CHAPTER 1

COPPER-CATALYZED AMINATION OF ARYL AND ALKENYL ELECTROPHILES

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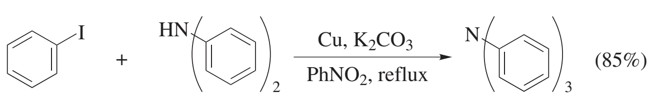
Organic Reactions, Vol. 85, Edited by Scott E. Denmark et al.

ACKNOWLEDGMENTS

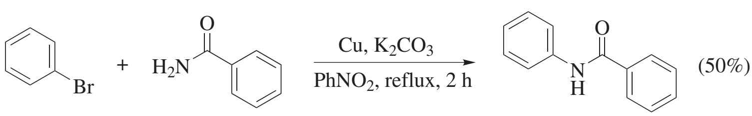
We thank Ms. Hannah Box for assistance in collecting references for this manuscript.

INTRODUCTION

Metal-catalyzed amination of aryl and alkenyl electrophiles has developed into a highly useful synthetic strategy for preparing *N*-aryl- and *N*-alkenyl- containing structures. Ullmann[1] first reported Cu-mediated *N*-arylation reactions of amines in 1903 (Scheme 1) followed closely by Goldberg's[2] report of amide *N*-arylations (Scheme 2). In these reactions, an aryl halide is condensed with an amine or amide in the presence of base and copper powder or a copper salt at high temperature. The need for stoichiometric amounts of copper and high reaction temperatures combined with the modest yields of product in most cases limits the application of these methods. Despite these limitations, Ullmann and Goldberg condensation reactions represented the state-of-the-art in metal-mediated C–N bond formation for nearly a century.[3] The development of efficient Pd-catalyzed C–N bond-forming reactions that could be carried out under mild conditions with less reactive substrates, such as aryl chlorides, resulted in palladium displacing copper as the preferred metal for aryl amination reactions in the late 1990s.[4–7]

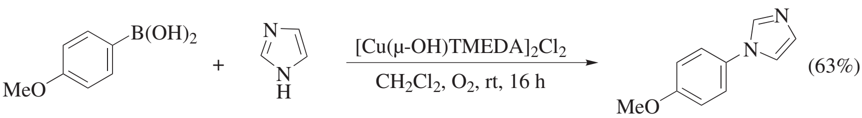


Scheme 1

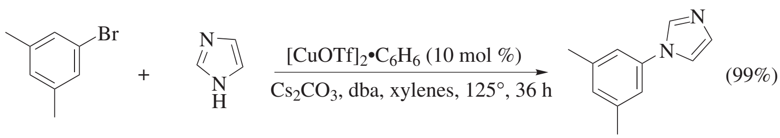


Scheme 2

Interest in Cu-mediated reactions was reinvigorated with the development of Cu(II)-mediated[8,9] and -catalyzed[10] oxidative couplings of carbon nucleophiles (e.g., arylboronic acids) and nitrogen nucleophiles (Scheme 3). Development of efficient, ligand-promoted, Cu-catalyzed coupling reactions of nitrogen nucleophiles and aryl or vinyl halide electrophiles further increased interest in the use of less expensive copper in place of palladium for C–N bond formation (Scheme 4).[11] The use of aryl halides is attractive due to their wider availability and lower cost compared to organoboron reagents. Copper-catalyzed *N*-arylation and alkenylation reactions are widely used in the synthesis of natural products, pharmaceuticals, electronics materials, and ligands.



Scheme 3



Scheme 4

Aromatic and heteroaromatic halides are the most common electrophiles in Cu-catalyzed C–N bond-forming reactions. The halide leaving group is typically an iodide or bromide, although chloride and even fluoride can be used in some cases. Alkenyl halides are also effective coupling partners in these reactions, with the iodides and bromides being most commonly used. Unlike Pd-catalyzed reactions, sulfonate leaving groups have not been successfully applied in Cu-catalyzed reactions. The nitrogen nucleophile can be nearly any class of compound with an N–H bond including aryl and alkyl amines, ammonia, azoles, amides, sulfonamides, carbamates, ureas, and guanidines. Copper-catalyzed systems are particularly useful with amide and azole substrates that prove challenging with Pd-catalyzed methods. In addition to amination reactions, Cu-catalyzed C–O, C–S, and C–C bond-forming reactions have been developed, but these reactions are outside the scope of this review.[12]

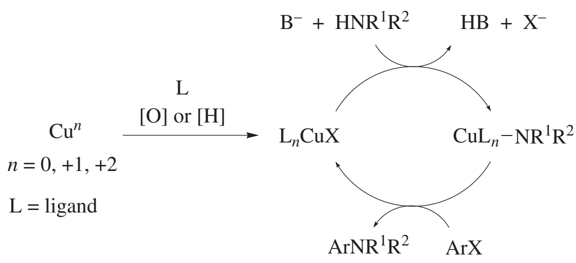
The catalysts used for the coupling of nitrogen nucleophiles and aryl or alkenyl halides can be broken down into two broad classes. Ligand-free catalyst systems based on the original Ullmann and Goldberg methods use copper powder or copper salts as the catalyst, and typically employ a polar aprotic solvent at high temperature (100–200°). Alternatively, copper salts in combination with ligands such as amines, ethers, or phosphines provide more active copper catalysts than ligand-free systems. Reactions using ligand-supported catalysts can often be carried out at lower temperature and with a wider range of substrates (i.e., aryl bromides and chlorides) than the ligand-free systems.

The goal of this chapter is to provide a critical and comprehensive review of the scope and mechanism of Cu-catalyzed amination of aryl and alkenyl electrophiles.

Copper-mediated or -catalyzed oxidative coupling reactions and couplings of preformed copper amides with aryl halides are not covered in this chapter, although they have previously been reviewed.[12] This review covers the literature through August 2010 with selected examples published through early 2011. Additional reactions reported mid-2011 through early 2014 are included only as references at the end of the bibliography, categorized according to the relevant table in the Tabular Survey. The patent literature is not covered in this chapter, but the relevant patent literature has been reviewed recently.[13] Several reviews have appeared in recent years that focus on the development of Cu-catalyzed amination reactions and their applications in complex target syntheses.[12,14–18]

MECHANISM

The mechanism of Cu-catalyzed C–N bond formation has proven more difficult to determine than that of the corresponding Pd-catalyzed cross-coupling reactions. The same general steps—nucleophile coordination to the metal center, activation of the C–X bond, and C–N bond formation—are involved in both the Pd- and Cu-catalyzed reactions, although the order of these steps is different. In the case of the Cu-catalyzed reactions, the order, exact mechanism of these steps, and identity of the active species continue to be debated.[19] The generally accepted sequence of steps begins with coordination of the deprotonated nucleophile to a Cu(I) center (Scheme 5). The Cu–amide complex then activates the organic halide to form the new C–N bond. The nature of the organic halide activation and C–N bond formation remains the least understood step in the catalytic cycle.



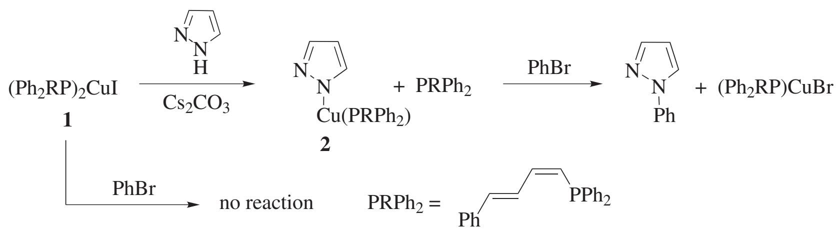
Scheme 5

Oxidation State of Catalytically Active Copper Species

The active form of copper is generally believed to be Cu(I) in these reactions. Copper precatalysts in 0, +1, and +2 oxidation states can be used to catalyze *N*-arylation reactions, however. When Cu(0) or Cu(II) sources are used, the active Cu(I) species is formed by in situ reduction or oxidation of the copper source. In kinetic studies of the Ullmann coupling of phenyl halides with diphenylamine, Cu(I) halides give reaction rates that are significantly higher than when Cu(II) salts are used.[20] When Cu(II) precursors are used, reduction to Cu(I) by alkoxide or amide reagents is observed.[20,21] Reduction of Cu(II) can be accelerated by ligands that stabilize the Cu(I) oxidation state, such as neocuproine.[22] Reduction of Cu(II) ions by amide or alkoxide ligands has been confirmed by electron paramagnetic resonance (EPR) spectroscopy of catalyst systems.[23,24] Amino acid complexes of Cu(I) ions are observed under catalytic conditions by electrospray–mass spectrometry (ESI–MS) analysis of reaction mixtures.[25] In the case of heterogeneous Cu(0) catalysts, the true catalyst may be formed by dissolving the Cu_2O coating found on copper metal catalysts.[20]

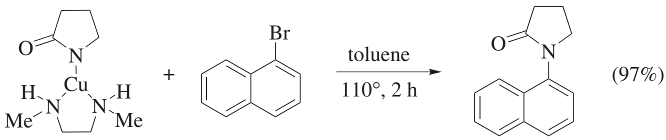
Nucleophile Coordination

In contrast to Pd-catalyzed coupling reactions where oxidative addition of the organic halide is the initial step, a strong body of evidence suggests that coordination of the nucleophile to copper occurs prior to activation of the organic halide. Support for this mechanism is provided by the ability of Cu–amido and –amidate complexes to react with aryl halides at catalytically competent rates. A *trans-N,N′*-dimethyl-1,2-diaminocyclohexane (DMCDA)-supported Cu–pyrrolidonate complex is kinetically competent in the arylation of pyrrolidone.[26] An NMR spectroscopic study of phosphine–copper complex **1** shows that this complex reacts with pyrazole in the presence of base to give a Cu–pyrazolate complex **2** (Scheme 6).[27] The pyrazolate complex reacts quantitatively with phenyl bromide to give 1-phenylpyrazole. Complex **1** is unreactive with phenyl bromide, however. Computational studies at the density functional theory (DFT) level suggest that a diamine Cu–amidate complex has a lower barrier to oxidative addition of the aryl halide than the analogous CuBr complex.[28]

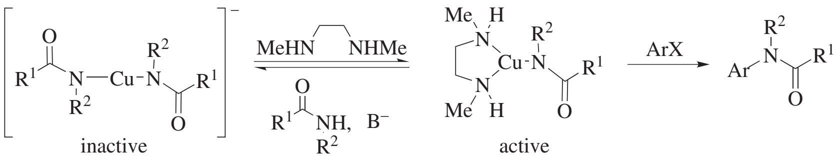


Scheme 6

A number of Cu(I)–amido and –amidate complexes have been prepared by metathesis of Cu(I) halides with nitrogen nucleophiles.[26,29–31] These complexes react stoichiometrically with aryl halides to give *N*-arylated products (Scheme 7), supporting the role of Cu(I) species in the catalytic cycle.[32] Copper–phthalimidate complexes react with aryl halides provided that the phthalimidate/Cu ratio is < 1.[29] With higher phthalimidate/Cu ratios, no reaction occurs. Part of the accelerating effect of chelating ligands in Cu-catalyzed coupling reactions appears to result from inhibition of the formation of catalytically inactive $[Cu(NR_2)_2]^-$ complexes (Scheme 8).[33,34]



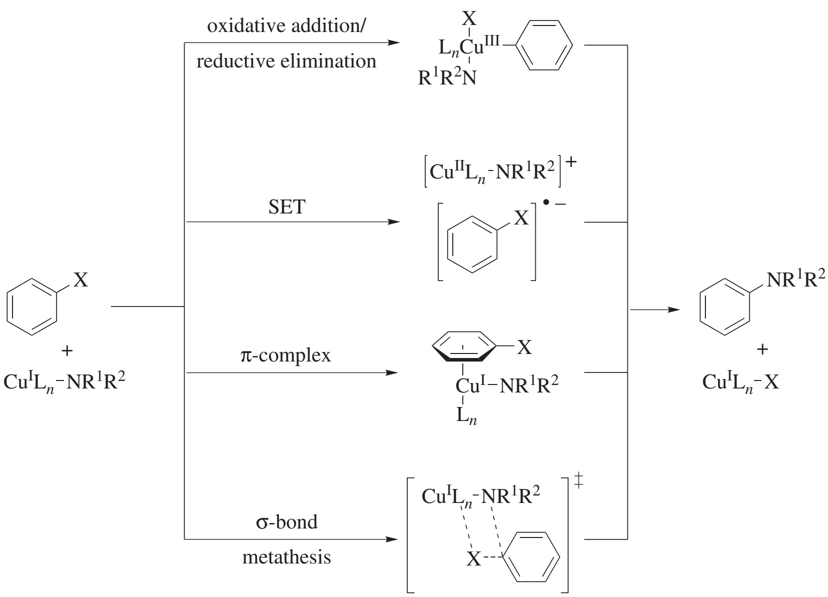
Scheme 7



Scheme 8

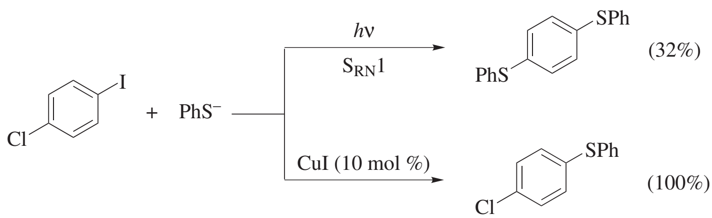
Organic Halide Activation Step

The mechanism for the aryl halide activation and C–N bond formation steps remains a matter of debate. Four major mechanisms have been proposed for this process (Scheme 9): (1) oxidative addition/reductive elimination, (2) substitution promoted by single-electron transfer (SET) from Cu(I) to the aryl halide, (3) nucleophilic aromatic substitution via π-complexation of copper to the aryl halide, and (4) σ-bond metathesis via a four-centered transition state. Mechanistic studies on the original Ullmann systems provide support for several of these mechanisms.[19]



Scheme 9

Several authors have postulated SET mechanisms analogous to $S_{RN}1$ reactions. Key mechanistic support for the SET mechanism is the observation of EPR signals from Cu(II) and organic radicals in the Cu-catalyzed amination of 1-bromoanthraquinone.[35] Evidence that seems to rule out free-radical intermediates has also been reported. The photochemical $S_{RN}1$ reaction of phenylthiolate with 1-chloro-4-iodobenzene gives the disubstituted product exclusively, whereas the CuI-catalyzed reaction gives only the monosubstituted product (Scheme 10).[36] Substrates with radical clocks are not rearranged by the Cu-catalyzed reactions. Both of these results suggest that radical intermediates are not formed, or have very short lifetimes. Reactions carried out under N_2 with Cu(I) salts are faster than reactions run in air.[23] In addition, the Cu(I) reactions run under a N_2 atmosphere show very weak EPR signals. These results suggest that the observed Cu(II) species are not catalytically relevant, but are formed by air oxidation of the active Cu(I) catalyst.



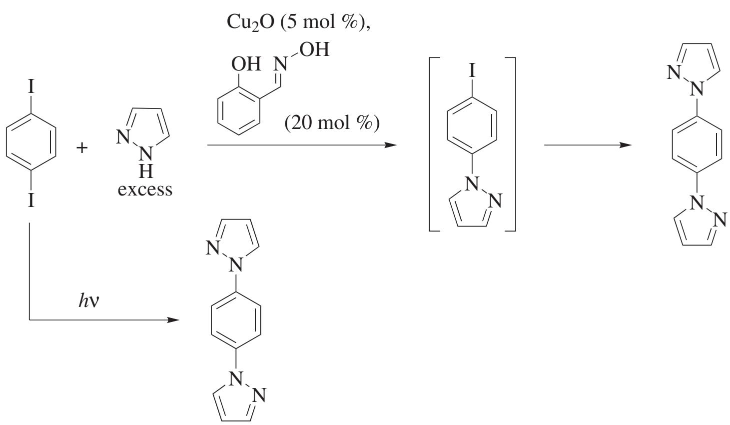
Scheme 10

Oxidative addition to give an aryl–Cu(III) intermediate followed by reductive elimination was first proposed on the basis of studies of the reaction of *N,N*-dimethyl *o*-halobenzamides with CuCl or CuCN.[37] Addition of benzoic acid results in hydrodehalogenation, which suggests an arylcopper intermediate is present that is protonated by the acid. A radical mechanism was discounted since no demethylation of the amide nitrogen occurs. The typical reactivity trend of ArI > ArBr > ArCl ≫ ArF is consistent with an oxidative addition mechanism and inconsistent with an S_NAr mechanism, which displays the opposite trend. In the amination of 1-haloanthraquinone, hydrodehalogenation occurs as a side reaction.[38] The halogen leaving group affects the rate of the reaction, but not the ratio of substitution to hydrodehalogenation. In addition, the hydrodehalogenation occurs by hydrogen transfer from the α-carbon of the amine. These results suggest a common $ArCu(III)(NR_2)$ intermediate that could form either the aryl amine product by reductive elimination or the hydrodehalogenation product by β-hydrogen elimination from the amine and then reductive elimination from the resulting aryl hydride complex.

The S_NAr mechanism via a copper π-complex was originally proposed in analogy to the known acceleration of S_NAr reactions in chromium–arene complexes as well as the observation of Cu–arene complexes.[23] This mechanism does not account for the aryl halide reactivity trend, however, which is opposite that of S_NAr reactions. In addition, this mechanism cannot explain the fact that *o*-halobenzoic acids undergo substitution at significantly higher rates than *p*-halobenzoic acids.[20] These substrates would be expected to react at similar rates in an S_NAr mechanism involving a copper π-complex. Substitution by a σ-bond metathesis mechanism has been proposed,[39] but there is little mechanistic evidence to support or refute this proposal due to the difficulty in differentiating the σ-bond metathesis mechanism from oxidative addition/reductive elimination.

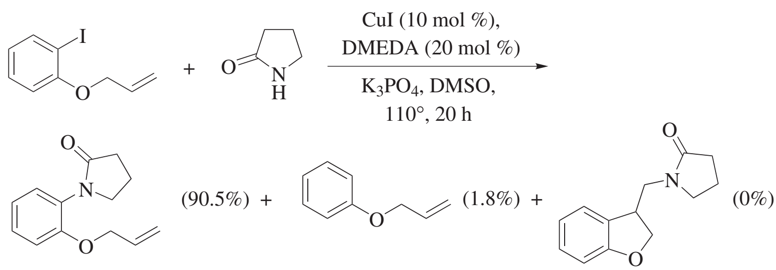
Mechanistic Studies of Aryl Halide Activation by Ligand-Supported Copper Species

Mechanistic studies of ligand-promoted Cu-catalyzed C–N bond formation also largely support an oxidative addition/reductive elimination mechanism. Several pieces of evidence suggest that long-lived radicals or radical anions are not involved in C–N bond formation catalyzed by copper complexes of a tetradentate nitrogen ligand.[40] This reaction is not affected by radical traps or initiators. Reaction of 1,4-diiodobenzene with excess pyrazole forms 1-(4-iodophenyl)pyrazole as an observable intermediate, which then is converted to 1,4-dipyrazolylbenzene (Scheme 11). In contrast, a radical mechanism would predict formation of the disubstituted product without intermediate formation of 1-(4-iodophenyl)pyrazole. The 1-(4-iodophenyl)pyrazole radical anion intermediate formed after the initial substitution would rapidly lose iodide leading to the second substitution without significant buildup of 1-(4-iodophenyl)pyrazole. Vinyl halides undergo substitution with retention of configuration, whereas a radical mechanism would result in scrambling of the alkene geometry. A number of features support the oxidative addition/reductive elimination mechanism in this system. The reactivity trend of aryl halides (ArI > ArBr > ArCl) and modest electronic effect [electron-withdrawing group (EWG) > electron-donating group (EDG)] are consistent with expected trends for oxidative addition. The fact that steric bulk on either the aryl halide or azole reduces the reaction rate suggests that both the aryl halide and azole must coordinate to copper prior to the rate-limiting step.

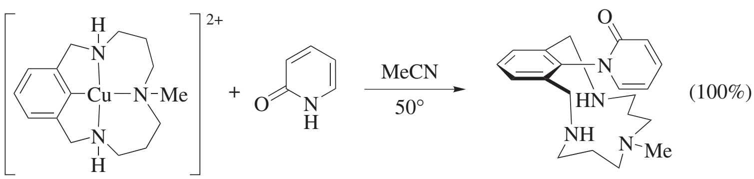


Scheme 11

The reactivities of 4-chlorobenzonitrile and 1-bromonaphthalene have been compared in the coupling of aryl halides and amides catalyzed by diamine copper complexes.[32] These substrates have similar reduction potentials and rates of halide dissociation from their radical anion forms. Therefore, these substrates would be expected to react at similar rates in an $S_{RN}1$-like mechanism. 1-Bromonaphthalene reacts with (DMEDA)Cu–pyrrolidonate to give *N*-1-naphthylpyrrolidone in 97% yield after 2 hours at 110° (Scheme 7). No reaction is seen when the copper complex is combined with 4-chlorobenzonitrile under identical conditions. In addition, coupling of *o*-allyloxyiodobenzene with pyrrolidone gives no cyclized product (Scheme 12). This result shows that any radical intermediate would have to be trapped significantly faster than the cyclization rate for the *o*-allyloxyphenyl radical (10^{12} s^{-1}). Evidence for reductive elimination from a Cu(III)(aryl)amido complex is provided by the rapid formation of *N*-arylamides by the reaction of preformed Cu(III)aryl complex **3** with amides (Scheme 13).[41,42]



Scheme 12



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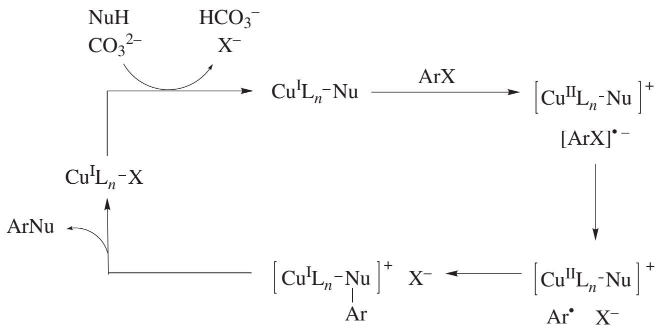
Scheme 13

Computational Studies of Copper-Catalyzed Amination Mechanisms

Computational studies show that the oxidative addition of aryl halides to ligand-supported copper amido or amidate complexes occurs with modest activation barriers that are consistent with experimentally determined activation barriers.[28,32,43–45] These studies only consider oxidative addition as a possible mechanism for the aryl halide activation step, so they cannot exclude the possibility of other mechanistic pathways. A computational study that evaluates oxidative addition/reductive elimination, σ-bond metathesis, SET, and atom-abstraction (IAT) mechanisms concludes that the SET pathway proceeding through a Cu(II) intermediate is the lowest-energy pathway for C–N bond formation catalyzed by copper phenanthroline and copper diketonate complexes.[46] The intermediates involved in the oxidative addition/reductive elimination and σ-bond metathesis mechanisms are calculated to be energetically inaccessible. The phenyl radical generated through SET from the Cu(I)-amido complex adds to the nitrogen to form the arylated Cu(I) amido complex (Scheme 14). The radical-trapping step in the SET mechanism is calculated to be strongly exothermic, suggesting that the caged Cu(II)-phenyl radical pair collapses at a very high rate. Rapid trapping of the caged radical would be consistent with experimental data that appears to exclude radical mechanisms.



Scheme 14

Thus, despite significant effort, the exact nature of the aryl halide activation step remains an open question. It is likely that both oxidative addition and SET-type mechanisms are energetically accessible. The preferred pathway is likely dependent on the copper complex, ligands, substrates, and reaction conditions. In reactions where the SET mechanism is favored, rapid radical capture may make this mechanism experimentally indistinguishable from the oxidative addition mechanism.

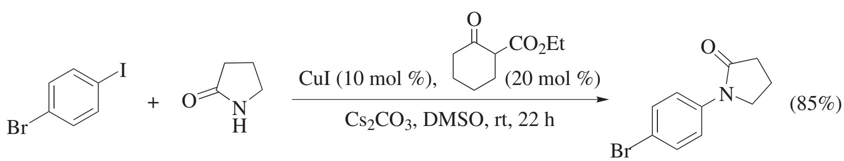
Mechanistic Studies of Ligand Effects on Copper-Catalyzed Amination

Experimental studies on the effect of ligands in Cu-catalyzed C–N bond formation suggest that an important role is preventing the formation of catalytically inactive, anionic $[Cu(NR_2)_n]^{(n-1)}$-species. Kinetic studies in the diamine-promoted amide arylations show that the reaction is first order in diamine at low ligand concentration, but the dependence saturates at higher ligand concentration. This result is interpreted to indicate that at low ligand concentrations catalytically inactive anionic diamidate copper complexes dominate. The diamine ligand pushes the equilibrium to the catalytically active ligand–Cu–amidate complex (Scheme 8).[33] With phenanthroline as the ligand, $[Cu(phen)_2][Cu(NR_2)]$ complexes (NR_2 = pyrrolidonate) are formed rather than $Cu(phen)(NR_2)$.[32] Although the phenanthroline ligand is not coordinated to the Cu–amidate, its presence is critical for reaction with aryl halides. Tetrabutylammonium salts of $[Cu(NR_2)]^-$ are unreactive with aryl iodides. The $[Cu(phen)_2][Cu(NR_2)]$ complex is proposed to be in equilibrium with $Cu(phen)(NR_2)$, which is the true catalytically active species. Computational studies also show that anionic Cu–diamidate complexes have significantly higher barriers for oxidative addition than Cu–(diamine)(amidate) species.[28]

SCOPE AND LIMITATIONS

The Carbon Electrophile

Aromatic Halides and Sulfonates. Aryl iodides and bromides are the most commonly employed substrates in Cu-catalyzed nitrogen arylations. The general reactivity trend for aryl halide substrates is ArI > ArBr > ArCl, whereas aryl fluoride and aryl sulfonate substrates are generally unreactive except in special cases. This order of reactivity is clearly demonstrated in a number of examples in which the more reactive halide can be selectively coupled in the presence of less reactive halide substituents. 1-Bromo-4-iodobenzene is coupled in high yield and selectivity at the iodide position with alkyl amine,[47] aniline,[48] imidazole,[40] and amide nucleophiles (Scheme 15).[49] Similarly, 1-bromo-4-chlorobenzene is selectively coupled at the bromine position in high yield with a variety of nitrogen nucleophiles.[47,49–51]

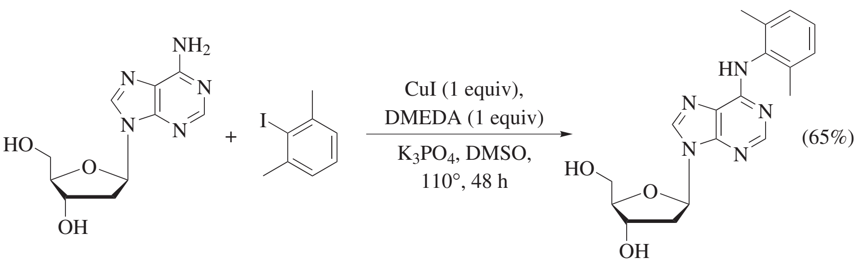


Scheme 15

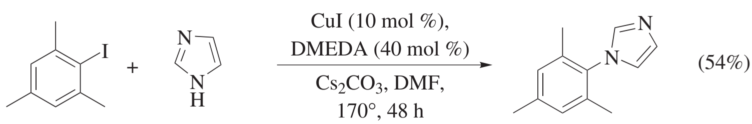
Steric and electronic properties of the aryl halide substrate can affect reactivity, although there are relatively few careful studies of these effects. A kinetic study of the coupling of 4-substituted aryl iodides with *n*-hexylamine catalyzed by a CuI/diketonate catalyst at room temperature shows that the reaction time increases from 40 minutes for 4-iodobenzonitrile to 110 minutes for 4-iodoanisole.[52] In a competitive coupling of 4-substituted aryl iodides with 2-pyridone, ethyl 4-iodobenzoate (relative rate = 4.7) gives the highest rate followed by 4-iodotoluene (1.4) and 4-iodoanisole (1.0).[53] At the higher temperatures and longer reaction times typically used in methodology studies, these small differences in reactivity are generally not noticeable.

Substituents adjacent to the halide leaving group can inhibit the coupling reaction. The vast majority of examples reported are 4-substituted aryl halides. With the exception of the special case of 2-halobenzoic acid derivatives, few examples of Cu-catalyzed coupling of 2-substituted aryl halides have been reported. With aryl amine nucleophiles, 2-halotoluene substrates give good yields.[50,54–56] Coupling of 1-iodo-2,6-dimethylbenzene with the N6 of adenosine gives incomplete conversion

(65% yield) after 48 hours using stoichiometric amounts of CuI/DMEDA at 110° in DMSO (Scheme 16).[57] Unhindered aryl iodides give complete conversion after 1–2 hours under identical conditions. Couplings with *N*-heteroaromatic substrates appear to be more tolerant of steric hindrance in the aryl halide substrate. Numerous examples of 2-substituted aryl halides coupling with azoles are known. Coupling of iodomesitylene and imidazole using CuI (10 mol %) and DMEDA (40 mol %) at 170° in DMF gives 1-mesitylimidazole in 54% yield after 48 hours (Scheme 17).[58] Under the same conditions, 2,6-diisopropyliodobenzene gives only a 19% yield.



Scheme 16



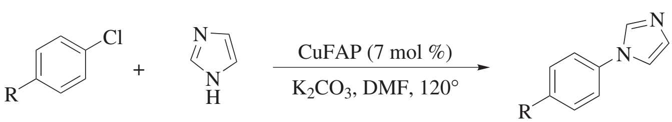
Scheme 17

Functional group tolerance is very high for these reactions. Nearly all classes of functional groups are tolerated by the copper catalyst systems. Electrophilic substituents such as esters, ketones, and aldehydes are unaffected. Free hydroxyl groups in carboxylic acids and alcohols do not need to be protected. Free amine or amide N–H bonds are generally tolerated provided they do not compete with the desired nitrogen nucleophile. As noted above, less reactive halogens than that in the desired reactive C–X bond are generally unaffected.

Aryl iodides are generally useful arylating agents for all classes of nitrogen nucleophiles and a wide range of copper catalyst systems. For ligand-free catalyst systems, reaction temperatures typically range from 80–150° for intermolecular couplings of unactivated aryl iodides. High yields are obtained at 40° for the coupling of aryl iodides with azoles using 20 mol % of CuI in DMF.[59] A coordinating solvent, such as DMF, DMSO, or NMP, is typically required for these ligand-free systems. Copper catalysts supported by proline,[60] acetylacetonate,[61] 2,2′-binaphthol,[62] or DMEDA[63] ligands promote coupling of electron-deficient and sterically unhindered aryl iodides at room temperature. Other ligand-promoted couplings of aryl iodides are generally carried out at 80–110°.

Although aryl bromides are less reactive than aryl iodides, they are generally useful electrophiles for Cu-catalyzed C–N bond-forming reactions with all classes of nitrogen nucleophiles. Ligand-free catalyst systems typically require temperatures between 100 and 140° when coordinating solvents are used. Ligand-supported copper catalysts are more general and the couplings can typically be carried out at lower temperatures (80–110°).

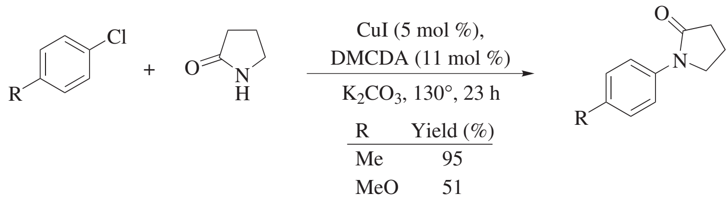
Aryl chlorides are much more challenging substrates for Cu-catalyzed C–N bond formation than aryl iodides or bromides. Although in some cases electron-deficient aryl chlorides can be coupled at relatively low temperatures (80–100°), temperatures between 110 and 150° are generally required. Substituent electronic properties have a significant effect on the ability of aryl chlorides to be coupled. Ligand-free copper catalyst systems are only effective for aryl chlorides that have strong electron-withdrawing substituents. In the few cases where non-activated chlorides are reported in ligand-free systems, the yields are typically much lower than for electron-deficient aryl chlorides.[64,65] For example, a Cu-exchanged fluorapatite catalyst (CuFAP) affords a 95% yield after six hours at 120° for the coupling of 4-chlorobenzonitrile and imidazole (Scheme 18).[66] In contrast, the coupling of 4-chloroanisole requires 36 hours and affords only a 52% yield under the same conditions. Ligand-free systems often give no conversion with unactivated aryl chlorides, such as chlorobenzene, under conditions where electron-deficient aryl chlorides are effectively coupled.[64,65]



R	Time (h)	Yield (%)
NC–	6	95
MeO	36	52

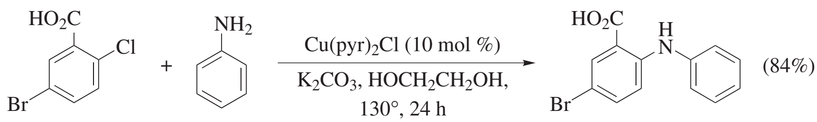
Scheme 18

Mixed results are obtained in the coupling of unactivated aryl chlorides and nitrogen nucleophiles with ligand-supported copper catalysts. Yields below 30% are obtained in the coupling of chlorobenzene with aniline derivatives using a CuI/pipecolinic acid catalyst system at 110°.[67] Chlorobenzene and 4-chlorotoluene give no conversion in coupling with indole or benzimidazole using a CuO/phenanthroline catalyst system at 140°.[68] A 95% yield is obtained in the arylation of 2-pyrrolidinone in neat 4-chlorotoluene using CuI/DMCDA (DMCDA = *N,N′*-dimethyl-*trans*-1,2-cyclohexanediamine) as the catalyst at 130°, but 4-chloroanisole gives only a 51% yield under identical conditions (Scheme 19).[69] Using the more electron-rich tributylphosphine ligand provides a more general catalyst for coupling of aryl chlorides and aniline derivatives at 135°.[56]



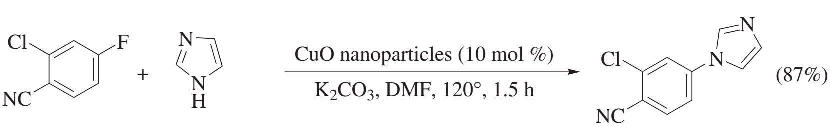
Scheme 19

Since Ullmann's original report,[1] 2-halobenzoic acids have been known to be particularly effective substrates for Cu-catalyzed C–N bond-forming reactions.[70–72] The proximity of the carboxylate group is critically important, since 4-halobenzoic acids do not give a similar acceleration. Therefore, the effect appears to be due to coordination rather than the electron-withdrawing property of the carboxylate group. The presence of a carboxylic acid group can reverse the normal reactivity order of carbon–halogen bonds. 5-Bromo-2-chlorobenzoic acid undergoes selective coupling with aniline at the chlorine position (Scheme 20).[71]



Scheme 20

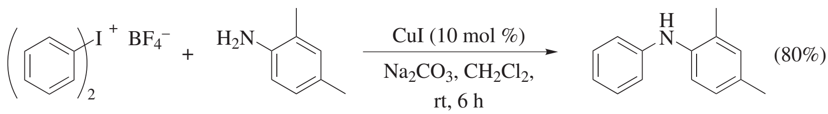
Aryl fluorides are generally inert toward Cu-catalyzed C–N bond formation unless activated by strong electron-withdrawing groups positioned *ortho* or *para* to the C–F bond. Activated aryl fluorides are efficiently coupled with imidazole at 120° using a nanoparticle CuO catalyst without supporting ligands (Scheme 21).[64] Aryl fluorides react faster than the corresponding aryl chlorides, which is inverse to the normal reactivity trend. In addition, 2-chloro-1-fluoro-4-nitrobenzene reacts selectively at the fluorine position. No reaction occurs in the absence of the CuO catalyst precluding a Cu-free S_NAr mechanism. The reactivity trend suggests that the Cu-promoted C–F activation follows an S_NAr-like mechanism, however. Similar reactivity of activated aryl fluorides with azoles has been reported for sulfonated Cu–salen complexes[73] and a Cu-exchanged fluorapatite catalyst.[66] In both cases, activated aryl fluorides react faster than aryl chlorides.



Scheme 21

Aryl sulfonates are generally unreactive in Cu-catalyzed C–N bond-forming reactions on the basis of a very small number of examples reported in the literature. No reaction is observed in the coupling of phenyl tosylate with benzamide or aniline using CuO oxide nanoparticles, although this system is also inactive for aryl bromides and chlorides.[74] Low yields of aniline derivatives are obtained in the coupling of electron-deficient aryl mesylates and sodium azide using a $CuSO_4$/proline catalyst in the presence of ascorbate as a reducing agent.[75]

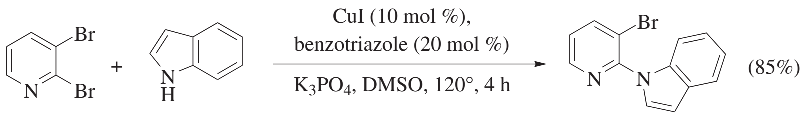
Diaryliodonium ions can also serve as electrophiles in Cu-catalyzed C–N bond-forming reactions. The diaryliodonium salts are highly reactive towards nucleophilic substitution and oxidative addition. Coupling of diaryliodonium salts with alkyl or aryl amines occurs in good yield (65–83%) at room temperature using CuI without a supporting ligand, whereas azole nucleophiles require 50° (Scheme 22).[76] Amide nucleophiles give lower yields (30–70%).



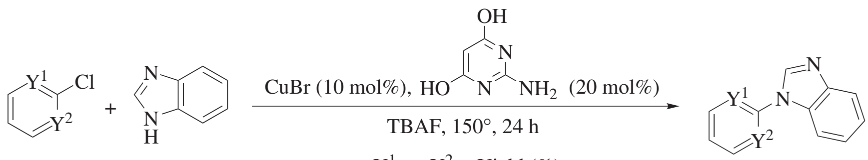
Scheme 22

Heteroaryl Halides. Heteroaromatic halide substrates can present challenges in metal-catalyzed cross-coupling reactions due to their ability to act as ligands for the catalyst. Copper catalysts seem to be largely unaffected by potential coordination to heteroaromatic substrates containing N, O, S, or Se. The main effect of heteroatoms on the reactivity of heteroaryl halides appears to be electronic. Since pyridine rings are more electron-deficient than benzene, halopyridine derivatives tend to be more reactive than aryl halides. Each additional π-bonded nitrogen further increases the reactivity of the heteroaryl halide. In contrast, five-membered-ring heterocycles, such as pyrrole, furan, and thiophene, in which the heteroatom contributes a lone pair to the π-system, are more electron-rich than benzene. Therefore, these heteroaryl halides tend to be less reactive than simple aryl halides.

Halogenated pyridines, pyrimidines, and pyrazines are generally reactive substrates in Cu-catalyzed C–N bond-forming reactions. Because of the high reactivity of simple aryl iodides, there is usually not a noticeable difference in reactivity between aryl iodides and heteroaryl iodides. Some authors have noted improved reactivity of bromopyridines compared with non-activated aryl bromides.[77,78] The effect is strongest for 2- or 4-halopyridines. Coupling of 3-bromopyridine with imidazole requires 24 hours using a CuI/diketonate catalyst system at 110° compared with 12 hours for 2-bromopyridine.[79] 2,3-Dibromopyridine is substituted selectively at the 2-position by indole (Scheme 23).[77] Chloropyridine derivatives show a significantly increased activity compared to non-activated aryl chlorides. In cases where direct comparisons can be made, 2-chloropyrimidine gives improved yields and reacts faster than 2-chloropyridine, which is more reactive than chlorobenzene (Scheme 24).[79,80] Like other electron-deficient aryl chlorides, chloropyridine and chloropyrimidine derivatives can be coupled under conditions where non-activated aryl chlorides give no conversion.[68,81]



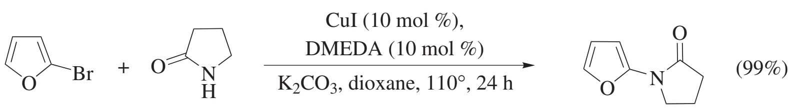
Scheme 23



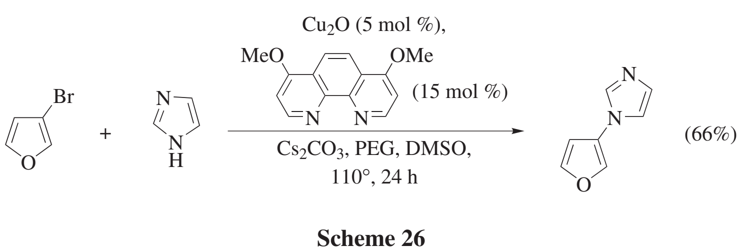
Y^1	Y^2	Yield (%)
CH	CH	40
N	CH	56
N	N	100

Scheme 24

Halogenated five-membered-ring heteroaromatic compounds have been used less extensively than pyridine derivatives due to their lower reactivity. The number of examples follows the trend in electron richness: halothiophenes/halothiazoles $\gg$ halofurans $\gg$ haloazoles. *N*-Methyl-4-iodopyrazole is coupled with pyrazole in good yield at 80° using a CuI/salicylaldehyde oxime catalyst system,[82] but no examples of bromo- or chloroazoles undergoing Cu-catalyzed coupling reactions are known. Only a few examples of the amination of 2- and 3-bromofurans are reported. Generally good yields are obtained in the coupling of 2- and 3-bromofurans with amides and carbamates using the CuI/DMEDA catalyst system at 110° (Scheme 25).[83] Coupling of 3-bromofuran with imidazole using Cu_2O/4,7-dimethoxyphenathroline as the catalyst affords a 66% yield of coupled product (Scheme 26).[84]

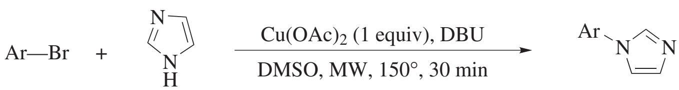


Scheme 25



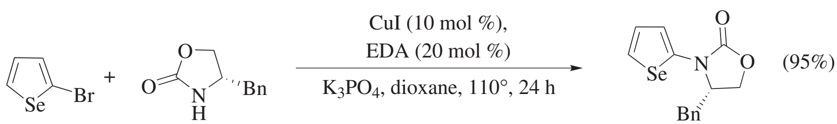
Scheme 26

Couplings of iodo- and bromothiophenes and thiazoles have been reported with a variety of nitrogen nucleophiles. When a ligand-free $Cu(OAc)_2$ catalyst is used with DBU as a base, bromothiophenes require higher temperature (150° vs. 130°) and afford lower yields than bromopyridine derivatives.[85] 2-Bromothiophene provides a lower yield than 3-bromothiophene (Scheme 27). In another study, yields increase along the trend 2-bromothiophene < 2-bromo-3-thiazole < 4-bromotoluene < 2-bromopyridine for the coupling of the halide with imidazole using a CuI/aminopyrrole catalyst system.[86] 2-Iodoselenophene undergoes coupling with amide and azole nucleophiles in modest to excellent yields using CuI/EDA (EDA = ethylenediamine) as the catalyst (Scheme 28),[87] but no conversion occurs with aniline or morpholine. To our knowledge, no examples are on record for amination of chlorinated five-membered-ring heterocycles using copper catalysts. Given the low reactivity of copper catalysts with aryl chlorides, the electron-rich chloroazoles, chlorofurans, or chlorothiophenes are likely unreactive.



Ar	Yield (%)
2-thienyl	63
3-thienyl	80

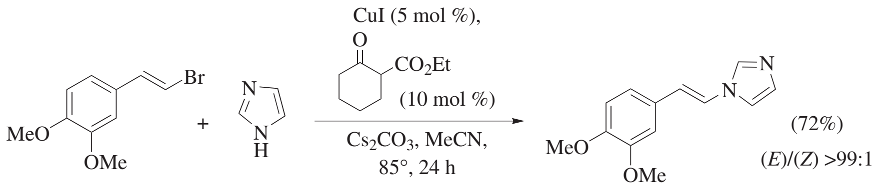
Scheme 27



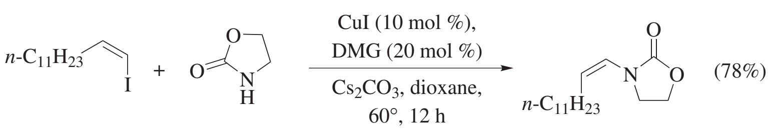
Scheme 28

Alkenyl Halides. Alkenyl halides are also useful substrates in Cu-catalyzed C–N bond-forming reactions. Examples of these couplings are largely limited to amide and azole nucleophiles that form stable *N*-alkenylated products. Alkenyl iodides and bromides have been coupled with diarylamines to give stable enamine products, but primary amine substrates afford the imine tautomers as the final products.[88] The general reactivity trends for alkenyl halides mirror those of the aryl halides (I > Br > Cl). No significant limitations to substitution at the alkenyl center are noted based on the examples published to date. Good yields are obtained with mono-, di-, and tri-substituted halogenated alkenes. Electronic effects from substituents do not seem to inhibit activation of the vinyl halogen bond.

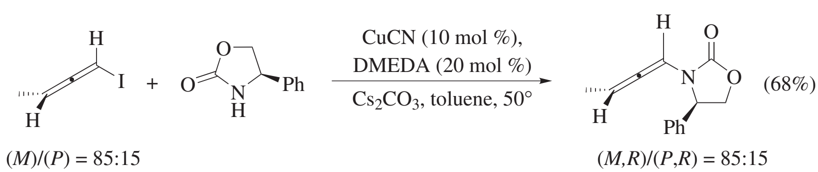
Alkenyl halides typically undergo Cu-catalyzed C–N bond formation with retention of alkene configuration. The strong preference for retention suggests a concerted C–X bond activation mechanism, rather than a process involving free-radical species. The coupling of (*E*)-β-halostyrenes with azole derivatives using a Cu_2O/β-keto ester catalyst system affords nearly exclusive formation of the (*E*)-substituted products (Scheme 29).[89] A few examples show a slight erosion of the alkene configurational purity [(*E*)/(*Z*) = 96:4], but no consistent trend accounts for the minor alkene isomerization. More hindered (*Z*)-haloalkenes also give (*Z*)-substituted products with complete retention of configuration in most cases (Scheme 30).[90] Axially chiral allenyl iodides undergo coupling with amides with complete retention of configuration as well. Coupling of (*M*)-1-iodo-1,2-butadiene [(*M*)/(*P*) = 85:15] with (*R*)-5-phenyloxazolidone using CuCN/DMEDA at 50° gives the coupled product as an 85:15 mixture of diastereomers (Scheme 31).[91]



Scheme 29

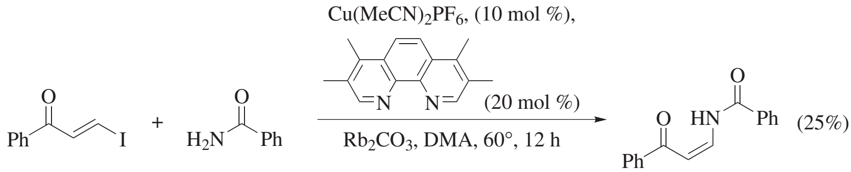


Scheme 30

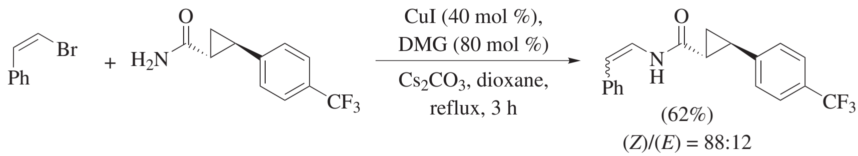


Scheme 31

Inversion of alkene configuration is observed in a few cases. In the coupling of conjugated amides with an (*E*)-β-iodoacryloyl amide, the thermodynamically more stable (*Z*)-product is obtained in low yield as the only coupling product (Scheme 32).[92] Coupling of (*Z*)-β-bromostyrene derivatives with amides using a CuI/DMG (DMG= *N,N*-dimethylglycine HCl) catalyst system in refluxing dioxane gives mixtures of (*Z*)- and (*E*)-alkenes in (*Z*)/(*E*) ratios ranging from 78:22 to 95:5 (Scheme 33).[93]

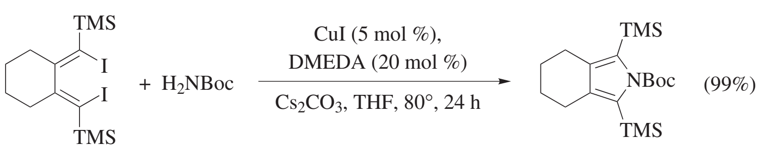


Scheme 32



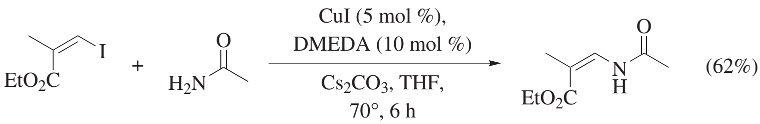
Scheme 33

Typical coupling temperatures for alkenyl iodides are between 50 and 100°, which is somewhat lower than the temperatures generally required for aryl iodides. Only a few examples of ligand-free Cu-catalyzed coupling of alkenyl iodides have been reported. Copper(II) oxide nanoparticles are an effective catalyst for coupling of (*E*)-β-iodostyrene and azole nucleophiles at 80°.[94] Coupling of vinyl iodides with amides catalyzed by copper thiophene-2-carboxylate (CuTC) without additional supporting ligands is used in the synthesis of several natural products.[95−97] More commonly, the catalyst derived from CuI and DMEDA is used for the coupling of alkenyl iodides with amides and azoles. Couplings of alkenyl iodides and amides are widely used in the synthesis of enamide natural products. Coupling of an alkenyl iodide with amides at room temperature with stoichiometric amounts of CuI/DMEDA is used in the synthesis of palmerolide A analogs.[98] Intramolecular coupling of an alkenyl iodide and amide catalyzed by CuI/DMEDA is used as the ring-closing step in the synthesis of abyssenine A.[99] These examples are discussed in more detail in the "Applications to Synthesis" section. The CuI/DMEDA system has also been used in the coupling of 1,4-diiodobutadienes and amides to give pyrroles (Scheme 34).[100]



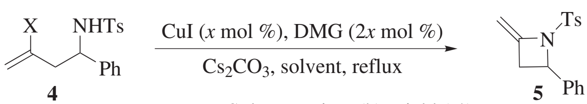
Scheme 34

Examples of coupling of alkenyl bromides are less common than those of iodides. Ligand-free couplings with CuO nanoparticles give good yields at 80°, but require approximately twice the reaction time compared to iodides.[94] Diamine-ligand-supported catalysts are most commonly used with alkenyl bromides. Typical reaction temperatures for these systems range from 100 to 120°. The scope of alkenyl halides is broad with (*E*) and (*Z*) 1-haloalkenes, 2-haloalkenes, and trisubstituted haloalkenes all giving good yields and complete retention of alkene configuration for couplings with amides and azoles (Scheme 35).[101,102] *N,N*-Dimethylglycine is also used as a ligand for coupling of alkenyl bromides and amides.[90,93]



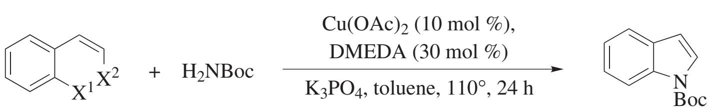
Scheme 35

The less reactive alkenyl chlorides have not been widely used in Cu-catalyzed C–N bond-forming reactions. Ligand-free catalyst systems give low yields in intermolecular couplings of alkenyl chlorides with azole nucleophiles in the few examples that have been reported.[94,103] Alkenyl chlorides show more utility in intramolecular couplings. Cyclization of 3-chloro-3-butenyl sulfonamide **4** provides a good yield of azetidine **5**, but the chloride substrate requires higher temperatures (100° vs. 68°) and higher catalyst loadings (20 vs. 10 mol % Cu) than the bromide substrate (Scheme 36).[104,105] Condensation of 2-bromo-β-chlorostyrene and *O-tert*-butyl carbamate provides a 56% yield of the Boc-protected indole in a cascade coupling reaction using $Cu(OAc)_2$/DMEDA as the catalyst (Scheme 37).[106] The yield is significantly lower than is obtained with the dibromo analog. Interestingly, switching the chloride and bromide positions (2-chloro-β-bromostyrene) leads to no conversion under identical conditions. No examples of vinyl fluoride or sulfonate substrates in Cu-catalyzed C–N couplings are known.



X	*x*	Solvent	Time (h)	Yield (%)
Br	10	THF	1	99
Cl	20	dioxane	2	99

Scheme 36



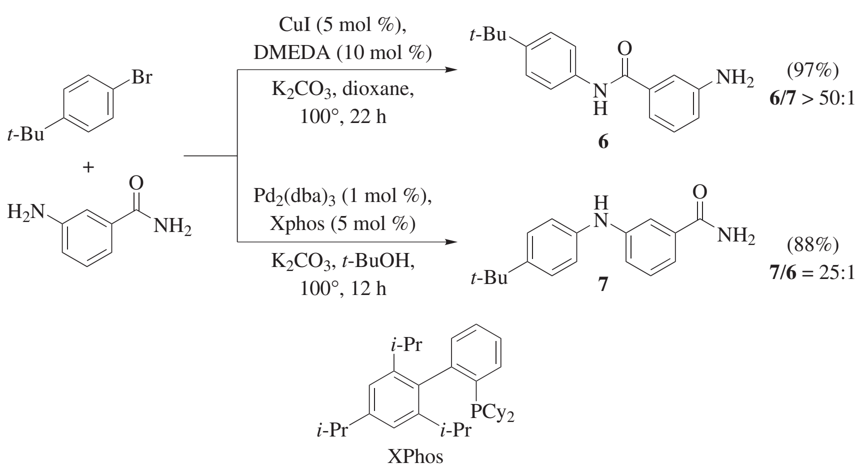
X^1	X^2	Yield (%)
Br	Br	88
Br	Cl	56
Cl	Br	0

Scheme 37

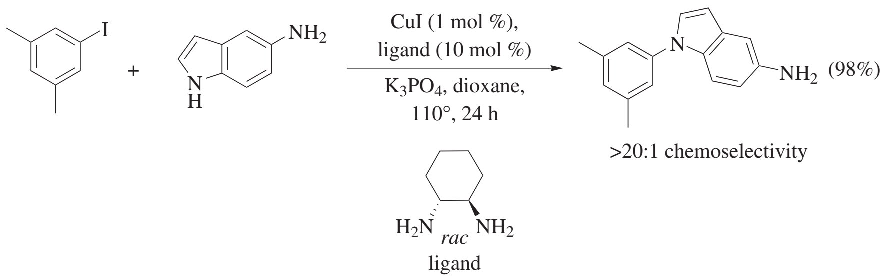
The Nitrogen Nucleophile

A broad range of nitrogen nucleophiles can be arylated under copper catalysis. Similarly to Pd-catalyzed reactions, primary and secondary aryl or alkyl amines can be arylated. The Cu-catalyzed reactions provide more general reactivity than palladium catalysts with more acidic N–H functionalities including azoles, amides, ureas, carbamates, and sulfonamides. The copper systems are also more general for the arylation of ammonia than palladium-based systems. Specific features of the main classes of nitrogen nucleophiles are highlighted here.

The general order of reactivity for nitrogen nucleophiles using copper catalysts is that amides and azoles are more reactive than amine substrates. For example, coupling of 3-aminobenzamide with an aryl bromide using a CuI/DMEDA catalyst system gives amide arylation product **6** exclusively (Scheme 38).[107] The observed selectivity is opposite to the strong preference for arylated amine product **7** seen with palladium catalysts using the same substrates. Similarly, 5-aminoindole is arylated exclusively on the indole nitrogen using the copper catalyst (Scheme 39),[107] whereas the Pd-catalyzed coupling gives exclusive arylation on the amine. The increased reactivity of amides and azoles in Cu-catalyzed couplings may be due to the increased acidity of azoles and amides compared to amines and aniline derivatives, or it is possible that Cu–amidate and –azolate complexes undergo oxidative addition with aryl halides faster than Cu–anilido complexes. Highly acidic N–H bonds, such as that in tetrazole, are poor coupling partners, however, presumably due to the low nucleophilicity of the nitrogen.[40] In substrates that contain both alkyl amine and aniline nucleophiles, selective arylation of the alkyl amine is observed.[52,107] This selectivity may be due to the stronger coordinating ability of the alkyl amine nitrogen compared to that of the aryl amine.

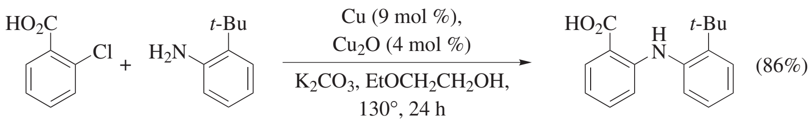


Scheme 38

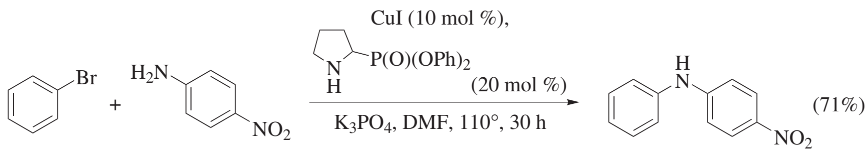


Scheme 39

Aromatic Amines. Aniline derivatives show broad scope in Cu-catalyzed *N*-arylation reactions. Sterically demanding anilines, such as 2,6-dimethylaniline, require reaction times and give yields comparable to those of unhindered substrates in the few examples reported.[67,108] 2-Substituted anilines with large substituents, such as phenyl or *tert*-butyl, are also successfully coupled with aryl halides (Scheme 40).[109] Substituent electronic effects have little influence on the coupling efficiency. Electron-withdrawing substituents would be expected to decrease the nucleophilicity of the amine making it less reactive in the C–N bond-forming step. This effect may be counteracted by the increased acidity of the N–H bond, which makes formation of the Cu–amido complex occur more readily. Careful studies of the electronic effect on coupling have not been reported. In a few cases, nitroanilines give significantly lower yields than more nucleophilic amines.[56] Other examples of successful coupling of nitroanilines with aryl halides are known, however (Scheme 41).[67,108]



Scheme 40

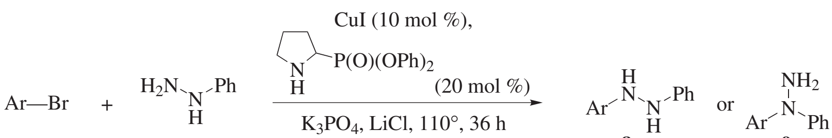


Scheme 41

In the arylation of primary anilines, both mono- and diarylation can occur to give either secondary or tertiary arylamines. To achieve monoarylation, the amine generally must be used in excess (2–4 equivalents) to avoid over-arylation. Under these conditions, high selectivity for the diaryl secondary amine is achieved. Use of a 2:1 ratio of aryl halide to aniline generally gives clean formation of the triarylamine product.

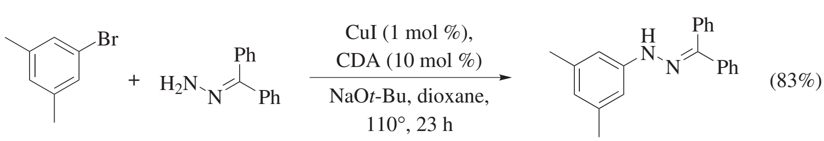
Ammonia, Hydrazine, and Hydroxylamine. The direct synthesis of primary aryl amines from ammonia and aryl halides has been a long-sought synthetic objective. Palladium catalysts are generally ineffective for direct coupling with ammonia, although a few recent systems have shown promise.[110] In contrast, Cu-catalyzed arylations of ammonia have a long history.[111] Selectivity for the monoarylated product is achieved by using a large excess (typically ≥10 equivalents) of ammonia relative to the aryl halide. Anhydrous ammonia at high pressure (80–100 psi) can be used as the NH_3 source.[110,112] A more convenient source of ammonia, at least in academic settings, is aqueous ammonia. A number of copper systems catalyze the arylation of aqueous ammonia in good yields under mild conditions.[113,114] Ammonium chloride can also be used as the NH_3 source.[60]

No examples of *N*-arylation of hydrazine or hydroxylamine are found in the literature. The majority of examples of arylation of hydrazine derivatives involve arylation of hydrazides on the more acidic amide N–H bond, which is discussed below. Arylation of phenylhydrazine occurs on the unsubstituted nitrogen to afford *N,N′*-diarylhydrazine **8** with 2-bromotoluene, whereas less hindered aryl halides selectively arylate the more acidic phenyl-substituted nitrogen to give *N,N*-diaryl hydrazine **9** (Scheme 42).[48] A CuI/CDA (CDA = *trans*-1,2-diaminocyclohexane) catalyst gives selective arylation on the unsubstituted NH_2 of benzoylhydrazide or benzophenone hydrazone (Scheme 43).[115]



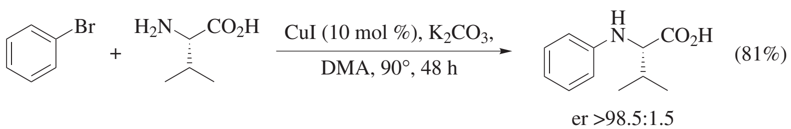
Ar	**8/9**	Yield (%)
2-MeC_6H_4	100:0	74
$4\text{-O}_2NC_6H_4$	0:100	82

Scheme 42

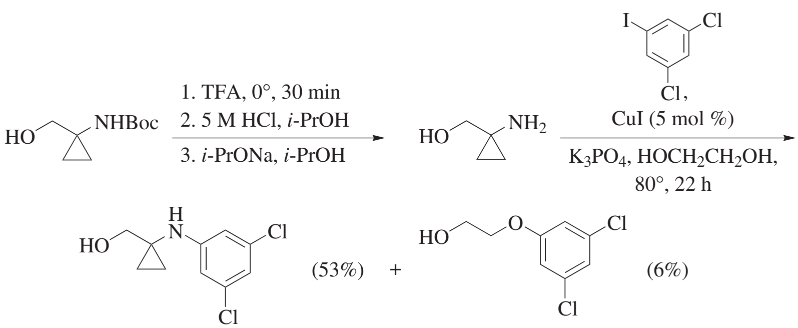


Scheme 43

Alkyl Amines. Primary and in some cases secondary alkyl amines are effective coupling partners in Cu-catalyzed C–N bond-forming reactions. Primary alkyl amines give high yields in couplings with aryl halides when the nitrogen is attached to primary or secondary carbons. Arylation of amino acids[116] and cyclohexylamine[117] has been successfully demonstrated with a number of systems. A smaller number of examples of arylation of amines attached to simple acyclic secondary carbons, such as isopropyl or *sec*-butyl amines are known.[118,119] Configurational purity at the amine α-carbon is retained (Scheme 44).[116,120] Examples of *N*-arylation of primary amines attached to tertiary carbons are rare. Arylation of 1-amino-1-hydroxymethylcyclopropane with 3,5-dichloro-1-iodobenzene gives a 53% yield of coupled product using CuI/ethylene glycol as the catalyst system (Scheme 45).[121]

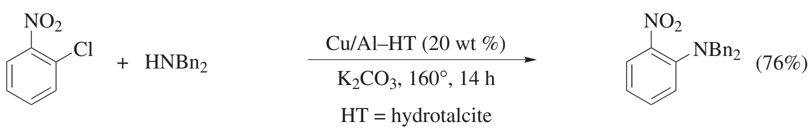


Scheme 44

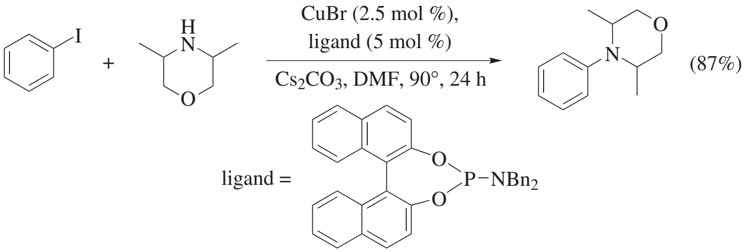


Scheme 45

Secondary alkyl amines often give significantly lower yields than primary amines or cyclic secondary amines.[47,122,123] Good yields for the coupling of dialkyl amines and activated aryl halides, such as 2-chloronitrobenzene, have been reported (Scheme 46).[117,122] In contrast to acyclic secondary amines, cyclic secondary amines, such as pyrrolidine, piperidine, and morpholine, generally give comparable yields to primary amines,[124,125] although some authors have noted lowered yields.[122,126] Even the sterically demanding 3,5-dimethylmorpholine can be arylated with phenyl iodide in 87% yield using a catalyst derived from CuBr and a phosphoramidite ligand (Scheme 47).[118]

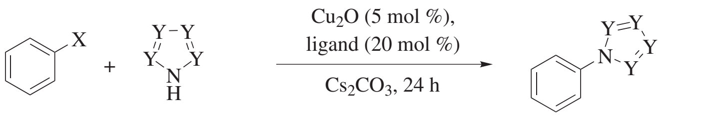


Scheme 46

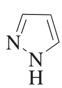
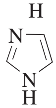
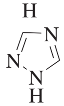
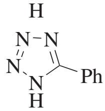


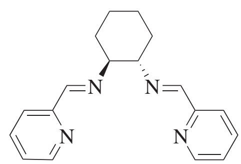
Scheme 47

Azole Nucleophiles. Five-membered-ring *N*-heteroaromatic compounds (azoles) are highly effective substrates for Cu-catalyzed C–N bond-forming reactions. Copper catalysts tend to be highly selective for *N*-arylation, whereas palladium catalysts often give mixtures of *N*- and *C*-arylated products.[127] Nearly all classes of *N*-heterocyclic compounds with an N–H bond are reactive, including pyrroles, imidazoles, pyrazoles, triazoles, and their benzannulated analogs. The order of reactivity among azoles is pyrazole > imidazole > indole > pyrrole, > 1,2,4-triazole ≫5-phenyltetrazole for arylations catalyzed by Cu_2O/tetradentate Schiff-base ligand at 80° (Scheme 48).[40] This trend may represent a balance of the acidity of the N–H bond, which would promote Cu–azolate formation, and the nucleophilicity of the resulting azolate anion, which would favor C–N bond formation. On the



Y = N, CH

Azole	X	Solvent	Temp (°)	Yield (%)
	Br	MeCN	82	93
	Br	MeCN	82	48
	I	MeCN	82	94
	I	DMF	82	79
	I	DMF	110	0

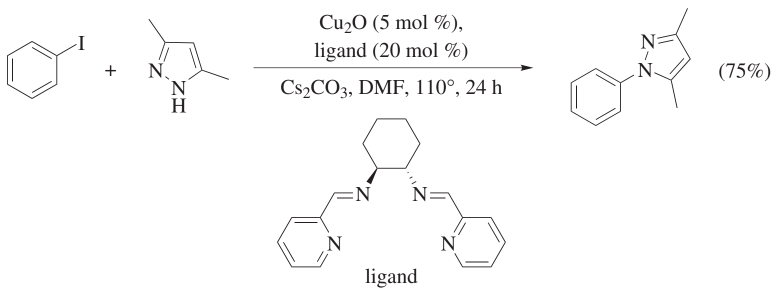


ligand

Scheme 48

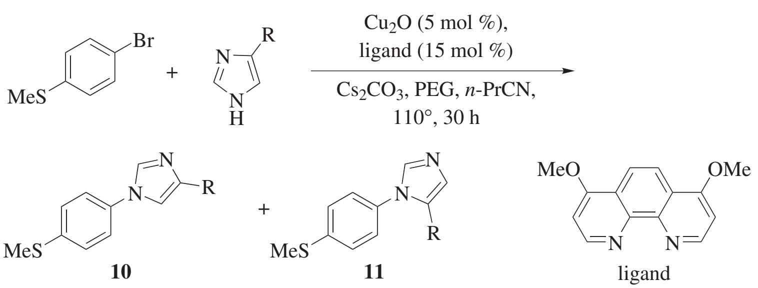
basis of nucleophilicity, pyrrole and indole would be expected to be most reactive towards arylation, but their higher pK_a values apparently slow the formation of the Cu–azolate intermediate. Thus, the more acidic pyrazole and imidazole substrates are most reactive. The presence of additional nitrogen atoms in the ring results in a decrease in activity. Presumably the lower nucleophilicity of triazoles and tetrazoles has a larger effect on reactivity than the increased acidity of the N–H bond. No successful examples of tetrazole arylation have been reported.

Azole *N*-arylation reactions are highly tolerant of substitution on the azole ring, but do show similar steric and electronic effects to other nitrogen nucleophiles. Substitution next to the nucleophilic nitrogen can reduce the rate of coupling, thus requiring higher temperatures and/or catalyst loadings to achieve high yields. Coupling of 3,5-dimethylpyrazole and iodobenzene provides a 12% yield of coupled product at 80° using a Cu_2O/salicylaldehyde oxime catalyst system, whereas unhindered pyrazoles give high yields under the same conditions.[82] Increasing the reaction temperature to 110° and changing the ligand to a tetradentate bis(imine) increases the yield to 75% (Scheme 49), which is still lower than that observed with unhindered pyrazoles. Electron-withdrawing substituents such as ester, ketone, or trifluoromethyl groups are generally tolerated without a significant effect on the coupling yield.[128]



Scheme 49

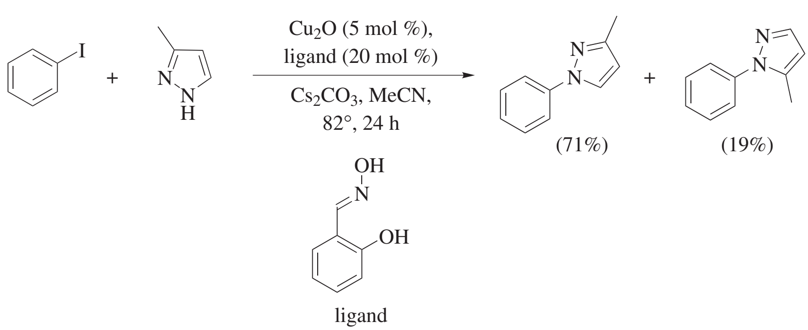
Arylation of azoles is generally highly selective for *N*-arylation over *C*-arylation. For non-symmetrical azoles with multiple nitrogen centers, mixtures of products are often obtained, since each nitrogen atom can share the negative charge due to resonance delocalization. Unsymmetrical, 4-substituted imidazoles often give mixtures of products with *N*-arylation at the less hindered nitrogen being favored. The size of substituents on the imidazole as well as the steric demand of the aryl group affect the selectivity. The coupling of 4-methylimidazole and 1-bromo-4-methylthiobenzene gives a 4.4:1 ratio of N1 (product **10**) and N3 (product **11**) arylation using a catalyst derived from Cu_2O/4,7-dimethoxyphenanthroline (Scheme 50).[84] With 4-phenylimidazole as the substrate, a complete selectivity for product **10** is obtained. Similarly, coupling of 4-methylimidazole and 1-bromo-2-isopropylbenzene affords a 44:1 selectivity for the N1 product.



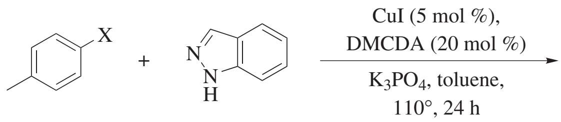
R	Yield (%)	**10/11**
Me	97	4.4:1
Ph	96	99:1

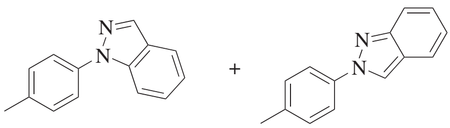
Scheme 50

Unsymmetrical pyrazoles can also give mixtures of products with the less-hindered nitrogen being the preferred site of arylation. Reaction of 3-methylpyrazole and iodobenzene gives a mixture of 3-methyl-1-phenylpyrazole and 3-methyl-2-phenylpyrazole in a 3.5:1 ratio using CuI/salicylaldehyde oxime as the catalyst system (Scheme 51).[82] Indazoles give mixtures of N1- and N2-arylated products. The selectivity is dependent upon the aryl halide. Aryl iodides give high selectivity (15–20:1) for the 1-arylindazole product using CuI/DMCDA as the catalyst system, whereas the corresponding aryl bromides give modest selectivities (<2:1) for the 1-arylindazole under the same conditions (Scheme 52).[128] Mixed results are obtained with 1,2,3-triazoles. A Cu_2O/phenanthroline-catalyzed coupling of iodobenzene and 1,2,3-triazole gives 1-phenyl-1,2,3-triazole as the sole product.[129] In contrast, the ligand-free Cu_2O/Fe(acac)$_3$ catalyst gives a nearly 1:1 mixture of 1-phenyl- and 2-phenyl-1,2,3-triazole (Scheme 53).[130] On the other hand, benzotriazole is arylated to give 1-arylbenzotriazoles with high selectivity in most reports,[128] although mixtures of products are obtained with a ligand-free catalyst system using TBAF as the base.[81] Complete selectivity for N1 is observed with 1,2,4-triazoles.[128]



Scheme 51

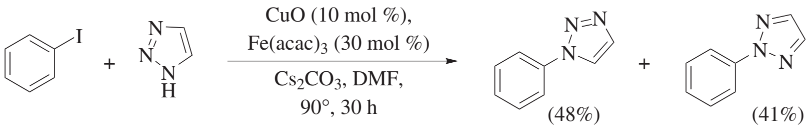




N1 arylation N2 arylation

X	N1 + N2 Yield	N1/N2
I	85%	17:1
Br	75% conv	1.8:1

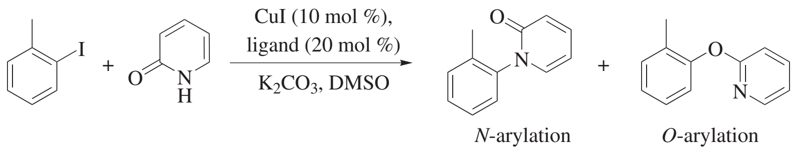
Scheme 52



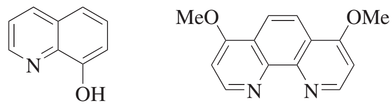
Scheme 53

Amides, Sulfonamides, and Related Compounds. Amides and related compounds, including carbamates, ureas, guanidines, and sulfonamides, are generally useful substrates for Cu-catalyzed C–N bond-forming reactions. The more acidic N–H bond of amides and related compounds typically results in their being more reactive than aryl and alkyl amines. Like azoles, Cu-based catalysts have proven to be much more general for coupling of amides than palladium catalysts. Although both the nitrogen and oxygen can act as the nucleophile in amidate anions, the nitrogen is generally the exclusive site of arylation. However, pyridones give competitive *O*-arylation with sterically hindered aryl halides. Coupling of 2-pyridone with 2-iodotoluene gives a 4.8:1 ratio of *O*- to *N*-arylation using 8-hydroxyquinoline as the ligand, whereas 4,7-dimethoxyphenanthroline gives a 1.8:1 preference for *N*-arylation (Scheme 54).[131] Unhindered aryl halides give complete selectivity for *N*-arylation using 4,7-dimethoxyphenanthroline as the ligand.

Primary amides are the most widely reported class of amide substrates. Arylations of primary amides are largely unaffected by steric and electronic effects, although careful analysis of these effects under common conditions has not been reported. Electron-deficient amides, such as trifluoroacetamide, are arylated in good yields.[132] Hydrazides undergo *N*-arylation on the more acidic amide nitrogen (Scheme 55),[133,134] although this selectivity can be reversed with more hindered aryl halides (Scheme 56).[135] Arylation of acyclic secondary amides has been less widely reported than that of primary amides or lactams. Some authors report lower yields or reaction rates with secondary amides, such as acetanilide.[136−138] Optimized systems based on CuI/diamine (diamine = DMEDA or DMCDA) catalysts give comparable yields for primary and secondary amides, however.[69,115] Lactams typically show comparable reactivity to primary amides, with pyrrolidinone being a commonly



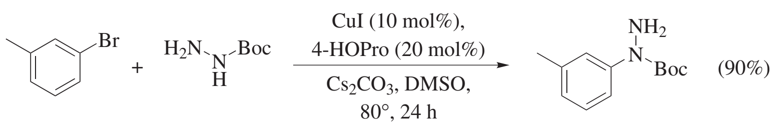
			Yield (%)		
Ligand	Temp (°)	Time (h)	*N*-Aryl	*O*-Aryl	*N*-Aryl/*O*-Aryl
A	120	48	14	67	1.0:4.8
B	150	96	40	22	1.8:1.0



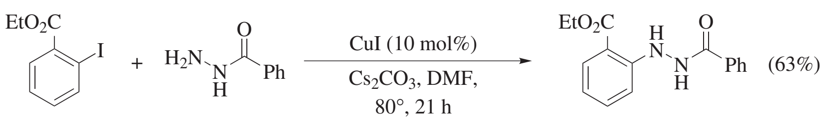
ligand **A** ligand **B**

Scheme 54

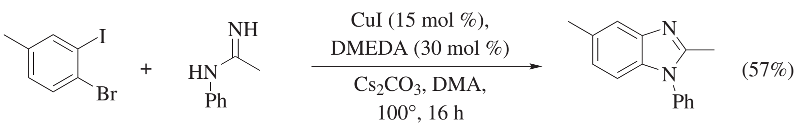
used model substrate. Both 2- and 4-hydroxypyridines are also effective substrates that give *N*-arylpyridones upon *N*-arylation.[131] Amidines are used primarily in tandem processes leading to benzimidazoles and quinazoline derivatives (Scheme 57).[139−143]



Scheme 55

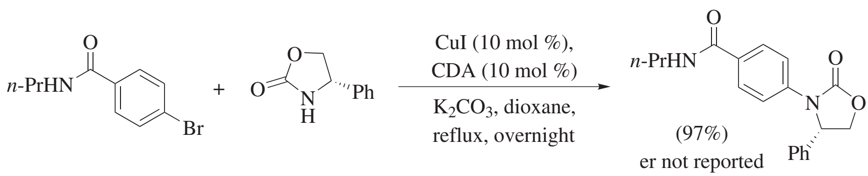


Scheme 56

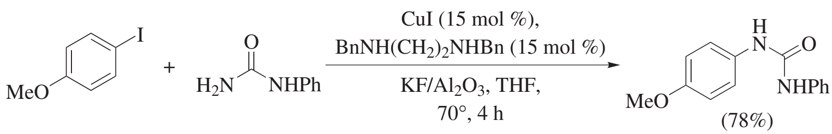


Scheme 57

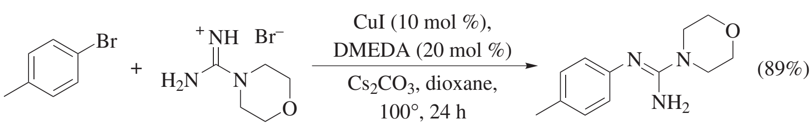
N-Arylation of carbamates, ureas, and guanidines has been reported for a number of catalyst systems. Carbamates typically show comparable reactivity to structurally similar amides. Examples of acyclic carbamates are largely limited to Boc-protected ammonia[83] and hydrazine (Scheme 55),[133,134] and hydroxylamine ethers.[144] The majority of examples of carbamate arylations involve oxazolidinone derivatives. Oxazolidinone-based chiral auxiliaries can be *N*-arylated without degradation of enantiomeric purity (Scheme 58).[87,145] Notably in this example, the cyclic carbamate nitrogen is cleanly arylated in the presence of the secondary amide. Both acyclic and cyclic ureas are effective nitrogen nucleophiles in Cu-catalyzed C–N bond-forming reactions, although the reported yields are modest (40–70%).[146−148] Mono-*N*-substituted ureas undergo exclusive arylation on the unsubstituted nitrogen (Scheme 59).[146] For symmetric ureas, mono- or diarylation can occur. Monoarylation requires an excess of the urea substrate.[148] Diarylation of guanidinium nitrate to give *N,N′*-diarylguanidines occurs in modest to good yields (30–90%) using a CuI/salicylamide catalyst system.[149] Higher yields (75–90%) are reported for the monoarylation of an unsymmetrical guanidine derivative using CuI/DMEDA as the catalyst precursor (Scheme 60).[141]



Scheme 58

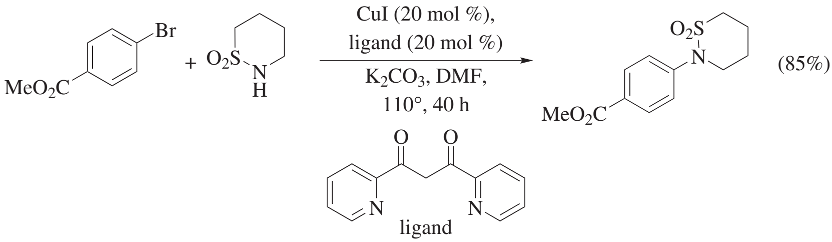


Scheme 59



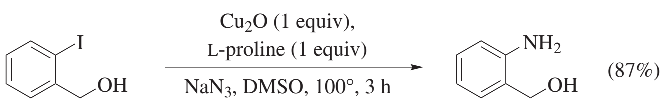
Scheme 60

Copper catalysts are effective for the *N*-arylation of sulfonamides. Primary and secondary sulfonamides are *N*-arylated with unhindered aryl halides in high yields.[150] Low yields are obtained with 2-substituted aryl halides and secondary sulfonamides, however. Sultams generally give modest to good yields (40–85%, Scheme 61).[151] In a direct comparison, a Pd/Xantphos (Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethyl-9*H*-xanthene) catalyst system provides higher yields than a Cu_2O/phen catalyst system for the *N*-arylation of 1,4-butanesultam.[152] A ligand-free system gives moderate yields for the coupling of aryl iodides and sulfonimidamides.[153]

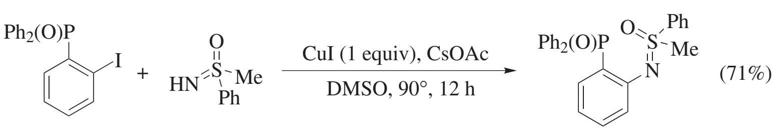


Scheme 61

Other Nitrogen Nucleophiles. Other nitrogen nucleophiles that have been applied to Cu-catalyzed C–N bond-forming reactions include azides and sulfoximines. Aryl azides are useful precursors to a variety of compounds. Copper catalysts provide high yields for the coupling of both aryl and vinyl halides with sodium azide under mild conditions.[154,155] At higher temperatures, the resulting aryl azide can be decomposed to give aniline products (Scheme 62).[75,156,157] A stoichiometric amount of copper is required to promote the azide reduction. Thus, azide nucleophiles can be used as an alternative to ammonia for the synthesis of primary aryl amines. Both ligand-free and DMEDA-supported copper catalysts provide good yields in the *N*-arylation of sulfoximines (Scheme 63).[158,159]



Scheme 62



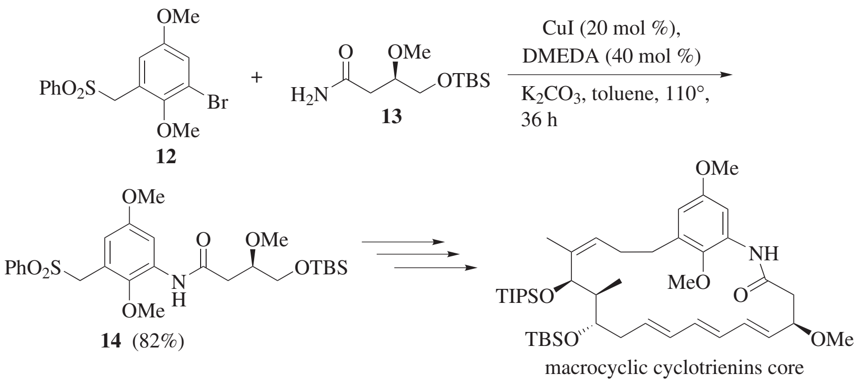
Scheme 63

APPLICATIONS TO SYNTHESIS

Synthesis of Natural Products and Biologically Active Compounds

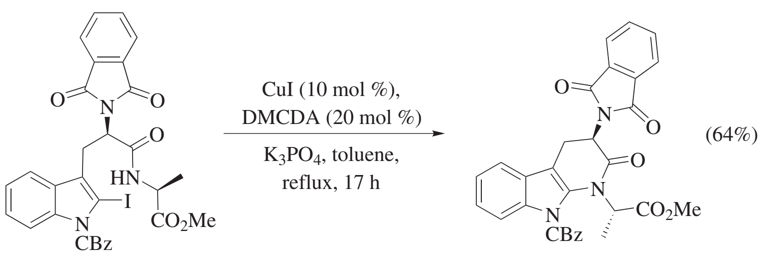
The ease and simplicity of Cu-catalyzed C–N bond formation along with the functional group tolerance of these reactions have made it a popular method in the synthesis of natural products.[16] Intramolecular and intermolecular amide arylation and vinylation reactions have been most widely used. Copper-catalyzed coupling of vinyl iodides and amides have been used in the synthesis of a large number of enamide-containing natural products. In this section, representative examples of the application of Cu-catalyzed C–N coupling reactions to the synthesis of natural products and pharmaceuticals are highlighted. Additional examples can be found in the "Tabular Survey" presented at the end of this chapter.

Amide arylation reactions have been used in the synthesis of a wide variety of alkaloid natural products. Intermolecular amide arylation is used in the early stages of the synthesis of the macrocyclic core of the cytotrienins **15** (Scheme 64).[160] Coupling of electron-rich aryl bromide **12** with functionalized amide **13** gives the aromatic segment **14**, which is further elaborated to provide **15**.



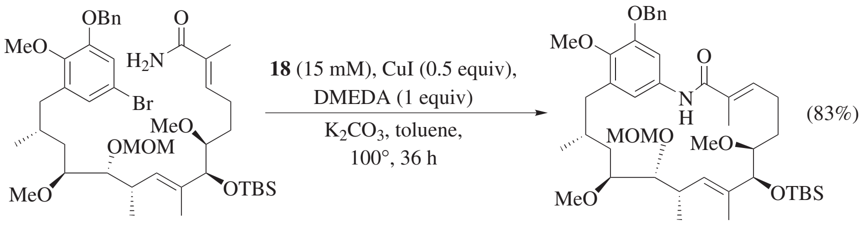
Scheme 64

A common application of Cu-catalyzed C–N bond formation is the synthesis of lactams through intramolecular amide arylation.[161] In the synthesis of chaetominine, the challenging intramolecular coupling of iodoindole **16** functionalized with a pendant hindered secondary amide affords a good yield of **17** (64%) using CuI/DMCDA as the catalyst in toluene at 110° with K_3PO_4 as base (Scheme 65).[162] No epimerization of the stereogenic centers is observed. Notably, there is no conversion when Pd/P(*o*-Tol)$_3$ is used as the catalyst.

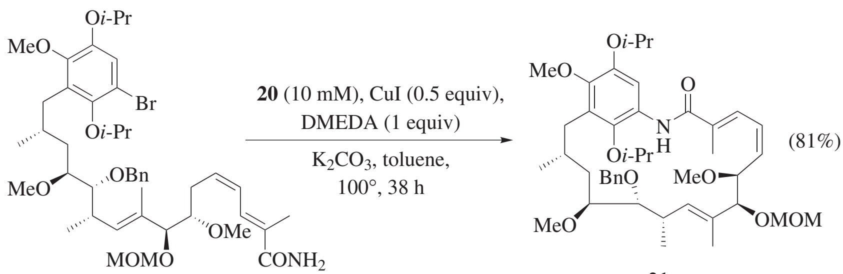


Scheme 65

Copper catalysts supported by diamine ligands are also effective at macrolactamization reactions. In the synthesis of reblastatin, intramolecular coupling of **18** gives 19-membered-ring lactam **19** in 83% yield using CuI/DMEDA (50 mol % Cu) at 100° for 36 hours at 0.015 M reaction concentration (Scheme 66).[163] This reaction is also used in the synthesis of the structurally similar macrolactam **21** in 81% yield from bromo amide **20** despite the presence of an isopropoxy group adjacent to the aryl bromide site (Scheme 67).[164] Deprotection of intermediate **21** provides geldanamycin.



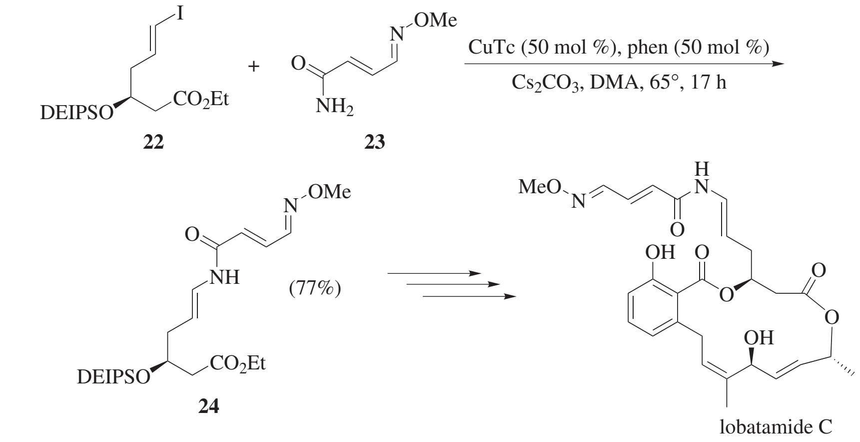
Scheme 66



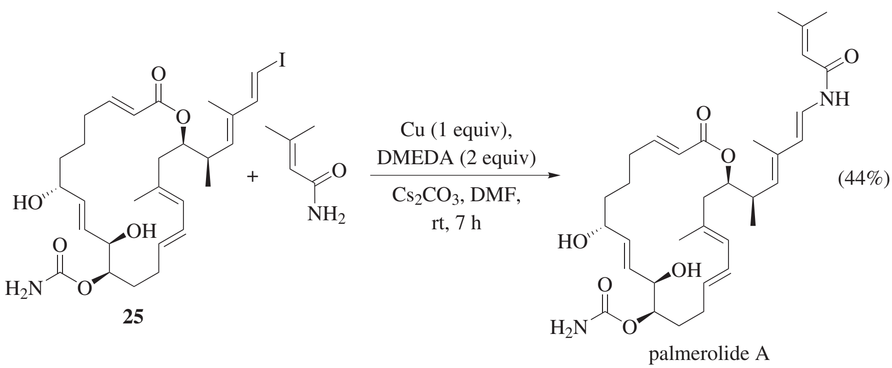
Scheme 67

Intermolecular coupling of vinyl iodides with amides is widely used in the synthesis of natural products with pendant enamide moieties. This approach was first used in the synthesis of lobatamide C (Scheme 68).[165] Coupling of enamide **23** with vinyl iodide **22** provides enamide **24**, which is then coupled with the lower portion of the macrocycle by sequential intermolecular esterification and Mitsunobu macrolactonization to provide lobatamide C.

Coupling of 3-methylbutenamide with late-stage intermediate macrocylic vinyl iodide **25** is the final step of the synthesis of palmerolide A (Scheme 69).[166] This method is used in the synthesis of a variety of structural analogs of palmerolide.[98]



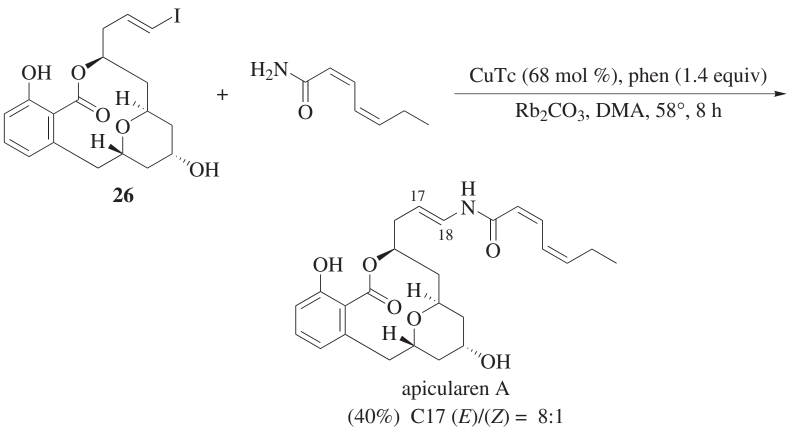
Scheme 68



Scheme 69

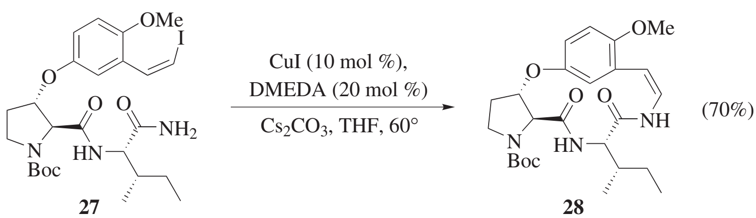
The synthesis of apicularen A highlights the functional-group tolerance of the Cu-catalyzed methodology. Coupling of (2*Z*,4*Z*)-2,4-heptadienamide with (*E*)-vinyl iodide **26** containing free phenol and alcohol groups affords apicularen A in 40% yield, predominantly with retention of the vinyl iodide configuration [(*E*)/(*Z*) = 8:1, Scheme 70].[167]

Intramolecular coupling of vinyl iodides and amides has been used to prepare a family of cyclopeptide alkaloids, including paliurines E and F, ziziphines N and Q, abyssenine A, and mucronine E.[168] These compounds contain 13–15-membered-ring lactams. The paliurine core **28** is synthesized in 70% yield from acyclic peptide **27** using CuI/DMEDA (Scheme 71). A similar strategy is used to prepare the ziziphine, abyssenine, and mucronine cores. Alternative macrocyclization reactions for the synthesis of cyclic peptide **28** were explored (Scheme 72), including ring-closing metathesis of diene **29** with Grubbs' second-generation catalyst (49%), Wacker-type cyclization of styrene amide precursor **30** (21%), and acid-catalyzed intramolecular

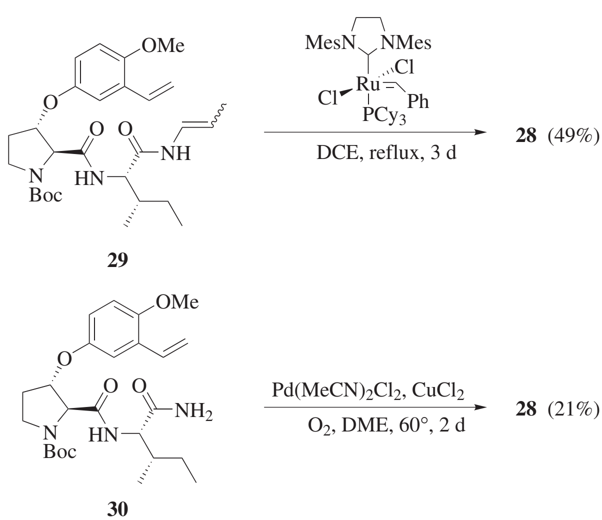


Scheme 70

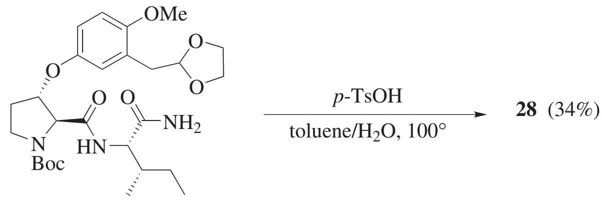
condensation of acetal-functionalized amide **31** (34%). The Cu-catalyzed cyclization proved superior to these alternative approaches under the conditions shown.



Scheme 71



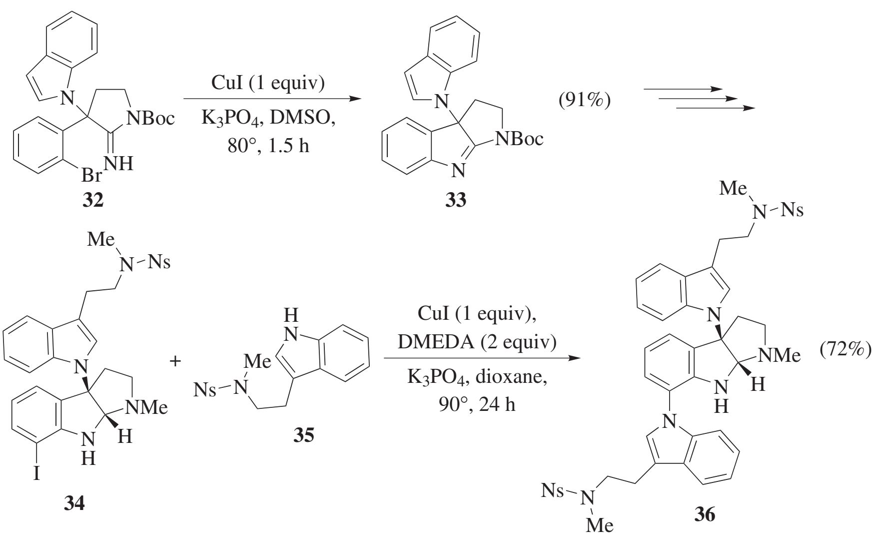
Scheme 72



31

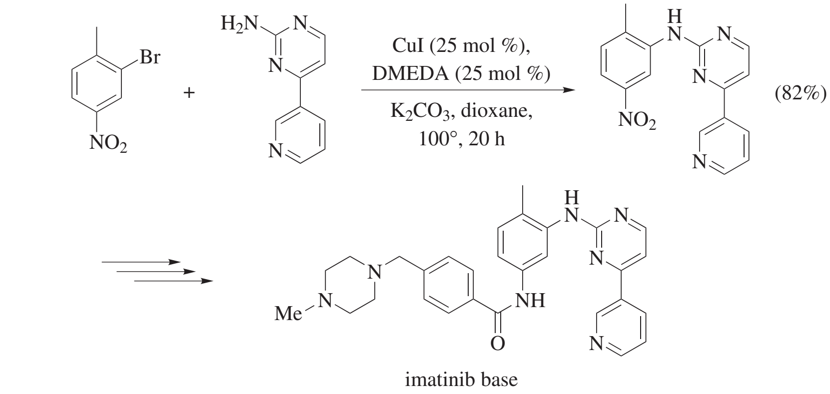
Scheme 72 (*Continued*)

Couplings with other nitrogen nucleophiles have received far less attention in the synthesis of natural products. Synthesis of the complex alkaloid psychotrimine involves two Cu-catalyzed C–N bond-forming reactions (Scheme 73).[169] The central ring system is formed by intramolecular cyclization of aryl bromide **32**. After further elaboration of pyrrolidinoindoline **33**, the final psychotrimine structure is formed by coupling of iodide **34** with indole **35** to afford protected psychotrimine **36**.

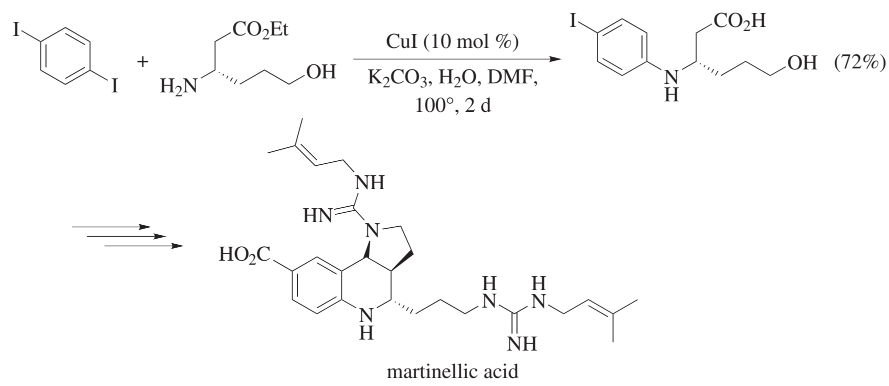


Scheme 73

Copper-catalyzed coupling of a 2-aminopyridine derivative and 2-bromo-4-nitrotoluene is used as the key step in a synthesis of the leukemia treatment imatinib (Scheme 74).[170] Arylation of ethyl (*S*)-3-amino-6-hydroxyhexanoate using CuI in aqueous DMF is used to prepare an early-stage intermediate in the synthesis of martinellic acid (Scheme 75).[171]



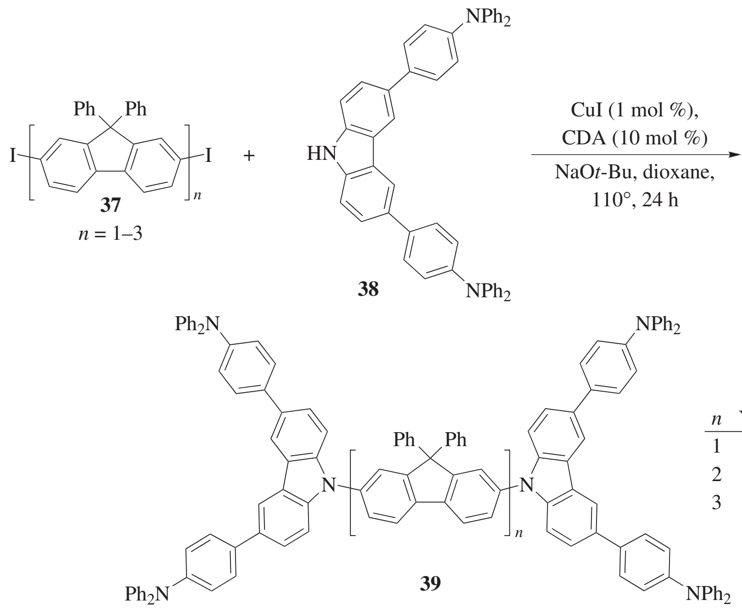
Scheme 74



Scheme 75

Electronic Materials

Aromatic amines are important components in many electronic materials. Triaryl amines are effective hole transport materials with applications in areas such as xerography, organic light-emitting diodes (OLEDs), and photovoltaics. The Cu-catalyzed coupling of diiodofluorene oligomers **37** with carbazole **38** provides oligocarbazoles **39** for use in OLED devices (Scheme 76).[172] Copper-catalyzed C–N bond formation has also been applied to the synthesis of ligands for luminescent metal complexes.[173,174] The ability to tolerate nitrogen-containing heteroaromatic substrates allows for the facile synthesis of chelating pyridine ligands. Triarylamine-based redox gradient dendrimers that can serve as charge storage molecules can be synthesized by successive Cu-catalyzed arylation of aniline derivatives.[175] The final dendrimer is prepared by condensation of aryl iodide **40** and triamine **41** to give dendrimer **42** (Scheme 77).



n	Yield (%)
1	45
2	51
3	55

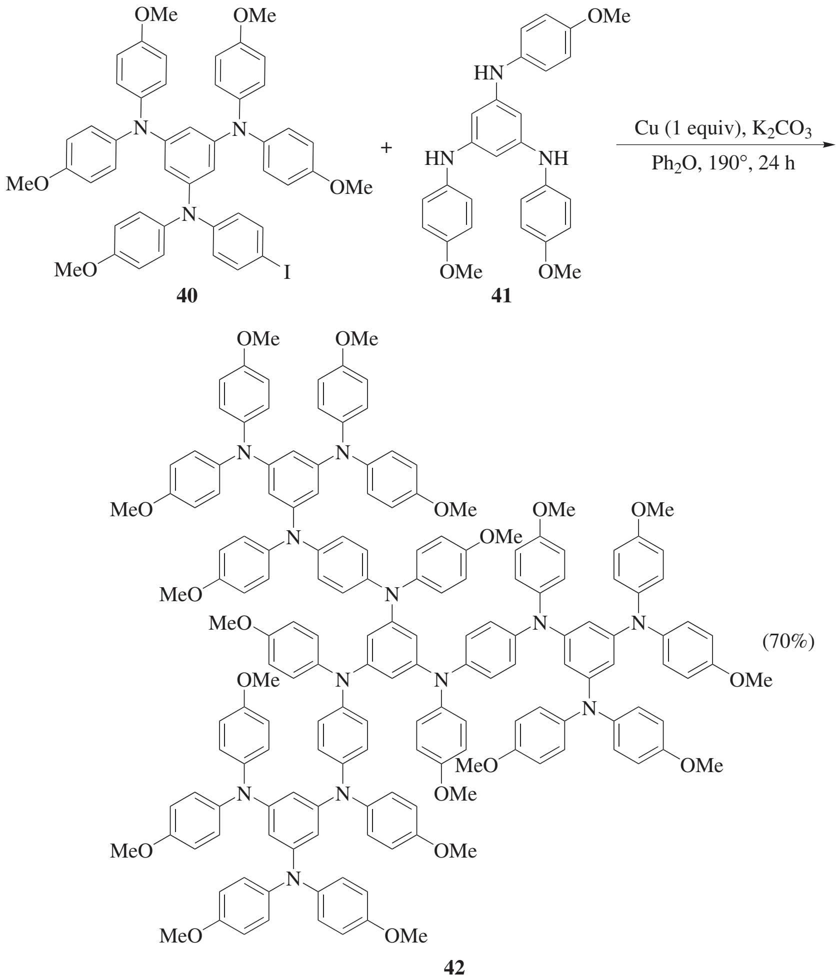
Scheme 76

Tandem Reactions for the Synthesis of Heterocyclic Compounds

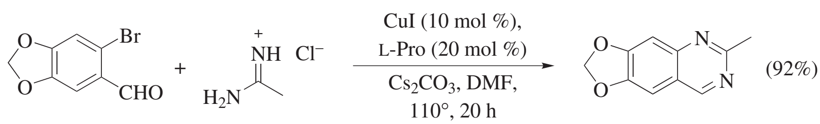
Copper-catalyzed C–N bond formation coupled with other reactions, such as condensations, substitutions, or other metal-catalyzed bond formations, has been widely used in the synthesis of heteroaromatic compounds. A full collection of these useful transformations is available in Tables 27 and 35 of the "Tabular Survey." Specific examples are highlighted here.

The most common approach is to couple an aryl halide having a reactive group in the *ortho* position with a nitrogen nucleophile having a complementary reaction partner in close proximity to the nitrogen. Condensation of bifunctional amidine nucleophiles with 2-halobenzaldehydes provides quinazolines by a sequence involving imine formation and Cu-catalyzed C–N bond formation (Scheme 78),[140] whereas condensation with 2-halo benzoic acids provides quinazolinones through an amide formation.[142] Larger rings, such as benzodiazepines, can be prepared by the condensation of 2-halobenzyl amines and amino acids (Scheme 79).[176] The configurational homogeneity of the amino acid is retained in these reactions, allowing the natural pool of chiral amino acids to be used.

An interesting alternative approach to seven-membered (e.g., benzodiazepines) or larger rings involves the coupling of aryl halides having a pendant nitrogen nucleophile with β-lactams. Subsequent attack by the pendant amine on the lactam provides the ring-expanded product (Scheme 80).[177] Copper-catalyzed coupling of acetanilides with ammonia followed by intramolecular condensation provides



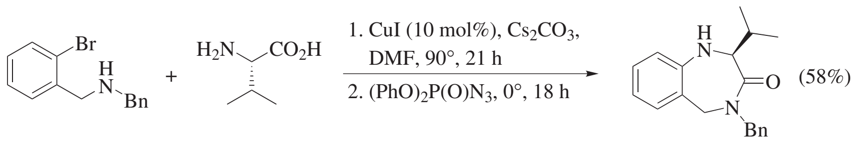
Scheme 77



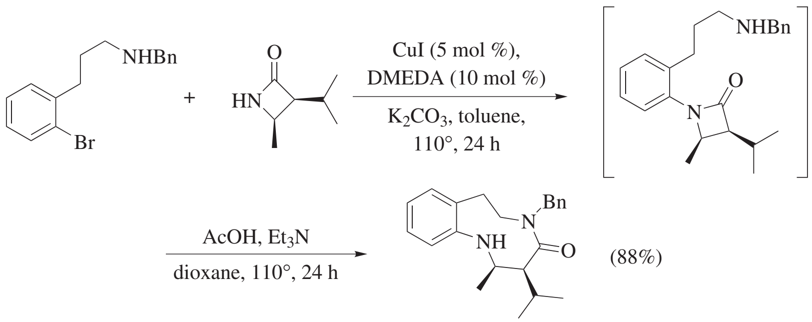
Scheme 78

benzimidazoles.[178] Condensation of α-halo acetamides with 2-halophenols is an effective way to prepare benzoxazin-3-(4*H*)-ones (Scheme 81).[179,180]

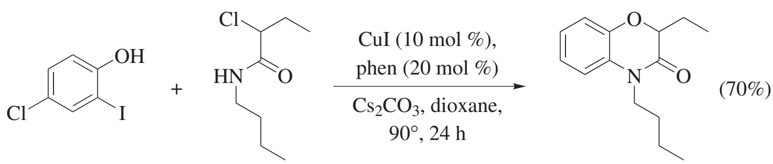
An alternative approach to tandem heterocycle synthesis is to generate the nitrogen nucleophile by initial nucleophilic attack on a nitrogen-containing electrophile,



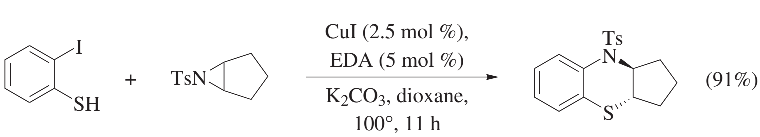
Scheme 79



Scheme 80

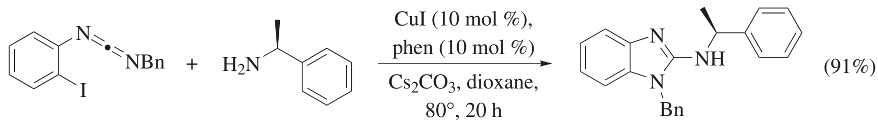


Scheme 81

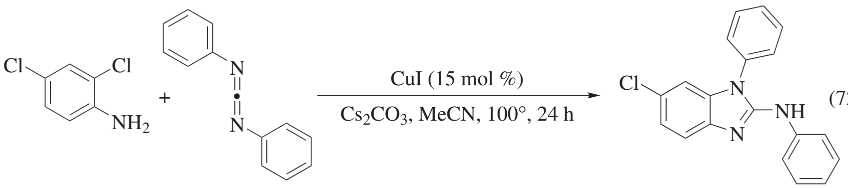


Scheme 82

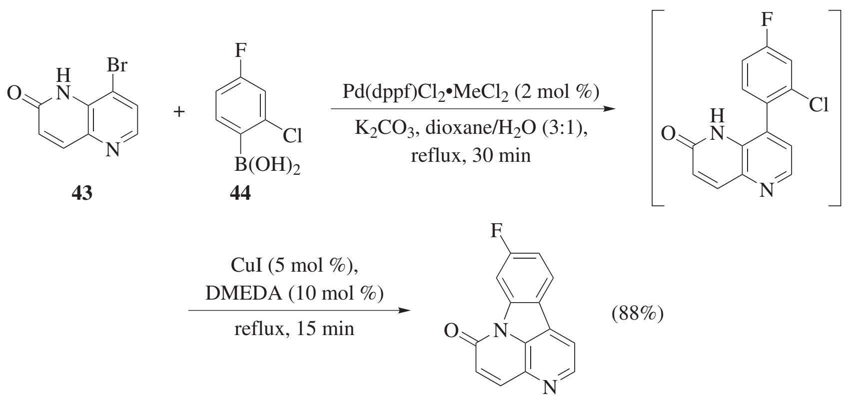
such as a carbodiimide or aziridine. Nucleophilic attack by 2-halophenols or 2-halothiophenols on protected aziridines generates an amido ion that undergoes intramolecular coupling with the pendant aryl halide to provide tricyclic heterocycles (Scheme 82).[181,182] Tandem nucleophilic attack on a carbodiimide followed by Cu-catalyzed arylation of the newly generated amidate anion provides access to benzimidazole and benzoxazole rings (Scheme 83).[183] Alternatively, a 2-halophenol or 2-haloaniline derivative can react intermolecularly with a carbodiimide followed by Cu-catalyzed C–N bond formation to give benzoxazole and benzimidazole derivatives (Scheme 84).[184]



Scheme 83

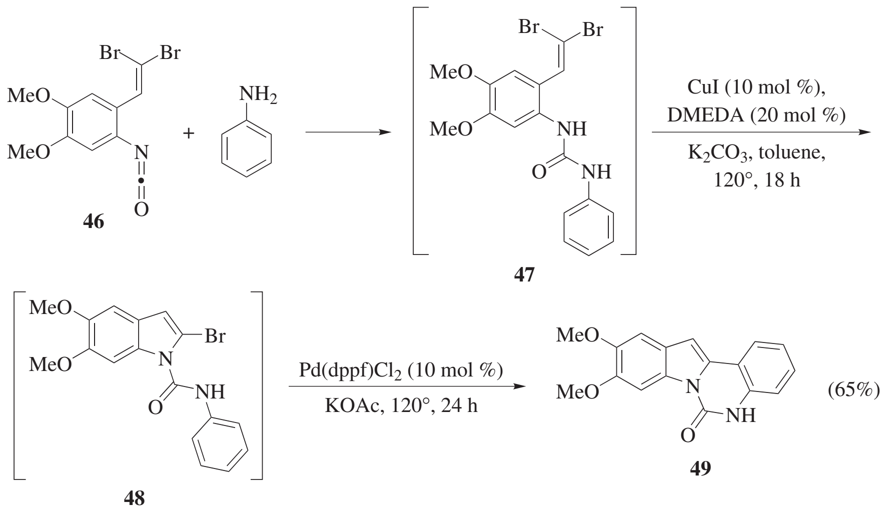


Scheme 84



Scheme 85

The complementary reactivity of copper and palladium catalysts can be used to generate complex organic structures by tandem catalysis. Canthin-6-one (**45**) can be prepared in high yield by the condensation of 2-chlorophenylboronic acid **44** with naphthyridone **43** via tandem Pd-catalyzed Suzuki coupling and Cu-catalyzed ring closure through a lactam arylation (Scheme 85).[185] This procedure can be carried out in one pot. Through proper reaction sequencing, highly complex ring systems can be developed from relatively simple precursors. A tandem Cu- and Pd-catalyzed coupling of *ortho-gem*-dibromovinylphenyl isocyanate **46** with aniline provides access to pyrimido[1,6-*a*]indol-1(2*H*)-one (**49**) by a one-pot cascade process (Scheme 86).[186] The cascade reaction involves nucleophilic attack by aniline on isocyanate **46** followed by intramolecular coupling of the generated urea **47** with the vinyl bromide. The final ring is formed by Pd-catalyzed intramolecular coupling of the bromoindole moiety in **48** with the proximal aryl group. In this reaction three new bonds and two new rings are formed in 60–87% yields.



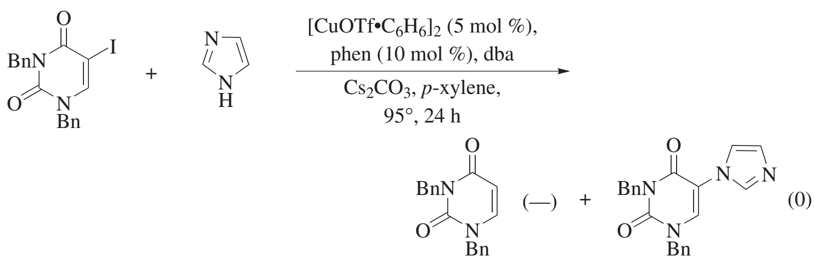
Scheme 86

SIDE REACTIONS

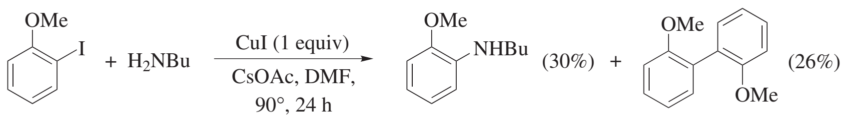
Relatively few side products have been identified in Cu-catalyzed C–N bond-forming reactions. Yields are generally high (>80%) for these reactions, but the identity of the remaining mass balance is usually not reported even in cases with lower yields. Hydrodehalogenation has been reported by a few authors. Deiodination is the only process observed in the reaction of a protected 5-iodouracil derivative with imidazole (Scheme 87), although coupling with heteroaryl and alkyl amines is achieved in good yields.[187] Dehydrobromination is observed in the coupling of 2-bromoanisole with piperidine using a CuCl/acac catalyst, whereas unhindered aryl bromides give the desired coupling product.[188] Homocoupled biaryl products are obtained in 26% yield in the coupling of 2-substituted aryl iodides with butylamine using stoichiometric amounts of CuI (Scheme 88).[189] In the coupling of an (*E*)/(*Z*) mixture (90:10) of β-bromostyrene with pyrazole, the (*E*)-isomer gives complete conversion to (*E*)-β-pyrazolylstyrene, whereas the (*Z*)-isomer undergoes elimination of HBr to give phenylacetylene (Scheme 89).[190]

The lack of chemoselectivity in substrates that contain more than one potential nucleophile is the most common cause of side products in Cu-catalyzed C–N bond-forming reactions. Arylation of amine ligands has been noted in some cases. When CDA or EDA is used as a ligand, the *N,N′*-diarylated ligands are observed in 1–10% yield.[69,115,191] The arylated ligands appear to be ineffective at promoting the coupling reaction, which is why CDA and EDA are less effective than DMCDA or DMEDA in most cases. The more hindered secondary amine ligands are not prone to arylation. Similarly, when *N*-methylglycine is used as a ligand, approximately

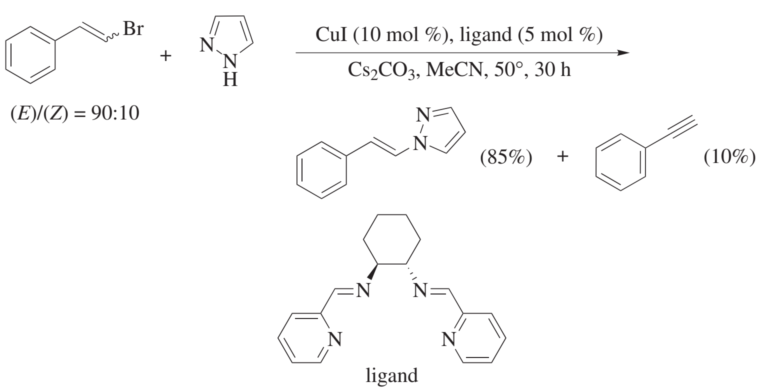
5% of the *N*-arylated glycine is obtained.[192] This side reaction can be avoided by using *N,N*-dimethylglycine (DMG) or L-proline instead. Alcohol solvents can also be competitively arylated to give aryl ethers as side products (Scheme 90).[193−195] By proper choice of ligand, complete selectivity for *N*-arylation over *O*-arylation can be achieved (Scheme 91).[196] Using 2-isobutyrylcyclohexanone, selective *N*-arylation occurs to give product **50**, whereas using 3,4,7,8-tetramethylphenanthroline as the ligand gives the *O*-arylation product **51** with high selectivity.



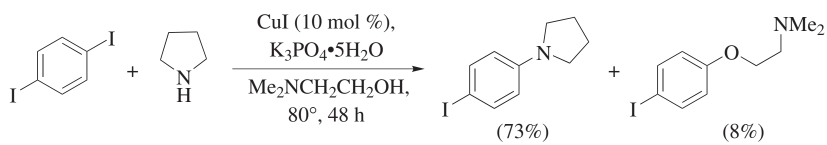
Scheme 87



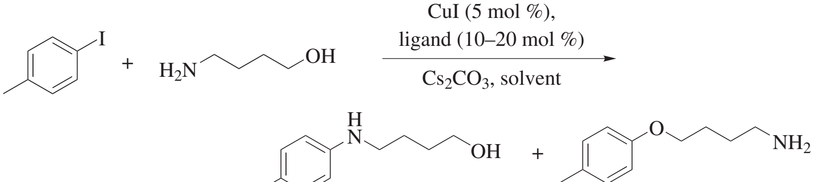
Scheme 88



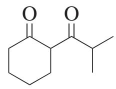
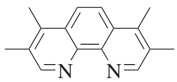
Scheme 89



Scheme 90

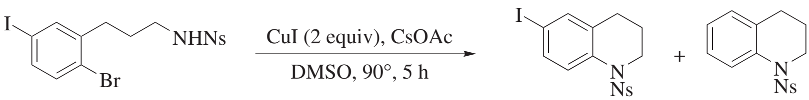


50 **51**

Ligand	Solvent	Temp	Yield (%)	**50/51**
	DMF	rt	99	>50:1
	toluene	80°	91	1:18

Scheme 91

Overall, Cu-catalyzed reactions appear to be fairly selective compared to Pd-catalyzed C–N bond formation. Copper-catalyzed reactions are more selective for substrates with multiple halogens than palladium catalysts. In the intramolecular cyclization of **52**, iodotetrahydroquinoline **53** is formed in 81% yield with only a 10% yield of the deiodinated product **54** (Scheme 92).[197] Using a palladium catalyst, iodotetrahydroquinoline **53** is obtained in <3% yield with the remaining material being a mixture of deiodinated compounds and oligomers. In the coupling of aryl bromide **55** bearing a benzylic alcohol moiety, palladium catalysts afford mixtures of ketone **56** and other unidentified products (Scheme 93).[198] In contrast, CuI in combination with a salicylamide ligand provides the desired amine product **57** without oxidation of the benzylic alcohol moiety.

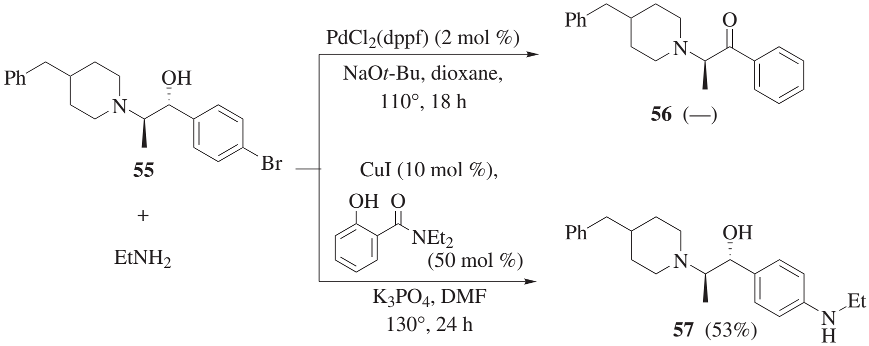


52 **53** (81%) **54** (10%)

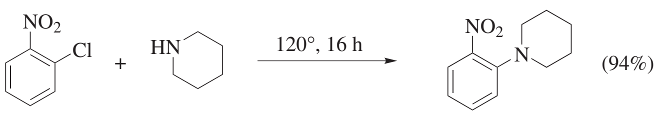
Scheme 92

COMPARISON WITH OTHER METHODS

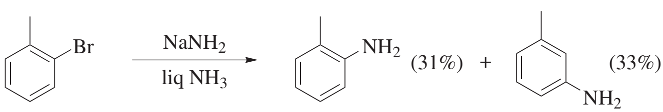
A number of classical routes are known for introduction of amine or amide nitrogens on aromatic rings, but these non-metal-catalyzed routes typically have significant limitations. A classic route is electrophilic nitration of aromatic rings followed by reduction of the nitro group to an amine. This method is limited to the normal electrophilic aromatic substitution patterns. In addition, only primary aniline derivatives can be made in this way. Nucleophilic addition of amines to electron-deficient aromatic rings via nucleophilic aromatic substitution provides a method to prepare a wider range of aryl amines (Scheme 94).[199] Ammonia and primary or secondary amines can be used in these reactions, but the aromatic ring must have one or more strongly electron-withdrawing groups positioned *ortho* and/or *para* to the leaving group. Nucleophilic substitution via the benzyne mechanism is possible with aryl halides lacking strong electron-withdrawing groups.[200] The benzyne mechanism requires strongly basic amido nucleophiles, which limits the functional-group tolerance of this methodology. In addition, for substituted aryl halides, mixtures of *ipso*- and *cine*-substitution products can be obtained (Scheme 95)[201] unless a substituent with an electronic directing effect is present. Naphthols can be converted into naphthylamines by the Bucherer reaction (Scheme 96).[202]



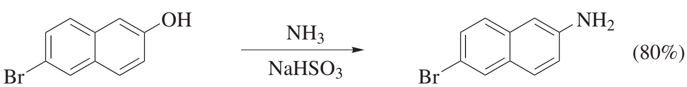
Scheme 93



Scheme 94

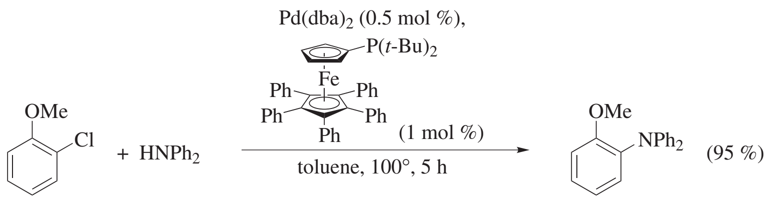


Scheme 95

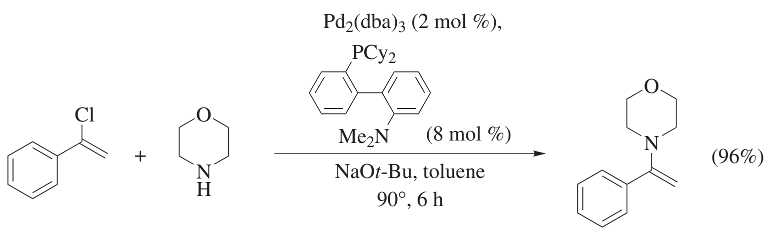


Scheme 96

Metal-catalyzed substitutions provide a more general approach to the synthesis of aryl and alkenyl amine derivatives. The classic Ullmann method represented the state-of-the-art for metal-mediated C–N bond formation until the 1990s, but the harsh conditions and modest yields limited its application. The development of Pd-catalyzed C–N bond formation largely replaced the use of traditional Ullmann-type couplings for arylation of amines. The mild conditions and improved scope of the Pd-catalyzed reactions, particularly with less reactive aryl bromide and chloride substrates, resulted in these methods becoming the dominant approach to amine *N*-arylation (Schemes 97 and 98).[6,7,203] Although the Pd-catalyzed method is highly useful, it does suffer from a number of drawbacks that has led to a resurgence of interest in the Cu-catalyzed methods. One obvious factor is cost. Palladium currently costs $20/g ($2,900/mole), whereas copper costs $0.01/g ($0.61/mole).[204] In addition, Pd-catalyst systems typically require expensive phosphines or *N*-heterocyclic carbene ligands, whereas Cu-catalyst systems rely on less expensive diamine or amino acid ligands. Even factoring in the use of higher catalyst loadings of copper (typically 5–20 mol %) compared to Pd (1–2 mol %), the cost difference is significant. Palladium catalysts tend to be more reactive toward aryl halides, so the reactions can generally be carried out at lower temperatures and lower catalyst loadings than are required for copper catalysts. Copper catalysts show limited reactivity with aryl chlorides and are ineffective with aryl sulfonate substrates, whereas optimized palladium systems can readily activate aryl chlorides and sulfonates.

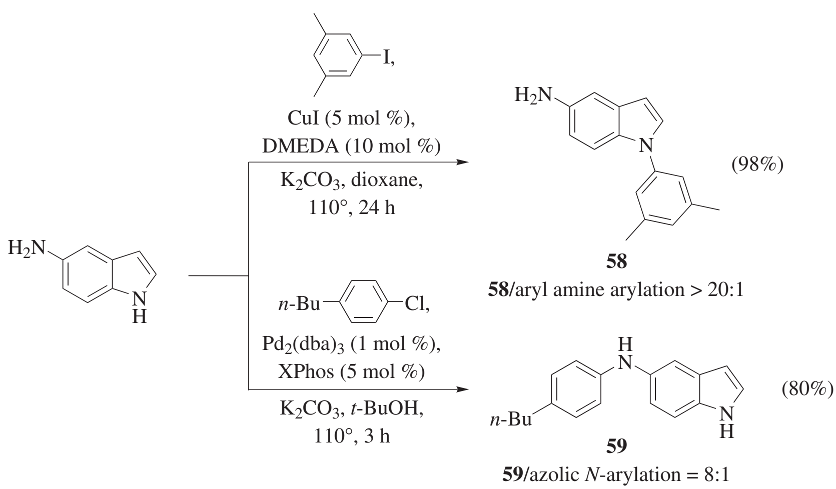


Scheme 97



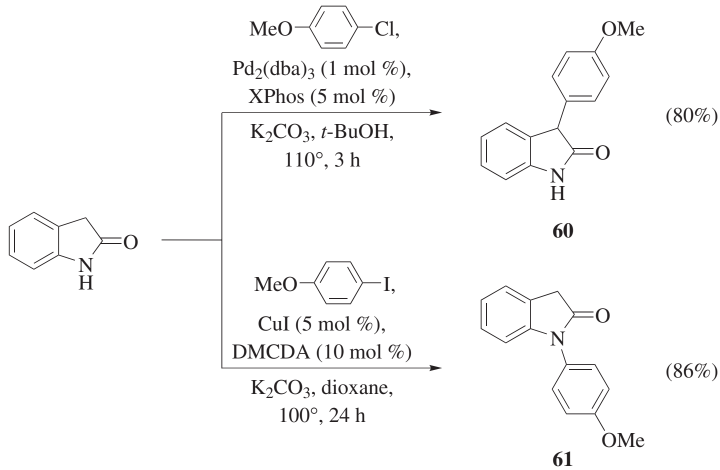
Scheme 98

Although there is overlap between the use of copper and palladium catalysts for nitrogen arylation, the two systems have complementary applications. Pd-catalyzed reactions are generally most useful for arylation of amines, but are less effective for the arylation of less nucleophilic nitrogen sources such as amides and azoles. In contrast, copper catalysts are highly effective for the coupling of amides and azoles. This complementary reactivity can be used to carry out highly selective functionalizations of substrates with two nitrogen nucleophiles. Using a CuI/DMEDA catalyst system, arylation of 2-, 3-, or 4-aminobenzamide with aryl bromides occurs selectively (>50:1) on the amide nitrogen (Scheme 38).[107] The copper catalyst also selectively arylates 5-aminoindole on the azolic nitrogen to afford **58** with >20:1 selectivity (Scheme 99). Arylation of the same substrate using a $Pd_2(dba)_3$/XPhos (XPhos = 2′,4′,6′-triisopropyl-2-dicylohexylphosphinobiphenyl) catalyst gives predominantly (>8:1) arylation on the aryl amine nucleophile (product **59**), rather than the azole nitrogen. Another example of this type of complementary reactivity between palladium and copper catalysts is seen in the arylation of oxindoles (Scheme 100).[205] Using Pd/XPhos, arylation occurs on the α-carbon to give arylated product **60**. With CuI/DMCDA, selective arylation of the amide nitrogen occurs to give *N*-arylated product **61**. DFT-level calculations show that the *N*-bound palladium intermediate is more stable than the *C*-bound intermediate by 4.8 kcal/mol, but that reductive elimination to form the C–C bond has a lower activation barrier than C–N bond formation by 2.4 kcal/mol, which is the selectivity-determining step. For the copper system, the Cu–amidate complex is more stable than the Cu–enolate complex by 14.1 kcal/mol. Thus, formation of the more stable amidate complex is the selectivity-determining step.

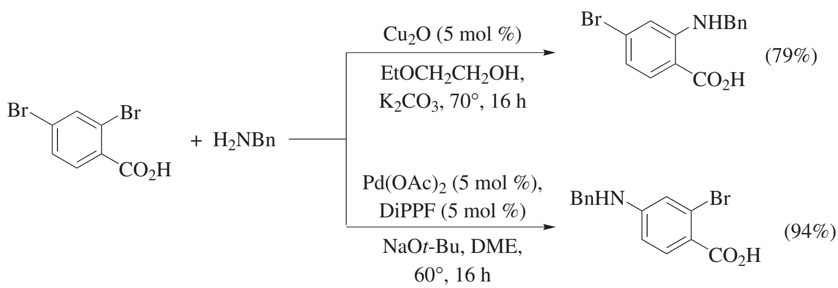


Scheme 99

Palladium and copper may also show different selectivities for aryl halide activation. 2-Halobenzoic acid derivatives show unusually high reactivity in Cu-catalyzed arylation reactions.[206] Coupling of 2,4-dibromobenzoic acid with amines using a copper catalyst leads to high selectivity for functionalization at the 2-position (Scheme 101). Use of a Pd/DiPPF (DiPPF = 1,1′-bis(diisopropylphosphino)ferrocene) catalyst gives selective arylation at the 4-position with >99:1 selectivity.

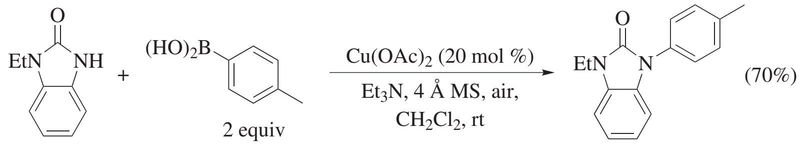


Scheme 100



Scheme 101

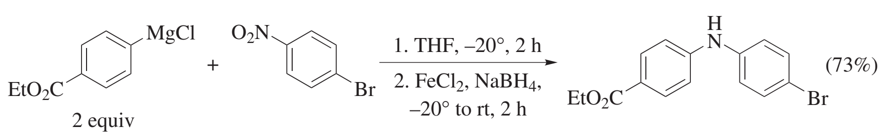
The oxidative coupling of organoboronic acids with nitrogen nucleophiles catalyzed by copper under mild conditions revitalized interest in Cu-catalyzed cross-coupling.[12] The initially reported systems involve the reaction of arylboronic acids with a range of nitrogen nucleophiles using stoichiometric amounts of $Cu(OAc)_2$ to mediate the reaction in the presence of a base.[8,9] These systems allow the Cu-promoted C–N bond formation to occur at room temperature, which is a significant improvement on the harsh conditions required for traditional Ullmann couplings. However, the reaction requires an excess of the boronic acid coupling partner in addition to a stoichiometric amount of copper. Catalytic versions were soon developed that utilize stoichiometric amounts of secondary oxidants, such as oxygen or amine *N*-oxides (Scheme 102).[10,207] Although these systems allow for the use of a catalytic amount of copper, they still typically require a 2:1 ratio of boronic acid to the nitrogen nucleophile. Because arylboronic acids are typically derived from aryl halides, and are significantly more expensive, the need to use superstoichoimetric amounts is undesirable. The development of efficient Cu-catalyzed couplings of aryl halides with nitrogen nucleophiles has largely supplanted the oxidative couplings with organometallic substrates.



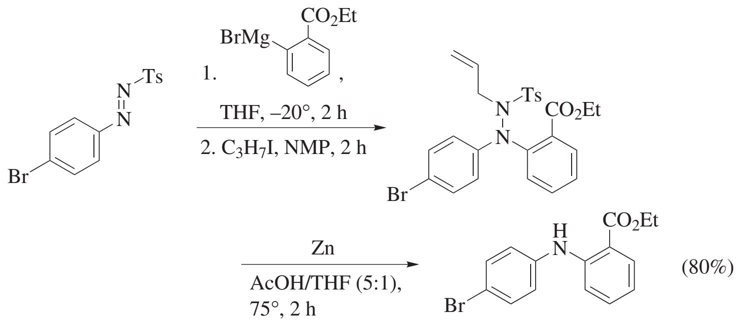
Scheme 102

A variety of other metals have been explored as potentially cheaper replacements for palladium catalysts for C–N bond formation. Nickel catalysts can also be effective in the arylation of amines. Ni(0) catalysts are generally more reactive with aryl chloride substrates than Pd(0) or Cu(I) catalysts.[208] In addition, nickel is significantly cheaper than palladium (\$0.03/g, \$1.54/mole).[204] Despite these advantages, nickel has received limited attention. In part, this may be attributable to the difficulty in reducing Ni(II) precatalysts or working with unstable Ni(0) precursors.[209,210] Iron-catalyzed C–N bond formation has received significant attention recently,[211–213] but the scope is limited to aryl iodides and yields are often modest. It appears that for some of these systems the active catalyst may be copper impurities in the iron salts used as precatalysts.[214] A catalyst derived from $CoCl_2$ and dppp (1,3-bis(diphenylphosphino)propane) provides modest yields in the coupling of amines with 2-chloropyridine derivatives.[215]

Although the majority of C–N bond-forming reactions involve reaction of a carbon electrophile with a nitrogen nucleophile, umpolung approaches in which the reaction polarity is reversed have also been developed. Diarylamines can be prepared by the reaction of two equivalents of an aryl Grignard reagent with nitroarenes followed by reductive workup with $FeCl_2$ and $NaBH_4$ (Scheme 103).[216] The first equivalent of the Grignard reagent reduces the nitro group to a nitroso group with formation of a phenoxide derivative.[217] The second equivalent then adds to the nitroso group. The need to use two equivalents of Grignard reagent can be eliminated by starting directly with the nitrosoarene. Arylazo tosylates are another class of nitrogen electrophiles that can be converted into diarylamines by reaction with Grignard reagents followed by reductive cleavage of the N–N bond (Scheme 104).[218]



Scheme 103



Scheme 104

EXPERIMENTAL CONDITIONS

Copper Precursors

Nearly any source of Cu(0), Cu(I), or Cu(II) can be used as a precatalyst for C–N bond formation. By far the most commonly used copper salts are the Cu(I) halides, with CuI being the most generally useful precatalyst. In a kinetic study of the coupling of 4-toluidine with two equivalents of 4-tolyl iodide, CuI, CuBr, and CuCl give nearly identical rates for the formation of tri(4-tolyl)amine.[219] Copper(I) oxide has also been used as a catalyst precursor with results comparable to Cu(I) halides. Copper thiophene-2-carboxylate (CuTC) has been used under both ligand-free conditions and with DMEDA for the coupling of vinyl halides and amides.[220] Copper(II) salts, such as CuO or $CuSO_4$, have also been successfully used under ligand-free conditions at high temperatures (150–200°). For ligand-promoted catalyst systems under milder conditions, the Cu(II) sources generally give lower yields than Cu(I) sources.[69,191,221] This lower activity is possibly due to slow reduction of the Cu(II) precatalyst to the Cu(I) active species. Copper(0) in the form of powder or bronze is commonly used in the traditional Ullmann conditions. The use of Cu(0) has largely been supplanted by the use of Cu(I) salts. Typical catalyst loadings range from 5–10 mol % of the copper source. Coupling of azoles with aryl iodides using $CuCl_2$ loadings as low as 10 ppm have been reported to give good yields.[222] Thus, it may be that the higher loadings commonly reported in the literature are not always required.

Commercially available CuO and Cu_2O nanoparticles have been shown to be effective catalysts under ligand-free conditions for the coupling of aryl and vinyl halides with azoles,[94,223] amines,[224] and amides.[225] The nanoparticle-based catalyst systems are generally limited to the coupling of aryl iodides, but a Cu_2O-coated Cu–nanoparticle system gives good yields with electron-deficient aryl chlorides.[223] Non-activated aryl chlorides, such as chlorobenzene, give no conversion with this system, however. An advantage of these nanoparticle-based systems is that they can be typically run in air. In addition, the insoluble nanoparticle catalyst can be recovered from the reaction mixture by centrifugation and reused.[224,225] A highly recyclable catalyst is formed by depositing CuO nanoparticles on acetylene black.[226]

The supported catalyst can be used for 10 cycles with no decrease in yield or conversion rate.

Copper catalysts supported by inorganic oxides have also been used successfully. Fluorapatite-supported copper catalysts are effective in the coupling of aryl iodides, bromides, chlorides, and even activated fluorides with azole nucleophiles.[66,227] An aluminum hydrotalcite-supported copper catalyst provides good activity for the coupling of aliphatic amines with non-activated aryl chlorides.[228] The heterogeneous catalyst can be recovered by centrifugation and reused for five reaction cycles with no degradation in product yield.

Ligands

The modern development of Cu-catalyzed C–N bond formation has relied on supporting ligands to provide more active and general catalysts that operate under milder conditions. Ligand-free systems are common, but generally require high temperatures, ultrasound activation, or highly reactive substrates, such as 2-halobenzoic acids. In addition, polar aprotic solvents are commonly used in "ligand-free" systems, presumably to help solubilize and stabilize the copper active species. The most commonly used supporting ligands are 1,2-diamines, such as EDA, CDA, DMEDA, or DMCDA, amino acids, such as proline or DMG, pyridine-based ligands, such as phenanthroline or 8-hydroquinoline, and oxygen-based ligands, such as diols and diketonates (Figure 1). All of the commonly used ligands, as well as ligand-free catalysts, have been successfully demonstrated with each class of nitrogen nucleophile. A 2:1 ligand/Cu ratio is most commonly used.

Careful studies comparing a wide range of ligand types for a given reaction class are rare. On the basis of comparisons of ligands and the data collected in the tables at the end of this chapter, certain trends can be deduced. Ligand-free catalysts are

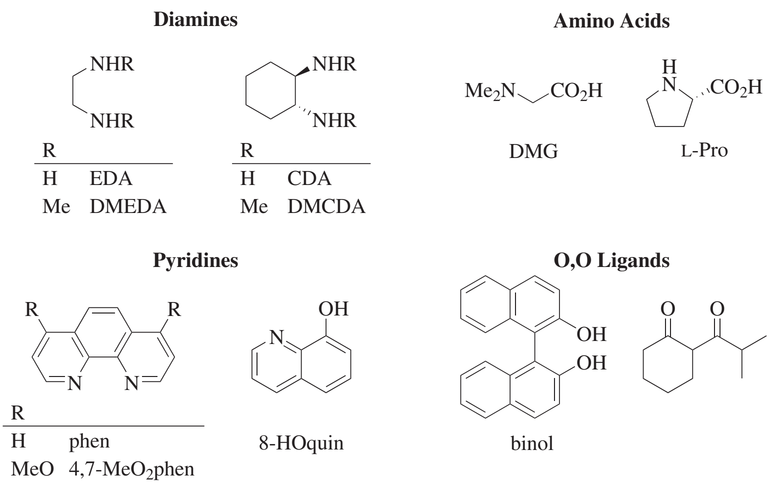


Figure 1. Common ligands for Cu-catalyzed C–N bond formation.

most widely used for arylation of aniline derivatives, although the use of ligand-free catalysts for amine, azole, and amide nucleophiles is also well precedented. A study of the coupling of aniline and iodobenzene shows that pyrrole-2-carboxylate in combination with CuI gives the best yield of diphenylamine after 17 hours at 80°.[50] Proline, phenanthroline, DMEDA, and 2-isobutyrylcyclohexanone all give significantly lower yields. Arylations of alkyl amines benefit from acidic oxygen-based ligands. Amino acids and diketonate ligands are commonly used for these reactions, whereas nitrogen-based ligands (diamines and pyridines) are less commonly reported. A kinetic study of the coupling of 5-iodo-*m*-xylene and *n*-hexylamine shows that 2-isobutyrylcyclohexanone is the most active catalyst with CuI, whereas a TMHD (TMHD = 2,2,6,6-tetramethylheptan-2,4-dionate)-derived catalyst gives a high initial rate, but incomplete conversion.[52] *N,N*-Diethyl salicylamide is a low-activity ligand. Ethylene glycol is the most effective alcohol-based ligand in the coupling of iodobenzene and benzylamine.[194] A 2:1 glycol/CuI ratio affords the highest yield. Substituted vicinal diols, diols with longer backbones (e.g., 1,3-propanediol), and polyols all give much less active catalysts.

More electron-deficient pyridine and Schiff base ligands work well with azole substrates. 4,7-Dimethoxyphenanthroline is the most active ligand in a survey of a wide range of nitrogen-based ligands for the coupling of 4-bromo-*tert*-butylbenzene and 2-methylimidazole using Cu_2O (5 mol %) as the catalyst. Vicinal diamines based on ethylenediamine or 1,2-diaminocyclohexane appear to be particularly effective for the arylation and vinylation of amide nucleophiles. In an extensive survey of ethylenediamine and 1,2-diaminocyclohexane derivatives, DMEDA and DMCDA are the best ligands in combination with CuI for the coupling of 5-bromo-*m*-xylene with pyrrolidine or *N*-benzyl formamide.[69] No conversion occurs with TMEDA as the ligand, whereas EDA and CDA give much lower conversions than DMEDA or DMCDA for each reaction.

The mechanistic basis for the effectiveness of ligands with specific nucleophiles is not well understood. Computational studies comparing diamine and diketonate ligands at the DFT level suggest that the acidity of the nitrogen nucleophile determines which ligands work best.[28,43] More acidic substrates, such as amides, require charge neutral diamine ligands. Less acidic amine nucleophiles have lower reaction barriers with anionic ligands, such as amino acids or diketonates. Further computational study of the Cu(diamine)-promoted arylation of amides shows that secondary diamine ligands, such as DMEDA or DMCDA, provide copper complexes that have lower oxidative addition barriers than either primary or tertiary diamine ligands.[28]

Bases

Inorganic bases, such as carbonates and phosphates, are most commonly used for Cu-catalyzed C–N bond-formation reactions. Potassium and cesium carbonate are most widely used because of the higher solubility of the larger cations in organic solvents. Potassium phosphate is also used in many systems, but less commonly than carbonates. In couplings of amides, phosphate often provides higher rates than carbonate with aryl iodide substrates. With less reactive aryl bromides, carbonate bases often give better results than phosphate bases. This difference is thought to result from the need to match the rate of nucleophile deprotonation with that of aryl halide activation.[229] With aryl bromides, the more basic phosphate provides too high a concentration of the amidate anion, which deactivates the catalyst. For aryl iodides, the less basic carbonate provides too low a concentration of the Cu–amidate active species. Carbonate and phosphate bases are attractive because of their low cost and tolerance of a wide range of functional groups. Stronger bases, such as alkoxides and hydroxides, are sometimes used with less acidic nucleophiles, but their use increases the chance of undesired side reactions with base-sensitive functional groups.

Solvents

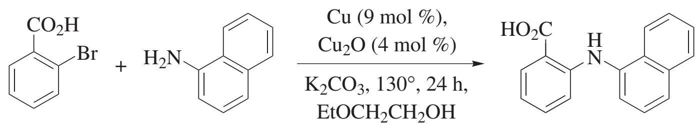
A wide range of solvents can be used in Cu-catalyzed C–N bond formation. The three most common classes of solvents are polar protic solvents, such as DMF, DMA, or DMSO; aromatics, such as toluene or xylene; and cyclic ethers, such as THF or dioxane. The choice of solvent depends in part on the catalyst system that is being used. Ligand-free catalyst systems most commonly are run with no solvent or a high-boiling dipolar aprotic solvent, such as DMF or DMSO. Because ligand-free systems often require high temperatures, high-boiling solvents are necessary. In addition, polar aprotic solvents can act as ligands to stabilize the copper catalyst species. Dipolar aprotic solvents are also the solvents of choice for amino acid- and diketonate-supported catalyst systems. With these anionic ligands, the polar solvent is likely needed to solubilize the ligand and the anionic copper intermediates. Catalysts supported by neutral diamine ligands give the best results with nonpolar solvents, such as toluene, dioxane, or THF.

Although the use of traditional organic solvents is most common, the use of non-traditional solvents has also been reported. Ionic liquids (IL) have been used as solvents for the arylation and vinylation of azoles using ligand-supported copper catalysts.[230–232] In the coupling of β-bromostyrene and imidazole, [bmin]BF_4 (bmin = 1-butyl-3-methylimidazolium) gives significantly higher yields than acetonitrile, DMF, or DMSO.[231] In contrast, little difference between [bmin]BF_4, DMF, and DMSO is seen in the coupling of benzimidazole with 2-bromothiophene.[230] The IL/Cu solution can be separated from the product and recycled up to four times without loss of activity.[230–232] Copper-catalyzed couplings can also be carried out in water. One approach is to use ligands with anionic substituents, such as sulfonates[233] or phenoxides.[78] Neutral, polar ligands with hydroxy, amino, or carbonyl substituents have also been used.[25,234–236] The advantage of using hydrophilic ligands is that the catalyst-containing aqueous phase can often be recovered and recycled.[233] Water-based systems are attractive for the arylation of ammonia, since aqueous ammonium hydroxide can be used as the ammonia source.[237,238]

Other Reaction Conditions

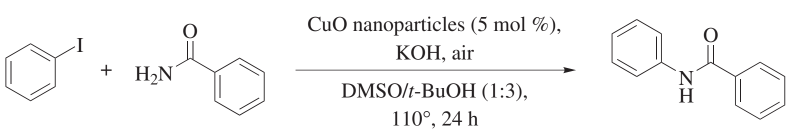
Microwave and ultrasound radiation have been used to accelerate Cu-catalyzed coupling reactions. Because of the high temperatures required in most ligand-free, Cu-catalyzed couplings, the use of microwave irradiation can give complete conversion with short reaction times. Whereas traditional heating generally requires reaction times of 12–24 hours, microwave heating often allows reactions to be completed in 5–20 minutes.[25,85,239,240] Ultrasound can also be used to significantly accelerate Cu-catalyzed coupling reactions. Higher yields are achieved in the coupling of 2-halobenzoic acids and amines with copper powder using ultrasound irradiation at room temperature for 15 minutes than in reactions performed at reflux in DMF for 3 hours.[241,242]

EXPERIMENTAL PROCEDURES



(97%)

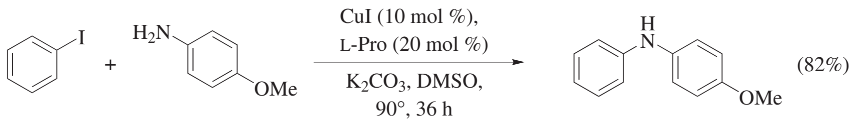
***N*-(1-Naphthyl)anthranilic Acid (Ligand-Free Ullmann Arylation of an Aryl Amine).**[70] A mixture of 1-aminonaphthalene (1.3 g, 9.3 mmol), 2-bromobenzoic acid (1.8 g, 8.8 mmol), K_2CO_3 (1.2 g, 8.8 mmol), Cu powder (0.2–0.3 micron, 50 mg, 0.80 mmol), Cu_2O (<5 micron, 60 mg, 0.40 mmol) and 3 mL of 2-ethoxyethanol was heated at reflux at 130° for 24 h under nitrogen. The cooled reaction mixture was poured into 30 mL of water to which decolorizing charcoal was added. The mixture was filtered through Celite. The crude product was obtained by precipitation upon acidification of the filtrate with diluted HCl (the pH was adjusted to 5–6). The solid residue was dissolved in 100 mL of 5% aqueous Na_2CO_3. The solution was filtered through Celite and the final product was obtained by precipitation as described above. *N*-(1-Naphthyl)anthranilic acid was obtained as an off-white grey powder (2.2 g, 97%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (br s, 1H), 8.08 (m, 2H), 7.92–7.89 (m, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.51–7.46 (m, 4H), 7.29–7.23 (m, 1H), 6.85 (d, J = 8.6 Hz, 1H), 6.73 (dd, J = 7.3 Hz, 7.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 151.2, 136.9, 136.0, 135.5, 133.1, 130.8, 129.1, 127.1, 126.5, 126.5, 123.5, 122.8, 117.5, 114.2, 110.5.



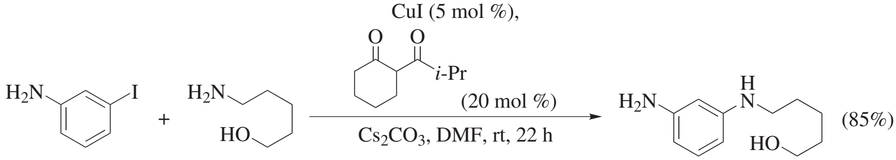
(74%)

***N*-Phenylbenzamide (Ligand-Free Goldberg Arylation of an Amide).**[74] A mixture of benzamide (150 mg, 1.2 mmol), phenyl iodide (200 mg, 1.0 mmol), CuO nanoparticles (4 mg, 0.05 mmol), and KOH (84 mg, 1.5 mmol) in DMSO/*t*-BuOH (1:3, 1 mL) was stirred at 110°. The progress of the reaction was monitored by TLC using a mixture of EtOAc and hexane as the eluent. After completion, the reaction mixture was treated with EtOAc (10 mL) and water (3 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL).

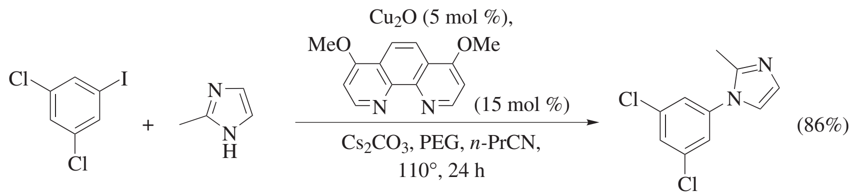
The combined organic solution was washed with brine (3 × 5 mL) and water (1 × 5 mL). The organic layer was dried over Na_2SO_4. The solvent was evaporated under reduced pressure to provide a residue, which was purified by passing through a short pad of silica gel using a mixture of EtOAc and hexane as eluent. The product was recovered as a colorless solid (146 mg, 74%): mp 163° (lit. mp 162–163°);[243] FTIR (KBr) 3310, 2995, 1659, 1604, 1533, 1420, 1315, 1233, 1185, 1090, 1023 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.2 Hz, 2H), 7.78 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 138.1, 135.2, 132.0, 129.3, 129.0, 127.2, 124.8, 120.5. Anal. Calcd for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.23; H, 5.65; N, 7.06.



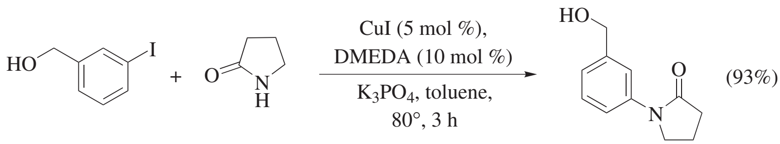
***N*-Phenyl-*p*-anisidine (CuI/L-Proline-Catalyzed Arylation of an Aniline Derivative).**[47] A mixture of phenyl iodide (610 mg, 30 mmol), *p*-anisidine (190 mg, 2.0 mmol), K_2CO_3 (550 mg, 4.0 mmol), CuI (38 mg, 0.20 mmol), and L-proline (40 mg, 0.40 mmol) in 3 mL of DMSO was heated at 90° for 36 h. The cooled mixture was partitioned between water and EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The residual oil was loaded on a silica gel column and the product was eluted with EtOAc/petroleum ether (1:10 to 1:8) to afford *N*-phenyl-*p*-anisidine as a pale yellow solid (163 mg, 82%): mp 102–103°; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21–7.19 (m, 2H), 7.09–7.05 (m, 2H), 6.91–6.77 (m, 5H), 5.49 (br s, 1H), 3.80 (s, 3H); EI–MS (*m/z*): 199 (M^+), 185, 184, 129, 128, 154, 77.



***N*-(3-Aminophenyl)-5-amino-1-pentanol (CuI/Diketonate-Catalyzed Arylation of an Alkyl Amine).**[196] An oven-dried, 10-mL Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, CuI (9.5 mg, 0.050 mmol), and Cs_2CO_3 (650 mg, 2.0 mmol). The tube was evacuated and refilled with argon. Under a counterflow of argon, 3-iodoaniline (219 mg, 1.0 mmol) and 5-amino-1-pentanol (155 mg, 1.5 mmol) were added followed by DMF (0.5 mL) and 2-isobutyroylcyclohexanone (34 mg, 0.2 mmol). The tube was sealed and the mixture was stirred under argon at ambient temperature (22°) for 22 h. After the starting material was consumed, the reaction mixture was diluted with dichloromethane and filtered. The solvent was removed by rotary evaporation, with heating if necessary, to ensure the removal of most of the DMF. The residue was purified by column chromatography on silica gel (EtOAc/hexanes). The product-containing fractions were concentrated by rotary evaporation and dried under high vacuum for at least 1 h to remove residual solvent. *N*-(3-Aminophenyl)-5-amino-1-pentanol was recovered as a yellow oil (165 mg, 85%): ^{1}H NMR ($CDCl_3$) δ 6.95 (pseudo t, 1H), 6.07–6.04 (m, 2H), 5.94 (pseudo t, 1H), 3.60 (t, J = 7 Hz, 2H), 3.28 (br s, 4H), 3.06 (t, J = 6 Hz, 2H), 1.64–1.53 (m, 4H), 1.47–1.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 149.8, 147.7, 130.2, 105.1, 104.3, 99.8, 62.8, 44.1, 32.6, 29.5, 23.6.

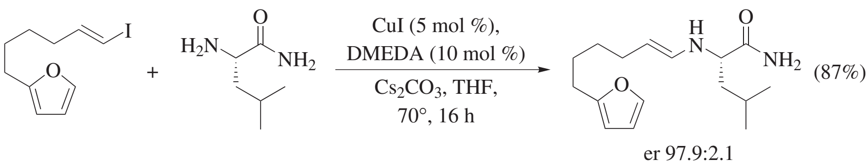


1-(3,5-Dichlorophenyl)-2-methyl-1*H*-imidazole (Cu/Phenanthroline-Catalyzed Arylation of an Azole).[84] An oven-dried screw-capped test tube (4 × 100 mm) was charged with Cu_2O (7.2 mg, 0.050 mmol), 4,7-dimethoxyphenanthroline (36 mg, 0.15 mmol), 2-methylimidazole (100 mg, 1.2 mmol), poly(ethylene glycol) (PEG) (200 mg), Cs_2CO_3 (0.45 g, 1.4 mmol), and a magnetic stir bar, and the reaction vessel was fitted with a rubber septum. The vessel was evacuated and back-filled with argon, and this sequence was repeated a second time. 1,3-Dichloro-5-iodobenzene (273 mg, 1.00 mmol) and butyronitrile (0.5 mL) were then added successively. The reaction tube was sealed and the mixture was stirred in a preheated oil bath for 24 h at 110°. The reaction mixture was cooled to rt, diluted with CH_2Cl_2 (15 mL), and filtered through a plug of Celite, eluting with additional CH_2Cl_2 (20 mL). The filtrate was concentrated, and the resulting residue was purified by flash chromatography (hexane/EtOAc, 1:3) to provide the title compound as white needles (194 mg, 86%): mp 122–125°; IR (KBr disc) 1534, 1501, 1463, 1451, 1405, 1305, 1176, 1143, 1115, 1099, 985, 850, 781 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (t, J = 1.8 Hz, 1H), 7.23 (d, J = 1.9 Hz, 2H), 7.05 (d, J = 1.2 Hz, 1H), 6.99 (d, J = 1.2 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 135.8, 128.5, 128.4, 124.1, 14.0. Anal. Calcd for $C_{10}H_8N_2Cl_2$: C 52.89, H 3.55. Found: C 52.95, H 3.44.



***N*-(3-Hydroxymethylphenyl)-2-pyrrolidinone (Cu/DMEDA-Catalyzed Arylation of an Amide).[69]** A 10-mL Schlenk tube was charged with CuI (9.6 mg, 0.050 mmol) and K_3PO_4 (430 mg, 2.03 mmol), evacuated, and backfilled with argon.

N,N′-Dimethylethylenediamine (11 μL, 0.10 mmol), 3-iodobenzyl alcohol (128 μL, 1.01 mmol), 2-pyrrolidinone (94 μL, 1.24 mmol), and toluene (1.0 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 80° for 3 h. The resulting white suspension was allowed to reach rt and was filtered through a 0.5 × 1 cm pad of silica gel, eluting with 10 mL of Et_2O/MeOH (5:1). The filtrate was concentrated and the residue was purified by flash chromatography on silica gel (CH_2Cl_2/MeOH 25:1) to give the product as a white solid (180 mg, 93%): mp 120–121°; IR (neat) 3331, 1663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, 1H), 7.55–7.50 (m, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.17–7.12 (m, 1H), 4.68 (d, J = 5.8 Hz, 2H), 3.86 (t, J = 7.0 Hz, 2H), 2.65 (t, J = 5.8 Hz, 1H), 2.60 (t, J = 8.0 Hz, 2H), 2.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 141.8, 139.3, 128.9, 123.0, 119.0, 118.5, 64.9, 48.9, 32.7, 17.9. Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85. Found: C, 69.05; H, 6.81.



(2*S*)-2-(*N*-((1*E*)-6-(2-Furyl)hex-1-enyl)amino)-4-methylpentanamide (Cu/DMEDA-Catalyzed Vinylation of an Amide).[244] A solution of (*E*)-6-(2-furyl)-1-iodo-1-hexene (0.150 mg, 0.543 mmol) and DMEDA (6.0 μL, 54 μmol) in THF (1 mL) was prepared in a flame-dried 5-mL conical flask. Separately, an oven-dried 10-mL Schlenk tube fitted with a septum was charged with the L-leucine amide (141 mg, 1.09 mmol), CuI (5.2 mg, 27 μmol), and Cs_2CO_3 (265 mg, 0.815 mmol), and then was evacuated and back-filled with dry nitrogen three times. The vinyl iodide solution was transferred to the Schlenk tube, the septum rapidly exchanged for a glass stopper, and the vessel sealed with Teflon tape. The reaction tube was immersed in a preheated oil bath and maintained at 70° for 16 h. After cooling to rt, the reaction mixture was diluted with EtOAc (2 mL) and placed directly atop a previously prepared silica gel column. Elution with CH_2Cl_2/MeOH (9:1) afforded a colorless oil (139 mg, 87%, er 97.9:2.1): er determined by chiral-phase GC (Alltech Associates, Chirasil-Val column, 25 m x 0.25 mm); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (br d, J = 9.7 Hz, 1H), 7.28 (dd, J = 1.9, 0.8 Hz, 1H), 6.71 (ddt, J = 14.0, 11.0, 1.4 Hz, 1H), 6.26 (dd, J = 3.1, 1.9 Hz, 1H), 5.96 (ddq, J = 3.1, 1.7, 0.9 Hz, 1H), 5.20 (dt, J = 14.3, 7.2 Hz, 1H), 3.41 (dd, J = 9.9, 3.6 Hz, 1H), 2.61 (t, J = 7.4 Hz, 2H), 2.06 (qd, J = 7.3, 1.4 Hz, 2H), 1.78–1.59 (m, 4H), 1.47–1.28 (m, 5H), 0.96 (d, J = 6.4 Hz, 3H), 0.93 (d, J = 6.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 156.3, 140.7, 122.4, 113.2, 110.0, 104.7, 53.2, 43.9, 29.5, 29.4, 27.8, 27.5, 24.9, 23.4, 21.3; HRMS–ESI–MS (m/z): $[M + H]^+$ calcd for $C_{16}H_{26}N_2O_2$, 279.2067; found, 279.2065.

TABULAR SURVEY

The tables incorporate reactions reported in the literature through August 2010. Some key examples published through early 2011 are also included. Additional reactions reported mid-2011 through early 2014 are included only as references at the end of the bibliography, sorted according to the table in which they would belong. The literature was extensively searched using the CAS databases. All examples of Cu-catalyzed C–N bond formation involving the coupling of an aryl or vinyl halide or pseudohalide with a nitrogen nucleophile are included in the following tables. Yields reported are isolated yields, except when only NMR, GC, or HPLC yields are reported. An em-dash (—) indicates that the authors did not report a yield for this example, but provided sufficient evidence that the product was formed. Attempted reactions that did not produce the desired product are included with 0% yield reported. In cases where multiple sets of conditions were reported as part of an optimization study, only the conditions giving the highest yields are listed.

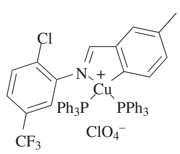
The list of tables can be found in the table of contents at the beginning of the chapter and is not repeated here. Tables 1A and 1B list reactions of all types of halogen electrophiles that lead to primary aryl and heteroaryl amines, respectively, in a single step. These two tables, as well as Table 25 (Preparation of Aryl and Heteroaryl Azides) and Table 33 (Preparation of Vinyl Azides) are organized by increasing carbon count of the halide electrophile, whereas in all other tables organization is by nitrogen nucleophile. Appropriate tables are sub-divided into *N*-arylations and *N*-heteroarylations. The latter contain electrophiles irrespective of whether the halide is attached to a heteroaryl group or an annulated aromatic ring. With the aim of grouping similar substrates together, protecting groups are excluded from the carbon count, as are simple groups on nitrogen, oxygen, and divalent sulfur, except when these groups are attached to the nucleophilic nitrogen. Tables 22A and 22B (*N*-Arylation and *N*-Heteroarylation of Ureas and Guanidines, respectively) also contain cyclic ureas such as 1*H*-imidazol-2(3*H*)-one and 1*H*-benzo[*d*]imidazol-2(3*H*)-one.

In addition to the standard abbreviations approved by the *Journal of Organic Chemistry*, the following abbreviations are used in the tables:

)))	ultrasound, sonication
L-4-HOPro	4-hydroxy L-proline
8-HOquin	8-hydroxyquinonline
AB	acetylene carbon black
Al–HT	aluminum hydrotalcite
An	4-methoxyphenyl (see also PMP)
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
binol	1,1′-binaphthyl-2,2′-diol
BtH	benzotriazole
C_4mim	1-butyl-3-methylimidazolium
CDA	*trans*-1,2-diaminocyclohexane

dba	dibenzylideneacetone
DEIPS	diethylisopropylsilyl
DIPP	diisopropylphosphoramidite
DiPrPhDAB	*N,N′*-(2,6-diisopropylphenyl)-1,4-diazabutadiene
DMCDA	*N,N′*-dimethyl-*trans*-1,2-cyclohexanediamine
DMEDA	*N,N′*-dimethyl-1,2-diaminoethane
DMG	*N,N*-dimethylglycine HCl
DPP	diphenyl pyrrolidine-2-phosphonate
EDA	ethylenediamine
FAP	fluorapatite
IPr	1,3-di-(2,6-diisopropylphenyl)imidazol-2-ylidine
L-Pro	L-proline
4,7-$(MeO)_2$phen	4,7-dimethoxyphenanthroline
Mes*	2,4,6-tri-*tert*-butylphenyl
mes_2DAB	*N,N′*-dimesityl-1,4-diazabutadiene
MTBD	7-methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-ene
Mtt	4-methylphenyldiphenylmethyl (4-methyltrityl)
MW	microwave heating
neocup	neocuproine
NMG	*N*-methylglycine
NP	nanoparticles
Np	naphthyl
PAnNF	poly(aniline) nanofiber
PEG	poly(ethylene glycol)
per-6-ABCD	per-6-amino-β-cyclodextrin
phen	1,10-phenanthroline
Phth	phthalimide
pip-2-CO_2H	piperidine-2-carboxylic acid
PMP	4-methoxyphenyl
PPAPM	pyrrolodine-2-phosphonic acid phenyl monoester
SEM	(2-trimethylsilylethoxy)methyl
TBAA	tetrabutylammonium adipate
TBPE	tetrabutylphosphonium acetate
TBPM	tetrabutylphosphonium malonate
TC	thiophene-2-carboxylic acid
TEAC	tetraethylammonium chloride
TMAH	tetramethylammonium hydroxide
THMD	2,2,6,6-tetramethylheptane-2,4-dionate
TM–BINAM	*N,N,N′,N′*-tetramethyldiaminobinaphthalene
TMU	*N,N,N′,N′*-tetramethylurea
xantphos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene

CHART 1. CATALYSTS USED IN TABLES



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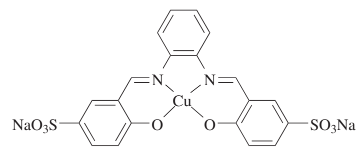

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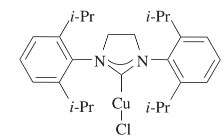

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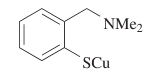

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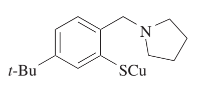
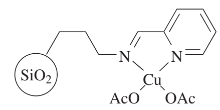


5



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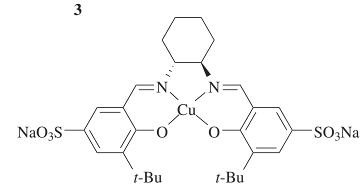

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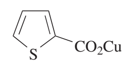

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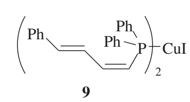

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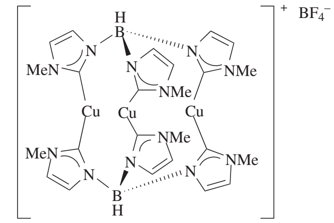

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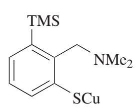

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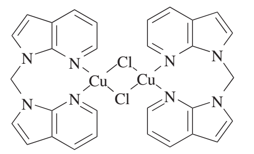

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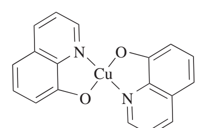
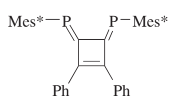


13

CHART 2. LIGANDS USED IN TABLES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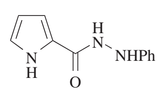
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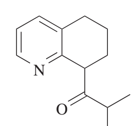
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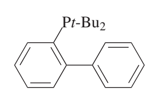
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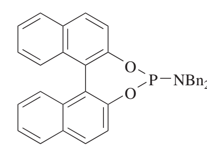
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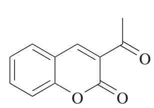
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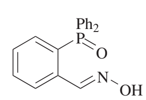
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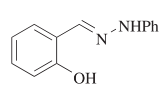
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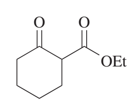
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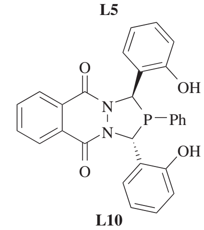
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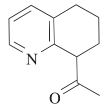
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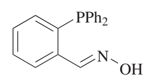
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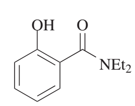
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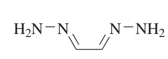
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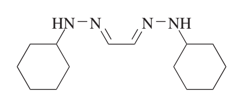
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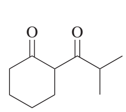
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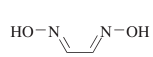
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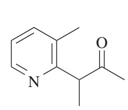
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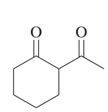
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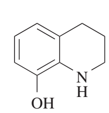
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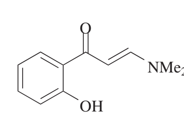
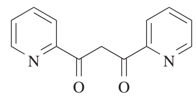

L21

CHART 2. LIGANDS USED IN TABLES (*Continued*)



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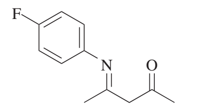

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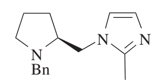

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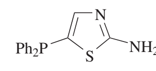

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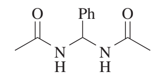

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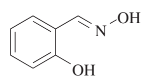

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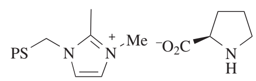

PS = polystyrene

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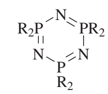
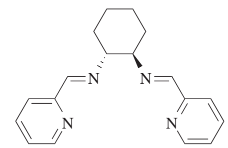


R = dendron

L29



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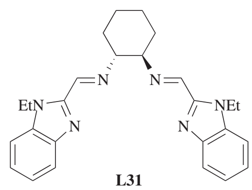

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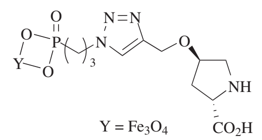

Y = Fe_3O_4

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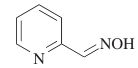

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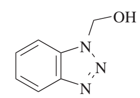

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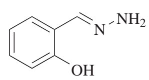

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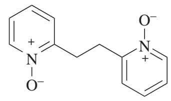

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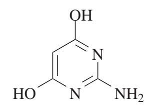

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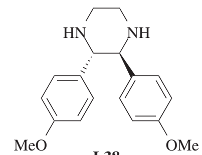

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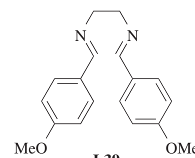

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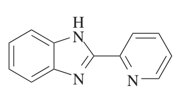

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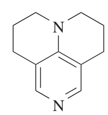

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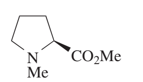

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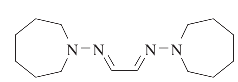

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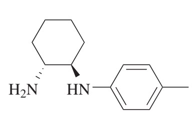

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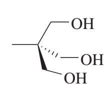

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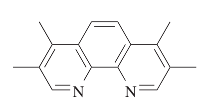

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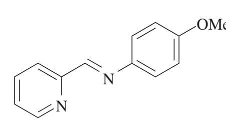

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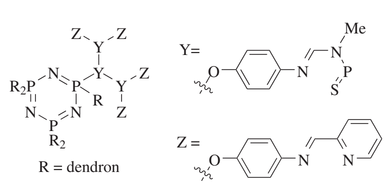


R = dendron

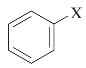
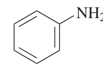
L48

TABLE 1A. PREPARATION OF PRIMARY ARYL AMINES

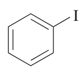
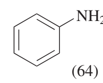
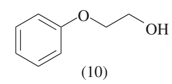
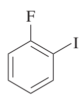
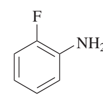
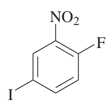
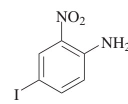
Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

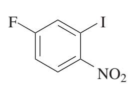
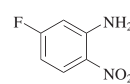
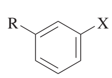
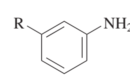
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_6

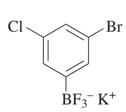
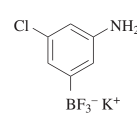
Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_3 (*y*)	Catalyst(s) (*x* amount)		

X	*y*	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
I	—	Cu, CuI	1 eq, 20 mol %	none	$HOCH_2CH_2OH$	50	10	(67)	237
Br	aq	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(85)	245
I	aq	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	rt	24	(85)	245
I	aq	CuI	10 mol %	Fe_2O_3 (10 mol %), NaOH	EtOH	90	16	(96)	246
Cl	aq	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	MW (150 W), 110	10	(93)	114
Br	aq	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	80	15	(99)	114
Br	aq	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	24	(78)	113
Br	aq	**2**	10 mol %	NaOH	H_2O	120	12	(85)	238
I	aq	**2**	5 mol %	NaOH	H_2O	120	12	(94)	238

Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_3	Cu_2O (10 mol %), $HOCH_2CH_2OH$, 80°, 16 h	 (64) +  (10)	193
	NH_3 (aq)	CuBr (5 mol %), **L3** (10 mol %), K_3PO_4, DMSO, rt, 24 h	 (93)	245
	NaN_3	$CuSO_4$•$5H_2O$ (20 mol %), L-Pro (20 mol %), Na ascorbate, DMSO/H_2O (9:1), 70°, 24 h	 (69)	75

Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3	$CuSO_4$•$5H_2O$ (20 mol %), L-Pro (20 mol %), Na ascorbate, DMSO/H_2O (9:1), 70°, 24 h	 (67)	75
	NH_3 (aq)	Catalyst (*x* mol %)		

R	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Cl	Br	CuBr	10	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(93)	245
Cl	I	CuBr	5	**L3** (20 mol %), K_3PO_4	DMSO	rt	24	(90)	245
Cl	Br	Cu_2O	5	none	H_2O/NMP (1:1)	80	15	(93)	114
Br	I	CuI	10	Fe_2O_3 (10 mol %), NaOH	EtOH	90	16	(89)	246

Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3	CuBr (10 mol %), DMEDA (20 mol %), Cs_2CO_3, DMSO, 90°, 12 h	 (91)	47

Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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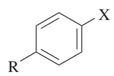
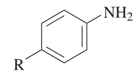
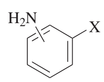


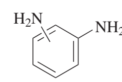
See table. Catalyst(s) (*x* amount)



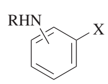
R	X	*N*-Nucleophile	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
F	Br	NH_3 (aq)	**3**	10 mol %	NaOH	H_2O	120	12	(88)	238
Cl	Br	NH_3 (aq)	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(60)	245
Cl	I	NH_3 (aq)	CuBr	5 mol %	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(90)	245
Cl	Br	NH_3	CuI	10 mol %	DMG (20 mol %), TBPM	DMSO	rt	24	(54)	61
Cl	I	NH_3	CuI	10 mol %	DMG (20 mol %), TBPM	DMSO	rt	24	(86)	61
Cl	Br	NH_3 (aq)	**2**	10 mol %	NaOH	H_2O	120	12	(83)	238
Cl	I	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(83)	238
Cl	Br	NH_3	**3**	5 mol %	K_2CO_3	MeOH/NMP	90	24	(72)	112
Cl	Br	NaN_3	CuI	1 eq	L-Pro (1 eq)	DMSO	100	16	(73)	156
Cl	Br	N_3TMS	CuF_2	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	24	(76)	157
Cl	I	$MeC(NH_2){=}NH_2^+\ Cl^-$	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	120	10	(72)	248
Br	I	NH_4Cl	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	H_2O/DMSO	rt	12	(80)	60
Br	I	NH_3	Cu, CuI	20 mol %, 1 eq	none	$HOCH_2CH_2OH$	50	10	(69)	237
Br	I	NH_3 (aq)	CuI	10 mol %	Fe_2O_3 (10 mol %), NaOH	EtOH	90	16	(82)	246
Br	Br	NH_3 (aq)	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	36	(41)	113



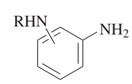
See table. Catalyst (*x* mol %)



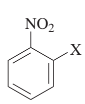
Isomer	*N*-Nucleophile	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
3	NH_3 (aq)	Br	Cu_2O	5	none	H_2O/NMP 1:1	80	24	(94)	114
4	NH_3 (aq)	I	CuI	10	Fe_2O_3 (10 mol %), NaOH	EtOH	90	16	(92)	246
4	$MeC(NH_2){=}NH_2^+\ Cl^-$	I	CuI	10	L-Pro (20 mol %), Cs_2CO_3	DMF	120	10	(94)	248



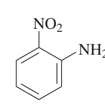
See table. Catalyst (*x* mol %)



Isomer	R	X	*N*-Nucleophile	Catalyst	*x*	Additive	Solvent(s)	Temp (°)	Time (h)		Refs.
2	Ac	Br	NH_3	**3**	5	K_2CO_3	MeOH/NMP	90	24	(73)	112
2	Ac	Br	NaN_3	CuI	10	DMEDA (20 mol %), Cs_2CO_3	EtOH	95	36	(52)	249
2	Bz	Cl	NaN_3	CuI	10	DMEDA (20 mol %), Cs_2CO_3	EtOH	90	12	(68)	249
4	Ac	I	NH_3 (aq)	CuBr	5	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(90)	245

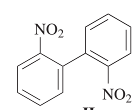


See table. Catalyst(s) (*x* amount)



I

or



II

X	*N*-Nucleophile	Catalyst(s)	*x*	Additive	Solvent(s)	Temp (°)	Time (h)	**I**	**II**	Refs.
Br	NH_3 (aq)	CuI	20 mol %	L-4-HOPro (40 mol%), K_2CO_3	DMSO	70	24	(78)	(0)	133
I	NH_3 (aq)	Cu, CuOTf	1.5 mol %, 1 eq	none	Me_2CO/MeCN (20:1)	rt	—	(0)	(92)	111
I	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(79)	(0)	238
Br	NaN_3	Cu	10 mol %	piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %)	EtOH	100	3	(52)	(0)	250
Cl	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	5	(75)	(0)	156
Cl	NaN_3	$CuSO_4$•5 H_2O	20 mol %	L-Pro (20 mol %), Na ascorbate	DMSO/H_2O (9:1)	70	24	(74)	(0)	75
I	NaN_3	$CuSO_4$•5 H_2O	20 mol %	L-Pro (20 mol %), Na ascorbate	DMSO/H_2O (9:1)	70	24	(76)	(0)	75
I	$MeC(NH_2){=}NH_2^+\ Cl^-$	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	110	10	(79)	(0)	251

TABLE 1A. PREPARATION OF PRIMARY ARYL AMINES (*Continued*)

Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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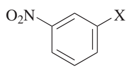
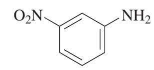
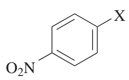


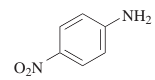
See table. Catalyst (*x* mol %)



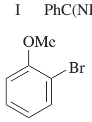
X	*N*-Nucleophile	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield (%)	Refs.
Br	NH_3 (aq)	CuI	20	L-4-HOPro (40 mol %), K_2CO_3	DMSO	50	24	(91)	133
I	NH_3 (aq)	CuI	20	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(92)	60
I	NH_4Cl	CuI	20	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(74)	60
Br	NH_3	**3**	5	K_2CO_3	MeOH/NMP	90	24	(93)	112
I	NaN_3	$CuSO_4$•5 H_2O	20	L-Pro (20 mol %), Na ascorbate	DMSO/H_2O (9:1)	70	24	(77)	75
I	$MeC(NH_2)=NH_2^+ Cl^-$	CuI	10	L-Pro (20 mol %), Cs_2CO_3	DMF	110	10	(92)	248
I	*n*-$PrC(NH_2)=NH_2^+ Cl^-$	CuI	10	L-Pro (20 mol %), Cs_2CO_3	DMF	110	10	(87)	248
I	$PhC(NH_2)=NH_2^+ Cl^-$	CuI	10	L-Pro (20 mol %), Cs_2CO_3	DMF	110	10	(65)	248



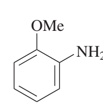
See table. Catalyst (*x* amount)



X	*N*-Nucleophile	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield (%)	Refs.
I	NH_3 (aq)	CuBr	5 mol %	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(92)	245
Br	NH_3 (aq)	CuI	20 mol %	L-4-HOPro (40 mol %), K_2CO_3	DMSO	50	24	(92)	133
I	NH_4Cl	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	H_2O/DMSO	rt	12	(94)	60
I	NH_3	CuI	20 mol %	DMG (20 mol %), TBPM	DMSO	rt	24	(86)	61
I	NH_3 (aq)	CuI	10 mol %	Fe_2O_3 (10 mol %), NaOH	EtOH	90	16	(61)	246
Cl	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	MW (150 W), 110	15	(79)	114
Br	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	80	15	(86)	114
I	NH_3 (aq)	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	24	(63)	113
Br	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(87)	238
I	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(91)	238
Cl	NaN_3	Cu	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	24	(32)	157
Br	NaN_3	Cu	10 mol %	piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %)	EtOH	100	3	(88)	250
Br	NaN_3	$CuSO_4$•5 H_2O	20 mol %	L-Pro (20 mol %), Na ascorbate	DMSO/H_2O (9:1)	70	24	(76)	75
I	NaN_3	$CuSO_4$•5 H_2O	20 mol %	L-Pro (20 mol %), Na ascorbate	DMSO/H_2O (9:1)	70	24	(86)	75
Br	N_3TMS	CuF_2	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	24	(95)	157
Br	$MeC(NH_2)=NH_2^+ Cl^-$	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	120	10	(75)	251
I	$MeC(NH_2)=NH_2^+ Cl^-$	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	110	10	(88)	248
I	*n*-$PrC(NH_2)=NH_2^+ Cl^-$	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	110	10	(80)	248
I	$PhC(NH_2)=NH_2^+ Cl^-$	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	110	10	(65)	248



See table. Catalyst (*x* mol %)



N-Nucleophile	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
NH_3 (aq)	CuBr	10	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(60)	245
NH_3 (aq)	CuI	20	L-4-HOPro (40 mol %), K_2CO_3	DMSO	70	24	(81)	133
NH_3 (aq)	**2**	5	NaOH	H_2O	120	12	(90)	238
NaN_3	Cu	10	piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %)	EtOH	100	3	(73)	250

Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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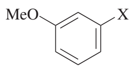
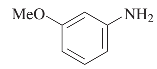
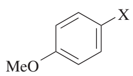


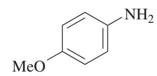
See table. Catalyst (*x* amount)



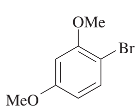
N-Nucleophile	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
NH_3 (aq)	Br	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(93)	245
NH_3 (aq)	Br	CuI	20 mol %	L-4-HOPro (40 mol %), K_2CO_3	DMSO	50	24	(83)	133
NH_3 (aq)	Br	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	24	(85)	113
NH_3 (aq)	Br	**2**	10 mol %	NaOH	H_2O	120	12	(88)	238
N_3TMS	Br	Cu	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	24	(81)	157
$MeC(NH_2)=NH_2^+\ Cl^-$	I	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	120	10	(72)	248



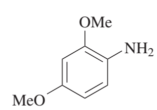
See table. Catalyst(s) (*x* amount)



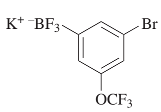
X	*N*-Nucleophile	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	NH_3 (aq)	Cu, CuI	20 mol %, 1 eq	none	$HOCH_2CH_2OH$	50	10	(71)	237
Br	NH_3 (aq)	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(86)	245
I	NH_3 (aq)	CuBr	5 mol %	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(81)	245
Br	NH_3	CuI	10 mol %	DMG (20 mol %), TBPM	DMSO	rt	24	(35)	61
I	NH_3	CuI	10 mol %	DMG (20 mol %), TBPM	DMSO	rt	24	(78)	61
Br	NH_3 (aq)	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	80	12	(44)	60
I	NH_3 (aq)	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(77)	60
I	NH_4Cl	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(32)	60
I	NH_3 (aq)	CuI	10 mol %	Fe_2O_3 (10 mol %), NaOH	EtOH	90	16	(81)	246
Cl	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	MW (150 W), 110	20	(85)	114
Br	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	80	20	(94)	114
I	NH_3 (aq)	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	24	(80)	113
Br	NH_3	**3**	5 mol %	K_2CO_3	MeOH/NMP	90	24	(79)	112
Br	NH_3 (aq)	**2**	10 mol %	NaOH	H_2O	120	12	(85)	238
I	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(90)	238
Br	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	16	(46)	156
Br	N_3TMS	Cu	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	24	(48)	157
I	$MeC(NH_2)=NH_2^+\ Cl^-$	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	120	10	(78)	248



See table. Catalyst (*x* amount)

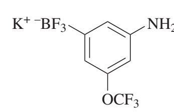


N-Nucleophile	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
NH_3	**3**	5 mol %	K_2CO_3	MeOH/NMP	90	24	(66)	112
NH_3 (aq)	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	70	24	(82)	133
NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	6	(71)	156

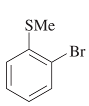


NaN_3

CuBr (10 mol %), DMEDA (20 mol %), Cs_2CO_3, DMSO, 90°, 12 h

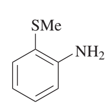


(83) 247



NaN_3

Cu (10 mol %), piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %), EtOH, 100°, 3 h

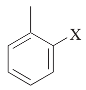


(64) 250

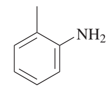
Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

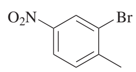
C_7



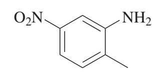
See table. Catalyst (x amount)



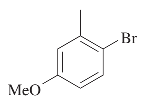
X	*N*-Nucleophile	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	NH_3 (aq)	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(52)	245
I	NH_3 (aq)	CuBr	5 mol %	**L3** (10 mol %), K_3PO_4	DMSO	80	24	(70)	245
Br	NH_3 (aq)	CuI	20 mol %	L-4-HOPro (40 mol %), K_2CO_3	DMSO	70	24	(55)	133
I	NH_3 (aq)	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	80	12	(34)	60
I	NH_4Cl	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(7)	60
Cl	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	MW (150 W) 110	15	(83)	114
Br	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	80	20	(99)	114
Br	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(70)	238
I	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(71)	238
Br	NH_3	**3**	5 mol %	K_2CO_3	MeOH/NMP	90	24	(80)	112
Br	NaN_3	CuI	1 eq	L-Pro (1 eq)	DMSO	100	18	(70)	156



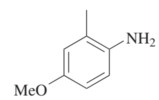
N_3TMS — CuF_2 (2 eq), $H_2NCH_2CH_2OH$, DMA, 95°, 24 h



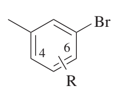
(75) 157



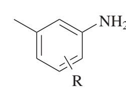
NH_3 (aq) — CuI (20 mol %), K_2CO_3, DMSO, L-4-HOPro (40 mol %), 70°, 24 h



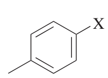
(78) 133



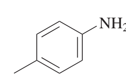
See table. Catalyst(s) (x amount), 50°



R	*N*-Nucleophile	Catalyst(s)	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
4-Br	NH_3 (aq)	CuI	20 mol %	L-4-HOPro (40 mol %), K_2CO_3	DMSO	50	24	(63)	133
6-NH_2	NH_3	Cu, CuI	20 mol %, 1 eq	none	$HOCH_2CH_2OH$	40	10	(37)	237
5-K^+ $^-BF_3$	NaN_3	CuBr	10 mol %	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	8	(93)	247



See table. Catalyst (x amount)



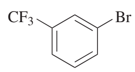
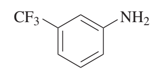
X	*N*-Nucleophile	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	NH_3 (aq)	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(86)	245
I	NH_3 (aq)	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	rt	24	(83)	245
I	NH_3 (aq)	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(80)	60
I	NH_4Cl	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(56)	60
Br	NH_3 (aq)	CuI	20 mol %	L-4-HO-Pro (40 mol %), K_2CO_3	DMSO	50	24	(55)	133
I	NH_3 (aq)	CuI	10 mol %	Fe_2O_3 (10 mol %), NaOH	EtOH	90	16	(72)	246
Cl	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP 1:1	MW (150 W), 110	12	(89)	114
Br	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP 1:1	80	15	(98)	114
Br	NH_3 (aq)	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	36	(79)	113
Br	NH_3 (aq)	**2**	10 mol %	NaOH	H_2O	120	12	(87)	238
I	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(94)	238
Br	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	16	(84)	156
I	$MeC(NH_2){=}NH_2^+\ Cl^-$	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	120	10	(72)	248

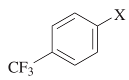
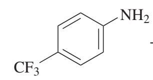
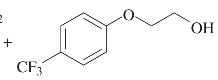
TABLE 1A. PREPARATION OF PRIMARY ARYL AMINES (*Continued*)

Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

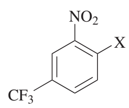
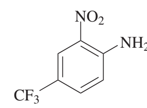
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

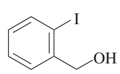
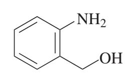
 NH_3 (aq) — CuI (20 mol %), K_2CO_3, DMSO, L-4-HOPro (40 mol %), 50°, 24 h —  (90) — 133

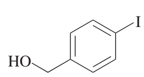
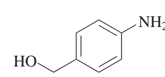
 See table. — Catalyst (*x* amount) —  **I** +  **II**

X	*N*-Nucleophile	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)	**I**	**II**	Refs.
Br	NH_3	CuI	10 mol %	DMG (20 mol %), TBPM	DMSO	rt	24	(62)	(—)	61
Br	NH_3 (aq)	CuI	20 mol %	L-4-HOPro (40 mol %), K_2CO_3	DMSO	50	24	(91)	(—)	133
I	NH_4Cl	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	H_2O/DMSO	rt	12	(80)	(—)	60
Br	NH_3	Cu_2O	10 mol %	none	$HOCH_2CH_2OH$	80	16	(54)	(18)	193
Br	NH_3	**3**	5 mol %	K_2CO_3	MeOH/NMP	90	24	(95)	(—)	112
I	NaN_3	$CuSO_4$•5 H_2O	20 mol %	L-Pro (20 mol %), Na ascorbate	DMSO/H_2O (9:1)	70	24	(57)	(—)	75
Br	N_3TMS	CuF_2	2 eq	Et_3N	DMA	95	24	(67)	(—)	157
I	N_3TMS	CuF_2	2 eq	Et_3N	DMA	95	24	(60)	(—)	157

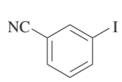
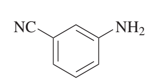
 NaN_3 — $CuSO_4$•5H_2O (20 mol %), L-Pro (20 mol %), Na ascorbate, DMSO/H_2O (9:1), 70°, 24 h —  — 75

X	
F	(78)
Cl	(76)
OMs	(42)

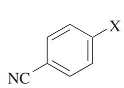
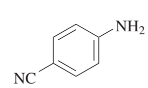
 NaN_3 — Cu_2O (1 eq), L-Pro (1 eq), DMSO, 100°, 16 h —  (87) — 156

 See table. — Catalyst (*x* mol %), DMSO, rt — 

N-Nucleophile	Catalyst	*x*	Additives	Time (h)		Refs.
NH_3 (aq)	CuBr	5	**L3** (10 mol %), K_3PO_4	24	(79)	245
NH_3 (aq)	CuI	20	L-Pro (40 mol %), K_2CO_3	12	(77)	60
NH_4Cl	CuI	20	L-Pro (40 mol %), K_2CO_3	12	(57)	60

 See table. — CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, rt, 12 h —  — 60

N-Nucleophile	
NH_3 (aq)	(97)
NH_4Cl/H_2O	(89)

 NH_3 (*y*) — Catalyst(s) (*x* amount) — 

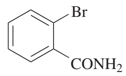
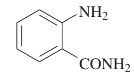
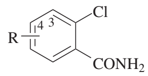
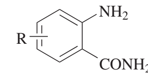
X	*y*	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	—	Cu, CuI	20 mol %, 1 eq	none	$HOCH_2CH_2OH$	50	10	(59)	237
I	aq	CuBr	5 mol %	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(93)	245
Br	aq	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	80	12	(88)	60
Br	aq	CuI	20 mol %	L-4-HO-Pro (40 mol %), K_2CO_3	DMSO	50	24	(91)	133
Cl	aq	Cu_2O	5 mol %	none	H_2O/NMP 1:1	MW (150 W), 110	20	(86)	114
Br	aq	Cu_2O	5 mol %	none	H_2O/NMP 1:1	80	15	(81)	114
Br	aq	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	36	(92)	113
I	aq	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	24	(94)	113
Br	—	**3**	5 mol %	K_2CO_3	MeOH/NMP	90	24	(93)	112

TABLE 1A. PREPARATION OF PRIMARY ARYL AMINES (*Continued*)

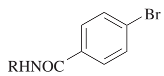
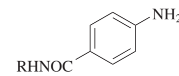
Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

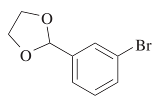
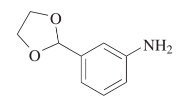
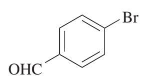
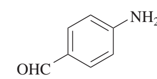
C_7

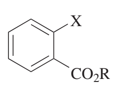
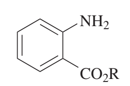
	NH_3	Catalyst **3** (5 mol %), K_2CO_3, MeOH/NMP, 90°, 24 h	 (93)	112
	NaN_3	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, EtOH, 95°		249

R	X	Time (h)	
H	Cl	36	(70)
H	Br	36	(79)
5-Cl	Br	56	(66)
5-Br	Br	48	(64)
$3\text{-}O_2N$	Br	36	(71)

	NH_3	Catalyst(s) (*x* amount)	

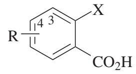
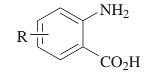
R	Catalyst(s)	*x*	Additive	Solvent(s)	Temp (°)	Time (h)		Refs.
H	**3**	5 mol %	K_2CO_3	MeOH/NMP	90	24	(93)	112
n-Bu	Cu, CuI	20 mol %, 1 eq	none	$HOCH_2CH_2OH$	50	10	(75)	237

	NH_3	Cu (20 mol %), CuI (1 eq), $HOCH_2CH_2OH$, 50°, 10 h	 (70)	237
	NH_3 (aq)	Cu_2O (5 mol %), H_2O/NMP (1:1), 80°, 15 h	 (79)	114

	See table.	Catalyst(s) (*x* amount)	

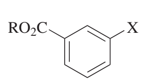
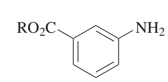
R	X	*N*-Nucleophile	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	Cl	NH_3 (aq)	Cu_2O	5 mol %	Cs_2CO_3	H_2O/NMP 1:1	80	24	(94)	114
H	Cl	NaN_3	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	EtOH	95	36	(90)	249
H	Br	NaN_3	CuI	10 mol %	Cs_2CO_3	EtOH	95	36	(91)	249
Me	Br	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP 1:1	80	24	(92)	114
Me	I	NH_3 (aq)	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	24	(23)	113
Me	I	NH_3 (aq)	Cu, CuOTf	1.5 mol %, 1 eq	none	Me_2CO/MeCN 20:1	rt	—	(80)	111
Me	Cl	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	12	(40)	156
Me	I	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	0.25	(64)	156
Et	Br	NaN_3	Cu	10 mol %	piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %)	EtOH	100	3	(91)	250
Et	Br	$TMSN_3$	CuF_2	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	24	(80)	157

C_{7-8}

	NaN_3	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, EtOH, 95°		249

R	X	Time (h)	
$3\text{-}O_2N$	Br	30	(95)
$4\text{-}O_2N$	Cl	36	(91)
$5\text{-}O_2N$	Cl	30	(79)
4-Me	Br	48	(65)

C_7

	See table.	Catalyst (*x* amount), 24 h	

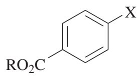
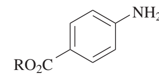
R	X	*N*-Nucleophile	Catalyst	*x*	Additive(s)	Solvent	Temp (°)		Refs.
Me	I	NH_3	CuI	10 mol %	DMG (20 mol %), TBPM	DMSO	rt	(93)	61
Me	Br	N_3Ts	CuF_2	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	(77)	157
Et	Br	N_3Ts	CuF_2	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	(80)	157

TABLE 1A. PREPARATION OF PRIMARY ARYL AMINES (*Continued*)

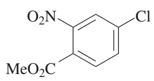
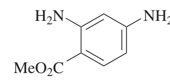
Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

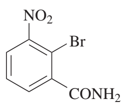
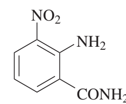
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

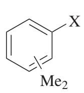
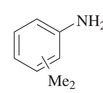
 See table. Catalyst (x amount) 

R	X	N-Nucleophile	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Me	I	N_3TMS	CuF_2	2 eq	none	Et_3N/DMA	95	24	(66)	157
Et	I	NH_3 (aq)	CuBr	5 mol %	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(89)	245
Et	I	NH_4Cl	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(97)	60
Et	Cl	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP 1:1	MW (150 W), 110	10	(84)	114
Et	Br	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP 1:1	80	15	(83)	114
Et	I	NaN_3	Cu	10 mol %	piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %)	EtOH	100	3	(87)	250
Et	Br	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	2	(93)	156
Et	Br	N_3TMS	CuF_2	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	24	(99)	157

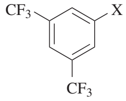
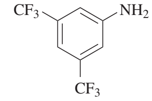
 NaN_3 — Cu_2O (1 eq), L-Pro (1 eq), DMSO, 100°, 48 h —  (20) — 156

 NaN_3 — CuI (10 mol %), Cs_2CO_3, EtOH, 95°, 36 h —  (71) — 249

C_8

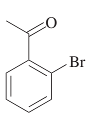
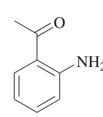
 See table. Catalyst(s) (x amount) 

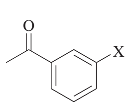
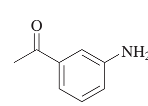
Isomer	X	N-Nucleophile	Catalyst(s)	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
2,4	Br	NH_3	Cu, CuI	20 mol %, 1 eq	none	$HOCH_2CH_2OH$	50	10	(7)	237
2,6	Br	NH_3	**3**	5 mol %	K_2CO_3	MeOH/NMP	120	48	(7)	112
2,6	Br	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(64)	238
3,5	I	NH_3 (aq)	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	rt	24	(90)	245
3,5	I	NH_3 (aq)	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(83)	60
3,5	I	NH_4Cl	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(62)	60
3,5	Br	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP 1:1	80	15	(99)	114

 NaN_3 — $CuSO_4$•5 H_2O (20 mol %), L-Pro (20 mol %), Na ascorbate, DMSO/H_2O (9:1), 70°, 24 h — 

X	
I	(68)
MsO	(24)

75

 NH_3 — Catalyst **3** (5 mol %), K_2CO_3, MeOH/NMP, 90°, 24 h —  (92) — 112

 NH_3 (y) — Catalyst(s) (x amount) — 

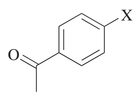
X	y	Catalyst(s)	x	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	—	Cu, CuI	20 mol %, 1 eq	$HOCH_2CH_2OH$	50	10	(82)	237
Cl	aq	Cu_2O	5 mol %	H_2O/NMP (1:1)	80	20	(82)	114
Br	aq	Cu_2O	5 mol%	H_2O/NMP (1:1)	80	15	(92)	114

TABLE 1A. PREPARATION OF PRIMARY ARYL AMINES (*Continued*)

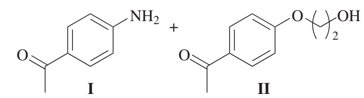
Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_8

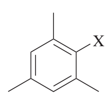


See table. Catalyst(s) (x amount)

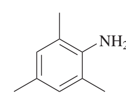


X	*N*-Nucleophile	Catalyst(s)	*x*	Additives	Solvent(s)	Temp (°)	Time (h)	**I**	**II**	Refs.
Br	NH_3	Cu, CuI	20 mol %, 1 eq	none	$HOCH_2CH_2OH$	50	10	(85)	(0)	237
Br	NH_3 (aq)	CuBr	10 mol %	**L3** (10 mol %), K_3PO_4	DMSO	110	24	(96)	(—)	245
I	NH_3 (aq)	CuBr	5 mol %	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(95)	(—)	245
Br	NH_3 (aq)	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	80	12	(91)	(—)	60
I	NH_4Cl	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	rt	12	(80)	(—)	60
I	NH_3 (aq)	CuI	10 mol %	Fe_2O_3 (10 mol %), NaOH	EtOH	90	16	(87)	(—)	246
Br	NH_3	Cu_2O	10 mol %	none	$HOCH_2CH_2OH$	80	16	(60)	(5)	193
Br	NH_3 (aq)	Cu(acac)	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	36	(92)	(—)	113
Br	NH_3 (aq)	**2**	10 mol %	NaOH	H_2O	120	12	(95)	(—)	238
I	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(95)	(—)	238
Br	NH_3	**3**	5 mol %	K_2CO_3	MeOH/NMP	90	24	(97)	(—)	112
Br	NaN_3	CuF_2	2 eq	none	Et_3N/DMA	95	24	(77)	(—)	157
Br	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	7	(87)	(—)	156
I	N_3TMS	CuF_2	2 eq	none	Et_3N/DMA	95	24	(81)	(—)	157

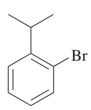
C_9



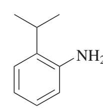
See table. Catalyst (x amount), DMSO



X	*N*-Nucleophile	Catalyst	*x*	Additive(s)	Temp (°)	Time (h)		Refs.
I	NH_3 (aq)	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	80	24	(60)	245
Br	NaN_3	Cu_2O	1 eq	DMEDA (1 eq)	100	10	(72)	156

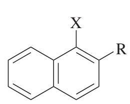


NH_3 (aq) — Cu_2O (5 mol %), H_2O/NMP (1:1), 90°, 48 h

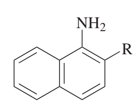


(82) — 114

$C_{10–11}$



See table. Catalyst (x amount)

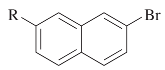


X	R	*N*-Nucleophile	Catalyst	*x*	Additives(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	H	NH_3 (aq)	CuBr	10 mol %	**L3** (10 mol %), K_3PO_4	DMSO	110	24	(89)	245
Br	H	NH_3 (aq)	CuI	20 mol %	L-4-HOPro (40 mol %), K_2CO_3	DMSO	50	36	(76)	133
I	H	NH_3	CuI	10 mol %	DMG (20 mol %), TBPM	DMSO	rt	24	(74)	61
Br	H	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	80	15	(90)	114
I	H	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	80	15	(96)	114
Br	H	NH_3 (aq)	Cu(acac)	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	24	(88)	113
I	H	NH_3 (aq)	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	24	(90)	113
Br	H	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(90)	238
Br	H	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	12	(59)	156
I	H	$MeC(NH_2){=}NH_2^+ Cl^-$	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMF	120	10	(67)	248
Br	OMe	NaN_3	Cu	10 mol %	piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %)	EtOH	100	3	(69)	250
Br	Me	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	14	(76)	156

Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

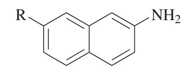
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{10}

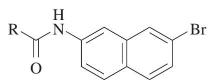


See table.

Catalyst (x amount)

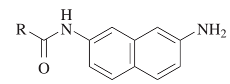


R	*N*-Nucleophile	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	NH_3	**3**	5 mol %	**L3** (5 mol %), K_2CO_3	MeOH/NMP	90	24	(75)	112
H	NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	12	(88)	156
$K^+\ ^-BF_3$	NaN_3	CuBr	10 mol %	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	12	(91)	247



NH_3 (aq)

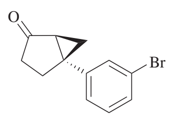
Cu_2O (30 mol %), $HOCH_2CH_2OH$/co-solvent (1:1), rt, 24 h



252

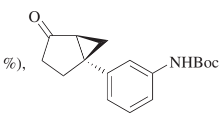
R	Co-solvent	
i-Pr	none	(65)
$BrCMe_2$	DME	(0)
$CH(Me)(CH_2)_3Me$	DME	(87)
n-C_6H_{13}	DME	(53)
Ph	none	(23)
Bn	DME	(10)

C_{12}

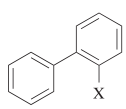


$BocNH_2$

CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 18 h

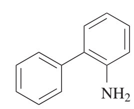


(45) 253

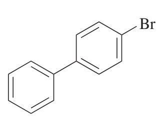


See table.

Catalyst (x amount)

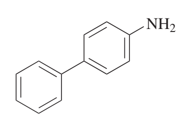


X	*N*-Nucleophile	Catalyst	x	Additive	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	NH_3 (aq)	Cu_2O	5 mol %	none	H_2O/NMP (1:1)	90	48	(75)	114
Br	NH_3	**3**	5 mol %	K_2CO_3	MeOH/NMP	90	24	(81)	112
Cl	NaN_3	CuI	1 eq	DMEDA (1 eq)	DMSO	100	18	(73)	156

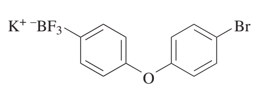


NH_3 (aq)

Catalyst (x mol %)

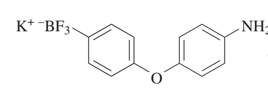


N-Nucleophile	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
NH_3 (aq)	CuI	20 mol %	L-4-HOPro (40 mol %), K_2CO_3	DMSO	50	24	(91)	133
NH_3 (aq)	Cu(acac)	10 mol %	TMHD (40 mol %), Cs_2CO_3	DMF	90	36	(98)	113
NaN_3	Cu_2O	1 eq	L-Pro (1 eq)	DMSO	100	14	(82)	156
N_3TMS	Cu	2 eq	none	$H_2N(CH_2)_2OH$/DMA	95	24	(95)	157



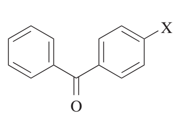
NaN_3

CuBr (10 mol %), DMEDA (20 mol %), Cs_2CO_3, DMSO, 90°, 12 h



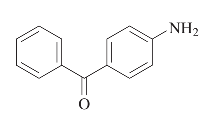
(91) 247

C_{13}



NH_3

CuI (10 mol %), DMG (20 mol %), TBPM, DMSO, rt, 24 h



X	
Br	(71)
I	(86)

61

TABLE 1A. PREPARATION OF PRIMARY ARYL AMINES (*Continued*)

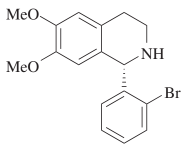
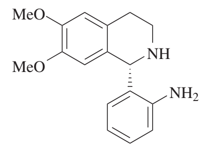
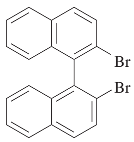
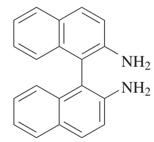
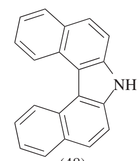
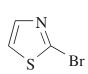
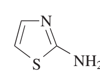
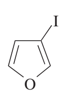
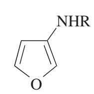
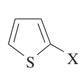
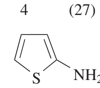
Aryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{15}				
	NH_3	Cu (40 mol %), CuCl (25 mol %), 70°, 45 bar, 120 h	 (82)	254
C_{24}				
	NaN_3	CuI (1 eq), DMEDA (1 eq), DMSO, 100°, 48 h	 (48) +  (48)	156

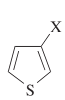
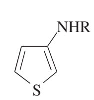
TABLE 1B. PREPARATION OF PRIMARY HETEROARYL AMINES

Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_3				
	NH_3	Cu_2O (10 mol %), $HOCH_2CH_2OH$, 80°, 16 h	 (94)	193
C_4				
	H_2NR	CuI (*x* mol %)		83

R	*x*	Additives	Solvent	Temp (°)	Time (h)	
Boc	10	DMEDA (10 mol %), K_2CO_3	—	110	24	(97)
Cbz	5	phen (20 mol %), Cs_2CO_3	DMF	80	4	(27)

Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_3 (*y*)	Catalyst (*x* mol %)		

X	*y*	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
I	aq	CuI	20	L-Pro (40 mol %), K_2CO_3	DMSO	80	12	(50)	60
Br	—	**3**	5	K_2CO_3	MeOH/NMP	120	48	(88)	112

Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_2R	Catalyst (x mol %)		

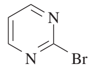
X	R	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
I	H (aq)	CuBr	5	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(79)	245
I	H (aq)	CuI	20	L-Pro (40 mol %), K_2CO_3	DMSO	80	12	(70)	60
Br	H	**3**	5	K_2CO_3	MeOH/NMP	120	48	(84)	112
I	Boc	CuI	10	DMEDA (10 mol %), K_2CO_3	—	110	24	(25)	83

TABLE 1B. PREPARATION OF PRIMARY HETEROARYL AMINES (*Continued*)

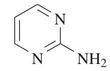
Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

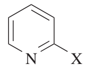
C_4



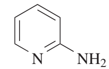
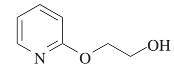
NH_3 (aq) — Cu_2O (5 mol %), DMEDA (10 mol %), K_2CO_3, $HOCH_2CH_2OH$, 60°, 16 h

 (85) — 255

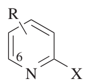
C_5



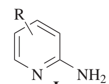
NH_3 (*y*) — Catalyst (*x* mol %)


I
+

II

X	*y*	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	I	II	Refs.
I	aq	CuBr	5	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(89)	(—)	245
Cl	—	Cu_2O	10	none	$HOCH_2CH_2OH$	80	16	(0)	(0)	193
Br	—	Cu_2O	10	none	$HOCH_2CH_2OH$	80	16	(52)	(13)	193
Br	aq	$Cu(acac)_2$	10	acac (40 mol %), Cs_2CO_3	DMF	90	36	(82)	(—)	113
Br	aq	**2**	5	NaOH	H_2O	120	12	(92)	(—)	238



NH_3 (*y*) — Cu_2O (*x* mol %), $HOCH_2CH_2OH$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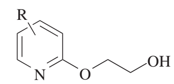
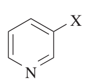
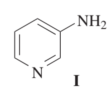
+

II

R	X	*y*	*x*	Additive(s)	Temp (°)	Time (h)	I	II	Refs.
5-Br	Br	—	10	none	80	16	(56)	(6)	193
5-NO_2	Cl	—	10	none	80	16	(85)	(0)	193
5-NO_2	Br	—	10	none	80	16	(99)	(0)	193
6-Br	Br	aq	5	DMEDA (10 mol %), K_2CO_3	60	16	(68)	(0)	255
6-$B(OH)_2$	Br	—	2	none	100	24	(69)	(0)	256
6-MeO	Br	—	2	none	100	24	(82)	(0)	256
6-MeO	Br	—	10	none	80	16	(69)	(6)	193
6-MeO	Br	aq	5	DMEDA (10 mol %), K_2CO_3	80	16	(94)	(0)	255



See table. — Catalyst(s) (*x* amount)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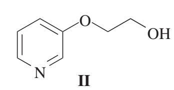
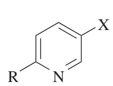
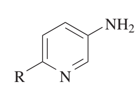

II

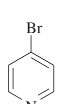
X	*N*-Nucleophile	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	I	II	Refs.
Br	NH_3	Cu, CuI	20 mol %, 1 eq	none	$HOCH_2CH_2OH$	50	10	(65)	(0)	237
I	NH_3 (aq)	CuBr	5 mol %	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(79)	(—)	245
I	NH_3 (aq)	CuI	10 mol %	Fe_2O_3 (10 mol %), NaOH	EtOH	90	16	(94)	(—)	246
Br	NH_3 (aq)	Cu_2O	5 mol %	DMEDA (10 mol %), K_2CO_3	$HOCH_2CH_2OH$	80	16	(80)	(0)	255
Br	NH_3 (aq)	Cu_2O	10 mol %	none	$HOCH_2CH_2OH$	80	16	(81)	(4)	193
Br	NH_3 (aq)	$Cu(acac)_2$	10 mol %	acac (40 mol %), Cs_2CO_3	DMF	90	36	(84)	(—)	113
Br	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(93)	(—)	238
I	NH_3 (aq)	**2**	5 mol %	NaOH	H_2O	120	12	(94)	(—)	238
I	NaN_3	**Cu**	10 mol %	piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %)	EtOH	100	3	(76)	(—)	250



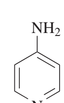
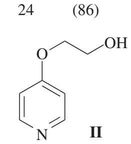
NH_3 (*y*) — Catalyst(s) (*x* amount)



R	X	*y*	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
Cl	Br	—	Cu, CuI	20 mol %, 1 eq	none	$HOCH_2CH_2OH$	50	10	(77)	237
Cl	I	aq	CuI	20 mol %	L-Pro (40 mol %), K_2CO_3	DMSO	80	12	(90)	60
MeO	Br	aq	CuBr	10 mol %	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(86)	245



NH_3 (*y*) — Cu_2O (*x* mol %), 80°

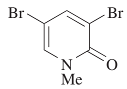
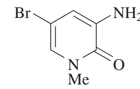

I
+

II

y	*x*	Solvent(s)	Time (h)	I	II	Refs.
aq	5	H_2O/NMP (1:1)	24	(74)	(—)	114
—	10	$HOCH_2CH_2OH$	16	(79)	(2)	193

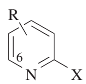
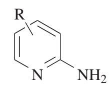
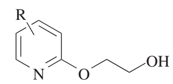
Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_5

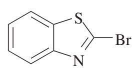
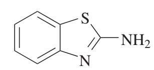
Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3	Cu (10 mol %), piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %), EtOH, 100°, 3 h	 (67)	250

C_6

Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_3 (*y*)	Catalyst (*x* mol %)	 **I** +  **II**	

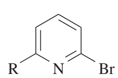
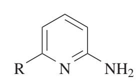
R	X	*y*	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
3-Me	Br	aq	Cu_2O	5	DMEDA (10 mol %), K_2CO_3	$HOCH_2CH_2OH$	60	16	(98)	(0)	255
5-CF_3	Br	aq	Cu_2O	5	DMEDA (10 mol %), K_2CO_3	$HOCH_2CH_2OH$	60	16	(86)	(0)	255
5-Me	Br	aq	CuBr	10	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(85)	(—)	245
6-Me	I	aq	CuBr	5	**L3** (10 mol %), K_3PO_4	DMSO	rt	24	(81)	(—)	245
6-Me	Br	—	Cu_2O	10	none	$HOCH_2CH_2OH$	80	16	(60)	(10)	193
6-Me	Br	—	Cu_2O	2	none	$HOCH_2CH_2OH$	100	24	(62)	(0)	256
6-Me	Br	aq	Cu_2O	5	DMEDA (10 mol %), K_2CO_3	$HOCH_2CH_2OH$	60	16	(88)	(0)	255

C_7

Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_3 (*y*)	Catalyst (*x* mol %)		

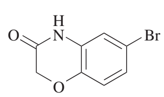
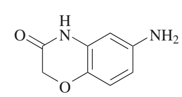
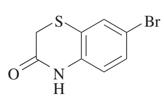
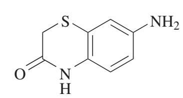
y	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield	Refs.
aq	CuBr	10	**L3** (20 mol %), K_3PO_4	DMSO	110	24	(81)	245
—	**3**	5	K_2CO_3	MeOH/NMP	120	48	(80)	112

$C_{8–9}$

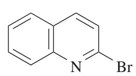
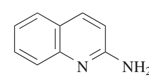
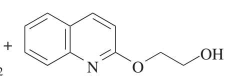
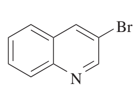
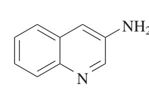
Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_3	Cu_2O (2 mol %), $HOCH_2CH_2OH$, 100°, 24 h		256

R	Yield
i-Pr	(66)
t-Bu	(75)

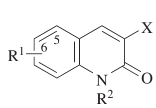
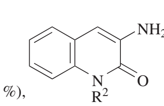
C_8

Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3	$CuSO_4$•$5H_2O$ (20 mol %), L-Pro (20 mol %), Na ascorbate, DMSO/H_2O (9:1), 70°, 24 h	 (68)	75
	NaN_3	$CuSO_4$•$5H_2O$ (20 mol %), L-Pro (20 mol %), Na ascorbate, DMSO/H_2O (9:1), 70°, 24 h	 (73)	75

C_9

Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_3	Cu_2O (10 mol %), $HOCH_2CH_2OH$, 80°, 16 h	 (76) +  (8)	193
	See table.	Catalyst (*x* mol %)		

N-Nucleophile	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Temp (°)	Yield	Refs.
NH_3	**3**	5	K_2CO_3	MeOH/NMP	120	120	(80)	112
NaN_3	Cu	10	piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %)	EtOH	100	100	(82)	250

Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaN_3	Cu (10 mol %), piperidine 2-carboxylic acid (30 mol %), ascorbic acid (20 mol %), EtOH, 100°, 3 h		250

R^1	R^2	X	Yield
H	H	Br	(50)
H	Me	Br	(98)
H	Et	I	(87)
H	EtO_2CCH_2	Br	(81)
H	PMB	Br	(90)
5-Br,	Me	Br	(65)
6-Br	Me	Br	(56)
6-MeO	Me	Br	(98)

TABLE 1B. PREPARATION OF PRIMARY HETEROARYL AMINES (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

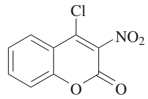
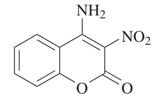
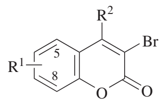
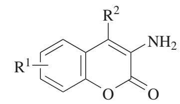
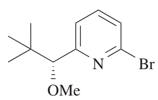
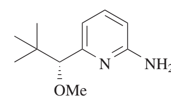
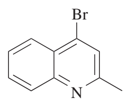
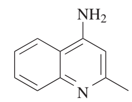
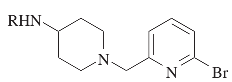
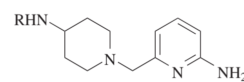
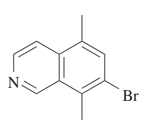
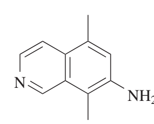
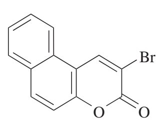
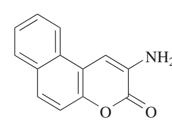
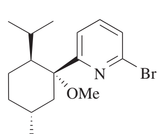
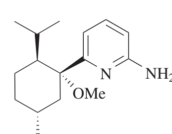
Heteroaryl Halide	Nitrogen Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	NaN_3	$CuSO_4•5H_2O$ (20 mol %), L-Pro (20 mol %), Na ascorbate, DMSO/H_2O (9:1), 70°, 24 h	 (76)	75
$C_{9–10}$				
	NaN_3	Cu (10 mol %), piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %), EtOH, 100°, 3 h	 R^1 / R^2: H / H (73); H / Ph (96); 6-F / Ph (43); 6-Cl / H (42); 6-MeO / H (72); 8-MeO / H (63); 8-Me / H (70); 7-MeO, 8-Me / Me (52)	250
C_{10}				
	NH_3	Cu_2O (2 mol %), $HOCH_2CH_2OH$, 100°, 24 h	 (68)	256
	NH_3 (aq)	Cu_2O (5 mol %), H_2O/NMP (1:1), 90°, 15 h	 (81)	114
C_{11}				
	NH_3	Cu_2O (10 mol %), $HOCH_2CH_2OH$, 80°, 16 h	 R: Ac (91); Boc (85)	193
	NH_3	Cu (40 mol %), CuCl (20 mol %), 195°, 24 h	 (76)	257
C_{13}				
	NaN_3	Cu (10 mol %), piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %), EtOH, 100°, 3 h	 (64)	250
C_{15}				
	NH_3	Cu_2O (2 mol %), $HOCH_2CH_2OH$, 100°, 24 h	 (68)	256

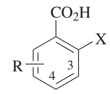
TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

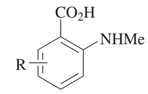
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_1

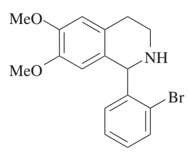
$MeNH_2$



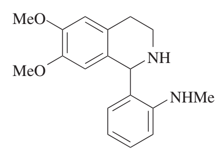
Catalyst (*x* mol %)



N-Nucleophile	R	X	Catalyst	*x*	Additive(s)	Solvent	Temp	Time		Refs.
free base	H	Cl	Cu	7.5	K_2CO_3	H_2O	))) (20 kHz), rt	20 min	(78)	241
free base	H	Cl	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(95)	258
free base	H	I	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(95)	258
HCl salt	H	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(96)	258
free base	5-Cl	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(84)	258
free base	5-Br	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(66)	258
free base	3-O_2N	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(68)	258
free base	4-O_2N	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(77)	258



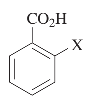
Cu (50 mol %),
CuCl (25 mol %),
70°, 120 h



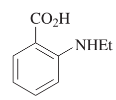
(80) 254

C_2

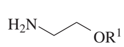
$EtNH_2$

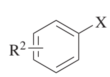


Catalyst (*x* mol %)

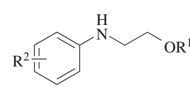


N-Nucleophile	X	Catalyst	*x*	Additive	Solvent	Temp	Time		Refs.
free base	Cl	Cu	7.5	K_2CO_3	H_2O	))) (20 kHz), rt	20 min	(74)	241
HCl salt	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(86)	258

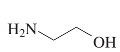


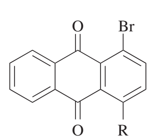


Catalyst (*x* mol %)

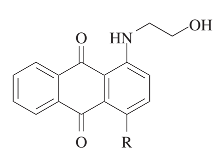


R^1	R^2	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	H	I	CuBr	5	**L10** (5 mol %), Cs_2CO_3	DMSO	80	30	(86)	259
H	H	I	CuI	10	L-Pro (20 mol %), TBAA	DMF	rt	24	(96)	61
H	H	I	CuI	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH/H_2O$	90	—	(90)	260
H	4-Cl	I	CuI	10	DMG (20 mol %), TBPE	NMP	0	5	(88)	61
H	3-MeO	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	80	29	(96)	47
H	4-MeO	I	CuBr	5	**L10** (6 mol %), Cs_2CO_3	DMSO	80	30	(82)	259
H	2,4-$(MeO)_2$	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	40	(93)	47
H	4-Me	I	CuI	5	Cs_2CO_3	DMF	rt	12	(92)	196
H	4-Me	I	CuBr	5	**L10** (5 mol %), Cs_2CO_3	DMSO	55	24	(80)	259
H	4-Me	I	CuI	10	**L11** (20 mol %), Cs_2CO_3	DMF	rt	8	(98)	261
H	4-CHO	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	80	27	(91)	47
Me	H	I	$Cu(acac)_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	MW, 150	0.5	(90)	262
Me	4-Ac	Br	CuI	4	**L13** (20 mol %), K_3PO_4	DMF	90	18	(81)	120





Cu (40 mol %),
DME/2-ethoxyethanol (4:1),
70°



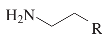
R		Refs.
H	(43)	263
NH_2	(49)	

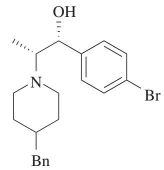
TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

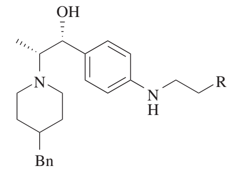
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{2-12}





CuI (10 mol %), K_3PO_4, DMF, 24 h

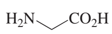


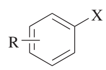
198

R	Additive	Temp (°)	
H_2N	none	90	(86)
HO	**L19** (20 mol %)	90	(5)
Me	**L19** (20 mol %)	90	(53)
$H_2N(CH_2)_2$	**L19** (20 mol %)	90	(61)
n-Pr	**L19** (20 mol %)	90	(50)
$H_2N(CH_2)_4$	**L19** (20 mol %)	130	(62)

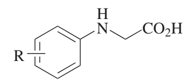
R	Additive	Temp (°)	
$BocHN(CH_2)_4$	**L19** (20 mol %)	130	(0)
$HO(CH_2)_4$	**L19** (20 mol %)	130	(51)
$H_2N(CH_2)_6$	**L19** (20 mol %)	130	(58)
$H_2N(CH_2)_8$	**L19** (20 mol %)	130	(57)
$H_2N(CH_2)_{10}$	**L19** (20 mol %)	130	(55)

C_2



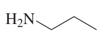


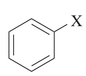
Catalyst (*x* mol %)



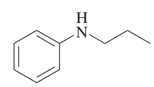
R	X	Catalyst	*x*	Additive	Solvent(s)	Temp (°)	Time		Refs.
H	Br	CuCl	20	TBAH (aq)	MeCN	reflux	24 h	(41)	264
H	Br	CuI	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH/H_2O$	90	—	(62)	260
H	I	CuI	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH/H_2O$	90	—	(87)	260
H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(66)	25
H	Br	CuI	10	K_2CO_3	DMF	MW, 140	20 min	(0)	265
2-HO_2C	Cl	Cu	7.5	K_2CO_3	H_2O	))) (20 kHz), rt	20 min	(87)	241
3-HO_2C	I	CuI	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH/H_2O$	90	—	(90)	260

C_3



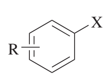


Cu_2O (5 mol %), NMP, 24 h

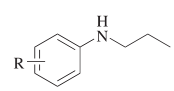


X	Temp (°)	
Cl	100	(92)
Br	80	(80)
I	80	(92)

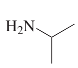
266

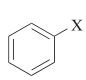


Catalyst (*x* mol %)

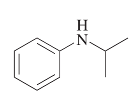


R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
4-Br	Br	CuBr	5	**L17** (20 mol %), TBAB, NaOH	H_2O	100	24 h	(81)	235
3-H_2N	Br	Cu_2O	5	none	NMP	110	24 h	(93)	266
3-O_2N	Cl	Cu_2O	5	none	NMP	100	24 h	(69)	266
3-O_2N	Br	Cu_2O	5	none	NMP	80	24 h	(88)	266
4-MeO	Br	Cu_2O	5	none	NMP	110	24 h	(81)	266
4-MeO	Br	CuO	25	**L17** (50 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(55)	267
4-MeS	Br	Cu_2O	5	none	NMP	110	24 h	(76)	266
3-Me	Cl	Cu_2O	5	NaO*t*-Bu	NMP	110	24 h	(87)	266
2-HO_2C	Cl	Cu	7.5	K_2CO_3	H_2O	))) (20 kHz), rt	20 min	(76)	241
2-HO_2C	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(68)	258
3-EtO_2C	Br	Cu_2O	5	none	NMP	80	24 h	(91)	266
1-Np	I	CuBr	5	**L17** (20 mol %), TBAB, NaOH	H_2O	100	24 h	(86)	235
2-Np	Br	Cu_2O	5	none	NMP	80	24 h	(94)	266





See table.

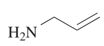
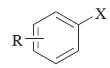
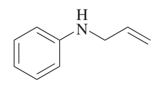


X	Catalyst	Additive(s)	Solvent	Temp (°)	Time		Refs.
I	CuBr (2.5 mol %)	**L5** (5 mol %), Cs_2CO_3	DMF	89	24 h	(96)	118, 119
Br	$Cu(OAc)_2$ (1 eq)	DBU	DMSO	MW, 130	10 min	(89)	85
I	$Cu(OAc)_2$ (1 eq)	DBU	DMSO	MW, 130	10 min	(90)	85

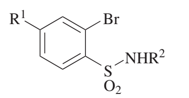
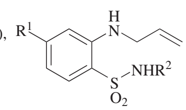
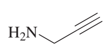
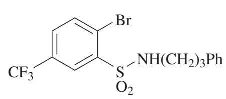
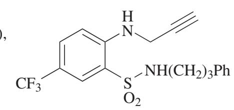
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

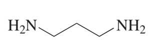
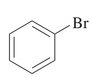
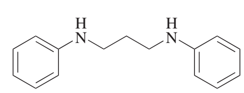
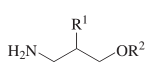
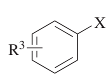
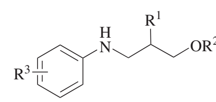
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

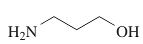
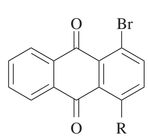
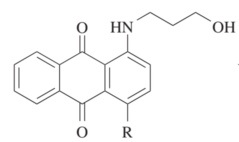
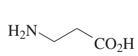
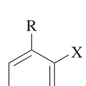
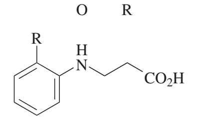
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (*x* amount)		

R	X	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	I	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	60	14	(80)	192
3-H_2N	I	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	90	40	(84)	47
3-H_2N	I	5 mol %	**L16** (20 mol %), Cs_2CO_3	DMF	rt	1	(90)	52
4-H_2N	I	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	rt	16	(80)	261
4-O_2N	I	1 eq	CsOAc	DMSO	90	24	(40)	189
2-MeO	I	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	90	40	(98)	47
4-NC	I	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	80	27	(96)	47
2-HO_2C	Cl	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16	(85)	258
2-HO_2C	Br	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16	(80)	258
2-HO_2C	I	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16	(85)	258
2-HO_2C, 4-Cl	Br	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16	(59)	258
2-HO_2C, 4-Br	Br	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16	(59)	258
2-Br, 3-O_2N	Br	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16	(86)	258
2-Br, 4-O_2N	Br	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16	(65)	258

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), phen (20 mol %), Cs_2CO_3, DMSO, MW, 150°, 11 min	 R^1 R^2: H Bn (96); F CH_2=$CHCH_2$ (94)	268
		CuI (10 mol %), phen (20 mol %), Cs_2CO_3, DMSO, MW, 150°, 11 min	 (69)	268

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cat. **8** (25 mol %), K_2CO_3, NMP, 160°, 16 h	 (43)	269
		Catalyst (*x* mol %)		

R^1	R^2	R^3	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	H	4-Me	I	CuBr	5	**L17** (20 mol %), TBAB, NaOH	H_2O	100	24	(86)	235
H	H	4-Me	I	CuI	5	**L16** (20 mol %), Cs_2CO_3	DMF	rt	12	(96)	196
HO	H	H	I	CuI	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$, H_2O	90	—	(92)	260
H	H	2-HO_2C	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16	(71)	258
H	Me	H	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	MW, 150	0.5	(93)	262

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (40 mol %), DME/$EtOCH_2CH_2OH$ (4:1), 70°	 R: H (31); H_2N (31)	263
		CuI (10 mol %)		

R	X	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	I	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$/H_2O	90	—	(73)	260
HO_2C	Br	binol (20 mol %), K_3PO_4	DMF	rt	16	(71)	258

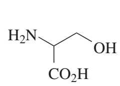
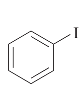
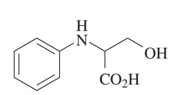
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$/H_2O, 90°	 (49)	260

TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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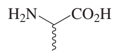
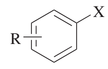
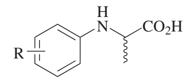
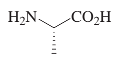


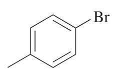


Catalyst (x mol %)

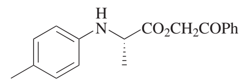


Config.	R	X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
(*S*)	H	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	40	10	(72)	62
(*S*)	H	Br	CuI	10	K_2CO_3	DMF/H_2O	90	24	(42)	270
(*S*)	H	Br	CuI	10	K_2CO_3	DMF/H_2O	90	48	(65)	116
(*R*,*S*)	H	Br	CuI	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH/H_2O$	90	—	(88)	260
(*R*,*S*)	H	I	CuI	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH/H_2O$	90	—	(85)	260
(*S*)	H	Cl	Cu_2O	5	NaO*t*-Bu	NMP	110	24	(76)	266
(*S*)	4-Cl	I	CuBr	5	**L17** (20 mol %), TBAB, NaOH	H_2O	100	24	(91)	235
(*S*)	4-Cl	I	CuI	10	**L8**, (20 mol %), K_3PO_4	DMF	30	3	(90)	271
(*S*)	2-O_2N	I	CuI	10	**L8**, (20 mol %), K_3PO_4	DMF	30	3	(68)	271



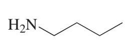


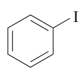
1. CuI (10 mol %), K_2CO_3, DMF, 90°
2. $PhCOCH_2Br$, Et_3N, EtOAc



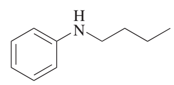
(36) 272

C_4

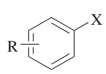




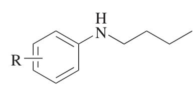
Catalyst (x amount)



Catalyst	x	Additives(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Cu	10 mol %	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	70	14	(94)	195
CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	89	24	(96)	118, 119
CuI	1 eq	CsOAc	DMSO	90	24	(96)	189
CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24	(13)	273
CuO nanoparticles	1.26 mol %	KOH	DMSO	110	13	(91)	224
$Cu(acac)_2$	10 mol %	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	MW, 150	0.5	(76)	262



Catalyst (x amount)



R	X	Catalyst	x	Additives(s)	Solvent(s)	Temp (°)	Time		Refs.
2-F	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(37)	274
2-F	I	CuI	1 eq	CsOAc	DMF	90	24 h	(20)	189
4-Br	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(76)	274
4-Br	I	CuI	1 eq	CsOAc	DMF	rt	24 h	(89)[a]	189
3-I	I	CuI	1 eq	CsOAc	DMSO	rt	24 h	(77)	189
3-I	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(50)	274
4-I	I	CuI	1 eq	CsOAc	DMSO	rt	24 h	(74)	189
4-H_2N	I	Cu	10 mol %	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	85	11 h	(66)	195
2-O_2N	I	CuI	1 eq	CsOAc	DMF	90	24 h	(8)	189
2-O_2N	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(78)	274
3-O_2N	I	CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	89	24 h	(96)	118
3-O_2N	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(95)	274
4-O_2N	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(99)	274
4-O_2N	I	CuI	1 eq	CsOAc	DMF	90	24 h	(89)	189
2-MeO	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(49)	274
2-MeO	I	CuI	1 eq	CsOAc	DMF	90	24 h	(30)	189
3-MeO	I	Cu	10 mol %	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	70	9 h	(89)	195
3-MeO	I	CuI	1 eq	CsOAc	DMSO	rt	24 h	(80)	189
3-MeO	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(89)	274

TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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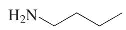
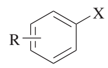
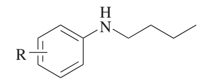
C_4

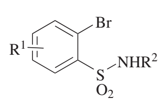




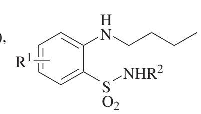
Catalyst (*x* amount)



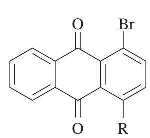
R	X	Catalyst	*x*	Additives(s)	Solvent(s)	Temp (°)	Time		Refs.
4-MeO	I	Cu	10 mol %	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	70	9 h	(87)	195
4-MeO	I	CuI	1 eq	CsOAc	DMF	90	24 h	(85)	189
4-MeO	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(84)	274
4-MeO	Br	CuI	5 mol %	**L2** (25 mol %), KOH, TBAB	H_2O	130	5 min	(80)	236
4-MeO	Br	CuO	5 mol %	**L14** (50 mol %), cyclohexanone, KOH, TBAB	H_2O	MW (100 W), 130	5 min	(86)	51
4-MeO	Br	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(50)	267
2,4-$(MeO)_2$	I	CuI	10 mol %	L-Pro (20 mol%), K_2CO_3	DMSO	90	40 h	(89)	47
2-Me	I	CuI	1 eq	CsOAc	DMSO	90	24 h	(20)	189
2-Me	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(21)	274
3-Me	I	CuI	1 eq	CsOAc	DMF	90	24 h	(77)	189
3-Me	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(99)	274
4-Me	I	Cu	10 mol %	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	60	12 h	(93)	195
4-Me	I	CuI	1 eq	CsOAc	DMF	90	24 h	(76)	189
4-Me	I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(86)	274
3-NC–	I	CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	89	24 h	(96)	118
2-HO_2C	Cl	Cu	7.5 mol %	K_2CO_3	H_2O	))) (20 kHz), rt	20 min	(81)	241
3-HO_2C	I	CuI	10 mol %	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	90	—	(73)	260



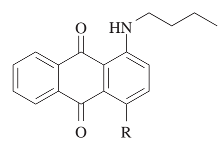
CuI (10 mol %), phen (20 mol %), Cs_2CO_3, DMSO, MW, 150°, 11 min



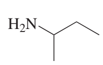
R^1	R^2		Refs.
3-F	*n*-Bu	(92)	268
4-CF_3	allyl	(95)	

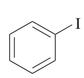


Cu (40 mol %), DME/$EtOCH_2CH_2OH$ (4:1), 70°

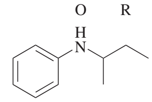


R		Refs.
H	(6)	263
NH_2	(9)	

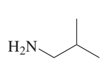


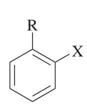


Catalyst (*x* mol %)

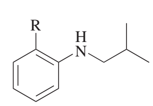


Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cu	5	binol (10 mol %), Cs_2CO_3	DMSO	90	24	(77)	124
Cu	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	80	26	(68)	195
CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	90	24	(98)	118, 119
Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18	(65)	125





Catalyst (*x* mol %)

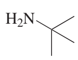
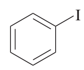
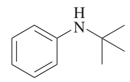
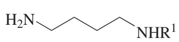
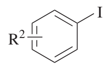
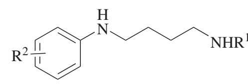


R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
H	I	Cu	5	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(77)	124
H	I	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	89	24 h	(96)	118, 119
H	I	Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18 h	(80)	125
HO_2C	Cl	Cu	7.5	K_2CO_3	H_2O	))) (20 kHz), rt	20 min	(80)	241

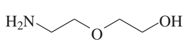
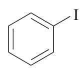
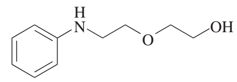
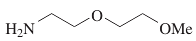
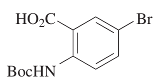
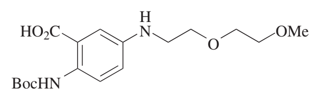
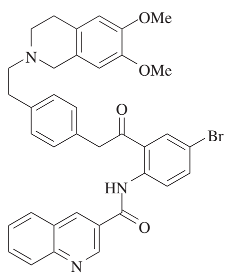
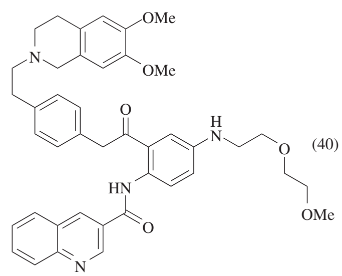
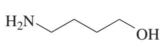
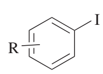
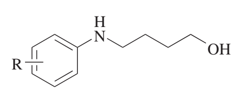
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

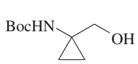
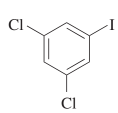
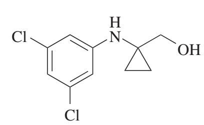
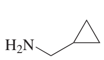
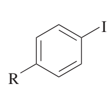
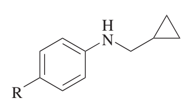
C_4

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, 90°, 48 h	 (3)	195
		CuI (*x* mol %)		

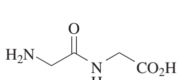
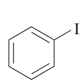
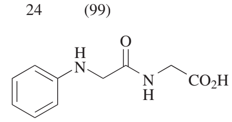
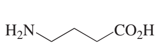
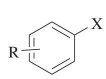
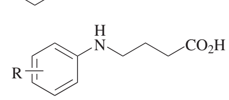
R^1	R^2	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Et	H	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	90	—	(86)	260
Boc	3,5-Me_2	5	**L16** (20 mol %), Cs_2CO_3	DMF	rt	4	(98)	52

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, H_2O, 90°	 (77)	260
		CuBr•Me_2S (20 mol %), **L13** (40 mol %), K_3PO_4, DMF, 90°, 24 h	 (60)	122
		CuI (40 mol %), **L16** (75 mol %), K_3PO_4, DMF, 90°, 24 h	 (40)	122
		CuI (5 mol %), DMF		

R	Additives	Temp (°)	Time (h)		Refs.
4-Me	**L16** (20 mol %), Cs_2CO_3	rt	12	(99)	196
3,5-Me_2	**L13** (20 mol %), K_3PO_4	90	18	(91)	120

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. TFA, 0°, 30 min 2. HCl, *i*-PrOH 3. NaO*i*-Pr 4. CuI, $HOCH_2CH_2OH$, K_3PO_4, *i*-PrOH, 80°, 22 h	 (53)	121
		CuI (*x* mol %), rt		

R	*x*	Additives	Solvent	Time (h)		Refs.
Br	5	**L16** (20 mol %), Cs_2CO_3	DMF	2	(98)	52
MeO	10	DMG (20 mol %), TBPM	DMSO	24	(82)	61
NC–	10	DMG (20 mol %), TBPM	DMSO	24	(99)	61

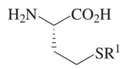
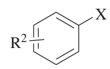
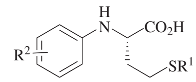
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, H_2O, 90°	 (40)	260
		CuI (10 mol %), DMF		

R	X	Additive(s)	Temp (°)	Time (h)		Refs.
H	Br	K_2CO_3, H_2O	110	24	(trace)	270
3,5-Me_2	I	**L16** (20 mol %), Cs_2CO_3	rt	4	(88)	52

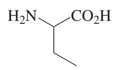
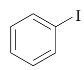
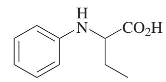
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

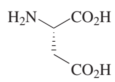
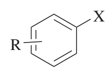
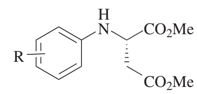
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

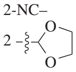


CuI (*x* mol %)


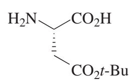
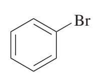
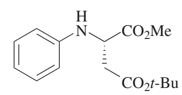
R^1	R^2	X	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Me	H	I	3	Cs_2CO_3	DMSO	90	48	(96)	275
Me	H	Br	10	K_2CO_3, H_2O	DMF	90	48	(76)	116
H	4-Cl	I	10	**L8** (20 mol %), K_3PO_4	DMF	30	3	(76)	271
H	2-O_2N	I	10	**L8** (20 mol %), K_3PO_4	DMF	30	3	(68)	271

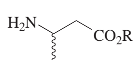
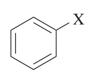
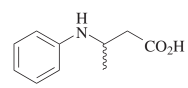


CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, H_2O, 90°

(80) 260



1. CuCl (20 mol %), TBAH (aq), MeCN, reflux, 24 h
2. AcCl, MeOH, reflux, 2 h

264

R	X		er
H	I	(37)	94.5:5.5
4-O_2N	Br	(32)	—
2-MeO	Br	(51)	—
3-MeO	Br	(86)	—
4-MeO	Br	(35)	—

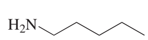
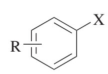
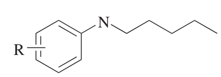
R	X		er
2-*t*-BuN=CH	Br	(55)	95:5
2-*t*-BuN=CH	I	(32)	—
2-NC–	Br	(31)	—
2-NC–	I	(22)	—
2 – 	Br	(64) R = 2-CHO	91:9



1. CuCl (20 mol %), TBAH (aq), MeCN, reflux, 24 h
2. AcCl, MeOH, reflux, 2 h

(27) er 97:3 264



CuI (10 mol %), K_2CO_3, H_2O, DMF, 100°, 48 h


R	X	Config.		Refs.
H	Br	(*R,S*)	(64)	270
Et	Br	(*R,S*)	(62)	
Et	I	(*R*)	(69)	

C_5



Catalyst(s) (*x* mol %)


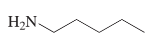
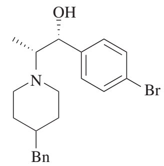
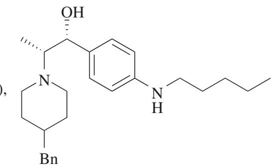
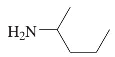
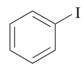
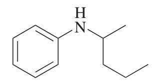
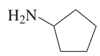
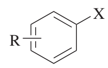
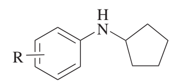
R	X	Catalyst(s)	*x*	Additives(s)	Solvent	Temp (°)	Time		Refs.
H	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	rt	4 h	(65)	62
H	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	24 h	(0)	276
H	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	8 h	(61)	276
H	Br	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	100	12 h	(76)	277
H	I	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	80	12 h	(84)	277
4-Cl	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	rt	5 h	(85)	62
4-Cl	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	1 h	(79)	271
4-Cl	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	6 h	(99)	276
4-Br	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	rt	4 h	(80)	62
4-Br	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	5 h	(92)	276
4-Br	I	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	80	12 h	(87)	277
2-O_2N	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	2 h	(99)	276
3-O_2N	Br	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	100	24 h	(81)	277
4-O_2N	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	4 h	(85)	276
4-O_2N	Br	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	90	12 h	(86)	277
4-MeO	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	6 h	(99)	276
2-Me	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	6 h	(0)	276
4-Me	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	40	8 h	(94)	62
4-Me	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	2 h	(73)	271
4-Me	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	9 h	(56)	276
4-Me	I	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	90	12 h	(73)	277
2-NC–	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	4 h	(75)	276
4-NC–	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	6 h	(63)	276
2-HO_2C	Cl	Cu	7.5	K_2CO_3	H_2O	))) (20 kHz), rt	20 min	(78)	241
2-HO_2C	Cl	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24 h	(85)	278
2-HO_2C	Br	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24 h	(97)	278
3-Ac	I	CuI	5	**L16** (20 mol %), Cs_2CO_3	DMF	rt	6 h	(92)	52

TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

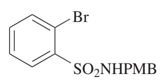
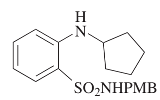
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

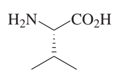
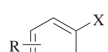
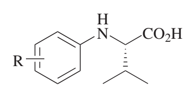
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_5

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (40 mol %), **L19** (20 mol %), K_3PO_4, DMF, 90°, 24 h	 (61)	198
		CuI–PAnNF (5 mol %), K_2CO_3, DMF, rt, 10 h	 (71)	276
		Catalyst (*x* amount)		

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	Cl	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	16	(0)	228
H	I	CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	89	24	(97)	118, 119
H	I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	5	(73)	276
H	I	Cu_2O	5 mol %	**L7** (20 mol %), Cs_2CO_3	MeCN	90	18	(88)	125
2-O_2N	Cl	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	8	(94)	228
2-O_2N	I	Cu–PAnNF	5 mol %	K_2CO_3	DMF	rt	3	(62)	276
4-O_2N	Cl	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	8	(90)	228
4-MeO	I	Cu_2O	5 mol %	**L7** (20 mol %), Cs_2CO_3	—	80	18	(64)	125
2-Me	Cl	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	20	(0)	228
2-NC–	Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	6	(93)	117

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), phen (20 mol %), Cs_2CO_3, DMSO, MW, 150°, 11 min	 (90)	268

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %)		

Config.	R	X	Catalyst	*x*	Additives(s)	Solvent(s)	Temp (°)	Time		Refs.
(*S*)	H	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	40	10 h	(61)	62
(*S*)	H	Cl	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(3)	116
(*S*)	H	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(81)	116
(*S*)	H	I	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(83)	116
(*S*)	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(58)	25
(*S*)	H	Br	CuI	10	K_2CO_3	DMF	MW, 140	15 min	(80)	265
(*S*)	H	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(86)	271
(*R*)	H	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(75)	116
(*R*, *S*)	H	Br	CuI	10	K_3PO_4•H_2O	$Me_2CH_2CH_2OH/H_2O$	90	—	(90)	260
(*R*,*S*)	H	I	CuI	10	K_3PO_4•H_2O	$Me_2CH_2CH_2OH/H_2O$	90	—	(82)	260
(*S*)	4-Cl	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(83)	116
(*S*)	4-Cl	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(88)	271
(*S*)	2-Br	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(58)	271
(*S*)	2-O_2N	I	CuI	10	K_2CO_3	DMF	MW, 140	15 min	(90)	265
(*S*)	2-O_2N	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(70)	271
(*S*)	2-HO	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(75)	116
(*S*)	2-MeO	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(75)	116
(*S*)	3-MeO	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(76)	25
(*S*)	3-MeO	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(85)	116
(*S*)	4-Me	Br	CuI	10	K_2CO_3	DMF	90	—	(83)	272
(*S*)	4-Me	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(84)	271
(*S*)	4-Me	Br	$Cu(OAc)_2$	10	K_2CO_3	DMF	MW, 140	25 min	(64)	265
(*S*)	2-$HOCH_2$	I	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(85)	116
(*S*)	2-$BnOCH_2$	I	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(47)	116

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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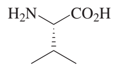
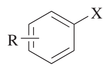
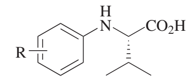
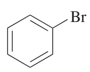
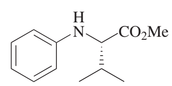
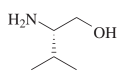
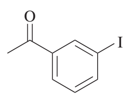
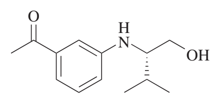
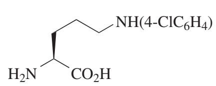
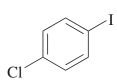
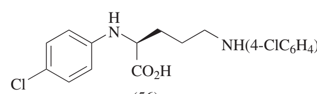
  Catalyst (*x* mol %) 

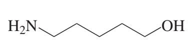
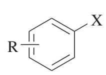
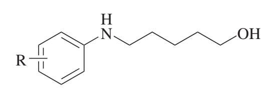
Config.	R	X	Catalyst	*x*	Additives(s)	Solvent(s)	Temp (°)	Time		Refs.
(*S*)	2-HO_2C	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(64)	116
(*S*)	2-HO_2C	I	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(64)	116
(*S*)	3-HO_2C	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(68)	271
(*S*)	3-HO_2C	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(92)	116
(*S*)	4-HO_2C	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(75)	116
(*S*)	2,5-Me_2	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(74)	116
(*S*)	2,6-Me_2	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(74)	116
(*S*)	3,5-Me_2	I	CuI	2.5	NaOH	DMSO/H_2O (2:1)	90	16.5 h	(88)	279
(*S*)	2-Ac	I	CuI	10	K_2CO_3	DMF	MW, 140	20 min	(78)	265
(*S*)	4-Ac	Br	CuI	10	K_2CO_3	DMF	MW, 140	20 min	(82)	265
(*S*)	4-Ac	I	CuI	10	K_2CO_3	DMF	MW, 140	18 min	(80)	265


1. CuCl (20 mol %), TBAH (aq), MeCN, reflux, 24 h
2. AcCl, MeOH, reflux, 2 h

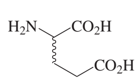
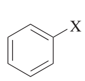
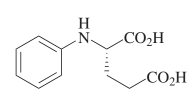
 (33) er 100:0 — 264

  CuI (2.5 mol %), NaOH, DMSO/H_2O (2:1), 90°, 16.5 h  (88) — 279

  CuI (10 mol %), **L8** (20 mol %), K_3PO_4, DMF, 30°, 3 h  (56) — 271

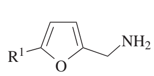
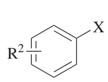
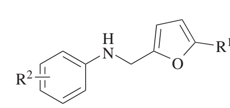
  Catalyst (*x* mol %) 

R	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	I	CuI	10	K_3PO_4•H_2O	$Me_2N(CH_2)_2OH$/H_2O	90	—	(81)	260
4-Cl	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	rt	6	(62)	62
4-Cl	Br	CuI	10	**L11** (20 mol %), Cs_2CO_3	DMF	65	17	(87)	261
3-Br	I	CuI	5	**L16** (20 mol %), Cs_2CO_3	DMF	rt	12	(97)	196
3-H_2N	I	CuI	5	**L16** (20 mol %), Cs_2CO_3	DMF	rt	12	(84)	196
4-Me	I	CuI	5	**L16** (20 mol %), Cs_2CO_3	DMF	rt	12	(97)	196
2-HO_2C, 6-O_2N	Br	CuBr	5	**L17** (20 mol %), NaOH, TBAB	H_2O	100	24	(81)	235

  CuI (10 mol %), 90° 

Config.	X	Additive	Solvents	Time (h)		Refs.
(*R,S*)	I	K_3PO_4•H_2O	$Me_2N(CH_2)_2OH$/H_2O	—	(32)	260
(*S*)	Br	K_2CO_3	H_2O/DMF	48	(0)	116

$C_{5–6}$

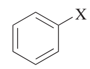
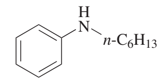
  Catalyst (*x* amount) 

R^1	R^2	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	H	I	CuO nanoparticles	1.26 mol %	KOH	DMSO	110	17	(85)	224
H	O_2N	I	CuI	1 eq	CsOAc	DMF	90	24	(40)	189
H	3,4-OCH_2O	Br	CuI	5 mol %	**L13** (20 mol %), K_3PO_4	DMF	90	18	(87)	120
Me	HO	I	CuI	5 mol %	**L16** (20 mol %), Cs_2CO_3	DMF	rt	20	(79)	52

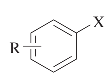
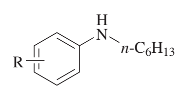
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_6

n-$C_6H_{13}NH_2$  Catalyst (x amount) 

X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
Br	Cu	5 mol %	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(69)	124
I	Cu	5 mol %	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(99)	124
Cl	Cu (active)	5 eq	none	H_2O	MW (100 W)	6 min	(80)	280
Br	Cu (active)	5 eq	none	H_2O	MW (100 W)	6 min	(84)	280
I	Cu (active)	5 eq	none	H_2O	MW (100 W)	6 min	(87)	280
I	CuCl	10 mol %	**L9** (10 mol %), TBAH	DMSO	80	24 h	(87)	281
Br	CuCl	10 mol %	TMHD (25 mol %), Cs_2CO_3	NMP	120	10 h	(78)	188
I	CuCl	5 mol %	TBAH (aq)	—	80	24 h	(77)	282
I	CuBr	5 mol %	**L10** (6 mol %), Cs_2CO_3	DMSO	80	30 h	(91)	259
I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	60	14 h	(87)	192
I	CuI	10 mol %	L-Pro (20 mol %), TBAA	DMF	rt	24 h	(91)	61
Br	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	80	24 h	(65)	273
I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(90)	273
I	CuI	10 mol %	DMG (20 mol %), TBPM	DMSO	rt	24 h	(94)	61
I	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	rt	10 h	(97)	261
I	Cu_2O	5 mol %	**L12** (20 mol %), Cs_2CO_3	MeCN	60	18 h	(78)	125
I	Cu_2O	5 mol %	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18 h	(88)	125

 Catalyst (x amount) 

R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
4-Cl	Br	CuCl	5 mol %	TBAH (aq)	—	80	24 h	(62)	282
4-Cl	I	CuCl	5 mol %	TBAH (aq)	—	80	24 h	(72)	282
4-Cl	I	CuCl	10 mol %	**L9** (10 mol %), TBAH	DMSO	80	24 h	(81)	281
4-Cl	I	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	rt	12 h	(91)	261
4-Cl	Br	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	80	24 h	(70)	273
4-Cl	I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(91)	273
4-Br	I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(92)	273
4-I	I	CuI	10 mol %	**L10** (6 mol %), Cs_2CO_3	DMSO	80	30 h	(87)	259
4-I	I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	60	9 h	(86)	192
2-H_2N	I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(80)	273
3-H_2N	Br	CuI	5 mol %	**L13** (5 mol %), K_3PO_4	—	100	22 h	(90)	120
3-H_2N	Br	CuI	5 mol %	**L13** (20 mol %), K_3PO_4	DMF	90	18 h	(80)	120
3-O_2N	I	CuBr	5 mol %	**L10** (6 mol %), Cs_2CO_3	DMSO	80	30 h	(90)	259
3-O_2N	Br	CuI	5 mol %	**L13** (20 mol %), K_3PO_4	DMF	90	18 h	(79)	120
4-O_2N	I	CuCl	10 mol %	**L9** (10 mol %), TBAH	DMSO	80	24 h	(68)	281
2-MeO	Br	CuI	5 mol %	**L13** (20 mol %), K_3PO_4	DMF	90	18 h	(88)	120
4-MeO	Br	Cu	5 mol %	binol (10 mol %), Cs_2CO_3	DMSO	90	40 h	(84)	124
4-MeO	I	Cu	5 mol %	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(84)	124
4-MeO	I	CuBr	20 mol %	binol (20 mol %), K_3PO_4	DMF	50	6 h	(55)	62
4-MeO	I	CuBr	5 mol %	**L10** (6 mol %), Cs_2CO_3	DMSO	80	30 h	(81)	259
4-MeO	I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	60	24 h	(79)	192
4-MeO	Br	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	80	24 h	(55)	273
4-MeO	I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(68)	273
4-MeO	Br	CuI	10 mol %	DMCDA (20 mol %), K_3PO_4	[bmim]BF_4	110	12 h	(95)	232

TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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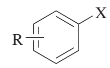
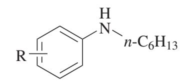
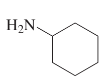
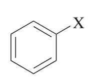
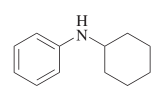
C_6

n-$C_6H_{13}NH_2$  Catalyst (x amount) 

R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
4-MeO	I	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	rt	12 h	(97)	261
4-MeO	I	Cu_2O	5 mol %	**L7** (20 mol %), Cs_2CO_3	toluene	80	18 h	(88)	125
4-Me	Br	Cu (active)	5 eq	none	H_2O	MW (100 W)	6 min	(78)	280
4-Me	I	CuCl	5 mol %	TBAH (aq)	—	80	24 h	(77)	282
4-Me	I	CuCl	10 mol %	**L9** (10 mol %), TBAH	DMSO	80	24 h	(74)	281
4-Me	I	CuBr	5 mol %	**L10** (6 mol %), Cs_2CO_3	DMSO	80	30 h	(87)	259
4-Me	I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(85)	273
3-CF_3	I	Cu_2O	5 mol %	**L7** (20 mol %), Cs_2CO_3	toluene	80	18 h	(76)	125
4-NC-	Br	CuI	5 mol %	**L9** (20 mol %), K_3PO_4	DMF	90	18 h	(73)	120
4-NC-	I	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	rt	8 h	(95)	261
2-$HOCH_2$	Br	CuI	5 mol %	**L13** (20 mol %), K_3PO_4	DMF	90	18 h	(88)	120
3-MeO_2C	I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(80)	273
3-MeO_2C	I	CuCl	10 mol %	**L9** (10 mol %), TBAH	DMSO	80	24 h	(59)	281
2-HO_2C, 4-Br	Br	Cu_2O	5 mol %	K_3PO_4	DMA	70	16 h	(83)	206
3,5-Me_2	I	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	rt	12 h	(97)	261
3,5-Me_2	Br	CuI	5 mol %	**L13** (5 mol %), K_3PO_4	—	100	22 h	(90)	120
3,5-Me_2	Br	CuI	5 mol %	**L13** (5 mol %), K_3PO_4	DMF	90	18 h	(91)	120
4-Ac	Br	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	80	24 h	(68)	273
4-Ac	Br	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	65	8 h	(95)	261

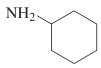
  Catalyst (x amount) 

X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
I	Cu/Fe–hydrotalcite	10 weight %	none	toluene	130	12	(81)	283
Br	CuBr	10 mol %	8-HOquin (20 mol %), Cs_2CO_3	DMSO	90	24	(82)	284
I	CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	89	24	(98)	118, 119
Br	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	24	(86)	67
I	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	20	(93)	67
I	CuI	10 mol %	DPP (20 mol %), K_3PO_4	DMF	90	24	(87)	108
I	CuI	10 mol %	**L8** (20 mol %), K_3PO_4	DMF	30	10	(62)	271
I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	60	14	(80)	192
I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	50	24	(64)	273
I	CuI	10 mol %	L-Pro (20 mol %), TBAA	DMF	rt	24	(94)	61
I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	5	(98)	276
I	CuO	10 mol %	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	80	12	(89)	277
I	Cu_2O	5 mol %	NaO*t*-Bu	NMP	110	24	(69)	266
I	$Cu(acac)_2$	10 mol %	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	MW, 150	0.5	(75)	262

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

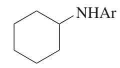
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_6

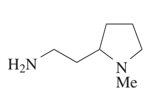


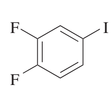
ArX

Catalyst(s) (x amount)

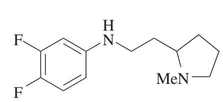


Ar	X	Catalyst(s)	x	Additive(s)	Solvent(s)	Temp (°)	Time	Yield	Refs.
4-ClC_6H_4	I	CuBr	5 mol %	**L17** (20 mol %), TBAB, NaOH	H_2O	100	24 h	(80)	235
4-ClC_6H_4	I	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	rt	19 h	(86)	261
4-ClC_6H_4	I	CuI	10 mol %	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(70)	271
4-ClC_6H_4	I	CuO	10 mol %	binol (20 mol %), $FeCl_3$ (10 mol %), Cs_2CO_3	DMF	90	12 h	(90)	277
2-$O_2NC_6H_4$	Cl	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	6 h	(99)	228
2-$O_2NC_6H_4$	Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	8 h	(91)	117
2-$O_2NC_6H_4$	I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	1 h	(99)	276
3-$O_2NC_6H_4$	Cl	CuI nanoparticles	1.25 mol %	Cs_2CO_3	DMF	110	3 h	(99)	285
3-$O_2NC_6H_4$	I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	6 h	(56)	276
3-$O_2NC_6H_4$	Br	CuO	10 mol %	binol (20 mol %), $FeCl_3$ (10 mol %), Cs_2CO_3	DMF	90	12 h	(88)	277
4-$O_2NC_6H_4$	Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	9 h	(71)	117
4-$O_2NC_6H_4$	Cl	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	8 h	(92)	228
4-$MeOC_6H_4$	I	Cu/Fe-hydrotalcite	10 wt %	none	toluene	130	12 h	(80)	283
4-$MeOC_6H_4$	I	CuBr	5 mol %	**L10** (6 mol %), Cs_2CO_3	DMSO	80	30 h	(70)	259
4-$MeOC_6H_4$	Br	CuI	10 mol %	piperidine 2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	20 h	(81)	67
4-$MeOC_6H_4$	Br	CuI	5 mol %	**L2** (25 mol %), TBAB, KOH, sealed tube	H_2O	130	5 min	(76)	236
4-$MeOC_6H_4$	Br	CuO	5 mol %	**L14** (50 mol %), cyclohexanone, TBAB, KOH	H_2O	MW (100 W), 130	5 min	(86)	51
4-$MeOC_6H_4$	Br	CuO	25 mol %	**L15** (50 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(73)	267
4-MeC_6H_4	I	CuBr	5 mol %	**L10** (6 mol %), Cs_2CO_3	DMSO	80	30 h	(75)	259
4-MeC_6H_4	I	CuI	10 mol %	**L8** (20 mol %), K_3PO_4	DMF	30	10 h	(90)	271
2-NCC_6H_4	Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	9 h	(59)	117
3-NCC_6H_4	Cl	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	14 h	(72)	228
4-$HOCH_2C_6H_4$	I	CuI	5 mol %	**L16** (20 mol %), Cs_2CO_3	DMF	rt	7 h	(88)	52
2-CHO, 5-ClC_6H_3	Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	8 h	(56)	117
4-$CHOC_6H_4$	Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	8 h	(89)	117
2-$HO_2CC_6H_4$	Cl	Cu, Cu_2O	10, 5 mol %	K_2CO_3	$EtOCH_2CH_2OEt$	130	24 h	(93)	278
2-$HO_2CC_6H_4$	Br	Cu, Cu_2O	9, 4 mol %	K_2CO_3	$EtOCH_2CH_2OH$	130	24 h	(65)	70
2-$HO_2CC_6H_4$	Br	Cu, Cu_2O	10, 5 mol %	K_2CO_3	$EtOCH_2CH_2OEt$	130	24 h	(82)	278
2-$HO_2CC_6H_4$	Br	CuI	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(85)	258
2-$HO_2CC_6H_4$	Br	$Cu(acac)_2$	10 mol %	binol (20 mol %), Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	MW, 130	0.5 h	(46)	262
2-HO_2C, 4-BrC_6H_3	Br	CuI	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(40)	258
2-HO_2C, 5-BrC_6H_3	Br	Cu_2O	5 mol %	K_3PO_4	DMA	70	16 h	(78)	206
2-HO_2C, 6-$O_2NC_6H_3$	Br	CuI	10 mol %	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(85)	258
4-$HO_2CC_6H_4$	Cl	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	14 h	(72)	228
4-$HO_2CC_6H_4$	Cl	Cu/Al–HTB	20 weight %	K_2CO_3	—	100	8 h	(88)	117
4-$HO_2CC_6H_4$	I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	4 h	(75)	276
4-$HO_2CC_6H_4$	Cl	CuI nanoparticles	1.25 mol %	Cs_2CO_3	DMF	110	3 h	(98)	285
1-Np	Br	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	65	18 h	(83)	261
2-Np	Br	CuBr	5 mol %	**L17** (20 mol %), NaOH, TBAB	H_2O	100	24 h	(81)	235

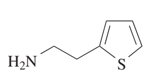


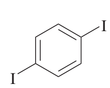


CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 1 h

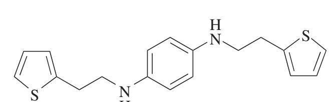


(98) 52

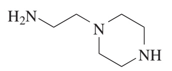
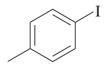
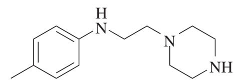
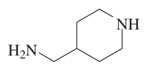
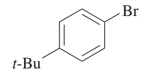
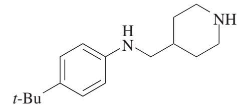
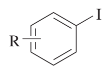
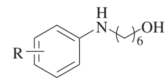
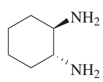
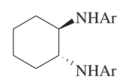
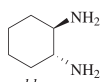
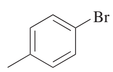
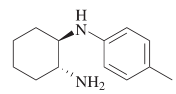
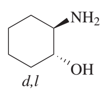
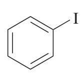
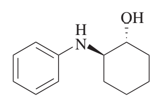
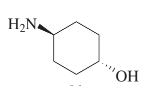
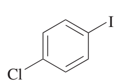
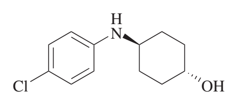
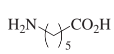
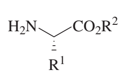
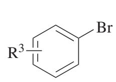
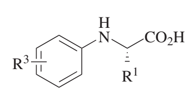




CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 20 h

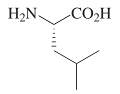
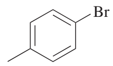
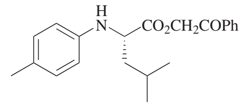
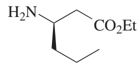
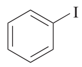
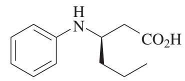
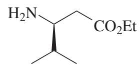
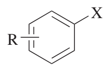
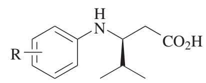


(82) 52

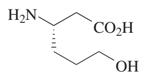
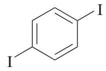
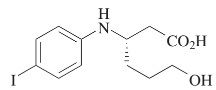
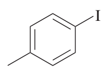
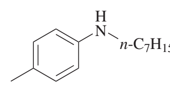
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		Cu (10 mol %), $K_3PO_4•H_2O$, $Me_2NCH_2CH_2OH$, 75°, 30 h	 (84)	195
		CuI (5 mol %), **L13** (20 mol %), K_3PO_4, DMF, 90°, 18 h	 (80)	120
		CuI (*x* mol %), Cs_2CO_3, additive (20 mol %), DMF, rt, 12 h	 *x* / R / Additive: 5 / 3,4-F_2 / **L16** (93); 10 / 4-Me / **L11** (93); 5 / 4-Me / **L16** (99)	196, 261, 196
 (1*R*,2*R*)	ArBr	CuBr (10 mol %), binol (20 mol %), K_3PO_4, DMF, 120°, 36 h	 Ar: Ph (78); 4-$O_2NC_6H_4$ (49); 4-$MeOC_6H_4$ (71); 4-MeC_6H_4 (61)	286
 *d,l*		CuI (20 mol %), K_3PO_4, dioxane, 110°, 23 h	 (66)	115
 *d,l*		CuI (2.5 mol %), NaOH, DMSO/H_2O (2:1), 90°, 15 h	 (87)	279
 *d,l*		CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 12 h	 (80)	196
	Ar I	CuI (10 mol %), $K_3PO_4•H_2O$, $Me_2N(CH_2)_2OH$, H_2O, 90°	 Ar: H (76); 3-$MeOC_6H_4$ (73); 4-$MeOC_6H_4$ (46); 2-$HO_2CC_6H_4$ (76); 3-$HO_2CC_6H_4$ (76); 4-$HO_2CC_6H_4$ (88)	260
$C_{6–7}$				
		Catalyst (*x* mol %)		

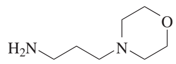
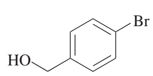
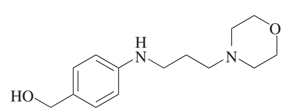
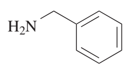
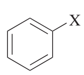
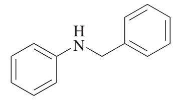
R^1	R^2	*N*-Nucleophile	R^3	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
n-Bu	H	free base	H	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(80)	271
n-Bu	H	free base	2-O_2N	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(73)	271
i-Bu	H	free base	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(71)	25
i-Bu	H	free base	H	I	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(92)	25
i-Bu	H	free base	H	Br	CuI	10	**L11** (20 mol %), Cs_2CO_3	DMF	65	12 h	(93)	261
i-Bu	H	HCl salt	H	Cl	Cu_2O	5	NaO*t*-Bu	NMP	110	24 h	(76)	266
i-Bu	Me	HCl salt	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(60)	25
i-Bu	*t*-Bu	HCl salt	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(64)	25
i-Bu	H	free base	4-Cl	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(87)	271
i-Bu	H	free base	3-(1-imidazolylmethyl)	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(67)	25
$EtCH(Me)CH_2$	H	free base	4-Cl	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(88)	271

TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_6				
		1. CuI (10 mol %), K_2CO_3, DMF, 90° 2. $PhCOCH_2Br$, Et_3N, EtOAc	 (53)	272
		CuI (10 mol %), K_2CO_3, H_2O, DMF, 100°, 48 h	 (74)	270
		CuI (10 mol %), K_2CO_3, H_2O, DMF, 100°, 48 h		270

R	X		R	X	
H	Br	(62)	4-AcNH	I	(17)
H	I	(74)	4-O_2N	I	(87)
2-Cl	I	(80)	4-MeO	Br	(0)
4-Br	Br	(72)	4-MeO	I	(31)
4-I	I	(83)	4-Me	I	(75)
4-H_2N	I	(0)			

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), K_2CO_3, H_2O, DMF, 100°, 48 h	 (72)	171
C_7				
n-$C_7H_{15}NH_2$		Cu (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, 60°, 40 h	 (88)	195

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), **L18** (20 mol %), Cs_2CO_3, DMF, 65°, 17 h	 (90)	261
		Catalyst (x mol %)		

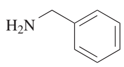
X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time		
Br	Cu	5	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(95)	124
I	Cu/Fe–hydrotalcite	10 (wt)	none	toluene	130	12 h	(79)	283
Br	CuCl	10	TMHD (25 mol %), Cs_2CO_3	NMP	120	10 h	(86)	188
I	CuCl	10	**L9** (10 mol %), TBAH	DMSO	80	24 h	(91)	281
Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	DMSO	90	24 h	(92)	284
I	CuBr	2.5	**L5**, (5 mol %), Cs_2CO_3	DMF	89	24 h	(98)	118, 119
I	CuBr	5	**L10** (6 mol %), Cs_2CO_3	DMSO	55	24 h	(92)	259
Br	CuI	2.5	K_2CO_3	NMP	160	16 h	(50)	287
I	CuI	2.5	K_2CO_3	NMP	160	16 h	(9)	287
I	CuI	5	K_3PO_4	$HOCH_2CH_2OH$/i-PrOH	80	8 h	(91)	194
Br	CuI	10	K_2CO_3	H_2O/DMF	110	24 h	(<4)	270
I	CuI	10	DMG (20 mol %), TBPM	DMSO	rt	24 h	(92)	61
I	CuI	10	DMG (20 mol %), TBPE	NMP	0	5 h	(87)	61
I	CuI	10	L-Pro (20 mol %), TBAA	DMF	rt	24 h	(95)	61
Br	CuI	2	**L1** (2 mol %), KOt-Bu	—	100	12 h	(72)	288
I	CuI	10	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(81)	273
I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(82)	271
Cl	CuI	5	**L2** (25 mol %), KOH, TBAH	H_2O	MW (100 W), 130	5 min	(trace)	236
I	CuI	5	**L2** (25 mol %), KOH, TBAH	H_2O	MW (100 W), 130	5 min	(82)	236
I	CuI–PAnNF	5	K_2CO_3	DMF	50	10 h	(99)	276
I	CuO nanoparticles	1.26	KOH	DMSO	110	4 h	(90)	224
Cl	CuO	5	**L14** (50 mol %), cyclohexanone, KOH, TBAB	H_2O	MW (100 W), 130	5 min	(trace)	51
I	CuO	5	**L14** (50 mol %), cyclohexanone, KOH, TBAB	H_2O	MW (100 W), 130	5 min	(86)	51

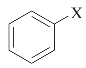
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

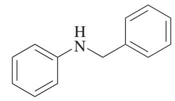
Continued from previous page.

C_7

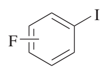




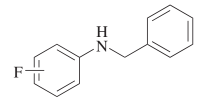
Catalyst (x mol %)



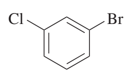
X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
Cl	CuO	25	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 80	2 min	(<5)	267
Br	CuO	25	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(78)	267
I	CuO	25	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 80	2 min	(78)	267
I	Cu_2O	10	Cs_2CO_3	DMF	100	18 h	(0)	221
I	Cu_2O	1	**L7** (20 mol %), Cs_2CO_3	—	80	18 h	(95)	125
I	$Cu(OAc)_2•H_2O$	20	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	20 h	(60)	289
I	$Cu(OAc)_2•H_2O$	15	(–)-sparteine, Cs_2CO_3	DMF	130	24 h	(75)	290
I	$Cu(OAc)_2•H_2O$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	MW, 150	30 min	(77)	262
Br	cat. **4**	25	K_2CO_3	NMP	160	16 h	(57)	269
Br	cat. **5**	2.5	K_2CO_3	NMP	160	16 h	(79)	291
I	cat. **6**	5	Cs_2CO_3	toluene	100	12 h	(90)	123



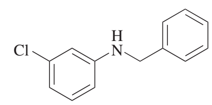
CuI (10 mol %), DMSO



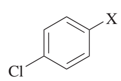
Isomer	Additives	Temp (°)	Time (h)		Refs.
2	DMG (20 mol %), TBPM	rt	24	(70)	61
3	L-Pro (20 mol%), K_2CO_3	60	14	(80)	192
4	DMG (20 mol %), TBPM	rt	24	(81)	61



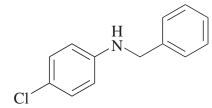
Cu (5 mol %), binol (10 mol %), Cs_2CO_3, DMSO, 90°, 24 h



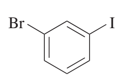
(93) 124



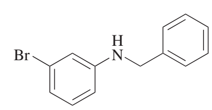
Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
Br	CuCl	5	TBAH (aq)	—	80	24 h	(96)	282
I	CuCl	5	TBAH (aq)	—	80	24 h	(80)	282
I	CuCl	10	**L9** (10 mol %), TBAH	DMSO	80	24 h	(78)	281
I	CuI	5	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	80	12 h	(84)	194
Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	70	22 h	(76)	192
I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(81)	271
I	CuI	10	DMG (20 mol %), TBPE	NMP	0	5 h	(91)	61
I	CuI	10	DMG (20 mol %), TBPM	DMSO	rt	24 h	(98)	61
I	CuI–PAnNF	5	K_2CO_3	DMF	rt	3 h	(85)	276
Br	CuO	5	**L14** (50 mol %), TBAB, cyclohexanone	H_2O	MW (100 W), 130	5 min	(86)	51
Br	CuO	25	**L15** (50 mol %), TBAB	H_2O	MW (100 W), 130	5 min	(81)	267



CuI (5 mol %), $HOCH_2CH_2OH$, K_3PO_4, *i*-PrOH, 80°, 6 h



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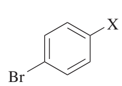
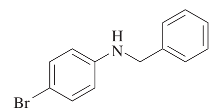


Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	CuCl	10	**L9** (10 mol %), TBAH	DMSO	80	24	(86)	281
I	CuCl	5	TBAH (aq)	—	80	24	(80)	282
Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	70	22	(82)	192
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	60	12	(81)	192, 47
I	CuI	10	L-Pro (20 mol %), TBAA	DMF	rt	24	(90)	61

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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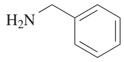
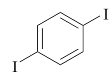
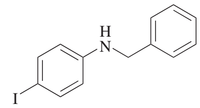
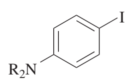




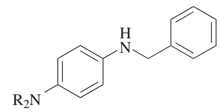
Catalyst (x mol %), DMSO



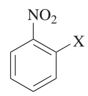
Catalyst	x	Additive(s)	Temp (°)	Time (h)		Refs.
CuBr	5	**L10** (6 mol %), Cs_2CO_3	55	24	(85)	259
CuI	10	NMG (20 mol %), K_2CO_3	40	13	(82)	47
CuI	10	L-Pro (20 mol %), K_2CO_3	60	14	(89)	192



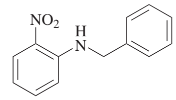
CuI (x mol %)



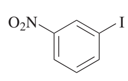
R	x	Additve(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	5	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	90	38	(62)	194
Me	10	DMG (20 mol), TBPM	DMSO	rt	24	(85)	61



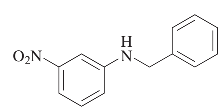
Catalyst (x amount), K_2CO_3



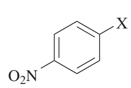
X	Catalyst	x	Solvent	Temp (°)	Time (h)		Refs.
Cl	Cu/Al–HTB	20 wt %	—	100	8	(80)	117
I	CuI–PAnNF	5 mol %	DMF	rt	4	(98)	276



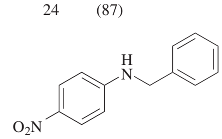
Catalyst (x mol %)



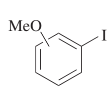
Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
CuBr	5	**L10** (6 mol %), Cs_2CO_3	DMSO	55	24	(83)	259
CuI	10	NMG (20 mol %), K_2CO_3	DMSO	40	23	(80)	47, 192
CuI	5	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	80	12	(91)	194
CuI	10	L-Pro (20 mol %), TBAA	DMF	rt	24	(96)	61
Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	toluene	80	24	(87)	125



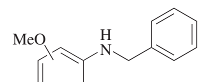
Catalyst (x amount)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	16 h	(77)	117
Br	CuO	5 mol %	**L14** (50 mol %), cyclohexanone, KOH, TBAB	H_2O	MW (100 W), 130	5 min	(63)	51
Br	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(50)	267



Catalyst (x mol %)



Isomer	X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time(h)		Refs.
2	Br	CuCl	10	TMHD (25 mol %), Cs_2CO_3	NMP	120	10	(11)	188
2	I	CuI	5	K_3PO_4	$HOCH_2CH_2OH$, *i*-PrOH	100	72	(91)	194
3	I	CuI	10	DMG (20 mol %), TBPE	NMP	0	5	(79)	61
3	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	80	30	(90)	47

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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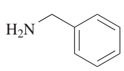
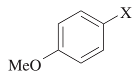
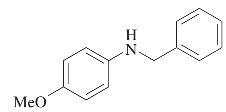
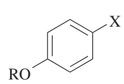




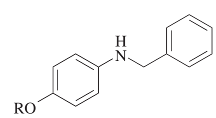
Catalyst (*x* amount)



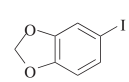
X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
Br	Cu	5 mol %	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(67)	124
I	Cu	5 mol %	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(82)	124
I	Cu/Fe–hydrotalcite	10 wt %	none	toluene	130	12 h	(81)	283
I	CuCl	5 mol %	TBAH (aq)	—	80	24 h	(96)	282
Br	CuCl	10 mol %	TMHD (25 mol %), Cs_2CO_3	NMP	120	10 h	(81)	188
I	CuCl	10 mol %	**L9** (10 mol %), TBAH	DMSO	80	24 h	(70)	281
I	CuBr	5 mol %	**L17** (20 mol %), TBAH, NaOH	H_2O	100	24 h	(74)	235
I	CuBr	5 mol %	**L10** (6 mol %), Cs_2CO_3	DMSO	55	24 h	(85)	259
Br	CuI	2.5 mol %	K_2CO_3	NMP	160	16 h	(25)	287
I	CuI	5 mol %	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	80	18 h	(89)	194
Br	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	65	14 h	(85)	261
I	CuI	10 mol %	**L11** (20 mol %), Cs_2CO_3	DMF	rt	13 h	(91)	261
I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	60	16 h	(84)	192, 47
I	CuI	10 mol %	L-Pro (20 mol %), TBAA	DMF	rt	24 h	(83)	61
I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	11 h	(23)	276
Cl	CuO	5 mol %	**L14** (50 mol %), cyclohexanone, TBAB, KOH	H_2O	MW (100 W), 130	5 min	(trace)	51
Br	CuO	5 mol %	**L14** (50 mol %), cyclohexanone, TBAB, KOH	H_2O	MW (100 W), 130	5 min	(91)	51
I	CuO	5 mol %	**L14** (50 mol %), cyclohexanone, TBAB, KOH	H_2O	MW (100 W), 130	5 min	(86)	51
Br	CuO	25 mol %	**L15** (50 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(82)	267
I	CuO	25 mol %	**L15** (50 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(82)	267
I	Cu_2O	1 mol %	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18 h	(90)	125
I	**6**	5 mol %	Cs_2CO_3	toluene	100	18 h	(72)	123



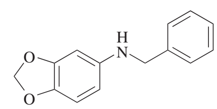
CuI (5 mol %), DMF



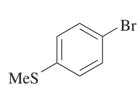
R	X	Additives	Temp (°)	Time (h)		Refs.
H	I	**L16** (20 mol %), Cs_2CO_3	rt	6	(80)	52
$HOCH_2CH_2$	Br	**L13** (20 mol %), K_3PO_4	90	18	(84)	120



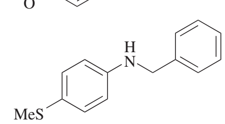
CuI (10 mol %),
DMG (20 mol %),
TBPM, DMSO, rt, 24 h



(81) 61



CuI (5 mol %),
L13 (20 mol %),
K_3PO_4, DMF, 90°, 18 h



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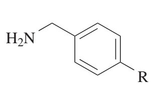
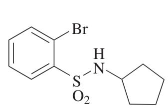
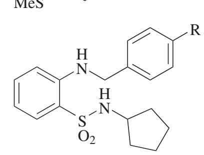
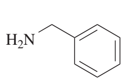


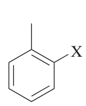


CuI (10 mol %),
phen (20 mol %),
Cs_2CO_3, DMSO,
MW, 150°, 11 min

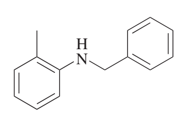


R		Refs.
H	(96)	268
Cl	(89)	
MeO	(90)	





Catalyst (*x* mol %)



X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time		Refs.
Br	Cu	5	binol (10 mol %), Cs_2CO_3	DMSO	90	40 h	(62)	124
I	CuI	10	DMG (20 mol %), TBPM	DMSO	rt	24 h	(62)	61
Br	CuO	20	**L14** (50 mol %), cyclohexanone, KOH, TBAB	H_2O	MW (100 W), 130	5 min	(65)	51

TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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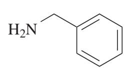
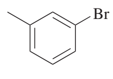
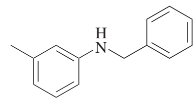
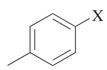




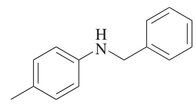
Catalyst (x mol %), Cs_2CO_3



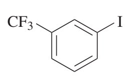
Catalyst	x	Additive	Solvent	Temp (°)	Time (h)		Refs.
Cu	5	binol (10 mol %)	DMSO	90	40	(93)	124
CuCl	10	TMHD (25 mol %)	NMP	120	10	(81)	188



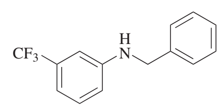
Catalyst (x mol %)



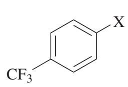
X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
Br	Cu	5	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(92)	124
I	CuCl	10	**L9** (10 mol %), TBAH	DMSO	80	24 h	(80)	281
I	CuBr	5	**L10** (6 mol %), Cs_2CO_3	DMSO	55	24 h	(82)	259
Br	CuBr	10	8-HOQ (20 mol %), Cs_2CO_3	DMSO	90	24 h	(22)	284
Br	CuI	2.5	K_2CO_3	NMP	160	16 h	(35)	287
I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	4 h	(76)	271
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	60	16 h	(85)	192, 47
I	CuI–PAnNF	5	K_2CO_3	DMF	rt	14 h	(37)	276
Br	CuO	5	**L14** (50 mol %), cyclohexanone, TBAB, KOH	H_2O	MW (100 W), 130	5 min	(85)	51
Br	CuO	25	**L15** (50 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(74)	267



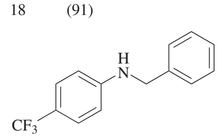
Catalyst (x mol %), Cs_2CO_3



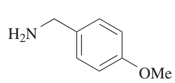
Catalyst	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
CuI	10	DMG (20 mol %), TBPE	NMP	0	5	(85)	61
Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	toluene	80	18	(91)	125

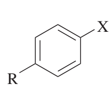


Catalyst (x mol %)

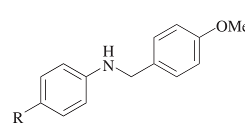


X	Catalyst	x	Additives	Solvent	Temp (°)	Time		Refs.
I	CuI	10	DMG (20 mol %), TBPM	DMSO	rt	24 h	(96)	61
Cl	CuO	5	**L14** (50 mol %), cyclohexanone, TBAB, KOH	H_2O	MW (100 W), 130	5 min	(trace)	51
Br	CuO	5	**L14** (50 mol %), cyclohexanone, TBAB, KOH	H_2O	MW (100 W), 130	5 min	(79)	51
Br	CuO	25	**L15** (50 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(57)	267





Catalyst (x mol %), Cs_2CO_3

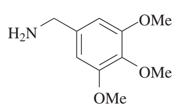
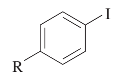
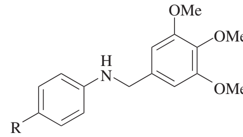
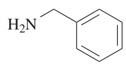
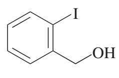
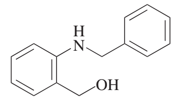
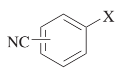
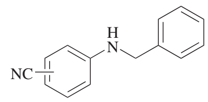


R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	I	**6**	5	none	toluene	100	12	(90)	123
MeO	Br	CuI	10	**L11** (20 mol %), Cs_2CO_3	DMF	65	14	(85)	261

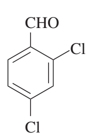
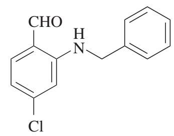
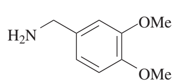
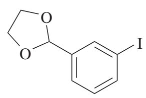
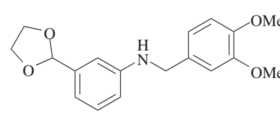
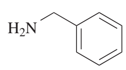
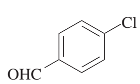
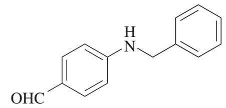
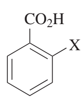
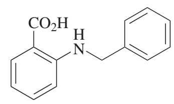
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuBr (5 mol %), **L10** (6 mol %), Cs_2CO_3, DMSO, 80°, 30 h	 R: H (95); MeO (80); Me (87)	259
		CuI (5 mol %), $HOCH_2CH_2OH$, K_3PO_4, *i*-PrOH, 100°, 24 h	 (95)	194
		Catalyst (*x* amount)		

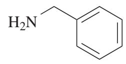
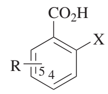
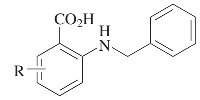
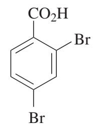
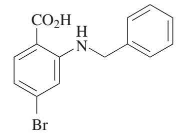
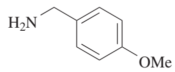
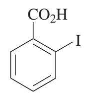
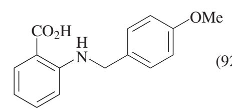
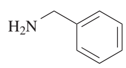
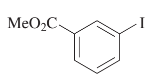
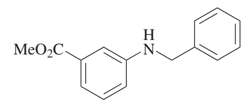
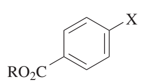
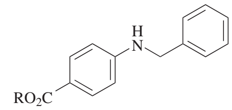
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
2	Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	8	(52)	117
2	I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	3	(59)	276
3	I	CuBr	5 mol %	**L10** (6 mol %), Cs_2CO_3	DMSO	55	24	(87)	259
3	I	CuI	10 mol %	L-Pro (20 mol %), TBAA	DMF	rt	24	(99)	61
3	I	CuI	5 mol %	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	80	12	(80)	194
3	I	Cu_2O	5 mol %	**L7** (20 mol %), Cs_2CO_3	toluene	80	24	(85)	125
4	Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	16	(45)	117
4	Cl	CuCl	10 mol %	TMHD (25 mol %), Cs_2CO_3	NMP	120	10	(5)	188
4	Br	CuCl	10 mol %	TMHD (25 mol %), Cs_2CO_3	NMP	120	10	(76)	188
4	I	CuI	5 mol %	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	80	12	(79)	194
4	I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	5	(41)	276

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu/Al–HTB (20 wt %), K_2CO_3, 100°, 12 h	 (69)	117
		CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 3 h	 (92)	52
		Cu/Al–HTB (20 wt %), K_2CO_3, 100°, 12 h	 (68)	117
		Catalyst(s) (*x* mol %)		

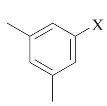
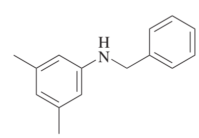
X	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
Cl	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24 h	(99)	278
Br	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24 h	(95)	278
Br	Cu, Cu_2O	9, 4	K_2CO_3	$EtOCH_2CH_2OEt$	130	24 h	(82)	70
Br	Cu	5	binol (20 mol %), Cs_2CO_3	DMSO	90	24 h	(75)	124
Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(80)	258
I	CuI	10	L-Pro (20 mol %), TBAA	DMF	rt	24 h	(89)	61
I	CuI	10	NMG (20 mol %), K_2CO_3	DMSO	40	12 h	(91)	192, 47
Cl	CuI	5	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	100	72 h	(48)	194
Br	CuI	5	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	100	48 h	(53)	194
I	CuI	5	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	80	18 h	(71)	194
Cl	CuO	25	**L15** (50 mol %), TBAB, KOH	H_2O	MW (100 W), 80	2 min	(55)	267

TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

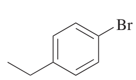
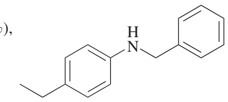
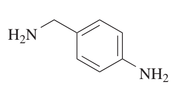
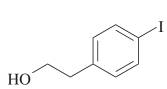
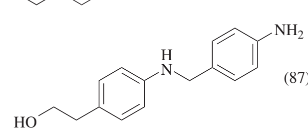
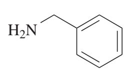
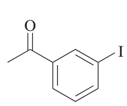
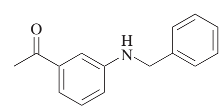
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Cu (10 mol %), Cu_2O (5 mol %), K_2CO_3, $EtOCH_2CH_2OEt$, 130°, 24 h	 R: 4-F (92); 5-O_2N (81); 5-MeO (85); 5-HO_2C (91)	278
		Cu_2O (5 mol %), K_3PO_4, $EtOCH_2CH_2OH$, 70°, 16 h	 (94)	206
		CuI (10 mol %), **L11** (20 mol %), Cs_2CO_3, DMF, rt, 10 h	 (92)	261
		CuI (10 mol %), DMG (20 mol %), TBPE, NMP, 0°, 5 h	 (94)	61
		Catalyst (*x* amount)		

R	X	Catalyst	*x*	Additive	Solvent(s)	Temp (°)	Time (h)		Refs.
H	Cl	Cu/Al–HTB	20 wt %	K_2CO_3	—	100	16	(46)	117
Et	I	CuI	5 mol %	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	90	12	(58)	194

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %)		

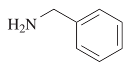
X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	Cu	5	binol (10 mol %), Cs_2CO_3	DMSO	90	24	(89)	124
Br	CuCl	10	TMHD (25 mol %), Cs_2CO_3	NMP	120	10	(84)	188
I	CuI	5	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	80	12	(89)	194
I	CuI	5	**L16** (20 mol %), Cs_2CO_3	DMF	rt	2	(90)	52
I	CuI	10	DMG (20 mol %), TBPM	DMSO	rt	24	(84)	61

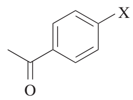
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuO (25 mol %), **L15** (50 mol %), KOH, TBAB, H_2O, MW (100 W), 130°, 5 min	 (70)	267
		CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 12 h	 (87)	196
		CuI (10 mol %), DMG (20 mol %), TBPM, DMSO, rt, 24 h	 (96)	61

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

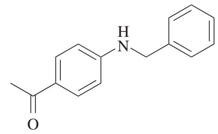
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

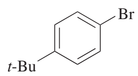




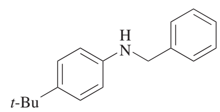
Catalyst (*x* mol %)



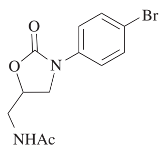
X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time	Yield (%)	Refs.
Br	Cu	5	binol (10 mol %), Cs_2CO_3	DMSO	90	40 h	(68)	124
I	CuCl	5	TBAH (aq)	—	80	24 h	(83)	282
I	CuCl	10	**L9** (10 mol %), TBAH	DMSO	80	24 h	(74)	281
I	CuI	5	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	80	5 h	(90)	194
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	80	40 h	(88)	47
I	CuI	10	L-Pro (20 mol %), TBAA	DMF	rt	24 h	(90)	61
Br	CuO	5	**L14** (50 mol %), cyclohexanone, TBAB, KOH	H_2O	MW (100 W), 130	5 min	(84)	51
Br	CuO	25	**L15** (50 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(50)	267



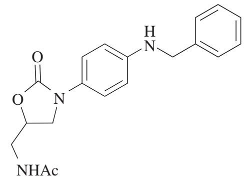
Cu (5 mol %), binol (10 mol %), Cs_2CO_3, DMSO, 90°, 24 h



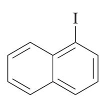
(92) 124



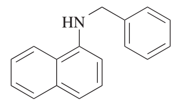
CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h



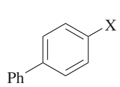
(65) 292



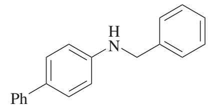
Catalyst (*x* mol %)



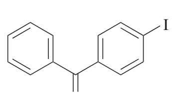
Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield (%)	Refs.
CuCl	10	**L9** (10 mol %), TBAH	DMSO	80	24	(68)	281
CuI	10	DMG (20 mol %), TBPM	DMSO	rt	24	(85)	61
CuI	5	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	90	12	(70)	194



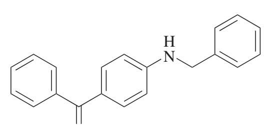
Catalyst (10 mol%)



X	Catalyst	Additives	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
Br	CuCl	TMHD (25 mol %), Cs_2CO_3	NMP	120	10	(76)	188
Br	CuI	L-Pro (20 mol %), K_2CO_3	DMSO	60	12	(66)	192
I	CuI	L-Pro (20 mol %), K_2CO_3	DMSO	80	30	(81)	47
I	CuI	DMG (20 mol %), TBPM	DMSO	rt	24	(90)	61



CuI (10 mol %), DMG (20 mol %), TBPM, DMSO, rt, 24 h

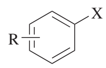
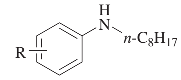


(97) 61

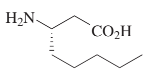
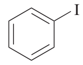
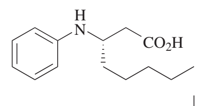
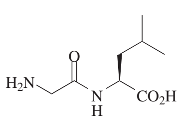
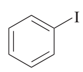
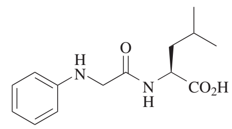
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

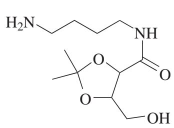
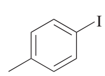
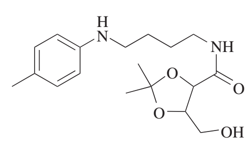
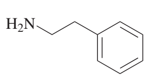
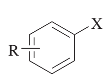
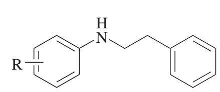
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_8

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
n-$C_8H_{17}NH_2$		Catalyst (x mol %)		

R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
H	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	24 h	(0)	228
2-O_2N	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	6 h	(89)	228
4-O_2N	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	8 h	(99)	228
2-$BnNHSO_2$	Br	CuI	10	phen (20 mol %), Cs_2CO_3	DMSO	MW, 150	11 min	(94)	268
2-Me	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	32 h	(42)	228
4-Me	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	28 h	(52)	228
2-NC–	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	10 h	(75)	228
4-NC–	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	12 h	(78)	228
2-CHO	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	8 h	(95)	228
2-CHO, 4-Cl	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	8 h	(95)	228
4-CHO	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	10 h	(90)	228
2-HO_2C	Cl	Cu	7.5	K_2CO_3	H_2O	))) (20 kHz), rt	20 min	(88)	241
4-HO_2C	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	8 h	(97)	228

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), K_2CO_3, H_2O, DMF, 110°, 48 h	 (73)	293
		CuI (10 mol %), $K_3PO_4 \cdot H_2O$, $Me_2NCH_2CH_2OH$, H_2O, 90°	 (46)	260

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 12 h	 (85)	196
		Catalyst (x mol %)		

R	X	Catalyst	x	Additives	Solvent(s)	Temp (°)	Time		Refs.
H	Cl	CuI	2	**L1** (2 mol %), KOt-Bu	—	100	12 h	(50)	288
H	Br	CuI	2	**L1** (2 mol %), KOt-Bu	—	100	12 h	(88)	288
H	I	CuI	2	**L1** (2 mol %), KOt-Bu	—	100	12 h	(88)	288
H	I	CuI	10	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(88)	273
H	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	MW, 150	30 min	(66)	262
4-Cl	I	CuI	10	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(89)	273
4-Br	I	CuI	5	**L16** (20 mol %), Cs_2CO_3	DMF	rt	20 h	(82)	52
2-$BnNHSO_2$	Br	CuI	10	phen (20 mol %), Cs_2CO_3	DMSO	MW, 150	11 min	(91)	268

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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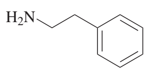
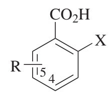
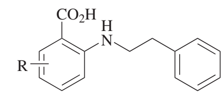
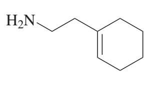
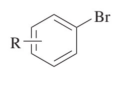
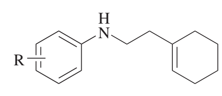
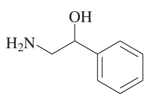
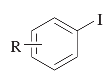
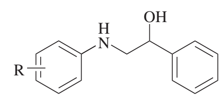
  Catalyst(s) (*x* mol %) 

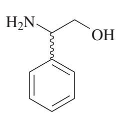
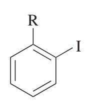
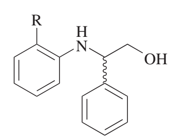
R	X	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	Cl	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(91)	278
H	Br	Cu, Cu_2O	10, 4	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(91)	278
H	Br	Cu, Cu_2O	9, 4	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(82)	70
H	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16	(62)	258
4-F	Br	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(94)	278
4-Cl	Cl	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(82)	278
4-Cl	Br	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(94)	278
5-Cl	Cl	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(94)	278
5-Br	Cl	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(84)	278
5-Br	Br	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(88)	278
4-O_2N	Cl	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(86)	278
3,4-$(MeO)_2$	Cl	Cu, Cu_2O	10, 5	K_2CO_3	$EtOCH_2CH_2OEt$	130	24	(84)	278

  CuI (5 mol %), **L13** (*x* mol %), K_3PO_4, 100°, 22 h 

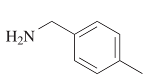
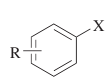
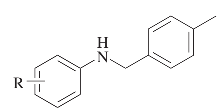
R	*x*		Refs.
4-Me	5	(79)	120
4-Me	20	(96)	
2,5-Me_2	20	(79)	

  CuI (2.5 mol %)  279

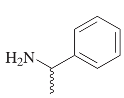
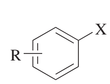
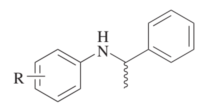
R	Additive	Solvents	Temp (°)	Time (h)	
2-H_2N	NaOH	DMSO/H_2O (2:1)	90	16.5	(86)
3-O_2N	K_3PO_4	$HOCH_2CH_2OH$/*i*-PrOH	75	16	(86)
2,6-Me_2	NaOH	DMSO/H_2O (2:1)	90	16.5	(86)

  Catalyst (*x* mol %) 

Config.	R	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
(*R,S*)	H	Cu_2O	1	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18	(91)	125
(*R*)	H	$Cu(OAc)_2$•H_2O	15	(–)-sparteine (30 mol %), Cs_2CO_3	DMF	130	24	(80)	290
(*R*)	Br	CuI	2.5	NaOH	*i*-PrOH	90	16	(84)	279

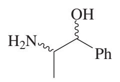
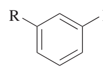
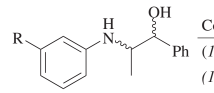
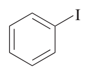
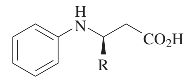
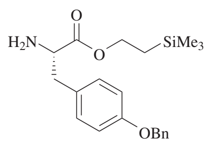
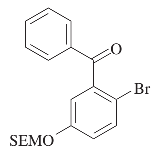
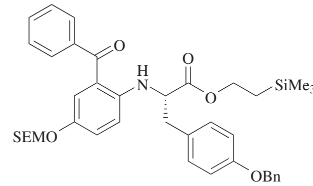
  Catalyst (*x* mol %), 100° 

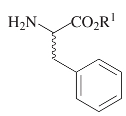
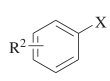
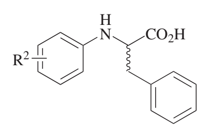
R	X	Catalyst	*x*	Additive(s)	Solvent	Time (h)		Refs.
H	Br	CuI	2	**L1** (2 mol %), KO*t*-Bu	—	12	(77)	288
H	I	**6**	5	Cs_2CO_3	toluene	12	(82)	123
2-HO_2C, 4-O_2N	Br	CuBr	5	**L17** (20 mol %), NaOH, TBAB	H_2O	24	(83)	235

  Catalyst (*x* mol %) 

Config.	R	X	Catalyst	x	Additives	Solvent	Temp (°)	Time (h)		er	Refs.
(*R*)	H	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	60	18	(65)	—	192
(*R*)	H	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	60	12	(75)	—	47
(*R*)	H	I	$Cu(OAc)_2$•H_2O	20	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	20	(48)	—	289
(*R*)	H	I	$Cu(OAc)_2$•H_2O	15	(–)-sparteine (30 mol %), Cs_2CO_3	DMF	130	24	(40)	—	290
(*S*)	H	I	CuI	10	**L11** (20 mol %), Cs_2CO_3	DMF	rt	15	(85)	—	261
(*R,S*)	4-Cl	I	CuI	10	DMG (20 mol %), TBPE	NMP	0	5	(78)	—	61
(*R,S*)	3,5-Me_2	I	CuI	5	**L16** (20 mol %), Cs_2CO_3	DMF	rt	10	(94)	—	52
(*R*)	3,5-Me_2	Br	CuI	5	**L13** (20 mol %), K_3PO_4	DMF	90	18	(71)	99:1	120

TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_9				
		CuI (2.5 mol %), NaOH, *i*-PrOH, 90°, 16.5 h	 Config. / R: (*1S,2R*) MeO (84); (*1R,2S*) $HOCH_2$ (84)	279
		CuI (10 mol %), K_2CO_3, H_2O, DMF, 100°, 48 h	 R: *n*-C_6H_{13} (76); *c*-C_6H_{11} (69); 4-$MeOC_6H_4$ (69)	270
		CuI (10 mol %), K_2CO_3, DMF, 90°, 72 h	 (50)	294

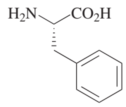
  Catalyst (*x* mol %) 

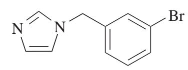
R^1	*N*-Nucleophile	Config.	R^2	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
H	free base	(*R/S*)	H	Br	CuI	10	K_3PO_4•H_2O	$Me_2N(CH_2)_2OH/H_2O$	90	—	(80)	260
H	free base	(*R*)	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(77)	25
H	free base	(*S*)	H	I	CuI	3	Cs_2CO_3	DMSO	90	48 h	(96)	275
H	free base	(*S*)	H	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(92)	116
H	free base	(*S*)	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(78)	25
H	free base	(*S*)	H	Br	CuI	10	K_2CO_3	DMF	MW, 140	20 min	(65)	265
Et	HCl salt	(*S*)	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(96)	25
allyl	HCl salt	(*S*)	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(57)	25
allyl	tosylate	(*S*)	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(93)	25
t-Bu	HCl salt	(*S*)	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(66)	25
Bn	HCl salt	(*S*)	H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(76)	25
H	free base	(*S*)	4-Cl	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(86)	271
H	free base	(*S*)	4-Cl	I	$La_{0.9}Ce_{0.1}Co_{0.6}Cu_{0.4}O_3$	2.5	Cs_2CO_3	toluene	110	48 h	(22)	295
H	free base	(*S*)	3-MeO	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(79)	25
H	free base	(*S*)	2-Me	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(43)	25
H	free base	(*S*)	4-Me	I	CuI	10	**L11** (20 mol %), Cs_2CO_3	DMF	rt	12 h	(85)	261
H	free base	(*S*)	4-Me	I	CuBr	5	**L17** (20 mol %), TBAB, NaOH	H_2O	100	24 h	(89)	235
H	free base	(*S*)	3-NC-	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(53)	25
H	free base	(*S*)	3-$HOCH_2$	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(87)	25
H	free base	(*S*)	3-Ac	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(94)	25
H	free base	(*S*)	4-*t*-Bu	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(41)	25
H	free base	(*S*)	4-Bz	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(18)	25

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

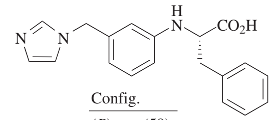
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_9



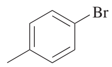


CuI (10 mol %),
K_2CO_3, KI,
H_2O, MW, 185°, 40 min

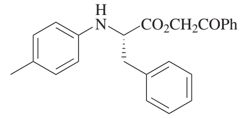


Config.	
(*R*)	(59)
(*S*)	(50)

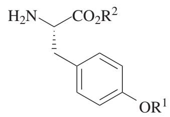
25

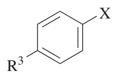


1. CuI (10 mol %),
K_2CO_3, DMF, 90°
2. $PhCOCH_2Br$, Et_3N, EtOAc

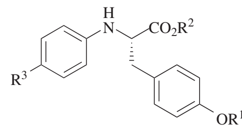


(59) 272

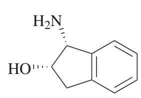


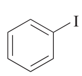


CuI (10 mol %)

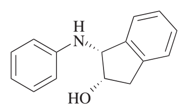


R^1	R^2	R^3	X	Additives	Solvent(s)	Temp (°)	Time		Refs.
H	H	H	I	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(78)	271
H	H	Cl	I	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(83)	271
H	Me	Cl	I	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(71)	271
H	H	Me	I	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(77)	271
allyl	H	*t*-Bu	Br	KI, K_2CO_3	H_2O/MeCN (4:1)	MW, 185	40 min	(64)	25
allyl	H	Bz	Br	KI, K_2CO_3	H_2O/MeCN (4:1)	MW, 185	40 min	(36)	25



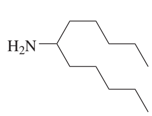


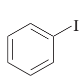
$Cu(OAc)_2$•H_2O (*x* mol %),
Cs_2CO_3, DMF



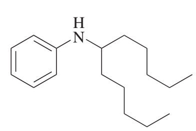
x	Additive	Temp (°)	Time (h)		Refs.
20	hippuric acid (20 mol %)	140	20	(47)	289
15	(–)-sparteine (30 mol %)	130	24	(72)	290

C_{11}

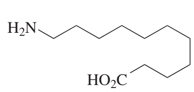


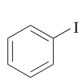


CuI–PAnNF (5 mol %),
K_2CO_3, DMF, rt, 10 h

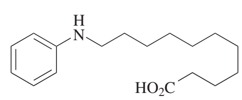


(79) 276

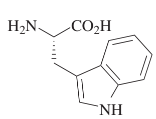


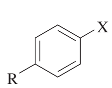


CuI (10 mol %), K_3PO_4•H_2O,
$Me_2NCH_2CH_2OH$, H_2O, 90°

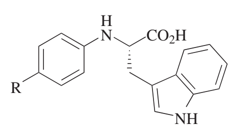


(87) 260





Catalyst (*x* mol %)



R	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
H	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	40	10 h	(81)	62
H	Br	CuI	10	KI, K_2CO_3	H_2O	MW, 185	40 min	(66)	25
H	Br	CuI	10	K_2CO_3	H_2O/DMF	90	48 h	(73)	116
Cl	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	3 h	(83)	271

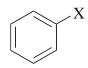
TABLE 2A. *N*-ARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

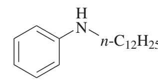
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{12}

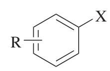
n-$C_{12}H_{25}NH_2$



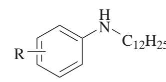
Catalyst(s) (x mol %)



X	Catalyst(s)	x	Additive(s)	Temp (°)	Time (h)		Refs.
I	CuBr	20	binol (20 mol %), K_3PO_4	rt	8	(83)	62
Br	CuI	10	DPP (20 mol %), K_3PO_4	90	24	(88)	108
Br	CuI	10	PPAPM (20 mol %), K_3PO_4	90	24	(87)	48
Cl	CuI–PAnNF	5	K_2CO_3	80	18	(7)	276
I	CuI–PAnNF	5	K_2CO_3	rt	4	(99)	276
I	CuO, $FeCl_3$	10, 10	binol (20 mol %), Cs_2CO_3	80	12	(76)	277



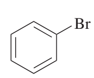
Catalyst (x mol %)



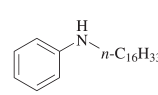
R		Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
4-Cl	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	rt	6 h	(83)	62
4-Cl	I	CuBr	5	**L17** (20 mol %), TBAB, NaOH	H_2O	100	24 h	(85)	235
4-Cl	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	1 h	(77)	271
4-Br	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	rt	10 h	(72)	62
2-O_2N	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	6 h	(95)	228
2-O_2N	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	2 h	(95)	276
3-O_2N	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	rt	10 h	(72)	62
3-O_2N	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	7 h	(76)	276
4-O_2N	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	6 h	(99)	228
4-O_2N	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	5 h	(93)	276
4-O_2N	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	4 h	(98)	276
4-MeO	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	10 h	(65)	276
4-MeO	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	8 h	(68)	276
4-Me	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	5 h	(71)	271
4-Me	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	12 h	(47)	276
4-Me	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	13 h	(68)	276
4-Me	I	CuO	10	binol (20 mol %), $FeCl_3$ (10 mol %), Cs_2CO_3	DMF	90	12 h	(72)	277
2-NC–	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	4 h	(78)	276
4-NC–	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	8 h	(64)	276
2-CHO, 5-Cl	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	4 h	(86)	276
3-CHO, 4-O_2N	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	1.5 h	(98)	276
4-CHO	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	4 h	(72)	276
2-HO_2C	Cl	Cu	7.5	K_2CO_3	H_2O	))) (20 kHz), rt	20 min	(88)	241
2-HO_2C	Br	CuBr	5	**L17** (20 mol %), TBAB, NaOH	H_2O	100	24 h	(83)	235
2-HO_2C	Br	CuI	10	binol (20 mol %), K_3PO_4	DMF	rt	16 h	(64)	258
4-HO_2C	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	2 h	(85)	276

C_{16}

n-$C_{16}H_{33}NH_2$



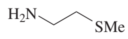
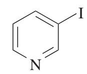
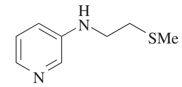
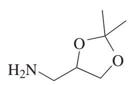
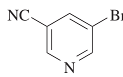
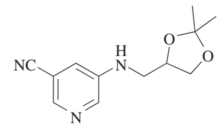
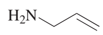
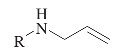
CuI (2 mol %), **L1** (2 mol %), KOt-Bu, 100°, 12 h

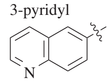


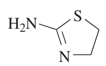
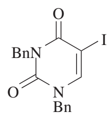
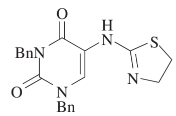
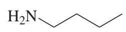
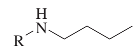
(65) 288

[a] 4-Iodo-*N*-(n-butyl)aniline was formed in 4% yield.

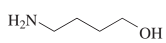
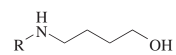
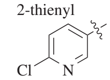
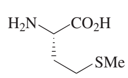
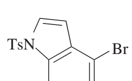
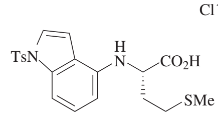
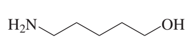
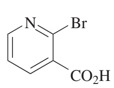
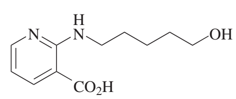
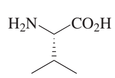
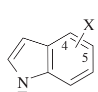
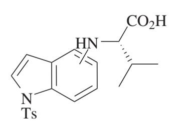
TABLE 2B. *N*-HETEROARYLATION OF PRIMARY ALKYL AMINES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_2				
		CuI (10 mol %), **L11** (20 mol %), Cs_2CO_3, DMF, rt, 20 h	 (95)	261
C_3				
		CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h	 (70)	292
	RX	CuI (*x* mol%)		

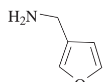
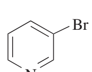
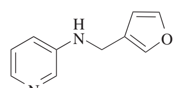
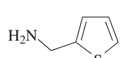
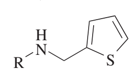
R	X	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
2-thienyl	I	5	**L11** (20 mol %), Cs_2CO_3	DMF	rt	17	(83)	52
3-pyridyl	Br	10	L-Pro (20 mol%), K_2CO_3	DMSO	90	40	(97)	47
	I	10	**L11** (20 mol %), Cs_2CO_3	DMF	rt	19	(87)	261

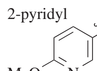
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$(CuOTf)_2$•C_6H_6 (5 mol %), phen (1 eq), dba (5 mol %), Cs_2CO_3, *p*-xylene, 95°, 24 h	 (0)	187
C_4				
	RX	Catalyst (*x* amount)		

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2-thienyl	I	Cu	10 mol %	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	60	11	(62)	296, 195
3-thienyl	Br	Cu	10 mol %	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	80	36	(85)	296
2-pyridyl	I	CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	89	24	(95)	119
2-pyridyl	I	CuI	1 eq	CsOAc	DMSO	90	24	(80)	189
2-pyridyl	I	CuI	10 mol %	CsOAc	DMSO	90	24	(70)	274
3-pyridyl	I	CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	89	24	(94)	119
3-pyridyl	I	CuI	10 mol %	CsOAc	DMSO	90	24	(96)	274

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	RI	CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 12 h	 R: 2-thienyl (85);  (84)	96
		CuI (10 mol %), Cs_2CO_3, DMSO, 90°, 48 h	 (40)	275
C_5				
		CuBr (5 mol %), **L17** (20 mol %), TBAB, NaOH, H_2O, 100°, 24 h	 (89)	235
		CuI (*x* mol %), 90°		275

Isomer	X	Additive(s)	Solvent	Time (h)	
4	Br	Cs_2CO_3	DMSO	48	(63)
4	I	K_2CO_3	DMA	52	(43)
5	Br	**L13** (20 mol %), K_3PO_4	DMF	18	(61)

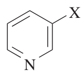
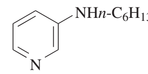
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), **L13** (20 mol %), K_3PO_4, DMF, 90°, 18 h	 (91)	120
	RX	CuI (*x* mol%), Cs_2CO_3, DMF		

R	X	*x*	Additive	Temp (°)	Time (h)		Refs.
2-pyrazinyl	I	5	**L16** (20 mol %)	rt	0.5	(99)	52
2-pyridyl	I	10	**L11** (20 mol %)	rt	14	(97)	261
	Br	10	**L11** (20 mol %)	65	12	(93)	261

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

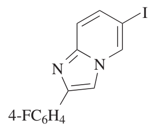
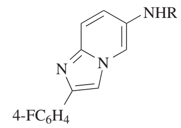
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_6

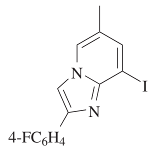
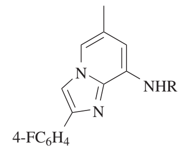
n-$C_6H_{13}NH_2$  Catalyst (5 mol %) 

X	Catalyst	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuCl	TBAH (aq)	—	80	24	(70)	282
I	CuCl	TBAH (aq)	—	80	24	(75)	282
Br	CuI	**L13** (5 mol %), K_3PO_4	—	100	22	(90)	120
Br	CuI	**L13** (20 mol %), K_3PO_4	DMF	90	18	(92)	120

C_{6-7}

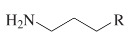
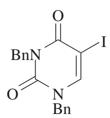
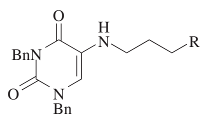
RNH_2  CuI (15 mol %), $HOCH_2CH_2OH$, K_3PO_4, i-PrOH, 85°, 48 h 

R		Refs.
c-C_6H_{11}	(72)	126
Bn	(85)	

 CuI (15 mol %), $HOCH_2CH_2OH$, K_3PO_4, i-PrOH, 85°, 48 h  297

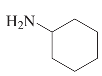
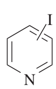
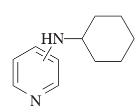
R	Temp (°)	Time (h)	
n-C_6H_{13}	85	48	(69)
c-C_6H_{11}	112	20	(57)
Bn	85	20	(62)

C_{6-8}

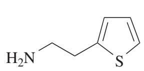
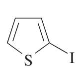
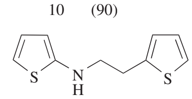
  $(Cu(OTf)_2 \cdot C_6H_6$ (50 mol %), phen (1 eq), dba, Cs_2CO_3. p-xylene, 95°, 24 h  187

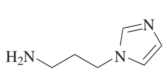
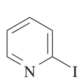
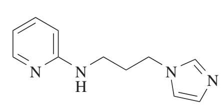
R	
1-(1H-imidazolyl)	(76)
1-morpholino	(77)
1-piperidinyl	(78)

C_6

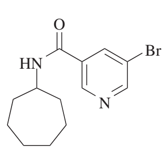
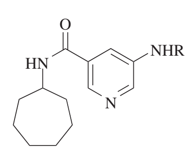
  Catalyst (x mol %), Cs_2CO_3, DMF 

Isomer	Catalyst	x	Additive	Temp (°)	Time (h)		Refs.
2	CuBr	2.5	**L5** (5 mol %)	89	24	(92)	119
3	CuBr	2.5	**L5** (5 mol %)	89	24	(90)	119
3	CuI	10	**L11** (20 mol %)	rt	24	(88)	261
3	CuI	5	**L16** (20 mol %)	rt	10	(90)	52

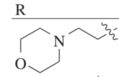
  CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 17 h  (82) 52

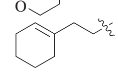
  CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 20 h  (90) 52

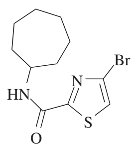
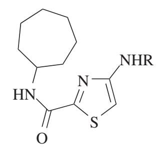
C_{6-8}

H_2NR  CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h  292

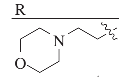
R

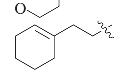
 (56)

 (50)

 CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h  292

R

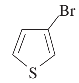
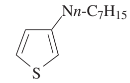
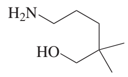
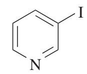
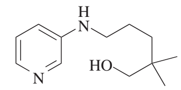
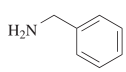
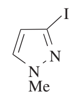
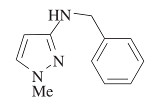
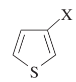
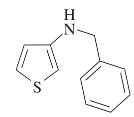
 (70)

 (70)

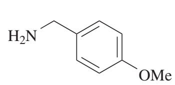
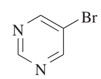
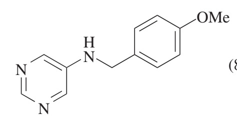
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

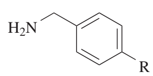
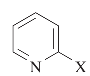
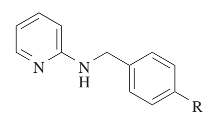
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

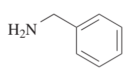
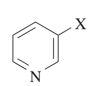
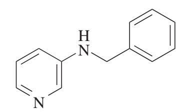
n-$C_7H_{15}NH_2$		Cu (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, 80°, 36 h	 (83)	296
		CuI (5 mol %), **L16** (20 mol %), Cs_2CO_3, DMF, rt, 20 h	 (85)	52, 196
		CuI (10 mol %), **L11** (20 mol %), Cs_2CO_3, DMF, rt, 19 h	 (87)	261
		Catalyst (10 mol %)		

X	Catalyst	Additive(s)	Solvent	Temp(°)	Time (h)		Refs.
Br	Cu	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	80	36	(86)	296
I	CuI	DMG (20 mol %), TBPM	DMSO	rt	24	(42)	61

		CuI (5 mol %), **L13** (20 mol %), K_3PO_4, DMF, 90°, 18 h	 (84)	120

		Catalyst (x mol %)		

R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	I	CuCl	10	**L9** (10 mol %), TBAH	DMSO	80	24	(72)	281
H	I	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	89	24	(97)	119
H	Br	**4**	25	K_2CO_3	NMP	160	16	(70)	269
MeO	I	CuI	10	**L11** (20 mol %), Cs_2CO_3	DMF	rt	17	(96)	261

		Catalyst (x mol %)		

X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	Cu	5	binol (10 mol %), Cs_2CO_3	DMSO	90	40	(96)	124
Br	CuCl	5	TBAH (aq)	—	80	24	(61)	282
I	CuCl	5	TBAH (aq)	—	80	24	(83)	282
I	CuCl	10	**L9** (10 mol %), TBAH	DMSO	80	24	(65)	281
Br	CuCl	10	TMHD (25 mol %), Cs_2CO_3	NMP	120	10	(55)	188
I	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	89	24	(96)	119
Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	40	(97)	47

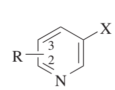
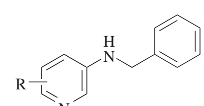
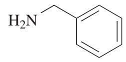
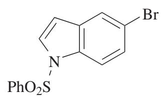
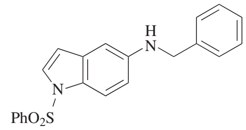
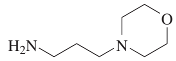
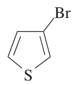
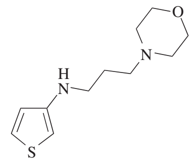
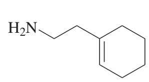
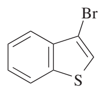
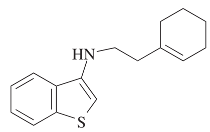
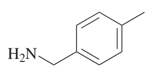
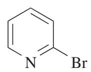
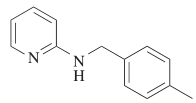
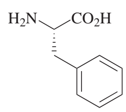
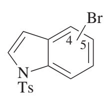
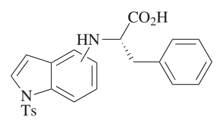
		CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h	 R: 2-AcNH (55); 3-NC– (70)	292

TABLE 2B. *N*-HETEROARYLATION OF PRIMARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_7				
		CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h	 (65)	292
		CuI (10 mol %), **L11** (20 mol %), Cs_2CO_3, DMF, rt, 14 h	 (90)	261
C_8				
		CuI (5 mol %), **L13** (20 mol %), K_3PO_4, DMF, 90°, 18 h	 (85)	120
		Cat. **4** (25 mol %), K_2CO_3, NMP, 160°, 16 h	 (90)	269
C_9				
		CuI (*x* mol %), 90°		275

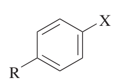
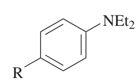
Isomer	*x*	Additive(s)	Solvent	Time (h)	
4	10	Cs_2CO_3	DMSO	48	(63)
5	5	**L13** (20 mol %), K_3PO_4,	DMF	18	(61)

TABLE 3A. *N*-ARYLATION OF ACYCLIC SECONDARY ALKYL AMINES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
Et_2NH		Catalyst (*x* mol %)		

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	I	Cu	10	$K_3PO_4•H_2O$	$Me_2NCH_2CH_2OH$	85	60	(2)	195
H	Cl	Cu_2O	5	NaO*t*-Bu	NMP	110	24	(79)	266
H	Br	Cu_2O	5	NaO*t*-Bu	NMP	100	24	(84)	266
H	I	Cu_2O	5	NaO*t*-Bu	NMP	100	24	(71)	266
MeO	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	40	(21)	47

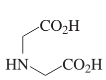
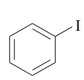
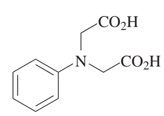
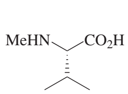
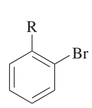
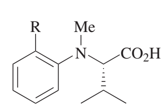
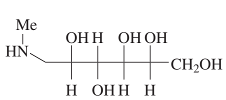
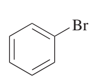
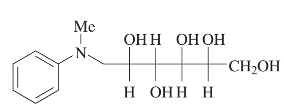
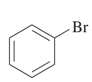
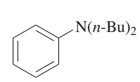
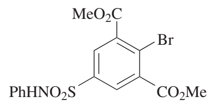
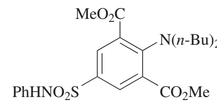
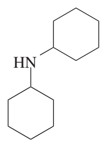
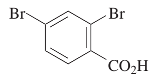
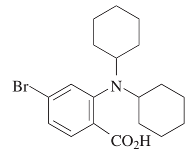
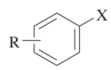
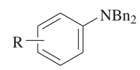
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), $K_3PO_4•H_2O$, $Me_2NCH_2CH_2OH$, H_2O, 90°	 (0)	260
C_5				
		CuI (10 mol %), K_2CO_3, DMA, 90°, 48 h	 R: H (46); $HOCH_2$ (17)	116
C_6				
		CuI (10 mol %), $K_3PO_4•H_2O$, $Me_2NCH_2CH_2OH$, H_2O, 90°	 (31)	260
C_8				
n-Bu_2NH		CuCl (10 mol%), TMHD (25 mol %), Cs_2CO_3, NMP, 120°, 10 h	 (9)	188

TABLE 3A. *N*-ARYLATION OF ACYCLIC SECONDARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_8				
n-Bu_2NH		Cu (15 mol %), K_2CO_3, dioxane, reflux, 24 h	 (79)	298
C_{12}				
		Cu_2O (5 mol %), K_3PO_4, DMA, 70°, 16 h	 (0)	206
C_{14}				
Bn_2NH		Catalyst (*x* amount)		

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	I	**6**	5 mol %	Cs_2CO_3	xylene	135	16	(0)	123
2-O_2N	Cl	Cu/Al–HTB	1 eq	K_2CO_3	—	160	16	(76)	117
4-MeO	I	CuI	10 mol %	DMG (20 mol %), K_2CO_3	DMSO	90	40	(<10)	47

TABLE 3B. *N*-HETEROARYLATION OF ACYCLIC SECONDARY ALKYL AMINES

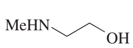
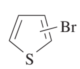
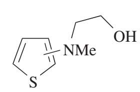
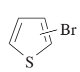
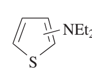
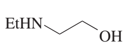
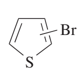
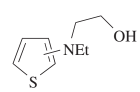
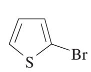
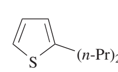
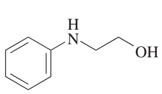
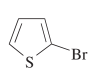
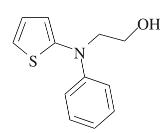
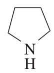
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)		Refs.
C_3					
		Cu (x mol %), CuI (10 mol %), K_3PO_4•H_2O, 80°, 24 h		Isomer / x 2 / 10 (81) 3 / 40 (90)	296
C_4					
Et_2NH		Cu (x mol %), CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$		Isomer / x / Temp (°) / Time (h) 2 / 40 / 80 / 48 (39) 3 / 10 / 85 / 60 (15)	296
		Cu (10 mol %), CuI (10 mol %), K_3PO_4•H_2O, 80°		Isomer / Time (h) 2 / 24 (81) 3 / 45 (45)	296
C_6					
n-Pr_2NH		Cu (40 mol%), CuI (10 mol%), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, 80°, 48 h		(35)	296
C_8					
		Cu (10 mol %), CuI (10 mol %), K_3PO_4•H_2O, 80°, 48 h		(15)	296

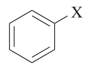
TABLE 4A. *N*-ARYLATION OF CYCLIC SECONDARY ALKYL AMINES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

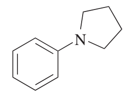
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

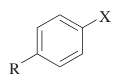




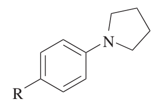
Catalyst (*x* mol %)



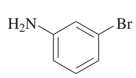
X	Catalyst	*x*	Additives(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	Cu	10	K_3PO_4•H_2O	$Me_3NCH_2CH_2OH$	80	48	(61)	195
I	Cu	10	binol (10 mol %), Cs_2CO_3	DMSO	90	24	(96)	124
I	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	90	24	(90)	118
I	CuI	10	CsOAc	DMSO	90	24	(68)	274
Br	CuI	10	DMG (20 mol %), TBPM	DMSO	rt	24	(83)	61
I	CuI–PAnNF	5	K_2CO_3	DMF	rt	6	(67)	276
I	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	90	12	(83)	277
I	CuO	1.26	KOH	DMSO	85	8	(93)	224



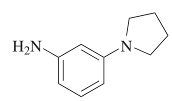
Catalyst (*x* mol %)



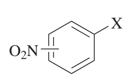
R	X	Catalyst	*x*	Additives(s)	Solvent	Temp (°)	Time (h)		Refs.
Cl	I	CuBr	20	BINAP (20 mol %), K_3PO_4	DMF	rt	5	(71)	62
Cl	Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	27	(89)	47
Cl	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	9	(68)	271
Cl	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	6	(82)	276
Br	Br	Cu	10	K_3PO_4•H_2O	$Me_3NCH_2CH_2OH$	80	48	(28)	195
Br	I	CuBr	20	BINAP (20 mol %), K_3PO_4	DMF	rt	10	(67)	62
Br	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	6	(75)	276
Br	I	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	90	12	(85)	277



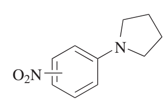
CuI (10 mol %),
L-Pro (20 mol %),
K_2CO_3, DMSO, 90°, 27 h



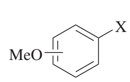
(94) 47



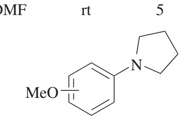
Catalyst (*x* amount %)



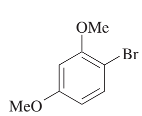
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
3	I	CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	90	24	(99)	119
3	I	Cu_2O	5 mol %	**L7** (20 mol %), Cs_2CO_3	MeCN	90	18	(73)	125
4	Cl	CuI nanoparticles	1.25 mol %	K_2CO_3, air	DMF	110	5	(95)	285
4	Br	CuI	1 eq	CsOAc	DMF	90	24	(89)	189
4	Cl	CuI–PAnNF	5 mol %	K_2CO_3	DMF	80	9	(95)	276
4	I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	5	(71)	276



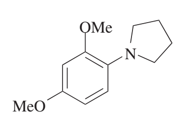
Catalyst (x mol %)



Isomer	X	Catalyst	*x*	Additives		Temp (°)	Time		Refs.
3	Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	31 h	(99)	47
4	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	65	27 h	(100)	47
4	I	CuI	5	**L2** (25 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(62)	236
4	Br	CuO	5	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	MW (100 W), 120	5 min	(50)	51
4	I	Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	90	18 h	(65)	125



CuI (10 mol %),
L-Pro (20 mol %),
K_2CO_3, DMSO, 90°, 40 h

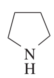


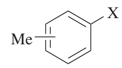
(86) 47

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

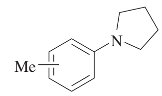
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

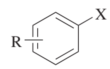




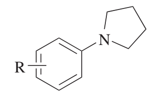
CuI (x mol %), DMF



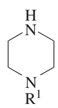
Isomer	X	x	Additives	Temp (°)	Time		Refs.
3	I	5	**L16** (20 mol %), Cs_2CO_3	rt	6 h	(90)	52
4	Br	10	L-Pro (20 mol %), K_2CO_3	MW (120 W)	15 min	(78)	299
4	I	10	**L8** (20 mol %), K_3PO_4	30	10 h	(66)	271

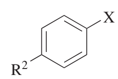


Catalyst (x mol %)

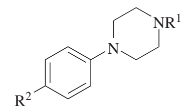


R	X	Catalyst	x	Additives	Solvent	Temp (°)	Time		Refs.
3-CF_3	I	Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	90	18 h	(72)	125
4-NC–	Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	27 h	(89)	47
4-CHO	Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMF	MW (120 W)	15 min	(72)	299
4-Ac	Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMF	MW (120 W)	15 min	(88)	299
4-Ac	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	65	20 h	(84)	47

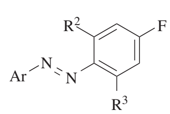




Catalyst (x mol %)

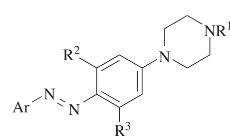


R^1	R^2	X	Catalyst	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
Me	H	Br	CuCl	10	TMHD (25 mol %), K_2CO_3	NMP	120	10	(17)	188, 195
Me	H	I	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	90	24	(86)	118, 119
Et	H	I	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	90	24	(90)	118, 119
Et	H	I	Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18	(72)	125
CO_2Et	MeO	I	Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	90	24	(60)	125
COEt	H	I	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	90	24	(83)	119



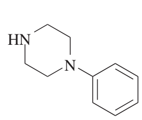
Ar = 4-$O_2NC_6H_4$

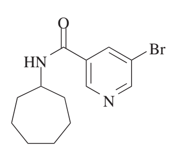
CuI (11 mol %), K_2CO_3, DMF, 100°, 24 h



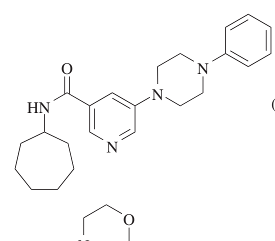
(—) 300

R^1	R^2	R^3	R^1	R^2	R^3	R^1	R^2	R^3	R^1	R^2	R^3
n-C_5H_{11}	F	H	n-C_6H_{13}	F	H	n-C_7H_{15}	F	H	n-C_8H_{17}	F	H
n-C_5H_{11}	F	F	n-C_6H_{13}	F	F	n-C_7H_{15}	F	F	n-C_8H_{17}	F	F
n-C_5H_{11}	Cl	H	n-C_6H_{13}	Cl	H	n-C_7H_{15}	Cl	H	n-C_8H_{17}	Cl	H

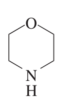


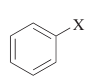


CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h

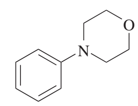


(42) 292





Catalyst (x amount)

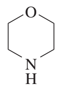


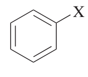
X	Catalyst	x	Additives(s)	Solvent(s)	Temp (°)	Time		Refs.
I	Cu	10 mol %	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(84)	124
Cl	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	8 h	(0)	228
I	Cu/Al–HTB	2.5 mol %	K_2CO_3	DMF	100	8 h	(90)	228
Br	CuCl	10 mol %	TMHD (25 mol %), Cs_2CO_3	NMP	120	10 h	(13)	188
I	CuBr	20 mol %	BINAP (20 mol %), K_3PO_4	DMF	rt	6 h	(73)	62
I	CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	90	24 h	(90)	118, 119
I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(83)	274

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

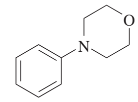
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

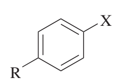




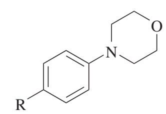
Catalyst (*x* amount)



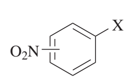
X	Catalyst	*x*	Additives(s)	Solvent(s)	Temp (°)	Time		Refs.
I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	80	26 h	(61)	192
I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	90	40 h	(77)	47
Br	CuI	10 mol %	DMG (20 mol %), TBPM	DMSO	rt	24 h	(70)	61
I	CuI	10 mol %	**L9** (10 mol %), TBAH	DMSO	80	24 h	(77)	281
I	CuI	10 mol %	DPP (20 mol %), K_3PO_4	DMF	110	30 h	(78)	108
Cl	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(70)	281
Br	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(80)	281
I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	5 h	(83)	276
Br	CuO	10 mol %	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	100	24 h	(82)	277
I	CuO	10 mol %	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	90	12 h	(85)	277
I	CuO	1.26 mol %	KOH	DMSO	110	6.5 h	(89)	224
I	Cu_2O	5 mol %	**L12** (20 mol %), Cs_2CO_3	MeCN	80	18 h	(85)	125
Br	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(93)	85
I	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(92)	85
Cl	$Cu(acac)_2$	10 mol %	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(0)	262
I	$Cu(acac)_2$	10 mol %	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(85)	262



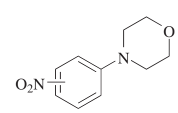
Catalyst (*x* mol %)



R	X	Catalyst	*x*	Additives(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Cl	I	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	8	(90)	228
Cl	I	CuBr	20	BINAP (20 mol %), K_3PO_4	DMF	rt	6	(75)	62
Cl	I	CuI	10	**L9** (10 mol %), TBAH	DMSO	80	24	(72)	281
Cl	Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	2	(95)	285
Cl	I	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	80	12	(90)	277
Cl	I	$Cu(acac)_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	0.5	(11)	262
Br	I	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	7	(99)	228
Br	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	6	(85)	276
I	I	CuI	10	K_3PO_4•H_2O	$Me_3NCH_2CH_2OH$	55	36	(54)	195



Catalyst (*x* mol %)

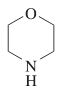


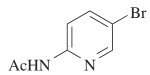
Isomer	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
2	Cl	Cu/A–HTB	2.5	K_2CO_3	DMF	100	6	(99)	228
2	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	3	(96)	276
3	I	CuBr	20	BINAP (20 mol %), K_3PO_4	DMF	rt	6	(73)	62
3	Br	CuO	10	binol (20 mol %), $FeCl_3$(10 mol %), Cs_2CO_3	DMF	100	12	(89)	277
4	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	8	(92)	228
4	Cl	CuI–PAnNF	5	K_2CO_3	DMF	80	4	(98)	276
4	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	4	(85)	276
4	I	$Cu(acac)_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	0.5	(39)	262

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

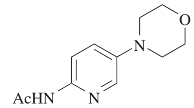
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

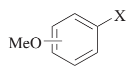




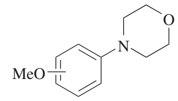
CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h



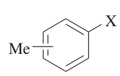
(58) 292



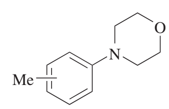
Catalyst (*x* mol %)



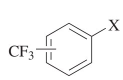
Isomer	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
2	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(36)	262
3	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(54)	262
4	I	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	90	24 h	(80)	118, 119
4	I	CuI	5	**L2** (25 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(62)	236
4	I	CuI	10	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	20 h	(80)	67
4	Br	CuI	5	EDA (10 mol %), K_2CO_3	PEG	80	4 h	(69)	301
4	I	CuI	10	PPAPM (20 mol %), K_3PO_4	DMF	90	30 h	(87)	48
4	I	CuI	10	DPP (20 mol %), K_3PO_4	DMF	110	30 h	(75)	108
4	Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	7 h	(95)	285
4	I	CuO	5	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	MW (100 W), 120	5 min	(60)	51
4	I	CuO	25	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(44)	267
4	I	Cu_2O	5	**L12** (20 mol %), Cs_2CO_3	MeCN	80	18 h	(85)	125
4	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(80)	262



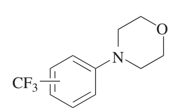
Catalyst (*x* mol %)



Isomer	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
2	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(trace)	262
3	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(45)	262
4	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	28 h	(52)	228
4	I	CuBr	20	BINAP (20 mol %), K_3PO_4	DMF	40	6 h	(91)	62
4	Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMF	MW (120 W)	15 min	(49)	299
4	I	CuI–PAnNF	5	K_2CO_3	DMF	rt	4 h	(65)	276
4	I	CuO	10	$FeCl_3$ (10 mol %), binol (20 mol %), Cs_2CO_3	DMF	100	12 h	(75)	277
4	Cl	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(0)	262
4	Br	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(20)	262
4	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O	MW, 150	30 min	(83)	262



Catalyst (*x* mol %), Cs_2CO_3

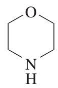


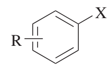
Isomer	X	Catalyst	*x*	Additive	Solvent(s)	Temp (°)	Time (h)		Refs.
2	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %)	DMSO/H_2O	MW, 150	0.5	(trace)	262
3	I	Cu_2O	5	**L7** (20 mol %)	MeCN	90	18	(70)	125
3	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %)	DMSO/H_2O	MW, 150	0.5	(62)	262
4	Br	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %)	DMSO/H_2O	MW, 150	0.5	(11)	262
4	I	Cu(acac)$_2$	10	Fe_2O_3 (20 mol %)	DMSO/H_2O	MW, 150	0.5	(25)	262

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

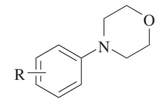
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

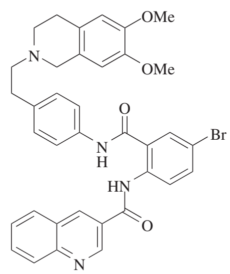




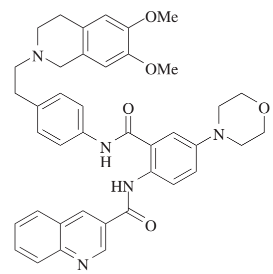
Catalyst (10 mol %)



R	X	Catalyst	Additive(s)	Solvent	Temp (°)	Time		Refs.
4-NC–	Br	CuCl	TMHD (25 mol %), Cs_2CO_3	NMP	120	10 h	(32)	188
4-CHO	Br	CuI	L-Pro (20 mol %), K_2CO_3	DMF	MW (120 W)	15 min	(69)	299
3-MeO_2C	I	CuI	**L9** (10 mol %), TBAH	DMSO	80	24 h	(67)	281
4-Ac	Br	CuI	L-Pro (20 mol %), K_2CO_3	DMF	MW (120 W)	15 min	(42)	299
4-Ph	Br	CuCl	TMHD (25 mol %), Cs_2CO_3	NMP	120	10 h	(23)	188

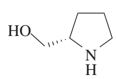


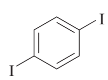
CuBr•DMS (20 mol %), L-Pro (40 mol %), K_3PO_4, DMSO, 90°



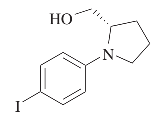
(75) 122

C_5





CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, rt, 20 h; then 40°, 28 h



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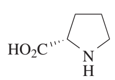
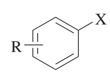
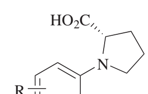
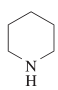


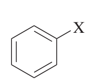


CuI (*x* mol %)

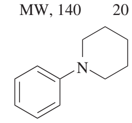


R	X	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
H	I	—	K_2CO_3	DMA	90	—	(—)	302
4-Cl	I	10	**L8** (20 mol %), K_3PO_4	DMF	30	12 h	(68)	271
2-O_2N	Br	10	K_2CO_3	DMF	MW, 140	15 min	(90)	265
4-O_2N	I	—	K_2CO_3	DMA	90	—	(—)	302
3-MeO	I	—	K_2CO_3	DMA	90	—	(—)	302
4-Me	Br	10	K_2CO_3	DMF	MW, 140	22 min	(65)	265
2-NC–	I	—	K_2CO_3	DMA	90	—	(—)	302
2-Ac	Br	10	K_2CO_3	DMF	MW, 140	20 min	(80)	265
4-Ac	Br	10	K_2CO_3	DMF	MW, 140	18 min	(80)	265
4-Ac	I	10	K_2CO_3	DMF	MW, 140	20 min	(83)	265





Catalyst (*x* amount)

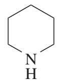


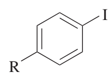
X	Catalyst	*x*	Additives(s)	Solvent	Temp (°)	Time		Refs.
Br	Cu	5 eq	none	H_2O	MW, 100	2 min	(91)	280
I	Cu	10 mol %	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(88)	124
I	Cu	10 mol %	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	70	9 h	(54)	195
Br	CuCl	10 mol %	TMHD (25 mol %), Cs_2CO_3	NMP	120	10 h	(39)	188
I	CuBr	2.5 mol %	**L5** (5 mol %), Cs_2CO_3	DMF	90	24 h	(87)	118, 119
I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	90	40 h	(83)	47
I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	80	26 h	(61)	192
I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(15)	273
I	CuI	10 mol %	**L9** (10 mol %), TBAH	DMSO	80	24 h	(82)	281
Cl	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(78)	281
Br	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(94)	281
$I^+Ph\ BF_4^-$	CuI	10 mol %	Na_2CO_3	CH_2Cl_2	rt	6 h	(65)	76
I	CuI–PAnNF	5 mol %	K_2CO_3	DMF	rt	6 h	(67)	276
I	CuO	1.26 mol %	KOH	DMF	110	7 h	(90)	224
I	CuFAP	—	K_2CO_3	DMF	110	12 h	(90)	227

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

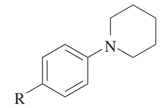
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_5

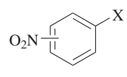




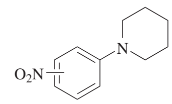
Catalyst (x mol %)



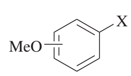
R	Catalyst	x	Additives(s)	Solvent	Temp (°)	Time (h)		Refs.
Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	9	(81)	228
Cl	CuBr	20	BINAP (20 mol %), K_3PO_4	DMF	rt	6	(67)	62
Cl	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	8	(64)	271
Br	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	10	(88)	228
I	CuI	10	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	45	20	(68)	195



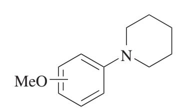
Catalyst (x mol %)



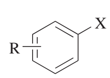
Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
3	I	Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	90	18	(68)	125
4	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	8	(94)	228
4	I	CuI–PAnNF	5	K_2CO_3	DMF	80	7	(96)	276
4	F	CuFAP	—	K_2CO_3	DMF	120	1	(85)	66
4	Cl	CuFAP	—	K_2CO_3	DMF	120	5	(80)	66
4	F	cat. **7**	1	K_2CO_3	DMF	110	1	(90)	73
4	Cl	cat. **7**	1	K_2CO_3	DMF	110	5	(87)	73



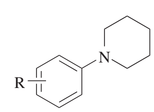
Catalyst (x mol %)



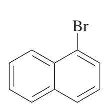
Isomer	X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
2	Cl	Cu/Al–HTB	2.5	K_2CO_3	DMF	100	24 h	(48)	228
4	I	Cu	10	binol (10 mol %), Cs_2CO_3	DMSO	90	24 h	(75)	124
4	I	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	90	24 h	(78)	118, 119
4	Br	CuI	10	DMEDA (20 mol %)	$[C_4mim]BF_4$	110	12 h	(87)	232
4	Br	CuI	5	**L16** (20 mol %), K_3PO_4	DMF	100	16 h	(90)	52
4	I	CuO	25	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(47)	267



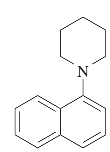
Catalyst (x amount)



R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
4-Me	Br	Cu	5 eq	none	H_2O	MW (100 W)	2 min	(87)	280
4-NC–	Br	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	90	40 h	(81)	47
3-MeO_2C	I	CuI	10 mol %	**L9** (10 mol %), TBAH	DMSO	80	24 h	(70)	281



CuI (5 mol %),
EDA (10 mol %),
PEG, K_2CO_3, 80°, 4 h



(69) 301

TABLE 4A. *N*-ARYLATION OF CYCLIC SECONDARY ALKYL AMINES (*Continued*)

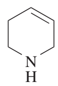
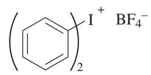
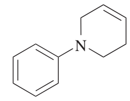
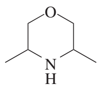
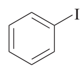
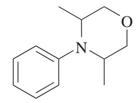
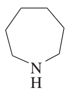
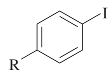
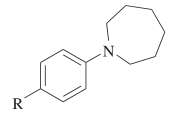
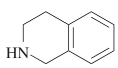
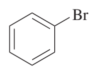
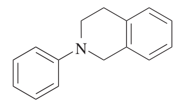
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_5				
		CuI (10 mol %), Na_2CO_3, $MeCl_2$, rt, 6 h	 (66)	76
C_6				
		CuBr (2.5 mol %), **L5** (5 mol %), Cs_2CO_3, DMF, 90°, 24 h	 (87)	118, 119
C_7				
		CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, 60°, 40 h	 R: Br (47); I (50)	195
C_9				
		CuI (2 mol %), **L1** (2 mol %), KO*t*-Bu, 100°, 12 h	 (94)	281

TABLE 4B. *N*-HETEROARYLATION OF CYCLIC SECONDARY ALKYL AMINES

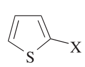
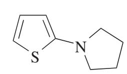
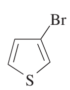
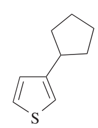
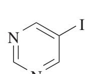
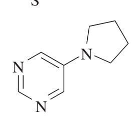
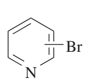
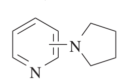
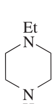
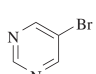
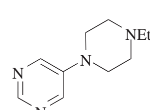
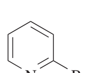
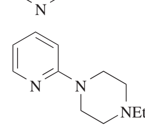
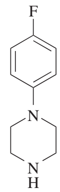
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		Cu (10 mol %), CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$	 X Temp (°) Time (h) Br 80 50 (81) Br 80 49 (81) I 60 10 (91) I 80 49 (91)	296
		Cu (10 mol %), CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, 80°, 45 h	 (83)	296
		CuBr (2.5 mol %), **L5** (5 mol %), Cs_2CO_3, DMF, 90°, 24 h	 (83)	119
		CuI (10 mol %), L-Pro (20 mol %), K_2CO_3 Isomer Solvent Temp Time 2 DMF MW (120 W) 15 min (84) 3 DMSO 90° 40 h (94)		299 47
		CuBr (2.5 mol %), **L5** (5 mol %), Cs_2CO_3, DMF, 90°, 24 h	 (80)	119
		CuBr (2.5 mol %), **L5** (5 mol %), Cs_2CO_3, DMF, 90°, 24 h	 (85)	119

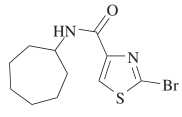
TABLE 4B. *N*-HETEROARYLATION OF CYCLIC SECONDARY ALKYL AMINES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

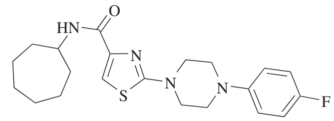
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_4





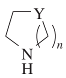
CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h

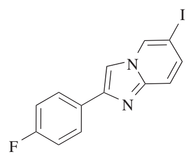


(85)

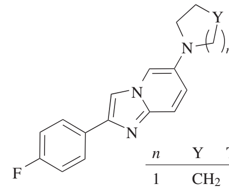
292

C_{4-5}



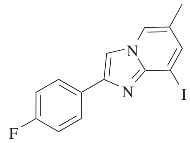


CuI (15 mol %), K_3PO_4, $HOCH_2CH_2OH$, *i*-PrOH, 85°

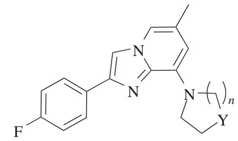


n	Y	Time (h)	
1	CH_2	20	(84)
2	O	48	(72)
2	CH_2	48	(70)

126



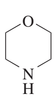
CuI (15 mol %), K_3PO_4, $HOCH_2CH_2OH$, *i*-PrOH

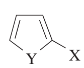


n	Y	Temp (°)	Time (h)	
1	CH_2	85	20	(60)
2	EtN	85	48	(69)
2	O	112	20	(55)
2	CH_2	85	48	(64)

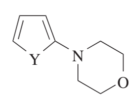
297

C_4

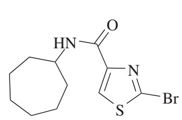




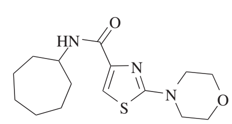
Catalyst(s) (10 mol %)



Y	X	Catalyst(s)	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
S	Br	Cu, CuI	K_3PO_4•H_2O	$Me_2NCH_2CH_2OH$	80	50	(65)	296
Se	I	CuI	EDA (20 mol %), K_3PO_4	dioxane	reflux	24	(0)	87

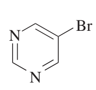


CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h

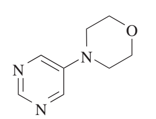


(65)

292

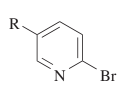


CuBr (2.5 mol %), **L5** (5 mol %), Cs_2CO_3, DMF, 90°, 24 h

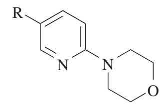


(86)

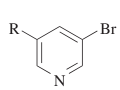
119



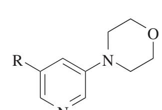
Catalyst (*x* mol %), 90°



R	Catalyst	*x*	Additives	Solvent	Time (h)		Refs.
H	CuBr	2.5	**L5** (5 mol %), Cs_2CO_3	DMF	24	(82)	119
Br	CuI	10	L-Pro (20 mol%), K_2CO_3	DMSO	40	(81)	47



CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h

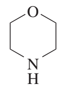
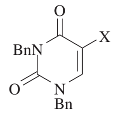
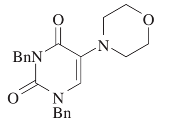


R	
H_2NCO	(52)
NC–	(65)

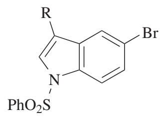
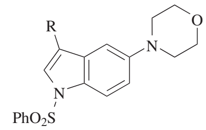
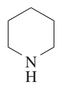
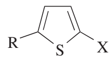
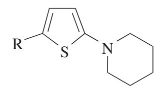
292

TABLE 4B. *N*-HETEROARYLATION OF CYCLIC SECONDARY ALKYL AMINES (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		Catalyst, (*x* mol %)		

X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	40	(81)	47
I	$(CuOTf)_2$•C_6H_6	50	phen (1 eq), dba (50 mol %), Cs_2CO_3	*p*-xylene	95	24	(73)	187

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h	 R: H (66); $CH_2CONHPh$ (0)	292
C_5				
		Cu (10 mol %), co-catalyst (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$		296

R	X	Co-Catalyst	Temp (°)	Time (h)	
H	Br	CuI	80	50	(73)
H	I	none	60	10	(91)
Me	Br	CuI	80	24	(71)
OHC	Br	CuI	65	48	(77)

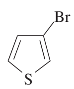
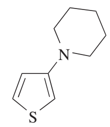
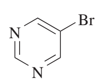
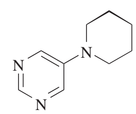
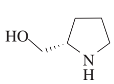
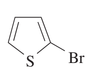
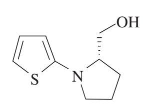
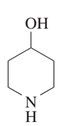
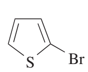
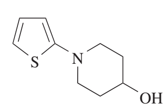
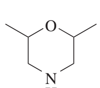
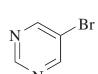
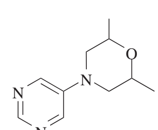
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (10 mol %), CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, 80°, 40 h	 (73)	296
		CuBr (2.5 mol %), **L5** (5 mol %), Cs_2CO_3, DMF, 90°, 24 h	 (85)	119
		Cu (10 mol %), CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, 80°, 50 h	 (71)	296
		Cu (10 mol %), CuI (10 mol %), K_3PO_4•H_2O, $Me_2NCH_2CH_2OH$, 80°, 50 h	 (91)	296
C_6				
		CuBr (2.5 mol %), **L5** (5 mol %), Cs_2CO_3, DMF, 90°, 24 h	 (78)	119

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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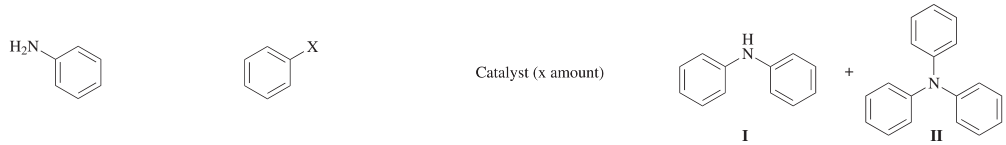


X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	I	II	Refs.
Br[a]	Cu	3 eq	none	—	270	—	(21)	(4)	303
I[a]	Cu	3 eq	none	—	180	—	(31)	(46)	303
I[b]	Cu	3 eq	none	—	220	—	(0)	(86)	303
I	Cu (active)	5 eq	none	H_2O	MW (100 W)	6 min	(74)	(0)	280
Br	CuCl	10 mol %	2,5-pentanedione (25 mol %), K_2CO_3	NMP	130	18 h	(30)	(30)	188
$I^+Ph\ BF_4^-$	CuI	10 mol %	Na_2CO_3	CH_2Cl_2	rt	6 h	(75)	(0)	76
I	CuI	10 mol %	CsOAc	DMSO	90	24 h	(24)	(0)	274
Cl	CuI	2 mol %	KO*t*-Bu	toluene	135	14 h	(12)	(28)	304
Br	CuI	2 mol %	KO*t*-Bu	toluene	135	14 h	(12)	(45)	304
I	CuI	2 mol %	KO*t*-Bu	toluene	135	14 h	(7)	(70)	304
Cl	CuI	3.6 mol %	PBu_3 (7.2 mol %), KO*t*-Bu	toluene	135	10.5 h	(82)	(0)	41
I	CuI	3.5 mol %	bipy (3.5 mol %), KO*t*-Bu	toluene	115	3.5 h	(2)	(95)	304
I	CuI	3.6 mol %	bipy (3.6 mol %), KO*t*-Bu	toluene	115	3.5 h	(0)	(95)	305
Br	CuI	10 mol %	PPAPM (20 mol %), K_3PO_4	DMF	110	36 h	(77)	(0)	48
I	CuI	5 mol %	DiPrPhDAB (6 mol %), KO*t*-Bu	toluene	120	48 h	(97)	(0)	306
I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	90	27 h	(66)	(0)	192, 47
Br	CuI	10 mol %	DPP (20 mol %), K_3PO_4	DMF	110	36 h	(57)	(0)	108
I	CuI	10 mol %	DMEDA (10 mol %), K_2CO_3	dioxane	100	21 h	(84)	(0)	55
Cl	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	36 h	(15)	(0)	67
Br	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	20 h	(72)	(0)	67
I	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	20 h	(79)	(0)	67
I	CuI	10 mol %	pyridine-2-carboxylic acid (20 mol %), K_3PO_4	DMSO	80	17 h	(68)	(0)	50

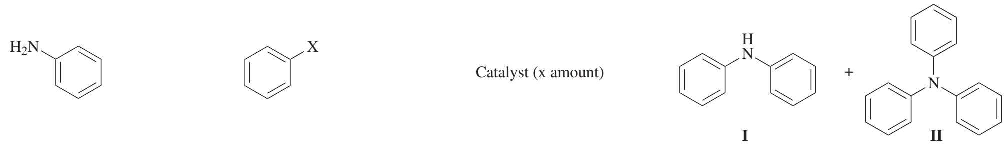
X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	I	II	Refs.
Cl	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(80)	(0)	288
Br	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(99)	(0)	288
Br	CuI	5 mol %	**L2** (25 mol %), KOH, TBAB	H_2O	MW (100 W), 135	5 min	(79)	(0)	236
Cl	CuO nanoparticles (33 nm)	1.3 mol %	KOH, air	DMSO	110	18 h	(60)	(0)	224
Br	CuO nanoparticles (33 nm)	1.3 mol %	KOH, air	DMSO	110	10 h	(80)	(0)	224
I	CuO nanoparticles (33 nm)	1.3 mol %	KOH, air	DMSO	110	2 h	(95)	(0)	224
Cl	CuO nanoparticles	5 mol %	KOH	DMSO/*t*-BuOH (3:1)	110	18 h	(0)	(0)	74
Br	CuO nanoparticles	5 mol %	KOH	DMSO/*t*-BuOH (3:1)	110	18 h	(0)	(0)	74
I	CuO nanoparticles	5 mol %	KOH	DMSO/*t*-BuOH (3:1)	110	18 h	(88)	(0)	74
OTs	CuO nanoparticles	5 mol %	KOH	DMSO/*t*-BuOH (3:1)	110	18 h	(0)	(0)	74
Br	CuO	5 mol %	NaO*t*-Bu	NMP	100	—	(79)	(0)	266
I	CuO	5 mol %	NaO*t*-Bu	NMP	100	—	(74)	(0)	266
Br	CuO	10 mol %	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	110	12 h	(76)	(0)	277
I	CuO	10 mol %	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	100	24 h	(78)	(0)	277
Br	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(49)	(0)	267
Br	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	reflux	10 h	(49)	(0)	267
I	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(57)	(0)	267
I	CuO/AB	5 mol %	KO*t*-Bu	toluene	180	18 h	(26)	(0)	226
Br	CuO	5 mol %	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	90	8 h	(70)	(0)	51
Br	CuO	5 mol %	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	MW, 120	5 min	(75)	(0)	51
I	CuO	5 mol %	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	MW, 120	5 min	(63)	(0)	51

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

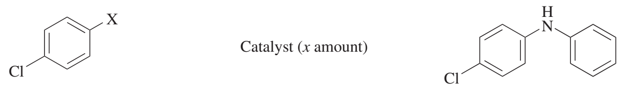
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Continued from previous page.

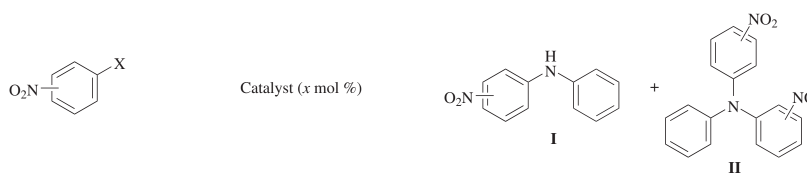
C_6



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	**I**	**II**	
I	Cu_2O	10 mol %	Cs_2CO_3	DMF	100	18 h	(0)	(0)	221
I	$Cu(OAc)_2$	4 mol %	phen (3 mol %), KOH	toluene	reflux	18 h	(0)	(—)	307
I	$Cu(acac)_2$	10 mol %	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	MW, 150	5 min	(35)	(0)	262
I	$Cu(TMHD)_2$	20 mol %	KO*t*-Bu	toluene	120	40 h	(0)	(94)	308
Br	Cu/Fe–hydrotalcite	10 wt %	none	toluene	130	14 h	(79)	(0)	283
I	Cu/Fe–hydrotalcite	10 wt %	none	toluene	130	12 h	(81)	(0)	283
I	**1**	1.25 mol %	KO*t*-Bu	toluene	90	12 h	(0)	(65)	309



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		
Br	CuI	5 mol %	**L2** (25 mol %), KOH, TBAB	H_2O	MW (100 W) 130	5 min	(66)	236
I	CuI	10 mol %	TBPM, 2,2'-biphenol (20 mol %)	dioxane	rt	12 h	(80)	61
Br	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W) 130	5 min	(81)	267
Br	CuO	5 mol %	KOH, TBAB, **L14** (50 mol %), hexane-2,5-dione	H_2O	90	8 h	(59)	51
Br	CuO	5 mol %	KOH, TBAB, **L14** (50 mol %), hexane-2,5-dione	H_2O	MW 120	5 min	(58)	51
Br	Cu/Fe–hydtotalcite	10 wt %	none	toluene	130	12 h	(76)	283

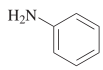


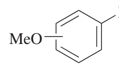
Isomer	X	Catalyst	*x*	Additives	Solvent(s)	Temp (°)	Time	**I**	**II**	
3	Br	CuI	10	DPP (20 mol %), K_3PO_4	DMF	110	30 h	(80)	(0)	108
3	Br	CuI	10	PPAPM (20 mol %), K_3PO_4	DMF	110	30 h	(89)	(0)	48
4	Cl	CuBr	2.5	**L4** (2.5 mol %), K_2CO_3	—	190	4 h	(89)	(0)	310
4	Cl	CuI	3.6	PBu_3 (7.2 mol %), KO*t*-Bu	toluene	135	10.5 h	(0)	(41)	56
4	Br	CuI	5	**L2** (25 mol %), KOH, TBAB	H_2O	MW (100 W) 130	5 min	(80)	(0)	236
4	Br	CuO	5	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	MW 120	5 min	(56)	(0)	51
4	I	CuO nanoparticles	5	KOH, air	DMSO/*t*-BuOH (3:1)	110	4 h	(85)	(0)	74
4	I	CuO nanoparticles (33 nm)	1.3	PBu_3 (7.2 mol %), KO*t*-Bu	DMSO	110	1.2 h	(93)	(0)	224

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

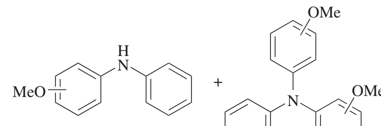
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_6



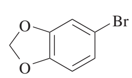


Catalyst (*x* amount)

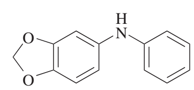


I + II

Isomer	X	Catalyst	*x*	Additive(s)	Solvents	Temp (°)	Time	I	II	
2	Br	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(99)	(0)	288
4	Cl	CuI	3.6 mol %	PBu_3 (7.2 mol %), KO*t*-Bu	toluene	135	10.5 h	(—)	(85)	56
4	Br	CuI	10 mol %	K_2CO_3, piperidine-2-carboxylic acid (20 mol %)	DMF	110	20 h	(67)	(0)	67
4	Br	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(99)	(0)	288
4	Br	CuI	3.6 mol %	PBu_3 (7.2 mol %), KO*t*-Bu	toluene	135	10.5 h	(0)	(85)	56
4	Br	CuI	10 mol %	1,2-CDA (20 mol %), K_3PO_4	[C_4mim][BF_4]	110	12 h	(83)	(0)	232
4	Br	CuI	5 mol %	**L2** (25 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(78)	(0)	236
4	4-MeOC$_6$H$_4$I$^+$	CuI	10 mol %	Na_2CO_3	CH_2Cl_2	rt	6 h	(38)	(0)	76
4	I	CuI	2 mol %	KO*t*-Bu	toluene	135	14 h	(8)	(81)	304
4	I	CuI	10 mol %	TBPM, 2,2'-biphenol (20 mol %)	dioxane	rt	12 h	(65)	(0)	61
4	Br	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(52)	(0)	267
4	Br	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	reflux	10 h	(52)	(0)	267
4	Br	CuO	5 mol %	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	MW, 120	5 min	(78)	(0)	51
4	I	CuO nanoparticles (33 nm)	1.3 mol %	KOH, air	DMSO	110	12 h	(22)	(0)	224
4	I	CuO nanoparticles	5 mol %	KOH	DMSO/*t*-BuOH (3:1)	110	24 h	(73)	(0)	74
4	Br	Cu/Fe–hydrotalcite	10 wt %	none	toluene	130	15 h	(80)	(0)	283
4	I	Cu/Fe–hydrotalcite	10 wt %	none	toluene	130	12 h	(82)	(0)	283



CuI (5 mol %), **L2** (25 mol %), KOH, TBAB, H_2O, MW (100 W), 130°, 5 min



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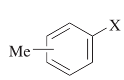
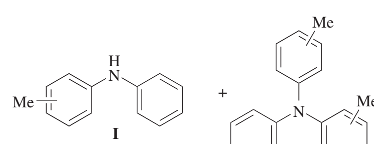


Catalyst (*x* amount)



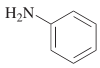
I + II

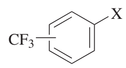
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time	I	II	
2	I	Cu	2 eq	K_2CO_3, 18-c-6	1,2-$Cl_2C_6H_4$	reflux	15 h	(0)	(95)	54
2	Cl	CuI	3.6 mol %	PBu_3 (7.2 mol %), KO*t*-Bu	toluene	135	10.5 h	(0)	(80)	56
4	Br	Cu (active)	5 mol %	none	H_2O	MW (100 W)	6 min	(71)	(0)	280
4	I	$CuCl_2$	4 mol %	phen (4 mol %), KOH	toluene	125	5 h	(0)	(73)	311
4	Br	CuI	7 mol %	L-Pro (14 mol %), K_2CO_3	DMSO	90	40 h	(51)	(0)	47
4	I	CuI	5 mol %	DiPrPhDAB (6 mol %), KO*t*-Bu	toluene	120	48 h	(92)	(0)	306
4	Cl	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(60)	(0)	288
4	Br	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12 h	(78)	(0)	288
4	Br	CuI	5 mol %	**L2** (25 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(74)	(0)	236
4	I	CuO	10 mol %	$FeCl_3$ (10 mol%), *rac*-binol (20 mol %), Cs_2CO_3	DMF	90	12 h	(79)	(0)	277
4	Br	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	reflux	10 h	(48)	(0)	51
4	Br	CuO	25 mol %	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(48)	(0)	51
4	Br	CuO	5 mol %	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	90	8 h	(70)	(0)	51
4	Br	CuO	5 mol %	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	MW, 120	5 min	(70)	(0)	51

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

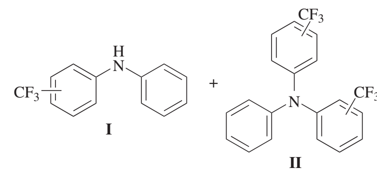
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_6

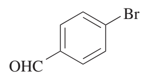




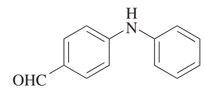
Catalyst (*x* mol %)



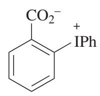
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time	I	II	Refs.
3	I	$Cu(TMHD)_2$	20	KO*t*-Bu	toluene	120	40 h	(0)	(82)	308
4	Br	CuI	5	**L2** (25 mol %), KOH, TBAB	H_2O	MW (100 W) 130	5 min	(47)	(0)	236
4	Br	CuO	5	**L14** (50 mol %), KOH, TBAB, hexane-2,5-dione	H_2O	MW 120	5 min	(45)	(0)	51



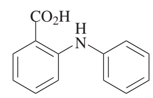
Cu/Fe–hydrotalcite (10 wt %), toluene, 130°, 12 h



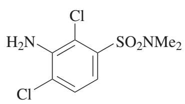
(79) 283

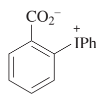


$Cu(OAc)_2$ (4 mol %), *i*-PrOH, reflux, 1 h

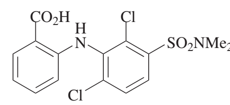


(68) 312

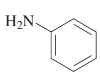


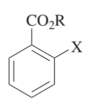


$Cu(OAc)_2$ (4 mol %), *i*-PrOH, reflux, 48 h

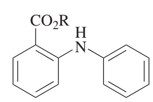


(38) 312





Catalyst(s) (*x* amount)



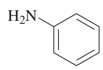
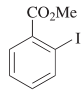
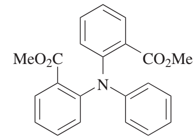
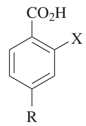
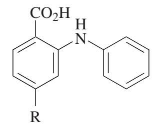
X	R	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
Cl	H	Cu	8 mol %	pyridine (15 wt %), K_2CO_3	amyl alcohol	reflux	1h	(69)	313
Cl	H	Cu	1 eq	none	—	reflux	—	(83)	1
Cl	H	Cu powder	—	pyridine, K_2CO_3	H_2O	)))	20 min	(88)	314
Cl	H	Cu, CuI	2, 0.6 mol %	K_2CO_3	DMF	))) (20 kHz), reflux	20 min	(25)	315
Cl	H	Cu, CuI	4, 9 mol %	K_2CO_3	$EtO(CH_2)_2OH$	130	24 h	(83)	109
Br	H	Cu, CuI	9, 4 mol %	K_2CO_3	$EtO(CH_2)_2OH$	130	24 h	(86)	70
Cl	H	CuO	6 mol %	K_2O_3	—	reflux	—	(93)	316
Cl	H	$CuSO_4$	16 mol %	K_2CO_3	H_2O	MW, 100	5 min	(98)	240
Cl	H	CuOAc	10 mol %	NaOAc	H_2O	reflux	4 h	(91)	317
Br	H	CuOAc	10 mol %	NaOAc	H_2O	reflux	2.5 h	(94)	317
I	H	CuOAc	10 mol %	NaOAc	H_2O	reflux	0.5 h	(97)	317
Cl	H	$Cu(OAc)_2$	14 mol %	K_2CO_3	—	MW (700 W)	6 min	(87)	72
Br	H	$Cu(OAc)_2$	14 mol %	K_2CO_3	—	MW (700 W)	6 min	(93)	72
Cl	H	$Cu(pyr)_2Cl_2$	10 mol %	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(72)	71
Cl	H	$Cu(pyr)_2Cl_2$	11 mol %	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(70)	318
Br	H	$Cu(pyr)_2Cl_2$	10 mol %	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(69)	71
Br	H	$Cu(pyr)_2Cl_2$	11 mol %	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(71)	318
I	H	$Cu(pyr)_2Cl_2$	10 mol %	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(81)	71
I	H	$Cu(pyr)_2Cl_2$	11 mol %	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(97)	317

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

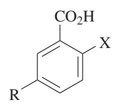
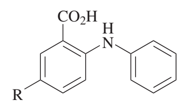
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

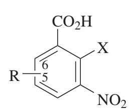
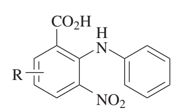
C_6

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (1 mol %), K_2CO_3, 18-c-6, 1,2-$Cl_2C_6H_4$, reflux, 48 h	 (81)	319
		Catalyst(s) (*x* mol %), K_2CO_3		

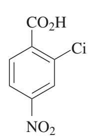
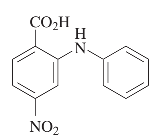
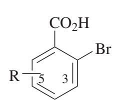
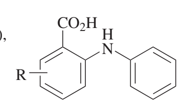
R	X	Catalyst(s)	*x*	Solvent	Temp (°)	Time		Refs.
F	Br	Cu, CuI	4, 9	$EtOCH_2CH_2OH$	130	24 h	(82)	70
Cl	Br	Cu, CuI	9, 4	$EtOCH_2CH_2OH$	130	24 h	(94)	70
Cl	Cl	$CuSO_4$	16	H_2O	MW, 100	10 min	(87)	240
Br	Cl	$Cu(pyr)_2Cl_2$	10	$HOCH_2CH_2OH$	130	24 h	(78)	71
Br	Br	$Cu(pyr)_2Cl_2$	10	$HOCH_2CH_2OH$	130	24 h	(83)	71
Br	I	$Cu(pyr)_2Cl_2$	10	$HOCH_2CH_2OH$	130	24 h	(88)	71

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst(s) (*x* mol %), K_2CO_3		

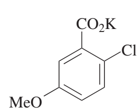
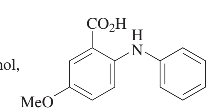
R	X	Catalyst(s)	*x*	Solvent	Temp (°)	Time		Refs.
Cl	Cl	Cu, CuI	2, 0.6	DMF	))) (20 kHz), reflux	20 min	(33)	315
Br	Br	Cu, CuI	9, 4	$EtOCH_2CH_2OH$	130	24 h	(84)	70
Br	Cl	$Cu(pyr)_2Cl_2$	11	$HOCH_2CH_2OH$	MW, 75	20 min	(79)	318
Br	Br	$Cu(pyr)_2Cl_2$	11	$HOCH_2CH_2OH$	MW, 75	20 min	(91)	318
Br	I	$Cu(pyr)_2Cl_2$	11	$HOCH_2CH_2OH$	MW, 75	20 min	(96)	318

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (4 mol %), *N*-ethylmorpholine, 2,3-butanediol, 70°, 15 h		320

R	X	
H	Br	(78)
5-Cl	Cl	(59)
6-Cl	Cl	(52)
4-MeO	I	(50)
5-Me	I	(89)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$CuSO_4$ (16 mol %), K_2CO_3, H_2O, MW, 100°, 5 min	 (95)	240
		Cu (9 mol %), CuI (4 mol %), K_2CO_3, $EtOCH_2CH_2OH$, 130°, 24 h		70

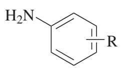
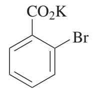
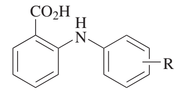
R	
3-Me	(58)
5-HO_2C	(99)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (1 mol %), isoamyl alcohol, reflux, 18 h	 (—)	321

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

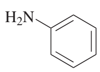
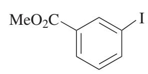
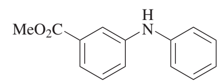
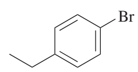
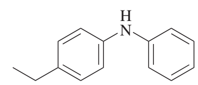
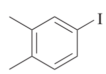
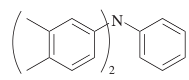
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

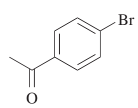
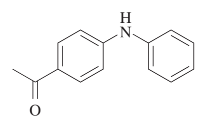
$C_{6–11}$

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu(OAc)$_2$ (6 mol %), DMF, 4-ethylmorpholine, 145°, 3 h	 (—)	322

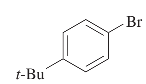
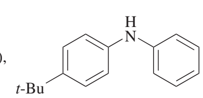
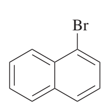
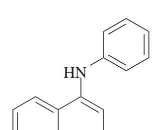
R	R	R	R	R	R	R	R
H	2,3,4-Cl$_3$	2,3-Br$_2$	3-Me	2-Me, 3-O$_2$N	3-Et	3-Ac	3,6-Me$_2$, 2-Cl
2-Cl	2,3,5-Cl$_3$	3-Me$_2$N	4-Me	2-Me, 3-O$_2$N, 6-Cl	3-Et, 2,6-Cl$_2$	3,5-(CF$_3$)$_2$	2,4,5-Me$_3$
3-Cl	2,4,5-Cl$_3$	3-O$_2$N	2-Me, 3-Cl	2-Me, 3-Me$_2$NO$_2$S	2-H$_2$N, 3,6-Me$_2$	2,3-Me$_2$	2,4,6-Me$_3$
4-Cl	2,4,6-Cl$_3$	2-MeO, 5,6-Cl$_2$	2-Me, 6-Cl	3-CF$_3$	3-Me$_2$N, 2,6-Me$_2$	2,4-Me$_2$	3-*n*-Pr
2,3-Cl$_2$	3,4,5-Cl$_3$	3-MeO	3-Me, 2-Cl	3-CF$_3$, 2,6-Cl$_2$	3-O$_2$N, 2,6-Me$_2$	2,5-Me$_2$	3-*n*-Bu
2,4-Cl$_2$	2,3,4,5-Cl$_4$	3-EtO	3-Me, 2,6-Cl$_2$	3-CF$_3$, 2-Br	2-Me, 3-CF$_3$	2,6-Me$_2$	3-NC–, 2,6-Me$_2$
2,5-Cl$_2$	2,3,4,6-Cl$_4$	3-MeS	3-Me, 5,6-Cl$_2$	3-NC–	3-MeS, 2,6-Me$_2$	3,4-Me$_2$	2,3,5,6-Me$_4$
3,4-Cl$_2$	2,3,4,5,6-Cl$_5$	3-Me$_2$NO$_2$S	3-Me, 2,4,6-Cl$_3$	3-NC–, 2,6-Cl$_2$	3-MeO$_3$S, 2,6-Me$_2$	2,5-Me$_2$, 3-Cl	2,6-Me$_2$, 3-Et
3,5-Cl$_2$	3-Br	2-Me	2-Me, 4,5,6-Cl$_3$	3-NC–, 2-Br	4-Me$_2$NO$_2$S, 2,6-Me$_2$	2,6-Me$_2$, 2-Cl	2,6-Et$_2$, 3-Me$_2$NO$_2$S
					2-Me, 3-CN–	2,6-Me$_2$, 3-Br	2,6-Me$_2$, 3-*n*-Pr

C_6

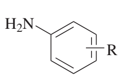
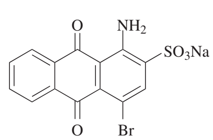
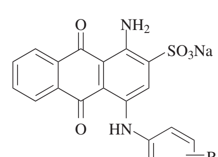
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), TBPM, 2,2'-biphenol (20 mol %), dioxane, rt, 12 h	 (85)	61
		CuO (25 mol %), **L15** (50 mol %), KOH, TBAB, H$_2$O, MW (100 W), 130°, 5 min	 (49)	267
		Cu(OAc)$_2$ (4 mol %), phen (3 mol %), KOH, toluene, reflux, 18 h	 (59)	307

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (5 mol %), H$_2$O, 5 min		

Catalyst	Additives	Temp (°)		Refs.
CuI	**L2** (25 mol %), KOH, TBAB	MW (100 W), 130	(75)	236
CuO	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	MW, 120	(66)	51

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (2 mol %), **L1** (2 mol %), KO*t*-Bu, 100°, 12 h	 (90)	288
		CuI (5 mol %), EDA (5 mol %), K$_2$CO$_3$, PEG-400, 80°, 24 h	 (58)	301

$C_{6–9}$

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (17 mol %), Na$_3$PO$_4$, H$_2$O, pH 6-7, MW, 80–120°, 2–20 min		323

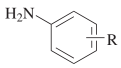
R		R		R		R		R	
H	(55)	3-H$_2$N	(70)	4-MeO	(85)	2-HO$_2$C, 5-Cl	(64)	4-HO$_2$CCH$_2$	(44)
4-F	(76)	4-H$_2$N	(90)	2-HO$_3$S	(30)	3-HO$_2$C	(76)	2,4,6-Me$_3$	(77)
3-Cl	(56)	2-HO	(58)	4-HO$_3$S	(40)	3-HO$_2$C, 5-H$_2$N	(70)		
4-Cl	(87)	4-HO	(72)	2-Me, 3-H$_2$N	(34)	3-HO$_2$C, 4-HO	(30)		
3-Br	(41)	2-MeO	(79)	2-HO$_2$C	(83)	4-HO$_2$C	(70)		
2-H$_2$N	(58)	3-MeO	(67)	2-HO$_2$C, 4-Cl	(43)	3,5-Me$_2$	(32)		

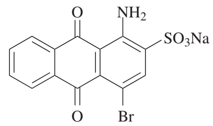
TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

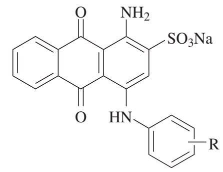
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{6-8}



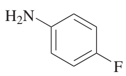


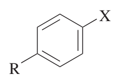
Catalyst (x mol %), Na_2CO_3, H_2O



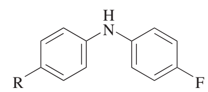
R	Catalyst	x	Additive	Temp (°)	Time (h)		Refs.
3-HO_2S, 4-H_2N	CuCl	30	Na_2SO_4	80	8	(—)	324
3-HO_2S, 4-H_2N	Cu_2SO_4	50	Zn (50 mol %)	60	24	(75)	325
2-Me	CuCl	50	Na_2SO_4	80	8	(—)	324
3-Me	CuCl	50	Na_2SO_4	80	8	(—)	324
4-Me	CuCl	50	Na_2SO_4	80	8	(—)	324
2,6-Me_2	CuCl	50	Na_2SO_4	80	8	(—)	324

C_6

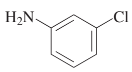


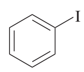


Catalyst (x mol %)

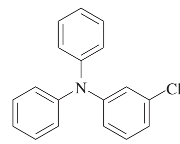


R	Catalyst	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
F	$Cu(OAc)_2$	4	phen (3 mol %), KOH	toluene	reflux	18	(—)	307
MeS	CuI	10	pyridine 2-carboxylic acid (20 mol %), K_3PO_4	DMSO	100	24	(71)	50

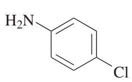


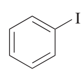


Cu, K_2CO_3

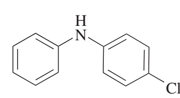


(50) 326

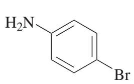


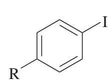


Catalyst (x mol %)

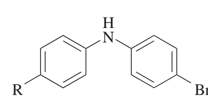


Catalyst	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
CuI	10	2,2'-biphenol (20 mol %), TBPM	dioxane	rt	12	(72)	61
CuO nanoparticles (33 nm)	1.3	KOH, air	DMSO	110	4	(92)	224

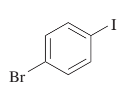




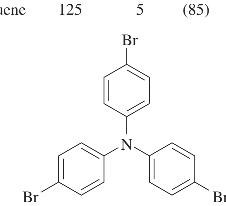
Catalyst (x mol %)



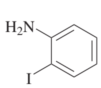
R	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	CuO nanoparticles (33 nm)	1.3	KOH, air	DMSO	110	4	(83)	224
H	**1**	1.25	KO*t*-Bu	toluene	90	12	(62)	309
Me	$CuCl_2$	4	phen (4 mol %), KOH	toluene	125	5	(85)	311

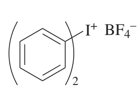


$CuCl_2$ (4 mol %), phen (4 mol %), KOH, toluene, 125°, 5 h

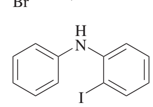


(85) 311





CuI (10 mol %), Na_2CO_3, CH_2Cl_2, rt, 6 h

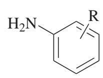


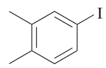
(70) 76

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

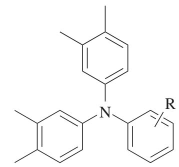
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_6

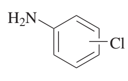


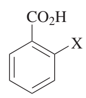


Catalyst (4 mol %),
phen (*x* mol %),
KOH, toluene

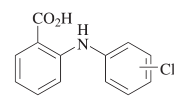


R	Catalyst	*x*	Temp (°)	Time (h)		Refs.
2-F	$Cu(OAc)_4$	3	reflux	18	(—)	307
3-F	$Cu(OAc)_4$	3	reflux	18	(—)	307
4-F	$Cu(OAc)_4$	3	reflux	18	(—)	307
2,4-F_2	$Cu(OAc)_4$	3	reflux	18	(—)	307
4-Cl	$Cu(OAc)_4$	3	reflux	18	(—)	307
4-Br	$CuCl_2$	4	125	5	(83)	311
4-Br	$Cu(OAc)_4$	3	reflux	18	(—)	307

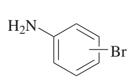


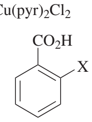


Catalyst(s) (*x* mol %)

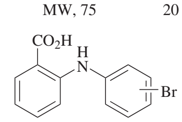


X	Isomer	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
Cl	2	Cu, CuI	2, 0.6	K_2CO_3	DMF	(20 kHz), reflux	20 min	(75)	315
Cl	2	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	15 min	(69)	72
Br	2	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	14.5 min	(75)	72
Cl	3	Cu	8	pyridine (15 wt %), K_2CO_3	amyl alcohol	reflux	1 h	(56)	313
Cl	3	Cu	8	pyridine (15 wt %), K_2CO_3	H_2O	reflux	1 h	(60)	313
Br	3	Cu	9	K_2CO_3	$EtO(CH_2)_2OH$	130	24 h	(84)	70
Cl	3	CuI	9	K_2CO_3	$EtO(CH_2)_2OH$	130	24 h	(99)	109
Cl	3	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	14 min	(73)	72
Br	3	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	12.5 min	(81)	72
Cl	3	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(78)	71
Br	3	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(83)	71
I	3	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(88)	71
Cl	4	Cu, CuI	2, 0.6	K_2CO_3	DMF	))) (20 kHz), reflux	20 min	(33)	315
Cl	4	Cu	7.5	K_2CO_3	DMF	reflux	2 h	(82)	327
Cl	4	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	13 min	(78)	72
Br	4	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	10 min	(86)	72
Cl	4	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(80)	318
Br	4	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(94)	318
I	4	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(96)	318





Catalyst(s) (*x* mol %)

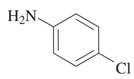
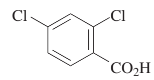
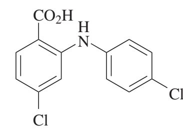
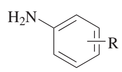
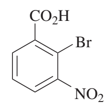
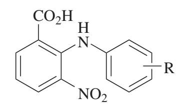


X	Isomer	Catalyst(s)	*x*	Additive	Solvent	Temp (°)	Time		Refs.
Cl	2	$Cu(OAc)_2$	14	K_2CO_3	—	MW (900 W)	12 min	(65)	72
Br	2	$Cu(OAc)_2$	14	K_2CO_3	—	MW (900 W)	11 min	(69)	72
Br	3	Cu, CuI	9, 4	K_2CO_3	$EtO(CH_2)_2OH$	130	24 h	(81)	70
Cl	3	$Cu(OAc)_2$	14	K_2CO_3	—	MW (900 W)	11 min	(74)	72
Br	3	$Cu(OAc)_2$	14	K_2CO_3	—	MW (900 W)	11 min	(80)	72
Cl	3	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(76)	71
Br	3	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(80)	71
I	3	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(86)	71
Cl	4	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(83)	318
Br	4	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(91)	318
I	4	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(95)	318

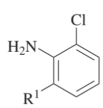
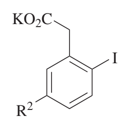
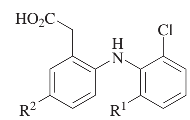
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

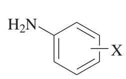
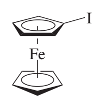
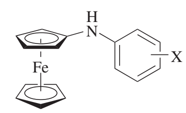
C_6

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$CuSO_4$ (16 mol %), K_2CO_3, H_2O, MW, 100°, 7 min	 (95)	240
		Cu (4 mol %), 4-ethylmorpholine, 2,3-butanediol, 70°, 15 h		320

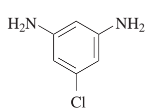
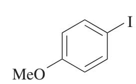
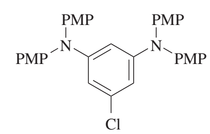
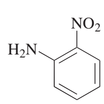
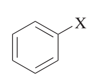
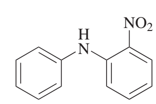
R		R		R	
2-F	(67)	2-F, 5-Cl	(31)	2-Cl	(58)
2,3-F_2	(57)	2,6-F_2	(58)	3-Cl	(40)
2,5-F_2	(62)	2-F, 6-Cl	(12)	4-Cl	(60)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (2 eq), K_2CO_3, NMP, 100°, 24 h		328

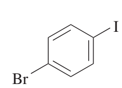
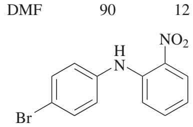
R^1	R^2	
Cl	H	(61)
F	Me	(41)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (10 mol %), K_2CO_3, xylene, 140°, 6 h		329

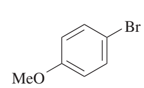
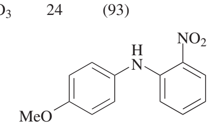
X	
2-Cl	(94)
4-Cl	(0)
2,4-Cl_2	(0)
2-Br	(46)
4-Br	(0)
2,4-Br_2	(38)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu powder (1 eq), K_2CO_3, Ph_2O, 190°, 36 h	 (52)	330
		Catalyst (10 mol %)		

X	Catalyst	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	CuI	CsOAc	DMSO	90	24	(63)	274
Cl	CuI	PPAPM (20 mol %), K_3PO_4	DMF	120	48	(32)	48
Br	CuI	PPAPM (20 mol %), K_3PO_4	DMF	110	36	(90)	48
Cl	CuI	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	36	(31)	67
Br	CuI	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	20	(87)	67
Br	CuI	DPP (20 mol %), K_3PO_4	DMF	110	36	(75)	108
I	CuO	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	90	12	(89)	277

Aryl Halide	Conditions	Product(s) and Yield(s) (%)
	CuI (10 mol %), DMF, 110°	

Additives	Time (h)		Refs.
PPAPM (20 mol %), K_3PO_4	30	(98)	48
piperidine-2-carboxylic acid (20 mol %), K_2CO_3	24	(93)	67

Aryl Halide	Conditions	Product(s) and Yield(s) (%)
	CuI (10 mol %), DMF, 110°	

Additives	Time (h)		Refs.
DPP (20 mol %), K_3PO_4	36	(70)	108
PPAPM (20 mol %), K_3PO_4	36	(82)	48
piperidine-2-carboxylic acid (20 mol %), K_2CO_3	20	(80)	67

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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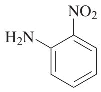
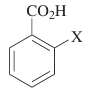
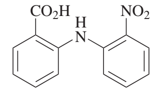
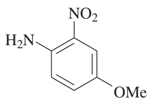


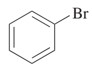


Catalyst (x mol %), K_2CO_3

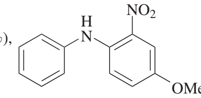


X	Catalyst	x	Additive	Solvent	Temp	Time (min)		Refs.
Cl	Cu powder	—	pyridine	H_2O	)))	20	(79)	314
Cl	$Cu(OAc)_2$	14	none	—	MW (700 W)	14	(70)	72
Br	$Cu(OAc)_2$	14	none	—	MW (700 W)	13	(78)	72

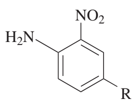


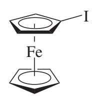


Cu/Fe–hydrotalcite (10 wt %), toluene, 130°, 16 h

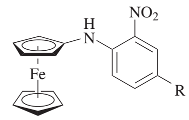


(77) 283

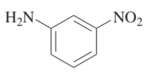


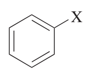


Cu (10 mol %), K_2CO_3, xylene, 140°, 6 h

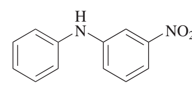


R		Refs.
H	(85)	329
NO_2	(0)	
Me	(89)	

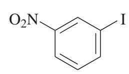




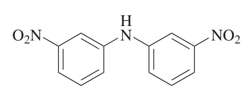
Catalyst (10 mol %)



X	Catalyst	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cl	CuI	K_2CO_3, piperidine-2-carboxylic acid (20%)	DMF	110	36	(31)	67
Br	CuI	K_3PO_4, PPAPM (20 mol %)	DMF	110	36	(83)	48
Br	CuI	K_3PO_4, DPP (20 mol %)	DMF	110	36	(73)	108
I	CuI	CsOAc	DMSO	90	24	(12)	274
I	CuO	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	90	12	(81)	277



Cu powder, K_2CO_3, 1,2-$Cl_2C_6H_4$, reflux, 20 h



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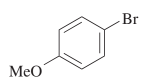
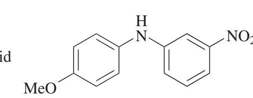


CuI (10 mol %), piperidine-2-carboxylic acid (20 mol %), K_2CO_3, DMF, 110°, 20 h



(29) 67

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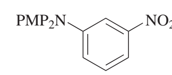
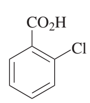
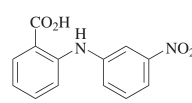


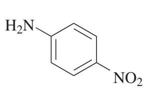
(23)

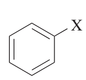


Cu (8 mol %), reflux

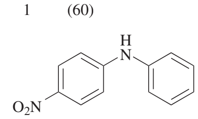


Additive(s)	Solvent	Time (h)		Refs.
KOH	H_2O	5	(49)	332
pyridine (15 wt %), K_2CO_3	H_2O	1	(62)	313
pyridine (15 wt %), K_2CO_3	amyl alcohol	1	(60)	313





Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cl	CuI	10	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	36	(25)	67
Br	CuI	10	DPP (20 mol %), K_3PO_4	DMF	110	36	(71)	108
Br	CuI	10	PPAPM (20 mol %), K_3PO_4	DMF	110	36	(86)	48
I	CuI	10	CsOAc	DMSO	90	24	(64)	274
I	CuI	10	2,2'-biphenol (20 mol %), TBPM	dioxane	rt	12	(53)	61
Br	CuO	10	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	110	24	(82)	277
I	CuO	10	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	100	12	(85)	277
I	CuO nanoparticles (33 nm)	1.3	KOH, air	DMSO	110	1.5	(70)	224
I	$Cu(acac)_2$	10	Fe_2CO_3, (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	MW, 150	0.5	(trace)	262

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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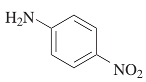
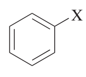
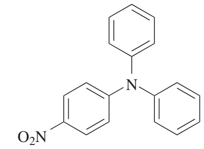
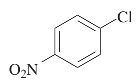
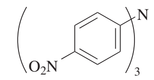
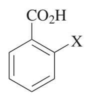
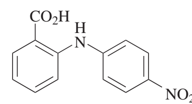
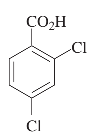
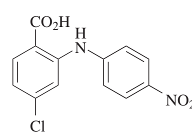
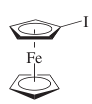
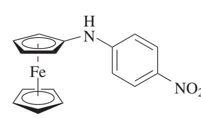
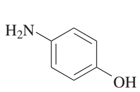
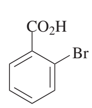
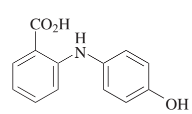
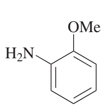
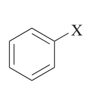
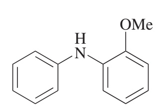
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (3.6 mol %), PBu_3 (7.2 mol %), KO*t*-Bu, toluene, 135°, 10.5 h	 X: Cl (31); Br (35)	56
		CuI (3.6 mol %), PBu_3 (7.2 mol %), KO*t*-Bu, toluene, 135°, 10.5 h	 (29)	56
		Catalyst(s) (*x* mol %), K_2CO_3		

X	Catalyst(s)	*x*	Solvent	Temp (°)	Time		Refs.
Br	Cu, CuI	9, 4	$EtO(CH_2)_2OH$	130	24 h	(53)	70
Cl	CuI	9, 4	$EtO(CH_2)_2OH$	130	24 h	(87)	109
Cl	$Cu(OAc)_2$	14	—	MW (700 W)	11 min	(75)	72
Br	$Cu(OAc)_2$	14	—	MW (700 W)	10 min	(81)	72
Cl	$Cu(pyr)_2Cl_2$	10	$HO(CH_2)_2OH$	130	24 h	(56)	71
Br	$Cu(pyr)_2Cl_2$	10	$HO(CH_2)_2OH$	130	24 h	(58)	71
I	$Cu(pyr)_2Cl_2$	10	$HO(CH_2)_2OH$	130	24 h	(64)	71
Cl	$Cu(pyr)_2Cl_2$	11	$HO(CH_2)_2OH$	MW 75	20 min	(62)	318
Br	$Cu(pyr)_2Cl_2$	11	$HO(CH_2)_2OH$	MW 75	20 min	(82)	318
I	$Cu(pyr)_2Cl_2$	11	$HO(CH_2)_2OH$	MW 75	20 min	(81)	318

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %), K_2CO_3		

Catalyst	*x*	Solvent(s)	Temp	Time		Refs.
Cu powder	—	pyridine/H_2O	)))	20 min	(61)	314
Cu	7.5	DMF	reflux	2 h	(49)	327

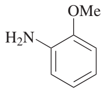
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (10 mol %), K_2CO_3, xylene, 140°, 6 h	 (0)	329
		Cu (9 mol %), CuI (4 mol %), K_2CO_3, $EtOCH_2CH_2OH$, 130°, 24 h	 (63)	70
		Catalyst (*x* amount)		

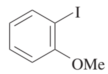
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	10 mol %	piperidine-2-carboxylic acid (20%), K_2CO_3	DMF	110	36	(76)	67
Br	CuI	10 mol %	PPAPM (20 mol %), K_3PO_4	DMF	110	36	(60)	108
Br	CuI	10 mol %	DPP (20 mol %), K_3PO_4	DMF	110	36	(60)	108
Br	CuI	10 mol %	CsOAc	DMSO	90	24	(44)	274
Br	Cu/Fe–hydrotalcite	10 wt %	none	toluene	130	12	(75)	283
I	CuO	10 mol %	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	80	12	(80)	277
I	CuO nanoparticles (33 nm)	1.3 mol %	KOH, air	DMSO	110	1.7	(98)	224

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

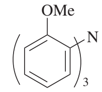
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_6

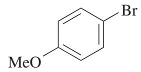




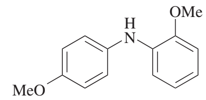
Cu powder, K_2CO_3, 1,2-$Cl_2C_6H_4$, reflux, 48 h



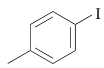
(91) 331



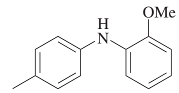
Catalyst (*x* amount)



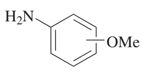
Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	36	(73)	67
Cu/Fe-hydrotalcite	10 wt %	none	toluene	130	12	(76)	283

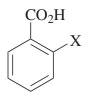


CuO (10 mol %), $FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3, DMF, 90°, 12 h

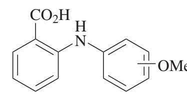


(82) 277

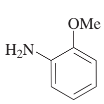


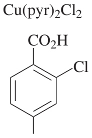


Catalyst(s) (*x* mol %)

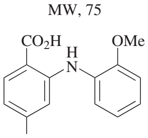


Isomer	X	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
2	Cl	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	8 min	(83)	72
2	Br	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	6 min	(91)	72
2	Cl	$CuSO_4$	16	K_2CO_3	H_2O	MW 100	7 min	(90)	240
3	Cl	Cu powder	—	K_2CO_3, pyridine	H_2O	)))	20 min	(82)	314
3	Cl	Cu	7.5	K_2CO_3	DMF	reflux	2 h	(72)	327
3	Cl	Cu, CuI	2, 0.6	K_2CO_3	DMF	))) (20 kHz), reflux	20 min	(54)	315
4	Cl	Cu	8	KOH	H_2O	reflux	5 h	(89)	332
4	Cl	Cu	8	K_2CO_3, pyridine (15 wt %)	H_2O	reflux	1 h	(86)	332
4	Cl	Cu	8	K_2CO_3, pyridine (15 wt %)	amyl alcohol	reflux	1 h	(75)	313
4	Br	Cu, CuI	9, 4	K_2CO_3	$EtO(CH_2)_2OH$	130	24 h	(88)	70
4	Cl	Cu, CuI	4, 9	K_2CO_3	$EtO(CH_2)_2OH$	130	24 h	(84)	109
4	Cl	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	6.5 min	(88)	72
4	Br	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	6 min	(97)	72
4	Cl	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(81)	71
4	Br	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(88)	71
4	I	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(90)	71
4	Cl	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(89)	318
4	Br	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(90)	318
4	I	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(94)	318

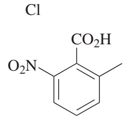




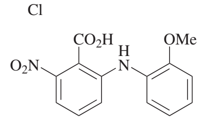
$CuSO_4$ (16 mol %), K_2CO_3, H_2O, MW, 100°, 8 min



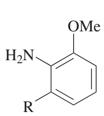
(94) 240

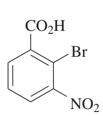


Cu/Zn, Na_2CO_3, EtOH, 2 h

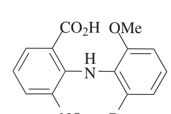


(76) 333





Cu (4 mol %), *N*-ethylmorpholine, 2,3-butanediol, 70°, 15 h



R	
H	(79)
MeO	(42)

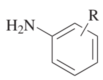
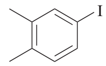
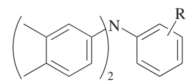
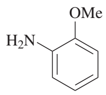
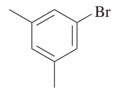
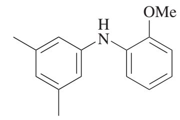
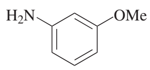
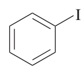
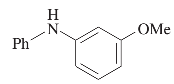
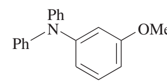
320

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

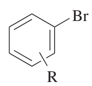
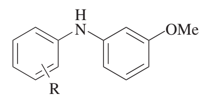
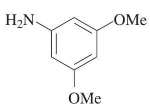
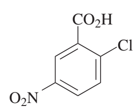
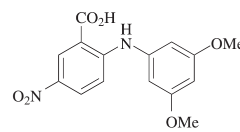
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

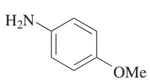
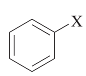
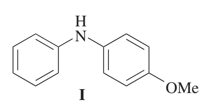
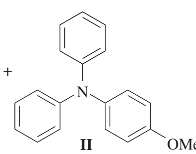
C_6

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = 2-, 3-, or 4-MeO		$Cu(OAc)_2$ (4 mol %), phen (3 mol %), KOH, toluene, reflux, 18 h	 (—)	307
		CuI (10 mol %), pyridine-2-carboxylic acid (20 mol%), K_3PO_4, DMSO, 90°, 24 h	 (70)	50
		Catalyst (*x* mol %)	 I +  II	

Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)	I	II	Refs.
Cu	—	K_2CO_3	—	—	—	(0)	(60)	326
CuI	10	CsOAc	DMSO	90	24	(4)	(0)	274

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), pyridine-2-carboxylic acid (20 mol %), K_3PO_4, DMSO, 100°		50
		Cu (17 mol %), KI, K_2CO_3, DMF, 120°, 6 h	 (25)	334

R	Time (h)	
2-Me	30	(67)
3-CF_3	24	(55)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %)	 I +  II	

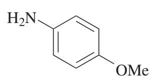
X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)	I	II	Refs.
I	CuI	7	Cs_2CO_3	$Si(OEt)_4$	145	38	(85)	(0)	335
I	CuI	10	CsOAc	DMSO	90	24	(38)	(0)	274
I	CuI	2	KO*t*-Bu	toluene	135	14	(8)	(81)	304
Cl	CuI	3.6	PBu_3 (7.2 mol %), KO*t*-Bu	toluene	135	10.5	(0)	(85)	56
Br	CuI	3.6	PBu_3 (7.2 mol %), KO*t*-Bu	toluene	135	10.5	(0)	(86)	56
I	CuI	10	2,2′-biphenol (20 mol %), TBPM	dioxane	rt	12	(86)	(0)	61
Br	CuI	7	L-Pro (14 mol %), K_2CO_3	DMSO	90	40	(90)	(0)	47
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	36	(82)	(0)	192, 336, 47
I	CuI	5	DiPrPhDAB (6 mol %), KO*t*-Bu	toluene	120	48	(76)	(0)	306
Br	CuI	2	**L1** (2 mol %), KO*t*-Bu	—	100	12	(71)	(0)	288
I	CuO nanoparticles (33 nm)	1.3	KOH, air	DMSO	110	1.5	(94)	(0)	224
Br	CuO	10	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	110	24	(79)	(0)	277
I	CuO	10	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	90	12	(85)	(0)	277
I	$Cu(acac)_2$	10	Fe_2O_3 (20 mol %), Cs_2CO_3	DMSO/H_2O (1:1)	150	0.5	(51)	(0)	262
I	**1**	1.25	KO*t*-Bu	toluene	90	12	(69)	(0)	309

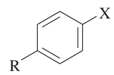
TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

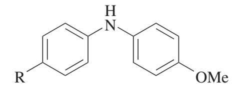
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_6

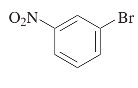




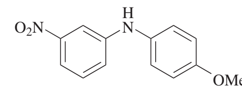
CuI (*x* mol %), DMSO



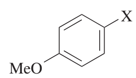
R	X	*x*	Additives	Temp (°)	Time (h)		Refs.
F	Br	10	pyridine-2-carboxylic acid (20 mol %), K_3PO_4	100	24	(76)	50
Cl	Br	7	L-Pro (14 mol %), K_2CO_3	90	40	(82)	47
Cl	Br	10	pyridine 2-carboxylic acid (20 mol %), K_3PO_4	100	24	(72)	50
Cl	I	5	pyridine 2-carboxylic acid (20 mol %), K_3PO_4	70	24	(82)	50



CuO (10 mol %), $FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3, DMF, 100°, 12 h



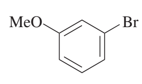
(86) 277



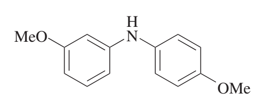
Catalyst (*x* mol %)

I + **II**

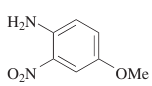
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
Cl	CuI	3.6	bipy (3.6 mol %), KO*t*-Bu	toluene	115	3.5	(0)	(87)	305
Br	CuI	3.6	PBu_3 (7.2 mol %), KO*t*-Bu	toluene	135	10.5	(0)	(87)	56
I	CuI	2	KO*t*-Bu	toluene	135	14	(14)	(71)	304
I	CuI	7	L-Pro (14 mol %), K_2CO_3	DMSO	90	27	(81)	(0)	47
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	27	(81)	(0)	192
I	CuI	20	Cs_2CO_3	$Si(OEt)_4$	145	32	(0)	(73)	335
I	$Cu(OAc)_2$	4	phen (3 mol %), KOH	toluene	reflux	18	(0)	(—)	307
I	$Cu(TMHD)_2$	20	KO*t*-Bu	toluene	120	40	(0)	(73)	308

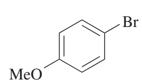


CuI (7 mol %), L-Pro (14 mol %), K_2CO_3, DMSO, 90°, 40 h

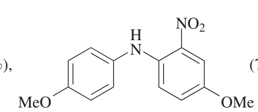


(97) 47

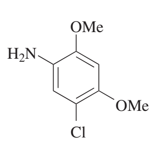


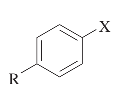


Cu/Fe–hydrotalcite (10 wt %), toluene, 130°, 16 h

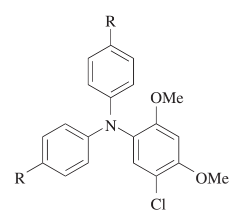


(74) 283

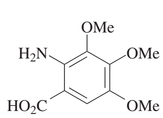


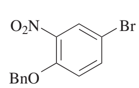


CuI (20 mol %), Cs_2CO_3, $Si(OEt)_4$, 145°, 38 h

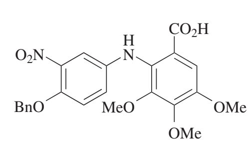


R	X	Time (h)		Refs.
H	Br	38	(5)	335
H	I	38	(82)	
MeO	I	30	(83)	

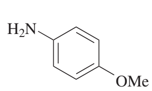


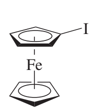


CuI (20 mol %), L-Pro (20 mol %), K_2CO_3, isoamyl alcohol, MW, 140°, 1 h

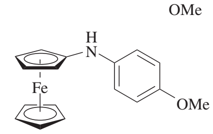


(83) 337





Cu (10 mol %), K_2CO_3, xylene, 140°, 6 h

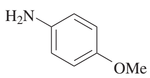


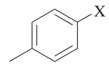
(0) 329

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

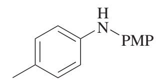
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_6





CuI (x mol %)



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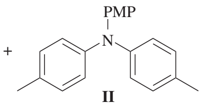
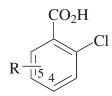
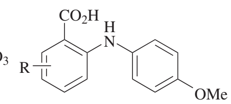


II

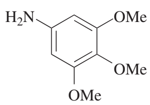
X	x	Additives	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
Br	7	L-Pro (14 mol %), K_2CO_3	DMSO	90	40	(90)	(0)	47
I	5	DiPrPhDAB (6 mol %), KO*t*-Bu	toluene	120	48	(75)	(0)	306
I	5	**L41** (10 mol %), NaO*t*-Bu	toluene	110	40	(0)	(60)	338

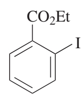


Catalyst(s) (x mol %), K_2CO_3

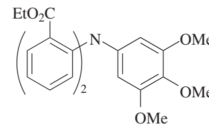


R	Catalyst(s)	x	Solvent(s)	Temp (°)	Time		Refs.
4-Cl	Cu powder	—	pyridine/H_2O	)))	20 min	(90)	314
4-Cl	Cu, CuI	4, 9	$EtOCH_2CH_2OH$	130	24 h	(86)	109
5-Br	Cu, CuI	4, 9	$EtOCH_2CH_2OH$	130	24 h	(85)	109
4-O_2N	Cu, CuI	4, 9	$EtOCH_2CH_2OH$	130	24 h	(99)	109
4-O_2N	$CuSO_4$	16	H_2O	MW, 100	5 min	(93)	240



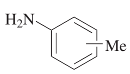


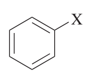
CuI (20 mol %), Cs_2CO_3, $Si(OEt)_4$, 145°, 28 h



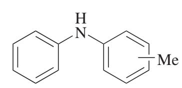
(93) 335

C_7





Catalyst (x mol %)



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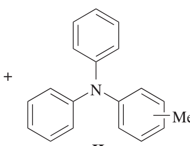
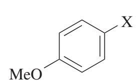
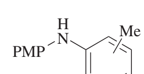


II

Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
2	Cl	CuI	3.6	PBu_3 (7.2 mol %), KO*t*-Bu	toluene	135	10.5	(0)	(80)	56
2	I	CuI	2	KO*t*-Bu	toluene	135	14	(8)	(81)	304
2	I	CuO particles (33 nm)	1.3	KOH, air	DMSO	110	1.6	(96)	(0)	224
3	I	CuI	5	KO*t*-Bu, DiPrPhDAB (6 mol %)	toluene	120	48	(84)	(0)	306
4	I	CuI	5	KO*t*-Bu, DiPrPhDAB (6 mol %)	toluene	120	48	(82)	(0)	55
4	I	CuI	10	TBPM, 2,2'-biphenol (20 mol %)	dioxane	rt	12	(84)	(0)	61
4	I	CuO	10	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), Cs_2CO_3	DMF	80	12	(68)	(0)	277
4	I	$Cu(PPh_3)_3Br$	20	Cs_2CO_3	toluene	110	24	(88)	(0)	339



Catalyst (x mol %)



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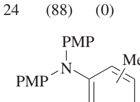


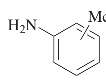
II

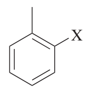
Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
2	I	CuI	2	KO*t*-Bu	toluene	135	14	(14)	(71)	304
4	Br	CuI	5	**L2** (25 mol %), TBAB, KOH	H_2O	MW (100 W), 130	5 min	(75)	(0)	236
4	Br	CuO	5	**L14** (50 mol %), hexane-2,5-dione, KOH, TBAB	H_2O	MW, 120	5 min	(75)	(0)	51
4	Br	CuO	25	**L15** (50 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(55)	(0)	267

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

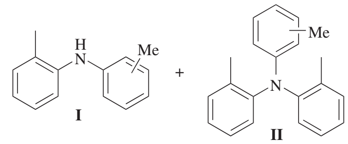
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

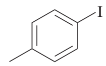




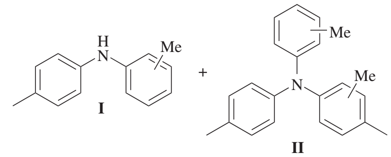
Catalyst (*x* mol %)



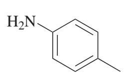
Isomer	X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
2	I	Cu	2	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	15	(0)	(90)	54
3	Br	CuI	10	pyridine-2-carboxylic acid (20 mol %), K_3PO_4	DMSO	100	30	(74)	(0)	50
3	I	CuI	10	pyridine-2-carboxylic acid (20 mol %), K_3PO_4	DMSO	80	24	(71)	(0)	50

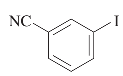


Catalyst (*x* mol %), toluene

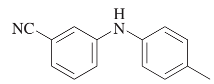


Isomer	Catalyst	*x*	Additive(s)	Temp (°)	Time (h)	**I**	**II**	Refs.
3	CuI	5	DiPrPhDAB (6 mol %), KO*t*-Bu	120	48	(73)	(0)	306
4	CuI	5	DiPrPhDAB (6 mol %), KO*t*-Bu	120	48	(82)	(0)	55, 170
4	$Cu(OAc)_2$	4	phen (3 mol %), KOH	reflux	18	(0)	(—)	307
4	$Cu(TMHD)_2$	20	KO*t*-Bu	120	40	(0)	(72)	308

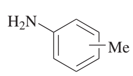


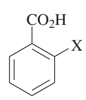


CuI (10 mol %), pyridine-2-carboxylic acid (20 mol %), K_3PO_4, DMSO, 80°, 24 h

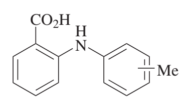


(73) 50



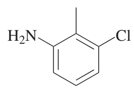
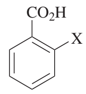
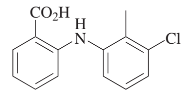
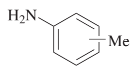
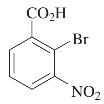
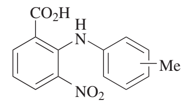
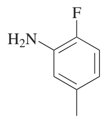
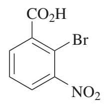
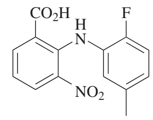
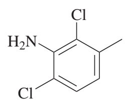
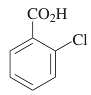
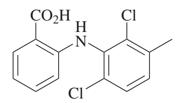
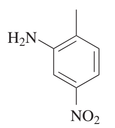
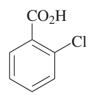
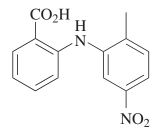
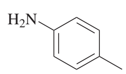
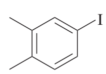
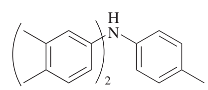


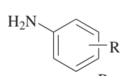
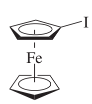
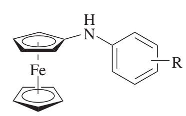
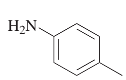
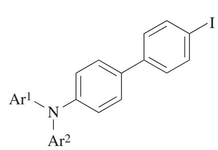
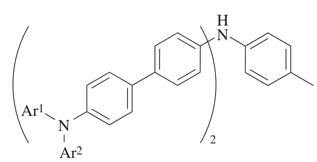
Catalyst(s) (*x* mol %)



Isomer	X	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
2	Cl	Cu, CuI	2, 0.6	K_2CO_3	DMF	))) (20 kHz), reflux	20 min	(70)	315
2	Cl	Cu, CuI	4, 9	Na_2CO_3	$EtO(CH_2)_2OH$	130	24 h	(92)	109
2	Cl	Cu, Cu_2O	3, 1.3	K_2CO_3	$MeO(CH_2)_2OH$	reflux	2 h	(55)	340
3	Cl	Cu	7.5	K_2CO_3	DMF	reflux	2 h	(63)	327
3	Cl	Cu, CuI	4, 9	K_2CO_3	$EtO(CH_2)_2OH$	130	24 h	(80)	109
3	Cl	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	7.5 min	(87)	72
3	Br	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	6.6 min	(95)	72
4	Cl	Cu	8	KOH	H_2O	reflux	5 h	(98)	332
4	Cl	Cu	8	K_2CO_3, pyridine (15 wt %)	H_2O	reflux	1 h	(75)	313
4	Cl	Cu	8	K_2CO_3, pyridine (15 wt %)	amyl alcohol	reflux	1 h	(84)	313
4	I	Cu, CuI	25, 5	K_2CO_3	Bu_2O	170	120 h	(70)	341
4	Cl	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	6.6 min	(85)	72
4	Br	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	6.3 min	(94)	72
4	Cl	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(82)	71
4	Br	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(90)	71
4	I	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HO(CH_2)_2OH$	130	24 h	(89)	71
4	Cl	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(80)	318
4	Br	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(91)	318
4	I	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HO(CH_2)_2OH$	MW, 75	20 min	(86)	318

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_7				
		$Cu(OAc)_2$ (14 mol %), K_2CO_3, MW (700 W)	 X Time (min): Cl 14 (75); Br 12.5 (84)	72
		Cu (4 mol %), *N*-ethylmorpholine, 2,3-butanediol, 70°, 15 h	 Isomer: 2 (67); 3 (58); 4 (63)	320
		Cu (4 mol %), *N*-ethylmorpholine, 2,3-butanediol, 70°, 15 h	 (64)	320
		Cu (7.5 mol %), K_2CO_3, DMF, reflux, 2 h	 (18)	327
		Cu (2 mol %), CuI (0.6 mol %), K_2CO_3, DMF,))) (20 kHz), reflux, 20 min	 (14)	315
		$Cu(OAc)_2$ (4 mol %), phen (3 mol %), KOH, toluene, reflux, 18 h	 (—)	307

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = 2- or 4-Me		Cu (10 mol %), K_2CO_3, xylene, 140°, 6 h	 (0)	329
		Catalyst (*x* mol %)		

Ar[1]	Ar[2]	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Ph	*o*-Tol	$CuCl_2$	4	phen (20 mol %), KOH	toluene	125	5	(—)	311
m-Tol	*m*-Tol	CuO	6	K_2O_3	—	reflux	—	(30)	342

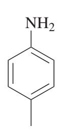
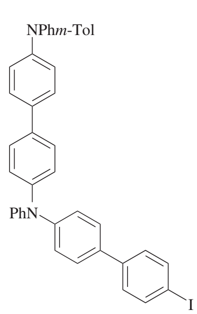
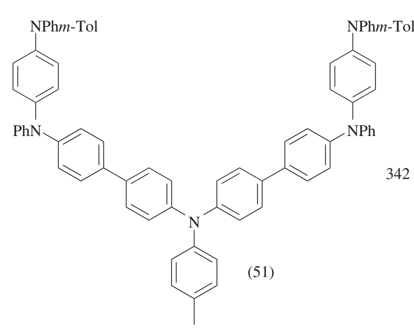
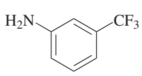
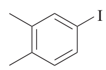
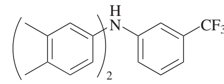
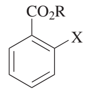
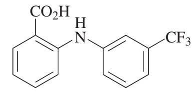
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuO (6 mol %), K_2O_3, reflux	 (51)	342

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

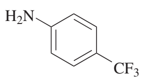
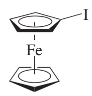
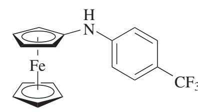
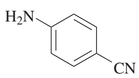
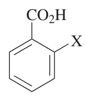
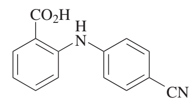
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

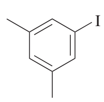
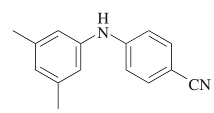
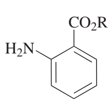
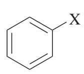
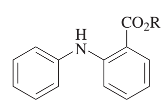
C_7

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Cu(OAc)_2$ (4 mol %), phen (3 mol %), KOH, toluene, reflux, 18 h	 (—)	307
		Catalyst (*x* mol %)		

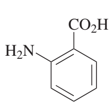
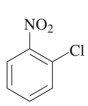
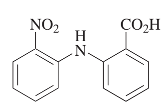
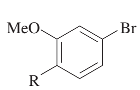
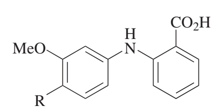
X	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
Cl	Cu, CuI	2, 0.6	K_2CO_3	DMF	))) (20 kHz), reflux	20 min	(24)	315
Cl	Cu	7.5	Na_2CO_3	DMF	reflux	2 h	(60)	327
I	Cu	25	K_2CO_3	H_2O	reflux	3 h	(61)	343
Cl	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	14.5 min	(72)	72
Br	$Cu(OAc)_2$	14	K_2CO_3	—	MW (700 W)	13 min	(76)	72

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (10 mol %), K_2CO_3, xylene, 140°, 6 h	 (0)	329
		Catalyst(s) (*x* mol %), K_2CO_3		

X	Catalyst(s)	*x*	Solvent	Temp (°)	Time		Refs.
Br	Cu, CuI	9, 4	$EtOCH_2CH_2OH$	130	24 h	(71)	70
Br	$Cu(pyr)_2Cl_2$	10	$HOCH_2CH_2OH$	130	24 h	(72)	71
Cl	$Cu(pyr)_2Cl_2$	11	$HOCH_2CH_2OH$	MW 75	20 min	(64)	318
Br	$Cu(pyr)_2Cl_2$	11	$HOCH_2CH_2OH$	MW 75	20 min	(75)	318
I	$Cu(pyr)_2Cl_2$	11	$HOCH_2CH_2OH$	MW 75	20 min	(89)	318

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), pyridine-2-carboxylic acid (20 mol %), K_3PO_4, DMSO, 90°, 24 h	 (52)	50
		Catalyst (*x* mol %), 110°		

R	X	Catalyst	x	Additive(s)	Solvent	Time (h)		Refs.
H	Br	CuI	10	K_3PO_4, DPP (20 mol %)	DMF	30	(70)	108
Me	Br	CuI	10	K_3PO_4, PPAPM (20 mol%)	DMF	30	(84)	48
Me	I	$Cu(Ph_3)_3Br$	20	Cs_2CO_3	toluene	24	(70)	339

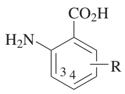
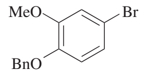
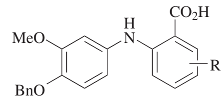
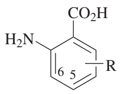
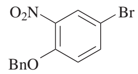
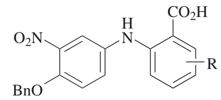
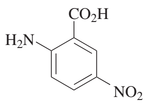
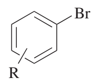
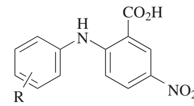
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (0.3 mol %), K_2CO_3, 220°	 (90)	345
		CuI (20 mol %), L-Pro (20 mol %), K_2CO_3, MW, 140°, 1 h		337

R	Solvent	
H	isoamyl alcohol	(78)
H	DMSO	(69)
BnO	isoamyl alcohol	(85)

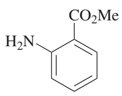
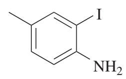
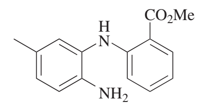
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

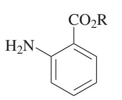
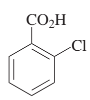
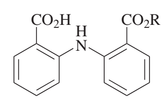
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

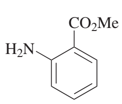
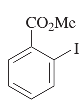
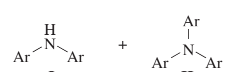
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (20 mol %), L-Pro (20 mol %), K_2CO_3, isoamyl alcohol, MW, 140°, 1 h	 R: 4,5-F_2 (38); 3-MeO (70)	337
		CuI (20 mol %), L-Pro (20 mol %), K_2CO_3, isoamyl alcohol, MW, 140°, 1 h	 R: H (83); 4,5-F_2 (54); 6-MeO (92); 4,5,6-$(MeO)_3$ (83)	337
		CuI (20 mol %), L-Pro (20 mol %), K_2CO_3, MW, 1 h		337

R	Solvent(s)	Temp (°)	
H	DMF/H_2O	160	(82)
4-MeO	DMF/H_2O	160	(76)
3-BnO	isoamyl alcohol	140	(82)
4-BnO	DMF/H_2O	160	(69)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu_2O (10 mol %), K_2CO_3, xylene, 145°, 8 h	 (70)	346

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst(s) (*x* mol %)		

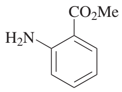
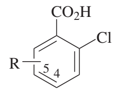
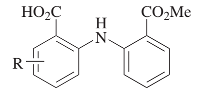
R	Catalyst(s)	*x*	Additive	Solvent(s)	Temp (°)	Time		Refs.
H	Cu	7.5	K_2CO_3	DMF	reflux	2 h	(81)	327
H	Cu powder	—	K_2CO_3	pyridine/H_2O	)))	20 min	(81)	314
H	$CuSO_4$	16	K_2CO_3	H_2O	MW, 100	10 min	(82)	240
Me	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	1 h	(87)	347

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %)	 **I** + **II**, Ar = 2-$MeO_2CC_6H_4$	

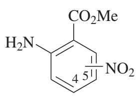
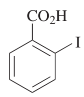
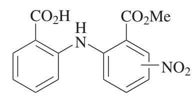
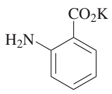
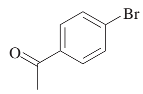
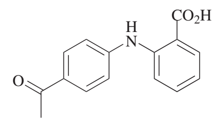
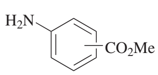
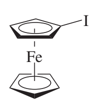
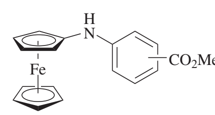
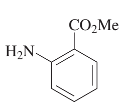
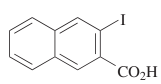
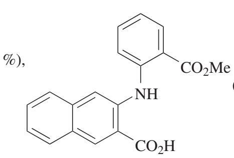
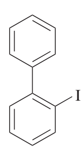
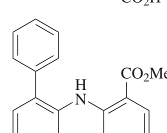
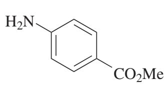
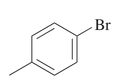
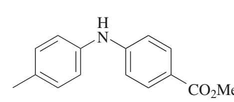
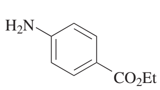
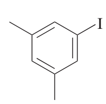
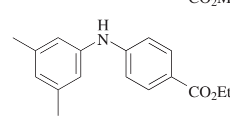
Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
Cu	1	K_2CO_3, 18-c-6	1,2-$Cl_2C_6H_4$	reflux	17	(0)	(55)	319
Cu	15	K_2CO_3	—	180	—	(70)	(0)	348
$Cu(PPh_3)_3Br$	20	Cs_2CO_3	toluene	110	24	(83)	(0)	339

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Catalyst(s) (x mol %)		

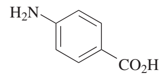
R	Catalyst(s)	x	Additive	Solvent	Temp (°)	Time		Refs.
4-Cl	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	20 h	(83)	347
5-Cl	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	20 h	(60)	347
4-O_2N	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	15 h	(64)	347
4-O_2N	Cu	7.5	K_2CO_3	DMF	reflux	2 h	(80)	327
4-O_2N	$CuSO_4$	16	K_2CO_3	H_2O	MW, 100	8 min	(85)	240
5-O_2N	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	2 h	(56)	347
4-MeO	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	3 h	(67)	347
5-MeO	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	2 h	(88)	347
6-MeO	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	2 h	(51)	347
5-Me	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	2 h	(70)	347
6-Me	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	2 h	(69)	347
4-HO_2C	Cu, CuI	8, 12	*N*-ethylmorpholine	2,3-butanediol	120	15 h	(61)	347

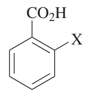
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (8 mol %), CuI (12 mol %), *N*-ethylmorpholine, 2,3-butanediol, 120°, 3 h	 Isomer: 4 (71); 5 (86)	347
		Cu (1 mol %), isoamyl alcohol, reflux, 21 h	 (56)	321
		Cu (10%), K_2CO_3, xylene, 140°, 6 h	 Isomer: 2 (81); 4 (0)	329
		Cu (8 mol %), CuI (12 mol %), *N*-ethylmorpholine, 2,3-butanediol, 120°, 20 h	 (72)	347
		Cu (50 mol %), K_2CO_3, nitrobenzene, 180°, 2.5 h	 (58)	349
		CuI (7 mol %), L-Pro (14 mol %), K_2CO_3, DMSO, 90°, 40 h	 (<5)	47
		CuI (10 mol %), 2-pyridinecarboxylic acid (20 mol %), K_3PO_4, DMSO, 90°, 24 h	 (50)	50

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

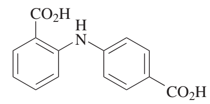
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7



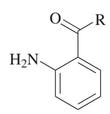


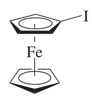
Catalyst(s) (x mol %)



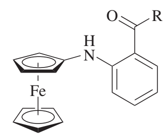
X	Catalyst(s)	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
Cl	Cu	7.5	K_2CO_3	DMF	reflux	2 h	(66)	327
Cl	Cu powder	—	K_2CO_3, pyridine	H_2O	)))	20 min	(65)	314
Cl	Cu, CuI	4, 9	K_2CO_3	$EtOCH_2CH_2OH$	130	24 h	(98)	109
Br	Cu, CuI	9, 4	K_2CO_3	$EtOCH_2CH_2OH$	130	24 h	(80)	70
Cl	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HOCH_2CH_2OH$	130	24 h	(59)	71
Br	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HOCH_2CH_2OH$	130	24 h	(61)	71
I	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HOCH_2CH_2OH$	130	24 h	(88)	71
Cl	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HOCH_2CH_2OH$	MW, 75	20 min	(61)	318
Br	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HOCH_2CH_2OH$	MW, 75	20 min	(72)	318
I	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HOCH_2CH_2OH$	MW, 75	20 min	(88)	318

C_{7-8}



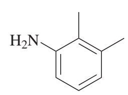


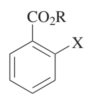
Cu (10 mol %), K_2CO_3, xylene, 140°, 6 h



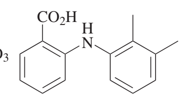
R		Refs.
H	(96)	329
Me	(92)	

C_8

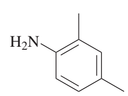


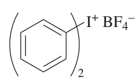


Catalyst(s) (x mol %), K_2CO_3

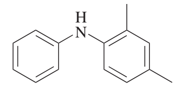


X	Catalyst(s)	x	Solvent	Temp (°)	Time		Refs.
Cl	Cu, CuI	2, 0.6	DMF	))) (20 KHz) reflux	20 min	(44)	315
Cl	Cu	7.5	DMF	reflux	2 h	(70)	327
Cl	$Cu(OAc)_2$	14	—	MW (700 W)	7 min	(83)	72
Br	$Cu(OAc)_2$	14	—	MW (700 W)	6.6 min	(90)	72

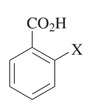




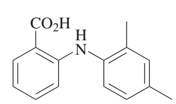
CuI (10 mol %), Na_2CO_3, CH_2Cl_2, rt, 6 h



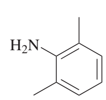
(70) 76

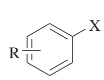


$Cu(OAc)_2$ (14 mol %), K_2CO_3, MW (700 W)

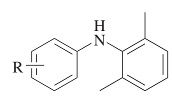


X	Time (min)		Refs.
Cl	7	(86)	72
Br	6.5	(91)	

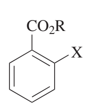




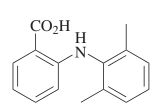
CuI (10 mol %), DMF, 110°



R	X	Additives	Time (h)		Refs.
H	I	PPAPM (20 mol %), K_3PO_4	30	(82)	48
H	I	DPP (20 mol %), K_3PO_4	36	(66)	108
H	Br	2-piperidinecarboxylic acid (20 mol %), K_2CO_3	36	(60)	67
3-O_2N	Br	PPAPM (20 mol %), K_3PO_4	36	(75)	48
3-O_2N	Br	DPP (20 mol %), K_3PO_4	36	(62)	108
4-MeO	Br	2-piperidinecarboxylic acid (20 mol %), K_2CO_3	36	(66)	67



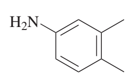
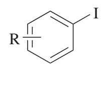
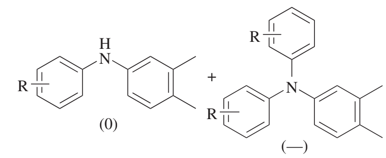
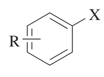
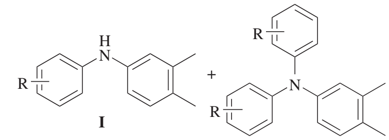
Catalyst(s) (x mol %)



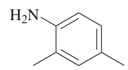
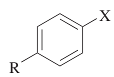
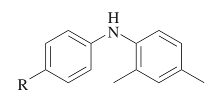
X	R	Catalyst(s)	x	Additive	Solvent	Temp (°)	Time (h)		Refs.
Cl	H	Cu, CuI	4, 9	K_2CO_3	$EtOCH_2CH_2OH$	130	24	(65)	109
Br	H	Cu, CuI	4, 9	K_2CO_3	$EtOCH_2CH_2OH$	130	24	(98)	70
Br	K	$Cu(OAc)_2$	6	4-ethylmorpholine	DMF	145	3	(24)	350

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

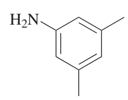
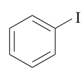
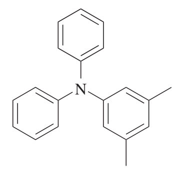
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

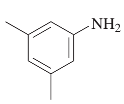
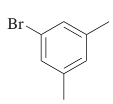
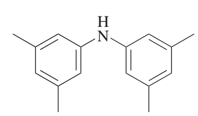
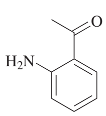
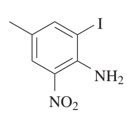
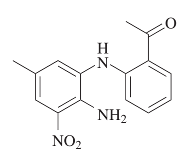
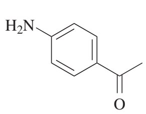
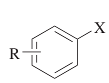
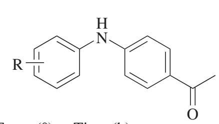
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	 R = H, 4-F, 3-MeO, 4-MeO, 4-Me, 3-CF_3, 4-*t*-Bu	$Cu(OAc)_2$ (4 mol %), phen (3 mol %), KOH, toluene, reflux, 18 h	 (0) + (—)	307
		Catalyst (*x* mol %)	 **I** + **II**	

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time	I	II	Refs.
2-HO_2C	Cl	$CuSO_4$	16	K_2CO_3	H_2O	MW, 100	7 min	(92)	(0)	240
3,4-Me_2	I	$CuCl_2$	4	phen (4 mol %), KOH	toluene	125	22 h	(0)	(70)	311

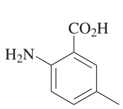
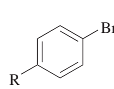
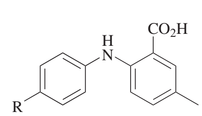
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %)		

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	$I^+Ph\ BF_4^-$	CuI	10	Na_2CO_3	CH_2Cl_2	rt	6	(70)	76
H	I	CuO nanoparticles (33 nm)	1.3	KOH, air	DMSO	110	5	(92)	224
Me	$I^+C_6H_4$-4-Me BF_4^-	CuI	10	Na_2CO_3	CH_2Cl_2	rt	6	(83)	76

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (20 mol %), Cs_2CO_3, $Si(OEt)_4$, 145°, 24 h	 (85)	335

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), **L16** (20 mol %), K_3PO_4, DMF, 110°, 24 h	 (75)	50
		Cu_2O (10 mol %), K_2CO_3, xylene, 145°, 12 h	 (85)	346
		CuI (10 mol %), K_3PO_4		

R	X	Additive	Solvent	Temp (°)	Time (h)		Refs.
H	Br	PPAPM (20 mol %)	DMF	110	36	(82)	48
H	Br	DPP (20 mol %)	DMF	110	36	(65)	108
4-Br	I	PPAPM (20 mol %)	DMF	110	36	(91)	48
4-Br	I	DPP (20 mol %)	DMF	110	36	(73)	108
3,5-Me_2	I	2-pyridinecarboxylic acid (20 mol %)	DMSO	90	24	(60)	50

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst(s) (*x* mol %)		

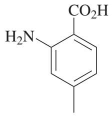
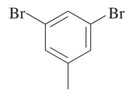
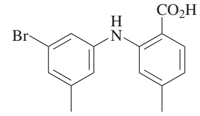
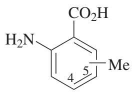
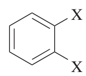
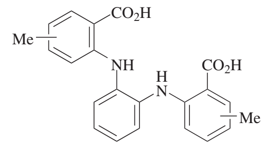
R	Catalyst(s)	*x*	Solvent	Temp (°)	Time (h)		Refs.
H	Cu	3	isoamyl alcohol	reflux	18	(83)	321
Me	Cu, CuI	1.5, 1.5	*n*-pentanol	150	5	(62)	351

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

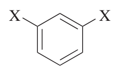
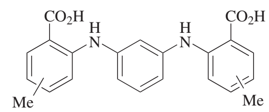
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

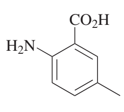
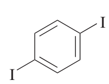
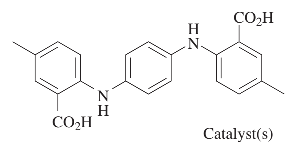
C_8

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu/CuI, K_2CO_3, *n*-pentanol, reflux	 (25)	352
		Catalyst(s) (*x* mol %), K_2CO_3, *n*-pentanol, reflux		

Isomer	X	Catalyst(s)	*x*	Time (h)	Yield	Refs.
4	Br	Cu, CuI	—	—	(10)	352
4	I	Cu, CuI	—	—	(30)	352
5	I	Cu	20	24	(40)	344
5	I	Cu, CuI	10, 8	24	(40)	344

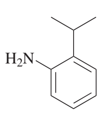
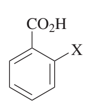
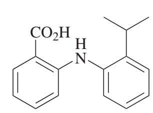
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst(s) (*x* mol %), K_2CO_3, *n*-pentanol, reflux		

Isomer	X	Catalyst(s)	*x*	Time (h)	Yield	Refs.
4	Br	Cu, CuI	—	—	(20)	352
4	I	Cu, CuI	—	—	(45)	352
5	I	Cu	20	24	(45)	344
5	I	Cu, CuI	10, 8	24	(65)	344

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst(s) (*x* mol %), K_2CO_3, *n*-pentanol, reflux, 24 h	 (60)	344

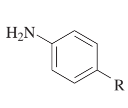
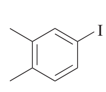
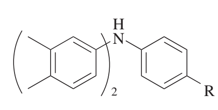
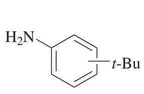
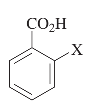
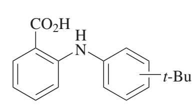
Catalyst(s)	*x*	Yield
Cu	20	(60)
Cu, CuI	10, 8	(45)

C_9

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalysts (*x* mol %), K_2CO_3		

X	Catalysts	*x*	Solvent	Temp (°)	Time	Yield	Refs.
Cl	Cu, CuI	4, 9	$EtOCH_2CH_2OH$	130	24 h	(73)	109
Cl	Cu, Cu_2O	3, 1.3	$MeOCH_2CH_2OH$	reflux	2 h	(77)	340
Br	Cu, CuI	9, 4	$EtOCH_2CH_2OH$	130	24 h	(78)	70

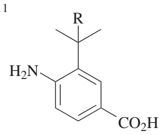
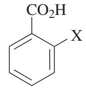
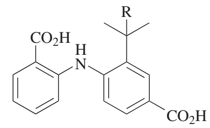
C_{10}

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Cu(OAc)_2$ (4 mol %), phen (3 mol %), KOH, toluene, reflux, 18 h	 R: *s*-Bu (—); *n*-Bu (—)	307
		Catalyst(s) (*x* mol %), 24 h		

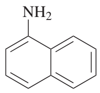
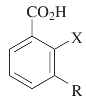
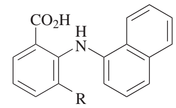
Isomer	X	Catalyst(s)	*x*	Additive	Solvent	Temp (°)	Yield	Refs.
2	Cl	Cu, CuI	4, 9	K_2CO_3	$EtOCH_2CH_2OH$	130	(86)	109
2	Br	Cu, CuI	4, 9	K_2CO_3	$EtOCH_2CH_2OH$	130	(53)	70
3	Cl	Cu, CuI	4, 9	K_2CO_3	$EtOCH_2CH_2OH$	130	(99)	109
4	Cl	Cu	2	none	DMF	reflux	(70)	353

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

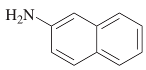
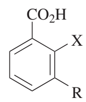
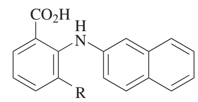
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-11} 		$Cu(pyr)_2Cl_2$ (11 mol %), K_2CO_3, $HO(CH_2)_2OH$, MW, 75°, 20 min		318

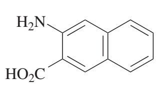
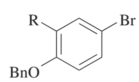
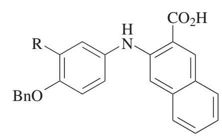
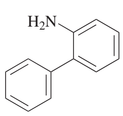
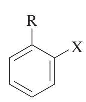
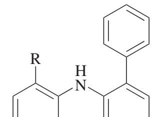
R	X	
H	Cl	(67)
H	Br	(79)
H	I	(90)
Me	Cl	(79)
Me	Br	(90)
Me	I	(94)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 		Catalyst(s) (*x* mol %)		

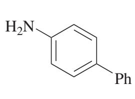
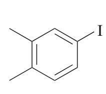
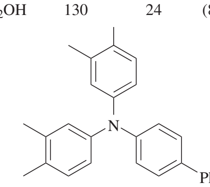
R	X	Catalyst(s)	*x*	Additive	Solvent	Temp (°)	Time		Refs.
H	Br	Cu, CuI	9, 4	K_2CO_3	$EtOCH_2CH_2OH$	130	24 h	(97)	70
H	Cl	Cu, CuI	4, 9	K_2CO_3	$EtOCH_2CH_2OH$	130	24 h	(96)	109
H	Cl	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HOCH_2CH_2OH$	MW, 75	20 min	(72)	318
H	Br	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HOCH_2CH_2OH$	MW, 75	20 min	(87)	318
H	I	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HOCH_2CH_2OH$	MW, 75	20 min	(98)	318
NO_2	Br	Cu	4	*N*-ethylmorpholine	2,3-butanediol	70	15 h	(35)	320

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst(s) (*x* mol %)		

R	X	Catalyst(s)	*x*	Additive	Solvent	Temp (°)	Time		Refs.
H	Br	Cu, CuI	9, 4	K_2CO_3	$EtOCH_2CH_2OH$	130	24 h	(90)	70
H	Cl	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HOCH_2CH_2OH$	130	24 h	(82)	71
H	Br	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HOCH_2CH_2OH$	130	24 h	(89)	71
H	I	$Cu(pyr)_2Cl_2$	10	K_2CO_3	$HOCH_2CH_2OH$	130	24 h	(91)	71
H	Cl	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HOCH_2CH_2OH$	MW, 75	20 min	(88)	318
H	Br	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HOCH_2CH_2OH$	MW, 75	20 min	(91)	318
H	I	$Cu(pyr)_2Cl_2$	11	K_2CO_3	$HOCH_2CH_2OH$	MW, 75	20 min	(91)	318
NO_2	Br	Cu	4	*N*-ethylmorpholine	2,3-butanediol	70	15 h	(62)	320

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		CuI (20 mol %), L-Pro (20 mol %), K_2CO_3, isoamyl alcohol, MW, 140°, 1 h	 R: O_2N (54); MeO (81)	337
C_{12} 		Catalyst(s) (*x* mol %)		

R	X	Catalyst(s)	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
H	$I^+Ph\ BF_4^-$	CuI	10	Na_2CO_3	CH_2Cl_2	rt	6	(72)	76
CO_2H	Cl	Cu, CuI	4, 9	K_2CO_3	$EtOCH_2CH_2OH$	130	24	(85)	109

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %), phen (*x* mol %), KOH, toluene		

Catalyst	*x*	Temp (°)	Time (h)		Refs.
$CuCl_2$	4	125	5	(83)	311
$Cu(OAc)_4$	3	reflux	18	(—)	307

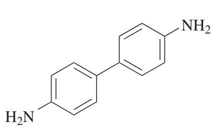
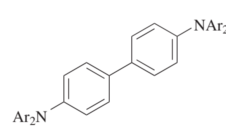
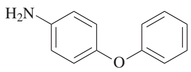
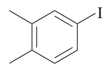
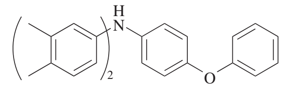
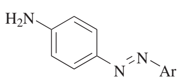
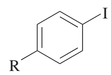
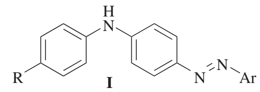
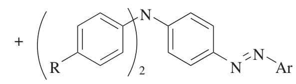
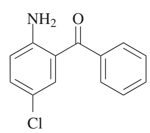
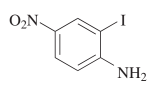
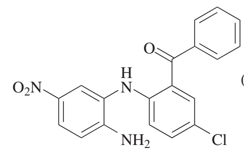
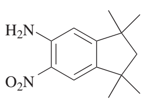
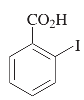
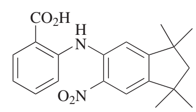
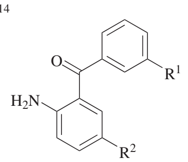
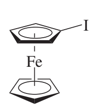
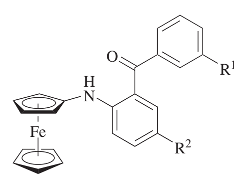
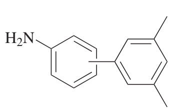
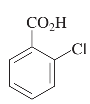
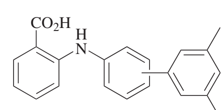
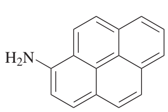
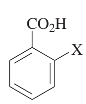
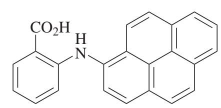
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	ArI	CuI (20 mol %), Cs_2CO_3, $Si(OEt)_4$, 145°, 38 h	 Ar: Ph (88); 4-$MeOC_6H_4$ (75); 2-$HO_2CC_6H_4$ (80)	335

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
		$Cu(OAc)_2$ (4 mol %), phen (3 mol %), KOH, toluene, reflux, 18 h	 (—)	307
 Ar = 4-$O_2NC_6H_4$		Cu, K_2CO_3, triglyme, 200–220°	 **I** +  **II**	354
C_{13}				
		Cu_2O (10 mol %), K_2CO_3, xylene, 145°, 20 h	 (75)	346
		Cu (70 mol %), $CaCO_3$	 (24)	355

R	I	II
i-PrC(O)NH	(19)	(40)
MeO	(0)	(40)

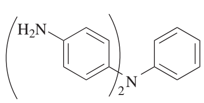
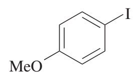
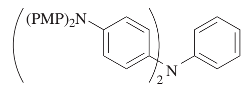
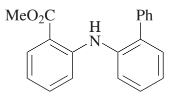
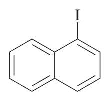
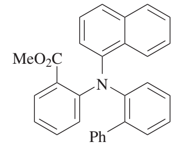
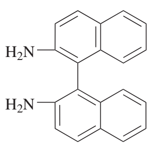
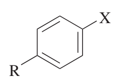
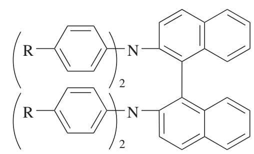
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{13–14}$				
		Cu (10 mol %), K_2CO_3, xylene, 140°, 6 h		329
C_{14}				
		Catalysts (*x* mol %), K_2CO_3		
C_{16}				
		Catalyst(s) (*x* mol %), K_2CO_3		

R^1	R^2	
H	Cl	(89)
H	Me	(84)
Me	Cl	(86)

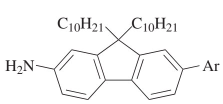
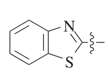
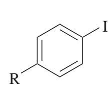
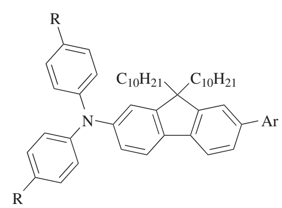
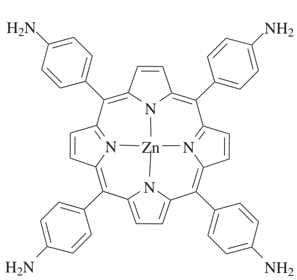
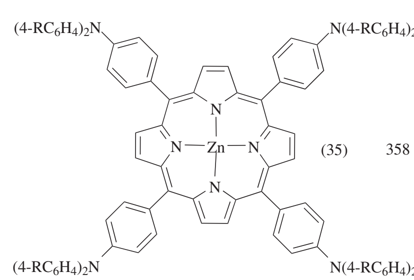
Isomer	Catalysts	*x*	Solvent	Temp (°)	Time (h)		Refs.
3	Cu, CuI	4, 9	$EtOCH_2CH_2OH$	130	24	(96)	109
4	Cu, Cu_2O	3, 1.3	$MeOCH_2CH_2OH$	reflux	2	(95)	356, 357

X	Catalyst(s)	*x*	Solvent	Temp (°)	Time		Refs.
Cl	Cu, CuI	4, 9	$EtOCH_2CH_2OH$	130	24 h	(73)	109
Br	Cu, CuI	9, 4	$EtOCH_2CH_2OH$	130	24 h	(55)	70
Cl	$Cu(pyr)_2Cl_2$	11	$HOCH_2CH_2OH$	MW, 75	20 min	(89)	318
Br	$Cu(pyr)_2Cl_2$	11	$HOCH_2CH_2OH$	MW, 75	20 min	(93)	318
I	$Cu(pyr)_2Cl_2$	11	$HOCH_2CH_2OH$	MW, 75	20 min	(96)	318

TABLE 5A. *N*-ARYLATION OF PRIMARY ARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*					
C_{18}					
		Cu (10 eq), 18-c-6 (3 eq), K_2CO_3, 1,2-$Cl_2C_6H_4$, reflux, 48 h		(35)	358
C_{19}					
		Cu (50 mol %), K_2CO_3, $PhNO_2$, 180°, 2.5 h		(18)	349
C_{24}					
		Catalyst (*x* mol %)			

Isomer	er	R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		er	Refs.
(*R*)	99:1	H	Br	CuBr	10	*rac*-binol (20 mol %), K_3PO_4	DMF	120	36	(83)	56.5:45.4	286
(*R*,*S*)	—	MeO	I	CuI	20	Cs_2CO_3	$Si(OEt)_4$	145	120	(87)	—	335

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{40}					
 Ar = 	 R = H, MeO	Cu-bronze, 18-c-6, K_2CO_3, 1,2-$Cl_2C_6H_4$, 180°, 43 h		(82)	359
C_{44}					
	4-RC_6H_4I R = MeO, $(PMP)_2N$	Cu (10 eq), 18-c-6 (3 eq), K_2CO_3, 1,2-$Cl_2C_6H_4$, reflux, 48 h		(35)	358

[a] The ratio of PhX to $PhNH_2$ was 2:1.

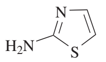
[b] The ratio of PhX to $PhNH_2$ was 29:1.

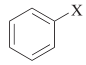
TABLE 5B. *N*-ARYLATION OF PRIMARY HETEROARYL AMINES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

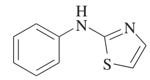
Please refer to the charts preceding the tables for structures indicated by the bold numbers.

C_3





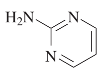
CuI (*x* amount), K_2CO_3, dioxane, 100°, 22 h

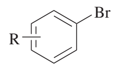


55

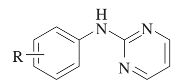
X	*x*	Additive(s)	
Br	50 mol %	DMEDA (50 mol %), KI	(62)
I	1 eq	DMEDA (1 eq)	(78)

C_4



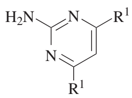


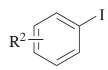
CuI (50 mol %), DMEDA (50 mol %), KI, K_2CO_3, dioxane, 100°



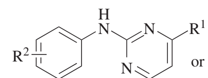
R	Time (h)	
H	22	(78)
2-MeO	24	(70)

55

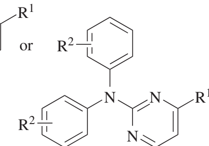




Catalyst (x mol %)

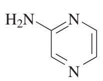


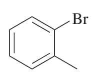
I or



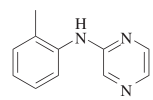
II

R^1	R^2	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
H	H	Cu/AB	5	KO*t*-Bu	toluene	180	18	(71)	(0)	226
MeO	4-MeO	CuI	20	Cs_2CO_3	$Si(OEt)_4$	145	40	(0)	(61)	335





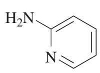
CuI (35 mol %), DMEDA (35 mol %), K_2CO_3, KI, dioxane, 100°, 22 h

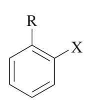


(74)

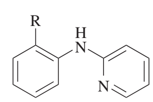
55

C_5

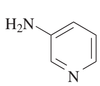


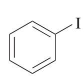


Catalyst (*x* mol %)

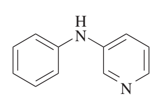


R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
H	Br	CuI	50	DMEDA (50 mol %), K_2CO_3	dioxane	100	24 h	(83)	55
H	I	CuI	25	DMEDA (25 mol %), K_2CO_3	dioxane	100	20 h	(83)	55
H	I	Cu/AB	5	KO*t*-Bu	toluene	180	18 h	(56)	226
CO_2H	Cl	Cu powder	—	K_2CO_3	DMF	)))	20 min	(71)	360



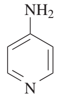


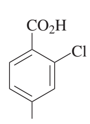
CuO/AB (5 mol %), KO*t*-Bu, toluene, 180°, 18 h



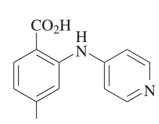
(89)

226





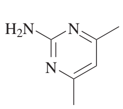
Cu (1 mol %), K_2CO_3, *n*-hexanol, reflux, 2 h

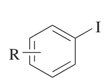


(75)

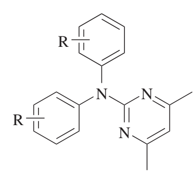
361

C_6





CuI (20 mol %), Cs_2CO_3, $Si(OEt)_4$, 145°, 42 h



R	Time (h)	
H	42	(70)
4-MeO	40	(81)
2-EtO_2C	18	(89)

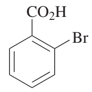
335

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

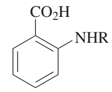
Please refer to the charts preceding the tables for structures indicated by the bold numbers.

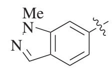
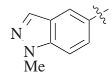
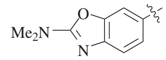
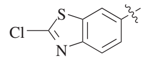
C_7

RNH_2

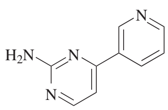


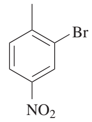
Cu (x mol %), K_2CO_3, 1-pentanol,



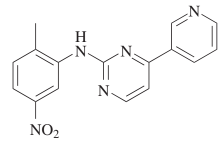
R	x	Additive	Time (h)		Refs.
	1.5	none	2.5	(68)	333
	1.5	none	2.5	(48)	333
	13	none	3	(90)	362
	1.5	KI	2	(76)	333

C_9

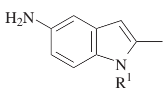


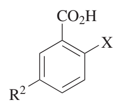


CuI (50 mol %), DMEDA (50 mol %), K_2CO_3, KI, dioxane, 100°, 24 h

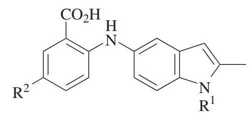


(82) 55, 170





CuI (10 mol %), K_2CO_3, DMSO, 80°



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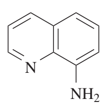
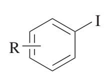
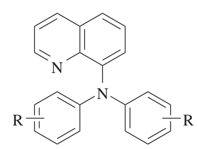
R^1	R^2	X	Time (min)	
H	H	Br	120	(80)
H	H	I	30	(86)
PhO_2S	H	Cl	120	(65)
PhO_2S	H	Br	30	(68)
PhO_2S	H	I	15	(71)
Me	H	Br	120	(82)
Me	H	I	30	(91)
H	MeO	Br	30	(81)
PhO_2S	Cl	I	30	(75)
PhO_2S	Br	I	15	(77)
Me	Cl	I	30	(87)
Me	Br	I	30	(79)
Me	O_2N	I	30	(84)





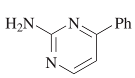
CuI (20 mol %), Cs_2CO_3, $Si(OEt)_4$, 145°, 42 h

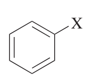


R	Time (h)	
H	38	(94)
4-MeO	30	(90)
$2\text{-}EtO_2C$	18	(90)

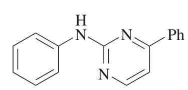
335

C_{10}



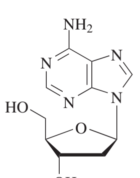


CuI (x amount), DMEDA (x amount), K_2CO_3, KI, dioxane, 100°



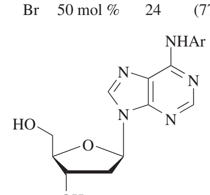
55

X	x	Time (h)	
Cl	1 eq	48	(<5)
Br	50 mol %	24	(77)



ArX

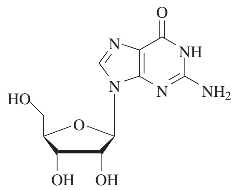
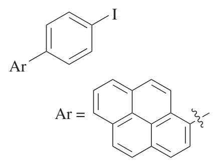
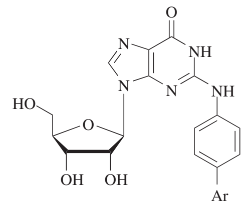
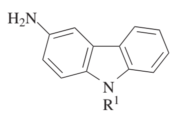
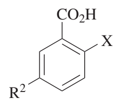
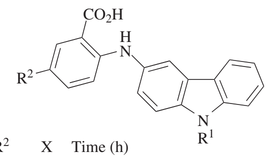
CuI (1 eq), DMEDA (1 eq), K_3PO_4, DMSO, 110°



57

Ar	X	Additive	Time (h)	
$4\text{-}ClC_6H_4$	I	none	1.5	(70)
$4\text{-}BrC_6H_4$	I	none	1.5	(—)
$4\text{-}O_2NC_6H_4$	I	none	1.5	(73)
$2\text{-}HOC_6H_4$	I	none	2.5	(—)
$4\text{-}MeOC_6H_4$	Br	NaI	3.5	(84)
$4\text{-}MeOC_6H_4$	I	none	2.5	(84)
$4\text{-}MeC_6H_4$	Cl	NaI	24	(0)
$4\text{-}MeC_6H_4$	I	none	2.5	(78)
$4\text{-}MeC_6H_4$	I	none	48	(65)
$2,3\text{-}Me_2C_6H_3$	I	none	2.5	(80)
$2,6\text{-}Me_2C_6H_3$	Br	none	6	(75)
$3,4\text{-}Me_2C_6H_3$	Br	none	6	(70)
9-phenanthryl	Br	NaI	3.5	(80)
1-pyrenyl	I	none	2.5	(88)

TABLE 5B. *N*-ARYLATION OF PRIMARY HETEROARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the bold numbers.				
C_{10}				
		CuI (15 mol %), Cs_2CO_3, DMSO, 140°, 24 h	 (59)	365
C_{12}				
		CuI (10 mol %), K_2CO_3, DMSO, 80°		364

R^1	R^2	X	Time (h)	
H	H	I	1	(73)
Et	H	Br	3	(64)
Et	H	I	1	(73)

R^1	R^2	X	Time (h)	
Et	Cl	I	1	(72)
Et	Br	I	1	(70)
H	O_2N	I	0.5	(74)

TABLE 5C. *N*-HETEROARYLATION OF PRIMARY ARYL AND HETEROARYL AMINES

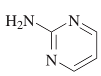
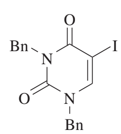
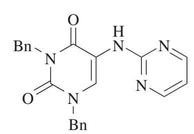
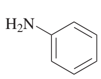
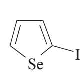
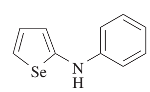
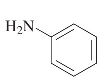
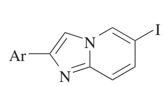
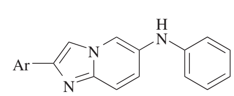
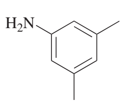
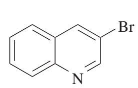
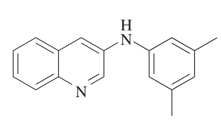
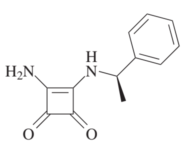
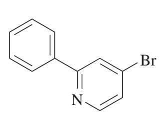
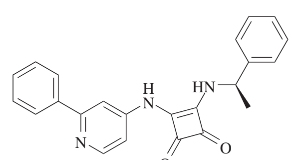
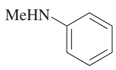
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 80°, 30 h	 (77)	47
C_6 		CuI (10 mol %), EDA (20 mol %), K_3PO_4, reflux, 24 h	 (0)	87
	 Ar = 4-FC_6H_4	CuI (5 mol %), $HO(CH_2)_2OH$, K_3PO_4, *i*-PrOH, 85°, 20 h	 (30)	126
C_8				
		CuI (10 mol %), K_3PO_4, DMSO, 2-pyridine-carboxylic acid (20 mol %), 100°, 24 h	 (51)	50
C_{12}				
		CuI (1 eq), DMEDA (1.5 eq), K_2HPO_3, DMF, 110°, 6.5 h	 (—)	366

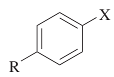
TABLE 6A. *N*-ARYLATION OF SECONDARY ARYL, ALKYL, AND DIARYL AMINES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

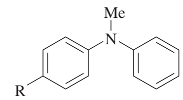
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

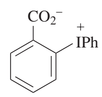




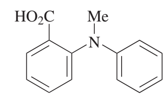
CuI (*x* mol %)



R	X	*x*	Additives	Solvent(s)	Temp (°)	Time (h)		Refs.
H	Cl	2	**L1** (2 mol %), KO*t*-Bu	—	100	12	(85)	288
H	Br	2	**L1** (2 mol %), KO*t*-Bu	—	100	12	(85)	288
Br	I	10	PPAPM (20 mol %), K_3PO_4	DMF	110	36	(60)	48
Br	I	10	DPP, K_3PO_4	DMF/H_2O (98:2)	110	36	(60)	108
MeO	Br	10	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	36	(57)	67
Me	I	5	**L41** (10 mol %), NaO*t*-Bu	toluene	110	40	(71)	338

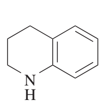


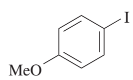
$Cu(OAc)_2$ (3 mol %), *i*-PrOH, reflux, 24 h



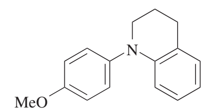
(44) 312

C_9





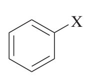
$Cu(THMD)_2$ (20 mol %), KO*t*-Bu, toluene, 120°, 12 h



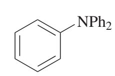
(83) 308

C_{12}

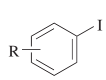
Ph_2NH



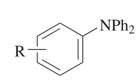
Catalyst (*x* amount)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
Br	Cu	4.7 eq	none	—	210	12 h	(86)	303
I	Cu	4.7 eq	none	—	210	12 h	(86)	303
I	Cu (active)	5 eq	none	none	MW (100 W)	6 min	(83)	280
I	Cu (active)	5 eq	none	H_2O	MW (100 W)	6 min	(85)	280
I	Cu	8 eq	KOH	*n*-$C_{16}H_{34}$	160	8 h	(88)	20
I	Cu	8 mol %	K_2CO_3	$PhNO_2$	reflux	24 h	(85)	367
I	CuI	5 mol %	mes_2DAB (6 mol %), KO*t*-Bu	toluene	120	20 h	(94)	306
Cl	Cu_2O	5 mol %	NaO*t*-Bu	NMP	110	24 h	(81)	266
Br	Cu_2O	5 mol %	NaO*t*-Bu	NMP	80	24 h	(83)	266
Cl	Cu(neocup)(PPh_3)Br	10 mol %	KO*t*-Bu	toluene	110	36 h	(49)	368
Br	Cu(neocup)(PPh_3)Br	10 mol %	KO*t*-Bu	toluene	110	36 h	(73)	368
I	Cu(neocup)(PPh_3)Br	10 mol %	KO*t*-Bu	toluene	110	6 h	(78)	368
I	$Cu(THMD)_2$	20 mol %	KO*t*-Bu	toluene	120	12 h	(95)	308
I	$Cu(PPh_3)_3Br$	20 mol %	Cs_2CO_3	toluene	120	24 h	(70)	339



Catalyst (*x* amount)



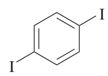
X	R	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2-Cl	H	Cu	8 eq	KOH	$C_{16}H_{34}$	160	27	(55)	20
2-I	H	Cu	8 eq	KOH	$C_{16}H_{34}$	160	27	(18)	20
3-Cl	H	Cu	2 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	21	(87)	54
3-Cl	H	CuI	5 mol %	KOH	$C_{16}H_{34}$	160	24	(82)	20
4-Cl	H	Cu	2 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	21	(78)	54
4-Br	H	CuI	1 mol %	CDA (10 mol %), NaO*t*-Bu	dioxane	reflux	24	(75)	172
4-Br	H	$Cu(PPh_3)_3Br$	20 mol %	Cs_2CO_3	toluene	120	24	(54)	339
4-I	H	Cu	8 eq	KOH	$C_{16}H_{34}$	160	16	(41)	20
4-I	H	Cu	1 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	200	48	(35)	369
4-I	H	CuI	2.5 mol %	BuLi	xylenes	reflux	2	(48)	370

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

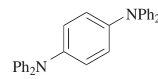
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{12}

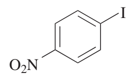
Ph_2NH



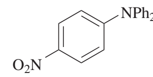
Catalyst (*x* amount)



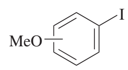
Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
Cu	8 eq	KOH	n-$C_{16}H_{34}$	160	24	(62)	20
CuI	2.5 mol %	BuLi	xylenes	reflux	2	(28)	370



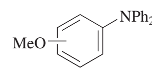
Catalyst (20 mol %), KO*t*-Bu, toluene, 120°



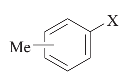
Catalyst	Time (h)		Refs.
$Cu(THMD)_2$	12	(90)	308
$Cu(PPh_3)_3Br$	24	(62)	339



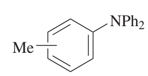
Catalyst (*x* amount)



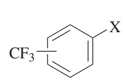
Isomer	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
3	Cu	2 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	21	(78)	54
4	Cu	1 eq	K_2CO_3	triglyme	200	26.5	(84)	371
4	Cu	2 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	19	(90)	54
4	Cu	8 eq	KOH	$C_{16}H_{34}$	160	5	(79)	20
4	CuI	5 mol %	mes_2DAB, KO*t*-Bu	toluene	120	20	(72)	306
4	CuI	5 mol %	9-AJ (10 mol %), NaO*t*-Bu	toluene	110	40	(96)	338
4	$Cu(THMD)_2$	20 mol %	KO*t*-Bu	toluene	120	12	(90)	308



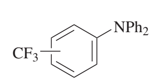
Catalyst (*x* amount)



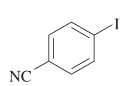
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
2	I	Cu	2 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	18 h	(92)	54
2	I	Cu	8 eq	KOH	$C_{16}H_{34}$	160	27 h	(81)	20
2	I	CuI	5 mol %	**L41** (10 mol %), NaO*t*-Bu	toluene	110	40 h	(85)	338
2	I	$Cu(PPh_3)_3Br$	20 mol %	Cs_2CO_3	toluene	120	24 h	(52)	339
2	I	$Cu(neocup)(PPh_3)_3Br$	10 mol %	KO*t*-Bu	toluene	110	36 h	(70)	368
3	I	Cu	2 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	18 h	(93)	54
3	I	Cu	8 eq	KOH	n-$C_{16}H_{34}$	160	24 h	(82)	20
4	Br	Cu (active)	5 eq	none	H_2O	MW (100 W)	6 min	(81)	280
4	I	Cu	2 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	16 h	(92)	54
4	I	CuI	5 mol %	**L41** (10 mol %), NaO*t*-Bu	toluene	110	40 h	(96)	338
4	I	CuI	5 mol %	mes_2DAB (6 mol %), KO*t*-Bu	toluene	120	20 h	(79)	306
4	I	$Cu(PPh_3)_3Br$	20 mol %	Cs_2CO_3	toluene	120	24 h	(52)	339
4	I	$Cu(THMD)_2$	20 mol %	KO*t*-Bu	toluene	120	12 h	(90)	308
4	I	$Cu(neocup)(PPh_3)Br$	10 mol %	KO*t*-Bu	toluene	110	36 h	(70)	339



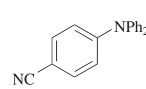
Cu (8 eq), KOH, n-$C_{16}H_{34}$, 160°



Isomer	Time (h)		Refs.
3	8	(64)	20
4	24	(56)	



CuI (5 mol %), **L41** (10 mol %), NaO*t*-Bu, toluene, 110°, 40 h



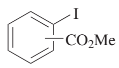
(96) 338

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

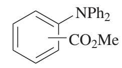
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{12}

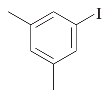
Ph_2NH



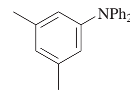
Catalyst (x mol %)



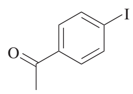
Isomer	Catalyst	x	Additive	Solvent	Temp (°)	Time (h)		Refs.
2	Cu	15	K_2CO_3	—	180	33	(67)	348
2	$Cu(PPh_3)_3Br$	20	Cs_2CO_3	toluene	120	24	(69)	339
4	$Cu(PPh_3)_3Br$	20	KO*t*-Bu	toluene	120	24	(62)	339



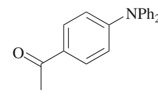
Catalyst (x eq)



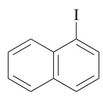
Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
$CuCl_2$	4	phen (4 mol %), KOH	—	125	6	(85)	311
CuI	1	CDA (10 mol %)	dioxane	110	23	(77)	115



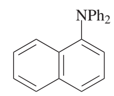
$Cu(PPh_3)_3Br$ (20 mol %), Cs_2CO_3, toluene, 120°, 24 h



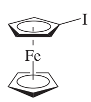
(68) 339



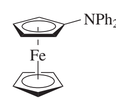
CuI (5 mol %), KOH, *n*-$C_{16}H_{34}$, 160°, 24 h



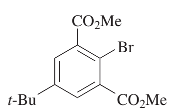
(59) 20



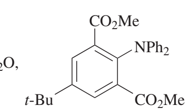
CuI (1 eq), K_2CO_3, DMSO, 90°, 18 h



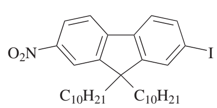
(43) 372



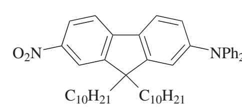
Cu (15 mol %), K_2CO_3, Ph_2O, 190°, 48 h



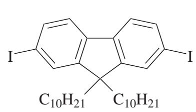
(85) 341



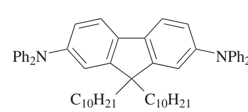
Cu-bronze, 18-c-6, K_2CO_3, 1,2-$Cl_2C_6H_4$, 180°, 43 h



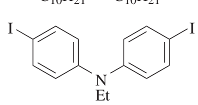
(80) 359



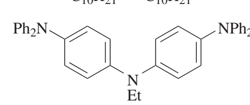
Cu-bronze, 18-c-6, K_2CO_3, 1,2-$Cl_2C_6H_4$, 180°, 43 h



(80) 359

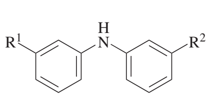


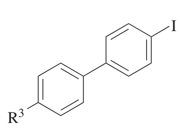
Cu (12 eq), 18-c-6, K_2CO_3, 1,2-$Cl_2C_6H_4$, reflux, 24 h



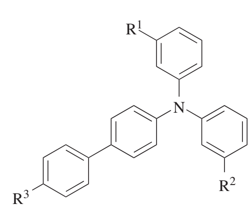
(69) 373

$C_{12–14}$





Catalyst (x amount)



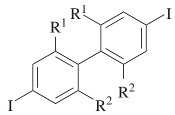
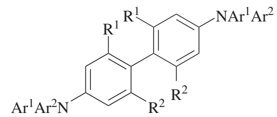
R^1	R^2	R^3	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	H	I	Cu	1 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	200	48	(54)	369
H	Me	I	Cu	1 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	200	48	(46)	369
H	Me	Br	$CuCl_2$	4 mol %	phen (4 mol %), KOH	—	125	5	(80)	311
Me	Me	I	Cu	—	18-c-6	xylene	160	40	(33)	342

TABLE 6A. *N*-ARYLATION OF SECONDARY ARYL, ALKYL, AND DIARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

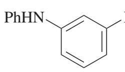
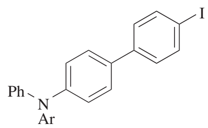
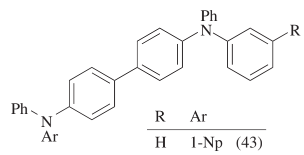
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{12-14}

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
Ar^1Ar^2NH		Catalyst (*x* amount)		

Ar^1	Ar	R^1	R^2	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Ph	Ph	H	H	CuI	5 mol %	**L41** (10 mol %), NaO*t*-Bu	toluene	110	40	(82)	338
Ph	Ph	H	H	CuI	5 mol %	mes_2DAB (6 mol %), KO*t*-Bu	toluene	120	20	(85)	306
Ph	Ph	H	H	$Cu(THMD)_2$	20 mol %	KO*t*-Bu	toluene	120	12	(81)	308
Ph	Ph	H	Me	Cu	1 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	15	(35)	374
Ph	Ph	Me	Me	Cu	1 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	15	(35)	374
Ph	2-$MeOC_6H_4$	H	H	$CuCl_2$	4 mol %	phen (4 mol %), KOH	—	130	5	(75)	311
Ph	2-MeC_6H_4	H	H	$CuCl_2$	4 mol %	phen (4 mol %), KOH	—	125	5	(85)	311
4-MeC_6H_4	4-MeC_6H_4	H	H	Cu	1 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	15	(47)	374
4-MeC_6H_4	4-MeC_6H_4	H	H	CuI	5 mol %	mes_2DAB (6 mol %), KO*t*-Bu	toluene	120	20	(38)	306
4-MeC_6H_4	4-MeC_6H_4	H	Me	Cu	1 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	15	(82)	374
4-MeC_6H_4	4-MeC_6H_4	Me	Me	Cu	1 eq	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	15	(35)	374

C_{12-13}

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (1 eq), 18-c-6, K_2CO_3, 1,2-$Cl_2C_6H_4$, 200°, 48 h		369

R	Ar	
H	1-Np	(43)
Me	1-Np	(43)
H	2-Np	(38)
Me	2-Np	(44)

C_{12}

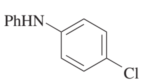
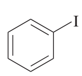
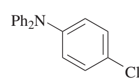
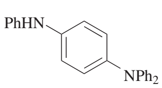
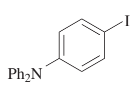
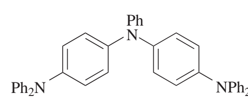
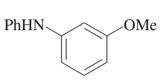
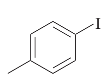
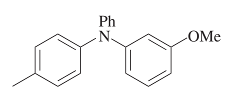
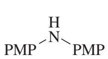
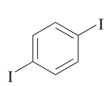
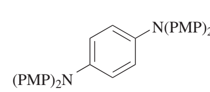
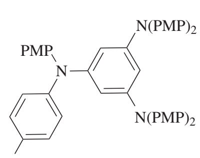
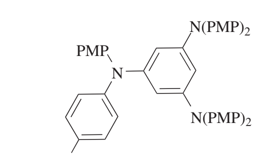
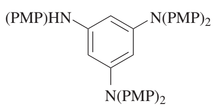
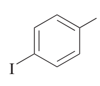
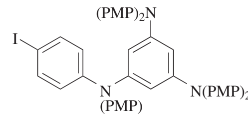
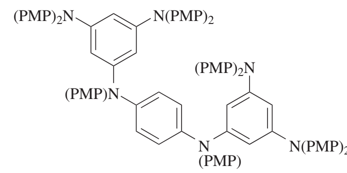
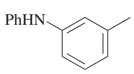
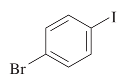
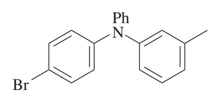
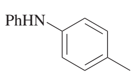
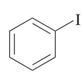
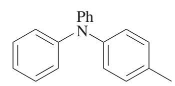
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (8 eq), KOH, *n*-$C_{16}H_{34}$, 160°, 27 h	 (88)	20
		CuI (2.5 mol %), BuLi, xylenes, reflux, 2 h	 (4)	370
		$CuCl_2$ (4 mol %), phen (4 mol %), KOH, 125°, 6 h	 (61)	311
		Cu (1 eq), K_2CO_3, Ph_2O, 190°, 48 h	 (75)	330
		Cu (1 eq), K_2CO_3, Ph_2O, 190°, 24 h	 (64)	330

TABLE 6A. *N*-ARYLATION OF SECONDARY ARYL, ALKYL, AND DIARYL AMINES (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
 **I**	 **II**	Cu (1 eq), K_2CO_3, Ph_2O, 190°, 48 h	 **III** or  **IV**	330

I/II	Time (h)	III	IV
1:4.5	24	(78)	(0)
2:1	48	(0)	(71)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		Cu (1 eq), 18-c-6, K_2CO_3, *o*-$Cl_2C_6H_4$, 200°, 48 h	 (30)	369
		Catalyst (*x* amount)		

Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cu	—	K_2CO_3, 18-c-6	1,2-$Cl_2C_6H_4$	—	—	(29)	375
Cu	8 eq	KOH	*n*-$C_{16}H_{34}$	160	24	(88)	306
$[Cu(phen)_2]Cl$	8 mol %	K_2CO_3, 18-c-6	1,2-$Cl_2C_6H_4$	reflux	15	(75)	376

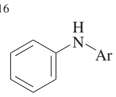
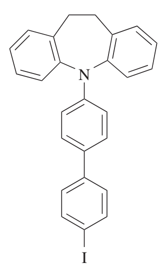
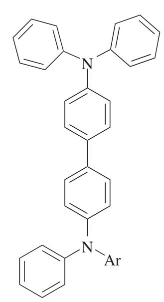
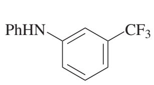
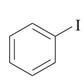
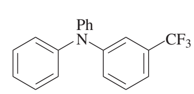
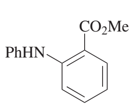
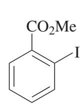
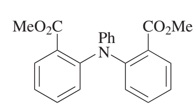
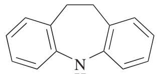
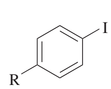
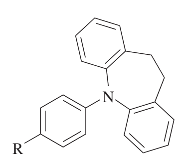
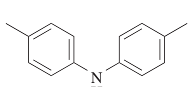
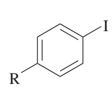
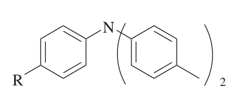
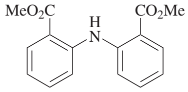
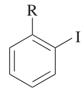
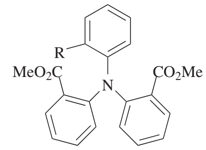
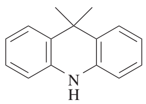
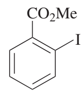
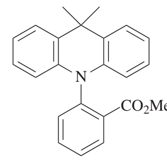
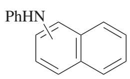
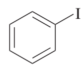
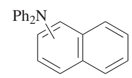
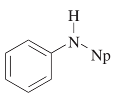
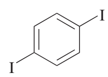
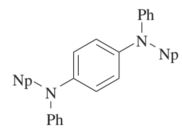
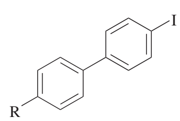
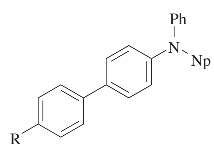
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{13–16}$				
		Cu (1 eq), 18-c-6, K_2CO_3, 1,2-$Cl_2C_6H_4$, 200°, 48 h	 Ar: 3-MeC_6H_4 (44); 1-Np (26)	369
C_{13}				
		Cu (8 eq), KOH, *n*-$C_{16}H_{34}$, 160°, 27 h	 (88)	20
		$Cu(PPh_3)_3Br$ (20 mol %), Cs_2CO_3, 1,2-$Cl_2C_6H_4$, 175°, 32 h	 (40)	339
C_{14}				
		Cu (1 eq), 18-c-6, K_2CO_3, 1,2-$Cl_2C_6H_4$, 200°, 48 h	 R: 4-IC_6H_4 (40); NPh(1-Np) (32)	369
		CuI (5 mol %), mes_2DAB (6 mol %), KO*t*-Bu, toluene, 120°, 20 h	 R: MeO (63); Me (87)	306

TABLE 6A. *N*-ARYLATION OF SECONDARY ARYL, ALKYL, AND DIARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{14}				
		Cu (15 mol %), K_2CO_3, 180°, 33 h	 R: H (46); CO_2Me (26)	348
C_{15}				
		Cu (25 mol %), $CaCO_3$	 (52)	355
C_{16}				
		CuI (*x* mol %)		

Isomer	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
1	4	NaH	n-$C_{16}H_{34}$	160	24	(23)	20
1	5	mes_2DAB (6 mol %), KO*t*-Bu	toluene	120	20	(38)	306
2	5	mes_2DAB (6 mol %), KO*t*-Bu	toluene	120	20	(88)	306

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (1 eq), 18-c-6, K_2CO_3, 1,2-$Cl_2C_6H_4$, 200°, 48 h	 Isomer: 1-Np (26); 2-Np (52)	369

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* eq), K_2CO_3		

Isomer	R	Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
1-Np	I	Cu	1	18-c-6	1,2-$Cl_2C_6H_4$	200	48	(42)	369
1-Np	I	$CuSO_4$	—	none	—	—	—	(—)	377
2-Np	I	Cu	1	18-c-6	1,2-$Cl_2C_6H_4$	200	48	(50)	369
2-Np	NPh_2	Cu	1	18-c-6	1,2-$Cl_2C_6H_4$	200	48	(31)	369

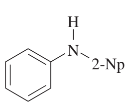
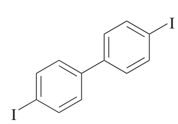
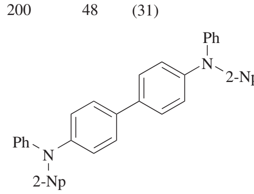
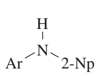
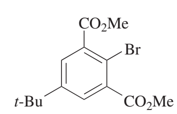
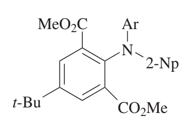
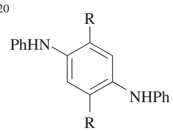
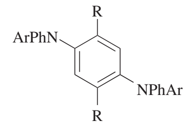
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), mes_2DAB (6 mol %), KO*t*-Bu, toluene, 120°, 20 h	 (87)	306
C_{16-20}				
		Cu (15 mol %), K_2CO_3, Ph_2O, 190°, 48 h	 Ar: Ph (83); 2-Np (83)	341

TABLE 6A. *N*-ARYLATION OF SECONDARY ARYL, ALKYL, AND DIARYL AMINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

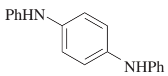
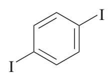
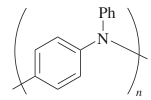
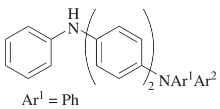
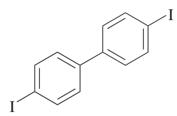
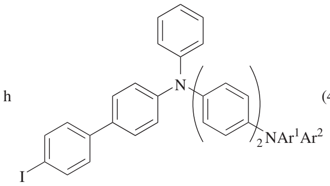
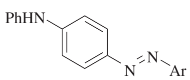
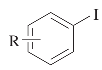
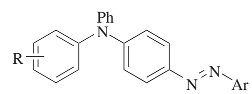
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{18-20}

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	ArI	Catalyst (*x* mol %)		

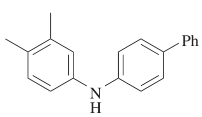
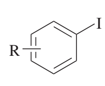
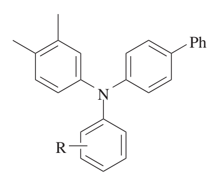
R	Ar	Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
H	Ph	CuI	2.5	BuLi	xylenes	reflux	2	(24)	370
H	4-$Ph_2NC_6H_4$	CuI	2.5	BuLi	xylenes	reflux	4	(4)	370
CO_2H	Ph	Cu	25	none	1-pentanol	195	3	(42)	378

C_{18}

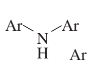
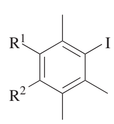
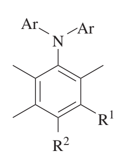
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (2.5 mol %), BuLi, dihexyl ether, reflux, 6 h	 (48)	370
 Ar^1 = Ph, Ar^2 = 3-MeC_6H_4		Cu, 18-c-6, xylene, 160°, 40 h	 (47)	342
 Ar = 4-$O_2NC_6H_4$		Cu, K_2CO_3, triglyme, 200–220°		354

R	
H	(81)
4-I	(74)
4-H_2N	(61)
4-*i*-PrCONH	(56)
3-MeO	(55)
4-MeO	(66)
4-*t*-$BuPh_2SiO(CH_2)_2O$	(50)

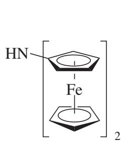
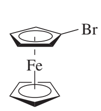
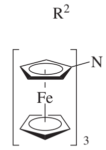
C_{20}

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$CuCl_2$ (4 mol %), phen (4 mol %), KOH, 125°, 5 h		311

R	
H	(80)
3-MeO	(80)
3,4,5-Me_3	(80)
4-Ph	(78)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
 Ar = 4-*t*-BuC_6H_4		Cu, K_2CO_3, 18-c-6, 1,2-$Cl_2C_6H_4$, reflux		379

R^1	R^2	
$(Mes)_2P$	Me	(66)
Me	$(Mes)_2P$	(46)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuBr (2.5 eq), $NaNH_2$, toluene, reflux, 20 h	 (97)	380

C_{22}

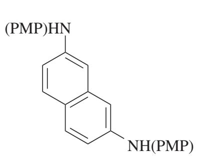
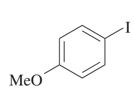
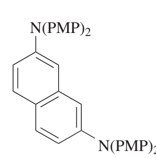
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (2 eq), K_2CO_3, Ph_2O, 190°, 36 h	 (52)	175

TABLE 6A. *N*-ARYLATION OF SECONDARY ARYL, ALKYL, AND DIARYL AMINES (*Continued*)

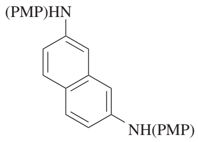
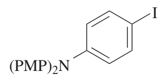
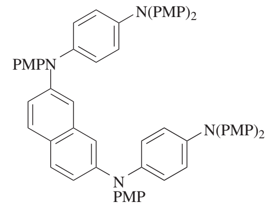
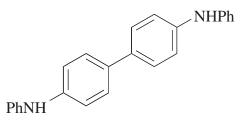
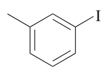
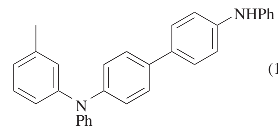
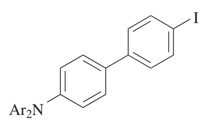
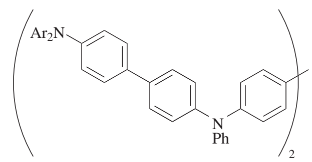
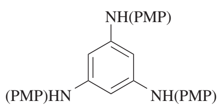
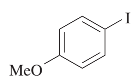
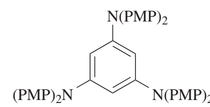
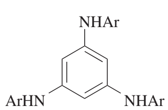
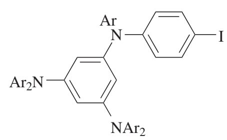
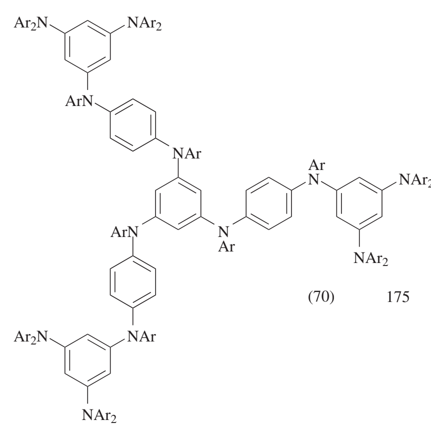
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{22}				
		Cu (2 eq), K_2CO_3, Ph_2O, 190°, 36 h	 (56)	175
C_{24}				
		Cu, 18-c-6, xylene, 160°, 40 h	 (16)	342
	 Ar = 3-MeC_6H_4	Cu, 18-c-6, xylene, 160°, 40 h	 (75)	342
		Cu (2 eq), K_2CO_3, Ph_2O, 190°, 36 h	 (28)	175
C_{24}				
 Ar = PMP		Cu (1 eq), K_2CO_3, Ph_2O, 190°, 24 h	 (70)	175

TABLE 6B. *N*-ARYLATION OF SECONDARY HETEROARYL AMINES

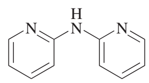
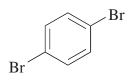
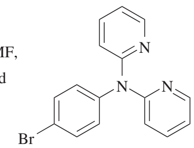
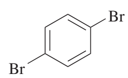
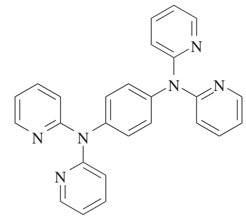
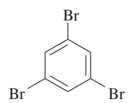
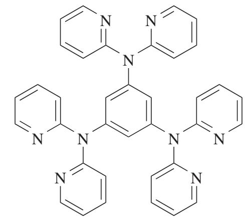
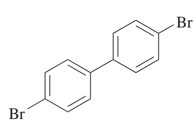
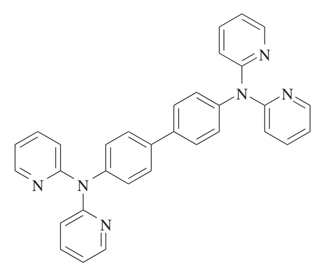
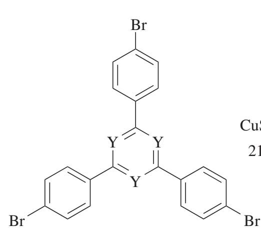
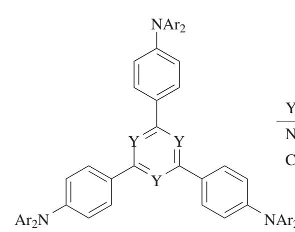
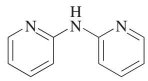
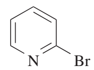
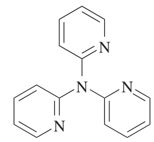
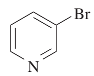
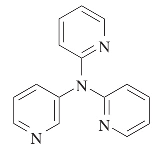
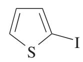
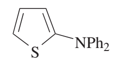
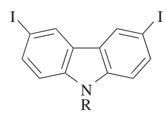
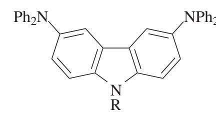
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		CuI (10 mol %), K_2CO_3, DMF, piperidine-2-carboxylic acid (20 mol %), 110°, 36 h	 (57)	67
		$CuSO_4$ (2 mol %), KOH, 180°, 5 h	 (29)	174
		$CuSO_4$ (5 mol %), K_2CO_3, 210°, 8 h	 (45)	381
		$CuSO_4$ (2 mol %), KOH, 180°, 5 h	 (33)	174
		$CuSO_4$ (10 mol %), K_2CO_3, 210°, 8 h	 Ar = 2-pyridyl; Y: N (60); CH (85)	N: 381; CH: 382, 381

TABLE 6C. *N*-HETEROARYLATION OF SECONDARY ARYL AND HETEROARYL AMINES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		$CuSO_4$ (2 mol %), KOH, 180°, 6 h	 (48)	383
		$CuSO_4$ (2 mol %), KOH, 180°, 6 h	 (48)	383
C_{12}				
Ph_2NH		CuI (1 eq), NaH, DMPU	 (40)	384
		See table.		

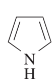
R	Catalyst	Additives	Solvent	Temp (°)	Time (h)		Refs.
Et	Cu (12 eq)	18-c-6, K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	36	(74)	373
4-MeC_6H_4	CuI (10 mol %)	18-c-6 (1 mol %), K_2CO_3	DMPU	170	20	(70)	385

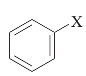
TABLE 7A. *N*-ARYLATION OF PYRROLES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

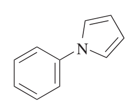
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4





Catalyst (*x* amount)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	Cu	20 mol %	Cs_2CO_3	*n*-PrCN	reflux	20	(81)	129
I	Cu	20 mol %	Cs_2CO_3	*n*-PrCN	reflux	7	(95)	129
I	CuCl	10 mol %	**L9** (10 mol %), TMAH	DMSO	80	24	(90)	281
I	CuCl	5 mol %	TBAH (40% aq)	H_2O	80	24	(86)	282
Br	CuBr	10 mol %	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12	(77)	284
I	CuBr	20 mol %	binol (20 mol %), K_3PO_4	DMF	rt	8	(52)	62
Br	CuI	20 mol %	Cs_2CO_3	DMF	120	40	(66)	386
I	CuI	10 mol %	K_3PO_4	DMF	110	24	(88)	387
Br	CuI	20 mol %	L-Pro (20 mol %), K_3PO_4	DMF	140	48	(67)	388
I	CuI	5 mol %	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(95)	388
Br	CuI	10 mol %	L-His (20 mol %), K_2CO_3	DMSO	100	48	(56)	389
Br	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	9	(81)	390
I	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	8	(85)	390
I	CuI	5 mol %	TBAB (5 mol %), NaOH	toluene	reflux	22	(95)	391
Br	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	24	(76)	67
I	CuI	5 mol %	oxazolidin-2-one (10 mol %), NaOMe	DMSO	80	10	(93)	392
Br	CuI	20 mol %	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24	(92)	393
Br	CuI	10 mol %	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(45)	394
I	CuI	10 mol %	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(92)	394
Br	CuI	10 mol %	**L22** (10 mol %), K_2CO_3	DMF	110	12	(71)	79
Br	CuI	5 mol %	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(72)	86
I	CuI	5 mol %	**L24** (10 mol %), Cs_2CO_3	DMF	90	24	(98)	86
Br	CuI	10 mol %	**L25** (20 mol %), Cs_2CO_3	MeCN	80	15	(80)	395
I	CuI	5 mol %	*N*-hydroxymaleimide (10 mol %), NaOMe	DMSO	90	12	(96)	396

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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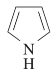
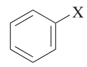
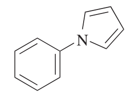
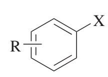




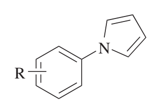
Catalyst (*x* amount)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	CuI	10 mol %	**L26** (10 mol %), NaOMe	DMSO	120	12	(69)	397
I	CuI/PAnNF	5 mol %	K_2CO_3	DMF	rt	8	(80)	276
Br	CuO	10 mol %	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %)	DMF	110	24	(75)	277
I	CuO	10 mol %	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %)	DMF	90	12	(78)	277
I	CuO	10 mol %	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30	(90)	130
I	CuO	2.5 mol %	KOH	DMSO	110	24	(91)	224
I	CuO	1.26 mol %	KOH	DMSO	110	2.5	(93)	224
I	CuO	0.1 mol %	DMEDA (20 mol %), K_3PO_4•H_2O	toluene	135	24	(11)	222
Cl	CuO on acetylene black	5 mol %	KO*t*-Bu	toluene	180	18	(74)	226
Br	CuO on acetylene black	5 mol %	KO*t*-Bu	toluene	180	18	(80)	226
I	CuO on acetylene black	5 mol %	KO*t*-Bu	toluene	180	18	(96)	226
I	Cu_2O	10 mol %	Cs_2CO_3	DMF	100	18	(93)	221
I	Cu_2O	10 mol %	KOH	DMSO	120	24	(91)	398
I	Cu_2O	10 mol %	ninhydrin (20 mol %), KOH	DMSO	110	48	(91)	399
I	Cu_2O	5 mol %	**L27** (20 mol %)	MeCN	82	24	(94)	40
Br	Cu_2O	10 mol %	**L23** (20 mol %), Cs_2CO_3	DMF	110	24	(82)	400
I	Cu_2O	5 mol %	**L23** (10 mol %), KO*t*-Bu	DMF	80	24	(95)	400
Br	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(90)	85
I	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(91)	85
I	$Cu(OAc)_2$•H_2O	20 mol %	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	30	(68)	289
I	$Cu(OAc)_2$•H_2O	15 mol %	(–)-sparteine (30 mol %), K_2CO_3	DMF	130	24	(78)	290
Br	$Cu(TMHD)_2$	20 mol %	KO*t*-Bu	DMF	120	24	(88)	308
I	$Cu(TMHD)_2$	20 mol %	KO*t*-Bu	DMF	120	24	(94)	308
Br	**8**	25 mol %	K_2CO_3	DMSO	135	35	(82)	65
I	**6**	5 mol %	Cs_2CO_3	toluene	100	10	(94)	123
Br	Cu fluorapatite	12.5 mol %	none	DMSO	110	10	(90)	227
I	Cu fluorapatite	12.5 mol %	none	DMSO	110	6	(92)	227



Catalyst (*x* mol %)



R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2-Br	I	Cu	20	Cs_2CO_3	*n*-PrCN	reflux	24	(83)	129
2-Br	I	CuI	10	benzotriazole (20 mol %), K_3PO_4	DMSO	100	30	(61)	77
2-I	I	CuI	10	benzotriazole (20 mol %), K_3PO_4	DMSO	100	30	(52)	77
3-Br	I	CuCl	5	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24	(75)	235
4-F	I	CuI	5	TBAB (5 mol %), NaOH	toluene	reflux	22	(77)	391
4-Cl	Br	Cu	20	Cs_2CO_3	*n*-PrCN	reflux	24	(77)	129
4-Cl	I	CuCl	5	TBAB (40% aq)	H_2O	80	24	(72)	282
4-Cl	I	CuCl	10	**L9** (10 mol %), TMAH	DMSO	80	24	(83)	281
4-Cl	I	CuBr	20	binol (20 mol %), K_3PO_4	DMF	rt	8	(51)	62
4-Cl	Br	CuCl	5	TBAB (40% aq)	H_2O	80	24	(57)	282
4-Cl	I	CuI	5	TBAB (5 mol %), NaOH	toluene	reflux	22	(80)	391
4-Cl	I	CuI	5	*N*-hydroxyphthalimide (10 mol %), NaOMe	DMSO	90	12	(95)	396
4-Cl	Br	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	80	10	(81)	392
4-Cl	I	CuI	5	oxazolidin-2-one (20 mol %), NaOMe	DMSO	80	8	(86)	392
4-Cl	Br	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(45)	394
4-Cl	I	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(92)	394
4-Cl	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	14	(67)	271
4-Cl	I	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12	(83)	397
4-Br	I	CuI	5	TBAB (5 mol %), NaOH	toluene	reflux	22	(90)	391
4-Br	I	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(81)	394
4-Br	I	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12	(68)	397
4-Br	I	CuI	10	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	24	(84)	67
4-Br	I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	36	(80)	47, 336
4-Br	I	CuI	5	L-Pro (10 mol %), K_2CO_3	DMSO	90	36	(80)	401
4-Br	I	CuO	10	$FeCl_3$ (10 mol %), *rac*-binol (20 mol %), $CsCO_3$	DMF	90	12	(89)	227

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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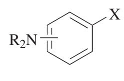
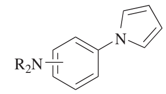
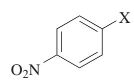


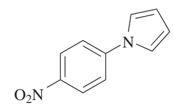
Catalyst (*x* mol %)



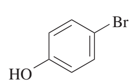
Isomer	R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	H	Br	CuI	5	DMCDA (20 mol %), K_3PO_4	toluene	110	24	(83)	128
3	H	I	CuI	5	oxazolidin-2-one (10 mol %), NaOMe	DMSO	80	10	(78)	392
3	H	I	CuI	5	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	90	12	(92)	396
4	H	I	Cu	20	Cs_2CO_3	*n*-PrCN	reflux	9	(85)	129
4	H	I	CuI	5	oxazolidin-2-one (10 mol %), NaOMe	DMSO	80	14	(92)	392
4	H	I	CuI	5	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	90	12	(98)	396
4	Me	Br	CuI	5	DMCDA (20 mol %), K_3PO_4	toluene	110	24	(94)	128



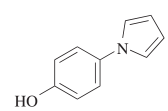
Catalyst (*x* mol %)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	Cu	20	Cs_2CO_3	*n*-PrCN	reflux	7	(92)	129
I	CuCl	10	**L9** (10 mol %), TMAH	DMSO	80	24	(74)	281
Br	CuCl	5	TBAH (40% aq)	H_2O	80	24	(43)	282
I	CuCl	5	TBAH (40% aq)	H_2O	80	24	(50)	282
Cl	CuI	5	*N*-hydroxymaleimide (10 mol %), NaOMe	DMSO	110	40	(45)	396
Cl	CuI	10	**L26** (10 mol %), NaOMe	DMSO	110	12	(93)	397
Cl	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24	(32)	392
Cl	CuO	8	K_2CO_3	pyridine	reflux	24	(1)	402
F	Cu fluorapatite	7	K_2CO_3	DMF	120	2	(85)	66
Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	4	(80)	66
Br	Cu fluorapatite	12.5	none	DMSO	110	4	(95)	227
I	Cu fluorapatite	12.5	none	DMSO	110	3	(95)	227
Cl	**7**	1	K_2CO_3	DMF	110	5	(80)	73
I	**7**	1	K_2CO_3	DMF	110	1.5	(92)	73



CuO on acetylene black (5 mol %), KO*t*-Bu, toluene, 180°, 18 h



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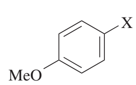
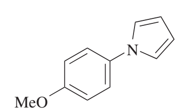


Catalyst (*x* mol %)



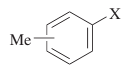
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	Cu	20	Cs_2CO_3	*n*-PrCN	reflux	20	(79)	129
I	Cu	20	Cs_2CO_3	*n*-PrCN	reflux	20	(93)	129
I	CuI	5	TBAB (5 mol %), NaOH	toluene	reflux	22	(84)	391
Br	CuI	10	phen (20 mol %), KF/Al_2O_3	toluene	reflux	10	(80)	390
I	CuI	10	phen (20 mol %), KF/Al_2O_3	toluene	reflux	9	(85)	390
Br	CuI	10	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	24	(71)	67
Br	CuI	10	DMG (20 mol %), Cs_2CO_3	DMSO	110	40	(46)	47
Br	CuI	20	L-Pro (20 mol %), K_3PO_4	DMF	140	48	(60)	388
I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(98)	388
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	36	(84)	47
I	CuI	5	L-Pro (20 mol %), K_2CO_3	DMSO	90	36	(84)	401
I	CuI	5	*N*-hydroxymaleimide (10 mol %), NaOMe	DMSO	90	12	(93)	396
Br	CuI	5	**L34** (10 mol %), KO*t*-Bu	DMSO	110	—	(91)	403
Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	5	(90)	285
I	CuI/PAnNF	5	K_2CO_3	DMF	rt	12	(55)	276
Br	CuO on acetylene black	5	KO*t*-Bu	toluene	180	18	(34)	226
I	**8**	25	K_2CO_3	DMSO	135	24	(82)	65
Br	Cu fluorapatite	12.5	none	DMSO	110	15	(85)	227
I	Cu fluorapatite	12.5	none	DMSO	110	14	(91)	227

TABLE 7A. *N*-ARYLATION OF PYRROLES (*Continued*)

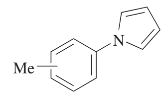
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

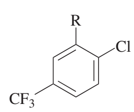
C_4



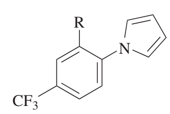
Catalyst (*x* mol %)



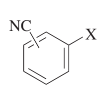
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	Br	CuI	5	DMCDA (20 mol %), K_3PO_4	toluene	110	24	(87)	128
2	I	CuI	5	TBAB (5 mol %), NaOH	toluene	reflux	22	(62)	391
2	I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	110	24	(90)	388
3	I	CuI	5	TBAB (5 mol %), NaOH	toluene	reflux	22	(83)	391
4	Br	CuCl	5	TBAH (40% aq)	H_2O	80	24	(65)	282
4	I	CuCl	5	TBAH (40% aq)	H_2O	80	24	(63)	282
4	I	CuCl	10	**L9** (10 mol %), TMAH	DMSO	80	24	(86)	281
4	I	CuI	5	TBAB (5 mol %), NaOH	toluene	reflux	22	(88)	391
4	I	CuI	10	phen (20 mol %), KF/Al_2O_3	toluene	reflux	8	(84)	390
4	Br	CuI	20	L-Pro (20 mol %), K_3PO_4	DMF	140	48	(57)	388
4	I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(98)	388
4	I	CuI	5	L-Pro (20 mol %), K_2CO_3	DMSO	90	42	(82)	401
4	I	CuI	10	**L8** (20 mol %), K_3PO_4	DMF	30	14	(64)	271
4	Br	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(39)	394
4	I	CuI/PAnNF	5	K_2CO_3	DMF	rt	12	(63)	276
4	Cl	CuO on acetylene black	5	KO*t*-Bu	toluene	180	18	(40)	226
4	Br	Cu fluorapatite	12.5	none	DMSO	110	15	(88)	227
4	I	Cu fluorapatite	12.5	none	DMSO	110	14	(83)	227
4	Br	Cu(II)-NaY zeolite	10	K_2CO_3	DMF	120	36	(99)	404
4	I	Cu(II)-NaY zeolite	10	K_2CO_3	DMF	120	20	(99)	404



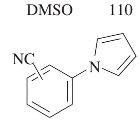
Catalyst (*x* mol %)



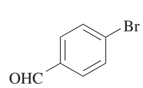
R	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	CuI	5	*N*-hydroxymaleimide (10 mol %), NaOMe	DMSO	110	40	(45)	396
H	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24	(35)	392
H	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	4	(95)	285
NO_2	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(87)	394
NO_2	CuI	10	**L26** (10 mol %), NaOMe	DMSO	110	12	(91)	397



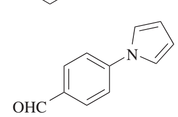
CuO (8 mol %), K_2CO_3,
pyridine,
reflux, 24 h



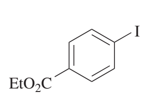
Isomer	X		Refs.
2	Cl	(6)	402
3	Br	(42)	



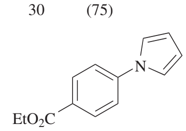
Catalyst (*x* mol %), DMSO



Catalyst	*x*	Additive	Temp (°)	Time (h)		Refs.
Cu fluorapatite	12.5	none	110	8	(90)	227
cat. **8**	25	K_2CO_3	135	30	(75)	65



Cu (20 mol %),
Cs_2CO_3, *n*-PrCN,
reflux, 10 h

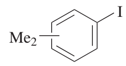


(95) 129

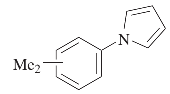
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

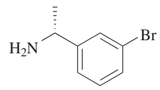
C_4



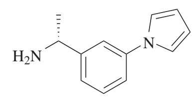
CuI (*x* mol %)



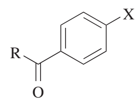
Isomer	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
2,4	5	TBAB (5 mol %), NaOH	toluene	reflux	22	(63)	391
3,5	1	CDA (10 mol %), K_3PO_4	dioxane	110	24	(99)	115
3,5	5	L-Pro (10 mol%), K_2CO_3	DMSO	90	36	(85)	401
3,5	10	EDA (10 mol %), K_3PO_4	dioxane	110	24	(87)	405



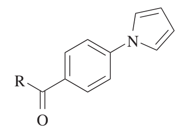
CuI (10 mol %),
K_2CO_3, NMP,
MW, 195°, 3 h



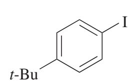
(66) 406



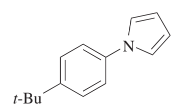
Catalyst (*x* mol %)



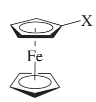
R	X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
Me	I	CuCl	10	**L9** (10 mol %), TMAH	DMSO	80	24	(70)	281
Me	Br	CuI	20	L-Pro (20 mol %), K_3PO_4	DMF	140	48	(68)	388
Me	I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(99)	388
Et	Br	CuI	5	DMCDA (20 mol %), K_3PO_4	toluene	110	24	(92)	128



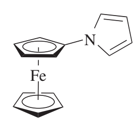
CuI (5 mol %),
TBAB (5 mol %), NaOH,
toluene, reflux, 22 h



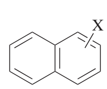
(86) 391



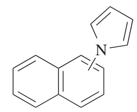
Catalyst (*x* amount),
DMSO



X	Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
I	CuI	1 eq	K_2CO_3	DMSO	90	18	(62)	372
Br	Cu(TMHD)$_2$	20 mol %	KO*t*-Bu	toluene	120	36	(34)	407
I	Cu(TMHD)$_2$	20 mol %	KO*t*-Bu	toluene	120	12	(74)	407



Catalyst (5 mol %)



Isomer	X	Catalyst	Additives	Solvent	Temp (°)	Time (h)		Refs.
1	I	CuI	oxazolidin-2-one (10 mol %), MeONa	DMSO	80	14	(92)	392
1	I	CuI	*N*-hydroxyphthalimide (10 mol %), MeONa	DMSO	90	12	(98)	396
2	Br	CuCl	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24	(69)	235

TABLE 7A. *N*-ARYLATION OF PYRROLES (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

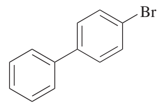
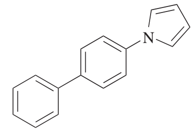
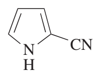
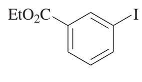
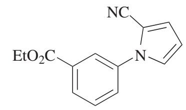
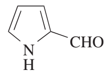
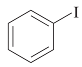
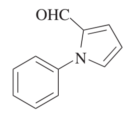
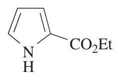
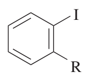
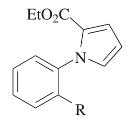
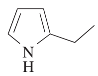
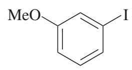
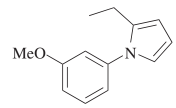
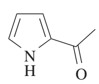
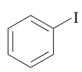
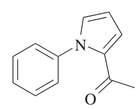
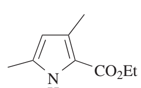
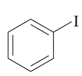
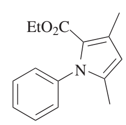
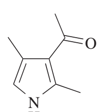
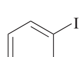
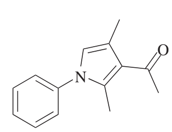
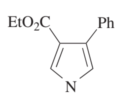
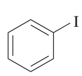
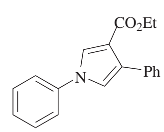
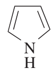
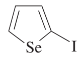
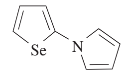
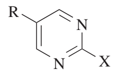
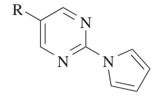
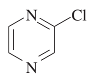
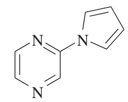
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CuI (5 mol %), NaOMe, DMSO, *N*-hydroxy-succinimide (10 mol %), 110°, 40 h	 (82)	396
C_5				
		CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 (85)	128
		CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 (88)	128
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 24 h	 R: MeO (96); Me (89)	128
C_6				
		CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 (92)	128
		CuI (5 mol %), toluene		
		Additives: DMCDA (20 mol %), K_3PO_4; Temp (°) 110; Time (h) 24	(96)	128
		Additives: TBAB (5 mol %), NaOH; Temp (°) reflux; Time (h) 22	(80)	391
C_7				
		CuI (5 mol %), DMEDA (20 mol %), K_3PO_4, 110°, 24 h	 (86)	128
C_8				
		CuI (5 mol %), DMEDA (20 mol %), K_3PO_4, 110°, 24 h	 (92)	128
C_{11}				
		Cu (20 mol %), Cs_2CO_3, *n*-PrCN, reflux, 15 h	 (95)	129

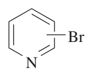
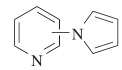
TABLE 7B. *N*-HETEROARYLATION OF PYRROLES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, reflux, 24 h	 (50)	87
		Catalyst (*x* mol %)		

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
H	Br	Cu fluorapatite	12.5	none	DMSO	110	2	(98)	227
Br	I	CuI	5	phen (10 mol %), Cs_2CO_3	DMF	80	24	(84)	408

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (*x* mol %), NaOMe, DMSO		

x	Additive	Temp (°)	Time (h)	Yield (%)	Refs.
5	*N*-hydroxyphthalimide (10 mol %)	110	24	(90)	396
10	oxazolidin-2-one (20 mol %)	120	20	(78)	392

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %), DMSO		

Isomer	Catalyst	*x*	Additive(s)	Temp (°)	Time (h)	Yield (%)	Refs.
2	CuI	5	*N*-hydroxyphthalimide (10 mol %), NaOMe	110	24	(96)	396
2	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	80	12	(88)	392
4	Cu fluorapatite	12.5	none	110	6	(92)	227

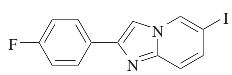
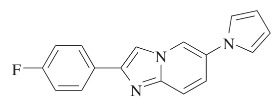
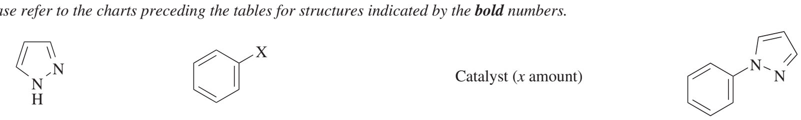
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 112°, 24 h	 (76)	409

TABLE 8A. *N*-ARYLATION OF PYRAZOLES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3



Catalyst (*x* amount)

X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
I	Cu	20 mol %	Cs_2CO_3	*n*-PrCN	reflux	8 h	(95)	129
I	CuBr	10 mol %	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24 h	(95)	259
Br	CuI	20 mol %	Cs_2CO_3	DMF	120	40 h	(84)	386
Br	CuI	20 mol %	phen (20 mol %), KF/Al_2O_3	xylene	140	15 h	(80)	410
I	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	xylene	140	13 h	(95)	411
Br	CuI	10 mol %	L-His (20 mol %), K_2CO_3	DMSO	100	48 h	(66)	389
I	CuI	10 mol %	DMG (20 mol %), TBPE	DMSO	rt	24 h	(81)	61
I	CuI	5 mol %	DMCDA (10 mol %), K_2CO_3	toluene	110	24 h	(93)	128
Br	CuI	20 mol %	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24 h	(98)	393
Br	CuI	10 mol %	**L25** (10 mol %), CTAB (20 mol %), Cs_2CO_3	H_2O	80	50 h	(67)	395
I	CuI	10 mol %	**L25** (10 mol %), CTAB (20 mol %), Cs_2CO_3	H_2O	80	50 h	(67)	395
I	CuI	5 mol %	**L2** (25 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(63)	236
Br	CuI	10 mol %	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(87)	86
Br	CuI	10 mol %	**L28** (20 mol %), K_2CO_3	DMSO	120	60 h	(93)	412
Br	CuI	10 mol %	**L29**, Cs_2CO_3	MeCN	80	2 h	(80)	413
I	CuI	10 mol %	**L29**, Cs_2CO_3	MeCN	80	2 h	(95)	413
Br	CuO	10 mol %	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30 h	(94)	130
I	CuO	10 mol %	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30 h	(91)	130
I	CuO on acetylene black	5 mol %	KO*t*-Bu	toluene	180	18 h	(96)	226
Cl	Cu_2O	10 mol %	Cs_2CO_3	DMF	100	18 h	(0)	221
Br	Cu_2O	10 mol %	Cs_2CO_3	DMF	100	18 h	(93)	221
I	Cu_2O	10 mol %	Cs_2CO_3	DMF	100	18 h	(98)	221
I	Cu_2O	10 mol %	KOH	DMSO	120	24 h	(92)	398

TABLE 8A. *N*-ARYLATION OF PYRAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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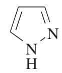
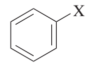
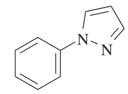
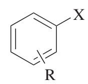
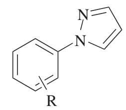
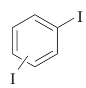
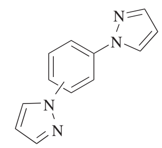
C_3   Catalyst (x amount) 

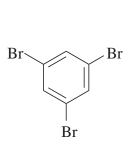
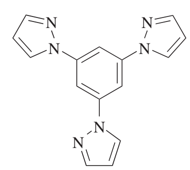
X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	Yield (%)	Refs.
I	Cu_2O	10 mol %	ninhydrin (20 mol %), KOH	DMSO	110	48 h	(92)	399
Br	Cu_2O	5 mol %	**L27** (20 mol %), Cs_2CO_3	MeCN	82	24 h	(96)	82
I	Cu_2O	5 mol %	**L27** (20 mol %), Cs_2CO_3	MeCN	82	24 h	(100)	82
I	Cu_2O	5 mol %	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18 h	(94)	125
Br	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(86)	85
I	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(89)	85
Br	[Cu(μ-I)((–)-sparteine)]$_2$	1 mol %	K_2CO_3	DMSO	115	7 h	(95)	414
Br	Cu fluorapatite	12.5 mol %	none	DMSO	110	10 h	(92)	227
I	**6**	5 mol %	Cs_2CO_3	toluene	100	12 h	(90)	123
Br	**9**	10 mol %	Cs_2CO_3	MeCN	reflux	4 h	(98)	27

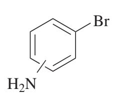
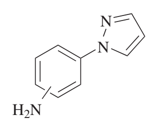
 Catalyst (x mol %) 

X	R	Catalyst	x	Additives	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
Br	2,4-Cl_2	Cu_2O	5	**L30** (20 mol %), Cs_2CO_3	DMF	110	48	(60)	82
I	4-Cl	CuI	10	DMG (20 mol %), TBPE	DMSO	rt	24	(98)	61
Br	4-Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	30	(82)	82
I	4-Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	30	(95)	82

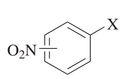
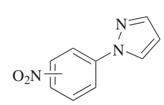
 CuI (5 mol %), **L30** (5 mol %), Cs_2CO_3, DMF, 100°, 24 h 

Isomer	Yield (%)	Refs.
1,3	(92)	415
1,4	(93)	

 CuI (20 mol %), K_2CO_3, $PhNO_2$, reflux, 3 h  (90) 416

 Catalyst (5 mol %) 

Isomer	Catalyst	Additives	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
2	CuI	DMCDA (10 mol %), K_2CO_3	toluene	110	24	(91)	128
4	Cu_2O	**L30** (20 mol %), Cs_2CO_3	MeCN	82	42	(91)	82

 Catalyst (x mol %) 

Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
2	Cl	CuO	8	K_2CO_3	pyridine	reflux	24	(31)	402
3	I	CuBr	10	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24	(95)	259
3	Cl	CuO	8	K_2CO_3	pyridine	reflux	24	(31)	402
3	Br	Cu_2O	10	Cs_2CO_3	DMF	110	18	(98)	221
3	Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	24	(91)	82
4	Br	CuI	10	**L25** (20 mol %), Cs_2CO_3	MeCN	80	15	(92)	395
4	Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24	(97)	417
4	Cl	CuO	8	K_2CO_3	pyridine	reflux	24	(24)	402
4	Br	CuO	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30	(90)	130
4	I	CuO	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30	(90)	130
4	I	Cu_2O	5	**L30** (20 mol %), Cs_2CO_3	MeCN	82	24	(90)	82
4	F	**7**	1	K_2CO_3	DMF	110	1	(92)	73
4	Cl	**7**	1	K_2CO_3	DMF	110	3	(87)	73
4	F	Cu fluorapatite	7	K_2CO_3	DMF	120	1	(80)	66
4	Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	12	(72)	66

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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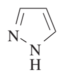
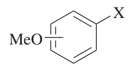
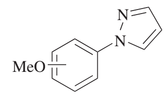
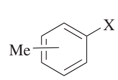




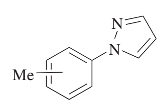
Catalyst (x mol %)



Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	Yield	Refs.
2	I	CuI	10	phen (10 mol %), KF/Al_2O_3	—	140	17 h	(82)	411
2	I	Cu_2O	10	Cs_2CO_3	DMF	110	18 h	(99)	221
3	Br	CuI	10	L-Glu (20 mol %), K_3PO_4	—	MW (200 W), 150	10 h	(32)	418
3	Br	CuI	10	**L25** (20 mol %), Cs_2CO_3	MeCN	80	15 h	(93)	395
3	Br	CuO	10	$Fe(acac)_3$, Cs_2CO_3	DMF	120	24 h	(86)	130
4	Br	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	20 h	(80)	228
4	I	CuF_2	50	phen (50 mol %), K_2CO_3	DMF	140	96 h	(98)	419
4	I	CuBr	10	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24 h	(85)	259
4	I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24 h	(78)	119
4	I	CuI	20	K_3PO_4	DMF	40	40 h	(71)	59
4	Br	CuI	20	phen (20 mol %), KF/Al_2O_3	xylene	140	16 h	(88)	410
4	I	CuI	10	phen (20 mol %), KF/Al_2O_3	—	140	15 h	(94)	411
4	I	CuI	10	DMG (20 mol %), Bu_4POAc	DMSO	rt	24 h	(70)	61
4	Br	CuI	10	DMG (20 mol %), K_2CO_3	DMSO	110	45 h	(71)	47
4	Br	CuI	10	L-Lys (20 mol %), K_2CO_3	—	MW (200 W), 150	10 h	(83)	418
4	I	CuI	5	L-Pro (10 mol %), K_2CO_3	DMSO	90	65 h	(91)	401, 47
4	I	CuI	5	**L2** (25 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(78)	236
4	Br	CuI	10	**L25** (20 mol %), Cs_2CO_3	MeCN	80	15 h	(82)	395
4	Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	4 h	(90)	285
4	Br	CuO	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	120	24 h	(80)	130
4	Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	40 h	(93)	82
4	I	Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18 h	(95)	125
4	Br	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	115	12 h	(82)	414
4	I	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	115	7 h	(91)	414
4	Br	**10**	1	Cs_2CO_3	DMSO	100	24 h	(16)	420
4	I	**10**	1	Cs_2CO_3	DMSO	100	24 h	(50)	420
4	I	Cu(IPr)Cl	10	Cs_2CO_3	DMSO	100	24 h	(23)	421



Catalyst (x mol %)



Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
2	Br	CuI	5	DMCDA (10 mol %), K_2CO_3	—	110	24	(92)	128
2	Br	CuI	20	phen (20 mol %), KF/Al_2O_3	xylene	140	18	(81)	410
2	I	Cu_2O	10	Cs_2CO_3	DMF	110	18	(91)	221
2	Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	DMF	110	48	(100)	82
2	I	Cu_2O	5	**L30** (20 mol %), Cs_2CO_3	MeCN	82	70	(94)	82
3	Br	CuI	10	L-Glu (20 mol %), K_3PO_4	—	MW (200 W), 150	3	(27)	418
4	Br	CuI	10	L-Glu (20 mol %), K_3PO_4	—	MW (200 W), 150	2	(37)	418
4	Br	CuI	10	**L25** (20 mol %), Cs_2CO_3	MeCN	80	15	(80)	395
4	Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24	(98)	417
4	Br	CuO	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	120	24	(57)	130
4	Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	36	(95)	82
4	I	Cu(IPr)Cl	10	Cs_2CO_3	DMSO	100	24	(54)	421
4	Br	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	36	(99)	404
4	I	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	22	(99)	404
4	I	**10**	1	Cs_2CO_3	DMSO	100	24	(21)	420
4	Br	**9**	10	Cs_2CO_3	MeCN	reflux	4	(97)	27
3,5	I	CuI	1	CDA (10 mol %), K_2CO_3	dioxane	110	24	(89)	115

TABLE 8A. *N*-ARYLATION OF PYRAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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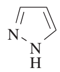
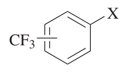
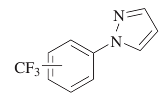
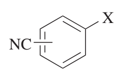




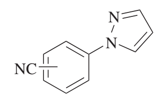
Catalyst (*x* mol %)



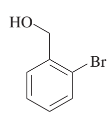
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
3	I	Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18	(81)	125
4	Br	CuO	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	140	24	(40)	130
4	Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	36	(96)	82
4	Cl	**9**	10	Cs_2CO_3	DMF	140	24	(70)	27



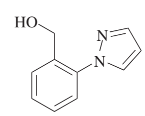
Catalyst(s) (*x* mol %)



Isomer	X	Catalyst(s)	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
3	I	CuBr	10	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24	(89)	259
4	Br	Cu, CuI	10, 5	binol (20 mol %), Cs_2CO_3	DMSO	110	36	(89)	124
4	Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	75	45	(96)	47
4	Br	CuI	10	**L25** (20 mol %), Cs_2CO_3	MeCN	80	15	(94)	395
4	Br	CuO	8	K_2CO_3	pyridine	reflux	24	(47)	402
4	Br	CuO	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30	(98)	130
4	I	Cu_2O	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30	(98)	130
4	Cl	Cu_2O	10	Cs_2CO_3	DMF	110	18	(98)	221
4	Br	Cu_2O	5	**L30** (20 mol %), Cs_2CO_3	MeCN	82	24	(91)	82
4	Br	**9**	10	Cs_2CO_3	MeCN	reflux	4	(98)	27



CuI (5 mol %),
DMCDA (10 mol %), K_2CO_3,
toluene, 110°, 24 h



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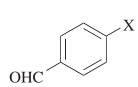
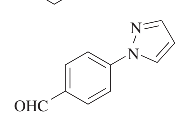
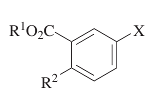


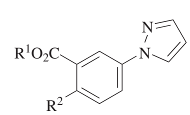
Catalyst (*x* mol %)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	5	**L31** (5 mol %), Cs_2CO_3	DMF	100	24	(72)	415
Cl	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	125	19	(65)	414
Br	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	115	8	(77)	414



Catalyst (*x* mol %)



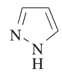
R^1	R^2	X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
Me	H	I	CuI	10	Me_2Gly (20 mol %), Bu_4POAc	DMSO	rt	24	(93)	61
Et	H	Br	Cu_2O	5	**L30** (20 mol %), Cs_2CO_3, 3 Å MS	MeCN	82	48	(50)	82
Me	Cl	I	CuI	5	DMCDA (10 mol %), K_2CO_3	toluene	110	24	(89)	128

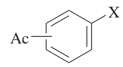
TABLE 8A. *N*-ARYLATION OF PYRAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

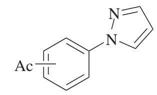
Please refer to the charts preceding the tables for structures indicated by the bold numbers.

C_3

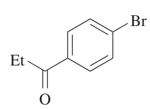




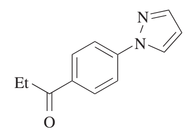
Catalyst (*x* mol %)



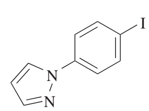
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
3	Br	CuI	10	L-Lys (20 mol %), K_3PO_4	—	MW (200 W), 150	10 h	(44)	418
3	Br	CuO	8	K_2CO_3	pyridine	reflux	48 h	(62)	402
4	I	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	8 h	(80)	228
4	Br	CuI	10	L-Glu (20 mol %), K_3PO_4	—	MW (200 W), 150	5 h	(59)	418
4	I	CuI	5	**L2** (25 mol %), KOH, TBAB	H_2O	MW (100 W), 130	5 min	(54)	236
4	Br	CuI	10	**L25** (20 mol %), Cs_2CO_3	MeCN	80	15 h	(95)	395
4	Br	CuI	5	**L31** (5 mol %), Cs_2CO_3	DMF	100	24 h	(91)	415
4	Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24 h	(98)	417
4	Br	CuO	8	K_2CO_3	pyridine	reflux	48 h	(75)	402
4	Br	CuO	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30 h	(81)	130
4	Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	24 h	(91)	82
4	Cl	Cu(IPr)Cl	10	Cs_2CO_3	DMSO	100	24 h	(50)	421
4	Br	Cu(IPr)Cl	10	Cs_2CO_3	DMSO	100	24 h	(60)	421
4	I	Cu(IPr)Cl	10	Cs_2CO_3	DMSO	100	24 h	(90)	421
4	Cl	**10**	1	Cs_2CO_3	DMSO	100	24 h	(44)	420
4	Br	**10**	1	Cs_2CO_3	DMSO	100	24 h	(93)	420
4	I	**10**	1	Cs_2CO_3	DMSO	100	24 h	(93)	420



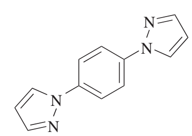
CuI (5 mol %),
DMCDA (10 mol %), K_2CO_3,
toluene, 110°, 24 h



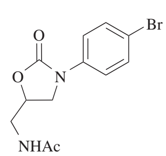
(98) 128



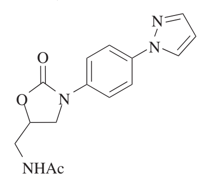
Cu_2O (5 mol %),
L27 (20 mol %), Cs_2CO_3,
MeCN, 82°, 48 h



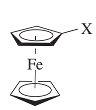
(91) 82



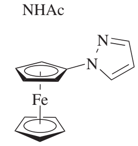
CuI (20 mol %),
L-Pro (40 mol %), K_2CO_3,
DMSO, 120°, 15 h



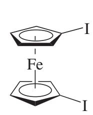
(70) 292



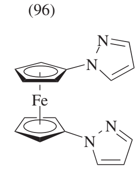
Catalyst (*x* amount),
DMSO, 90°



X	Catalyst	*x*	Additive	Time (h)		Refs.
I	CuI	1 eq	K_2CO_3	18	(84)	372
Br	$Cu(TMHD)_2$	20 mol %	KO*t*-Bu	12	(80)	407
I	$Cu(TMHD)_2$	10 mol %	KO*t*-Bu	12	(96)	407



CuI (1 eq), K_2CO_3,
DMSO, 90°, 18 h



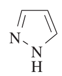
(50) 372

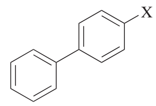
TABLE 8A. *N*-ARYLATION OF PYRAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

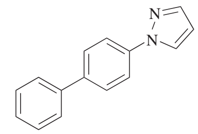
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3



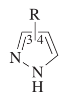


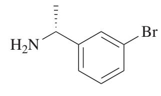
Catalyst (10 mol %), Cs_2CO_3



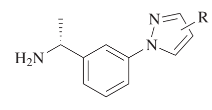
X	Catalyst	Additive	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	**L25** (20 mol %)	MeCN	80	15	(98)	395
Br	CuO	$Fe(acac)_3$ (30 mol %)	DMF	120	24	(93)	130
I	CuO	$Fe(acac)_3$ (30 mol %)	DMF	120	24	(93)	130

C_{3-5}



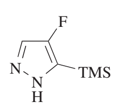


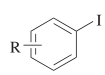
CuI (10 mol %), K_2CO_3, NMP, MW, 195°



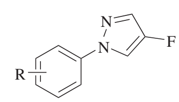
406

R	Time (h)	
H	2	(71)
3-Me	17	(32) (3-Me) + (32) (1-Me)
4-Me	1	(90)
3,5-Me_2	22	(49)



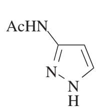


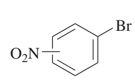
CuI (10 mol %), **L33** (20 mol %), Cs_2CO_3, MeCN



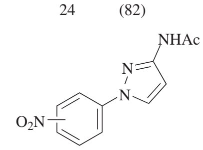
422

R	Temp (°)	Time (h)		R	Temp (°)	Time (h)	
H	60	24	(76)	2-MeO_2C	60	24	(89)
4-O_2N	60	24	(98)	4-EtO_2C	60	24	(76)
3-MeO	60	24	(67)	2,4-Me_2	70	144	(trace)
4-NC	60	24	(98)	2-Et	70	144	(69)
4-CF_3	60	24	(86)	4-Ac	60	24	(82)





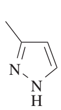
Cu_2O (12 mol %), K_2CO_3, pyridine, reflux, 24 h

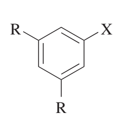


Isomer	
2	(45)
3	(39)
4	(40)

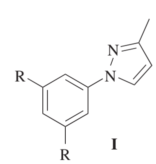
423

C_4



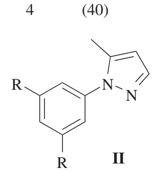


Catalyst (*x* mol %)



I

+



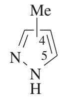
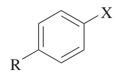
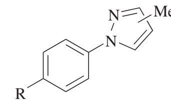
II

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
H	I	CuI	20	Cs_2CO_3	DMF	120	40	(64)	(21)	386
H	Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	96	(52)	(16)	82
H	I	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	96	(71)	(19)	82
Me	I	CuI	1	CDA (10 mol %), K_2CO_3	dioxane	110	24	(84)	(0)	115

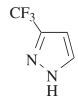
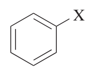
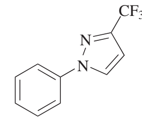
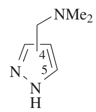
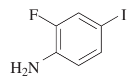
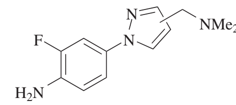
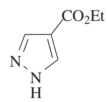
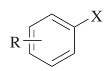
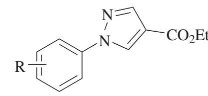
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

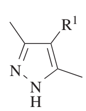
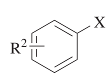
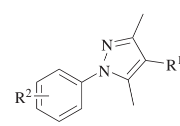
C_4

		Catalyst (*x* mol %)		

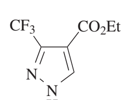
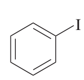
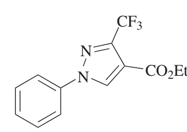
Isomer	R	X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
4	H	I	CuI	5	DMCDA (20 mol %), Cs_2CO_3	DMF	110	24	(74)	128
4	H	I	CuI	10	phen (10 mol %), KF/Al_2O_3	—	140	13	(95)	411
4	H	Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	96	(100)	82
4	H	I	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	24	(98)	82
5	HO	Br	CuI	5	DMCDA (10 mol %), K_2CO_3	toluene	110	24	(78)	128

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu_2O (5 mol %), **L27** (20 mol %), Cs_2CO_3, MeCN, 82°, 96 h	 X: Br (81); I (81)	82
		CuI, 8-HOquin, K_2CO_3, DMSO, 130°	 Isomer: 4 (—); 5 (—)	424
		CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 R, X: 2-Me, Br (77); 4-EtO_2C, I (79)	128

C_5

		Catalyst (*x* amount)		

R^1	R^2	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	H	I	CuI	20 mol %	Cs_2CO_3	DMF	120	40	(63)	386
H	H	I	CuI	5 mol %	DMCDA (20 mol %), Cs_2CO_3	DMF	110	24	(98)	128
H	H	I	CuI	10 mol %	**L22** (10 mol %), K_2CO_3	DMF	90	12	(71)	79
H	H	I	Cu_2O	5 mol %	**L30** (20 mol %), Cs_2CO_3	MeCN	82	54	(94)	82
H	4-MeO	I	CuF_2	25 mol %	phen (25 mol %), K_2CO_3	DMF	140	96	(81)	419
Br	4-MeO	I	CuF_2	50 mol %	phen (50 mol %), K_2CO_3	DMF	140	96	(83)	419
H	4-Me	I^+4-MeC_6H_4 BF_4^-	$Cu(acac)_2$	1 eq	K_2CO_3	toluene	50	6	(80)	76
H	2-CH_2NH_2	I	CuI	5 mol %	DMCDA (10 mol %), K_2CO_3	—	110	24	(71)	128

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMCDA (10 mol %), K_2CO_3, 110°, 24 h	 (77)	128

C_9

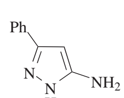
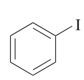
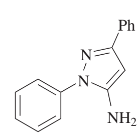
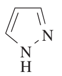
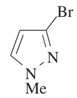
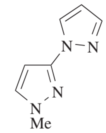
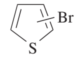
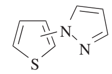
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMCDA (10 mol %), K_2CO_3, 110°, 24 h	 (68)	128

TABLE 8B. *N*-HETEROARYLATION OF PYRAZOLES

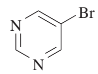
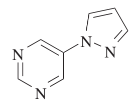
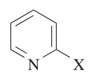
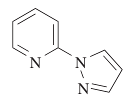
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

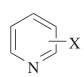
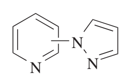
C_3

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu_2O (5 mol %), **L27** (20 mol %), Cs_2CO_3, MeCN, 82°, 54 h	 (92)	82
		Cu_2O (*x* mol %), Cs_2CO_3		

Isomer	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
2	5	**L27** (20 mol %)	MeCN	82	24	(91)	82
2	10	none	DMF	110	18	(95)	221
3	5	**L27** (20 mol %)	MeCN	82	54	(92)	82

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (10 mol %), CuI (5 mol %), binol (20 mol %), Cs_2CO_3, DMSO, 110°, 40 h	 (82)	124
		Catalyst (*x* mol %)		

X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cl	Cu	5	binol (20 mol %), Cs_2CO_3	DMSO	110	36	(89)	124
Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	60	45	(94)	47
Br	CuI	10	**L25** (20 mol %), Cs_2CO_3	MeCN	80	15	(94)	395
Br	CuI	5	**L31** (5 mol %), Cs_2CO_3	DMF	100	24	(85)	415
Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24	(95)	417
Br	CuO	8	K_2CO_3	pyridine	reflux	16	(42)	402
Br	Cu_2O	5	**L27** (20 mol %), Cs_2CO_3	MeCN	82	24	(93)	82

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst(s) (*x* mol %)		

Isomer	X	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
3	Br	Cu, CuI	10, 5	binol (20 mol %), Cs_2CO_3	DMSO	110	36	(98)	124
3	Br	CuO	8	K_2CO_3	pyridine	reflux	60	(41)	402
4	Cl	CuO	8	K_2CO_3	pyridine	reflux	60	(6)	402

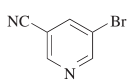
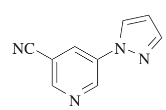
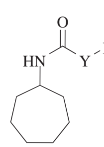
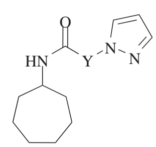
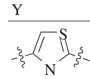
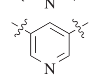
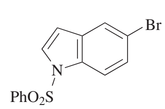
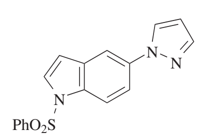
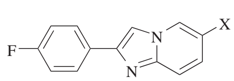
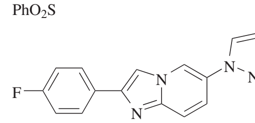
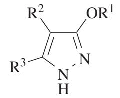
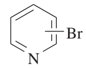
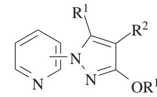
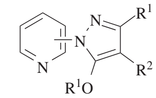
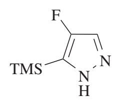
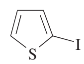
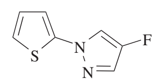
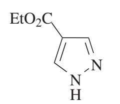
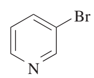
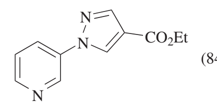
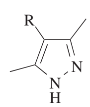
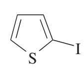
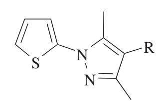
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h	 (30)	292
		CuI (20 mol %), L-Pro (40 mol%), K_2CO_3, DMSO, 120°, 15 h	 Y:  (65);  (77)	292
		CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 120°, 15 h	 (68)	292
		CuI (5 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 112°, 24 h	 X: Br (44); I (79)	409

TABLE 8B. *N*-HETEROARYLATION OF PYRAZOLES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{3-16}				
		Cu_2O (0.5 mol %), **L30** (1 mol %), Cs_2CO_3, 4 Å MS, MeCN, MW, 180°	 **I** +  **II**	425

R^1	R^2	R^3	Isomer	Time (h)	**I**	**II**
Et	H	H	2	6	(70)	(0)
Et	H	Me	2	2	(55)	(26)
i-Pr	H	Me	2	2	(53)	(25)
Et	H	Ph	2	6	(36)	(41)
Et	H	Bn	2	2	(41)	(25)
Et	F	Me	2	6	(67)	(9)
Et	EtO_2C	H	2	2	(72)	(0)
Et	EtO_2CCH_2	H	2	6	(7)	(0)
Et	Ph	Me	2	6	(79)	(5)
Et	Bn	Ph	2	6	(66)	(7)
i-Pr	H	Me	3	6	(30)	(2)
i-Pr	H	Me	4	6	(17)	(10)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		CuI (10 mol %), **L33** (20 mol %), Cs_2CO_3, MeCN, 70°, 144 h	 (46)	422
C_4				
		CuI (5 mol %), DMCDA (10 mol %), K_2CO_3, toluene, 110°, 24 h	 (84)	128
C_5				
		CuF_2 (*x* mol %), phen (*x* mol %), K_2CO_3, DMF, 140°, 96 h	 R, *x*: H, 50, (65); Br, 25, (37)	419

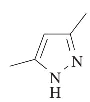
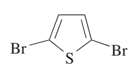
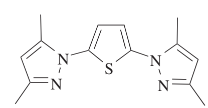
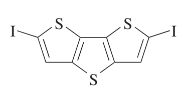
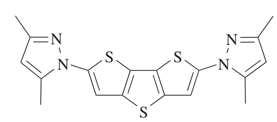
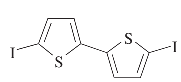
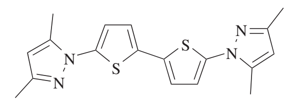
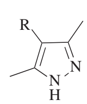
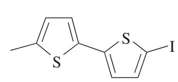
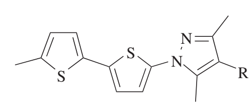
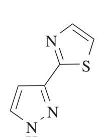
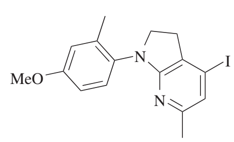
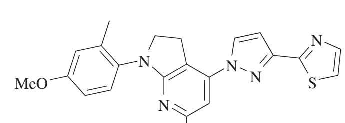
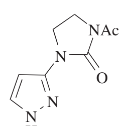
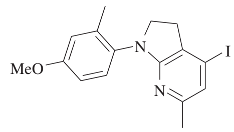
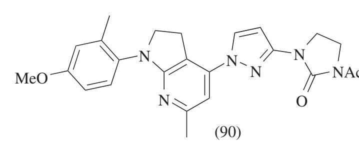
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuF_2 (50 mol %), phen (50 mol %), K_2CO_3, DMF, 140°, 96 h	 (36)	419
		CuF_2 (50 mol %), phen (50 mol %), K_2CO_3, DMF, 140°, 96 h	 (20)	419
		CuF_2 (50 mol %), phen (50 mol %), K_2CO_3, DMF, 140°, 96 h	 (87)	419
		CuF_2 (25 mol %), phen (25 mol %), K_2CO_3, DMF, 140°, 96 h	 R: H (67); Br (71)	419
C_6				
		CuI (10 mol %), DMG (30 mol %), DBU, DMSO, 110°, 7 h	 (75)	426
		CuI (10 mol %), DMG (30 mol %), DBU, DMSO, 110°, 7 h	 (90)	426

TABLE 9A. *N*-ARYLATION OF IMIDAZOLES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
I	Cu	20 mol %	Cs_2CO_3	*n*-PrCN	reflux	9 h	(95)	129
Cl	Cu/Al–hydrotalcite	2.5 mol %	K_2CO_3	DMF	100	18 h	(80)	228
Br	Cu/Al–hydrotalcite	2.5 mol %	K_2CO_3	DMF	100	18 h	(92)	228
I	Cu/Al–hydrotalcite	2.5 mol %	K_2CO_3	DMF	100	18 h	(92)	228
Cl	Cu on cellulose	2 mol %	K_2CO_3	DMSO	130	48 h	(20)	427
Br	Cu on cellulose	1 mol %	K_2CO_3	DMSO	130	24 h	(70)	427
I	Cu on cellulose	1 mol %	K_2CO_3	DMSO	130	12 h	(95)	427
Br	CuBr	2.5 mol %	K_2CO_3	NMP	160	16 h	(86)	287
I	CuBr	2.5 mol %	K_2CO_3	DMSO	160	16 h	(86)	287
Br	CuBr	10 mol %	**L9** (20 mol %), Cs_2CO_3	DMSO	75	22 h	(87)	49
I	CuBr	10 mol %	**L9** (20 mol %), Cs_2CO_3	DMSO	45	25 h	(96)	49
Br	CuBr	10 mol %	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12 h	(92)	284
I	CuBr	10 mol %	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24 h	(98)	259
I	CuI	20 mol %	K_3PO_4	DMF	40	40 h	(93)	59
I	CuI	10 mol %	K_3PO_4	DMF	110	24 h	(91)	387
Br	CuI	20 mol %	Cs_2CO_3	DMF	120	40 h	(91)	386
I	CuI	5 mol %	TBAB, KOH	—	110	6 h	(85)	428
I	CuI	5 mol %	TBAB, NaOH	toluene	reflux	22 h	(84)	391
Br	CuI	20 mol %	phen (20 mol %), KF/Al_2O_3	xylene	140	15 h	(72)	410
I	CuI	10 mol %	phen (10 mol %), KF/Al_2O_3	—	140	13 h	(92)	411
Br	CuI	20 mol %	per-6-ABCD, K_2CO_3	DMSO	110	24 h	(98)	393
I	CuI	10 mol %	PPAPM (20 mol %), K_3PO_4	DMF	100	24 h	(86)	48
I	CuI	5 mol %	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	90	12 h	(98)	396
I	CuI	5 mol %	oxazolidin-2-one (10 mmol %), NaOMe	DMSO	80	10 h	(91)	392

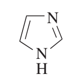
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
I	CuI	10 mol %	DMG (20 mol %), TBPE	DMSO	rt	24 h	(90)	61
I	CuI	5 mol %	L-Pro (20 mol %), K_3PO_4	dioxane	100	24 h	(90)	388
Br	CuI	10 mol %	L-His (20 mol %), K_2CO_3	DMSO	100	36 h	(82)	389
I	CuI	10 mol %	L-His (20 mol %), K_2CO_3	DMSO	100	18 h	(91)	389
Br	CuI	20 mol %	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	24 h	(84)	429
I	CuI	10 mol %	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(93)	273
Br	CuI	10 mol %	**L22** (10 mol %), K_2CO_3	DMF	110	24 h	(90)	79
Br	CuI	5 mol %	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(96)	86
Br	CuI	10 mol %	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12 h	(43)	394
I	CuI	10 mol %	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12 h	(88)	394
I	CuI	10 mol %	**L26** (10 mol %), NaOMe	DMSO	120	12 h	(85)	397
I	CuI	5 mol %	**L31** (5 mol %), Cs_2CO_3	DMF	80	24 h	(82)	415
Cl	CuI nanoparticles	1.25 mol %	K_2CO_3, air	DMF	110	16 h	(56)	285
I	CuI nanoparticles	1.25 mol %	K_2CO_3, air	DMF	110	4 h	(95)	285
I	CuI/PAnNF	5 mol %	K_2CO_3	DMF	rt	6 h	(99)	276
I	CuO	10 mol %	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30 h	(90)	130
I	CuO on acetylene black	5 mol %	KO*t*-Bu	toluene	180	18 h	(100)	226
Cl	CuO nanoparticles	10 mol %	K_2CO_3	DMF	120	24 h	(0)	64
Br	CuO	5 mol %	**L14** (50 mol %), TBAB, 2,5-hexanedione, K_3PO_4	H_2O	MW (100 W), 140	5 min	(67)	51
I	CuO	5 mol %	**L14** (50 mol %), TBAB, 2,5-hexanedione, K_3PO_4	H_2O	MW (100 W), 140	5 min	(88)	51
Br	Cu_2O	20 mol %	KOH	DMSO	130	24 h	(85)	398
Cl	Cu_2O	20 mol %	ninhydrin (30 mol %), KOH	DMSO	130	48 h	(49)	399
Br	Cu_2O	10 mol %	ninhydrin (20 mol %), KOH	DMSO	130	24 h	(91)	399
Cl	Cu_2O	10 mol %	phen (20 mol %), TBAF	—	145	24 h	(48)	68
Br	Cu_2O	10 mol %	phen (20 mol %), TBAF	—	145	24 h	(98)	68
I	Cu_2O	5 mol %	phen (10 mol %), TBAF	—	115	24 h	(98)	68
I	Cu_2O	2.5 mol %	$(MeO)_2$phen (7.5 %), PEG, Cs_2CO_3	*n*-PrCN	110	24–48 h	(95)	84
I	Cu_2O	2.5 mol %	$(MeO)_2$phen (7.5 %), PEG, Cs_2CO_3	NMP	110	3 h	(92)	430
I	Cu_2O	5 mol %	$(MeO)_2$phen (7.5 %), PEG, Cs_2CO_3	DMF	110	3 h	(95)	430, 84

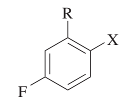
TABLE 9A. *N*-ARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

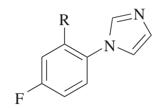
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

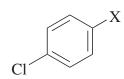




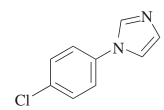
Catalyst (x mol %), DMSO



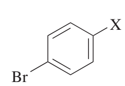
R	X	Catalyst	x	Additive(s)	Temp (°)	Time (h)		Refs.
H	Br	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	110	22	(90)	429
H	Cl	Cu_2O/Cu NP	5	Cs_2CO_3	150	18	(97)	223
F	Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	80	12	(94)	284



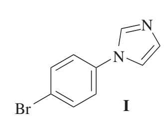
Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
Br	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	8 h	(98)	228
I	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	6 h	(99)	228
I	CuCl	5	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24 h	(92)	235
Br	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	75	24 h	(93)	49
I	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	45	23 h	(91)	49
Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	3 h	(95)	285
I	CuI	5	DMEDA (10 mol %), CsF	THF	60	24 h	(82)	63
Br	CuI	10	oxazolidin-2-one (20 mmol %), NaOMe	DMSO	120	24 h	(78)	392
Br	CuI	20	per-6-ABCD, K_2CO_3	DMSO	110	24 h	(99)	393
Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	110	24 h	(80)	230
I	CuI	5	8-HOquin (10 mol %), CsF	DMSO	100	1 h	(87)	63
I	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12 h	(87)	397
Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24 h	(87)	79
Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	130	24 h	(95)	400
Cl	Cu_2O/Cu NP	5	Cs_2CO_3	DMSO	150	18 h	(69)	223
Br	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(85)	85
I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(92)	85
Br	$Cu(OAc)_2$•H_2O	20	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	30 h	(53)	289
I	$Cu(OAc)_2$•H_2O	20	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	20 h	(99)	289
I	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	40 h	(99)	404
I	**6**	5	Cs_2CO_3	toluene	100	10 h	(90)	123



Catalyst (x mol %)



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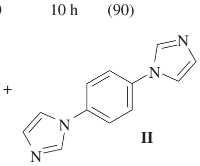


II

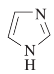
X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	**I**	**II**	Refs.
I	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	1 h	(99)	(0)	285
I	CuI	20	K_3PO_4	DMF	40	40 h	(87)	(0)	59
I	CuI	10	PPAPM (20 mol %), K_3PO_4	DMF	100	24 h	(89)	(0)	48
I	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8 h	(96)	(0)	431
I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24 h	(80)	(0)	388
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(87)	(0)	86
I	CuI	1	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12 h	(83)	(0)	394
Br	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12 h	(43)	(0)	397
I	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12 h	(76)	(0)	397
I	CuI/PAnNF	5	K_2CO_3	DMF	rt	8 h	(75)	(0)	276
Br	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), PEG, Cs_2CO_3	NMP	110	24 h	(0)	(97)	430
Br	Cu_2O	5	$(MeO)_2$phen (15 mol %), PEG, Cs_2CO_3	NMP	110	48 h	(0)	(97)	84
Br	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), PEG, Cs_2CO_3	*n*-PrCN	110	24 h	(82)[a]	(0)	430
I	Cu_2O	5	$(MeO)_2$phen (7.5 mol %), PEG, Cs_2CO_3	*n*-PrCN	110	24 h	(84)	(0)	430, 84
Br	Cu_2O	10	$(MeO)_2$phen (15 mol %), PEG, Cs_2CO_3	*n*-PrCN	110	24 h	(0)	(97)	430, 84
I	Cu_2O	5	**L35** (20 mol %)	MeCN	50	36 h	(89)	(0)	40
I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(89)	(0)	85
I	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24 h	(90)	(0)	234
I	**2**	2	NaOH, TBAB	H_2O	100	12 h	(86)	(0)	233

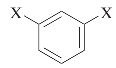
TABLE 9A. *N*-ARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

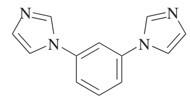
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_3

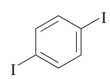




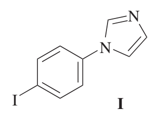
Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuO	25	K_2CO_3	DMSO	150	48	(77)	432
Br	**11**	2.5	K_2CO_3	NMP	180	16	(98)	291
I	CuI	10	CDA (40 mol %), Cs_2CO_3	dioxane	95	24	(95)	58
I	CuI	5	**L31** (5 mol %), Cs_2CO_3	DMF	100	24	(94)	415



Catalyst (x mol %)



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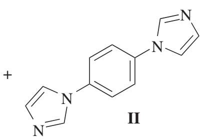
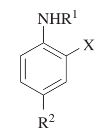
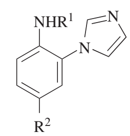


II

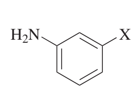
Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	I	II	Refs.
CuBr	10	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24	(85)	(0)	259
CuI	5	**L31** (5 mol %), Cs_2CO_3	DMF	100	24	(0)	(97)	415
Cu_2O	5	**L35** (20 mol %)	MeCN	82	48	(0)	(89)	40
6	5	Cs_2CO_3	toluene	100	16	(90)	(0)	123



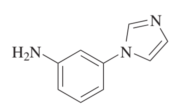
Catalyst (x mol %)



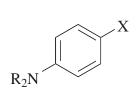
R^1	R^2	X	Catalyst	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
Ac	H	I	Cu_2O	5	phen (10 mol %), TBAF	—	115	48	(80)	68
CF_3CO	Me	Br	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	60	20	(90)	429



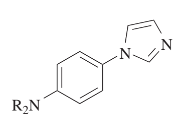
Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	20	Cs_2CO_3	DMF	120	40	(80)	386
I	CuI	20	K_3PO_4	DMF	40	40	(66)	59
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	36	(90)	393
Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(99)	412
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(85)	386
I	Cu_2O	10	KOH	DMSO	125	24	(85)	398
Br	Cu_2O	10	$(MeO)_2$phen (15 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	24	(92)	430, 84



Catalyst (x mol %)



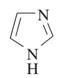
R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12	(78)	284
H	I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(69)	119
H	I	CuI	20	K_3PO_4	DMF	40	40	(73)	59
H	Br	CuI	20	Cs_2CO_3	DMF	120	40	(79)	386
H	I	CuI	5	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	90	12	(98)	396
H	Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(86)	412
H	Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24	(83)	79
H	Br	CuI	10	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(82)	86
H	Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	130	24	(85)	400
H	Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(46)	234
H	Br	cat. **2**	2	NaOH, TBAB	H_2O	100	24	(64)	233
Me	Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	130	24	(98)	400

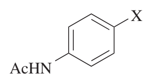
TABLE 9A. *N*-ARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

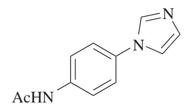
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

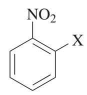




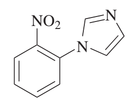
CuI (*x* mol %),



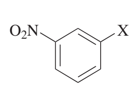
X	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	24	(72)	429
Br	10	**L22** (10 mol %), K_2CO_3	DMF	110	24	(82)	79
I	20	K_3PO_4	DMF	40	40	(98)	59



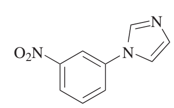
Catalyst (*x* mol %)



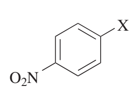
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cl	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	6	(92)	228
I	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	6	(99)	228
Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	2	(99)	285
I	CuI/PAnNF	5	K_2CO_3	DMF	rt	4	(99)	276
F	CuO nanoparticles	10	K_2CO_3	DMF	120	2	(89)	64
Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	4	(86)	64
Cl	CuO	8	K_2CO_3	pyridine	reflux	24	(64)	402
Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	3	(88)	66
Cl	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	125	12	(92)	414
Cl	**8**	25	K_2CO_3	DMSO	135	24	(90)	65
Br	**8**	25	K_2CO_3	DMSO	135	18	(90)	65
F	**7**	1	K_2CO_3	DMF	110	1.5	(93)	73
Cl	**7**	1	K_2CO_3	DMF	110	3	(91)	73



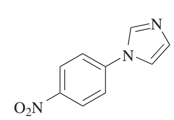
Catalyst (*x* mol %)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	CuBr	10	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24	(97)	259
I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(87)	119
Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	80	40	(72)	47
Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	17	(81)	64
Cl	CuO	8	K_2CO_3	pyridine	reflux	24	(30)	402
I	Cu_2O	2.5	(MeO)$_2$phen (7.5 mol %), Cs_2CO_3, PEG	*n*-PrCN	90	24	(92)	430, 84



Catalyst (*x* mol %)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
Cl	Cu on cellulose		K_2CO_3	DMSO	130	24 h	(95)	427
Cl	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	8 h	(90)	228
I	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	8 h	(95)	228
Br	CuCl	5	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24 h	(85)	235
Cl	CuBr	10	**L37** (20 mol %), TBAF	none	150	24 h	(trace)	80
Br	CuBr	10	**L37** (20 mol %), TBAF	none	150	24 h	(96)	80
Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	3 h	(95)	235
Cl	CuI	20	Cs_2CO_3	DMF	120	40 h	(95)	386
I	CuI	5	KOH, TBAB	—	110	4 h	(95)	428
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	18 h	(87)	393
Cl	CuI	5	*N*-hydroxyphthalimide (10 mol %), NaOMe	DMSO	110	40 h	(62)	396
Br	CuI	10	Me_2Gly (20 mol %), K_2CO_3	DMSO	MW, 162	5 min	(79)	299
Cl	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	36 h	(78)	389

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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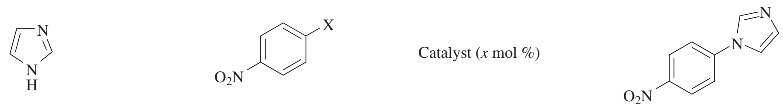
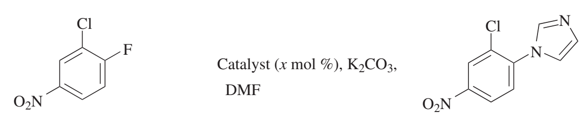
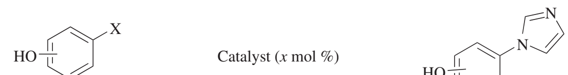


X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
Br	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	48 h	(92)	389
I	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	30 h	(91)	389
Br	CuI	10	L-Glu (20 mol %), K_3PO_4	—	MW (200 W), 130	7 h	(51)	418
Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	110	24 h	(62)	230
Cl	CuI	10	**L26** (10 mol %), NaOMe	DMSO	110	12 h	(91)	397
Cl	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(98)	86
Cl	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	30 h	(74)	412
Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24 h	(97)	79
Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24 h	(96)	417
Cl	CuI/PAnNF	5	K_2CO_3	DMF	80	6 h	(93)	276
F	CuO nanoparticles	10	K_2CO_3	DMF	120	30 min	(91)	64
Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	1.5 h	(88)	64
I	CuO nanoparticles	5	KOH	DMSO/*t*-BuOH (1:3)	110	11 h	(89)	74
Cl	CuO	8	K_2CO_3	pyridine	reflux	24 h	(54)	402
Br	Cu_2O	10	**L23** (20 mol %), Cs_2CO_3	DMF	130	24 h	(70)	400
I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(89)	85
Br	$Cu(OAc)_2$•H_2O	20	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	30 h	(70)	289
I	$Cu(OAc)_2$•H_2O	20	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	30 h	(99)	289
Cl	$Cu(OAc)_2$•H_2O	15	(–)-sparteine (30 mol %), K_2CO_3	DMF	130	36 h	(48)	290
Br	$Cu(OAc)_2$•H_2O	15	(–)-sparteine (30 mol %), K_2CO_3	DMF	130	36 h	(83)	290
Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24 h	(95)	234
Cl	Cu(II)-NaY zeolite	10	K_2CO_3	DMF	120	20 h	(92)	404
Cl	$[Cu(\mu\text{-}I)((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	125	12 h	(91)	414
Br	$[Cu(\mu\text{-}I)((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	115	6 h	(96)	414
F	Cu fluorapatite	7	K_2CO_3	DMF	120	30 min	(85)	66
Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	1 h	(90)	66
Br	Cu fluorapatite	12.5	none	DMSO	110	4 h	(95)	227
Br	**3**	2	NaOH, TBAB	H_2O	100	12 h	(85)	233
I	**3**	2	NaOH, TBAB	H_2O	100	12 h	(93)	233
Br	**6**	5	Cs_2CO_3	toluene	100	12 h	(90)	123
I	**6**	5	Cs_2CO_3	toluene	100	3 h	(90)	123
Cl	**8**	25	K_2CO_3	DMSO	135	24 h	(95)	65
Br	**8**	25	K_2CO_3	DMSO	135	18 h	(96)	65
F	**7**	1	K_2CO_3	DMF	110	1 h	(95)	73
Cl	**7**	1	K_2CO_3	DMF	110	1.5 h	(94)	73



Catalyst	x	Temp (°)	Time (h)		Refs.
Cu fluorapatite	7	120	1	(85)	66
7	1	110	3	(91)	73



Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	48	(61)	86
2	Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(74)	412
4	Br	CuI	20	Cs_2CO_3	DMF	120	40	(85)	386
4	I	CuI	20	K_3PO_4	DMF	40	40	(63)	59
4	Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(97)	412
4	Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(70)	86
4	Br	Cu_2O	5	$(MeO)_2$phen (15 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	24	(84)	430, 84
4	Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	130	24	(95)	400
4	Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(38)	234
4	Br	cat. **2**	2	NaOH, TBAB	H_2O	100	24	(58)	233

TABLE 9A. *N*-ARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the **bold** *numbers.*

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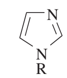
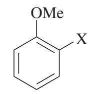
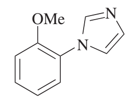
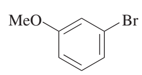




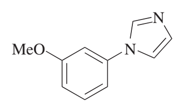
Catalyst (x mol %)



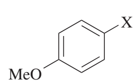
R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	Yield (%)	Refs.
H	I	Cu on cellulose	1	K_2CO_3	DMSO	130	12 h	(40)	427
H	I	CuI	20	K_3PO_4	DMF	40	40 h	(78)	59
H	Br	CuI	20	Cs_2CO_3	DMF	120	40 h	(57)	386
H	Br	CuI	10	L-Lys (20 mol %), K_3PO_4	—	MW (200 W), 130	6.5 h	(95)	418
H	I	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8 h	(93)	431
H	Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	48 h	(78)	386
H	Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	6 h	(90)	412
H	I	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	110	24 h	(90)	399
H	Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	130	24 h	(72)	400
H	I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(92)	85
H	Br	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	115	24 h	(72)	414
H	I	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	115	12 h	(92)	414
Na	I	CuI	10	none	DMF	150	4 h	(47)	433



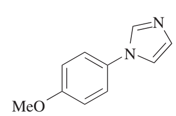
Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	Yield (%)	Refs.
I	CuI	10	DMG (20 mol %), TBPE	DMSO	rt	24 h	(93)	61
Br	CuI	10	L-Lys (20 mol %), K_3PO_4	—	MW (200 W), 130	5 h	(99)	418
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	18 h	(90)	393
Br	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	130	24 h	(90)	399
Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	130	24 h	(91)	400
I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(90)	85
Br	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	115	12 h	(86)	414



Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time	Yield (%)	Refs.
I	Cu on cellulose	1	K_2CO_3	DMSO	130	12 h	(89)	427
Cl	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	8 h	(59)	228
I	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	8 h	(90)	228
I	CuF_2	50	phen (50 mol %), K_2CO_3	DMF	140	96 h	(80)	419
Br	CuBr	2.5	K_2CO_3	NMP	160	16 h	(91)	287
Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12 h	(85)	284
I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24 h	(78)	119
Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	5 h	(95)	285
Br	CuI	20	Cs_2CO_3	DMF	120	40 h	(89)	386
I	CuI	20	K_3PO_4	DMF	40	40 h	(95)	59
I	CuI	5	KOH, TBAB	—	110	6 h	(93)	428
I	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8 h	(95)	431
I	CuI	10	PPAPM (20 mol %), K_3PO_4	DMF	100	24 h	(85)	48
Br	CuI	5	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	110	40 h	(88)	396
Br	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	12 h	(83)	392
I	CuI	10	CDA(20 mol %), K_3PO_4	[C_4mim][BF_4]	110	12 h	(75)	232
Br	CuI	20	phen (20 mol %), KF/Al_2O_3	xylene	140	16 h	(89)	410
I	CuI	10	phen (10 mol %), KF/Al_2O_3	—	140	15 h	(94)	411
Br	CuI	10	DMG (20 mol %), K_2CO_3	DMSO	110	45 h	(95)	47
Br	CuI	10	DMG (20 mol %), K_2CO_3	DMSO	MW, 171	0.25 h	(61)	299
Br	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	24 h	(73)	429
Br	CuI	10	L-Lys (20 mol %), K_3PO_4	—	MW (200 W), 130	5 h	(99)	418
Br	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	48 h	(70)	389
I	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	30 h	(86)	389
Br	CuI	20	L-Pro (20 mol %), K_3PO_4	DMF	140	48 h	(75)	388

TABLE 9A. *N*-ARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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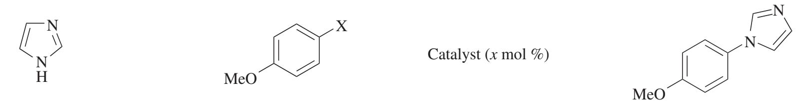
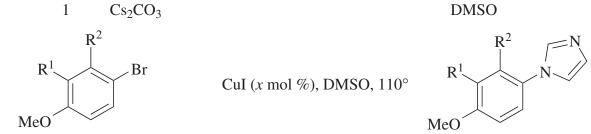


X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24 h	(40)	388
I	CuI	5	L-Pro (10 mol %), K_2CO_3	DMSO	90	36 h	(91)	401, 47
Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	36 h	(85)	79
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(88)	86
Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60 h	(97)	412
Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24 h	(30)	417
I	CuI	10	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(81)	273
I	CuI/PAnNF	5	K_2CO_3	DMF	rt	12 h	(65)	276
Br	CuO	5	**L14** (50 mol %), TBAB, 2,5-hexanedione, K_3PO_4	H_2O	MW (100 W), 140	5 min	(89)	51
I	CuO	5	**L14** (50 mol %), TBAB, 2,5-hexanedione, K_3PO_4	H_2O	MW (100 W), 140	5 min	(77)	51
I	CuO nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	11 h	(64)	74
I	Cu_2O	10	KOH	DMSO	125	24 h	(90)	398
Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24 h	(89)	68
I	Cu_2O	5	phen (10 mol %), TBAF	—	115	48 h	(90)	68
I	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	110	24 h	(89)	399
Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	130	24 h	(92)	400
I	Cu_2O	5	**L27** (20 mol %)	MeCN	82	72 h	(97)	40
Cl	Cu_2O/Cu NP	5	Cs_2CO_3	DMSO	150	18 h	(0)	223
Br	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(87)	85
I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(92)	85
I	$Cu(OTf)_2$•C_6H_6	10	phen (1 eq), dba, Cs_2CO_3	xylenes	110	48 h	(96)	11
Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24 h	(32)	234
I	Cu(IPr)Cl	10	Cs_2CO_3	DMSO	100	24 h	(67)	421
Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	36 h	(52)	66
Br	$[Cu(\mu\text{-I})((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	115	12 h	(85)	414
I	$[Cu(\mu\text{-I})((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	115	7 h	(95)	414
Br	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	48 h	(85)	404
I	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	36 h	(99)	404
Br	**8**	25	K_2CO_3	DMSO	135	48 h	(89)	65
I	**8**	25	K_2CO_3	DMSO	135	24 h	(88)	65
Br	**6**	5	Cs_2CO_3	toluene	100	24 h	(20)	123
I	**6**	5	Cs_2CO_3	toluene	100	16 h	(94)	123
Br	**2**	2	NaOH, TBAB	H_2O	100	24 h	(41)	233
I	**10**	1	Cs_2CO_3	DMSO	100	24 h	(50)	420



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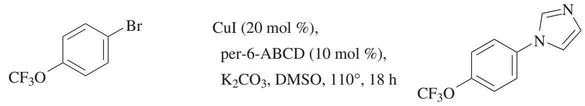
R1	R2	*x*	Additive(s)	Time (h)		Refs.
H	MeO	10	DMG (20 mol %), K_2CO_3	40	(62)	47
MeO	H	20	D-glucosamine (40 mol%), Cs_2CO_3	24	(79)	429



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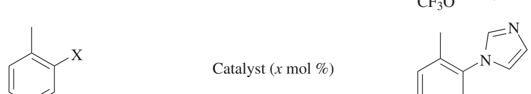

X	Catalyst	*x*	Additives	Solvent(s)	Temp (°)	Time (h)		Refs.
Cl	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	19	(18)	228
I	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	19	(65)	228
I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(65)	119
Br	CuI	20	Cs_2CO_3	DMF	120	40	(75)	386
I	CuI	5	KOH, TBAB	—	110	8	(55)	428
Br	CuI	20	phen (20 mol %), KF/Al_2O_3	xylene	140	18	(80)	410
Br	CuI	10	L-Lys (20 mol %), K_3PO_4	—	MW (200 W), 130	6.5	(95)	418
Br	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	48	(55)	429
Br	CuI	10	8-HOquin (20 mol %), TEAC	DMF/H_2O	130	16	(47)	434
I	CuI	10	8-HOquin (10 mol %), TEAC	DMF	130	16	(74)	434
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24	(95)	393
I	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8	(92)	431
Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(89)	412

TABLE 9A. *N*-ARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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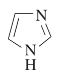
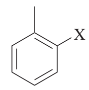
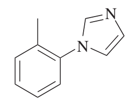
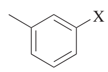




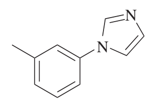
Catalyst (x mol %)



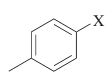
X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield	Refs.
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(78)	86
Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24	(81)	79
I	Cu_2O	10	KOH	DMSO	125	24	(88)	398
Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(84)	68
I	Cu_2O	5	phen (10 mol %), TBAF	—	115	48	(81)	68
Br	Cu_2O	10	$(MeO)_2$phen (15 mol %), Cs_2CO_3	NMP	110	24	(85)	430, 84
I	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	110	24	(89)	399
I	Cu_2O	5	**L35** (20 mol %)	MeCN	82	36	(92)	40
Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	130	24	(92)	400
I	$Cu(TMHD)_2$	20	KO*t*-Bu	DMF	120	24	(74)	308
Br	cat. **8**	25	K_2CO_3	DMSO	135	48	(60)	65
I	cat. **8**	25	K_2CO_3	DMSO	135	38	(75)	435
I	cat. **6**	5	Cs_2CO_3	toluene	100	24	(79)	123



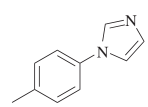
Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield	Refs.
I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(75)	119
I	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8	(98)	431
Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	110	24	(75)	230
Cl	CuI	10	8-HOquin (20 mol %), TEAC	DMF/H_2O	130	60	(40)	434
I	Cu_2O	10	KOH	DMSO	125	24	(90)	398
I	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	110	24	(91)	399



Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
Cl	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	12	(27)	228
I	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	12	(89)	228
I	CuCl	5	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24	(88)	235
Br	CuBr	2.5	K_2CO_3	NMP	160	16	(89)	287
I	CuBr	10	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24	(85)	259
Br	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	75	28	(90)	49
Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12	(80)	284
Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	14	(36)	285
Br	CuI	20	Cs_2CO_3	DMF	120	40	(80)	386
I	CuI	20	K_3PO_4	DMF	40	40	(80)	59
I	CuI	5	KOH, TBAB	—	110	8	(70)	428
I	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8	(96)	431
Br	CuI	5	*N*-hydroxyphthalimide (10 mol %), NaOMe	DMSO	110	40	(73)	396
Br	CuI	20	L-Pro (20 mol %), K_3PO_4	DMF	140	48	(89)	388
I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(88)	388
Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	110	24	(82)	230
Br	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	48	(71)	389
I	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	110	30	(89)	389
Br	CuI	20	L-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	24	(80)	429
Br	CuI	10	L-Lys (20 mol %), K_3PO_4	—	MW (200 W), 130	2.5	(49)	418
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24	(96)	393
I	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12	(48)	397
I	CuI	10	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24	(90)	273
Br	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(43)	394
Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24	(84)	79

TABLE 9A. *N*-ARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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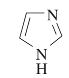
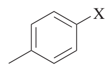
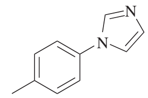
C_3

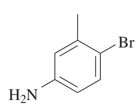




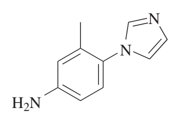
Catalyst (*x* mol %)



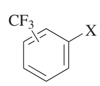
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(89)	86
Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60 h	(98)	412
I	CuI/PAnNF	5	K_2CO_3	DMF	rt	14 h	(55)	276
Br	CuO	5	**L14** (50 mol %), TBAB, 2,5-hexanedione, K_3PO_4	H_2O	MW (100 W), 140	5 min	(76)	51
Br	Cu_2O	20	KOH	DMSO	130	24 h	(88)	398
I	Cu_2O	10	KOH	DMSO	125	24 h	(91)	398
I	Cu_2O	5	phen (10 mol %), TBAF	—	115	24 h	(94)	68
Cl	Cu_2O	20	ninhydrin (30 mol %), KOH	DMSO	130	48 h	(46)	399
I	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	110	24 h	(91)	399
Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	130	24 h	(99)	400
I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(91)	85
Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	48 h	(47)	234
I	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24 h	(78)	234
Br	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	36 h	(90)	404
I	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	24 h	(99)	404
Br	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	115	12 h	(88)	414
Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	36 h	(85)	66
Br	**8**	25	K_2CO_3	DMSO	135	24 h	(91)	65
I	**6**	5	Cs_2CO_3	toluene	100	8 h	(90)	123
Br	**2**	2	NaOH, TBAB	H_2O	100	24 h	(47)	233
I	**2**	2	NaOH, TBAB	H_2O	100	12 h	(78)	233
I	**10**	3	Cs_2CO_3	DMSO	100	24 h	(93)	421
I	**10**	1	Cs_2CO_3	DMSO	100	24 h	(20)	420



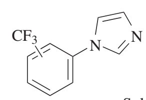
CuI (20 mol %),
per-6-ABCD (10 mol%),
K_2CO_3, DMSO,
110°, 24 h



(81) 393



Catalyst (*x* mol %)

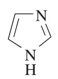


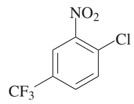
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
2	Cl	Cu/Al-hydrotalcite	2.5	K_2CO_3	DMF	100	7 h	(97)	228
2	I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(trace)	85
3	I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24 h	(85)	119
3	I	CuI	10	phen (10 mol %), KF/Al_2O_3	—	140	11 h	(98)	411
3	Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	18 h	(93)	393
3	I	Cu_2O	10	KOH	DMSO	110	16 h	(92)	398
3	I	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	90	16 h	(92)	399
3	I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(94)	85
3	I	$Cu(OTf)_2$•C_6H_6	10	phen (1 eq), dba, Cs_2CO_3	xylenes	110	24 h	(94)	11
4	Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	5 h	(95)	285
4	Cl	CuI	5	*N*-hydroxymaleimide (10 mol %), NaOMe	DMSO	110	24 h	(48)	396
4	Br	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24 h	(45)	392
4	Br	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	24 h	(72)	429
4	Cl	Cu_2O	10	KOH	DMSO	130	24 h	(88)	398
4	Br	Cu_2O	10	KOH	DMSO	110	24 h	(90)	398
4	Cl	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	130	24 h	(90)	399
4	Br	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	110	24 h	(91)	399
4	Br	Cu_2O	5	**L27** (20 mol %)	MeCN	82	72 h	(94)	40
4	I	Cu_2O	5	**L35** (20 mol %)	MeCN	50	24 h	(100)	40
4	Cl	Cu_2O/Cu NP	5	Cs_2CO_3	DMSO	150	18 h	(90)	223
4	Br	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(87)	85
4	I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(92)	85
4	Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24 h	(88)	234
4	Cl	Cu(II)-NaY zeolite	10	K_2CO_3	DMF	120	30 h	(97)	404
4	Cl	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	125	15 h	(89)	414
4	Cl	**8**	25	K_2CO_3	DMSO	135	30 h	(85)	65
4	Br	**2**	2	NaOH, TBAB	H_2O	100	12 h	(88)	233

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

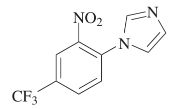
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

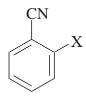




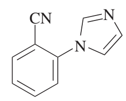
CuI (10 mol %), 12 h



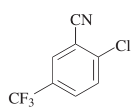
Additives	Solvent	Temp (°)		Refs.
L21 (20 mol %), Cs_2CO_3	MeCN	reflux	(79)	394
L21 (20 mol %), Cs_2CO_3	MeCN	reflux	(43)	397
L26 (10 mol %), NaOMe	DMSO	130	(90)	397



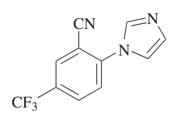
Catalyst (*x* mol %)



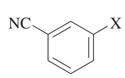
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cl	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	12	(99)	228
Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	2	(87)	285
Cl	CuI	5	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	110	24	(52)	396
F	CuO nanoparticles	10	K_2CO_3	DMF	120	1.5	(91)	64
Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	12	(91)	64
Cl	CuO	8	K_2CO_3	pyridine	reflux	50	(43)	402
F	Cu fluorapatite	7	K_2CO_3	DMF	120	1	(82)	66
Cl	$[Cu(\mu\text{-}I)((-)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	125	14	(86)	414
F	**7**	1	K_2CO_3	DMF	110	1.5	(92)	73
Cl	**7**	1	K_2CO_3	DMF	110	5	(88)	73
Cl	**8**	25	K_2CO_3	DMSO	135	24	(84)	65



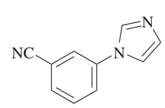
Catalyst (*x* mol %), K_2CO_3, DMF



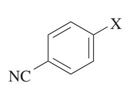
Catalyst	*x*	Temp (°)	Time (h)		Refs.
Cu fluorapatite	7	120	3	(92)	66
cat. **7**	1	110	2	(95)	73



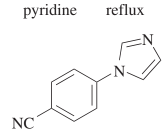
Catalyst (*x* mol %)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	CuBr	10	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24	(93)	259
I	CuI	5	8-HOquin (10 mol %), CsF	DMSO	80	4	(85)	63
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	18	(99)	393
I	Cu_2O	5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	MeCN	80	24	(95)	430, 84
Br	CuO	8	K_2CO_3	pyridine	reflux	50	(13)	402



Catalyst (*x* mol %)

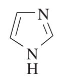


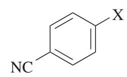
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cl	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	8	(95)	228
Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12	(94)	284
Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	4	(65)	285
Cl	CuI	20	Cs_2CO_3	DMF	120	40	(90)	386
Br	CuI	20	Cs_2CO_3	DMF	120	40	(98)	386
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	36	(93)	336
I	CuI	5	L-Pro (10 mol %), K_2CO_3	DMSO	80	34	(93)	401

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

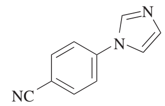
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_3

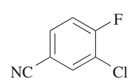




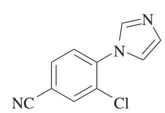
Catalyst (x mol %)



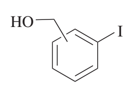
X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	Yield (%)	Refs.
Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	80	48 h	(97)	47
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	80	34 h	(93)	47
Br	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	36 h	(43)	389
Cl	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(92)	86
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(95)	86
Cl	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	30 h	(97)	412
Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	90	60 h	(95)	412
Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24 h	(68)	417
F	CuO nanoparticles	10	K_2CO_3	DMF	120	12 h	(83)	64
Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	12 h	(84)	64
Br	CuO	8	K_2CO_3	pyridine	reflux	50 h	(73)	402
I	Cu_2O	10	KOH, 4 Å MS	DMSO	100	24 h	(88)	398
Br	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(92)	85
I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(94)	85
Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24 h	(82)	234
Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	6 h	(95)	66
Cl	Cu(II)-NaY zeolite	10	K_2CO_3	DMF	120	24 h	(99)	404
Cl	$[Cu(\mu\text{-I})((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	125	14 h	(89)	414
Br	$[Cu(\mu\text{-I})((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	115	7 h	(95)	414
Br	**2**	2	NaOH, TBAB	H_2O	100	12 h	(82)	233
F	**7**	1	K_2CO_3	DMF	110	1 h	(96)	73
Cl	**7**	1	K_2CO_3	DMF	110	6 h	(90)	73



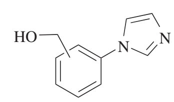
CuO nanoparticles (10 mol %), K_2CO_3, DMF, 120°, 1.5 h



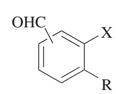
(85) 64



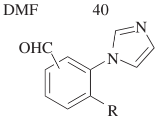
Catalyst (x mol %)



Isomer	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
2	Cu_2O	5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	24	(94)	430, 84
3	CuI	20	K_3PO_4	DMF	40	40	(54)	59



Catalyst (x mol %)



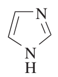
Isomer	R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	Yield (%)	Refs.
2	H	Cl	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	8 h	(90)	228
2	H	Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12 h	(77)	284
2	H	Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	6 h	(99)	285
4	H	Cl	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	10 h	(73)	228
4	H	Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	2 h	(87)	285
4	H	I	CuI	20	K_3PO_4	DMF	40	40 h	(98)	59
4	H	Br	CuI	10	DMG (20 mol %), K_2CO_3	DMSO	MW, 169	5 min	(86)	299
4	H	Br	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	36 h	(86)	389
4	H	Br	CuI	5	**L31** (5 mol %), Cs_2CO_3	DMF	100	24 h	(92)	415
4	H	Br	CuI	10	**L22** (10 mol %, K_2CO_3	DMF	110	24 h	(94)	79
4	H	F	CuO nanoparticles	10	K_2CO_3	DMF	120	2 h	(85)	64
4	H	Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	18 h	(83)	64
4	H	Cl	Cu_2O/Cu NP	5	Cs_2CO_3	DMSO	150	18 h	(85)	223
4	H	Br	$Cu(OAc)_2•H_2O$	20	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	20 h	(32)	289
4	H	F	Cu fluorapatite	7	K_2CO_3	DMF	120	1 h	(80)	66
4	H	Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	10 h	(82)	66
4	H	Cl	$[Cu(\mu\text{-I})((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	125	18 h	(75)	414
4	H	Br	$[Cu(\mu\text{-I})((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	115	8 h	(91)	414
4	H	Br	**8**	25	K_2CO_3	DMSO	135	30 h	(70)	435
4	H	F	**7**	1	K_2CO_3	DMF	110	1.5 h	(93)	73
4	H	Cl	**7**	1	K_2CO_3	DMF	110	6 h	(88)	73
4	Cl	F	CuO nanoparticles	10	K_2CO_3	DMF	120	2 h	(94)	64

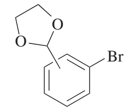
TABLE 9A. *N*-ARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

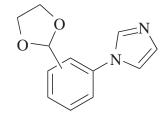
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_3

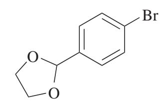




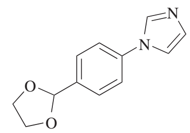
1. NaH, DMF
2. Cu (10 mol %), 150°, 4 h



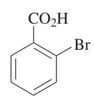
Isomer		
2	(87)	436
3	(84)	
4	(65)	



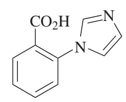
CuI (10 mol %), DMG (20 mol %), K_2CO_3, DMSO, MW, 173°, 15 min



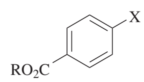
(69) 299



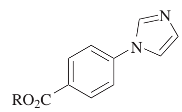
CuCl (5 mol %), **L17** (10 mol %), TBAB, NaOH, H_2O, 100°, 24 h



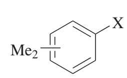
(97) 235



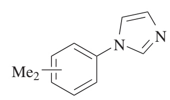
Catalyst (*x* mol %)



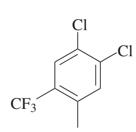
R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
Me	I	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(89)	85
Et	Br	CuI	20	Cs_2CO_3	DMF	120	40 h	(69)	386
Et	I	CuI	20	K_3PO_4	DMF	40	40 h	(91)	59
Et	Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(61)	86
Et	Br	CuI	5	8-HOquin (10 mol %), CsF	DMSO	100	7 h	(65)	63
Et	I	Cu_2O	10	KOH, 4 Å MS	DMSO	100	24 h	(85)	398
Et	I	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, 3 Å MS, PEG	MeCN	80	24–48 h	(87)	430, 84



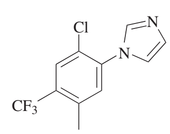
Catalyst (*x* mol %)



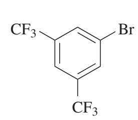
Isomer	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
2,4	I	CuI	5	KOH, TBAB	—	110	7	(65)	428
2,5	Br	$Cu(OTf)_2•C_6H_6$	10	phen (1 eq), dba, Cs_2CO_3	xylenes	125	48	(79)	11
3,4	Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	110	24	(70)	230
3,5	I	CuCl	5	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24	(87)	235
3,5	Br	CuI	10	8-HOquin (10 mol %), Cs_2CO_3	DMF/H_2O	130	16	(80)	434
3,5	I	CuI	5	phen (10 mol %), Cs_2CO_3	dioxane	110	24	(91)	128, 115
3,5	Br	Cu_2O	20	KOH	DMSO	130	24	(90)	398
3,5	Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(86)	68
3,5	Br	$Cu(OTf)_2•C_6H_6$	10	phen (1 eq), dba, Cs_2CO_3	xylenes	125	36	(99)	11
3,5	I	$Cu(OTf)_2•C_6H_6$	10	phen (1 eq), dba, Cs_2CO_3	xylenes	110	30	(96)	11



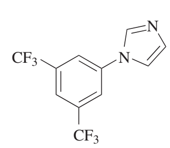
CuI (10 mol %), **L26** (10 mol %), NaOMe, DMSO, 130°, 12 h



(50) 397



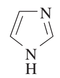
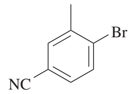
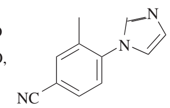
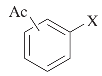
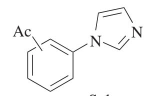
CuI (*x* mol %), Cs_2CO_3



x	Additive	Solvent	Temp (°)	Time (h)		Refs.
20	D-glucosamine (40 mol %)	DMSO	110	20	(91)	429
10	**L21** (20 mol %)	MeCN	reflux	12	(39)	394

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)		Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3 		CuI (20 mol%), per-6-ABCD (10 mol %), K_2CO_3, DMSO, 110°, 18 h		(85)	393
		Catalyst (*x* mol %)			

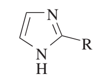
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		
2	Br	CuO	8	K_2CO_3	pyridine	reflux	7 h	(33)	402
3	Br	CuI	10	L-Lys (20 mol%), K_3PO_4	—	MW (200 W), 130	5 h	(73)	418
3	Br	CuO	8	K_2CO_3	pyridine	reflux	48 h	(68)	402
4	Cl	Cu on cellulose	1	K_2CO_3	DMSO	130	24 h	(50)	427
4	Br	Cu on cellulose	1	K_2CO_3	DMSO	130	24 h	(70)	427
4	I	Cu/Al-hydrotalcite	2.5	K_2CO_3	DMF	100	18 h	(95)	228
4	Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12 h	(95)	284
4	Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	5 h	(99)	285
4	Br	CuI	20	Cs_2CO_3	DMF	120	40 h	(92)	386
4	Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	18 h	(94)	393
4	Br	CuI	10	DACA (20 mol %), K_3PO_4	$[C_4mim][BF_4]$	110	12 h	(100)	232
4	Br	CuI	10	Me_2Gly (20 mol %), K_2CO_3	DMSO	MW, 169	5 min	(88)	299
4	I	CuI	10	Me_2Gly (20 mol %), Bu_4POAc	DMSO	rt	24 h	(96)	61
4	Br	CuI	10	L-Glu (20 mol %), K_3PO_4	—	MW (200 W), 130	6,5 h	(69)	418
4	Br	CuI	20	L-Pro (20 mol %), K_3PO_4	DMF	140	48 h	(90)	388
4	I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24 h	(97)	388
4	Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	95	40 h	(93)	47
4	Br	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	36 h	(83)	389
4	I	CuI	10	**L6** (20 mol %), Cs_2CO_3	DMF	rt	24 h	(95)	273
4	Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(99)	86
4	Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	90	60 h	(92)	412
4	Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24 h	(98)	79
4	Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24 h	(98)	417
4	Br	CuI	5	**L31** (5 mol %), Cs_2CO_3	DMF	100	24 h	(84)	415

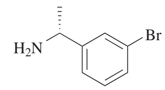
4	F	CuO nanoparticles	10	K_2CO_3	DMF	120	2 h	(83)	64
4	Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	12 h	(89)	64
4	Br	CuO	8	K_2CO_3	pyridine	reflux	48 h	(82)	402
4	Br	CuO	5	**L14** (50 mol %), TBAB, 2,5-hexanedione, K_3PO_4	H_2O	MW (100 W), 140	5 min	(77)	51
4	I	CuO	5	**L14** (50 mol %), TBAB, 2,5-hexanedione, K_3PO_4	H_2O	MW (100 W), 140	5 min	(84)	51
4	Cl	Cu_2O/Cu NP	5	Cs_2CO_3	DMSO	150	18 h	(91)	223
4	Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24 h	(100)	68
4	Br	Cu_2O	10	$(MeO)_2$phen (15 mol %), PEG, Cs_2CO_3	*n*-PrCN	110	24 h	(90)	430, 84
4	Br	Cu_2O	10	**L23** (20 mol %), Cs_2CO_3	DMF	130	24 h	(73)	400
4	Br	$Cu(OAc)_2$•H_2O	20	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	20 h	(49)	289
4	Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24 h	(69)	234
4	Cl	Cu(IPr)Cl	10	Cs_2CO_3	DMSO	100	24 h	(56)	421
4	Br	Cu(IPr)Cl	10	Cs_2CO_3	DMSO	100	24 h	(86)	421
4	I	Cu(IPr)Cl	10	Cs_2CO_3	DMSO	100	24 h	(86)	421
4	Cl	$[Cu(\mu\text{-}I)((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	125	17 h	(79)	414
4	Br	$[Cu(\mu\text{-}I)((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	115	7 h	(97)	414
4	Cl	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	48 h	(95)	404
4	Br	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	20 h	(99)	404
4	Br	**2**	2	NaOH, TBAB	H_2O	100	12 h	(79)	233
4	Br	**6**	5	Cs_2CO_3	toluene	100	18 h	(90)	123
4	I	**6**	5	Cs_2CO_3	toluene	100	4 h	(92)	123
4	Cl	**8**	25	K_2CO_3	DMSO	135	40 h	(81)	65
4	Br	**8**	25	K_2CO_3	DMSO	135	30 h	(85)	65
4	Cl	**10**	1	Cs_2CO_3	DMSO	100	24 h	(50)	420
4	Br	**10**	1	Cs_2CO_3	DMSO	100	24 h	(70)	420
4	I	**10**	1	Cs_2CO_3	DMSO	100	24 h	(99)	420

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

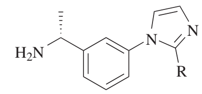
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{3-4}



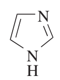


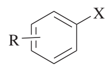
CuI (10 mol %), K_2CO_3, NMP, MW, 195°, 2 h



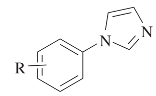
R	Time (h)		Refs.
H	2	(76)	406
Me	3	(68)	

C_3

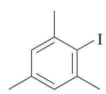




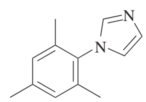
Catalyst (*x* mol %)



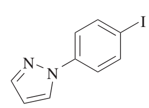
R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
4-Et	Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	90	60	(91)	412
4-HC≡C	I	CuI	20	K_3PO_4	DMF	40	40	(82)	59
4-*n*-Pr	Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12	(84)	284
2-*i*-Pr	I	Cu_2O	5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	24	(94)	430, 84
3-*i*-Pr	I	Cu_2O	5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	24	(94)	430
4-*t*-Bu	Br	Cu_2O	5	$(MeO)_2$phen (15 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	48	(93)	84
4-*t*-Bu	I	$(CuOTf)_2$•C_6H_6	10	phen (1 eq), dba, Cs_2CO_3	xylenes	110	24	(97)	11



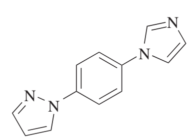
Catalyst (*x* mol %), Cs_2CO_3



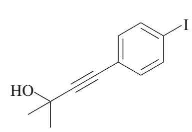
Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
CuI	10	DMEDA (40 mol %)	DMF	170	48	(54)	58
CuI	10	EDA (40 mol %)	DMF	170	48	(50)	58
Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), PEG	DMSO	150	24	(44)	84



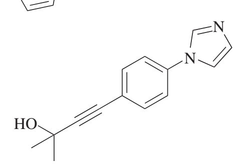
Cu_2O (5 mol%), **L35** (20 mol %), MeCN, 82°, 24 h



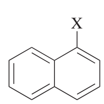
(100) 40



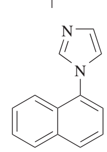
CuI (20 mol %), K_3PO_4, DMF, 40°, 40 h



(93) 59



Catalyst (*x* mol %)

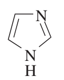


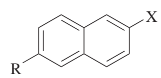
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	20	Cs_2CO_3	DMF	120	40	(56)	386
Br	CuI	10	CDA (40 mol %), Cs_2CO_3	dioxane	95	24	(57)	58
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24	(86)	393
I	CuI	10	phen (10 mol %), KF/Al_2O_3	—	140	15	(74)	411
Br	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	24	(68)	429
Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	48	(77)	79
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(66)	86
Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(62)	412
I	Cu_2O	10	KOH	DMSO	110	24	(90)	398
I	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	100	24	(90)	399
I	Cu_2O	10	$(MeO)_2$phen (15 mol %), Cs_2CO_3	NMP	110	24	(93)	430, 84
Br	Cu_2O	10	**L20** (20 mol %), Cs_2CO_3	DMSO	80	12	(68)	284
Br	Cu_2O	10	**L23** (20 mol %), KO*t*-OBu	DMF	130	24	(92)	400

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

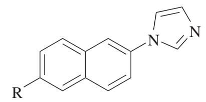
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

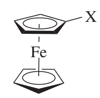




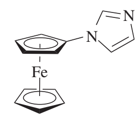
CuI (x mol %)



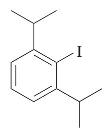
R	X	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	Br	10	EDA (40 mol %), Cs_2CO_3	DMF	170	48	(80)	58
H	Br	10	DMEDA (40 mol %), Cs_2CO_3	DMF	170	48	(80)	437
H	Br	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24	(90)	393
H	Br	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	22	(86)	429
H	I	10	**L26** (10 mol %), NaOMe	DMSO	130	24	(48)	397
MeO	Br	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	110	24	(85)	230



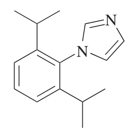
Catalyst (x amount), DMSO, 90°



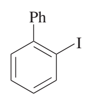
X	Catalyst	x	Additive	Time (h)		Refs.
I	CuI	1 eq	K_2CO_3	18	(31)	372
Br	$Cu(TMHD)_2$	20 mol %	KO*t*-Bu	12	(22)	407
I	$Cu(TMHD)_2$	10 mol %	KO*t*-Bu	12	(46)	407



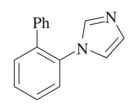
CuI (10 mol %), EDA (40 mol %), Cs_2CO_3, DMF, 170°, 48 h



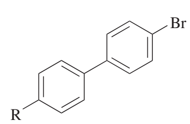
(19) 58



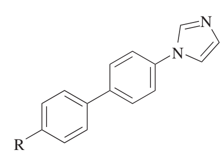
Cu_2O (10 mol %), $(MeO)_2$phen (15 mol %), Cs_2CO_3, PEG, *n*-PrCN, 110°, 24 h



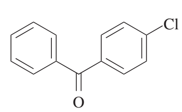
(94) 430, 84



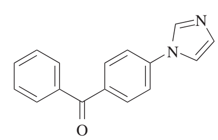
CuI (10 mol %), DMSO



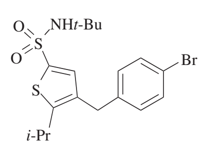
R	Additives	Temp (°)	Time (h)		Refs.
H	DMG (20 mol %), K_2CO_3	110	40	(81)	47
Br	**L26** (10 mol %), NaOMe	130	12	(40)	397



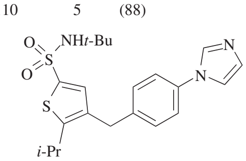
Catalyst (x mol %), K_2CO_3, DMF



Catalyst	x	Temp (°)	Time (h)		Refs.
CuO nanoparticles	10	120	11	(87)	64
Cu fluorapatite	7	120	6	(88)	66
cat. **7**	1	110	5	(88)	73



CuI (1 mol %), DMCDA (4 mol %), Cs_2CO_3, DMF, MW, 180°, 40 min

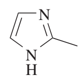


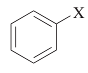
(27) 438

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

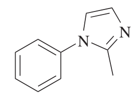
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

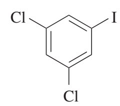




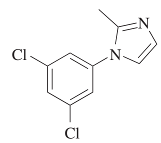
Catalyst (*x* amount)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
Br	CuBr	10 mol %	**L20** (20 mol %), Cs_2CO_3	DMSO	90	24 h	(73)	284
I	CuI	5 mol %	TBAB, KOH	—	110	7 h	(78)	428
Br	CuI	10 mol %	**L22** (10 mol %), K_2CO_3	DMF	110	24 h	(63)	79
Br	CuI	20 mol %	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24 h	(86)	393
Br	CuI	10 mol %	**L28** (20 mol %), K_2CO_3	DMSO	120	60 h	(68)	412
Br	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(53)	85
I	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(62)	85

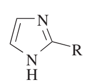


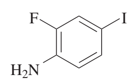
Catalyst (5 mol %), 24 h



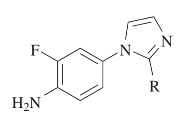
Catalyst	Additives	Solvent	Temp (°)		Refs.
CuI	8-HOquin (10 mol %), CsF	DMSO	100	(78)	63
Cu_2O	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	(84)	430, 84

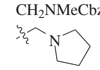
C_{4-8}



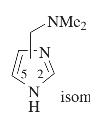


CuI (20 mol %), K_2CO_3, DMSO, 120°, 12 h

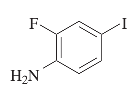


R		Refs.
Me	(53)	439
Et	(55)	
i-Pr	(50)	
CH_2NMe_2	(67)	
$CH_2NMeCbz$	(65)	
	(55)	

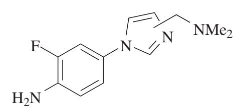
C_4



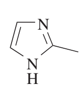
isomer 2, 4, or 5

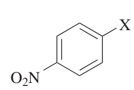


CuI, DMSO, 8-HOquin, K_2CO_3, 130°

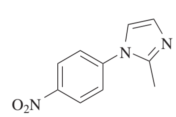


(—) 424

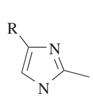


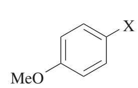


Catalyst (*x* mol %)

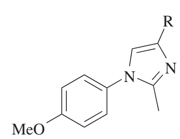


X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Cl	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12	(43)	397
I	CuO nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	11	(83)	74
Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(85)	234
Br	cat. **2**	2	NaOH, TBAB	H_2O	100	12	(82)	233





Catalyst (*x* mol %)

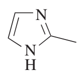


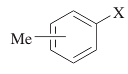
R	X	Catalyst	*x*	Additve(s)	Solvent(s)	Temp (°)	Time		Refs.
H	I	CuO nanoparticles	10	KOH	*t*-BuOH/DMSO (3:1)	110	11 h	(86)	74
H	Br	CuO	5	**L14** (50 mol %), TBAB, 2,5-hexanedione, K_3PO_4	H_2O	MW (100 W), 140	5 min	(70)	51
H	I	$Cu(OTf)\bullet C_6H_6$	10	phen (1 eq), dba, Cs_2CO_3	xylenes	125	48 h	(62)	11
Br	I	Cu_2O	5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3	MeCN	110	24 h	(76)	84

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

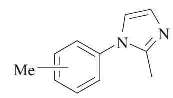
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

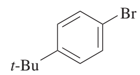




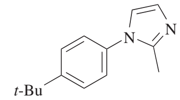
Catalyst (x mol %)



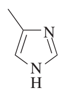
Isomer	X	Catalyst	x	Additives	Solvent(s)	Temp (°)	Time (h)		Refs.
2	I	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	NMP	150	24	(86)	84
3,5	Br	CuI	10	8-HOquin (10 mol %), TEAC	DMF/H_2O	130	16	(64)	434
2,4,6	I	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	DMSO	150	24	(44)	84

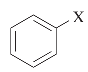


Cu_2O (5 mol %),
$(MeO)_2$phen (15 mol %),
Cs_2CO_3, PEG,
n-PrCN, 110°, 24 h

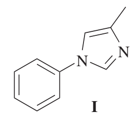


(95) 430, 84





Catalyst (x amount)



I

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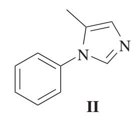
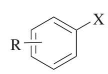
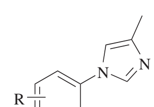


II

X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	I	II	Refs.
Br	CuI	20 mol %	Cs_2CO_3	DMF	120	40 h	(50)	(12)	386
Br	CuI	20 mol %	phen (20 mol %), KF/Al_2O_3	xylene	140	15 h	(91)	(0)	410
I	CuI	10 mol %	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12 h	(63)	(10)	394
Br	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(91)	(0)	85
I	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(90)	(0)	85
I	$Cu(OTf)_2$•C_6H_6	10 mol %	phen (1 eq), dba, Cs_2CO_3	xylenes	110	36 h	(77)	(17)	11



Catalyst (x mol %)



I

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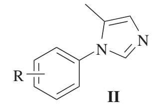
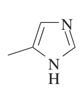
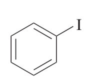


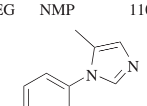
II

R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	I	II	Refs.
4-F	Br	Cu_2O	5	$(MeO)_2$phen (15 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	30	(78)	(15)	84
2-Cl	I	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	24	(96)	(0)	84
2-Cl	I	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	NMP	110	48	(90)	(6)	84
4-MeO	I	CuI	20	K_3PO_4	DMF	40	40	(62)	(4)	59
4-MeS	Br	Cu_2O	5	$(MeO)_2$phen (15 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	24	(97)	(0)	84
2-Me	I	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	NMP	110	48	(86)	(5)	84
2-*i*-Pr	I	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	NMP	110	48	(82)	(0)	84

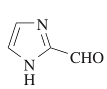


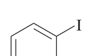


CuO (2.5 mol %), KOH,
DMSO, 110°, 24 h

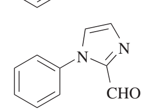


(96) 224



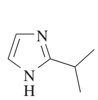


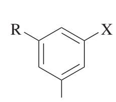
CuI (5 mo l%),
DMCDA (20 mol %),
K_3PO_4, toluene,
110°, 24 h



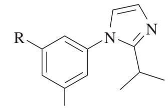
(88) 128

C_6





Catalyst (x amount)



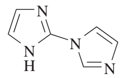
R	X	Catalyst	x	Additive	Solvent(s)	Temp (°)	Time		Refs.
H	Br	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(34)	85
H	I	$Cu(OAc)_2$	1 eq	DBU	DMSO	MW, 130	10 min	(42)	85
Me	Br	CuI	10 mol %	8-HOquin (10 mol %), Cs_2CO_3	DMF/H_2O	130	16 h	(40)	434

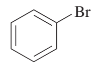
TABLE 9A. *N*-ARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

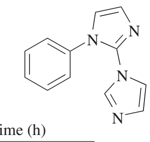
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_6



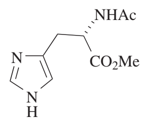


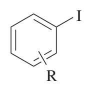
CuI (*x* mol %), Cs_2CO_3, DMF



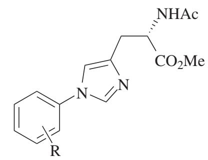
386

x	Additive	Temp (°)	Time (h)	
20	none	120	40	(53)
5	**L24** (10 mol %)	110	24	(62)





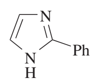
$(CuOTf)_2$•C_6H_6 (5 mol %), phen (5 mol %), dba (5 mol %), Cs_2CO_3, DMF/xylene (1:5), 115°, 48 h

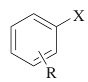


R	
H	(78)
4-Cl	(10–15)
3-Br	(10–15)
4-Br	(10–15)
4-MeO	(10–15)
3-Me	(10–15)
4-Me	(10–15)

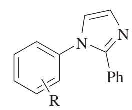
440

C_9

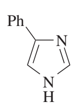


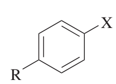


Catalyst (*x* mol %)

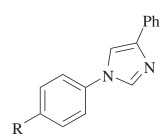


R	X	Catalyst	*x*	Additives	Solvent(s)	Temp (°)	Time (h)		Refs.
H	Br	CuI	10	8-HOquin (10 mol %), TEAC	DMF/H_2O	130	36	(trace)	434
H	Br	Cu_2O	20	$(MeO)_2$phen (30 mol %), Cs_2CO_3, PEG	*n*-PrCN	120	24	(92)	430, 84
4-F	I	Cu_2O	5	$(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	24	(85)	430, 84, 441
4-O_2N	Cl	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(56)	80
4-O_2N	Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(63)	68



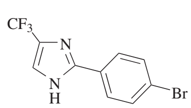


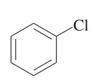
Catalyst (*x* mol %)



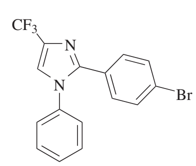
R	X	Catalyst	*x*	Additives	Solvents	Temp (°)	Time (h)		Refs.
H	I	CuI	5	DMCDA (20 mol %), Cs_2CO_3	DMF	110	24	(87)	128
H	I	$Cu(OTf)_2$•C_6H_6	10	phen (1 eq), dba, Cs_2CO_3	xylenes	110	36	(93)	11
Cl	I	CuI	5	8-HOquin (10 mol %), CsF	DMSO	100	5	(99)	63
MeS	Br	Cu_2O	5	$(MeO)_2$phen (15 mol %), Cs_2CO_3, PEG	*n*-PrCN	110	24	(96)	84

C_{10}





$Cu(OAc)_2$•H_2O (20 mol %), hippuric acid (20 mol %), Cs_2CO_3, DMF, 140°, 20 h



(64)

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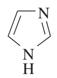
[a] The product was a 6:1 mixture of 4-bromo- and 4-iodoimidazoylbenzene.

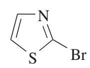
TABLE 9B. *N*-HETEROARYLATION OF IMIDAZOLES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

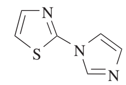
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

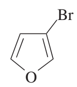




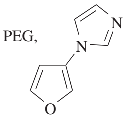
CuI (x mol %)



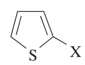
x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
20	Cs_2CO_3	DMF	120	40	(83)	386
5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(85)	86
10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(86)	412



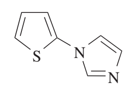
Cu_2O (5 mol %), Cs_2CO_3, PEG, $(MeO)_2$phen (15 mol %), DMSO, 110°, 24 h



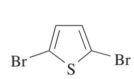
(60) 84



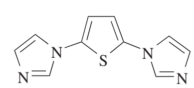
Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
I	CuF_2	50	phen (50 mol %), K_2CO_3	DMF	140	96 h	(59)	419
Br	CuI	20	Cs_2CO_3	DMF	120	40 h	(72)	386
Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	110	24 h	(74)	230
Br	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	12 h	(79)	392
Br	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	22 h	(82)	429
Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	48 h	(76)	79
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(75)	86
Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60 h	(60)	412
Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24 h	(98)	417
I	Cu_2O	2.5	$(MeO)_2$phen (7.5 %), PEG, Cs_2CO_3	DMSO	110	24 h	(83)	84
Br	$Cu(acac)_2$	100	DBU	DMSO	MW, 150	10 min	(63)	85



CuI (0.9 eq), L-Pro (1.8 eq), $[C_4mim][BF_4]$, 115°, 50 h



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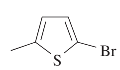
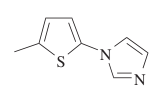


CuI (30 mol%), L-Pro (60 mol %), $[C_4mim][BF_4]$, 110°, 48 h



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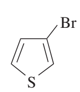
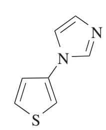
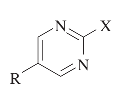


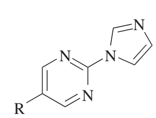
Catalyst (x mol %)



Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	20 h	(83)	429
CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24 h	(97)	393
CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	12 h	(68)	79
$Cu(OAc)_2$	100	DBU	DMSO	MW, 150	10 min	(80)	85



CuI (x mol %), 24 h



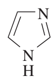
R	X	x	Additives	Solvent	Temp (°)		Refs.
H	Br	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	(98)	393
Br	I	5	phen (10 mol %), Cs_2CO_3	DMF	80	(65)	408

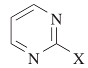
TABLE 9B. *N*-HETEROARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

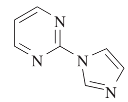
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

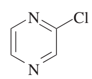




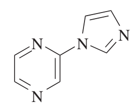
Catalyst (x mol %)



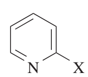
X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time	Yield (%)	Refs.
Cl	CuBr	10	**L37** (20 mol %), TBAF	none	150	24 h	(90)	80
Cl	CuI	20	Cs_2CO_3	DMF	120	40 h	(97)	386
Br	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	18 h	(95)	429
Cl	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24 h	(87)	79
Cl	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24 h	(97)	86
Cl	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60 h	(94)	412
Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	1 h	(94)	64
Cl	Cu_2O	10	phen (20 mol %), TBAF	—	145	24 h	(72)	68
Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24 h	(86)	68
Br	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(90)	85
Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	1 h	(90)	66
Cl	**2**	1	K_2CO_3	DMF	110	1 h	(87)	73



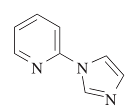
CuI (x mol %), NaOMe,
DMSO



x	Additive	Temp (°)	Time (h)	Yield (%)	Refs.
10	oxazolidin-2-one (20 mol%)	120	16	(67)	392
5	*N*-hydroxyphthalimide (10 mol%)	110	24	(94)	396
10	**L26** (10 mol %)	130	12	(86)	397



Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
Cl	Cu_2O-coated Cu nanoparticles	5	Cs_2CO_3	DMSO	150	18	(88)	223
Br	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(76)	119
Br	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(96)	80
Br	CuI	20	Cs_2CO_3	DMF	120	40	(98)	386
Br	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8	(98)	431
Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	60	45	(93)	47
Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	110	18	(74)	230
Br	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	24	(78)	429
Br	CuI	5	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	110	24	(98)	396
Br	CuI	20	phen (20 mol %), KF/Al_2O_3	xylene	140	15	(90)	410
Br	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	80	15	(85)	392
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24	(92)	393
Br	CuI	10	DACA (20 mol %), K_3PO_4	$[C_4mim][BF_4]$	110	12	(100)	232
Br	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(79)	394
Cl	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24	(65)	79
Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	12	(99)	79
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(98)	86
Br	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12	(92)	397
Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(99)	412
Br	CuI	5	**L31** (5 mol %), Cs_2CO_3	DMF	100	24	(94)	415
I	CuI	5	**L31** (5 mol %), Cs_2CO_3	DMF	90	24	(86)	415
Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24	(68)	417
Br	CuO	8	K_2CO_3	pyridine	reflux	48	(37)	402
Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	16	(87)	64

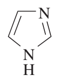
TABLE 9B. *N*-HETEROARYLATION OF IMIDAZOLES (*Continued*)

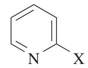
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

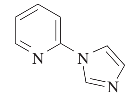
Continued from previous page.

C_3

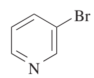




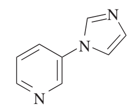
Catalyst (*x* mol %)



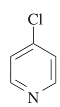
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cl	Cu_2O	20	KOH	DMSO	130	24	(89)	398
Br	Cu_2O	10	KOH	DMSO	110	24	(91)	398
Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(53)	68
Cl	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	130	24	(91)	399
Br	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	110	24	(92)	399
Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(74)	234
Br	$Cu(OAc)_2$	100	DBU	DMSO	MW, 130	10 min	(89)	85
Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	7	(92)	66
Br	**2**	2	NaOH, TBAB	H_2O	100	12	(81)	233
Cl	**7**	1	K_2CO_3	DMF	110	2	(95)	73



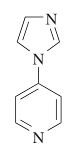
Catalyst (*x* mol %)



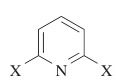
Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(74)	119
CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24	(92)	79
CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	24	(78)	429
CuO	8	K_2CO_3	pyridine	reflux	16	(51)	402



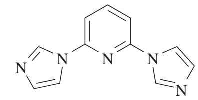
Catalyst (*x* mol %)



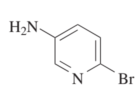
Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
Cu_2O-covered Cu nanoparticles	5	Cs_2CO_3	DMSO	150	18	(86)	223
CuO	8	K_2CO_3	pyridine	reflux	24	(51)	402
CuO nanoparticles	10	K_2CO_3	DMF	120	18	(92)	64



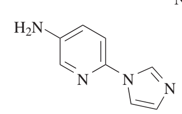
CuI (10 mol %),
L22 (10 mol %), K_2CO_3,
DMF, 110°



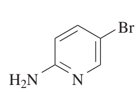
X	Time (h)		Refs.
Cl	12	(67)	79
Br	48	(88)	



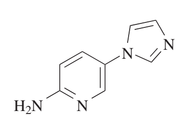
CuI (10 mol %),
L28 (20 mol %), K_2CO_3,
DMSO, 120°, 60 h



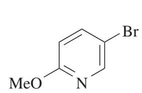
(90) 412



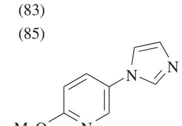
CuI (*x* mol %), Cs_2CO_3, DMF



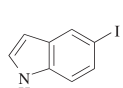
x	Additive	Temp (°)	Time (h)		Refs.
5	**L24** (10 mol %)	110	24	(83)	86
20	none	120	40	(85)	386



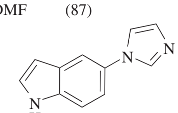
CuI (*x* mol %), 110°, 24 h



x	Additives	Solvent		Refs.
20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	(71)	429
10	**L22** (10 mol %), K_2CO_3	DMF	(87)	79



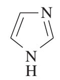
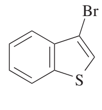
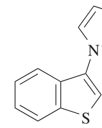
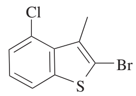
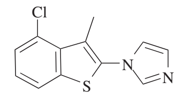
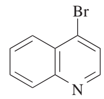
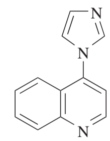
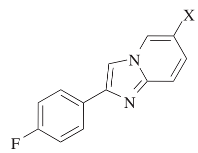
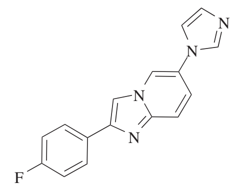
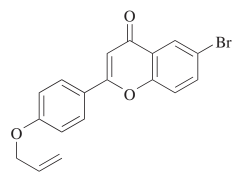
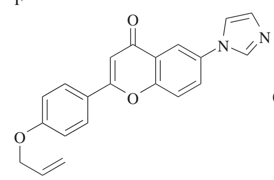
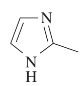
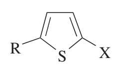
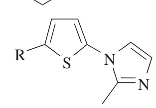
Cu_2O (2.5 mol %),
(MeO_2)phen (7.5 mol %),
Cs_2CO_3, *n*-PrCN, 110°, 24 h



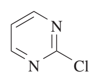
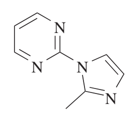
(83) 84

TABLE 9B. *N*-HETEROARYLATION OF IMIDAZOLES (*Continued*)

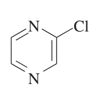
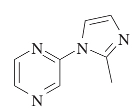
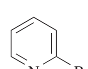
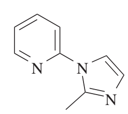
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		Cu_2O (5 mol %), $(MeO)_2$phen (15 mol %), Cs_2CO_3, PEG, DMSO, 110°, 24 h	 (79)	84
		CuI (30 mol %), L-Pro (60 mol %), $[C_4mim][BF_4]$, 110°, 48 h	 (19)	230
		Cu_2O (5 mol %), $(MeO)_2$phen (15 mol %), Cs_2CO_3, PEG, DMSO, 110°, 24 h	 (85)	84
		CuI (5 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 112°, 24 h	 X: Br (18); I (55)	409
		CuI (20 mol %), L-Lys (40 mol %), K_3PO_4, MW (200 W), 140°, 10 h	 (64)	418
C_4 		Catalyst (*x* mol %), 110°		

R	X	Catalyst	*x*	Additive(s)	Solvent	Time (h)		Refs.
H	Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	48	(62)	230
H	I	Cu_2O	2.5	$(MeO)_2$phen (7.5 mol %), PEG, Cs_2CO_3	DMSO	24	(70)	84
Me	Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	48	(46)	230

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (10 mol %), TBAF, 24 h		

Catalyst	Additive	Solvent	Temp (°)		Refs.
CuBr	**L37** (20 mol %)	none	150	(100)	80
Cu_2O	phen (20 mol %)	—	145	(98)	68

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), **L26** (10 mol %), NaOMe, DMSO, 130°, 12 h	 (85)	397
		Catalyst (*x* mol %)		

Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	110	48	(71)	230
CuI	10	oxazolidin-2-one (10 mol %), NaOMe	DMSO	80	12	(81)	392
CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12	(82)	297
$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(72)	234
2	2	NaOH, TBAB	H_2O	100	12	(80)	233

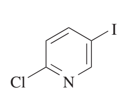
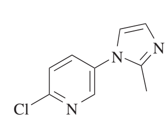
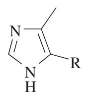
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu_2O (2.5 mol %), $(MeO)_2$phen (7.5 mol %), Cs_2CO_3, PEG, DMSO, 110°, 24 h	 (76)	84

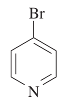
TABLE 9B. *N*-HETEROARYLATION OF IMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

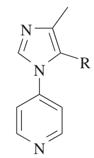
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{4-5}





CuO (10 mol %), K_2CO_3, reflux, 20 h



I

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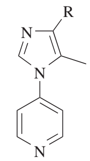
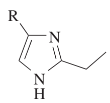
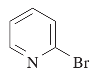


II

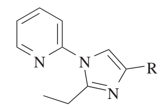
R	I	II	Refs.
H	(38)	(7)	442
Me	(63)	(0)	

C_{5-6}



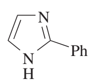


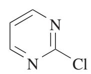
Catalyst (*x* mol %)



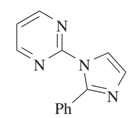
R	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	CuI	5	*N*-hydroxyphthalimide (10 mol %), NaOMe	DMSO	110	24	(92)	396
H	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(64)	234
Me	**2**	2	NaOH, TBAB	H_2O	100	12	(73)	233

C_9





Catalyst (10 mol %), TBAF, 24 h



Catalyst	Additive	Solvent	Temp (°)		Refs.
CuBr	**L37** (20 mol %)	none	150	(trace)	80
Cu_2O	phen (20 mol %)	—	145	(trace)	68

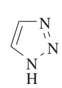
TABLE 10A. *N*-ARYLATION OF TRIAZOLES

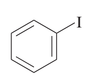
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

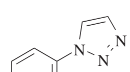
1,2,3-Triazoles

C_2





Catalyst (x mol %)



I

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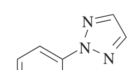
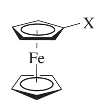
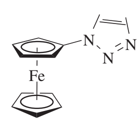


II

Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
Cu	20	Cs_2CO_3	*n*-PrCN	reflux	48	(45)	(—)	129
CuO	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30	(48)	(41)	130
Cu_2O	5	phen (10 mol %), TBAF	—	115	48	(85)	(—)	68

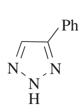


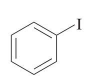
$Cu(TMHD)_2$ (10 mol %), KO*t*-Bu, DMSO, 90°, 12 h



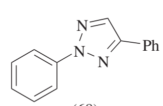
X		Refs.
Br	(14)	407
I	(28)	

C_8





CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°



(68)

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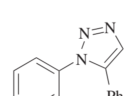
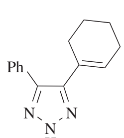
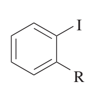


(11)

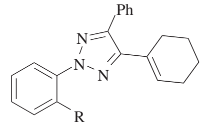
443

C_{14}



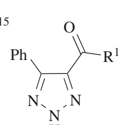


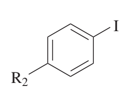
CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°



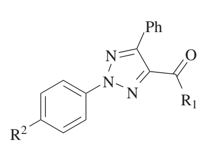
R		Refs.
H	(85)	443
Me	(70)	

C_{14-15}



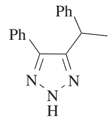
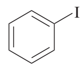
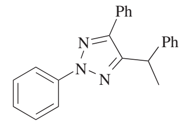
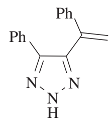
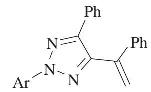
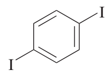
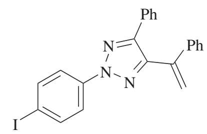
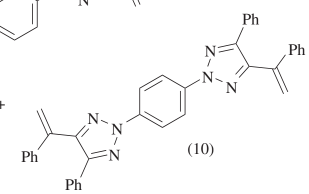
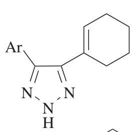
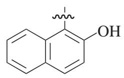
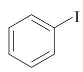
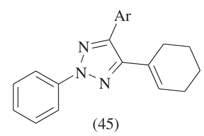
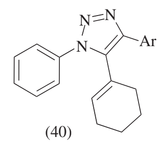


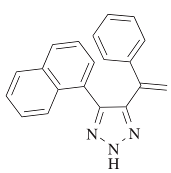
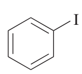
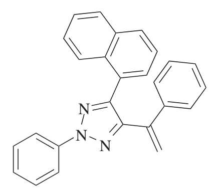
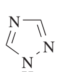
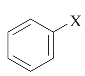
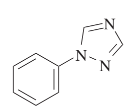
CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°



R^1	R^2		Refs.
$HO(CH_2)_5$	H	(60)	443
Ph	H	(85)	
Ph	O_2N	(88)	

TABLE 10A. *N*-ARYLATION OF TRIAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{16}				
		CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°	 (85)	443
	ArI	CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°	 Ar: Ph (87); 4-$MeOC_6H_4$ (85); 4-MeC_6H_4 (86); 1-Np (70)	443
		CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°	 (67) +  (10)	443
C_{18}				
 Ar = 		CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°	 (45) +  (40)	443

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}				
		CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°	 (87)	443
1,2,4-Triazoles				
C_2				
		Catalyst (*x* mol %)		

X	Catalyst	*x*	Additve(s)	Solvent	Temp (°)	Time (h)		Refs.
I	Cu	20	Cs_2CO_3	*n*-PrCN	reflux	48	(54)	129
Br	CuI	20	Cs_2CO_3	DMF	120	40	(85)	386
I	CuI	5	DMCDA (10 mol %), K_3PO_4	DMF	110	24	(89)	128
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24	(98)	393
I	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(93)	412
I	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	90	24	(96)	86
I	CuO	10	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30	(83)	130
I	Cu_2O	10	Cs_2CO_3	DMF	100	18	(76)	221
Br	Cu_2O	5	phen (10 mol %), TBAF	—	110	24	(55)	68
I	Cu_2O	5	phen (10 mol %), TBAF	—	110	24	(90)	68
I	Cu_2O	5	**L30** (20 mol %)	DMF	82	48	(91)	40
I	$Cu(TMHD)_2$	20	KO*t*-Bu	DMF	120	24	(51)	308

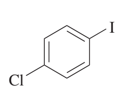
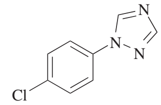
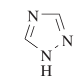
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), 8-HOquin (10 mol %), CsF, DMSO, 100°, 7 h	 (85)	63

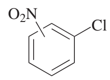
TABLE 10A. *N*-ARYLATION OF TRIAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

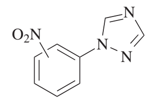
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_2

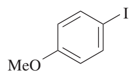




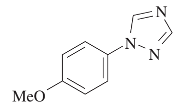
CuO (8 mol %), K_2CO_3, pyridine, reflux, 24 h



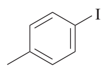
Isomer		Refs.
2	(68)	402
3	(6)	
4	(13)	



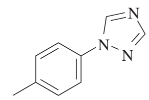
Catalyst (*x* mol %)



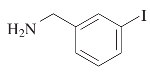
Catalyst	*x*	Additve(s)	Solvent	Temp (°)	Time (h)		Refs.
CuI	20	K_3PO_4	DMF	50	40	(84)	59
CuI	5	DMCDA (10 mol %), K_3PO_4	DMF	110	24	(82)	128
Cu_2O	5	phen (10 mol %), TBAF	—	145	48	(85)	68
$Cu(TMHD)_2$	20	KO*t*-Bu	DMF	120	24	(51)	308
10	1	Cs_2CO_3	DMSO	100	24	(84)	420



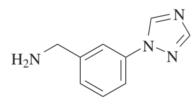
Catalyst (*x* mol %)



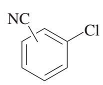
Catalyst	*x*	Additve(s)	Solvent	Temp (°)	Time (h)		Refs.
CuI	5	phen (10 mol %), TBAF	—	145	48	(61)	68
10	1	Cs_2CO_3	DMSO	100	24	(22)	420



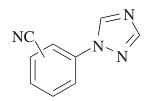
CuI (5 mol %), DMEDA (10 mol %), K_3PO_4, DMF, 110°, 24 h



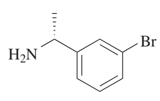
(79) — 128



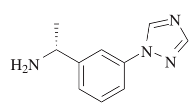
CuO (8 mol %), K_2CO_3, pyridine, reflux



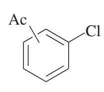
Isomer	Time (h)		Refs.
2	165	(10)	402
3	64	(8)	
4	50	(12)	



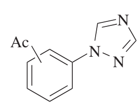
CuI (10 mol %), K_2CO_3, NMP, MW, 195°, 1 h



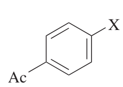
(96) — 406



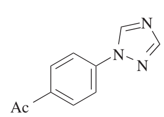
CuO (8 mol %), K_2CO_3, pyridine, reflux



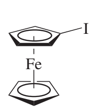
Isomer	Time (h)		Refs.
2	48	(37)	402
3	50	(11)	
4	48	(5)	



Catalyst (*x* mol %), 24 h



X	Catalyst	*x*	Additve(s)	Solvent	Temp (°)		Refs.
I	CuI	5	DMCDA (10 mol %), K_3PO_4	DMF	110	(83)	128
Cl	**10**	1	Cs_2CO_3	DMSO	100	(14)	420
Br	**10**	1	Cs_2CO_3	DMSO	100	(54)	420
I	**10**	1	Cs_2CO_3	DMSO	100	(99)	420, 421



CuI (1 eq), K_2CO_3, DMSO, 90°, 18 h

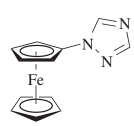


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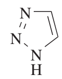
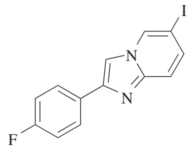
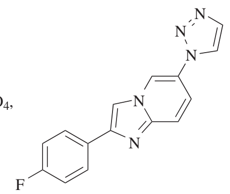
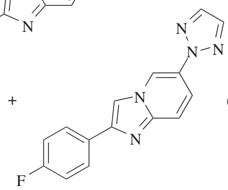
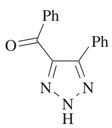
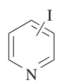
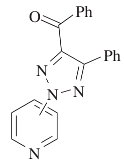
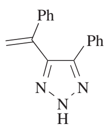
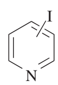
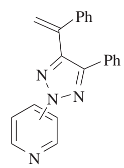
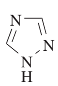
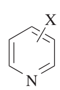
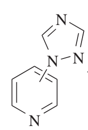
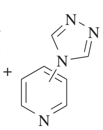
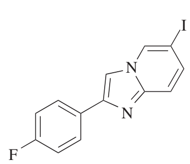
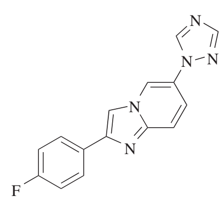
TABLE 10B. *N*-HETEROARYLATION OF TRIAZOLES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
1,2,3-Triazoles				
C_2				
		CuI (5 mol %), DMCDA (15 mol %), K_3PO_4, DMF, 112°, 24 h	 (26) +  (33)	409
C_{15}				
		CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°	 Isomer 2 (88) 4 (80)	443
C_{16}				
		CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°	 Isomer 2 (85) 3 (70) 4 (70)	443
1,2,4-Triazoles				
C_2				
		CuO (8 mol %), K_2CO_3, pyridine, reflux	 I +  II	402
		CuI (5 mol %), DMCDA (15 mol %), K_3PO_4, DMF, 112°, 24 h	 (45)	409

Isomer	X	Time (h)	I	II
2	Br	16	(29)	(3)
3	Br	17	(11)	(0.4)
4[a]	Cl	22	(6)	(2)

[a] 4-Chloropyridine hydrochloride was used as the halide.

TABLE 11A. *N*-ARYLATION OF INDOLES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_8

X	Catalyst(s)	*x*	Additve(s)	Solvent	Temp (°)	Time (h)		Refs.
I	Cu	20 mol %	Cs_2CO_3	*n*-PrCN	reflux	10	(95)	129
I	Cu on cellulose	1 mol %	K_2CO_3	DMSO	130	24	(60)	427
Br	Cu/Fe–hydrotalcite	10 wt %	none	toluene	130	12	(85)	283
I	Cu/CuI	1.3 eq/7 mol %	K_2CO_3	—	210	8	(87)	444
I	CuBr	10 mol %	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24	(71)	259
Br	CuBr	10 mol %	**L20** (20 mol %), Cs_2CO_3	DMSO	90	24	(84)	284
$I^+Ph\ BF_4^-$	CuI	10 mol %	K_2CO_3	DMF	150	7	(80)	445
I	CuI	5 mol %	K_3PO_4	DMF	110	24	(95)	387
I	CuI	5 mol %	NaOH, TBAB (5 mol %)	toluene	reflux	22	(80)	391
I	CuI	5 mol %	EDA (10 mol %), K_2CO_3	PEG-400	80	12	(86)	301
I	CuI	10 mol %	PPAPM (20 mol %), K_3PO_4	DMF	100	24	(96)	48
I	CuI	10 mol %	TM-BINAM (10 mol %), K_2CO_3	MeCN	reflux	26	(98)	446
I	CuI	0.2 mol %	DMCDA (1 mol %), K_3PO_4	toluene	110	48	(98)	191
Br	CuI	20 mol %	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	36	(93)	393
Br	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	8	(86)	390
I	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	7	(90)	390
I	CuI	5 mol %	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	90	12	(97)	396
Br	CuI	10 mol %	L-Pro (20 mol %), Cs_2CO_3	DMSO	90	40	(33)	47
I	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	DMSO	90	40	(85)	47
I	CuI	5 mol %	L-Pro (10 mol %), K_2CO_3	DMSO	90	40	(85)	401
I	CuI	20 mol %	L-Pro (20 mol %), K_3CO_4	DMF	140	48	(92)	388
Cl	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	24	(36)	67
Br	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	24	(91)	67
I	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	24	(95)	67

I	CuI	5 mol %	oxazolidin-2-one (10 mol %), NaOMe	DMSO	80	13	(90)	392
Br	CuI	10 mol %	**L21** (10 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(42)	394
I	CuI	10 mol %	**L21** (10 mol %), Cs_2CO_3	MeCN	reflux	12	(78)	394
Br	CuI	10 mol %	**L22** (10 mol %), K_2CO_3	DMF	110	48	(85)	79
I	CuI	5 mol %	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(98)	86
Br	CuI	10 mol %	**L25** (20 mol %), Cs_2CO_3	MeCN	80	15	(78)	395
I	CuI	10 mol %	**L26** (10 mol %), NaOMe	DMSO	90	12	(65)	397
Br	CuI	10 mol %	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(68)	412
I	CuI	10 mol %	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(99)	412
I	CuI	10 mol %	**L38** (10 mol %), K_3PO_4	toluene	reflux	24	(96)	447
I	CuI	10 mol %	**L39** (10 mol %), K_3PO_4	toluene	reflux	24	(95)	447
Br	CuO	6 mol %	K_2CO_3	DMF	reflux	24	(50)	448
I	CuO	1.3 mol %	KOH	DMSO	110	3.5	(94)	224
I	CuO	10 mol %	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30	(94)	130
Br	CuO	10 mol %	*rac*-binol (20 mol %), $FeCl_3$ (10 mol %), Cs_2CO_3	DMF	90	12	(89)	277
I	CuO	10 mol %	*rac*-binol (20 mol %), $FeCl_3$ (10 mol %), Cs_2CO_3	DMF	90	12	(89)	277
I	Cu_2O	10 mol %	KOH	DMSO	120	24	(90)	398
I	Cu_2O	10 mol %	Cs_2CO_3	DMF	100	18	(95)	221
I	Cu_2O	10 mol %	ninhydrin (20 mol %), KOH	DMSO	110	24	(90)	399
Cl	Cu_2O	10 mol %	phen (20 mol %), TBAF	—	145	48	(trace)	68
Br	Cu_2O	10 mol %	phen (20 mol %), TBAF	—	145	24	(91)	68
I	Cu_2O	5 mol %	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18	(64)	125
Br	Cu_2O	10 mol %	**L23** (20 mol %), KO*t*-Bu	DMF	130	24	(40)	431
I	Cu_2O	5 mol %	**L23** (10 mol %), KO*t*-Bu	DMF	110	24	(95)	431
I	Cu_2O	5 mol %	**L30** (20 mol %)	MeCN	82	24	(92)	40

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Continued from previous page.

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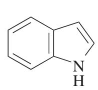
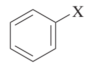
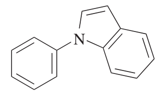
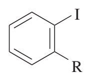




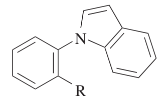
Catalyst(s) (*x* amount)



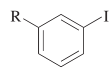
X	Catalyst	*x*	Additve(s)	Solvent	Temp (°)	Time (h)		Refs.
I	$Cu(OAc)_2$	1.1 eq	none	DMA	160	48	(76)	127
Br	$Cu(OAc)_2•H_2O$	15 mol %	(–)-sparteine (30 mol %), K_2CO_3	DMF	130	30	(63)	290
I	$Cu(OAc)_2•H_2O$	15 mol %	(–)-sparteine (30 mol %), K_2CO_3	DMF	130	24	(90)	290
I	$Cu(OAc)_2•H_2O$	20 mol %	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	30	(91)	289
I	$CuSO_4$	10 mol %	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(90)	234
I	$Cu(TMHD)_2$	20 mol %	KO*t*-Bu	DMF	120	24	(92)	308
Br	Cu fluorapatite	12.5 mol %	none	DMSO	110	15	(88)	227
Br	**2**	2 mol %	NaOH, TBAB	H_2O	100	24	(94)	233
I	**6**	5 mol %	Cs_2CO_3	toluene	100	14	(88)	123



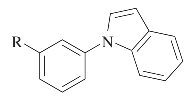
CuI (*x* mol %), K_3PO_4



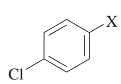
R	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
Br	5	DMCDA (20 mol %)	toluene	110	24	(72)	191
Br	10	BtH (20 mol %)	DMSO	120	30	(65)	77
I	10	BtH (20 mol %)	DMSO	120	30	(65)	77



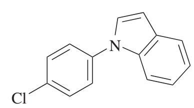
Catalyst (*x* mol %)



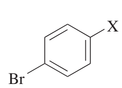
R	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
F	CuI	5	L-Pro (10 mol %), K_2CO_3	DMSO	80	34	(88)	401
F	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	80	34	(88)	47
Cl	CuCl	5	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24	(93)	235
Cl	CuI	5	**L40** (5 mol %), K_3PO_4	DMF	110	24	(89)	449



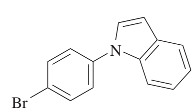
Catalyst(s) (*x* amount)



X	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	Cu/CuI	1.3 eq/7 mol %	K_2CO_3	—	210	8	(82)	444
$I^+C_6H_4Cl$-4 BF_4^-	CuI	10 mol %	K_2CO_3	DMF	80	3	(92)	445
I	CuI	5 mol %	DMEDA (10 mol %), CsF	THF	60	24	(86)	63
Br	CuI	10 mol %	oxazolidin-2-one (20 mol %), NaOMe	DMSO	80	18	(85)	392
I	CuI	5 mol %	*N*-hydroxyphthalimide (10 mol %), NaOMe	DMSO	90	12	(99)	396
I	CuI	5 mol %	*N*-hydroxymaleimide (10 mol %), NaOMe	DMSO	110	24	(48)	396
Br	CuI	10 mol %	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(52)	394
I	CuI	10 mol %	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(89)	394
I	CuI	5 mol %	**L40** (5 mol %), K_3PO_4	DMF	110	24	(86)	449
I	$Cu(OAc)_2•H_2O$	20 mol %	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	30	(43)	289



CuI (*x* mol %)



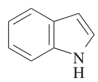
X	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I^+Ph BF_4^-	10	K_2CO_3	DMF	80	3	(81)	445
I	5	K_3PO_4	DMF	110	24	(76)	387
Br	10	PPAPM (20 mol %), K_3PO_4	DMF	100	36	(87)	48
I	10	PPAPM (20 mol %), K_3PO_4	DMF	100	24	(96)	48
I	5	oxazolidin-2-one (10 mol %), NaOMe	DMSO	80	16	(83)	392
I	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(60)	388
I	5	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	110	24	(86)	396
I	10	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	24	(94)	67
I	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(91)	394

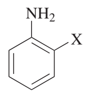
TABLE 11A. *N*-ARYLATION OF INDOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

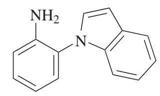
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_8

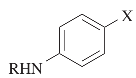




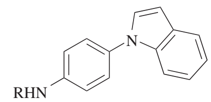
CuI (5 mol %)



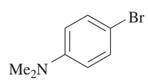
X	Additives	Solvent	Temp (°)	Time (h)		Refs.
Br	EDA (10 mol %), K_2CO_3	PEG-400	80	24	(79)	301
I	EDA (10 mol %), K_2CO_3	PEG-400	80	18	(84)	301
I	DMEDA (20 mol %), K_3PO_4	toluene	110	24	(88)	191



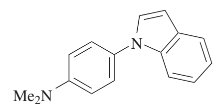
CuI (x mol %)



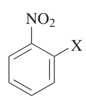
R	X	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Ac	$I^+C_6H_4NHAc$-4 BF_4^-	10	K_2CO_3	DMF	80	3	(72)	445
Ac	I	5	DMCDA (20 mol %), K_3PO_4	toluene	110	24	(72)	191
Boc	I	5	DMCDA (20 mol %), K_3PO_4	toluene	110	24	(75)	191



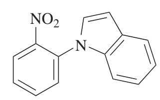
CuI (5 mol %),
DMCDA (20 mol %),
K_3PO_4, toluene, 110°, 24 h



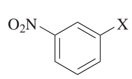
(93) 191



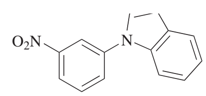
Catalyst (x mol %)



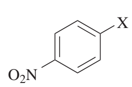
X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(<5)	388
Cl	CuO	6	K_2CO_3	DMF	reflux	24	(48)	448
Cl	CuO	8	K_2CO_3	pyridine	reflux	18	(50)	402
I	Cu_2O	10	Cs_2CO_3	PEG-3400	MW, 150	1	(89)	450



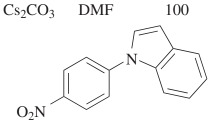
Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
$I^+C_6H_4NO_2$-3 BF_4^-	CuI	10	K_2CO_3	DMF	80	3	(76)	445
I	CuI	5	L-Pro (10 mol %), K_2CO_3	DMSO	75	42	(93)	401
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	75	42	(93)	47
I	CuI	10	TM–BINAM (10 mol %), K_2CO_3	MeCN	reflux	20	(95)	446
Br	CuO	6	K_2CO_3	DMF	reflux	24	(38)	448
Cl	CuO	8	K_2CO_3	pyridine	reflux	48	(80)	402
I	CuO	10	*rac*-binol (20 mol %), $FeCl_3$ (10 mol %), Cs_2CO_3	DMF	100	12	(89)	277



Catalyst(s) [x amount(s)]



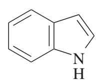
X	Catalyst(s)	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	Cu/CuI	1.3 eq/7 mol %	K_2CO_3	—	210	8	(60)	444
I	$CuBr_2$	10 mol %	TBAF	—	145	4	(64)	81
Br	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	9	(89)	390
I	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	8	(94)	390
I	CuI	1 mol %	CDA (10 mol %), K_3PO_3	dioxane	110	24	(99)	115
Cl	CuI	5 mol %	*N*-hydroxyphthalimide (10 mol %), NaOMe	DMSO	110	40	(62)	396
Cl	CuI	10 mol %	**L26** (10 mol %), NaOMe	DMSO	90	12	(57)	397
I	CuO nanoparticles	5 mol %	KOH	*t*-BuOH/DMSO (3:1)	110	11	(45)	74
Cl	CuO nanoparticles	10 mol %	K_2CO_3	DMF	120	9	(89)	64
Cl	CuO	8 mol %	K_2CO_3	pyridine	reflux	19	(15)	402
Br	CuO	6 mol %	K_2CO_3	DMF	reflux	24	(77)	448
I	Cu_2O	10 mol %	Cs_2CO_3	PEG-3400	MW, 150	1	(47)	450
I	CuOAc	1.1 eq	none	DMA	160	48	(66)	127
Cl	$Cu(OAc)_2$•H_2O	20 mol %	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	20	(55)	289
I	$Cu(OAc)_2$•H_2O	20 mol %	hippuric acid (20 mol %), Cs_2CO_3	DMF	140	30	(43)	289
Cl	$Cu(OAc)_2$•H_2O	15 mol %	(–)-sparteine (30 mol %), K_2CO_3	DMF	130	36	(34)	290
Br	$Cu(OAc)_2$•H_2O	1 mol %	(–)-sparteine (30 mol %), K_2CO_3	DMF	130	36	(71)	290
I	$Cu(TMHD)_2$	20 mol %	KO*t*-Bu	DMF	120	24	(87)	308
F	**7**	1 mol %	K_2CO_3	DMF	110	5	(85)	73
Cl	**7**	1 mol %	K_2CO_3	DMF	110	1	(82)	73

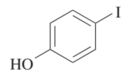
TABLE 11A. *N*-ARYLATION OF INDOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

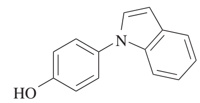
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_8

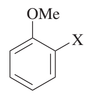




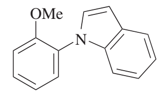
CuOAc (1.1 eq), DMA, 160°, 48 h



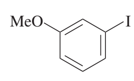
(49) 127



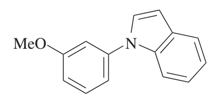
Catalyst (*x* mol %)



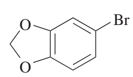
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	10	phen (20 mol %), KF/Al_2O_3	toluene	reflux	12	(73)	390
I	CuI	10	phen (20 mol %), KF/Al_2O_3	toluene	reflux	11	(78)	390
I	CuI	1	CDA (10 mol %), K_3PO_4	dioxane	110	24	(100)	115
I	CuI	10	BtH (20 mol %), K_3PO_4	DMSO	120	30	(68)	77
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	48	(79)	47
I	CuI	5	L-Pro (10 mol %), K_2CO_3	DMSO	90	48	(79)	401
I	Cu_2O	10	Cs_2CO_3	PEG-3400	MW, 150	1	(83)	450



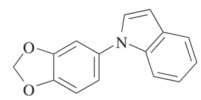
CuI (10 mol %), K_2CO_3, TM–BINAM (10 mol %), MeCN, reflux, 40 h



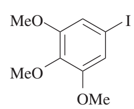
(90) 446



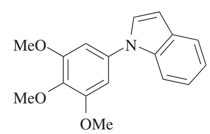
CuI (5 mol %), EDA (10 mol %), K_2CO_3, PEG-400, 80°, 24 h



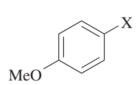
(60) 301



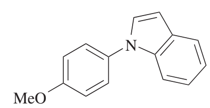
CuOAc (1.1 eq), DMA, 160°, 48 h



(36) 127



Catalyst(s) [*x* amount(s)]

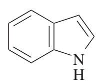


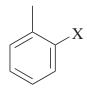
X	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time		Refs.
I	Cu/CuI	1.3 eq/7 mol %	K_2CO_3	—	210	8 h	(79)	444
I	CuF_2	25 mol %	phen (25 mol %), K_2CO_3	DMF	140	96 h	(72)	419
I	$CuBr_2$	10 mol %	TBAF	—	145	24 h	(47)	81
$I^+C_6H_4OMe$-4 BF_4^-	CuI	10 mol %	K_2CO_3	DMF	80	3 h	(80)	445
I	CuI	10 mol %	K_3PO_4	DMF	110	24 h	(81)	387
Br	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	9 h	(84)	390
I	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	8 h	(87)	390
Br	CuI	20 mol %	L-Pro (20 mol %), K_3PO_4	DMF	140	48 h	(85)	388
I	CuI	5 mol %	L-Pro (20 mol %), K_3PO_4	dioxane	100	24 h	(99)	388
I	CuI	10 mol %	BtH (20 mol %), K_3PO_4	DMSO	120	30 h	(87)	77
Br	CuI	5 mol %	EDA (10 mol %), K_2CO_3	PEG-400	80	24 h	(79)	301
I	CuI	10 mol %	TM–BINAM (10 mol %), K_2CO_3	MeCN	reflux	36 h	(76)	446
Br	CuI	5 mol %	**L34** (5 mol %), KO*t*-Bu	DMSO	110	—	(94)	403
Cl	CuI	10 mol %	**L39** (10 mol %), K_3PO_4	DMF	reflux	24 h	(trace)	447
I	CuI	5 mol %	**L40** (5 mol %), K_3PO_4	DMF	110	24 h	(83)	449
Br	CuO	5 mol %	**L14** (50 mol %), TBAB, 2,5-hexanedione, K_3PO_4	H_2O	MW (100 W), 140	5 min	(52)	51
I	Cu_2O	10 mol %	Cs_2CO_3	PEG-3400	MW, 150	1 h	(76)	450
Br	Cu_2O	10 mol %	phen (20 mol %), TBAF	—	145	24 h	(74)	68
Br	Cu–Fe hydrotalcite	10 wt %	none	toluene	130	12 h	(87)	283
I	$Cu(TMHD)_2$	20 mol %	KO*t*-Bu	DMF	120	24 h	(86)	308
I	**6**	5 mol %	Cs_2CO_3	toluene	100	24 h	(82)	123

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

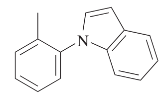
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_8

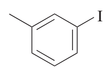




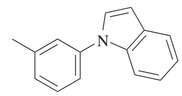
Catalyst (*x* mol %)



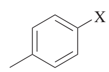
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	Cu	200	18-c-6 (10 mol %), K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	36	(87)	444
Br	CuI	10	phen (20 mol %), KF/Al_2O_3	toluene	reflux	10	(76)	390
I	CuI	10	phen (20 mol %), KF/Al_2O_3	toluene	reflux	9	(81)	390
Br	CuI	5	DMCDA (20 mol %), K_3PO_4	toluene	110	24	(91)	191
I	CuI	5	**L40** (5 mol %), K_3PO_4	DMF	110	24	(73)	449



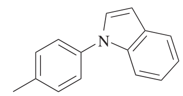
Cu (1.3 eq), CuI (7 mol %), K_2CO_3, 210°, 8 h



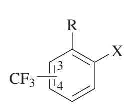
(84) 444



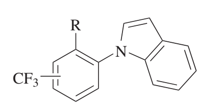
Catalyst(s) [*x* amount(s)]



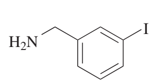
X	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
I	Cu/CuI	1.3 eq/7 mol %	K_2CO_3	—	210	8	(84)	444
$I^+C_6H_4Me$-4 BF_4^-	CuI	10 mol %	K_2CO_3	DMF	80	3	(87)	445
Br	CuI	1 mol %	DMCDA (5 mol %), K_3PO_4	toluene	110	24	(96)	191
I	CuI	10 mol %	TM–BINAM (10 mol %), K_2CO_3	MeCN	reflux	36	(76)	446
Br	CuI	20 mol %	L-Pro (20 mol %), K_3PO_4	DMF	140	48	(90)	388
I	CuI	5 mol %	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(80)	388
I	CuI	5 mol %	NaOH, TBAB (5 mol %)	toluene	reflux	22	(64)	391
Br	CuI	10 mol %	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24	(52)	392
I	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	7	(89)	390
Br	CuI	5 mol %	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	110	24	(52)	396
Br	CuI	10 mol %	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(51)	394
Br	CuI	10 mol %	**L38** (10 mol %), K_3PO_4	DMF	reflux	24	(95)	447
Br	CuI	10 mol %	**L39** (10 mol %), K_3PO_4	DMF	reflux	24	(95)	447
I	CuI	5 mol %	**L40** (5 mol %), K_3PO_4	DMF	110	24	(83)	449
I	CuI	5 mol %	**L41** (10 mol %), NaO*t*-Bu	toluene	reflux	40	(99)	451
I	Cu_2O	10 mol %	Cs_2CO_3	PEG-3400	MW, 150	1	(57)	450
Br	Cu(II)–NaY zeolite	10 mol %	Cs_2CO_3	DMF	120	20	(99)	404
I	Cu(II)–NaY zeolite	10 mol %	Cs_2CO_3	DMF	120	22	(99)	404



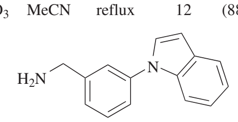
Catalyst [*x* amount(s)]



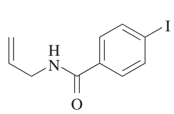
Isomer	R	Catalyst(s)	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
3	H	Cu/CuI	1.3 eq/7 mol %	K_2CO_3	—	210	8	(35)	444
4	H	CuOAc	1.1 eq	none	DMA	160	48	(66)	127
4	NO_2	CuI	10 mol %	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(88)	394



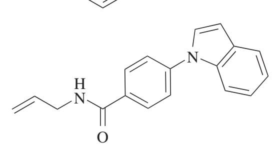
CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 80°, 24 h



(90) 191



CuI (5 mol%), DMCDA (20 mol%), K_3PO_4, toluene, 110°, 24 h

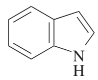


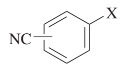
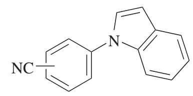
(83) 191

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

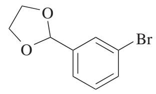
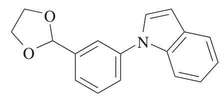
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

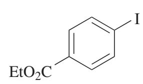
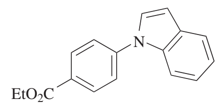
C_8

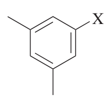
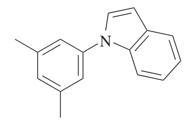


 Catalyst (*x* mol %) 

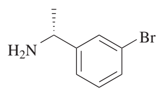
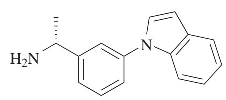
Isomer	X	Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
2	Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	18	(83)	64
4	Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	18	(76)	64
4	Br	CuO	8	K_2CO_3	pyridine	reflux	39	(77)	402
4	I	Cu_2O	10	Cs_2CO_3	PEG-3400	MW, 150	1	(80)	450

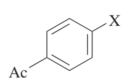
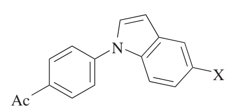
 CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 80°, 24 h  (78) 191

 CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h  (90) 191

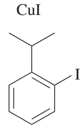
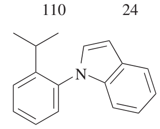
 Catalyst (*x* mol %) 

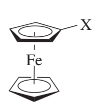
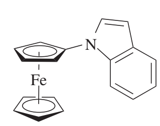
X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
I	CuI	10	TM–BINAM (10 mol %), K_2CO_3	MeCN	reflux	36	(60)	446
I	CuI	10	EDA (10 mol %), Cs_2CO_3	dioxane	110	24	(96)	405
I	CuI	1	CDA (10 mol %), K_3PO_4	dioxane	110	24	(99)	115
Br	$[CuOTf]_2•C_6H_6$	5	4,7-Cl_2-phen (10 mol %), Cs_2CO_3	NMP	125	41	(94)	452

 CuI (10 mol %), K_2CO_3, NMP, MW, 195°, 22 h  (49) 406

 Catalyst (*x* mol %) 

X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
I	CuI	10	TM–BINAM (10 mol %), K_2CO_3	MeCN	reflux	28	(94)	446
Br	CuI	20	L-Pro (20 mol %), K_3PO_4	DMF	140	48	(91)	388
I	CuI	5	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(99)	388
I	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	75	42	(90)	47
I	CuO	5	L-Pro (10 mol %), K_2CO_3	DMSO	80	22	(90)	401
Br	CuO	8	K_2CO_3	pyridine	reflux	45	(93)	402
Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24	(85)	417

 CuI (1 mol %), DMCDA (5 mol %), K_3PO_4, toluene, 110°, 24 h  (86) 191

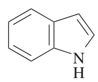
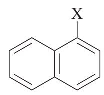
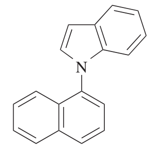
 Catalyst (*x* amount) 

X	Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
I	CuI	1 eq	K_2CO_3	DMSO	90	18	(73)	372
Br	$Cu(TMHD)_2$	20 mol %	KO*t*-Bu	toluene	120	36	(61)	407
I	Cu(TMHD)	10 mol %	KO*t*-Bu	DMSO	90	12	(95)	407

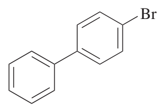
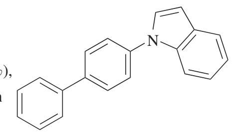
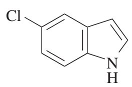
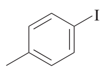
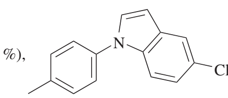
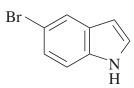
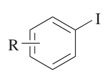
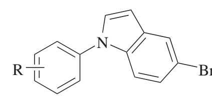
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

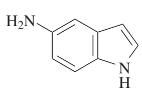
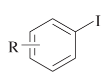
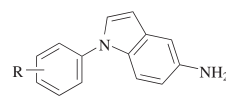
C_8

		Catalyst(s) [*x* amount(s)]		

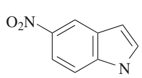
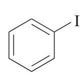
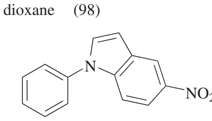
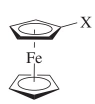
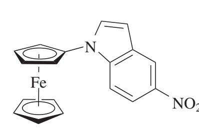
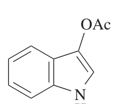
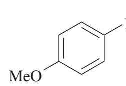
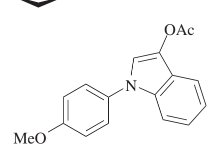
X	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
I	Cu/CuI	1.3 eq/7 mol %	K_2CO_3	—	210	8	(84)	444
I	CuI	5 mol %	L-Pro (20 mol %), K_3PO_4	dioxane	100	24	(85)	388
Br	CuI	20 mol %	L-Pro (20 mol %), K_3PO_4	DMF	140	48	(80)	388
Br	CuI	5 mol %	EDA (10 mol %), K_2CO_3	PEG-400	80	24	(92)	301
Br	CuI	10 mol %	**L38** (10 mol %), K_3PO_4	DMF	reflux	24	(82)	447
Br	CuI	10 mol %	**L39** (10 mol %), K_3PO_4	DMF	reflux	24	(82)	447

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), oxazolidin-2-one (20 mol %), MeONa, DMSO, 120°, 24 h	 (45)	392
		CuI (5 mol %), **L40** (5 mol %), K_3PO_4, DMF, 110°, 24 h	 (82)	449
		CuI (10 mol%), K_2CO_3, TM–BINAM (10 mol %), MeCN, reflux		446

R	Time (h)	
H	36	(34)
3-MeO	72	(65)
4-MeCO	28	(93)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), 110°, 24 h		

R	Additives	Solvent		Refs.
4-Me	**L40** (5 mol %), K_3PO_4	DMF	(76)	449
3,5-Me_2	DMEDA (10 mol %), K_2CO_3	dioxane	(98)	107, 115

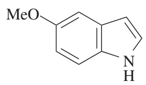
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol%), DMCDA (10 mol %), K_3PO_4, toluene, 110°, 24 h	 (96)	191
		$Cu(TMHD)_2$ (20 mol %), KO*t*-Bu, DMSO, 90°		407
		CuOAc (1.1 eq), DMA, 160°, 48 h	 (49)	127

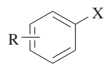
X	Time (h)	
Br	36	(30)
I	12	(68)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

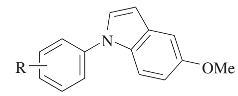
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_8

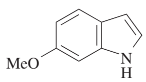


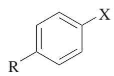


Catalyst (*x* mol %)

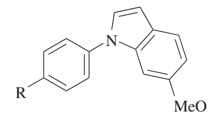


R	X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	I	CuI	10	TM–BINAM (10 mol %), K_2CO_3	MeCN	reflux	36	(66)	446
2-Br	I	CuI	10	BtH (20 mol %), K_3PO_4	DMSO	120	30	(70)	77
2-I	I	CuI	10	BtH (20 mol %), K_3PO_4	DMSO	120	30	(68)	77
3-MeO	I	CuI	10	TM–BINAM (10 mol %), K_2CO_3	MeCN	reflux	72	(97)	446
4-Me	I	CuI	5	**L40** (5 mol %), K_3PO_4	DMF	110	24	(83)	449
3,5-Me_2	Br	$(Cu(OTf)_2{\bullet}C_6H_6$	5	4,7-Cl_2phen (10 mol %), Cs_2CO_3	NMP	125	89	(100)	452
3,5-Me_2	I	CuI	10	CDA (10 mol %), K_3PO_4	dioxane	110	24	(100)	115



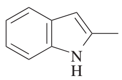


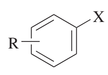
CuCl (5 mol %), **L17** (10 mol %), TBAB, NaOH, H_2O, 100°, 24 h



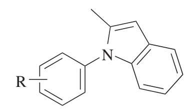
R	X		Refs.
Br	Br	(79)	235
O_2N	I	(96)	

C_9

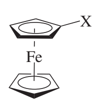




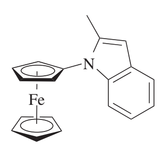
CuI (*x* mol %)



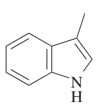
R	X	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	Br	40	8-HOquin (10 mol %), TEAC	H_2O	130	36	(45)	434
H	I	20	Cs_2CO_3	DMF	120	40	(65)	386
4-MeO	I	10	BtH (20 mol %), K_3PO_4	DMSO	100	30	(87)	77
4-MeO	I	10	L-Pro (20 mol %), K_2CO_3	DMSO	90	40	(75)	47
4-MeO	I	5	L-Pro (10 mol %), K_2CO_3	DMSO	90	40	(75)	401
3-Me	I	10	BtH (20 mol %), K_3PO_4	DMSO	80	8	(90)	77
4-Me	I	10	BtH (20 mol %), K_3PO_4	DMSO	100	30	(89)	77
4-Me	I	5	**L40** (5 mol %), K_3PO_4	DMF	110	24	(23)	449
3,5-Me_2	I	1	CDA (10 mol %), K_3PO_4	dioxane	110	24	(94)	115

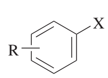


$Cu(TMHD)_2$ (20 mol %), KO*t*-Bu, toluene, 120°

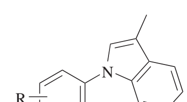


X	Time (h)		Refs.
Br	36	(52)	407
I	12	(88)	

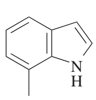


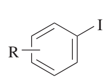


CuI (*x* mol %), K_3PO_4

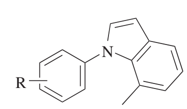


R	X	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
H	I	10	BtH (20 mol %)	DMSO	100	30	(85)	77
2-Br	I	10	BtH (20 mol %)	DMSO	120	30	(72)	77
2-I	I	10	BtH (20 mol %)	DMSO	120	30	(70)	77
2-O_2N	I	10	BtH (20 mol %)	DMSO	80	8	(98)	77
4-MeO	I	10	BtH (20 mol %)	DMSO	100	30	(90)	77
4-Me	Br	10	BtH (20 mol %)	DMSO	120	30	(55)	77
4-Me	I	10	BtH (20 mol %)	DMSO	120	30	(91)	77
4-Me	Br	1	DMCDA (5 mol %)	toluene	110	24	(85)	191
4-Me	I	5	**L40** (5 mol %)	DMF	110	24	(83)	449
2-NC–	I	10	BtH (20 mol %)	DMSO	80	8	(98)	77





CuI (*x* mol %), K_3PO_4, 110°

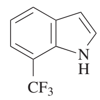
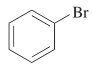
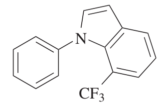


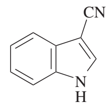
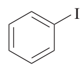
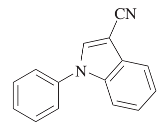
R	*x*	Additive	Solvent	Time (h)		Refs.
H	5	DMCDA (20 mol %)	toluene	24	(92)	191
4-Me	5	**L40** (5 mol %)	DMF	24	(92)	449
3,5-Me_2	1	CDA (10 mol %)	dioxane	48	(62)	115

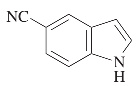
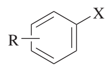
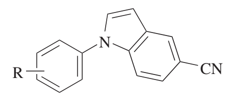
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

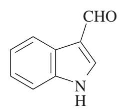
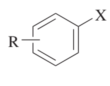
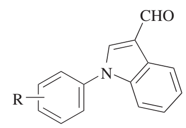
C_9

  Cu_2Br_2 (14 mol %), K_2CO_3, pyridine, 160°, 18 h  (3) 453

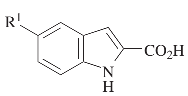
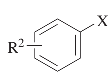
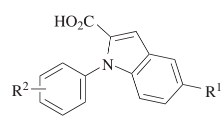
  CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h  (92) 191

  Catalyst (5 mol %) 

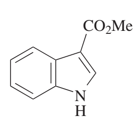
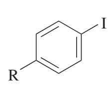
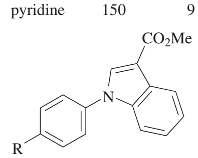
R	X	Catalyst	Additives	Solvent	Temp (°)	Time (h)		Refs.
4-Me	I	CuI	**L40** (5 mol %), K_3PO_4	DMF	110	24	(88)	449
3,5-Me_2	Br	$(CuOTf)_2$•C_6H_6	4,7-Cl_2phen (10 mol %), Cs_2CO_3	NMP	125	89	(100)	452

  Catalyst (*x* amount) 

R	X	Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
H	Br	CuO	6 mol %	K_2CO_3	DMF	reflux	24	(60)	448
2-O_2N	Cl	CuO	6 mol %	K_2CO_3	DMF	reflux	24	(56)	448
3-O_2N	Br	CuO	6 mol %	K_2CO_3	DMF	reflux	24	(76)	448
4-O_2N	Br	CuO	6 mol %	K_2CO_3	DMF	reflux	24	(88)	448
4-O_2N	I	CuOAc	1.1 eq	none	DMA	160	48	(55)	127
4-MeO	I	CuOAc	1.1 eq	none	DMA	160	48	(54)	127

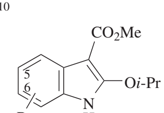
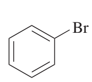
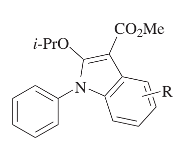
  Catalyst (*x* mol %) 

R^1	R^2	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	H	Br	CuO	6	K_2CO_3	DMF	reflux	24	(67)	448
MeO	H	Br	CuO	30	KOH	DMF	reflux	6	(93)	454
H	3-O_2N	Br	CuO	6	K_2CO_3	DMF	reflux	24	(50)	448
H	4-O_2N	Br	CuO	6	K_2CO_3	DMF	reflux	24	(45)	448
BnO	4-MeO	I	CuF_2	50	phen (50 mol %), K_2CO_3	DMF	140	96	(60)	419
H	3-CF_3	Br	Cu_2Br_2	14	K_2CO_3	pyridine	150	9	(68)	453
H	4-CF_3	Br	Cu_2Br_2	14	K_2CO_3	pyridine	150	9	(95)	453

  Catalyst (*x* amount) 

R	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	CuI	5 mol %	DMCDA (10 mol %), K_3PO_4	toluene	110	24	(96)	191
MeO	CuOAc	1.1 eq	none	DMA	160	48	(60)	127
Me	CuI	5 mol %	**L40** (5 mol %), K_3PO_4	DMF	110	24	(97)	449

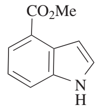
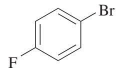
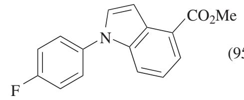
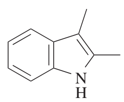
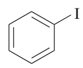
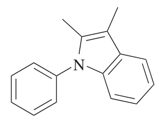
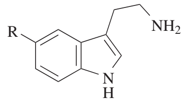
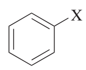
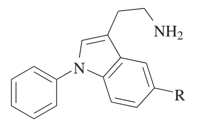
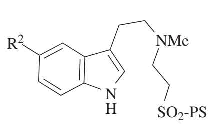
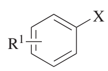
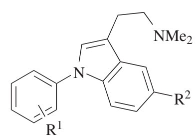
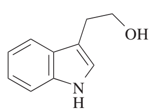
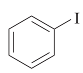
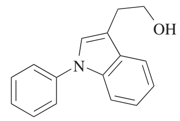
C_{9-10}

  CuBr (10 mol %), K_2CO_3, KOH, 140°, 21 h  454

R	
5,6-Cl_2	(93)
6-Br	(—)
6-MeO	(—)
6-Me	(—)

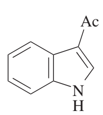
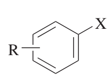
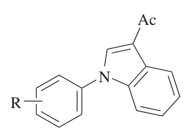
TABLE 11A. *N*-ARYLATION OF INDOLES (*Continued*)

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

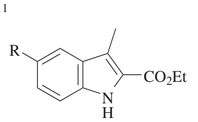
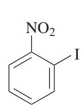
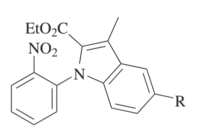
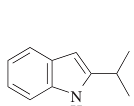
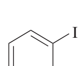
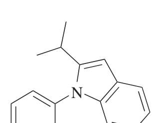
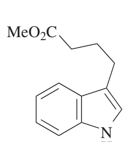
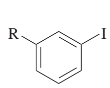
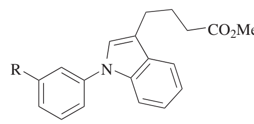
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		CuO, K_2CO_3, reflux	 (95)	435
C_{10}				
		CuI (5 mol %), DMCDA (10 mol %), K_3PO_4, toluene, 110°, 24 h	 (98)	191
		CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 see table below	191
 PS = polystyrene		1. CuI (1 eq), CDA (1 eq), KO*t*-Bu, dioxane, 80°, 24 h 2. MeI, DMF 3. *i*-Pr_2NEt, CH_2Cl_2	 see table below	455
		CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 (90)	191

X	R	
I	H	(90)
Br	MeO	(76)

R^1	R^2	
H	H	(10–20)
2-F	H	(10–20)
3,4-Cl_2	H	(10–20)
3-HO	H	(10–20)
4-MeO	MeO	(74)
4-PhO	H	(10–20)
4-Me	H	(10–20)
3-Ph	H	(10–20)
4-Ph	H	(10–20)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %), reflux		

R	X	Catalyst	*x*	Additive(s)	Solvent	Time (h)		Refs.
H	I	CuI	10	TM–BINAM (10 mol %), K_2CO_3	MeCN	48	(38)	446
H	Br	CuO	6	K_2CO_3	DMF	24	(62)	448
2-O_2N	Br	CuO	6	K_2CO_3	DMF	24	(70)	448
3-O_2N	Br	CuO	6	K_2CO_3	DMF	24	(68)	448
4-O_2N	Br	CuO	6	K_2CO_3	DMF	24	(97)	448

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{10–11}$				
 R = H, Cl, MeO, EtO, Me		CuO (6 mol %), K_2CO_3, pyridine, reflux, 18 h	 (~50)	456
C_{11}				
		CuI (5 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 (70)	191
C_{12}				
		CuI (10 mol %), TM–BINAM (10 mol %), K_2CO_3, MeCN, reflux	 see table below	446

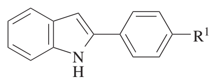
R	Time (h)	
H	30	(65)
MeO	48	(82)

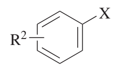
TABLE 11A. *N*-ARYLATION OF INDOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

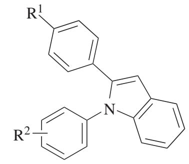
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{14}



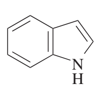
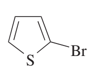
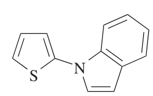
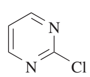
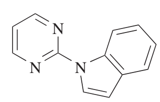
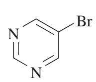
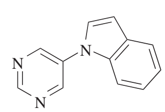
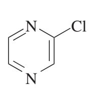
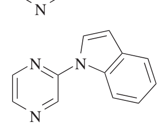


Catalyst (x mol %), reflux



R^1	R^2	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	H	I	CuI	5	DMCDA (10 mol %), K_3PO_4	toluene	110	24	(67)	191
H	2-O_2N	Cl	CuO	6	K_2CO_3	DMF	reflux	24	(52)	448
H	3-O_2N	Br	CuO	6	K_2CO_3	DMF	reflux	24	(34)	448
H	4-O_2N	Br	CuO	6	K_2CO_3	DMF	reflux	24	(48)	448
H	4-Me	I	CuI	5	**L40** (5 mol %), K_3PO_4	DMF	110	24	(38)	449
H	3,5-Me_2	I	CuI	1	CDA (10 mol %), K_3PO_4	dioxane	110	48	(72)	115
F	3,5-Me_2	I	CuI	1	CDA (10 mol %), K_3PO_4	dioxane	110	48	(65)	115

TABLE 11B. *N*-HETEROARYLATION OF INDOLES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_8				
		Cu_2O (10 mol %), phen (20 mol %), TBAF, 145°, 24 h	 (74)	68
		CuO nanoparticles (10 mol %), K_2CO_3, DMF, 120°, 1.5 h	 (94)	64
		$[Cu(OTf)]_2 \cdot C_6H_6$ (5 mol %), 4,7-Cl_2phen (10 mol %), Cs_2CO_3, NMP, 125°, 17 h	 (100)	452
		Catalyst (10 mol %)		

Catalyst	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
$CuBr_2$	TBAF	—	145	2.5	(58)	81
CuI	**L26** (10 mol %), NaOMe	DMSO	130	12	(70)	397

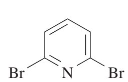
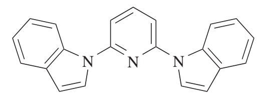
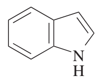
		CuI (10 mol %), **L22** (10 mol %), K_2CO_3, DMF, 110°, 24 h	 (76)	79

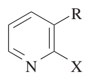
TABLE 11B. *N*-HETEROARYLATION OF INDOLES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

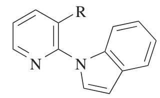
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_8

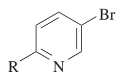




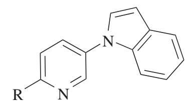
Catalyst (*x* mol %)



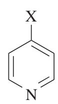
R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
H	I	CuI	10	BtH (20 mol %), K_3PO_4	DMSO	100	30	(92)	77
H	Br	CuI	5	*N*-hydroxysuccinimide (10 mol %), NaOMe	DMSO	110	24	(68)	396
H	Br	CuI	10	phen (20 mol %), KF/Al_2O_3	toluene	reflux	7	(91)	390
H	Br	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(92)	394
H	Cl	CuO nanoparticles	10	K_2CO_3	DMF	120	23	(77)	64
H	Br	CuO	8	K_2CO_3	pyridine	reflux	17	(79)	402
H	Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(86)	68
Br	Br	CuI	10	BtH (20 mol %), K_3PO_4	DMSO	120	30	(85)	77



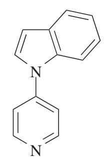
Catalyst (*x* mol %), 24 h



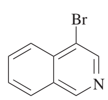
R	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Yield (%)	Refs.
H	CuI	5	DMCDA (20 mol %), K_3PO_4	toluene	80	(93)	191
H	CuO	8	K_2CO_3	pyridine	reflux	(75)	402
H_2N	CuI	5	DMCDA (20 mol %), K_3PO_4	toluene	110	(78)	191



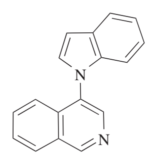
Catalyst (*x* mol %)



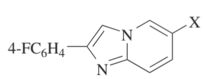
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
Cl	CuO	8	K_2CO_3	pyridine	reflux	22	(3)	402
Br	$[Cu(OTf)]_2 \bullet C_6H_6$	5	4,7-Cl_2-phen (10 mol %), Cs_2CO_3	NMP	125	17	(100)	452



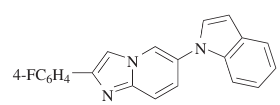
CuI (5 mol %),
DMCDA (20 mol %),
K_3PO_4, toluene, 110°, 24 h



(72) 191



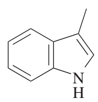
CuI (5 mol %),
DMCDA (15 mol %),
K_3PO_4, toluene, 112°, 24 h

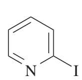


X	
Br	(72)
I	(74)

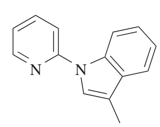
409

C_9



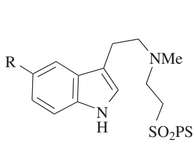


CuI (10 mol %),
BtH (20 mol %),
K_3PO_4, DMSO, 100°, 30 h



(93) 77

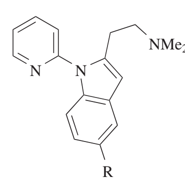
C_{10}



PS = polystyrene

ArBr

1. CuI (1 eq), CDA (1 eq), KO*t*-Bu, dioxane, 80°, 24 h
2. MeI, DMF
3. *i*-Pr_2NEt, CH_2Cl_2



455

R	Ar	
H	2-thiazolyl	(—)
H	2-furyl	(—)
H	3-pyrimidyl	(—)
H	2-pyridyl	(—)
BnO	2-pyridyl	(—)
H	3-quinolyl	(—)

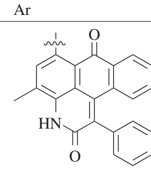
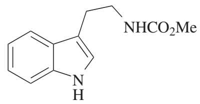
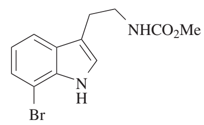
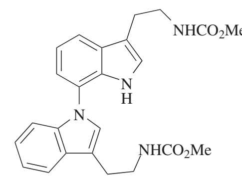
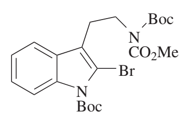
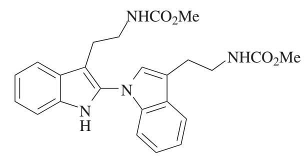
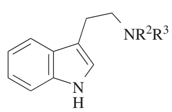
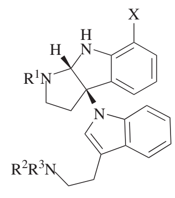
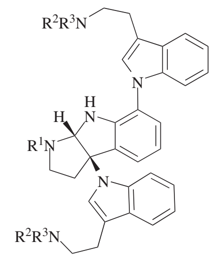
R	Ar	
H		(—)

TABLE 11B. *N*-HETEROARYLATION OF INDOLES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{10} 		CuI (30 mol %), DMCDA (60 mol %), K_2CO_3, dioxane, 101°, 20 h	 (45)	457
		1. CuI (1 eq), DMCDA (20 mol %), K_3PO_4, dioxane, 101°, 24 h 2. TFA/$MeCl_2$ (1:4), rt, 1 h	 (22)	457
		CuI (*x* amount), dioxane		

R^1	R^2	R^3	X	*x*	Additives	Temp (°)	Time (h)		Refs.
Me	Me	2-$O_2NC_6H_4SO_2$	I	1 eq	DMEDA (2 eq), K_3PO_4	90	24	(72)	169
MeO_2C	MeO_2C	H	Br	30 mol %	DMCDA (60 mol %), K_2CO_3	101	9	(89)	457

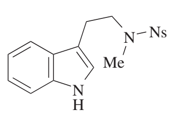
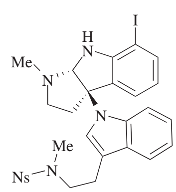
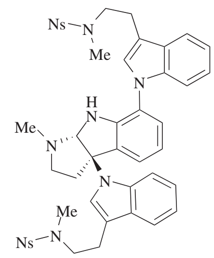
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (1 eq), DMEDA (2 eq), K_3PO_4, dioxane, 90°	 (72)	169

TABLE 12A. *N*-ARYLATION OF INDAZOLES

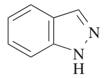
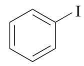
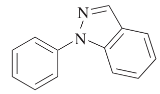
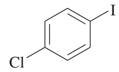
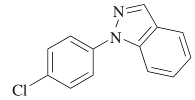
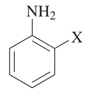
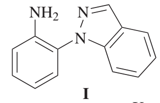
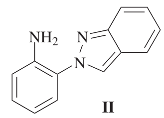
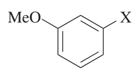
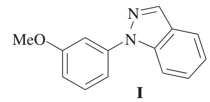
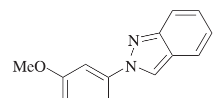
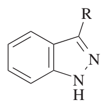
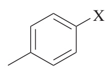
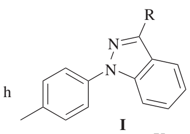
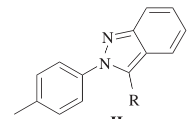
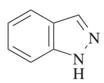
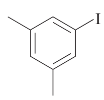
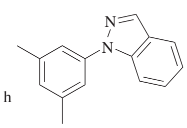
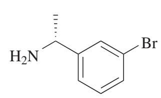
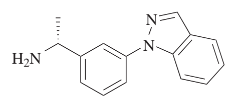
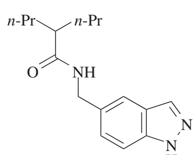
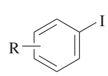
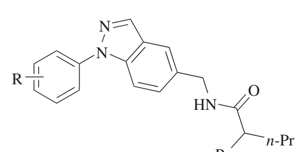
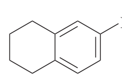
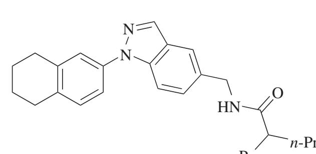
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CuI (5 mol %), TBAB (5 mol %), NaOH, toluene, reflux, 22 h	 (50)	391
		CuI (5 mol %), DMEDA (10 mol %), CsF, THF, 60°, 24 h	 (88)	63
		CuI (7 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 **I** +  **II** X | **I** | **II** Br | (41) | (29) I | (80) | (0)	128
		CuI (7 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 **I** +  **II** X | **I** | **II** Br | (49) | (25) I | (92) | (0)	128
		CuI (7 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 24 h	 **I** +  **II** X | R | **I** | **II** Br | H | (48) | (27) I | H | (85) | (0) Br | Cl | (86) | (0)	128
		CuI (1 mol %), CDA (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 (91)	115
		CuI (10 mol %), K_2CO_3, NMP, MW, 195°, 2 h	 (72)	406
C_8				
	 R = H, 2-F, 3-F, 4-F, 4-Cl, 2-MeO, 3-MeO, 4-MeO, 2-Me, 3-Me, 4-Me, 2,3-Me, 2,6-Me_2, 4-CO_2t-Bu, 4-Ac	CuI, DMCDA, K_3PO_4, dioxane, 110°, 12 h	 (—)	458
		CuI, DMCDA, K_3PO_4, dioxane, 110°, 12 h	 (—)	458

TABLE 12A. *N*-ARYLATION OF INDAZOLES (*Continued*)

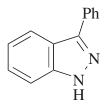
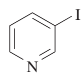
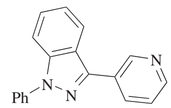
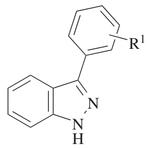
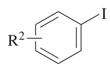
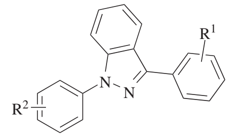
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)				Refs.
C_{13}							
		CuI (7 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 18 h	 (94)				459
C_{13-14}							
		CuI (7 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 18 h		R^1	R^2		459
				H	H	(86)	
				2,4-F_2	H	(98)	
				3-Cl	H	(93)	
				3-Me	H	(80)	
				H	2-F	(28)	
				H	3-F	(65)	
				H	4-F	(75)	
				H	2-H_2N	(73)	
				H	3-H_2N	(86)	
				H	4-H_2N	(75)	
				H	3-O_2N	(97)	
				H	2-MeO	(30)	
				H	3-MeO	(62)	
				H	4-MeO	(84)	
				H	4-Me	(68)	

TABLE 12B. *N*-HETEROARYLATION OF INDAZOLES

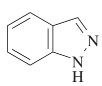
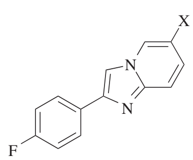
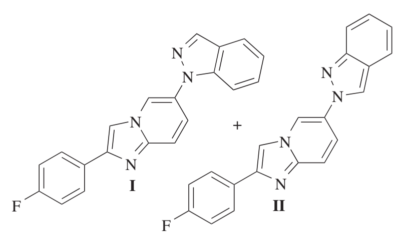
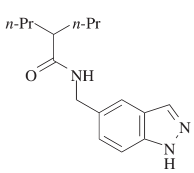
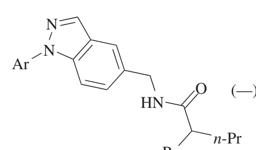
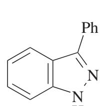
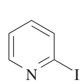
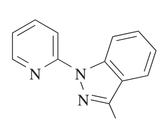
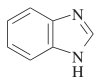
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CuI (5 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 112°, 24 h	 I + II X / I / II Br / (36) / (16) I / (83) / (3)	409
C_8				
	ArI Ar = 2-pyrimidinyl, 2-pyrazinyl, 2-pyridinyl, 4-pyridinyl, 3-(5-MeO-pyridinyl), 3-(2-MeO-pyridinyl)	CuI, DMCDA, K_3PO_4, dioxane, 110°, 12 h	 (—)	458
C_{13}				
		CuI (7 mol %), DMCDA (20 mol %), K_3PO_4, toluene, 110°, 18 h	 (98)	459

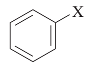
TABLE 13A. *N*-ARYLATION OF BENZIMIDAZOLES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

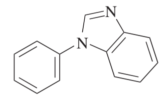
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7





Catalyst (*x* mol %)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	Cu on cellulose	1	K_2CO_3	DMSO	130	24	(40)	427
I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(82)	119
Br	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	75	28	(72)	49
I	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	60	25	(85)	49
I	CuBr	10	**L10** (12 mol %), Cs_2CO_3	DMSO	80	24	(78)	259
Br	CuBr	10	**L20** (20 mol %), Cs_2CO_3	DMSO	90	24	(87)	284
Cl	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(40)	80
Br	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(86)	80
$I^+Ph\ BF_4^-$	CuI	10	K_2CO_3	DMF	80	3	(80)	460
I	CuI	20	Cs_2CO_3	DMF	120	40	(91)	386
I	CuI	5	K_3PO_4	DMF	110	24	(72)	387
I	CuI	5	KOH, TBAB	—	110	6	(72)	428
Br	CuI	20	phen (20 mol %), KF/Al_2O_3	xylene	140	15	(90)	410
I	CuI	10	phen (20 mol %), KF/Al_2O	—	140	13	(94)	410
I	CuI	10	CDA (20 mol %), K_3PO_4	$[C_4bmim][BF_4]$	110	12	(96)	232
Br	CuI	10	L-His (20 mol %), K_2CO_3	DMSO	100	36	(78)	389
I	CuI	5	oxazolidin-2-one (10 mol %), NaOMe	DMSO	80	15	(87)	392
Br	CuI	10	8-HOquin (20 mol %), TEAC	DMF	130	24	(85)	434
Br	CuI	20	per-6-ABCD (10 mol %), K_2CO_3	DMSO	110	24	(99)	393
Br	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(29)	394
I	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(73)	394
Br	CuI	10	**L22** (10 mol %), K_2CO_3	DMF	110	24	(73)	79
Br	CuI	5	**L24** (10 mol %), Cs_2CO_3	DMF	110	24	(98)	86
I	CuI	10	**L26** (10 mol %), NaOMe	DMSO	120	12	(52)	397

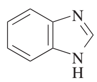
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(69)	412
I	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(99)	412
I	CuO	2.5	KOH	DMSO	110	29	(98)	224
I	Cu_2O	10	Cs_2CO_3	DMF	100	18	(86)	221
I	Cu_2O	10	KOH	DMSO	120	24	(88)	398
Cl	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(82)	68
I	Cu_2O	10	ninhydrin (20 mol %), KOH	DMSO	110	24	(88)	399
I	Cu_2O	5	**L7** (20 mol %), Cs_2CO_3	MeCN	80	18	(60)	125
Br	Cu_2O	10	**L23** (20 mol %), KO*t*-Bu	DMF	110	24	(90)	400
$I^+Ph\ BF_4^-$	$Cu(acac)_2$	100	K_2CO_3	toluene	50	6	(80)	76
I	$Cu(OAc)_2•H_2O$	15	(–)-sparteine (30 mol %), K_2CO_3	DMF	130	24	(85)	290
Br	$Cu(TMHD)_2$	20	KO*t*-Bu	DMF	120	24	(70)	308
I	$Cu(TMHD)_2$	20	KO*t*-Bu	DMF	120	24	(90)	308
Br	**8**	25	K_2CO_3	DMSO	135	35	(85)	65

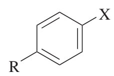
TABLE 13A. *N*-ARYLATION OF BENZIMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

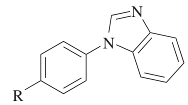
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

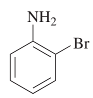




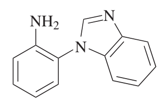
Catalyst (*x* mol %)



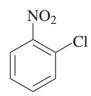
R	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
F	I	CuCl	5	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24	(83)	235
F	Br	Cu_2O	5	$(MeO)_2$phen (15 mol %), Cs_2CO_3	*n*-PrCN/PEG	110	30	(81)	84
Cl	$I^+C_6H_4$-4-Cl BF_4^-	CuI	10	K_2CO_3	DMF	80	3	(68)	460
Cl	I	CuI	5	8-HOquin (10 mol %), CsF	DMSO	100	24	(88)	63
Cl	Br	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(33)	394
Cl	I	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(63)	394
Br	$I^+C_6H_4$-4-Br BF_4^-	CuI	10	K_2CO_3	DMF	80	3	(68)	460
Br	I	CuI	5	K_3PO_4	DMF	110	24	(76)	387
Br	I	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	reflux	12	(61)	394



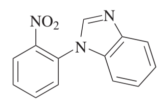
Catalyst (10 mol %),
110°, 24 h



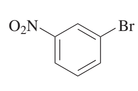
Catalyst	Additives	Solvents		Refs.
CuI	8-HOquin (20 mol %), TEAC	DMF/H_2O	(67)	434
Cu_2O	$(MeO)_2$phen (20 mol %), Cs_2CO_3	DMSO/PEG	(71)	84



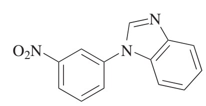
CuO (8 mol %),
K_2CO_3, pyridine,
reflux, 7 h



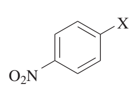
(45) 402



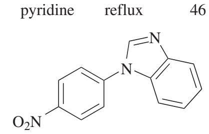
Catalyst (*x* mol %)



X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuCl	5	**L17** (10 mol %), KI, NaOH, TBAB	H_2O	100	24	(66)	235
I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(90)	119
$I^+C_6H_4NO_2$-3 BF_4^-	CuI	10	K_2CO_3	DMF	80	3	(54)	460
Cl	CuO	8	K_2CO_3	pyridine	reflux	46	(8)	402



Catalyst (*x* mol %)



X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Cl	Cu on cellulose	1	K_2CO_3	DMSO	130	24	(85)	427
Cl	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(74)	80
Br	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(95)	80
Cl	$CuBr_2$	10	TBAF	—	145	3	(81)	81
I	$CuBr_2$	10	TBAF	—	145	4.5	(86)	81
I	CuI	100	CsOAc	DMF	90	24	(73)	189
Cl	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12	(48)	397
I	CuO nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	10	(74)	74
Cl	CuO	8	K_2CO_3	pyridine	reflux	3.5	(28)	402
Cl	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(98)	68
Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(87)	234
I	$Cu(TMHD)_2$	20	KO*t*-Bu	DMF	120	24	(74)	308
Cl	$[Cu(\mu\text{-I})((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	110	12	(83)	414
Br	$[Cu(\mu\text{-I})((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	115	6	(95)	414
F	Cu fluorapatite	7	K_2CO_3	DMF	120	2	(85)	66
Cl	Cu fluorapatite	7	K_2CO_3	DMF	120	4	(85)	66
Cl	**8**	25	K_2CO_3	DMSO	135	24	(89)	65

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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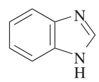
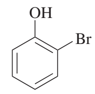
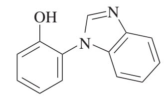
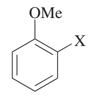


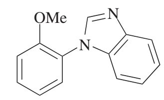


CuI (10 mol %), 8-HOquin (20 mol %), TEAC, DMF, H_2O, 120°, 70 h

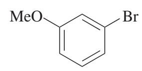
 (85) 434



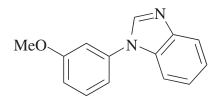
CuI (*x* mol %),



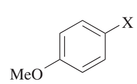
X	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
I	20	K_3PO_4	DMF	60	40	(51)	59
Br	20	phen (20 mol %), KF/Al_2O_3	xylene	140	18	(71)	410
I	10	phen (10 mol %), KF/Al_2O_3	—	140	17	(76)	411
Br	10	8-HOquin (20 mol %), TEAC	DMF/H_2O	110	64	(64)	434



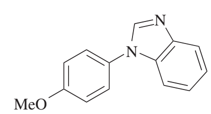
Catalyst (*x* mol %)



Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
CuI	20	phen (20 mol %), KF/Al_2O_3	xylene	140	16	(91)	410
CuI	10	8-HOquin (20 mol %), TEAC	DMF/H_2O	130	16	(87)	434
Cu_2O	10	$(MeO)_2$phen (20 mol %), MTBD	DMSO	130	24	(82)	84



Catalyst (*x* mol %)



X	Catalyst(s)	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
I	CuF_2	50	phen (50 mol %), K_2CO_3	DMF	140	96	(16)	419
I	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(80)	119
Br	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(81)	80
Cl	$CuBr_2$	10	TBAF	—	145	15	(0)	81
Br	$CuBr_2$	10	TBAF	—	145	24	(8)	273
I	$CuBr_2$	10	TBAF	—	145	24	(18)	81
Cl	CuI nanoparticles	1.25	K_2CO_3, air	DMF	110	9	(78)	285
$I^+C_6H_4OMe$-4 BF_4^-	CuI	10	K_2CO_3	DMF	80	3	(71)	460
Br	CuI	20	phen (20 mol %), KF/Al_2O	xylene	140	17	(91)	410
I	CuI	10	phen (10 mol %), KF/Al_2O	—	140	15	(86)	411
Br	CuI	10	8-HOquin (20 mol %), TEAC	DMF/H_2O	130	16	(88)	434
I	CuI	5	oxazolidin-2-one (10 mol %), NaOMe	DMSO	80	12	(92)	392
I	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8	(94)	431
I	CuI	10	CDA (20 mol %), K_3PO_4	$[C_4bmim][BF_4]$	110	12	(97)	232
I	CuO nanoparticles	10	KOH	*t*-BuOH/DMSO (3:1)	110	11	(10)	74
Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(66)	68
I	Cu_2O	5	phen (10 mol %), TBAF	—	115	48	(85)	68
Br	$[Cu(\mu\text{-I})((-)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	115	13	(88)	414
I	$[Cu(\mu\text{-I})((-)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	115	7	(95)	414
I	Cu/Al–hydrotalcite	2,5	K_2CO_3	DMF	100	18	(85)	228
Br	**8**	25	K_2CO_3	DMSO	135	48	(85)	435

TABLE 13A. *N*-ARYLATION OF BENZIMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

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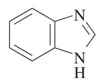
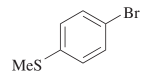
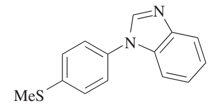
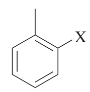




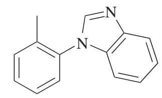
CuI (10 mol %), 8-HOquin (20 mol %), TEAC, DMF, H_2O, 130°, 16 h



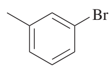
(83) 434



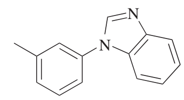
Catalyst (5 mol %)



X	Catalyst	Additive	Solvent(s)	Temp (°)	Time (h)	Yield (%)	Refs.
I	CuBr	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(67)	119
I	CuI	BtH (10 mol %), KO*t*-Bu	DMSO	110	8	(95)	431
Br	Cu_2O	$(MeO)_2$phen (15 mol %), Cs_2CO_3	DMSO/PEG	110	24	(76)	84



CuBr (5 mol %), **L5** (10 mol %), Cs_2CO_3, DMF, 90°, 24 h



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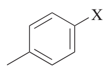
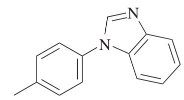
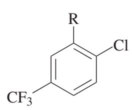


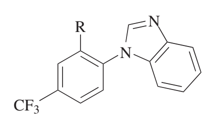
Catalyst (*x* mol %)



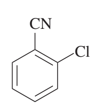
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
$I^+C_6H_4Me$-4 BF_4^-	CuI	10	K_2CO_3	DMF	80	3	(76)	460
I	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8	(95)	431
Br	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(34)	394
Cl	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(trace)	68
Br	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(89)	68
Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(71)	234
$I^+C_6H_4Me$-4 BF_4^-	$Cu(acac)_2$	100	K_2CO_3	toluene	50	6	(94)	76
Br	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	48	(99)	404
I	Cu(II)–NaY zeolite	10	K_2CO_3	DMF	120	36	(99)	404
Br	**2**	2	NaOH, TBAB	H_2O	100	12	(81)	233



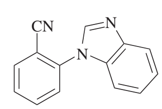
CuI (10 mol %)



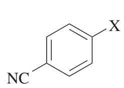
R	Additives	Solvent(s)	Temp (°)	Time (h)	Yield (%)	Refs.
H	8-HOquin (20 mol %), TEAC	DMF/H_2O	130	60	(50)	434
NO_2	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(90)	394



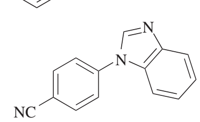
$[Cu(\mu\text{-}I)((–)\text{-sparteine})]_2$ (1 mol %), K_2CO_3, DMSO, 125°, 16 h



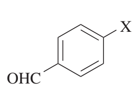
(82) 414



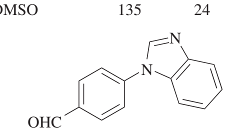
Catalyst (*x* mol %)



X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield (%)	Refs.
Br	CuI	10	L-Pro (20 mol %), K_2CO_3	DMSO	95	42	(99)	47
Br	CuI	10	CDA (20 mol %), K_3PO_4	$[C_4mim][BF_4]$	110	12	(70)	232
Br	CuI	10	8-HOquin (20 mol %), TEAC	DMF/H_2O	110	24	(87)	434
Br	CuO	8	K_2CO_3	pyridine	reflux	101	(42)	402
Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(82)	234
Cl	$[Cu(\mu\text{-}I)((–)\text{-sparteine})]_2$	1	K_2CO_3	DMSO	125	14	(86)	414
Br	**2**	2	NaOH, TBAB	H_2O	100	12	(92)	233
Cl	**8**	25	K_2CO_3	DMSO	135	24	(90)	435



$[Cu(\mu\text{-}I)((–)\text{-sparteine})]_2$ (1 mol %), K_2CO_3, DMSO, 115°, 8 h

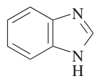


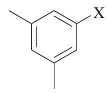
X	Time (h)	Yield (%)	Refs.
Cl	19	(77)	414
Br	8	(90)	

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

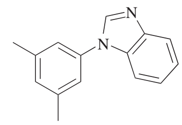
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_7

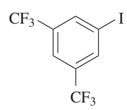




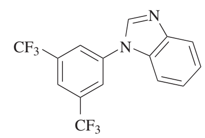
Catalyst (*x* mol %)



X	Catalyst	*x*	Additives	Solvent(s)	Temp (°)	Time (h)		Refs.
I	CuI	10	phen (20 mol %), Cs_2CO_3	dioxane	110	24	(91)	115
I	CuI	10	phen (20 mol %), Cs_2CO_3	DMF	110	24	(80)	128
Br	CuI	10	8-HOquin (10 mol %), Cs_2CO_3	DMF/H_2O	120	70	(90)	434
Br	Cu(OAc)•H_2O	5	4,7-Cl_2phen (10 mol %), KO*t*Bu	NMP	125	22	(99)	452
I	$(CuOTf)_2$•C_6H_6	10	phen (1 eq), dba, Cs_2CO_3	xylenes	125	48	(91)	11



CuI (10 mol %), DMEDA (20 mol %), TEAC, DMF, 110°, 10 h



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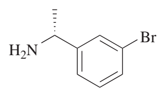
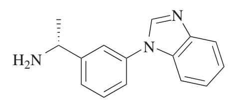
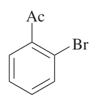


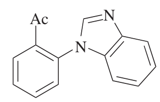
CuI (10 mol %), K_2CO_3, NMP, MW, 195°, 2 h



(88) 406



CuO (8 mol %), K_2CO_3, pyridine, reflux, 3 h



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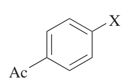
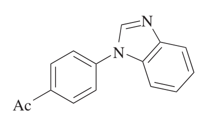
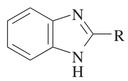


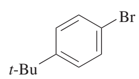
Catalyst (*x* mol %)



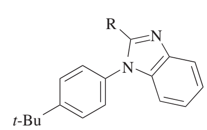
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuCl	5	**L17** (10 mol %), NaOH, TBAF	H_2O	100	24	(62)	235
Br	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(92)	80
Br	CuI	10	DMG (20 mol %), K_2CO_3	DMSO	110	40	(75)	47
Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24	(80)	417
Br	CuO	8	K_2CO_3	pyridine	reflux	80	(48)	402
I	Cu/Al–hydrotalcite	2.5	K_2CO_3	DMF	100	15	(88)	228
Br	[Cu(μ-I)((–)-sparteine)]$_2$	1	K_2CO_3	DMSO	115	8	(92)	414
Br	**8**	25	K_2CO_3	DMSO	135	30	(82)	65

$C_{7–8}$



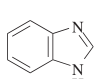


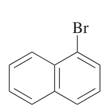
Cu_2O (5 mol %), MeO_2phen (15 mol %), Cs_2CO_3, PEG, DMSO, 110°, 24 h



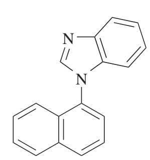
R		Refs.
H	(98)	84
Me	(82)	

C_7





CuI (20 mol %), phen (20 mol %), KF/Al_2O_3, xylene, 140 °C, 17 h



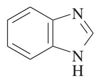
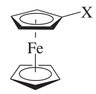
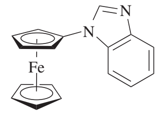
(71) 410

TABLE 13A. *N*-ARYLATION OF BENZIMIDAZOLES (*Continued*)

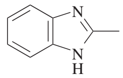
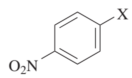
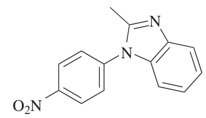
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_7

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Cu(TMHD)_2$ (20 mol %), KO*t*-Bu, DMSO, 90°, 12 h	 X: Br (18); I (35)	407

C_8

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (10 mol %)		

X	Catalyst	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
Cl	CuI	**L26** (10 mol %), NaOMe	DMSO	110	12	(50)	397
Cl	Cu_2O	phen (20 mol %), TBAF	—	145	24	(trace)	68
Br	Cu_2O	phen (20 mol %), TBAF	—	145	24	(63)	68

C_{12}

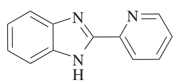
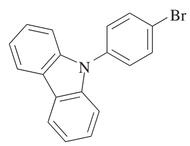
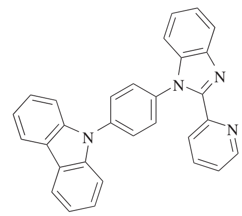
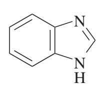
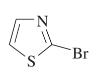
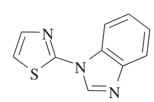
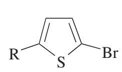
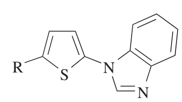
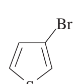
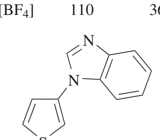
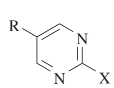
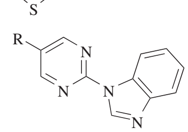
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), 18-c-6 (3 mol %), K_2CO_3, DMPU, 230°, 13 h	 (67)	461

TABLE 13B. *N*-HETEROARYLATION OF BENZIMIDAZOLES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_7 		CuBr (10 mol %), **L37** (20 mol %), TBAF, 150°, 24 h	 (55)	80
		Catalyst (*x* mol %)		

R	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(62)	80
H	CuI	30	L-Pro (60 mol%)	$[C_4mim][BF_4]$	110	24	(76)	230
H	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24	(80)	417
Me	CuI	30	L-Pro (60 mol%)	$[C_4mim][BF_4]$	110	36	(73)	230

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (30 mol %), L-Pro (60 mol %), $[C_4mim][BF_4]$, 110°, 36 h	 (75)	230
		Catalyst (*x* mol %), 24 h		

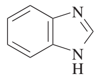
R	X	Catalyst	*x*	Additives	Solvent	Temp (°)		Refs.
H	Cl	CuBr	10	**L37** (20 mol %), TBAF	none	150	(100)	80
H	Br	CuBr	10	**L37** (20 mol %), TBAF	none	150	(100)	80
H	I	CuI	5	phen (10 mol %), Cs_2CO_3	DMF	110	(50)	408
H	Br	CuI	5	**L30** (10 mol %), Cs_2CO_3	MeCN	reflux	(78)	408
H	Cl	Cu_2O	10	phen (10 mol %), TBAF	—	145	(77)	68
Br	I	CuI	5	phen (10 mol %), Cs_2CO_3	DMF	80	(57)	408

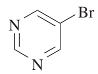
TABLE 13B. *N*-HETEROARYLATION OF BENZIMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

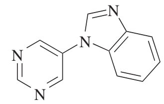
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

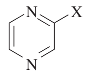




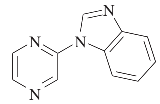
CuBr (5 mol %), **L5** (10 mol %), Cs_2CO_3, DMF, 90°, 24 h



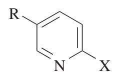
(73) 119



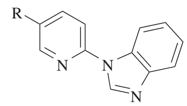
Catalyst (*x* mol %)



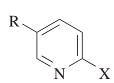
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
Cl	$CuBr_2$	10	TBAF	—	145	1	(76)	81
I	CuI	5	phen (10 mol %), Cs_2CO_3	DMF	110	24	(50)	408
Cl	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12	(88)	397



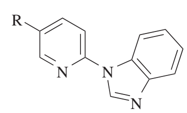
Catalyst (*x* mol %),



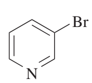
R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
H	Cl	Cu	5	binol (20 mol %), Cs_2CO_3	DMSO	110	36	(88)	124
H	Br	CuCl	5	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24	(87)	235
H	Br	CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	24	(78)	119
H	Cl	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(56)	80
H	Br	CuBr	10	**L37** (20 mol %), TBAF	none	150	24	(99)	80
H	Br	$CuBr_2$	10	TBAF	—	145	4	(90)	81
H	Br	CuI	30	L-Pro (60 mol %)	$[C_4mim][BF_4]$	100	10	(87)	230
H	Br	CuI	5	BtH (10 mol %), KO*t*-Bu	DMSO	110	8	(98)	431
H	Br	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	80	12	(94)	392
H	Br	CuI	10	CDA (20 mol %), K_3PO_4	$[C_4mim][BF_4]$	110	12	(78)	232
H	Br	CuI	10	**L26** (10 mol %), NaOMe	DMSO	110	12	(90)	397
H	Br	CuI	10	**L32** (20 mol %), Cs_2CO_3	DMF	110	24	(90)	417



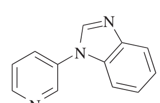
Catalyst (*x* mol %),



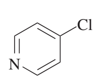
R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
H	Br	CuO	8	K_2CO_3	pyridine	reflux	24	(46)	402
H	Cl	Cu_2O	10	phen (20 mol %), TBAF	—	145	24	(95)	68
H	Br	$CuSO_4$	10	**L36** (20 mol %), Cs_2CO_3	H_2O	120	24	(78)	234
H	Br	**2**	2	NaOH, TBAB	H_2O	100	12	(58)	233
Br	I	CuI	5	phen (10 mol %), Cs_2CO_3	DMF	80	24	(90)	408



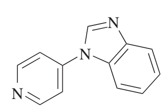
Catalyst (*x* mol %), 24 h



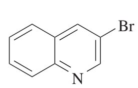
Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Yield	Refs.
CuBr	5	**L5** (10 mol %), Cs_2CO_3	DMF	90	(77)	119
CuO	8	K_2CO_3	pyridine	reflux	(33)	402



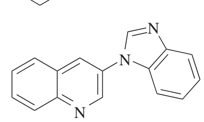
CuO (8 mol %), K_2CO_3, pyridine, reflux, 19.5 h



(21) 402



CuBr (10 mol %), **L37** (20 mol %), TBAF, neat, 150°, 24 h

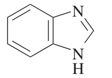
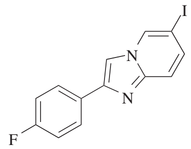
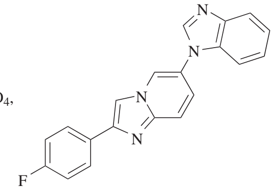
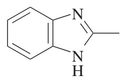
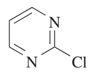
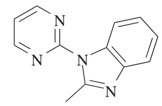


(63) 80

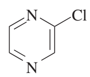
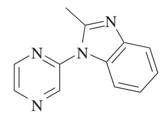
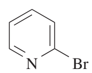
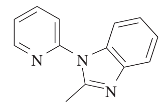
TABLE 13B. *N*-HETEROARYLATION OF BENZIMIDAZOLES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		CuI (5 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 112°, 24 h	 (9)	409
C_8 		Catalyst (10 mol %), 24 h		

Catalyst	Additives	Solvent	Temp (°)		Refs.
CuBr	**L37** (20 mol %), TBAF	none	150	(78)	80
Cu_2O	phen (20 mol %), TBAF	—	145	(66)	68

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), **L26** (10 mol %), NaOMe, DMSO, 130°, 12 h	 (66)	397
		Catalyst (10 mol %),		

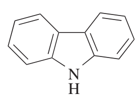
Catalyst	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
CuBr	**L37** (20 mol %), TBAF	none	150	24	(95)	80
CuI	**L26** (10 mol %), NaOMe	DMSO	130	12	(88)	397

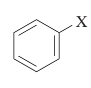
TABLE 14A. *N*-ARYLATION OF CARBAZOLES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

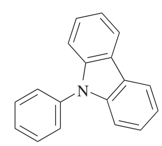
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{12}

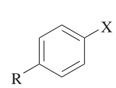




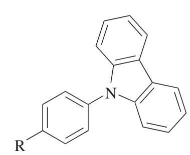
Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	Cu	20	Cs_2CO_3	*n*-PrCN	reflux	20	(81)	129
I	Cu	20	K_2CO_3	$PhNO_2$	reflux	24	(99)	348
Br	CuI	10	phen (20 mol %), KF/Al_2O_3	toluene	reflux	7	(90)	390
I	CuI	10	phen (20 mol %), KF/Al_2O	toluene	reflux	7	(90)	390
I	CuO	0.1	DMEDA (20 mol %), $K_3PO_4 \cdot H_2O$	toluene	135	24	(25)	222

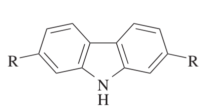


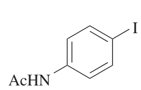
CuI (x mol %)



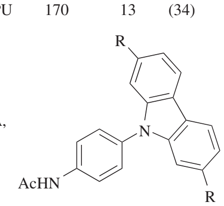
R	X	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
Cl	I	5	DMEDA (10 mol %), CsF	THF	60	25	(88)	63
Br	Br	10	18-c-6 (3 mol %), K_2CO_3	DMPU	170	13	(34)	461

$C_{12–36}$





Cu_2O (1.5 eq), DMA, 160°, 24 h

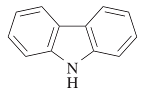


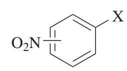
R		Refs.
H	(55)	462
1-carbazolyl	(99)	

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

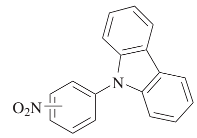
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{12}

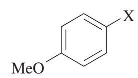




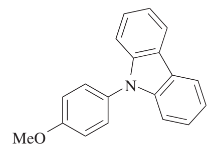
Catalyst (x mol %)



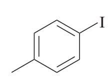
Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	Cl	CuO	8	K_2CO_3	pyridine	reflux	16	(90)	402
3	Cl	CuO	8	K_2CO_3	pyridine	reflux	16	(90)	402
4	Br	CuCl	5	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24	(85)	235
4	Cl	CuO	8	K_2CO_3	pyridine	reflux	18	(0.2)	402



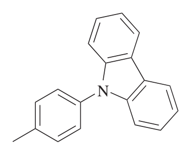
Catalyst (x amount)



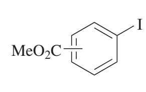
X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
I	CuI	10 mol %	L-Pro (10 mol %), K_2CO_3	DMSO	90	40	(75)	47
I	CuI	5 mol %	L-Pro (10 mol %), K_2CO_3	DMSO	90	40	(93)	401
Br	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	10	(83)	390
I	CuI	10 mol %	phen (20 mol %), KF/Al_2O_3	toluene	reflux	8	(89)	390
I	Cu_2O	2 eq	none	DMA	160	24	(82)	463



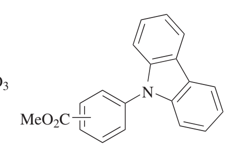
Catalyst (5 mol %)



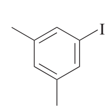
Catalyst	Additives	Solvent	Temp (°)	Time (h)		Refs.
CuCl	**L17** (10 mol %), NaOH, TBAB	H_2O	100	24	(89)	235
CuI	**L41** (10 mol %), NaO*t*-Bu	toluene	reflux	40	(86)	338



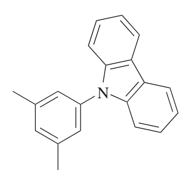
Cu (x mol %), K_2CO_3



Isomer	x	Solvent	Temp (°)	Time (h)		Refs.
2	50	$PhNO_2$	180	40	(59)	349
2	20	$PhNO_2$	reflux	24	(60)	348
4	3	xylene	200	1	(60)	464



CuI (x mol %)



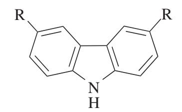
x	Additives	Solvent	Temp (°)	Time (h)		Refs.
1	CDA (10 mol %), K_3PO_4	dioxane	110	24	(90)	115
5	L-Pro (10 mol%), K_2CO_3	DMSO	90	40	(90)	401

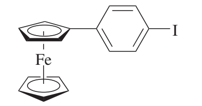
TABLE 14A. *N*-ARYLATION OF CARBAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

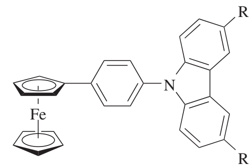
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{12-108}





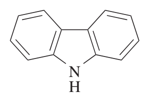
CuI (10 mol %), CDA (15 mol %), K_3PO_4, dioxane, 110°, 24 h

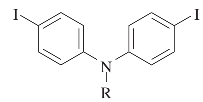


Ref. 465

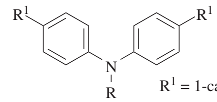
R	
H	(77)
1-carbazolyl	(47)
3,6-bis(1-carbazolyl)-1-carbazolyl	(54)
3,6-bis[3,6-bis(1-carbazolyl)-1-carbazolyl]-1-carbazolyl	(54)

C_{12}





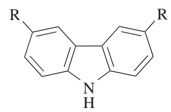
Cu (*x* eq), K_2CO_3, 24 h

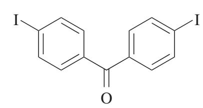


R^1 = 1-carbazolyl

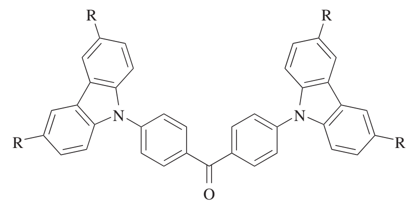
R	*x*	Additive	Solvent	Temp (°)		Refs.
n-Bu	2	18-c-6 (10 mol %)	1,2-$Cl_2C_6H_4$	reflux	(69)	373
4-$MeOC_6H_4$	1	none	triglyme	200	(74)	371

C_{12-108}



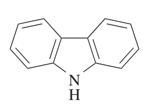


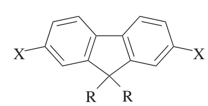
Catalyst (*x* amount)



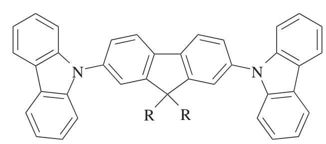
R	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	Cu_2O	3 eq	none	DMA	165	48	(83)	466
H	CuI	5 mol %	CDA (10 mol %), K_3PO_4	dioxane	110	24	(80)	465
1-carbazolyl	Cu_2O	3 eq	none	DMA	165	48	(46)	466
1-carbazolyl	CuI	5 mol %	CDA (10 mol %), K_3PO_4	dioxane	110	24	(77)	465
3,6-bis(1-carbazolyl)-1-carbazolyl	CuI	5 mol %	CDA (10 mol %), K_3PO_4	dioxane	110	24	(85)	465
3,6-bis[3,6-bis(1-carbazolyl)-1-carbazolyl]-1-carbazolyl	CuI	5 mol %	CDA (10 mol %), K_3PO_4	dioxane	110	24	(32)	465

C_{12}

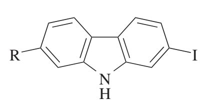


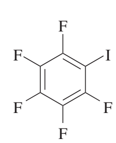


Catalyst (*x* mol %), 24 h

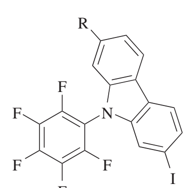


R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)		Refs.
Et	I	CuI	20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	(48)	467
n-C_6H_{13}	Br	Cu	45	K_2CO_3	$PhNO_2$	reflux	(98)	468
n-C_8H_{17}	Br	Cu	44	K_2CO_3	$PhNO_2$	reflux	(93)	469

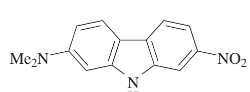


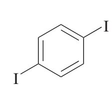


Cu, 18-c-6, K_2CO_3, reflux

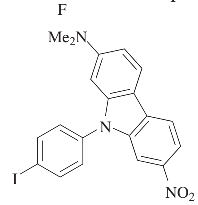


R		Refs.
H	(78)	470
I	(65)	471



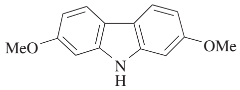
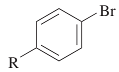
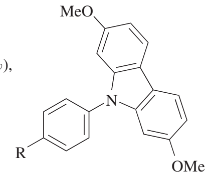
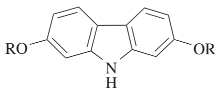
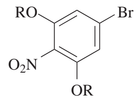
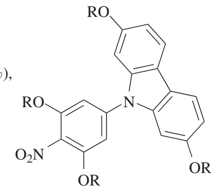
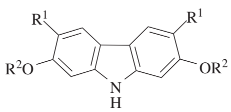
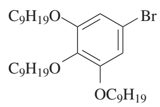
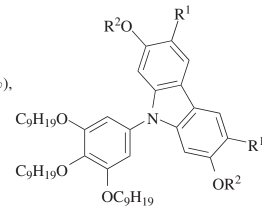
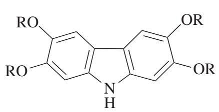
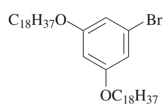
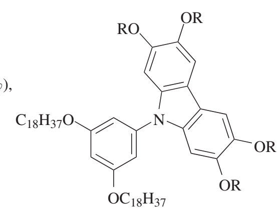
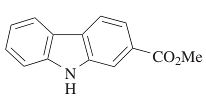
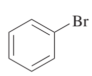
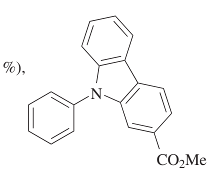
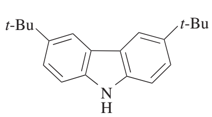
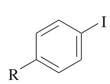
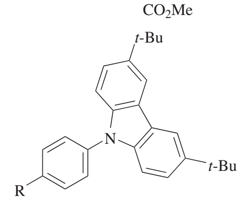


Cu (10 mol %), Na_2SO_4, K_2CO_3, $PhNO_2$, 180°, 23 h

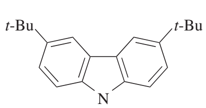
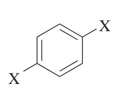
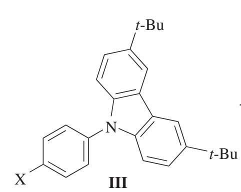
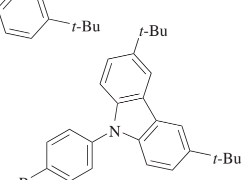
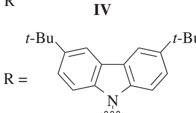


(50) 472

TABLE 14A. *N*-ARYLATION OF CARBAZOLES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{12}				
		Cu-bronze (14 mol %), K_2CO_3, DMA, 160°, 12 h	 R: O_2N (98); MeO (98)	473
		Cu-bronze (14 mol %), K_2CO_3, DMA, 160°, 12 h	 R: Me (98); *n*-$C_{18}H_{37}$ (98)	473
 R^1 = H or C_9H_{19}; R^2 = C_9H_{19}		Cu-bronze (14 mol %), K_2CO_3, DMA, 160°, 12 h	 (94)	473
 R = C_9H_{19}		Cu-bronze (14 mol %), K_2CO_3, DMA, 160°, 12 h	 (85)	473
C_{13}				
		Cu-bronze (14 mol %), K_2CO_3, DMA, 160°, 12 h	 (72)	473
C_{20}				
		Catalyst (*x* eq), 24 h		

R	Catalyst	*x*	Additive	Solvent	Temp (°)	Yield (%)	Refs.
H	Cu	1	K_2CO_3	$PhNO_2$	170	(92)	474
O_2N	Cu	1	K_2CO_3	$PhNO_2$	170	(92)	444
MeO	Cu_2O	2	none	DMA	160	(83)	463
CHO	Cu	1	K_2CO_3	$PhNO_2$	170	(80)	444

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
 **I**	 **II**	Cu (1 eq), K_2CO_3, $PhNO_2$, 170°, 24 h	 **III** +  **IV** R = 	474

X	**I**/**II**	**III**	**IV**
Br	excess of **II**	(55)	(—)
I	excess of **II**	(80)	(—)
I	2:1	(—)	(55)

TABLE 14A. *N*-ARYLATION OF CARBAZOLES (*Continued*)

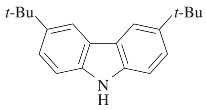
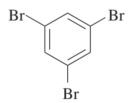
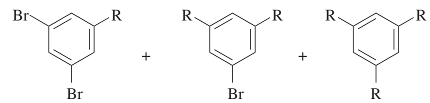
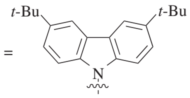
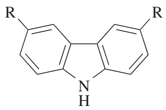
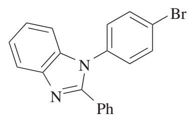
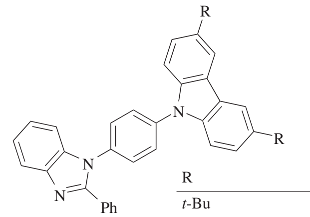
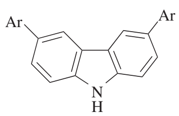
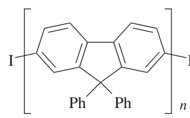
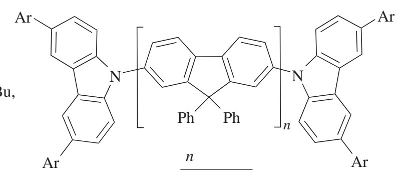
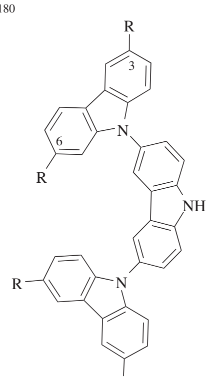
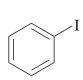
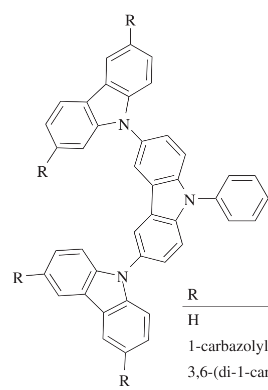
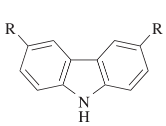
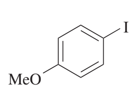
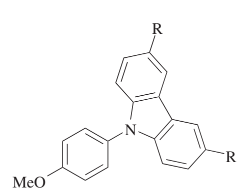
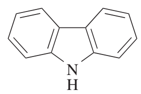
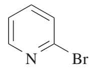
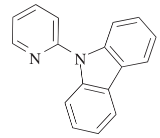
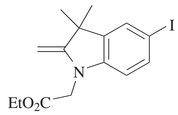
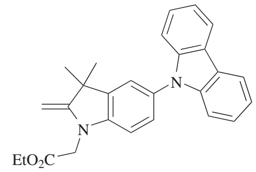
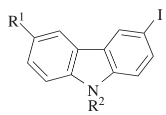
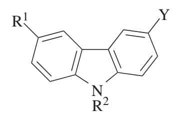
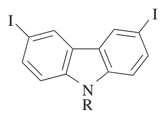
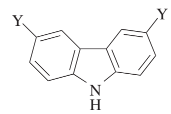
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{20}				
 **I**	 **II**	Cu (1 eq), K_2CO_3, $PhNO_2$, 170°, 24 h	 **III** + **IV** + **V** R =  **I/II** — **III** — **IV** — **V** 1:2 — (50) — (—) — (—) 2:1 — (—) — (27) — (—) slight excess of **II** — (—) — (—) — (0)	474
$C_{20–52}$				
		CuI (5 mol %), 18-c-6 (5 mol %), K_2CO_3, DMPU, 190°, 24 h	 R *t*-Bu (86) 3,6-(*t*-Bu)$_2$-1-carbazolyl (72)	475
C_{24}				
 Ar = 4-$Ph_2NC_6H_4$		CuI (1 mol %), CDA (10 mol %), NaO*t*-Bu, dioxane, 110°, 24 h	 *n* 1 (45) 2 (51) 3 (55)	172
$C_{36–180}$				
		CuI (5 mol %), CDA (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 R H (40) 1-carbazolyl (32) 3,6-(di-1-carbazolyl)-1-carbazolyl (47)	465
C_{52}				
 R = 3,6-di(*t*-Bu)$_2$-1-carbazolyl		Cu_2O (2 eq), DMA, 160°, 24 h	 (76)	463

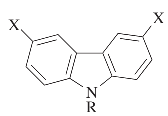
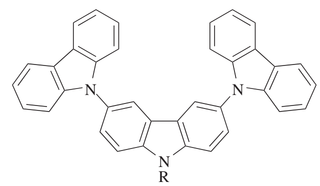
TABLE 14B. *N*-HETEROARYLATION OF CARBAZOLES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 		CuO (8 mol %), K_2CO_3, pyridine, reflux, 26 h	 (59)	402
		CuI (6 mol %), DMCDA (12 mol %), Cs_2CO_3, dioxane, 100°, 17 h	 (53)	476
		Catalyst (*x* eq)	 Y = 1-carbazolyl	

R^1	R^2	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	*n*-C_6H_{13}	Cu	2	18-6-c (10 mol %), K_2CO_3	1,2-$Cl_2C_6H_4$	reflux	36	(63)	477
H	Ts	Cu_2O	—	none	DMA	170	24	(76)	478
CHO	*n*-Bu	Cu	2.5	none	DMA	190	24	(63)	479

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		See table.	 Y = 1-carbazolyl	

R	Conditions		Refs.
Ac	1. Cu_2O (1.5 eq), DMA, 160°, 24 h 2. KOH, H_2O, DMSO, THF	(55)	462
Boc	1. CuI (10 mol %), CDA (15 mol %), K_3PO_4, dioxane, 110°, 24 h 2. TFA, H_2O, anisole, toluene	(58)	465

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (*x* amount), K_2CO_3		

R	X	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
n-Bu	I	2 eq	18-c-6 (10 mol %)	1,2-$Cl_2C_6H_4$	reflux	24	(69)	373
Bn	I	—	18-c-6	DMF	170	24	(67)	480
n-C_8H_{17}	Br	44 mol %	none	$PhNO_2$	reflux	24	(87)	469
n-C_8H_{17}	I	2 eq	18-c-6 (10 mol %)	1,2-$Cl_2C_6H_4$	reflux	36	(77)	477
n-$C_{10}H_{21}$	I	2 eq	18-c-6 (10 mol %)	1,2-$Cl_2C_6H_4$	reflux	36	(63)	477

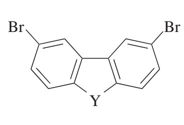
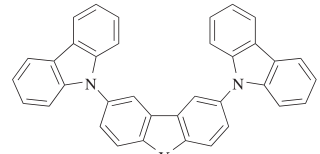
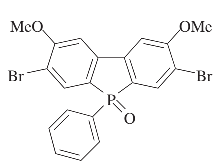
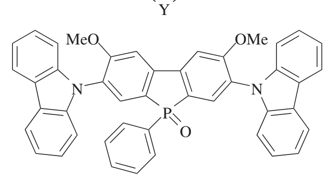
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu (44 mol %), K_2CO_3, $PhNO_2$, reflux, 24 h	 Y: O (70); S (68)	469
		Cu (44 mol %), K_2CO_3, $PhNO_2$, reflux, 24 h	 (55)	469

TABLE 14B. *N*-HETEROARYLATION OF CARBAZOLES (*Continued*)

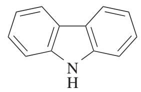
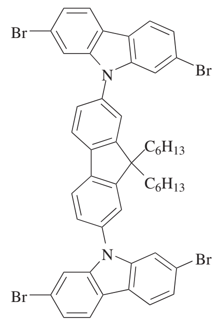
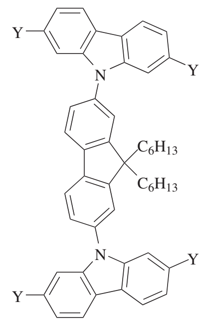
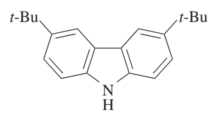
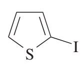
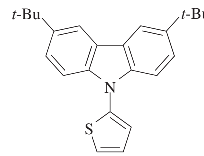
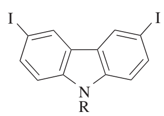
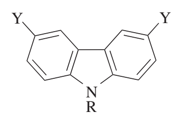
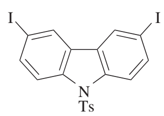
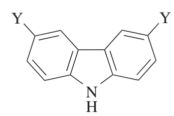
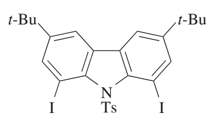
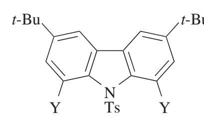
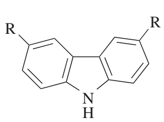
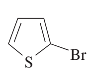
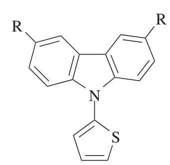
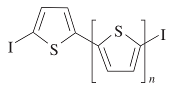
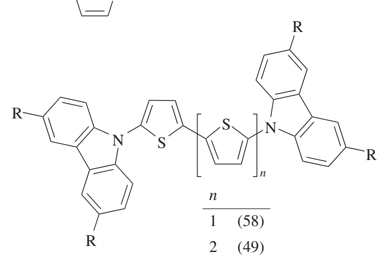
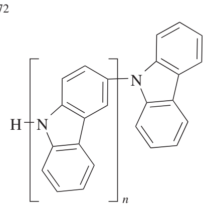
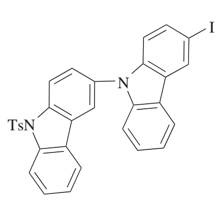
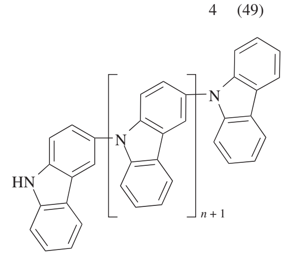
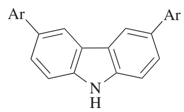
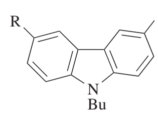
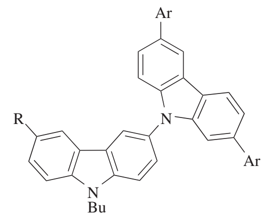
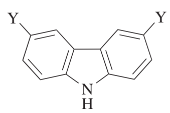
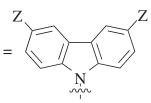
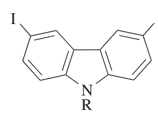
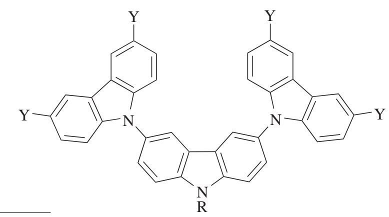
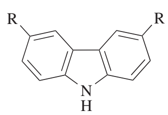
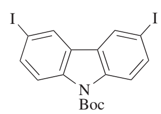
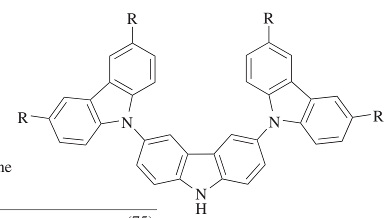
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
		Cu (45 mol %), K_2CO_3, $PhNO_2$, reflux, 24 h	 (55) Y = 1-carbazolyl	468
C_{20}				
		Cu (1 eq), K_2CO_3, $PhNO_2$, 170°, 24 h	 (52)	474
		Cu (*x* eq), K_2CO_3, $PhNO_2$, 170°, 24 h	 Y = 3,6-(*t*-Bu)$_2$-1-carbazolyl R / *x* Bn 1 (82) Ts 1 (66) Ts 2.3 (66)	 474 474 481
		1. Cu_2O (2 eq), DMA, 180°, 24 h 2. KOH, H_2O, DMSO, THF reflux, 4 h	 (83) Y = 3,6-(*t*-Bu)$_2$-1-carbazolyl	463
		Cu (1 eq), K_2CO_3, $PhNO_2$, 170°, 24 h	 (65) Y = 3,6-(*t*-Bu)$_2$-1-carbazolyl	474
C_{24}				
 R = 4-$Ph_2NC_6H_4$		CuI (25 mol %), CDA (2.5 eq), NaO*t*-Bu, dioxane, 110°, 40 h	 (74)	474
		CuI (25 mol %), CDA (2.5 eq), NaO*t*-Bu, dioxane, 110°, 40 h	 *n* 1 (58) 2 (49) 3 (82) 4 (49)	482
$C_{24–72}$				
		1. Cu_2O, DMA, 170°, 24 h 2. KOH, H_2O, DMSO, THF, reflux	 *n* 1 (38) 3 (35) 5 (22)	478

TABLE 14B. *N*-HETEROARYLATION OF CARBAZOLES (*Continued*)

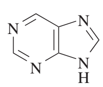
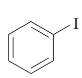
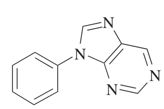
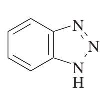
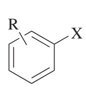
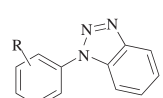
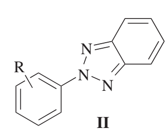
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{36}				
 Ar =1-carbazolyl		Cu_2O (2.5 eq), DMAc, 190°, 24 h	 R: H (68); CHO (51)	479
$C_{36–52}$				
 Y = 		Cu_2O (x eq), DMA, 24 h		

R	Z	x	Temp (°)		Refs.
4-AcNHC$_6$H$_4$	H	1.5	160	(37)	462
4-MeOC$_6$H$_4$	t-Bu	2	160	(64)	463

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{36–180}$				
		1. CuI (10 mol %), CDA (15 mol %), K_3PO_4, dioxane, 110°, 24 h 2. TFA, H_2O, anisole, toluene		466

R	
1-carbazolyl	(75)
3,6-bis(1-carbazolyl)-1-carbazolyl	(75)
3,6-bis[3,6-bis(1-carbazolyl)-1-carbazolyl]-1-carbazolyl	(47)

TABLE 15A. *N*-ARYLATION OF MISCELLANEOUS HETEROAROMATIC NITROGEN NUCLEOPHILES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
9*H*-Purines				
C_5				
		CuI (5 mol %), DMCDA (20 mol %), Cs_2CO_3, DMF, 70°, 24 h	 (66)	128
1*H*-Benzo[*d*][1,2,3]triazoles				
C_6				
		Catalyst (*x* mol %)	 I +  II	

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
H	Br	CuI	10	**L28** (20 mol %), K_2CO_3	DMSO	120	60	(93)	(—)	412
H	I	CuI	5	DMCDA (10 mol %), K_3PO_4	DMF	110	24	(89)	(—)	128
H	I	Cu_2O	5	phen (10 mol %), TBAF	—	145	48	(19)	(—)	68
H	$I^+Ph\ BF_4^-$	$Cu(acac)_2$	100	K_2CO_3	toluene	50	6	(80)	(—)	76
4-O_2N	I	$CuBr_2$	10	TBAF	—	145	24	(35)	(13)	81
4-O_2N	Cl	$CuBr_2$	10	TBAF	—	145	15	(38)	(30)	81
4-O_2N	Cl	CuI	10	**L26** (10 mol %), NaOMe	DMSO	130	12	(65)	(—)	397
4-Me	$I^+C_6H_4Me\text{-}4\ BF_4^-$	$Cu(acac)_2$	100	K_2CO_3	toluene	50	6	(94)	(—)	76
2-O_2N, 4-CF_3	Cl	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(95)	(—)	397
2-O_2N, 4-CF_3	Cl	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	reflux	12	(89)	(—)	394
4-Ac	I	CuI	5	DMCDA (20 mol %), K_3PO_4	DMF	110	24	(67)	(—)	128

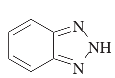
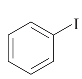
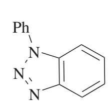
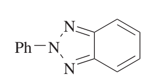
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
2*H*-Benzo[*d*][1,2,3]triazoles				
C_6				
		CuCl (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, MW, 160°	 (60) +  (8)	443

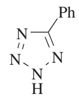
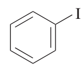
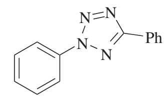
TABLE 15A. *N*-ARYLATION OF MISCELLANEOUS HETEROAROMATIC NITROGEN NUCLEOPHILES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

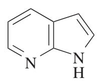
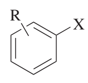
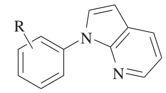
2*H*-Tetrazoles

C_7

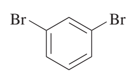
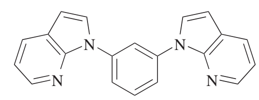
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Cu_2O (5 mol %), **L30** (20 mol %), DMF, 110°, 24 h	 (0)	40

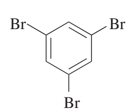
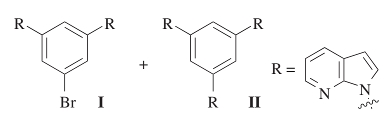
1*H*-Pyrrolo[3,2-*b*]pyridines

C_7

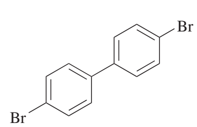
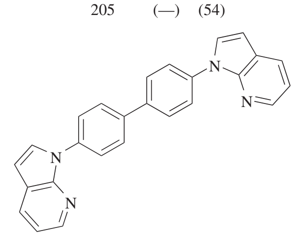
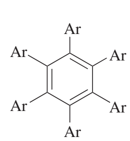
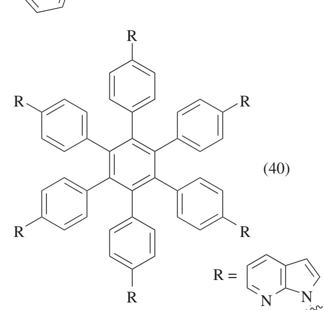
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %)		

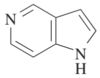
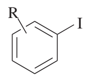
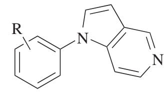
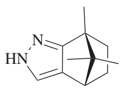
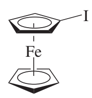
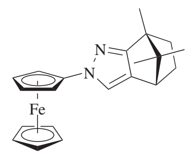
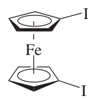
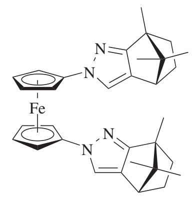
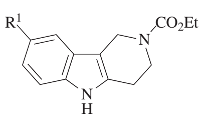
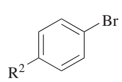
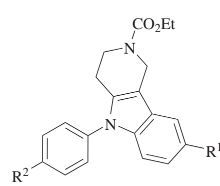
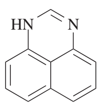
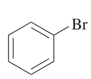
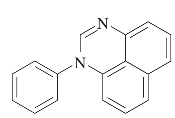
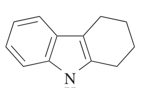
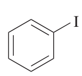
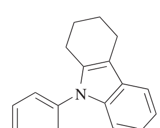
R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
H	I	CuO	0.001	DMEDA (20 mol %), $K_3PO_4 \cdot H_2O$	toluene	135	24	(86)	425
4-F	I	CuI	10	LiCl, K_2CO_3	DMF	120	24	(75)	483
3,5-F_2	I	CuI	10	LiCl, K_2CO_3	DMF	120	24	(78)	483
4-Cl	I	CuI	5	DMEDA (10 mol %), CsF	THF	rt	24	(88)	63
4-Br	I	CuI	10	LiCl, K_2CO_3	DMF	120	24	(60)	483
4-Br	Br	$CuSO_4$	5	K_2CO_3	—	220	6	(43)	76, 484
2-EtO_2C	I	CuI	10	LiCl, K_2CO_3	DMF	120	36	(92)	483
3,5-Me_2	I	CuI	1	CDA (10 mol %), K_3PO_4	dioxane	110	24	(99)	115

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$CuSO_4$ (2 mol %), K_2CO_3, 210°, 6 h	 (85)	437

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$CuSO_4$ (2.5 mol %), K_2CO_3, 9 h		

Temp (°)	I	II	Refs.
210	(32)	(54)	437
205	(—)	(54)	485

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		$CuSO_4$ (4 mol %), K_2CO_3, 210°, 12 h	 (63)	437
	 Ar = 4-BrC_6H_4	CuI (5 mol %), DMCDA (50 mol %), K_3PO_4, toluene, reflux	 (40)	486

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
1*H*-Pyrrolo[3,2-*c*]pyridines				
C_7				
		CuI (10 mol %), LiCl, K_2CO_3, DMF, 120°, 24 h	 R: H (70); 4-Cl (85); 4-MeO (65); 2-EtO_2C (88)	483
4,5,6,7-Tetrahydro-4,7-methano-2-indazoles				
C_{11}				
		CuI (1 eq), K_2CO_3, DMSO, 90°, 18 h	 (70)	372
		CuI (1 eq), K_2CO_3, DMSO, 90°, 18 h	 (31)	372
2,3,4,5-Tetrahydro-1*H*-pyrido[4,3-*b*]indoles				
C_{11-12}				
		CuBr (10 mol %), Na_2CO_3, DMF, 200°, 8 h	 R^1, R^2: H, H (40); F, H (61); Cl, H (65); Br, H (46); MeO, H (47); Me, H (62); F, F (78); Cl, F (69); MeO, F (47)	487
1*H*-Perimidines				
C_{11}				
		CuI (10 mol %), **L22** (10 mol %), K_2CO_3, DMF, 110°, 24 h	 (53)	79
2,3,4,9-Tetrahydro-1*H*-carbazoles				
C_{12}				
		Catalyst (*x* mol %), reflux		

Catalyst	*x*	Additive(s)	Solvent	Time (h)		Refs.
Cu	20	Cs_2CO_3	*n*-PrCN	10	(95)	129
CuI	10	TM–BINAM (10 mol %), K_2CO_3	MeCN	36	(72)	446

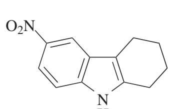
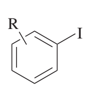
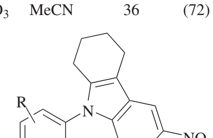
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	 R = 2-EtO_2C, 3-EtO_2C, 4-EtO_2C	CuI, DMEDA, K_2CO_3, toluene, reflux	 (—)	488

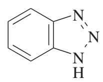
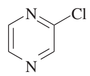
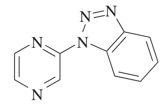
TABLE 15B. *N*-HETEROARYLATION OF MISCELLANEOUS HETEROAROMATIC NITROGEN NUCLEOPHILES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

1*H*-Benzo[*d*][1,2,3]triazoles

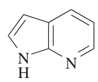
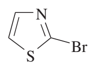
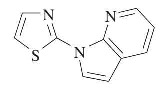
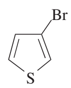
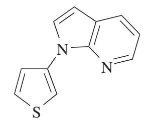
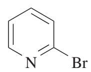
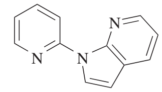
C_6

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (10 mol %)		

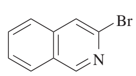
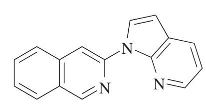
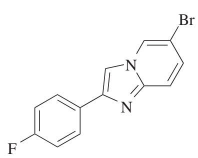
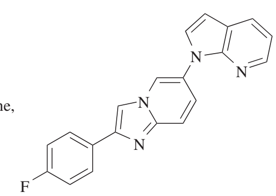
Catalyst	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
$CuBr_2$	TBAF	—	145	2.5	(76)	81
CuI	**L26** (10 mol %), NaOMe	DMSO	130	12	(94)	397

1*H*-Pyrrolo[3,2-*b*]pyridines

C_7

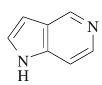
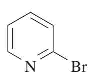
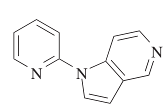
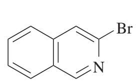
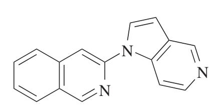
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), LiCl, K_2CO_3, DMF, 120°, 48 h	 (40)	483
		CuI (10 mol %), LiCl, K_2CO_3, DMF, 120°, 48 h	 (40)	483
		CuI (*x* mol %)		

x	Additives	Solvent	Temp (°)	Time (h)		Refs.
10	LiCl, K_2CO_3	DMF	120	36	(85)	483
20	D-glucosamine (40 mol %), Cs_2CO_3	DMSO	110	22	(64)	467

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), LiCl, K_2CO_3, DMF, 120°, 48 h	 (50)	483
		CuI (5 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 112°, 24 h	 (94)	409

1*H*-Pyrrolo[3,2-*c*]pyridines

C_7

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), LiCl, K_2CO_3, DMF, 120°, 36 h	 (75)	483
		CuI (10 mol %), LiCl, K_2CO_3, DMF, 120°, 36 h	 (80)	483

1*H*-Perimidines

C_{11}

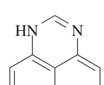
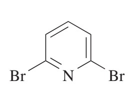
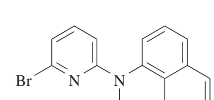
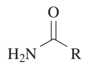
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), **L22** (10 mol %), K_2CO_3, DMF, 110°, 48 h	 (62)	79

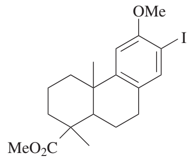
TABLE 16A. *N*-ARYLATION OF PRIMARY AMIDES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

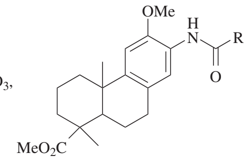
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{1-8}





CuI (1 mol %), DMEDA (2 mol %), K_2CO_3, dioxane, 100°, 24 h

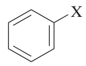


R	
H	(82)
Me	(84)
Et	(81)
n-Pr	(84)
Ph	(80)
Bn	(92)

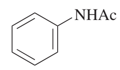
489

C_2

NH_2Ac

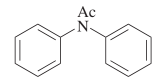


Catalyst (*x* amount)



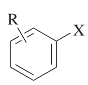
I

+

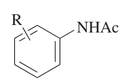


II

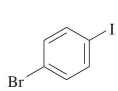
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
Br	Cu	3 eq	none	—	210	12	(79)	(0)	303
I	Cu	3 eq	none	—	180	12	(64)	(0)	303
I	CuBr	10 mol %	**L9** (20 mol %), Cs_2CO_3	DMSO	75	28	(84)	(0)	49
I	CuI	10 mol %	K_3PO_4	DMF	110	24	(65)	(0)	387
I	CuI	5 mol %	KOH, TBAB	—	110	6	(87)	(0)	428
I	CuI	10 mol %	phen (10 mol %), KF/Al_2O_3	toluene	110	5	(97)	(0)	490
I	CuI	5 mol %	Gly (20 mol %), K_3PO_4	dioxane	100	24	(95)	(0)	136
I	CuI	15 mol %	L-Pro (15 mol %), KF/Al_2O	toluene	110	5	(80)	(0)	491
I	CuI	10 mol %	PPAPM (20 mol %), K_3PO_4	—	110	30	(89)	(0)	48
I	CuI	7.5 mol %	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	2	(95)	(0)	137
I	CuI	10 mol %	oxazolidin-2-one (20 mol %), Na_2CO_3	DMSO	120	24	(88)	(0)	492
Cl	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	30	(24)	(0)	67
Br	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	36	(78)	(0)	67
I	CuI	10 mol %	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	36	(86)	(0)	67
I	CuI	5 mol %	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(50)	(11)	138
I	Cu_2O	5 mol %	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(76)	(0)	493
I	Cu_2O nanoparticles	5 mol %	KOH	PEG 4000	120	3	(73)	(0)	225
I	Cu_2O	5 mol %	Cs_2CO_3	NMP	80	18	(88)	(0)	266
Br	Cu_2O	5 mol %	NaO*t*-Bu	NMP	110	18	(72)	(0)	266
I	Cu_2O	5 mol %	**L30** (20 mol %), Cs_2CO_3, 3 Å MS	DMF	82	75	(81)	(7)	40



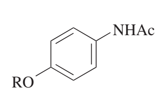
CuI (*x* mol %)



R	X	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2-Cl	I	10	oxazolidin-2-one (20 mol %), K_2CO_3	DMSO	120	24	(80)	492
4-Br	I	10	PPAPM (20 mol %), K_3PO_4	—	110	20	(94)	48
4-Br	I	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(91)	136
2-NO_2	I	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(88)	136
2-MeO	I	1	CDA (10 mol %), K_3PO_4	dioxane	90	23	(94)	115
2-MeO	I	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	4	(90)	137
2-MeO	I	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	5.5	(70)	137
4-MeO	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(85)	494
4-MeO	I	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	2	(90)	137
4-MeO	I	0.2	CDA (5 mol %), K_3PO_4	dioxane	110	23	(99)	115
4-MeO	I	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(90)	136
4-MeO	I	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	5.5	(90)	491
4-MeO	I	10	phen (10 mol %), KF/Al_2O_3	toluene	110	9.5	(90)	490
4-MeO	I	10	oxazolidin-2-one (20 mol %), K_2CO_3	DMSO	120	24	(80)	492
2-Me	I	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	6	(0)	491
2-Me	I	1	DMEDA (10 mol %), K_3PO_4	DMF	80	23	(95)	69
2-Me	I	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	4	(90)	137
4-Me	I	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(92)	136
4-Me	I	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	2	(90)	137
4-Me	I	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	5	(90)	491
4-Ac	Br	20	DMG (20 mol %)	DMF	reflux	48	(86)	494
4-Ac	I	5	Gly (20 mol%)	dioxane	100	24	(62)	136

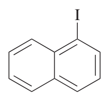
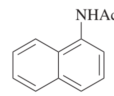
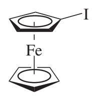
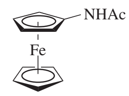
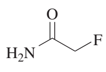
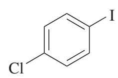
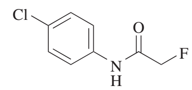
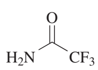
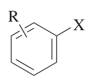
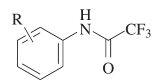


1. CuI (15 mol %), DMG (20 mol %), K_3PO_4, DMSO, 80°, 24 h
2. ROH, 120°, 48 h

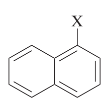
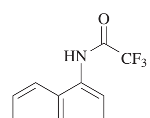


R	
Ph	(65)
4-ClC_6H_4	(60)
2-$MeOC_6H_4$	(65)
4-$MeOC_6H_4$	(70)
2-Np	(66)

495

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_2				
NH_2Ac		CuI (10 mol %), oxazolidin-2-one (20 mol %), K_2CO_3, DMSO, 120°, 24 h	 (76)	492
		CuI (1 eq), K_2CO_3, DMSO, 90°, 18 h	 (70)	372
		CuI (5 mol %), DMEDA (10 mol %), CsF, THF, rt, 24 h	 (98)	63
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, 4 Å MS, DMF, 36 h		132

R	X	Temp (°)	
H	Br	75	(96)
H	I	45	(95)
4-Br	I	45	(94)
2-H_2N	I	45	(6)
4-Me_2N	Br	75	(99)
4-O_2N	I	45	(94)
2-MeO	I	45	(26)
4-MeO	Br	75	(93)
4-MeO	I	45	(93)
2-Me	I	45	(15)
4-Me	I	45	(94)
3-NC–	Br	75	(83)
4-NC–	Br	75	(84)
4-EtO_2C	I	45	(83)
4-Ac	Br	75	(81)
4-Ac	I	45	(90)
4-Ph	Br	75	(98)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMEDA (10 mol %), K_3PO_4, 4 Å MS, DMF, 36 h		132

X	Temp (°)	
Br	75	(61)
I	45	(21)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	ArX	1. CuI (5 mol %), K_3PO_4, DMEDA (10 mol %), 4 Å MS, DMF, temp, 36 h 2. MeOH/H_2O, rt, 12 h	$ArNH_2$	132

Ar	X	Temp (°)	
Ph	Br	75	(93)
Ph	I	45	(91)
4-BrC_6H_4	I	45	(80)
4-$O_2NC_6H_4$	Br	75	(93)
4-$MeOC_6H_4$	Br	75	(87)
4-MeC_6H_4	Br	75	(91)
4-MeC_6H_4	I	45	(95)
3-NCC_6H_4	Br	75	(95)
4-NCC_6H_4	Br	75	(99)
4-$EtO_2CC_6H_4$	I	45	(99)
4-AcC_6H_4	I	45	(98)
4-PhC_6H_4	Br	75	(93)
1-Np	Br	75	(50)

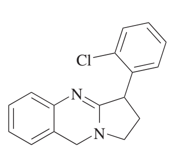
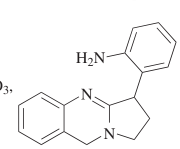
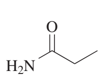
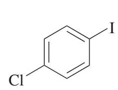
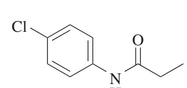
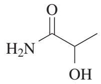
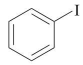
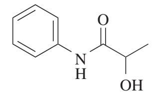
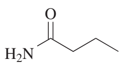
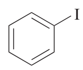
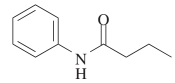
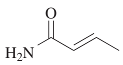
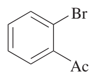
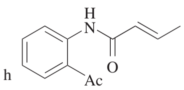
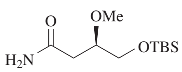
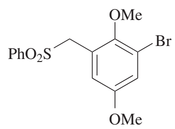
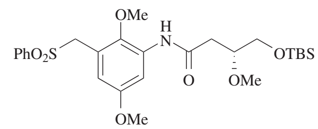
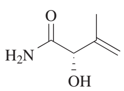
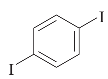
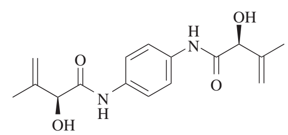
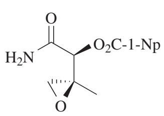
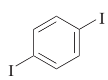
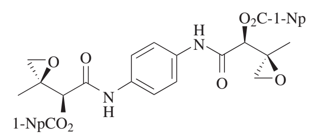
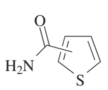
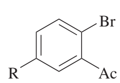
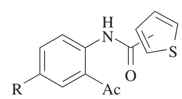
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CuI (25 mol %), DCDA (50 mol %), K_2CO_3, dioxane, 140°, 21 h 2. HCl, H_2O	 (37)	496
C_3				
		CuI (5 mol %), DMEDA (10 mol %), CsF, THF, rt, 24 h	 (94)	63

TABLE 16A. *N*-ARYLATION OF PRIMARY AMIDES (*Continued*)

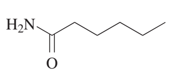
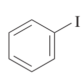
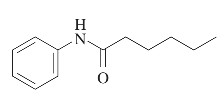
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		CuI (1 mol %), DMEDA (10 mol %), K_3PO_4, DMF, 60°, 23 h	 (90)	69
C_4				
		CuO (0.1 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 135°, 24 h	 (56)	222
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, 5 Å MS, 110°, 24 h	 (68)	497
		CuI (20 mol %), DMEDA (40 mol %), K_2CO_3, toluene, 110°	 (82)	160
C_5				
		CuI (1 eq), DMEDA (2 eq), K_3PO_4, dioxane, 50°, 22 h	 (63)	498
		CuI (1 eq), DMEDA (2 eq), K_3PO_4, dioxane, 50°, 22 h	 (10)	498

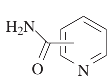
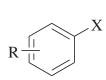
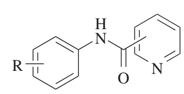
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMEDA (20 mol %), K_2CO_3, 110°, 24 h		497

Isomer	R	Additive	
2	H	none	(81)
2	MeO	5 Å MS	(72)
3	H	none	(81)

C_6

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (5 mol %), KOH		

Catalyst	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
CuI	TBAB	—	110	4	(75)	428
Cu_2O nanoparticles	none	PEG 4000	120	3	(75)	225

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (10 mol %)		

Isomer	R	X	Catalyst	Additives	Solvent	Temp (°)	Time (h)		Refs.
2	4-MeO	I	CuI	EDA (10 mol %), K_3PO_4	dioxane	110	24	(59)	405
2	3,5-Me_2	I	CuI	EDA (10 mol %), K_3PO_4	dioxane	110	24	(50)	405
2	2-Ac, 5-F	Br	CuI	DMEDA (20 mol %), K_2CO_3, 5 Å MS	—	110	24	(77)	497
3	H	I	CuBr	**L9** (20 mol %), Cs_2CO_3	DMSO	60	24	(83)	49
3	2-Ac	Br	CuI	DMEDA (20 mol %), K_2CO_3, 5 Å MS	—	110	24	(86)	497
4	2-Ac	Br	CuI	DMEDA (20 mol %), K_2CO_3	—	110	24	(80)	497
4	2-Ac	Br	CuI	DMEDA (20 mol %), K_3PO_4, 5 Å MS	—	110	42	(71)	497

C_7

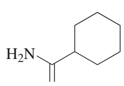
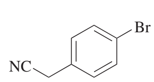
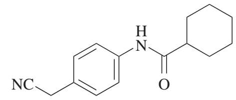
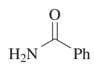
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 24 h	 (83)	69

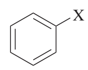
TABLE 16A. *N*-ARYLATION OF PRIMARY AMIDES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

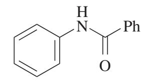
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

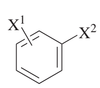




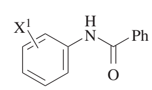
Catalyst (x mol %)



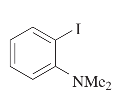
X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	Cu	—	K_2CO_3	—	reflux	2	(50)	2
Br	Cu	300	none	—	210	12	(79)	303
I	Cu	300	none	—	180	12	(64)	303
$I^+Ph\ BF_4^-$	CuI	5	K_2CO_3	toluene	50	6	(42)	76
I	CuI	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(97)	136
I	CuI	5	KOH, TBAB	—	110	5	(75)	428
Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(84)	494
I	CuI	5	EDA (5 mol %), K_2CO_3	PEG-400	80	8	(75)	301
I	CuI	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	1.5	(95)	137
I	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24	(70)	492
I	CuI	10	phen (10 mol %), KF/Al_2O_3	toluene	110	1.5	(99)	490
Br	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	8	(25)	491
I	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	4	(80)	491
I	CuI	5	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(71)	138
Br	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	82	12	(32)	394
I	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	82	12	(79)	394
I	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(76)	493
Cl	Cu_2O nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	24	(0)	74
Br	Cu_2O nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	24	(0)	74
I	Cu_2O nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	24	(73)	74
TsO	Cu_2O nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	24	(0)	74
I	Cu_2O nanoparticles	5	KOH	PEG-4000	120	10	(73)	225
Br	Cu_2O	5	NaO*t*-Bu	NMP	105	32	(97)	266
I	Cu_2O	5	Cs_2CO_3	NMP	90	24	(97)	266
I	Cu_2O	5	**L30** (20 mol %), Cs_2CO_3, 3 Å MS	DMF	82	48	(91)	40
I	$Cu(OAc)_2{\bullet}H_2O$	15	sparteine (30 mol %), K_2CO_3	DMF	130	13	(45)	290



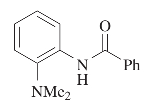
Catalyst (x mol %)



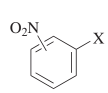
X^1	X^2	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
4-F	Br	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	82	12	(46)	394
4-F	I	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	82	12	(81)	394
2-Cl	I	CuI	10	oxazolidin-2-one (20 mol %), K_2CO_3	DMSO	120	24	(86)	492
4-Cl	I	CuI	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	4.5	(80)	491
4-Br	I	CuI	5	KOH, TBAB	—	110	5	(75)	428
4-Br	I	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	5.5	(75)	491
4-Br	I	Cu_2O nanoparticles	5	KOH	PEG-4000	120	12	(76)	225



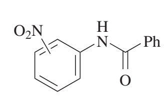
CuI (1 mol %),
CDA (10 mol %), K_3PO_4,
dioxane, 110°, 23 h



(96) — 115, 69



Catalyst (x mol %)



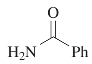
Isomer	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
2	5	DMEDA (10 mol %), K_3PO_4	toluene	80	7	(88)	69
2	1	CDA (10 mol %), K_3PO_4	dioxane	110	23	(69)	115
4	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	2	(95)	137
4	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	6	(75)	491

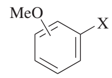
TABLE 16A. *N*-ARYLATION OF PRIMARY AMIDES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

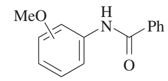
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

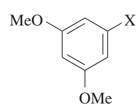




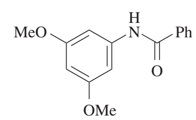
Catalyst (*x* mol %)



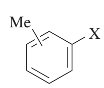
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	I	CuI	5	KOH, TBAB	—	110	8	(72)	428
2	I	CuI	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	4	(90)	137
2	I	CuI	1	DMCDA (10 mol %), K_2CO_3	dioxane	110	15	(84)	115
2	I	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	5	(80)	491
2	I	Cu_2O nanoparticles	5	KOH	PEG-4000	120	17	(70)	225
2	Br	Cu_2O	5	NaO*t*-Bu	NMP	105	24	(84)	266
3	I	Cu_2O	5	Cs_2CO_3	NMP	90	24	(92)	266
4	I	CuI	5	KOH, TBAB	—	110	6	(82)	428
4	Br	CuI	5	EDA (5 mol %), K_2CO_3	PEG-400	80	8	(70)	301
4	I	CuI	10	EDA (10 mol %), K_3PO_4	dioxane	110	24	(60)	405
4	I	CuI	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	1.5	(95)	137
4	I	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24	(85)	492
4	I	CuI	10	DMCDA (20 mol %), K_3PO_4	$[C_4mim][BF_4]$	110	12	(83)	232
4	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(73)	494
4	Br	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	5.5	(trace)	491
4	I	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	4	(85)	491
4	I	CuI	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(71)	136
4	I	CuI	10	phen (10 mol %), KF/Al_2O_3	toluene	110	3.5	(99)	490
4	I	Cu_2O nanoparticles	5	KOH	PEG-4000	120	15	(75)	225
4	I	**10**	3	Cs_2CO_3	DMSO	100	24	(<1)	420



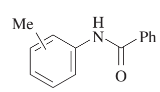
CuI (10 mol %), **L21** (20 mol %), Cs_2CO_3, MeCN, 82°, 12 h



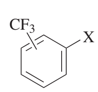
X	Additive		Refs.
Br	KI	(42)	394
I	none	(78)	



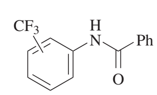
Catalyst (*x* mol %)



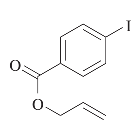
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
2	I	CuI	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	4 h	(90)	137
2	I	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	5 h	(80)	491
4	Br	Cu (active)	500	none	—	MW, 100 W	10 min	(71)	280
4	I	CuI	5	KOH, TBAB	—	110	5 h	(75)	428
4	Cl	CuI	5	DMEDA (11 mol %), K_2CO_3	—	110	23 h	(93)	115
4	I	CuI	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	2 h	(90)	137
4	I	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	3.5 h	(90)	491
4	Cl	CuI	5	DMCDA (11 mol %), K_2CO_3	—	110	23 h	(93)	69
4	Br	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	82	12 h	(41)	394
4	I	Cu_2O nanoparticles	5	KOH	PEG-4000	120	12 h	(75)	225



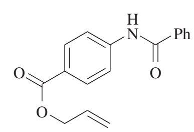
Cu_2Br_2 (1 mol %), K_2CO_3



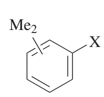
Isomer	Temp (°)	Time (h)		Refs.
2	160	55	(35)	453
3	180	26	(75)	



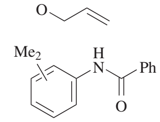
CuI (1 mol %), CDA (10 mol %), K_3PO_4, dioxane, 110°, 23 h



(86) 115, 69



Catalyst (*x* mol %)



Isomer	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
2,3	Br	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	82	12	(36)	394
2,3	I	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	82	12	(71)	394
2,4	I	CuI	5	KOH, TBAB	—	110	6	(91)	428
2,4	I	Cu_2O nanoparticles	5	KOH	PEG-4000	120	16	(72)	225
3,5	I	CuI	5	DMEDA (10 mol %), Cs_2CO_3	H_2O, THF	rt	7	(99)	69
3,5	I	CuI	1	DMCDA (10 mol %), K_2CO_3	dioxane	110	15	(90)	115
3,5	I	CuI	5	**L44** (10 mol %), Cs_2CO_3	dioxane	rt	46	(96)	115
3,5	I	Cu_2O	5	Cs_2CO_3	NMP	90	24	(98)	266

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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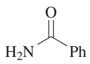
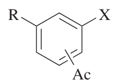
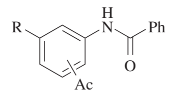
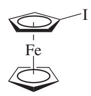




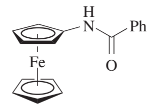
Catalyst (x mol %)



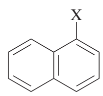
Isomer	R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	H	Br	CuI	10	DMEDA (20 mol %), K_2CO_3, 5 Å MS	—	90	24	(86)	497
2	F	Br	CuI	10	DMEDA (20 mol %), K_2CO_3, 5 Å MS	—	110	24	(78)	497
4	H	I	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	5.5	(75)	491
4	H	Cl	**10**	3	Cs_2CO_3	DMSO	100	24	(10)	420
4	H	Br	**10**	3	Cs_2CO_3	DMSO	100	24	(31)	420
4	H	I	**10**	3	Cs_2CO_3	DMSO	100	24	(73)	420



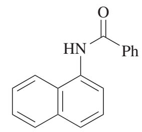
CuI (1 eq), K_2CO_3, DMSO, 90°, 18 h



(57) 372



Catalyst (x mol %)



X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Br	CuI	5	EDA (5 mol %), K_2CO_3	PEG-400	80	8	(73)	301
I	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24	(79)	492
I	CuI	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	6	(60)	491
I	Cu_2O nanoprticles	5	KOH	PEG-4000	120	12	(80)	225

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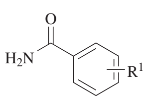
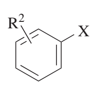
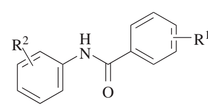




CuI (10 mol %), **L21** (20 mol %), Cs_2CO_3, MeCN, 82°, 12 h



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R^1	R^2	X	
4-F	4-Br	I	(81)
4-F	3,5-$(CF_3)_2$	Br	(42)
4-F	4-Me	Br	(40)
4-Cl	4-F	Br	(81)
4-Cl	4-F	I	(81)
4-Cl	3,5-$(MeO)_2$	Br	(37)
4-Cl	3,5-$(MeO)_2$	I	(83)

R^1	R^2	X	
3,5-$(MeO)_2$	4-Br	I	(67)
3,5-$(MeO)_2$	4-Me	Br	(45)
2,3-Me_2	4-Br	Br	(36)
2,3-Me_2	4-Me	I	(71)

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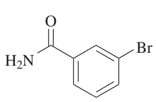
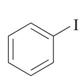
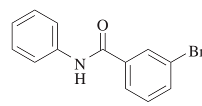




CuI (5 mol %), TBAB, KOH, 110°, 6 h



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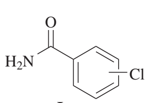
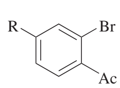
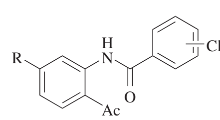


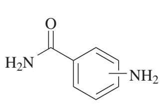
I

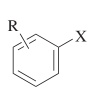


CuI (10 mol %), DMEDA (20 mol %), K_2CO_3, 5 Å MS, 110°, 24 h

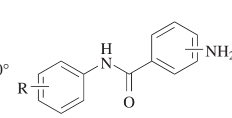


I Isomer	R		Refs.
2	F	(67)	497
3	H	(83)	
3	MeO	(72)	





CuI (x mol %), dioxane, 110°



Isomer	R	X	x	Additives	Time (h)		Refs.
2	H	Br	5	DMEDA (10 mol %), K_2CO_3	24	(97)	107
3	4-*t*-Bu	Br	5	DMEDA (10 mol %), K_2CO_3	24	(97)	107
4	3,5-Me_2	Br	5	DMEDA (10 mol %), K_2CO_3	24	(97)	107
4	3,5-Me_2	I	1	CDA (10 mol %), K_3PO_4	23	(81)	115, 69

TABLE 16A. *N*-ARYLATION OF PRIMARY AMIDES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

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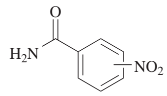
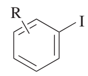
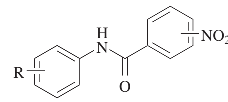
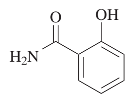
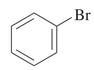



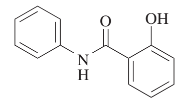
CuI (*x* mol %), 110°



Isomer	R	*x*	Additives	Solvent	Time (h)		Refs.
2	4-MeO	10	EDA (10 mol %), K_3PO_4	dioxane	24	(61)	405
2	3,5-Me_2	10	EDA (10 mol %), K_3PO_4	—	24	(68)	405
3	H	5	TBAB, KOH	—	7	(63)	428
4	H	5	TBAB, KOH	—	6	(58)	428
4	4-MeO	10	EDA (10 mol %), K_3PO_4	dioxane	24	(67)	405

Cu, K_2CO_3, reflux, 2 h



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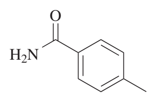
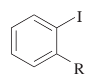
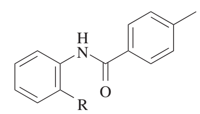
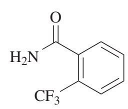
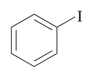



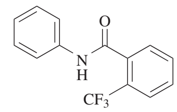
CuI (*x* mol %)



R	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	5	TBAB, KOH	—	110	5	(76)	428
Cl	10	oxazolidinone (20 mol %), K_2CO_3	DMSO	120	24	(78)	492

Cu_2Br_2 (1 mol %), K_2CO_3, 180°, 26 h



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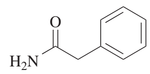
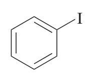
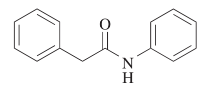
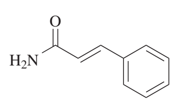
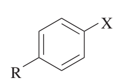



CuI (10 mol %), NaOMe, DMSO, oxazolidinone (20 mol %), 120°, 24 h

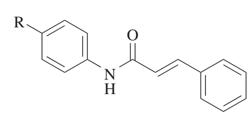


(69) 492

C_9

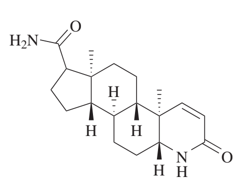
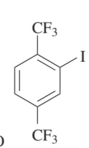



CuI (5 mol %), 110°

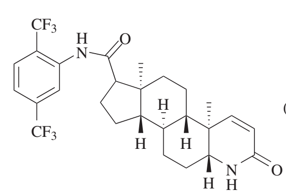


R	X	Additives	Solvent	Time (h)		Refs.
H	I	KOH, TBAB	—	5	(52)	428
Me_2N	Br	DMCDA (10 mol %), K_2CO_3	toluene	24	(99)	69

C_{19}

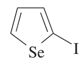
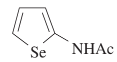
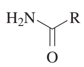
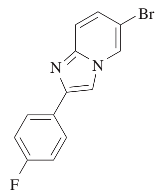
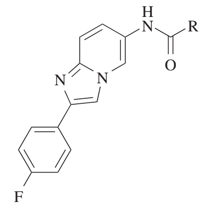
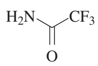
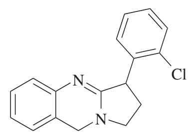
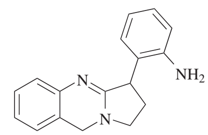
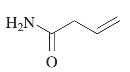
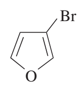
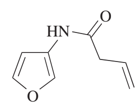
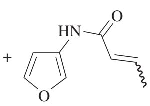
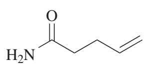
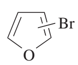
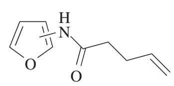



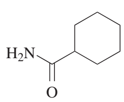
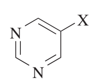
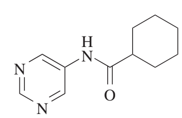
Cu (3 eq), K_2CO_3, *o*-xylene, 140°, 52 h



(53) 499

TABLE 16B. *N*-HETEROARYLATION OF PRIMARY AMIDES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
NH_2Ac		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, reflux, 24 h	 (48)	87
C_{2-7}				
		CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 20 h	 R: Me (85); Ph (99)	500
C_2				
		1. CuI (25 mol %), DMCDA (50 mol %), K_3CO_3, dioxane, 140°, 21 h 2. HCl, H_2O	 (37)	496
C_4				
		CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, dioxane, 110°, 24 h	 (12) +  (12)	83
C_5				
		CuI (10 mol %), DMEDA (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 Isomer: 2 (43); 3 (82)	501

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CuI (*x* mol %), DMEDA (*y* mol %)		

X	*x*	*y*	Additive	Solvent	Temp (°)	Time (h)		Refs.
Br	10	20	K_2CO_3	—	110	23	(87)	441
Br	10	10	K_3PO_4	dioxane	110	24	(86)	69
I	2	10	K_3PO_4	diglyme	120	24	(99)	115

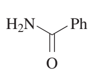
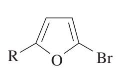
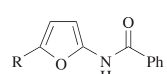
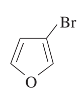
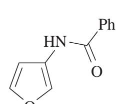
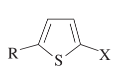
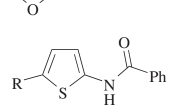
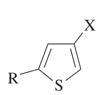
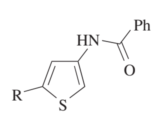
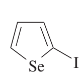
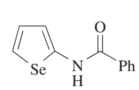
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMEDA (10 mol %), dioxane, 110°, 24 h	 R / Additive: CHO K_2CO_3 (71); CHO K_3PO_4 (98); MeO_2C K_3PO_4 (67)	83; 501; 501
		CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, dioxane, 110°, 24 h	 (98)	83, 501
		CuI (10 mol %), additive (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 R / X / Additive: H I EDA (42); Me Br DMEDA (66)	405; 83
		CuI (10 mol %), additive (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 R / X / Additive: H Br CDA (97); H I DMCDA (99); CHO Br DMEDA (39)	69; 115; 83
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, reflux, 24 h	 (77)	87

TABLE 16B. *N*-HETEROARYLATION OF PRIMARY AMIDES (*Continued*)

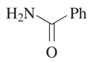
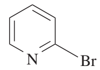
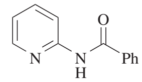
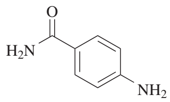
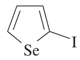
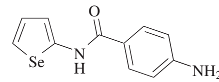
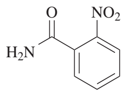
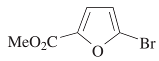
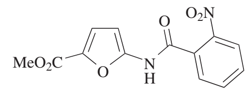
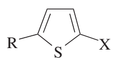
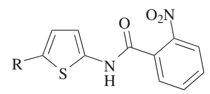
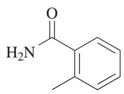
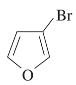
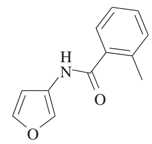
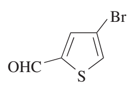
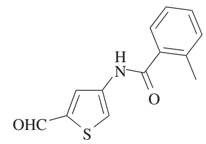
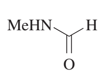
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CuI (10 mol %), oxazolidinone (20 mol %), NaOMe, DMSO, 120°, 24 h	 (80)	492
		CuI (10 mol %), DMEDA (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 (45)	87
		CuI (10 mol %), DMEDA (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 (30)	83
		CuI (10 mol %), additive (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 R X Additive H I EDA (52) Me Br DMEDA (33)	 405 83
C_8				
		CuI (10 mol %), DMEDA (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 (86)	83, 501
		CuI (10 mol %), DMEDA (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 (43)	83

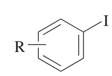
TABLE 17A. *N*-ARYLATION OF ACYCLIC SECONDARY AMIDES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

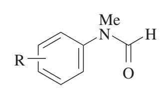
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_2



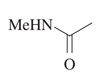


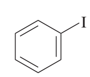
CuI (x mol %)



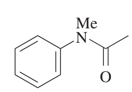
R	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	5	DMEDA (20 mol %), K_3PO_4	toluene	110	23	(87)	69
4-Cl	5	DMEDA (10 mol %), CsF	THF	rt	24	(98)	63
2-MeO	1	CDA (10 mol %), K_3PO_4	dioxane	110	23	(95)	115, 69
4-MeO	0.2	CDA (10 mol %), K_3PO_4	dioxane	110	23	(99)	69

C_3



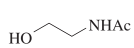


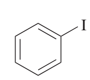
Catalyst (5 mol %)



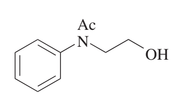
Catalyst	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
CuI	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(79)	493
CuI	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(25)	138
Cu_2O	NaO*t*-Bu	NMP	100	18	(81)	266

C_4



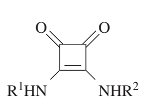


CuI (5 mol %),
Gly (20 mol %), K_3PO_4,
dioxane, 100°, 24 h



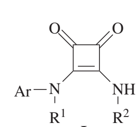
(84) 136

$C_{6–28}$



ArBr

CuI (25 mol %),
L-Pro (25 mol %), K_2CO_3,
DMF, 120°, 18 h



I

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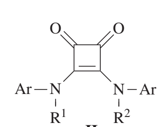


II

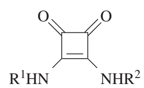
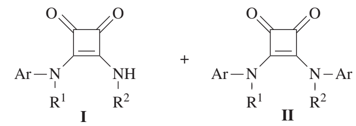
502

R^1	R^2	Ar	**I**	**II**
Me	Me	Ph	(12)	(65)
Me	Me	4-ClC_6H_4	(0)	(44)
Me	Me	4-$Me_2NC_6H_4$	(0)	(55)
Me	Me	4-$O_2NC_6H_4$	(0)	(0)

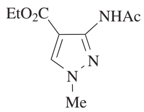
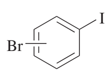
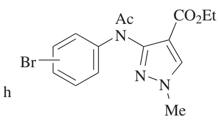
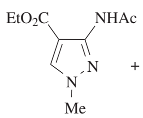
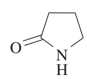
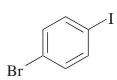
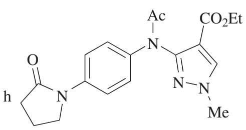
TABLE 17A. *N*-ARYLATION OF ACYCLIC SECONDARY AMIDES (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

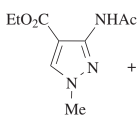
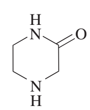
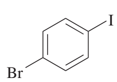
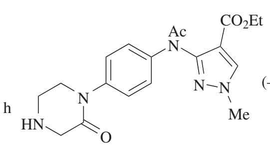
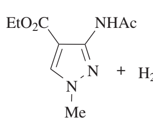
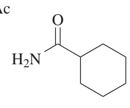
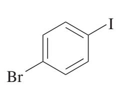
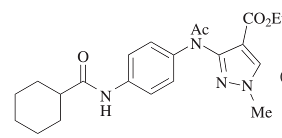
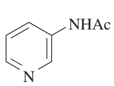
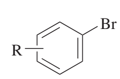
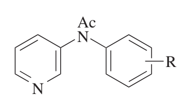
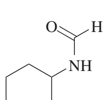
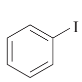
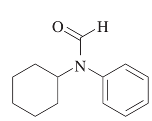
Continued from previous page.

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-28} 	ArBr	CuI (25 mol %), L-Pro (25 mol %), K_2CO_3, DMF, 120°, 18 h	 I + II	502

R^1	R^2	Ar	I	II
Me	Me	2-MeC_6H_4	(0)	(20)
Me	Me	4-MeC_6H_4	(0)	(70)
Me	Me	3-$MeO_2CC_6H_4$	(0)	(10)
Me	Me	4-$MeOCC_6H_4$	(0)	(10)
Me	Me	4-$EtO_2CCH_2C_6H_4$	(0)	(45)
Me	Me	1-Np	(10)	(35)
Me	Me	9-anthracenyl	(12)	(0)
Me	Me	1-phenanthrenyl	(30)	(14)
Me	Me	1-pyrenyl	(55)	(0)
t-Bu	*t*-Bu	Ph	(96)	(0)
c-C_6H_{11}	*c*-C_6H_{11}	Ph	(85)	(0)
n-$C_{12}H_{25}$	*n*-$C_{12}H_{25}$	4-$EtO_2CCH_2C_6H_4$	(35)	(18)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		CuI (10 mol %), DMCDA (20 mol %), K_3PO_4, dioxane, 110°, 22 h		503
 + 		CuI (20 mol %), DMCDA (40 mol %), K_3PO_4, dioxane, 110°, 22 h	 (53)	504

Isomer	
2	(0)
3	(67)
4	(70)

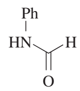
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
 + 		CuI (20 mol %), DMCDA (40 mol %), K_3PO_4, dioxane, 110°, 22 h	 (—)	504
 + 		CuI (20 mol %), DMCDA (40 mol %), K_3PO_4, dioxane, 110°, 22 h	 (—)	504
C_7 		CuCl (10 mol %), K_2CO_3, $N(CH_2CH_2OCH_2–CH_2OMe)_3$, xylene, reflux, 22 h		505
		CuI (5 mol %), CDA (20 mol %), K_3PO_4, toluene, 110°, 25 h	 (63)	69

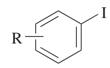
R	X	
H	Br	(74)
2-F	Br	(44)
3-F	Br	(68)
4-F	Br	(74)
2,3,4,5,6-F_5	Br	(0)
2-Cl	Cl	(82)
3-Cl	Cl	(56)
4-Cl	Br	(73)
2-CF_3	Br	(22)
3-CF_3	Br	(69)
4-CF_3	Br	(73)
4-CF_3O	Br	(53)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

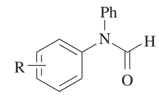
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7



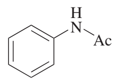


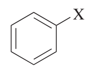
CuI (5 mol %)



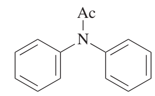
R	X	Additives	Solvent	Temp (°)	Time (h)	Yield	Refs.
H	I	CDA (20 mol %), K_3PO_4	toluene	80	4	(93)	69
4-Cl	I	DMEDA (10 mol %), CsF	THF	rt	24	(98)	63
3-Ac	Br	DMCDA (10 mol %), K_2CO_3	toluene	110	24	(91)	69

C_8



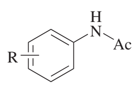


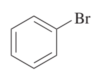
Catalyst (*x* mol %)



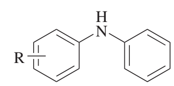
X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time	Yield	Refs.
Br	Cu bronze	100	none	—	180	—	(36)	506
I	CuI	10	K_3PO_4	DMF	110	24 h	(90)	387
Br	CuI	2.5	K_2CO_3	NMP	MW (250 W)	40 min	(76)	239
Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48 h	(88)	494
I	CuI	15	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	6 h	(30)	137
I	CuI	7.5	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	3 h	(50)	137
I	CuI	10	phen (10 mol %), KF/Al_2O_3	toluene	110	6 h	(95)	490
I	CuI	5	Gly (20 mol %), K_3PO_4	dioxane	100	24 h	(84)	136
I	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5 h	(75)	493
I	CuI	5	**L43** (10 mol %), K_3PO_4	DMSO	110	5 h	(30)	138
I	CuO	0.1	DMEDA (20 mol %), K_2CO_3	toluene	135	24 h	(38)	222

C_{8-10}



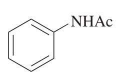


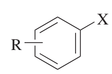
1. CuI, K_2CO_3, $PhNO_2$, reflux, 15 h
2. HCl, EtOH, reflux, 3 h



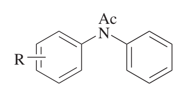
R	Yield	Refs.
H	(60)	507
3-O_2N	(80)	
4-Me	(33)	
2,4-Me_2	(80)	

C_8





Catalyst (*x* amount)



R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time	Yield	Refs.
2-F	Br	Cu bronze	1 eq	none	—	180	—	(42)	506
4-F	Br	Cu bronze	1 eq	none	—	180	—	(35)	506
4-Br	I	CuI	5 mol %	Gly (20 mol %), K_3PO_4	dioxane	100	24 h	(80)	136
4-H_2N	I	CuI	1 mol %	CDA (1 mol %), K_3PO_4	dioxane	110	23 h	(81)	115, 69
2-O_2N	I	CuI	5 mol %	Gly (20 mol %), K_3PO_4	dioxane	100	24 h	(98)	136
4-O_2N	Br	Cu bronze	1 eq	none	—	180	—	(35)	506
2-MeO	Br	CuI	2.5 mol %	K_2CO_3	NMP	MW (250 W)	40 min	(56)	239
2-MeO	I	CuI	7.5 mol %	DMEDA (7.5 %), KF/Al_2O_3	toluene	110	8 h	(40)	137
2-MeO	I	CuI	15 mol %	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	8 h	(trace)	491
2,6-$(MeO)_2$	Br	Cu	10 mol %	I_2, K_2CO_3	$PhNO_2$	reflux	24 h	(3)	508
4-MeO	Br	Cu bronze	1 eq	none	—	180	—	(19)	506
4-MeO	I	CuI	5 mol %	Gly (20 mol %), K_3PO_4	dioxane	100	24 h	(88)	136
4-MeO	I	CuI	15 mol %	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	6 h	(trace)	137
4-MeO	I	CuI	7.5 mol %	DMEDA (7.5 mol %), KF/Al_2O_3	toluene	110	3 h	(40)	137
4-MeO	Br	CuI	20 mol %	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(81)	494
4-MeO	I	CuI	10 mol %	phen (10 mol %), KF/Al_2O_3	toluene	110	8 h	(95)	490
4-MeO	I	CuI	10 mol %	DMCDA (20 mol %), K_3PO_4	[C_4min][BF_4]	110	12 h	(87)	232
3-MeS	Br	Cu	5 mol %	K_2CO_3	—	220	2 h	(64)	509
3-CF_3S	Br	Cu	5 mol %	K_2CO_3	—	220	2 h	(72)	509
3-MeO_2S	Br	Cu	5 mol %	K_2CO_3	—	220	2 h	(30)	509
2-Me	Br	Cu bronze	1 eq	none	—	180	—	(60)	506
2-Me	I	CuI	15 mol %	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	9 h	(trace)	491
2-Me	I	CuI	15 mol %	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	5 h	(20)	137
4-Me	I	CuI	5 mol %	Gly (20 mol %), K_3PO_4	dioxane	100	24 h	(82)	136
4-Me	I	CuI	15 mol %	L-Pro (15 mol %), KF/Al_2O_3	toluene	110	7 h	(30)	491
4-Me	I	CuI	7.5 mol %	DMEDA (7.5 mol %), KF/Al_2O	toluene	110	2 h	(40)	137
4-NC–	Br	Cu bronze	1 eq	none	—	180	—	(35)	506
4-CHO	Br	Cu bronze	1 eq	none	—	180	—	(38)	506
2,5-Me_2	Br	Cu bronze	1 eq	none	—	180	—	(27)	506

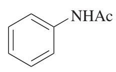
TABLE 17A. *N*-ARYLATION OF ACYCLIC SECONDARY AMIDES (*Continued*)

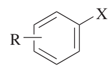
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

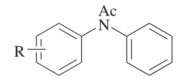
Continued from previous page.

C_8

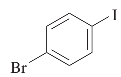




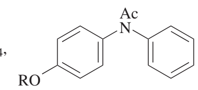
Catalyst (*x* amount)



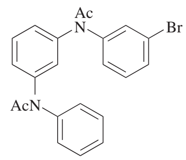
R	X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time		Refs.
3,5-Me_2	I	CuI	1 mol %	CDA (10 mol %), K_3PO_4	dioxane	110	24 h	(96)	115, 69
4-Ac	I	CuI	5 mol %	Gly (20 mol %), K_3PO_4	dioxane	100	24 h	(62)	136



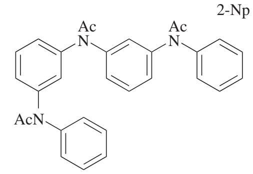
1. CuI (15 mol %), DMG (20 mol %), K_3PO_4, DMSO, 80°, 24 h
2. ROH, 120°, 48 h



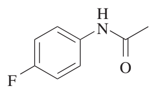
R		Refs.
Ph	(77)	495
4-ClC_6H_4	(71)	
2-$MeOC_6H_4$	(80)	
4-$MeOC_6H_4$	(81)	
2-Np	(70)	

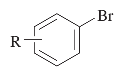


CuI, K_2CO_3, 215°, 4 d

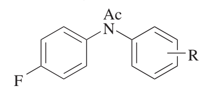


(45) 510

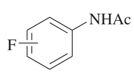


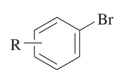


Cu bronze (1 eq), 180°

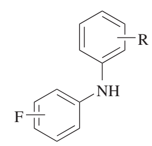


R		Refs.
H	(13)	506
2-Me	(19)	
2,5-Me_2	(21)	



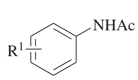


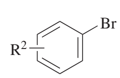
1. Cu (30 mol %), CuI (10 mol %), KI, I_2, K_2CO_3, $PhNO_2$, reflux, 17 h
2. KOH, EtOH, reflux, 3 h



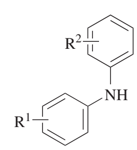
Isomer	R		Refs.
2	4-MeO	(70)	511
2	4-Me	(65)	
4	2-Cl	(72)	
4	2-MeO	(80)	
4	4-MeO	(63)	
4	4-Me	(75)	

$C_{8–11}$



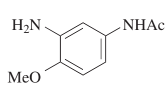


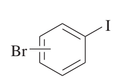
1. CuI (10 mol %), K_2CO_3, benzene
2. KOH, EtOH, reflux (*x* hours)



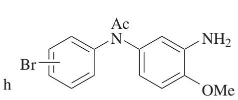
R^1	R^2	*x*		Refs.
4-Cl	H	—	(80)	512
2-Me	H	2	(69)	
2-Me	2-Me	2	(90)	
2,4-Me_2	H	3	(80)	
2,4-Me_2	2-Me	2	(80)	
2,6-Me_2	H	2	(88)	
2,4,6-Me_3	H	2	(84)	
2,4,6-Me_3	2,6-Me_2	2	(84)	

C_8

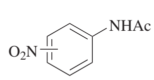


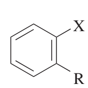


CuI (10 mol %), DMCDA (20 mol %), K_3PO_4, dioxane, 110°, 22 h

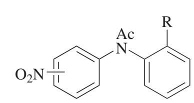


Isomer		Refs.
2	(0)	503
3	(78)	
4	(80)	

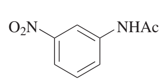


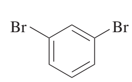


Catalyst (*x* amount)

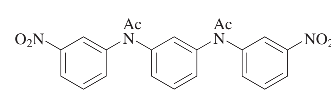


Isomer	R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	H	I	CuI	5 mol %	Gly (20 mol %), K_3PO_4	dioxane	100	24	(75)	136
3	H	I	CuI	—	K_2CO_3	—	180	18	(50)	510
4	2-Me	Br	Cu bronze	1 eq	none	—	180	—	(4)	506

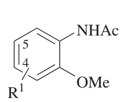


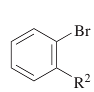


CuI, K_2CO_3, 180°, 2 d

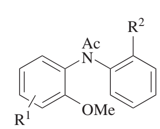


(45) 510





Cu (10 mol %), I_2, K_2CO_3, $PhNO_2$, reflux,

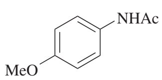
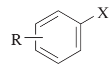
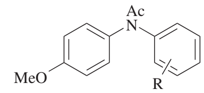


R^1	R^2	Time (h)		Refs.
H	H	34	(81)	513
4-Cl	H	34	(81)	
5-Cl	H	34	(82)	
6-MeO	H	24	(83)	
4-Cl, 6-MeO	CO_2Et	8	(83)	

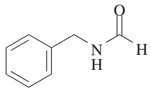
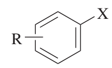
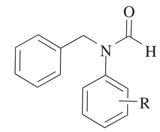
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_8

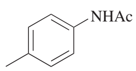
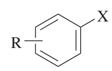
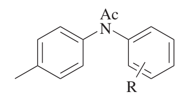


Catalyst (*x* amount)


R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	I	CuI	5 mol %	TBAB. KOH	—	110	4	(79)	428
4-O_2N	Br	Cu bronze	1 eq	none	—	180	—	(40)	506
2-Me	Br	Cu bronze	1 eq	none	—	180	—	(58)	506

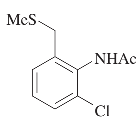
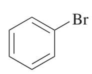
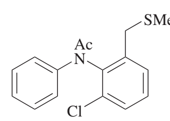


CuI (*x* mol %), 110°


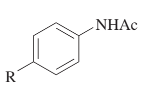
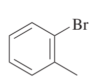
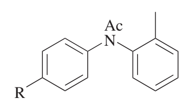
R	X	*x*	Additives	Solvent	Time (h)		Refs.
4-MeS	Br	5	DMEDA (10 mol %), K_2CO_3	toluene	24	(95)	69
3,5-Me_2	I	1	CDA (10 mol %), K_3PO_4	dioxane	23	(93)	115, 69

C_9



CuI (*x* mol %), K_3PO_4


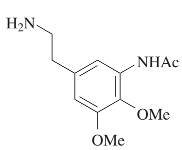
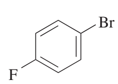
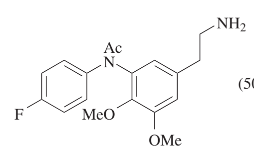
R	X	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
H	Br	20	DMG (20 mol %)	DMF	reflux	48	(85)	494
H	I	5	Gly (20 mol %)	dioxane	100	24	(74)	136
4-MeO	Br	20	DMG (20 mol %)	DMF	reflux	48	(83)	494
2-Me	Br	20	DMG (20 mol %)	DMF	reflux	48	(72)	494
4-Ac	Br	20	DMG (20 mol %)	DMF	reflux	48	(87)	494



Cu (10 mol %), I_2, K_2CO_3, $PhNO_2$, reflux, 24 h

(85) 508

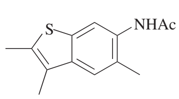
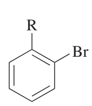
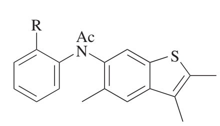


Cu bronze (1 eq), 180°


R		Refs.
NC–	(18)	506
CHO	(4)	

C_{10}

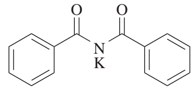
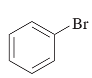
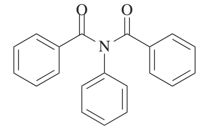


Cu_2O, K_2CO_3

(50) 435

C_{13}



Cu_2O (1 eq), 180°


R	X	Time (h)		Refs.
H	Br	8	(84)	514
Br	I	12	(40)[a]	

C_{14}



CuI (1 eq), DMA, 165°, 24 h

(62) 515

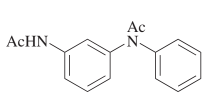
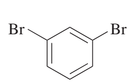
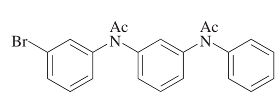
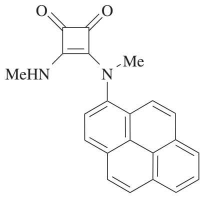
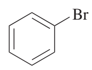
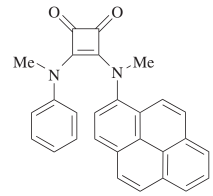
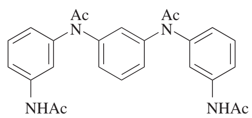
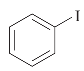
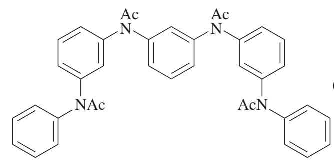


CuI, K_2CO_3, 185°, 5 d

(90) 510

TABLE 17A. *N*-ARYLATION OF ACYCLIC SECONDARY AMIDES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*					
C_{21}					
		CuI (25 mol %), L-Pro (25 mol %), K_2CO_3, DMF, 120°, 18 h		(15)	502
C_{22}					
		CuI, K_2CO_3, 190°, 4 d		(60)	510

[a] A mixture of R = Br and R = I was formed.

TABLE 17B. *N*-HETEROARYLATION OF ACYCLIC SECONDARY AMIDES

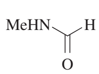
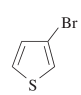
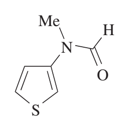
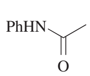
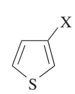
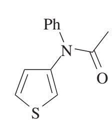
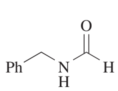
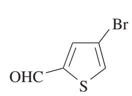
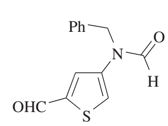
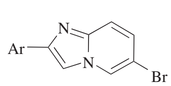
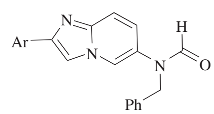
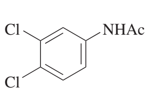
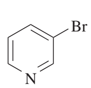
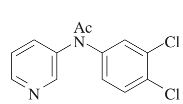
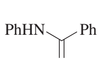
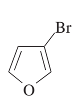
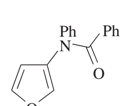
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
		CuI (5 mol %), DMCDA (10 mol %), K_3PO_4, dioxane, 110°, 24 h	 (99)	115
C_8				
		CuI (10 mol %), additive (*x* mol %), K_3PO_4, dioxane, 110°, 24 h	 X / Additive / *x*: Br / CDA / 20 (81); I / DMCDA / 10 (99)	69 115
		CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, dioxane, 110°, 24 h	 (43)	83
	 Ar = 4-FC_6H_4	CuI (10 mol %), DMCDA (10 mol %), K_3PO_4, toluene, 110°, 20 h	 (71)	500
		CuCl (10 mol %), K_2CO_3, xylene, $N(CH_2CH_2–OCH_2CH_2OMe)_3$, reflux, 27 h	 (61)	505
C_{13}				
		CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, dioxane, 110°, 24 h	 (11)	83

TABLE 17B. *N*-HETEROARYLATION OF ACYCLIC SECONDARY AMIDES (*Continued*)

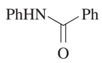
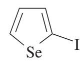
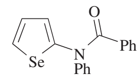
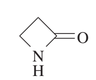
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, reflux, 24 h	 (70)	87

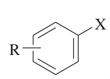
TABLE 18A. *N*-ARYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

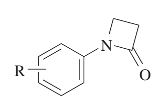
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

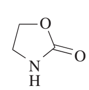


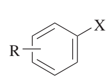


Catalyst (x mol %)

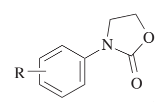


R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
H	$I^+Ph\ BF_4^-$	$Cu(acac)_2$	5	K_2CO_3	toluene	50	6	(70)	76
4-MeO	Br	CuI	1	DMCDA (10 mol %), K_2CO_3	dioxane	110	24	(90)	69
4-MeO	I	CuI	1	DMCDA (10 mol %), K_2CO_3	dioxane	110	15	(99)	115
3,5-Me_2	I	CuI	1	CDA (10 mol %), K_3PO_4	dioxane	110	23	(99)	115, 69





Catalyst (x mol %)

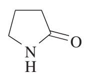


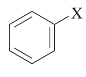
R	X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield (%)	Refs.
H	Br	Cu/SiO_2	10	KOAc	—	reflux	4	(73)	516
H	Br	CuI	3	CDA (10 mol %), K_2CO_3	dioxane	110	15	(85)	517
H	I	CuI	5	KOH, TBAB	—	110	4	(85)	428
H	I	CuO nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	24	(90)	74
3-F	I	CuI	10	DMEDA (10 mol %), K_2CO_3	MeCN	80	21	(99)	518
4-I	Br	CuI	10	DMCDA (20 mol %), K_3PO_4	dioxane	110	22	(95)	503
4-O_2N	Br	CuI	3	CDA (10 mol %), K_2CO_3	dioxane	110	15	(50)	517
4-O_2N	I	CuO nanoparticles	5	K_2CO_3	*t*-BuOH/DMSO (3:1)	110	24	(95)	74
2-MeO	I	CuI	10	DMEDA (10 mol %), K_2CO_3	MeCN	80	21	(99)	518
2-MeO	Br	CuI	3	CDA (10 mol %), K_2CO_3	dioxane	110	15	(83)	517
4-MeO	I	CuI	10	DMEDA (10 mol %), K_2CO_3	MeCN	80	21	(99)	518
4-MeO	Br	CuI	5	CDA (10 mol %), K_2CO_3	dioxane	110	15	(82)	517
4-MeO	I	CuO nanoparticles	10	K_2CO_3	*t*-BuOH/DMSO (3:1)	110	24	(54)	74
4-MeS	Br	CuI	3	CDA (10 mol %), K_2CO_3	dioxane	110	15	(86)	517
2-Me	I	CuI	10	DMEDA (10 mol %), K_2CO_3	MeCN	80	21	(99)	518
3-Me	Br	CuI	3	CDA (10 mol %), K_2CO_3	dioxane	110	15	(80)	517
4-NC–	Br	CuI	3	CDA (10 mol %), K_2CO_3	dioxane	110	15	(81)	517
4-CHO	Br	CuI	3	CDA (10 mol %), K_2CO_3	dioxane	110	15	(30)	517
4-MeO_2C	I	CuI	10	DMEDA (10 mol %), K_2CO_3	MeCN	80	21	(92)	518
3-Ac	I	CuI	10	DMEDA (10 mol %), K_2CO_3	MeCN	110	21	(93)	518
4-Ac	Br	CuI	3	CDA (10 mol %), K_2CO_3	dioxane	110	15	(98)	517

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

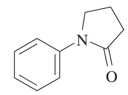
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

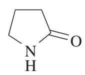
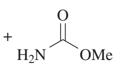


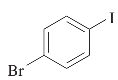


Catalyst (*x* mol %)

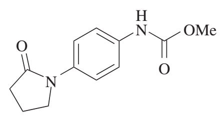


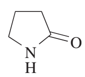
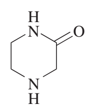
X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	Cu/SiO_2	14	KOAc	—	reflux	—	(91)	516
I	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	rt	22	(96)	49
I	CuI	1	K_2CO_3	DMF	150	6	(89)	519
$I^+Ph\ BF_4^-$	CuI	5	K_2CO_3	touene	50	6	(65)	76
I	CuI	5	K_3PO_4	DMF	110	24	(98)	387
Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(90)	494
I	CuI	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(98)	136
I	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24	(85)	492
I	CuI	10	**L21** ((20 mol %), Cs_2CO_3	MeCN	82	12	(86)	394
I	CuI	10	**L45** (10 mol %), Cs_2CO_3	dioxane/DMF (9:1)	110	24	(98)	520
Cl	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(3)	493
Br	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(11)	493
I	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(90)	493
I	CuO	1	$Fe(acac)_3$ (30 mol %), Cs_2CO_3	DMF	90	30	(81)	130
I	Cu_2O	5	**L30** (20 mol %), Cs_2CO_3, 3 Å MS	DMF	82	40	(92)	40
I	**12**	5	K_3PO_4	dioxane	110	24	(99)	521

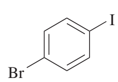
 + 



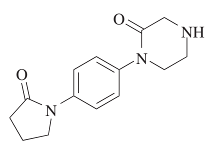
CuI (20 mol %), DMCDA (40 mol %), K_3PO_4, dioxane, 110°, 22 h

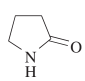
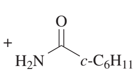
 (60) 504

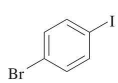
 + 



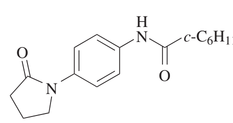
CuI (20 mol %), DMCDA (40 mol %), K_3PO_4, dioxane, 110°, 22 h

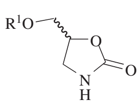
 (70) 504

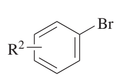
 + 



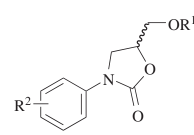
CuI (20 mol %), DMCDA (40 mol %), K_3PO_4, dioxane, 110°, 22 h

 (64) 504



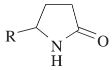


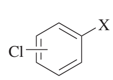
CuI (*x* mol %), CDA (10 mol %), K_2CO_3, dioxane



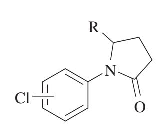
R^1	Config.	R^2	*x*	Temp (°)	Time (h)		Refs.
H	(*R*,*S*)	H	5	110	15	(20)	517
THP	(*R*,*S*)	H	5	110	15	(85)	517
THP	(*R*,*S*)	3-F, 4-(1-morpholino)	5	110	15	(85)	517
CPh_3	(*S*)	4-Ac	10	reflux	24	(95)	145

$C_{4–5}$





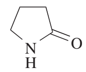
Catalyst (*x* mol %)

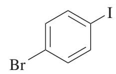
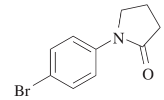


Isomer	R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	H	Cl	Cu/SiO_2	14	KOAc	—	reflux	—	(37)	516
3	H	Br	Cu/SiO_2	14	KOAc	—	reflux	—	(44)	516
4	H	I	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	rt	23	(90)	49
4	H	I	CuI	5	DMEDA (10 mol %), CsF	EtOAc	rt	24	(99)	63
4	H	Br	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	82	12	(61)	394
4	H	I	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	82	12	(92)	394
4	H	I	**12**	5	K_3PO_4	dioxane	110	24	(98)	521
4	Me	I	CuI	5	DMEDA (10 mol %), CsF	THF	rt	24	(83)	63

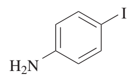
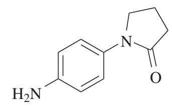
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

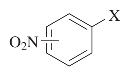
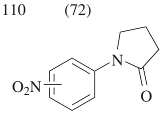
C_4 

 Catalyst (x mol %) 

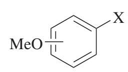
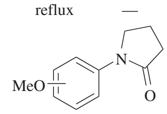
Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	rt	22	(85)	49
CuI	5	DMEDA (10 mol %), CsF	EtOAc	rt	24	(99)	63
CuI	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(93)	136
CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(89)	493
12	5	K_3PO_4	dioxane	110	24	(70)	521

 Catalyst (5 mol %), 24 h 

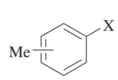
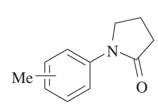
Catalyst	Additive(s)	Solvent	Temp (°)		Refs.
CuI	DMEDA (10 mol %), CsF	THF	rt	(99)	63
12	K_3PO_4	dioxane	110	(72)	521

 Catalyst (x mol %) 

Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	Cl	Cu/SiO_2	14	KOAc	—	reflux	—	(45)	516
2	I	CuI	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(95)	136
3	Cl	Cu/SiO_2	14	KOAc	—	reflux	—	(41)	516

 Catalyst (x mol %) 

Isomer	X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
2	I	CuI	10	**L45** (10 mol %), Cs_2CO_3	dioxane/DMF (9:1)	110	24	(91)	520
2	I	cat. **12**	5	K_3PO_4	dioxane	110	24	(93)	521
4	Br	CuBr	10	**L5** (20 mol %), Cs_2CO_3	DMSO	75	30	(76)	49
4	I	CuBr	10	**L5** (20 mol %), Cs_2CO_3	DMSO	75	25	(85)	49
4	I	CuI	10	EDA (10 mol %), K_3PO_4	dioxane	110	24	(85)	405
4	Cl	CuI	5	DMEDA (11 mol %), K_2CO_3	—	130	23	(51)	115
4	Cl	CuI	5	DMCDA (11 mol %), K_2CO_3	—	130	23	(51)	69
4	Br	CuI	10	oxazolidin-2-one (10 mol %), NaOMe	DMSO	120	24	(74)	492
4	I	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(89)	494
4	I	CuI	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(95)	136
4	I	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(88)	493
4	I	CuI	5	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(82)	138
4	I	CuI	10	**L45** (10 mol %), Cs_2CO_3	dioxane/DMF (9:1)	110	24	(96)	520
4	I	cat. **12**	5	K_3PO_4	dioxane	110	24	(89)	521

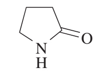
 Catalyst (x mol %) 

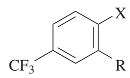
Isomer	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
2	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(78)	494
2	I	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(86)	493
2	I	CuI	5	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(86)	138
4	Br	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	75	26	(81)	49
4	I	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	60	24	(86)	49
4	$I^+C_6H_4Me\text{-}4\ BF_4^-$	CuI	5	K_2CO_3	toluene	50	6	(68)	76
4	Cl	CuI	5	DMEDA (11 mol %), K_2CO_3	—	130	23	(95)	115
4	Cl	CuI	5	DMCDA (11 mol %), K_2CO_3	—	130	23	(95)	69
4	I	CuI	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(95)	136
4	Br	CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24	(76)	492
4	Br	CuI	10	**L21** (20 mol %), KI, Cs_2CO_3	MeCN	82	12	(58)	394
4	I	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(93)	493
4	I	CuI	5	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(91)	138

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

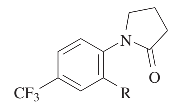
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

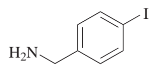




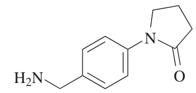
Catalyst (*x* mol %)



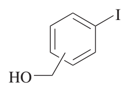
R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
H	I	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(89)	493
H	I	CuI	5	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(81)	138
H	I	**12**	5	K_3PO_4	dioxane	110	24	(99)	521
O_2N	Cl	CuI	10	**L21** (20 mol %), Cs_2CO_3	MeCN	82	12	(22)	394



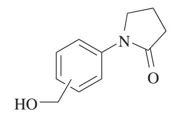
CuI (5 mol %),
DMEDA (10 mol %),
CsF, THF, rt, 24 h



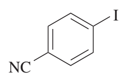
(93) 63



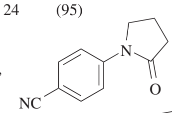
CuI (5 mol %),
DMEDA (10 mol %)



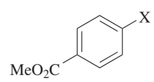
Isomer	Additive	Solvent	Temp (°)	Time (h)	Yield	Refs.
3	K_3PO_4	toluene	80	23	(97)	69
4	CsF	THF	rt	24	(95)	63



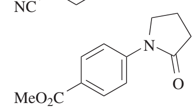
CuI (5 mol %),
DMEDA (10 mol %), CsF,
THF, rt, 24 h



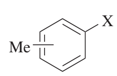
(89) 63



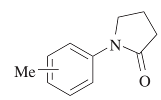
CuI (5 mol %)



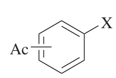
X	Additives	Solvent	Temp (°)	Time (h)	Yield	Refs.
Cl	DMEDA (11 mol %), K_2CO_3	—	130	23	(62)	115
Cl	DMCDA (11 mol %), K_2CO_3	—	110	23	(62)	69
I	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(85)	493



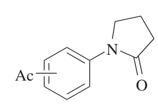
Catalyst (*x* mol %)



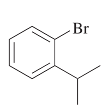
Isomer	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
3,5	I	CuI	10	EDA (10 mol %), Cs_2CO_3	dioxane	110	24	(68)	405
3,5	I	CuI	1	CDA (10 mol %), K_3PO_4	dioxane	110	23	(99)	115
3.5	I	**12**	5	K_3PO_4	dioxane	110	24	(85)	521
2,4,6	Br	Cu/SiO_2	14	KOAc	—	reflux	—	(48)	516



Catalyst (*x* mol %)



Isomer	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield	Refs.
2	Br	CuI	5	DMEDA (10 mol %), K_2CO_3, 5 Å MS	—	110	24	(89)	497
4	I	CuI	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(98)	136
4	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(90)	494
4	I	CuI	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(90)	493
4	I	CuI	5	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(62)	138
4	I	CuI	10	**L45** (10 mol %), Cs_2CO_3	dioxane/DMF (9:1)	110	34	(86)	520
4	Br	**10**	3	Cs_2CO_3	DMSO	100	24	(<1)	420
4	I	**10**	3	Cs_2CO_3	DMSO	100	24	(100)	420



CuI (5 mol %),
DMCDA (10 mol %),
K_2CO_3, toluene, 110°, 24 h

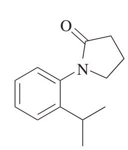


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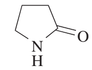
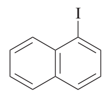
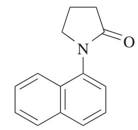
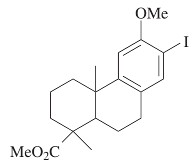
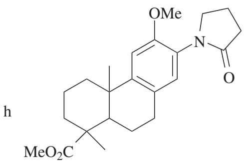
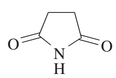
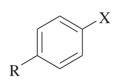
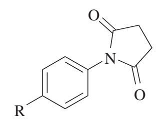
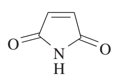
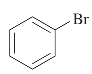
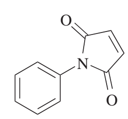
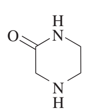
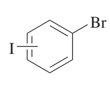
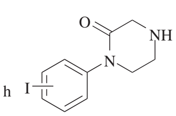
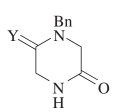
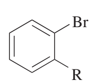
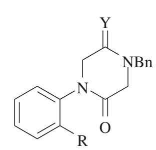
TABLE 18A. *N*-ARYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES (*Continued*)

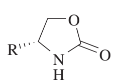
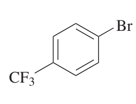
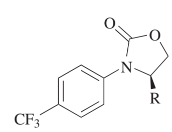
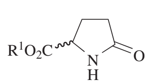
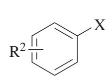
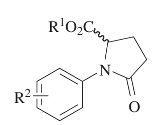
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CuI (5 mol %), additive (10 mol %), K_3PO_4, DMSO, 110°, 5 h	 Additive: **L42** (93)	493
			L43 (92)	138
		CuI (1 mol %), DMEDA (2 mol %), K_2CO_3, dioxane, 100°, 24 h	 (81)	489
		Catalyst (*x* eq)		

R	X	Catalyst	*x*	Solvent	Temp (°)	Time		Refs.
H	Cl	Cu	3	—	210	12 h	(100)	303
H	Br	Cu	3	—	210	12 h	(100)	303
H	I	Cu	3	—	150	12 h	(97)	303
H	I	Cu (active)	5	—	MW (100 W)	10 min	(87)	280
H	Br	CuI	1	DMA	165	24 h	(62)	515
Me	Br	Cu (active)	5	—	MW (100 W)	6 min	(83)	280

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (1 eq), DMA, 165°, 24 h	 (62)	515
		CuI (10 mol %), DMCDA (20 mol %), K_3PO_4, dioxane, 110°, 22 h	 Isomer: 2 (—); 3 (57); 4 (60)	503
		CuI (2.5 mol %), K_2CO_3, NMP, MW (250 W)		239

R	Y	Time	
H	CH_2	1 h	(57)
H	O	20 min	(51)
MeO	CH_2	1 h	(57)

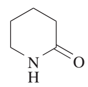
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-10}				
		CuI (10 mol %), CDA (10 mol %), K_2CO_3, dioxane, reflux, 24 h	 R: Et (90); Bn (95)	145
C_5				
		CuI (5 mol %)		

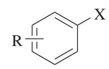
R^1	R^2	X	Config.	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Me	H	Br	(*R,S*)	Cs_2CO_3	dioxane	rt	36	(90)	522
Me	4-F	Br	(*R,S*)	Cs_2CO_3	dioxane	60	8	(81)	522
Me	4-Cl	I	(*S*)	DMEDA (10 mol %), CsF	THF	rt	24	(99)	63
H	4-MeO	I	(*R,S*)	K_2CO_3	DMSO	80	5	(75)	522
Me	4-MeO	Br	(*R,S*)	Cs_2CO_3	dioxane	rt	12	(90)	522
Me	3,4-OCH_2O	Br	(*R,S*)	Cs_2CO_3	dioxane	60	6	(85)	522
Me	2-Me	Br	(*R,S*)	Cs_2CO_3	dioxane	60	12	(90)	522
Me	4-Me	Br	(*R,S*)	Cs_2CO_3	dioxane	60	15	(95)	522
Me	3-CF_3	Br	(*R,S*)	Cs_2CO_3	dioxane	60	16	(91)	522
Me	4-NC–	Br	(*R,S*)	Cs_2CO_3	dioxane	60	9	(91)	63

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

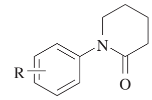
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_5



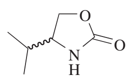


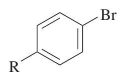
CuI (*x* mol %)



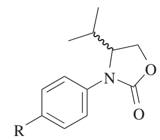
R	X	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
H	I	10	phen (10 mol %), KF/Al_2O_3	toluene	110	8	(99)	490
H	I	5	**L42** (10 mol %), K_3PO_4	DMSO	110	5	(81)	493
H	I	5	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(74)	138
4-Br	I	5	K_3PO_4	DMF	110	24	(95)	387
2-Me	Br	5	DMEDA (20 mol %), K_2CO_3	toluene	110	24	(49)	69
4-Me	I	5	K_3PO_4	DMF	110	24	(93)	387
4-H_2NCH_2	I	5	DMEDA (10 mol %), K_2CO_3	toluene	100	18	(95)	69
4-EtO_2C	Br	5	DMEDA (10 mol %), K_2CO_3	toluene	110	24	(94)	69

C_6

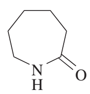


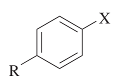


CuI (*x* mol %),
CDA (10 mol %),
K_2CO_3, dioxane

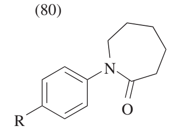


Config.	R	*x*	Temp (°)	Time (h)	Yield	Refs.
(*R,S*)	MeO	3	110	15	(50)	517
(*R,S*)	NC–	3	110	15	(99)	517
(*R*)	Ac	10	reflux	24	(80)	145

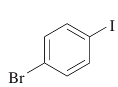




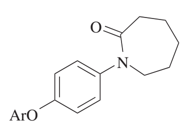
CuI (*x* mol %)



R	X	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
H	Br	10	K_3PO_4	DMF	110	24	(trace)	387
H	I	5	K_3PO_4	DMF	110	24	(98)	387
H	Cl	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(26)	136
H	Br	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(62)	136
H	I	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(97)	136
H	I	10	PPAPM (20 mol %), K_3PO_4	—	110	30	(89)	48
H	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(87)	494
H	Br	10	piperidine-2-carboxylic acid (20 mol %), K_2CO_3	DMF	110	36	(70)	67
Br	I	5	K_3PO_4	toluene	110	24	(94)	387
MeO	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(88)	494
MeO	I	10	DMCDA (20 mol %), K_3PO_4	$[C_4min][BF_4]$	110	12	(78)	232
MeO	I	5	Gly (20 mol %), K_3PO_4	dioxane	100	24	(92)	136
Ac	I	10	K_3PO_4	toluene	110	24	(95)	387
Ac	I	5	Gly (20 mol %), K_3PO_4	dioxane	110	24	(98)	136



1. CuI (15 mol %),
DMG (20 mol %), K_3PO_4,
DMSO, 80°, 24 h
2. ArOH, 120°, 48 h

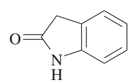


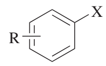
Ar	Yield	Refs.
Ph	(82)	
4-ClC_6H_4	(75)	495
2-$MeOC_6H_4$	(82)	
4-$MeOC_6H_4$	(87)	
4-$HO_2CC_6H_4$	(0)	
4-AcC_6H_4	(45)	
2-Np	(85)	

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

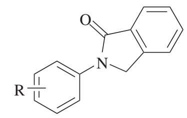
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_8



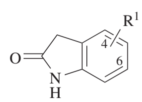


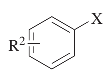
CuI (x mol %), K_2CO_3



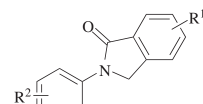
R	X	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	Br	10	DMEDA (10 mol %)	MeCN	80	21	(43)	518
4-F	I	1	DMCDA (4 mol %)	dioxane	100	24	(94)	205
4-Cl	Br	10	DMCDA (20 mol %)	dioxane	100	24	(77)	205
3,4-Cl_2	Br	10	DMEDA (10 mol %)	MeCN	80	21	(50)	518
4-Br	I	5	DMCDA (10 mol %)	dioxane	40	24	(61)	205
4-Me_2N	Br	10	DMCDA (20 mol %)	dioxane	100	24	(73)	205
4-HO	I	10	DMEDA (10 mol %)	MeCN	80	21	(73)	518
4-MeO	I	5	DMCDA (10 mol %)	dioxane	100	24	(86)	205
3,4-OCH_2O	Br	10	DMEDA (10 mol %)	MeCN	80	21	(50)	518
2-F, 4-Me	Br	10	DMEDA (10 mol %)	MeCN	80	21	(50)	518
4-CF_3	Br	10	DMEDA (10 mol %)	MeCN	80	21	(50)	518
4-CF_3	I	1	DMCDA (4 mol %)	dioxane	80	24	(69)	518
4-NC–	I	5	DMCDA (10 mol %), 4 Å MS	dioxane	80	24	(72)	205
3-MeO_2C	Br	10	DMEDA (10 mol %)	MeCN	80	21	(40)	518
3-MeO_2C	I	10	DMEDA (10 mol %)	MeCN	80	21	(74)	518
3,4-Me_2	I	10	DMEDA (10 mol %)	MeCN	80	21	(86)	518
3,5-Me_2	Br	10	DMCDA (20 mol %)	dioxane	100	24	(71)	205
3,5-Me_2	I	10	DMEDA (10 mol %)	MeCN	80	21	(86)	518

$C_{8–14}$



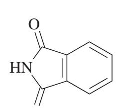


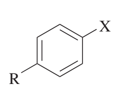
CuI (x mol %), K_2CO_3



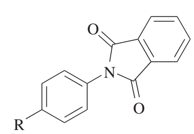
R^1	R^2	X	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
5-F	3-MeO_2C	I	10	DMEDA (10 mol %)	MeCN	80	21	(61)	518
4-Cl	3-EtO_2C	I	5	DMCDA (10 mol %), 4 Å MS	dioxane	80	24	(87)	205
5-Cl	4-*n*-Pr	Br	10	DMEDA (10 mol %)	MeCN	80	21	(50)	518
6-Cl	3-MeO_2C	I	10	DMEDA (10 mol %)	MeCN	80	21	(82)	518
6-Cl	3.5-Me_2	I	10	DMEDA (10 mol %)	MeCN	80	21	(69)	518
6-Br	3,4-Me_2	I	10	DMEDA (10 mol %)	MeCN	80	21	(72)	518
6-Me	3-O_2N	I	5	DMCDA (10 mol %)	dioxane	80	24	(87)	205
6-Me	3-MeO	Br	10	DMCDA (20 mol %)	dioxane	100	24	(62)	205
6-Me	2,4-Me_2	Br	10	DMEDA (10 mol %)	MeCN	80	24	(50)	518
6-CF_3	3-MeO_2C	I	10	DMEDA (10 mol %)	MeCN	80	21	(65)	518
6-CF_3	3,4-Me_2	I	10	DMEDA (10 mol %)	MeCN	80	21	(77)	518
6-MeO_2C	3,4-Me_2	I	10	DMEDA (10 mol %)	MeCN	80	21	(66)	518
6-Ph	3,4-Me_2	Br	10	DMEDA (10 mol %)	MeCN	80	21	(50)	518

C_8





Catalyst (x amount)

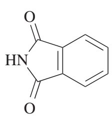


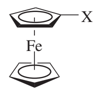
R	X	Catalyst	x	Additive(s)	Solvent	Temp (°)	Time		Refs.
H	I	Cu (active)	5 eq	none	—	MW (100 W)	8 min	(81)	280
H	Br	Cu	3 eq	none	—	240	12 h	(100)	303
H	Br	CuI	1 eq	none	DMA	165	24 h	(62)	515
H	I	CuI	10 mol %	K_2CO_3	DMF	150	6 h	(32)	519
H	Br	CuI	20 mol %	DMG (20 mol %), K_3PO_4	DMF	reflux	48 h	(60)	494
H	I	CuI	5 mol %	Gly (20 mol %), K_3PO_4	dioxane	100	24 h	(53)	136
H	Br	Cu_2O	60 mol %	none	collidine	—	—	(80)	523
H	I	Cu_2O	60 mol %	none	collidine	—	—	(92)	523
F	Br	Cu	3 eq	none	—	240	12 h	(98)	303
MeO	Br	Cu	3 eq	none	—	240	12 h	(86)	303
Me	Br	Cu	3 eq	none	—	240	12 h	(100)	303

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

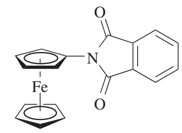
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_8



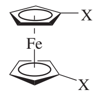


Cu_2O (60 mol %)

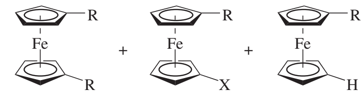


X	Solvent
Br	4-picoline (71)
I	pyridine (73)

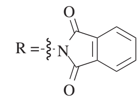
523



Cu_2O (60 mol %), 4-picoline, reflux, 24 h

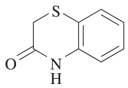


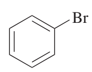
I + II + III



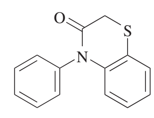
X	I	II	III
Br	(47)	(0)	(8)
I	(35)	(11)	(21)

523



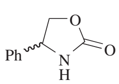


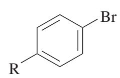
Cu/SiO_2 (14 mol %), KOAc, reflux



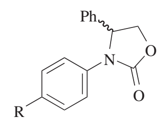
(72) 516

C_9

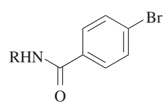




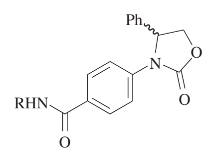
CuI (*x* mol %), CDA (10 mol %), K_2CO_3, dioxane



Config.	R	x	Temp (°)	Time (h)		Refs.
(*R*)	H	10	reflux	24	(95)	145
(*R,S*)	MeO	3	110	15	(98)	517
(*R,S*)	Me	10	reflux	24	(85)	145
(*R,S*)	NC–	3	110	15	(98)	517
(*R*)	NC–	10	reflux	24	(82)	145

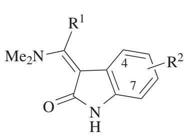


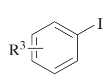
CuI (*x* mol %), K_2CO_3



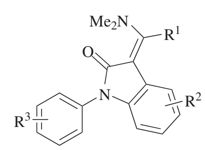
Config.	R	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
(*R*)	*n*-Pr	10	CDA (10 mol %)	dioxane	reflux	24	(97)	145
(*R*)	*i*-Pr	—	DMEDA	—	—	—	(97)	524
(*S*)	*i*-Pr	10	CDA (10 mol %)	dioxane	reflux	24	(95)	145

C_{9-10}





1. NaH
2. CuBr (1 eq), DMF, 100°, 24 h



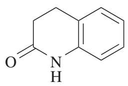
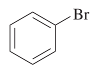
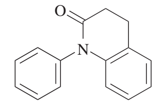
525

R^1	R^2	R^3	
H	H	2-Cl	(12)
H	4-Cl	3-Cl	(5)
H	5-Cl	3-Cl	(24)
H	6-Cl	3-Cl	(2)
H	7-Cl	3-Cl	(31)
H	5-MeO	3-Cl	(9)
H	H	4-Cl	(10)
H	H	2,5-Cl_2	(19)
H	H	3,4-Cl_2	(28)
H	H	3,5-Cl_2	(72)
H	H	3-Br	(24)
H	H	4-Me_2N	(32)
H	H	3-O_2N	(51)
H	H	3-HO	(83)
H	H	3-MeO	(83)
H	H	4-MeO	(42)
H	H	3-F, 4-MeO	(38)

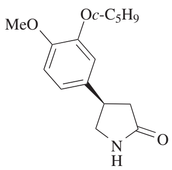
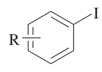
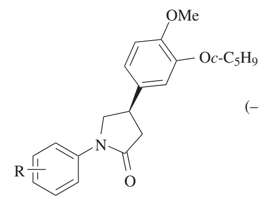
R^1	R^2	R^3	
H	H	3-Cl, 4-MeO	(38)
H	H	3-Cl, 6-MeO	(27)
H	H	3,4-$(MeO)_2$	(6)
H	H	3-EtO	(17)
H	H	3-Cl, 4-MeO, 5-Me	(33)
H	H	4-MeS	(32)
H	H	2-Me	(10)
H	H	3-Me	(38)
Me	H	3-Me	(8)
H	H	4-Me	(23)
H	H	3-Me, 4-MeO	(18)
H	H	3-CF_3	(21)
H	H	3-NC–	(22)
H	H	3-Me_2NCO	(14)
H	H	3-CHO	(18)
H	H	3-Et	(39)
H	H	3-Ph	(39)

TABLE 18A. *N*-ARYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES (*Continued*)

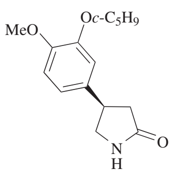
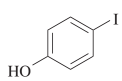
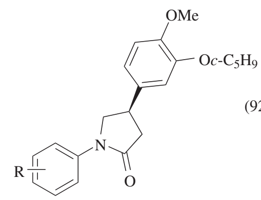
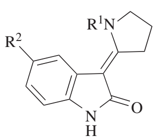
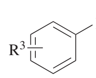
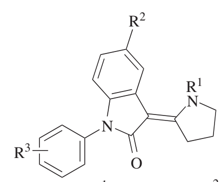
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		CuI (x mol %), K_2CO_3		

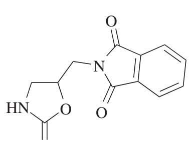
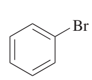
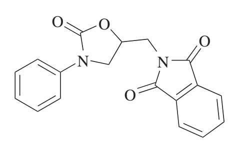
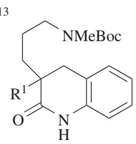
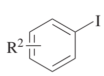
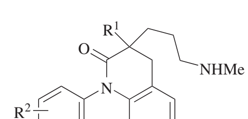
x	Additive	Solvent	Temp (°)	Time (h)		Refs.
2.5	none	NMP	reflux	—	(77)	239
20	DMCDA (20 mol %)	dioxane	125	—	(80)	526

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		CuI, CDA, K_3PO_4, DMF, 110°, 12 h	 (—)	527

R = H;
2-H_2N, 3-H_2N, 4-H_2N, 5-H_2N, 3,5-$(H_2N)_2$;
3-F, 3-O_2N;
3-MeSO, 3-$MeSO_2$, 4-MeSO, 4-$MeSO_2$;
2-Me, 3-Me, 4-Me;
2-CF_3, 3-CF_3, 4-CF_3;
2-NC–, 3-NC–, 4-NC–
2 R groups = 3-H_2N and 2-Me; 3-H_2N and 4-Me

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI, CDA, K_3PO_4, DMF, 110°, 12 h	 (92)	527
C_{12}				
		1. NaH 2. CuBr (1 eq), DMF, 100°, 24 h		525

R^1	R^2	R^3	
Me	Cl	3-Cl	(43)
Me	H	4-Cl	(48)
Me	H	3-MeO	(20)
Me	H	3-NC-	(16)
Me	H	3-Me_2NCO	(17)
4-$ClC_6H_4CH_2$	H	3-Cl	(29)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), CDA (10 mol %), K_2CO_3, dioxane, 110°, 15 h	 (65)	517
C_{12-13}				
		1. CuI (20 mol %), CDA (20 mol %), K_2CO_3, dioxane, 125° 2. TFA, CH_2Cl_2, rt, 2 h	 (>80)	526

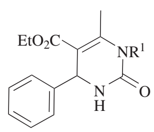
R^1	R^2	R^1	R^2
H	H	H	3,4-Cl_2
Me	H	Me	3,5-Cl_2
H	3-F	Me	3- Me
H	4-F	H	4- Me
Me	3,4-F_2	Me	4-Me
Me	3,5-F_2	H	4-CF_3
H	3-Cl	H	4-Et
H	4-Cl	Me	4-*i*-Pr

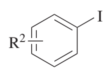
TABLE 18A. *N*-ARYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

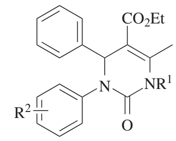
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{12}





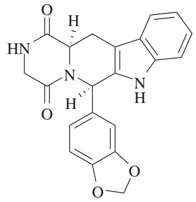
CuI (20 mol %), Cs_2CO_3, DMF, 180°, 40 min

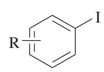


R^1	R^2	
H	H	(36)
H	4-EtO_2C	(13)
Me	H	(69)
Me	4-Cl	(70)
Me	4-O_2N	(49)
Me	3-MeO	(63)
Me	4-Me	(34)
Me	2-MeO_2C	(83)
Me	4-EtO_2C	(80)
Me	4-MeCO	(67)

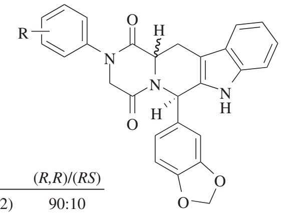
528

C_{20}





CuI (10 mol %), CDA (10 mol %), K_3PO_4, dioxane, 14°, 14 d

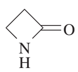
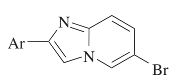
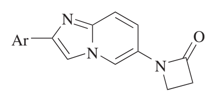
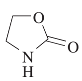
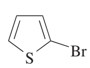
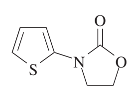
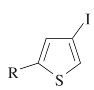
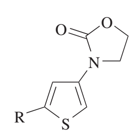


R		(*R,R*)/(*RS*)	R		(*R,R*)/(*RS*)
H	(80)	—[a]	4-MeO	(52)	90:10
3-Cl	(81)	80:20	3-Me	(52)	—[a]
4-Cl	(43)	66:34	4-CF_3	(50)	60:40
4-O_2N	(60)	17:83	4-*n*-Bu	(63)	76:24

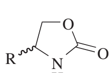
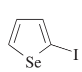
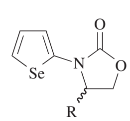
529

[a] Only the (*R,R*)-isomer was isolated.

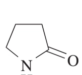
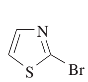
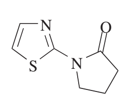
TABLE 18B. *N*-HETEROARYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_3				
	 Ar = 4-FC_6H_4	CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 20 h	 (80)	500
		CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, MeCN, 80°, 21 h	 (99)	518
		CuI (*x* mol %)		

R	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	1	DMEDA (1 mol %), K_2CO_3	dioxane	110	24	(99)	501
H	10	DMEDA (10 mol %), K_2CO_3	—	110	24	(99)	83
CHO	1	phen (10 mol %), Cs_2CO_3	DMF	80	21	(85)	501
CHO	10	DMEDA (10 mol %), K_2CO_3	—	110	24	(85)	83

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-10}				
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, reflux, 24 h		87

R	Config.	
H	—	(90)
i-Pr	(*S*)	(43)
(*S*)-*s*-Bu	(*R*)	(65)
Bn	(*S*)	(95)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CuI (10 mol %), DMEDA (10 mol %), dioxane, 110°, 24 h		

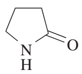
Additive		Refs.
K_2CO_3	(58)	83
K_3PO_4	(58)	501

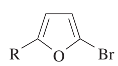
TABLE 18B. *N*-HETEROARYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

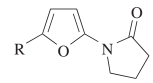
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

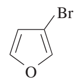




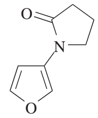
CuI (10 mol %), DMEDA (10 mol %), dioxane, 110°, 24 h



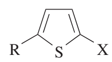
R	Additive		Refs.
H	K_2CO_3	(99)	83
H	K_3PO_4	(82)	501
MeO_2C	K_2CO_3	(77)	83
MeO_2C	K_3PO_4	(77)	501



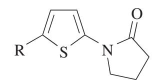
CuI (10 mol %), DMEDA (10 mol %), dioxane, 110°, 24 h



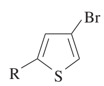
Additive		Refs.
K_2CO_3	(80)	83
K_3PO_4	(80)	501



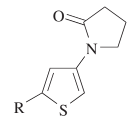
CuI (*x* mol %), dioxane, 110°



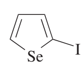
R	X	*x*	Additives	Time (h)		Refs.
H	Br	10	CDA (10 mol %), K_3PO_4	24	(96)	69
H	I	1	CDA (10 mol %), K_3PO_4	23	(97)	69
H	Br	10	DMEDA (10 mol %), K_2CO_3	24	(99)	83
H	I	10	EDA (10 mol %), K_3PO_4	24	(95)	405
H	I	1	DMCDA (10 mol %), K_3PO_4	24	(99)	115
Me	Br	10	DMEDA (10 mol %), K_2CO_3	24	(90)	83, 501



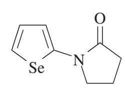
CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, dioxane, 110°, 24 h



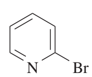
R	Additive		Refs.
H	K_2CO_3	(99)	83
CHO	K_3PO_4	(48)	501



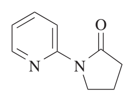
CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, reflux, 24 h



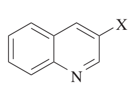
(77) 87



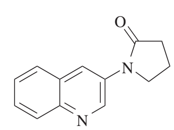
Catalyst (*x* mol %)



Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cu/SiO_2	14	KOAc	—	reflux	—	(51)	516
CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	60	22	(95)	49
CuI	10	oxazolidin-2-one (20 mol %), NaOMe	DMSO	120	24	(89)	492

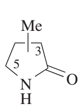


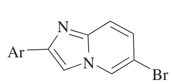
CuI (2 mol %), DMEDA (*x* mol %), K_2CO_3, diglyme, 110°, 24 h



X	*x*	Temp (°)		Refs.
Br	20	110	(98)	69
I	10	120	(99)	115

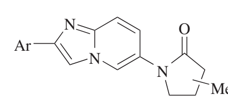
C_5



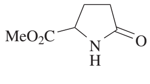


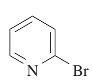
Ar = 4-FC_6H_4

CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 20 h

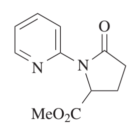


Isomer		Refs.
3	(83)	500
5	(83)	

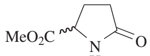


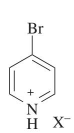


CuI (5 mol %), Cs_2CO_3, dioxane, 60°, 36 h

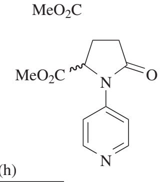


(73) 522





CuI (50 mol %), Cs_2CO_3, dioxane, 100°, 23 h

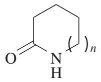
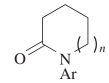


X	Config.	Temp (°)	Time (h)		Refs.
Cl	(*S*)	reflux	24	(68)	530
Br	(*R*,*S*)	100	23	(68)	522

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

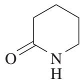
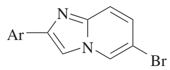
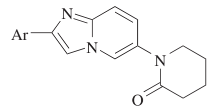
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{5-6}

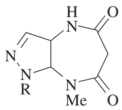
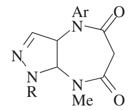
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	ArX	CuI (10 mol %), dioxane, 24 h		

n	Ar	X	Additives	Time (h)		Refs.
1	3-furyl	Br	DMEDA (10 mol %), K_2CO_3	110	(19)	83
1	selenophen-2-yl	I	EDA (20 mol %), K_3PO_4	reflux	(23)	87
2	3-furyl	Br	DMEDA (10 mol %), K_2CO_3	110	(80)	83
2	selenophen-2-yl	I	EDA (20 mol %), K_3PO_4	reflux	(21)	87

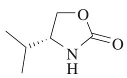
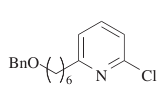
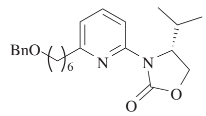
C_5

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	 Ar = 4-FC_6H_4	CuI (10 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 20 h	 (80)	500

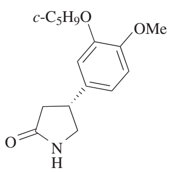
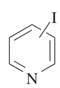
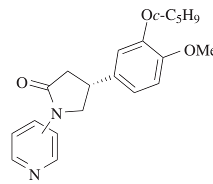
C_6

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	ArBr	Cu/SiO_2 (14 mol %), KOAc, reflux		516

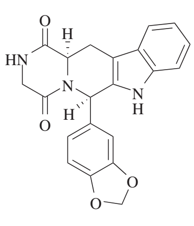
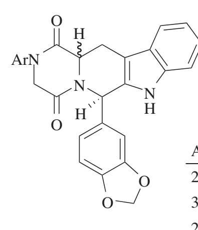
Ar	R	
2-thienyl	Bn	(78)
3-thienyl	Bn	(80)
2-pyridyl	Me	(77)
2-pyridyl	Bn	(73)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (15 mol %), DMEDA (30 mol %), K_2CO_3, toluene, 140°, 72 h	 (90)	531

C_{10}

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	 2-, 3-, or 4-I	CuI, CDA, K_3PO_4, DMF, 110°, 12 h	 (—)	527

C_{20}

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
	ArI	CuI (10 mol %), CDA (10 mol %), K_3PO_4, dioxane, 14°, 15 d		529

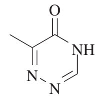
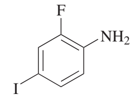
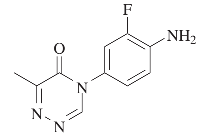
Ar		(*R*,*R*)/(*R*,*S*)
2-thienyl	(43)	58:42
3-thienyl	(77)	78:22
2-pyrazinyl	(35)	47:53
3-pyridyl	(66)	66:34

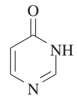
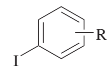
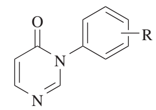
TABLE 19A. *N*-ARYLATION OF HETEROAROMATIC LACTAMS

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

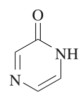
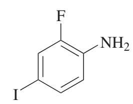
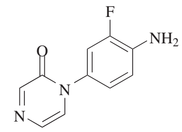
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4

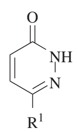
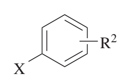
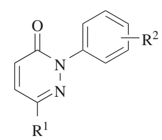
  CuI (15 mol %), 8-HOquin (15 mol %), K_2CO_3, DMSO, 130°, 18 h  (22) 532

  CuI (*x* mol %), K_2CO_3 

R	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
H	1	none	DMF	150	6	(0)	519
3-F, 4-NH_2	15	8-HOquin	DMSO	130	18	(28)	532

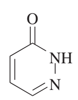
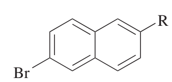
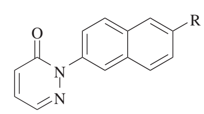
  CuI (15 mol %), 8-HOquin (15 mol %), K_2CO_3, DMSO, 130°, 18 h  (43) 532

C_{4-5}

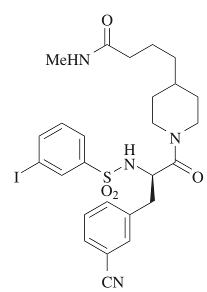
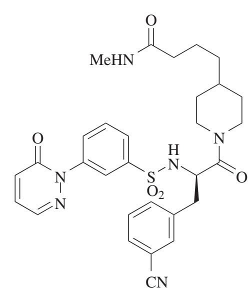
  Catalyst (*x* mol %) 

R^1	R^2	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	H	I	Cu_2O	5	**L30** (20 mol %), Cs_2CO_3, 3 Å MS	MeCN	82	100	(89)	40
H	4-MeO	Br	**13**	5	K_2CO_3	DMF	140	18	(85)	533
H	3-NC–	I	**13**	5	K_2CO_3	DMF	140	18	(80)	533
H	4-NC–	I	**13**	5	K_2CO_3	DMF	140	18	(94)	533
H	3,5-Me_2	I	**13**	5	K_2CO_3	DMF	140	18	(80)	533
Me	3-F, 4-NH_2	I	CuI	15	8-HOquin (15 mol %), K_2CO_3	DMSO	130	18	(59)	532
Me	4-MeO	Br	**13**	5	K_2CO_3	DMF	140	18	(80)	533

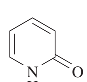
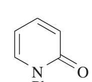
C_4

  Cat. **13** (5 mol %), K_2CO_3, DMF, 140°, 18 h 

R		Refs.
Br	(85)	533
$HOCH_2CH_2$	(70)	

 CuI (4 mol %), DMCDA (10 mol %), K_3PO_4, DMF, 110°, 1.5 h  (—) 534

C_5

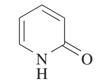
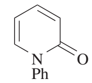
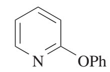
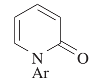
 PhX See table. 

X	Catalyst	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
Br	Cu (3 eq)	none	—	180	12	(100)	303
Br	Cu/SiO_2 (14 mol %)	KOAc	—	reflux	—	(57)	516
I	CuBr (10 mol %)	**L9** (20 mol %), Cs_2CO_3	DMSO	60	22	(95)	49
I	CuI (1 mol %)	K_2CO_3	DMF	150	6	(72)	519
Br	CuI (20 mol%)	DMCDA (1 eq), K_2CO_3	toluene	reflux	24	(91)	535
I	CuI (20 mol %)	DMCDA (1 eq), K_2CO_3	toluene	reflux	24	(84)	535
I	CuI (5 mol %)	**L43** (10 mol %), K_3PO_4	DMSO	110	5	(70)	138

TABLE 19A. *N*-ARYLATION OF HETEROAROMATIC LACTAMS (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	PhI	Cu_2O (5 mol %), **L30** (20 mol %), Cs_2CO_3, 3 Å MS, MeCN, 82°, 24 h	 (90) +  (2)	40
	ArX	Catalyst (*x* mol %)		

Ar	X	Catalyst	*x*	Additives	Solvent(s)	Temp (°)	Time (h)		Refs.
4-ClC_6H_4	I	CuI	10	4,7-(MeO)$_2$phen (15 mol %), K_2CO_3	DMSO	110	30	(80)	131
4-ClC_6H_4	I	CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(40)	53
$3\text{-H}_2NC_6H_4$	Br	CuI	5	4,7-(MeO)$_2$phen (7.5 mol %), K_2CO_3	DMSO	110	30	(78)	131
$3\text{-H}_2NC_6H_4$	I	Cu_2O	5	**L30** (20 mol %), Cs_2CO_3, 3 Å MS	MeCN	82	48	(82)	40
$4\text{-Ph}_2NC_6H_4$	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(59)	535
$4\text{-Ph}_2NC_6H_4$	I	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(79)	535
2-MeOC_6H_4	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(2)	535
3-MeOC_6H_4	I	CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(84)	53
4-MeOC_6H_4	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(89)	535
4-MeOC_6H_4	Br	CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(82)	53
4-MeOC_6H_4	I	CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(78)	53
3-Br, 4-MeOC_6H_4	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(37)	535
4-MeSC_6H_4	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(80)	535
2-MeC_6H_4	I	CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(40)	53
4-MeC_6H_4	I	CuBr	10	**L9** (20 mol %), Cs_2CO_3	DMSO	60	24	(86)	49
4-MeC_6H_4	Br	CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(88)	53
4-MeC_6H_4	I	CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(81)	53
4-NCC_6H_4	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(70)	535
$4\text{-MeO}_2CC_6H_4$	I	CuI	15	8-HOquin (15 mol %), K_2CO_3	DMSO	130	18	(22)	532
$4\text{-EtO}_2CC_6H_4$	Br	CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(91)	53
$4\text{-EtO}_2CC_6H_4$	I	CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(82)	53
$4\text{-CH}_2\text{=CHC}_6H_4$	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(82)	535
4-PhC_6H_4	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(70)	535
1-Np	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(37)	535
2-Np	Br	CuI	29	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(82)	535

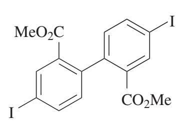
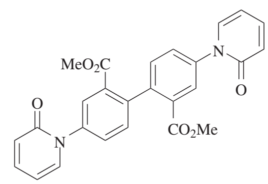
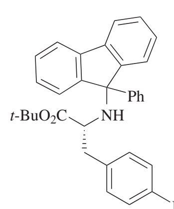
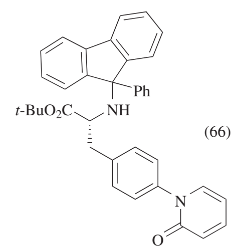
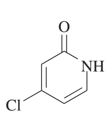
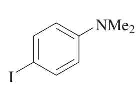
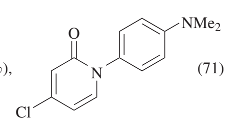
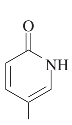
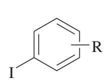
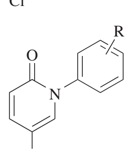
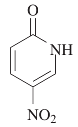
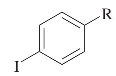
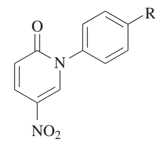
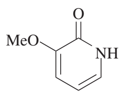
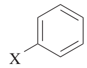
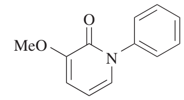
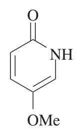
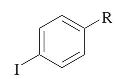
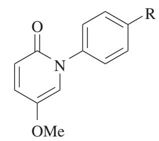
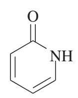
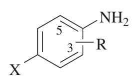
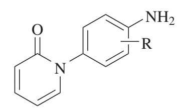
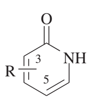
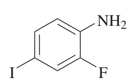
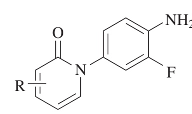
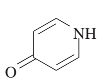
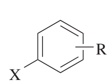
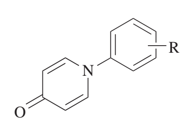
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (20 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 20 h	 (81)	535
		CuI, Cs_2CO_3, DMF, 150°	 (66)	536
		CuI (10 mol %), 4,7-(MeO)$_2$phen (15 mol %), K_2CO_3, DMSO, 120°, 30 h	 (71)	131
		CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, dioxane, 110°, 24 h	 R: 4-Cl (50); 3-MeO (90); 4-MeO (67); 4-Me (68); 4-EtO$_2$C (83)	53

TABLE 19A. *N*-ARYLATION OF HETEROAROMATIC LACTAMS (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_5				
		CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, dioxane, 110°, 24 h	 R MeO (trace) EtO_2C (trace)	53
		$Cu(OAc)_2$ (1 eq), DBU, DMSO, MW, 130°, 10 min	 X Br (81) I (84)	85
		CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, dioxane, 110°, 24 h	 R 4-Cl (75) 3-MeO (82) 4-MeO (90) 4-Me (87) 4-EtO_2C (81)	53
		CuI (15 mol %), 8-HOquin (15 mol %), K_2CO_3, DMSO, 130°, 18 h	 R X 3-F I (62) 3,5-F_2 Br (41) 3-Cl Br (11) 3-Cl I (31) 3-*i*-PrO Br (56)	532

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-6}				
		CuI (15 mol %), 8-HOquin (15 mol %), K_2CO_3, DMSO, 130°, 18 h		532

R		R	
3-F	(31)	3-PMBO	(55)
3,5-F_2	(58)	4-MeO	(74)
6-Cl	(0)	3-EtS	(51)
3-H_2N	(38)	3-Me	(78)
3-BocNH	(2)[a]	4-Me	(81)
3-O_2N	(4)	5-Me	(81)
3-HO	(0)	6-Me	(6)
3-AcO	(0)	3-CF_3	(30)
3-BnO$(CH_2)_2$O	(49)	5-EtO_2C	(81)

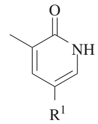
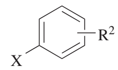
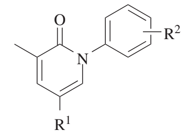
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		CuI (*x* mol %), K_2CO_3, DMSO, 110°, 30 h		131

R	X	*x*	Additive	
3-MeO	I	5	4,7-$(MeO)_2$phen (7.5 mol %)	(95)
2-Me	I	5	TMHD (40 mol %)	(60)
3,5-Me_2	I	2	TMHD (8 mol %)	(90)
4-EtOC	Br	5	TMHD (20 mol %)	(92)

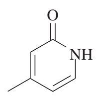
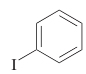
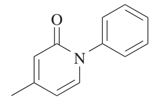
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

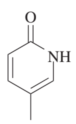
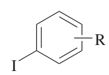
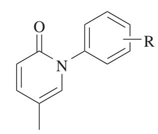
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_6

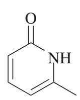
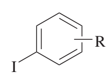
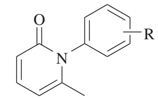
  See table. 

R^1	R^2	X	Catalyst	Additive(s)	Solvent	Temp (°)	Time		Refs.
H	H	Br	$Cu(OAc)_2$ (1 eq)	DBU	DMSO	MW, 130	10 min	(81)	85
H	H	I	$Cu(OAc)_2$ (1 eq)	DBU	DMSO	MW, 130	10 min	(84)	85
H	4-Cl	I	CuI (20 mol %)	DMEDA (40 mol %), K_3PO_4	dioxane	110	24 h	(85)	53
H	3-MeO	I	CuI (20 mol %)	DMEDA (40 mol %), K_3PO_4	dioxane	110	24 h	(95)	53
H	4-MeO	I	CuI (20 mol %)	DMEDA (40 mol %), K_3PO_4	dioxane	110	24 h	(97)	53
H	4-Me	I	CuI (20 mol %)	DMEDA (40 mol %), K_3PO_4	dioxane	110	24 h	(82)	53
H	3-H_2NCH_2	I	CuI (15 mol %)	8-HOquin (15 mol %), K_2CO_3	DMSO	130	18 h	(37)	532
H	4-NC–	I	CuI (15 mol %)	8-HOquin (15 mol %), K_2CO_3	DMSO	130	18 h	(58)	532
H	4-EtO_2C	I	CuI (20 mol %)	DMEDA (40 mol %), K_3PO_4	dioxane	110	24 h	(83)	53
NO_2	3,5-Me_2	I	CuI (10 mol %)	4,7-$(MeO)_2$phen (15 mol %), K_2CO_3	DMSO	150	30 h	(0)	131

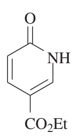
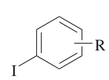
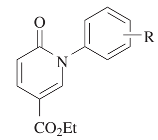
  CuI (1 mol %), K_2CO_3, DMF, 150°, 6 h  (87) 519

  CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, dioxane, 110°, 24 h  53

R	
4-Cl	(85)
3-MeO	(78)
4-MeO	(91)
4-Me	(94)
4-EtO_2C	(92)

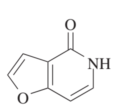
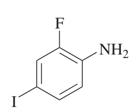
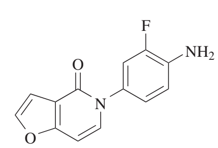
  CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, dioxane, 110°, 24 h  53

R	
4-MeO	(trace)
4-EtO_2C	(trace)

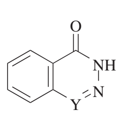
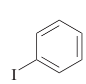
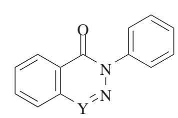
  CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, dioxane, 110°, 24 h  53

R	
4-Cl	(55)
3-MeO	(92)
4-MeO	(69)
4-Me	(77)
4-EtO_2C	(95)

C_7

  CuI (15 mol %), 8-HOquin (15 mol %), K_2CO_3, DMSO, 130°, 18 h  (92) 532

C_{7-8}

  CuI (10 mol %), K_2CO_3, DMF, 150°, 6 h  519

Y	
N	(14)
CH	(78)

C_9

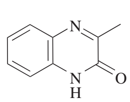
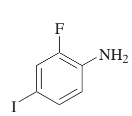
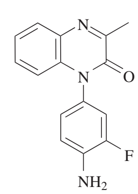
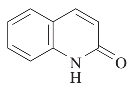
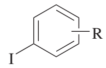
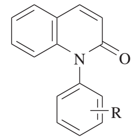
  CuI (15 mol %), 8-HOquin (15 mol %), K_2CO_3, DMSO, 130°, 18 h  (40) 532

TABLE 19A. *N*-ARYLATION OF HETEROAROMATIC LACTAMS (*Continued*)

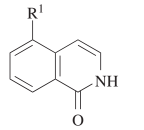
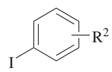
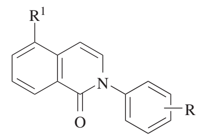
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

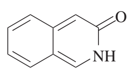
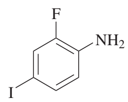
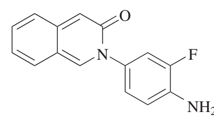
C_9

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (*x* mol %), K_2CO_3		

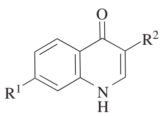
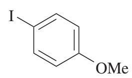
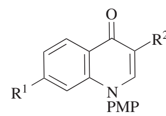
R	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
H	10	none	DMF	150	6	(0)	519
3-F, 4-H_2N	15	8-HOquin (15 mol %)	DMSO	130	18	(54)	532

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (*x* mol %), K_2CO_3		

R^1	R^2	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
H	3-F, 4-H_2N	15	8-HOquin (15 mol %)	DMSO	130	18	(66)	532
HO	H	10	none	DMF	150	6	(32)	519

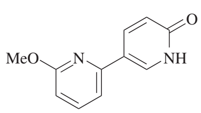
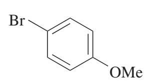
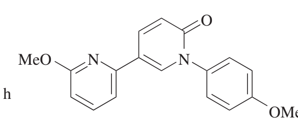
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (15 mol %), 8-HOquin (15 mol %), K_2CO_3, DMSO, 130°, 18 h	 (0)	532

$C_{9–11}$

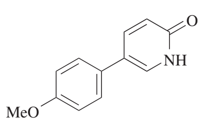
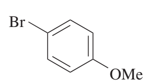
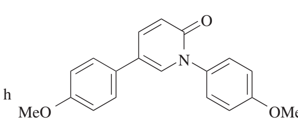
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), K_3PO_4, DMSO, TMHD (40 mol %), 30 h		131

R^1	R^2	Temp (°)	
Cl	H	120	(68)
CF_3	CO_2Et	140	(0)

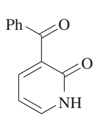
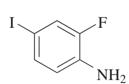
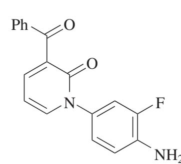
C_{10}

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 20 h	 (74)	537

C_{11}

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 20 h	 (82)	537

C_{12}

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (15 mol %), 8-HOquin (15 mol %), K_2CO_3, DMSO, 130°, 18 h	 (47)	532

C_{14}

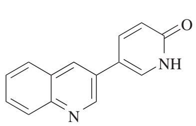
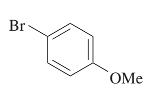
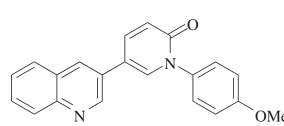
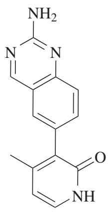
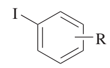
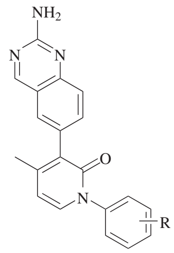
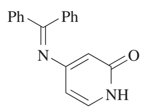
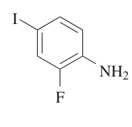
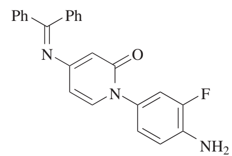
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 20 h	 (66)	537

TABLE 19A. *N*-ARYLATION OF HETEROAROMATIC LACTAMS (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)			Refs.
C_{14}						
		CuI (40 mol %), DMEDA (1 eq), K_3PO_4, NMP, 85°, 6 h		R		538
				3-F, 4-Cl	(—)	
				4-Cl	(—)	
				4-(4-morpholino)	(—)	
				3-MeO	(—)	
				4-MeO	(—)	
				3-F, 4-Me	(—)	
				3-Me, 4-F	(—)	
				3-CF_3	(91)	
				4-EtO_2C	(—)	
				4-Ac	(—)	
				4-*t*-Bu	(—)	
				4-(1-pyrazolyl)	(—)	
				4-(2-oxazolyl)	(—)	
C_{18}						
		CuI (15 mol %), 8-HOquin (15 mol %), K_2CO_3, DMSO, 130°, 18 h		(81)		532

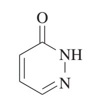
[a] The deprotected free amine was formed in 14% yield.

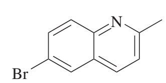
TABLE 19B. *N*-HETEROARYLATION OF HETEROAROMATIC LACTAMS

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

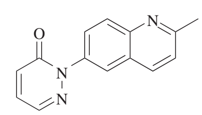
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_4



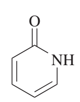


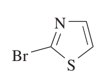
13 (5 mol %), K_2CO_3, DMF, 140°, 18 h



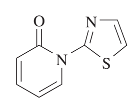
(90) 533

C_5

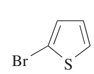




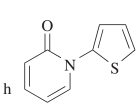
CuI (x mol %)



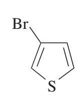
x	Additives	Solvent	Temp (°)	Time (h)		Refs.
5	4,7-(MeO)$_2$phen (7.5 mol %), K_2CO_3	DMSO	110	30	(85)	131
20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(27)	53
20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	16	(33)	535



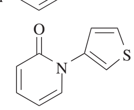
CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, dioxane, 110°, 24 h



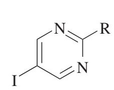
(81) 53



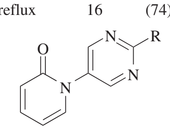
Catalyst (x mol %)



Catalyst	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
Cu/SiO$_2$	14	KOAc	—	reflux	—	(84)	516
CuI	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(80	53
CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	16	(74)	535



CuI (x mol %), K_2CO_3, DMSO



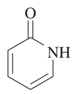
R	x	Additive	Temp (°)	Time (h)		Refs.
H	5	4,7-(MeO)$_2$phen (7.5 mol %)	110	30	(47)	131
NH$_2$	15	8-HOquin (15 mol %)	130	18	(59)	532

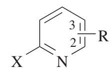
TABLE 19B. *N*-HETEROARYLATION OF HETEROAROMATIC LACTAMS (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

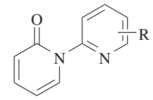
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_5

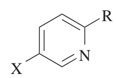




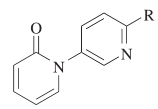
Catalyst (*x* mol %), reflux



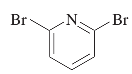
R	X	Catalyst	*x*	Additive(s)	Solvent	Time (h)		Refs.
H	Br	Cu/SiO_2	14	KOAc	—	—	(76)	516
H	Cl	CuI	20	DMCDA (1 eq), K_2CO_3	toluene	24	(7)	535
H	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	16	(68)	535
H	I	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	16	(44)	535
2-O_2N	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	16	(62)	535
3-Me	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	20	(36)	535
4-Me	Br	CuI	20	DMCDA (20 mol %), K_2CO_3	toluene	20	(57)	535



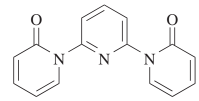
CuI (*x* mol %)



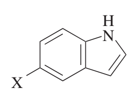
R	X	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	Br	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(8)	53
H	Br	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	16	(76)	535
H	Br	15	8-HOquin (15 mol %), K_2CO_3	DMSO	130	18	(46)	532
H_2N	I	15	8-HOquin (15 mol %), K_2CO_3	DMSO	130	18	(59)	532
t-BuO	Br	20	DMCDA (20 mol %), K_2CO_3	toluene	reflux	20	(63)	535
t-BuO	Br	20	DMCDA (20 mol %), 18-c-6 (20 mol %), K_2CO_3	toluene	reflux	24	(63)	539



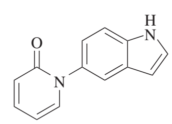
CuI (20 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 16 h



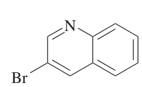
(65) 535



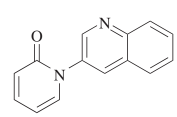
CuI (*x* mol%)



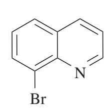
X	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
Br	20	DMEDA (40 mol %), K_3PO_4	dioxane	110	24	(16)	53
I	10	DMCDA (20 mol %), K_2CO_3	DMSO	100	30	(75)	131



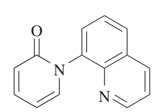
CuI (5 mol %), 4,7-$(MeO)_2$phen (7.5 mol %), K_2CO_3, DMF, 110°, 30 h



(82) 131



CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, dioxane, 110°, 24 h



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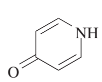
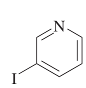
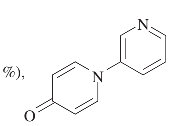




CuI (7 mol %), 4,7-$(MeO)_2$phen (7.5 mol %), K_2CO_3, DMSO, 110°, 30 h



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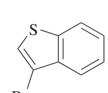

CuI (5 mol%), TMHD (40 mol %), K_2CO_3, DMSO, 110°, 30 h

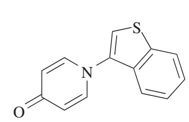

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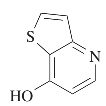
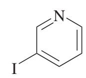
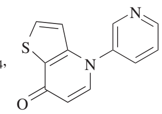
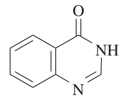
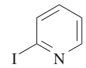
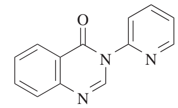
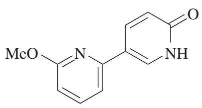
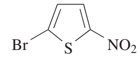
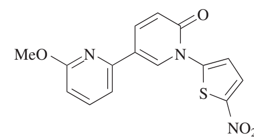
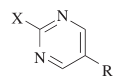
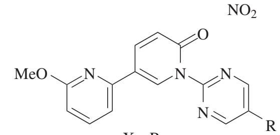
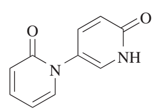
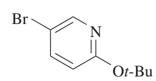
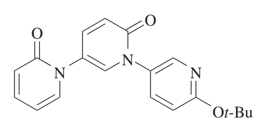
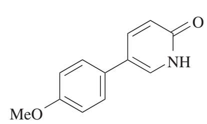
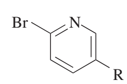
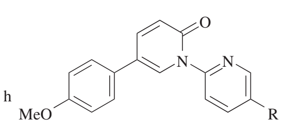
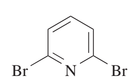
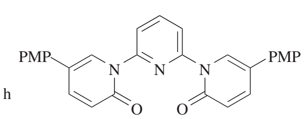
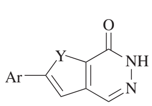
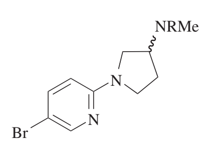
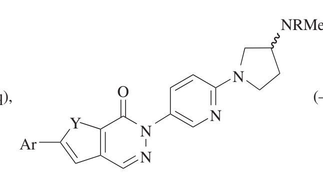
TABLE 19B. *N*-HETEROARYLATION OF HETEROAROMATIC LACTAMS (*Continued*)

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CuI (10 mol %), TMHD (40 mol %), K_3PO_4, DMSO, 120°, 30 h	 (65)	131
C_8				
		CuI (10 mol %), oxazolidinone (20 mol %), NaOMe, DMSO, 120°, 24 h	 (93)	492
C_{10}				
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 20 h	 (60)	537
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 20 h		537
		CuI (20 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux	 (82)	535
C_{11}				
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 20 h		537
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 20 h	 (69)	537
$C_{12–14}$				
		CuI (1 eq), DMCDA (1.4 eq), dioxane, 110°, 9 h	 (—)	540

Pyrimidine products (ref. 537):

X	R	
I	Br	(51)
Br	NH_2	(40)

Ref. 535 conditions:

Additive	Time (h)	
none	20	(82)
18-c-6	24	(82)

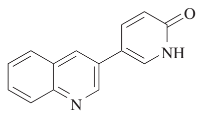
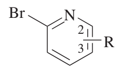
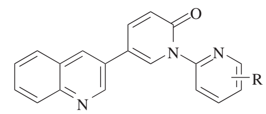
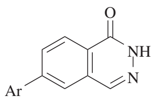
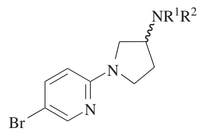
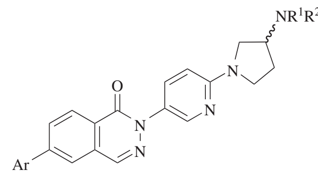
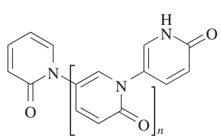
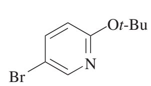
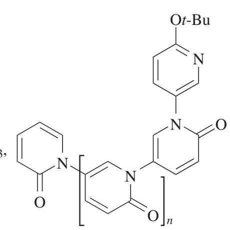
Ref. 537 (C_{11}) products:

R	
F	(77)
O_2N	(83)
CF_3	(80)

Ref. 540 products:

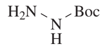
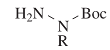
Ar	Y	R	Config.
$4\text{-}FC_6H_4$	S	H	(*R*)
$4\text{-}FC_6H_4$	S	H	(*S*)
$4\text{-}ClC_6H_4$	S	H	(*S*)
$4\text{-}MeOC_6H_4$	S	H	(*S*)
$4\text{-}CF_3C_6H_4$	NMe	Me	(*R*)
$4\text{-}CF_3C_6H_4$	O	Me	(*R*)
$4\text{-}CF_3C_6H_4$	S	H	(*R*)
$4\text{-}CF_3C_6H_4$	S	H	(*S*)
$4\text{-}CF_3C_6H_4$	S	Me	(*R*)
$4\text{-}CF_3C_6H_4$	Se	H	(*R*)
$4\text{-}EtC_6H_4$	S	H	(*S*)

TABLE 19B. *N*-HETEROARYLATION OF HETEROAROMATIC LACTAMS (*Continued*)

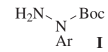
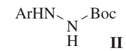
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{14}				
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 20 h	 R 2-MeO (72) 3-CF_3 (72)	537
C_{14-15}				
		CuI (1 eq), DMCDA (1.4 eq), dioxane, 110°, 9 h		540
C_{15-20}				
		CuI (20 mol %), DMCDA (20 mol %), 18-c-6, (20 mol %), K_2CO_3, toluene, reflux, 24 h	 *n* 1 (53) 2 (18)	539

Ar	R^1	R^2	Config.	
4-ClC_6H_4	Me	H	(*R*)	(—)
4-ClC_6H_4	Me	H	(*S*)	(—)
4-ClC_6H_4	Et	H	(*R*)	(—)
4-ClC_6H_4	Et	H	(*S*)	(—)
4-ClC_6H_4	Me	Me	(*R*)	(—)
4-ClC_6H_4	Me	Me	(*S*)	(39)
4-ClC_6H_4	—$(CH_2)_4$—		(*R*)	(—)
4-ClC_6H_4	—$(CH_2)_4$—		(*S*)	(—)
2-Me-3-$MeOC_6H_3$	Me	H	(*R*)	(—)
4-$CF_3C_6H_4$	Me	H	(*R*)	(—)
4-$CF_3C_6H_4$	Me	H	(*S*)	(—)

TABLE 20. *N*-ARYLATION AND *N*-HETEROARYLATION OF HYDRAZINE DERIVATIVES

Nitrogen Nucleophile	(Hetero)aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_0 	RX	CuI (*x* mol %), Cs_2CO_3, 80°		

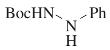
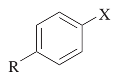
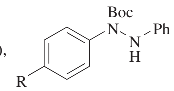
R	X	*x*	Additive	Solvent	Time (h)	Yield (%)	Refs.
3-thienyl	Br	10	4-HOPro (20 mol %)	DMSO	24	(43)	133
3-pyridyl	Br	10	4-HOPro (20 mol %)	DMSO	15	(82)	133
3-pyridyl	I	5	2-picoline (10 mol %)	DMF	24	(52)	134
4-pyridyl	I	10	4-HOPro (20 mol %)	DMSO	24	(91)	133

ArX — CuI (*x* mol %), Cs_2CO_3 —  **I** +  **II**

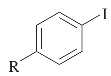
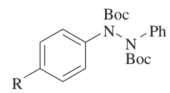
Ar	X	*x*	Additive	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
Ph	I	1	phen (10 mol %)	DMF	80	21	(97)	(0)	135
3-FC_6H_4	I	5	none	DMSO	50	2.5	(92)	(0)	133
3-FC_6H	Br	10	4-HOPro (20 mol %)	DMSO	80	24	(91)	(0)	133
4-FC_6H_4	I	5	none	DMSO	50	4	(86)	(0)	133
4-FC_6H_4	Br	10	4-HOPro (20 mol %)	DMSO	80	15	(66)	(0)	133
4-FC_6H_4	I	5	2-picoline (10 mol %)	DMF	80	24	(65)	(0)	134
4-ClC_6H_4	I	5	2-picoline (10 mol %)	DMF	80	24	(65)	(0)	134
4-BrC_6H_4	I	5	none	DMSO	50	2.5	(75)	(0)	133
4-BrC_6H_4	I	5	phen (20 mol %)	DMF	80	21	(71)	(0)	135
3-$H_2NC_6H_4$	Br	10	4-HOPro (20 mol %)	DMSO	80	16	(73)	(0)	133
4-$H_2NC_6H_4$	I	5	none	DMSO	50	4	(76)	(0)	133
4-$H_2NC_6H_4$	Br	10	4-HOPro (20 mol %)	DMSO	80	24	(64)	(0)	133
4-$H_2NC_6H_4$	I	5	2-picoline (10 mol %)	DMF	80	24	(62)	(0)	134
4-$H_2NC_6H_4$	I	1	phen (20 mol %)	DMF	80	21	(78)	(0)	135
3-$O_2NC_6H_4$	I	5	none	DMSO	50	2.5	(75)	(0)	133
4-$O_2NC_6H_4$	I	10	4-HOPro (20 mol %)	DMSO	80	4	(43)	(0)	133
4-HOC_6H_4	I	5	none	DMSO	50	2.5	(65)	(0)	133
4-HOC_6H_4	Br	10	4-HOPro (20 mol %)	DMSO	80	20	(70)	(0)	133
4-HOC_6H_4	I	1	phen (10 mol %)	DMF	80	21	(67)	(0)	135
3-$MeOC_6H_4$	I	5	none	DMSO	50	2.5	(92)	(0)	133
3-$MeOC_6H_4$	Br	10	4-HOPro (20 mol %)	DMSO	80	15	(78)	(0)	133
3-$MeOC_6H_4$	I	1	phen (10 mol %)	DMF	80	21	(80)	(0)	135
4-$MeOC_6H_4$	I	5	none	DMSO	50	2.5	(92)	(0)	133

Ar	X	*x*	Additive	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
4-$MeOC_6H_4$	I	1	phen (10 mol %)	DMF	80	21	(85)	(0)	135
4-$MeOC_6H_4$	I	5	2-picoline (10 mol %)	DMF	80	24	(61)	(0)	134
2-MeC_6H_4	I	5	none	DMSO	50	2.5	(33)	(9)	133
2-MeC_6H_4	I	5	2-picoline (10 mol %)	DMSO	80	24	(28)	(0)	134
2-MeC_6H_4	Br	10	5-HOPro (20 mol %)	DMSO	80	15	(56)	(0)	133
3-MeC_6H_4	I	5	none	DMSO	50	2.5	(92)	(0)	133
3-MeC_6H_4	Br	10	5-HOPro (20 mol %)	DMSO	80	16	(90)	(0)	133
3-MeC_6H_4	I	5	2-picoline (10 mol %)	DMF	80	24	(70)	(0)	134
4-MeC_6H_4	Br	10	5-HOPro (20 mol %)	DMSO	80	15	(80)	(0)	133
4-MeC_6H_4	I	5	none	DMSO	50	2.5	(85)	(0)	133
4-MeC_6H_4	I	5	2-picoline (10 mol %)	DMF	80	24	(67)	(0)	134
3-$CF_3C_6H_4$	Br	10	5-HOPro (20 mol %)	DMSO	80	15	(79)	(0)	133
4-$CF_3C_6H_4$	I	5	none	DMSO	50	4	(86)	(0)	133
4-$CF_3C_6H_4$	I	5	2-picoline (10 mol %)	DMF	80	24	(67)	(0)	134
3-$HOCH_2C_6H_4$	Br	10	5-HOPro (20 mol %)	DMSO	80	24	(89)	(0)	133
3-$HOCH_2C_6H_4$	I	5	2-picoline (10 mol %)	DMF	80	24	(30)	(0)	134
3-$HOCH_2C_6H_4$	I	1	phen (10 mol %)	DMF	80	21	(89)	(0)	135
3-NCC_6H_4	I	5	2-picoline (10 mol %)	DMF	80	24	(52)	(0)	134
4-NCC_6H_4	I	1	phen (10 mol %)	DMF	80	4	(78)	(0)	135
3-$MeO_2CC_6H_4$	I	5	none	DMSO	50	4	(88)	(0)	133
3-$EtO_2CC_6H_4$	I	5	phen (10 mol %)	DMF	80	21	(78)	(0)	135
4-$MeO_2CC_6H_4$	I	5	none	DMSO	50	3	(90)	(0)	133
4-$MeO_2CC_6H_4$	Br	10	5-HOPro (20 mol %)	DMSO	80	24	(34)	(41)	133
4-$EtO_2CC_6H_4$	I	5	phen (10 mol %)	DMF	80	21	(88)	(0)	135
3,5-$Me_2C_6H_3$	I	5	2-picoline (10 mol %)	DMF	80	24	(73)	(0)	134
3,5-$Me_2C_6H_3$	I	1	phen (10 mol %)	DMF	80	21	(90)	(0)	135
4-AcC_6H_4	I	10	5-HOPro (20 mol %)	DMSO	80	24	(60)	(0)	133
4-AcC_6H_4	I	1	phen (10 mol %)	DMF	80	4	(43)	(0)	135
4-*i*-PrC_6H_4	I	1	phen (10 mol %)	DMF	80	21	(87)	(0)	135
4-PhC_6H_4	Br	10	5-HOPro (20 mol %)	DMSO	80	15	(80)	(0)	133

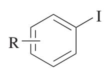
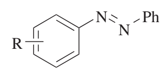
TABLE 20. *N*-ARYLATION AND *N*-HETEROARYLATION OF HYDRAZINE DERIVATIVES (*Continued*)

Nitrogen Nucleophile	(Hetero)aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		CuI (10 mol %), phen (10 mol %), Cs_2CO_3, DMF, 80°		541

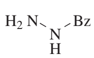
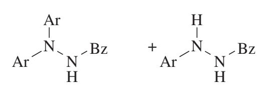
R	X	Time (h)	
H	I	22	(87)
O_2N	I	5	(51)
MeO	I	22	(87)
NC–	Br	47	(56)
EtO_2C	Br	48	(45)

Nitrogen Nucleophile	(Hetero)aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (1 eq), phen (10 mol %), Cs_2CO_3, DMF, 80°		541

R	Time (h)	
H	3	(99)
I	18	(99)
O_2N	3	(99)
MeO	18	(86)
Me	3	(99)
$HOCH_2$	3	(95)
NC–	3	(99)
MeO_2C	3	(99)
Ph	34	(99)

Nitrogen Nucleophile	(Hetero)aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (1 eq), phen (10 mol %), Cs_2CO_3, DMF, 110°		541

R	Time (d)	
H	6.5	(64)
4-I	3	(45)
4-O_2N	2	(50)
4-MeO	4	(43)
4-Me	6.5	(46)
4-$HOCH_2$	7	(trace)
3-NC–	3	(60)
4-MeO_2C	2	(69)
4-Ac	4	(50)
4-Ph	3	(67)

Nitrogen Nucleophile	(Hetero)aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	ArX	CuI (*x* amount)	 **I** + **II**	

Ar	X	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	**I**	**II**	Refs.
Ph	I	1 eq	*t*-BuOK	HMPA	100	1	(30)	(0)	542
4-$MeOC_6H_4$	I	1 eq	*t*-BuOK	HMPA	100	1	(13)	(0)	542
2-MeC_6H_4	I	1 eq	*t*-BuOK	HMPA	100	1	(20)	(0)	542
2-MeC_6H_4	Br	10 mol %	PPAPM (20 mol %), K_2CO_3, LiCl	DMF	110	36	(0)	(74)	48
4-MeC_6H_4	I	1 eq	*t*-BuOK	HMPA	100	1	(32)	(0)	542
3,5-$Me_2C_6H_3$	I	1 mol %	CDA (10 mol %), K_2CO_3	dioxane	110	23	(0)	(62)	115
4-Ph	I	1 eq	*t*-BuOK	HMPA	100	1	(26)	(0)	542
1-Np	I	1 eq	*t*-BuOK	HMPA	100	1	(13)	(21)	542

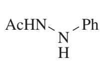
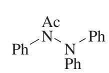
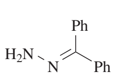
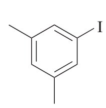
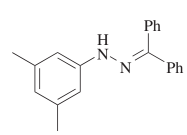
Nitrogen Nucleophile	(Hetero)aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	PhI	CuI (5 mol %), Gly (20 mol %), K_3PO_4, dioxane, 100°, 24 h	 (91)	136
C_{13}				
		CuI (1 mol %), CDA (10 mol %), NaO*t*-Bu, dioxane, 110°, 23 h	 (83)	115

TABLE 21. *N*-ARYLATION OF HYDROXYLAMINE DERIVATIVES

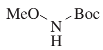
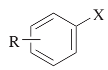
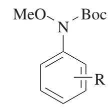
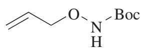
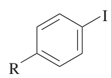
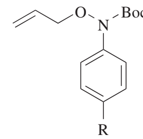
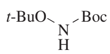
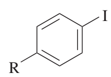
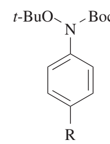
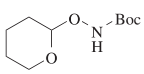
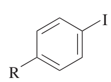
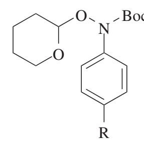
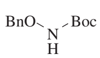
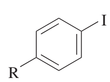
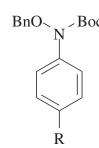
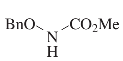
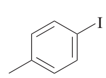
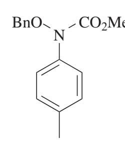
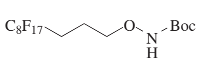
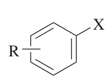
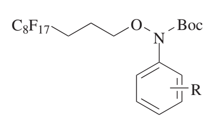
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
		CuI (5 mol %), phen (50 mol %), Cs_2CO_3, DMF, 80°, 24 h	 R, X: H, Br (0); H, I (89); H, OTf (0); 4-F, I (72); 3-Br, I (74); 4-O_2N, I (77); 4-MeO, I (69); 2-Me, I (0); 4-Me, I (72); 3-EtO_2C, I (84); 4-Ac, I (73)	543
C_3				
		CuI (5 mol %), phen (50 mol %), Cs_2CO_3, DMF, 80°, 24 h	 R: O_2N (70); Me (57)	543
C_4				
		CuI (5 mol %), phen (50 mol %), Cs_2CO_3, DMF, 80°, 24 h	 R: F (70); O_2N (68); MeO (86); Me (74); NC– (86)	543
C_5				
		CuI (5 mol %), phen (50 mol %), Cs_2CO_3, DMF, 80°, 24 h	 R: Me (70); NC– (76)	543
C_7				
		CuI (5 mol %), phen (50 mol %), Cs_2CO_3, DMF, 80°, 24 h	 R: H (83); F (70); MeO (65); Me (74); NC– (65)	543
C_8				
		CuI (5 mol %), phen (50 mol %), Cs_2CO_3, DMF, 80°, 24 h	 (68)	543
C_{11}				
		CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 110°, 16 h	 R: 4-F (96); 3-Cl (94); 4-Br (99); 3-HO (86); 3-MeO (96); 3-$O(CH_2)_2O$-4 (96); 2-MeS (68); 4-CF_3 (93); 2-$BocMeNCH_2$ (74); 4-$HOCH_2$ (92); 4-NC– (84); 4-CHO (89); 3-EtO_2C (89); 4-EtO_2C (90); 4-Ac (89); 4-*i*-Pr (99)	144

TABLE 21. *N*-ARYLATION OF HYDROXYLAMINE DERIVATIVES (*Continued*)

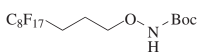
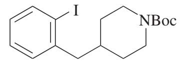
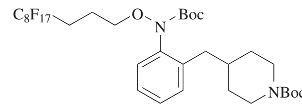
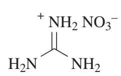
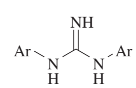
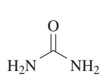
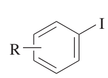
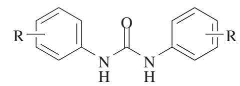
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{11}					
		CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 110°, 16 h		(96)	144

TABLE 22A. *N*-ARYLATION OF UREAS AND GUANIDINES

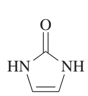
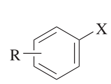
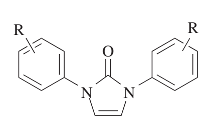
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_1				
	ArI	CuI (*x* mol %), **L13** (20 mol %), K_3PO_4, 80°, 24 h		149

Ar	*x*	Solvent	
Ph	15	MeCN	(83)
$2\text{-}FC_6H_4$	10	dioxane	(33)
$3\text{-}FC_6H_4$	10	dioxane	(53)
3-F, $4\text{-}BrC_6H_3$	10	toluene	(55)
$4\text{-}FC_6H_4$	10	dioxane	(62)
$4\text{-}ClC_6H_4$	10	MeCN	(35)
$4\text{-}BrC_6H_4$	10	MeCN	(19)
$4\text{-}O_2NC_6H_4$	15	MeCN	(46)

Ar	*x*	Solvent	
$2\text{-}MeOC_6H_4$	10	MeCN	(47)
$2\text{-}MeC_6H_4$	10	MeCN	(92)
$3\text{-}MeC_6H_4$	15	MeCN	(64)
$4\text{-}MeC_6H_4$	15	MeCN	(49)
3-Cl,$4\text{-}MeC_6H_3$	10	MeCN	(67)
$4\text{-}EtC_6H_4$	10	MeCN	(39)
$2,4\text{-}Me_2C_6H_3$	10	MeCN	(80)
4-*t*-BuC_6H_4	10	MeCN	(30)
2-Np	10	MeCN	(50)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), CDA (10 mol %), K_3PO_4, DMF, 80°, 24 h		147

R	
H	(60)
4-Cl	(57)
3-Me	(63)
4-Me	(56)
$3\text{-}CF_3$	(29)
4-*t*-Bu	(65)

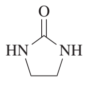
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		Catalyst (*x* mol %), dioxane		544

R	X	Catalyst	*x*	Additives	Temp (°)	Time (h)	
4-Me	I	CuI	10	CDA (10 mol %), K_3PO_4	120	15	(80)
4-Me	I	$Cu(OTf)_2•C_6H_6$	5	CDA (50 mol %), Cs_2CO_3	120	15	(67)
4-Me	I	$Cu(OTf)_2•C_6H_6$	10	phen (2 eq), Cs_2CO_3	MW, 180°	0.5	(44)
$3\text{-}CF_3$	Br	$Cu(OTf)_2•C_6H_6$	5	CDA (10 mol %), Cs_2CO_3	120	15	(52)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

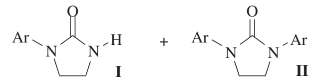
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3

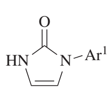


ArX

CuI (10 mol %), K_2CO_3

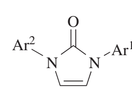


Ar	X	Additive	Solvent	Temp (°)	Time (h)	I	II	Refs.
Ph	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(74)	(17)	148
Ph	Br	DMCDA (20 mol %)	toluene	reflux	24	(—)	(85)	545
2-FC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(60)	(—)	148
3-FC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(67)	(—)	148
4-FC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(67)	(—)	148
2-ClC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(49)	(—)	148
3-ClC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(53)	(—)	148
4-ClC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(65)	(—)	148
4-BrC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(48)	(—)	148
4-$H_2NC_6H_4$	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(54)	(—)	148
4-$O_2NC_6H_4$	Br	DMCDA (20 mol %)	toluene	reflux	24	(—)	(82)	545
4-HOC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(61)	(—)	148
2-$MeOC_6H_4$	Br	DMCDA (20 mol %)	toluene	reflux	24	(—)	(82)	545
2-$MeOC_6H_4$	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(70)	(—)	148
3-$MeOC_6H_4$	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(71)	(—)	148
4-$MeOC_6H_4$	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(54)	(—)	148
4-$MeOC_6H_4$	Br	DMCDA (20 mol %)	toluene	reflux	24	(—)	(88)	545
4-$MeSC_6H_4$	Br	DMCDA (20 mol %)	toluene	reflux	24	(—)	(76)	545
2-MeC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(55)	(—)	148
3-MeC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(65)	(—)	148
4-MeC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(61)	(—)	148
4-NCC_6H_4	Br	DMCDA (20 mol %)	toluene	reflux	24	(—)	(84)	545
4-NCC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(46)	(—)	148
4-$EtO_2CC_6H_4$	Br	DMCDA (20 mol %)	toluene	reflux	24	(—)	(73)	545
4-AcC_6H_4	Br	DMCDA (20 mol %)	toluene	reflux	24	(—)	(82)	545
4-AcC_6H_4	I	DMEDA (30 mol %)	*n*-BuOH	100	5	(45)	(—)	148
1-Np	Br	DMCDA (20 mol %)	toluene	reflux	24	(—)	(88)	545

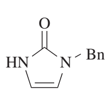


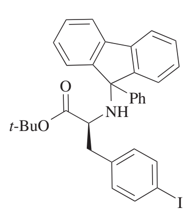
Ar^2X

$(CuOTf)_2$•C_6H_6 (10 mol %), DMCDA (50 mol %), dba (10 mol %), Cs_2CO_3, dioxane, MW, 150°, 30 min

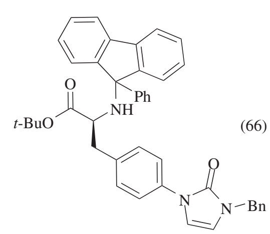


Ar^1	Ar^2	X		Refs.
Ph	3-$O_2NC_6H_4$	I	(73)	544
Ph	4-$O_2NC_6H_4$	Br	(96)	
Ph	4-$O_2NC_6H_4$	I	(100)	
Ph	4-MeC_6H_4	I	(97)	
Ph	4-$CF_3C_6H_4$	Br	(83)	
4-$MeOC_6H_4$	4-$O_2NC_6H_4$	I	(74)	
4-MeC_6H_4	4-MeC_6H_4	Br	(84)	
4-MeC_6H_4	4-MeC_6H_4	I	(86)	



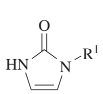


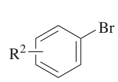
CuI (cat.), Cs_2CO_3, DMF, 150°



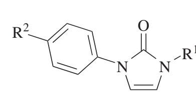
(66) 536

C_{3-9}



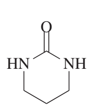


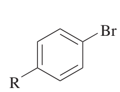
CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 24 h



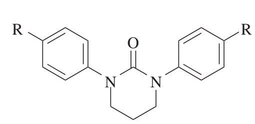
R^1	R^2		Refs.
t-Bu	SMe	(94)	545
4-$MeSC_6H_4$	EtO_2C	(76)	

C_4



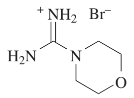
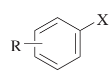
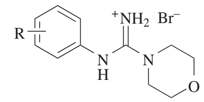
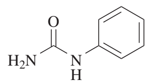
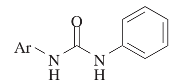
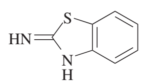
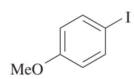
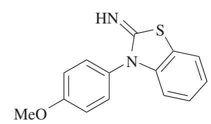


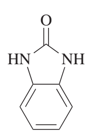
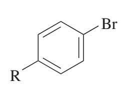
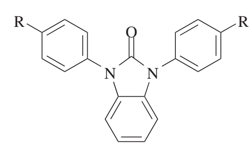
CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 24 h



R		Refs.
O_2N	(67)	545
MeO	(84)	

TABLE 22A. *N*-ARYLATION OF UREAS AND GUANIDINES (*Continued*)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_5				
		CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, dioxane, 100°, 24 h	 R, X: 3,4-Cl_2, I (86); 4-O_2N, I (93); 4-MeO, I (75); 4-Me, Br (35); 4-Me, I (86); 4-NC–, I (84); 4-Ac, I (83)	141
C_7				
	ArI	CuI (15 mol %), KF/Al_2O_3, BnNH(CH)$_2$NHBn (15 mol %), THF, 70°, 4 h	 Ar: Ph (83); 4-BrC_6H_4 (88); 4-$O_2NC_6H_4$ (75); 2-$MeOC_6H_4$ (75); 4-$MeOC_6H_4$ (78); 2-MeC_6H_4 (75); 4-MeC_6H_4 (70); 3-$CF_3C_6H_4$ (73); 4-EtCO (70); 1-Np (67)	146
		CuI (10 mol %), pyrrole-2-carboxylic acid (20 mol %), K_3PO_4, DMSO, 90°, 24 h	 (82)	50

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (x mol %), K_2CO_3, 24 h		

R	x	Additive	Solvent	Temp (°)	Yield	Refs.
Br	20	none	DMF	150	(28)	546
O_2N	10	DMCDA (20 mol %)	toluene	reflux	(82)	545
MeO	10	DMCDA (20 mol %)	toluene	reflux	(82)	545

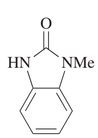
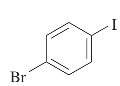
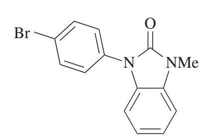
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 80°, 24 h	 (81)	408

TABLE 22B. *N*-HETEROARYLATION OF UREAS AND GUANIDINES

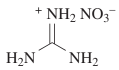
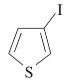
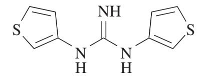
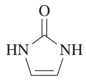
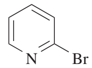
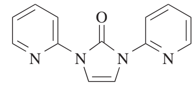
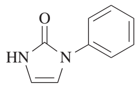
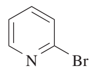
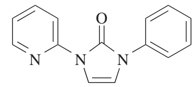
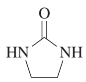
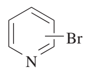
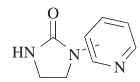
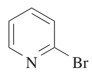
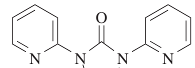
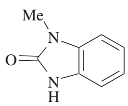
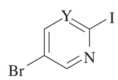
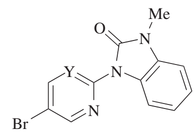
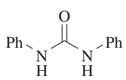
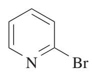
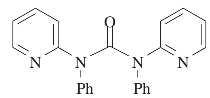
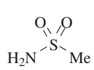
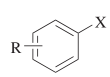
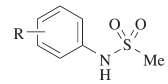
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_1				
		CuI (10 mol %), **L13** (20 mol %), K_3PO_4, dioxane, 80°, 24 h	 (75)	149
C_3				
		$(CuOTf)_2•C_6H_6$ (10 mol %), phen (20 mol %), Cs_2CO_3, dioxane, MW, 150°, 30 min	 (32)	544
		$(CuOTf)_2•C_6H_6$ (10 mol %), DMCDA (50 mol %), dba (10 mol %), Cs_2CO_3, dioxane, MW, 150°, 30 min	 (96)	544
		CuI (10 mol %), DMEDA (30 mol %), K_2CO_3, *n*-BuOH, 100°, 5 h	 Isomer: 2 (45); 3 (46)	148
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 24 h	 (82)	545
C_7				
		CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 80°, 24 h	 Y: N (76); CH (94)	408
C_{13}				
		CuI (10 mol %), DMCDA (20 mol %), K_2CO_3, toluene, reflux, 24 h	 (21)	545

TABLE 23A. *N*-ARYLATION OF SULFONAMIDES AND SULFONIMIDAMIDES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

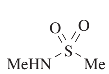
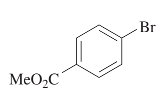
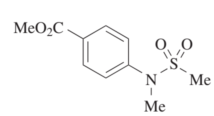
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_1

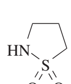
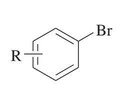
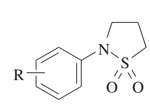
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (*x* mol %)		

R	X	x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	Br	10	K_2CO_3	NMP	MW, 195	2	(67)	547
H	I	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(99)	150
H	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(99)	150
2-MeO	I	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(60)	150
4-MeO	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(80)	150
2-Me	I	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(80)	150
4-Me	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(89)	150
3-MeO_2C	I	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(99)	150
4-MeO_2C	Br	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(75)	151
4-EtO_2C	I	10	NMG (20 mol %), K_3PO_4	DMF	100	24	(95)	150
4-Ac	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(96)	150

C_2

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (20 mol %), **L22** (20 mol %), K_2CO_3, DMF, 110°, 40 h	 (75)	151

C_3

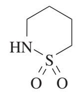
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (20 mol %), **L22** (20 mol %), K_2CO_3, DMF		151

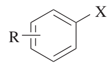
R	Temp (°)	Time (h)	
4-MeO	120	36	(40)
3-Me, 4-NH_2, 5-O_2N	110	40	(75)
4-MeO_2C	110	40	(63)

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

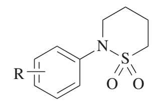
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_4



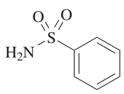


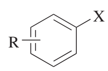
Catalyst (x mol %)



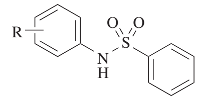
R	X	Catalyst	x	Additives	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
2-O_2N	I	Cu_2O	40	bpy (40 mol %), K_3PO_4	NMP	120	18	(44)	152
2-MeO	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(10)	151
3-MeO	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(43)	151
4-MeO	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	120	36	(43)	151
2-Me	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(14)	151
2-Me, 5-O_2N	Br	Cu_2O	40	bpy (40 mol %), K_3PO_4	NMP	120	48	(50)	152
3-Me, 4-H_2N, 5-O_2N	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(64)	151
3-NC–	Br	Cu_2O	40	bpy (40 mol %), K_3PO_4	NMP	120	24	(35)	152
4-NC–	Br	Cu_2O	40	bpy (40 mol %), K_3PO_4	NMP	120	15	(35)	152
2-MeO_2C	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(0)	151
3-MeO_2C	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(60)	151
4-EtO_2C	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	120	36	(85)	151
2,6-Me_2	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(0)	151

C_6

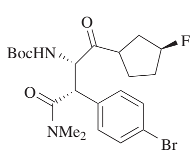




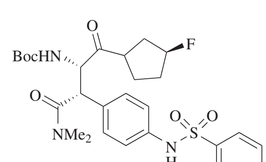
Catalyst (x mol %)



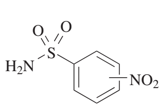
R	X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield (%)	Refs.
H	Br	CuI	10	K_2CO_3	NMP	MW, 195	3	(66)	547
H	I	CuI	10	K_2CO_3	NMP	MW, 195	3	(90)	547
H	I	CuI	10	NMG (20 mol %), K_3PO_4	DMF	100	24	(95)	150
H	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(95)	150
4-O_2N	I	CuO nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	24	(54)	74
2-MeO	I	CuI	10	NMG (20 mol %), K_3PO_4	NMP	100	24	(55)	150
3-MeO	Br	CuI	10	K_2CO_3	NMP	MW, 195	3	(90)	547
3-MeO	I	CuI	10	K_2CO_3	NMP	MW, 195	2	(83)	547
4-MeO	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(75)	150
2-Me	I	CuI	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(56)	150
4-Me	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(96)	150
4-NC–	Br	CuI	10	K_2CO_3	NMP	MW, 195	2	(88)	547
3-MeO_2C	I	CuI	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(99)	150
4-EtO_2C	I	CuI	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(99)	150
3,5-Me_2	Br	CuI	10	K_2CO_3	NMP	MW, 195	2	(81)	547
3,5-Me_2	I	CuI	10	K_2CO_3	NMP	MW, 195	3	(88)	547
4-Ac	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(91)	150
4-*t*-Bu	Br	CuI	10	K_2CO_3	NMP	MW, 195	2	(78)	547
4-*t*-Bu	I	CuI	10	K_2CO_3	NMP	MW, 195	2	(88)	547

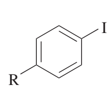


CuI (1 eq), DMEDA (3 eq), K_2CO_3, toluene, 110°, 48 h

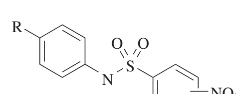


(80) 548





CuI (2 eq), Cs_2CO_3, DMSO, 90°, 18 h



Isomer	R	Yield (%)
2	H	(91)
4	EtO_2C	(82)

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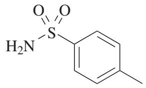
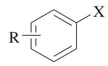
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

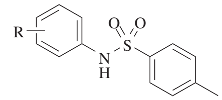
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_7

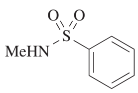


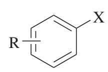


Catalyst (x mol %)

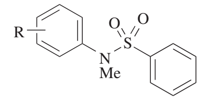


R	X	Catalyst	x	Additive(s)	Solvent(s)	Temp (°)	Time (h)	Yield	Refs.
H	Br	CuI	10	K_2CO_3	NMP	MW, 195	3	(70)	547
H	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(99)	150
H	I	CuO nanoparticles	5	KOH	*t*-BuOH/DMSO (3:1)	110	24	(45)	74
H	I	$Cu(OAc)_2$•H_2O	15	sparteine (30 mol %), K_2CO_3	DMF	130	24	(80)	290
2-MeO	I	CuI	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(76)	150
4-MeO	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(85)	150
2-Me	I	CuI	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(50)	150
4-Me	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(91)	150
3-MeO_2C	I	CuI	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(99)	150
4-EtO_2C	I	CuI	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(99)	150
4-EtO_2C	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(51)	151
4-Ac	Br	CuI	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(95)	150

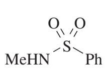
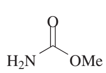


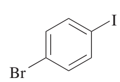


CuI (x mol %)

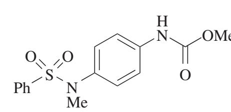


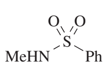
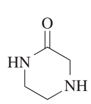
R	X	x	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
H	Br	10	K_2CO_3	NMP	MW, 195	4	(54)	547
H	I	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(82)	150
H	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(82)	150
2-MeO	I	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(trace)	150
4-MeO	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(68)	150
2-Me	I	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(trace)	150
4-Me	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(99)	150
3-MeO_2C	I	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(99)	150
4-MeO_2C	Br	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(51)	151
4-EtO_2C	I	5	NMG (20 mol %), K_3PO_4	DMF	100	24	(95)	150
4-Ac	Br	20	DMG (20 mol %), K_3PO_4	DMF	reflux	48	(90)	150

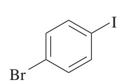
 + 



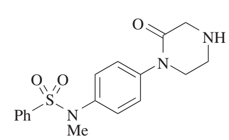
CuI (20 mol %), DMCDA (40 mol %), K_3PO_4, dioxane, 110°, 22 h

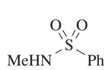
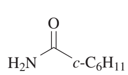
 (83) 504

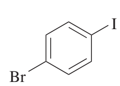
 + 



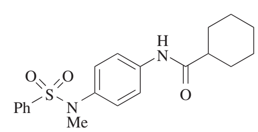
CuI (20 mol %), DMCDA (40 mol %), K_3PO_4, dioxane, 110°, 22 h

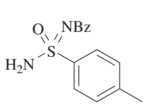
 (81) 504

 + 



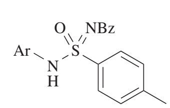
CuI (20 mol %), DMCDA (40 mol %), K_3PO_4, dioxane, 110°, 22 h

 (70) 504



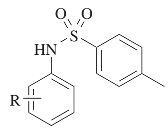
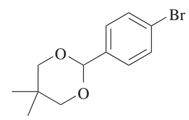
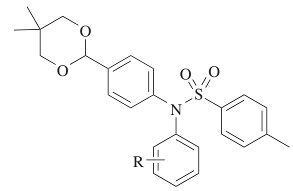
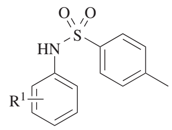
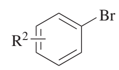
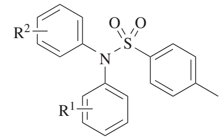
ArX

CuCl (1 eq), K_2CO_3, DMSO, 100°, 20 h



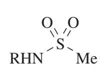
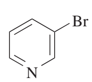
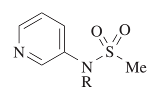
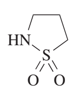
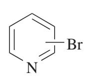
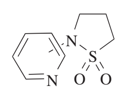
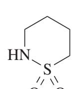
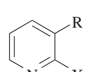
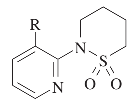
Ar	X	Yield	Refs.
Ph	I	(50)	153
4-FC_6H_4	I	(51)	
2-ClC_6H_4	I	(55)	
3-ClC_6H_4	I	(59)	
4-ClC_6H_4	I	(75)	
4-IC_6H_4	I	(65)	
4-$MeOC_6H_4$	Br	(59)	
4-$MeOC_6H_4$	I	(68)	
3-MeC_6H_4	I	(62)	
4-MeC_6H_4	I	(59)	
2-Np	I	(66)	

TABLE 23A. *N*-ARYLATION OF SULFONAMIDES AND SULFONIMIDAMIDES (*Continued*)

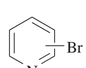
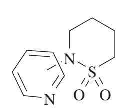
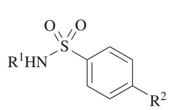
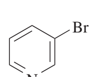
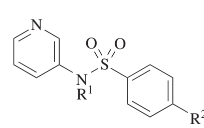
Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{13}				
		Cu (2.3 eq), K_2CO_3, reflux, 13 h	 R 2,3-$(MeO)_2$ (25) 3,4,5-$(MeO)_3$ (67)	549
C_{13-15}				
		Cu (2.3 eq), K_2CO_3, reflux, 13 h		549

R^1	R^2	
2-MeO	2,5-Me_2	(67)
4-MeO	3-Me, 5-MeO	(45)
3,5-$(MeO)_2$	2,5-Me_2	(21)
3,4-OCH_2O–	2,5-Me_2	(35)
3,4,5-$(MeO)_3$	2,5-Me_2	(12)
2,5-Me_2	H	(17)
2,5-Me_2	3-MeO	(63)
2,5-Me_2	2,5-$(MeO)_2$	(52)

TABLE 23B. *N*-HETEROARYLATION OF SULFONAMIDES

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{1-2}				
		CuI (20 mol %), **L22** (20 mol %), K_2CO_3, DMF, 110°, 40 h	 R: H (42); Me (91)	151
C_3				
		CuI (20 mol %), **L22** (20 mol %), K_2CO_3, DMF, 110°, 40 h	 Isomer: 2 (85); 3 (70); 4[a] (60)	151
C_4				
		Catalyst (*x* mol %)		

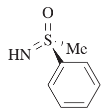
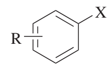
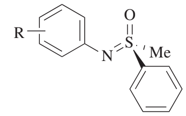
R	X	Catalyst	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	Br	CuI	20	**L22** (20 mol %), K_2CO_3	DMF	110	40	(70)	151
H	Br	Cu_2O	40	bpy (40 mol %), K_3PO_4	NMP	120	6	(93)	152
NC–	Cl	Cu_2O	40	bpy (40 mol %), K_3PO_4	NMP	120	36	(35)	152

Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (20 mol %), **L22** (20 mol %), K_2CO_3, DMF, 110°, 40 h	 Isomer: 3 (61); 4[a] (86)	151
C_{6-8}				
		CuI (20 mol %), **L22** (20 mol %), K_2CO_3, DMF, 120°, 36 h		151

R^1	R^2	
H	Cl	(55)
H	O_2N	(33)
H	MeO	(54)
H	Me	(90)
Me	Me	(99)

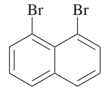
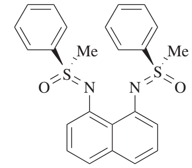
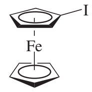
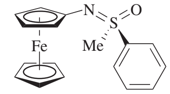
[a] The heteroaryl halide was the HCl salt.

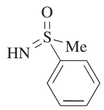
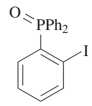
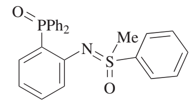
TABLE 24A. *N*-ARYLATION OF SULFOXIMINES

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		Catalyst (*x* amount)		

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
H	Br	CuI	10 mol %	DMEDA (20 mol %), NaI, Cs_2CO_3	dioxane	110	22	(93)	159
H	I	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(95)	159
H	Br	Cu_2O	10 mol %	Cs_2CO_3	DMF	110	18	(89)	221
H	I	Cu_2O	10 mol %	Cs_2CO_3	DMF	100	18	(95)	221
2-F	I	CuI	10 mol %	DMEDA (20 mol %), NaI, Cs_2CO_3	dioxane	110	22	(86)	159
2,4,6-Cl_3	I	CuI	1 eq	CsOAc	DMSO	90	—	(85)	158
2,4,6-Cl_3	I	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(93)	159
2-Br	I	CuI	1 eq	Cs_2CO_3	DMSO	90	—	(68)	158
2-AcNH, 3-O_2N	I	CuI	1 eq	Cs_2CO_3	DMSO	90	—	(48)	158
2-AcNH, 5-O_2N	Br	CuI	1 eq	Cs_2CO_3	DMSO	90	—	(65)	158
2-O_2N	Br	CuI	1 eq	CsOAc	DMSO	90	—	(78)	158
2-O_2N	I	CuI	1 eq	CsOAc	DMSO	90	—	(83)	158
2-O_2N	I	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(93)	159
2-O_2N, 4-F	I	CuI	1 eq	CsOAc	DMSO	90	—	(95)	158
2-O_2N, 4-MeO	I	CuI	1 eq	CsOAc	DMSO	90	—	(80)	158
2-O_2N, 4-CF_3	Br	CuI	1 eq	CsOAc	DMSO	90	—	(83)	158
3-O_2N	I	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(98)	159
4-O_2N	I	CuI	1 eq	Cs_2CO_3	DMSO	90	—	(82)	158
4-O_2N	I	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(92)	159
2-MeO	I	CuI	1 eq	Cs_2CO_3	DMSO	90	—	(72)	158
2-MeO	Br	CuI	10 mol %	DMEDA (20 mol %), NaI, Cs_2CO_3	dioxane	110	22	(97)	159
2-MeO	I	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(99)	159
4-MeO	Br	CuI	10 mol %	DMEDA (20 mol %), NaI, Cs_2CO_3	dioxane	110	22	(84)	159

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
2-Me	I	CuI	1 eq	Cs_2CO_3	DMSO	90	—	(84)	158
2-Me	Br	CuI	10 mol %	DMEDA (20 mol %), NaI, Cs_2CO_3	dioxane	110	22	(93)	159
4-Me	I	CuI	1 eq	Cs_2CO_3	DMSO	90	—	(93)	158
4-Me	I	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(95)	159
3-NC–	I	CuI	1 eq	CsOAc	DMSO	90	—	(94)	158
3-NC–	I	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(99)	159
4-CHO	I	CuI	1 eq	Cs_2CO_3	DMSO	90	—	(85)	158
4-EtO_2C	I	CuI	1 eq	Cs_2CO_3	DMSO	90	—	(88)	158
4-EtO_2C	I	CuI	10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(92)	159
3,5-Me_2	Br	CuI	10 mol %	DMEDA (20 mol %), NaI, Cs_2CO_3	dioxane	110	22	(82)	159

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (2 eq), CsOAc, DMSO, 90°	 (56)	158
		CuI (1 eq), K_2CO_3, DMSO, 90°, 18 h	 (80)	372

Nitrogen Nucleophile	Aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7  (racemic)		CuI (*x* amount)		

x	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
1 eq	CsOAc	DMSO	90	—	(71)	158
10 mol %	DMEDA (20 mol %), Cs_2CO_3	toluene	110	22	(86)	159

TABLE 24B. *N*-HETEROARYLATION OF SULFOXIMINES

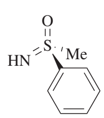
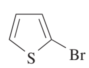
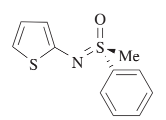
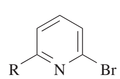
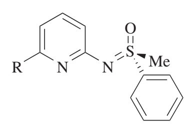
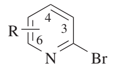
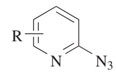
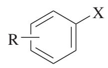
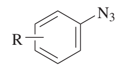
Nitrogen Nucleophile	Heteroaryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CuI (10 mol %), DMEDA (20 mol %), NaI, Cs_2CO_3, dioxane, 110°, 22 h	 (89)	159
		CuI (10 mol %), DMEDA (20 mol %), NaI, Cs_2CO_3, dioxane, 110°, 22 h	 R: H (96), Me (97)	159

TABLE 25. PREPARATION OF ARYL AND HETEROARYL AZIDES

(Hetero)aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-6} 	NaN_3, CuBr (10 mol %), DMEDA (20 mol %), Cs_2CO_3, DMSO, 90°	 R / Time (h): 5-$K^+ F_3B^-$ 1 (98); 3-Me, 5-$K^+ F_3B^-$ 1 (95); 6-$K^+ F_3B^-$ 3 (98)	247
C_{6-8} 	NaN_3, catalyst (*x* mol %)		

R	X	Catalyst	*x*	Additives	Solvent(s)	Temp (°)	Time		Refs.
H	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	20 min	(96)	154
H	Br	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	10 h	(93)	155
H	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	5 h	(92)	155
H	I	$CuSO_4$•H_2O	20	L-Pro (20 mol %), Na ascorbate, Na_2CO_3	DMSO/H_2O (9:1)	70	24 h	(92)	75
2-$K^+ F_3B^-$	Br	CuBr	10	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	24 h	(73)	247
3-$K^+ F_3B^-$	Br	CuBr	10	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	9 h	(90)	247
3-$K^+ F_3B^-$	I	CuBr	10	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	5 h	(93)	247
4-$K^+ F_3B^-$	Br	CuBr	10	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	7 h	(95)	247
4-$K^+ F_3B^-$	I	CuBr	10	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	1 h	(95)	247
2-F	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	24 h	(82)	155
3-F	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	10 h	(85)	155
4-Cl	Br	CuI	10	L-Pro (20 mol %), NaOH	DMSO	95	24 h	(91)	155
4-Cl	Br	CuI	10	L-Pro (20 mol %), NaOH	EtOH/H_2O	95	24 h	(90)	336
4-Cl	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	20 min	(84)	154
3-Br	I	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	30 min	(77)	154
4-Br	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	10 h	(82)	155
3-H_2N	Br	CuI	10	L-Pro (20 mol %), NaOH	DMSO	95	24 h	(77)	155
4-H_2N	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	10 h	(77)	155
3-HO	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	30 min	(99)	154
4-HO	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	40 min	(99)	154
4-HO	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	10 h	(87)	155
2-MeO	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	24 h	(67)	155
2,4-$(MeO)_2$	Br	CuI	10	L-Pro (20 mol %), NaOH	DMSO	95	30 h	(70)	155
3-MeO	Br	CuI	10	L-Pro (20 mol %), NaOH	DMSO	95	24 h	(92)	155

R	X	Catalyst	*x*	Additives	Solvent(s)	Temp (°)	Time		Refs.
3-MeO	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	40 min	(95)	154
3-$K^+ F_3B^-$, 5-MeO	Br	CuBr	10	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	4 h	(92)	247
4-MeO	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	5 h	(92)	155
4-MeO	Br	CuI	10	L-Pro (20 mol %), NaOH	DMSO	95	10 h	(93)	155
4-MeO	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	20 min	(90)	154
2-Me	Br	CuI	10	L-Pro (20 mol %), NaOH	DMSO	95	24 h	(90)	155
3-Me, 4-H_2N	I	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	50 min	(99)	154
3-$K^+ F_3B^-$, 5-Me	Br	CuBr	10	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	8 h	(93)	247
4-Me	Br	CuI	10	L-Pro (20 mol %), NaOH	DMSO	95	10 h	(91)	155
4-Me	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	5 h	(92)	155
4-Me	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	10 min	(89)	154
4-Me	I	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	15 nin	(91)	154
3-H_2N, 4-Me	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	30 min	(90)	154
4-$HOCH_2$	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	24 h	(81)	155
4-$HOCH_2$	I	CuI	10	DMEDA, Na ascorbate	EtOH/H_2O (7:3)	MW, 100	40 min	(81)	550
2-HO_2C	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	7 h	(58)	155
2-HO_2C	I	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	1 h	(84)	154
2-MeO_2C	I	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	15 min	(91)	154
3-HO_2C	Br	CuI	10	L-Pro (20 mol %), NaOH	DMSO	95	30 h	(66)	155
3-HO_2C	I	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	1 h	(99)	154
3,5-Me_2	I	CuI	10	L-Pro (20 mol %), NaOH	DMSO	60	5 h	(92)	155
2,5-Me, 4-$K^+ F_3B^-$	Br	CuBr	10	DMEDA (20 mol %), Cs_2CO_3	DMSO	90	12 h	(90)	247
3-Me, 4-HO_2C	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	1 h	(82)	154
3-Ac	Br	CuI	10	DMCDA (15 mol %), Na ascorbate	EtOH/H_2O (7:3)	reflux	30 min	(88)	154

TABLE 25. PREPARATION OF ARYL AND HETEROARYL AZIDES (*Continued*)

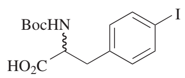
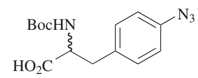
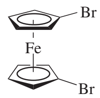
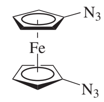
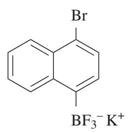
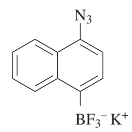
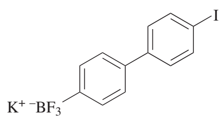
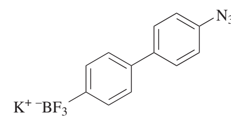
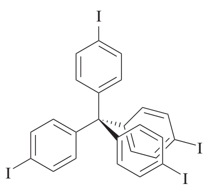
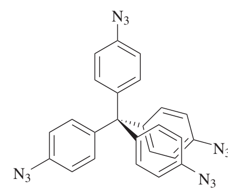
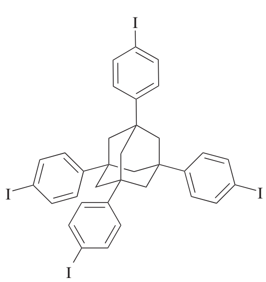
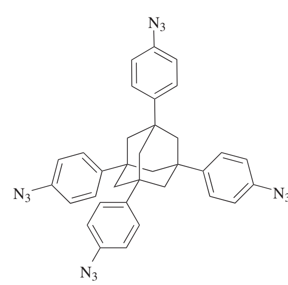
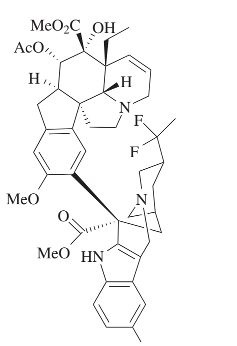
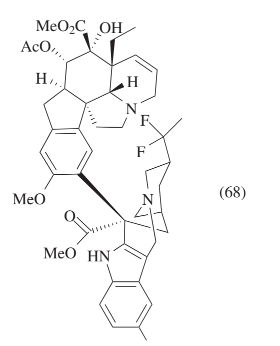
(Hetero)aryl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	NaN_3, CuI (10 mol %), L-Pro (20 mol %), NaOH, DMSO, 60°, 5 h	 Config. (*R*) (91); (*S*) (91)	155
C_{10}			
	NaN_3, CuCl (1 eq), EtOH/H_2O (9:1), rt, 48 h	 (59)	551
	NaN_3, CuBr (10 mol %), DMEDA (20 mol %), Cs_2CO_3, DMSO, 90°, 4 h	 (92)	247
C_{12}			
	NaN_3, CuBr (10 mol %), DMEDA (20 mol %), Cs_2CO_3, DMSO, 90°, 5 min	 (96)	247
C_{25}			
	NaN_3, CuI (80 mol %), DMEDA (1.2 eq), Na ascorbate, DMSO/H_2O (5:1), 100°, 48 h	 (65)	552
C_{34}			
	NaN_3, CuI (80 mol %), DMEDA (1.2 eq), Na ascorbate, DMSO/H_2O (5:1), 100°, 48 h	 (34)	552
C_{41}			
	NaN_3, CuI, L-Pro, NaOH, DMSO	 (68)	553

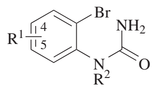
TABLE 26. INTRAMOLECULAR ARYLATIONS

A. SYNTHESIS OF FIVE-MEMBERED NITROGEN HETEROCYCLES

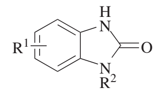
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{7-8}

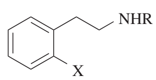


CuI (8.5 mol %), TMEDA (3.5 eq), H_2O, 120°, 15 h

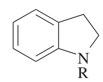


R^1	R^2		Refs.
H	Et	(71)	554
H	allyl	(71)	
H	*n*-Bu	(60)	
H	Ph	(69)	
H	$4\text{-}ClC_6H_4$	(71)	
H	Bn	(87)	
H	$4\text{-}FC_6H_4CH_2$	(62)	
H	$3\text{-}MeOC_6H_4CH_2$	(78)	
H	$4\text{-}MeOC_6H_4CH_2$	(74)	
H	$2\text{-}NpCH_2$	(72)	
4-F	Ph	(60)	
4-F	Bn	(74)	
$4,6\text{-}F_2$	Bn	(51)	
$5\text{-}O_2N$	Bn	(79)	
4-MeO	Bn	(87)	
4-Me	Bn	(76)	
4-Me	$4\text{-}FC_6H_4CH_2$	(92)	
$4\text{-}CF_3$	*n*-Bu	(80)	
$4\text{-}CF_3$	Ph	(54)	

C_{8-15}

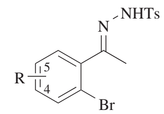
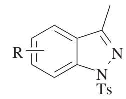
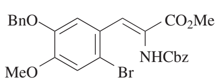
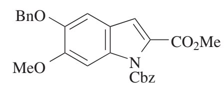
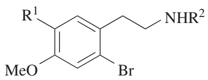
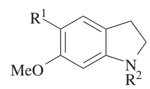
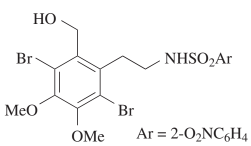
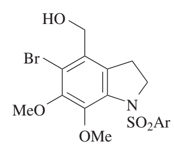
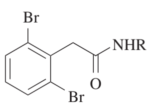
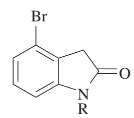
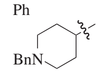
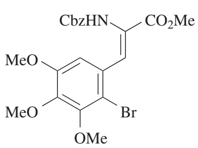
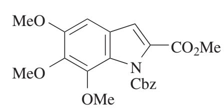
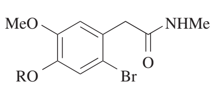
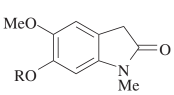
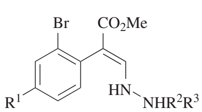
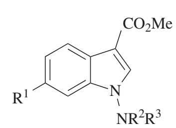


Catalyst (*x* amount)



R	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	Br	CuI	2 eq	CsOAc	DMSO	rt	1	(47)	197
H	I	CuI	2 eq	CsOAc	DMSO	rt	1	(44)	197
H	Br	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	rt	1	(47)	274
H	Cl	CuI	10 mol %	L-proline (20 mol %), K_2CO_3	DMSO	70	45	(71)	47
H	I	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	rt	1	(44)	274

R	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	Br	CuI	2 mol %	**L1** (2 mol %), KO*t*-Bu	—	100	12	(99)	288
H	Cl	CuI	5 mol %	**L16** (20 mol %), Cs_2CO_3	DMF	rt	0.5	(90)	52
H	Br	CuI	5 mol %	**L16** (20 mol %), Cs_2CO_3	DMF	rt	0.5	(90)	182
H	Br	CuOAc	5 mol %	**L13** (20 mol %), K_3PO_4	DMF	35	12	(88)	120
H	Br	$Cu(acac)_2$	10 mol %	Fe_2O_3 (20 mol %), Cs_2CO_3	$DMSO/H_2O$	MW, 150	0.5	(52)	262
CHO	Cl	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	H_2O	100	—	(88)	69
CHO	Br	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	H_2O	rt	—	(100)	69
Ac	Br	CuI	2 eq	CsOAc	DMSO	90	24	(66)	197
Ac	I	CuI	2 eq	CsOAc	DMSO	90	24	(96)	197
Ac	Br	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	24	(82)	274
Ac	I	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	24	(96)	274
Boc	Br	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	24	(82)	274
Boc	I	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	24	(93)	274
$CH_2{=}CHCH_2O_2C$	Br	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	24	(75)	274
$CH_2{=}CHCH_2O_2C$	I	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	24	(81)	274
$2\text{-}O_2NC_6H_4SO_2$	Br	CuI	2 eq	CsOAc	DMSO	90	1	(92)	197
$2\text{-}O_2NC_6H_4SO_2$	I	CuI	2 eq	CsOAc	DMSO	90	24	(90)	197
$2\text{-}O_2NC_6H_4SO_2$	Br	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	24	(92)	274
$2\text{-}O_2NC_6H_4SO_2$	I	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	1	(87)	274
$2\text{-}O_2NC_6H_4SO_2$	Br	CuI	1 mol %	CsOAc	DMSO	90	24	(97)	274
Bn	Br	CuI	2 eq	CsOAc	DMSO	rt	4	(87)	197
Bn	Br	CuI	5 mol %	CsOAc	DMSO	90	24	(83)	274
Bn	Br	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	rt	5	(87)	274
Cbz	Br	CuI	2 eq	CsOAc	DMSO	90	24	(64)	197
Cbz	I	CuI	2 eq	CsOAc	DMSO	90	24	(95)	197
Cbz	Br	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	24	(77)	274
Cbz	I	CuI	5 mol %	DMEDA (10 mol %), Cs_2CO_3	DMSO	90	24	(95)	274

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_8			
	CuI (10 mol %), DMEDA (30 mol %), Na_2CO_3, EtOH/H_2O (1:1), rt, 10 min	 R: H (98); 5-MeO (98); 4,5-$(MeO)_2$ (99); 4-$O(CH_2)_2O$-5 (98)	555
C_9			
	CuI (5 mol %), Cs_2CO_3, DMSO, 90°, 24 h	 (80)	556
C_{9-10}			
	CuI (1 eq), NaH, DMF, 80°, 12 h	 R^1, R^2: H, Ac (52); MeO, CO_2Me (66); MeO, Ac (74)	557
C_9			
 Ar = 2-$O_2NC_6H_4$	CuI (10 mol %), CsOAc, DMSO, 80°, 24 h	 (95)	556
C_{9-20}			
	CuCl (10 mol %), acac (25 mol %), K_2CO_3, NMP, 85°	 R, Time (h): Me, 1 (84); *t*-Bu, 22 (83); 4-pyridyl, 1 (66); Ph, 1 (83); , 3.5 (55)	558
C_9			
	CuI (1.5 eq), CsOAc, DMSO, rt, 24 h	 (98)	559
	CuI (1 eq), NaH, DMF, 80°, 12 h	 R: Me (63); Bn (73)	557
	CuI (5 mol %), K_3PO_4		

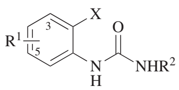
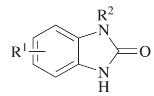
R^1	R^2	R^3	Solvent	Temp (°)	Time (h)		Refs.
H	Boc	H	DMF	85	2	(0)	560
H	Boc	Boc	DMF	85	2	(0)	560
H	Me	Me	DMF	85	2	(82)	560
H	*c*-C_3H_7	H	$HOCH_2CH_2OH$	75	4	(78)	561
H	*t*-Bu	H	DMF	75	20	(32)	561
H	*c*-C_6H_{11}	H	DMF	75	20	(57)	561
H	Ph	H	DMF	85	2	(0)	560
H	Ph	Boc	DMF	85	2	(78)	560
H	4-$MeOC_6H_4$	H	$HOCH_2CH_2OH$	75	4	(94)	561
H	2-MeC_6H_4	H	DMF	75	9	(65)	561
H	3-$CF_3C_6H_4$	H	$HOCH_2CH_2OH$	75	4	(74)	561
H	Bn	H	$HOCH_2CH_2OH$	75	4	(91)	561
H	3-$MeC_6H_4CH_2$	H	DMF	85	2	(68)	560
H	(*R*)-PhMeCH	H	DMF	75	9	(68)	561
H	$PhCH_2CH_2$	H	$HOCH_2CH_2OH$	75	6	(80)	561
H	2,4,6-$Me_3C_6H_2$	H	DMF	75	6	(77)	561
MeO	2-$ClC_6H_4CH_2$	Boc	DMF	85	2	(86)	560
MeO	3-$MeC_6H_4CH_2$	H	DMF	85	2	(65)	560

TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)
A. SYNTHESIS OF FIVE-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

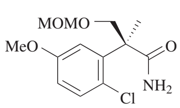
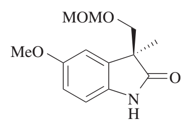
C_{10-15}

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	CuI (20 mol %), DBU, DMSO, MW, 20 min		562

R^1	R^2	X	Additve	Temp (°)	
H	allyl	I	none	140	(60)
H	2-thiazolyl	I	none	120	(72)
H	*i*-Bu	Br	L-Pro (50 mol %)	140	(65)
H	*i*-Bu	I	none	140	(71)
H	4-pyridyl	I	none	120	(83)
H	4-BrC_6H_4	I	none	120	(92)
H	2-MeOC_6H_4	I	none	120	(93)
H	4-MeOC_6H_4	I	none	120	(95)
H	4-MeC_6H_4	Br	L-Pro (50 mol %)	120	(79)
H	4-Me	I	none	120	(90)
H	$2\text{-CF}_3C_6H_4$	I	none	120	(89)
H	$4\text{-CF}_3C_6H_4$	Br	L-Pro (50 mol %)	120	(79)
H	$4\text{-CF}_3C_6H_4$	I	none	120	(93)

R^1	R^2	X	Additive	Temp (°)	
H	3-NC–	I	none	120	(89)
H	4-EtO_2C	I	none	120	(81)
H	4-ethenyl	Br	L-Pro (50 mol %)	120	(77)
H	4-ethenyl	I	none	120	(86)
H	3-ethynyl	Br	L-Pro (50 mol %)	120	(73)
H	3-ethynyl	I	none	120	(85)
H	$4\text{-FC}_6H_4CH_2$	I	none	140	(85)
H	$n\text{-C}_8H_{17}$	I	none	140	(59)
5-F	4-pyridyl	I	none	120	(81)
4-Cl, 6-F	*i*-Bu	I	none	120	(66)
4-Cl, 6-F	4-FC_6H_4	I	none	120	(77)
5-MeO	Bn	I	none	120	(70)
3-CF_3	4-FC_6H_4	I	none	120	(73)
4-MeO_2C	4-FC_6H_4	I	none	120	(75)

C_{10}

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	CuI (50 mol %), DMEDA (1 eq), K_2CO_3, DMF, reflux, 12 h	 (96)	563

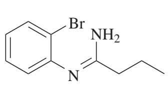
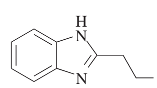
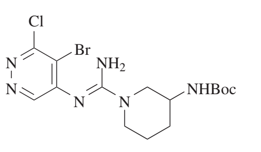
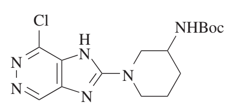
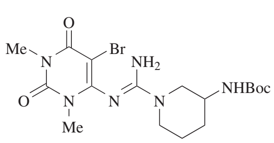
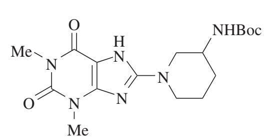
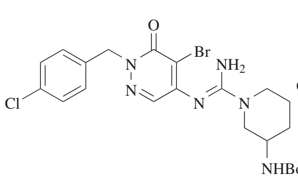
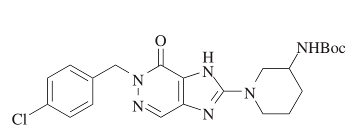
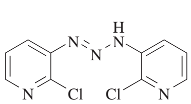
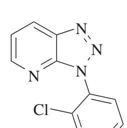
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	CuI (50 mol %), NaH, THF, reflux, 1 h	 (37)	139
	CuI (50 mol %), NaH, THF, reflux, 1 h	 (73)	139
	CuI (50 mol %), NaH, THF, reflux, 1 h	 (77)	139
	CuI (50 mol %), NaH, THF, reflux, 1 h	 (81)	139
	CuI (10 mol %), K_2CO_3, PEG, H_2O, 110°, 6.5 h	 (84)	564

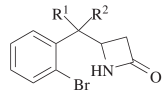
TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

A. SYNTHESIS OF FIVE-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

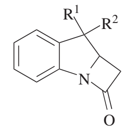
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{10-12}

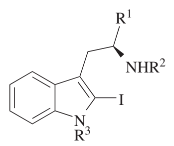


Catalyst (5 eq)

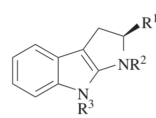


R^1	R^2	Catalyst	Solvent	Temp (°)	Time		Refs.
H	H	Cu	DMF	135	8 h	(8)	565
H	H	Cu (active)	—	MW (100 W)	6 min	(69)	280
EtO_2C	H	Cu (active)	—	MW (100 W)	8 min	(78)	280
BnO_2C	H	Cu	DMF	135	8 h	(19)	565
BnO_2C	BnO_2C	Cu	DMF	135	8 h	(23)	565
BnO_2C	BnO_2C	Cu (active)	—	MW (100 W)	6 min	(69)	280

C_{10-11}



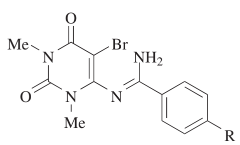
CuI (10 mol %), DMEDA (20 mol %), K_3PO_4, toluene, 110°, 16 h



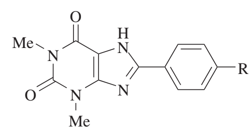
R^1	R^2	R^3	
H	Boc	Ac	(50)
$TBSOCH_2$	Boc	Ac	(51)
MeO_2C	Ac	Boc	(98)
MeO_2C	Boc	Ac	(87)
MeO_2C	Cbz	H	(85)
MeO_2C	Cbz	Ac	(93)
MeO_2C	Cbz	Boc	(73)
BnO_2C	Boc	Boc	(62)

566

C_{11}

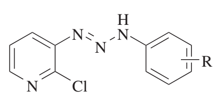


CuI (50 mol %), NaH, THF, reflux, 1 h

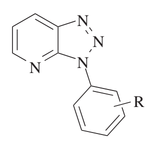


R	
H	(82)
Br	(53)

139



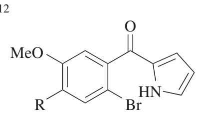
CuI (10 mol %), K_2CO_3, PEG, H_2O, 110°, 6 h



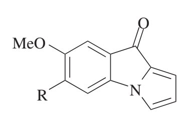
R	Time (h)	
4-Cl	6	(88)
2,4-Cl_2	6	(88)
4-O_2N	6.5	(75)
4-Me	6	(86)

564

C_{11-12}



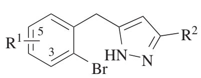
CuBr (1.3 eq), NaOH, H_2O, DMF, rt, 3 h



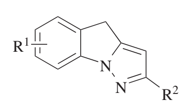
R	
MeO	(52)
Me	(53)

567

C_{11-20}



CuI (5 mol %), phen (10 mol %), K_2CO_3, dioxane, 110°, 20 h



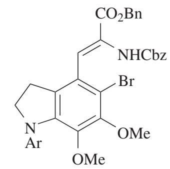
R^1	R^2	
H	Me	(89)
H	Ph	(98)
H	4-$O_2NC_6H_4$	(97)
H	4-$MeOC_6H_4$	(86)
5-F	Ph	(95)
5-Cl	Ph	(83)
5-MeO	Ph	(96)
3-$(CH{=}CH)_2$–4	Ph	(45)

568

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

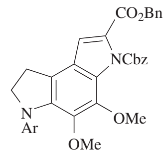
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{11}



Ar = 2-$O_2NC_6H_4$

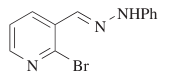
CuI (1 eq), CsOAc, DMSO, rt, 12 h



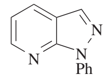
(77)

569, 556

C_{12}

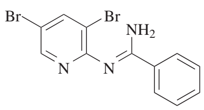


CuI (5 mol %), phen (10 mol %), KOH, dioxane, 100°, 5 h

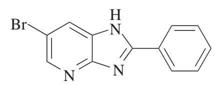


(71)

570



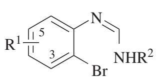
CuI (50 mol %), NaH, THF, reflux, 1 h



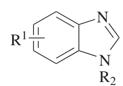
(73)

139

$C_{12–21}$



CuI (20 mol %), DBU, DMSO, 120°

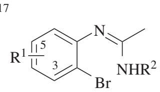


571

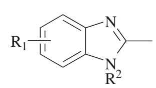
R^1	R^2	Temp (°)	Time	
H	2-pyridyl	120	1 h	(87)
H	2-BrC_6H_4	110	1.3 h	(99)
H	2,4,6-$Me_3C_6H_2$	120	4.5 h	(85)
H	2,6-(i-Pr)$_2C_6H_3$	120	5 h	(96)
H	1-adamantyl	140	6 h	(95)
H	9-anthracenyl	120	2 h	(92)
4-Cl	2,4-$Cl_2C_6H_4$	120	190 h	(53)
4,6-Cl_2	2,4,6-$Cl_3C_6H_2$	120	171 h	(49)

R^1	R^2	Temp (°)	Time	
4,6-Br_2	2,4,6-$Br_3C_6H_2$	120	70 min	(93)
4,6-Br_2	2,4,6-$Me_3C_6H_2$	120	75 min	(98)
5-CF_3	2-Br-5-$CF_3C_6H_3$	120	75 min	(92)
3,5-Me_2	2-Br-3,5-$Me_2C_6H_2$	120	23 h	(93)
4,6-Me_2	2-t-BuC_6H_4	120	96.5 h	(85)
4,6-Me_2	2-Br-4,6-$Me_2C_6H_2$	120	70 min	(97)
4,6-Me_2	2,4,6-$Me_3C_6H_2$	120	90 min	(99)
3,5-Me_2, 4-Br	2,4-Br_2-3,5-Me_2C_6H	120	24 h	(99)

$C_{12–17}$



CuO nanoparticles (5 mol %), KOH, DMSO, 110°

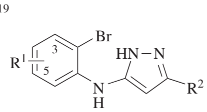


572

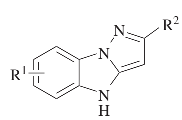
R^1	R^2	Time (h)	
H	n-Bu	5	(83)
H	Ph	4	(94)
H	Bn	6	(95)
H	2,4-$(MeO)_2C_6H_4CH_2$	6	(82)
4-Cl	Bn	4	(92)
4-Cl, 6-Br	Ph	4	(94)
4-MeO	Bn	3	(93)

R^1	R^2	Time (h)	
4-Me	c-C_6H_{11}	16	(91)
4-Me	Ph	5	(95)
4-Me	Bn	8	(93)
4,5-Me_2	Ph	24	(93)
4,5-Me_2	Bn	13	(92)
4,6-Me_2	Ph	4	(90)
4,6-Me_2	Bn	15	(88)

$C_{12–19}$



CuI (10 mol %), L-Pro (20 mol %), NaH, DMF, 90°

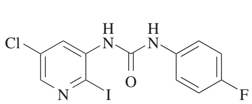


573

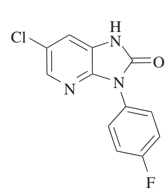
R^1	R^2	Time (h)	
H	2-furyl	1.5	(94)
H	2-thienyl	2.5	(80)
H	2-pyridyl	0.5	(78)
H	4-ClC_6H_4	1.5	(73)
H	4-$MeOC_6H_4$	1	(84)
4-F	4-FC_6H_4	1	(53)

R^1	R^2	Time (h)	
4-MeO	Ph	1.5	(0)
4,5-$(MeO)_2$	i-Pr	0.75	(81)
4-Me	Ph	1.25	(83)
4-i-Pr	4-pyridyl	2.5	(80)
4-i-Pr	4-$CF_3C_6H_4$	1	(84)

C_{12}



CuI (20 mol %), DBU, DMSO, MW, 120°, 40 min



(54)

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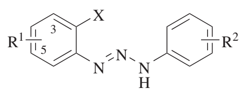
TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

A. SYNTHESIS OF FIVE-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

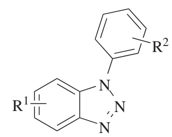
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{12-13}



CuI (10 mol %), K_2CO_3, PEG, H_2O, 110°, 2.5 h

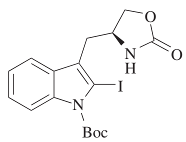


564

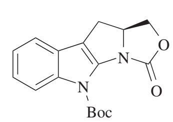
R^1	R^2	X	Time (h)	
H	H	I	2.5	(92)
H	2,5-Cl_2	Br	3	(90)
H	2-Br	I	2.5	(90)
H	2-I	I	2.5	(92)
H	3-O_2N	I	3	(89)
H	4-Me	I	2.5	(92)
5-Cl	2,4-Cl_2	Br	3	(91)

R^1	R^2	X	Time (h)	
4-Cl	4-Me	I	2.5	(92)
5-Cl	2-O_2N	Cl	6	(82)
5-Cl	3-O_2N	Cl	6	(84)
5-Cl	4-O_2N	Cl	6.5	(84)
4-Me	4-Cl	Br	2.5	(92)
4-Me	2,4-Cl_2	Br	3	(91)

C_{12}

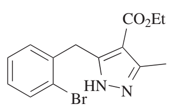


CuI (10 mol %), CDA (20 mol %), K_3PO_4, toluene, 110°, 16 h

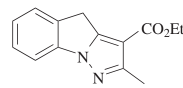


(55)

566



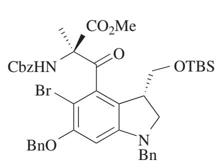
1. CuI (5 mol %), DMG (20 mol %), K_2CO_3, MeCN, reflux, 12 h
2. HCl



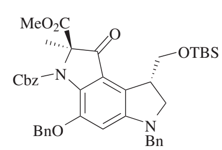
(82)

568

C_{13}



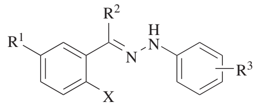
CuI (2 eq), CsOAc, DMSO, rt, 8 h



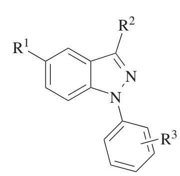
(100)

559

C_{13-14}



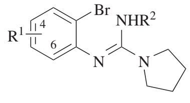
CuI (5 mol %), phen (10 mol %), KOH, dioxane, 100°, 5 h



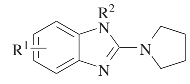
570

R^1	X	R^2	R^3	
H	Cl	H	H	(10)
H	Br	H	H	(82)
H	Br	H	4-F	(70)
H	Br	H	4-O_2N	(85)
H	Br	H	4-MeO	(80)
H	Br	H	4-Me	(90)
H	Br	Me	H	(71)
F	Br	H	H	(77)
MeO	Br	H	H	(63)

C_{13-18}



CuO nanoparticles (5 mol %), KOH, DMSO, 110°



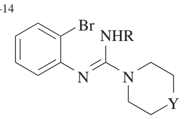
572

R^1	R^2	Time (h)	
H	Ph	5	(95)
H	2-$MeOC_6H_4$	5	(88)
H	4-$MeOC_6H_4$	5	(78)
H	4-MeC_6H_4	4	(93)
H	Bn	4	(93)
H	2,4-$Me_2C_6H_4$	5	(83)
H	2,6-$Me_2C_6H_4$	5	(80)
H	3,5-$Me_2C_6H_4$	4	(93)
4-Me	Bn	14	(89)
4,6-Me_2	Bn	12	(90)

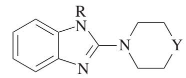
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{13-14}



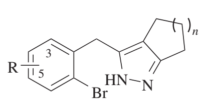
CuO nanoparticles (5 mol %), KOH, DMSO, 110°



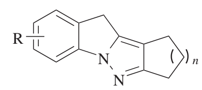
R	Y	Time (h)	
Ph	BocN	4	(90)
Bn	O	18	(88)

572

C_{13-18}



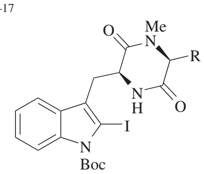
CuI (5 mol %), phen (10 mol %), K_2CO_3, dioxane, 110°, 20 h



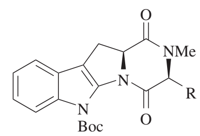
R	*n*	
H	1	(89)
H	2	(91)
H	3	(78)
5-F	2	(77)
5-Cl	2	(81)
3-Me	2	(88)
3-(CH=CH)$_2$-4	2	(44)

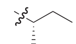
568

C_{13-17}



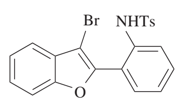
CuI (10 mol %), CDA (20 mol %), K_3PO_4, toluene, 110°, 16 h



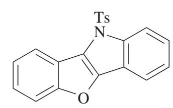
R	
H	(40)
i-Bu	(40)
	(65)

566

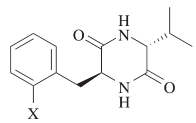
C_{14}



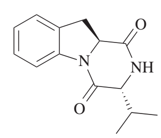
CuI (8.5 mol %), DMEDA (3.5 eq), H_2O, 120°

 (85)

575



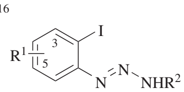
CuI (1 eq), CsOAc, DMSO, 90°, 12 h



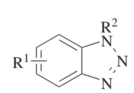
Config.	X	
(3*S*,6*R*)	Br	(84)
(3*S*,6*R*)	I	(99)
(3*R*,6*R*)	Br	(13)

576

C_{14-16}



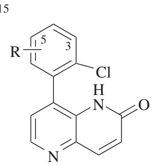
CuI (10 mol %), K_2CO_3, PEG, H_2O, 110°, 3 h



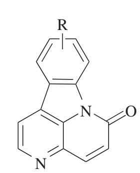
R^1	R^2	Time (h)	
H	3-quinolyl	3	(82)
H	6-quinolyl	3	(75)
5-Cl	3-quinolyl	2.5	(88)
4-Me	Bn	2.5	(92)
4-Me	3-quinolyl	3	(90)

564

C_{14-15}



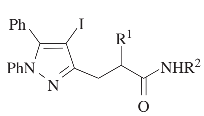
CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, H_2O, dioxane, reflux, 1 h



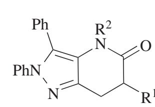
R	
H	(99)
4-Cl	(96)
5-Cl	(97)
6-Cl	(94)
3-MeO	(91)
5-MeO	(98)
4-CF$_3$	(99)

185

C_{15-16}



CuI (20 mol %), EDA (40 mol %), Cs_2CO_3, DMF, 100°



R^1	R^2	Time (h)	
H	*i*-Pr	24	(69)
H	*c*-Pr	24	(69)
Me	*i*-Pr	48	(49)
Me	*c*-Pr	48	(78)

577

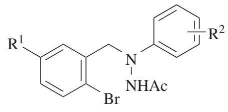
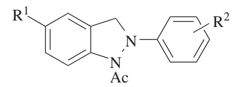
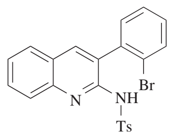
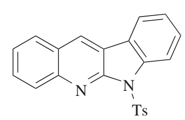
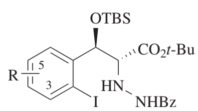
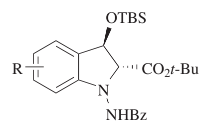
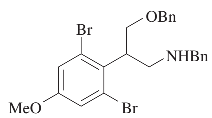
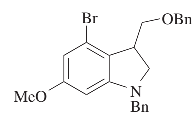
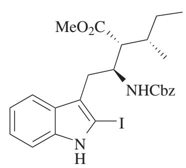
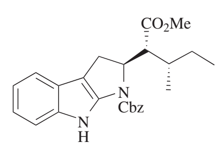
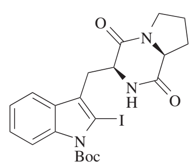
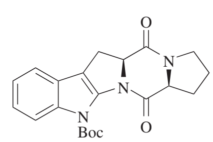
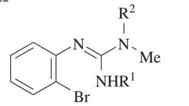
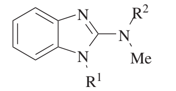
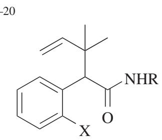
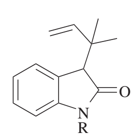
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{15-16}			
	CuI (5 mol %), Cs_2CO_3, 105°, 20 h	 R^1 / R^2 H / H (95) H / 4-F (98) H / 4-Cl (95) H / 4-MeO (85) H / 4-Me (92) H / 3-CF_3 (81) H / 3-NC– (96) F / H (89) MeO / H (85)	578
C_{15}			
	CuI (5 eq), NaH, diglyme, rt, 30 min	 (86)	579
C_{16-17}			
	CuI (10 mol %), DMEDA (10 mol %), Cs_2CO_3, DMSO, rt, 10 min	 R 6-F (71) 4-Cl (71) 4,5-$(MeO)_2$ (70) 3-Me (29)	580
C_{16}			
	CuI (2 eq), CsOAc, DMF, rt, 20 min	 (60)	274
	CuI (10 mol %), DMEDA (20 mol %), K_3PO_4, toluene, 110°, 16 h	 (67)	566
	CuI (10 mol %), CDA (20 mol %), K_3PO_4, toluene, 110°, 16 h	 (81)	566
C_{17-22}			
	CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DME, 80°, 16 h	 R^1 / R^2 Ph / Bn (83) Bn / $NC(CH_2)_2$ (87) Bn / (*S*)-PhMeCH (97)	581
C_{17-20}			
	Cu(phen)(PPh_3)Br (10 mol %), K_3PO_4, toluene, 115°, 72 h	 R / X *n*-Bu / Br (53) *n*-Bu / I (75) *i*-Pr / Br (18) *i*-Pr / I (79) *n*-C_5H_{11} / Br (43) *n*-C_5H_{11} / I (85) Ph / I (78) Bn / Br (78) Bn / I (87)	582

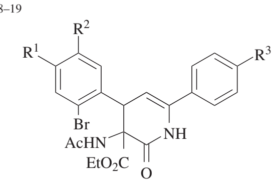
TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

A. SYNTHESIS OF FIVE-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

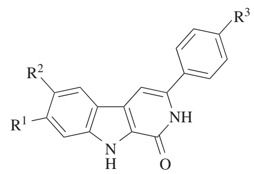
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{18-19}



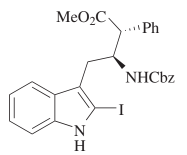
1. CuCl (2 eq), NaH, DME, 90°, 2 h
2. aq NH_4OH



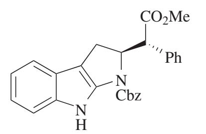
R^1	R^2	R^3	
H	H	H	(68)
H	H	Cl	(67)
H	H	Me	(70)
MeO	MeO	H	(65)
MeO	MeO	Cl	(77)
MeO	MeO	Me	(60)
—OCH_2O—		H	(60)
—OCH_2O—		Cl	(64)
—OCH_2O—		Me	(64)

583

C_{18}

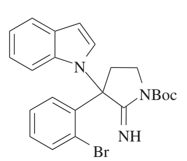


CuI (10 mol %), DMEDA (20 mol %), K_3PO_4, toluene, 110°, 16 h

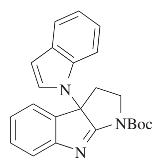


(45)

566



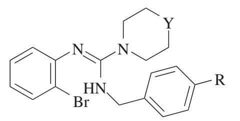
CuI (1 eq), K_3PO_4, DMSO, 80°, 1.5 h



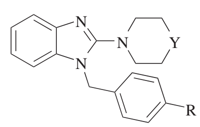
(91)

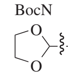
169

C_{18-19}



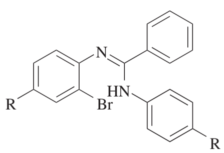
CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DME, 80°, 16 h



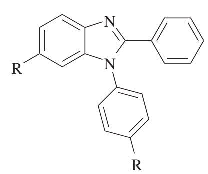
R	Y	
MeO	BocN	(97)
H		(96)

581

C_{19-21}



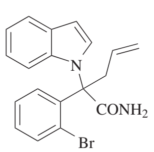
CuO nanoparticles (5 mol %), KOH, DMSO, 110°, 3 h



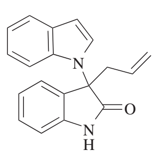
R	
H	(97)
Me	(96)

572

C_{19}



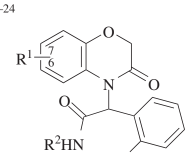
CuI (1 eq), Cs_2CO_3, DMSO, 90°



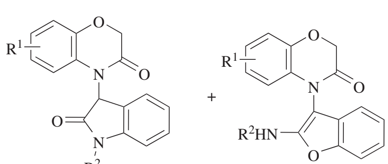
(86)

169

C_{21-24}



CuI (10 mol %), MeCN, K_3PO_4•$3H_2O$, MW



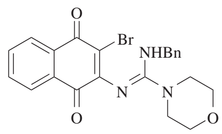
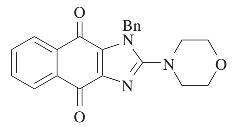
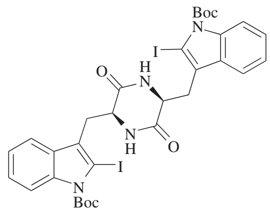
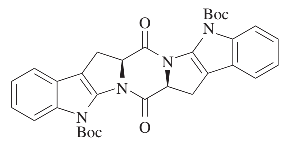
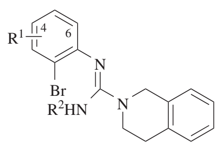
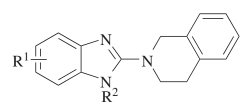
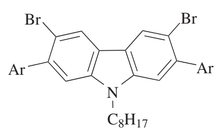
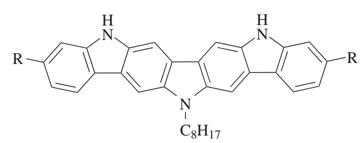
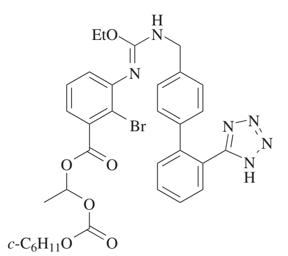
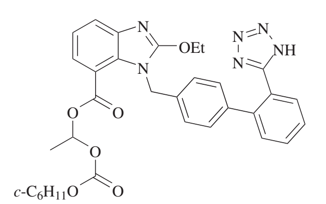
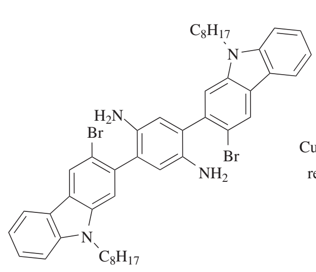
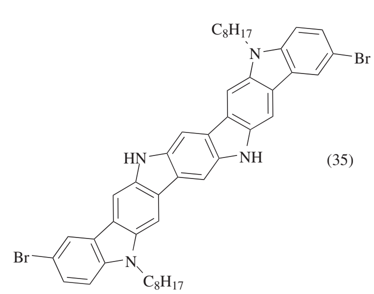
I + **II**

R^1	R^2	X	Additive	Solvent	Temp (°)	Time (min)	I	II	Refs.
6-Cl	Bn	Br	L-Pro (20 mol %)	MeCN	150	50	(59)	(0)	584
6-Cl	Bn	Br	none	DMF	150	35	(80)	(0)	585
6-Me	Bn	Br	L-Pro (20 mol %)	MeCN	150	50	(85)	(0)	584
6-Me	Bn	Br	none	DMF	150	35	(89)	(0)	585
7-Me	*t*-Bu	Br	L-Pro (20 mol %)	MeCN	180	60	(60)	(17)	584
7-Me	*t*-Bu	I	L-Pro (20 mol %)	MeCN	180	60	(25)	(15)[a]	584
7-Me	*c*-C_6H_{11}	Br	L-Pro (20 mol %)	MeCN	180	80	(40)	(11)	584
7-Me	Bn	Br	L-Pro (20 mol %)	MeCN	150	35	(90)	(0)	584
7-Me	Bn	Br	none	DMF	150	35	(93)	(0)	585

TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

A. SYNTHESIS OF FIVE-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}			
	CuI (50 mol %), NaH, THF, reflux, 1 h	 (84)	139
	CuI (10 mol %), DMEDA (20 mol %), K_3PO_4, toluene, 110°, 16 h	 (72)	566
C_{22-24}			
	CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DME, 80°, 16 h		581
C_{24}			
 Ar = 2-H_2N-4-RC_6H_3	Cu (50 mol %), CuI (10 mol %), K_2CO_3, $(n\text{-Bu})_2O$, reflux, 12 h		586
C_{25}			
	CuI (50 mol %), L-Pro (1 eq), K_2CO_3, DMSO, 70°, 3 h	 (75)	587
C_{30}			
	Cu, CuI, K_2CO_3, $(n\text{-Bu})_2O$, reflux, 24 h	 (35)	588

C_{22-24} entry:

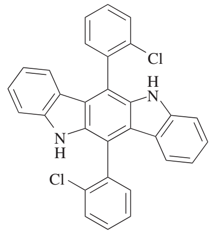
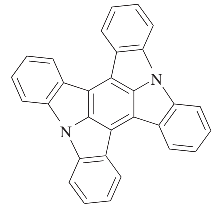
R^1	R^2	
H	Ph	(58)
H	Bn	(83)
H	4-$MeOC_6H_4CH_2$	(95)
4-Cl	Bn	(90)
4-Me	Bn	(90)
4-Me, 6-Br	Bn	(90)
5-CF_3	Bn	(90)

C_{24} entry:

R	
H	(57)
Cl	(68)

TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

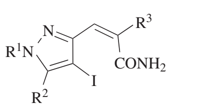
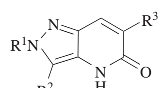
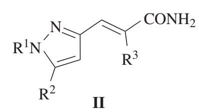
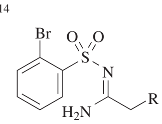
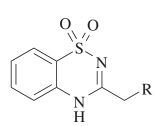
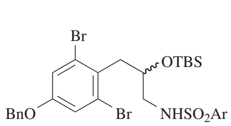
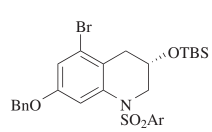
A. SYNTHESIS OF FIVE-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

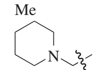
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{30}			
	CuI (10 mol %), TBAH, DMF, 120°, 20 h	 (74)	589

[a] The dehalogenated substrate was formed in 22% yield.

TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

B. SYNTHESIS OF SIX-MEMBERED NITROGEN HETEROCYCLES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{7-18} 	CuI (20 mol %), EDA (40 mol %), Cs_2CO_3, DMF, 100°, 18 h	 **I** +  **II**	577
C_{8-14} 	CuI (10 mol %), phen (20 mol %), Cs_2CO_3, DMF, 80°, 16 h		590
C_9  Ar = 2-$O_2NC_6H_4$	CuI (50 mol %), DMSO		569, 556

R^1	R^2	R^3	**I**	**II**
Me	H	Me	(70)	(7)
Ph	Ph	Me	(86)	(8)
Ph	4-ClC_6H_4	Me	(87)	(6)
Ph	4-MeC_6H_4	Me	(90)	(5)
Ph	Ph		(88)	(7)

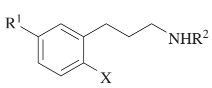
R	
TMS	(72)
n-Bu	(86)
Ph	(75)

Isomer	Additive	Temp (°)	Time (h)		Refs.
(*R*)	CsOAc	60	24	(83)	569
(*S*)	Cs_2CO_3	50	15	(89)	556

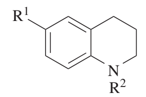
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{9-16}

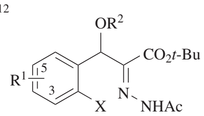


Catalyst (*x* amount)

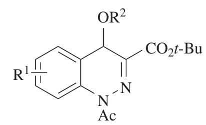


R^1	R^2	X	Catalyst	*x*	Additive(s)	Solvent(s)	Temp (°)	Time (h)		Refs.
H	H	Br	CuI	10 mol %	CsOAc	DMSO	90	24	(54)	197
H	H	Br	CuI	2 eq	CsOAc	DMSO	rt	1	(54)	274
H	H	I	CuI	2 eq	CsOAc	DMSO	rt	24	(56)	197
H	H	I	CuI	2 eq	CsOAc	DMSO	rt	24	(56)	274
H	H	Br	CuOAc	5 mol %	**L13** (20 mol %), K_3PO_4	DMF	40	18	(80)	120
H	$SO_2C_4F_9$	Br	CuI	2 eq	CsOAc	DMSO	90	5	(98)	274
H	$SO_2C_4F_9$	Br	CuI	2 eq	CsOAc	DMSO	90	4.5	(98)	197
H	Bn	Br	CuI	2 eq	CsOAc	DMSO	90	9	(71)	197, 274
H	Bn	I	CuI	2 eq	CsOAc	DMSO	90	9	(54)	197, 274
H	2-$O_2NC_6H_4O_2S$	I	CuI	2 eq	CsOAc	DMSO	90	4	(99)	274
H	2-$O_2NC_6H_4O_2S$	I	CuI	2 eq	CsOAc	DMSO	90	4	(81)	197
I	$C_4F_9O_2S$	Br	CuI	2 eq	CsOAc	DMSO	90	24	(81)	274

C_{11-12}

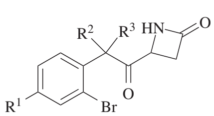


CuI (*x* amount), DMSO

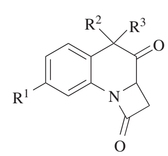


580

R^1	R^2	X	*x*	Additive(s)	Temp (°)	Time	
H	H	Br	10 mol %	DMEDA (10 mol %), Cs_2CO_3	rt	10 min	(89)
H	H	I	10 mol %	DMEDA (10 mol %), Cs_2CO_3	rt	10 min	(89)
H	TBS	Br	2 eq	NaOAc	50	19 h	(65)
H	TBS	I	10 mol %	DMEDA (10 mol %), Cs_2CO_3	rt	10 min	(93)
6-F	TBS	I	10 mol %	DMEDA (10 mol %), Cs_2CO_3	rt	10 min	(100)
4-Cl	TBS	I	10 mol %	DMEDA (10 mol %), Cs_2CO_3	rt	10 min	(100)
4,5-$(MeO)_2$	TBDPS	I	10 mol %	DMEDA (10 mol %), Cs_2CO_3	rt	10 min	(61)
3-Me	TBS	I	10 mol %	DMEDA (10 mol %), Cs_2CO_3	rt	10 min	(58)

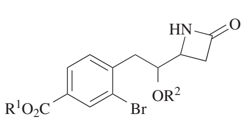


Catalyst (5 eq)

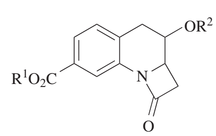


R^1	R^2	R^3	Catalyst	Solvent	Temp (°)	Time		Refs.
H	H	H	Cu	DMF	135	8 h	(13)	565
H	H	H	Cu (active)	—	MW (100 W)	10 min	(72)	280
H	BnO_2C	BnO_2C	Cu (active)	—	MW (100 W)	10 min	(68)	280
MeO_2C	H	H	Cu	DMF	135	8 h	(10)	565

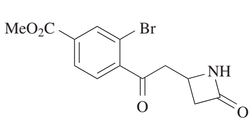
C_{12}



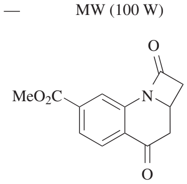
Catalyst (5 eq)



R^1	R^2	Catalyst	Solvent	Temp (°)	Time		Refs.
Me	Ac	Cu	DMF	135	8 h	(65)	565
Me	Ac	Cu (active)	—	MW (100 W)	10 min	(84)	280
t-Bu	H	Cu	DMF	135	8 h	(41)	565
t-Bu	Ac	Cu	DMF	135	8 h	(50)	565
Bn	H	Cu	DMF	135	8 h	(68)	565
Bn	H	Cu (active)	—	MW (100 W)	8 min	(83)	280

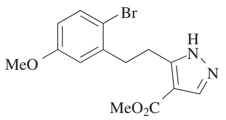
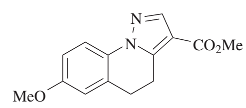
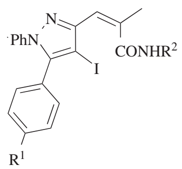
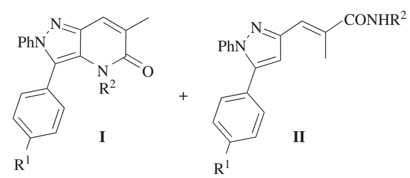


Active Cu (5 eq), MW (100 W), 8 min

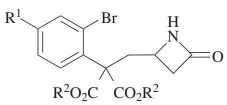
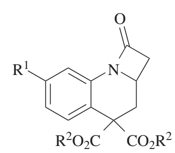


(75) 280

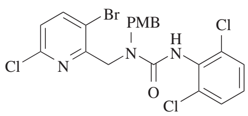
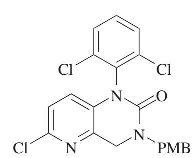
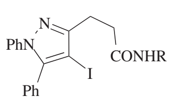
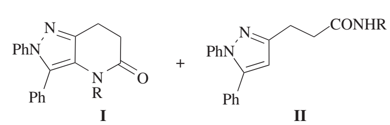
TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)
B. SYNTHESIS OF SIX-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{12}			
	CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, reflux, 18 h	 (70)	591
C_{13-21}			
	CuI (20 mol %), EDA (40 mol %), Cs_2CO_3, DMF, 100°, 24 h		577

R^1	R^2	I	II
Ph	H	(39)	(21)
Ph	*n*-Pr	(54)	(14)
Ph	*i*-Pr	(21)	(43)
Ph	*c*-Pr	(57)	(21)
Ph	*s*-Bu	(10)	(47)
Ph	*c*-C_6H_{11}	(14)	(49)
Ph	Ph	(39)	(27)
Ph	3-ClC_6H_4	(28)	(20)
Ph	4-ClC_6H_4	(13)	(22)
Ph	4-$MeOC_6H_4$	(58)	(18)
Ph	4-MeC_6H_5	(62)	(22)
Ph	Bn	(47)	(22)
Ph	$Ph(CH_2)_2$	(38)	(31)
Cl	H	(32)	(18)
Cl	*c*-Pr	(50)	(28)
Cl	Ph	(37)	(19)
Cl	Bn	(46)	(33)
Me	H	(35)	(16)
Me	*c*-Pr	(54)	(21)
Me	Ph	(33)	(23)
Me	Bn	(57)	(24)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13-14}			
	Cu (5 eq), DMF, 135°, 8 h		565

R^1	R^2	
H	Et	(60)
H	Bn	(5)
EtO_2C	Et	(45)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	CuI (1.5 eq), K_2CO_3, pyridine, 160°, 1 h	 (35)	592
C_{14}			
	CuI (20 mol %), EDA (40 mol %), Cs_2CO_3, DMF, 100°, 48 h		577

R	I	II
i-Pr	(42)	(45)
c-Pr	(69)	(28)

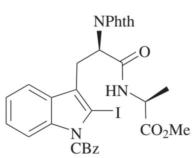
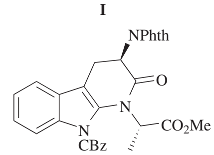
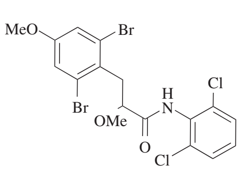
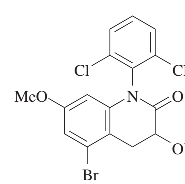
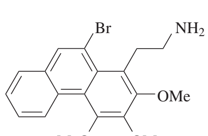
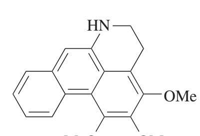
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	CuI (10 mol %), DMCDA (10 mol %), K_3PO_4, toluene, 110°	 (64)	162
C_{15}			
	CuI, K_2CO_3, 150°	 (84)	593
C_{16}			
	CuI, CsOAc, DMSO	 (71)	594

TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

B. SYNTHESIS OF SIX-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

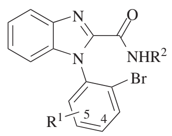
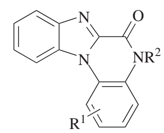
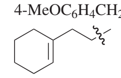
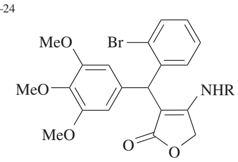
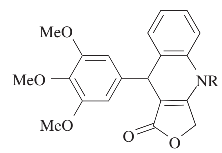
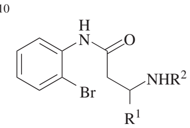
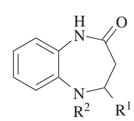
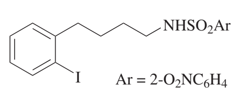
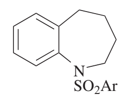
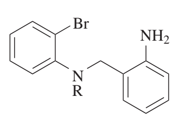
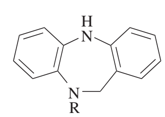
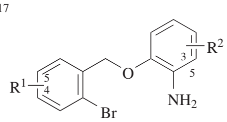
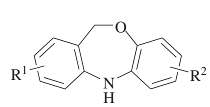
Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_{18-23}					
	CuI (20 mol %), DMG (20 mol %), K_3PO_4, DMF, 150°, 12 h		R^1	R^2	595
			H	$PhCH_2CH_2$ (56)	
			4-CF_3O	*n*-Bu (trace)	
			4-CF_3O	Bn (66)	
			4-CF_3O	2,4-$Cl_2C_6H_4CH_2$ (44)	
			4-CF_3O	4-$MeOC_6H_4CH_2$ (71)	
			4-CF_3O	 (42)	
			4-CF_3O	$PhCH_2CH_2$ (56)	
			5-CF_3	$PhCH_2CH_2$ (40)	
C_{23-24}					
	CuI (1.2 eq), Cs_2CO_3, DMF, 90°, 16 h		R		596
			Ph (82)		
			Bn (100)		
			4-$MeOC_6H_4CH_2$ (84)		

TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)
C. SYNTHESIS OF SEVEN-MEMBERED NITROGEN HETEROCYCLES

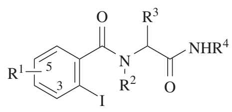
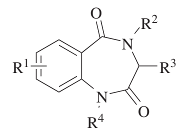
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10}			
	CuI (5 mol %), L-Pro (10 mol %), K_2CO_3, toluene, 110°, 60 h	 R^1 R^2: H DIPP (63); Me Boc (60)	597
C_9			
 Ar = 2-$O_2NC_6H_4$	CuI (1 eq), CsOAc, DMSO, 120°, 24 h	 (74)	274, 197
C_{13}			
	CuI (10 mol %), Cs_2CO_3, $HOCH_2CH_2OH$, 100°, 3 h	 R: H (82); Me (94)	598
C_{13-17}			
	CuI (10 mol %), L-Pro (20 mol %), DABCO•$6H_2O$, DMSO, H_2O, 90°		599

R^1	R^2	Time (h)	
H	4-Cl	72	(40)
H	3-Me	72	(93)
H	4-Me	72	(73)
H	6-Me	72	(66)
5-MeO	H	48	(35)
5-MeO	3-Me	24	(90)

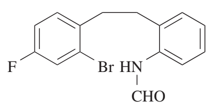
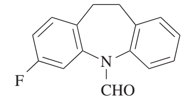
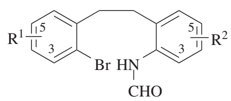
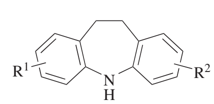
R^1	R^2	Time (h)	
3-t-BuO_2C	H	24	(81)
3-t-BuO_2C	3-Me	24	(71)
3-t-BuO_2C	4-Me	24	(65)
5-t-BuO_2C	H	24	(80)
5-t-BuO_2C	3-Me	24	(92)
4-Ac	4-Me	48	(63)
3-$(CH=CH)_2$-4	H	48	(75)

TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

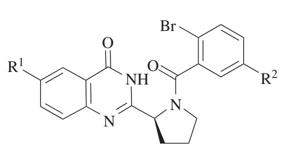
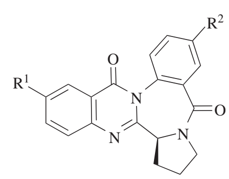
C. SYNTHESIS OF SEVEN-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14-19}			
	CuI (10 mol %), thiophene-2-carboxylic acid (20 mol %), K_2CO_3, DMSO, 100°		600

R^1	R^2	R^3	R^4	Temp (°)	Time (h)	
H	Me	H	2-$IC_6H_4CH_2$	100	15	(52)
H	*n*-Bu	*i*-Pr	MeO_2CCH_2	110	16	(88)
H	Bn	*i*-Pr	1-morpholinyl-$(CH_2)_2$	110	16	(99)
H	Bn	*i*-Pr	2,4-$(MeO)_2C_6H_4CH_2$	110	16	(95)
H	Bn	$CbzHN(CH_2)_4$	MeO_2CCH_2	110	16	(88)
H	Bn	$AcO(CH_2)_4$	MeO_2CCH_2	110	16	(74)
H	Bn	*n*-C_6H_{13}	MeO_2CCH_2	110	16	(86)
H	2,4-$(MeO)_2C_6H_4CH_2$	*i*-Pr	4-morpholinyl-$(CH_2)_2$	110	16	(97)
5-Me	Bn	*i*-Pr	4-morpholinyl-$(CH_2)_2$	110	16	(95)
4-$(CH{=}CH)_2$-5	Bn	*i*-Pr	MeO_2CCH_2	110	16	(50)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	Cu (80 mol %), K_2CO_3, DMSO, 160°, 24 h	 (61)	601
	1. Cu (80 mol %), K_2CO_3, DMSO, 160°, 24 h 2. 6 M NaOH, EtOH, reflux, 1 h		601

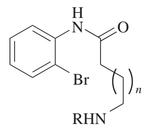
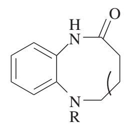
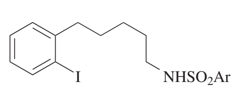
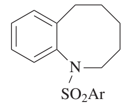
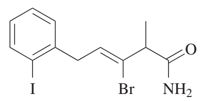
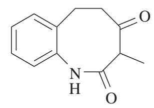
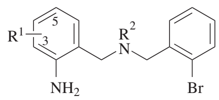
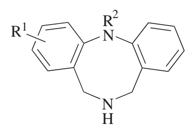
R^1	R^2	
H	4-Cl	(53)
H	4-MeO	(46)
3-F	3-F	(61)
4-Cl	4-Cl	(75)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	CuI (20 mol %), L-Pro (30 mol %), NaH, DMF, 120°, 10 h		602

R^1	R^2	
H	H	(84)
H	MeO	(91)
MeO	H	(89)
MeO	MeO	(90)

TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

D. SYNTHESIS OF EIGHT- AND HIGHER-MEMBERED NITROGEN HETEROCYCLES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-18}			
	CuI (5 mol %), L-Pro (10 mol %), K_2CO_3, toluene, 110°, 72 h	 R / n: DIPP 1 (68); Boc 1 (62); DIPP 2 (64); DIPP 3 (63); DIPP 5 (60); DIPP 9 (61)	597
C_{11}			
 Ar = 2-$O_2NC_6H_4$	CuI (*x* eq), CsOAc, DMSO, 120°	 *x* / Time (h): 1, 24 (0); 2, 4 (0)	274 197
C_{12}			
	1. CuI (5 mol %), DMG (20 mol %), K_2CO_3, MeCN, reflux, 12 h 2. HCl	 (62)	603
C_{14-15}			
	CuI (10 mol %), Cs_2CO_3, $HOCH_2CH_2OH$, 100°, 3 h	 R^1 / R^2: H H (64); H Me (91); H allyl (97); H Bn (80); 5-Cl H (53); 5-Cl Me (86); 5-Br Me (84); 5-HO Me (62); 4,5-$(MeO)_2$ Me (77); 4-CF_3 Me (96); 5-MeO_2C Me (45)	598

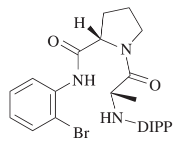
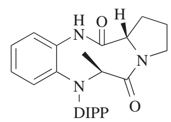
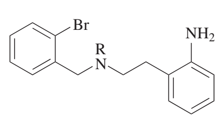
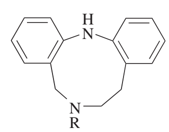
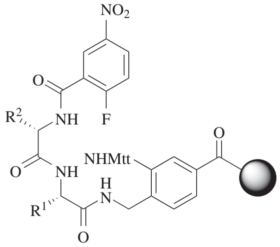
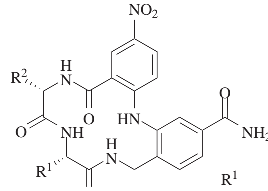
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	CuI (5 mol %), L-Pro (10 mol %), K_2CO_3, toluene, 110°, 84 h	 (53)	597
C_{15}			
	CuI (10 mol %), $HOCH_2CH_2OH$, Cs_2CO_3, 100°, 3 h	 R: H (82); Me (93)	598
C_{22-26}			
  = Rapp HypoGel 200 RAM resin	1. TFA, $HSi(i\text{-}Pr)_3$, CH_2Cl_2 2. CuI, K_2CO_3, DMF, rt, 2 d 3. TFA, $HSi(i\text{-}Pr)_3$, H_2O	 (—) R^1 / R^2: H / $H_2N(CH_2)_3$; $HOCH_2$ / $H_2N(CH_2)_3$; Me(OH)CH / $H_2N(CH_2)_3$; HO_2CCH_2 / $H_2NN(=NH)(CH_2)_3$; $H_2N(CH_2)_3$ / $HOCH_2$; $H_2NN(=NH)(CH_2)_3$ / $HOCH_2$; $HO_2C(CH_2)_2$ / $H_2N(CH_2)_3$; *s*-Bu / $H_2N(CH_2)_3$; *s*-Bu / $H_2NN(=NH)(CH_2)_3$	604

TABLE 26. INTRAMOLECULAR ARYLATIONS (*Continued*)

D. SYNTHESIS OF EIGHT- AND HIGHER-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

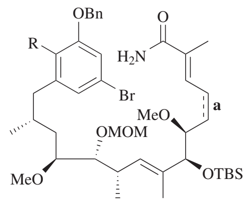
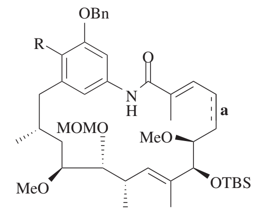
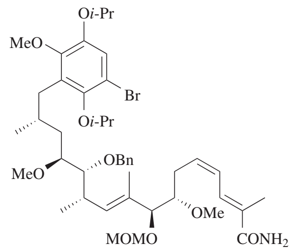
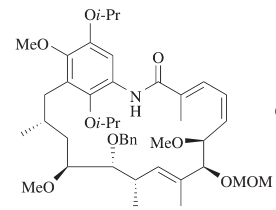
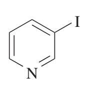
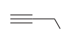
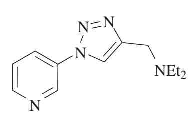
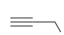
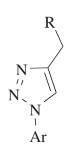
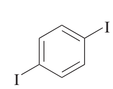
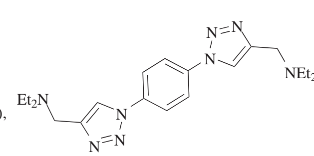
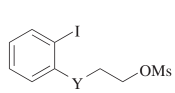
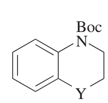
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{25} 	CuI (50 mol %), DMEDA (1 eq), K_2CO_3, toluene, 100°, 36 h	 R / Bond **a**: H, single (82); MeO, single (>80); MeO, double, (*Z*) (82)	605
C_{26} 	CuI (50 mol %), DMEDA (1 eq), K_2CO_3, toluene, 100°, 36 h	 (81)	164

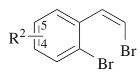
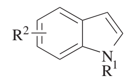
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS
A. SYNTHESIS OF FIVE-MEMBERED RINGS

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_0				
NaN_3		 NEt_2, $CuSO_4$•$5H_2O$ (5 mol %), Na ascorbate, L-Pro (20 mol %), Na_2CO_3, DMSO/H_2O (9:1), 60°, 18 h	 (94)	606
	ArI	 R, $CuSO_4$•$5H_2O$ (5 mol %), Na ascorbate, L-Pro (20 mol %), Na_2CO_3, DMSO/H_2O (9:1), 60°, 18 h	 Ar / R Ph / Et_2N (90) Ph / 4-ClC_6H_4O (98) Ph / 4-$MeOC_6H_4O$ (76) Ph / 4-AcC_6H_4O (87) Ph / $HO(CH_2)_3$ (98) Ph / $HO_2C(NH_2)CH$ (52) Ph / 1-cyclohexenyl (74) Ph / Ph (84) Ph / 3-$H_2NC_6H_4$ (74) 4-BrC_6H_4 / Et_2N (78)	606
		NEt_2, $CuSO_4$•$5H_2O$ (5 mol %), Na ascorbate, L-Pro (20 mol %), Na_2CO_3, DMSO/H_2O (9:1), 60°, 18 h	 (66)	606
H_2NBoc		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, 16 h	 Y O (76) CH_2 (74)	607

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

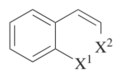
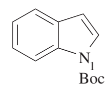
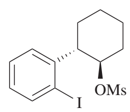
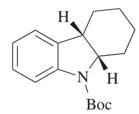
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{0-6}

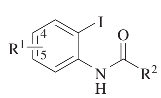
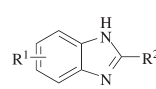
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
H_2NR^1		CuOAc (10 mol %), K_3PO_4, toluene, DMEDA (20 mol%), reflux, 24 h		106

R^1	R^2	
EtO_2C	H	(81)
BnO_2C	H	(84)
Et(O)C	H	(89)
n-C_5H_{11}(O)C	H	(87)
n-C_6H_{13}(O)C	H	(21)
Ph	H	(80)
Boc	5-F	(80)
Boc	5-Br	(53)
Boc	4,5-$(MeO)_2$	(82)
Boc	4-(OCH_2O)-5	(62)
Boc	4-Me	(80)
Boc	5-Ac	(70)

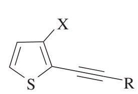
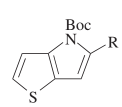
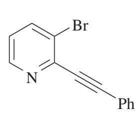
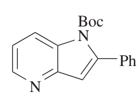
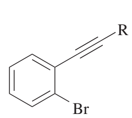
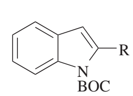
C_0

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
H_2NBoc		CuOAc (10 mol %), K_3PO_4, toluene, DMEDA (20 mol%), reflux, 24 h		106
		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, 16 h	 (94)	607

X^1	X^2	
Cl	Br	(56)
Br	Cl	(80)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
NH_3		1. CuI (10 mol %), L-Pro (20 mol %), NaOH, DMSO, rt, 7 h 2. HOAc, 80°, 12 h		178

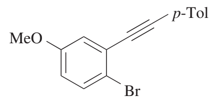
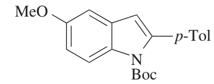
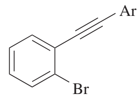
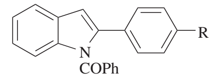
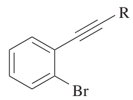
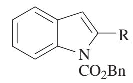
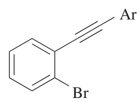
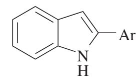
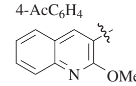
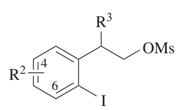
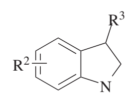
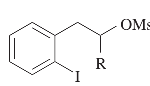
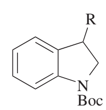
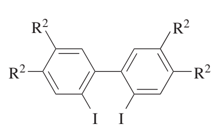
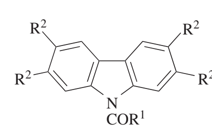
R^1	R^2		R^1	R^2		R^1	R^2	
H	$BocHNCH_2$	(82)	4-Cl	4-ClC_5H_4	(82)	5-MeO	Ph	(77)
H	2-furyl	(77)	4-Cl	Bn	(72)	4-Me	2-furyl	(65)
H	Ph	(83)	4-Br	n-Pr	(81)	4-n-PrHNCO	MeO	(74)
H	Bn	(79)	4-I, 6-Cl	Ph	(61)	4-MeO_2C	n-Pr	(86)
4-F	2-furyl	(81)	4-O_2N	MeO	(78)	4-Ac	MeO	(72)
4-F	Ph	(74)	4-O_2N	Ph	(66)	4-Ac	Ph	(79)
4-Cl	Ph	(68)	4-MeO	Ph	(75)	4-6-Me_2	MeO	(76)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
H_2NBoc		Cu (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, 15 h		608
		CuI (10 mol %), DMEDA (30 mol %), K_2CO_3, toluene, 105°, 24 h	 (63)	609
		CuI (10 mol %), DMEDA (30 mol %), K_2CO_3, toluene, 105°, 24 h		609

R	X	
n-Bu	Br	(83)
n-Bu	I	(83)
3-thienyl	Br	(84)

R	
2-thienyl	(61)
Ph	(73)
3-$MeOC_6H_4$	(65)
4-MeC_6H_4	(63)
3-NCC_6H_4	(63)
4-Ac	(52)

TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
A. SYNTHESIS OF FIVE-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_0				
H_2NBoc		CuI (10 mol %), DMEDA (30 mol %), K_2CO_3, toluene, 105°, 24 h	 (58)	609
H_2NCOPh		CuI (10 mol %), DMEDA (30 mol %), K_2CO_3, toluene, 105°, 24 h	 Ar: Ph (62); PMP (71)	609
H_2NCO_2Bn		CuI (10 mol %), DMEDA (30 mol %), K_2CO_3, toluene, 105°, 24 h	 R: *n*-Bu (52); Ph (57); 4-$MeOC_6H_4$ (56); 4-$CF_3C_6H_4$ (55)	609
H_2NBoc		1. CuI (10 mol %), DMEDA (30 mol %), K_2CO_3, toluene, 105°, 24 h 2. TFA, $MeCl_2$, rt	 Ar: Ph (69); 4-$AcHNC_6H_4$ (55); 2-$MeOC_6H_4$ (50); 3-$MeOC_6H_4$ (64); 4-$MeOC_6H_4$ (65); 4-MeC_6H_4 (63); 4-$CF_3C_6H_4$ (72); 3-NCC_6H_4 (63); 4-AcC_6H_4 (54);  (64)	609
H_2NCOR^1		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, 15 h		607
H_2NBoc		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, 15 h	 R: H (89); Me (96); $TBSOCH_2$ (91); $BzOCH_2$ (88); Et (*S*) (94)	607
C_{0-7}				
H_2NCOR^1		CuI (20 mol %), DMCDA (20 mol %), K_2CO_3, toluene, 110°, 48 h		610

Products of H_2NCOR^1 (ref. 607):

R^1	R^2	R^3	
MeO	H	H	(90)
t-BuO	H	Me	(95)
t-BuO	H	$Ph(CH_2)_2$	(92)
t-BuO	6-F	H	(95)
t-BuO	4,5-$(MeO)_2$	H	(75)
t-BuO	4-(OCH_2O)-5	H	(82)
BnO	H	H	(90)
Me	H	H	(87)

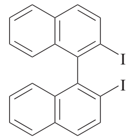
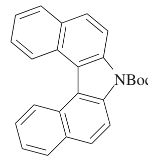
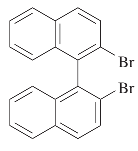
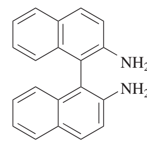
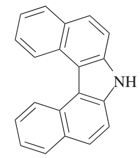
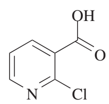
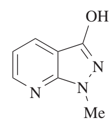
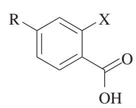
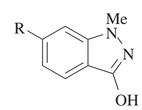
Products of H_2NCOR^1 (ref. 610):

R^1	R^2	
EtO	H	(58)
EtO	MeO	(47)
EtO	Me	(47)
n-Bu	H	(85)
n-Bu	MeO	(55)

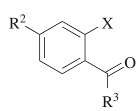
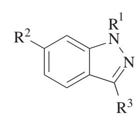
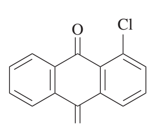
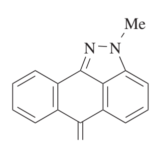
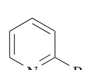
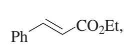
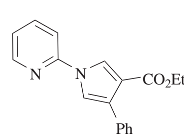
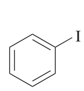
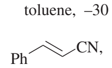
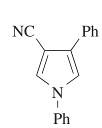
R^1	R^2	
Ph	Me	(41)
4-$H_2NC_6H_4$	H	(65)
4-$MeOC_6H_4$	H	(84)
Bn	H	(85)

TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)

A. SYNTHESIS OF FIVE-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_0				
H_2NBoc		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 110°, 24 h	 (75)	100
NaN_3		CuI (1 eq), DMEDA (1 eq), DMSO, 100°, 48 h	 (48) +  (48)	156
C_1				
H_2NNHMe		CuO (2 mol %), K_2CO_3, C_6H_6, 110°, 20 h	 (54)	611
		CuO (2 mol %), K_2CO_3, C_6H_6, 110°, 20 h	 R X: H Cl (20); H Br (22); Cl Cl (16); O_2N Cl (26); MeO Cl (22)	611

R	X	Yield (%)
H	Cl	(20)
H	Br	(22)
Cl	Cl	(16)
O_2N	Cl	(26)
MeO	Cl	(22)

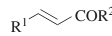
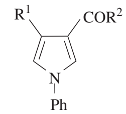
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{1-6}				
H_2NNHR^1		CuO (2 mol %), K_2CO_3, C_6H_6, 110°, 20 h		611
C_1				
H_2NNHMe		CuO (2 mol %), K_2CO_3, DMA/THF, 110°, 20 h	 (43)	611
C_2				
$CNCH_2Ts$		, CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, NaO*t*-Bu, toluene, –30 to 110°, 5 h	 (62)	612
		, CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, NaO*t*-Bu, toluene, –30 to 110°, 8 h	 (70)	612

R^1	R^2	R^3	X	Yield (%)
Me	O_2N	Ph	Cl	(80)
Me	MeO	Me	F	(83)
$HO(CH_2)_2$	H	Me	F	(30)
t-Bu	H	Me	F	(32)
Ph	H	Me	F	(40)
Me	H	Me	F	(50)
Me	H	Me	Cl	(54)
Me	H	Et	F	(63)
Me	H	Ph	Cl	(43)
Me	Cl	Me	F	(30)

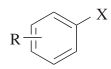
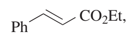
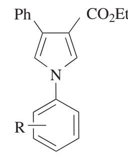
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
A. SYNTHESIS OF FIVE-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

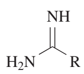
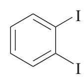
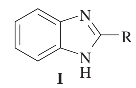
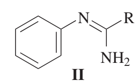
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 $CNCH_2Ts$	PhI	, CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, NaO*t*-Bu, toluene, –30 to 110°		612

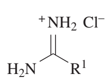
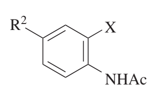
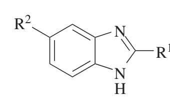
R^1	R^2	Time (h)	
Me	EtO	8	(45)
EtO_2C	EtO	6	(52)
Ph	Me	10	(50)
Ph	Ph	8	(68)
$2\text{-}BrC_6H_4$	Ph	8	(50)
$4\text{-}O_2NC_6H_4$	Ph	7	(62)
$4\text{-}MeC_6H_4$	Ph	7	(62)
Bn	EtO	8	(50)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		, CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, NaO*t*-Bu, toluene, –30 to 110°		612

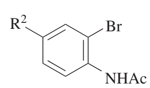
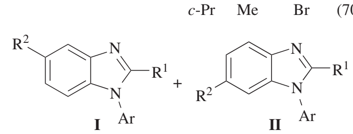
R	X	Time (h)	
H	Br	24	(55)
H	I	8	(50)
4-F	Br	24	(56)
3-Cl	Br	5	(62)
$4\text{-}O_2N$	I	5	(61)
3-MeO	Br	5	(62)
4-MeO	Br	24	(52)
2-Me	Br	24	(0)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{2–7}$ 		CuI (15 mol %), DMEDA (30 mol %), Cs_2CO_3, DMA	 **I** +  **II**	141

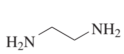
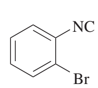
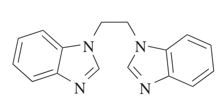
R	Temp (°)	Time (h)	**I**	**II**
NHMe	165	16	(36)	(0)
NMe_2	130	16	(59)	(0)
NHAc	165	16	(29)	(0)
i-Pr	170	24	(66)	(22)
t-Bu	170	24	(64)	(23)
1-pyrrolidinyl	150	16	(47)	(0)
2-furyl	170	24	(64)	(23)
4-pyridyl	170	24	(32)	(—)
Ph	170	24	(64)	(23)
$3\text{-}O_2NC_6H_4$	170	24	(45)	(31)
$3\text{-}(OCH_2O)\text{-}4\text{-}C_6H_3$	170	24	(45)	(31)
PhHN	130	16	(32)	(0)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{2–4}$ 		CuBr (10 mol %), Cs_2CO_3, DMSO, 90–120°, 72 h		613

R^1	R^2	X	
Me	H	Br	(82)
Me	H	I	(80)
Me	Br	Br	(89)
Me	O_2N	Br	(74)
Me	Me	Br	(75)
n-Pr	H	Br	(63)
n-Pr	H	I	(65)
n-Pr	Br	Br	(65)
n-Pr	O_2N	Br	(80)
n-Pr	Me	Br	(62)
c-Pr	H	Br	(65)
c-Pr	Br	Br	(62)
c-Pr	Me	Br	(70)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CuBr (10 mol %), Cs_2CO_3, DMSO, 70–120°, 72 h 2. ArI, **L46** (20 mol %)	 **I** + **II**	613

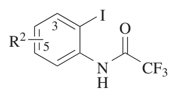
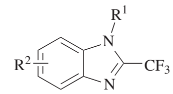
R^1	R^2	Ar	**I**	**II**
Me	H	Ph	(65)	(—)
Me	H	$4\text{-}ClC_6H_4$	(70)	(—)
Me	H	$3\text{-}O_2NC_6H_4$	(49)	(—)
Me	H	$4\text{-}MeC_6H_4$	(62)	(—)
Me	Br	Ph	(62)	(0)
Me	Me	Ph	(33)	(24)
Me	Me	$4\text{-}ClC_6H_4$	(33)	(27)
n-Pr	H	Ph	(65)	(—)
n-Pr	H	$4\text{-}ClC_6H_4$	(57)	(—)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 		CuBr (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 20–90°, 16 h	 (42)	614

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

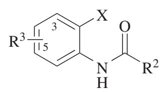
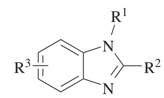
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

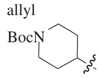
C_{2-6}

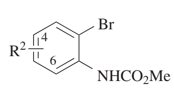
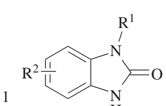
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
H_2NR^1		CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, rt		251

R^1	R^2	Time (h)	
$HOCH_2CH_2$	H	24	(92)
$HOCH_2CH_2$	6-MeO	15	(89)
$HOCH_2CH_2$	6-MeO_2C	24	(72)
$HOCH_2CH_2$	4,6-Me_2	17	(92)
$HOCH_2CH_2$	6-Ac	24	(90)
allyl	H	10	(92)
n-C_6H_{13}	H	24	(90)

C_{2-9}

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
H_2NR^1		1. CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, temp 1, time 1 2. AcOH, temp 2, time 2		251

R^1	R^2	R^3	X	Temp 1 (°)	Time 1 (h)	Temp 2 (°)	Time 2 (h)	
$HOCH_2CH_2$	Me	H	I	40	2	40	4	(75)
$HOCH_2CH_2$	CF_3	H	Br	40	36	70	12	(90)
allyl	CF_3	H	Br	50	10	50	6	(80)
allyl	CF_3	H	I	40	2	40	4	(81)
	CF_3	4-Ac	Br	rt	24	50	1	(85)
n-C_6H_{13}	CF_3	H	Br	rt	10	50	2	(80)
n-C_6H_{13}	Bn	H	I	40	6	40	10	(90)
c-C_6H_{11}	CF_3	H	Br	rt	10	50	5	(75)
c-C_6H_{11}	CF_3	H	I	rt	24	50	5	(94)
c-C_6H_{11}	2-furyl	H	I	40	10	60	12	(88)
c-C_6H_{11}	2-furyl	5-MeO_2C	I	40	8	60	12	(75)
c-C_6H_{11}	2-furyl	4-Ac	Br	50	12	80	12	(70)
c-C_6H_{11}	Ph	4-MeO	Br	50	10	90	10	(62)
c-C_6H_{11}	Bn	H	Br	45	10	50	6	(70)
(S)-BnCH(CO_2Me)	CF_3	H	I	40	36	70	12	(61)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CuI (10 mol %), 4-HOPro (20 mol %), K_2CO_3, DMSO, 70°, time 1 2. 130°, time 2		615

R^1	R^2	Time 1 (h)	Time 2 (h)	
HO_2CCH_2	H	5	4	(73)
i-Pr	4-$TBSOCH_2$	11	14	(75)
allyl	4-MeO	11	8	(62)
2-furylmethyl	4-O_2N	4	10	(82)
2-furylmethyl	4-n-PrHNCO	5	4	(82)
n-C_6H_{13}	4-Ac	10	9	(70)
c-C_6H_{11}	4-n-PrNHCO	21	12	(66)
Bn	H	4	6	(77)
Bn	4-MeO_2C	12	12	(74)
(S)-Bn(CONHMe)CH	4,6-Me_2	22	24	(76)

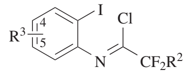
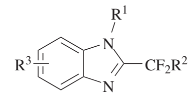
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)

A. SYNTHESIS OF FIVE-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

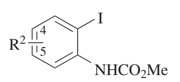
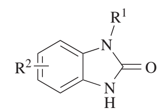
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

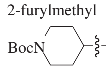
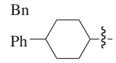
C_{2-7}

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
H_2NR^1		CuI (10 mol %), K_2CO_3, DMF		616

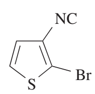
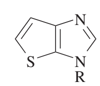
R^1	R^2	R^3	Temp (°)	
$HOCH_2CH_2$	F	H	40	(87)
$HOCH_2CH_2$	Br	H	60	(68)
allyl	F	H	60	(70)
allyl	Br	H	60	(68)
n-Bu	F	H	rt	(78)
n-Bu	Br	H	60	(76)
n-Bu	Br	4-Cl	80	(91)
n-Bu	F	4-O_2N	80	(73)
n-Bu	F	5-O_2N	80	(76)
n-Bu	Br	4-Me	80	(68)
c-C_6H_{11}	F	H	80	(69)
c-C_6H_{11}	Br	H	60	(76)
4-ClC_6H_4	F	H	80	(62)
4-ClC_6H_4	Br	H	80	(31)
4-$O_2NC_6H_4$	F	H	80	(64)
4-$O_2NC_6H_4$	Br	H	80	(58)
4-$MeOC_6H_4$	F	H	80	(91)
4-$MeOC_6H_4$	Br	H	60	(67)
4-MeC_6H_4	F	H	60	(93)
4-MeC_6H_4	Br	H	60	(74)
Bn	Br	H	60	(82)

C_{3-12}

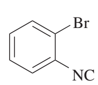
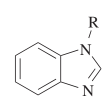
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
H_2NR^1		1. CuI (20 mol %), 4-HOPro (40 mol %), K_3PO_4, DMSO, 50°, time 1 2. 130°, time 2		615

R^1	R^2	Time 1 (h)	Time 2 (h)	
allyl	H	4	6	(82)
allyl	4-Br	7	5	(66)
2-furylmethyl	4-Ac	12	12	(82)
	H	7	5	(74)
Bn	H	3	3	(81)
Bn	5-MeO	7	3	(80)
	H	7	3	(85)

C_{3-10}

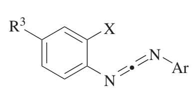
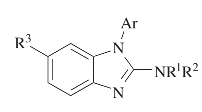
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
H_2NR		CuBr (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 20–90°, 16 h		614

R	
$BnO(CH_2)_3$	(44)
Bn	(49)
3-indolylethyl	(44)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuBr (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 20–90°, 16 h		614

R	
n-Pr	(65)
c-Pr	(40)
$BnO(CH_2)_3$	(66)
2-furylmethyl	(46)
c-C_6H_{11}	(46)
4-MeC_6H_4	(41)
Bn	(70)
2-$MeOC_6H_4CH_2$	(67)
3,5-$(MeO)_2C_6H_3CH_2$	(65)
4-$CF_3C_6H_4CH_2$	(55)
3-indolylethyl	(59)

C_{3-8}

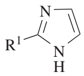
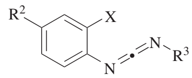
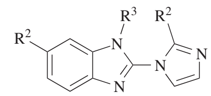
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
HNR^1R^2		CuI (10 mol %), additive (20 mol %), Cs_2CO_3, dioxane, 80°		183

R^1	R^2	R^3	Ar	X	Additive	Temp (°)	Time (h)	
Me	$HOCH_2CH_2$	Me	Ph	I	L-Pro	80	30	(78)
H	*c*-C_6H_{11}	H	4-$MeOC_6H_4$	I	phen	80	20	(86)
H	Bn	H	4-$MeOC_6H_4$	I	phen	80	20	(88)
H	(*S*)-PhMeCH	H	Ph	I	phen	80	20	(91)
Me	Bn	Me	Ph	Br	phen	80	20	(85)
n-Bu	*n*-Bu	Me	Ph	I	L-Pro	70	30	(83)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

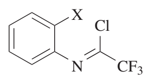
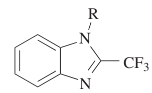
C_{3-4}

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), phen (20 mol %), Cs_2CO_3, dioxane		183

R^1	R^2	R^3	X	Temp (°)	Time (h)	
H	H	Ph	Br	80	20	(90)
H	H	4-$MeOC_6H_4$	I	100	24	(85)
H	H	4-MeC_6H_4	I	80	20	(86)
H	H	Bn	I	80	20	(92)
H	Cl	Ph	I	80	20	(82)
H	Me	Ph	Br	100	24	(90)

R^1	R^2	R^3	X	Temp (°)	Time (h)	
H	Me	Ph	I	80	24	(91)
H	Me	3-ClC_6H_4	Br	80	24	(87)
H	Me	4-MeC_6H_4	I	80	20	(86)
Me	H	4-MeC_6H_4	I	100	36	(73)
Me	Cl	Ph	Br	100	36	(75)

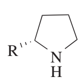
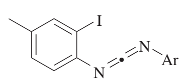
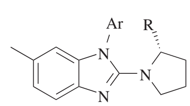
C_{4-8}

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
H_2NR		CuI (10 mol %), TMEDA (20 mol %), Cs_2CO_3, toluene, 110°, 8 h		617

R	X	
n-Bu	I	(79)
4-ClC_6H_4	I	(92)
4-$O_2NC_6H_4$	I	(62)
2-$MeOC_6H_4$	I	(70)
3-$MeOC_6H_4$	I	(73)
4-$MeOC_6H_4$	I	(86)
2-MeC_6H_4	I	(76)
4-MeC_6H_4	Cl	(70)
4-MeC_6H_4	Br	(77)

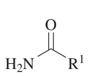
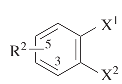
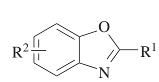
R	X	
Bn	Cl	(76)
Bn	Br	(89)
2-$FC_6H_4CH_2$	I	(89)
4-$FC_6H_4CH_2$	I	(95)
2-$ClC_6H_4CH_2$	I	(98)
4-$ClC_6H_4CH_2$	I	(88)
4-$MeOC_6H_4CH_2$	I	(93)
4-$MeC_6H_4CH_2$	I	(98)
PhMeCH	I	(83)

C_{4-5}

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), L-Pro (20 mol %), Cs_2CO_3, dioxane		183

R	Ar	Temp (°)	Time (h)	
H	4-MeC_6H_4	70	20	(90)
$HOCH_2$	Ph	80	30	(75)

C_{4-9}

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, reflux, 24 h	 (68)	618

R^1	R^2	X^1	X^2	
n-Pr	H	Br	Br	(68)
i-Pr	H	Br	Br	(68)
t-Bu	H	Br	Br	(92)
2-pyridyl	H	Br	Br	(78)

R^1	R^2	X^1	X^2	
Ph	H	Cl	Cl	(0)
Ph	H	Cl	Br	(95)
Ph	H	Br	Br	(95)
Ph	H	I	I	(89)

R^1	R^2	X^1	X^2	
Ph	3-Cl	Cl	Br	(75)
Ph	4-Cl	Cl	Br	(72)
Ph	4-(OCH_2O)-5	Br	Br	(88)
Ph	4-CF_3	Cl	Br	(59)

R^1	R^2	X^1	X^2	
2-FC_6H_4	H	Br	Br	(86)
4-$H_2NC_6H_4$	H	Br	Br	(67)
4-$MeOC_6H_4$	H	Br	Br	(72)
(*E*)-PhCH=CH	H	Br	Br	(77)

C_5

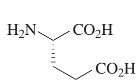
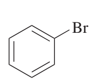
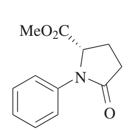
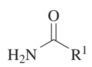
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CuCl (10 mol %), aq TBAH, MeCN, reflux, 24 h 2. AcCl, MeOH, reflux, 2 h	 (38)	264

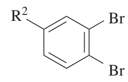
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
A. SYNTHESIS OF FIVE-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

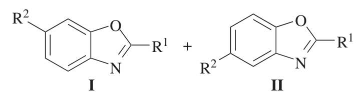
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{5-12}





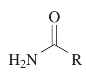
CuI (10 mol %), DMEDA (20 mol %), K_3PO_4, toluene, 110°, 48 h

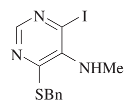


I + II — 619

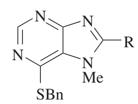
R^1	R^2	**I**	**II**
2-thienyl	H	(58)	(—)
Ph	H	(74)	(—)
Ph	Me	(36)	(36)
2-MeC_6H_4	H	(58)	(—)
n-$C_{11}H_{23}$	H	(77)	(—)

C_{5-8}





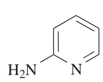
CuI (10 mol %), DMCDA (40 mol %), Cs_2CO_3, dioxane, 90°

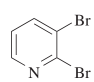


620

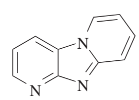
R		R	
n-Bu	(45)	3-ClC_6H_4	(68)
2-pyridyl	(66)	4-ClC_6H_4	(75)
3-pyridyl	(61)	3-$O_2NC_6H_4$	(68)
Ph	(61)	4-$O_2NC_6H_4$	(75)
2-FC_6H_4	(73)	3-$MeOC_6H_4$	(75)
3-FC_6H_4	(67)	4-$MeOC_6H_4$	(65)
4-FC_6H_4	(70)	2-MeC_6H_4	(80)

C_5

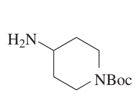


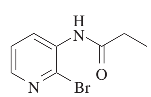


Cu (7.5 mol %), phen (15 mol %), Cs_2CO_3, DME, 95°, 17 h

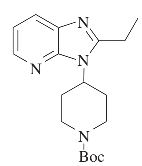


(95) — 621

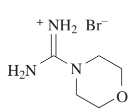


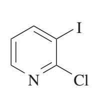


1. CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 45°, 6 h
2. 150°, 12 h

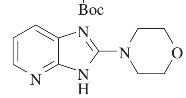


(76) — 251

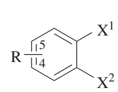




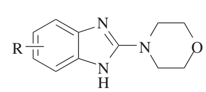
CuI (15 mol %), DMEDA (30 mol %), Cs_2CO_3, DMA, 150°, 16 h



(16) — 141



CuI (x mol %), Cs_2CO_3



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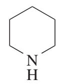
R	X^1	X^2	x	Additive	Solvent	Temp (°)	Time	
H	Cl	Cl	15	DMEDA (30 mol %)	DMA	150	16 h	(0)
H	Br	Cl	15	DMEDA (30 mol %)	DMA	150	16 h	(51)
H	I	Cl	15	DMEDA (30 mol %)	DMA	150	16 h	(25)
H	I	Br	15	DMEDA (30 mol %)	DMA	150	16 h	(76)
H	Br	Br	15	DMEDA (30 mol %)	DMA	150	16 h	(40)
H	I	I	15	DMEDA (30 mol %)	DMA	150	16 h	(52)
4-Cl	I	Cl	15	DMEDA (30 mol %)	DMA	165	16 h	(26)
4-O_2N	I	Cl	20	DBU	DMSO	MW, 130	10 min	(15)
5-Me	I	Br	15	DMEDA (30 mol %)	DMA	165	16 h	(53)
5-CF_3	I	Cl	15	DMEDA (30 mol %)	DMA	165	16 h	(18)

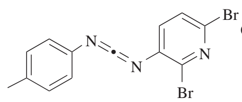
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
A. SYNTHESIS OF FIVE-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

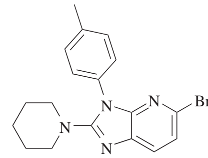
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_5

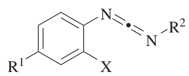




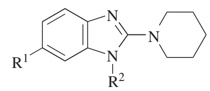
CuI (10 mol %), DMG (20 mol %), K_3PO_4, DMSO, 90°, 24 h



(92) 183



CuI (10 mol %), additive (20 mol %), Cs_2CO_3, dioxane



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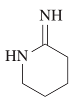
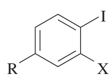
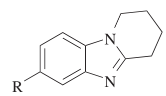
R^1	R^2	X	Additive	Temp (°)	Time (h)	
H	Bn	I	phen	80	20	(92)
Cl	Ph	I	L-Pro	70	20	(93)
O_2N	$4\text{-}MeC_6H_4$	I	L-Pro	70	30	(59)
Me	Ph	Br	phen	80	20	(91)
Me	Ph	I	L-Pro	70	20	(95)
Me	$3\text{-}ClC_6H_4$	I	L-Pro	70	20	(84)
Me	$4\text{-}MeOC_6H_4$	I	L-Pro	70	30	(96)
Me	$4\text{-}MeC_6H_4$	I	L-Pro	80	30	(68)
Me	$3\text{-}CF_3C_6H_4$	I	L-Pro	80	30	(70)



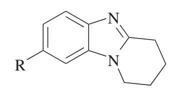


CuI (15 mol %), DMEDA (30 mol %), Cs_2CO_3



I

\+



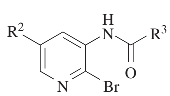
II

143

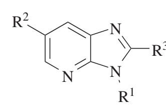
R	X	Solvent	Temp (°)	Time (h)	**I**	**II**
H	I	DMA	170	24	(52)	(**I + II**)
Me	Br	NMP	150	16	(24)	(5)

C_{6-7}

H_2NR^1



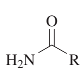
1. CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, temp, time
2. See table.

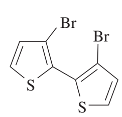


251

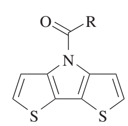
R^1	R^2	R^3	Temp (°)	Time (h)	Conditions 2	
$n\text{-}C_6H_{13}$	H	CF_3	50	10	AcOH, 90°, 4 h	(72)
Bn	H	Et	45	7	150°, 12 h	(78)
Bn	Br	CF_3	40	7	AcOH, 90°, 4 h	(78)

C_{6-12}





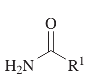
CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, reflux, 24 h

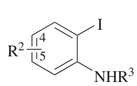


R	
$n\text{-}C_5H_{11}$	(24)
$c\text{-}C_6H_{11}$	(24)
Ph	(36)
$n\text{-}C_7H_{15}$	(38)
$n\text{-}C_{11}H_{23}$	(19)

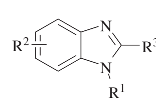
622

C_{6-9}





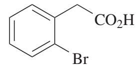
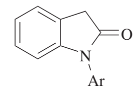
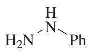
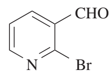
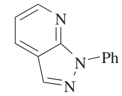
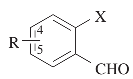
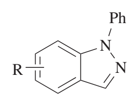
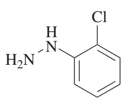
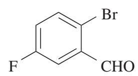
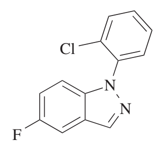
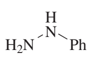
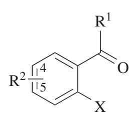
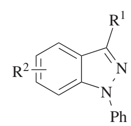
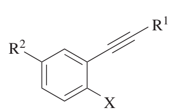
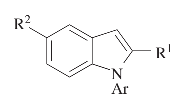
1. CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, dioxane, 110°, 17 h
2. See table.



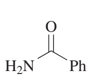
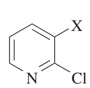
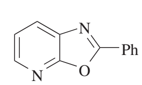
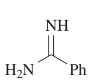
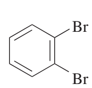
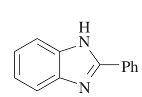
623

R^1	R^2	R^3	Conditions 2	
$n\text{-}C_5H_{11}$	H	$c\text{-}C_6H_{11}CH_2$	AcOH, 75°	(85)
$n\text{-}C_5H_{11}$	4-Me	Et	K_3PO_4, *t*-BuOH, 110°	(68)
$n\text{-}C_5H_{11}$	5-Me	Et	K_3PO_4, *t*-BuOH, 110°	(76)
$n\text{-}C_5H_{11}$	$4\text{-}CF_3$	Et	K_3PO_4, *t*-BuOH, 110°	(75)
$n\text{-}C_5H_{11}$	$5\text{-}CF_3$	Et	K_3PO_4, *t*-BuOH, 110°	(75)
$c\text{-}C_6H_{11}$	H	$c\text{-}C_6H_1CH_{21}$	AcOH, 75°	(80)
Ph	H	Me	K_3PO_4, *t*-BuOH, 110°	(80)
Ph	H	$c\text{-}C_6H_{11}CH_2$	K_3PO_4, *t*-BuOH, 110°	(68)
Ph	4-Me	Et	K_3PO_4, *t*-BuOH, 110°	(85)
Ph	5-Me	Et	K_3PO_4, *t*-BuOH, 110°	(79)
Ph	$4\text{-}CF_3$	Et	K_3PO_4, *t*-BuOH, 110°	(82)
Ph	$5\text{-}CF_3$	Et	K_3PO_4, *t*-BuOH, 110°	(82)
(*E*)-PhCH=CH	H	$c\text{-}C_6H_{11}CH_2$	AcOH, 75°	(60)

TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
A. SYNTHESIS OF FIVE-MEMBERED RINGS (*Continued*)

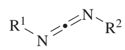
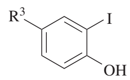
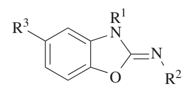
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_6				
NH_2Ar		Cu_2O (30 mol %), K_2CO_3, 240°, 4 h	 Ar: 3-ClC_6H_4 (75); 3-$MeOC_6H_4$ (82)	326
		1. NMP, MW, 160°, 10 min 2. CuI (5 mol %), DMCDA (10 mol %), K_2CO_3, MW, 160°, 10 min	 (95)	624
		1. NMP, MW, 160°, 10 min 2. CuI (5 mol %), DMCDA (10 mol %), K_2CO_3, MW, 10 min	 R / X / Temp (°): H / Cl / 160 (87); H / Br / 160 (91); H / I / 120 (87); 5-F / Br / 160 (84); 5-O_2N / Br / 120 (95); 4,5-$(MeO)_2$ / Br / 160 (82)	624
		1. NMP, MW, 160°, 10 min 2. CuI (5 mol %), DMCDA (10 mol %), K_2CO_3, MW, 160°, 10 min	 (82)	624
		1. NMP, MW, 160°, 10 min 2. CuI (5 mol %), DMCDA (10 mol %), K_2CO_3, MW, 10 min	 R^1 / R^2 / X / Temp (°): Me / H / Br / 160 (75); Me / 5-CF_3 / Cl / 160 (78); Et / 4-Cl / Cl / 120 (69)	624
$C_{6–10}$				
H_2NAr		CuI (10 mol %), KO*t*-Bu, toluene, 105°		

Ar	R^1	R^2	X	Time (h)	Yield (%)	Refs.
Ph	*n*-C_6H_{13}	H	Br	2	(84)	626, 609
4-ClC_6H_4	*n*-C_6H_{13}	H	Br	12	(70)	609
2-$MeOC_6H_4$	*n*-Bu	H	Br	12	(69)	626, 609
4-$MeOC_6H_4$	*n*-C_6H_{13}	H	Br	12	(60)	609
2-Cl, 5-$MeOC_6H_3$	*n*-C_6H_{13}	H	Br	12	(60)	609
4-MeC_6H_4	*n*-Bu	H	Br	2	(75)	626, 609
4-MeC_6H_4	*n*-C_6H_{13}	H	Br	12	(67)	609
4-MeC_6H_4	*n*-C_6H_{13}	CF_3	Cl	2	(53)	626, 609
4-MeC_6H_4	Ph	H	Cl	2	(21)	626
2-Cl, 4-MeC_6H_3	*n*-Bu	H	Br	12	(72)	609
1-Np	*n*-C_6H_{13}	H	Br	12	(77)	609

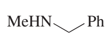
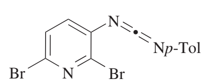
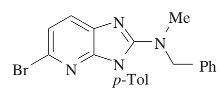
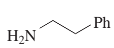
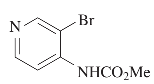
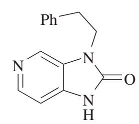
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, reflux, 24 h	 X: Cl (0); Br (77)	618
		CuI (10 mol %), DMEDA (20 mol %), K_3PO_4, xylenes, 150°, 48 h	 (27)	619

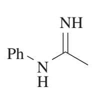
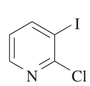
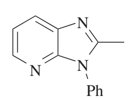
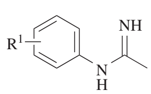
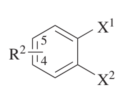
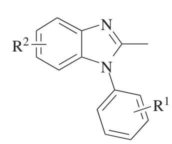
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

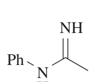
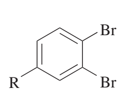
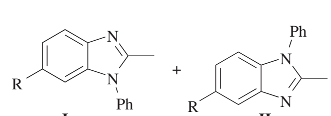
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-15} 		CuI (*x* mol %), 24 h		184

R^1	R^2	R^3	*x*	Additive(s)	Solvent	Temp (°)	
i-Pr	*i*-Pr	H	15	Cs_2CO_3	MeCN	100	(—)
i-Pr	Ph	H	15	Cs_2CO_3	MeCN	100	(83)
Ph	Ph	H	15	Cs_2CO_3	MeCN	100	(93)
Ph	Ph	F	15	Cs_2CO_3	MeCN	100	(85)
Ph	Ph	Cl	15	Cs_2CO_3	MeCN	100	(86)
Ph	Ph	Me	10	sparteine (20 mol %), K_3PO_4	NMP	130	(92)
Ph	Ph	*t*-Bu	15	Cs_2CO_3	MeCN	100	(85)
4-ClC_6H_4	4-ClC_6H_4	H	15	Cs_2CO_3	MeCN	100	(83)
4-ClC_6H_4	4-ClC_6H_4	Cl	10	sparteine (20 mol %), K_3PO_4	NMP	130	(74)
4-$CF_3OC_6H_4$	4-$CF_3OC_6H_4$	H	15	Cs_2CO_3	MeCN	100	(83)
2-MeC_6H_4	2-MeC_6H_4	H	10	sparteine (20 mol %), K_3PO_4	NMP	130	(75)
2-MeC_6H_4	2-MeC_6H_4	Cl	15	Cs_2CO_3	MeCN	100	(75)
4-MeC_6H_4	4-MeC_6H_4	H	15	Cs_2CO_3	MeCN	100	(89)
4-MeC_6H_4	4-MeC_6H_4	*t*-Bu	15	Cs_2CO_3	MeCN	100	(83)
3-$CF_3C_6H_4$	3-$CF_3C_6H_4$	H	15	Cs_2CO_3	MeCN	100	(78)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		CuI (10 mol %), phen (20 mol %), Cs_2CO_3, dioxane, 85°, 18 h	 (72)	183
C_8 		CuI (20 mol %), 4-HOPro (40 mol %), K_3PO_4, DMSO, 70°, 10 h; 130°, 12 h	 (62)	615

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		CuI (15 mol %), DMEDA (30 mol %), Cs_2CO_3, DMA, 150°, 16 h	 (39)	143
C_{8-9} 		CuI (15 mol %), DMEDA (30 mol %), Cs_2CO_3		143

R^1	R^2	X^1	X^2	Solvent	Temp (°)	Time (h)	
H	3-Cl	I	Cl	NMP	150	24	(24)
H	4-Cl	I	Cl	NMP	150	16	(41)
H	4-O_2N	I	Cl	NMP	150	16	(0)
H	3-Me	Br	Cl	NMP	150	24	(10)
H	4-Me	I	Br	NMP	150	24	(53)
H	5-Me	I	Br	NMP	150	24	(57)
H	6-Me	I	Cl	NMP	150	24	(38)
H	5-CF_3	I	Cl	NMP	150	16	(24)
H	4-NC–	I	Br	NMP	130	16	(31)
H	3,5-Me_2	I	I	NMP	150	24	(51)
4-MeO	4-Me	I	Br	NMP	150	16	(48)
2-Me	4-Me	I	Br	NMP	150	16	(49)
4-NC–	4-Me	I	Br	DMA	100	16	(41)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		CuI (15 mol %), DMEDA (30 mol %), Cs_2CO_3, NMP, 150°, 24 h	 **I** + **II**	143

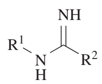
R	**I**	**II**
Me	(6)	(5)
t-Bu	(8)	(6)

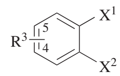
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
A. SYNTHESIS OF FIVE-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

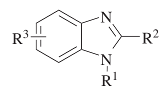
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{8-14}



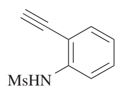


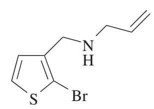
CuI (15 mol %), DMEDA (30 mol %), Cs_2CO_3, 150°, 16 h



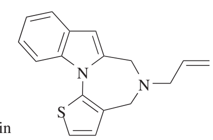
R^1	R^2	R^3	X^1	X^2	Solvent	Temp (°)	Time (h)		Refs.
Me	Ph	4-Me	I	Br	NMP	150	16	(48)	143
i-Pr	Ph	4-Me	I	Br	NMP	150	16	(24)	143
Ph	4-pyridyl	4-Me	I	Br	DMA	150	16	(56)	143
Ph	Ph	H	I	I	DMA	170	24	(58)	141
Ph	Ph	3-Cl	I	Cl	NMP	150	16	(29)	143
Ph	Ph	4-Me	I	Br	NMP	150	16	(56)	143
Ph	Ph	5-Me	Br	Cl	NMP	150	16	(20)	143
Ph	4-MeOC_6H_4	4-Me	I	Br	NMP	150	16	(0)	143
$4\text{-O}_2NC_6H_4$	Ph	4-Me	I	Br	NMP	150	16	(11)	143
Bn	Ph	4-Me	I	Br	NMP	150	16	(16)	143

C_8





1. CuI (2.5 mol %), $(H_2CO)_n$, dioxane, MW, 170°, 40 min
2. NaOMe, MW, 170°, 20 min



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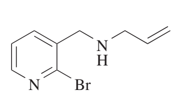
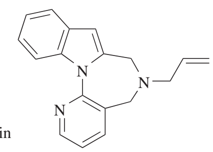


1. CuI (2.5 mol %), $(H_2CO)_n$, dioxane, MW, 170°, 40 min
2. NaOMe, MW, 170°, 20 min



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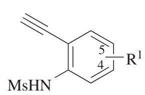
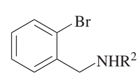
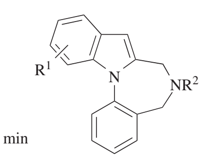
C_{8-9}



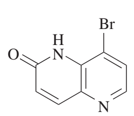


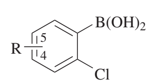
1. CuI (2.5 mol %), $(H_2CO)_n$, dioxane, MW, 170°, 40 min
2. NaOMe, MW, 170°, 20 min



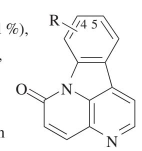
R^1	R^2		Refs.
H	Me	(51)	627
H	allyl	(81)	
H	*n*-Bu	(88)	
H	Bn	(83)	
5-Me	allyl	(85)	
4-CF_3	allyl	(53)	
5-CF_3	allyl	(81)	
5-$MeCO_2$	allyl	(23)	

C_8

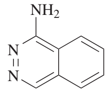


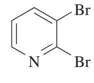


1. $Pd(dppf)Cl_2\bullet MeCl_2$ (2 mol %), K_2CO_3, dioxane/H_2O (3:1), reflux, 30 min
2. CuI (5 mol %), DMEDA (*x* mol %), 15 min

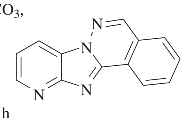


R	*x*		Refs.
H	10	(95)	185
4-F	10	(88)	
3-Cl	10	(82)	
4-Cl	10	(82)	
5-Cl	10	(77)	
6-Cl	10	(0)	
4-MeO	20	(92)	
6-MeO	20	(trace)	
4-Me	20	(92)	
4-CF_3	20	(78)	
5-CF_3	20	(71)	

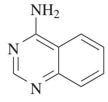


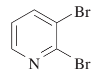


1. $Pd_2(dba)_3$ (4 mol %), Cs_2CO_3, DME, xantphos (9 mol %), reflux, 17 h
2. CuI (10 mol %), CDA (20 mol %), reflux, 8 h

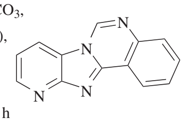


(65) 628





1. $Pd_2(dba)_3$ (6 mol %), Cs_2CO_3, DME, xantphos (13 mol %), reflux, 17 h
2. CuI (10 mol %), CDA (20 mol %), reflux, 8 h

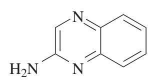


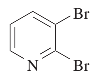
(93) 628

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

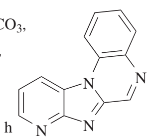
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_8



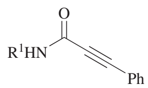


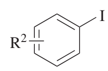
1. $Pd_2(dba)_3$ (4 mol %), Cs_2CO_3, DME, xantphos (9 mol %), reflux, 17 h
2. CuI (10 mol %), CDA (20 mol %), reflux, 8 h



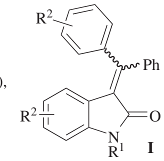
(99) 628

C_{10-16}



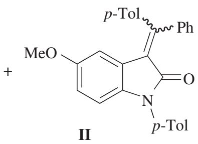


1. CuI (10 mol %), DMEDA (20 mol %), K_2CO_3, DMF/MeCN (1:1), 110°, 12 h
2. $Pd(OAc)_2$ (10 mol %), 100°, 12 h



I

\+

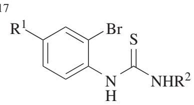


II

630

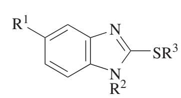
R^1	R^2	**I**	(*E*)/(*Z*)	**II**
Me	4-MeO	(33)	3:1	(—)
Ph	H	(45)	—	(—)
2-$MeOC_6H_4$	2-MeO	(32)	1:1	(—)
4-$MeOC_6H_4$	H	(27)	—	(—)
4-$MeOC_6H_4$	4-Me	(37)	2:1	(27)
2-MeC_6H_4	2-Me	(21)	3:1	(—)
3-MeC_6H_4	3-Me	(55)	2:1	(—)
4-MeC_6H_4	4-Me	(53)	2:1	(—)
Bn	4-MeO	(36)	2:1	(—)

C_{11-17}



Intramolecular

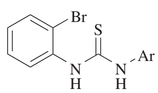
1. Et_3N, R^3X
2. CuI (5 mol %), phen (10 mol %), K_2CO_3, dioxane, 85°, time



631

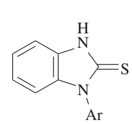
R^1	R^2	R^3X	Time (h)	
H	4-morphonlinyl	MeI	8	(86)
H	2-furylmethyl	MeI	12	(78)
H	2-pyridyl	MeI	8	(79)
H	Ph	CH_2=$CHCH_2I$	8	(88)
H	Ph	BnBr	12	(87)
H	Ph	4-$MeOC_6H_4CH_2Br$	20	(48)
H	4-FC_6H_4	MeI	4	(83)
H	4-$MeOC_6H_4$	MeI	4	(93)
H	3,4-$(MeO)_2C_6H_3CH_2CH_2$	MeI	20	(48)
H	3,5-$(MeO)_2C_6H_3$	MeI	4	(88)
H	4-MeC_6H_4	MeI	4	(91)
H	Bn	MeI	8	(81)
H	2,3-$Me_2C_6H_3$	MeI	4	(74)
H	4-*t*-BuC_6H_4	MeI	4	(78)
Br	Ph	CH_2=$CHCH_2I$	12	(87)
MeO	Ph	MeI	4	(82)
MeO	Ph	4-$O_2NC_6H_4CH_2Br$	20	(84)
MeO	Ph	4-$MeOC_6H_4CH_2Br$	20	(48)
MeO	Bn	EtI	12	(74)
Me	Ph	MeI	4	(85)
Me	4-F_6H_4	EtI	4	(81)
Me	4-Me_6H_4	EtI	4	(78)

C_{13-14}



Intramolecular

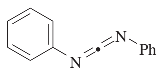
1. Et_3N, 4-$MeOC_6H_4CH_2Br$
2. CuI (5 mol %), phen (10 mol %), K_2CO_3, dioxane, 85°
3. TFA, reflux

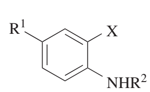


Ar	
Ph	(68)
4-FC_6H_4	(71)
4-MeC_6H_4	(72)

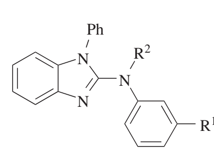
631

C_{13}





CuI (15 mol %), Cs_2CO_3, MeCN, 100°, 24 h



R^1	R^2	X	
H	H	Br	(62)
H	H	I	(81)
H	Me	I	(63)
Cl	H	I	(72)
Me	H	Br	(64)
Me	H	I	(70)

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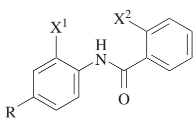
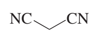
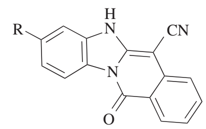
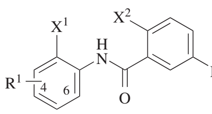
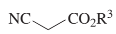
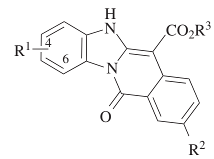
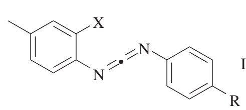
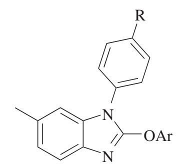
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
A. SYNTHESIS OF FIVE-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{13-14}				
		CuCl (10 mol %), Na_2CO_3, DMSO, 100°, 12 h		632
		CuCl (10 mol %), Na_2CO_3, DMSO, 100°, 12 h		632

R^1	X^1	X^2	
H	Br	Cl	(71)
H	Cl	Br	(70)
H	Br	Br	(85)
Me	Br	Br	(80)

R^1	R^2	X^1	X^2	R^3	
H	H	Br	Br	Me	(87)
H	H	Cl	Br	Et	(75)
H	H	Br	Cl	Et	(82)
H	H	Br	Br	Et	(90)
H	H	Br	Br	*n*-Bu	(87)
H	Cl	Br	Br	Me	(65)
H	Cl	Br	Br	Et	(78)
H	Cl	Br	Br	*n*-Bu	(65)
4-Me	H	Br	Br	Me	(89)
4-Me	H	Br	Br	Et	(91)
4-Me	H	Br	Br	*n*-Bu	(63)
4-Me	Cl	Br	Br	Me	(81)
5-MeO_2C	H	Br	Br	Me	(81)
5-MeO_2C	H	Br	Br	Et	(72)
5-MeO_2C	H	Br	Br	*n*-Bu	(72)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14-15}				
	Intramolecular	ArOH, CuI (10 mol %), DMG (20 mol %), K_3PO_4, DMSO, 90°, 24 h		183

R	X	Ar	
H	I	Ph	(76)
H	I	4-MeC_6H_4	(71)
H	Br	2-Np	(68)
Me	I	Ph	(72)

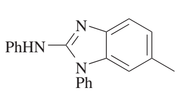
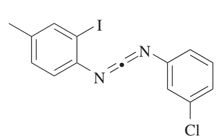
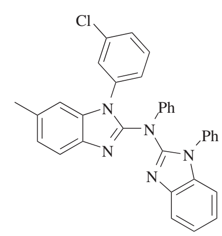
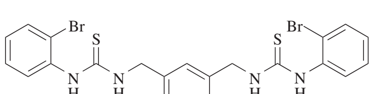
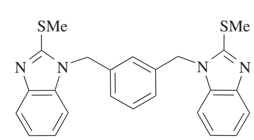
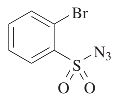
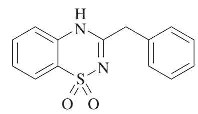
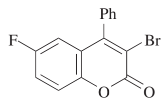
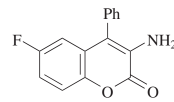
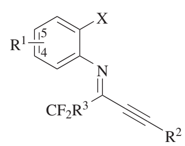
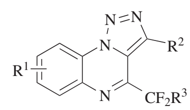
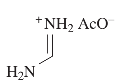
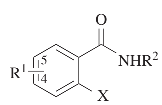
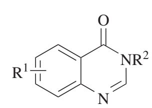
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
		CuI (15 mol %), Cs_2CO_3, MeCN, 100°, 24 h	 (62)	184
C_{22}				
		1. Et_3N, MeI 2. CuI (5 mol %), phen (10 mol %), K_2CO_3, dioxane, 85°, 20 h	 (54)	631

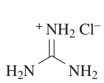
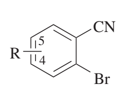
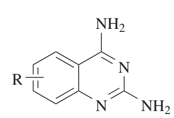
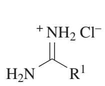
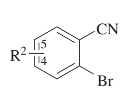
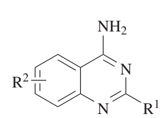
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
B. SYNTHESIS OF SIX-MEMBERED RINGS

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_0				
NH_4Cl		1. Ph—≡, CuI (10 mol %), Et_3N, $MeCl_2$, rt, 1 h 2. Phen (10 mol %), Cs_2CO_3, DMF, 80°, 16 h	 (77)	590
NaN_3		Cu (10 mol %), piperidine-2-carboxylic acid (30 mol %), ascorbic acid (20 mol %), EtOH, 100°, 3 h	 (43)	250
		CuI (10 mol %), L-Pro (20 mol %), DMSO		634

R^1	R^2	R^3	X	Temp (°)	Time (h)	
H	$AcOCH_2$	F	I	rt	10	(65)
H	MeO_2C	F	I	60	10	(56)
H	*n*-Bu	F	I	rt	0.5	(97)
H	*n*-Bu	Cl	I	60	2	(70)
H	*t*-Bu	F	I	rt	1	(91)
H	2-thienyl	F	I	60	10	(92)
H	Ph	F	Cl	130	10	(65)
H	Ph	F	Br	60	10	(95)
H	Ph	Cl	I	60	10	(70)
H	$4\text{-}ClC_6H_4$	F	I	80	10	(87)
H	$4\text{-}MeC_6H_4$	F	I	rt	0.5	(94)
4-F	Ph	F	I	60	10	(80)
$5\text{-}O_2N$	Ph	F	I	80	10	(70)
5-MeO	Ph	F	I	60	4	(87)
4-Me	Ph	F	I	rt	1.5	(90)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
		CuI (10 mol %), K_2CO_3, DMF, 80°, 6 h		635

R^1	R^2	X	
H	H	I	(82)
H	Me	Br	(3)
H	Me	I	(81)
H	Et	I	(63)
H	*i*-Pr	I	(55)
H	2-thiazolyl	I	(91)
H	Ph	I	(77)
H	$4\text{-}ClC_6H_4$	I	(56)
H	$4\text{-}BrC_6H_4$	I	(71)
H	$4\text{-}O_2NC_6H_4$	I	(20)
H	$2\text{-}MeOC_6H_4$	I	(72)
H	$3\text{-}MeOC_6H_4$	I	(73)
H	$4\text{-}MeOC_6H_4$	I	(83)
H	$2\text{-}MeC_6H_4$	I	(67)
H	$3\text{-}MeC_6H_4$	I	(62)
H	$4\text{-}MeC_6H_4$	I	(69)
H	$4\text{-}NCC_6H_4$	I	(66)
H	$4\text{-}AcC_6H_4$	I	(75)
H	Bn	I	(84)
4-Cl	H	I	(66)
5-Me	H	I	(69)

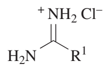
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMEDA (20 mol %), K_2CO_3, DMF, 80°, 12 h	 R: H (57); $4\text{-}O_2N$ (85); 5-Me (66)	636
C_{2-7}				
		CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, DMF, 80°, 12 h		636

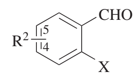
R^1	R^2	
Me	H	(69)
Me	$4\text{-}O_2N$	(63)
Me	5-Me	(75)
n-Pr	H	(79)
n-Pr	$4\text{-}O_2N$	(76)
n-Pr	5-Me	(79)
c-Pr	H	(72)
c-Pr	5-Me	(55)
Ph	H	(85)
Ph	5-Me	(67)

TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
B. SYNTHESIS OF SIX-MEMBERED RINGS (*Continued*)

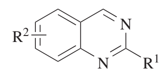
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{2-7}

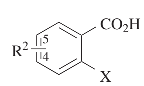




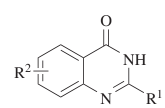
CuI (10 mol %), Cs_2CO_3



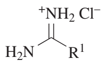
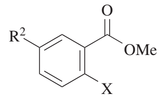
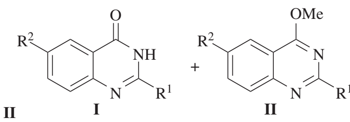
R^1	R^2	X	Additive	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
Me	H	Br	L-Pro (20 mol %)	DMF	110	24	(75)	140
Me	4-(OCH_2O)-5	Br	L-Pro (20 mol %)	DMF	110	24	(92)	140
n-Pr	H	Br	L-Pro (20 mol %)	DMF	110	24	(82)	140
n-Pr	4-(OCH_2O)-5	Br	L-Pro (20 mol %)	DMF	110	20	(95)	140
c-Pr	H	I	none	MeOH	60	18	(87)	637
5-pyrimidinyl	H	I	none	MeOH	60	18	(53)	637
2-pyridyl	H	I	none	MeOH	60	18	(59)	637
4-pyridyl	H	I	none	MeOH	60	18	(80)	637
Ph	H	Br	L-Pro (20 mol %)	DMF	110	24	(55)	140
Ph	H	I	none	MeOH	60	18	(89)	637
Ph	4-F	I	none	MeOH	60	18	(62)	637
Ph	4,5-$(MeO)_2$	I	none	MeOH	60	18	(89)	637
Ph	4-(OCH_2O)-5	Br	L-Pro (20 mol %)	DMF	110	20	(89)	140
4-FC_6H_4	H	I	none	MeOH	60	18	(82)	637
4-ClC_6H_4	H	I	none	MeOH	60	18	(88)	637
3-$O_2NC_6H_4$	H	I	none	MeOH	60	18	(83)	637
2-$MeOC_6H_4$	H	I	none	MeOH	60	18	(86)	637
3-$MeOC_6H_4$	H	I	none	MeOH	60	18	(83)	637
4-$MeOC_6H_4$	H	I	none	MeOH	60	18	(61)	637
2-MeC_6H_4	H	I	none	MeOH	60	18	(86)	637
3-MeC_6H_4	H	I	none	MeOH	60	18	(94)	637
4-MeC_6H_4	H	I	none	MeOH	60	18	(89)	637
4-$CF_3C_6H_4$	H	I	none	MeOH	60	18	(70)	637



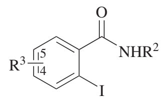
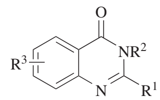
Catalyst (*x* mol %), Cs_2CO_3



R^1	R^2	X	Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
Me	H	Br	$Cu(acac)_2$	10	Fe_2O_3 (20 mol %)	DMSO	MW, 130	0.5	(48)	262
Me	H	Br	CuI	20	none	DMF	rt	12	(81)	142
Me	H	I	CuI	20	none	DMF	rt	12	(89)	142
Me	4-Cl	Br	CuI	20	none	DMF	rt	12	(83)	142
Me	5-O_2N	Br	CuI	20	none	DMF	rt	12	(69)	142
n-Pr	H	Cl	CuI	20	none	DMF	rt	12	(79)	142
n-Pr	H	Br	CuI	20	none	DMF	rt	12	(79)	142
n-Pr	H	I	CuI	20	none	DMF	rt	12	(90)	142
n-Pr	4-Cl	Br	CuI	20	none	DMF	rt	12	(87)	142
n-Pr	5-O_2N	Br	CuI	20	none	DMF	rt	12	(89)	142
n-Pr	4-(OCH_2O)-5	Br	CuI	20	none	DMF	rt	12	(40)	142
c-Pr	H	Br	CuI	20	none	DMF	rt	12	(84)	142
c-Pr	4-Cl	Br	CuI	20	none	DMF	rt	12	(75)	142
c-Pr	5-O_2N	Br	CuI	20	none	DMF	rt	12	(68)	142
1-pyrrolidinyl	H	I	CuI	20	none	DMF	rt	12	(72)	142
1-piperidinyl	H	I	CuI	20	none	DMF	rt	12	(70)	142
Ph	H	Cl	CuI	20	none	DMF	rt	12	(79)	142
Ph	H	Br	CuI	20	none	DMF	rt	12	(79)	142
Ph	H	I	CuI	20	none	DMF	rt	12	(97)	142
Ph	4-Cl	Br	CuI	20	none	DMF	rt	12	(66)	142
Ph	5-O_2N	Br	CuI	20	none	DMF	rt	12	(79)	142
Ph	4-(OCH_2O)-5	Br	CuI	20	none	DMF	rt	12	(79)	142

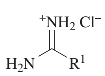
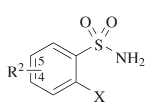
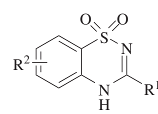
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-7}				
		CuI (10 mol %), L-Pro (20 mol%), Cs_2CO_3, DMF, 110°		140

R^1	R^2	X	Time (h)	I	II
Me	H	Cl	20	(90)	(0)
Me	H	Br	16	(91)	(0)
Me	Cl	Br	16	(87)	(0)
n-Pr	H	Cl	20	(77)	(18)
n-Pr	H	Br	16	(74)	(22)
n-Pr	Cl	Br	16	(95)	(0)
Ph	Cl	Br	16	(86)	(0)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), K_2CO_3, DMF, 80°		635

R^1	R^1	R^3	Time (h)	
Me	H	H	6	(78)
Me	H	5-Cl	6	(65)
Me	H	5-Me	6	(60)
Me	Me	H	6	(52)
Me	Ph	H	6	(69)

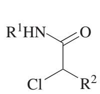
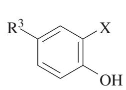
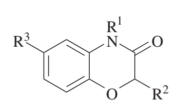
R^1	R^1	R^3	Time (h)	
Ph	H	H	6	(81)
Ph	H	4-Cl	16	(86)
Ph	H	6-MeO	6	(65)
Ph	H	$6\text{-}O_2N$	16	(86)
Ph	H	5-Me	6	(66)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-4}				
		CuI (15 mol %), DMEDA (30 mol %), Cs_2CO_3, DMA, 170°		638

R^1	R^2	X	Time (h)	
Me	H	Br	24	(77)
Me	5-Br	Br	12	(70)
Me	5-Me	I	24	(81)
Me	$4\text{-}CF_3$	Br	10	(77)
Me	$4,5\text{-}Me_2$	Br	10	(70)

R^1	R^2	X	Time (h)	
n-Pr	H	Br	24	(80)
n-Pr	5-Br	Br	12	(68)
n-Pr	5-Me	I	10	(78)
n-Pr	$4\text{-}CF_3$	Br	10	(75)
n-Pr	$4,5\text{-}Me_2$	Br	10	(65)

R^1	R^2	X	Time (h)	
c-Pr	H	Br	24	(75)
c-Pr	5-Br	Br	12	(65)
c-Pr	5-Me	I	10	(80)
c-Pr	$4\text{-}CF_3$	Br	10	(80)
c-Pr	$4,5\text{-}Me_2$	Br	10	(80)

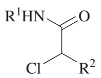
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-9}				
		CuI (*x* mol %), Cs_2CO_3		

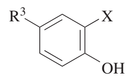
R^1	R^2	R^3	X	*x*	Additive(s)	Solvent	Temp (°)	Time		Refs.
H	H	Cl	Br	10	phen (10 mol %)	dioxane	90	24 h	(55)	179
H	H	Me	I	10	phen (10 mol %)	dioxane	90	6 h	(71)	179
H	H	*t*-Bu	I	10	phen (10 mol %)	dioxane	90	24 h	(80)	179
$HOCH_2CH_2$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(70)	180
n-Pr	H	H	I	20	DBU	DMSO	MW, 130	10 min	(82)	180
$c\text{-}PrCH_2$	H	Me	I	20	DBU	DMSO	MW, 130	10 min	(65)	180
n-Bu	H	H	Br	10	phen (10 mol %)	dioxane	reflux	24 h	(55)	179
n-Bu	H	H	I	10	phen (10 mol %)	dioxane	90	24 h	(84)	179
n-Bu	H	Cl	I	10	phen (10 mol %)	dioxane	reflux	24 h	(70)	179
n-Bu	H	Me	I	10	phen (10 mol %)	dioxane	90	24 h	(51)	179
n-Bu	H	*t*-Bu	I	10	phen (10 mol %)	dioxane	reflux	24 h	(98)	179
n-Bu	Et	H	I	10	phen (10 mol %)	dioxane	90	24 h	(73)	179
2-pyridyl	H	H	I	20	DBU	DMSO	MW, 130	10 min	(67)	180
2-pyridyl	H	H	I	10	phen (10 mol %)	dioxane	90	6 h	(45)	179

TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
B. SYNTHESIS OF SIX-MEMBERED RINGS (*Continued*)

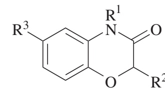
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

C_{2-9}

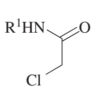


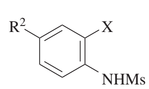


CuI (x mol %), Cs_2CO_3

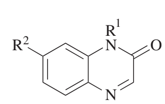


R^1	R^2	R^3	X	x	Additive	Solvent	Temp (°)	Time		Refs.
Ph	H	H	I	10	phen (10 mol %)	dioxane	90	24 h	(97)	179
Ph	H	H	I	20	DBU	DMSO	MW, 130	10 min	(68)	180
Ph	H	Cl	I	10	phen (10 mol %)	dioxane	90	24 h	(83)	179
Ph	H	Me	I	10	phen (10 mol %)	dioxane	90	24 h	(98)	179
Ph	H	*t*-Bu	I	10	phen (10 mol %)	dioxane	90	24 h	(99)	179
Ph	Me	H	Br	10	phen (10 mol %)	dioxane	reflux	24 h	(97)	179
Ph	Me	F	I	10	phen (10 mol %)	dioxane	reflux	24 h	64)	179
$3\text{-}ClC_6H_4$	H	H	I	10	phen (10 mol %)	dioxane	90	24 h	(71)	179
$4\text{-}BrC_6H_4$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(75)	180
$4\text{-}BrC_6H_4$	H	*t*-Bu	I	20	DBU	DMSO	MW, 130	10 min	(82)	180
$2\text{-}MeOC_6H_4$	H	H	Br	20	DBU	DMSO	MW, 130	20 min	(86)	180
$2\text{-}MeOC_6H_4$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(82)	180
$2\text{-}MeOC_6H_4$	H	*t*-Bu	I	20	DBU	DMSO	MW, 130	10 min	(75)	180
$3\text{-}MeOC_6H_4$	H	H	Br	20	DBU	DMSO	MW, 130	20 min	(51)	180
$3\text{-}MeOC_6H_4$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(82)	180
$3\text{-}MeOC_6H_4$	H	*t*-Bu	I	20	DBU	DMSO	MW, 130	10 min	(82)	180
$4\text{-}MeOC_6H_4$	H	H	Br	10	phen (10 mol %)	dioxane	reflux	24 h	(86)	179
$4\text{-}MeOC_6H_4$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(86)	180
$4\text{-}MeOC_6H_4$	Me	H	I	20	DBU	DMSO	MW, 130	10 min	(73)	180
$4\text{-}MeOC_6H_4$	Me	Me	Br	20	DBU	DMSO	MW, 130	10 min	(61)	180
$2\text{-}MeC_6H_4$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(85)	180
$2\text{-}MeC_6H_4$	H	Me	Br	20	DBU	DMSO	MW, 130	10 min	(55)	180
$2\text{-}MeC_6H_4$	Me	H	I	20	DBU	DMSO	MW, 130	10 min	(70)	180
$3\text{-}MeC_6H_4$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(84)	180
$3\text{-}MeC_6H_4$	H	Me	Br	20	DBU	DMSO	MW, 130	10 min	(56)	180
$3\text{-}MeC_6H_4$	Me	H	I	20	DBU	DMSO	MW, 130	10 min	(75)	180
$4\text{-}MeC_6H_4$	H	H	Br	10	phen (10 mol %)	dioxane	reflux	24 h	(80)	179
$4\text{-}MeC_6H_4$	H	H	Br	20	DBU	DMSO	MW, 130	20 min	(89)	180
$4\text{-}MeC_6H_4$	H	H	I	10	phen (10 mol %)	dioxane	90	24 h	(98)	179
$4\text{-}MeC_6H_4$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(89)	180
$4\text{-}MeC_6H_4$	H	Me	Br	20	DBU	DMSO	MW, 130	10 min	60)	180
$4\text{-}MeC_6H_4$	Me	H	I	20	DBU	DMSO	MW, 130	10 min	(82)	180
$4\text{-}CF_3C_6H_4$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(72)	180
$4\text{-}EtO_2CC_6H_4$	H	H	I	20	DBU	DMSO	MW, 130	10 min	(75)	180
$4\text{-}EtO_2CC_6H_4$	H	*t*-Bu	I	20	DBU	DMSO	MW, 130	10 min	(82)	180
$4\text{-}EtO_2CC_6H_4$	Me	H	I	20	DBU	DMSO	MW, 130	10 min	(82)	180
$4\text{-}EtO_2CC_6H_4$	Me	Me	Br	20	DBU	DMSO	MW, 130	10 min	(59)	180
Bn	H	H	I	10	phen (10 mol %)	dioxane	90	24 h	(71)	179





CuI (x mol %),
DMCDA (y mol %)



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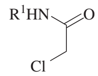
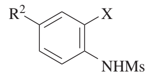
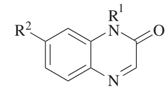
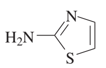
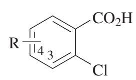
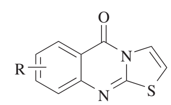
R^1	R^2	X	x	y	Additive	Solvent	Temp (°)	Time (h)	
H	Me	Br	20	40	K_3PO_4	DMF	115	36	(52)
n-Pr	H	I	7	14	Cs_2CO_3	dioxane	100	9	(62)
n-Pr	Cl	I	20	40	K_3PO_4	DMF	115	36	(60)
n-Bu	Me	I	7	14	Cs_2CO_3	dioxane	100	9	(68)
Ph	Cl	I	7	14	K_3PO_4	dioxane	100	13	(76)
$3\text{-}ClC_6H_4$	Me	I	7	14	K_3PO_4	dioxane	100	13	(60)
$4\text{-}MeOC_6H_4$	H	I	7	14	K_3PO_4	dioxane	100	13	(86)
$4\text{-}MeOC_6H_4$	CF_3O	Br	20	40	K_3PO_4	dioxane	115	36	(55)

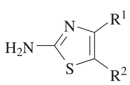
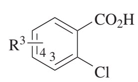
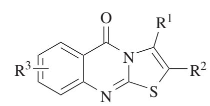
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
B. SYNTHESIS OF SIX-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
Continued from previous page.				
C_{2-9}				
		CuI (x mol %), DMCDA (y mol %)		639

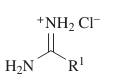
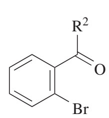
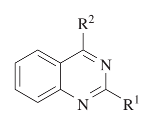
R^1	R^2	X	x	y	Additive	Solvent	Temp (°)	Time (h)	
4-$MeOC_6H_4$	Me	I	7	14	K_3PO_4	dioxane	100	13	(91)
4-MeC_6H_4	H	Br	20	40	K_3PO_4	dioxane	115	24	(58)
4-MeC_6H_4	H	I	7	14	K_3PO_4	dioxane	100	13	(91)
4-MeC_6H_4	Cl	I	7	14	K_3PO_4	dioxane	100	13	(87)
4-MeC_6H_4	CF_3O	Br	20	40	K_3PO_4	DMF	115	36	(61)
4-MeC_6H_4	Me	I	7	14	K_3PO_4	dioxane	100	13	(94)
Bn	H	I	7	14	Cs_2CO_3	dioxane	100	9	(80)
Bn	Cl	I	20	40	K_3PO_4	DMF	reflux	36	(70)
Bn	Me	I	7	14	Cs_2CO_3	dioxane	100	9	(88)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		Cu (7.5 mol %), K_2CO_3, DMF, rt		242

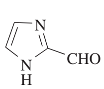
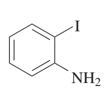
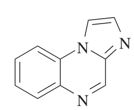
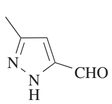
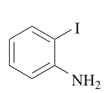
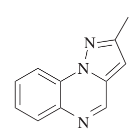
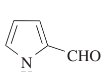
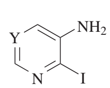
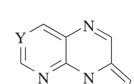
R	Time (min)	
H	15	(88)
3-F	25	(90)
6-F	25	(86)
3-Cl	25	(86)
6-Me	15	(85)
3,5-Me_2	15	(90)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-5}				
		Cu (7.5 mol %), K_2CO_3, DMF, rt		242

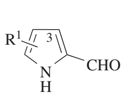
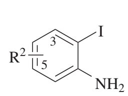
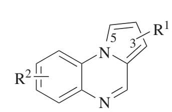
R^1	R^2	R^3	Time (min)	
H	Me	6-F	25	(91)
Me	H	H	15	(88)
Me	Me	6-Me	15	(91)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-7}				
		CuI (10 mol %), L-Pro (20 mol %), Cs_2CO_3, DMF, 110°		140

R^1	R^2	Time (h)	
n-Pr	Me	20	(86)
n-Pr	Ph	24	(81)
Ph	Me	20	(84)
Ph	Ph	24	(81)

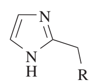
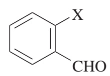
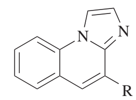
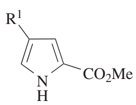
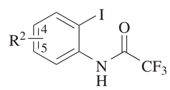
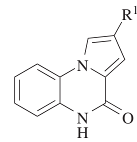
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CuI (10 mol %), sparteine (20 mol %), K_3PO_4, NMP, 130°, 24 h	 (51)	640
C_5				
		CuI (10 mol %), sparteine (20 mol %), K_3PO_4, NMP, 130°, 24 h	 (83)	640
		CuI (10 mol %), sparteine (20 mol %), K_3PO_4, NMP, 130°, 24 h		640

Y	
N	(63)
CH	(78)

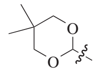
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-11}				
		CuI (10 mol %), sparteine (20 mol %), K_3PO_4, NMP, 130°, 24 h		640

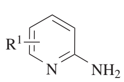
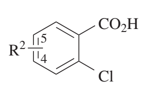
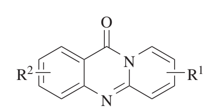
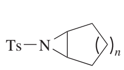
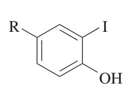
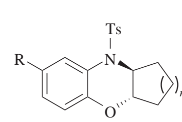
R^1	R^2	Time (h)	
H	H	24	(83)
H	5-F	24	(83)
H	4-CF_3	24	(69)
H	4-NC–	24	(48)
H	4-MeO_2C	24	(61)
3,5-Me_2	H	36	(82)
5-Ph	H	36	(78)

TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
B. SYNTHESIS OF SIX-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-11} 		CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 8 h		641
C_{5-7} 		1. CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 80°, time 1 2. H_2O, 60°, time 2		642

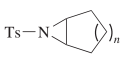
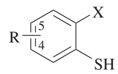
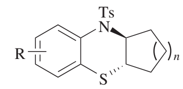
R	X	Temp (°)	
NC–	Cl	80	(35)
NC–	I	rt	(53)
Bz	Cl	110	(23)
Bz	Br	80	(62)
Bz	I	rt	(75)

R^1	R^2	Time 1 (h)	Time 2 (h)	
H	H	23	11	(93)
H	4-F	40	10	(75)
H	4-MeO	23	12	(97)
H	4-Me	23	11	(93)
H	4-Ac	36	15	(44)
Cl	H	23	11	(85)
Cl	4-MeO	20	15	(84)
	5-Ac	36	15	(72)
MeO_2C	H	35	12	(86)
MeO_2C	5-MeO	29	13	(72)
Et	H	23	11	(83)
Et	4-MeO	20	12	(81)
Ac	H	25	11	(84)
Ac	4-Me	26	15	(88)
Ac	5-Et	38	12	(89)

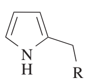
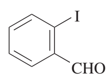
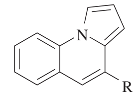
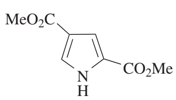
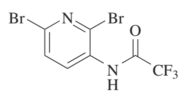
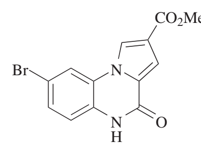
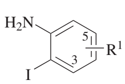
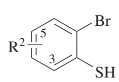
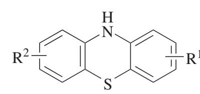
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		Cu (8 mol %), K_2CO_3, DMF, reflux, 6 h		643
C_{5-8} 		CuI (2.5 mol %), EDA (5 mol %), K_2CO_3, DMF, 110°		182

R^1	R^2	
H	H	(64)
H	4-Cl	(49)
H	3-O_2N	(52)
H	4-O_2N	(25)
H	5-O_2N	(72)
H	3,5-$(O_2N)_2$	(84)
H	5-MeO	(72)
3-O_2N	5-O_2N	(45)
5-O_2N	5-O_2N	(77)

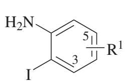
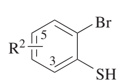
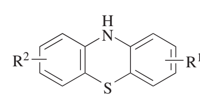
n	R	Time (h)	
1	H	20	(78)
1	Cl	12	(89)
2	H	15	(99)
2	Cl	14	(94)
2	*t*-Bu	16	(85)
3	H	13	(80)
3	Cl	15	(92)
3	*t*-Bu	16	(89)
3	Ph	16	(92)
4	H	26	(48)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-8} 		CuI (2.5 mol %), EDA (5 mol %), K_2CO_3, dioxane, 100°, 48 h		181

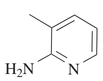
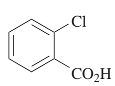
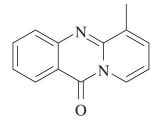
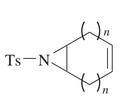
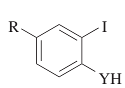
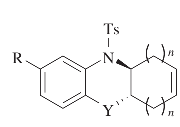
n	R	X	Time (h)	
1	H	Cl	48	(60)
1	H	Br	28	(92)
1	4-Cl	Cl	38	(70)
1	5-Me	Br	21	(85)
2	H	Cl	32	(74)
2	H	Br	17	(97)
2	H	I	12	(97)
2	4-Cl	Cl	48	(82)
2	5-Me	Br	24	(92)
3	H	Br	48	(74)
3	H	I	24	(74)
4	H	Br	48	(94)
4	5-Me	Br	28	(65)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		CuI (10 mol %), L-Pro (20 mol %), Cs_2CO_3, DMSO, 50°, 8 h	 R: NC– (30); EtO_2C (25)	641
		1. CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 80°, 13 h 2. H_2O, 60°, 13 h	 (77)	642
		CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, DMSO, 90°		644

R^1	R^2	Time (h)	
H	3,5-Me_2	70	(46)
4-Cl, 6-F	H	48	(80)
4-Cl, 6-F	3,5-Me_2	48	(81)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-8} 		1. CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, $MeOCH_2CH_2OH$, 90°, time 1 2. 110°, time 2		644

R^1	R^2	Time 1 (h)	Time 2 (h)	
5-F	H	28	72	(85)
5-Cl	H	28	72	(85)
4-O_2N	H	30	72	(84)
4-MeO	H	40	48	(73)
5-MeO	H	40	50	(71)
5-Me	H	40	60	(75)
4-CF_3	H	26	72	(86)
5-CF_3	H	28	72	(83)
5-CF_3	5-Me	26	72	(85)
4-NC–	H	30	72	(82)
4-MeO_2C	H	35	68	(85)
4,5-Me_2	H	48	60	(64)
4-Ac	H	30	67	(77)
4-Ac	4-F	30	72	(84)
5-Ac	H	30	70	(79)
5-Ac	5-Me	28	70	(88)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		Cu (8 mol %), K_2CO_3, DMF, reflux, 6 h	 (54)	643
C_{6-8} 		CuI (2.5 mol %), EDA (5 mol %), K_2CO_3, DMF, 110°		182

n	R	Y	Time (h)	
1	H	O	10	(93)
1	Cl	O	14	(88)
1	Ph	O	16	(94)
1	H	S	24	(74)
2	H	O	12	(91)
2	Cl	O	16	(98)

TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
B. SYNTHESIS OF SIX-MEMBERED RINGS (*Continued*)

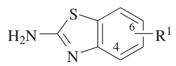
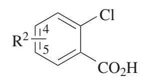
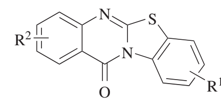
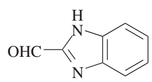
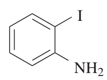
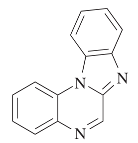
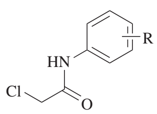
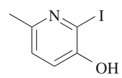
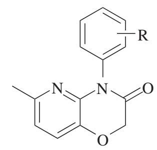
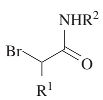
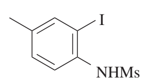
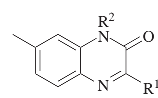
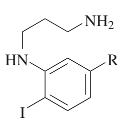
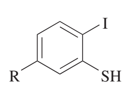
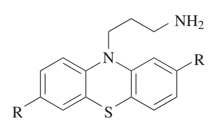
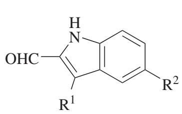
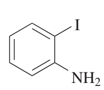
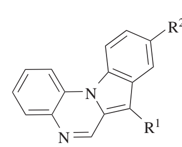
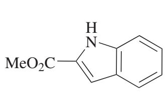
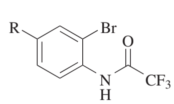
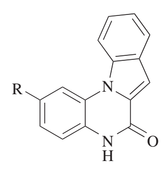
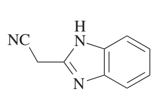
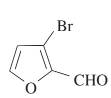
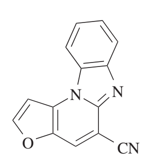
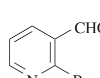
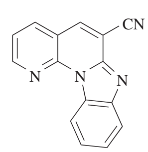
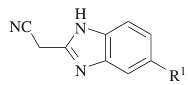
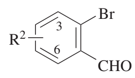
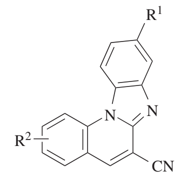
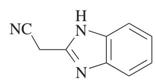
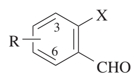
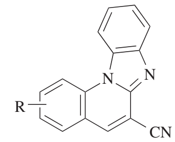
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8}				
		Cu (7.5 mol %), K_2CO_3, DMF, rt, 25 min	 R^1 / R^2: H, H (85) H, 4-F (93) H, 4-Cl (83) H, 5-Cl (95) H, 4-O_2N (86) H, 5-O_2N (92) 6-MeO, H (92) 6-EtO, H (90) 4-Me, H (94) 6-Me, H (94)	242
C_8				
		CuI (10 mol %), sparteine (20 mol %), K_3PO_4, NMP, 130°, 24 h	 (50)	640
		CuI (20 mol %), Cs_2CO_3, DBU, DMSO, MW, 130°, 10 min	 R: 4-MeO (59) 2-Me (78) 3-Me (65) 4-Me (71)	180
C_{9-11}				
		CuI (20 mol %), DMCDA (40 mol %), Cs_2CO_3, dioxane, reflux, 36 h	 R^1 / R^2: Me, Ph (51) Et, Bn (35)	639
		1. CuI (20 mol %), L-Pro (40 mol %), K_2CO_3, $MeOCH_2CH_2OH$, 90° 2. 110°	 R: Cl (78) CF_3 (81) Ac (75)	644
C_{9-10}				
		CuI (10 mol %), sparteine (20 mol %), K_3PO_4, NMP, 130°, 24 h	 R^1 / R^2: H, H (71) H, OMe (64) Me, F (78)	640
C_9				
		1. CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 80°, 38 h 2. H_2O, 60°, 12 h	 R: Me (74) Ac (63)	642
		CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 80°, 6 h	 (62)	641
		CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 80°, 6 h	 (93)	641

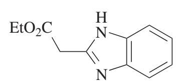
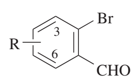
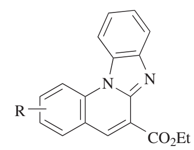
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
B. SYNTHESIS OF SIX-MEMBERED RINGS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10}				
		1. Piperidine, dioxane, rt 2. CuI (10 mol %), phen (20 mol %), K_2CO_3, 90°, 7 h		645

R^1	R^2	
H	H	(84)
H	5-Cl	(79)
H	5-HO	(43)
H	5-MeO	(75)
H	4-Me	(68)
Cl	H	(81)
Me	H	(88)
Me	5-MeO	(72)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO		641

R	X	Temp (°)	Time (h)	
H	Br	80	6	(87)
4-Cl	Cl	80	6	(50)
5-Cl	Br	80	6	(91)
5-Br	I	rt	8	(82)
5-O_2N	I	rt	8	(85)
5-HO	I	50	8	(89)
5-MeO	I	50	8	(89)
3,4-$(MeO)_2$	Cl	110	8	(47)
4,5-$(MeO)_2$	Br	80	6	(43)
5-Me	Br	80	6	(45)
5-CF_3	Br	80	6	(81)
5-NC–	I	rt	8	(90)
4-MeO_2C	I	rt	8	(85)
4,5-Me_2	I	50	8	(85)
3-$(CH{=}CH)_2$-4	Br	80	6	(80)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Piperidine, dioxane, rt 2. CuI (10 mol %), phen (20 mol %), K_2CO_3, 90°, 7 h	 R: H (40); 4-Cl (45); 5-Cl (37); 5-MeO (20)	645

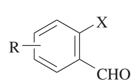
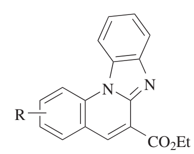
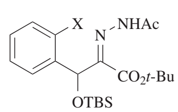
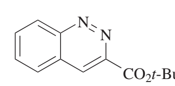
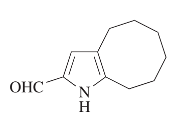
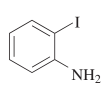
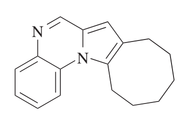
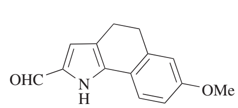
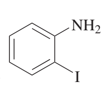
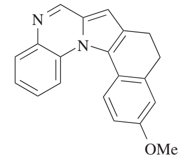
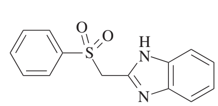
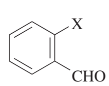
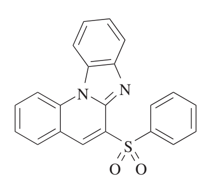
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 8 h	 X / Temp (°): Cl 110 (30); Br 80 (60); I rt (72)	641
C_{11}				
	Intramolecular	CuI (2 eq), CsOAc, DMSO, rt	 X / Time: Br 15 h (30); I 10 min (100)	580
		CuI (10 mol %), sparteine (20 mol %), K_3PO_4, NMP, 130°, 236 h	 (74)	640
C_{13}				
		CuI (10 mol %), sparteine (20 mol %), K_3PO_4, NMP, 130°, 48 h	 (63)	640
C_{14}				
		CuI (10 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 80°, 8 h	 X: Br (62); I (65)	641

TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
B. SYNTHESIS OF SIX-MEMBERED RINGS (*Continued*)

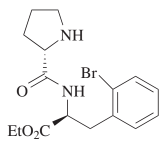
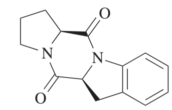
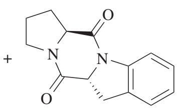
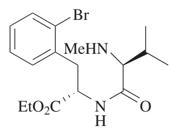
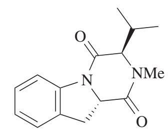
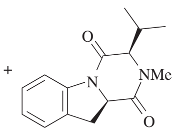
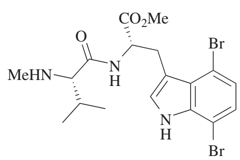
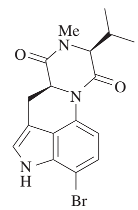
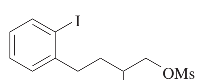
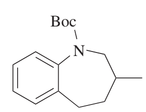
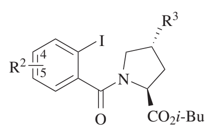
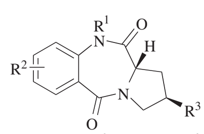
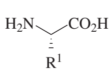
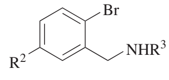
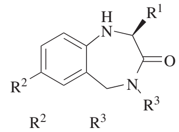
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
	Intramolecular	CuI (1 eq), Cs_2CO_3, DMSO, 90°, 12 h	 (48) +  (12)	576
	Intramolecular	CuI (1 eq), Cs_2CO_3, DMSO, 90°, 12 h	 (59) +  (18)	576
C_{16}				
	Intramolecular	CuI (1 eq), Cs_2CO_3, DMSO, 90°, 12 h	 (63)	576

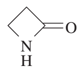
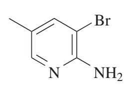
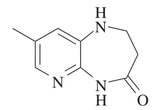
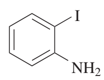
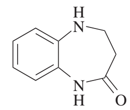
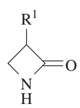
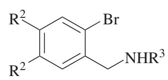
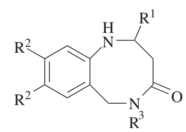
TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
C. SYNTHESIS OF SEVEN- AND HIGHER-MEMBERED RINGS

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_0				
H_2NBoc		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, 16 h	 (57)	607
C_{2-8}				
H_2NR^1		1. Cu_2O (20 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 80°, 24 h 2. 1 N HCl, 110°, 5 h		646

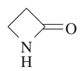
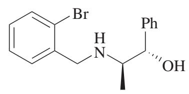
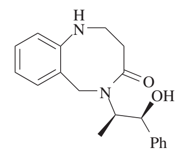
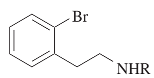
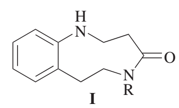
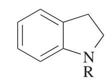
R^1	R^2	R^3	
$BocHNCH_2CH_2$	H	H	(62)
$BocHNCH_2CH_2$	5-Cl	TBSO	(50)
t-BuO_2CCH_2	H	TBSO	(66)
n-Pr	H	H	(76)
allyl	H	H	(82)
c-Pr	H	H	(63)
$TBSO(CH_2)_3$	H	H	(46)
c-$PrCH_2$	H	H	(70)
Bn	5-F	H	(56)
Bn	5-Cl	H	(81)
Bn	4,5-$(MeO)_2$	H	(85)
Bn	5-Me	H	(80)
4-$MeOC_6H_4CH_2$	H	H	(60)
3,4-$(OCH_2O)C_6H_3CH_2$	H	H	(81)
3,4,5-$(MeO)_3C_6H_2$	H	H	(64)
3,4,5-$(MeO)_3C_6H_2$	4,5-$(MeO)_2$	H	(75)
4-$CF_3C_6H_4CH_2$	H	H	(75)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-11}				
		1. CuI (10 mol %), Cs_2CO_3, DMF, 90°, 24 h 2. DPPA, 5°, 8 h		176

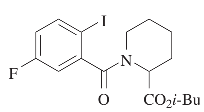
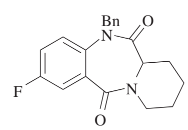
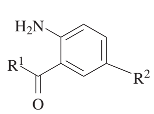
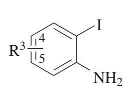
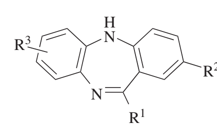
R^1	R^2	R^3	
Me	H	Bn	(50)
i-Pr	H	allyl	(52)
i-Pr	H	n-Bu	(57)
i-Pr	H	Bn	(58)
i-Pr	F	Bn	(48)
i-Pr	O_2N	Bn	(44)
i-Pr	MeO	Bn	(35)
i-Pr	MeO_2C	Bn	(48)
Bn	H	Bn	(51)
4-$HOC_6H_4CH_2$	H	Bn	(52)
3-indolylmethyl	H	Bn	(40)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		1. Cu (5 mol %), K_2CO_3, toluene, DMEDA (10 mol %), 100°, 24 h 2. Ti(O*i*-Pr)$_4$ (50 mol %), dioxane, 110°, 24 h	 (59)	177
		1. Cu (5 mol %), K_2CO_3, toluene, DMEDA (10 mol %), 100°, 24 h 2. Ti(O*i*-Pr)$_4$ (50 mol %), dioxane, 110°, 24 h	 (92)	177
C_{3-9}				
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 24 h		177

R^1	R^2	R^3	
H	H	H	(96)
H	H	HO(CH$_2$)$_5$	(90)
H	MeO	Bn	(90)
Ph	H	H	(88)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		1. CuI (5 mol %), K_2CO_3, toluene, DMEDA (10 mol %), 110°, 24 h 2. AcOH, THF, 60°, 4 h	 (90)	177
		CuI (5 mol %), K_2CO_3, toluene, 110°, 24 h	 **I** +  **II**	177

R	Additive	I	II
H	none	(68)	(18)
Bn	DMEDA (10 mol %)	(78)	(17)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
H_2NBn		1. Cu_2O (20 mol %), L-Pro (20 mol %), K_2CO_3, DMSO, 80°, 24 h 2. 1 N HCl, 110°, 5 h	 (65)	646
C_{7-14}				
		Cu_2O (10 mol %), K_2CO_3, xylene, 145°		346

R^1	R^2	R^3	Time (h)	
H	H	4-Me	7	(60)
Me	H	4-Cl	4.5	(85)
Me	H	4-Br	6	(75)
Me	H	4-Me	8	(88)
Me	H	4,5-Me$_2$	8	(90)
Ph	H	4-Me	5	(80)

R^1	R^2	R^3	Time (h)	
Ph	Cl	4-Me	8	(80)
Ph	Cl	4,5-Me$_2$	2.5	(78)
Ph	Me	4-Cl	7	(80)
Ph	Me	4,5-Me$_2$	2.5	(76)
3-MeC$_6$H$_4$	Cl	H	20	(40)
3-MeC$_6$H$_4$	Cl	4-Br	13	(68)
3-MeC$_6$H$_4$	Cl	4-Me	6	(82)

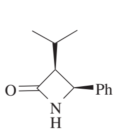
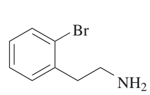
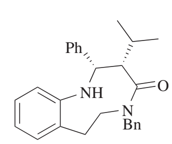
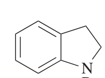
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
		1. CuI (5 mol %), K_2CO_3, toluene, DMEDA (10 mol %), 110°, 24 h 2. AcOH, NEt_3, dioxane, 110°, 24 h	 (78) +  (17)	177

TABLE 27. *N*-ARYLATIONS IN MULTI-STEP REACTIONS (*Continued*)
C. SYNTHESIS OF SEVEN- AND HIGHER-MEMBERED RINGS (*Continued*)

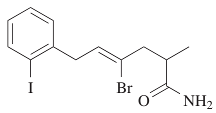
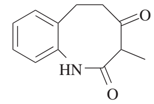
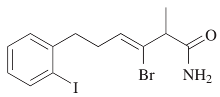
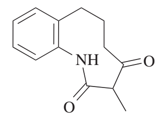
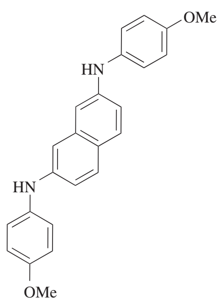
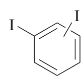
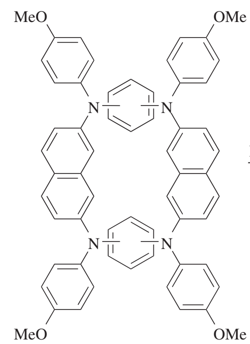
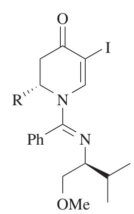
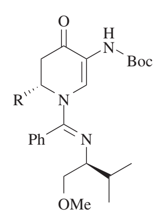
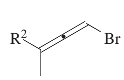
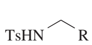
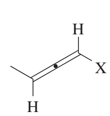
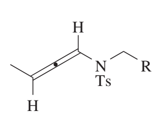
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
	Intramolecular	1. CuI (10 mol %), DMG (20 mol %), K_2CO_3, MeCN, reflux, 12 h 2. 2 N HCl, THF	 (90)	603
	Intramolecular	1. CuI (10 mol %), DMG (20 mol %), K_2CO_3, MeCN, reflux, 12 h 2. 2 N HCl, THF	 (99)	603
		Cu (4 eq), K_2CO_3, Ph_2O, 190°, 48 h	 Isomer 1,3 (21) 1,4 (28)	633

TABLE 28. *N*-VINYLATION OF AMINES

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_0				
H_2NBoc		CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 90°		647
C_{2-10}				
$TsNHR^1$		**8** (15 mol %), DMEDA (13 mol %), Cs_2CO_3, 24 h		625
C_{5-7}				
		Catalyst (*x* mol %), DMEDA (*y* mol %), Cs_2CO_3, toluene		

R	
Et	(93)
CH_2=CH(CH_2)$_5$	(93)

R^1	R^2	Solvent	Temp (°)	
t-BuO_2CCH_2	Me	dioxane	reflux	(41)
CH_2=CHCH_2	Me	toluene	80	(89)
(*E*)-MeCH=CHCH_2	Me	toluene	80	(82)
Me_2C=CHCH_2	Me	toluene	80	(74)
Me_2C=CHCH_2	Et	toluene	80	(67)
(*E*)-*n*-PrCH_2CH=CH	Me	toluene	80	(72)

R	R^2	Solvent	Temp (°)	
Ph	Me	dioxane	reflux	(56)
2-AcC_6H_4	Me	dioxane	reflux	(63)
(*E*)-PhCH_2CH=CH	Me	toluene	40	(53)
(*E*)-4-Me$C_6H_4$$CH_2$CH=CH	Me	toluene	40	(20)
(*E*)-4-$CF_3$$C_6H_4$$CH_2$CH=CH	Me	toluene	40	(52)

R	X	Catalyst	*x*	*y*	Temp (°)	Time (h)		Refs.
Me_2C=CH_2	Br	**8**	15	30	80	24	(35)	625
Ph	I	CuCN	10	20	50	—	(60)	91

TABLE 28. *N*-VINYLATION OF AMINES (*Continued*)

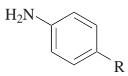
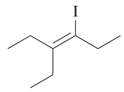
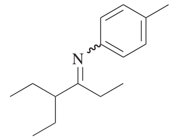
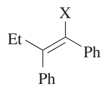
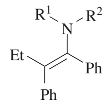
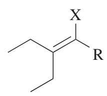
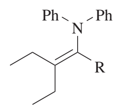
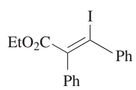
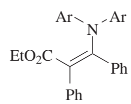
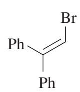
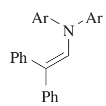
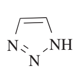
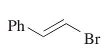
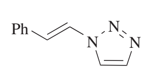
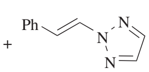
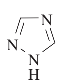
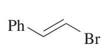
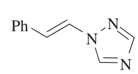
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{6-7}				
		CuI (10 mol %), DMEDA (20 mol %), NaO*t*-Bu, toluene, 140°, 24 h	 R | (*E*)/(*Z*) H (64) 1:1 Me (88) 1:1	88
C_{7-14}				
HNR^1R^2		CuI (10 mol %), DMEDA (20 mol %), NaO*t*-Bu, toluene, 140°	 R^1 | R^2 | X | Time (h) Me | Ph | I | 36 (85) Et | Ph | I | 36 (85) Ph | Ph | Br | 16 (60) Ph | Ph | I | 16 (89) Ph | 1-Np | I | 16 (87) 4-ClC_6H_4 | 4-ClC_6H_4 | I | 48 (81) 4-MeC_6H_4 | 4-MeC_6H_4 | I | 48 (81)	88
C_{12}				
$HNPh_2$		CuI (10 mol %), DMEDA (20 mol %), NaO*t*-Bu, toluene, 140°	 R | X | Time (h) Et | I | 16 (63) *n*-Pr | Br | 36 (67) *n*-Pr | I | 36 (42)	88
C_{12-14}				
$HNAr_2$		CuI (10 mol %), DMEDA (20 mol %), NaO*t*-Bu, toluene, 140°	 Ar | Time (h) Ph | 16 (55) 4-MeC_6H_4 | 24 (67)	88
		CuI (10 mol %), DMEDA (20 mol %), NaO*t*-Bu, toluene, 140°, 24 h	 Ar Ph (89) 4-MeC_6H_4 (89)	88

TABLE 29A. *N*-VINYLATION OF PYRROLES, PYRAZOLES, TRIAZOLES, AND TETRAZOLES

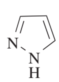
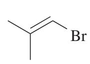
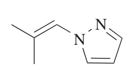
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_2

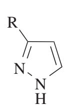
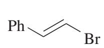
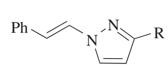
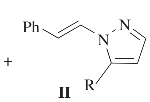
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), **L30** (5 mol %), Cs_2CO_3, DMF, 110°, 24 h	 (38) +  (50)	190
		CuI (10 mol %), **L30** (5 mol %), Cs_2CO_3, DMF, 110°, 24 h	 (94)	190

C_3

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), ligand (20 mol %), Cs_2CO_3, MeCN, 80°		

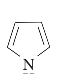
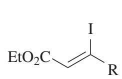
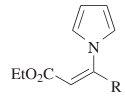
Ligand	Time (h)		Refs.
L30	36	(70)	648
L47	24	(47)	190

C_{3-4}

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (10 mol %), Cs_2CO_3	 I +  II	

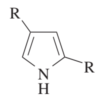
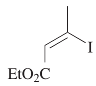
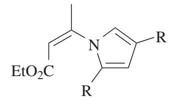
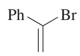
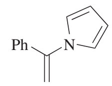
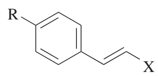
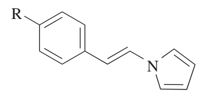
R	Catalyst	Additive	Solvent	Temp (°)	Time (h)	I	II	Refs.
H	CuI	none	DMF	120	36	(95)	(—)	103
H	CuI	**L25** (10 mol %)	MeCN	80	15	(90)	(—)	395
H	CuI	**L30** (5 mol %)	MeCN	50	30	(94)	(—)	190
H	CuI	**L47** (10 mol %)	MeCN	80	2	(100)	(—)	413
H	CuI	**L48** (0.21 mol %)	MeCN	80	2	(100)	(—)	413
H	**9**	none	MeCN	82	4	(100)	(—)	27
Me	CuI	**L30** (5 mol %)	MeCN	50	30	(62)	(27)	190
CF_3	CuI	**L30** (5 mol %)	MeCN	50	30	(98)	(0)	190

C_4

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (50 mol %), DMEDA (1 eq), K_3PO_4, toluene, 65°		649

R	
t-Bu	(77)
n-C_5H_{11}	(63)
Ph	(54)

TABLE 29A. *N*-VINYLATION OF PYRROLES, PYRAZOLES, TRIAZOLES, AND TETRAZOLES (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{4-5}				
		CuI (50 mol %), DMEDA (1 eq), K_3PO_4, toluene, 65°	 R: H (70); Me (40)	649
C_4				
		CuI (20 mol %), EDA (40 mol %), K_3PO_4, dioxane, 110°, 48 h	 (21)	102
		CuI (10 mol %), Cs_2CO_3		

R	X	Additive	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
H	Cl	none	DMF	120	50	(7)	103
H	Br	none	DMF	120	36	(75)	103
H	Br	**L30** (5 mol %)	MeCN	80	24	(89)	190
MeO	Cl	none	DMF	120	50	(13)	103
MeO	Br	none	DMF	120	36	(93)	103

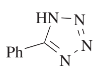
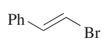
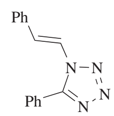
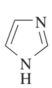
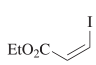
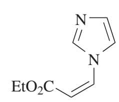
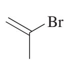
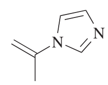
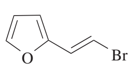
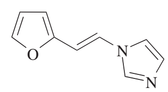
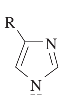
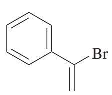
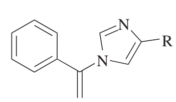
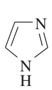
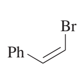
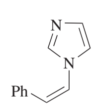
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CuI (10 mol %), **L30** (5 mol %), Cs_2CO_3, MeCN, 80°, 24 h	 (0)	190

TABLE 29B. *N*-VINYLATION OF IMIDAZOLES

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_3				
		CuO nanoparticles (1.5 eq), KOH, DMSO, 80°, 5 h	 (0)	94
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 48 h	 (58)	102
		Cu_2O (5 mol %), **L9** (10 mol %), Cs_2CO_3, MeCN, 85°, 24 h	 (70)	89
$C_{3–4}$				
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 48 h	 R: H (41); Me (25)	102
C_3				
		CuI (10 mol %), Cs_2CO_3		

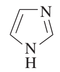
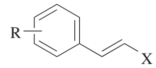
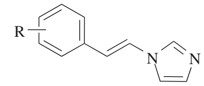
Additive	Solvent	Temp (°)	Time (h)	Yield (%)	Refs.
none	DMF	120	50	(61)	103
L9 (30 mol %)	DMSO	80	24	(0)	650

585

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

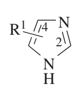
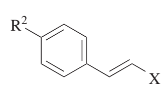
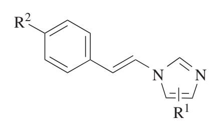
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3



Catalyst (*x* amount)


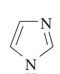
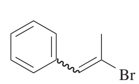
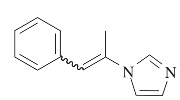
R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	Cl	CuI	10 mol %	Cs_2CO_3	DMF	120	50	(22)	103
H	Br	CuI	10 mol %	L-Pro (20 mol%), K_2CO_3	$[C_4mim][BF_4]$	110	20	(87)	231
H	Br	CuI	15 mol %	**L9** (30 mol %), Cs_2CO_3	DMSO	60	24	(88)	650
H	Br	CuI	10 mol %	**L30** (5 mol %), Cs_2CO_3	MeCN	60	24	(100)	190
H	Cl	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(20)	89
H	Cl	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	130	45	(53)	89
H	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(98)	89
H	Cl	CuO nanoparticles	2 eq	KOH	DMSO	80	11	(20)	94
H	Br	CuO nanoparticles	2 eq	KOH	DMSO	80	11	(89)	94
H	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(98)	94
3-F	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(88)	94
4-F	Br	CuI	15 mol %	**L9** (30 mol %), Cs_2CO_3	DMSO	60	24	(90)	650
4-F	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(99)	89
4-Cl	Br	CuI	10 mol %	L-Pro (20 mol%), K_2CO_3	$[C_4mim][BF_4]$	110	20	(93)	231
4-Cl	Br	CuO nanoparticles	2 eq	KOH	DMSO	80	11	(82)	94
4-Cl	Br	CuI	15 mol %	**L9** (30 mol %), Cs_2CO_3	DMSO	60	24	(87)	650
4-Cl	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(99)	89
4-Cl	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(91)	94
4-MeO	Cl	CuI	10 mol %	Cs_2CO_3	DMF	140	36	(66)	103
4-MeO	Br	CuI	10 mol %	Cs_2CO_3	DMF	120	36	(57)	103
4-MeO	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(92)	89
4-MeO	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(98)	94
3,4-$(MeO)_2$	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(72)	89
4-Me	Br	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	$[C_4mim][BF_4]$	110	20	(86)	231
4-Me	Br	CuI	15 mol %	**L9** (30 mol %), Cs_2CO_3	DMSO	60	24	(85)	650
4-Me	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(91)	89
4-Me	Br	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(80)	94
4-Me	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(90)	94

C_{3-9}

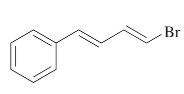
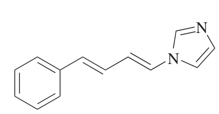


Catalyst (*x* amount)


R^1	R^2	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
4-O_2N	H	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(10)	94
2-Me	H	Br	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	$[C_4mim][BF_4]$	110	30	(60)	231
2-Me	H	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(62)	89
4-NC–	H	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(0)	94
4-Ph	H	Br	CuO nanoparticles	2 eq	KOH	DMSO	80	11	(79)	94
4-Ph	H	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(87)	94
4-Ph	Cl	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(89)	94
4-Ph	MeO	Br	CuO nanoparticles	2 eq	KOH	DMSO	80	11	(84)	94
4-Ph	MeO	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(91)	94
4-Ph	Me	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(84)	94

C_3



CuI (10 mol %)


(*E*)/(*Z*)	Additive(s)	Solvent	Temp (°)	Time (h)		(*E*)/(*Z*)	Refs.
58:42	Cs_2CO_3	DMF	120	50	(70)	67:33	103
—	L-Pro (20 mol %), K_2CO_3	$[C_4mim][BF_4]$	110	20	(87)	—	231


Cu_2O (5 mol %), **L9** (10 mol %), Cs_2CO_3, MeCN, 85°, 24 h

(60) 89

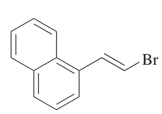
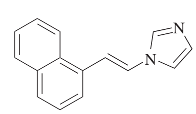
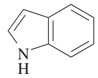
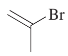
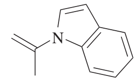
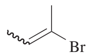
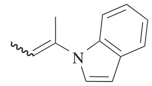
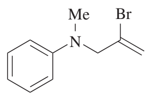
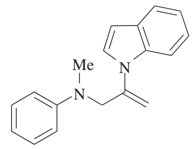
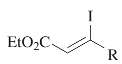
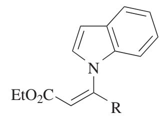
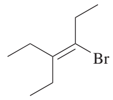
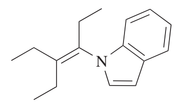
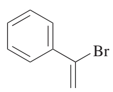
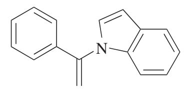
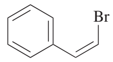
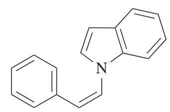
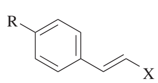
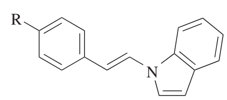

Cu_2O (5 mol %), **L9** (10 mol %), Cs_2CO_3, MeCN, 85°, 24 h

(98) 89

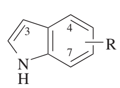
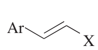
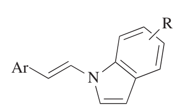
TABLE 29C. *N*-VINYLATION OF INDOLES

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 24 h	 (85)	102
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 24 h	 (63)	102
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 24 h	 (88)	102
		CuI (50 mol %), DMEDA (1 eq), K_3PO_4, toluene, 65°	 R: Me (60); n-C_5H_{11} (69)	649
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 24 h	 (78)	102
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 24 h	 (85)	102
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 24 h	 (76)	102

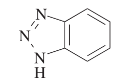
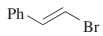
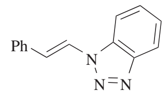
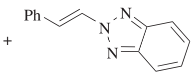
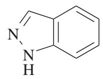
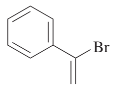
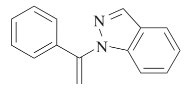
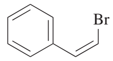
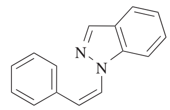
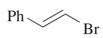
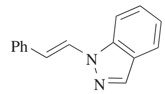
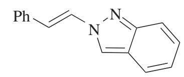
 CuI (10 mol %) 

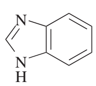
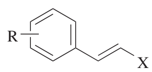
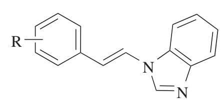
R	X	Additive(s)	Solvent	Temp (°)	Time (h)	Yield	Refs.
H	Cl	Cs_2CO_3	DMF	120	50	(7)	103
H	Br	Cs_2CO_3	DMF	120	36	(80)	103
H	Br	EDA (20 mol %), K_3PO_4	dioxane	110	24	(80)	102
H	Br	**L30** (5 mol %), Cs_2CO_3	MeCN	80	24	(83)	190
H	Br	L-Pro (20 mol %), K_2CO_3	$[C_4mim][BF_4]$	110	20	(91)	231
MeO	Cl	Cs_2CO_3	DMF	120	50	(35)	103

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), Cs_2CO_3, DMF, 120°		103

Ar	R	X	Time (h)	Yield
4-$BnOC_6H_4$	H	Br	36	(71)
4-$BnOC_6H_4$	MeO	Br	36	(91)
3-MeC_6H_4	H	Br	36	(70)
3-MeC_6H_4	MeO	Br	36	(82)
3-$OHCC_6H_4$	H	Cl	50	(17)
3-$OHCC_6H_4$	H	Br	36	(63)
3-$OHCC_6H_4$	MeO	Cl	50	(25)
3-$OHCC_6H_4$	MeO	Br	36	(80)
3-AcC_6H_4	H	Br	36	(48)
3-AcC_6H_4	MeO	Br	36	(93)

TABLE 29D. *N*-VINYLATION OF INDAZOLES, BENZIMIDAZOLES, BENZOTRIAZOLES, AND CARBAZOLES

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_6				
		CuI (10 mol %), **L30** (5 mol %), Cs_2CO_3, DMF, 110°, 24 h	 (87) +  (7)	190
C_7				
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 48 h	 (57)	102
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 48 h	 (72)	102
		CuI (10 mol %), **L30** (5 mol %), Cs_2CO_3, MeCN, 80°, 24 h	 (80) +  (9)	190

  Catalyst (*x* amount) 

R	X	Catalyst	*x*	Additive(s)	Solvent	Temp (°)	Time (h)		Refs.
H	Br	CuI	10 mol %	Cs_2CO_3	DMF	120	36	(69)	103
H	Br	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	[C_4mim][BF_4]	110	20	(88)	231
H	Br	CuI	15 mol %	**L9** (30 mol %), Cs_2CO_3	DMSO	80	24	(82)	650
H	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(82)	89
H	Br	CuO nanoparticles	2 eq	KOH	DMSO	80	11	(78)	94
H	I	CuO nanoparticles	1.5eq	KOH	DMSO	80	5	(90)	94
3-F	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(85)	94
4-F	Br	CuI	15 mol %	**L9** (30 mol %), Cs_2CO_3	DMSO	60	24	(88)	650
4-F	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(91)	89
4-Cl	Br	CuI	15 mol %	**L9** (30 mol %), Cs_2CO_3	DMSO	60	24	(84)	650
4-Cl	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(78)	89
4-MeO	Br	CuI	10 mol %	Cs_2CO_3	DMF	120	36	(91)	103
4-MeO	Br	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	[C_4mim][BF_4]	110	20	(85)	231
4-MeO	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(54)	89
4-MeO	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(88)	94
3,4-$(MeO)_2$	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(60)	89
4-Me	Br	CuI	10 mol %	L-Pro (20 mol %), K_2CO_3	[C_4mim][BF_4]	110	20	(86)	231
4-Me	Br	CuI	15 mol %	**L9** (30 mol %), Cs_2CO_3	DMSO	80	24	(85)	650
4-Me	Br	Cu_2O	5 mol %	**L9** (10 mol %), Cs_2CO_3	MeCN	85	24	(71)	89
4-Me	I	CuO nanoparticles	1.5 eq	KOH	DMSO	80	5	(88)	94

TABLE 29D. *N*-VINYLATION OF INDAZOLES, BENZIMIDAZOLES, BENZOTRIAZOLES, AND CARBAZOLES (*Continued*)

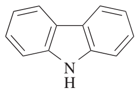
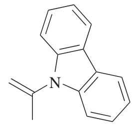
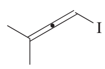
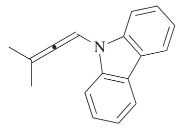
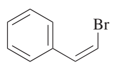
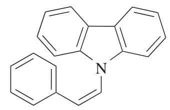
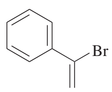
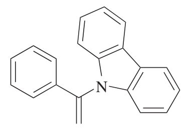
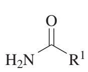
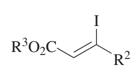
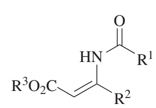
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{12} 		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 24 h	 (78)	102
		**8** (7 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 85°, 16 h	 (94)	651
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 39 h	 (90)	102
		CuI (10 mol %), EDA (20 mol %), K_3PO_4, dioxane, 110°, 30 h	 (78)	102

TABLE 30A. *N*-VINYLATION OF PRIMARY ACYCLIC AMIDES

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

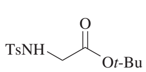
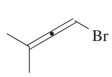
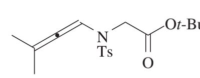
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{2-6}

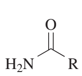
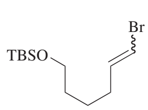
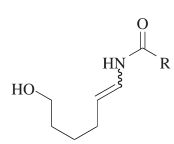
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (x mol %), Cs_2CO_3		

R^1	R^2	R^3	x	Additive	Solvent	Temp (°)	Time (h)		Refs.
Me	H	Et	10	DMG (20 mol %)	dioxane	60	12	(78)	90
Me	H	Et	5	DMEDA (10 mol %)	THF	70	5	(67)	101
Me	Me	Et	5	DMEDA (10 mol %)	THF	70	6	(62)	101
(*E,E*)-Me(CH=CH)$_2$	H	Et	10	DMG (20 mol %)	dioxane	60	12	(73)	90
(*E,E*)-Me(CH=CH)$_2$	H	allyl	10	DMG (20 mol %)	dioxane	60	12	(87)	90

C_2

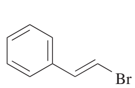
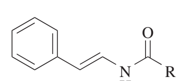
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		**8** (15 mol %), DMEDA (30 mol %), Cs_2CO_3, dioxane, reflux, 24 h	 (41)	625

C_{2-8}

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CuI (10 mol %), DMEDA (20 mol%), Cs_2CO_3, toluene, 70°, 20 h 2. TBAF, THF, 24 h		652

R	Config.	
Me	(*E*)	(85)
Me	(*Z*)	(86)
c-Pr	(*E*) + (*Z*)	(86)
Bn	(*E*) + (*Z*)	(86)

C_{2-7}

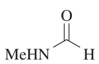
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (1 eq), HMPA, KH, 130°		653

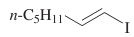
R	Time (h)	
Me	3	(45)
CF_3	2	(83)
Ph	1	(38)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

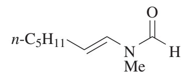
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_2



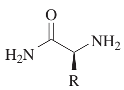


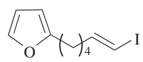
8 (30 mol %), Cs_2CO_3, NMP, 90°, 12 h



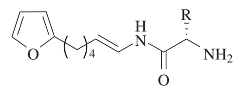
(75) 165

C_{2-11}





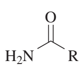
CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF, 16 h

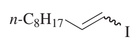


244

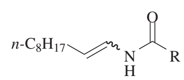
R	Temp (°)		R	Temp (°)	
H	70	(32)	*i*-Bu	70	(87)
Me	70	(82)	(*S*)-EtMeCH	70	(63)
$MeSCH_2CH_2$	70	(77)	Bn	70	(87)
i-Pr	70	(58)	$4\text{-}HOC_6H_4CH_2$	50	(30)
$H_2NCOCH_2CH_2$	50	(31)	3-indolylCH_2	50	(50)

C_{2-9}





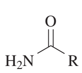
CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF,

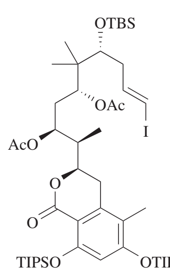


101

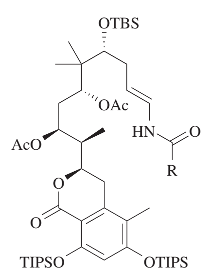
R	Config.	Temp (°)	Time (h)	
Me	(*E*)	rt	15	(82)
Me	(*Z*)	50	12	(84)
(*E*)-PhCH=CH	(*E*)	70	14	(86)

C_{2-11}





CuI (50 mol %), DMEDA (1 eq), Cs_2CO_3, toluene, 70°, 20 h



654

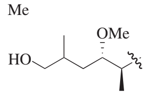
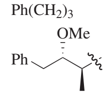
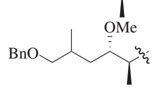
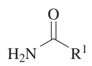
R		R	
Me	(80)	$Ph(CH_2)_3$	(90)
	(80)		(90)
	(95)		

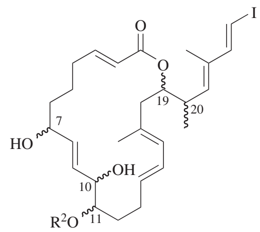
TABLE 30A. *N*-VINYLATION OF PRIMARY ACYCLIC AMIDES (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

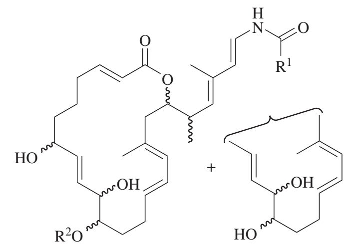
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{2-7}





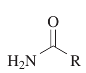
CuI (1.5 eq), DMEDA (*x* eq), K_2CO_3, DMF, rt, 1 h

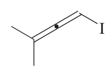


I + II

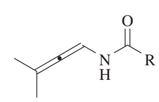
R^1	R^2	C–7	C–10	C–11	C–19	C–20	*x*	I	II	Refs.
		Configuration								
Me	H_2NCO	(*S*)	(*S*)	(*S*)	(*R*)	(*R*)	3	(47)	(—)	98
i-Bu	H_2NCO	(*S*)	(*S*)	(*S*)	(*R*)	(*R*)	3	(41)	(—)	98
Me_2C=CH	H	(*S*)	(*S*)	(*S*)	(*R*)	(*R*)	3	(51)	(—)	655
Me_2C=CH	H_2NCO	(*R*)	(*S*)	(*S*)	(*R*)	(*R*)	3	(46)	(<5)	655
Me_2C=CH	H	(*R*)	(*R*)	(*R*)	(*R*)	(*R*)	2	(45)	(—)	655
Me_2C=CH	H_2NCO	(*R*)	(*R*)	(*R*)	(*R*)	(*R*)	3	(31)	(<5)	655
Me_2C=CH	H	(*R*)	(*R*)	(*R*)	(*S*)	(*R*)	3	(45)	(—)	655
Me_2C=CH	H_2NCO	(*R*)	(*R*)	(*R*)	(*S*)	(*R*)	3	(37)	(10)	655
Me_2C=CH	H	(*R*)	(*R*)	(*R*)	(*S*)	(*S*)	3	(54)	(—)	655
Me_2C=CH	H_2NCO	(*R*)	(*R*)	(*R*)	(*S*)	(*S*)	3	(55)	(<5)	655
Me_2C=CH	H	(*R*)	(*R*)	(*R*)	(*R*)	(*S*)	3	(42)	(—)	655
Me_2C=CH	H_2NCO	(*R*)	(*R*)	(*R*)	(*R*)	(*S*)	2	(44)	(10)	166, 655
2-methyl-4-thiazolyl	H_2NCO	(*S*)	(*S*)	(*S*)	(*R*)	(*R*)	3	(40)	(—)	98
2-pyridyl	H_2NCO	(*S*)	(*S*)	(*S*)	(*R*)	(*R*)	3	(31)	(—)	98
3-pyridyl	H_2NCO	(*S*)	(*S*)	(*S*)	(*R*)	(*R*)	3	(54)	(—)	98
Ph	H_2NCO	(*S*)	(*S*)	(*S*)	(*R*)	(*R*)	3	(44)	(—)	98

C_{3-7}



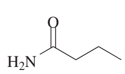


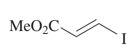
8 (7 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 85°



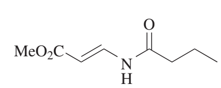
R	Time (h)		Refs.
Et	4.5	(24)	651
Ph	11	(47)	

C_4



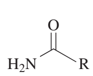


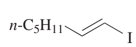
CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, toluene, 75°, 5 h



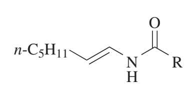
(42) 656

C_{4-7}

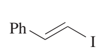




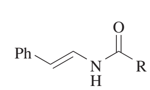
8 (*x* mol %), 90°



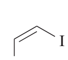
R	*x*	Additive(s)	Solvent	Time (h)		Refs.
(*Z*)-MeON=CHCH=CH	50	DMEDA (50 mol %), Rb_2CO_3	DMA	12	(52)	165
(*Z*)-MeON=CHCH=CH	30	Rb_2CO_3	NMP	1.5	(36)	220
(*E*)-MeON=CHCH=CH	30	Cs_2CO_3	NMP	12	(57)	165, 220
$Me(CH{=}CH)_2$	30	Cs_2CO_3	NMP	12	(69)	165
Ph	30	Cs_2CO_3	NMP	12	(71)	165



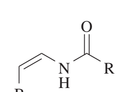
8 (30 mol %), Cs_2CO_3, NMP, 90°, 12 h



R		Refs.
(*E*)-MeON=CHCH=CH	(52)	220, 165
n-C_5H_{11}	(71)	220
(*E,E*)-$Me(CH{=}CH)_2$	(36)	165
Ph	(57)	220, 165



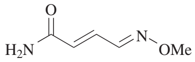
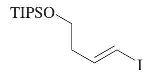
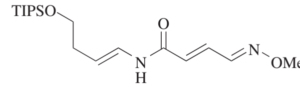
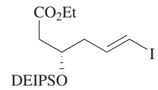
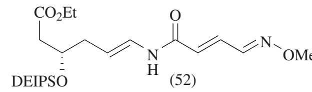
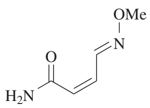
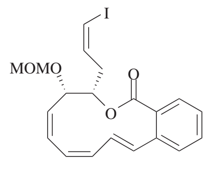
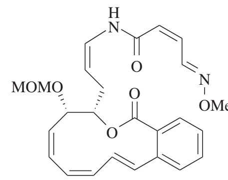
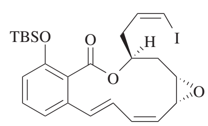
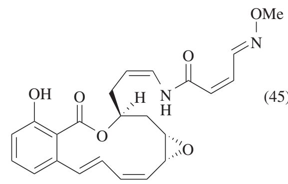
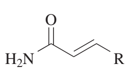
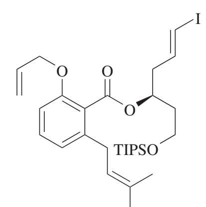
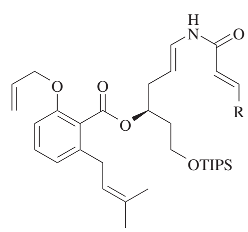
8 (30 mol %), Cs_2CO_3, NMP, 90°, 12 h



R		Refs.
(*E*)-MeON=CHCH=CH	(55)	165
Ph	(23)	

TABLE 30A. *N*-VINYLATION OF PRIMARY ACYCLIC AMIDES (*Continued*)

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		**8** (30 mol %), Cs_2CO_3, NMP, 90°, 12 h	 (50)	165
		**8** (50 mol %), phen, dba, Cs_2CO_3, DMA, 65°, 20 h	 (52)	657, 165
		**8** (57 mol %), DMEDA (1.1 eq), K_2CO_3, DMA, rt, 1 h	 (44)	658
		1. TBAF, THF, rt 2. **8**, DMEDA, K_2CO_3, DMA, 50°, 1 h	 (45)	659
C_{4-7}				
		**8** (45 mol %), DMEDA (90 mol %), Cs_2CO_3, THF, DMA, 50°, 11 h		660

R	
HON=CH	(50)
(*E*)-CH_2=CHCH$_2O_2$CNHCH$_2$CH=CH	(51)

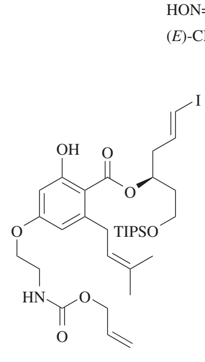
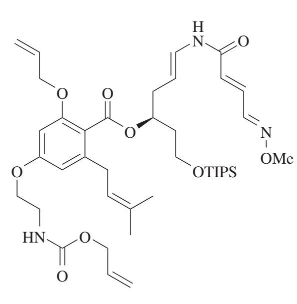
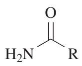
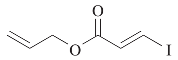
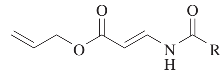
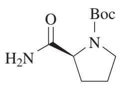
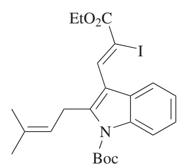
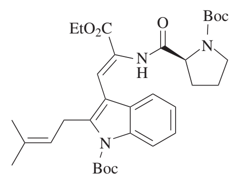
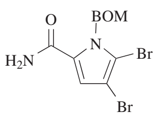
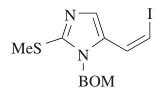
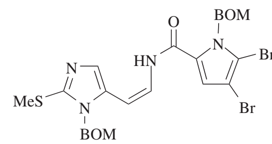
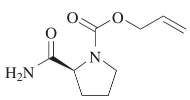
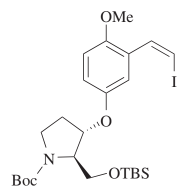
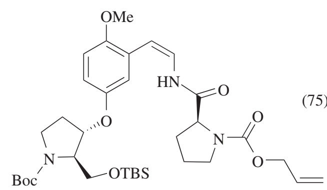
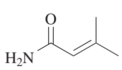
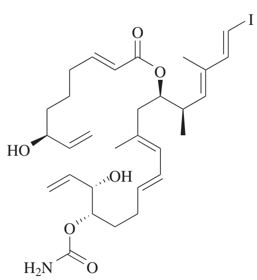
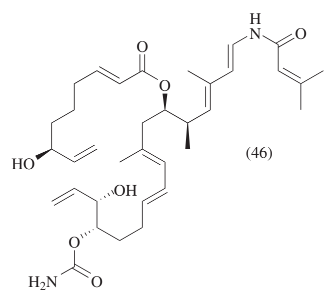
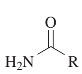
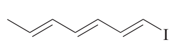
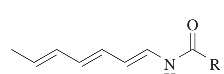
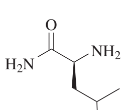
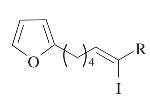
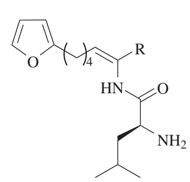
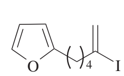
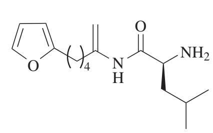
C_4				
		1. NaHMDS, allyl bromide 2. **8** (45 mol %), DMEDA (90 mol %), Cs_2CO_3, THF, DMA, 50°, 11 h	 (50)	660

TABLE 30A. *N*-VINYLATION OF PRIMARY ACYCLIC AMIDES (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{5-6}				
		$Cu(MeCN)_4PF_6$ (10 mol %), phen (20 mol %), Rb_2CO_3, DMA, 12 h		92
C_5				
		CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 100°, 13 h	 (57)	661
		CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, toluene, 75°, 5 h	 (42)	656
		CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF, 50°, 24 h	 (75)	662
		CuI (1.5 eq), DMEDA (3 eq), K_2CO_3, DMF, rt, 1 h	 (46)	655
C_{6-7}				
		Cat. **8** (30 mol %), Cs_2CO_3, NMP, 90°, 12 h	 R: n-C_5H_{11} (69); Ph (58)	220
C_6				
		CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF, 70°, 16 h	 R: H (50); Me (41)	244
		CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF, 70°, 16 h	 (20)	244

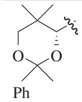
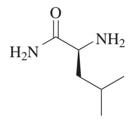
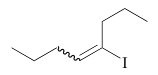
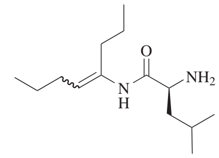
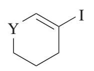
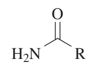
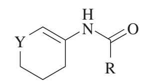
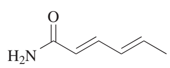
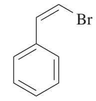
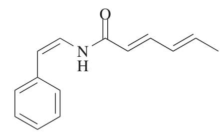
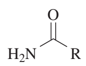
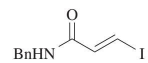
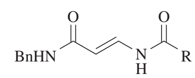
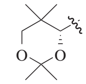
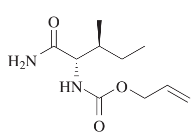
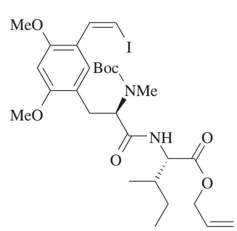
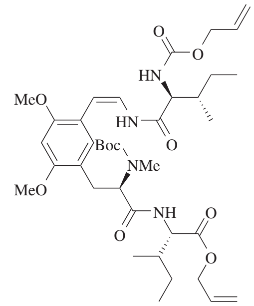
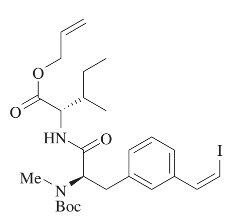
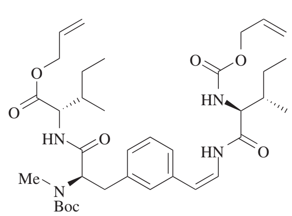
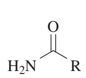
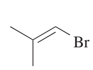
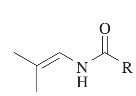
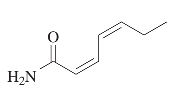
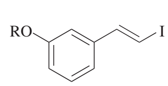
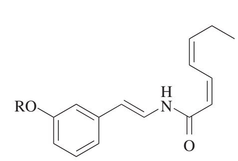
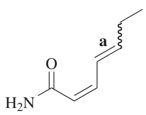
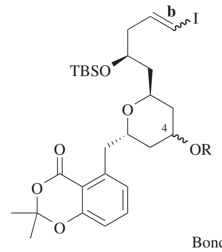
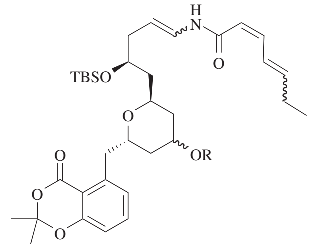
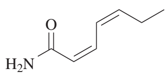
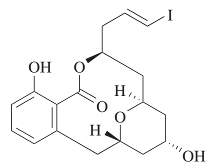
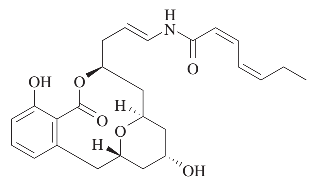
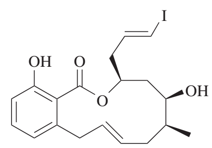
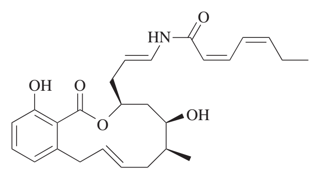
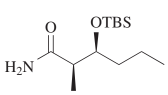
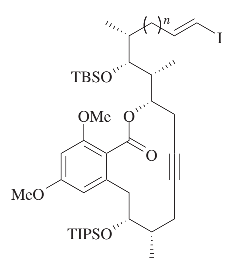
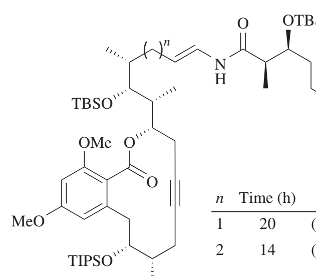
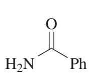
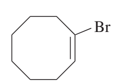
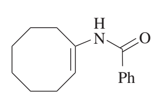
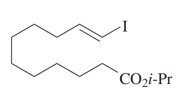
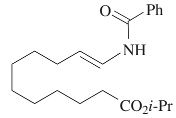
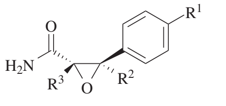
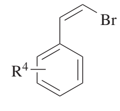
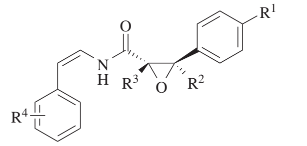
R	Temp (°)		R	Temp (°)	
2-tetrahydrofuryl	rt	(61)		45	(90)
(E,E)-Me(CH=CH)$_2$	45	(58)	Ph	45	70)
c-C_5H_{11}	45	(6)			
2-pyridyl	45	(43)			

TABLE 30A. *N*-VINYLATION OF PRIMARY ACYCLIC AMIDES (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_6				
		CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF, 70°, 16 h	 R / Config. H (*E*) (35) H (*Z*) (34) Cbz (*E*) (54) Boc (*E*) (90)	244
		CuI (10 mol %), DMG (20 mol %), Cs_2CO_3, dioxane, 60°, 12 h	 R / Y Me(CH=CH)$_2$ CH$_2$ (74) Ph CH$_2$ (81) Ph C=O (82)	90
		CuI (10 mol %), DMG (20 mol %), Cs_2CO_3, dioxane, 80°, 24 h	 (65)	90
		$Cu(MeCN)_4PF_6$ (10 mol %), phen (20 mol %), Rb_2CO_3, DMA, 60°, 12 h	 R (*E*,*E*)-Me(CH=CH)$_2$ (18)  (70) Ph (72)	92

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		CuI, DMG, Cs_2CO_3, dioxane	 (60)	451
		CuI, DMG, Cs_2CO_3, dioxane	 (61)	451
C_7				
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 24 h	 R *c*-C_6H_{11} (84) 2-$H_2NC_6H_4$ (81)	101
		**8** (50 mol %), Rb_2CO_3, DMA, 90°, 2 h	 R H (86) Me (89)	95

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_7				
		**8** (50 mol %), Rb_2CO_3, DMA, 90°, 12 h		97
		**8** (68 mol %), phen (1.4 eq), Rb_2CO_3, DMA, 58°, 8 h	 (40)	167
		**8** (50 mol %), Rb_2CO_3, DMA, 90°, 2 h	 (57)	95
		CuI (50 mol %), DMEDA (1 eq), Cs_2CO_3, THF, 60°		663
		CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 100°	 (94)	664
		**8** (30 mol %), Cs_2CO_3, NMP, 90°, 12 h	 (70)	95
C_{9-10}				
		CuI (40 mol %), DMG (80 mol %), Cs_2CO_3, dioxane, reflux, 3 h		93

Bond **a**	Bond **b**	C–4	R	
(*E*)	(*E*)	(*R*)	Ac	(41)
(*Z*)	(*E*)	(*R*)	Ac	(90)
(*E*)	(*Z*)	(*S*)	TBS	(41)

n	Time (h)	
1	20	(82)
2	14	(85)

R^1	R^2	R^3	R^4		dr
H	H	H	H	(82)	93:7
H	H	H	4-Cl	(64)	84:16
H	H	H	2-Me	(49)	84:16
H	H	H	3-Me	(62)	92:8
H	H	H	4-Me	(54)	88:12
H	H	H	4-CF_3	(62)	78:22
H	Me	H	H	(79)	95:5
H	H	Me	H	(91)	83:17
Cl	H	H	H	(54)	93:7
Me	H	H	H	(74)	83:17

TABLE 30A. *N*-VINYLATION OF PRIMARY ACYCLIC AMIDES (*Continued*)

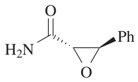
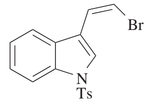
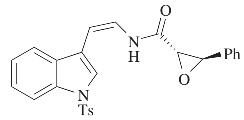
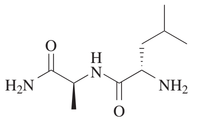
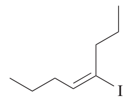
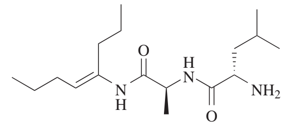
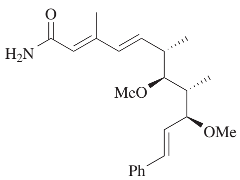
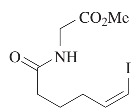
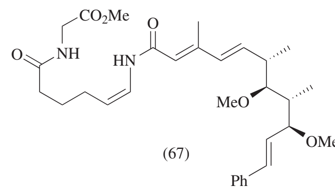
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_9				
		CuI (40 mol %), DMG (80 mol %), Cs_2CO_3, dioxane, reflux, 3 h	 (63)	93
		CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF, 70°, 16 h	 (54)	244
C_{20}				
		CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF, 70°, 15 h	 (67)	665

TABLE 30B. *N*-VINYLATION OF SECONDARY ACYCLIC AMIDES

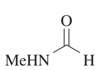
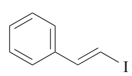
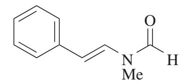
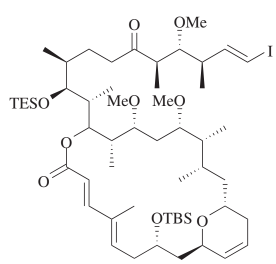
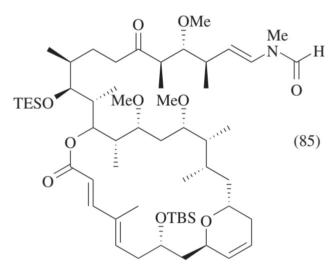
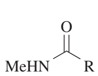
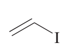
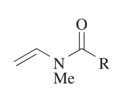
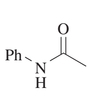
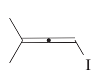
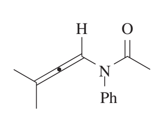
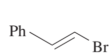
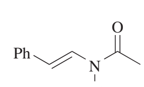
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_2				
		**8** (30 mol %), Cs_2CO_3, NMP, 90°, 12 h	 (70)	165
		CuI (50 mol %), DMEDA (1.1 eq), dioxane, 60°, 13 h	 (85)	666
C_{7-8}				
		**8** (30 mol %), Cs_2CO_3, NMP, 90°, 12 h	 R: *n*-C_5H_{11} (75); Ph (70)	220
C_8				
		**8** (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 50°	 (52)	91
		CuI (1 eq), KH, HMPA, 130°, 3 h	 (38)	653

TABLE 30B. *N*-VINYLATION OF SECONDARY ACYCLIC AMIDES (*Continued*)

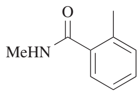
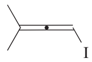
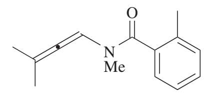
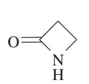
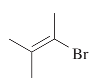
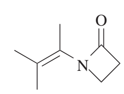
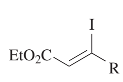
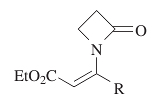
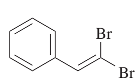
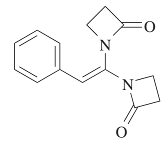
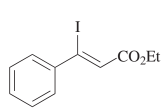
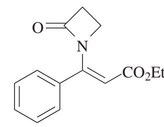
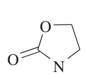
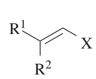
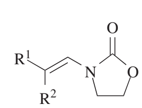
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_9				
		**8** (7 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 85°, 22 h	 (20)	651

TABLE 30C. *N*-VINYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_3				
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 25 h	 (88)	101
		CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, toluene, 65°	 R / Time (h): Me, 3, (66); n-C_5H_{11}, 24, (79)	649
		CuI (10 mol %), DMG (20 mol %), K_3PO_4, NH_4OAc, MeCN, reflux, 24 h	 (84)	574
		CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, toluene, 65°, 23 h	 (65)	649
		CuI (x mol %)		

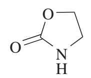
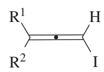
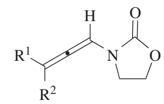
R^1	R^2	X	x	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	EtO_2C	I	10	DMG (20 mol %), Cs_2CO_3	dioxane	60	12	(82)	90
H	4-$MeOC_6H_4$	I	10	DMG (20 mol %), Cs_2CO_3	dioxane	60	12	(78)	90
H	n-$C_{11}H_{23}$	I	10	DMG (20 mol %), Cs_2CO_3	dioxane	60	12	(78)	90
Me	Me	Br	5	DMEDA (10 mol %), K_2CO_3	toluene	90	22	(94)	101

TABLE 30C. *N*-VINYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES (*Continued*)

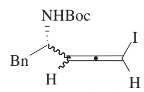
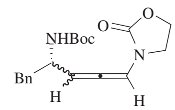
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

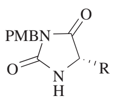
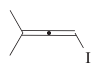
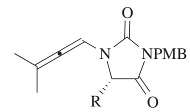
C_3

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %), toluene		

R^1	R^2	Catalyst	*x*	Additives	Temp (°)	Time (h)		Refs.
H	Me	CuCN	10	DMEDA (20 mol %), Cs_2CO_3	50	—	(90)	91
H	*n*-Pr	**8**	7	DMCDA (15 mol %), K_3PO_4	85	5	(100)	651
Me	Me	**8**	7	DMCDA (15 mol %), K_3PO_4	85	7	(97)	651

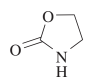
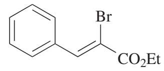
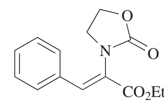
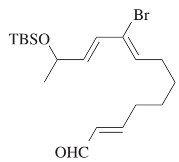
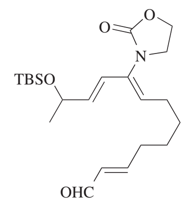
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	 er 75:25	CuCN (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 50°	 Config. (*P*) (73); (*M*) (65)	91

C_{3-7}

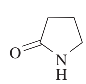
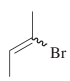
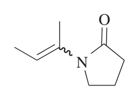
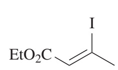
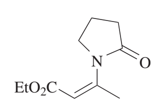
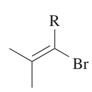
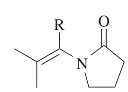
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		**8** (7 mol %), K_3PO_4, toluene, DMCDA (15 mol %), 85°		651

R	Time (h)	
H	6	(99)
i-Bu	7	(100)

C_3

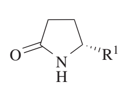
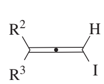
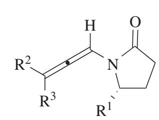
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMG (20 mol %), Cs_2CO_3, dioxane, 80°, 24 h	 (63)	90
		CuI (50 mol %), DMEDA (2.5 eq), K_2CO_3, toluene, reflux, 21 h	 (65)	667

C_4

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMG (20 mol %), Cs_2CO_3, dioxane, 80°, 24 h	 (63)	90
		CuI (20 mol %), DMEDA (40 mol %), K_3PO_4, toluene, 65°, 19 h	 (64)	649
		CuI (*x* mol %)		

R	*x*	Additives	Solvent	Temp (°)	Time (h)		Refs.
H	10	DMG (20 mol %), Cs_2CO_3	dioxane	80	24	(62)	90
H	5	DMEDA (10 mol %), K_2CO_3	toluene	90	22	(93)	101
Me	5	DMEDA (10 mol %), K_2CO_3	toluene	110	25	(91)	101

C_{4-11}

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		**8** (*x* mol %), toluene		

R^1	R^2	R^3	X	*x*	Additives	Temp (°)	Time (h)		Refs.
H	H	Me	I	10	DMEDA (20 mol %), Cs_2CO_3	50	—	(54)	91
Bn	Me	Me	Br	7	DMCDA (15 mol %, K_3PO_4	85	8	(96)	651

C_4

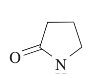
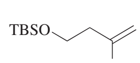
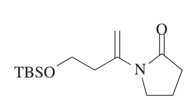
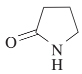
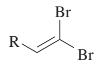
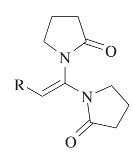
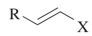
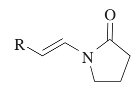
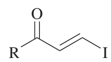
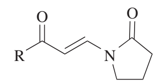
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 14 h	 (90)	101

TABLE 30C. *N*-VINYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES (*Continued*)

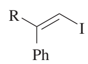
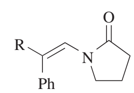
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

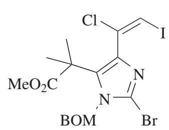
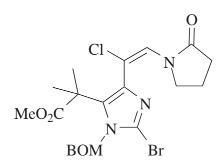
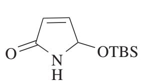
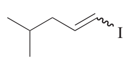
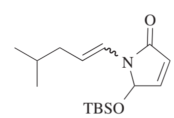
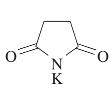
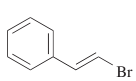
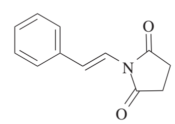
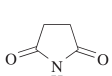
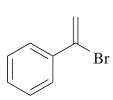
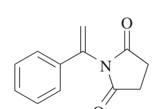
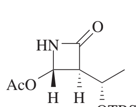
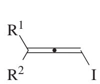
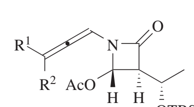
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CuI (10 mol %), DMG (20 mol %), K_3PO_4, NH_4OAc, MeCN, reflux, 24 h	 R: $TBDPSOCH_2$ (60); 2-thienyl (73); Ph (94); $3\text{-}O_2NC_6H_4$ (60); $4\text{-}MeOC_6H_4$ (56); (*E*)-PhCH=CH (85); 2-Np (58)	668
		Catalyst (*x* amount)		

R	X	Catalyst	*x*	Additive	Solvent	Temp (°)	Time (h)		Refs.
n-C_5H_{11}	I	**8**	30 mol %	Cs_2CO_3	NMP	90	12	(59)	165
Ph	Br	CuI	1 eq	KH	HMPA	130	22	(43)	653

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* amount), 12 h		

R	Catalyst	*x*	Additives	Solvent	Temp (°)		Refs.
$CH_2=CHCH_2O_2C$	CuI	1 eq	DMG (1 eq), Cs_2CO_3	dioxane	45	(70)	90
$CH_2=CHCH_2O_2C$	$Cu(MeCN)_4PF_6$	10 mol %	phen (20 mol %), Rb_2CO_3	DMA	rt	(92)	92
BnNHCO	$Cu(MeCN)_4PF_6$	10 mol %	phen (20 mol %), Rb_2CO_3	DMA	60	(72)	92

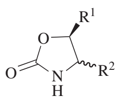
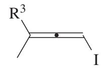
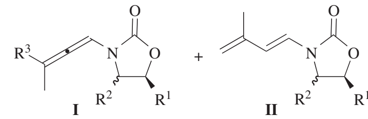
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF, 70°, 24 h	 R: Cl (92); Br (21)	669

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 50°, 45 h	 (43)	669
		**8** (10 mol %), DMCDA (20 mol %), K_3PO_4, dioxane, 90°, 24 h	 Config.: (*E*) 72); (*Z*) (56)	670
		CuI (1 eq), HMPA, 130°, 3 h	 (72)	653
		CuI (1 eq), HMPA, KH, 130°, 23 h	 (28)	653
C_5				
		**8** (7 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 85°, 5 h	 R^1, R^2: H, *n*-Pr (36); Me, Me (47)	651

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

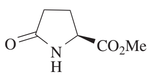
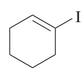
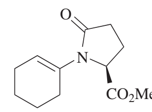
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{5-10}

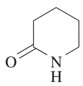
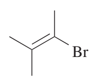
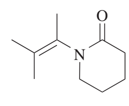
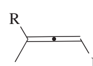
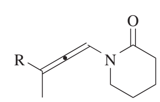
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %), toluene		

R^1	R^2	Config.	R^3	Catalyst	*x*	Additives	Temp (°)	Time (h)	I	II	Refs.
H	CH_2=CH	(*R*)	Me	**8**	7	DMCDA (15 mol %), K_3PO_4	85	7	(53)	(26)	651
H	*i*-Pr	(*S*)	H	CuCN	10	DMEDA (20 mol %), Cs_2CO_3	50	—	(60	(0)	91
H	(2-furyl)-CH_2CH_2	(*R*)	H	CuCN	10	DMEDA (20 mol %), Cs_2CO_3	50	—	(55)	(0)	91
H	Ph	(*R*)	Me	CuCN	10	DMEDA (20 mol %), Cs_2CO_3	50	—	(51)	(0)	91
H	Bn	(*R*)	H	CuCN	10	DMEDA (20 mol %), Cs_2CO_3	rt	—	(84)	(0)	91
H	Bn	(*R*)	Me	CuCN	10	DMEDA (20 mol %), Cs_2CO_3	50	—	(30)	(0)	91
H	Bn	(*S*)	Me	**8**	7	DMCDA (15 mol %), K_3PO_4	85	6	(95)	(0)	651
Me	Ph	(*R*)	Me	**8**	7	DMCDA (15 mol %), K_3PO_4	85	6	(99)	(0)	651

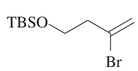
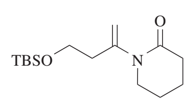
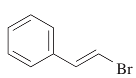
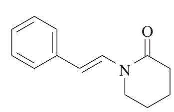
C_5

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), Cs_2CO_3, dioxane, 60°, 12 h		90

Additive	
$Me_2NCH_2CH_2CO_2H$ (20 mol %)	(78)
DMG (20 mol %)	(78)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 115°, 30 h	 (76)	101
		**8** (*x* mol %), toluene		101

R	*x*	Additives	Temp (°)	Time (h)	
H	10	DMEDA (20 mol %), Cs_2CO_3	50	—	(27)
Me	7	DMCDA (15 mol %), K_3PO_4	85	9	(28)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 14 h	 (84)	101
		CuI (1 eq), HMPA, KH, 130°, 5 h	 (31)	653

C_6

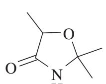
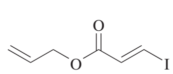
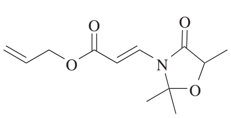
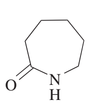
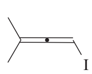
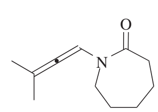
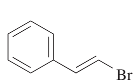
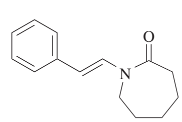
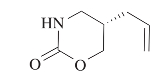
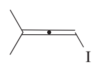
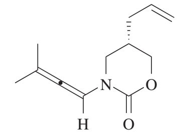
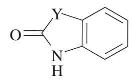
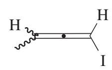
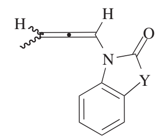
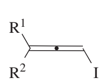
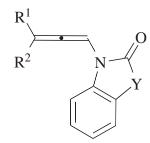
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Cu(MeCN)_4$ PF_6 (10 mol %), phen (20 mol %), Rb_2CO_3, DMA, 45°, 12 h	 (72)	92
		Cat. **8** (7 mol %), K_3PO_4, DMCDA (15 mol %), toluene, 85°, 7 h	 (46)	651
		CuI (1 eq), HMPA, KH, 130°, 5 h	 (38)	653

TABLE 30C. *N*-VINYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES (*Continued*)

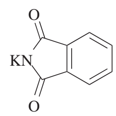
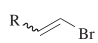
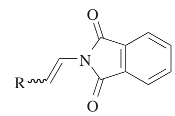
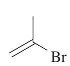
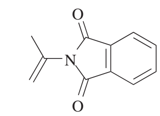
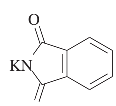
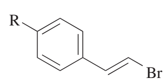
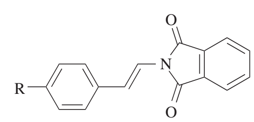
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CuCN (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 50°	 (35)	91
C_{7-8}				
		CuCN (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene		91

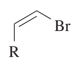
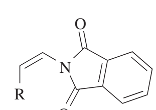
Y	Config.	er	Temp (°)	
NMe_2	(*P*)	75:25	50	(63)
NMe_2	(*M*)	87.5:24.5	50	(79)
NMe_2	(*P*,*M*)	—	50	(65)
CH_2	(*P*)	75:25	rt	(75)
CH_2	(*M*)	87.5:24.5	rt	(71)
CH_2	(*P*,*M*)	—	50	(60)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		**8** (7 mol %), K_3PO_4, DMCDA (15 mol %), toluene, 85°, 6 h		651

Y	R^1	R^2	
O	H	*n*-Pr	(100)
CH_2	Me	Me	(68)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		CuI (1 eq), DMA, 165°, 24 h	 R: H (73); Me (63)	515
		CuI (1 eq), DMA, 165°, 24 h	 (80)	515
		CuI (1 eq)		

R	Solvent	Temp (°)	Time (h)		Refs.
H	TMU	130	7	(95)	653
H	DMA	165	24	(72)	515
O_2N	DMA	165	24	(82)	515
MeO	DMA	165	24	(93)	515

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (1 eq), HMPA, 130°		653

R	Time (h)	
n-C_6H_{13}	42	(69)
Ph	4	(77)
4-ClC_6H_4	24	(76)
4-$MeOC_6H_4$	21	(57)

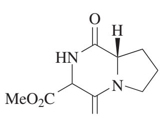
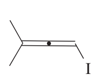
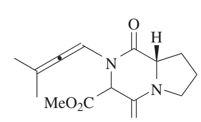
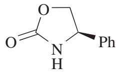
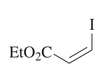
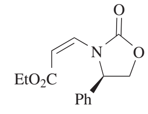
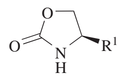
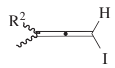
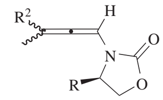
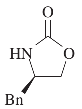
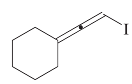
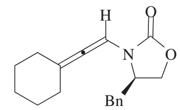
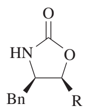
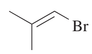
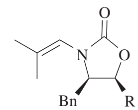
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		**8** (7 mol %), DMCDA (15 mol %), K_3PO_4, toluene, 85°, 12 h	 (63)	651
C_9				
		CuI (10 mol %), DMG (20 mol %), Cs_2CO_3, dioxane, 60°, 12 h	 (76)	90

TABLE 30C. *N*-VINYLATION OF LACTAMS, OXAZOLIDINONES, AND CYCLIC IMIDES (*Continued*)

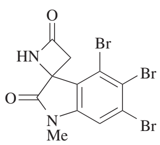
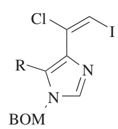
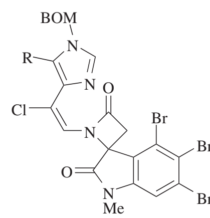
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10}				
		CuCN (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene		91

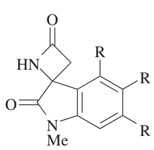
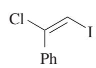
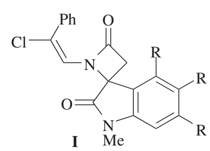
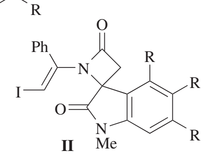
R^1	R^2	Config.	er	
Ph	Me	(*M*)	85:15	(68)
Ph	Me	(*P*)	75:25	(68)
Ph	(*S*)-*i*-PrCH(NHBoc)	(*M*)	—	(44)
Ph	(*S*)-*i*-PrCH(NHBoc)	(*P*)	—	(45)
Bn	Me	(*M*)	85:15	(62)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		CuCN (10 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 50°	 (41)	91
C_{10-11}				
		CuI (5 mol %), DMEDA (10 mol %), K_2CO_3, toluene, 110°, 16 h		101

R	
H	(95)
Me	(94)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		CuI (5 mol %), DMEDA (10 mol %), Cs_2CO_3, THF, 70°, 24 h		669

R	Temp (°)	
H	50	(91)
$MeO_2C(Me_2)C$	70	(45)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 70°, 24 h	 **I** +  **II**	669

R	I	II
H	(75)	(16)
Br	(43)	(0)

TABLE 31. *N*-VINYLATION OF HYDRAZINE DERIVATIVES

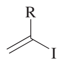
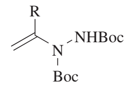
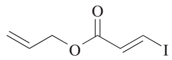
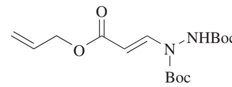
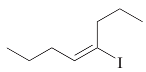
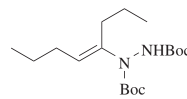
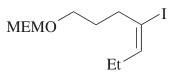
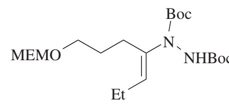
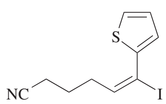
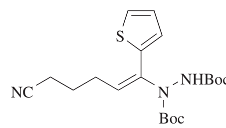
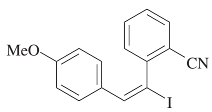
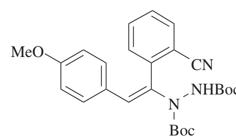
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_0 BocHN—NHBoc		CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 80°, 13 h	 R: Me (75); *n*-C_8H_{17} (75)	671
		CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 80°, 13 h	 (70)	671
		CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 80°, 13 h	 (87)	671
		CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 100°	 (85)	671
		CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 80°, 13 h	 (85)	671
		CuI (5 mol %), phen (10 mol %), Cs_2CO_3, DMF, 80°, 13 h	 (94)	671

TABLE 32. *N*-VINYLATION OF SULFOXIMINES

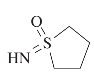
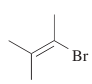
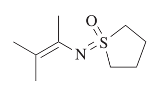
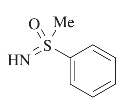
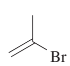
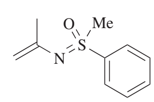
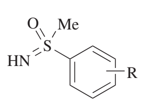
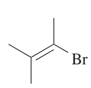
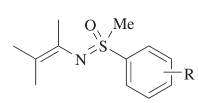
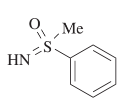
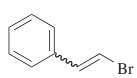
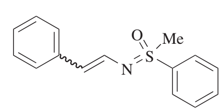
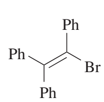
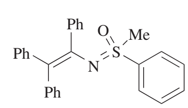
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CuI (1 eq), DMEDA (2 eq), K_2CO_3, toluene, reflux, 24 h	 (91)	672
C_7				
		CuI (1 eq), DMEDA (2 eq), K_2CO_3, toluene, reflux, 24 h	 (97)	672
C_{7-8}				
		CuI (1 eq), DMEDA (2 eq), K_2CO_3, toluene, reflux, 24 h	 R: H (94); 2-MeO (93); 4-Me (92)	672
C_7				
		CuI (1 eq), DMEDA (2 eq), K_2CO_3, toluene, reflux, 24 h	 (90)	672
		CuI (1 eq), DMEDA (2 eq), K_2CO_3, toluene, reflux, 24 h	 (78)	672

TABLE 33. PREPARATION OF VINYL AZIDES

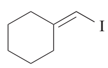
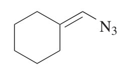
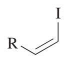
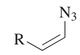
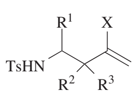
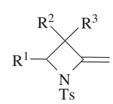
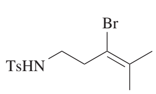
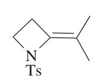
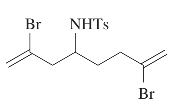
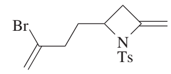
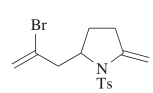
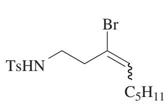
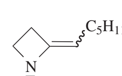
Vinyl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	NaN_3, CuI (10 mol %), L-Pro (20 mol %), DMSO, 70°, 4 h	 (78)	155
C_{8-13}			
	NaN_3, CuI (10 mol %), L-Pro (20 mol %), DMSO, 70°, 4 h	 R Ph (70) 4-ClC_6H_4 (76) 4-$MeOC_6H_4$ (64) *n*-$C_{11}H_{23}$ (82)	155

TABLE 34. INTRAMOLECULAR VINYLATIONS

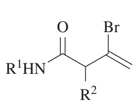
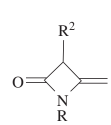
A. SYNTHESIS OF FOUR-MEMBERED NITROGEN HETEROCYCLES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-10} 	CuI (x mol %), DMEDA (y mol %), Cs_2CO_3		104

R^1	R^2	R^3	X	x	y	Solvent	Temp (°)	Time (h)	
H	H	H	I	10	20	THF	40	1	(94)
H	Me	H	Cl	20	40	dioxane	100	4	(99)
H	Me	Me	Cl	20	40	dioxane	100	3	(99)
Me	H	H	Br	10	20	THF	68	1	(99)
n-Pr	H	H	Cl	20	40	dioxane	100	2	(99)
n-Pr	H	H	Br	10	20	THF	68	2	(99)
Ph	H	H	Cl	20	40	dioxane	100	2	(99)
Ph	H	H	Br	10	20	THF	68	2	(99)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	CuI (10 mol %), DMEDA (40 mol %), Cs_2CO_3, THF, 68°, 6 h	 (99)	104
C_8 	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, dioxane, 68°, 3 h	 (66) +  (33)	105
C_9 	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, THF, 68°		104

Config.	Time (h)	
(*E*)	3	(86)
(*Z*)	12	(89)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-17} 	CuI (5 mol %), DMG (10 mol %), K_2CO_3, THF, reflux		603

R^1	R^2	Time (h)	
c-C_6H_{11}	H	24	(70)
Ph	H	17	(94)
Ph	Bn	18	(99)
4-$MeOC_6H_4$	H	16	(99)
4-MeC_6H_4	H	18	(98)
Bn	H	16	(92)

TABLE 34. INTRAMOLECULAR VINYLATIONS (*Continued*)

A. SYNTHESIS OF FOUR-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

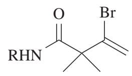
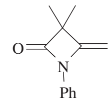
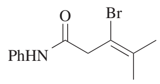
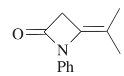
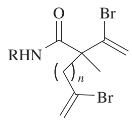
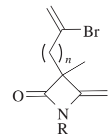
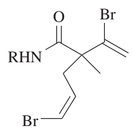
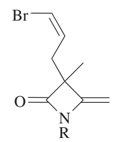
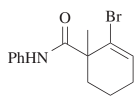
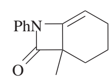
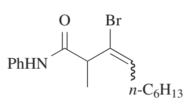
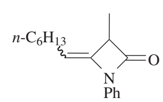
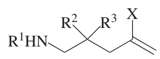
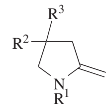
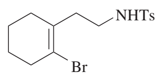
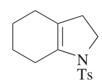
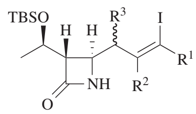
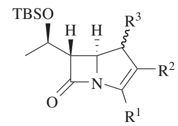
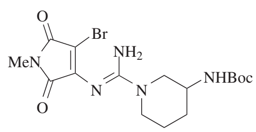
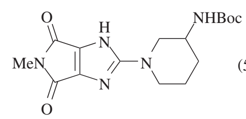
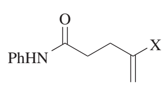
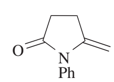
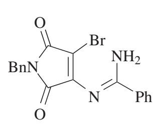
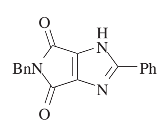
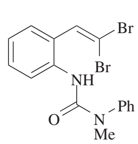
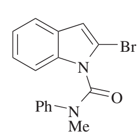
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-18} 	CuI (5 mol %), DMG (10 mol %), K_2CO_3, THF, reflux	 R / Time (h): Ph 18 (99) 4-$MeO_2CC_6H_4$ 20 (89) *n*-$C_{12}H_{25}$ 35 (95)	603
C_{12} 	CuI (5 mol %), DMG (10 mol %), K_2CO_3, THF, reflux, 24 h	 (99)	603
C_{14-16} 	CuI (5 mol %), DMG (10 mol %), K_2CO_3, THF, reflux	 R / *n* / Time (h): Ph 1 18 (99) Ph 2 21 (92) Bn 1 25 (70) Bn 2 17 (98)	603
C_{14-15} 	CuI (5 mol %), DMG (10 mol %), K_2CO_3, THF, reflux	 R / Time (h): Ph 19 (99) Bn 17 (98)	603
C_{14} 	CuI (5 mol %), DMG (10 mol %), K_2CO_3, THF, reflux, 21 h	 (99)	603
C_{17} 	CuI (5 mol %), DMG (10 mol %), K_2CO_3, THF, reflux	 Config. / Time (h): (*E*) 28 (97) (*Z*) 32 (99)	603

TABLE 34. INTRAMOLECULAR VINYLATIONS (*Continued*)

B. SYNTHESIS OF FIVE-MEMBERED NITROGEN HETEROCYCLES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-7}			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°	 (see below)	105
C_8			
	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, dioxane, 68°, 2 h	 (99)	105
C_{8-10}			
	CuI (20 mol %), bpy (40 mol %), K_3PO_4, toluene, 40°, 18 h	 (see below)	629
C_{10}			
	CuI (50 mol %), NaH, THF, reflux, 1 h	 (55)	139
C_{11}			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 (see below)	673
	CuI (50 mol %), NaH, THF, reflux, 1 h	 (94)	139
C_{15}			
	CuI (10 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 120°, 24 h	 (92)	186

C_{5-7} products:

R^1	R^2	R^3	X	Temp (°)	Time (h)	
Ms	H	H	Cl	100	4	(99)
Ts	H	H	Cl	100	4	(99)
Ts	H	H	Br	68	2	(99)
Ts	H	H	I	20	24	(92)
Ts	Me	H	Cl	100	4	(99)
Ts	Me	Me	Cl	100	4	(99)

C_{8-10} products:

R^1	R^2	R^3	Time (h)	
H	I	H	18	(97)
Me	I	H	22	(96)
$AcOCH_2$	I	H	22	(91)
$BnOCH_2$	I	H	24	(95)
EtO_2C	Cl	H	12	(85)
EtO_2C	Br	H	13	(92)
EtO_2C	I	H	21	(94)
EtO_2C	I	Me (*R*)	24	(92)
EtO_2C	I	Me (*S*)	28	(85)
$PNBO_2C$	I	H	18	(94)

C_{11} products:

X	
Br	(trace)
I	(95)

TABLE 34. INTRAMOLECULAR VINYLATIONS (*Continued*)

C. SYNTHESIS OF SIX-MEMBERED NITROGEN HETEROCYCLES

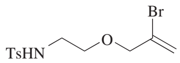
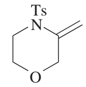
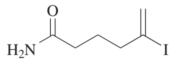
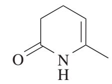
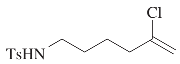
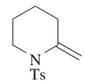
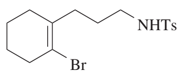
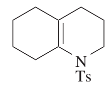
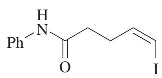
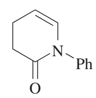
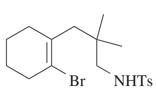
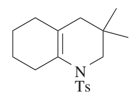
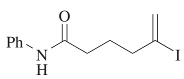
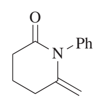
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, dioxane, 68°, 8 h	 (99)	105
C_6			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 (86)	673
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 144 h	 (19)	105
C_9			
	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, dioxane, 100°, 3 h	 (91)	105
C_{11}			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 (91)	673
	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, dioxane, 68°, 3 h	 (99)	105
C_{12}			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 (86)	673

TABLE 34. INTRAMOLECULAR VINYLATIONS (*Continued*)

D. SYNTHESIS OF SEVEN-MEMBERED NITROGEN HETEROCYCLES

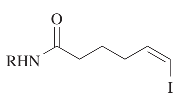
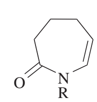
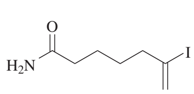
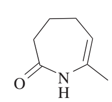
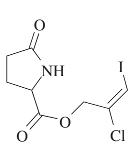
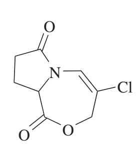
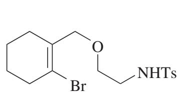
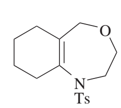
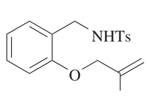
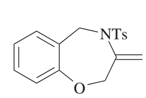
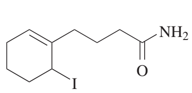
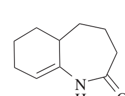
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-7}			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 R: H (44); Me (91)	673
C_7			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 (46)	673
C_8			
	CuI (15 mol %), DMEDA (30 mol %), Cs_2CO_3, THF, 70°, 12 h	 (82)	669
C_9			
	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, dioxane, 100°, 3 h	 (90)	105
C_{10}			
	CuI (50 mol %), DMEDA (1 eq), Cs_2CO_3, dioxane, 68°, 12 h	 (66)	105
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 (45)	673

TABLE 34. INTRAMOLECULAR VINYLATIONS (*Continued*)

D. SYNTHESIS OF SEVEN-MEMBERED NITROGEN HETEROCYCLES (*Continued*)

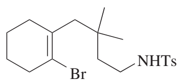
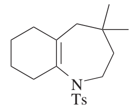
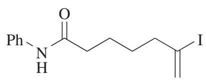
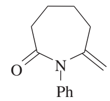
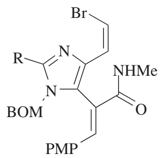
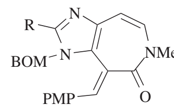
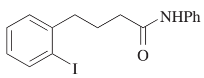
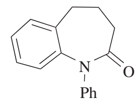
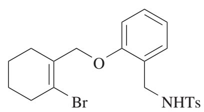
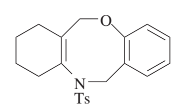
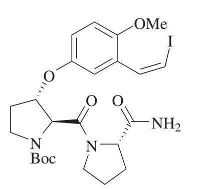
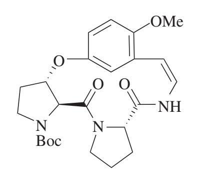
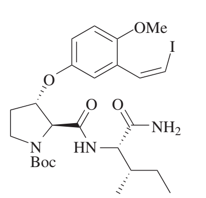
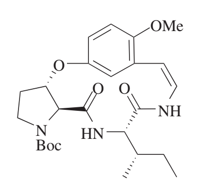
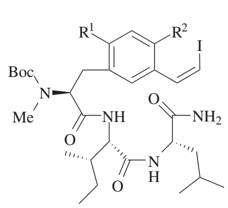
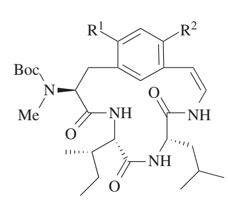
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, dioxane, 100°, 3 h	 (96)	105
C_{13}			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 (91)	673
C_{15}			
	CuI (1 eq), DMEDA (2 eq), Cs_2CO_3, THF, rt, 24 h	 R / Temp (°): Cl / 75 / (80); MeS / rt / (92)	674; 675, 674
C_{16}			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 (83)	673

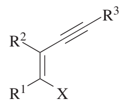
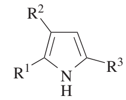
TABLE 34. INTRAMOLECULAR VINYLATIONS (*Continued*)

E. SYNTHESIS OF EIGHT- AND HIGHER-MEMBERED NITROGEN HETEROCYCLES

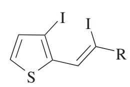
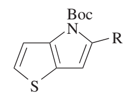
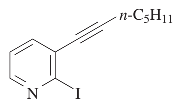
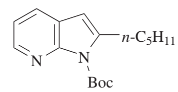
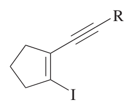
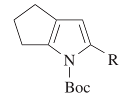
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	CuI (20 mol %), DMEDA (40 mol %), Cs_2CO_3, dioxane, 153°, 48 h	 (62)	105
C_{18}			
	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 60°	 (82)	168
C_{19}			
	CuI (10 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 60°	 (70)	676, 168
C_{23}			
	CuI (x mol %), DMEDA (y mol %), Cs_2CO_3, THF		

R^1	R^2	x	y	Temp (°)	Time (h)		Refs.
HO	MeO	10	20	60	—	(84)	168
MeO	H	20	40	reflux	72	(83)	99, 677
MeO	MeO	10	20	60	—	(82)	168

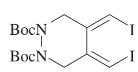
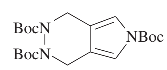
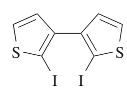
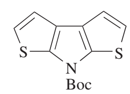
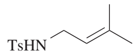
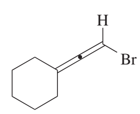
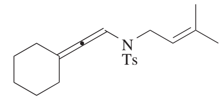
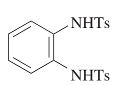
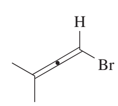
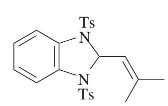
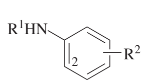
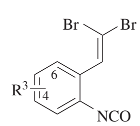
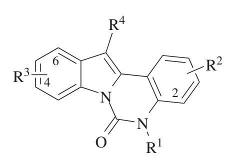
TABLE 35. *N*-VINYLATIONS IN MULTI-STEP REACTIONS

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_0				
H_2NBoc		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°		608

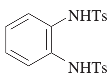
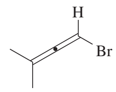
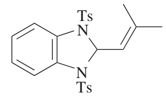
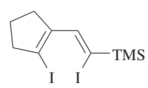
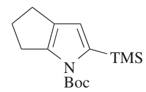
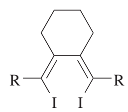
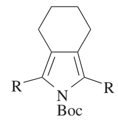
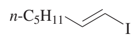
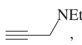
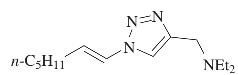
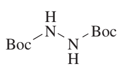
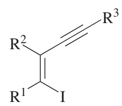
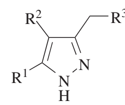
R^1	R^2	R^3	X	Time (h)	
TBS	4-MeC_6H_4	4-MeC_6H_4	I	14	(95)
$TIPSOCH_2$	H	n-C_5H_{11}	I	7	(83)
MeO_2C	H	n-C_5H_{11}	Br	14	(82)
MeO_2C	H	1-cyclohexenyl	Br	14	(81)
n-Pr	H	n-Pr	Br	14	(70)
n-Pr	H	n-Pr	I	8	(74)
n-Pr	n-Pr	H	I	8	(68)
n-Bu	Et	n-C_8H_{17}	I	14	(85)
1-cyclohexenyl	H	n-Pr	I	5	(84)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 15 h	 R: n-Bu (83); 3-thienyl (74)	608
		CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 15 h	 (71)	608
		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°		608

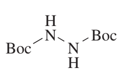
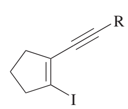
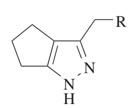
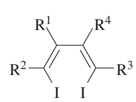
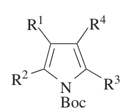
R	Time (h)	
$Cl(CH_2)_3$	4	(78)
Ph	6	(52)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, 16 h	 (78)	100
		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 110°, 7 h	 (78)	100
C_5				
		**8** (15 mol %), DMEDA (30 mol %), Cs_2CO_3, toluene, 80°, 24 h	 (65)	625
C_6				
		**8** (15 mol %), DMEDA (30 mol %), Cs_2CO_3, THF, reflux, 24 h	 (63)	625
C_{7-13}				
		1. CuI (10 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 120°, time 1 2. $Pd(dppf)Cl_2$ (10 mol %), KOAc, toluene, 120°, time 2		186

R^1	R^2	R^3	R^4	Time 1 (h)	Time 2 (h)	
Me	H	5-Cl	H	24	24	(63)
Me	H	4-Br	H	24	24	(57)
Me	H	5-Br	H	24	24	(78)
Me	H	4,5-$(MeO)_2$	H	18	24	(65)
Me	H	H	CF_3	24	24	(67)
Me	4-Cl	H	H	26	24	(77)
Me	4-Br	H	H	24	24	(71)
Me	4-MeO	H	H	18	24	(67)
Me	4-CF_3O	H	H	30	36	(69)
Me	2-Me	H	H	30	24	(62)
Me	3-Me	H	H	30	36	(68)
Me	4-Me	H	H	24	36	(80)
Me	3,5-Me_2	H	H	26	36	(64)
Me	2-$(CH{=}CH)_2$-3	H	H	16	36	(69)
Bn	H	H	H	24	24	(87)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		**8** (15 mol %), DMEDA (30 mol %), Cs_2CO_3, THF, reflux, 24 h	 (63)	625
		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, 6 h	 (94)	100
		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°	 R: H, Time (h) 7 (99); TMS, 10 (99)	100
NaN_3		 , $CuSO_4$•$5H_2O$ (5 mol %), Na ascorbate, L-Pro (20 mol %), Na_2CO_3, DMSO/H_2O (9:1), 60°, 18 h	 (73)	606
		1. CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, time 2. TFA, $MeCl_2$, rt		608

R^1	R^2	R^3	Time (h)		R^1	R^2	R^3	Time (h)	
H	H	*n*-C_5H_{11}	9	(92)	*n*-Bu	H	EtO_2C	16	(81)
H	H	Ph	9	(93)	*n*-Bu	Et	*n*-C_8H_{17}	14	(66)
$TIPSOCH_2$	H	*n*-C_5H_{11}	11	(78)	Ph	Et	*n*-C_5H_{11}	14	(72)
n-Pr	H	*n*-Pr	9	(83)	Bn	H	$BnO(CH_2)_2$	9	(72)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_0				
		1. CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°, time 2. TFA, $MeCl_2$, rt	 R: $Cl(CH_2)_3$, Time (h) 13 (89); Ph, 6 (86)	608
H_2NBoc		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, THF, 80°		100

R^1	R^2	R^3	R^4	Time (h)		R^1	R^2	R^3	R^4	Time (h)	
H	H	*n*-Pr	*n*-Pr	5	(73)	TMS	*n*-Bu	H	$Cl(CH_2)_4$	9	(92)
TMS	H	*n*-Pr	*n*-Pr	6	(89)	Me	Me	Me	Me	14	(97)
TMS	Me	Me	TMS	8	(97)	*n*-Bu	H	*t*-BuO_2C	TBS	8	(98)
TMS	*n*-Bu	H	$THPO(CH_2)_2$	10	(86)	3-thienyl	H	CH_2=C(Me)	TMS	10	(97)
TMS	*n*-Bu	*n*-Pr	*n*-Pr	14	(78)						

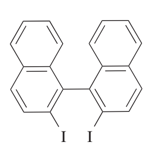
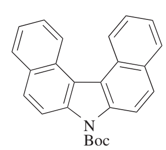
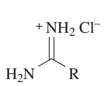
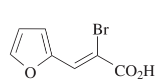
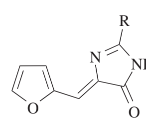
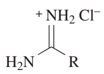
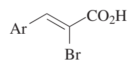
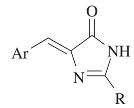
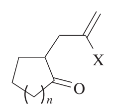
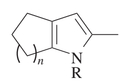
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 110°, 24 h	 (75)	100
C_{2-7}				
		Cu_2O (20 mol %), Cs_2CO_3, DMF, 100°, 12 h	 R: Me (48); *n*-Pr (45); *c*-Pr (94); Ph (67)	678

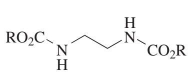
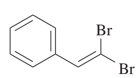
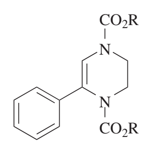
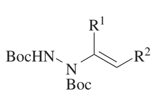
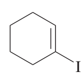
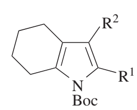
TABLE 35. *N*-VINYLATIONS IN MULTI-STEP REACTIONS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-7} 		Cu_2O (20 mol %), Cs_2CO_3, DMF, 80°, 12 h		678

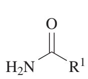
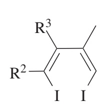
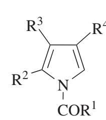
Ar	R	
$4\text{-}MeC_6H_4$	H	(53)
$4\text{-}MeC_6H_4$	MeO	(70)
$4\text{-}MeC_6H_4$	Me	(44)
$4\text{-}n\text{-}PrC_6H_4$	H	(66)
$4\text{-}n\text{-}PrC_6H_4$	Cl	(60)
$4\text{-}n\text{-}PrC_6H_4$	MeO	(75)
$4\text{-}n\text{-}PrC_6H_4$	Me	(52)
$4\text{-}c\text{-}PrC_6H_4$	H	(55)
$4\text{-}c\text{-}PrC_6H_4$	Cl	(62)
$4\text{-}c\text{-}PrC_6H_4$	MeO	(68)
$4\text{-}c\text{-}PrC_6H_4$	Me	(86)
$4\text{-}PyC_6H_4$	Cl	(62)
$4\text{-}PyC_6H_4$	MeO	(82)
$4\text{-}PyC_6H_4$	Me	(44)
$4\text{-}PhC_6H_4$	H	(75)
$4\text{-}PhC_6H_4$	MeO	(87)
$4\text{-}PhC_6H_4$	Me	(71)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-7} H_2NR		CuI (10 mol %), DMG (20 mol %), K_3PO_4, NH_4OAc, MeCN, reflux		574

n	R	X	Time (h)	
1	Ph	Br	24	(95)
2	allyl	Br	15	(99)
2	$n\text{-}C_5H_{11}$	Br	15	(99)
2	$c\text{-}C_6H_{11}$	Br	22	(78)
2	$4\text{-}MeOC_6H_4$	Br	12	(92)
2	Bn	Cl	24	(86)
2	Bn	Br	10	(99)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		CuI (10 mol %), DMG (20 mol %), K_3PO_4, NH_4OAc, toluene, 80°, 24 h	 R: Me (43); allyl (37)	668
C_{4-8} 		1. CuI (10 mol %), phen (20 mol %), Cs_2CO_3, DMF, 80°, 24 h 2. Xylene, 140°, 24 h		671

R^1	R_2	
Me	MeO_2C	(49)
$MEMO(CH_2)_4$	Et	(61)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-8} 		CuI (20 mol %), DMCDA (20 mol %), Cs_2CO_3, dioxane, 100°		679, 610

R^1	R^2	R^3	R^4	Time (h)	
n-Bu	H	*n*-Bu	*n*-Bu	24	(95)
Ph	H	*n*-Bu	*n*-Bu	18	(54)
Ph	H	Ph	Ph	3	(54)
Ph	*n*-Pr	*n*-Pr	*n*-Bu	24	(54)
Ph	Ph	Ph	*n*-Bu	20	(32)
$4\text{-}H_2NC_6H_4$	H	*n*-Bu	*n*-Bu	18	(71)
$4\text{-}H_2NC_6H_4$	*n*-Pr	*n*-Pr	*n*-Bu	24	(70)
$4\text{-}MeC_6H_4$	H	*n*-Bu	*n*-Bu	24	(71)
Bn	H	*n*-Bu	*n*-Bu	24	(73)
Bn	H	Ph	Ph	4	(48)

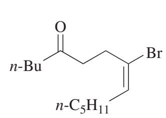
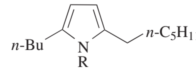
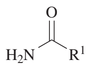
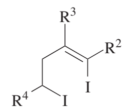
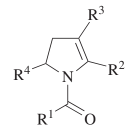
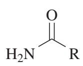
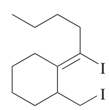
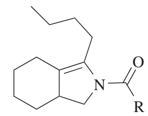
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-7} H_2NR		CuI (10 mol %), DMG (20 mol %), K_3PO_4, NH_4OAc, MeCN, reflux, 24 h	 R: $n\text{-}C_5H_{11}$ (93); Bn (93)	574

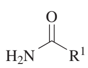
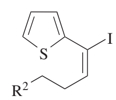
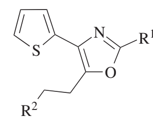
TABLE 35. *N*-VINYLATIONS IN MULTI-STEP REACTIONS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-8}				
		CuI (20 mol %), DMCDA (20 mol %), K_2CO_3, 48 h		

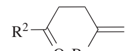
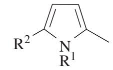
R^1	R^2	R^3	R^4	Solvent	Temp (°)		Refs.
n-Bu	Et	Et	H	toluene	reflux	(70)	680, 610
n-Bu	*n*-Pr	*n*-Pr	H	toluene	reflux	(69)	680
n-Bu	*n*-Pr	*n*-Pr	H	dioxane	110	(69)	610
n-Bu	Ph	Ph	TMS	dioxane	110	(41)	680, 610
Ph	*n*-Pr	*n*-Pr	H	toluene	reflux	(65)	680
Ph	*n*-Pr	*n*-Pr	H	dioxane	110	(46)	610
Ph	Ph	Ph	H	toluene	reflux	(65)	680
Ph	Ph	Ph	H	dioxane	reflux	(65)	610
4-MeC_6H_4	Et	Et	H	toluene	reflux	(64)	680, 610
4-MeC_6H_4	Ph	Ph	H	dioxane	reflux	(47)	610
4-MeC_6H_4	Ph	Ph	H	toluene	reflux	(47)	680

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-7}				
		CuI (20 mol %), DMCDA (20 mol %), K_2CO_3, 48 h		

R	Solvent	Temp (°)		Refs.
n-Bu	toluene	reflux	(57)	680
n-Bu	dioxane	110	(57)	610
PMP	toluene	reflux	(32)	680
PMP	dioxane	110	(47)	610

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-6}				
		1. CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 8 h 2. I_2, DBU, rt to 80°, 10 h		664

R^1	R^2	
2-furyl	$NCCH_2$	(63)
Ph	$NCCH_2$	(68)
Ph	TIPSO	(72)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-7}				
H_2NR^1		CuI (10 mol %), DMG (20 mol %), K_3PO_4, NH_4OAc, MeCN, reflux, 24 h		574

R^1	R^2	
n-C_5H_{11}	Bn	(68)
Bn	Me	(90)
Bn	Bn	(85)

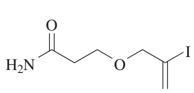
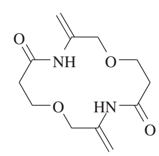
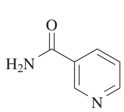
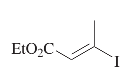
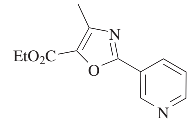
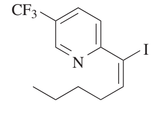
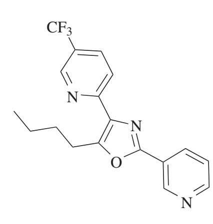
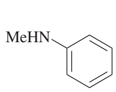
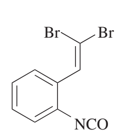
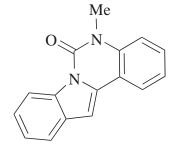
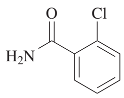
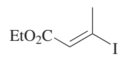
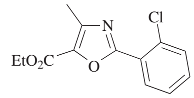
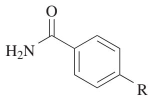
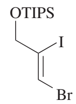
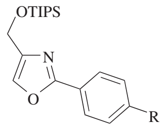
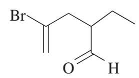
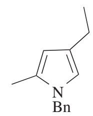
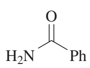
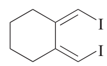
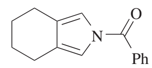
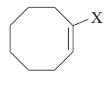
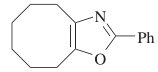
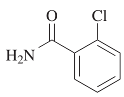
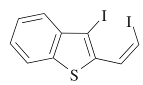
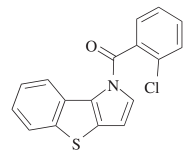
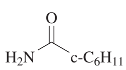
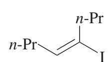
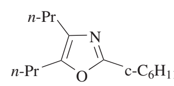
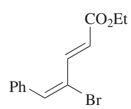
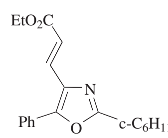
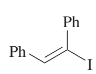
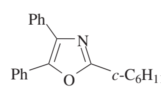
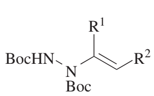
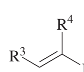
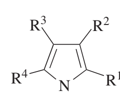
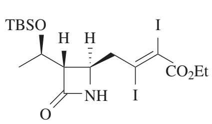
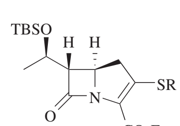
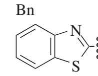
Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	Intramolecular	CuI (1 eq), DMEDA (2 eq), Cs_2CO_3, dioxane, reflux, 4 h	 (86)	673
		1. CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 8 h 2. I_2, DBU, rt to 80°, 10 h	 (70)	664
		1. CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 8 h 2. I_2, DBU, rt to 80°, 10 h	 (74)	664
C_7				
		1. CuI (10 mol %), K_2CO_3, DMEDA (20 mol %), toluene, 120°, 24 h 2. $Pd(dppf)Cl_2$ (10 mol %), KOAc, toluene, 120°, 24 h	 (78)	157

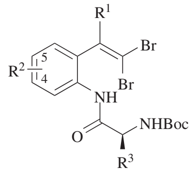
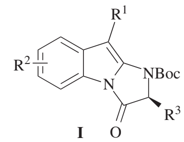
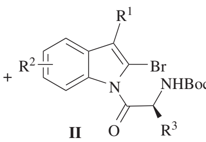
TABLE 35. *N*-VINYLATIONS IN MULTI-STEP REACTIONS (*Continued*)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 8 h 2. I_2, DBU, rt to 80°, 10 h	 (77)	664
C_{7-8}				
		CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°	 R / Time (h) H / 8 / (98) Cl / 8 / (99) CF_3 / 10 / (99)	664
C_7				
H_2NBn		CuI (10 mol %), DMG (20 mol %), K_3PO_4, NH_4OAc, MeCN, reflux, 24 h	 (83)	574
		CuI (20 mol %), DMCDA (20 mol %), Cs_2CO_3, dioxane, 100°, 20 h	 (89)	679, 610
		1. CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 8 h 2. I_2, DBU, rt to 80°, 10 h	 X Br (74) I (78)	664
		CuI (5 mol %), DMEDA (20 mol %), Cs_2CO_3, toluene, 110°, 6 h	 (83)	100
C_7				
		$CuSO_4$•$5H_2O$ (5 mol %), L-Pro (20 mol %), Na ascorbate, Na_2CO_3, DMSO/H_2O (9:1), 60°, 18 h	 (56)	664
		1. CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 8 h 2. I_2, DBU, rt to 80°, 10 h	 (63)	664
		1. CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 8 h 2. I_2, DBU, rt to 80°, 10 h	 (79)	664
C_{8-10}				
		1. CuI (10 mol %), phen (20 mol %), Cs_2CO_3, DMF, 80°, 24 h 2. xylene, 140°, 24 h 3. *p*-TsOH, rt, 6 h		671

R^1	R^2	R^3	R^4	
n-Pr	*n*-Pr	EtO_2C	Me	(59)
n-Pr	*n*-Pr	CH_2=$CHCH_2O_2C$	H	(66)
n-Pr	*n*-Pr	$BnO(CH_2)_2$	Me	(61)
n-Pr	*n*-Pr	*n*-C_8H_{17}	H	(68)

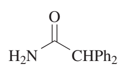
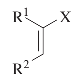
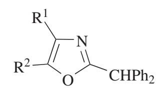
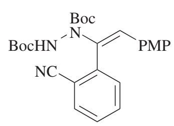
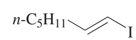
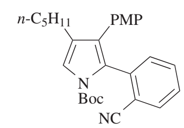
R^1	R^2	R^3	R^4	
$MEMO(CH_2)_3$	Et	MeO_2C	H	(49)
$MEMO(CH_2)_3$	Et	$BnO(CH_2)_2$	Me	(61)
$MEMO(CH_2)_3$	Et	Ph	Ph	(60)
2-thienyl	$NC(CH_2)_3$	*n*-Pr	*n*-Pr	(49)
n-C_8H_{17}	H	*n*-Pr	*n*-Pr	(62)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	Intramolecular	1. CuI (20 mol %), bpy (20 mol %), K_3PO_4, toluene, H_2O, 60° 2. RSH, phen (20 mol %), PPh_3 (40 mol %)	 R $TBSO(CH_2)_2$ (75) $PNBO_2CCH_2$ (77) $PNBO_2CNH(CH_2)_2$ (62) Ph (68) Bn (76)  (89)	629

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-16}				
	Intramolecular	CuI (2.5 mol %), CDA (5 mol %), K_2CO_3, toluene, 120°	 I +  II	681

R^1	R^2	R^3	Time (h)	I	er	II
H	H	H	22	(74)	—	(0)
H	H	Me	13	(84)	93:7	(0)
H	H	$BnO_2CCH_2CH_2$	15	(71)	53:47	(0)
H	H	*i*-Pr	22	(63)	52:48[a]	(0)
H	H	$BocHN(CH_2)_4$	15	(69)	96.5:3.5	(0)
H	H	*i*-Bu	22	(68)	94.5:5.5	(0)
H	H	Bn	18	(73)	88:12	(0)
H	4-F	Me	13	(65)	94.5:5.5	(0)

R^1	R^2	R^3	Time (h)	I	er	II
H	3-MeO	Me	49	(56)	64:36	(0)
H	4,5-$(BnO)_2$	Me	14	(69)	94.5:5.5	(0)
H	6-Me	Me	13	(78)	86.5:13.5	(0)
H	4-CF_3	Me	12	(67)	82:12	(0)
H	5-MeO, 6-BnO	Me	13	(67)	90.5:9.5	(0)
4-FC_6H_4	H	H	14	(52)[b]	—	(0)
4-FC_6H_4	H	H	13	(40)	—	(28)

Nitrogen Nucleophile	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
		1. CuI (5 mol %), DMEDA (20 mol %), K_2CO_3, toluene, 80°, 8 h 2. I_2, DBU, rt to 80°, 10 h		664
C_{15}				
		1. CuI (10 mol %), phen (20 mol %), Cs_2CO_3, DMF, 80°, 24 h 2. xylene, 140°, 24 h 3. *p*-TsOH, rt, 6 h	 (54)	671

R^1	R^2	X	
Me	EtO_2C	I	(82)
$NC(CH_2)_3$	2-thienyl	I	(72)
Ph	Ph	Br	(79)
Ph	Ph	I	(79)

[a] The er of the substrate was 52:48.

[b] The amount of CuI was 10 mol % and that of CDA, 20 mol %.

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