Organic Structures from Spectra

SIXTH EDITION

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WILEY

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PREFACE

This is the Sixth Edition of the text "Organic Structures from Spectra". The original text, published in 1986 by J R Kalman and S Sternhell, was a remarkable instructive text at a time where spectroscopic analysis, particularly NMR spectroscopy, was becoming widespread and routinely available in many chemical laboratories. The original text was founded on the premise that the best way to learn to obtain "structures from spectra" is to build up skills by practising on simple problems. Editions two through five of the text have been published at about five-yearly intervals and each revision has taken account of new developments in spectroscopy as well as dropping out techniques that have become less important or obsolete over time. The collection has grown substantially and we are deeply indebted to Dr John Kalman and to Emeritus Professor Sev Sternhell for their commitment and contribution to all of the previous editions of "Organic Structures from Spectra".

Edition Six of the text has been expanded to include a new selection of problems and many of the problems now incorporate 2D NMR spectra (COSY, TOCSY, NOESY, C–H Correlation spectroscopy or HMBC).

The overarching philosophy remains the same as in previous editions of the text:

a. Theoretical exposition is kept to a minimum, consistent with gaining an understanding of those aspects of the various spectroscopic techniques which are actually used in solving problems. Experience tells us that both mathematical detail and in-depth theoretical description of advanced techniques merely confuse or overwhelm the average student.

b. The learning of data is kept to a minimum. There are now many sources of spectroscopic data available online. It is much more important to learn to use a range of generalised data well, rather than to achieve a superficial acquaintance with extensive sets of data. This book contains summary tables of essential spectroscopic data and these tables become critical reference material, particularly in the early stages of gaining experience in solving problems. ix

c. We emphasise the concept of identifying "structural elements or fragments" and building the logical thought processes needed to produce a structure out of the structural elements.

The derivation of structural information from spectroscopic data is now an integral part of Organic Chemistry courses at all universities. At the undergraduate level, the principal aim is to teach students to solve simple structural problems efficiently by using combinations of the major spectroscopic techniques (UV, IR, NMR and MS). We have evolved courses both at the University of New South Wales and at the University of Sydney which achieve this aim quickly and painlessly. The text is tailored specifically to the needs and approach of these courses.

The courses have been taught in the second and third years of undergraduate chemistry, at which stage students have usually completed an elementary course of Organic Chemistry in their first year and students have also been exposed to elementary spectroscopic theory, but are, in general, unable to relate the theory to actually solving spectroscopic problems.

We have delivered courses of about 9 lectures outlining the basic theory, instrumentation and the structure–spectra correlations of the major spectroscopic techniques. The treatment is highly condensed and elementary and, not surprisingly, the students do initially have great difficulties in solving even the simplest problems. The lectures are followed by a series of problem solving workshops (about 2 hours each) with a focus on 5 to 6 problems per session. The students are permitted to work either individually or in groups and may use any additional resource material that they can find. At the conclusion of the course, the great majority of the class is quite proficient and has achieved a satisfactory level of understanding of all methods used. Clearly, most of the real teaching is done during the hands-on problem seminars. At the end of the course, there is an examination usually consisting essentially of 3 or 4 problems from the book and the results are generally very satisfactory. The students have always found this a rewarding course since the practical skills acquired are obvious to them. Solving these real puzzles is also addictive – there is a real sense of achievement, understanding and satisfaction,

since the challenge in solving the graded problems builds confidence even though the more difficult examples are quite demanding.

Problems 1–19 are introductory questions designed to develop the understanding of molecular symmetry, the analysis of simple spin systems as well as how to navigate the common 2D NMR experiments.

Problems 20–294 are of the standard "structures from spectra" type and are arranged roughly in order of increasing difficulty. A number of problems deal with related compounds (sets of isomers) which differ mainly in symmetry or the connectivity of the structural elements and are ideally set together. The sets of related examples include Problems 33 and 34; 35 and 36; 40–43; 52 and 53; 57–61; 66–71; 72 and 73; 74–77; 82 and 83; 84–86; 92–94; 95 and 96; 101 and 102; 106 and 107; 113 and 114; 118–121; 126 and 127; 129–132; 133 and 134; 137–139; 140–142; 154 and 155; 157–164; 165–169; 176–180; 185–190; 199–200; 205–206; 208–209; 211–212; 245–247; 262–264; and 289–290.

A number of problems (218, 219, 220, 221, 242, 273, 278, 279, 280, 285, 286 and 287) exemplify complexities arising from the presence of chiral centres, and some problems illustrate restricted rotation about amide bonds (191, 275 and 281). There are a number of problems dealing with the structures of compounds of biological, environmental or industrial significance (41, 49, 64, 91, 92, 93, 94, 98, 146, 151, 152, 160, 179, 180, 191, 198, 219, 225, 231, 235, 236, 269, 285, 277, 278, 279, 284, 286 and 287).

Problems 295–300 are again structures from spectra, but with the data presented in a textual form such as might be encountered when reading the experimental section of a paper or report.

Problems 301–309 deal with the use of NMR spectroscopy for quantitative analysis and for the analysis of mixtures of compounds.

In Chapter 9, there are also three worked solutions (to problems 117, 146 and 77) as an illustration of a logical approach to solving problems. However, with the exception that we insist that students perform all routine measurements first, we do not recommend a mechanical attitude to problem solving – intuition has an important place in solving structures from spectra as it has elsewhere in chemistry.

Bona fide instructors may obtain a list of solutions (at no charge) by writing to the authors or EMAIL: L.Field@unsw.edu.au

We wish to thank the many graduate students and research associates who, over the years, have supplied us with many of the compounds used in the problems.

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January 2020

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INTRODUCTION

1.1 GENERAL PRINCIPLES OF ABSORPTION SPECTROSCOPY

Spectroscopy involves resolving electromagnetic radiation into its component wavelengths (or frequencies) and absorption spectroscopy is the absorption of electromagnetic radiation by matter as a function of wavelength.

In Organic Chemistry, we typically deal with molecular spectroscopy, *i.e.* the spectroscopy of atoms that are bound together in molecules rather than absorption by individual atoms or ions.

An absorption spectrum is a plot or graph of the absorption of energy (radiation) as a function of its wavelength (λ) or frequency (ν). A schematic absorption spectrum is given in Figure 1.1.

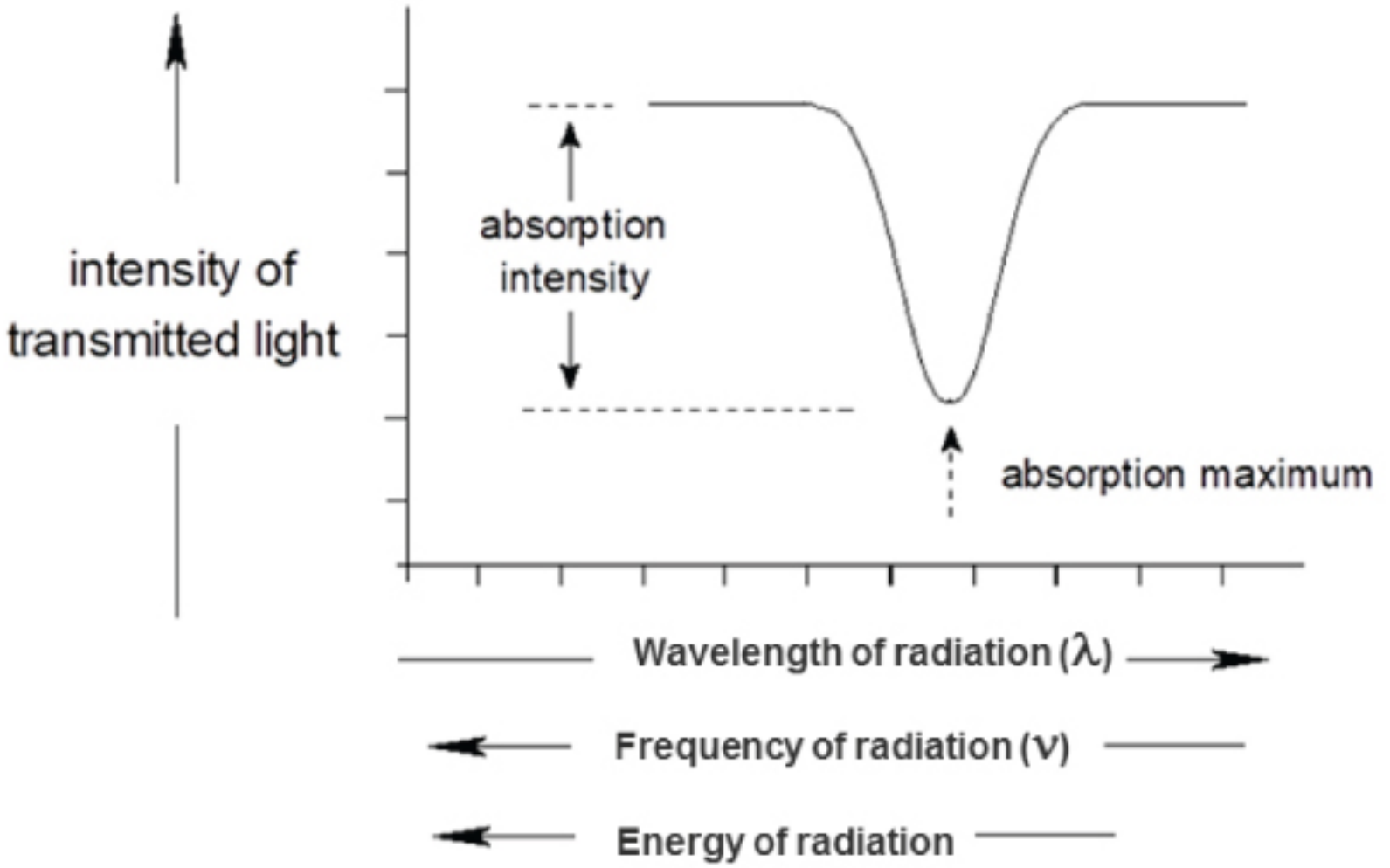


Figure 1.1 Schematic Absorption Spectrum

It follows that the *x*-axis in Figure 1.1 is an **energy** scale, since the frequency, wavelength and energy (E) of electromagnetic radiation are interrelated by the Planck–Einstein relation:

$$E = h.\nu$$

$$\text{and} \quad \nu.\lambda = c$$

where ν is the frequency of the electromagnetic radiation, λ is the wavelength of the electromagnetic radiation, and *c* is the velocity of light.

An absorption band can be characterised primarily by two parameters:

a. the wavelength (or frequency) at which maximum absorption occurs

b. the intensity of absorption at this wavelength compared to base-line (or background) absorption

A spectroscopic transition takes a molecule from one energy state to a state of higher energy. For any spectroscopic transition between energy states (*e.g.* E_1 and E_2 in Figure 1.2), the change in energy (ΔE) is given by:

$$\Delta E = h\nu$$

where h is Planck's constant and ν is the frequency of the electromagnetic energy absorbed.

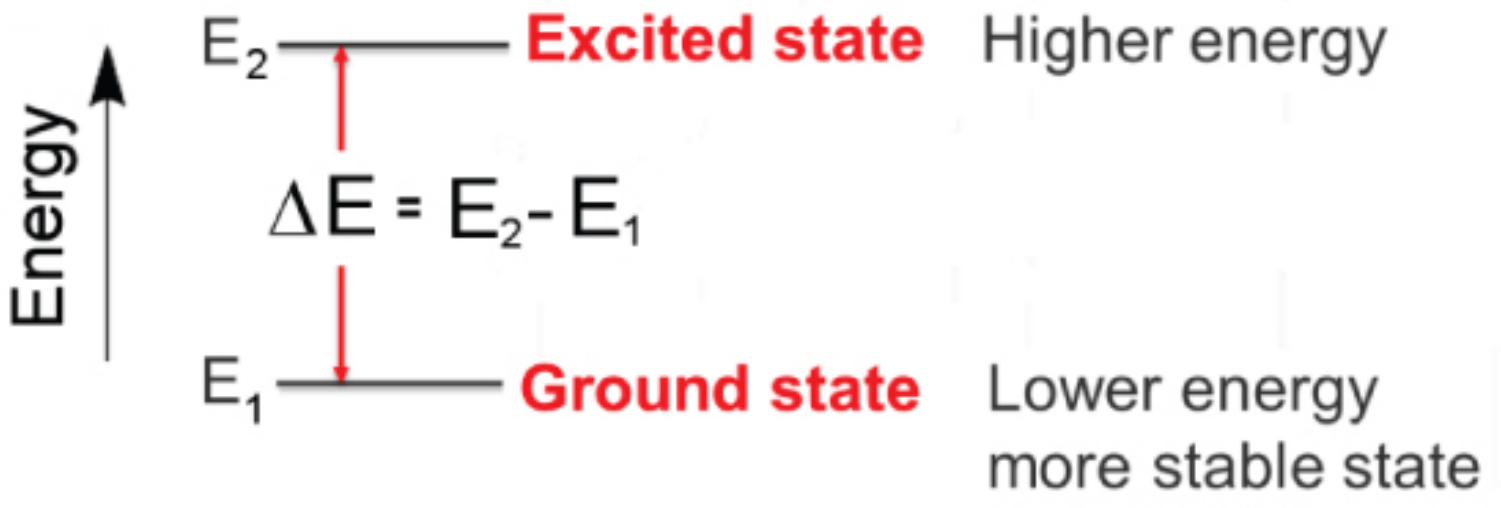


Figure 1.2 Definition of a Spectroscopic Transition

It follows that $\Delta E \propto \nu$ and that $\Delta E \propto 1/\lambda$; *i.e.* the larger ΔE, the *higher* the frequency of radiation required for absorption to take place or the *shorter* the wavelength of radiation required for absorption to take place.

The *y*-axis in Figure 1.1 measures the intensity of the absorption band and this depends on the number of molecules observed (the Beer–Lambert Law) and the probability of the transition between the energy levels.

A spectrum consists of distinct bands or transitions because the absorption (or emission) of energy is quantised. The energy gap for a transition (and hence the absorption frequency) is a ***molecular property*** and it is ***characteristic of molecular structure***. The absorption intensity is also a molecular property and both the frequency and the intensity of a transition can provide structural information.

1.2 CHROMOPHORES

In general, any spectral feature, *i.e.* a band or group of bands, is due not to the whole molecule, but to an identifiable part of the molecule, which we loosely call a *chromophore*.

A chromophore may correspond to a functional group (*e.g.* a hydroxyl group or the double bond in a carbonyl group). However, it may equally well correspond to a single atom within a molecule or to a group of atoms (*e.g.* a methyl group) that is not normally associated with chemical functionality.

The detection of a chromophore permits us to deduce the presence of a *structural fragment* or a *structural element* in the molecule. The fact that it is the chromophores and not the molecule as a whole that give rise to spectral features is fortunate because it permits complete molecular structures to be built up piece-by-piece from the molecular fragments.

1.3 DEGREE OF UNSATURATION

Traditionally, the molecular formula of a compound was derived from elemental analysis and its molecular weight, and these were determined independently. The concept of the **degree of unsaturation** of an organic

compound derives simply from the tetravalency of carbon. For a non-cyclic hydrocarbon (*i.e.* an alkane) the number of hydrogen atoms must be twice the number of carbon atoms plus two, any "deficiency" in the number of hydrogens must be due to the presence of unsaturation, *i.e.* double bonds, triple bonds or rings in the structure.

The degree of unsaturation can be calculated from the molecular formula for all compounds containing C, H, N, O, S or the halogens. There are three basic steps in calculating the degree of unsaturation:

Step 1 – take the molecular formula and replace all halogens by hydrogens

Step 2 – omit all of the sulfur or oxygen atoms

Step 3 – for each nitrogen, omit the nitrogen and omit one hydrogen

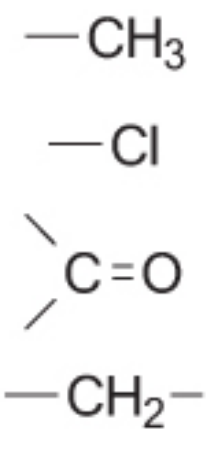
After these three steps, the molecular formula is reduced to C_nH_m and the degree of unsaturation is given by:

$$\text{Degree of Unsaturation} = n - \frac{m}{2} + 1$$

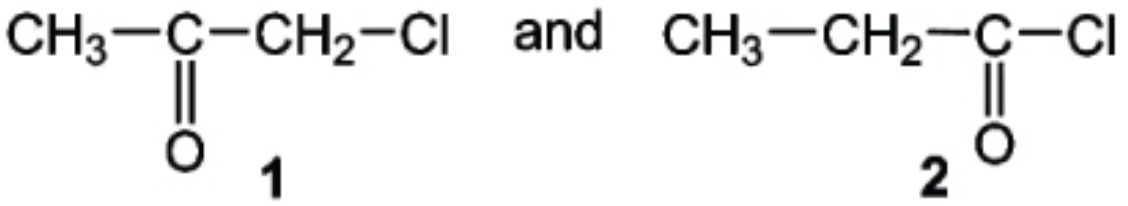
The degree of unsaturation indicates the number of π bonds or rings that the compound contains. For example, a compound whose molecular formula is $C_4H_9NO_2$ is reduced to C_4H_8, which gives a degree of unsaturation of 1. This indicates that the molecule must have one π bond or one ring. Note that a triple bond (*e.g.* the −C≡C− bond in an alkyne or the −C≡N bond in a nitrile) contributes two units of unsaturation (two π bonds). Note also that any compound that contains an aromatic ring always has a degree of unsaturation greater than or equal to 4, since the aromatic ring contains a ring plus three π bonds. Similarly, if a compound has a degree of unsaturation greater than or equal to 4, one should suspect the possibility that the structure contains an aromatic ring.

1.4 CONNECTIVITY

Even if it were possible to identify sufficient structural elements in a molecule to account for the molecular formula, it may not be possible to deduce the structural formula from a knowledge of the structural elements alone. For example, it could be demonstrated that a substance of molecular formula C_3H_5OCl contains the structural elements:



and this leaves two possible structures:



Not only the presence of various structural elements, but also their juxtaposition, must be determined to establish the structure of a molecule. Fortunately, spectroscopy often gives valuable information concerning the *connectivity* of structural elements and in the above example it would be very easy to determine whether there is a ketonic carbonyl group (as in **1**) or an acid chloride (as in **2**). In addition, it is possible to determine independently whether the methyl ($-CH_3$) and methylene ($-CH_2-$) groups are separated (as in **1**) or adjacent (as in **2**).

1.5 SENSITIVITY

Sensitivity is generally taken to signify the limits of detectability of a chromophore. Some methods (*e.g.* ^{1}H NMR spectroscopy) detect all chromophores accessible to them with equal sensitivity while in other techniques (*e.g.* UV spectroscopy) the range of sensitivity towards different chromophores spans many orders of magnitude. Mass spectroscopy is the most sensitive of the common spectroscopic techniques and requires only very small amounts of sample (< 10^{-10} g) whereas ^{13}C NMR typically requires tens of milligrams of sample. In terms of overall sensitivity:

$$\text{MS} > \text{UV} > \text{IR} > {}^1\text{H NMR} > {}^{13}\text{C NMR}$$

but the relative sensitivity of different spectroscopic techniques often depends on the specific chromophores present in a molecule.

1.6 PRACTICAL CONSIDERATIONS

The five major spectroscopic methods (MS, UV, IR, ^{1}H NMR and ^{13}C NMR) have become established as the principal tools for the determination of the structures of organic compounds because, between them, they detect a wide variety of structural elements.

The instrumentation and skills involved in the use of all five major spectroscopic methods are now widely spread, but the ease of obtaining and interpreting the data from each method under real laboratory conditions varies.

In very general terms:

a. While the ***cost*** of each type of instrumentation differs greatly (NMR instruments cost between $50,000 and several million dollars), as an overall guide, MS and NMR instruments are much more costly than UV and IR spectrometers. With increasing cost comes increasing difficulty in maintenance and the required operator expertise, thus compounding the total outlay.

b. In terms of ***ease of usage*** for routine operation, most UV and IR instruments are comparatively straightforward bench-top laboratory instruments. NMR spectrometers are also common as "hands-on" instruments in most chemistry laboratories and the users require routine training and a degree of basic computer literacy. Similarly some mass spectrometers are now designed to be used by researchers as "hands-on" routine instruments. However, the more advanced NMR spectrometers and most mass spectrometers are still sophisticated instruments that are usually operated and maintained by specialists.

c. The ***scope*** of each spectroscopic method can be defined as the amount of useful information it provides. This is a function of the total amount of information obtainable and also how difficult the data are to

interpret. The scope of each method varies from problem to problem, and each method has its aficionados and specialists, but the overall utility undoubtedly decreases in the order:

$$\text{NMR} > \text{MS} > \text{IR} > \text{UV}$$

with the combination of ^{1}H and ^{13}C NMR spectroscopy providing the most useful information.

d. The ***theoretical background*** needed for each method varies with the nature of the experiment, but the minimum overall amount of theory needed decreases in the order:

$$\text{NMR} >> \text{MS} > \text{UV} \approx \text{IR}$$

2
ULTRAVIOLET (UV) SPECTROSCOPY

2.1 THE NATURE OF ULTRAVIOLET SPECTROSCOPY

The term "UV spectroscopy" generally refers to the excitation of *electronic transitions* by absorption of energy in the ultraviolet region of the electromagnetic spectrum (λ in the range approximately 200–380 nm) accessible to standard UV spectrometers.

Electronic transitions are also responsible for absorption in the visible region of the spectrum (approximately 380–800 nm) which is easily accessible instrumentally but of less importance when solving structural problems because most organic compounds are colourless. An extensive region at wavelengths shorter than ~200 nm ("vacuum ultraviolet") also corresponds to electronic transitions, but this region is not readily accessible with standard instruments. UV spectra used for determination of structures are invariably obtained in solution.

2.2 BASIC INSTRUMENTATION

Basic instrumentation for both UV and IR spectroscopies consists of an energy *source*, a *dispersing device* (prism or grating), a *sample cell* and a *detector*, arranged as schematically shown in Figure 2.1.

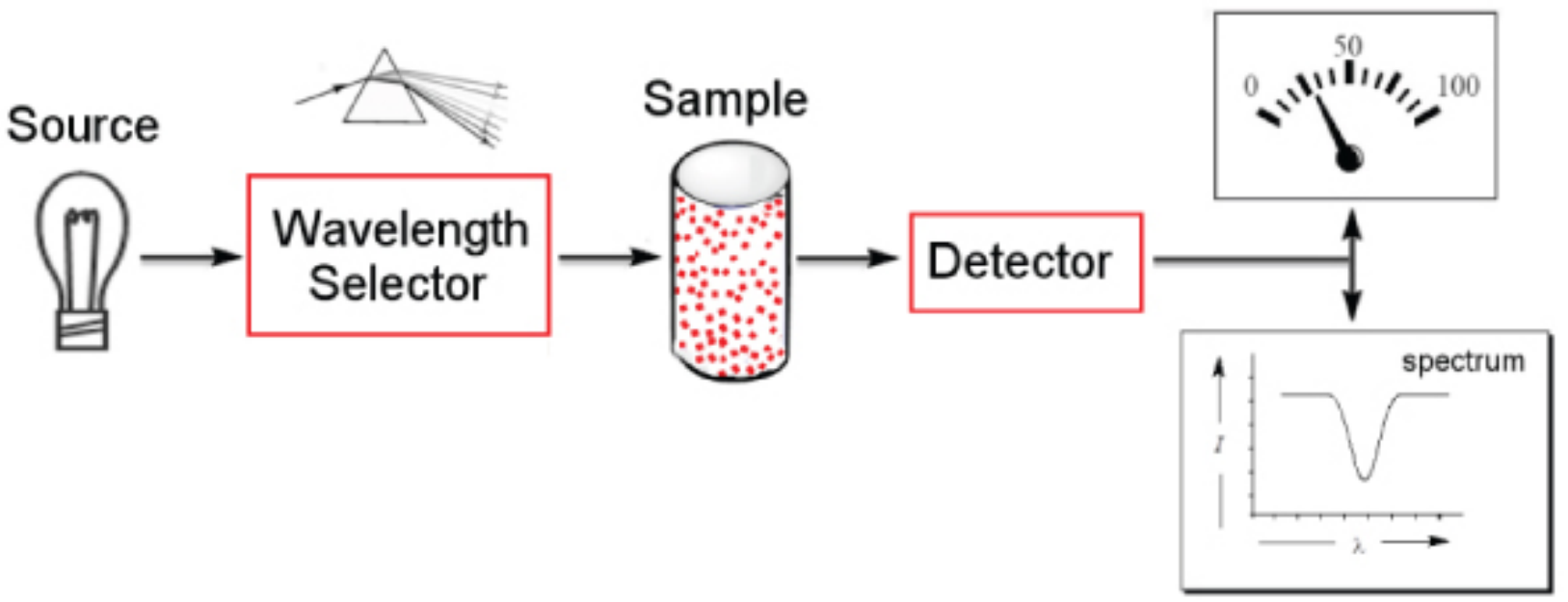


Figure 2.1 Schematic Representation of an IR or UV Spectrometer

The dispersing device scans through the range of wavelengths produced by the source and these pass through the sample. The drive of the dispersing device is synchronised with the x-axis of the recorder or fed directly to a computer, so that the x-axis tracks the wavelength of radiation reaching the detector. The signal from the detector is transmitted to the *y*-axis of the recorder or to a computer and this records how much radiation is absorbed by the sample at any particular wavelength.

In practice, almost all instruments are *double-beam* spectrometers and in this type of instrument, the beam is split and part of the beam goes through a *reference cell*, containing only solvent, and part of the beam goes through the sample. The absorbance of the reference cell is subtracted from the absorbance of the sample cell. Double-beam instruments eliminate any absorbance from the solvent and also cancel out absorption resulting from the atmosphere in the optical path (Figure 2.2).

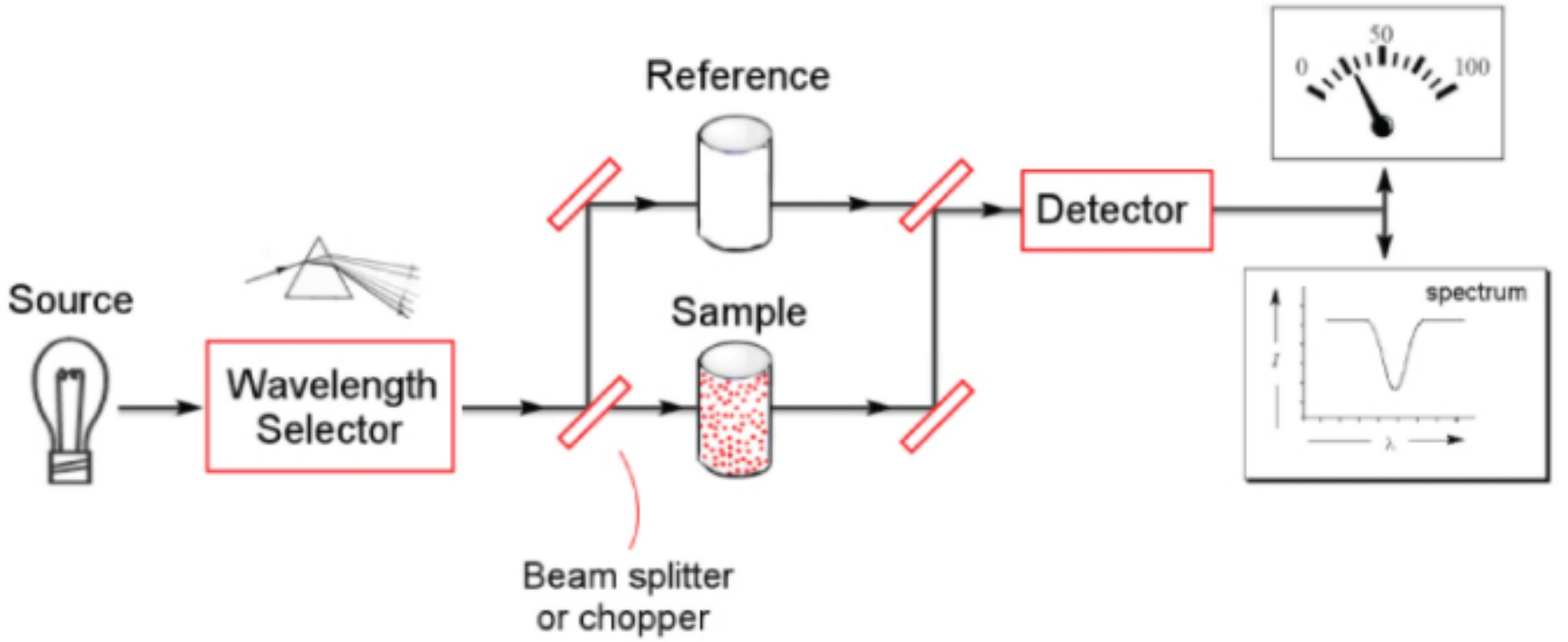


Figure 2.2 Schematic Representation of a Double-Beam Absorption Spectrometer

The energy source must be appropriate for the wavelengths of radiation being scanned. For UV spectroscopy the source is usually a deuterium lamp in which an electrical discharge through a lamp filled with deuterium gas produces a broad spectrum of light across the UV range in the electromagnetic spectrum.

The samples for UV spectroscopy are typically dissolved in solution and contained in small cells (cuvettes). The cells and optical components must be as transparent as possible to wavelengths being scanned and are typically made of quartz or fused silica. Note that conventional glass and most plastics absorb UV radiation very strongly so these materials are not used in cells for UV spectroscopy. Ethanol, hexane, water or dioxane are usually chosen as solvents as these have minimal absorption in the UV region of the spectrum.

2.3 QUANTITATIVE ASPECTS OF ULTRAVIOLET SPECTROSCOPY

The *y*-axis of a UV spectrum may be calibrated in terms of the intensity of transmitted light (*i.e.* the percentage of transmission or absorption) or it may be calibrated on a logarithmic scale, *i.e.* in terms of *absorbance* (A) (Figure 2.3).

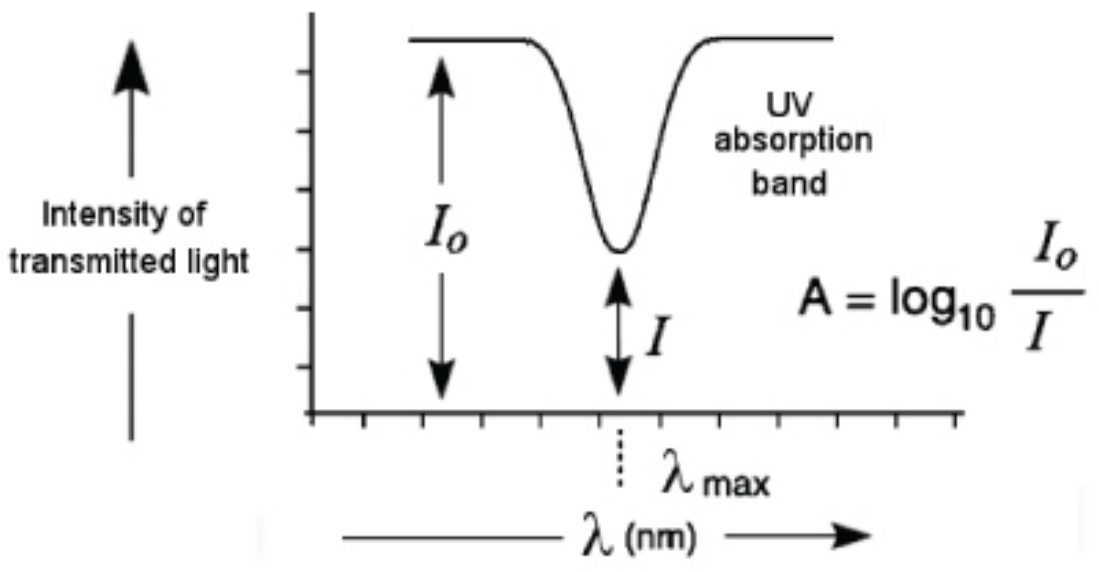


Figure 2.3 Definition of Absorbance (A)

Absorbance is proportional to concentration and path length (the Beer–Lambert Law). The intensity of absorption is usually expressed in terms of *molar absorbance* or the *molar extinction coefficient* (ε) given by:

$$\varepsilon = \frac{M\,A}{C\,l}$$

where M is the molecular weight, C the concentration (in grams per litre) and *l* is the path length through the sample in centimetres.

UV absorption bands (Figure 2.3) are characterised by the wavelength of the absorption maximum (λ_{max}) and ε. The values of associated with commonly encountered chromophores vary between 10 and 10^5. For convenience, extinction coefficients are usually tabulated as $\log_{10}(\varepsilon)$ as this gives numerical values that are easier to manage. The fact that some species may have very large extinction coefficients means that care must be taken in the preparation of samples because the presence of small amounts of strongly absorbing impurities may lead to errors in the interpretation of UV data.

2.4 CLASSIFICATION OF UV ABSORPTION BANDS

UV absorption bands have fine structure because of the presence of vibrational sub-levels, but this is rarely observed in solution due to collisional broadening. As the transitions are associated with changes of electron orbitals, they are often described in terms of the orbitals involved, *e.g.*

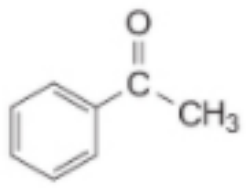
$\sigma \rightarrow \sigma^*$	where *n* denotes a non-bonding orbital,
$\pi \rightarrow \pi^*$	the asterisk denotes an antibonding orbital
$n \rightarrow \pi^*$	and σ and π have the usual meaning in
$n \rightarrow \sigma^*$	terms of bonding categories.

Another method of classification uses the symbols:

B	(for benzenoid)
E	(for ethylenic)
R	(for radical-like)
K	(for conjugated – from the German "konjugierte")

A molecule may give rise to more than one band in its UV spectrum, either because it contains more than one chromophore or because more than one transition of a single chromophore is observed. However, UV spectra typically contain far fewer features (bands) than IR, MS or NMR spectra and therefore have a lower information content. The ultraviolet spectrum of acetophenone in ethanol contains three easily observed bands (Table 2.1).

Table 2.1 Observable UV Absorption Bands for Acetophenone

	λ_{max}(nm)	ε	$\log_{10}(\varepsilon)$	Assignment	
 acetophenone	244	12,600	4.1	$\pi \rightarrow \pi^*$	K
	280	1,600	3.2	$\pi \rightarrow \pi^*$	B
	60	317	1.8	$n \rightarrow \pi^*$	R

2.5 SPECIAL TERMS IN UV SPECTROSCOPY

Auxochromes (auxiliary chromophores) are groups that have little UV absorption by themselves, but which often have significant effects on the absorption (both λ_{max} and ε) of a chromophore to which they are attached. Generally, auxochromes contain atoms with one or more lone pairs, *e.g.* –OH, –OR, $-NR_2$, –halogen.

If a structural change, such as the attachment of an auxochrome, leads to the absorption maximum being shifted to a longer wavelength, the phenomenon is termed a *bathochromic shift*. A shift towards shorter wavelength is called a *hypsochromic shift*.

2.6 IMPORTANT UV CHROMOPHORES

Most of the reliable and useful data are due to relatively strongly absorbing chromophores (ε > 200) that are mainly indicative of conjugated or aromatic systems. The examples listed below encompass most of the commonly encountered effects.

2.6.1 DIENES AND POLYENES

Extension of conjugation in a carbon chain is always associated with a pronounced shift towards longer wavelength, and usually towards greater absorption intensity (Table 2.2).

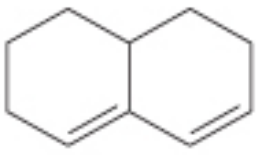
Table 2.2 The Effect of Extended Conjugation on UV Absorption

Alkene	λ_{max} (nm)	ε	$\log_{10}(\varepsilon)$
$CH_2=CH_2$	165	10,000	4.0
$CH_3-CH_2-CH=CH-CH_2-CH_3$ (*trans*)	184	10,000	4.0
$CH_2=CH-CH=CH_2$	217	20,000	4.3
$CH_3-CH=CH-CH=CH_2$ (*trans*)	224	23,000	4.4
$CH_2=CH-CH=CH-CH=CH_2$ (*trans*)	263	53,000	4.7
$CH_3-(CH=CH)_5-CH_3$ (*trans*)	341	126,000	5.1

When there are more than eight conjugated double bonds, the absorption maximum of polyenes is further shifted such that they absorb light strongly in the visible region of the spectrum.

There are empirical rules (Woodward's Rules) of good predictive value and these allow the estimation of the positions of the absorption maxima in conjugated alkenes and conjugated carbonyl compounds.

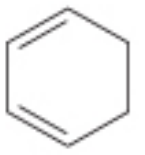
The stereochemistry and the presence of substituents also influence UV absorption by the diene chromophore. For example:



λ_{max} = 214 nm

ε = 16,000

$\log_{10}(\varepsilon)$ = 4.2



λ_{max} = 253 nm

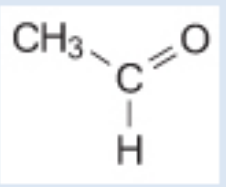
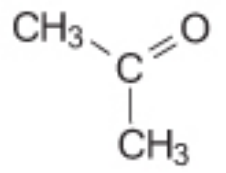
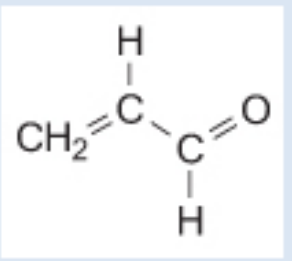
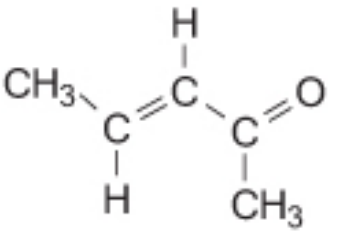
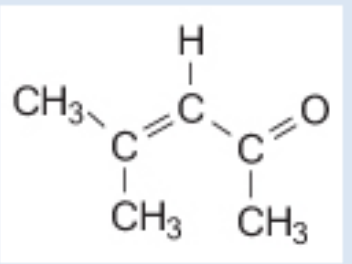
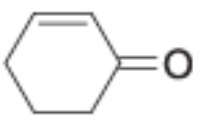
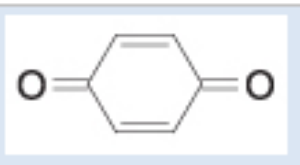
ε = 8,000

$\log_{10}(\varepsilon)$ = 3.9

2.6.2 CARBONYL COMPOUNDS

All carbonyl derivatives exhibit weak (ε < 100) absorption between 250 and 350 nm, and this is only of marginal use in determining structure. However, conjugated carbonyl derivatives always exhibit strong UV absorption (Table 2.3).

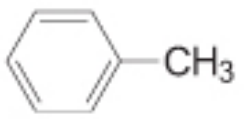
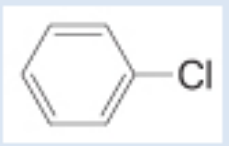
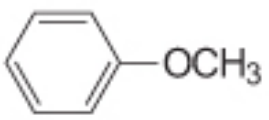
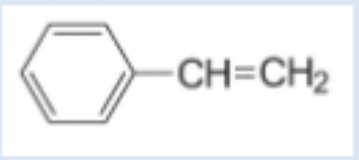
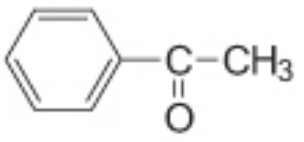
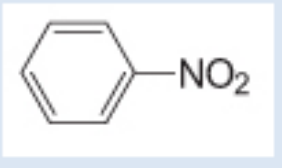
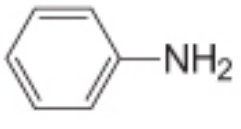
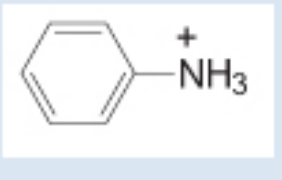
Table 2.3 UV Absorption Bands in Common Carbonyl Compounds

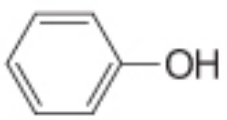
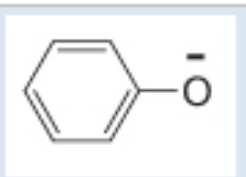
Compound	Structure	λ_{max} (nm)	ε	$\log_{10}(\varepsilon)$
Acetaldehyde		293 (hexane solution)	12	1.1
Acetone		279 (hexane solution)	15	1.2
Propenal		207	12,000	4.1
		328 (ethanol solution)	20	1.3
(E)-Pent-3-en-2-one		221	12,000	4.1
		312 (ethanol solution)	40	1.6
4-Methylpent-3-en-2-one		238	12,000	4.1
		316 (ethanol solution)	60	1.8
Cyclohex-2-en-1-one		225	7,950	3.9
Benzoquinone		247	12,600	4.1
		292	1,000	3.0
		363	250	2.4

2.6.3 BENZENE DERIVATIVES

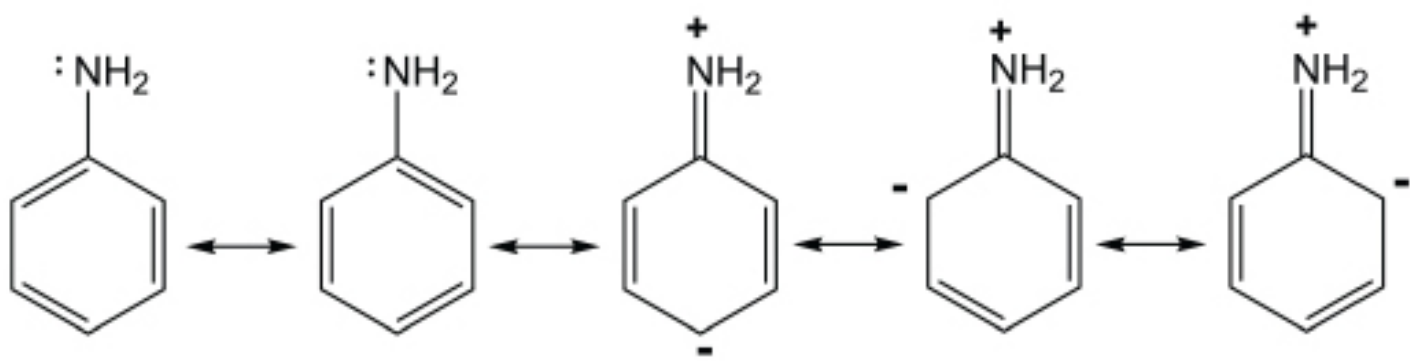
Benzene derivatives exhibit medium to strong absorption in the UV region. Bands usually have characteristic fine structure and the intensity of the absorption is strongly influenced by substituents. Examples listed in Table 2.4 include weak auxochromes (−CH_3, −Cl, −OCH_3), groups which increase conjugation (−$CH{=}CH_2$, −C(=O)−R, −NO_2) and auxochromes whose absorption is pH dependent (−NH_2 and −OH).

Table 2.4 UV Absorption Bands in Common Benzene Derivatives

Compound	Structure	λ_{max} (nm)	ε	$\log_{10}(\varepsilon)$
Benzene		184	60,000	4.8
		204	7,900	3.9
		256	200	2.3
Toluene		208	8,000	3.9
		261	300	2.5
Chlorobenzene		216	8,000	3.9
		265	240	2.4
Anisole		220	8,000	3.9
		272	1,500	3.2
Styrene		244	12,000	4.1
		282	450	2.7
Acetophenone		244	12,600	4.1
		280	1,600	3.2
Nitrobenzene		251	9,000	4.0
		280	1,000	3.0
		330	130	2.1
Aniline		230	8,000	3.9
		281	1,500	3.2
Anilinium ion		203	8,000	3.9

		254	160	2.2
Phenol		211	6,300	3.8
		270	1,500	3.2
Phenoxide ion		235	9,500	4.0
		287	2,500	3.4

Aniline and phenoxide ion have strong UV absorptions resulting from the overlap of the lone pair on the nitrogen (or oxygen) with the π-system of the benzene ring. This may be visualised in the usual Valence Bond terms:



The striking changes in the ultraviolet spectra accompanying protonation of aniline and phenoxide ion are because of the loss (or substantial reduction) of the overlap between the lone pairs and the benzene ring.

2.7 THE EFFECT OF SOLVENTS

Solvent polarity may affect the absorption characteristics, in particular λ_{max}, since the polarity of a molecule usually changes when an electron is moved from one orbital to another. Solvent effects of up to 20 nm may be observed with carbonyl compounds. Thus the $n \rightarrow \pi^*$ absorption of acetone occurs at 279 nm in *n*-hexane, 270 nm in ethanol and at 265 nm in water.

3
INFRARED (IR) SPECTROSCOPY

3.1 ABSORPTION RANGE AND THE NATURE OF IR ABSORPTION

Infrared spectroscopy generally refers to absorption of energy in the infrared region of the electromagnetic spectrum (λ in the range approximately 2.5 to 15 μm) Infrared absorption spectra are calibrated in units of wavelength expressed in micrometers:

$$1\ \mu m = 10^{-6}\ m$$

or in frequency-related *wave numbers* (cm^{-1}) which are the reciprocals of wavelengths:

$$\text{wave number } \bar{\nu}\ (cm^{-1}) = \frac{1\times10^{4}}{\text{wavelength (in } \mu m)}$$

The range accessible for standard IR instrumentation is usually:

$$\bar{\nu} = 4000 \text{ to } 666\ cm^{-1}, \text{ or}$$
$$\lambda = 2.5 \text{ to } 15\ \mu m$$

Infrared absorption intensities are rarely described quantitatively, except for the general classifications of s (strong), m (medium) or w (weak).

The transitions responsible for IR bands are due to *molecular vibrations, i.e.* due to periodic motions involving stretching or bending of bonds. Polar bonds are associated with strong IR absorption ***while symmetrical bonds with no dipole moment may not absorb at all.***

Every bond in a molecule can stretch or bend and each type of bond has a characteristic frequency in the IR range of the electromagnetic spectrum. The vibrational frequency, *i.e.* the position of the IR bands in the spectrum, depends on the nature of the bond. Shorter and stronger bonds have their stretching vibrations at the higher energy end (*i.e.* at higher frequency or shorter wavelength) of the IR spectrum than the longer and weaker bonds. Similarly, bonds to lighter atoms (*e.g.* bonds to hydrogen), always vibrate at higher energy than bonds between heavier atoms.

IR bands often have rotational sub-structure, but this is normally resolved only in spectra taken in the gas phase.

3.2 EXPERIMENTAL ASPECTS OF INFRARED SPECTROSCOPY

The basic layout of a simple dispersive IR spectrometer is the same as for an UV spectrometer (Figure 2.1), except that all components must now match the different energy range of electromagnetic radiation.

For IR spectroscopy, the source is usually a heated bar or filament that is heated with an electric current to produce a broad spectrum of radiation across the infrared range in the electromagnetic spectrum.

The optical components of IR spectrometers must be as transparent as possible to the wavelengths being scanned; these components are typically made of solid sodium chloride or potassium bromide.

The samples for IR spectroscopy can be solids, liquids, gases or solutions. In solution, samples are contained in small cells constructed with IR-transparent windows. Solution spectra are generally obtained in chloroform or carbon tetrachloride as solvents but this does lead to loss of information at longer wavelengths where there is considerable absorption of energy by the solvent. Neat liquids are most conveniently studied by sandwiching a film of the liquid between two NaCl plates. IR spectra for solids can be recorded as a mull where a sample is powdered and mixed into a thick suspension in a supporting fluid (typically Nujol®, which is a heavy paraffin oil). Solid samples are often mixed with KBr, ground to a powder and then compressed to a thin disk. IR spectra on solids can also be recorded by reflectance.

Many modern infrared spectrometers are more sophisticated Fourier Transform Infrared (FTIR) instruments, which record an infrared interference pattern generated by a moving mirror. The interference pattern is then transformed by a computer into an infrared spectrum. From the perspective of characterising compounds by IR spectroscopy, simple dispersive IR instruments and FTIR instruments produce IR spectra which are identical. FTIR instruments have the advantage that spectra can be obtained relatively quickly (in seconds) so many spectra can be accumulated and added together to improve sensitivity.

To a first approximation, the absorption frequencies due to the important IR chromophores are the same in solid and liquid states and in solution.

3.3 GENERAL FEATURES OF INFRARED SPECTRA

Almost all organic compounds contain C–H bonds and this means that there is invariably an absorption band in the IR spectrum between 2900 and 3100 cm^{-1} at the C–H stretching frequency.

Molecules generally have a large number of bonds and each bond may have several IR-active *vibrational modes*. As well as individual bond vibrations, there are also composite vibrations where different parts of a molecule may vibrate or bend in a concerted fashion. IR spectra are complex and there are many overlapping absorption bands. IR spectra are sufficiently complex that the spectrum for each compound is unique – this makes IR spectra very useful for identifying compounds by direct comparison with spectra from authentic samples *("fingerprinting")*.

Characteristic IR vibrations are influenced strongly by small changes in molecular structure thus making it difficult to identify structural fragments from IR data alone. However, there are some groups of atoms that are readily recognised from IR spectra. IR chromophores are most useful for the determination of structure if:

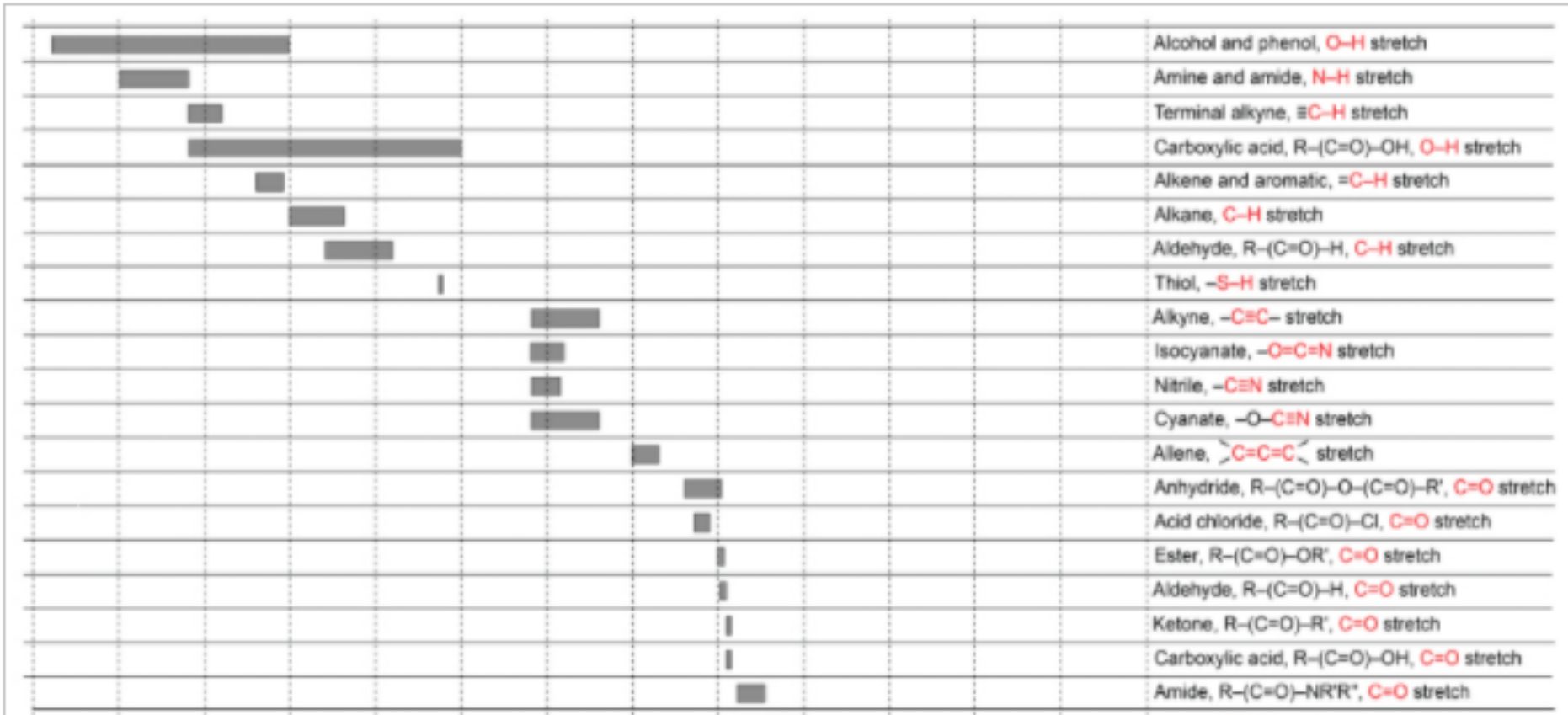
a. The chromophore does not absorb in the most *crowded region* of the spectrum (600–1400 cm^{-1}) where strong overlapping stretching absorptions from C–X single bonds (X = O, N, S, P and halogens) make assignment difficult.

b. The chromophores *absorb strongly* since this avoids confusion with weak harmonics. However, in otherwise empty regions *e.g.* 1800–2500 cm^{-1}, even weak absorptions can be assigned with confidence.

c. The absorption frequency must be structure dependent in an *interpretable* manner. This is particularly true of the very important bands due to the C=O stretching vibrations, which generally occur between 1630 and 1850 cm^{-1}.

Table 3.1 summarises the regions of the IR spectrum where there are characteristic absorptions for different functional groups.

IR Absorption Frequencies for Common Organic Functional Groups



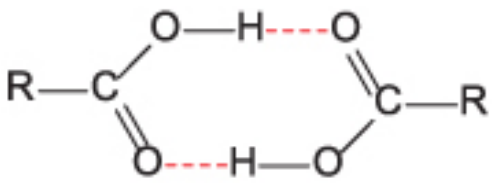
3.4 IMPORTANT IR CHROMOPHORES

3.4.1 –O–H AND –N–H STRETCHING VIBRATIONS

–OH and –NH stretching vibrations are observed in the region from *ca.* 3000 cm^{-1} up to *ca.* 3600 cm^{-1}. This region is relatively isolated from the rest of the IR spectrum and the presence of a strong absorption above 3000 cm^{-1} is a strong indication of the presence of an –OH or –NH group in the molecule (and equally as importantly, the absence of a strong absorption above 3000 cm^{-1} is a strong indication of the absence of any –OH or –NH group in the molecule).

Non-hydrogen-bonded ("free") alcohols typically have a strong absorption near 3600 cm^{-1} whereas hydrogen-bonded alcohols have absorption frequencies in the range 3100–3200 cm^{-1}; the difference between hydrogen-bonded and free O–H frequencies is clearly related to the weakening of the O–H bond as a consequence of hydrogen bonding.

Carboxylic acids also have an –O–H group and usually display a strong but very broad absorption in the range 2500–3300 cm^{-1}. The broadness of the –O–H stretch for carboxylic acids and the shift to lower frequencies is attributed to strong hydrogen bonding and the formation of hydrogen-bonded dimers.

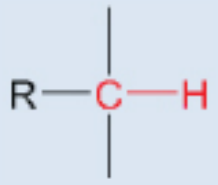
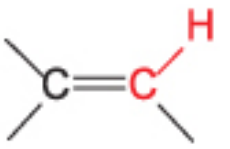
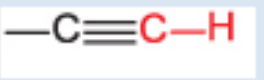
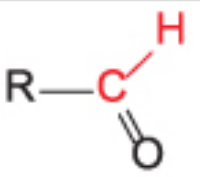


The N–H stretch of amines and amides typically appears in the range 3300–3500 cm^{-1}. Compared to the –O–H stretch of alcohols, the –N–H stretches are typically sharper and less intense. Primary amines (R–NH_2) and primary amides (R–(C=O)–NH_2) often have two bands in the NH stretching region (due to symmetric and asymmetric stretches) whereas secondary amines (R^1R^2–NH) and secondary amides (R^1–(C=O)–NH–R^2) typically give only one stretch.

3.4.2 C–H STRETCHING VIBRATIONS

C–H stretching vibrations are observed in the region from *ca.* 2700 cm^{-1} up to *ca.* 3100 cm^{-1}. Almost all organic compounds contain C–H bonds so there is always a strong absorption in this region from multiple C–H bonds. Table 3.2 gives the characteristic stretching frequencies for C–H bonds in different functional groups. Whilst this region has strong overlapping signals, some C–H stretching frequencies, such as those for a terminal alkyne or for an aldehyde, are often separated from the remaining C–H absorptions and often provide confirmatory evidence for the presence (or absence) of these functional groups.

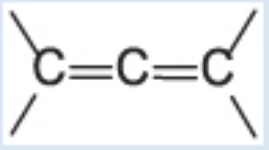
Table 3.2 C–H IR Absorption Frequencies in Common Functional Groups

C–H group	Structure	$\bar{\nu}$ (cm^{-1})
alkane		2850–2960
alkene		3020–3100
terminal alkyne		3200–3300
aldehyde		2700–2900

3.4.3 –C≡N AND –C≡C– STRETCHING VIBRATIONS

C≡N and –C≡C– stretching vibrations as well as vibrations for cumulenes (C=C=C), isonitriles (R–$^+$N≡C^-), azides (R–N=$^+$N=N^-) and isocyanates (R–N=C=O) are observed in the region from *ca.* 1900 cm^{-1} up to *ca.* 2400 cm^{-1} (Table 3.3). These absorptions are typically quite sharp but can be weak, particularly for internal alkynes where the dipole moment is small.

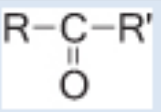
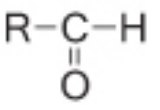
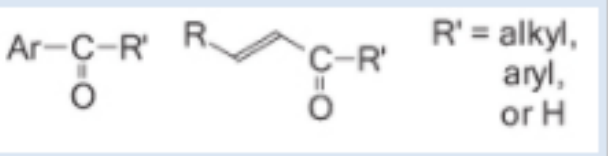
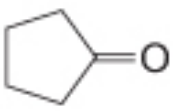
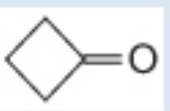
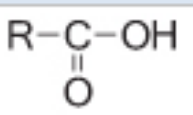
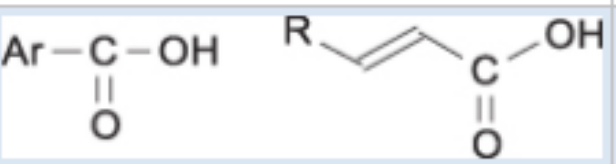
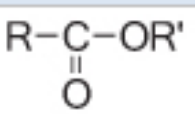
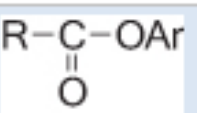
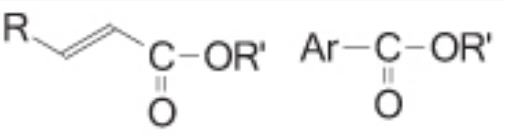
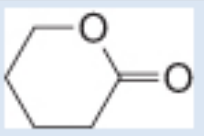
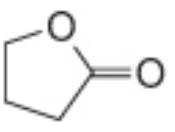
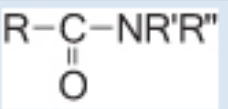
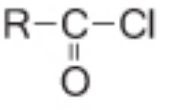
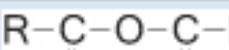
Table 3.3 C≡N and C≡C Absorption Frequencies in Common Functional Groups

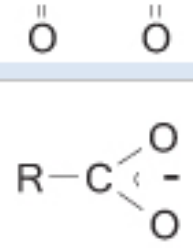
Functional group	Structure	$\bar{\nu}$ (cm^{-1})	Intensity
alkyne	—C≡C—	2100–2300	weak to medium
nitrile	—C≡N	2215–2280	medium
cyanate	—O—C≡N	2130–2270	strong
thiocyanate	—S—C≡N	2130–2175	medium
isocyanate	—N=C=O	2200–2300	strong broad
isothiocyanate	—N=C=S	2000–2200	strong
allene		1900–2000	strong

3.4.4 CARBONYL GROUPS

Carbonyl groups always give rise to a **strong** absorption between 1630 and 1850 cm^{-1} as a result of C=O stretching vibrations. When present, the carbonyl absorption is often the strongest absorption in an IR spectrum. Moreover, carbonyl groups in different functional groups are associated with well-defined regions of IR absorption (Table 3.4). Esters have an absorption at the high frequency end of the carbonyl range (typically between 1735 and 1750 cm^{-1}) whilst amides absorb typically between 1630 and 1690 cm^{-1}.

Table 3.4 C=O IR Absorption Frequencies in Common Functional Groups

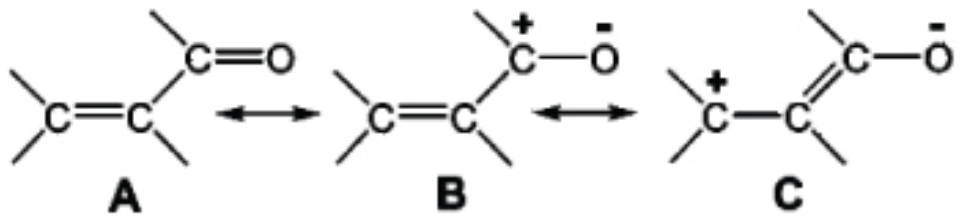
Carbonyl group	Structure	$\bar{\nu}$ (cm^{-1})
Ketones		1700–1725
Aldehydes		1720–1740
Aryl aldehydes or ketones, α,β-unsaturated aldehydes or ketones		1660–1720
Cyclopentanones		1740–1750
Cyclobutanones		1760–1780
Carboxylic acids [‡]		1700–1725
α,β-unsaturated and aryl carboxylic acids [‡]		1680–1715
Esters [§]		1735–1750
Phenolic esters [§]		1760–1800
Aryl or α,β-unsaturated esters [§]		1715–1730
δ-Lactones [§]		1735–1750
γ-Lactones [§]		1760–1780
Amides		1630–1690
Acid chlorides		1770–1815
Acid anhydrides (two bands)		1740–1850

Carboxylates		1550–1610 1300–1450

† Carboxylic acids also exhibit an O–H stretch near 3000 cm^{-1}

§ Esters and lactones also exhibit a strong C–O stretch in the range 1100–1300 cm^{-1}

There is a characteristic shift toward lower frequency associated with the introduction of α, β–unsaturation or conjugation with an aromatic ring. The effect of conjugation can be rationalised by considering the Valence Bond description of an enone:



The additional structure **C**, which cannot be drawn for an unconjugated carbonyl derivative, implies that the carbonyl bond in an enone has more single bond character than in an unconjugated carbonyl and is therefore weaker and its absorption frequency will be lower. The involvement of a carbonyl group in hydrogen bonding also reduces the frequency of the carbonyl stretching vibration by about 10 cm^{-1}.

Even though the ranges for individual types of carbonyls often overlap, it is often possible to make a definite identification of the functional group from information derived from other regions of the IR spectrum. Esters also exhibit strong C–O stretching absorption between 1100 and 1300 cm^{-1} while carboxylic acids exhibit an additional O–H stretching absorption near 3000 cm^{-1}.

3.4.5 OTHER POLAR FUNCTIONAL GROUPS

Many other functional groups have characteristic IR absorptions and these are summarised in Table 3.5.

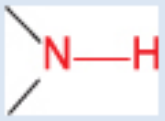
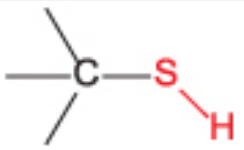
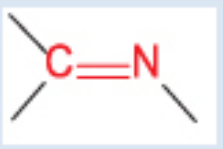
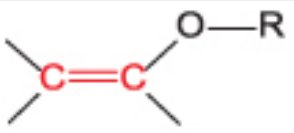
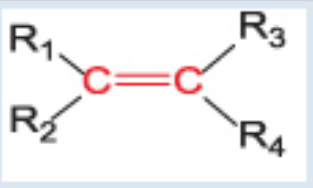
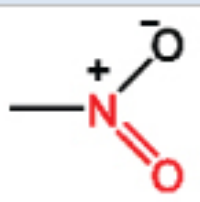
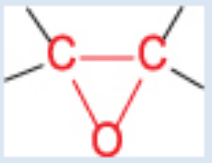
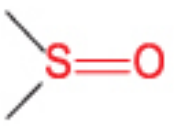
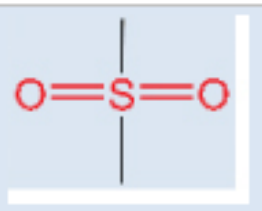
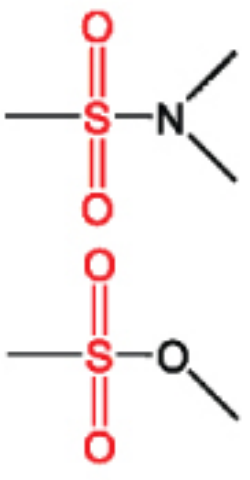
Carbon–carbon double bonds in unconjugated alkenes usually exhibit weak to moderate absorptions due to C=C stretching in the range 1660–1640 cm^{-1}. Disubstituted, trisubstituted and tetrasubstituted alkenes usually absorb near 1670 cm^{-1}. The more polar carbon–carbon double bonds in enol ethers and enones usually absorb strongly between 1600 and 1700 cm^{-1}. Alkenes conjugated with an aromatic ring absorb strongly near 1625 cm^{-1}.

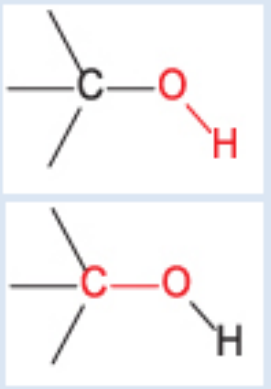
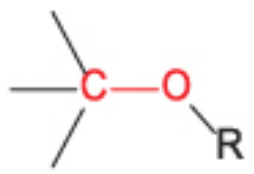
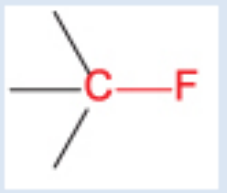
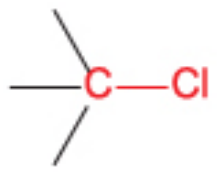
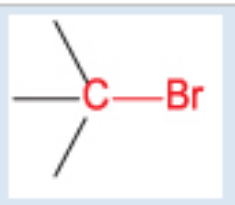
3.4.6 THE FINGERPRINT REGION

The region of the IR spectrum below about 1500 cm^{-1} is typically a crowded region of the spectrum with "composite vibrations" arising from the interaction of many groups with each other. Because it is a complex set of vibrations, every molecule is different, so this becomes a region of the spectrum which is a unique molecular signature.

For a known compound, once this region of the spectrum has been recorded into a database, the compound can always be identified again by searching for its unique infrared signature. Most IR instruments now come pre-loaded with compound libraries which can be routinely searched to assist with compound identification.

Table 3.5 Characteristic IR Absorption Frequencies for Functional Groups

Functional group	Structure	$\bar{\nu}$ (cm^{-1})	Intensity
Amine		3300–3500	strong
Thiols		2550–2560	weak
Imines		1480–1690	strong
Enol ethers		1600–1660	strong
Alkenes		1640–1680	weak to medium
Nitro groups		1500–1650 1250–1400	strong medium
Epoxides		1250 810–950	strong
Sulfoxides		1010–1070	strong
Sulfones		1300–1350 1100–1150	strong strong
Sulfonamides and Sulfonate esters		1140–1180 1300–1370	strong strong
Alcohols		3000–3600 1000–1260	strong strong

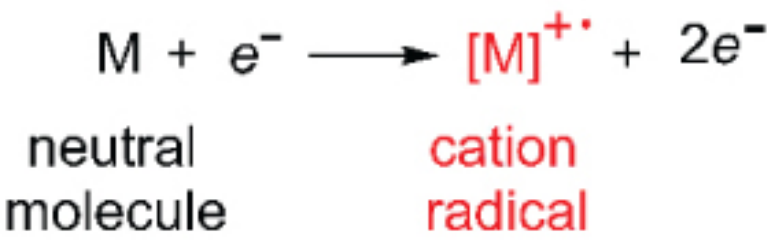
			
Ethers		1085–1150	strong
Alkyl fluorides		1000–1400	strong
Alkyl chlorides		580–780	strong
Alkyl bromides		560–800	strong
Alkyl iodides		500–600	strong

4
MASS SPECTROMETRY

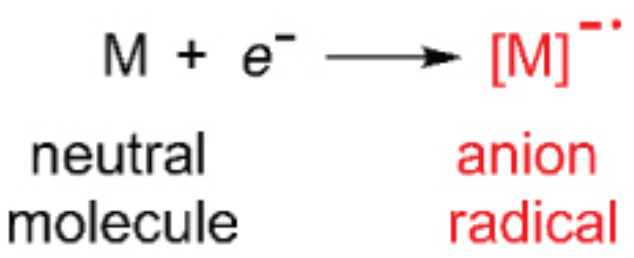
Mass spectrometry is an analytical method for measuring the mass of molecules (or fragments of molecules) in a sample. Mass spectrometry provides the molecular weight of a compound (and the molecular masses of fragments of a molecule). Molecules are ionised in the gas phase and then injected into a mass spectrometer which separates the ions and determines the masses of individual ions. Strictly speaking, it is only possible to measure their mass/charge ratio (*m/e*), but as multi-charged ions are very much less abundant than those with a single electronic charge (*e* = 1), *m/e* is for all practical purposes equal to the mass of the ion, *m*. The principal experimental problems in mass spectrometry are firstly to volatilise the substrate (which implies high vacuum) and secondly to ionise the neutral molecules to charged species.

4.1 IONISATION PROCESSES

The most common method of ionisation involves *Electron Impact* (EI) and there are two general courses of events following a collision of a molecule M with an electron *e*. By far the most probable event involves electron ejection which yields an odd-electron positively charged *cation radical* $[M]^{+\cdot}$ of the same mass as the initial molecule M.



The cation radical produced is known as the *molecular ion* and its mass gives a direct measure of the molecular weight of a substance. An alternative, far less probable process, also takes place and it involves the capture of an electron to give a negative *anion radical*, $[M]^{-\cdot}$.



Electron impact mass spectrometers are generally set up to detect only positive ions, but negative-ion mass spectrometry is also possible.

The energy of the electron responsible for the ionisation process can be varied. It must be sufficient to knock out an electron and this threshold, typically about 10–12 eV, is known as the *appearance potential* (1 eV = 95 kJ mol^{-1}). In practice much higher energies (~70 eV) are used and this large excess energy causes further *fragmentation* of the molecular ion.

The two important types of fragmentation are:

$$[M]^{+\cdot} \longrightarrow A^{+} \text{ (even electron cation)} + B^{\cdot} \text{ (neutral radical)}$$

$$\text{or} \quad [M]^{+\cdot} \longrightarrow C^{+\cdot} \text{ (cation radical)} + D \text{ (neutral molecule)}$$

As only species bearing a positive charge will be detected in a mass spectrometer, the mass spectrum will show signals due not only to $[M]^{+\cdot}$ but also due to A^{+}, $C^{+\cdot}$ and to fragment ions resulting from subsequent fragmentation of A^{+} and $C^{+\cdot}$.

As any species may fragment in a variety of ways, the typical mass spectrum consists of many signals. The mass spectrum (Figure 4.1) consists of a plot of the masses of ions against their relative abundance. The strongest peak in the spectrum (the *base peak*) is assigned a relative intensity of 100%. The peak at highest mass in the spectrum will be the *molecular ion* and then there will be multiple *fragment ions* resulting from fragmentation of the molecular ion. In some case, the molecular ion may be weak if there are very favourable fragmentation processes.

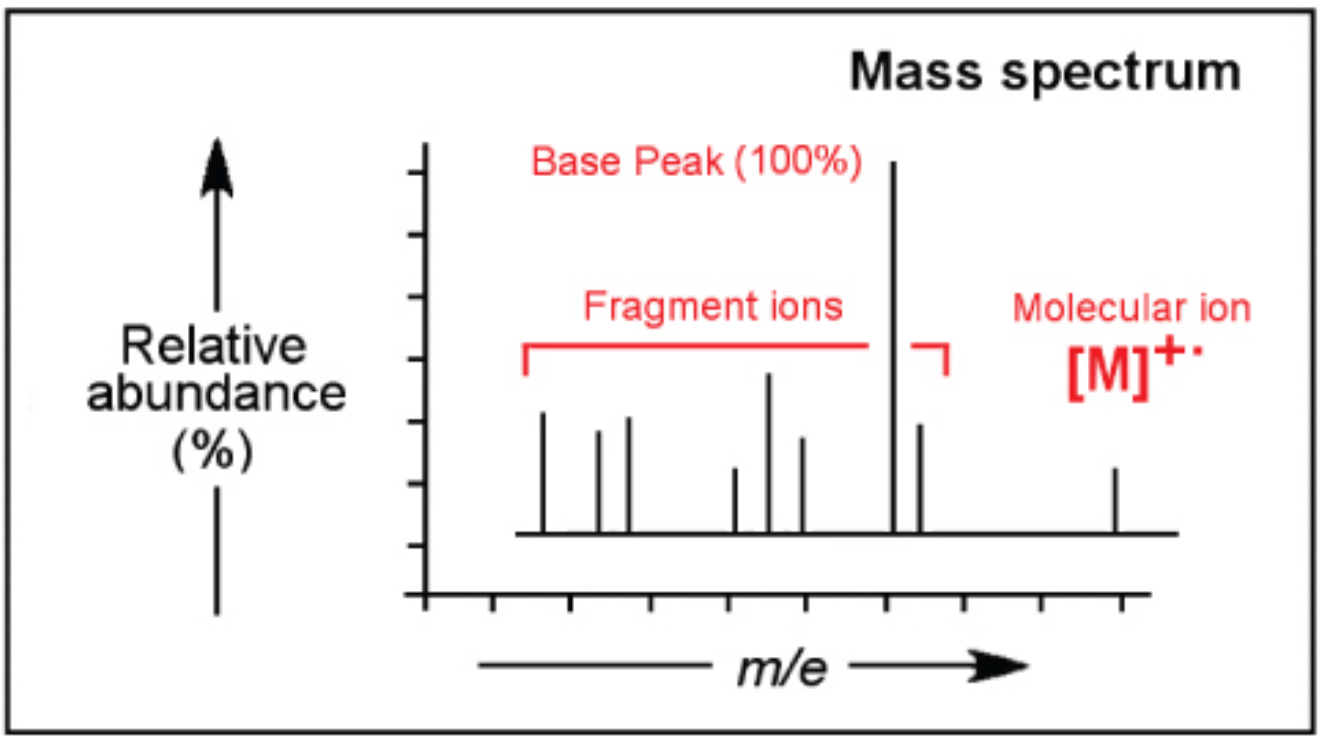


Figure 4.1 Schematic Mass Spectrum

There are a number of other methods for ionising the sample in a mass spectrometer. The most important alternative ionisation method to electron impact is *Chemical Ionisation* (CI). In CI mass spectrometry, an intermediate substance (generally methane or ammonia) is introduced at a higher concentration than that of the substance being investigated. The carrier gas is ionised by electron impact and the substrate is then ionised by collisions with the ionised carrier gas. CI is a much gentler method of ionisation than EI and consequently leads to less fragmentation of the molecular ion.

Another common method of ionisation is *Electrospray Ionisation* (ESI). In this method, the sample is dissolved in a polar, volatile solvent and pumped through a fine metal nozzle, the tip of which is charged with a high voltage. The metal nozzle produces charged droplets from which the solvent rapidly evaporates to leave naked ions which pass into the mass spectrometer. ESI is also a relatively mild form of ionisation and is suitable for biological samples that are usually quite soluble in polar solvents but are relatively difficult to vaporise in the solid state. Electrospray ionisation also tends to lead to far less fragmentation of the molecular ion than EI.

Matrix-Assisted Laser Desorption Ionisation (MALDI) uses a pulse of laser light to bring about ionisation. The sample is usually mixed with a highly absorbing compound that acts as a supporting matrix. The laser pulse

ionises and vaporises both the matrix and the sample to give ions that pass into the mass spectrometer. Again MALDI is a relatively mild form of ionisation which tends to give less fragmentation of the molecular ion than EI.

4.2 INSTRUMENTATION

In a magnetic sector mass spectrometer (Figure 4.2), the positively charged ions of mass, *m*, and charge, *e* (generally *e* = 1) are subjected to an accelerating voltage *V* to increase their speed and then they pass through a magnetic field *H*. A charged particle moving through a magnetic field will be deflected into a curved path of radius *r*. The amount of deflection depends on the velocity of the ion, the strength of the magnetic field and mass of the ion. The quantities are connected by the relationship:

$$\frac{m}{e} = \frac{H^2 r^2}{2V}$$

The values of *H* and *V* are known, *r* is determined experimentally and *e* is assumed to be unity thus permitting us to determine the mass *m*. In practice the magnetic field is scanned so that streams of ions of different mass pass sequentially to the detecting system (ion collector). The whole system (Figure 4.2) is under high vacuum (less than 10^{-6} Torr) to permit the volatilisation of the sample and so that the passage of ions is not impeded. The introduction of the sample into the ion chamber at high vacuum requires a relatively complex sample inlet system.

The magnetic scan is synchronised with the *x*-axis of a recorder and calibrated to appear as *mass number* (strictly *m/e*). The amplified current from the ion collector gives the relative abundance of ions on the *y*-axis. The signals are usually pre-processed by a computer that assigns a relative abundance of 100% to the strongest peak (*base peak*).

Many modern mass spectrometers do not use a magnet to bend the ion beam to separate ions but rather use the "*time of flight*" (TOF) of an ion over a fixed distance to measure its mass. In these spectrometers, ions are generated (usually using a very short laser pulse) then accelerated to constant energy in an electric field. Lighter ions have a higher velocity as they leave the accelerating field and their time of flight over a fixed distance will vary depending on the speed that they are travelling. Time of flight mass spectrometers have the advantage that they do not require large, high-precision magnets to bend and disperse the ion beam so they tend to be much smaller, less expensive, more compact and less complex (desktop size) instruments.

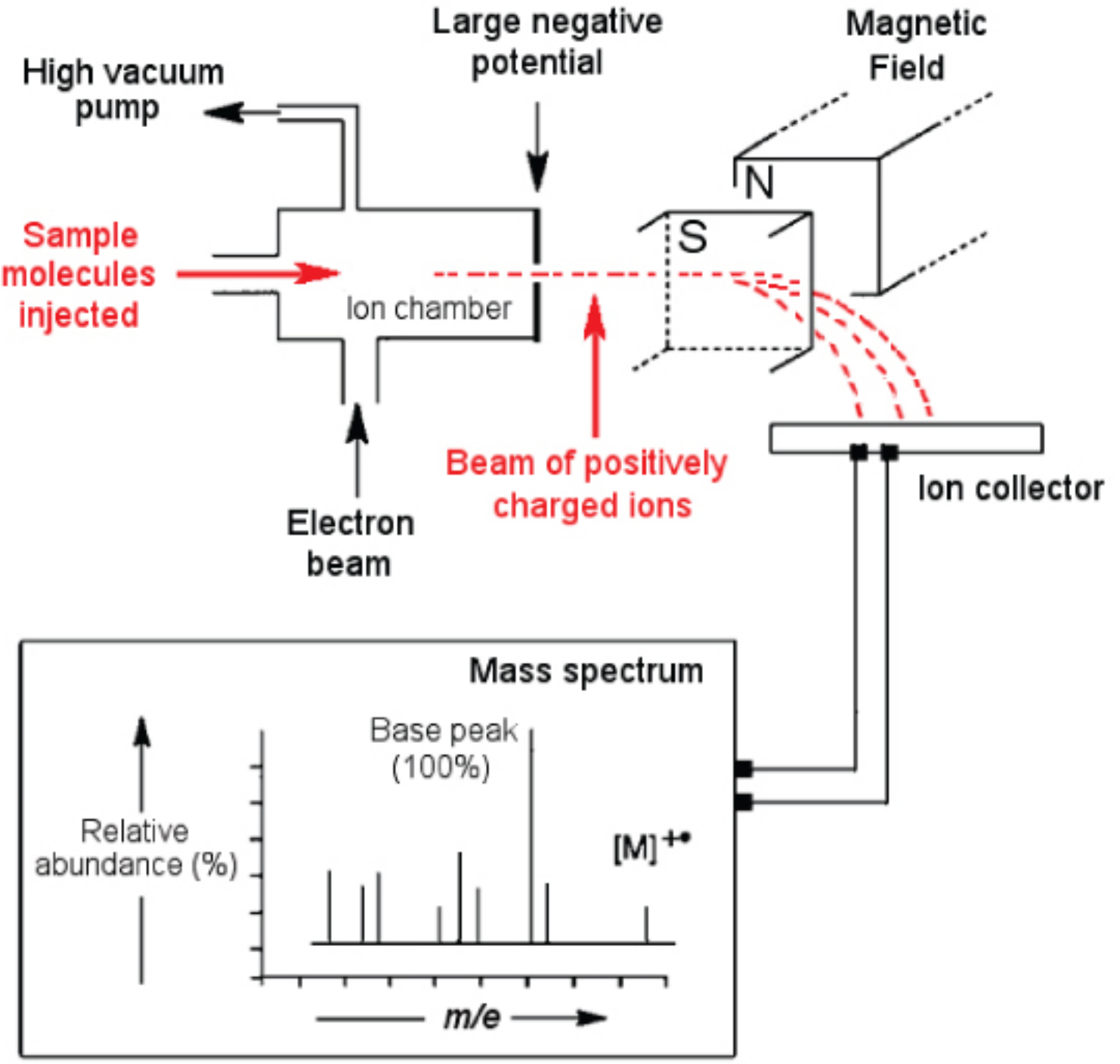


Figure 4.2 Schematic Diagram of an Electron-Impact Magnetic Sector Mass Spectrometer

4.3 MASS SPECTRAL DATA

As well as giving the molecular weight of a substance, the molecular ion of a compound may provide additional information. The **"nitrogen rule"** states that a molecule with an even molecular weight must contain no nitrogen atoms or an even number of nitrogen atoms. This means that a molecule with an odd molecular weight must contain an odd number of nitrogen atoms.

4.3.1 HIGH RESOLUTION MASS SPECTRA

The **mass of an ion** is routinely determined to the nearest unit value. Thus the mass of $[M]^{+\cdot}$ gives a direct measure of molecular weight. It is not usually possible to assign a molecular formula to a compound on the basis of the integer *m/e* value of its parent ion. For example, a parent ion at *m/e* 72 could be due to a compound whose molecular formula is C_4H_8O or one with a molecular formula $C_3H_4O_2$ or one with a molecular formula $C_3H_8N_2$.

However, using a *double-focussing* mass spectrometer or a *time-of-flight* mass spectrometer, the mass of an ion or any fragment can be determined to an accuracy of approximately ±0.00001 of a mass unit *(a high resolution*

mass spectrum). Since the masses of the atoms of each element are known to high accuracy, molecules that have the same mass when measured only to the nearest integer mass unit, can be cleanly distinguished when the mass is measured with high precision. Based on the accurate masses of ^{12}C, ^{16}O, ^{14}N and ^{1}H (Table 4.1) ions with the formulas $C_4H_8O^{+\cdot}$, $C_3H_4O_2^{+\cdot}$ or $C_3H_8N_2^{+\cdot}$ have accurate masses of 72.0575, 72.0211 and 72.0688, respectively, so these could easily be distinguished by high resolution mass spectrometry. In general, if the mass of any fragment in the mass spectrum can be accurately determined, there is usually only one combination of elements that can give rise to that signal since there are only a limited number of elements and their masses are accurately known. By examining a mass spectrum at sufficiently high resolution, one can unambiguously obtain the exact composition of *each ion* in a mass spectrum. Most importantly, determining the accurate mass of $[M]^{+\cdot}$ *gives the molecular formula of the compound.*

Table 4.1 Accurate Masses of Selected Isotopes

Isotope	Natural Abundance (%)	Mass
^{1}H	99.98	1.00783
^{2}H	0.016	2.01410
^{12}C	98.9	12.0000
^{13}C	1.1	13.00336
^{14}N	99.6	14.0031
^{15}N	0.37	15.0001
^{16}O	99.8	15.9949
^{17}O	0.037	16.9991
^{18}O	0.20	17.9992
^{19}F	100	18.99840
^{28}Si	92.28	27.9769
^{29}Si	4.7	28.9765
^{30}Si	3.02	29.9738
^{31}P	100	30.97376
^{32}S	95.0	31.9721
^{33}S	0.75	32.9715
^{34}S	4.2	33.9679
^{35}Cl	75.8	34.9689
^{37}Cl	24.2	36.9659
^{79}Br	50.7	78.9183
^{81}Br	49.3	80.9163
^{127}I	100	126.9045

4.3.2 MOLECULAR FRAGMENTATION

In addition to the molecular ion peak, the mass spectrum (see Figure 4.1) consists of a number of peaks at lower mass numbers and these result from fragmentation of the molecular ion. The **fragmentation pattern** is a molecular fingerprint. The principles determining the mode of fragmentation are reasonably well understood, and it is possible to derive structural information from the fragmentation pattern in several ways.

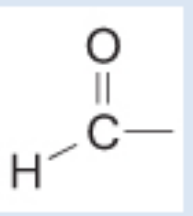
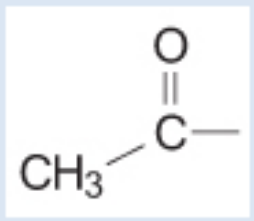
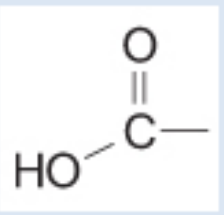
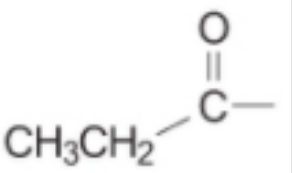
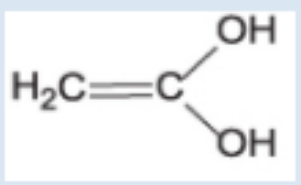
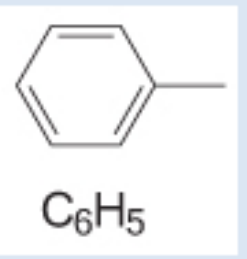
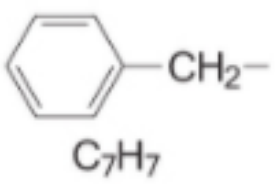
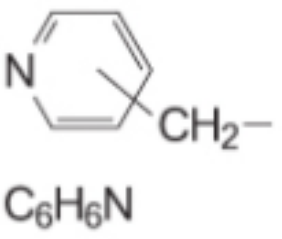
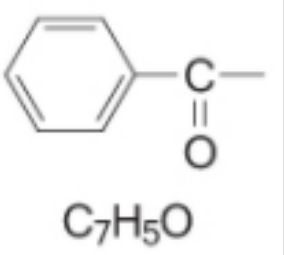
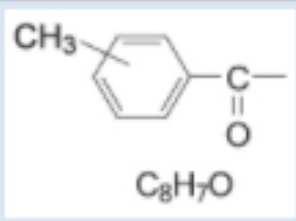
a. The appearance of prominent peaks at certain mass numbers can be correlated empirically with certain structural elements (Table 4.2), *e.g.* a prominent peak at *m/e* = 43 is a strong indication of the presence of a CH_3–CO– group in the molecule.

b. Information can also be obtained from *differences* between the masses of two peaks. Thus a prominent fragment ion that occurs 15 mass numbers below the molecular ion, suggests strongly the loss of a $-CH_3$ group and therefore that a methyl group was present in the substance examined.

c. The knowledge of the principles governing the **mode of fragmentation** of ions makes it possible to confirm the structure assigned to a compound and, quite often, to determine the juxtaposition of structural fragments and to distinguish between isomeric substances. For example, the mass spectrum of benzyl methyl ketone, Ph–CH_2–CO–CH_3 contains a strong peak at *m/e* = 91 resulting from the stable ion Ph–CH_2^+ but this ion is absent in the mass spectrum of the isomeric propiophenone Ph–CO–CH_2–CH_3 where the structural elements Ph– and –CH_2– are separated. Instead, a prominent peak occurs at *m/e* = 105 due to the stable ion Ph–C≡O^+.

Electronic databases of the mass spectral fragmentation patterns of known molecules can be rapidly searched by computer. The pattern and intensity of fragments in the mass spectrum are characteristic of an individual compound so comparison of the experimental mass spectrum of a compound with those in a library can be used to positively identify it, if its spectrum has been recorded previously.

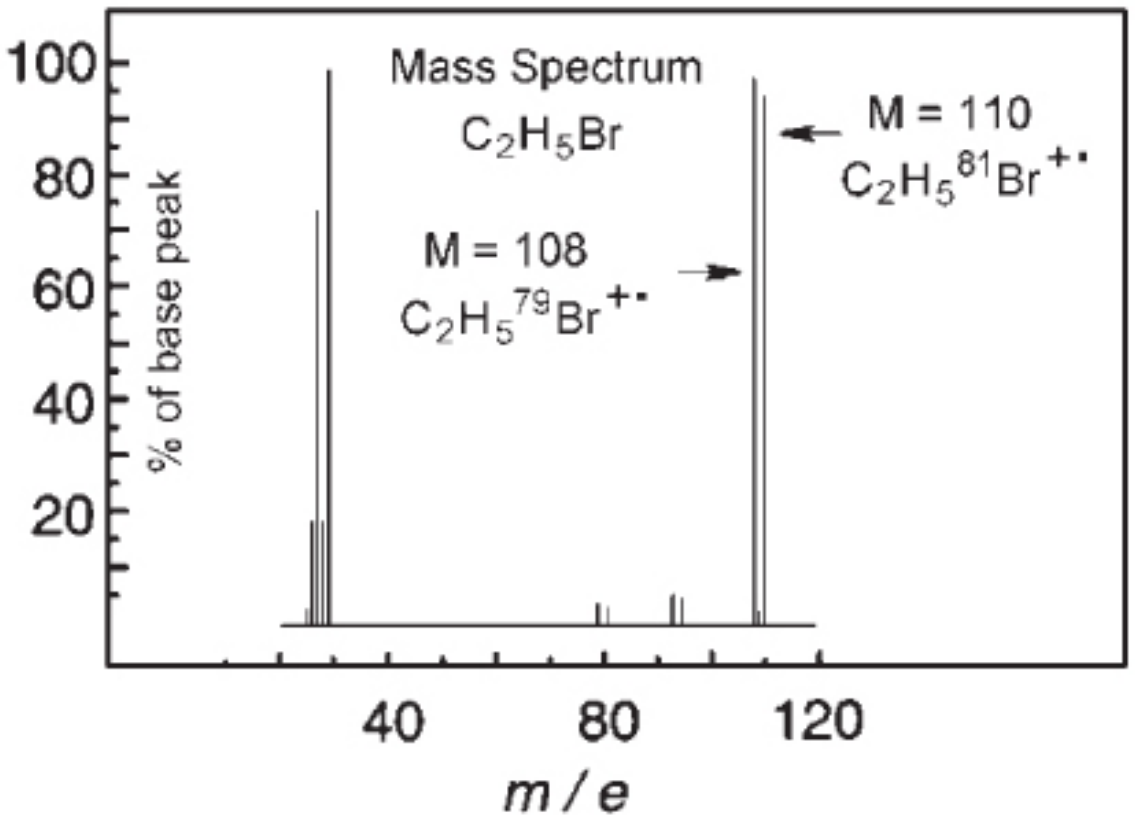
Table 4.2 Common Fragments and their Masses

Fragment	Mass	Fragment	Mass	Fragment	Mass
$CH_3—$	15	$CH_3CH_2—$	29		29
NO	30	$—CH_2OH$	31	$CH_2{=}CH{-}CH_2—$	41
	43		45	$—NO_2$	46
$C_4H_7—$	55	$C_4H_9—$	57		57
	60	$C_5H_5—$	65		77
	91		92		105
	119		127		

4.3.3 ISOTOPE RATIOS

For some elements (most notably bromine and chlorine), there is more than one isotope of high natural abundance, *e.g.* bromine has two abundant isotopes – ^{79}Br 51% and ^{81}Br 49%; chlorine also has two abundant isotopes – ^{35}Cl 75% and ^{37}Cl 25% (Table 4.1). The presence of Br or Cl, or other elements that contain significant proportions (≥ 1%) of minor isotopes, is often obvious simply by inspection of ions near the molecular ion.

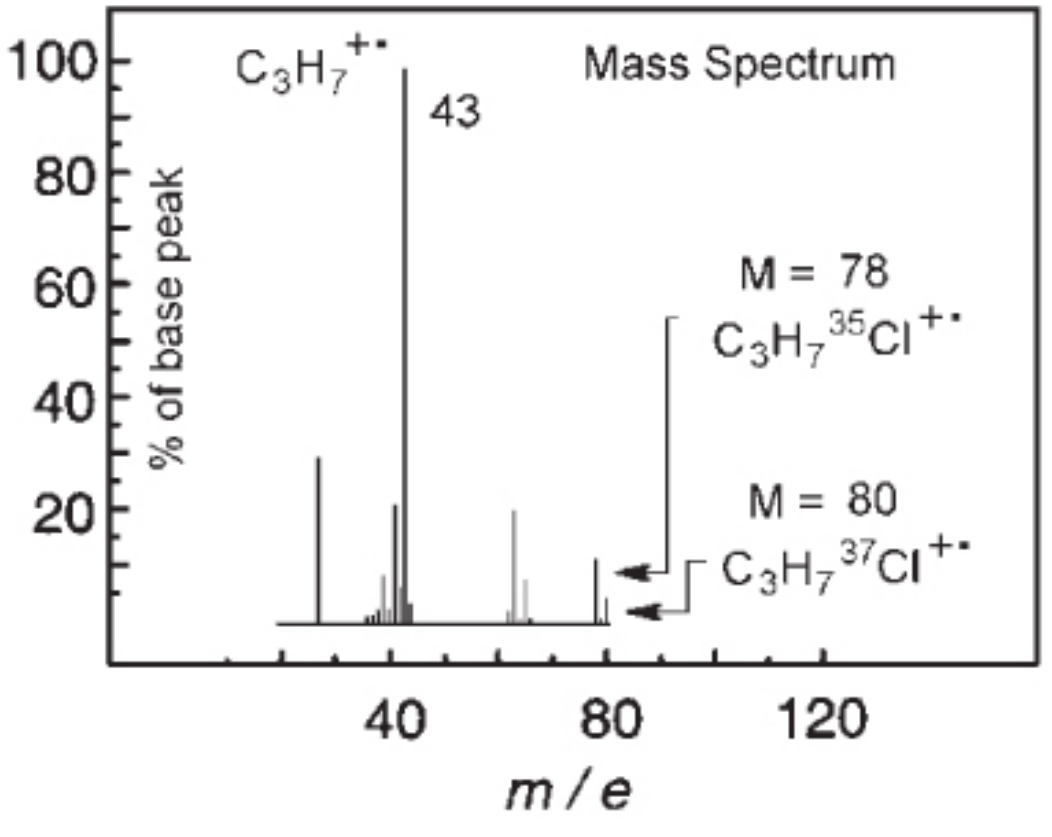
The relative intensities of the $[M]^{+\cdot}$, $[M+1]^{+\cdot}$ and $[M+2]^{+\cdot}$ ions exhibit a characteristic pattern depending on the specific isotopes that make up the ion. For any molecular ion (or fragment) that contains one bromine atom, the mass spectrum will contain two peaks separated by two *m/e* units, one for the ions that contain ^{79}Br and one for the ions that contain ^{81}Br. For bromine-containing fragments, the relative intensities of the two ions will be approximately the same, since the natural abundances of ^{79}Br and ^{81}Br are approximately equal.



In the mass spectrum of 1-bromoethane, there are two molecular ions of almost equal intensity. The peak at *m/e* 108 corresponds to the molecular ions in the sample that contain ^{79}Br; the peak at *m/e* 110 corresponds to the molecular ions in the sample that contain ^{81}Br.

Similarly, for any molecule (or fragment of a molecule) that contains one chlorine atom, the mass spectrum will contain two fragments separated by two *m/e* units, one for the ions that contain ^{35}Cl and one for the ions that contain ^{37}Cl. For chlorine-containing ions, the relative intensities of the two ions will be approximately 3:1 since this reflects the natural abundances of ^{35}Cl and ^{37}Cl.

In the mass spectrum of 2-chloropropane, there are two molecular ions at 78 and 80 with intensities approximately in the ratio 3:1. The peak at *m/e* 78 corresponds to the molecular ions in the sample that contain ^{35}Cl; the peak at *m/e* 80 corresponds to the molecular ions in the sample that contain ^{37}Cl. Note that the base peak at *m/e* 43 is only a single ion so this ion must contain no chlorine. The pair of ions at *m/e* 63 and 65 clearly corresponds to a fragment that still contains a chlorine atom.



Any molecular ion (or fragment) that contains two bromine atoms will have a pattern of ions M:M+2:M+4 with signals in the ratio 1:2:1 and any molecular ion (or fragment) that contains two chlorine atoms will have a pattern of M:M+2:M+4 with signals in the ratio 10:6.5:1 (Figure 4.3).

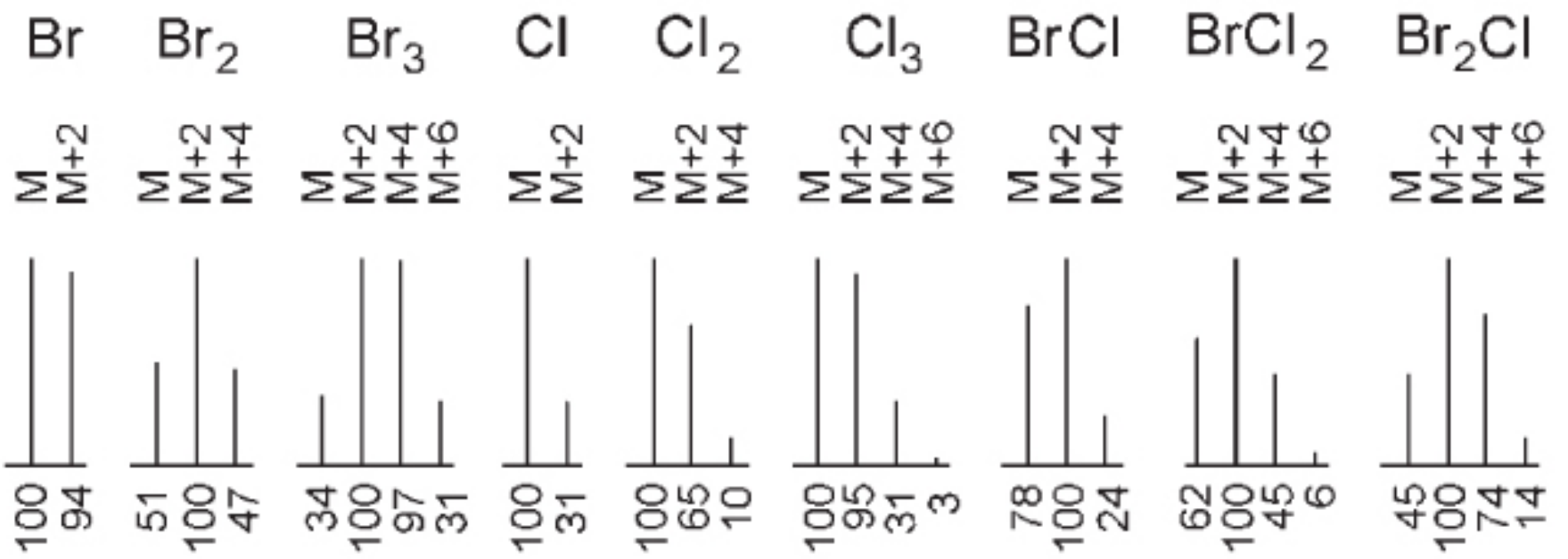


Figure 4.3 Relative Intensities of the Cluster of Molecular Ions for Molecules Containing Combinations of Bromine and Chlorine Atoms

4.3.4 CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY

It is now common to couple an instrument for separating a mixture of organic compounds, *e.g.* using gas chromatography (GC) or high performance liquid chromatography (HPLC), directly to the input of a mass spectrometer. In this way, as each individual compound is separated from the mixture, its mass spectrum can be recorded and compared automatically with the library of known compounds and identified immediately if it is a known compound.

4.3.5 METASTABLE PEAKS

Metastable peaks in a mass spectrum arise if the fragmentation process

$$[a]^+ \longrightarrow [b]^+ + M$$

cation — new cation — neutral molecule

takes place *within the ion-accelerating region of the mass spectrometer* (Figure 4.2). Ion peaks corresponding to the masses of $[a]^+$ and to $[b]^+$ (m_a and m_b) may be accompanied by a broader peak at mass m^*, such that:

$$m^* = \frac{m_b^2}{m_a}$$

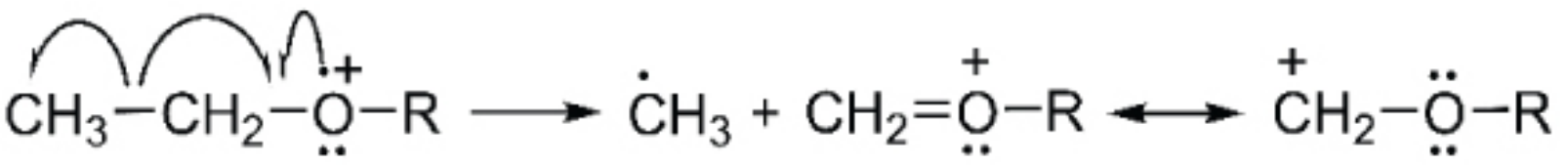
The presence of metastable peaks in a mass spectrum often permits positive identification of a particular fragmentation path.

4.4 REPRESENTATION OF FRAGMENTATION PROCESSES

As fragmentation reactions in a mass spectrometer involve the breaking of bonds, they can be represented by the standard "arrow notation" used in organic chemistry. For some purposes a radical cation (*e.g.* a generalised ion of the molecular ion) can be represented without attempting to localise the missing electron:

$$[M]^{+\bullet} \text{ or } [CH_3-CH_2-O-R]^{+\bullet}$$

However, to show a fragmentation process, it is generally necessary to speculate reasonably "from where the electron is missing". In the case of the molecular ion corresponding to an alkyl ethyl ether, it can be reasonably inferred that the missing electron resided on the oxygen. The application of standard arrow notation permits us to represent a commonly observed process, *e.g.* the loss of a methyl fragment from the $[H_3C-CH_2-O-R]^{+\bullet}$ molecular ion:



4.5 FACTORS GOVERNING FRAGMENTATION PROCESSES

Three factors dominate the fragmentation processes:

a. **Weak bonds** tend to be broken most easily;

b. **Stable fragments** (not only ions, but also the accompanying radicals and molecules) tend to be formed most readily;

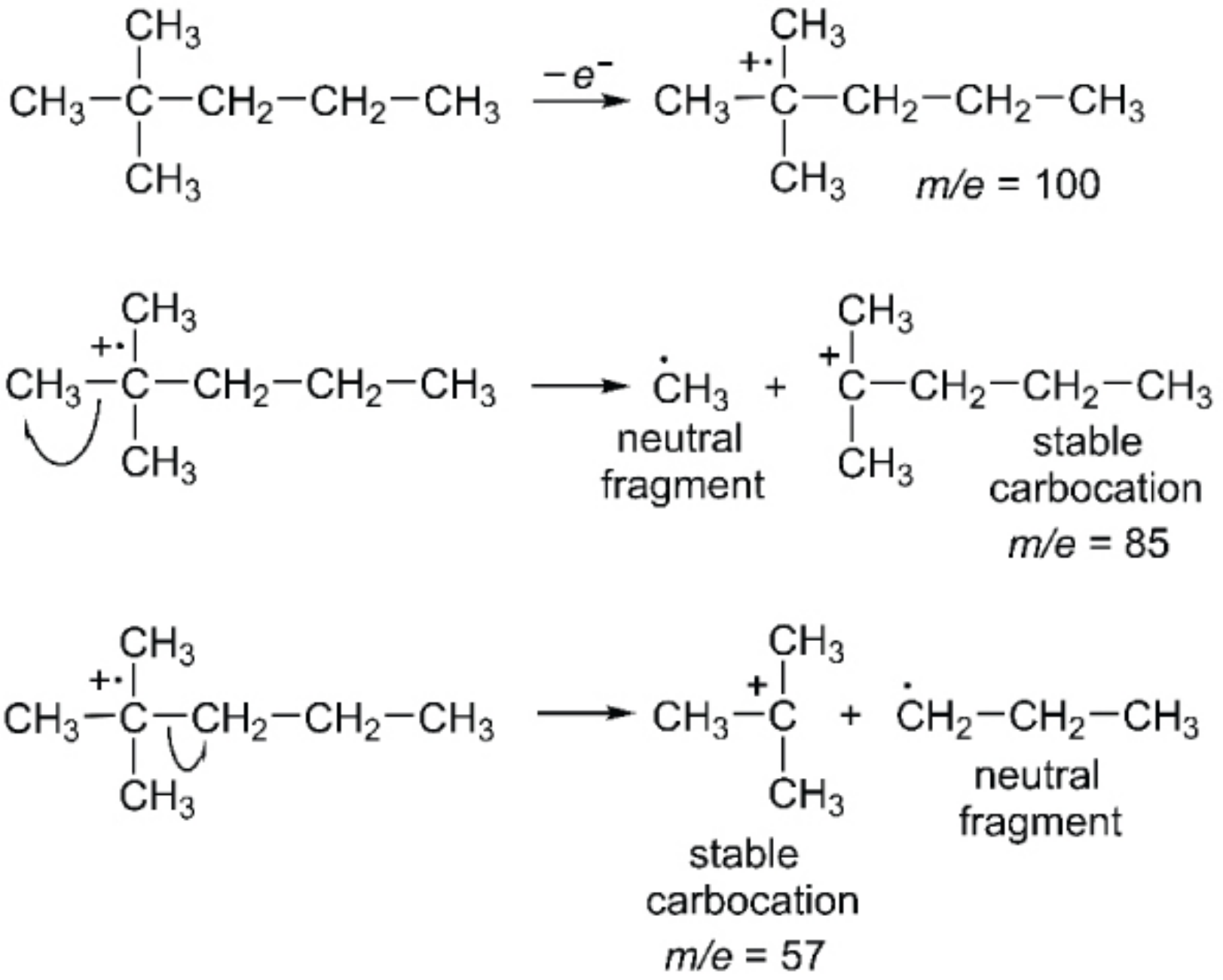
c. Some fragmentation processes depend on the ability of molecules to assume cyclic transition states. Favourable fragmentation processes naturally occur more often and ions thus formed give rise to strong peaks in the mass spectrum.

4.6 EXAMPLES OF COMMON TYPES OF FRAGMENTATION

There are a number of common types of cleavage that are characteristic of various classes of organic compounds. These result in the loss of well-defined fragments that are characteristic of certain functional groups or structural elements.

4.6.1 CLEAVAGE AT BRANCH POINTS

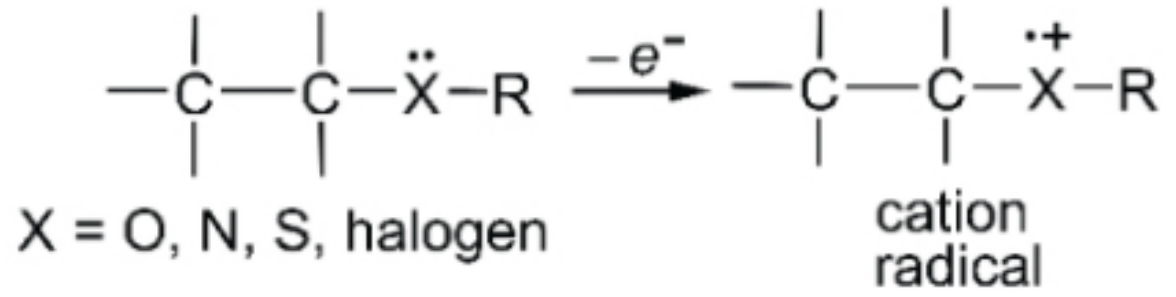
Cleavage of aliphatic carbon skeletons at branch points is favoured as it leads to more substituted (and hence more stable) carbocations. The mass spectrum of 2,2-dimethylpentane shows strong peaks at *m/e* = 85 and *m/e* = 57 where cleavage leads to the formation of stable tertiary carbocations.

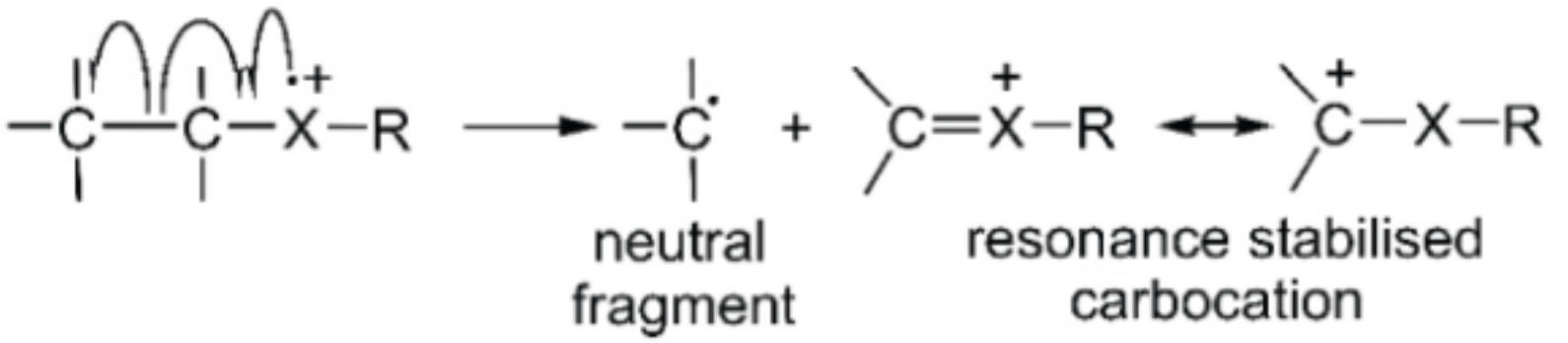


4.6.2 β–CLEAVAGE

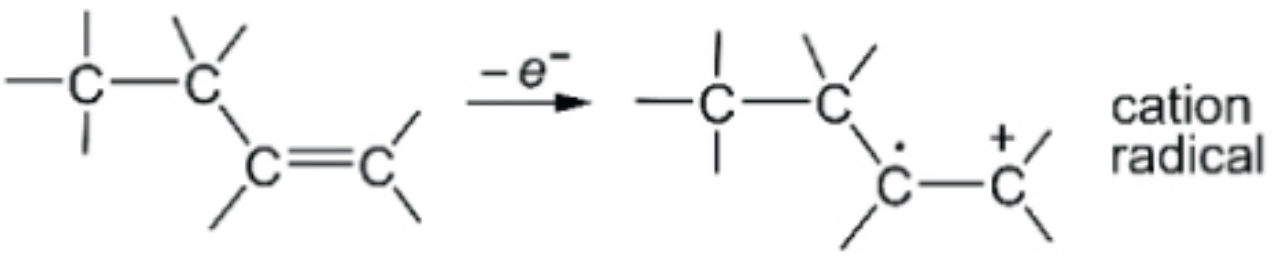
Chain cleavage tends to occur β to heteroatoms, double bonds and aromatic rings because relatively stable, delocalised carbocations result in each case.

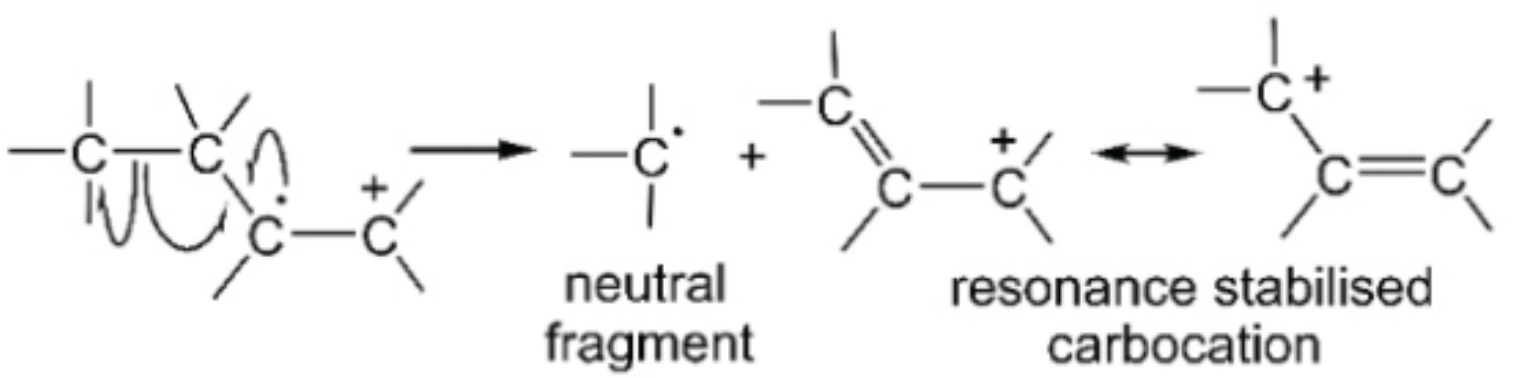
(a)



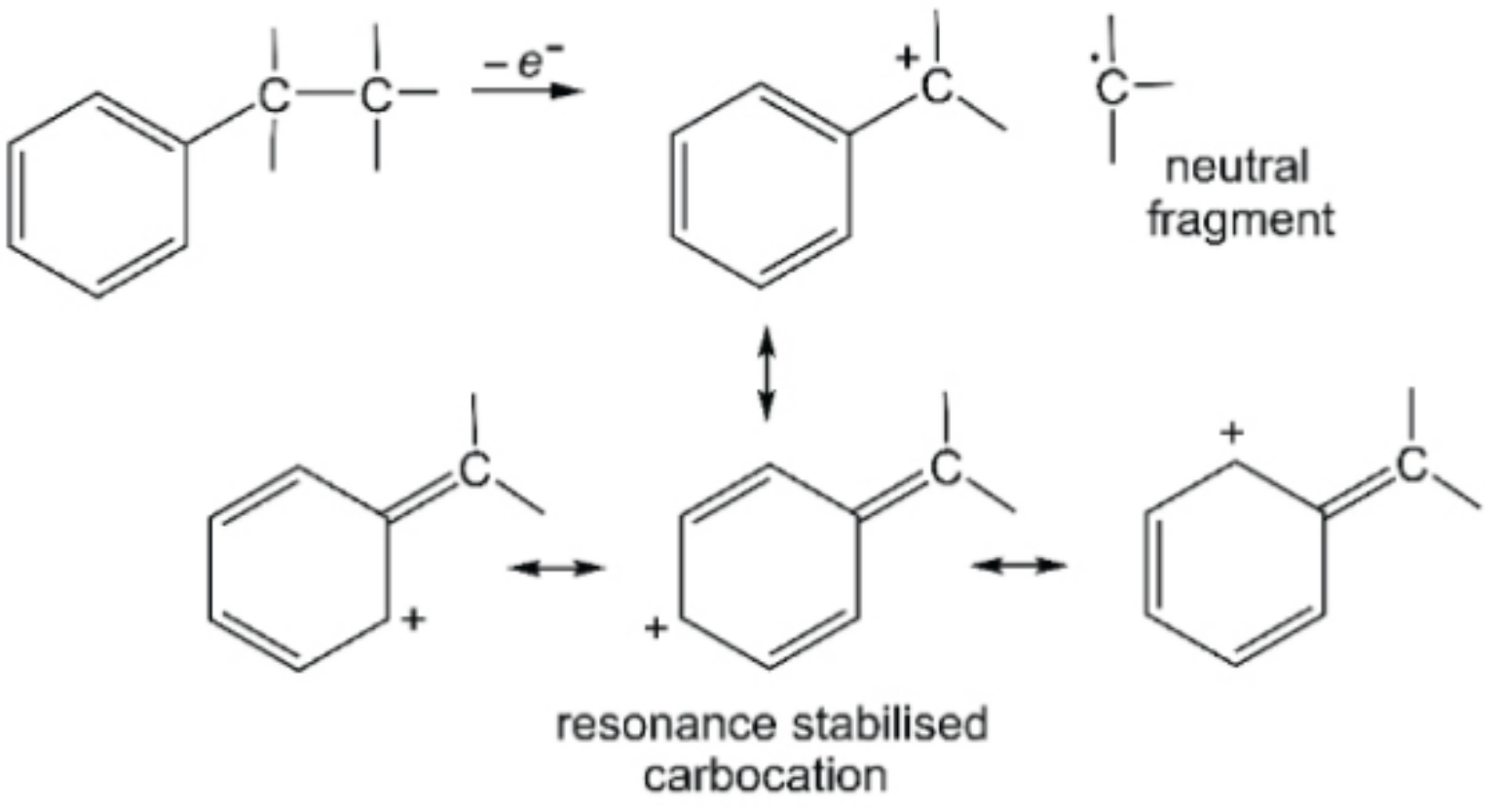


(b)



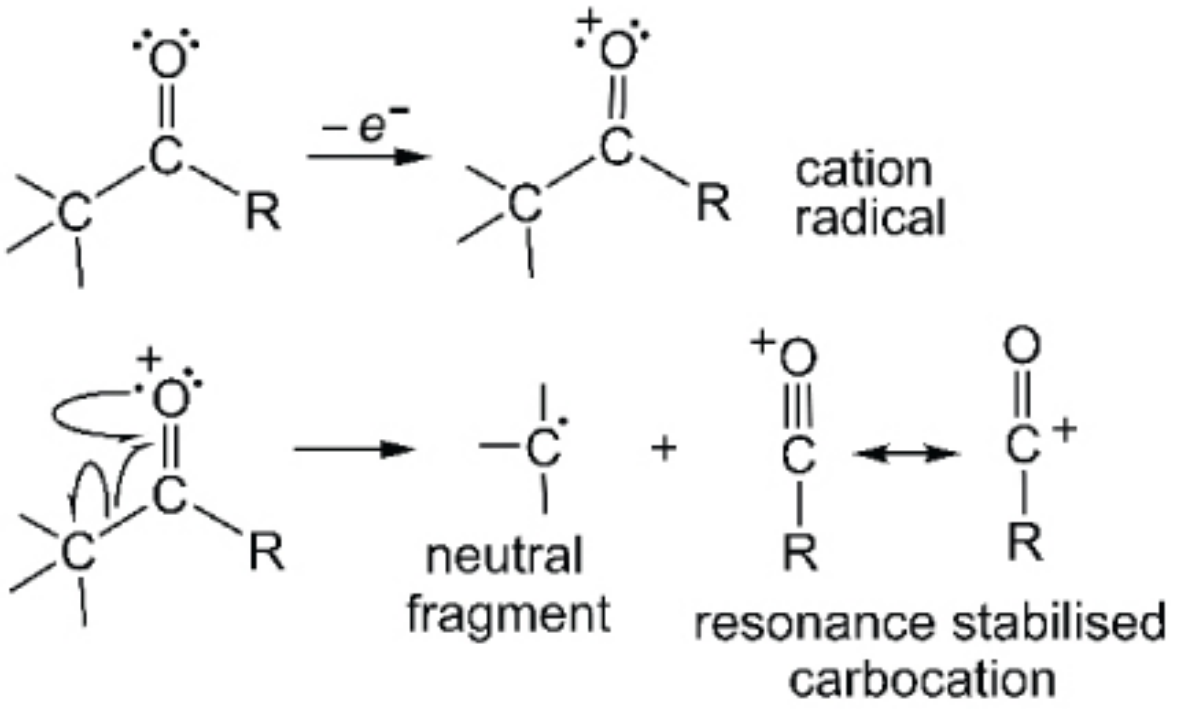


(c)



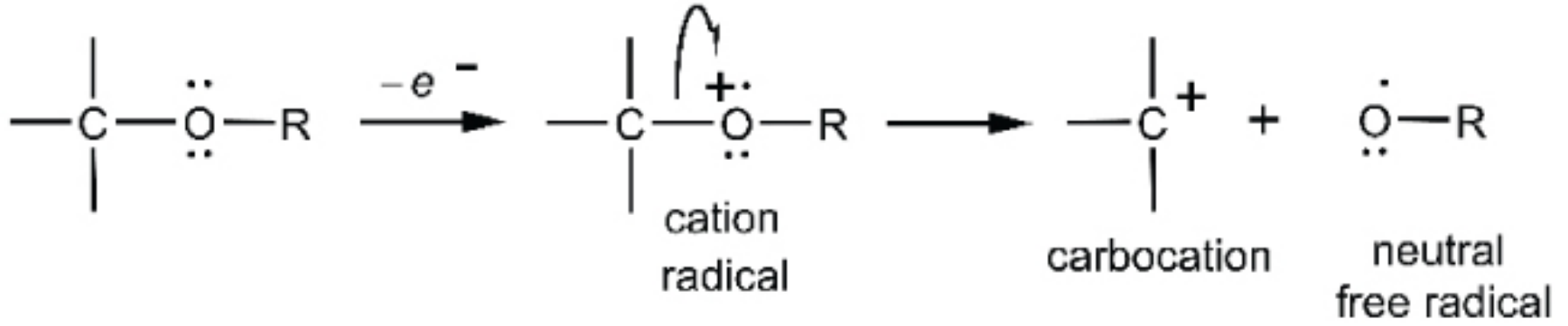
4.6.3 CLEAVAGE TO CARBONYL GROUPS

Cleavage tends to occur α to carbonyl groups to give stable acylium cations. R may be an alkyl, –OH or –OR group.



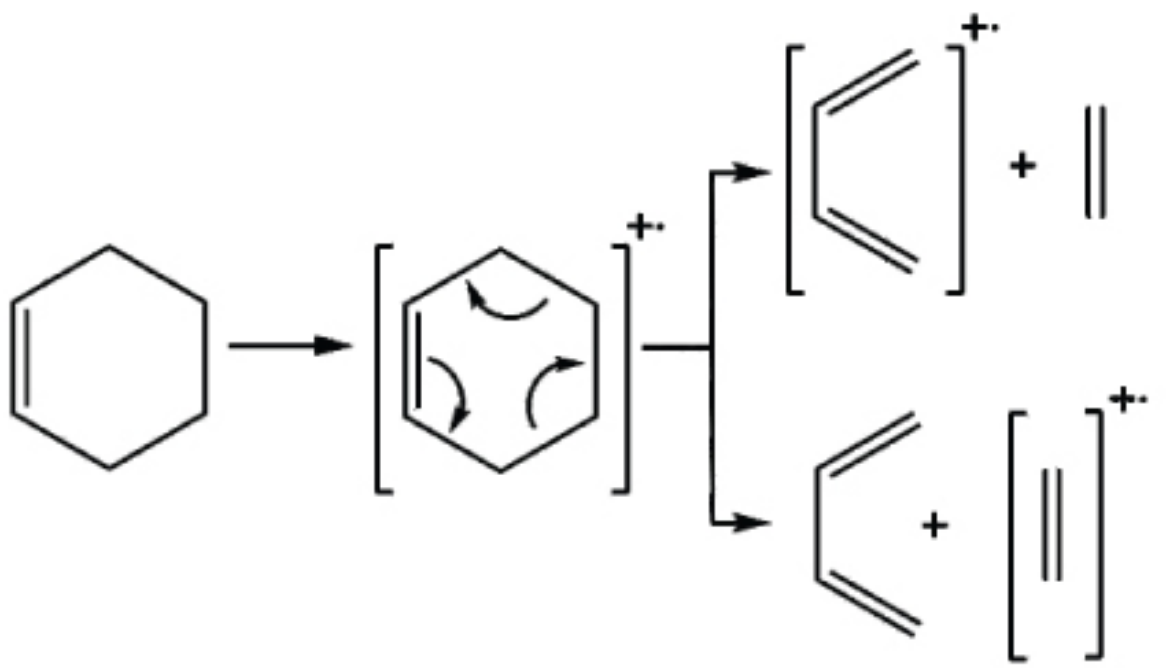
4.6.4 CLEAVAGE α TO HETEROATOMS

Cleavage of chains may also occur to heteroatoms, *e.g.* in the case of ethers:



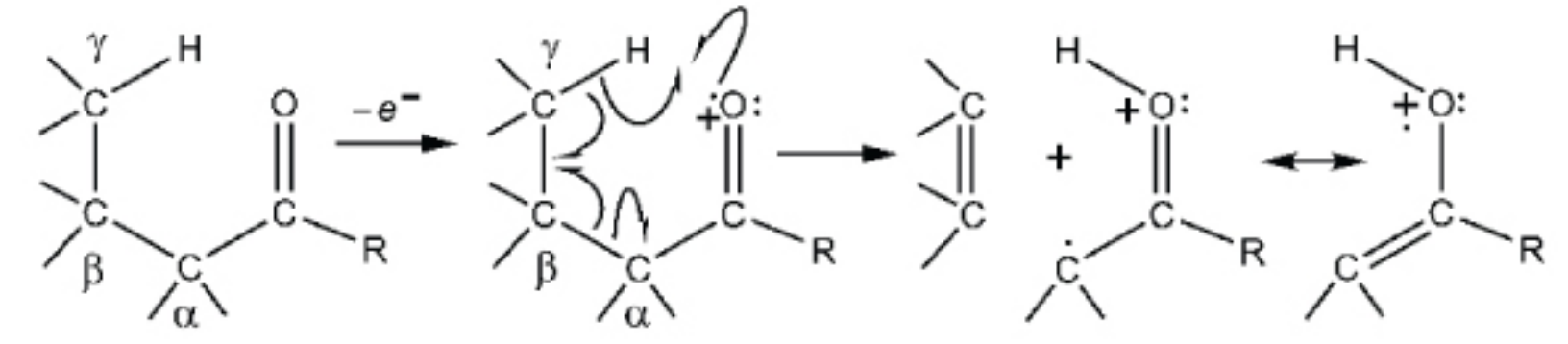
4.6.5 RETRO DIELS–ALDER REACTION

After ionisation, cyclohexene derivatives often undergo a retro Diels–Alder reaction to give either the diene cation radical and a neutral alkene and/or an alkene cation radical and a neutral diene:



4.6.6 THE McLAFFERTY REARRANGEMENT

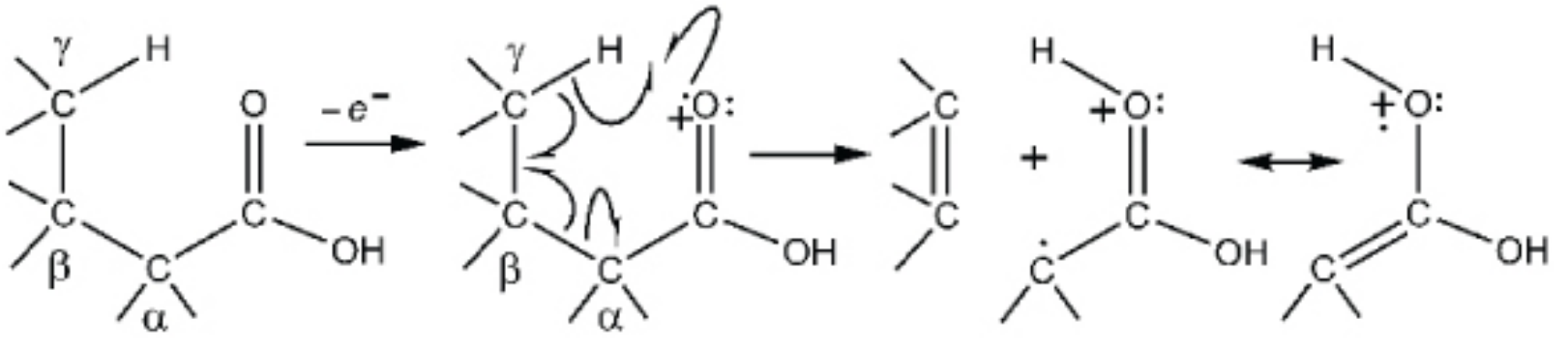
Compounds where the molecular ion can assume the appropriate six-membered cyclic transition state usually undergo a cyclic fragmentation, known as the **McLafferty rearrangement**. This rearrangement involves the transfer of a γ hydrogen atom to an oxygen atom and breaks the carbon–carbon bond between the α- and β-carbons. The McLafferty rearrangement is a common fragmentation for ketones, acids and esters:



aldehyde, ketone, ester

cation radical

resonance stabilised cation radical

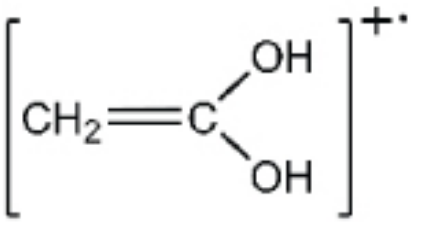


carboxylic acid

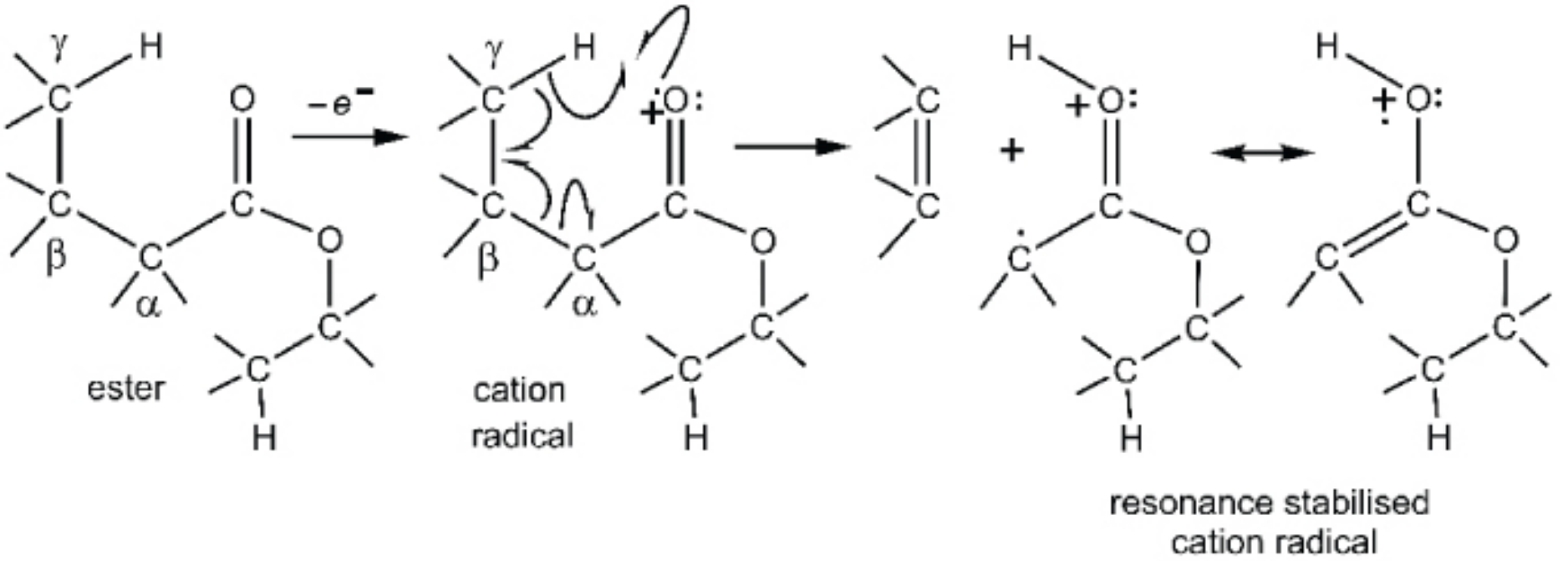
cation radical

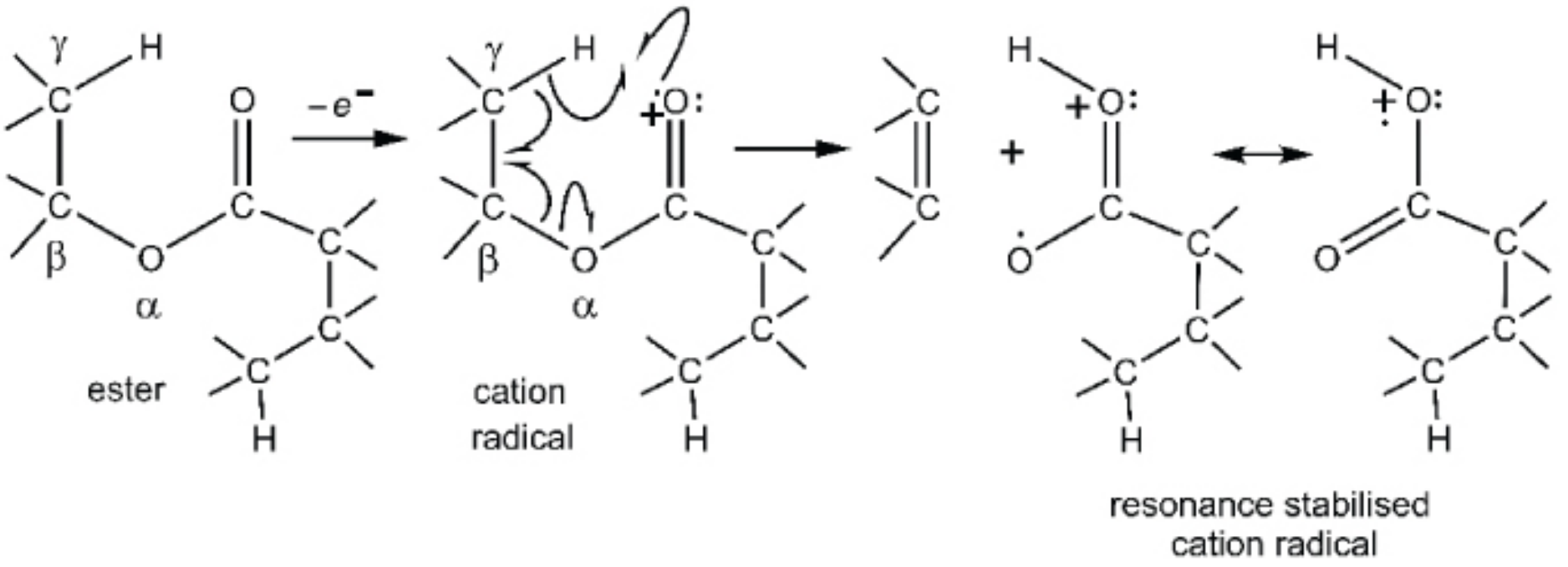
resonance stabilised cation radical

With carboxylic acids that are unsubstituted at the α-carbon, R–CH_2–COOH, the McLafferty rearrangement leads to a characteristic peak at *m/e* = 60 for $[C_2H_4O_2]^{+\cdot}$.



With esters, two types of McLafferty rearrangements may be observed and ions resulting from either fragmentation pathway are commonly observed in the mass spectrum:


γ
H
C
O
−e⁻
β
α
ester
cation
radical
+O:
resonance stabilised
cation radical


γ
H
C
O
−e⁻
β
α
ester
cation
radical
+O:
resonance stabilised
cation radical

5
^{1}H NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

NMR Spectroscopy involves the absorption of radiofrequency radiation by the nuclei of some atoms in a molecule when they are placed in a magnetic field. NMR spectroscopy provides information about the number of different environments in a molecule, the functional groups in a molecule and the relationship (connectivity) between different groups in a molecule. NMR is one of the most powerful spectroscopic methods for unravelling molecular structure.

5.1 THE PHYSICS OF NUCLEAR SPINS AND NMR INSTRUMENTS

5.1.1 THE LARMOR EQUATION AND NUCLEAR MAGNETIC RESONANCE

All nuclei have charge because they contain protons and some of them also behave as if they spin. Any nucleus that has an odd number of protons and/or neutrons has a property called "nuclear spin" and at least in principle, these nuclei can be observed by Nuclear Magnetic Resonance (NMR) spectroscopy. A spinning charge generates a magnetic dipole and is associated with a small magnetic field **H** (Figure 5.1). Such nuclear magnetic dipoles are characterised by nuclear magnetic **spin quantum numbers** which are designated by the letter **I** and can take up values equal to 0, ½, 1, $^{3}/_{2}$ ... *etc.*

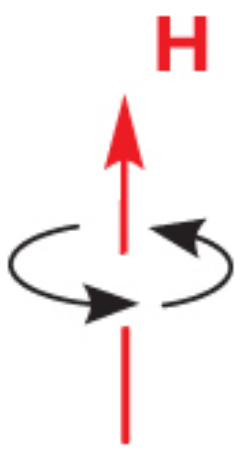


Figure 5.1 A Spinning Positive Charge Generates a Magnetic Field and Behaves like a Small Magnet

It is useful to consider three types of nuclei:

Type 1: Nuclei with **I** = 0. These nuclei are "NMR-silent". They do not interact with the applied magnetic field and they **are not NMR chromophores**. These nuclei cannot be observed by NMR spectroscopy. Nuclei with **I** = 0 have an even number of protons and an even number of neutrons. **Note** that nuclear spin is a property characteristic of certain **isotopes** rather than of certain elements. The most prominent examples of nuclei with **I** = 0 are ^{12}C and ^{16}O, and while ^{12}C and ^{16}O are NMR-silent, we can observe NMR spectra for the less abundant isotopes of carbon and oxygen, ^{13}C and ^{17}O.

Type 2: Nuclei with **I** = ½. These nuclei have a non-zero magnetic moment and they are NMR visible. The two most important nuclei for NMR spectroscopy belong to this category: ^{1}H (ordinary hydrogen) and ^{13}C (a non-radioactive isotope of carbon occurring to the extent of 1.06% at natural abundance). Also, two other commonly observed nuclei ^{19}F and ^{31}P have **I** = ½. Together, NMR data for ^{1}H and ^{13}C account for well over 90% of all NMR observations in the literature.

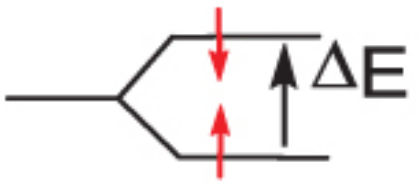
Type 3: Nuclei with **I** > ½. These nuclei have both a magnetic moment and they also have an electric quadrupole. These nuclei are NMR-visible but they are generally more difficult to observe and the spectra are generally very broad. This group includes some common important isotopes *e.g.* ^{2}H, ^{14}N and ^{11}B.

Each nucleus with a non-zero spin **I** has a magnetic moment μ, and the magnetic moment is proportional to the nuclear spin (Equation 5.1).

$$\mu = \gamma . \mathbf{I} \qquad 5.1$$

The constant of proportionality, γ, is known as the magnetogyric ratio and γ is unique for each NMR-active isotope. Table 5.1 provides a summary of the nuclear spins and magnetogyric ratios of some of the common NMR-active nuclei.

The most important consequence of nuclear spin is that if the nucleus is placed in a strong uniform magnetic field (H_0), a nucleus of spin **I** may assume 2**I** + 1 different orientations. For nuclei with **I** = ½, like ^{1}H or ^{13}C, there are two possible orientations (since 2 × ½ + 1 = 2) and these can be viewed as having the nuclear magnet aligned either parallel or antiparallel to the applied field. These two orientations are of unequal energy, and the energy gap (ΔE) is proportional to the strength of the applied magnetic field (H_0) according to Equation 5.2:



$$\Delta E = \frac{h.\gamma.H_0}{2\pi} \qquad 5.2$$

where h is Planck's constant.

Table 5.1 Nuclear Spins and Magnetogyric Ratios for Common NMR-Active Nuclei

Nucleus	Nuclear Spin I	Natural Abundance (%)	Magnetogyric Ratio (γ × 10^7 rad/T/s)
^{1}H	½	99.98	26.75
^{2}H	1	0.015	4.11
^{10}B	3	19.58	2.87
^{11}B	$^{3}/_{2}$	80.42	8.58
^{13}C	½	1.108	6.73
^{14}N	1	99.63	1.93
^{15}N	½	0.37	−2.71
^{17}O	$^{5}/_{2}$	0.037	−3.63
^{19}F	½	100.0	25.17
^{29}Si	½	4.7	−5.31
^{31}P	½	100.0	10.83

Nuclei in a lower energy orientation can be excited to the higher energy orientation by a radiofrequency (Rf) pulse of the correct frequency (ν) according to Equation 5.3:

$$\nu = \Delta E/h \qquad 5.3$$

It follows from Equations 5.2 and 5.3 that the fundamental equation that relates frequency (ν) to magnetic field strength (H_0) is Equation 5.4 which is known as the Larmor Equation:

$$\nu = (\gamma . H_0)/2\pi \qquad 5.4$$

Note that the frequency required to excite an NMR-active nucleus is proportional to the strength of the magnetic field and proportional to the magnetogyric ratio of the nucleus being observed. For magnetic fields that are currently accessible routinely for NMR spectroscopy (up to about 23.5 T), the frequencies required to observe most common NMR active nuclei fall in the Rf range of the electromagnetic spectrum (up to about 1 GHz).

Unlike other forms of spectroscopy, in NMR the frequency of the absorbed electromagnetic radiation is not an absolute value for any particular transition, but has a different value depending on the strength of the applied magnetic field. For every value of H_o, there is a matching value of ν corresponding to the condition of *resonance* according to Equation 5.4. Thus for ^{1}H and ^{13}C, *resonance frequencies* corresponding to magnitudes of applied magnetic field (H_o) commonly found in commercial instruments are given in Table 5.2.

Table 5.2 Resonance Frequencies of ^{1}H and ^{13}C Nuclei in Magnetic Fields of Different Strengths

H_o (Tesla)	^{1}H (MHz)	^{13}C (MHz)
1.4093	60.0	15.087
2.1139	90.0	22.629
2.3488	100.0	25.144
4.6975	200.0	50.288
7.0462	300.0	75.432
9.3950	400.0	100.577
11.744	500.0	125.720
14.0923	600.0	150.864
17.616	750.0	188.580
21.128	900.0	226.296
23.488	1000.0	250.288

In common jargon, NMR spectrometers are commonly known by the frequency they use to observe ^{1}H, *i.e.* as "60 MHz", "200 MHz" or "400 MHz" instruments, even if the spectrometer is set to observe a nucleus other than ^{1}H.

5.2 BASIC NMR INSTRUMENTATION AND THE NMR EXPERIMENT

5.2.1 CONTINUOUS WAVE AND PULSED NMR SPECTROMETERS

Samples for NMR spectroscopy are typically liquids (solutions) or solids. In order to observe Nuclear Magnetic Resonance, the sample must be placed in a strong, very uniform, magnetic field.

There are essentially two different types of NMR instruments – Continuous Wave (CW) and pulsed spectrometers. In a CW NMR spectrometer, the transmitter scans across a range of frequencies and the receiver records the frequencies where there is absorption of radiation (Figure 5.2). A complete CW spectrum typically takes several minutes to record.

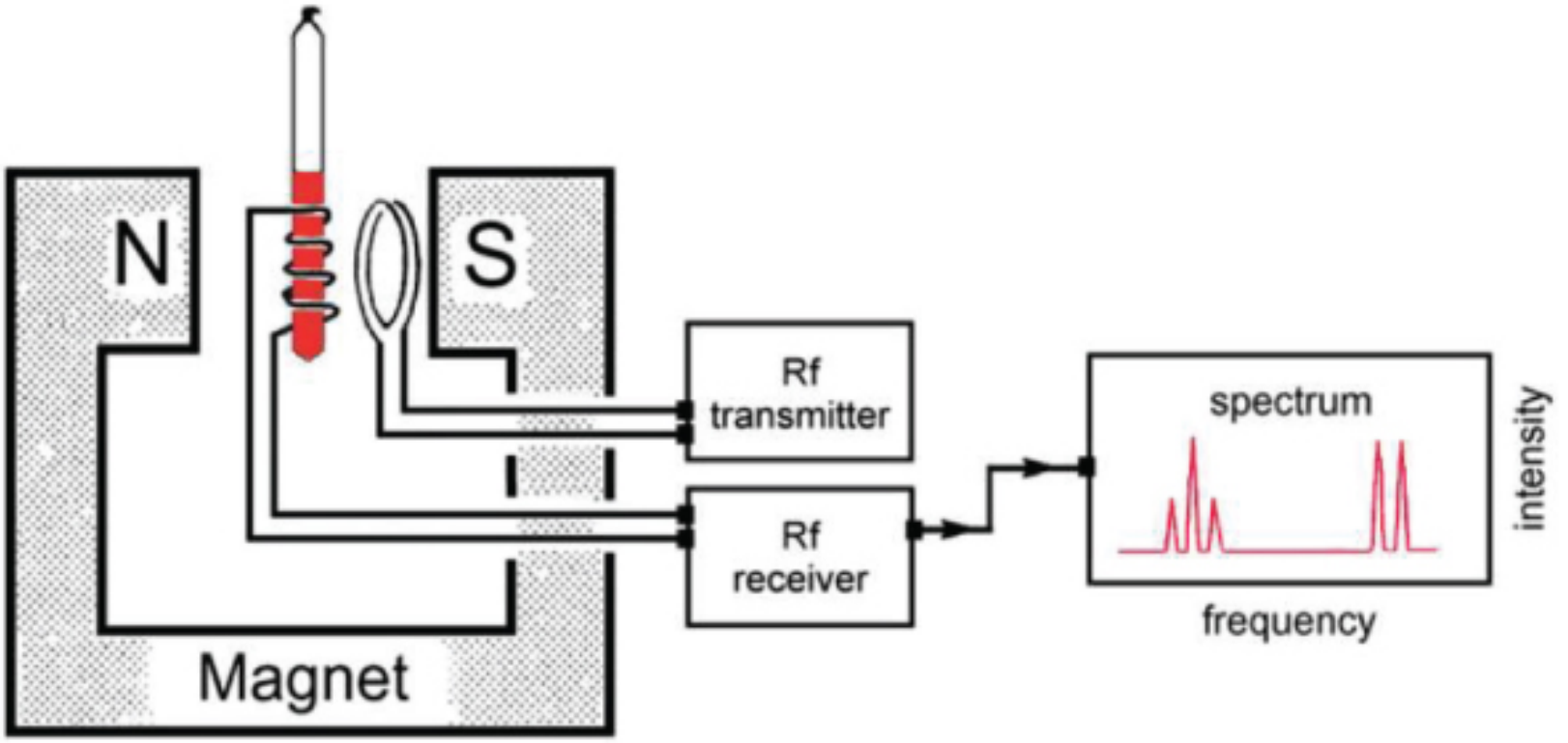


Figure 5.2 Schematic Representation of a CW NMR Spectrometer

In a pulsed NMR spectrometer, the transmitter provides intense short pulses of Rf radiation which excite all nuclei near the frequency of the pulse. The receiver records the signals from all excited nuclei simultaneously and a computer performs a Fourier Transformation to extract the frequencies in the form of a conventional spectrum (Figure 5.3).

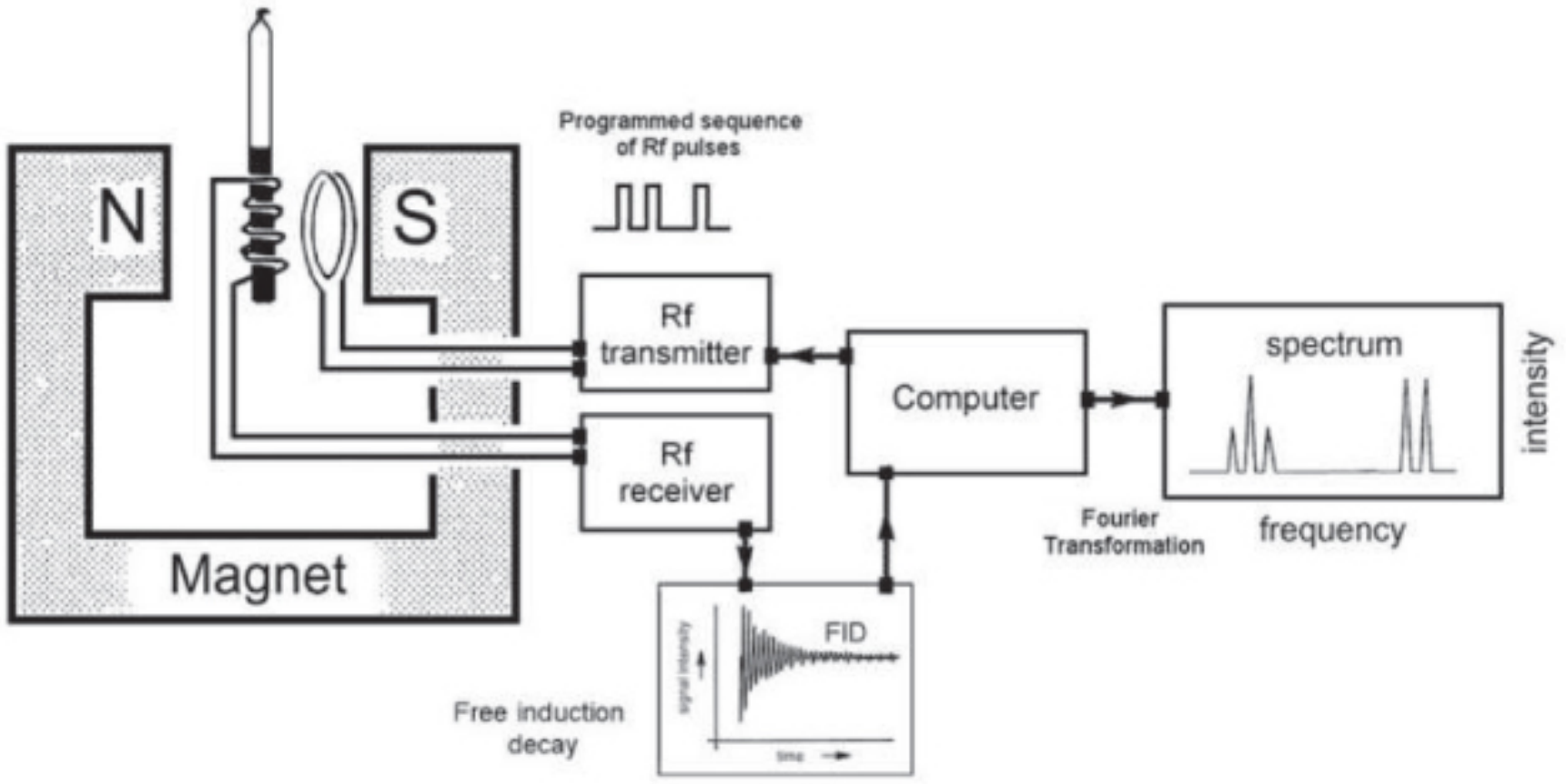


Figure 5.3 Schematic Representation of a Pulsed NMR Spectrometer

In a pulsed NMR spectrometer, a short burst or pulse of radiofrequency radiation will simultaneously excite all of the nuclei whose resonance frequencies are close to the frequency of the pulse. If a sample placed in a magnetic field of 9.395 T contains ^{1}H nuclei, then a pulse whose frequency is close to 400 MHz will excite all of the ^{1}H nuclei in the sample (see Table 5.2). Typically, the excitation pulse is very short in duration (microseconds)

and once the pulse is switched off, the magnetism which builds up in the sample begins to decay exponentially with time. A pulsed NMR spectrometer measures the decrease in sample magnetisation following a pulse as a function of time, and records the ***free-induction decay*** (FID). The FID is a time-domain signal (*i.e.* a signal whose amplitude is a function of time), and the FID contains information for each resonance in the sample, superimposed on the information for all the other resonances. The FID is an interference pattern arising from many different frequencies and the signal may be transformed into a frequency-domain spectrum (*i.e.* a spectrum whose amplitude is a function of frequency), by a mathematical procedure known as ***Fourier transformation*** (FT) (Figure 5.4). The frequency-domain spectrum is the typical NMR spectrum that is used to provide information about chemical compounds. An NMR spectrum which contains intensity information as a function of one frequency domain is termed a *one-dimensional (1D) NMR spectrum.*

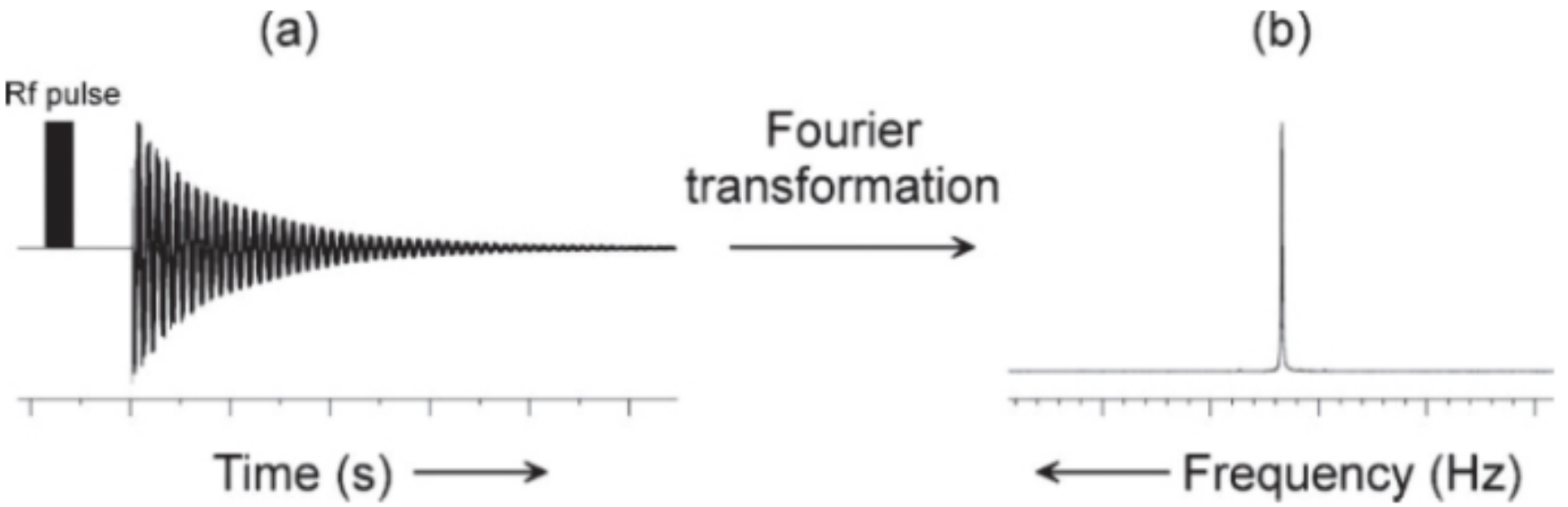


Figure 5.4 ^{1}H NMR Spectra: (a) Time Domain Spectrum (FID); (b) Frequency Domain Spectrum Obtained after Fourier Transformation of (a)

Almost all modern NMR spectrometers are pulsed Fourier transform spectrometers. Whilst pulsed spectrometers are generally more expensive and more complex to operate, spectra can be recorded rapidly (typically a few seconds) and the fact that the data is digitised into a computer means that it is much easier to store, visualise and add (or subtract) spectra.

Adding spectra is valuable since acquiring multiple spectra and adding them together improves the signal intensity of NMR spectra and this means that even weak samples can give good NMR spectra. The signal-to-noise ratio of the NMR spectrum is proportional to the square root of the number of scans which are added together, so the quality of NMR spectra is vastly improved as more scans are added. It is the ability to add spectra easily, brought about by the introduction of FT NMR spectroscopy, that has permitted the routine observation of nuclei whose natural abundance is low, *e.g.* ^{13}C.

Although it is possible to acquire many spectra in rapid succession using pulsed NMR methods, the speed with which multiple FIDs can be acquired is restricted by the fact that the nuclei in the sample need to relax between acquisitions (Section 5.2.2). If successive FIDs are acquired too rapidly, intensity information will be distorted because those nuclei which relax slowly will not be fully relaxed when subsequent scans are acquired and they will contribute less to the resulting signal. To ensure that the signal intensities are accurate, the repetition rate needs to be such that even any slowly relaxing nuclei in the sample are fully relaxed between scans.

In addition, the FID can be manipulated mathematically to enhance sensitivity (*e.g.* for routine ^{13}C NMR) at the expense of resolution, or to enhance resolution (often important for ^{1}H NMR) at the expense of sensitivity. It is also possible to devise **sequences** of Rf pulses to extract specific information from the sample, *e.g.* using two-dimensional NMR (see Chapter 7).

5.2.2 NUCLEAR RELAXATION

All of the frequencies listed in Table 5.2 correspond to the radio frequency region of the electromagnetic spectrum and inserting these values into Equation 5.2 gives the size of the energy gap between the states in an NMR experiment. A resonance frequency of 100 MHz corresponds to an energy gap of approximately 4×10^{-5} kJ mol^{-1}. Compared to other forms of spectroscopy, the energy gap for NMR spectroscopy is extremely small.

Any absorption signal observed in a spectroscopic experiment must originate from excess of the population in the lower energy state, the so called *Boltzmann excess*, which is equal to $N_\beta - N_\alpha$, where N_β and N_α are the populations in the lower (β) and upper (α) energy states.

For molar quantities, the general Boltzmann relation (Equation 5.5) shows that:

$$\frac{N_\beta}{N_\alpha} = e^{\frac{\Delta E}{RT}} \qquad 5.5$$

As the energy gap (ΔE) approaches zero, the right hand side of Equation 5.5 approaches 1 and the Boltzmann excess becomes very small. For the NMR experiment, the population excess in the lower energy state is typically of the order of 1 in 10^5 which renders NMR spectroscopy an **inherently insensitive** spectroscopic technique.

Equation 5.2 shows that the energy gap (and therefore ultimately the Boltzmann excess and sensitivity), increases with increasing applied magnetic field. Improving sensitivity is one of the reasons why NMR spectroscopists strive to use higher and higher magnetic fields in NMR spectrometers.

Even at the highest fields, the NMR experiment would not be practicable if mechanisms did not exist to restore the Boltzmann equilibrium that is perturbed as the result of the absorption of electromagnetic radiation in taking an NMR spectrum. These mechanisms are known by the general term of **relaxation**. The NMR experiment only works because there are processes that restore the system back to equilibrium once it has been excited by absorption of Rf energy.

If relaxation is too efficient (*i.e.* it takes a short time for the nuclear spins to relax after being excited in an NMR experiment) the lines observed in the NMR spectrum are very broad. If relaxation is too slow (*i.e.* it takes a long time for the nuclear spins to relax after being excited in an NMR experiment) then the populations of the upper and lower states equalise (*i.e.* the nuclei become *saturated*) and only a very weak signal can be observed.

The most important relaxation processes in NMR involve interactions with other nuclear spins that are in a state of random thermal motion. This is called *spin–lattice relaxation* and results in a simple exponential recovery process after the spins are disturbed in an NMR experiment. The exponential recovery is characterised by a time constant T_1 that can be measured for different types of nuclei. For organic liquids and samples in solution, T_1 is typically of the order of several seconds. In the presence of paramagnetic impurities or in very viscous solvents, relaxation of the spins can be very efficient and NMR spectra become broad.

Nuclei in solid samples typically relax very efficiently and give rise to very broad spectra. NMR spectra of solid samples can only be acquired using specialised spectroscopic equipment. This technique is known as solid state NMR spectroscopy and will not be discussed further.

5.2.3 MAGNETS FOR NMR SPECTROSCOPY

Magnets for NMR spectroscopy may be either permanent magnets or electromagnets. Most modern magnets are electromagnets based on superconducting solenoids, cooled to liquid helium temperature (4 degrees Kelvin). Irrespective of the type of magnet, for NMR spectroscopy, the magnetic field must be:

a. ***Strong***. This is partly due to the fact that the sensitivity of the NMR experiment increases as the strength of the magnet increases, but more importantly it ensures adequate **dispersion** of signals, *i.e.* less overlap of

signals.

b. Extremely ***homogeneous*** or uniform so that all portions of the sample experience exactly the same magnetic field. Any inhomogeneity of the magnetic field will result in broadening and distortion of spectral bands. When determining the structure of organic compounds, the highest attainable degree of magnetic field homogeneity is desirable, because useful information may be lost if the width of the NMR spectral lines exceeds about 0.2 Hz. Clearly, 0.2 Hz in, say, 100 MHz implies a homogeneity of about 2 parts in 10^9, and this is a very stringent requirement for homogeneity over the whole volume of an NMR sample.

c. Very ***stable*** over time so that it does not drift during the acquisition of the spectrum. This also means that there is a requirement for NMR instruments to be relatively isolated from sources of magnetic interference such as the movement of large metal objects (*e.g.* trucks, trains, metal cylinders, heavy machinery, elevators, *etc*).

5.2.4 THE NMR SPECTRUM

An NMR spectrum is effectively a graph of the intensity of absorption of Rf radiation (*y*-axis) against the frequency of the Rf radiation (*x*-axis). Since frequency and magnetic field strength are linked by the Larmor equation, the *x*-axis could also be calibrated in units of magnetic field strength.

The frequency axis of the spectrum is usually calibrated in dimensionless units called "parts per million" (abbreviated to ppm) although the horizontal scale is a frequency scale, the units are usually converted to ppm by dividing the observed frequencies by the frequency of the spectrometer so that the scale has the same numbers **irrespective of the strength of the magnetic field** in which the measurement was made.

The frequency scale in ppm, termed the δ scale, is usually referenced to the resonance of some standard substance whose frequency is chosen as 0.0 ppm. Tetramethylsilane, $(CH_3)_4Si$, (abbreviated commonly as TMS) is the usual reference compound chosen for both ^1H and ^{13}C NMR and it is normally added directly to the solution of the substance to be examined.

The frequency difference between the resonance of a nucleus and the resonance of the reference compound is termed the **chemical shift**.

$$\text{chemical shift } (\delta) \text{ in ppm} = \frac{\text{frequency difference from TMS in Hz}}{\text{spectrometer frequency in MHz}}$$

By convention, the δ scale runs (with increasing values) from right–to–left. Note that for a spectrometer operating at 200 MHz, 1 ppm corresponds to 200 Hz, *i.e.* for a spectrometer operating at x MHz, 1.00 ppm corresponds to exactly x Hz. A sample ^1H NMR spectrum is given in Figure 5.5.

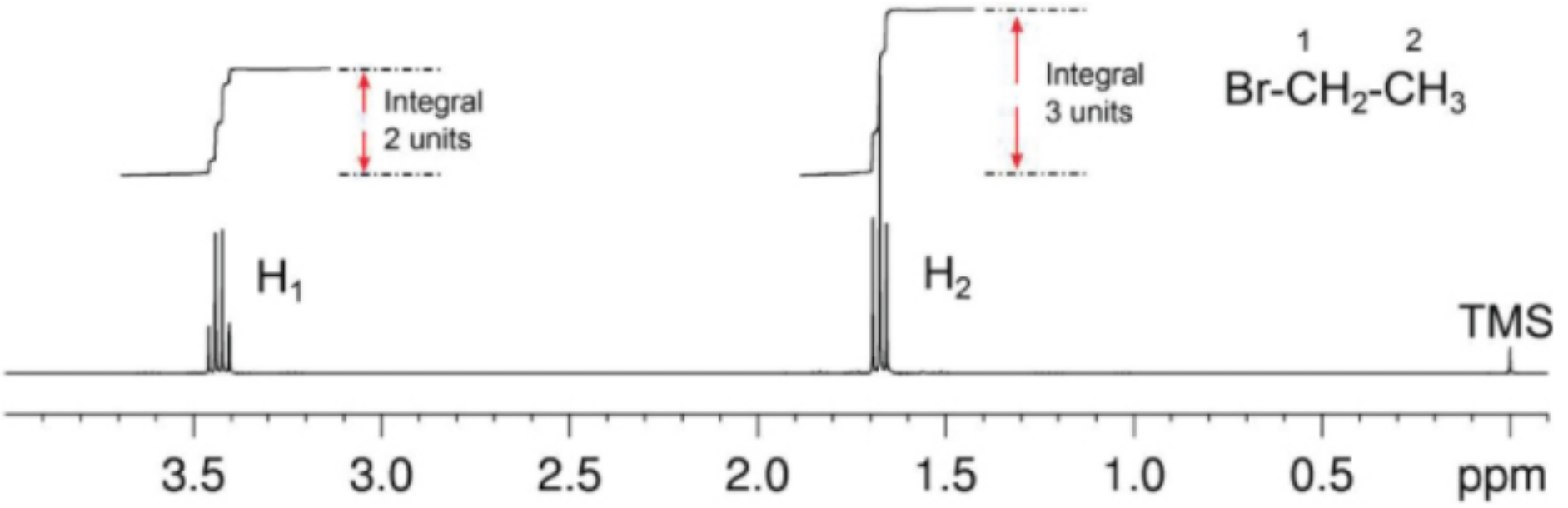


Figure 5.5 ^{1}H NMR Spectrum of Bromoethane (400 MHz, $CDCl_3$)

TMS has the following advantages as a reference compound:

a. it is a relatively inert, low boiling (b.p. 26.5°C) liquid which can be easily removed after use;

b. it gives a sharp single signal in both ^{1}H and ^{13}C because the compound has only one type of hydrogen and one type of carbon;

c. the chemical environment of both carbon and hydrogen in TMS is unusual due to the presence of silicon and hence the TMS signal occurs outside the normal range observed for organic compounds so the reference signal is unlikely to overlap with the signal from the substance examined;

d. the chemical shift of TMS is not substantially affected by complexation or solvent effects because the molecule doesn't contain any polar groups.

NMR spectroscopy is a quantitative technique and ^{1}H NMR spectra are usually recorded with an **integral** which indicates the relative areas of the absorption peaks in the spectrum. The area of a peak is proportional to the number of protons which give rise to the signal. In most NMR spectrometers, the integral is represented as a horizontal line plotted over the spectrum (see Figure 5.5). Whenever a peak is encountered, the vertical displacement of the integral line is proportional to the area of the peak. ^{1}H NMR spectroscopy is an excellent tool for the analysis of mixtures – if a sample contains more than one compound then the areas of the signals belonging to each species in the NMR spectrum will reflect the relative concentrations of the species in the mixture.

5.3 CHEMICAL SHIFTS IN 1H NMR SPECTROSCOPY

The real utility of NMR spectroscopy in chemistry is based on the *chemical shift* and on *spin–spin coupling* between nuclei and, to a lesser extent, on effects related to the *time-scale* of the NMR experiment.

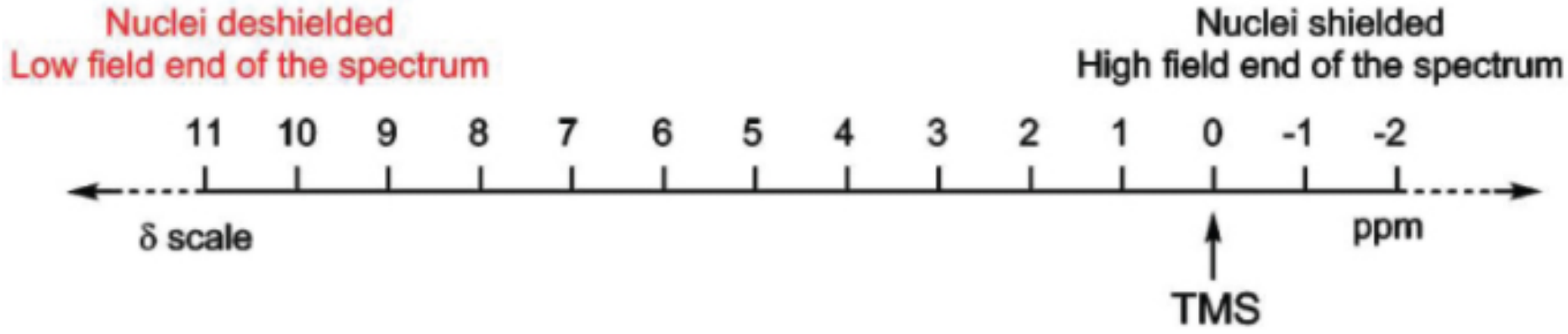
For the majority of organic compounds, the chemical shift range for ^{1}H covers approximately the range 0–10 ppm (from TMS) and for ^{13}C covers approximately the range 0–220 ppm (from TMS).

All ^{1}H nuclei in a sample are not necessarily equivalent, and the chemical environment that each ^{1}H finds itself in within the structure of the molecule determines its exact resonance frequency. Each nucleus is **screened or shielded** from the applied magnetic field by the electrons that surround it. Unless two ^{1}H environments are precisely identical (by symmetry) *their resonance frequencies must be slightly different*. When two nuclei have identical molecular environments and hence the same chemical shift, they are termed **chemically equivalent nuclei** or *isochronous* nuclei. Non-equivalent nuclei that coincidentally have chemical shifts that are so close that their signals are indistinguishable are termed ***accidentally equivalent nuclei***.

Nuclei that are close to strongly electron-withdrawing functional groups have the local electronic environment distorted and may have less electron density to screen or shield them from the magnetic field. These nuclei are said to be **deshielded** and these nuclei resonate at higher chemical shift values (*i.e.* towards the left hand or low-field end of an NMR spectrum). Nuclei that are in electron-rich sections of a molecule have more electron density to screen or shield them from the magnetic field. These nuclei are said to be **shielded** and these nuclei resonate at lower chemical shift values (*i.e.* towards the right hand or high-field end of an NMR spectrum).

Any effect which alters the density or spatial distribution of electrons around a ^{1}H nucleus will alter the degree of shielding and hence its chemical shift. ^{1}H chemical shifts are sensitive to both the hybridisation of the atom to which the ^{1}H nucleus is attached (sp^2, sp^3, *etc.*) and to electronic effects (the presence of neighbouring electronegative/electropositive groups).

The chemical shift of a nucleus reflects its local environment in a molecular structure and this makes NMR spectroscopy a powerful tool for obtaining structural information. **Every hydrogen and carbon atom in an organic molecule is a "chromophore"** for NMR spectroscopy.



Electron withdrawing substituents (–OH, –OCOR, –OR, –NO_2, halogen) attached to an aliphatic carbon chain cause a **downfield shift** of 2–4 ppm when present at C_α and have less than half of this effect when present at C_β.

When sp^2 hybridised carbon atoms (carbonyl groups, olefinic fragments, aromatic rings) are present in an aliphatic carbon chain they cause a downfield shift of 1–2 ppm when present at C_α. When present at C_β, sp^2 hybridised carbons have less than half of this effect.

Tables 5.3 and 5.4 give characteristic shifts for ^{1}H nuclei in some representative organic compounds. Table 5.5 gives characteristic chemical shifts for protons in common alkyl derivatives. Table 5.6 provides approximate ranges for proton chemical shifts in organic compounds.

Table 5.3 Typical ^1H Chemical Shift Values (δ) in Selected Organic Compounds

Compound	^1H (ppm from TMS)
CH_4	0.23
CH_3-Cl	3.05
CH_2Cl_2	5.33
$CHCl_3$	7.27
CH_3-CH_3	0.86
$CH_2{=}CH_2$	5.25
C_6H_6(benzene)	7.26
$CH_3{-}C(=O){-}H$	2.20 (-CH_3), 9.80 (-CHO)
CH_3-CH_2-CH_2-Cl	1.06 (-CH_3), 1.81 (-CH_2-), 3.47 (-CH_2-Cl)

Table 5.4 Typical ^1H Chemical Shift Values (δ) of Selected Protons*

Group	^1H (ppm from TMS)
Si(CH_3)$_4$ tetramethylsilane (TMS)	0.0
CH_3- attached to sp^3-hybridised carbon	0.8–1.2
-CH_2- attached to sp^3-hybridised carbon	1.0–1.5
>C–H attached to sp^3-hybridised carbon	1.2–1.8
—C≡C–H attached to *sp*-hybridised carbon	2.0–3.5
>C=C<, H attached to sp^2-hybridised carbon	5–8
protons attached to aromatic and heterocyclic rings	6–9
R–C(=O)–H attached to sp^2-hybridised aldehyde carbon	9–10

* -OH protons in alcohols, phenols or carboxylic acids; -SH protons in thiols; -NH protons in amines or amides do not have reliable chemical shift ranges (see Section 5.8).

Table 5.5 ^{1}H Chemical Shift Values (δ) for Protons in Common Alkyl Derivatives

	CH_3–X	CH_3–CH_2–X		$(CH_3)_2$CH–X	
X	CH_3–	CH_3–	–CH_2–	CH_3–	>CH–
–H	0.23	0.86	0.86	0.91	1.33
–CH=CH_2	1.71	1.00	2.00	0.91	2.50
–Ph	2.35	1.21	2.63	1.25	2.89
–Cl	3.06	1.33	3.47	1.55	4.14
–Br	2.69	1.66	3.37	1.73	4.21
–I	2.16	1.88	3.16	1.89	4.24
–OH	3.39	1.18	3.59	1.16	3.94
–OCH_3	3.24	1.15	3.37	1.08	3.55
–O–Ph	3.73	1.38	3.98	1.31	4.51
–OCO–CH_3	3.67	1.21	4.05	1.22	4.94
–OCO–Ph	3.89	1.38	4.37	1.36	5.30
–CO–CH_3	2.09	1.05	2.47	1.08	2.54
–CO–Ph	2.55	1.18	2.92	1.22	3.58
–CO–OCH_3	2.01	1.12	2.28	1.15	2.48
–NH_2	2.47	1.10	2.74	1.03	3.07
–NH–$COCH_3$	2.71	1.12	3.21	1.13	4.01
–C≡N	1.98	1.31	2.35	1.35	2.67
–NO_2	4.29	1.58	4.37	1.53	4.44

Approximate ^{1}H Chemical Shifts (δ) for Olefinic Protons

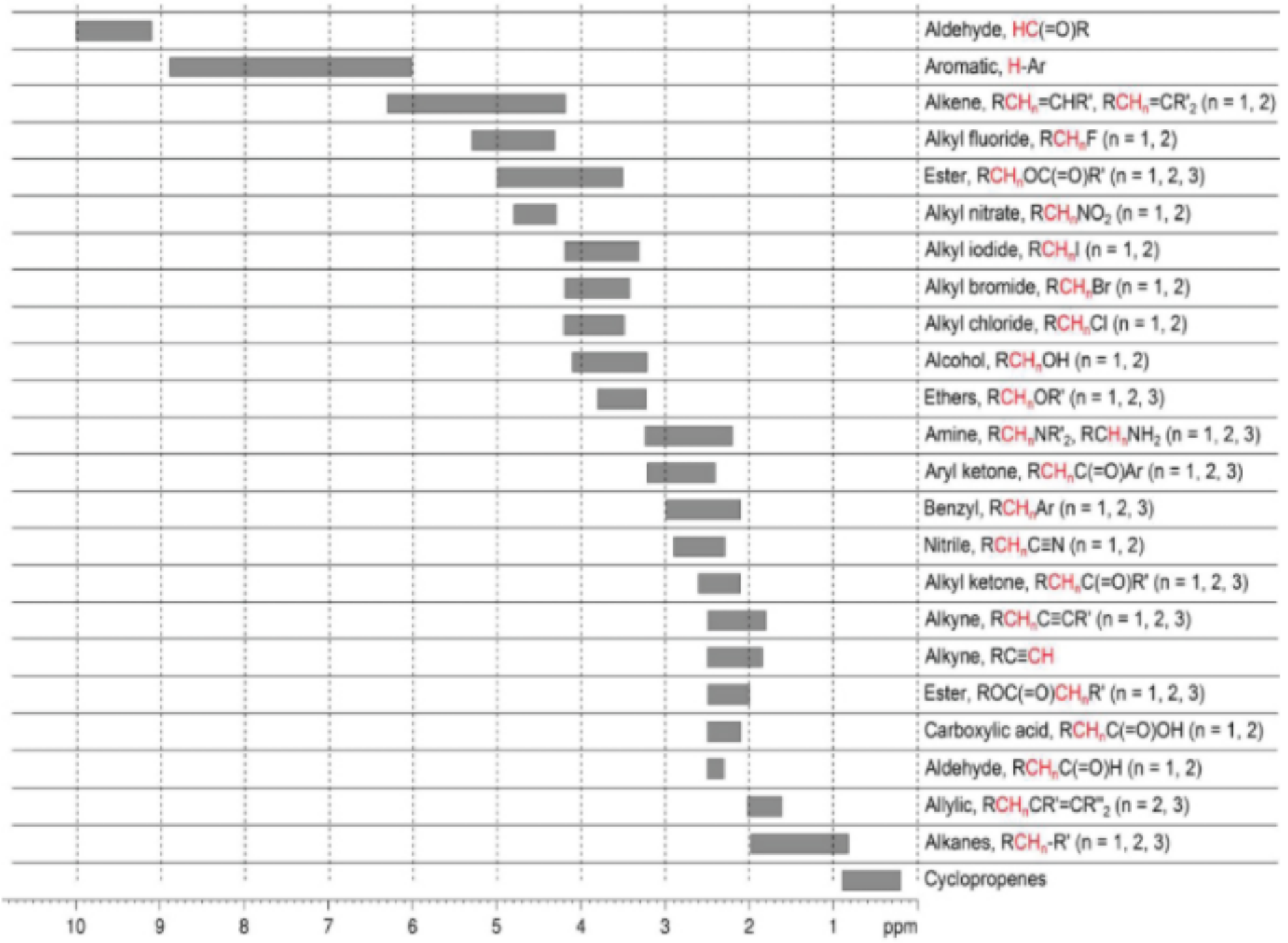


Table 5.7 gives characteristic chemical shifts for the olefinic protons in common substituted alkenes. To a first approximation, the shifts induced by substituents attached to an alkene are additive. So, for example, an olefinic proton which is *trans* to a −CN group and has a geminal alkyl group will have a chemical shift of approximately 6.25 ppm [5.25 + 0.55(*trans*-CN) + 0.45(*gem*-alkyl)].

Table 5.7 Approximate ^{1}H Chemical Shifts (δ) for Olefinic Protons

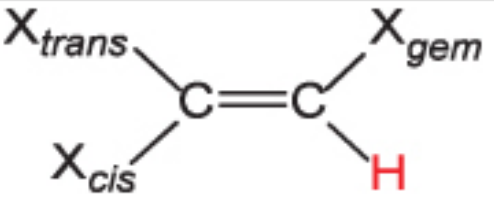
$\delta_{C=C-H} = 5.25 + \sigma_{gem} + \sigma_{cis} + \sigma_{trans}$			
X	σ_{gem}	σ_{cis}	σ_{trans}
-H	0.0	0.0	0.0
-alkyl	0.45	−0.22	−0.28
-aryl	1.38	0.36	−0.07
$-CH=CH_2$	1.00	−0.09	−0.23
-CH=CH-conjugated	1.24	0.02	−0.05
-C≡C-H	0.47	0.38	0.12
-CO-R	1.10	1.12	0.87
-CO-OH	0.80	0.98	0.32
-CO-OR	0.78	1.01	0.46
-C≡N	0.27	0.75	0.55
-Cl	1.08	0.18	0.13
-Br	1.07	0.45	0.55
-OR	1.22	−1.07	−1.21
$-NR_2$	0.80	−1.26	−1.21

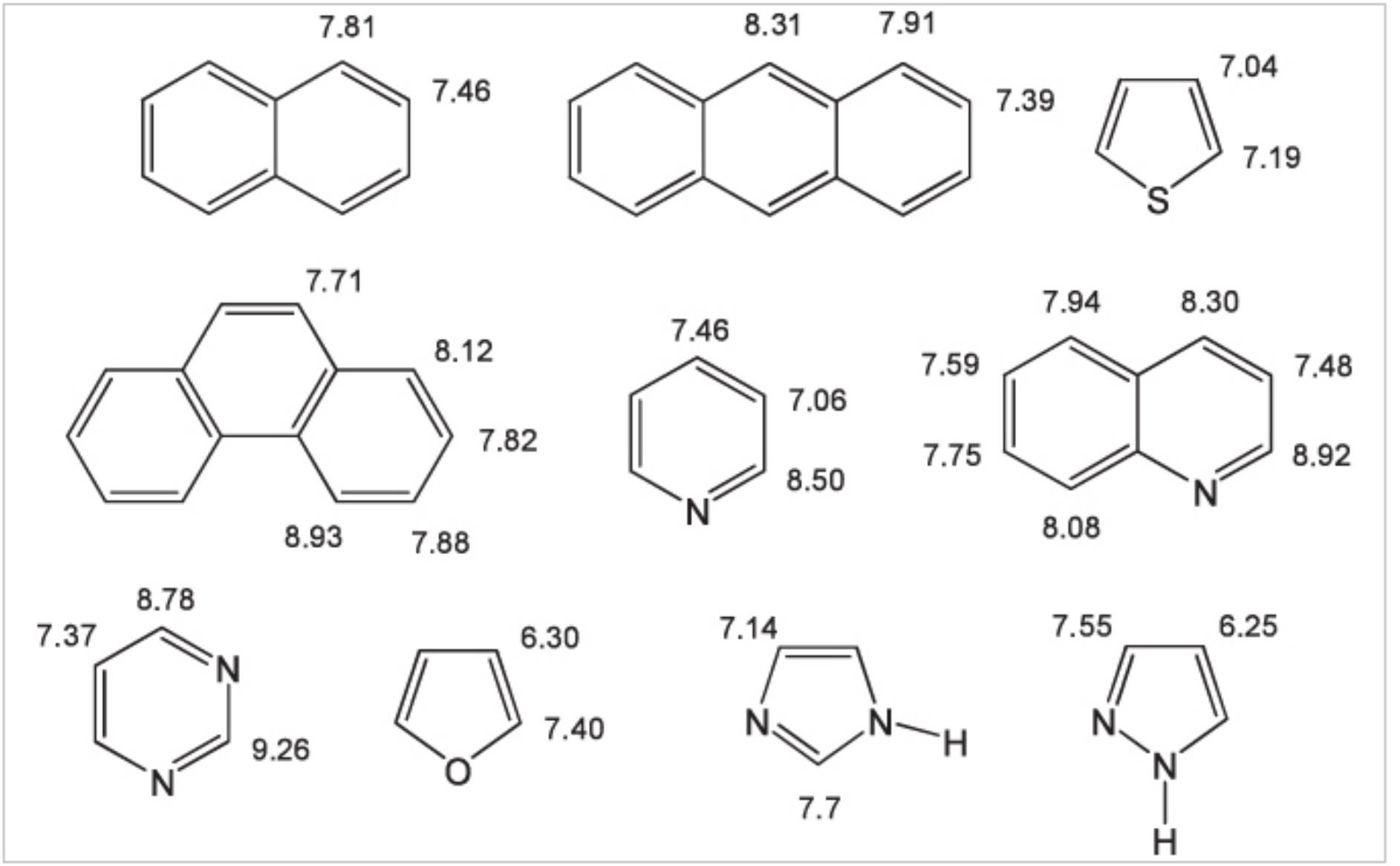
Table 5.8 gives characteristic ^{1}H chemical shifts for the aromatic protons in benzene derivatives. To a first approximation, the shifts induced by substituents are additive. So, for example, an aromatic proton which has a $-NO_2$ group in the *para* position and a −Br group in the *ortho* position will appear at approximately 7.82 ppm [(7.26 + 0.38(*p*-NO_2) + 0.18(*o*-Br))].

Table 5.9 gives characteristic chemical shifts for ^{1}H nuclei in some polynuclear aromatic compounds and heteroaromatic compounds.

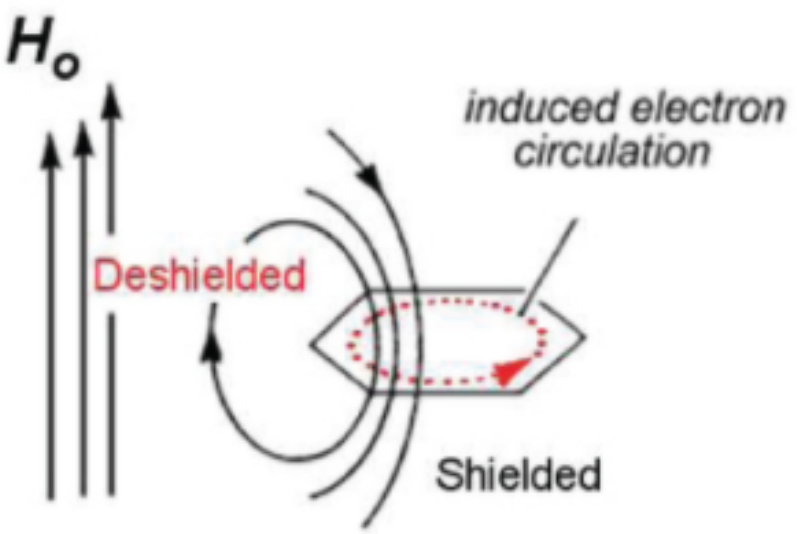
Table 5.8 Approximate ^1H Chemical Shifts (δ) for Aromatic Protons in Benzene Derivatives Ph–X in ppm Relative to Benzene at δ 7.26 ppm (positive sign denotes a downfield shift)

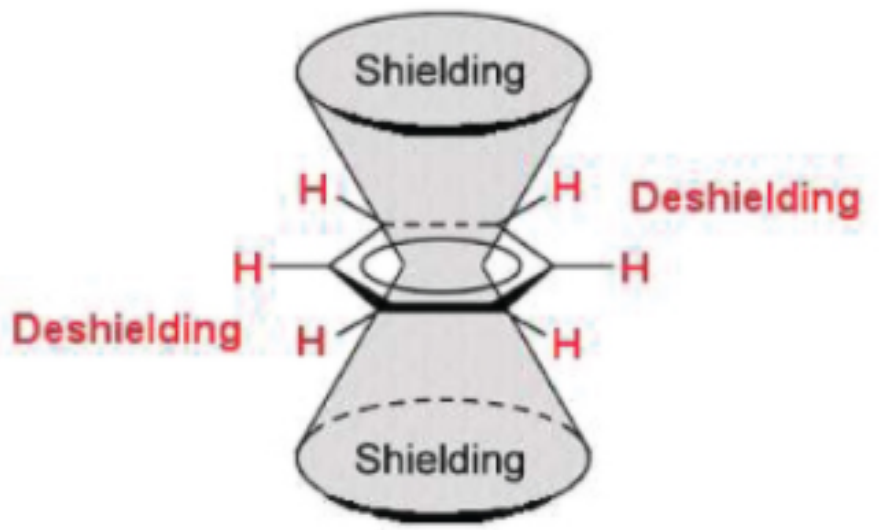
X	ortho	meta	para
–H	0.0	0.0	0.0
$-CH_3$	–0.20	–0.12	–0.22
$-C(CH_3)_3$	–0.03	–0.08	0.20
$-CH=CH_2$	0.06	–0.03	–0.10
–C≡C–H	0.16	–0.04	–0.02
–CO–OR	0.71	0.11	0.21
–CO–R	0.62	0.14	0.21
–OCO–R	-0.25	0.03	–0.13
$-OCH_3$	–0.48	–0.09	–0.44
–OH	–0.56	–0.12	–0.45
–Cl	0.03	–0.02	–0.09
–Br	0.18	–0.08	–0.04
–C≡N	0.36	0.18	0.28
$-NO_2$	0.95	0.26	0.38
$-NR_2$	–0.66	–0.18	–0.67
$-NH_2$	–0.75	–0.25	–0.65

Table 5.9 ^{1}H Chemical Shifts (δ) for Protons in some Polynuclear Aromatic Compounds and Heteroaromatic Compounds



The chemical shift of a nucleus may also be affected by the presence in its vicinity of a *magnetically anisotropic* group (*e.g.* an aromatic ring or carbonyl group). In an aromatic ring, the "circulation" of electrons effectively forms a current loop which gives rise to an induced magnetic field. This is called the **ring current effect** and the induced field opposes the applied magnetic field of the spectrometer (H_0) inside the loop and enhances the field outside the loop. The resonance of a nucleus which is located close to the face of an aromatic ring will be shifted to high field (towards TMS) because it experiences the effect of both the main spectrometer magnetic field but also the magnetic field from the ring current effect of the aromatic ring. Conversely a proton which is in the plane of an aromatic ring is deshielded by the ring current effect.

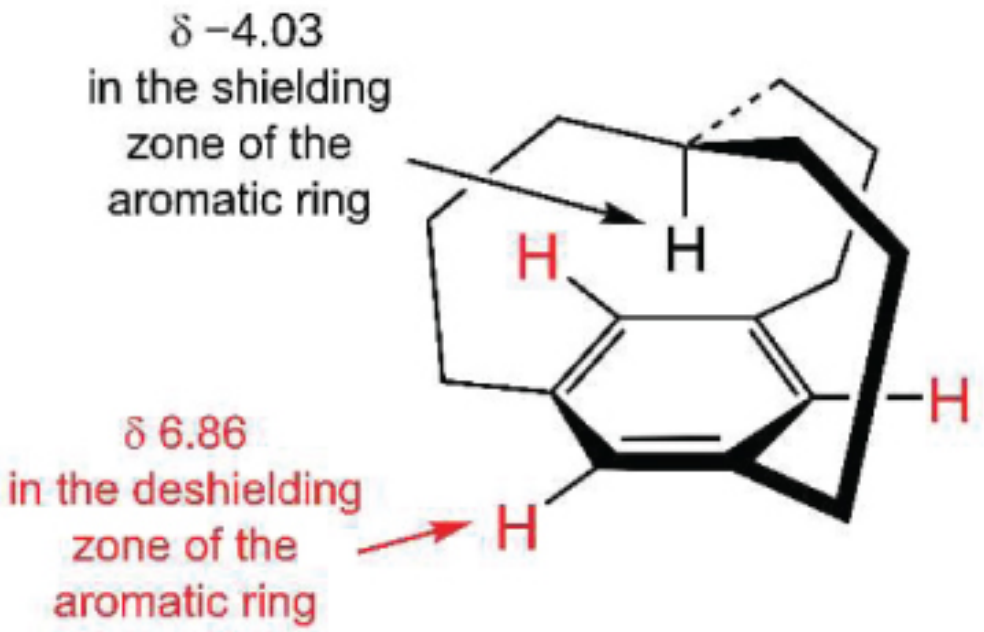




The ring current effect is the main reason that protons attached to aromatic rings typically appear at the low field end of the ^{1}H NMR spectrum (near 7 ppm from TMS) since they are in the deshielded zone of the aromatic

ring.

Shielding and deshielding by an aromatic ring is clearly illustrated by the compound on the right, in which the aromatic protons are deshielded, and resonate at 6.86 ppm, while the central bridge-head proton, which is constrained in the shielding zone of the aromatic ring, resonates at −4.03 ppm, well upfield of most other proton signals.[1]



18-annulene

The compound 18-annulene ($C_{18}H_{18}$) is aromatic. The structure is planar with 12 hydrogens on the outside of the ring (in the deshielding zone of the aromatic system) and 6 hydrogens on the inside of the ring (in the shielding zone of the aromatic ring). The protons in the shielding zone resonate at −1.92 ppm, well upfield of most other proton signals.[2]

There are also a number of common non-aromatic organic functional groups which are magnetically anisotropic and influence the magnetic field experienced by nearby nuclei. The greatest influence comes from multiple bonds and in particular, the C≡C group, the C≡N group, and C=C, N=O and C=O groups have strong magnetic anisotropies. Figure 5.6 depicts the shielding and deshielding zones around common non-aromatic functional groups.

Shielding effects diminish with distance but are useful qualitative indicators of what groups are close by and also their geometric relationship in the three-dimensional structure of the molecule.

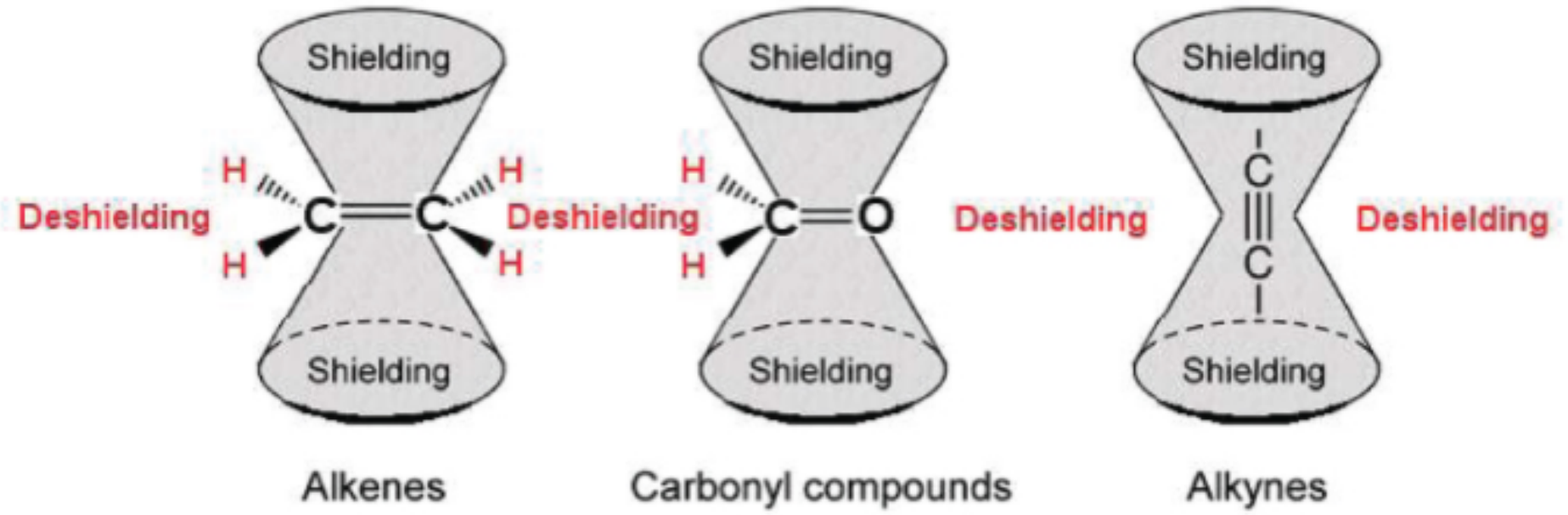
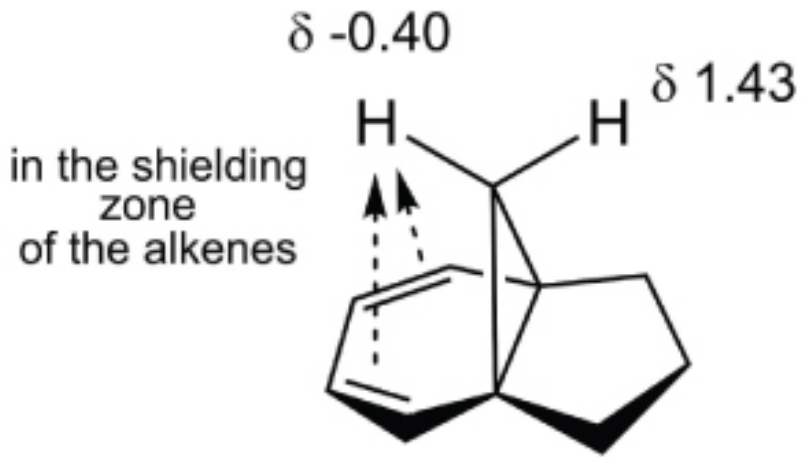
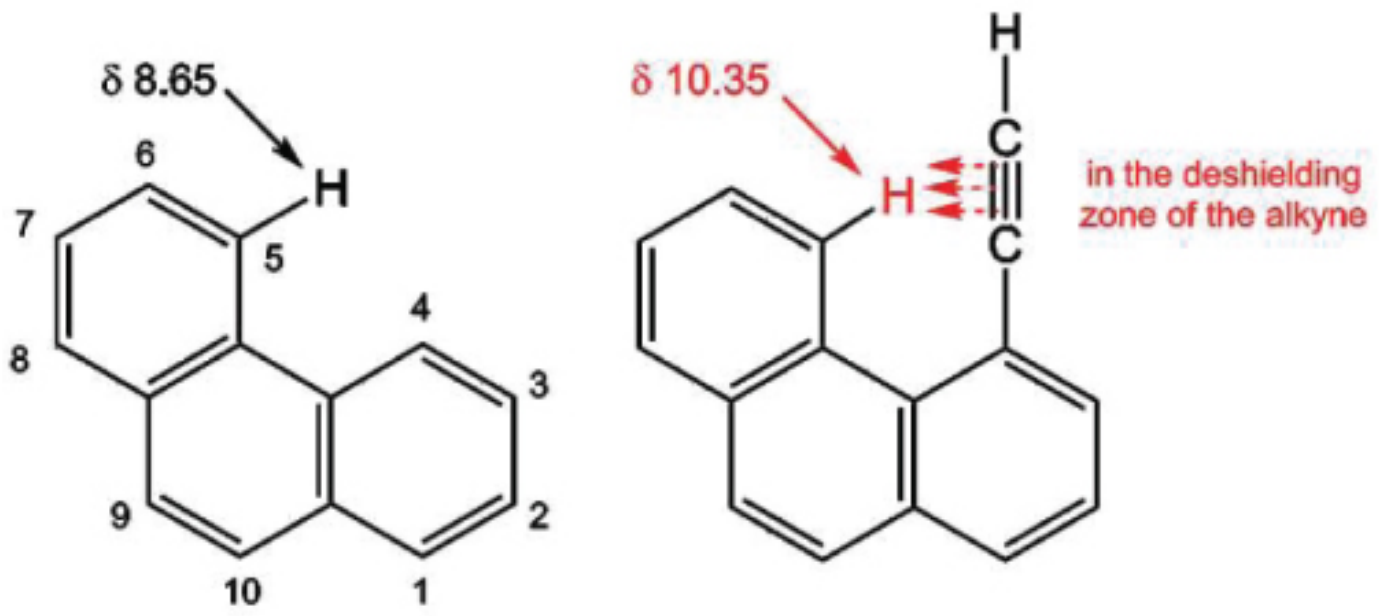


Figure 5.6 Shielding/deshielding Zones for Common Non-aromatic Functional Groups

The tricyclic alkene, [4.3.1]propella-2,4-diene, has two protons attached to a three-membered ring. One proton (δ −0.40) is constrained in the shielding zone of the alkene double bonds. The other proton is not. The proton in the shielding zone is shifted about 1.8 ppm to higher field due to the shielding influence of the alkenes.[3]



In the structure of 4-ethynylphenanthrene, the proton at position 5 (δ 10.38) is constrained in the deshielding zone of the alkyne triple bond.[4] Compared to the phenanthrene without the alkyne substituent, the proton in the alkyne shielding zone resonates 1.7 ppm to lower field due to the deshielding influence of the triple bond.



5.4 SPIN–SPIN COUPLING IN 1H NMR SPECTROSCOPY

A typical organic molecule contains more than one magnetic nucleus (*e.g.* more than one ^{1}H, or ^{1}H and ^{31}P *etc.*) and splitting or multiplicity arises when one nucleus can sense the presence of other magnetic nuclei ***through the bonds of the molecule***. Signal splitting is due to spin–spin coupling and arises because a magnetic nucleus will have different energy depending on the spin state of nuclei that it can sense.

The fine structure caused by spin–spin coupling is not only the principal cause of difficulty in interpreting ^{1}H NMR spectra, but also provides valuable structural information when correctly interpreted. The **coupling constant** (related to the size of the splittings in the multiplet) is given the symbol *J* and is measured in Hz. By convention, a superscript before the symbol "*J*" represents the number of intervening bonds between the coupled nuclei. Labels identifying the coupled nuclei are usually indicated as subscripts after the symbol "*J*", *e.g.* $^{2}J_{ab}$ = 2.7 Hz would indicate a coupling of 2.7 Hz between nuclei *a* and *b* that are separated by two bonds.

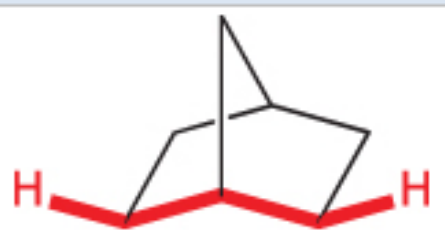
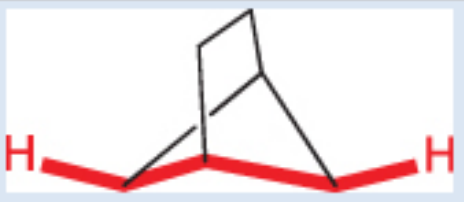
Because *J* is a property of the bonding in a molecule, it is **independent of the applied magnetic field**. The magnitude of *J* provides valuable structural information.

Two important observations that relate to ^{1}H–^{1}H spin–spin coupling:

a. No **inter-molecular** spin–spin coupling is observed. Spin–spin coupling is transmitted through the bonds of a molecule and doesn't occur between nuclei in different molecules.

b. The effect of coupling falls off as the number of bonds between the coupled nuclei increases. ^{1}H–^{1}H coupling is generally unobservable across more than three intervening bonds. Unexpectedly large couplings across many bonds *(long-range coupling)* may occur if there is a particularly favourable bonding pathway, *e.g.* extended π-conjugation or a rigid σ-bonding skeleton (Table 5.10).

Table 5.10 Typical ^{1}H–^{1}H Coupling Constants

Group	J (Hz)
$CH_3CH_2CH_2CH_3$	$^{2}J_{HH} = -16$
$CH_3CH_2CH_2CH_3$	$^{3}J_{HH} = 7.2$
$CH_3CH_2CH_2CH_3$	$^{4}J_{HH} = 0.3$
$CH_2{=}C{=}C{=}CH_2$	$^{5}J_{HH} = 7$
$CH_2{=}CH{-}CH{=}CH_2$	$^{5}J_{HH} = 1.3$
	$^{4}J_{HH} = 1.5$
	$^{4}J_{HH} = 7.0$

5.4.1 SIGNAL MULTIPLICITY – THE N+1 RULE.

Spin–spin coupling gives rise to multiplet splittings in ^{1}H NMR spectra. The NMR signal of a nucleus coupled to ***n*** equivalent hydrogens will be split into a multiplet with (***n*** + 1) lines (see for example Figure 5.7).

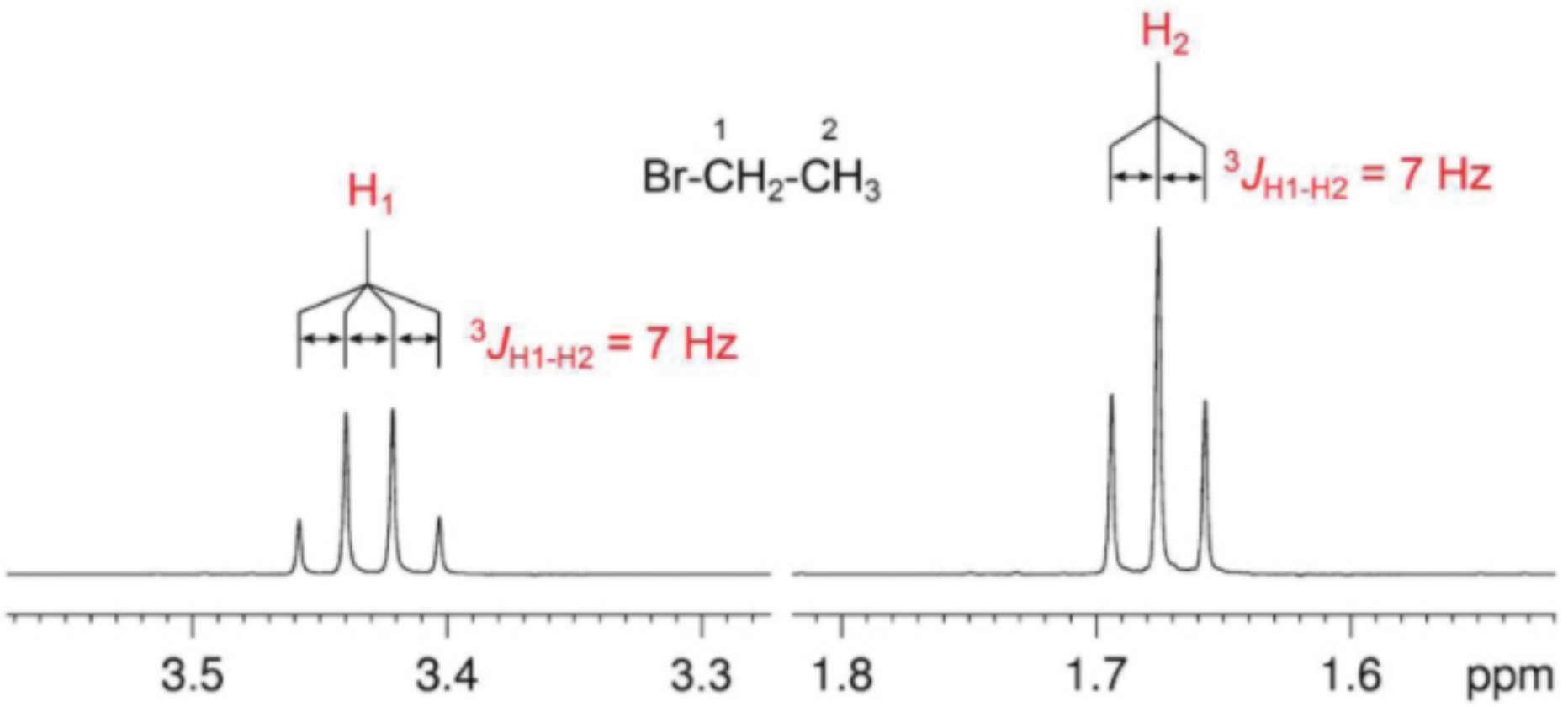


Figure 5.7 ^{1}H NMR Spectrum of Bromoethane (400 MHz, $CDCl_3$) Showing the Multiplicity of the Two ^{1}H Signals

For simple multiplets, the spacing between the lines (in Hz) is the coupling constant. The relative intensity of the lines in multiplets is given by the binomial coefficients of order "***n***" (Table 5.11).

Table 5.11 Relative Line Intensities for Simple Multiplets

n	Multiplicity *n+1*	Relative line intensities	Multiplet name
0	1	1	singlet
1	2	1:1	doublet
2	3	1:2:1	triplet
3	4	1:3:3:1	quartet
4	5	1:4:6:4:1	quintet
5	6	1:5:10:10:5:1	sextet
6	7	1:6:15:20:15:6:1	septet
7	8	1:7:21:35:35:21:7:1	octet
8	9	1:8:28:56:70:56:28:8:1	nonet

These simple multiplet patterns give rise to characteristic "fingerprints" for common fragments of organic structures. A methyl group, $-CH_3$, (isolated from coupling to other protons in the molecule) will always occur as a singlet. A CH_3-CH_2- group, (isolated from coupling to other protons in the molecule) will appear as a quartet ($-CH_2-$) and a triplet (CH_3-). Figure 5.8 shows the schematic appearance of the NMR spectra of various common molecular fragments encountered in organic molecules.

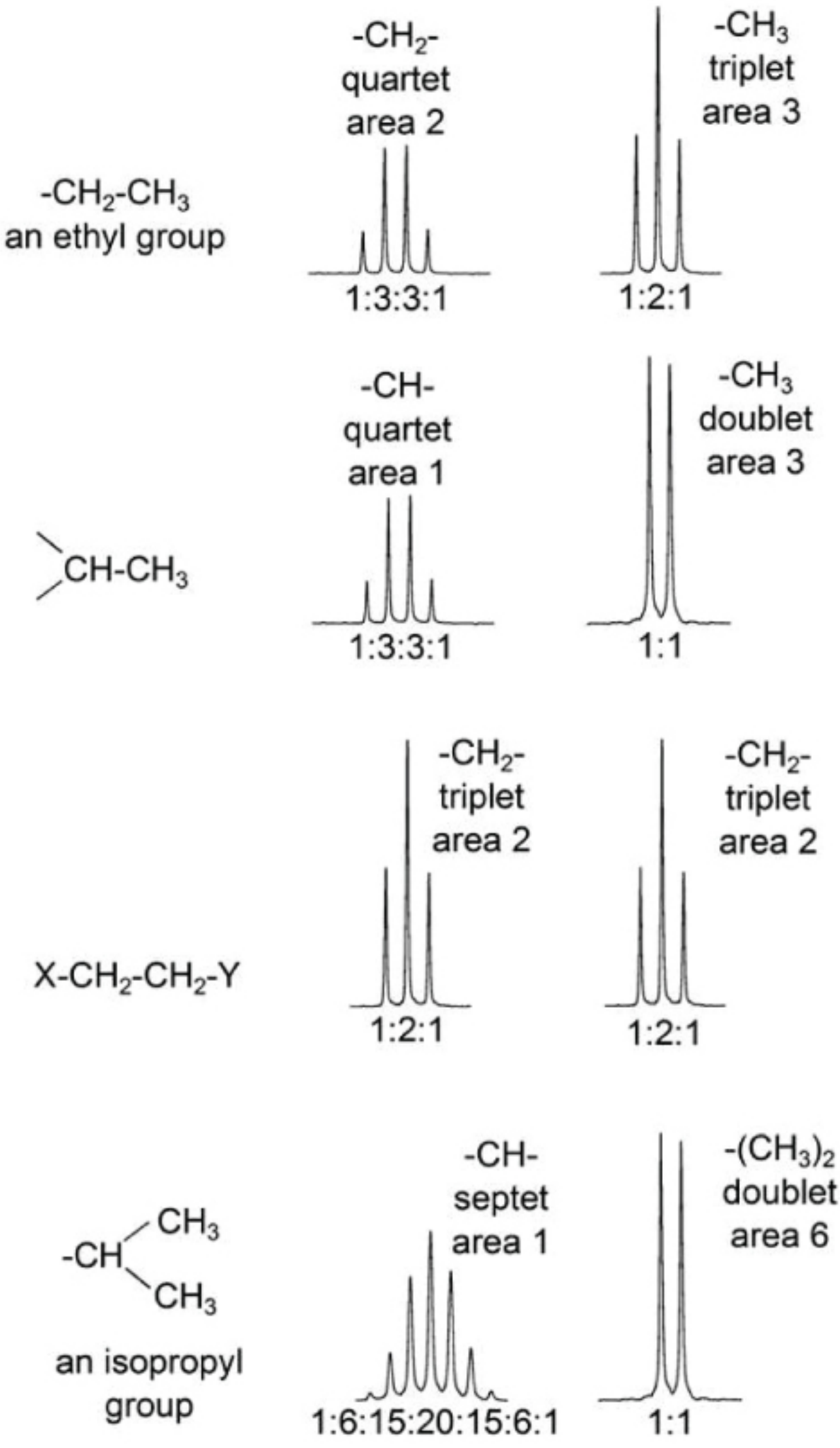


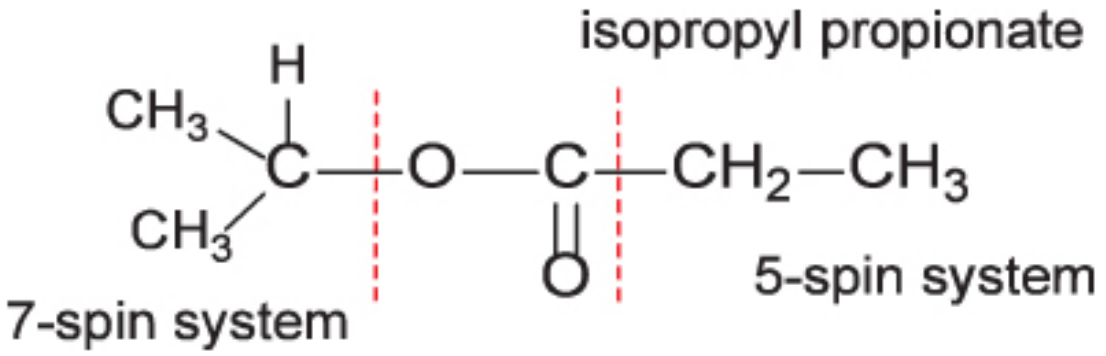
Figure 5.8 Characteristic Multiplet Patterns for Common Organic Fragments

5.5 ANALYSIS OF 1H NMR SPECTRA

To obtain structurally useful information from NMR spectra, one must solve two separate problems. Firstly, the spectrum must be **analysed** to obtain the NMR parameters (chemical shifts and coupling constants) for all the protons and, secondly, the values of the chemical shifts and coupling constants must be **interpreted** in terms of established relationships between the parameters and structure.

5.5.1 SPIN SYSTEMS

A spin system is defined as a group of coupled protons. Clearly, a spin system cannot extend beyond the bounds of a molecule, but it might not include a whole molecule. For example, isopropyl propionate comprises **two** separate and isolated proton spin systems, a seven-proton system for the isopropyl residue and a five-proton system for the propionate residue. The ester group effectively provides an "insulating barrier" across which there is no (or very small) H–H coupling and therefore isolates the two different spin systems. Any molecule may contain a number of different spin systems.



5.5.2 STRONGLY AND WEAKLY COUPLED SPIN SYSTEMS

The terms "strongly or weakly coupled" protons refers to the **ratio** of the separation of chemical shifts expressed in Hz ($\Delta\nu$) to the coupling constant J between them. For most purposes, if $\Delta\nu/J$ is larger than ~3, the spin system is termed *weakly coupled*. When this ratio is smaller than ~3, the spins are termed *strongly coupled*.

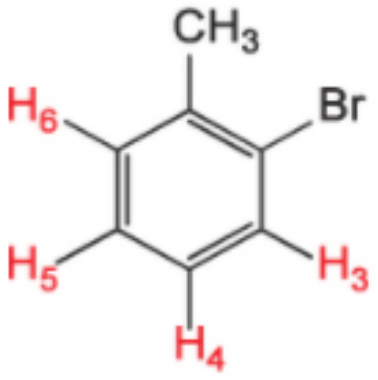
In weakly coupled systems, multiplets are typically well separated and the line intensities in the multiplets approximately follow the binomial intensities given in Table 5.11. Weakly coupled systems are also termed "first-order" spin systems and these can always be analysed by inspection, i.e. the coupling constants and chemical shifts can be measured directly from the spectra.

Note the following:

a. The chemical shifts of the nuclei (expressed in Hz) are proportional to the strength of the magnetic field (see Section 5.1). Nuclei move further apart (in Hz) from each other as the magnetic field strength increases, *i.e.* **there is better dispersion in the spectrum**. However, spin–spin coupling is a molecular property that is independent of the magnetic field of the spectrometer. So the splittings in an NMR spectrum due to spin–spin coupling, remain constant, irrespective of the magnetic field strength of the spectrometer.

   Spin systems become progressively more weakly coupled as the spectrometer frequency increases. Since **weakly coupled spin systems are much easier to analyse than strongly coupled spin systems**, spectrometers operating at higher frequencies (and therefore at higher applied magnetic fields) will yield spectra which are more easily analysed and interpreted. ^{1}H NMR spectra of 2-bromotoluene are given in Figure 5.9 where spectra on the same sample have been recorded using three different NMR spectrometers each operating at a different magnetic field strength.

   There are four different aromatic proton resonances. At the lowest field (4.7 Tesla), there is significant overlap of the resonances. The resonances for H_5 and H_6 are severely distorted and this is not a first-order spectrum. At 14.1 Tesla (600 MHz) dispersion is much better and the spectrum is a first-order spectrum that could be analysed by first-order rules.



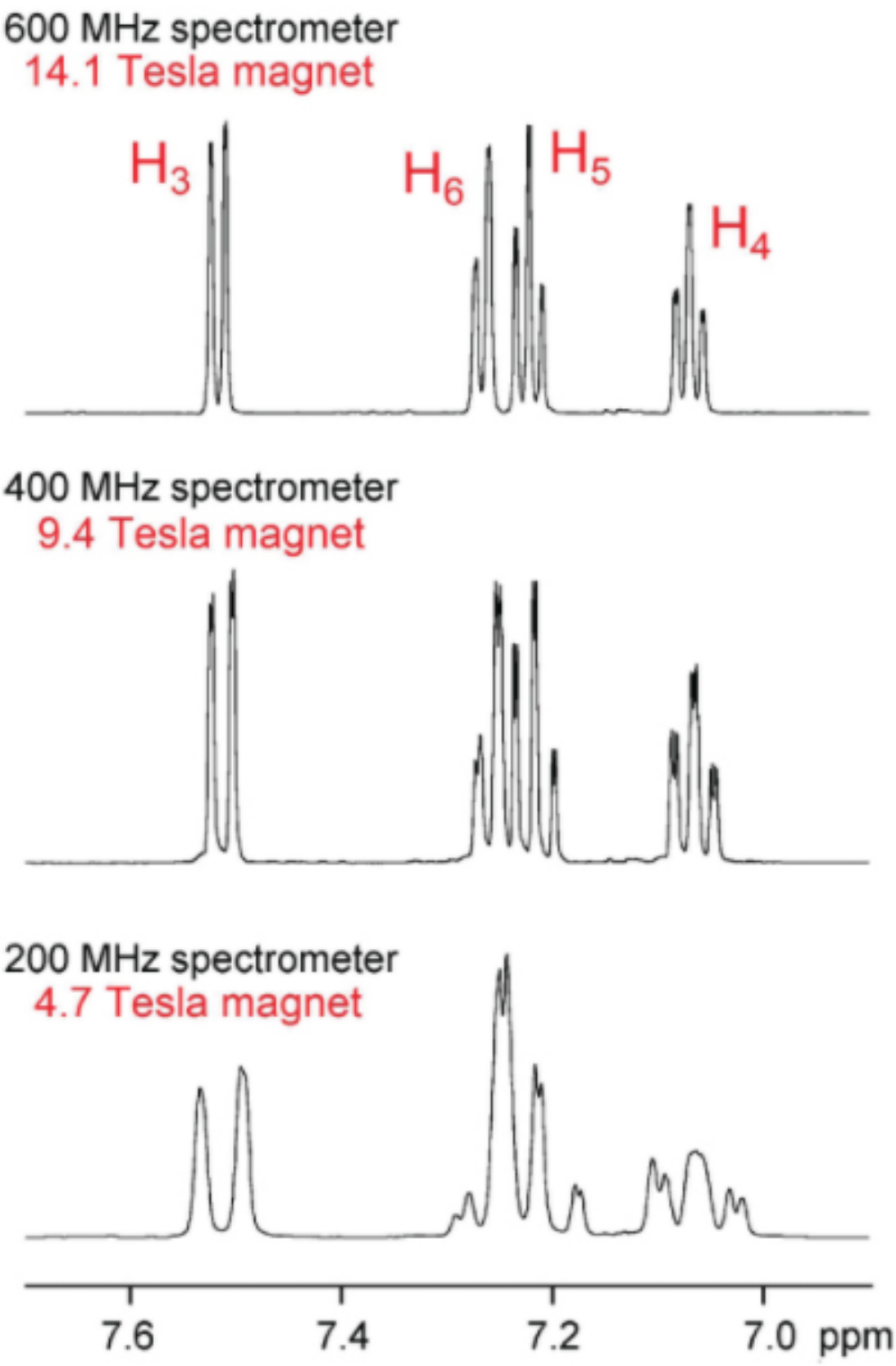


Figure 5.9 Aromatic Region of the ^{1}H NMR Spectrum of 2-Bromotoluene (acetone-d_6 solution) in Three Different Magnetic Field Strengths

b. A spin system comprising just two protons is always exceptionally easy to analyse because, independent of the value of the ratio of $\Delta\nu/J$, the spectrum always consists of just four lines with each pair of lines separated by the coupling constant J. As $\Delta\nu$ decreases, the main distortion from the first-order pattern consists of the gradual reduction of intensities of the outer lines in favour of the inner lines, a characteristic "sloping" or "tenting" towards the coupling partner. A series of simulated spectra of 2-spin systems are shown in Figure 5.10.

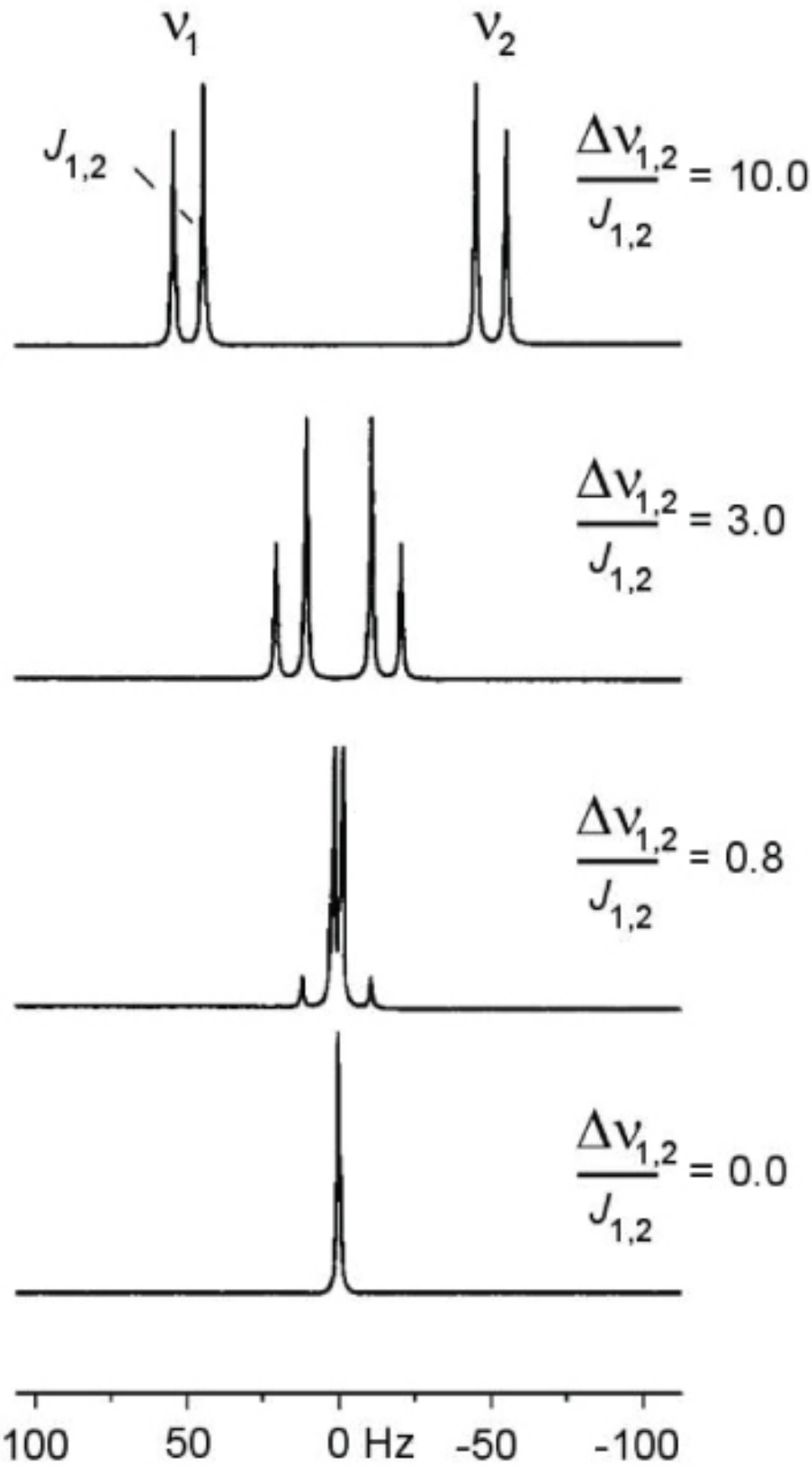


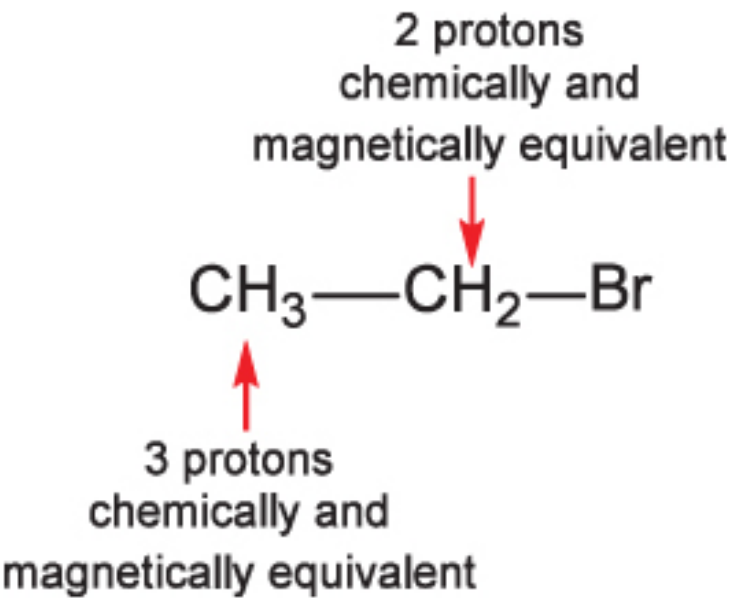
Figure 5.10 Simulated ^{1}H NMR Spectra of a 2-Spin System as the Ratio $\Delta\nu/J$ is Systematically Decreased from 10.0 to 0.0

c. Within a spin system, some pairs of nuclei or groups of nuclei may be strongly coupled and others weakly coupled. It is possible for a spin-system to be *partially strongly coupled.*

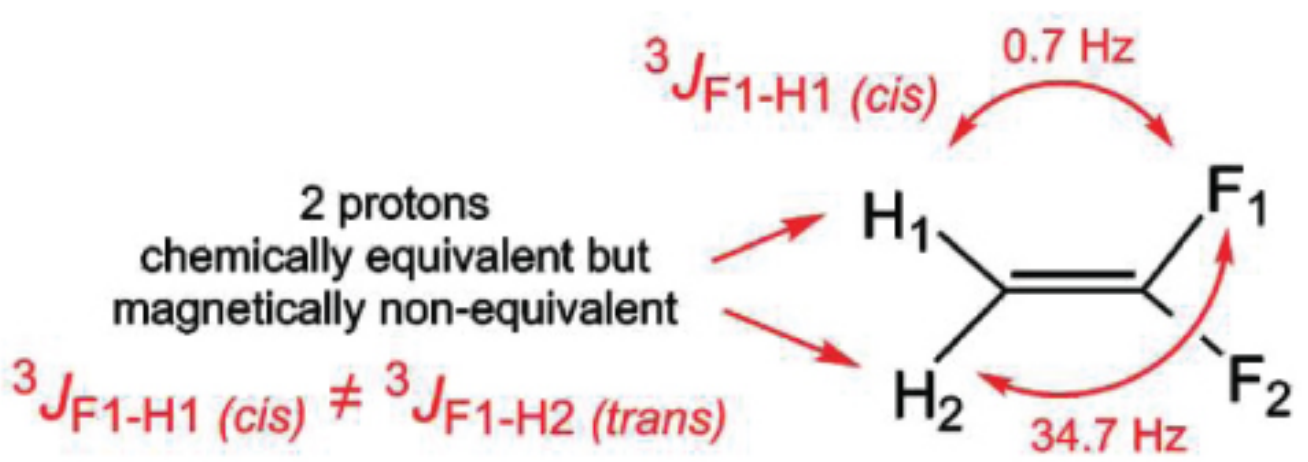
5.5.3 MAGNETIC EQUIVALENCE

A group of nuclei are ***chemically equivalent*** when they have identical chemical shifts. A group of nuclei are ***magnetically equivalent*** when they have the same chemical shift but they also have identical spin–spin coupling to each individual nucleus **outside** the group.

In bromoethane, all three protons in the $-CH_3$ group are chemically equivalent. Similarly, the two protons of the $-CH_2-$ group in bromoethane are chemically equivalent. The $-CH_3$ protons are also magnetically equivalent because from the perspective of the $-CH_2-$group all three of the $-CH_3$ protons have the same coupling so a proton in the $-CH_2-$ group cannot distinguish between the three protons in the $-CH_3$ group. The $-CH_2-$ protons are chemically and magnetically equivalent. The $-CH_3$ protons are also chemically and magnetically equivalent.



In 1,1-difluoroethylene, the two protons are chemically equivalent. Similarly, the two fluorines are chemically equivalent. However, from the perspective of F_1, the two protons appear to be quite different. H_1 is coupled to F_1 with a coupling of 0.7 Hz whereas H_2 is coupled to F_1 with a coupling of 34.7 Hz. F_1 can clearly distinguish H_1 and H_2. So while H_1 and H_2 in 1,1-difluoroethylene have the same chemical shift (chemically equivalent), they are magnetically non-equivalent.



When a spin system contains nuclei that are chemically equivalent but magnetically non-equivalent, the spectrum will be complex and the spectrum no longer follows first order rules – none of the multiplets will appear as doublets, triplets, quartets, *etc.* The spin–spin coupling constants cannot be extracted by simple measurement of splittings in the spectrum. Spectra containing nuclei that are chemically equivalent but magnetically non-equivalent can be analysed but this typically requires computer simulation of the spectrum and iteratively fitting the computed spectrum to the experimental spectrum to extract the coupling constants in the spin system.

5.5.4 CONVENTIONS FOR NAMING SPIN SYSTEMS

Consecutive letters of the alphabet (*e.g.* A, B, C, D, ...) are used to describe groups of protons which are strongly coupled, *i.e.* their chemical shifts are relatively close together. Subscripts are used to give the number of protons that are magnetically equivalent. Primes are used to denote protons that are chemically equivalent but not magnetically equivalent. A break in the alphabet indicates weakly coupled groups, *i.e.* their chemical shifts are relatively far apart. For example:

ABC denotes a strongly coupled 3-spin system

AMX denotes a weakly coupled 3-spin system

ABX denotes a *partially* strongly coupled 3-spin system

A_3BMXY denotes a 7-spin system in which the three magnetically equivalent A nuclei are strongly coupled to the B nucleus, but weakly coupled to the M, X and Y nuclei. The nucleus X is strongly coupled to the nucleus Y but weakly coupled to all the other nuclei. The nucleus M is weakly coupled to all the other 6 nuclei.

AA′XX′ is a 4-spin system described by two chemical shift parameters (for the nuclei A and X) but where $J_{A,X} \neq J_{A,X'}$. A and A′ (as well as X and X′) are pairs of nuclei which are chemically equivalent but magnetically non-equivalent.

The process of deriving the NMR parameters (chemical shifts and coupling constants) from a set of multiplets in a spin system is known as *spectral analysis of the NMR spectrum*. In principle, **any** spectrum arising from a spin system, no matter how complicated, can be analysed but some will require calculations or simulations performed by a computer.

5.5.5 SPECTRAL ANALYSIS OF FIRST-ORDER NMR SPECTRA

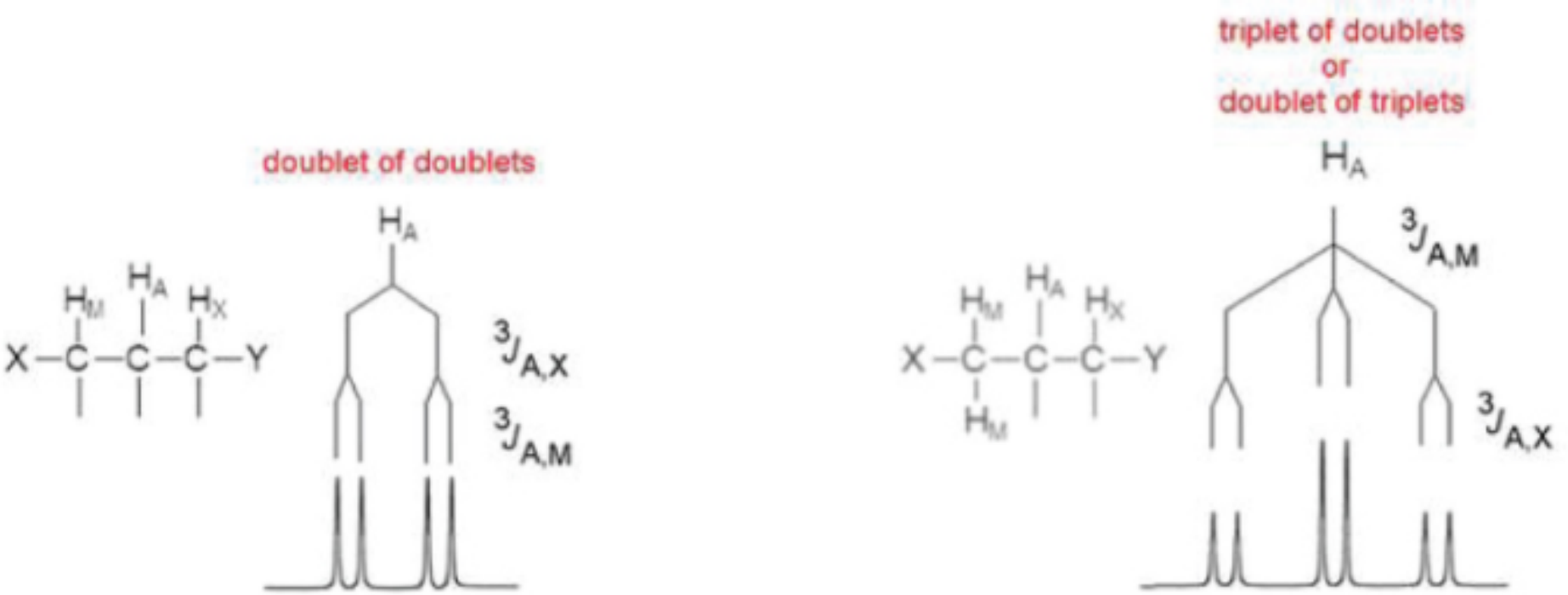
Rule 1 A group of ***n*** magnetically equivalent protons will split a resonance of an interacting group of protons into ***n*** + 1 lines. For example, the resonance due to the A protons in an A_nX_m system will be split into ***m*** + 1 lines, while the resonance due to the X protons will be split into ***n*** + 1 lines. More generally, splitting by ***n*** nuclei of spin quantum number I, results in $2n\mathbf{I}+1$ lines. This simply reduces to ***n*** + 1 for protons where **I** = ½.

Rule 2 The spacing (measured in Hz) of the lines in the multiplet is equal to the coupling constant.

Rule 3 The true chemical shift of each group of interacting protons lies in the centre of the (always symmetrical) multiplet.

Rule 4 The relative intensities of the lines within each multiplet will be in the ratio of the binomial coefficients (Table 5.11). Note that, in the case of higher multiplets, the outside components of multiplets are relatively weak and may be lost in the instrumental noise, *e.g.* a septet may appear as a quintet if the outer lines are not clearly visible.

Rule 5 When a group of magnetically equivalent protons interacts with more than one group of protons, its resonance will take the form of a *multiplet of multiplets*. For example, the resonance due to the A protons in a system $A_nM_pX_m$ will have the multiplicity of $(p+1)(m+1)$. The multiplet patterns are chained, *e.g.* a proton coupled to two different protons will be split to a doublet by coupling to the first proton then each of the component of the doublet will be split further by coupling to the second proton resulting in a symmetrical multiplet with four lines (a doublet of doublets). A proton coupled to two equivalent protons as well as a different proton will be split into a triplet by coupling to the two equivalent protons then each of the component of the triplet will be split further by coupling to the third proton resulting in a symmetrical multiplet with six lines (a doublet of triplets).



The appropriate coupling constants will control splitting and relative intensities will obey rule 4.

Rule 6 Protons that are magnetically equivalent do not split each other. Any system A_n will give rise to a singlet.

Rule 7 Spin systems that contain groups of chemically equivalent protons that are not magnetically equivalent **cannot be analysed by first-order methods** and these spin systems can only be analysed by computer simulation.

Rule 8 If $\Delta\nu_{A,B}/J_{A,B}$ is less than ~3, for **any** pair of nuclei A and B in the spin system, the spectra become distorted from the expected ideal multiplet patterns. Such spectra **cannot be analysed by first-order methods** and these spin systems can only be analysed by computer simulation.

5.5.6 SPLITTING DIAGRAMS

The knowledge of the rules listed above permits the development of a simple procedure for the analysis of any spectrum that is suspected of being first-order. The first step consists of drawing a *splitting diagram*, from which the line spacings can be measured and splittings can be identified (Figure 5.11).

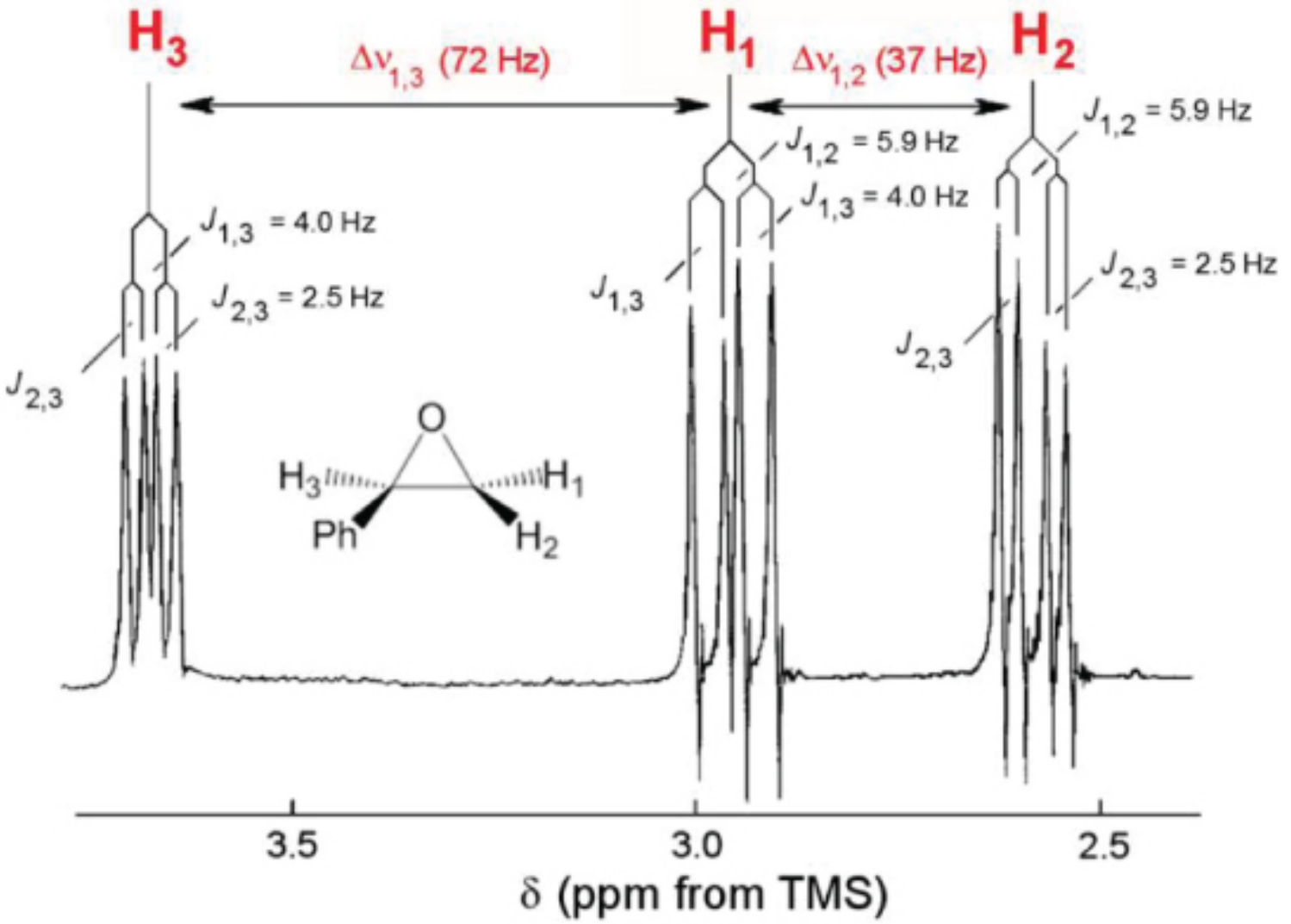


Figure 5.11 A Portion of the ^{1}H NMR Spectrum of Styrene Epoxide (100 MHz as a 5% solution in CCl_4)

The section of the spectrum of styrene epoxide (Figure 5.11) clearly contains the signals from three separate protons (identified as H_1, H_2 and H_3) with H_1 at δ 2.95, H_2 at δ 2.58 and H_3 at δ 3.67 ppm. Each signal appears as a doublet of doublets and the chemical shift of each proton is simply obtained by locating the centre of each multiplet. The pair of nuclei giving rise to each splitting is clearly indicated by the splitting diagram above each multiplet with $^2J_{H1-H2} = 5.9$ Hz, $^3J_{H1-H3} = 4.0$ Hz and $^3J_{H2-H3} = 2.5$ Hz.

The validity of a first-order analysis can be verified by calculating the ratio $\Delta\nu/J$ for each pair of nuclei and establishing that it is greater than 3.

From Figure 5.11

$$\frac{\Delta\nu_{1,2}}{J_{1,2}} = \frac{37}{5.9} = 6.3 \qquad \frac{\Delta\nu_{1,3}}{J_{1,3}} = \frac{72}{4.0} = 18.0 \qquad \frac{\Delta\nu_{2,3}}{J_{2,3}} = \frac{109}{2.5} = 43.6$$

Each ratio is greater than 3 so a first order analysis is justified and the 100 MHz spectrum of the aliphatic protons of styrene epoxide is indeed a first order spectrum and could be labelled as an AMX spin system.

The 60 MHz ^{1}H spectrum of a 4-spin AMX_2 system is given in Figure 5.12. This system contains three separate proton signals (in the intensity ratios 1:1:2, identified as H_A, H_M and H_X). The multiplicity of H_A is a triplet of doublets, the multiplicity of H_M is a triplet of doublets and the multiplicity of H_X is a doublet of doublets. Again, the nuclei giving rise to each splitting are clearly indicated by the splitting diagram above each multiplet and the chemical shifts of each multiplet are simply obtained by measuring the centres of each multiplet.

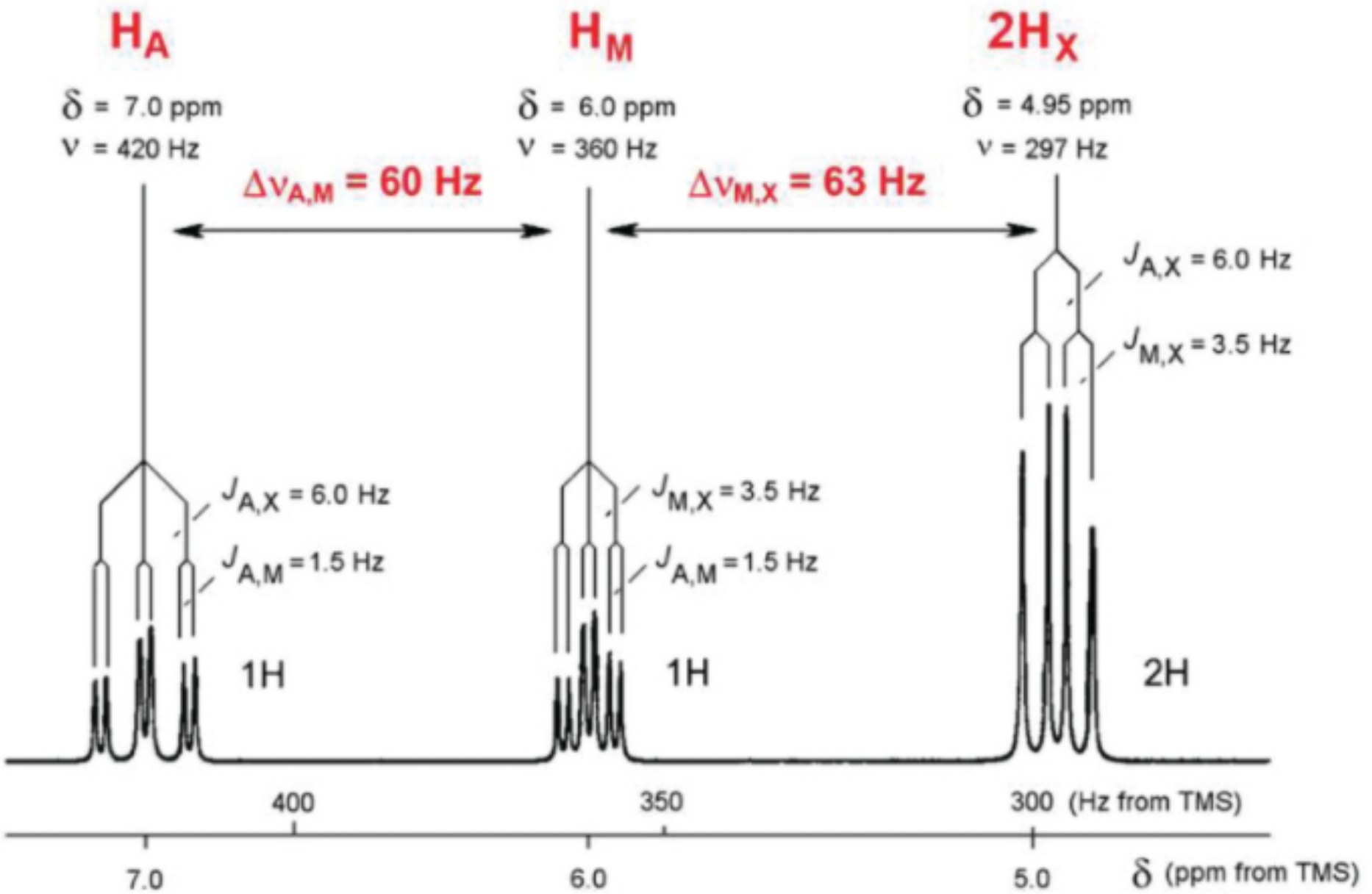
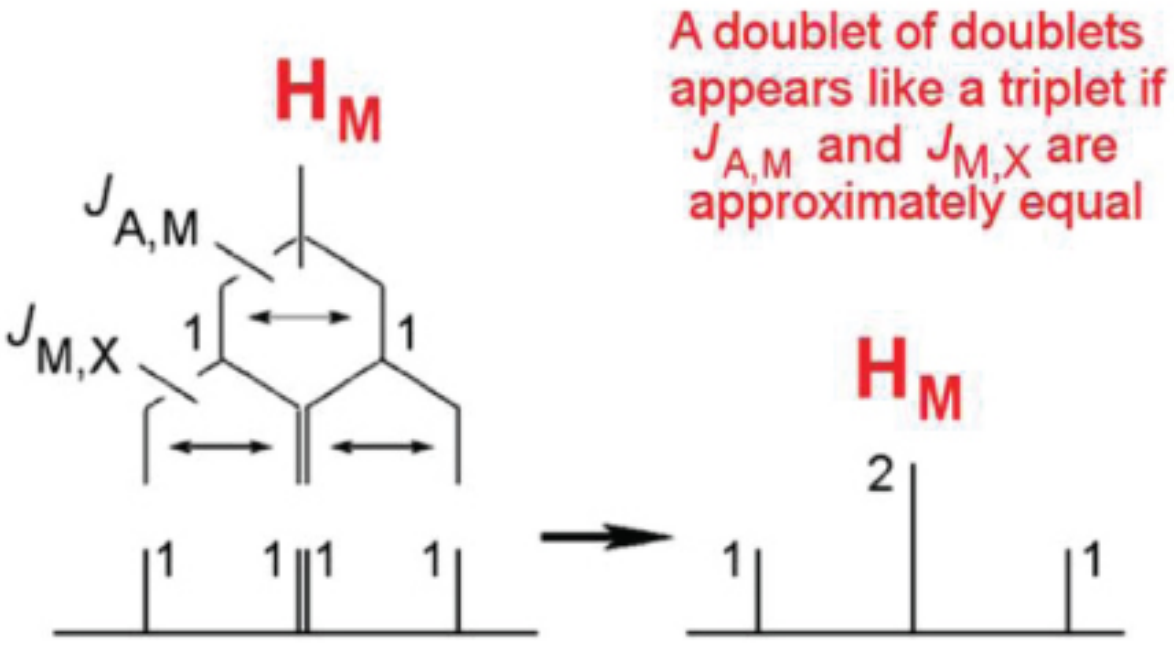


Figure 5.12 The 60 MHz ^{1}H NMR Spectrum of a 4-Spin AMX_2 Spin System

Coincidentally Equivalent Coupling Constants.

An AMX spin system. First-order analysis rules predict that the resonance for H_M in an AMX spin system will be a doublet of doublets (four lines) since H_M will be split by coupling to H_A and to H_X. All lines of the multiplet will have equal intensity and the spacings in the multiplet will be $J_{A,M}$ and $J_{M,X}$.

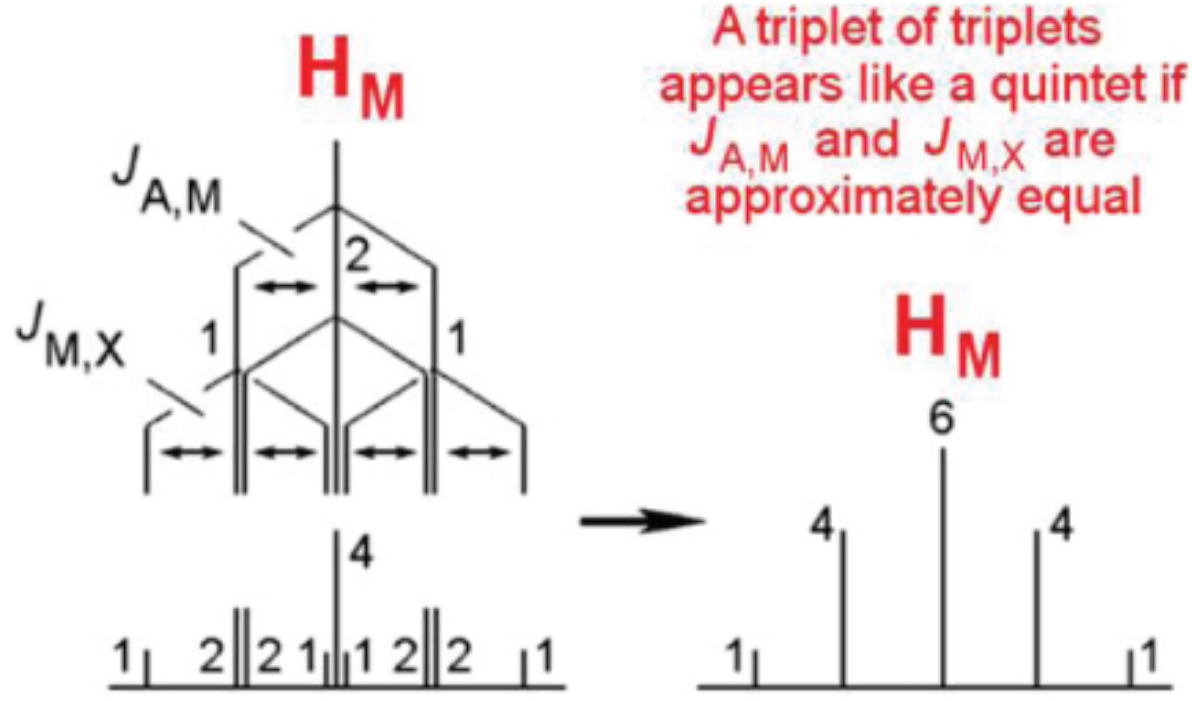
However, in the case where $J_{A,M}$ and $J_{M,X}$ are approximately equal, the central lines of the multiplet overlap to give what appears to be a single line whose intensity is twice as high as the outer lines. While the multiplet is technically a doublet of doublets, it appears as a triplet (three lines) with intensities in the ratio 1:2:1.



An $A_2M_2X_2$spin system. First-order analysis rules predict that the resonance for H_M in an $A_2M_2X_2$ spin system will be a triplet of triplets (9 lines) since H_M will be split by coupling to 2 × H_A nuclei and to 2 × H_X nuclei. The relative intensities of the lines in the multiplet can be predicted easily using Table 5.11. The spacings in the multiplet will be equal to $J_{A,M}$ and $J_{M,X}$.

However, in the case where $J_{A,M}$ and $J_{M,X}$ are approximately equal, there is overlap between the lines of the multiplet.

While the multiplet is technically a triplet of triplets, it appears as a quintet (five lines) with intensities in the ratio 1:4:6:4 1.



This is not an uncommon situation in flexible alkyl chains (X–CH_2–CH_2–CH_2–Y) since the three-bond vicinal coupling between protons on adjacent carbons typically falls within a narrow range of about 6–8 Hz.

5.5.7 SPIN DECOUPLING

In the signal of a proton that is a multiplet due to spin–spin coupling, it is possible to remove the splitting effects by irradiating the sample with an additional Rf source at the exact resonance frequency of the proton giving rise to the splitting. The additional radiofrequency causes rapid flipping of the irradiated nuclei and as a consequence nuclei coupled to them cannot sense them as being in either a spin-up or spin-down state for long enough to cause splitting. The irradiated nuclei are said to be **decoupled** from other nuclei in the spin system.

Decoupling simplifies the appearance of complex multiplets by removing some of the splittings. In addition, decoupling is a powerful tool for assigning spectra because a skilled spectroscopist can use a series of decoupling experiments to sequentially identify which nuclei are coupled.

Figure 5.13 (a) shows the ^{1}H NMR spectrum of bromoethane. The spectrum shows the characteristic quartet (for the $-CH_2-$ group at C_1 and this is coupled to the $-CH_3$ group) and a triplet (for the $-CH_3$ group at C_2 and this is coupled to the $-CH_2-$ group). The spectrum in Figure 5.13 (b) shows the result after irradiation at the $-CH_2-$, which causes the multiplet structure of the triplet for H_2 to collapse to a singlet. Figure 5.13 (c) shows the effect of irradiation at the frequency of the $-CH_3$ group where the multiplet structure of the quartet for H_1 collapses to a singlet.

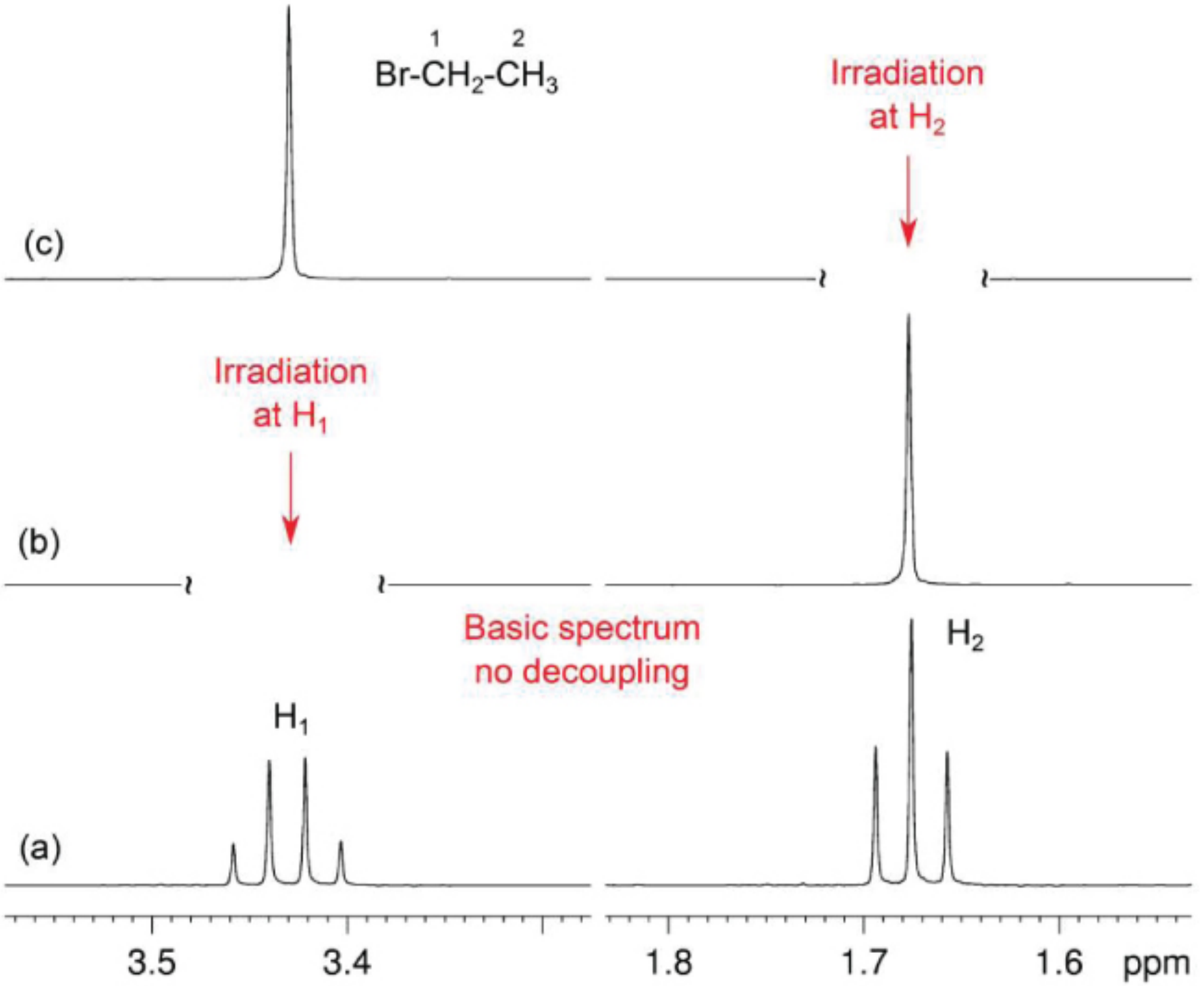


Figure 5.13 Selective Decoupling in the ^{1}H NMR Spectrum of Bromoethane

In a 4-spin AM_2X spin system, the signal for proton H_A would appear as a doublet of triplets (with the triplet splitting due to coupling to the 2 M protons and the doublet splitting due to coupling to the X proton). Irradiation at the frequency of H_X reduces the multiplicity of the A signal to a triplet (with the remaining splitting due to $J_{A,M}$) and irradiation at the frequency of H_M reduces the multiplicity of the A signal to a doublet (with the remaining splitting due to $J_{A,X}$) (Figure 5.14).

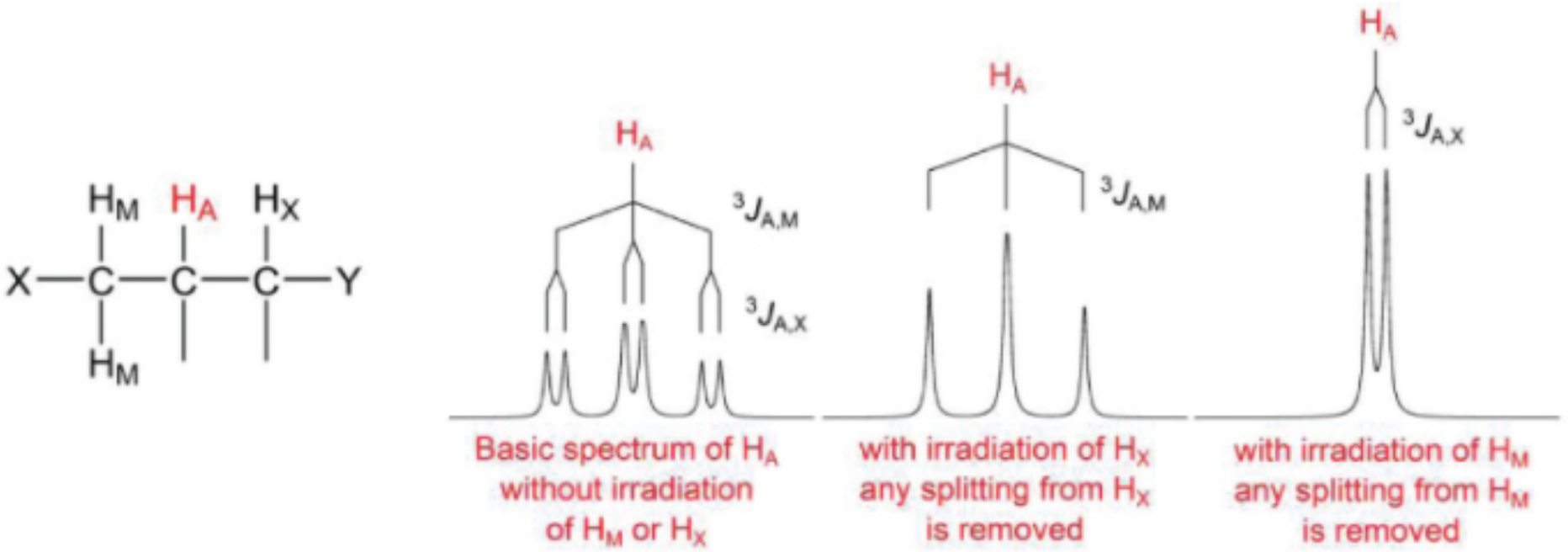


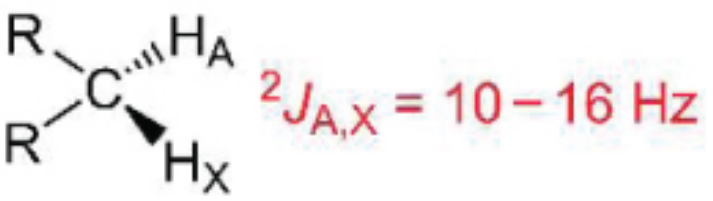
Figure 5.14 Selective Decoupling in a Simple 4-Spin System

5.6 CORRELATION OF 1H–1H COUPLING WITH STRUCTURE

Interproton spin–spin coupling constants are of real value in obtaining structural data about a molecule, in particular information about the connectivity of structural elements and the relative disposition of various protons.

5.6.1 NON-AROMATIC SPIN SYSTEMS

In saturated systems, the magnitude of the *geminal* coupling constant $^{2}J_{\text{H-C-H}}$ (two protons attached to the same carbon atom) is typically between 10 and 16 Hz but values between 0 and 22 Hz have been recorded in some unusual structures.



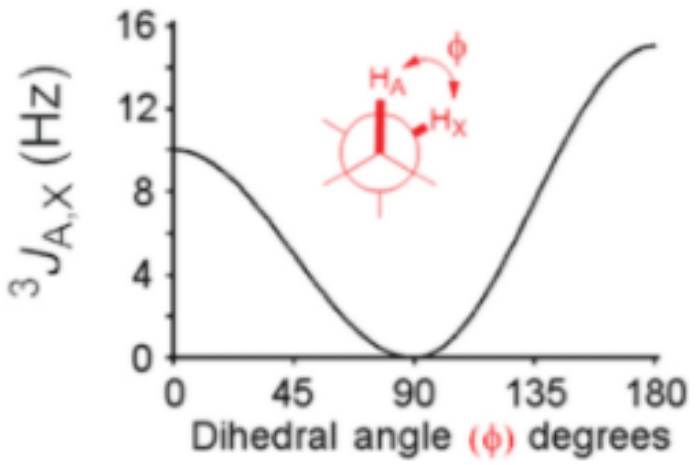
The *vicinal* coupling (protons on adjacent carbon atoms) $^{3}J_{\text{H-C-C-H}}$ have values 0–16 Hz depending mainly on the dihedral angle ϕ.

The **Karplus relationship** expresses, **approximately**, the angular dependence of the vicinal coupling constant as:

$$^{3}J_{\text{H-C-C-H}} = 10\cos^{2}\phi \quad \text{for } 0 < \phi < 90°$$

and

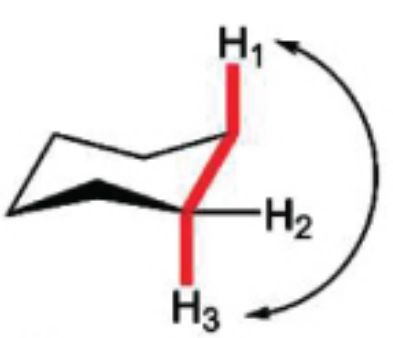
$$^{3}J_{\text{H-C-C-H}} = 15\cos^{2}\phi \quad \text{for } 90 < \phi < 180°$$



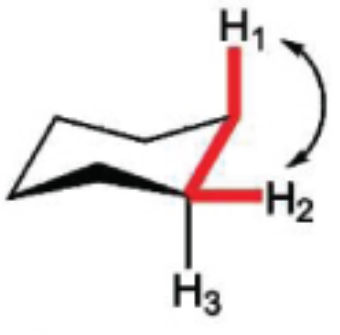
It follows from these equations that if the dihedral angle ϕ between two vicinal protons is near 90° then the coupling constant will be very small and, conversely, if the dihedral angle ϕ between two vicinal protons is near 0° or 180° then the coupling constant will be relatively large. The Karplus relationship is particularly valuable in

determining the stereochemistry of organic molecules but must be treated with some caution because vicinal coupling constants also depend markedly on the nature of substituents. In systems that assume an average conformation, such as a flexible hydrocarbon chain, $^3J_{H-H}$ generally lies between 6 and 8 Hz.

In conformationally rigid systems, such as substituted cyclohexanes, there can be pronounced differences in $^3J_{H-H}$. The axial–axial coupling ($^3J_{H1-H3}$) between vicinal protons in cyclohexanes, where the dihedral angle is near 180°, is typically large (about 13 Hz). The axial–equatorial and equatorial–equatorial couplings where the dihedral angles are typically closer to 60°, are much smaller, typically in the range of 3–6 Hz.

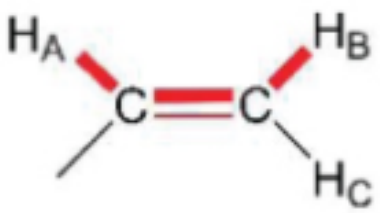


$^3J_{1,3}$ = 13 Hz

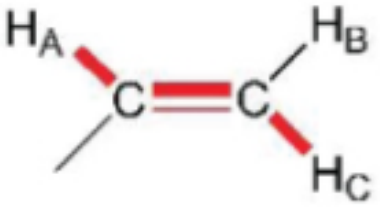


$^3J_{1,2}$ = 3 Hz

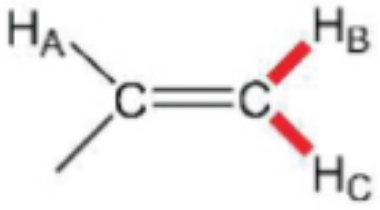
The coupling constants in unsaturated (olefinic) systems depend on the nature of the substituents attached to the C=C but for the vast majority of substituents, the ranges for $^3J_{H-C=C-H\,(cis)}$ and $^3J_{H-C=C-H\,(trans)}$ do not overlap. This means that the stereochemistry of a double bond can be determined by measuring the coupling constant between vinylic protons. Where the C=C bond is in a ring, the $^3J_{H-C=C-H}$ coupling reflects the ring size.



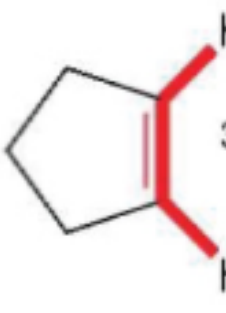
$^3J_{A,B\,(cis)}$ = 6 – 11 Hz



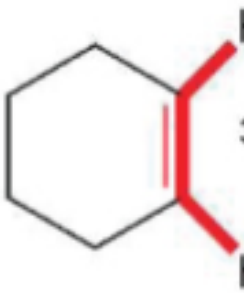
$^3J_{A,C\,(trans)}$ = 12 – 19 Hz



$^2J_{B,C\,(gem)}$ = 0 – 3 Hz



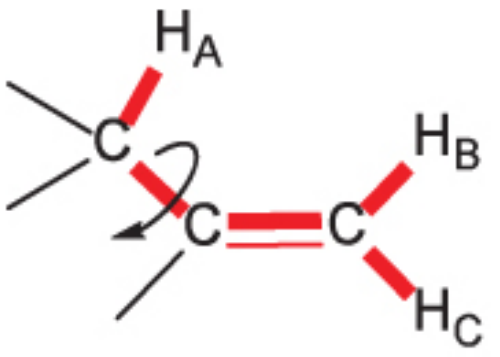
$^3J_{A,B\,(cis)}$ = 5 – 7 Hz



$^3J_{A,B\,(cis)}$ = 9 – 11 Hz

In alkyl-substituted alkenes, the long-range allylic couplings, ($^4J_{A,B}$ and $^4J_{A,C}$) are typically in the range 0–3 Hz.

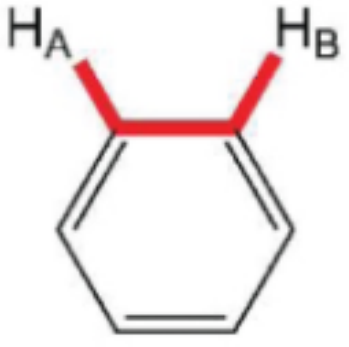
In systems that are stereochemically constrained, the magnitude of the coupling is a function of the dihedral angle between the C–H_A bond and the plane of the double bond in a relationship reminiscent of the Karplus relation.



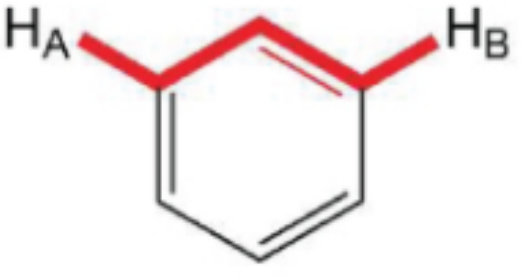
$^4J_{A,B}$; $^4J_{A,C}$ = 0–3 Hz

5.6.2 AROMATIC SPIN SYSTEMS

The coupling constant between protons attached to an aromatic ring is diagnostic of the relative position of the coupled protons, *i.e.* whether they are *ortho*, *meta* or *para*.



$^3J_{A,B\ (ortho)}$ = 6 – 10 Hz

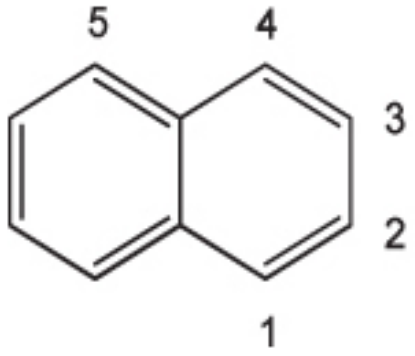
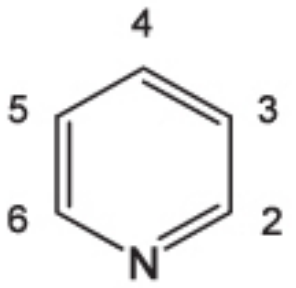
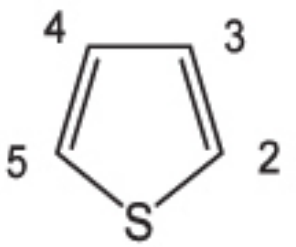
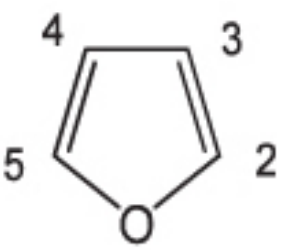
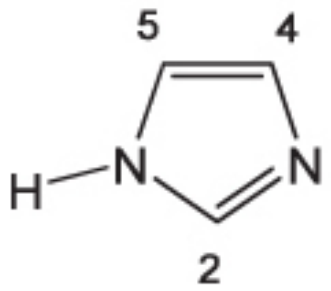
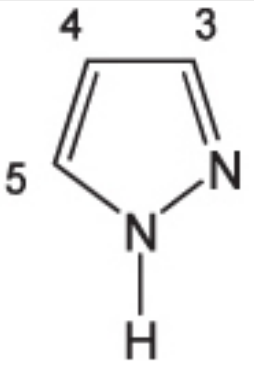
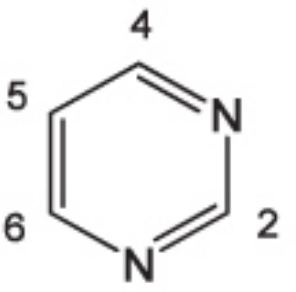
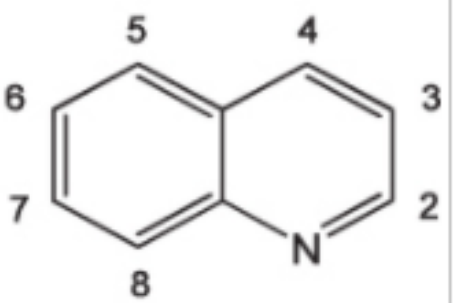


$^4J_{A,B\ (meta)}$ = 1 – 3 Hz

$^5J_{A,B\ (para)}$ = 0 – 1.5 Hz

Similarly in condensed polynuclear aromatic compounds and heterocyclic compounds, the magnitude of the coupling constants between protons in the aromatic rings reflects the relative position of the coupled protons (Table 5.12).

Table 5.12 Proton–Proton Coupling Constants in Aromatic and Heteroaromatic Rings

			
$^{3}J_{1,2}$ = 8.3–9.1 Hz	$^{3}J_{2,3}$ = 4.0–5.7 Hz	$^{3}J_{2,3}$ = 4.7 Hz	$^{3}J_{2,3}$ = 1.8 Hz
$^{3}J_{2,3}$ = 6.1–6.9 Hz	$^{3}J_{3,4}$ = 6.8–9.1 Hz	$^{3}J_{3,4}$ = 3.4 Hz	$^{3}J_{3,4}$ = 3.5 Hz
$^{4}J_{1,3}$ = 1.2–1.6 Hz	$^{4}J_{2,4}$ = 0.0–2.5 Hz	$^{4}J_{2,4}$ = 1.0 Hz	$^{4}J_{2,4}$ = 0.8 Hz
$^{5}J_{1,4}$ = 0–1.0 Hz	$^{4}J_{3,5}$ = 0.5–1.8 Hz	$^{4}J_{2,5}$ = 2.9 Hz	$^{4}J_{2,5}$ = 1.6 Hz
$^{5}J_{1,5}$ = 0–1.5 Hz	$^{4}J_{2,6}$ = 0.0–0.6 Hz		
	$^{5}J_{2,5}$ = 0.0–2.3 Hz		
			
$^{4}J_{2,4}$; $^{4}J_{2,5}$ = 1.0 Hz	$^{3}J_{3,4}$; $^{3}J_{4,5}$ = 2.1 Hz	$^{4}J_{2,4}$; $^{4}J_{2,6}$ = 0 Hz	$^{3}J_{2,3}$ = 4.3 Hz
		$^{5}J_{2,5}$ = 1.5 Hz	$^{4}J_{2,4}$ = 1.8 Hz
		$^{3}J_{4,5}$; $^{3}J_{5,6}$ = 5.0 Hz	$^{3}J_{3,4}$ = 8.3 Hz
			$^{5}J_{4,8}$ = 0.9 Hz
			$^{3}J_{5,6}$ = 8.2 Hz
			$^{4}J_{5,7}$ = 1.6 Hz
			$^{5}J_{5,8}$ = 0.3 Hz
			$^{3}J_{6,7}$ = 6.8 Hz
			$^{4}J_{6,8}$ = 1.1 Hz
			$^{3}J_{7,8}$ = 8.3 Hz

The splitting patterns of the protons in the aromatic region of the ^{1}H spectrum are frequently used to establish the substitution pattern of an aromatic ring. For example, a trisubstituted aromatic ring has three remaining protons and they can have relative positions 1,2,3-; 1,2,4-; or 1,3,5- and each substitution pattern has a characteristic arrangement of signals in the aromatic region of the spectrum (Figure 5.15).

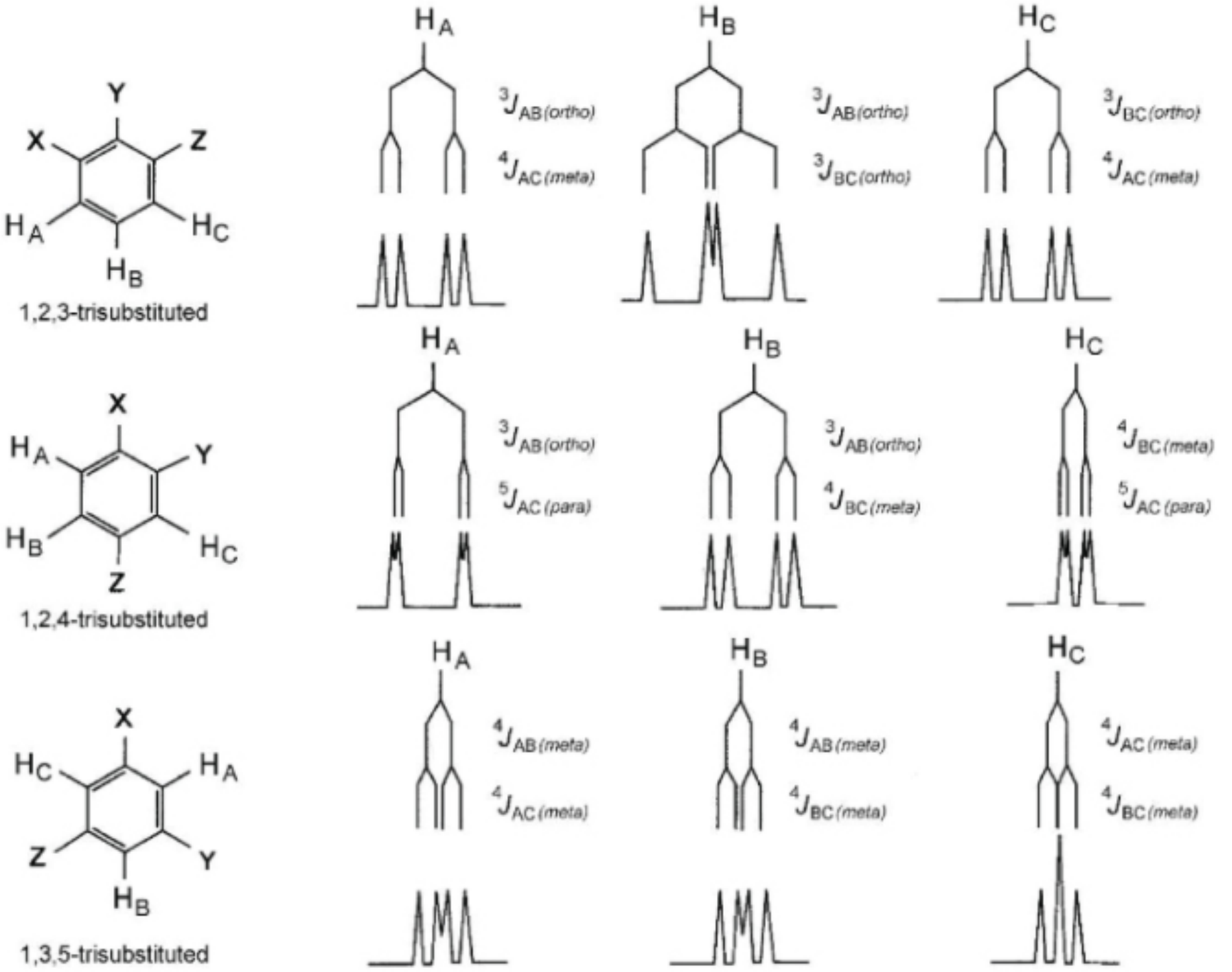


Figure 5.15 Characteristic Aromatic Splitting Patterns in the ^1H NMR Spectra for some Tri-substituted Benzenes

Likewise the 1,2-disubstituted and 1,3-disubstituted benzenes also have a characteristic four-proton splitting pattern (Figure 5.16).

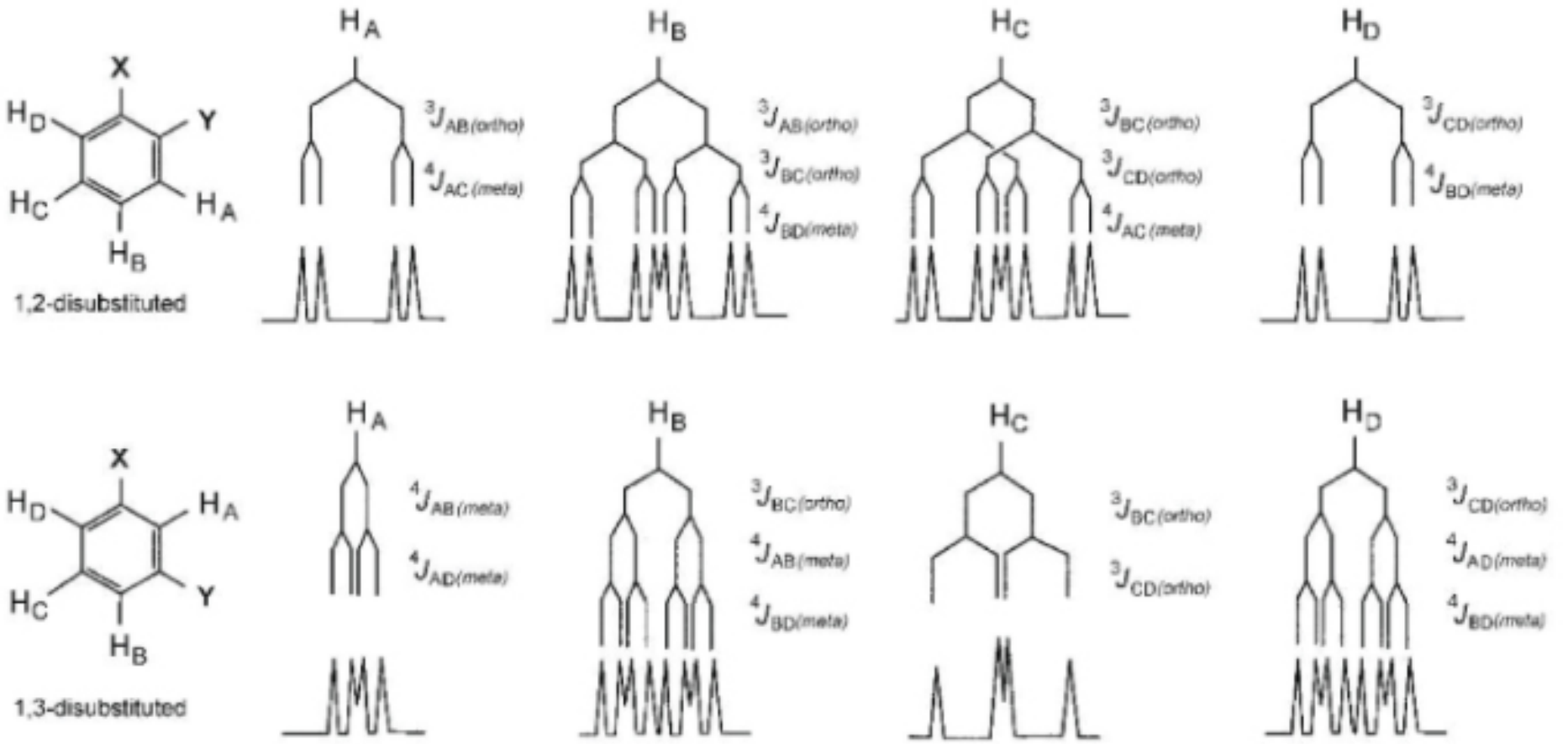


Figure 5.16 Characteristic Aromatic Splitting Patterns in the ^{1}H NMR Spectra for some Di-substituted Benzenes (ignoring the small *para* couplings)

para-Disubstituted Benzenes

para-Disubstituted benzenes have characteristically "simple" and symmetrical ^{1}H NMR spectra in the aromatic region. Superficially, the spectra of *p*-disubstituted benzenes always appear as two strong doublets with the line positions symmetrically disposed about a central frequency. The spectra are in fact far more complex (many lines make up the pattern for the NMR spectrum when it is analysed in detail) but the symmetry of the pattern of lines makes 1,4-disubstituted benzenes very easy to recognise from their ^{1}H NMR spectra. The ^{1}H NMR spectrum of *p*-nitrophenylacetylene is given in Figure 5.17. The expanded section shows the two strong prominent signals in the aromatic region, characteristic of 1,4-substitution on a benzene ring.

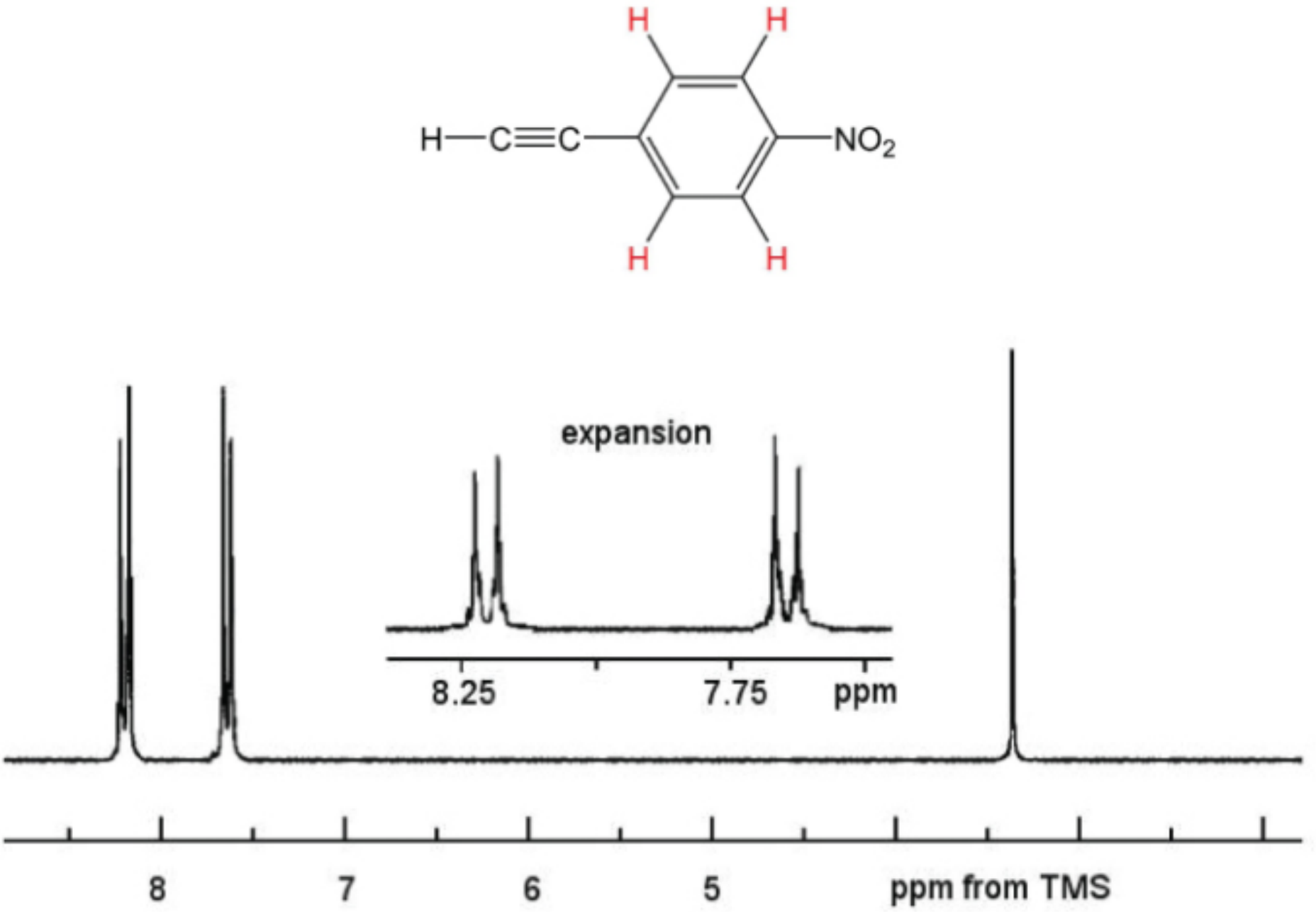


Figure 5.17 ^{1}H NMR Spectrum of *p*-Nitrophenylacetylene (200 MHz as a 10% solution in $CDCl_3$)

5.7 THE NUCLEAR OVERHAUSER EFFECT (NOE) IN 1H NMR SPECTROSCOPY

Irradiation of one nucleus while observing the resonance of another may result in a change in the **amplitude** of the observed resonance *i.e.* an enhancement of the signal intensity. This is known as the *nuclear Overhauser effect* (NOE). The NOE is a "through space" effect and its magnitude is inversely proportional to the sixth power of the distance between the interacting nuclei. Because of the distance dependence of the NOE, it is an important method for establishing which groups are close together in space and, because the NOE can be measured quite accurately, it is a very powerful means for determining the three dimensional structure (and stereochemistry) of organic compounds.

Figure 5.18(i) shows the aromatic region of the ^{1}H NMR spectrum of 2,4-dinitrotoluene. Figure 5.18(ii) shows the same spectrum but with irradiation of the $-CH_3$ groups at about δ 2.7 ppm. There is an enhancement in the intensity of H_6 (by about 10%). The enhancements are often quite small and they are best visualised by difference spectroscopy. Figure 5.18(iii) is the difference spectrum with spectrum (ii) minus spectrum (i) and the enhancement of H_6 is clear. In this experiment, irradiation of the $-CH_3$ group enhances the resonance of H_6, which is the closest proton in space to the $-CH_3$ group. Note that the effect drops off dramatically with distance and H_3 and H_5 show negligible enhancement.

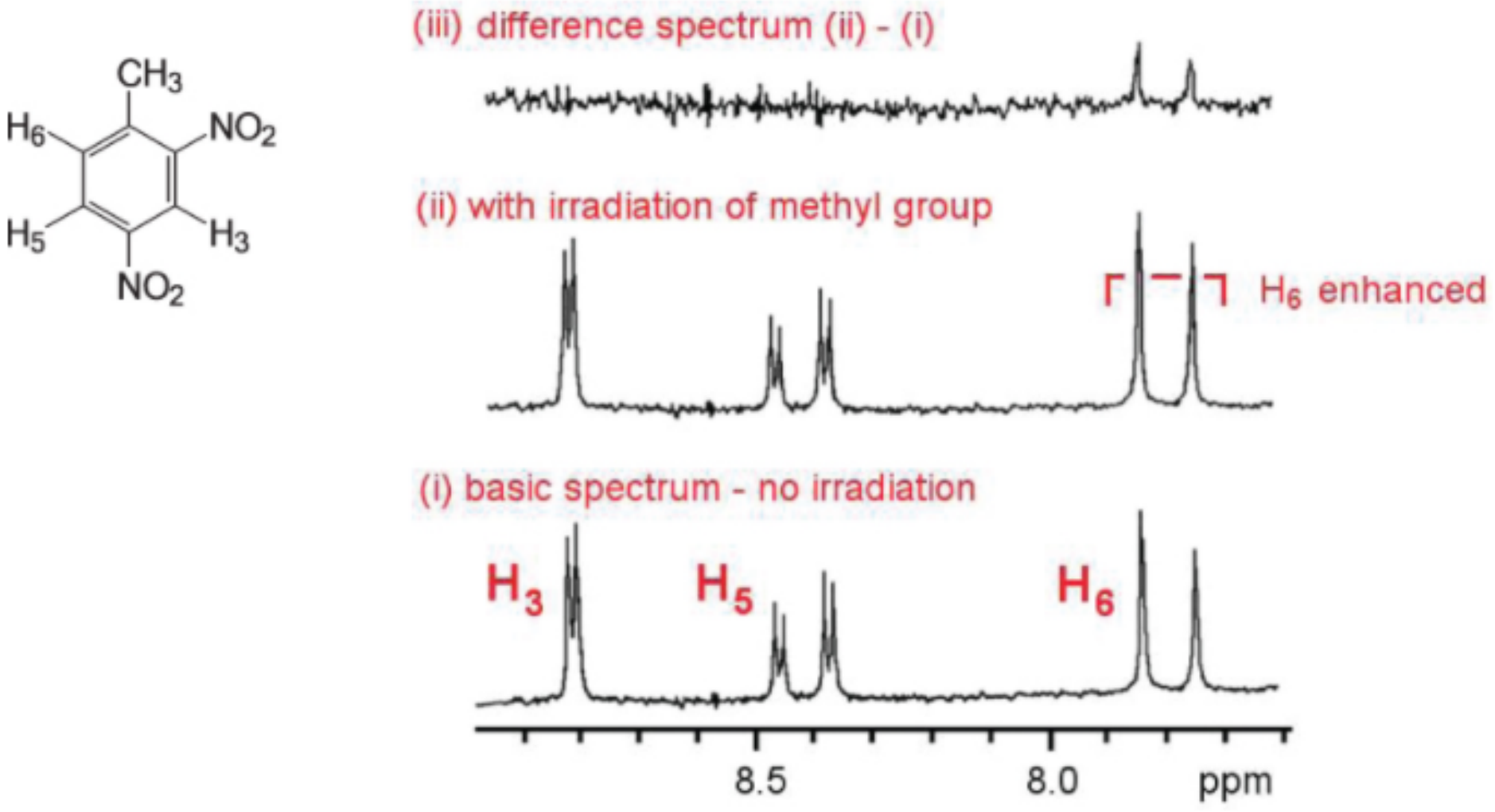


Figure 5.18 Aromatic Region of the ^1H NMR Spectrum of 2,4-Dinitrotoluene. (i) Basic NMR Spectrum; (ii) NMR Spectrum with Irradiation of the $-CH_3$ Group at δ 2.7; (iii) Difference Spectrum: Spectrum (ii) minus Spectrum (i).

5.8 LABILE AND EXCHANGEABLE PROTONS

Protons in groups such as alcohols (R–OH) amines (R–NH–), carboxylic acids (R–COOH), thiols (R–SH) and to a lesser extent amides (R–CO–NH–) are classified as labile or readily exchangeable protons.

Labile protons frequently give rise to broadened resonances in the ^1H NMR spectrum and their chemical shifts are critically dependent on the solvent, concentration, and on temperature. *They do not have reliable characteristic chemical shift ranges.*

Labile protons exchange rapidly with each other and also with protons in water or with the deuterons in D_2O.

Labile protons can always be positively identified by *in situ* exchange with D_2O. In practice, a normal ^1H NMR spectrum is recorded then deuterium exchange of labile protons is achieved by simply adding a drop of deuterated water (D_2O) to the NMR sample. Labile protons in –OH, –COOH, $-NH_2$ and –SH groups exchange rapidly for deuterons in D_2O and the ^1H NMR is recorded again. Since deuterium is invisible in the ^1H NMR spectrum, labile protons disappear from the ^1H NMR spectrum and can be readily identified by comparison of the spectra before and after addition of D_2O.

In Figure 5.19, the spectrum of 1-propanol shows the expected four signals. On addition of 1 drop of D_2O, one of the signals disappears from the spectrum, clearly identifying this as the –OH proton.

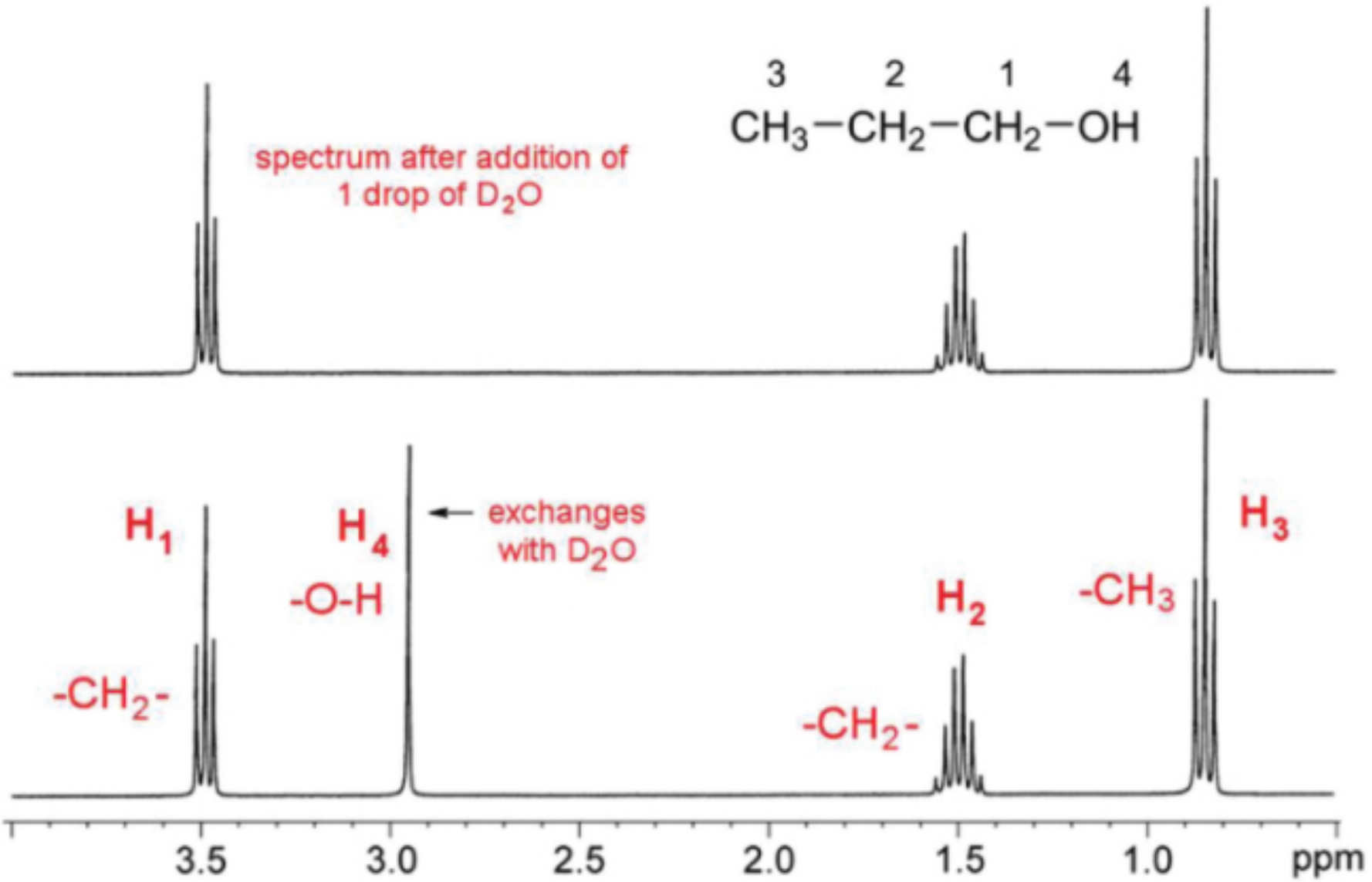


Figure 5.19 D_2O Exchange in the ^1H NMR Spectrum of 1-Propanol (300 MHz, $CDCl_3$ solution)

The N–H protons of primary and secondary amides are slow to exchange and usually require heating or base catalysis; this is one way an amide functional group can be distinguished from other functional groups.

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6
^{13}C NMR SPECTROSCOPY

The most abundant isotope of carbon (^{12}C) cannot be observed by NMR. ^{13}C is a rare nucleus (1.1% natural abundance) and its low concentration, coupled with the fact that ^{13}C has a relatively low resonance frequency, leads to its relative insensitivity as an NMR-active nucleus (about 1/6000 as sensitive as ^{1}H). However, with pulsed FT NMR spectrometers, it is now common to acquire many spectra and add them together (Section 5.2.1), so ^{13}C NMR spectra of good quality can be obtained readily.

6.1 COUPLING AND DECOUPLING IN ^{13}C NMR SPECTRA

Because the ^{13}C nucleus is isotopically rare, it is extremely unlikely that any two adjacent carbon atoms in a molecule will *both* be ^{13}C. As a consequence, **^{13}C–^{13}C coupling is not observed** in ^{13}C NMR spectra, *i.e.* there is no signal multiplicity or splitting in a ^{13}C NMR spectrum due to ^{13}C–^{13}C coupling. ^{13}C couples strongly to any protons that may be attached ($^{1}J_{C-H}$ is typically about 125 Hz for saturated carbon atoms in organic molecules). It is the usual practice to irradiate the ^{1}H nuclei during ^{13}C acquisition so that all ^{1}H spins are fully decoupled from the ^{13}C nuclei (usually termed **broadband decoupling** or **noise decoupling**). **^{13}C NMR spectra usually appear as a series of singlets** (when ^{1}H is fully decoupled) and *each distinct ^{13}C environment in the molecule gives rise to a separate signal.*

If ^{1}H is **not decoupled** from the ^{13}C nuclei during acquisition, the signals in the ^{13}C spectrum appear as multiplets where the major splittings are due to the $^{1}J_{C-H}$ couplings (about 125 Hz for sp^3 hybridised carbon atoms, about 160 Hz for sp^2 hybridised carbon atoms, about 250 Hz for sp hybridised carbon atoms). CH_3– signals appear as quartets, –CH_2– signals appear as triplets, –CH– groups appear as doublets and quaternary C (no attached H) appear as singlets. The **multiplicity information**, taken together with chemical shift data, is useful in identifying and assigning the ^{13}C resonances.

In ^{13}C spectra acquired without proton decoupling, there is usually much more *"long-range"* coupling information visible in the fine structure of each multiplet. The fine structure arises from coupling between the carbon and protons that are not directly bonded to it (e.g. from $^{2}J_{C-C-H}$, $^{3}J_{C-C-C-H}$). The magnitude of long range C–H coupling is typically <10 Hz and this is much less than $^{1}J_{C-H}$. Sometimes a more detailed analysis of the long-range C–H couplings can be used to provide additional information about the structure of the molecule.

6.2 THE NUCLEAR OVERHAUSER EFFECT (NOE) IN 13C NMR SPECTROSCOPY

In most ^{13}C spectra, ^{13}C nuclei that have directly attached protons receive a significant (but not easily predictable) signal enhancement when the protons are irradiated as a result of the nuclear Overhauser effect (see Section 5.7). The intensity of ^{13}C resonances may be increased by up to 200% when ^{1}H nuclei that are directly bonded to the carbon atom are irradiated. The efficiency of the proton/carbon NOE varies from carbon-to-carbon and, as a consequence, peak intensity in ^{13}C NMR does not necessarily reflect the number of ^{13}C nuclei giving rise to the signal.

This effect is very important in increasing the intensity of ^{13}C spectra when they are proton decoupled. While the intensity of protonated carbon atoms can be increased significantly by NOE, non-protonated carbons

(quaternary carbon atoms) receive little NOE and non-protonated carbons are usually the weakest signals in a proton decoupled ^{13}C NMR spectrum.

It is not usually possible to integrate routine ^{13}C spectra directly unless specific precautions have been taken. However with proper controls, ^{13}C NMR spectroscopy can be used quantitatively and it is a valuable technique for the analysis of mixtures. To record ^{13}C NMR spectra where the relative signal intensity can be reliably determined, the spectra must be recorded with techniques to suppress the nuclear Overhauser effect and with a long delay between the acquisitions of successive spectra to ensure that all of the carbon atoms in the molecule are completely relaxed between spectral acquisitions.

6.3 DETERMINING 13C SIGNAL MULTIPLICITY USING DEPT

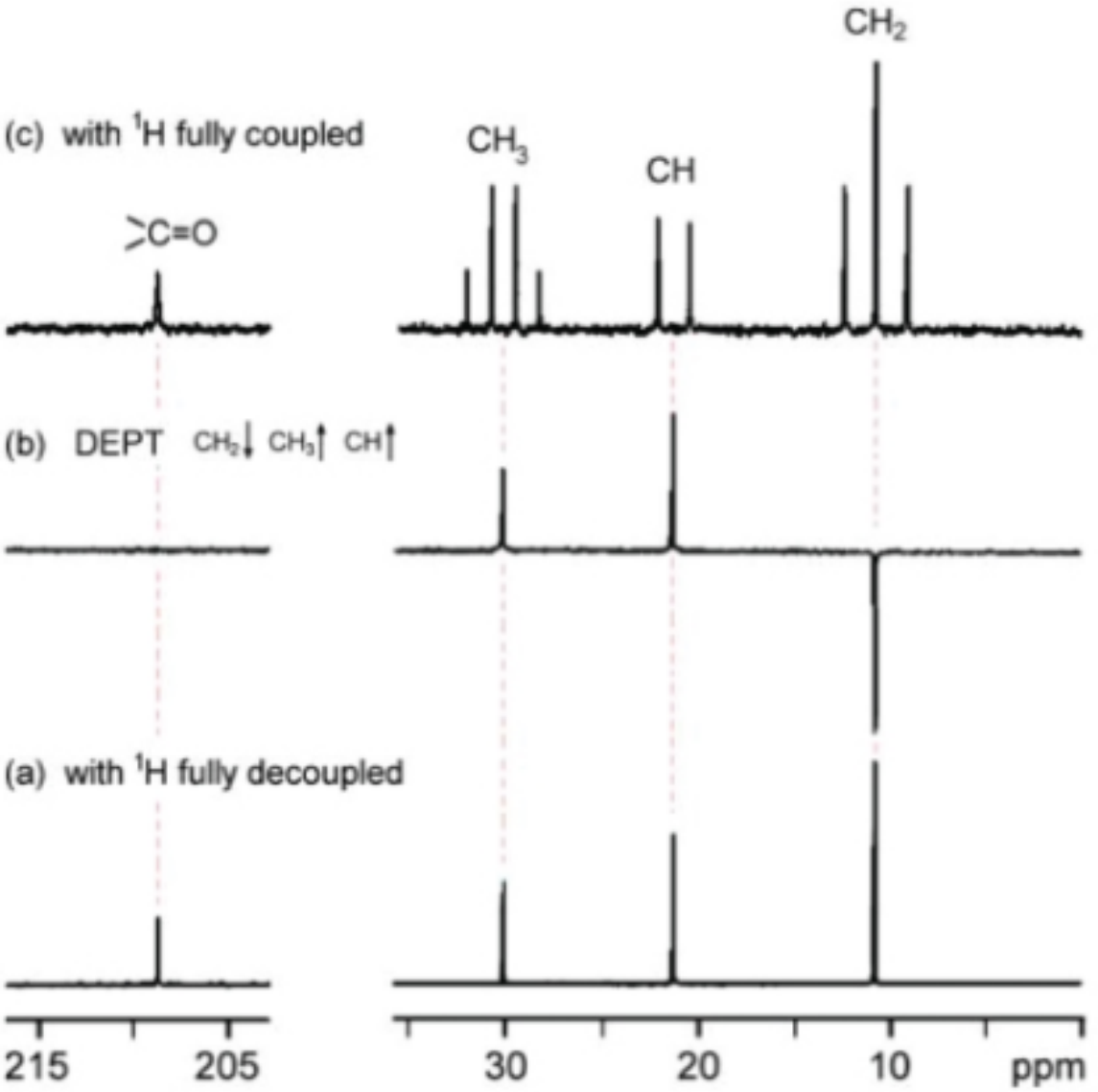
With most modern NMR instrumentation, the DEPT experiment (**D**istortionless **E**nhancement by **P**olarisation **T**ransfer) is the most commonly used method to determine the multiplicity of ^{13}C signals. The DEPT experiment is a pulsed NMR experiment that requires a series of programmed Rf pulses to both the ^{1}H and ^{13}C nuclei in a sample. The resulting ^{13}C DEPT spectrum contains only signals arising from protonated carbons (**non-protonated carbons do not give signals in the ^{13}C DEPT spectrum**). The signals arising from carbons in CH_3 and CH groups (*i.e.* those with an odd number of protons) appear oppositely phased from those in CH_2 groups (*i.e.* those with an even number of protons). Signals from CH_3 and CH groups point upwards and signals from CH_2 groups point downwards (Figure 6.1b).

In more advanced applications, the ^{13}C DEPT experiment can be used to separate the signals arising from carbons in CH_3, CH_2 and CH groups. This is termed spectral editing and can be used to produce separate ^{13}C sub-spectra of just the CH_3 carbons, just the CH_2 carbons or just the CH carbons.

Figure 6.1 shows various ^{13}C spectra of methyl cyclopropyl ketone. The ^{13}C spectrum acquired with full proton decoupling (Figure 6.1a) shows four singlet peaks, one for each of the four different carbon environments in the molecule.

The DEPT spectrum (Figure 6.1b) shows only the three resonances for the protonated carbons. The carbon atoms that have an odd number of attached hydrogens (CH and CH_3 groups) point upwards and those with an even number of attached hydrogen atoms (the signals of CH_2 groups) point downwards. Note that the carbonyl carbon does not appear in the DEPT spectrum since it has no attached protons.

In the carbon spectrum with no proton decoupling (Figure 6.1c), all of the protonated carbons appear as multiplets and the multiplet structure is due to coupling to the attached protons. The CH_3 (methyl) group appears as a quartet, the CH_2 (methylene) groups appear as a triplet and the CH (methine) group appears as a doublet while the carbonyl carbon (with no attached protons) is a singlet. In Figure 6.1c, the $^{1}J_{C-H}$ coupling constants could be measured directly from the spectrum.



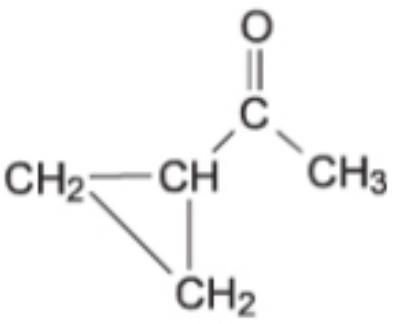
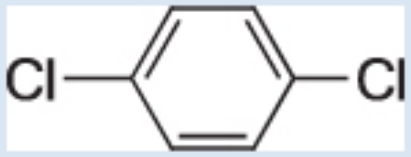
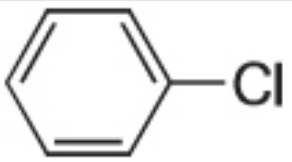
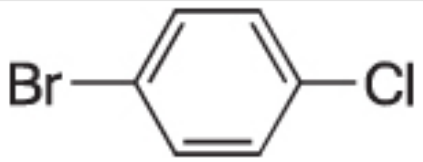
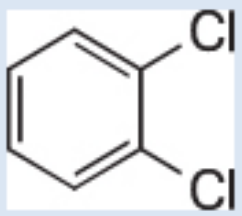
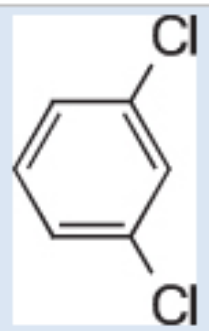
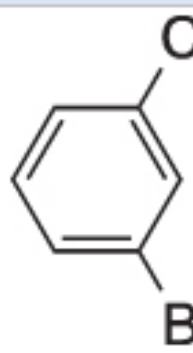
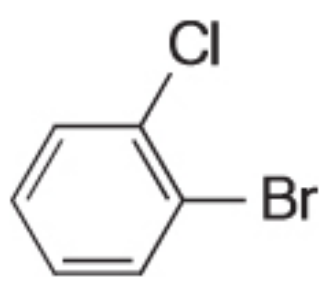


Figure 6.1 ^{13}C NMR Spectra of Methyl Cyclopropyl Ketone ($CDCl_3$ solvent, 100 MHz). *(a)* with Broadband Decoupling of ^{1}H ; *(b)* DEPT Spectrum *(c)* with no Decoupling of ^{1}H.

For the purpose of assigning a ^{13}C spectrum, two different types of ^{13}C spectra are usually obtained. Firstly, a spectrum with complete ^{1}H decoupling to maximise the intensity of signals and provide sharp singlets to minimise any signal overlap. This is the best spectrum to count the number of resonances and accurately determine their chemical shifts. Secondly, a spectrum which is sensitive to the number of protons attached to each C to permit partial sorting of the ^{13}C signals according to whether they are methyl, methylene, methine or quaternary carbon atoms. This could be a DEPT spectrum or a ^{13}C spectrum with no proton decoupling.

The number of resonances visible in a ^{13}C NMR spectrum immediately indicates **the number of distinct ^{13}C environments in the molecule** (Table 6.1). If the number of ^{13}C environments is less than the number of carbons in the molecule, then the molecule must have some symmetry that dictates that some ^{13}C nuclei are in identical environments. This is particularly useful in establishing the **substitution pattern** (position where substituents are attached) in aromatic compounds.

Table 6.1 The Number of Aromatic ^{13}C Resonances in Benzenes with Different Substitution Patterns

Molecule	Number of aromatic ^{13}C resonances	Molecule	Number of aromatic ^{13}C resonances
	1		2
	4		4
	3		6
	4		6

6.4 SHIELDING AND CHARACTERISTIC CHEMICAL SHIFTS IN 13C NMR SPECTRA

The general trends of ^{13}C chemical shifts somewhat parallel those in ^{1}H NMR spectra. However, ^{13}C nuclei have access to a greater variety of hybridisation states (bonding geometries and electron distributions) than ^{1}H nuclei and both hybridisation and changes in electron density have a significantly larger effect on ^{13}C nuclei than ^{1}H nuclei. As a consequence, the ^{13}C chemical shift scale spans some 250 ppm, *cf.* the 10 ppm range commonly encountered for ^{1}H chemical shifts (Tables 6.2–6.3).

Table 6.2 Typical ^{13}C Chemical Shift Values in Selected Organic Compounds

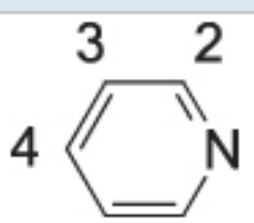
Compound	δ ^{13}C (ppm from TMS)
CH_4	−2.1
CH_3CH_3	7.3
CH_3OH	50.2
CH_3Cl	25.6
CH_2Cl_2	52.9
$CHCl_3$	77.3
$CH_3CH_2CH_2Cl$	11.5 (CH_3) 26.5 (−CH_2−) 46.7 (−CH_2−Cl)
$CH_2=CH_2$	123.3
$CH_2=C=CH_2$	208.5 (=C=) 73.9 (=CH_2)
CH_3CHO	31.2 (−CH_3) 200.5 (−CHO)
CH_3COOH	20.6 (−CH_3) 178.1 (−COOH)
CH_3COCH_3	30.7 (−CH_3) 206.7 (−CO−)
	128.5
	149.8 (C-2) 123.7 (C-3) 135.9 (C4)

Table 6.3 Typical ^{13}C Chemical Shift Ranges in Organic Compounds

Group	^{13}C shift (ppm)
TMS	0.0
$-CH_3$ (with only –H or –R at C_α and C_β)	0–30
$-CH_2$ (with only –H or –R at C_α and C_β)	20–45
–CH (with only –H or –R at C_α and C_β)	30–60
C quaternary (with only –H or –R at C_α and C_β)	30–50
$O-CH_3$	50–60
$N-CH_3$	15–45
C≡C	70–95
C=C	105–160
C (aromatic)	110–155
C (heteroaromatic)	105–165
–C≡N	115–125
C=O (acids, acyl halides, esters, amides)	155–185
C=O (aldehydes, ketones)	185–225

In ^{13}C NMR spectroscopy, the ^{13}C signal resulting from the carbon atom in $CDCl_3$ appears as a triplet centred at δ 77.0 with peak intensities in the ratio 1:1:1 (due to spin–spin coupling between ^{13}C and ^{2}H). This resonance serves as a convenient reference for the chemical shifts of ^{13}C NMR spectra recorded in this solvent.

Table 6.4 gives the typical chemical shift ranges for carbons in organic molecules. Table 6.5 lists characteristic ^{13}C chemical shifts for some sp^3-hybridised carbon atoms in common functional groups. Table 6.6 gives characteristic ^{13}C chemical shifts for some sp^2-hybridised carbon atoms in substituted alkenes and Table 6.7 gives characteristic ^{13}C chemical shifts for some *sp*-hybridised carbon atoms in alkynes.

Approximate ^{13}C Chemical Shift Ranges (δ) for Carbons in Organic Compounds

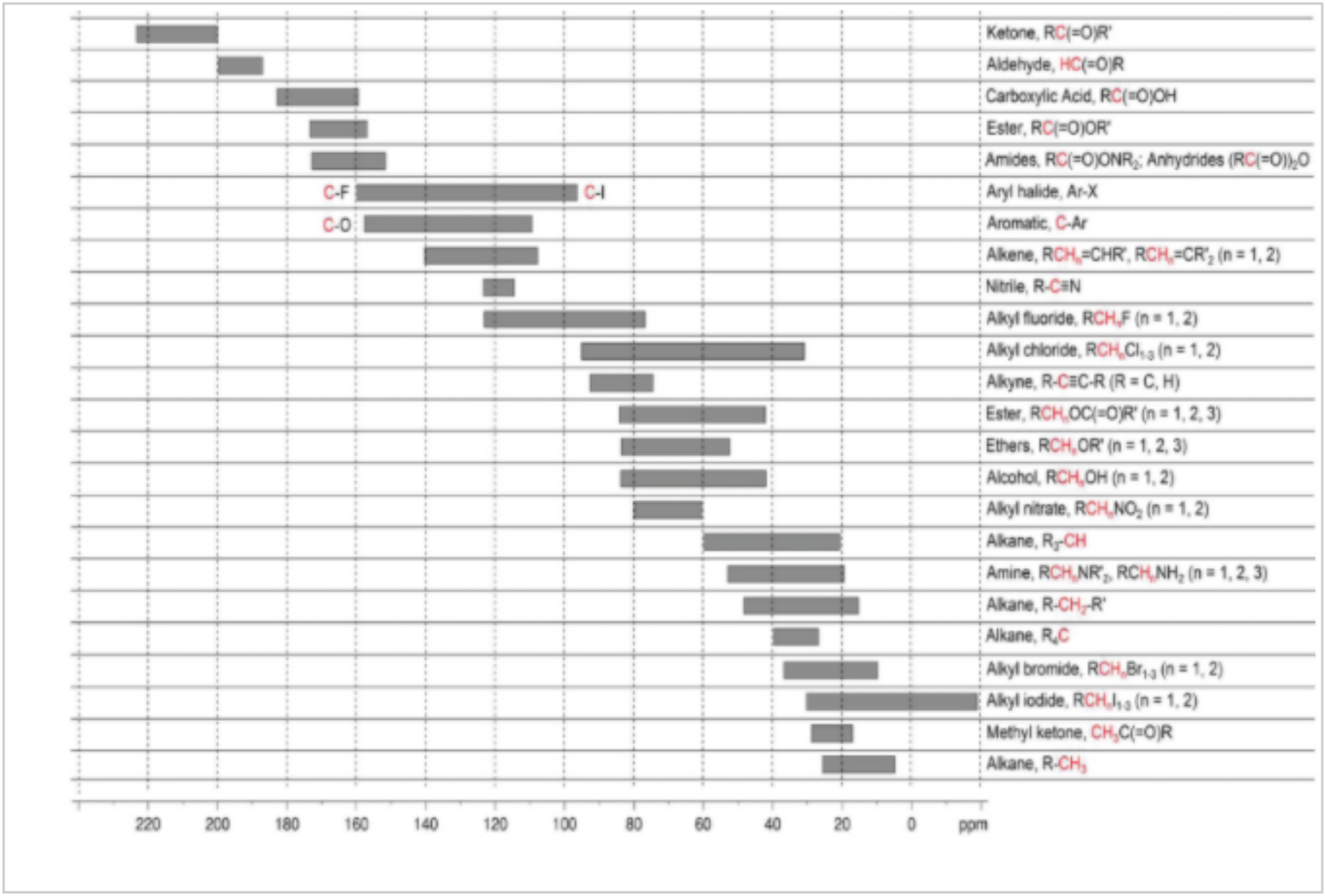


Table 6.5 ^{13}C Chemical Shifts (δ) for sp^3-hybridised Carbons in Alkyl Derivatives

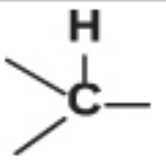
	CH_3–X	CH_3CH_2–X		$(CH_3)_2CH$–X	
X	–CH_3	–CH_3	–CH_2–	–CH_3	
–H	–2.3	7.3	7.3	15.4	15.9
–CH=CH_2	18.7	13.4	27.4	22.1	32.3
–Ph	21.4	15.8	29.1	24.0	34.3
–Cl	25.6	18.9	39.9	27.3	53.7
–OH	50.2	18.2	57.8	25.3	64.0
–OCH_3	60.9	14.7	67.7	21.4	72.6
–OCO–CH_3	51.5	14.4	60.4	21.9	67.5
–CO–CH_3	30.7	7.0	35.2	18.2	41.6
–CO–OCH_3	20.6	9.2	27.2	19.1	34.1
–NH_2	28.3	19.0	36.9	26.5	43.0
–NH–$COCH_3$	26.1	14.6	34.1	22.3	40.5
–C≡N	1.7	10.6	10.8	19.9	19.8
–NO_2	61.2	12.3	70.8	20.8	78.8

Table 6.6 ^{13}C Chemical Shifts (δ) for sp^2-hybridised Carbons in Vinyl Derivatives: CH_2=CH–X

X	CH_2=	=CH–X
–H	123.3	123.3
$-CH_3$	115.9	136.2
$-C(CH_3)_3$	108.9	149.8
–Ph	112.3	135.8
$-CH=CH_2$	116.3	136.9
–C≡C–H	129.2	117.3
$-CO-CH_3$	128.0	137.1
$-CO-OCH_3$	130.3	129.6
–Cl	117.2	126.1
$-OCH_3$	84.4	152.7
$-OCO-CH_3$	96.6	141.7
–C≡N	137.5	108.2
$-NO_2$	122.4	145.6
$-N(CH_3)_2$	91.3	151.3

Table 6.7 ^{13}C Chemical Shifts (δ) for *sp*-hybridised Carbons in Alkynes: X–C C–Y

X	Y	X–C≡	≡C–Y
H–	–H	73.2	73.2
H–	$-CH_3$	66.9	79.2
H–	$-C(CH_3)_3$	67.0	92.3
H–	$-CH=CH_2$	80.0	82.8
H–	–C≡C–H	66.3	67.3
H–	–Ph	77.1	83.4
H–	$-COCH_3$	81.8	78.1
H–	$-OCH_2CH_3$	22.0	88.2
CH_3–	$-CH_3$	72.6	72.6
CH_3–	–Ph	79.7	85.8
CH_3–	$-COCH_3$	97.4	87.0
Ph–	–Ph	89.4	89.4
$-COOCH_3$	$-COOCH_3$	74.6	74.6

Table 6.8 gives characteristic ^{13}C chemical shifts for the aromatic carbons in benzene derivatives. To a first approximation, the shifts induced by substituents are additive. So, for example, an aromatic carbon which has a –

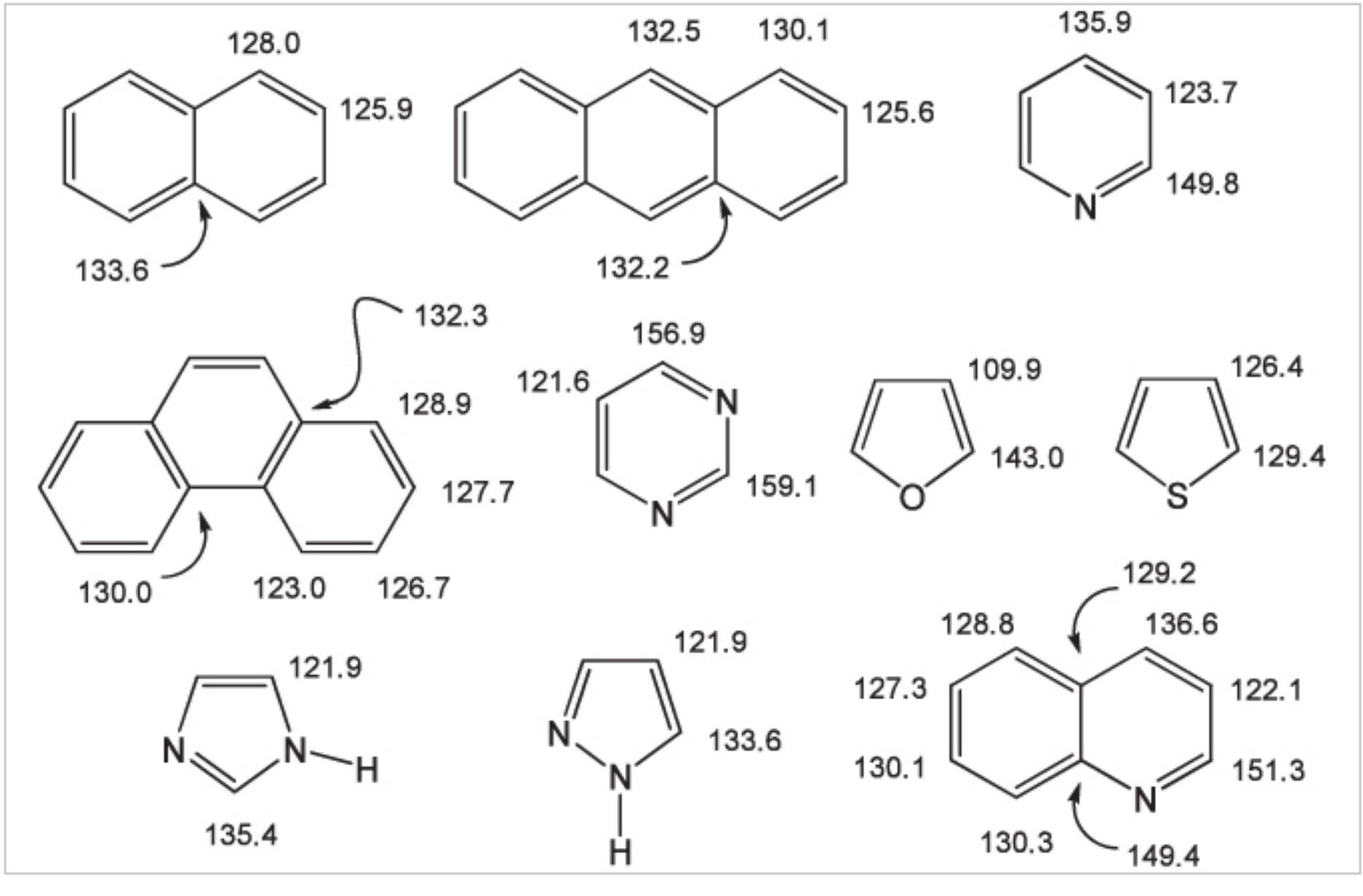
NO_2 group in the *para* position and a –Br group in the *ortho* position will appear at approximately 137.9 ppm [(128.5 + 6.1(*p*-NO_2) + 3.3(*o*-Br))].

Table 6.8 Approximate ^{13}C Chemical Shifts (δ) for Aromatic Carbons in Benzene Derivatives Ph–X in ppm Relative to Benzene at δ 128.5 ppm (a positive sign denotes a downfield shift)

X	*ipso*	*ortho*	*meta*	*para*
–H	0.0	0.0	0.0	0.0
$-NO_2$	19.9	–4.9	0.9	6.1
$-CO-OCH_3$	2.0	1.2	–0.1	4.3
$-CO-NH_2$	5.0	–1.2	0.1	3.4
$-CO-CH_3$	8.9	0.1	–0.1	4.4
–C≡N	–16.0	3.5	0.7	4.3
–Br	–5.4	3.3	2.2	–1.0
$-CH=CH_2$	8.9	–2.3	–0.1	–0.8
–Cl	5.3	0.4	1.4	–1.9
$-CH_3$	9.2	0.7	–0.1	–3.0
$-OCO-CH_3$	22.4	–7.1	0.4	–3.2
$-OCH_3$	33.5	–14.4	1.0	–7.7
$-NH_2$	18.2	–13.4	0.8	–10.0

Table 6.9 gives characteristic shifts for ^{13}C nuclei in some polynuclear aromatic compounds and heteroaromatic compounds.

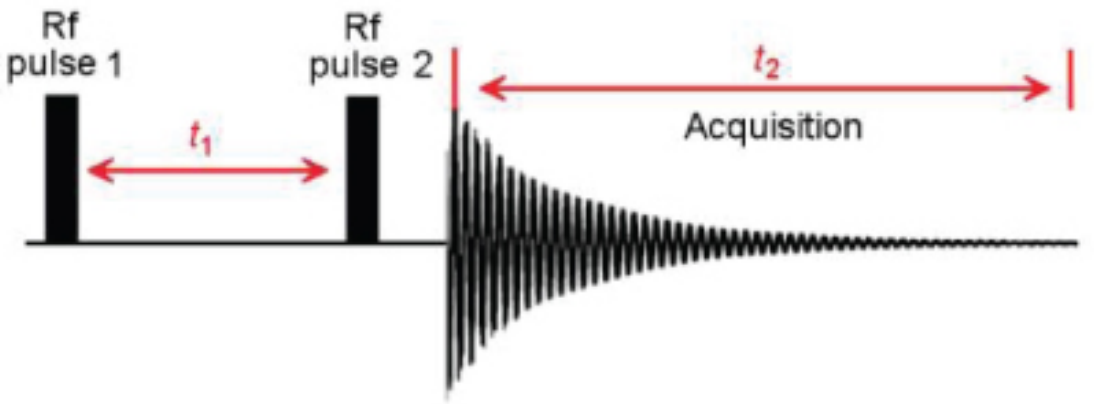
Table 6.9 Characteristic ^{13}C Chemical Shifts (δ) in some Polynuclear Aromatic Compounds and Heteroaromatic Compounds



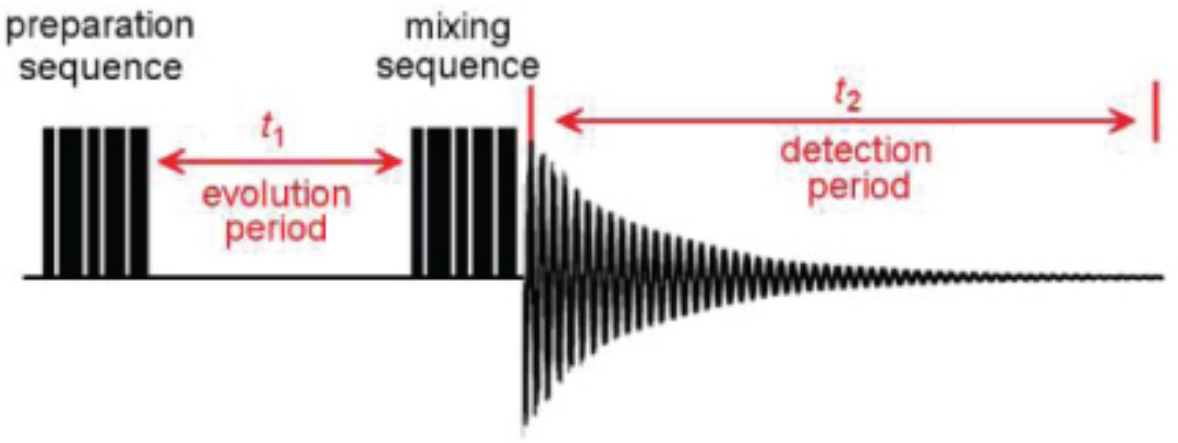
7
2-DIMENSIONAL NMR SPECTROSCOPY

Two-dimensional NMR spectra have two frequency axes rather than one.

A 2D spectrum is acquired using a pulse sequence which contains a delay period "t_1", which can be varied systematically as the experiment is repeated. The acquisition of a 2D NMR spectrum involves the use of two, or more, radiofrequency (Rf) pulses, separated by an intervening time period, t_1.



The first Rf pulse excites nuclei in the sample that interact with each other during t_1 through spin–spin coupling, dipolar interactions or by a range of other mechanisms. After the last pulse is applied, the free induction decay (FID) is acquired. The value of t_1 is then incremented, and the sequence is repeated to acquire a new FID. The experiment is repeated many times (typically 512 or 1024), with a different delay "t_1" in the pulse sequence for each experiment. One FID is acquired for each experiment giving an array of "N" individual FIDs, each of which has been acquired with a slightly different pulse sequence.



In practice, most 2D NMR experiments use more than two pulses and some heteronuclear sequences apply pulses to both ^{1}H and ^{13}C nuclei in the sample. To generalise the 2D NMR experiment, there are four important periods in the pulse sequence: *(i)* the preparation period; *(ii)* the evolution period (t_1); *(iii)* the mixing sequence; and *(iv)* the detection period (t_2).

Each FID represents the variation of detected signal as a function of time and successive FIDs in the array differ as a function of the time variable t_1 *within* the preparation period of the pulse sequence.

Fourier transformation of the two-dimensional array of data with respect to t_2 affords a series of spectra which vary systematically as a function of t_1. A second Fourier transformation, this time with respect to t_1, gives a two-dimensional spectral array (which is a function of two frequency domains F_1 and F_2) (Figure 7.1).

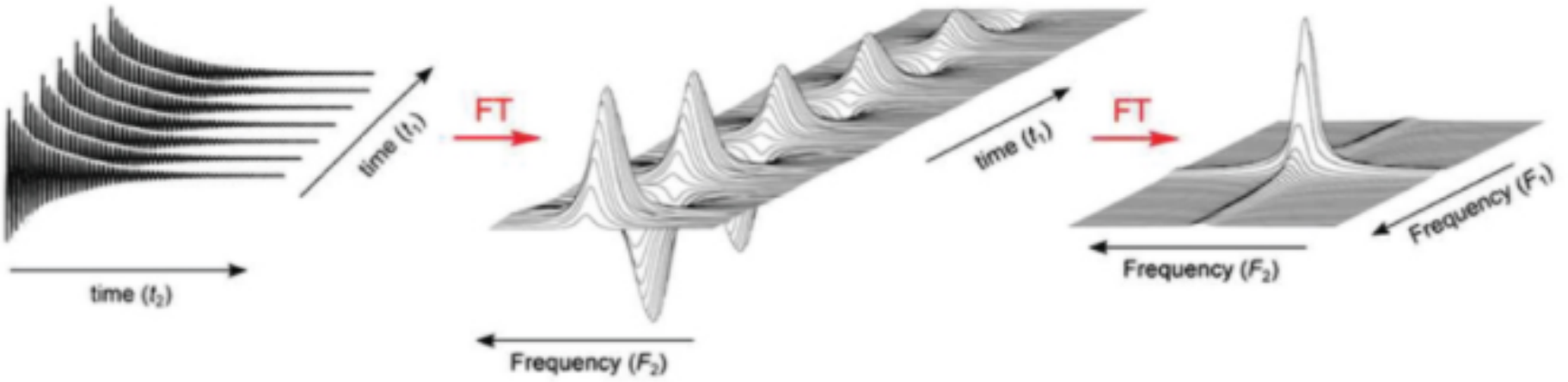


Figure 7.1 Acquisition of a 2D NMR spectrum: a series of individual FIDs are acquired; each individual FID is subjected to a Fourier transformation; a second Fourier transformation in the remaining time dimension gives the final 2D spectrum.

Two-dimensional spectra usually have the appearance of surfaces, generally with two frequency axes corresponding to chemical shift and the third (vertical) axis corresponding to peak intensity.

Two-dimensional spectra can be displayed in a number of formats. Firstly, the "**stacked plot**" (Figure 7.2a) is an aerial view across the 2D surface. This format provides a useful indication of the relative importance (size and positioning) of distinctive features on the 2D landscape. Secondly the "**contour plot**" (Figure 7.2b) provides a more convenient representation for making quantitative measurements or precise peak assignments.

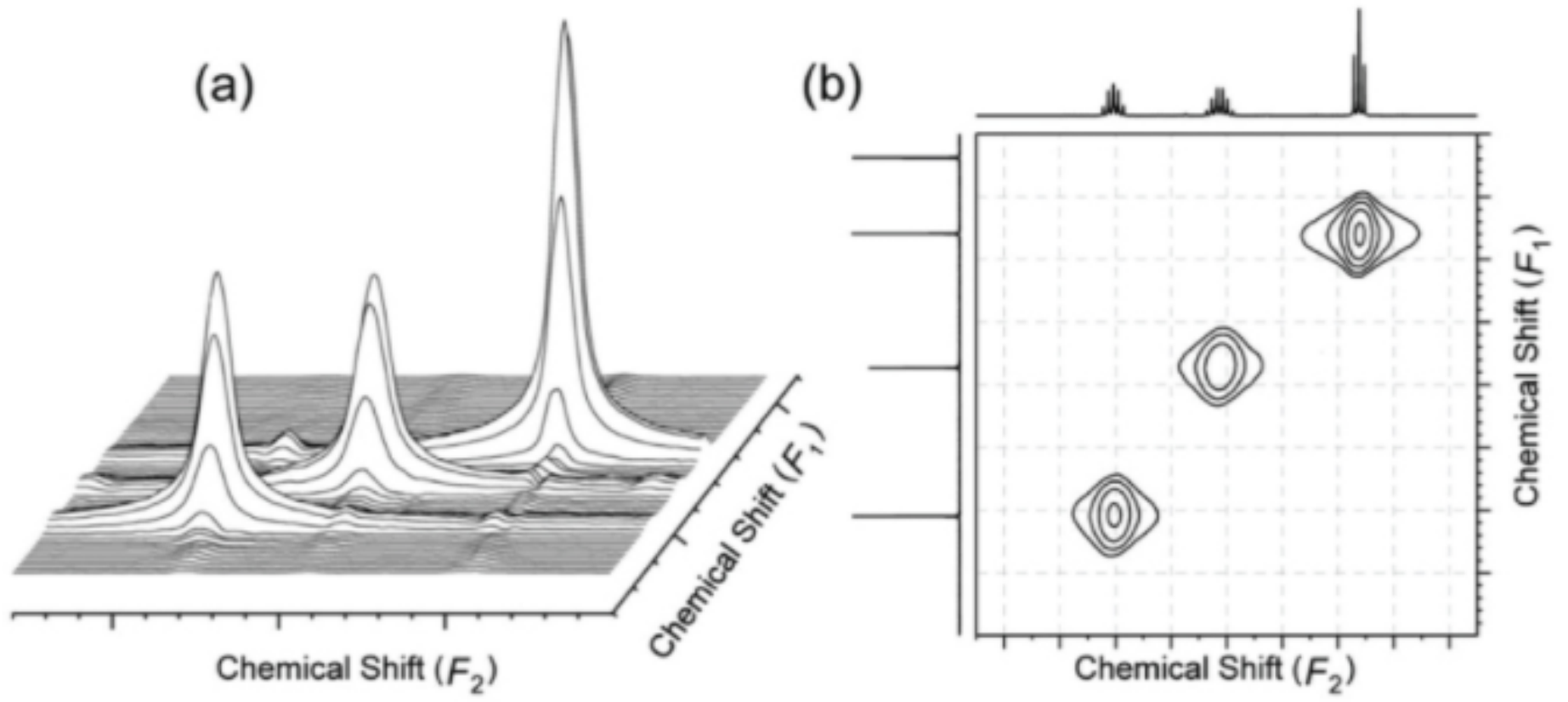


Figure 7.2 Representations of 2D NMR Spectra: (a) Stacked Plot; (b) Contour Plot

Two-dimensional NMR spectra may be acquired as either "magnitude" or as "phase-sensitive" spectra. Magnitude spectra are obtained by taking the absolute value of each point in the 2D spectrum so all of the intensities will be positive. Phase-sensitive spectra can contain both positive and negative signals and, for some 2D experiments, there is useful information in the relative phases of the peaks. In general, the peak widths of the peaks in phase-sensitive spectra are narrower and better resolved than in magnitude spectra. When phase-sensitive 2D NMR spectra are presented as contour plots, different colours are typically used to represent those peaks which are positive (usually black) and those which are negative (usually red) (Figure 7.3).

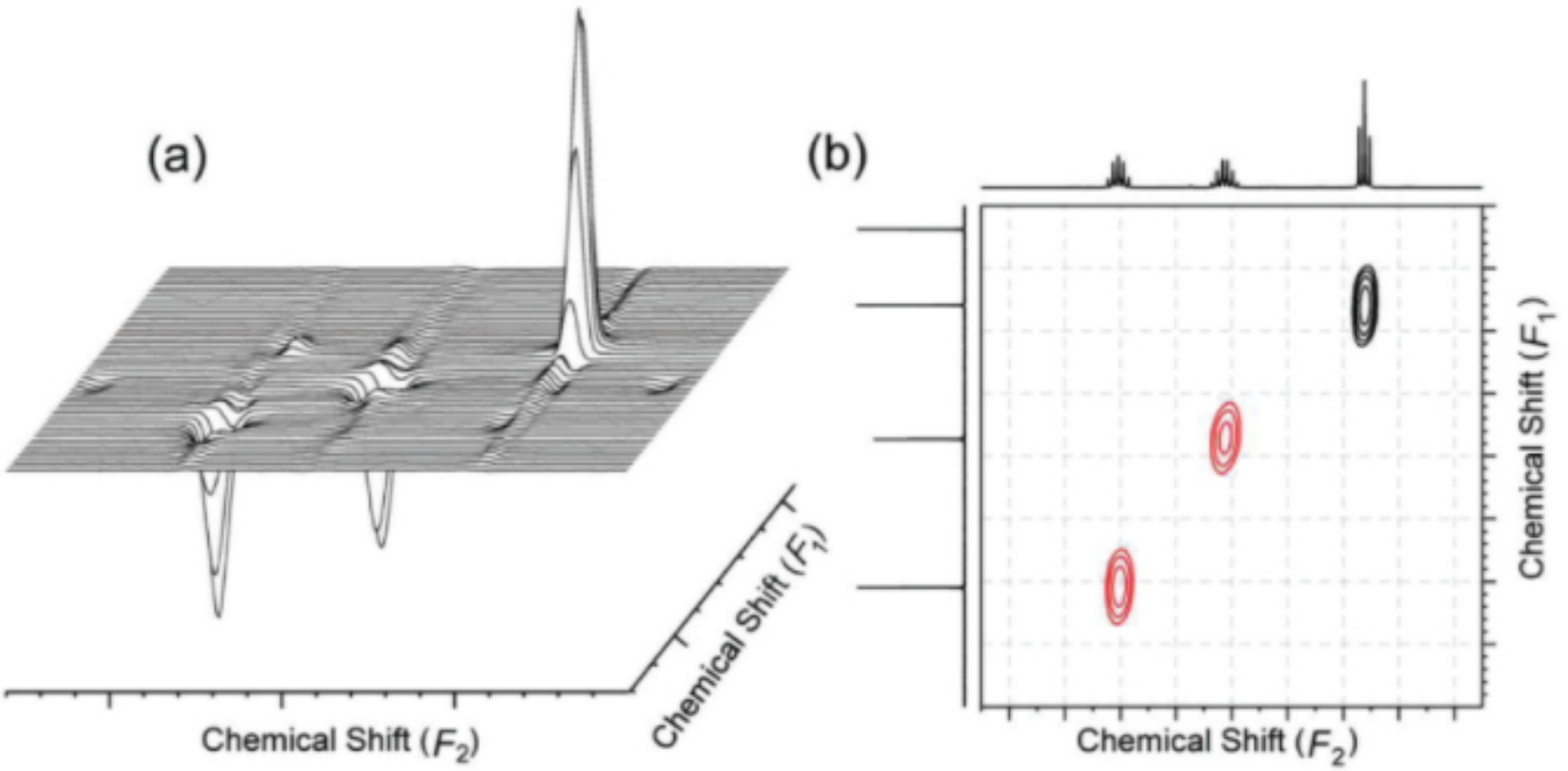


Figure 7.3 Representations of Phase-sensitive 2D NMR Spectra: (a) Stacked Plot; (b) Contour Plot

The number of possible two-dimensional experiments is essentially unlimited. Different pulse sequences in the preparation period give rise to different two-dimensional spectra which can be tailored to exhibit various properties of the sample.

The technical detail behind multi-dimensional NMR experiments, and the pulse sequences used to generate 2D spectra, is beyond the scope of this book. However, the most important two-dimensional NMR experiments for solving structural problems are COSY (COrrelation SpectroscopY), NOESY (Nuclear Overhauser Enhancement SpectroscopY), HSQC (Heteronuclear Single Quantum Correlation) or HSC (Heteronuclear Shift Correlation), HMBC (Heteronuclear Multiple Bond Correlation) and TOCSY (TOtal Correlation SpectroscopY). Most modern high-field NMR spectrometers have the capability to routinely and automatically acquire COSY, NOESY, HSQC, HMBC and TOCSY spectra.

7.1 PROTON–PROTON INTERACTIONS BY 2D NMR

7.1.1 COSY (CORRELATION SPECTROSCOPY)

The COSY spectrum shows which pairs of protons in a molecule are coupled to each other. The COSY spectrum is a symmetrical spectrum that has the ^{1}H NMR spectrum of the substance as both of the chemical shift axes (F_1 and F_2).

It is usual to plot a normal (one-dimensional) NMR spectrum along each of the F_1 and F_2 axes to give reference spectra for the peaks that appear in the two-dimensional spectrum. A COSY spectrum of 1-iodobutane ($CH_3CH_2CH_2CH_2I$) is given below (Figure 7.4).

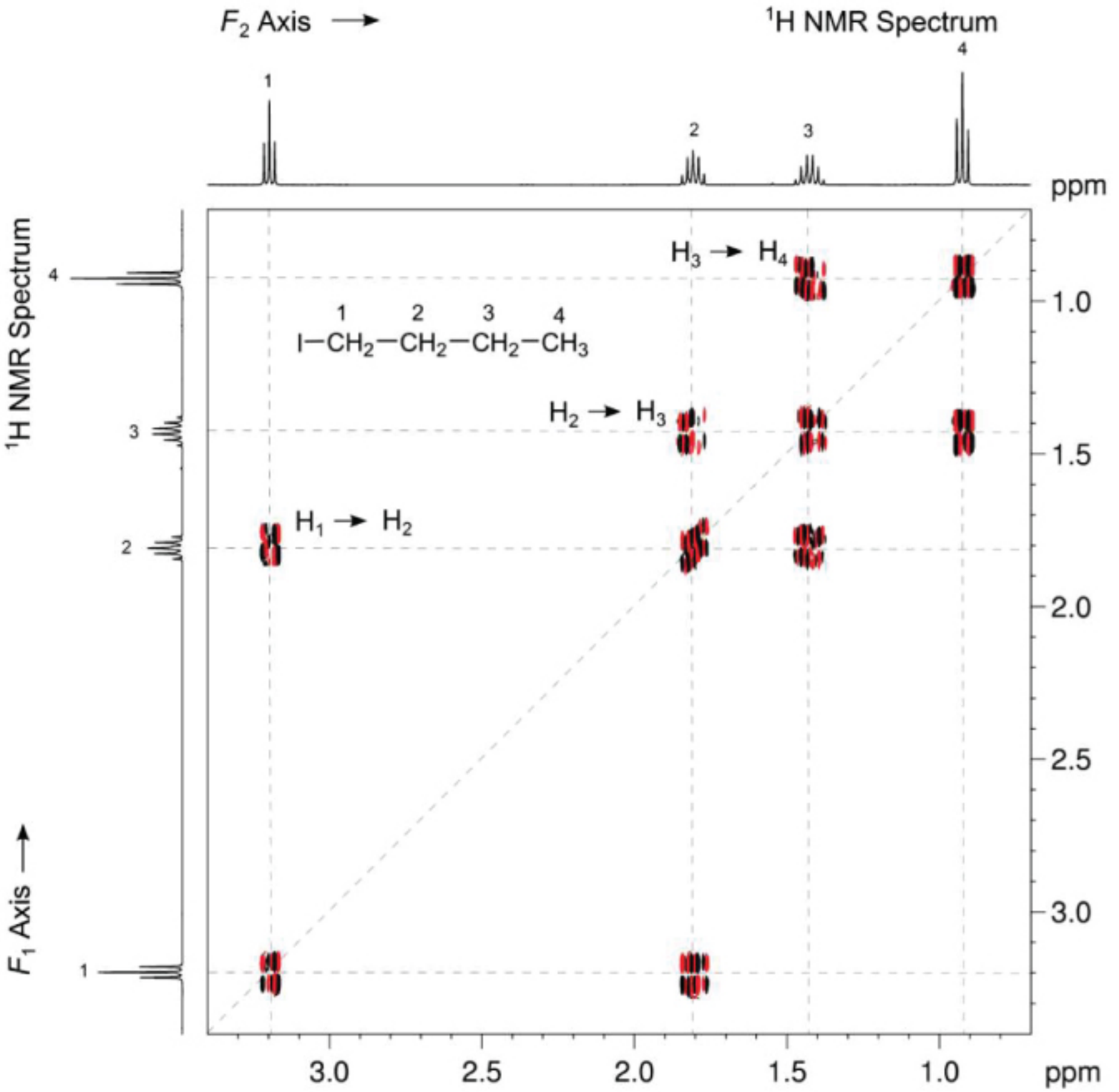
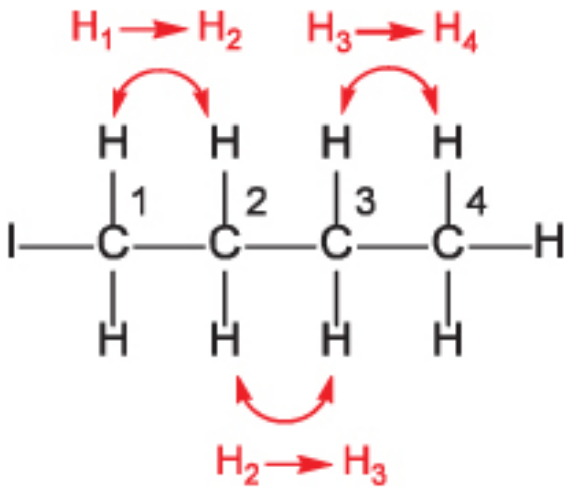


Figure 7.4 ^{1}H COSY Spectrum of 1-Iodobutane ($CDCl_3$ solvent, 298K, 400 MHz)

The COSY spectrum of 1-iodobutane has a set of four peaks on the diagonal as well as peaks that are off the diagonal. The COSY spectrum is always symmetrical about the diagonal – the off-diagonal peaks above the diagonal are mirrored on the lower side of the diagonal. The off-diagonal peaks are the important signals, since these only occur at positions where there is coupling between a proton on the F_1 axis and a proton on the F_2 axis. The off-diagonal peaks are typically multiplets, reflecting the multiplet structure of the signal, with some components of the multiplet pointing upwards (positive signals, black contours) and some components pointing downwards (negative signals, red contours). The protons which are part of the $-CH_2I$ group (H_1) are easy to identify since the halogen substituent characteristically moves these to about δ 3.2 ppm. There are three off-diagonal peaks on each side of the diagonal – one indicates the coupling between H_1 and H_2; the second

indicates coupling between H_2 and H_3 and the third indicates coupling between H_3 and H_4. If you can identify one of the proton signals, then you can identify the protons that are coupled to it and then work sequentially along a coupled network until all the protons that are coupled together in the spin system are identified.



In a single COSY spectrum all of the coupling pathways in a molecule can be identified.

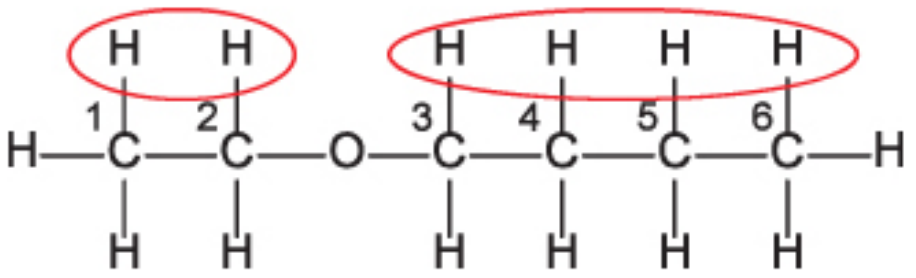
7.1.2 TOCSY (TOTAL CORRELATION SPECTROSCOPY)

The TOCSY spectrum is useful in identifying all of the protons that belong to the same isolated spin system. Like the COSY experiment, TOCSY relies on spin–spin coupling but rather than showing pairs of nuclei which are directly coupled together, the TOCSY shows a cross-peak (off-diagonal peak) for every nucleus which is part of the same coupled spin system – not just those that are directly coupled to each other.

Like the COSY spectrum, the TOCSY has peaks along a diagonal at the frequencies of all of the resonances in the spectrum. The TOCSY spectrum is also symmetrical around the diagonal and it is usual to plot a normal (one-dimensional) NMR spectrum along each of the F_1 and F_2 axes to give reference spectra for the peaks that appear in the two-dimensional spectrum.

A TOCSY spectrum of butyl ethyl ether ($CH_3CH_2CH_2CH_2OCH_2CH_3$) is given in Figure 7.5.

Butyl ethyl ether has two separate spin systems – a butyl fragment and an ethyl fragment which are isolated (and insulated) from each other by the ether oxygen bridge. Butyl ethyl ether has six proton resonances and the TOCSY shows six peaks on the diagonal. There are seven off-diagonal peaks above the diagonal and a corresponding set of mirrored peaks below the diagonal.



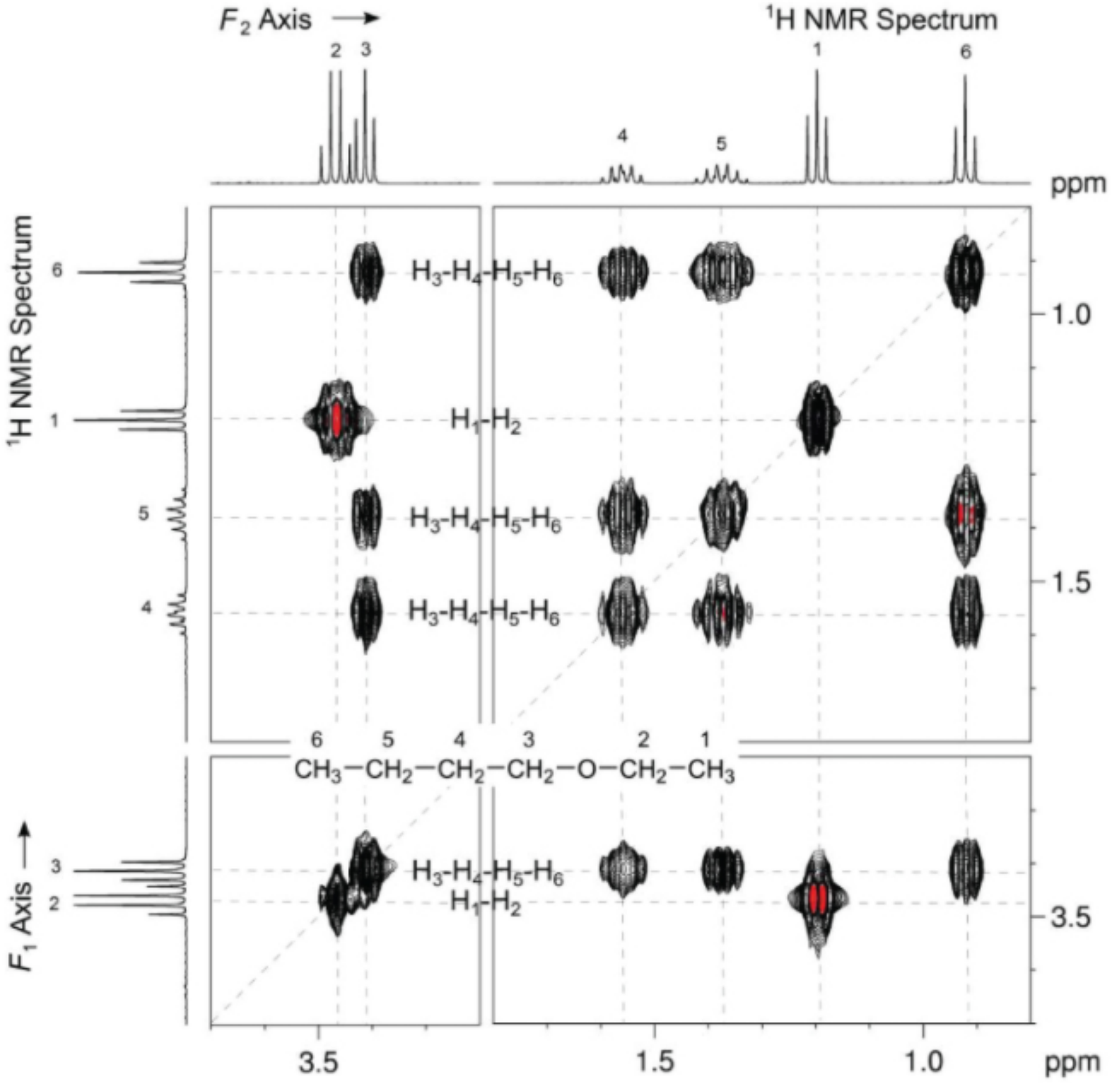


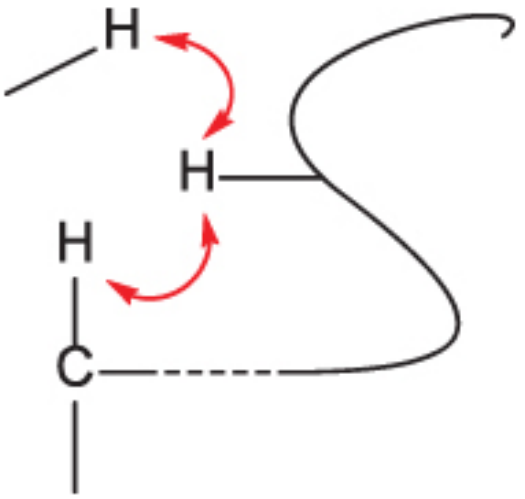
Figure 7.5 ^{1}H TOCSY Spectrum of Butyl Ethyl Ether ($CDCl_3$ solvent, 298K, 400 MHz)

At the frequency corresponding to each resonance in F_1, all of the nuclei in the same coupled spin system are identified by a series of peaks. At the frequency corresponding to H_6 in the F_1 dimension, a horizontal line will show peaks in the F_2 dimension for H_3, H_4, H_5 and H_6 which are all the signals for the butyl fragment of butyl ethyl ether. At the frequency corresponding to H_1 in the F_1 dimension, a horizontal line will show peaks in the F_2 dimension for H_1 and H_2 which are all the signals for the ethyl fragment of butyl ethyl ether. There is a significant amount of redundant information in a TOCSY spectrum.

The TOCSY spectrum is useful where there are a number of isolated spin systems in the sample, particularly if the spectra are heavily overlapped.

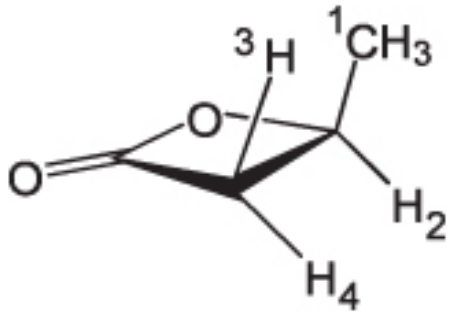
7.1.3 NOESY (NUCLEAR OVERHAUSER EFFECT SPECTROSCOPY)

The NOESY spectrum relies on the nuclear Overhauser effect (Section 5.7) and shows which pairs of nuclei in a molecule are close together in space.



The NOESY spectrum is very similar in appearance to a COSY spectrum. The NOESY spectrum is symmetrical about the diagonal and has the ^{1}H NMR spectrum as both of the chemical shift axes (F_1 and F_2). Again, it is usual to plot a normal (one-dimensional) NMR spectrum along each of the axes to give reference spectra for the peaks that appear in the two-dimensional spectrum.

From the analysis of a NOESY spectrum, it is possible to determine the three dimensional structure of a molecule or parts of a molecule. The NOESY spectrum is particularly useful for establishing the stereochemistry (*e.g.* the *cis/trans* configuration of a double bond or a ring junction) of a molecule where more than one possible stereoisomer exists. A NOESY spectrum of β-butyrolactone is given in Figure 7.6.



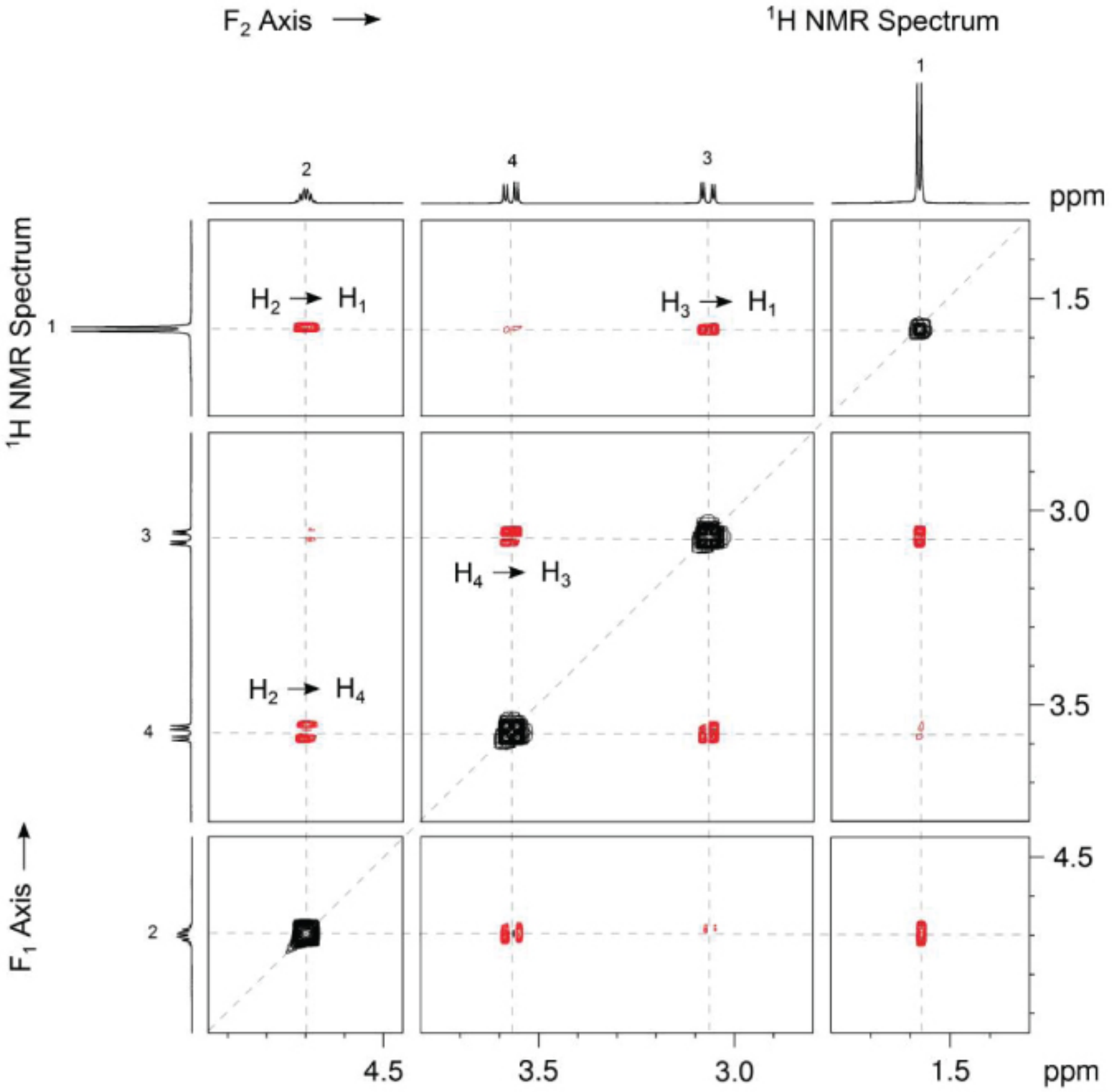
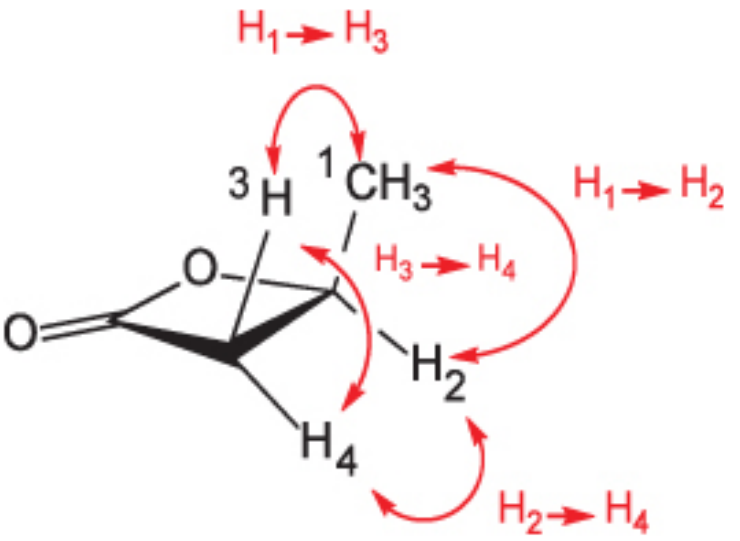


Figure 7.6 ^{1}H NOESY Spectrum of β-Butyrolactone ($CDCl_3$ solvent, 298K, 600 MHz)

β-Butyrolactone is a cyclic compound (four-membered ring) with a methyl group and three protons. The ring structure dictates that the methyl group (H_1) and one of the protons (H_3) are on one face of the molecule and two protons (H_2 and H_4) are on the other face. The NOESY spectrum contains strong cross-peaks between H_1 and H_2 (geminal groups, *i.e.* attached to the same carbon); strong cross-peaks between H_3 and H_4 (also geminal groups) as well as strong cros-speaks between H_2 and H_4 (same face of the molecule) and cross-peaks between H_1 and H_3 (same face of the molecule).

From the NOESY spectrum it is very clear which proton signal derives from H_3 and which from H_4. The spectrum also shows weak cross-peaks between H_2 and H_3 indicating that these protons are still sufficiently

close in space to have a weak NOE interaction.



7.2 PROTON–CARBON INTERACTIONS BY 2D NMR

7.2.1 HETERONUCLEAR SINGLE BOND CORRELATION: THE HSQC (HETERONUCLEAR SINGLE QUANTUM CORRELATION) OR HSC (HETERONUCLEAR SHIFT CORRELATION) SPECTRUM

The HSQC (Heteronuclear Single Quantum Correlation) and the HMQC (Heteronuclear Multiple Quantum Correlation) experiments are the heteronuclear analogues of the COSY spectrum and these experiments identify which protons are directly attached to which carbons in a molecule. The HSQC is often also called the HSC (Heteronuclear Shift Correlation) or the HETCOR (Heteronuclear Correlation) experiment. While there are differences in the pulse sequences that an NMR spectrometer uses to acquire the HSQC and HMQC spectra, in practice, these experiments provide essentially the same information. The HSQC spectrum has the ^{1}H NMR spectrum on one axis (F_2) and the ^{13}C spectrum (or the spectrum of some other nucleus) on the second axis (F_1).

It is usual to plot a normal (one-dimensional) ^{1}H NMR spectrum along the proton dimension (the F_2 axis) and a normal (one-dimensional) ^{13}C NMR spectrum along the ^{13}C dimension (the F_1 axis) to give reference spectra for the cross-peaks that appear in the two-dimensional spectrum. The HSQC spectrum does not have diagonal peaks. The peaks in an HSQC spectrum occur at positions where a proton in the spectrum on the F_2 axis is directly coupled to a carbon in the spectrum on the F_1 *axis via a one-bond C–H coupling*. Note that non-protonated carbons cannot have any cross-peaks in the HSQC spectrum.

The **multiplicity-edited HSQC (*me*-HSQC)** is a variation on the HSQC experiment that provides additional information about whether the signals arise from CH, CH_2 or CH_3 groups in much the same way that a DEPT experiment provides multiplicity information in one-dimensional ^{13}C spectra (see Section 6.3). In the *me*-HSQC spectrum, the carbon atoms with an even number of attached protons (CH_2 carbons) usually point downwards (plotted in red) while the carbons with an odd number of protons (the CH and CH_3 carbons) point upwards (plotted in black).

If the proton spectrum of a molecule can be assigned using chemical shift information or spin–spin coupling information (*e.g.* using a COSY experiment) then the resonances in the ^{13}C spectrum can be assigned using the HSQC experiment.

A *me*-HSQC spectrum of 1-iodobutane ($CH_3CH_2CH_2CH_2I$) is given in Figure 7.7.

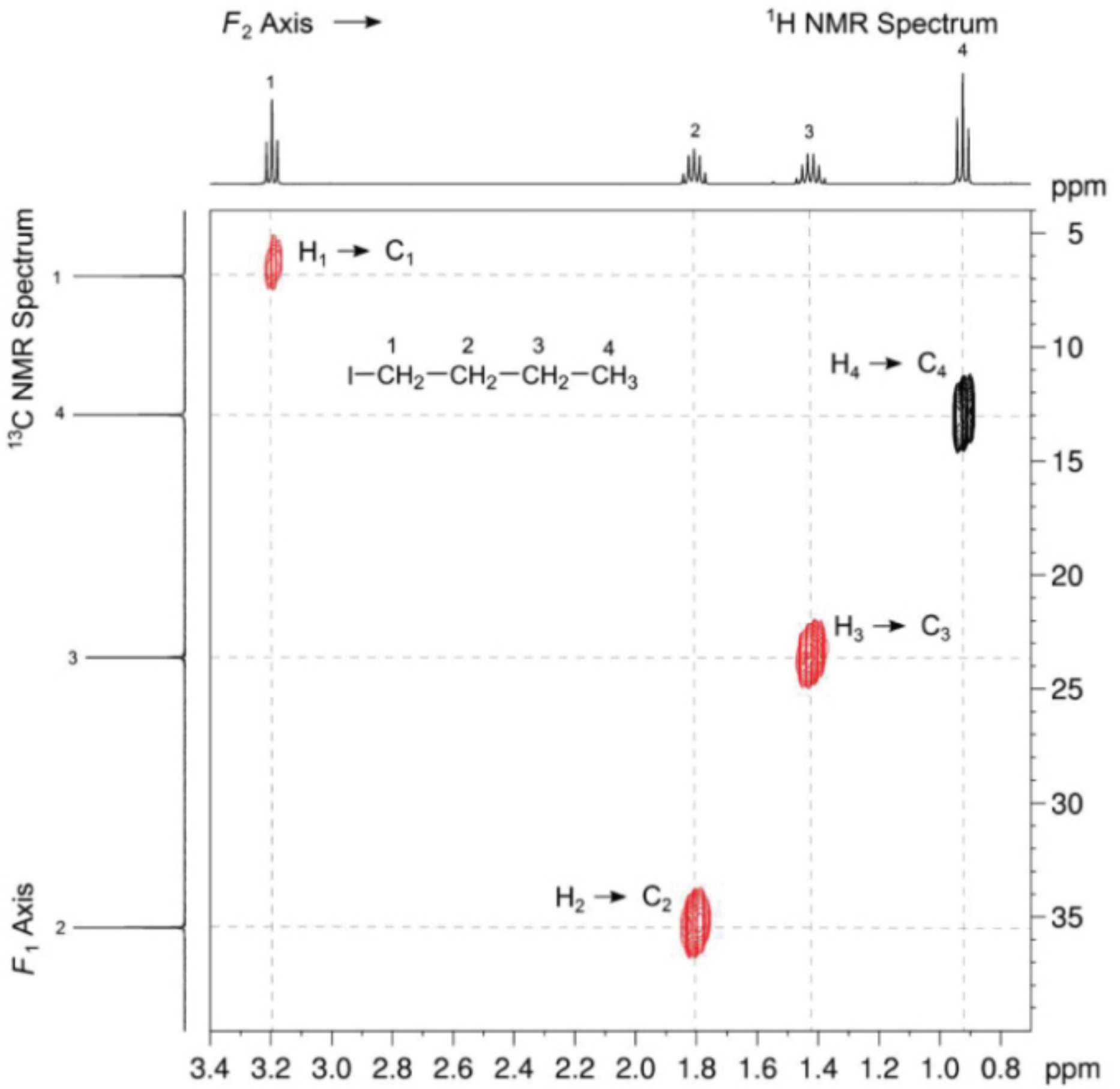
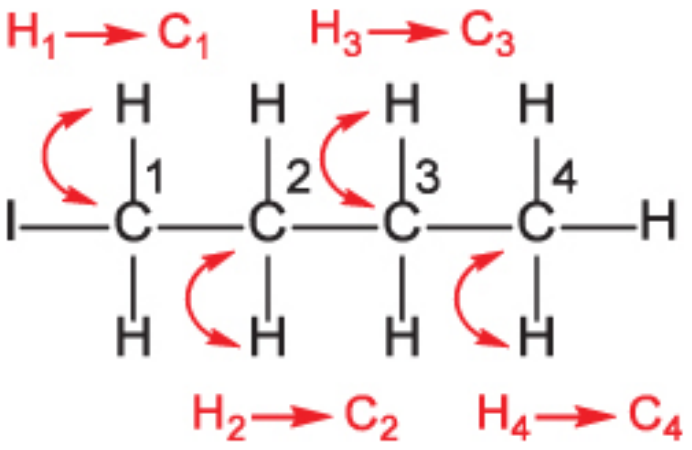


Figure 7.7 ^{1}H–^{13}C *me*-HSQC Spectrum of 1-Iodobutane (CDCl>$_3$ solvent, 298K, ^{1}H 400 MHz, ^{13}C 100 MHz)

1-Iodobutane has four carbon resonances and the *me*-HSQC spectrum shows four cross-peaks. Having assigned all of the resonances in the ^{1}H spectrum (see Section 7.1.1), then the resonances in the carbon spectrum can simply be assigned by the positions of the cross-peaks corresponding to each proton resonance.



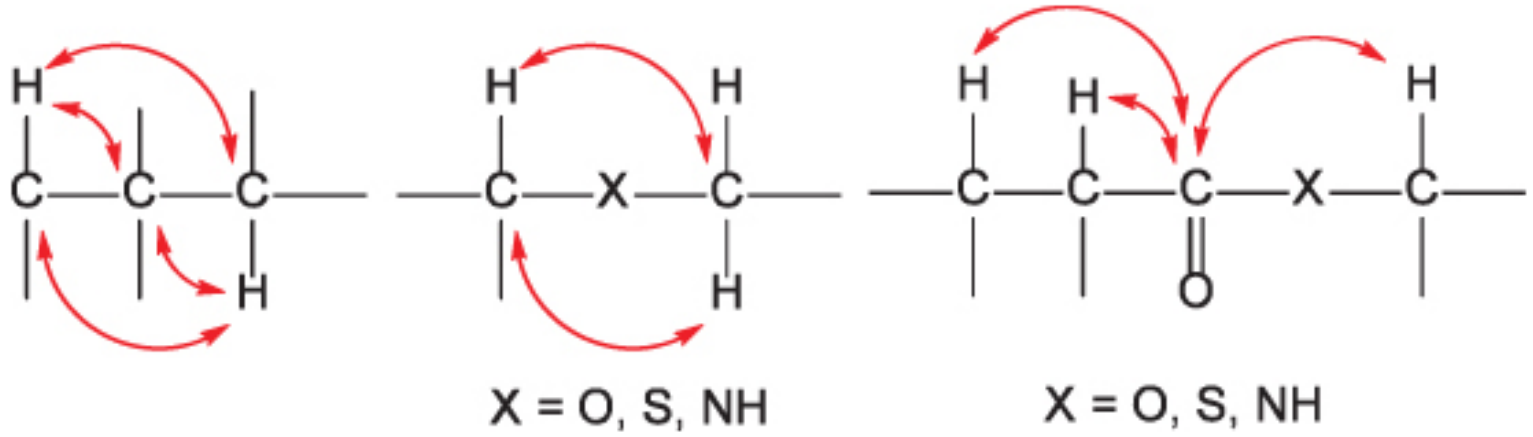
Note that in the *me*-HSQC spectrum, there are three cross-peaks in red corresponding to the negative signals from the CH_2 groups and one cross-peak which is black corresponding to the positive signal from the CH_3 group.

7.2.2 HMBC (HETERONUCLEAR MULTIPLE BOND CORRELATION)

The HMBC spectrum correlates chemical shifts of hydrogen nuclei with carbon nuclei which are separated by two or more chemical bonds. The HMBC experiment is frequently used to assign quaternary and carbonyl carbons that don't have any directly bound protons, which makes them "invisible" in the HSQC experiment.

The HMBC experiment is designed to filter out correlations resulting from large C–H coupling constants (120–160 Hz) resulting from protons directly bound to carbon and to select for smaller couplings (around 10 Hz), which are typical C–H couplings over two or three bonds.

The HMBC is a very powerful method for making the connection between two parts of a molecule that may be isolated from each other by a carbonyl, an ether, an ester, an amide or by some other functional group.



It is usual to plot a normal (one-dimensional) ^{1}H NMR spectrum along the proton dimension (the F_2 axis) and a normal (one-dimensional) ^{13}C NMR spectrum along the ^{13}C dimension (the F_1 axis) to give reference spectra for the peaks that appear in the two-dimensional spectrum.

The HMBC spectrum does not have diagonal peaks. The peaks in an HMBC spectrum occur at positions where a proton in the spectrum on the F_2 axis is coupled to a carbon in the spectrum on the F_1 axis *via a two-bond or three-bond C–H coupling*.

A HMBC spectrum of 1-iodobutane ($CH_3CH_2CH_2CH_2I$) is given in Figure 7.8. The spectrum has four carbon resonances and the HMBC spectrum shows ten peaks. H_1 correlates to C_2 (two-bond coupling) and to C_3 (three-bond coupling). H_2 correlates to C_1 and to C_3 (two-bond couplings) as well as to C_4 (three-bond coupling); H_3 correlates to C_2 and to C_4 (two-bond couplings) as well as to C_1 (three-bond coupling); H_4 correlates to C_3 (two-bond coupling) as well as to C_2 (three-bond coupling). Because the HMBC provides long-range information, it is an exceptionally useful experiment to tie together pieces of a molecule as parts are systematically identified.

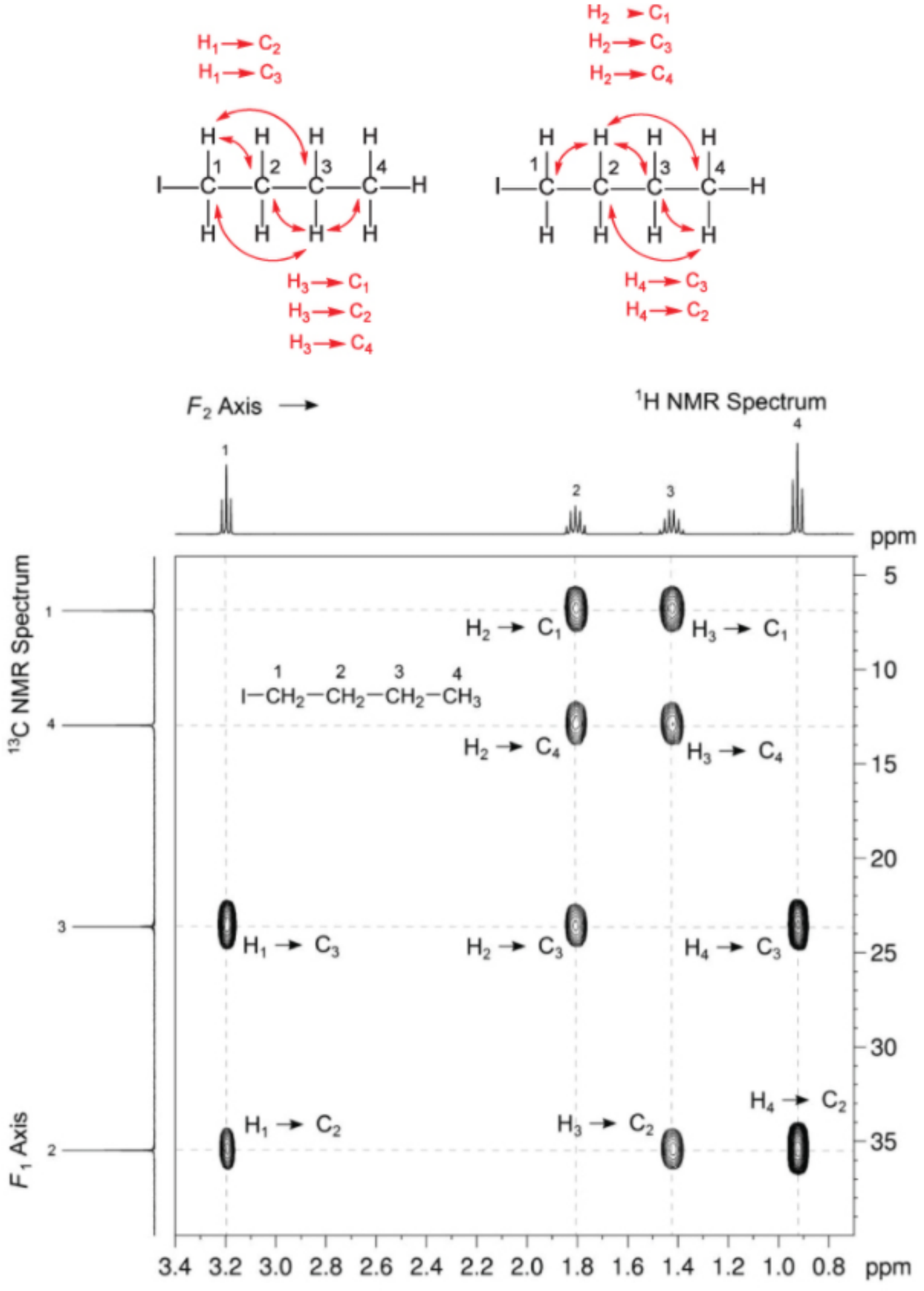
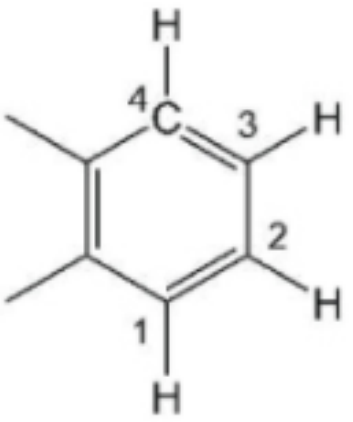

H1 → C2
H1 → C3
H2 → C1
H2 → C3
H2 → C4
H3 → C1
H3 → C2
H3 → C4
H4 → C3
H4 → C2
F2 Axis →
1H NMR Spectrum
ppm
13C NMR Spectrum
F1 Axis
I—CH2—CH2—CH2—CH3
H1 → C2
H1 → C3
H2 → C1
H2 → C3
H2 → C4
H3 → C1
H3 → C2
H3 → C4
H4 → C2
H4 → C3
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm

Figure 7.8 ^{1}H–^{13}C HMBC Spectrum of 1-Iodobutane ($CDCl_3$ solvent, 298K, ^{1}H 400 MHz, ^{13}C 100 MHz)

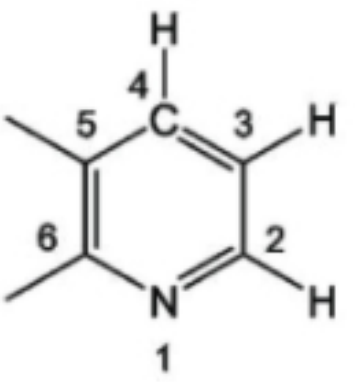
In aromatic systems, and in heteroaromatic systems, it is typically the three-bond (*meta*) J_{C-H} which is the largest of the long-range C–H couplings, so the HMBC cross-peaks between aromatic protons and the carbons which are three bonds away are typically the strongest.



$^{2}J_{H3-C4} = 1$ Hz

$^{3}J_{H2-C4} = 7$ Hz

$^{4}J_{H1-C4} = -1$ Hz



$^{2}J_{H3-C2} = 2$ Hz

$^{3}J_{H4-C2} = 7$ Hz

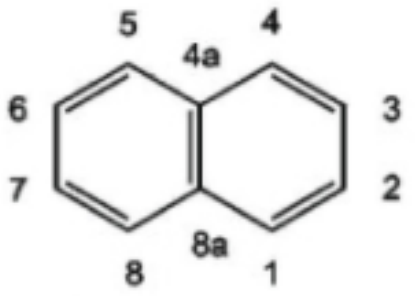
$^{3}J_{H6-C2} = 12$ Hz

$^{2}J_{H2-C3} = 7$ Hz

$^{2}J_{H4-C3} = 2$ Hz

$^{3}J_{H2-C4} = 4$ Hz

$^{3}J_{H3-C5} = 6$ Hz



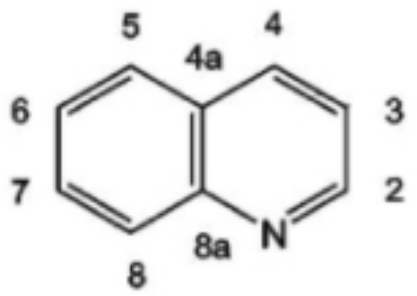
$^{3}J_{H3-C1} = 8$ Hz

$^{3}J_{H8-C1} = 5$ Hz

$^{3}J_{H4-C2} = 9$ Hz

$^{3}J_{H1-C4a} = 8$ Hz

$^{3}J_{H3-C4a} = 8$ Hz



$^{2}J_{H3-C2} = 4$ Hz

$^{3}J_{H4-C2} = 8$ Hz

$^{2}J_{H2-C3} = 10$ Hz

$^{3}J_{H2-C4} = 5$ Hz

$^{3}J_{H5-C4} = 5$ Hz

$^{3}J_{H4-C5} = 5$ Hz

$^{3}J_{H7-C5} = 7$ Hz

$^{3}J_{H8-C6} = 9$ Hz

$^{3}J_{H5-C7} = 9$ Hz

$^{3}J_{H6-C8} = 7$ Hz

$^{3}J_{H3-C4a} = 7$ Hz

$^{3}J_{H6-C4a} = 7$ Hz

$^{3}J_{H8-C4a} = 5$ Hz

$^{3}J_{H2-C8a} = 13$ Hz

$^{3}J_{H4-C8a} = 6$ Hz

$^{3}J_{H5-C8a} = 5$ Hz

$^{3}J_{H7-C8a} = 7$ Hz

The HMBC experiment is a powerful method for assigning the ^{13}C chemical shifts of the substituted (*i.e.* non-protonated) carbons in an aromatic framework.

The HMBC spectrum showing the aromatic protons and carbons of 2-bromophenol is given in Figure 7.9.

2-Bromophenol is a disubstituted aromatic compound. It has four aromatic protons and six aromatic carbons. There are four protonated carbons and two substituted (*i.e.* unprotonated) carbons. The proton assignments are given in Figure 7.9.

The HMBC spectrum of 2-bromophenol shows eight strong correlations and all of the strong peaks correspond to three-bond *meta* couplings. H_3 correlates to C_1 and to C_5; H_4 correlates to C_2 and to C_6; H_5 correlates to C_3 and to C_1; H_6 correlates to C_2 and to C_4.

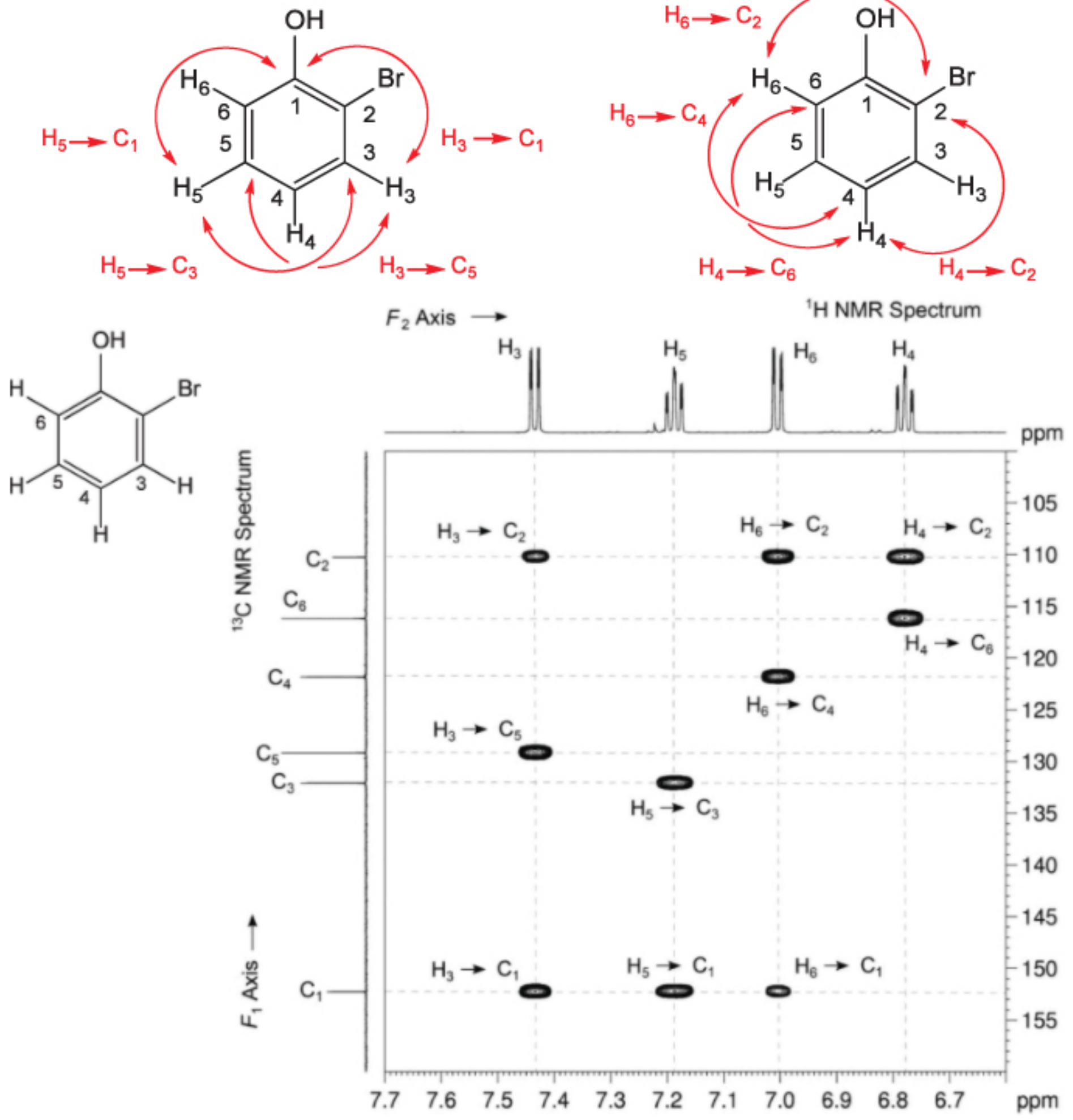
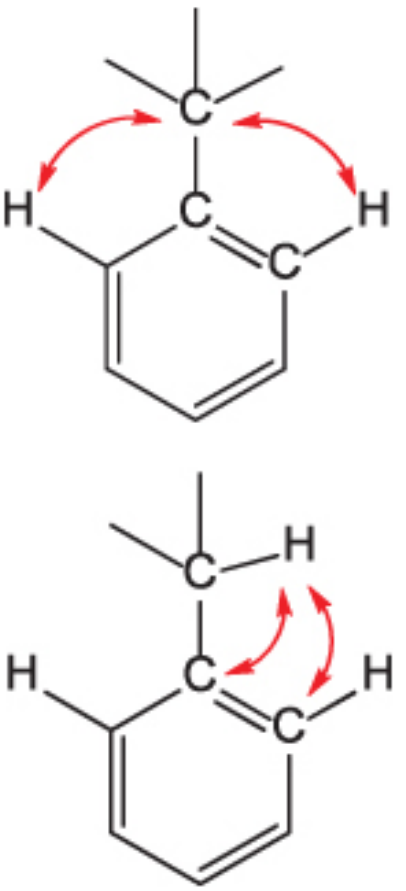
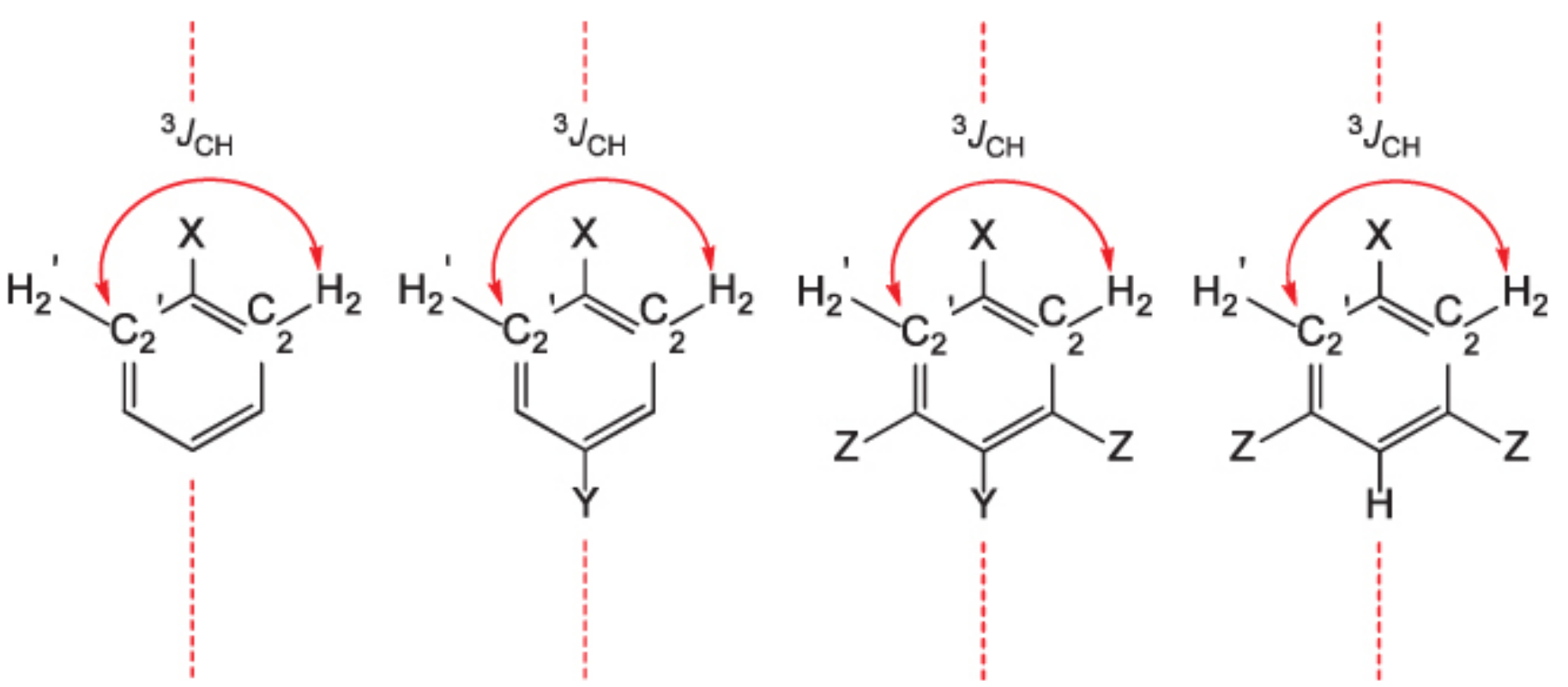


Figure 7.9 ^{1}H–^{13}C HMBC Spectrum of 2-Bromophenol ($CDCl^3$ solvent, 298K, ^{1}H 400 MHz, ^{13}C 100 MHz)

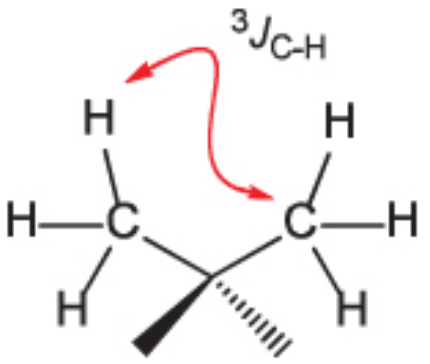
In substituted aromatic systems where there is a carbon bound to the aromatic ring, the protons *ortho* to a substituent will show correlations to a carbon directly bonded to the aromatic ring. Conversely protons on a benzylic carbon will correlate to the ring carbon to which the substituent is attached and also to the carbons ortho to where the substituent is attached. This is an excellent method for identifying the positions where alkyl-, acyl-, vinyl- or alkynyl- substituents (or other substituents which have a carbon directly bound to the aromatic ring) are attached to an aromatic ring.



In the HMBC spectra of *para*-disubstituted benzenes and in monosubstituted benzenes, or in 1,3,5- or 1,3,4,5-tetrasubstituted benzenes where there is a mirror plane of symmetry through the aromatic ring, it is usual to see what appear to be 1-bond correlations for some of the aromatic carbons. These occur for those carbons which are symmetry related, *i.e.* for those carbons which have a chemically identical carbon across the mirror plane of the molecule and the correlations arise from the $^{3}J_{H-C}$ interaction of a proton with the carbon that is *meta* to it.



It is also common to observe apparent one-bond C–H correlations in the HMBC spectra of the methyl groups in *t*-butyl groups, isopropyl groups or in compounds with *gem*-dimethyl groups. Again while the correlation appears to be a one-bond correlation, the HMBC correlation arises from the $^{3}J_{H-C}$ interaction of the protons of one of the methyl groups with the chemically equivalent carbon that is three bonds away.


$^3J_{C-H}$
H
H
H
C
C
H
H
H

8
MISCELLANEOUS TOPICS

8.1 SOLVENTS FOR NMR SPECTROSCOPY

NMR spectra are almost invariably obtained in solution. The solvents of choice:

a. should have adequate dissolving power.

b. should not associate strongly with solute molecules as this is likely to produce appreciable effects on chemical shifts. This requirement must sometimes be sacrificed to achieve adequate solubility.

c. should be essentially free of interfering signals. Thus for ^{1}H NMR, the best solvents are proton-free.

d. should preferably contain deuterium, ^{2}H. Deuterium is an isotope of hydrogen which is relatively easy to obtain and incorporate into common solvents in place of hydrogen with insignificant changes to the properties of the solvent. Almost all NMR instruments use the deuterium resonance of the solvent as a convenient "locking" signal to stabilise the magnetic field of the NMR magnet and to provide a strong signal to tune and optimise the homogeneity of the NMR magnet to produce a high-quality spectrum.

The most commonly used organic solvent is **deuterochloroform**, $CDCl_3$, which is an excellent solvent and is only weakly associated with most organic substrates. $CDCl_3$ contains no protons and has a deuterium atom. For ionic compounds or hydrophilic compounds, the most common solvent is deuterated water, D_2O.

Almost all deuterated solvents are not 100% deuterated and they typically contain a small residual protonated impurity. With the sensitivity of modern NMR instruments, the signal from residual protons in the deuterated solvent is usually visible in the ^{1}H NMR spectrum. Table 8.1 provides the chemical shifts of the residual signals from solvents which are commonly used in NMR spectroscopy.

For many spectra, the signal from residual protons or the ^{13}C signal from the solvent can be used as a reference signal (instead of adding TMS) since the chemical shifts of most common solvents are known accurately. In $CDCl_3$, the residual $CHCl_3$ has a shift of 7.27 ppm in the ^{1}H NMR spectrum and the ^{13}C shift of $CDCl_3$ is 77.0 ppm. Solvents that are miscible with water (and are difficult to "dry" completely), *e.g.* $CD_3(CO)CD_3$, $CD_3(SO)CD_3$ and D_2O, also commonly contain a small amount of residual water. The residual water typically appears as a broad resonance in the region 2.5–5 ppm in the ^{1}H NMR spectrum.

Table 8.1 1H and 13C Chemical Shifts for Common NMR solvents*

Solvent	Formula	Residual ^{1}H signal(s)* (multiplicity)	^{13}C signal(s)* (multiplicity)
acetone-d_6	$CD_3(C=O)CD_3$	2.05 (5)	29.9 (7); 206.7 (1)
acetonitrile-d_3	$CD_3C\equiv N$	1.94 (5)	1.4 (7); 118.7 (1)
benzene-d_6	C_6D_6	7.16 (1)	128.4 (3)
chloroform-d_1	$CDCl_3$	7.27 (1)	77.0 (3)
cyclohexane-d_{12}	C_6D_{12}	1.38 (3)	26.4 (5)
deuterium oxide-d_2	D_2O	4.81 (1)	–
dichloromethane-d_2	CD_2Cl_2	5.32 (3)	53.8 (5)
dimethylsulfoxide-d_6	$CD_3(S=O)CD_3$	2.50 (5)	39.5 (7)
1,4-dioxane-d_6	$C_4D_8O_2$	3.53 (3)	66.7 (5)
methanol-d_4	CD_3OD	4.87 (1); 3.31 (5)	49.2 (7)
pyridine-d_5	C_6D_5N	8.74 (1); 7.58 (1); 7.22 (1)	150.4 (3); 135.9 (3); 123.9 (3)
toluene-d_8	$C_6D_5CD_3$	7.09 (1); 7.00 (1); 6.98 (1); 2.09 (5)	137.9 (1); 129.4 (3); 128.3 (3); 125.5 (3); 20.4 (7)

* ppm from TMS

8.2 SOLVENT-INDUCED SHIFTS

Generally solvents chosen for NMR spectroscopy do not associate with the solute. However, solvents which are capable of both association and inducing differential chemical shifts in the solute are sometimes deliberately used to remove accidental chemical equivalence. The most useful solvents for the purpose of inducing *solvent-shifts* are aromatic solvents, in particular hexadeuterobenzene (C_6D_6), and the effect is called *aromatic solvent-induced shift* (ASIS). The numerical values of ASIS are usually of the order of 0.1–0.5 ppm and they vary with the molecule studied depending mainly on the geometry of the solvent/solute complexation.

8.3 DYNAMIC NMR SPECTROSCOPY – THE NMR TIME-SCALE

Two magnetic nuclei situated in different molecular environments must give rise to separate signals in the NMR spectrum, say $\Delta\nu$ Hz apart (Figure 8.1a). However, if some process interchanges the environments of the two nuclei at a rate (k) much faster than $\Delta\nu$ times per second, the two nuclei will be observed as a single signal at an averaged frequency (Figures 8.1d and 8.1e). When the rates (k) of the exchange process are comparable to $\Delta\nu$, *exchange broadened* spectra (*e.g.* Figures 8.1b, 8.1c and 8.1d) are observed. From the exchange broadened spectra, the rate constants for the exchange process (and hence the activation parameters $\Delta G^{\neq}$, $\Delta H^{\neq}$, $\Delta S^{\neq}$) can be derived. At the point where signals coalesce (Figure 8.1c) from being two separate signals to a single averaged signal, the rate constant for the exchange can be approximated as $k = \pi.\Delta\nu / \sqrt{2}$.

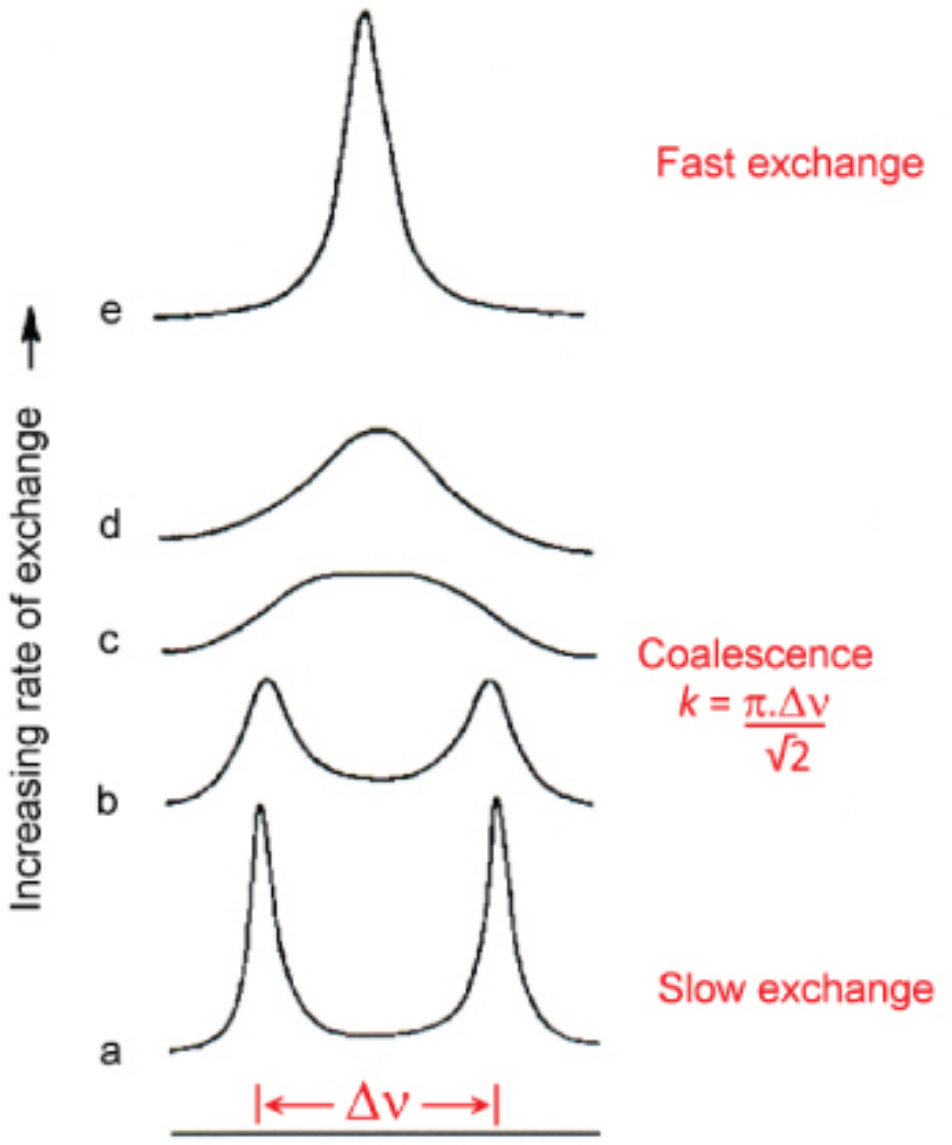


Figure 8.1 Schematic NMR Spectra of Two Exchanging Nuclei

In practice, a compound where an exchange process operates can give rise to a series of spectra of the type shown in Figure 8.1, if the NMR spectra are recorded at different temperatures. Changing the sample temperature alters the rate constant for the exchange (increasing the temperature increases the rate of an exchange process) and the spectra will have a different appearance depending on whether the rate constant, k (expressed in sec^{-1}) is large or small compared to the chemical shift differences between exchanging nuclei ($\Delta\nu$ expressed in Hz).

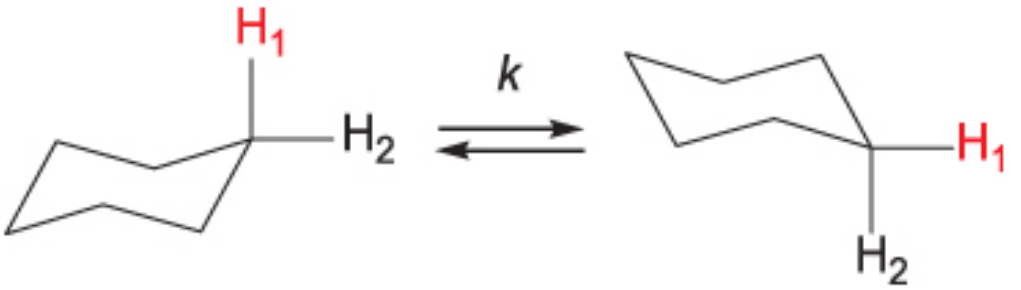
Molecules where there are exchange processes taking place may also give rise to different NMR spectra in different NMR spectrometers because $\Delta\nu$ depends on the strength of the magnetic field. An NMR spectrum which shows evidence of exchange broadening will tend to give a slow exchange spectrum if the spectrum is re-run in a spectrometer with a higher magnetic field.

The averaging effects of exchange apply to any dynamic process that takes place in a molecule (or between molecules). However, many processes occur at rates that are too fast or too slow to give rise to visible broadening of NMR spectra. The **NMR time-scale** happens to coincide with the rates of a number of common chemical processes that give rise to variation of the appearance of NMR spectra with temperature.

8.3.1 CONFORMATIONAL EXCHANGE PROCESSES

Conformational processes can give rise to exchange broadening in NMR spectra when a molecule exchanges between two or more conformations. Fortunately most conformational processes are so fast on the NMR time-scale that normally only averaged spectra are observed. In particular, in molecules which are not unusually sterically bulky, the rotation about C–C single bonds is normally fast on the NMR time-scale so, for example, the three hydrogen atoms of a methyl group appear as a singlet as a result of averaging of the various rotational conformers.

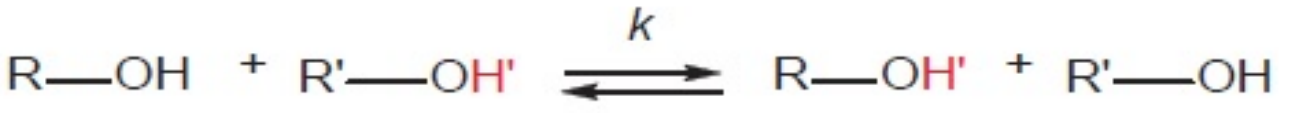
In molecules where there are very bulky groups, steric hindrance can slow the rotation about single bonds and give rise to broadening in NMR spectra. In molecules containing rings, the exchange between various ring conformations (*e.g.* chair–boat–chair) can exchange nuclei.



For example, cyclohexane gives a single averaged resonance in the ^{1}H NMR at room temperature (fast exchange), but separate signals are seen for the axial and equatorial hydrogens when spectra are acquired at very low temperature (slow exchange).

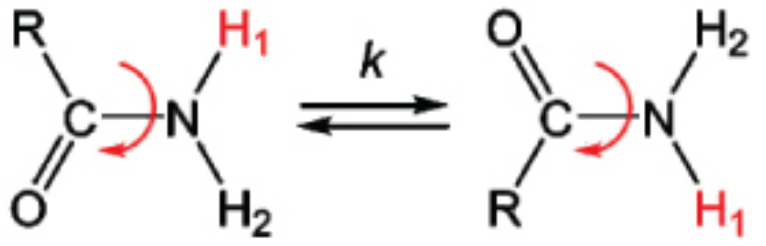
8.3.2 INTERMOLECULAR EXCHANGE OF LABILE PROTONS

Functional groups such as –OH, –COOH, –NH_2 and –SH have labile protons which exchange with each other in solution. Depending on the rate of exchange, the –OH protons of a mixture of two different alcohols may give rise to either an averaged signal (fast exchange) or to distinct separate signals (slow exchange). The rate of exchange depends on many factors including temperature, the polarity of the solvent, the concentrations of the solutes and the presence of acids or bases which can catalyse the exchange process.

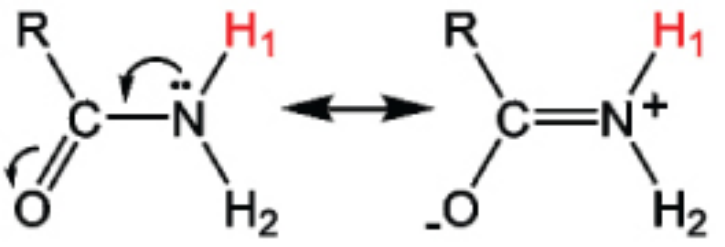


8.3.3 ROTATION ABOUT PARTIAL DOUBLE BONDS

Exchange broadening is frequently observed in amides as a result of restricted rotation about the N–C bond of the amide group.



The restricted rotation about amide bonds often occurs at a rate that gives rise to observable broadening in NMR spectra. At higher temperatures amide protons may appear as a single averaged resonance (fast exchange) and at lower temperatures the amide protons may resolve to separate distinct resonances (slow exchange).



The restricted rotation in amide bonds results from the partial double bond character of the C–N bond as a result of delocalisation of the lone pair of electrons on N.

8.4 THE EFFECT OF CHIRALITY

In an achiral solvent, enantiomers will give identical NMR spectra. However in a chiral solvent or in the presence of a chiral additive, enantiomers will have different spectra and this is frequently used to establish the

enantiomeric purity of compounds. The resonances of one enantiomer can be integrated against the resonances of the other to quantify the enantiomeric purity of a compound.

In molecules that contain a stereogenic centre, the NMR spectra can sometimes be more complex than would otherwise be expected. Groups such as $-CH_2-$ groups (or any $-CX_2-$ group such as $-C(Me)_2-$ or $-CR_2-$) require particular attention in molecules that contain a stereogenic centre. The carbon atom of a $-CX_2-$ group is termed a **prochiral carbon** if there is a stereogenic centre (a chiral centre) elsewhere in the molecule. A prochiral carbon atom is a carbon in a molecule that would be chiral if one of its substituents was replaced by a different substituent. From an NMR perspective, the important fact is that the presence of a stereogenic centre makes the substituents on a prochiral carbon atom **chemically non-equivalent**. So whereas the protons of a $-CH_2-$ group in an acyclic aliphatic compound would normally be expected to be equivalent and resonate at the same frequency in the ^1H NMR spectrum, *if there is a stereogenic centre in the molecule, each of the protons of the* $-CH_2-$ *group will appear at different chemical shifts.* Also, since they are non-equivalent, the coupling between the protons will be visible as a splitting, typically with a large coupling of about 15 Hz.

The effect of chirality is particularly important in the spectra of natural products including amino acids, proteins or peptides. Many molecules derived from natural sources contain a stereogenic centre and they are typically obtained as a single pure enantiomer. In these molecules, the resonances for all of the methylene groups (*i.e.* $-CH_2-$ groups) in the molecule will be complicated by the fact that the two protons of the methylene groups will be non-equivalent and there will be splittings due to the coupling between the methylene protons. Figure 8.2 shows the aliphatic protons in the ^1H NMR spectrum of the amino acid cysteine ($HSCH_2CHNH_3^+COO^-$). Cysteine has a stereogenic centre and the signals of the methylene group appear as separate signals at 3.18 and 2.92 ppm. Each of the methylene protons is split into a doublet of doublets due to coupling firstly to the other methylene proton and secondly to the proton on the α-carbon (Hα).

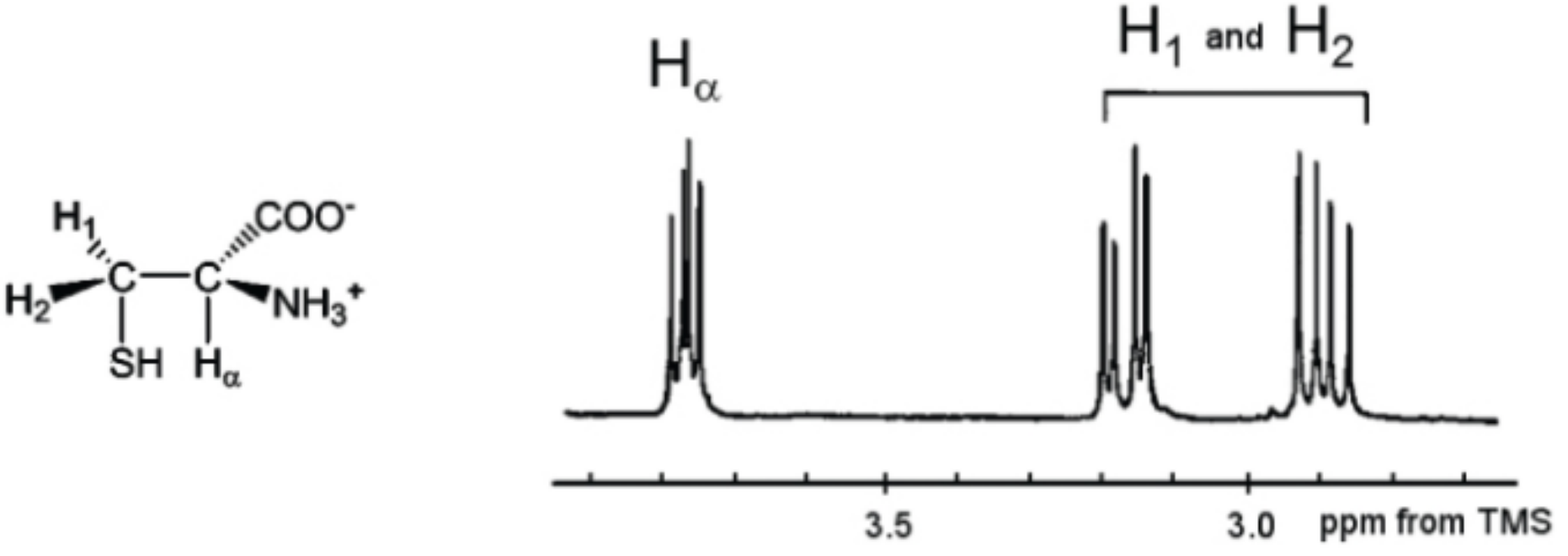


Figure 8.2 ^1H NMR Spectrum of the Aliphatic Region of Cysteine

8.5 THE NMR SPECTRA OF "OTHER NUCLEI"

^1H and ^{13}C NMR spectroscopy accounts for the overwhelming proportion of all NMR observations. However, there are many other isotopes which are NMR observable and they include the common isotopes ^{19}F, ^{31}P and ^2H. The NMR spectroscopy of these "other nuclei" has had surprisingly little impact on the solution of structural problems in organic chemistry and will not be discussed here. It is however important to be alert for the presence of other magnetic nuclei in the molecule, because they often cause additional multiplicity in ^1H and ^{13}C NMR spectra due to spin–spin coupling.

9
DETERMINING THE STRUCTURE OF ORGANIC COMPOUNDS FROM SPECTRA

The main purpose of this book is to present a collection of suitable problems to teach and train researchers in the most important methods of spectroscopy.

The problems are generally relatively straight forward and are arranged roughly in order of increasing complexity. No solutions to the problems are given. It is important to assign NMR spectra as completely as possible and to rationalise *all numbered peaks* in the mass spectrum as well as accounting for all of the significant features in the UV and IR spectra.

Collection of Spectra

The spectra presented in the problems were obtained under conditions stated on the individual problem sheets. Mass spectra were obtained on an AEI MS-9 spectrometer, a Hewlett Packard MS-Engine mass spectrometer or a Thermo Scientific DSQII quadrupole mass spectrometer. 100 MHz ^{1}H NMR spectra were obtained on a Varian XL-100 spectrometer, 200 MHz ^{1}H NMR spectra and 50 MHz ^{13}C NMR spectra were obtained on a Bruker AC-200 spectrometer, 400 MHz ^{1}H NMR spectra and 100 MHz ^{13}C NMR spectra were obtained on Bruker AMX-400 or DRX-400 spectrometers, and 500 and 600 MHz ^{1}H NMR spectra were obtained on a Bruker DRX-500 or AMX-600 or DRX-600 spectrometers.

Ultraviolet spectra were recorded on a Perkin-Elmer 402 UV spectrophotometer or Hitachi 150-20 UV spectrophotometer and infrared spectra on Perkin-Elmer 710B, Perkin-Elmer 1600 series, Nicolet Avatar 360 or Nicolet iS50 FTIR spectrometers.

The following collections are useful sources of spectroscopic data on organic compounds and some of the data for literature compounds have been derived from these collections:

a. http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng website maintained by the National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

b. http://webbook.nist.gov/chemistry/ website, which is the NIST Chemistry WebBook, NIST Standard Reference Database Number 69, June 2005, Eds. PJ Linstrom and WG Mallard.

c. E Pretch, P Bühlmann and C Affolter, "Structure Determination of Organic Compounds, Tables of Spectral Data", 3rd edition, Springer, Berlin 2000.

9.1 SOLVING PROBLEMS

The only way to acquire expertise in obtaining "organic structures from spectra" is to practice, and some students have found the following **general approach to solving structural problems by a combination of spectroscopic methods** helpful:

1. Perform all **routine operations:**
    a. Determine the molecular weight from the Mass Spectrum.
    b. Determine relative numbers of protons in different environments from the ^{1}H NMR spectrum.
    c. Determine the number of carbons in different environments and the number of quaternary carbons, methine carbons, methylene carbons and methyl carbons from the ^{13}C NMR spectrum.

d. Examine the problem for any additional data concerning composition and determine the molecular formula if possible. From the molecular formula, determine the degree of unsaturation.

e. Determine the molar absorbance in the UV spectrum, if applicable.

2. Examine each spectrum (IR, mass spectrum, UV, ^{13}C NMR, ^{1}H NMR) in turn for obvious **structural elements:**

   a. Examine the IR spectrum for the presence or absence of groups with diagnostic absorption bands *e.g.* carbonyl groups, hydroxyl groups, NH groups, C≡C or C≡N, *etc.*

   b. Examine the mass spectrum for typical fragments *e.g.* $PhCH_2-$, CH_3CO-, CH_3- *etc.*

   c. Examine the UV spectrum for evidence of conjugation, aromatic rings *etc.*

   d. Examine the ^{1}H NMR spectrum for CH_3- groups, CH_3CH_2- groups, aromatic protons, $-CH_nX$, exchangeable protons *etc.*

3. Write down all structural elements you have determined. Note that some are monofunctional (*i.e.* must be end-groups, such as $-CH_3$, $-C\equiv N$, $-NO_2$) whereas some structural elements are bifunctional (*e.g.* $-CO-$, $-CH_2-$, $-COO-$), or trifunctional (*e.g.* CH, N).

   Add up the atoms of each structural element and compare the total with the molecular formula of the unknown. The difference (if any) may give a clue to the nature of the undetermined structural elements (*e.g.* an ether oxygen). At this stage, elements of symmetry may become apparent.

4. Try to assemble the structural elements. Note that **there may be more than one way of fitting them together.** Spin–spin coupling data or information about conjugation may enable you to make a definite choice between possibilities.

5. Return to each spectrum (IR, UV, mass spectrum, ^{13}C NMR, ^{1}H NMR) in turn and *rationalise all major features* (especially all major fragments in the mass spectrum and all features of the NMR spectra) in terms of your proposed structure. Ensure that no spectral features are inconsistent with your proposed structure.

Note on the use of data tables. Tabulated data typically give characteristic absorptions or chemical shifts for representative compounds and these may not correlate *exactly* with those from an unknown compound. The data contained in data tables should always be used indicatively (not mechanically).

9.2 WORKED EXAMPLES

This section works through three problems from the text to indicate a reasonable process for obtaining the structure of the unknown compound from the spectra provided. It should be emphasised that the logic used here is by no means the only way to arrive at the correct solution but it does provide a systematic approach to obtaining structures by assembling structural fragments identified by each type of spectroscopy.

PROBLEM 117

(1) Perform all Routine Operations

a. From the molecular ion, the molecular weight is 198/200. The molecular ion has two peaks of equal intensity separated by two mass units. This is the characteristic pattern for a compound containing one bromine atom.

b. The molecular formula is $C_9H_{11}Br$ so one can determine the degree of unsaturation (see Section 1.3). Replace the Br by H to give an effective molecular formula of C_9H_{12} (C_nH_m) which gives the degree of unsaturation as $(n - m/2 + 1) = 9 - 6 + 1 = 4$. The compound must contain the equivalent or 4 π bonds and/or

rings. This degree of unsaturation would be consistent with one aromatic ring (with no other elements of unsaturation).

c. The total integral <u>across all peaks</u> in the ^{1}H spectrum is 55 mm. From the molecular formula, there are 11 protons in the structure so this corresponds to 5 mm per proton. The relative numbers of protons in different environments:

δ ^{1}H (ppm)	Integral (mm)	Relative No. of hydrogens (rounded)
~ 7.25	10	2 (2H)
~ 7.15	15	3 (3H)
~ 3.3	10	2 (2H)
~ 2.7	10	2 (2H)
~ 2.1	10	2 (2H)

Note that this analysis gives a total of 2+3+2+2+2 = 11 protons which is consistent with the molecular formula provided.

d. From the ^{13}C spectrum there are 7 carbon environments: 4 carbons are in the typical aromatic/olefinic chemical shift range and 3 carbons in the aliphatic chemical shift range. The molecular formula is $C_9H_{11}Br$ so there must be an element (or elements) of symmetry to account for the 2 carbons not apparent in the ^{13}C spectrum.

e. From the ^{13}C DEPT spectrum there are 3 CH resonances in the aromatic/olefinic chemical shift range and 3 CH_2 carbons in the aliphatic chemical shift range.

f. The same information in *(d)* and *(e)* is obtained from the ^{1}H–^{13}C *me*-HSQC spectrum where the 5-proton CH ^{1}H resonances at δ 7.25 and 7.15 correlate to the 3 ^{13}C resonances at δ 126–128.5 and the 3 CH_2 ^{1}H resonances at δ 3.3, 2.7 and 2.1 correlate to the ^{13}C resonances at δ 33–34. There is no correlation to the ^{13}C signal at δ 140 indicating it is due to a quaternary carbon.

g. Calculate the extinction coefficient from the UV spectrum:

$$\varepsilon_{255} = \frac{199 \times 0.95}{0.53 \times 1.0} = 357$$

(2) Identify any <u>Structural Elements</u>

a. There is no useful additional information from the infrared spectrum.

b. In the mass spectrum there is a strong fragment at *m/e* = 91 and this indicates a possible Ph–CH_2– group.

c. The ultraviolet spectrum shows a typical benzenoid absorption without further conjugation or auxochromes. This would also be consistent with the Ph–CH_2– group.

d. From the ^{13}C NMR spectrum, there is one resonance in the $^{13}C\{^{1}H\}$ spectrum which does not appear in the ^{13}C DEPT spectrum. This indicates one quaternary (non-protonated) carbon. There are 4 ^{13}C resonances in the aromatic region, 3 CH and 1 quaternary carbon, which is typical of a monosubstituted benzene ring.

e. From the ^{1}H NMR spectrum, there are 5 protons near δ ~7.2 which strongly suggests a monosubstituted benzene ring, consistent with *(b)*, *(c)* and *(d)*. The Ph–CH_2– group is confirmed.

The triplet at approximately δ 3.3 of intensity 2H suggests a $-CH_2-$ group. The downfield chemical shift suggests a $-CH_2-X$ group with X being an electron withdrawing group (probably bromine). The triplet splitting indicates that there must be another $-CH_2-$ as a neighbouring group. In the expanded proton spectrum 0.1 ppm = 6 mm and since this is a 400 MHz NMR spectrum, therefore 40 Hz = 6 mm. The triplet spacing is measured to be 1 mm *i.e.* 7 Hz and this is typical of vicinal coupling ($^3J_{HH}$).

The triplet at approximately δ 2.8 of intensity 2H in the ^1H NMR spectrum suggests a $-CH_2-$ with one $-CH_2-$ as a neighbour. The spacing of this triplet is almost identical with that observed for the triplet near δ 3.3.

The quintet at approximately δ 2.2 of intensity 2H has the same spacings as observed in the triplets near δ 2.8 and δ 3.3. This signal is consistent with a $-CH_2-$ group coupled to *two* flanking $-CH_2-$ groups. A sequence $-CH_2-CH_2-CH_2-$ emerges in agreement with the ^{13}C data.

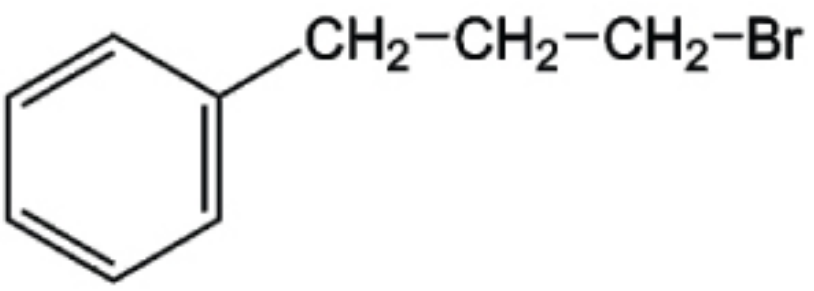
Thus the structural elements are:

1. $Ph-CH_2-$
2. $-CH_2-CH_2-CH_2-$
3. $-Br$

(3) Assemble the Structural Elements

Clearly there must be some common segments in these structural elements since the total number of C and H atoms adds to more than is indicated in the molecular formula. One of the CH_2 groups in structural element (2) must be the benzylic CH_2 group of structural element (1).

The structural elements can be assembled in only one way and this identifies the compound as 1-bromo-3-phenylpropane.



(4) Check that the answer is consistent with all spectra.

There are no additional strong fragments in the mass spectrum.

In the infrared spectrum there are two strong absorptions between 600 and 800 cm^{-1} which are consistent with the C–Br stretch of alkyl bromide.

PROBLEM 146

(1) Perform all Routine Operations

a. The molecular formula is given as $C_9H_{11}NO_2$. The molecular ion in the mass spectrum gives the molecular weight as 165.

b. From the molecular formula, $C_9H_{11}NO_2$, determine the degree of unsaturation (see Section 1.3). Ignore the O atoms and ignore the N and remove one H to give an effective molecular formula of C_9H_{10} (C_nH_m) which gives the degree of unsaturation as $(n - m/2 + 1) = 9 - 5 + 1 = 5$. The compound must contain the equivalent

or 5 π bonds and/or rings. This degree of unsaturation would be consistent with one aromatic ring with one other ring or double bond.

c. The total integral across all peaks in the ^{1}H spectrum is 97 mm. From the molecular formula, there are 11 protons in the structure so this corresponds to 8.8 mm per proton.

The relative numbers of protons in different environments:

δ ^{1}H (ppm)	Integral (mm)	Relative No. of hydrogens (rounded)
~ 7.9	17.5	2 (2H)
~ 6.6	17.5	2 (2H)
~ 4.3	18	2 (2H)
~ 4.0	17.5	2 (2H)
~ 1.4	26.5	3 (3H)

Note that this analysis gives a total of 2+2+2+2+3 = 11 protons which is consistent with the molecular formula provided.

d. From the ^{13}C spectrum there are 7 carbon environments: 4 carbons are in the typical aromatic/olefinic chemical shift range, 2 carbons in the aliphatic chemical shift range and 1 carbon at low field (167 ppm) characteristic of a carbonyl carbon. The molecular formula is given as $C_9H_{11}NO_2$ so there must be an element (or elements) of symmetry to account for the 2 carbons not apparent in the ^{13}C spectrum.

e. From the ^{13}C DEPT spectrum there are 2 × CH resonances in the aromatic/olefinic chemical shift range, 1 × $-CH_2-$ and 1 × $-CH_3$ carbon in the aliphatic chemical shift range.

f. The same information in *(d)* and *(e)* is obtained from the ^{1}H–^{13}C *me*-HSQC spectrum where the 2 CH ^{1}H resonances at δ 7.9 and 6.6 correlate to ^{13}C resonances at δ 131 and 113 respectively, the CH_2 ^{1}H resonance at δ 4.3 correlates to the ^{13}C resonance at δ 60 and the CH_3 ^{1}H resonance at δ 1.4 correlates to the ^{13}C resonance at δ 14. There are no correlations to the ^{13}C signals at δ 120, 152 and 167 indicating these are quaternary carbons. Note that the broad ^{1}H signal at δ 4.0 does not correlate to any ^{13}C signal.

g. Calculate the extinction coefficient from the UV spectrum:

$$\varepsilon_{292} = \frac{165 \times 0.90}{0.0172 \times 0.5} = 17{,}267$$

(2) Identify the Structural Elements

a. From the infrared spectrum, there is a strong absorption at 1680 cm^{-1} and this is probably a C=O stretch at an unusually low frequency (such as an amide or strongly conjugated ketone).

b. In the mass spectrum there are no obvious fragment peaks, but the difference between 165 (M) and 137 = 28 suggests loss of ethylene (CH_2=CH_2) or CO.

c. In the UV spectrum, the presence of extensive conjugation is apparent from the large extinction coefficient (ε ≈ 17,000).

d. In the ^{1}H NMR spectrum:

The appearance of a 4 proton symmetrical pattern in the aromatic region near δ 7.9 and 6.6 is strongly indicative of a *para* disubstituted benzene ring. This is confirmed by the presence of two quaternary ^{13}C resonances at δ 152 and 120 in the ^{13}C spectrum and two CH ^{13}C resonances at δ 131 and 113.

Note that the presence of a *para* disubstituted benzene ring also accounts for the element of symmetry identified above. The triplet of 3H intensity at approximately δ ~ 1.4 and the quartet of 2H intensity at approximately δ ~ 4.3 have the same spacings. On this 400 MHz NMR spectrum, 400 Hz (1 ppm) corresponds to 90 mm so the measured splitting of 1.5 mm corresponds to a coupling of about 6.7 Hz that is typical of a vicinal coupling constant. The triplet and quartet clearly correspond to an ethyl group and the downfield shift of the CH_2 resonance (δ ~ 4.3) indicates that it must be attached to a heteroatom so this is possibly an $-O-CH_2-CH_3$ group.

e. In the ^{13}C NMR spectrum:

The signals at δ 14 ($-CH_3$) and δ 60 ($-CH_2-$) in the ^{13}C NMR spectrum confirm the presence of the ethoxy group and the 4 resonances in the aromatic region (2 × CH and 2 × quaternary carbons) confirm the presence of a *p*-disubstituted benzene ring.

The quaternary carbon signal at δ 167 in the ^{13}C NMR spectrum indicates an ester or an amide carbonyl group.

The following structural elements have been identified so far:

C_6H_4

ethoxy group C_2H_5O

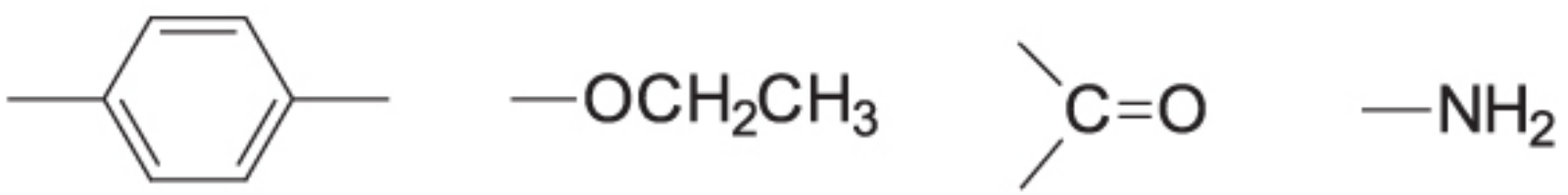
carbonyl group CO

In total this accounts for $C_9H_9O_2$ and this differs from the given molecular formula only by NH_2. The presence of an $-NH_2$ group is confirmed by the exchangeable signal at δ 4.0 in the ^1H NMR spectrum and the characteristic N–H stretching vibrations at 3200–3350 cm^{-1} in the IR spectrum.

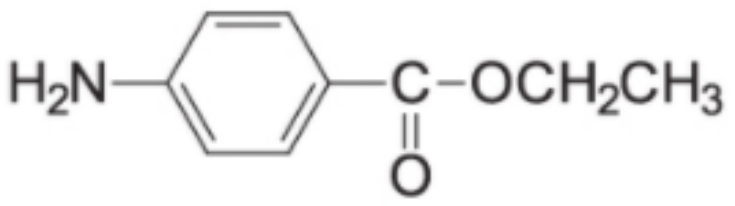
f. The presence of one aromatic ring plus the double bond in the carbonyl group is consistent with the calculated degree of unsaturation – there can be no other rings or multiple bonds in the structure.

(3) Assemble the Structural Elements

The structural elements:

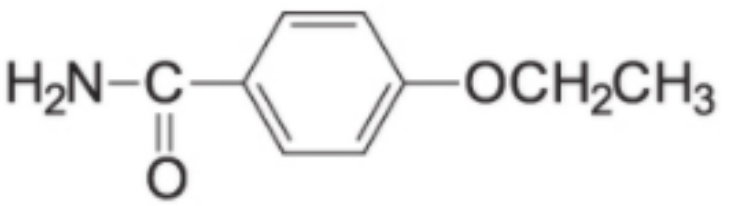


can be assembled as either:



(A)

or

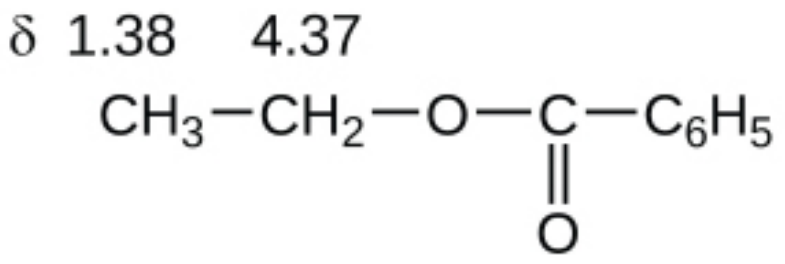


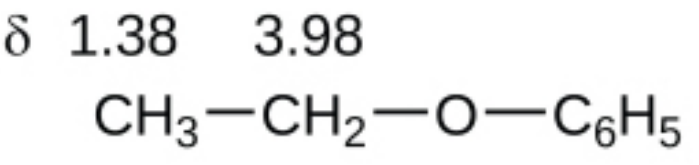
(B)

These possibilities can be distinguished because:

a. The **amine** $-NH_2$ group in (A) is "exchangeable with D_2O" as stated in the data but the **amide** $-NH_2$ group in (B) would require heating or base catalysis.

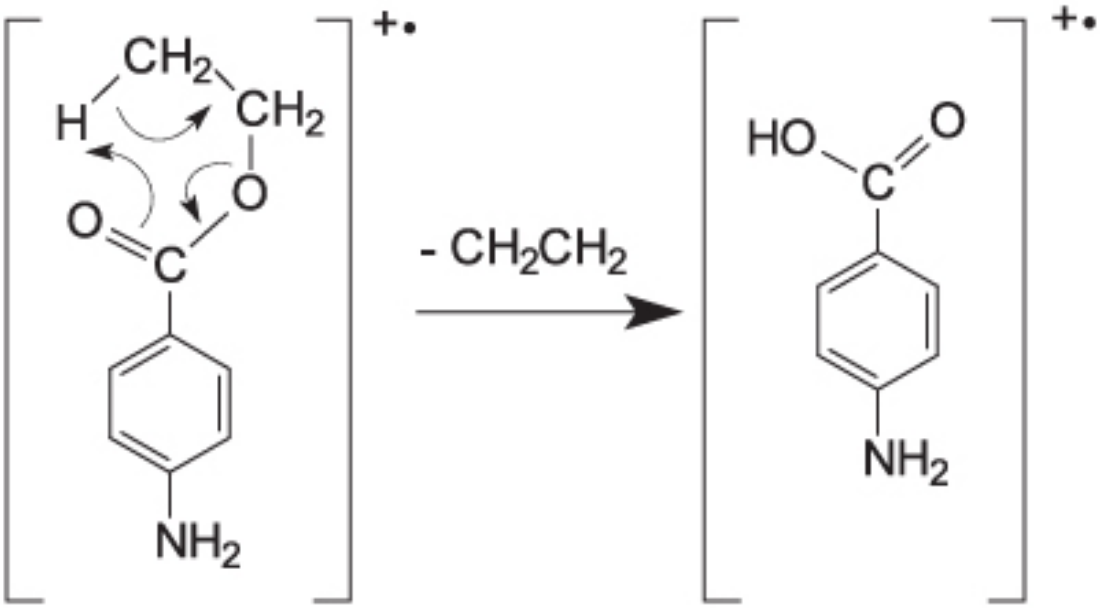
b. From Table 5.5, the ^1H chemical shift of the $-O-CH_2-$ group fits better to the ester structure in (A) than the phenoxy ether structure in (B) given the models:



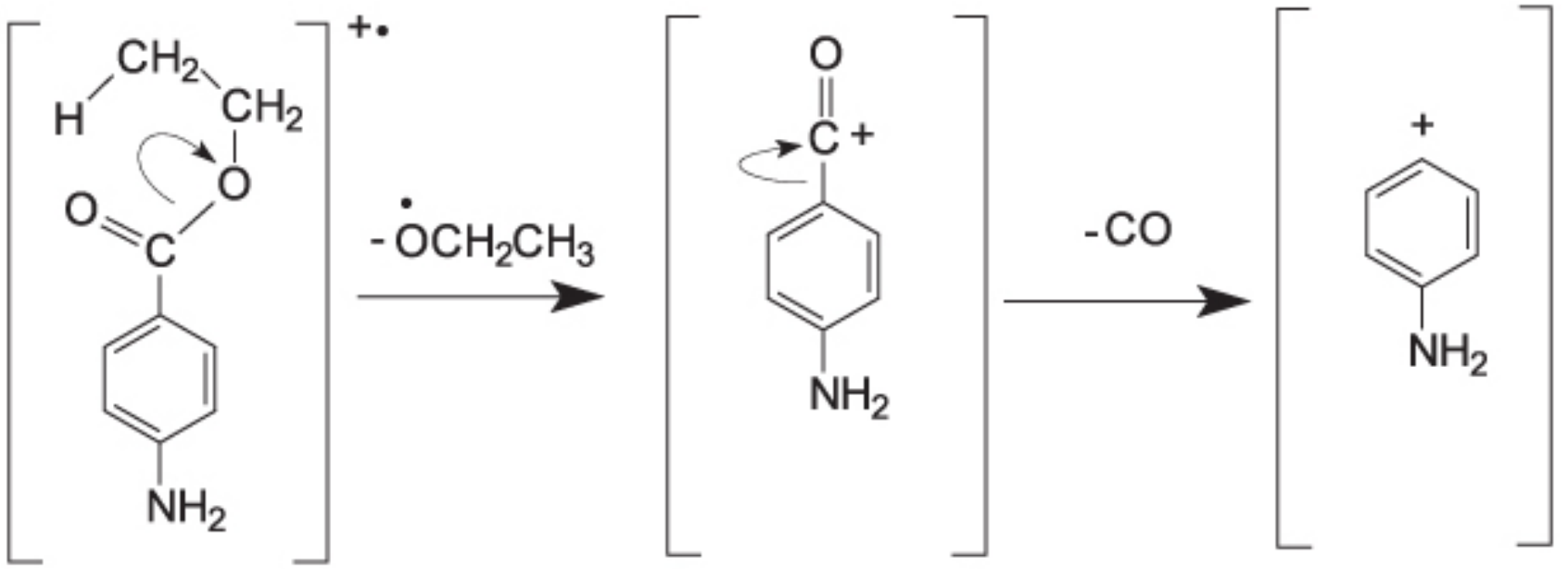


c. The ^{13}C chemical shifts of the quaternary carbons in the aromatic ring are at approximately 152 and 119 ppm. From Table 6.8, these shifts would be consistent with a $-NH_2$ and an ester substituent on an aromatic ring (structure A) but for an –OEt substituent (as in structure B), the *ipso* carbon would be expected at much lower field (between 160 and 170 ppm). The ^{13}C chemical shifts are consistent with structure (A).

d. The fragmentation pattern in the mass spectrum shown below fits (A) but not (B). The key fragments at *m/e* 137, 120 and 92 can be rationalised only from (A). This is decisive and ethyl 4-aminobenzoate (A) must be the correct answer.



m/z = 165 *m/z* = 137



m/z = 165 *m/z* = 120 *m/z* = 92

PROBLEM 77

(1) Perform all Routine Operations

a. From the molecular formula, $C_8H_{14}O_3$, determine the degree of unsaturation. Ignore the O atoms to give an effective molecular formula of C_8H_{14} (C_nH_m) which gives the degree of unsaturation as $(n - m/2 + 1) = 8 - 7 + 1 = 2$. The compound must contain the equivalent of 2 π bonds and/or rings.

b. The total integral across all peaks in the ^1H spectrum is 60.5 mm. From the molecular formula, there are 14 protons in the structure so this corresponds to 4.3 mm per proton.

Determine the relative numbers of protons in different environments.

δ ^1H (ppm)	Integral (mm)	Relative No. of hydrogens (rounded)
~ 4.6	8.5	2 (2H)

~ 2.2	12.5	2.9 (3H)
~ 1.3	39.5	9.2 (9H)

Note that this analysis gives a total of 2+3+9 = 14 protons which is consistent with the molecular formula provided.

c. From the ^{13}C spectrum there are 6 carbon environments: 4 carbons are in the typical aliphatic chemical shift range and 2 carbons at low field (202 and 178 ppm) characteristic for carbonyl carbons.

d. From the ^{13}C DEPT spectrum there are 2 CH_3 and 1 CH_2 carbons in the aliphatic chemical shift range.

e. The same information in *(c)* and *(d)* is obtained from the ^{1}H–^{13}C *me*-HSQC spectrum where the 2-proton CH_2 ^{1}H resonance at δ 4.6 correlates to the ^{13}C resonance at δ 68, the 3-proton CH_3 ^{1}H resonance at δ 2.2 correlates to the ^{13}C resonance at δ 26 and the 9-proton CH_3 ^{1}H resonance at δ 1.3 correlates to the ^{13}C resonance at δ 27. There are no correlations to the ^{13}C signals at δ 202, 178 and 39, indicating they are due to quaternary carbons.

(2) Identify any Structural Elements

a. From the infrared spectrum, there is a strong absorption at 1726 cm^{-1} for a C=O stretch.

b. From the ^{13}C NMR spectrum, the quaternary carbon resonance at δ 202 indicates a ketone group while the quaternary carbon resonance at δ 178 indicates an ester group. The presence of both ketone and ester groups account for all three O atoms in the molecular formula and the 2 degrees of unsaturation.

c. From the ^{1}H and ^{13}C NMR spectra, the remaining quaternary carbon at δ 39 and the 9-proton singlet at δ 1.3 indicate a *tert*-butyl group (–$C(CH_3)_3$). This can also be inferred from the ^{1}H–^{13}C HMBC spectrum where the 9-proton ^{1}H signal at δ 1.3 correlates to the quaternary carbon signal at δ 39. Note that the apparent 1-bond correlation of the ^{1}H signal at δ 1.3 to the ^{13}C signal at δ 27 in the HMBC spectrum arises from the $^{3}J_{HC}$ interaction of the protons of one of the methyl groups with the chemically equivalent carbon that is three bonds away.

d. From the ^{1}H NMR spectrum, the downfield chemical shift for the CH_2 protons at δ 4.6 indicates it must be attached to an O atom. Note that the ^{1}H signals at δ 4.6 and 2.2 are singlets which indicates the –OCH_2– and –CH_3 groups are isolated from one another.

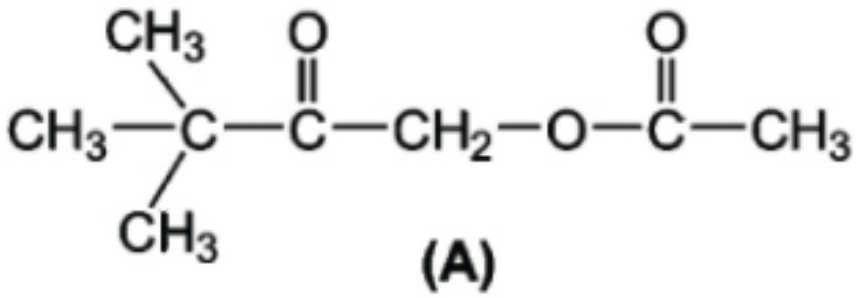
Thus the structural elements are:

1. –OCH_2–
2. –CH_3
3. –$C(CH_3)_3$
4. –C(=O)–
5. –C(=O)O–

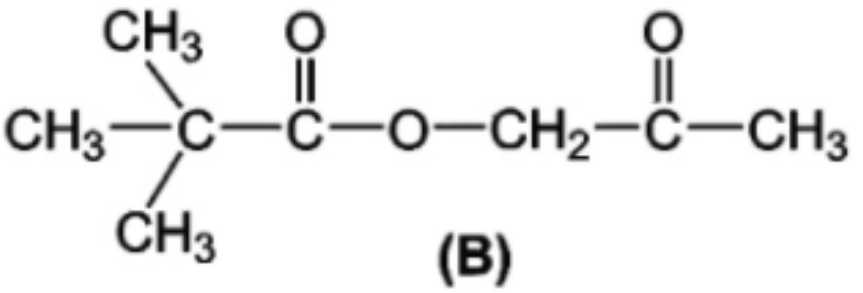
(3) Assemble the Structural Elements

Clearly there must be common segments in these structural elements since the total number of O atoms adds to more than is indicated in the molecular formula. The –OCH_2– group in structural element (1) must be part of the ester group of structural element (5).

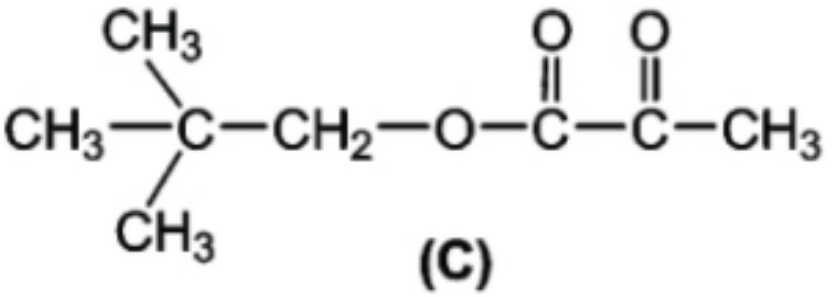
The structural elements can be assembled in three possible ways:



(A)



(B)



(C)

These possibilities can be distinguished by analysing the HMBC spectrum.

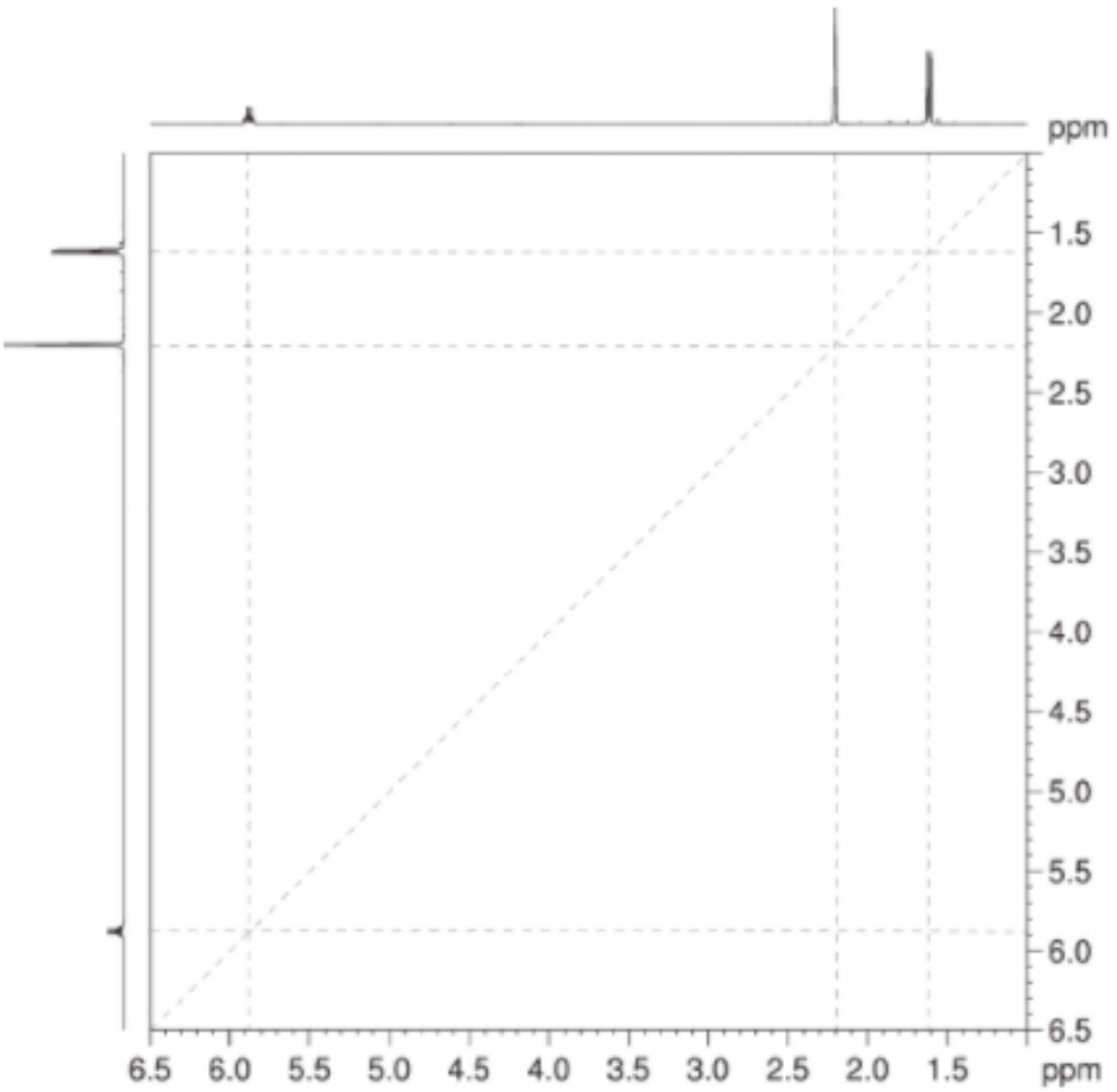
a. The CH_2 ^1H signal at δ 4.6 has correlations to both the ester carbon signal at δ 178 and the ketone carbon signal at δ 202. There are also no correlations from the CH_2 ^1H signal to the carbon signals of the *tert*-butyl group which excludes structure **C**. The carbonyl signals would also be expected to be lower in structure **C** due to conjugation which is not the case here.

b. The CH_3 ^1H signal at δ 2.2 has correlations to the CH_2 carbon signal at δ 68 and the ketone carbon signal at δ 202 which fits with structure B.

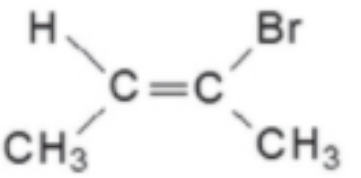
c. The ^1H signal of the CH_3 from the *tert*-butyl group at δ 1.3 has a correlation to the ester carbon signal at δ 178 which also fits with structure B.

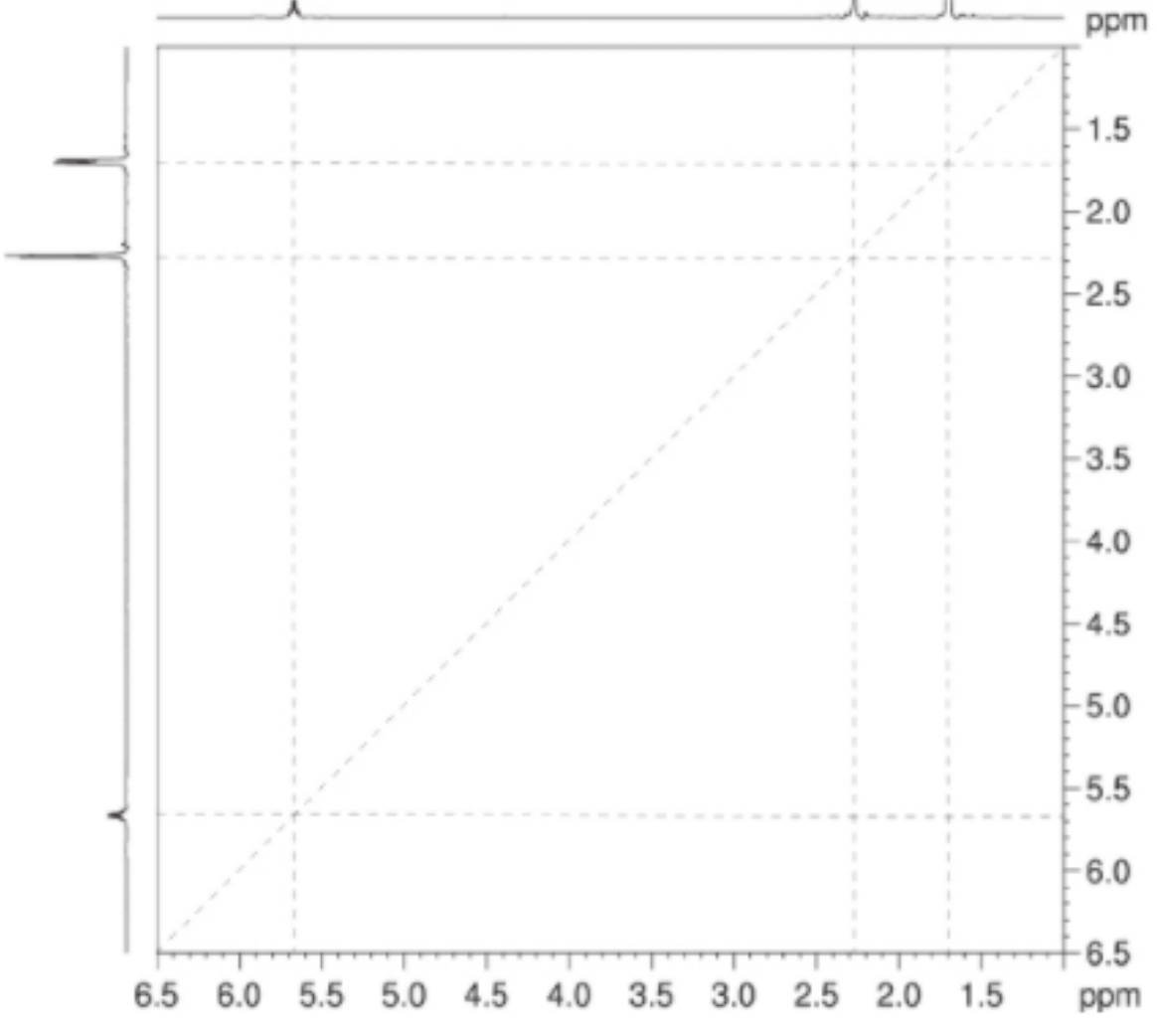
(4) Check that the answer is consistent with all spectra.

In the mass spectrum there is a strong fragment at *m/e* 57 which is consistent with both $-C(CH_3)_3$ and CH_3COCH_2- groups.

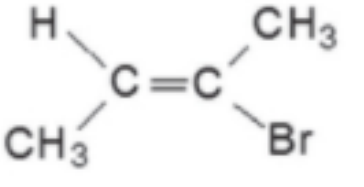


^{1}H NOESY spectrum of *(E)*-2-bromo-2-butene (400 MHz in $CDCl_3$ solution)





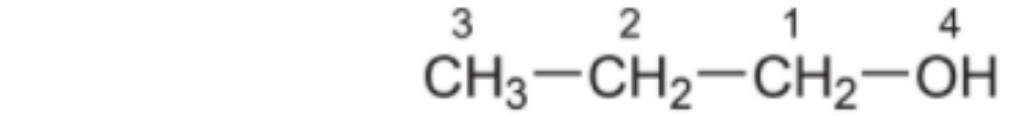
^{1}H NOESY spectrum of *(Z)*-2-bromo-2-butene (400 MHz in $CDCl_3$ solution)



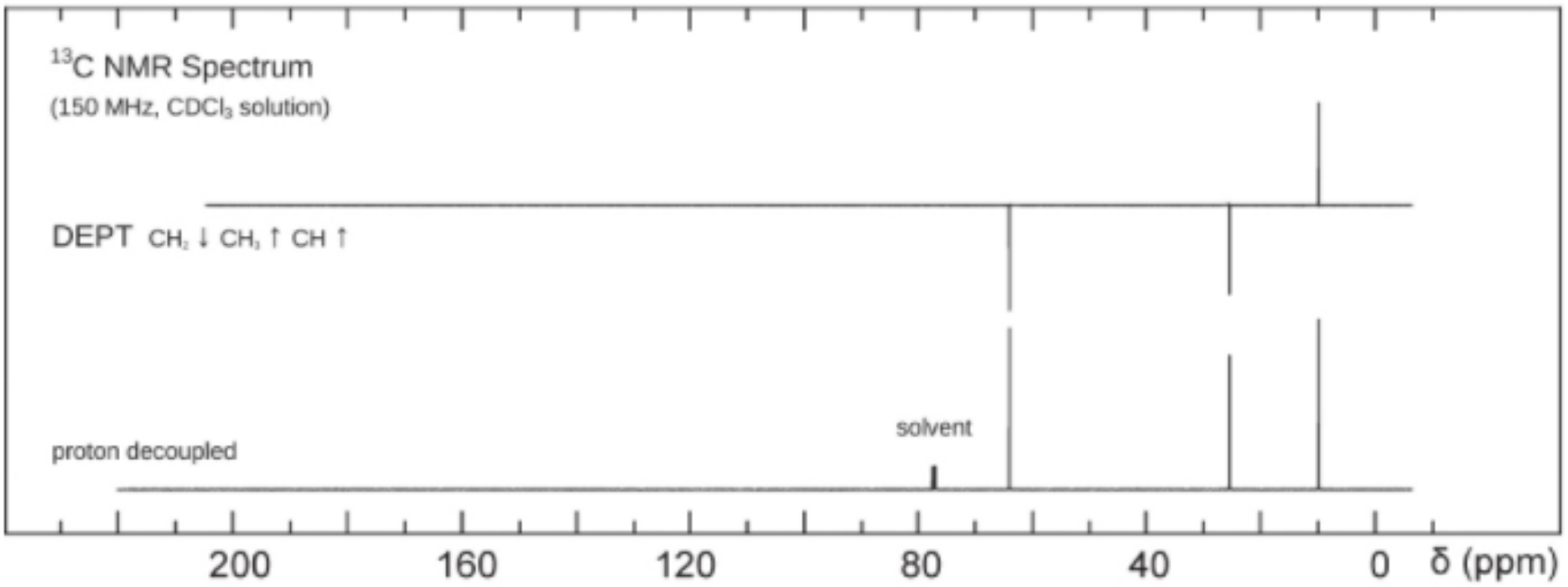
Problem 9

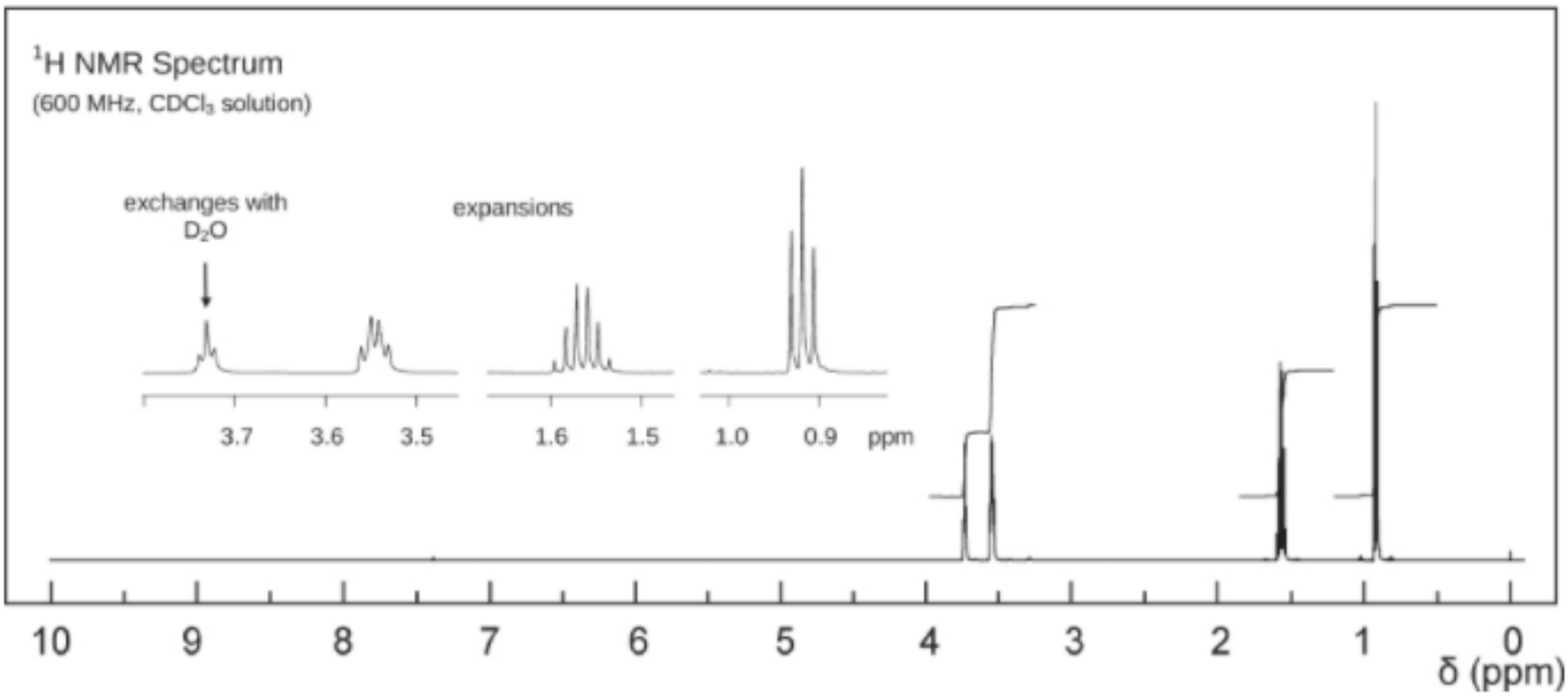
The ^{1}H and proton-decoupled ^{13}C NMR spectra of 1-propanol (C_3H_8O) recorded in $CDCl_3$ solution at 298 K and 600 MHz are given below. The ^{1}H NMR spectrum has signals at δ 0.92, 1.56, 3.54 and 3.73 ppm. The ^{13}C spectrum has signals at δ 10.0, 25.6 and 64.1 ppm.

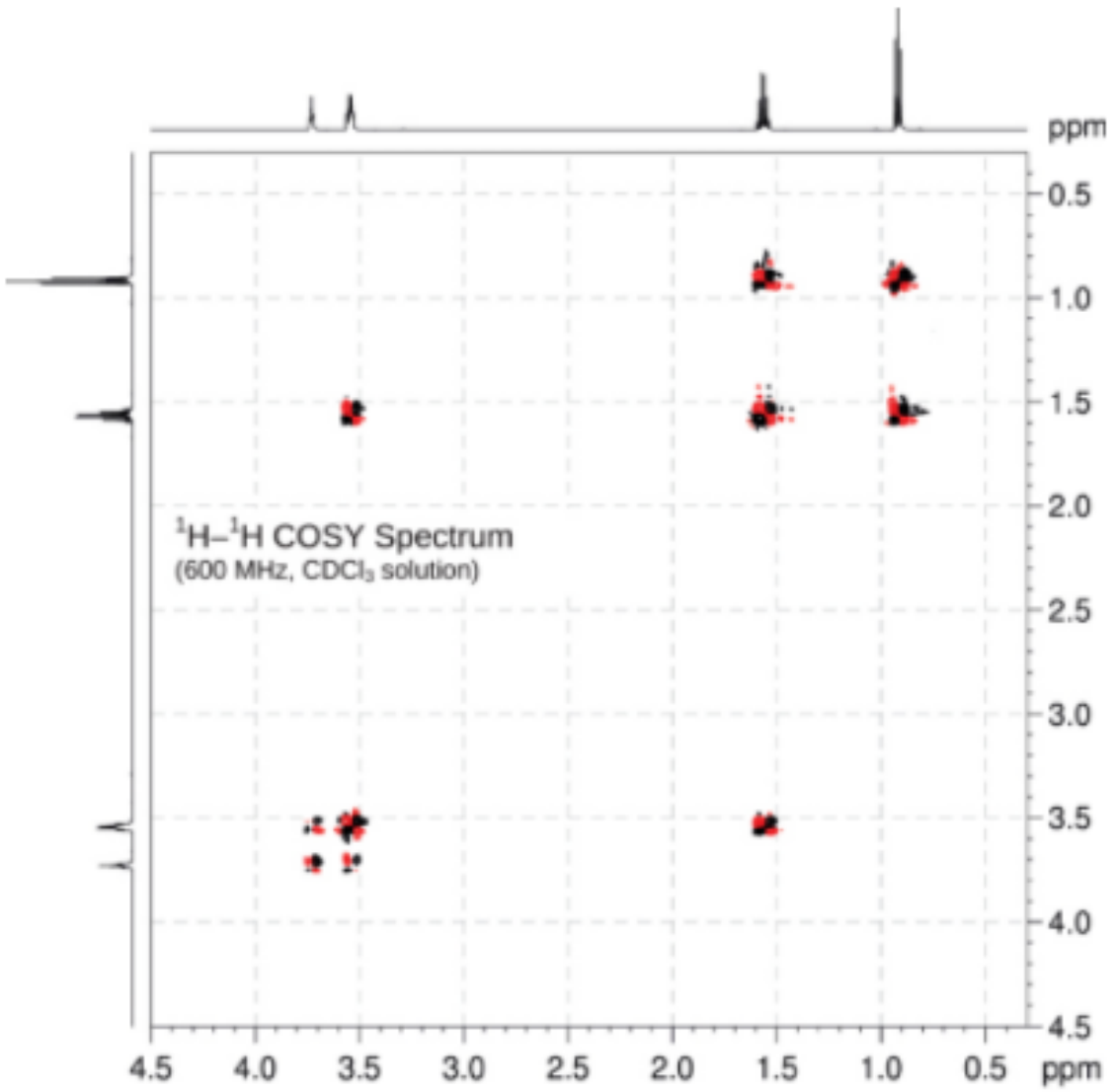
The 2-dimensional ^{1}H–^{1}H COSY spectrum and the ^{1}H–^{13}C *me*-HSQC correlation spectrum are given on the following page. From the COSY spectrum, assign the proton spectrum and then use the C–H correlation spectrum to assign the ^{13}C spectrum, *i.e.* determine the chemical shift corresponding to each of the protons and each of the carbons in the molecule.



Proton	Chemical Shift (δ) in ppm	Carbon	Chemical Shift (δ) in ppm
H1		C1	
H2		C2	
H3		C3	
H4			






ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
^{1}H–^{1}H COSY Spectrum
(600 MHz, $CDCl_3$ solution)
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

ppm
10
20
30
40
50
60
70
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

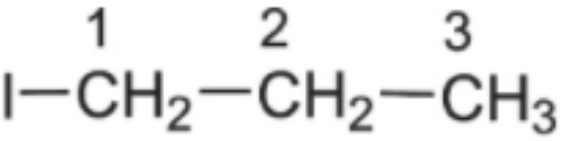
Problem 10

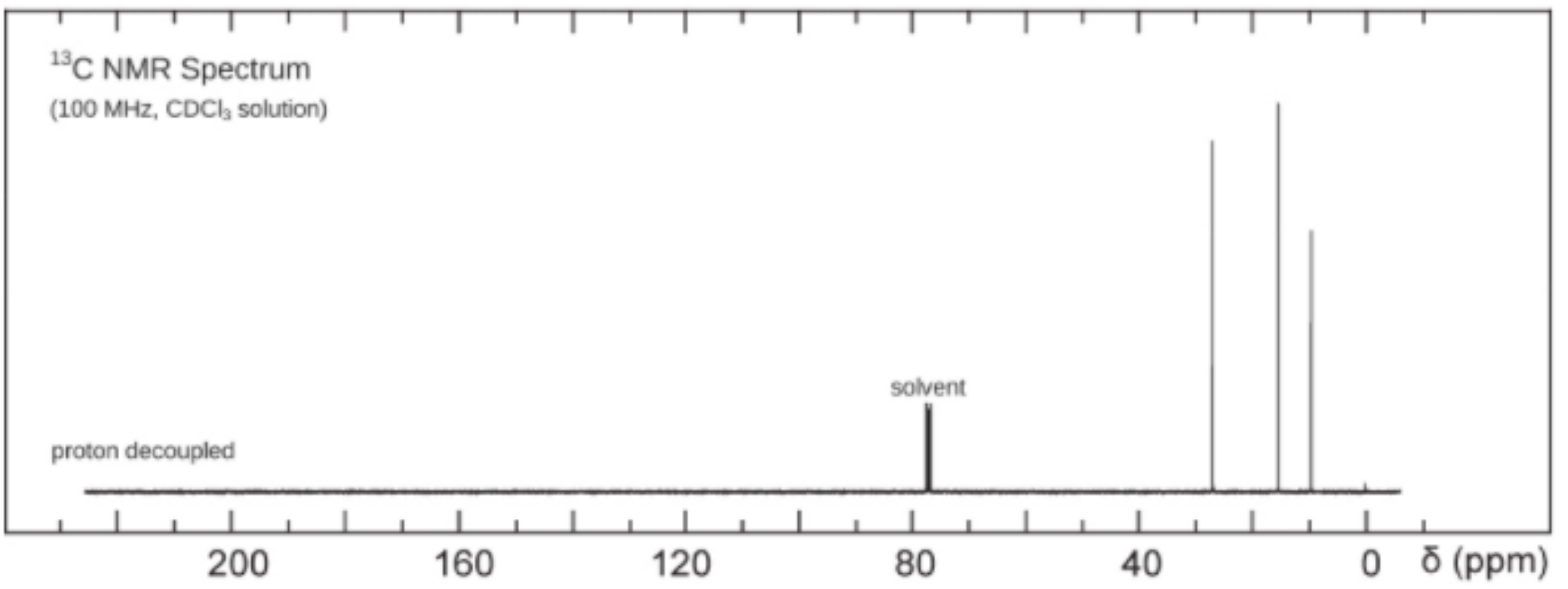
The ^{1}H and proton-decoupled ^{13}C NMR spectra of 1-iodopropane (C_3H_7I) recorded in $CDCl_3$ solution at 298 K and 400 MHz are given below.

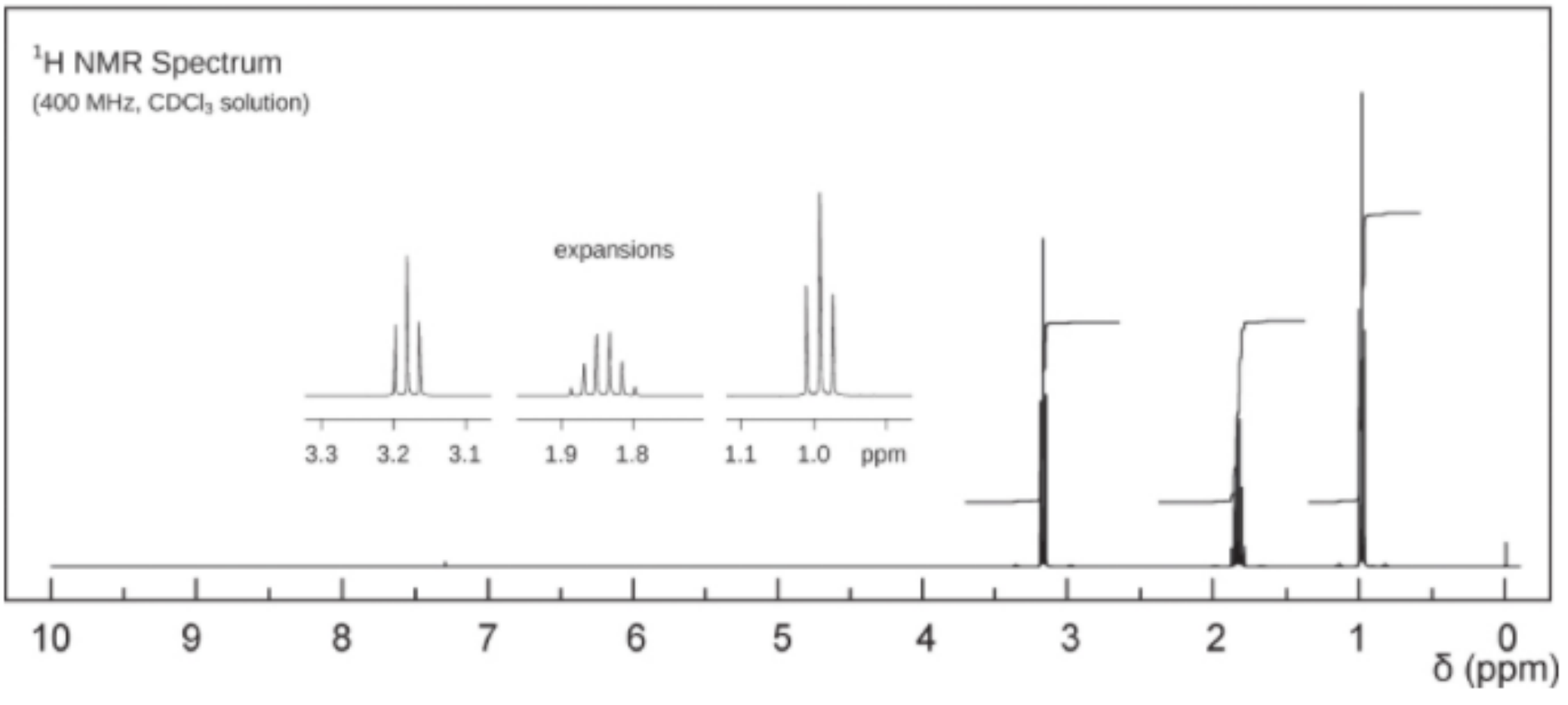
The ^{1}H NMR spectrum has signals at δ 0.99 (H_3), 1.84 (H_2) and 3.18 (H_1) ppm.

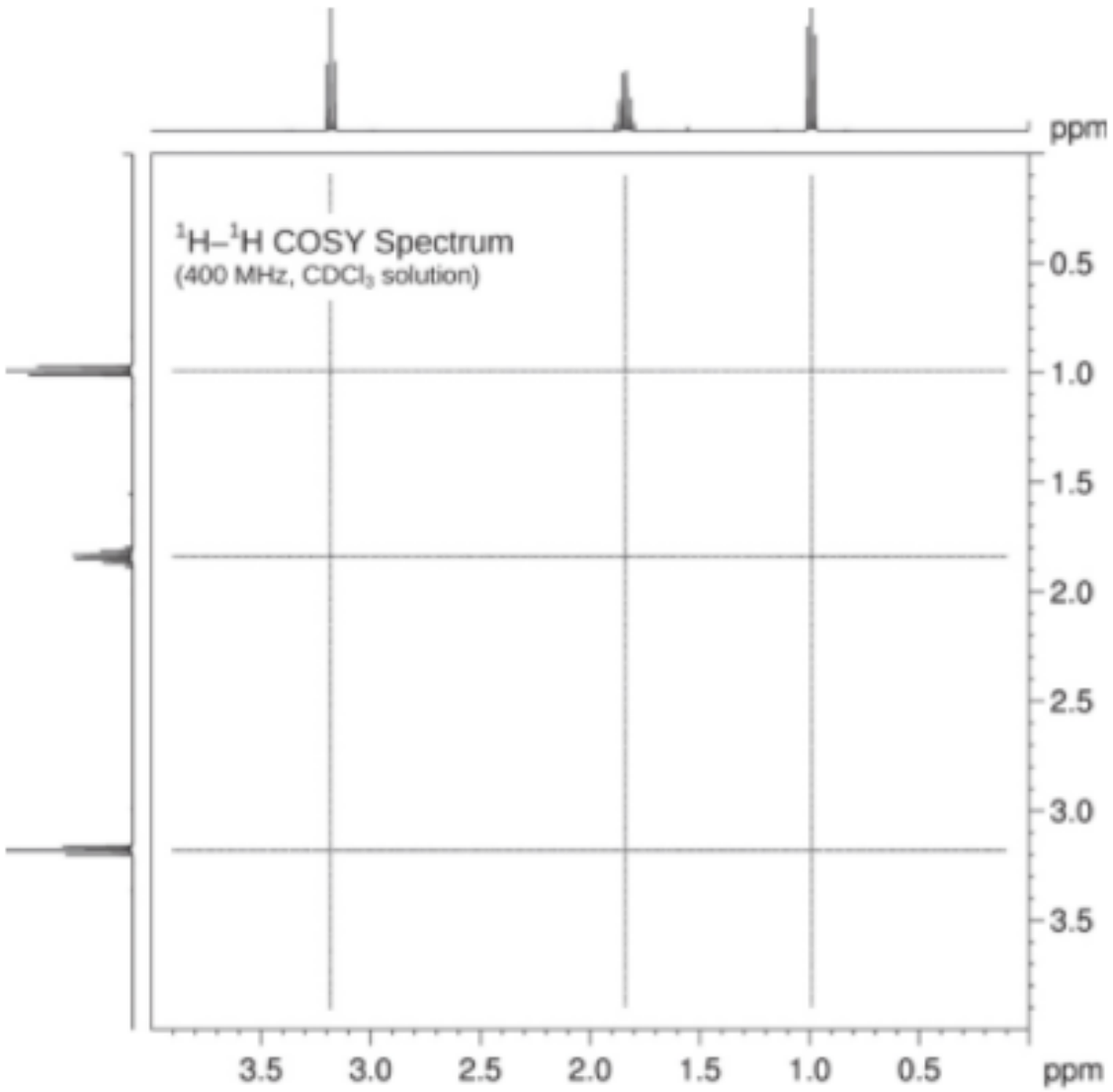
The ^{13}C NMR spectrum has signals at δ 9.6 (C_1), 15.3 (C_3) and 26.9 (C_2) ppm.

Use this information to produce schematic diagrams of the COSY, *me*-HSQC and HMBC spectra, showing where all of the cross-peaks and diagonal peaks would be.

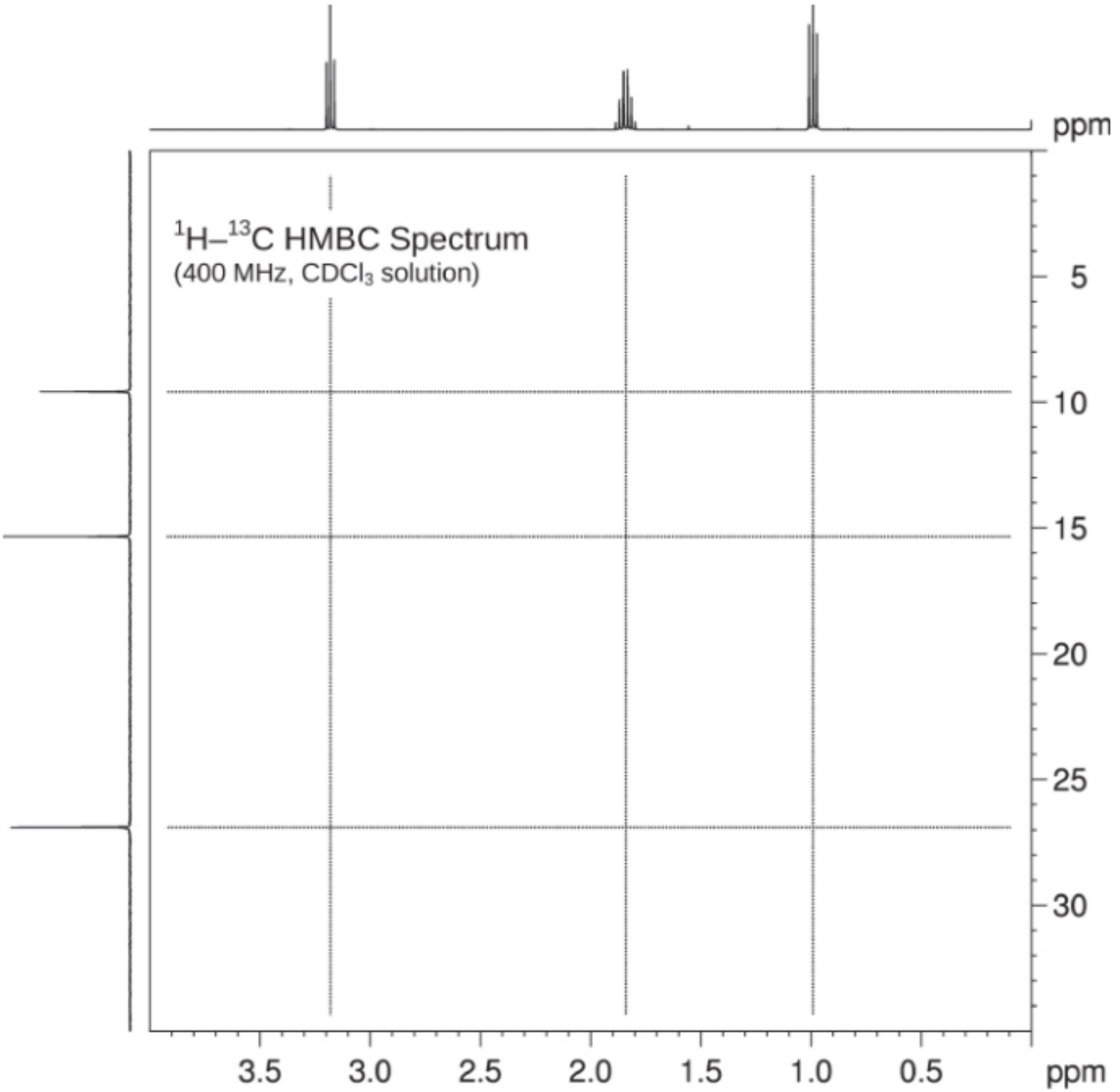


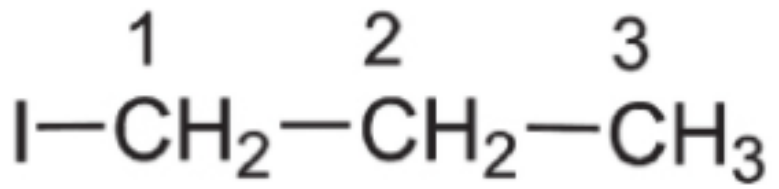





ppm
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

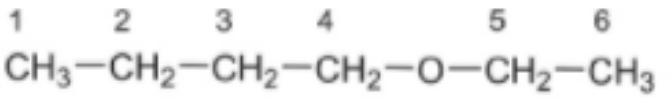
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
5
10
15
20
25
30
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
5
10
15
20
25
30
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

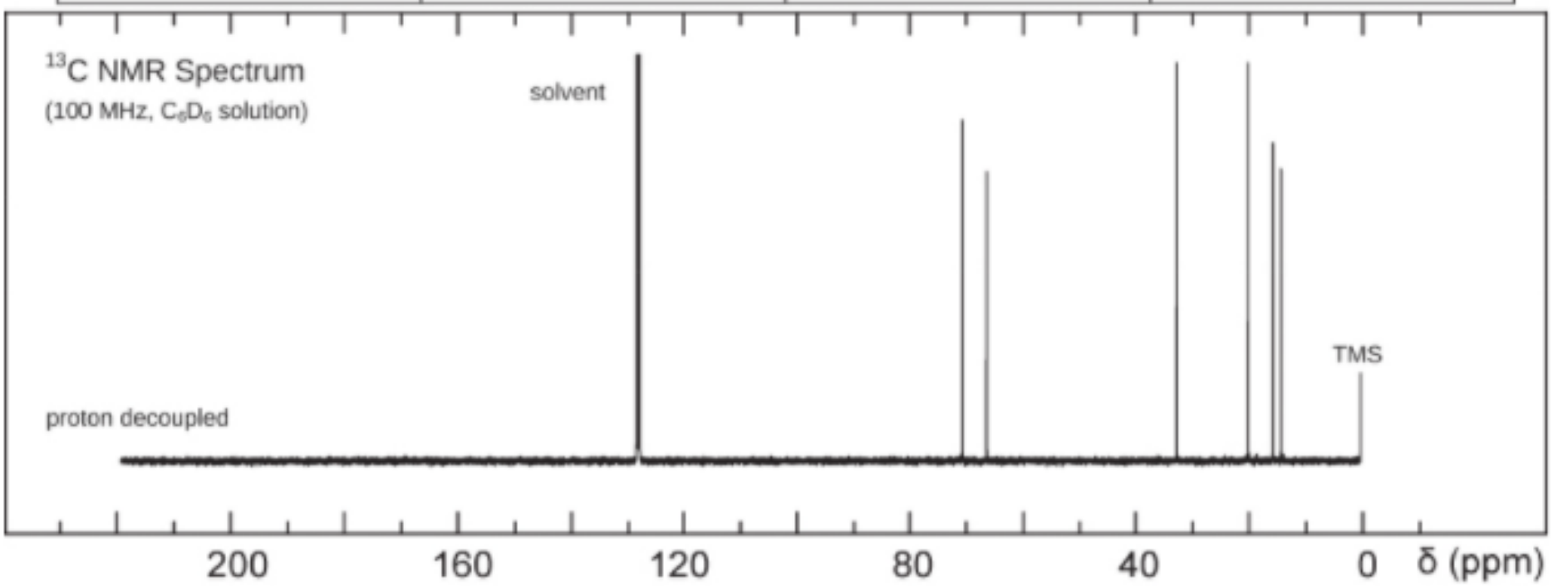

1
2
3
I—CH2—CH2—CH3

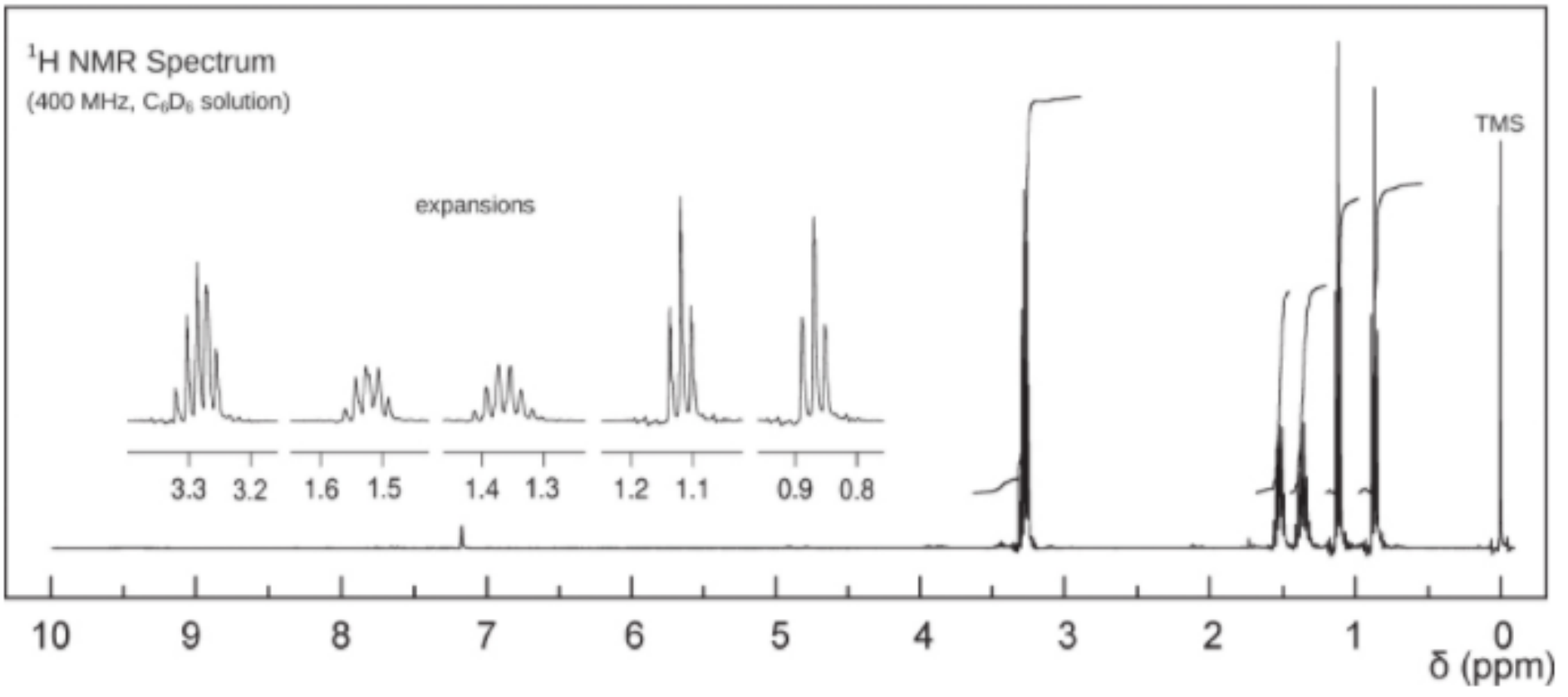
Problem 11

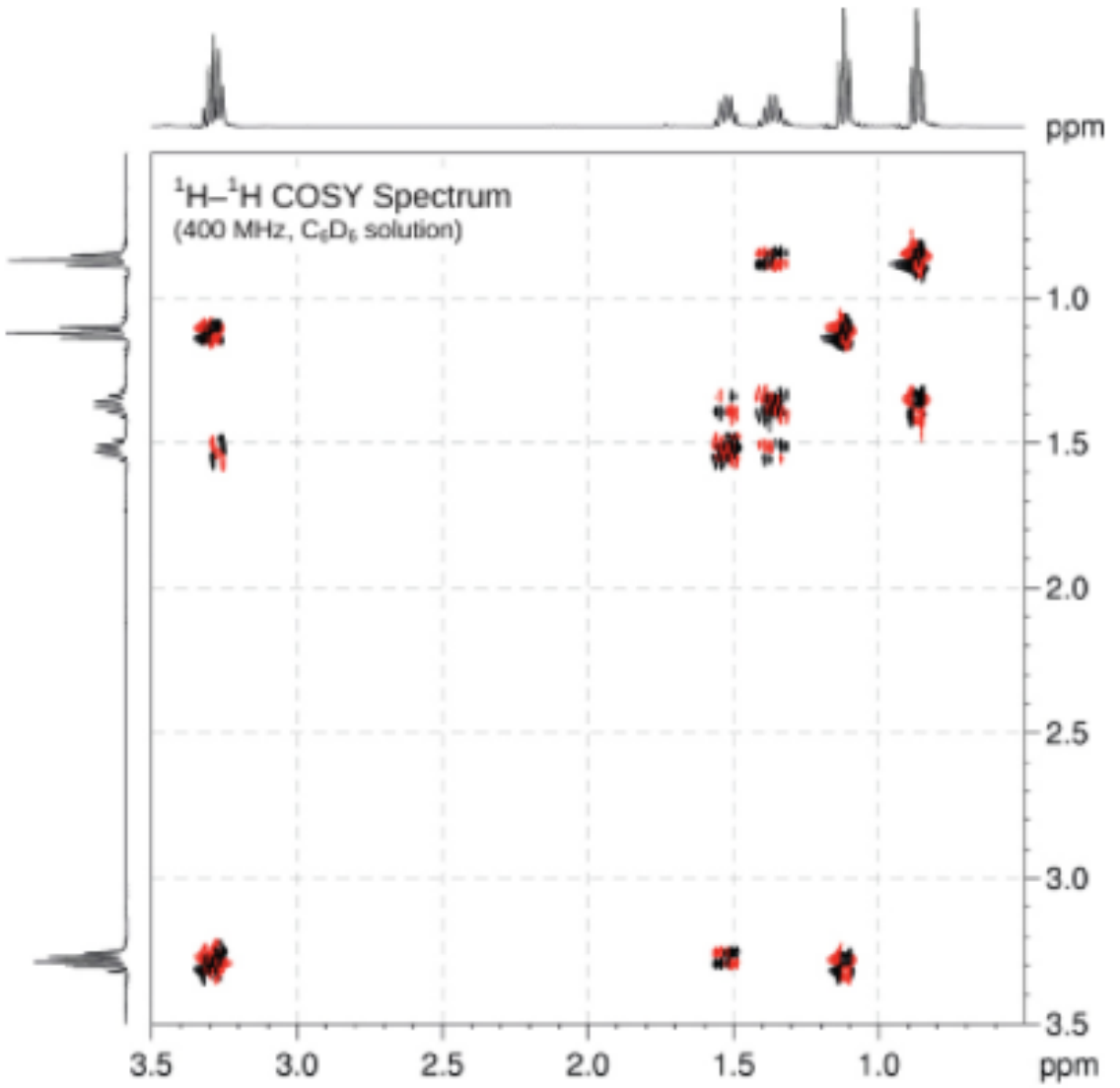
The ^{1}H and proton-decoupled ^{13}C NMR spectra of butyl ethyl ether ($C_6H_{14}O$) recorded at 298K in $CDCl_3$ solution, are given below. The ^{1}H spectrum has signals at δ 0.87, 1.12, 1.37, 1.53, 3.27 and 3.29 (partly overlapped) ppm. The ^{13}C spectrum has signals at δ 14.1, 15.5, 19.9, 32.5, 66.2 and 70.6 ppm. The 2-dimensional ^{1}H–^{1}H COSY spectrum and the *me*-HSQC spectrum are given on the facing page. From the COSY spectrum, assign the proton spectrum and use this information to assign the ^{13}C spectrum and then draw in the strong peaks that you would expect to see in the schematic HMBC on the following page.

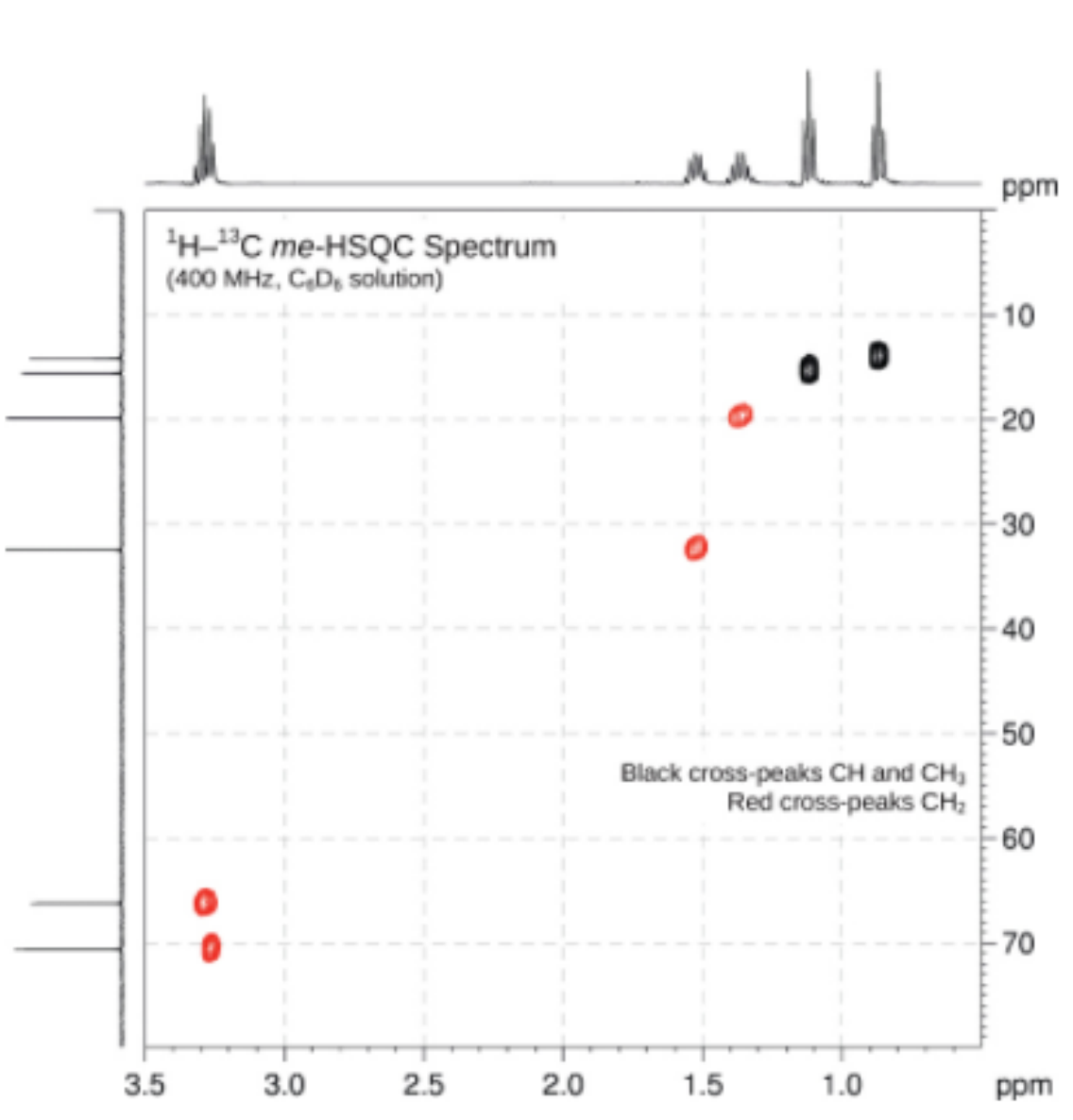


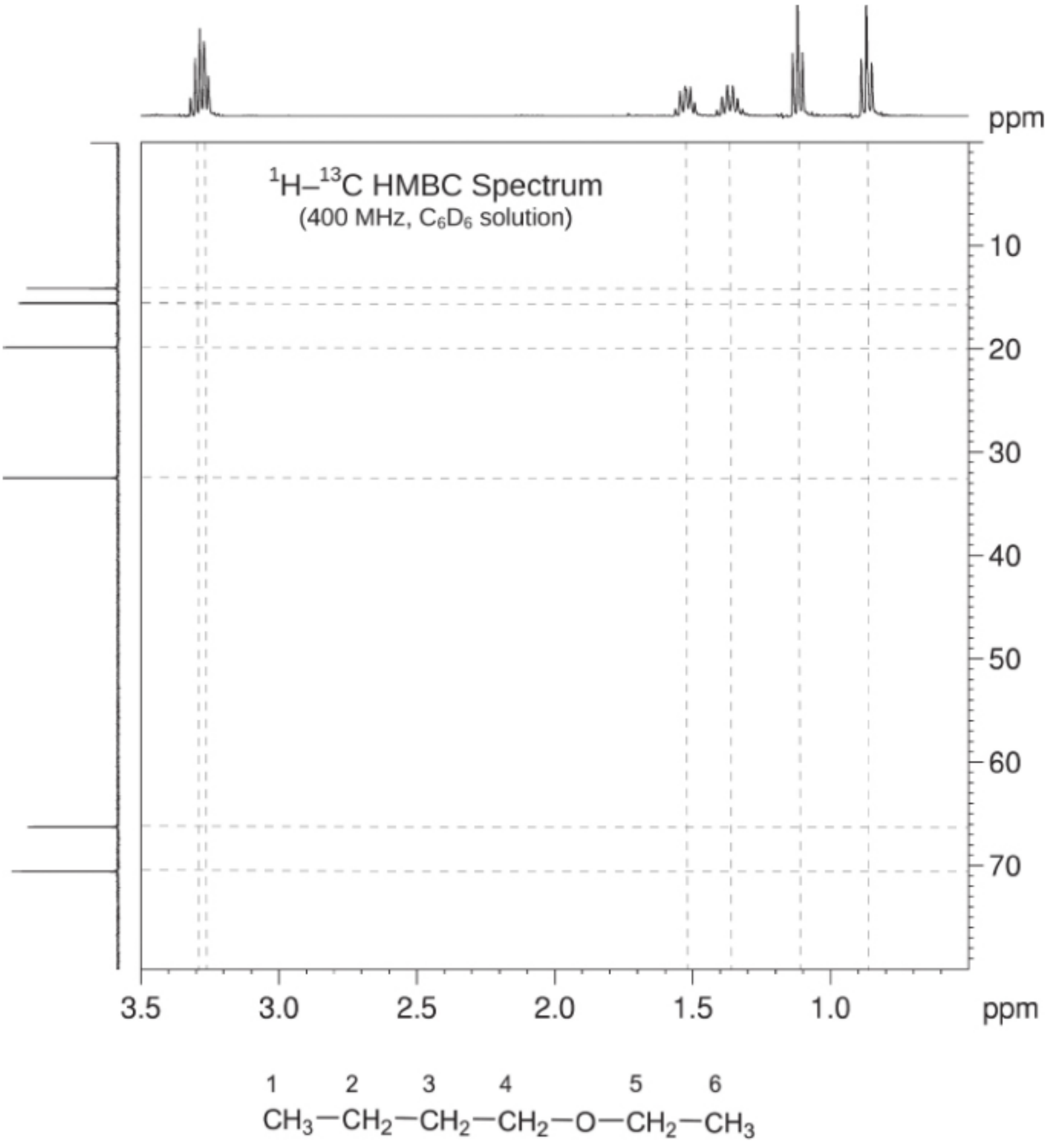
Proton	Chemical Shift (δ) in ppm	Carbon	Chemical Shift (δ) in ppm
H1		C1	
H2		C2	
H3		C3	
H4		C4	
H5		C5	
H6		C6	






^{1}H–^{1}H COSY Spectrum
(400 MHz, C_6D_6 solution)
ppm
1.0
1.5
2.0
2.5
3.0
3.5
3.5
3.0
2.5
2.0
1.5
1.0
ppm


^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, C_6D_6 solution)
ppm
10
20
30
40
50
60
70
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
3.5
3.0
2.5
2.0
1.5
1.0
ppm



1 2 3 4 5 6

$CH_3—CH_2—CH_2—CH_2—O—CH_2—CH_3$

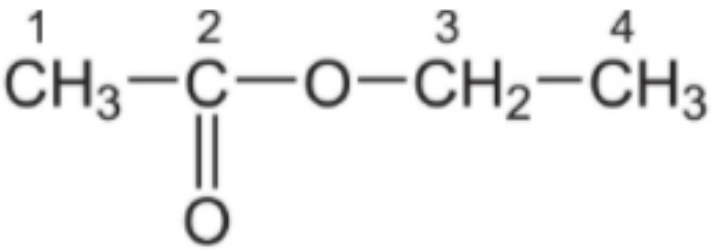
Problem 12

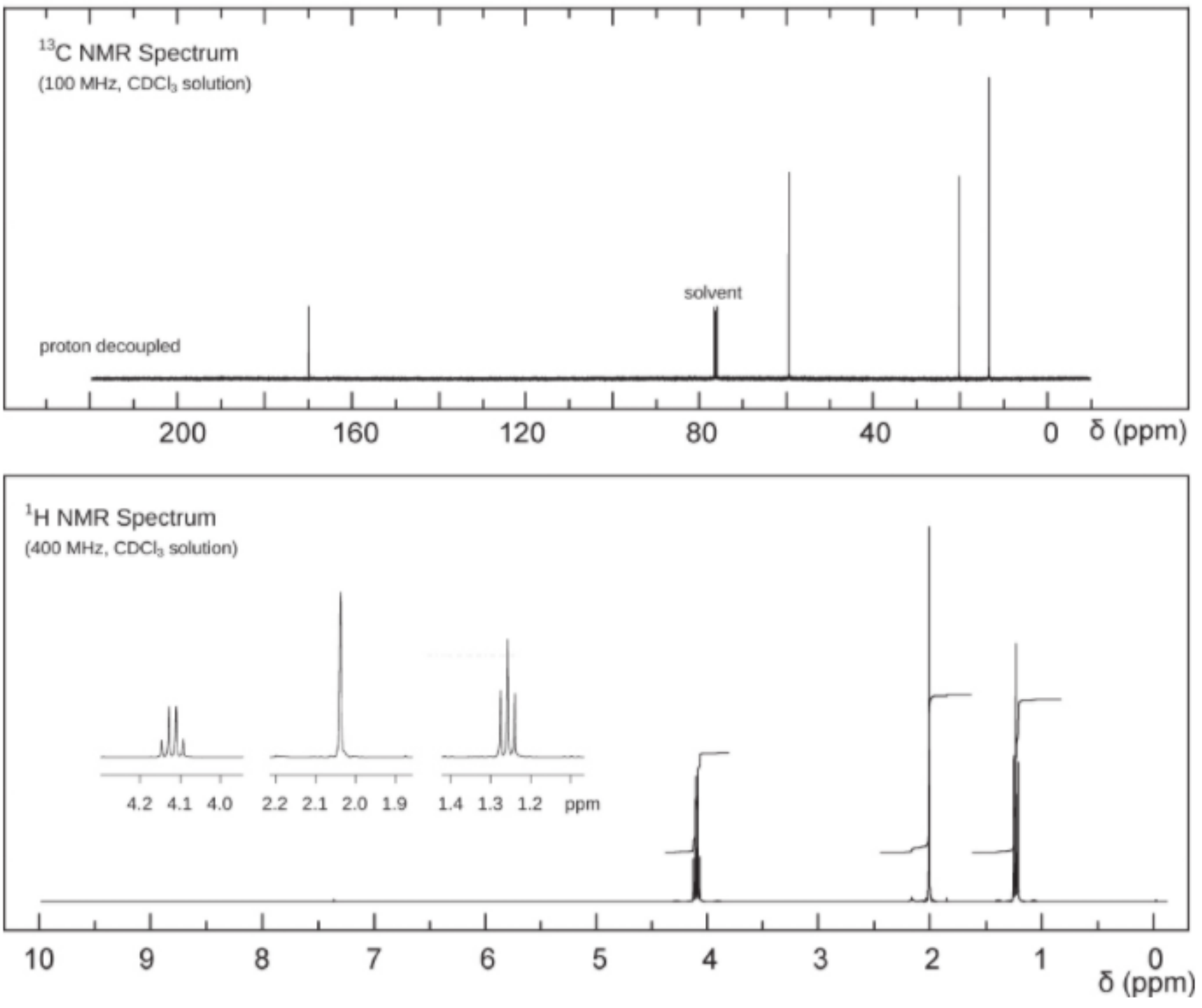
The ^{1}H and proton-decoupled ^{13}C NMR spectra of ethyl acetate ($C_4H_8O_2$) recorded in $CDCl_3$ solution at 298 K and 400 MHz are given below.

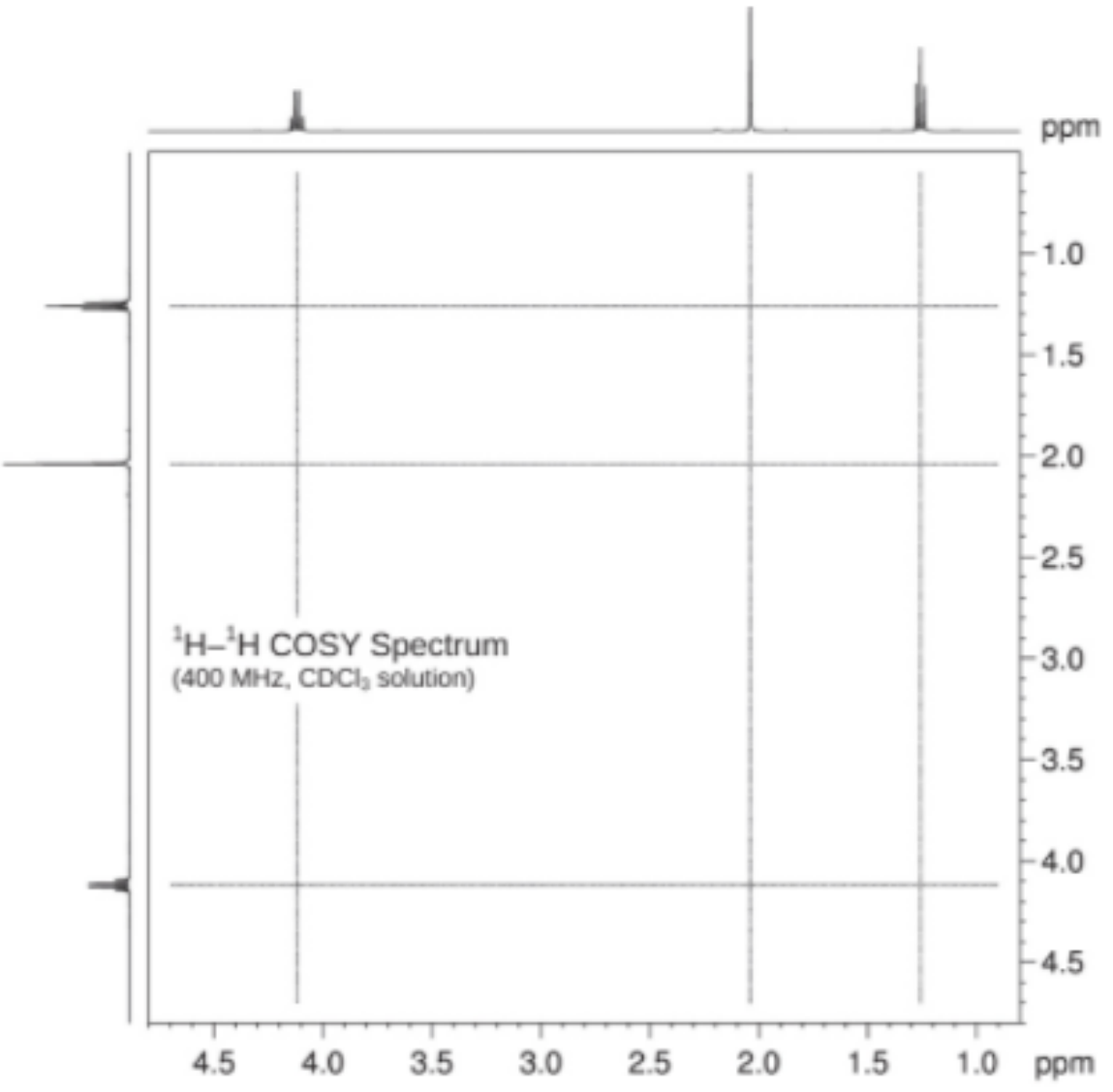
The ^{1}H NMR spectrum has signals at δ 1.28 (H_4), 2.04 (H_1) and 4.12 (H_3) ppm.

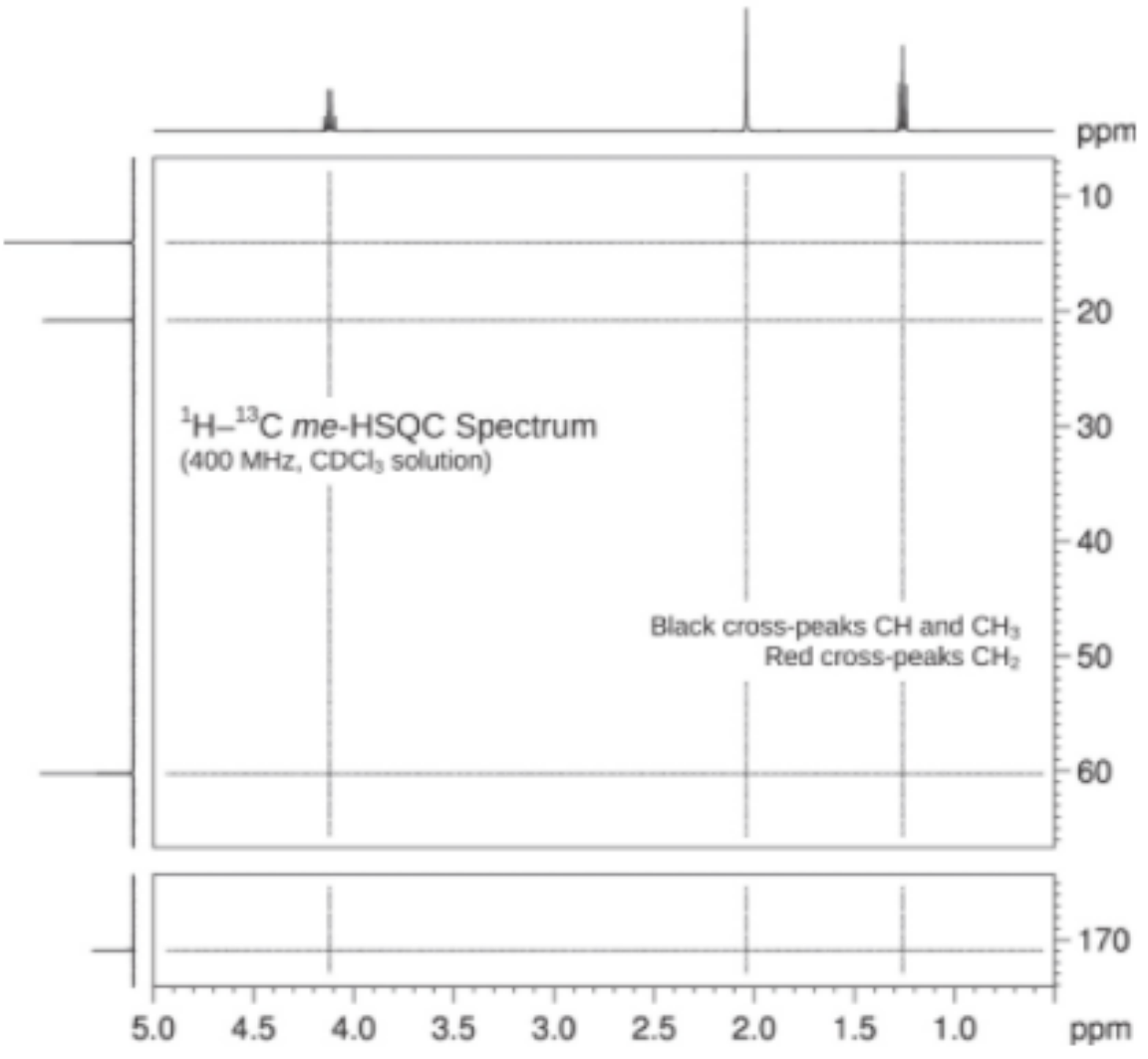
The ^{13}C NMR spectrum has signals at δ 14.0 (C_4), 20.8 (C_1), 60.2 (C_3) and 170.9 (C_2) ppm.

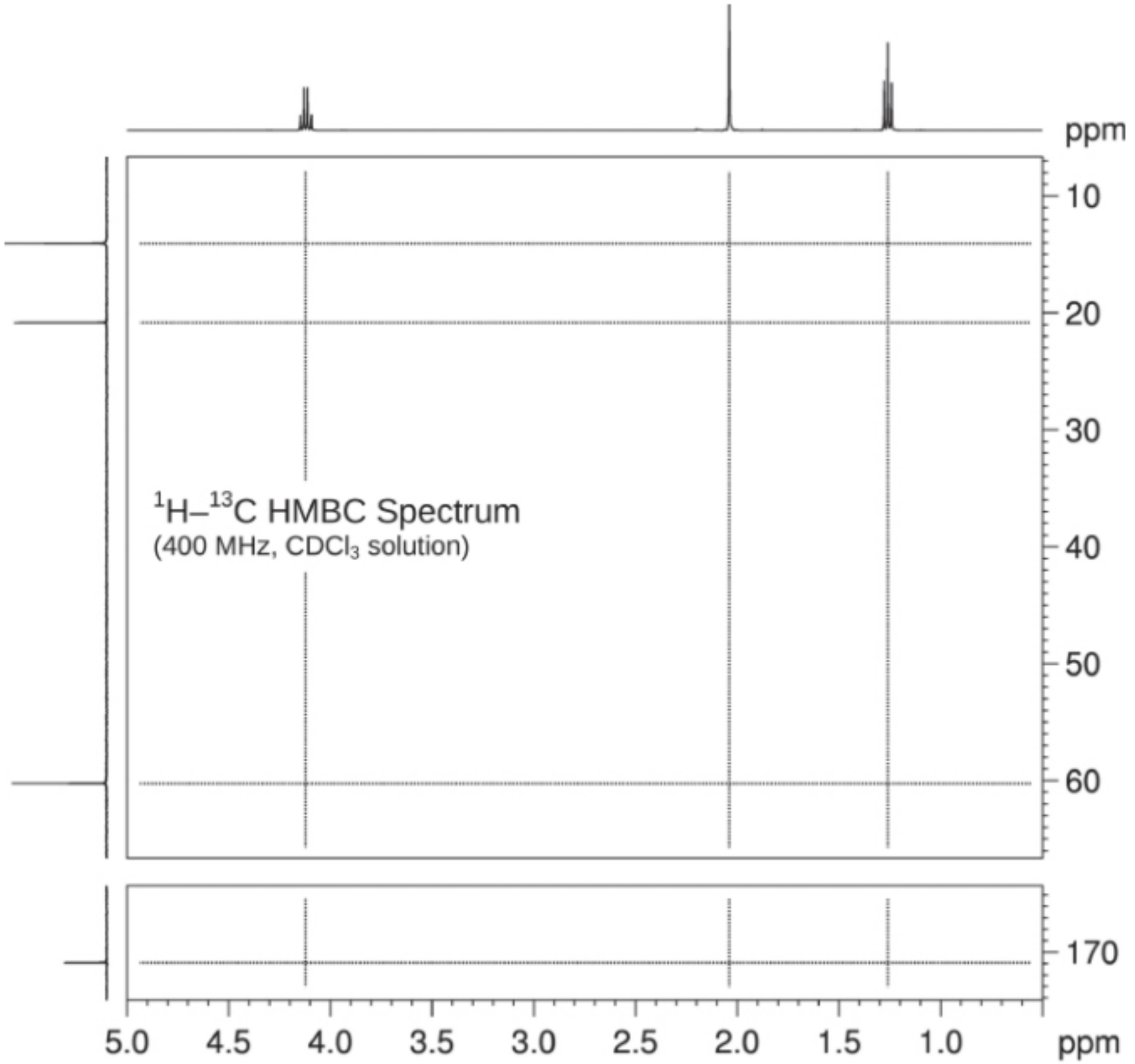
Use this information to produce schematic diagrams of the COSY, *me*-HSQC and HMBC spectra, showing where all of the cross-peaks and diagonal peaks would be.

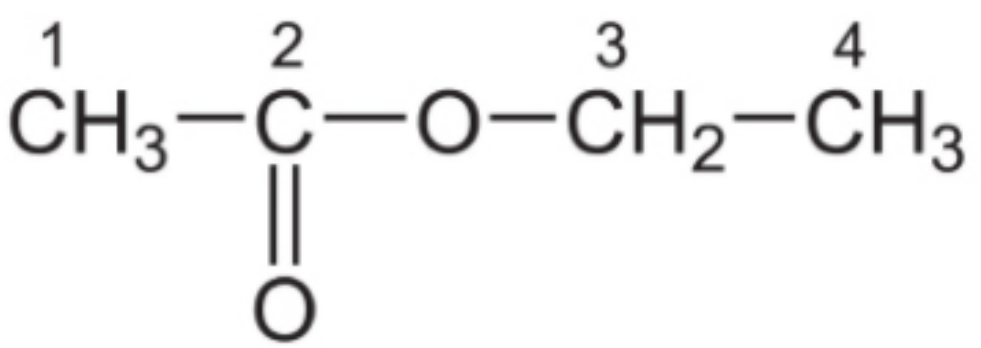





ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

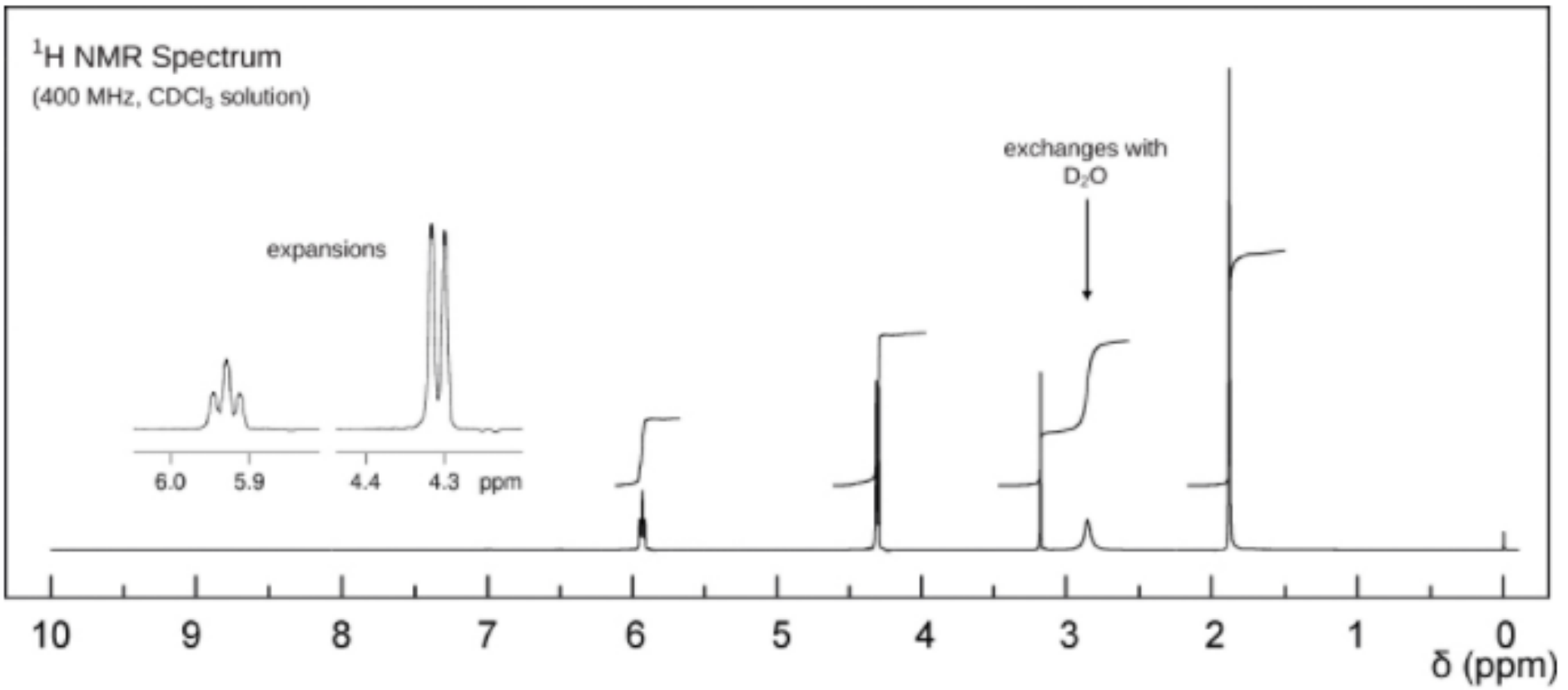

ppm
10
20
30
40
50
60
170
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

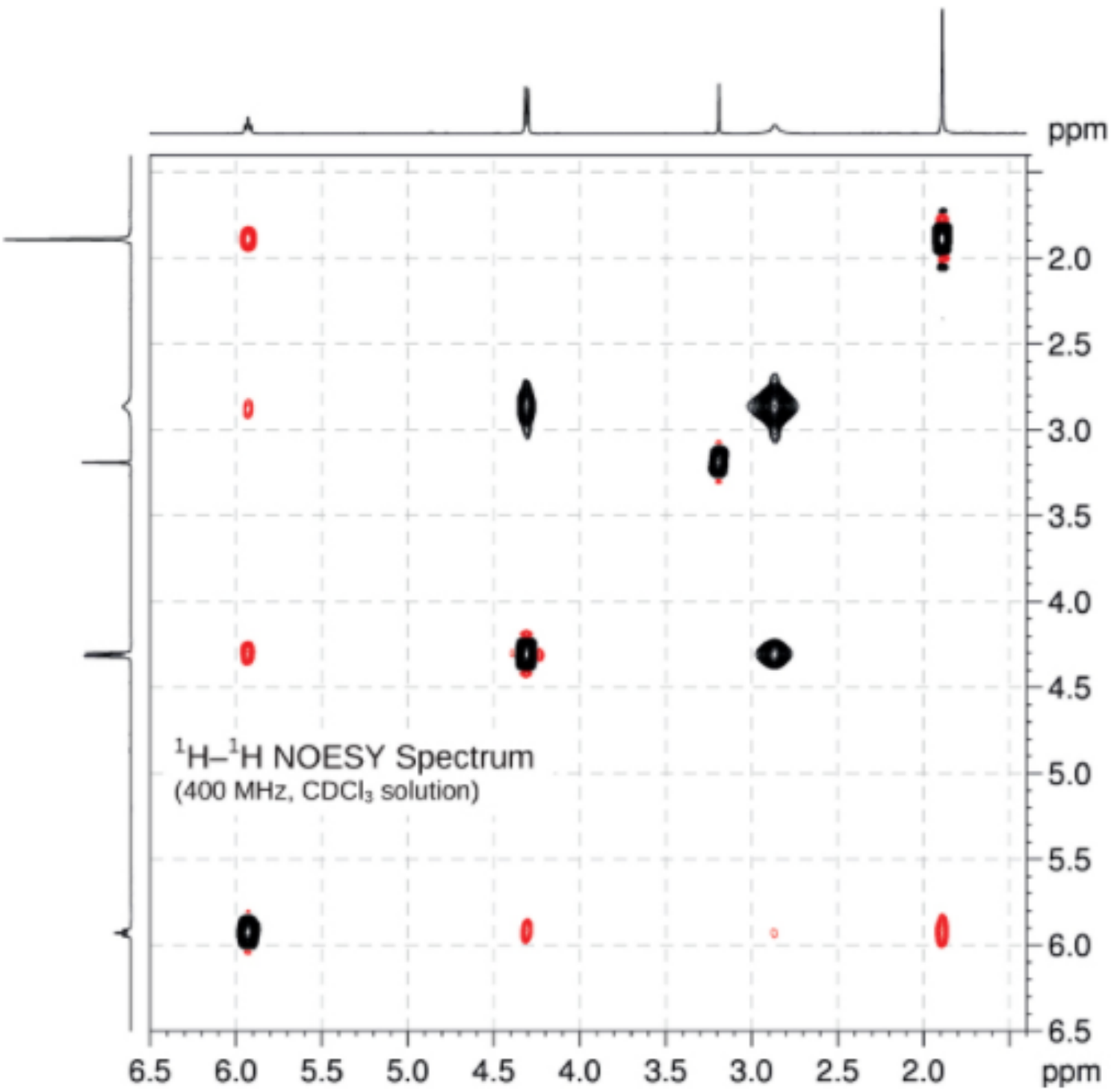

ppm
10
20
30
40
50
60
170
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


1
2
3
4
CH3—C—O—CH2—CH3
O

Problem 13

The ^{1}H NMR spectrum of one stereoisomer of 3-methylpent-2-en-4-yn-1-ol ($HC{\equiv}C(CH_3)\ C{=}CHCH_2OH$) recorded in $CDCl_3$ solution at 298 K and 400 MHz is given below. The 2-dimensional $^{1}H{-}^{1}H$ NOESY spectrum is also given. Determine the stereochemistry of the compound and draw a structural formula for the compound indicating the stereochemistry.


^{1}H NMR Spectrum
(400 MHz, $CDCl_3$ solution)
exchanges with D_2O
expansions
6.0
5.9
4.4
4.3
ppm
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
^{1}H–^{1}H NOESY Spectrum
(400 MHz, $CDCl_3$ solution)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

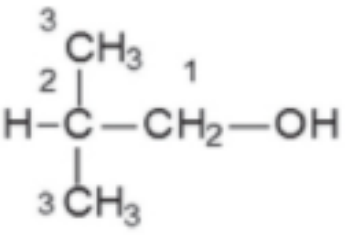
Problem 14

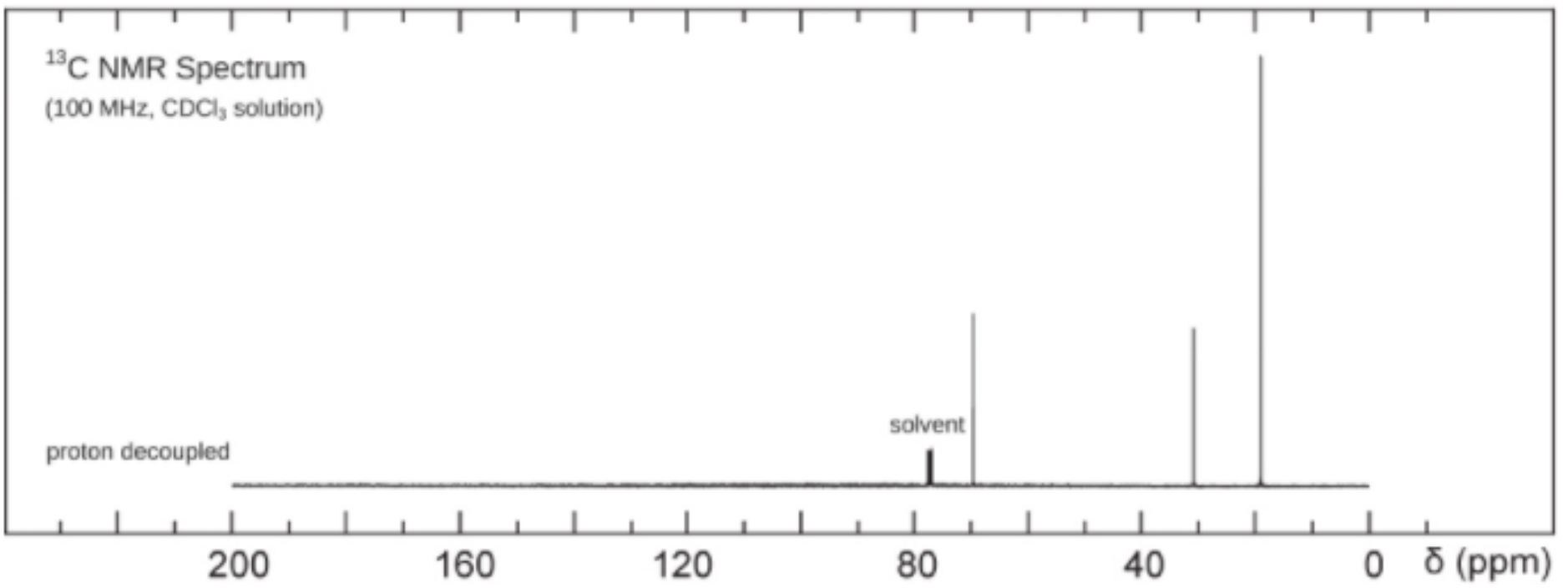
The ^{1}H and proton-decoupled ^{13}C NMR spectra of isobutanol (2-methyl-1-propanol, $C_4H_{10}O$) recorded in $CDCl_3$ solution at 298K, are given below.

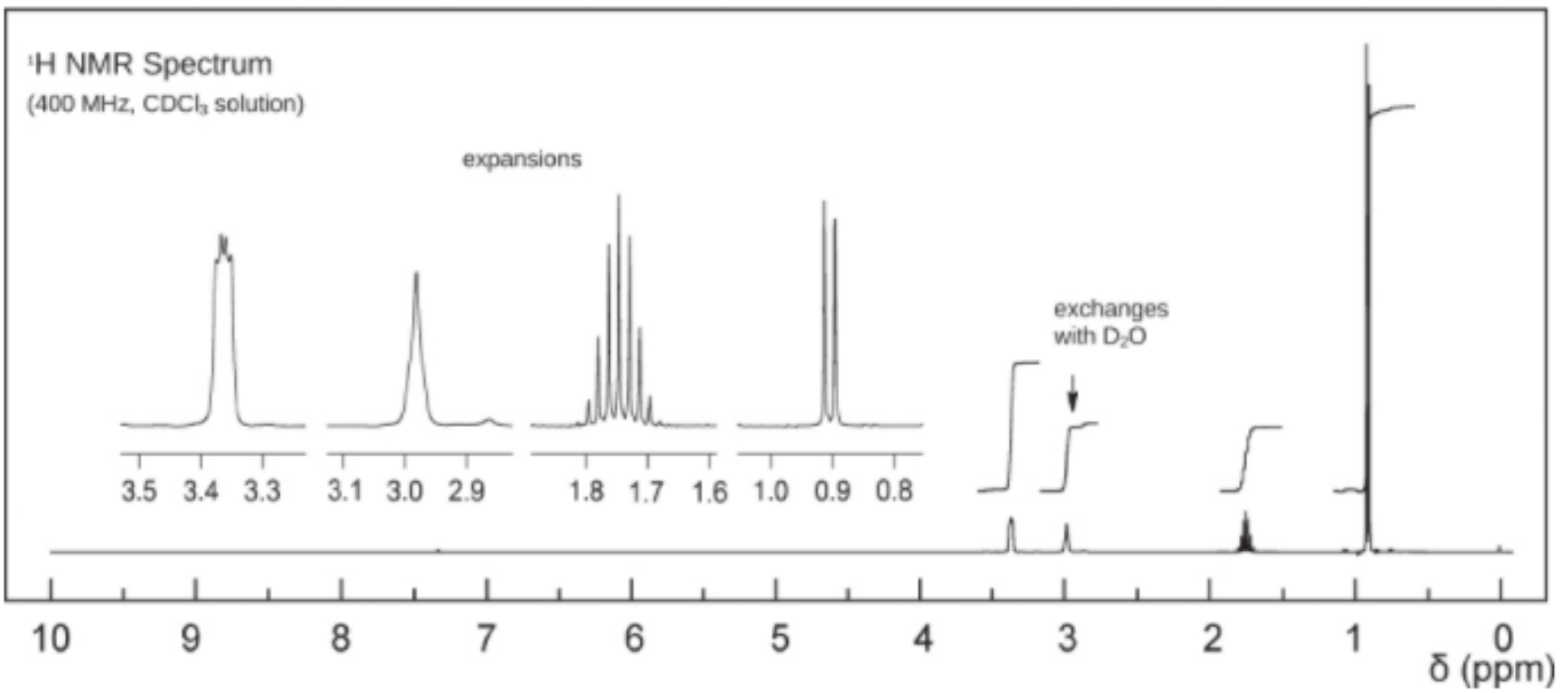
The ^{1}H spectrum contains signals at δ 3.37 (H_1), 2.98 (OH), 1.74 (H_2) and 0.90 (H_3) ppm.

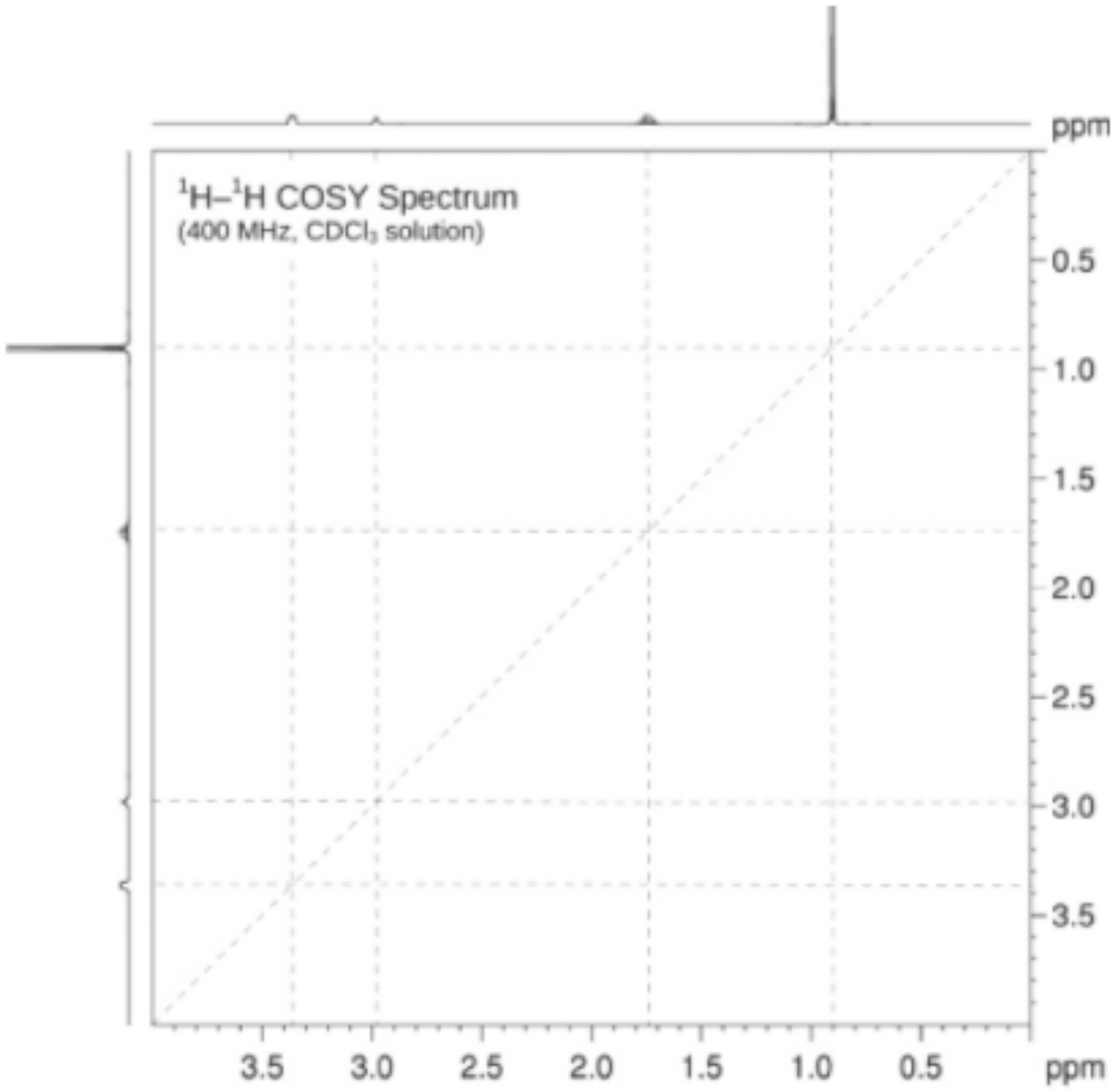
The ^{13}C spectrum contains signals at δ 69.5 (C_1), 30.9 (C_2) and 19.0 (C_3) ppm.

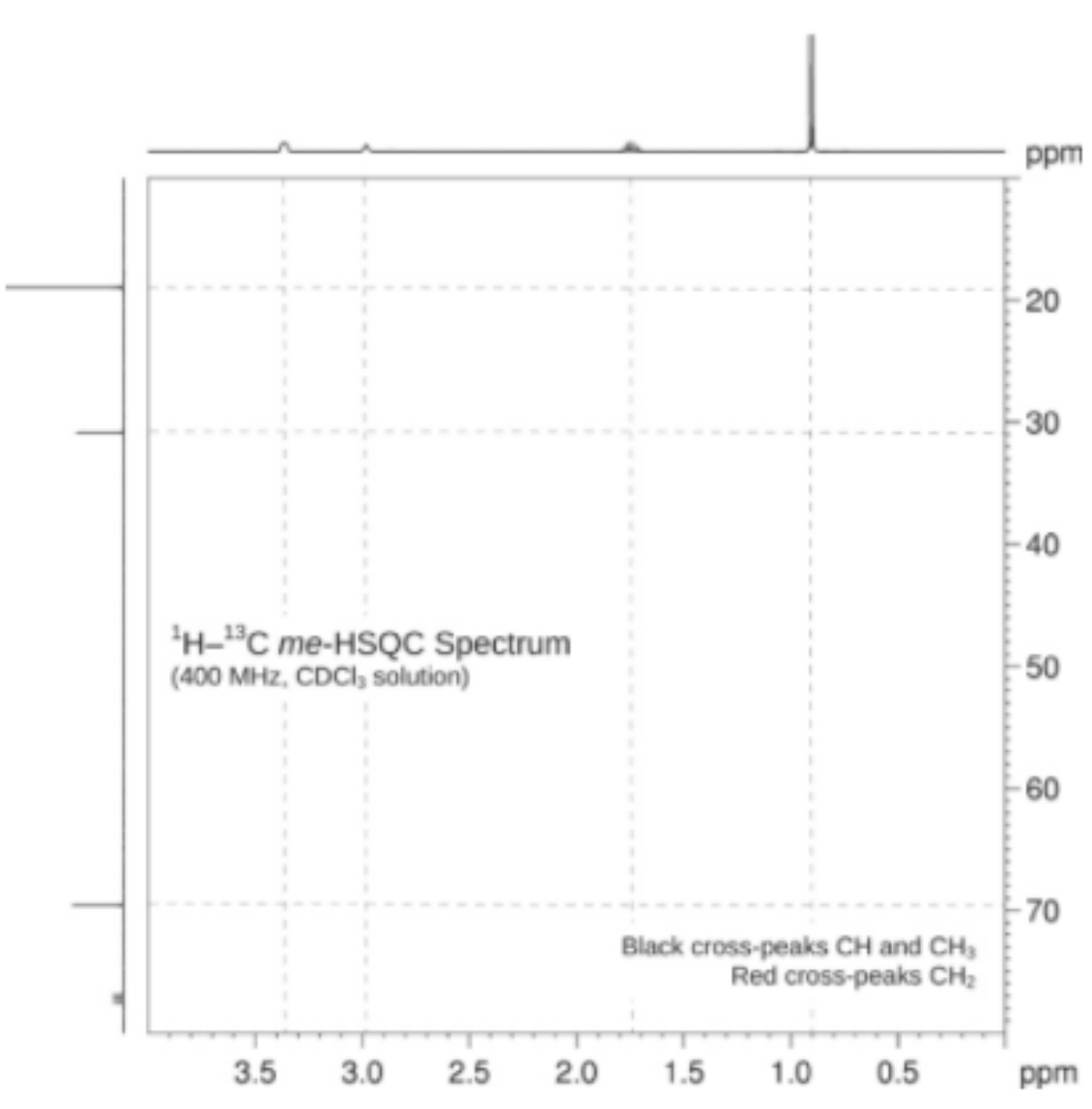
On the facing page, produce a schematic diagram of the COSY and the *me*–HSQC spectra for this molecule showing where all of the cross-peaks and diagonal peaks would be.





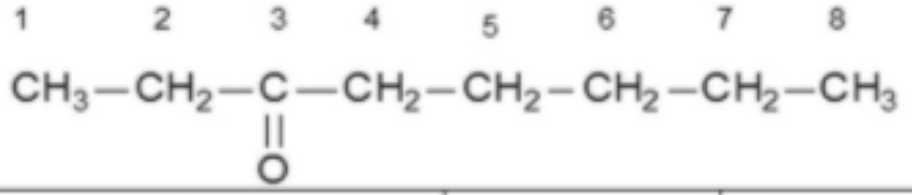



ppm
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


ppm
20
30
40
50
60
70
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

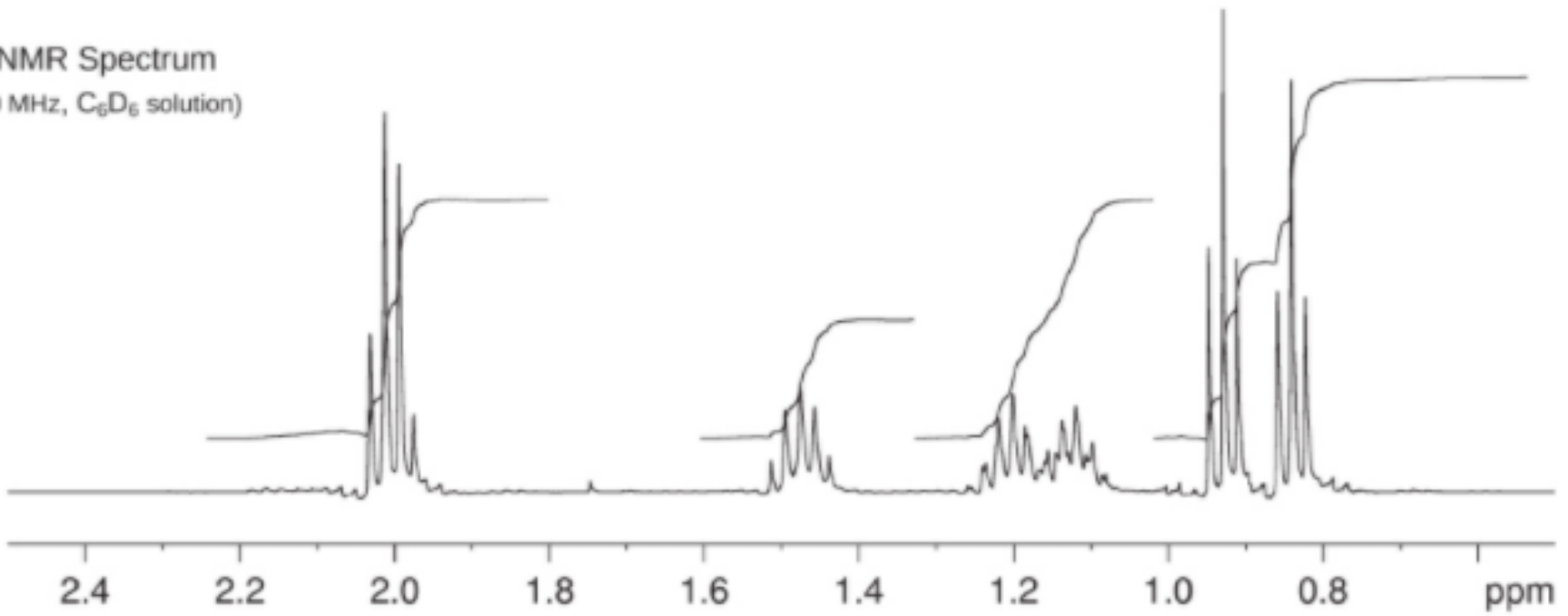
Problem 15

The ^{1}H and proton-decoupled ^{13}C spectra of 3-octanone ($C_8H_{16}O$) recorded in C_6D_6 solution at 298K at 400 MHz, are given below. The ^{1}H spectrum has signals at δ 0.84, 0.93, 1.12, 1.20, 1.48, 1.99 and 2.00 (partly overlapped) ppm. The ^{13}C spectrum has signals at δ 8.0, 14.2, 23.0, 23.9, 31.9, 35.6, 42.3 and 209.3 ppm. The 2-D ^{1}H–^{1}H COSY spectrum and the *me*-HSQC spectrum are given on the facing page. From the COSY spectrum, assign the proton spectrum and use this information to assign the ^{13}C spectrum.

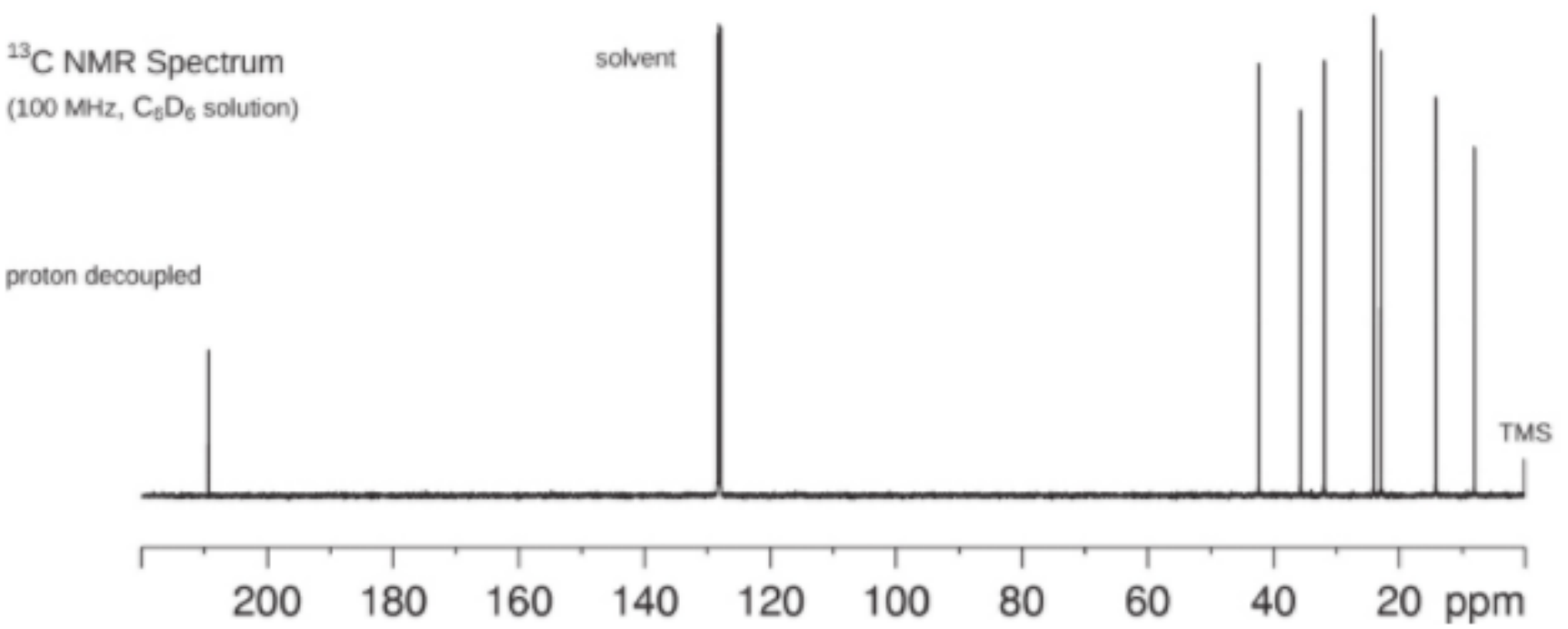


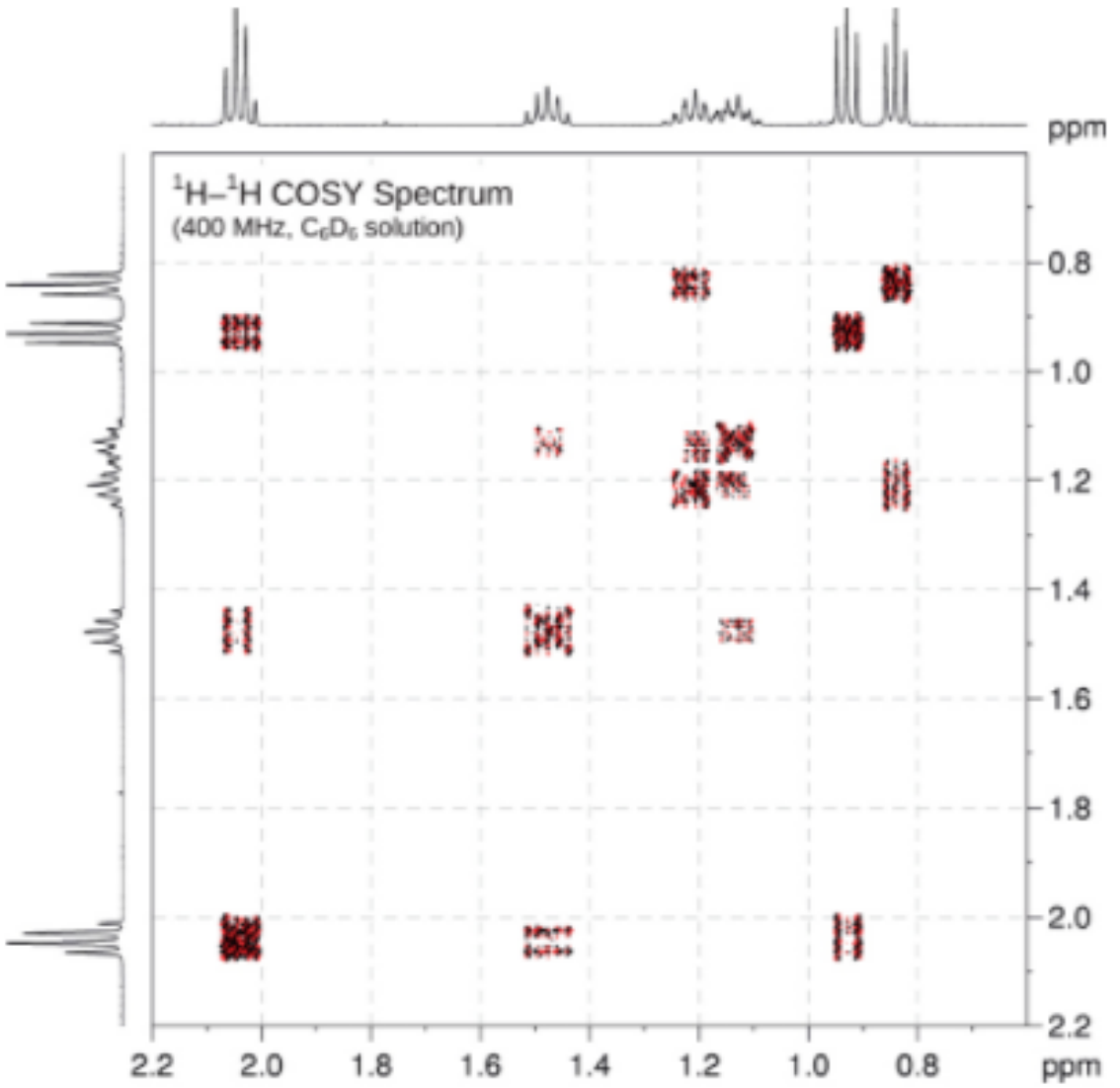
Proton	Chemical Shift (δ) in ppm	Carbon	Chemical Shift (δ) in ppm
H1		C1	
H2		C2	
		C3	
H4		C4	
H5		C5	
H6		C6	
H7		C7	
H8		C8	

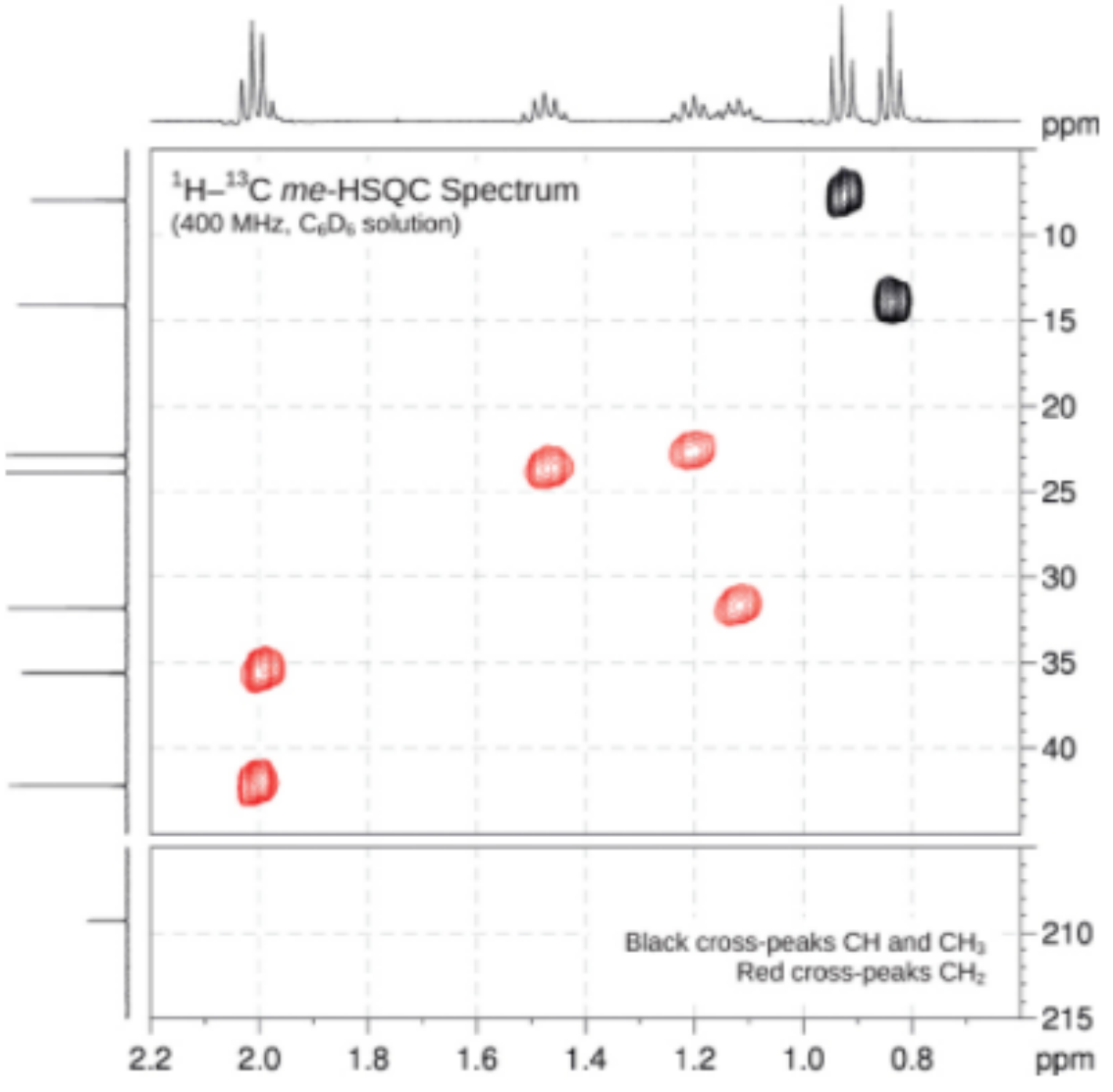
^{1}H NMR Spectrum
(400 MHz, C_6D_6 solution)



^{13}C NMR Spectrum
(100 MHz, C_6D_6 solution)



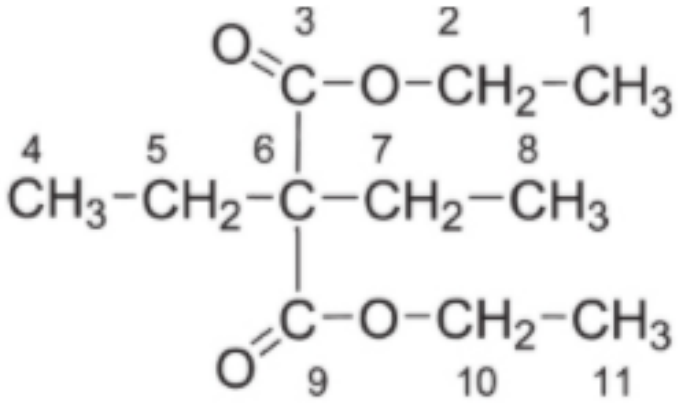

^{1}H–^{1}H COSY Spectrum
(400 MHz, C_6D_6 solution)
ppm
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm


^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, C_6D_6 solution)
ppm
10
15
20
25
30
35
40
210
215
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm

Problem 16

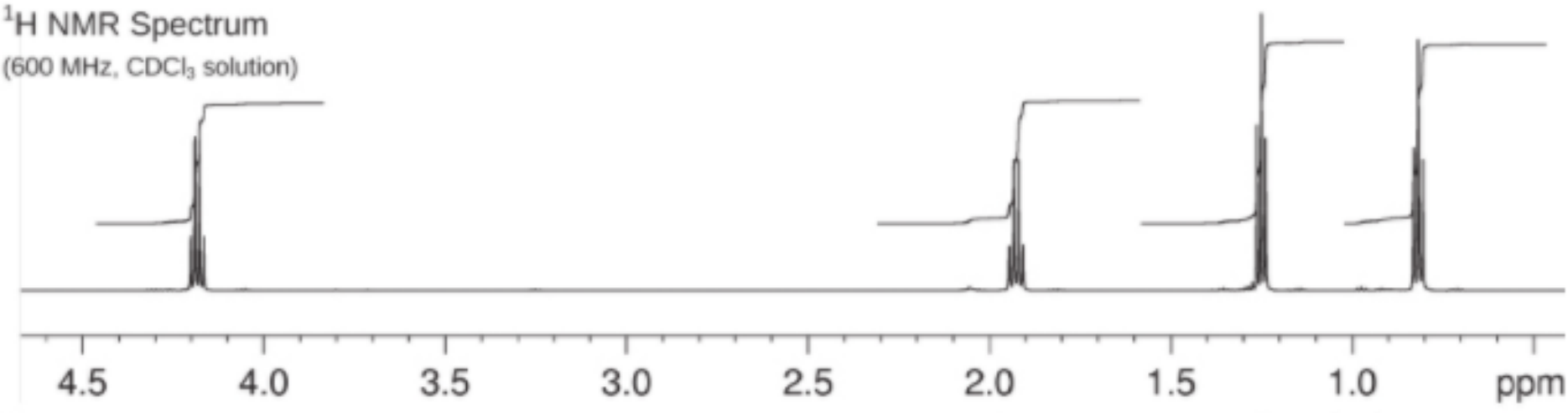
The ^{1}H and proton-decoupled ^{13}C NMR spectra of diethyl diethylmalonate ($C_{11}H_{20}O_4$) recorded in $CDCl_3$ solution at 298 K and 600 MHz are given below. The ^{1}H NMR spectrum has signals at δ 0.82, 1.25, 1.92 and 4.18 ppm. The ^{13}C spectrum has signals at δ 8.2, 14.0, 24.5, 58.3, 60.8 and 171.7 ppm.

The 2-dimensional ^{1}H–^{1}H COSY spectrum and the ^{1}H–^{13}C *me*-HSQC correlation spectrum are given on the following page. From the COSY spectrum, assign the proton spectrum and then use the *me*-HSQC spectrum to assign the ^{13}C spectrum, *i.e.* determine the chemical shift corresponding to each of the protons and each of the carbons in the molecule.

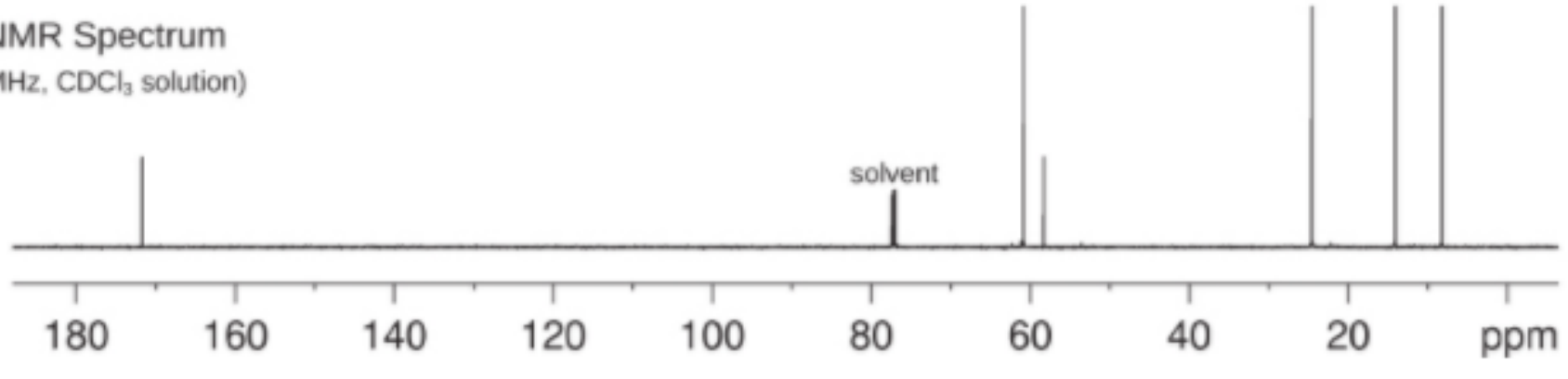


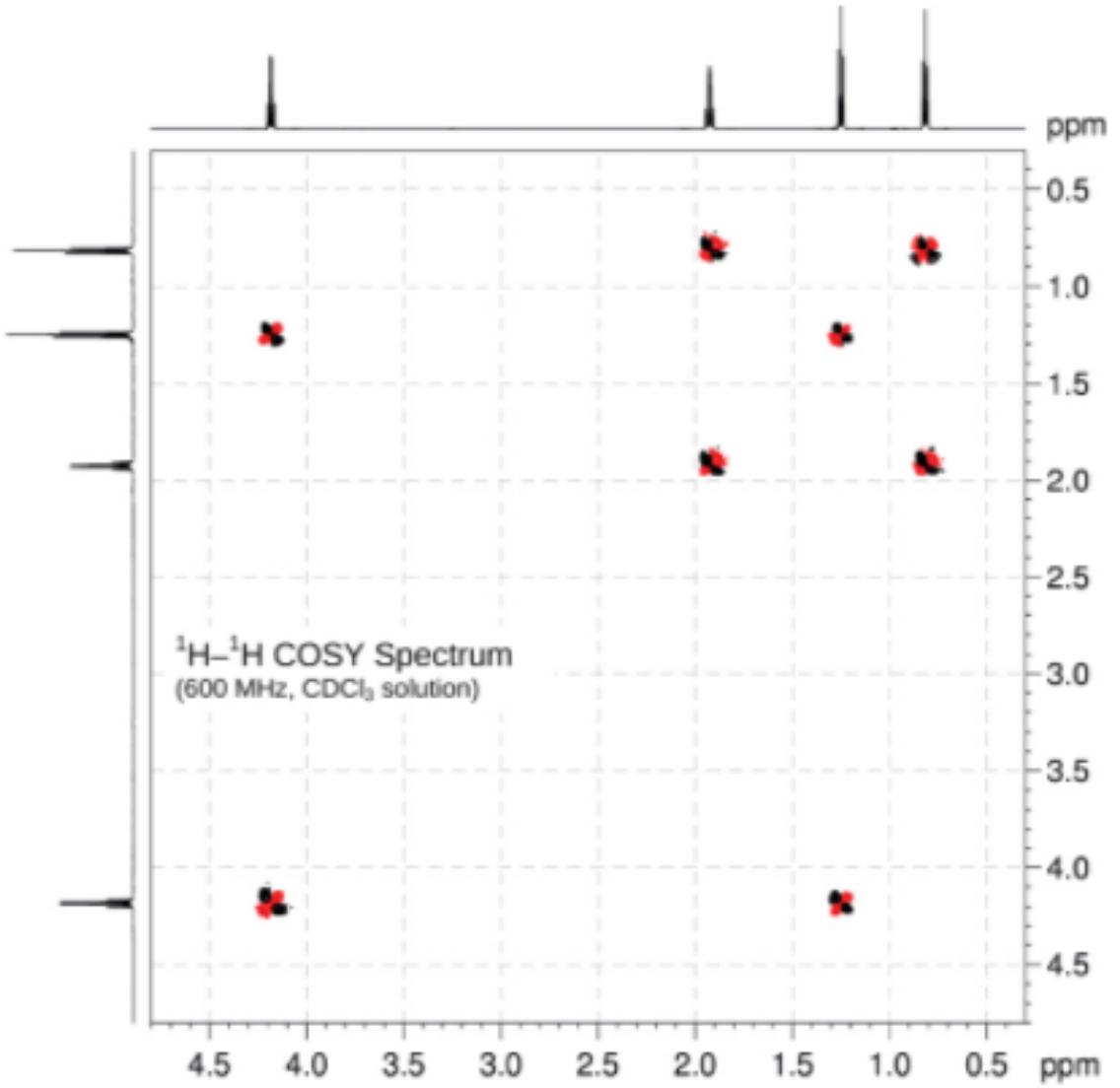
Proton	Chemical Shift (δ) in ppm	Carbon	Chemical Shift (δ) in ppm
H1		C1	
H2		C2	
		C3	
H4		C4	
H5		C5	
		C6	
H7		C7	
H8		C8	
		C9	
H10		C10	
H11		C11	

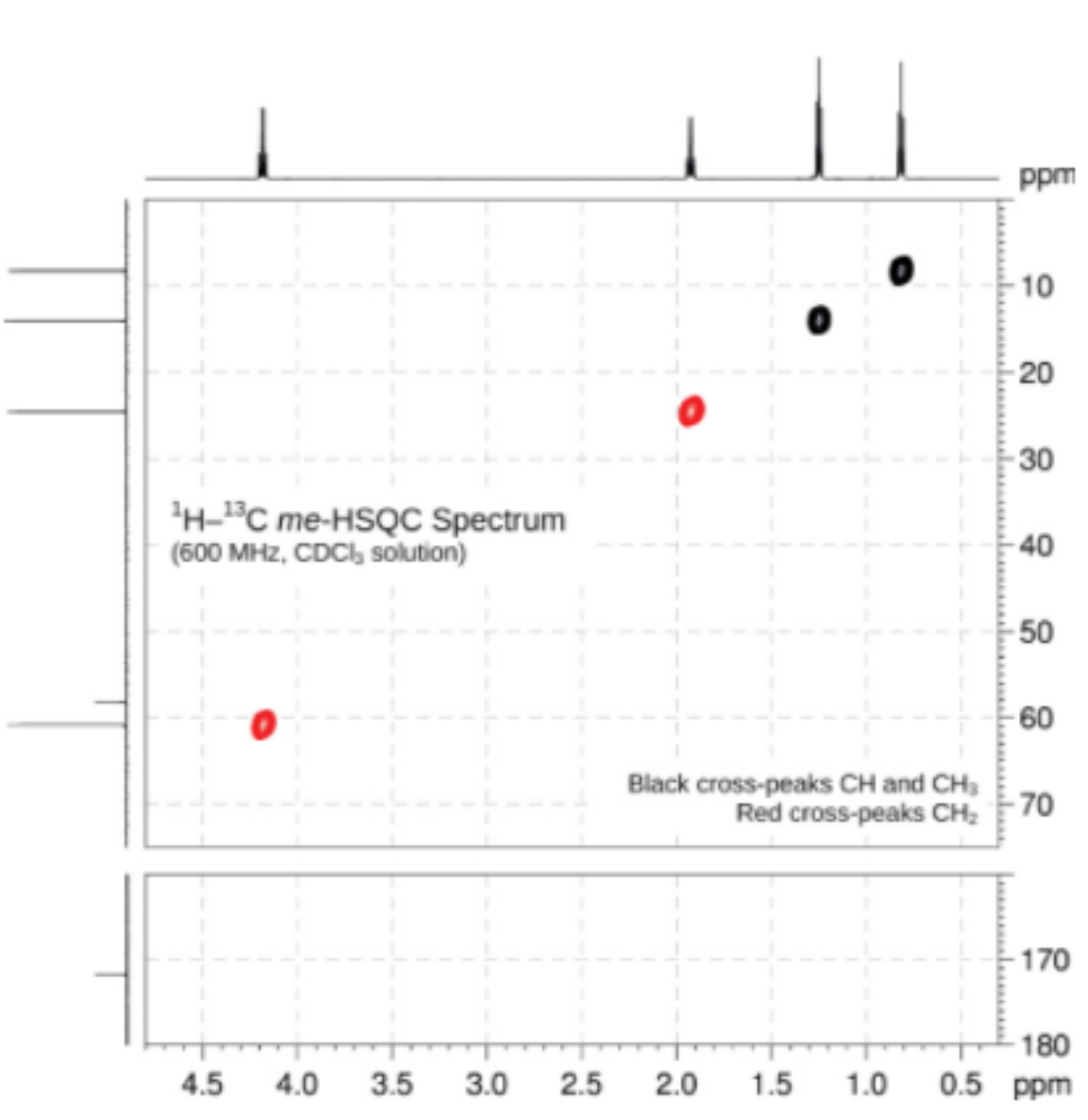
^{1}H NMR Spectrum
(600 MHz, $CDCl_3$ solution)



^{13}C NMR Spectrum
(150 MHz, $CDCl_3$ solution)



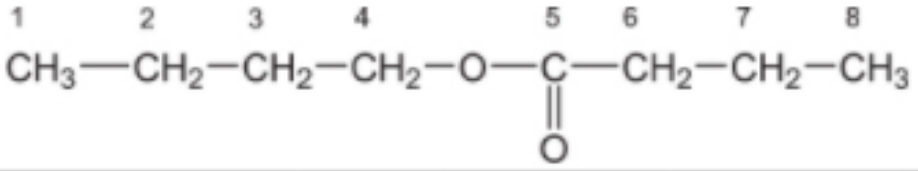

ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
^{1}H–^{1}H COSY Spectrum
(600 MHz, $CDCl_3$ solution)
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


ppm
10
20
30
40
50
60
70
170
180
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

Problem 17

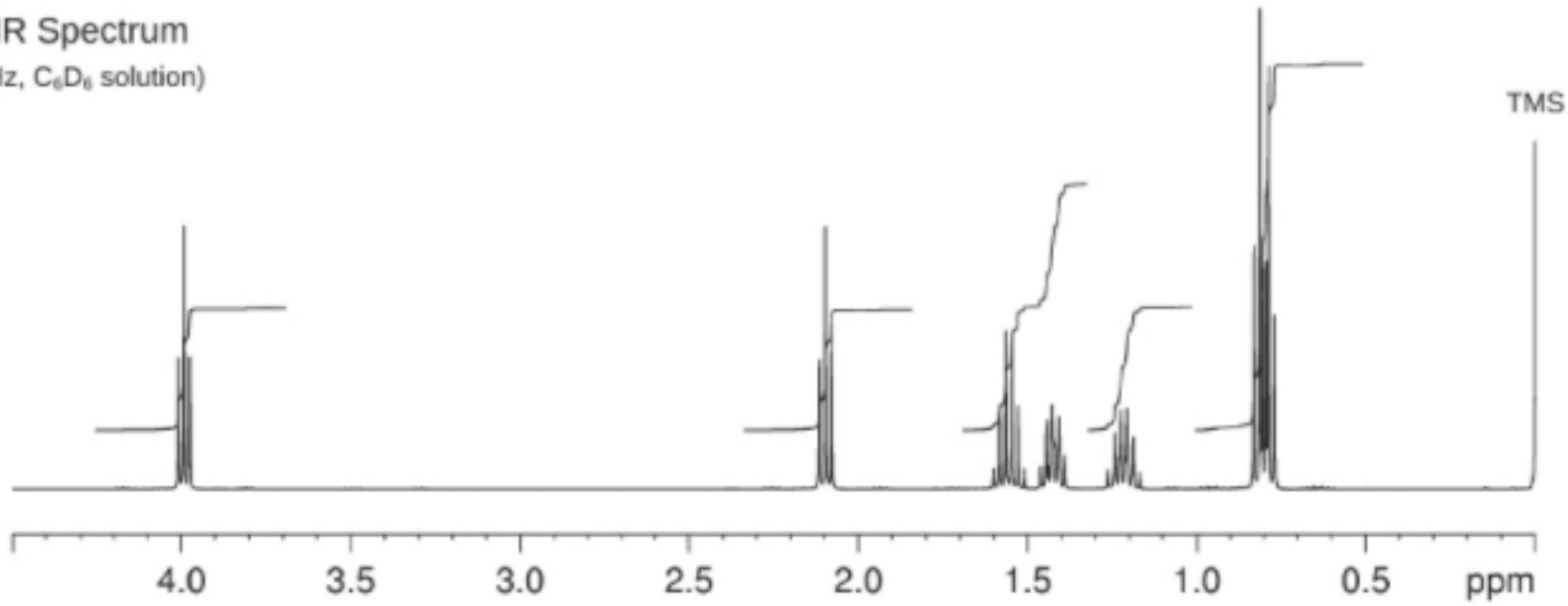
The ^{1}H and proton-decoupled ^{13}C NMR spectra of butyl butyrate recorded in C_6D_6 solution at 298K and 400 MHz are given below. The ^{1}H NMR spectrum has signals at δ 0.79, 0.81, 1.22, 1.43, 1.55, 2.10 and 3.99 ppm. The ^{13}C spectrum has signals at δ 13.7, 13.8, 18.8, 19.5, 31.2, 36.2, 63.9 and 172.8 ppm.

The 2-dimensional ^{1}H–^{1}H COSY spectrum and the ^{1}H–^{13}C *me*-HSQC correlation spectrum are given on the facing page. From the COSY spectrum, assign the proton spectrum and use the *me*–HSQC spectrum to assign the ^{13}C spectrum, *i.e.* determine the chemical shift corresponding to each of the protons and each of the carbons in the molecule.

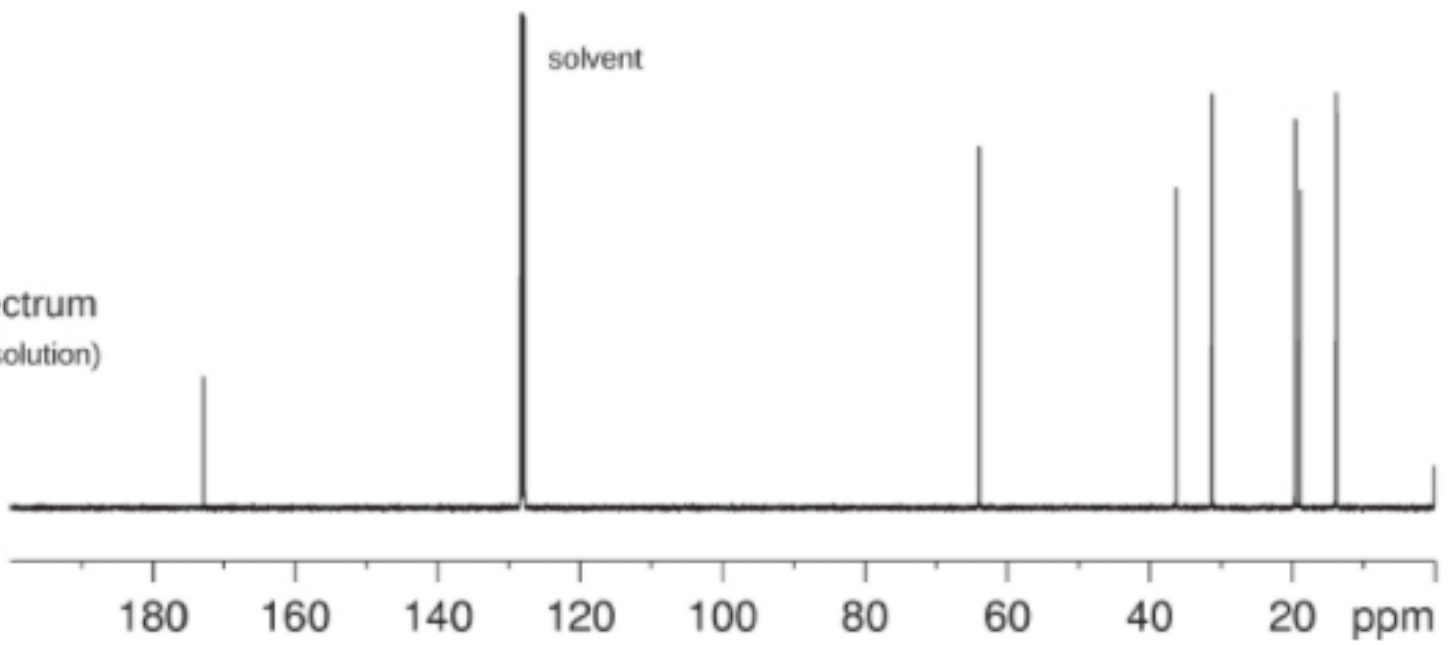


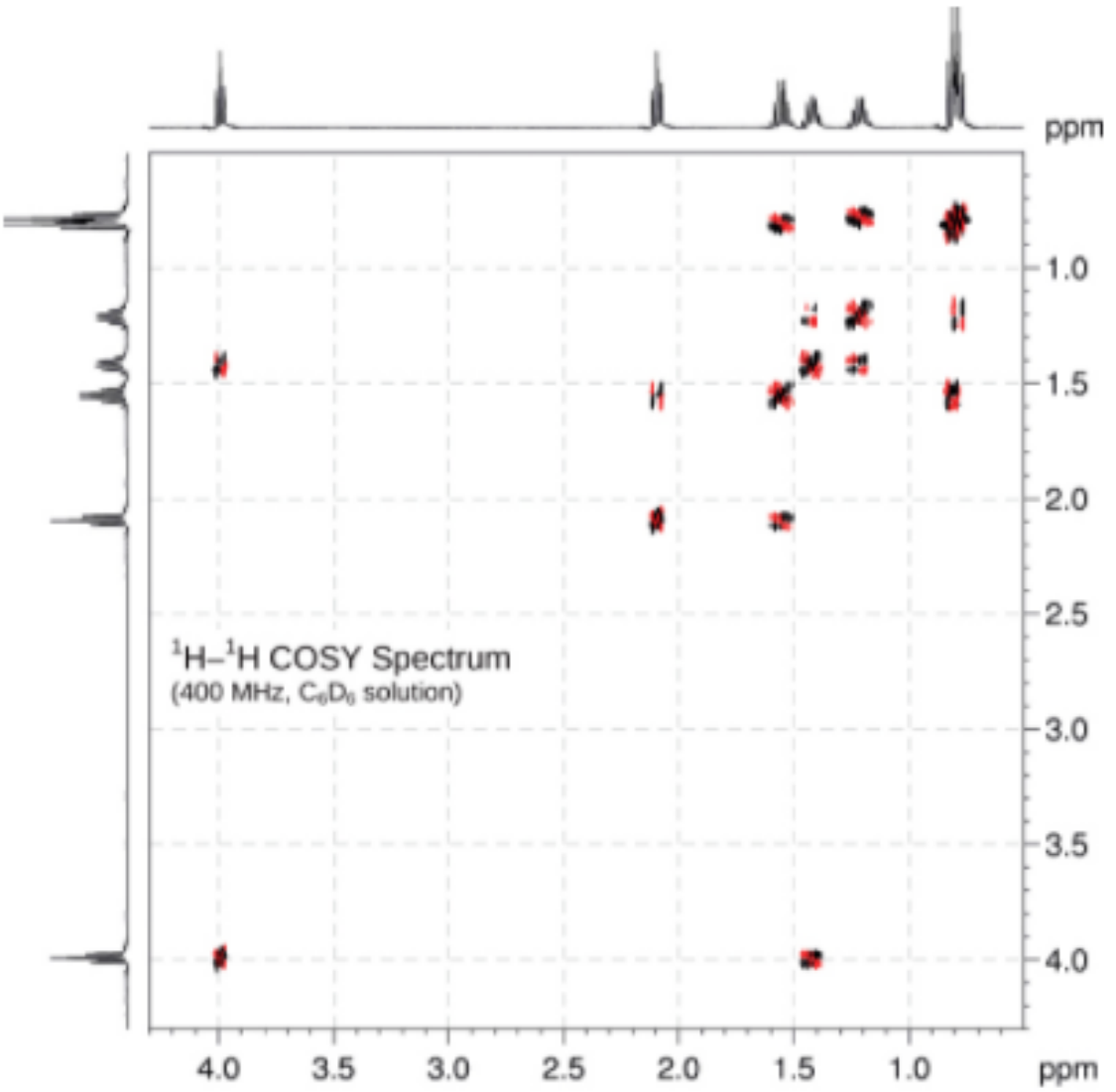
Proton	Chemical Shift (δ) in ppm	Carbon	Chemical Shift (δ) in ppm
H1		C1	
H2		C2	
H3		C3	
H4		C4	
		C5	
H6		C6	
H7		C7	
H8		C8	

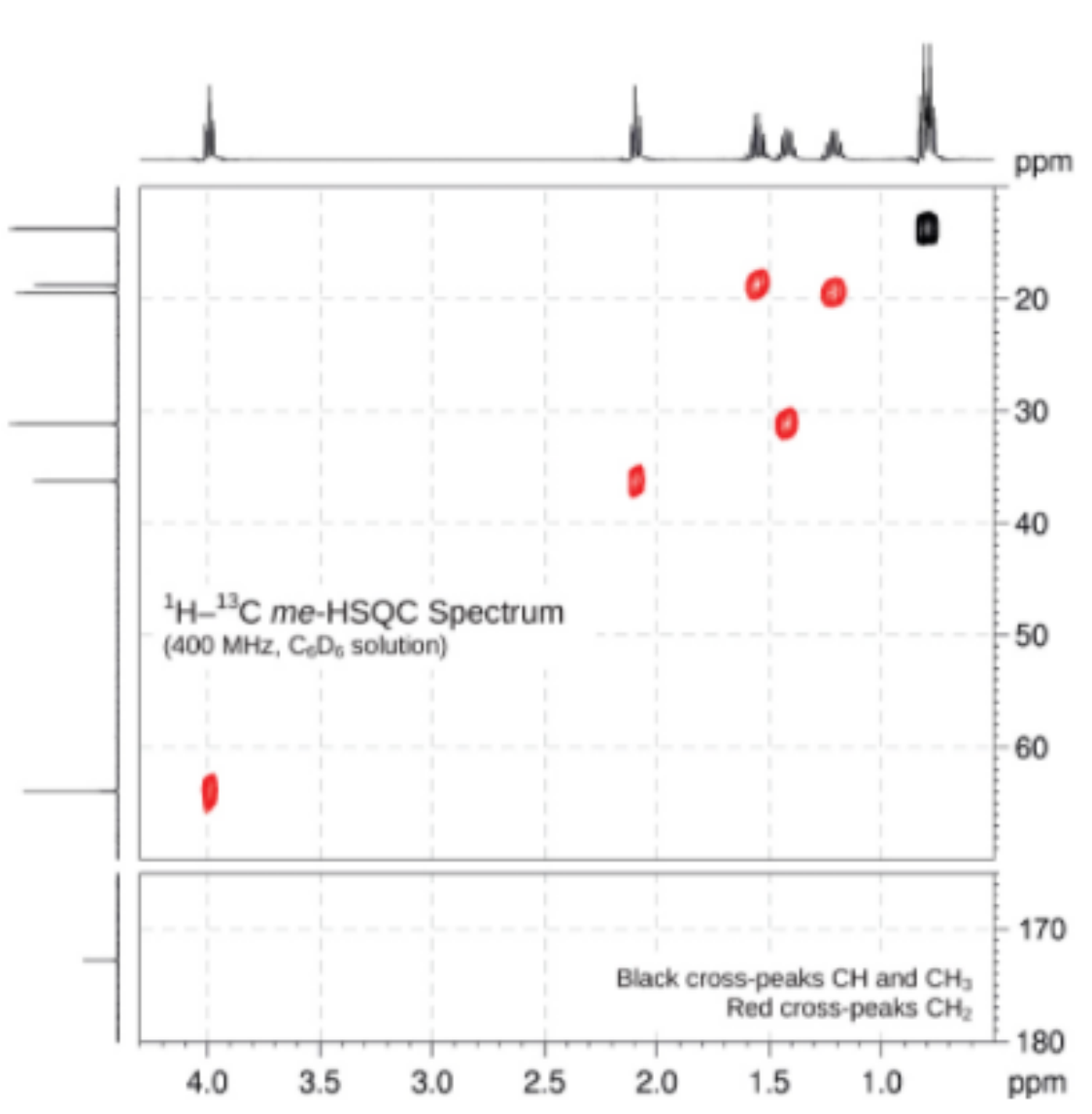
^{1}H NMR Spectrum
(400 MHz, C_6D_6 solution)



^{13}C NMR Spectrum
(100 MHz, C_6D_6 solution)

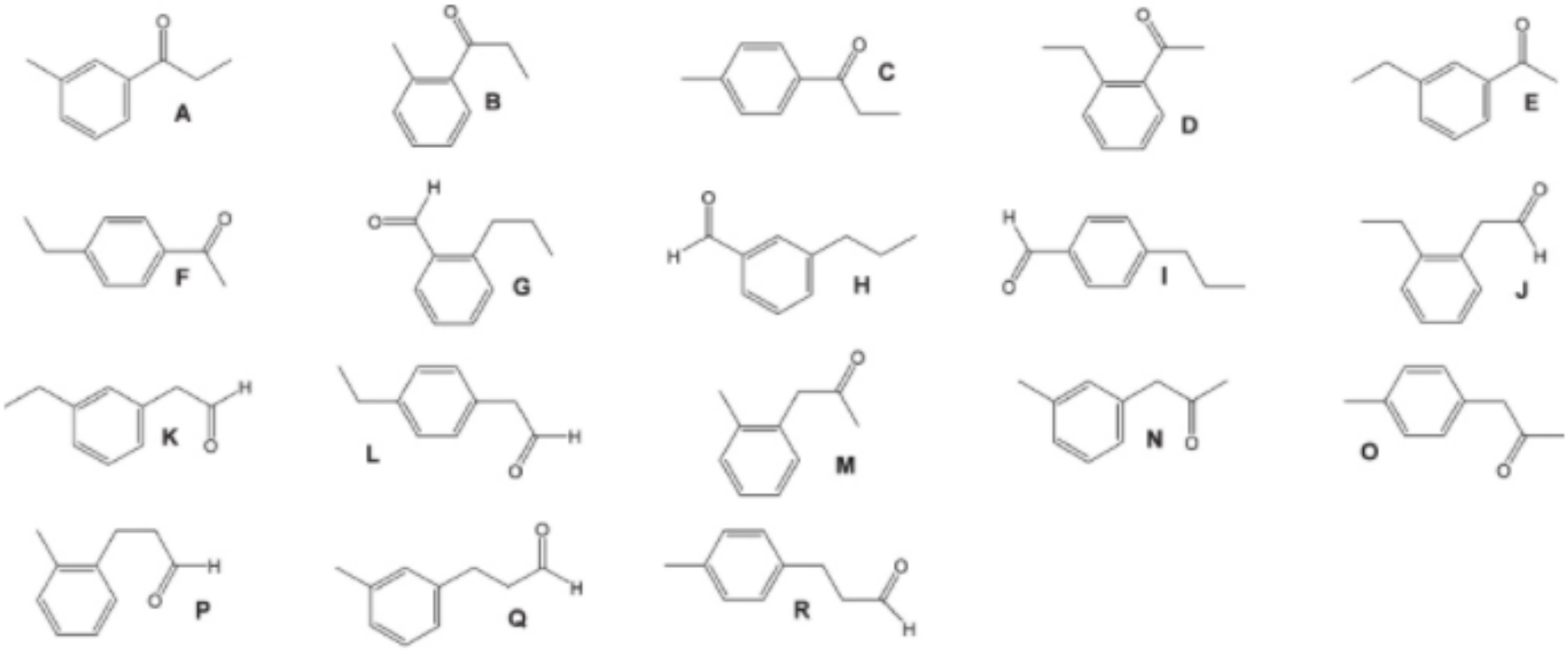


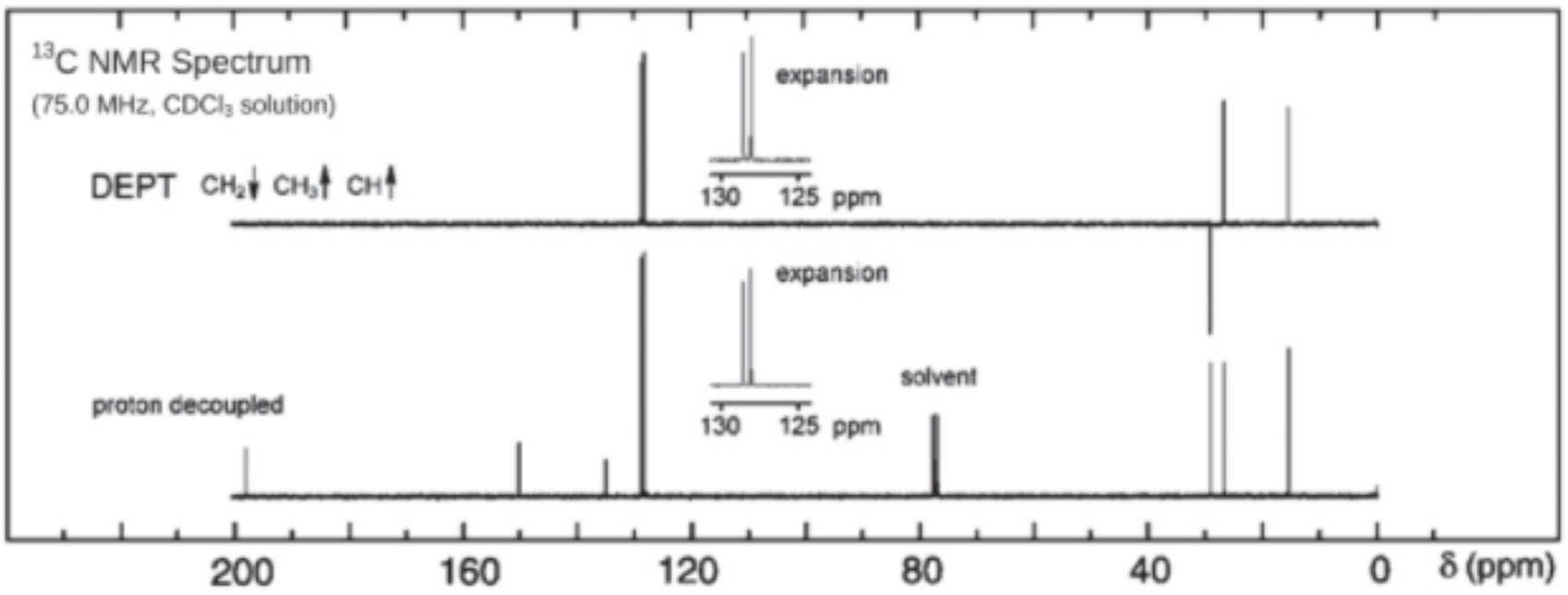

ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
ppm
4.0
3.5
3.0
2.5
2.0
1.5
1.0
^{1}H–^{1}H COSY Spectrum
(400 MHz, C_6D_6 solution)

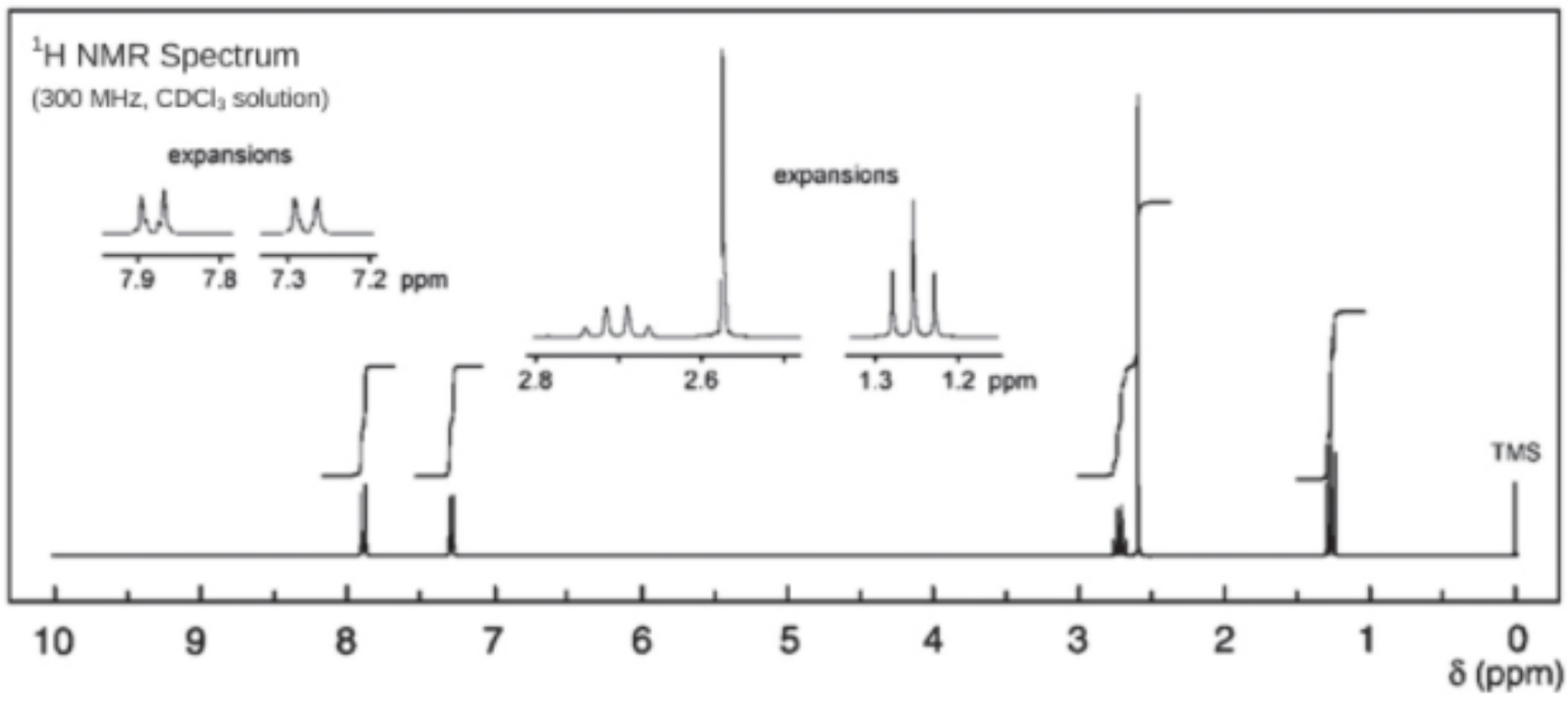

ppm
20
30
40
50
60
170
180
ppm
4.0
3.5
3.0
2.5
2.0
1.5
1.0
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, C_6D_6 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

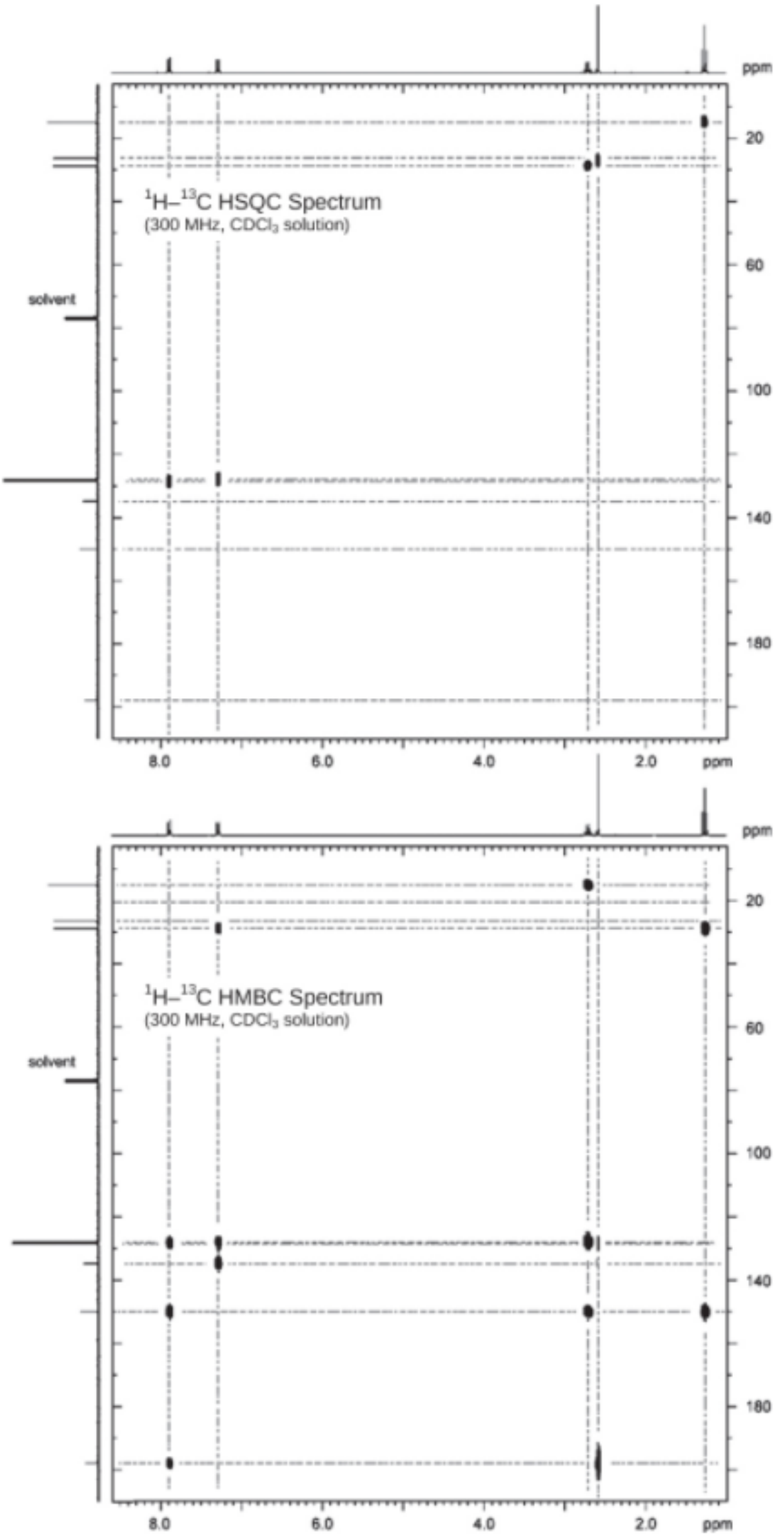
Problem 18

Given below are 18 aromatic carbonyl compounds which are isomers of $C_{10}H_{12}O$. The ^{1}H and ^{13}C NMR spectra of one of the isomers, recorded at 298K in $CDCl_3$ solution, is given below. The 2-dimensional C–H correlation and HMBC spectra are given on the facing page. To which of these compounds do the spectra belong?


A
B
C
D
E
F
G
H
I
J
K
L
M
N
O
P
Q
R


^{13}C NMR Spectrum
(75.0 MHz, $CDCl_3$ solution)
DEPT CH2 CH3 CH
expansion
130 125 ppm
expansion
130 125 ppm
solvent
proton decoupled
200 160 120 80 40 0 δ (ppm)

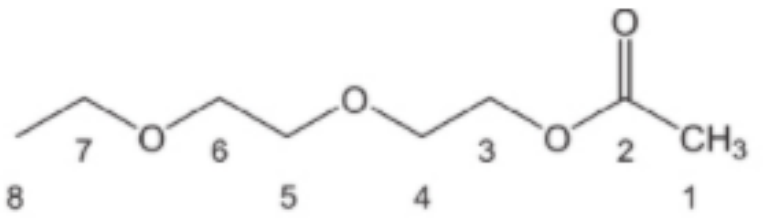

^{1}H NMR Spectrum
(300 MHz, $CDCl_3$ solution)
expansions
7.9 7.8 7.3 7.2 ppm
expansions
2.8 2.6
1.3 1.2 ppm
TMS
10 9 8 7 6 5 4 3 2 1 0
δ (ppm)


$^{1}H–^{13}C$ HSQC Spectrum
(300 MHz, $CDCl_3$ solution)
solvent
ppm
20
60
100
140
180
8.0
6.0
4.0
2.0
ppm
$^{1}H–^{13}C$ HMBC Spectrum
(300 MHz, $CDCl_3$ solution)
solvent
20
60
100
140
180
8.0
6.0
4.0
2.0
ppm

Problem 19

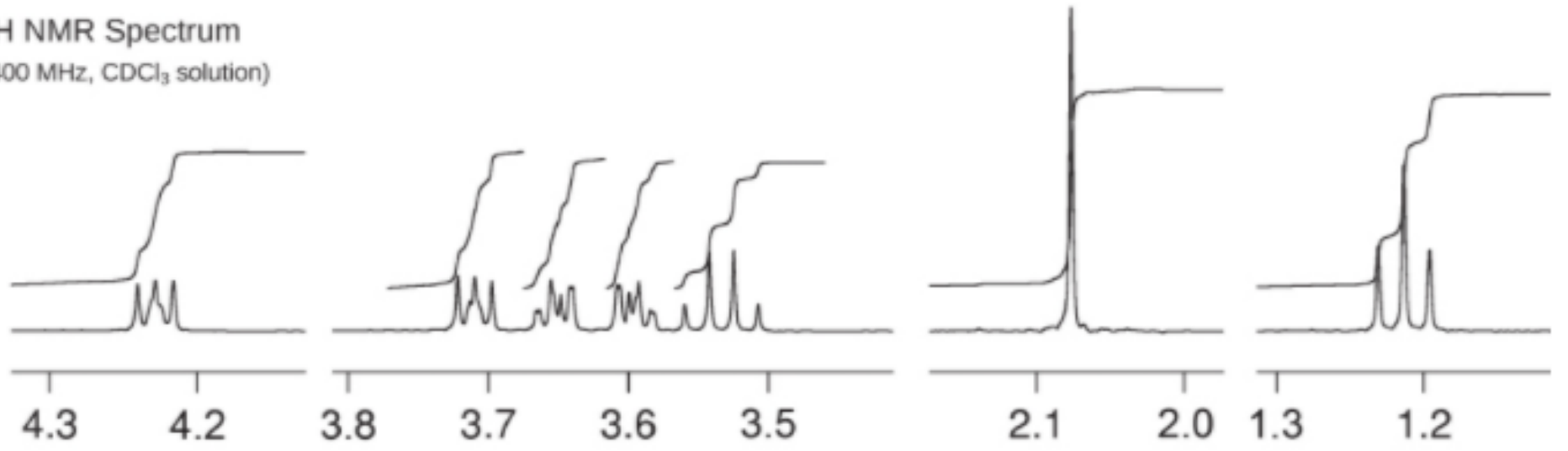
The ^{1}H and proton-decoupled ^{13}C NMR spectra of diethyleneglycol ethyl ether acetate ($C_8H_{10}O_4$) recorded in $CDCl_3$ solution at 298K and 400 MHz are given below. The ^{1}H NMR spectrum has signals at δ 4.23, 3.71, 3.65, 3.60, 3.53, 2.08 and 1.22 ppm. The ^{13}C spectrum has signals at δ 171.0, 70.7, 69.8, 69.1, 66.7, 63.6, 20.9 and 15.2 ppm.

The 2-dimensional ^{1}H–^{1}H COSY spectrum, the ^{1}H–^{13}C *me*-HSQC correlation spectrum and the ^{1}H–^{13}C HMBC spectrum are given on the following pages. Use the spectra to assign all of the ^{1}H and ^{13}C resonances in the spectrum, *i.e.* determine the chemical shift corresponding to each of the protons and each of the carbons in the molecule.

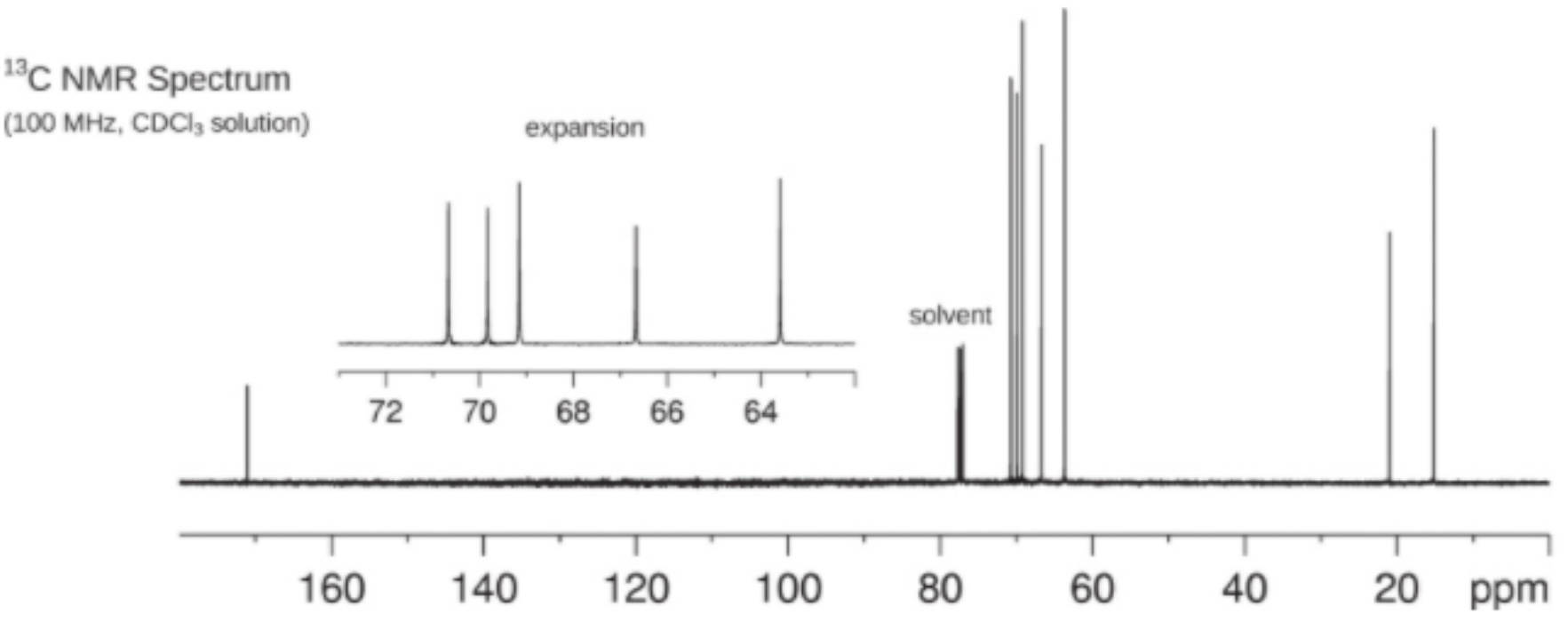


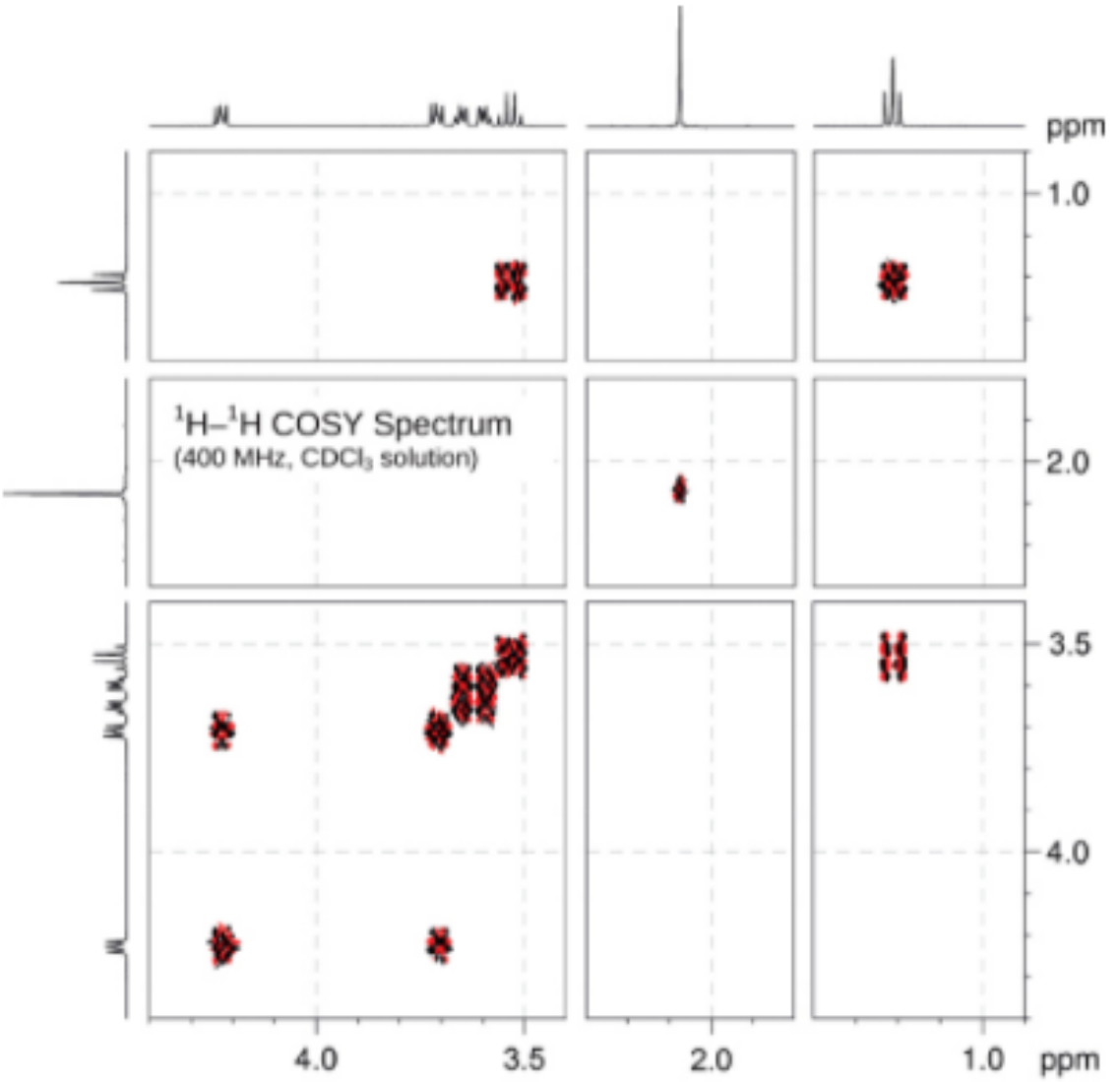
Proton	Chemical Shift (δ) in ppm	Carbon	Chemical Shift (δ) in ppm
H1		C1	
		C2	
H3		C3	
H4		C4	
H5		C5	
H6		C6	
H7		C7	
H8		C8	

^{1}H NMR Spectrum
(400 MHz, $CDCl_3$ solution)

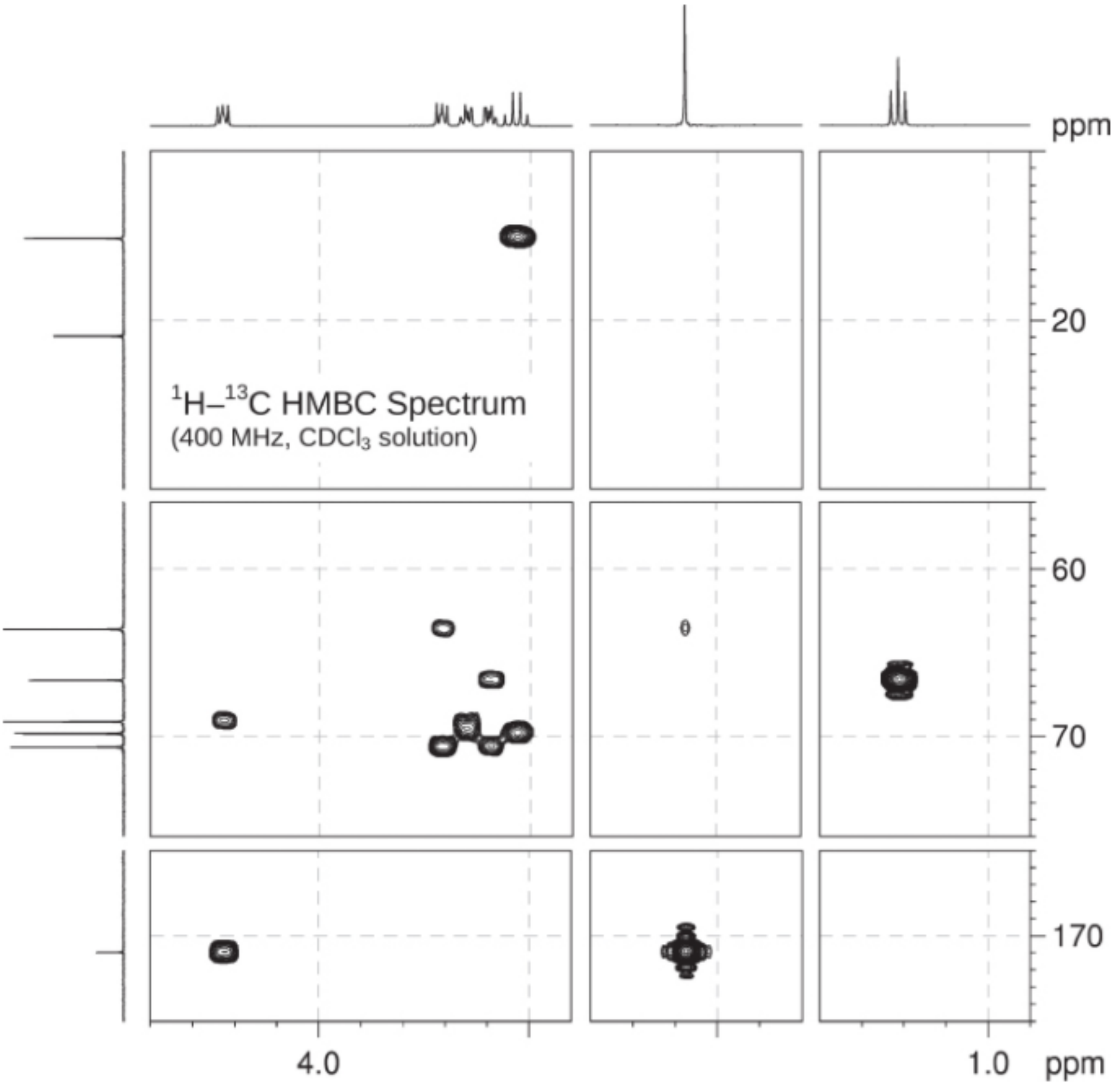


^{13}C NMR Spectrum
(100 MHz, $CDCl_3$ solution)

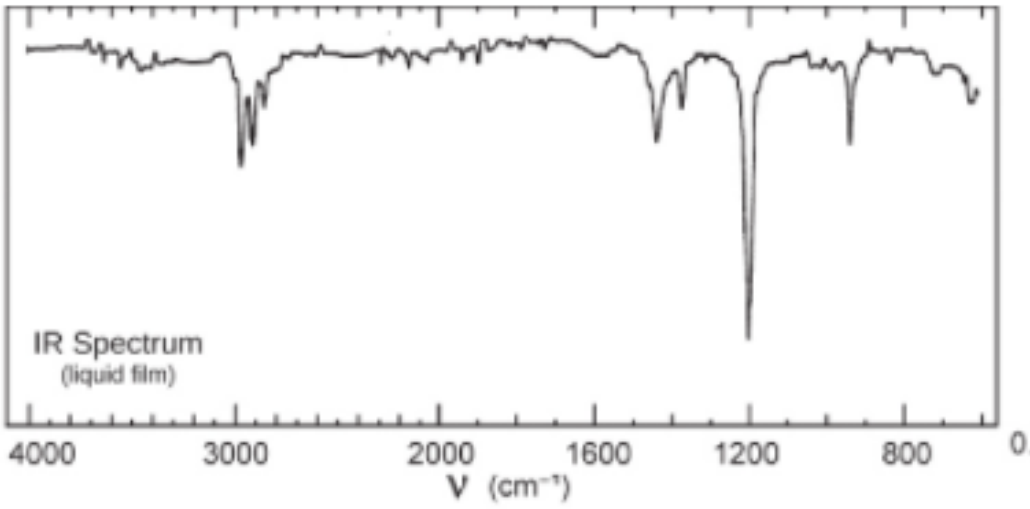


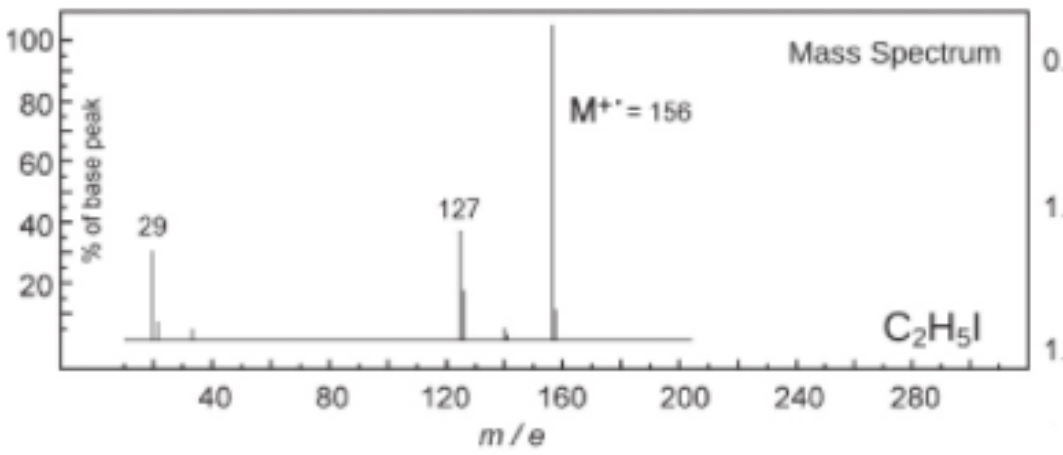

ppm
1.0
2.0
3.5
4.0
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
4.0
3.5
2.0
1.0
ppm

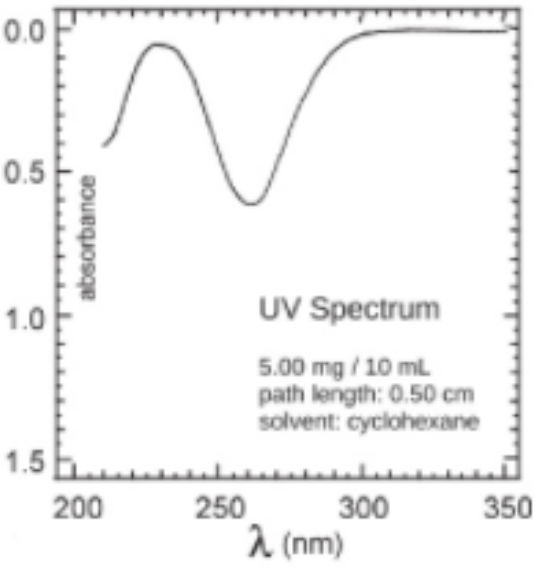
ppm
20
60
70
170
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
4.0
3.5
2.0
1.0
ppm

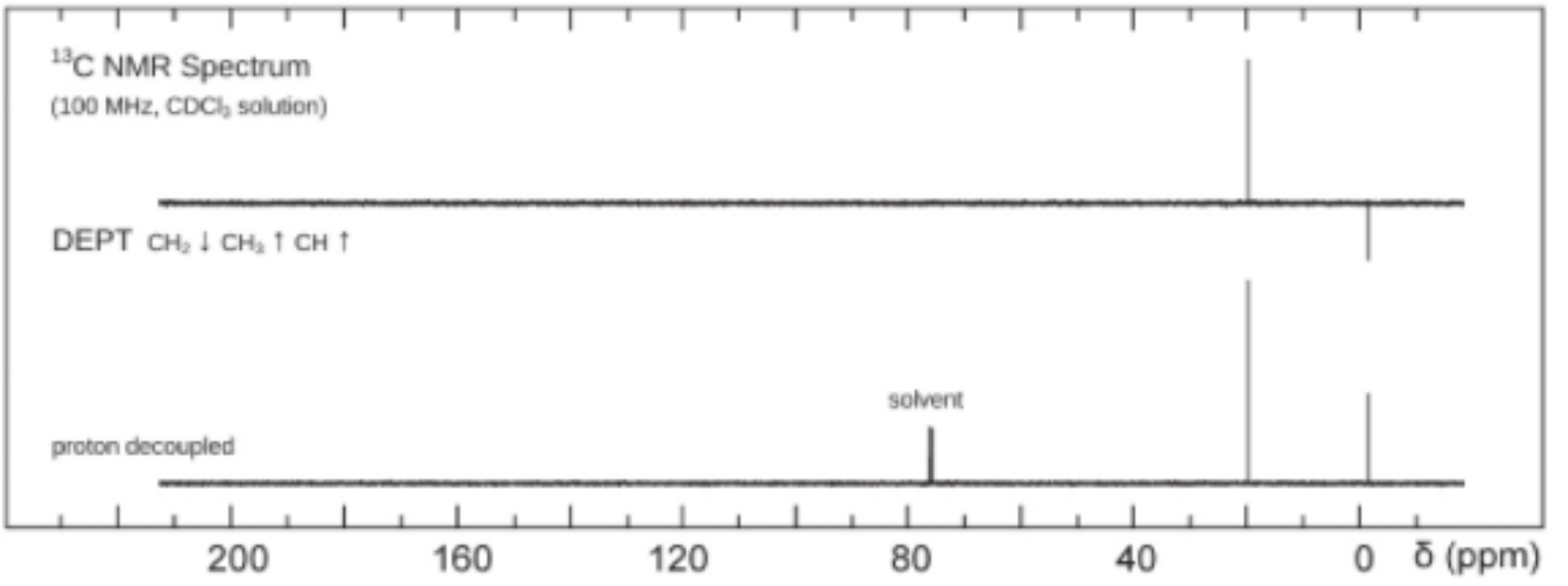

ppm
20
60
70
170
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
4.0
1.0
ppm

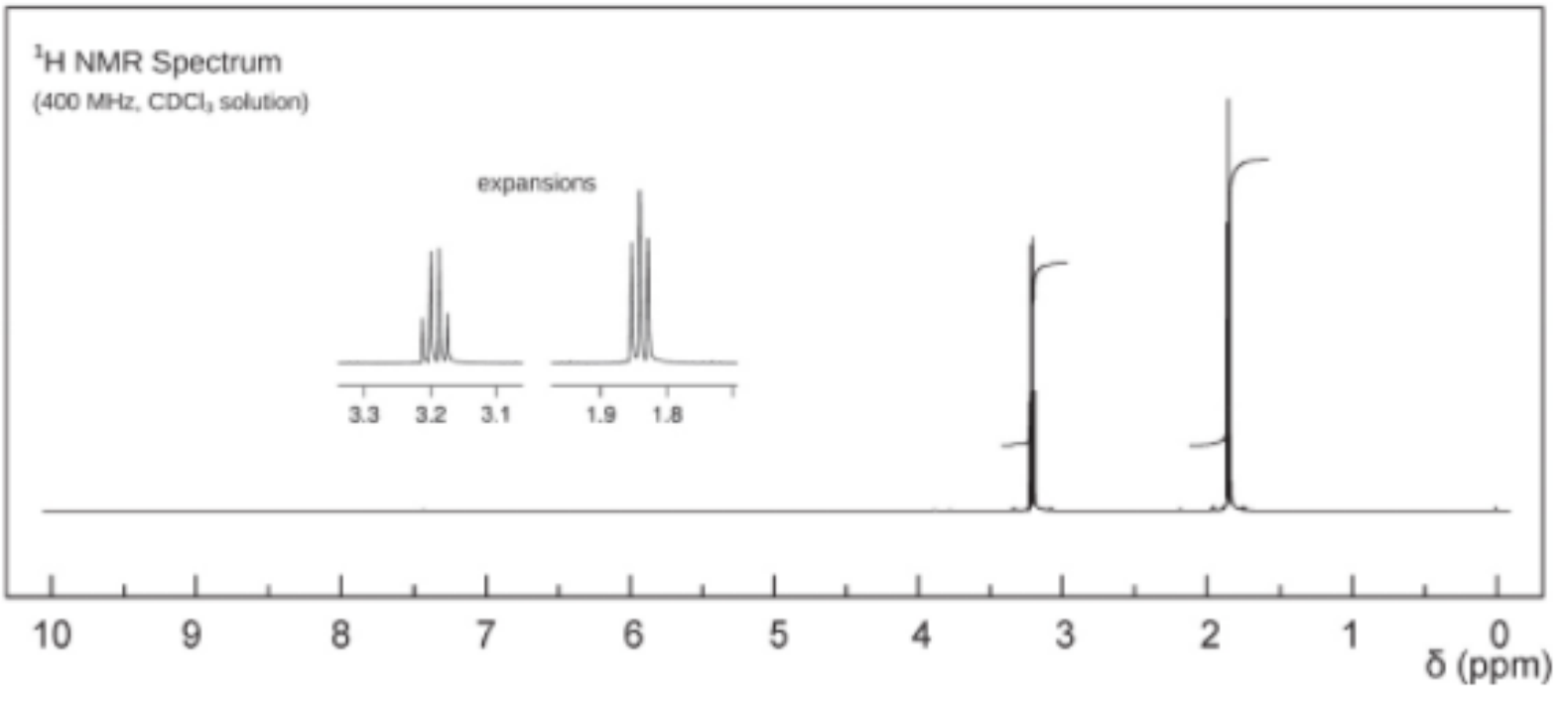
Problem 20


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

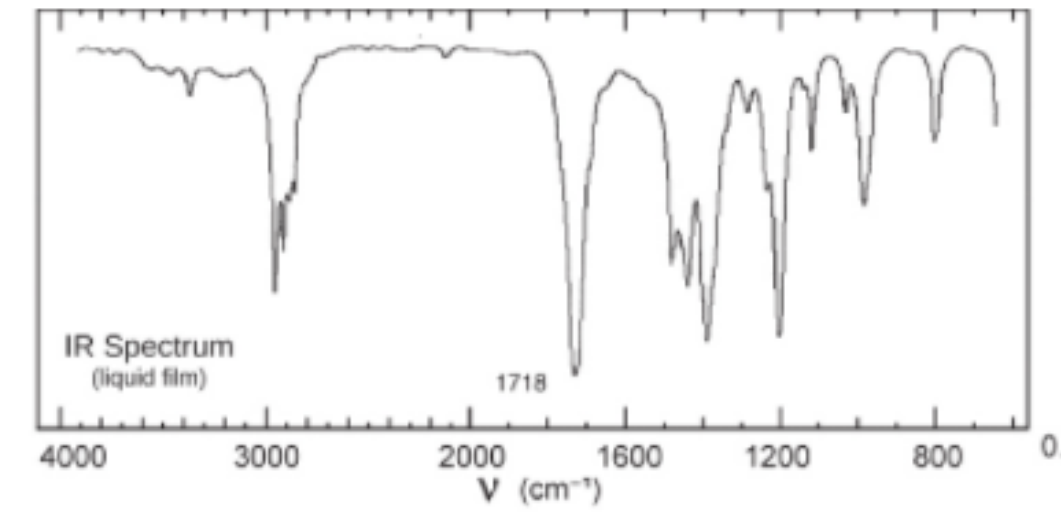

Mass Spectrum
% of base peak
100
80
60
40
20
M+· = 156
127
29
C2H5I
40
80
120
160
200
240
280
m / e

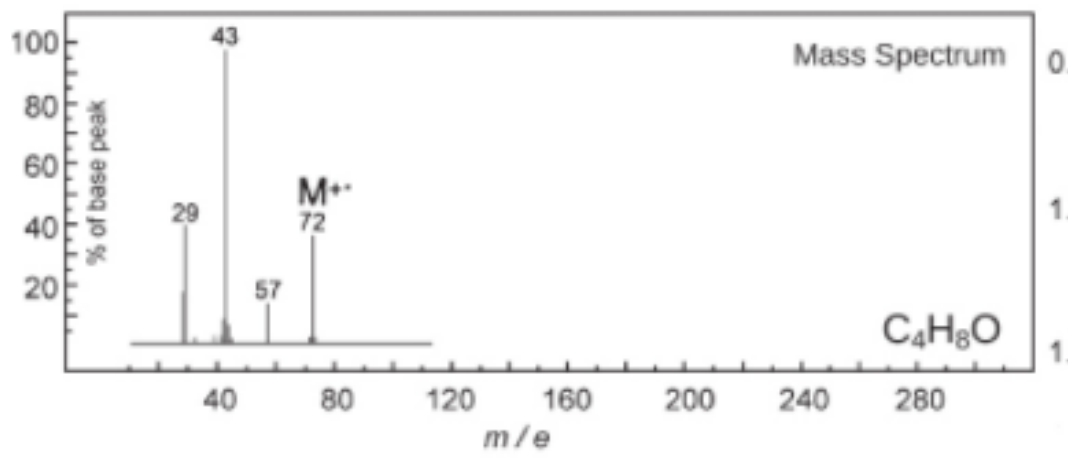

0.0
0.5
1.0
1.5
absorbance
UV Spectrum
5.00 mg / 10 mL
path length: 0.50 cm
solvent: cyclohexane
200
250
300
350
λ (nm)

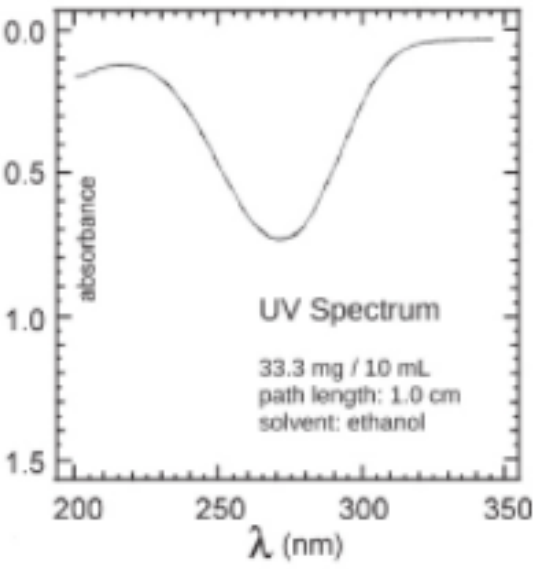

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

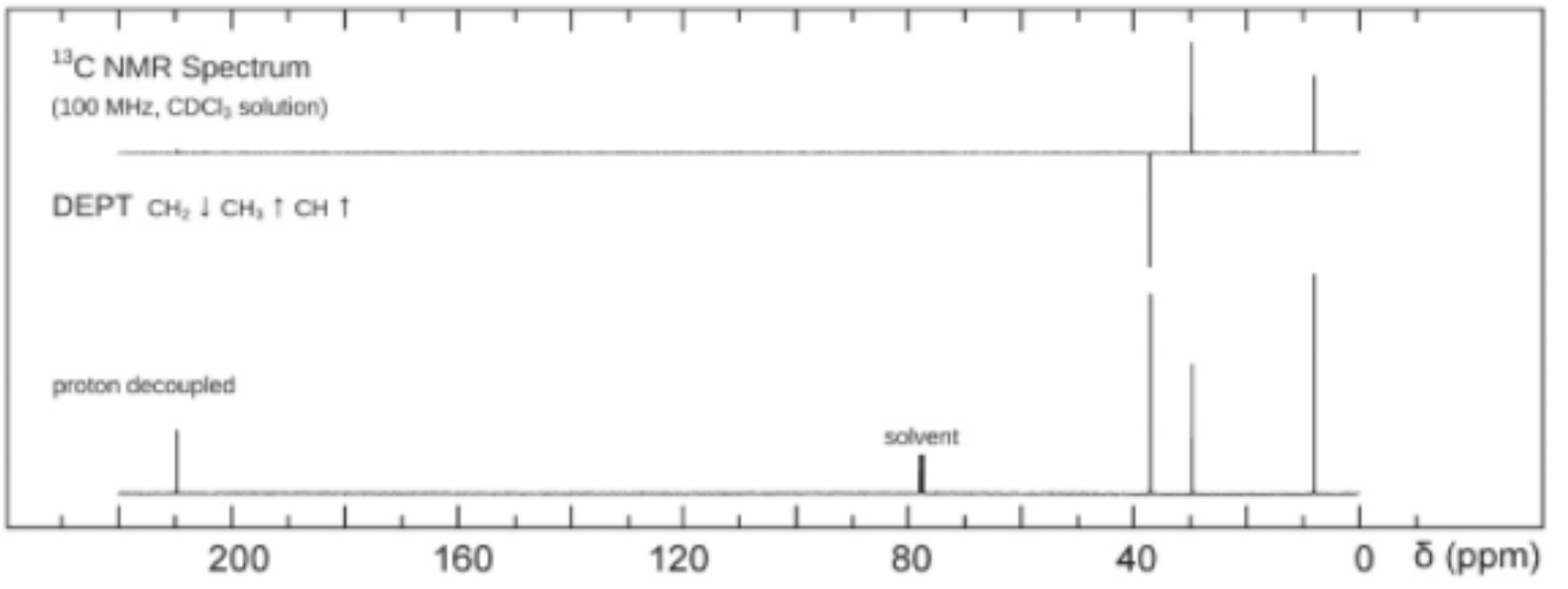

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
3.3
3.2
3.1
1.9
1.8
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

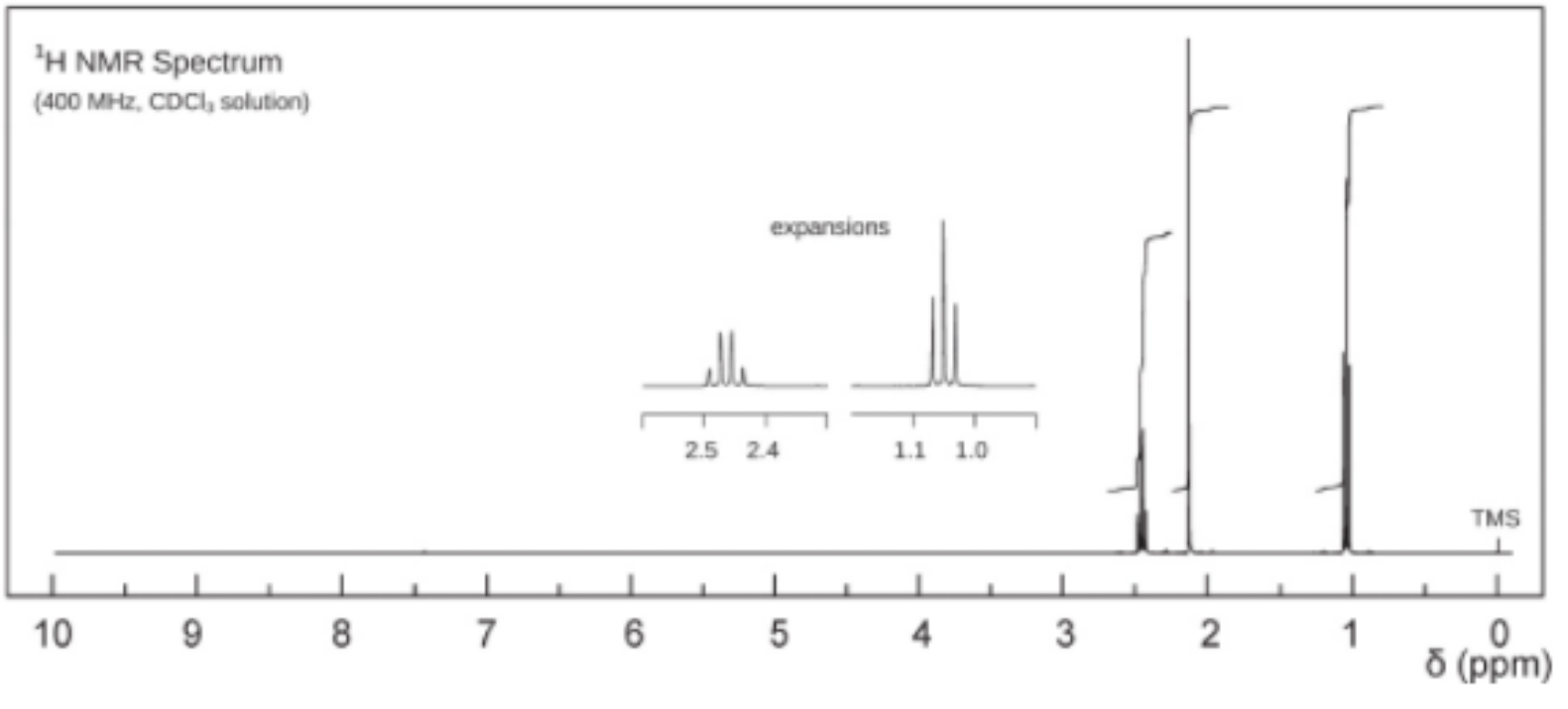
Problem 21


IR Spectrum
(liquid film)
1718
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

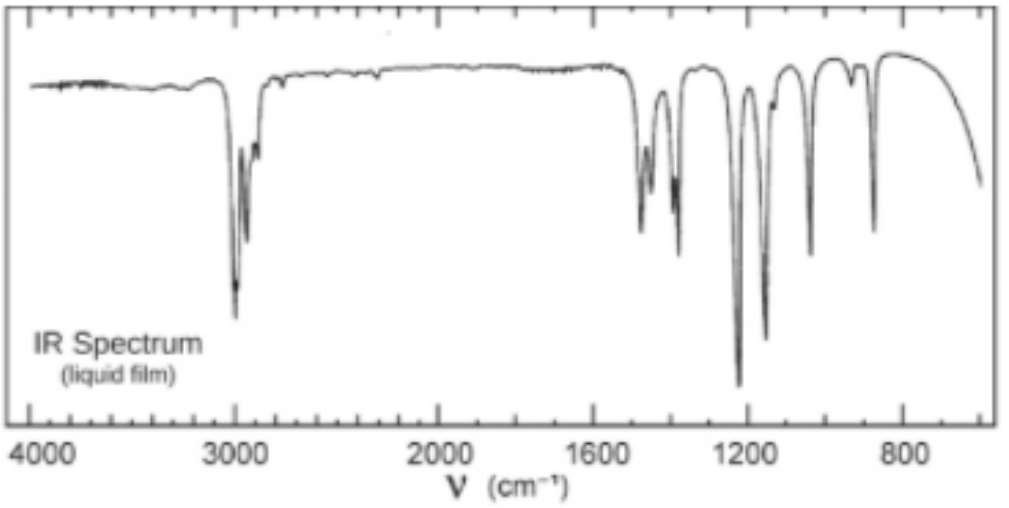

Mass Spectrum
% of base peak
100
80
60
40
20
43
29
M+·
72
57
C4H8O
40
80
120
160
200
240
280
m/e

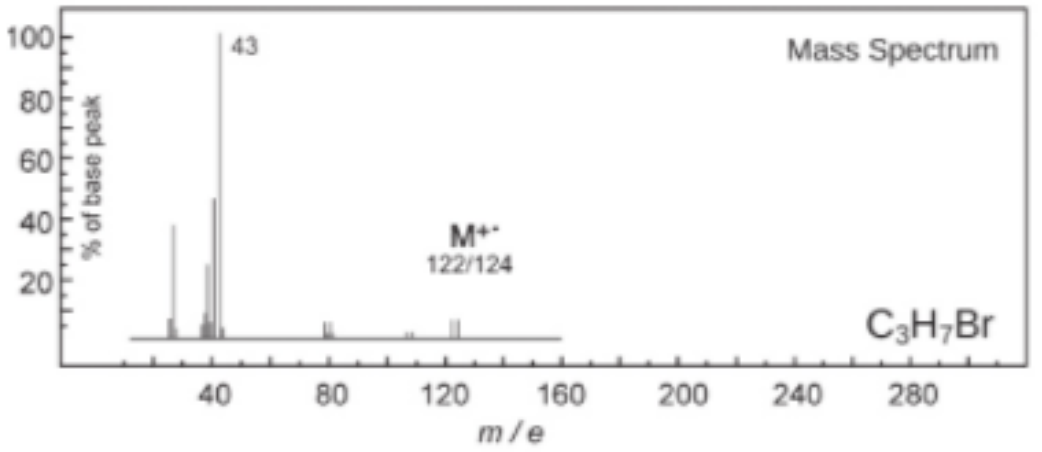

absorbance
0.0
0.5
1.0
1.5
UV Spectrum
33.3 mg / 10 mL
path length: 1.0 cm
solvent: ethanol
200
250
300
350
λ (nm)


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

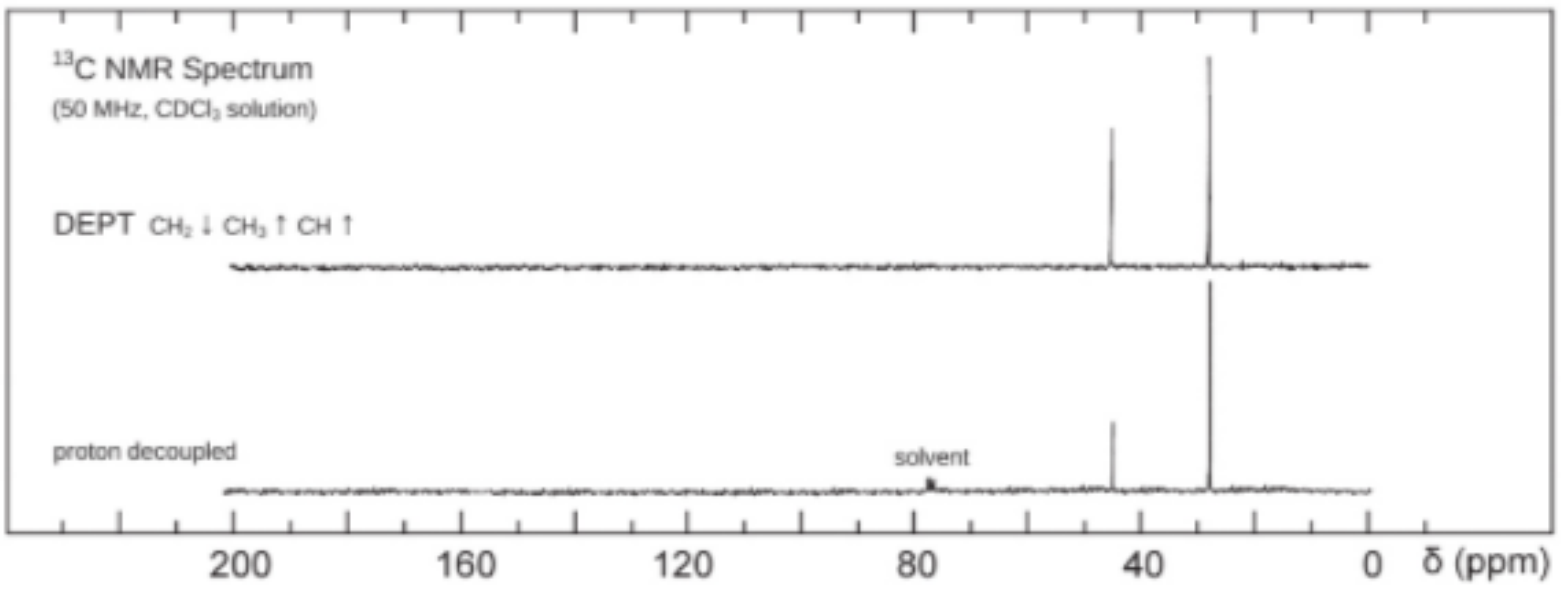

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
2.5
2.4
1.1
1.0
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

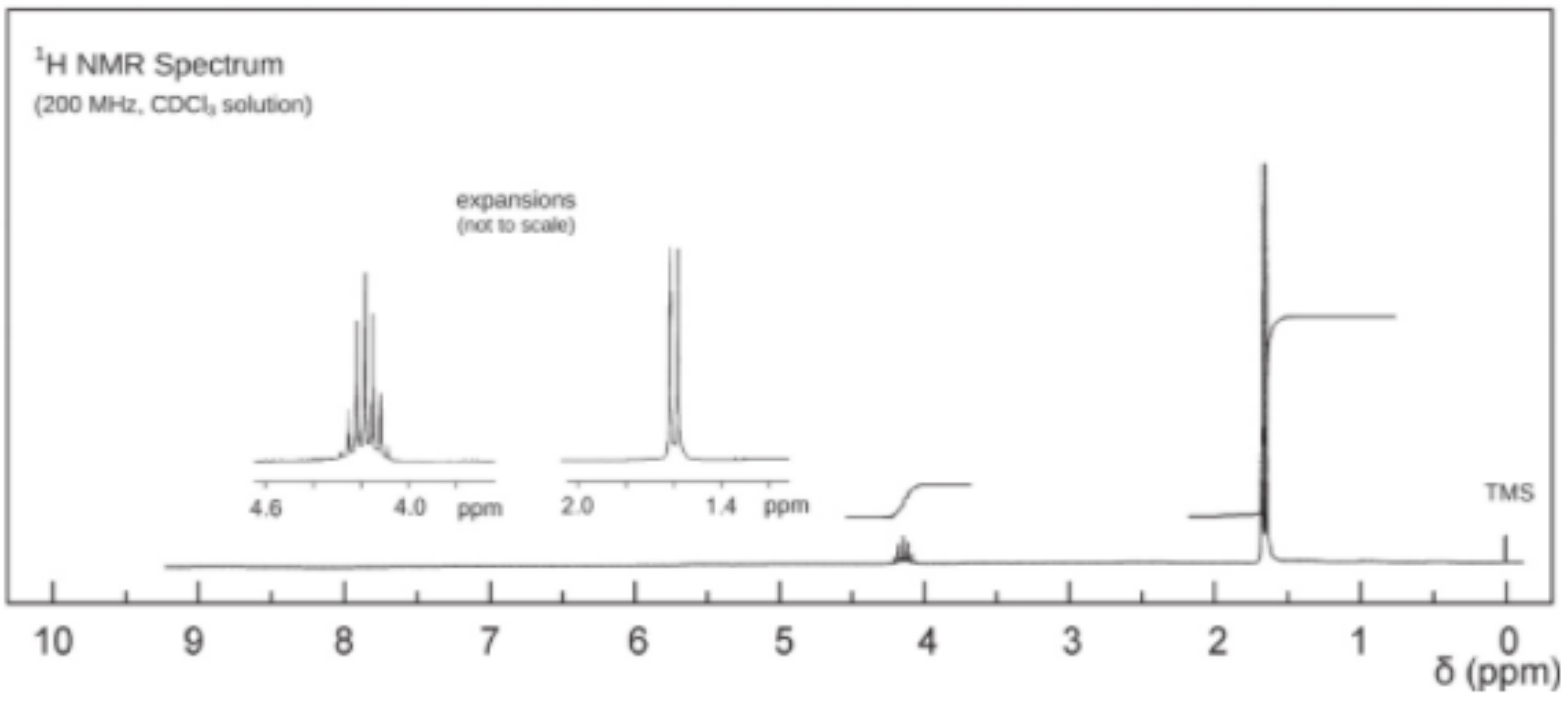
Problem 22



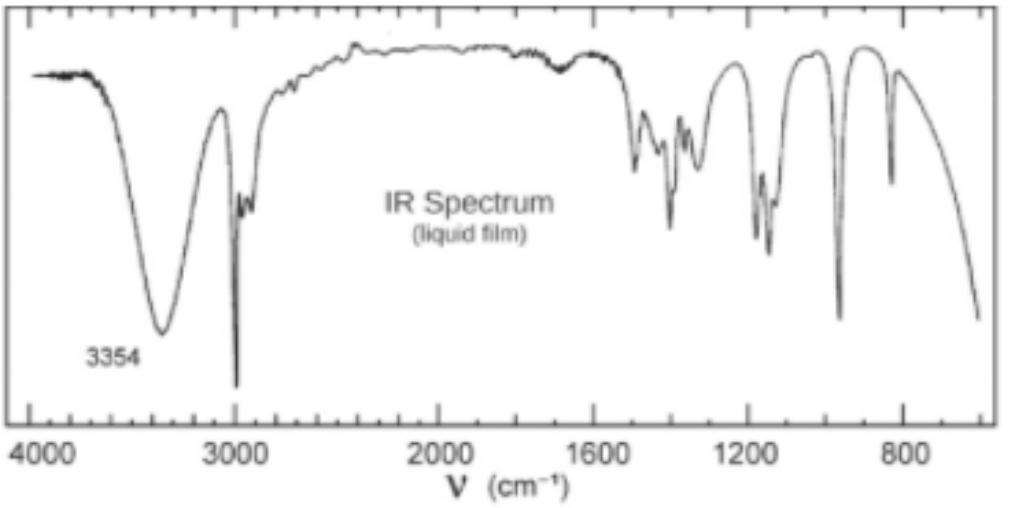


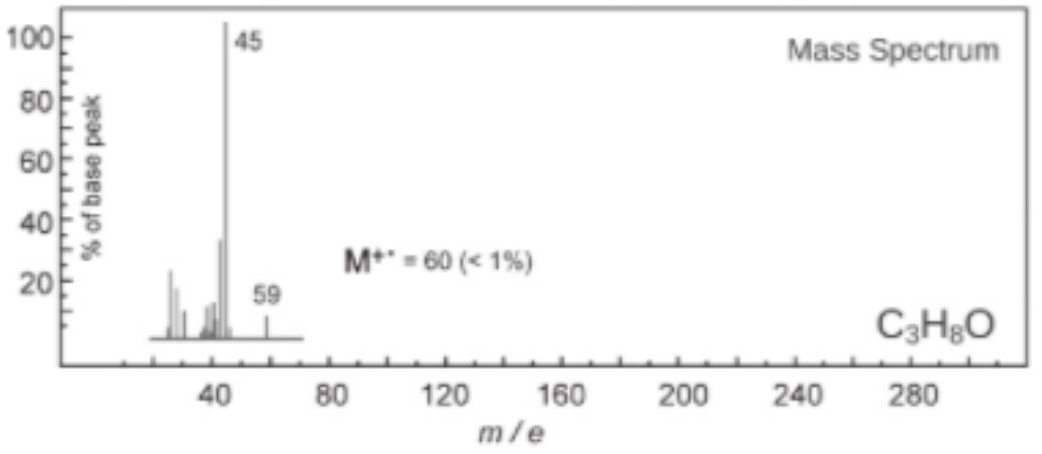
No significant UV absorption above 220 nm



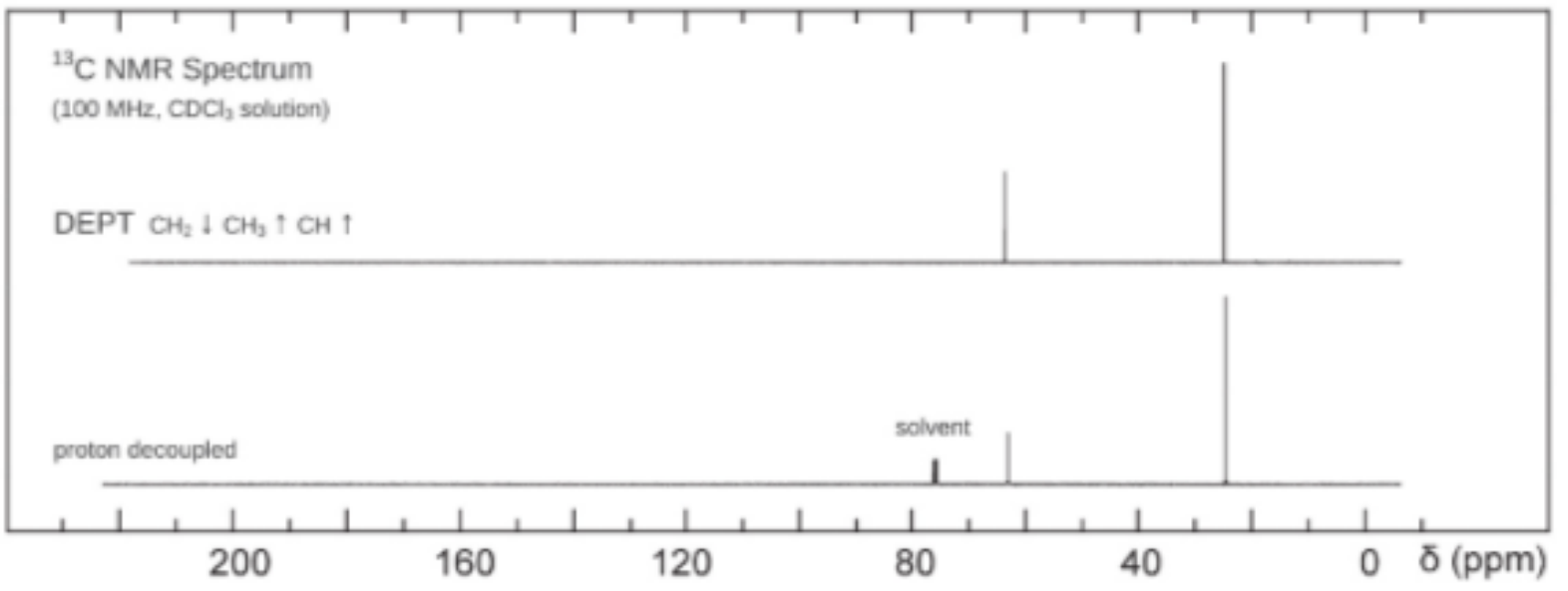


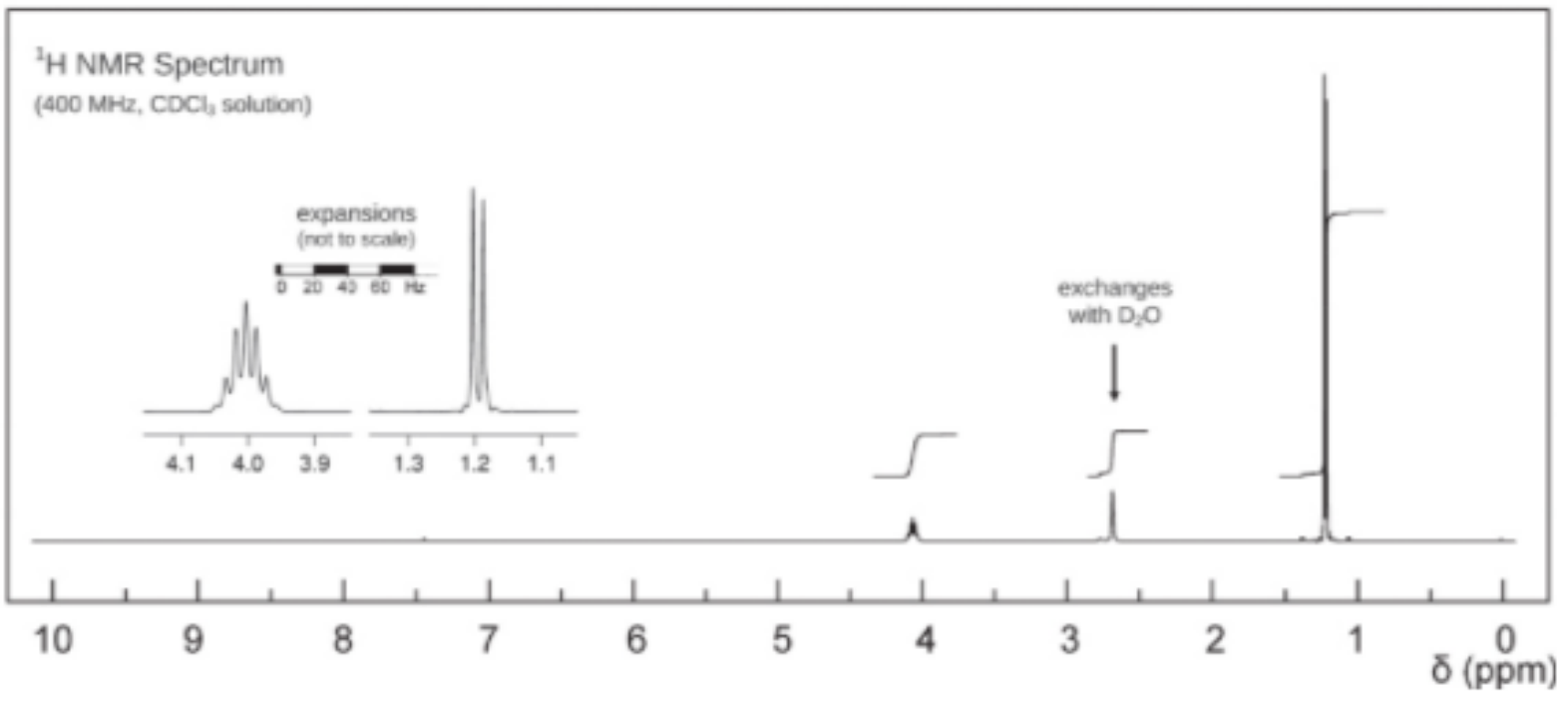
Problem 23

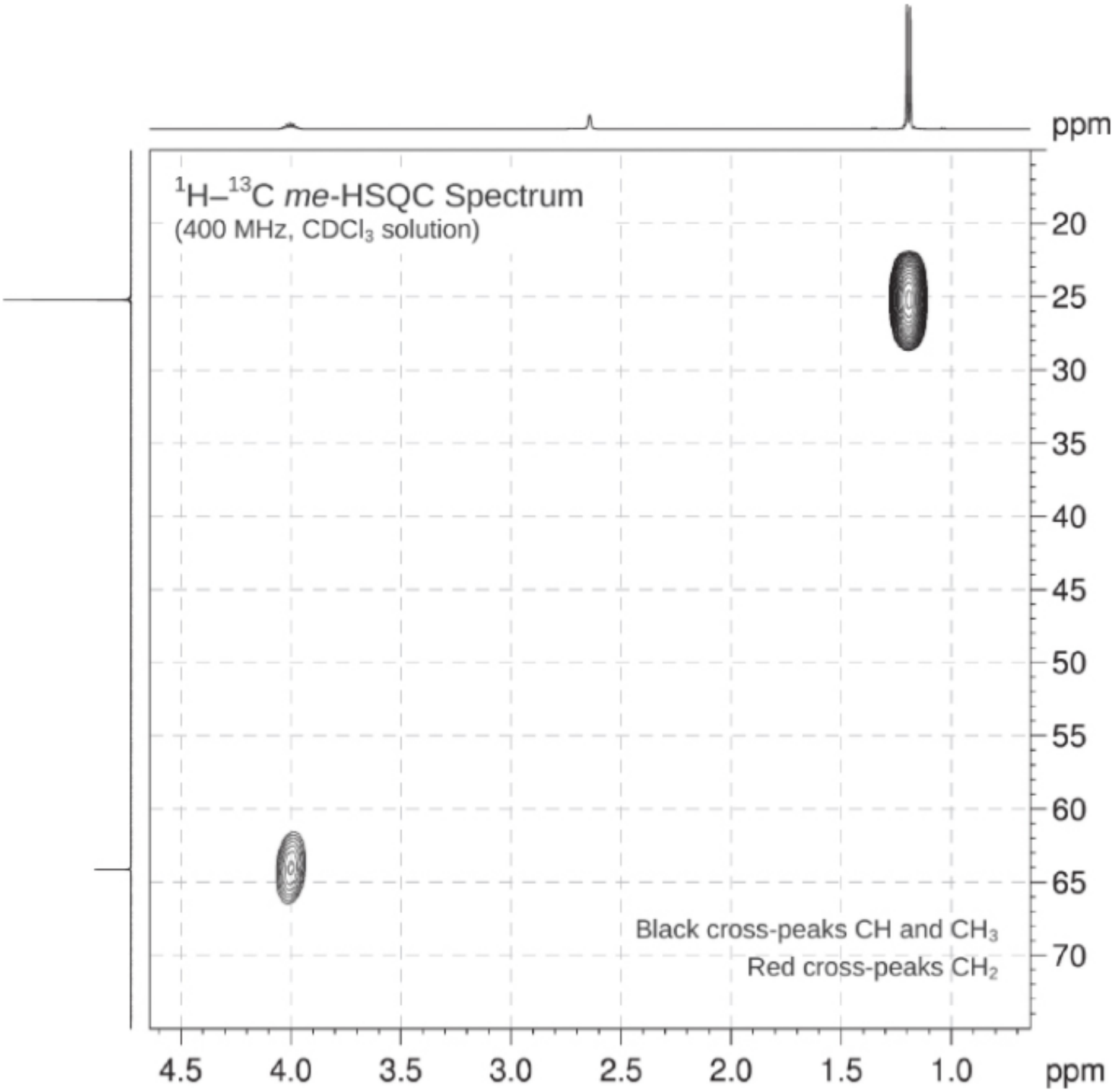




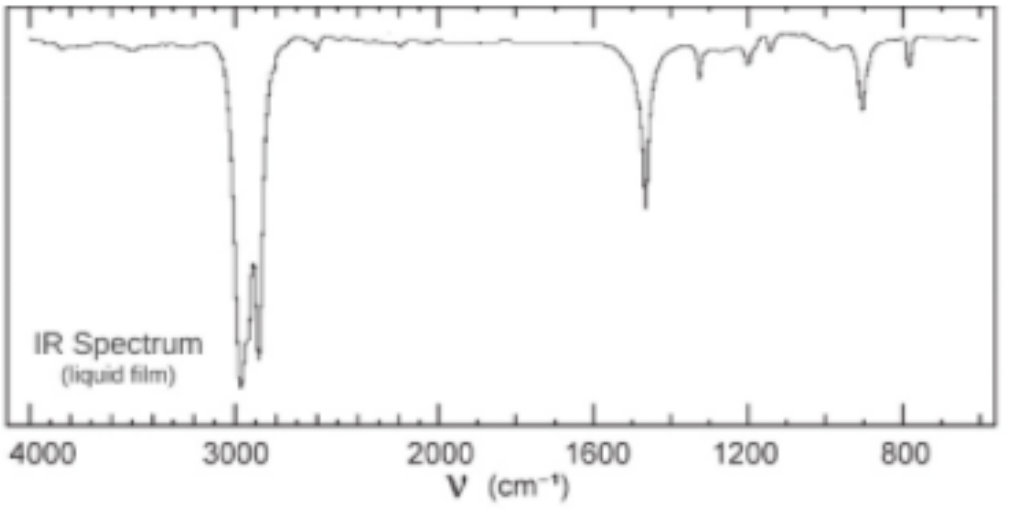
No significant UV absorption above 220 nm

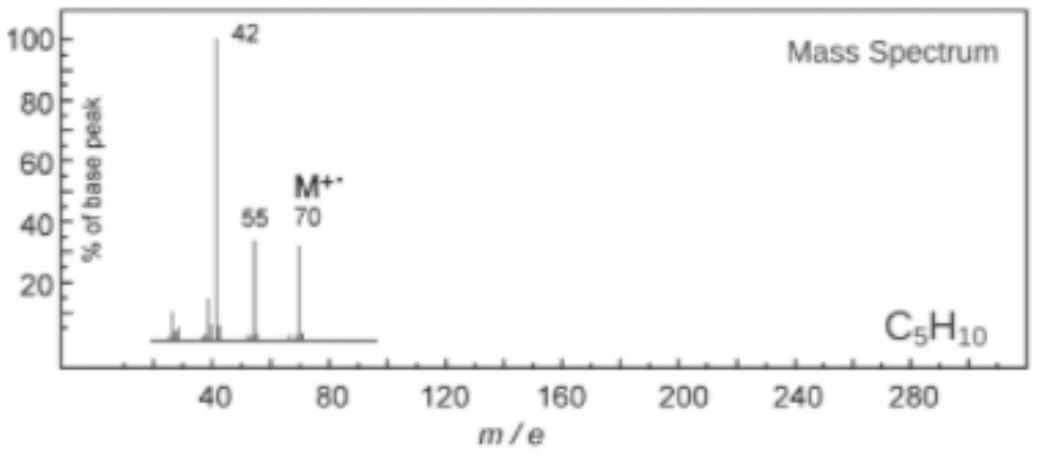




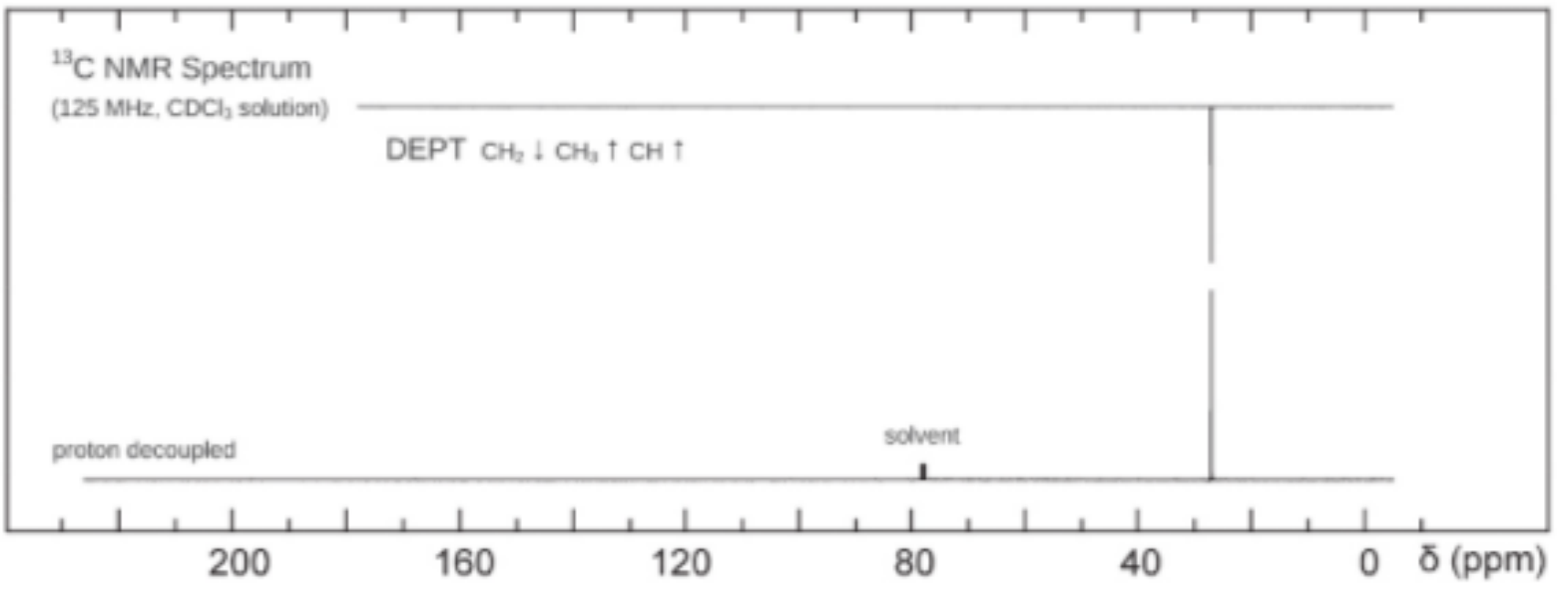

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
20
25
30
35
40
45
50
55
60
65
70
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

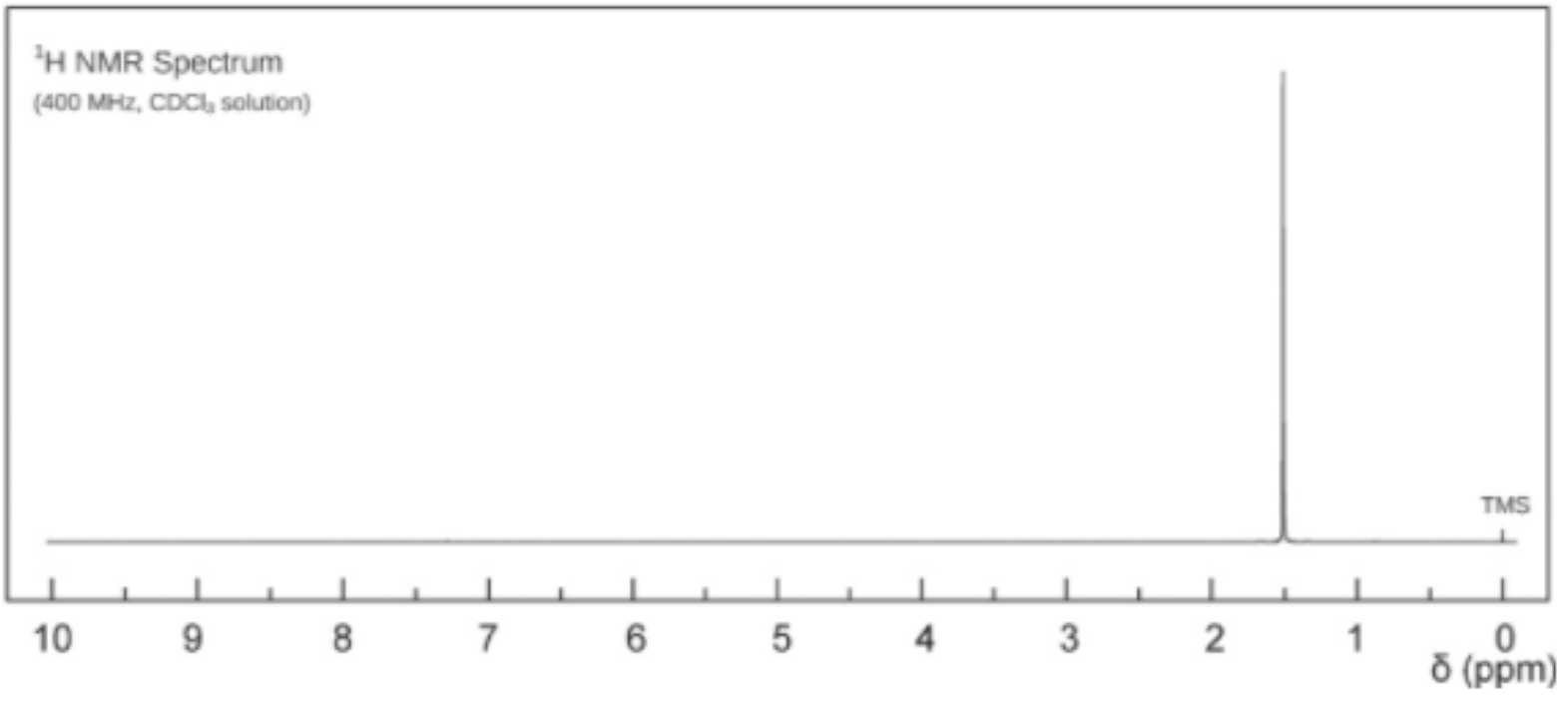
Problem 24



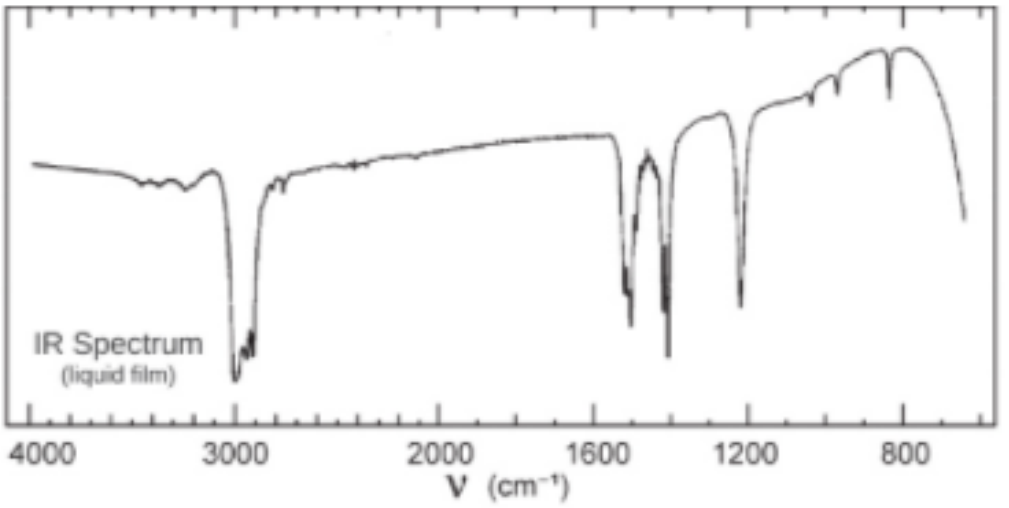


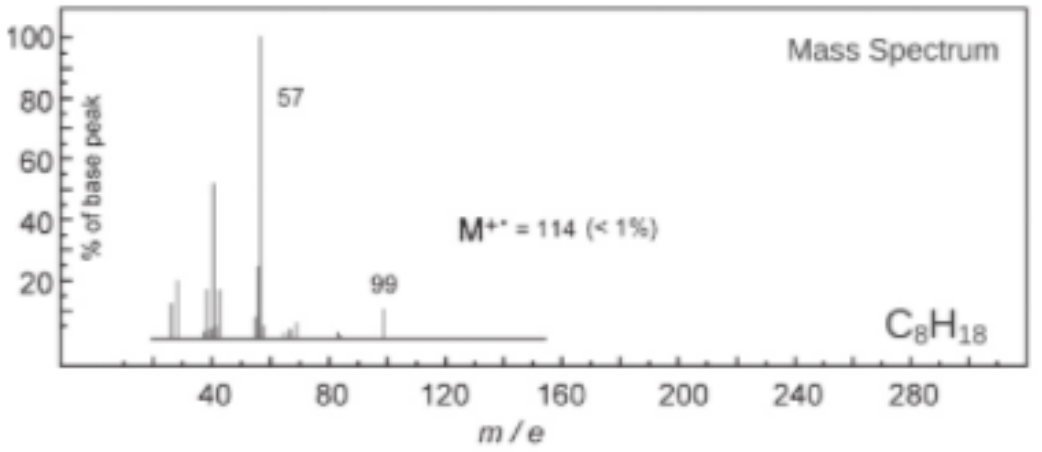
No significant UV absorption above 220 nm



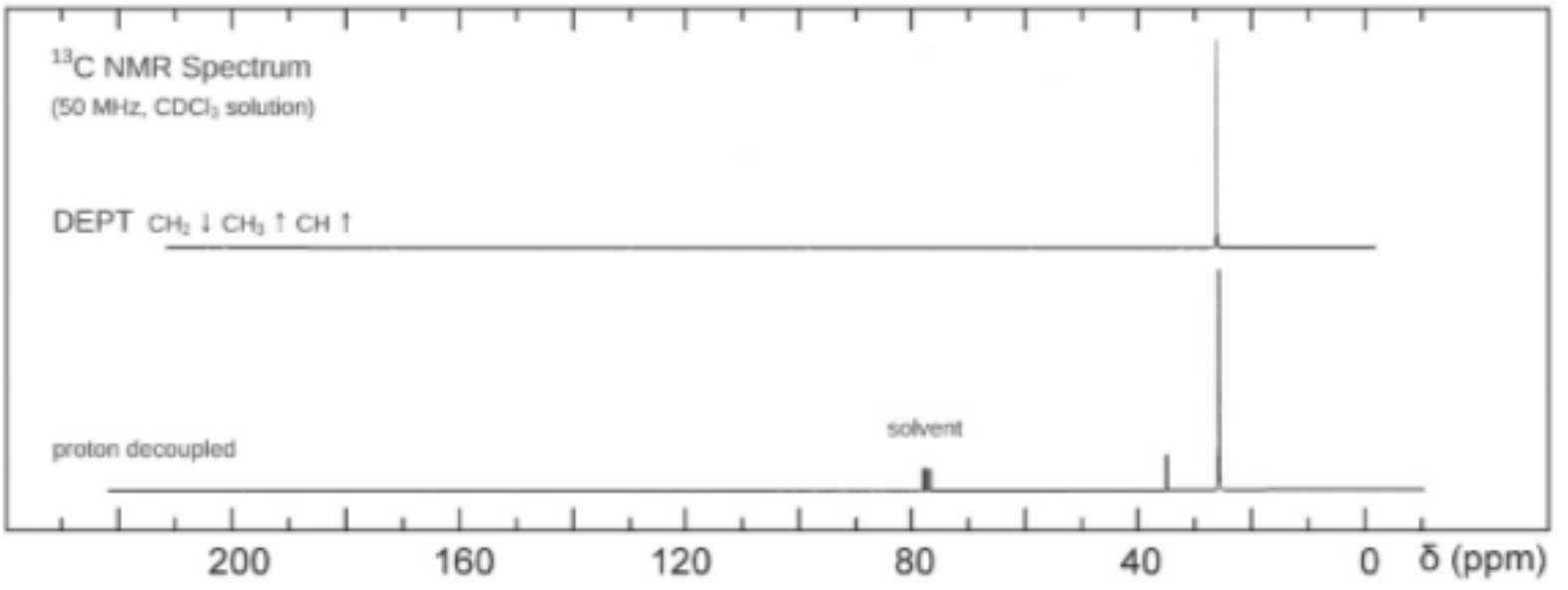


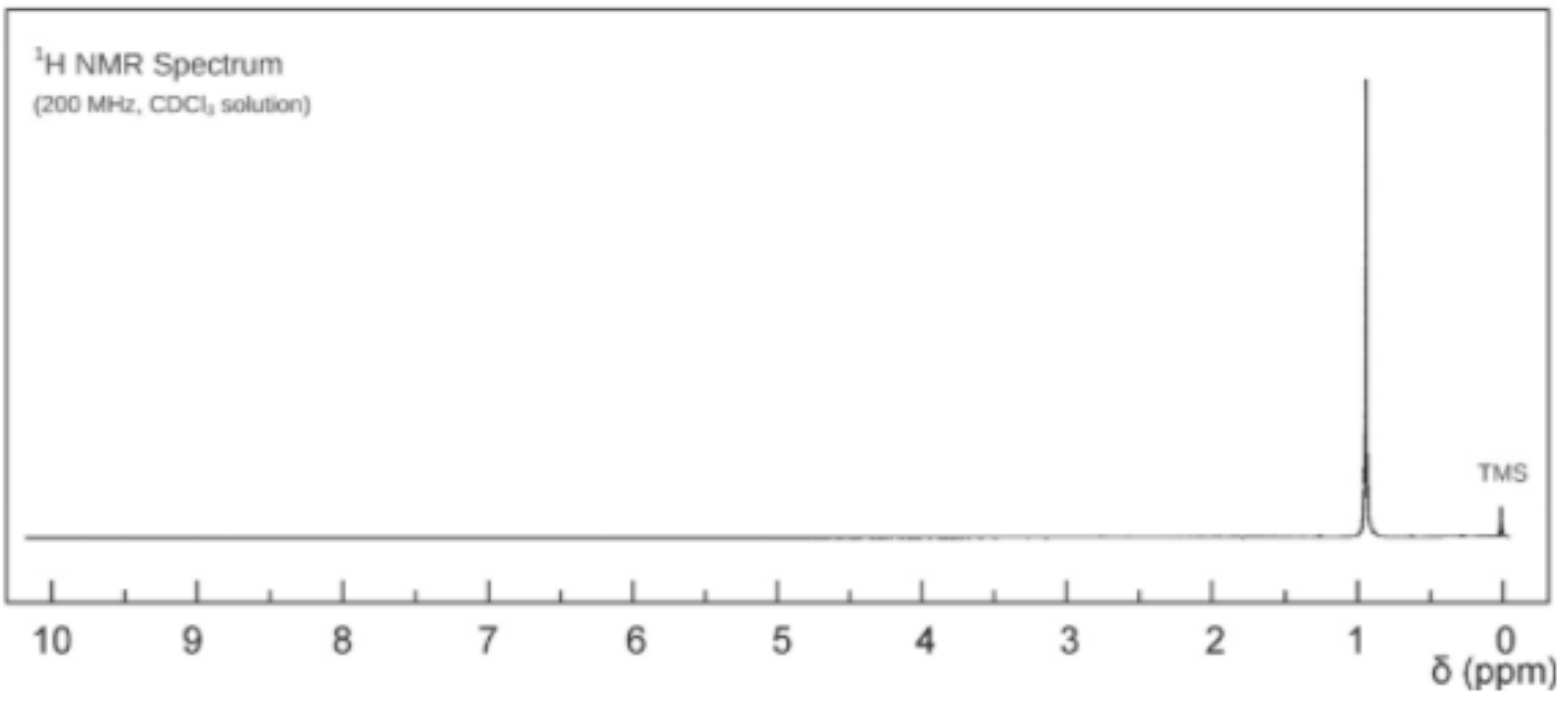
Problem 25



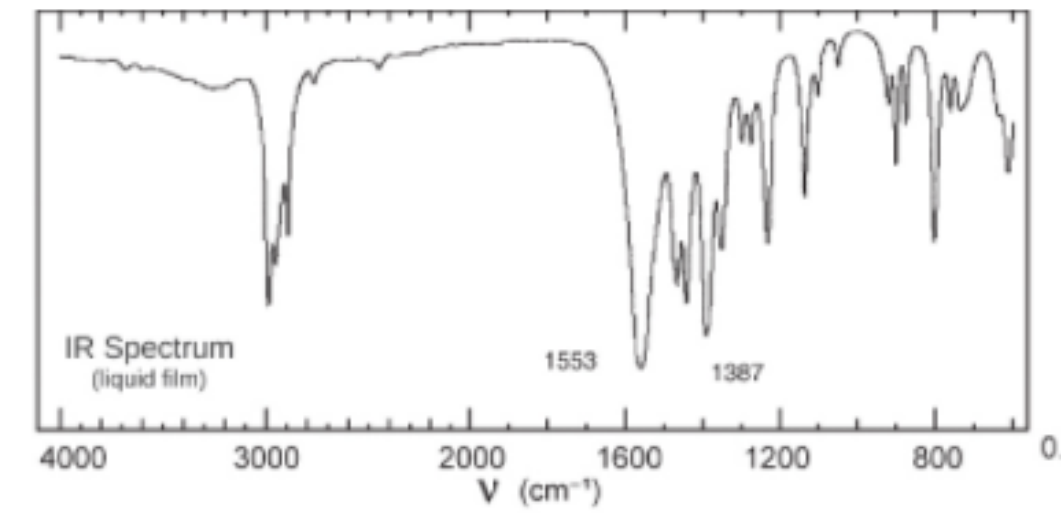


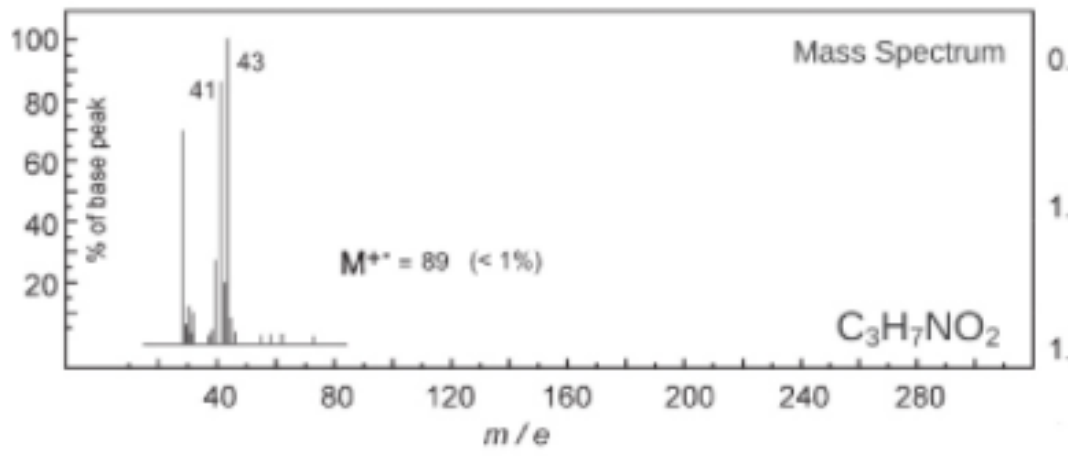
No significant UV absorption above 220 nm

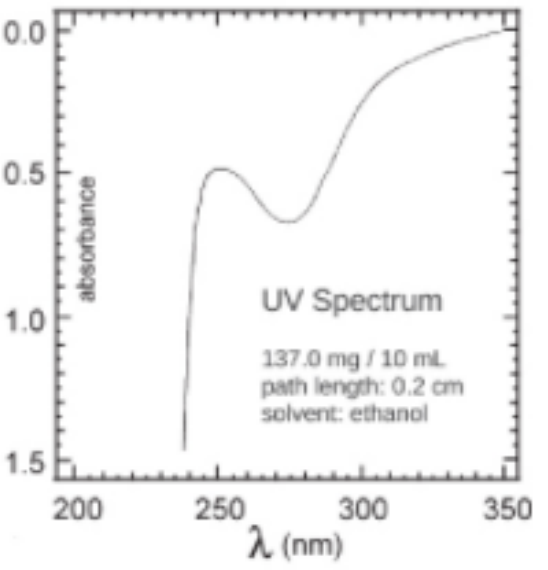


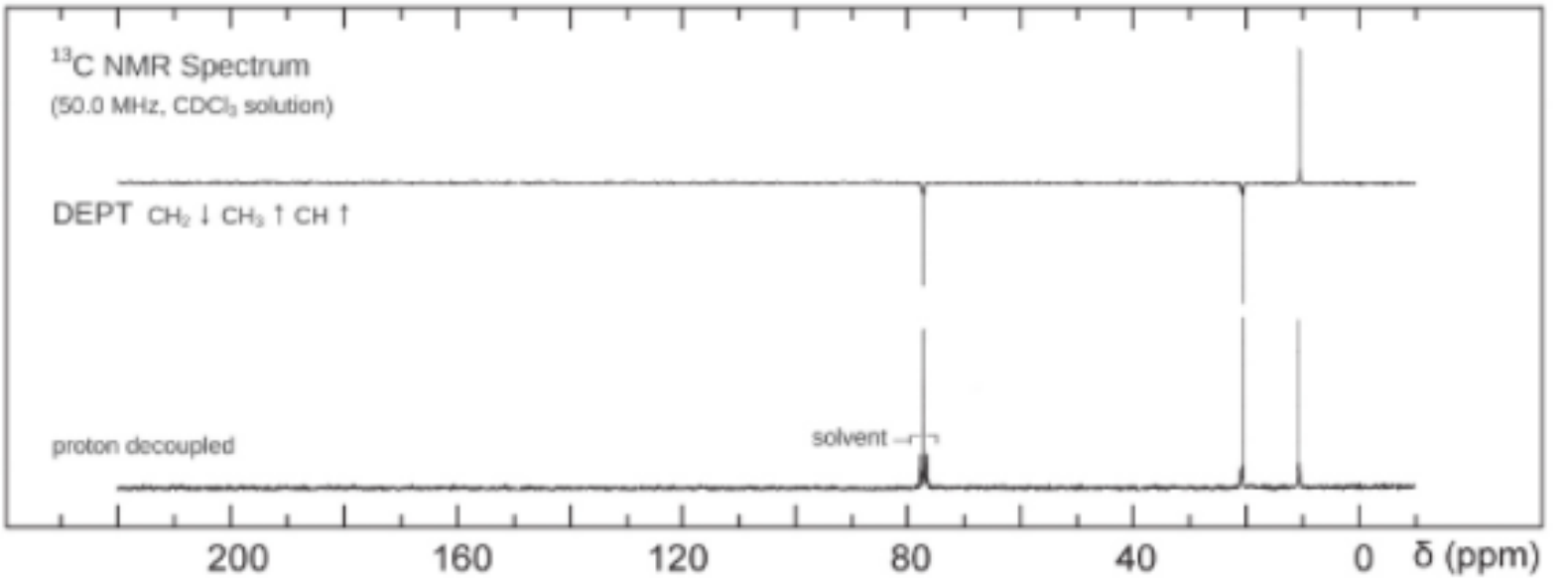


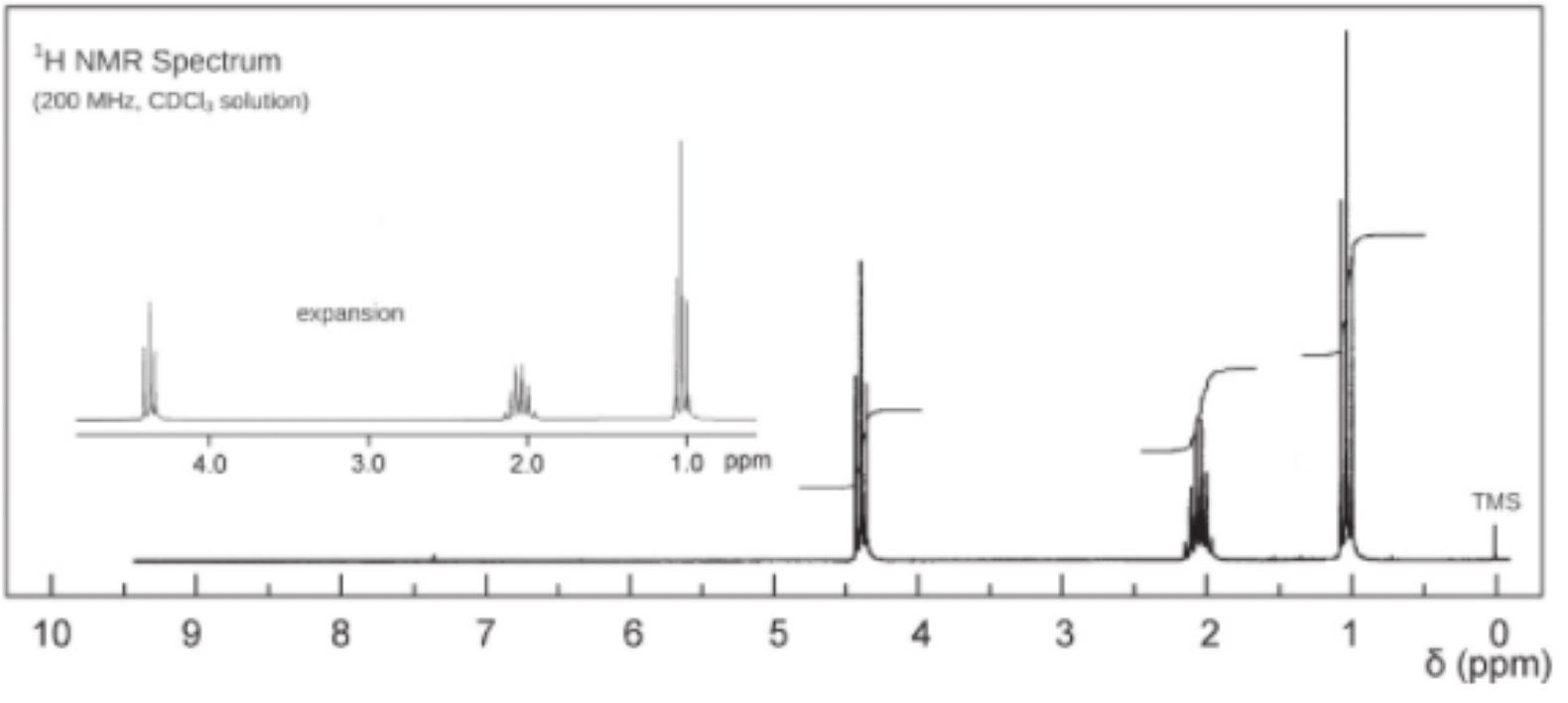
Problem 26


IR Spectrum
(liquid film)
1553
1387
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

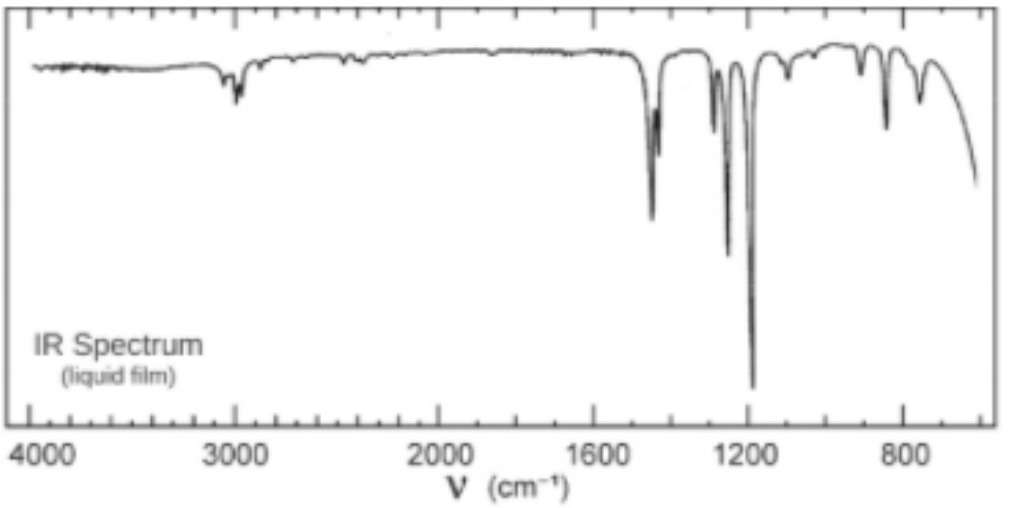

Mass Spectrum
% of base peak
100
80
60
40
20
41
43
M+· = 89 (< 1%)
C3H7NO2
40
80
120
160
200
240
280
m / e

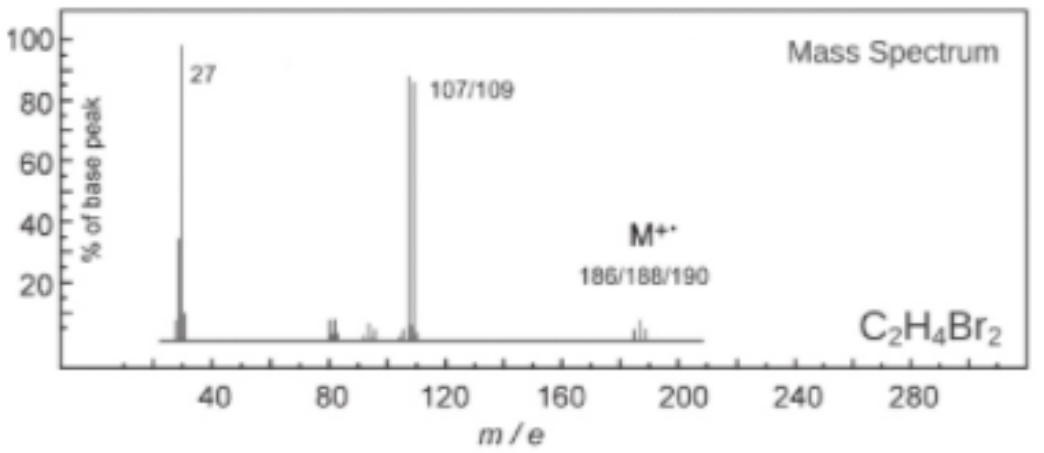

UV Spectrum
137.0 mg / 10 mL
path length: 0.2 cm
solvent: ethanol
absorbance
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)


13C NMR Spectrum
(50.0 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

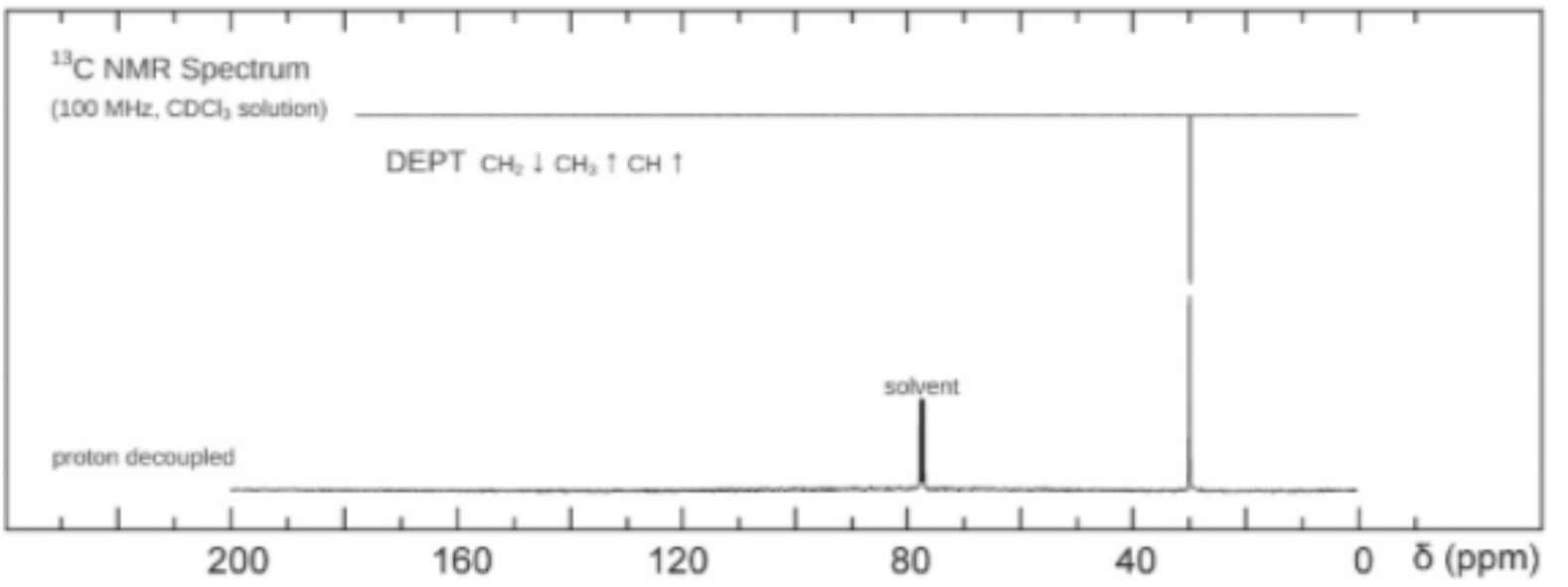

1H NMR Spectrum
(200 MHz, CDCl3 solution)
expansion
4.0
3.0
2.0
1.0 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

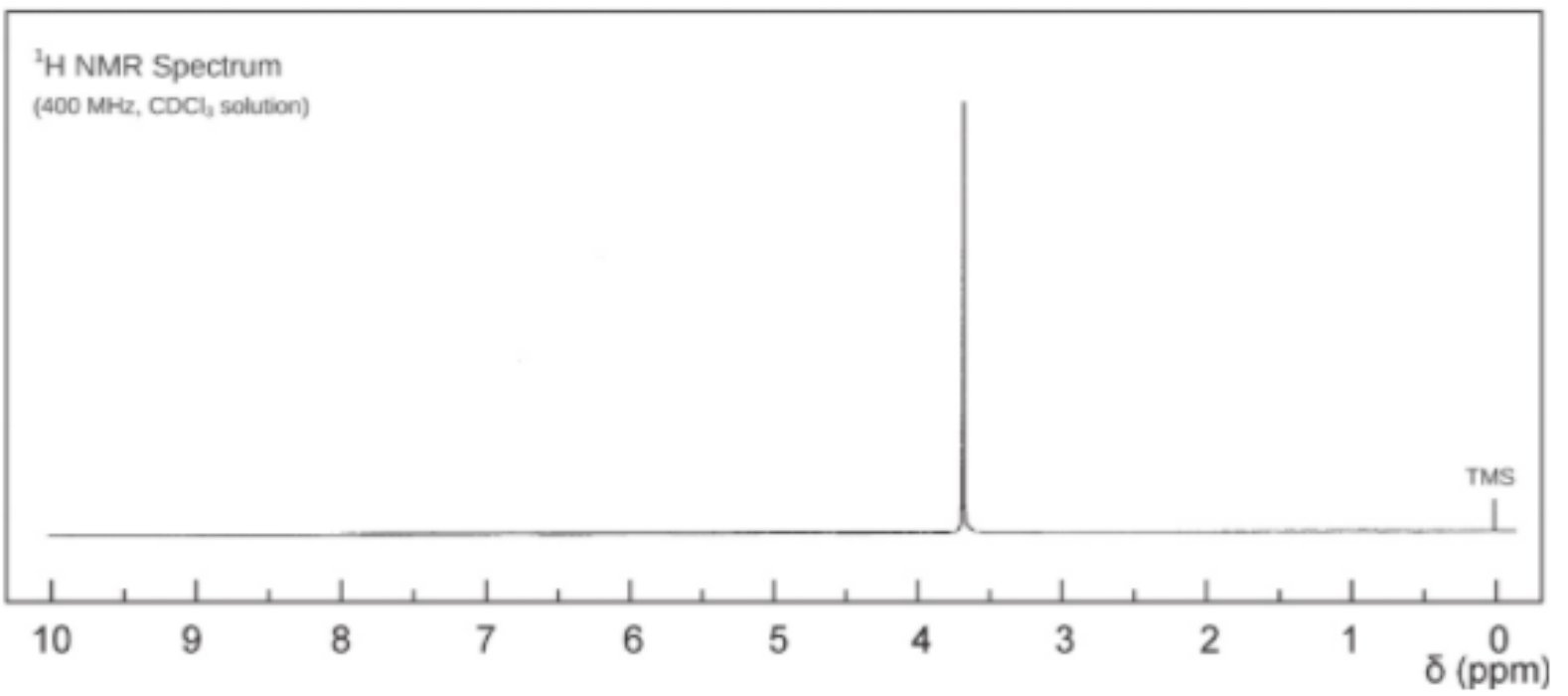
Problem 27



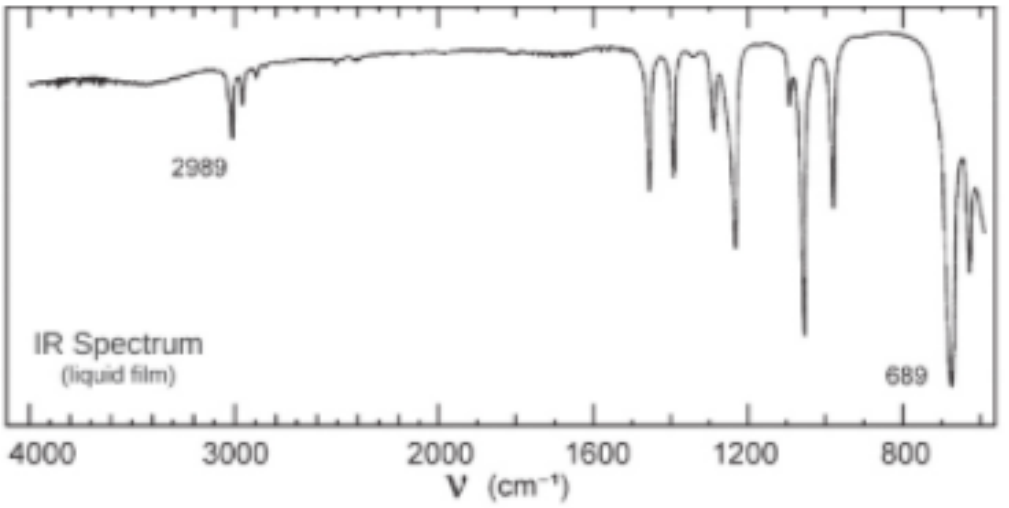


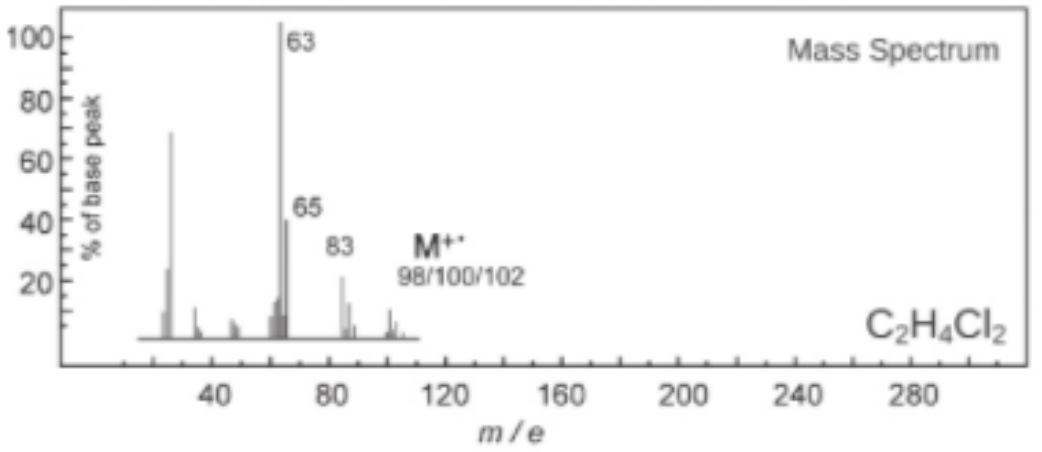
No significant UV absorption above 220 nm



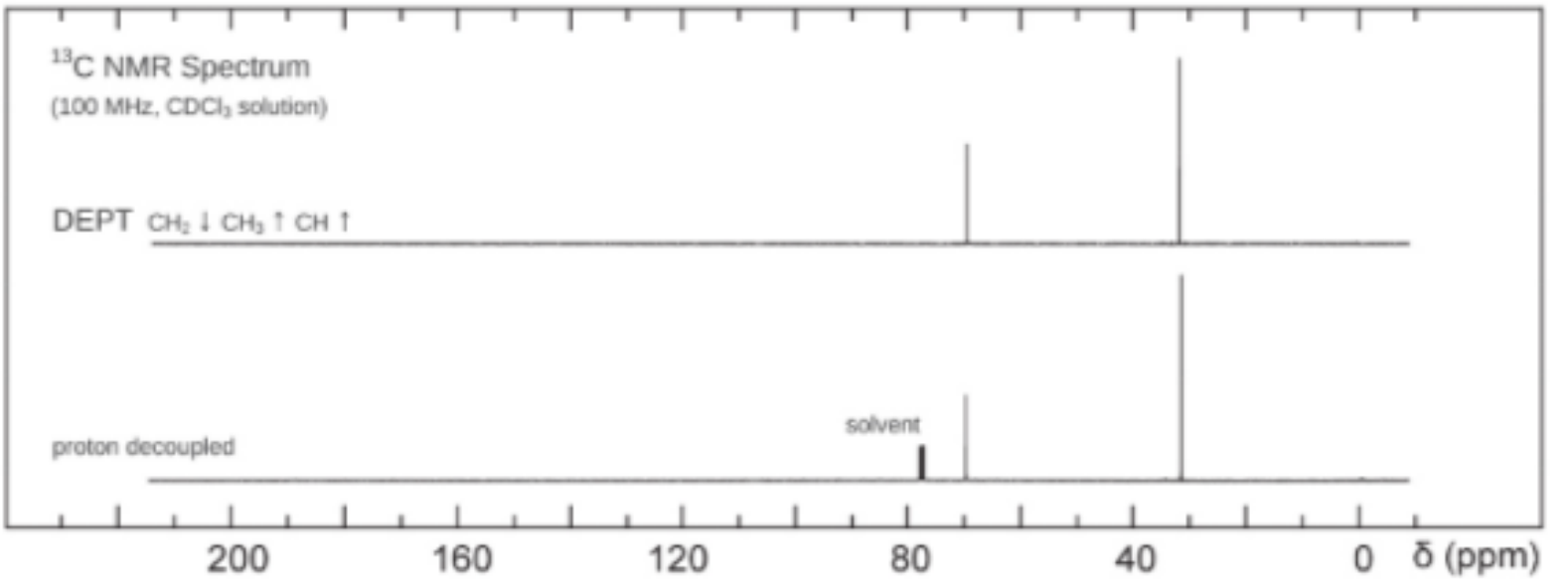


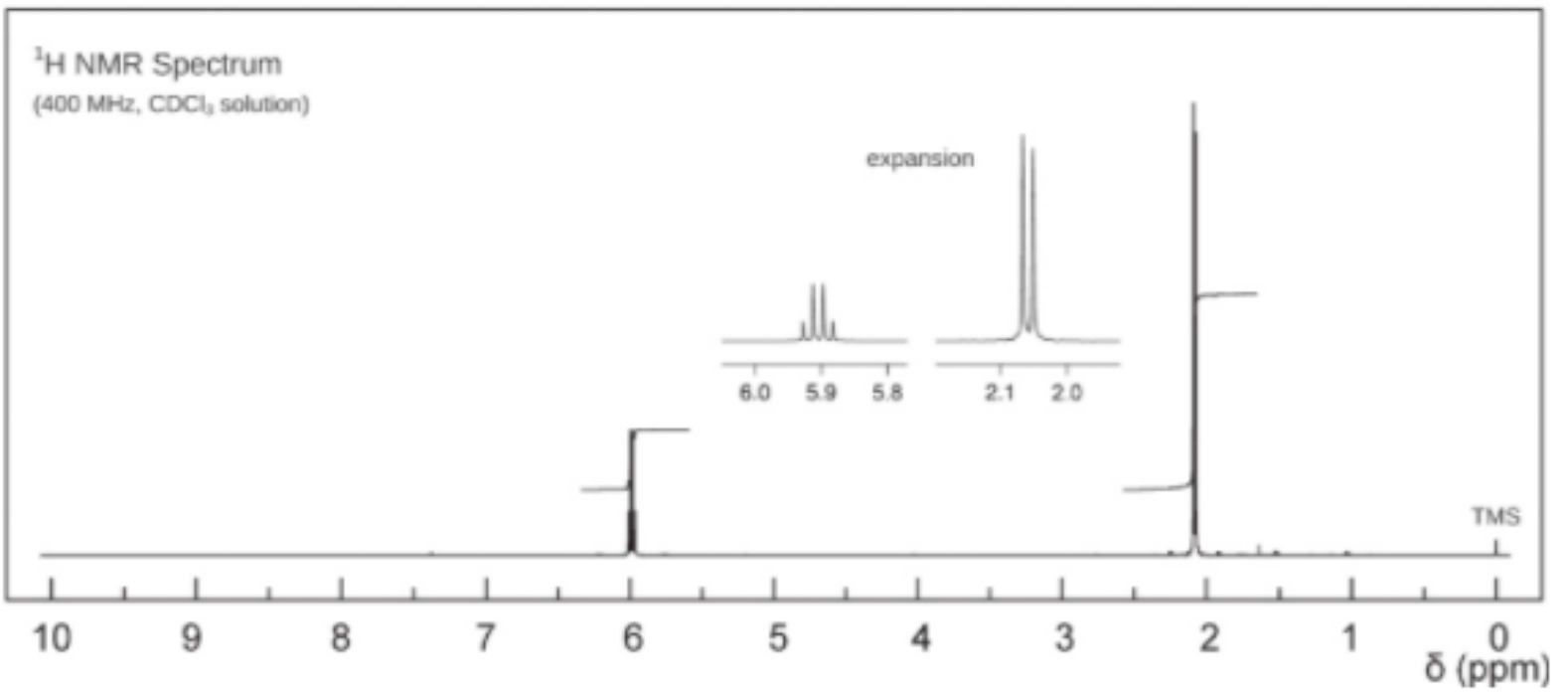
Problem 28



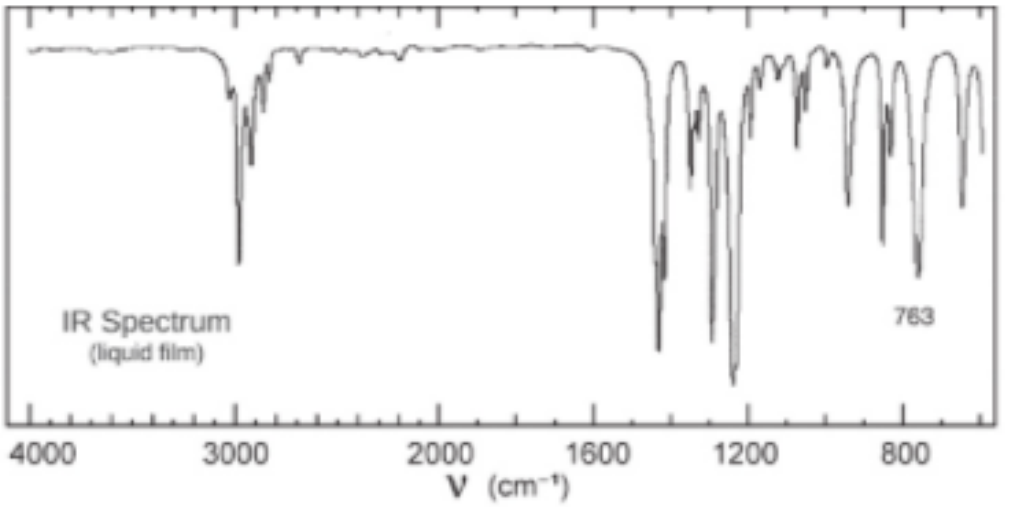


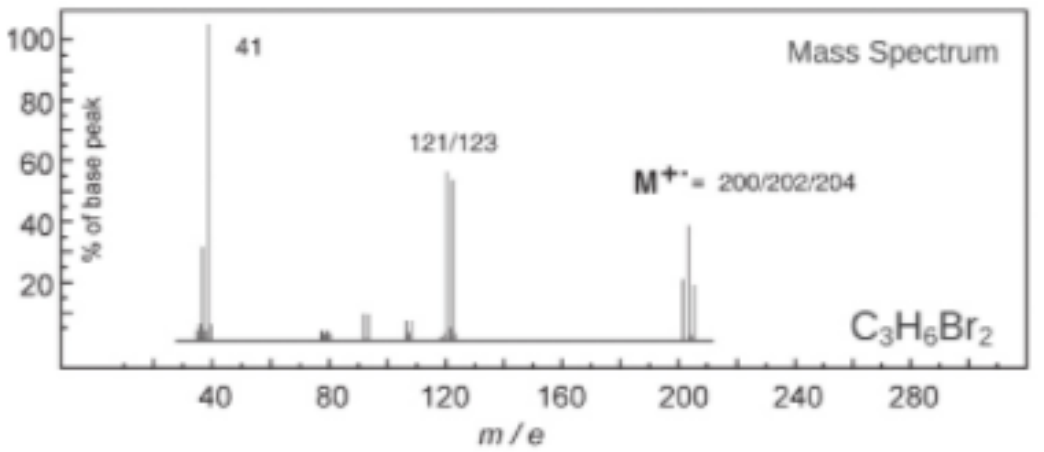
No significant UV absorption above 220 nm



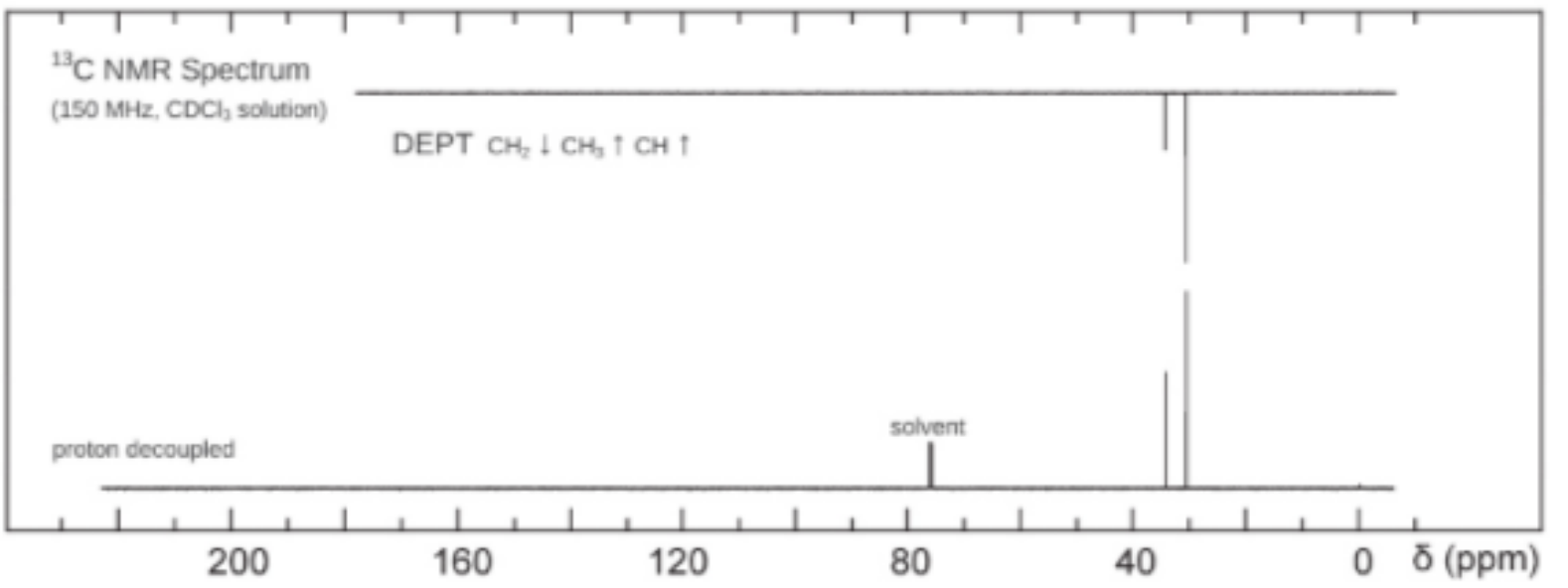


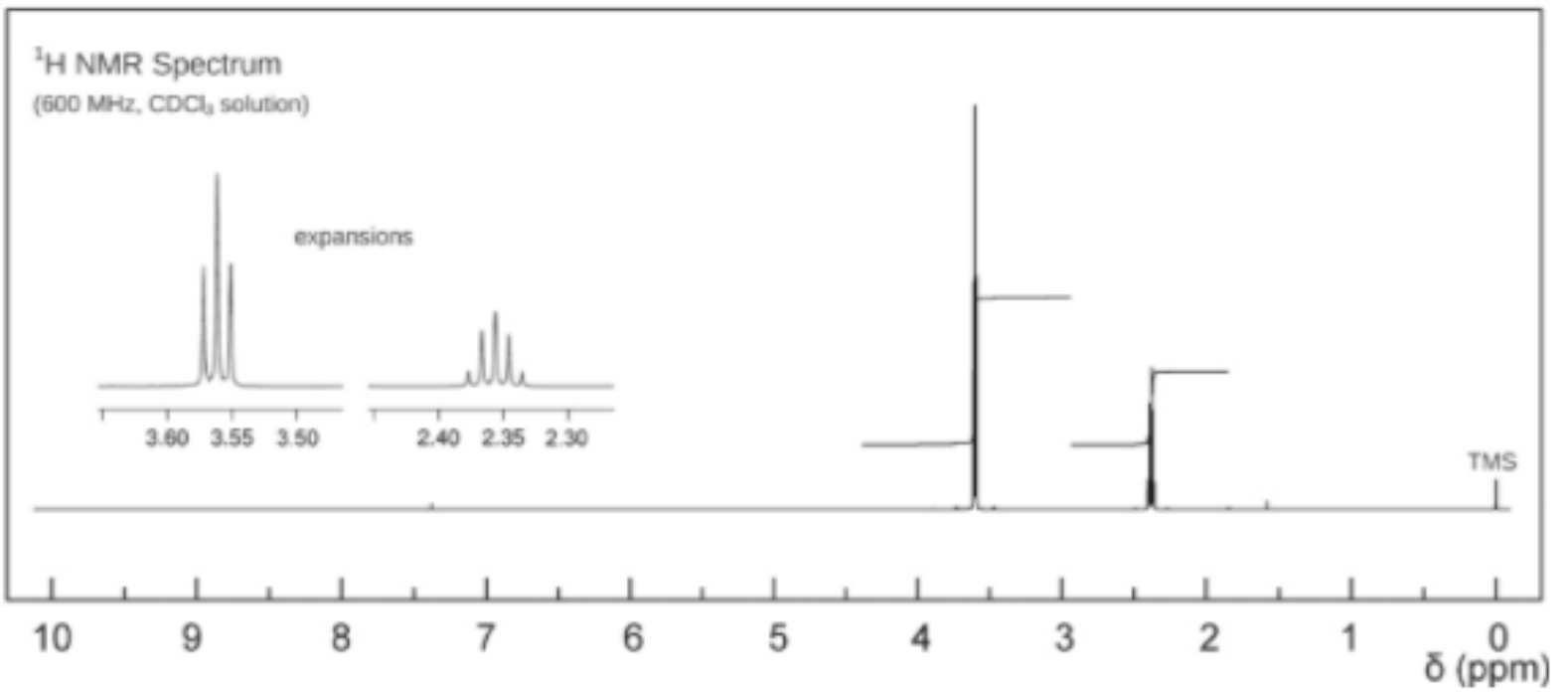
Problem 29



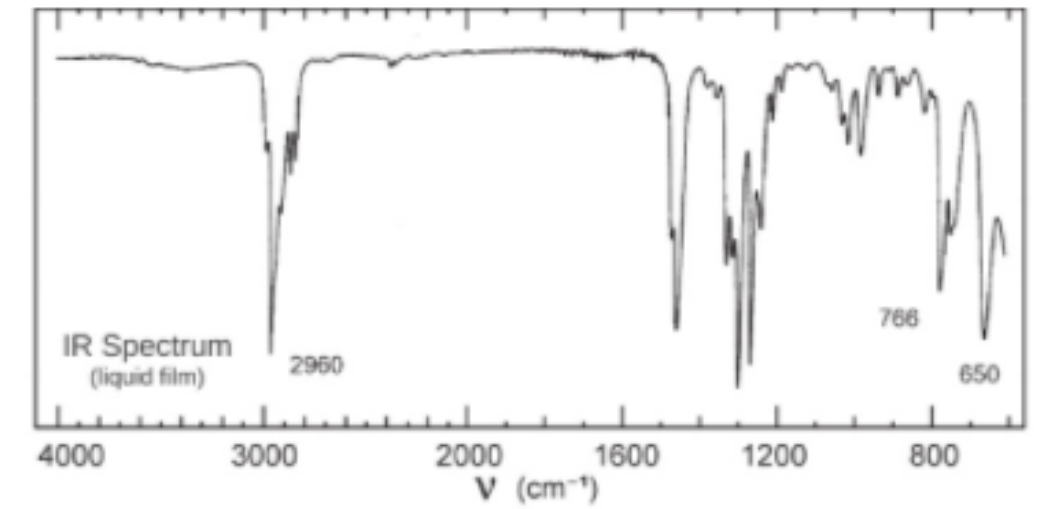


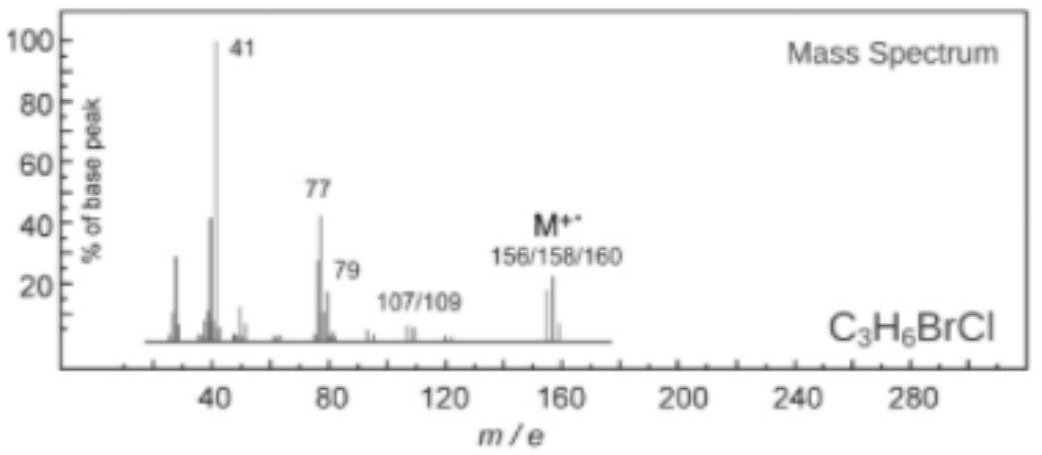
No significant UV absorption above 220 nm



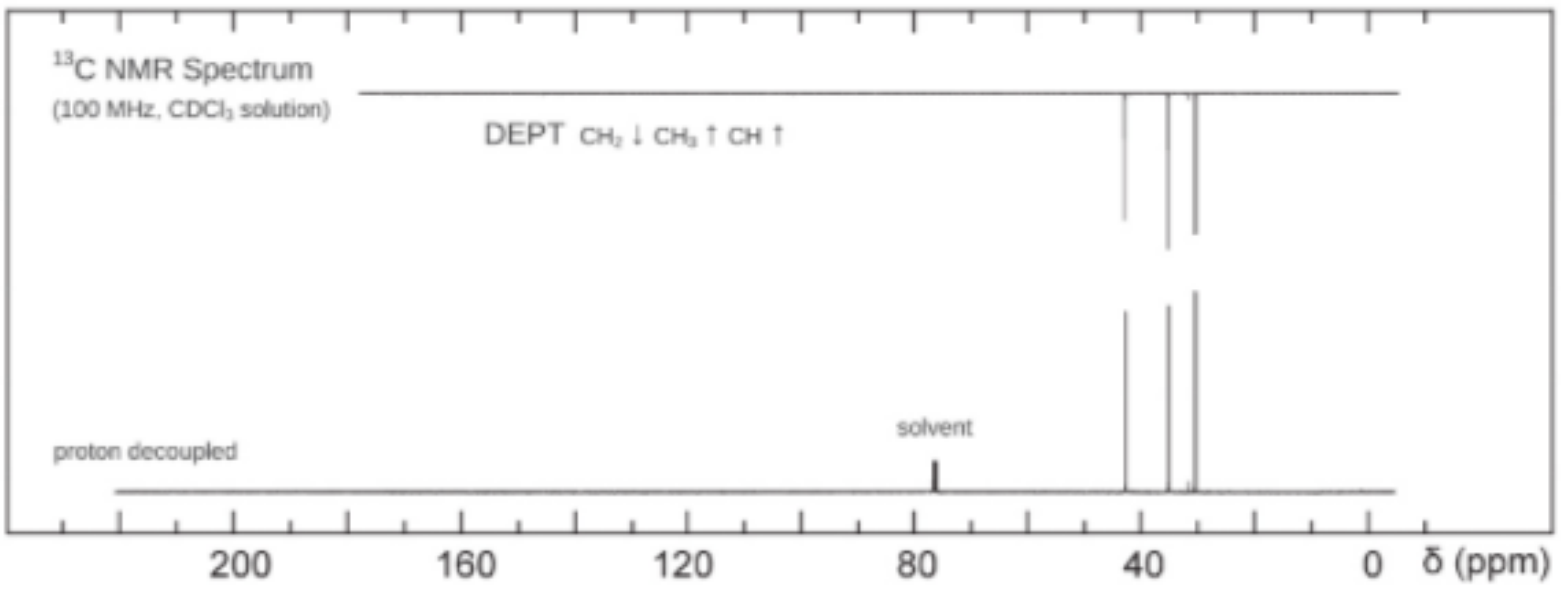


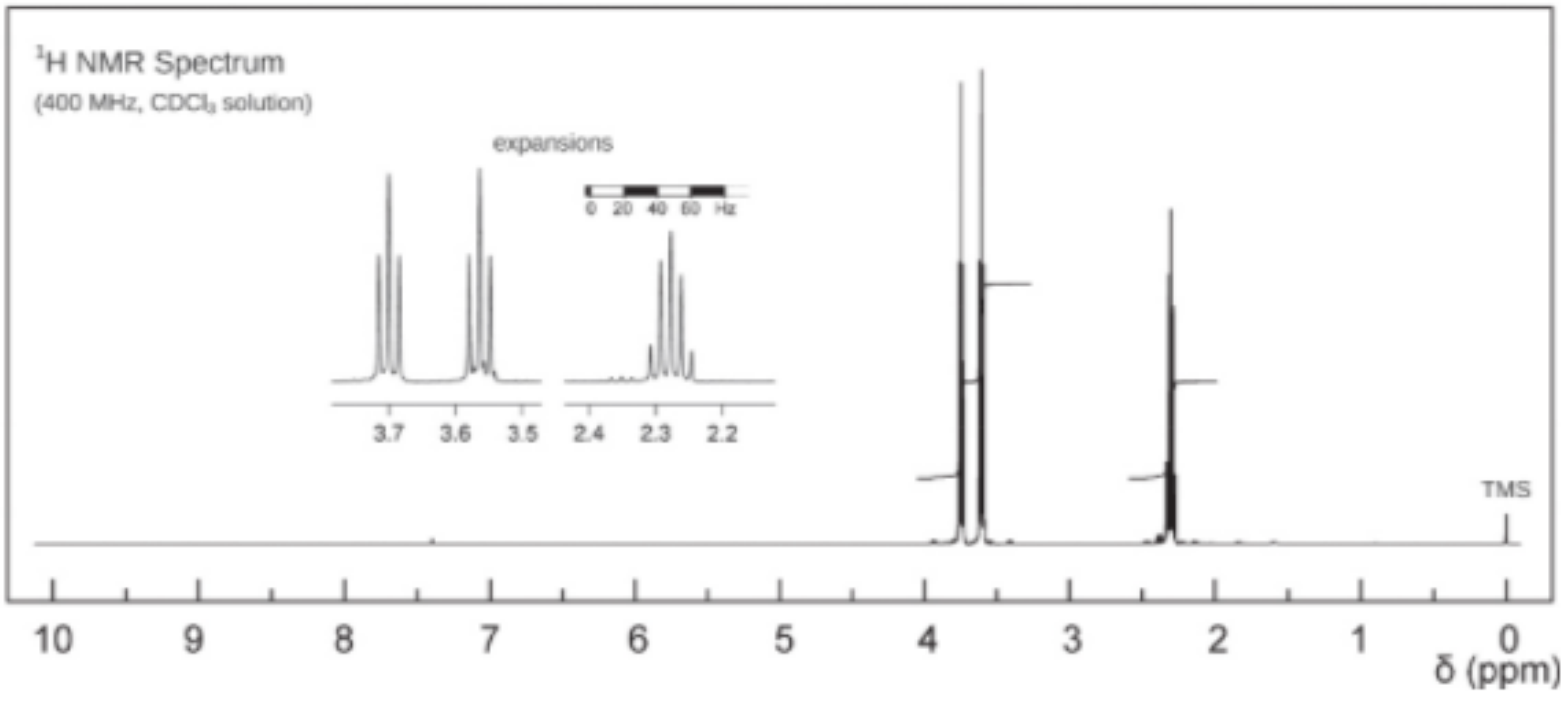
Problem 30

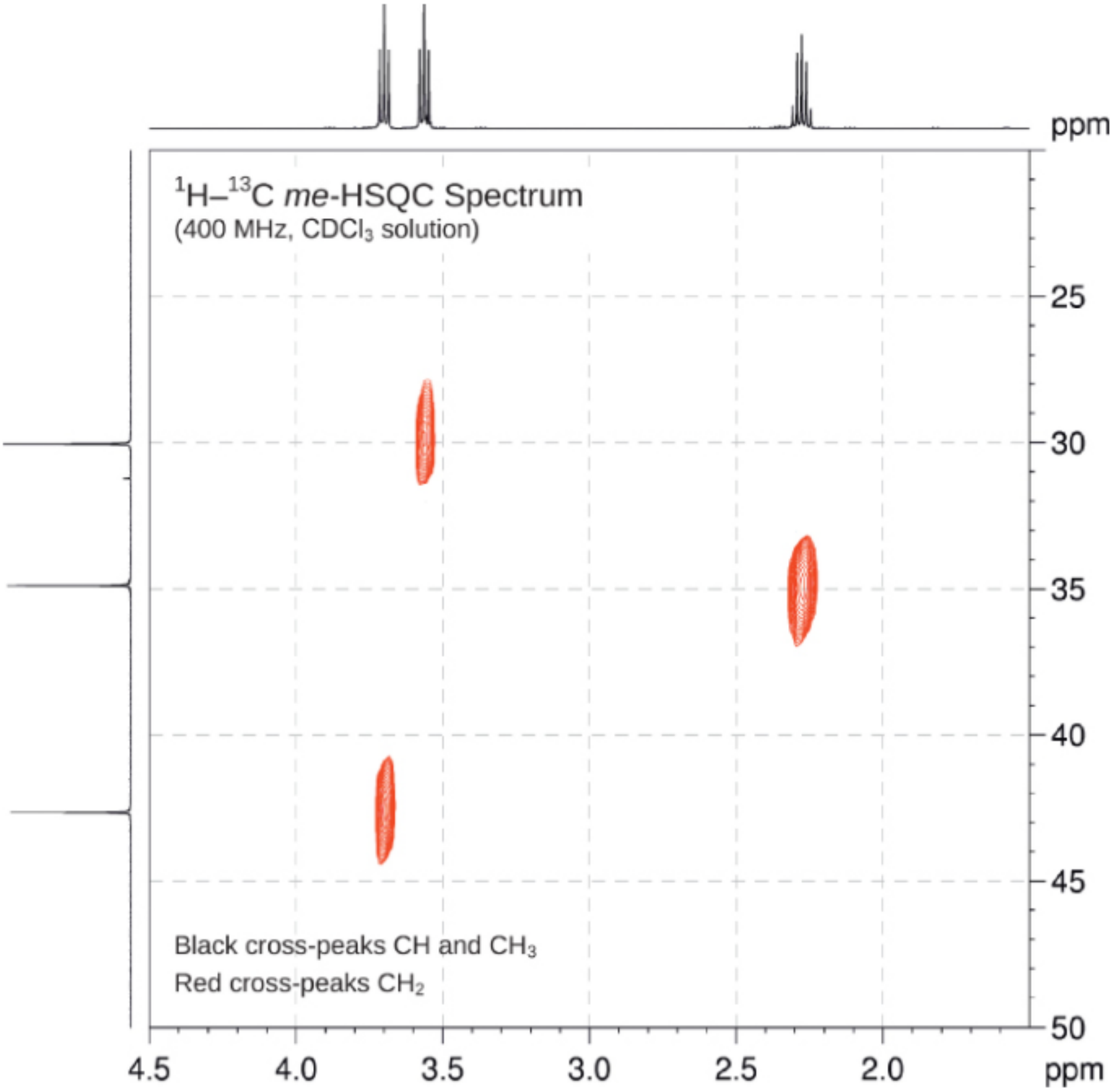




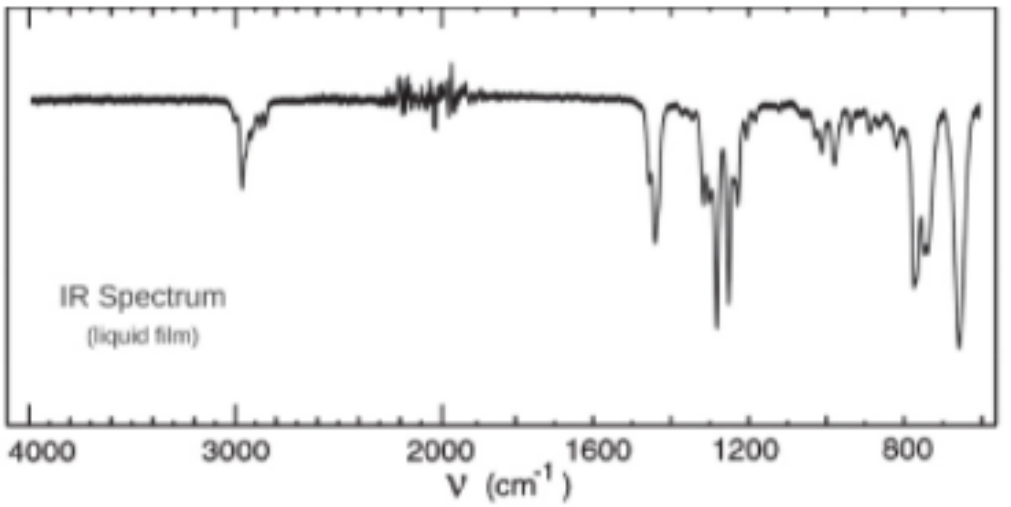
No significant UV absorption above 220 nm

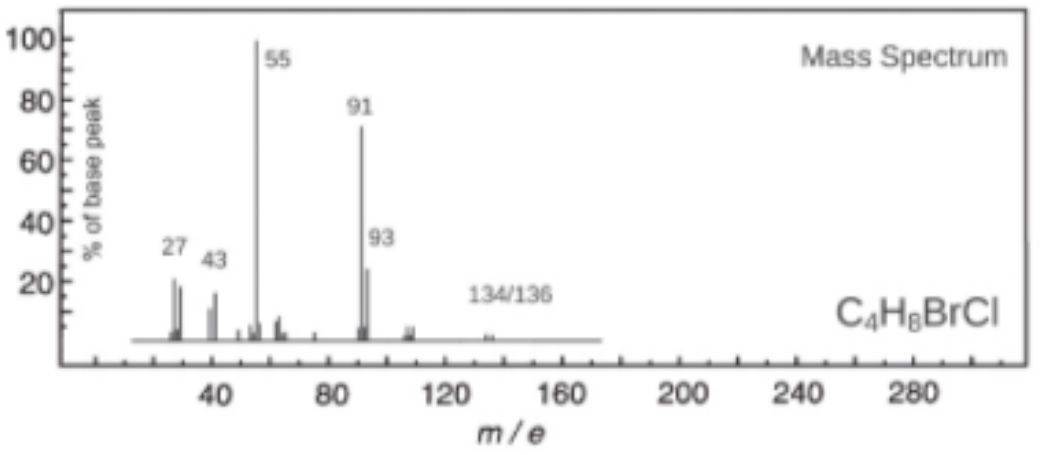


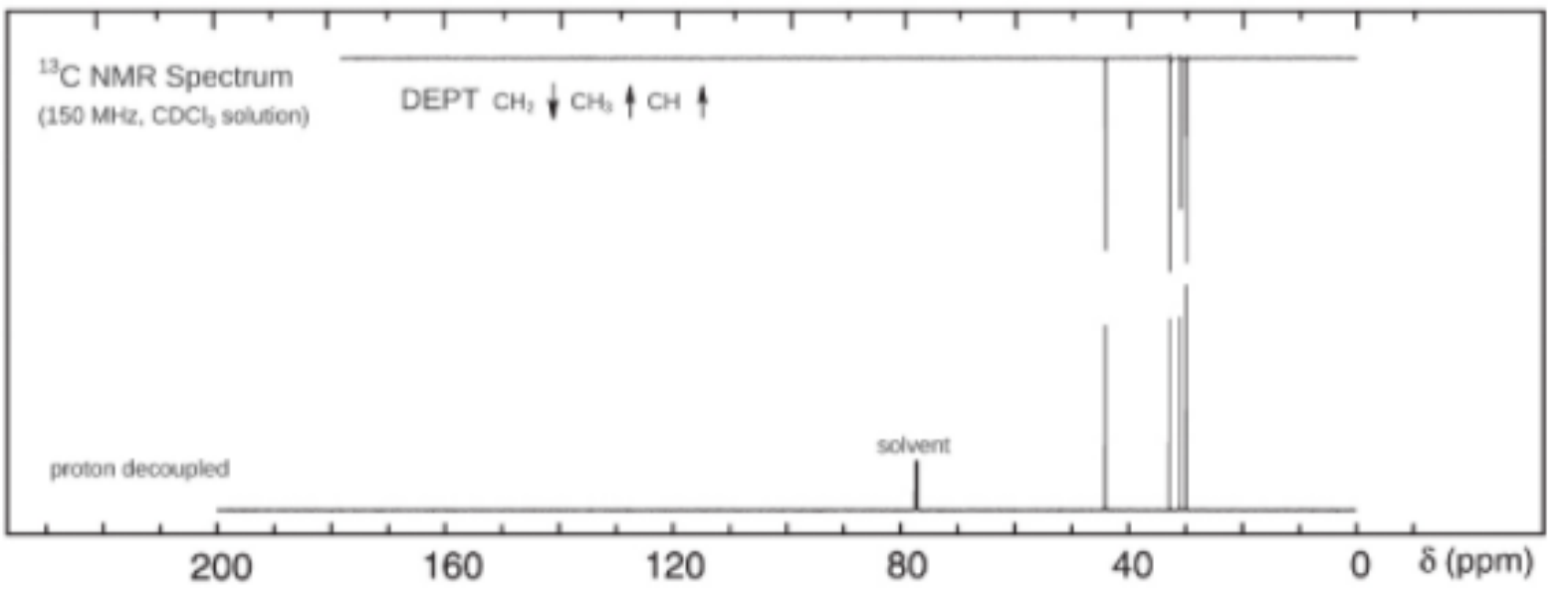


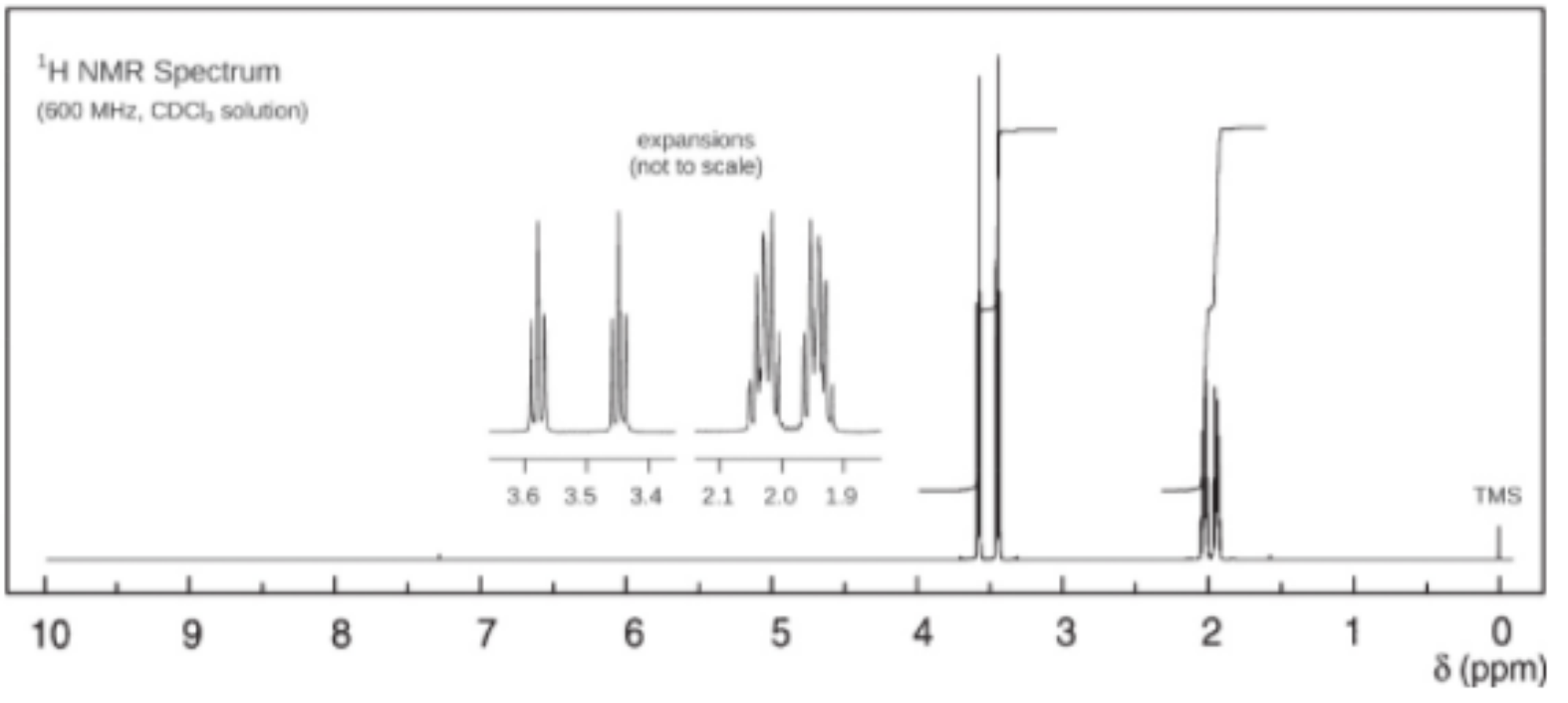

ppm
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
25
30
35
40
45
50
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
4.5
4.0
3.5
3.0
2.5
2.0
ppm

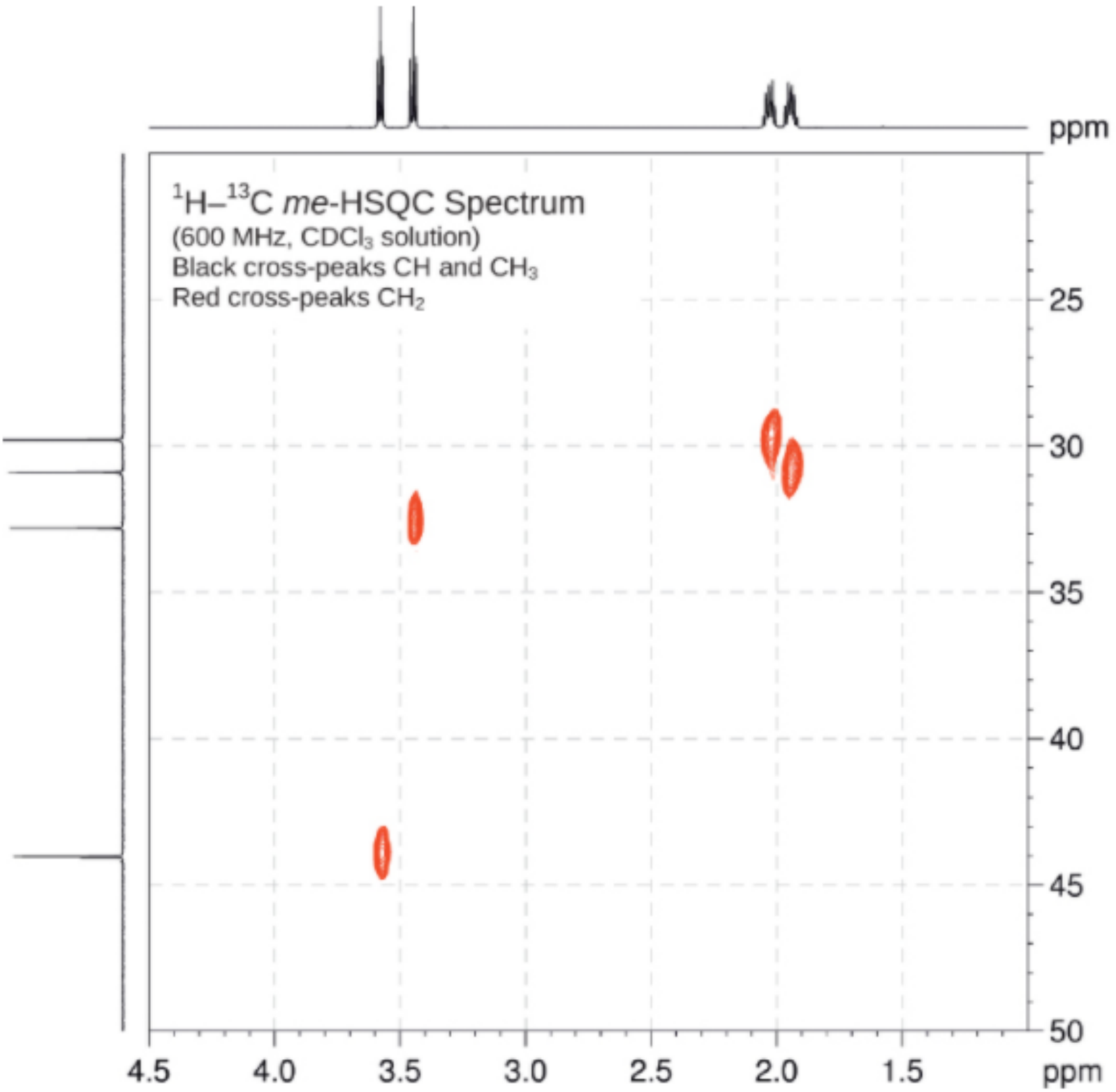
Problem 31


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

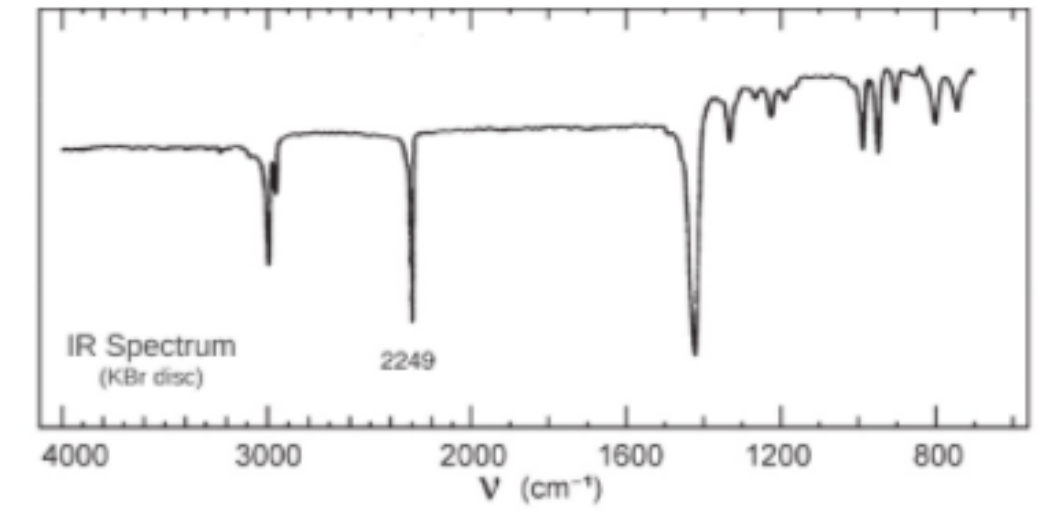

Mass Spectrum
% of base peak
100
80
60
40
20
55
91
93
27
43
134/136
C4H8BrCl
40
80
120
160
200
240
280
m/e

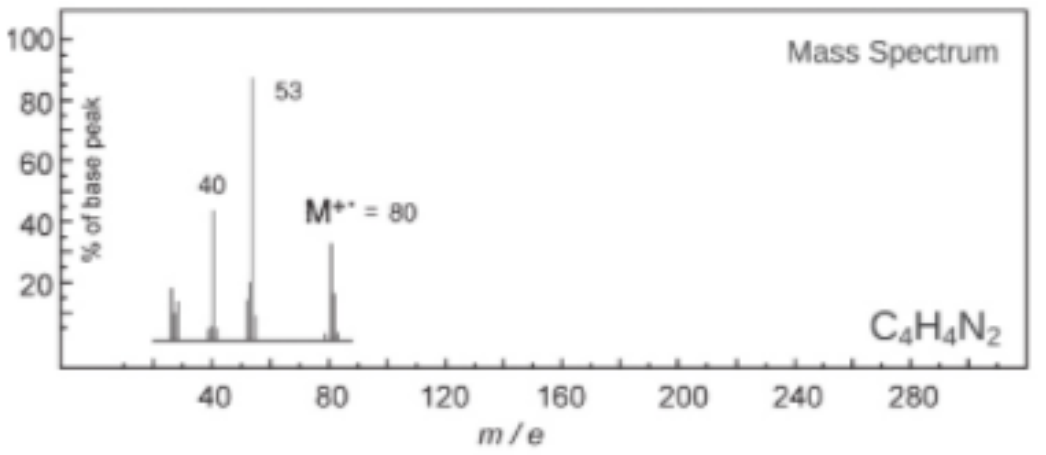

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansions
(not to scale)
3.6
3.5
3.4
2.1
2.0
1.9
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

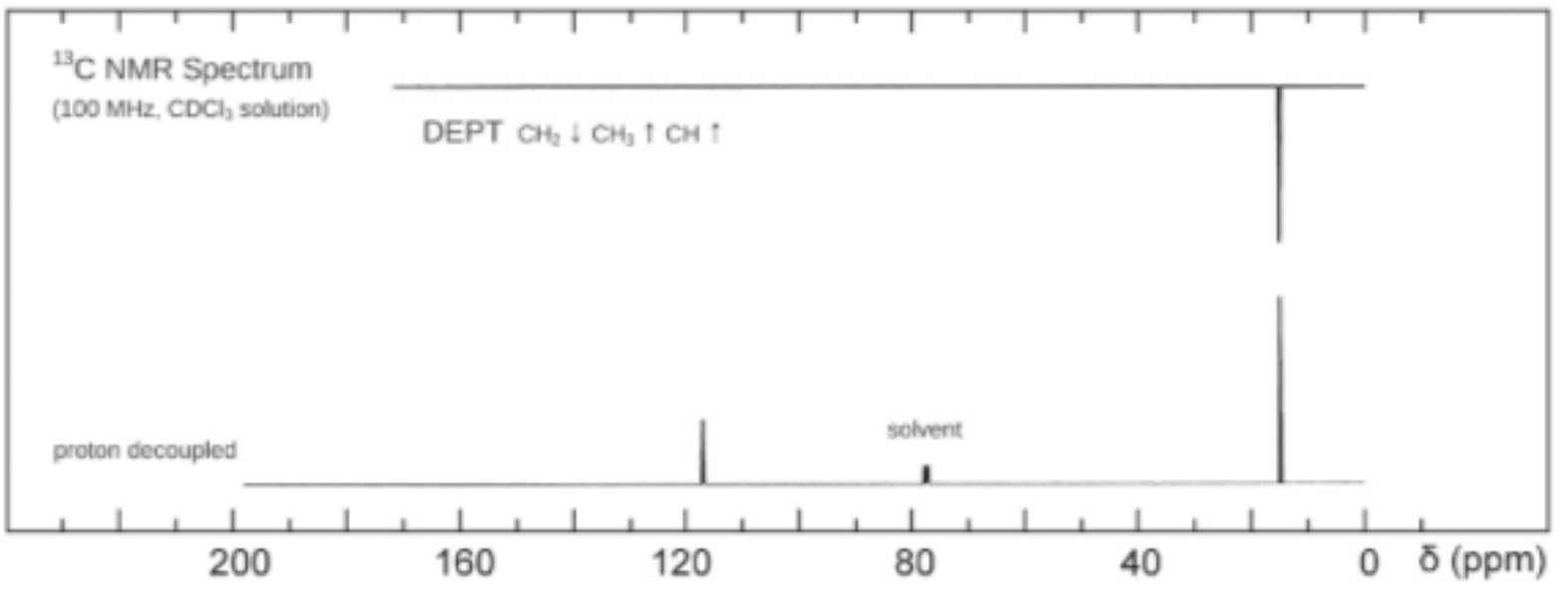

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
25
30
35
40
45
50
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

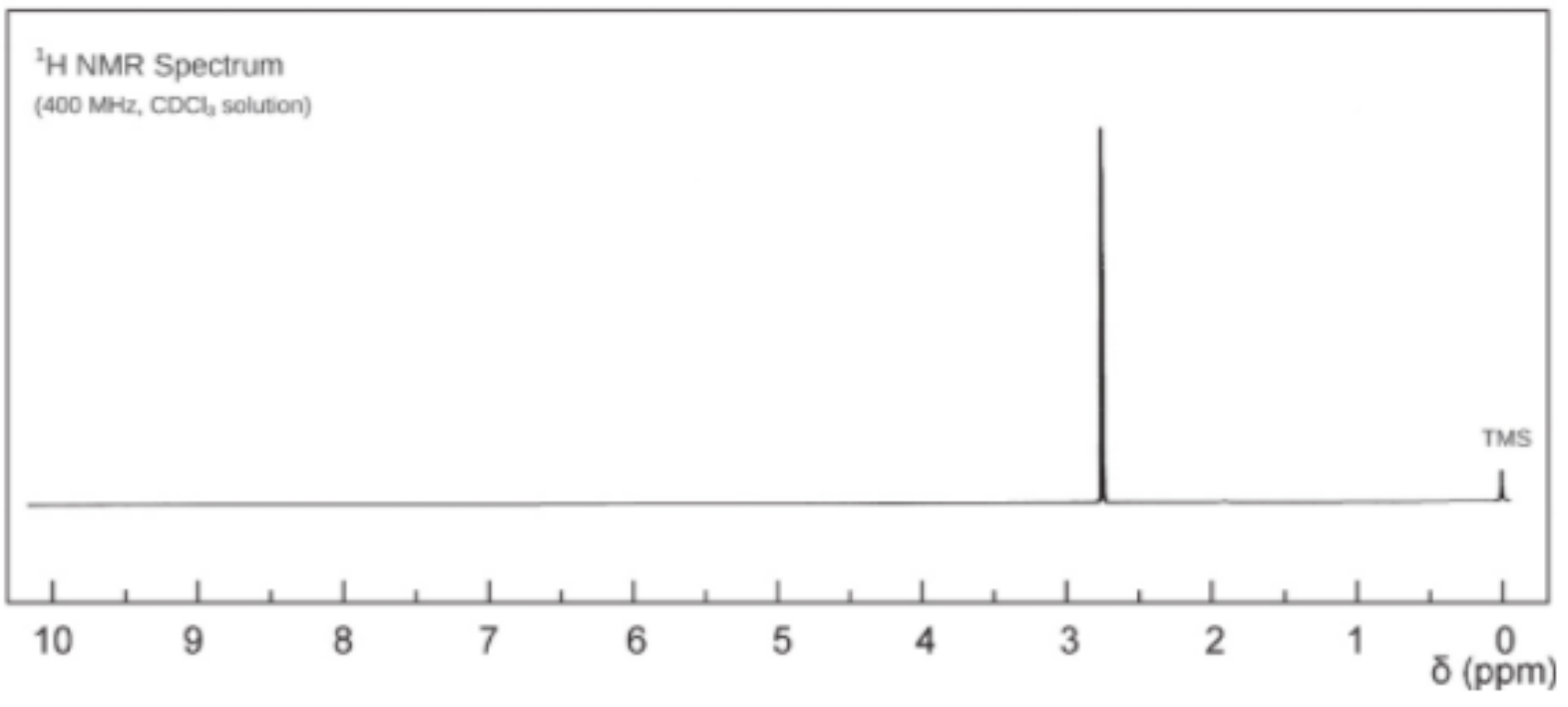
Problem 32



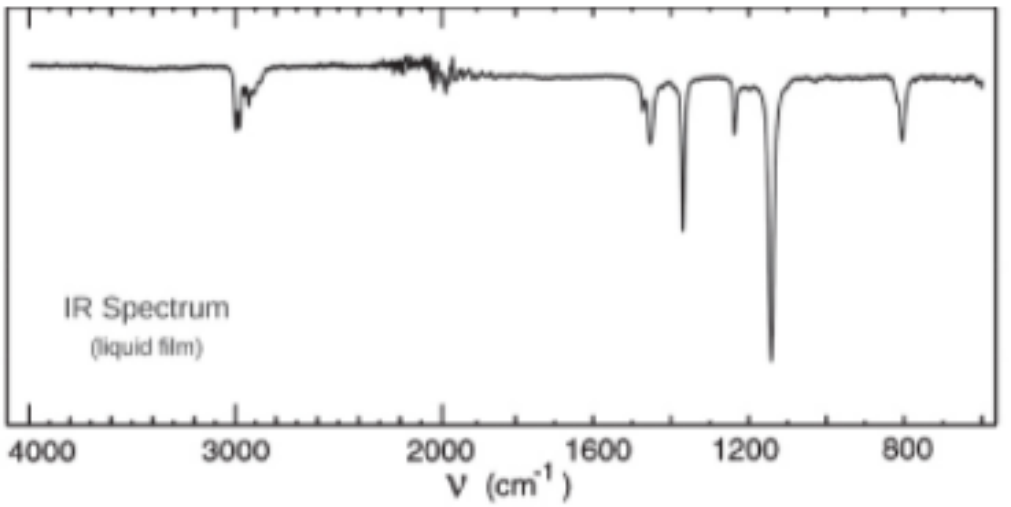


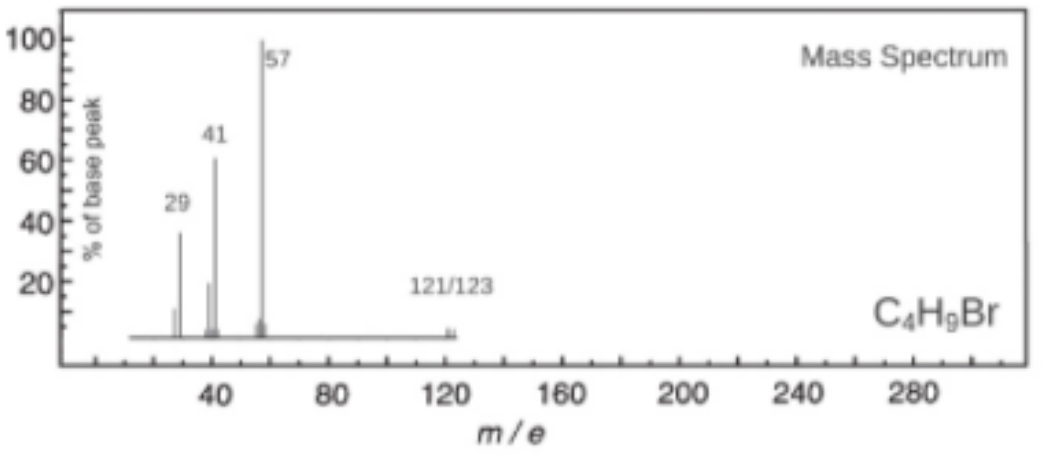
No significant UV absorption above 220 nm

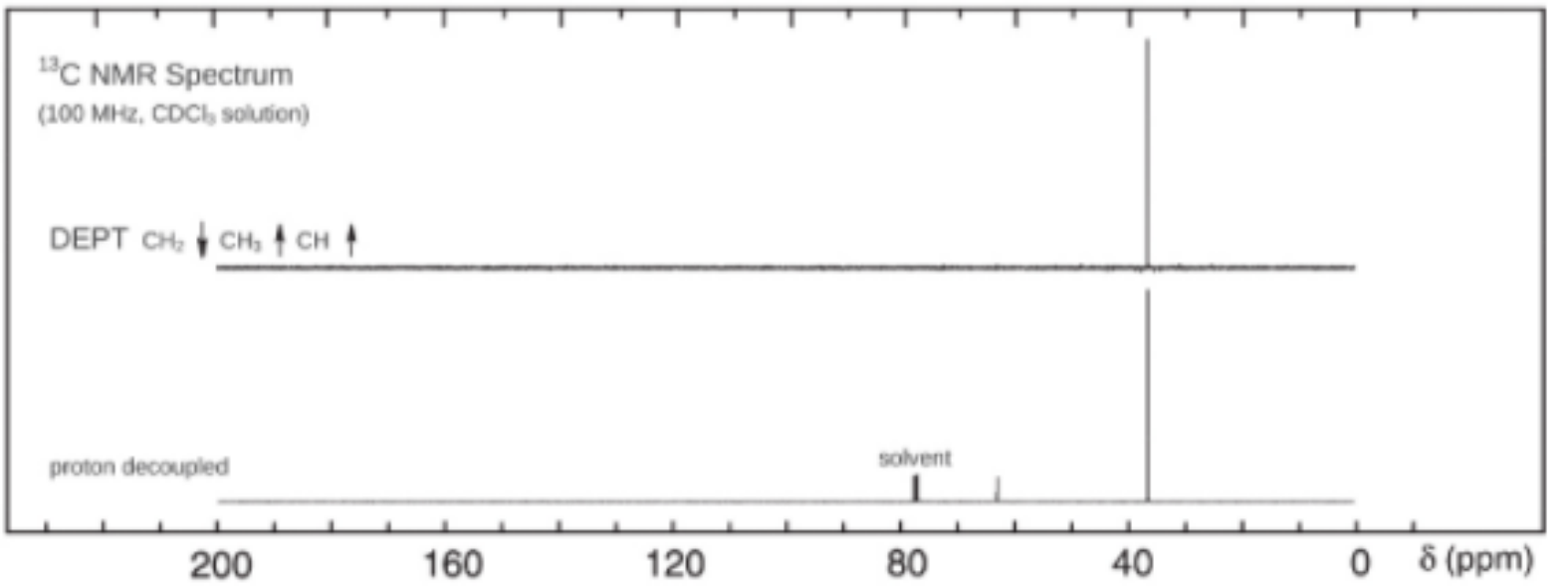


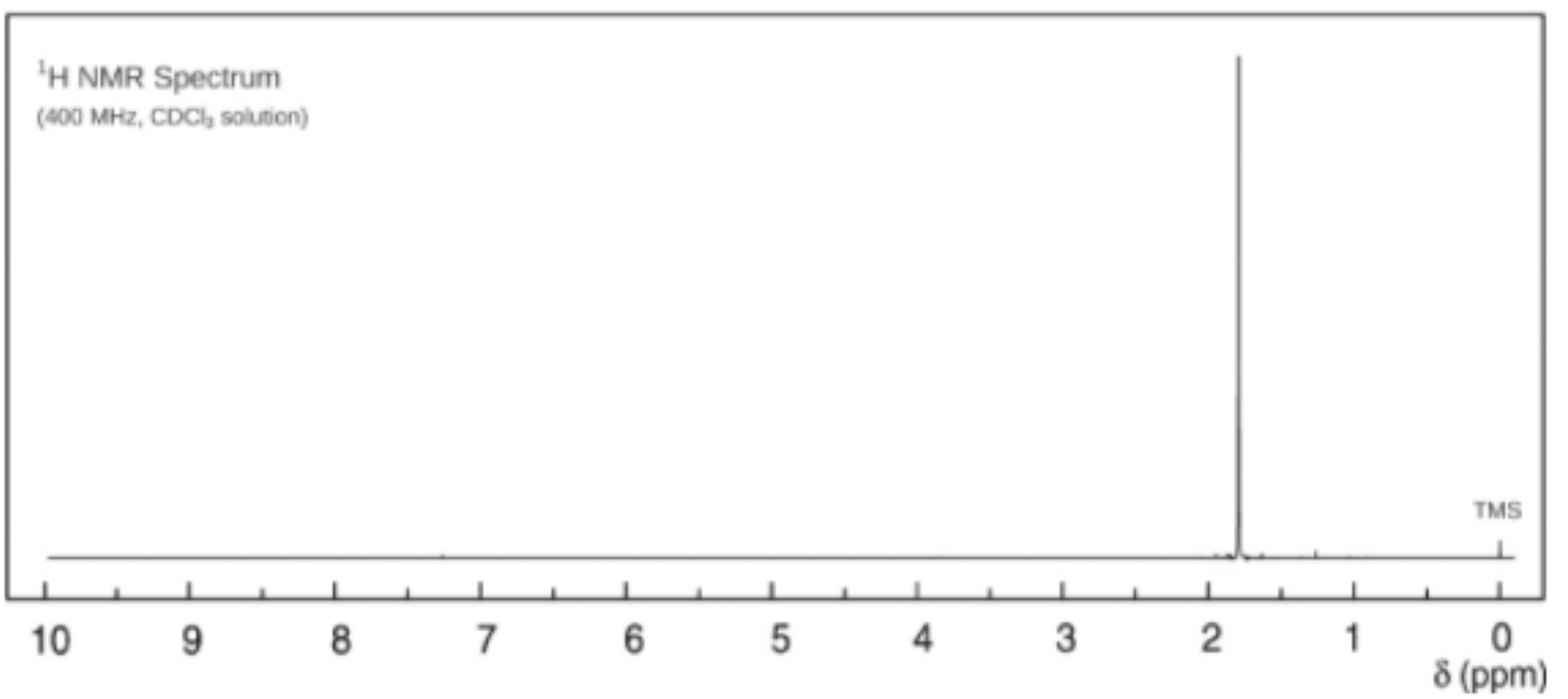


Problem 33

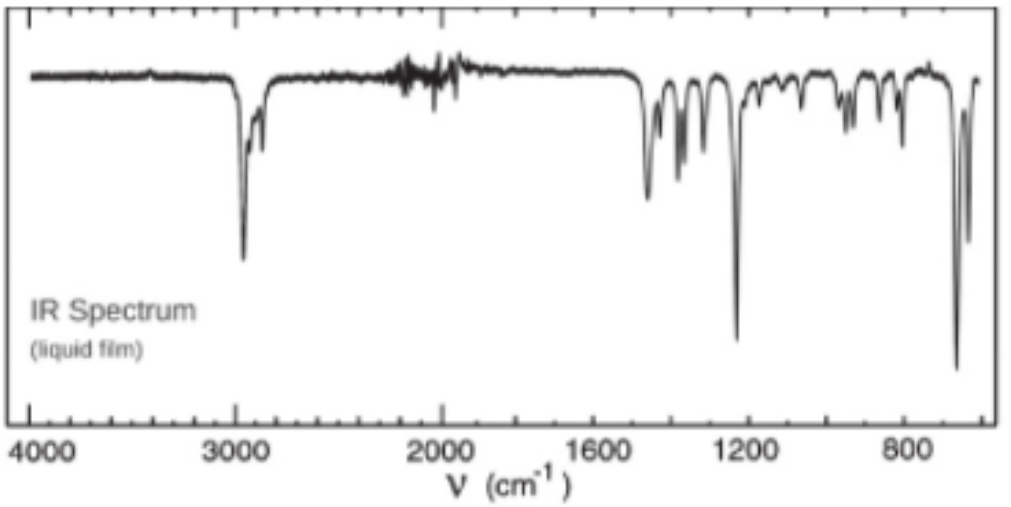

IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

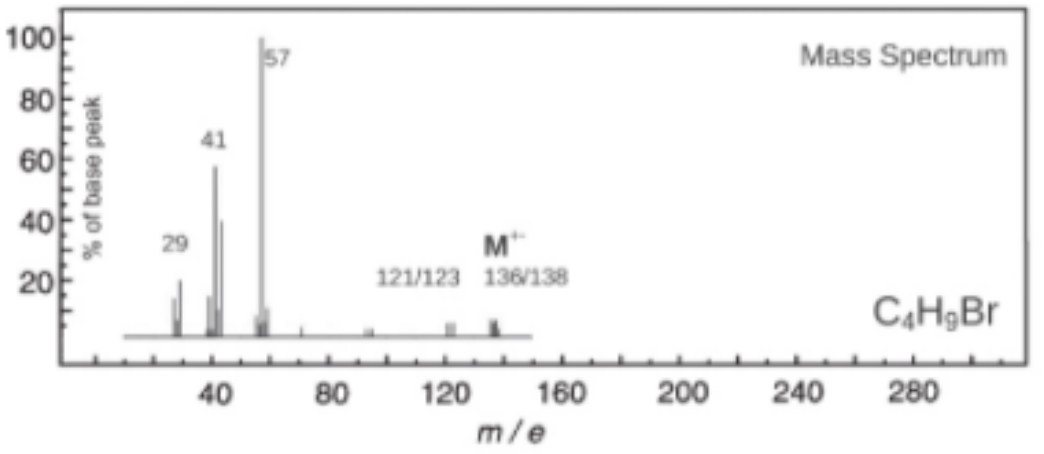

Mass Spectrum
% of base peak
100
80
60
40
20
57
41
29
121/123
C4H9Br
40
80
120
160
200
240
280
m / e

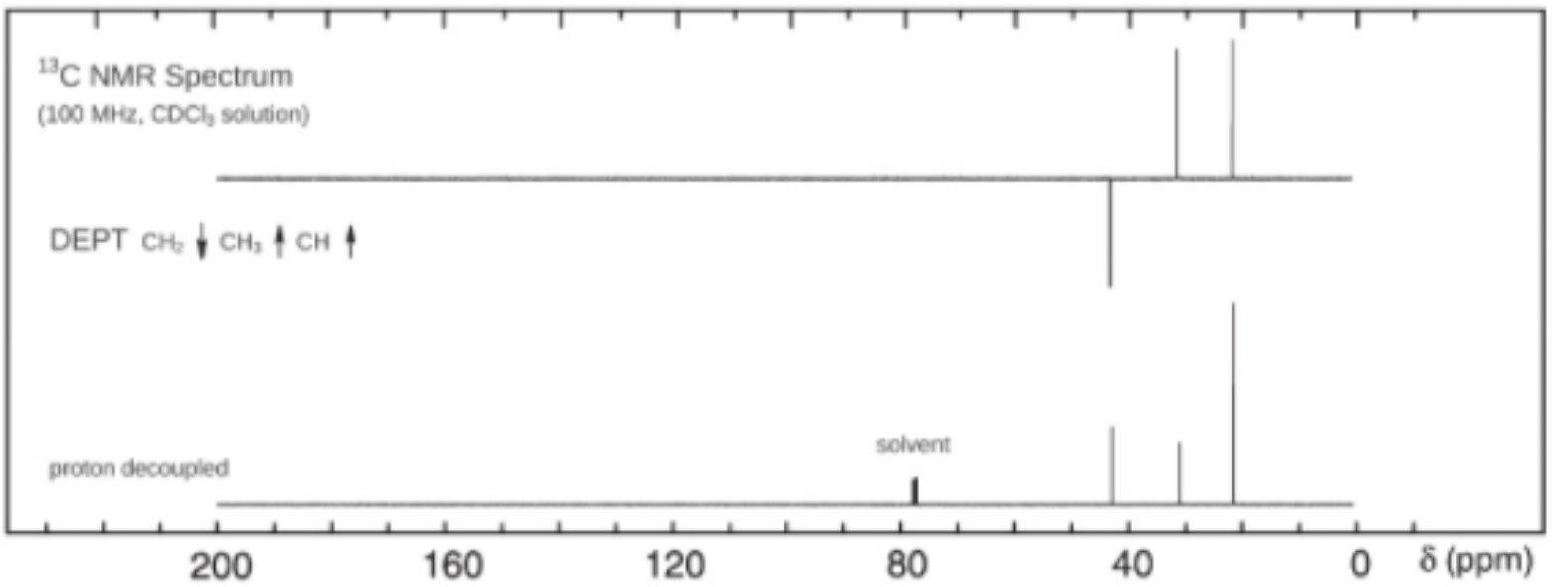

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

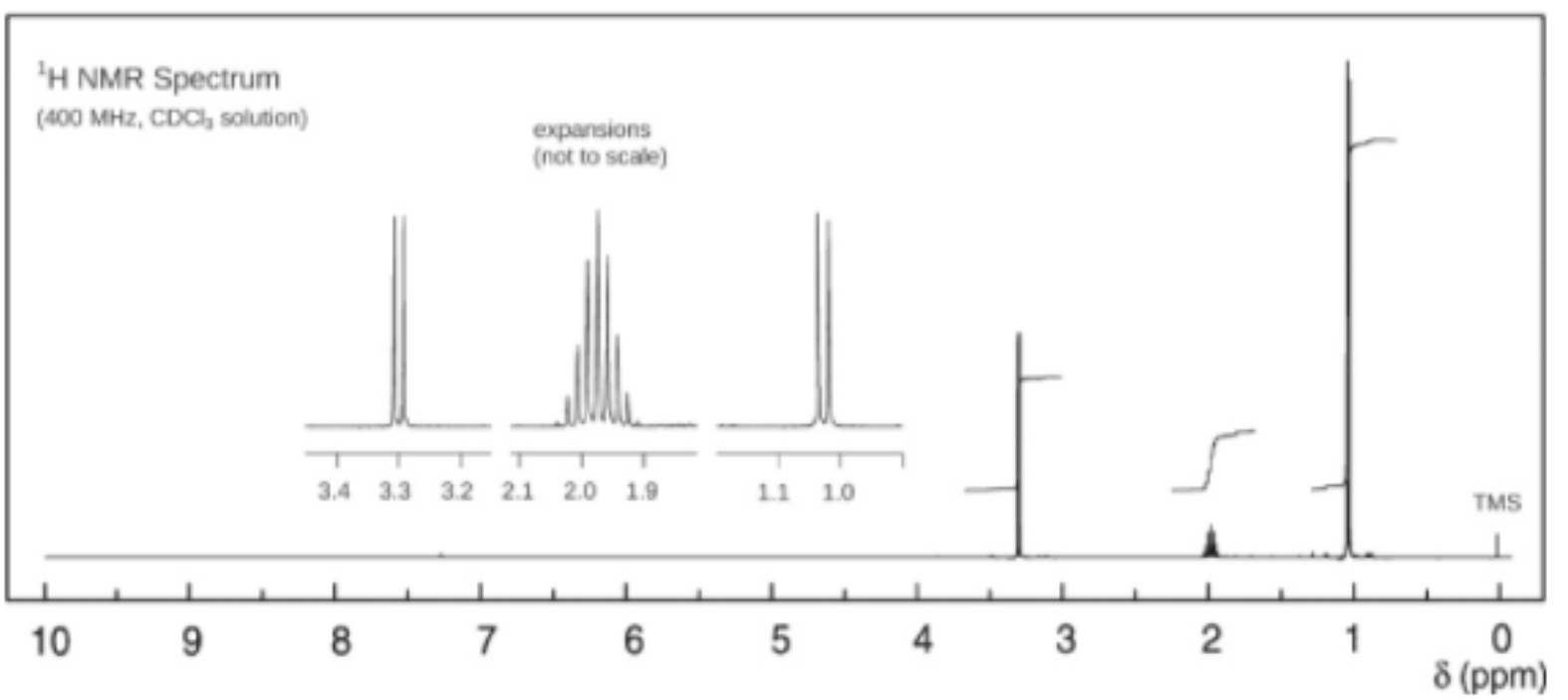

1H NMR Spectrum
(400 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

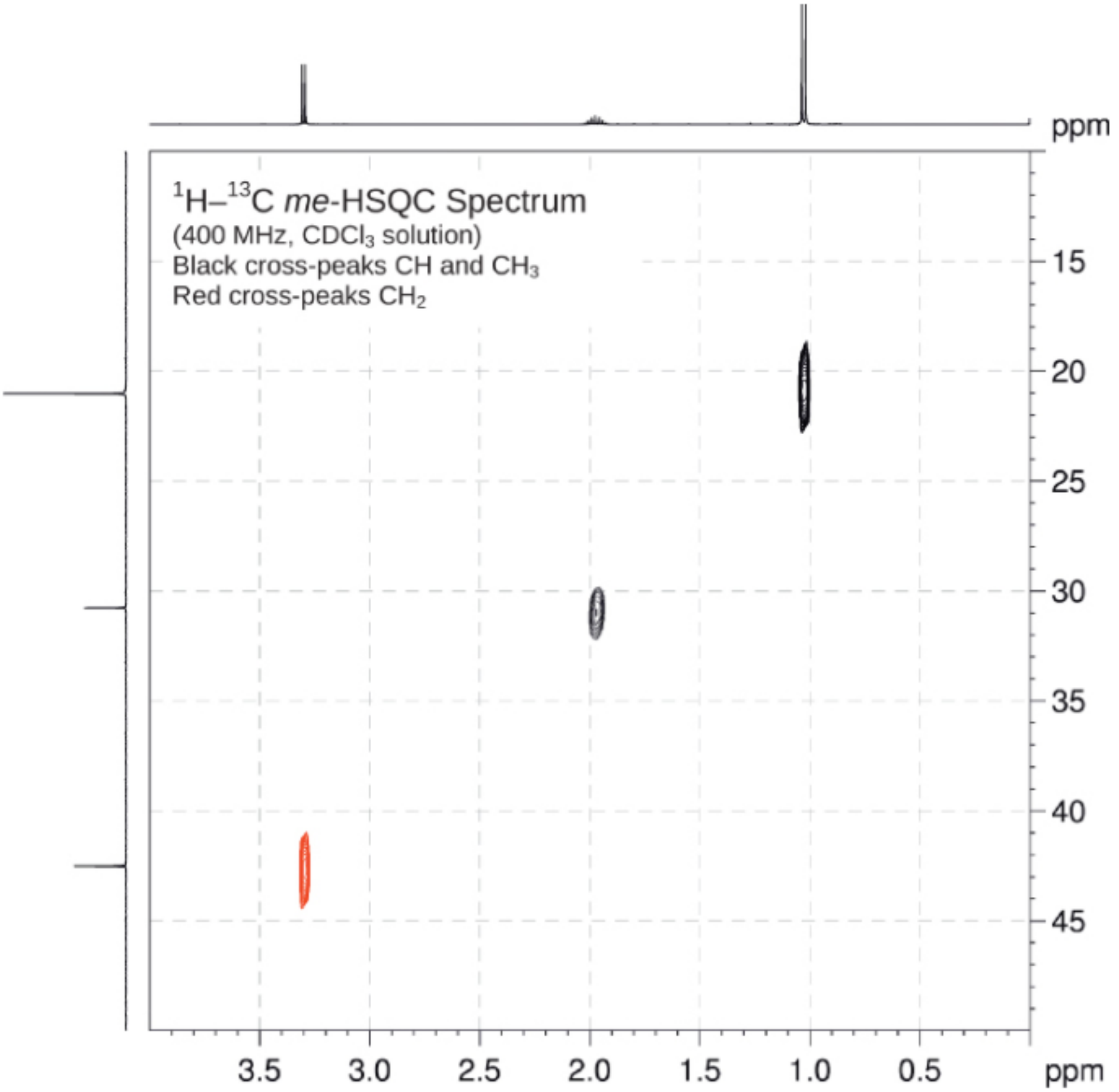
Problem 34


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

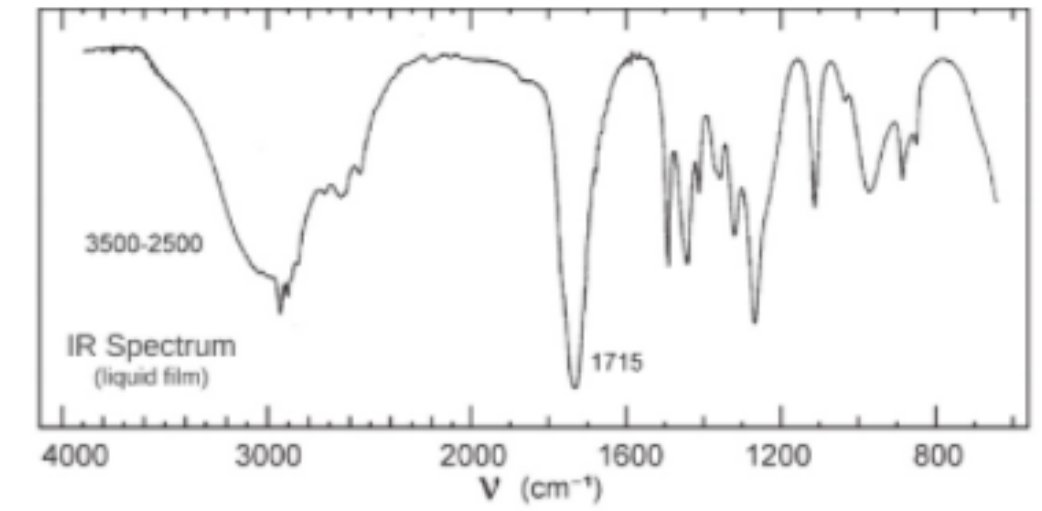

Mass Spectrum
% of base peak
100
80
60
40
20
57
41
29
M+·
121/123
136/138
C4H9Br
40
80
120
160
200
240
280
m / e

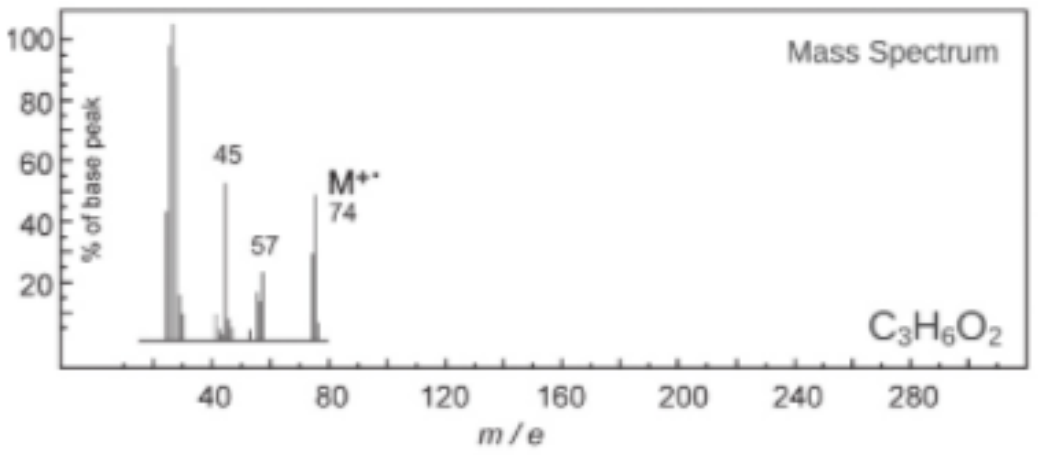

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
(not to scale)
3.4
3.3
3.2
2.1
2.0
1.9
1.1
1.0
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

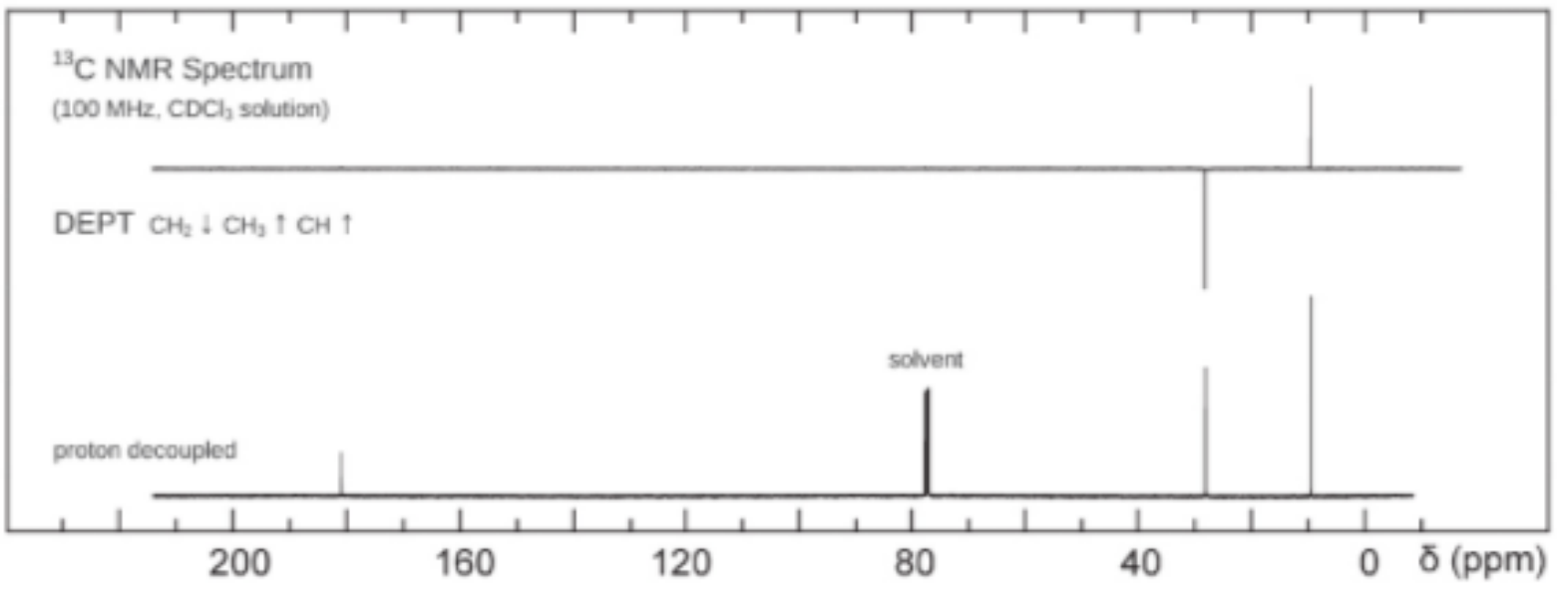

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
15
20
25
30
35
40
45
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

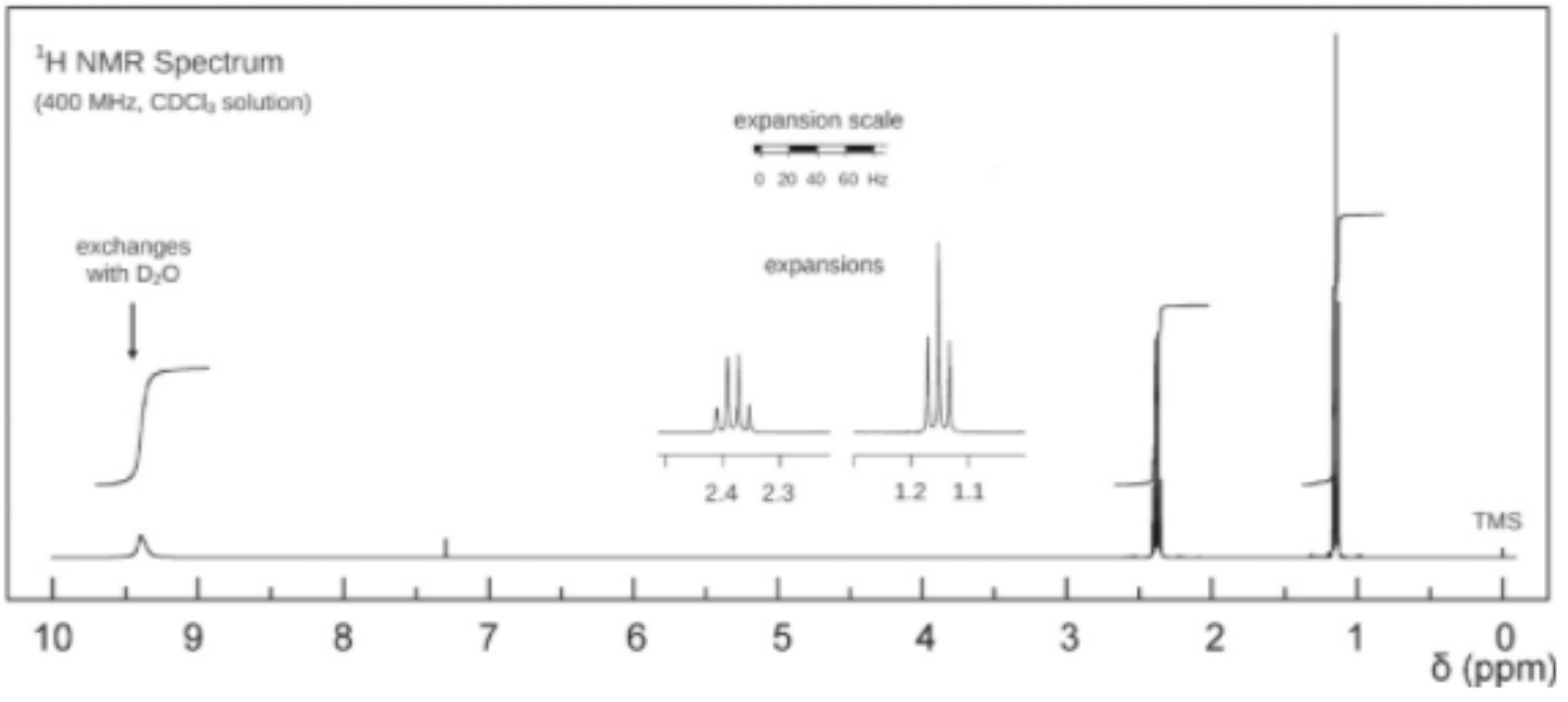
Problem 35



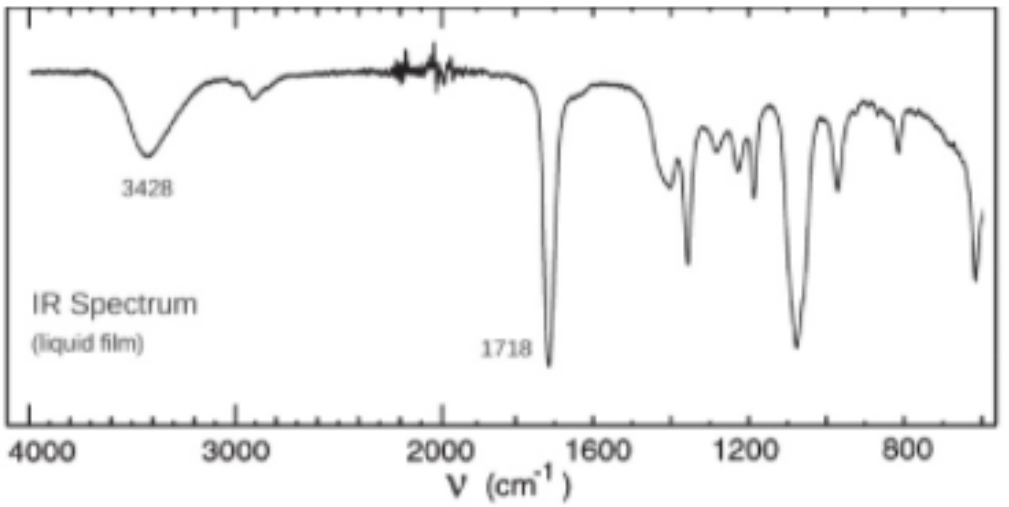


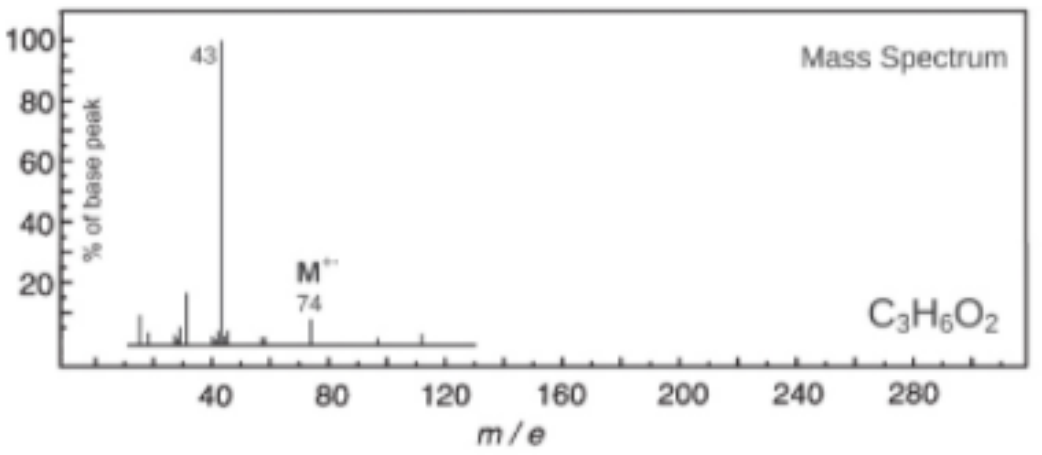
No significant UV absorption above 220 nm

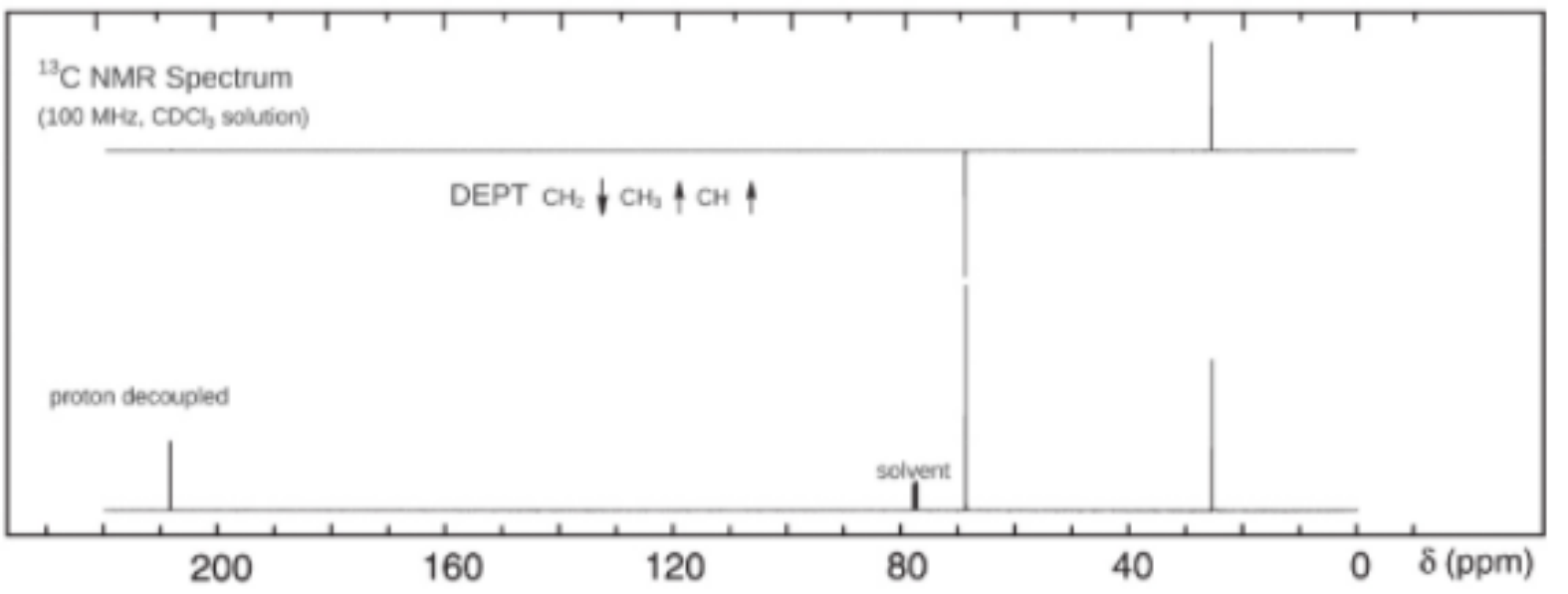


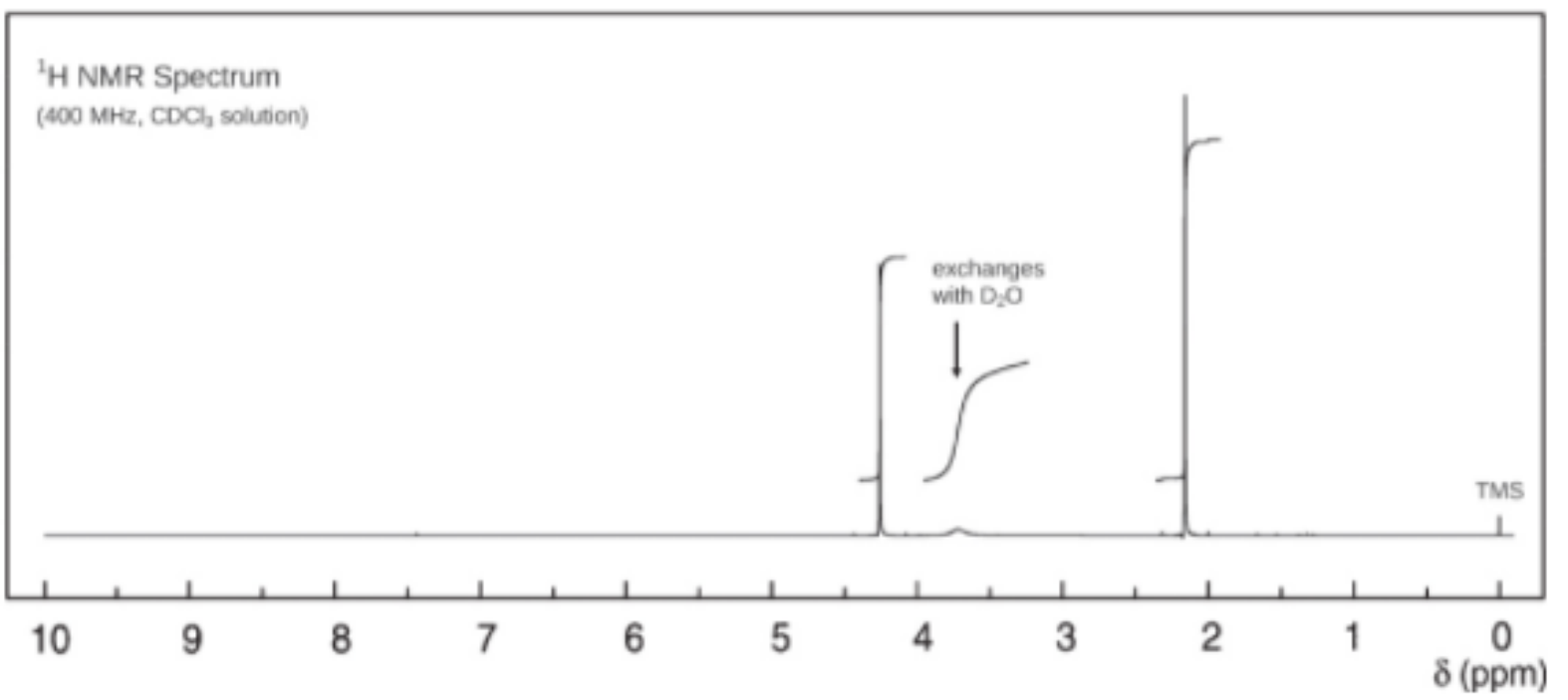


Problem 36

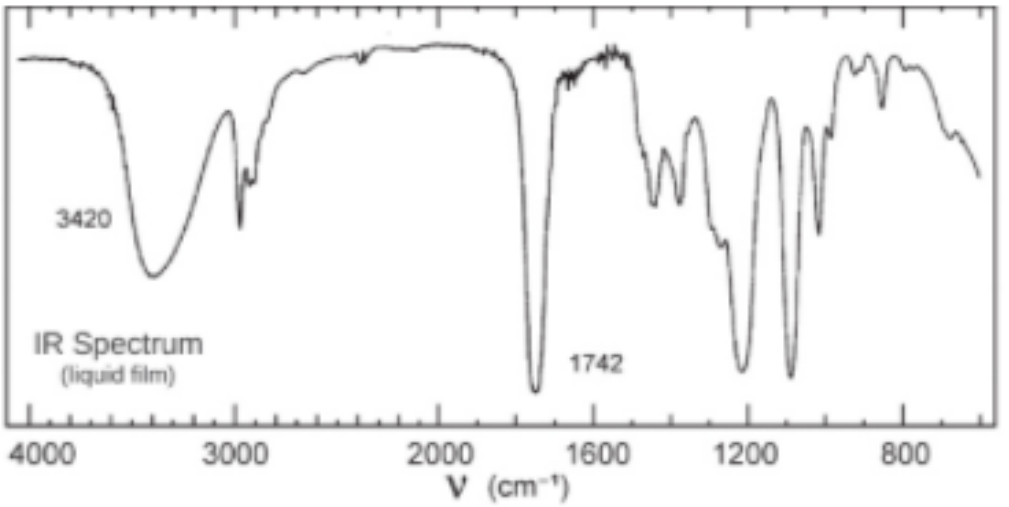

3428
IR Spectrum
(liquid film)
1718
4000
3000
2000
1600
1200
800
ν (cm-1)

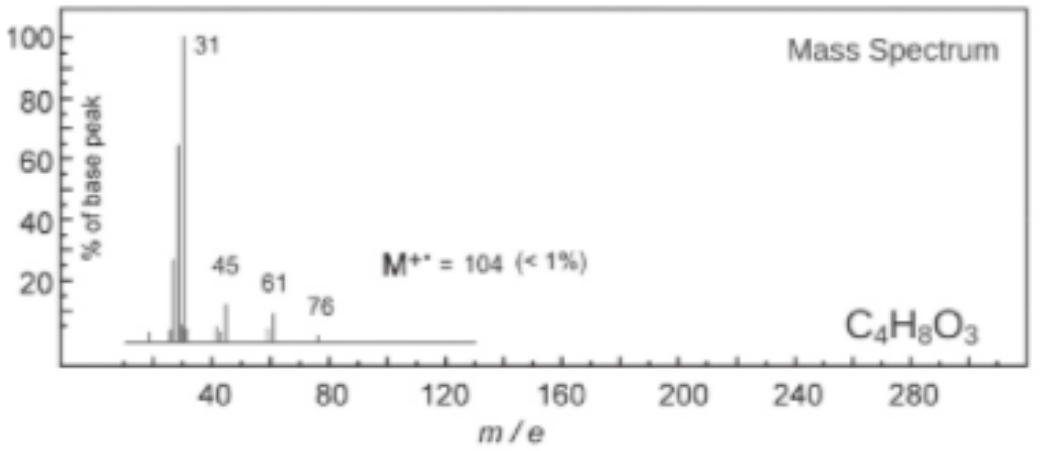

100
80
60
40
20
% of base peak
43
Mass Spectrum
M+·
74
C3H6O2
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

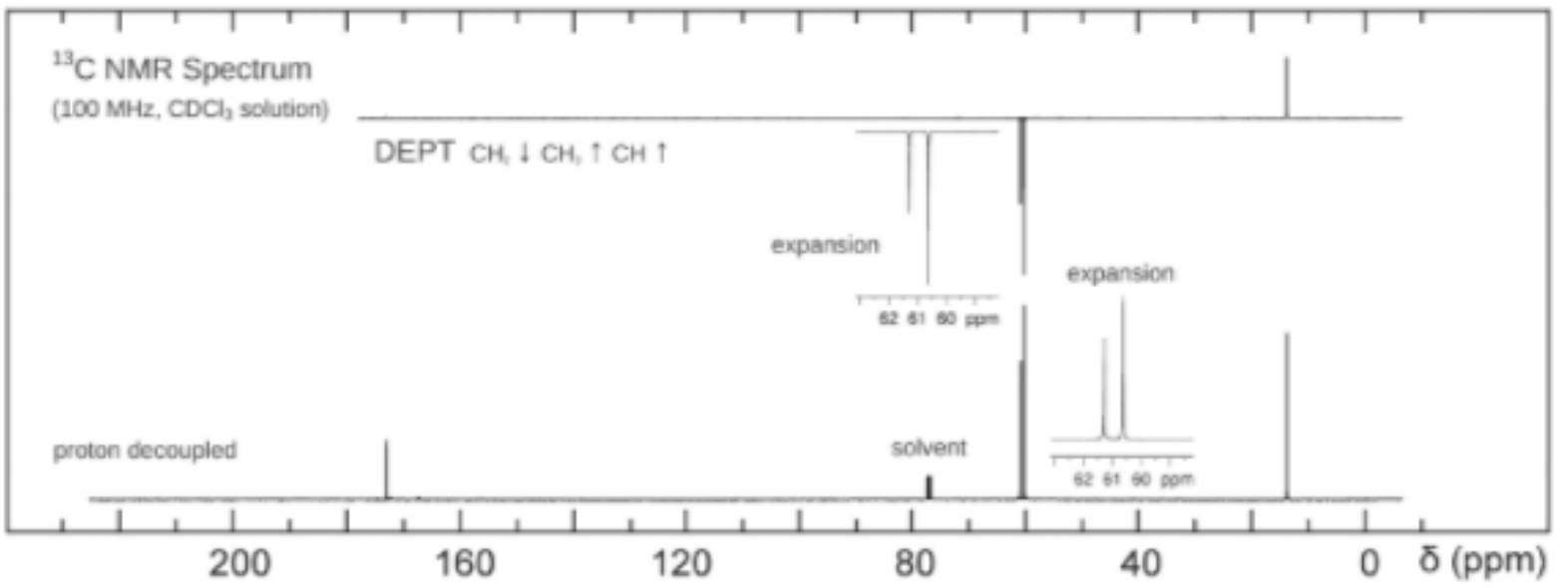

1H NMR Spectrum
(400 MHz, CDCl3 solution)
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

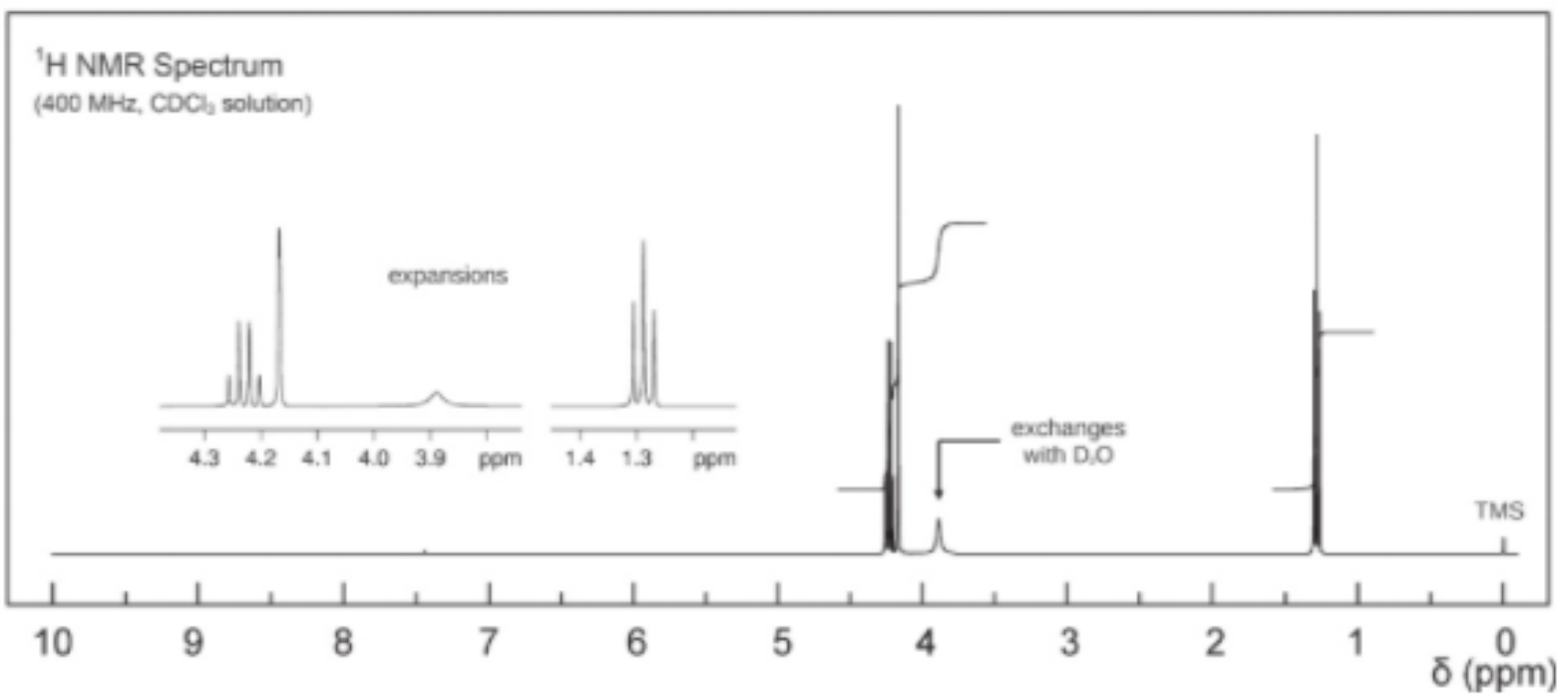
Problem 37



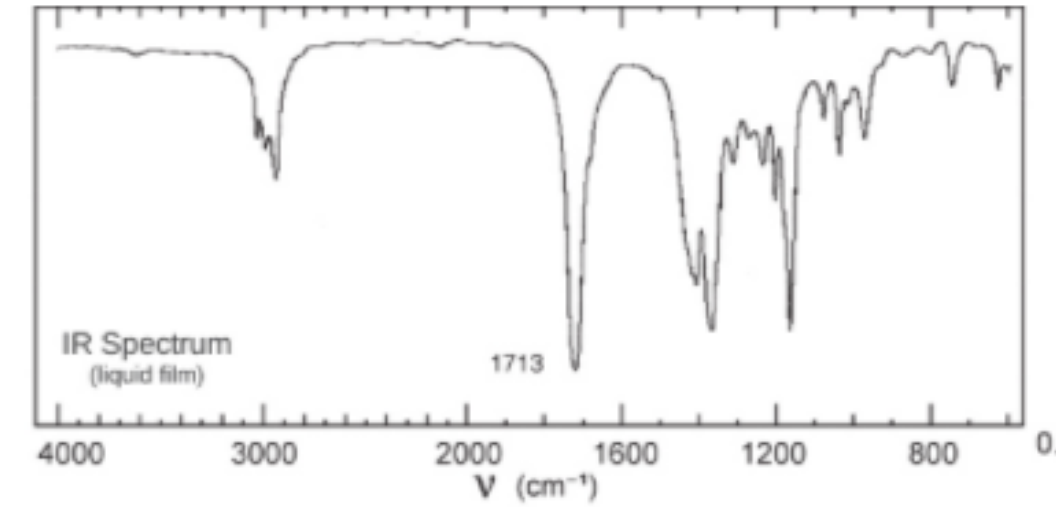


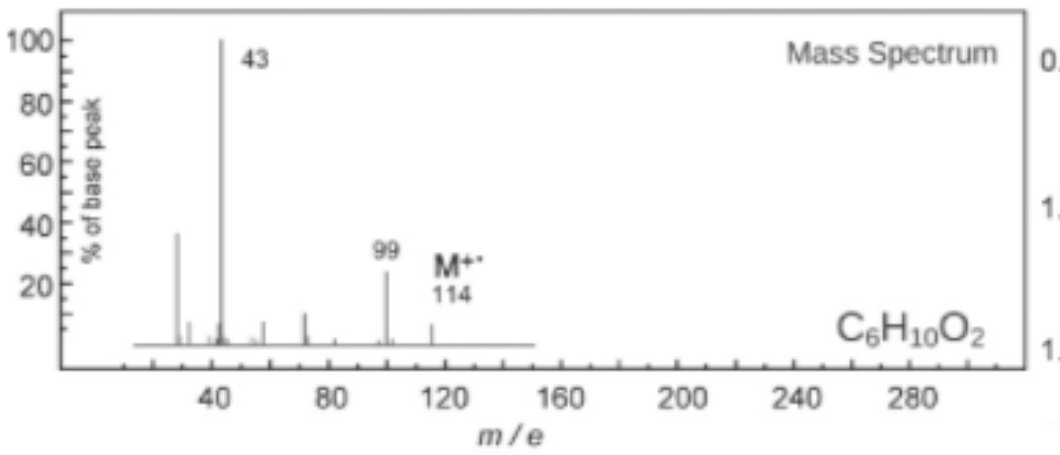
No significant UV absorption above 220 nm

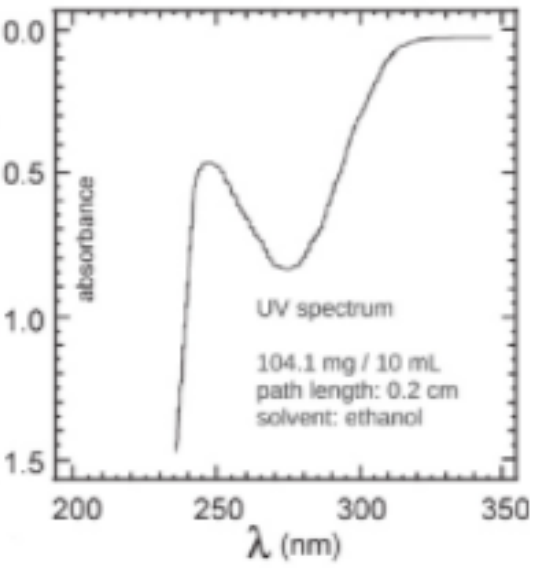


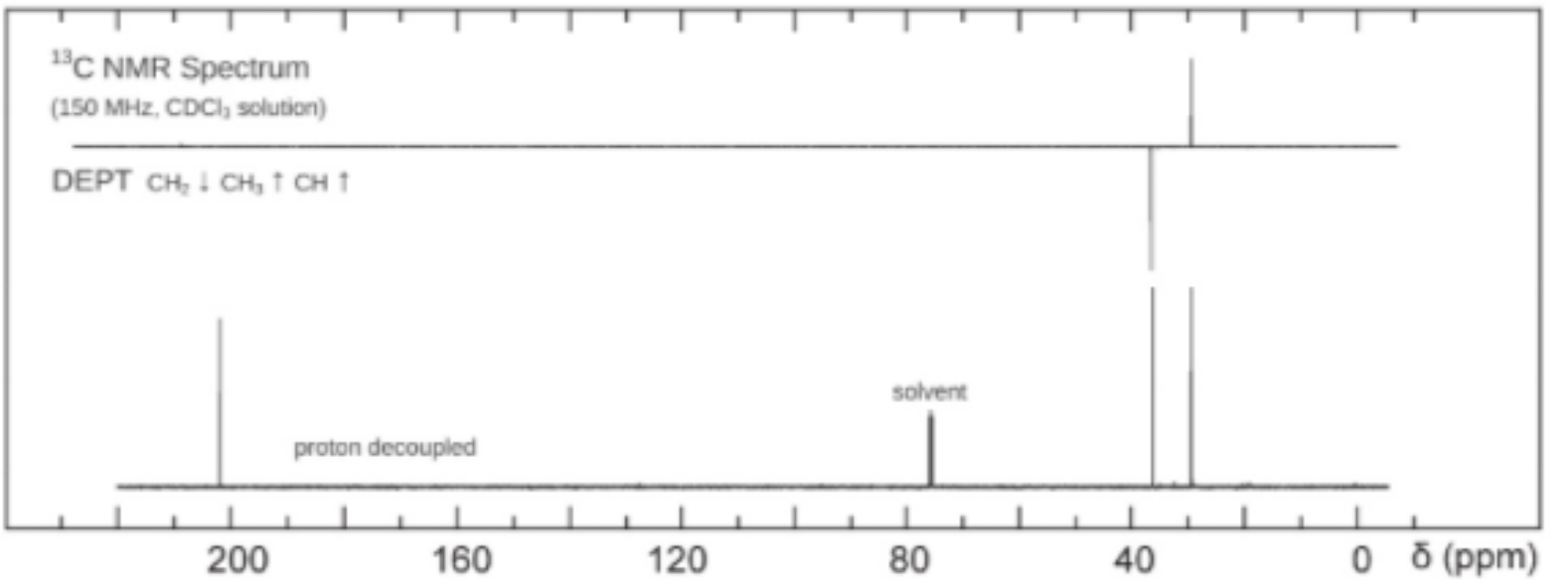


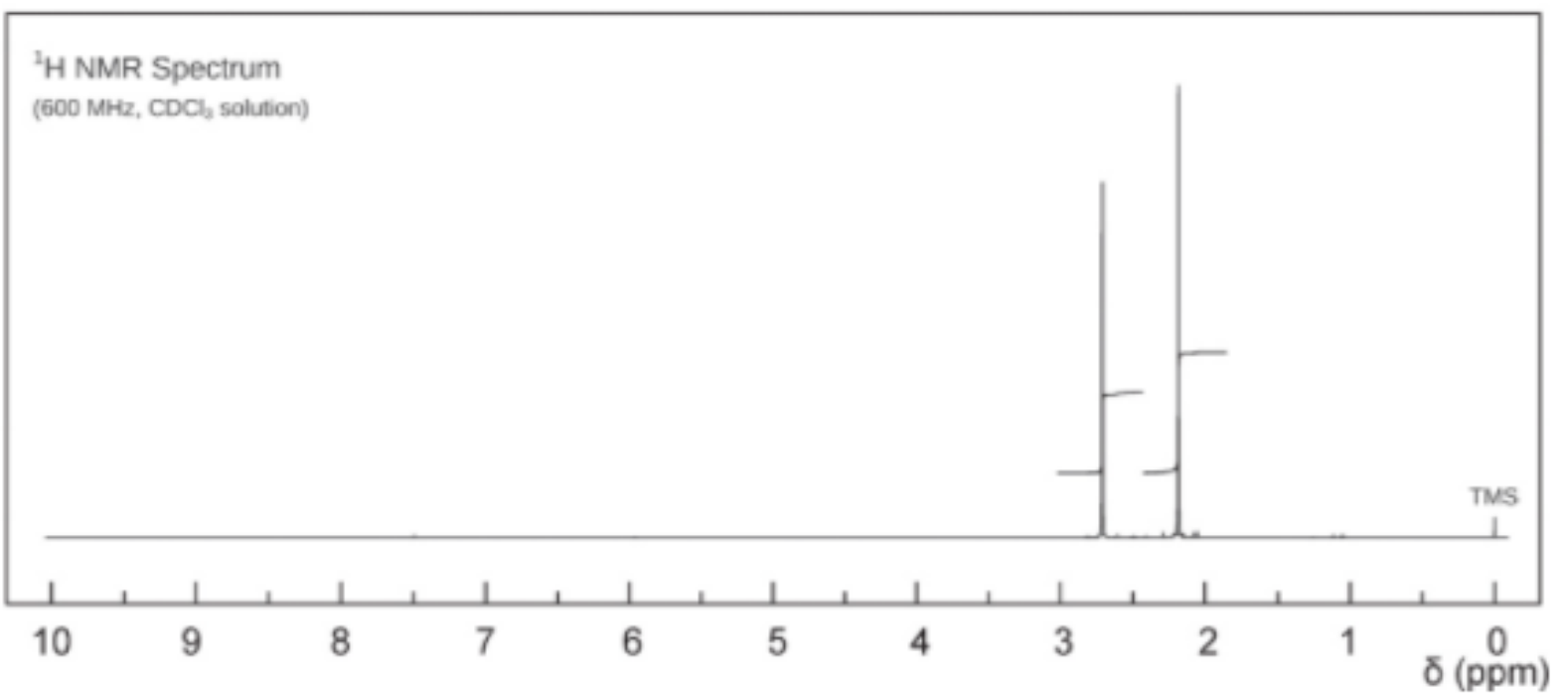
Problem 38


IR Spectrum
(liquid film)
1713
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

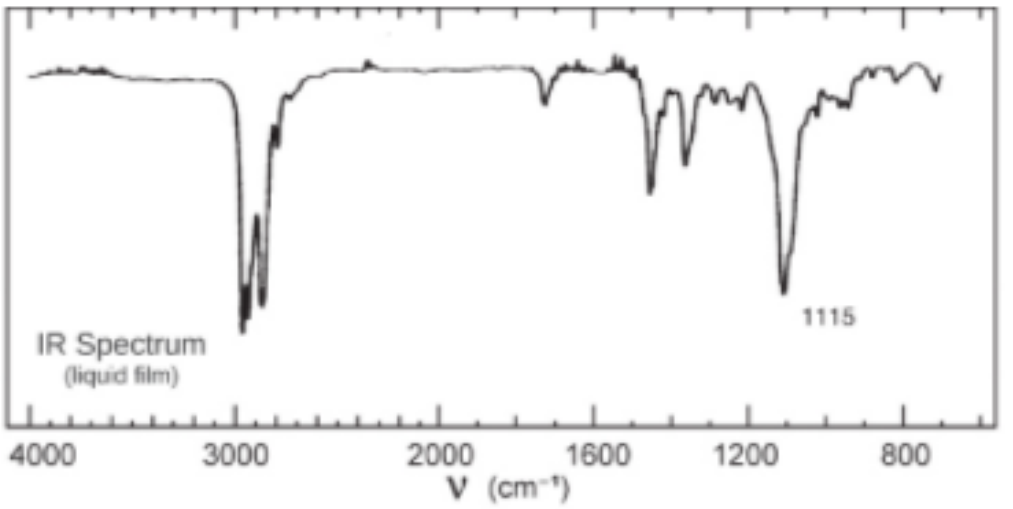

Mass Spectrum
% of base peak
100
80
60
40
20
43
99
M+·
114
C6H10O2
40
80
120
160
200
240
280
m/e

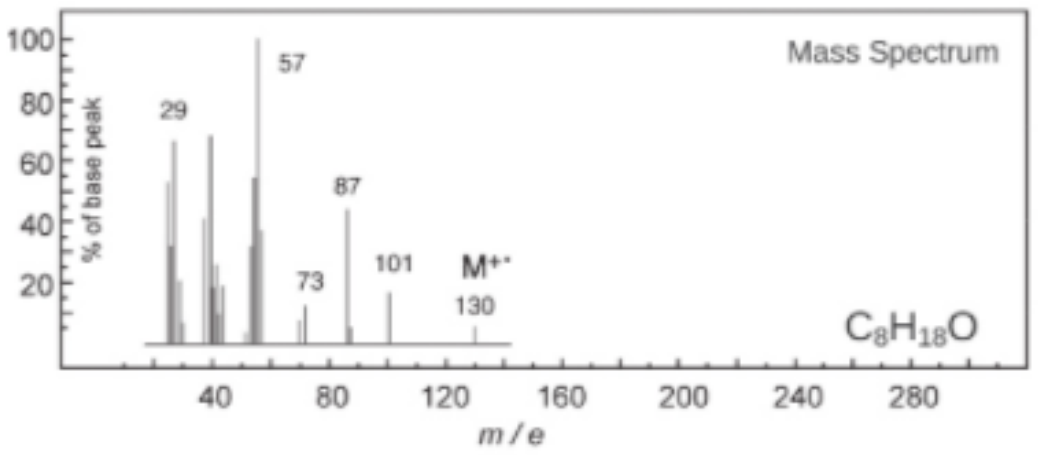

absorbance
0.0
0.5
1.0
1.5
UV spectrum
104.1 mg / 10 mL
path length: 0.2 cm
solvent: ethanol
200
250
300
350
λ (nm)


13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

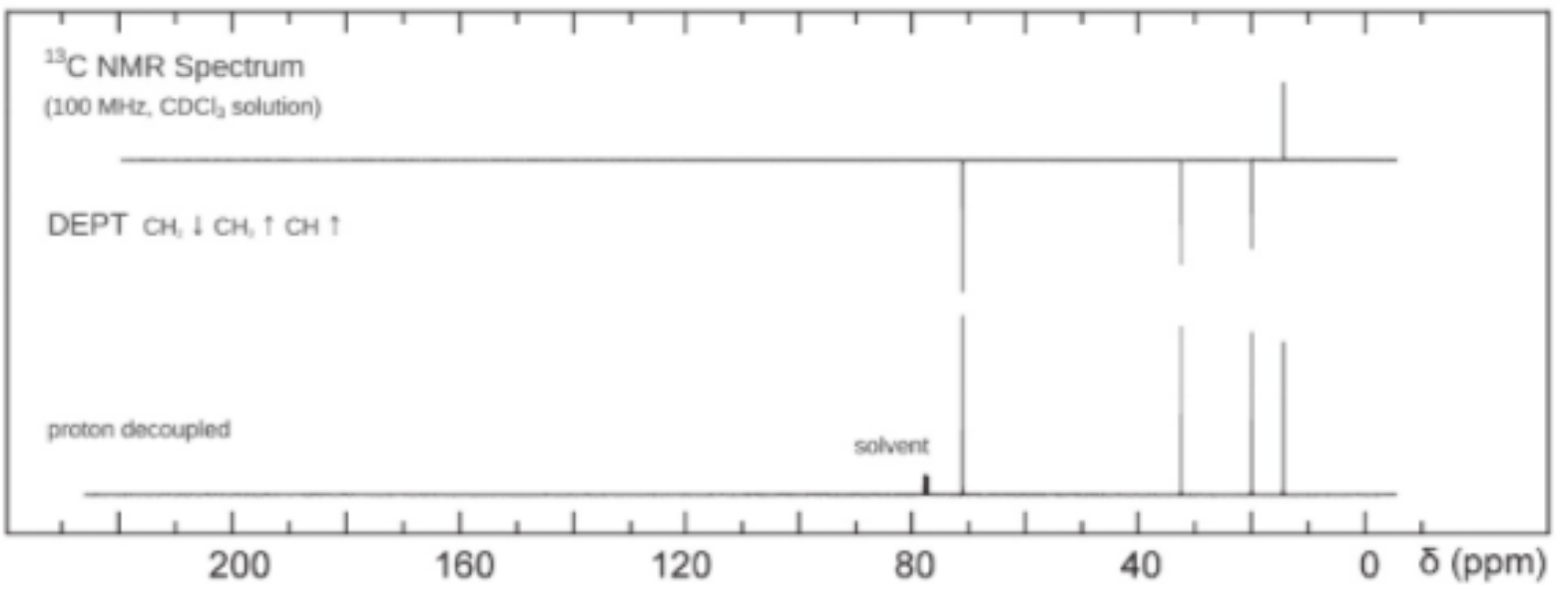

1H NMR Spectrum
(600 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

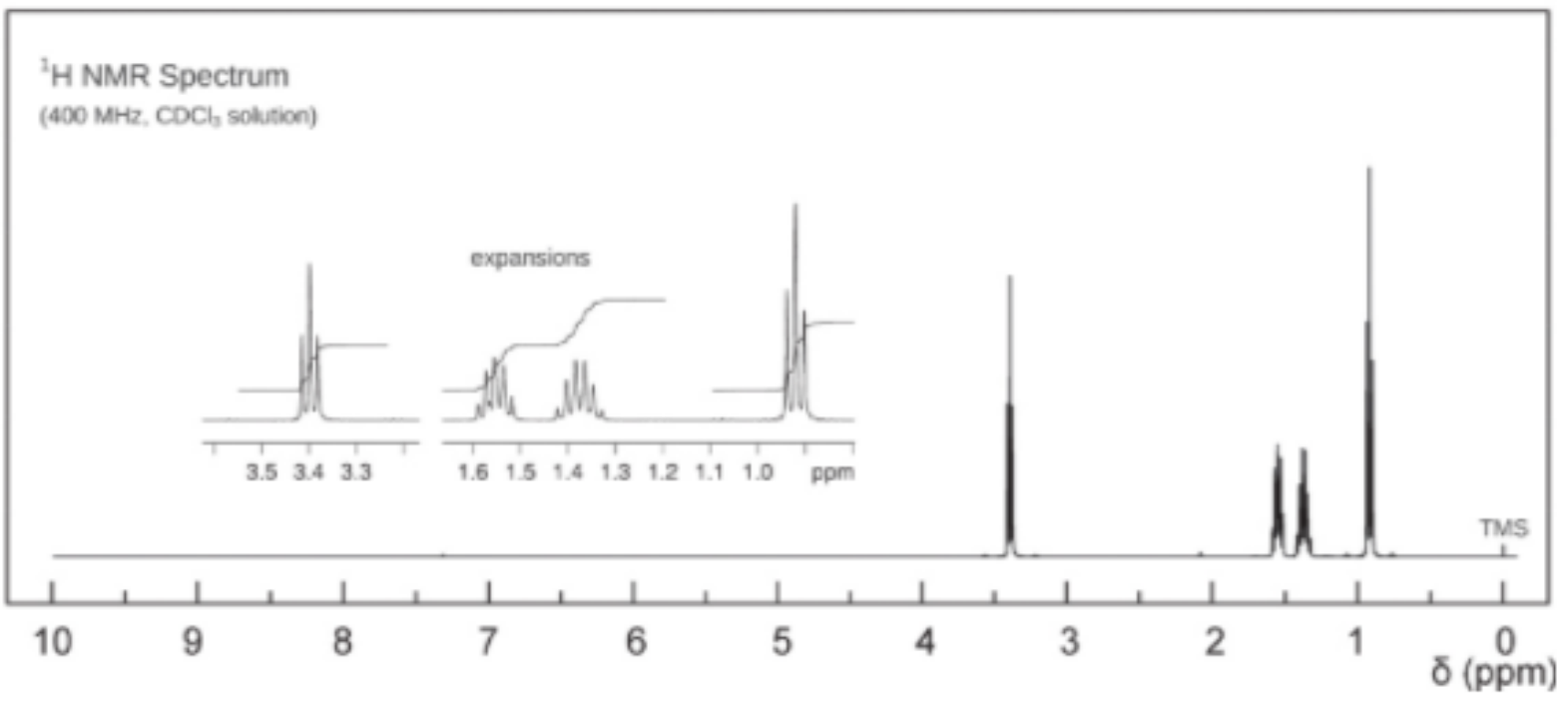
Problem 39

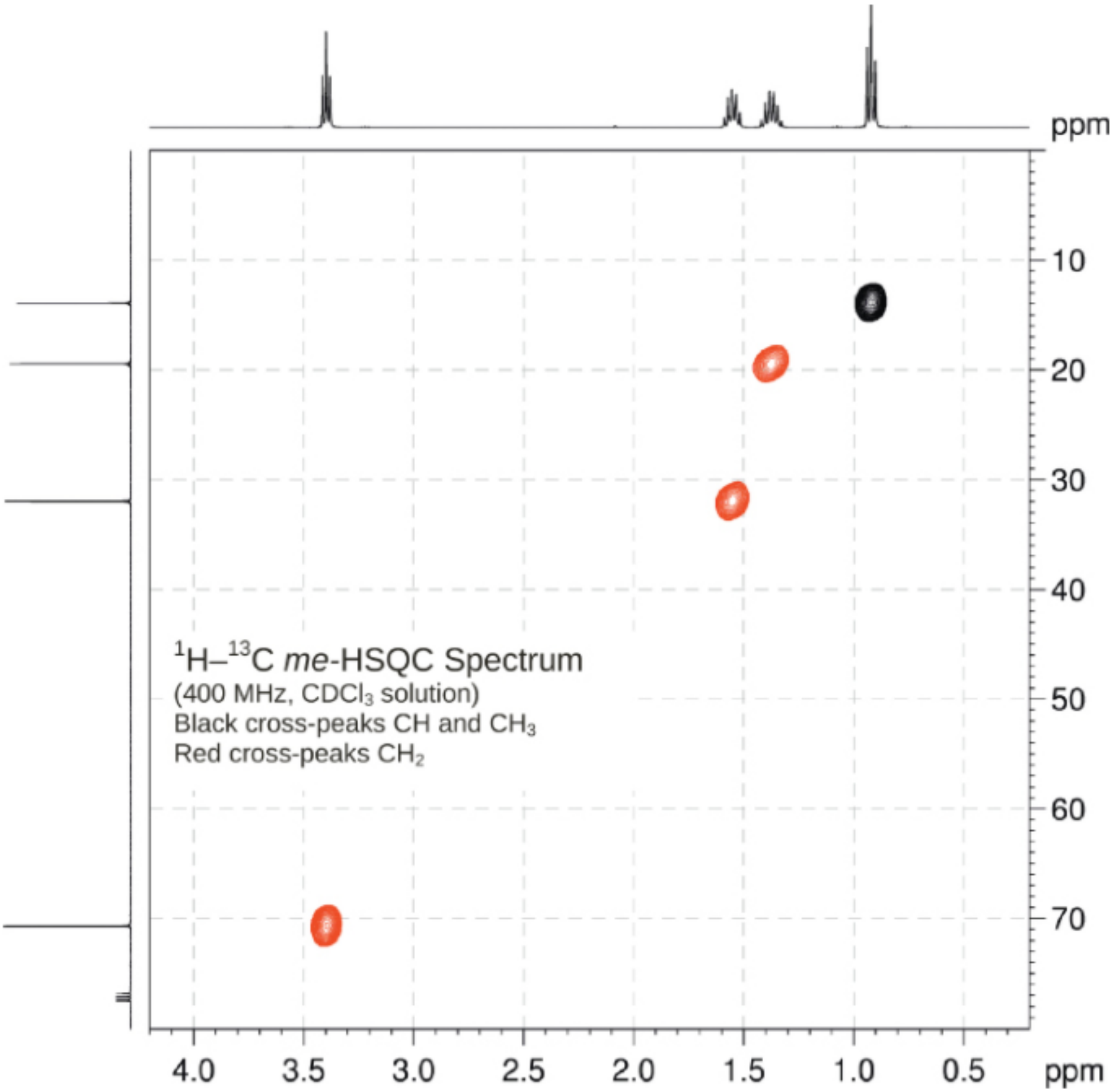




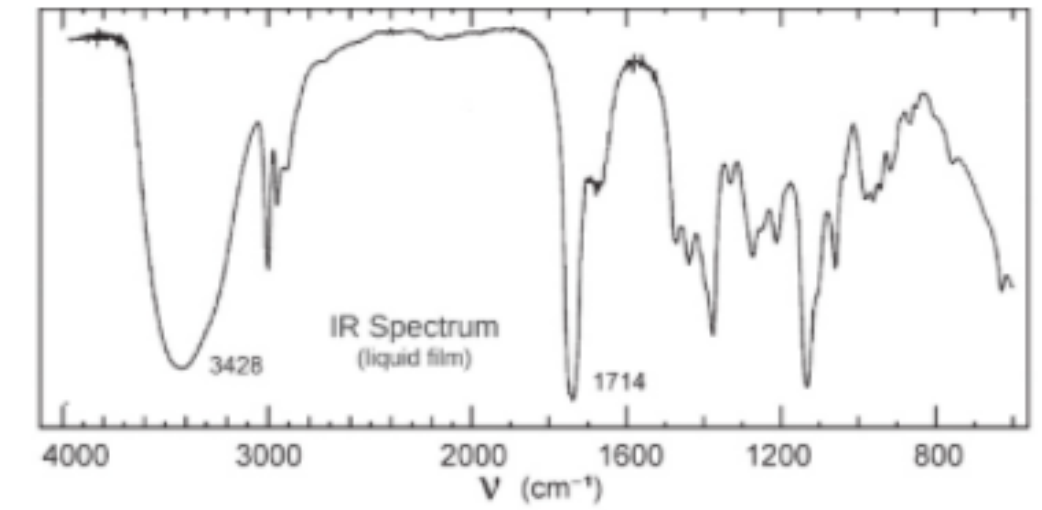
No significant UV absorption above 220 nm

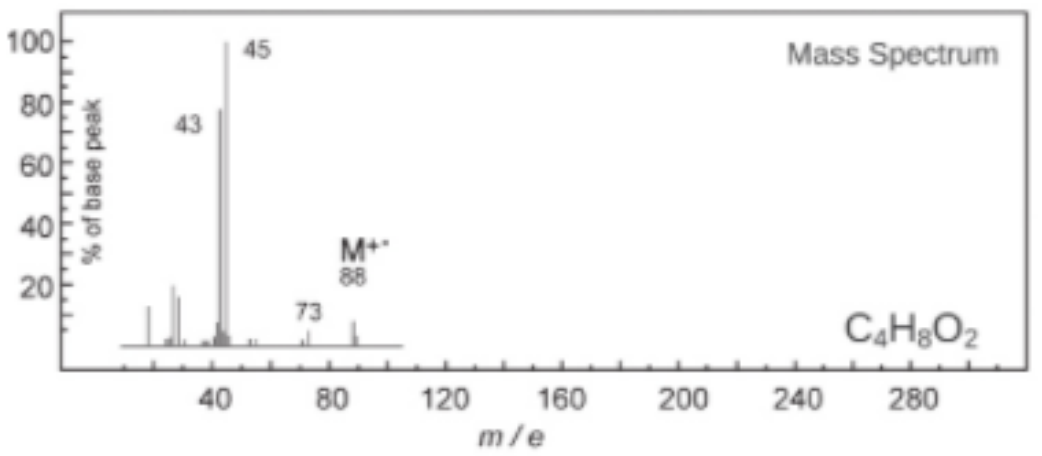




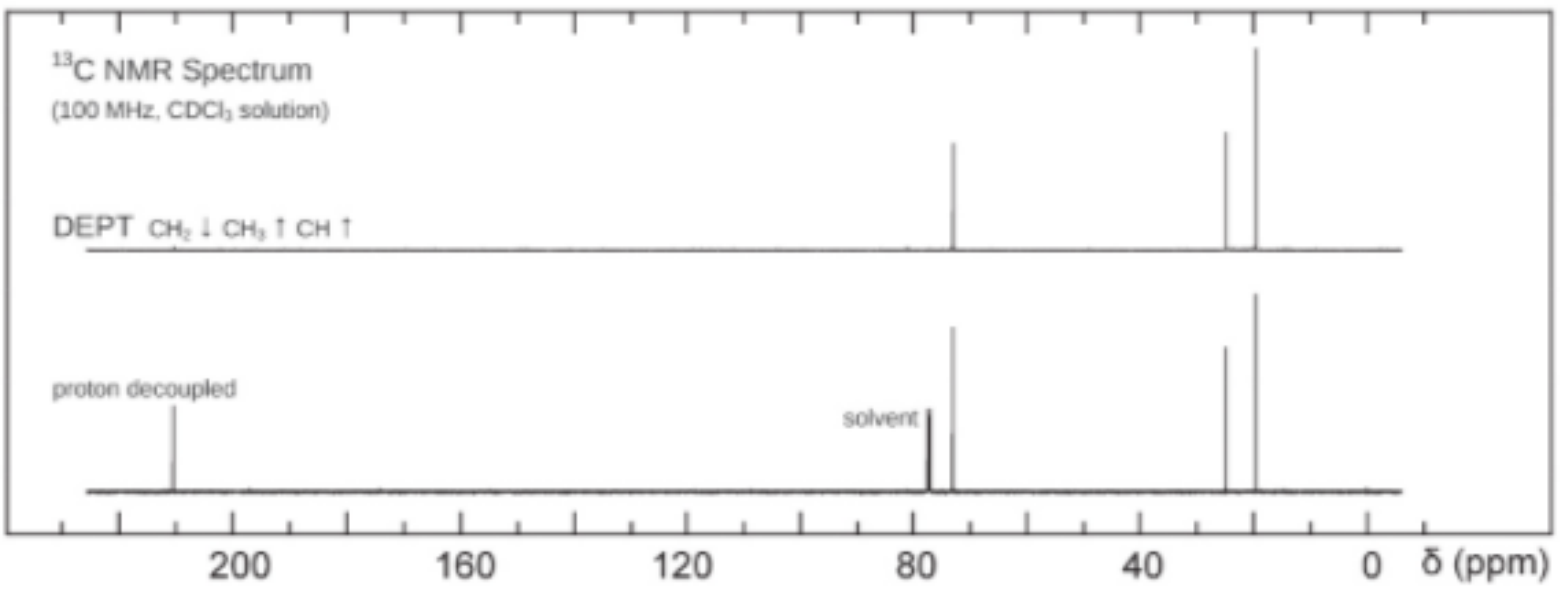

ppm
10
20
30
40
50
60
70
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

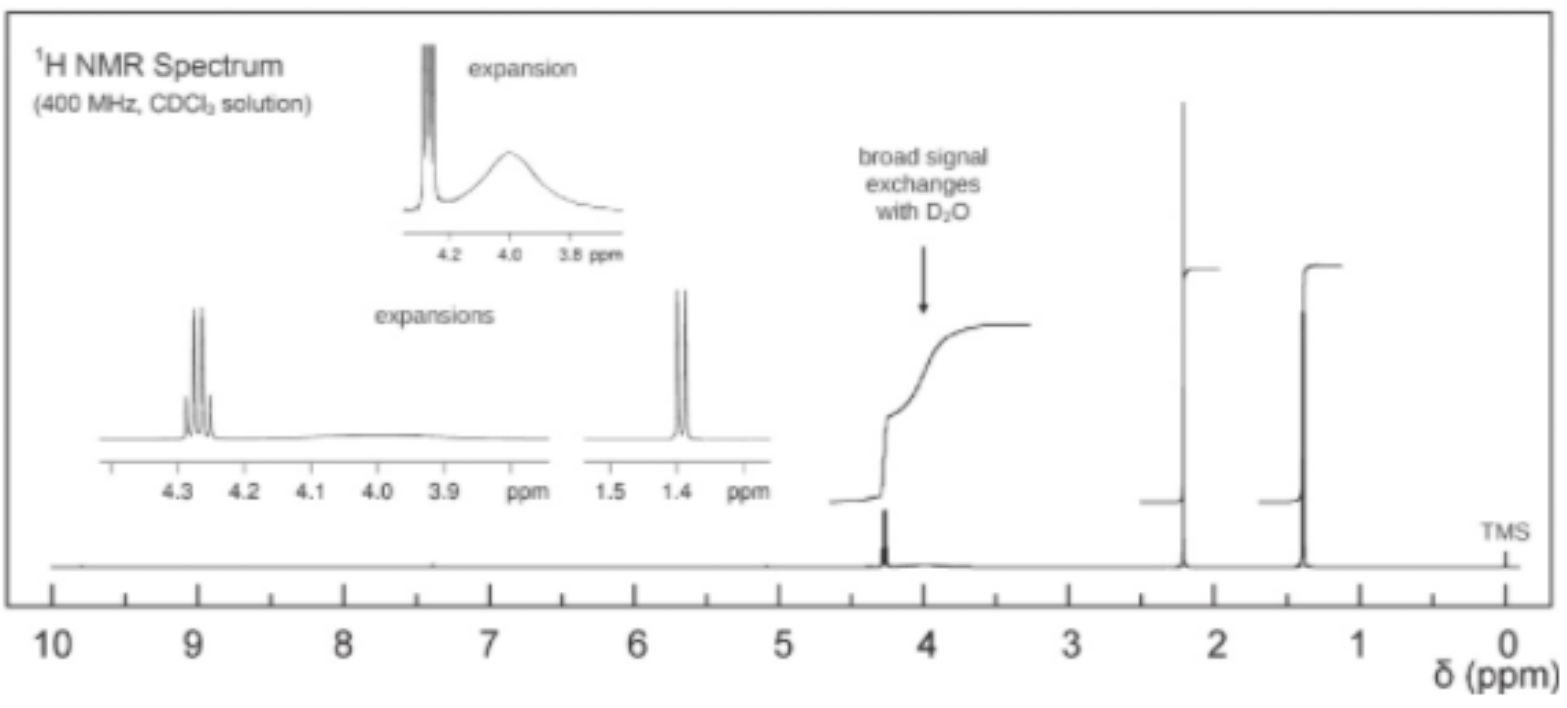
Problem 40

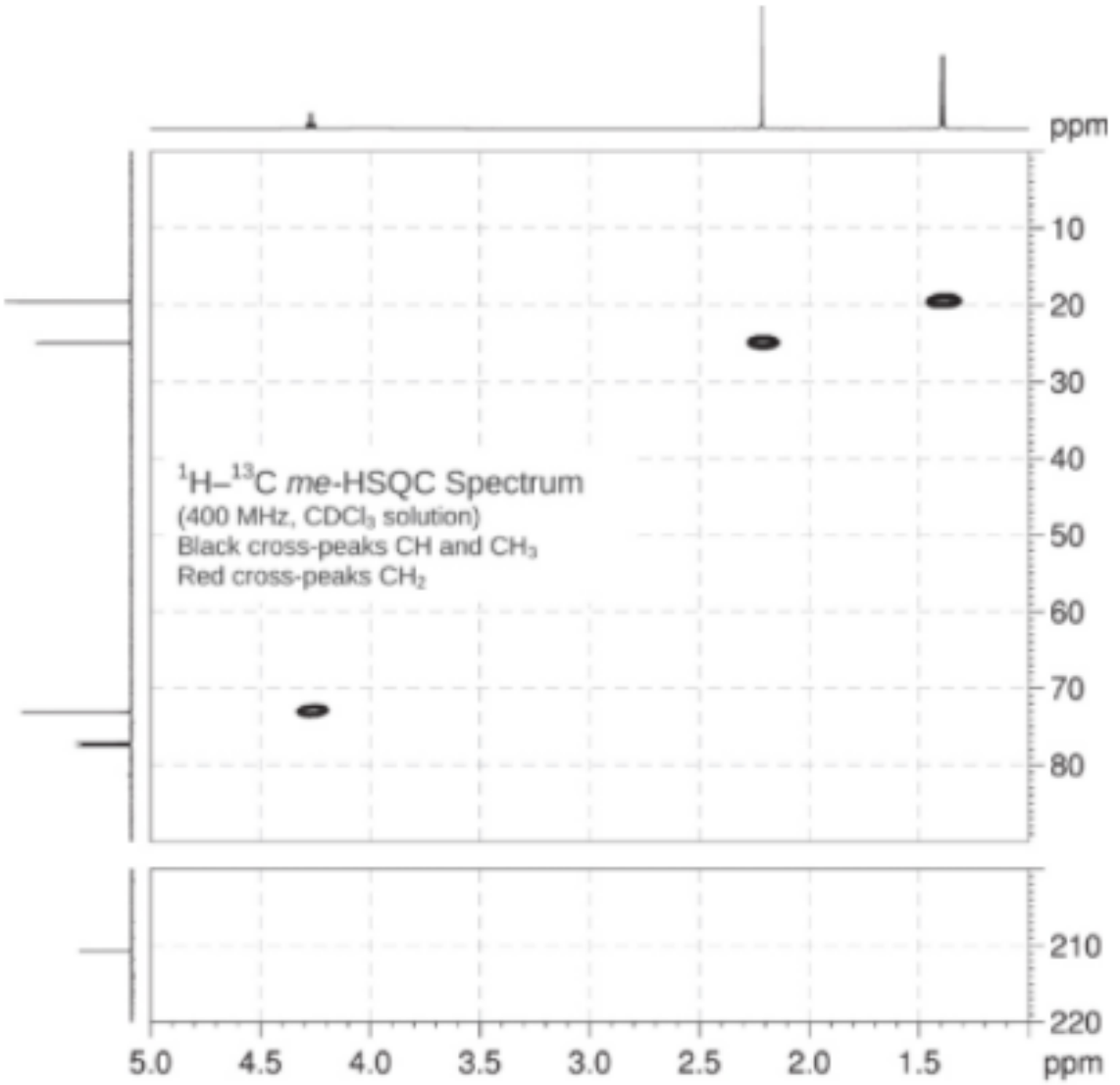


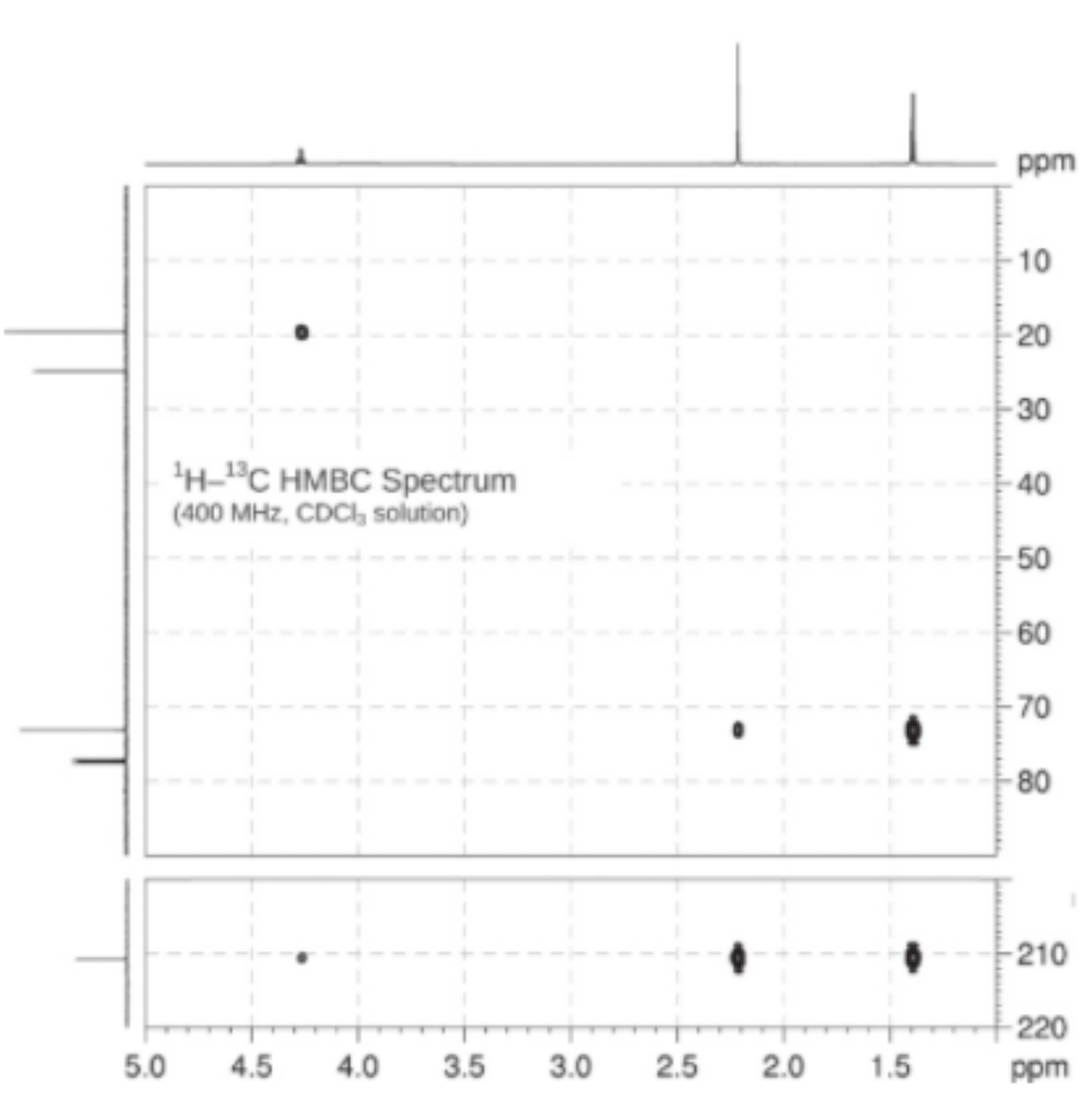


No significant UV absorption above 220 nm

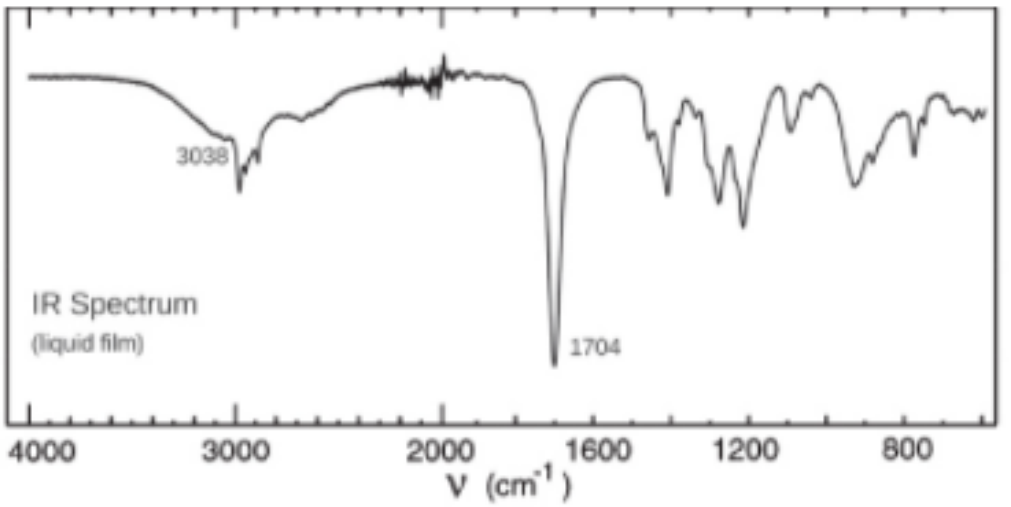


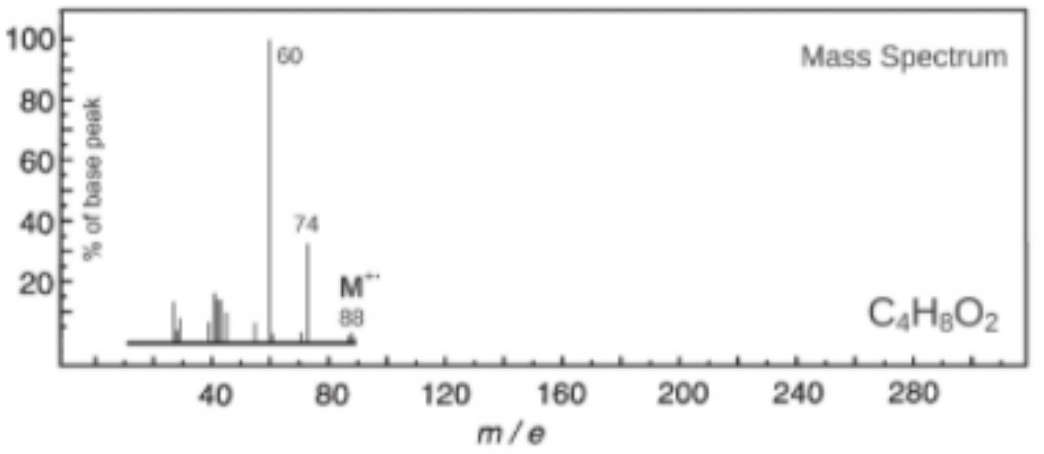


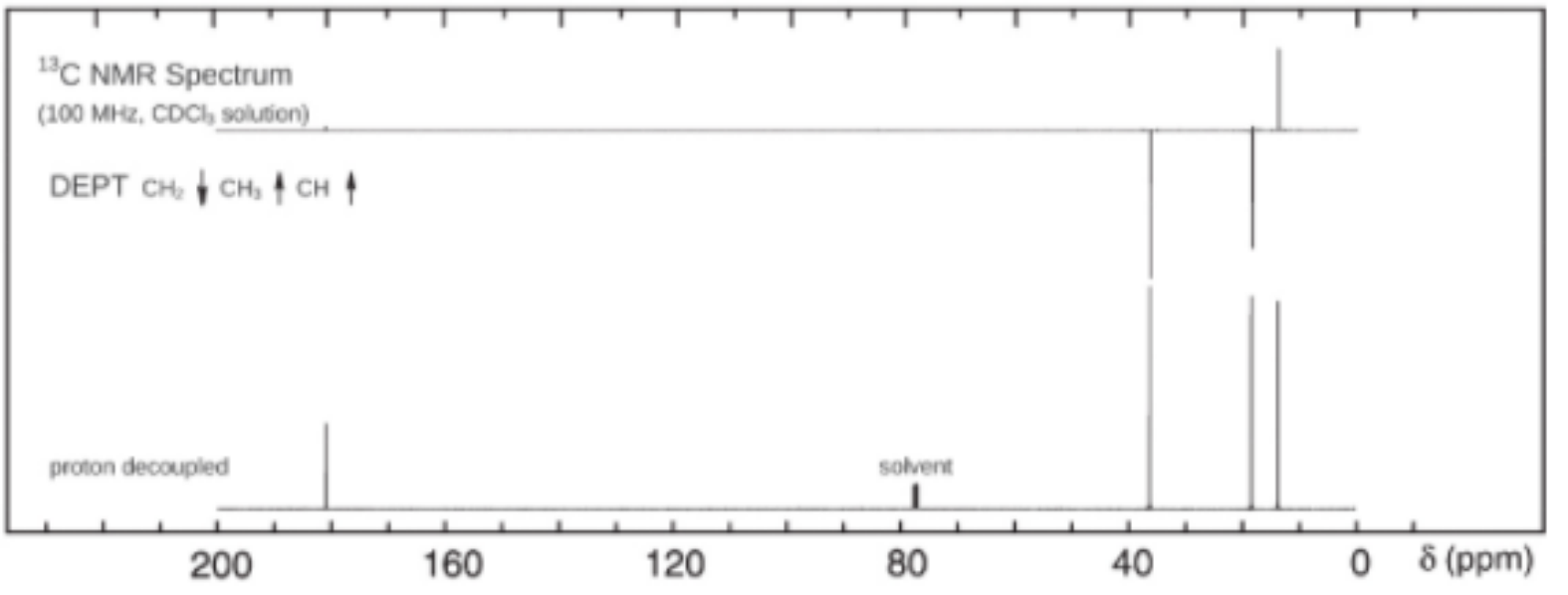

ppm
10
20
30
40
50
60
70
80
210
220
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

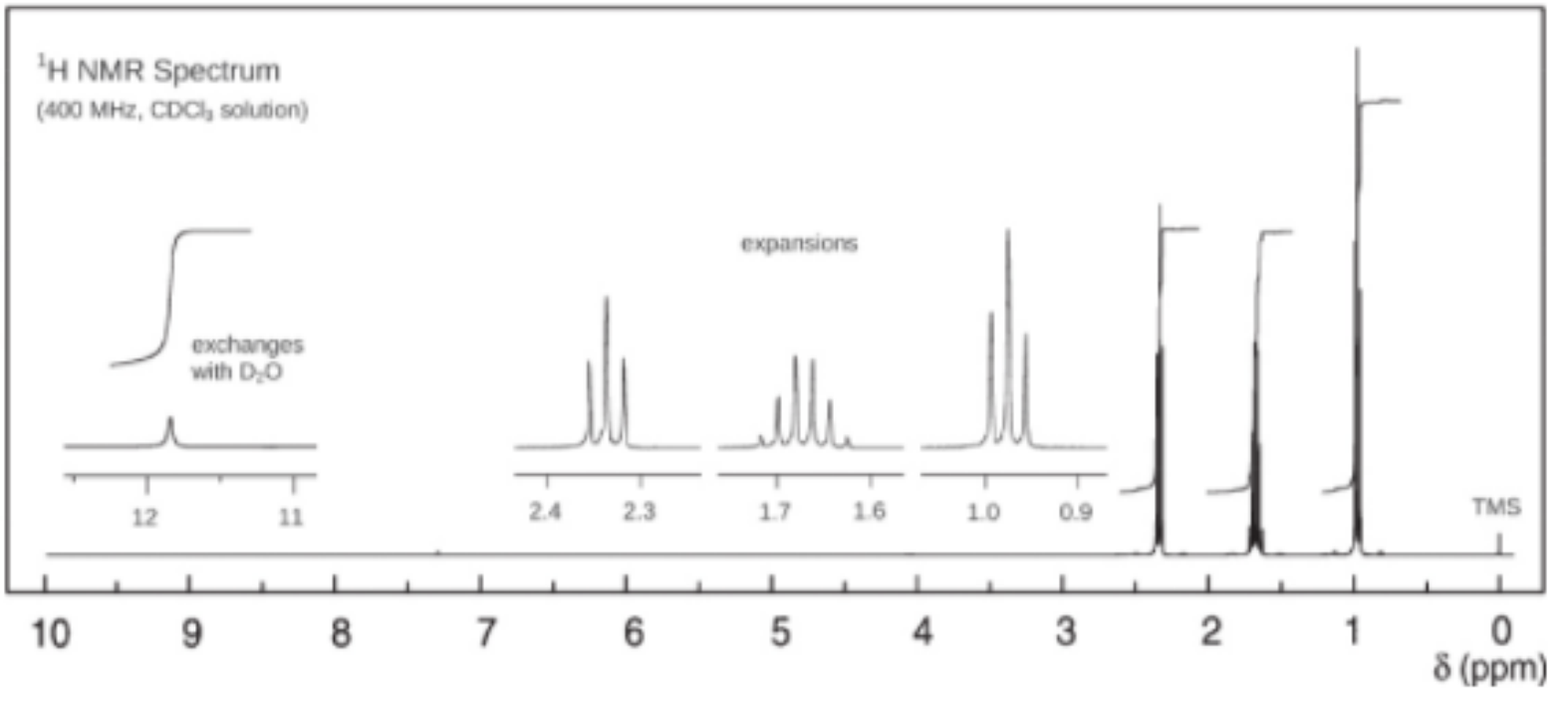

ppm
10
20
30
40
50
60
70
80
210
220
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)

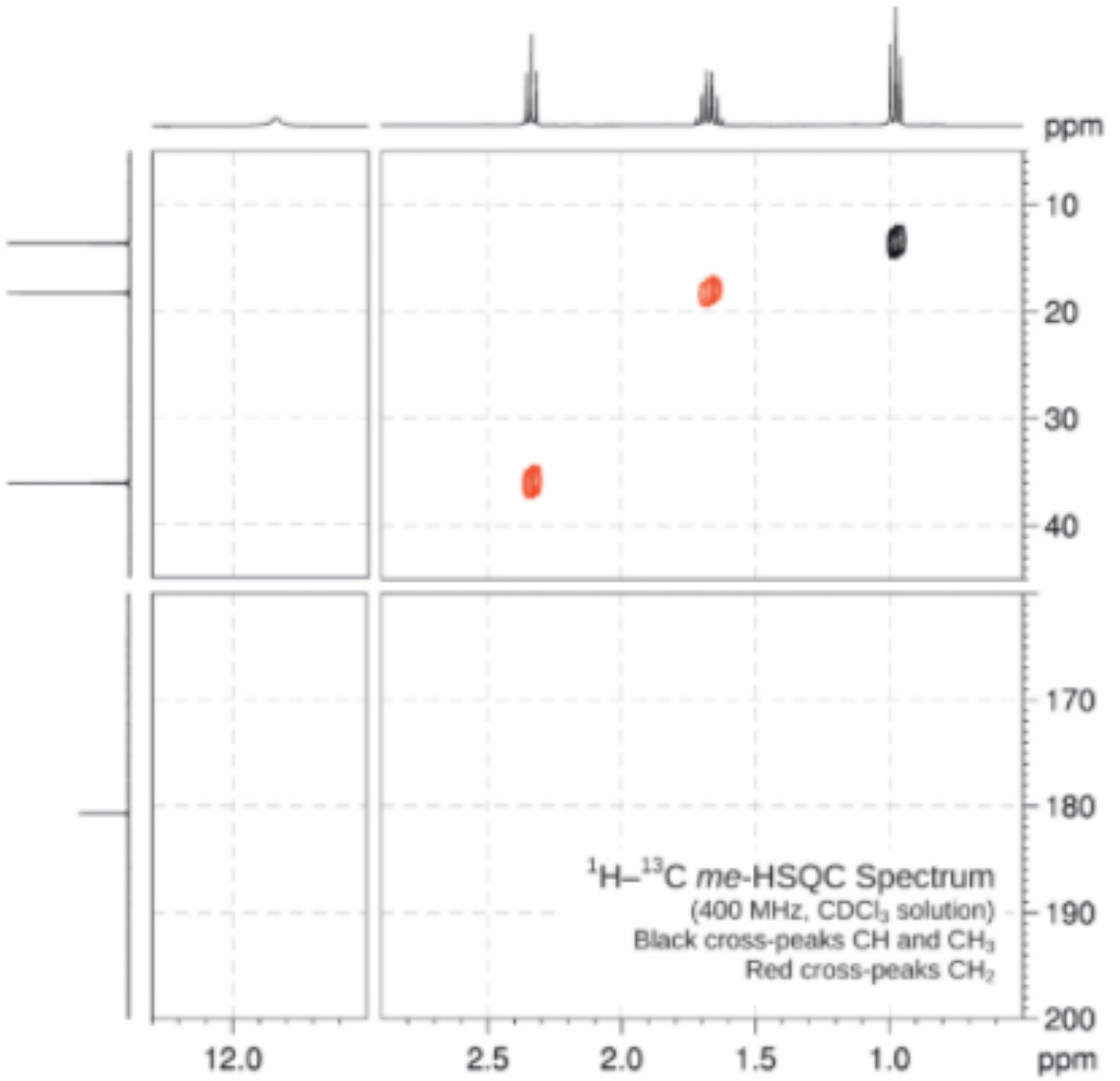
Problem 41


3038
IR Spectrum
(liquid film)
1704
4000
3000
2000
1600
1200
800
ν (cm-1)


100
80
60
40
20
% of base peak
60
74
M+·
88
Mass Spectrum
C4H8O2
40
80
120
160
200
240
280
m / e

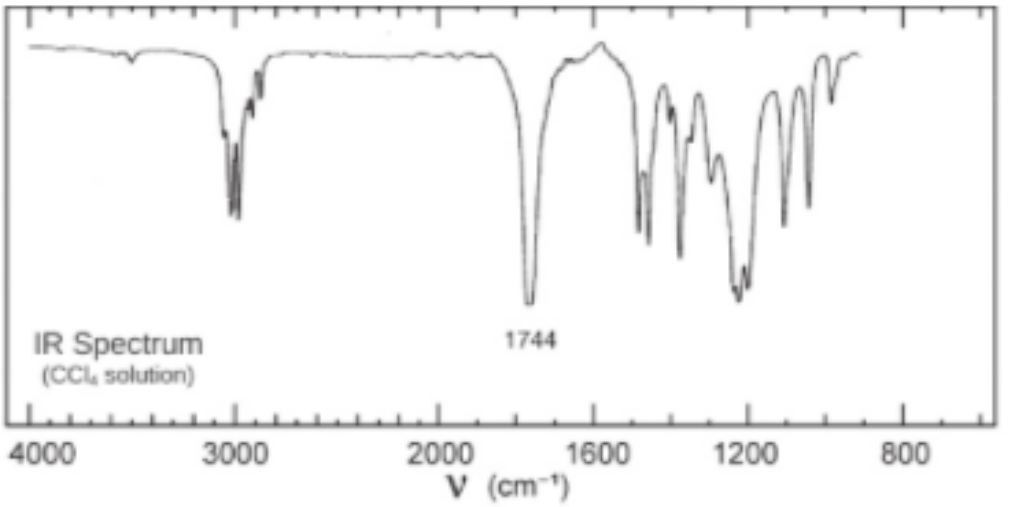

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

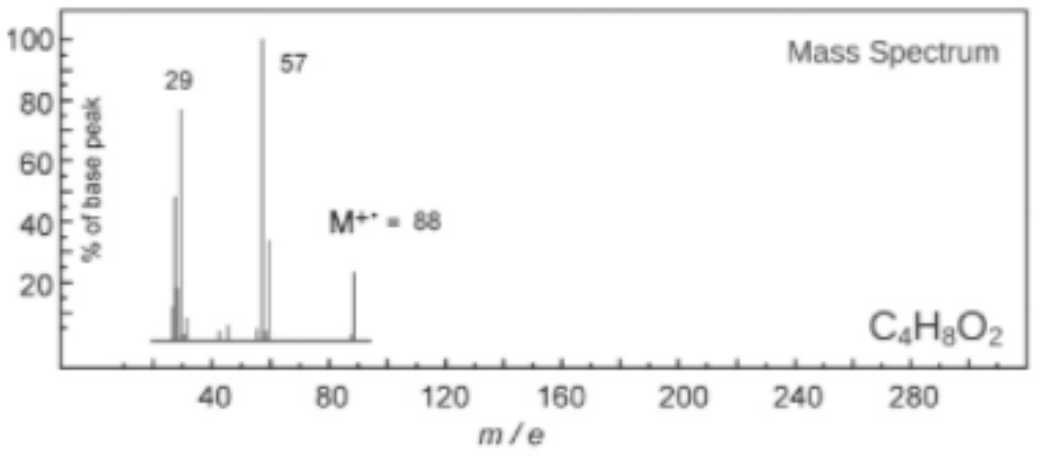

1H NMR Spectrum
(400 MHz, CDCl3 solution)
exchanges
with D2O
12
11
expansions
2.4
2.3
1.7
1.6
1.0
0.9
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
10
20
30
40
170
180
190
200
12.0
2.5
2.0
1.5
1.0
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

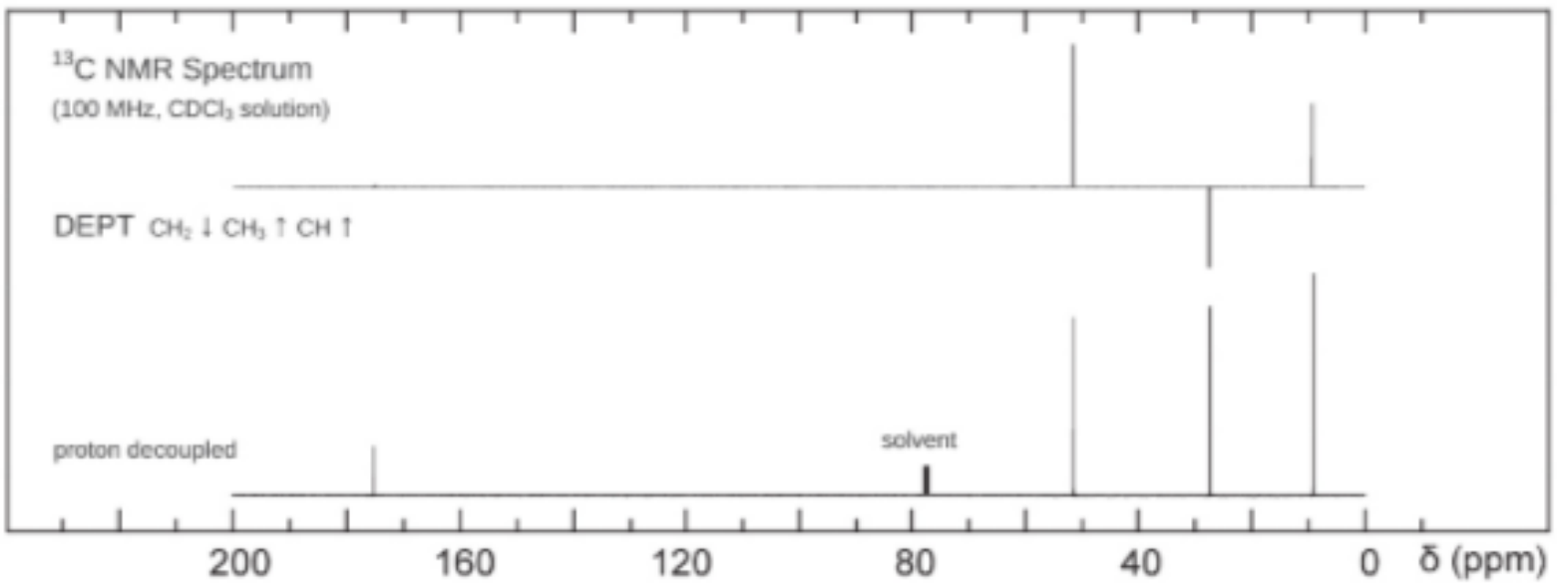
ppm
10
20
30
40
170
180
190
12.0
2.5
2.0
1.5
1.0
ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)

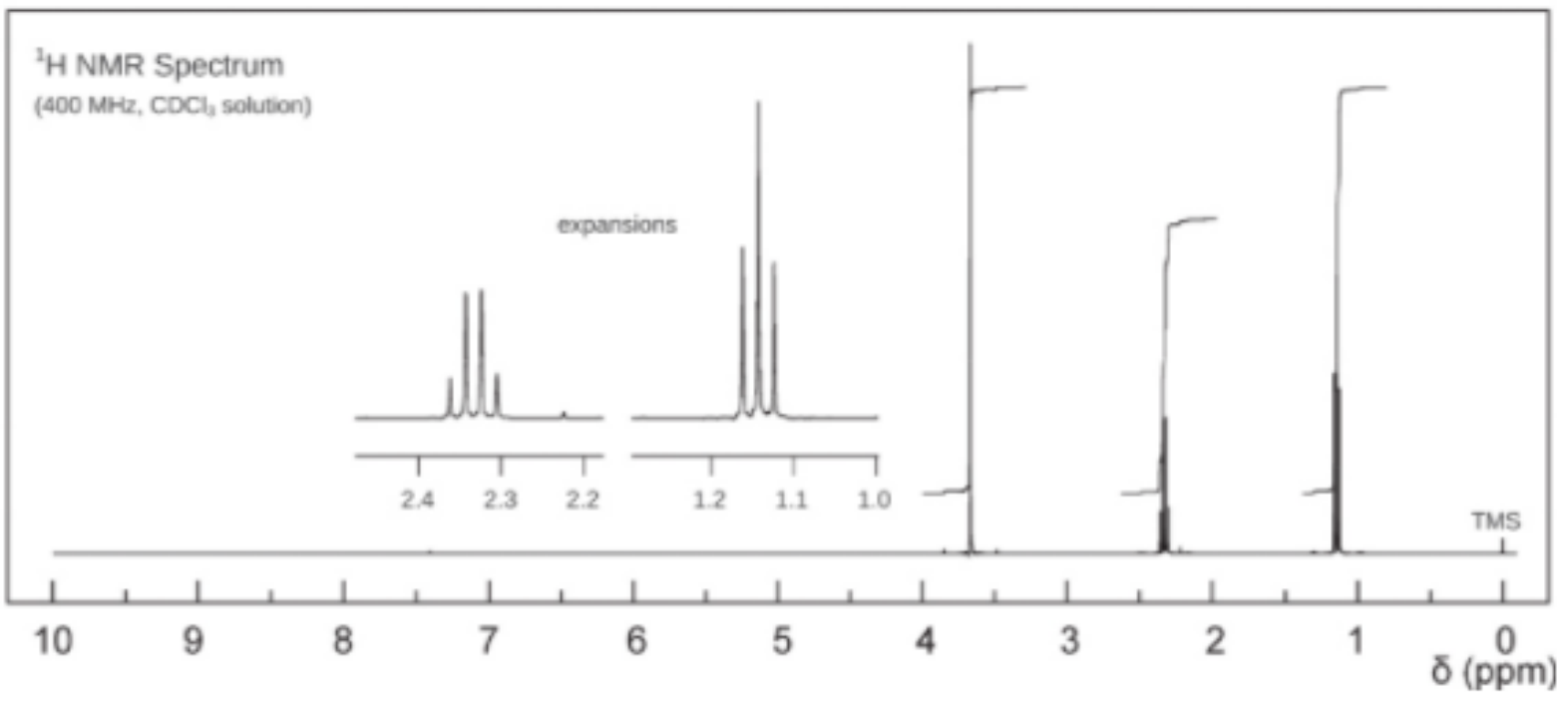
Problem 42

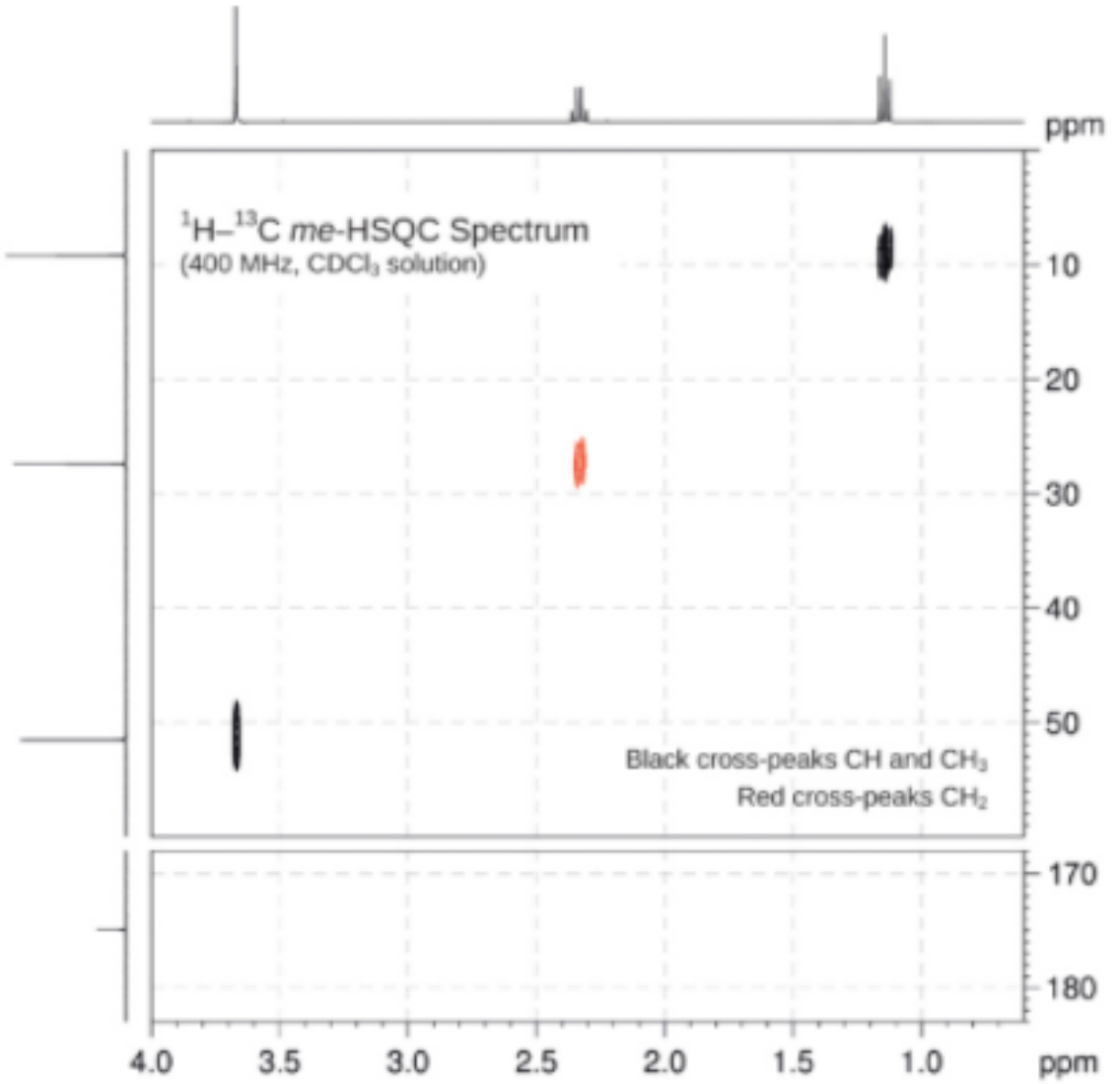


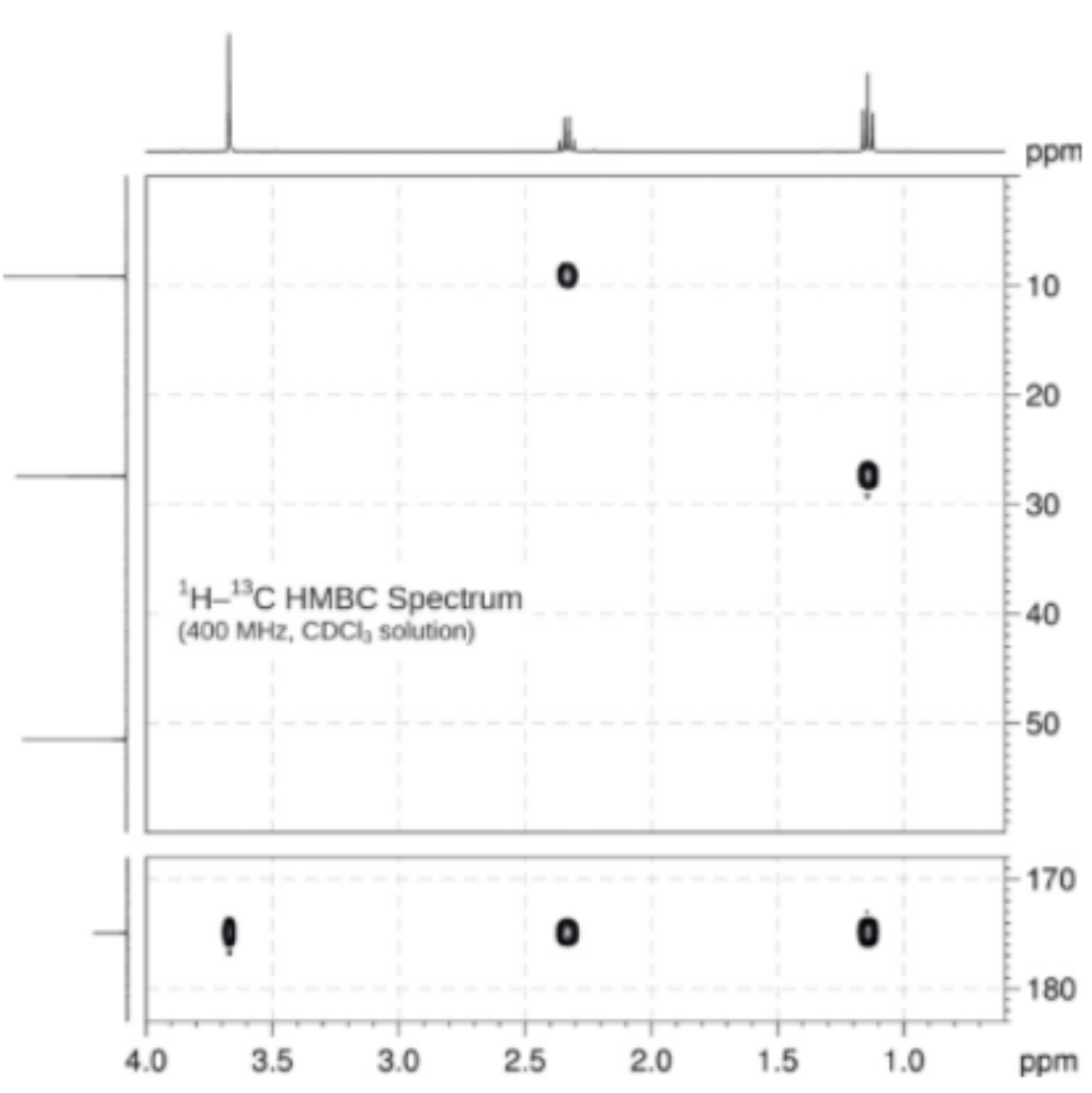


No significant UV absorption above 220 nm

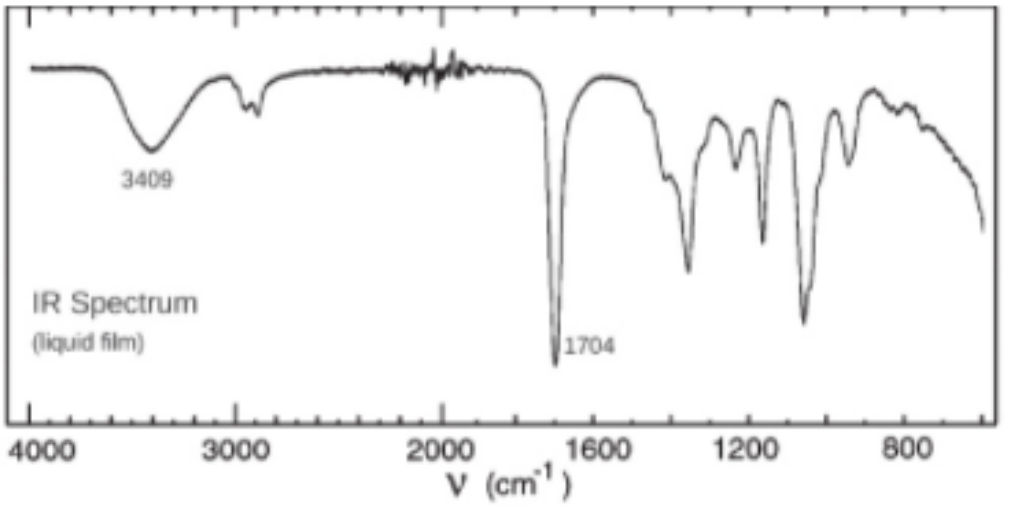


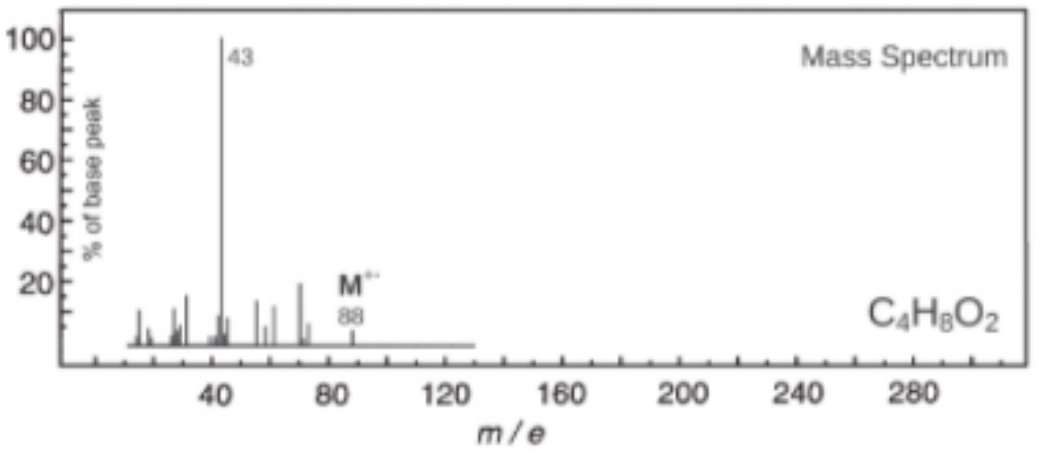


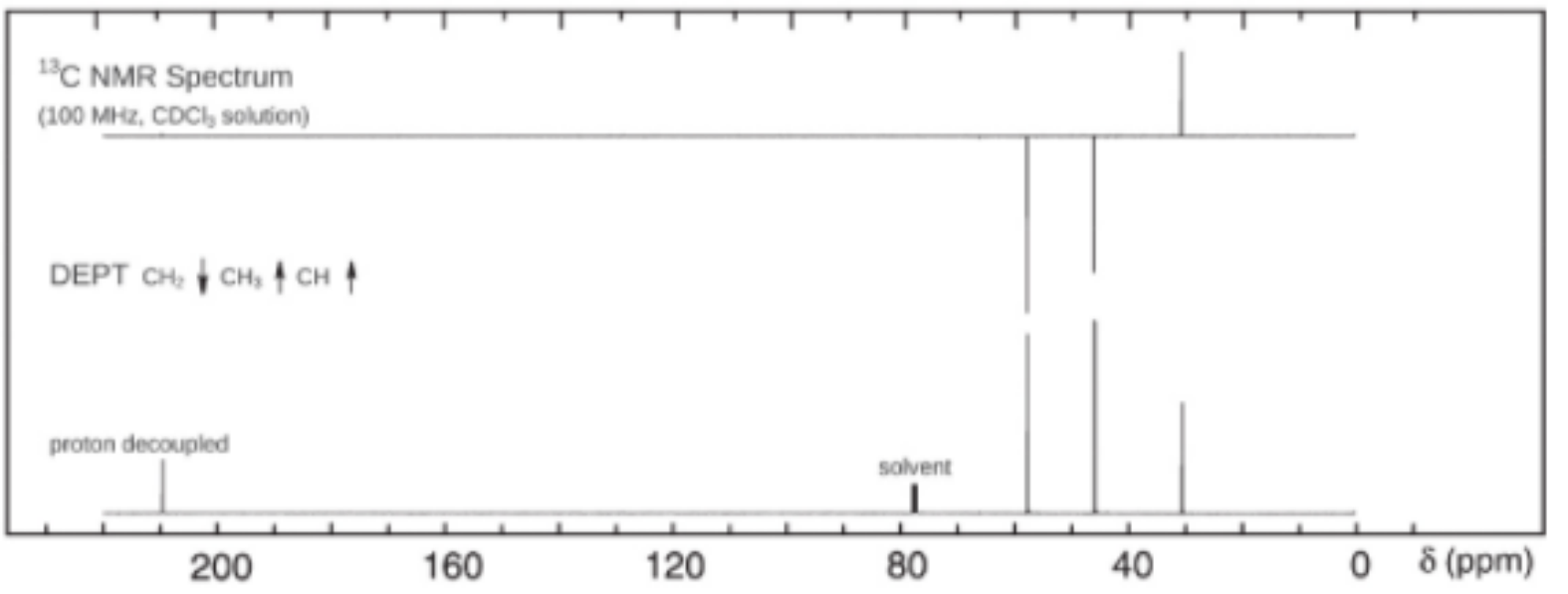

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
10
20
30
40
50
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
170
180
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

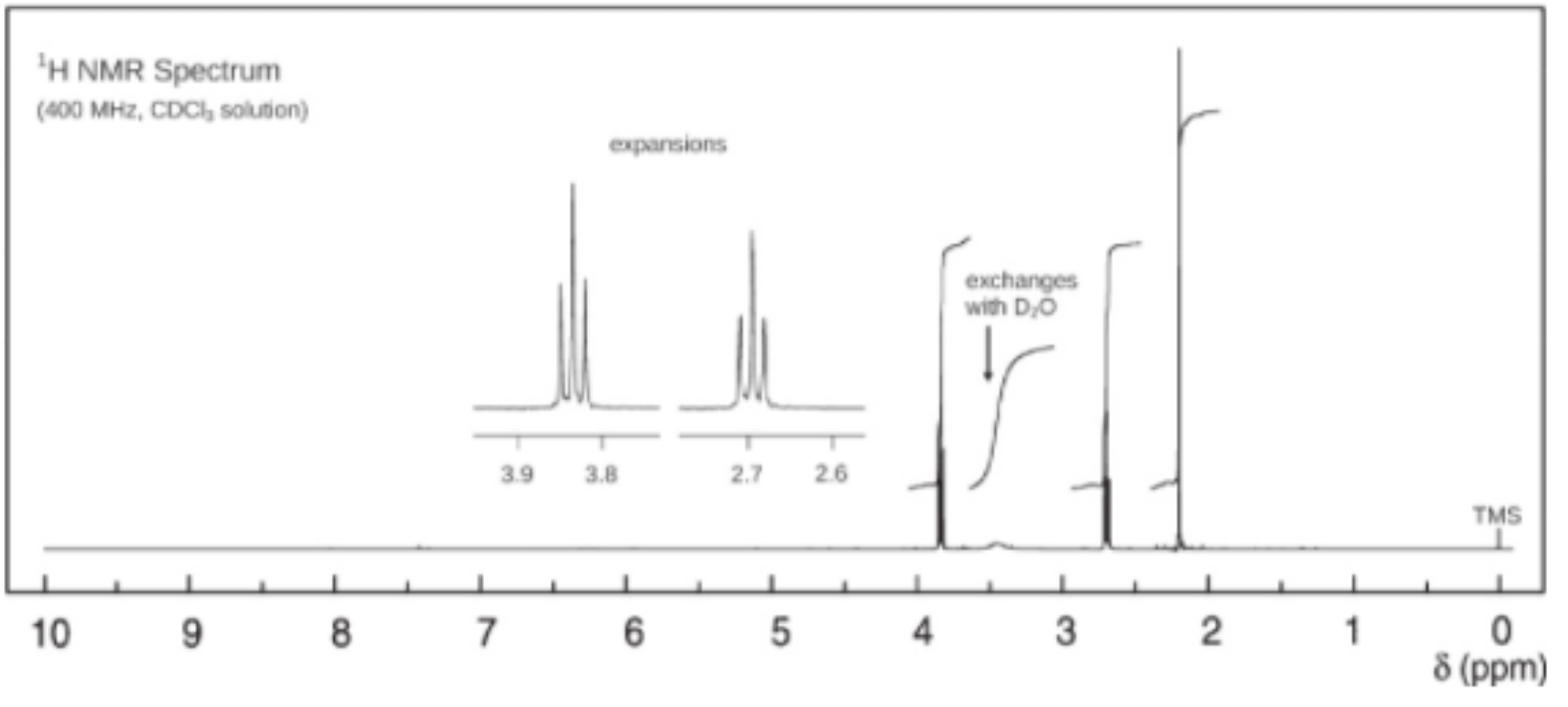

ppm
10
20
30
40
50
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
170
180
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

Problem 43

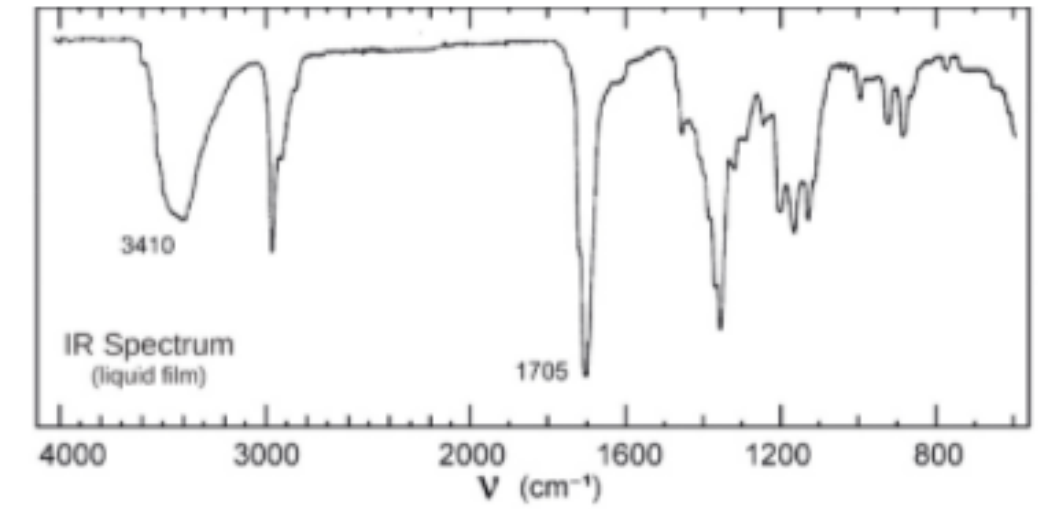

3409
IR Spectrum
(liquid film)
1704
4000
3000
2000
1600
1200
800
ν (cm-1)

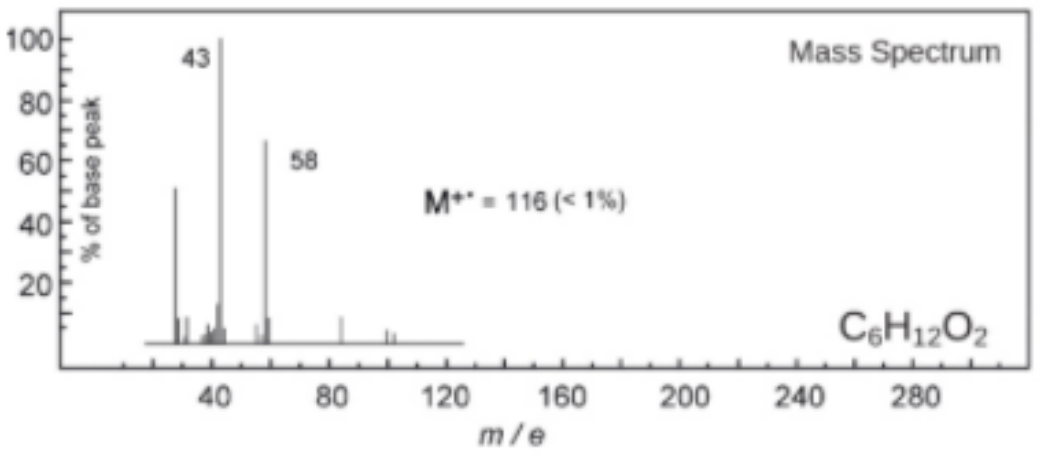

100
80
60
40
20
% of base peak
43
Mass Spectrum
M+·
88
C4H8O2
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
3.9
3.8
2.7
2.6
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 44

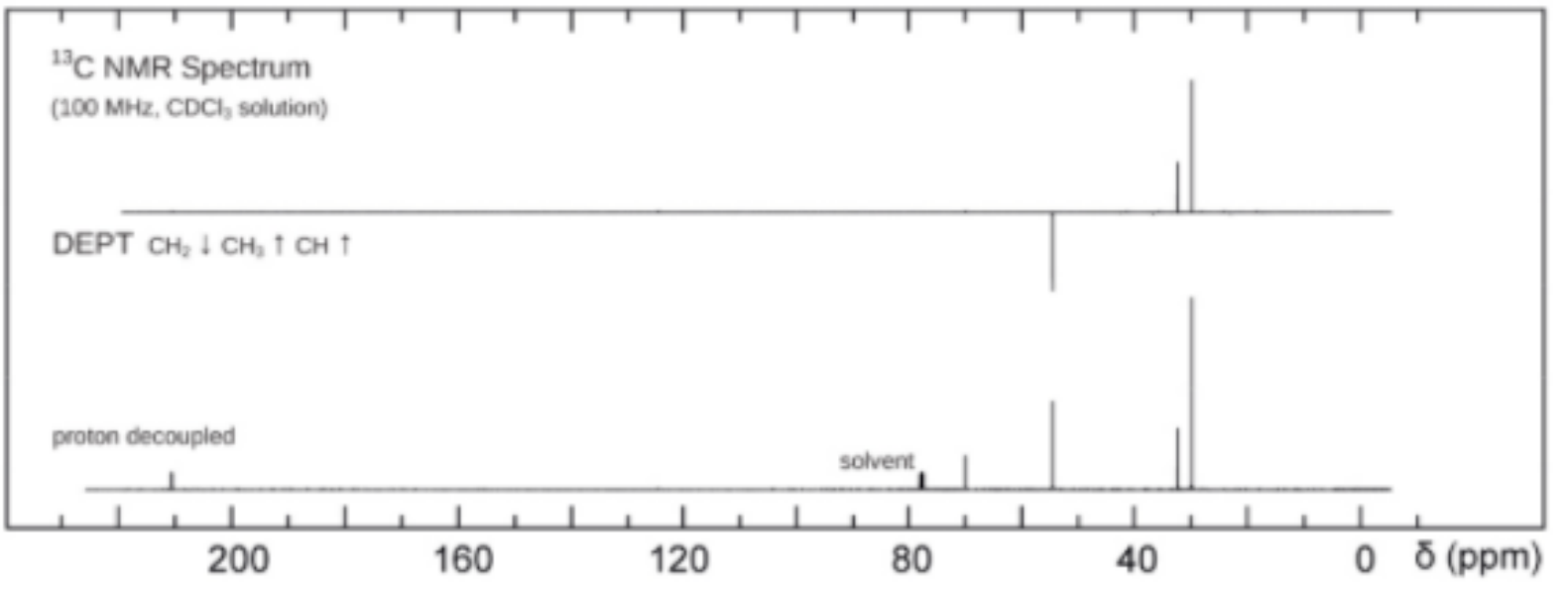


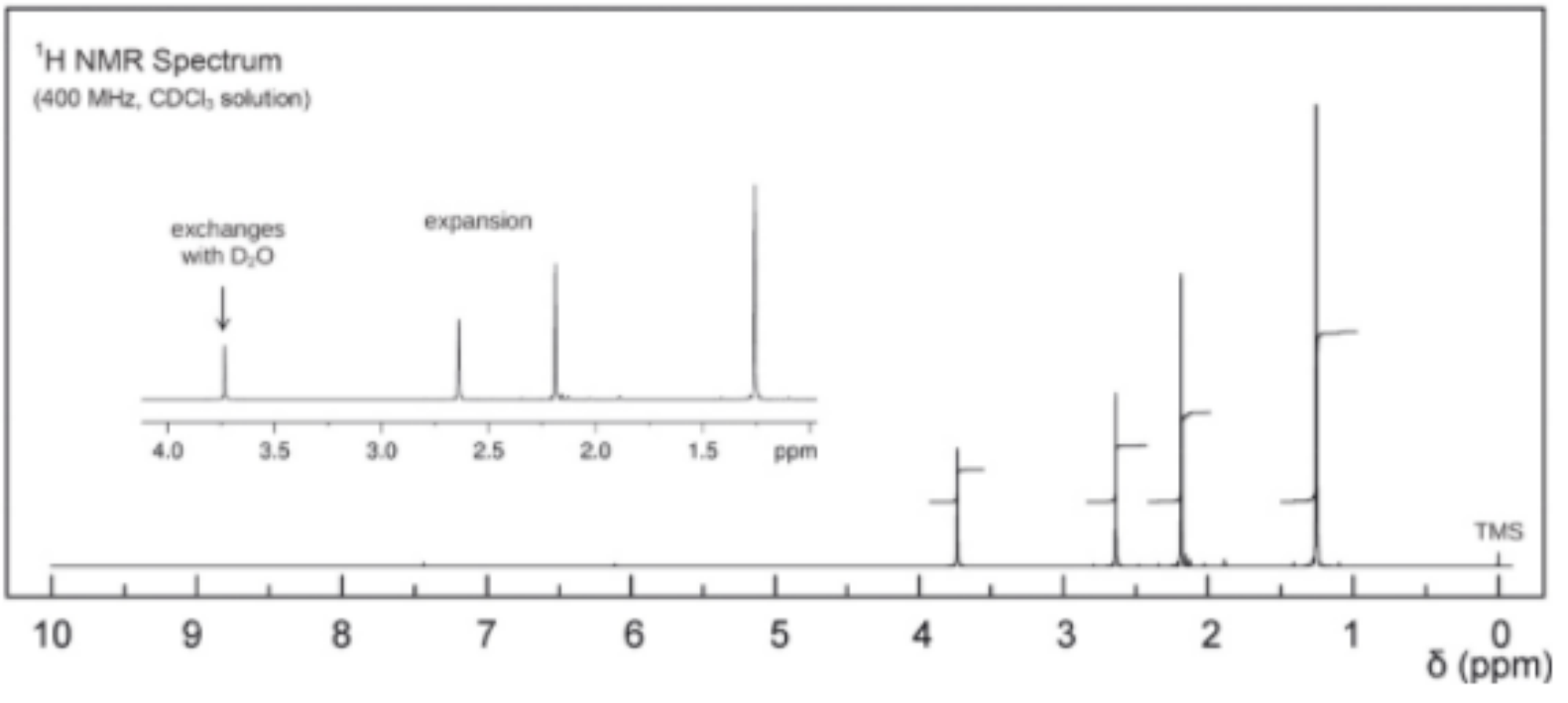


UV Spectrum

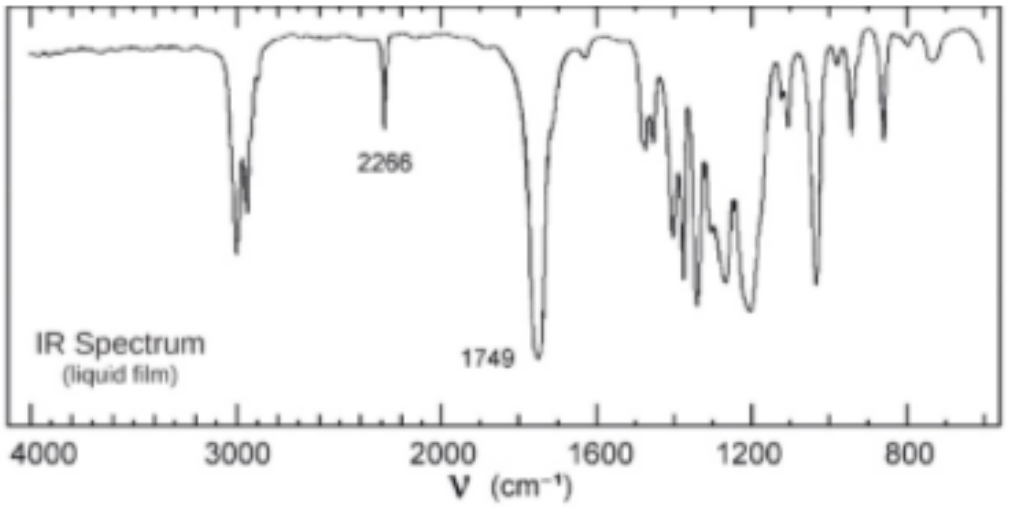
λ_{max} 283 nm ($\log_{10}\varepsilon$ 1.4)

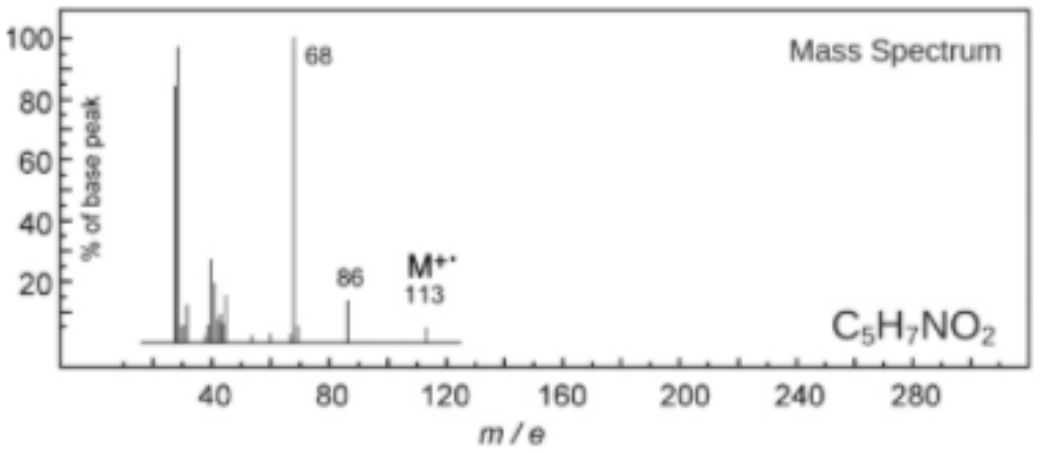
solvent: methanol



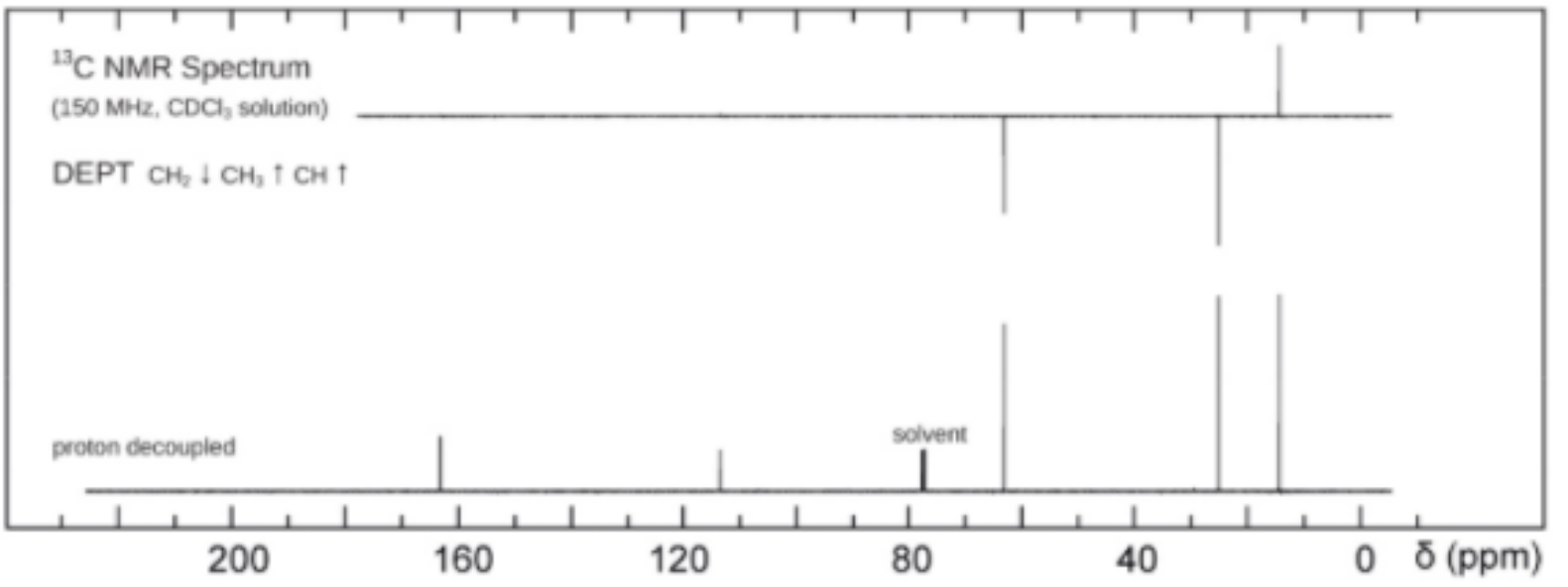


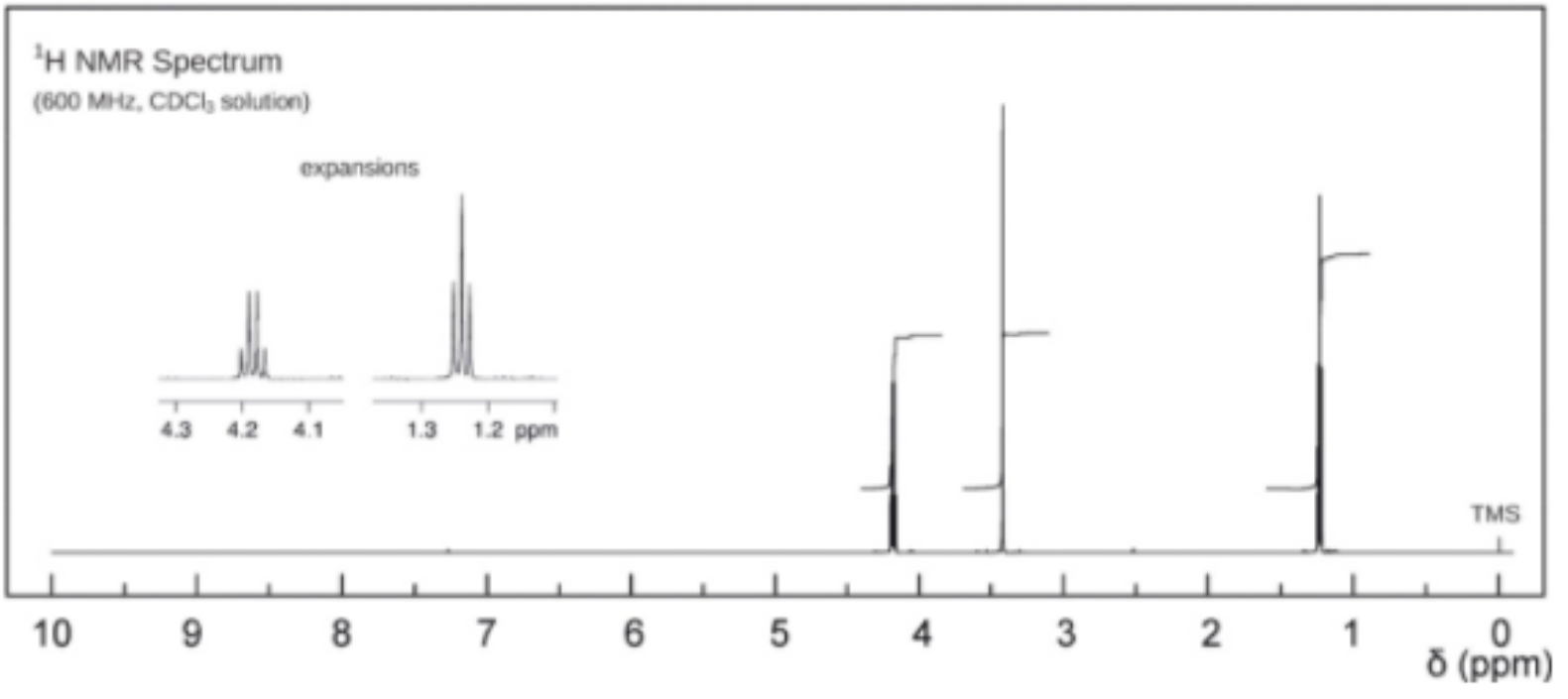
Problem 45

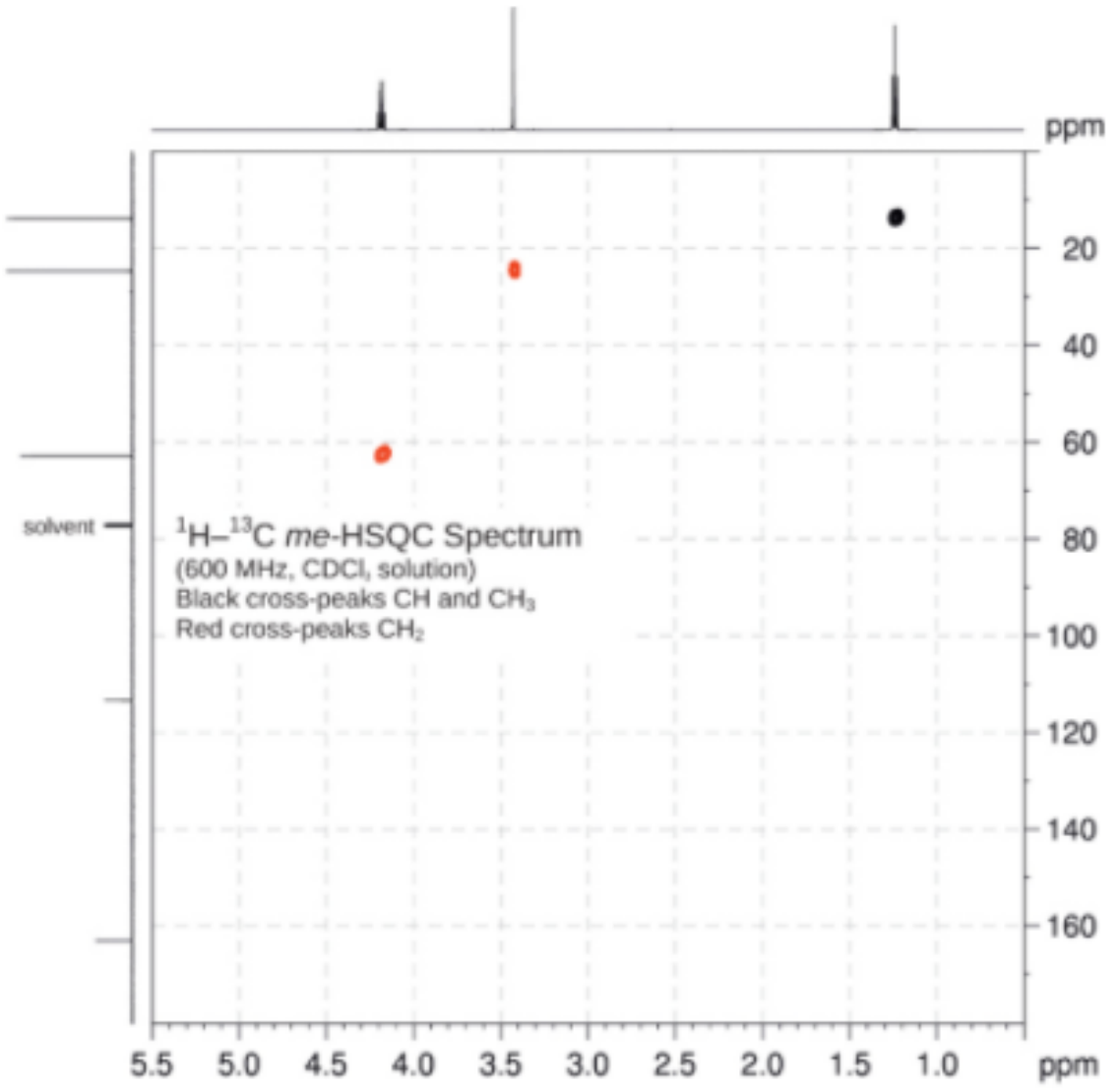


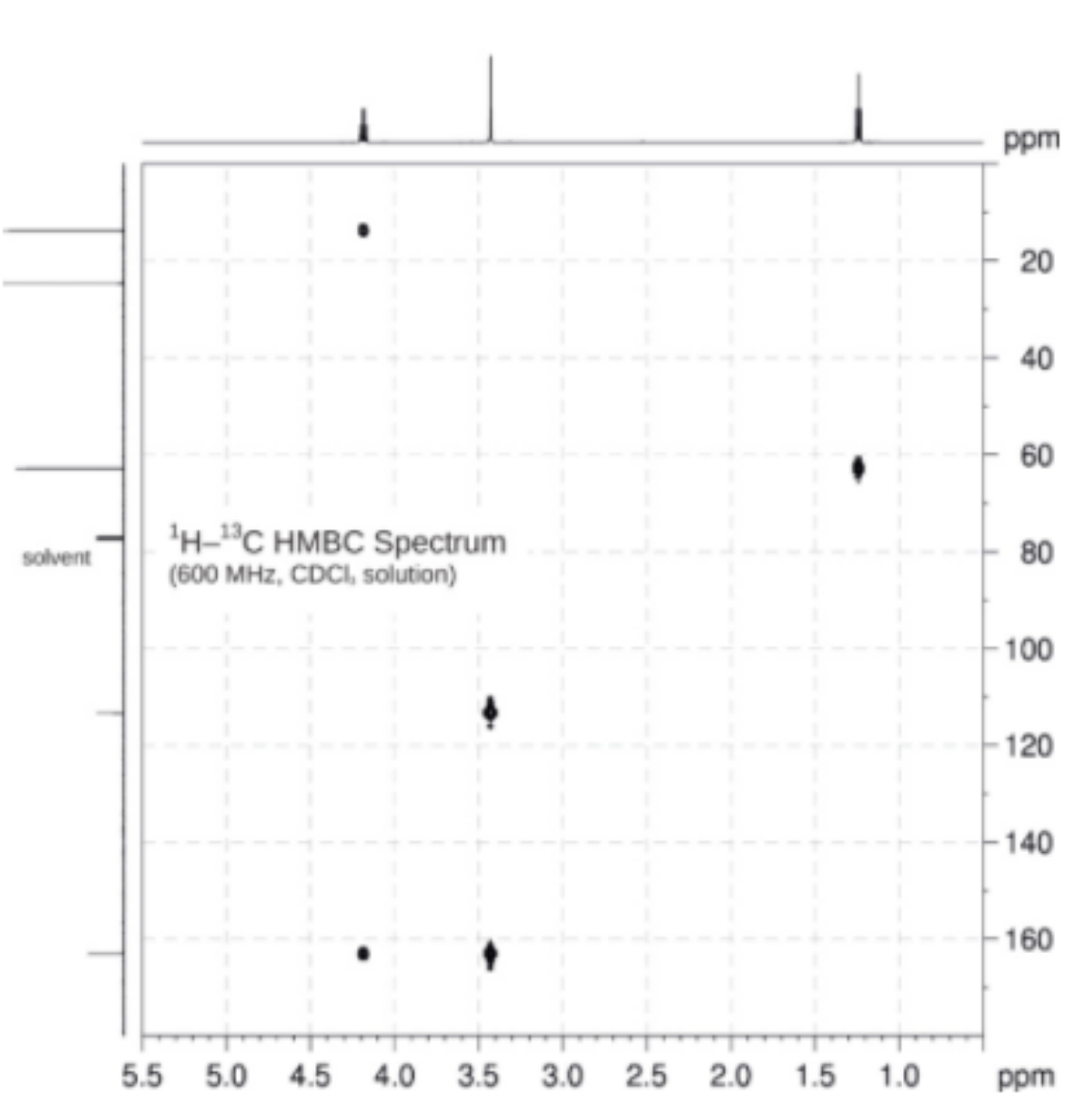


No significant UV absorption above 220 nm

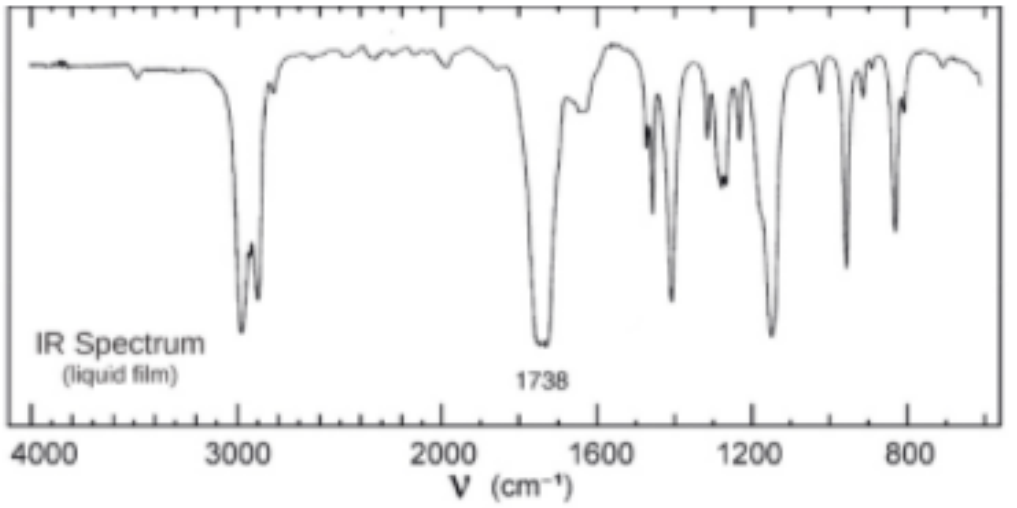


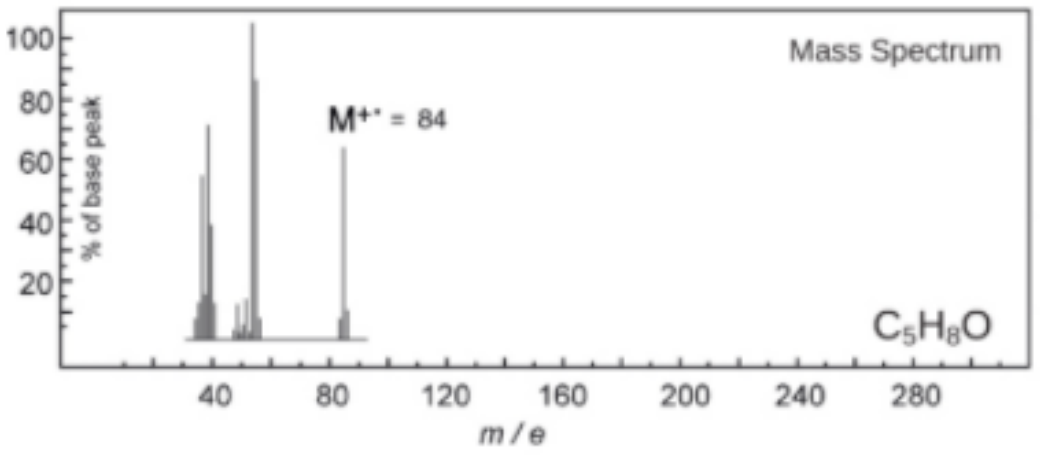



ppm
20
40
60
80
100
120
140
160
solvent
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, CDCl, solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

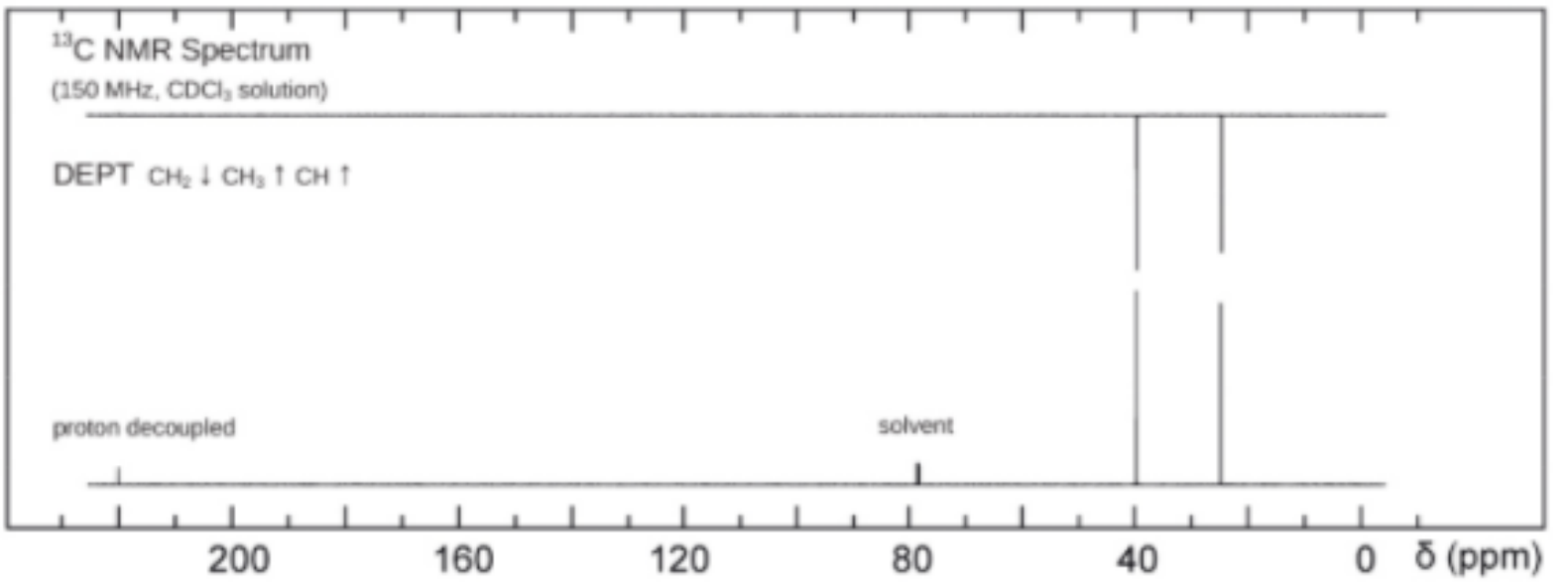

ppm
20
40
60
80
100
120
140
160
solvent
^{1}H–^{13}C HMBC Spectrum
(600 MHz, CDCl, solution)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

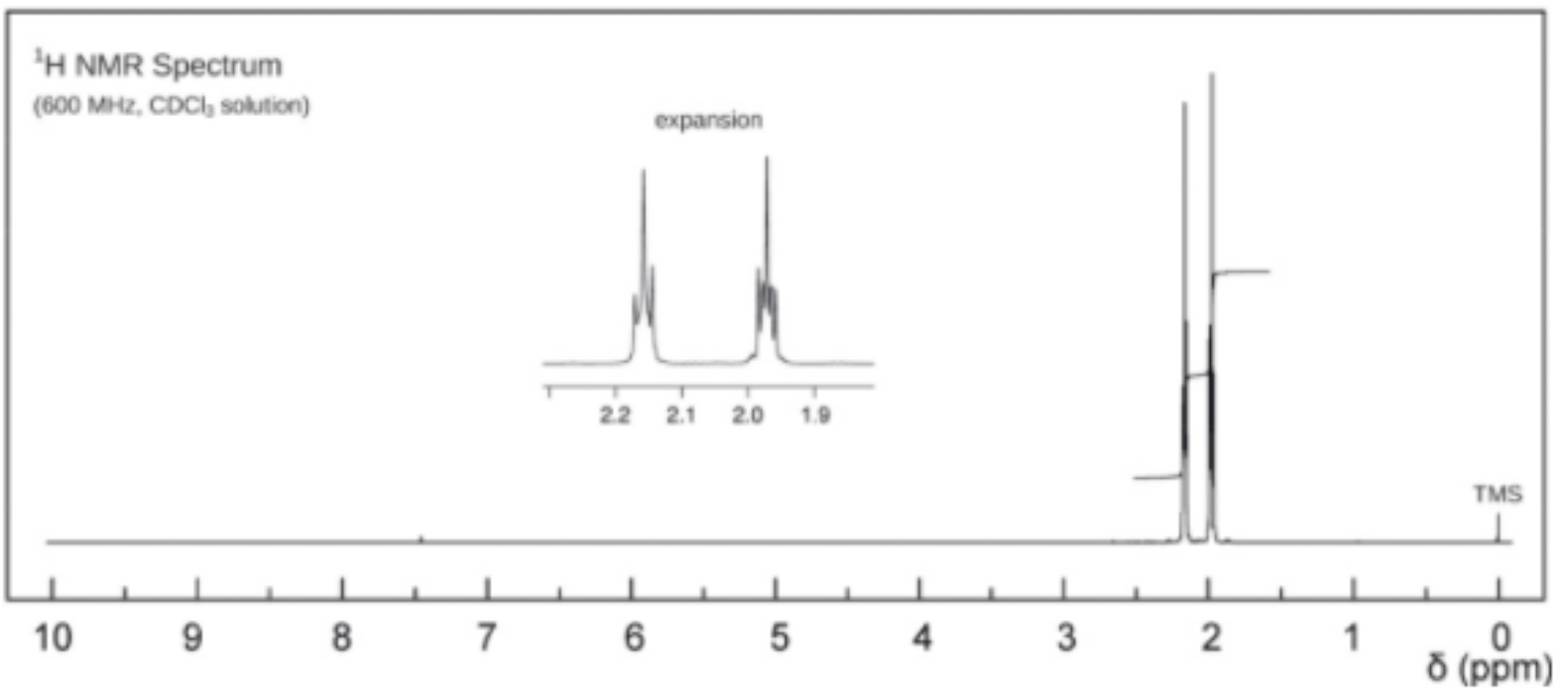
Problem 46

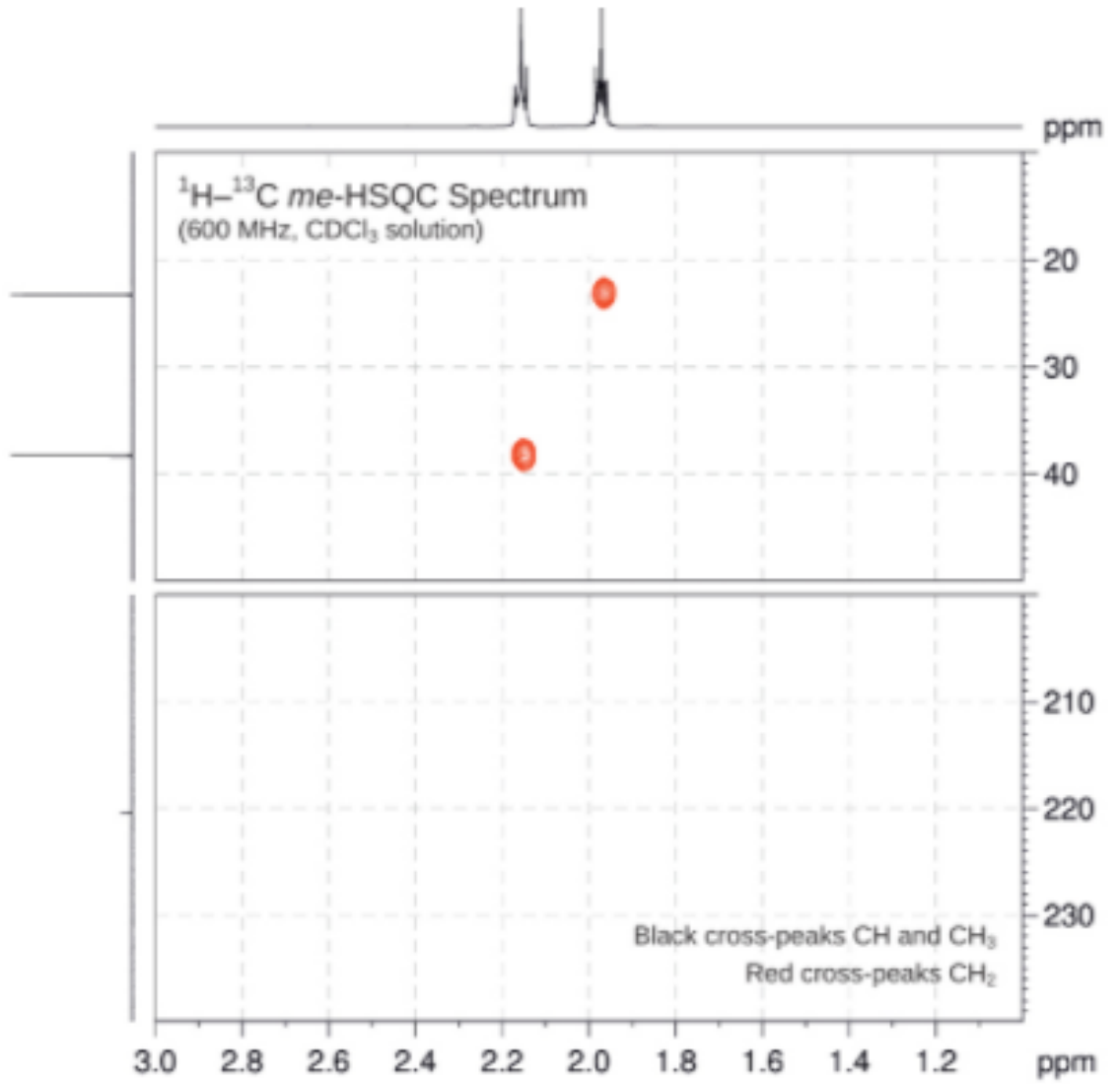


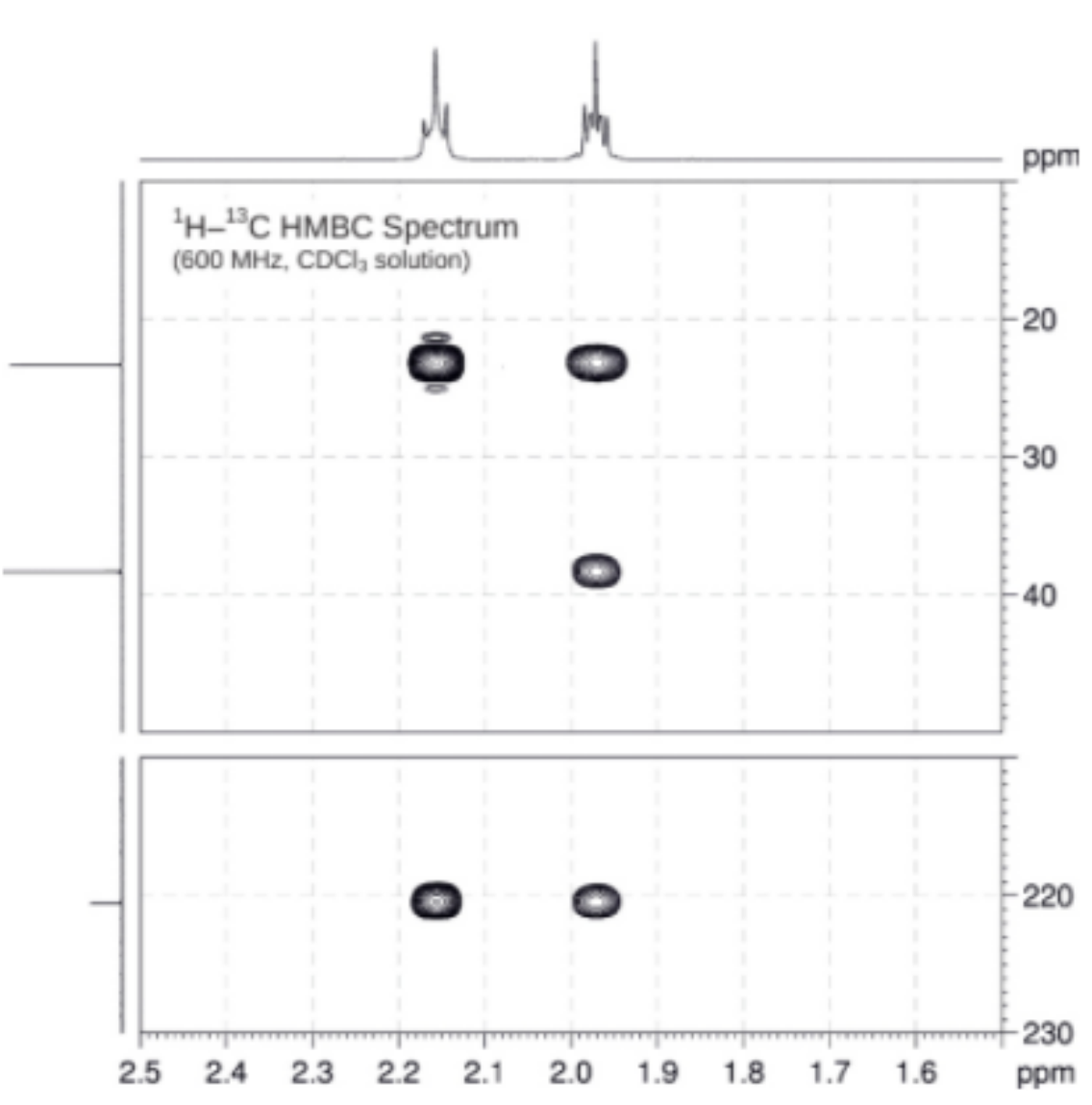


No significant UV absorption above 220 nm

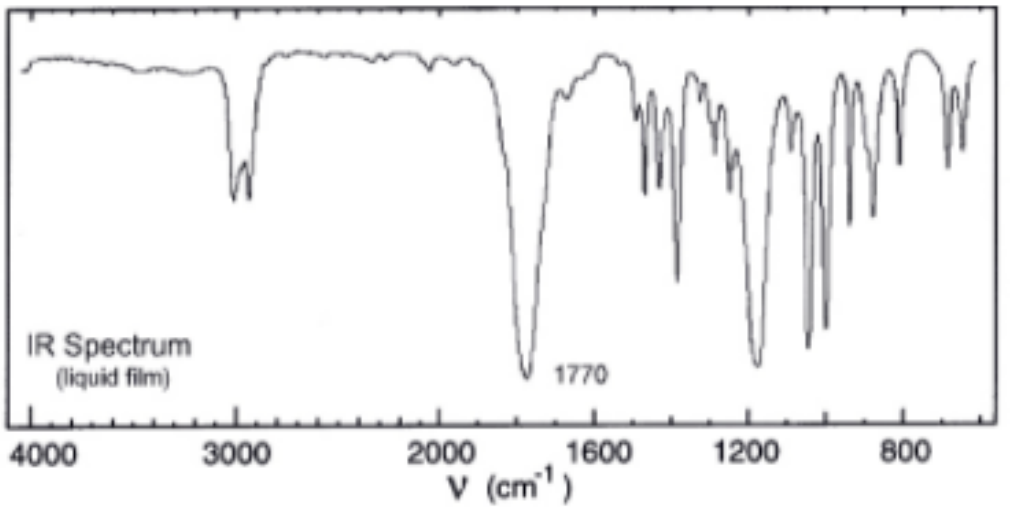


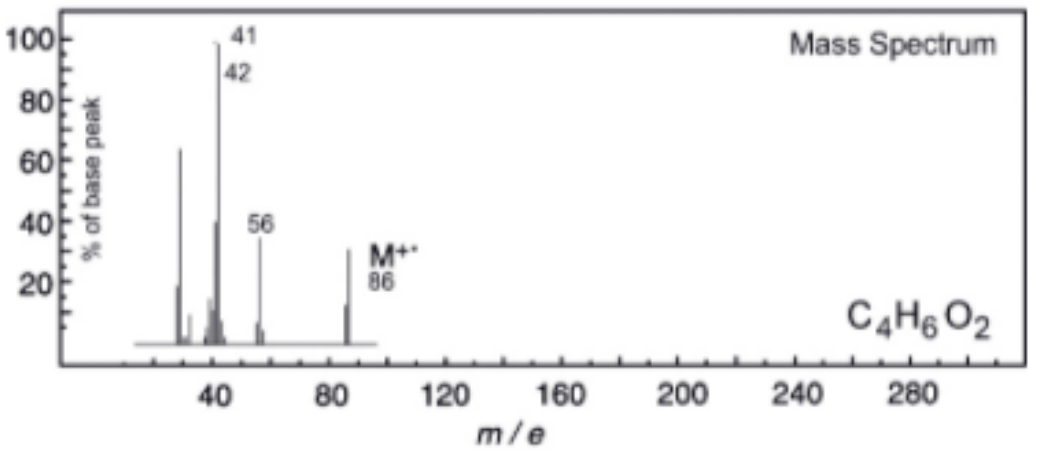



ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
20
30
40
210
220
230
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
ppm

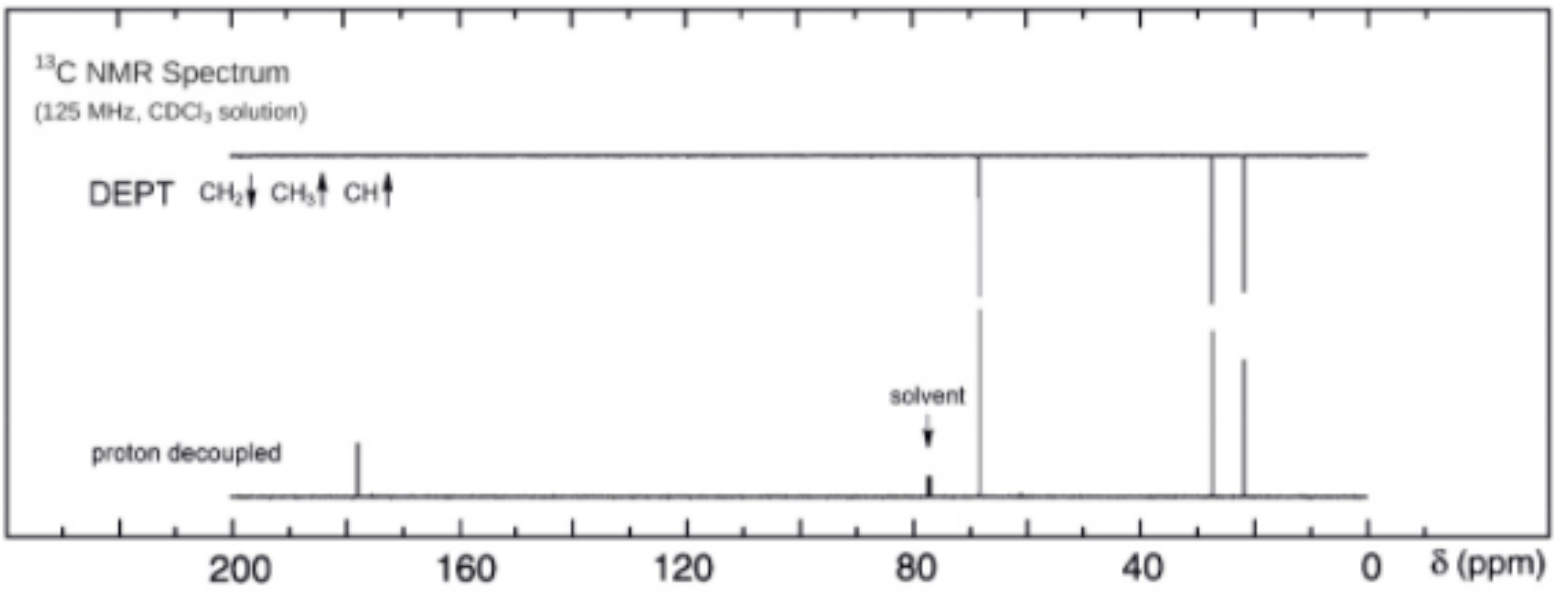

ppm
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)
20
30
40
220
230
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
ppm

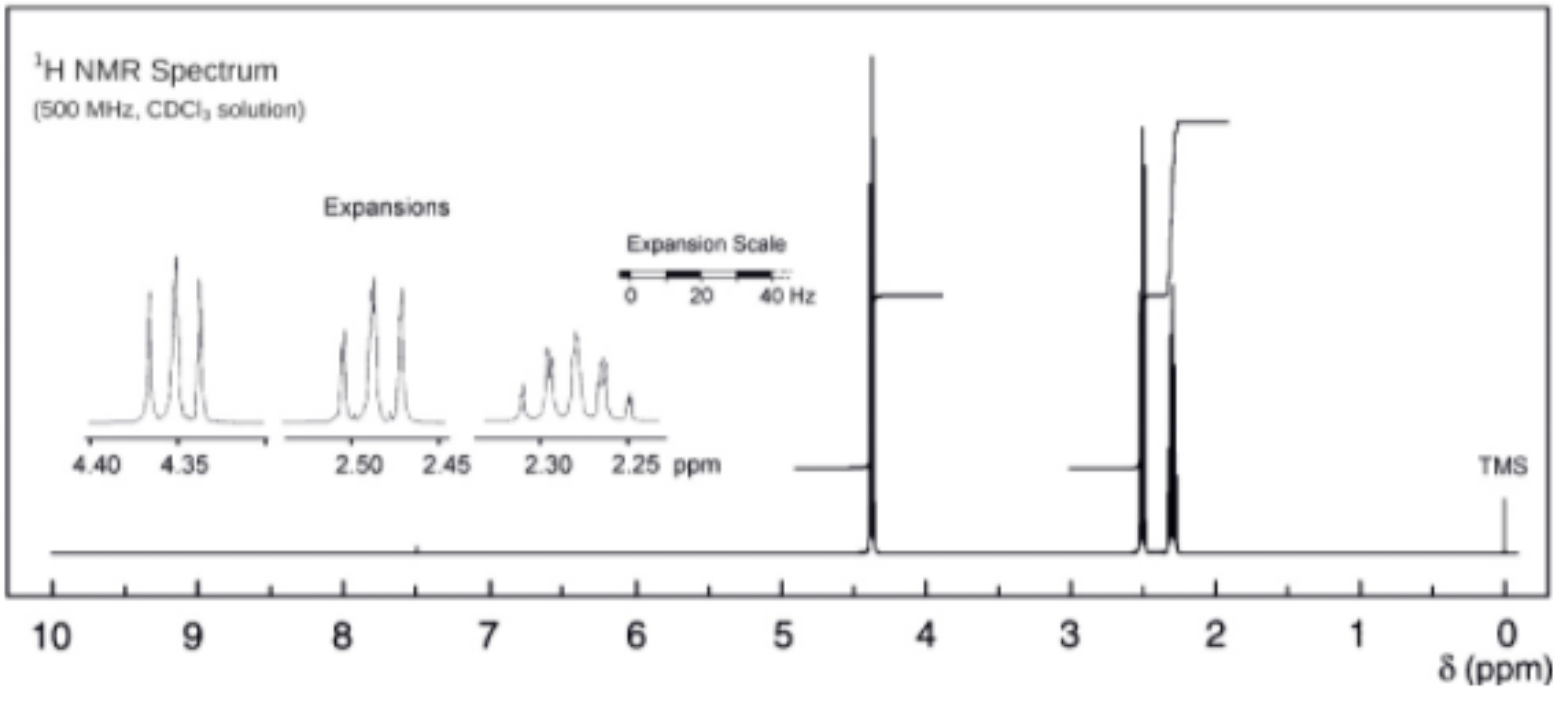
Problem 47

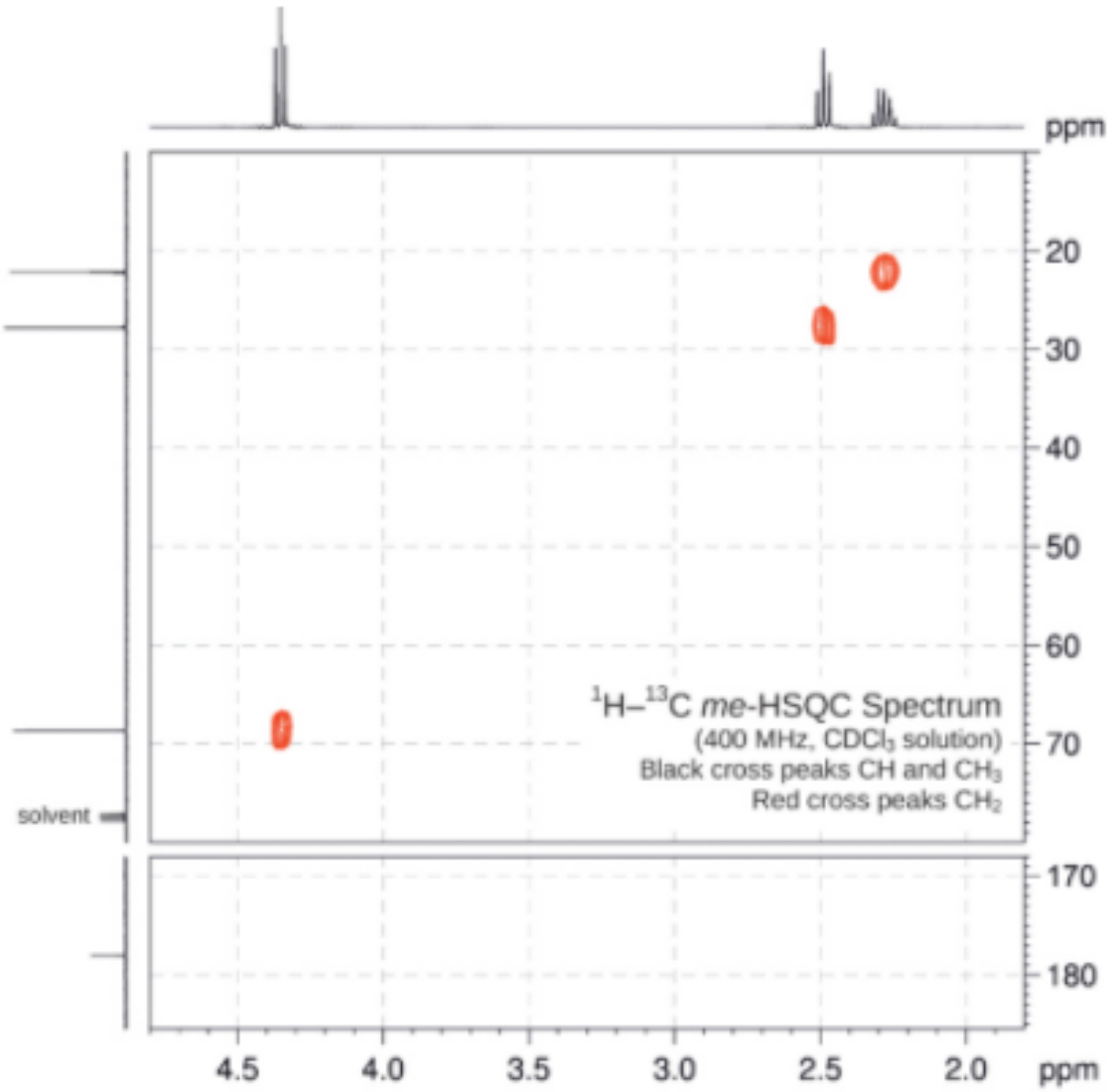




No significant UV absorption above 220 nm

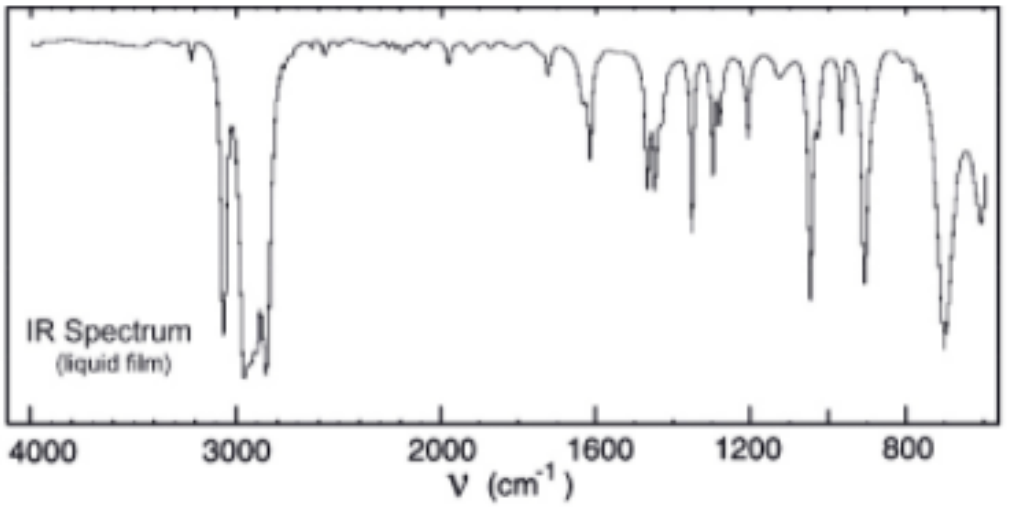


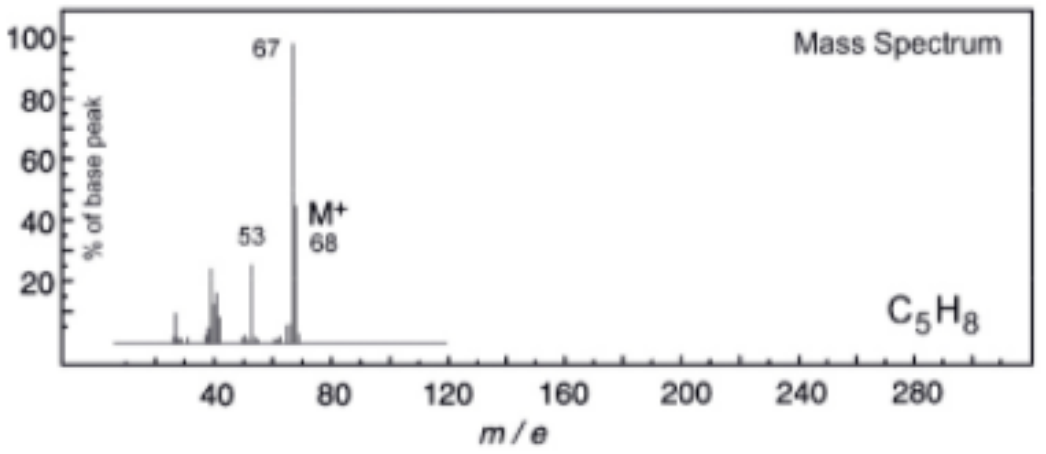



ppm
20
30
40
50
60
70
170
180
solvent
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross peaks CH and CH_3
Red cross peaks CH_2
4.5
4.0
3.5
3.0
2.5
2.0
ppm

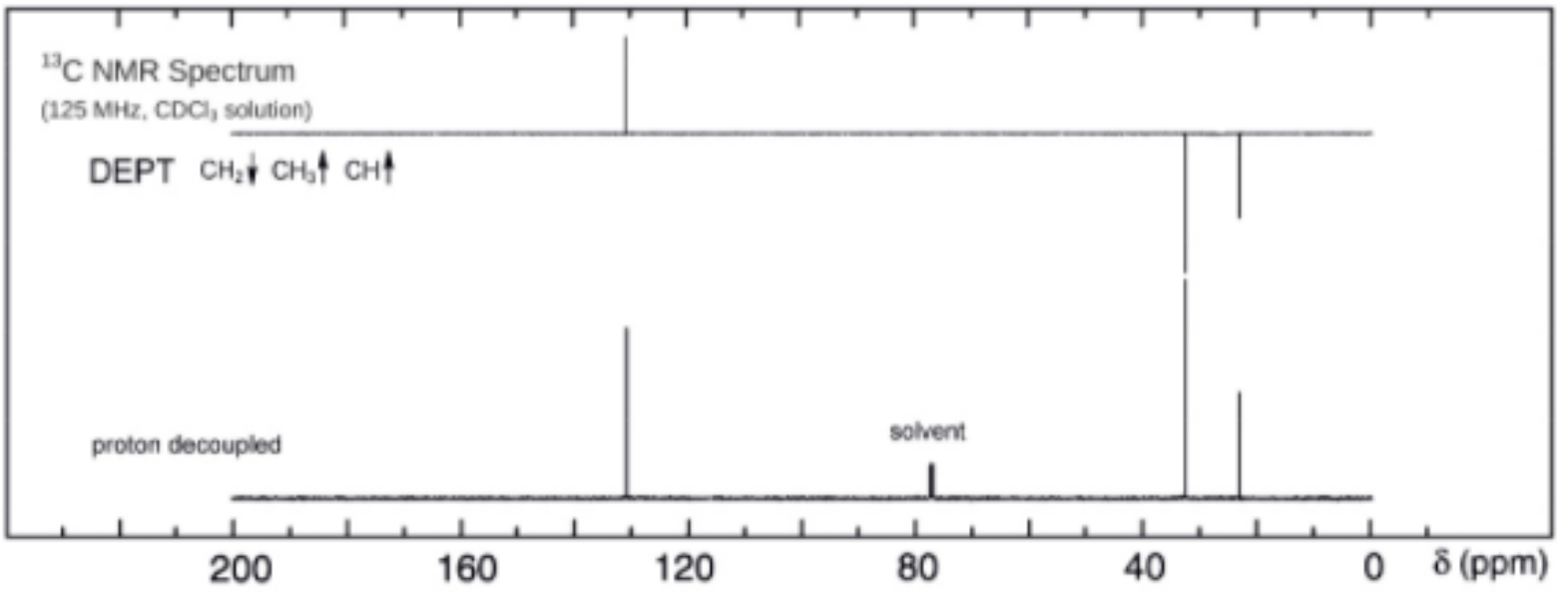
ppm
2.0
2.5
3.0
3.5
4.0
4.5
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
4.5
4.0
3.5
3.0
2.5
2.0
ppm

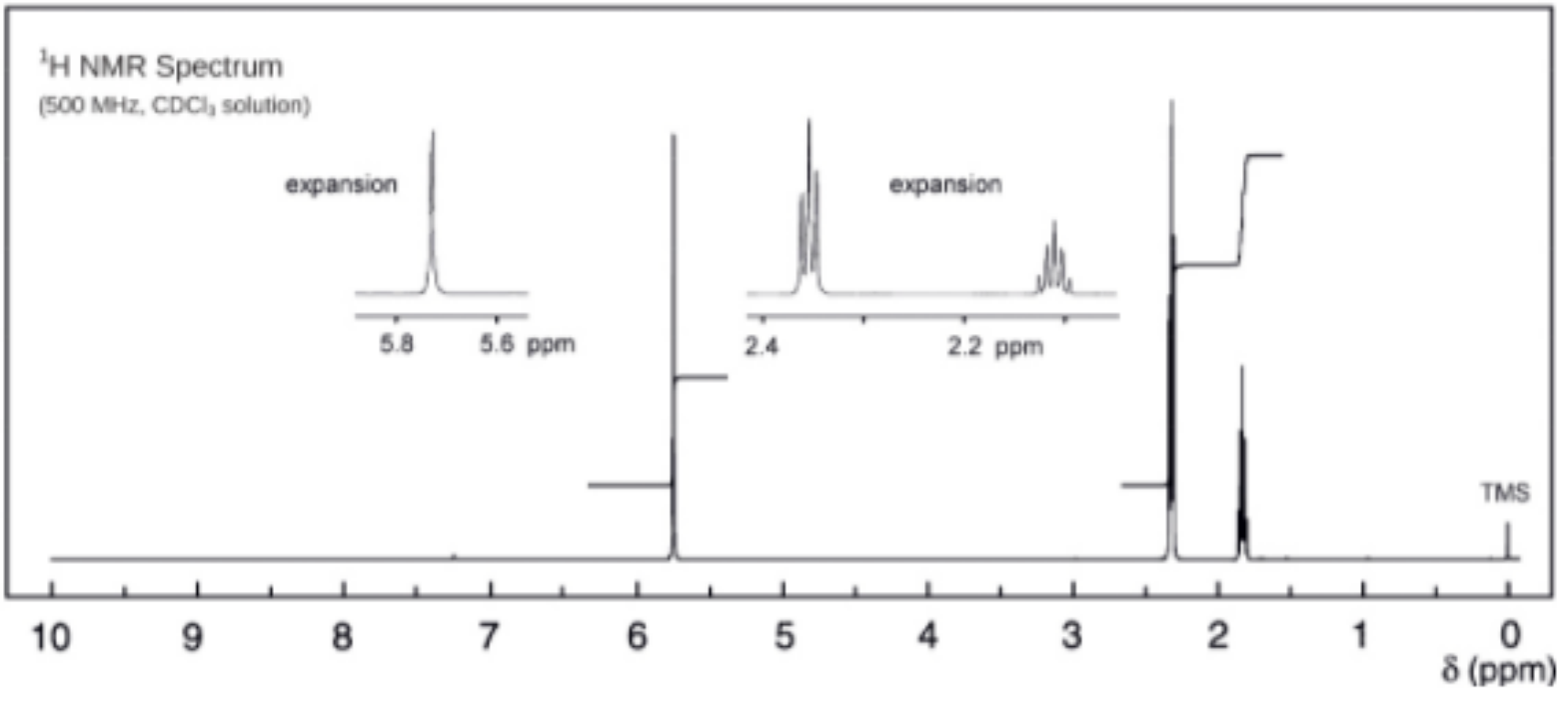
Problem 48



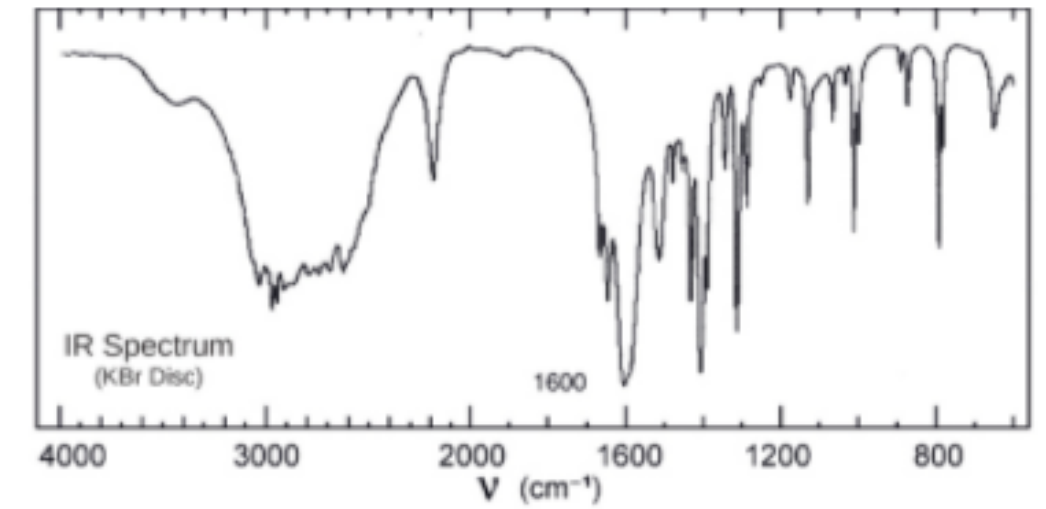


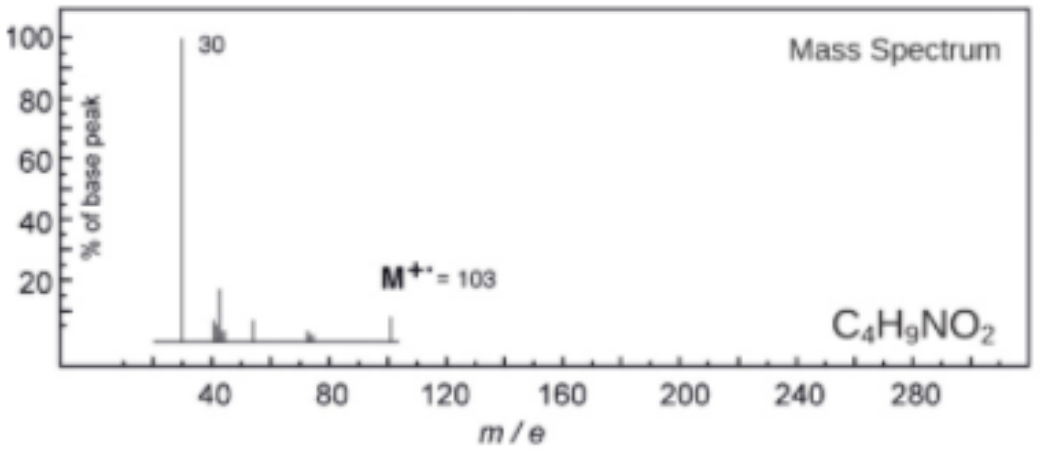
No significant UV absorption above 220 nm



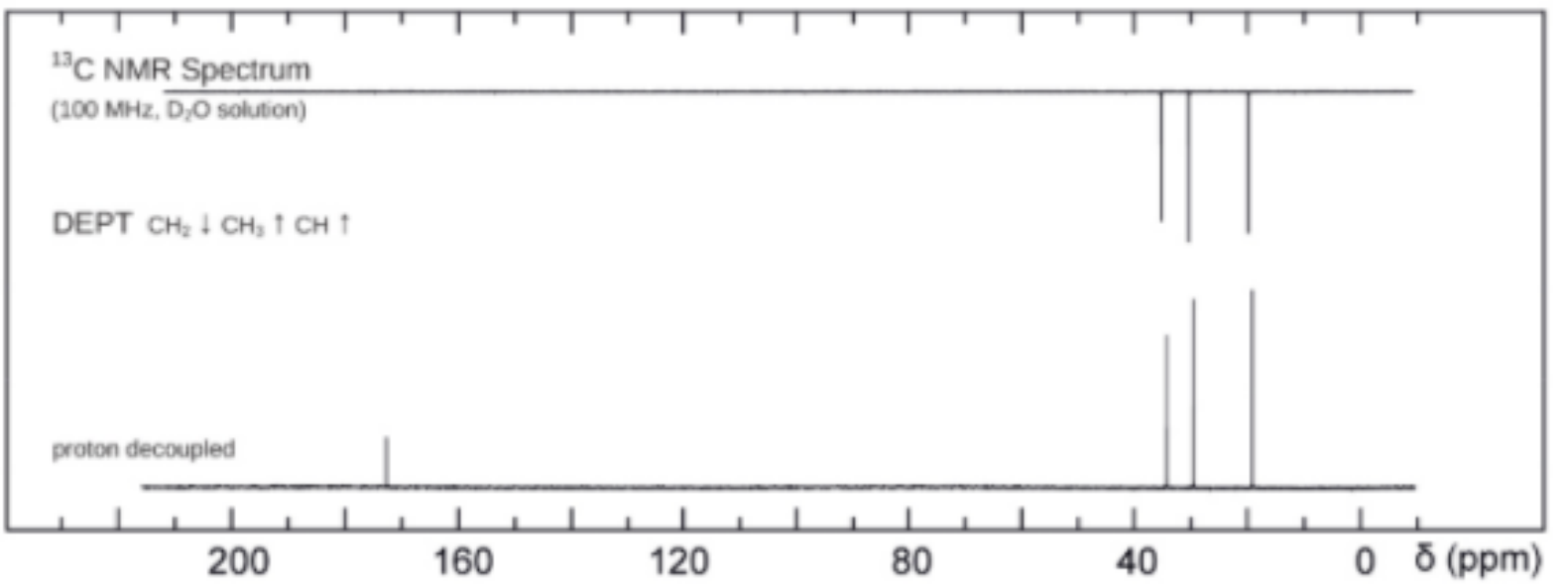


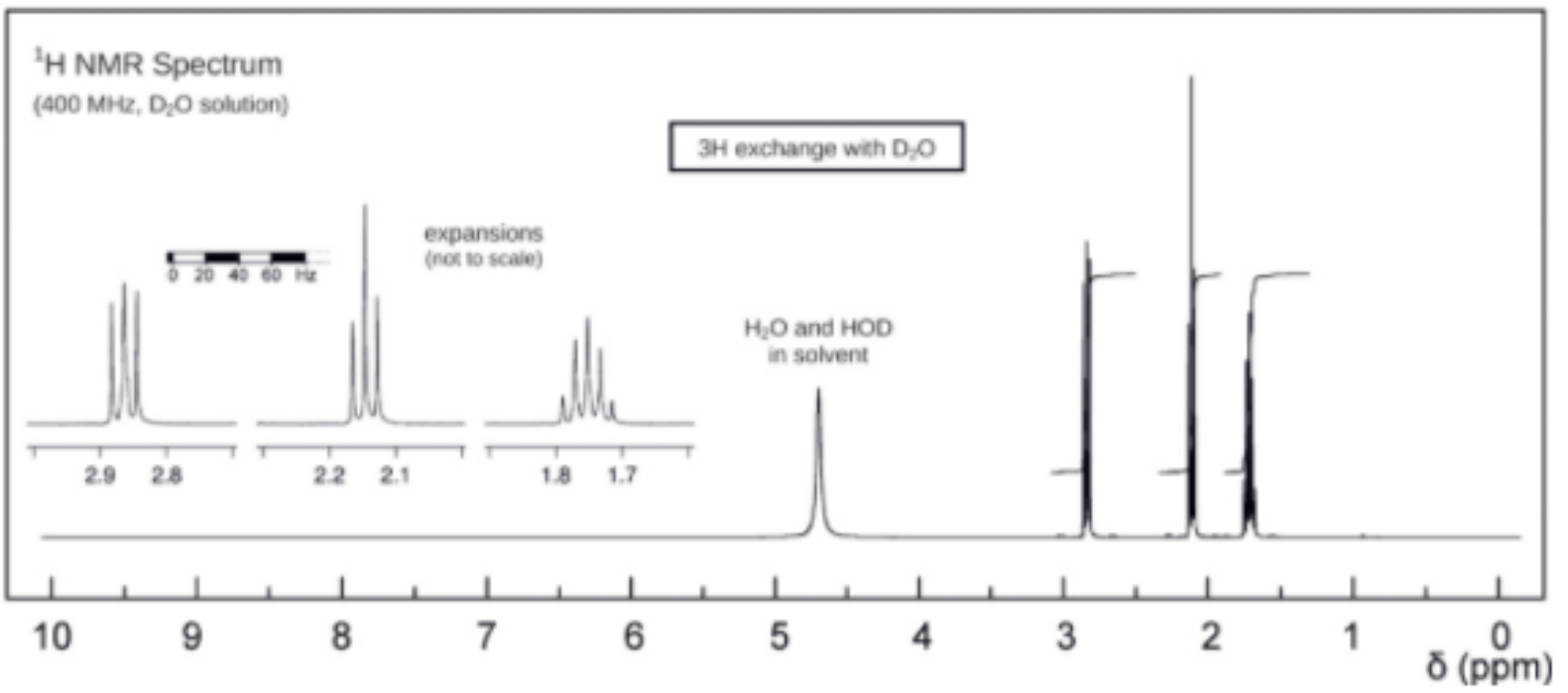
Problem 49



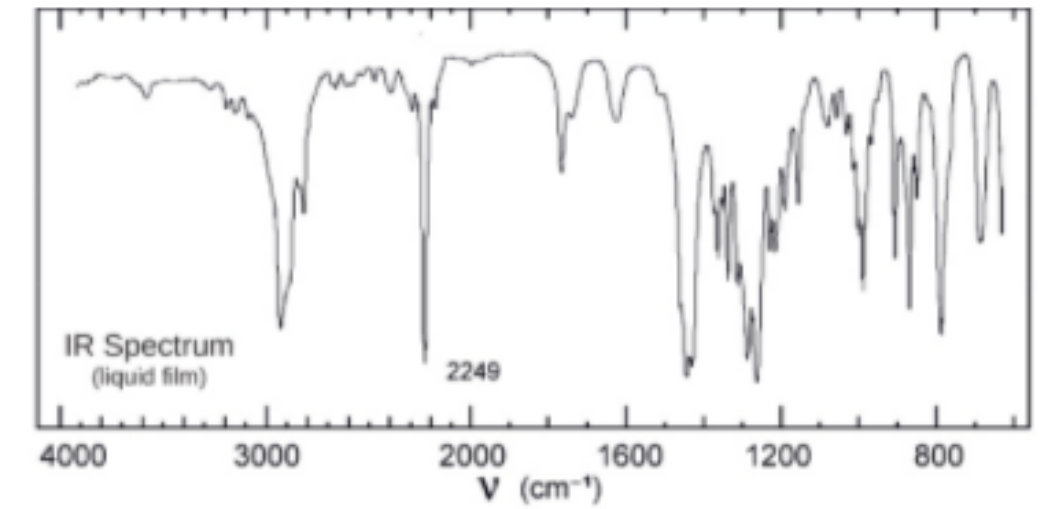


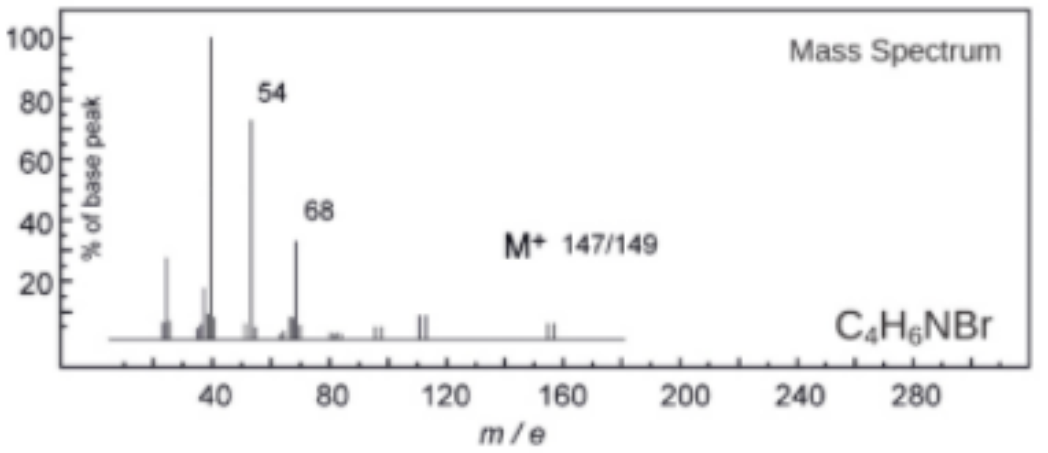
No significant UV absorption above 220 nm



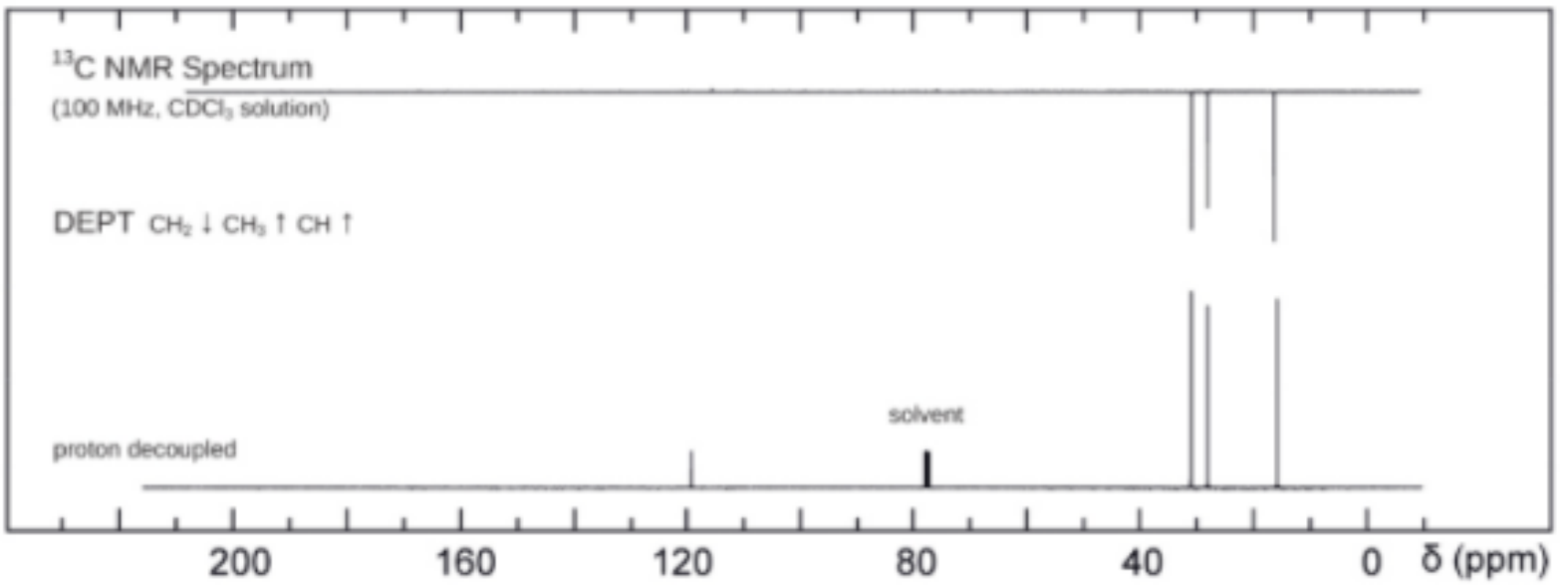


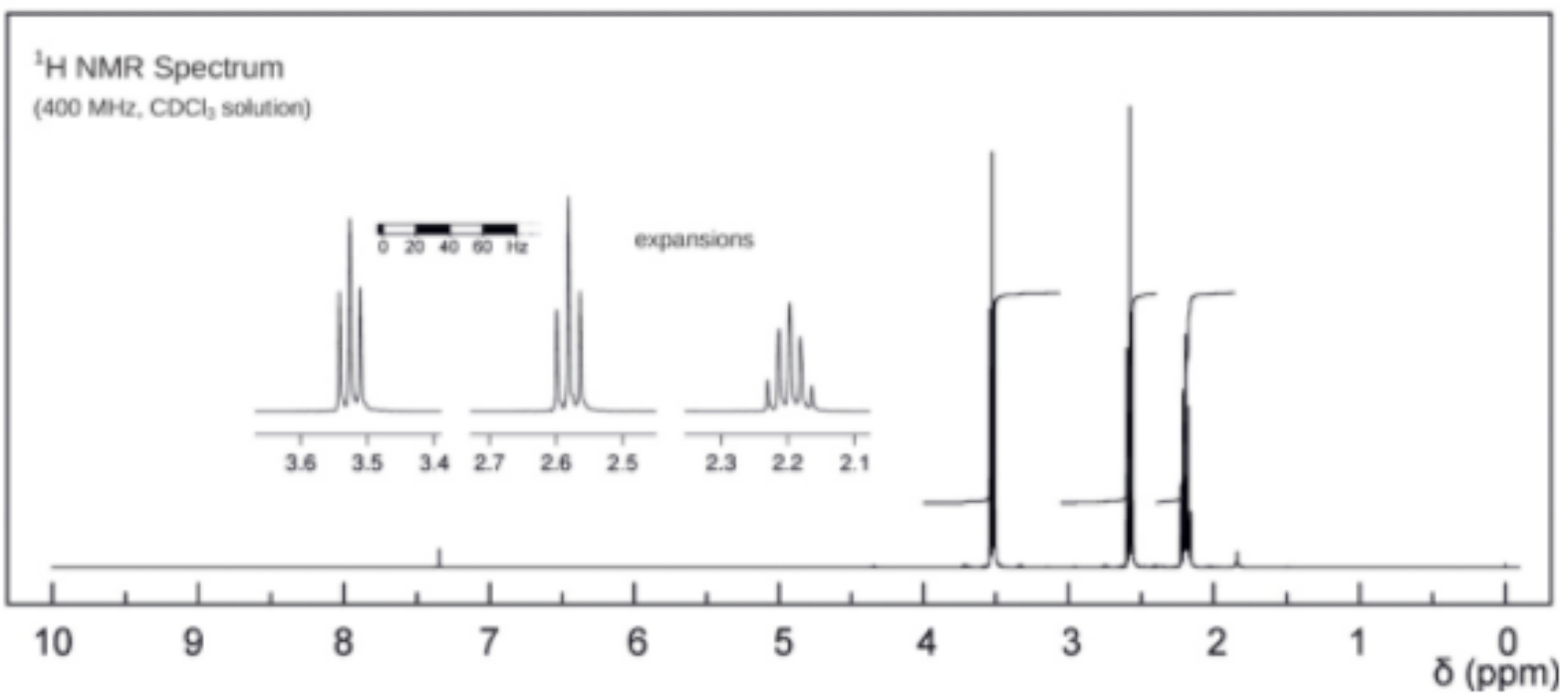
Problem 50

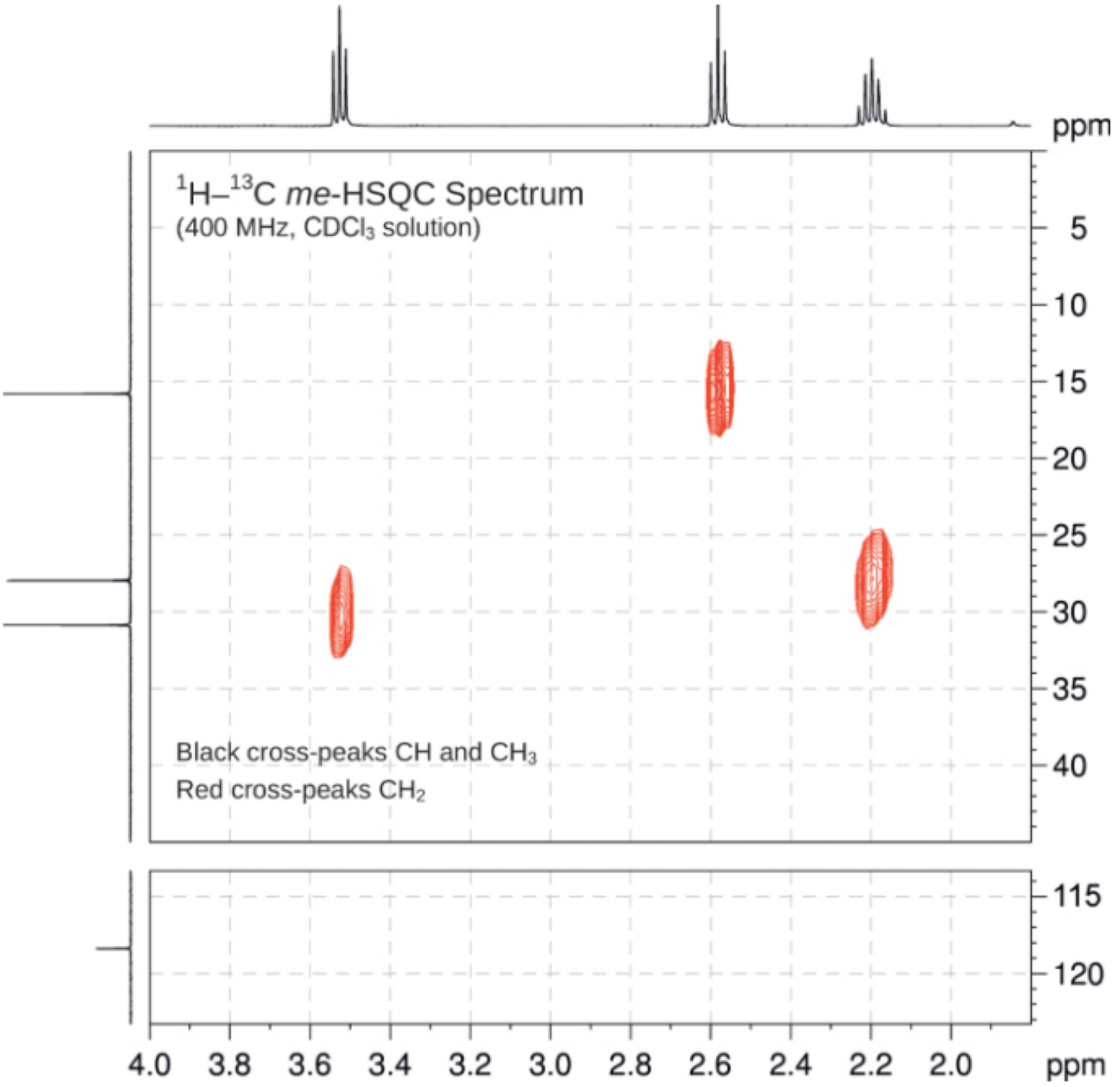




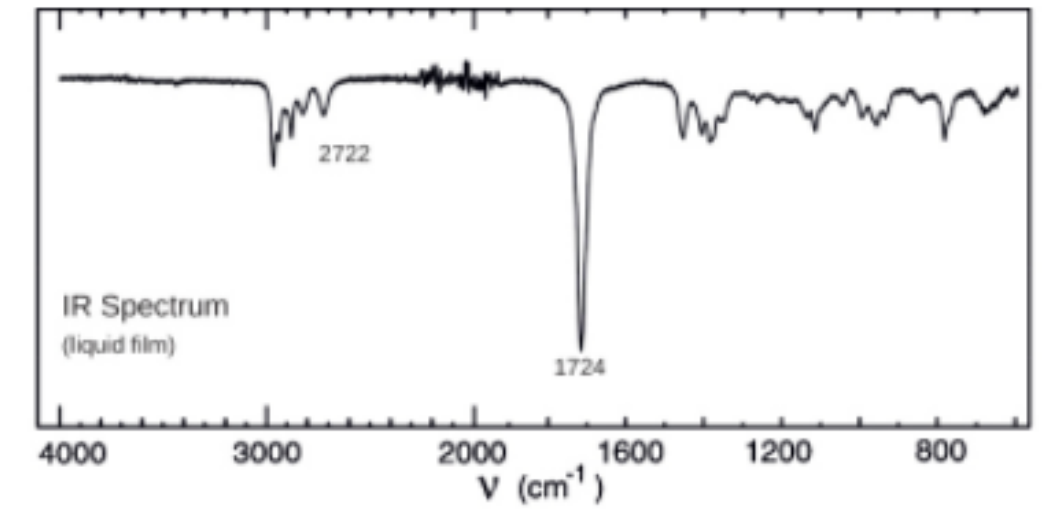
No significant UV absorption above 220 nm

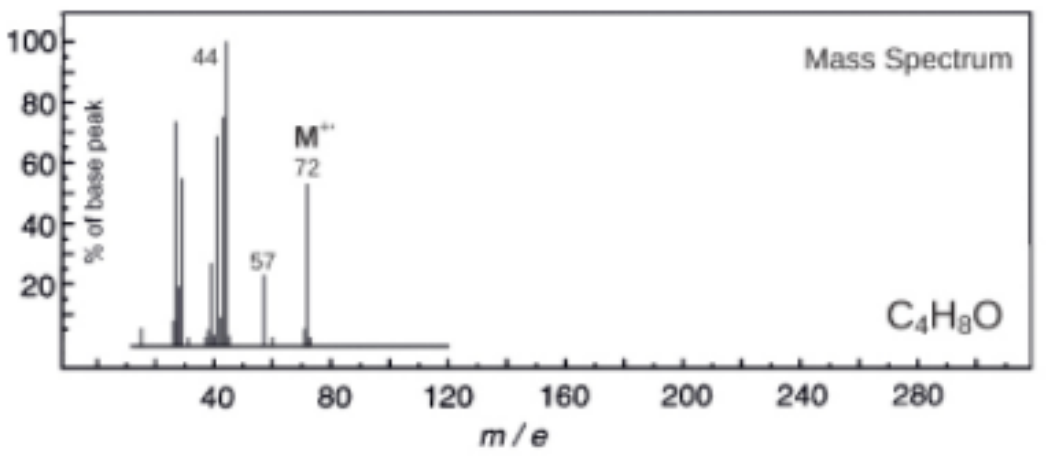


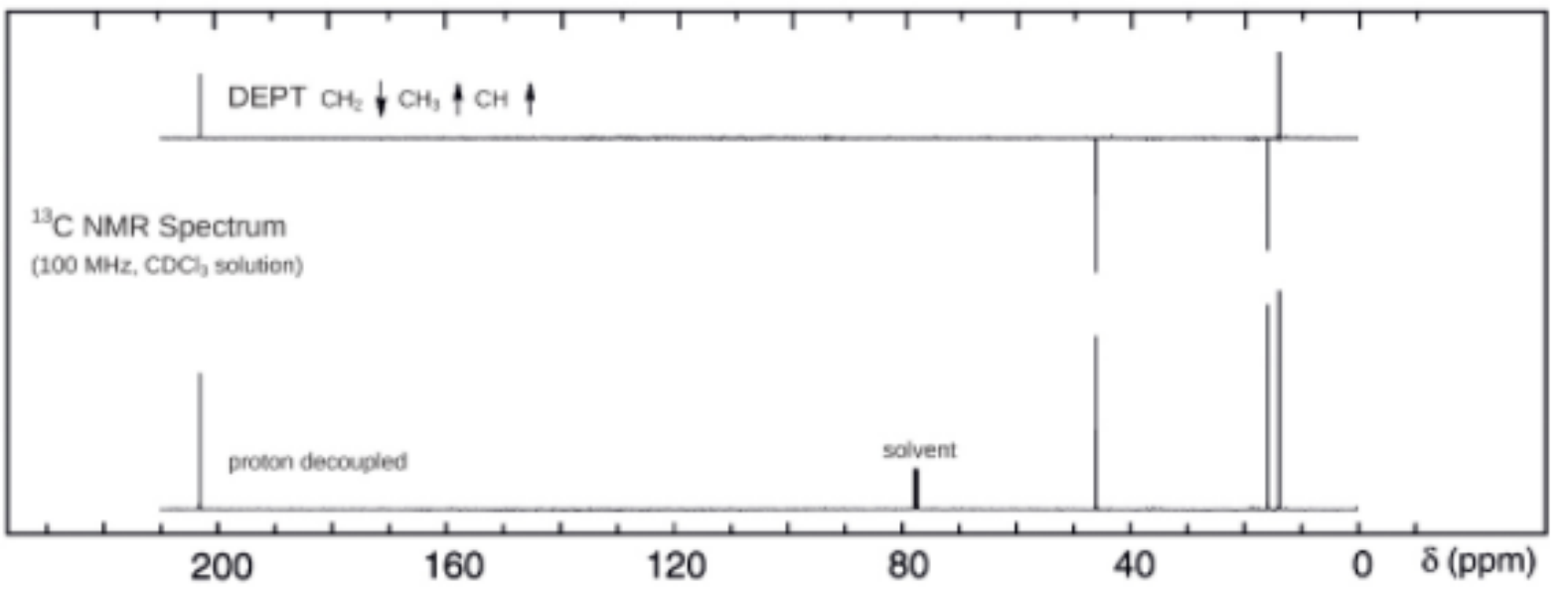


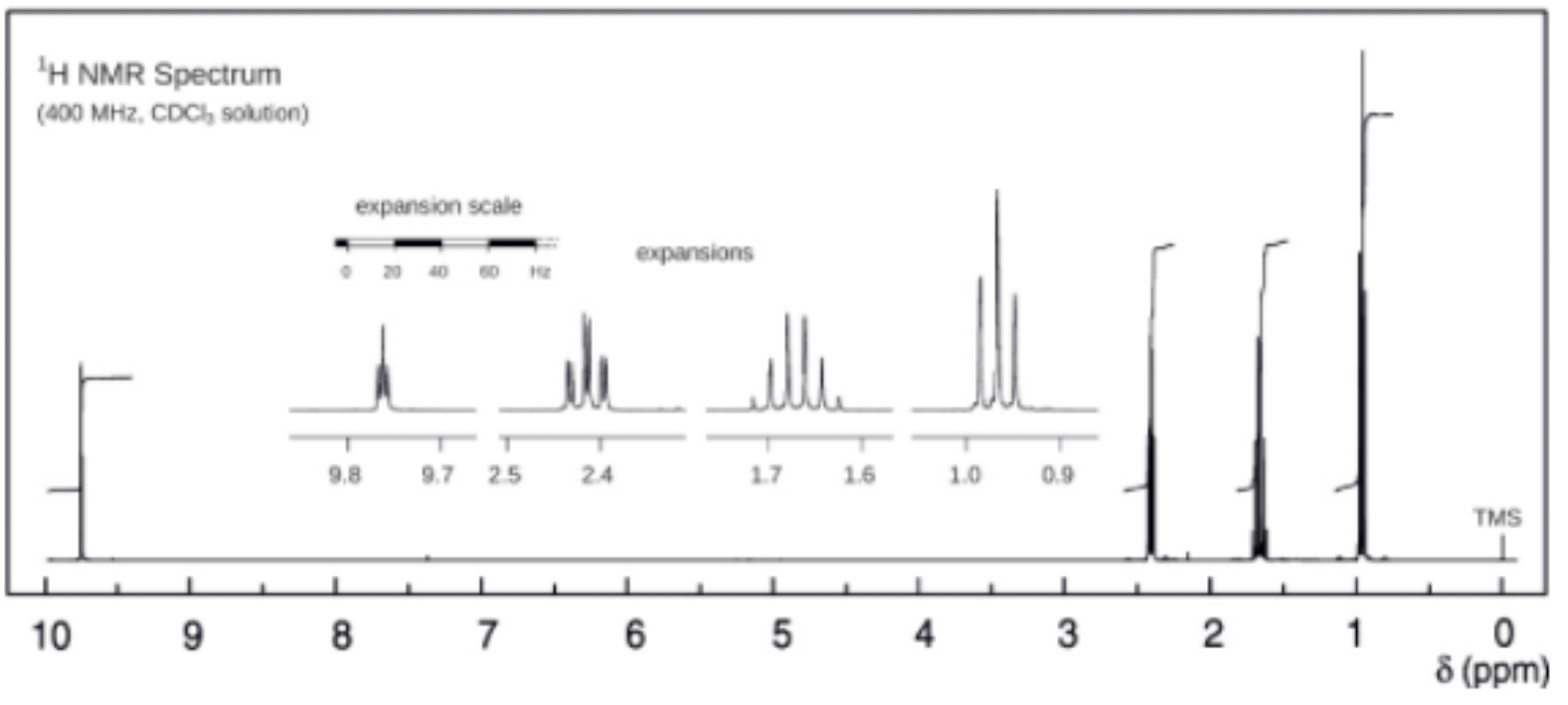

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
5
10
15
20
25
30
35
40
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
115
120
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
ppm

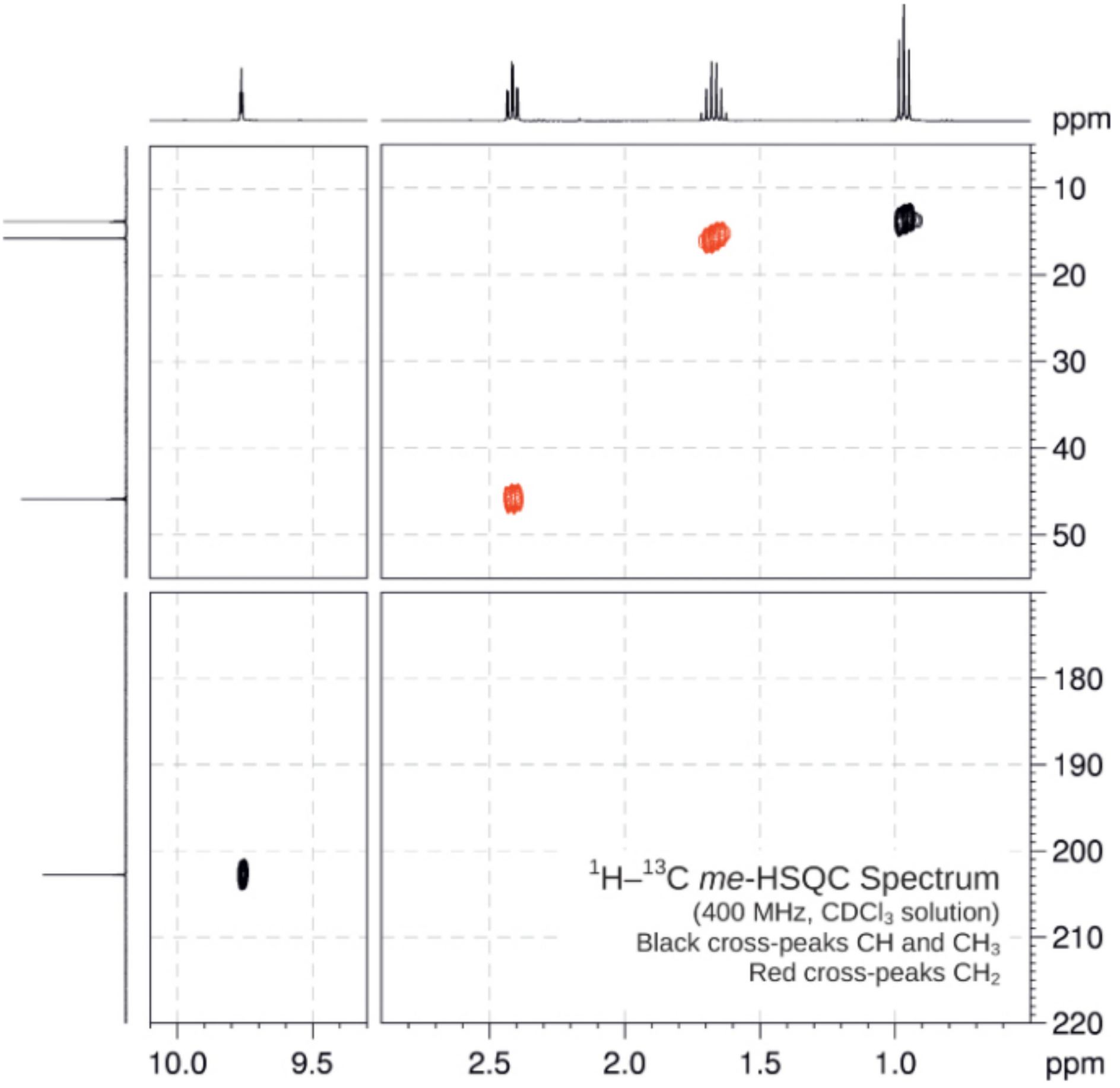
Problem 51


IR Spectrum
(liquid film)
2722
1724
4000
3000
2000
1600
1200
800
ν (cm-1)

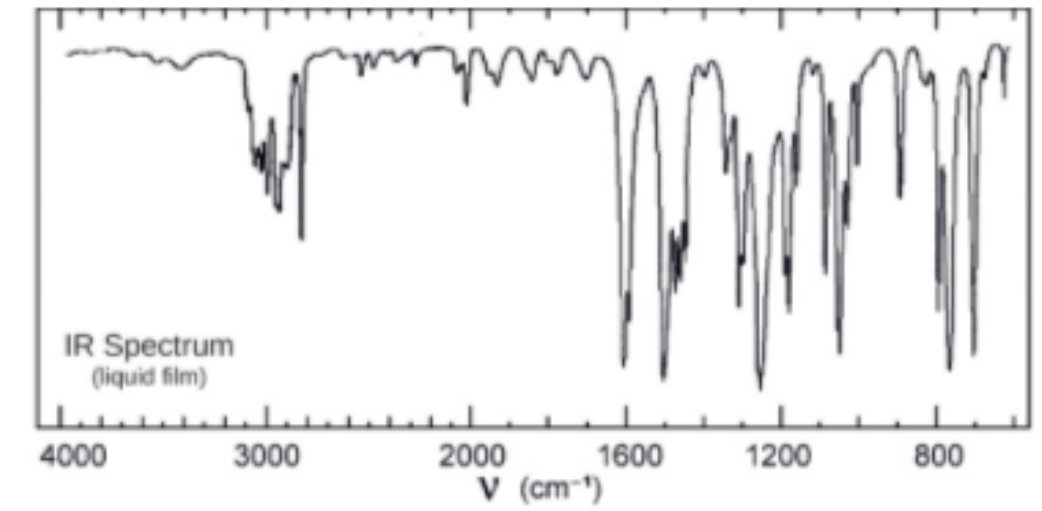

Mass Spectrum
% of base peak
100
80
60
40
20
44
M+·
72
57
C4H8O
40
80
120
160
200
240
280
m/e

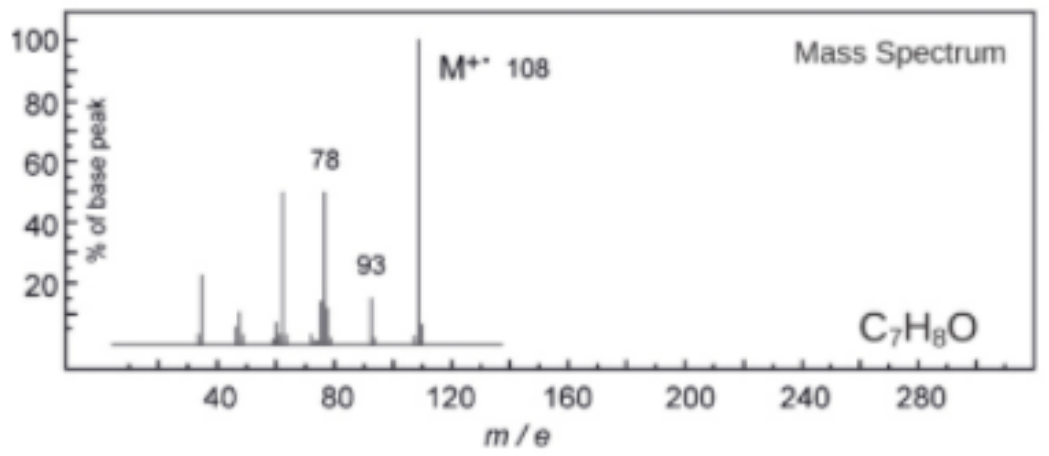

DEPT CH2 CH3 CH
13C NMR Spectrum
(100 MHz, CDCl3 solution)
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion scale
0 20 40 60 Hz
expansions
9.8
9.7
2.5
2.4
1.7
1.6
1.0
0.9
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
10
20
30
40
50
180
190
200
210
220
10.0
9.5
2.5
2.0
1.5
1.0
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

Problem 52

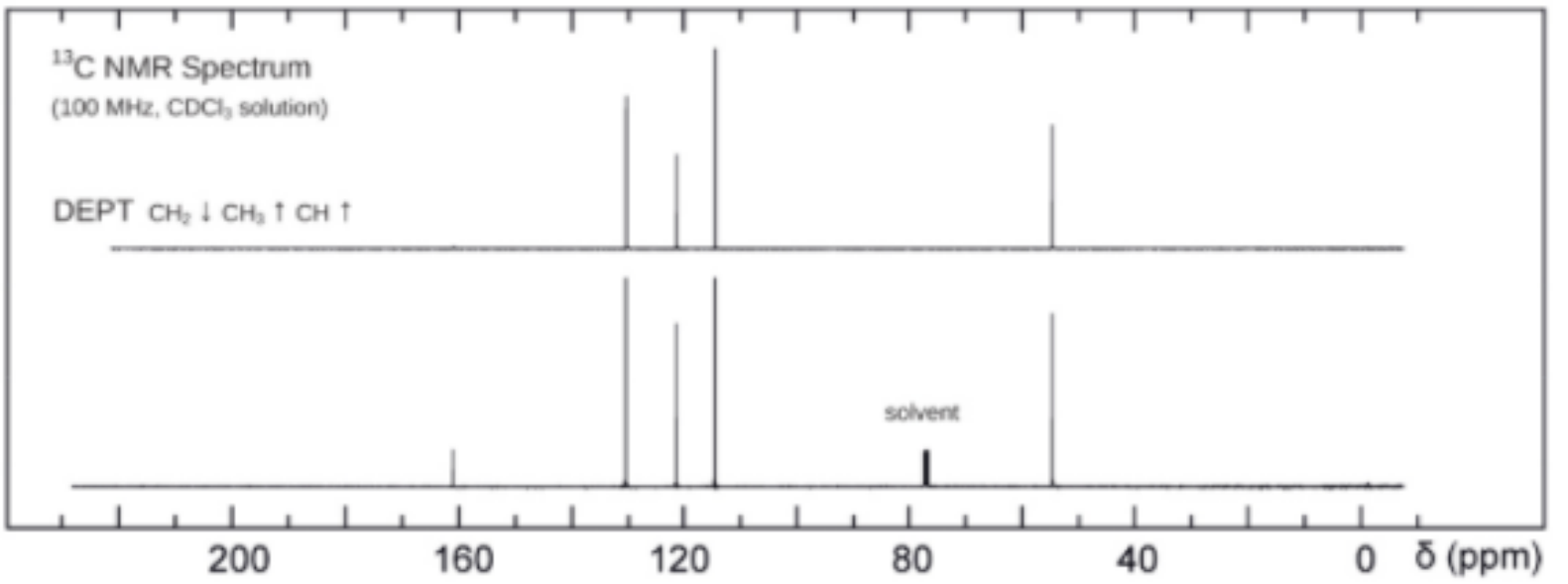


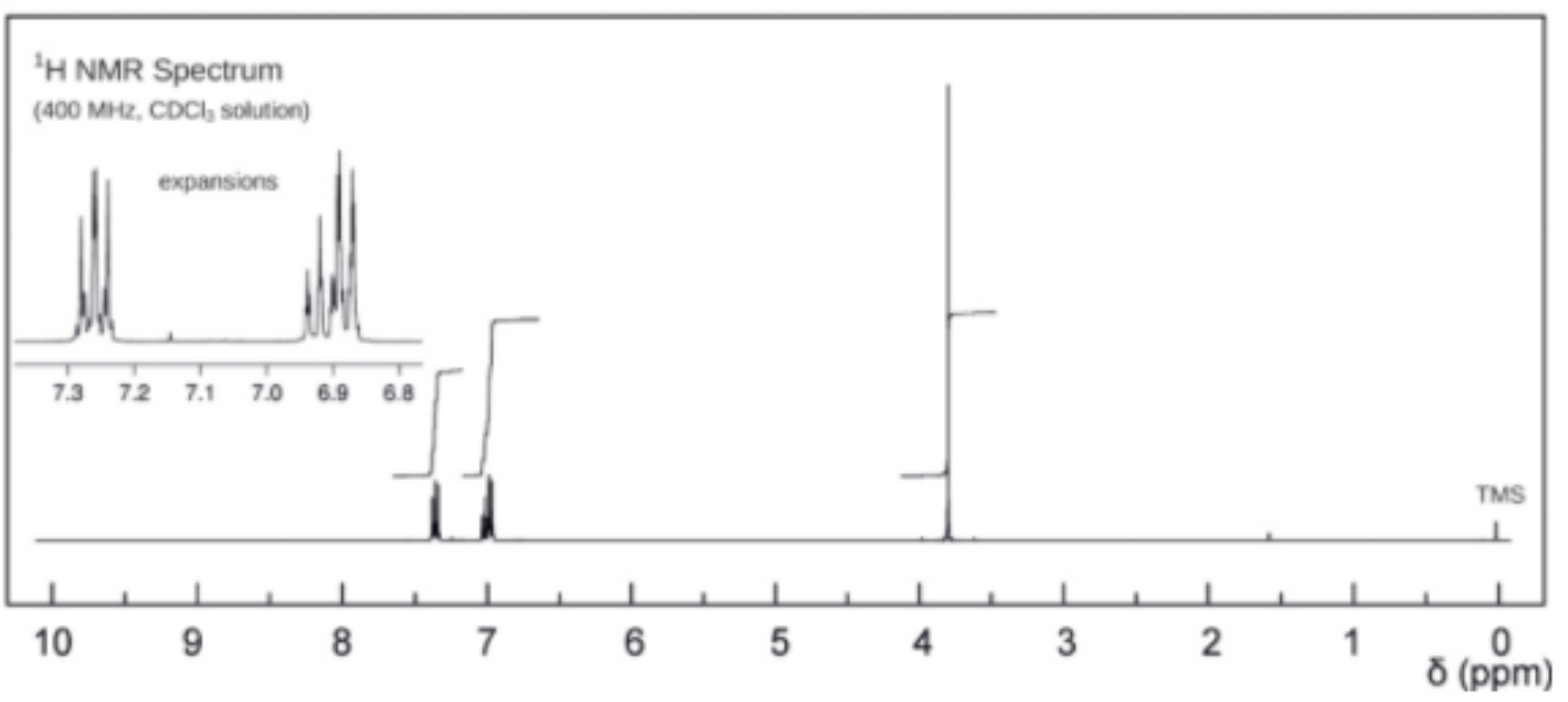


UV Spectrum

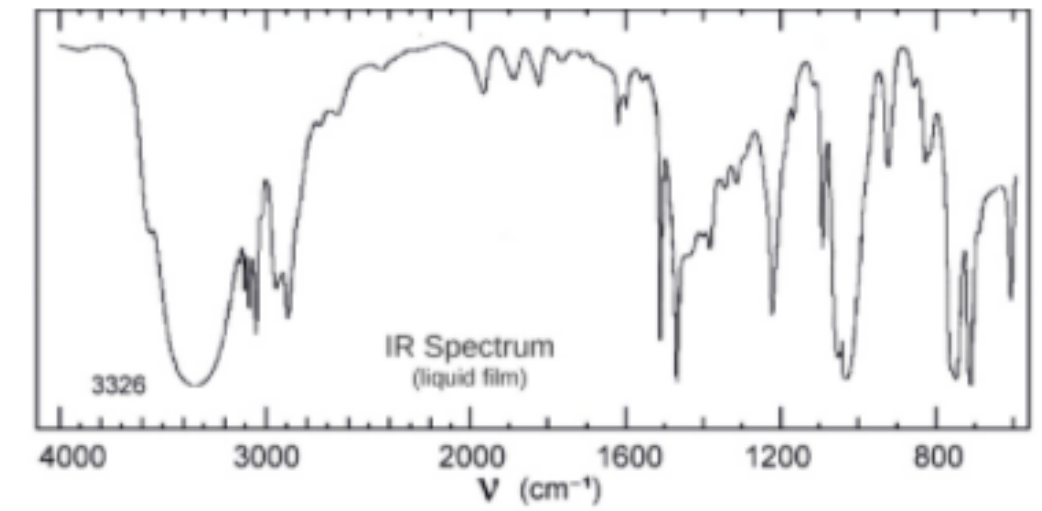
λ_{max} 269 nm ($\log_{10}\varepsilon$ 3.2)

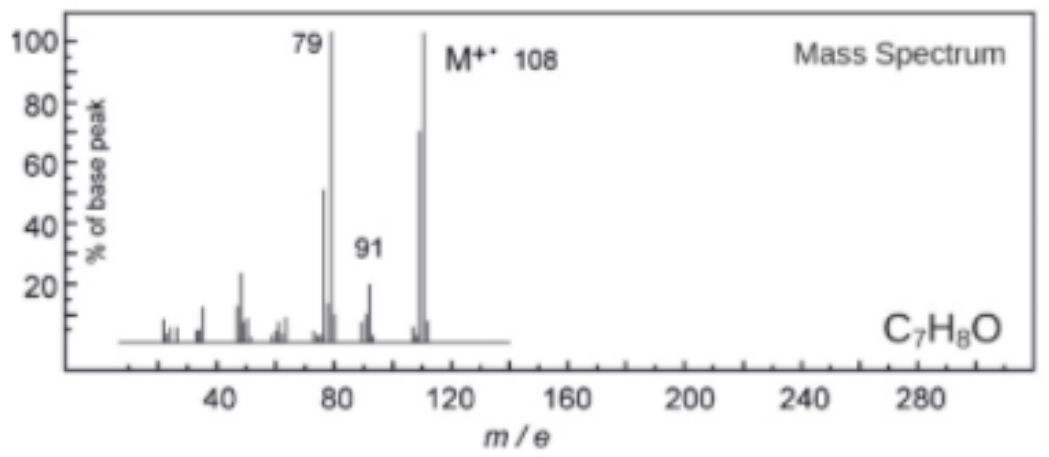
solvent: methanol





Problem 53

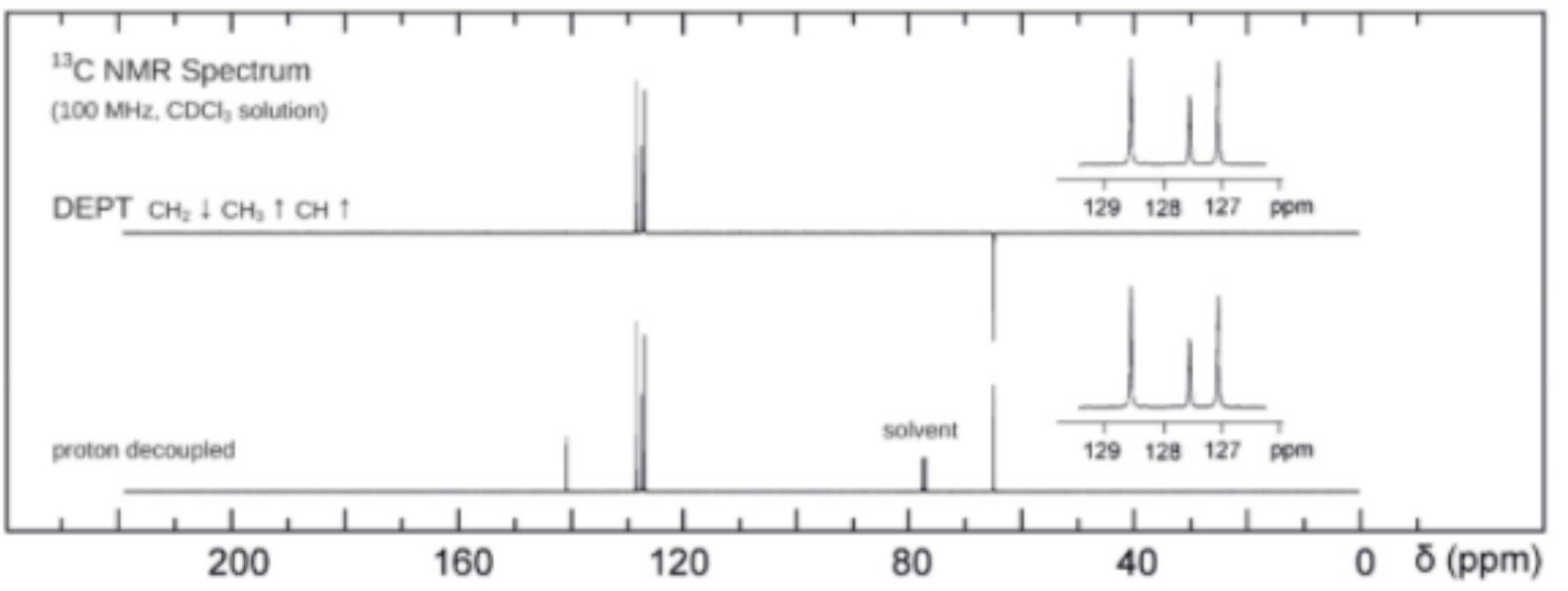


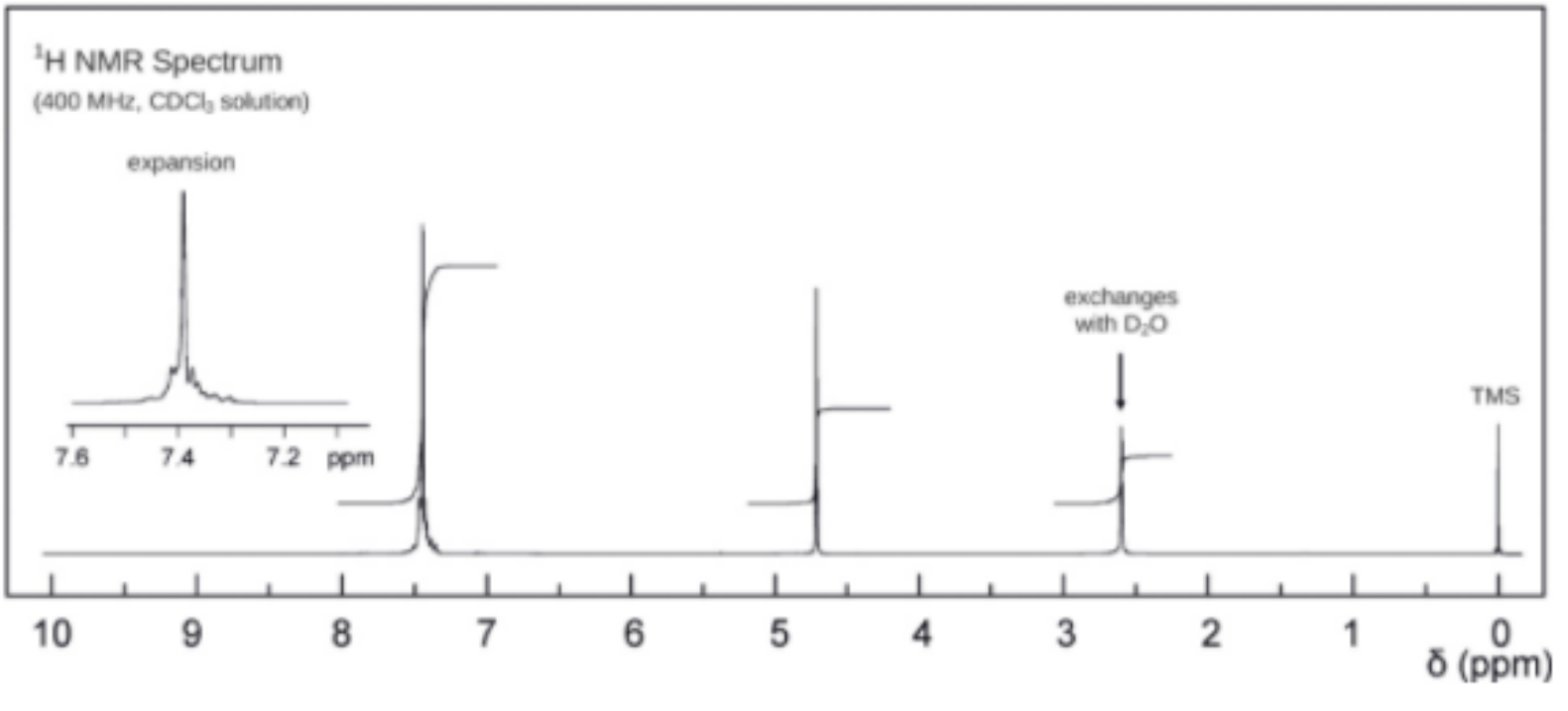


UV Spectrum

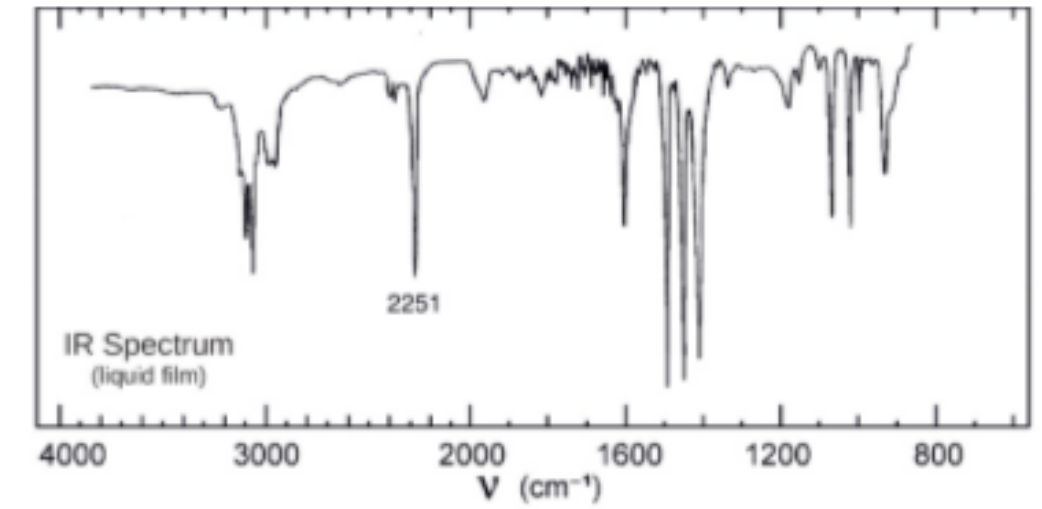
λ_{max} 243 nm ($\log_{10}\varepsilon$ 1.9)
λ_{max} 248 nm ($\log_{10}\varepsilon$ 2.1)
λ_{max} 252 nm ($\log_{10}\varepsilon$ 2.2)
λ_{max} 258 nm ($\log_{10}\varepsilon$ 2.3)
λ_{max} 264 nm ($\log_{10}\varepsilon$ 2.1)
λ_{max} 268 nm ($\log_{10}\varepsilon$ 1.9)

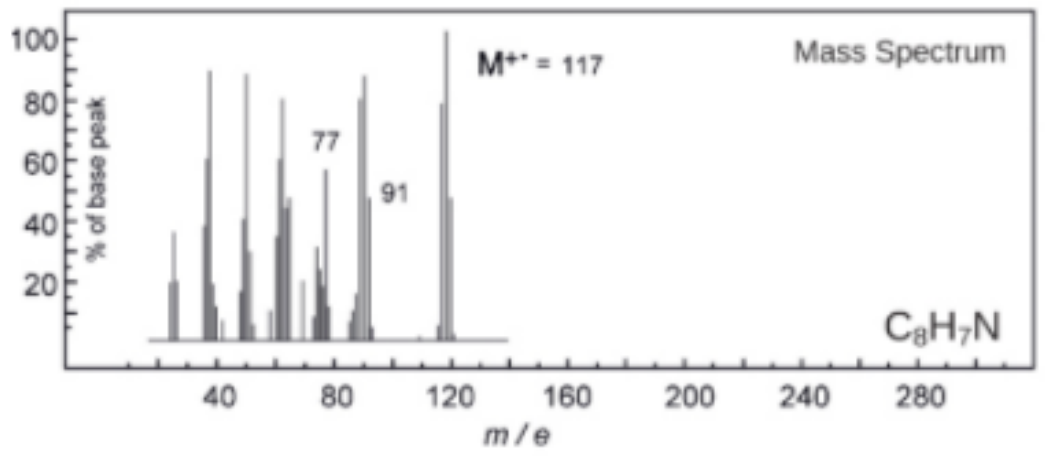
solvent: ethanol

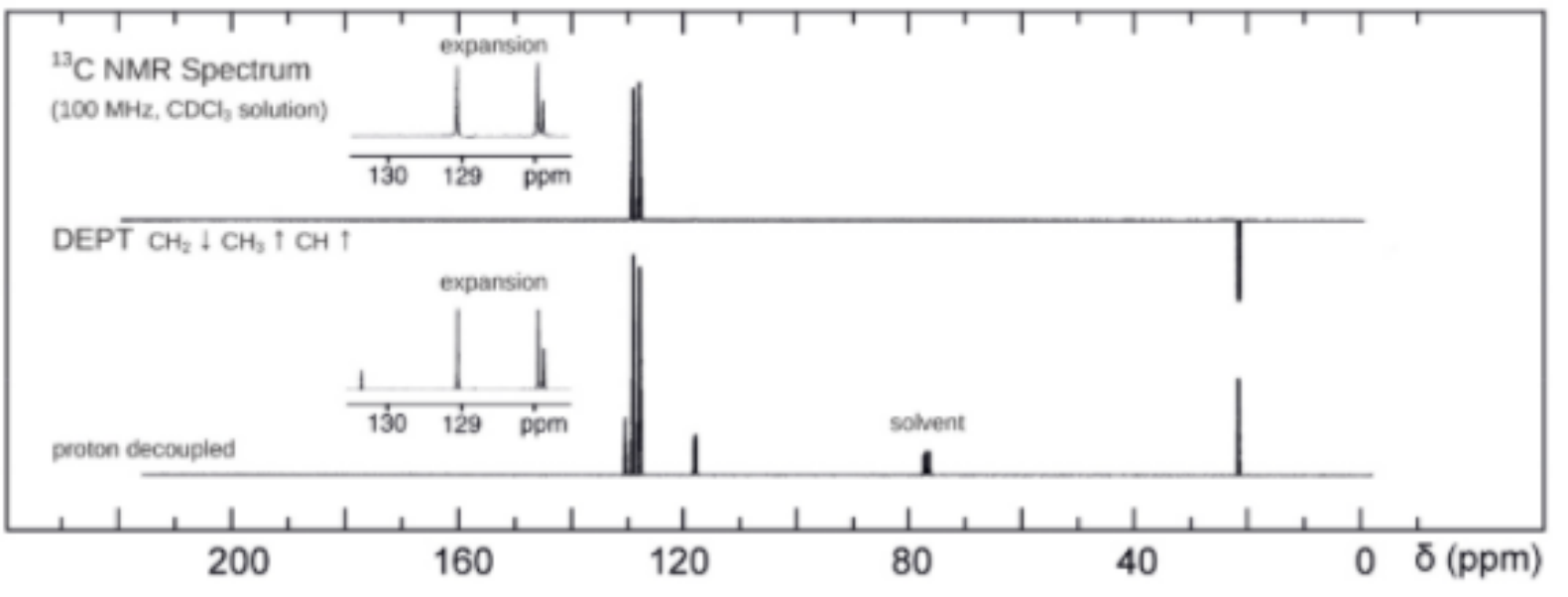


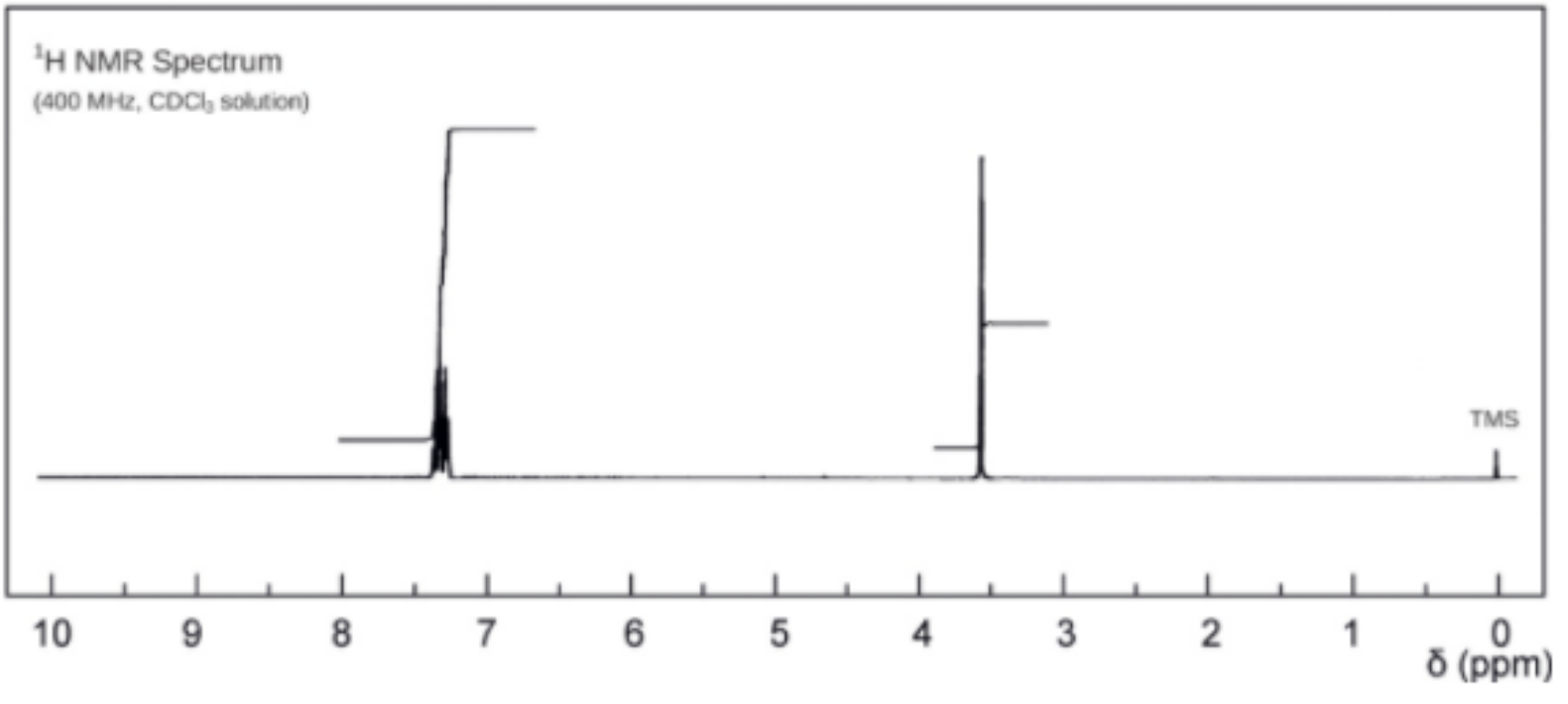


Problem 54

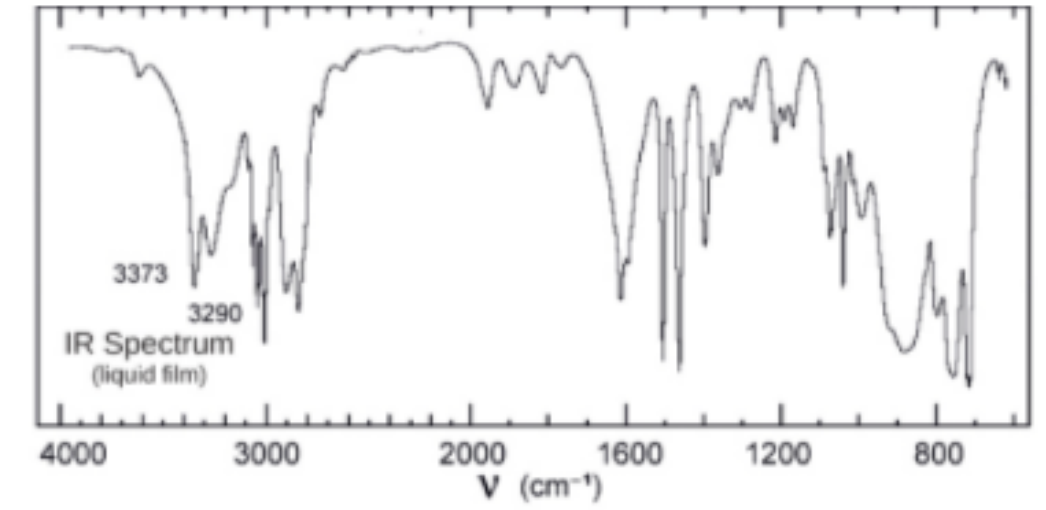

IR Spectrum
(liquid film)
2251
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

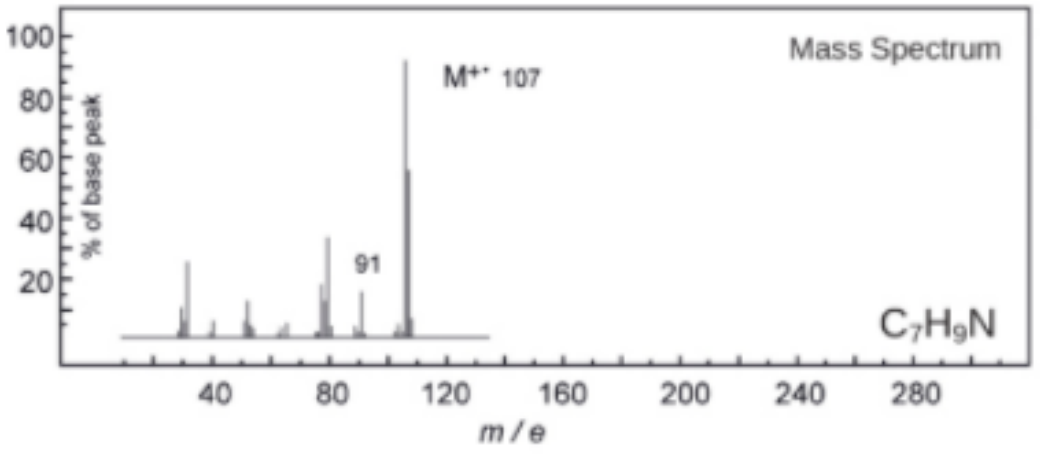

Mass Spectrum
M+· = 117
77
91
% of base peak
100
80
60
40
20
C8H7N
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
130
129
ppm
DEPT CH2 ↓ CH3 ↑ CH ↑
expansion
130
129
ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 55

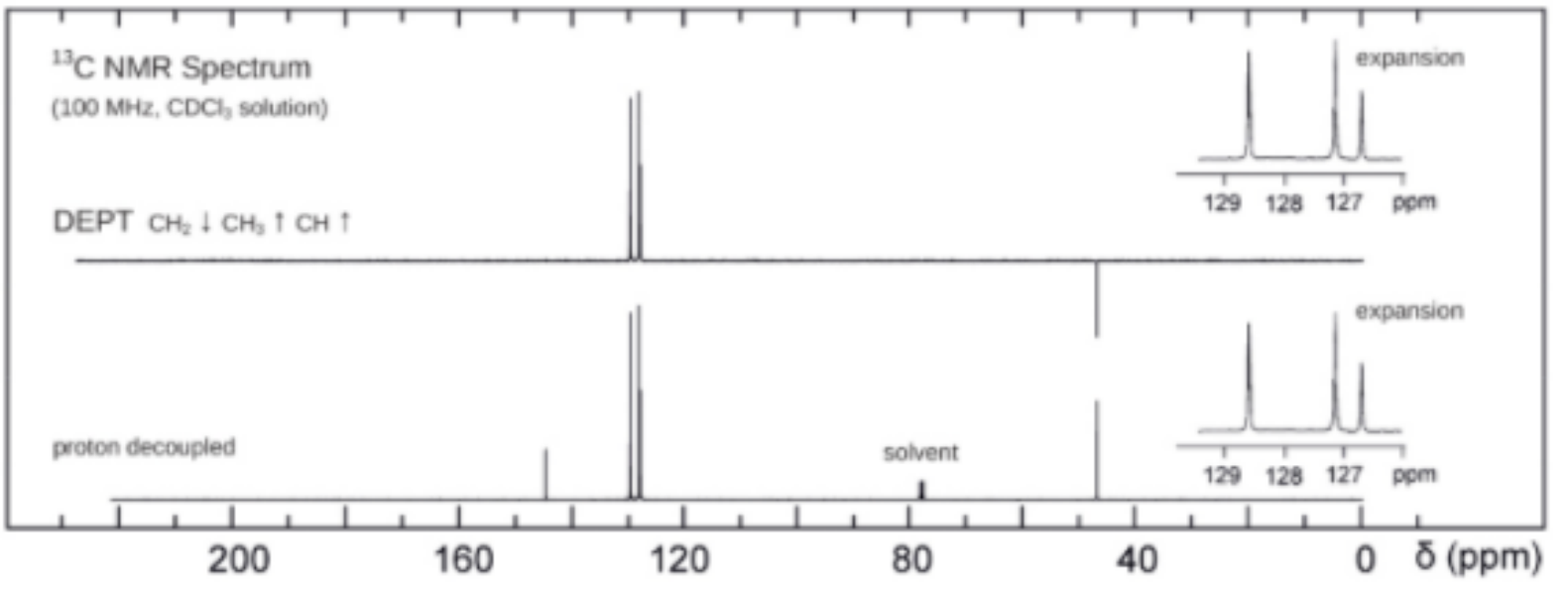


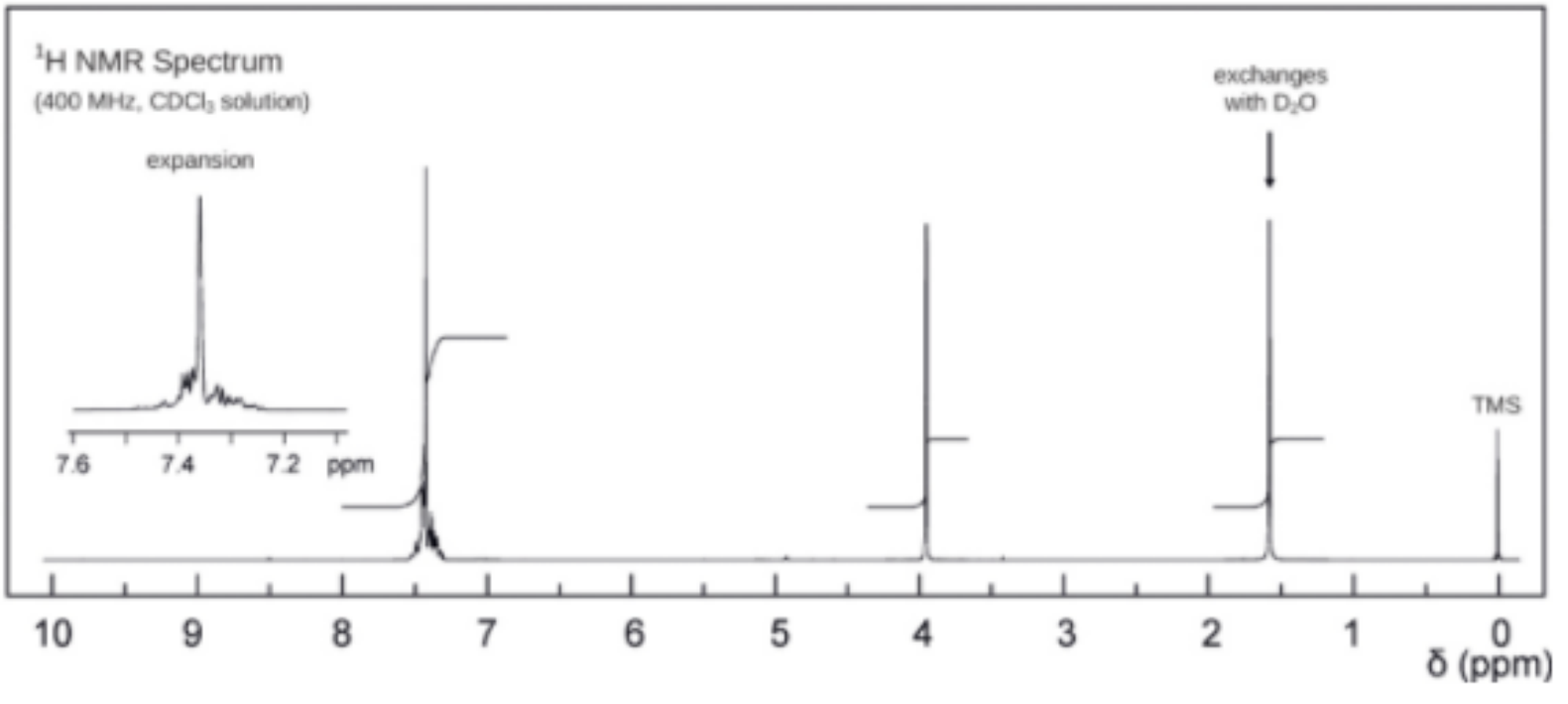


UV Spectrum

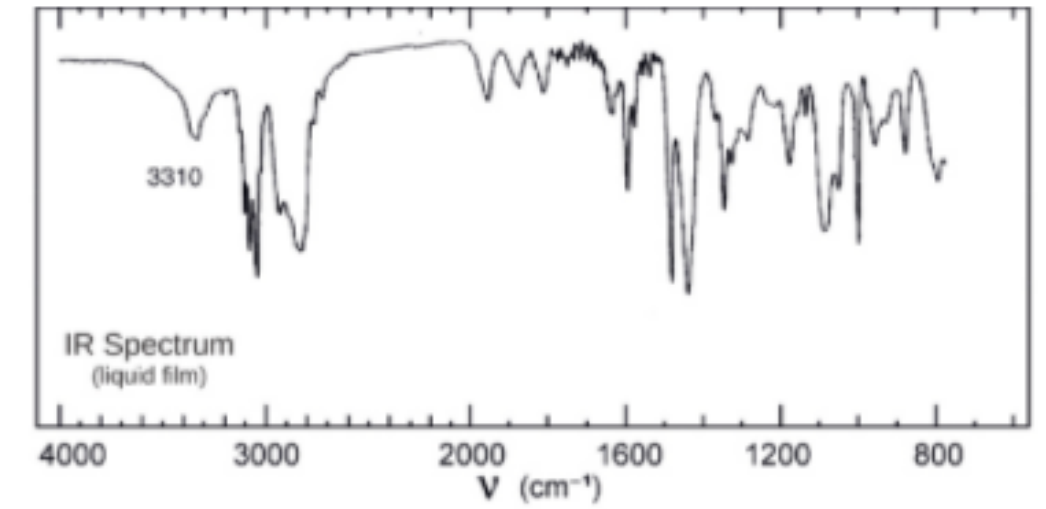
λ_{max} 256 nm ($\log_{10}\varepsilon$ 2.2)
λ_{max} 264 nm ($\log_{10}\varepsilon$ 2.1)

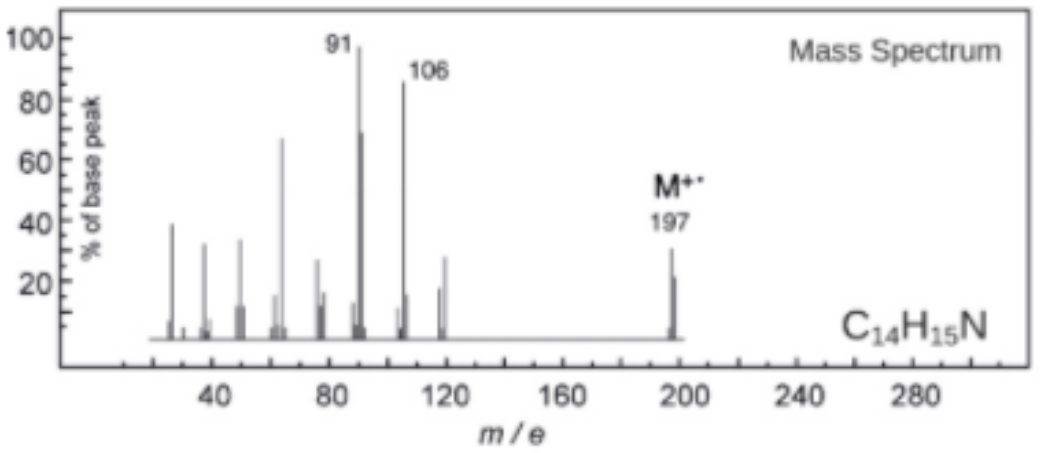
solvent: ethanol

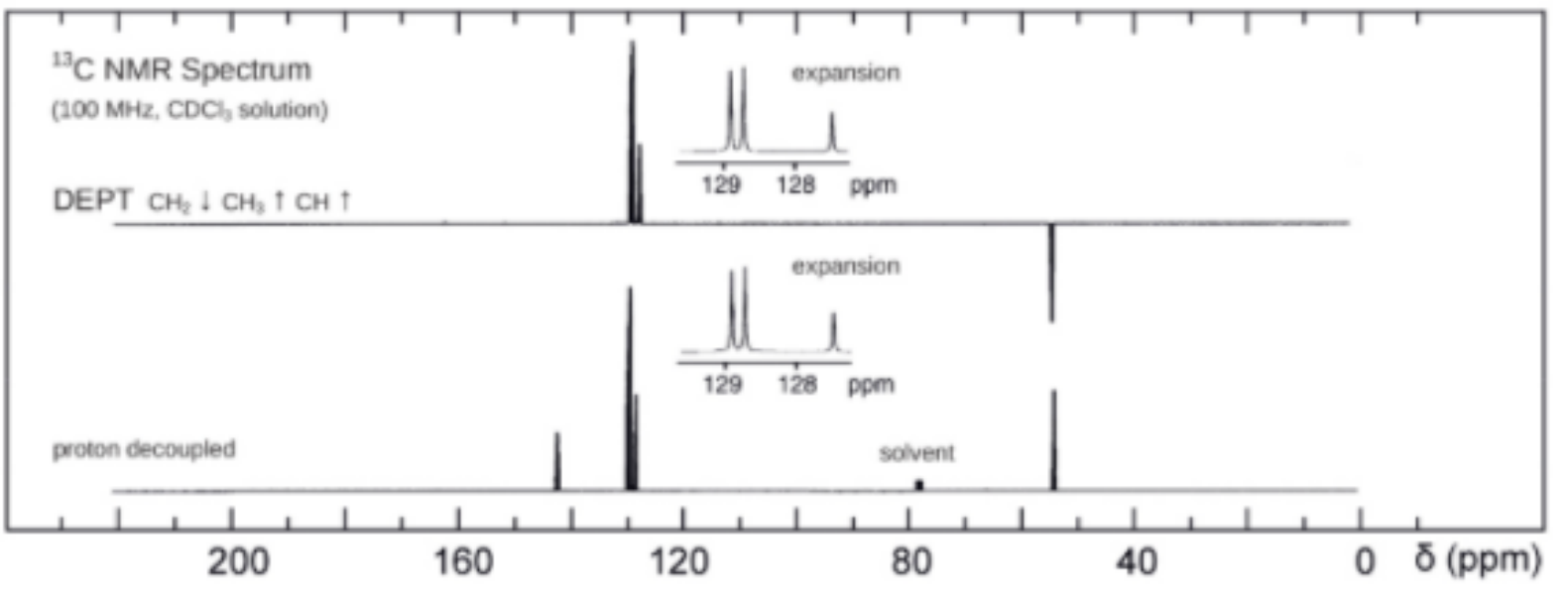


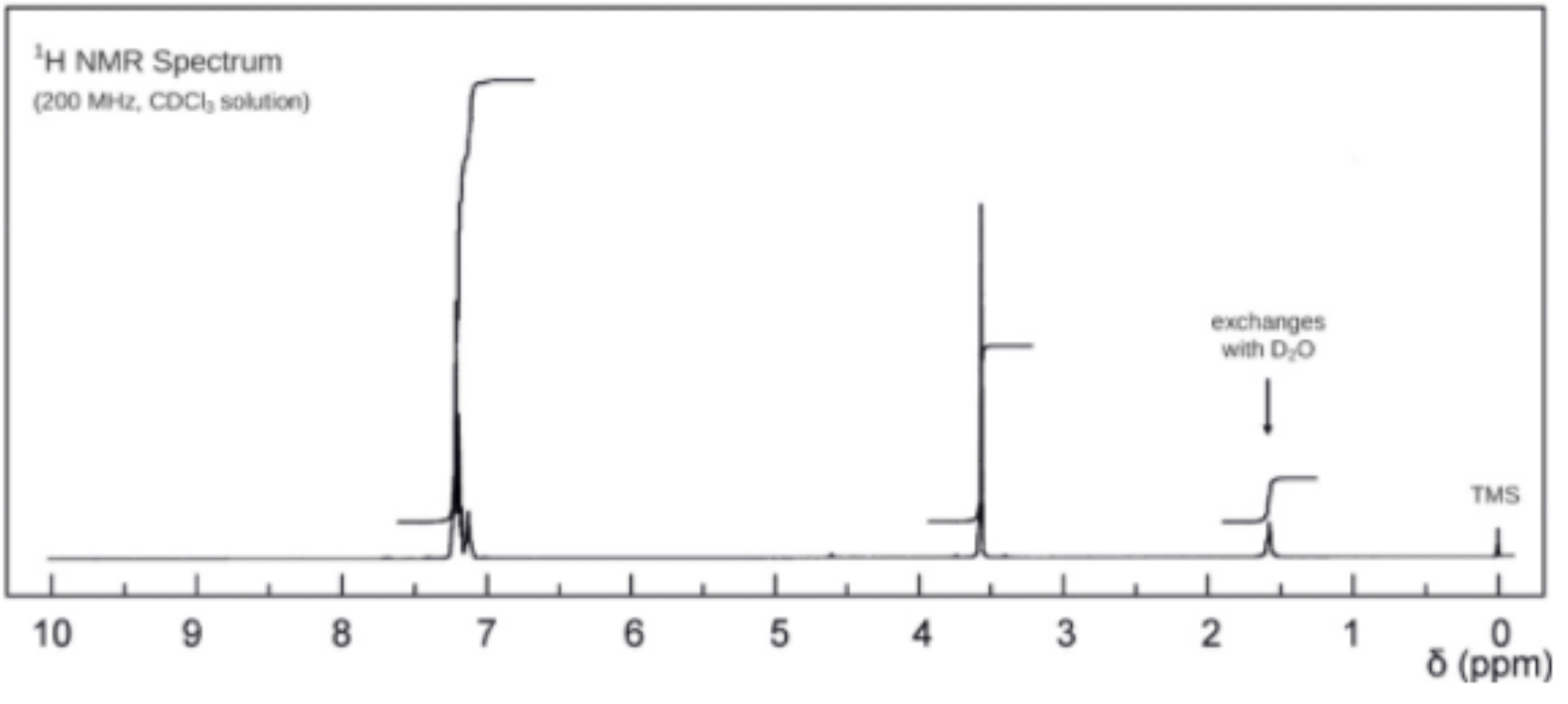


Problem 56

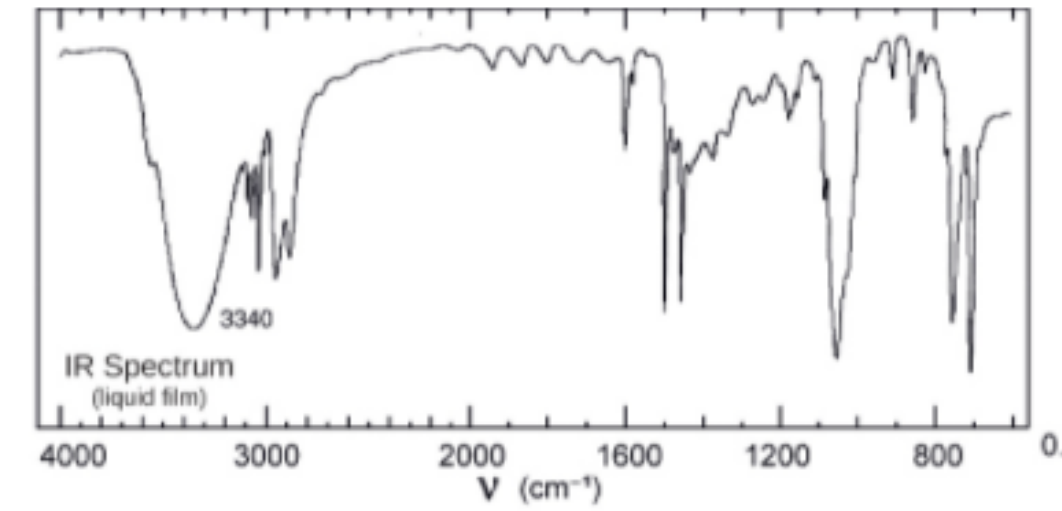

3310
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

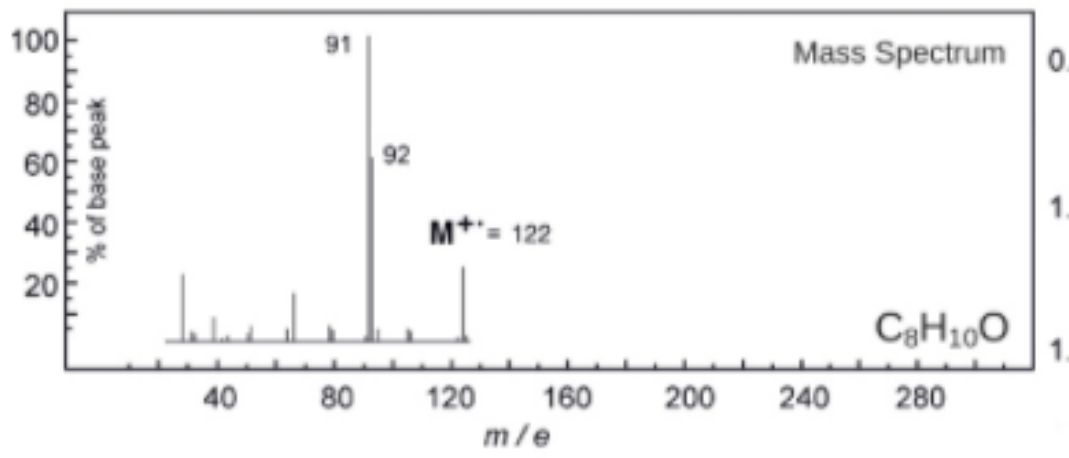

Mass Spectrum
91
106
M+·
197
C14H15N
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m / e

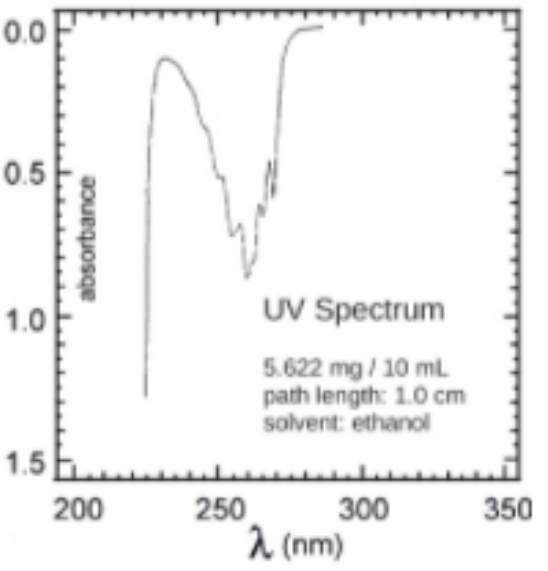

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
expansion
129
128
ppm
expansion
129
128
ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

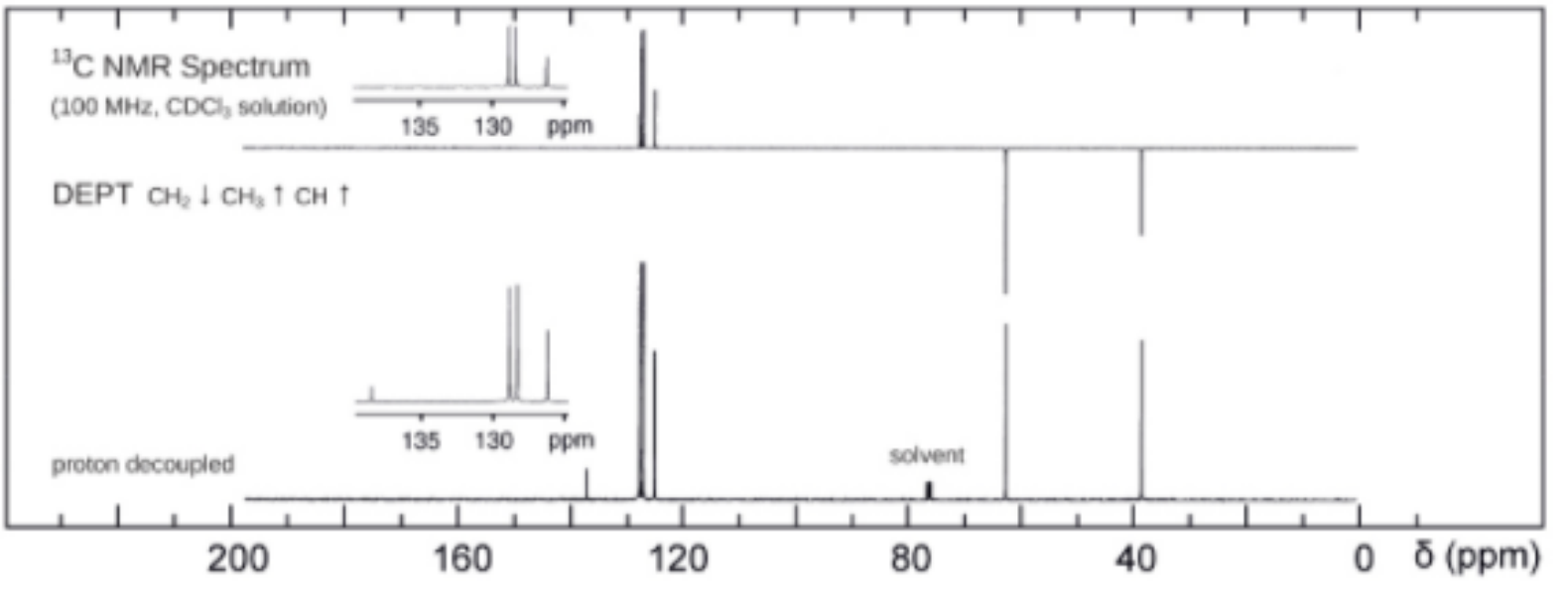

1H NMR Spectrum
(200 MHz, CDCl3 solution)
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

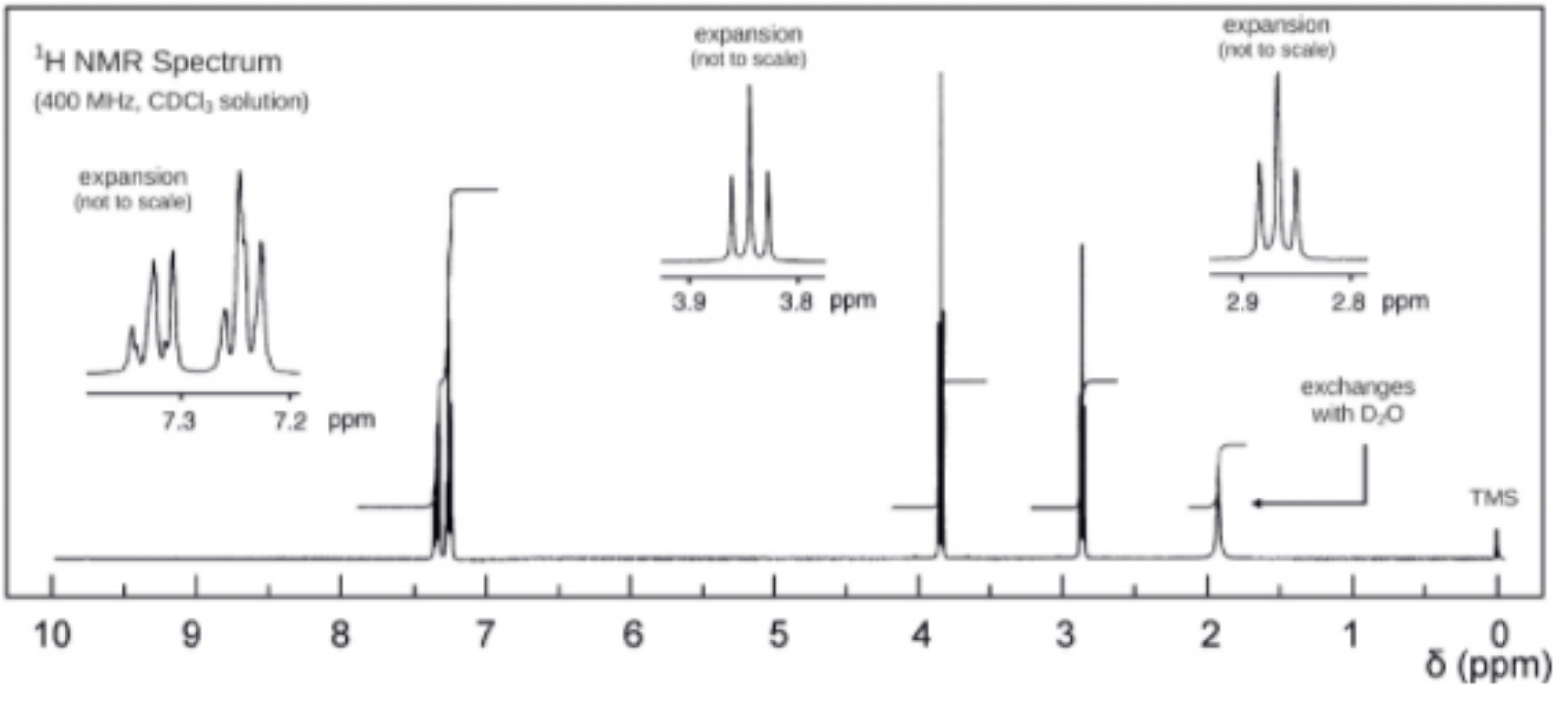
Problem 57


3340
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

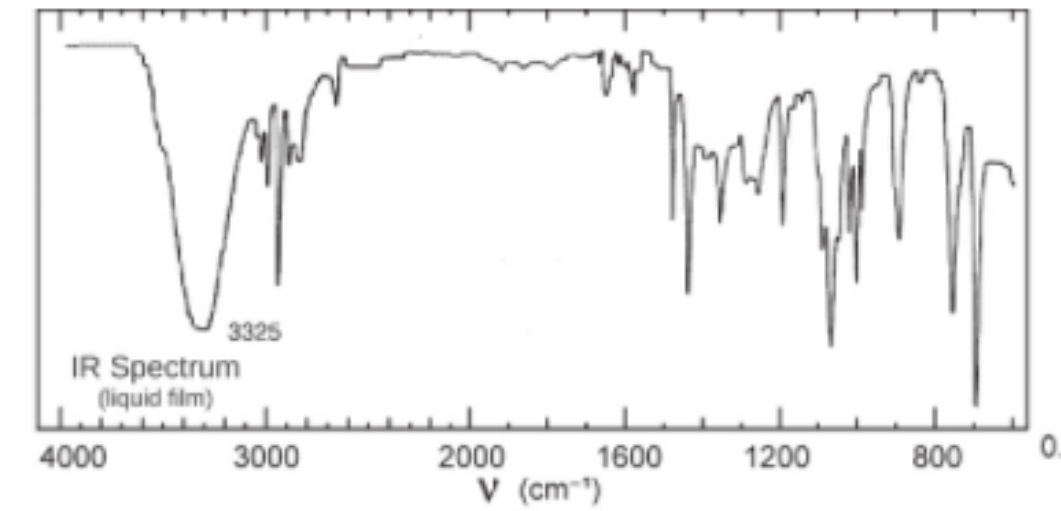

Mass Spectrum
91
92
M+· = 122
% of base peak
100
80
60
40
20
C8H10O
40
80
120
160
200
240
280
m/e

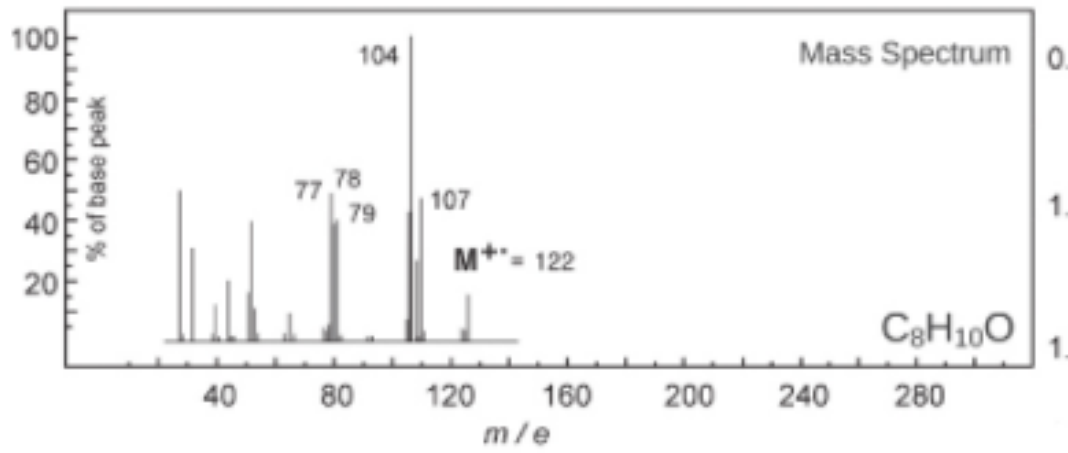

absorbance
0.0
0.5
1.0
1.5
UV Spectrum
5.622 mg / 10 mL
path length: 1.0 cm
solvent: ethanol
200
250
300
350
λ (nm)

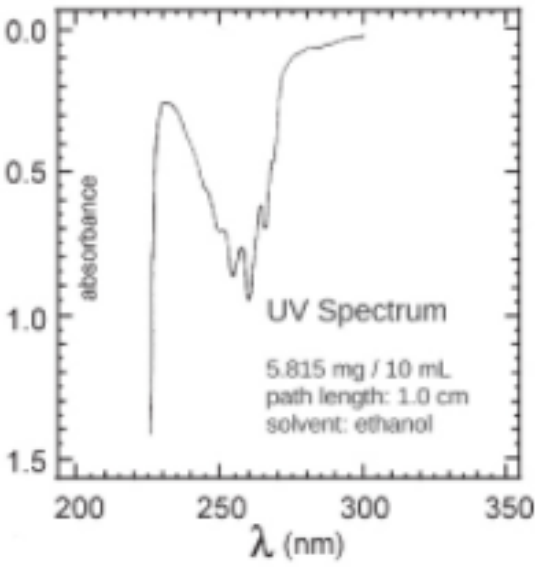

13C NMR Spectrum
(100 MHz, CDCl3 solution)
135
130
ppm
DEPT CH2 ↓ CH3 ↑ CH ↑
135
130
ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

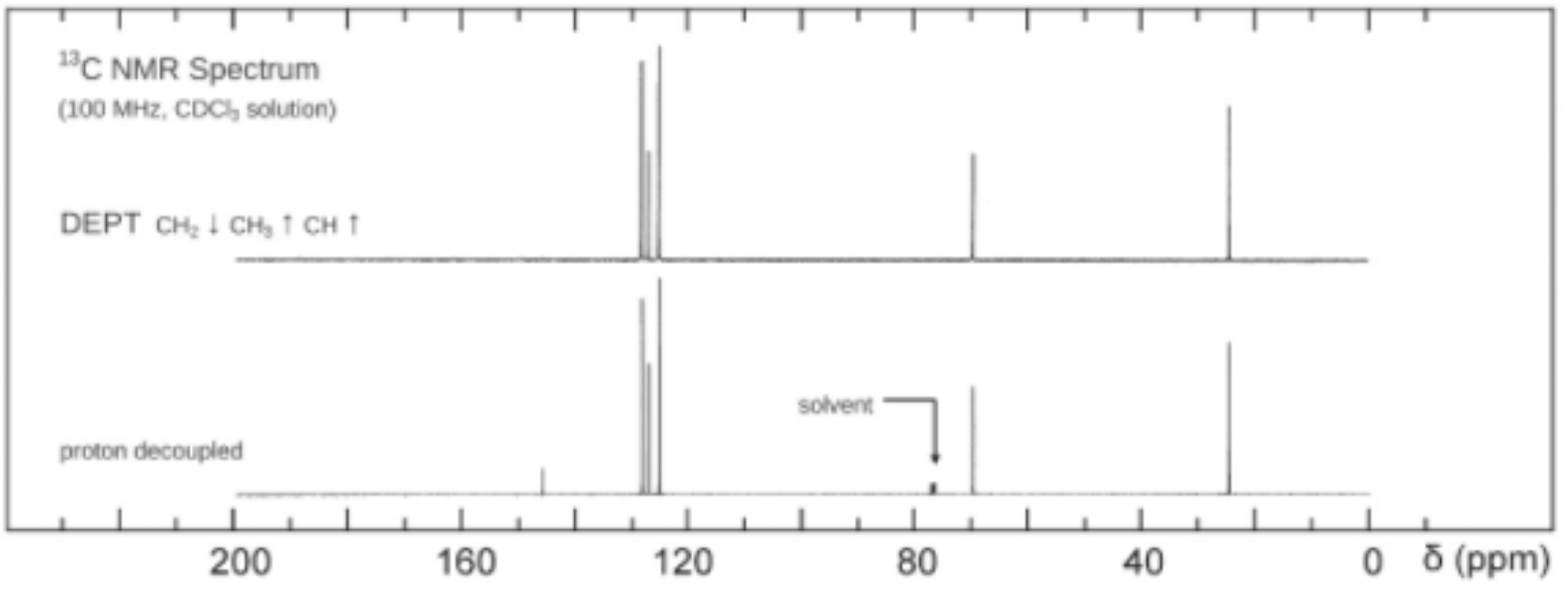

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
(not to scale)
7.3
7.2
ppm
expansion
(not to scale)
3.9
3.8
ppm
expansion
(not to scale)
2.9
2.8
ppm
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

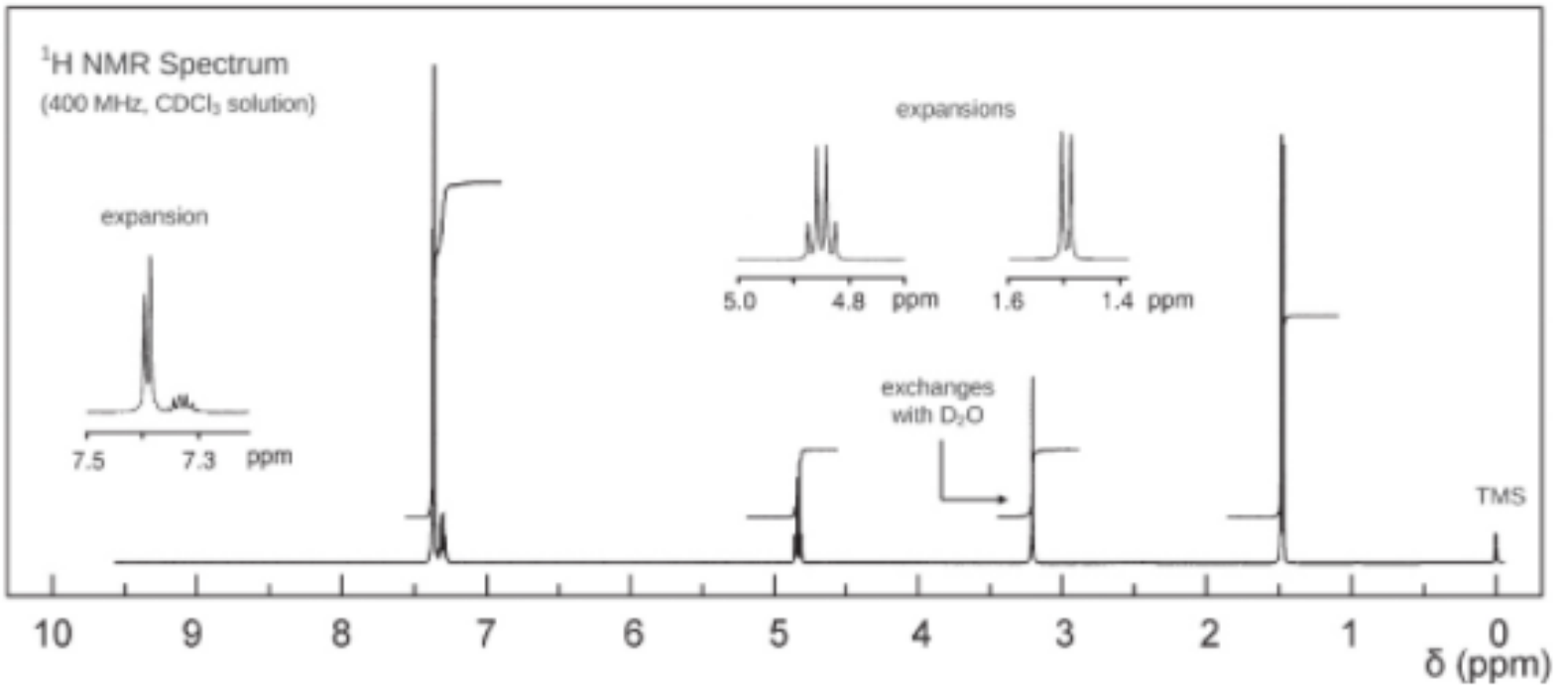
Problem 58


3325
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

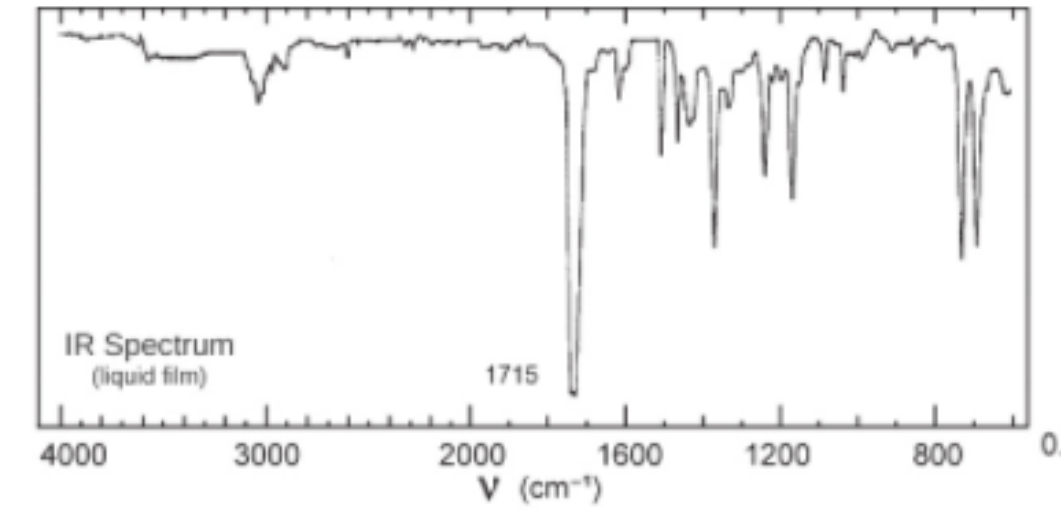

Mass Spectrum
% of base peak
104
77
78
79
107
M+• = 122
C8H10O
m/e

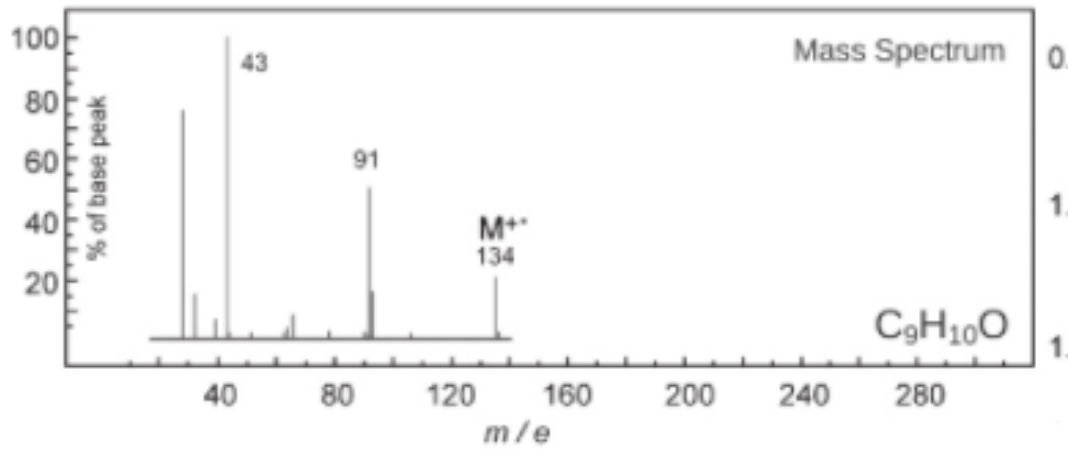

absorbance
UV Spectrum
5.815 mg / 10 mL
path length: 1.0 cm
solvent: ethanol
λ (nm)

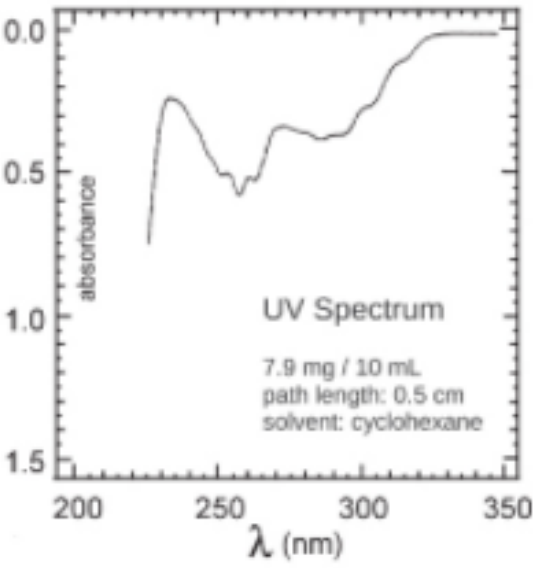

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
δ (ppm)

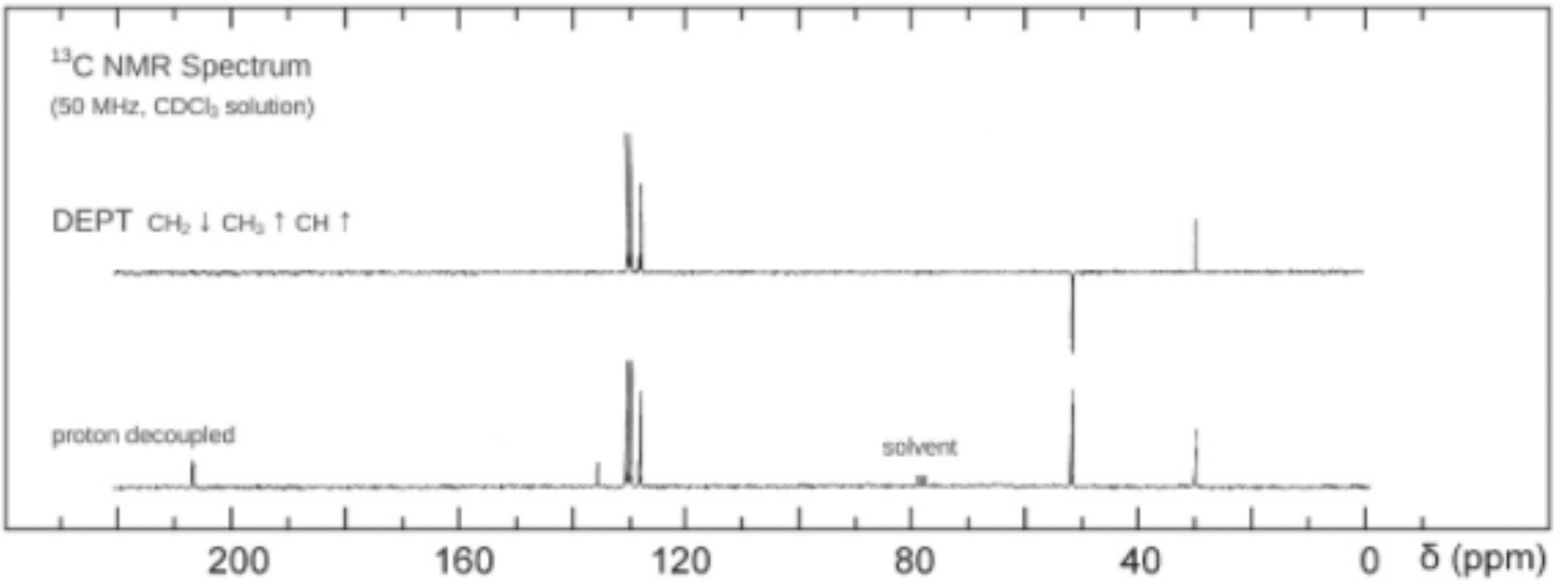

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.5
7.3
ppm
expansions
5.0
4.8
ppm
1.6
1.4
ppm
exchanges
with D2O
TMS
δ (ppm)

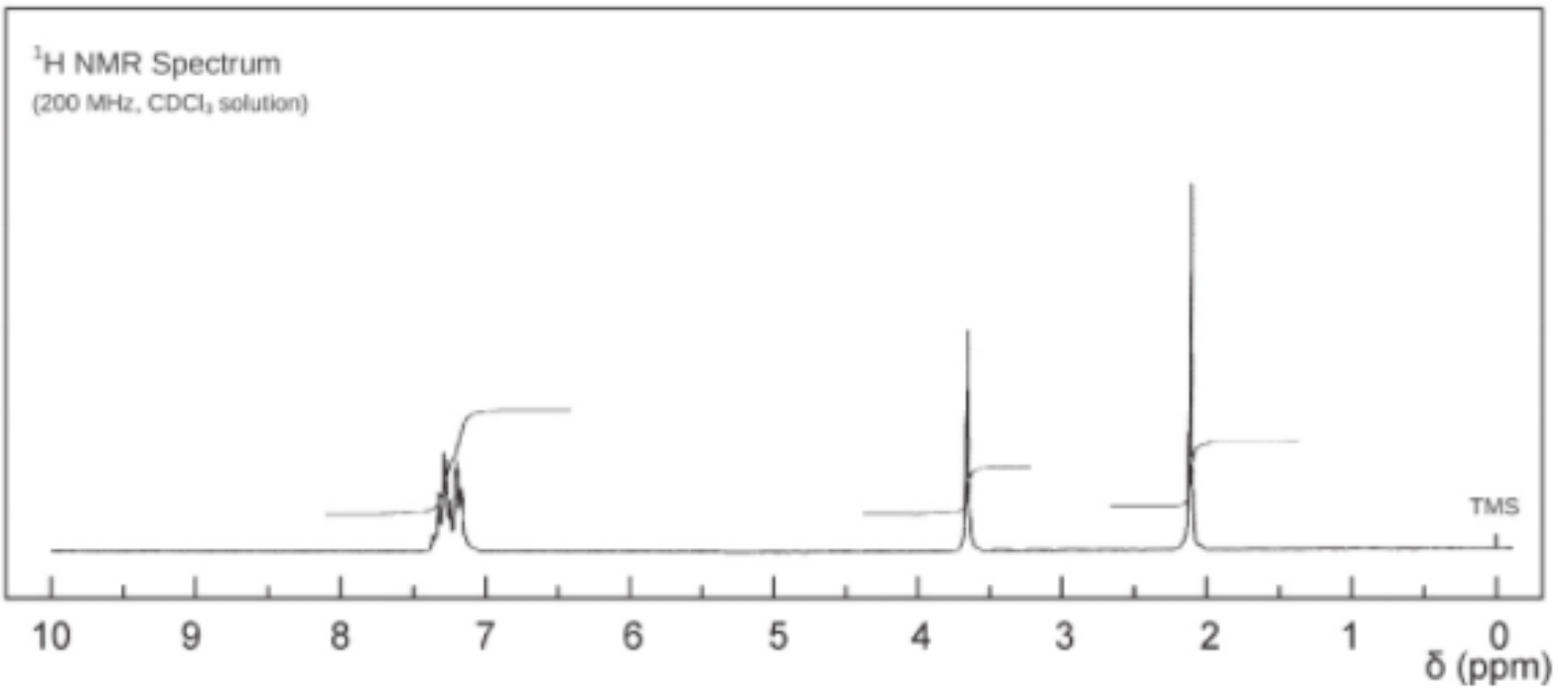
Problem 59


IR Spectrum
(liquid film)
1715
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

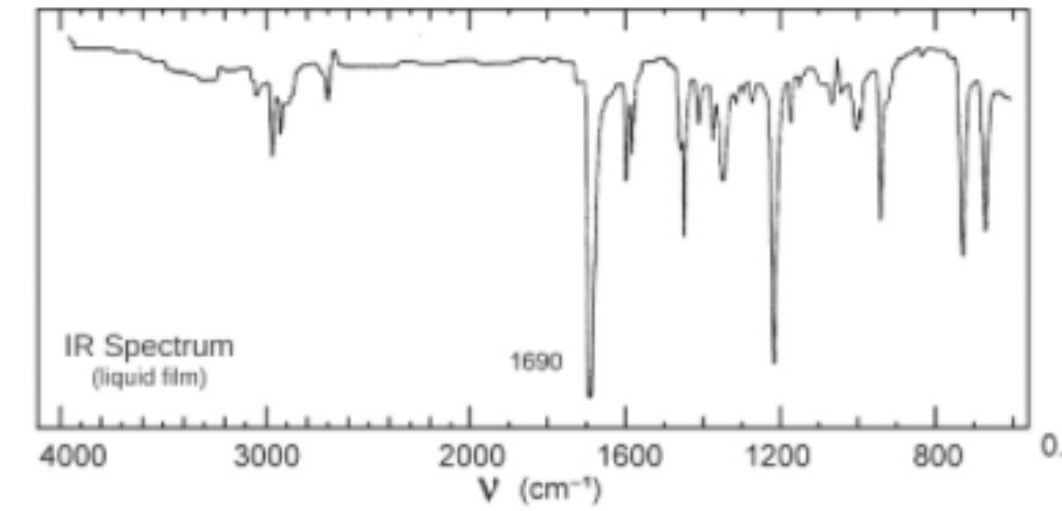

Mass Spectrum
% of base peak
100
80
60
40
20
43
91
M+·
134
C9H10O
40
80
120
160
200
240
280
m/e

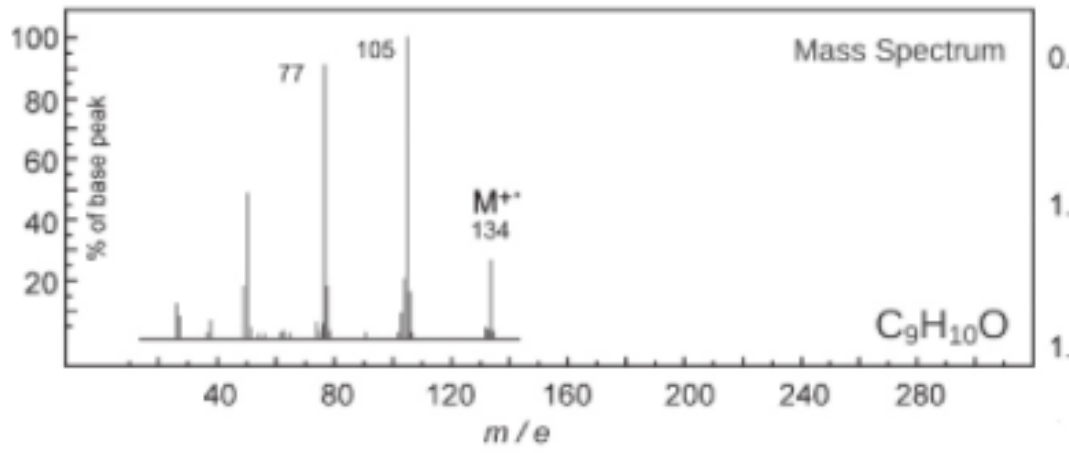

absorbance
0.0
0.5
1.0
1.5
UV Spectrum
7.9 mg / 10 mL
path length: 0.5 cm
solvent: cyclohexane
200
250
300
350
λ (nm)

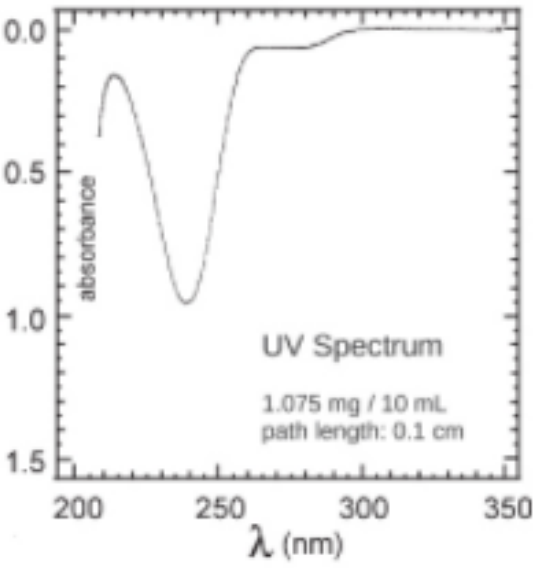

13C NMR Spectrum
(50 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

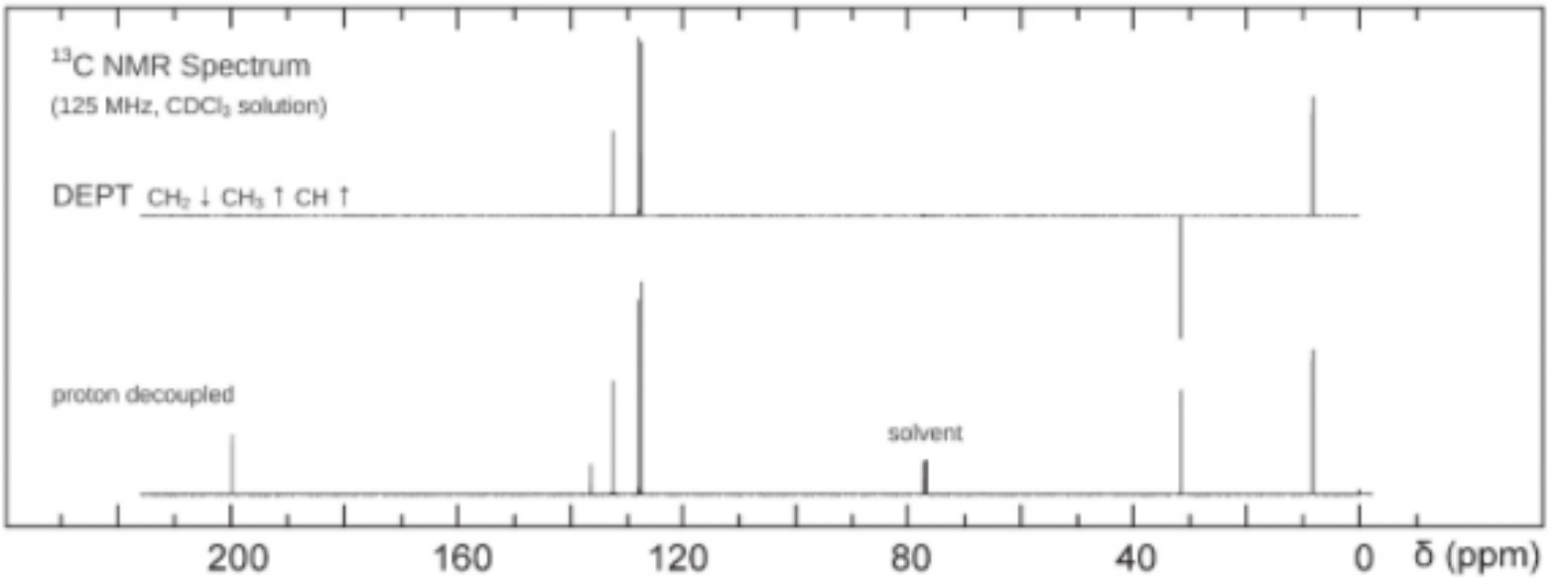

1H NMR Spectrum
(200 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

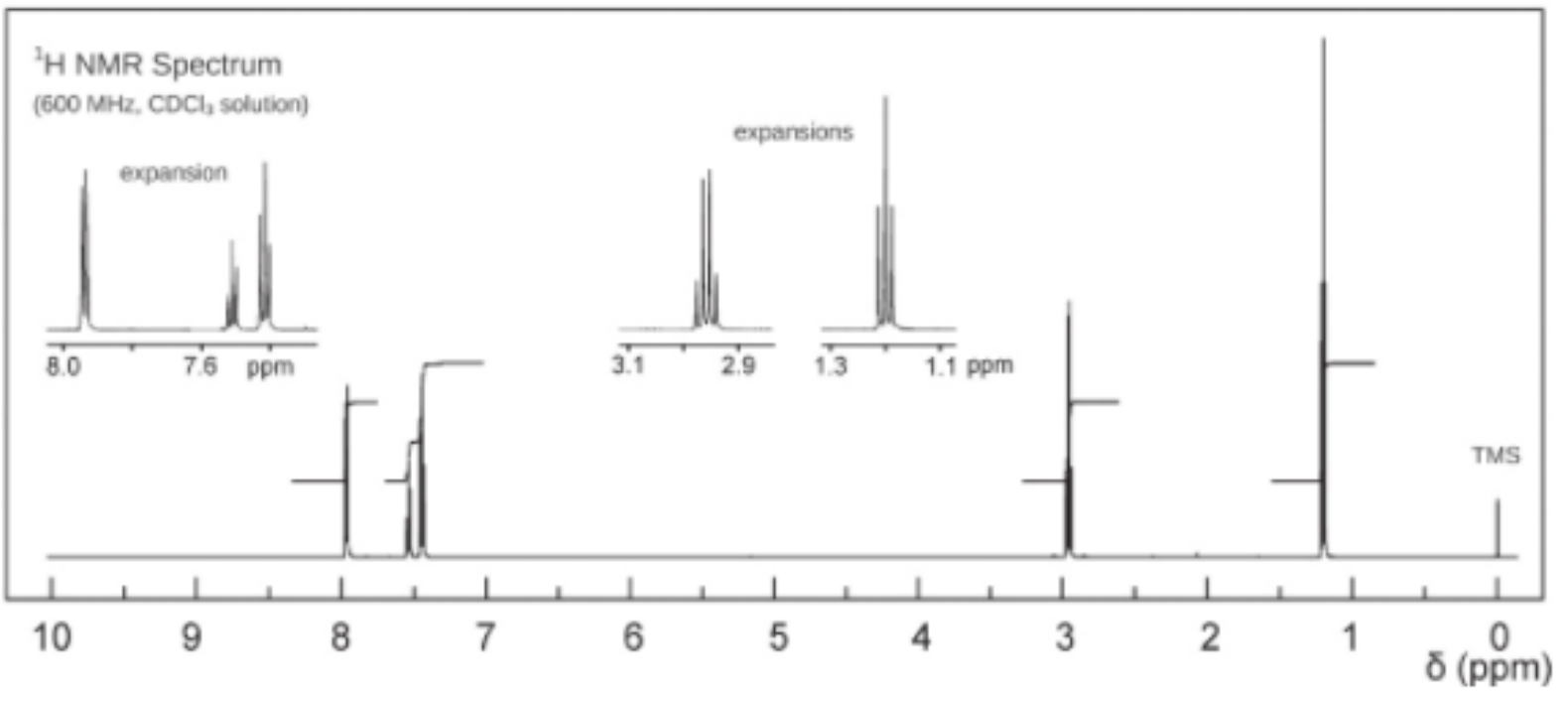
Problem 60


IR Spectrum
(liquid film)
1690
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

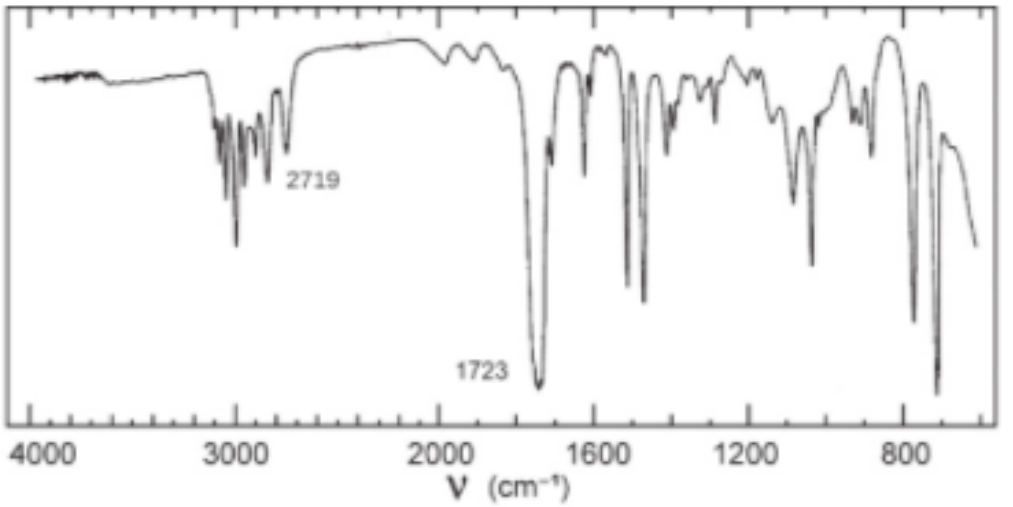

Mass Spectrum
% of base peak
100
80
60
40
20
77
105
M+·
134
C9H10O
40
80
120
160
200
240
280
m / e

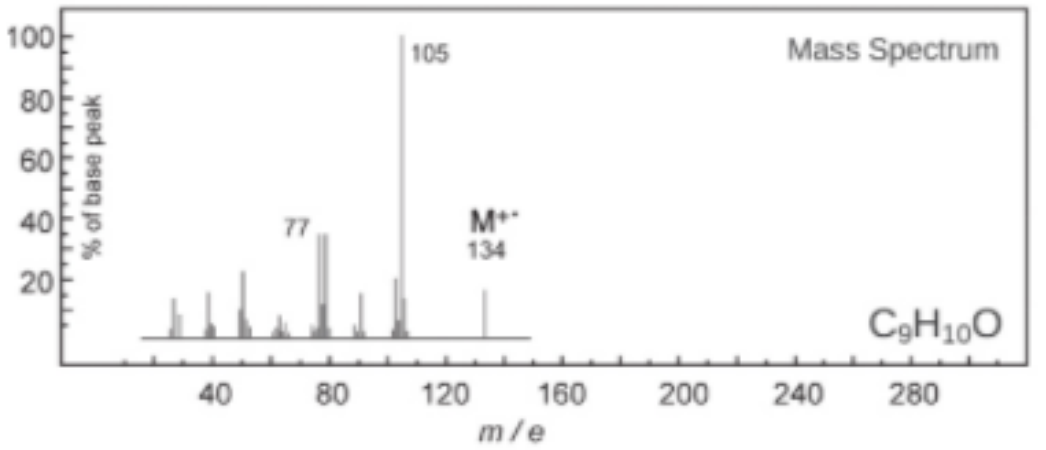

absorbance
0.0
0.5
1.0
1.5
UV Spectrum
1.075 mg / 10 mL
path length: 0.1 cm
200
250
300
350
λ (nm)

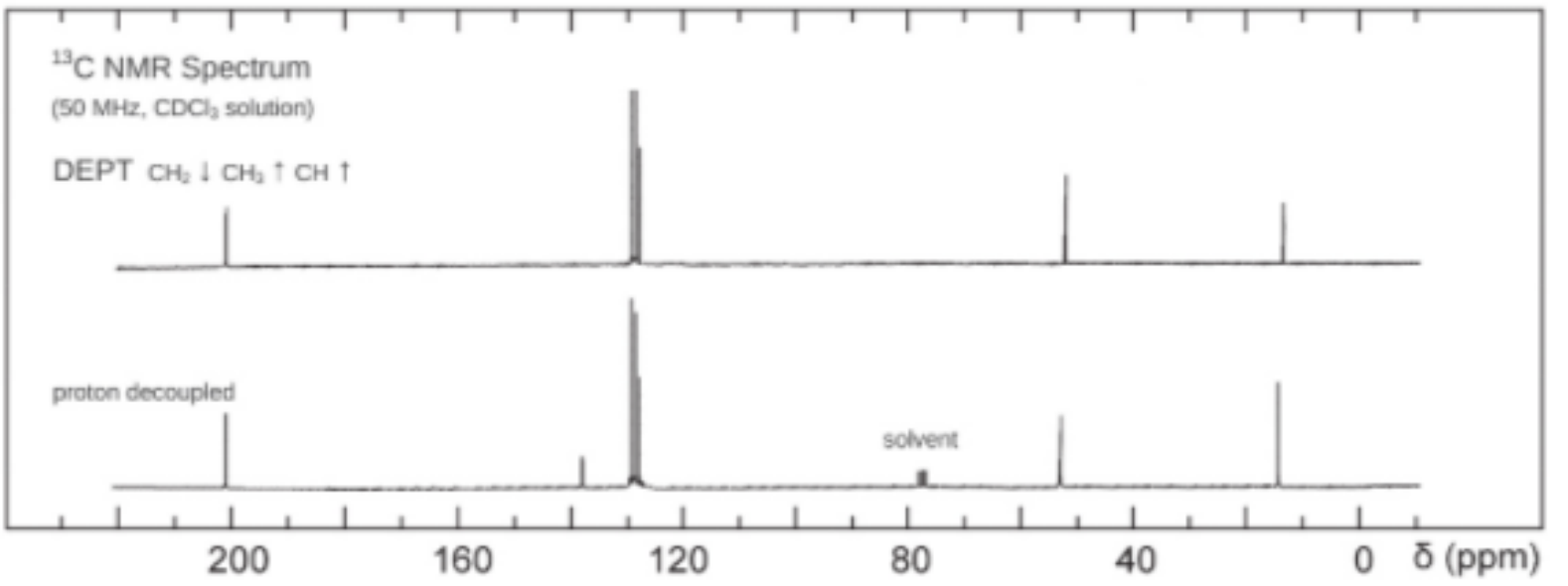

13C NMR Spectrum
(125 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

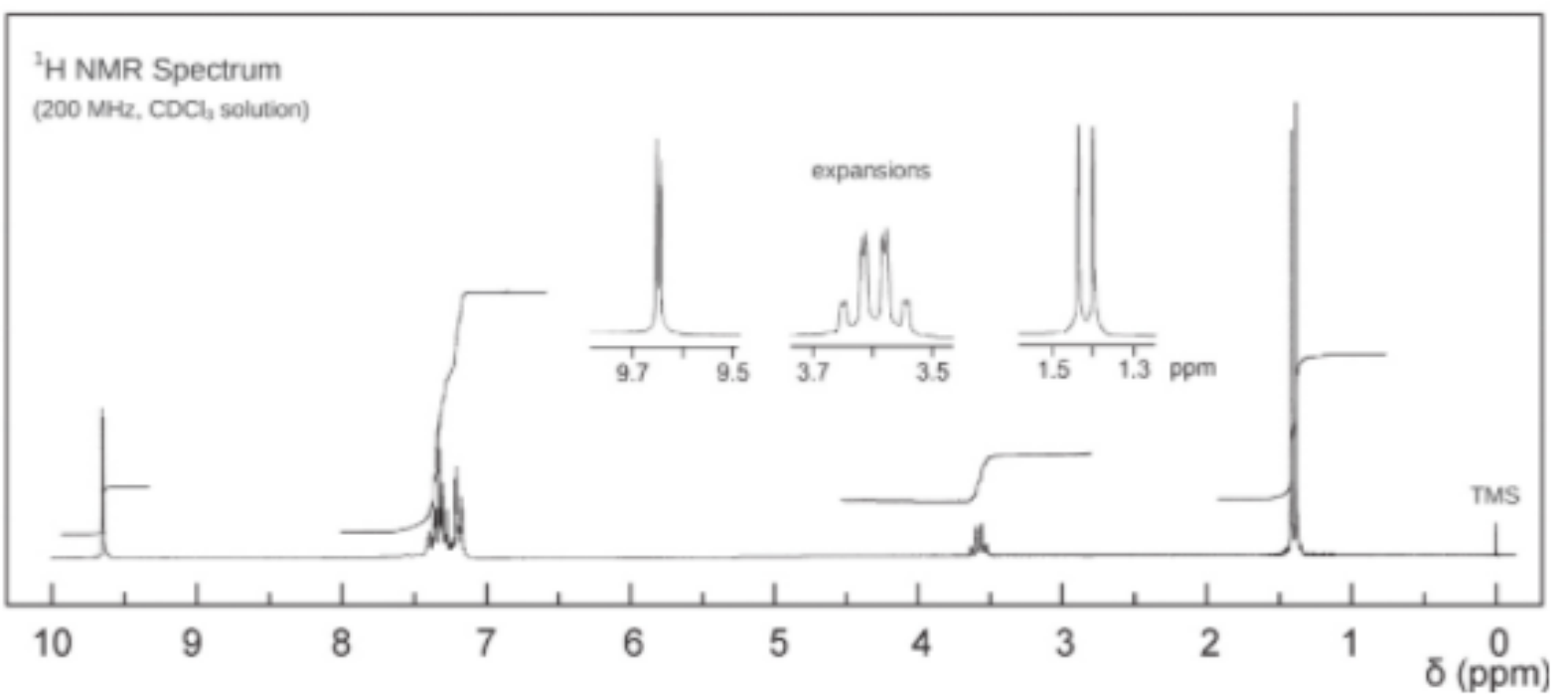

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion
8.0
7.6
ppm
expansions
3.1
2.9
1.3
1.1 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 61

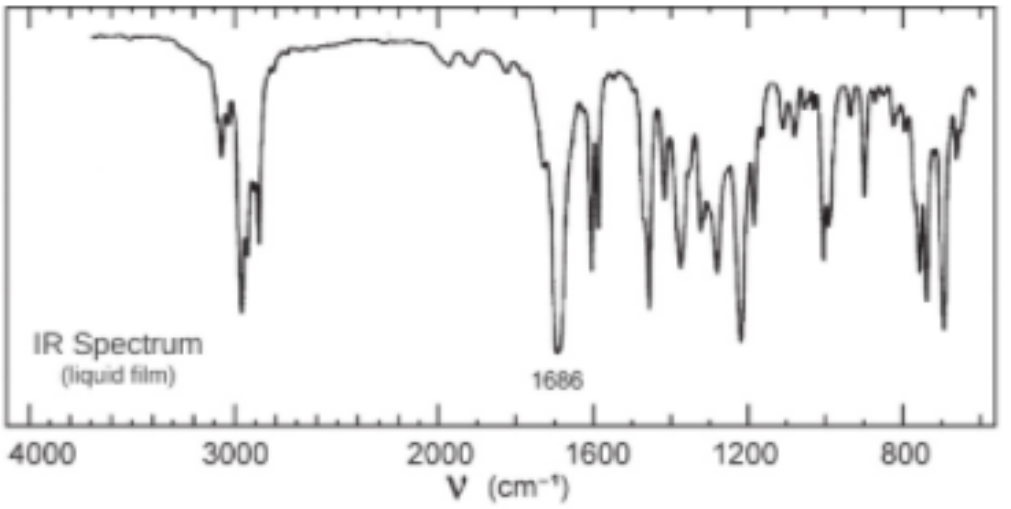

2719
1723
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

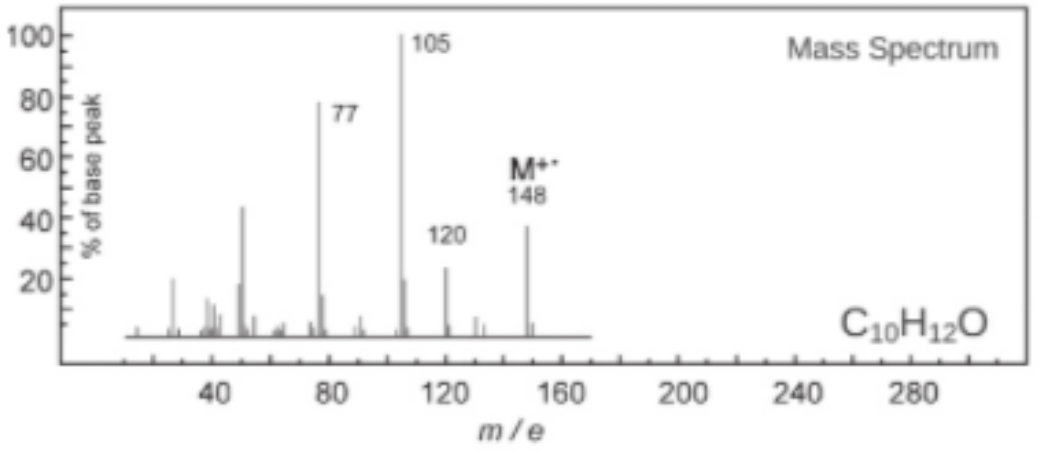

Mass Spectrum
105
77
M+·
134
% of base peak
100
80
60
40
20
C9H10O
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(50 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(200 MHz, CDCl3 solution)
expansions
9.7
9.5
3.7
3.5
1.5
1.3
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 62

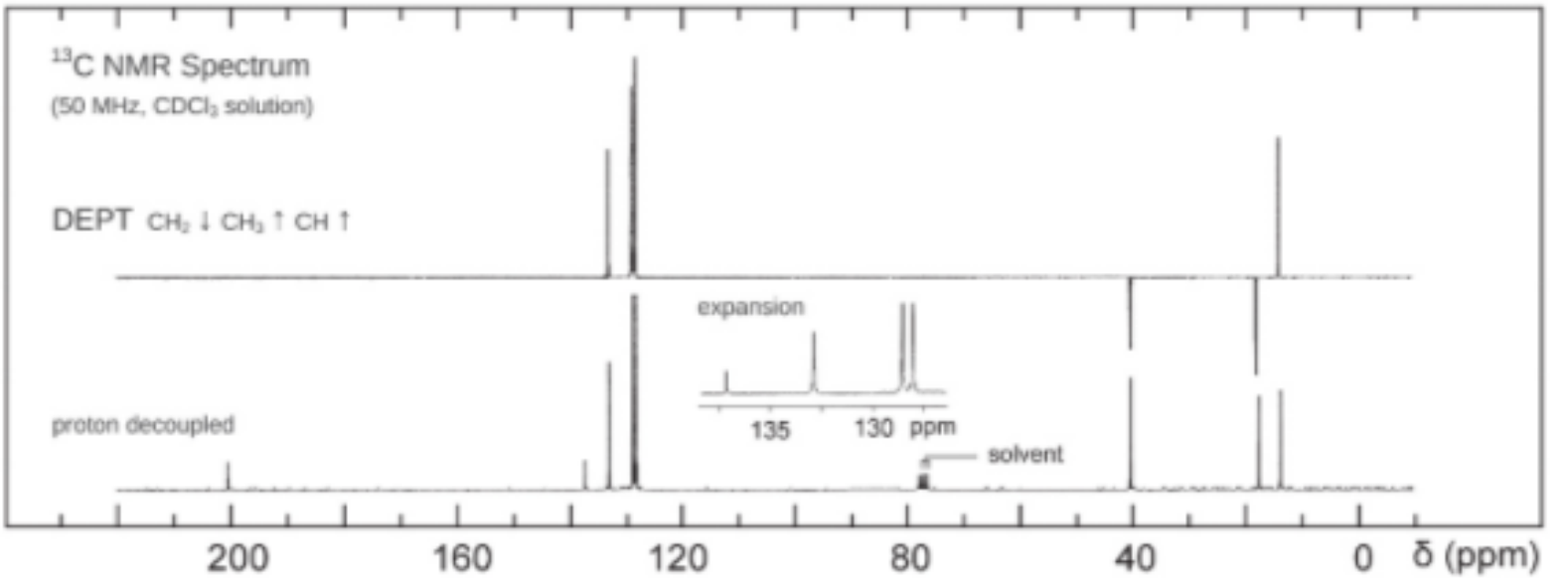


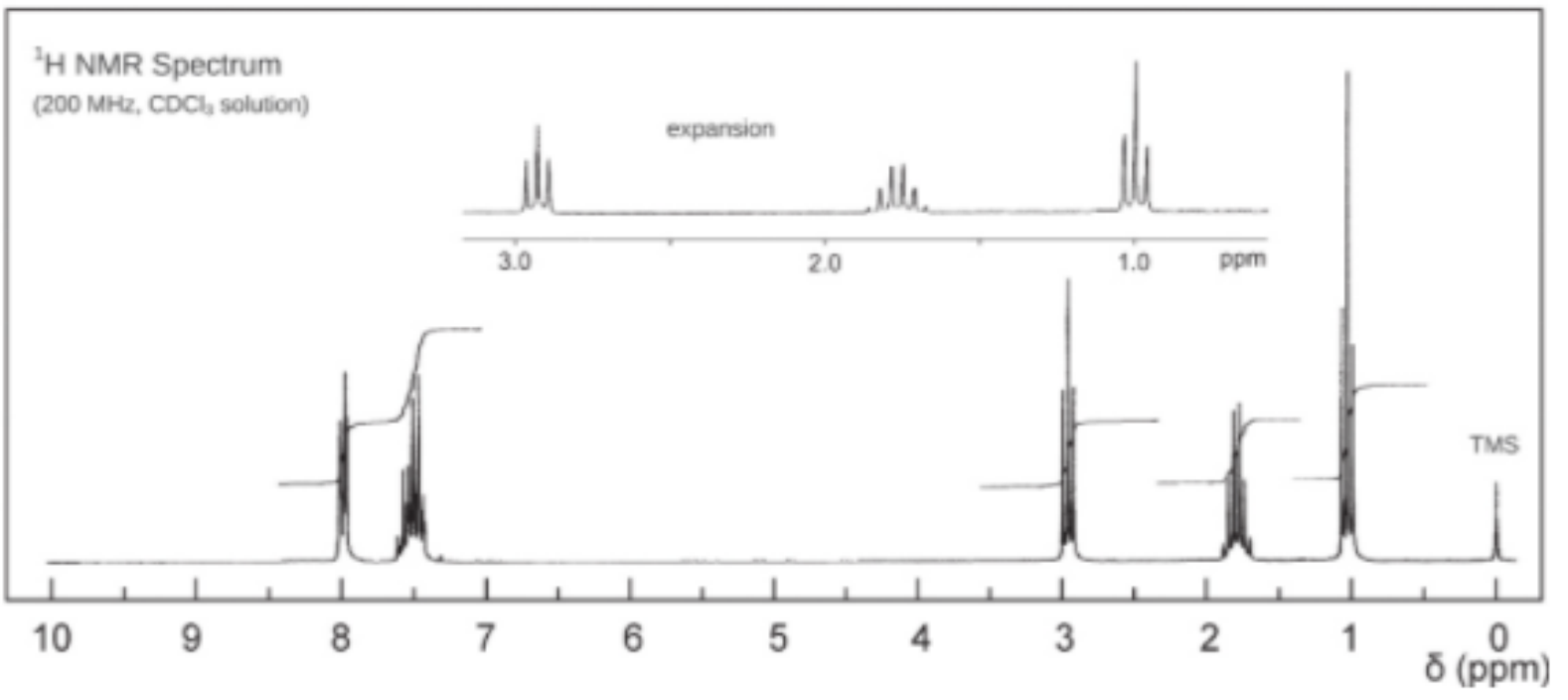


UV Spectrum

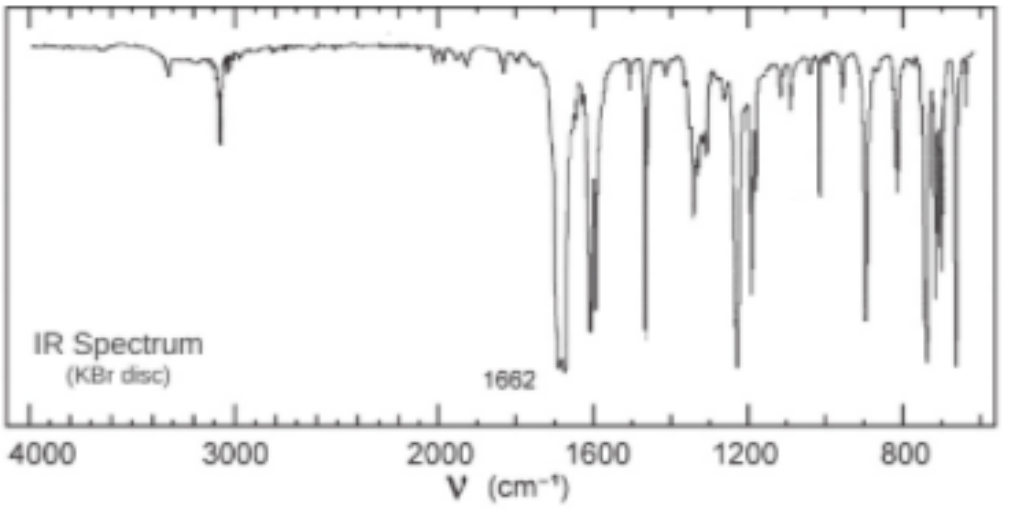
λ_{max} 241 nm ($\log_{10}\varepsilon$ 4.1)

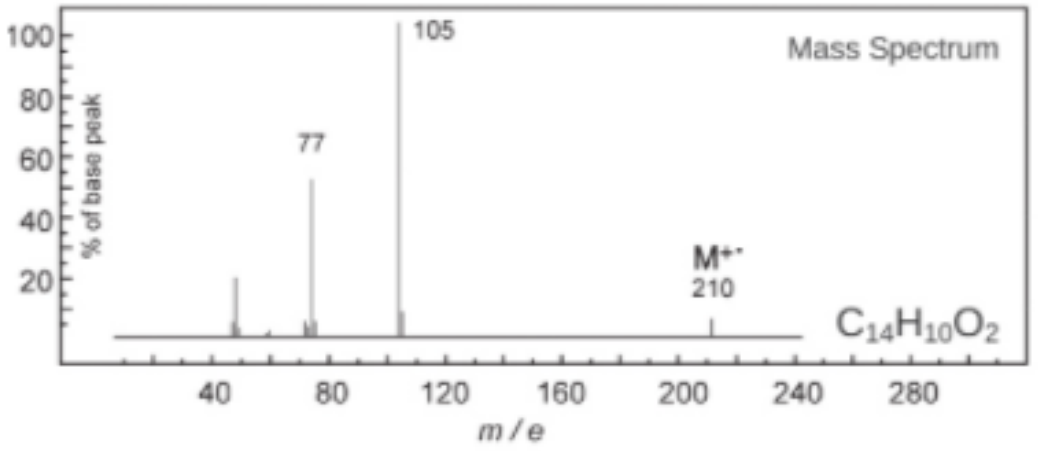
solvent: methanol





Problem 63





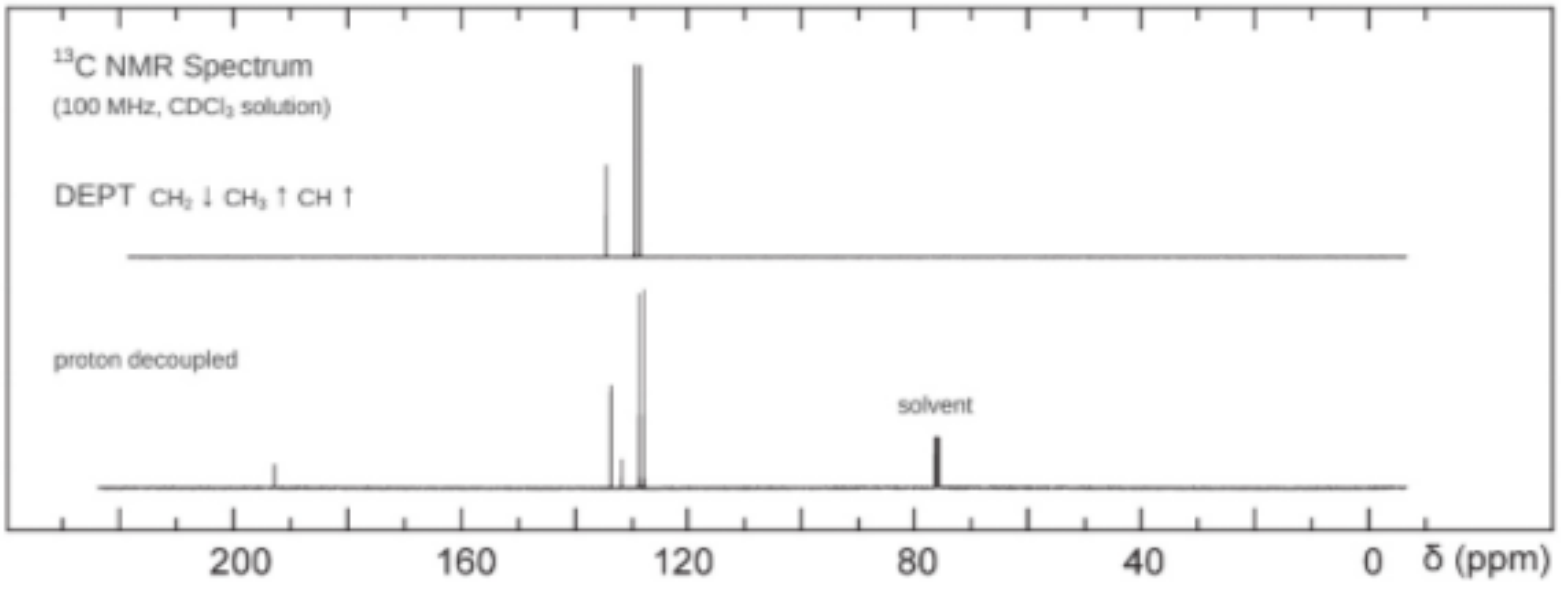
UV Spectrum

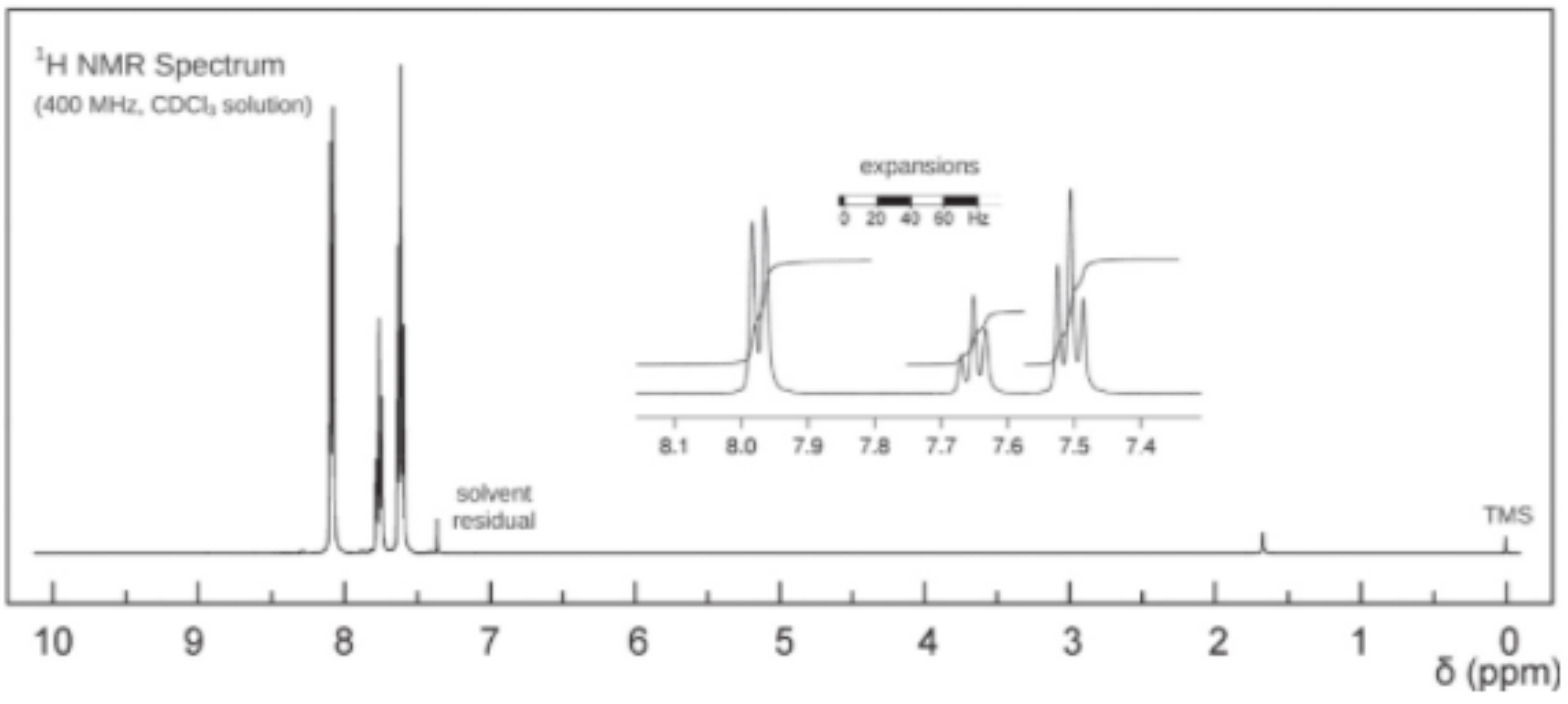
λ_{max} 258 nm ($\log_{10}\varepsilon$ 4.2)

λ_{max} 330 nm ($\log_{10}\varepsilon$ 2.8)

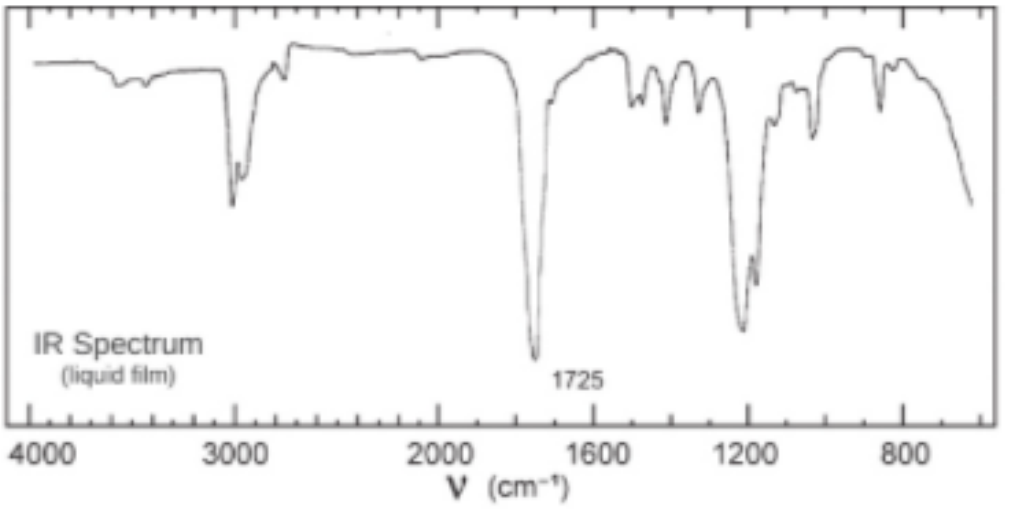
λ_{max} 388 nm ($\log_{10}\varepsilon$ 2.2)

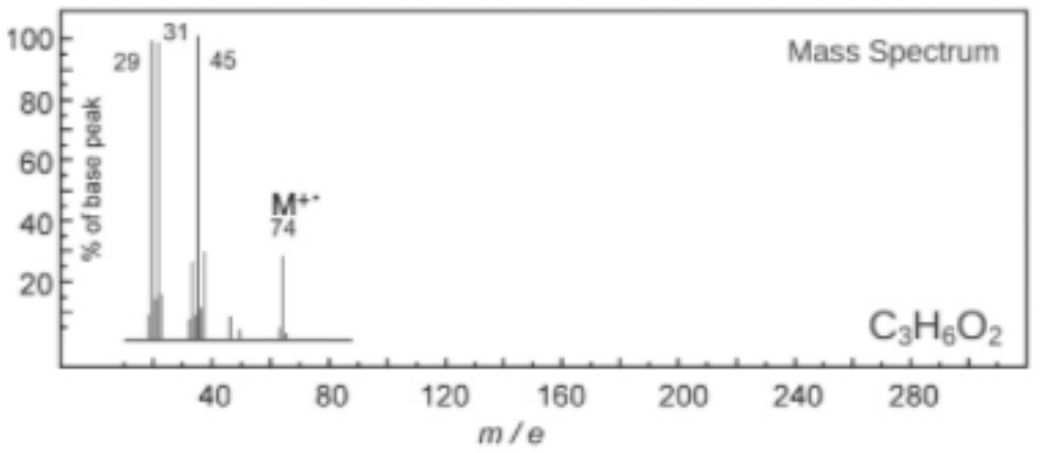
solvent: ethanol



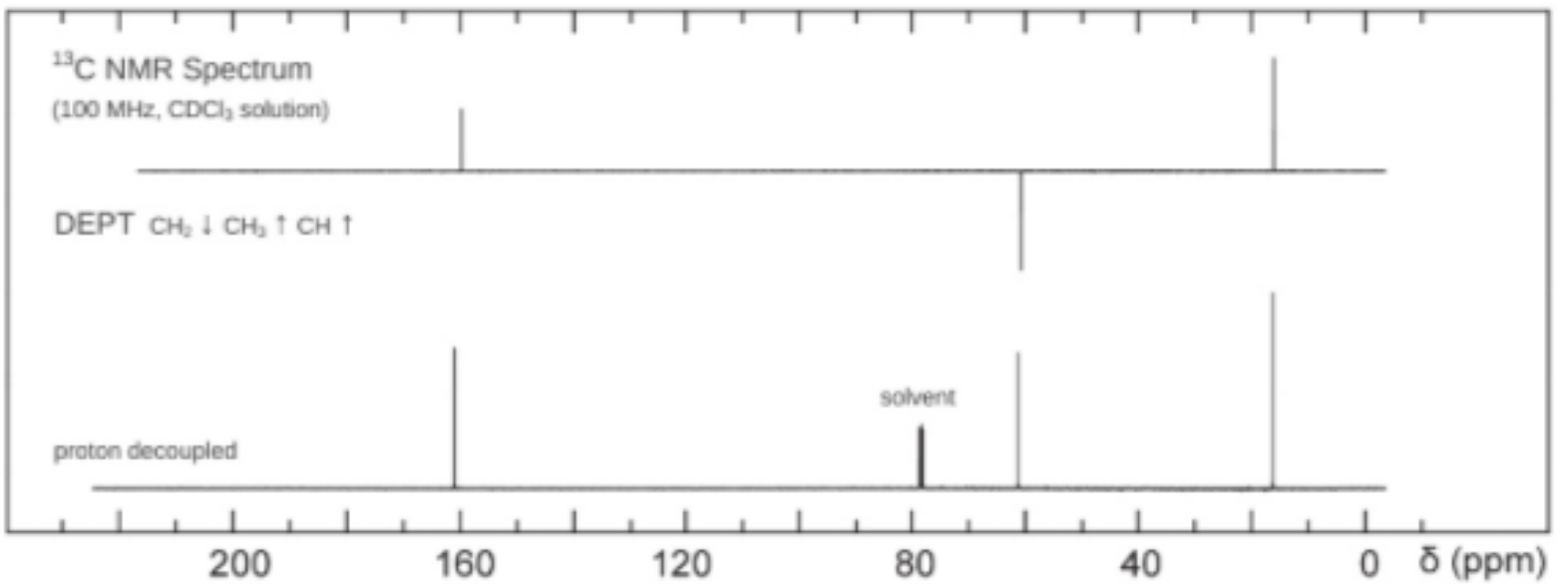


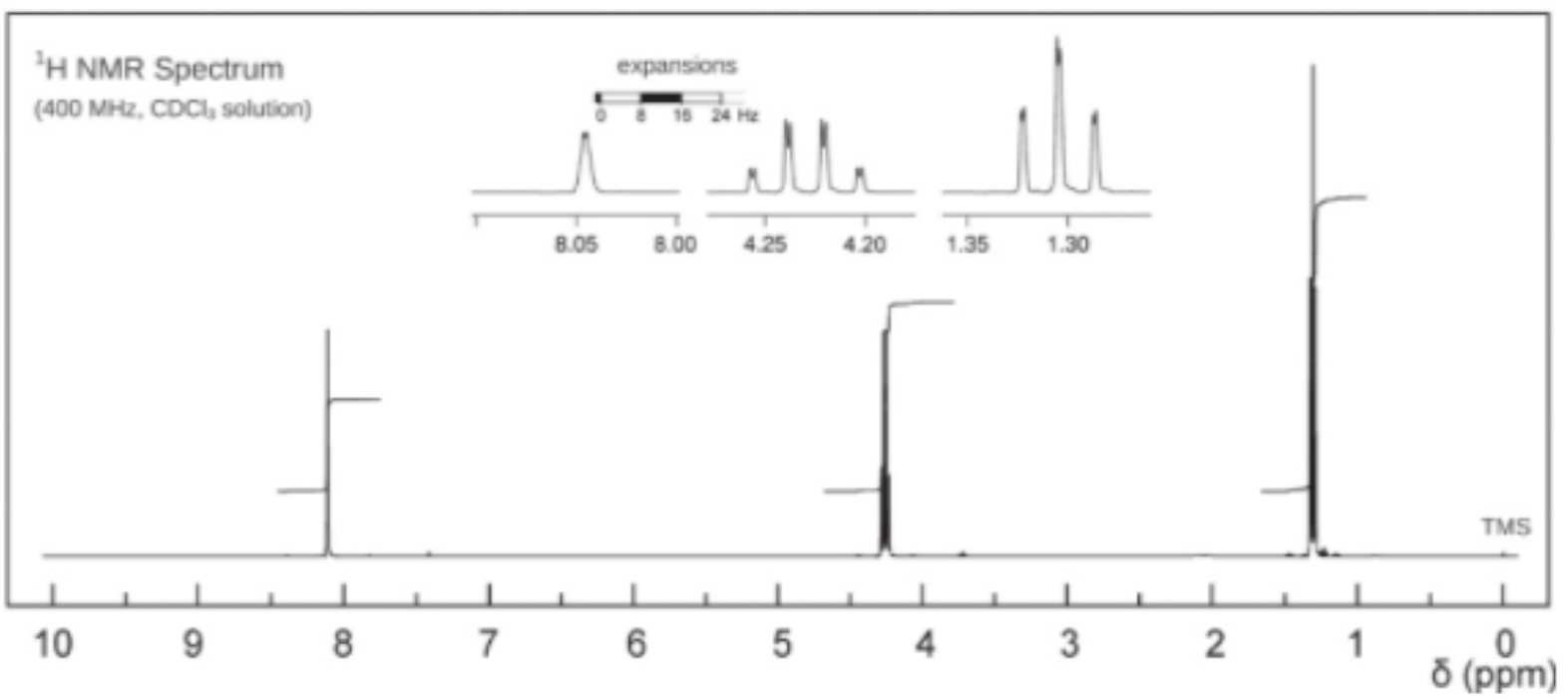
Problem 64



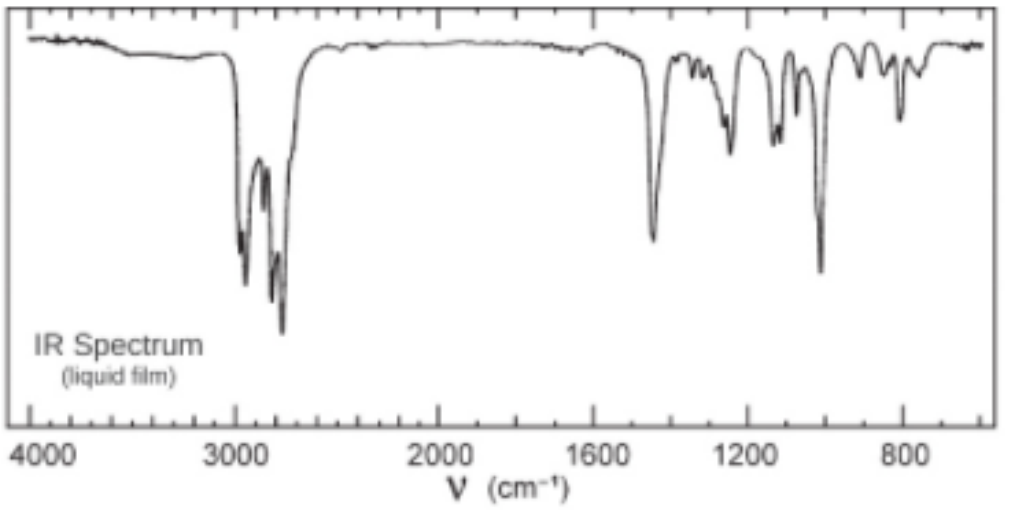


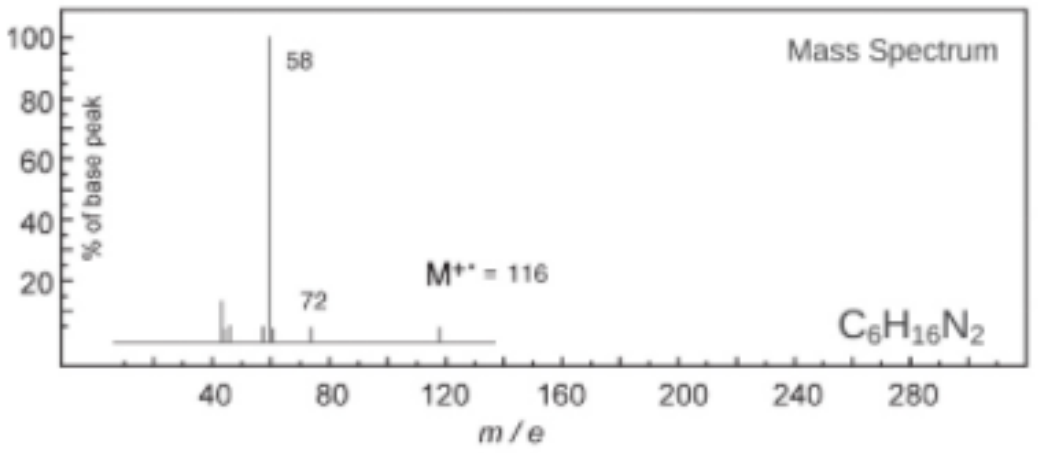
No significant UV absorption above 220 nm



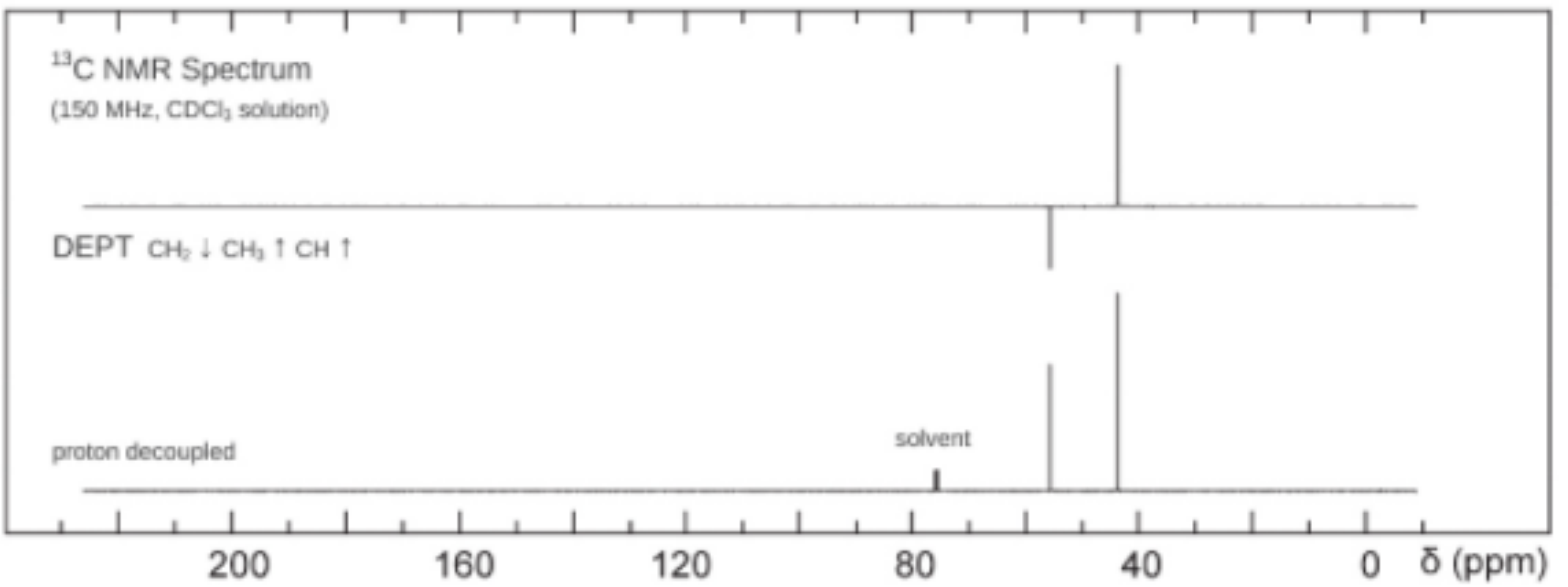


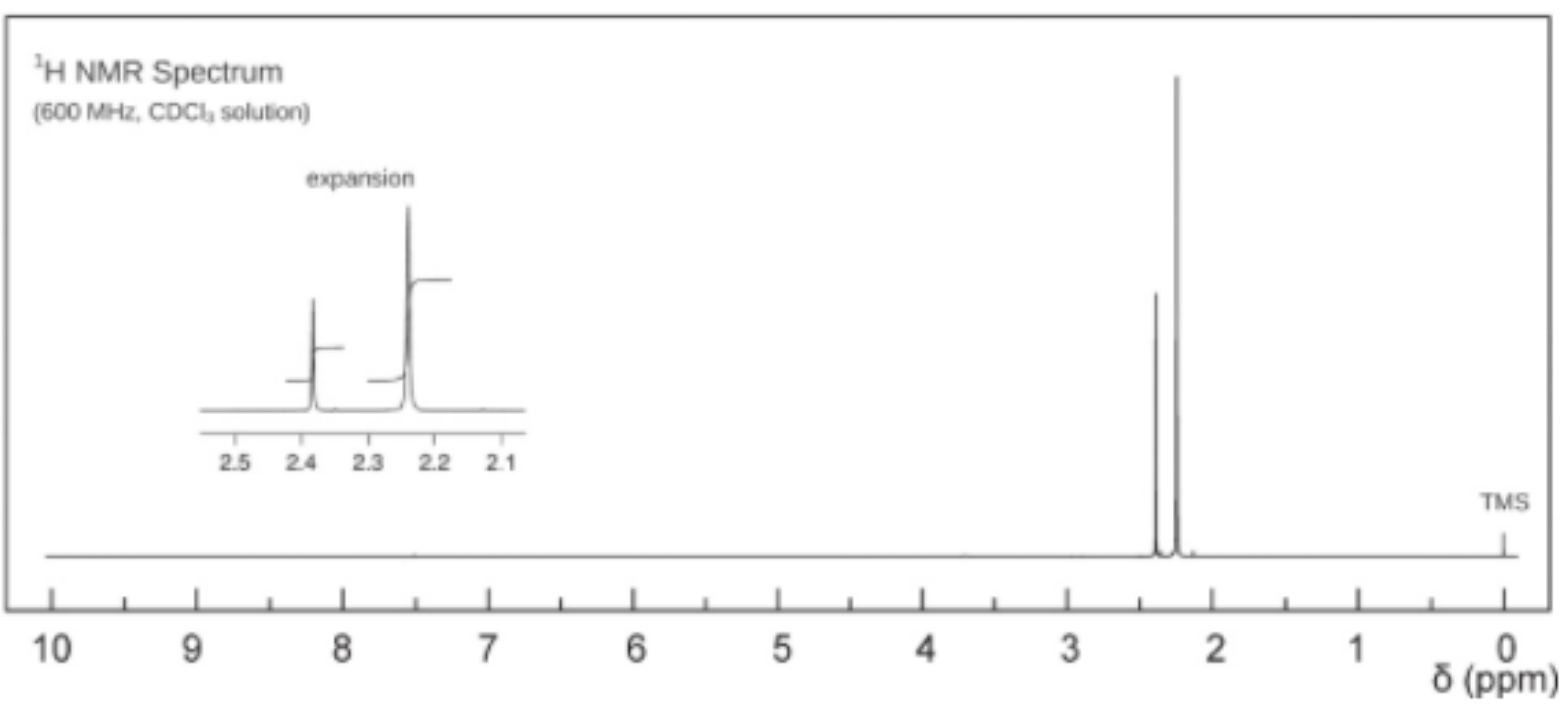
Problem 65



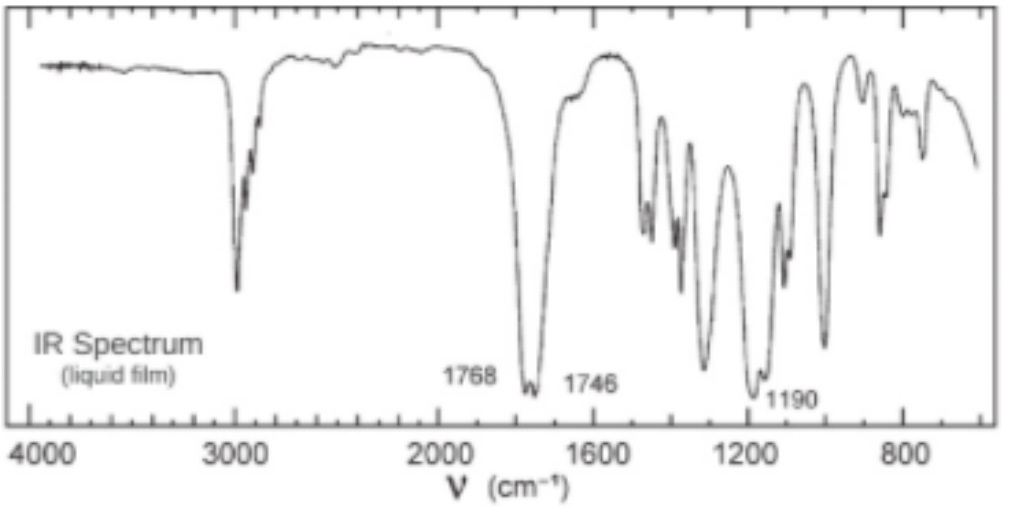


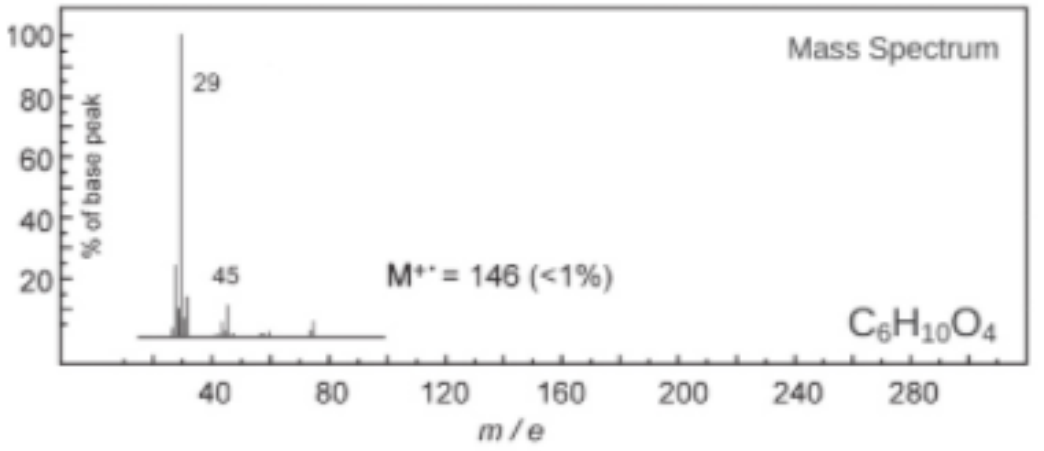
No significant UV absorption above 220 nm

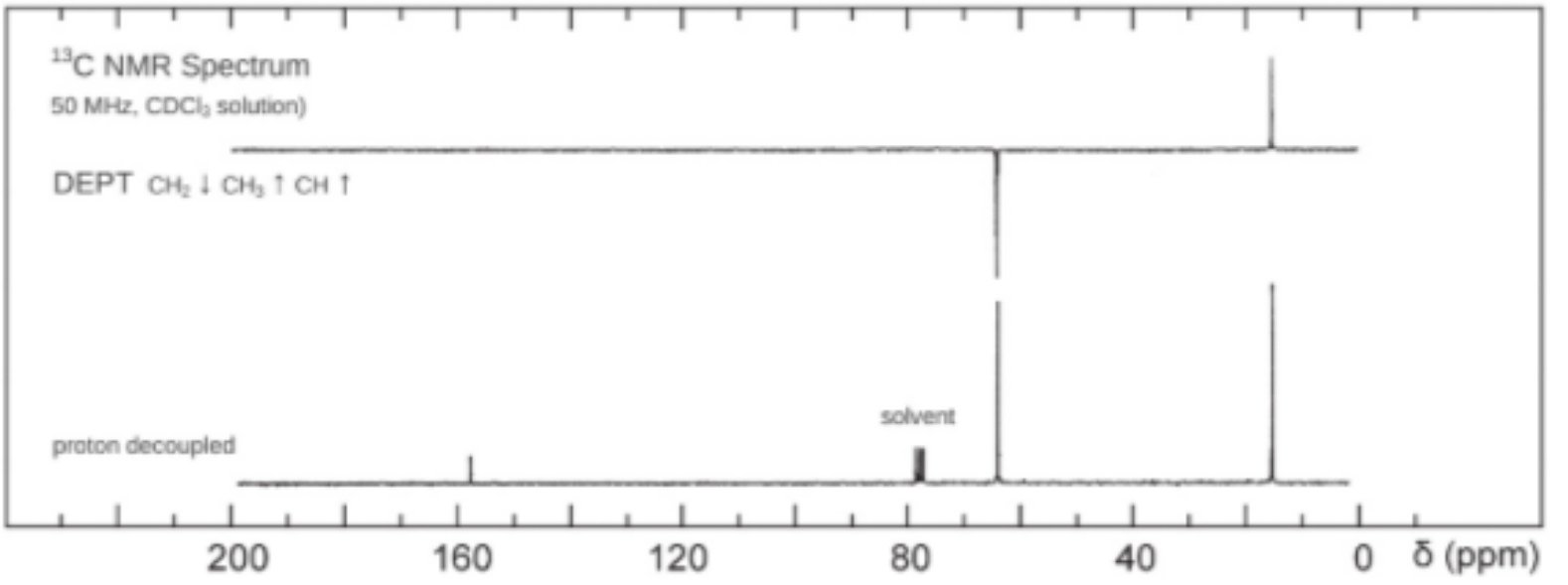


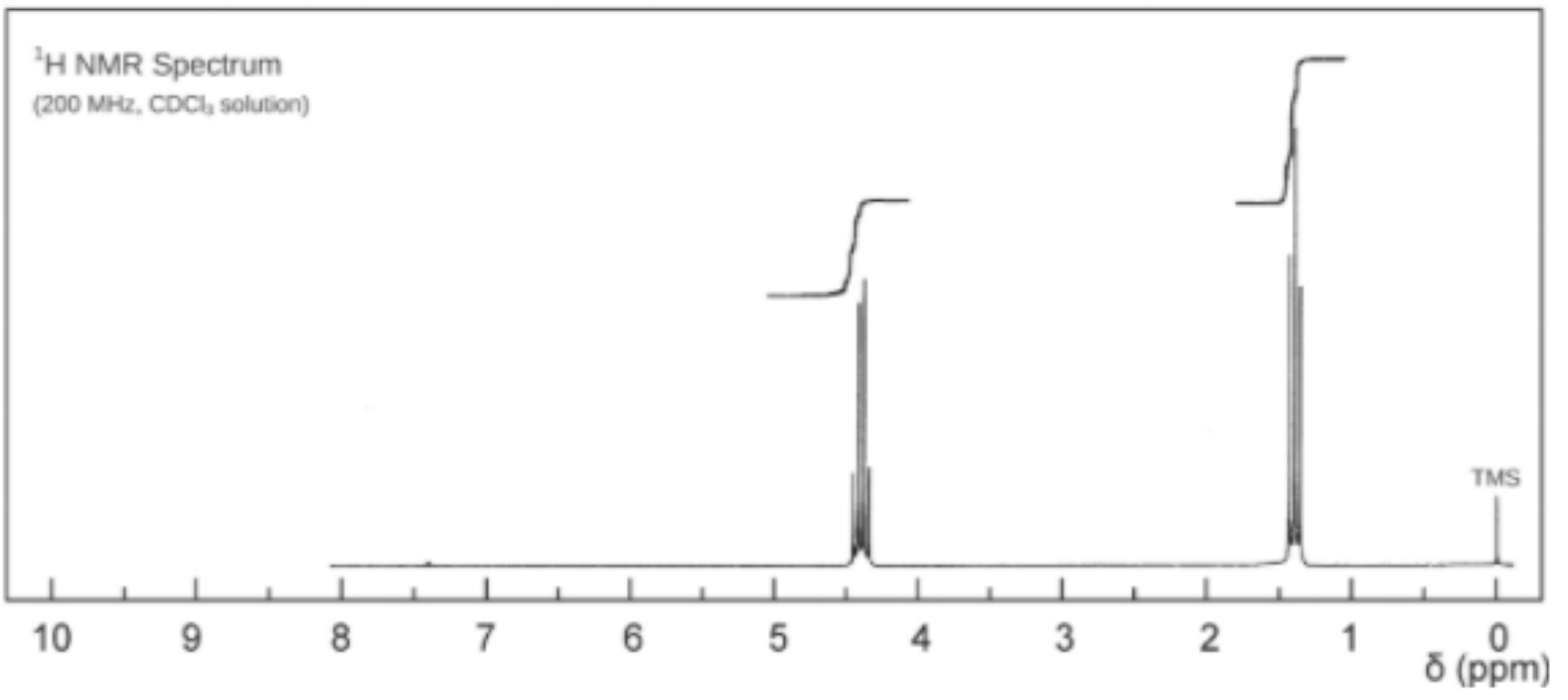


Problem 66

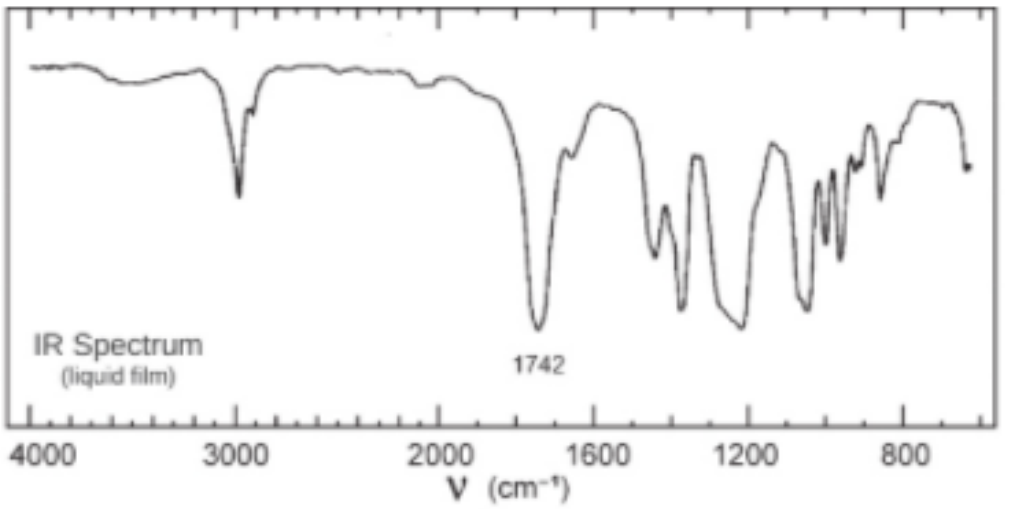

IR Spectrum
(liquid film)
1768
1746
1190
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

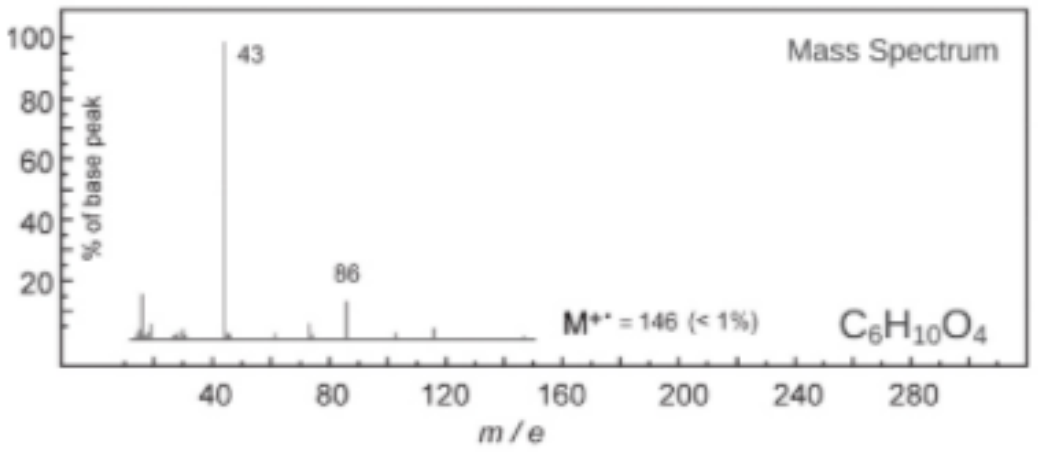

Mass Spectrum
100
80
60
40
20
% of base peak
29
45
M+· = 146 (<1%)
C6H10O4
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
50 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

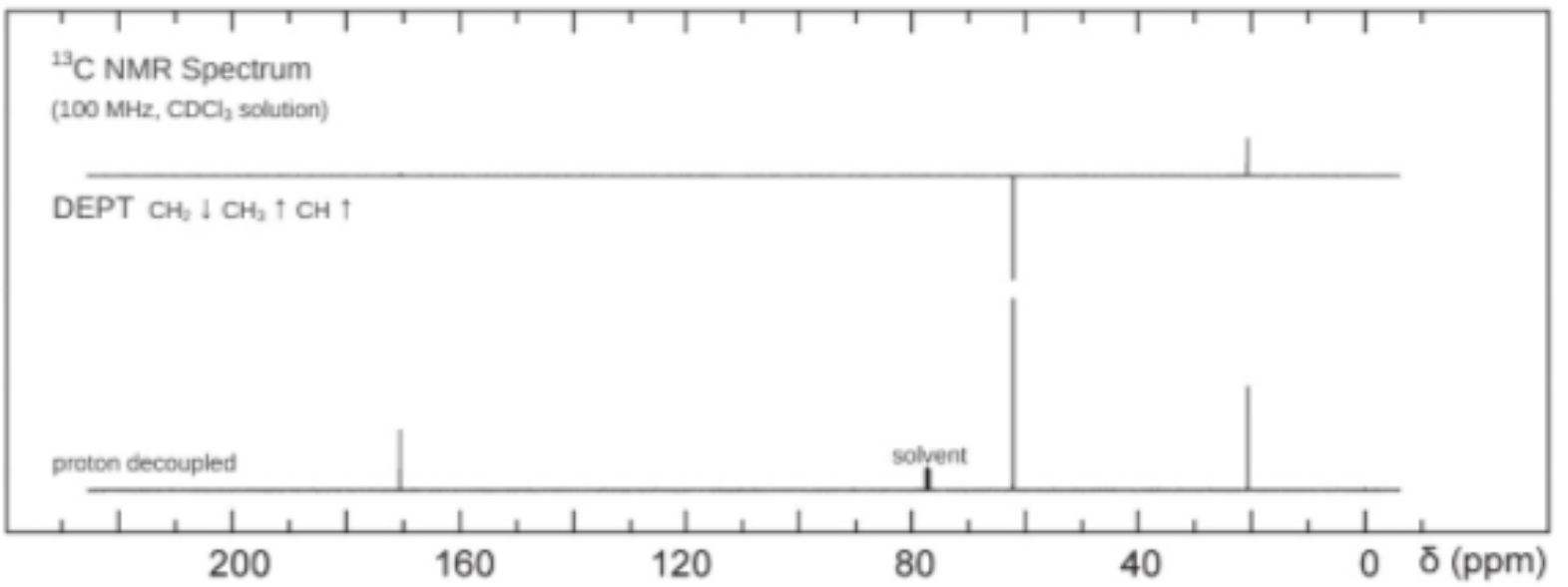

1H NMR Spectrum
(200 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

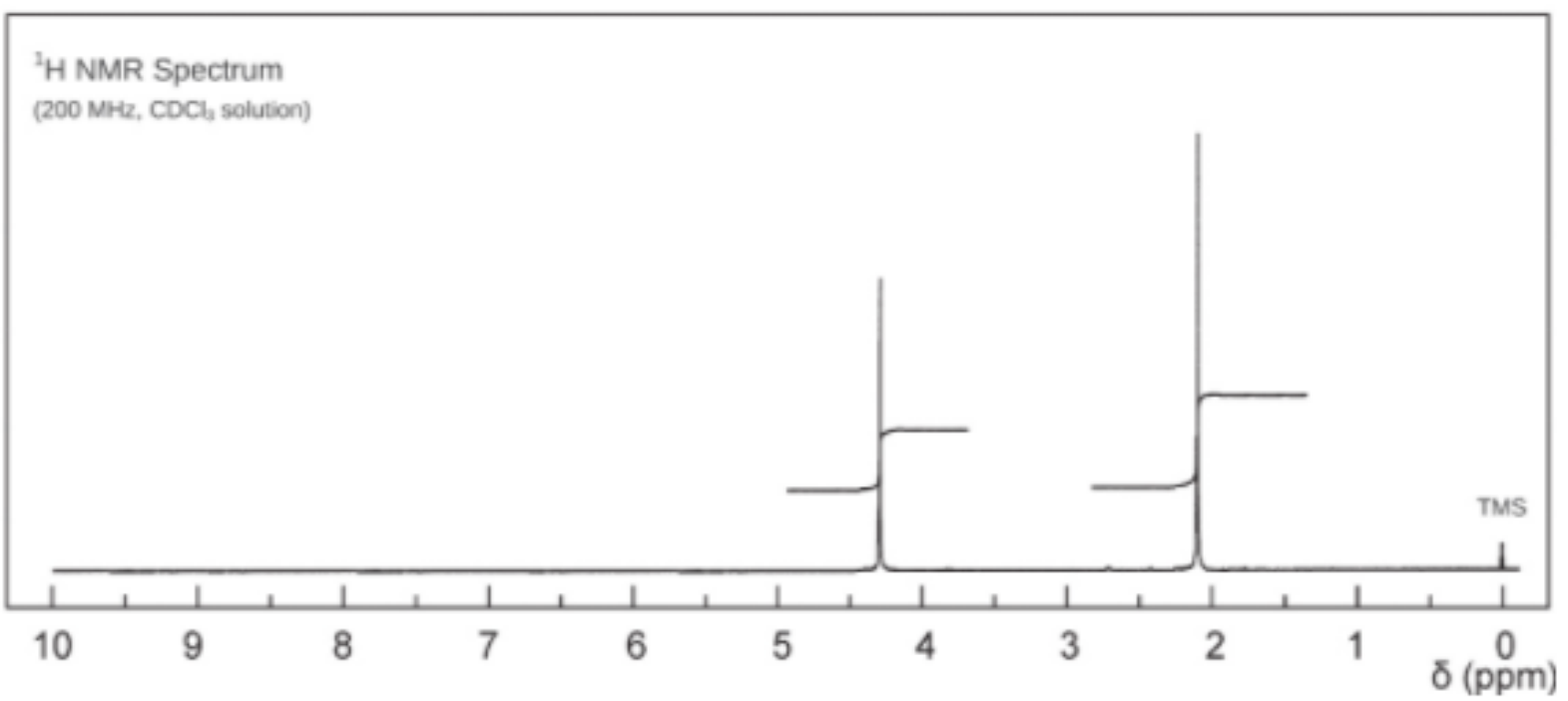
Problem 67



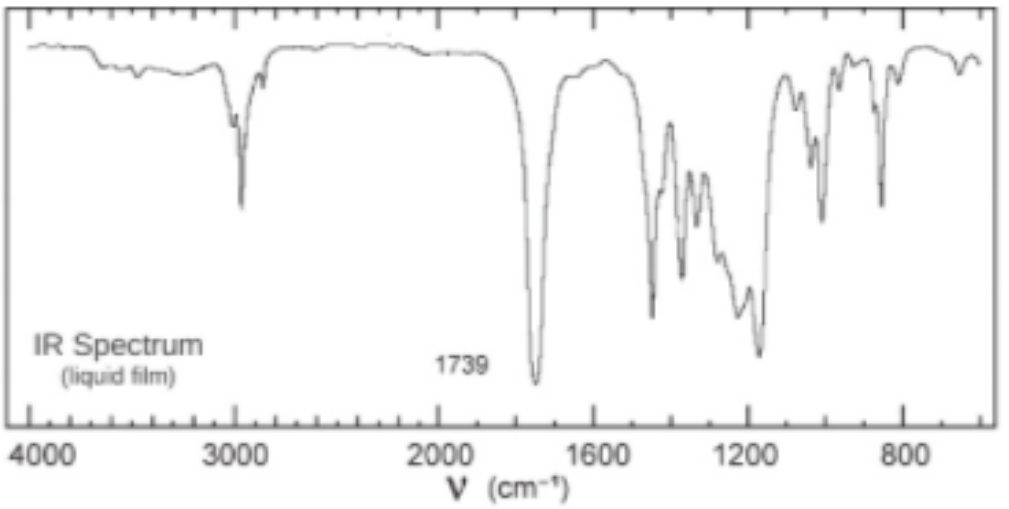


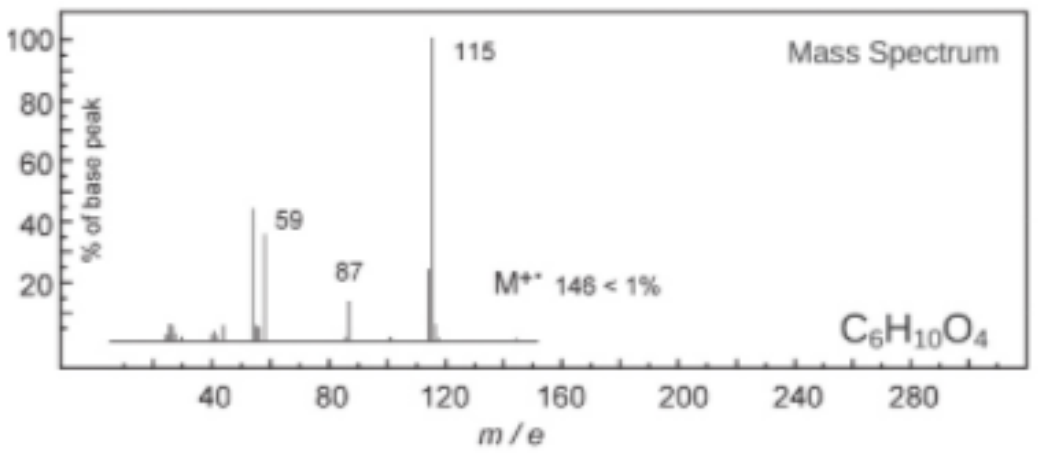
No significant UV absorption above 220 nm



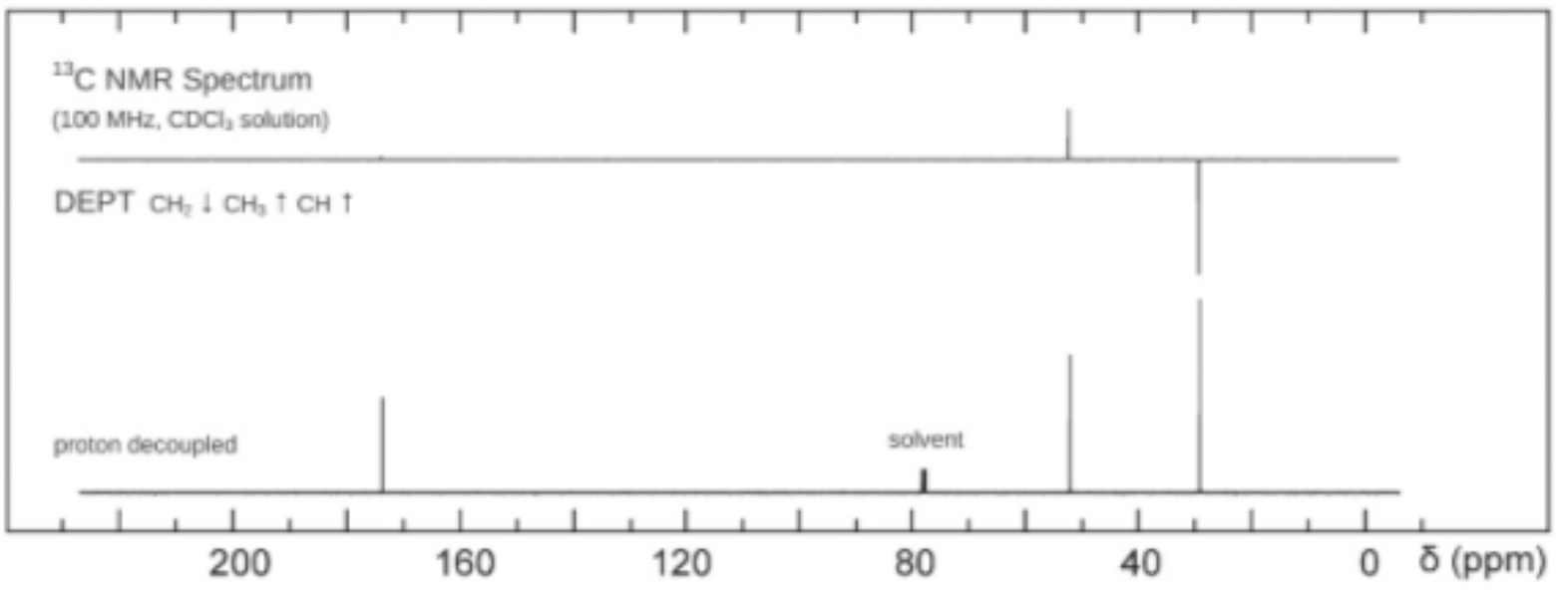


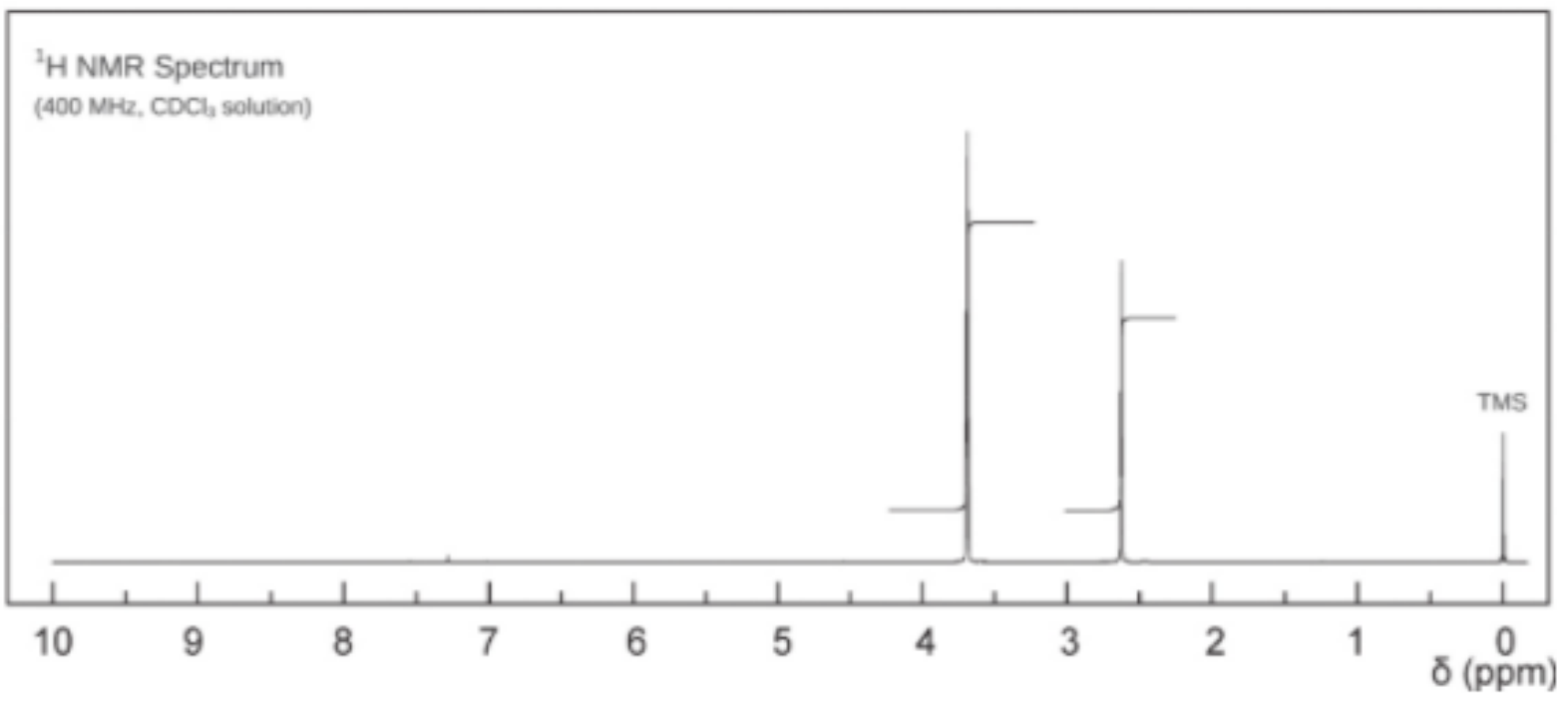
Problem 68



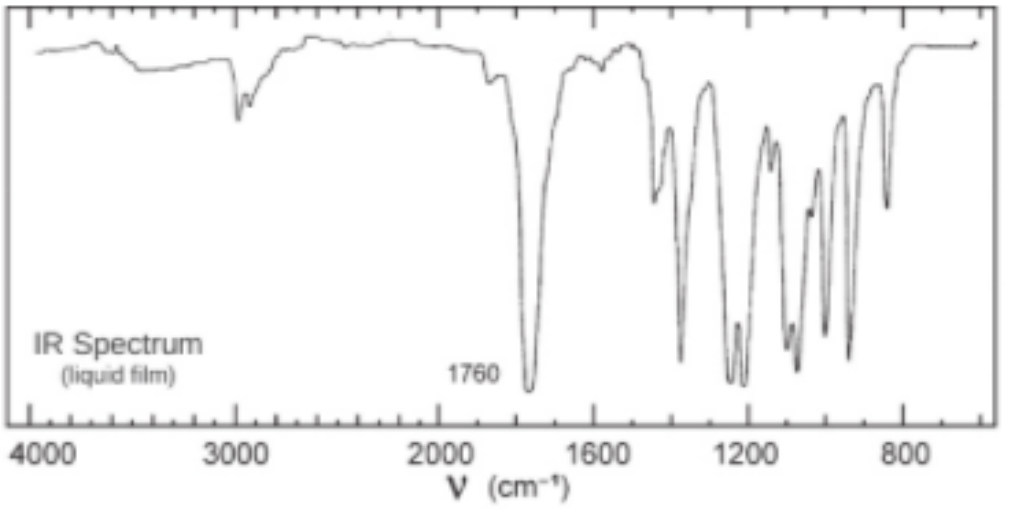


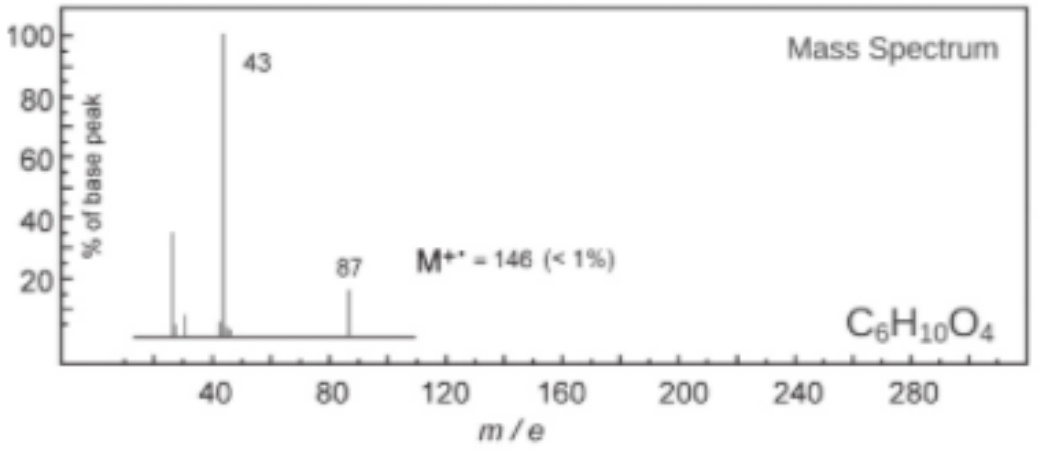
No significant UV absorption above 220 nm



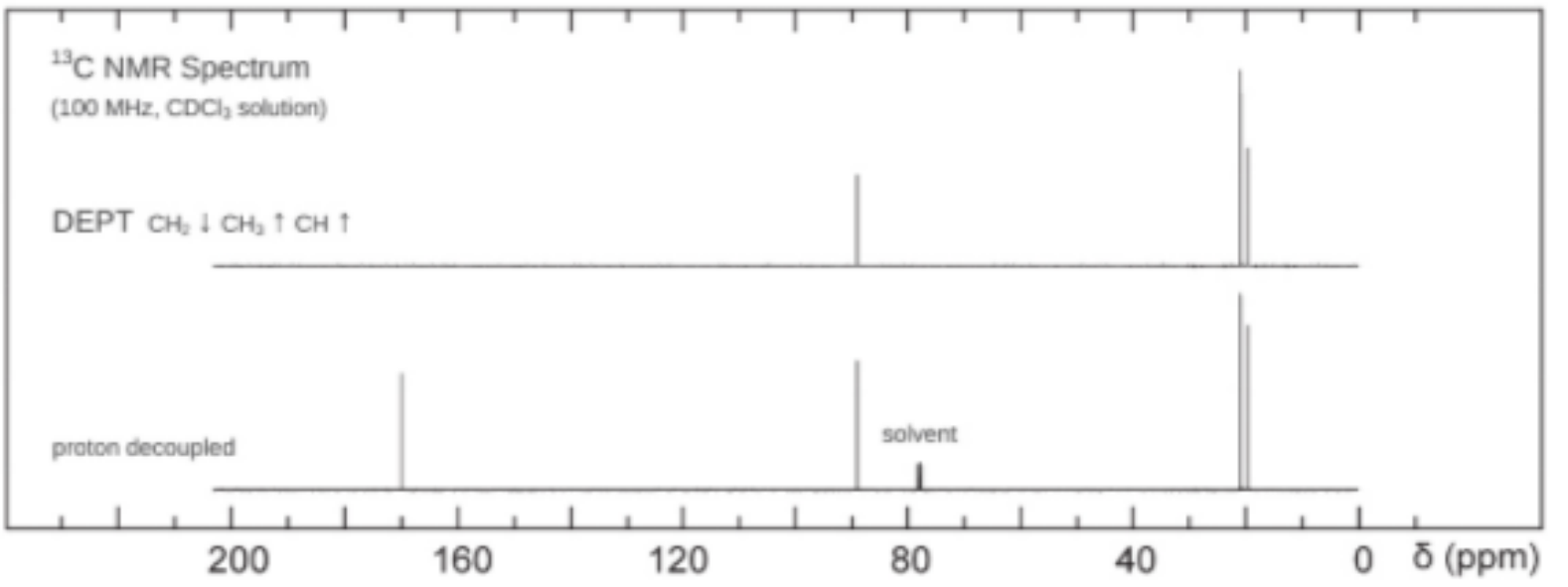


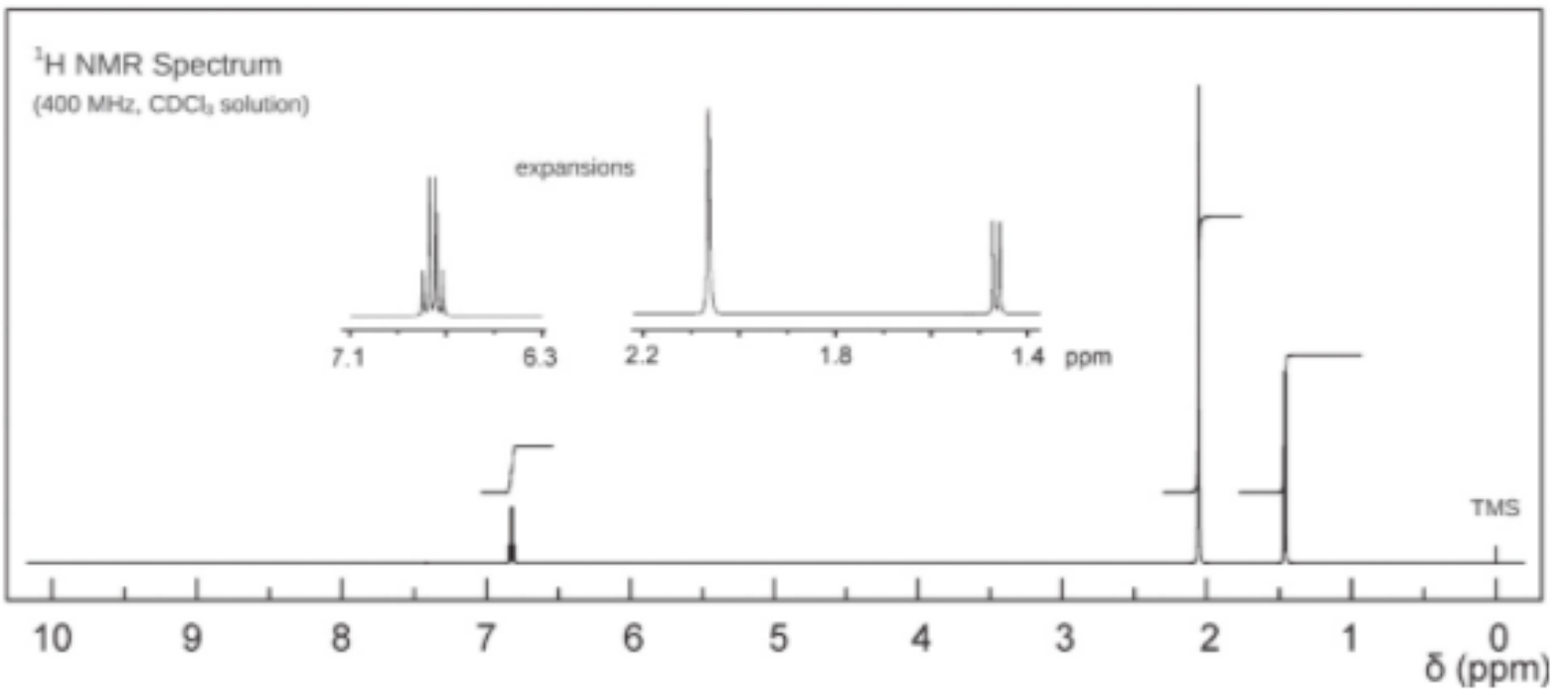
Problem 69



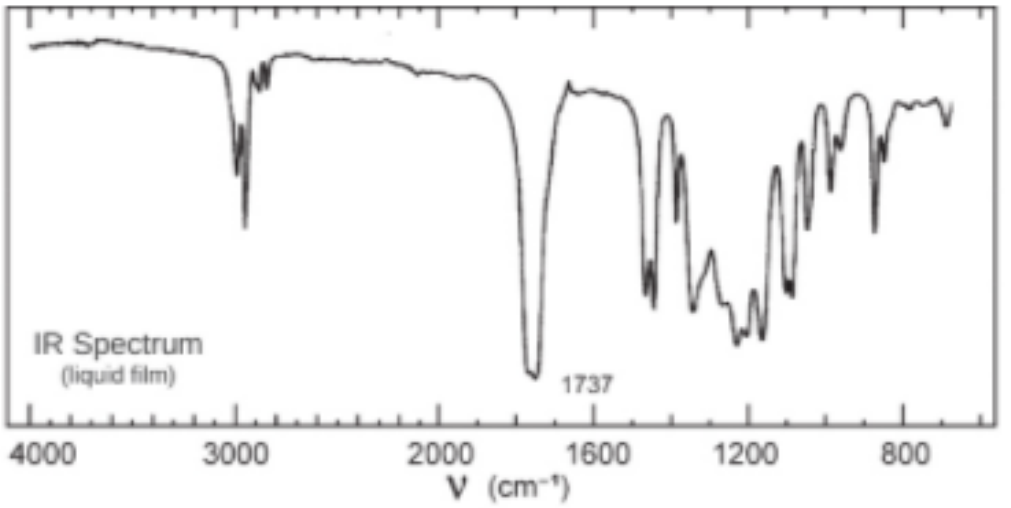


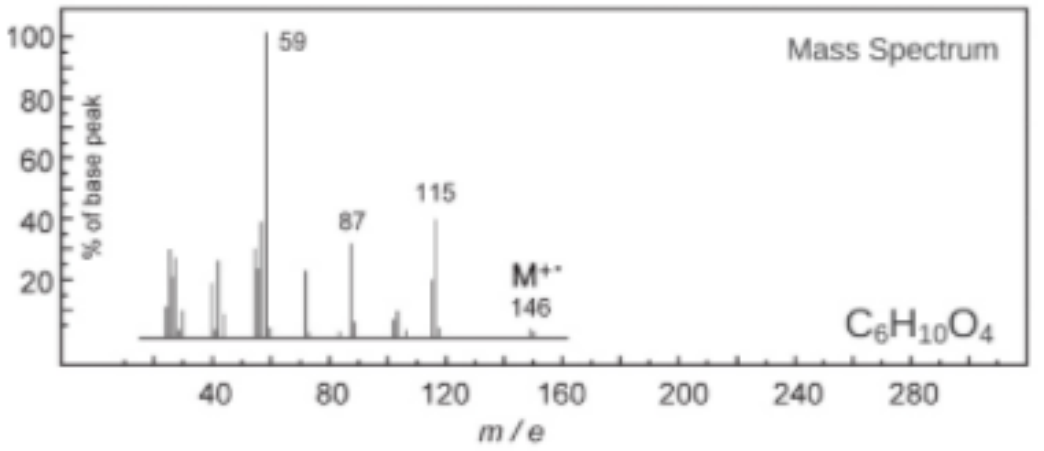
No significant UV absorption above 220 nm



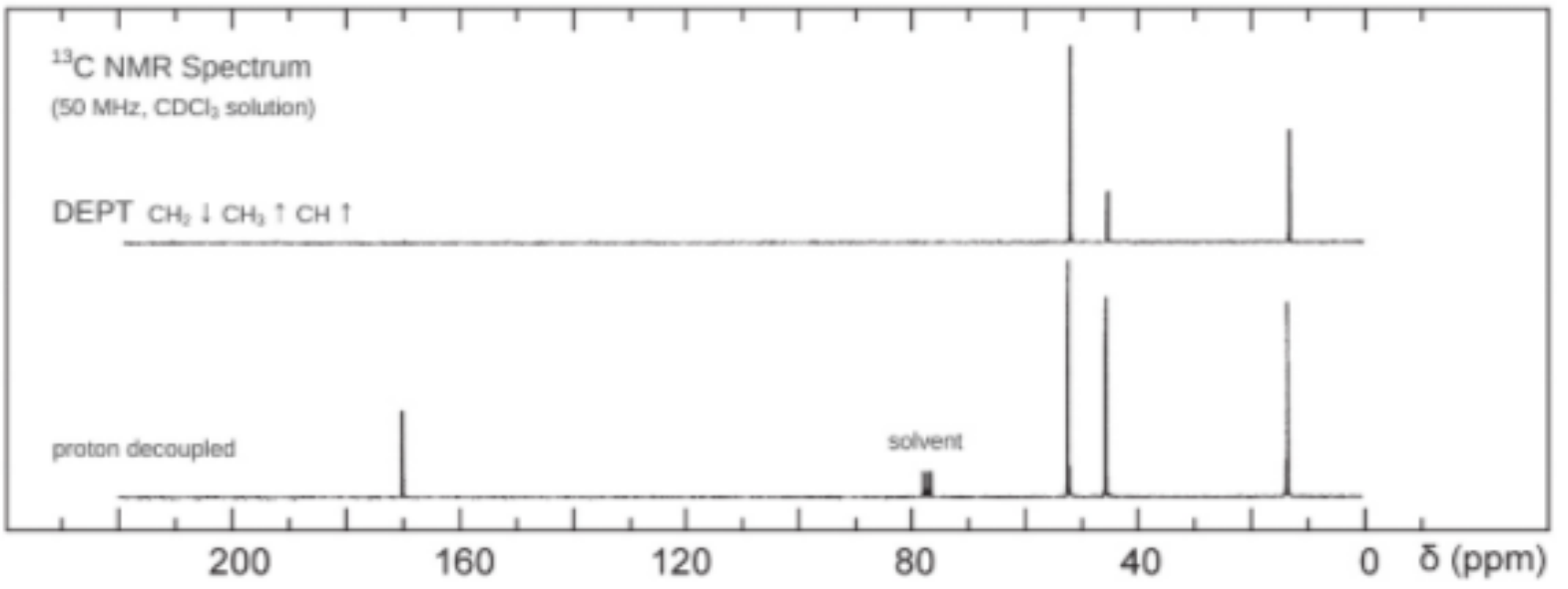


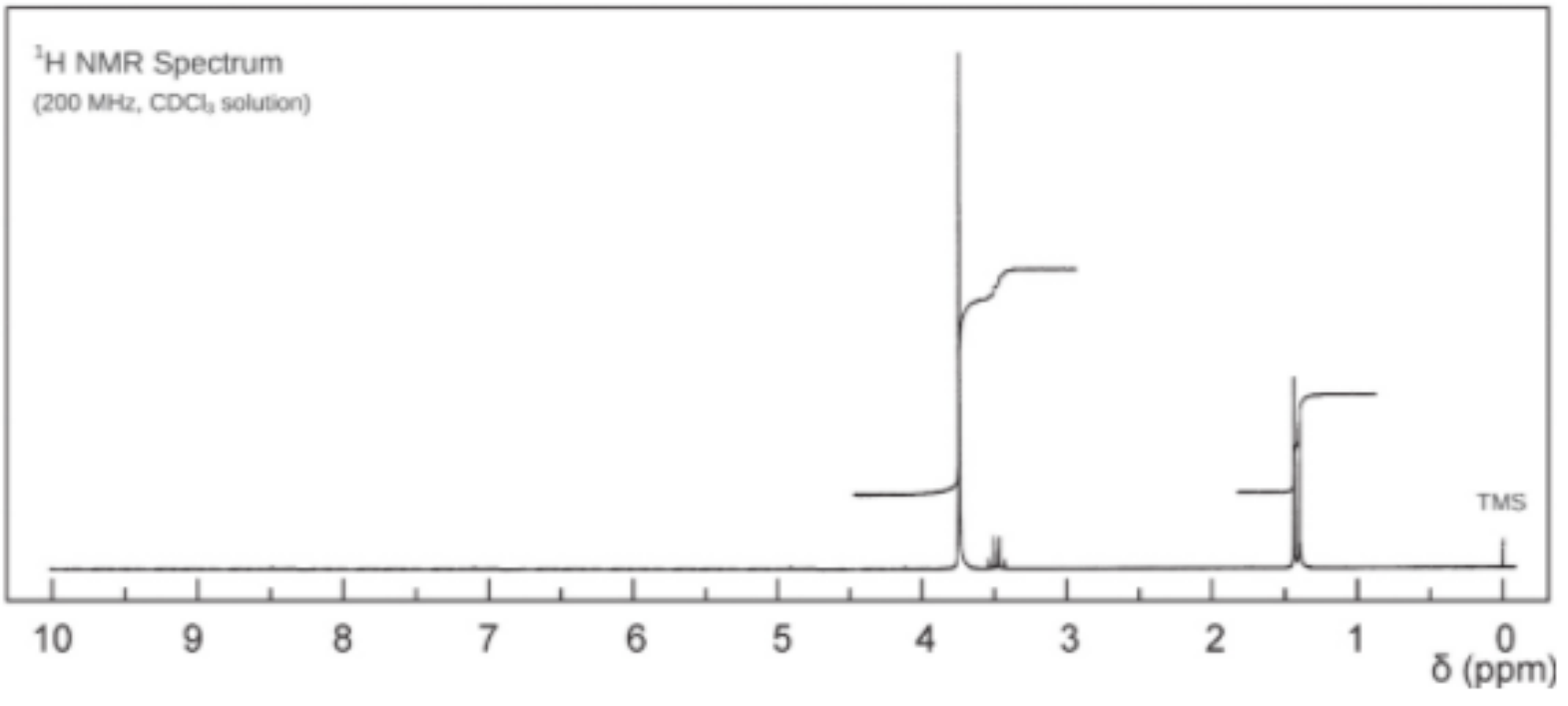
Problem 70



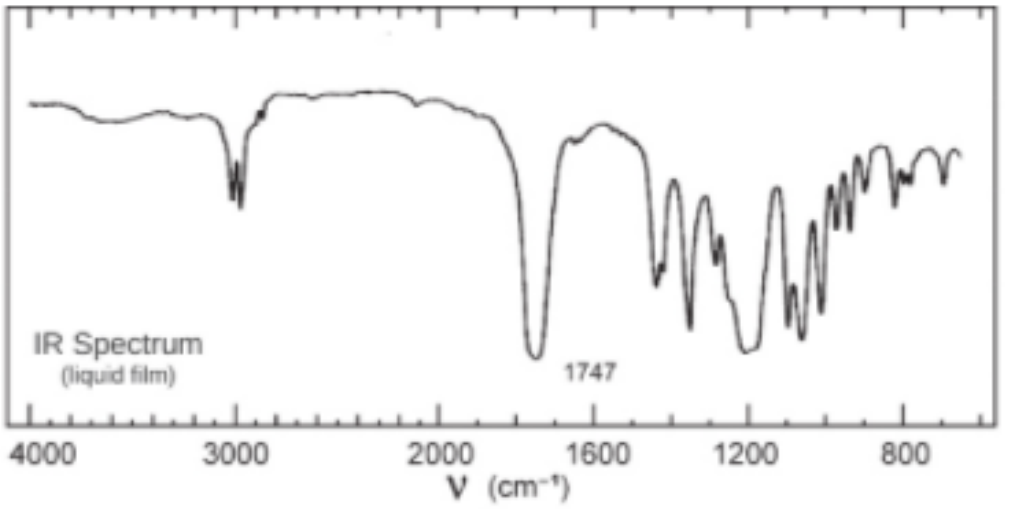


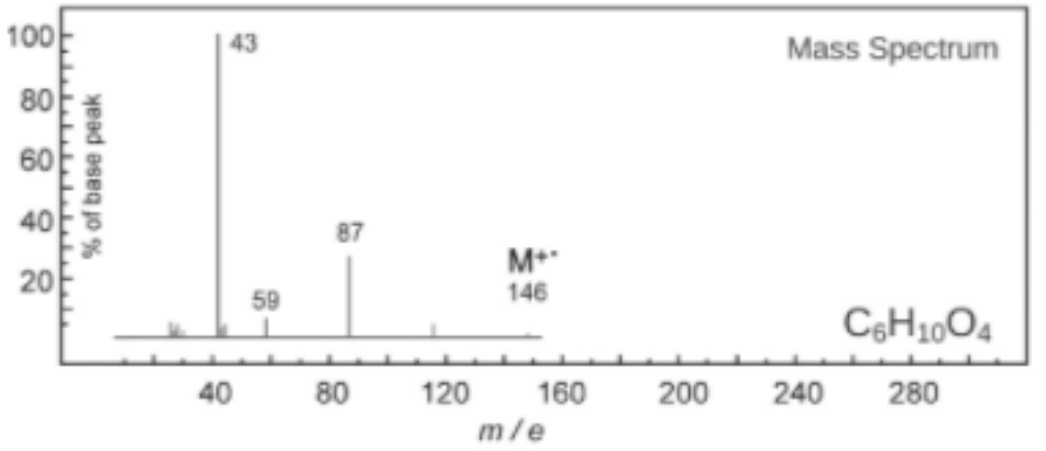
No significant UV absorption above 220 nm



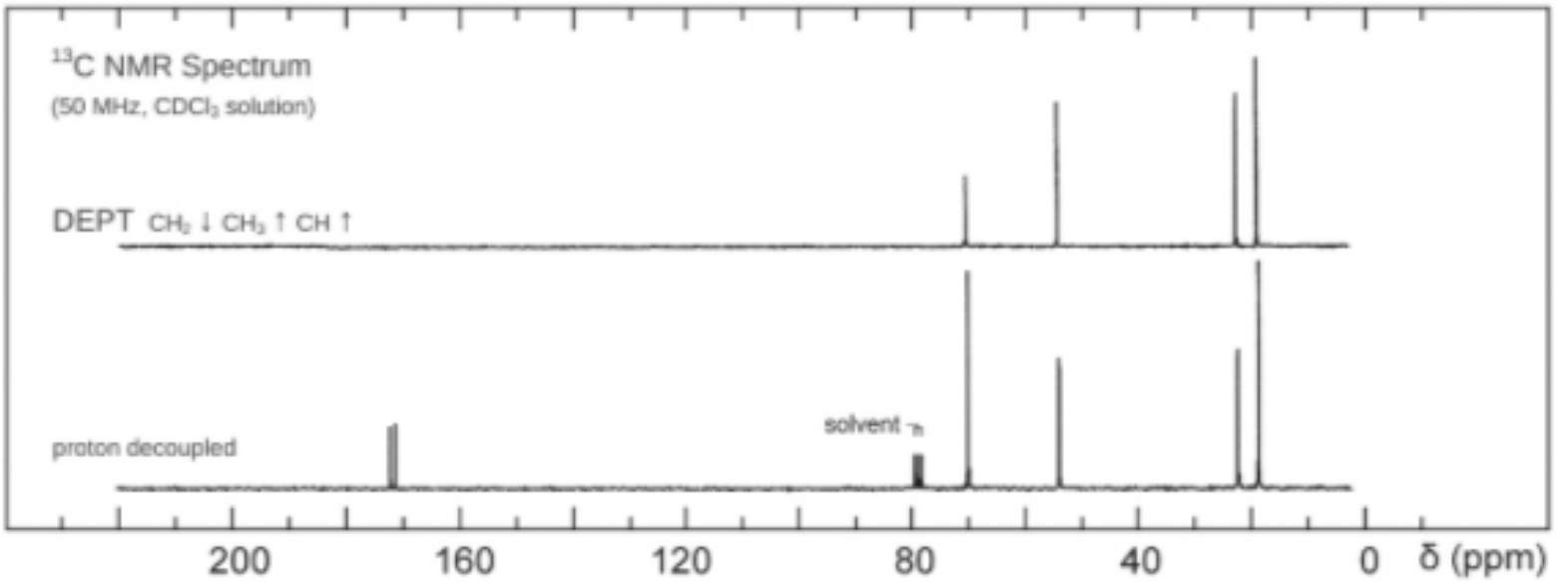


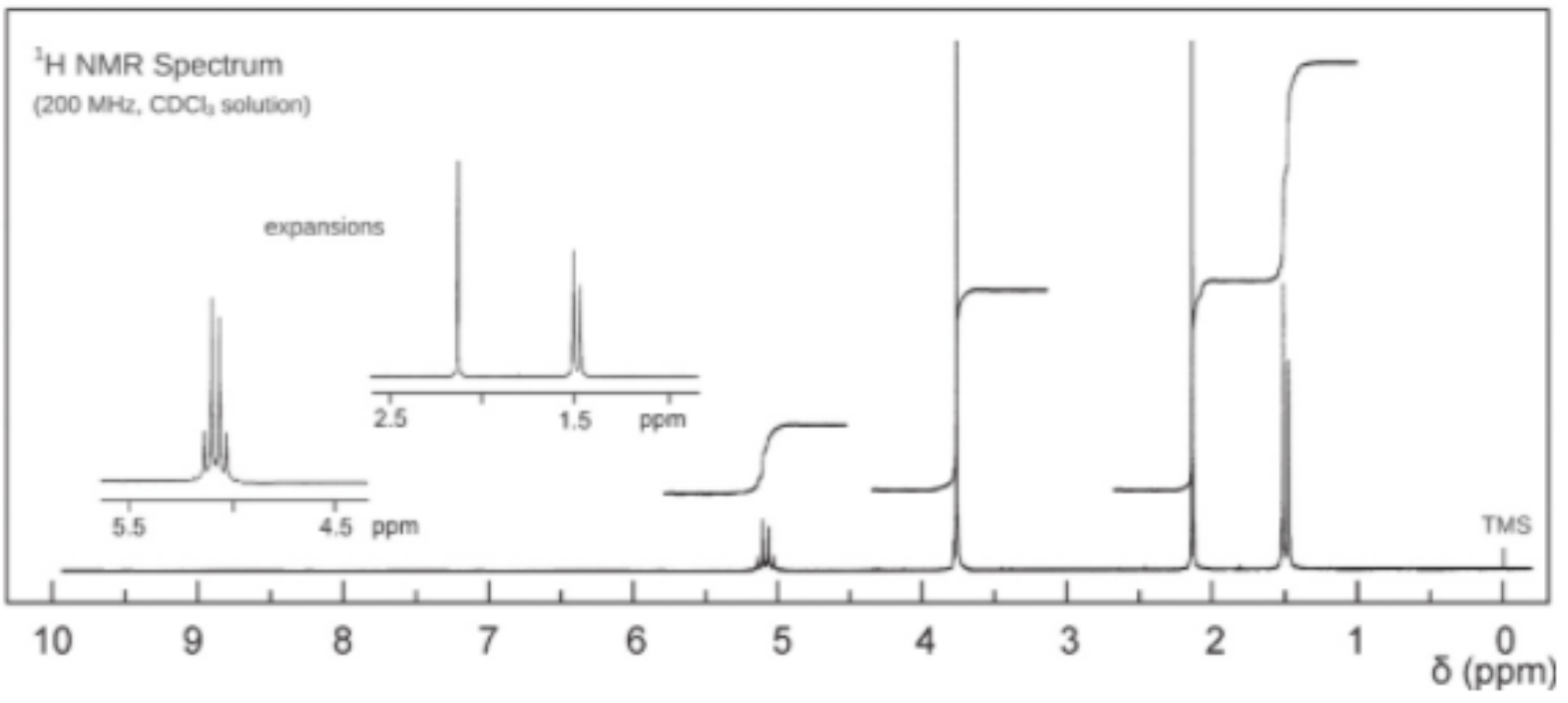
Problem 71



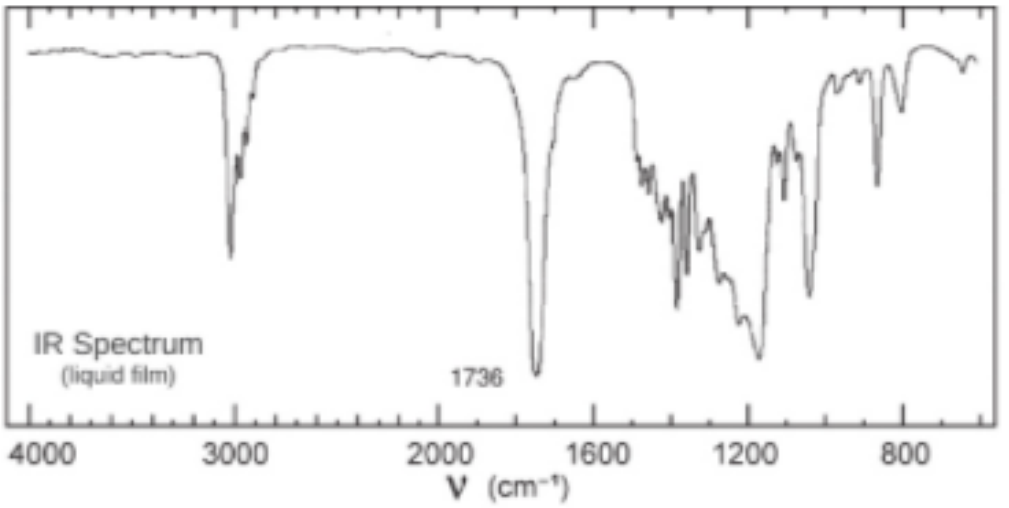


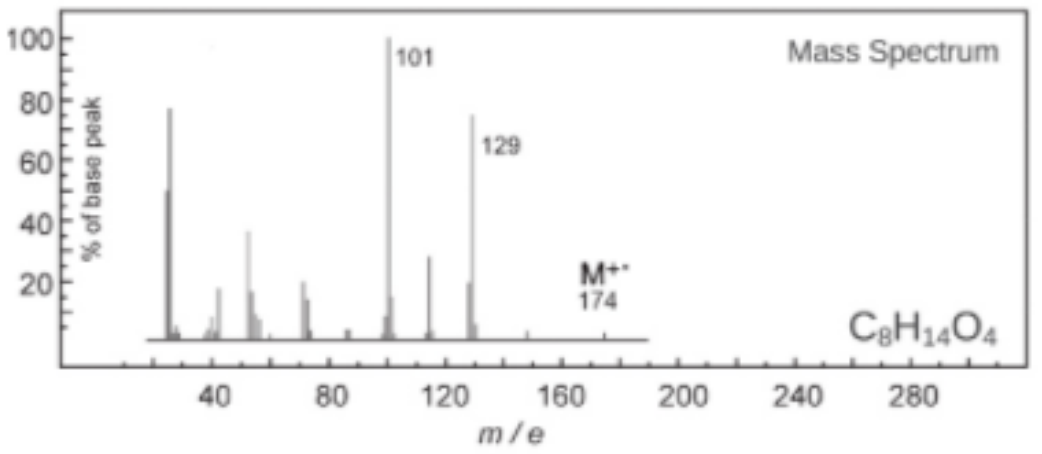
No significant UV absorption above 220 nm



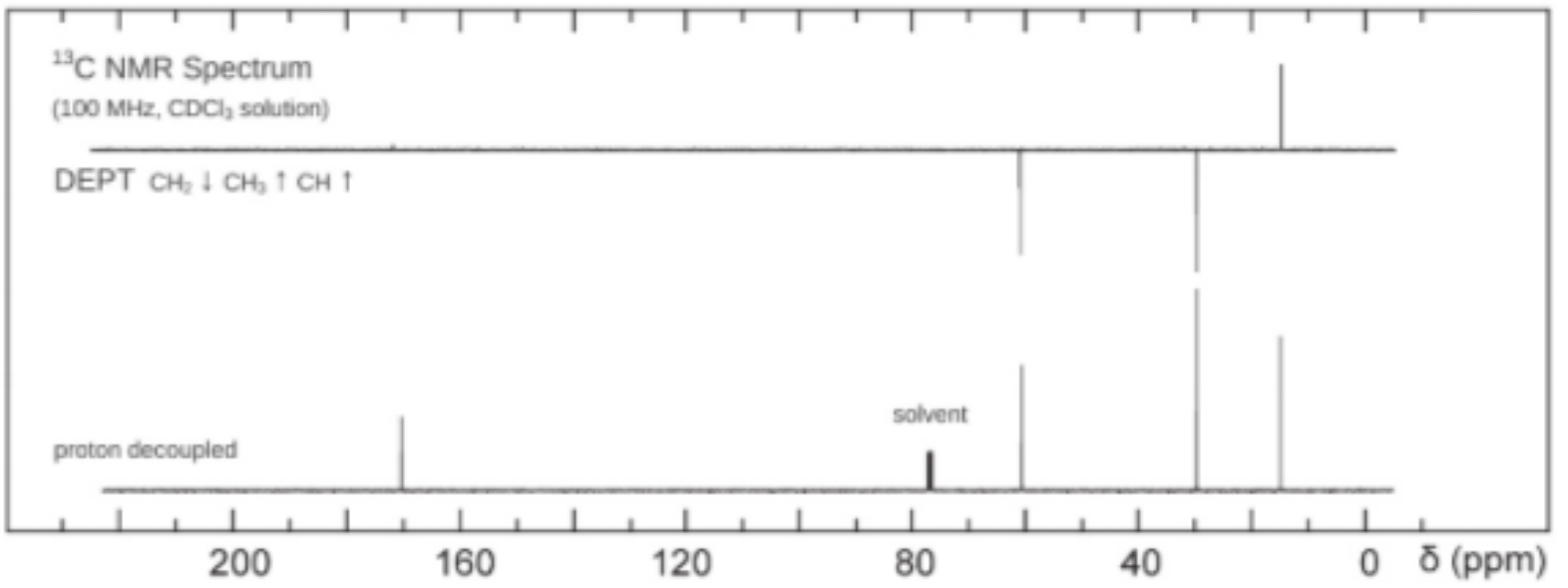


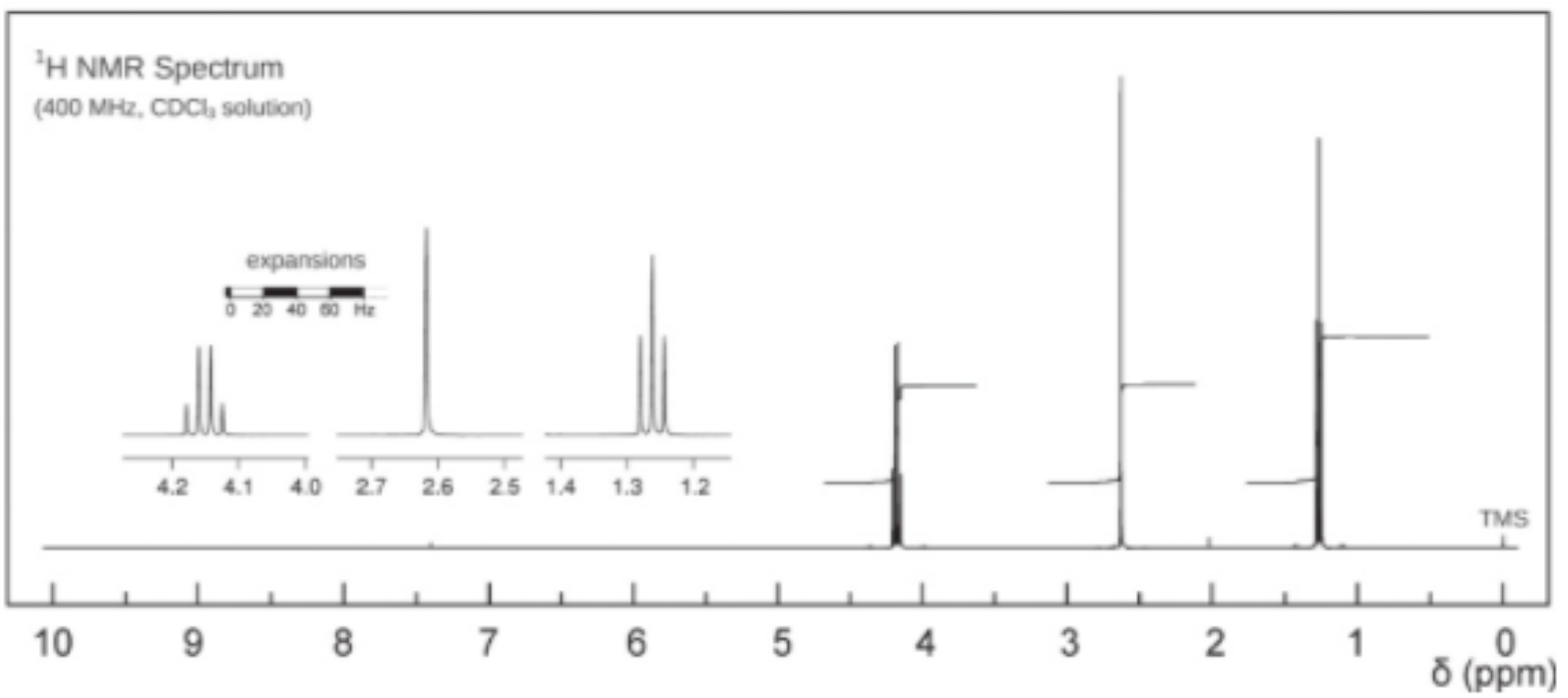
Problem 72



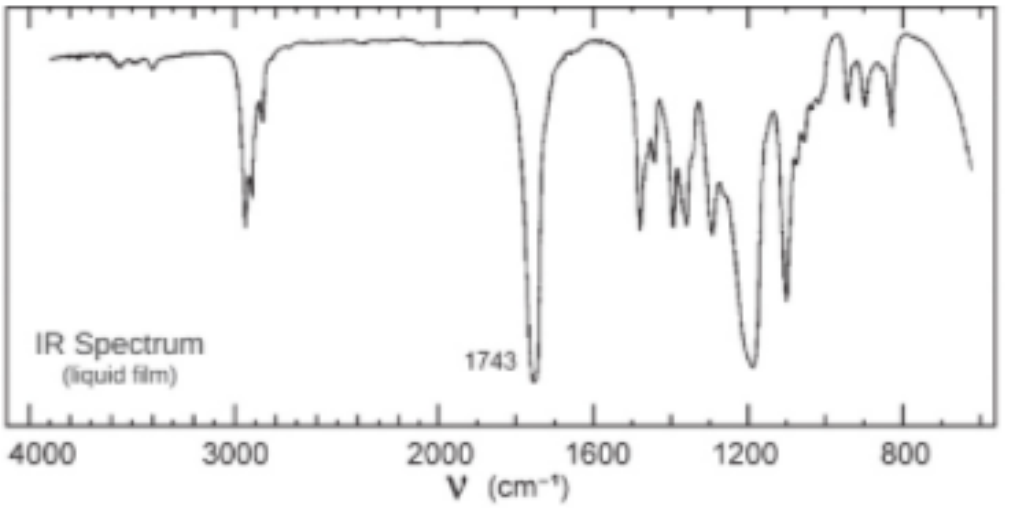


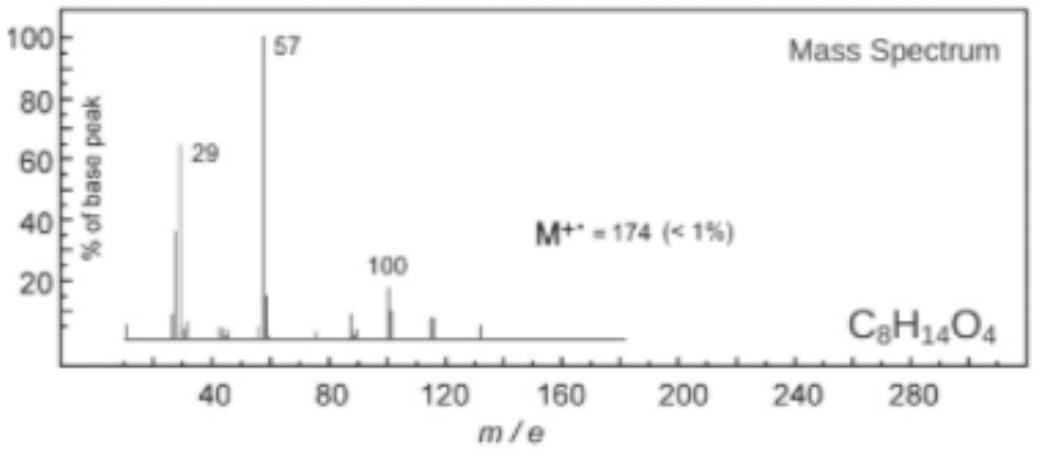
No significant UV absorption above 220 nm



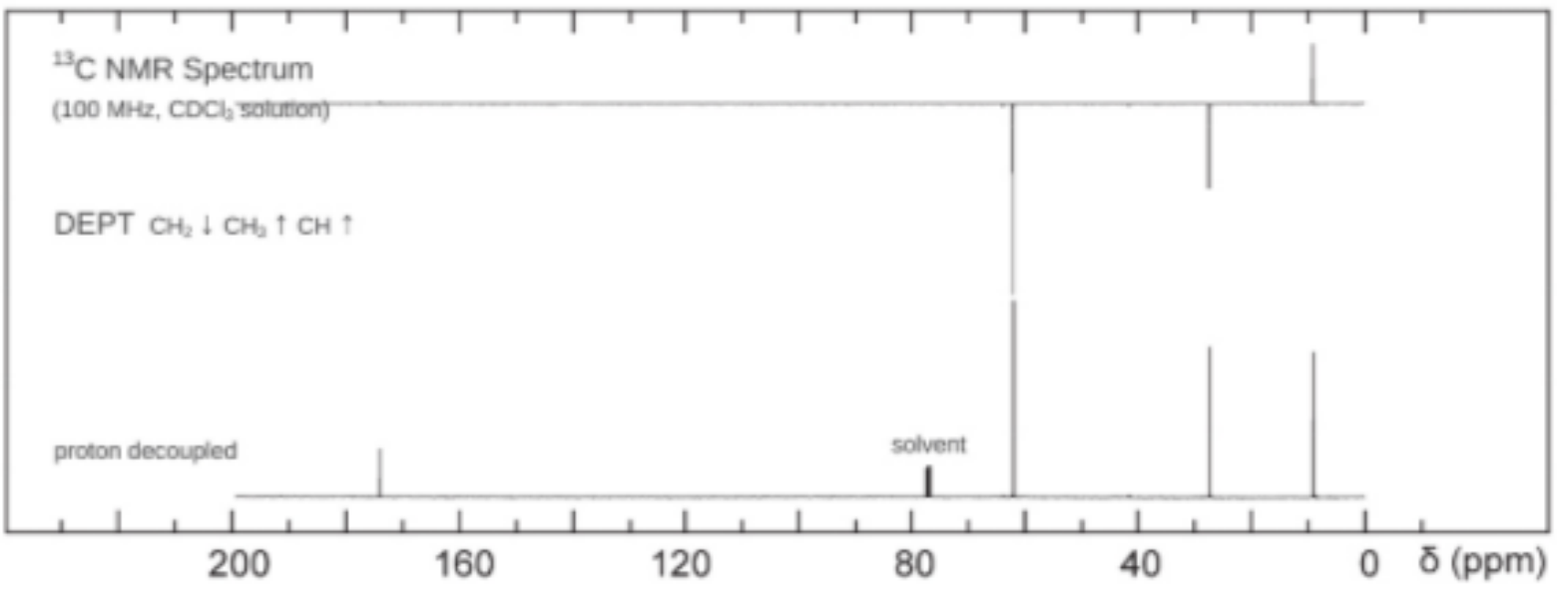


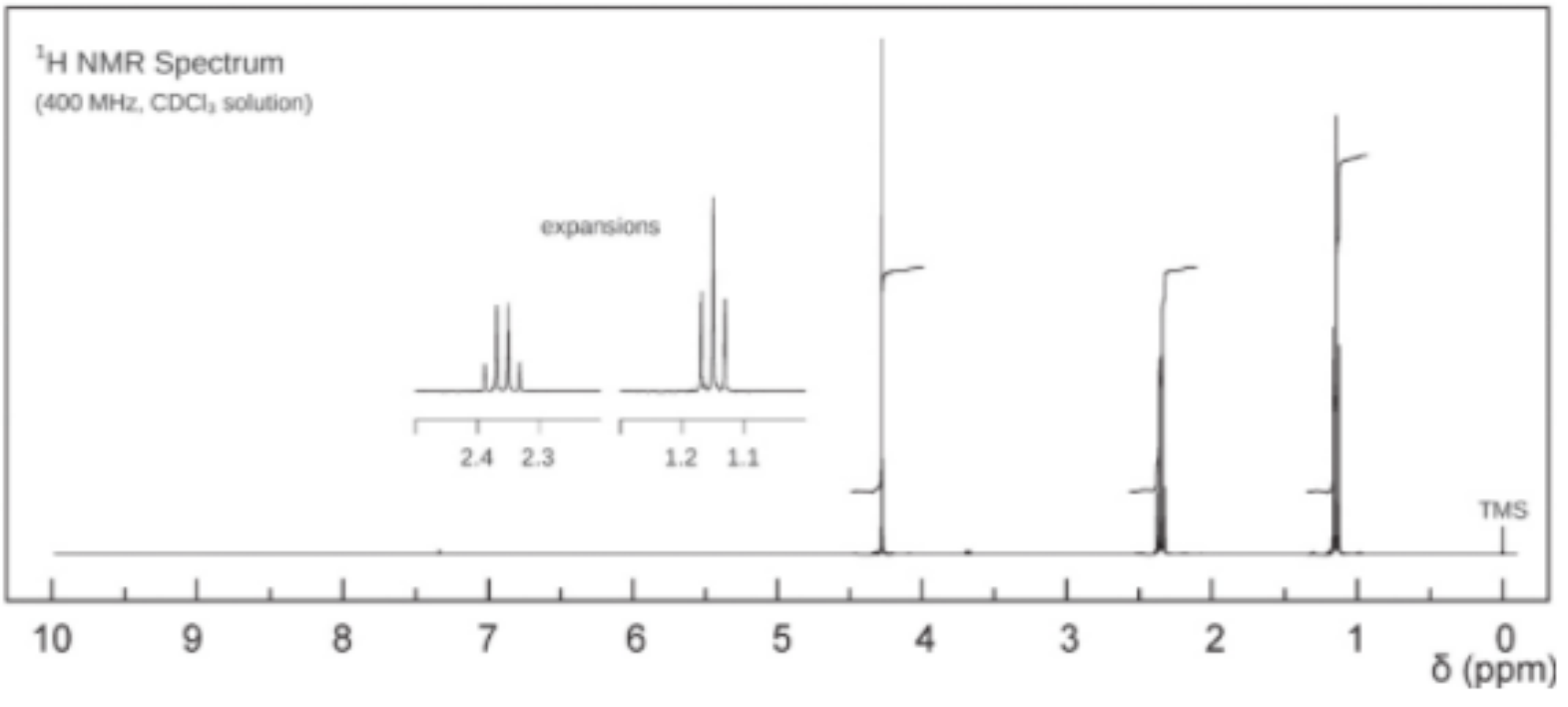
Problem 73



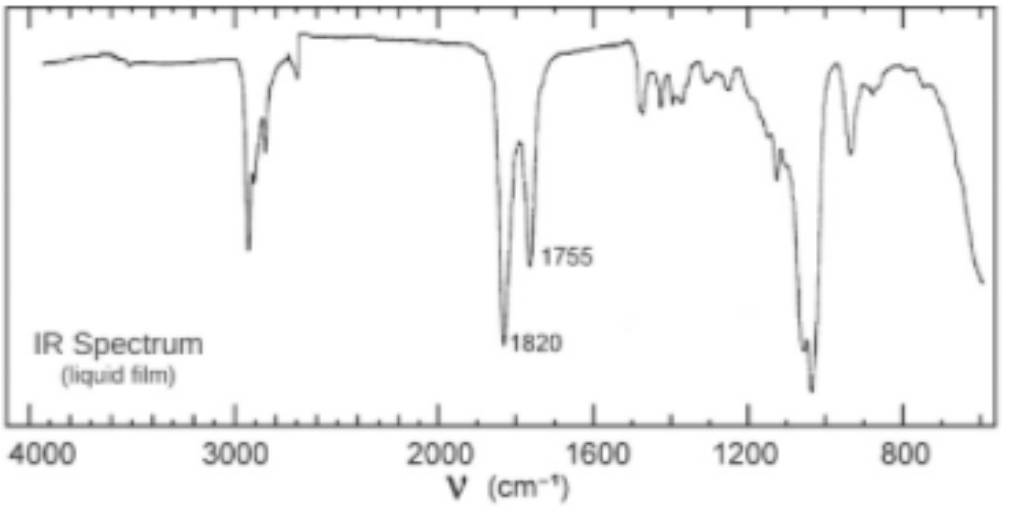


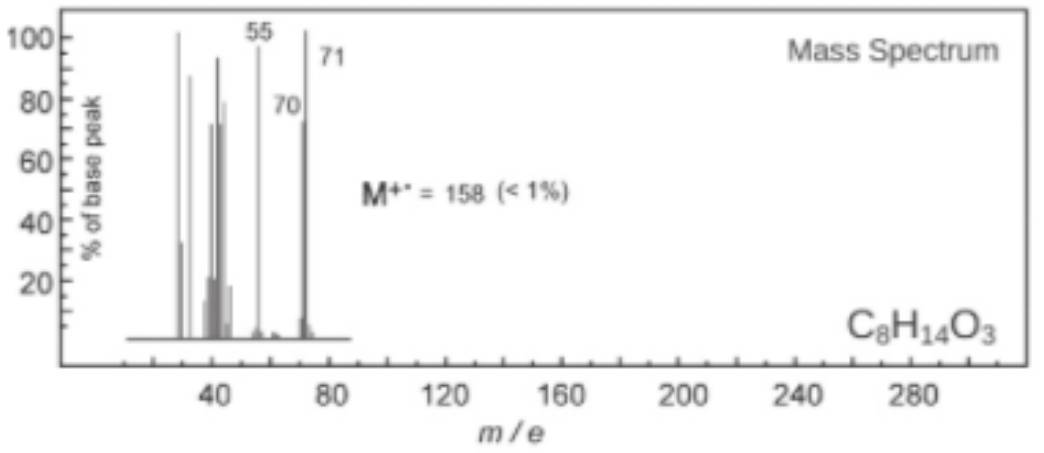
No significant UV absorption above 220 nm



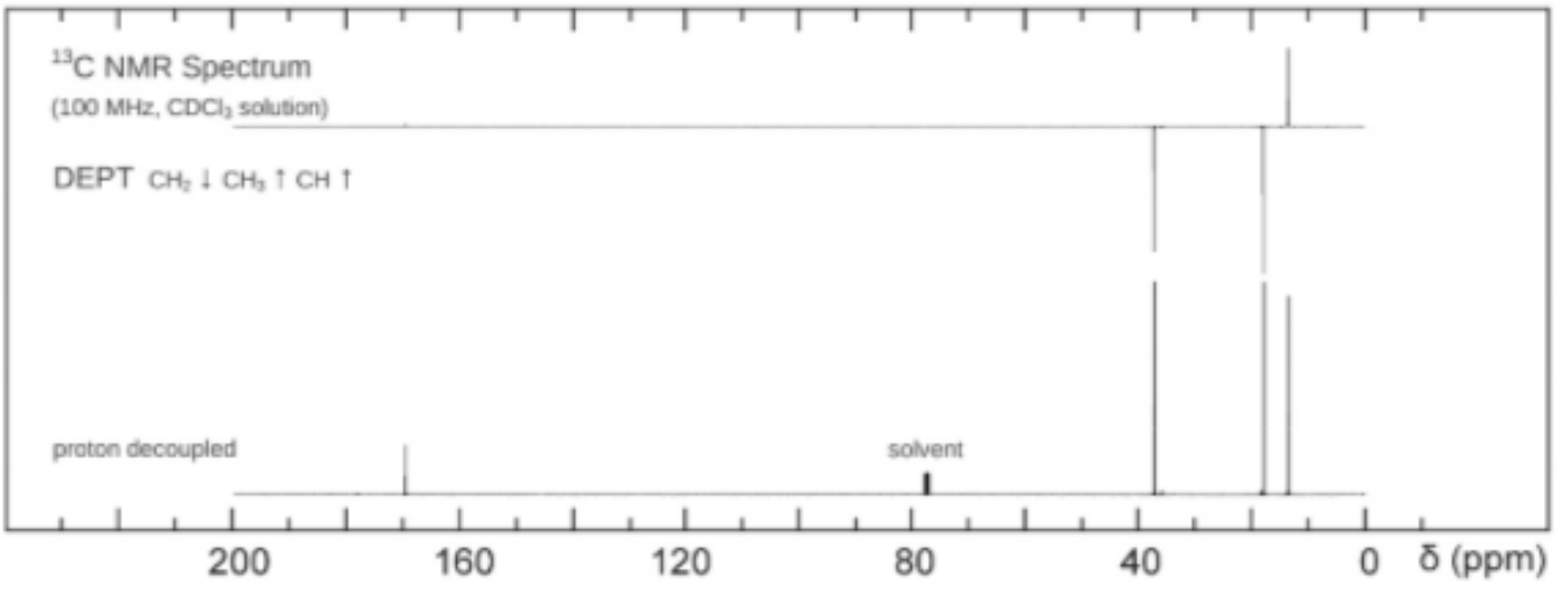


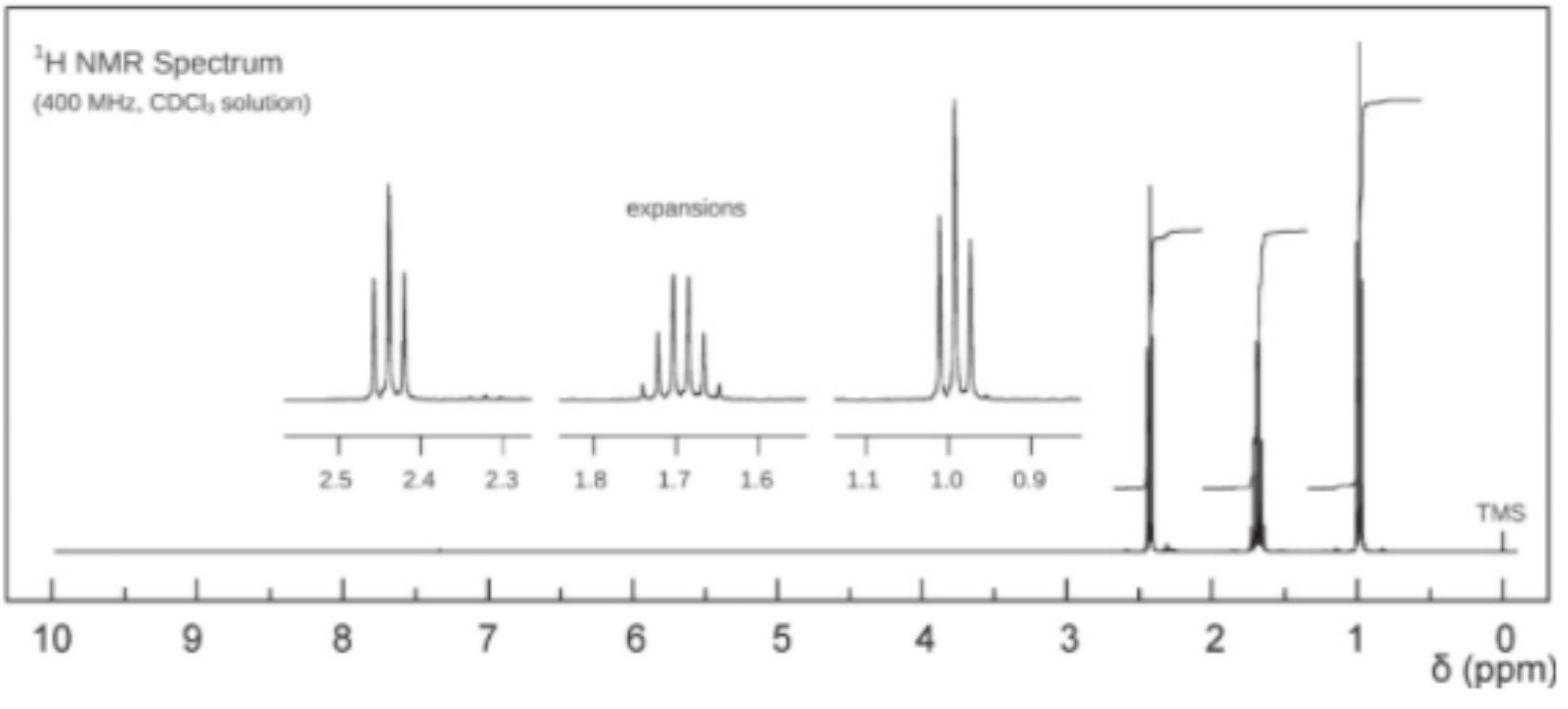
Problem 74

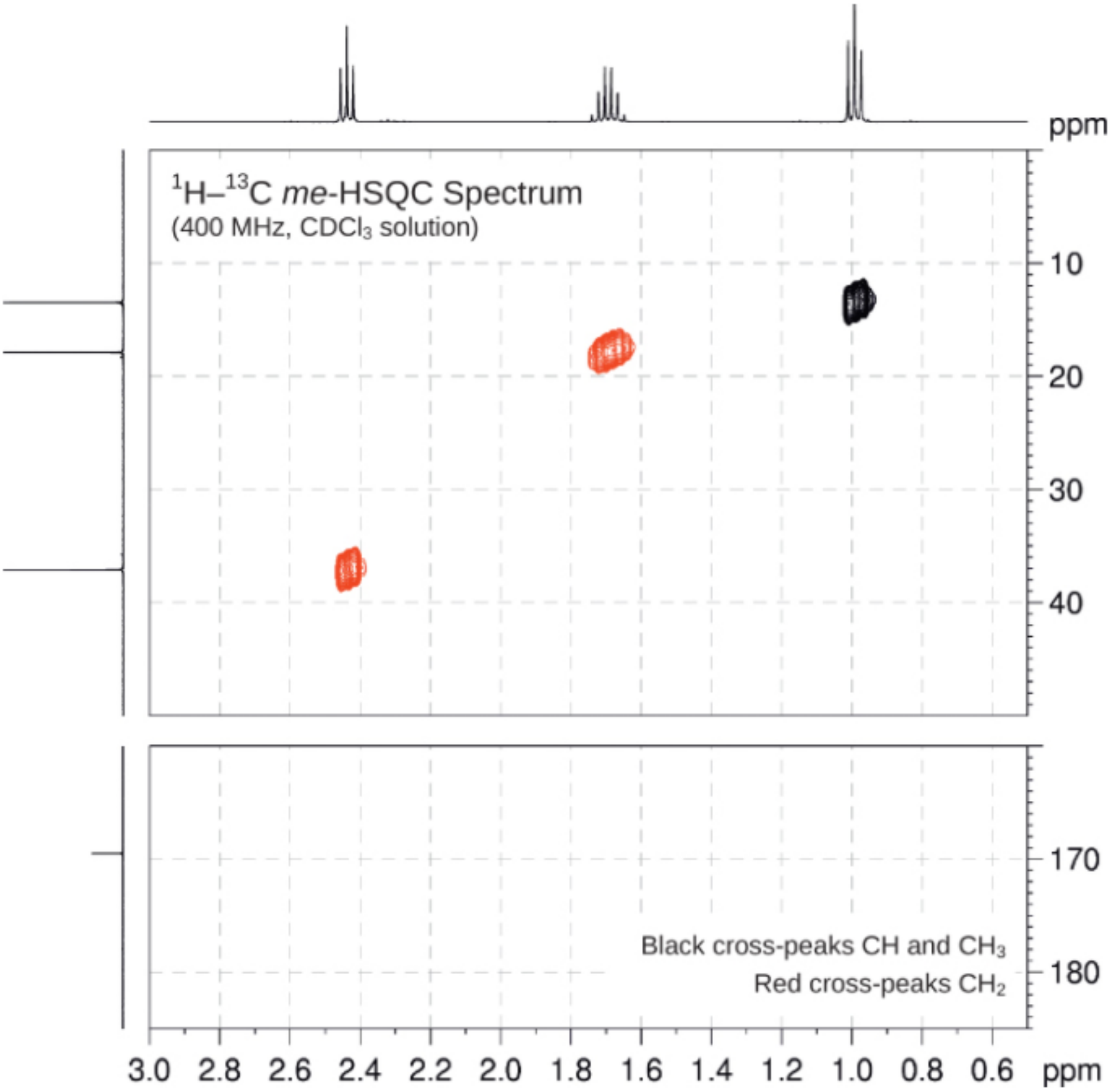




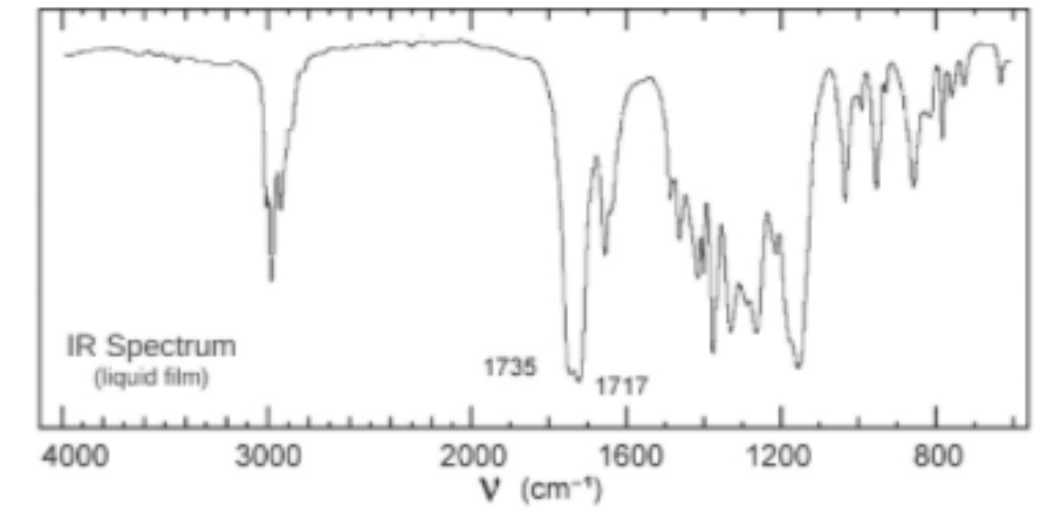
No significant UV absorption above 220 nm

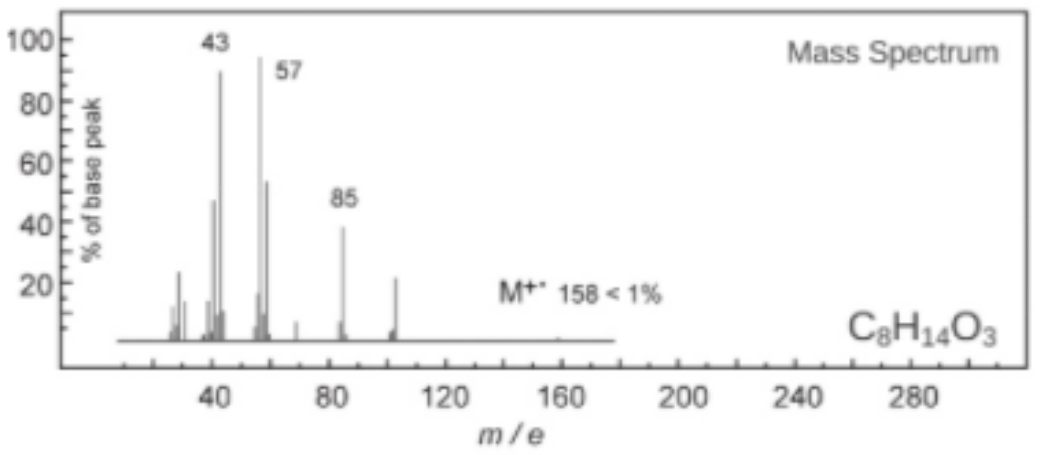




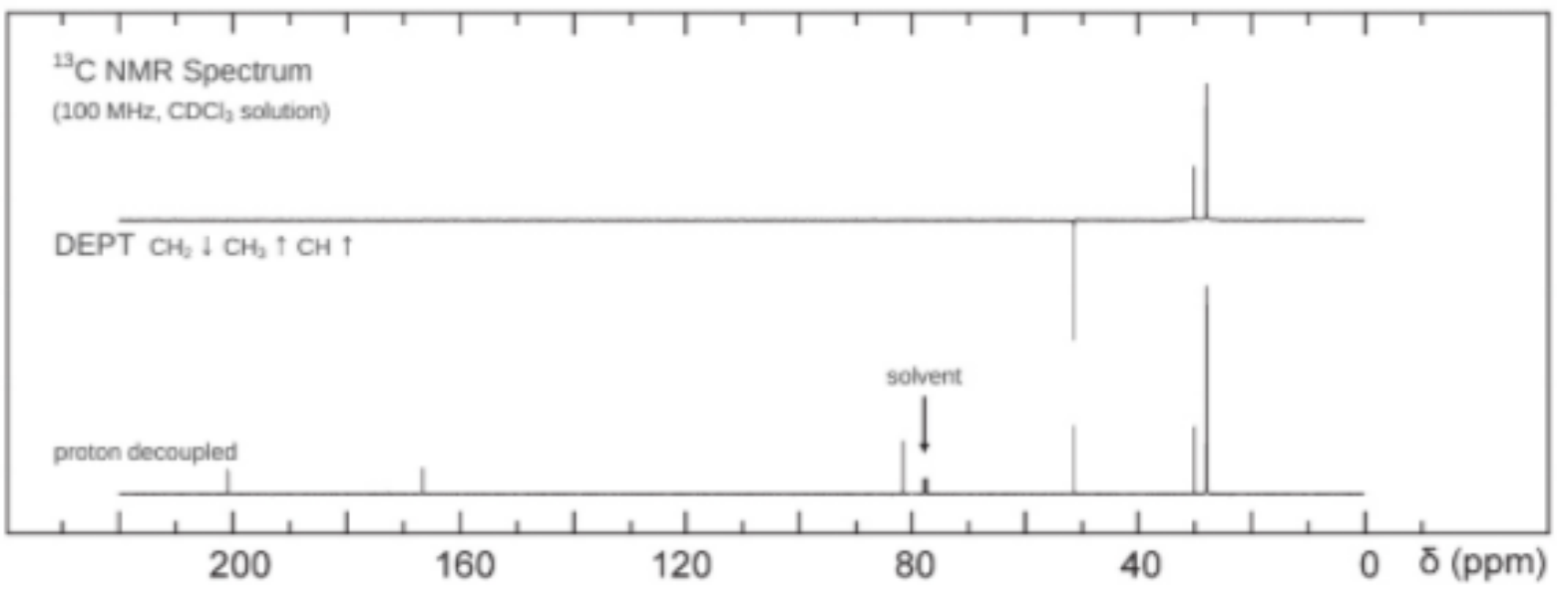

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
10
20
30
40
170
180
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 ppm

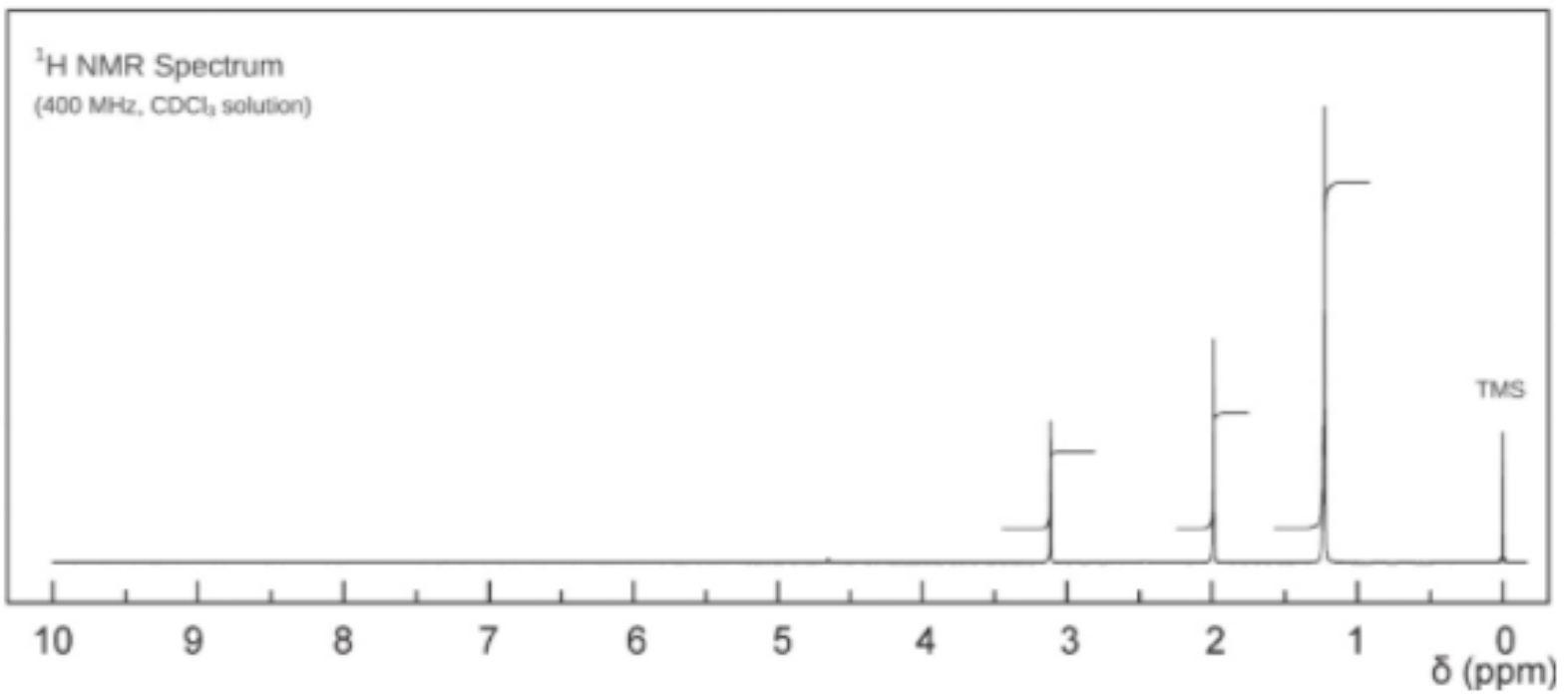
Problem 75

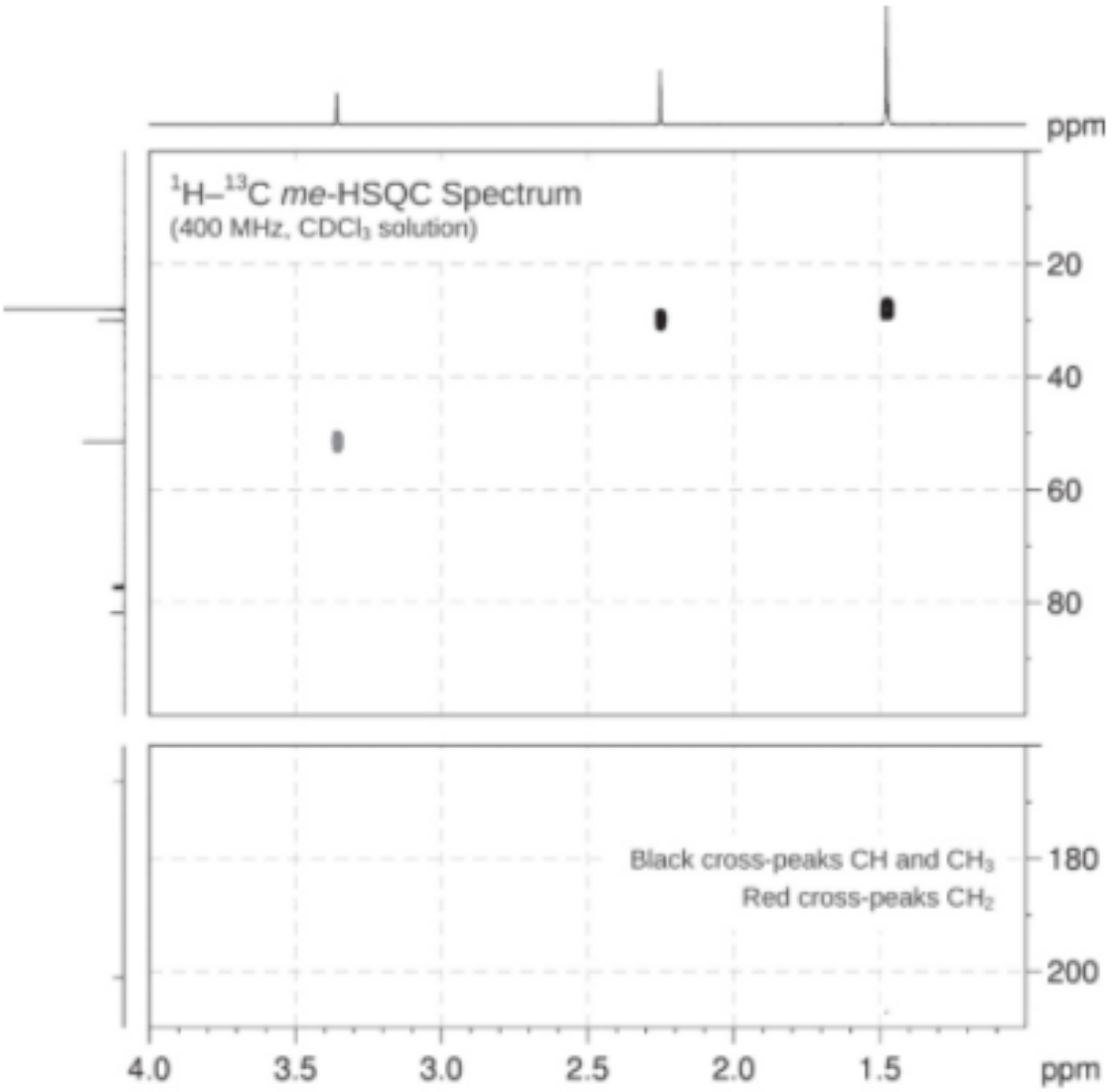


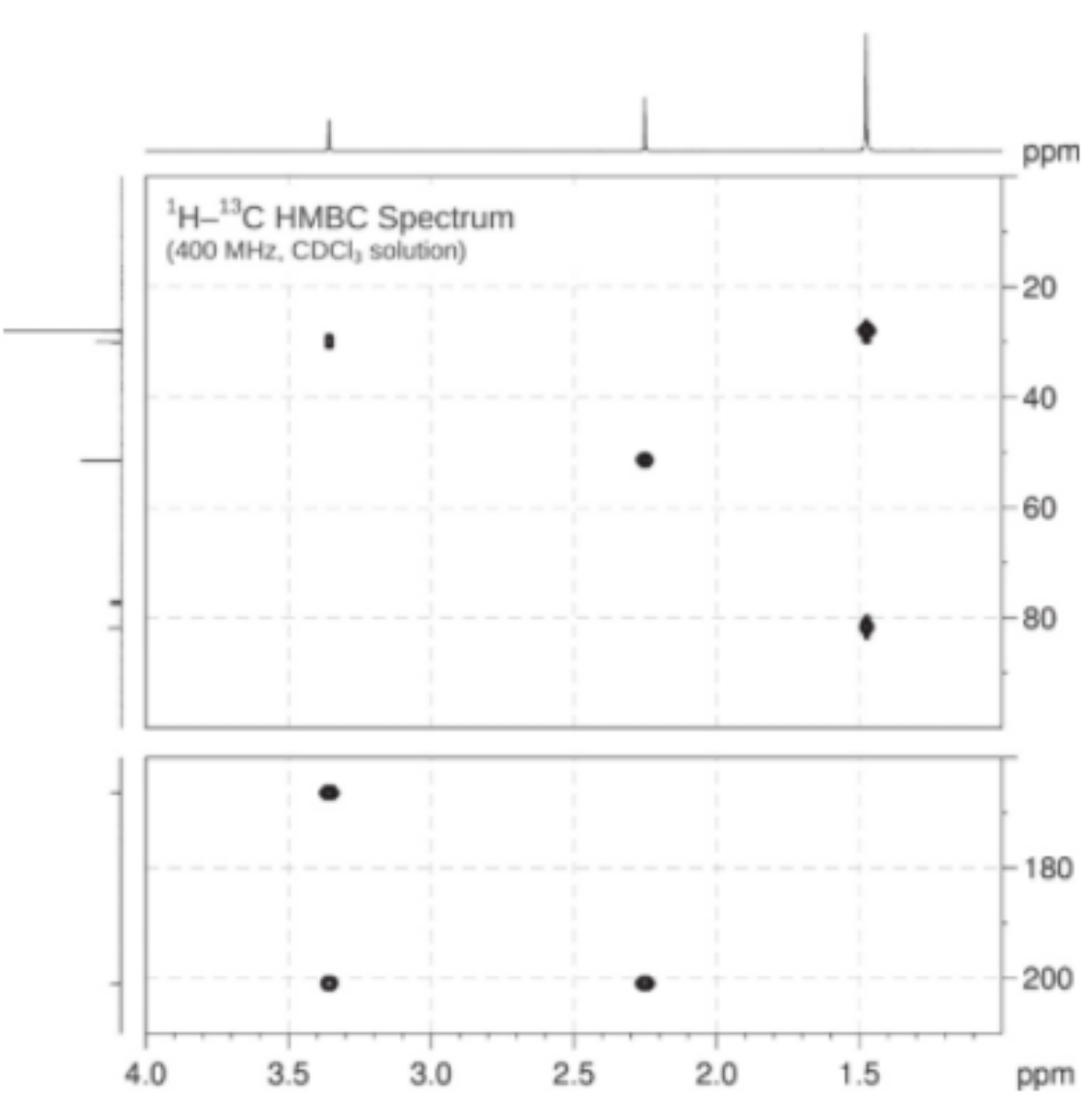


No significant UV absorption above 220 nm

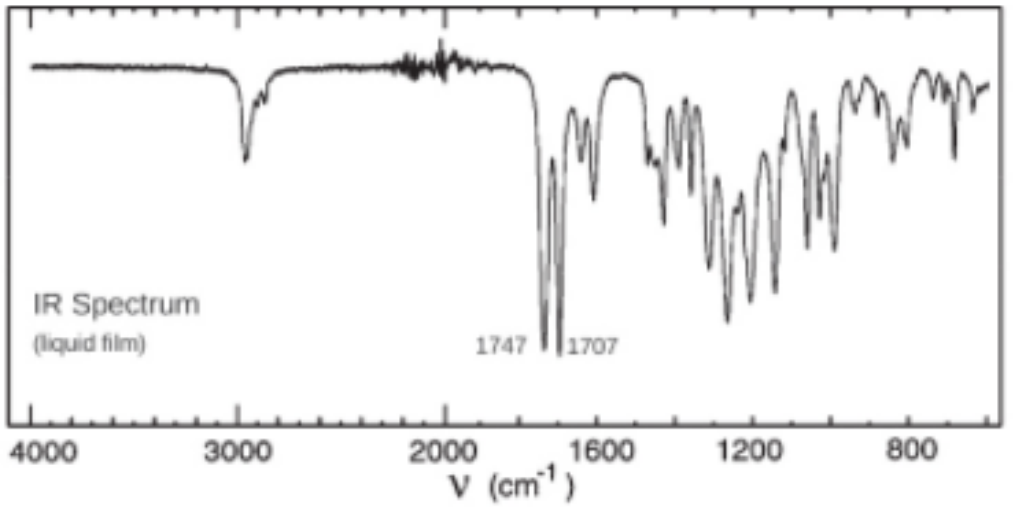


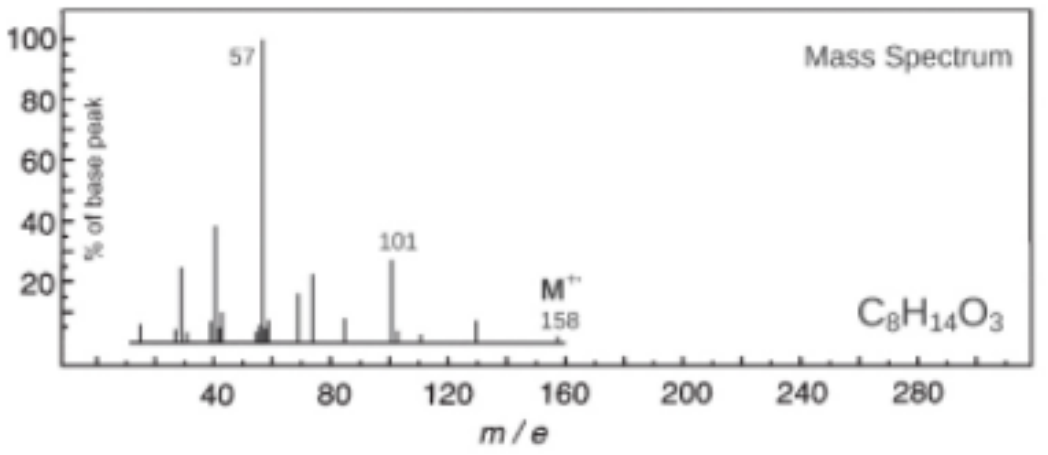


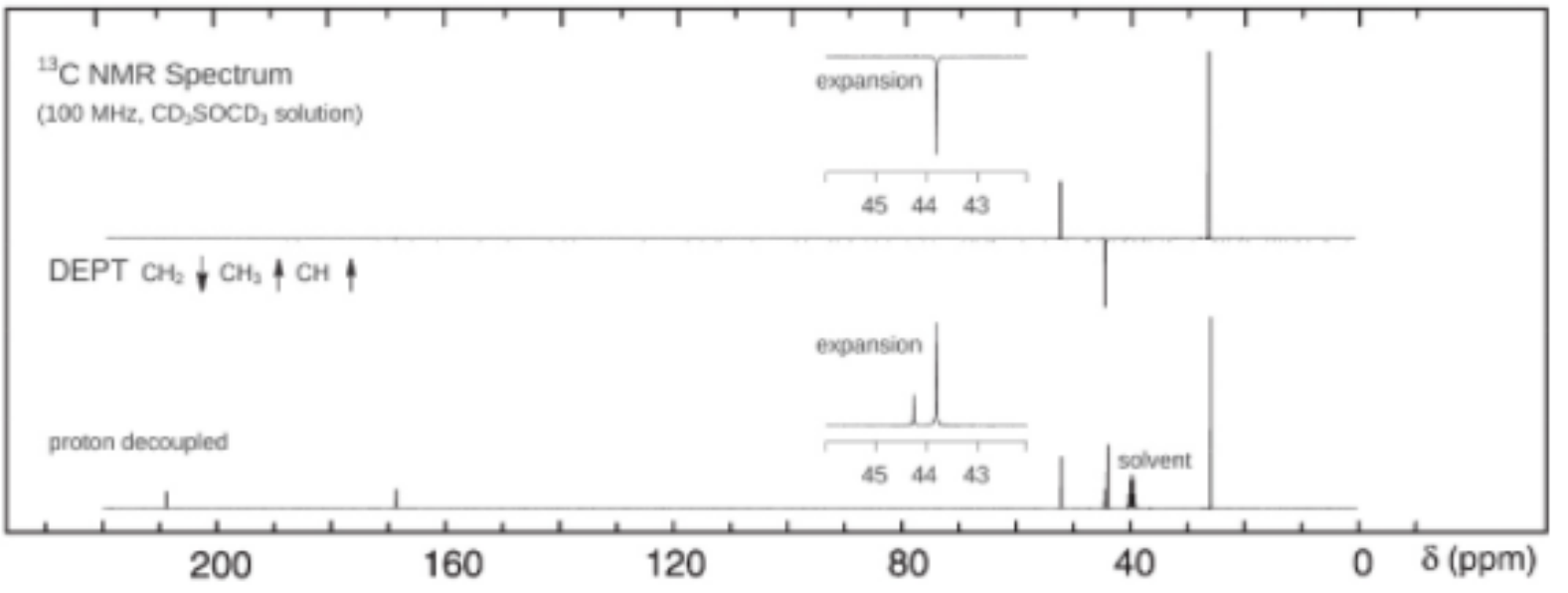

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
20
40
60
80
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
180
200
4.0
3.5
3.0
2.5
2.0
1.5
ppm

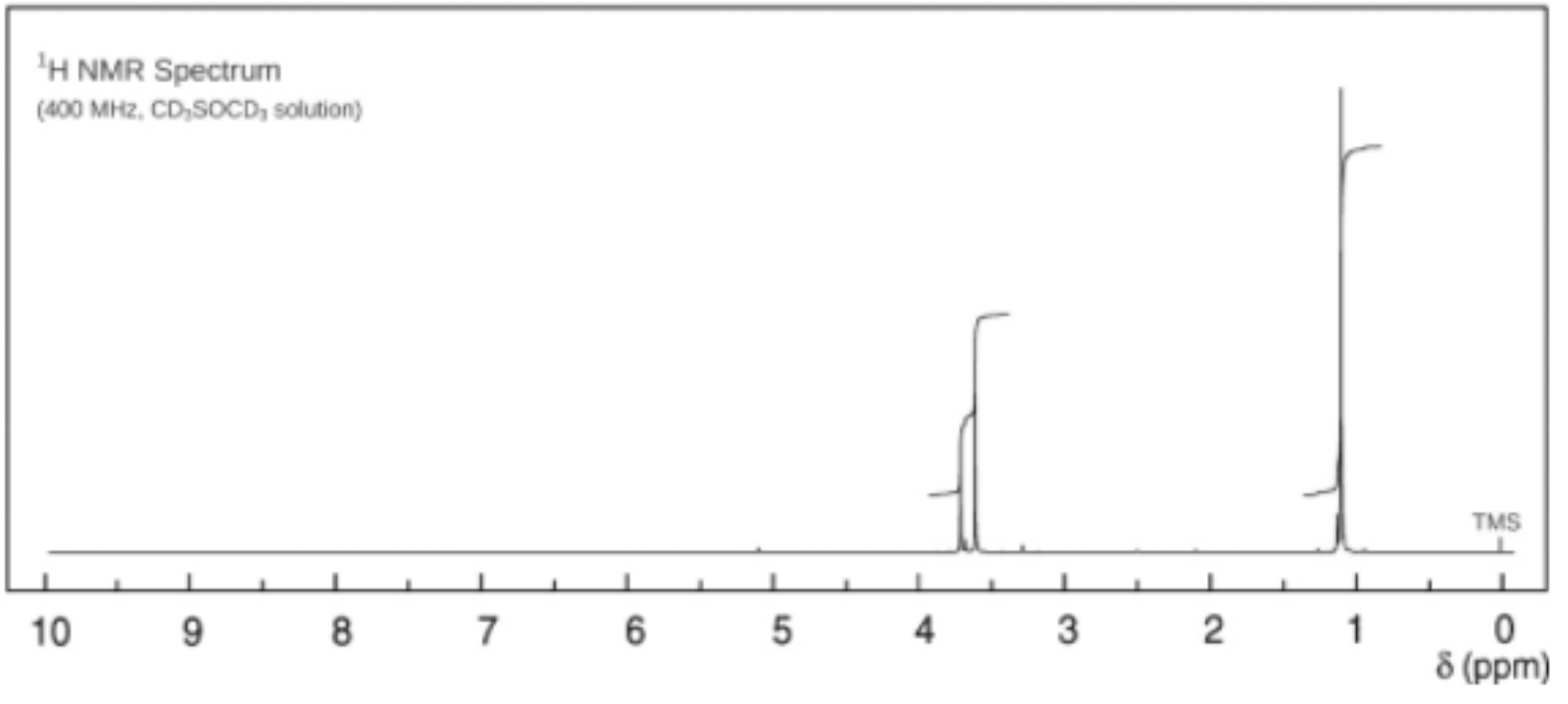

ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
20
40
60
80
180
200
4.0
3.5
3.0
2.5
2.0
1.5
ppm

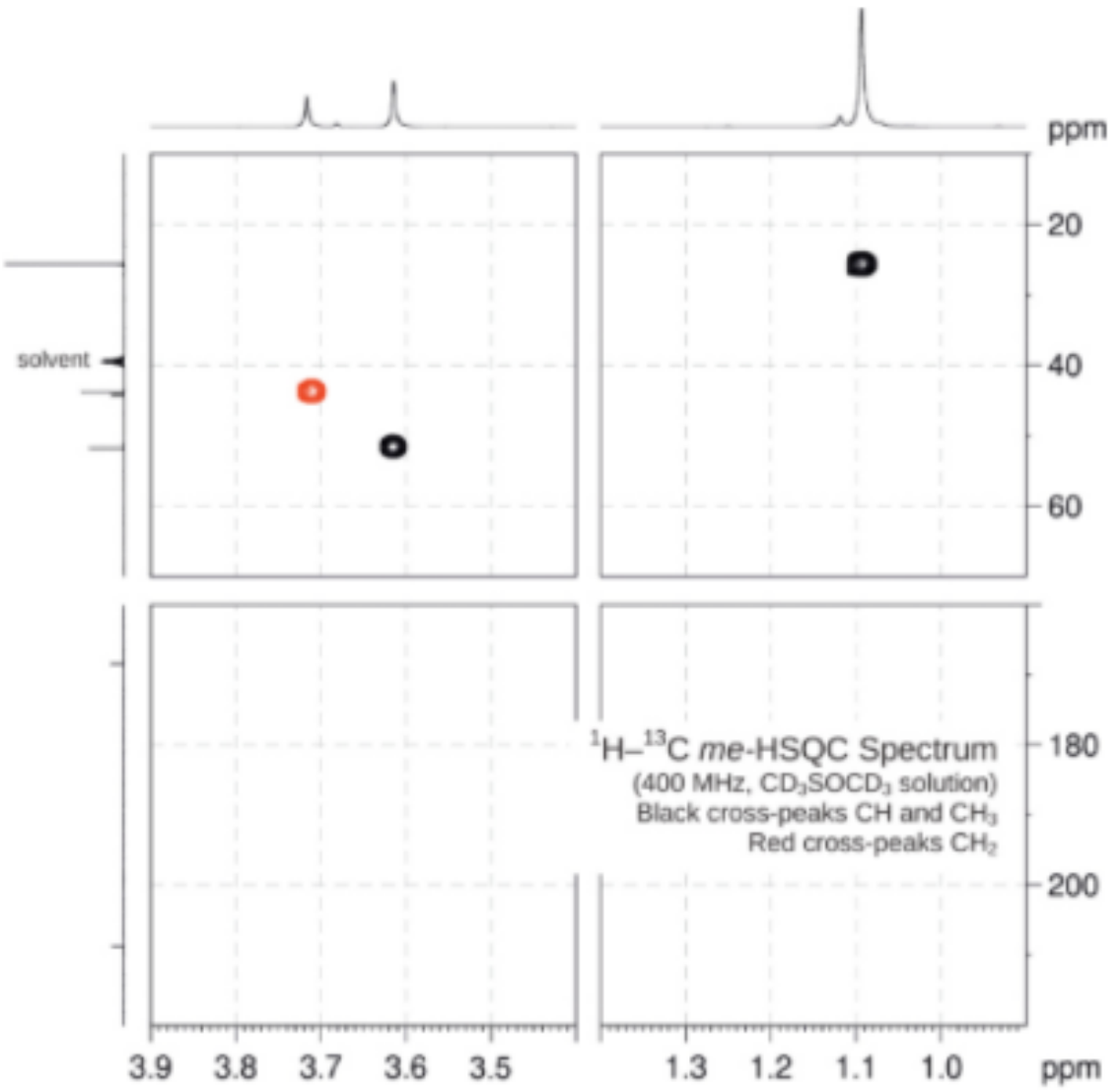
Problem 76


IR Spectrum
(liquid film)
1747
1707
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
100
80
60
40
20
57
101
M+·
158
C8H14O3
40
80
120
160
200
240
280
m / e

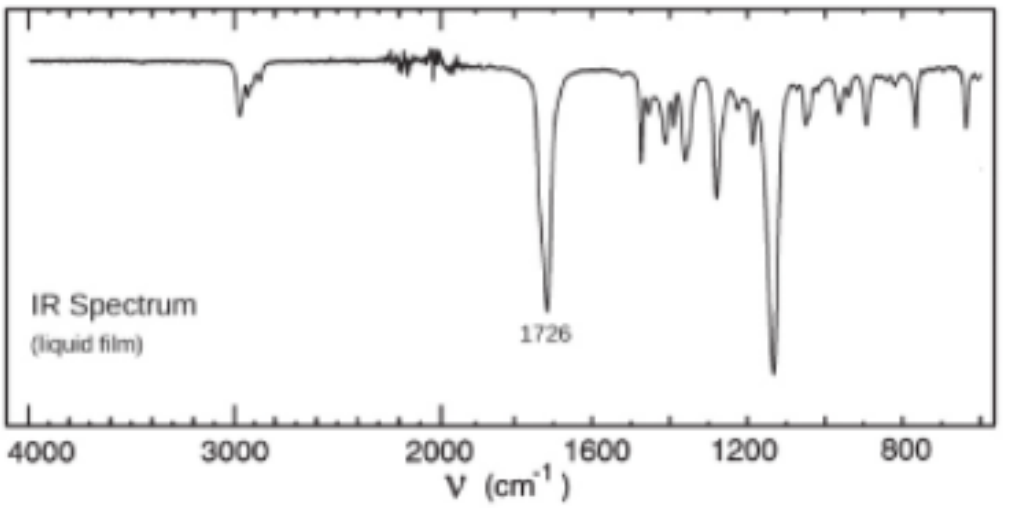

13C NMR Spectrum
(100 MHz, CD3SOCD3 solution)
expansion
45 44 43
DEPT CH2 CH3 CH
expansion
45 44 43
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

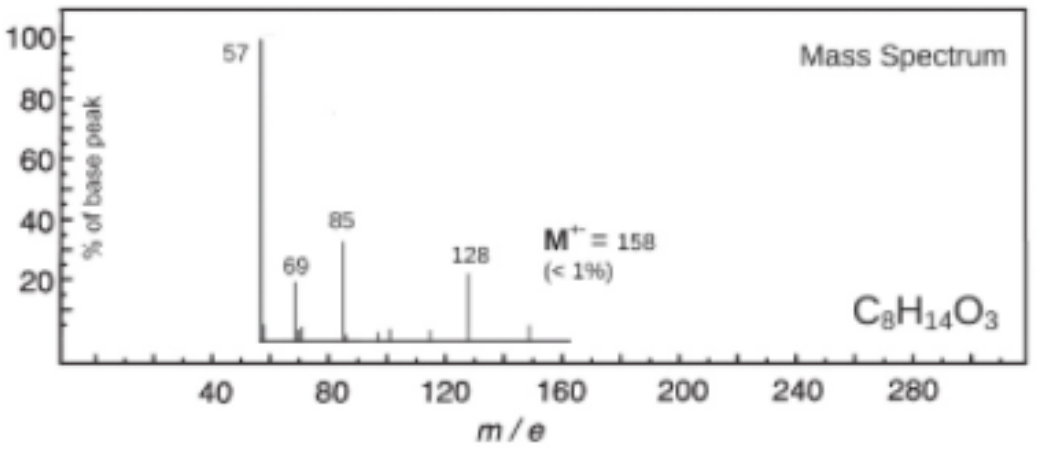

1H NMR Spectrum
(400 MHz, CD3SOCD3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

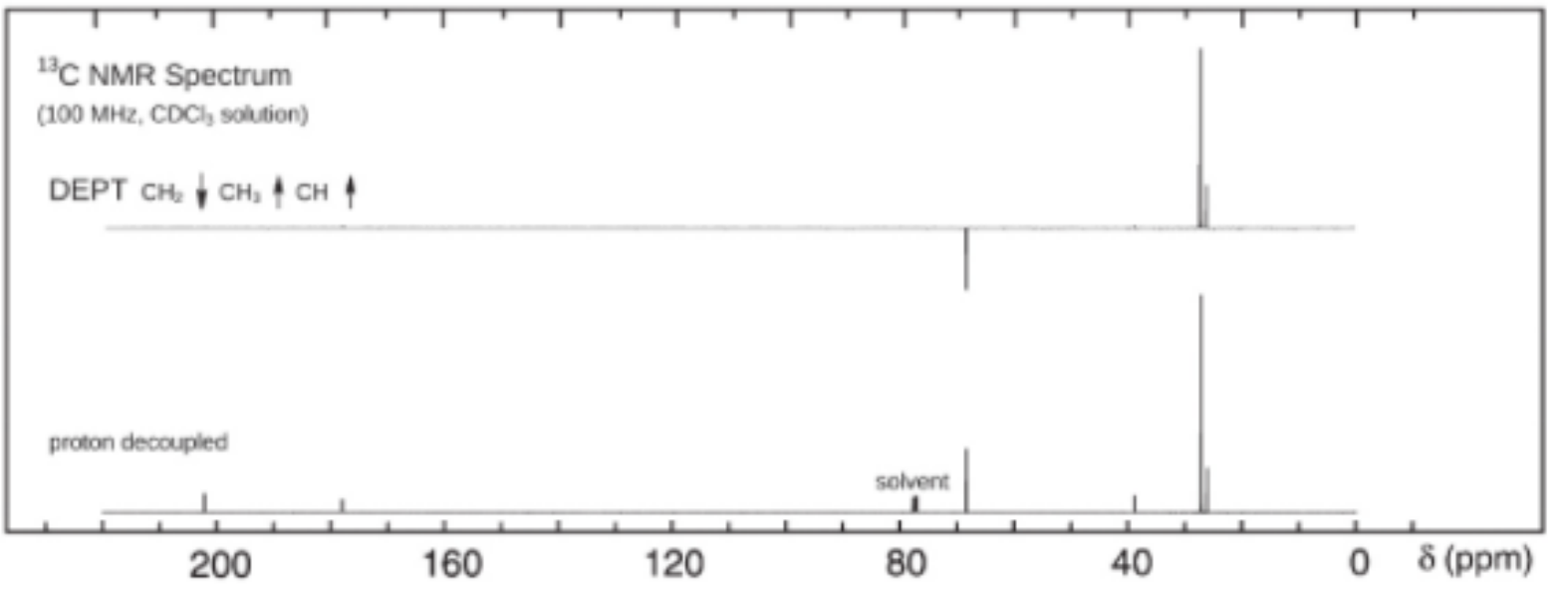

ppm
20
40
60
solvent
180
200
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, CD_3SOCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
3.9
3.8
3.7
3.6
3.5
1.3
1.2
1.1
1.0
ppm

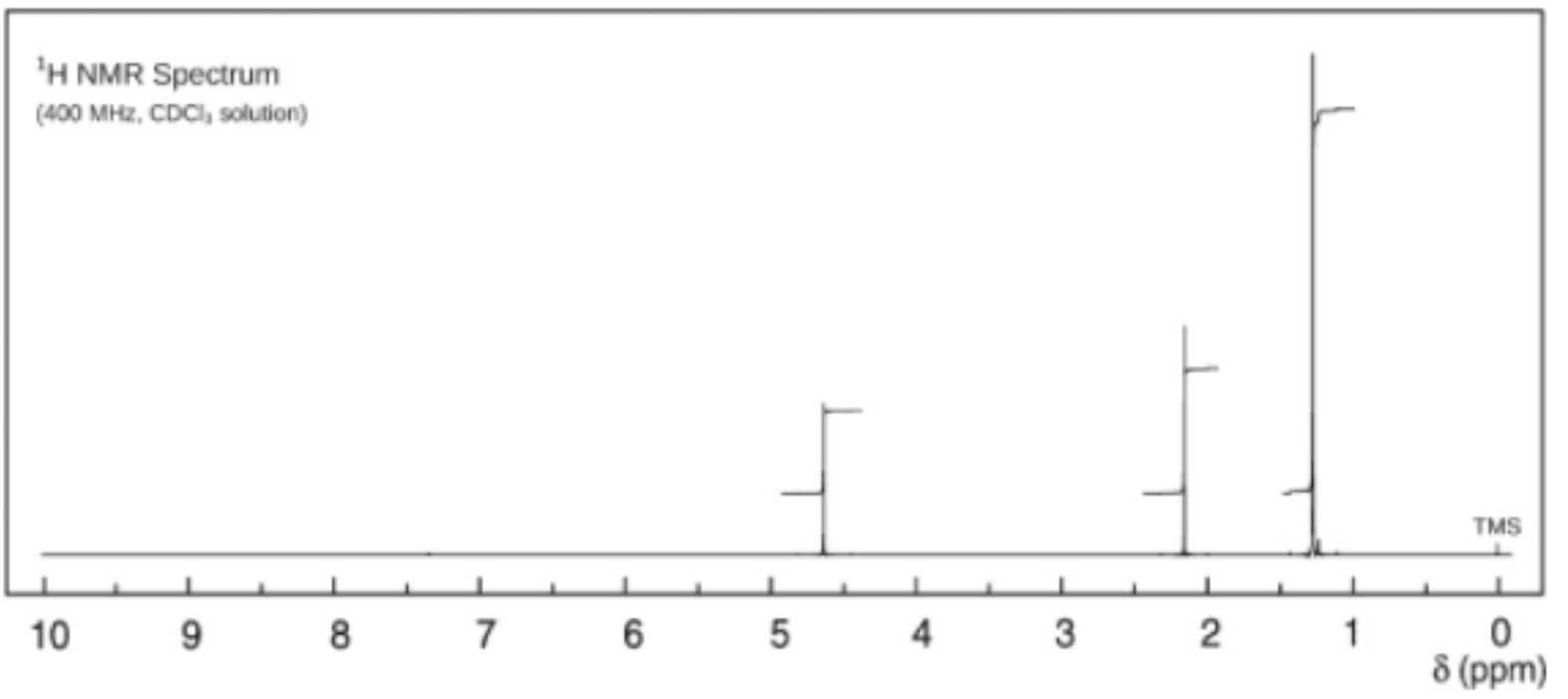
ppm
20
40
60
solvent
180
200
^{1}H–^{13}C HMBC Spectrum
(400 MHz, CD_3SOCD_3 solution)
3.9
3.8
3.7
3.6
3.5
1.3
1.2
1.1
1.0
ppm

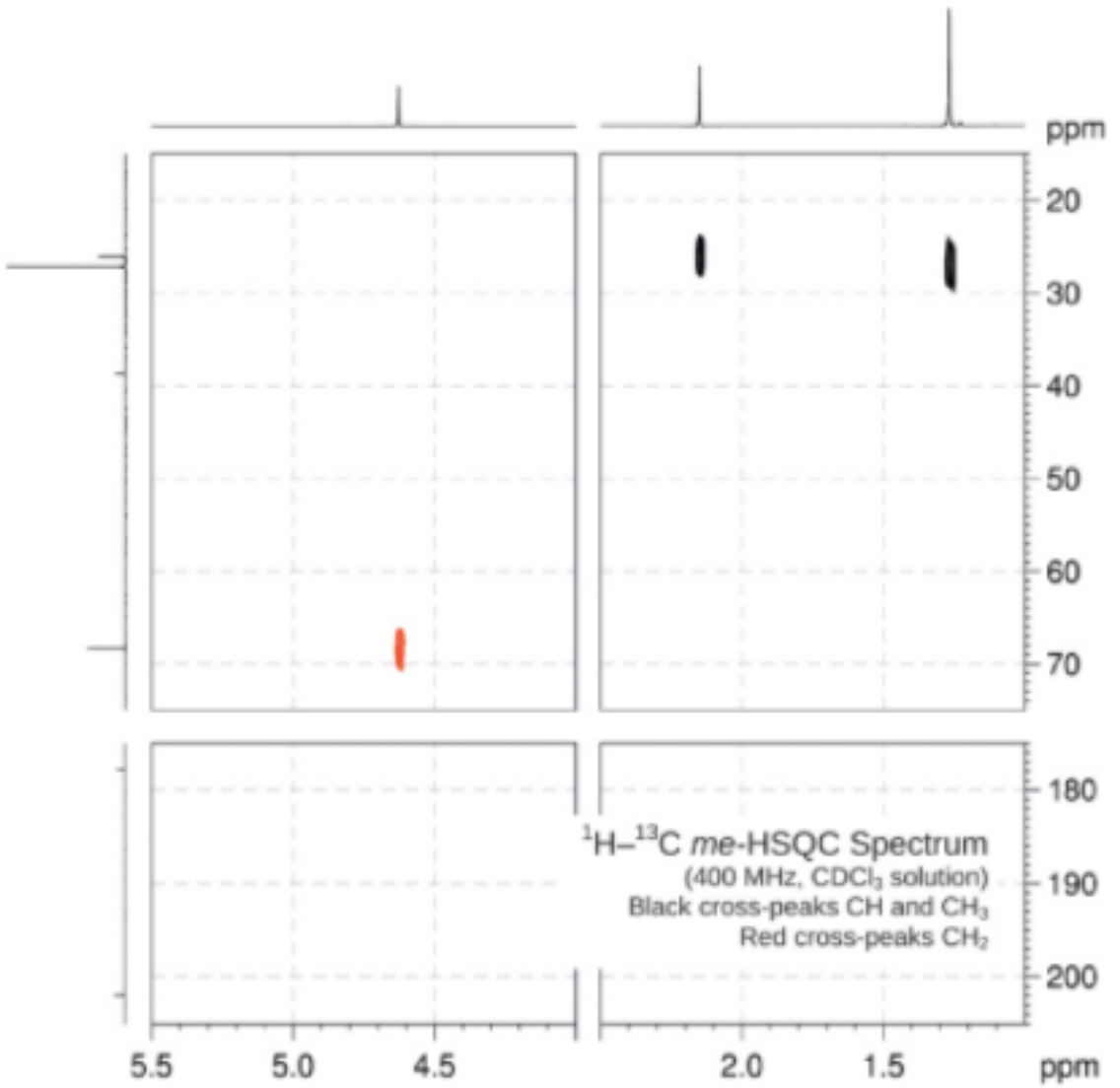
Problem 77


IR Spectrum
(liquid film)
1726
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
100
80
60
40
20
57
85
69
128
M+· = 158
(< 1%)
C8H14O3
40
80
120
160
200
240
280
m / e

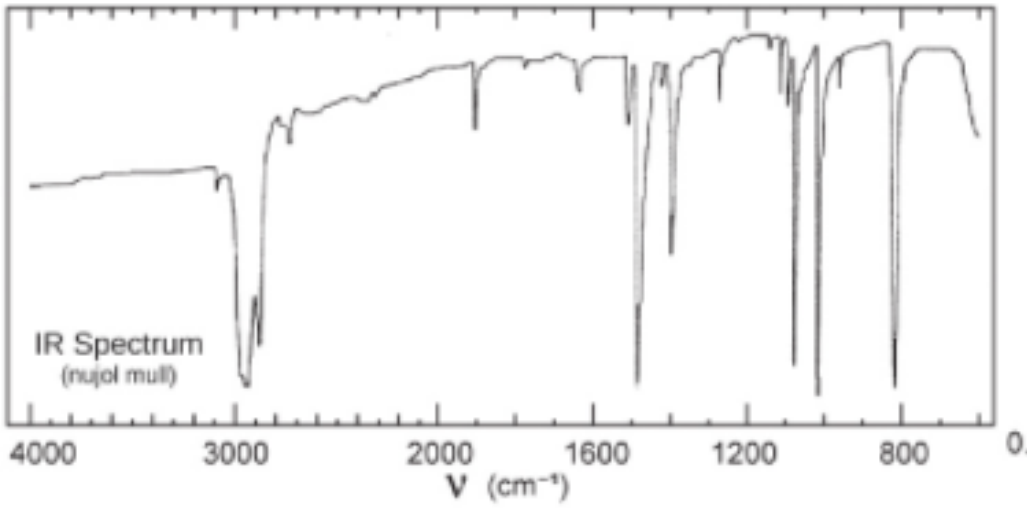

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

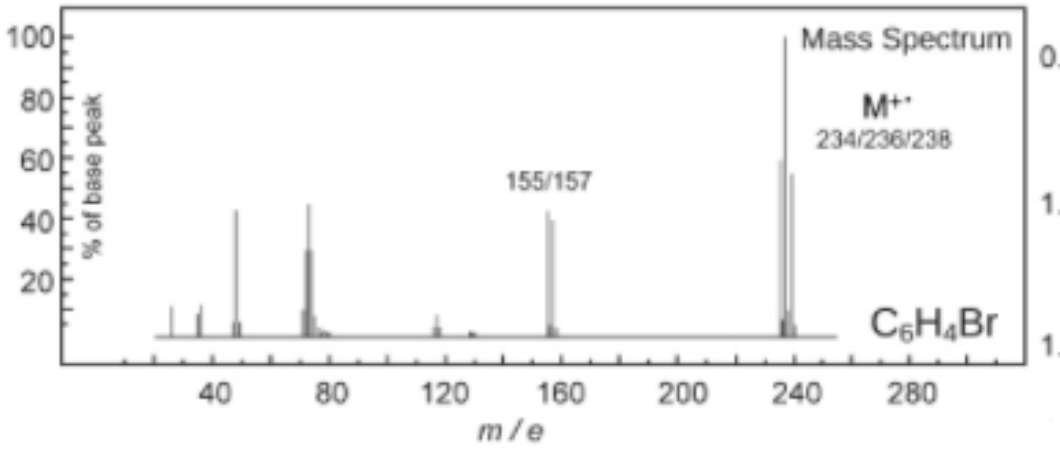

1H NMR Spectrum
(400 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

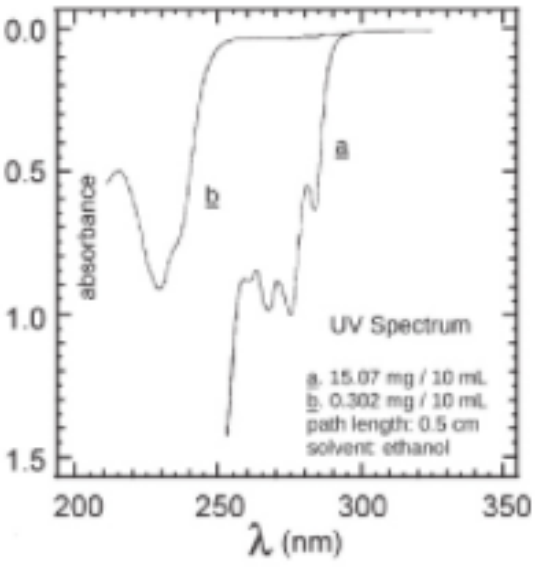

ppm
20
30
40
50
60
70
180
190
200
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
5.5
5.0
4.5
2.0
1.5
ppm

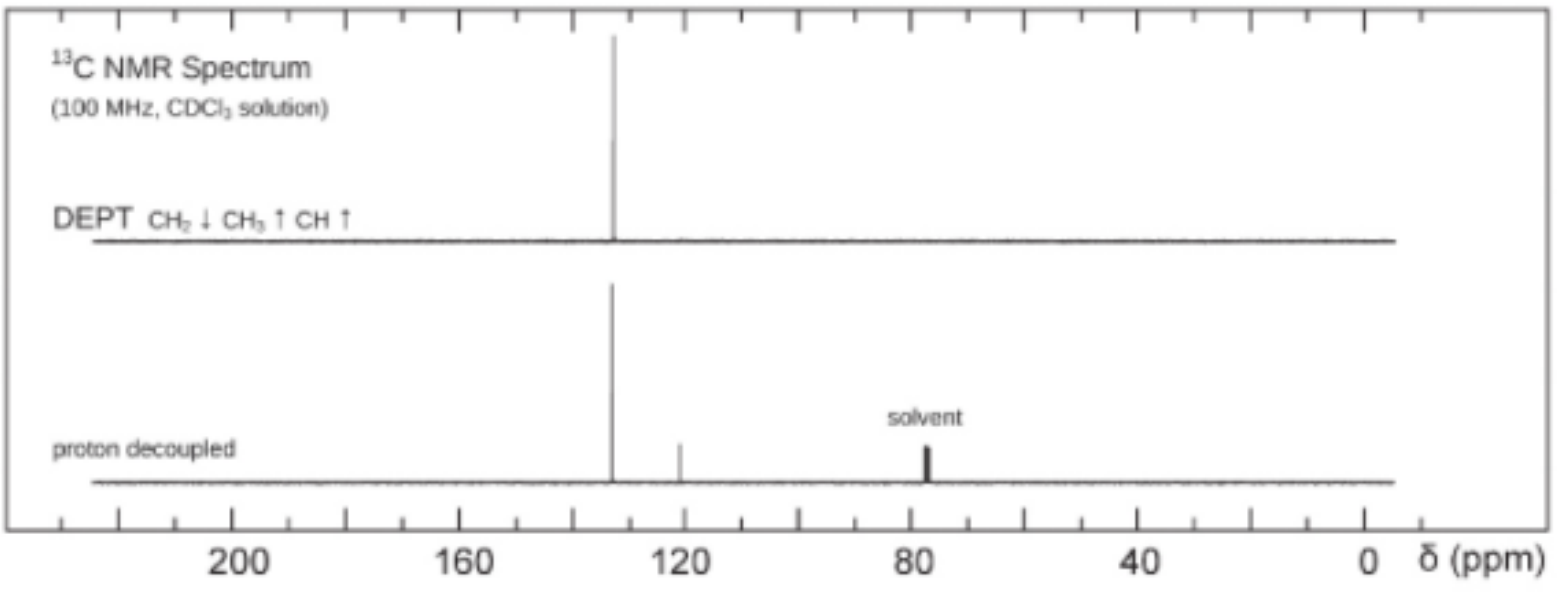
ppm
20
30
40
50
60
70
180
190
200
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
5.5
5.0
4.5
2.0
1.5
ppm

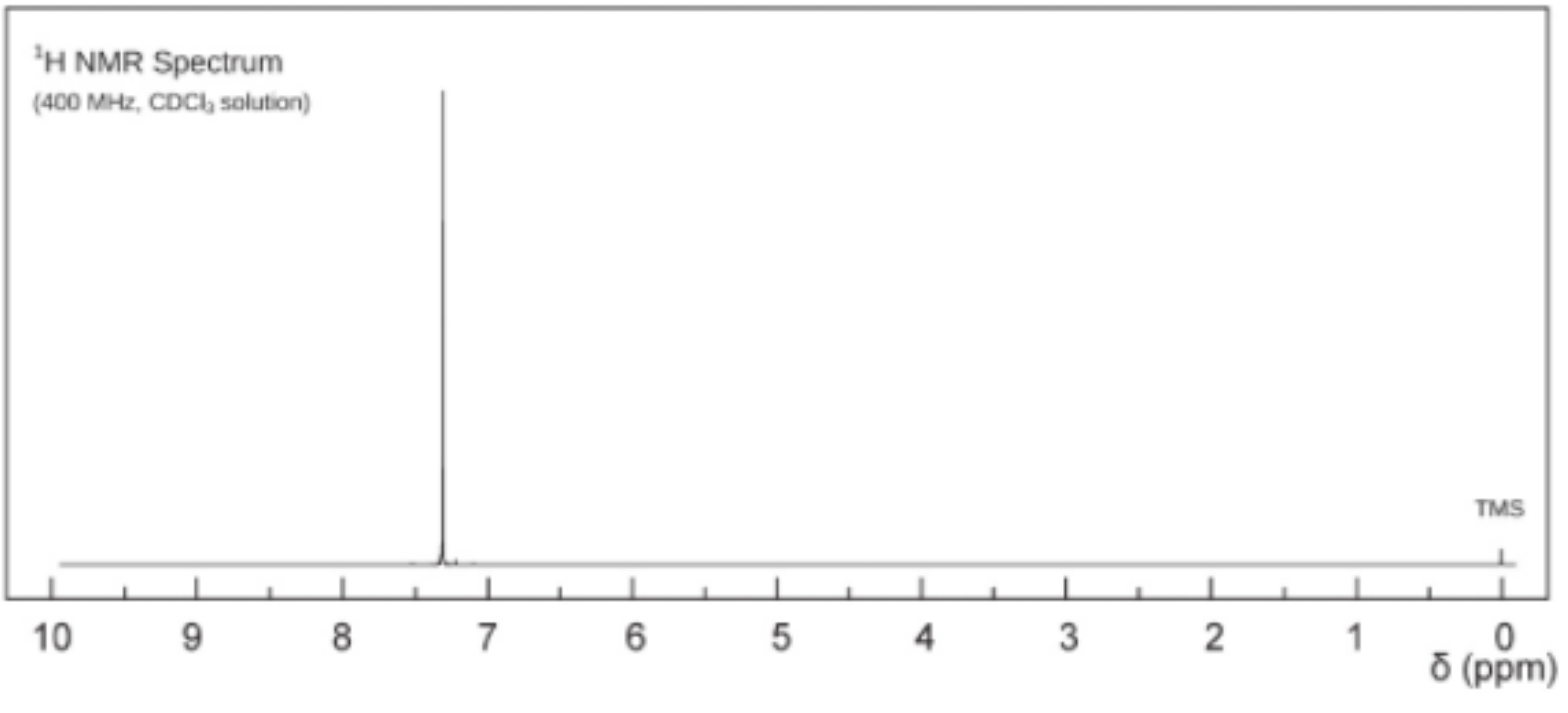
Problem 78


IR Spectrum
(nujol mull)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

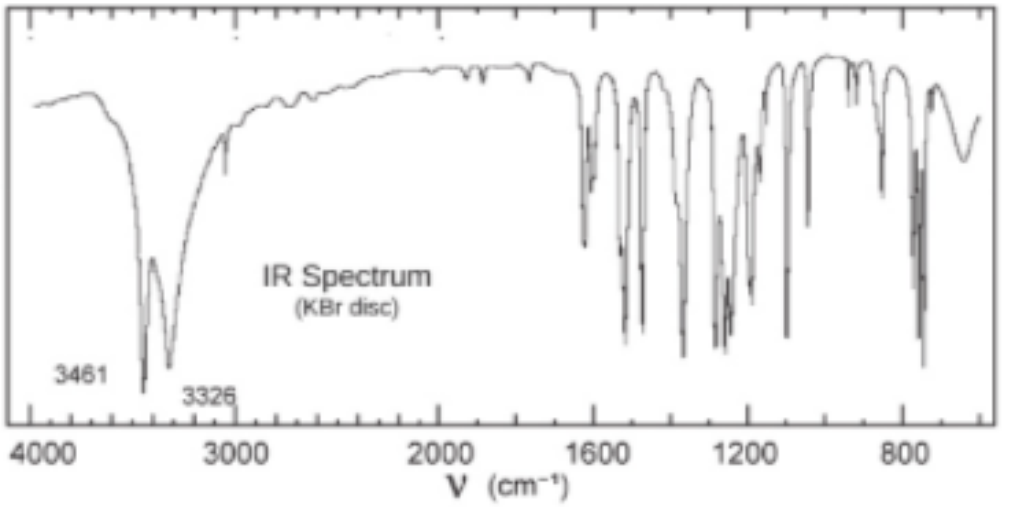

Mass Spectrum
M+·
234/236/238
155/157
C6H4Br
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m / e

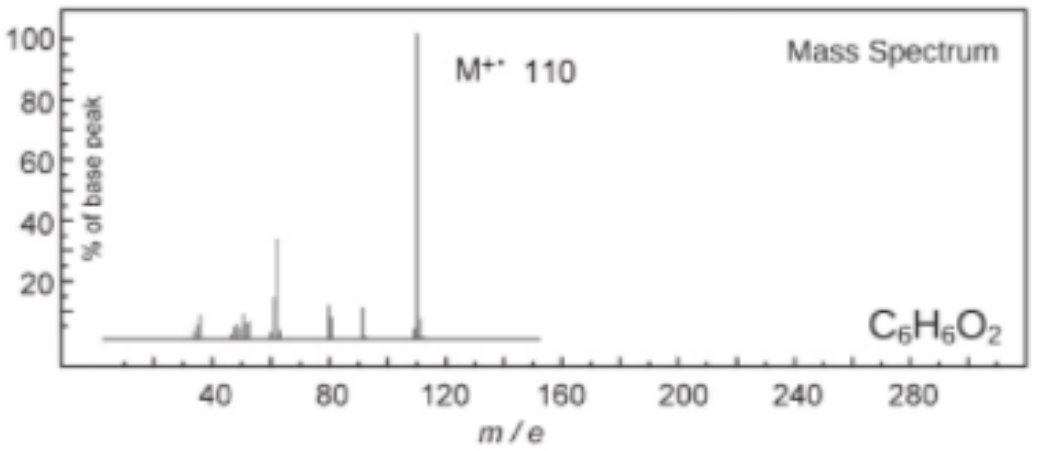

UV Spectrum
a. 15.07 mg / 10 mL
b. 0.302 mg / 10 mL
path length: 0.5 cm
solvent: ethanol
absorbance
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 79

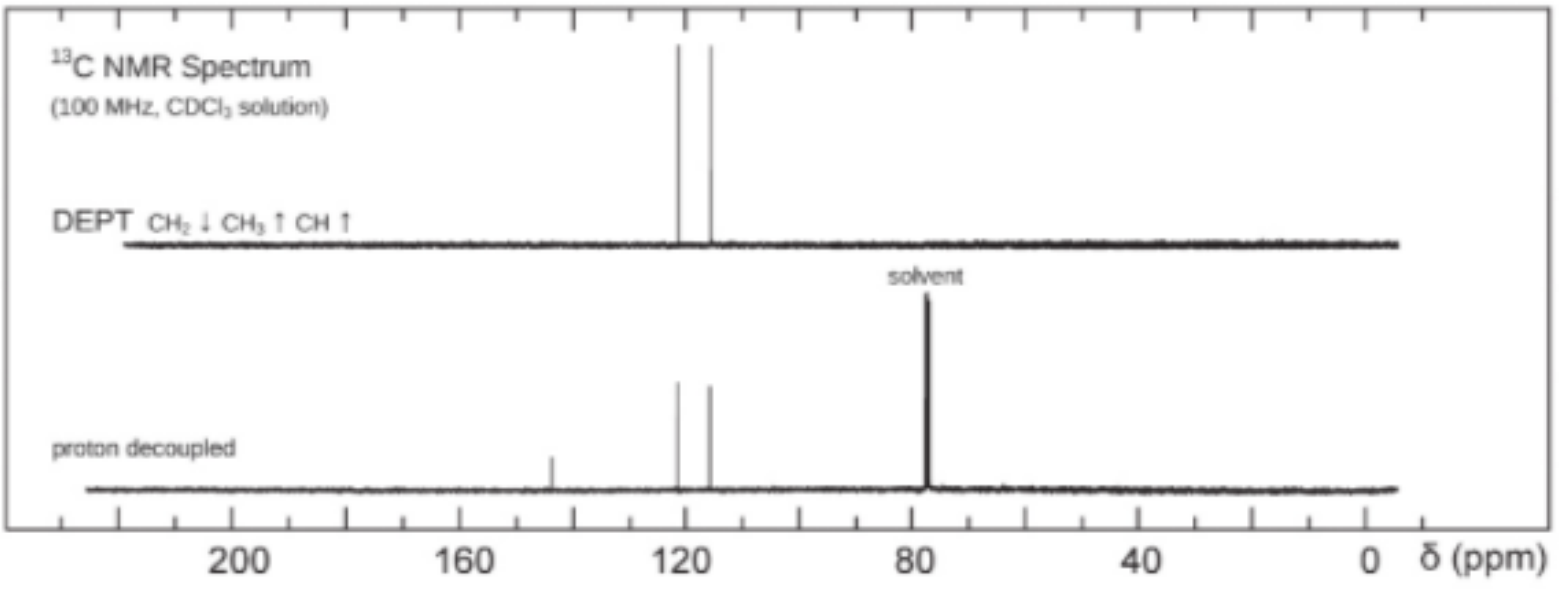


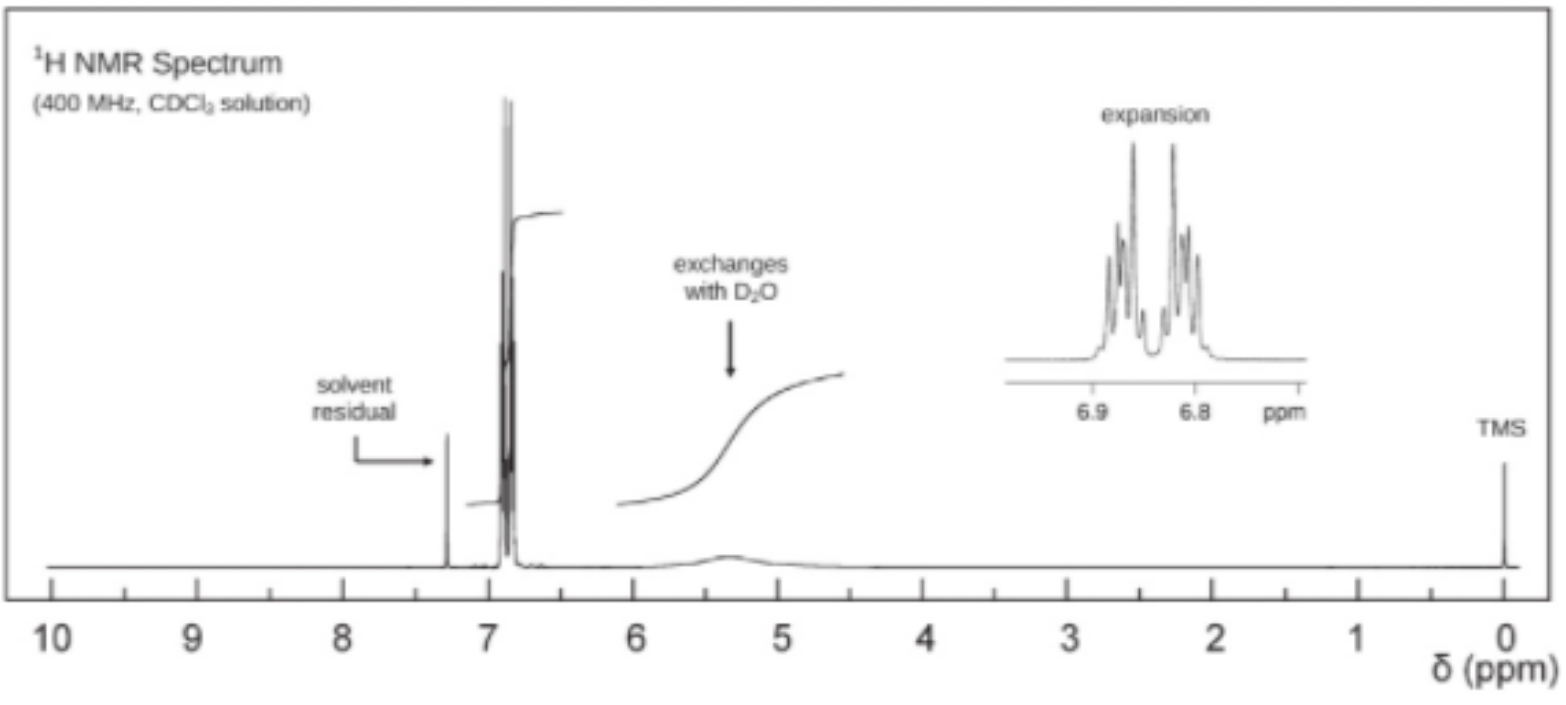


UV Spectrum

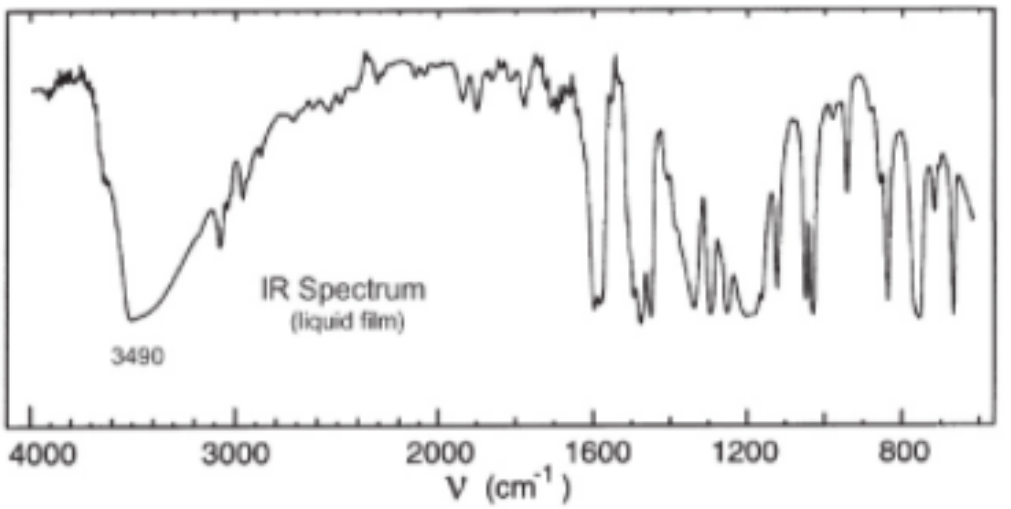
λ_{max} 225 nm ($\log_{10}\varepsilon$ 3.5)
λ_{max} 276 nm ($\log_{10}\varepsilon$ 3.4)
λ_{max} 283 nm ($\log_{10}\varepsilon$ 3.3)

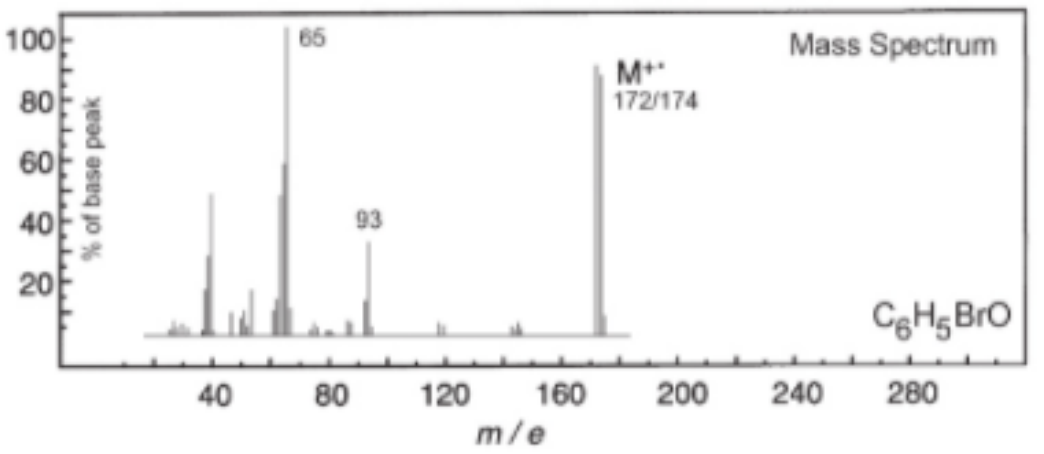
solvent: methanol





Problem 80

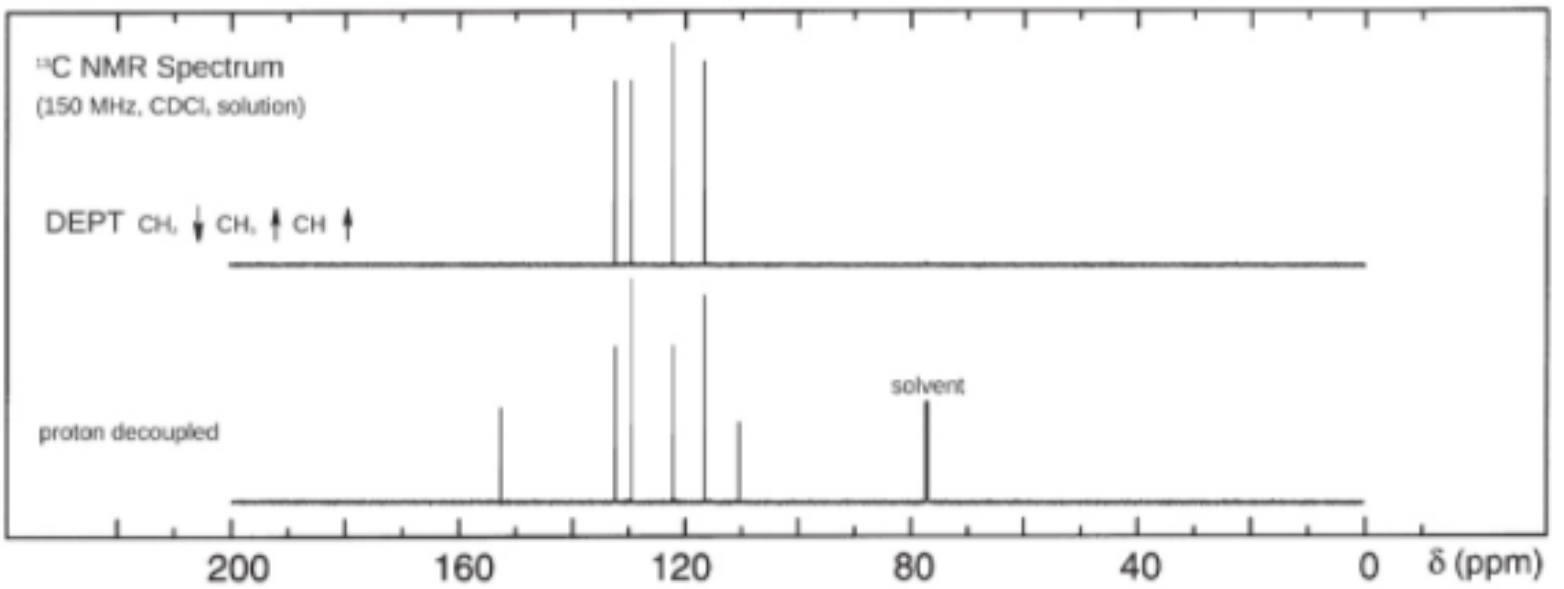


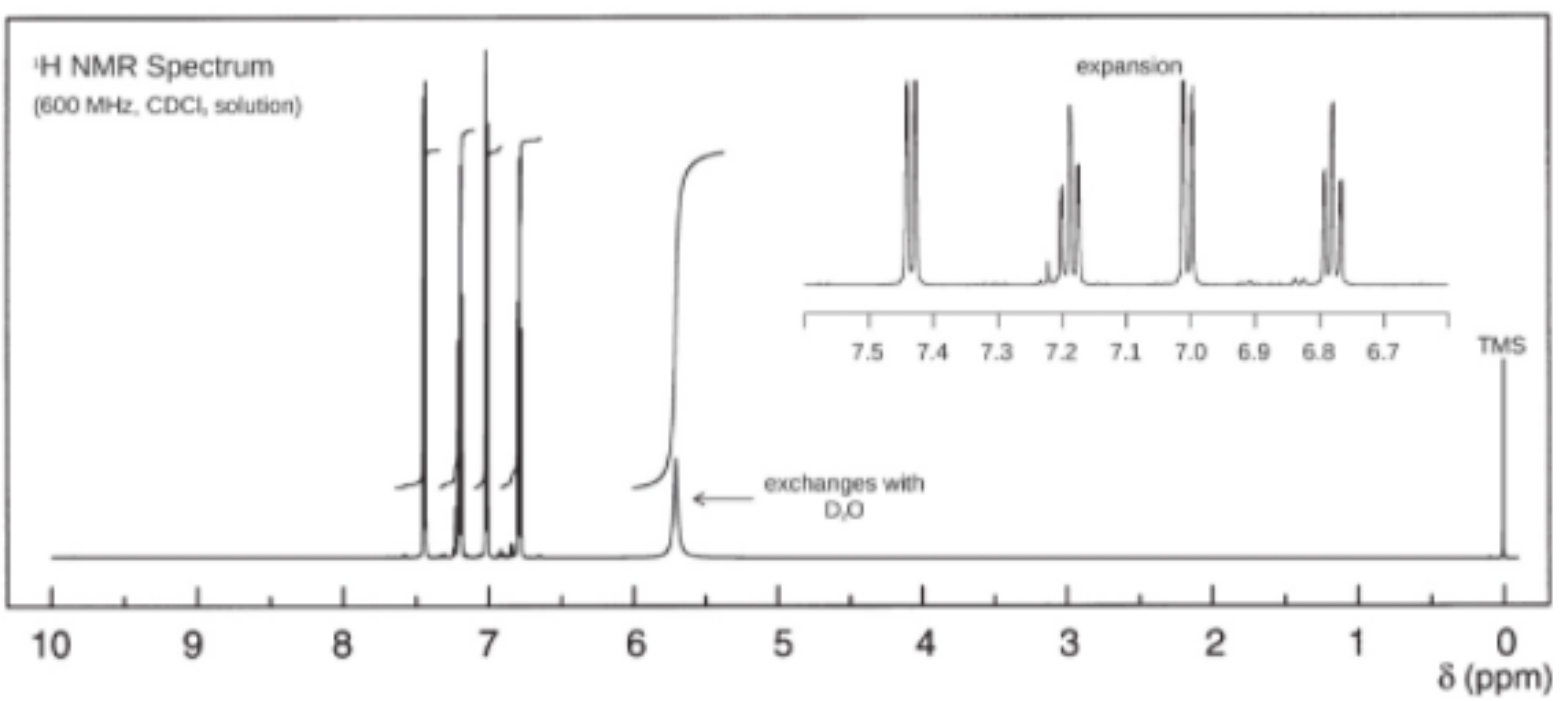


UV Spectrum

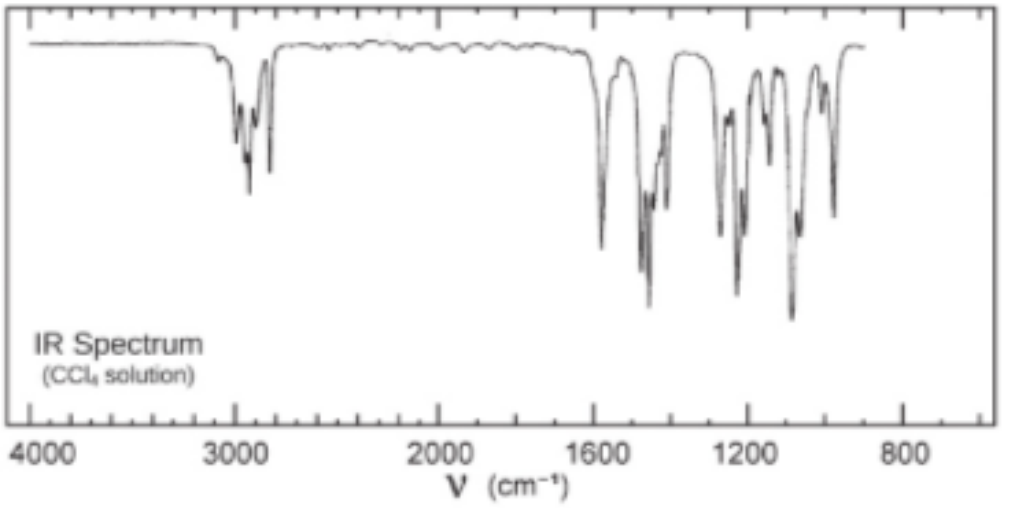
λ_{max} 277 nm ($\log_{10}\varepsilon$ 3.4)

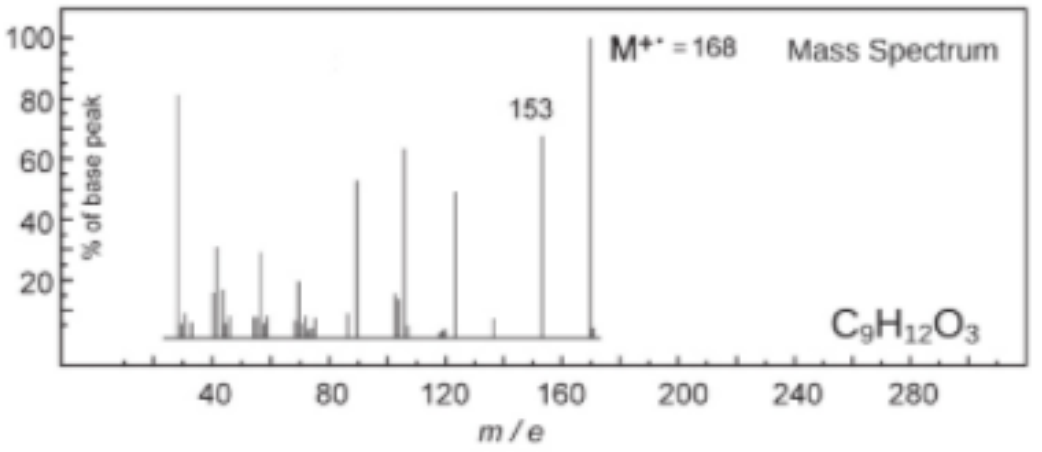
solvent : methanol





Problem 81

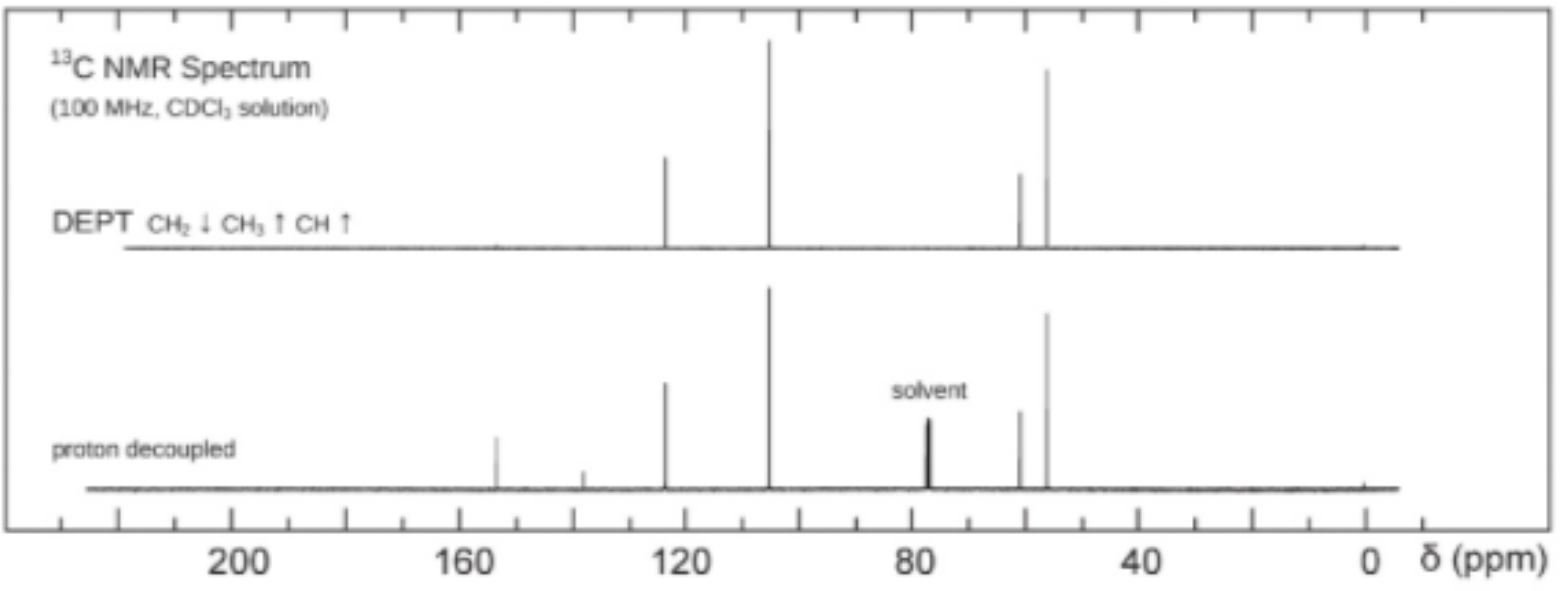


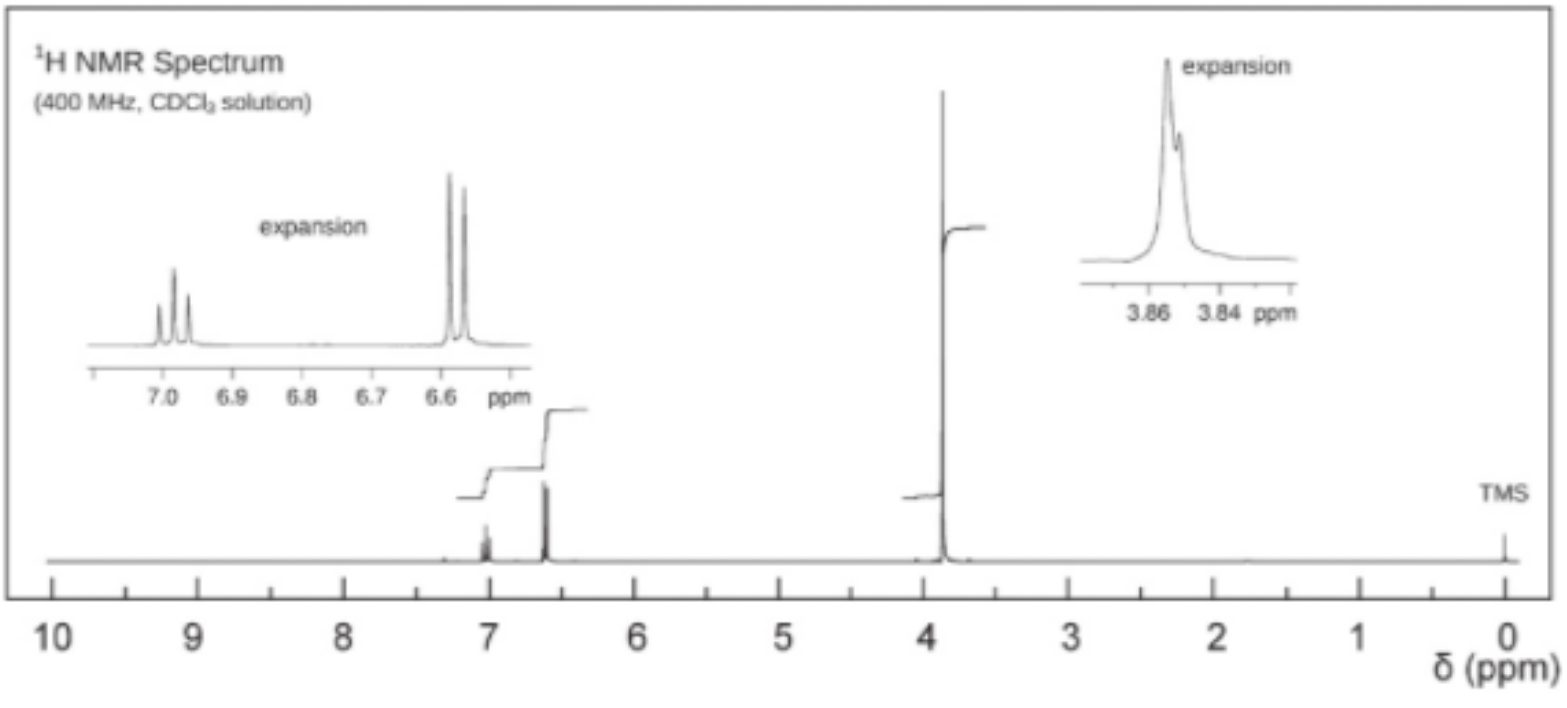


UV Spectrum

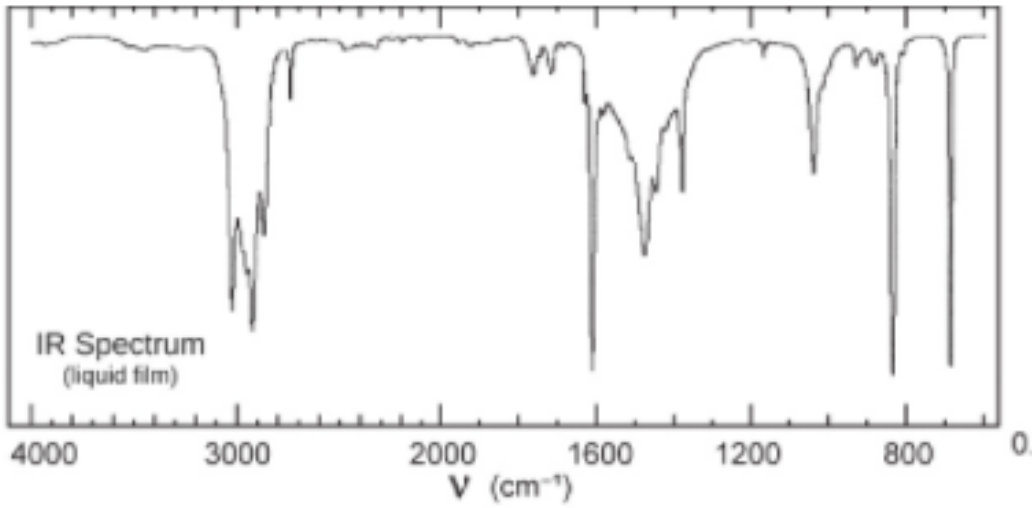
λ_{max} 267 nm ($\log_{10}\varepsilon$ 2.8)

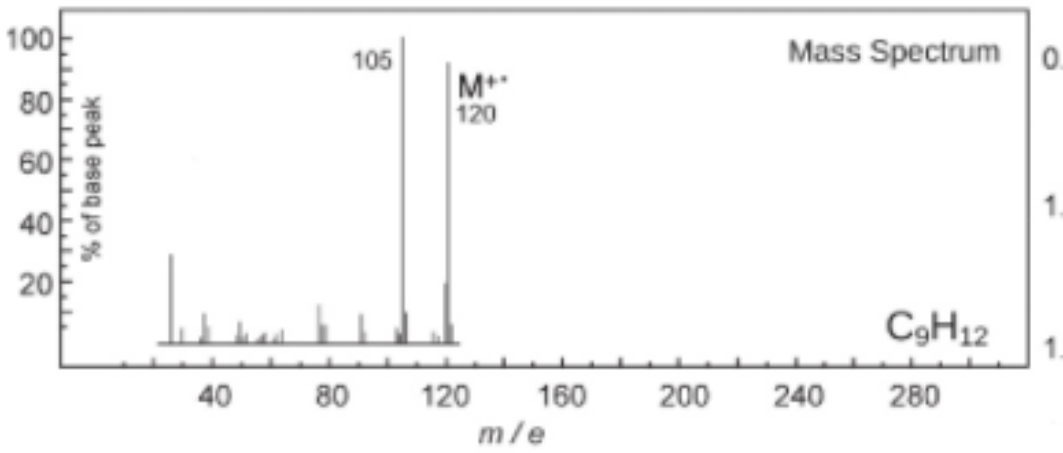
solvent: ethanol

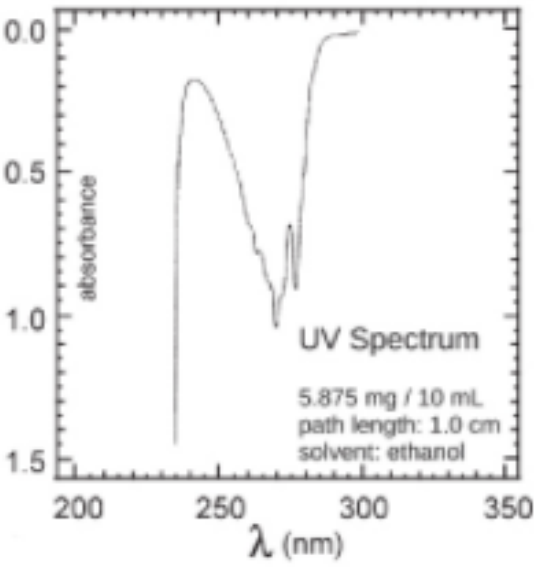


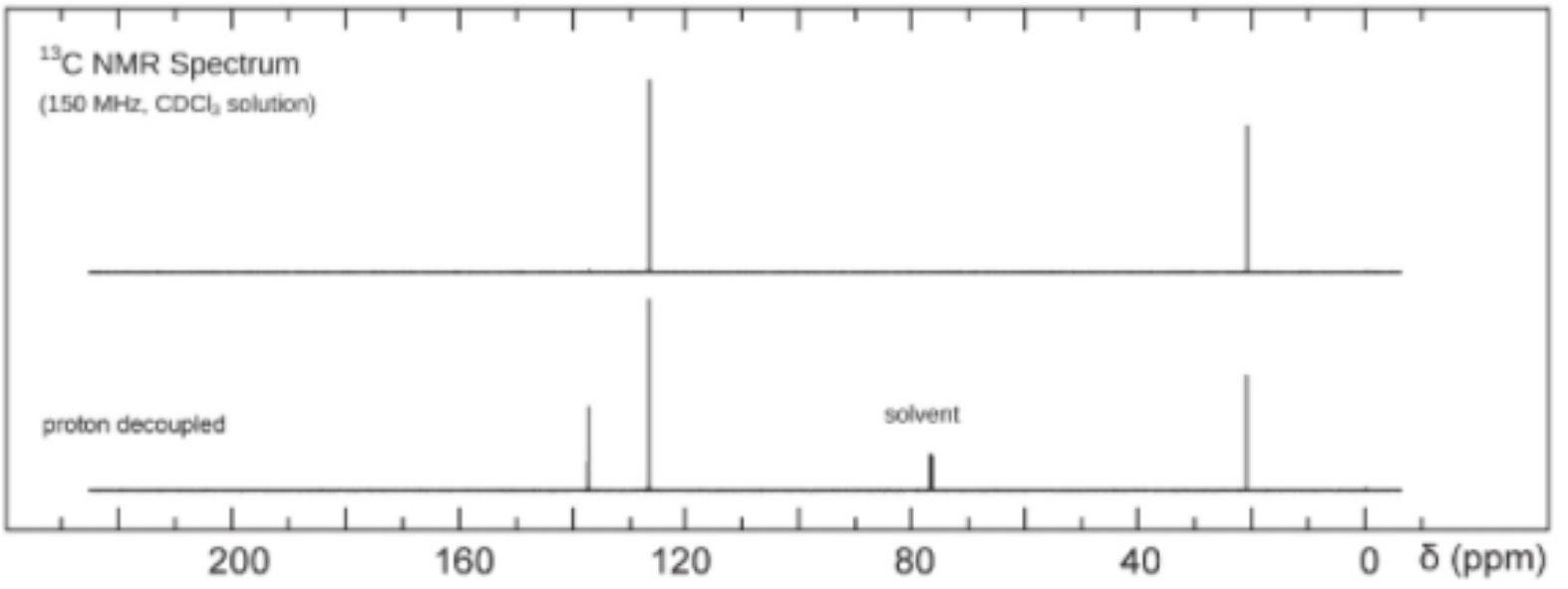


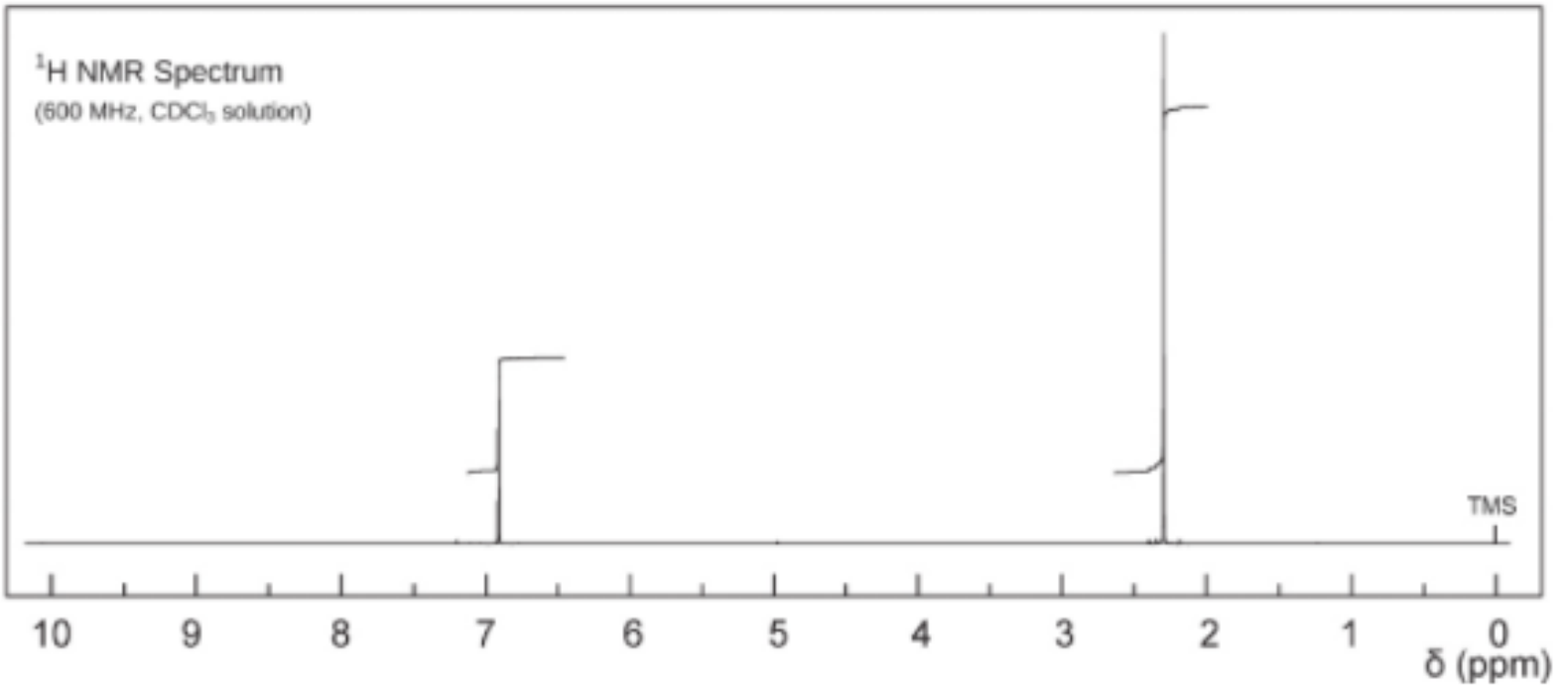
Problem 82


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

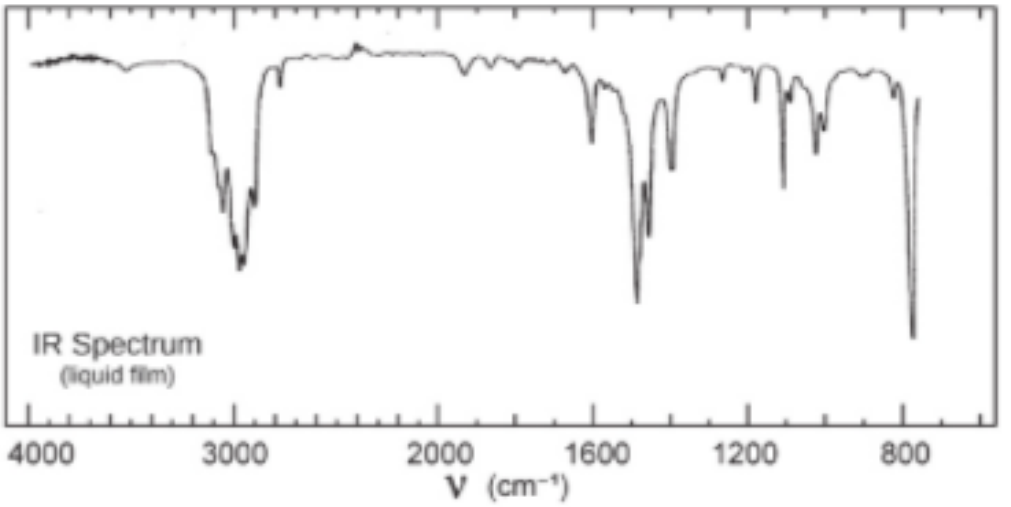

Mass Spectrum
105
M+·
120
% of base peak
100
80
60
40
20
C9H12
40
80
120
160
200
240
280
m / e

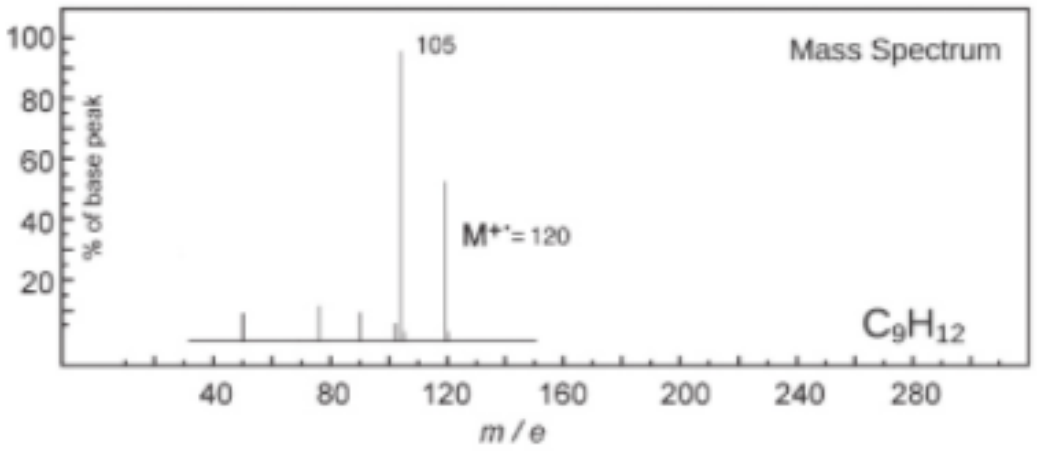

absorbance
0.0
0.5
1.0
1.5
UV Spectrum
5.875 mg / 10 mL
path length: 1.0 cm
solvent: ethanol
200
250
300
350
λ (nm)


13C NMR Spectrum
(150 MHz, CDCl3 solution)
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(600 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 83

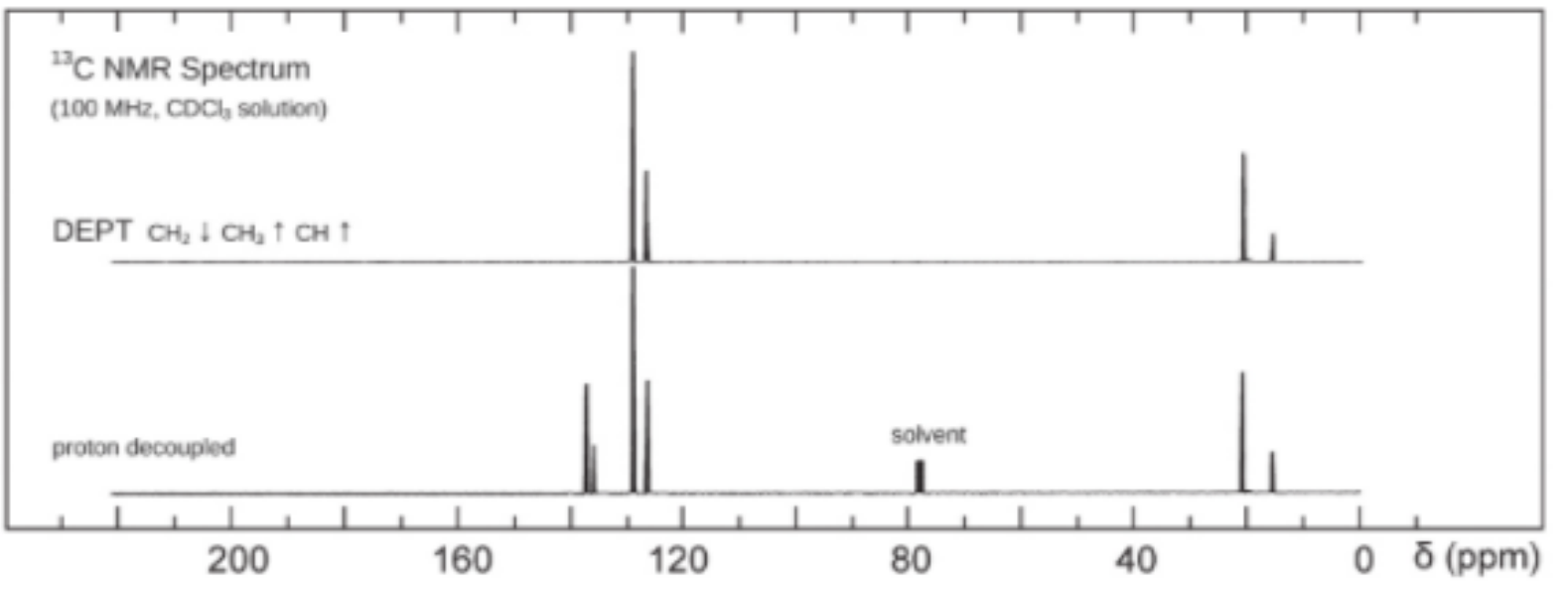


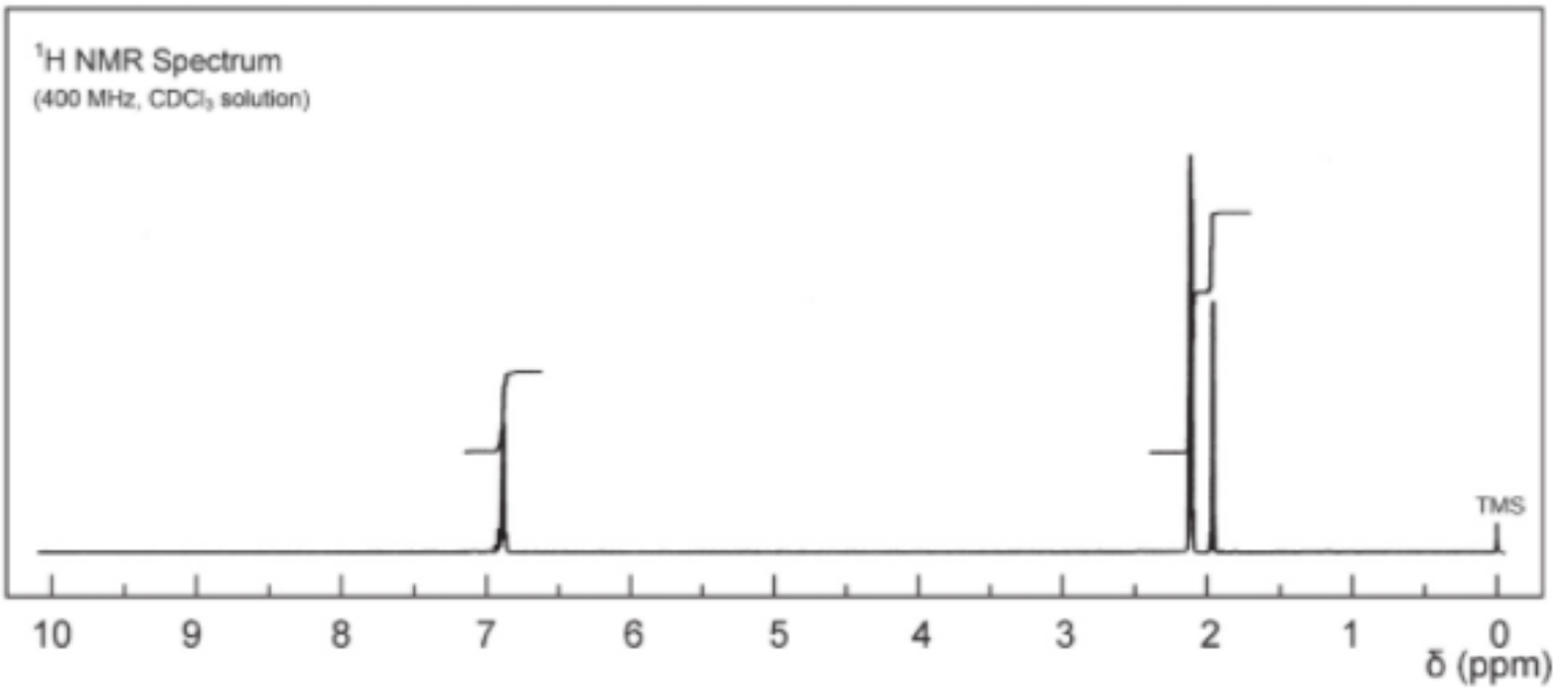


UV Spectrum

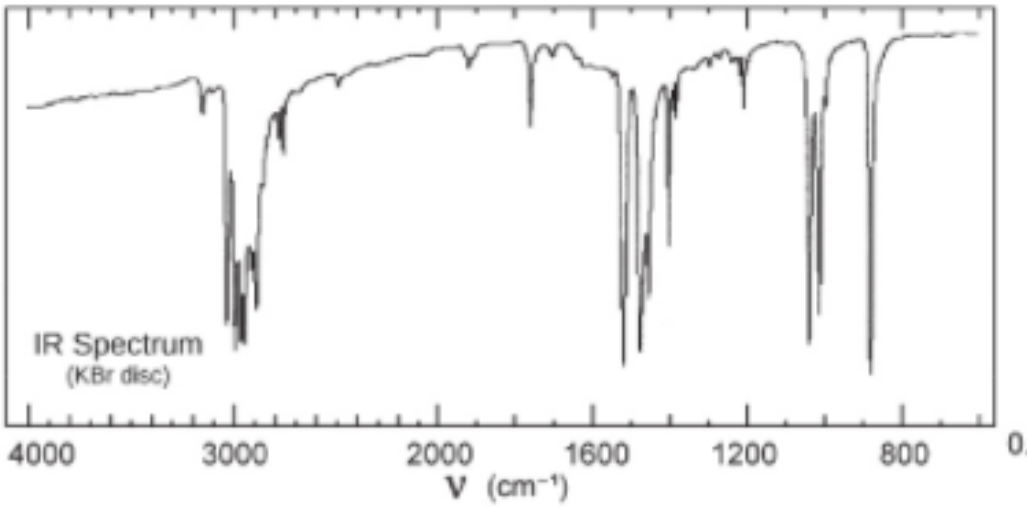
λ_{max} 261 nm ($\log_{10}\varepsilon$ 2.7)
λ_{max} 269 nm ($\log_{10}\varepsilon$ 2.5)

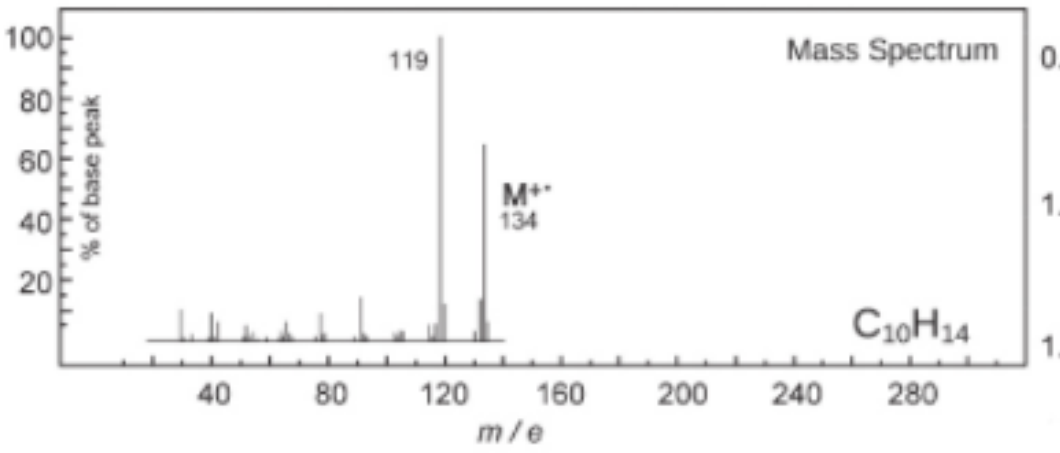
solvent: methanol

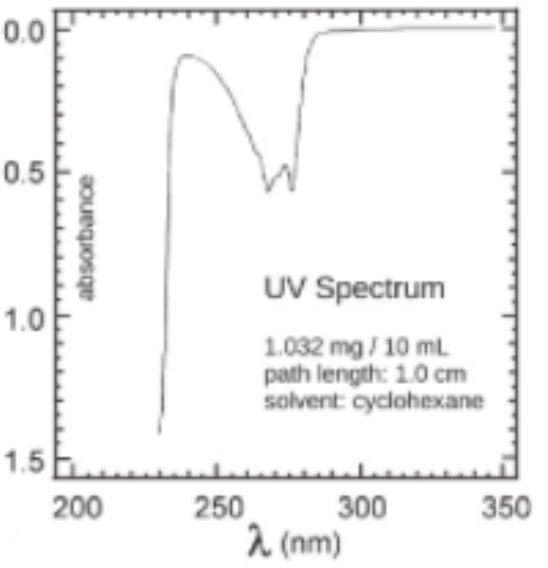


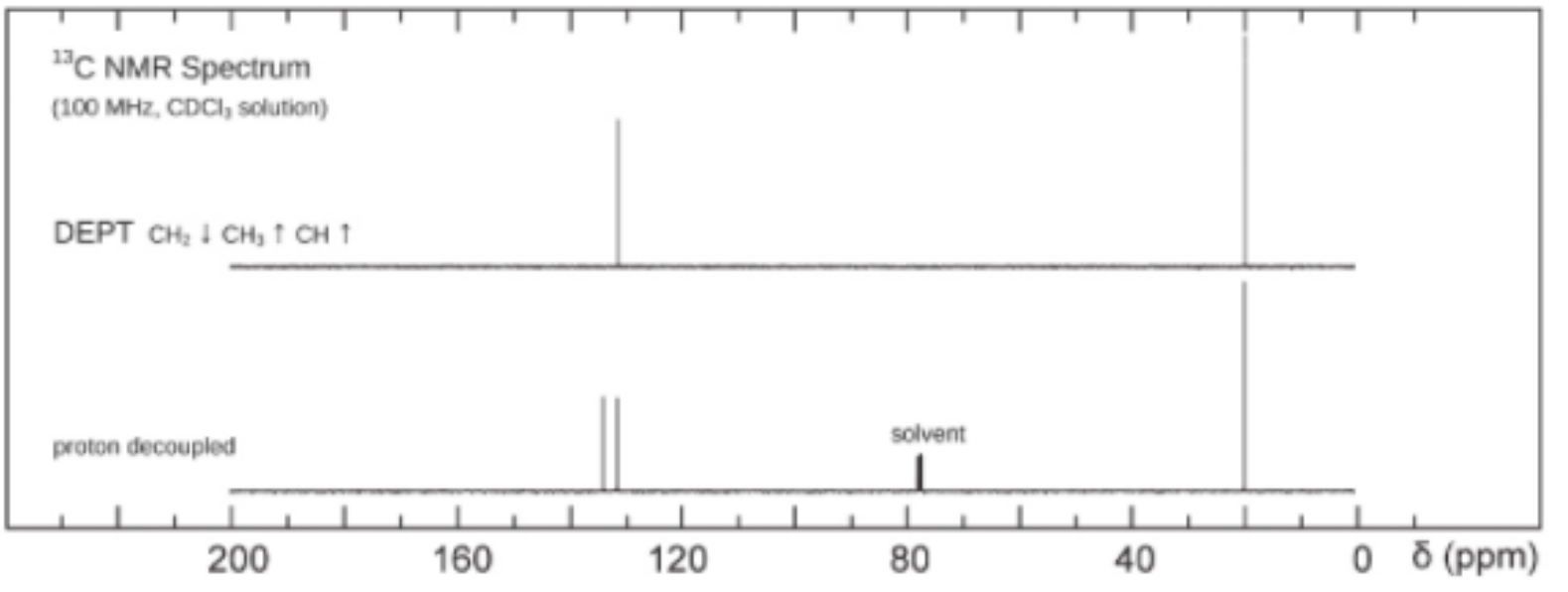


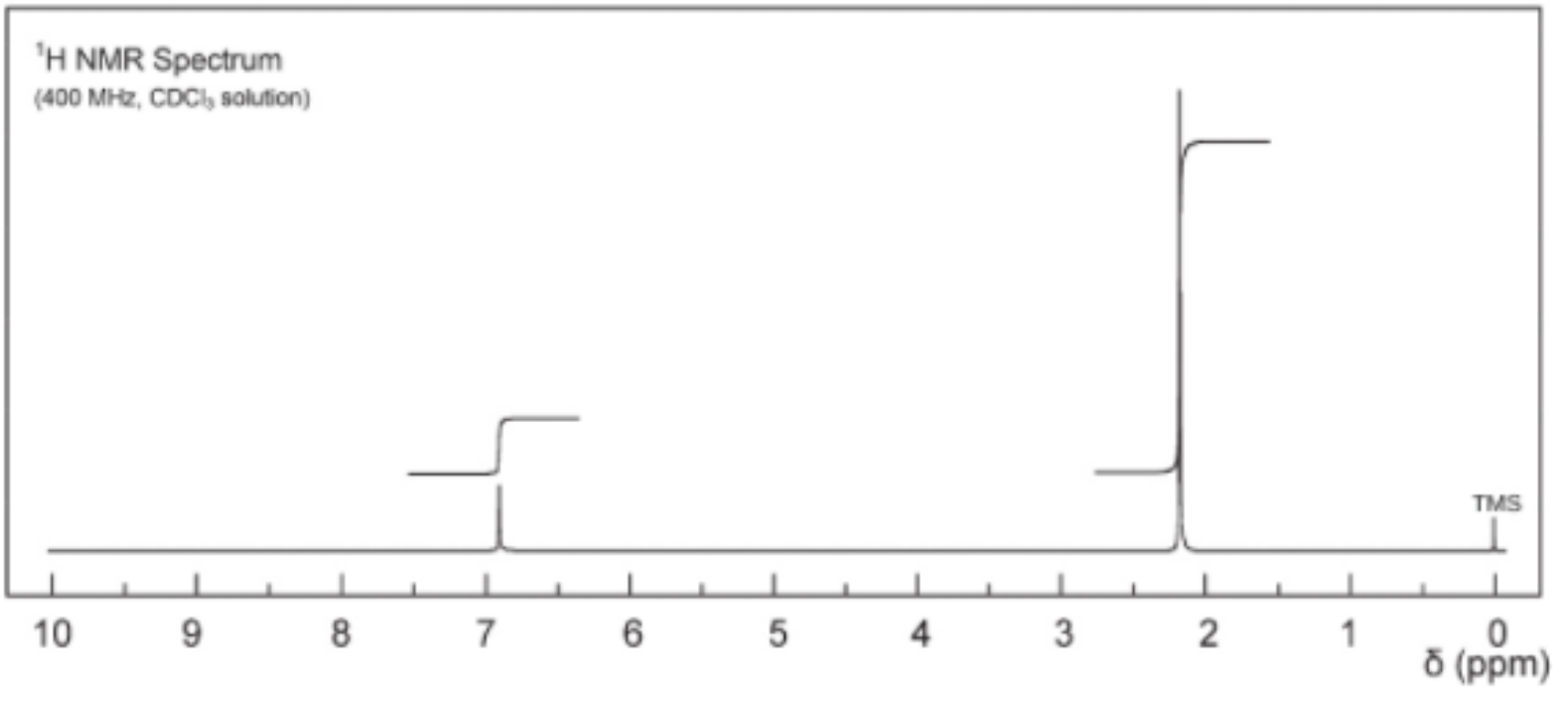
Problem 84


IR Spectrum
(KBr disc)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

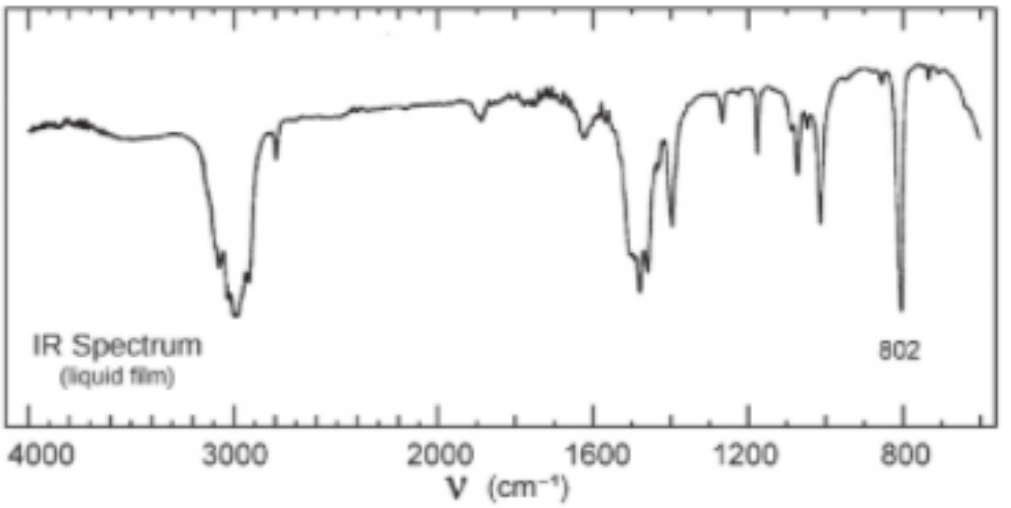

Mass Spectrum
119
M+·
134
% of base peak
100
80
60
40
20
C10H14
40
80
120
160
200
240
280
m / e

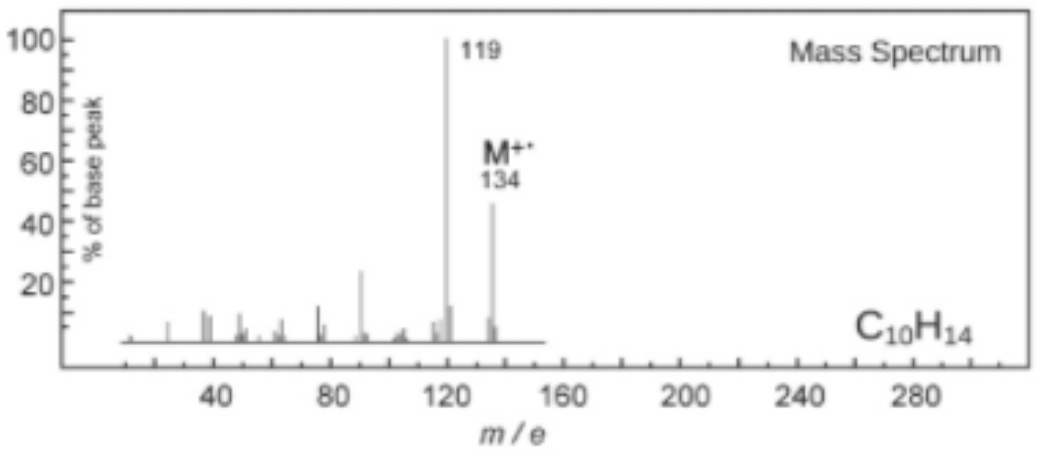

UV Spectrum
1.032 mg / 10 mL
path length: 1.0 cm
solvent: cyclohexane
absorbance
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)

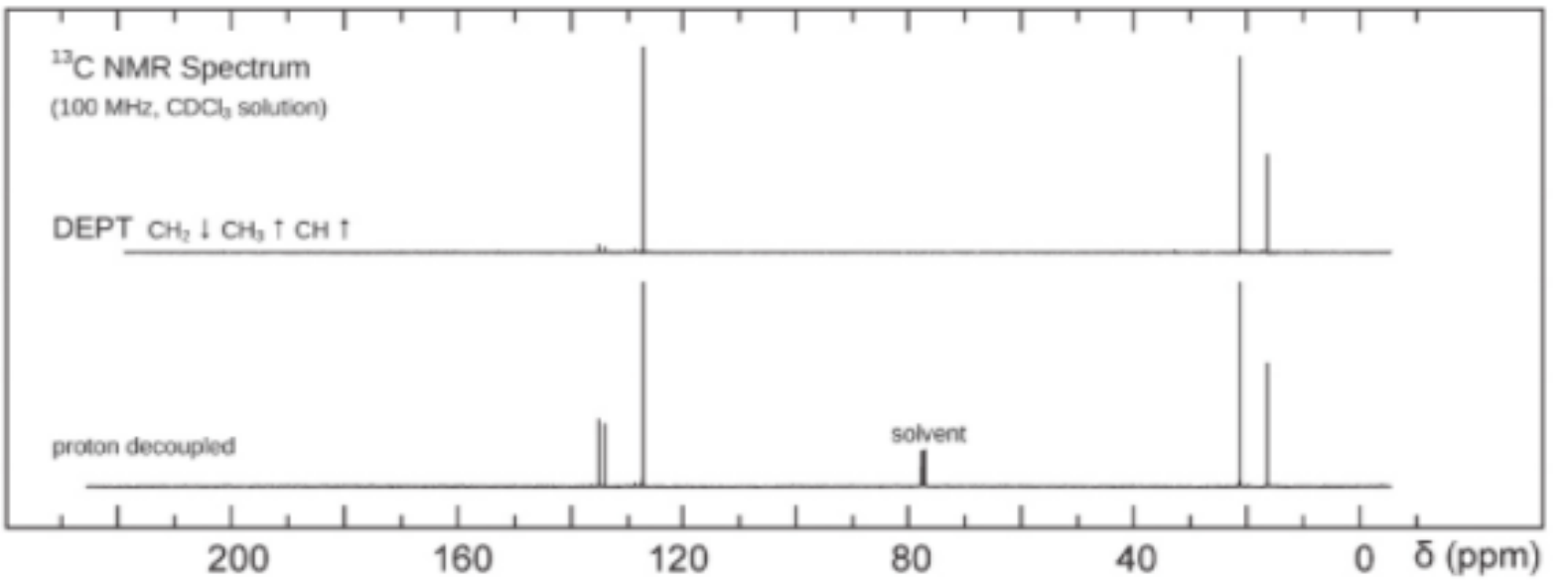

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

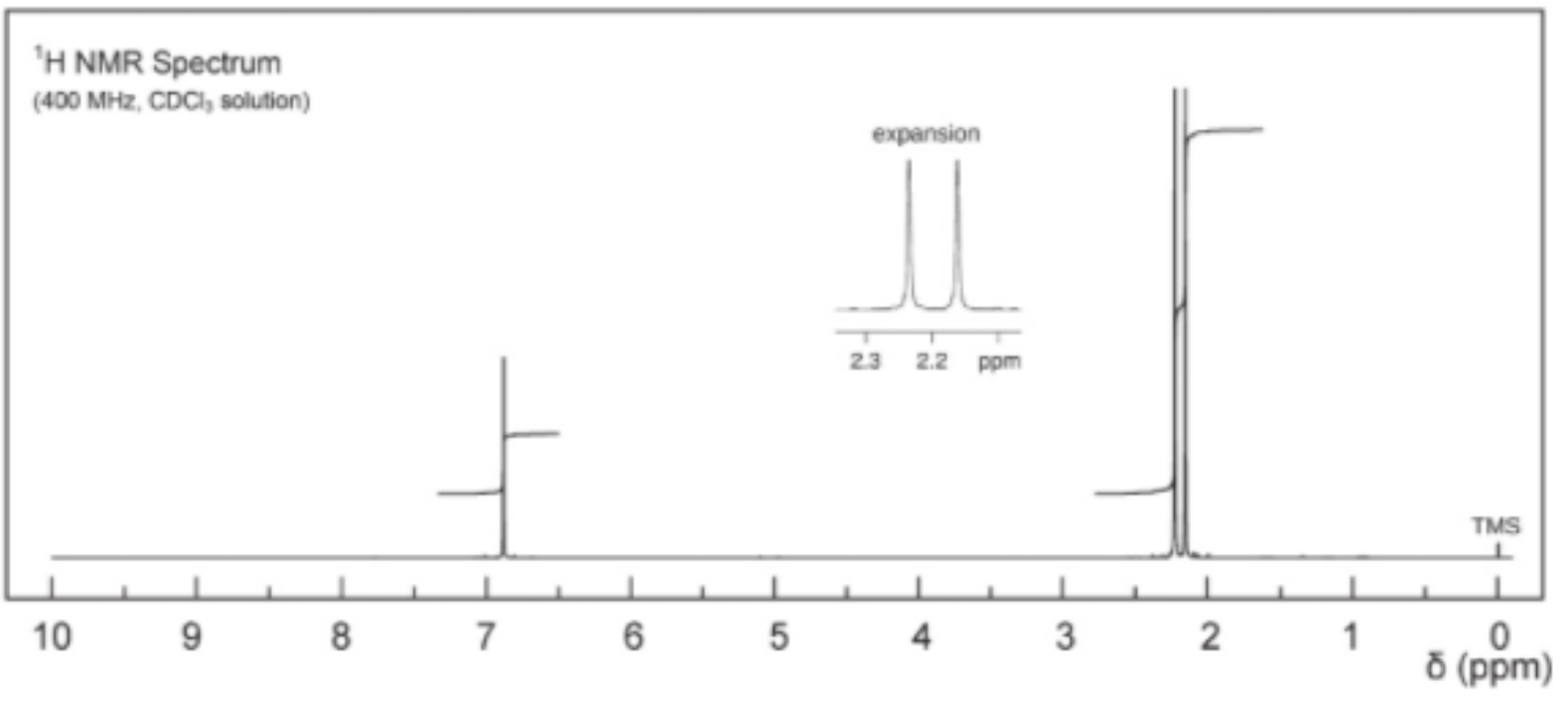

1H NMR Spectrum
(400 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 85

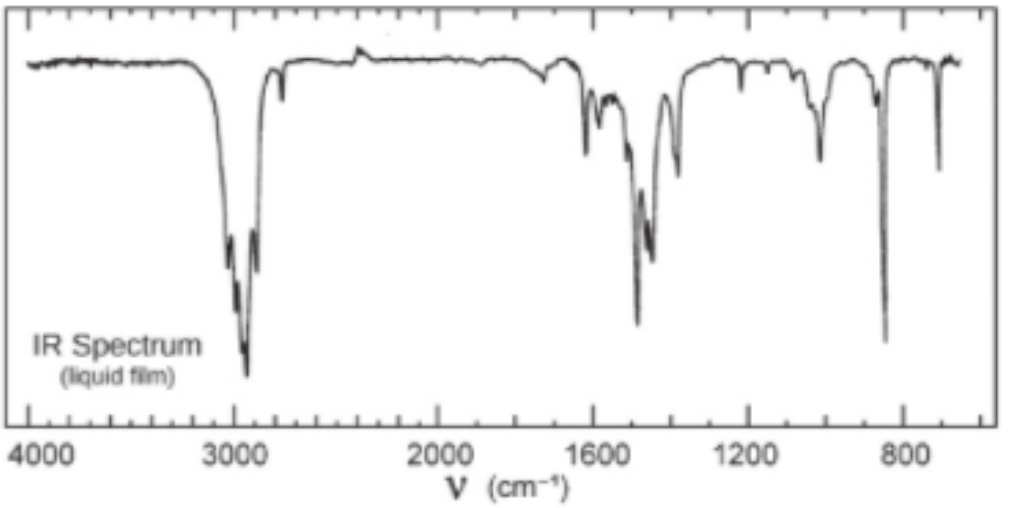

IR Spectrum
(liquid film)
802
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

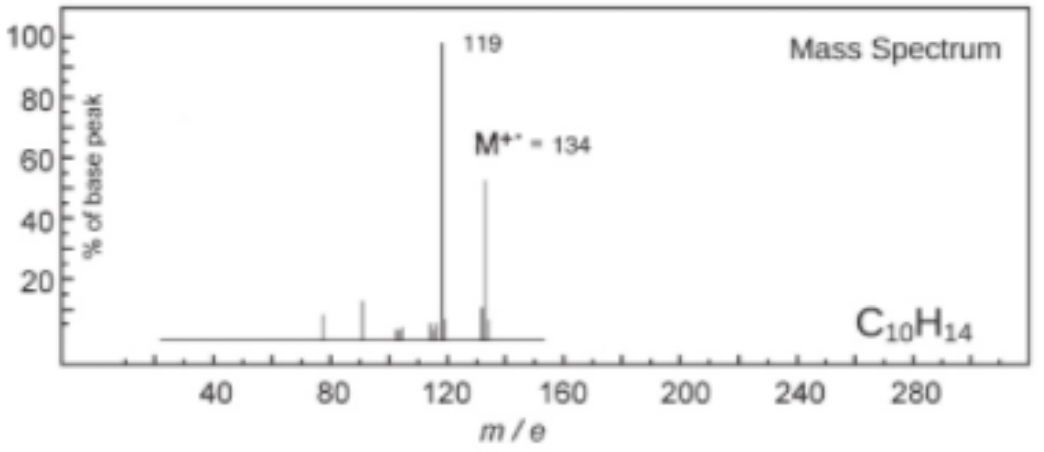

Mass Spectrum
119
M+·
134
% of base peak
100
80
60
40
20
C10H14
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
2.3
2.2
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 86

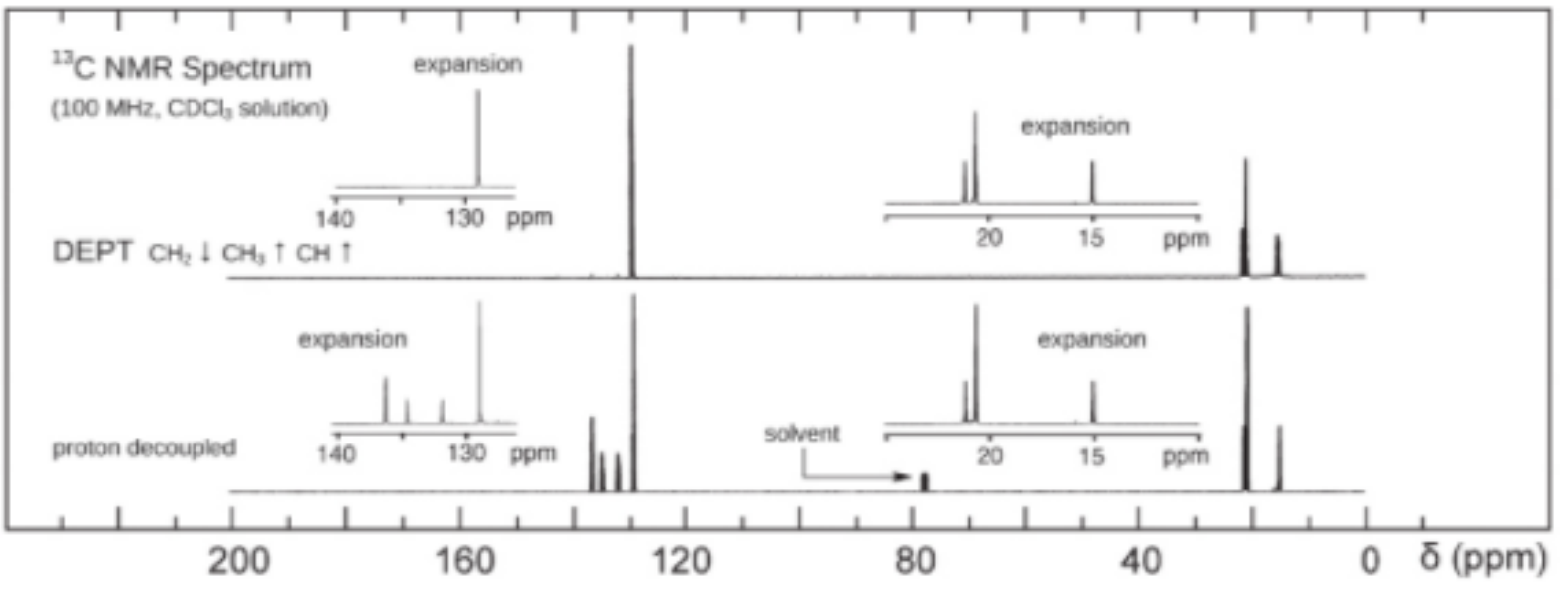


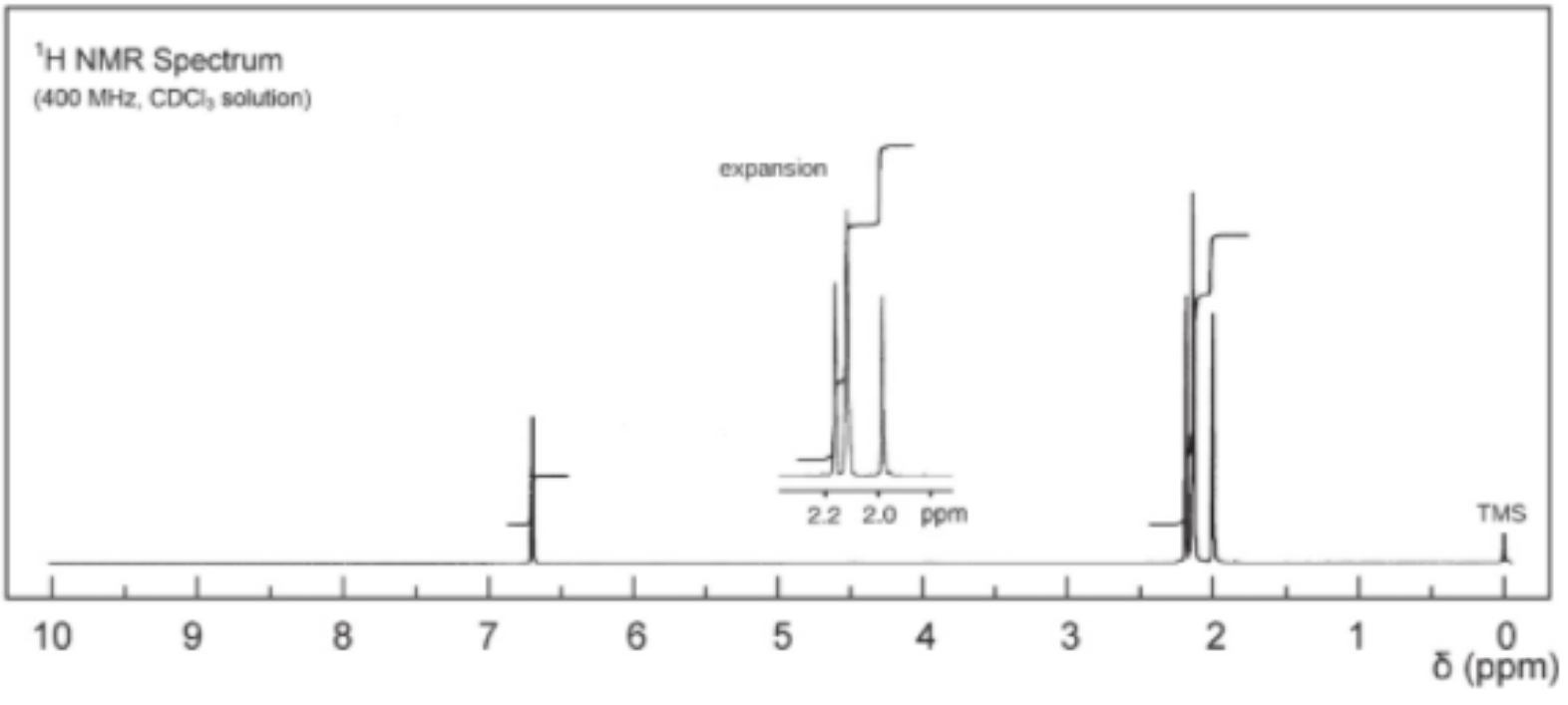


UV Spectrum

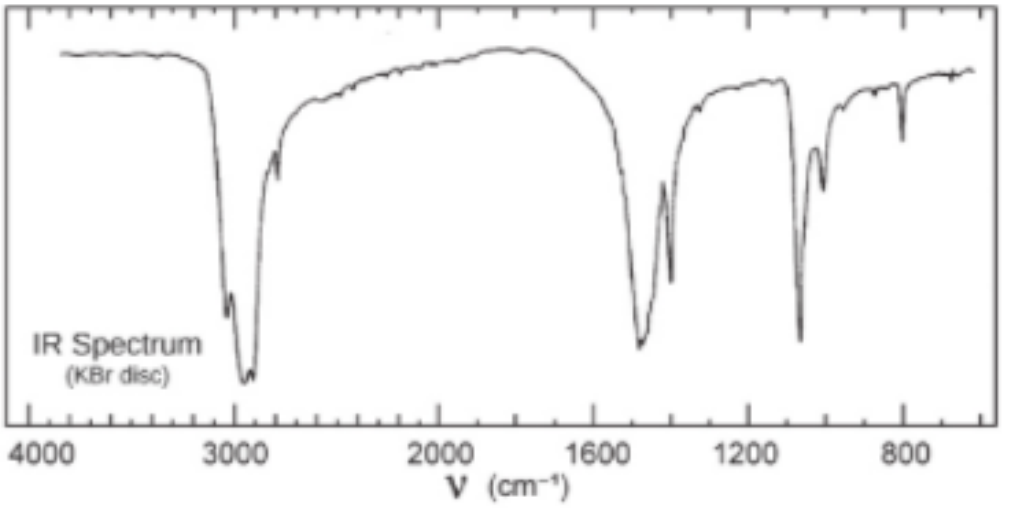
λ_{max} 274 nm ($\log_{10}\varepsilon$ 2.3)
λ_{max} 277 nm ($\log_{10}\varepsilon$ 2.3)

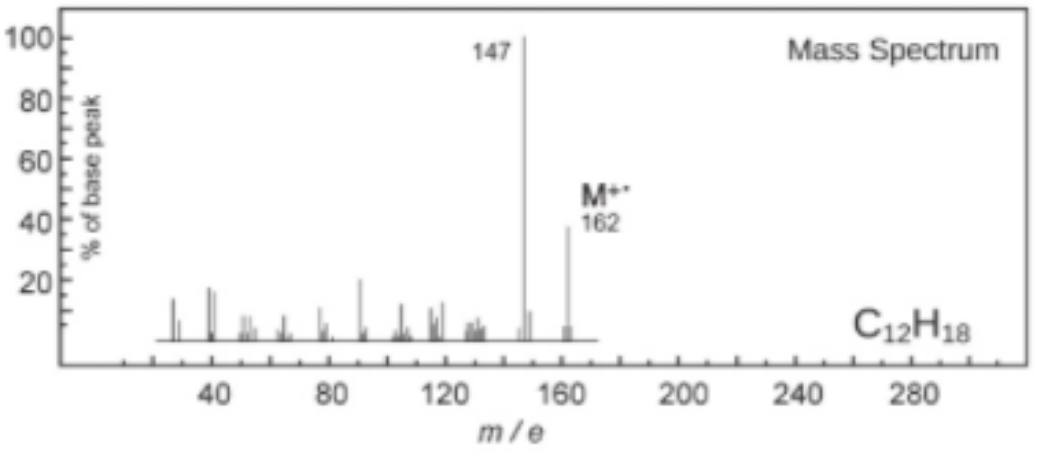
solvent: cyclohexane





Problem 87

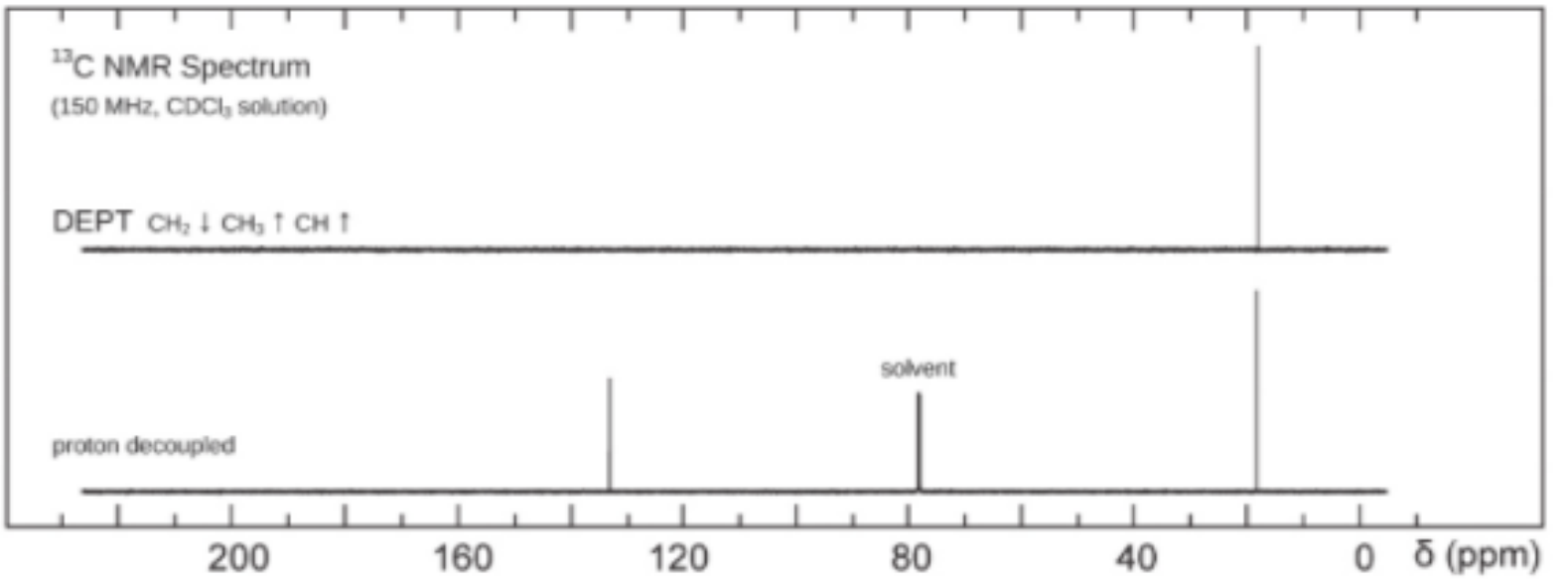


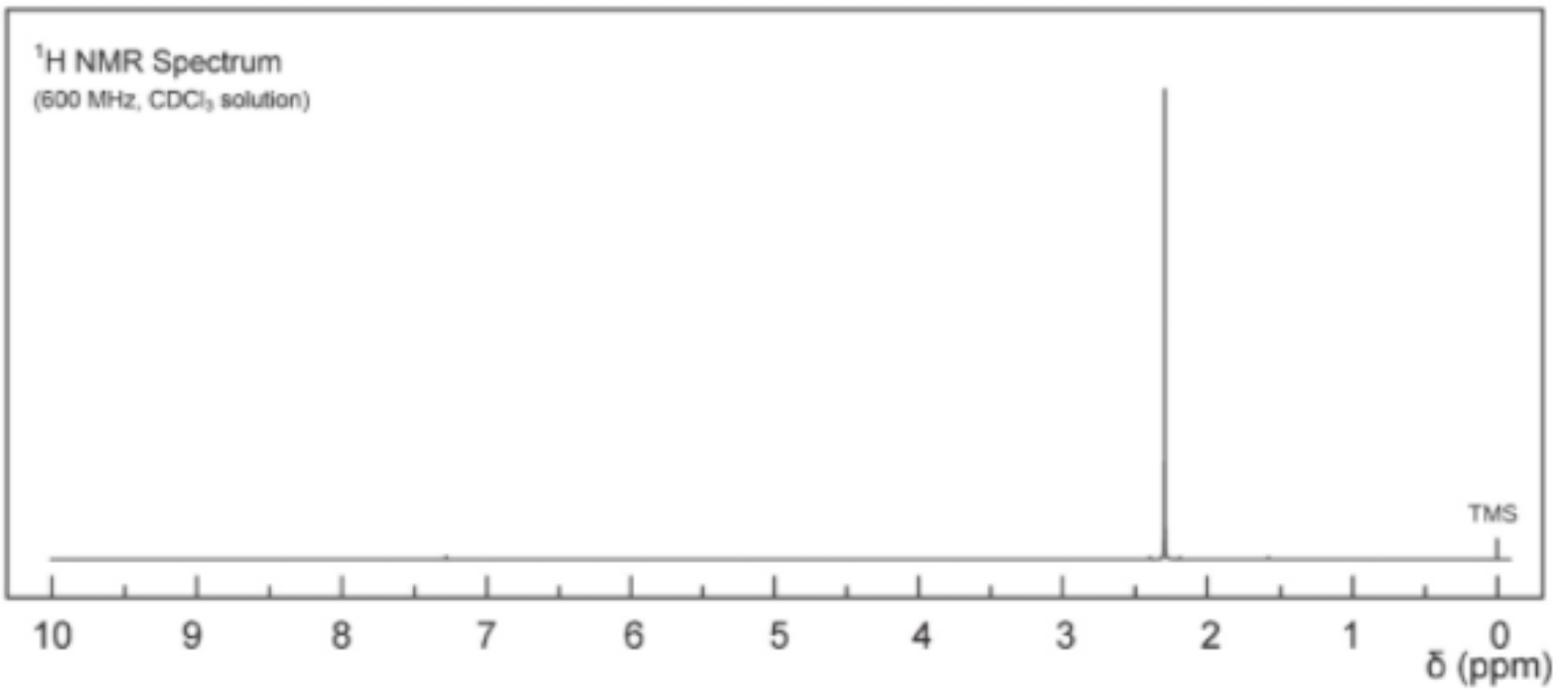


UV Spectrum

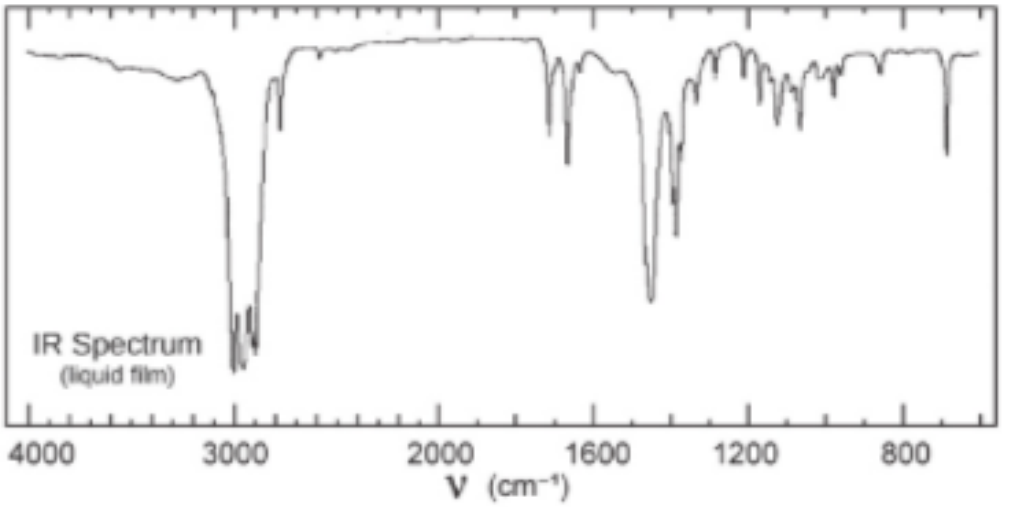
λ_{max} 270 nm ($\log_{10}\varepsilon$ 2.5)
λ_{max} 274 nm ($\log_{10}\varepsilon$ 2.4)
λ_{max} 278 nm ($\log_{10}\varepsilon$ 2.4)

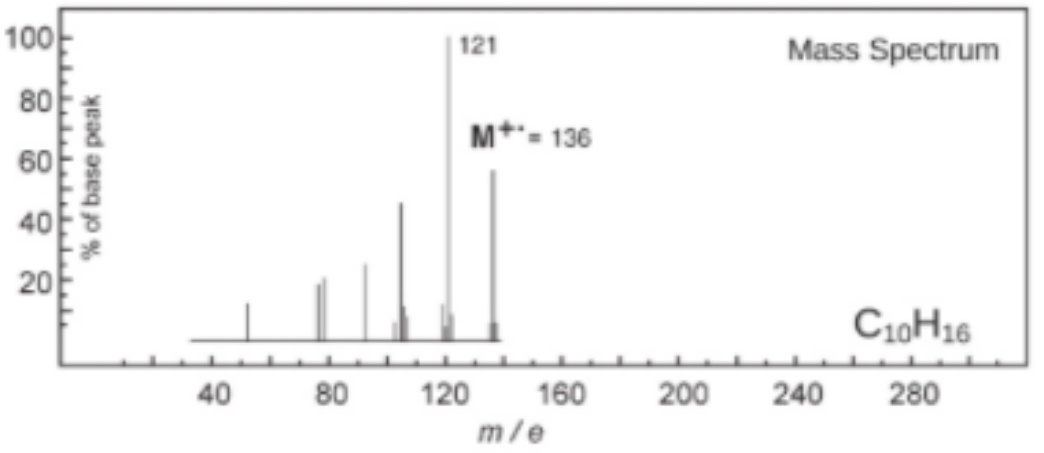
solvent: methanol





Problem 88

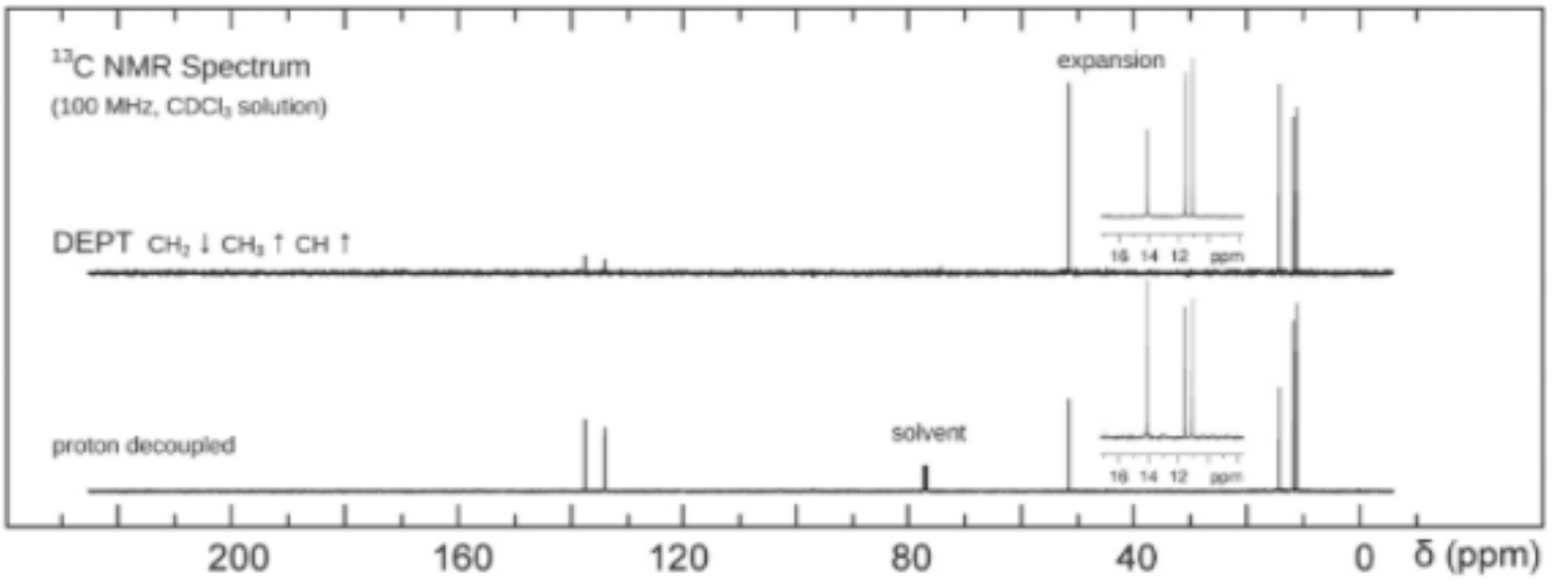


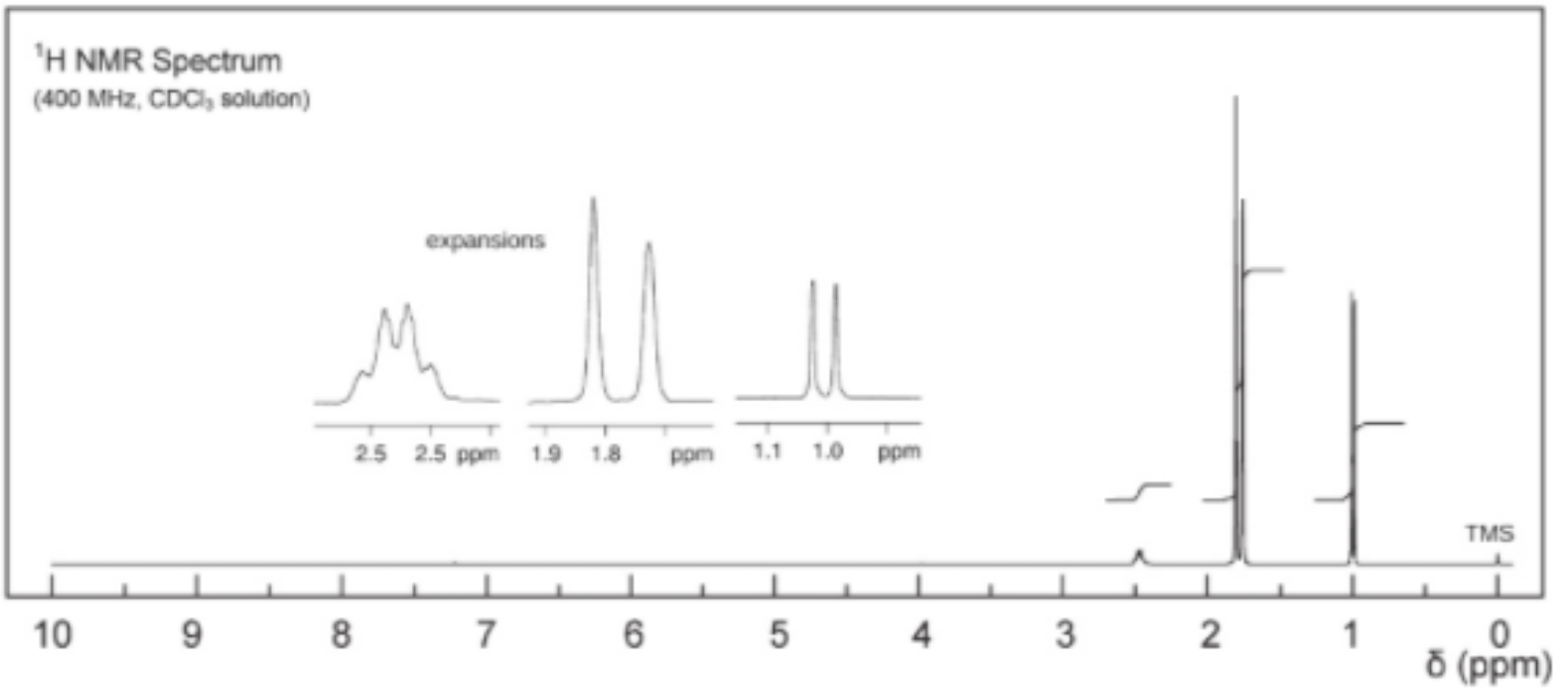


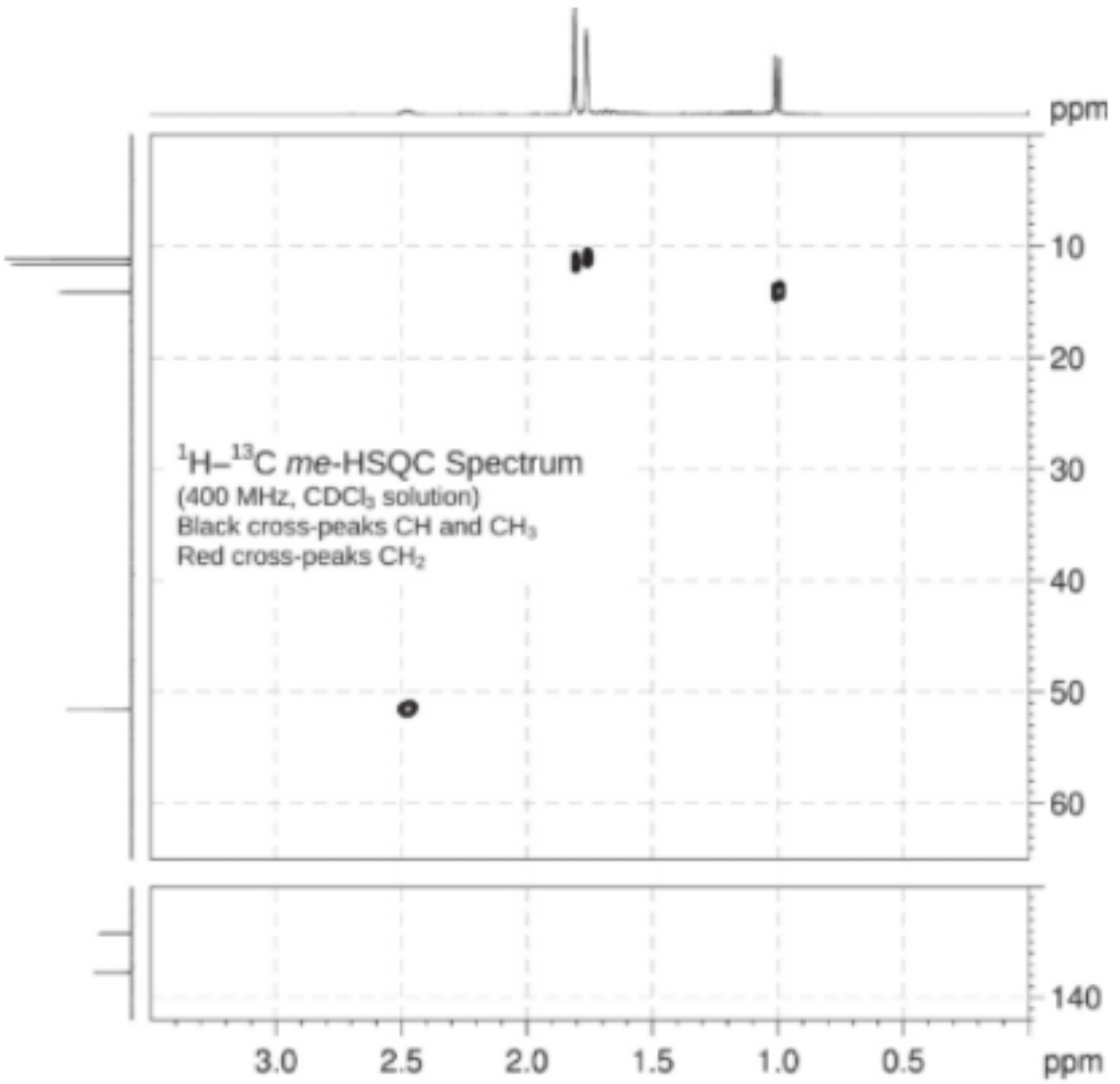
UV Spectrum

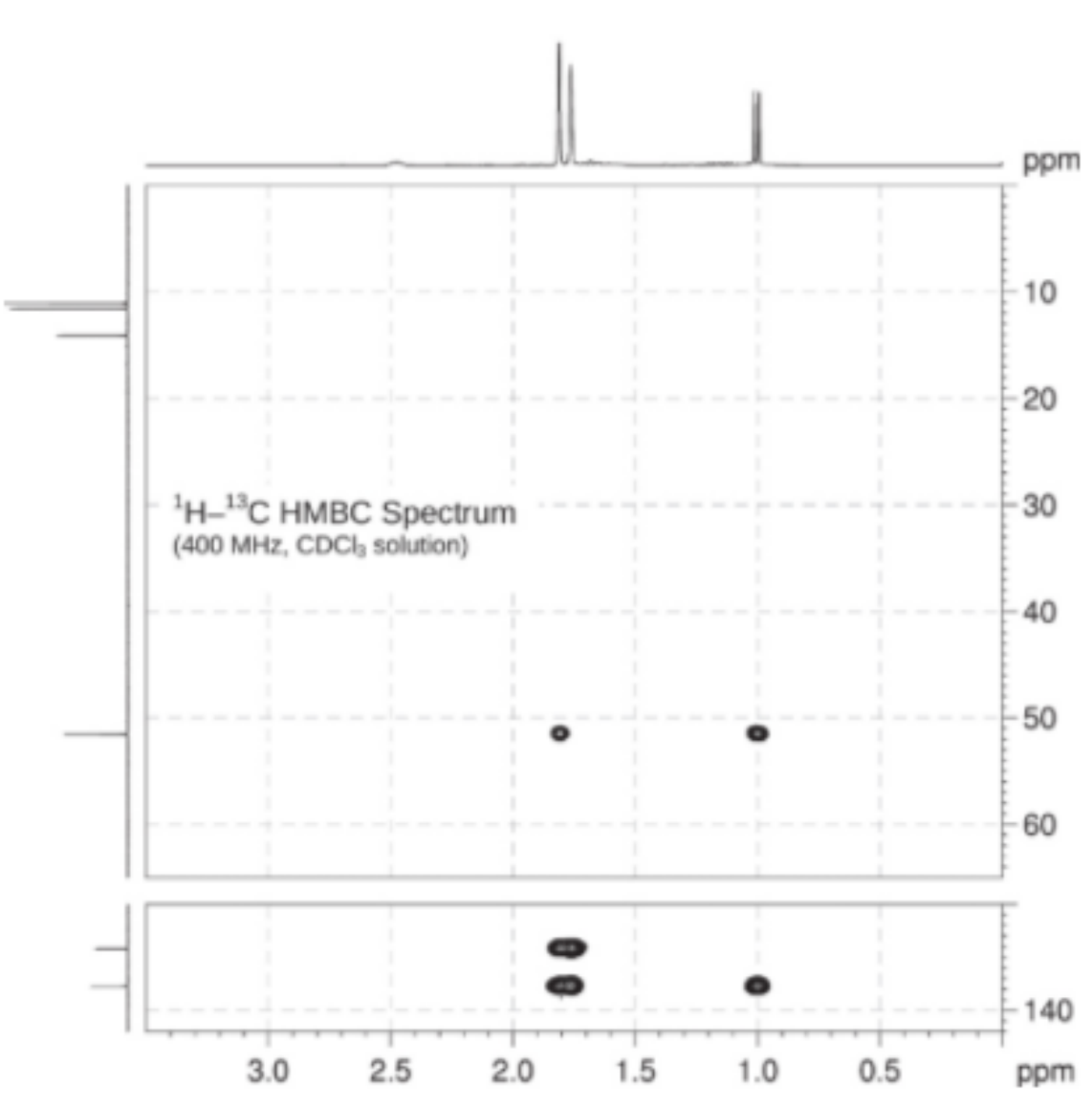
λ_{max} 232 nm ($\log_{10}\varepsilon$ 3.4)
λ_{max} 248 nm ($\log_{10}\varepsilon$ 3.5)
λ_{max} 265 nm ($\log_{10}\varepsilon$ 3.4)

solvent: isooctane

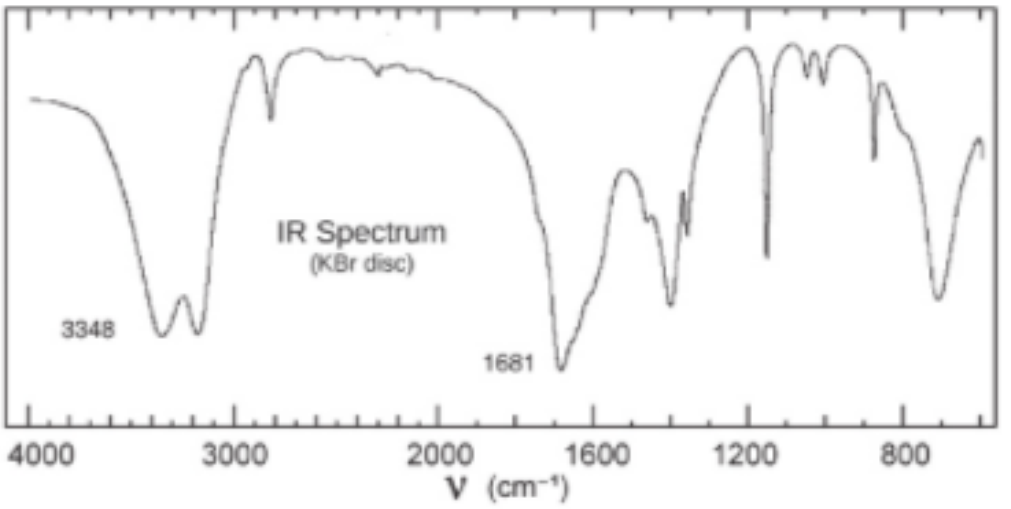


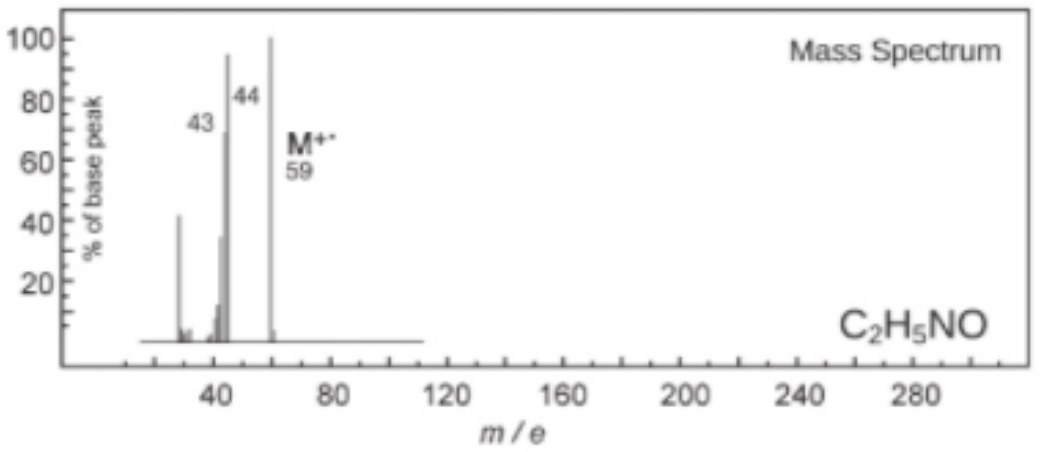



ppm
10
20
30
40
50
60
140
3.0
2.5
2.0
1.5
1.0
0.5
ppm
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

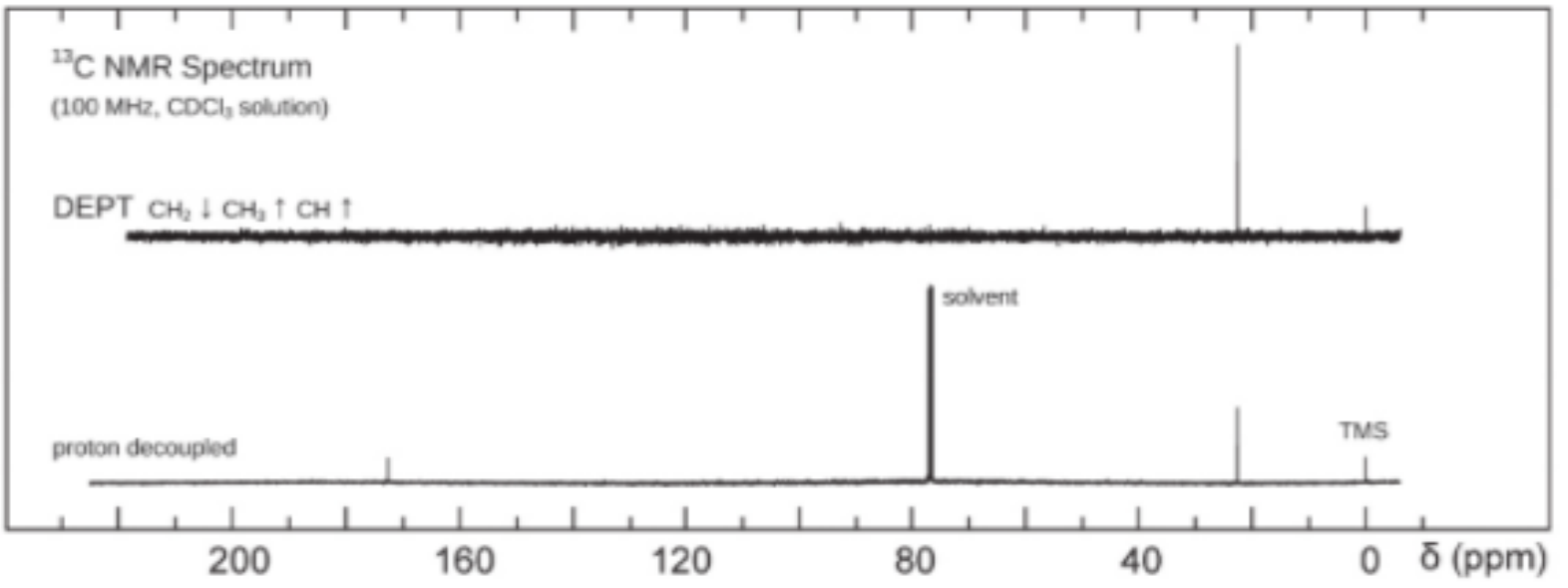

ppm
10
20
30
40
50
60
140
3.0
2.5
2.0
1.5
1.0
0.5
ppm
$^{1}H–^{13}C$ HMBC Spectrum
(400 MHz, $CDCl_3$ solution)

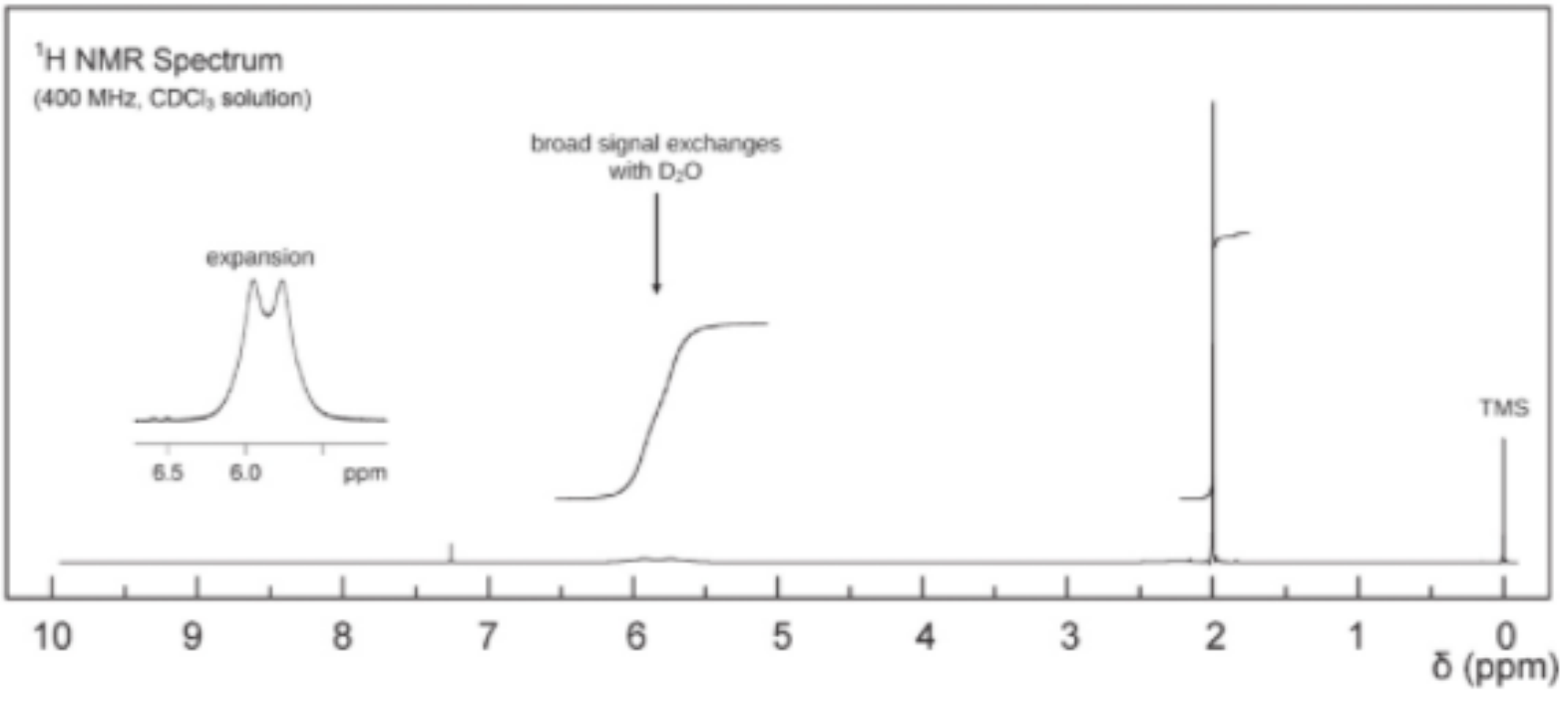
Problem 89



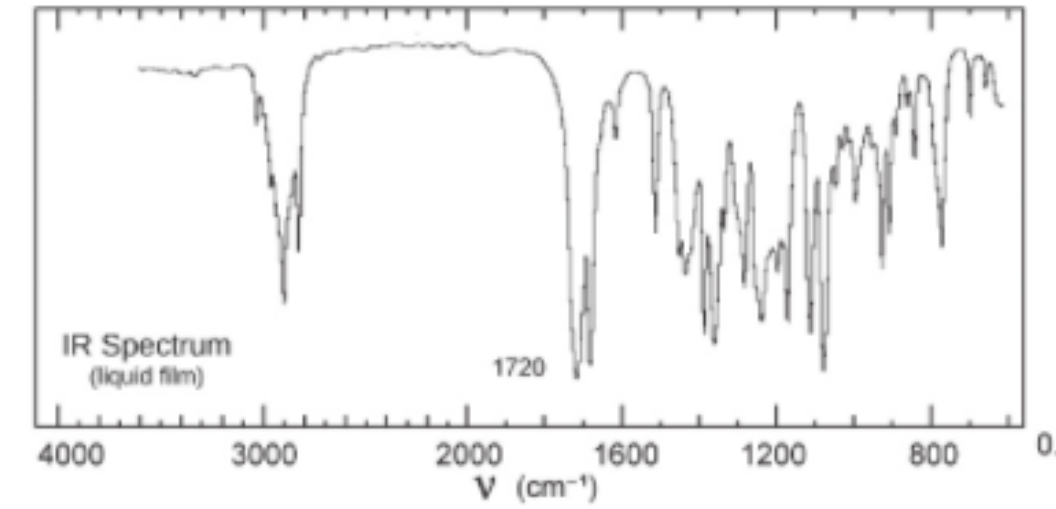


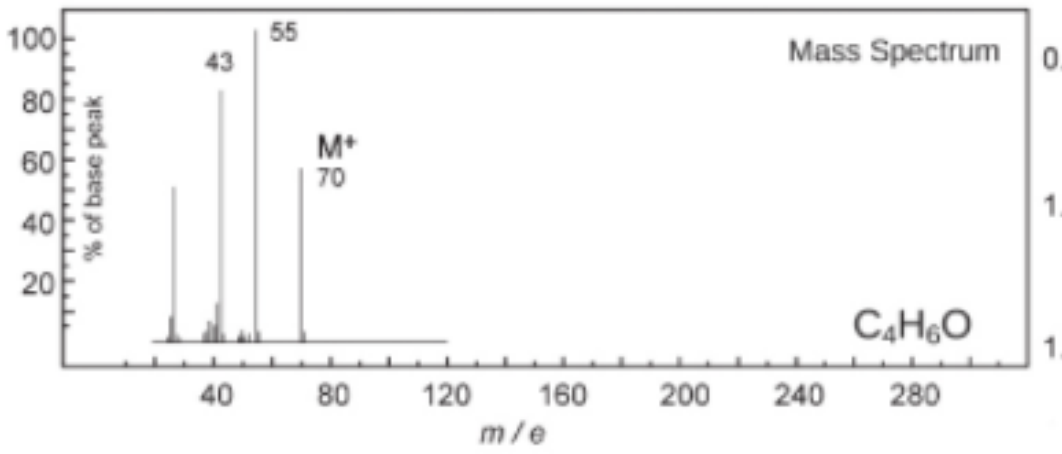
No significant UV absorption above 220 nm

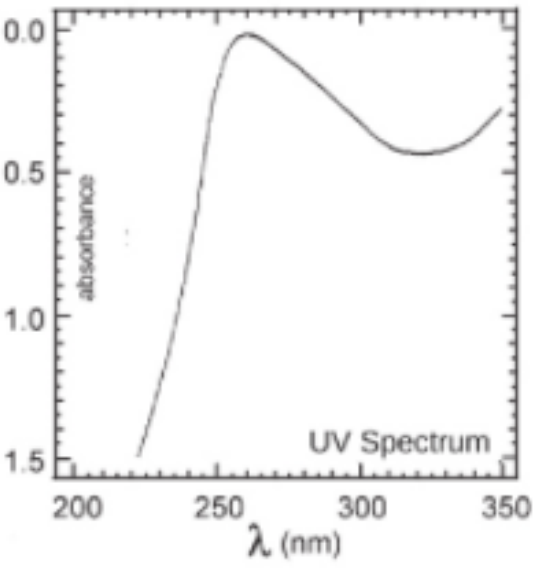


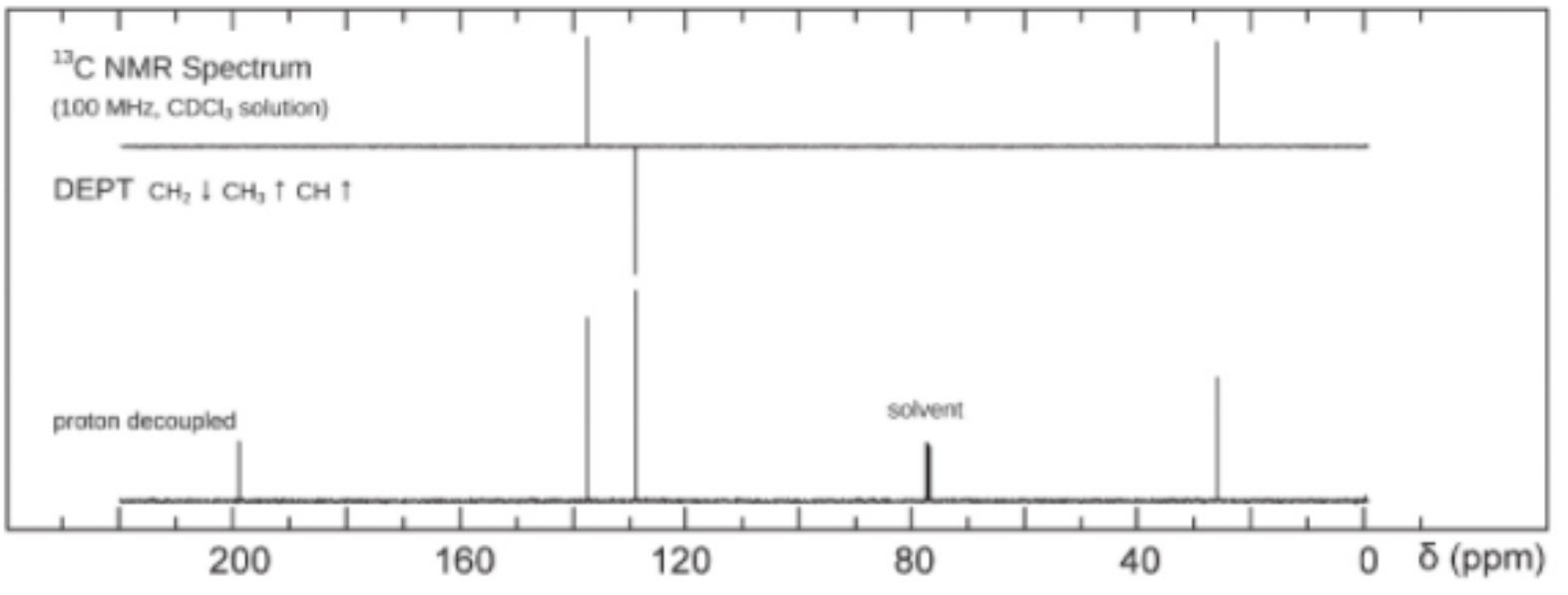


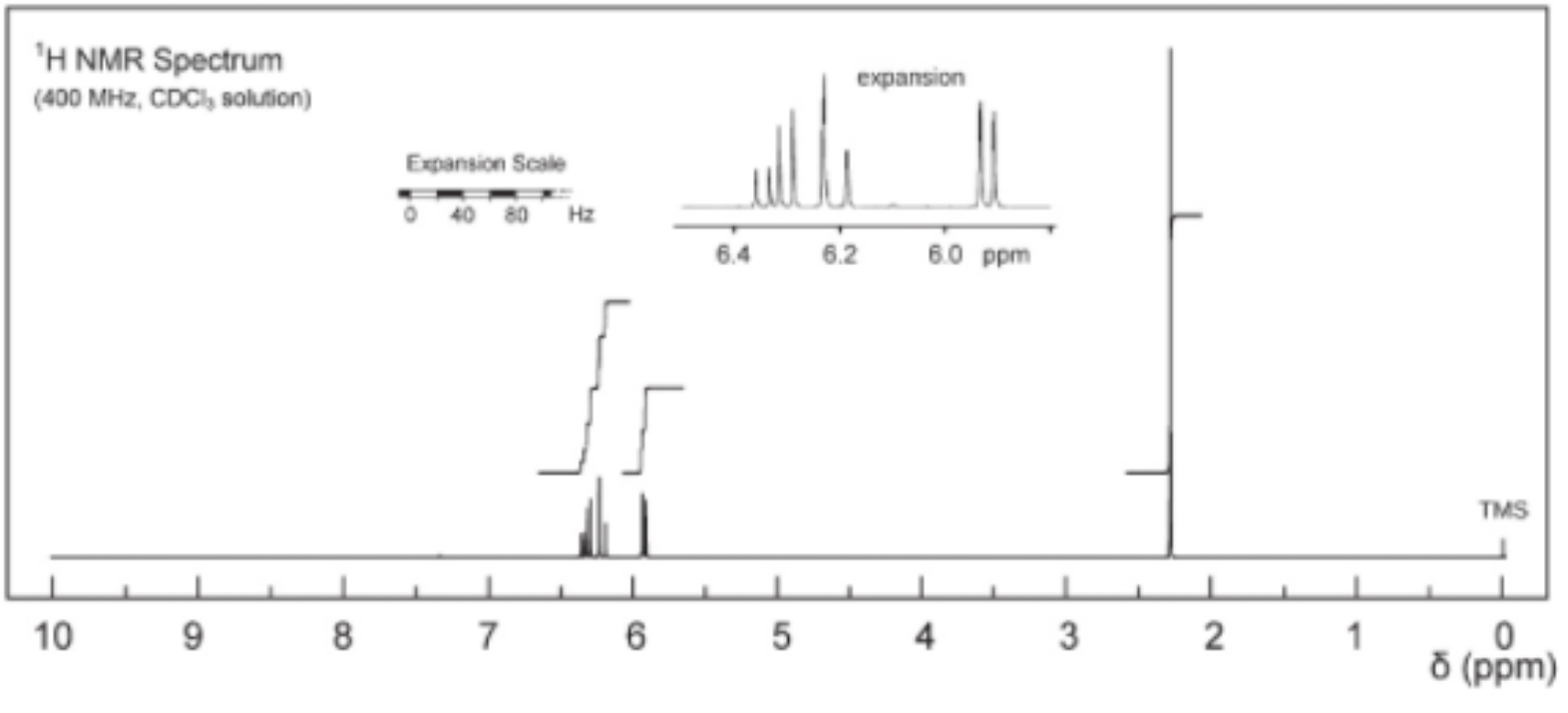
Problem 90


IR Spectrum
(liquid film)
1720
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

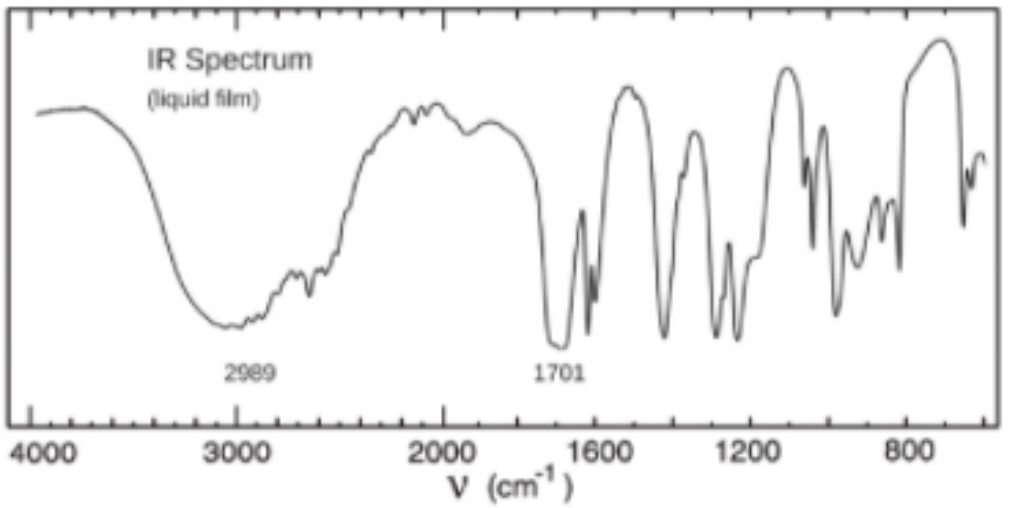

Mass Spectrum
% of base peak
100
80
60
40
20
43
55
M⁺
70
C4H6O
40
80
120
160
200
240
280
m / e

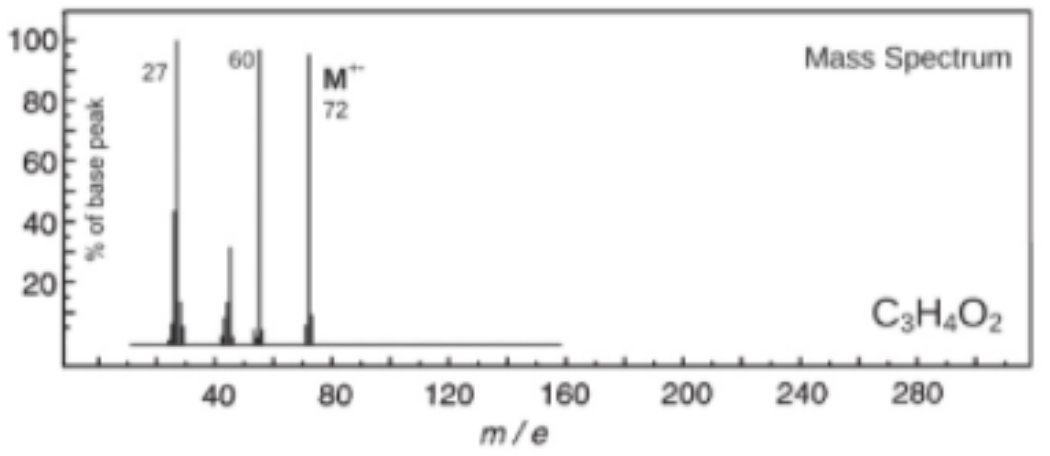

absorbance
0.0
0.5
1.0
1.5
UV Spectrum
200
250
300
350
λ (nm)

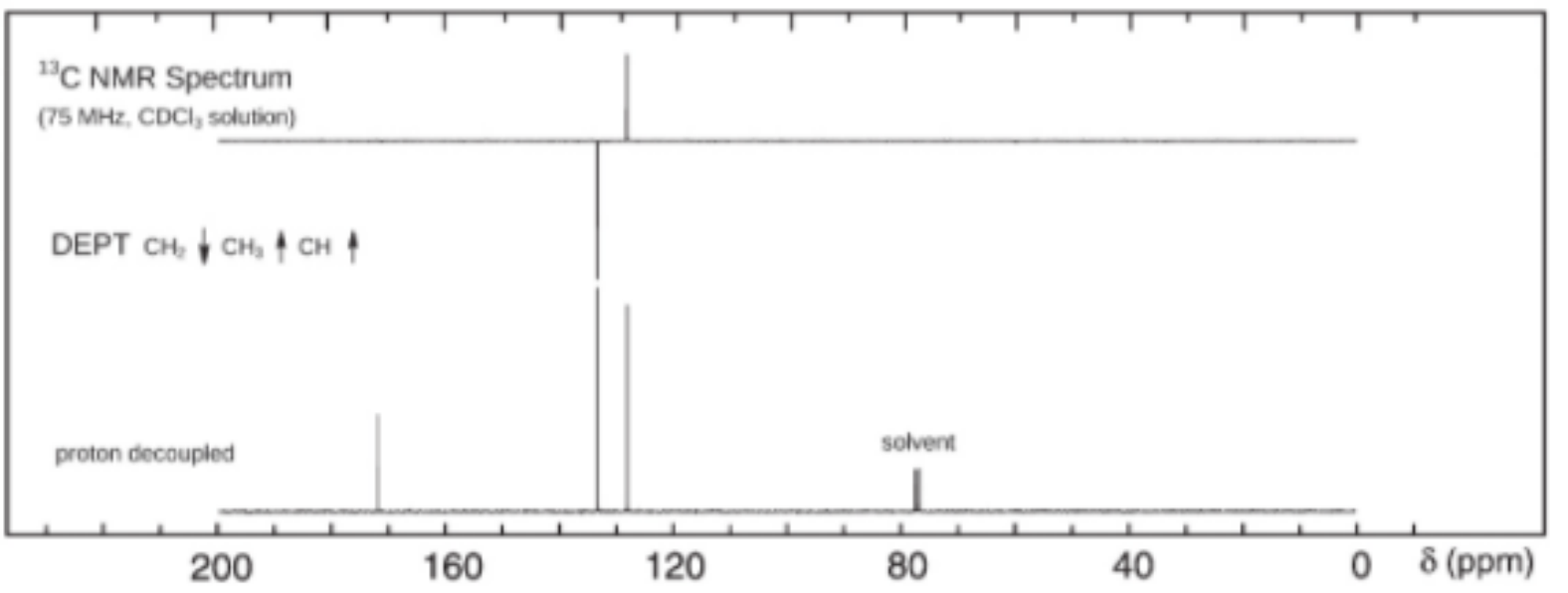

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

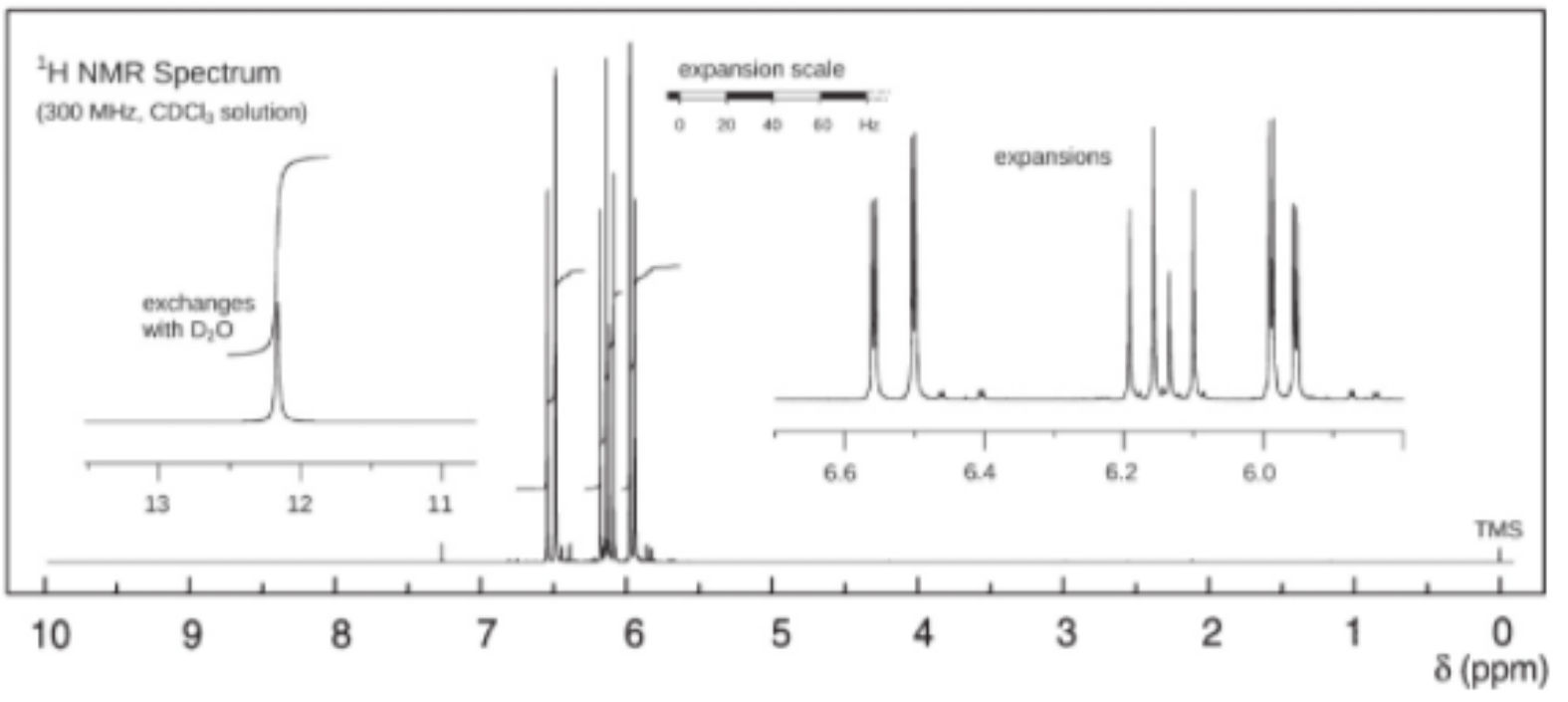

1H NMR Spectrum
(400 MHz, CDCl3 solution)
Expansion Scale
0 40 80 Hz
expansion
6.4
6.2
6.0 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

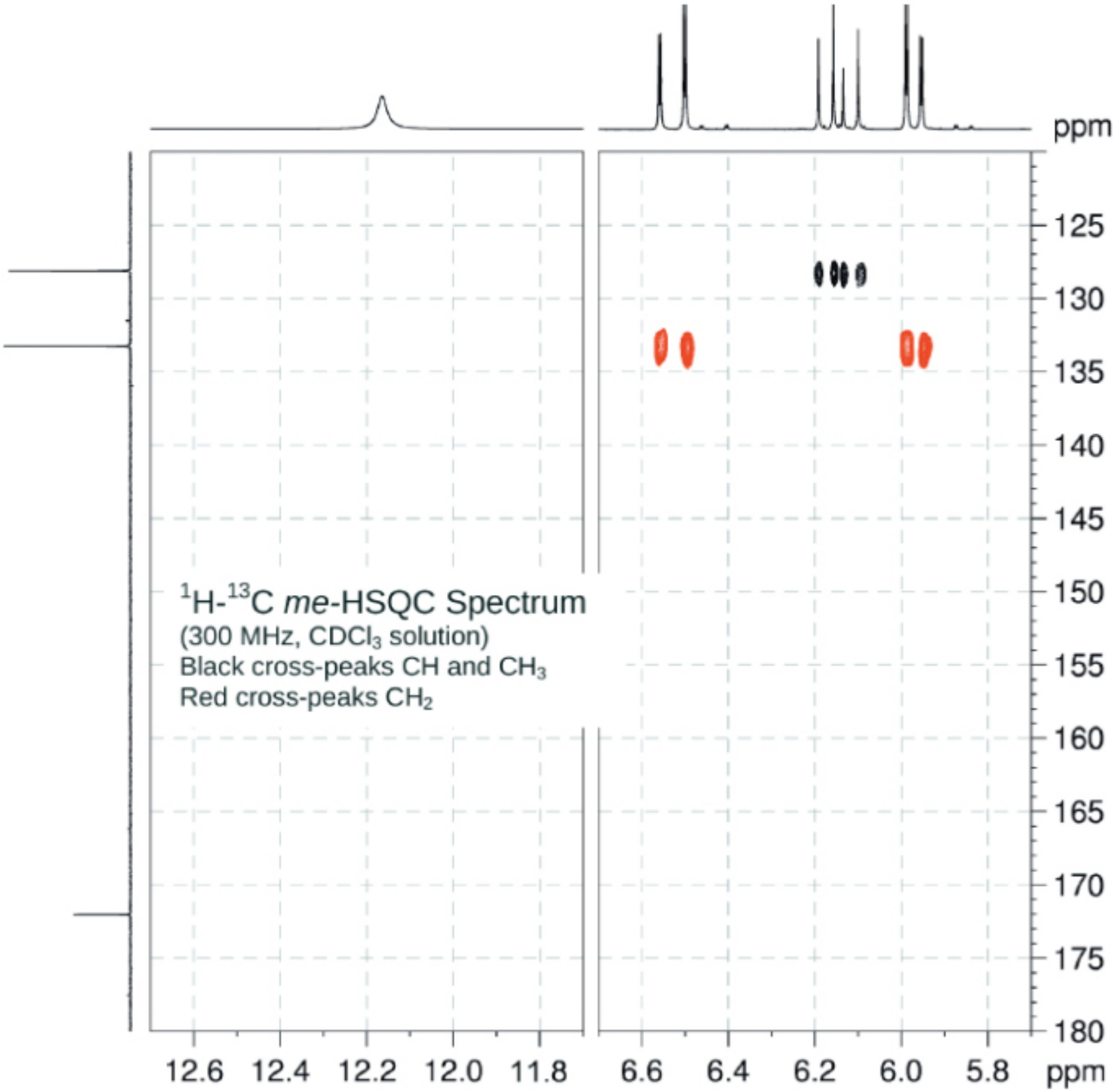
Problem 91


IR Spectrum
(liquid film)
2989
1701
4000
3000
2000
1600
1200
800
ν (cm-1)

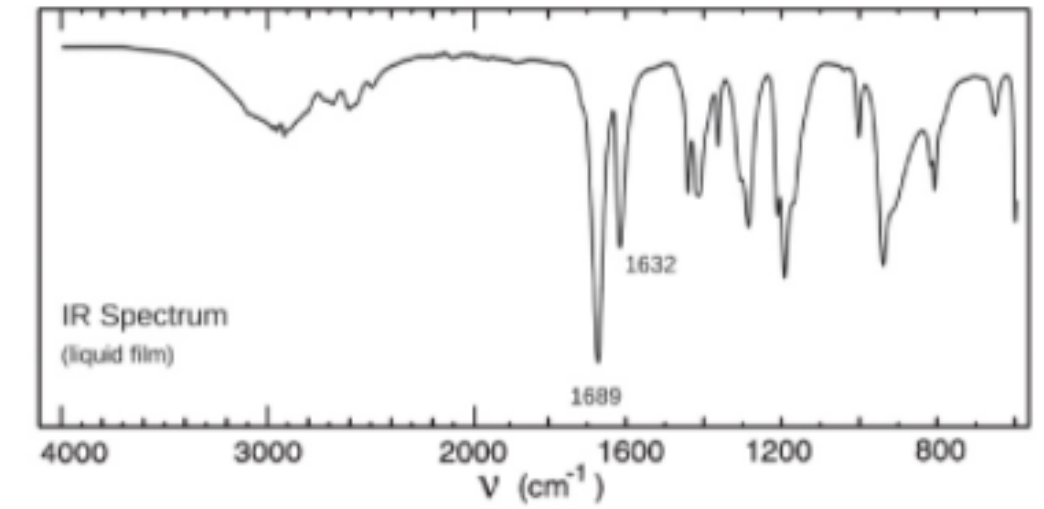

Mass Spectrum
% of base peak
100
80
60
40
20
27
60
M+·
72
C3H4O2
40
80
120
160
200
240
280
m/e

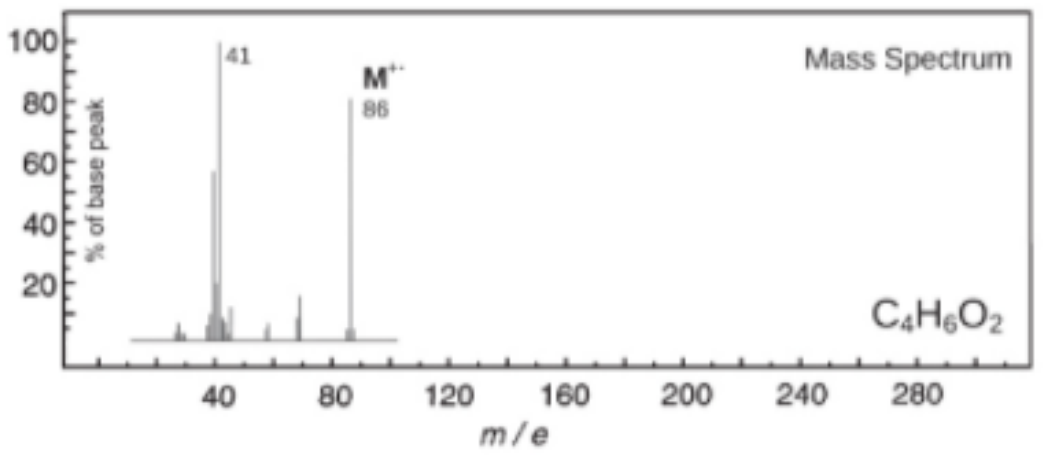

13C NMR Spectrum
(75 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

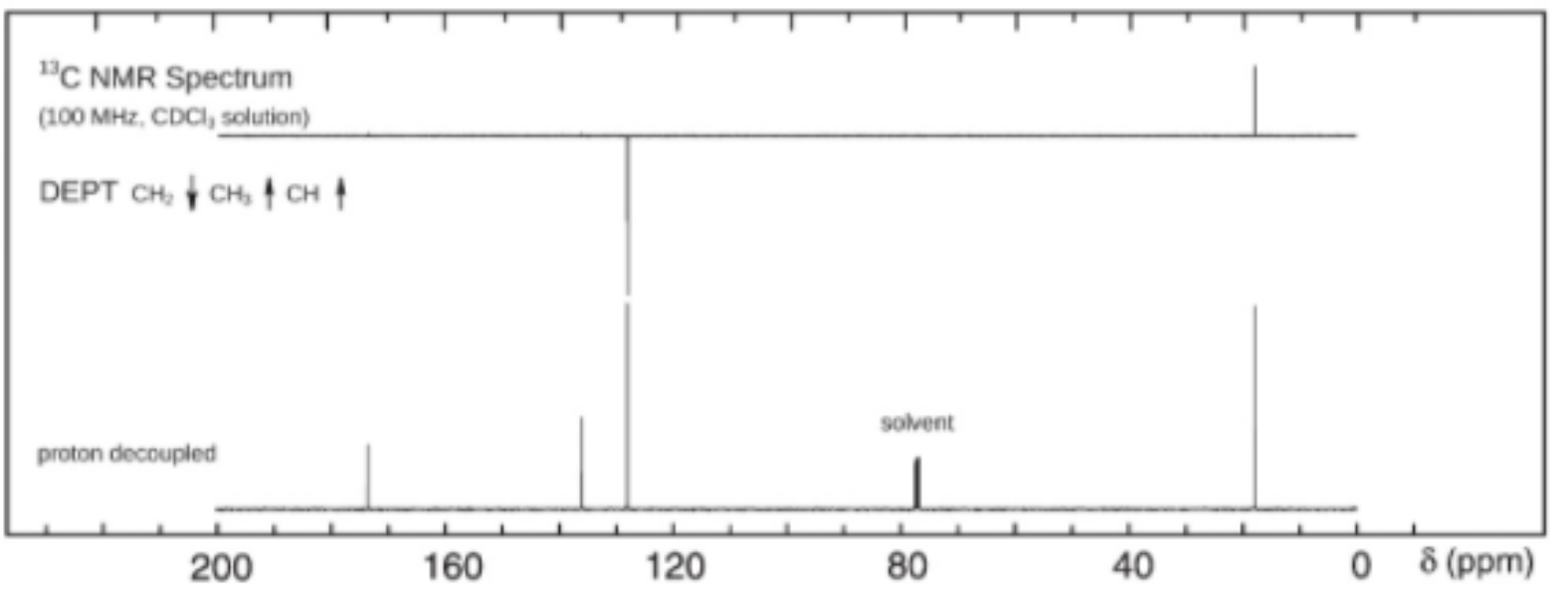

1H NMR Spectrum
(300 MHz, CDCl3 solution)
expansion scale
0 20 40 60 Hz
expansions
exchanges
with D2O
13
12
11
6.6
6.4
6.2
6.0
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

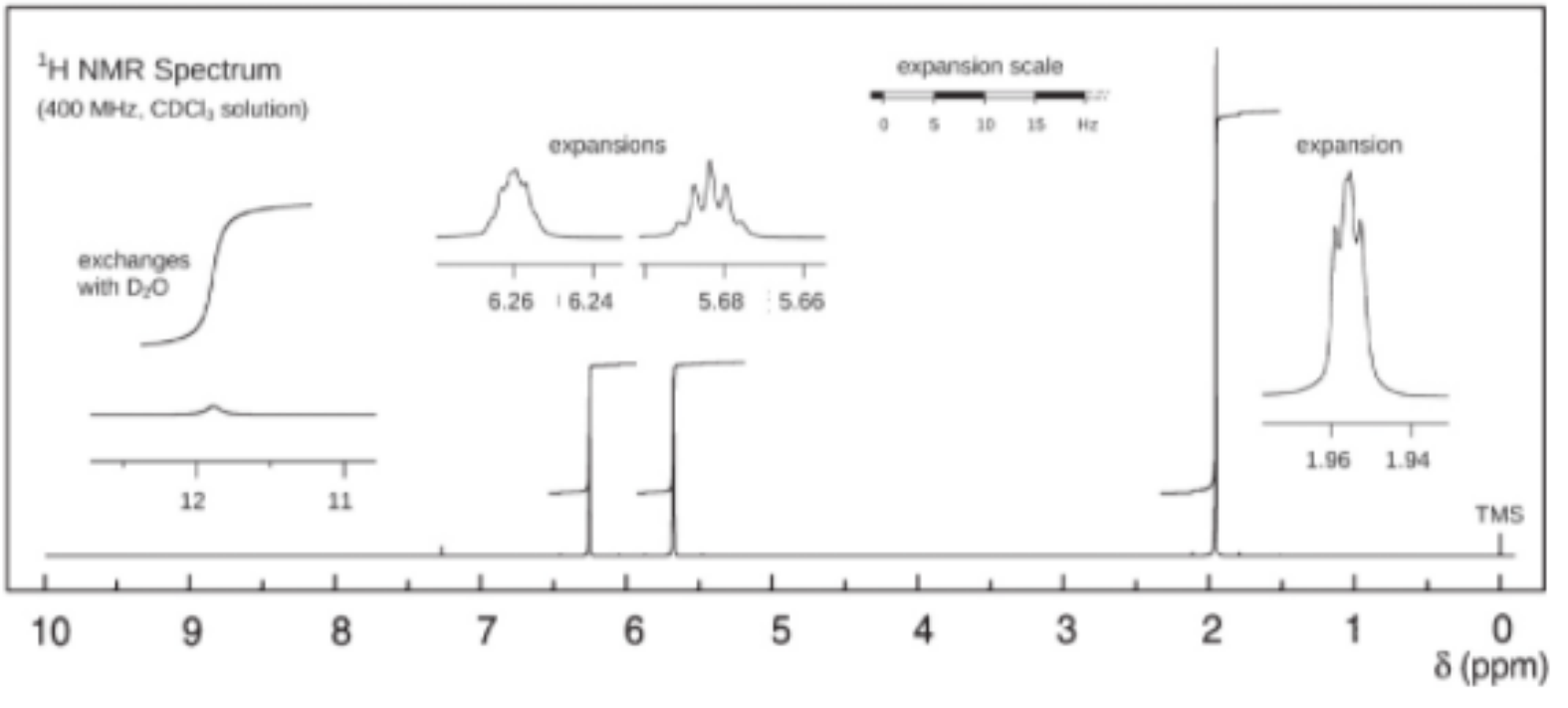

ppm
125
130
135
140
145
150
155
160
165
170
175
180
12.6
12.4
12.2
12.0
11.8
6.6
6.4
6.2
6.0
5.8
ppm
^{1}H-^{13}C *me*-HSQC Spectrum
(300 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

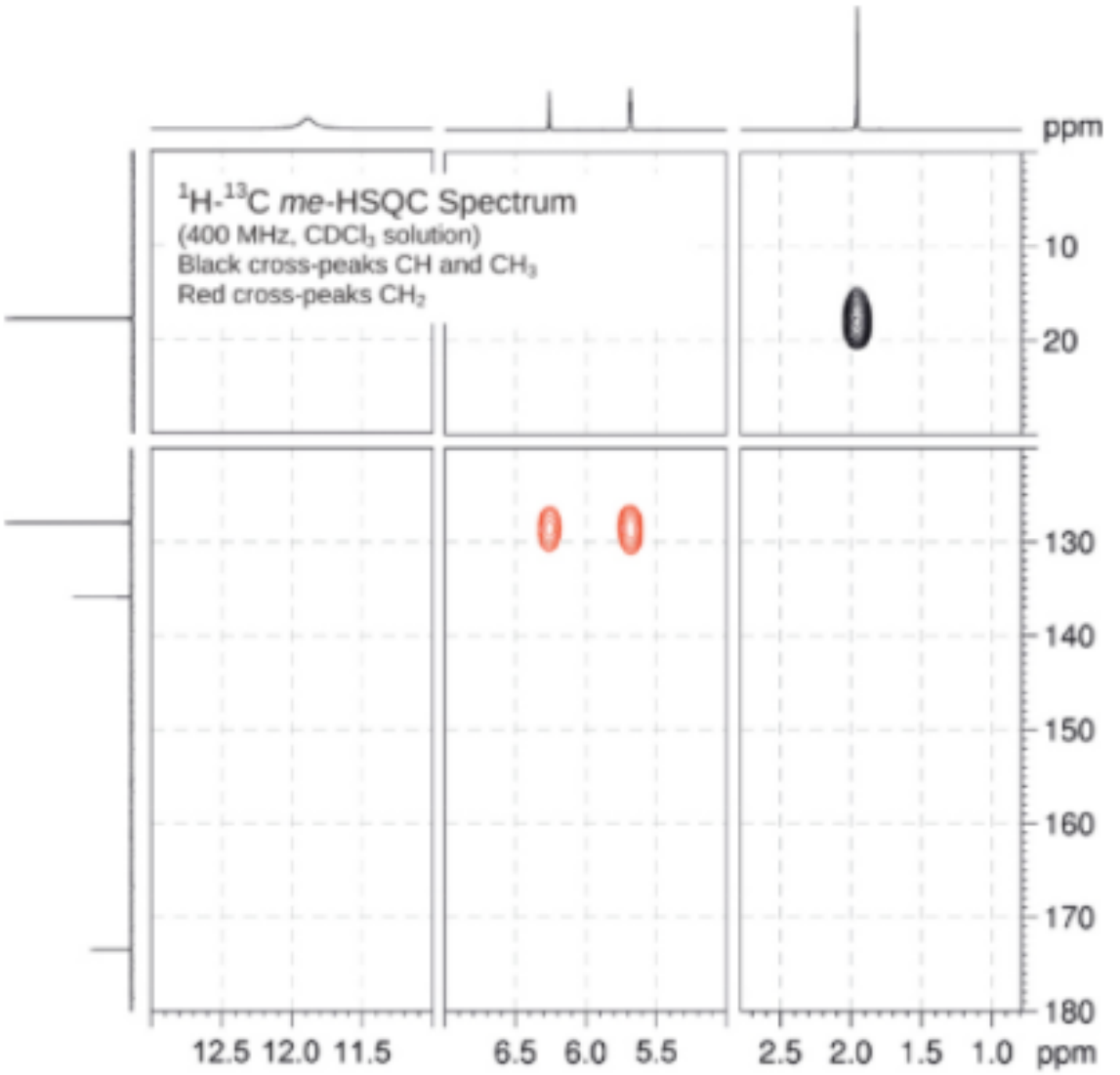
Problem 92


IR Spectrum
(liquid film)
1632
1689
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
100
80
60
40
20
41
M+·
86
C4H6O2
40
80
120
160
200
240
280
m/e

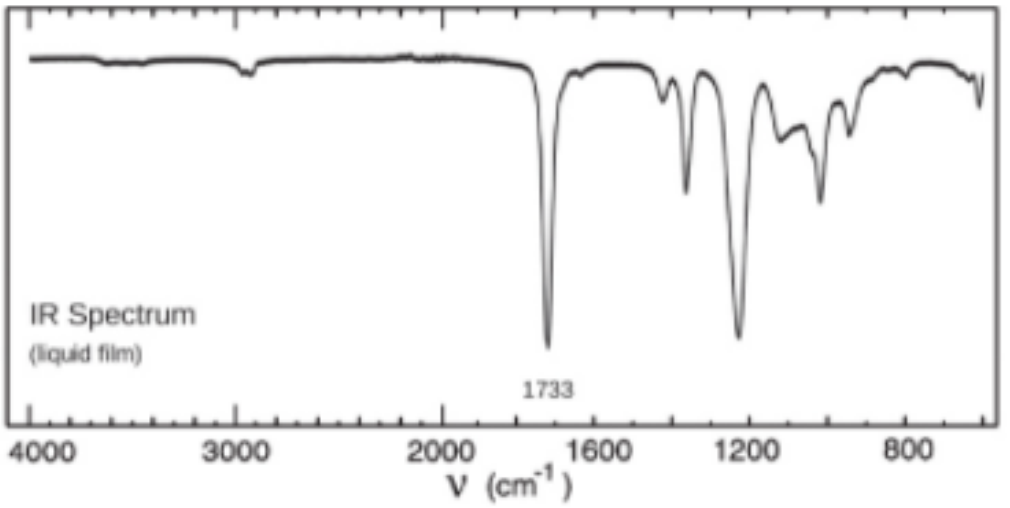

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

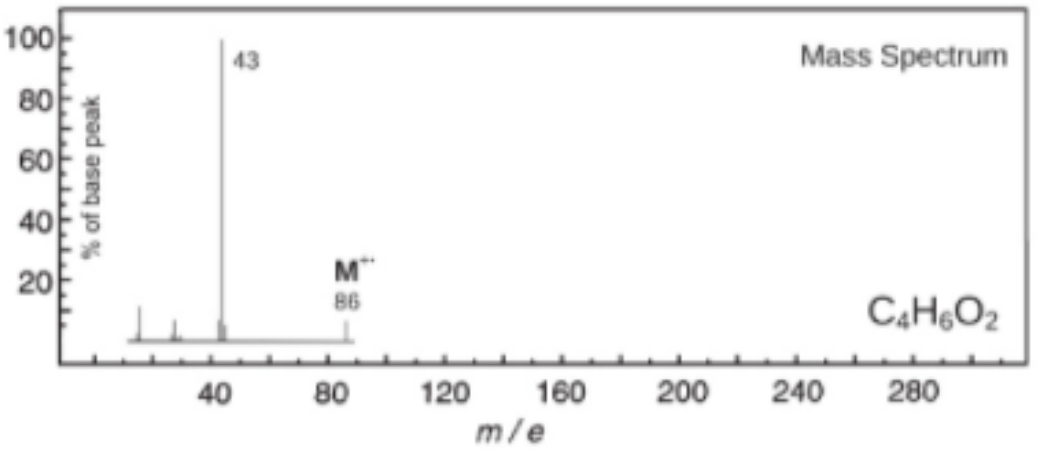

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion scale
0 5 10 15 Hz
expansions
6.26 6.24
5.68 5.66
expansion
1.96 1.94
exchanges with D2O
12
11
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

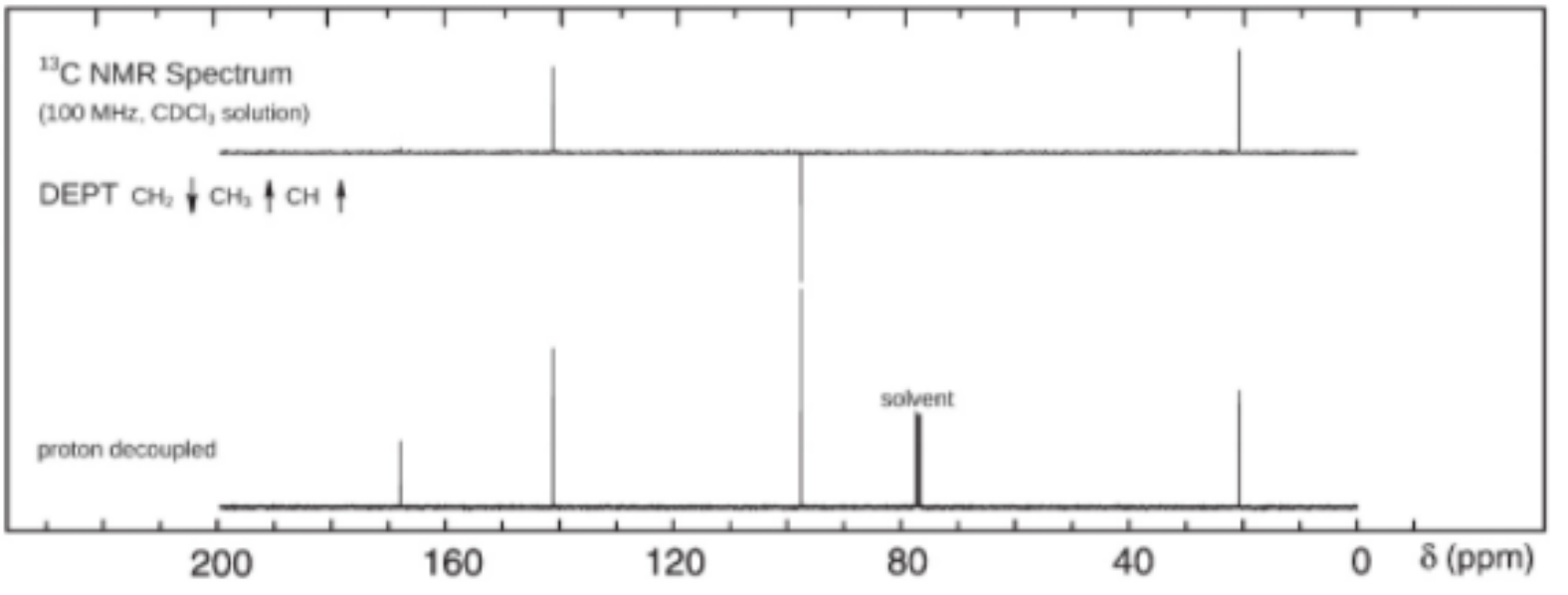

^{1}H-^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
ppm
10
20
130
140
150
160
170
180
12.5 12.0 11.5
6.5 6.0 5.5
2.5 2.0 1.5 1.0
ppm

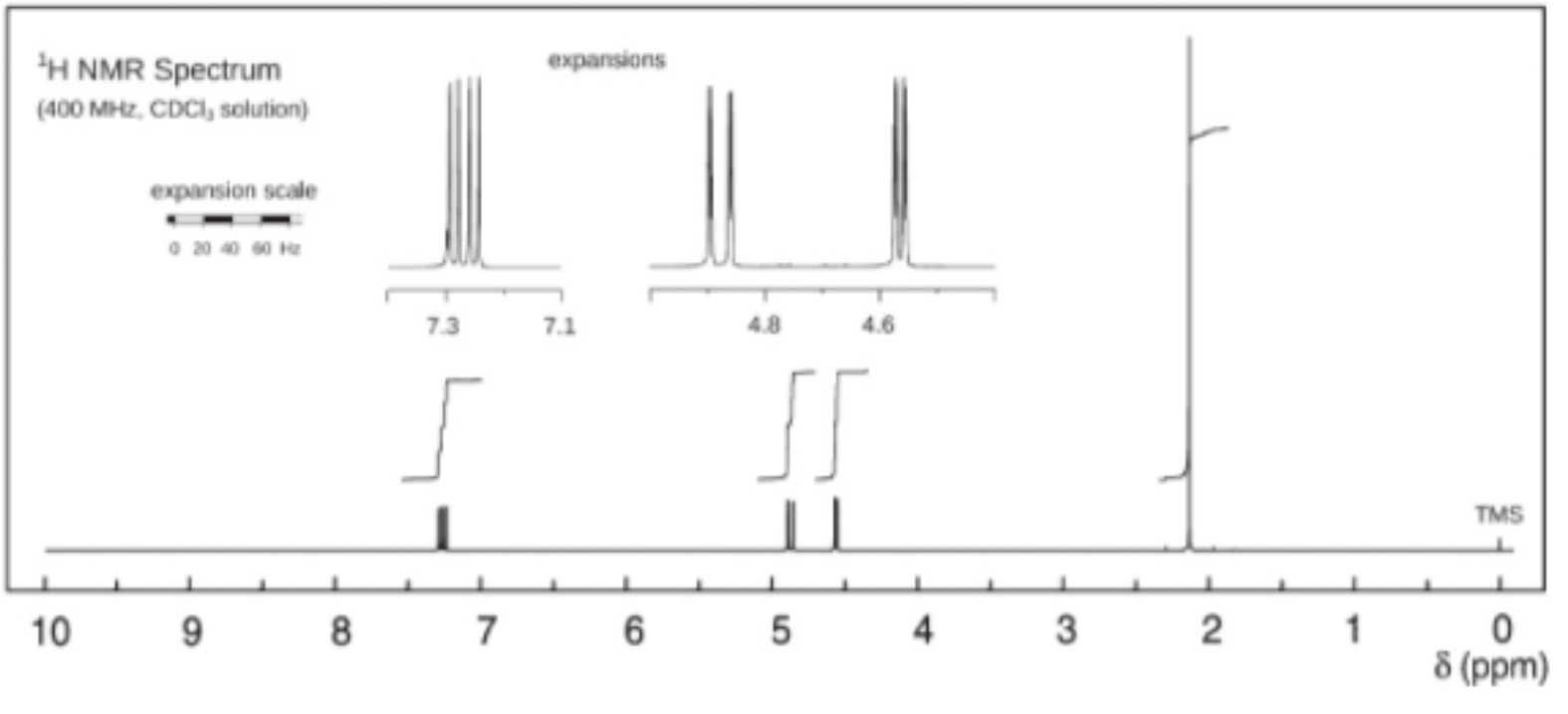
ppm
1.5
2.0
2.5
5.5
6.0
6.5
11.5
12.0
12.5
^{1}H-^{1}H NOESY Spectrum
(400 MHz, $CDCl_3$ solution)
12.5 12.0 11.5
6.5 6.0 5.5
2.5 2.0 1.5
ppm

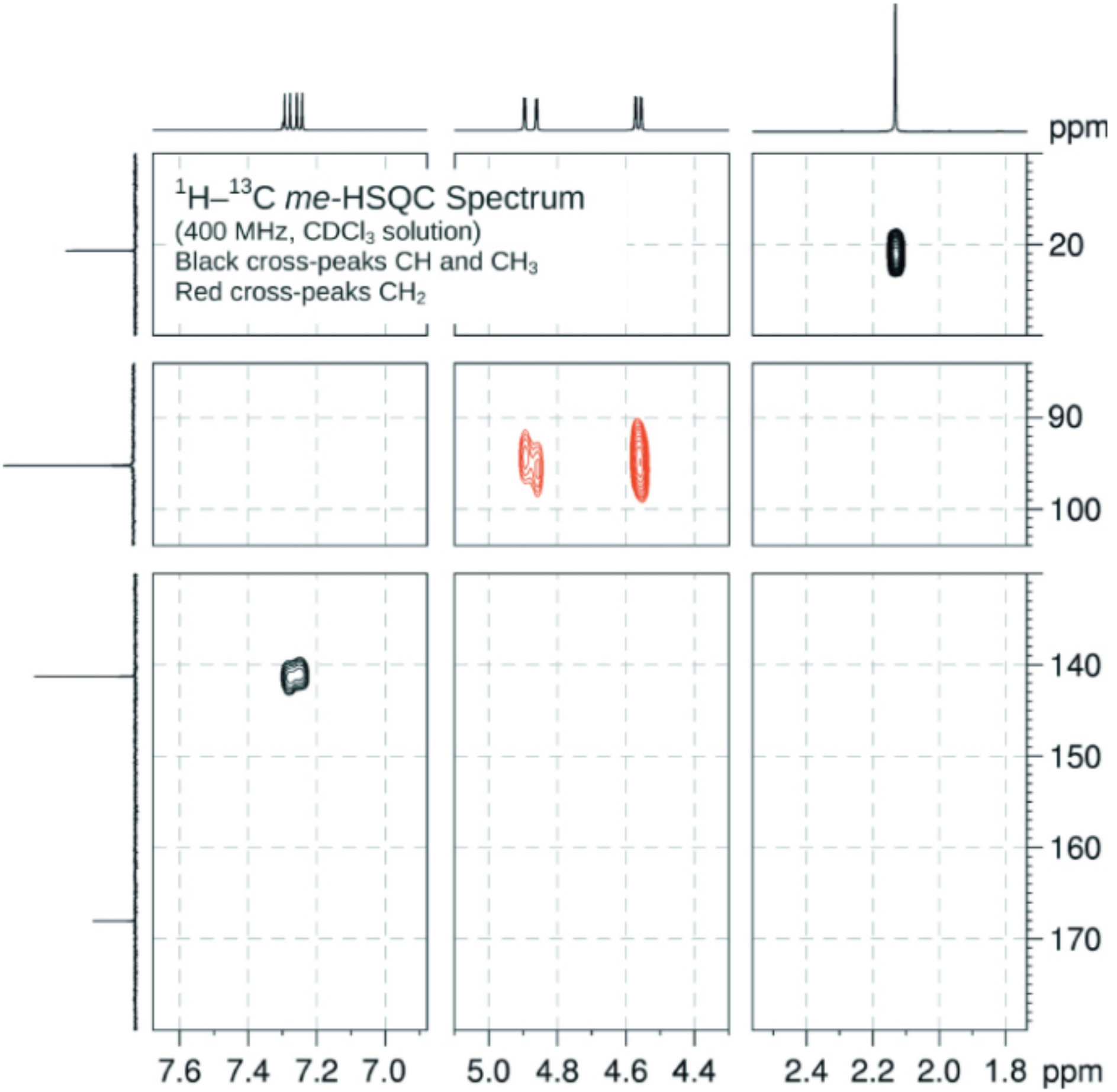
Problem 93


IR Spectrum
(liquid film)
1733
4000
3000
2000
1600
1200
800
ν (cm-1)

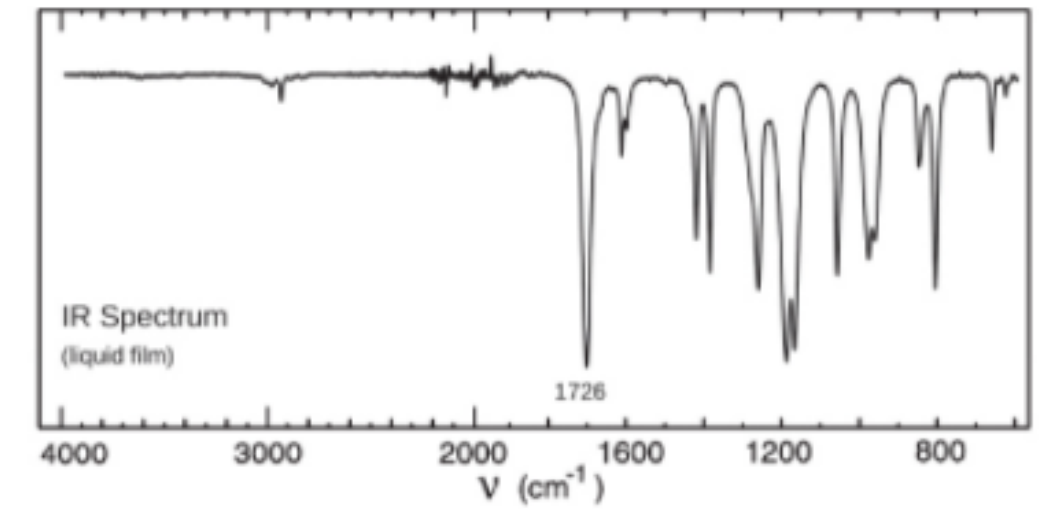

Mass Spectrum
% of base peak
100
80
60
40
20
43
M+·
86
C4H6O2
40
80
120
160
200
240
280
m/e

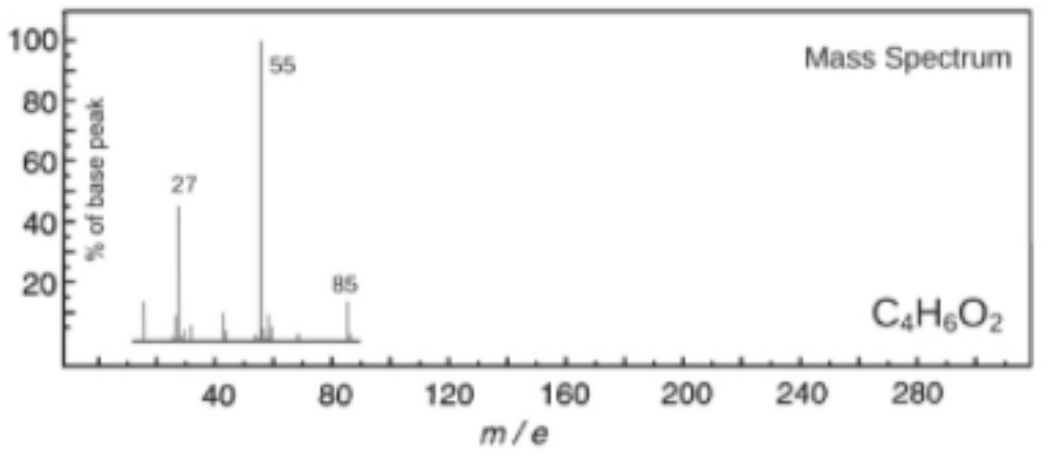

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

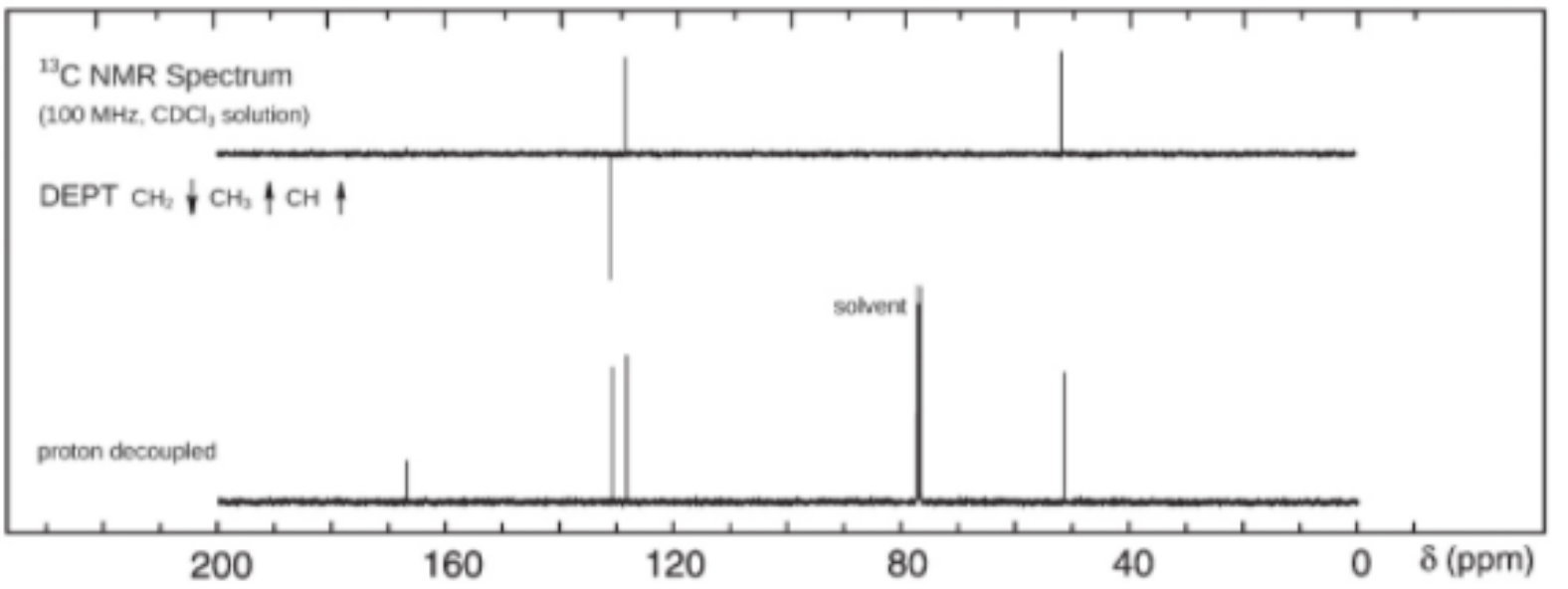

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion scale
0 20 40 60 Hz
expansions
7.3
7.1
4.8
4.6
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

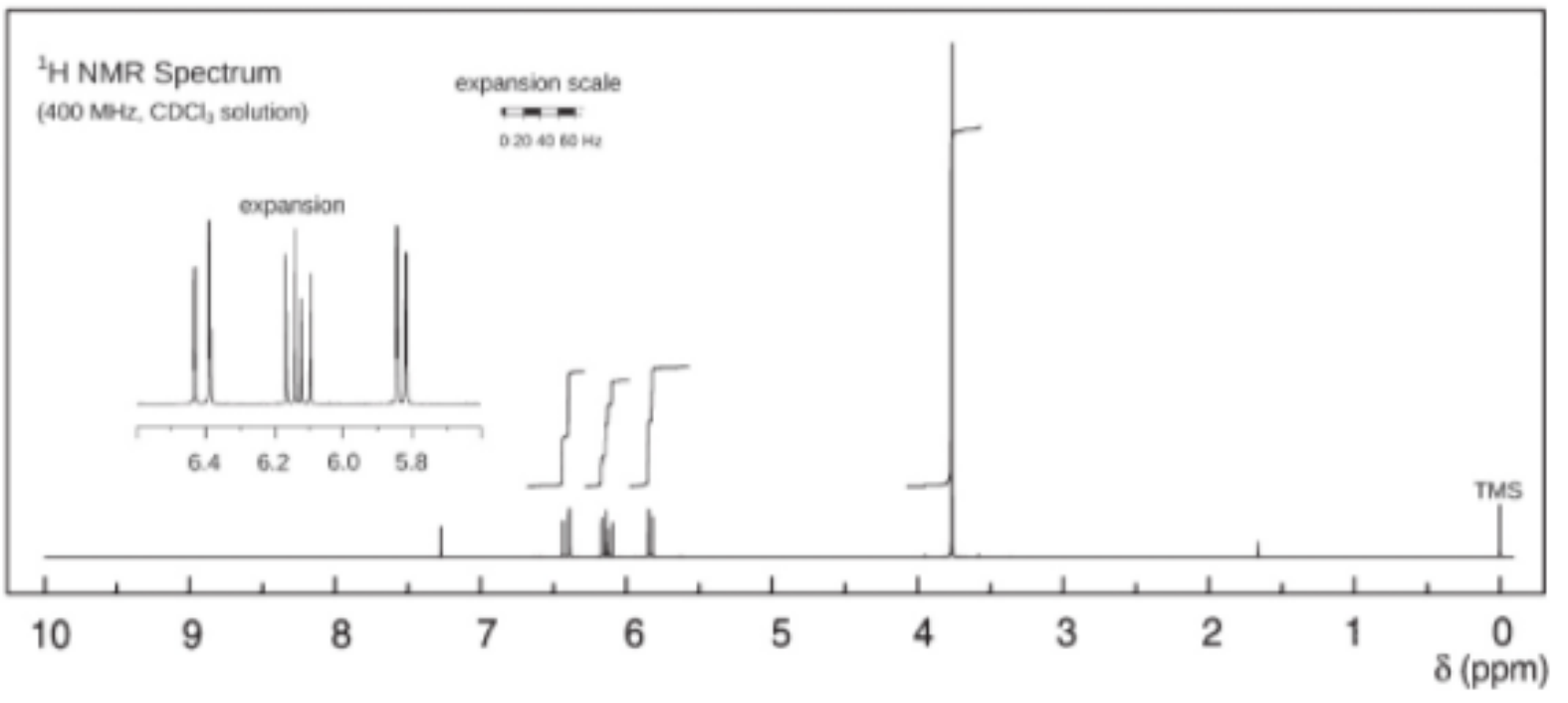

^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
ppm
20
90
100
140
150
160
170
7.6 7.4 7.2 7.0
5.0 4.8 4.6 4.4
2.4 2.2 2.0 1.8 ppm

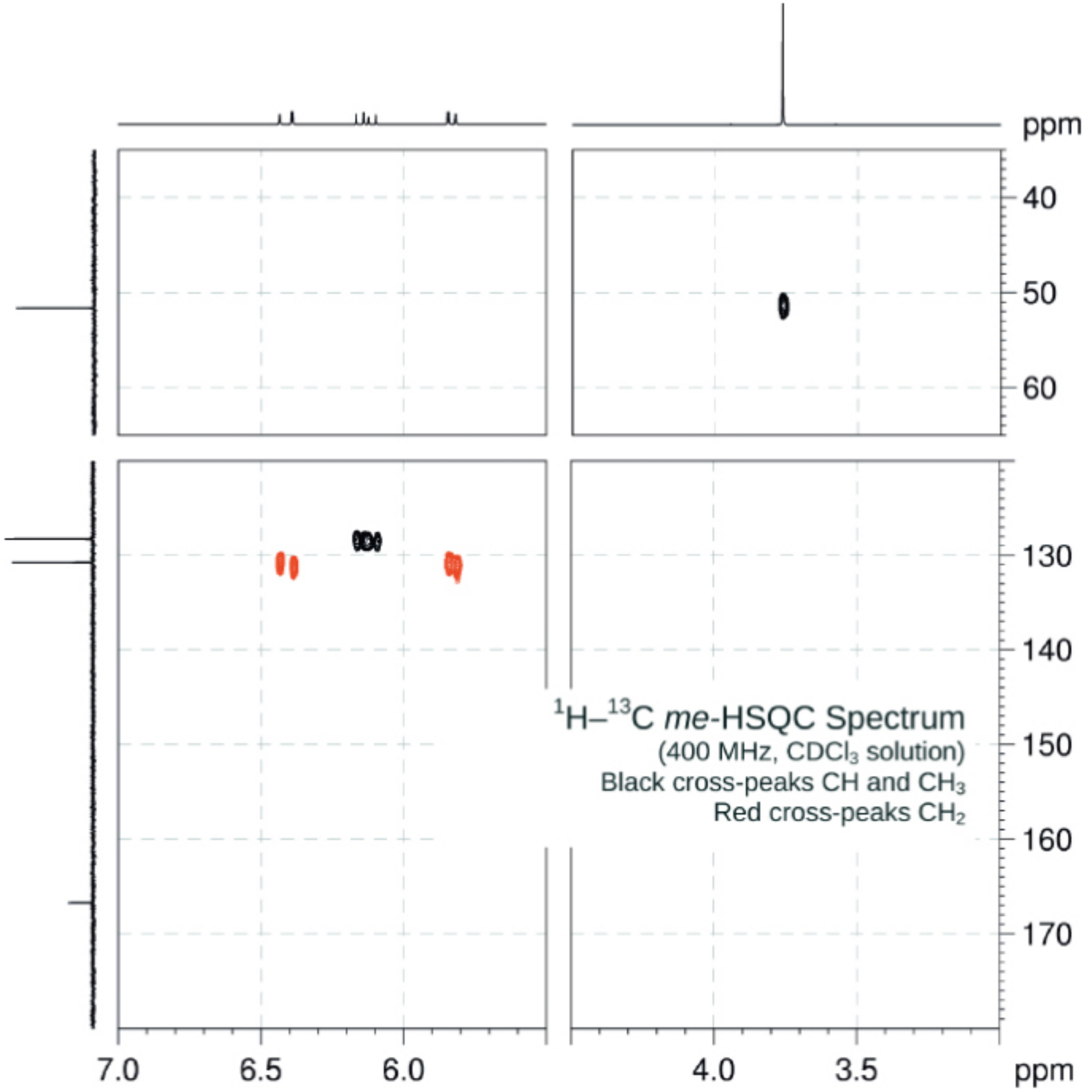
Problem 94


IR Spectrum
(liquid film)
1726
4000
3000
2000
1600
1200
800
ν (cm-1)

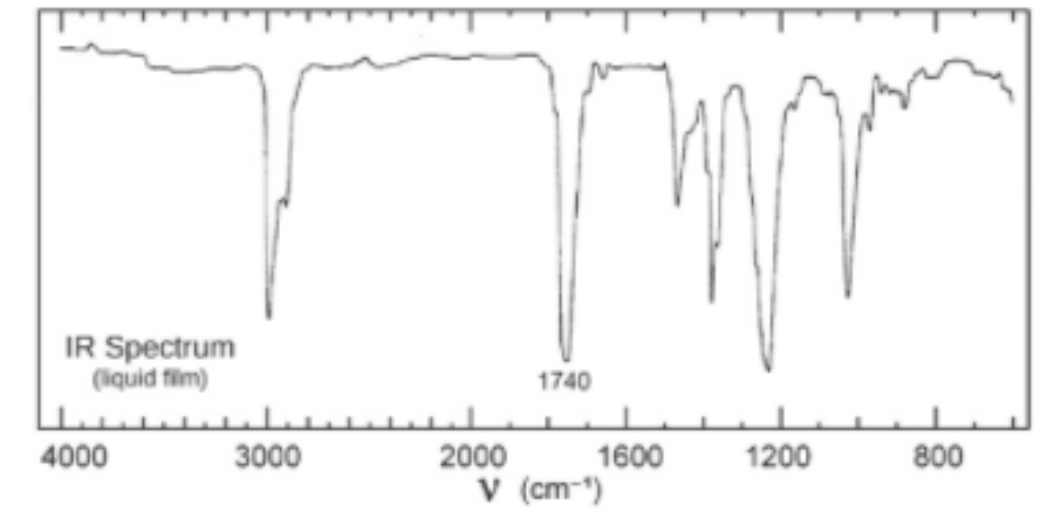

Mass Spectrum
% of base peak
100
80
60
40
20
55
27
85
C4H6O2
40
80
120
160
200
240
280
m/e

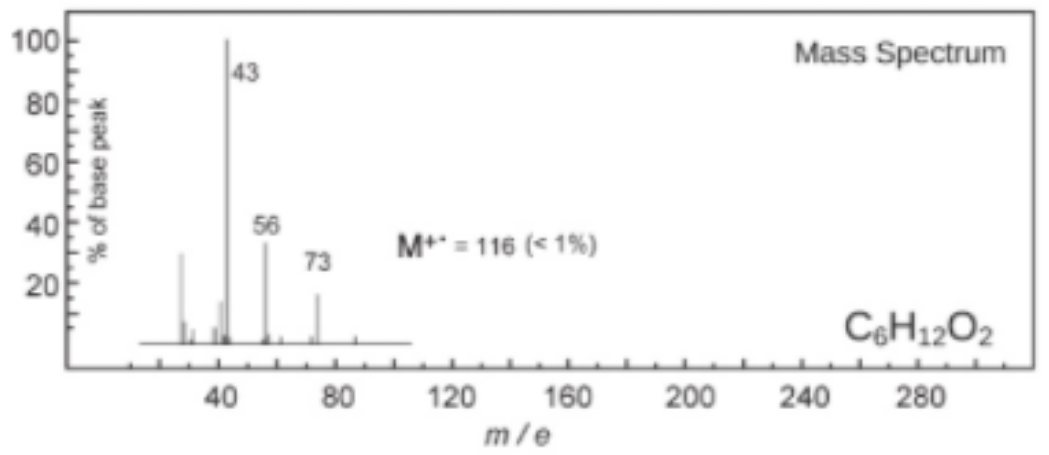

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion scale
0 20 40 60 Hz
expansion
6.4
6.2
6.0
5.8
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

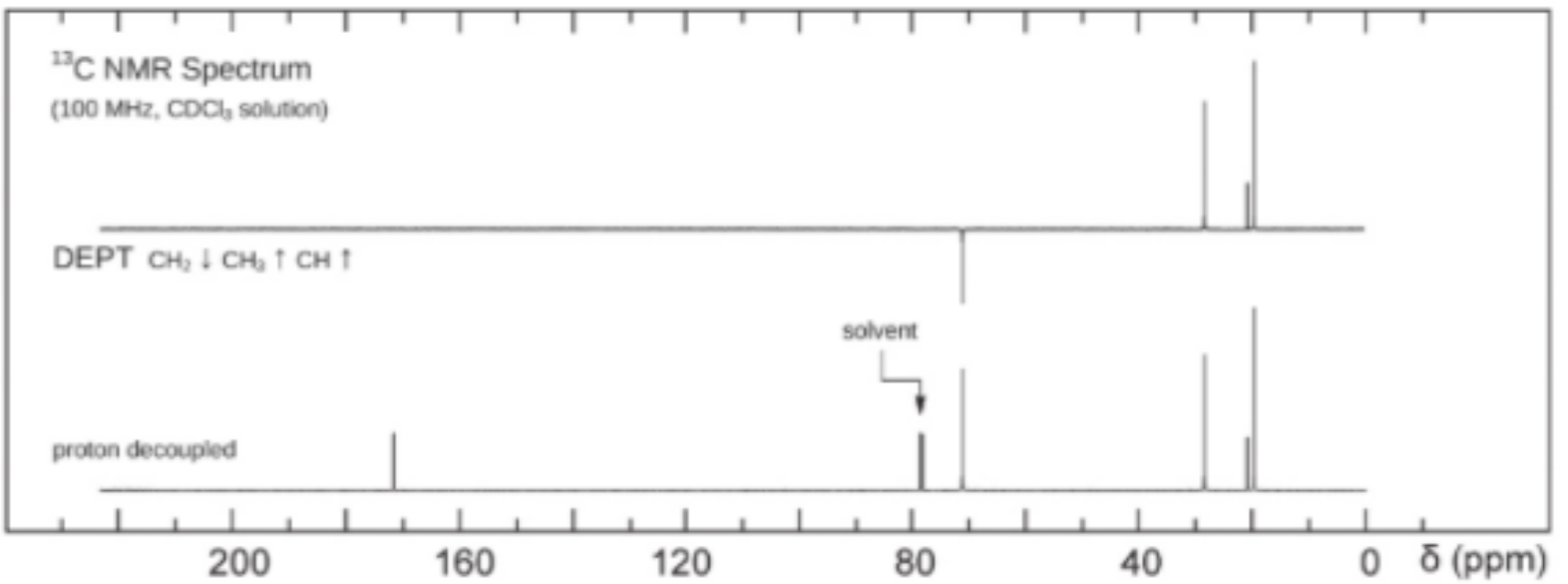

ppm
40
50
60
130
140
150
160
170
7.0
6.5
6.0
4.0
3.5
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

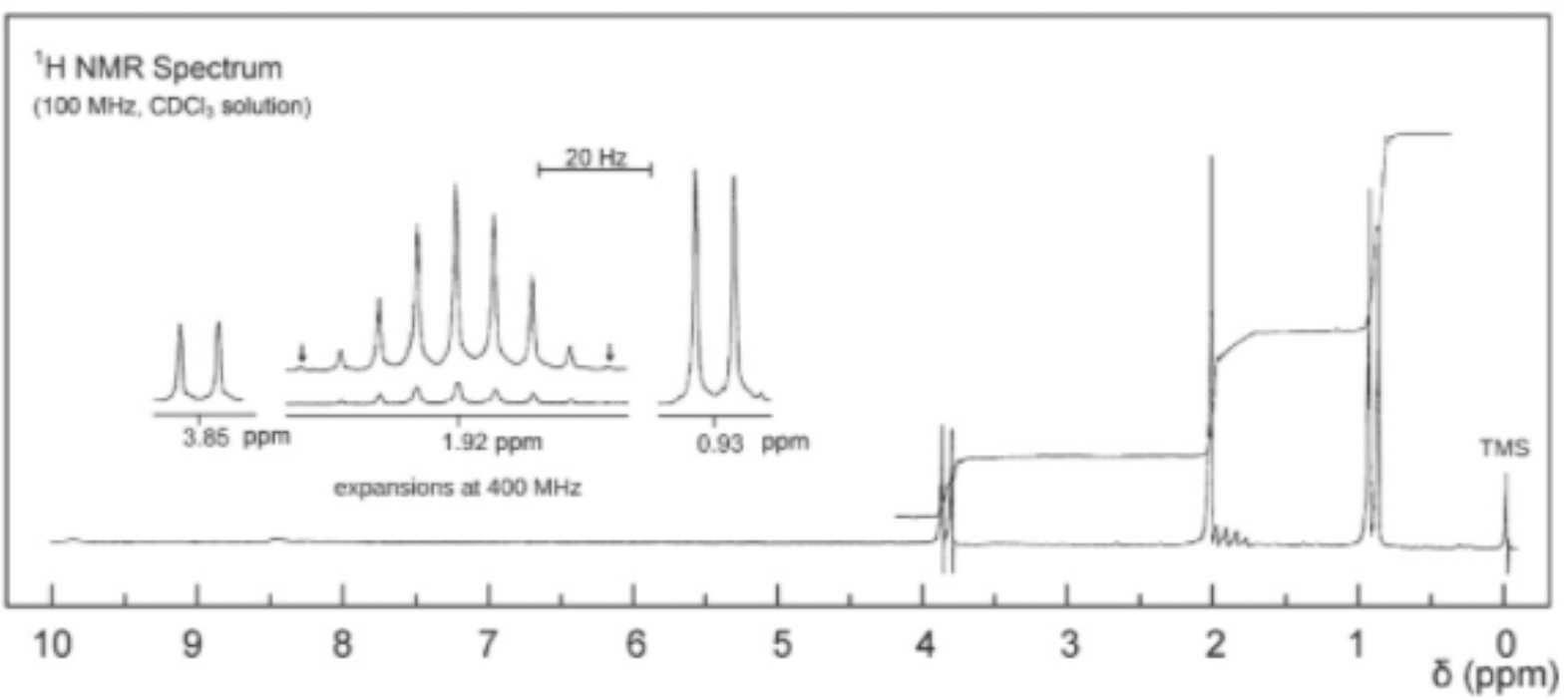
Problem 95



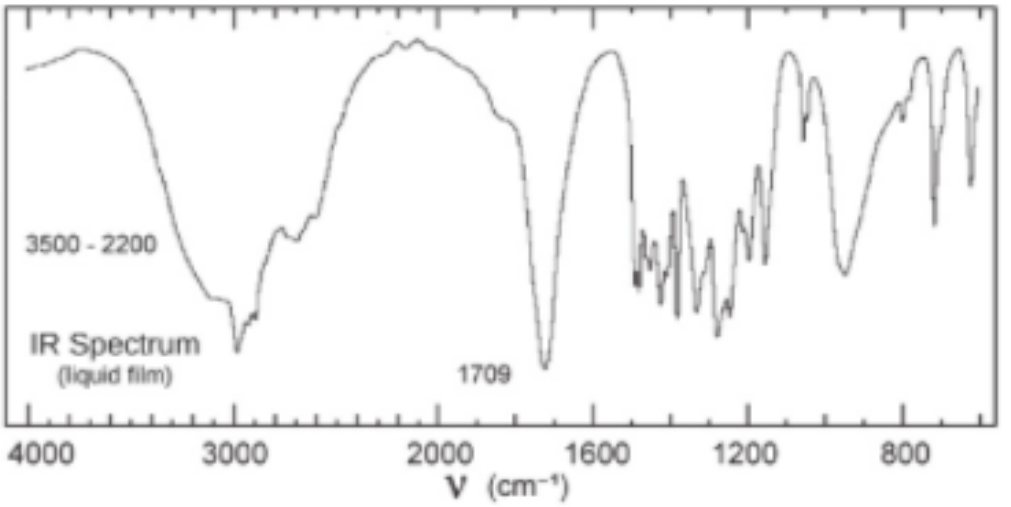


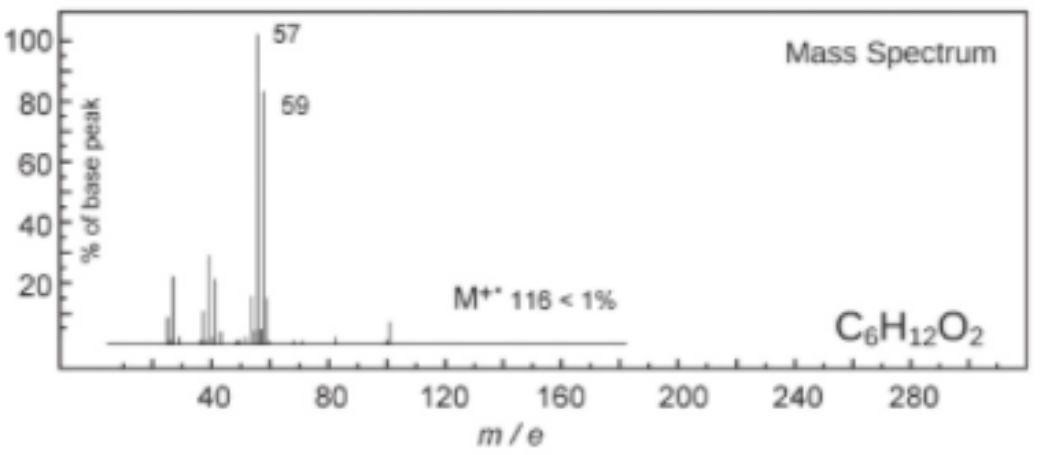
No significant UV absorption above 220 nm



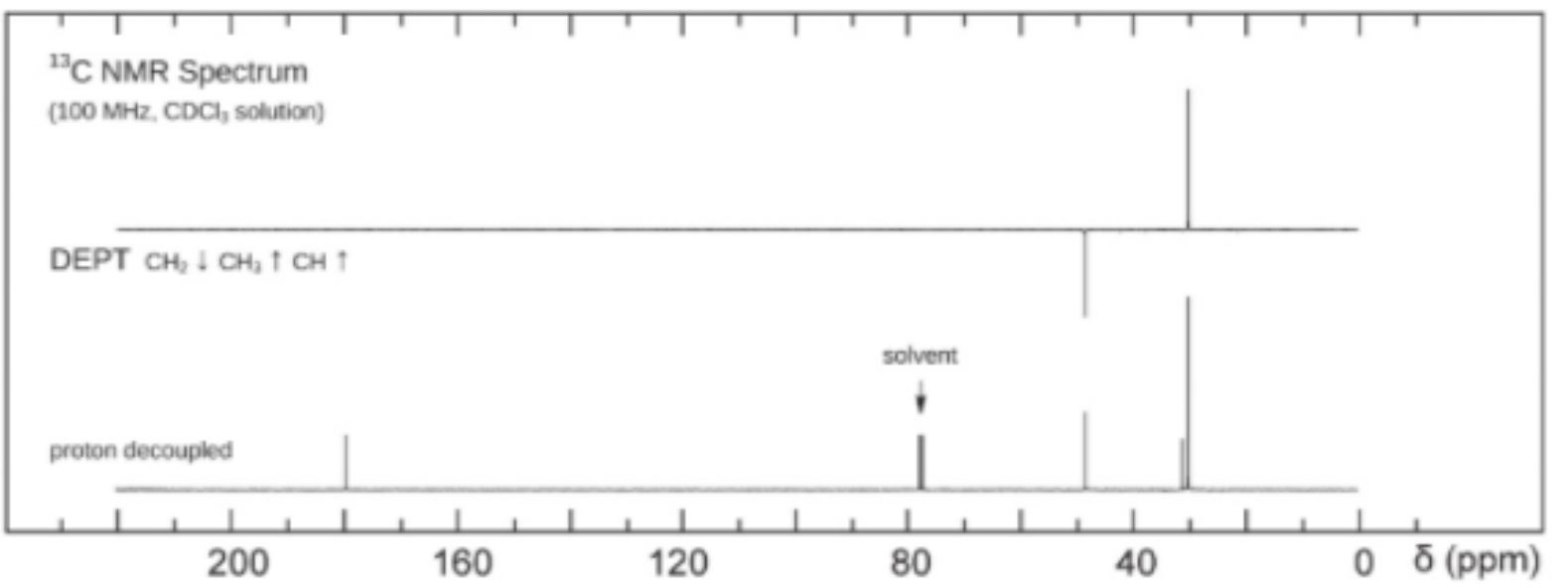


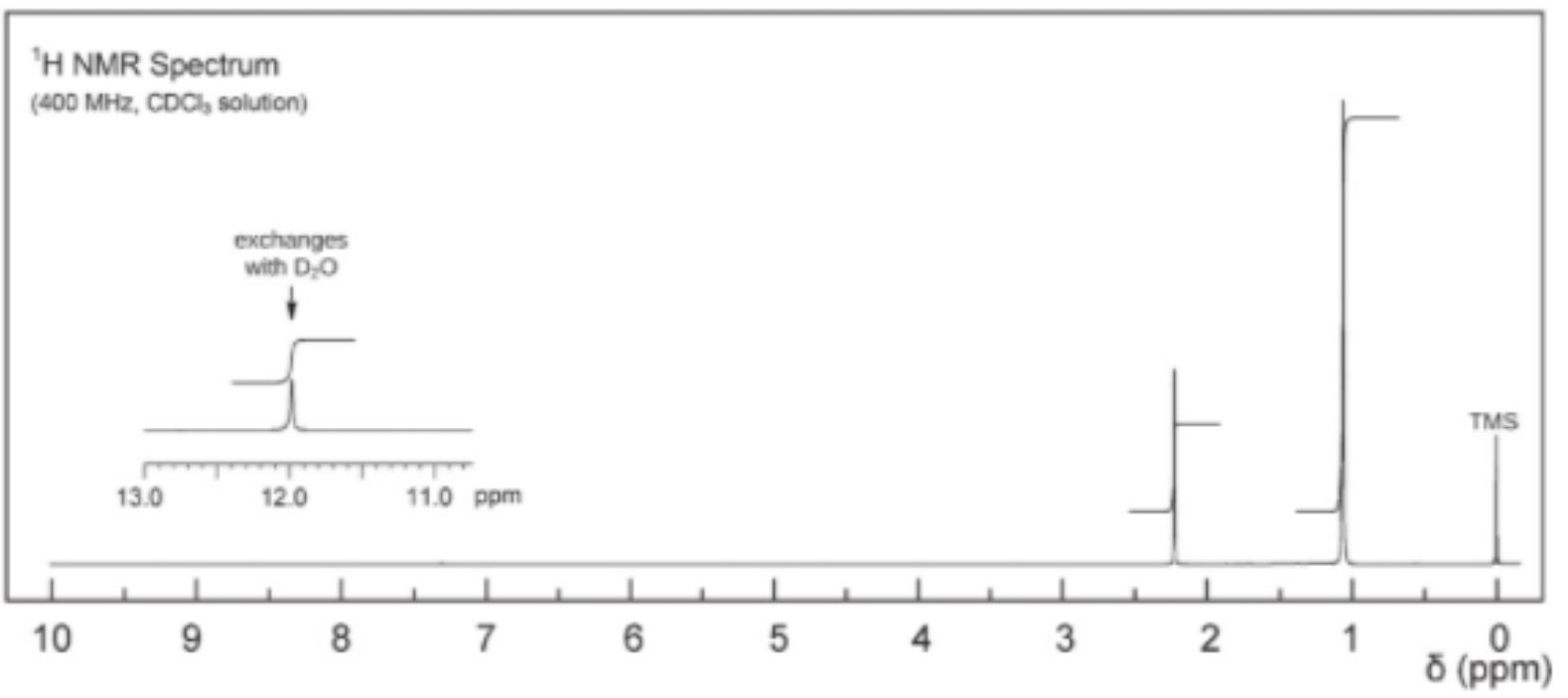
Problem 96



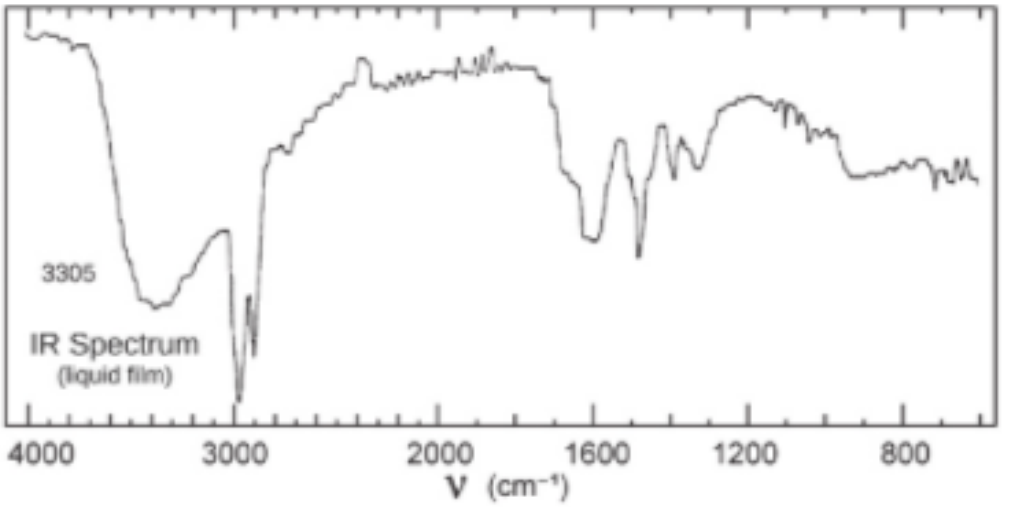


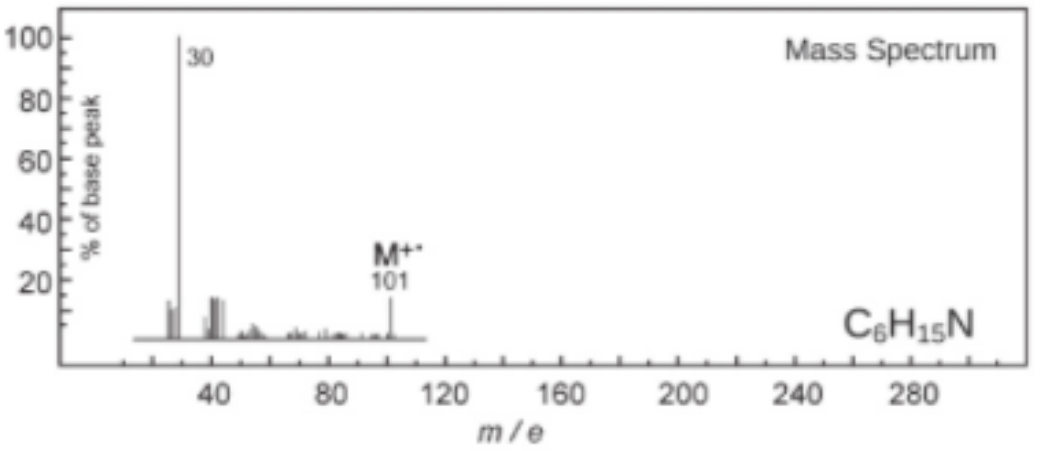
No significant UV absorption above 220 nm



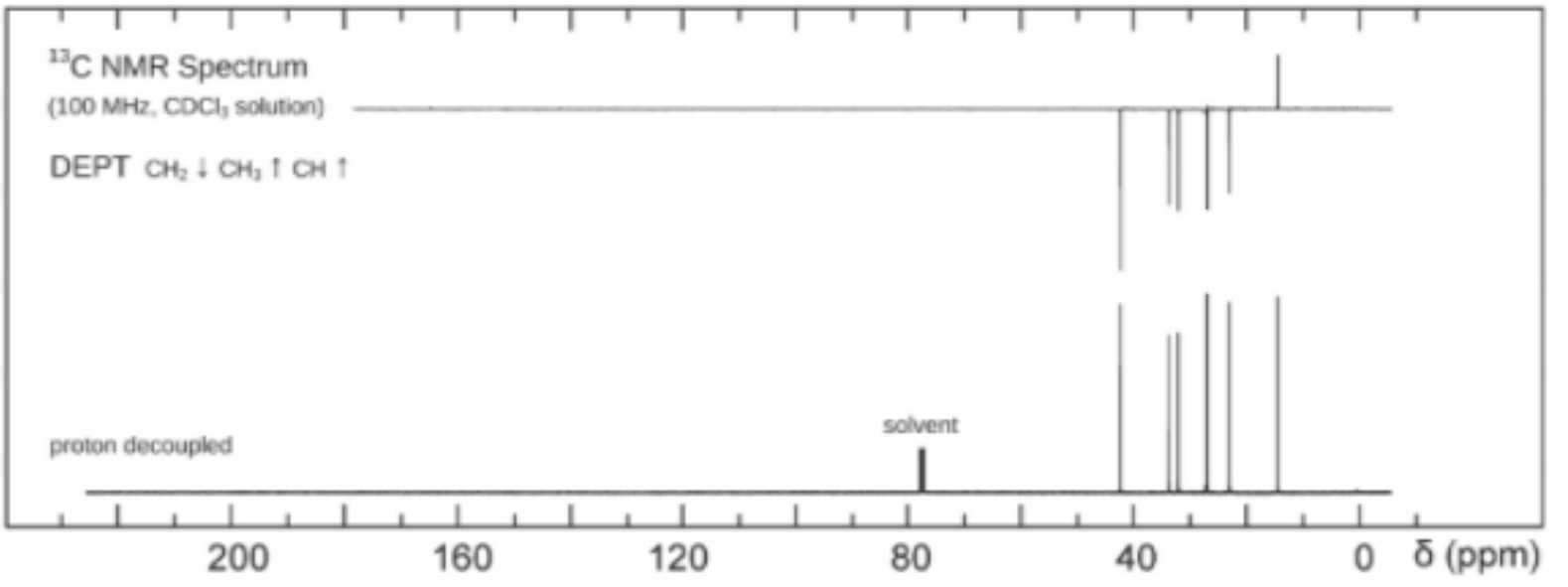


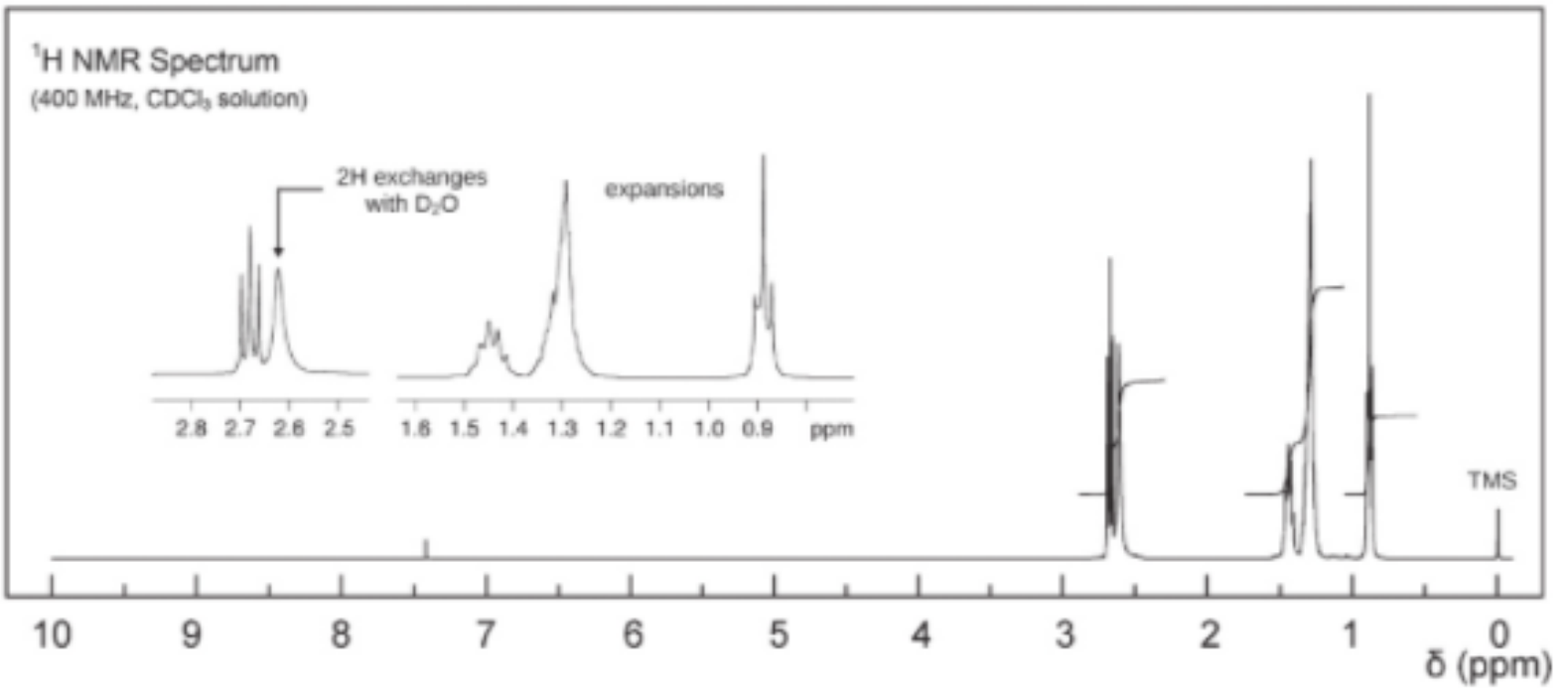
Problem 97

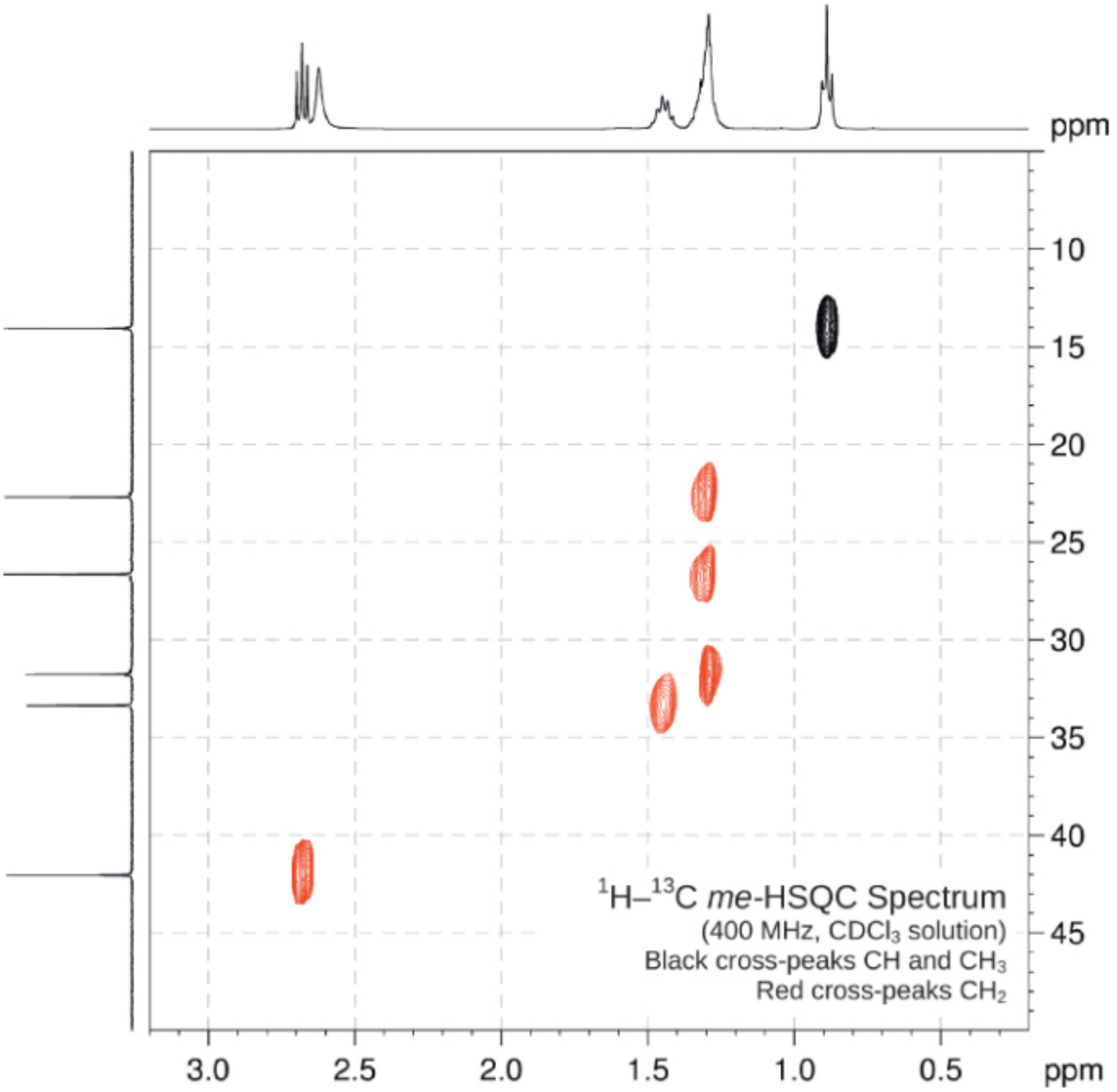




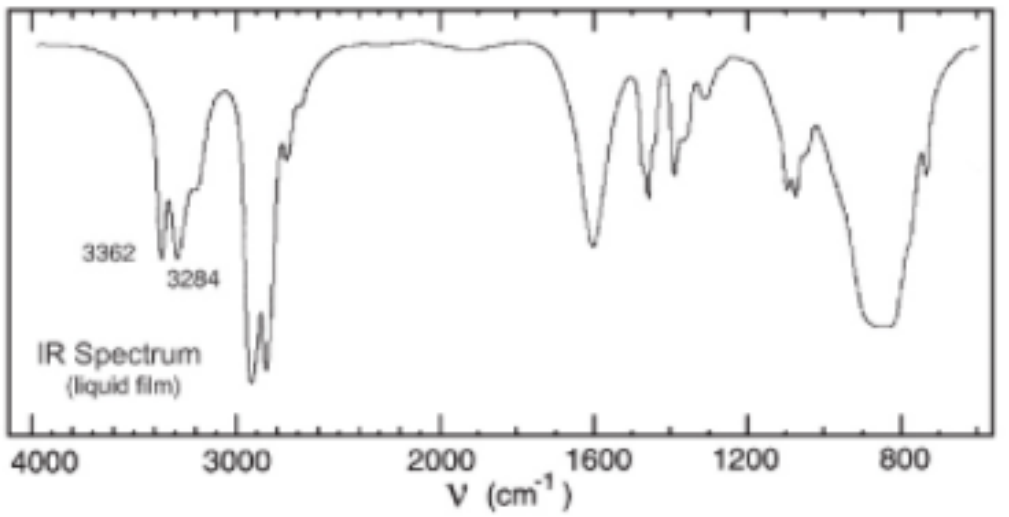
No significant UV absorption above 220 nm

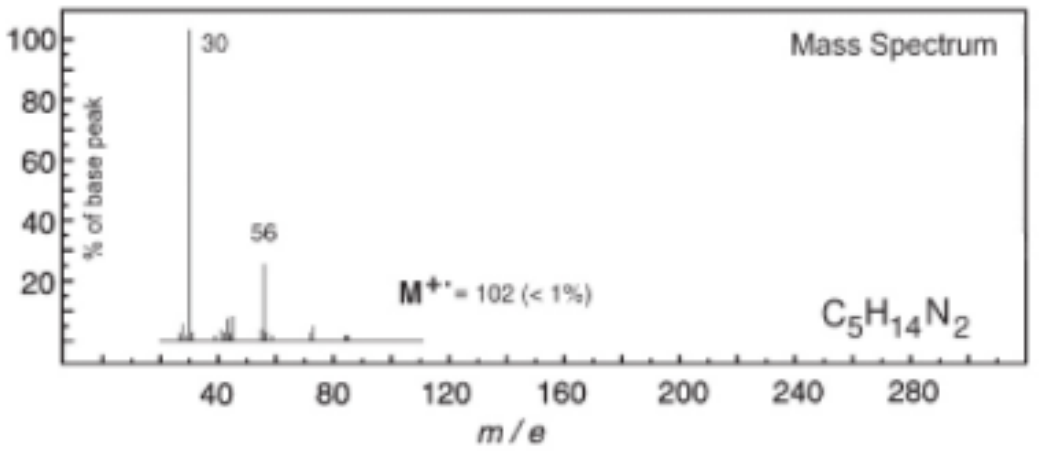




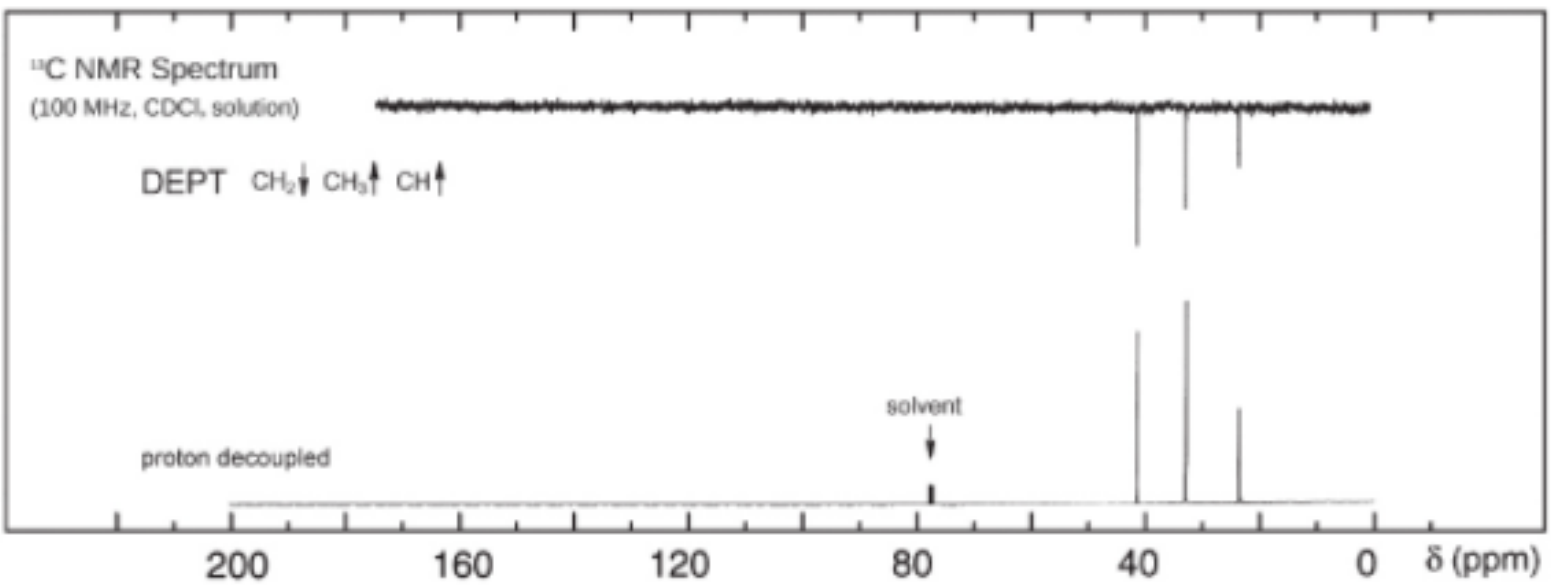

ppm
10
15
20
25
30
35
40
45
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
3.0
2.5
2.0
1.5
1.0
0.5
ppm

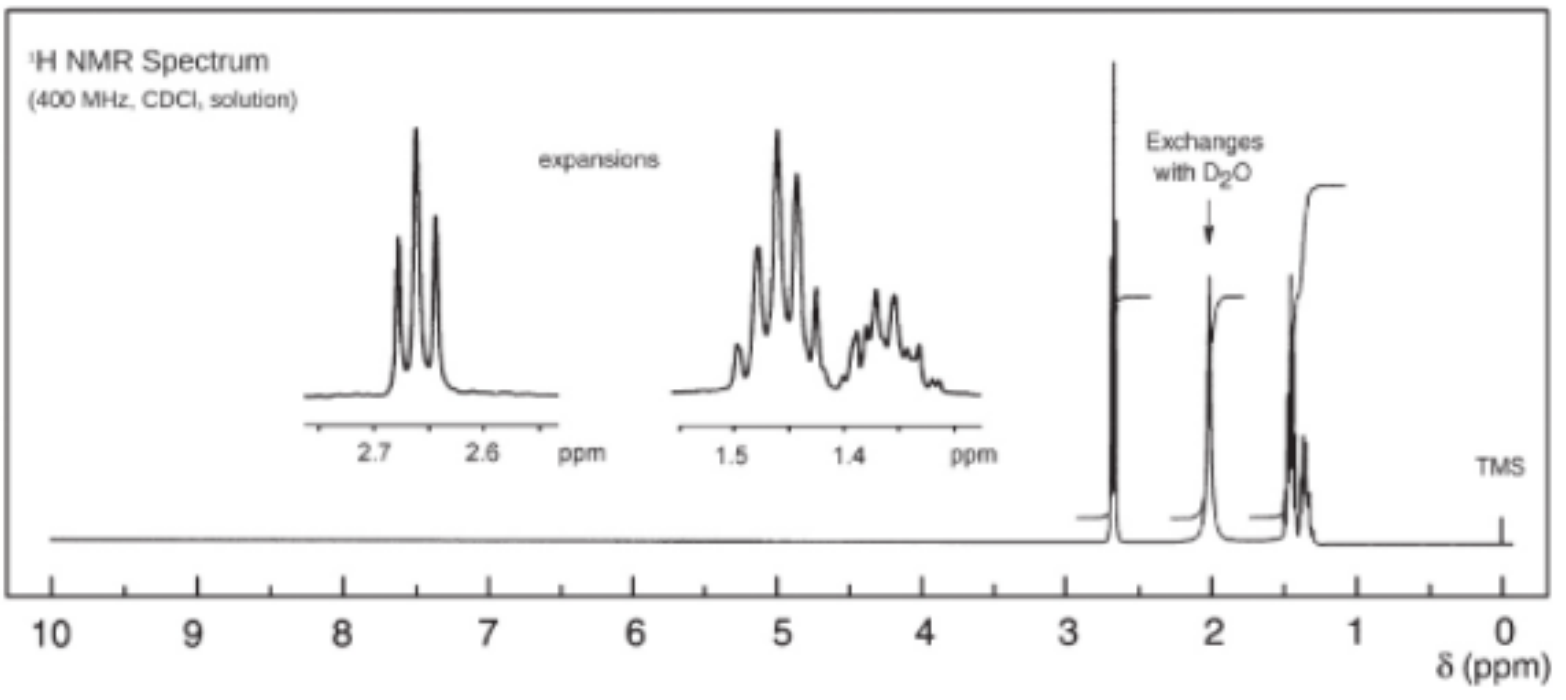
Problem 98



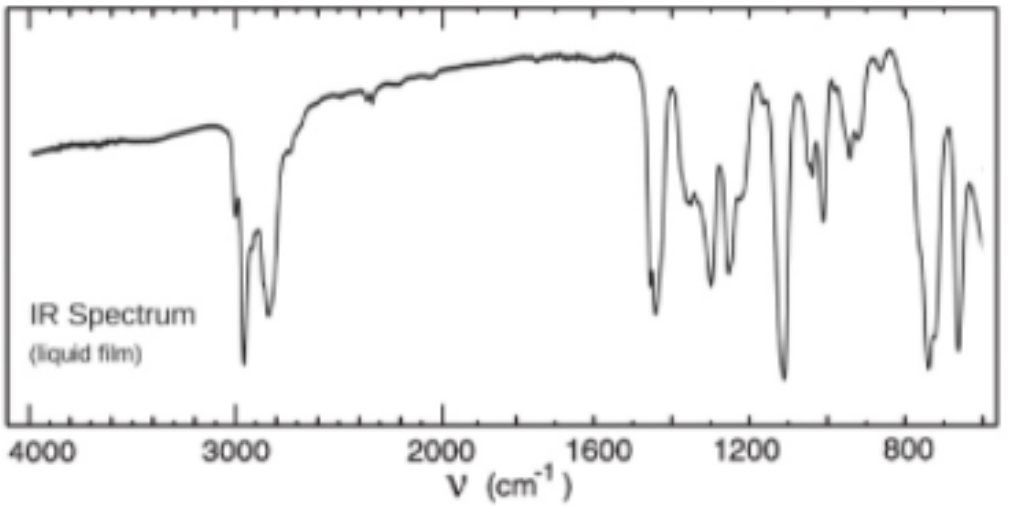


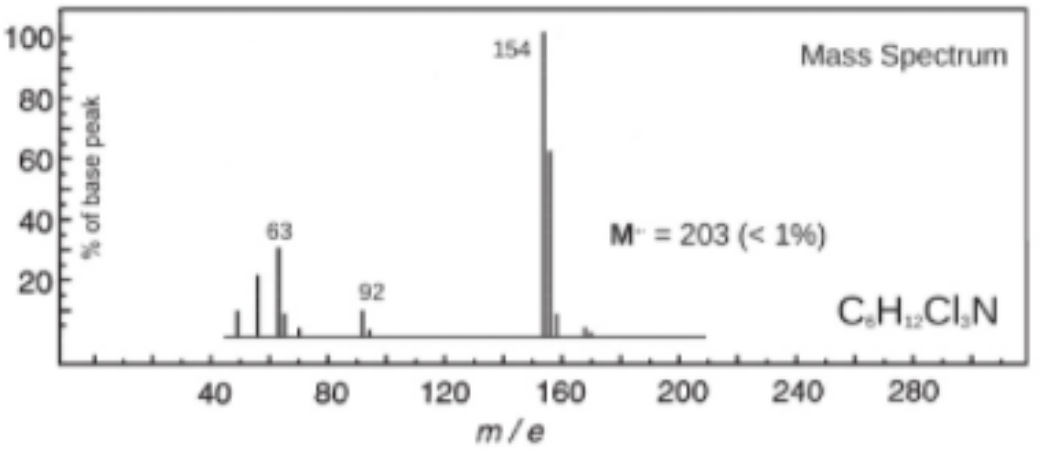
No significant UV
absorption above 220 nm

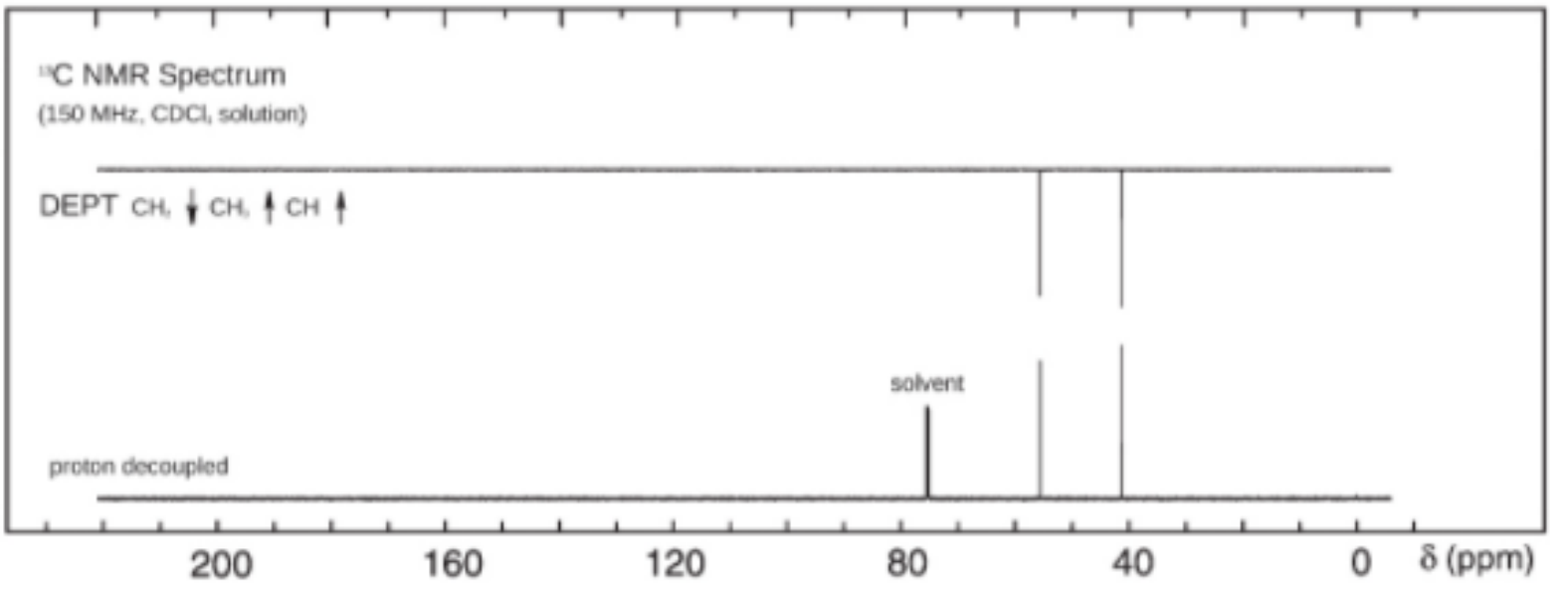


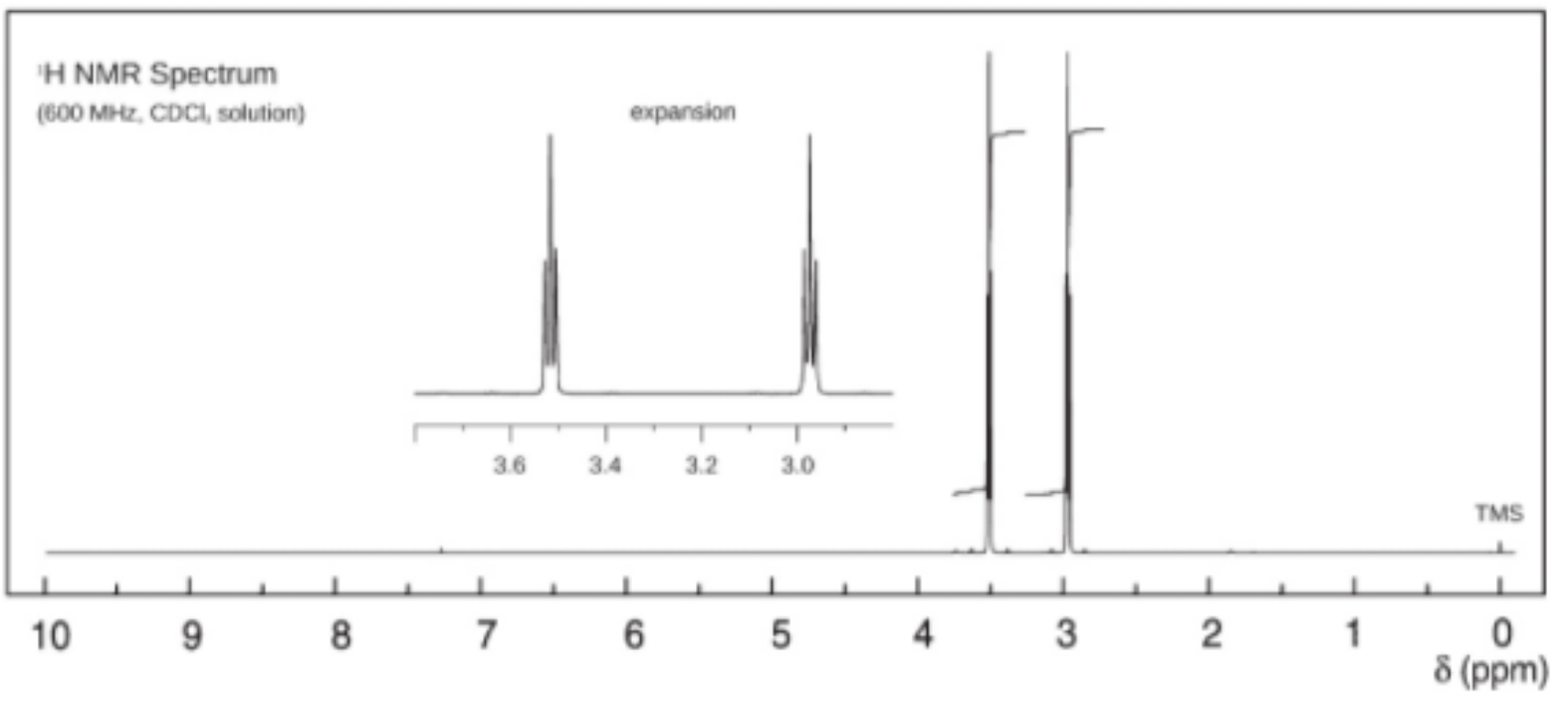


Problem 99

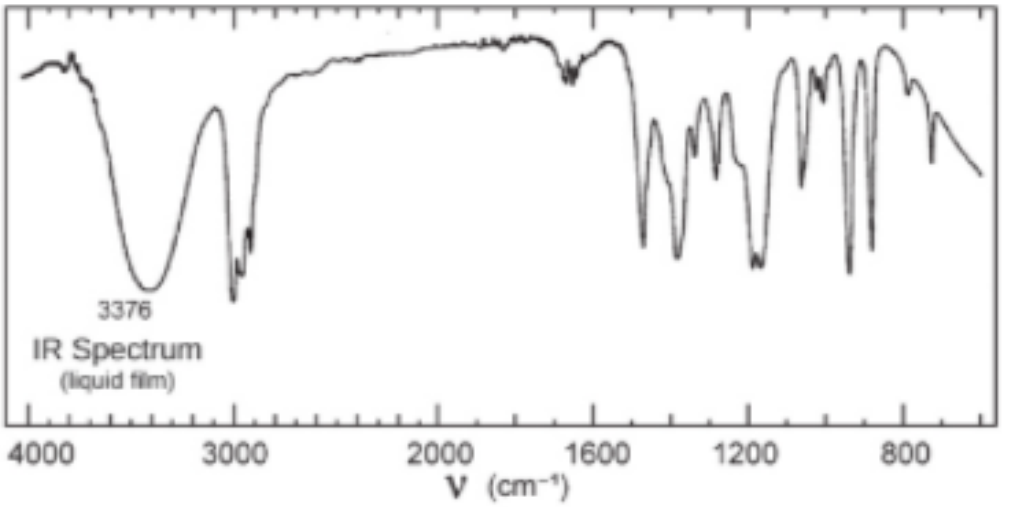

IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

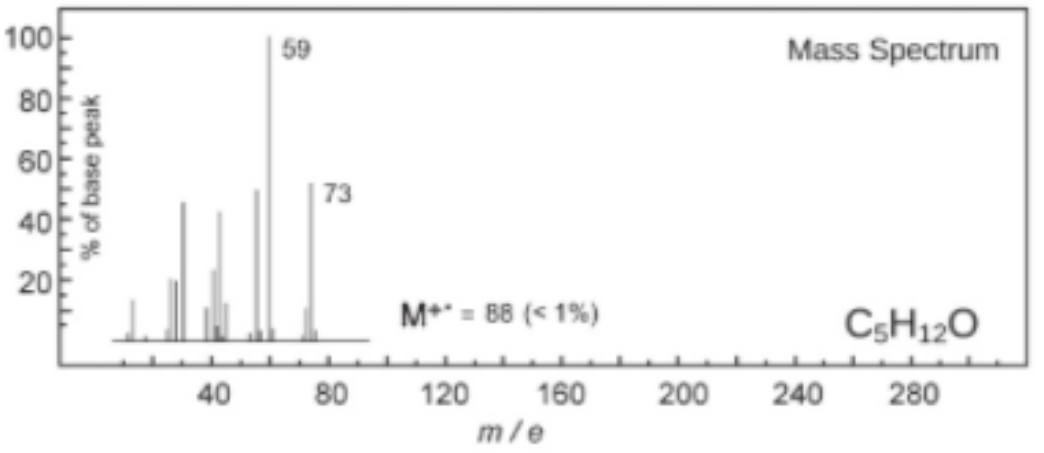

Mass Spectrum
100
80
60
40
20
% of base peak
154
63
92
M+· = 203 (< 1%)
C6H12Cl3N
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH3 ↓ CH2 ↑ CH ↑
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

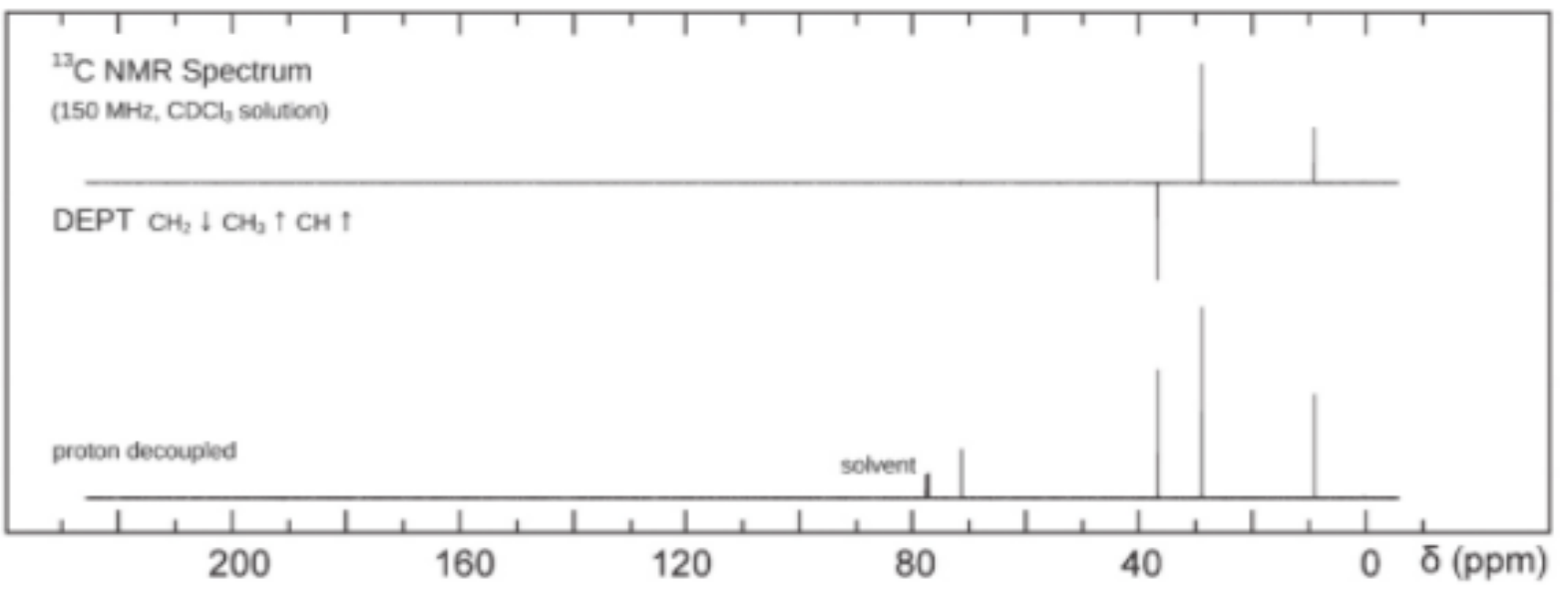

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion
3.6
3.4
3.2
3.0
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

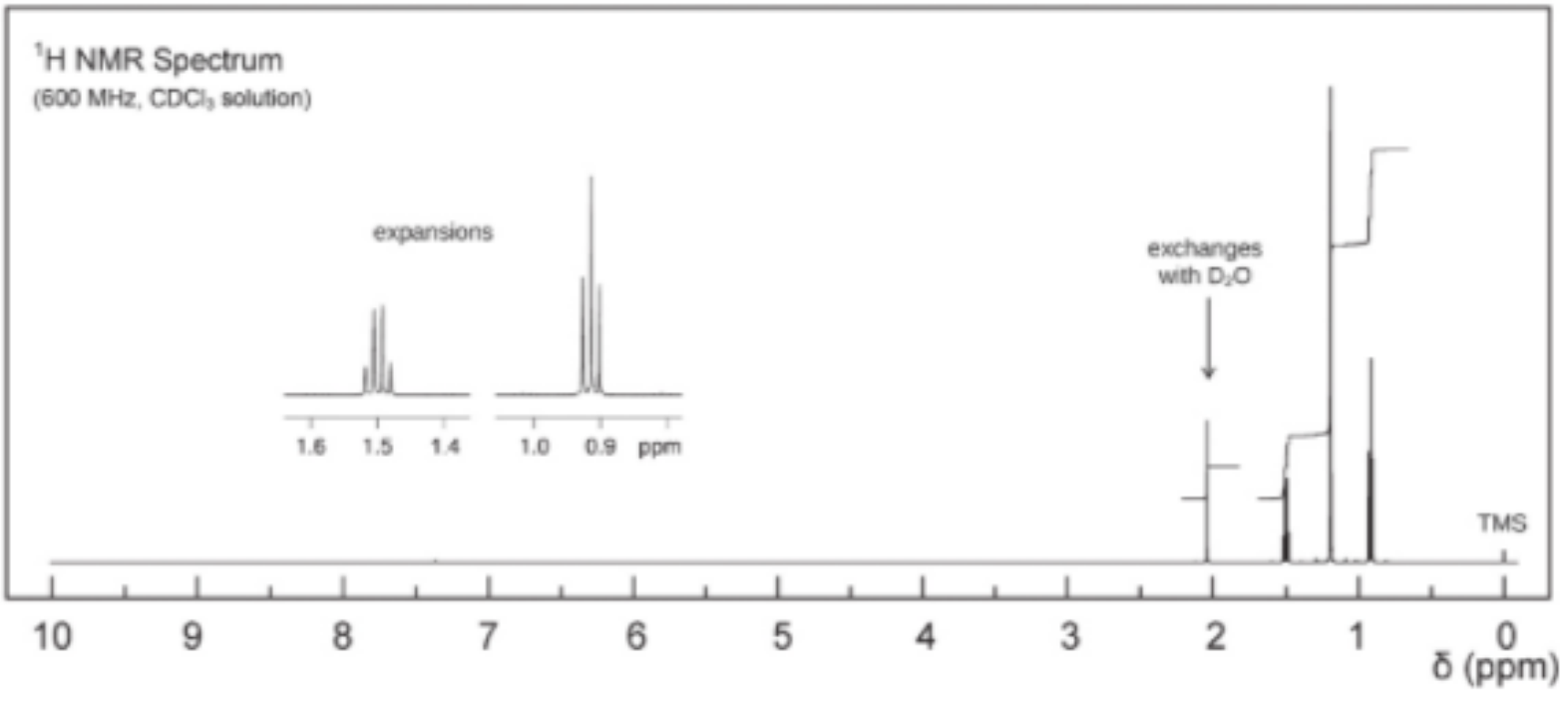
Problem 100



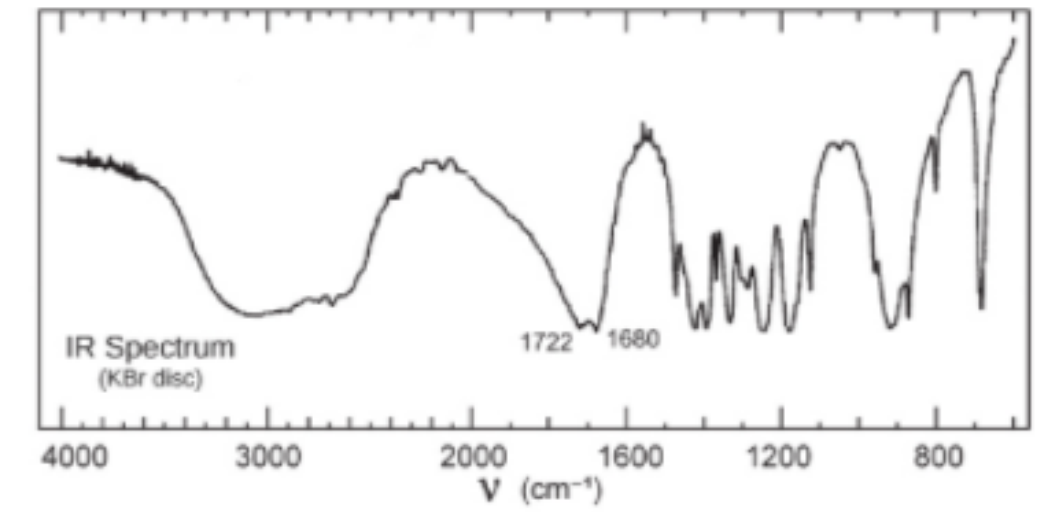


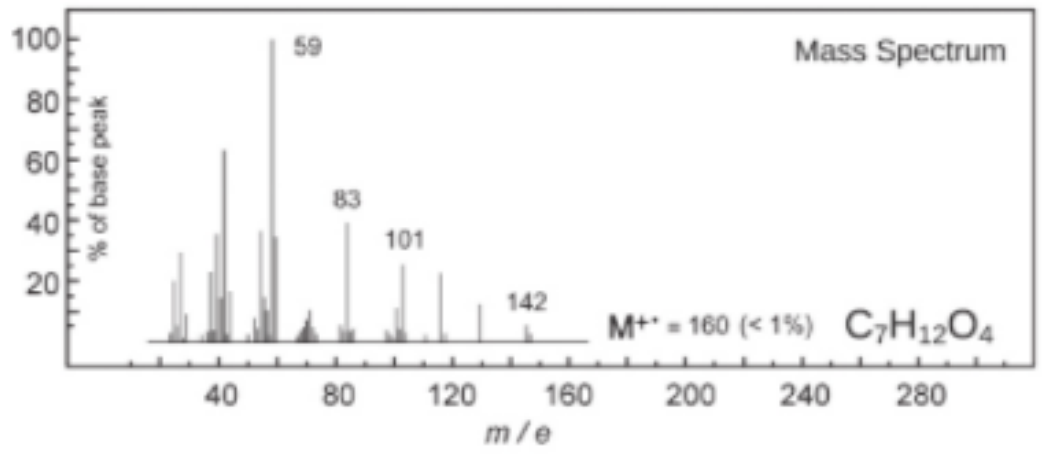
No significant UV absorption above 220 nm



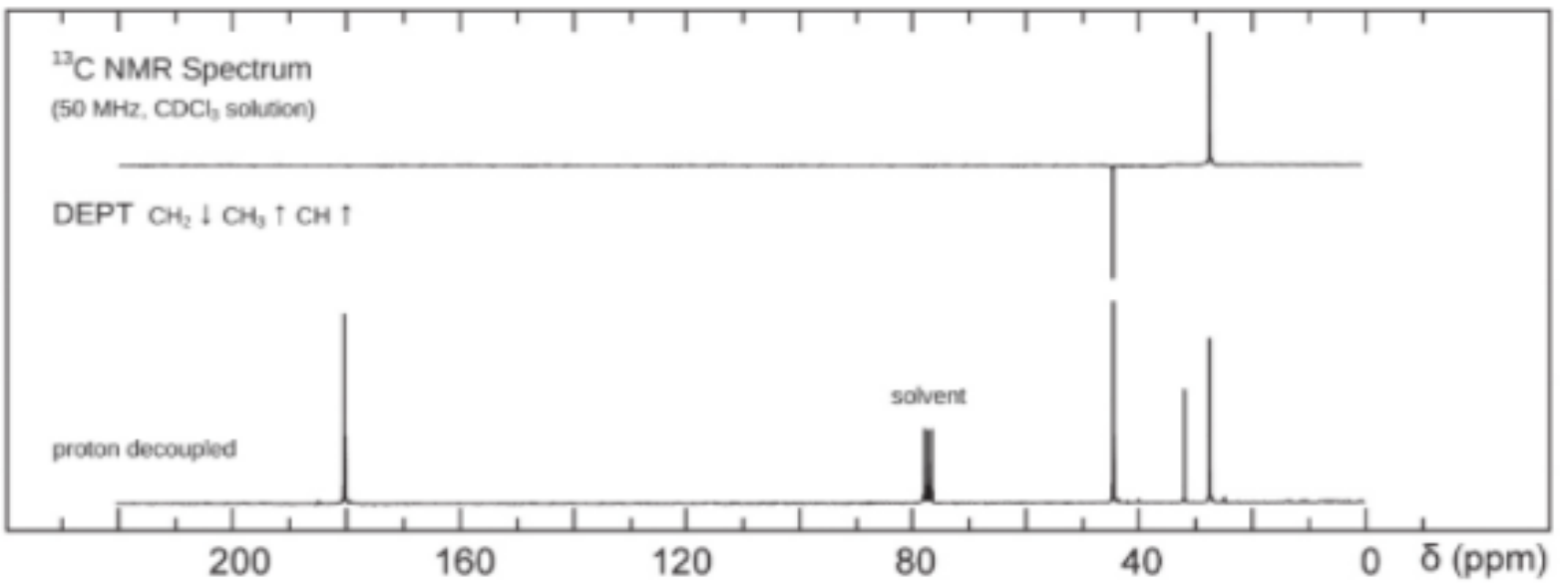


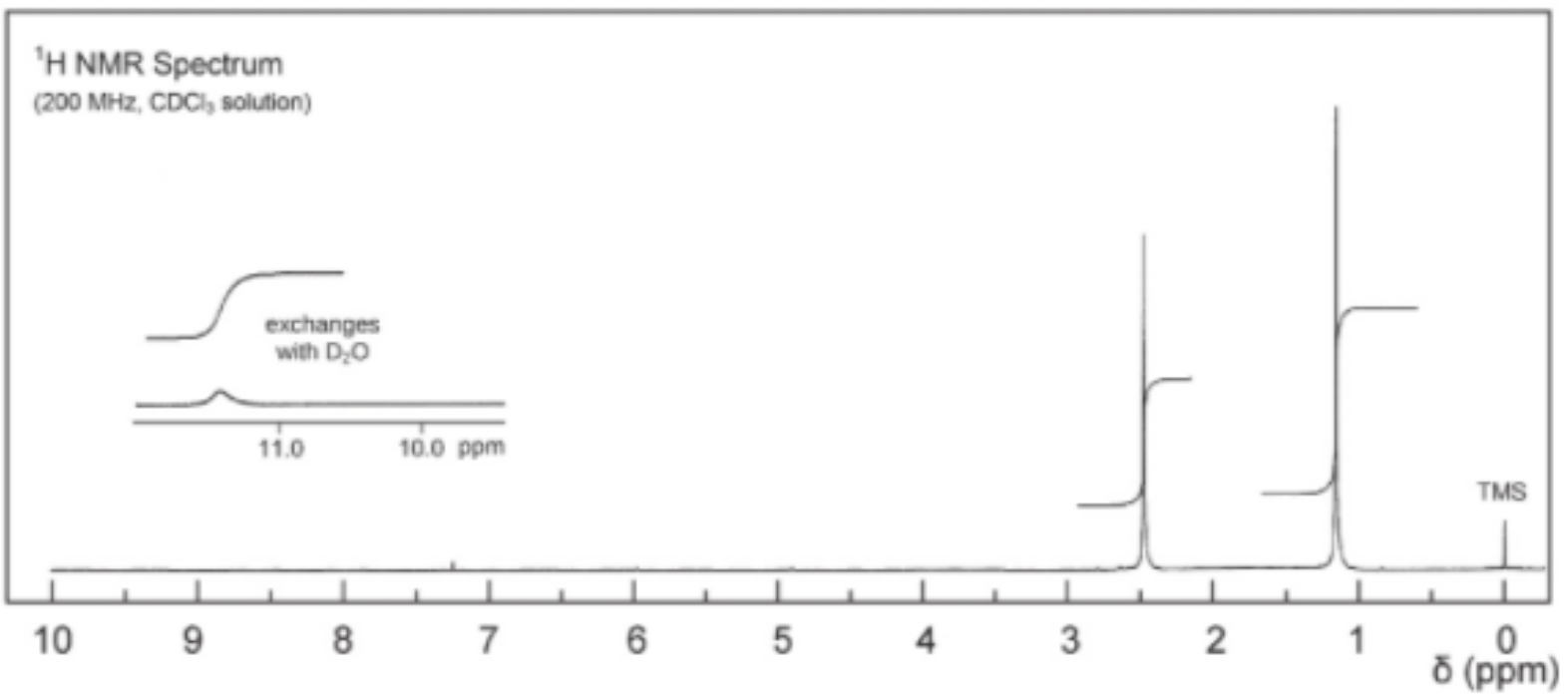
Problem 101



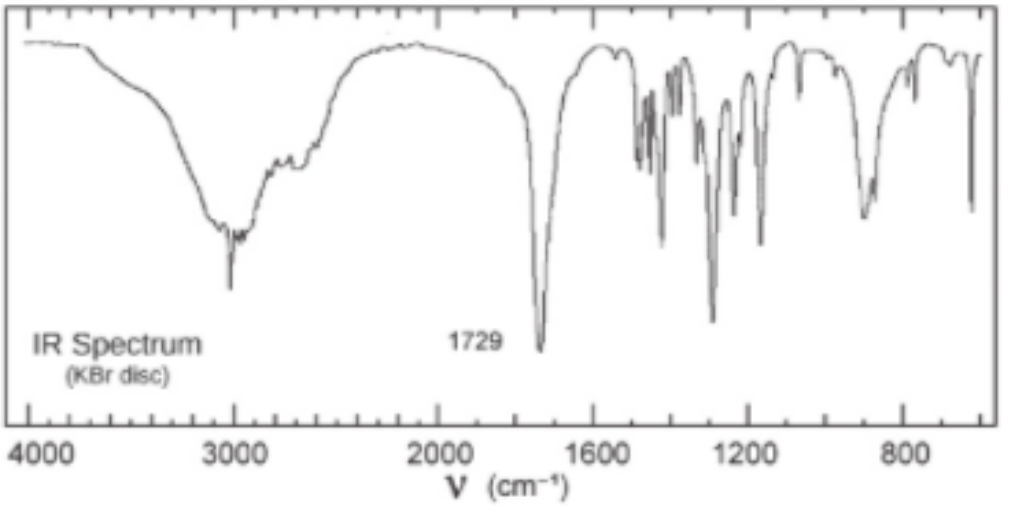


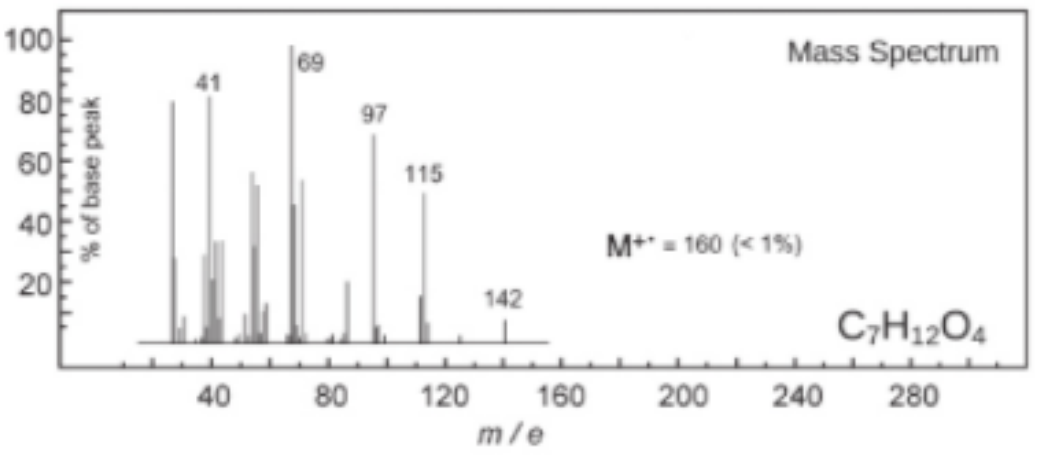
No significant UV absorption above 220 nm



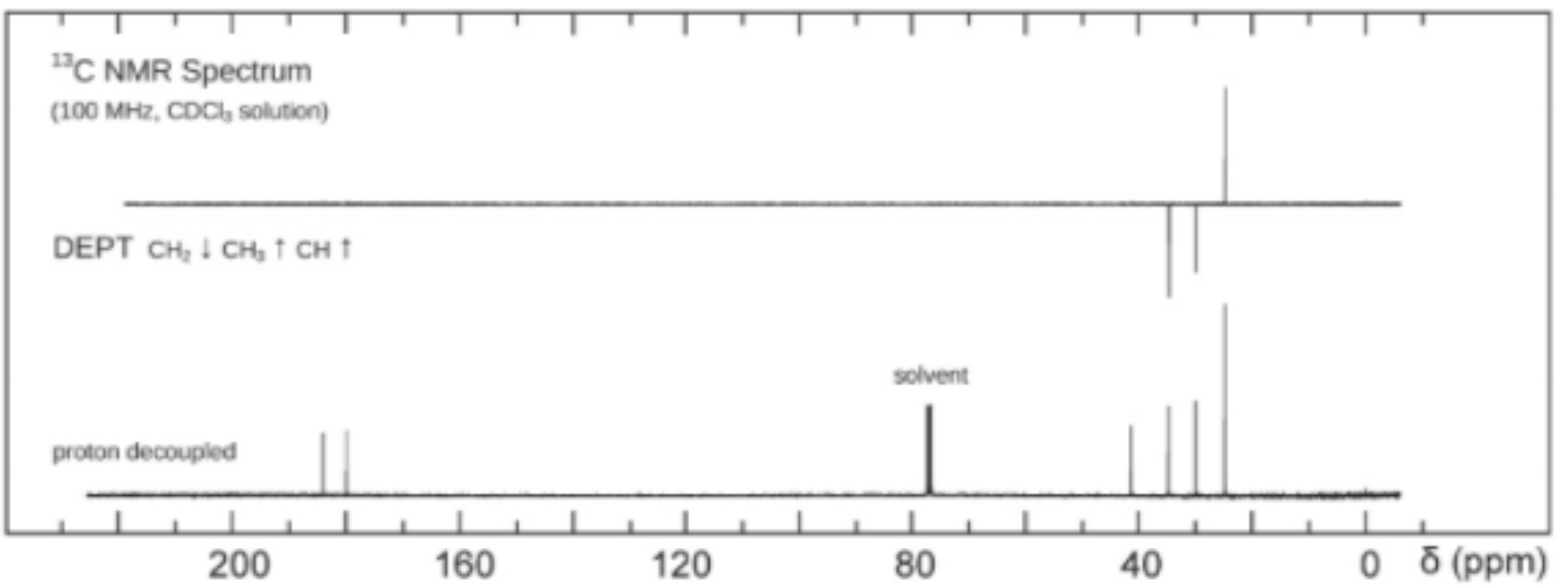


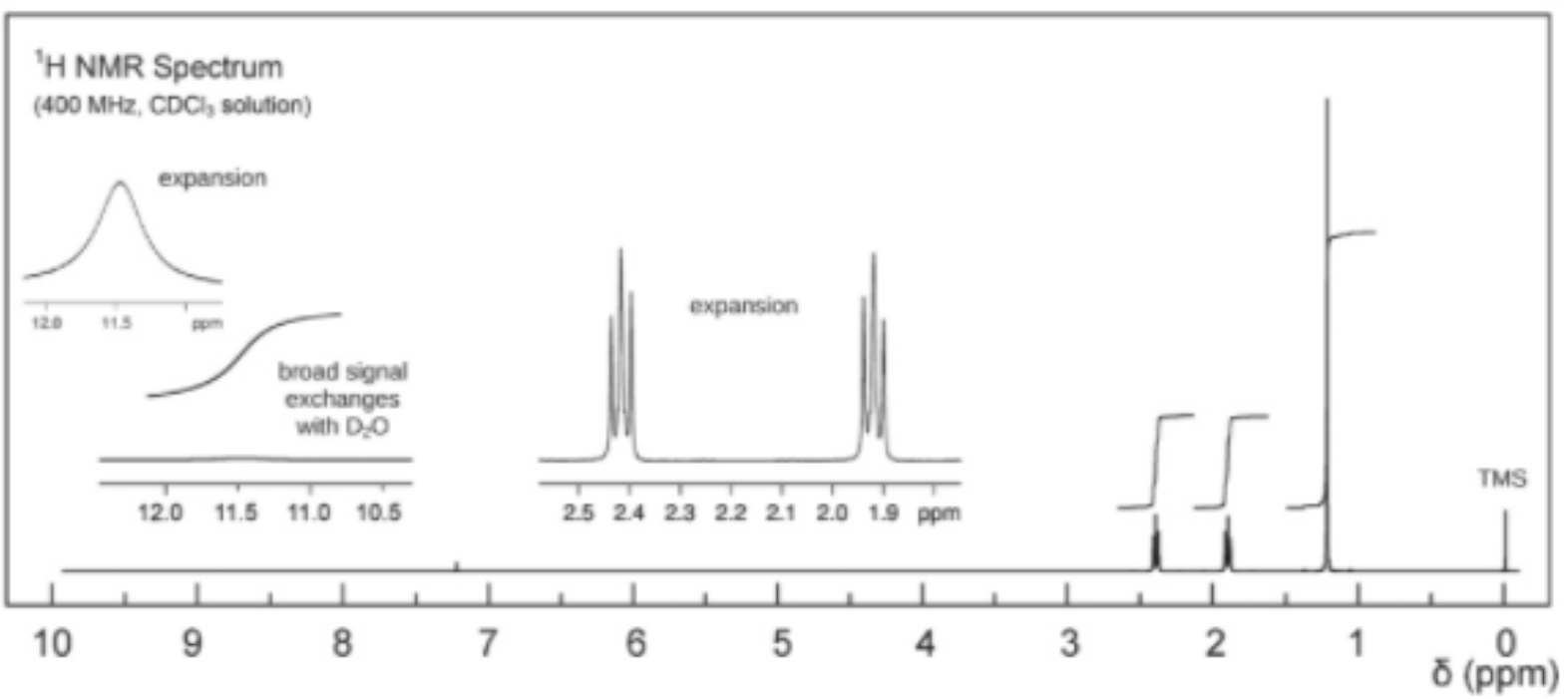
Problem 102



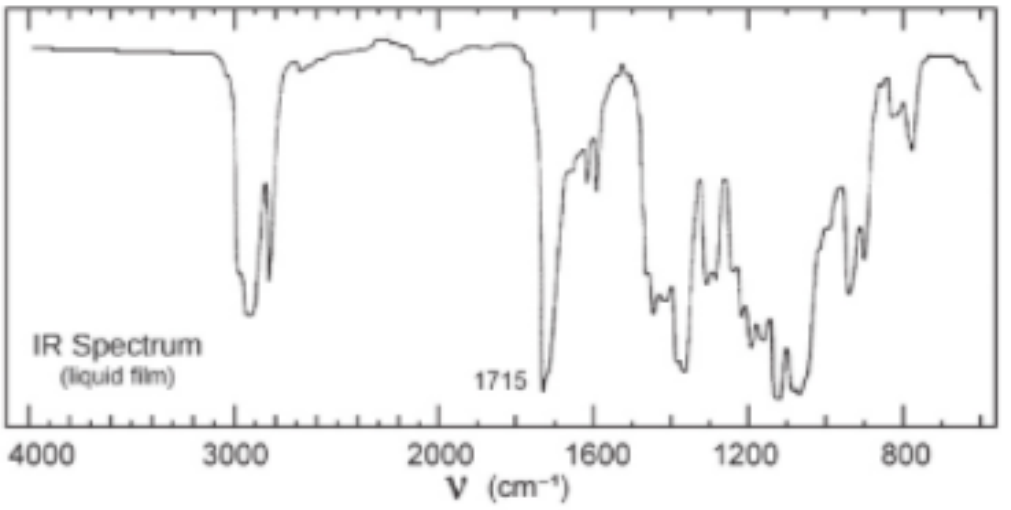


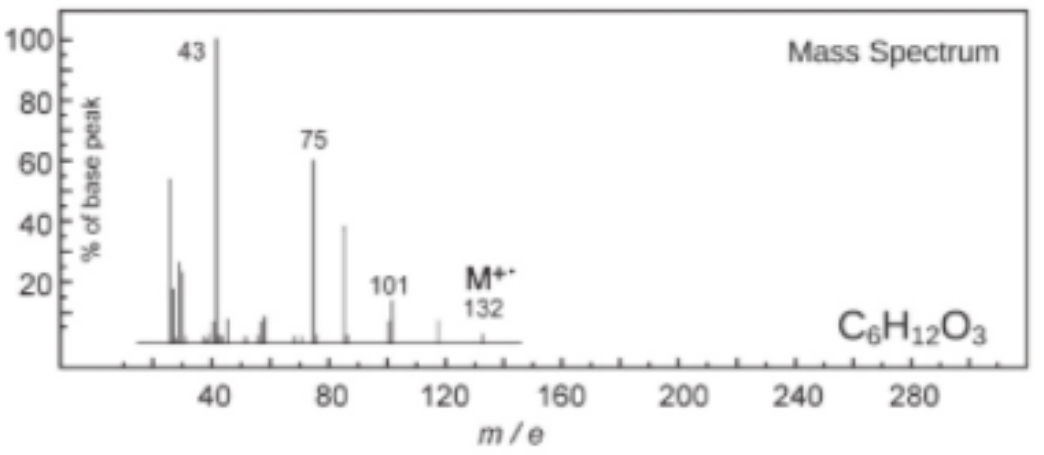
No significant UV absorption above 220 nm



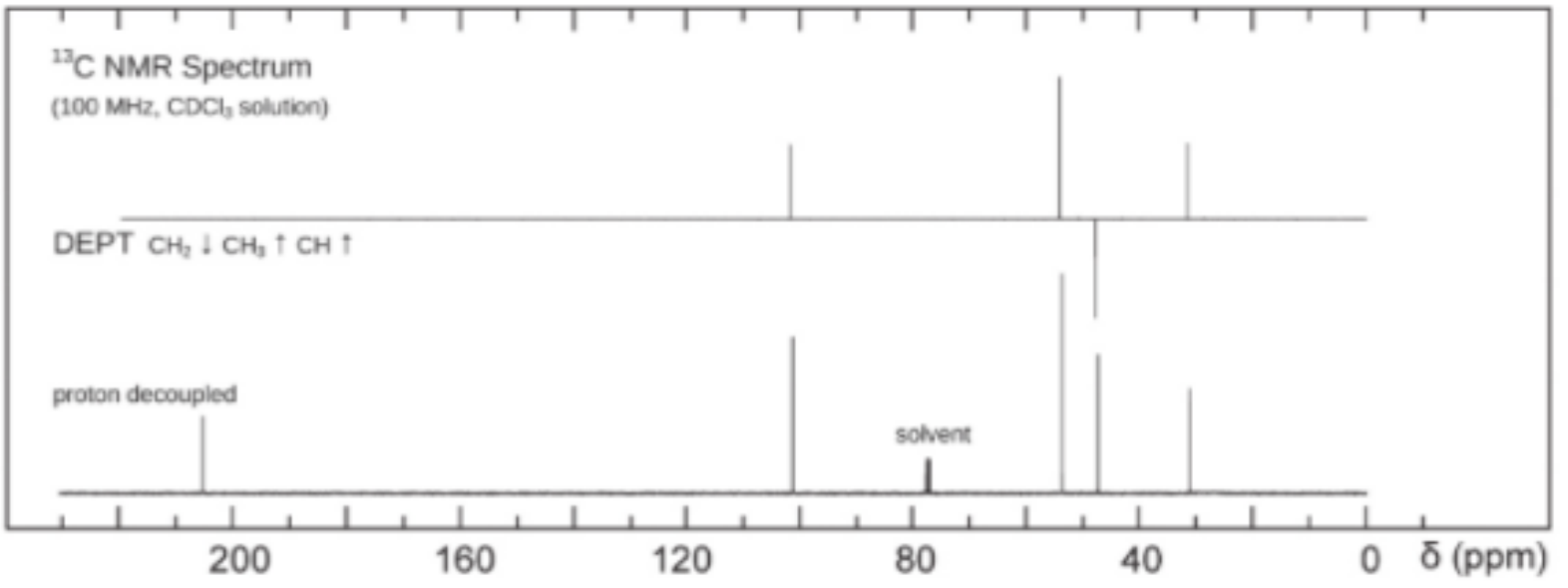


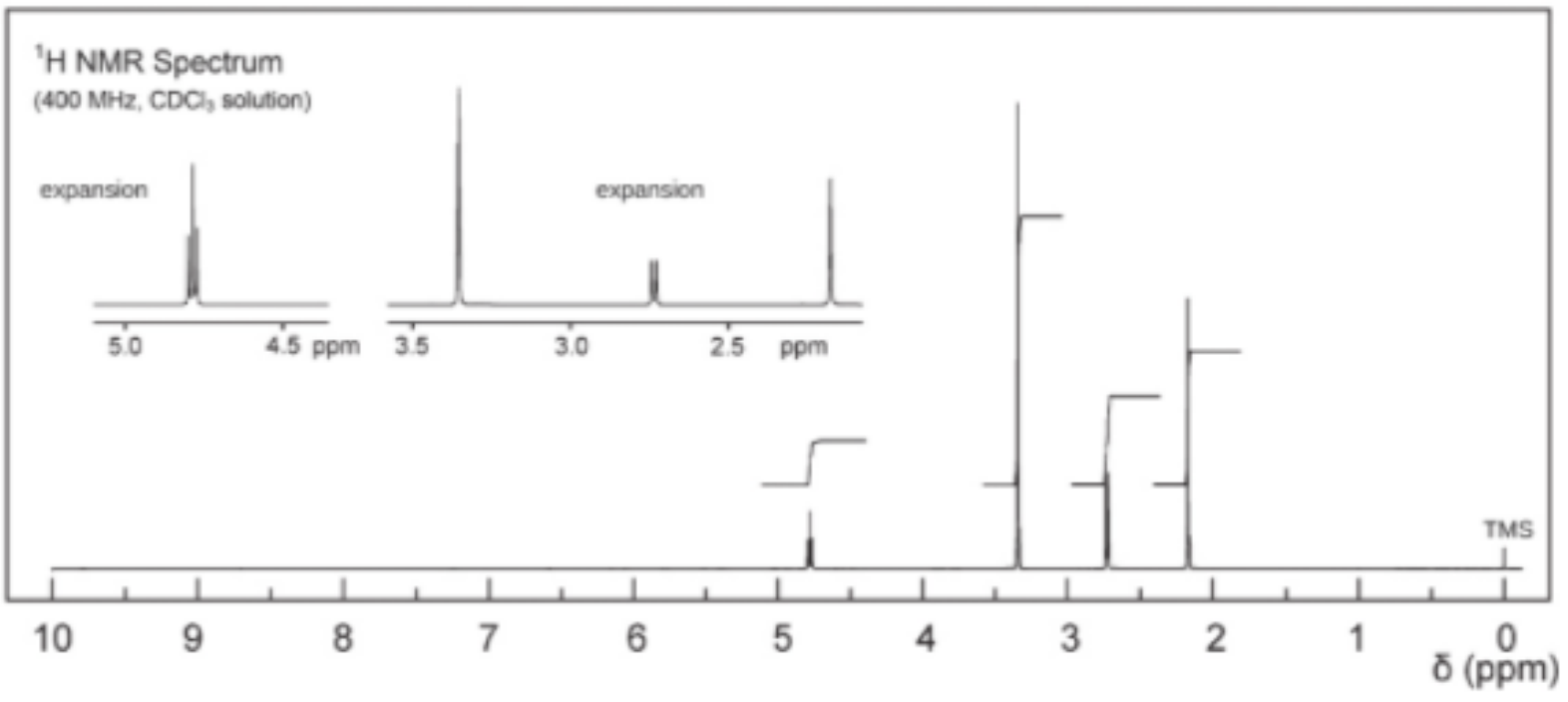
Problem 103



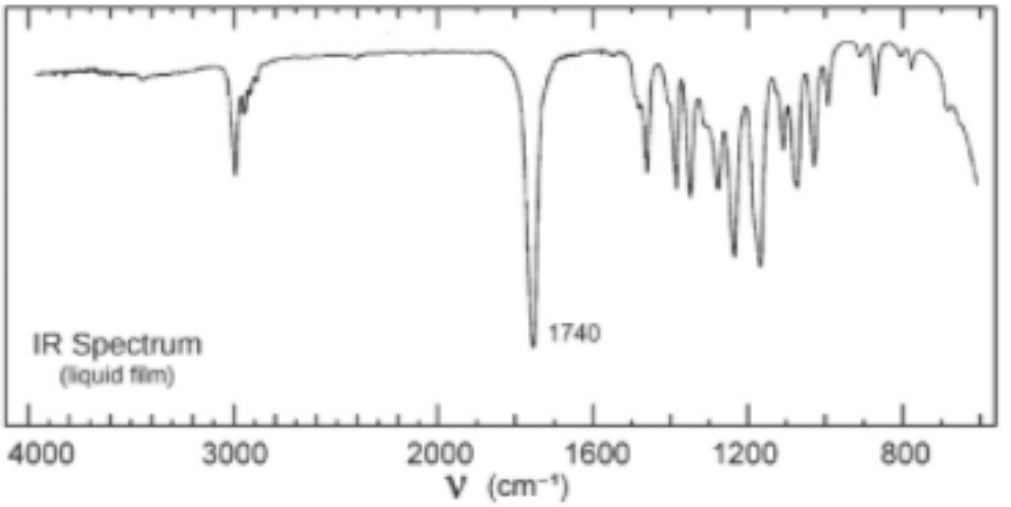


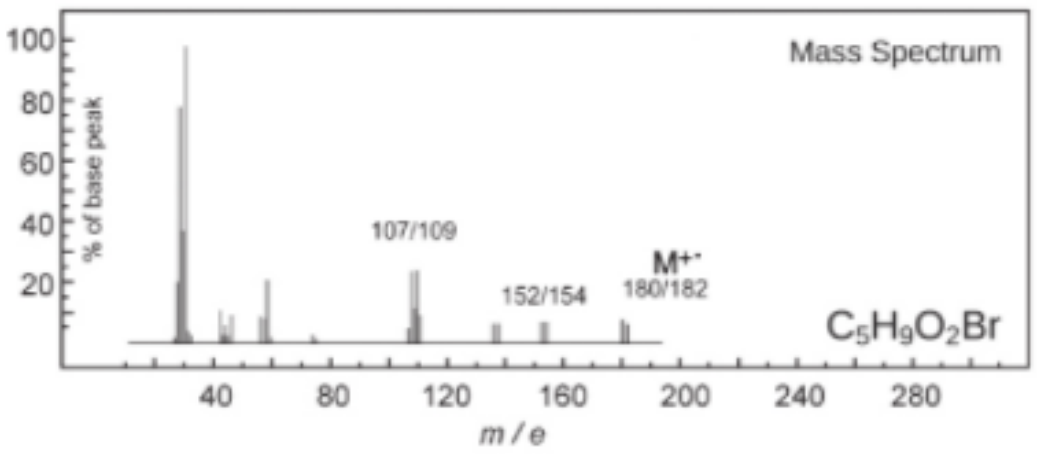
No significant UV absorption above 220 nm



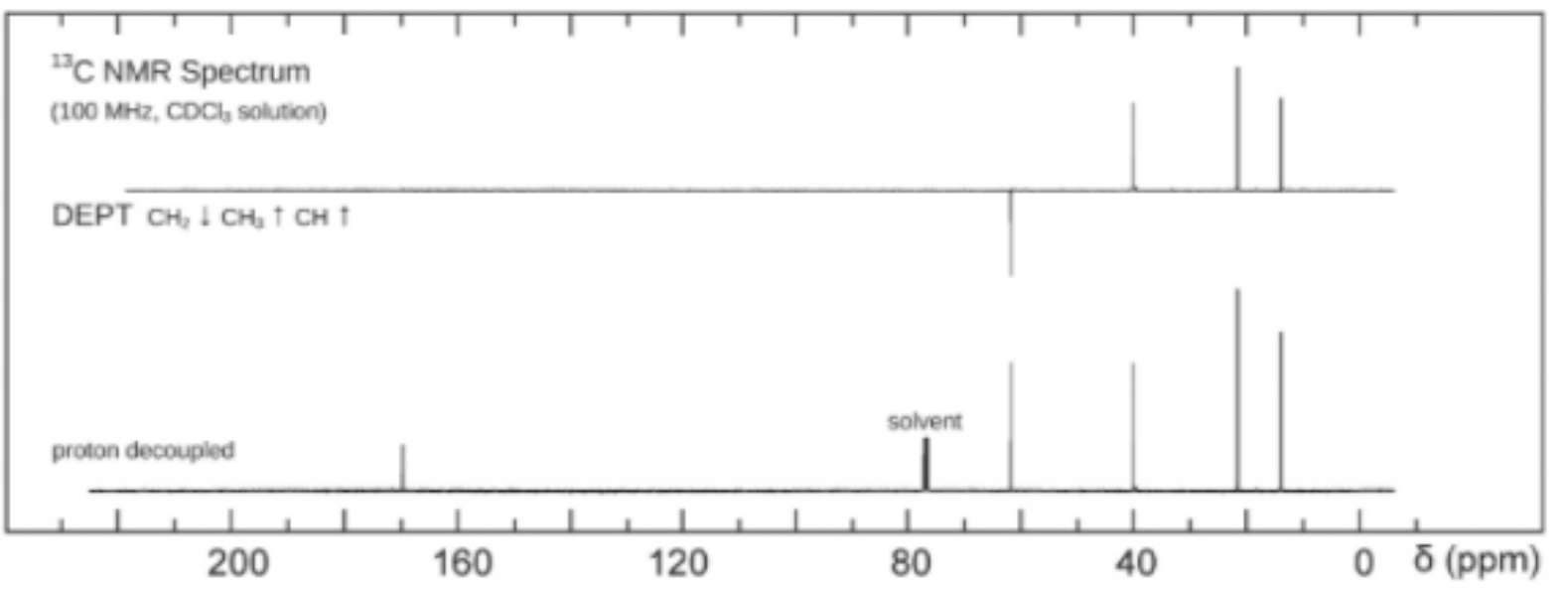


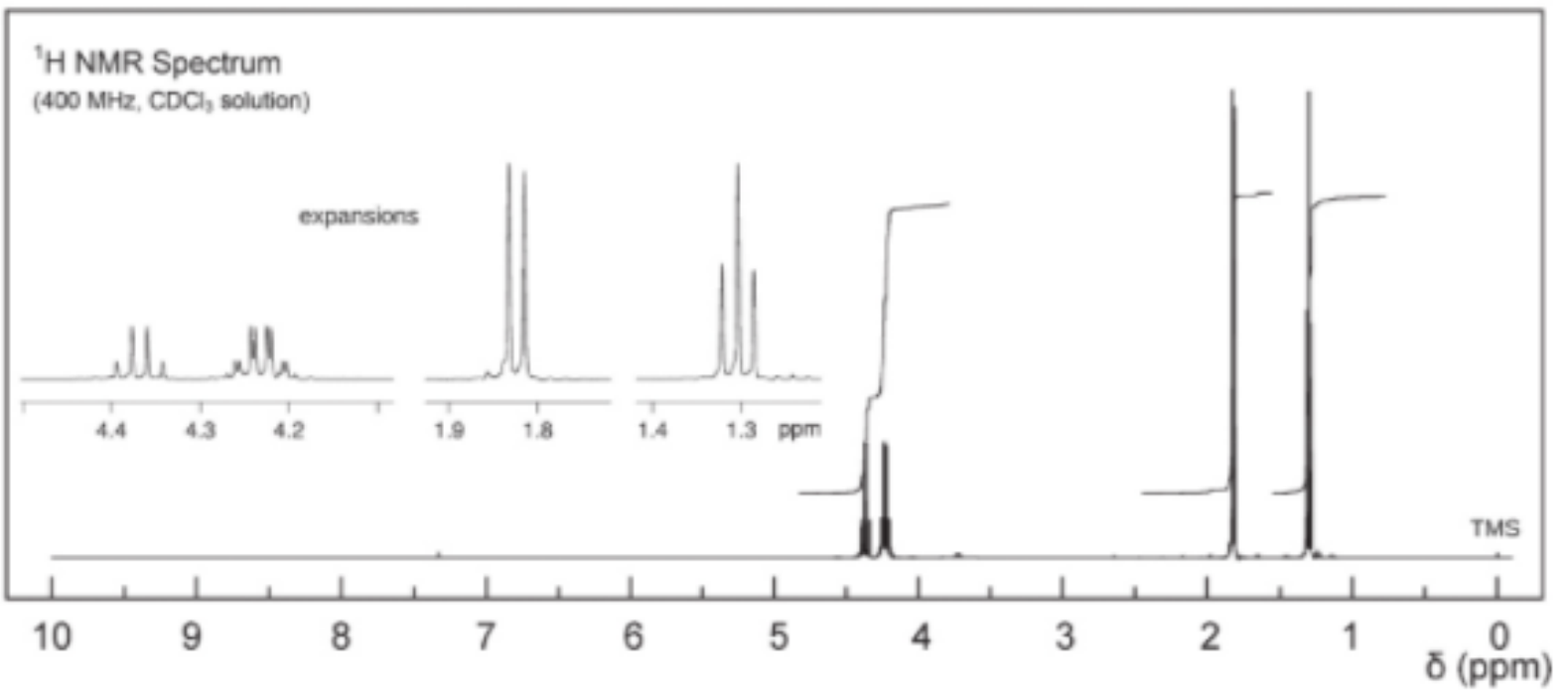
Problem 104

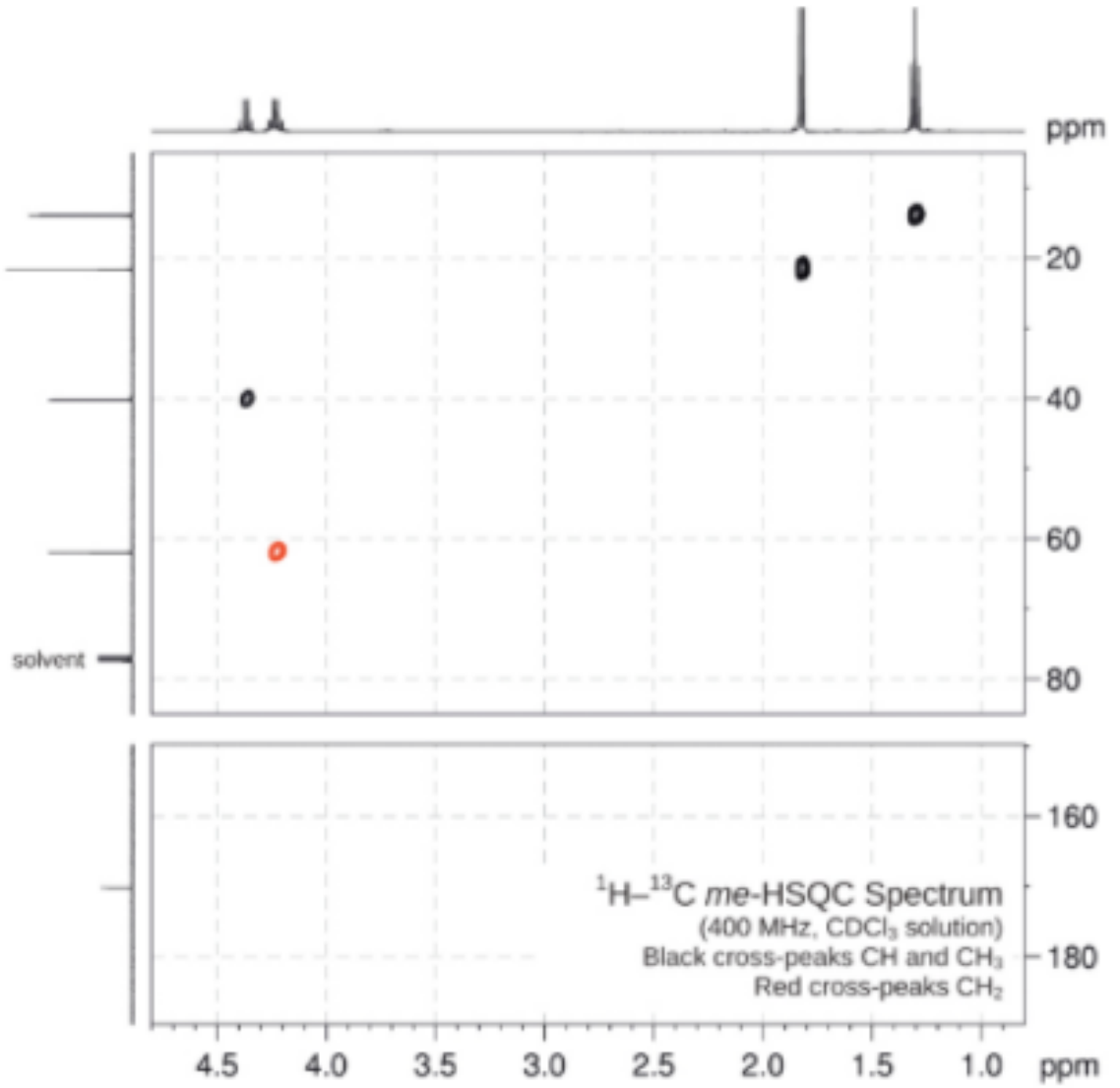




No significant UV absorption above 220 nm

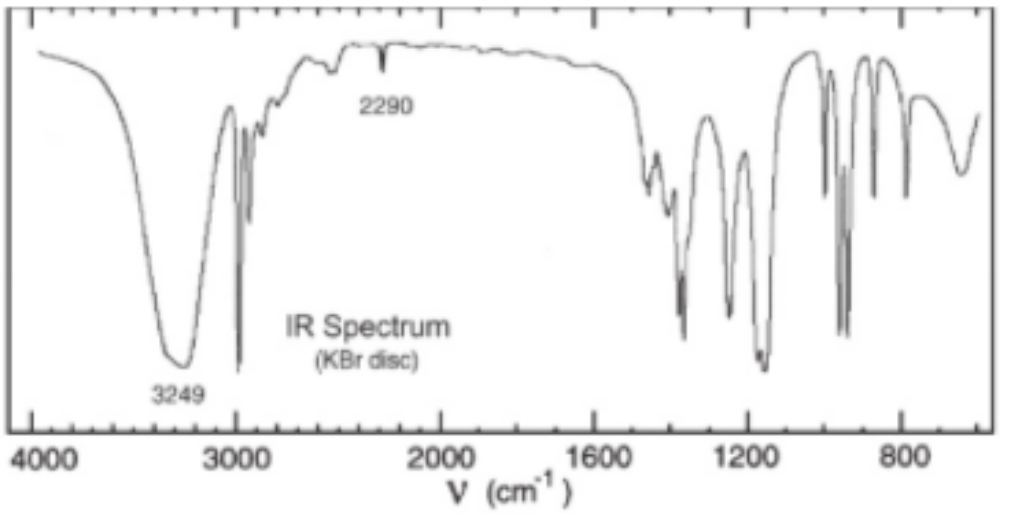


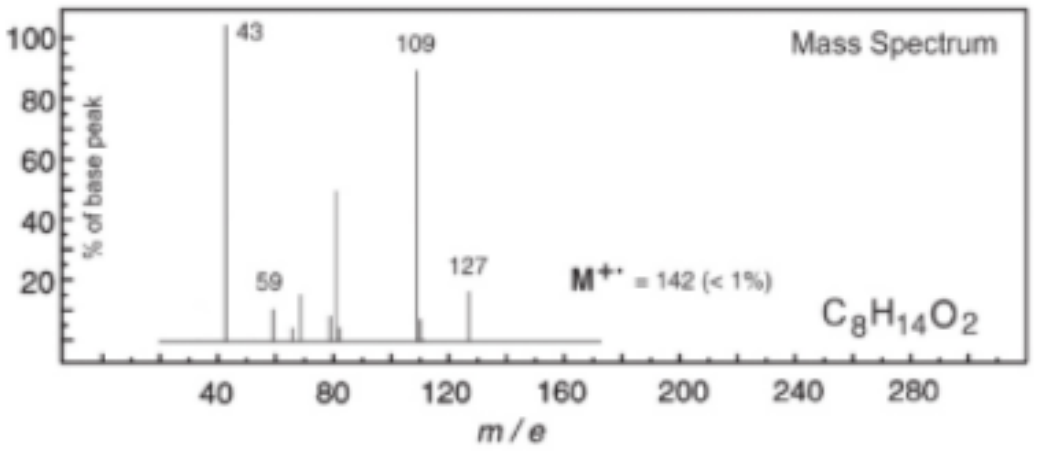


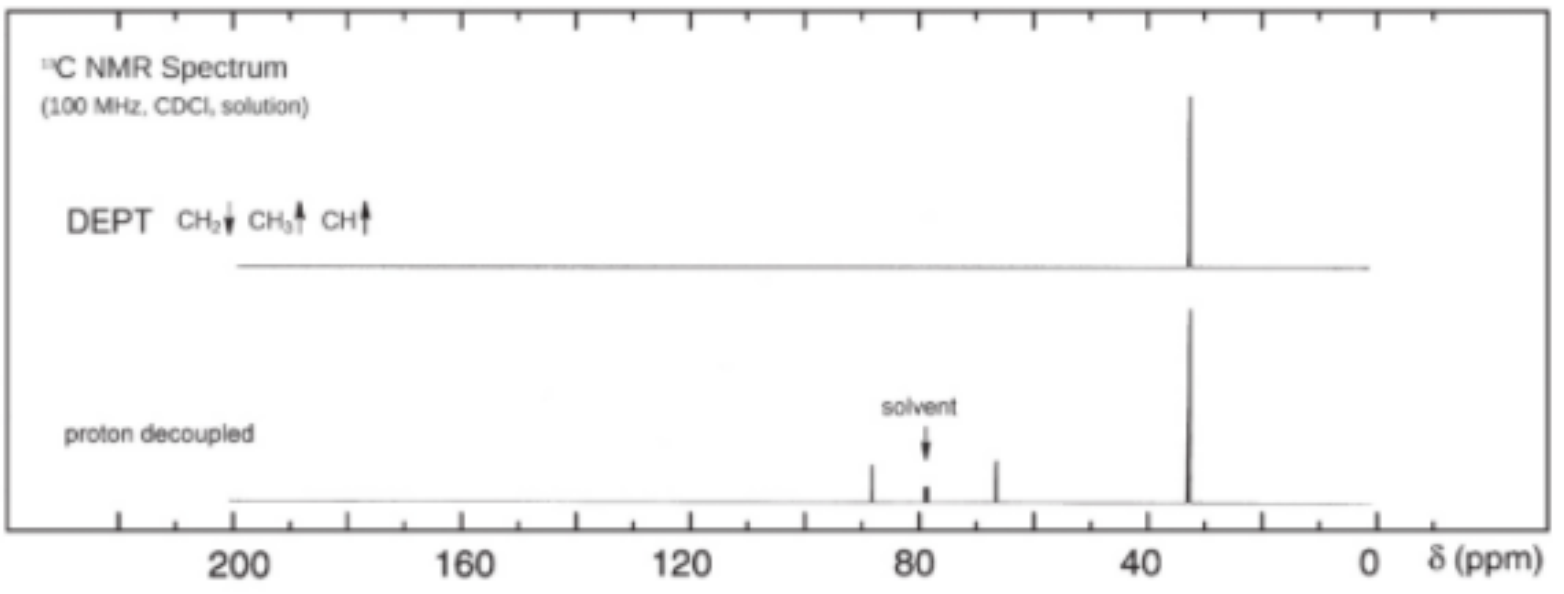

ppm
20
40
60
solvent
80
160
180
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

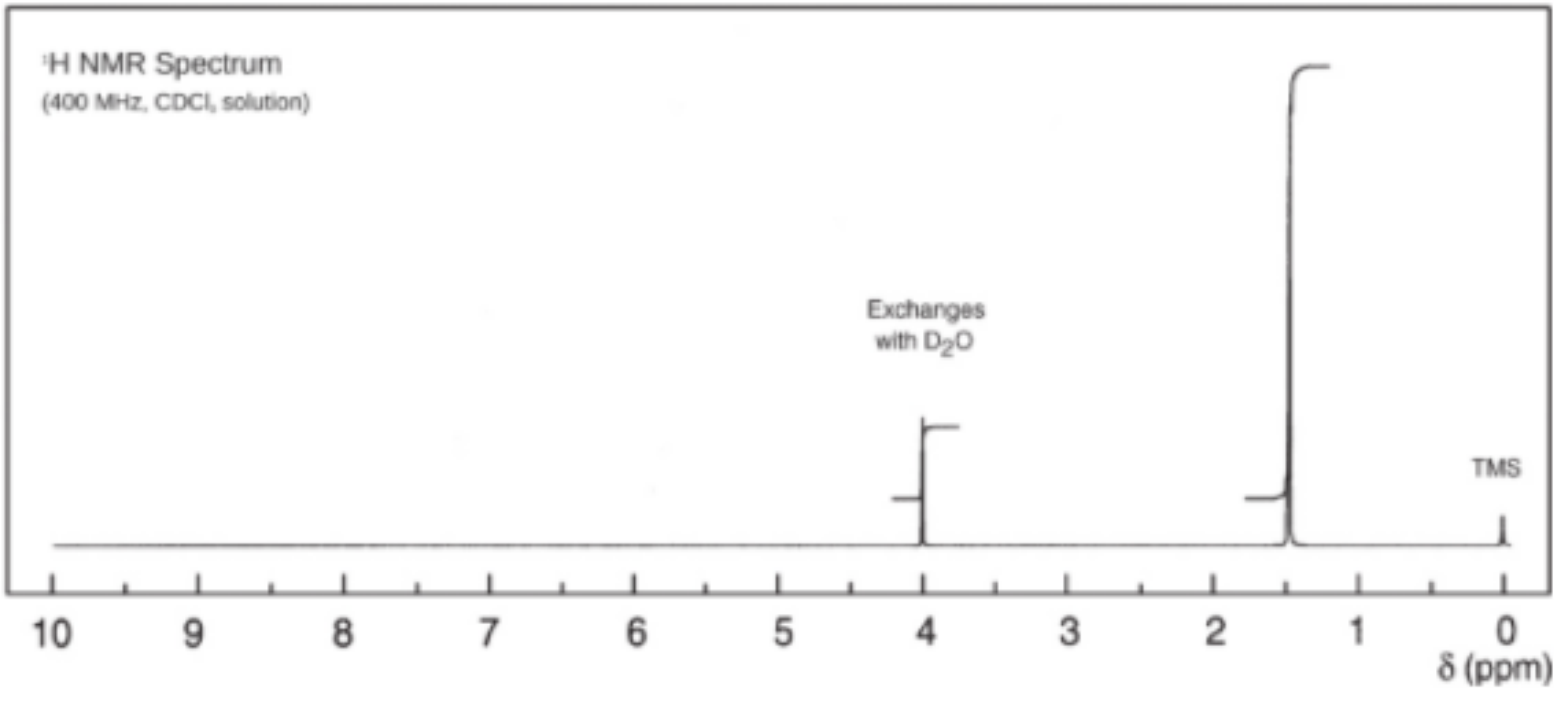
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

Problem 105

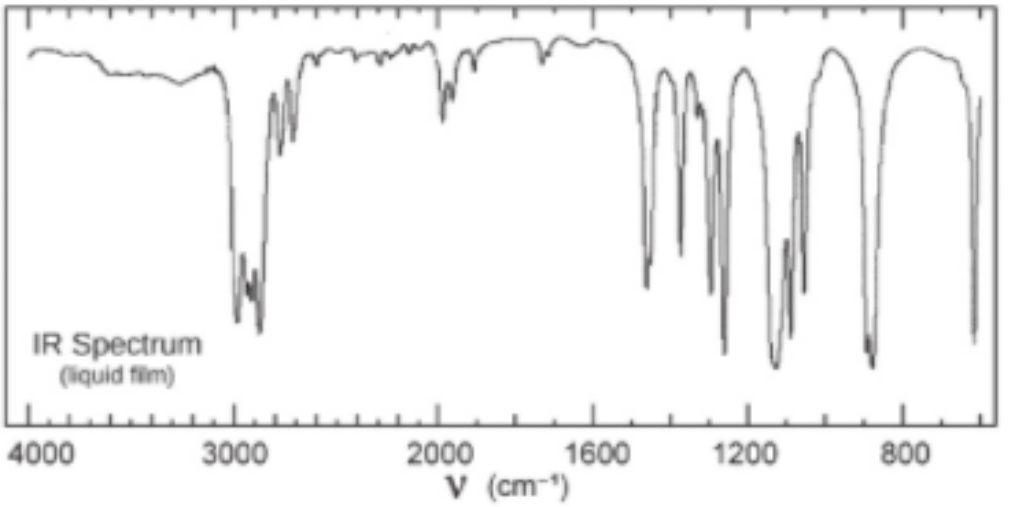

2290
IR Spectrum
(KBr disc)
3249
4000
3000
2000
1600
1200
800
ν (cm-1)

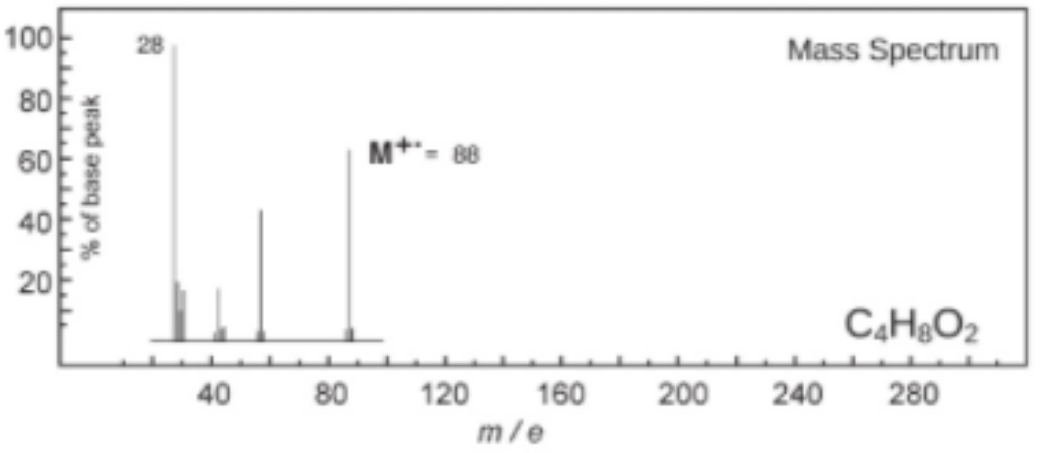

100
80
60
40
20
% of base peak
43
109
59
127
M+· = 142 (< 1%)
Mass Spectrum
C8H14O2
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(100 MHz, CDCl, solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

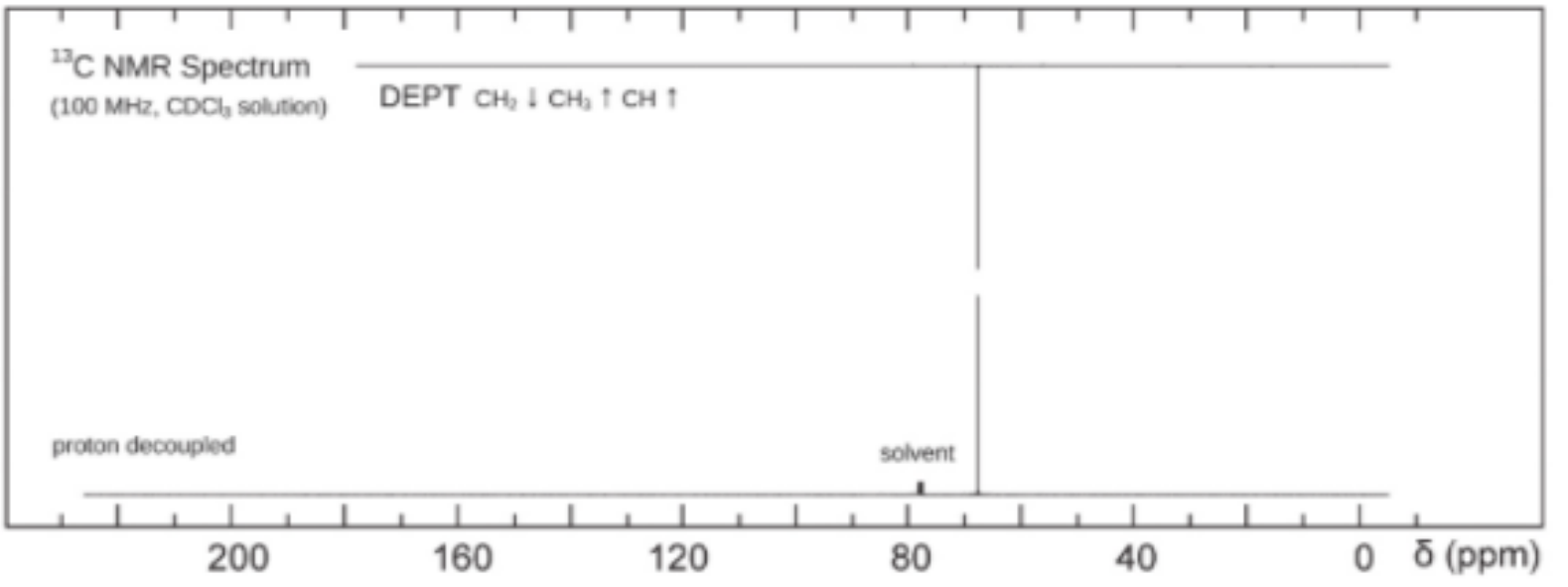

1H NMR Spectrum
(400 MHz, CDCl, solution)
Exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

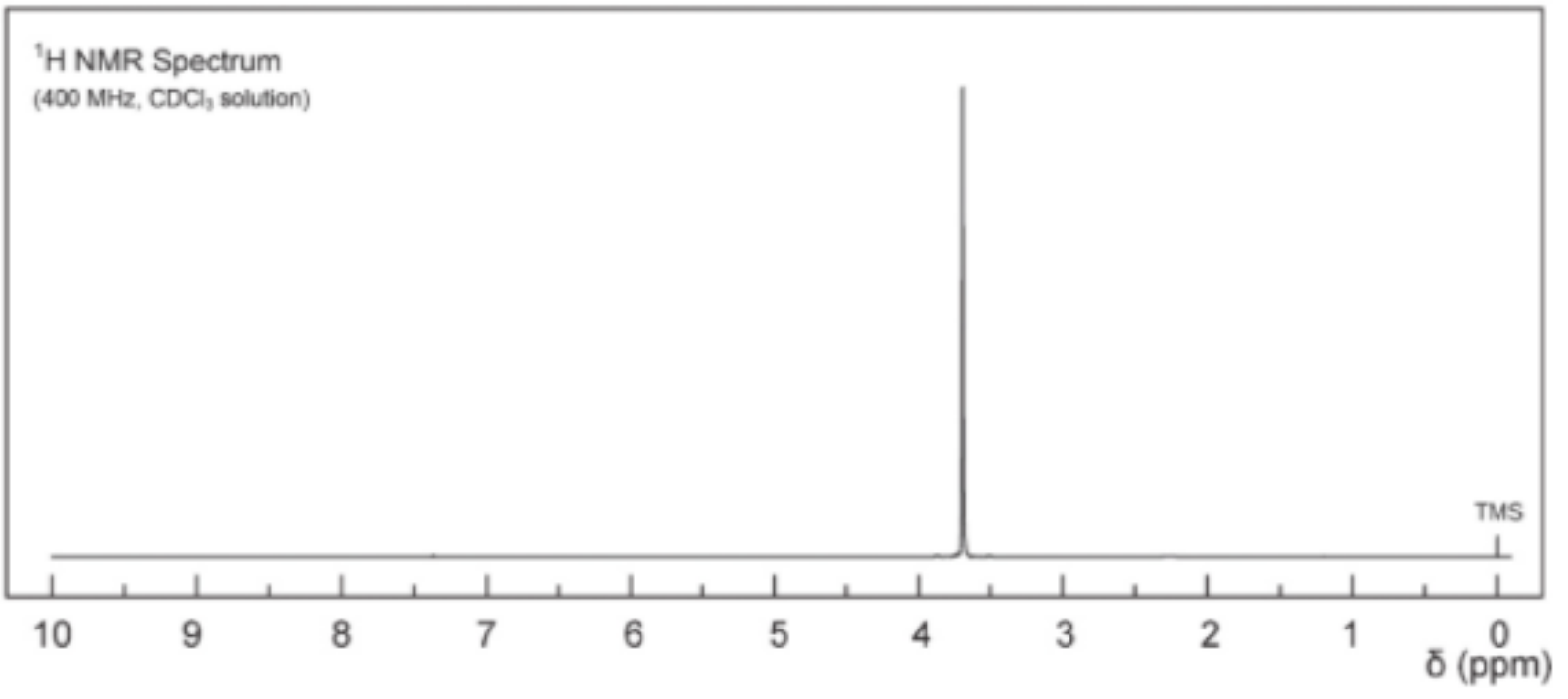
Problem 106



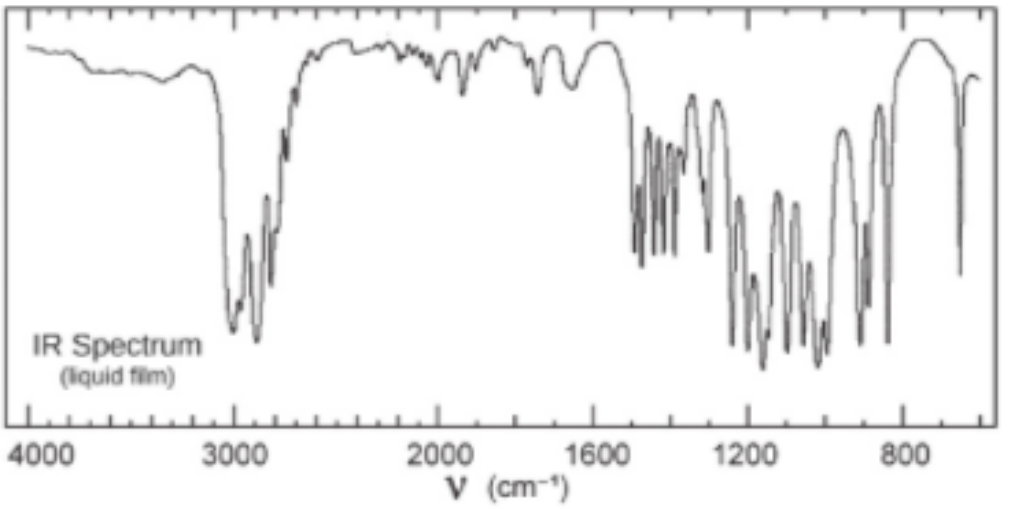


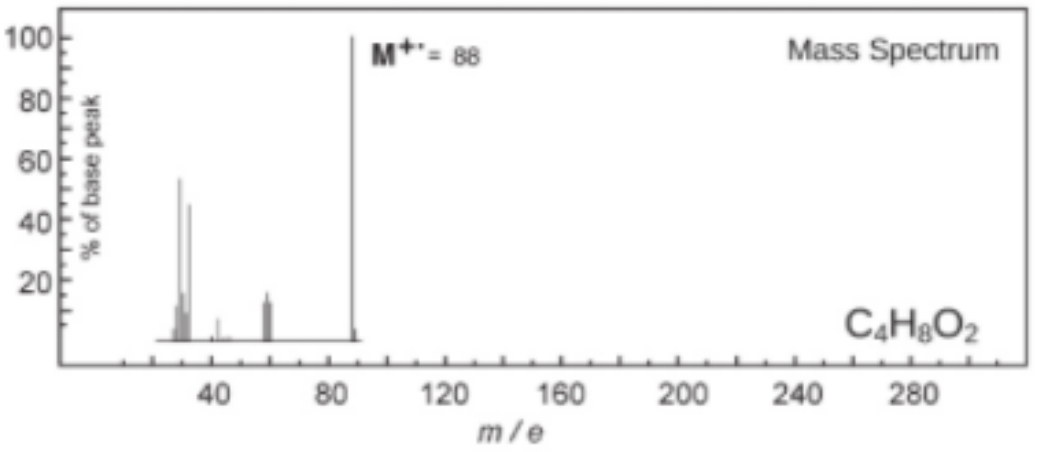
No significant UV absorption above 220 nm



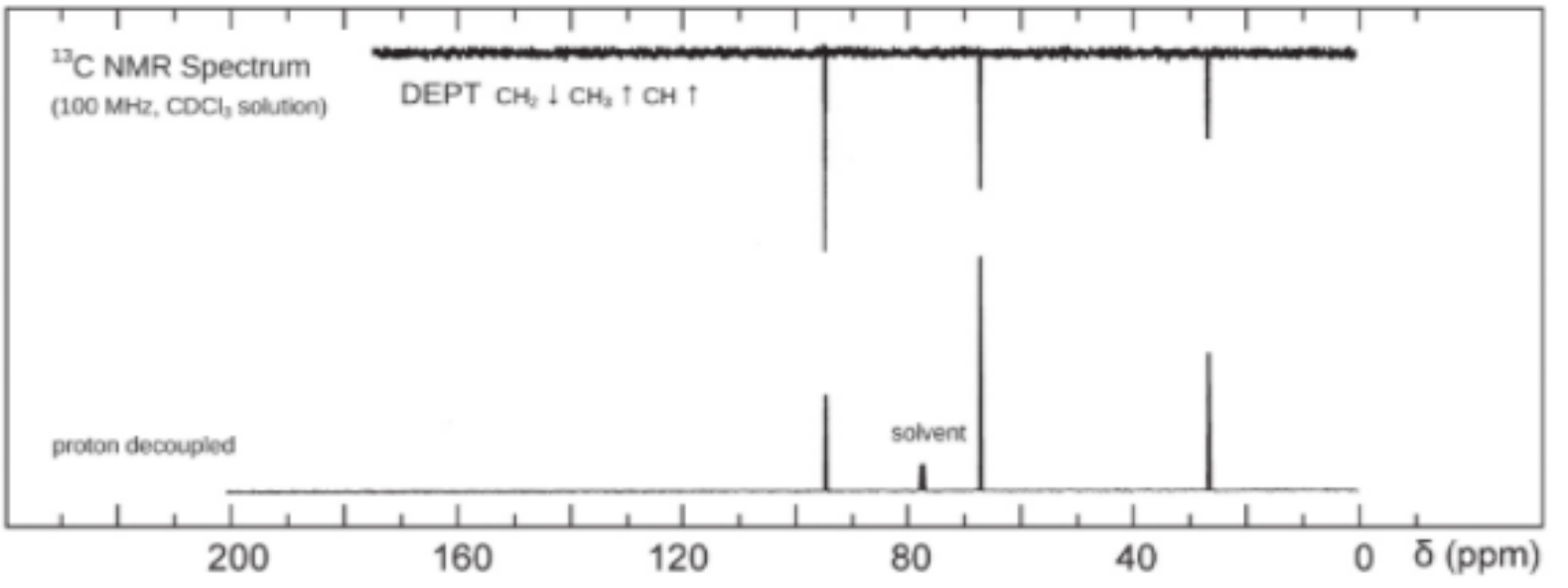


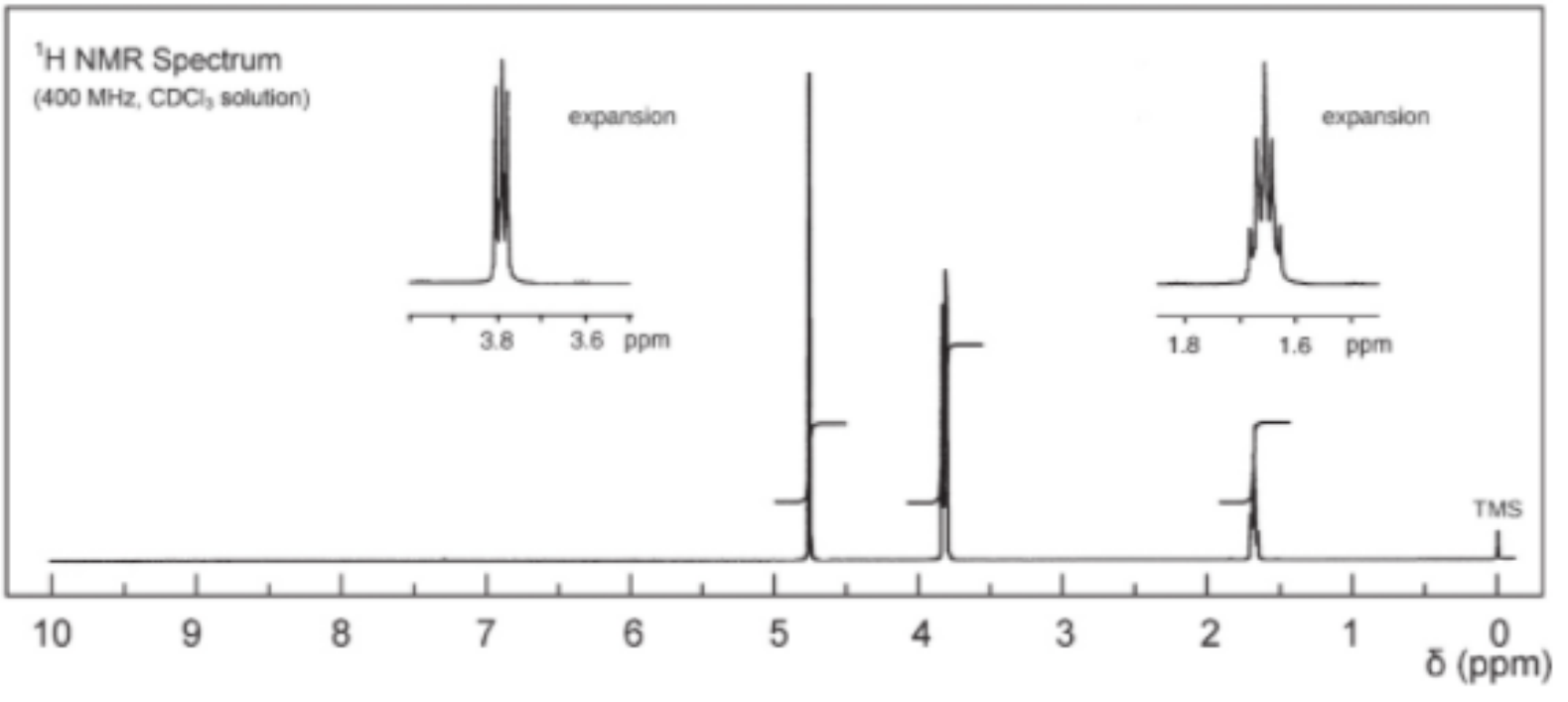
Problem 107



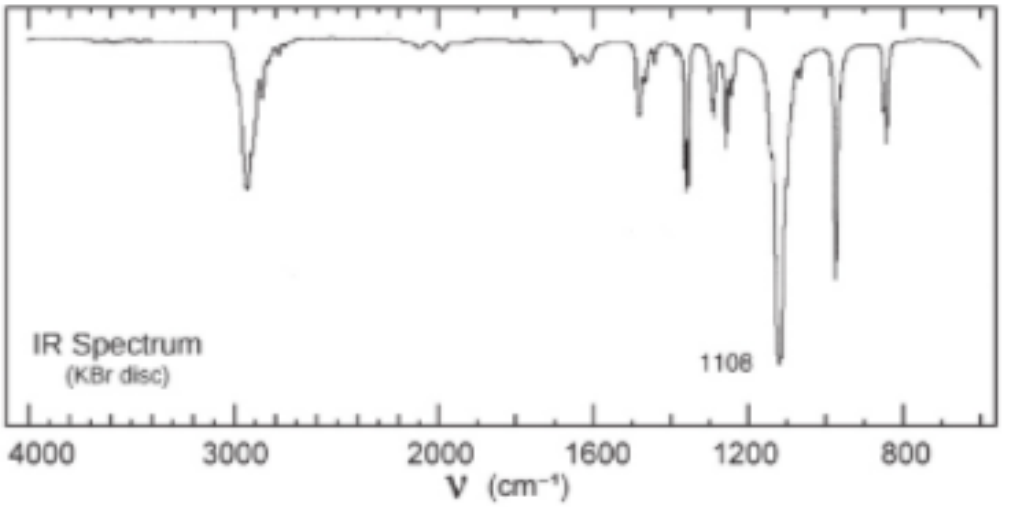


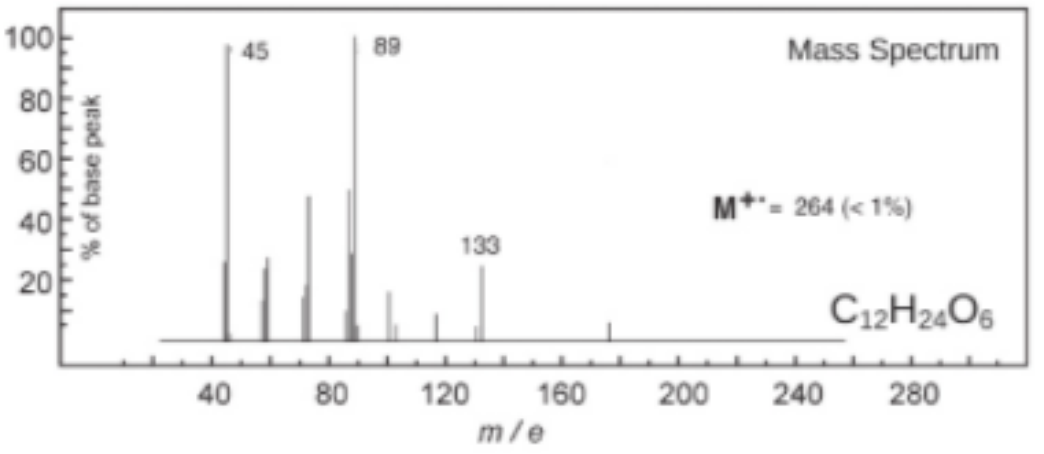
No significant UV absorption above 220 nm



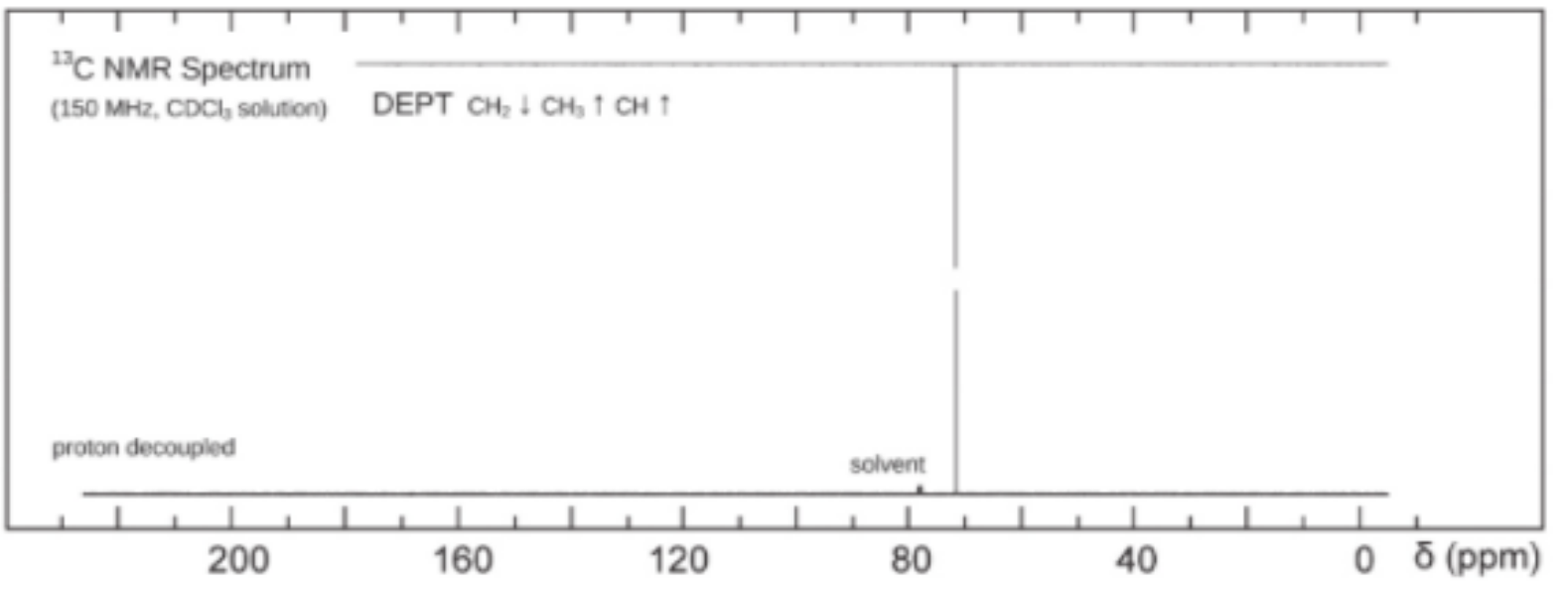


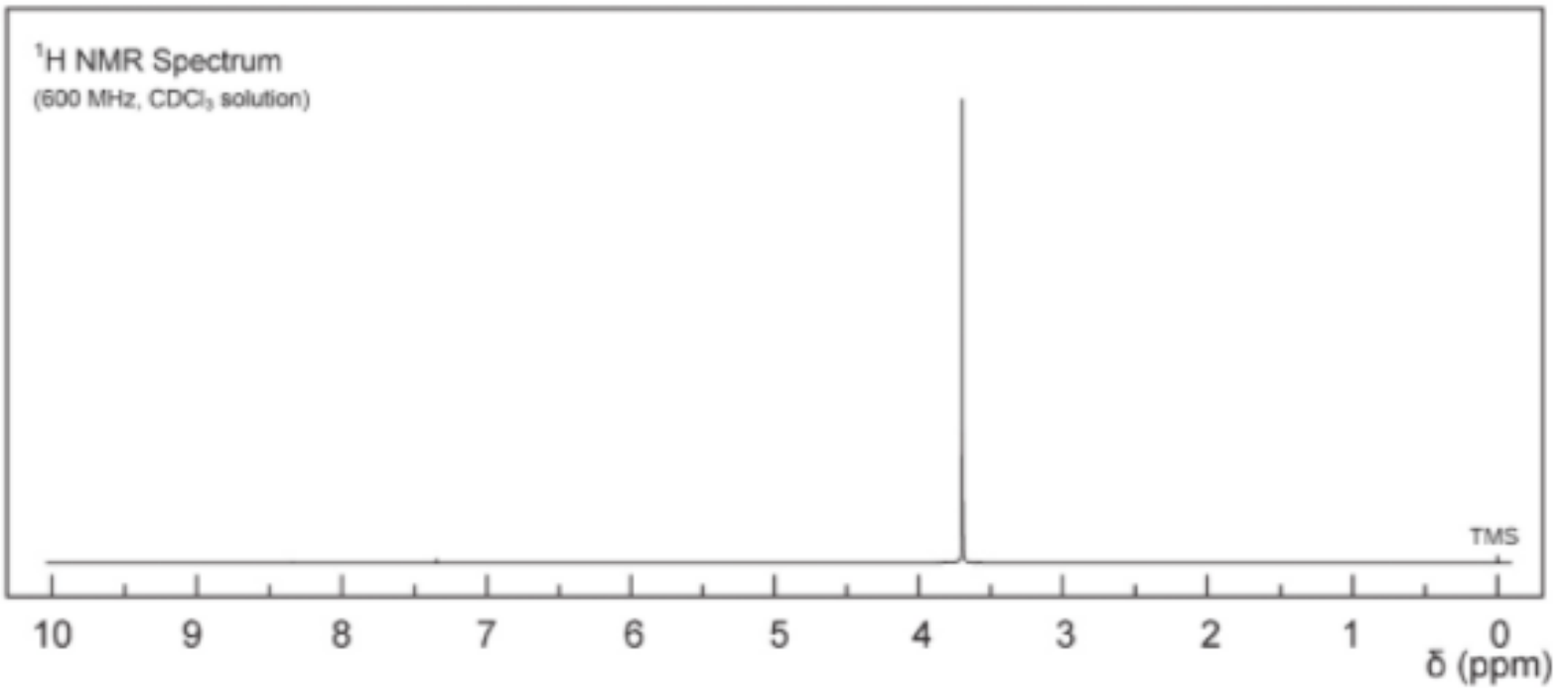
Problem 108



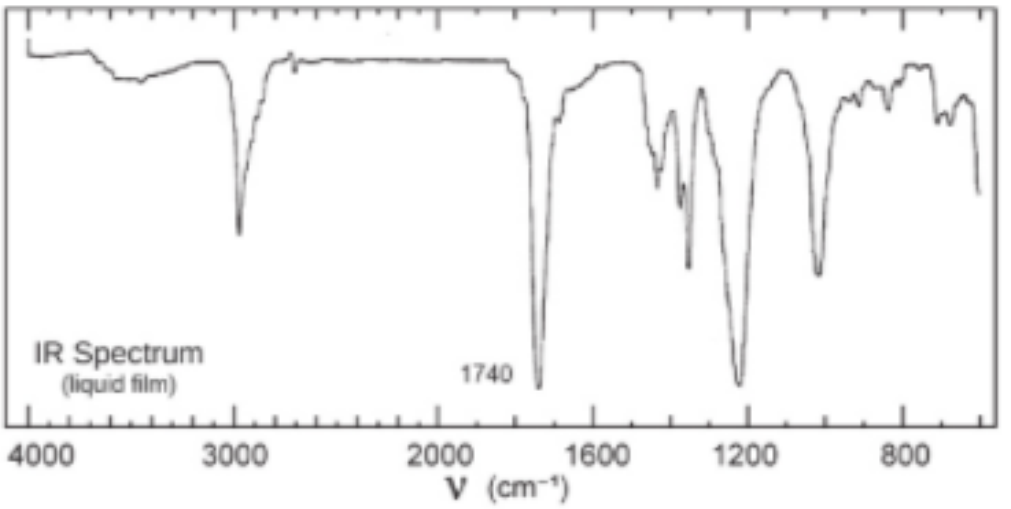


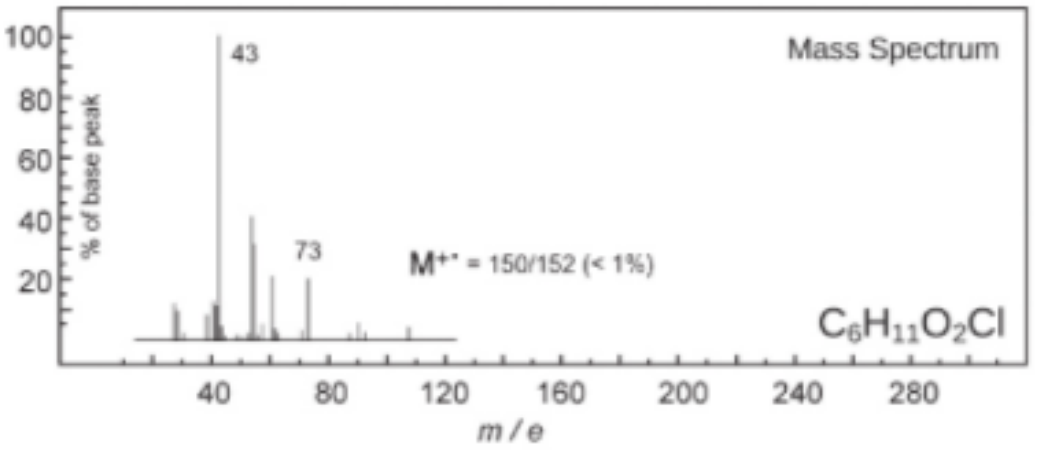
No significant UV absorption above 220 nm



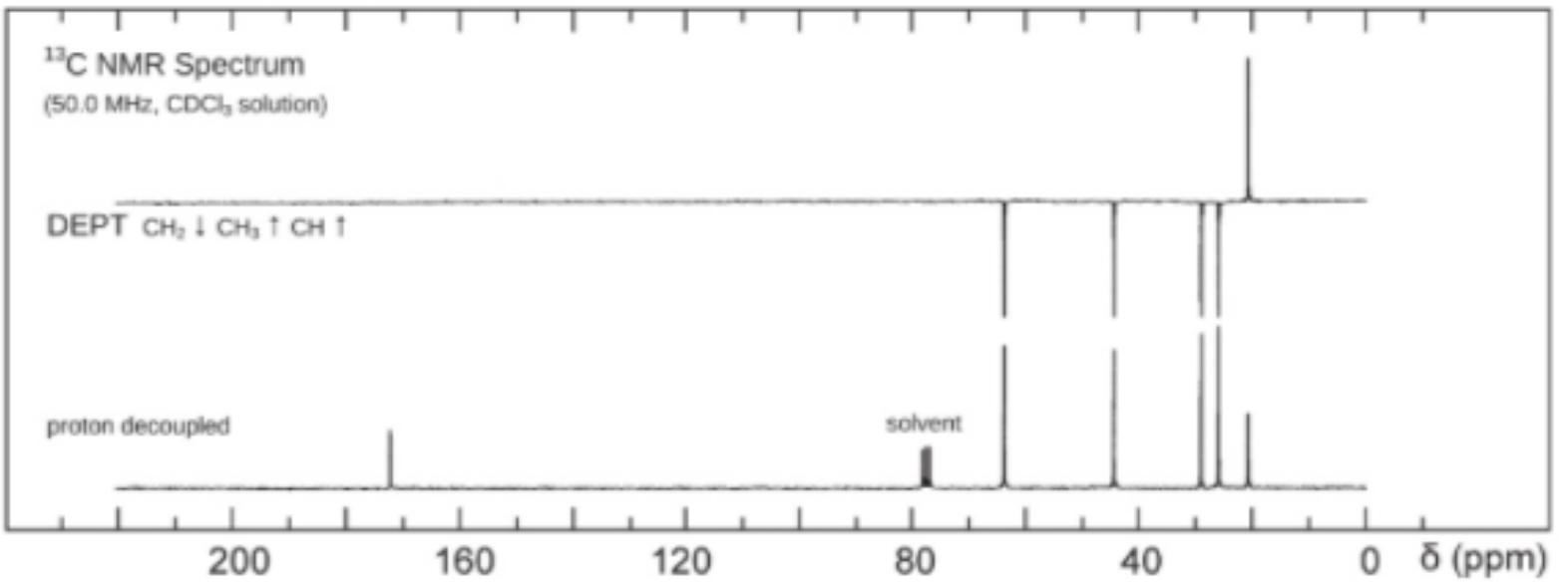


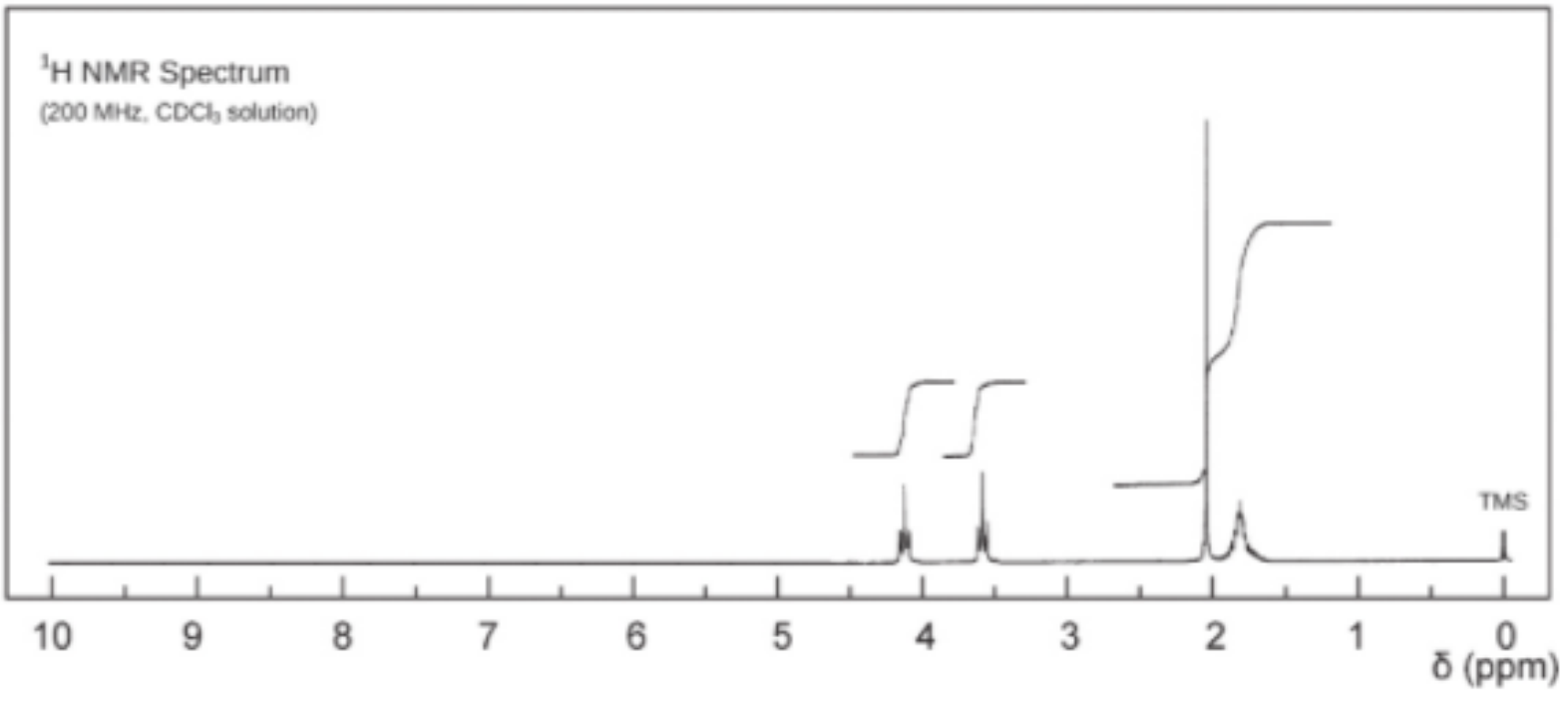
Problem 109



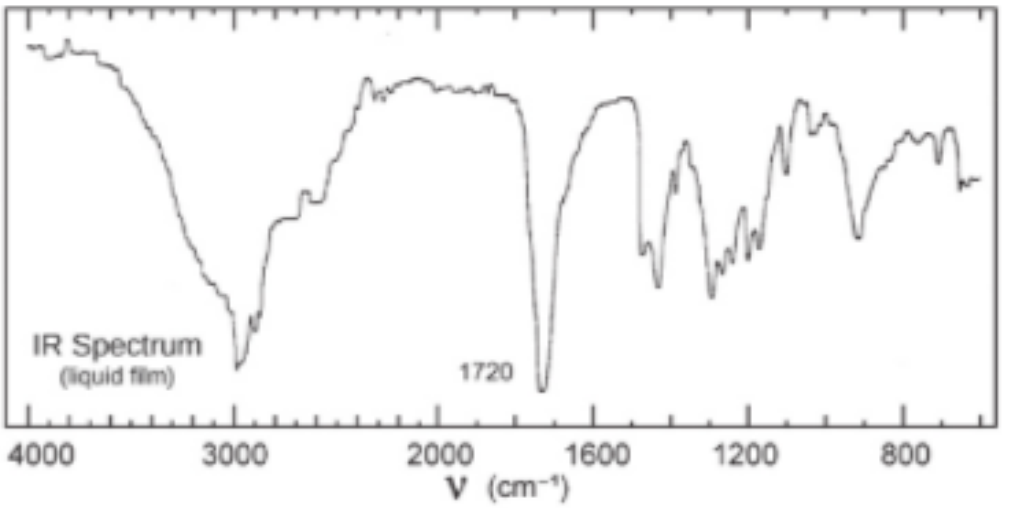


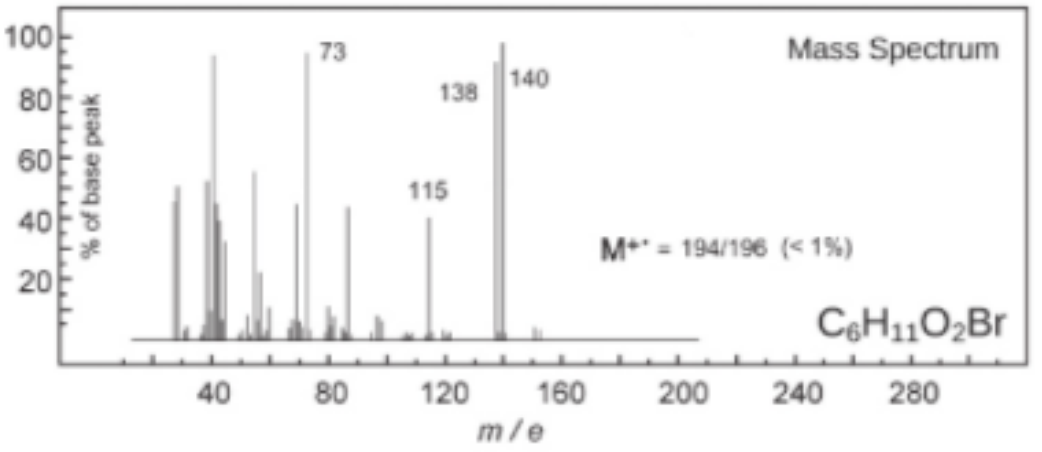
No significant UV absorption above 220 nm



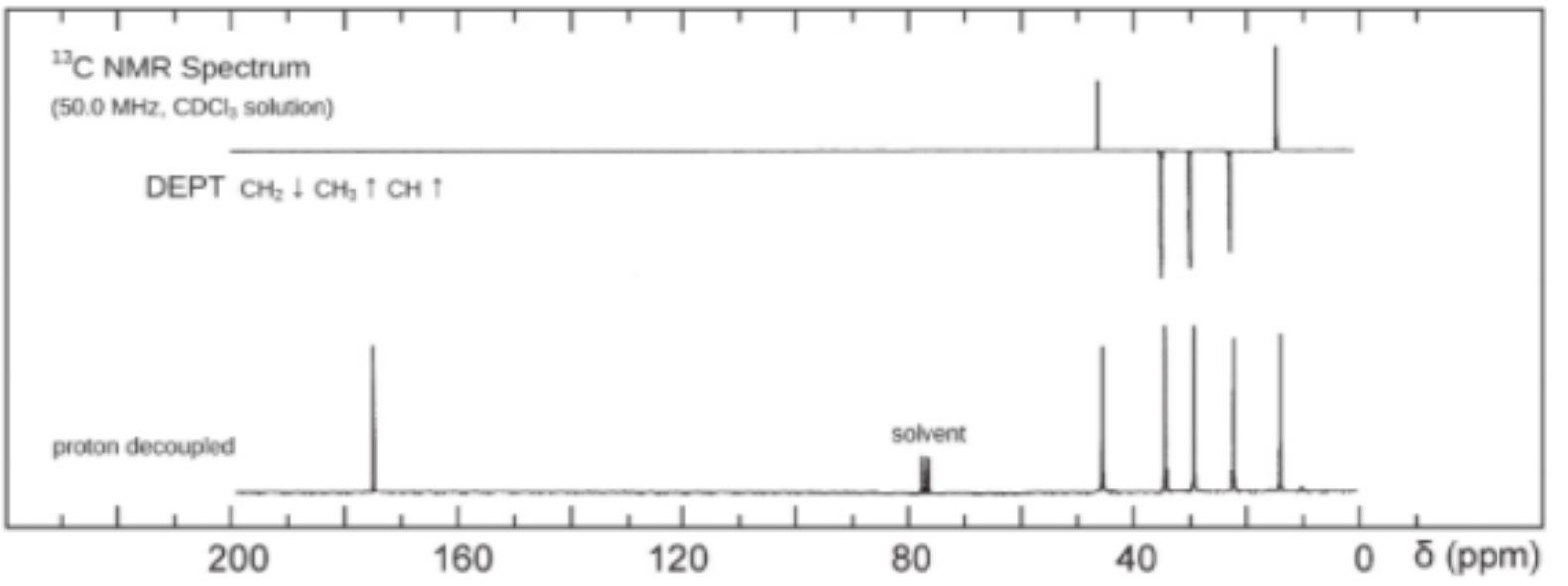


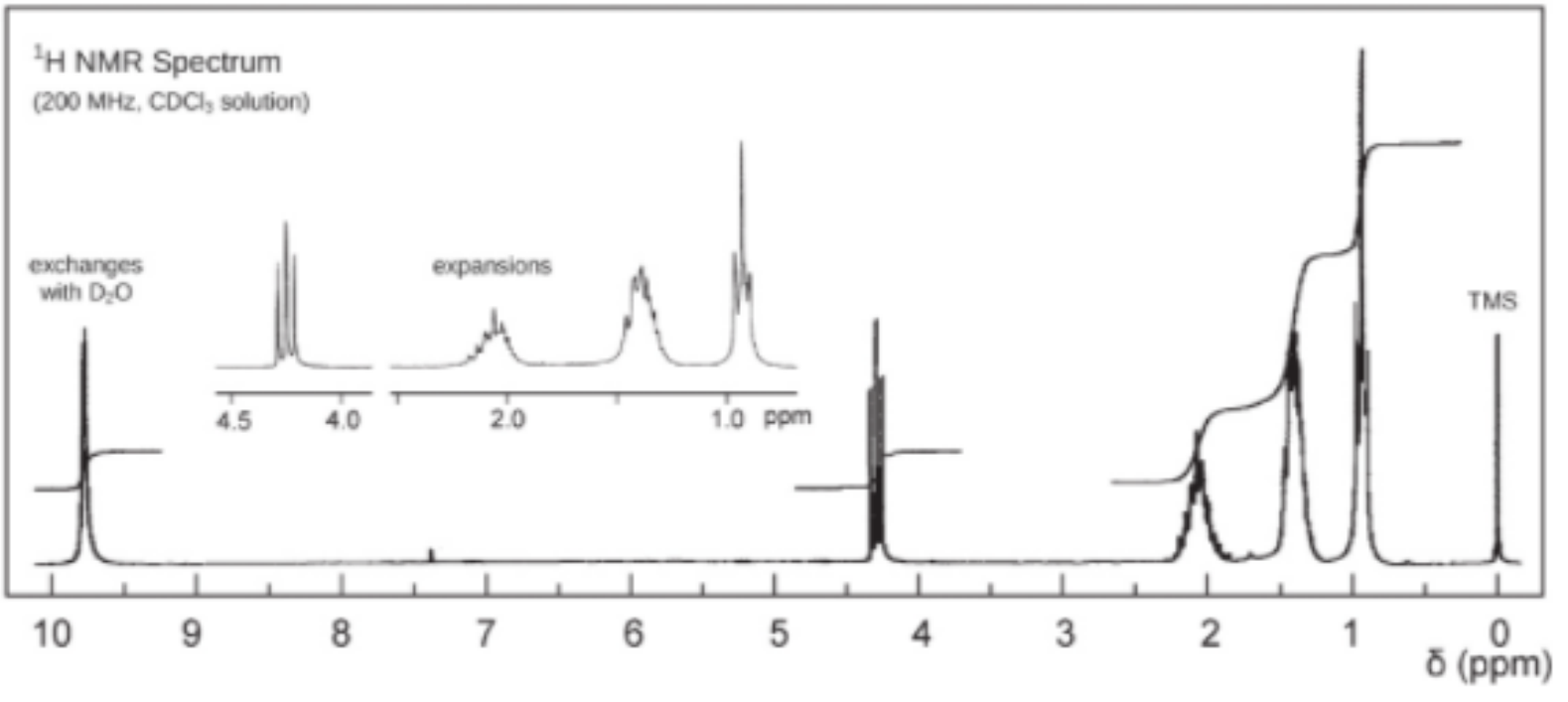
Problem 110



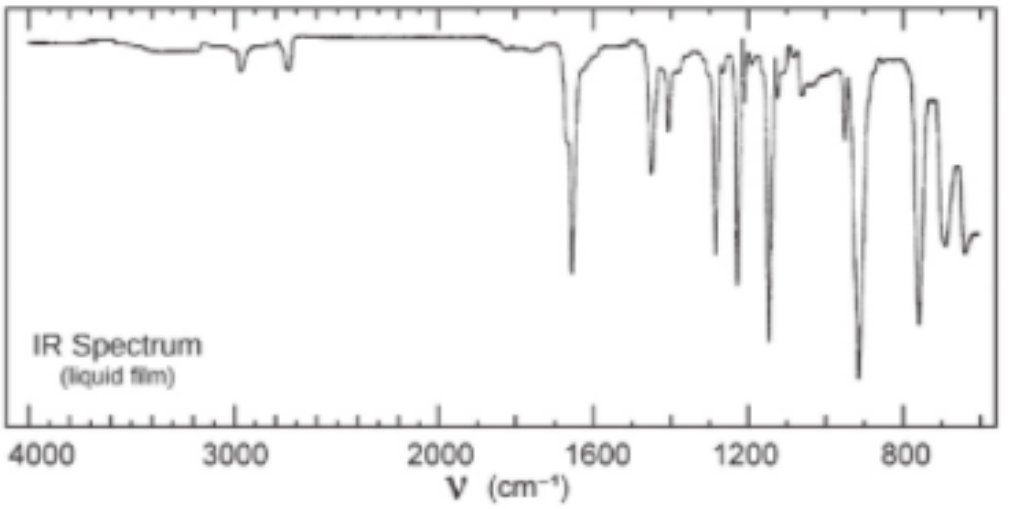


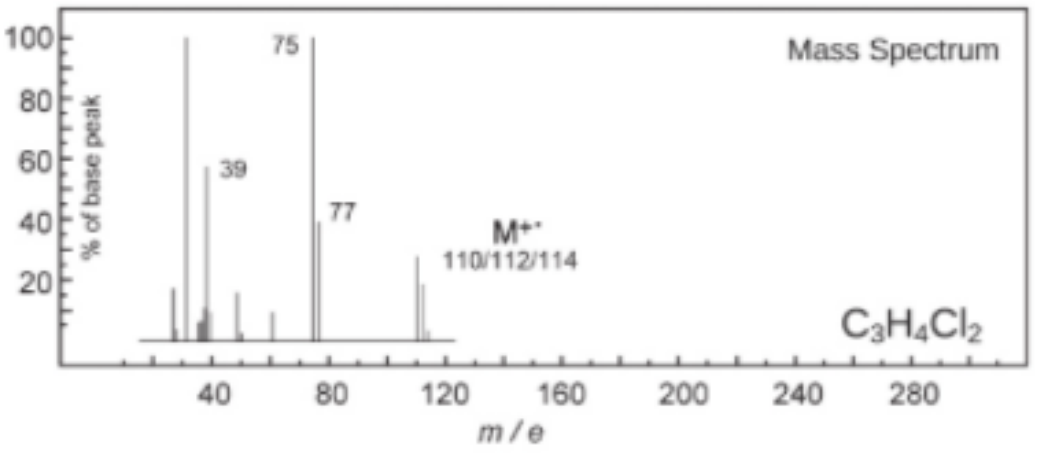
No significant UV absorption above 220 nm



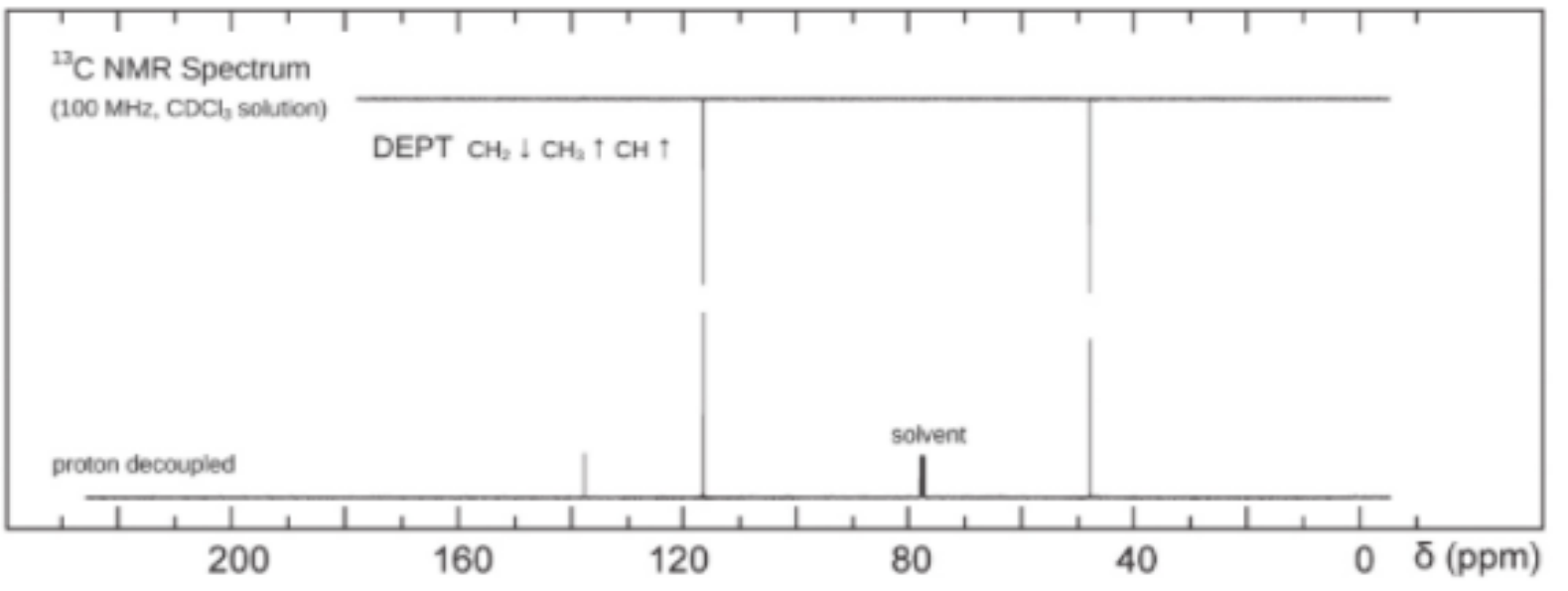


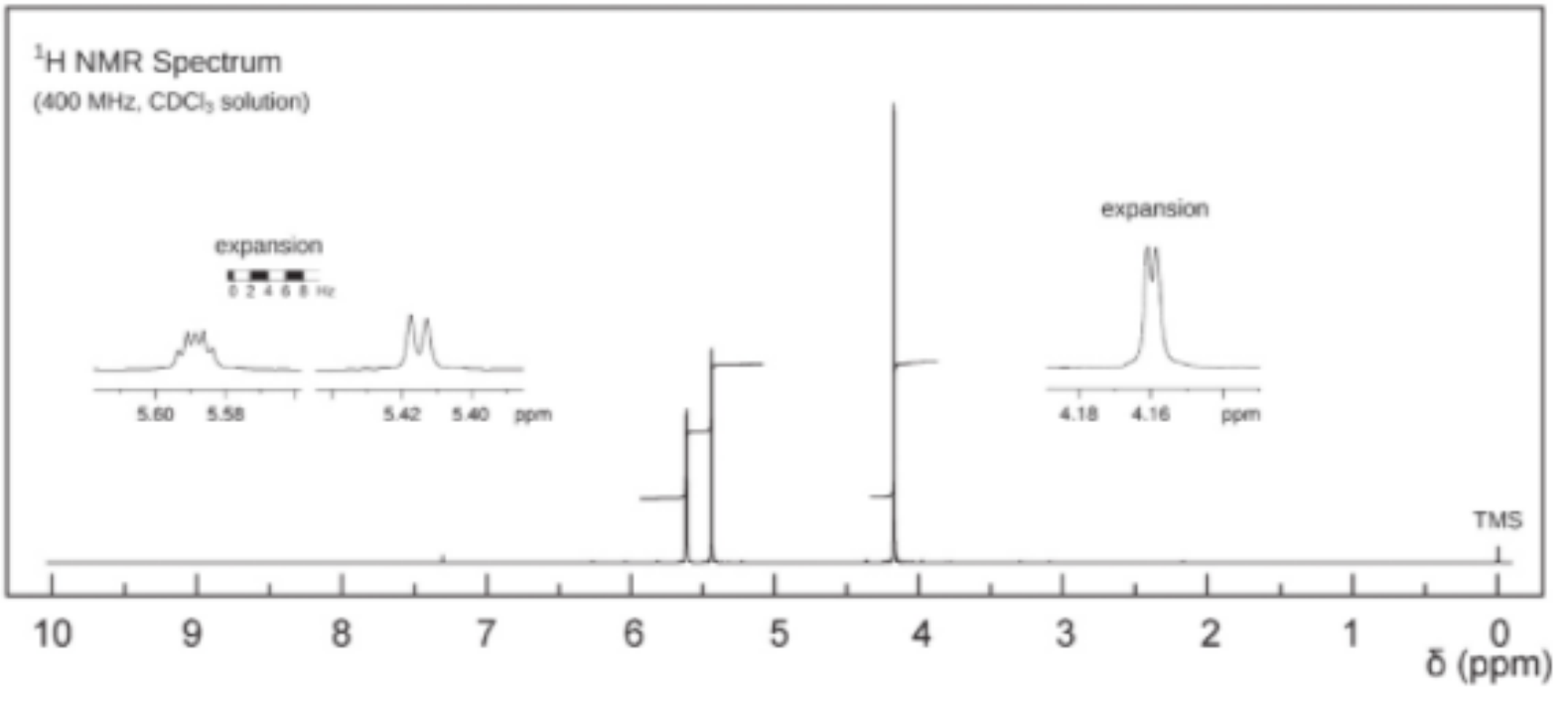
Problem 111

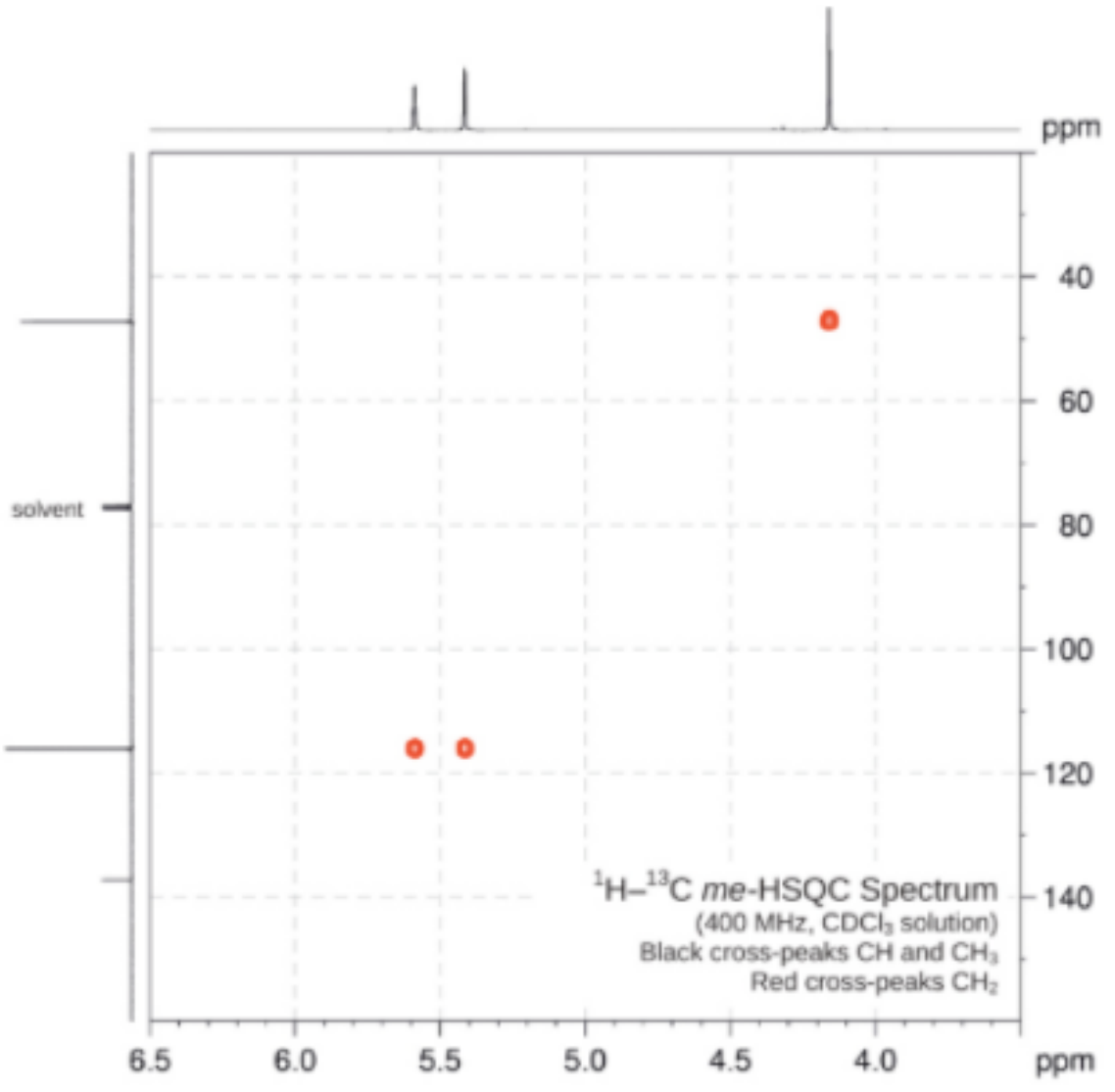


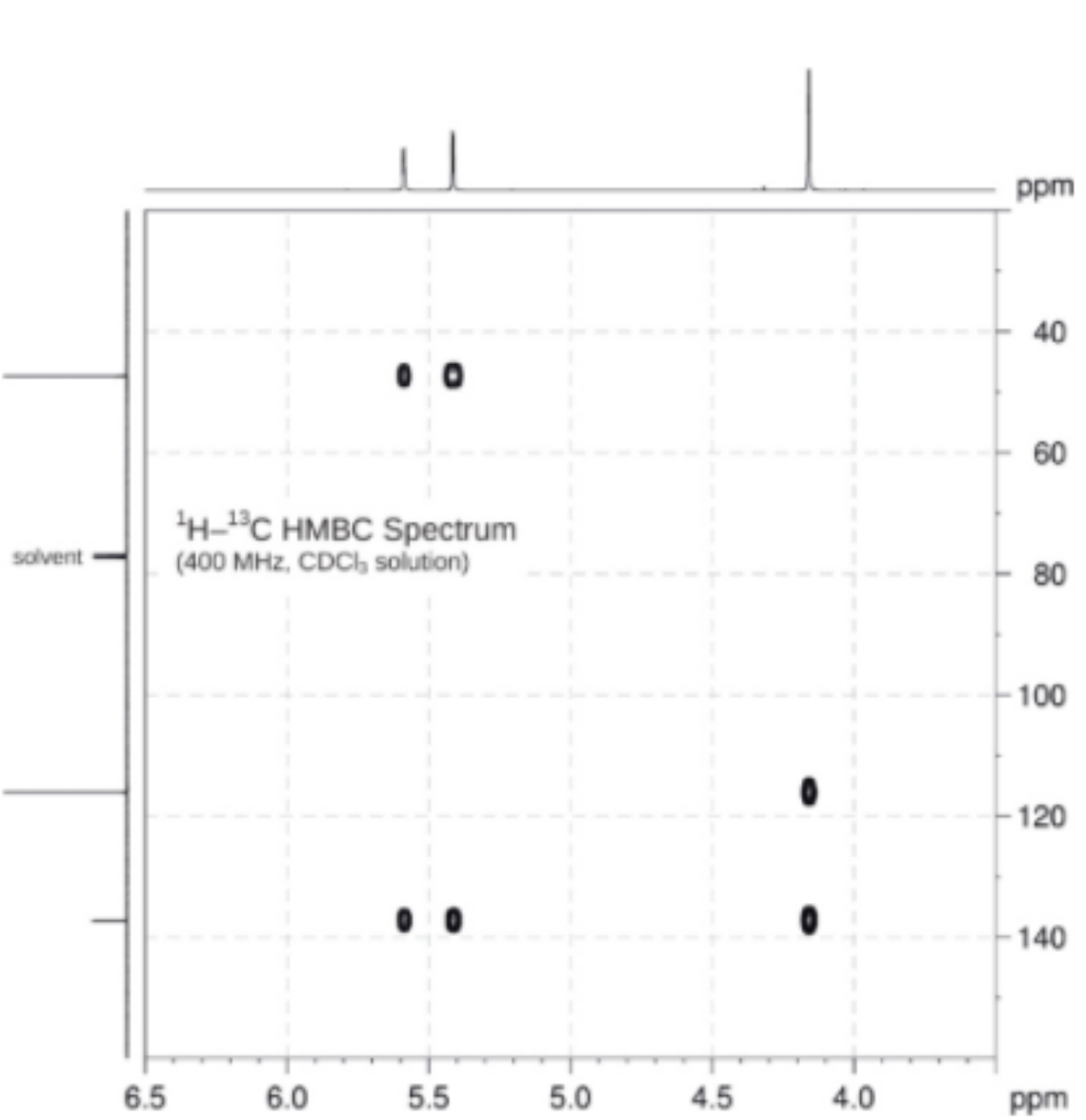


No significant UV absorption above 220 nm

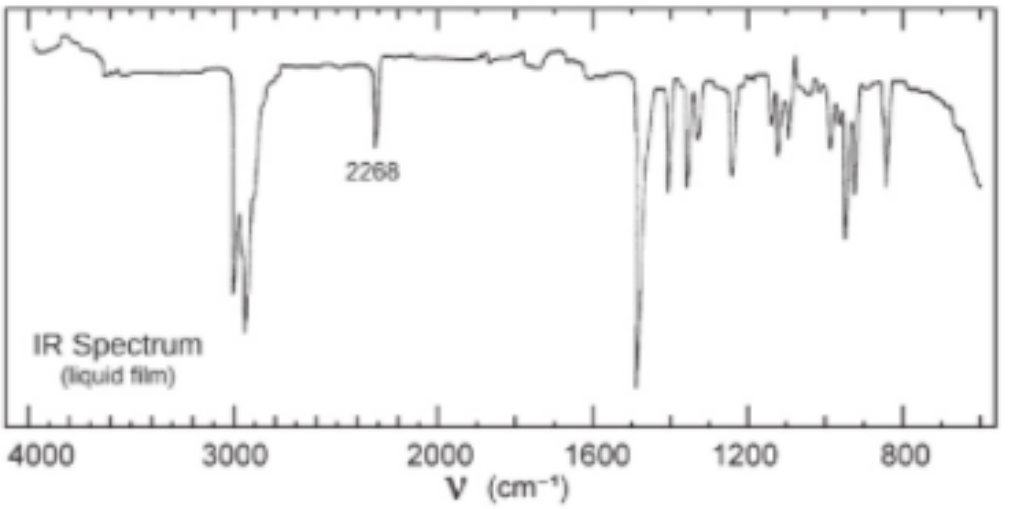


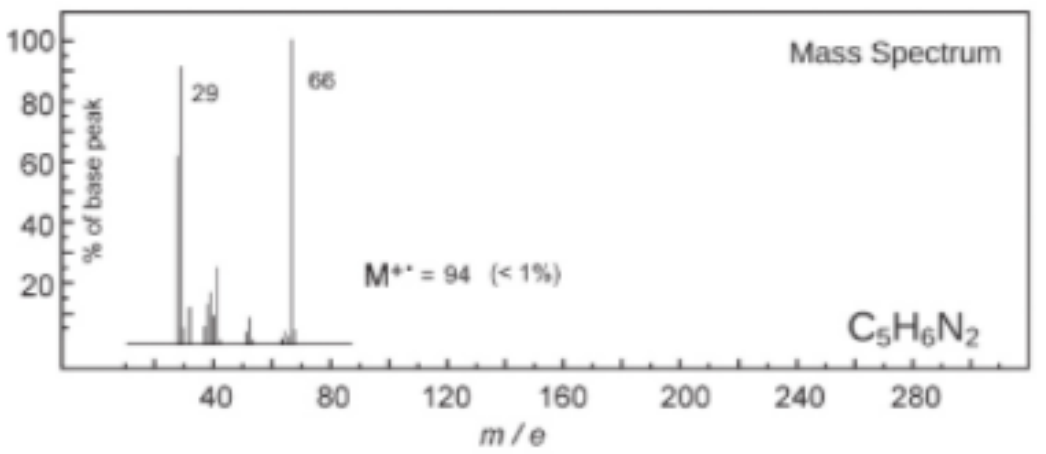



ppm
40
60
80
100
120
140
solvent
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
6.5
6.0
5.5
5.0
4.5
4.0
ppm

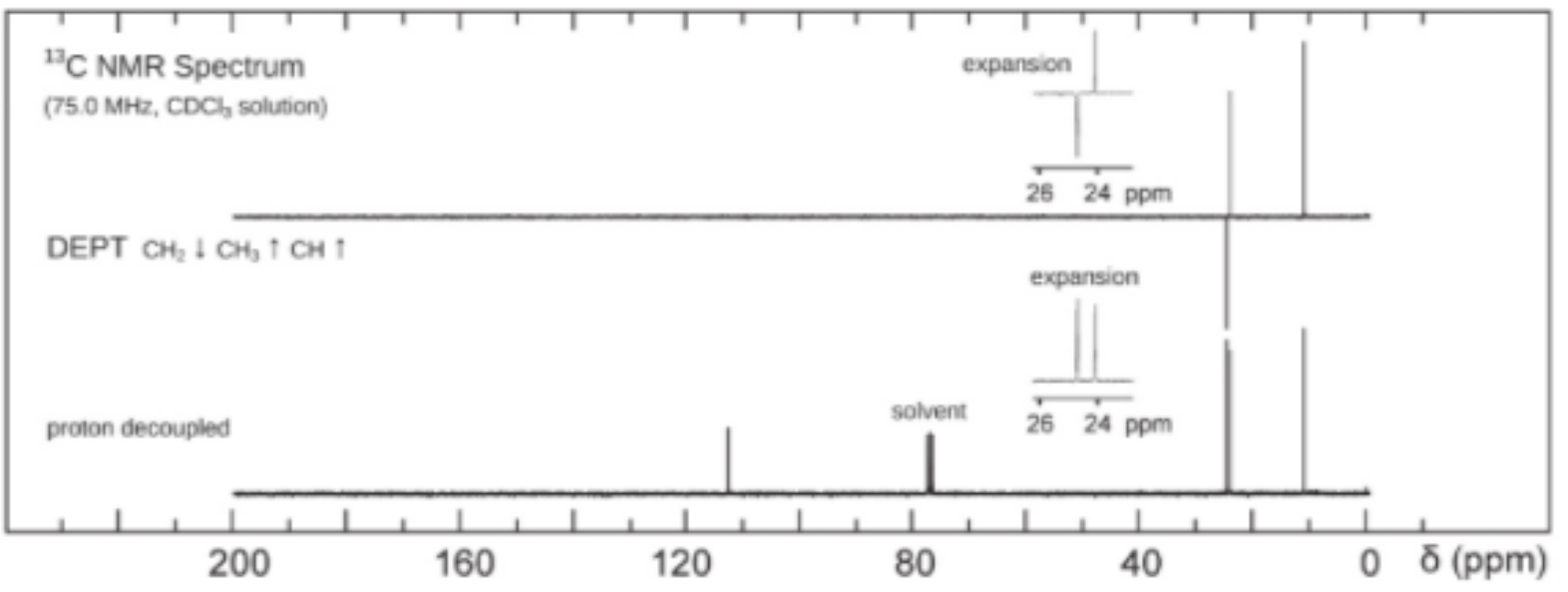

ppm
40
60
80
100
120
140
solvent
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
6.5
6.0
5.5
5.0
4.5
4.0
ppm

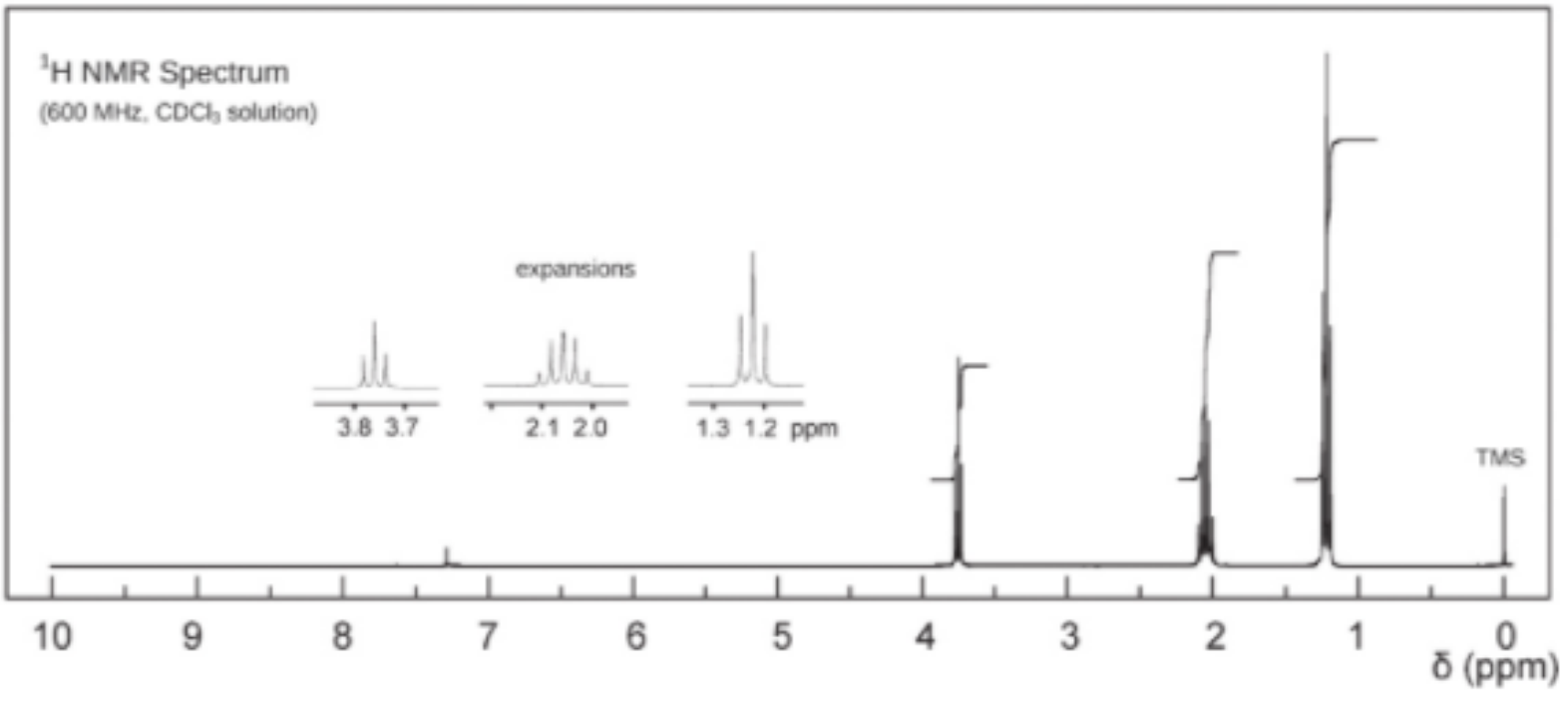
Problem 112



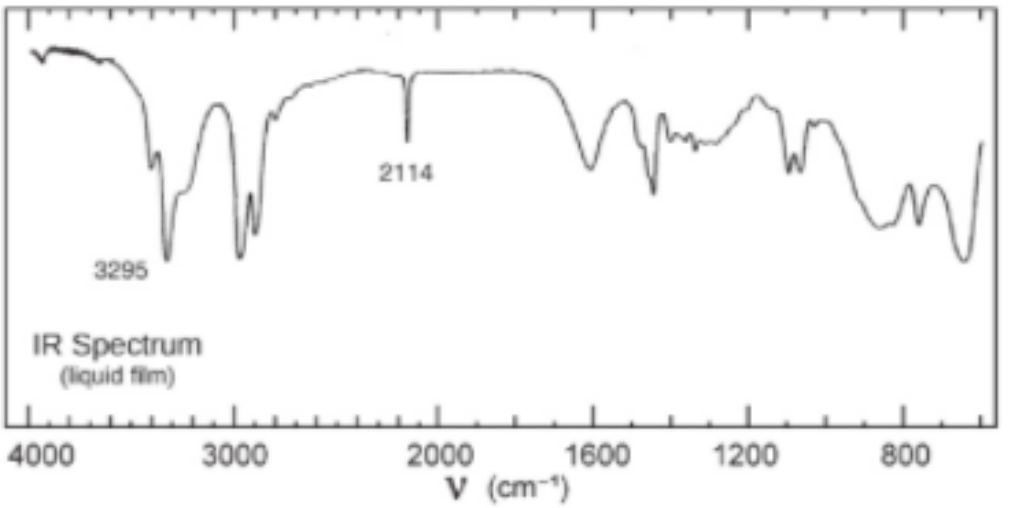


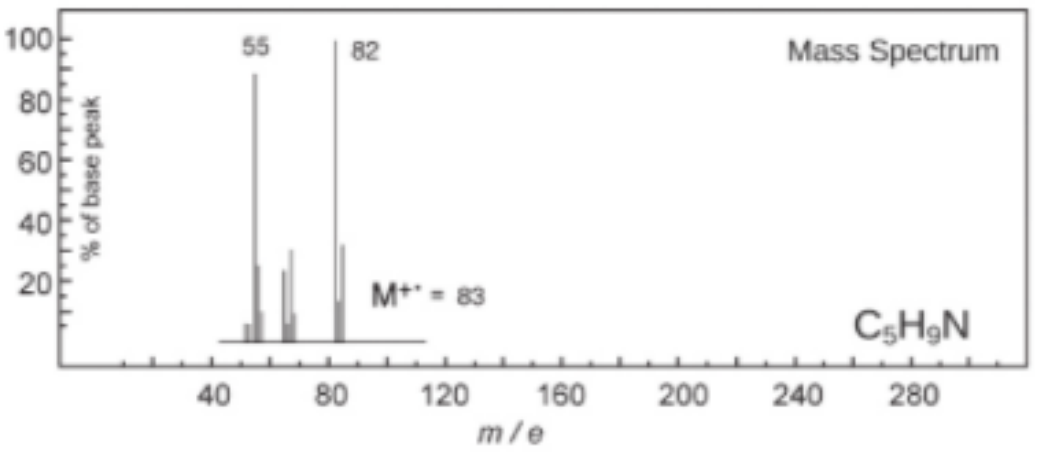
No significant UV absorption above 220 nm



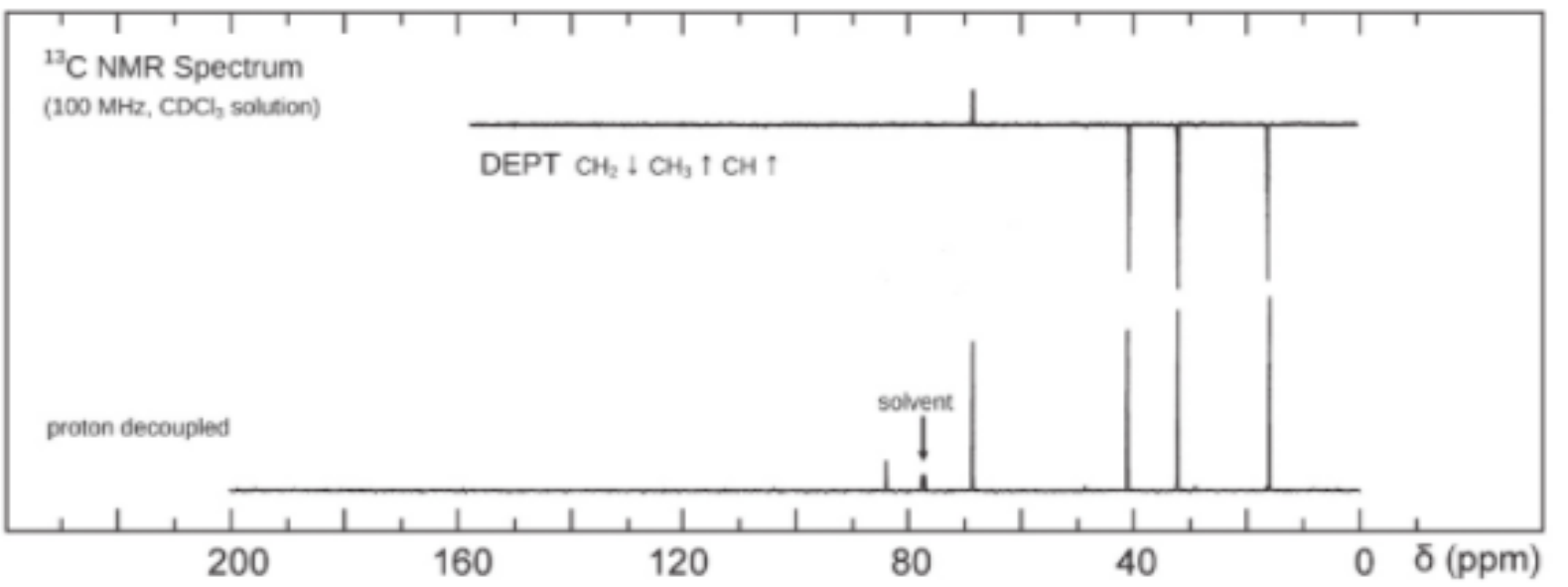


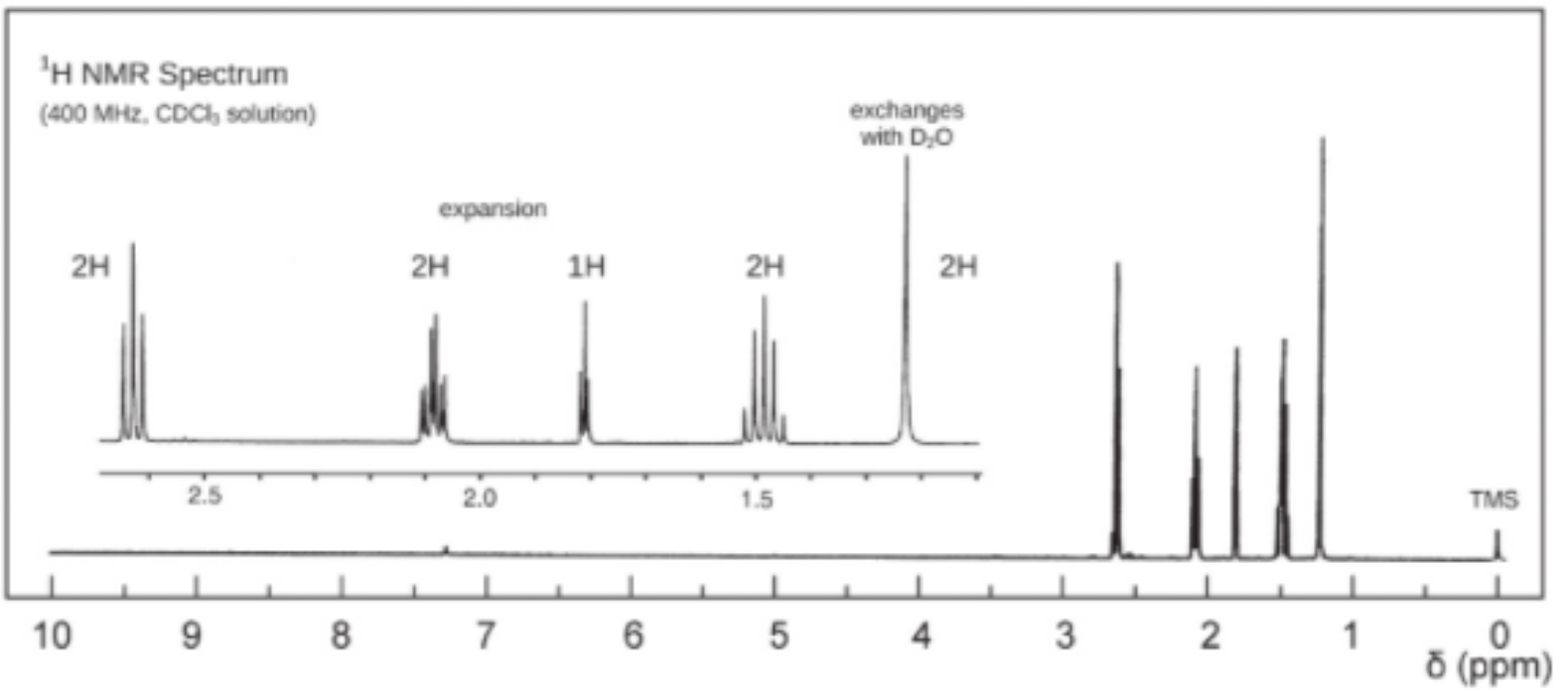
Problem 113



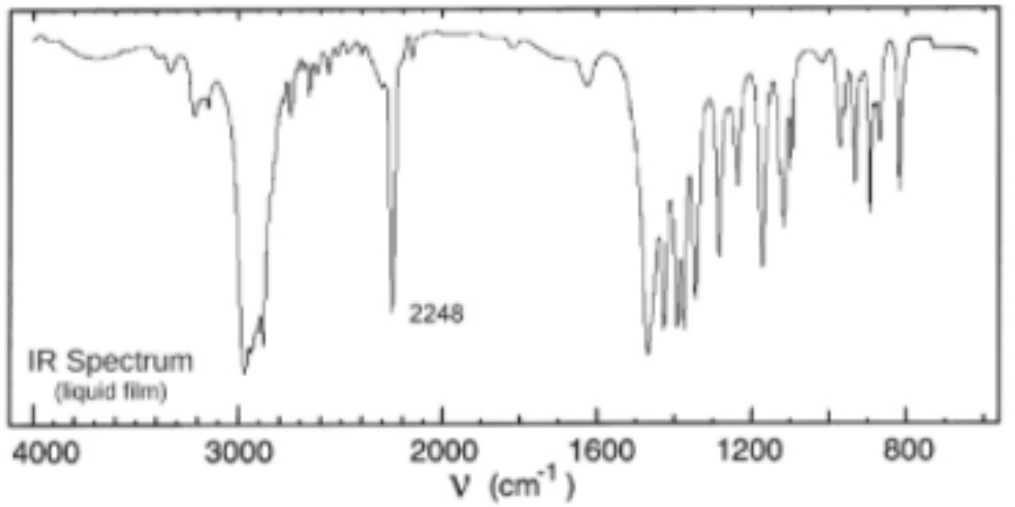


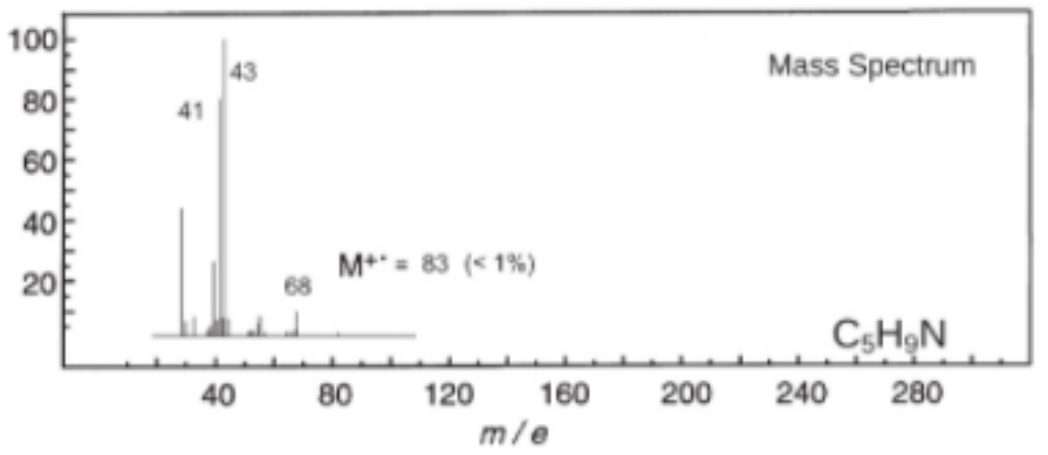
No significant UV absorption above 220 nm



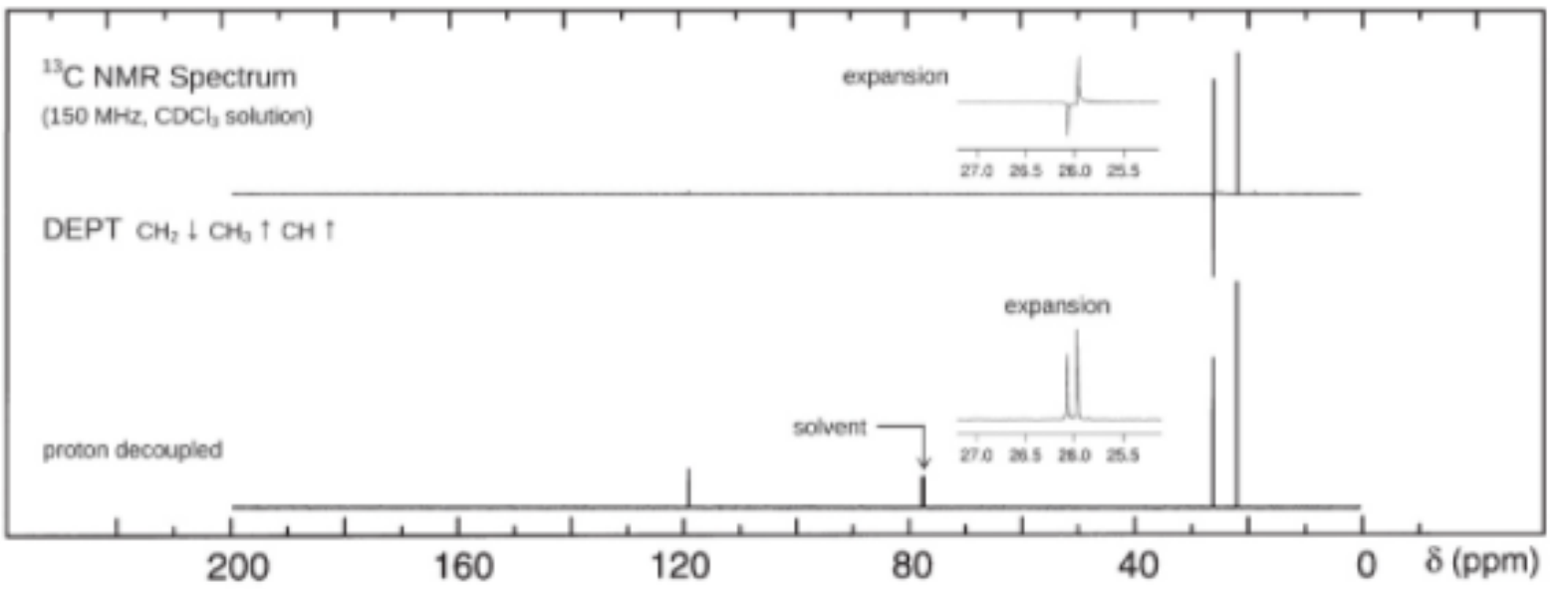


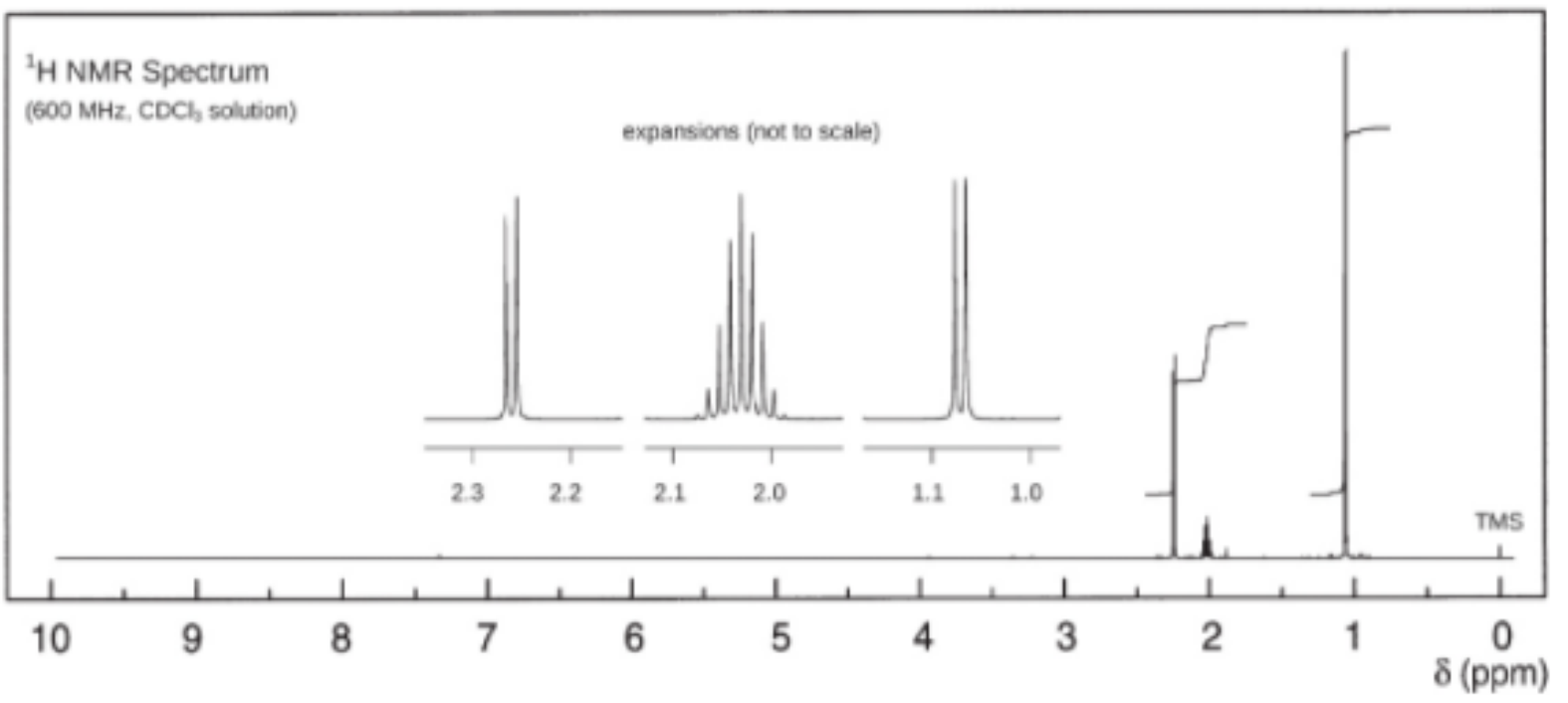
Problem 114

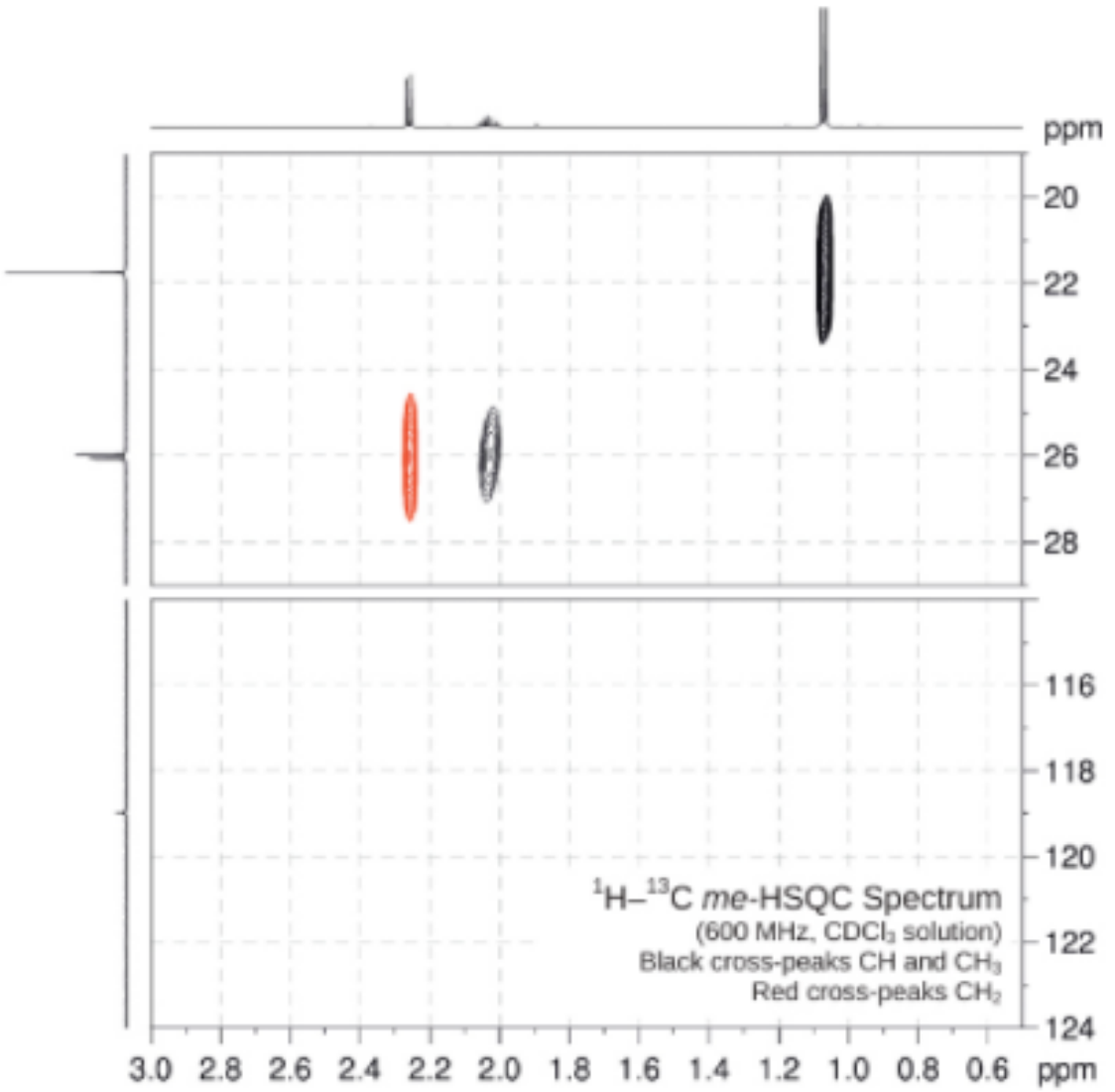




No significant UV absorption above 220 nm

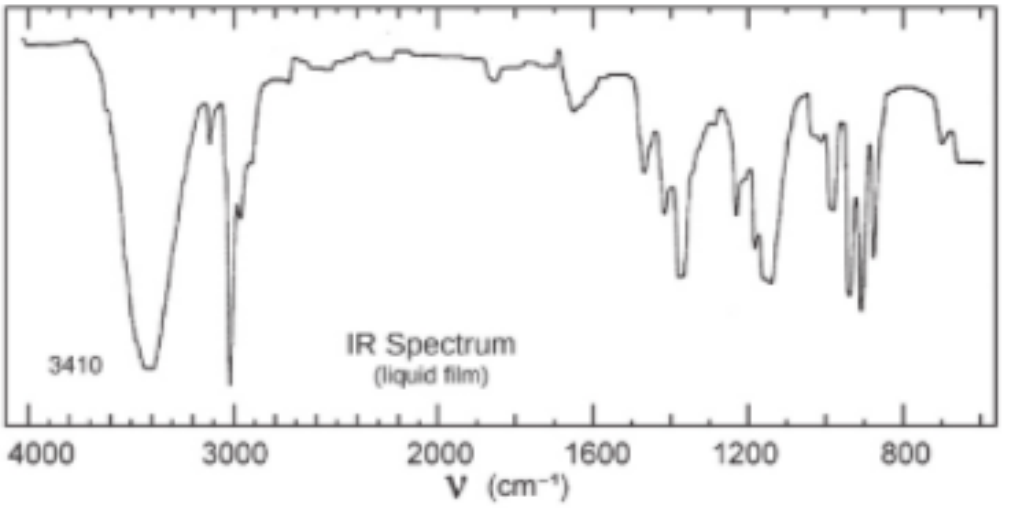


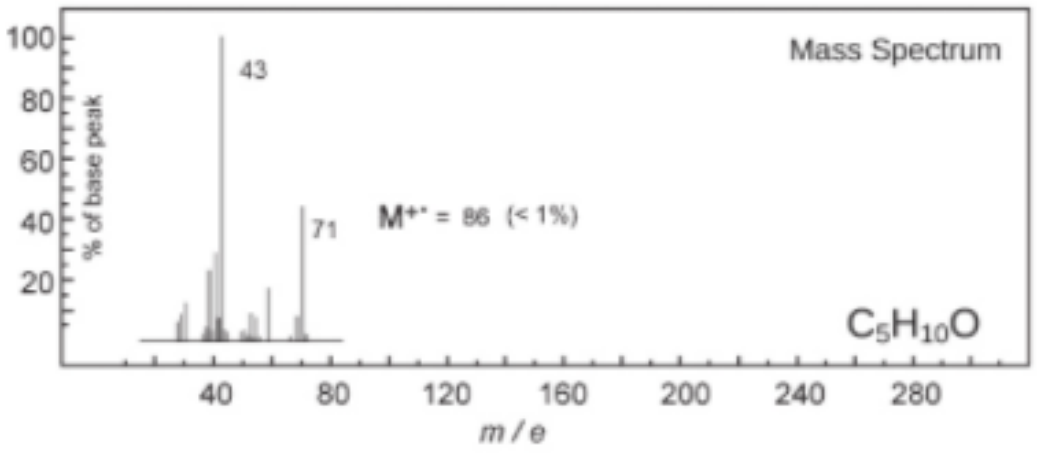



ppm
20
22
24
26
28
116
118
120
122
124
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

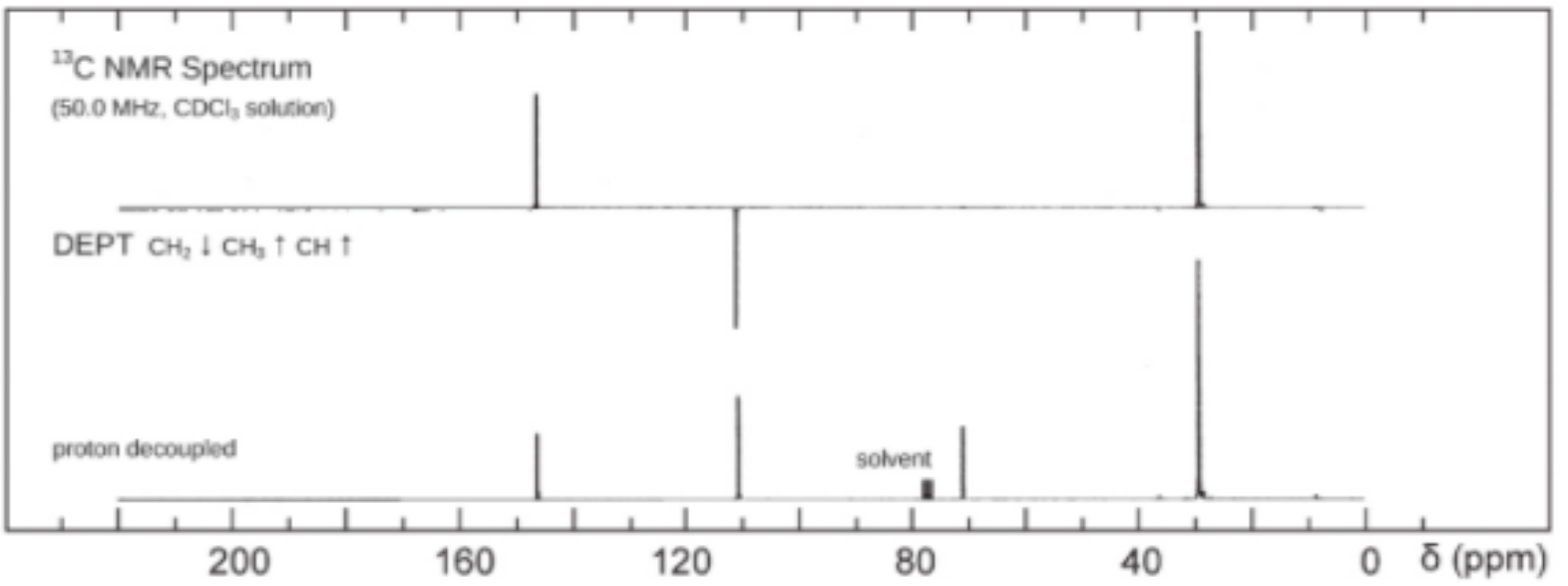
ppm
20
22
24
26
28
116
118
120
122
124
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 ppm
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)

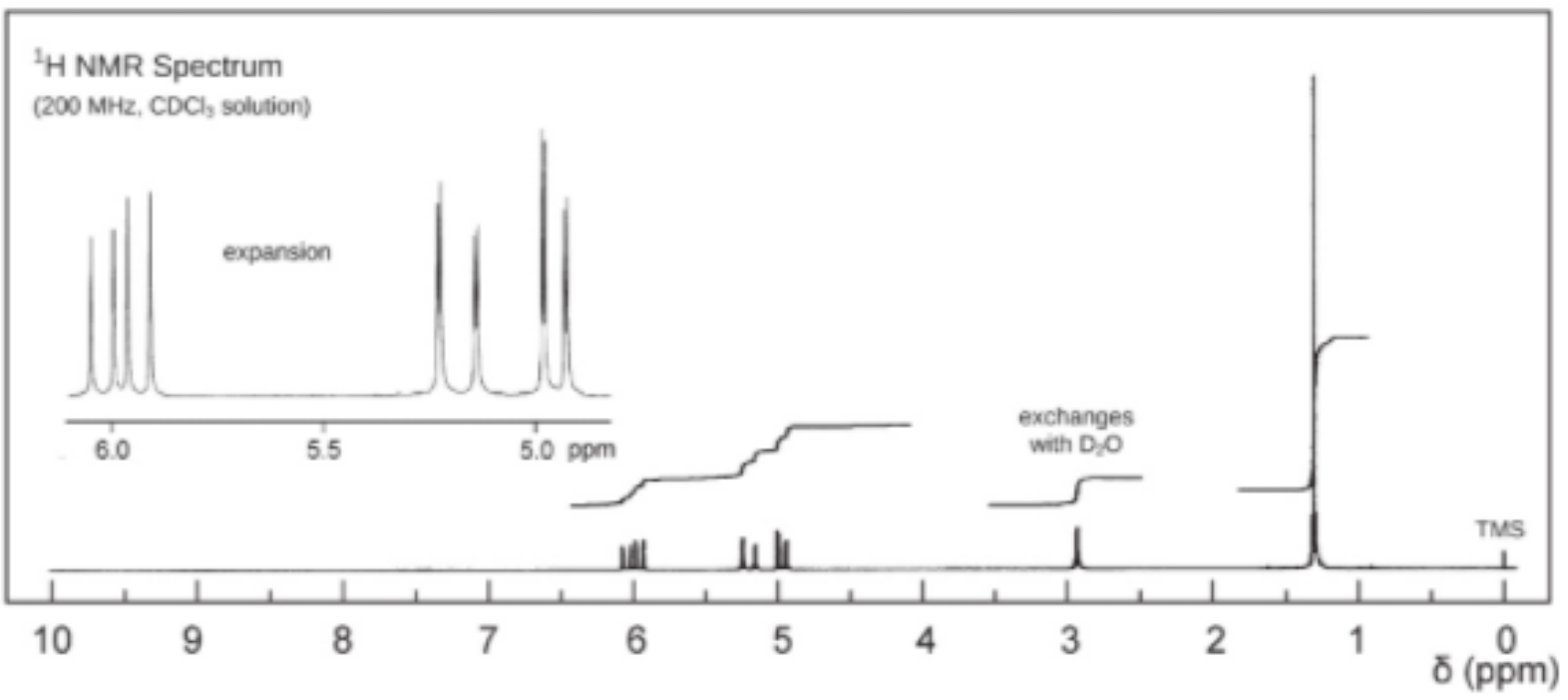
Problem 115



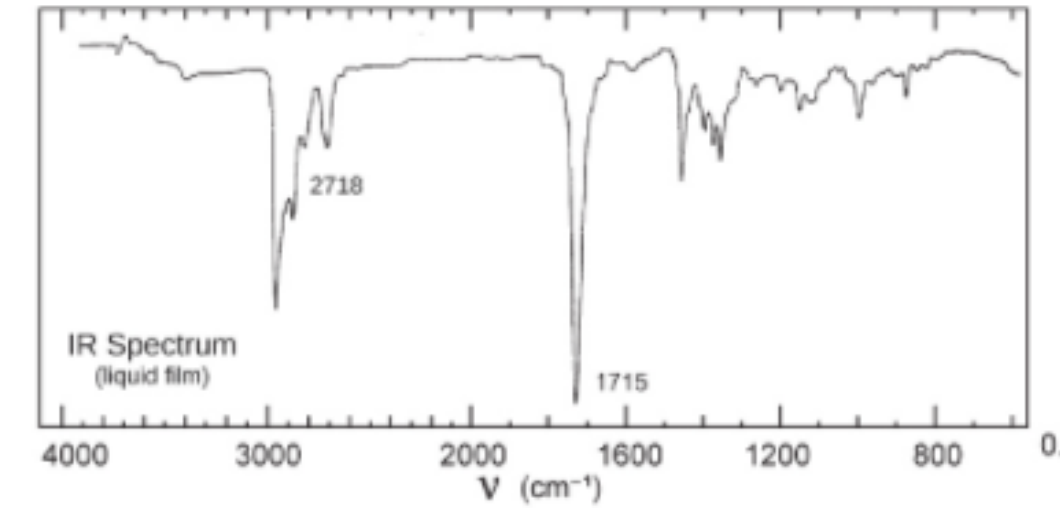


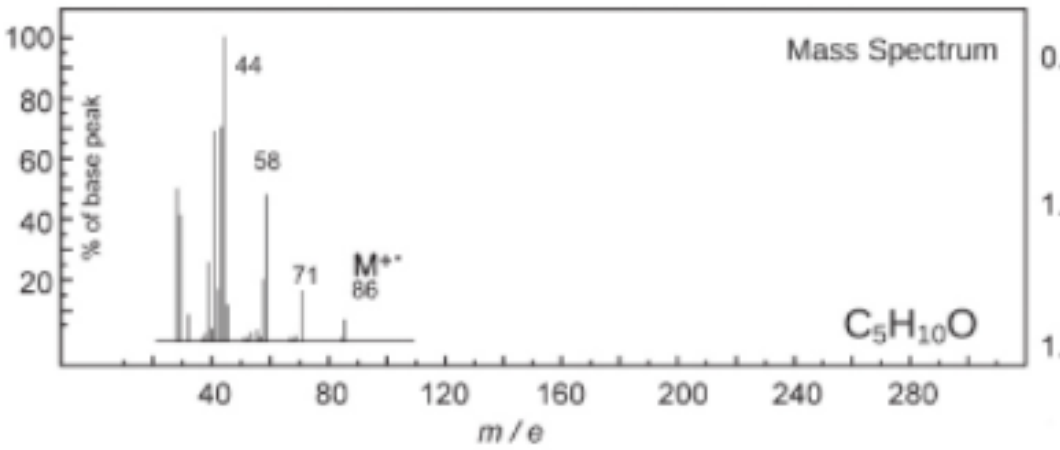
No significant UV absorption above 220 nm

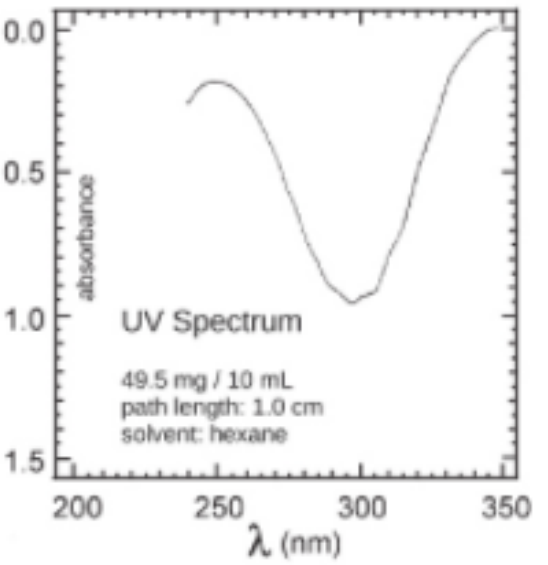


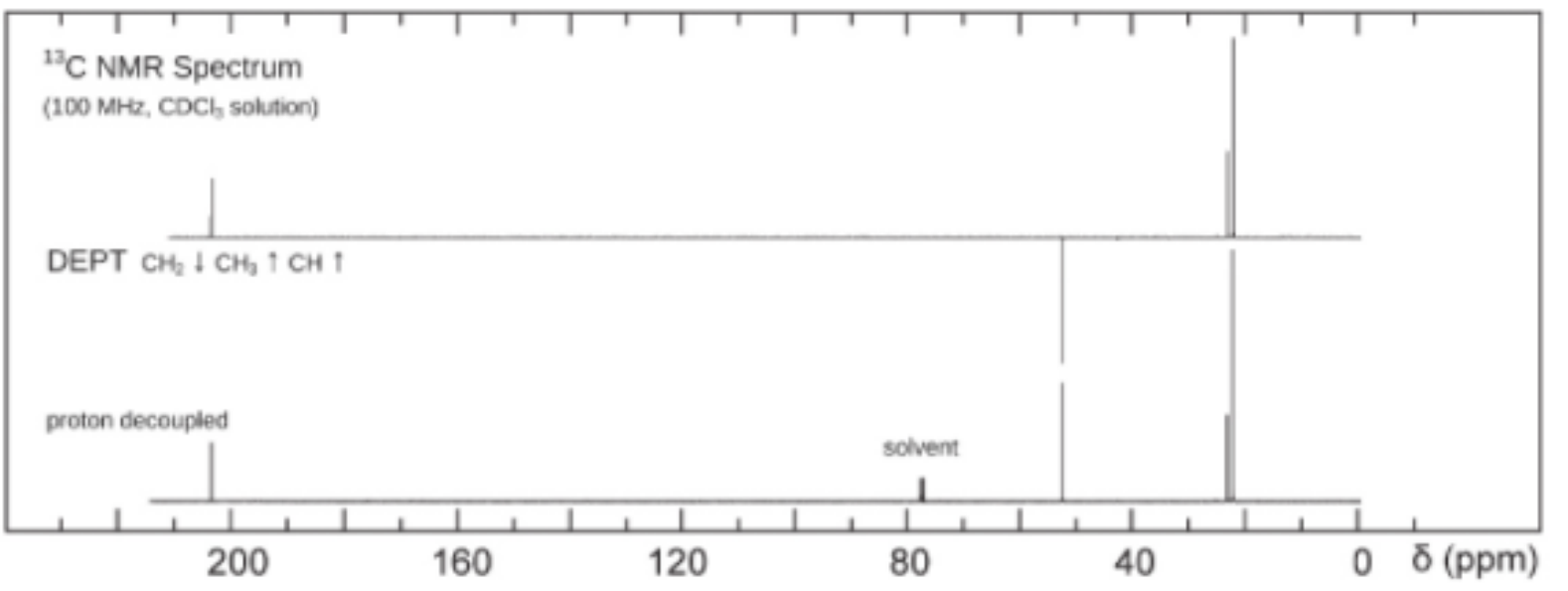


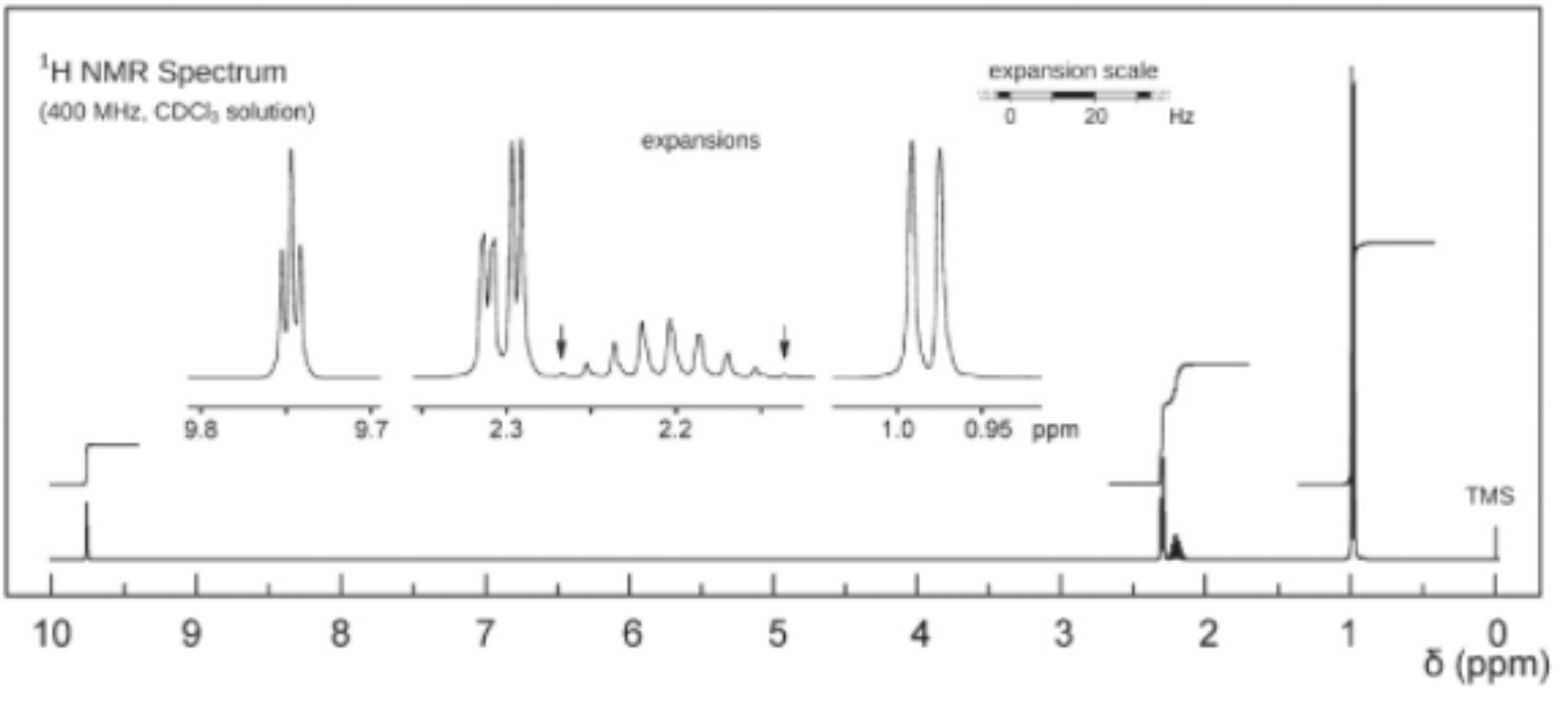
Problem 116


IR Spectrum
(liquid film)
2718
1715
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

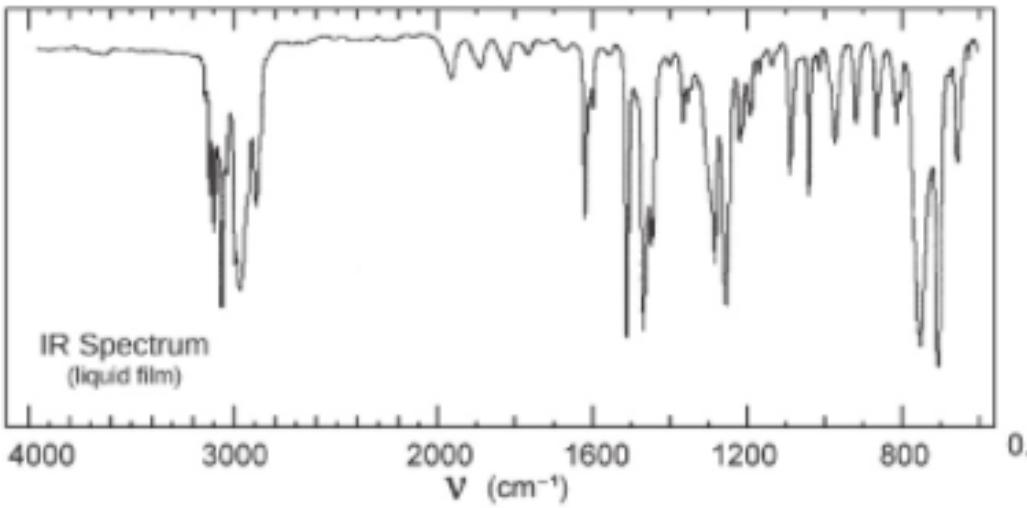

Mass Spectrum
% of base peak
100
80
60
40
20
44
58
71
M+·
86
C5H10O
40
80
120
160
200
240
280
m / e

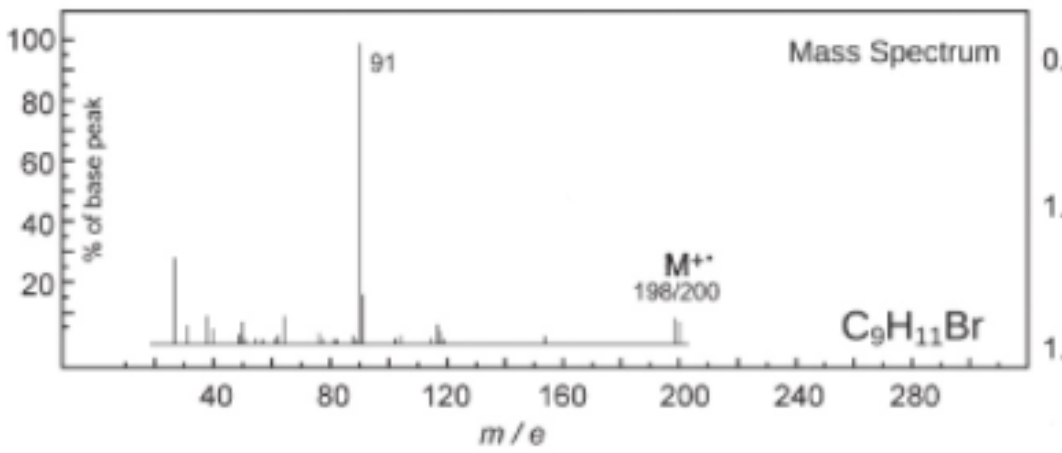

absorbance
0.0
0.5
1.0
1.5
UV Spectrum
49.5 mg / 10 mL
path length: 1.0 cm
solvent: hexane
200
250
300
350
λ (nm)

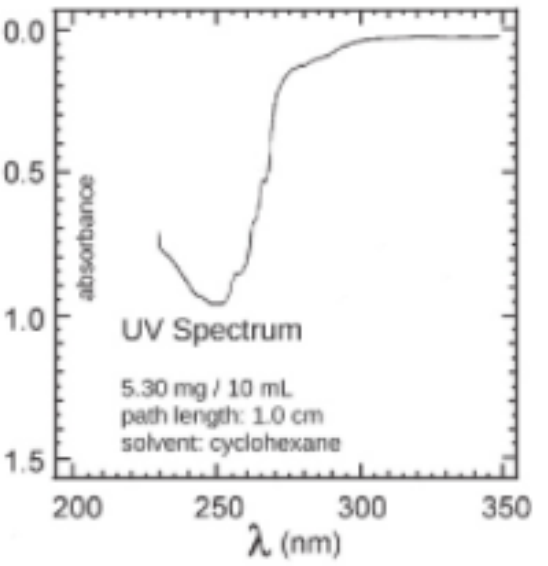

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

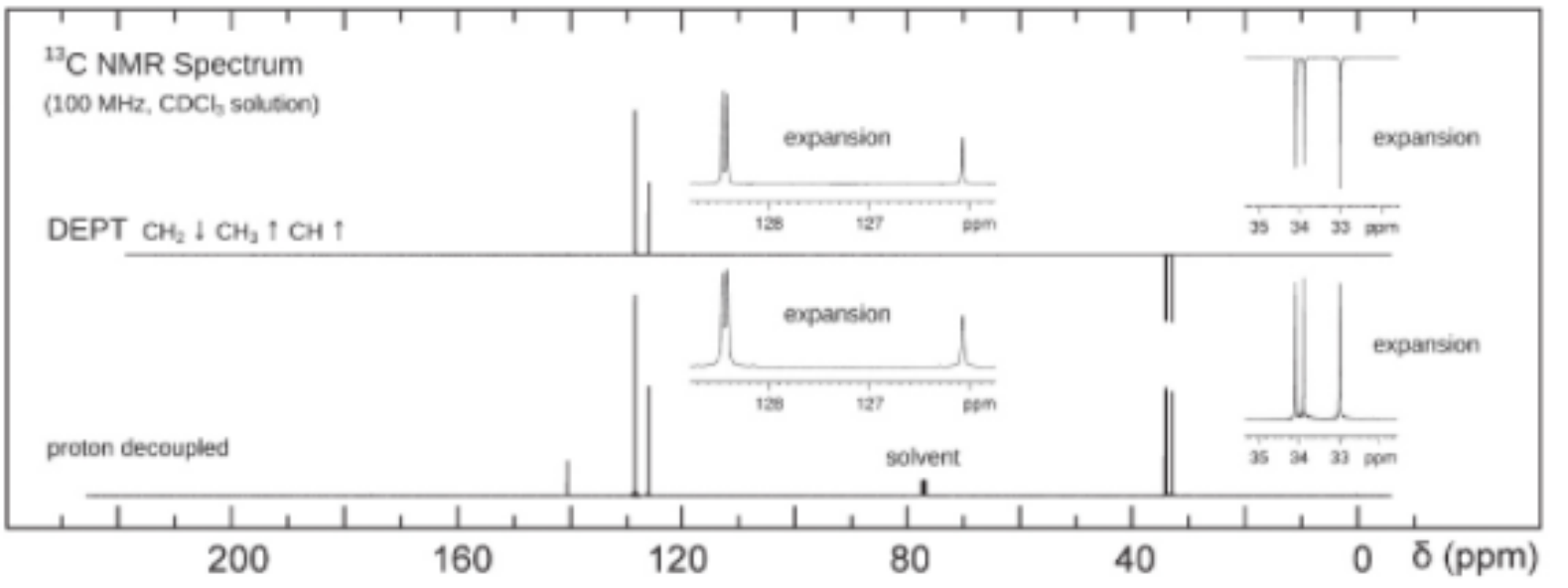

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion scale
0
20
Hz
expansions
9.8
9.7
2.3
2.2
1.0
0.95
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

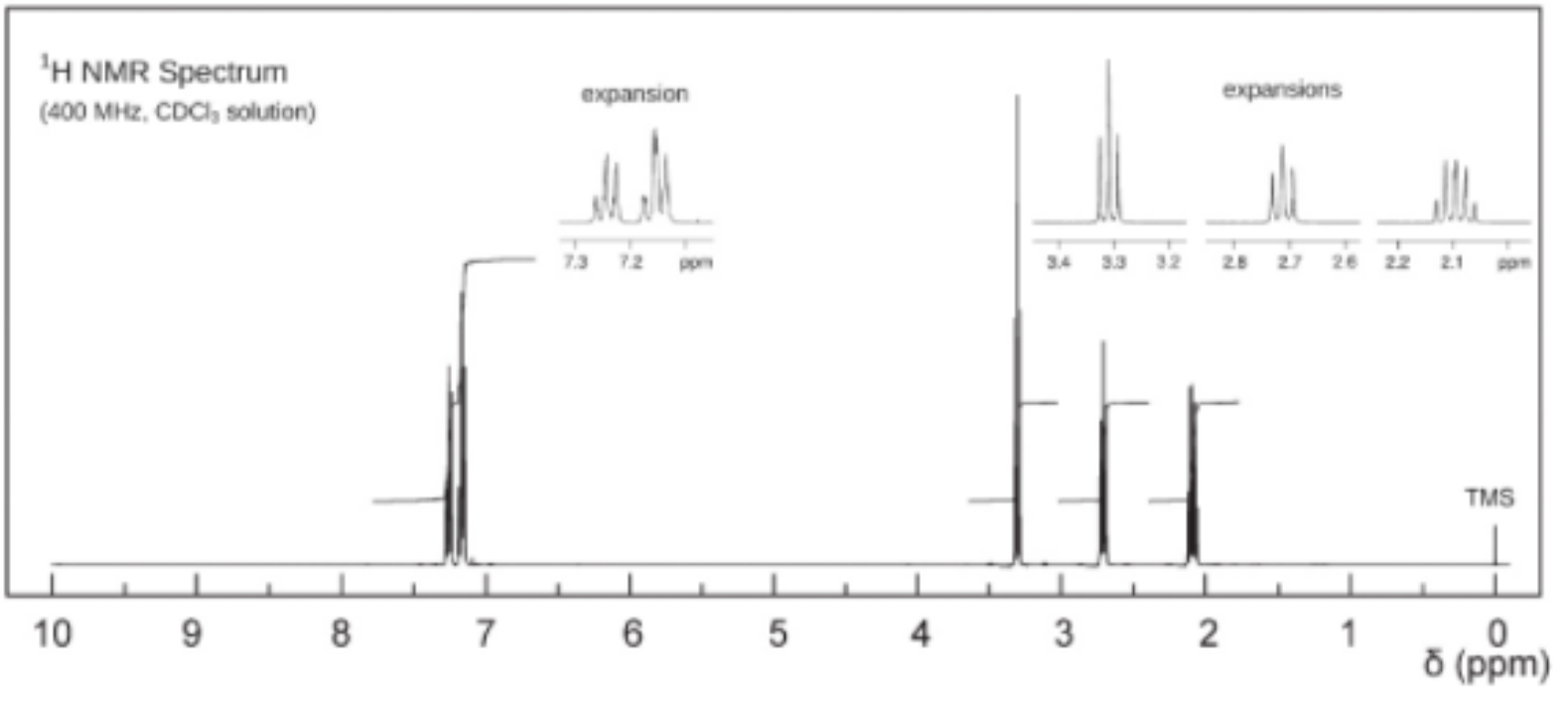
Problem 117


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

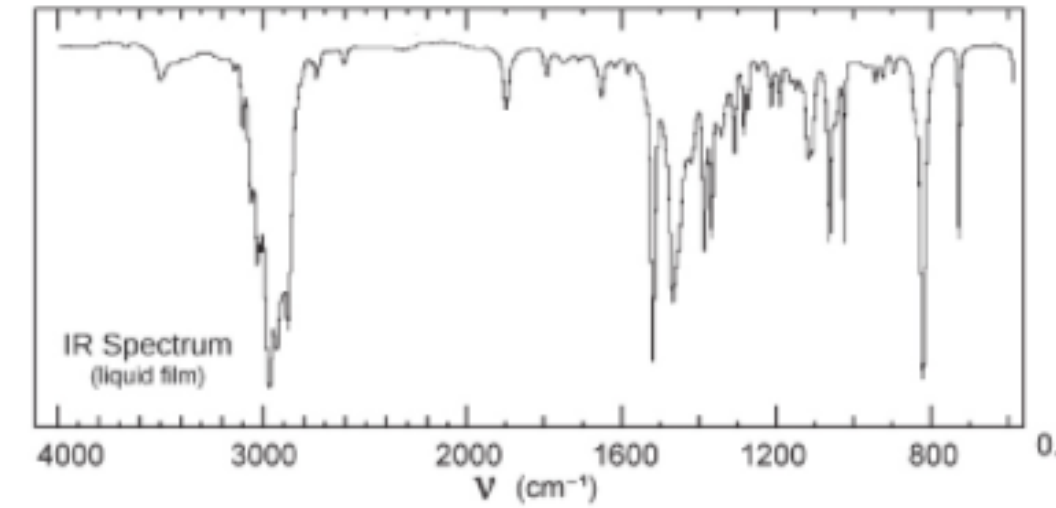

Mass Spectrum
% of base peak
100
80
60
40
20
91
M+·
198/200
C9H11Br
40
80
120
160
200
240
280
m / e

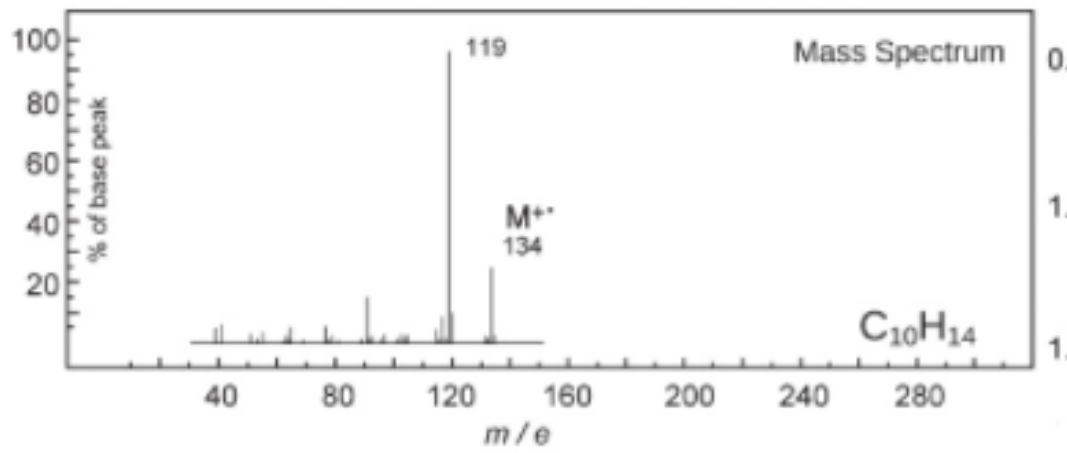

absorbance
0.0
0.5
1.0
1.5
UV Spectrum
5.30 mg / 10 mL
path length: 1.0 cm
solvent: cyclohexane
200
250
300
350
λ (nm)

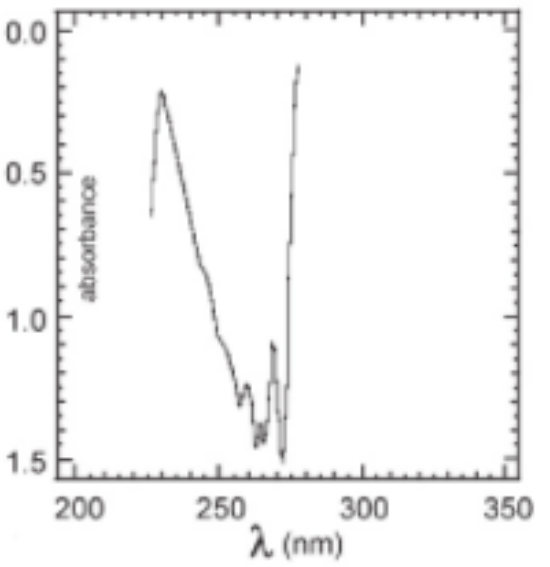

13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
128
127
ppm
expansion
35
34
33
ppm
DEPT CH2 ↓ CH3 ↑ CH ↑
expansion
128
127
ppm
expansion
35
34
33
ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

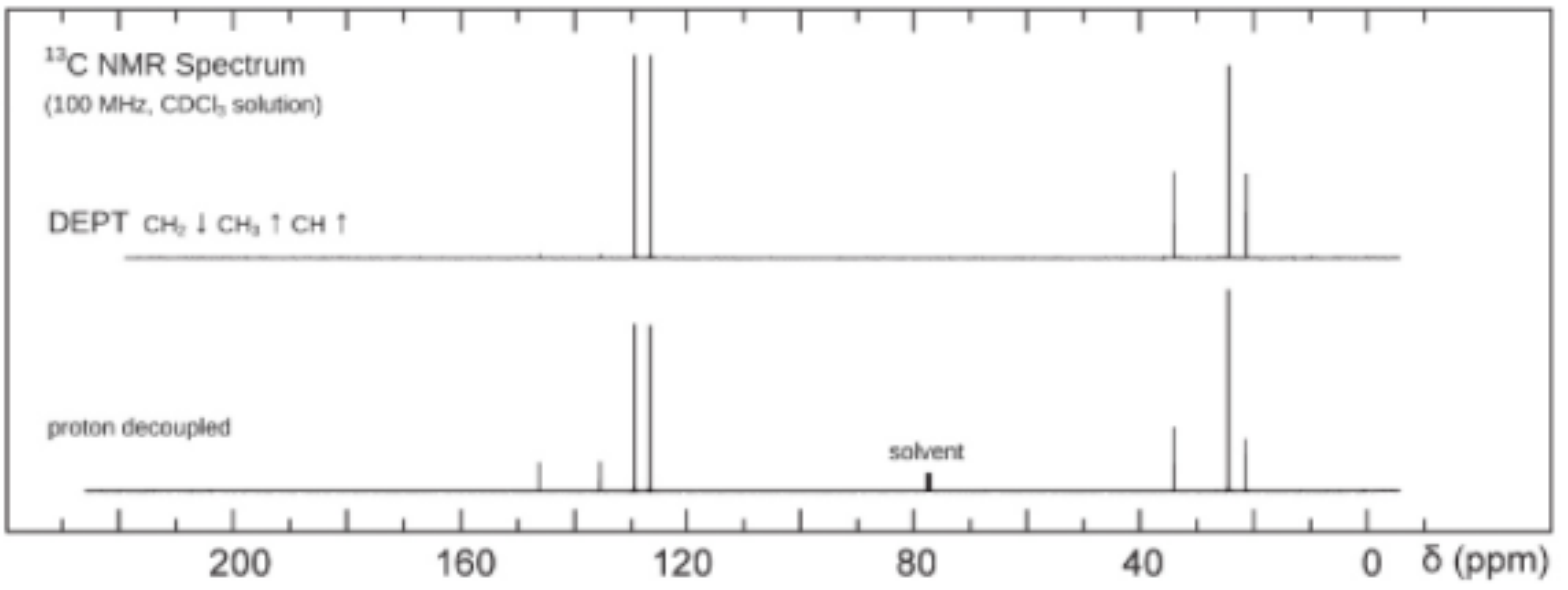

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.3
7.2
ppm
expansions
3.4
3.3
3.2
2.8
2.7
2.6
2.2
2.1
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

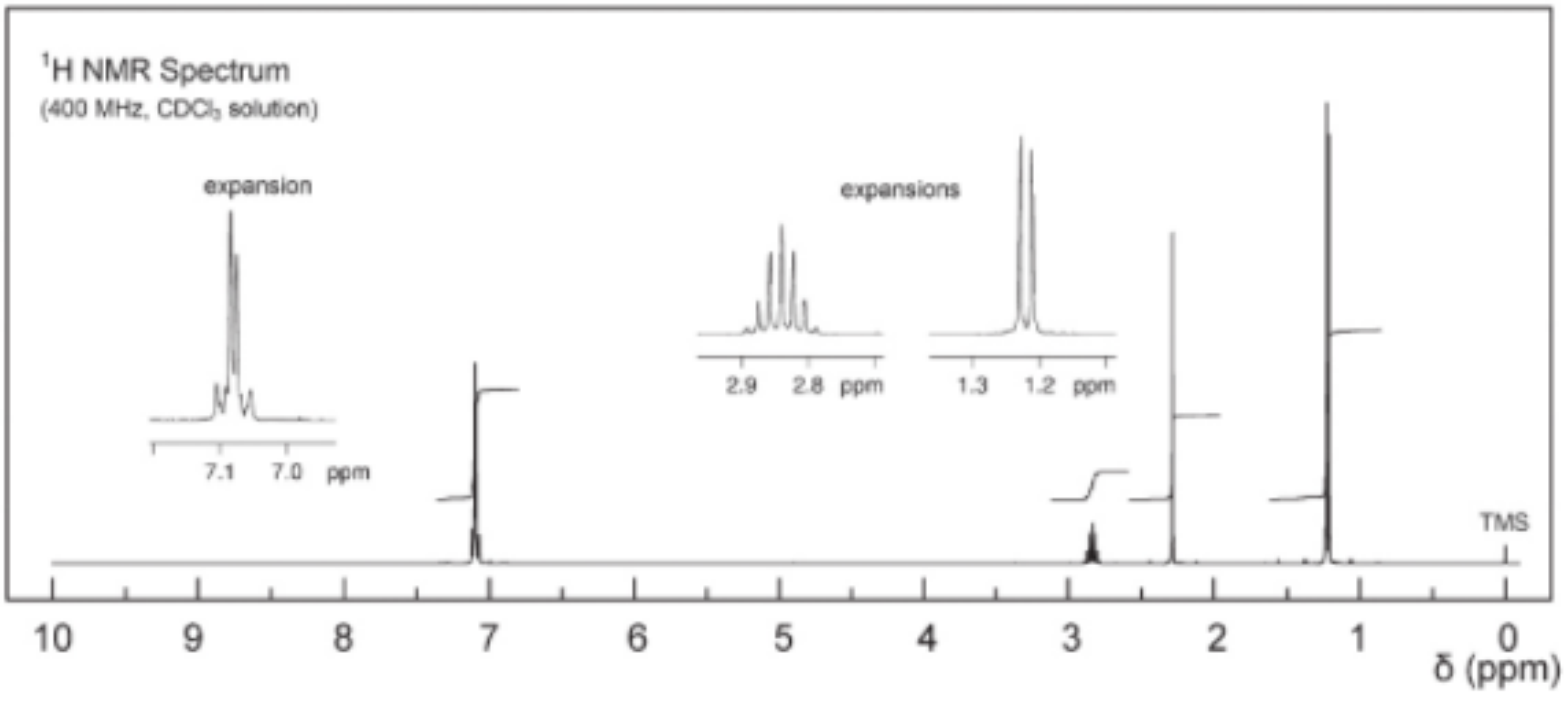
Problem 118


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

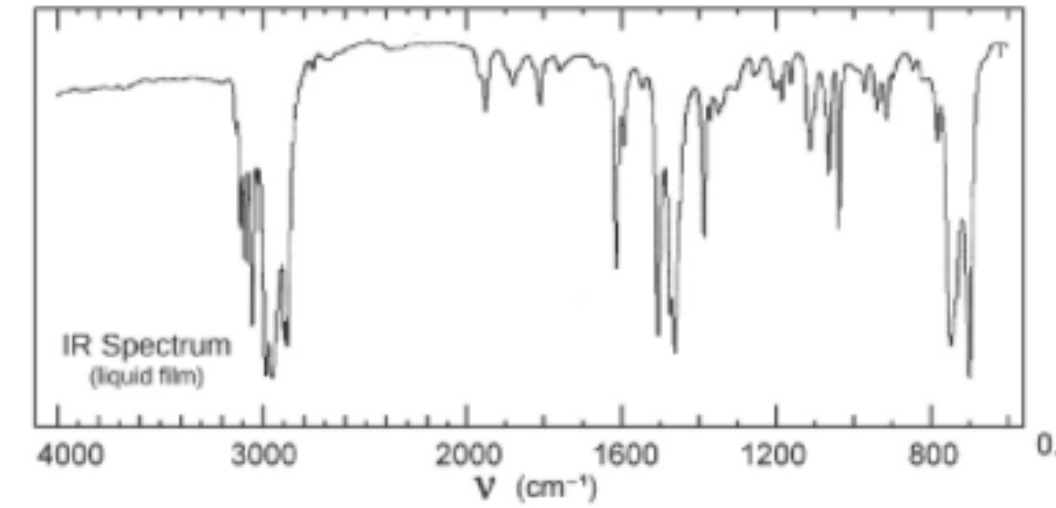

Mass Spectrum
119
M+·
134
% of base peak
100
80
60
40
20
C10H14
40
80
120
160
200
240
280
m / e

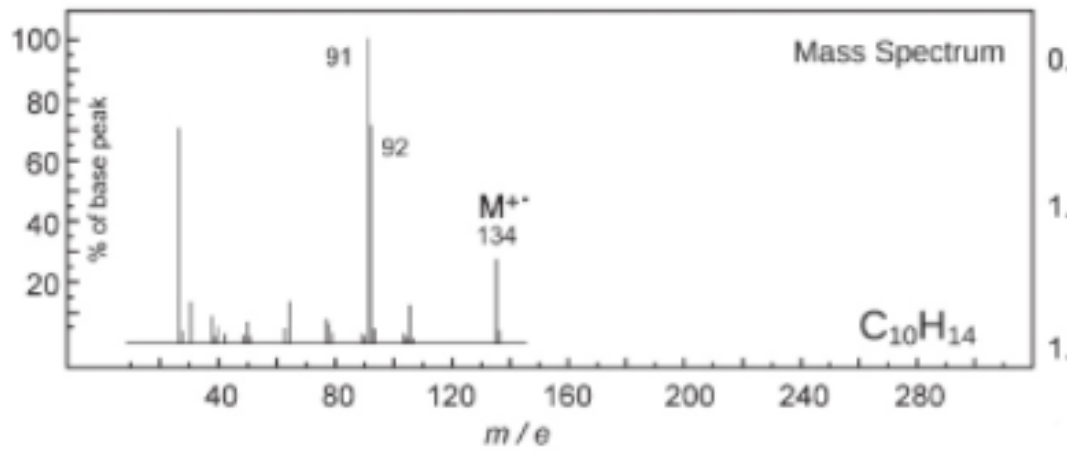

absorbance
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)

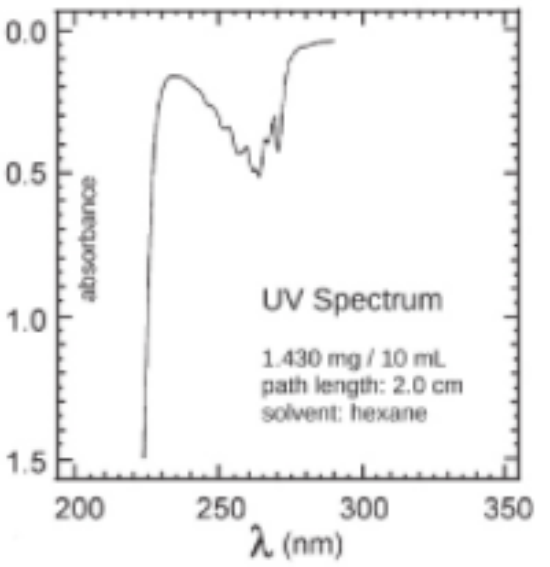

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

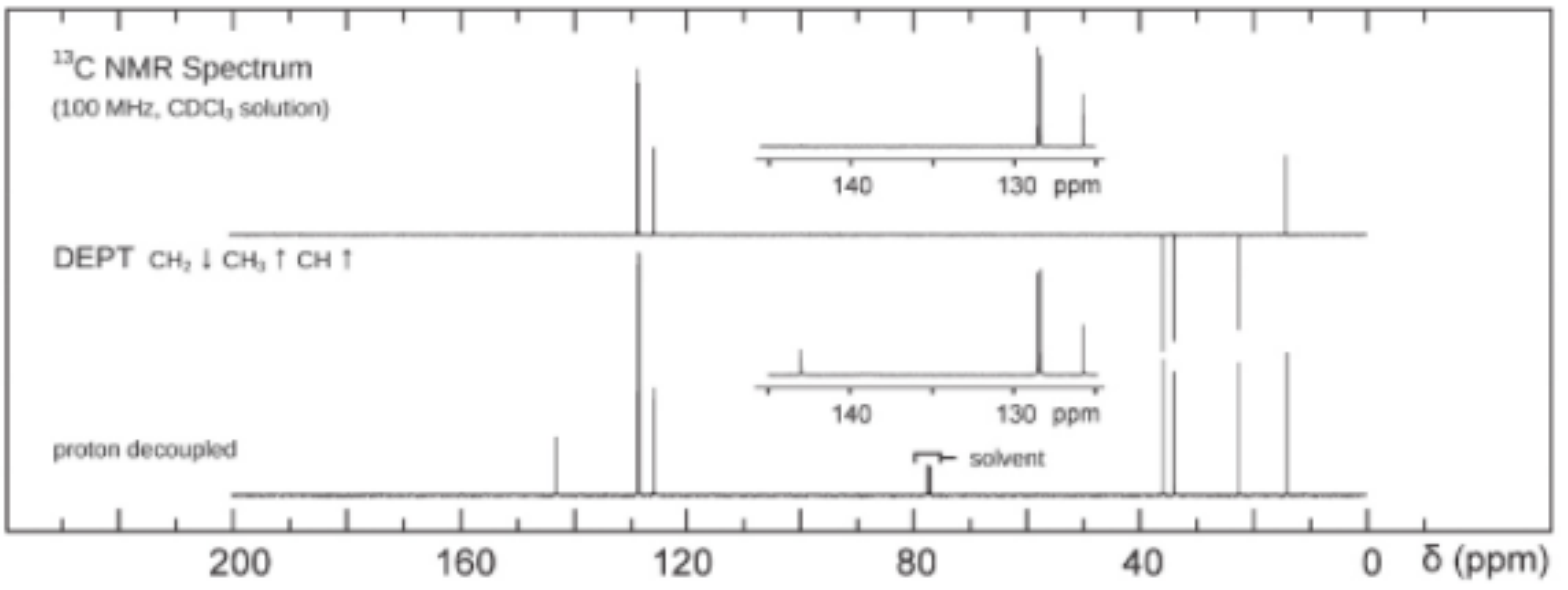

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.1
7.0
ppm
expansions
2.9
2.8
ppm
1.3
1.2
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

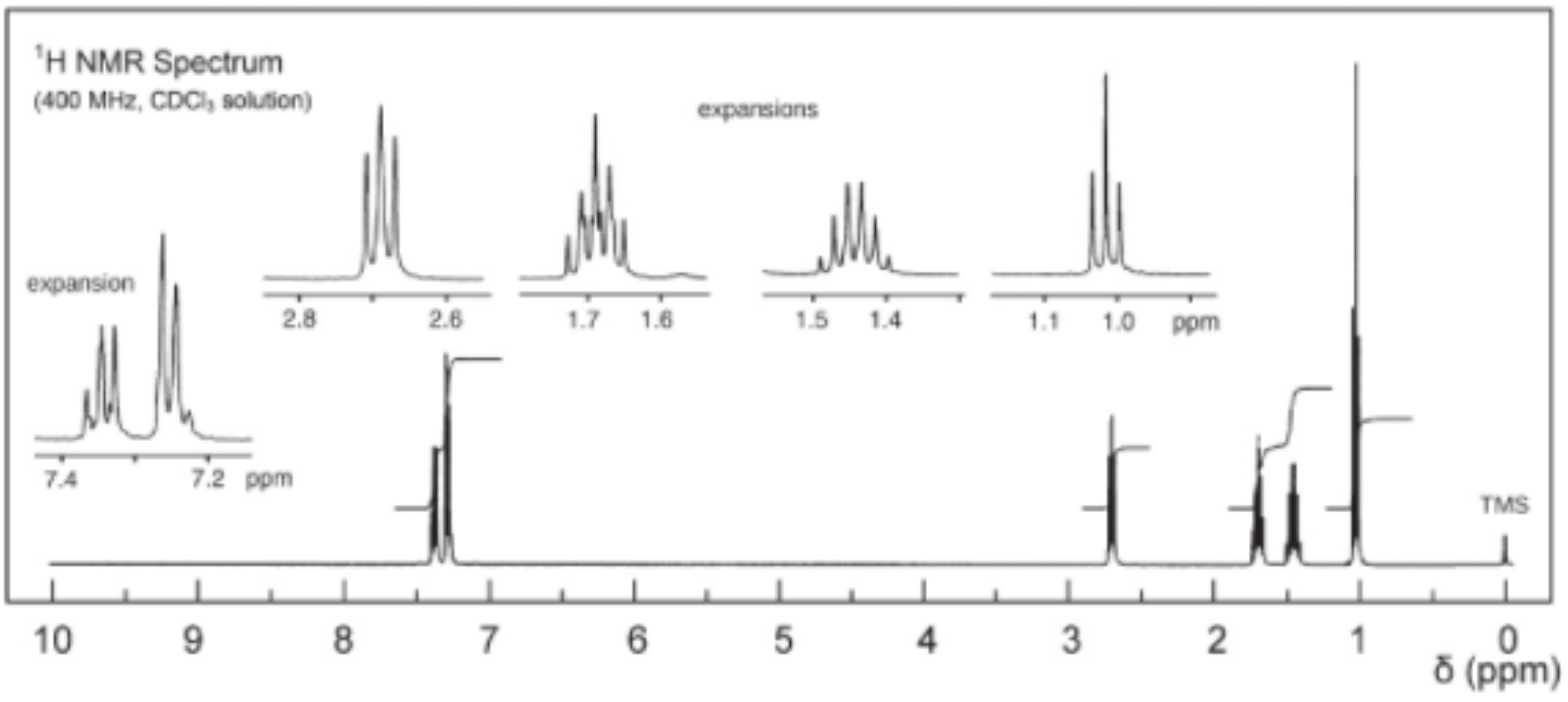
Problem 119


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

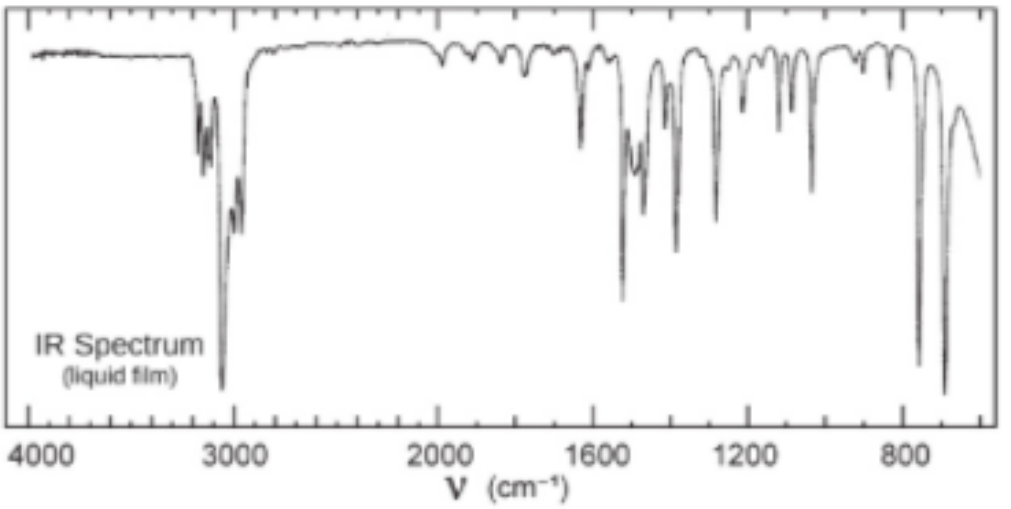

Mass Spectrum
% of base peak
100
80
60
40
20
91
92
M+·
134
C10H14
40
80
120
160
200
240
280
m / e

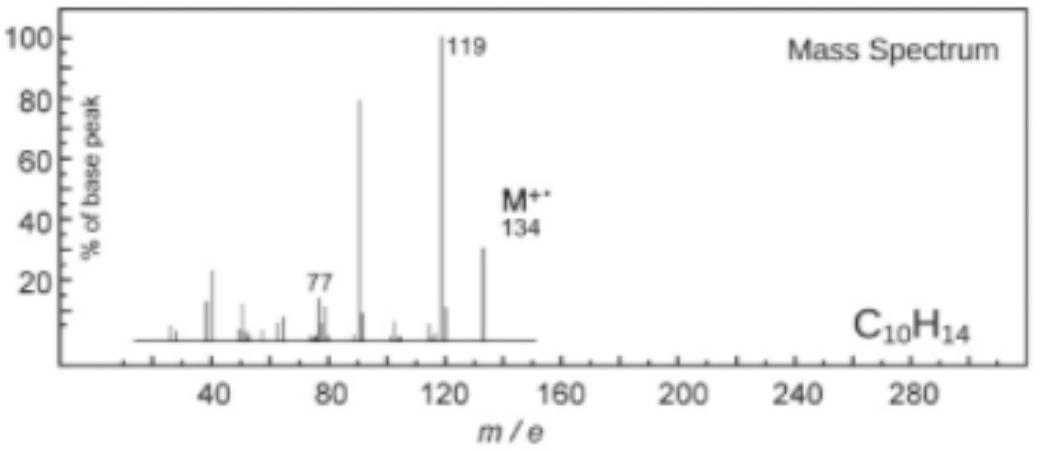

absorbance
0.0
0.5
1.0
1.5
UV Spectrum
1.430 mg / 10 mL
path length: 2.0 cm
solvent: hexane
200
250
300
350
λ (nm)


13C NMR Spectrum
(100 MHz, CDCl3 solution)
140
130 ppm
DEPT CH2 ↓ CH3 ↑ CH ↑
140
130 ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
expansion
2.8
2.6
1.7
1.6
1.5
1.4
1.1
1.0
ppm
7.4
7.2
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 120

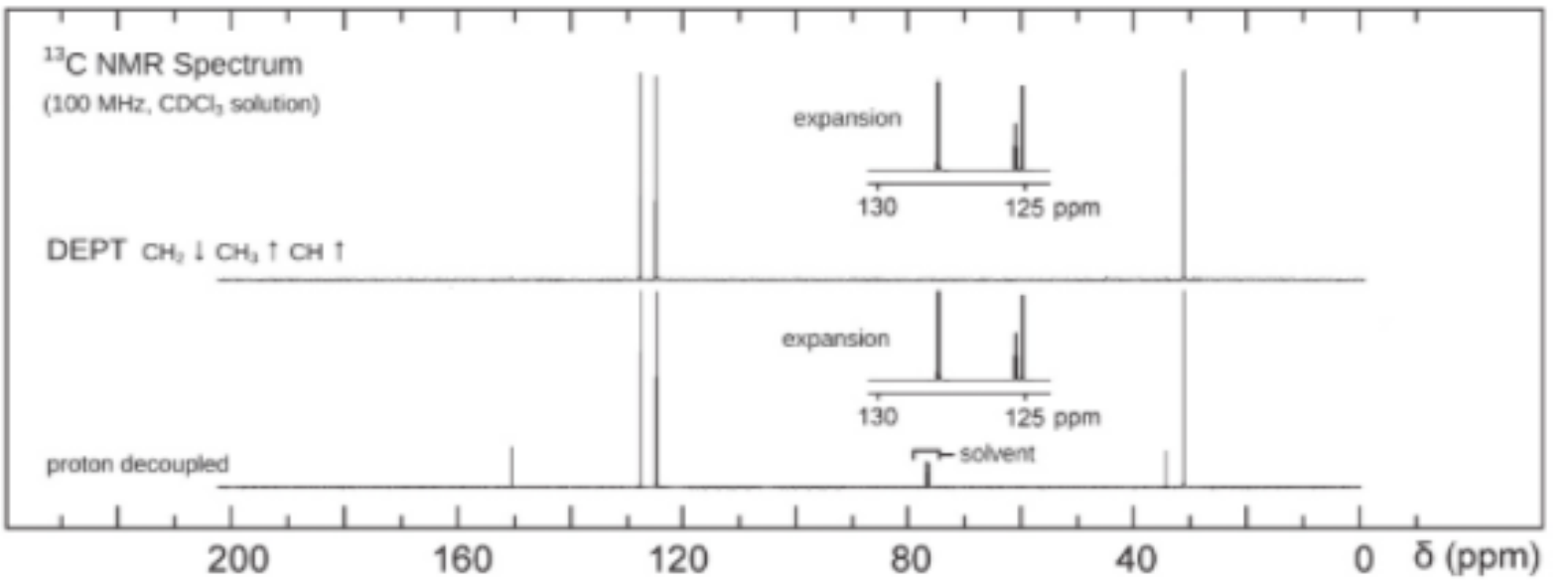


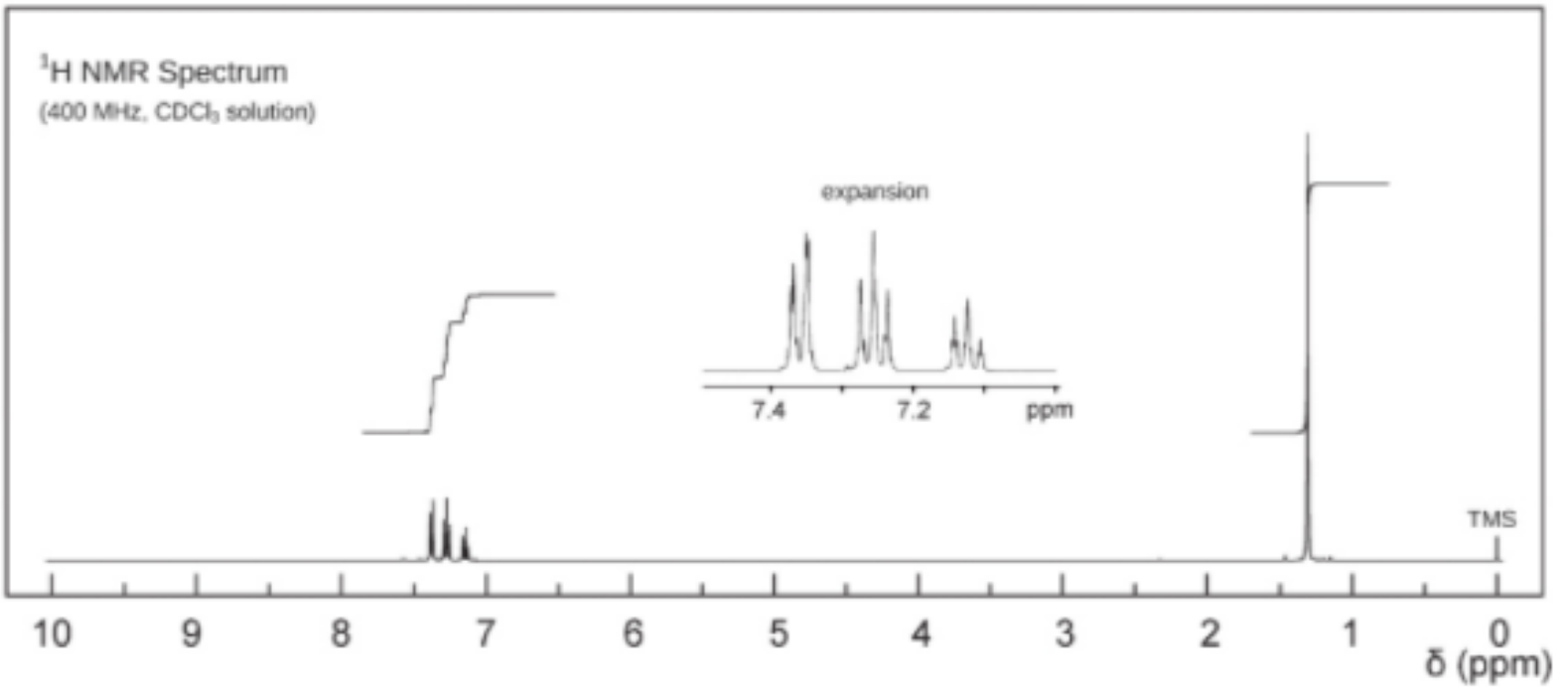


UV Spectrum

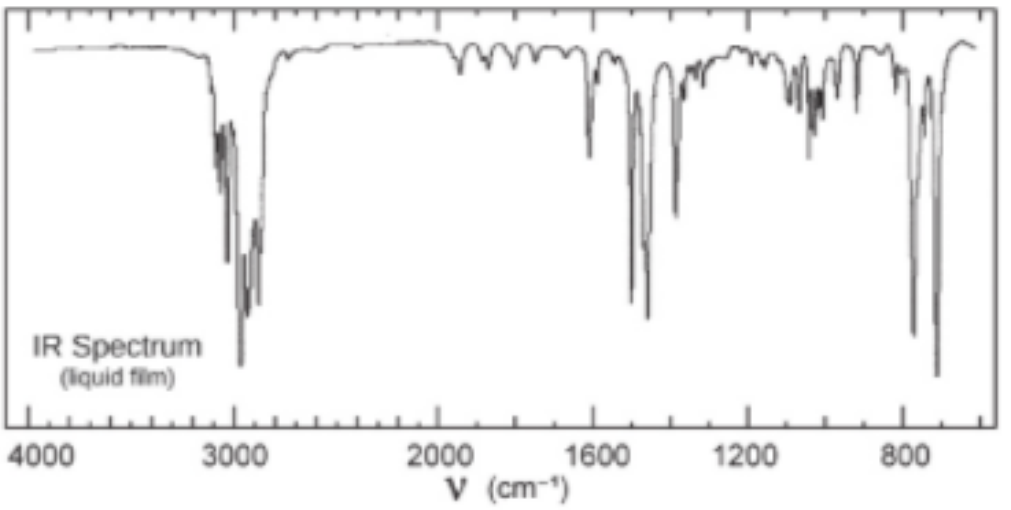
λ_{max} 262 nm ($\log_{10}\varepsilon$ 2.5)

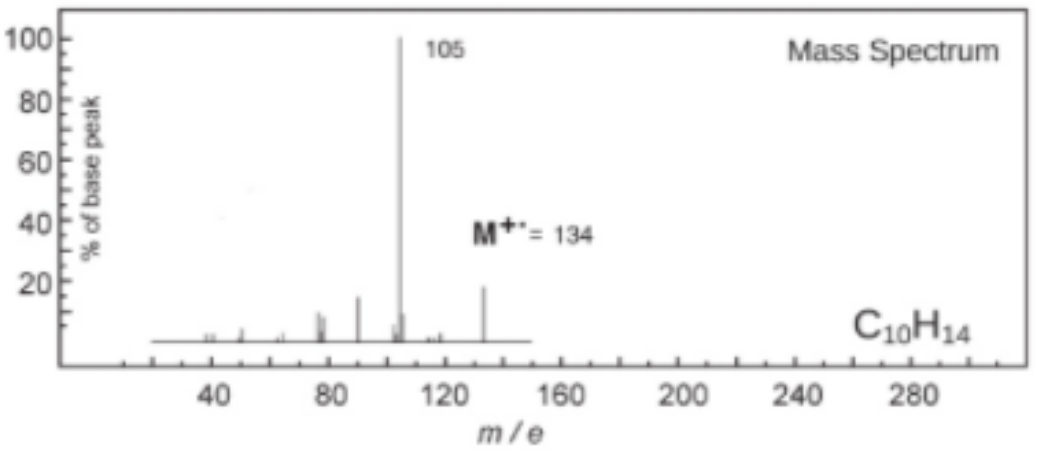
solvent: ethanol





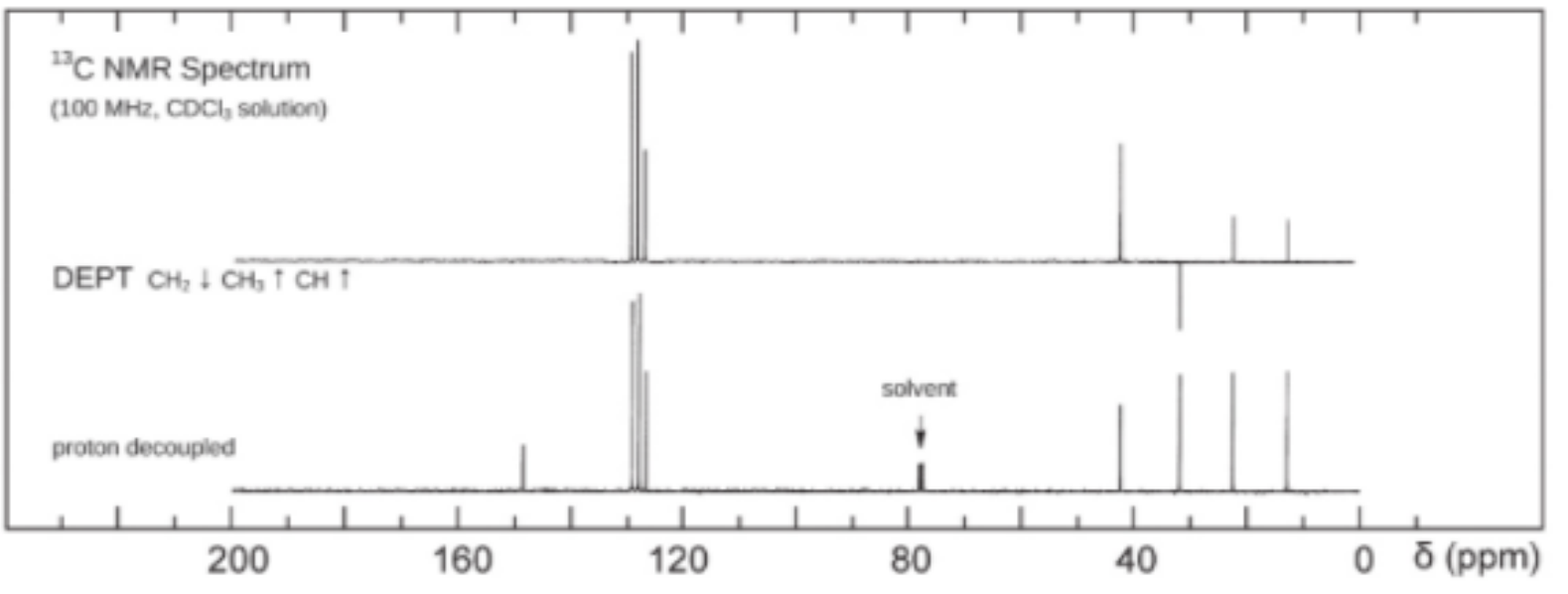
Problem 121

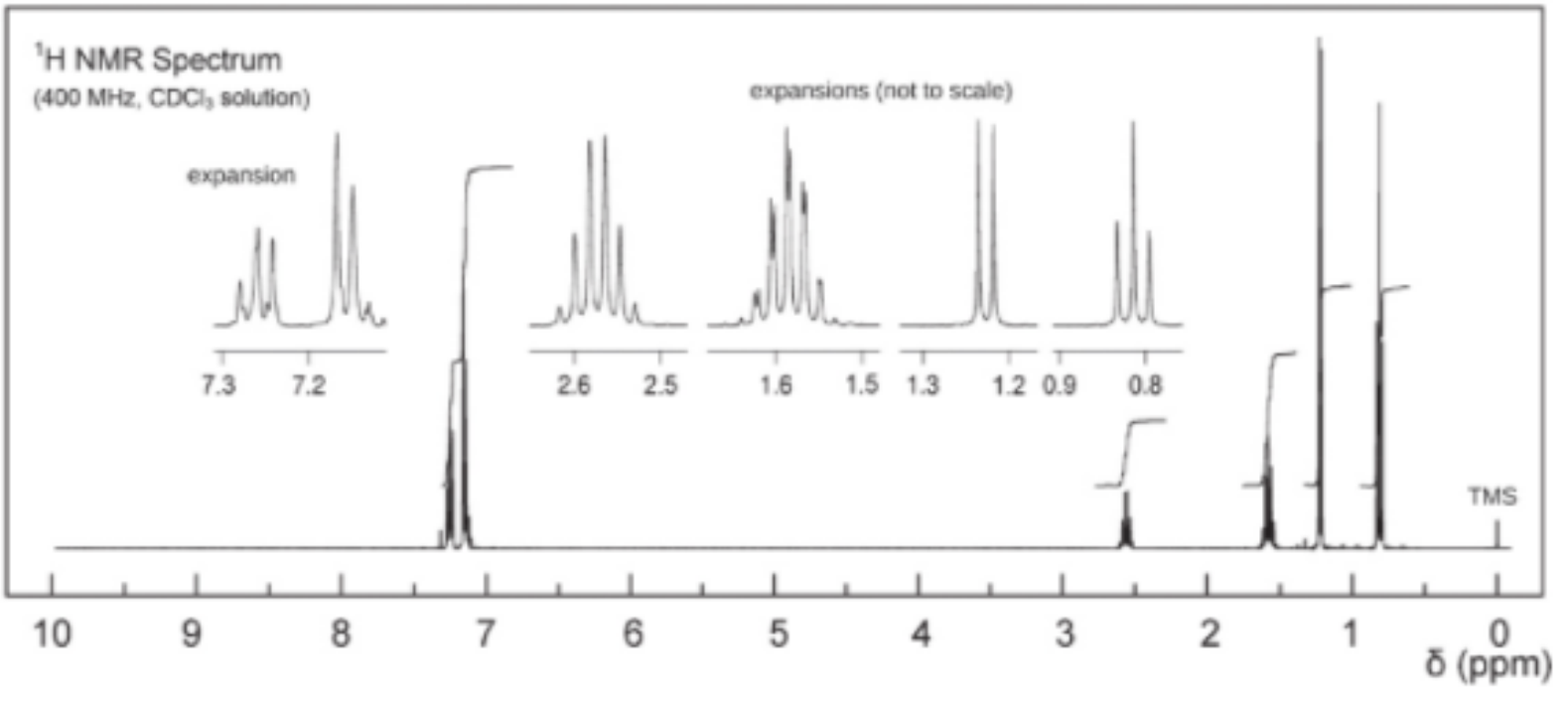


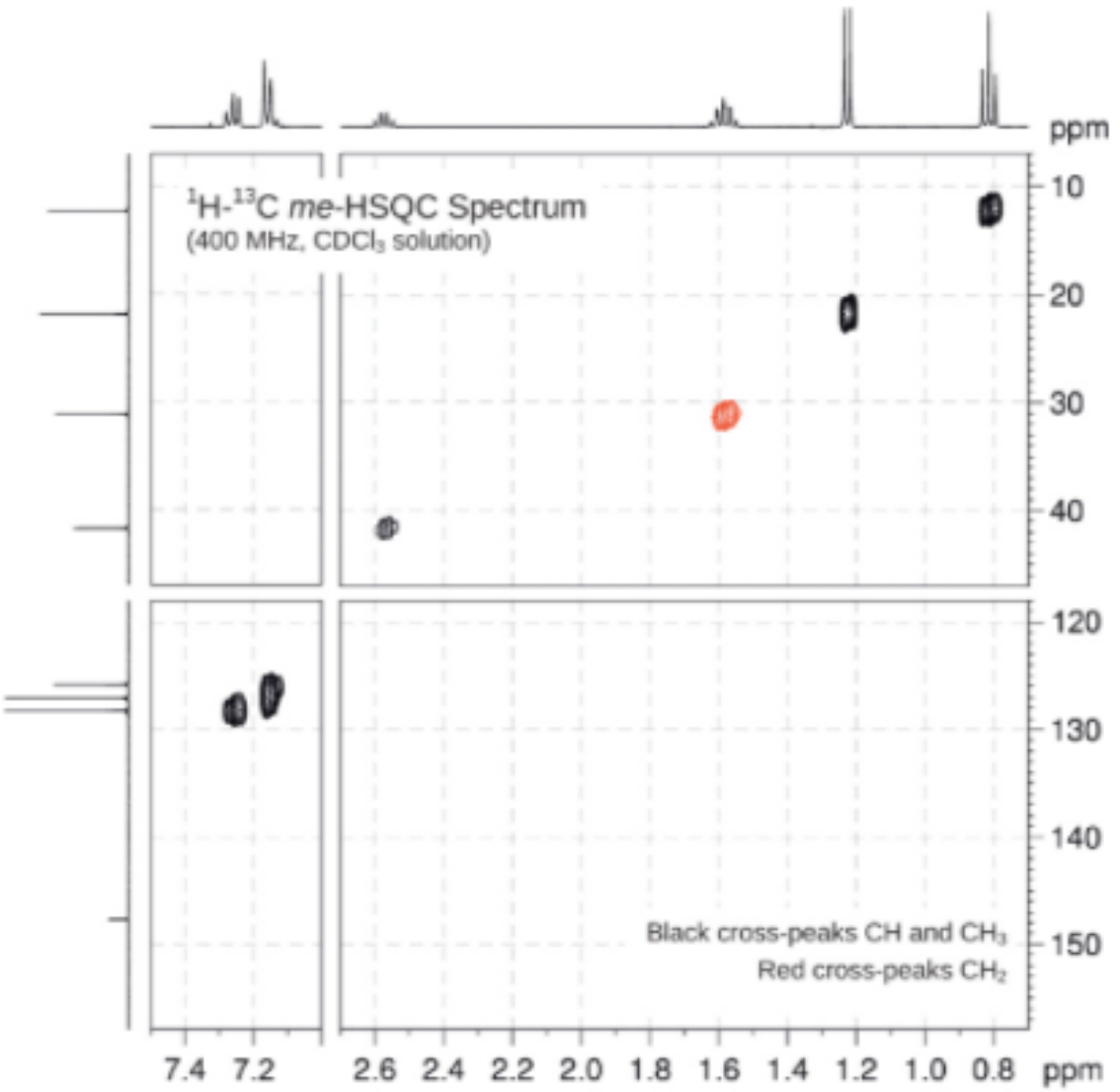


UV Spectrum

$\lambda_{max} \approx 260$ nm ($\log_{10}\varepsilon \approx 2.5$)

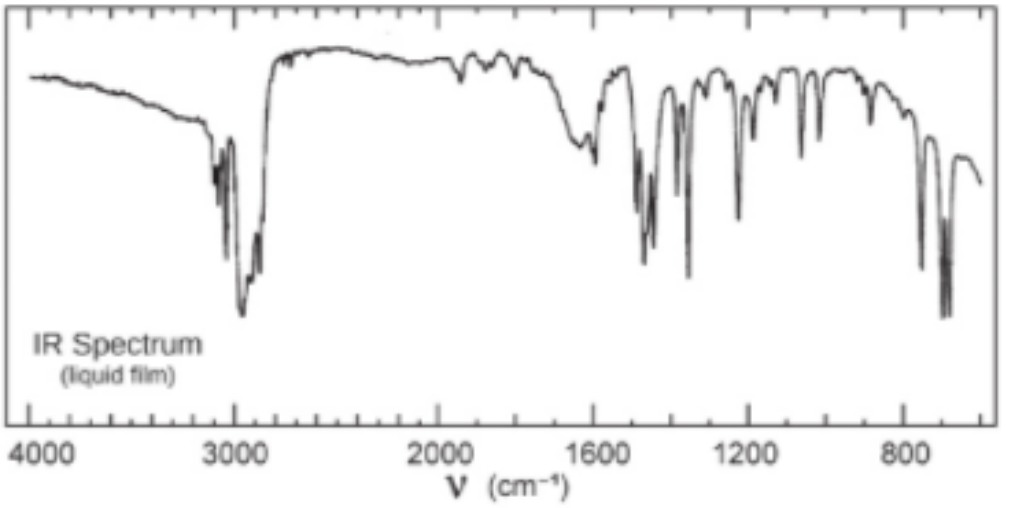


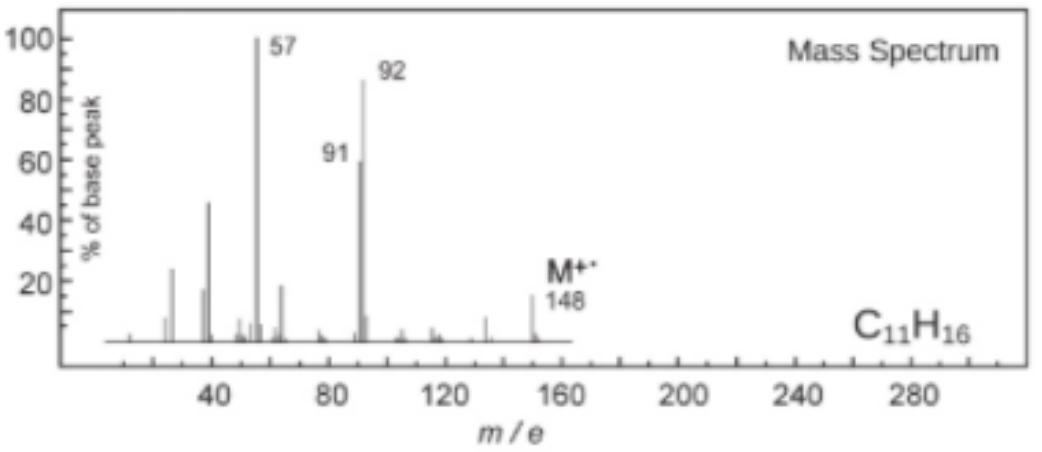



^{1}H-^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
ppm
10
20
30
40
120
130
140
150
7.4 7.2
2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
ppm

^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
ppm
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
7.2
7.4
7.4 7.2
2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
ppm

Problem 122

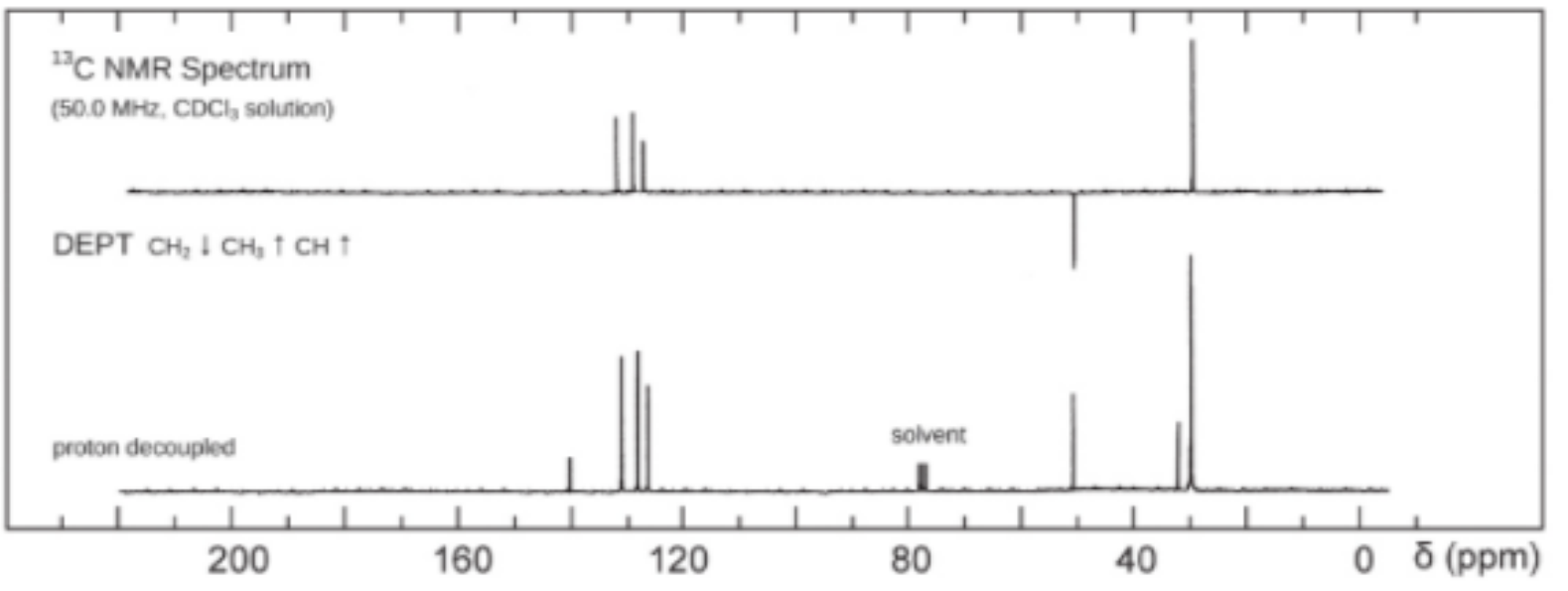


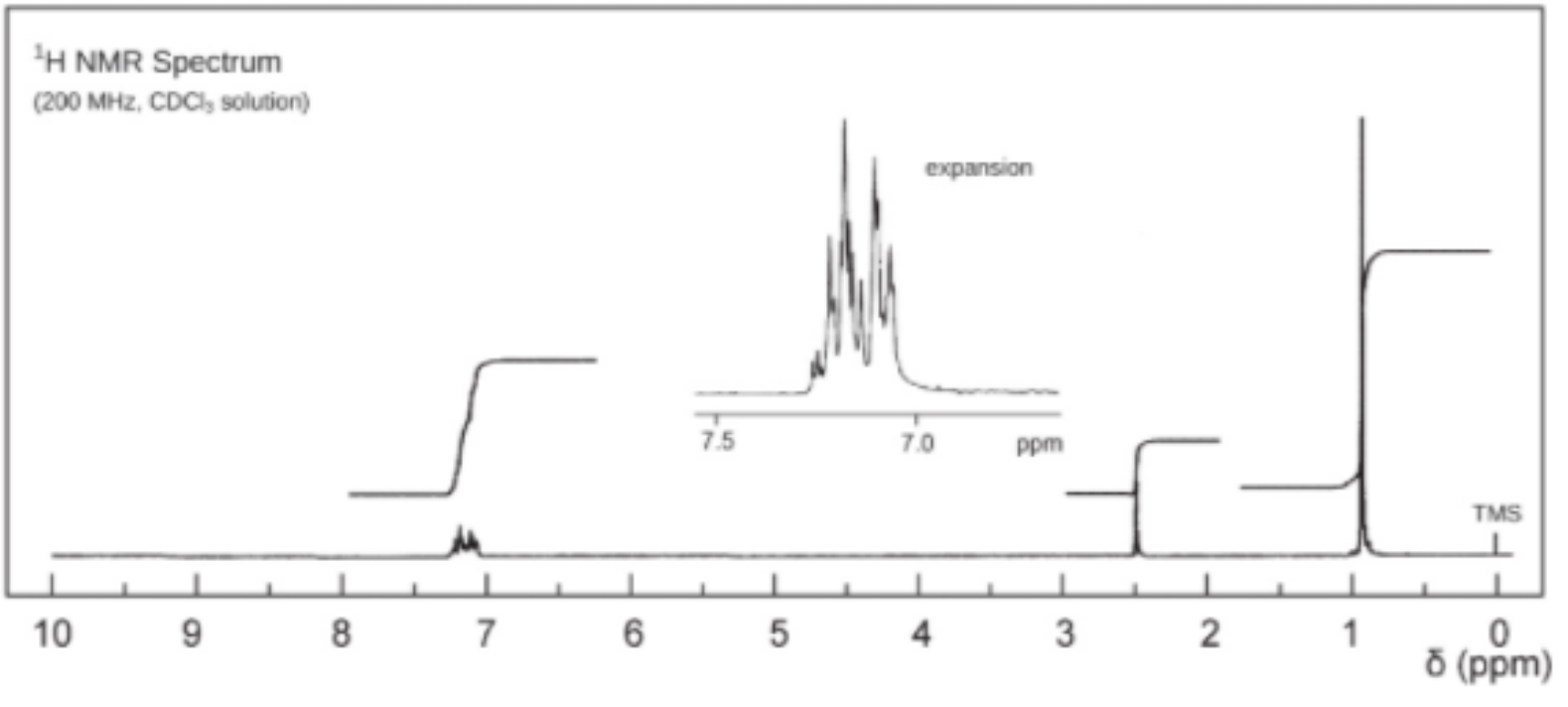


UV Spectrum

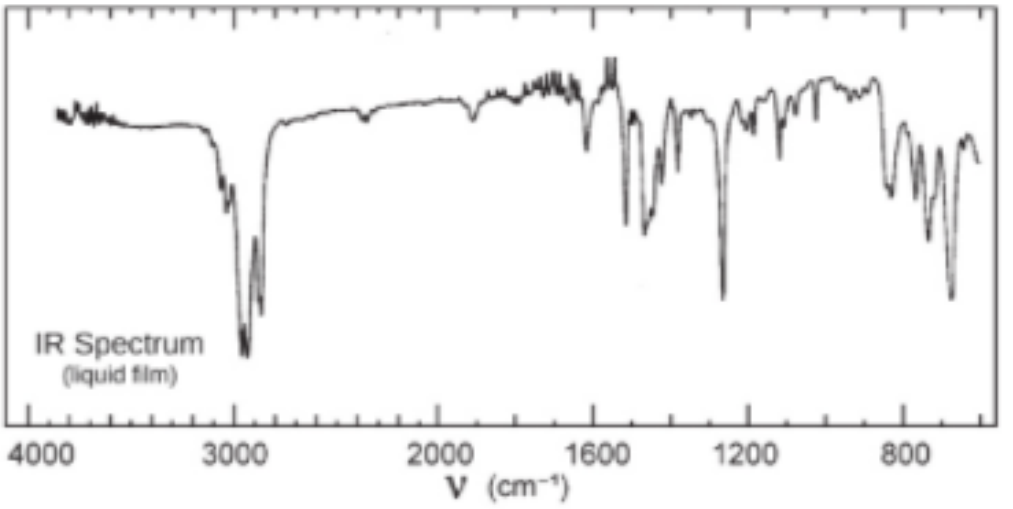
λ_{max} 260 nm ($\log_{10}\varepsilon$ 2.5)

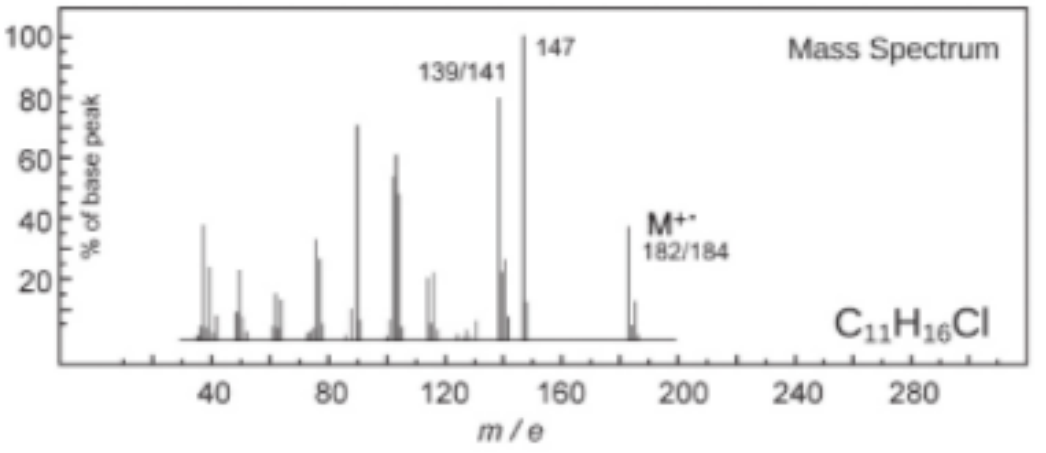
solvent: methanol

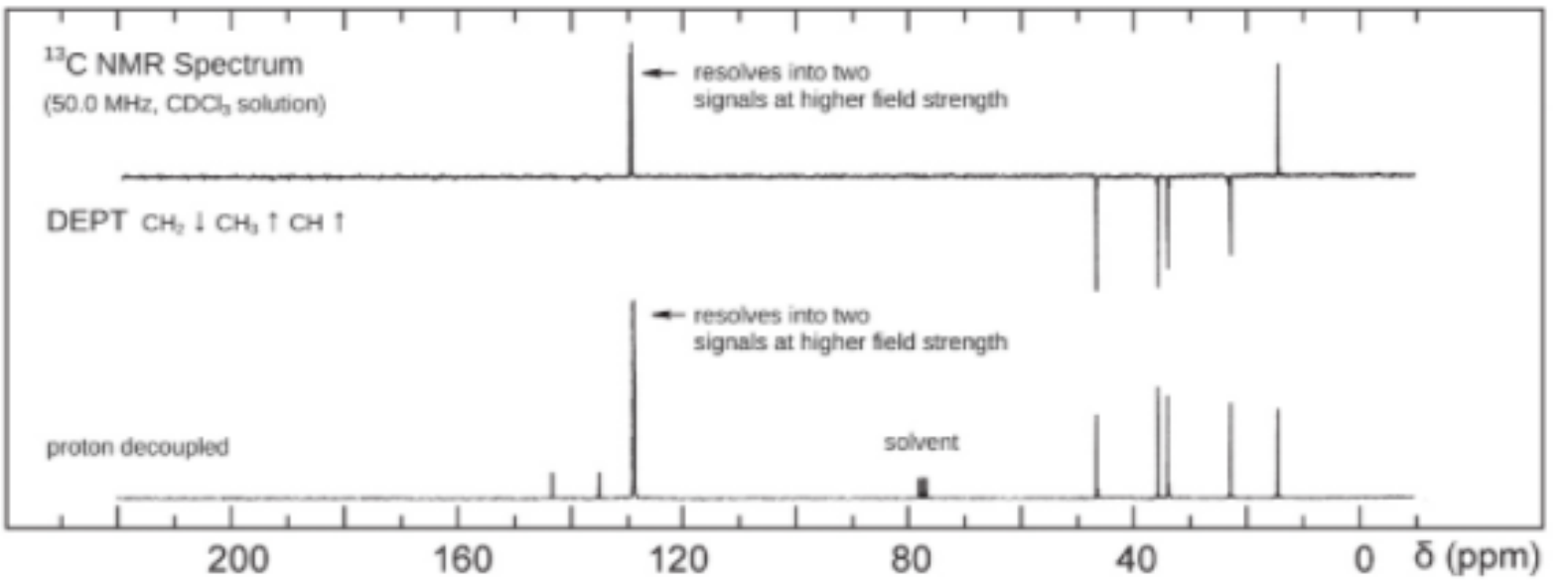


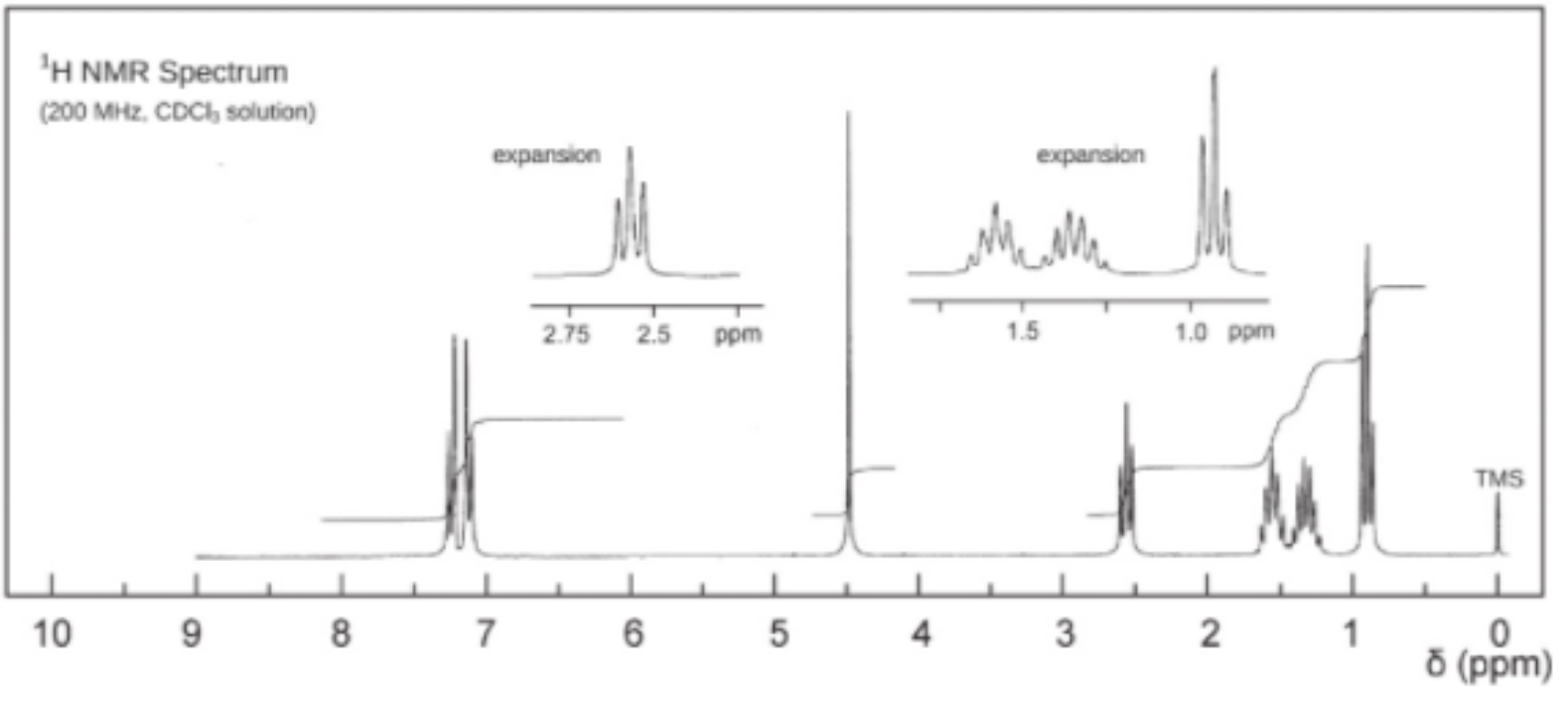


Problem 123

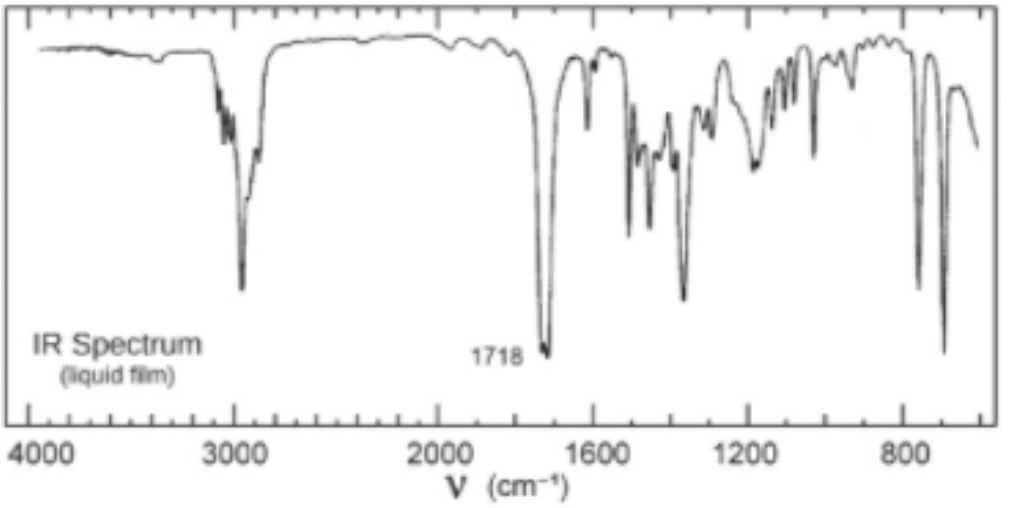

IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

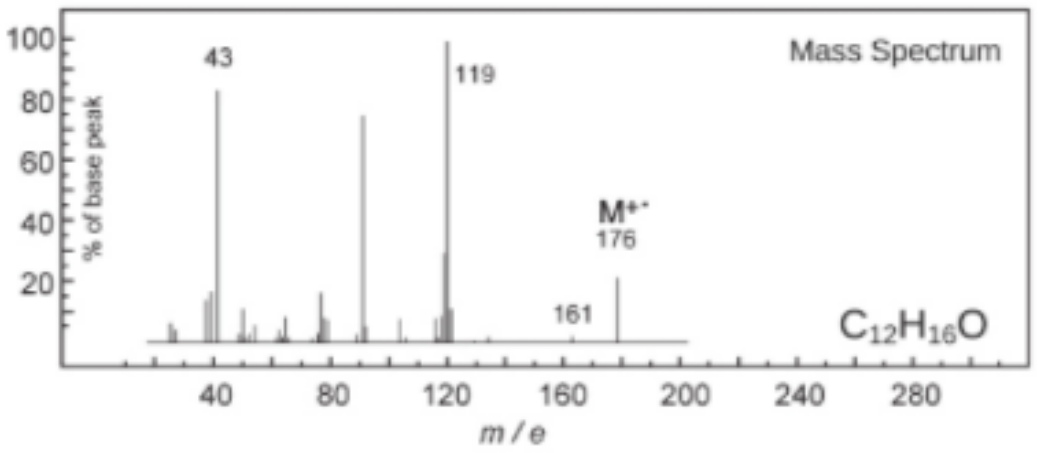

Mass Spectrum
100
80
60
40
20
% of base peak
139/141
147
M+·
182/184
C11H16Cl
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(50.0 MHz, CDCl3 solution)
resolves into two
signals at higher field strength
DEPT CH2 ↓ CH3 ↑ CH ↑
resolves into two
signals at higher field strength
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(200 MHz, CDCl3 solution)
expansion
2.75
2.5
ppm
expansion
1.5
1.0
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 124

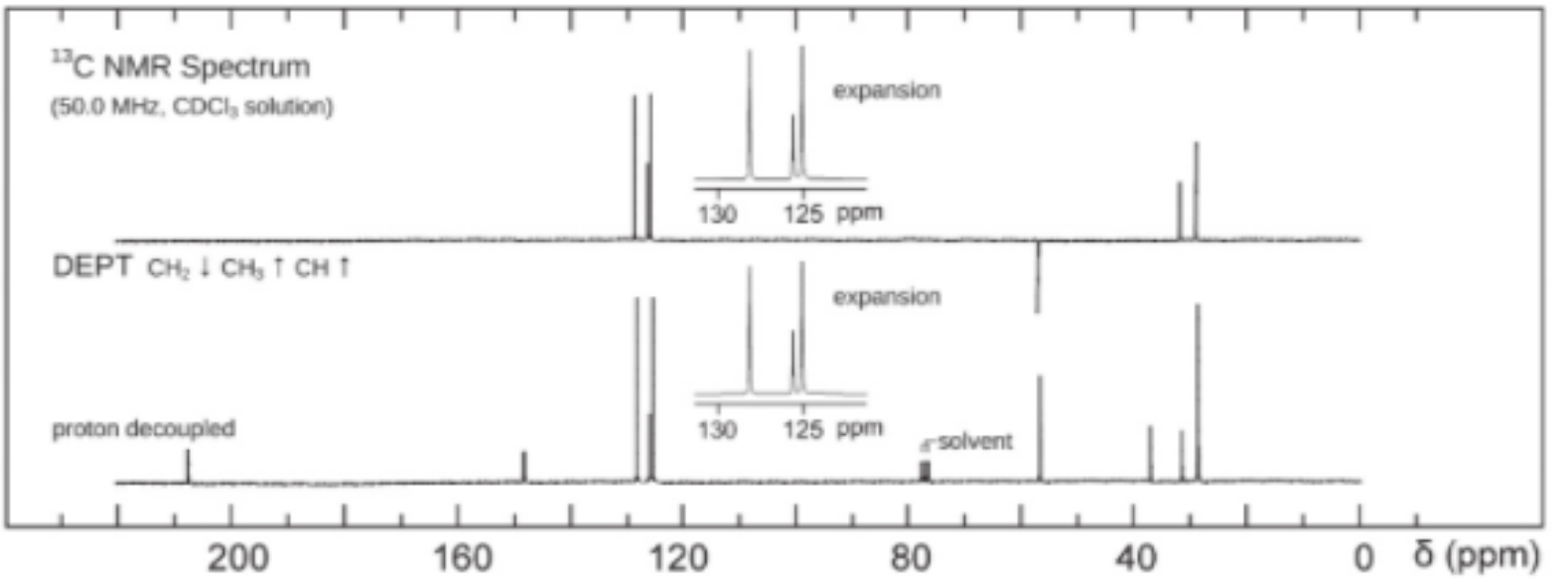


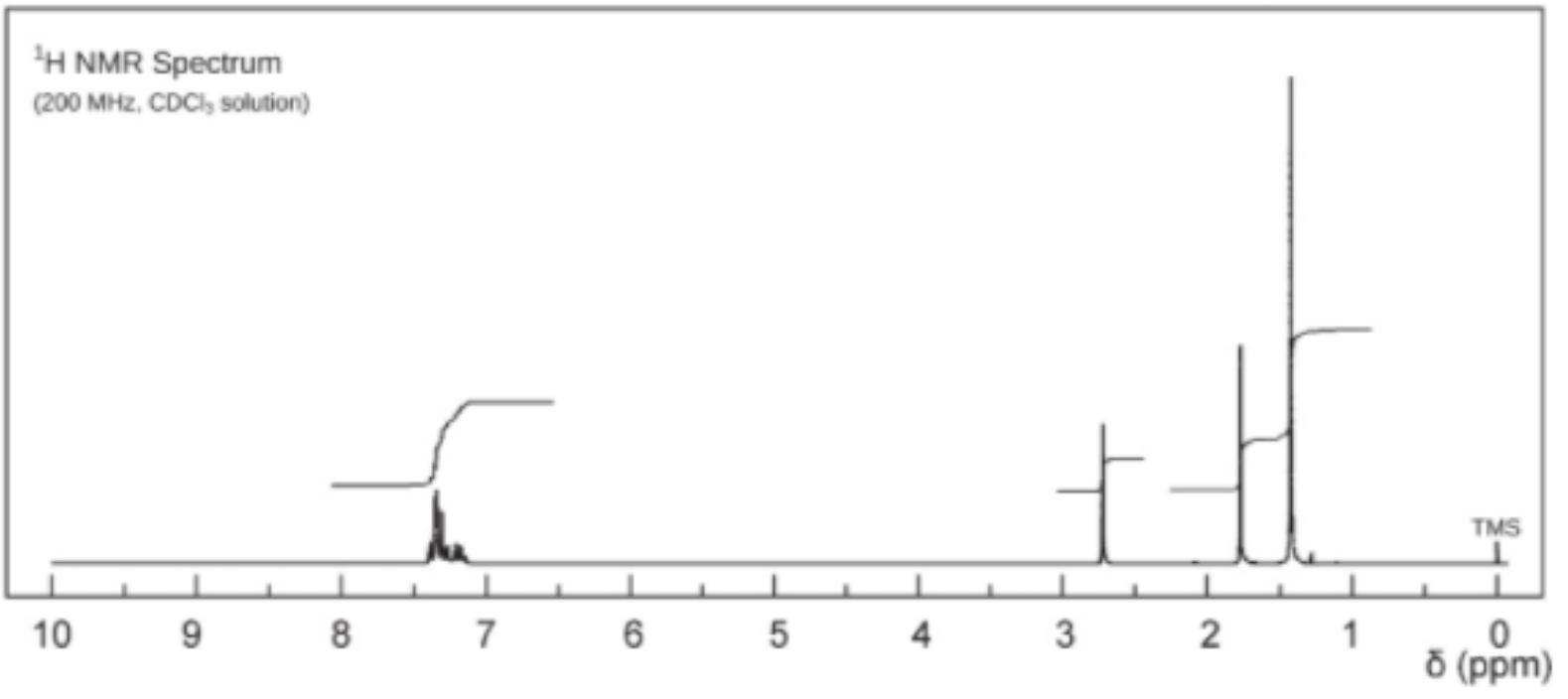


UV Spectrum

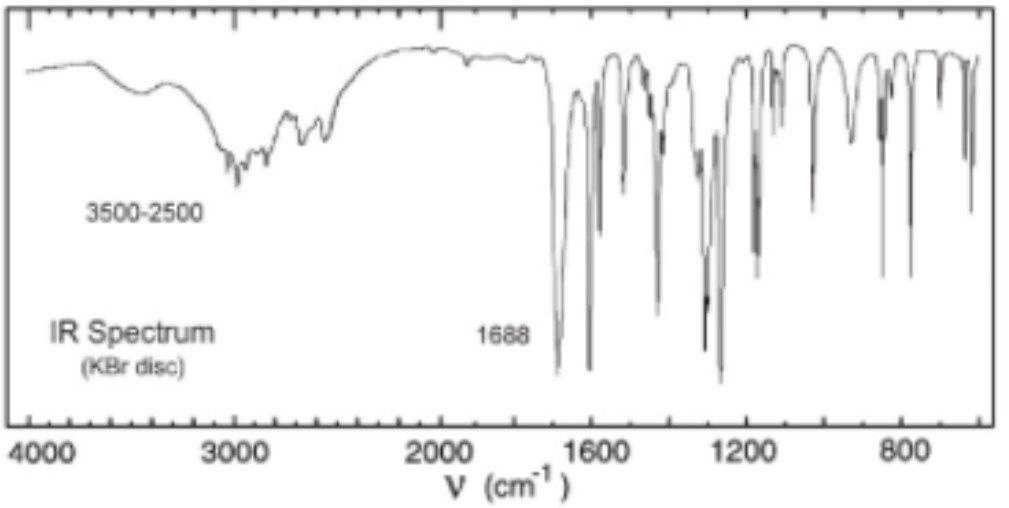
λ_{max} 262 nm ($\log_{10}\varepsilon$ 2.5)

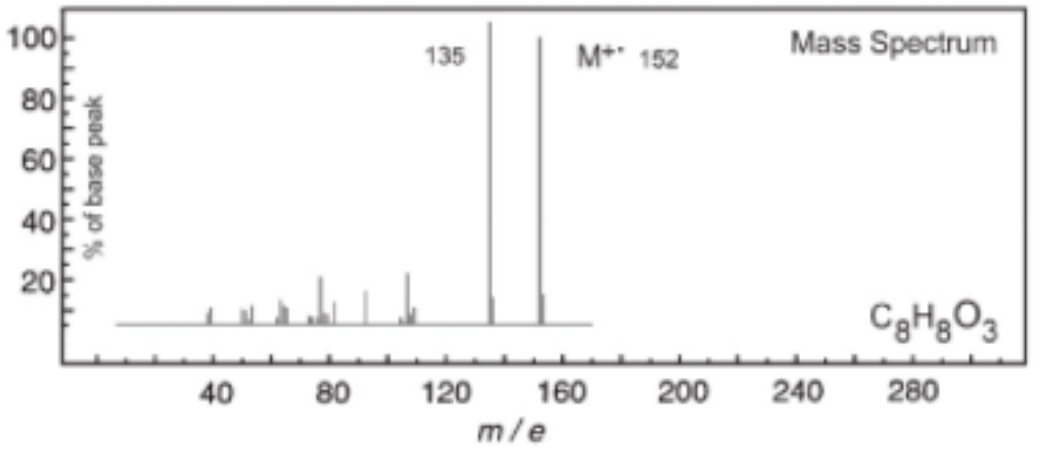
solvent: methanol





Problem 125

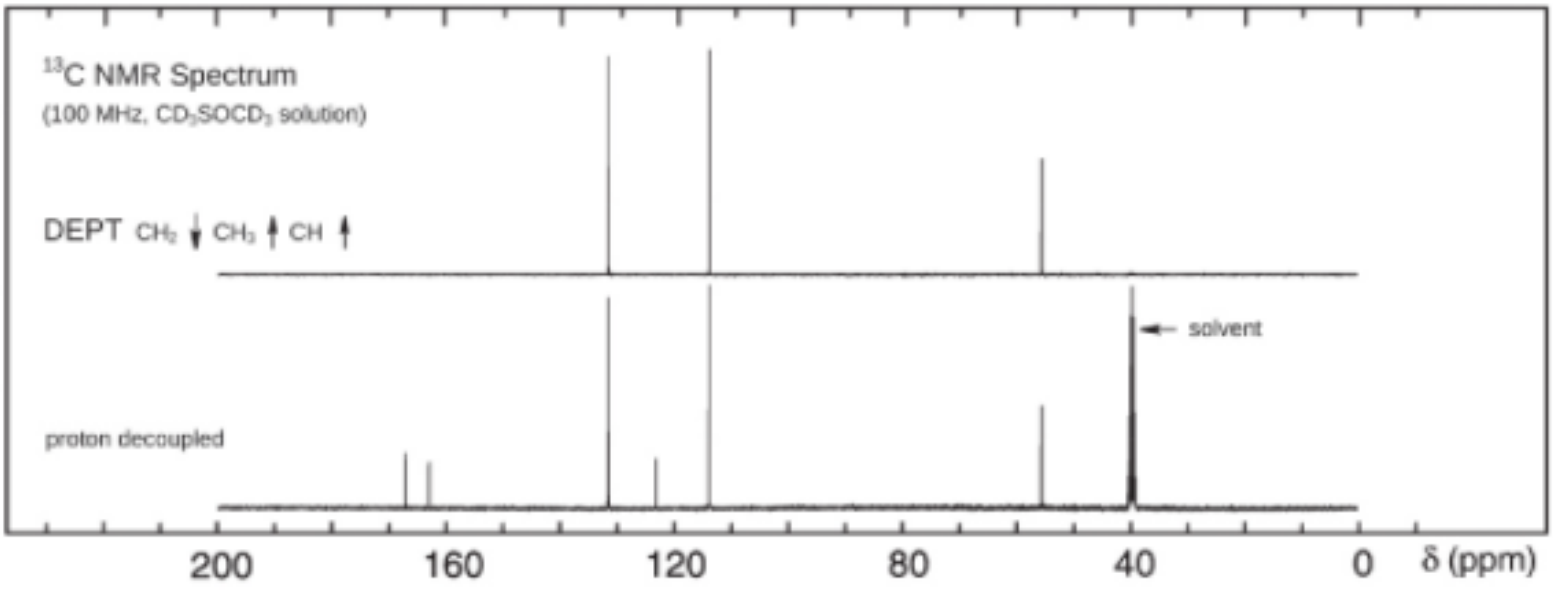


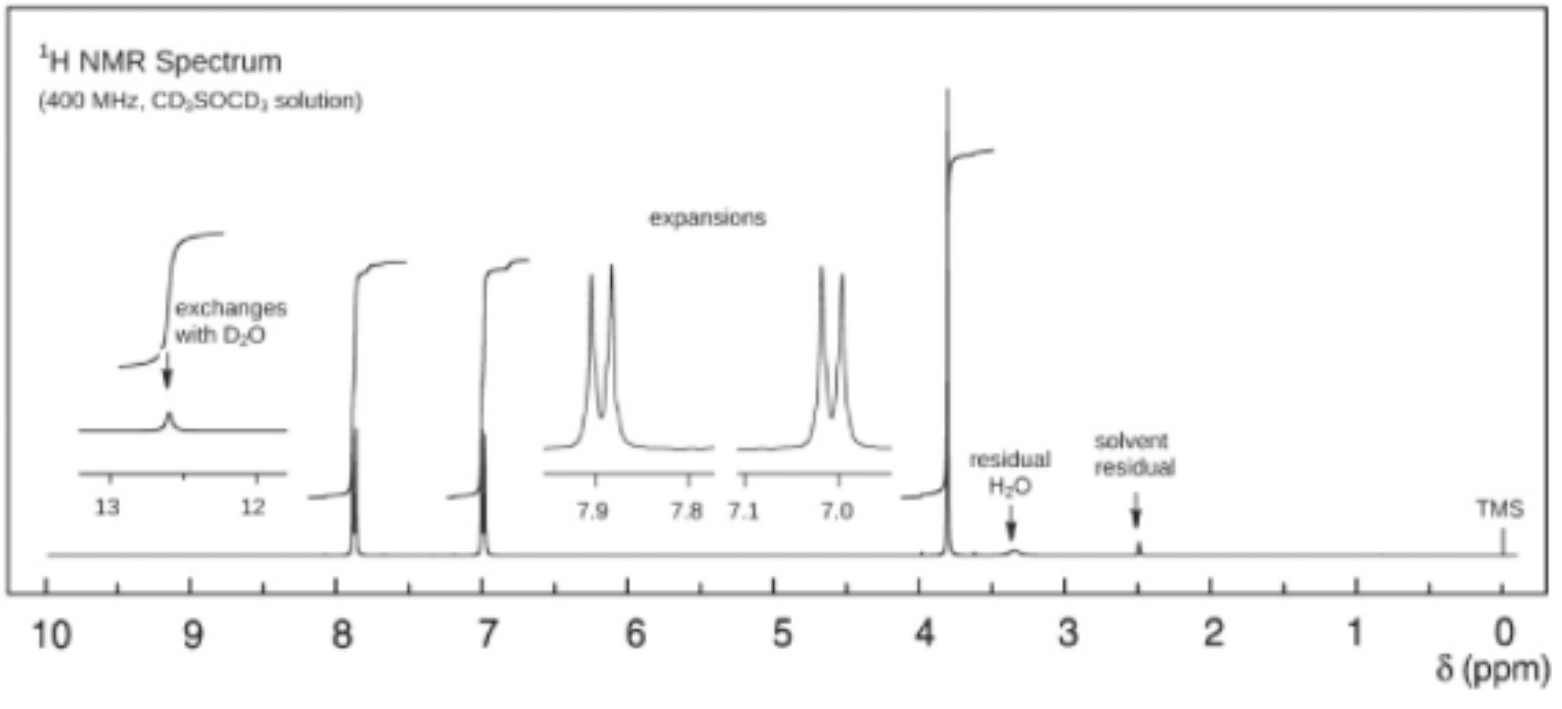


UV Spectrum

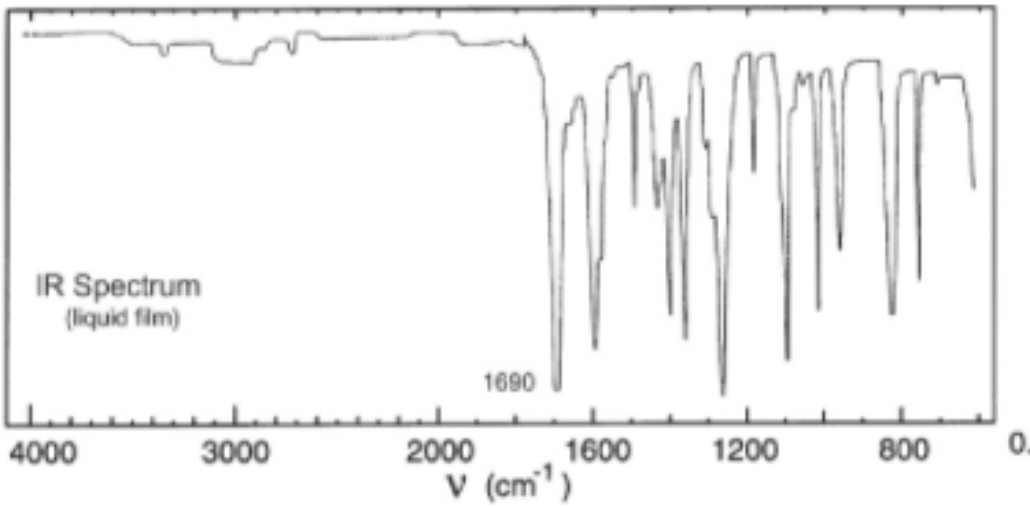
λ_{max} 224 nm ($\log_{10}\varepsilon$ 3.4)

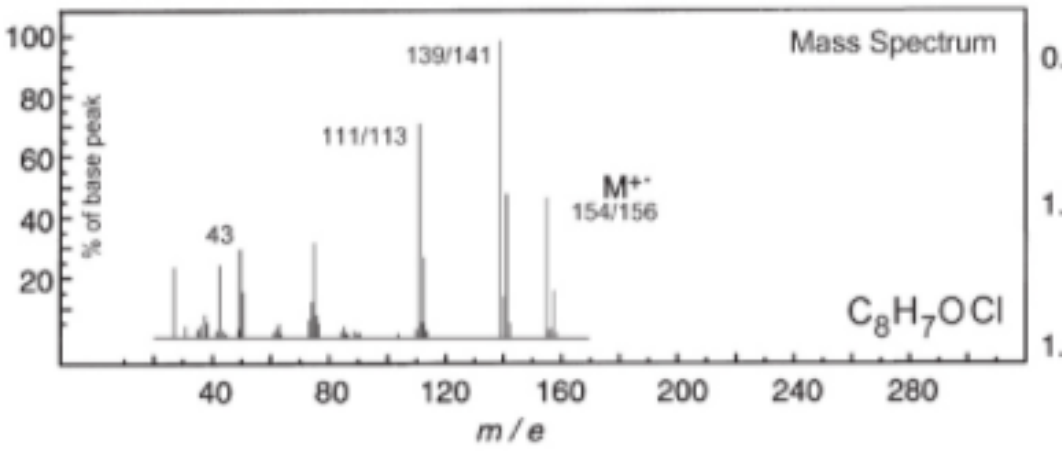
solvent : methanol

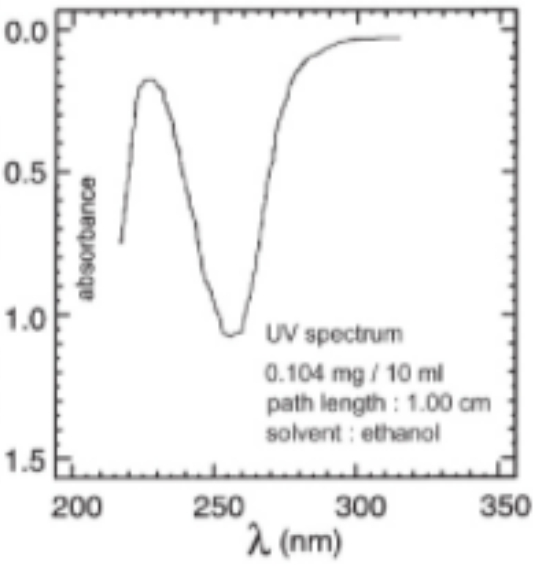


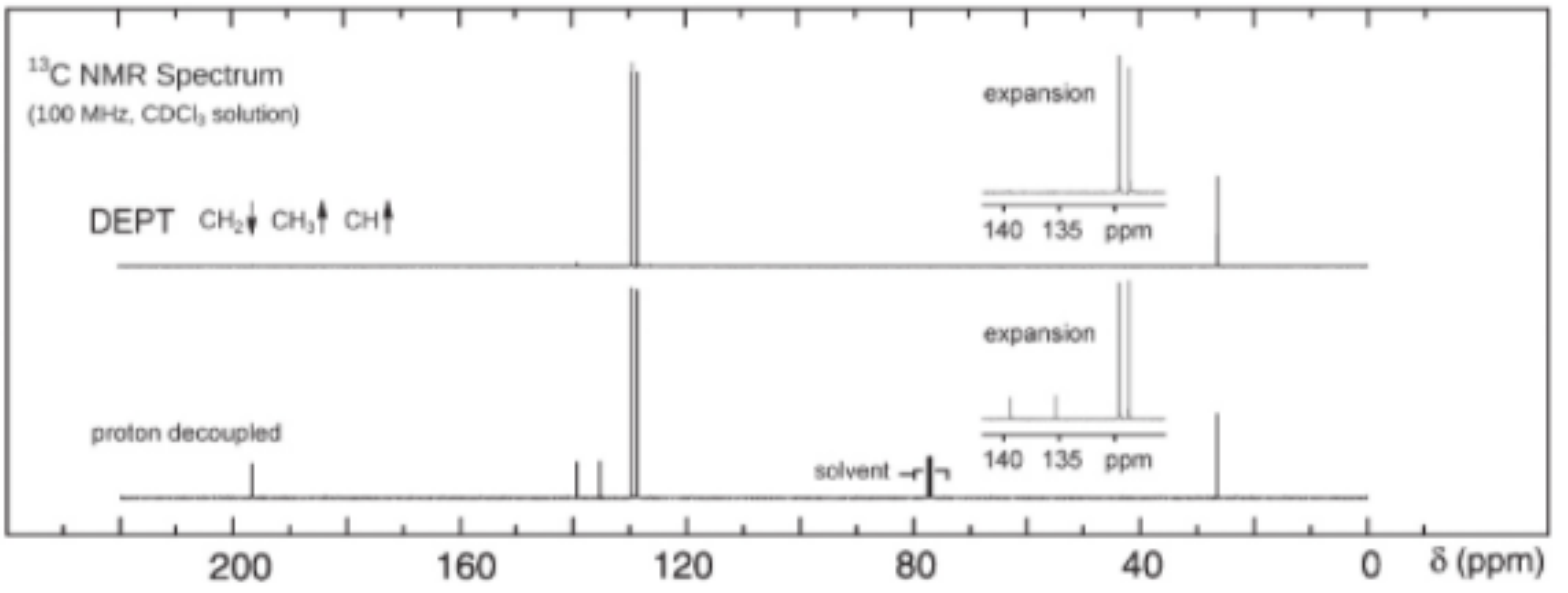


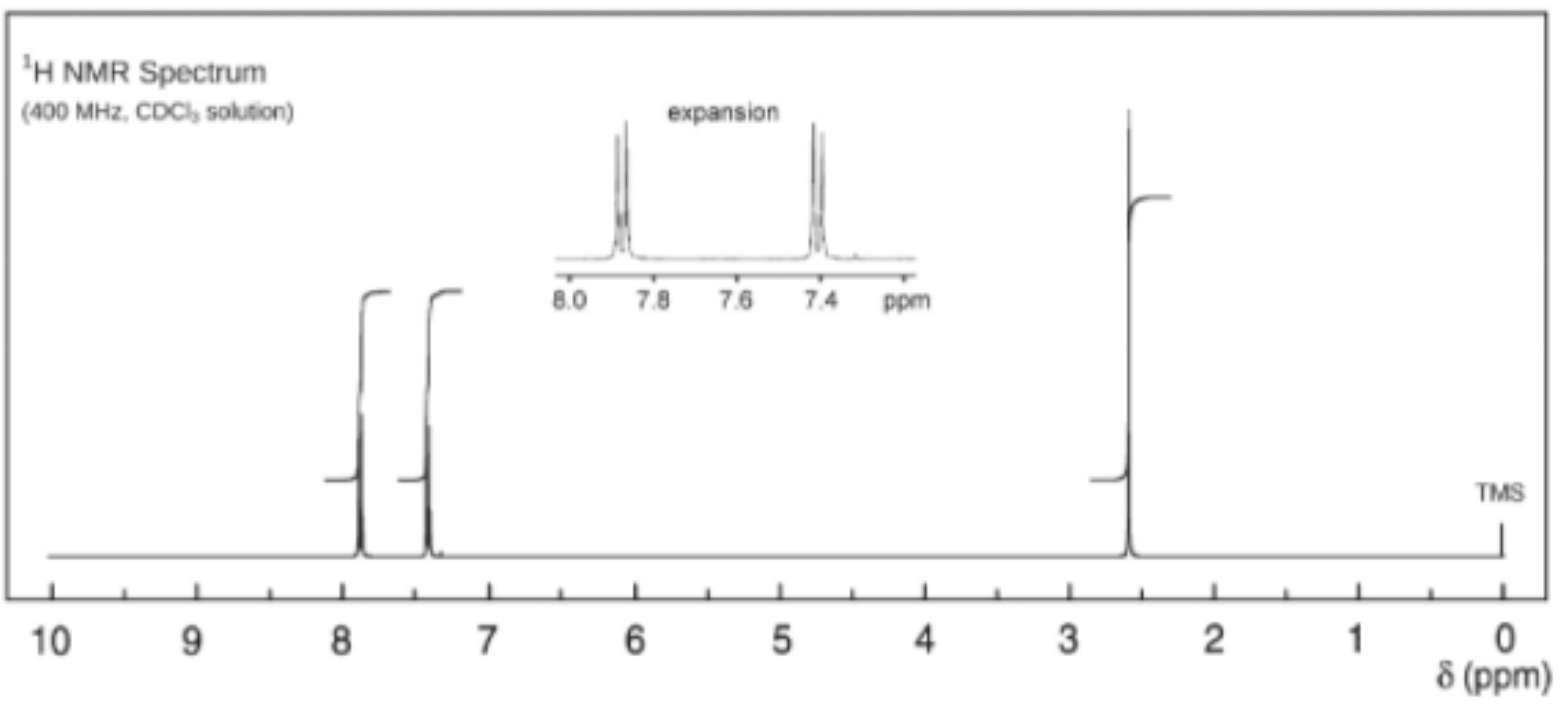
Problem 126

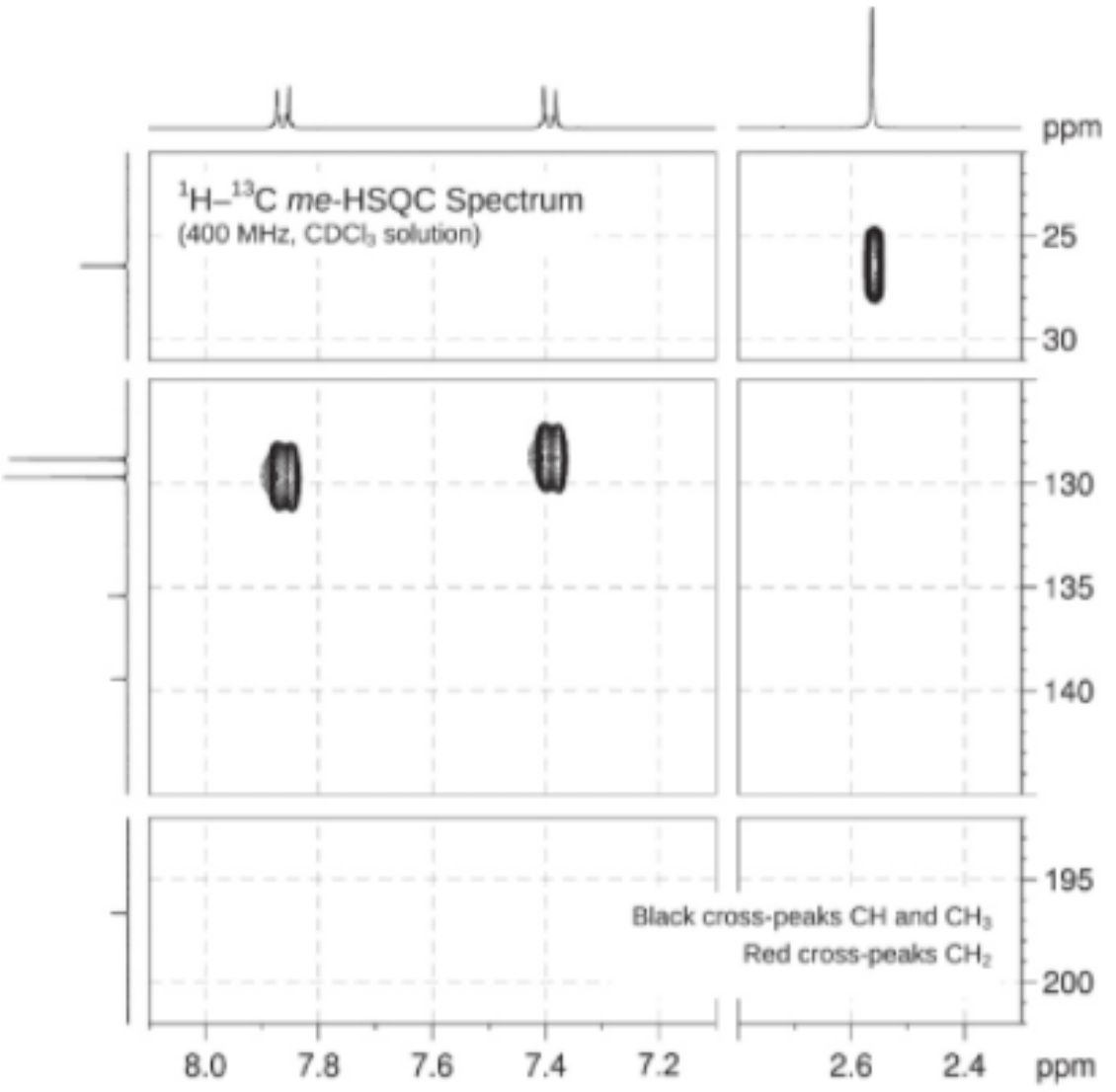

IR Spectrum
(liquid film)
1690
4000
3000
2000
1600
1200
800
ν (cm-1)

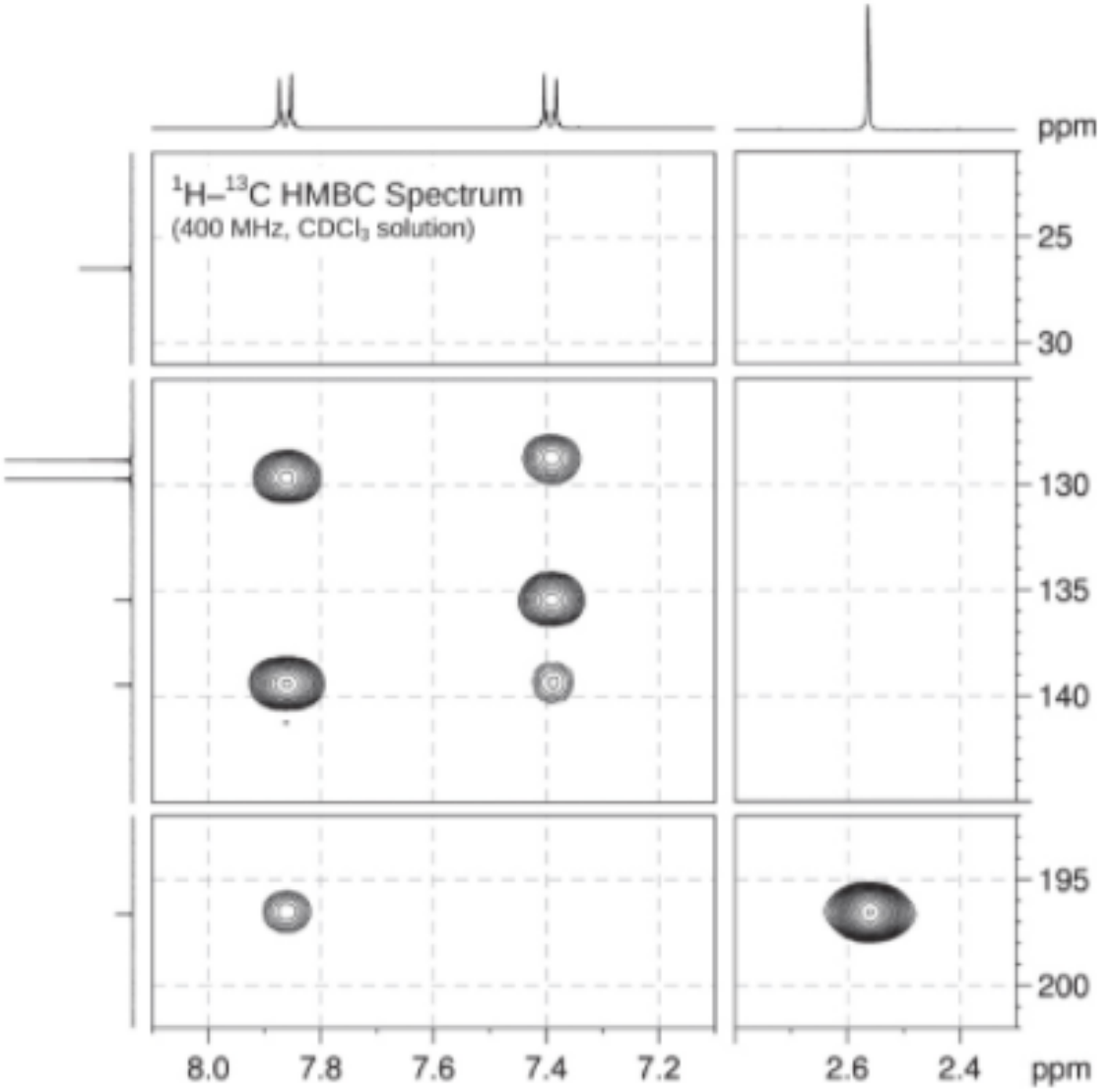

Mass Spectrum
% of base peak
100
80
60
40
20
139/141
111/113
M+·
154/156
43
C8H7OCl
40
80
120
160
200
240
280
m / e


absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.104 mg / 10 ml
path length : 1.00 cm
solvent : ethanol
200
250
300
350
λ (nm)

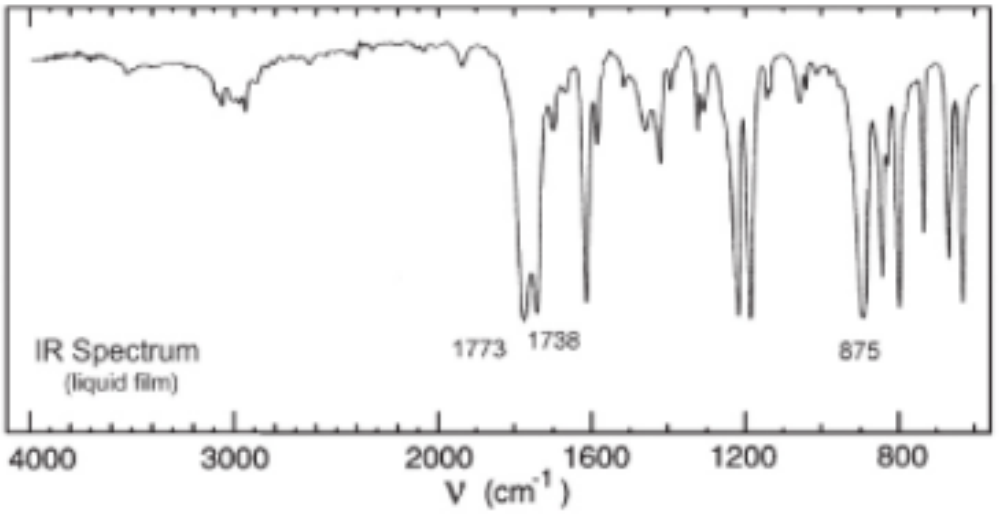

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
expansion
140 135 ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

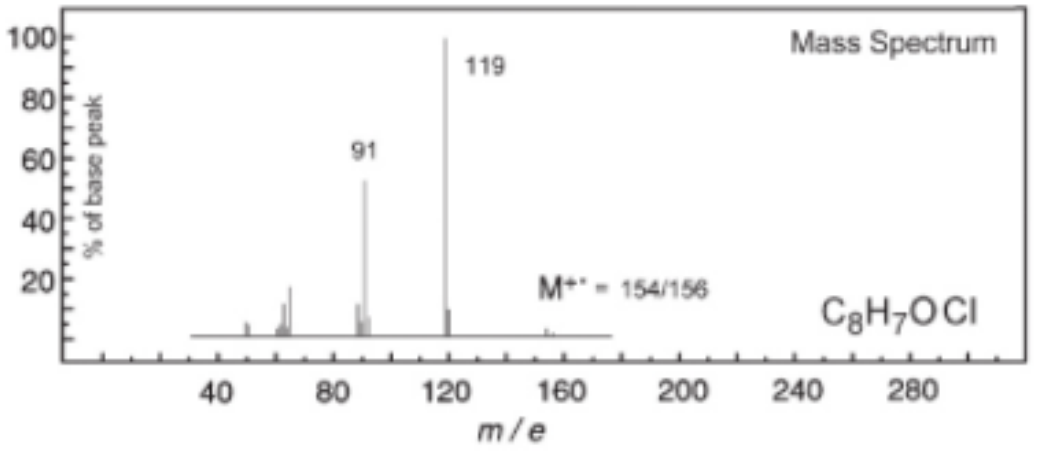

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
8.0 7.8 7.6 7.4 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
ppm
25
30
130
135
140
195
200
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
8.0
7.8
7.6
7.4
7.2
2.6
2.4
ppm


^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
ppm
25
30
130
135
140
195
200
8.0
7.8
7.6
7.4
7.2
2.6
2.4
ppm

Problem 127





UV Spectrum

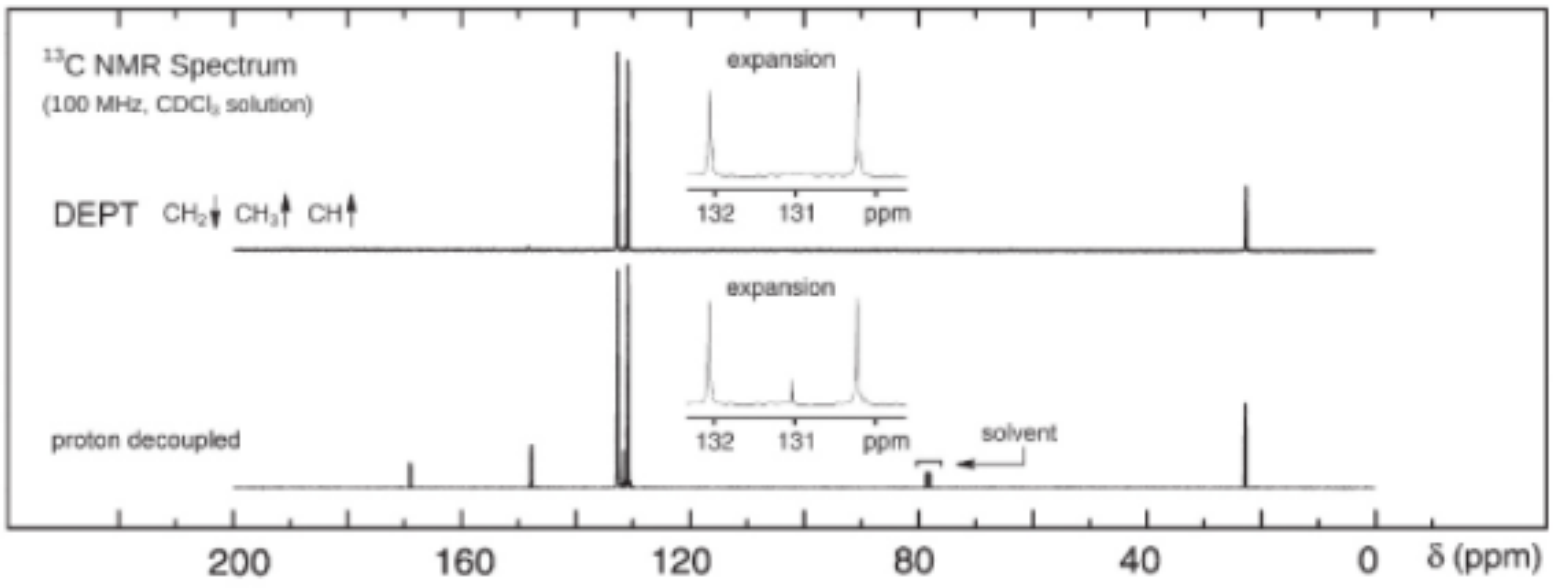
λ_{max} 254 nm ($\log_{10}\varepsilon$ 4.3)

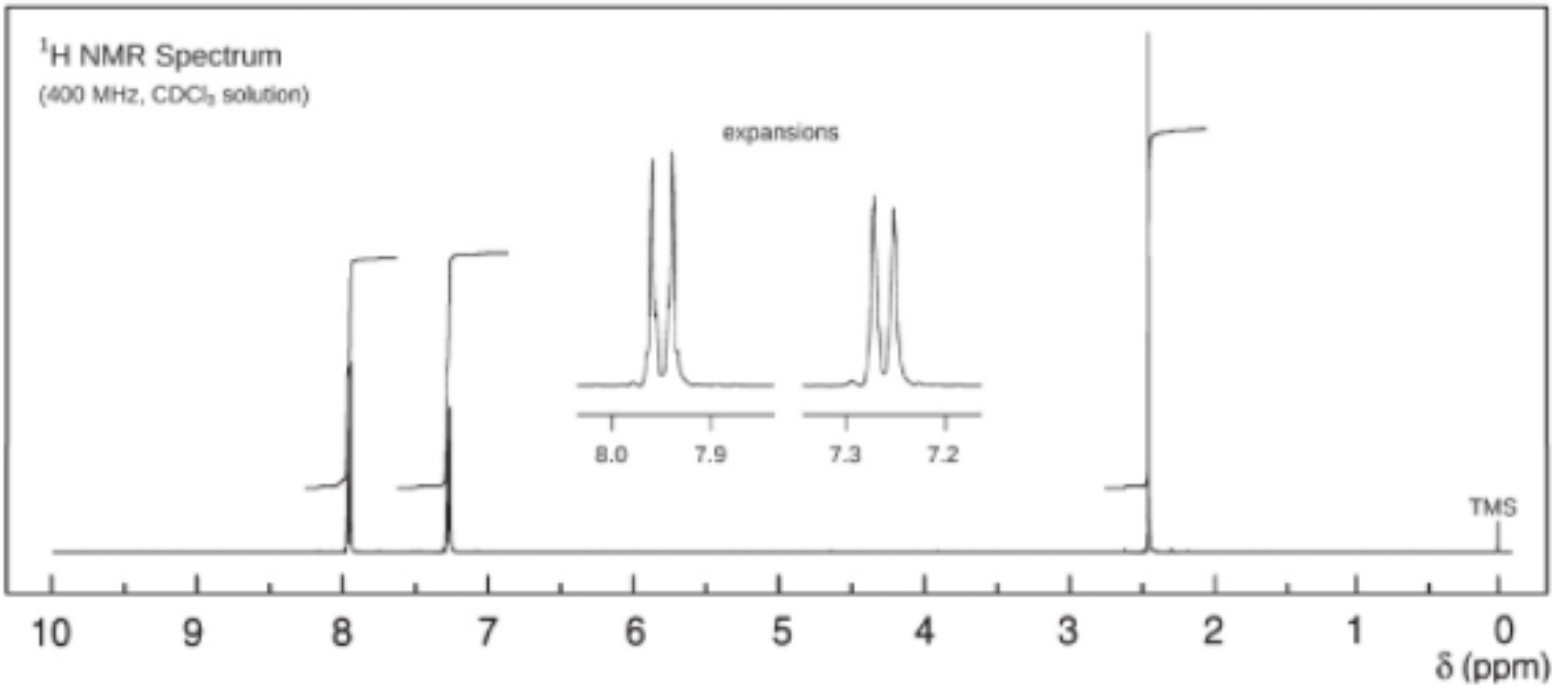
λ_{max} 258 nm ($\log_{10}\varepsilon$ 4.2)

λ_{max} 279 nm ($\log_{10}\varepsilon$ 3.3)

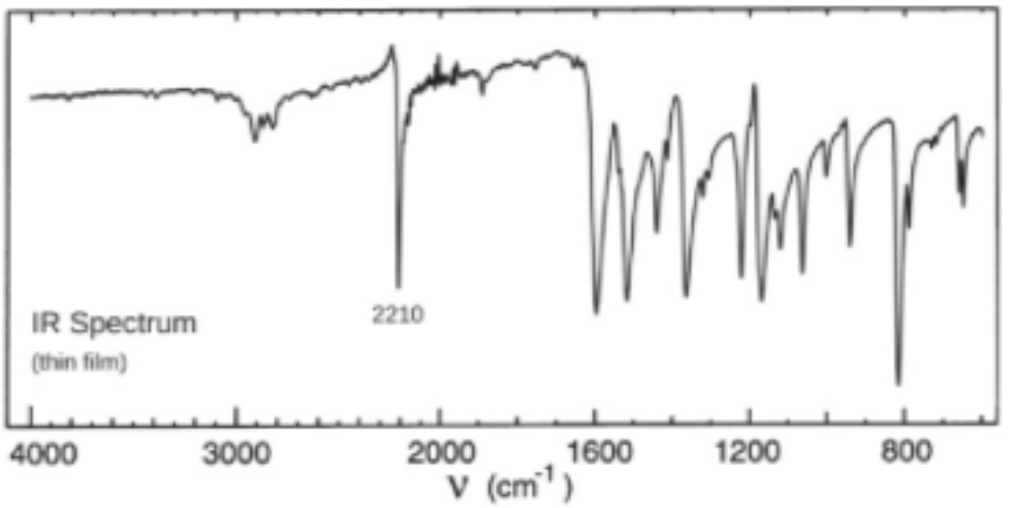
λ_{max} 290 nm ($\log_{10}\varepsilon$ 3.0)

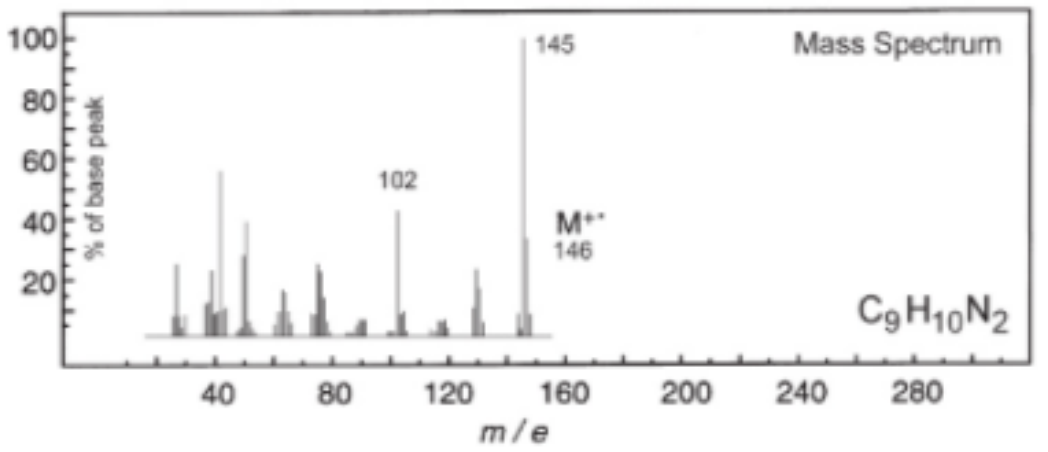
solvent : hexane

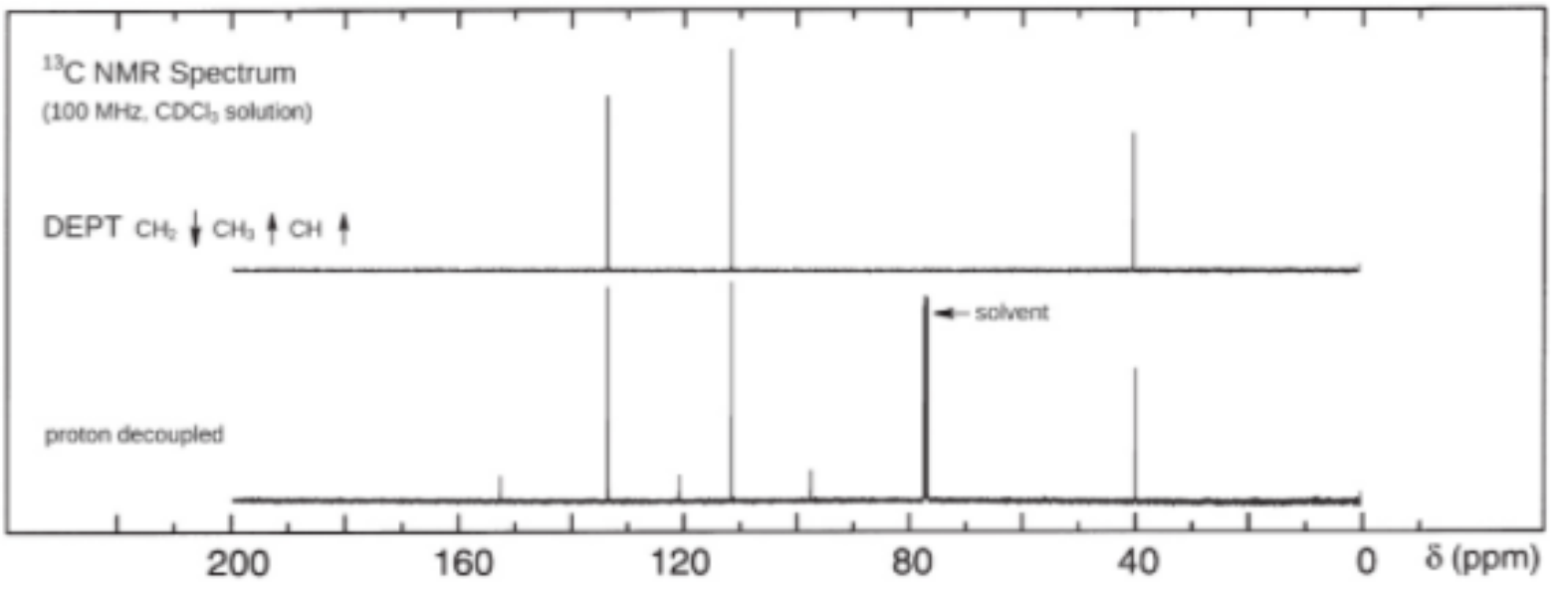


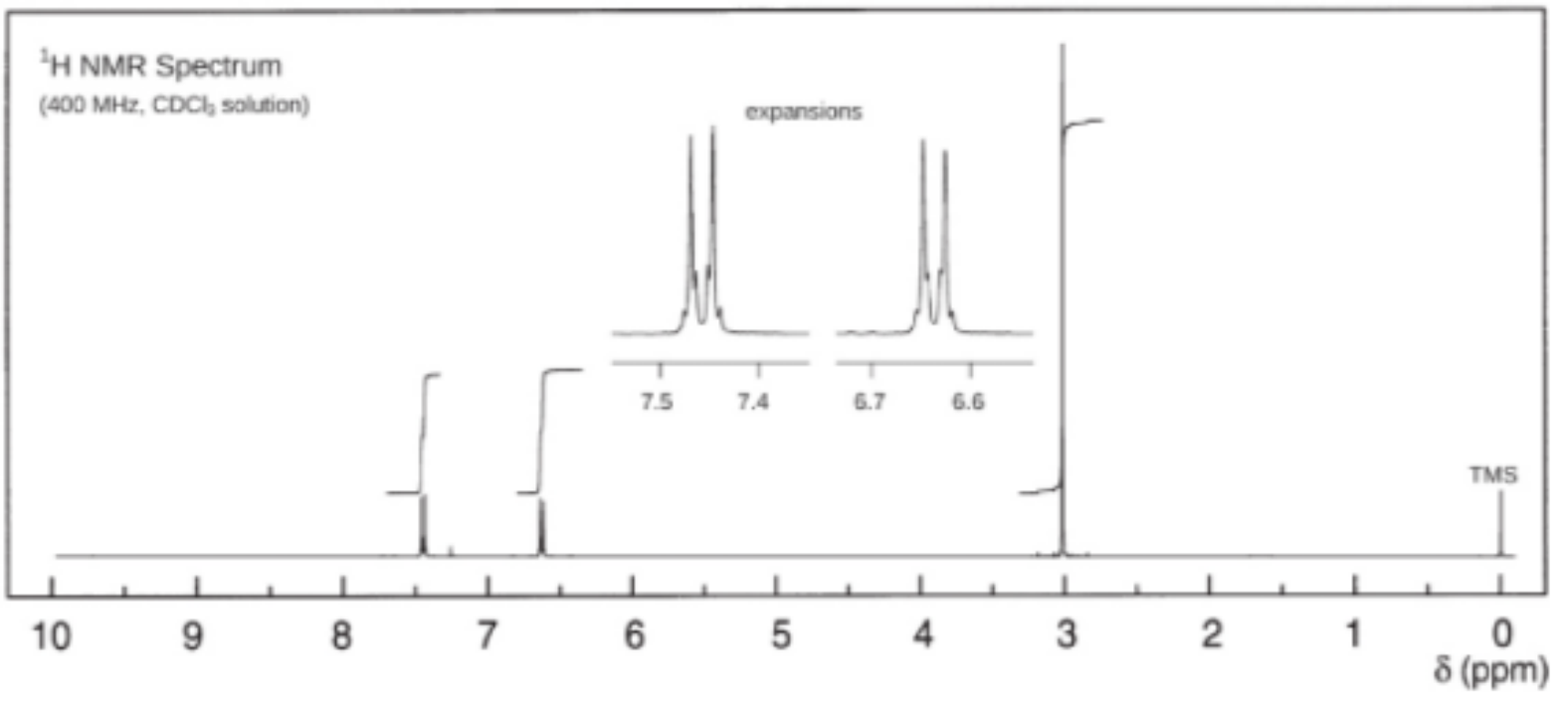


Problem 128

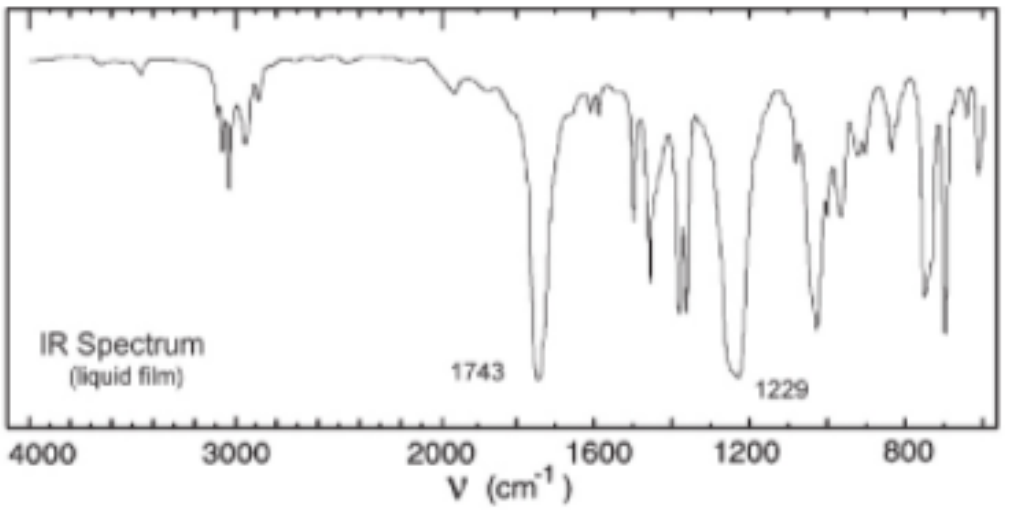

IR Spectrum
(thin film)
2210
4000
3000
2000
1600
1200
800
ν (cm-1)

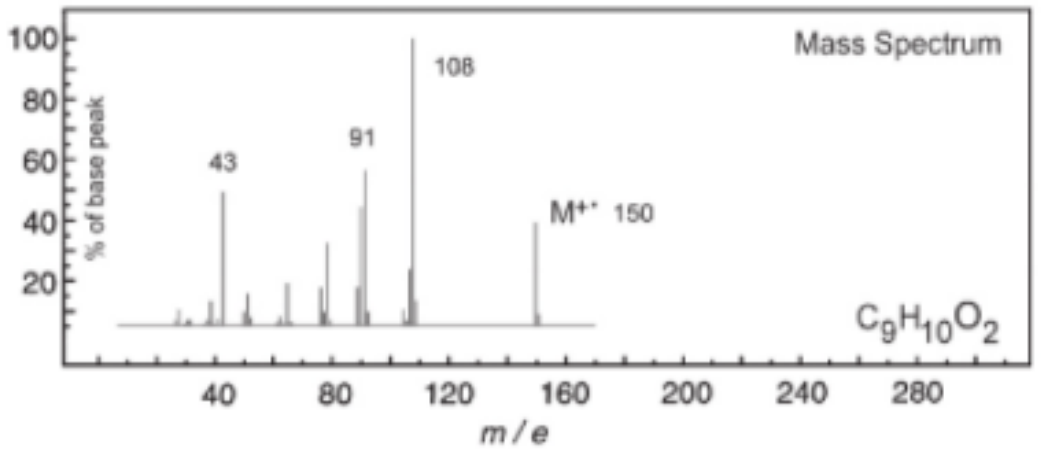

Mass Spectrum
% of base peak
100
80
60
40
20
145
102
M+·
146
C9H10N2
40
80
120
160
200
240
280
m/e


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
7.5
7.4
6.7
6.6
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 129

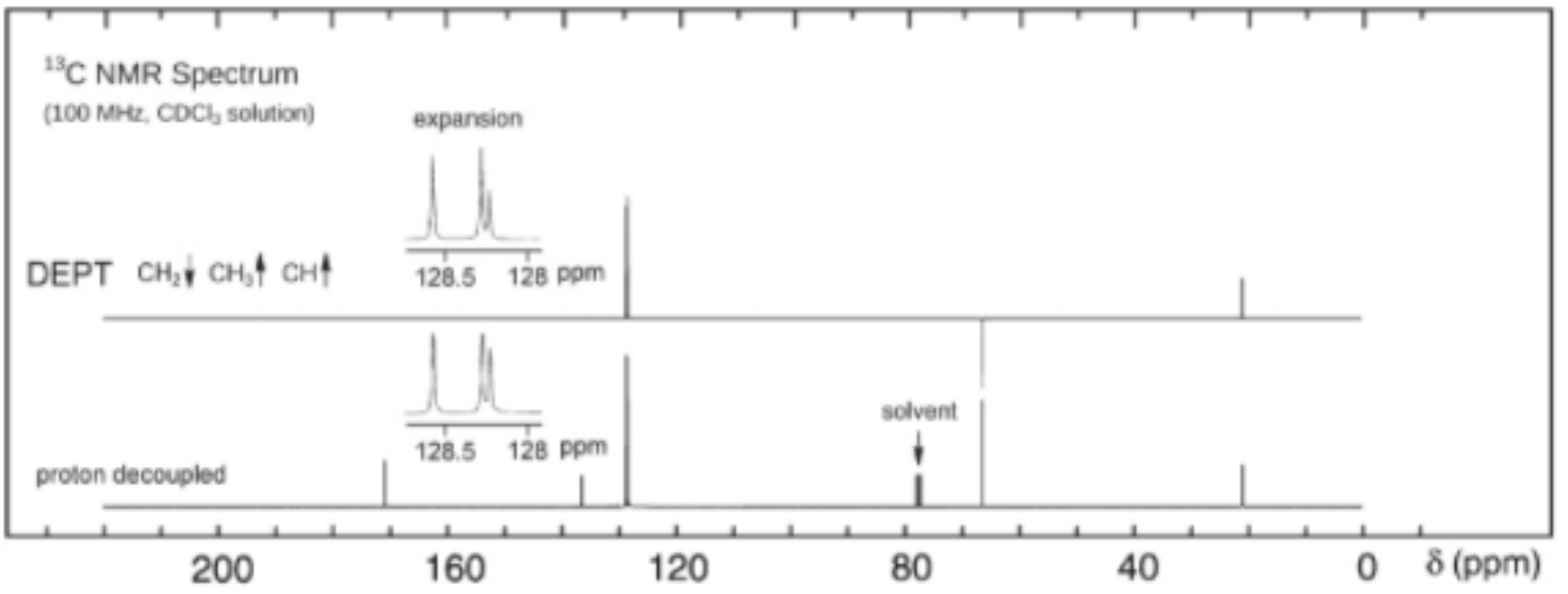


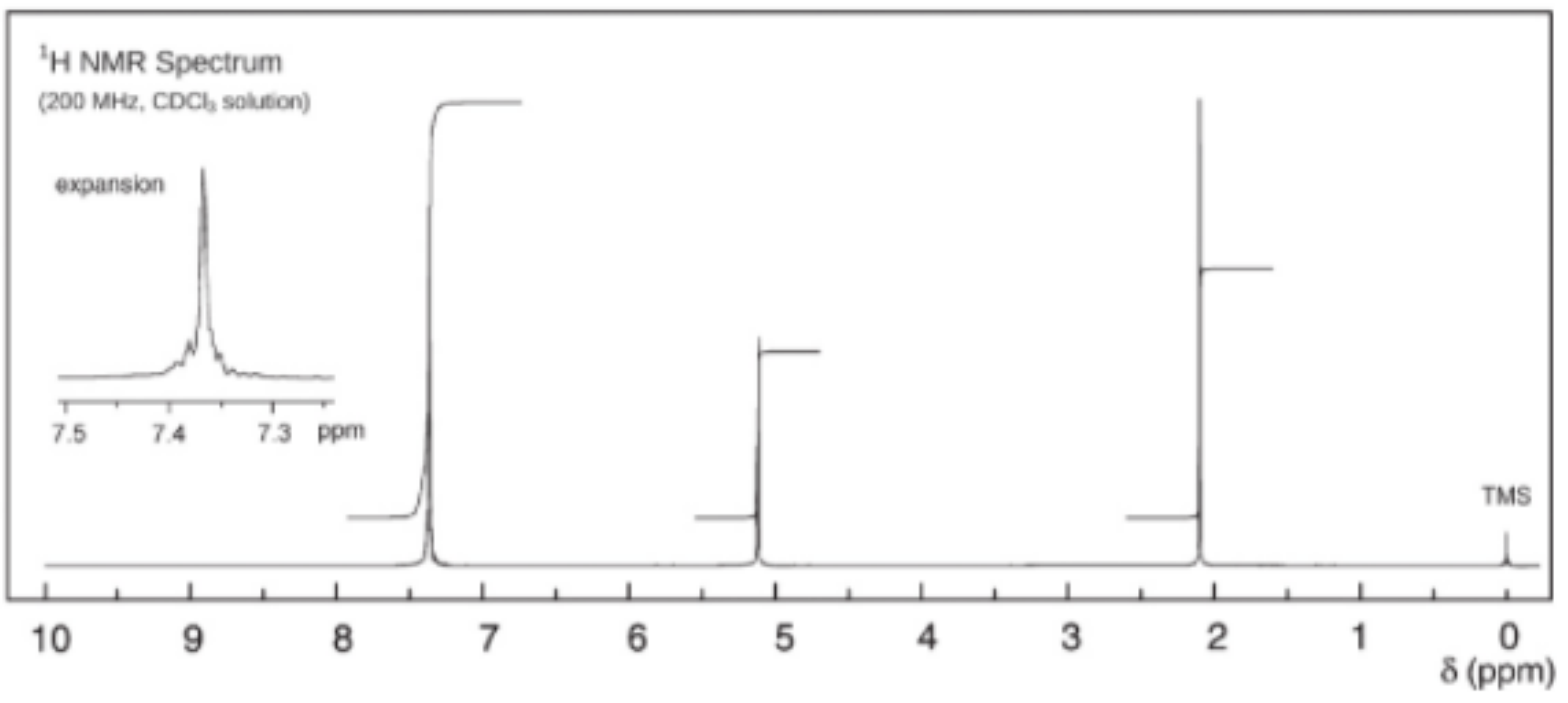


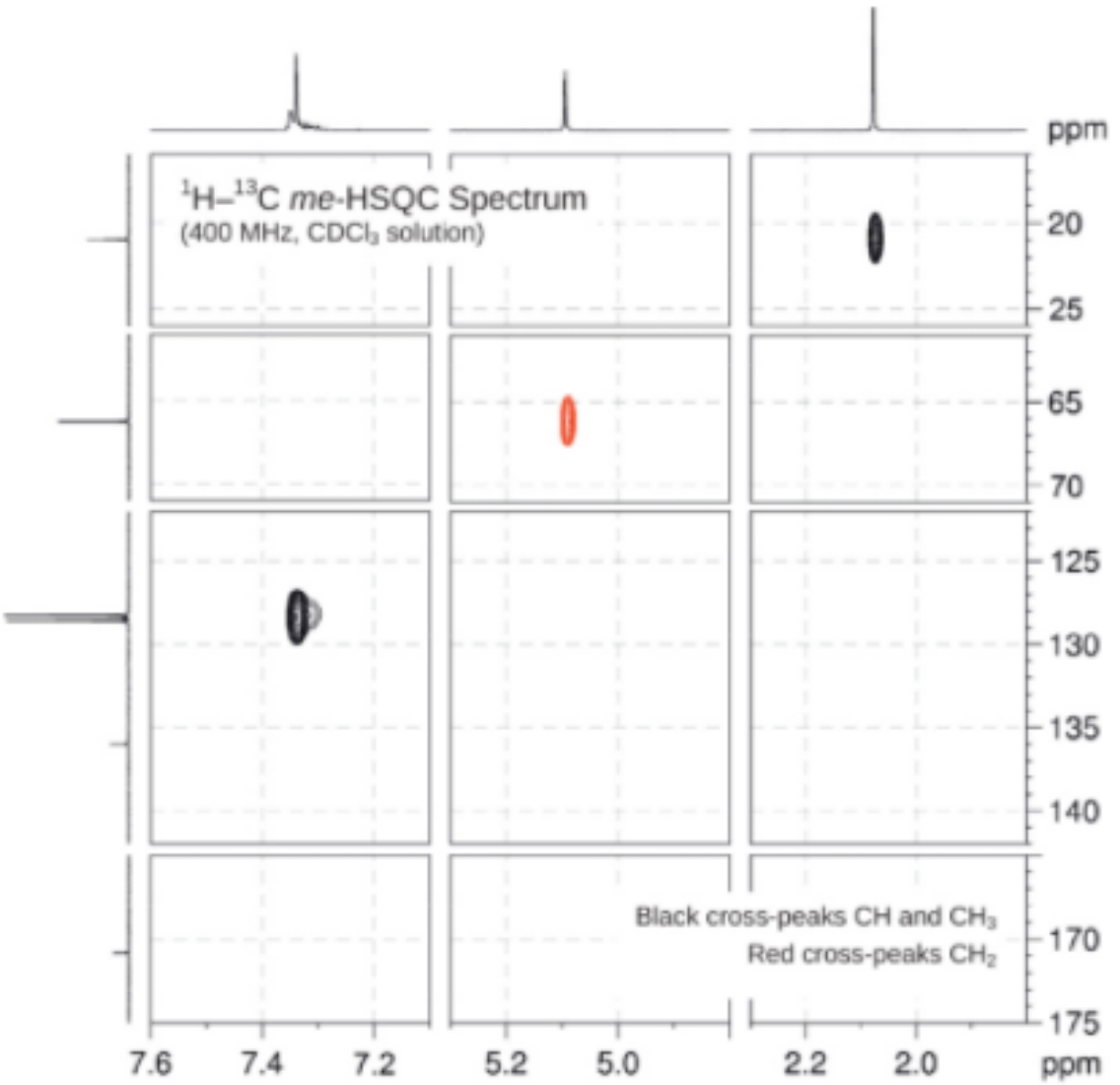
UV Spectrum

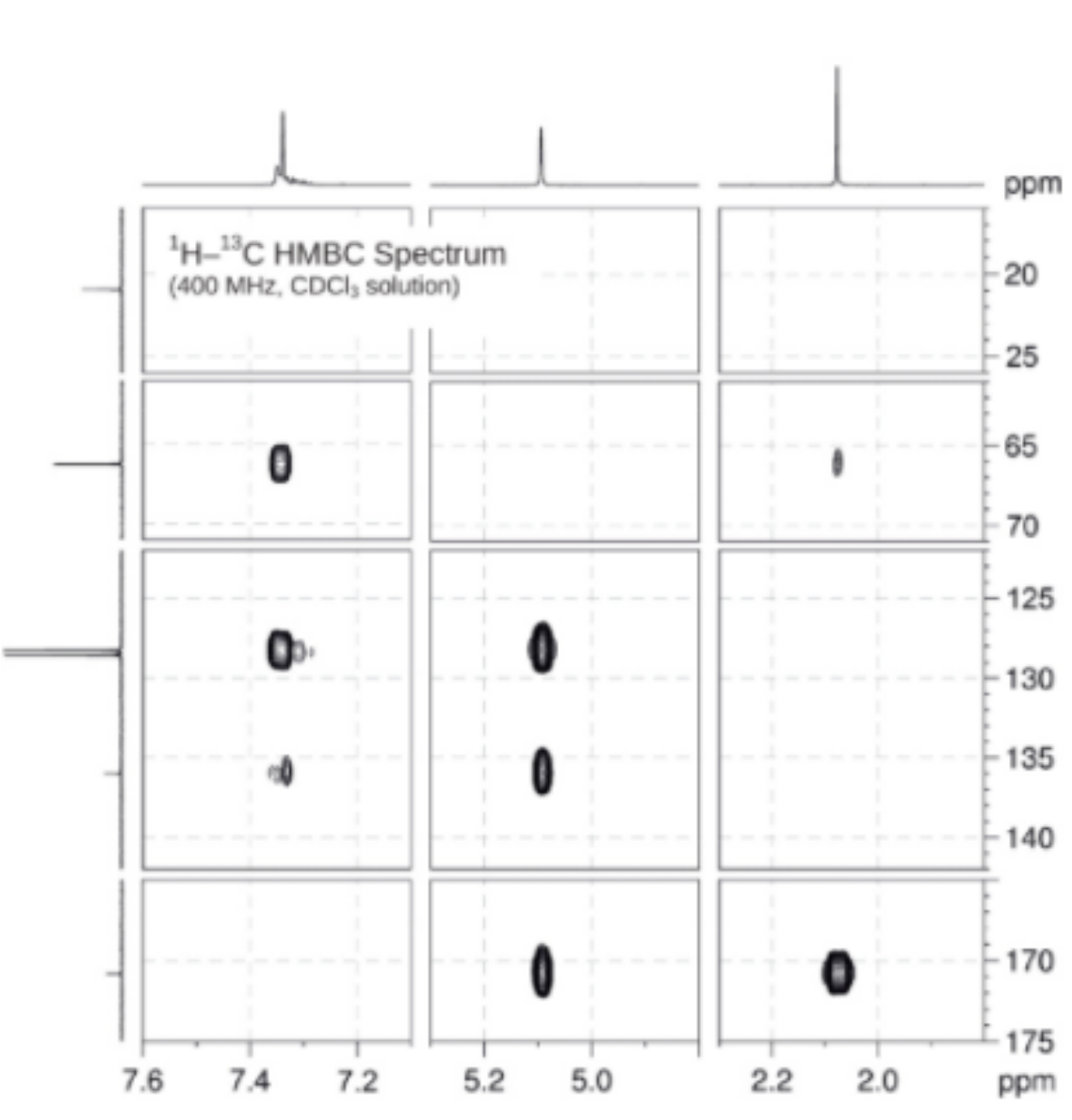
λ_{max} 252 nm ($\log_{10}\varepsilon$ 2.2)
λ_{max} 257 nm ($\log_{10}\varepsilon$ 2.3)
λ_{max} 262 nm ($\log_{10}\varepsilon$ 2.2)
λ_{max} 264 nm ($\log_{10}\varepsilon$ 2.2)
λ_{max} 268 nm ($\log_{10}\varepsilon$ 2.0)

solvent : ethanol

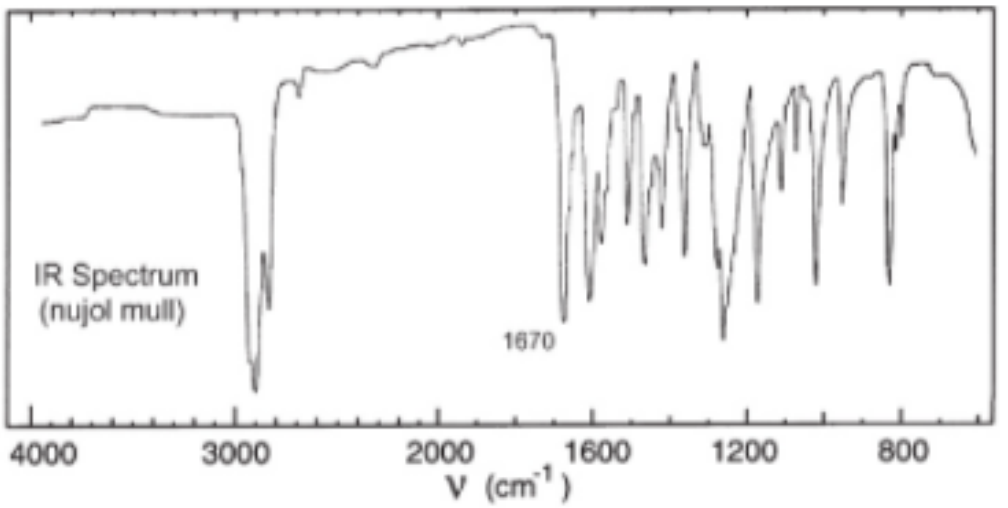


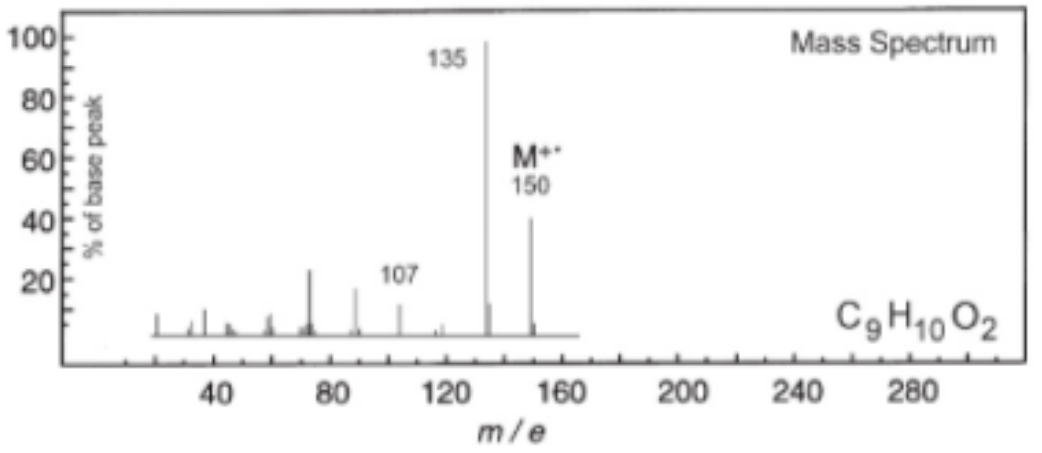



^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
ppm
20
25
65
70
125
130
135
140
170
175
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.6
7.4
7.2
5.2
5.0
2.2
2.0
ppm


^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
ppm
20
25
65
70
125
130
135
140
170
175
7.6
7.4
7.2
5.2
5.0
2.2
2.0
ppm

Problem 130

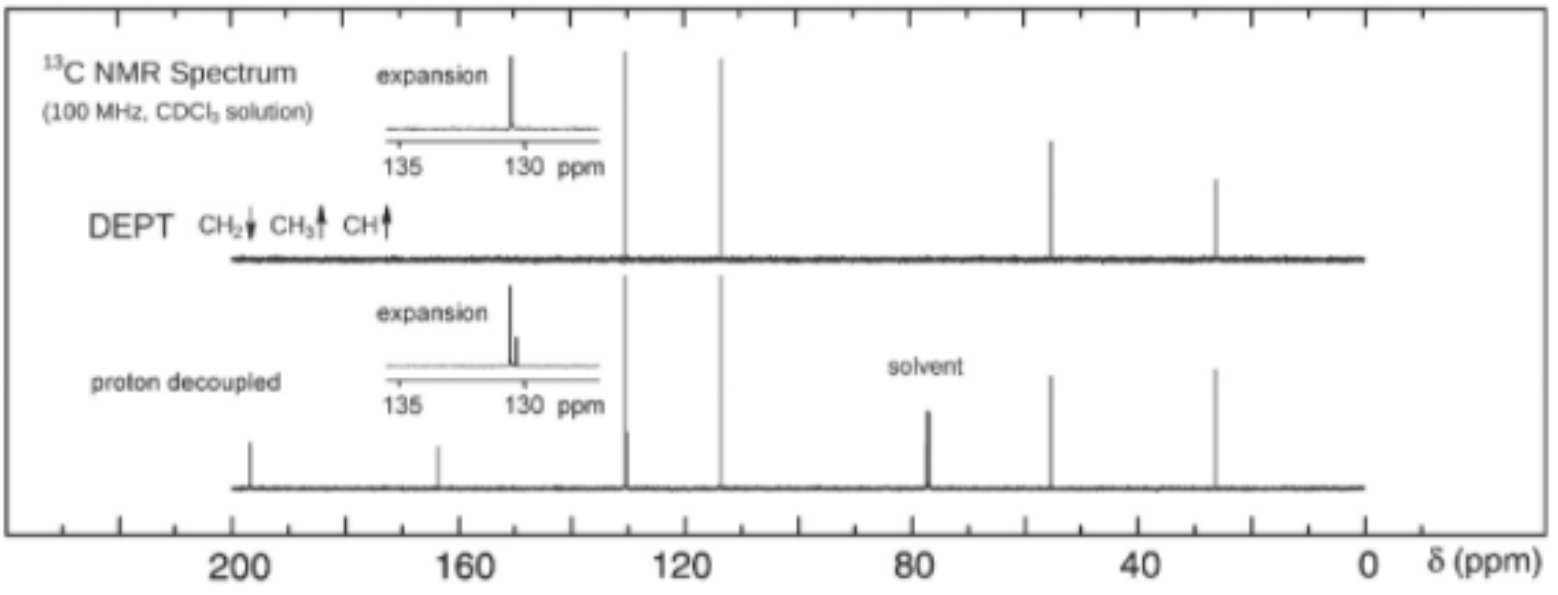


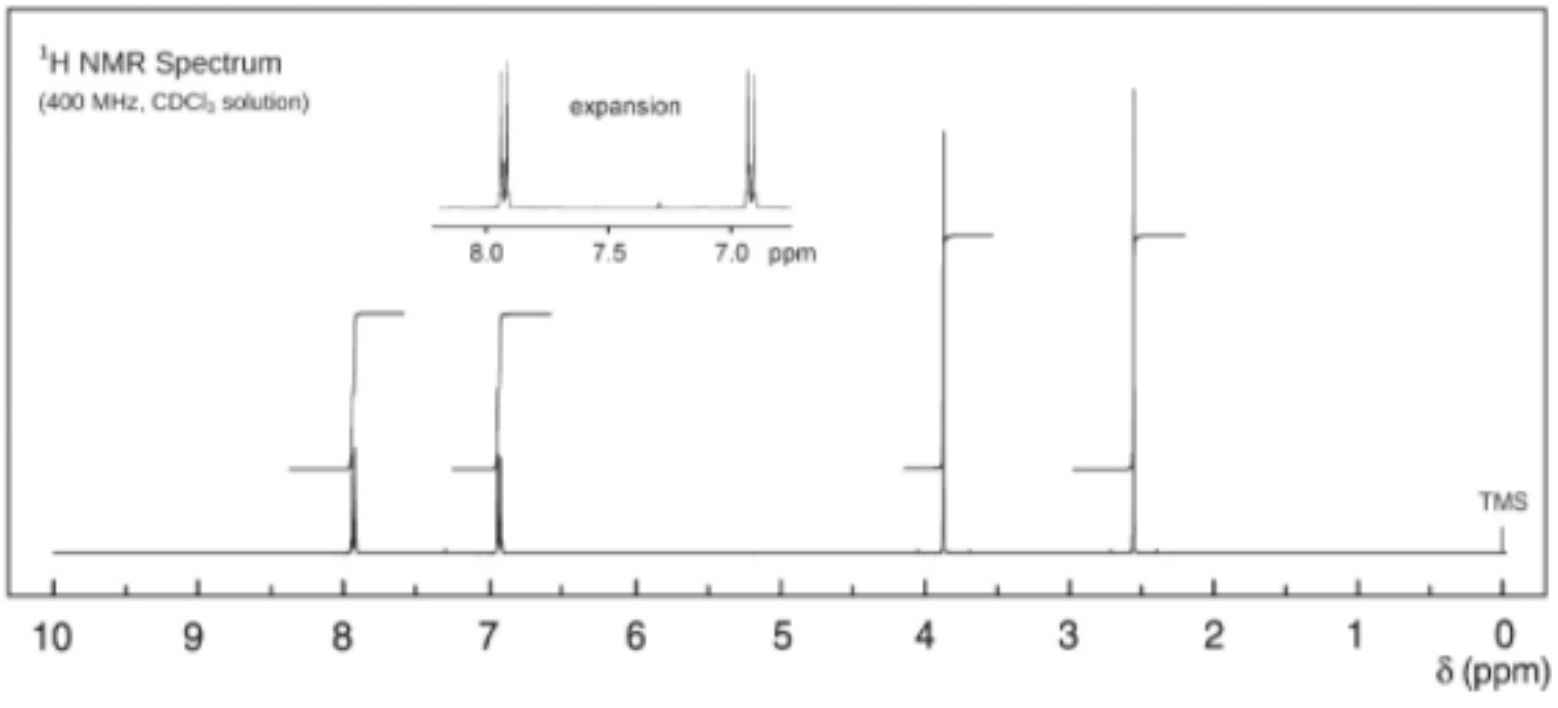


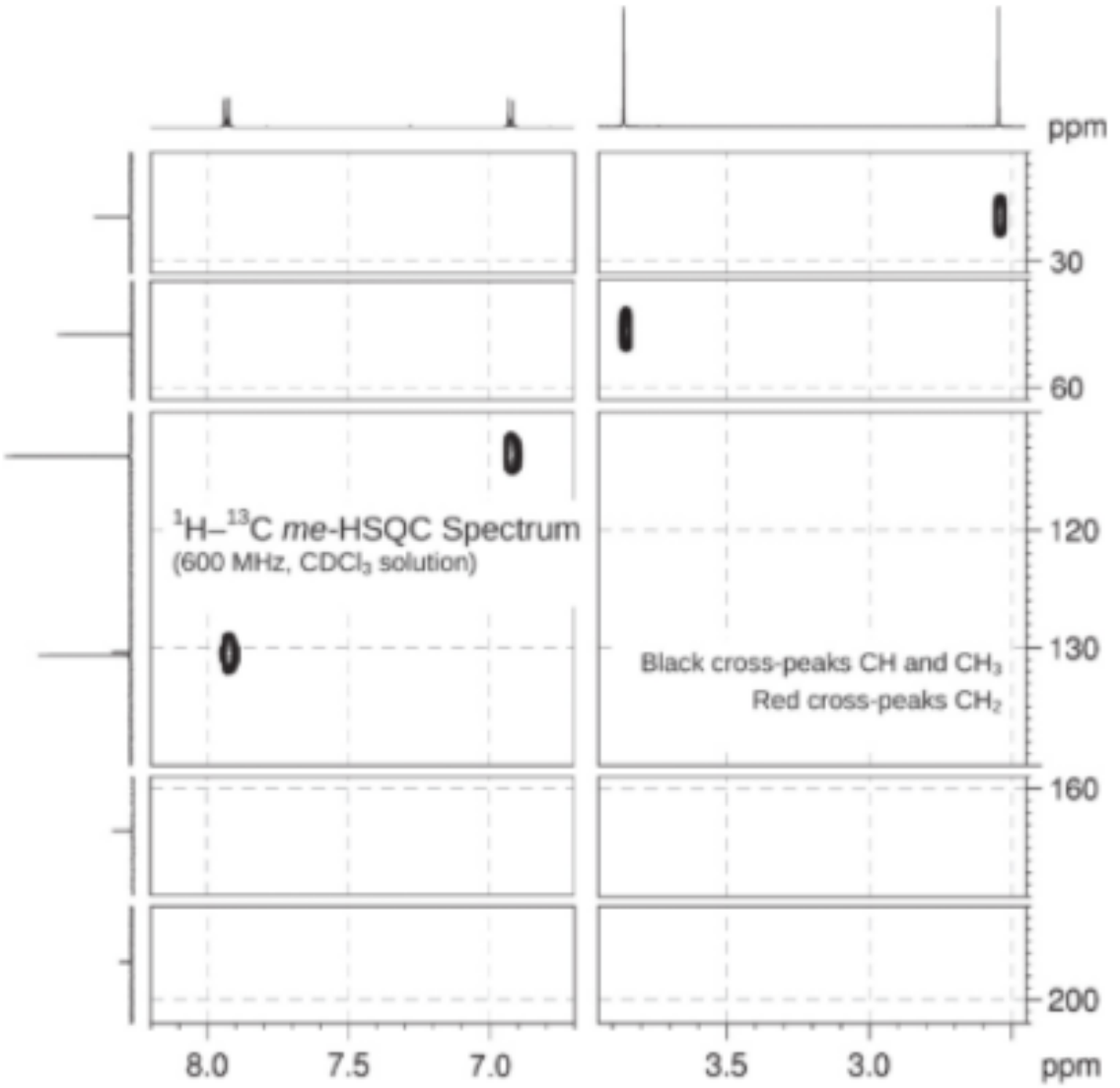
UV Spectrum

λ_{max} 270 ($\log_{10}\varepsilon$ 4.2)

solvent : methanol

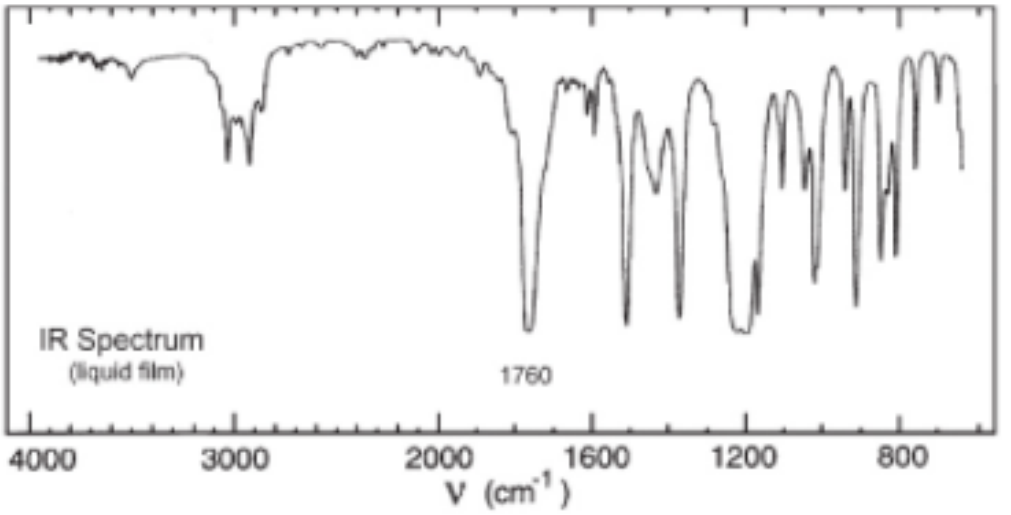


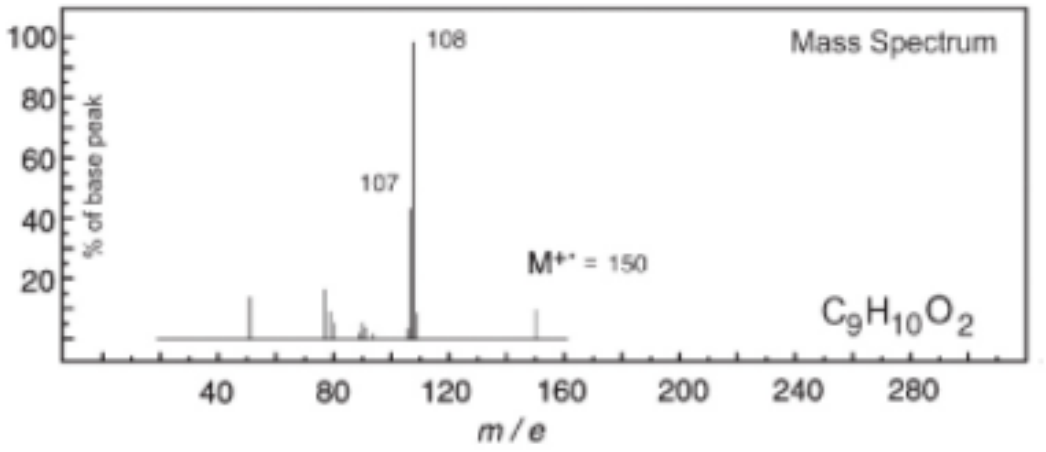



ppm
30
60
120
130
160
200
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
8.0
7.5
7.0
3.5
3.0
ppm

ppm
30
60
120
130
160
200
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)
8.0
7.5
7.0
3.5
3.0
ppm

Problem 131



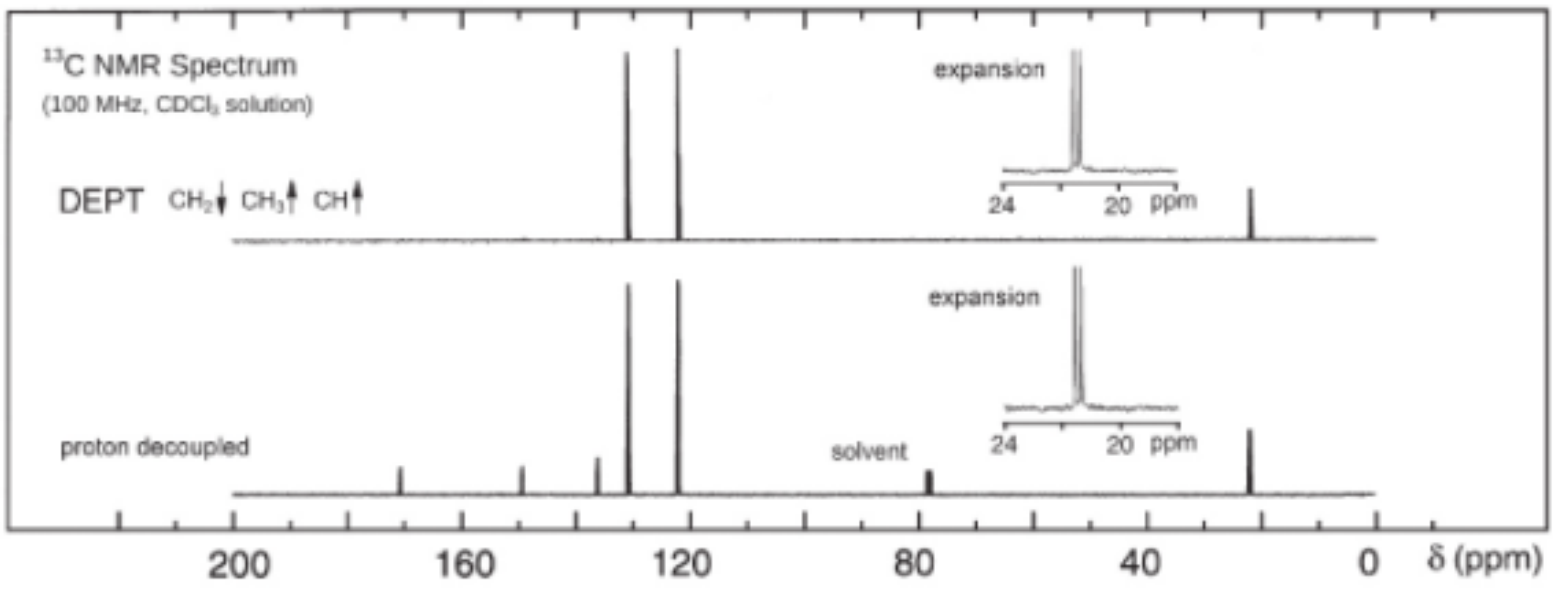


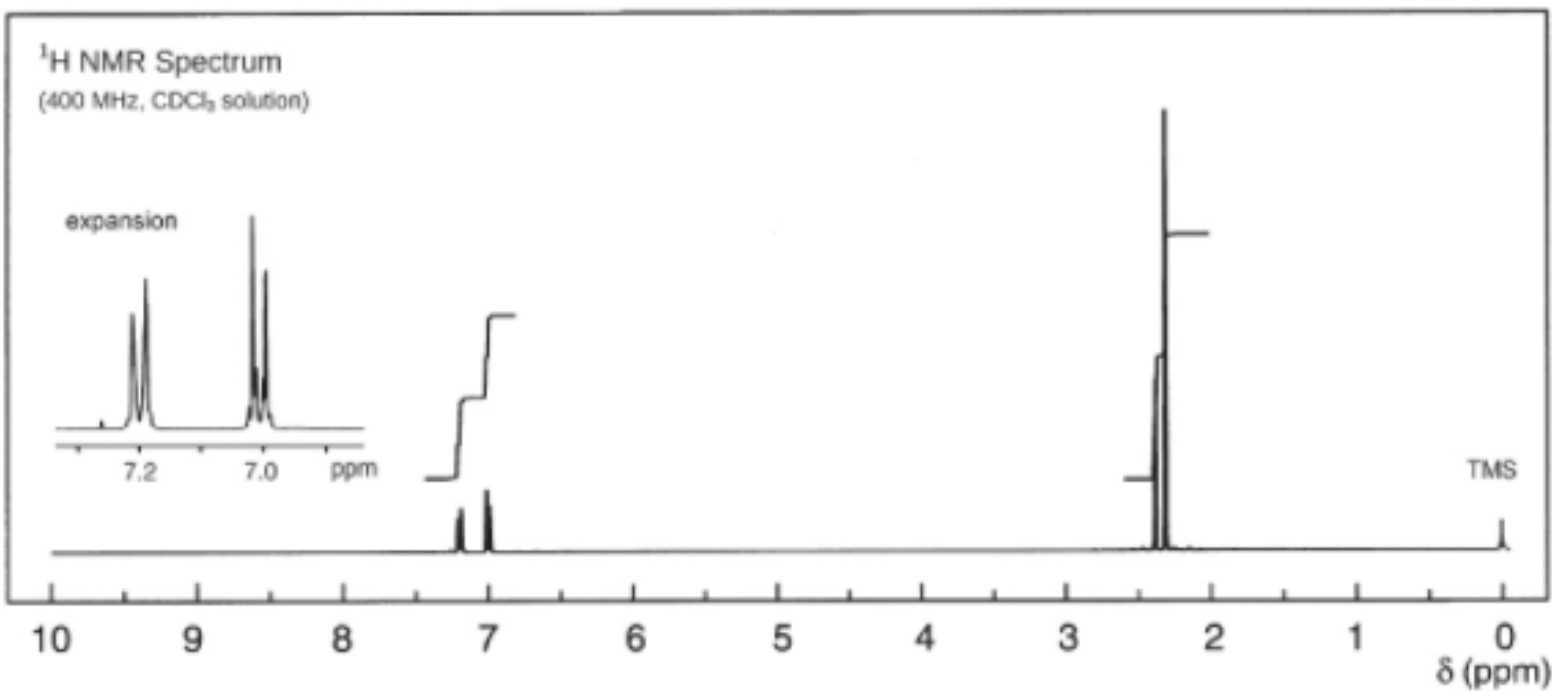
UV Spectrum

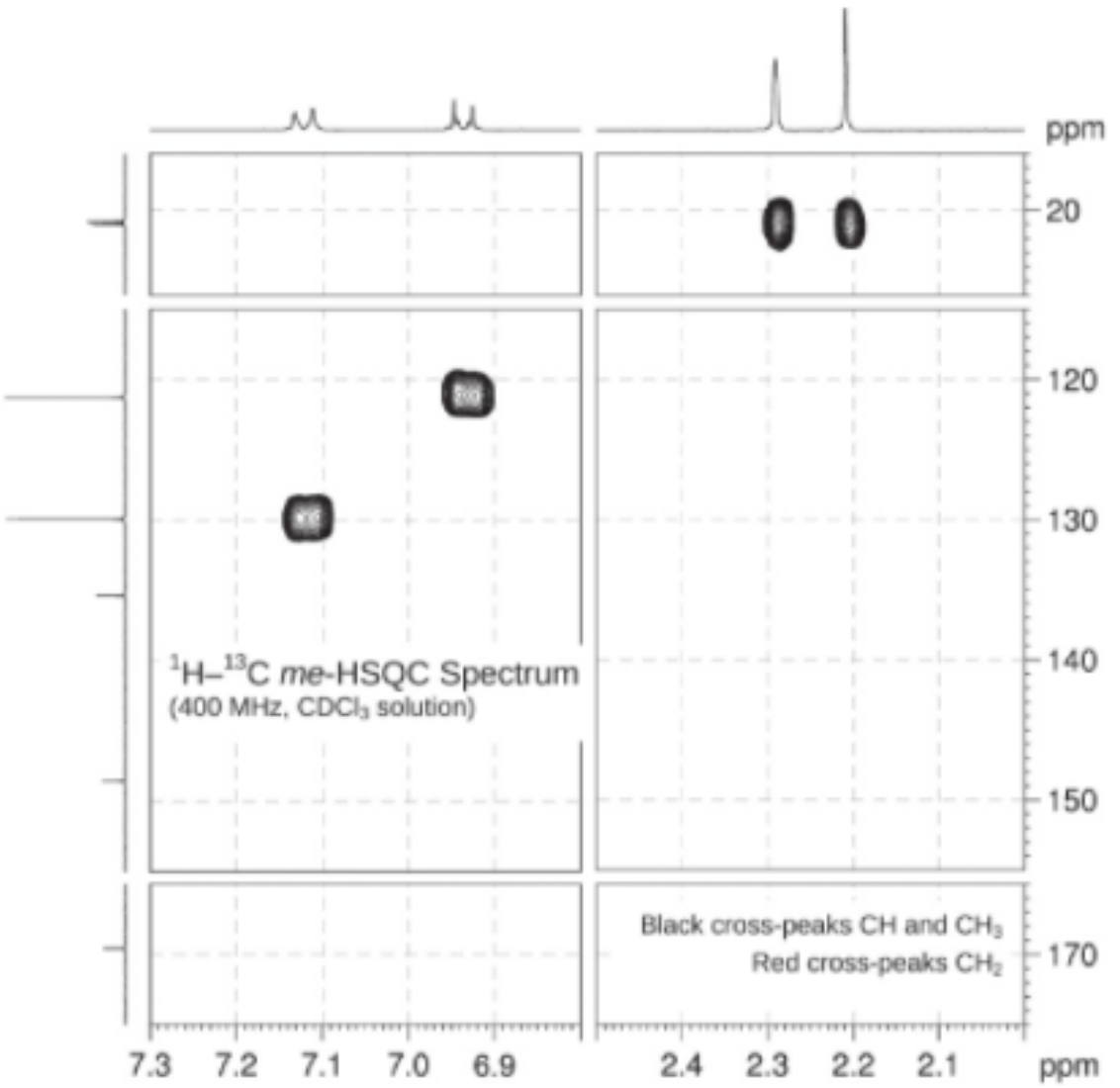
λ_{max} 265 nm ($\log_{10}\varepsilon$ 2.6)

λ_{max} 271 nm ($\log_{10}\varepsilon$ 2.6)

solvent : methanol

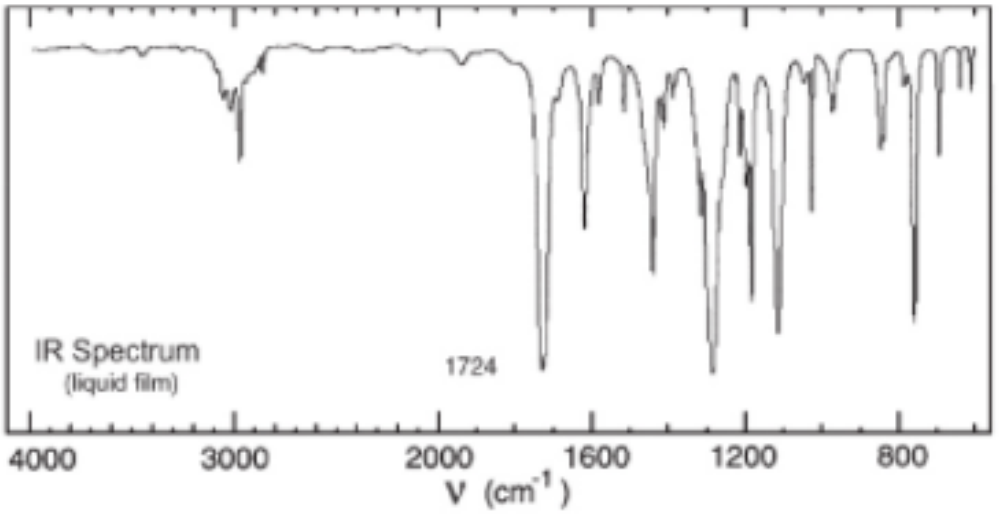


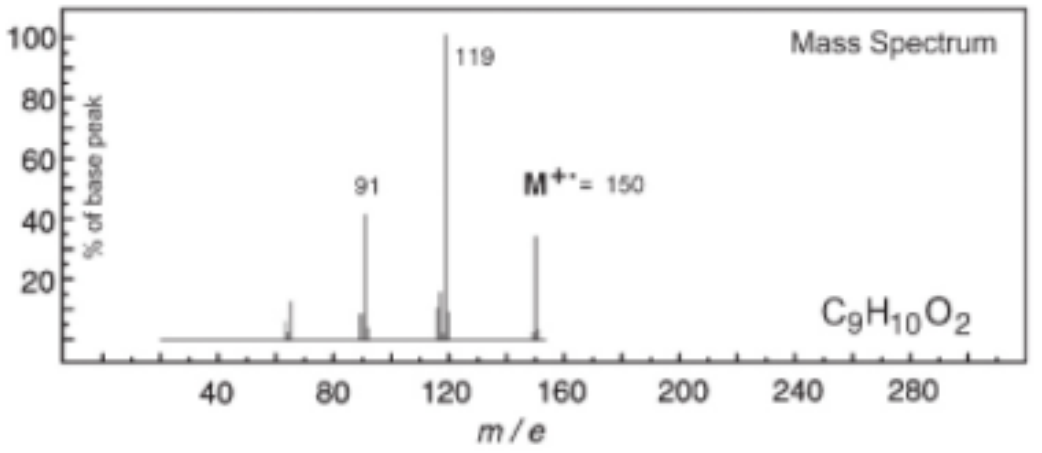



ppm
20
120
130
140
150
170
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.3
7.2
7.1
7.0
6.9
2.4
2.3
2.2
2.1
ppm

ppm
20
120
130
140
150
170
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
7.3
7.2
7.1
7.0
6.9
2.4
2.3
2.2
2.1
ppm

Problem 132



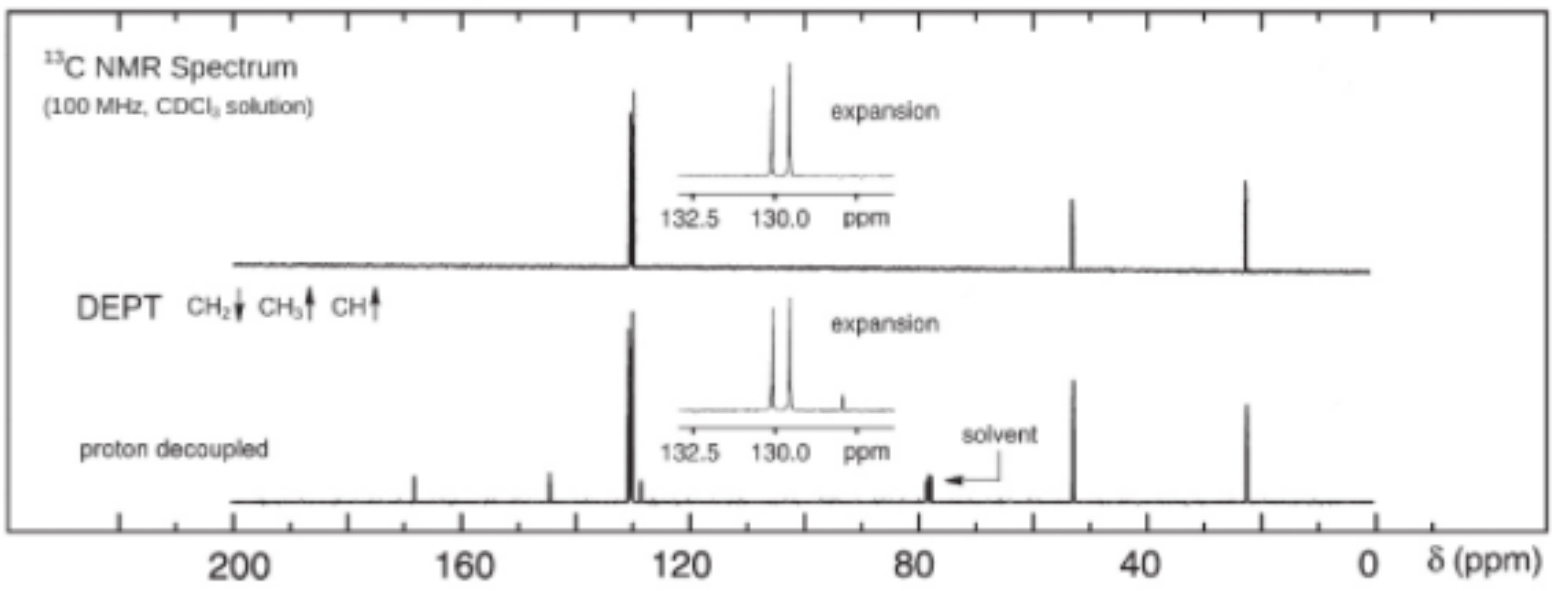


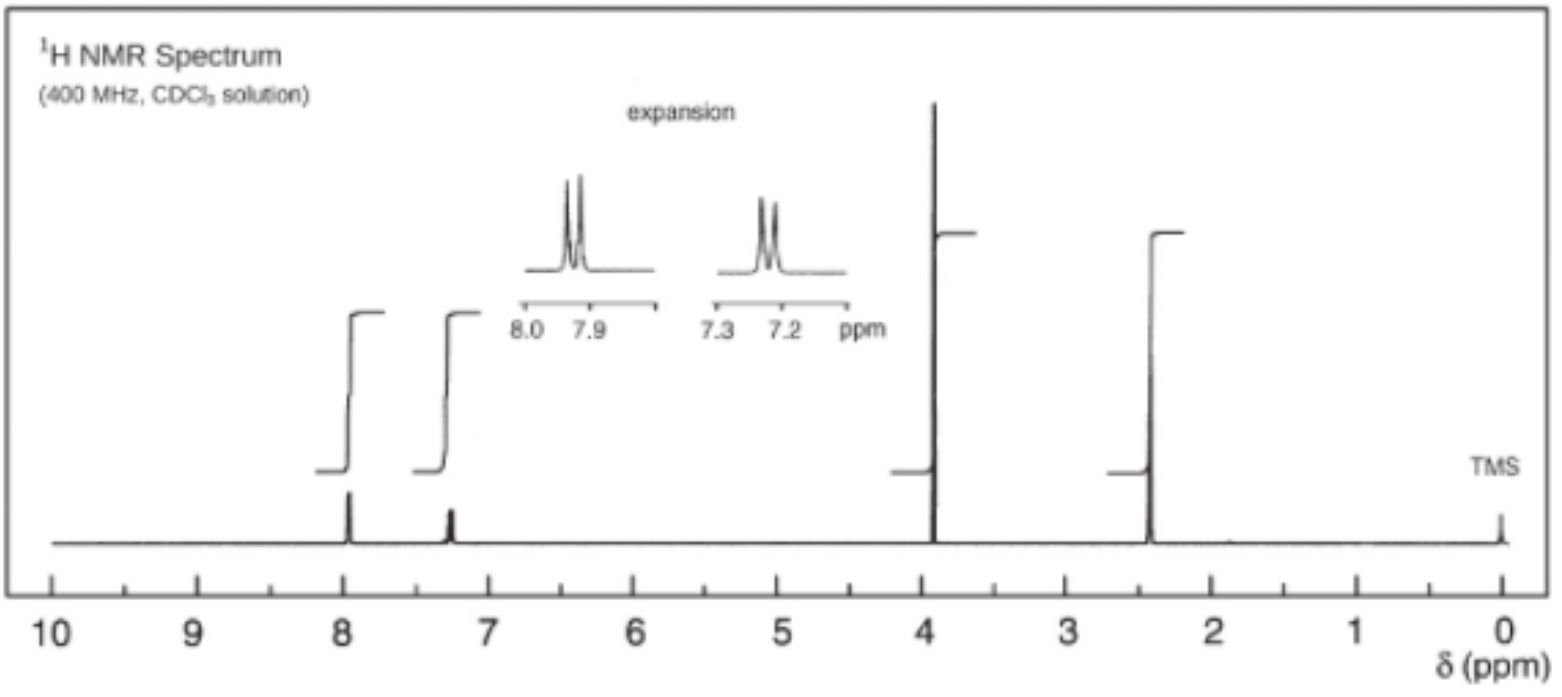
UV Spectrum

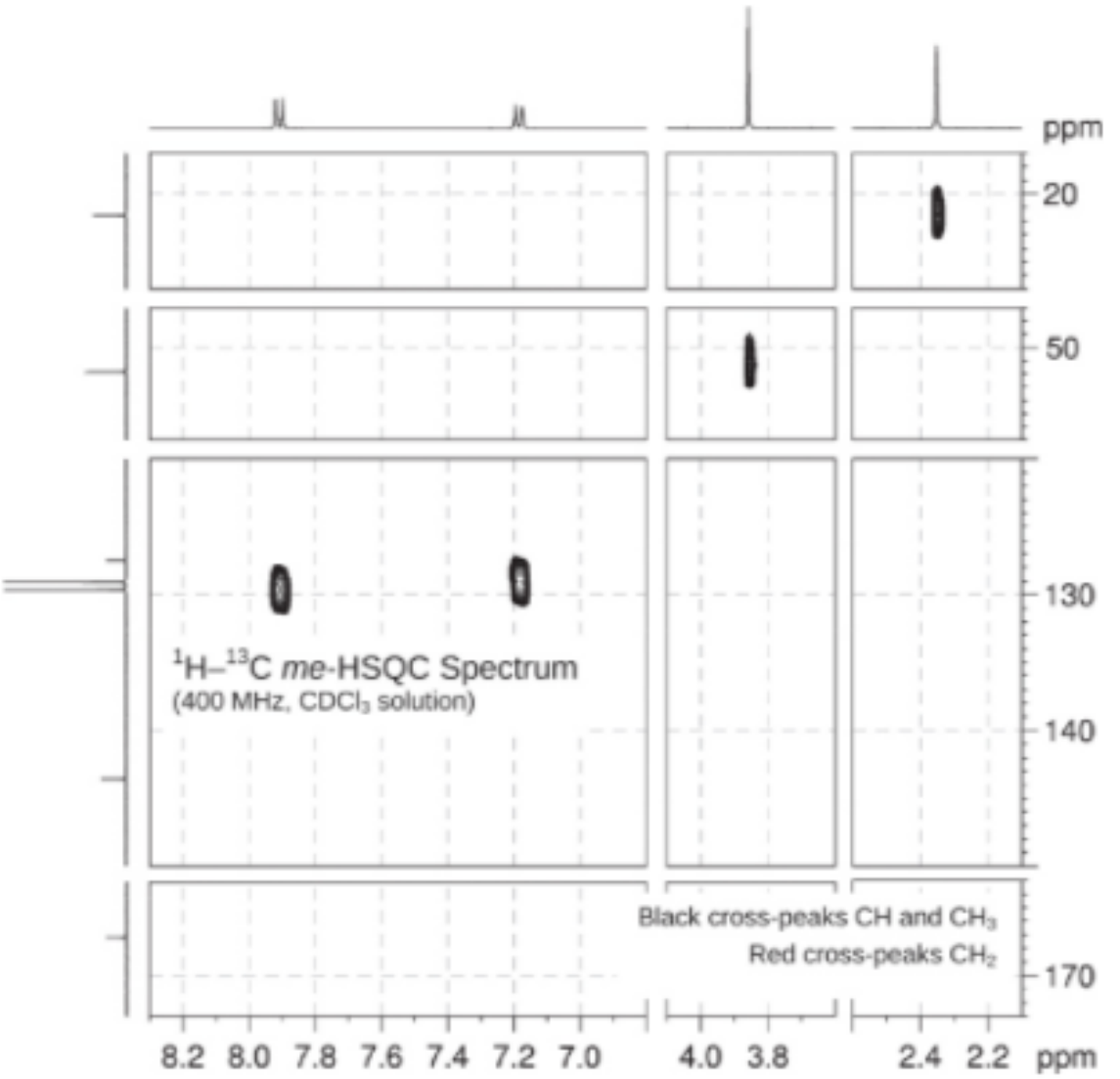
λ_{max} 238 nm ($\log_{10}\varepsilon$ 4.2)

λ_{max} 281 nm ($\log_{10}\varepsilon$ 2.7)

solvent : methanol

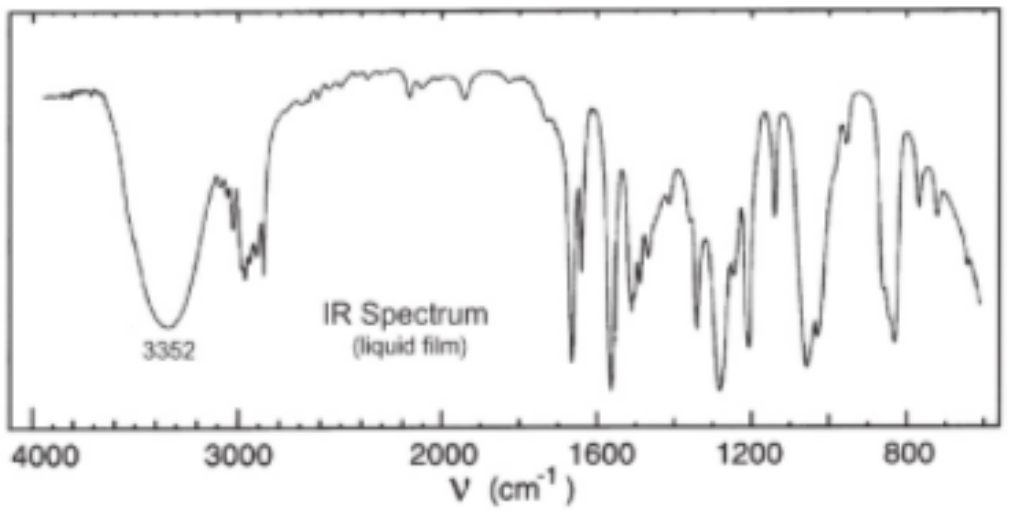


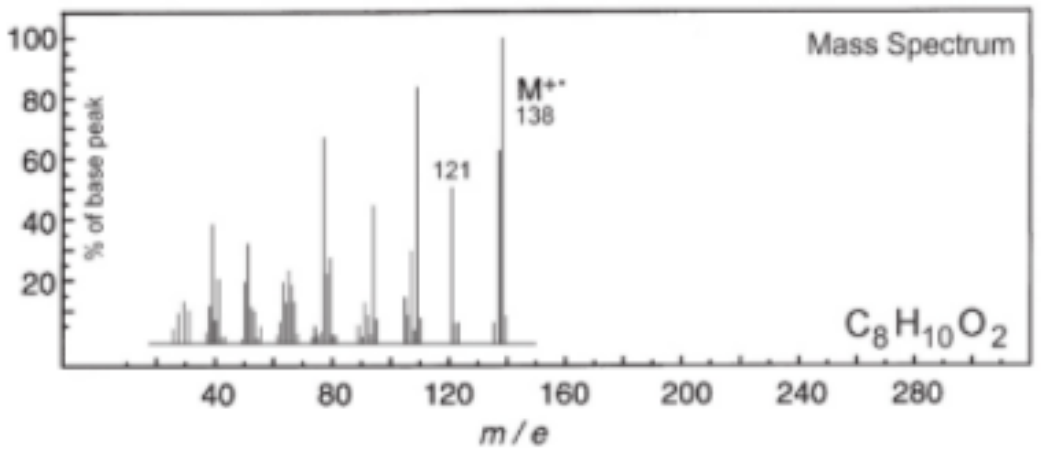



ppm
20
50
130
140
170
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
8.2 8.0 7.8 7.6 7.4 7.2 7.0
4.0 3.8
2.4 2.2
ppm

ppm
20
50
130
140
170
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
8.2 8.0 7.8 7.6 7.4 7.2 7.0
4.0 3.8
2.4 2.2
ppm

Problem 133





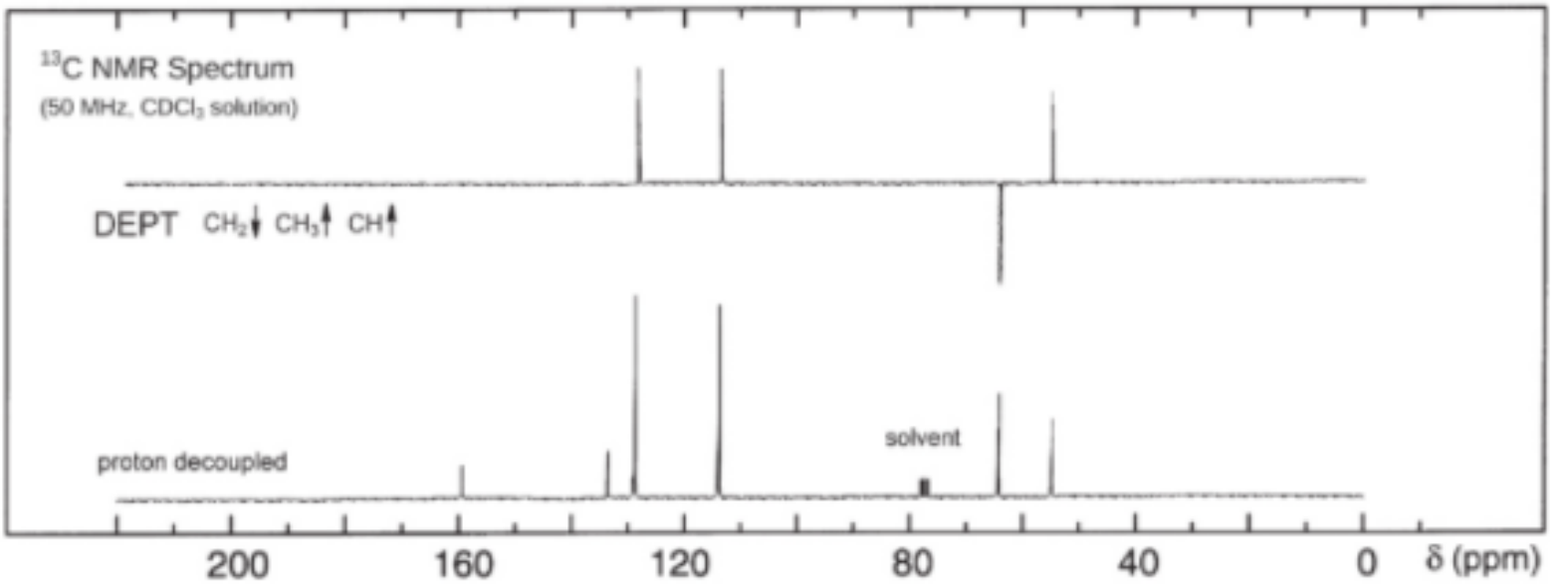
UV Spectrum

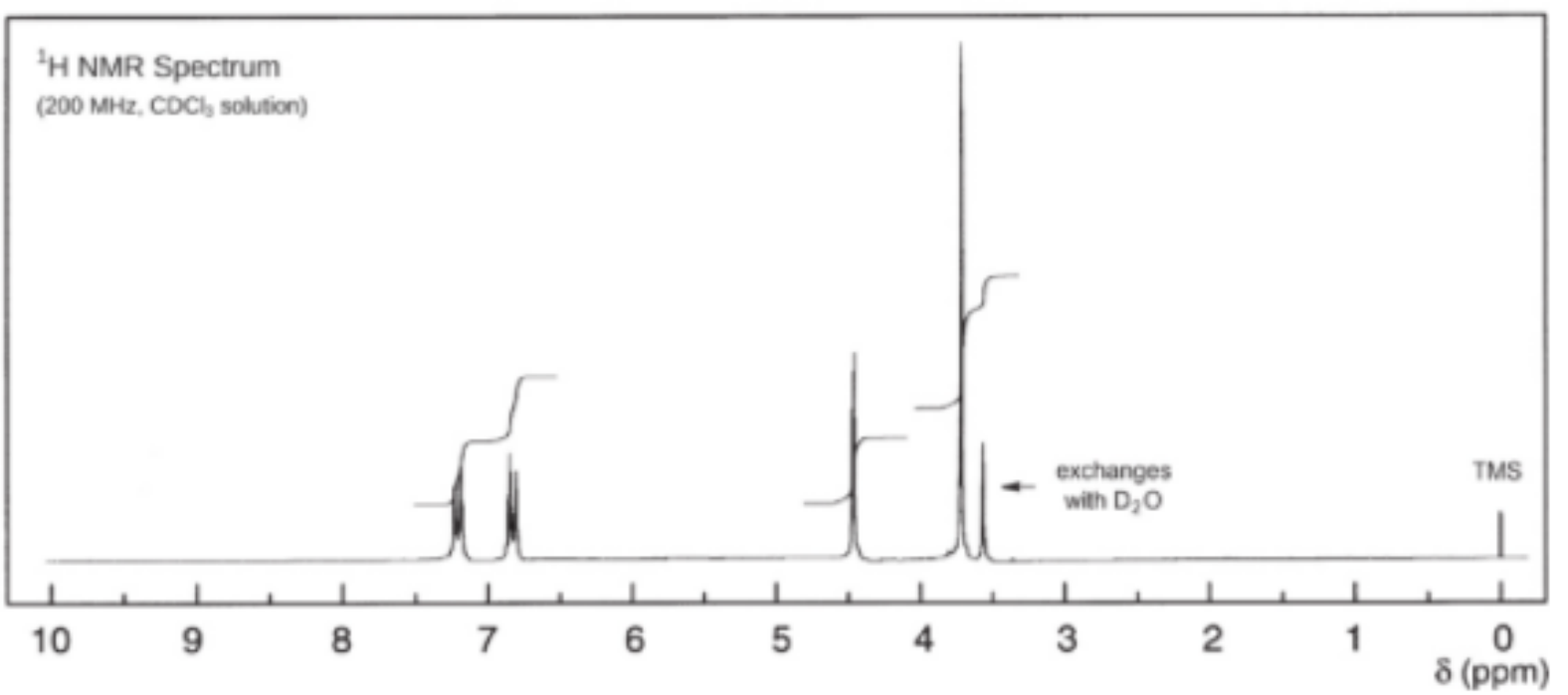
λ_{max} 270 nm ($\log_{10}\varepsilon$ 3.1)

λ_{max} 282 nm ($\log_{10}\varepsilon$ 3.1)

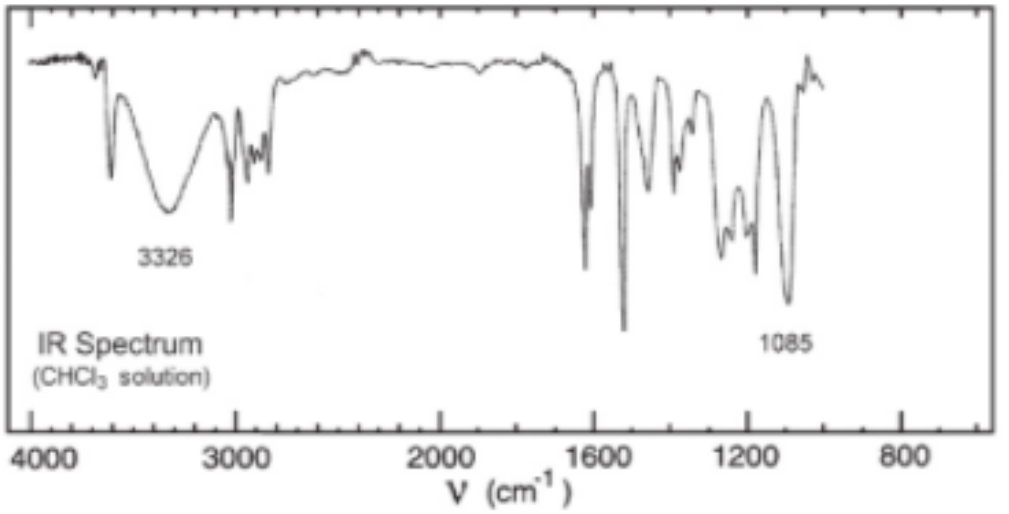
solvent : hexane

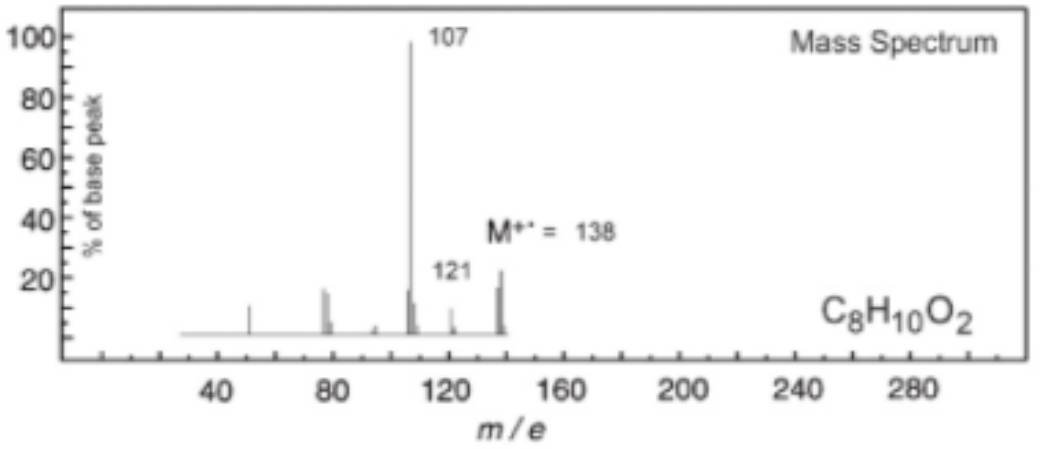
Note: UV spectrum not changed significantly on addition of base





Problem 134

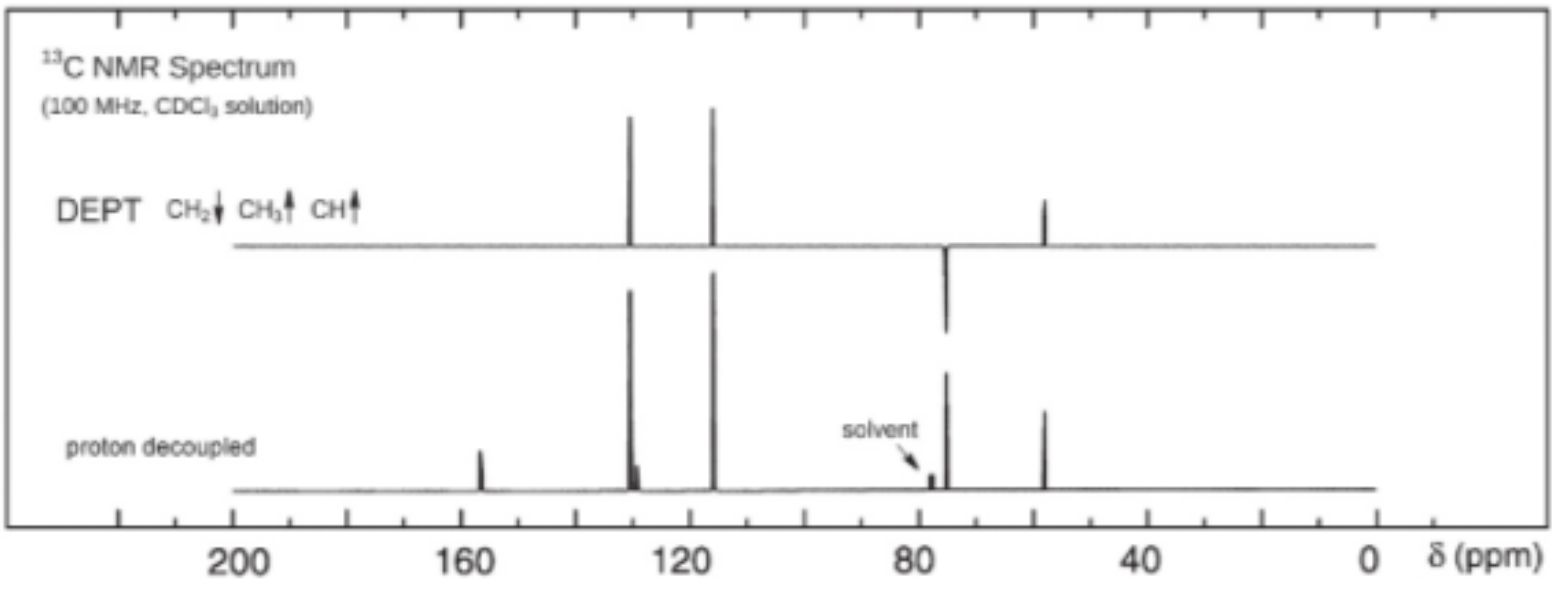


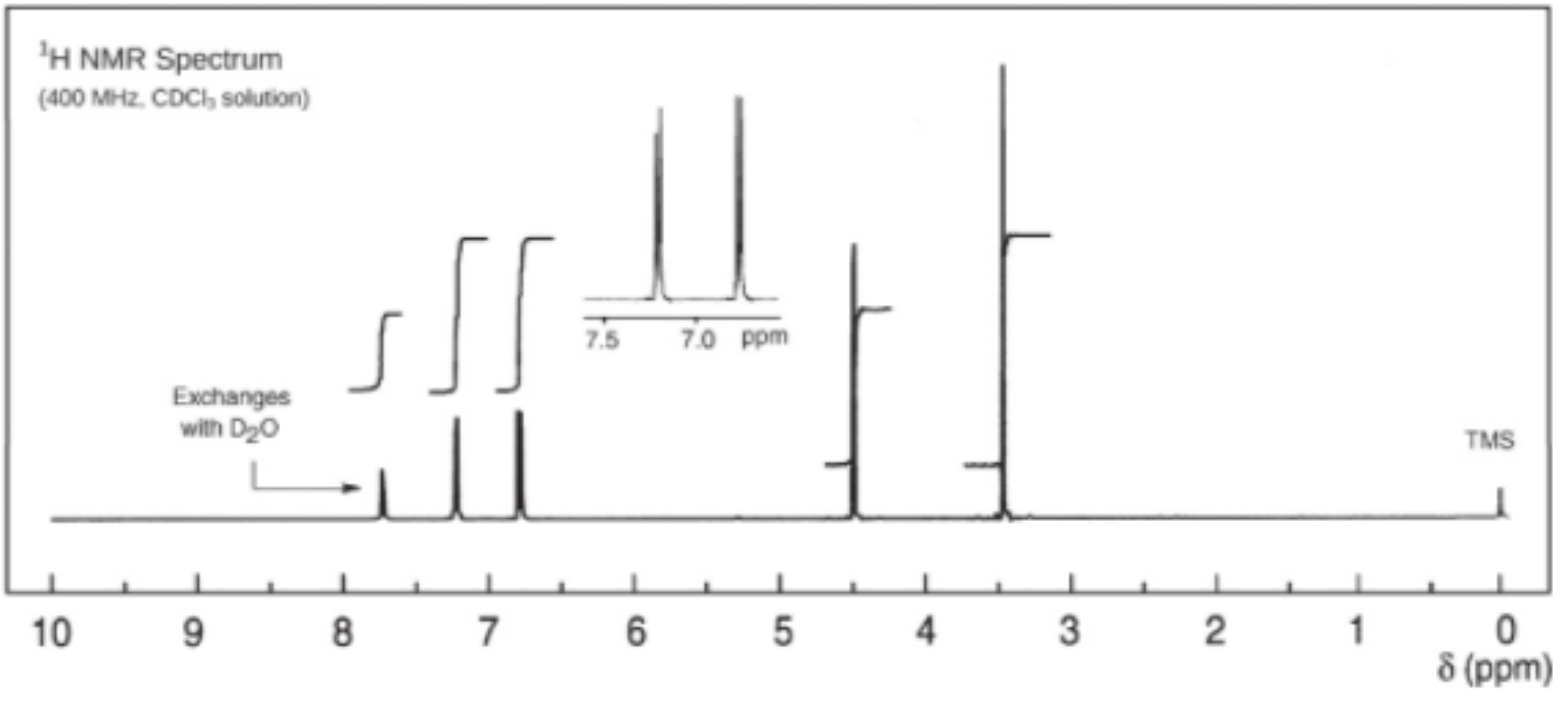


UV Spectrum

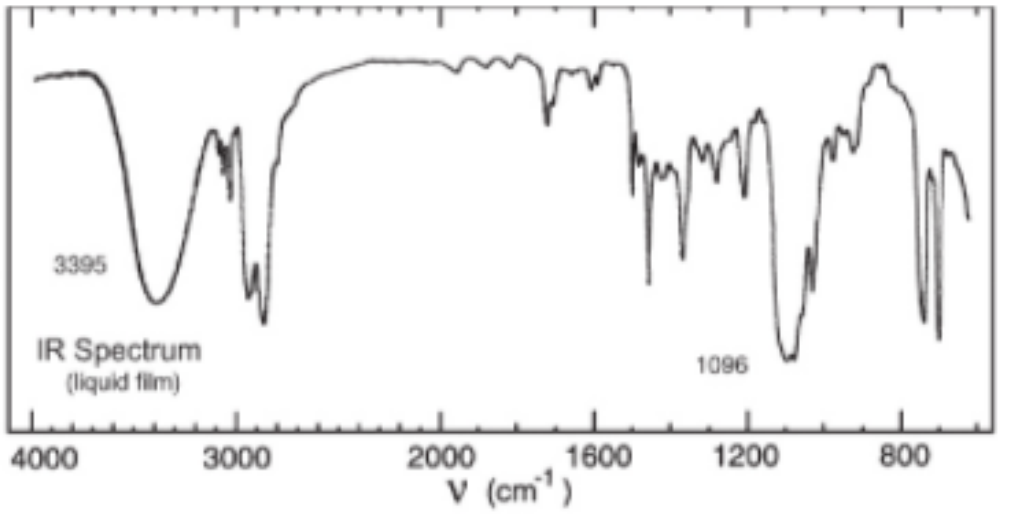
$\log_{10}\varepsilon \approx 3 - 4$

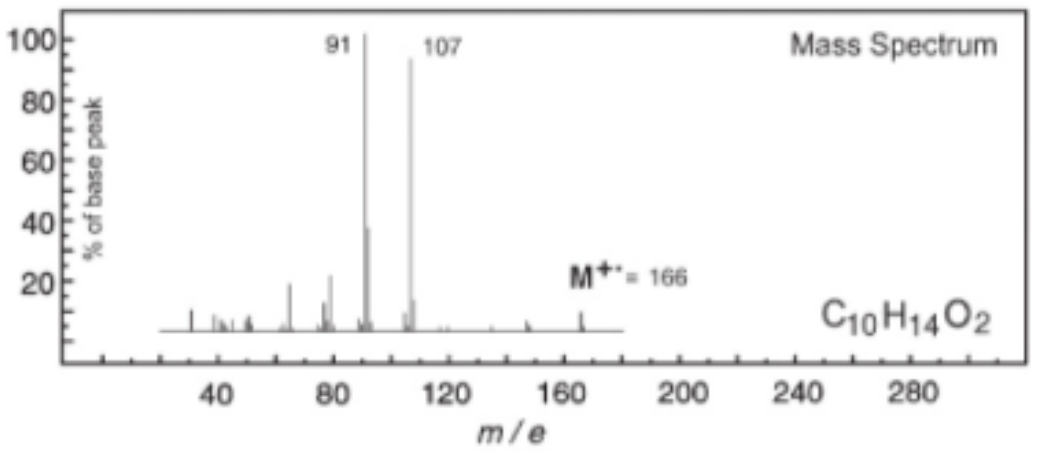
Note: UV spectrum changed significantly on addition of base

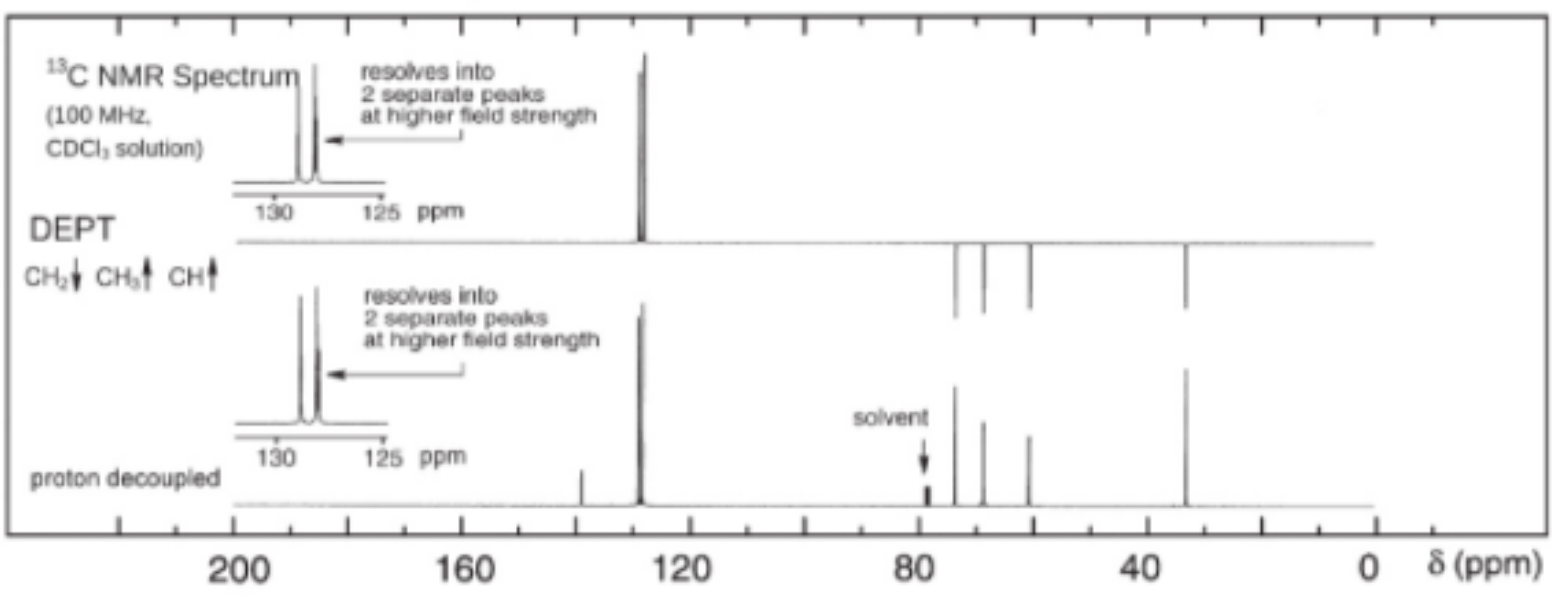


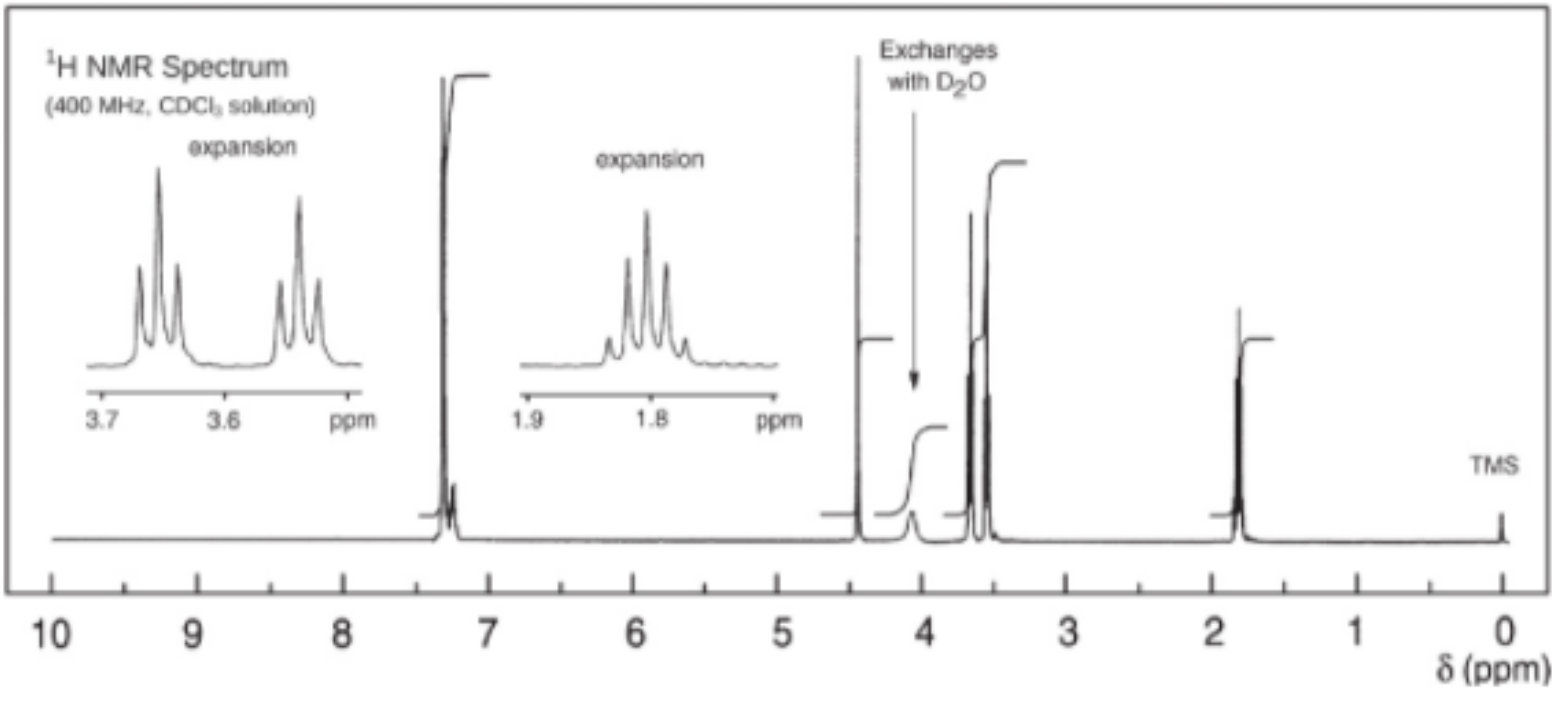


Problem 135

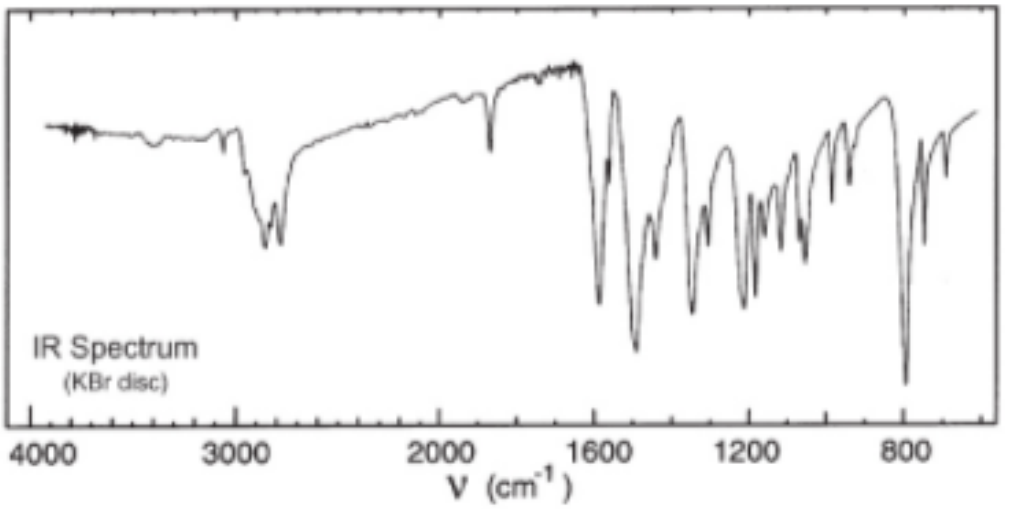

3395
IR Spectrum
(liquid film)
1096
4000
3000
2000
1600
1200
800
ν (cm-1)

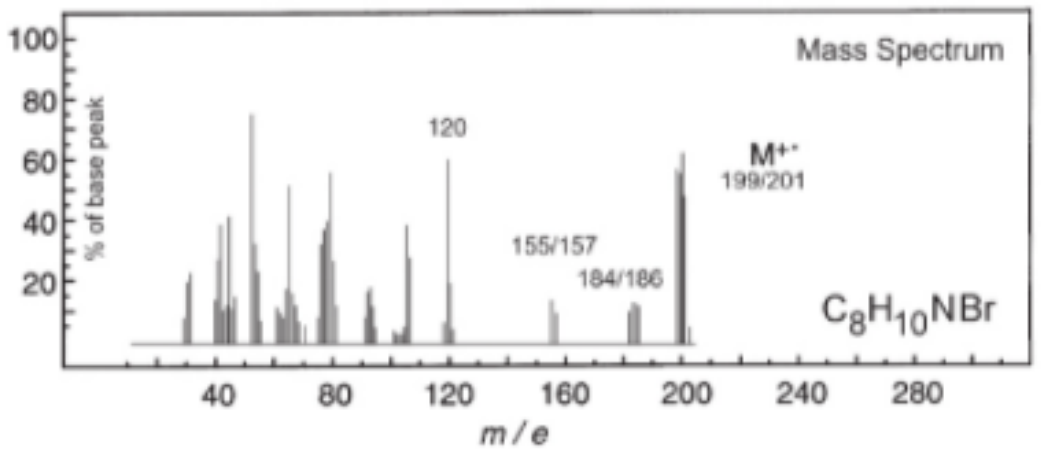

100
80
60
40
20
% of base peak
91
107
Mass Spectrum
M+· = 166
C10H14O2
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(100 MHz,
CDCl3 solution)
resolves into
2 separate peaks
at higher field strength
130
125 ppm
DEPT
CH2 CH3 CH
resolves into
2 separate peaks
at higher field strength
130
125 ppm
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
3.7
3.6
ppm
expansion
1.9
1.8
ppm
Exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 136





UV Spectrum

λ_{max} 310 nm ($\log_{10}\varepsilon$ 3.3)

λ_{max} 261 nm ($\log_{10}\varepsilon$ 4.3)

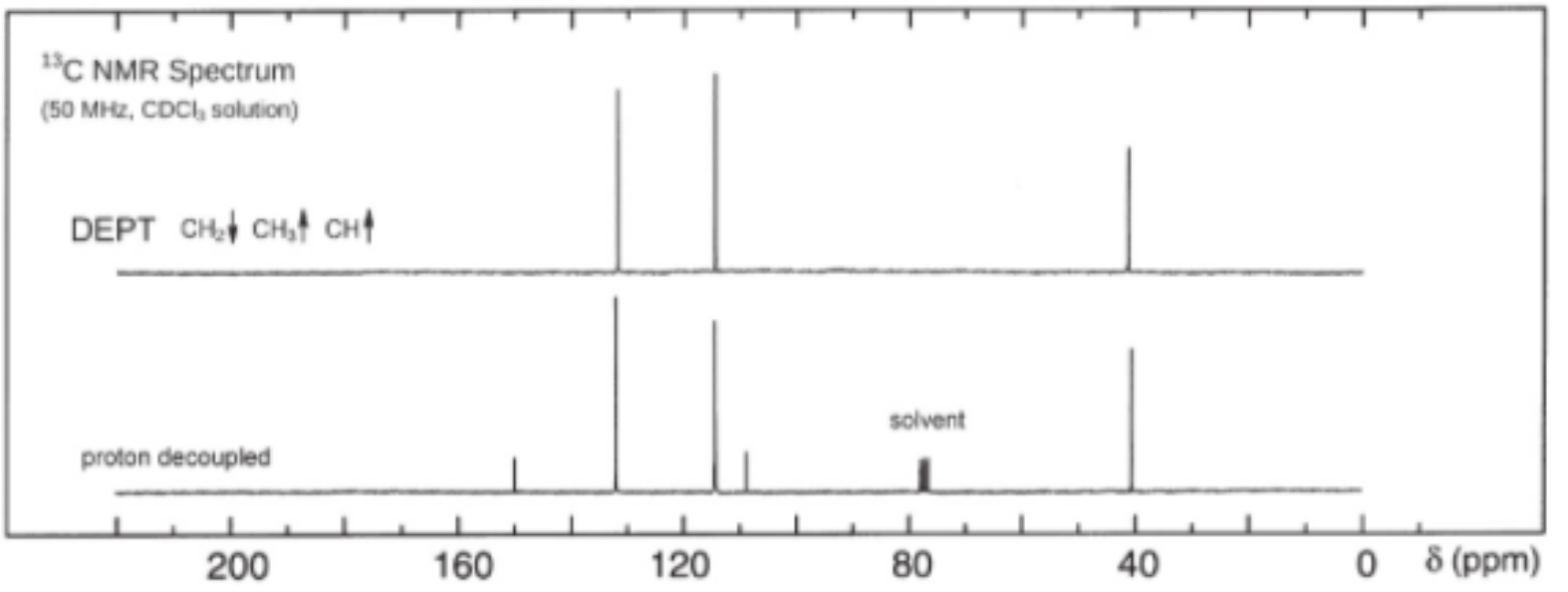
solvent : methanol

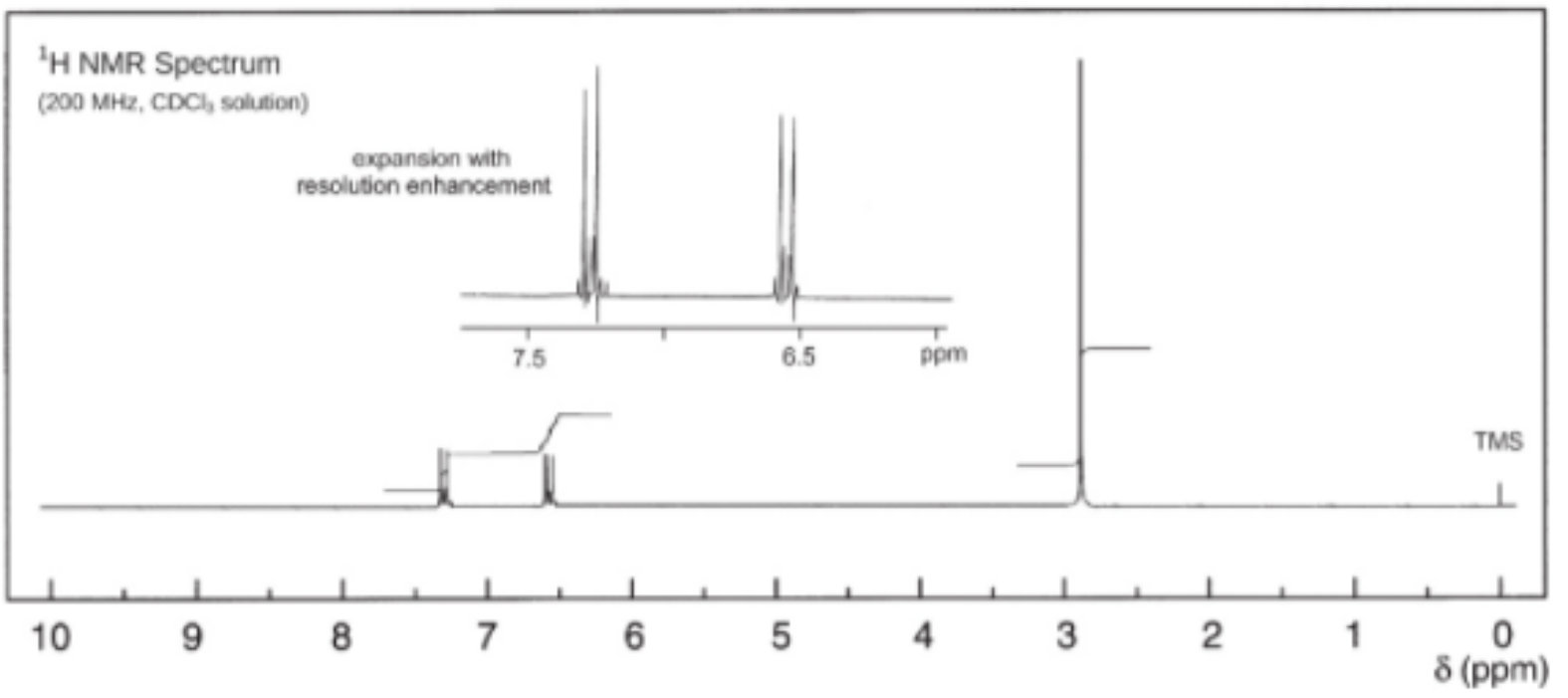
λ_{max} 262 nm ($\log_{10}\varepsilon$ 3.0)

λ_{max} 257 nm ($\log_{10}\varepsilon$ 3.0)

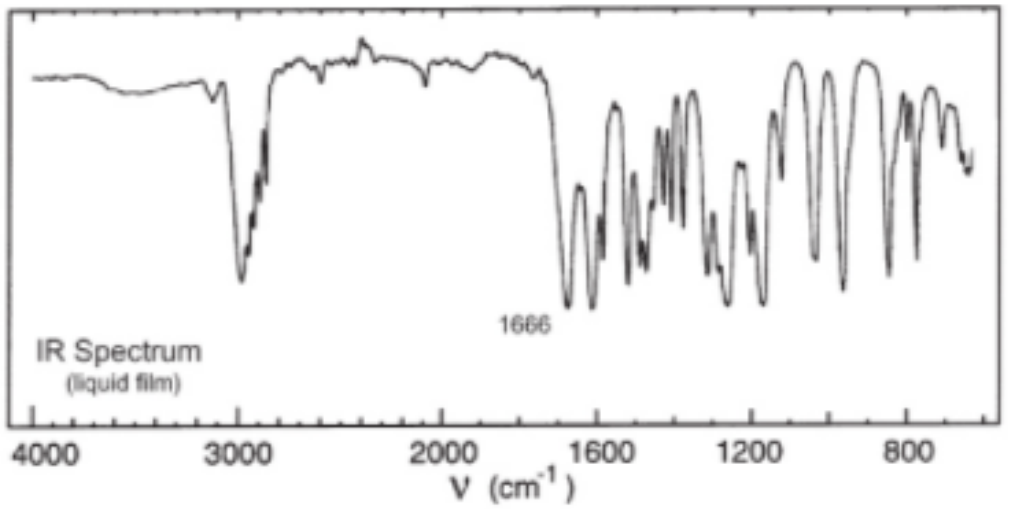
λ_{max} 222 nm ($\log_{10}\varepsilon$ 4.0)

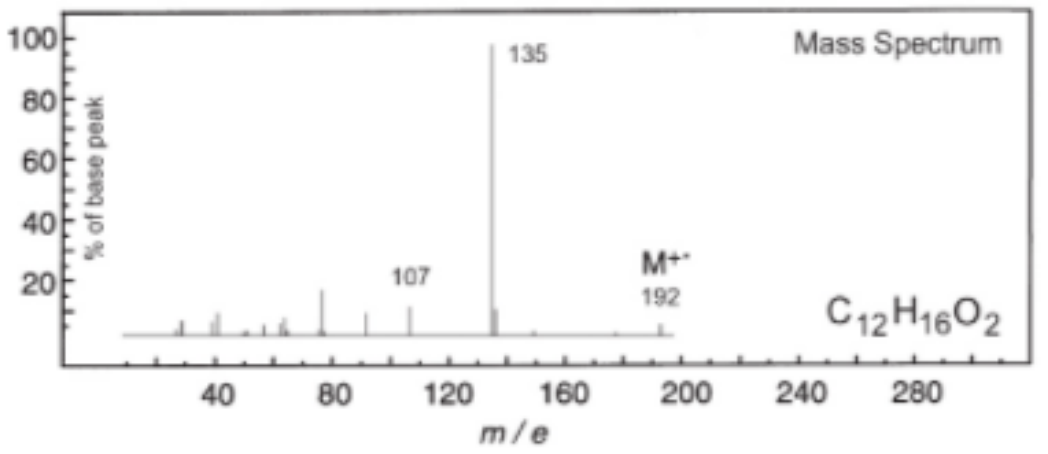
solvent : methanol / HCl





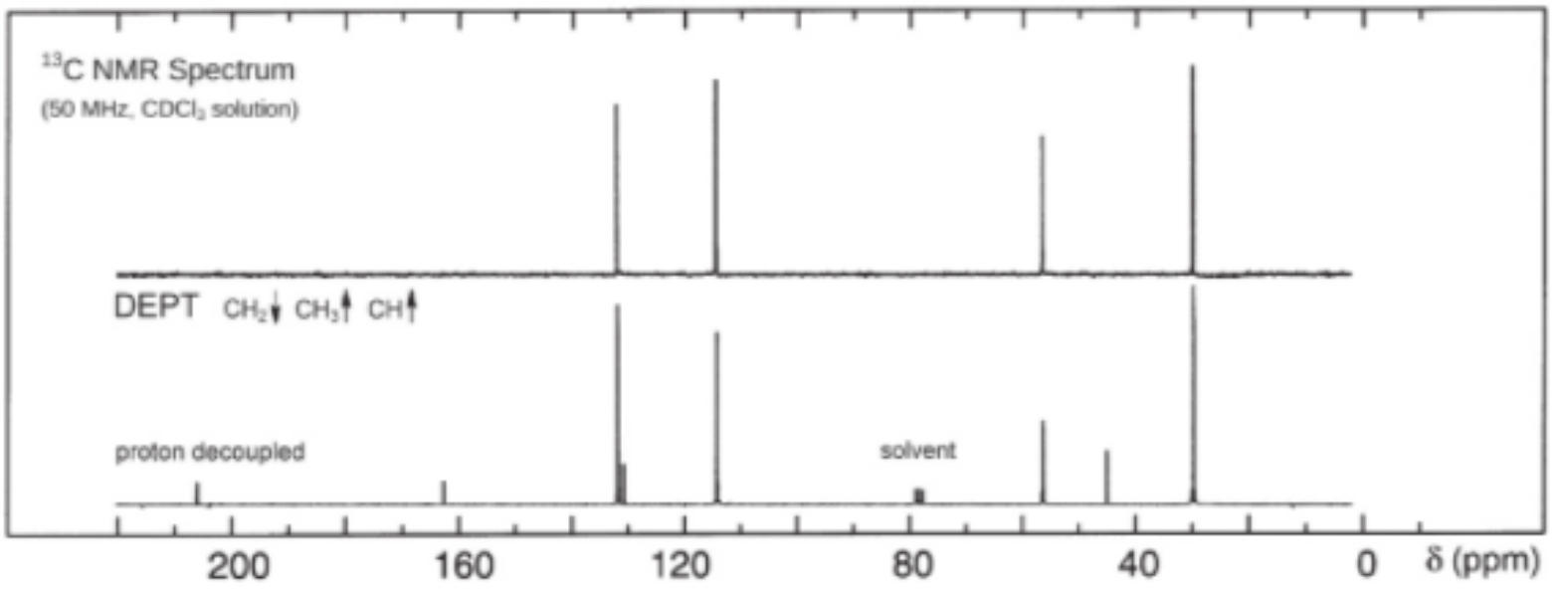
Problem 137

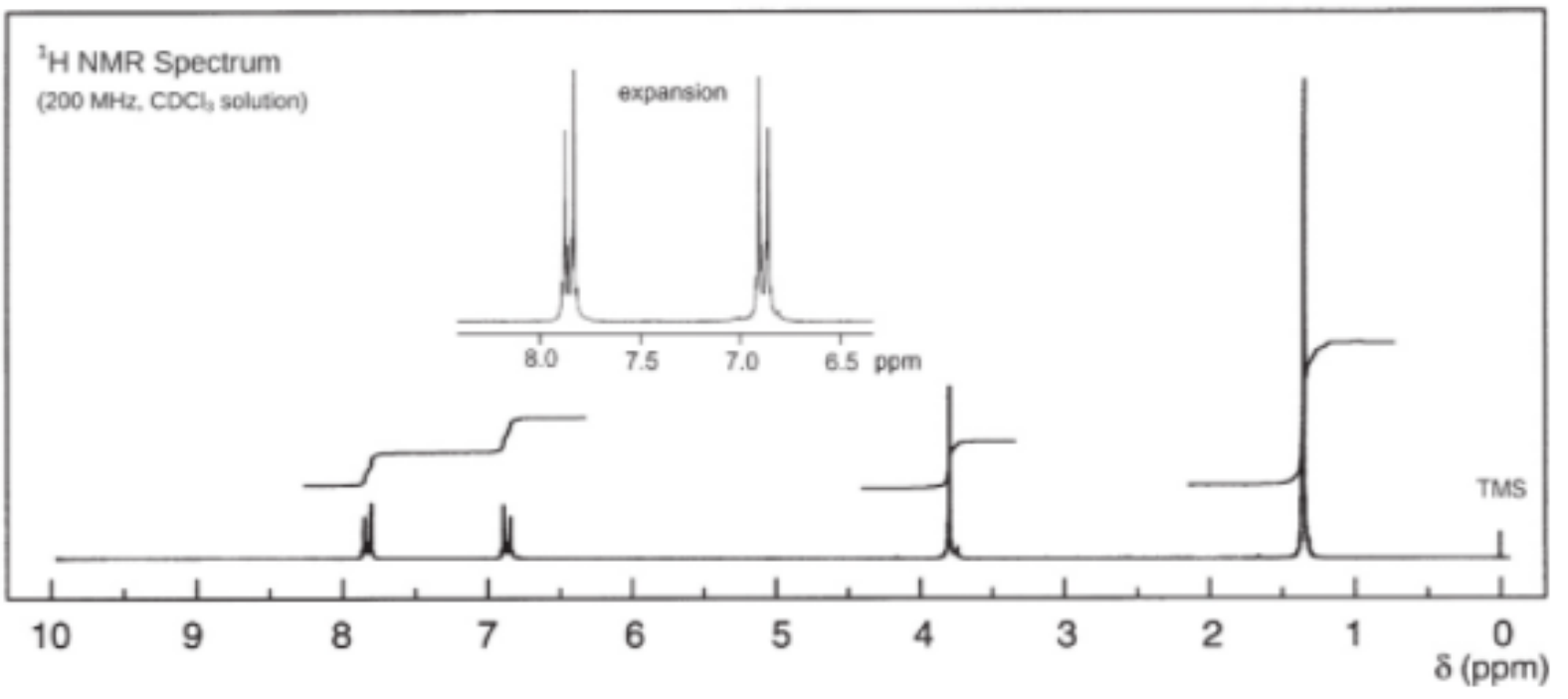




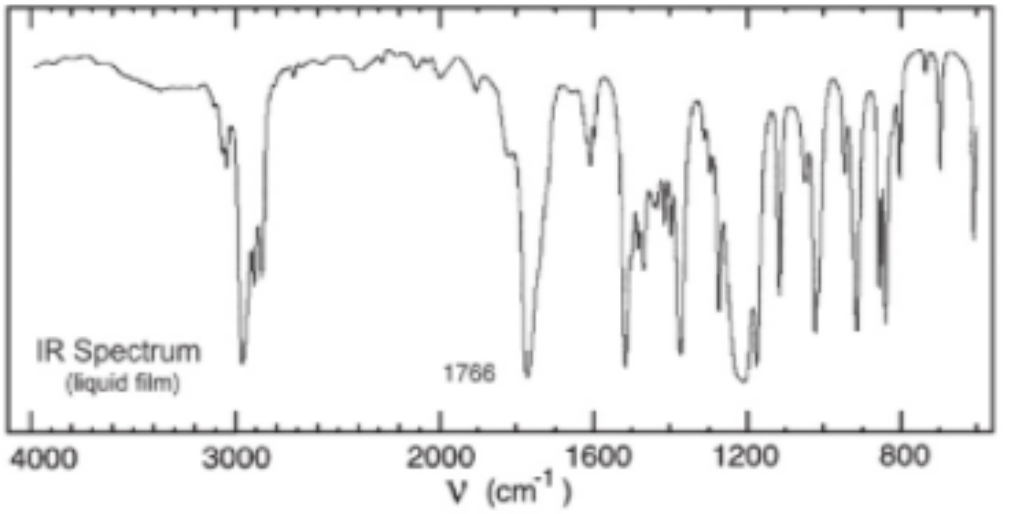
UV Spectrum

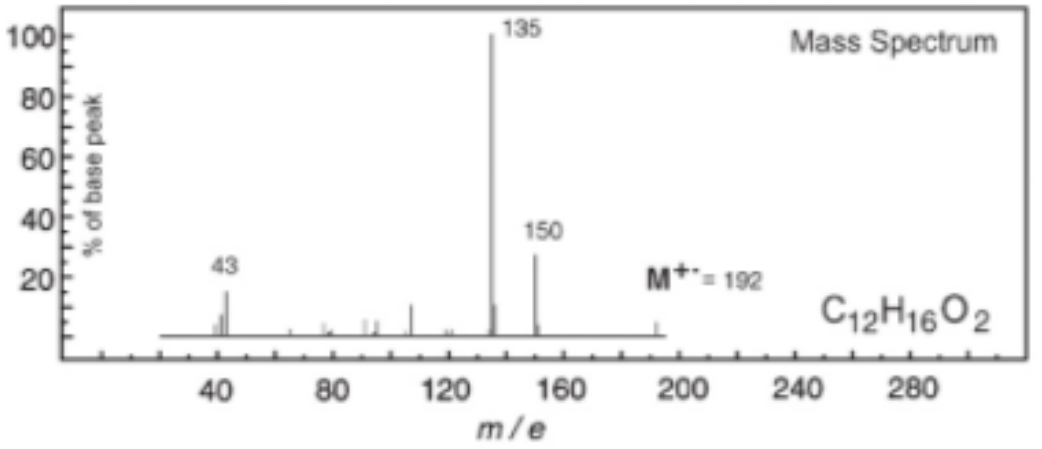
$\log_{10}\varepsilon \approx 4$





Problem 138



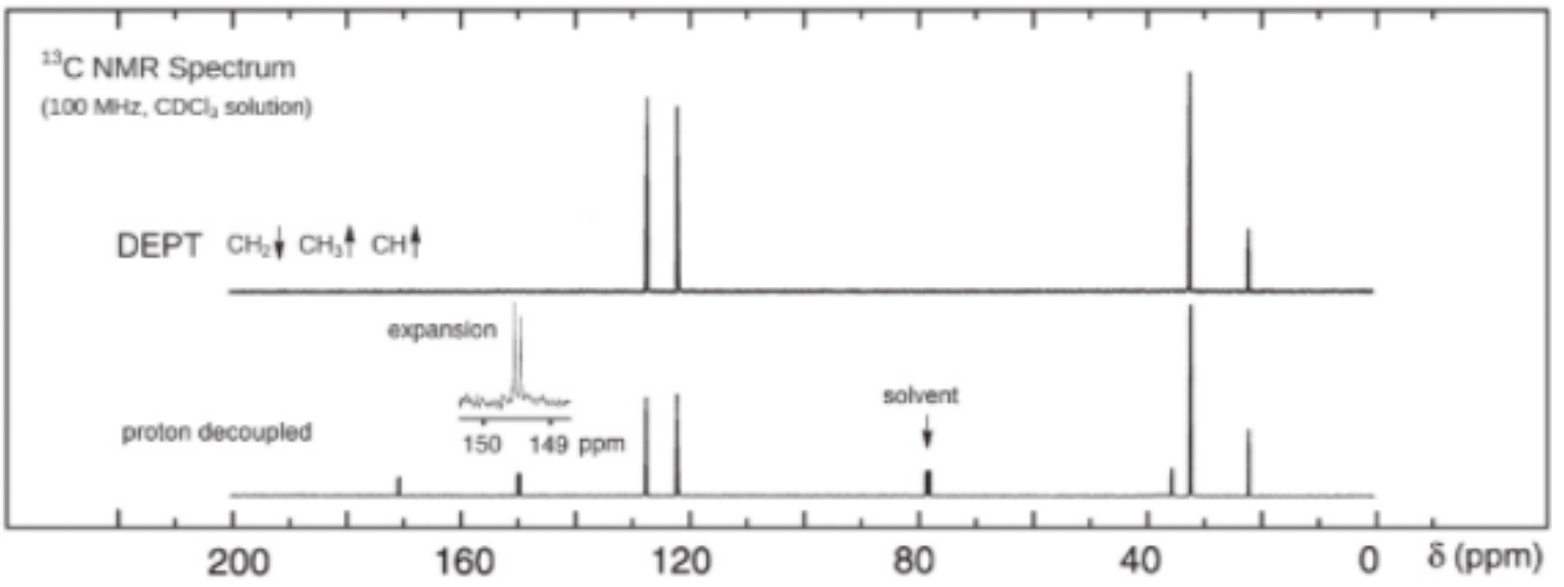


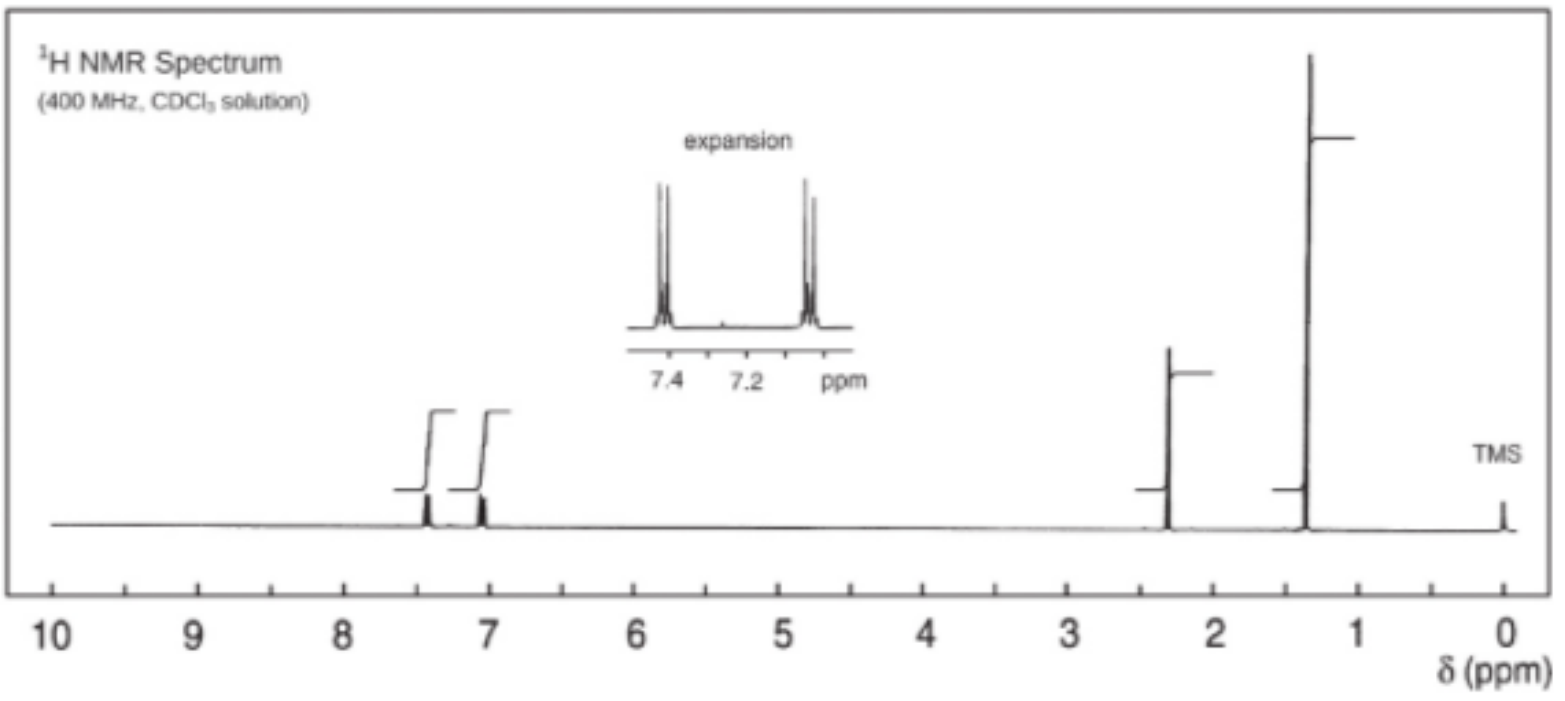
UV Spectrum

λ_{max} 262 nm ($\log_{10}\varepsilon$ 2.6)

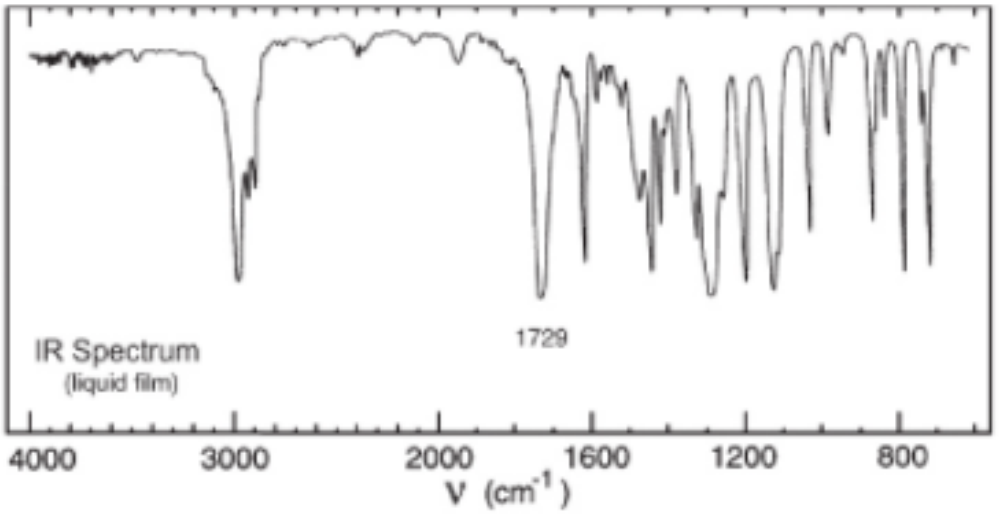
λ_{max} 269 nm ($\log_{10}\varepsilon$ 2.6)

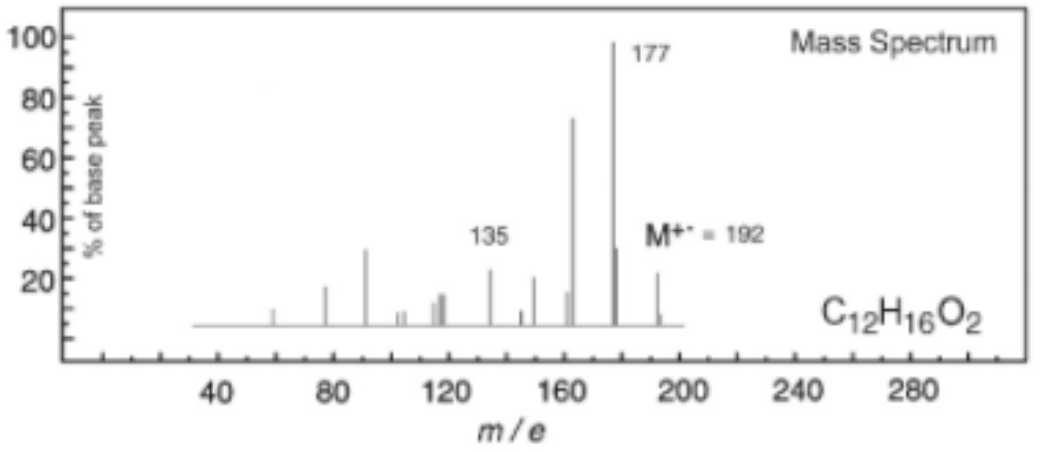
solvent : methanol





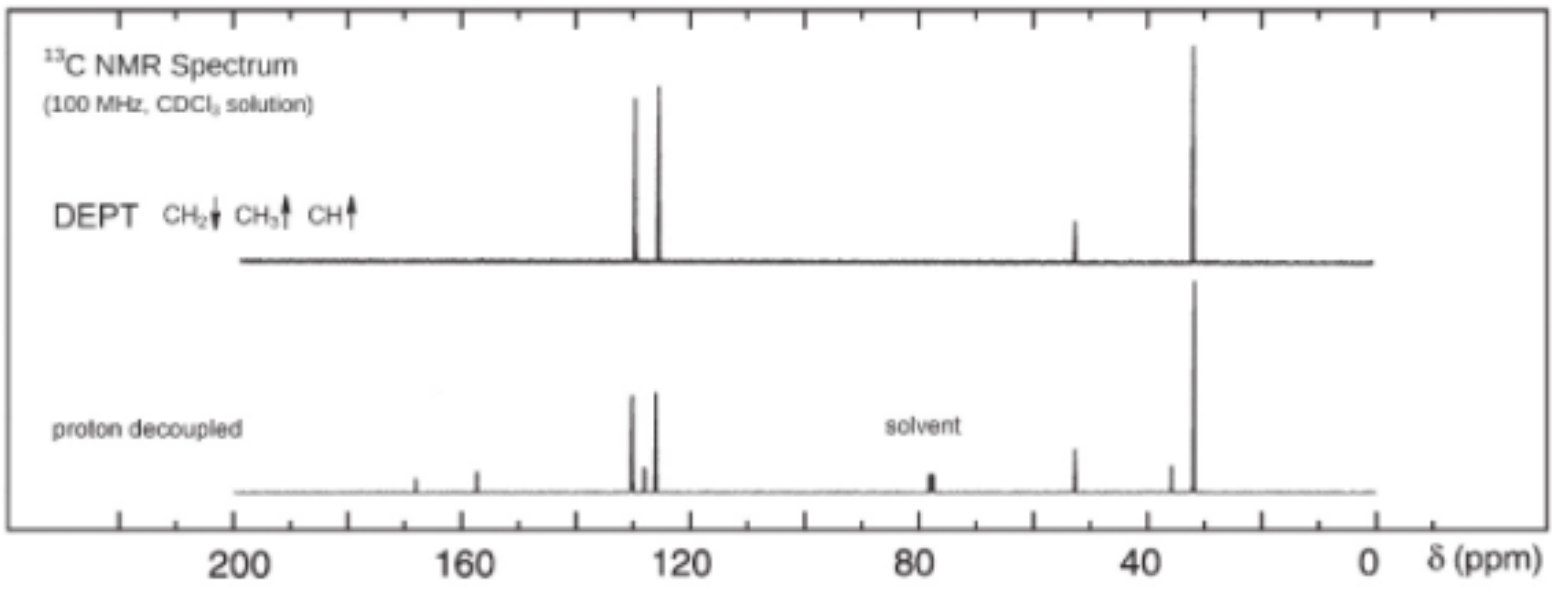
Problem 139

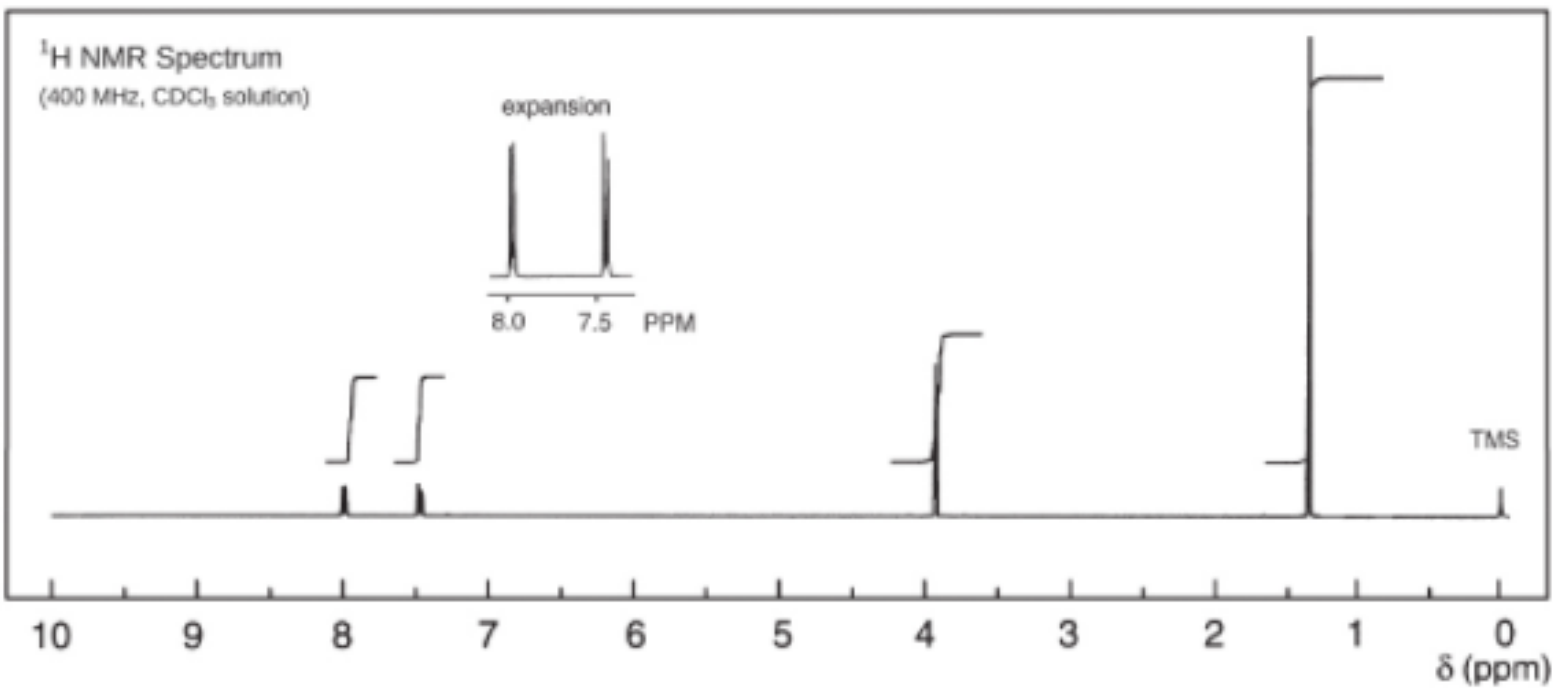




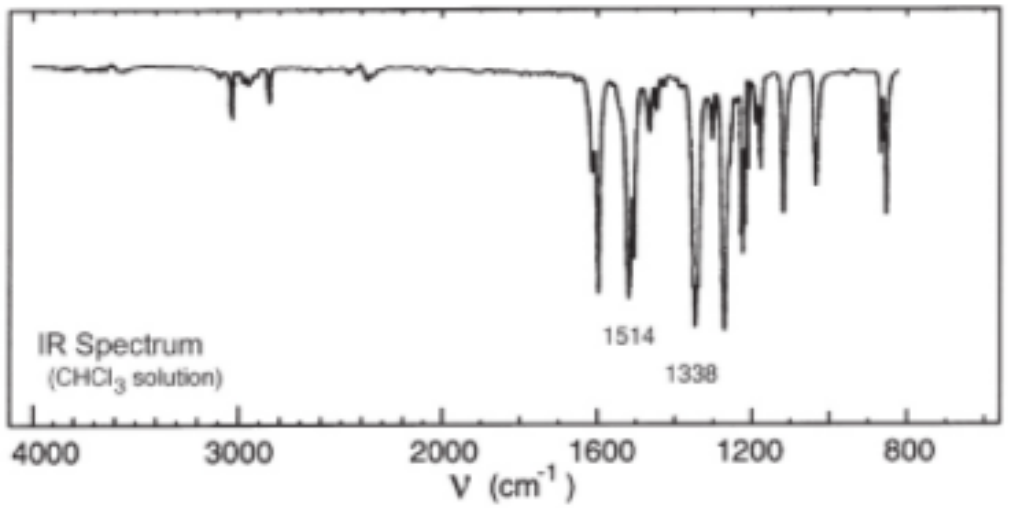
UV Spectrum

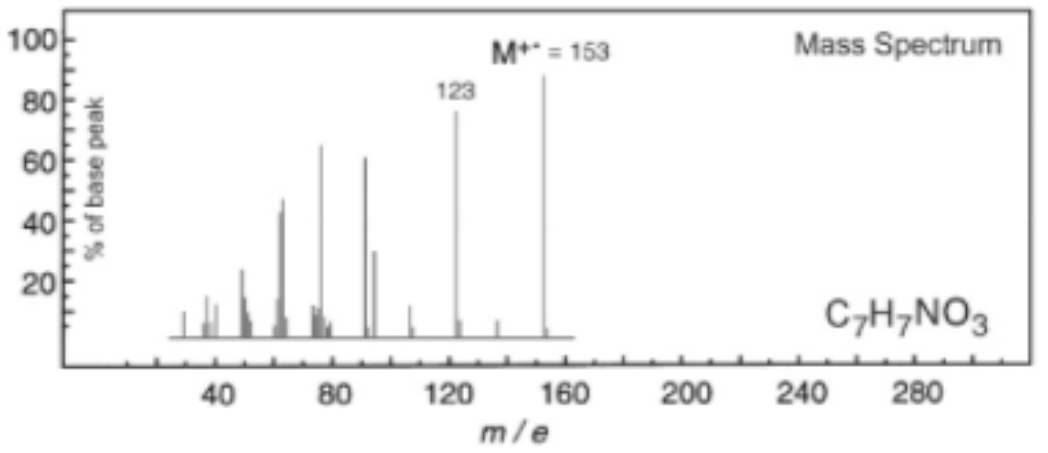
$\lambda_{max} \approx 240$ nm $(\log_{10}\varepsilon > 4.0)$





Problem 140



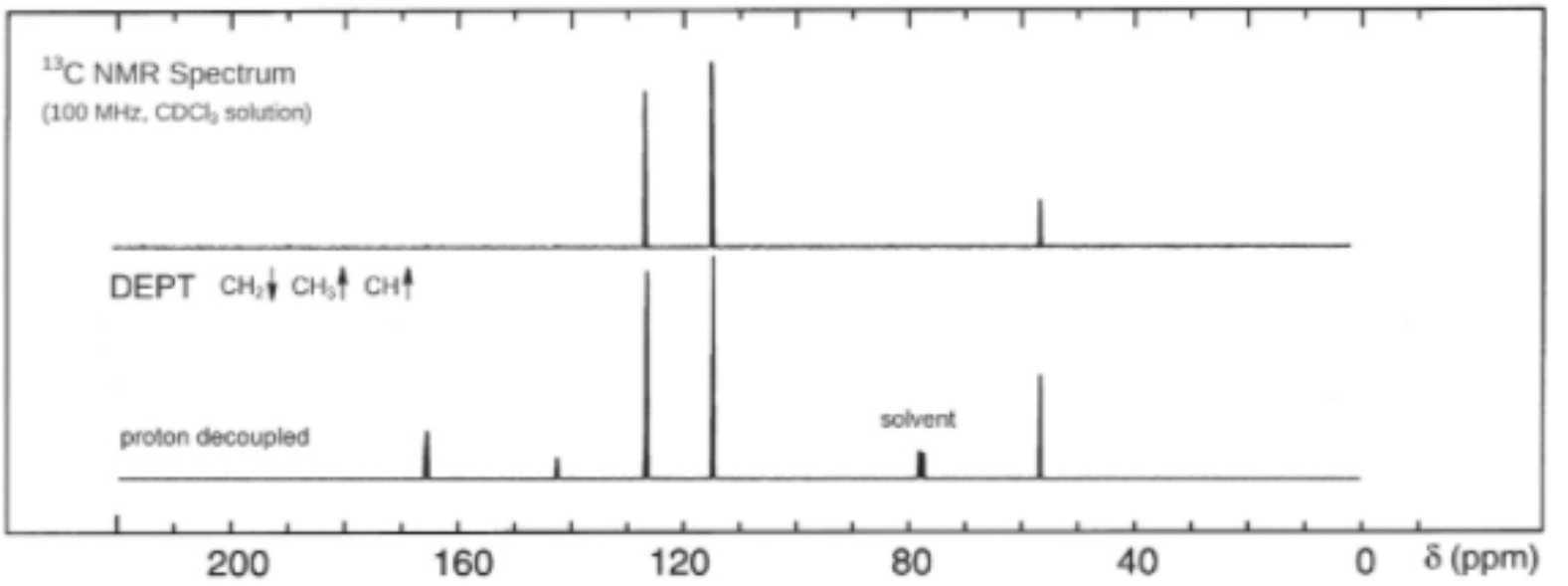


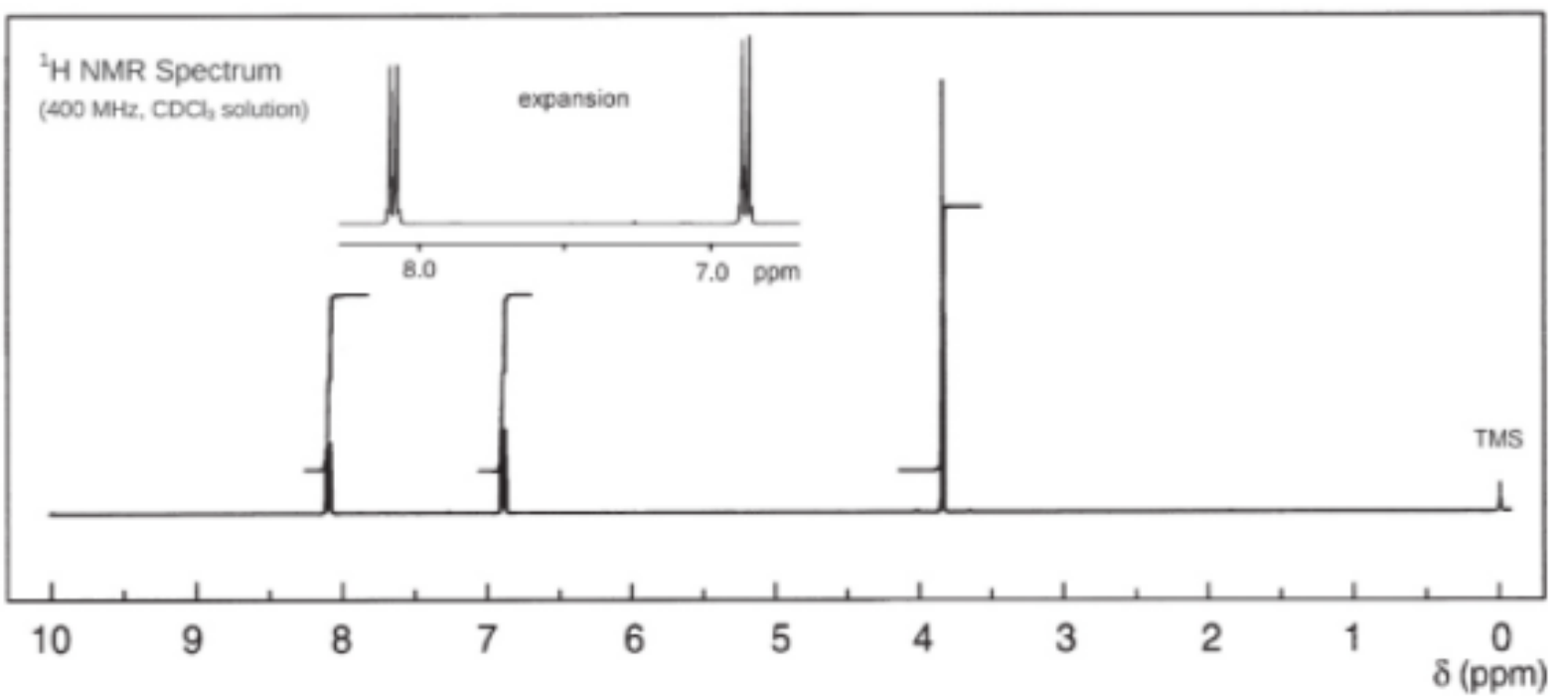
UV Spectrum

λ_{max} 227 nm ($\log_{10}\varepsilon$ 3.9)

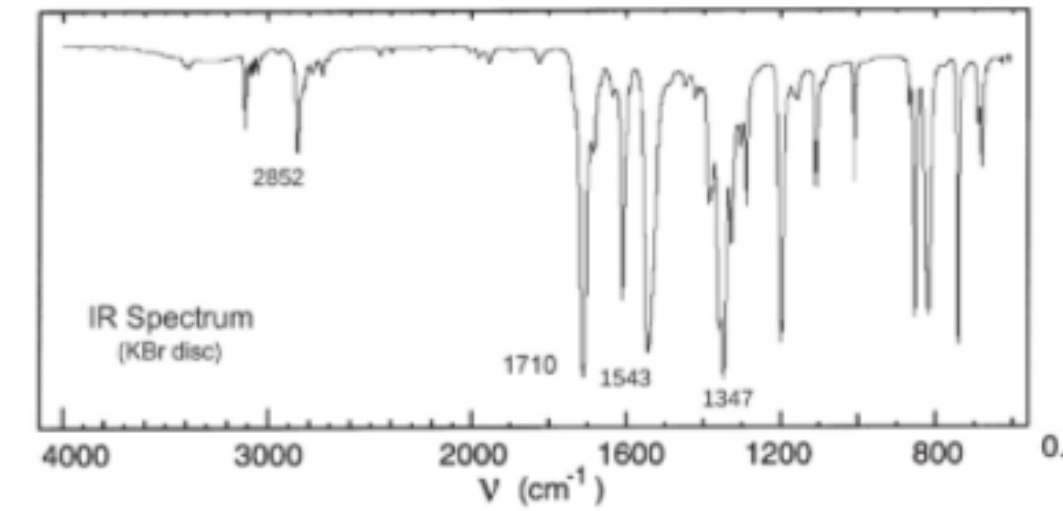
λ_{max} 305 nm ($\log_{10}\varepsilon$ 4.0)

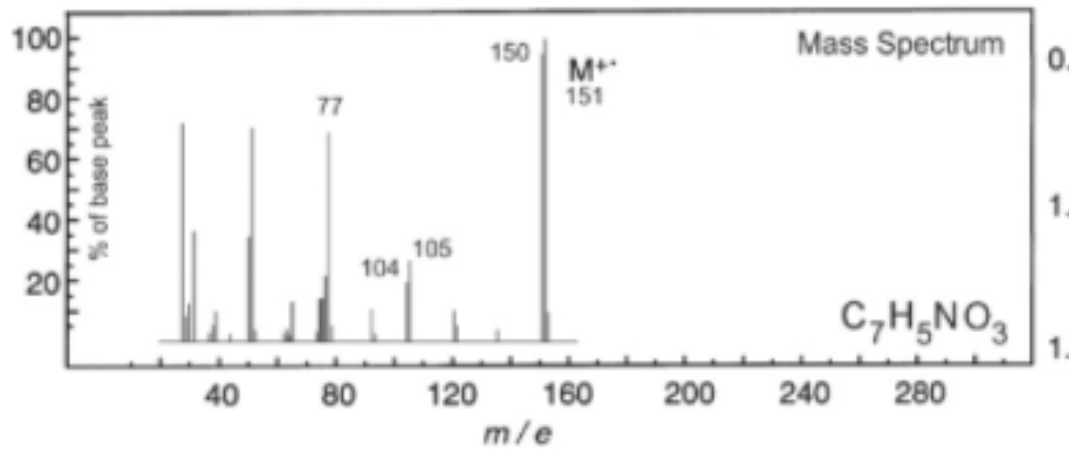
solvent : methanol

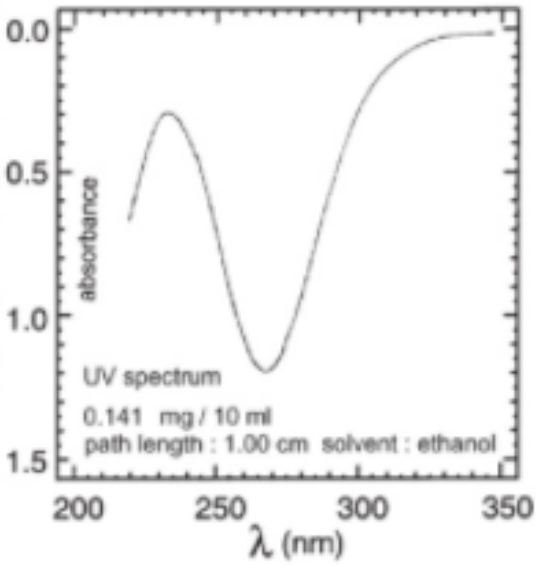


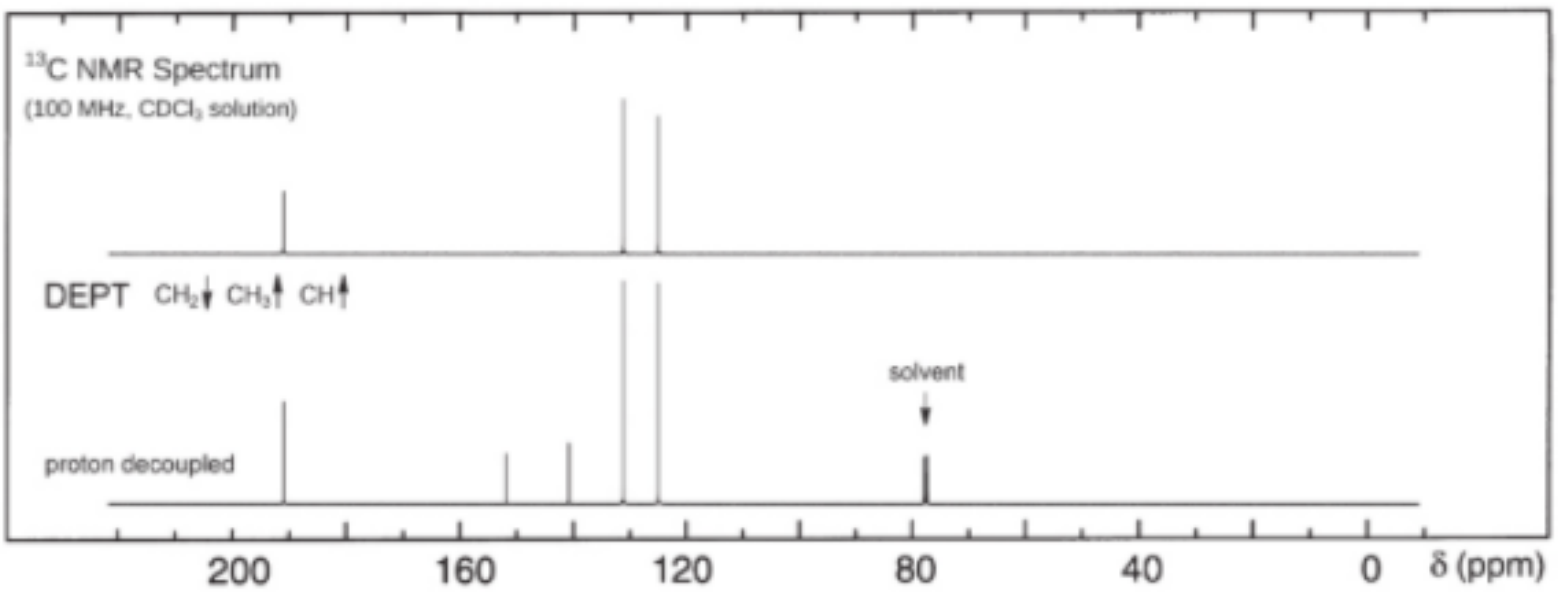


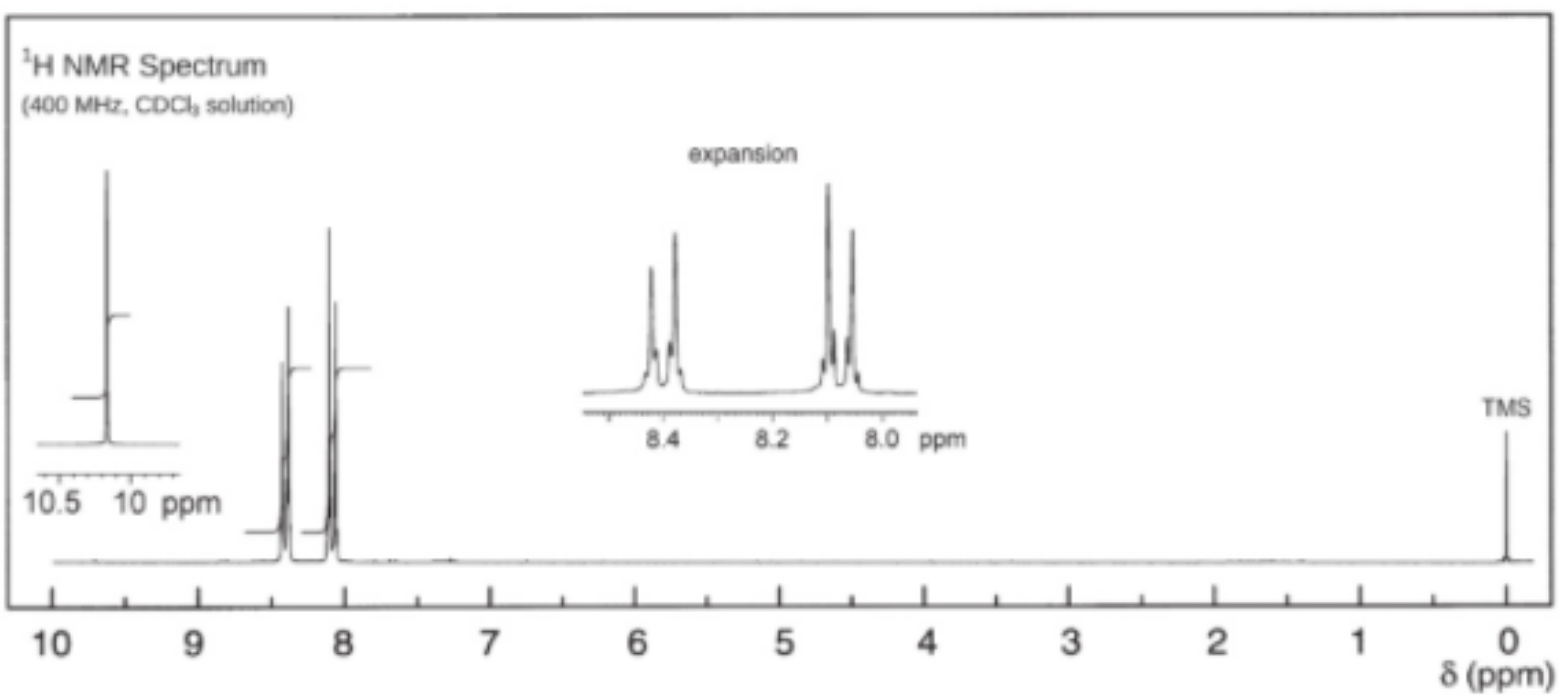
Problem 141

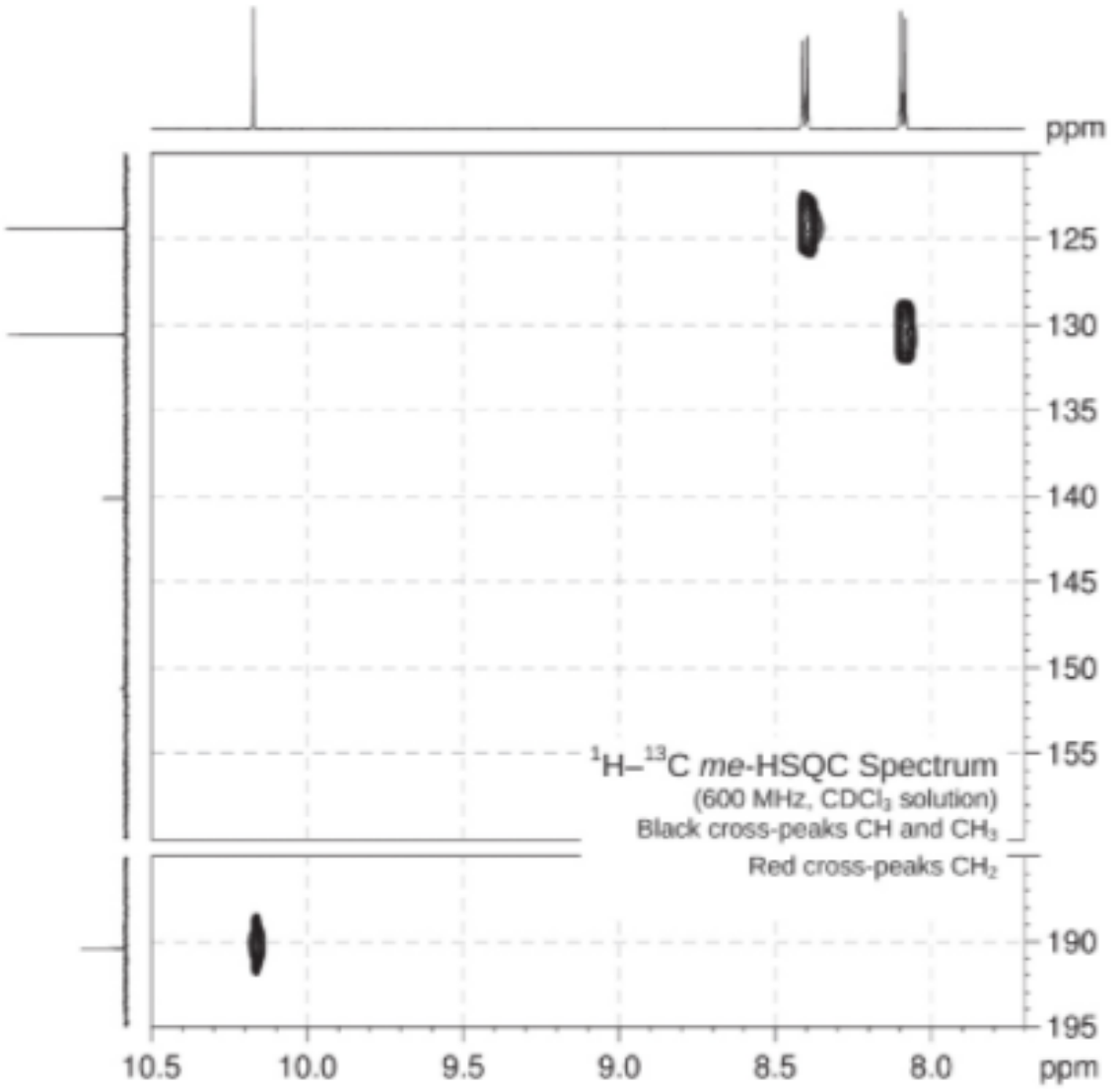

2852
IR Spectrum
(KBr disc)
1710
1543
1347
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
150
M+·
151
77
104
105
% of base peak
100
80
60
40
20
C7H5NO3
40
80
120
160
200
240
280
m/e


absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.141 mg / 10 ml
path length : 1.00 cm solvent : ethanol
200
250
300
350
λ (nm)

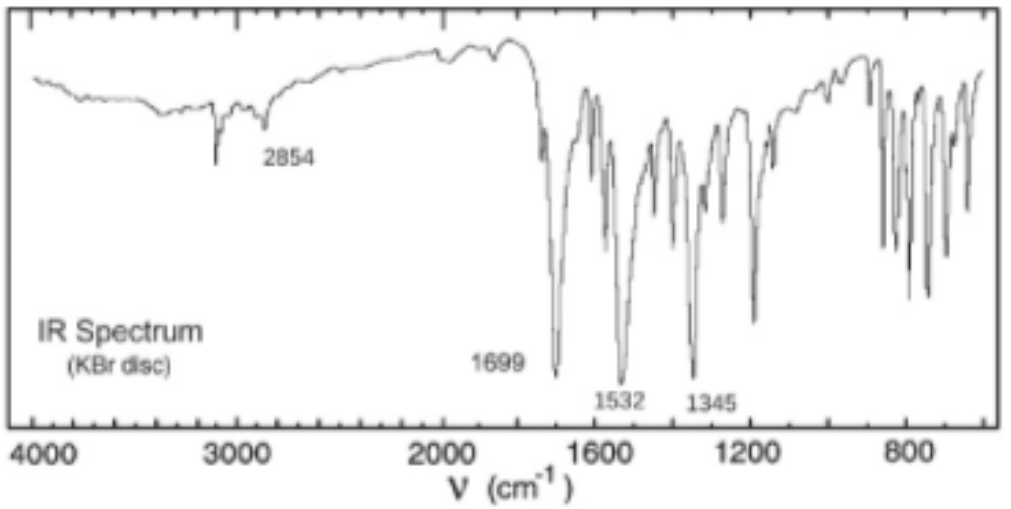

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

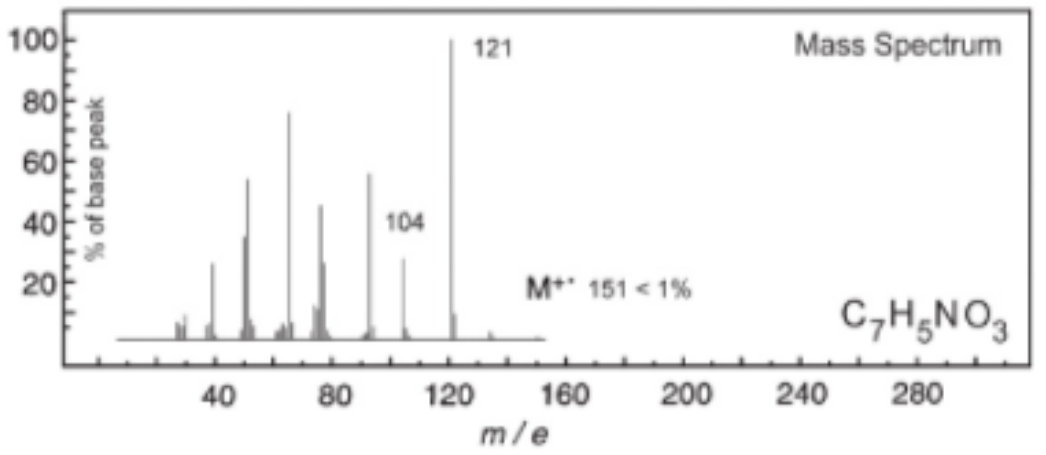

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
8.4
8.2
8.0 ppm
10.5
10 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
125
130
135
140
145
150
155
190
195
10.5
10.0
9.5
9.0
8.5
8.0
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

ppm
125
130
135
140
145
150
155
190
195
10.5
10.0
9.5
9.0
8.5
8.0
ppm
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)

Problem 142

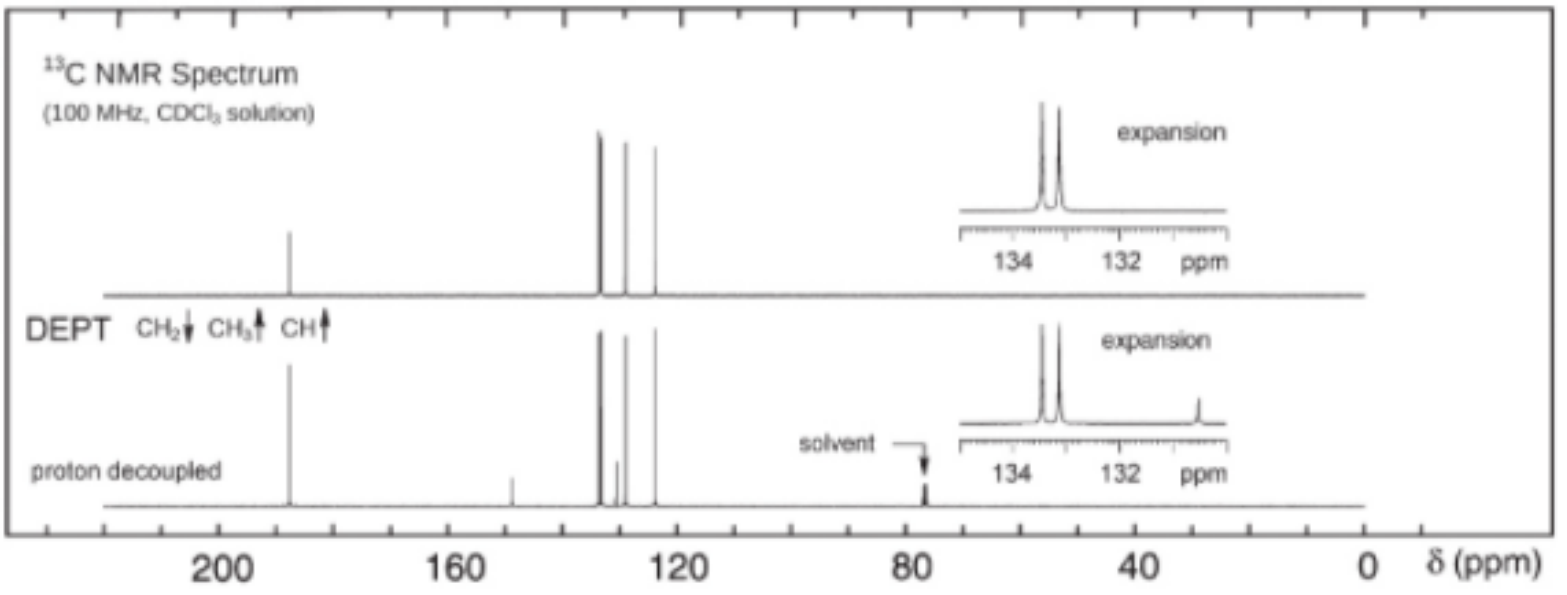


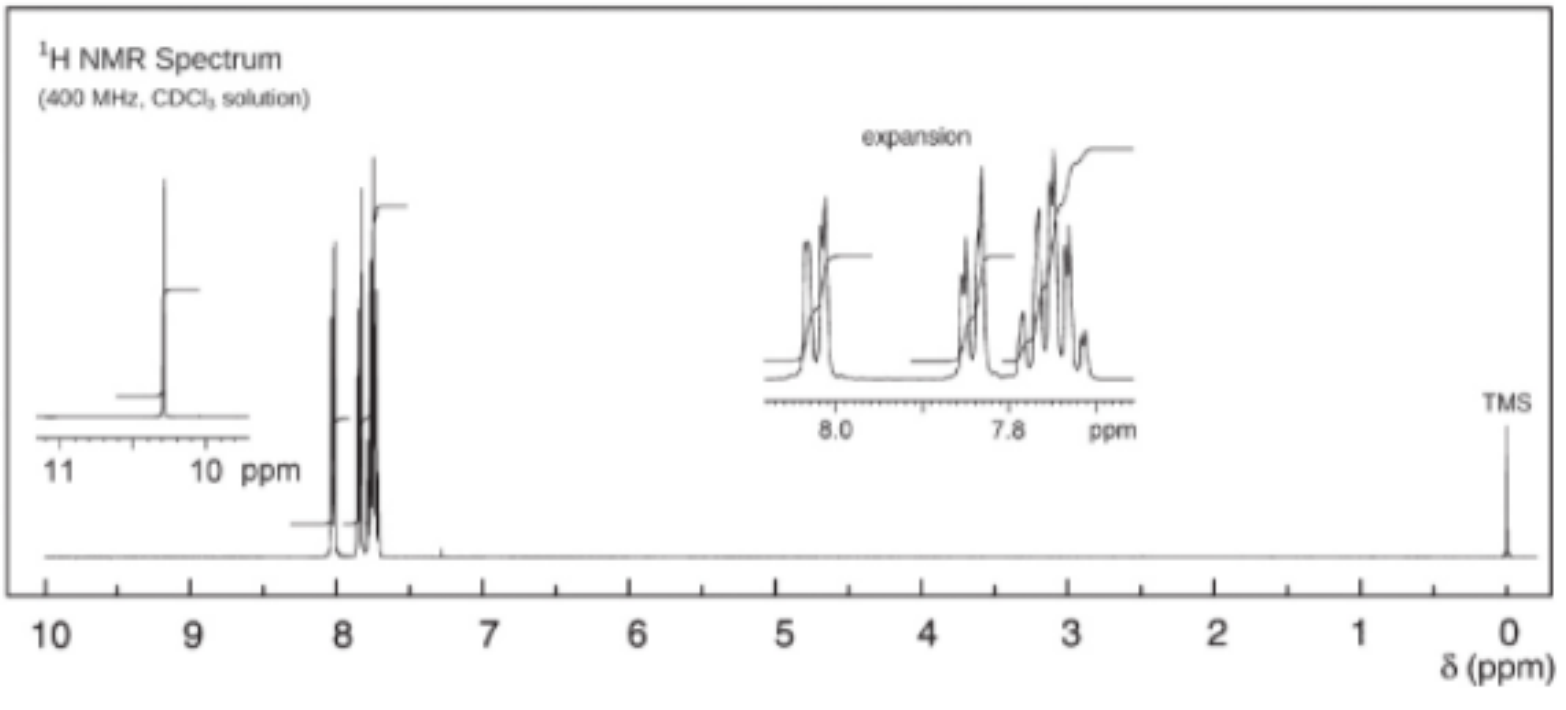


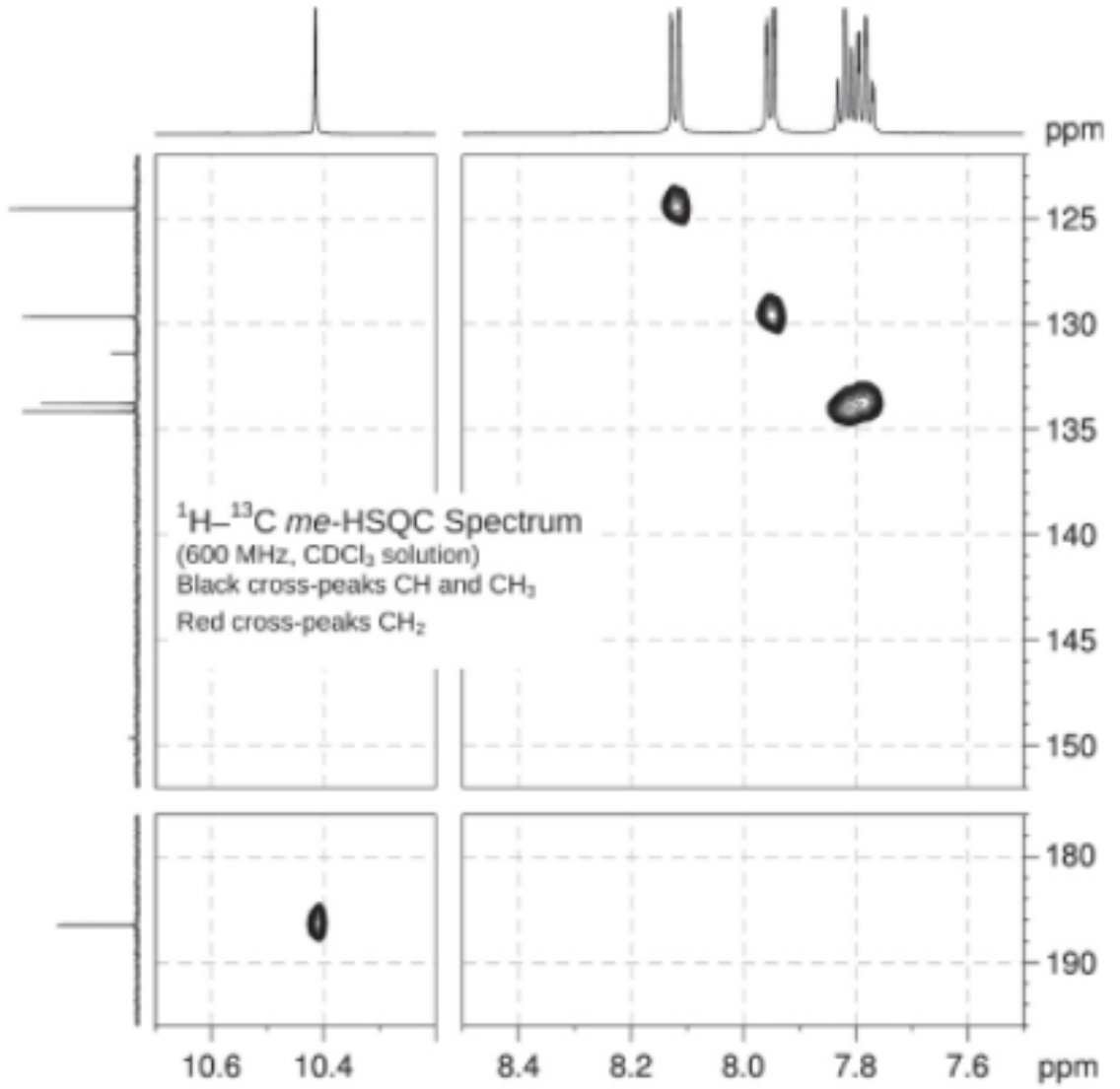
UV Spectrum

λ_{max} 225 nm ($\log_{10}\varepsilon$ 4.2)
λ_{max} 250 nm ($\log_{10}\varepsilon$ 3.8)
λ_{max} 293 nm ($\log_{10}\varepsilon$ 3.2)
λ_{max} 330 nm ($\log_{10}\varepsilon$ 2.6)

solvent : methanol

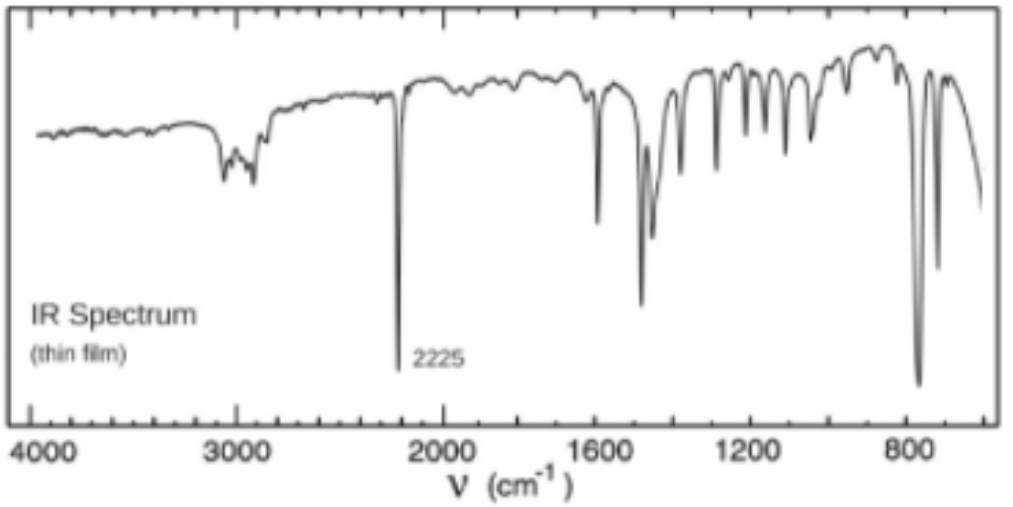


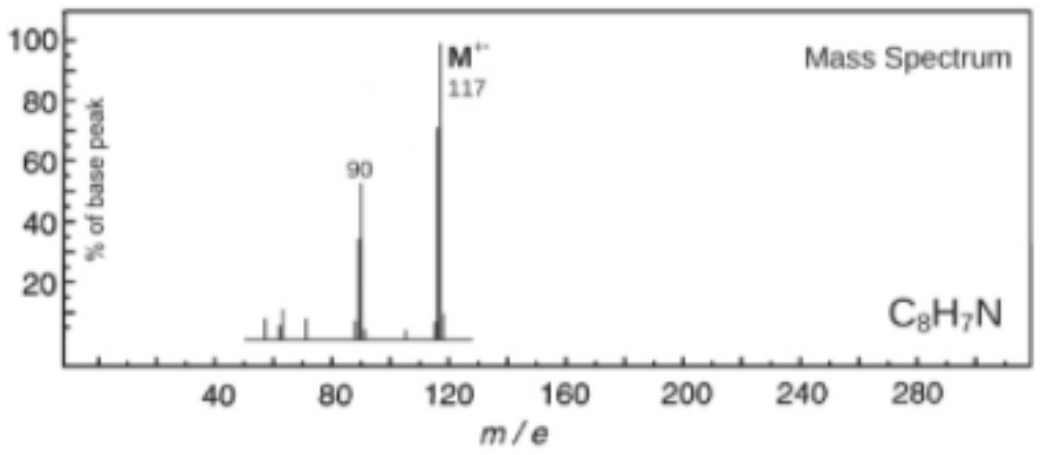


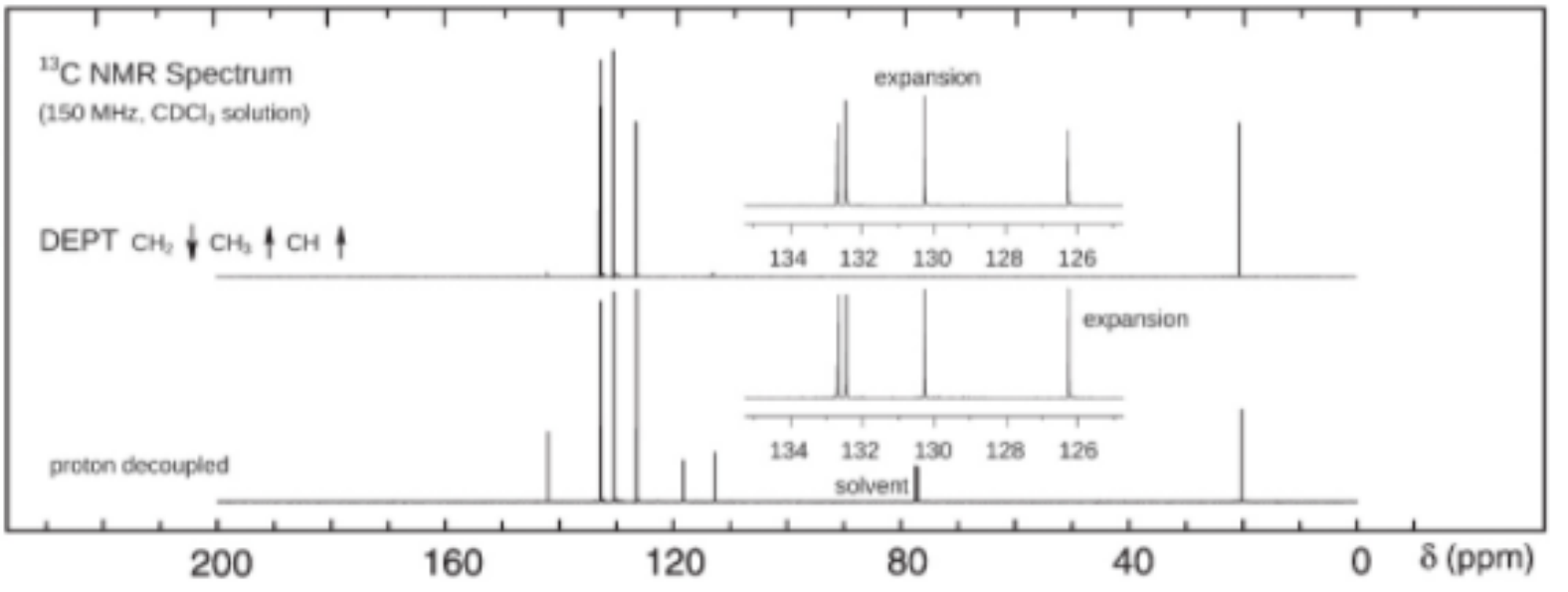

ppm
125
130
135
140
145
150
180
190
10.6
10.4
8.4
8.2
8.0
7.8
7.6
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

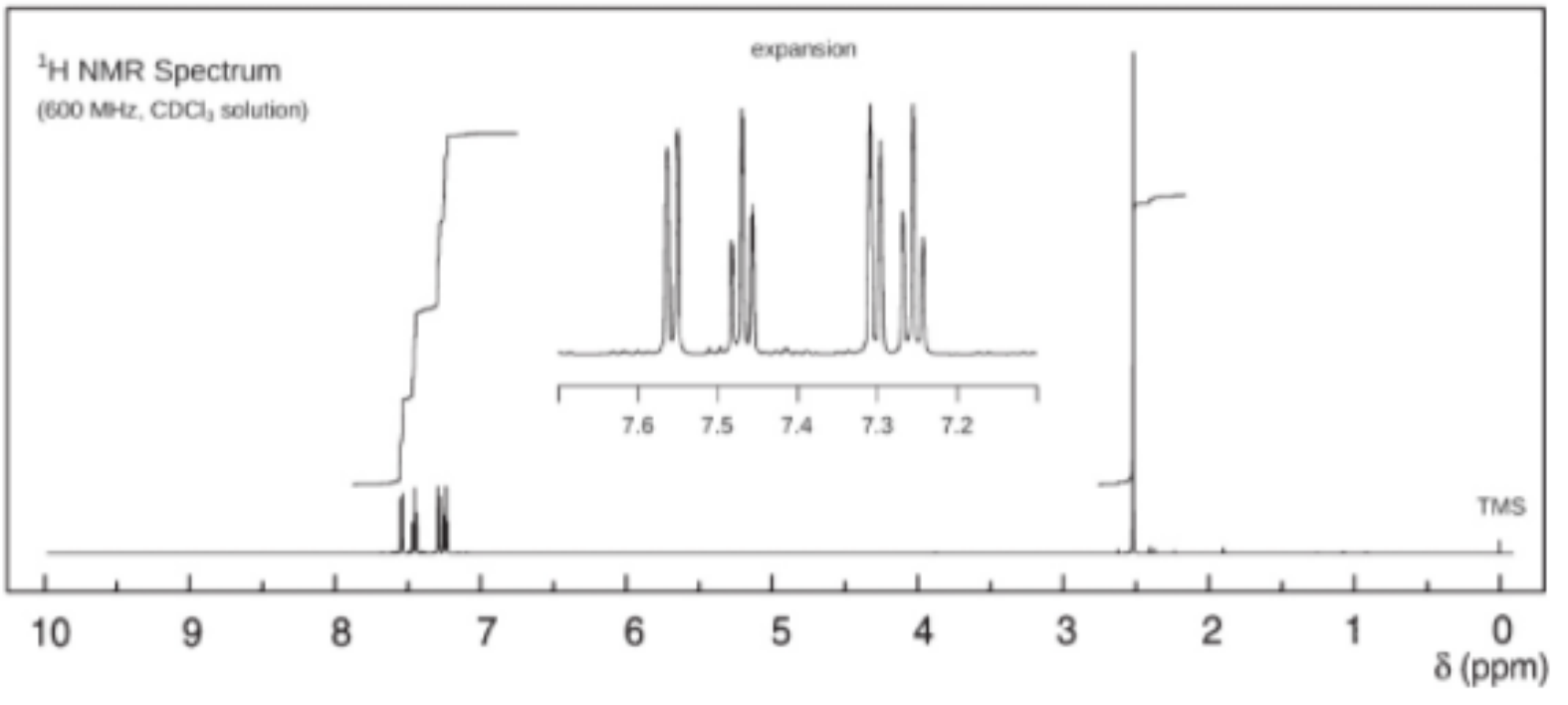
ppm
125
130
135
140
145
150
180
190
10.6
10.4
8.4
8.2
8.0
7.8
7.6
ppm
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)

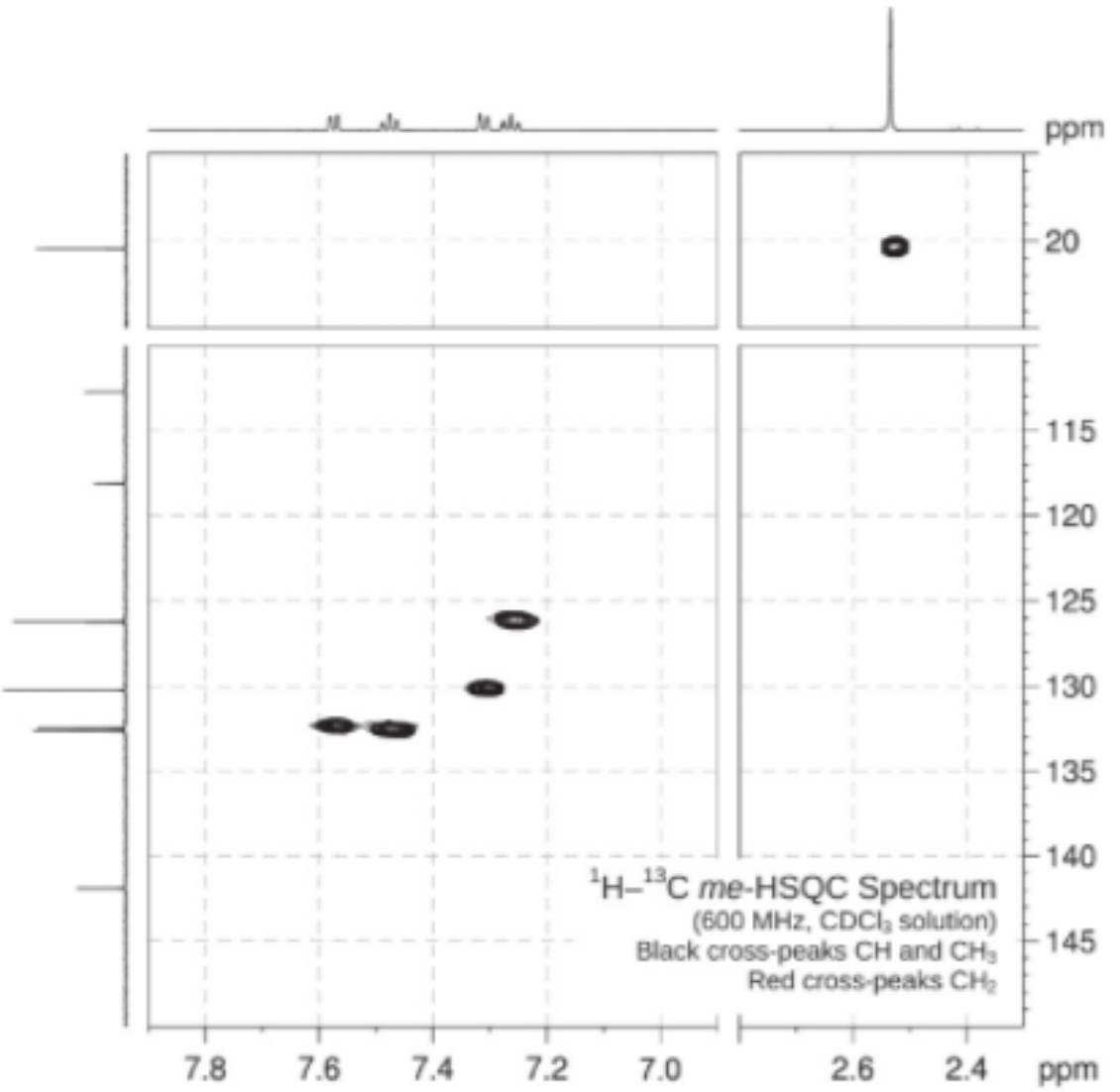
Problem 143


IR Spectrum
(thin film)
2225
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
M+·
117
90
% of base peak
100
80
60
40
20
C8H7N
40
80
120
160
200
240
280
m/e

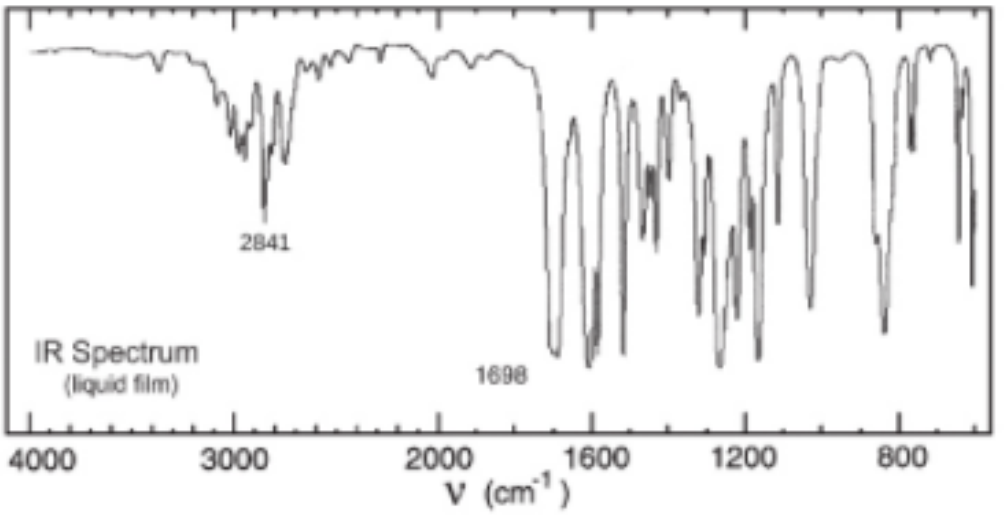

13C NMR Spectrum
(150 MHz, CDCl3 solution)
expansion
134
132
130
128
126
DEPT CH2 CH3 CH
expansion
134
132
130
128
126
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

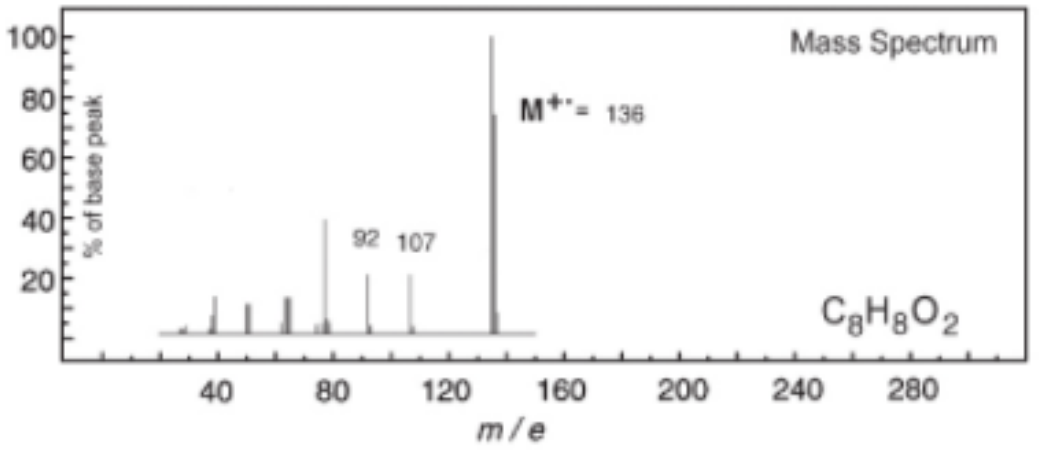

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion
7.6
7.5
7.4
7.3
7.2
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
20
115
120
125
130
135
140
145
7.8
7.6
7.4
7.2
7.0
2.6
2.4
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

ppm
20
115
120
125
130
135
140
145
7.8
7.6
7.4
7.2
7.0
2.6
2.4
ppm
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)

Problem 144

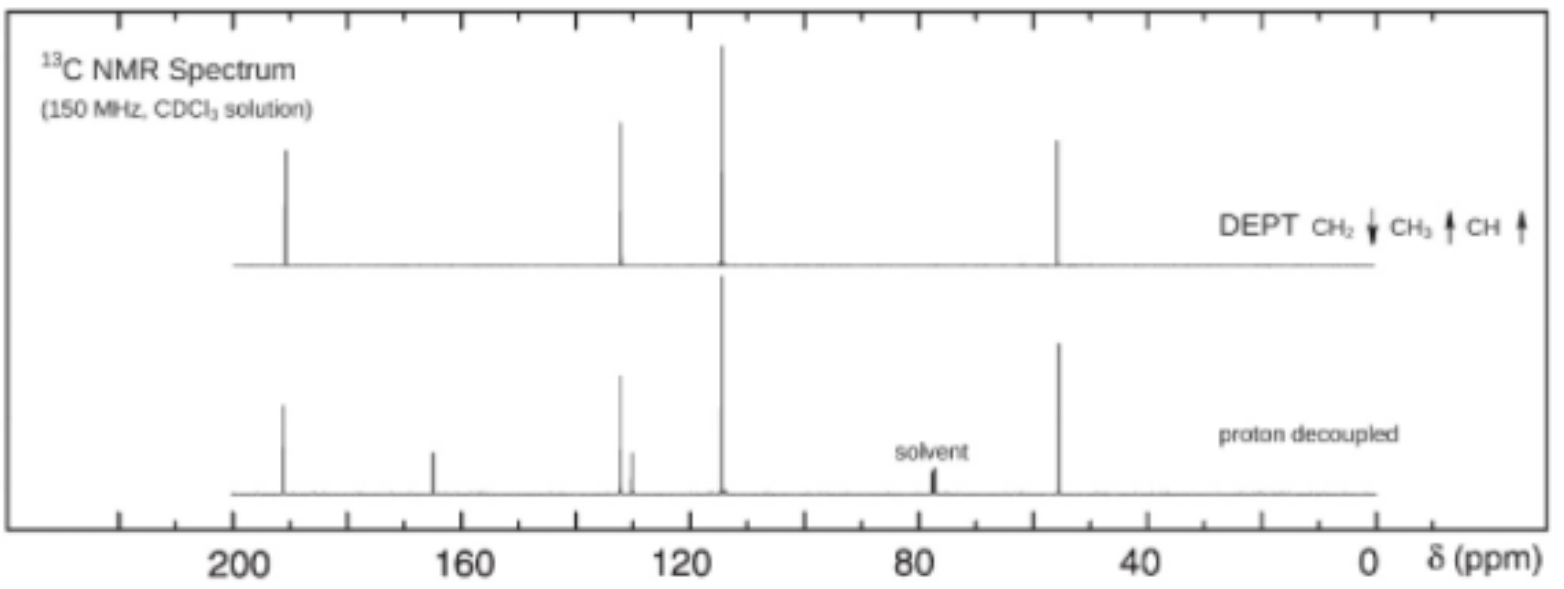


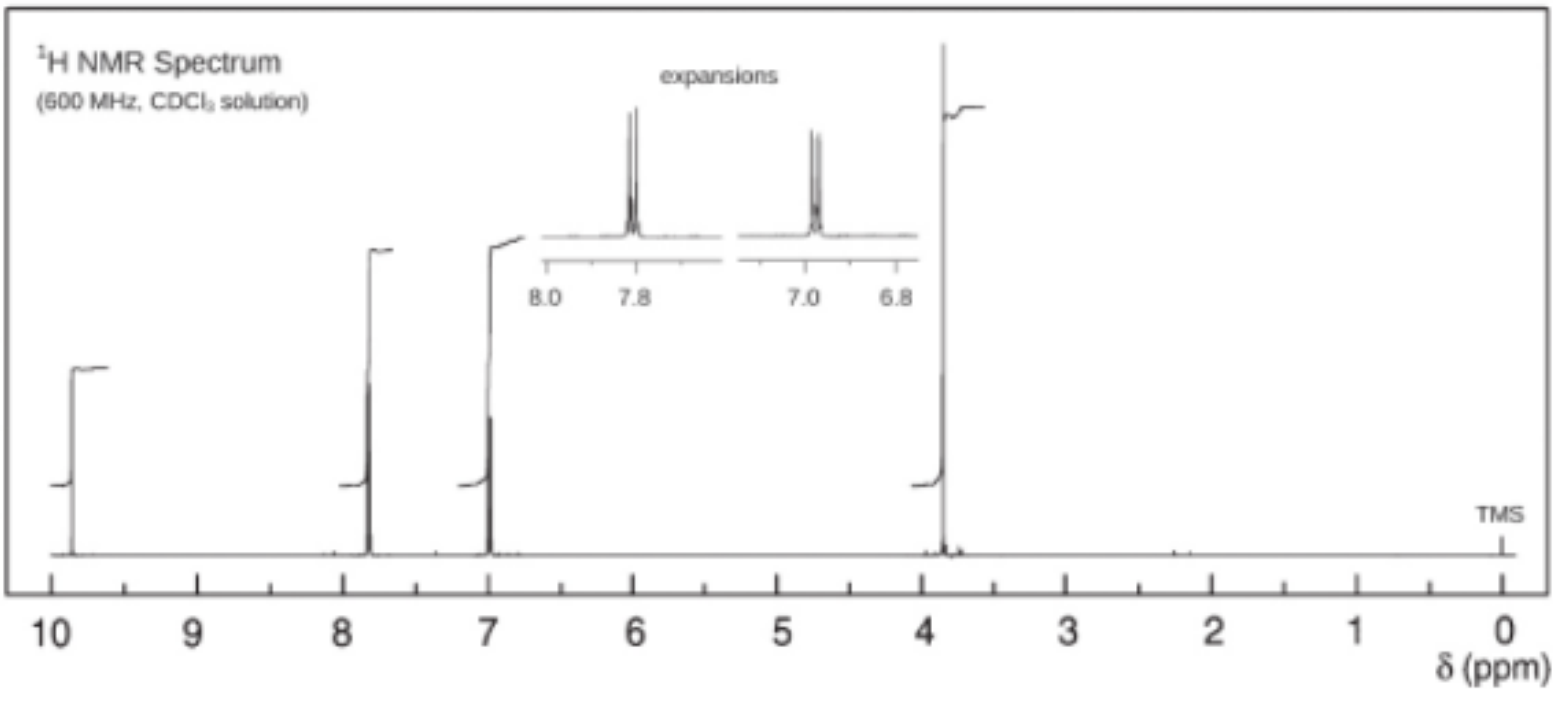


UV Spectrum

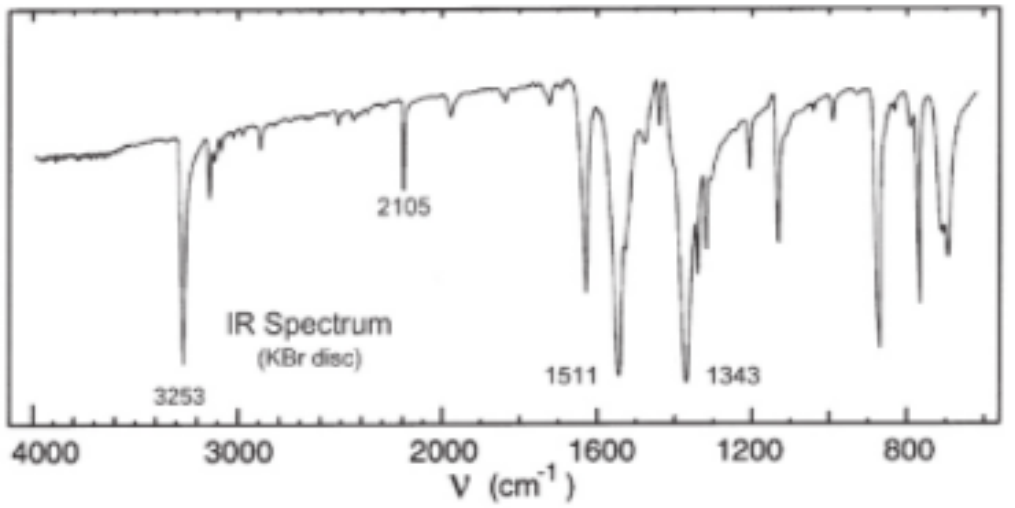
λ_{max} 277 nm ($\log_{10}\varepsilon$ 4.2)

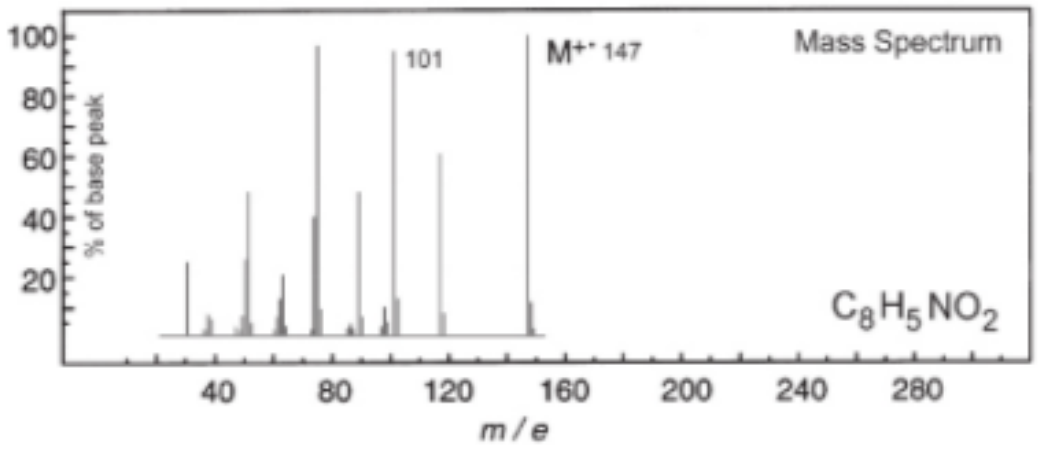
solvent : methanol





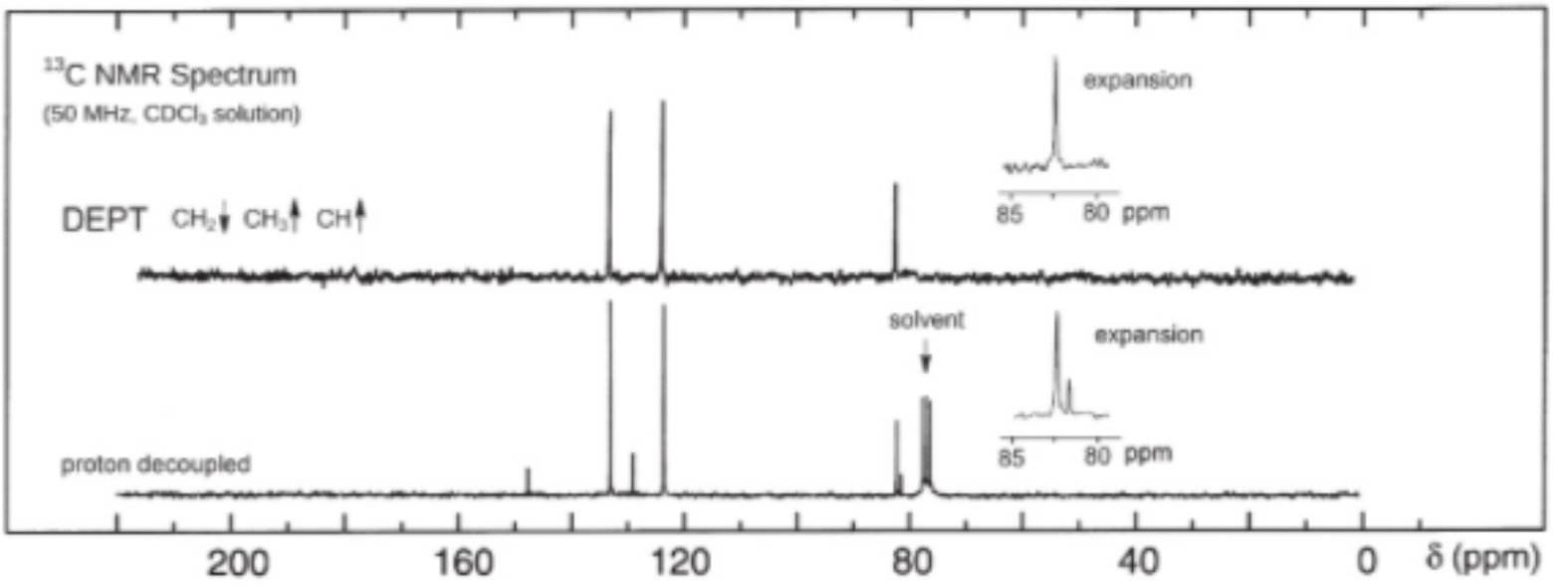
Problem 145

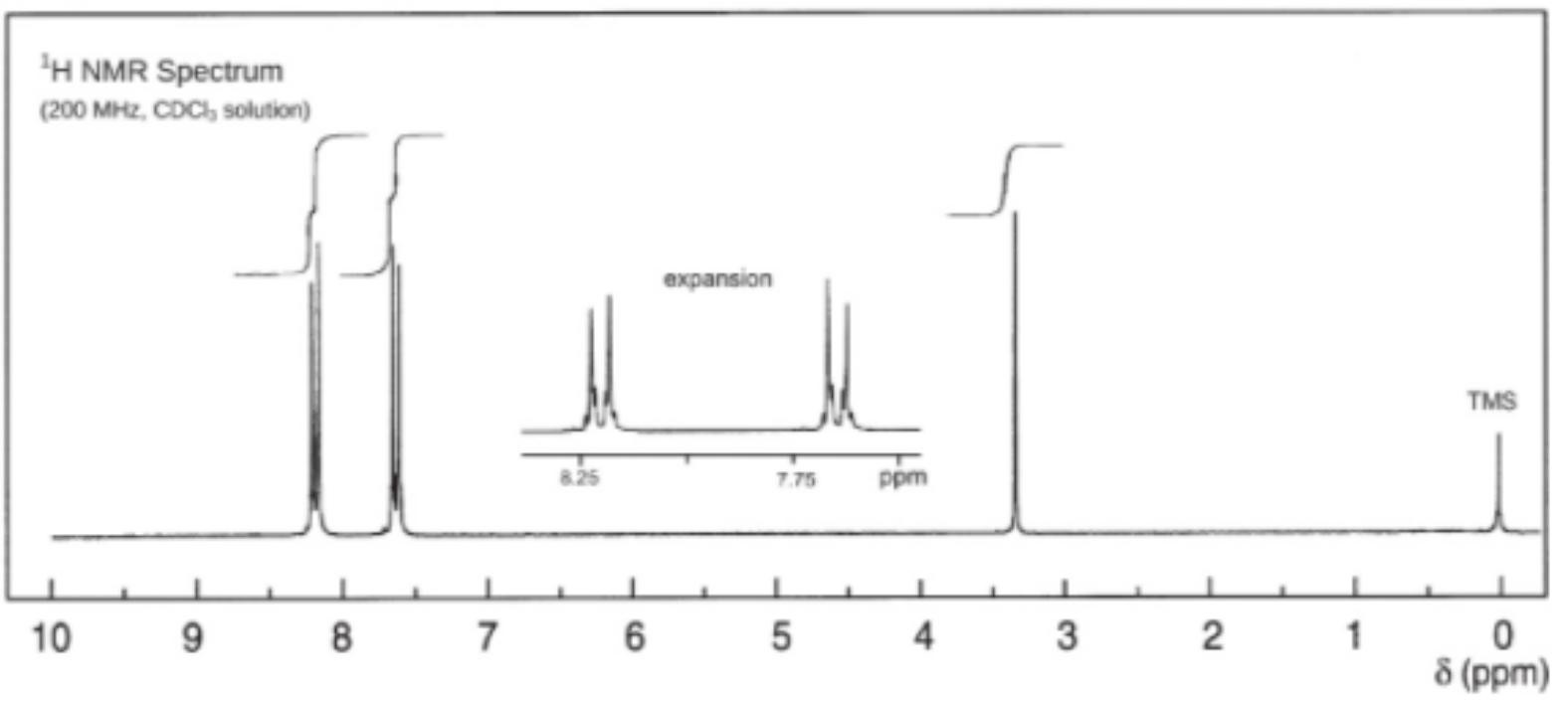




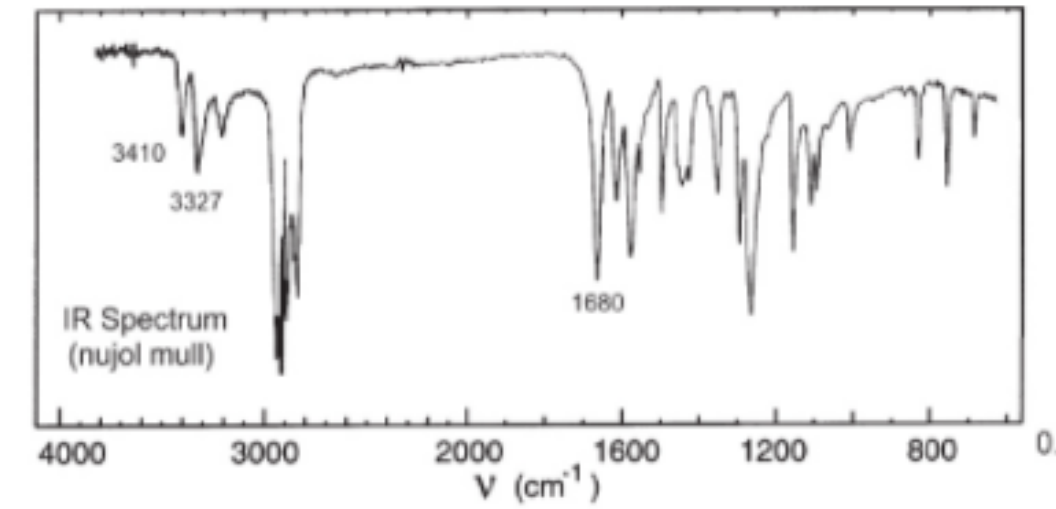
UV Spectrum

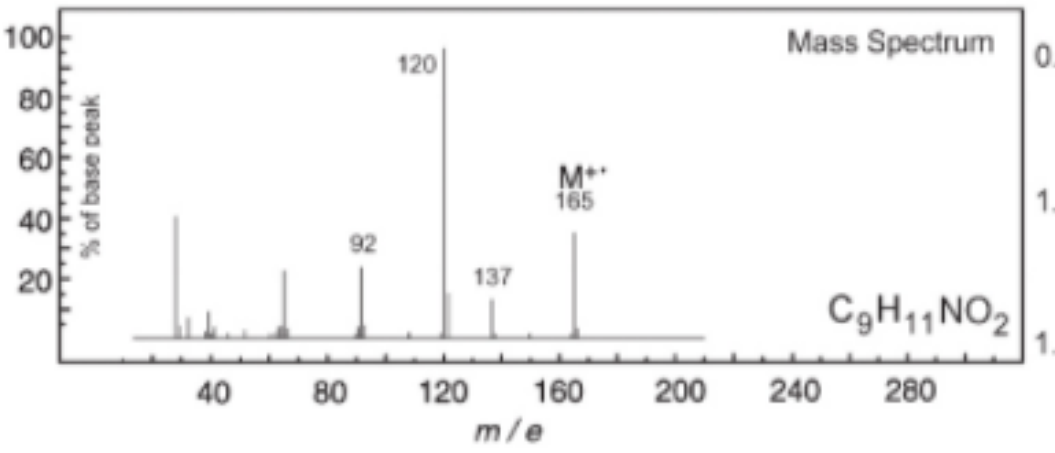
$\log_{10}\varepsilon > 4$

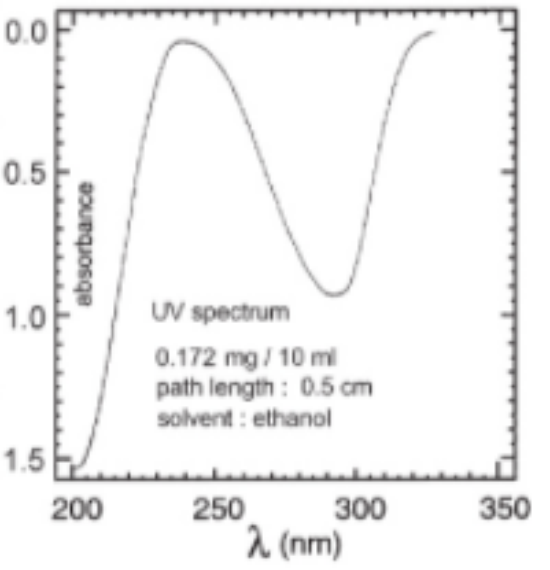


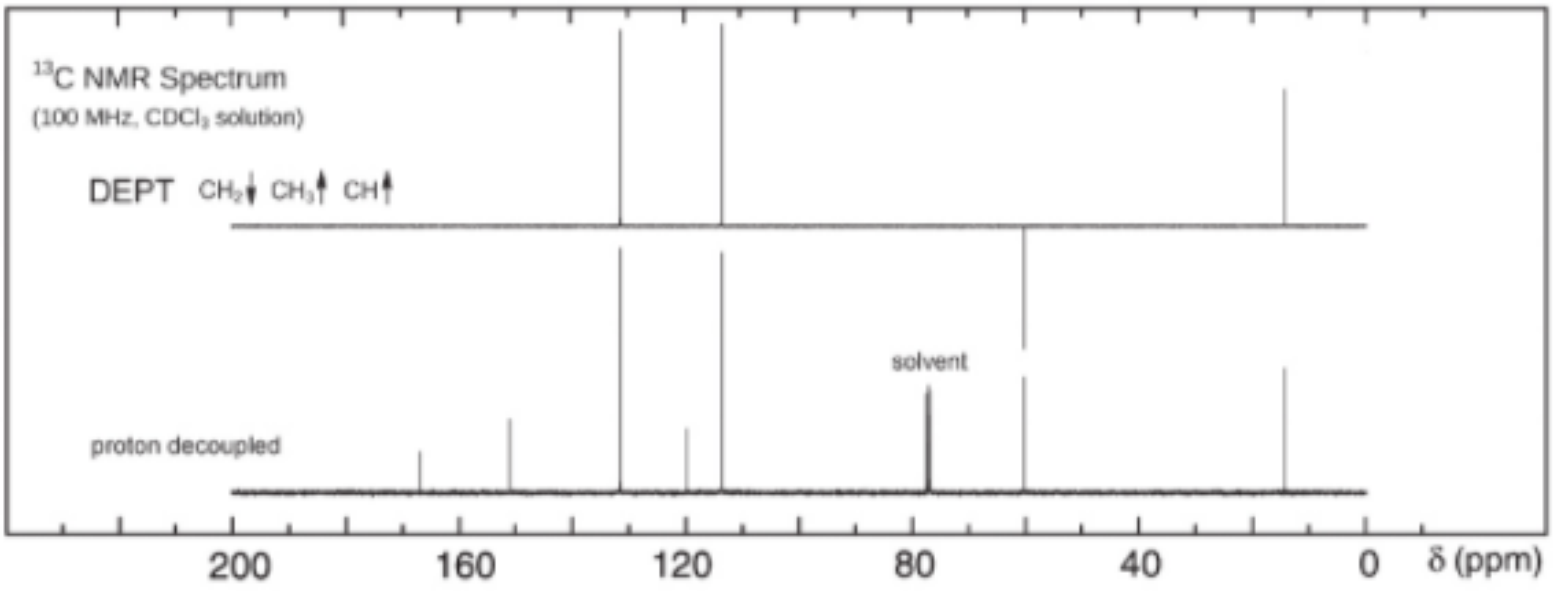


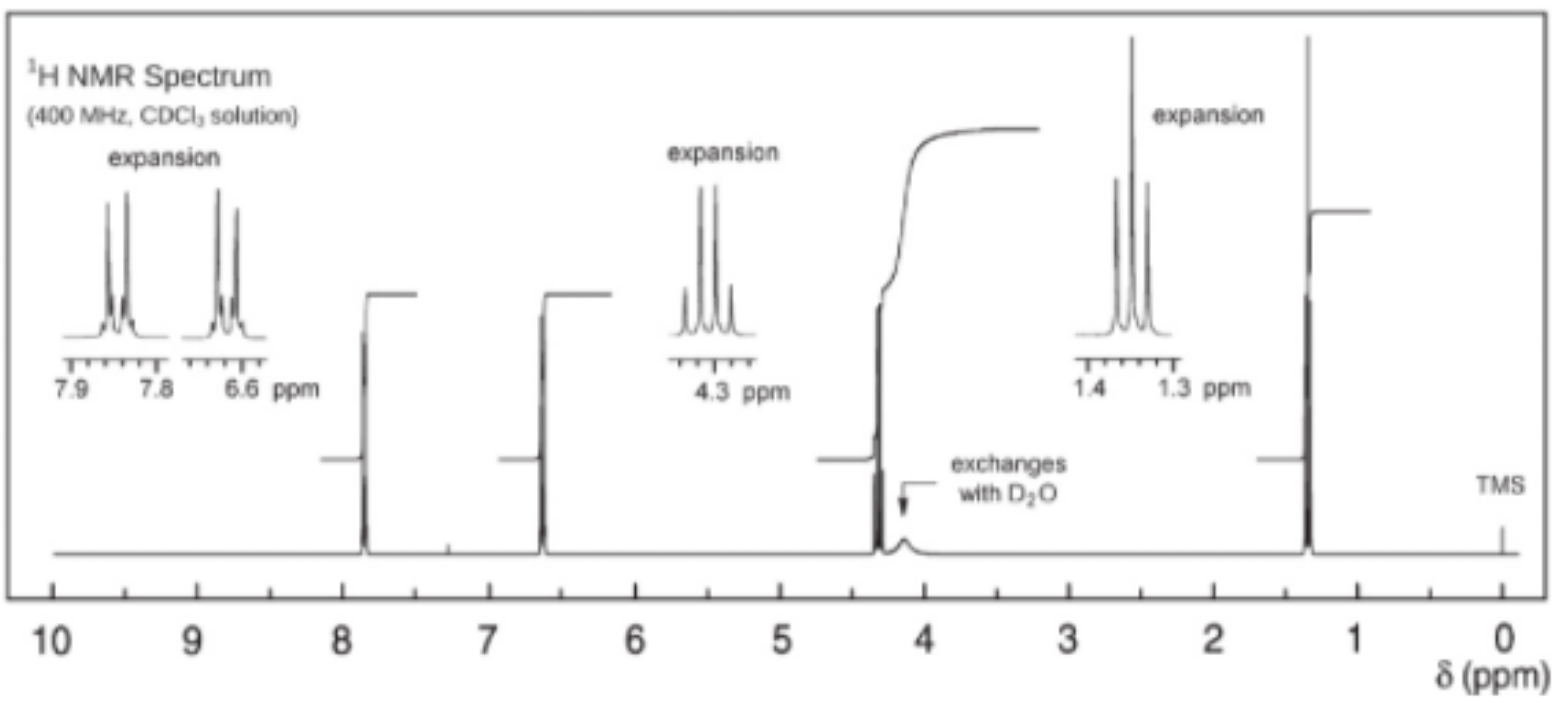
Problem 146

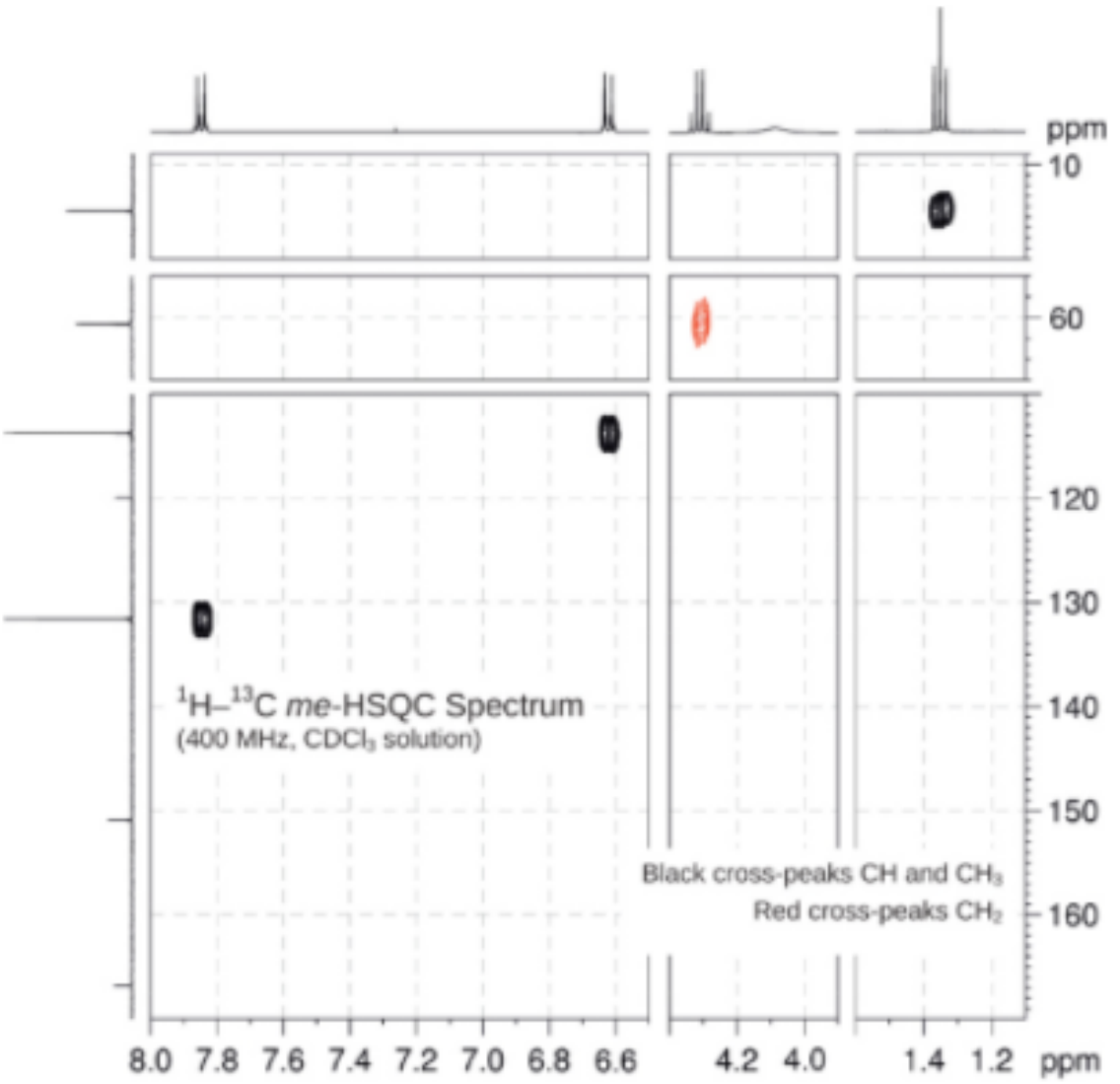

3410
3327
1680
IR Spectrum
(nujol mull)
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
120
M+·
165
92
137
C9H11NO2
100
80
60
40
20
40
80
120
160
200
240
280
m/e


absorbance
UV spectrum
0.172 mg / 10 ml
path length : 0.5 cm
solvent : ethanol
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)

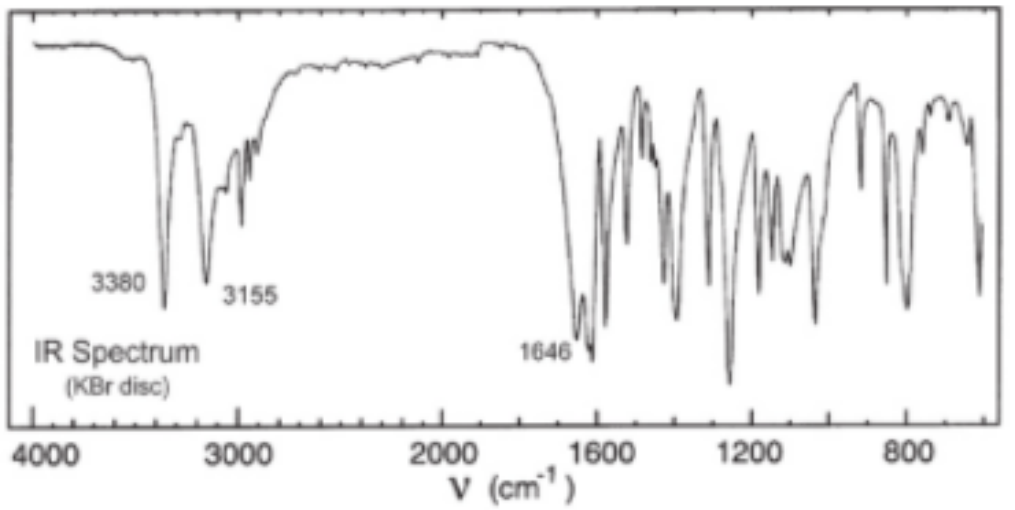

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

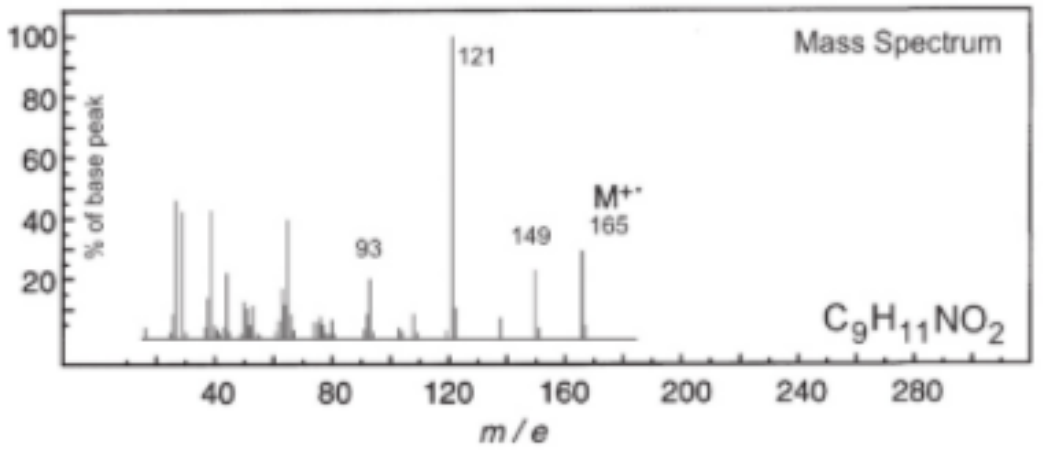

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.9
7.8
6.6 ppm
expansion
4.3 ppm
expansion
1.4
1.3 ppm
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

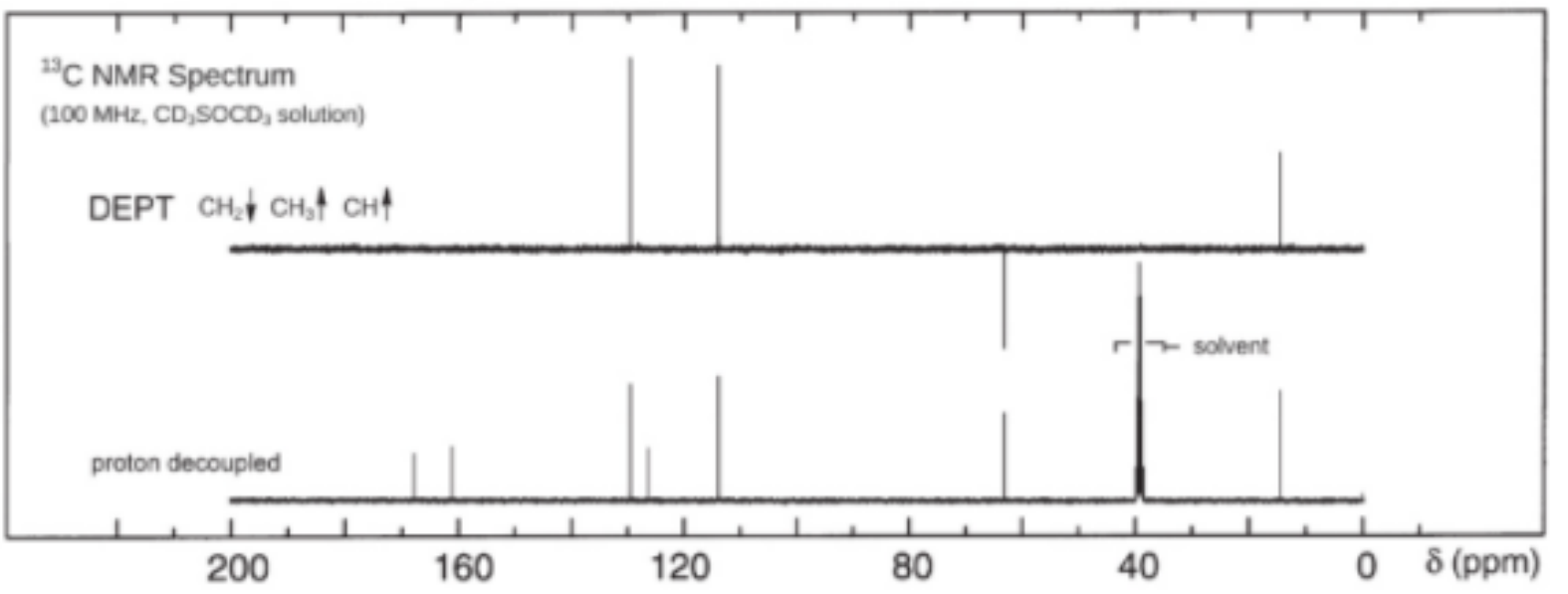

ppm
10
60
120
130
140
150
160
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
4.2 4.0
1.4 1.2
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

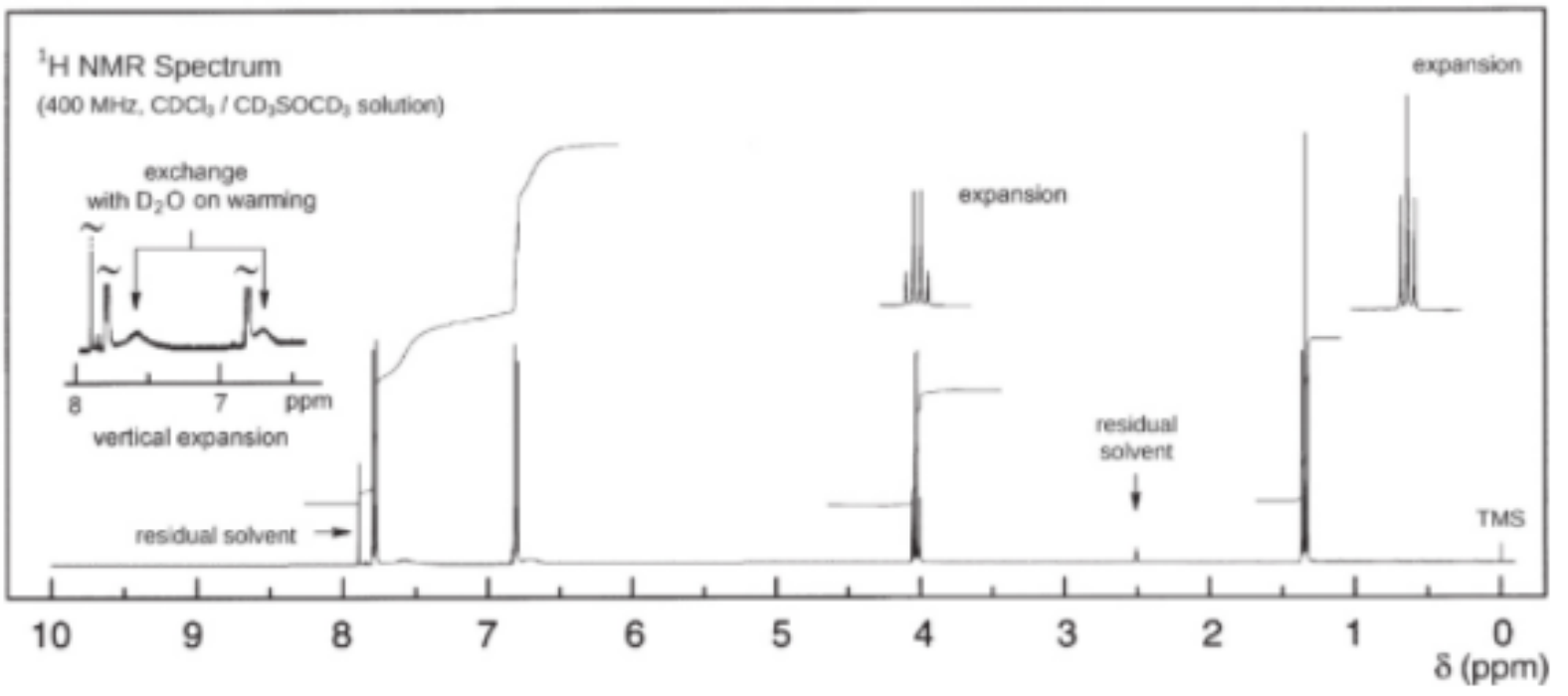
ppm
10
60
120
130
140
150
160
170
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
4.2 4.0
1.4 1.2
ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)

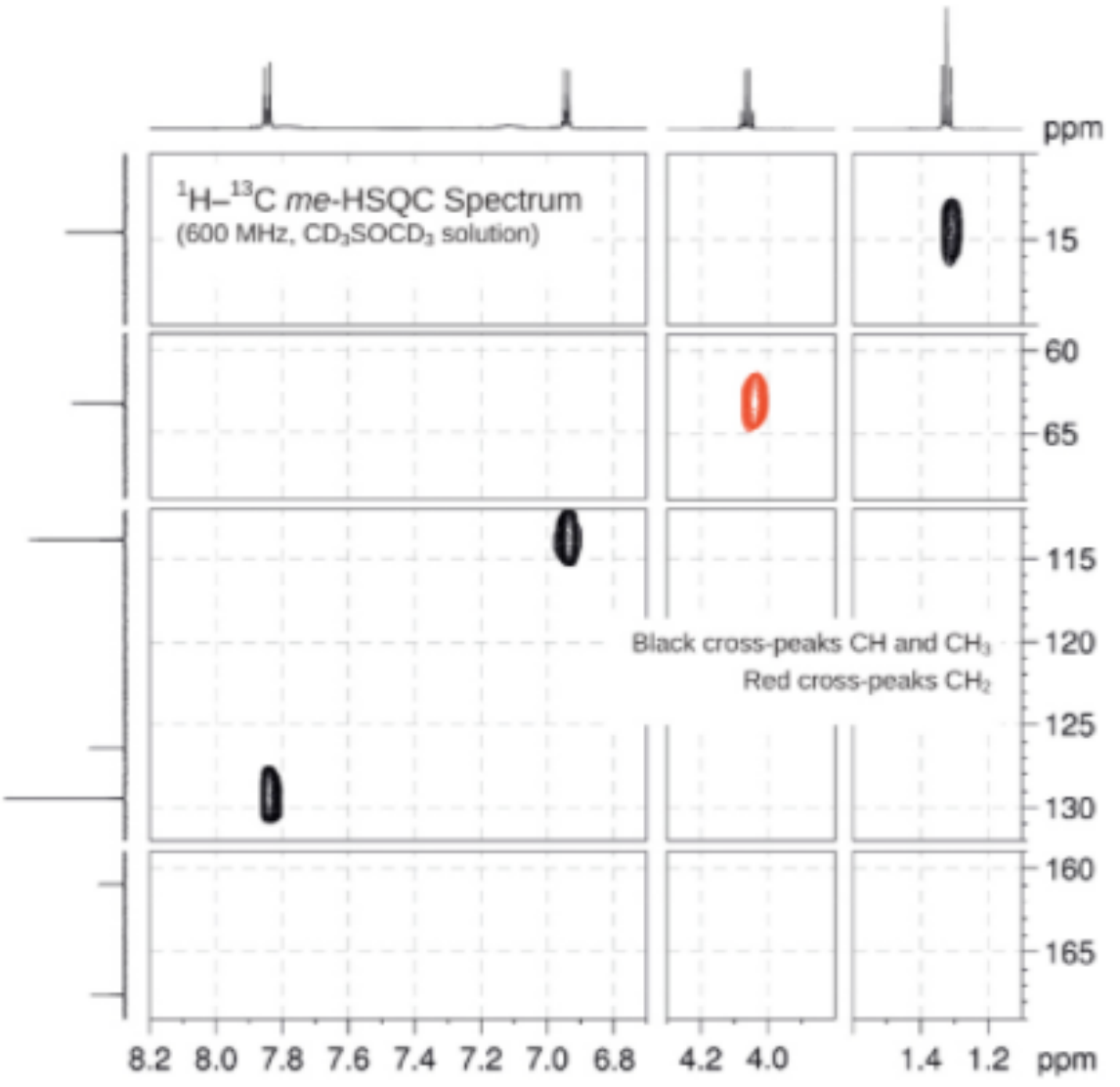
Problem 147

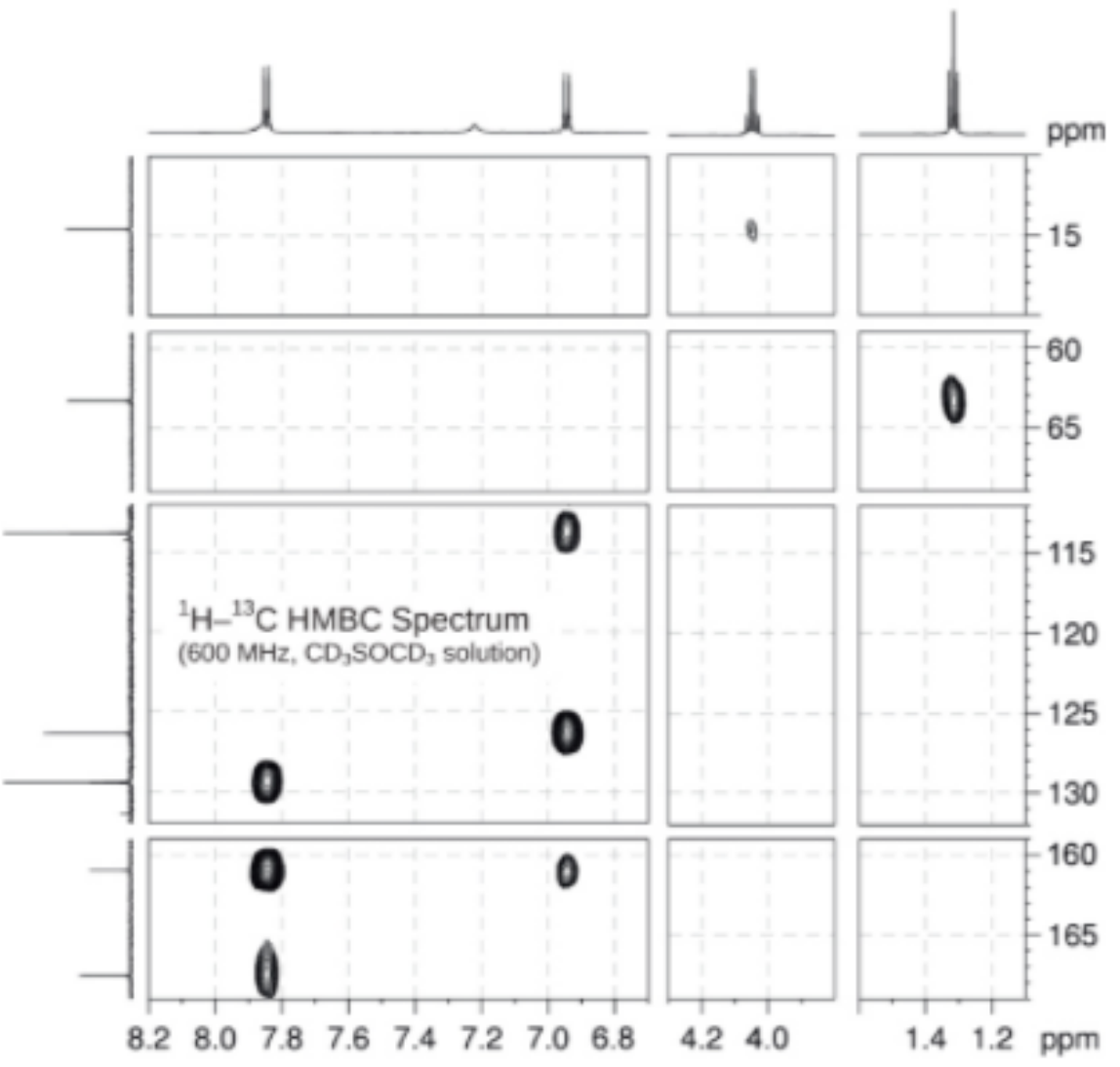

3380
3155
1646
IR Spectrum
(KBr disc)
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
100
80
60
40
20
121
93
149
M+·
165
C9H11NO2
40
80
120
160
200
240
280
m/e

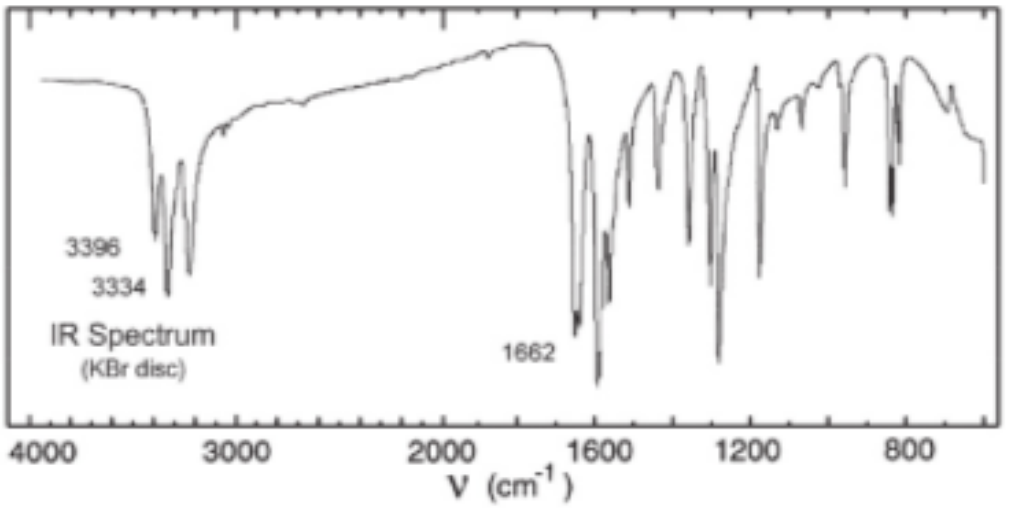

13C NMR Spectrum
(100 MHz, CD3SOCD3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

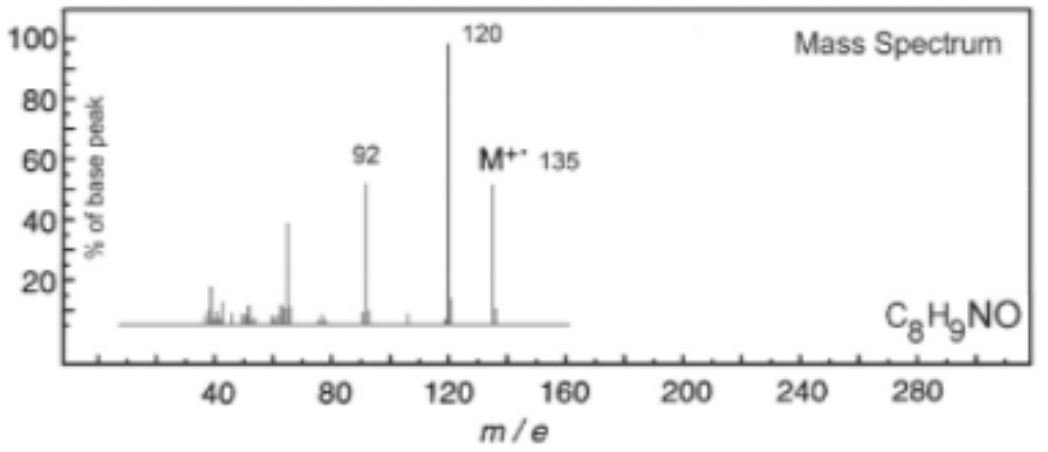

1H NMR Spectrum
(400 MHz, CDCl3 / CD3SOCD3 solution)
exchange
with D2O on warming
8
7
ppm
vertical expansion
residual solvent
expansion
expansion
residual
solvent
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, CD_3SOCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
ppm
15
60
65
115
120
125
130
160
165
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
4.2 4.0
1.4 1.2
ppm


^{1}H–^{13}C HMBC Spectrum
(600 MHz, CD_3SOCD_3 solution)
ppm
15
60
65
115
120
125
130
160
165
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
4.2 4.0
1.4 1.2
ppm

Problem 148

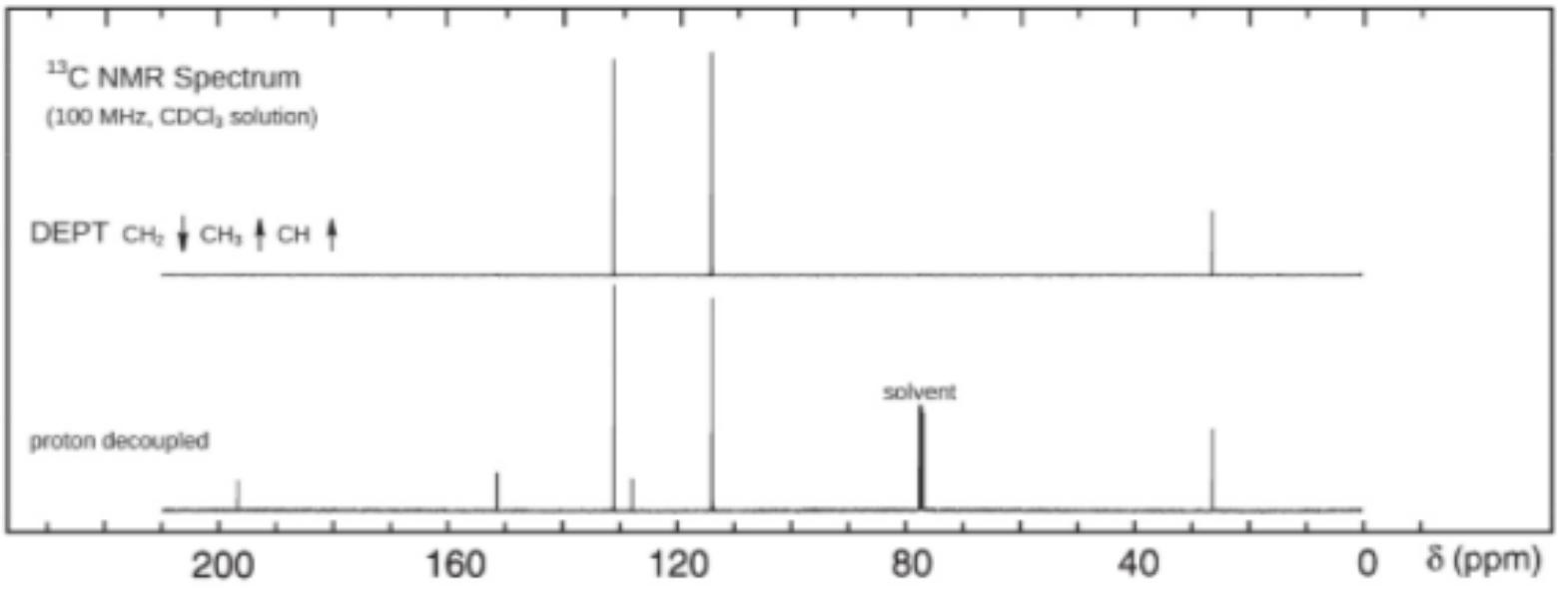


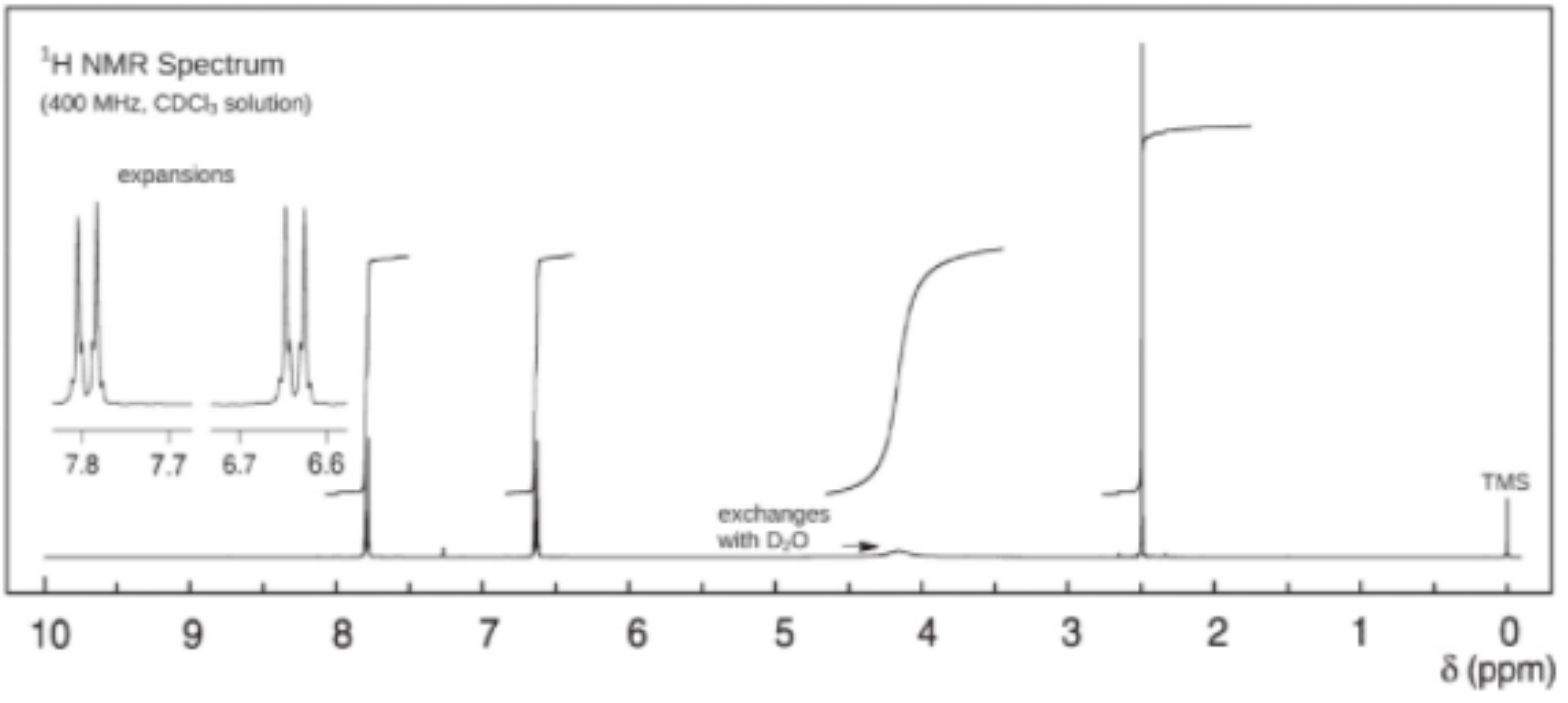


UV Spectrum

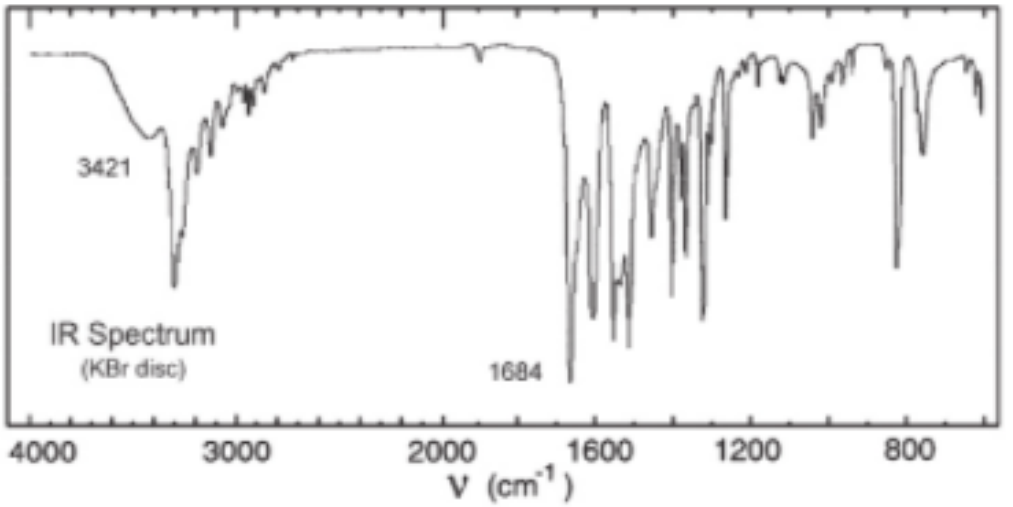
λ_{max} 312 nm ($\log_{10}\varepsilon$ 4.3)

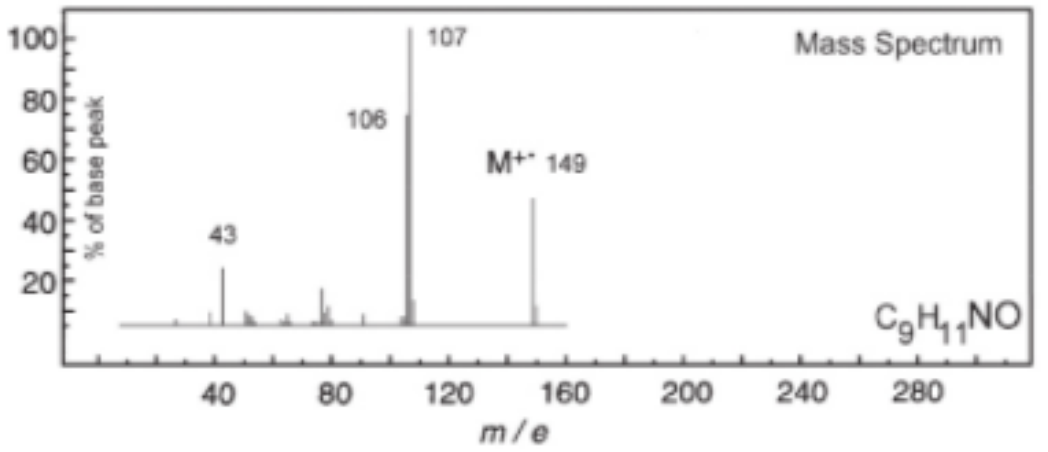
solvent : methanol





Problem 149



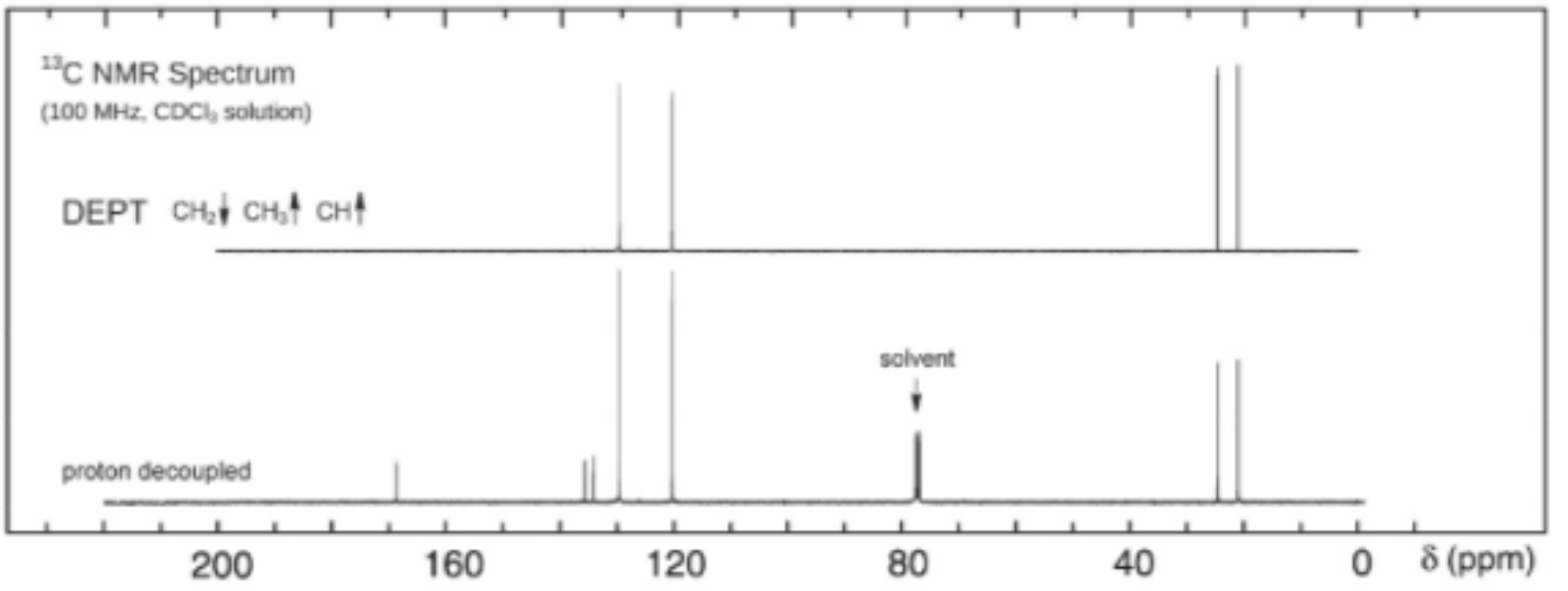


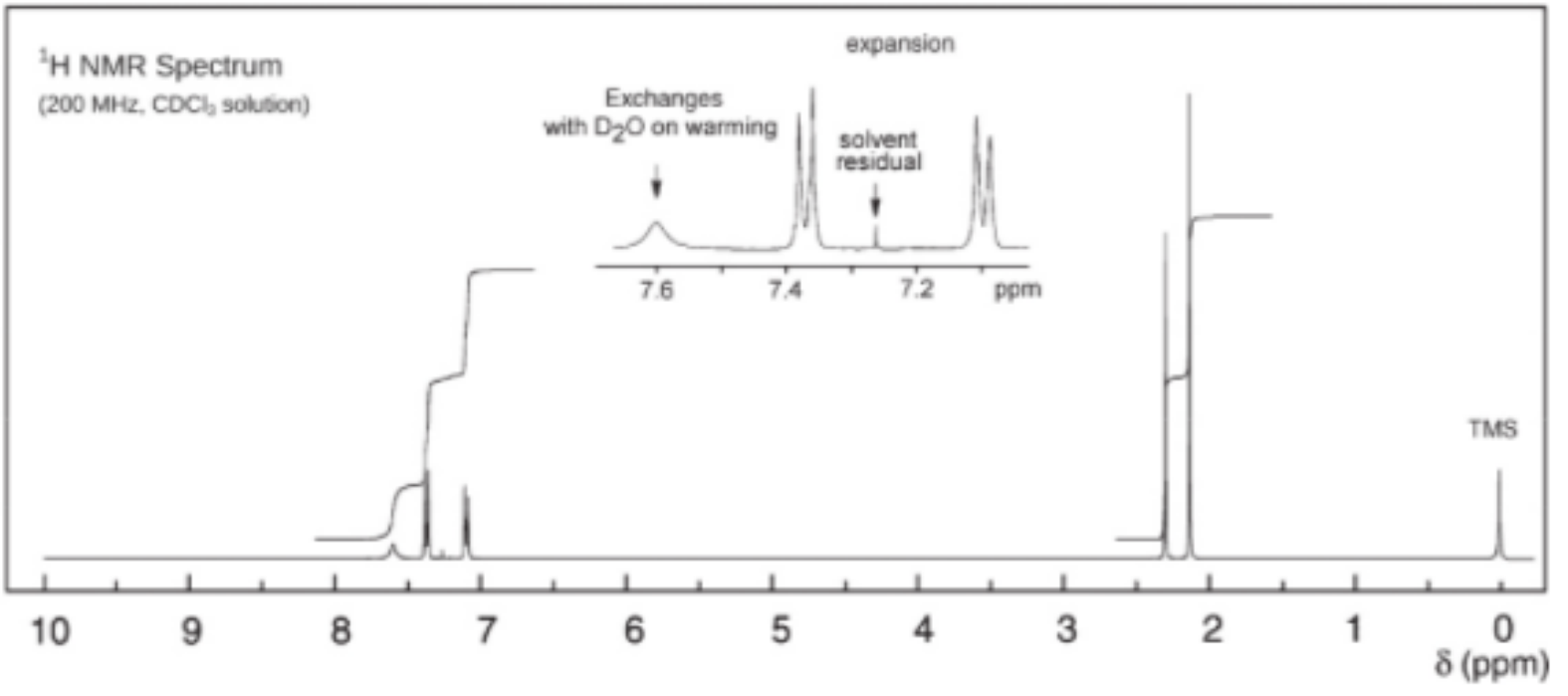
UV Spectrum

λ_{max} 246 nm ($\log_{10}\varepsilon$ 4.2)

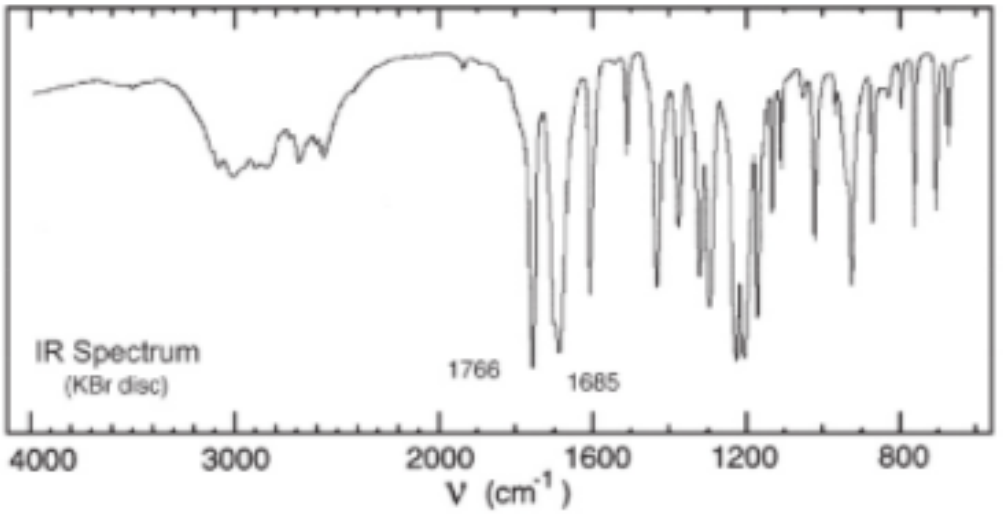
λ_{max} 280 nm ($\log_{10}\varepsilon$ 3.1)

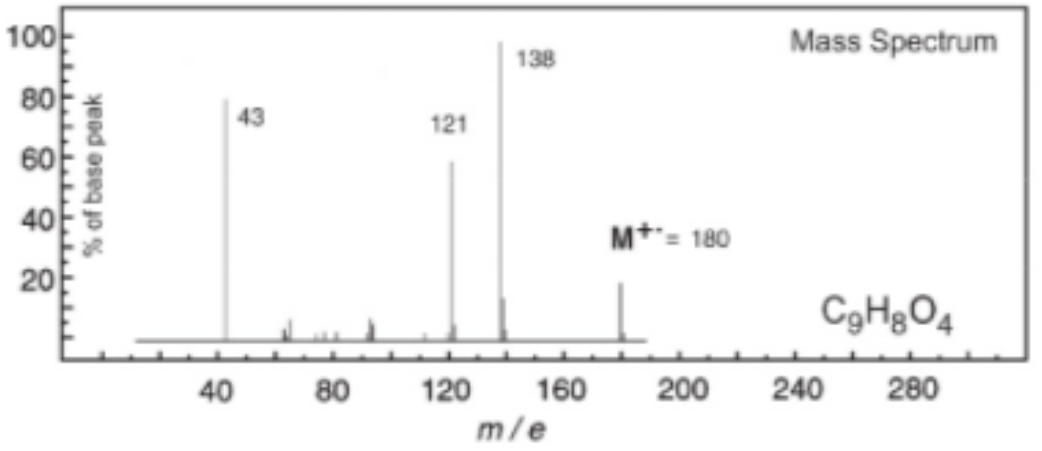
solvent : methanol





Problem 150



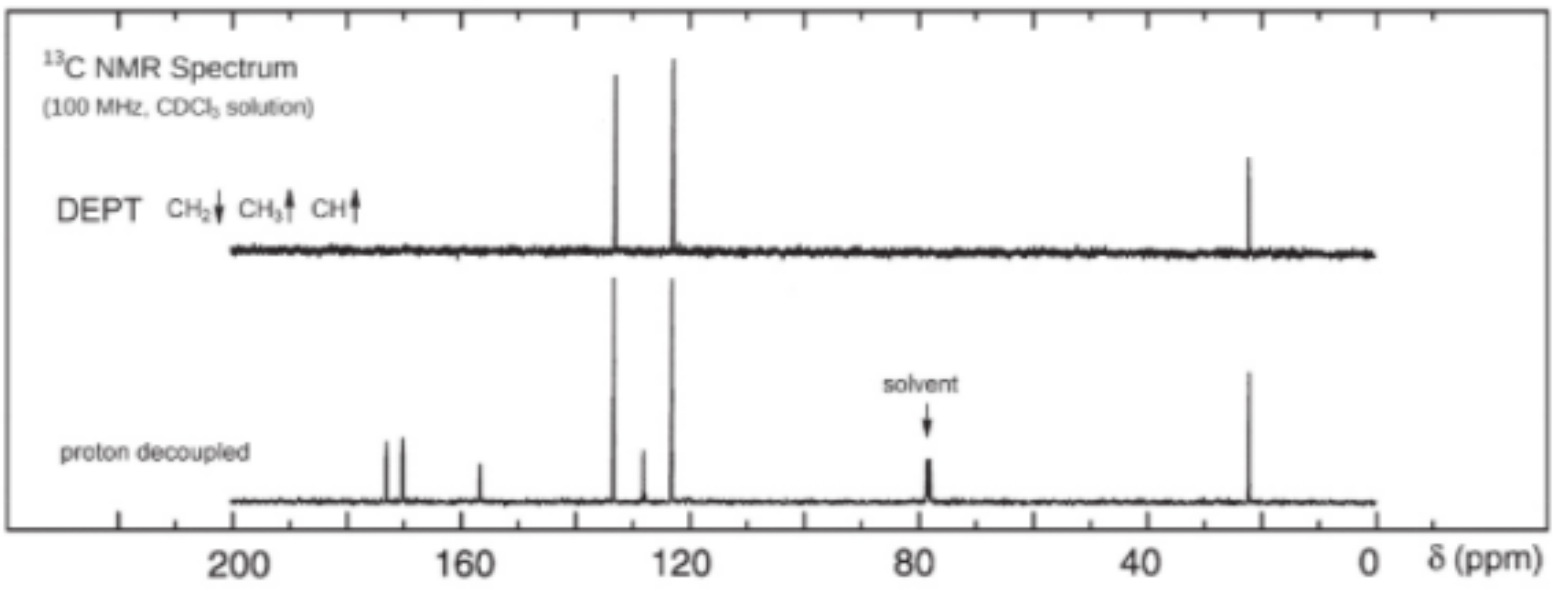


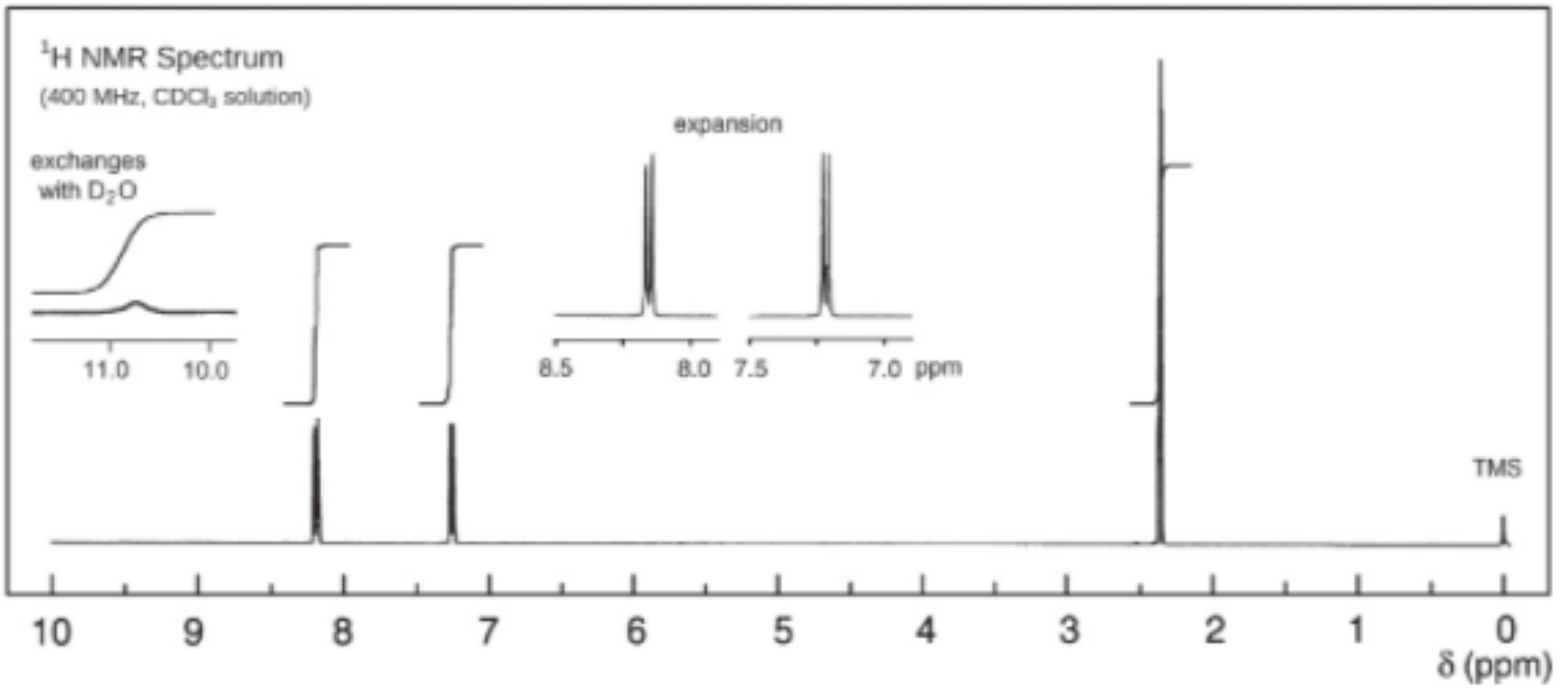
UV Spectrum

λ_{max} 235 nm ($\log_{10}\varepsilon$ 4.1)

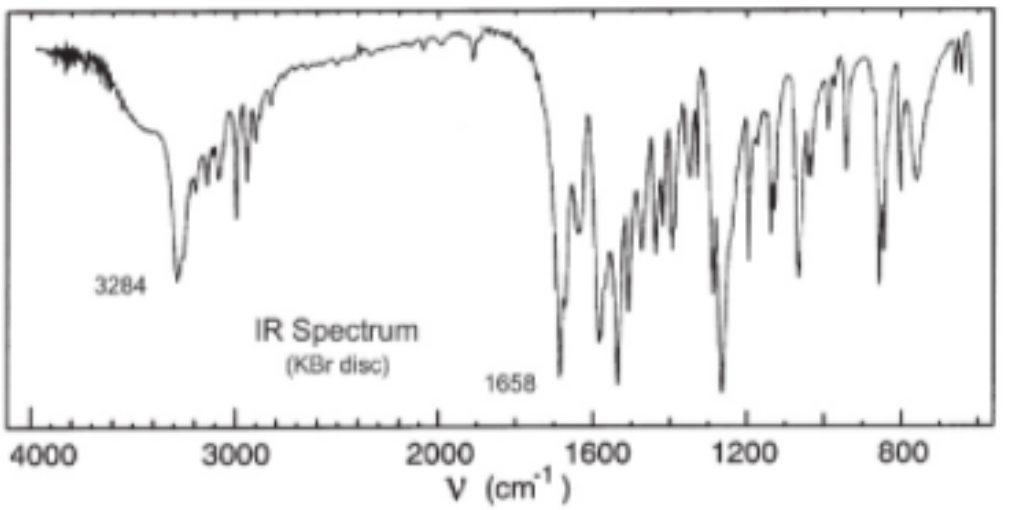
λ_{max} 265 nm ($\log_{10}\varepsilon$ 3.0)

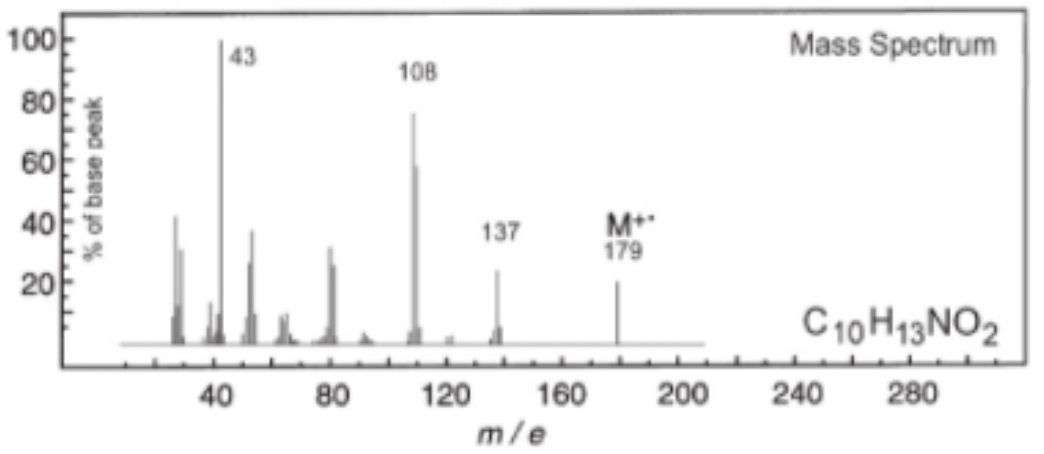
solvent : ethanol





Problem 151



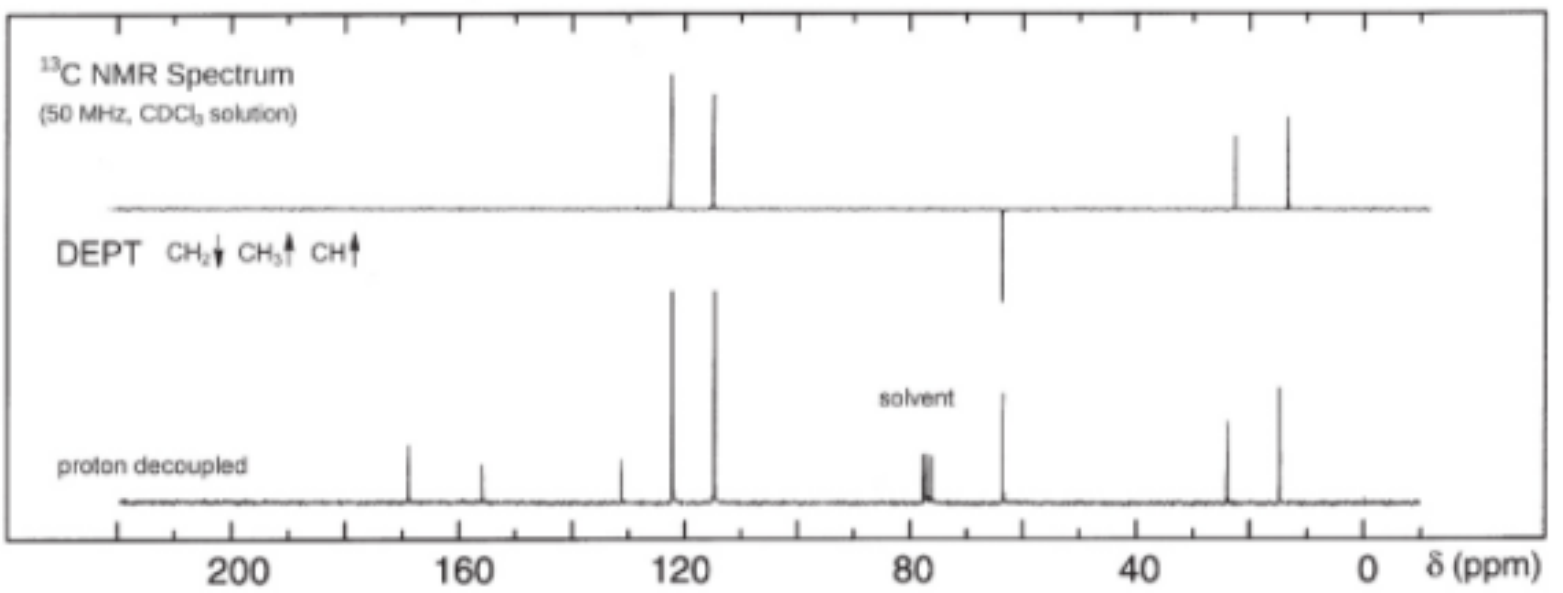


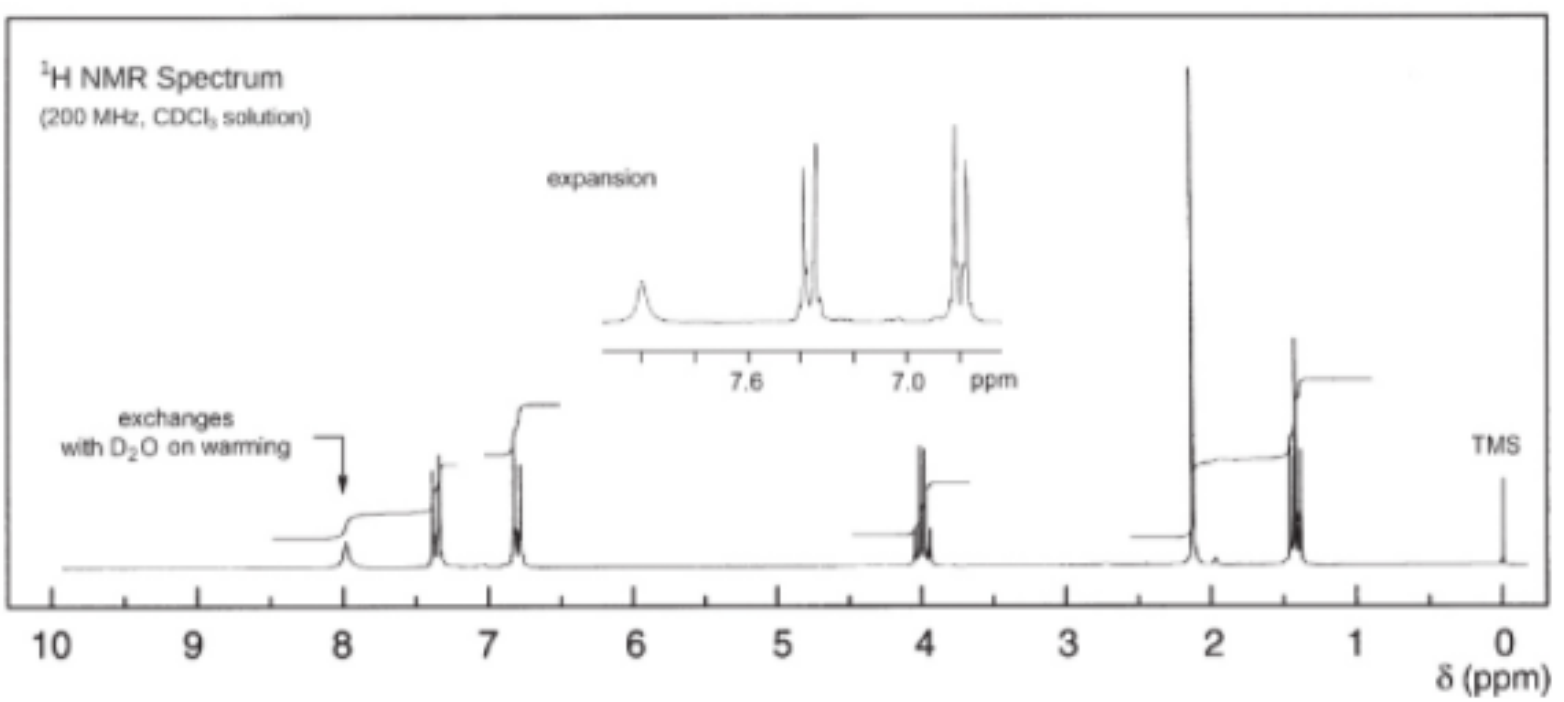
UV Spectrum

λ_{max} 250 nm ($\log_{10}\varepsilon$ 3.1)

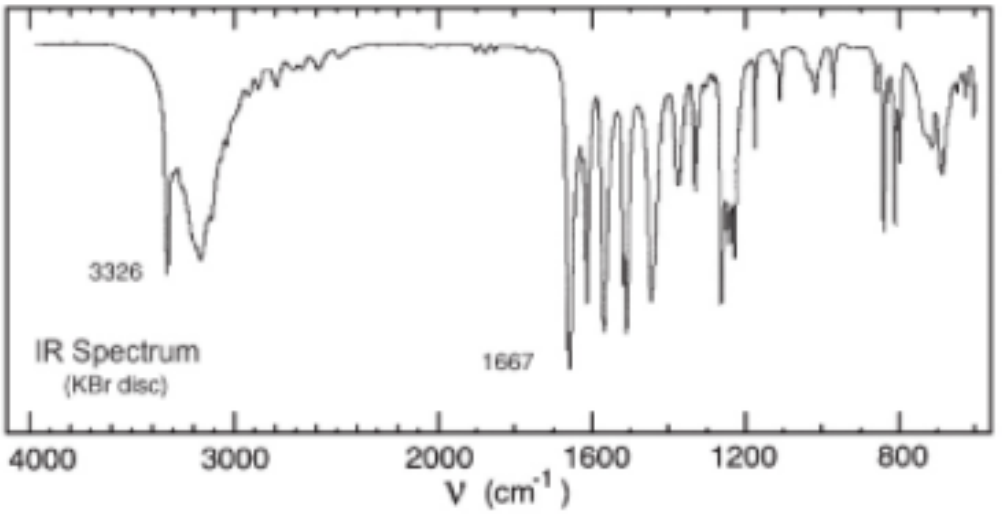
λ_{max} 287 nm ($\log_{10}\varepsilon$ 2.2)

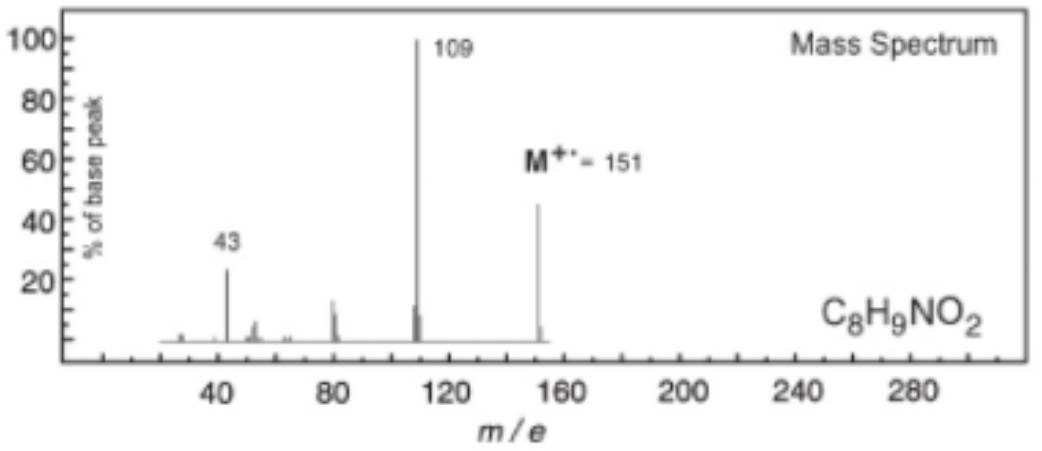
solvent : chloroform





Problem 152



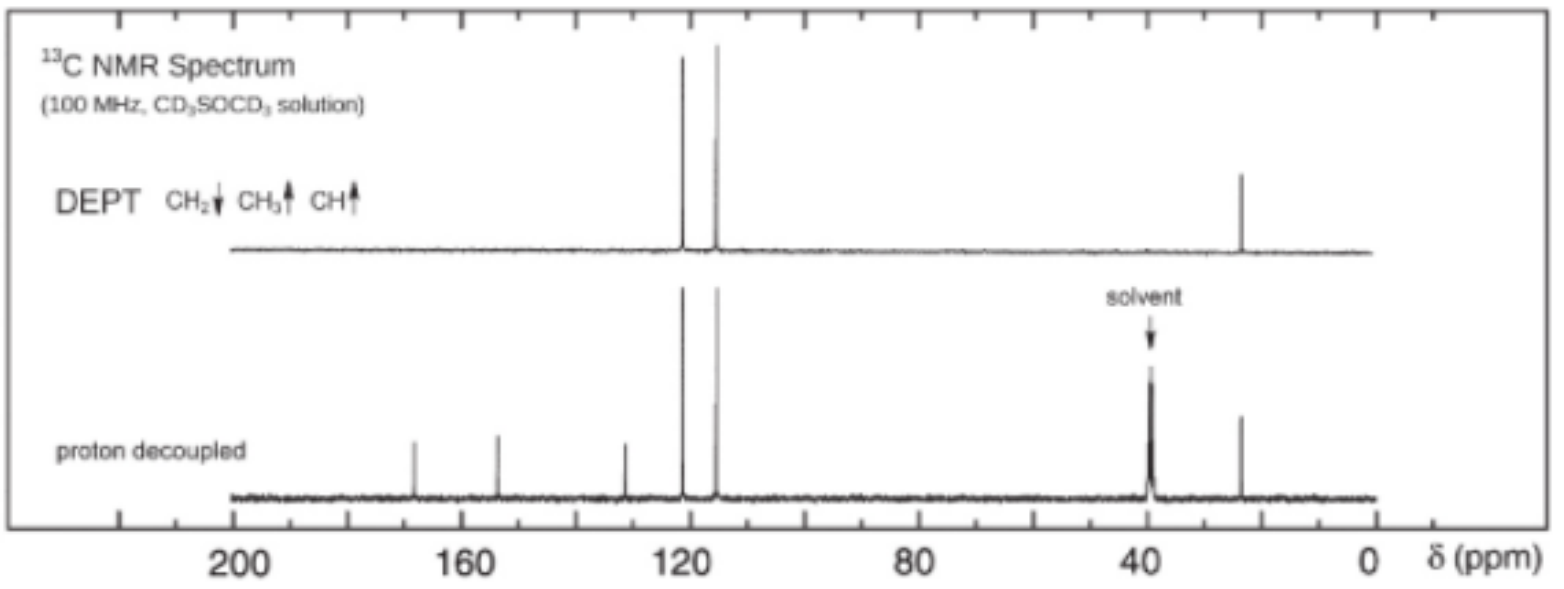


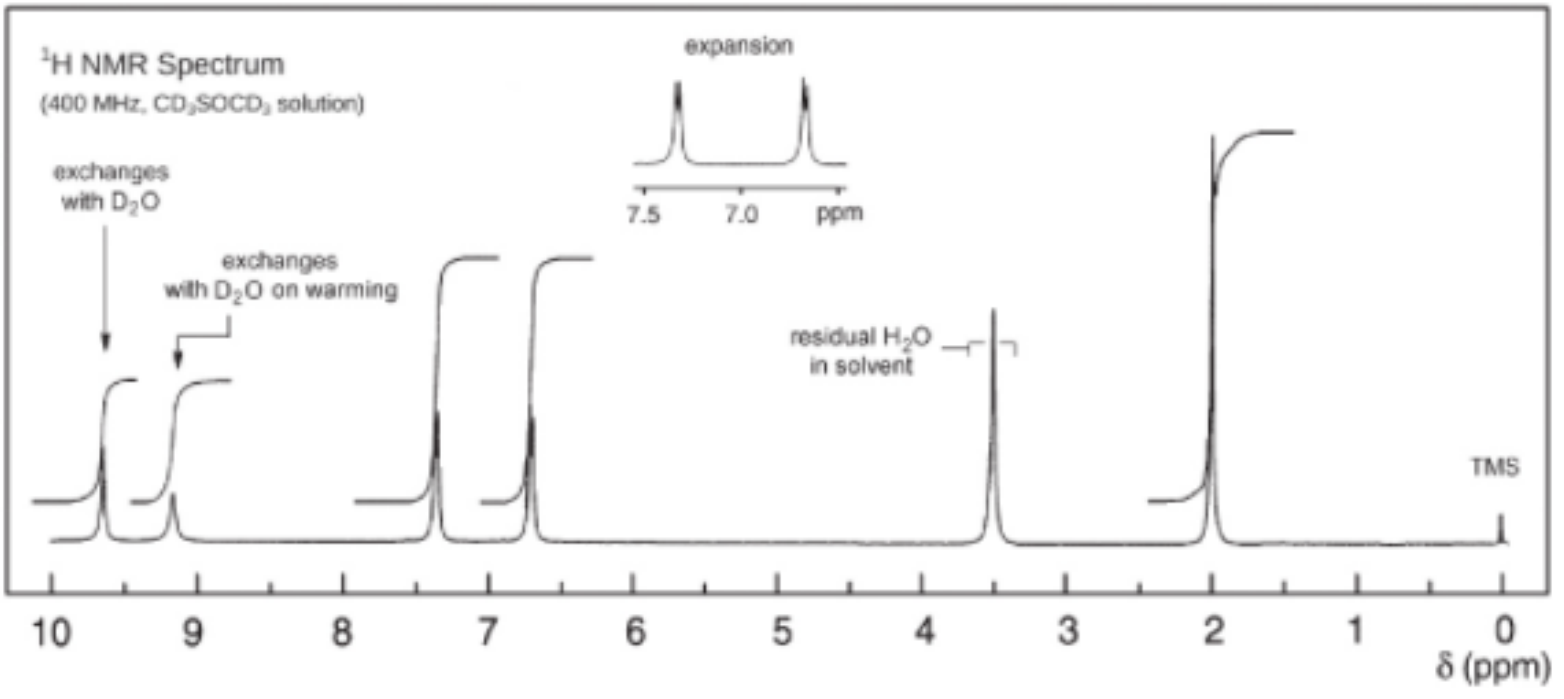
UV Spectrum

λ_{max} 250 nm ($\log_{10}\varepsilon$ 4.1)

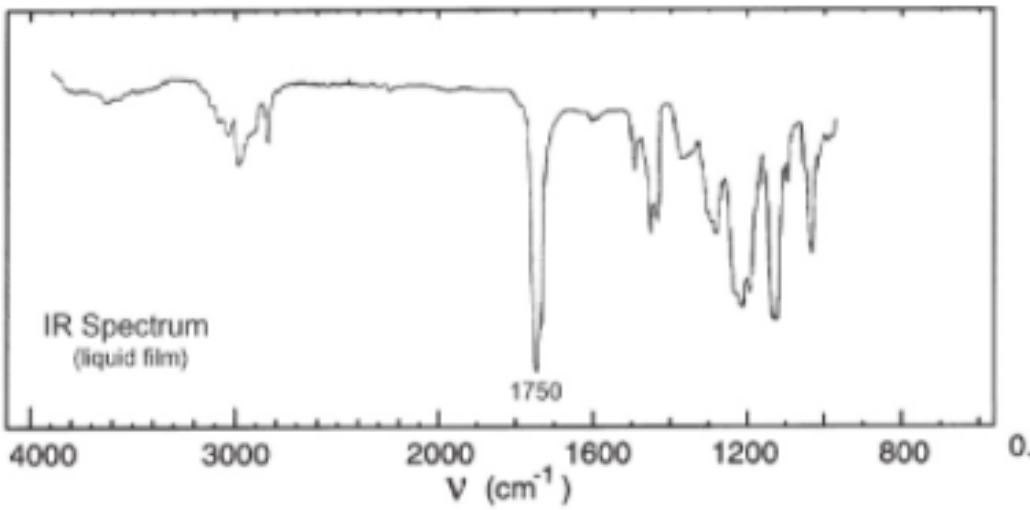
λ_{max} 285 nm ($\log_{10}\varepsilon$ 3.6)

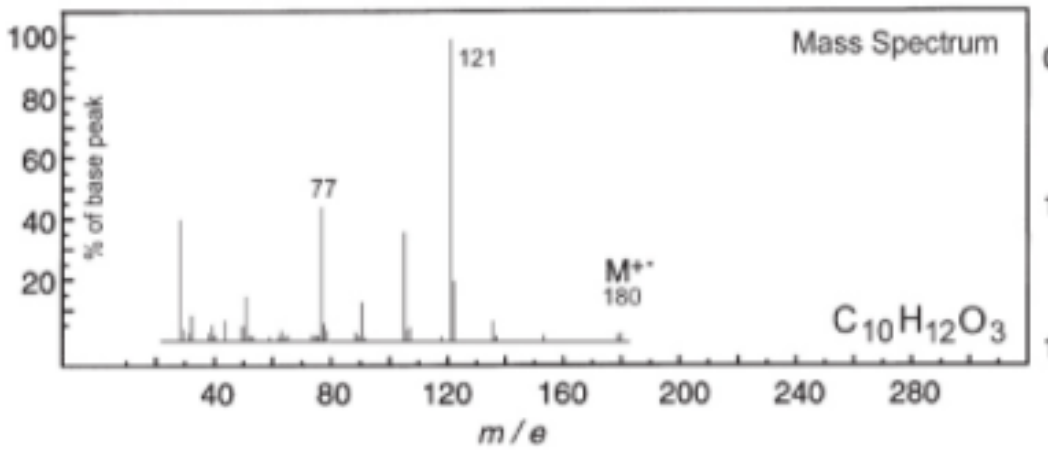
solvent : ethanol

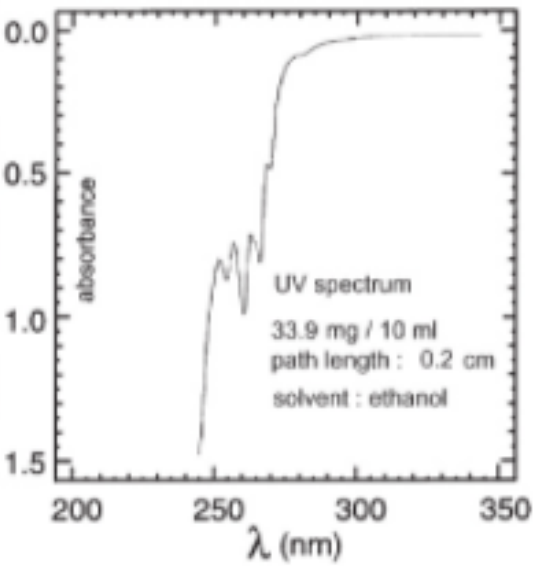


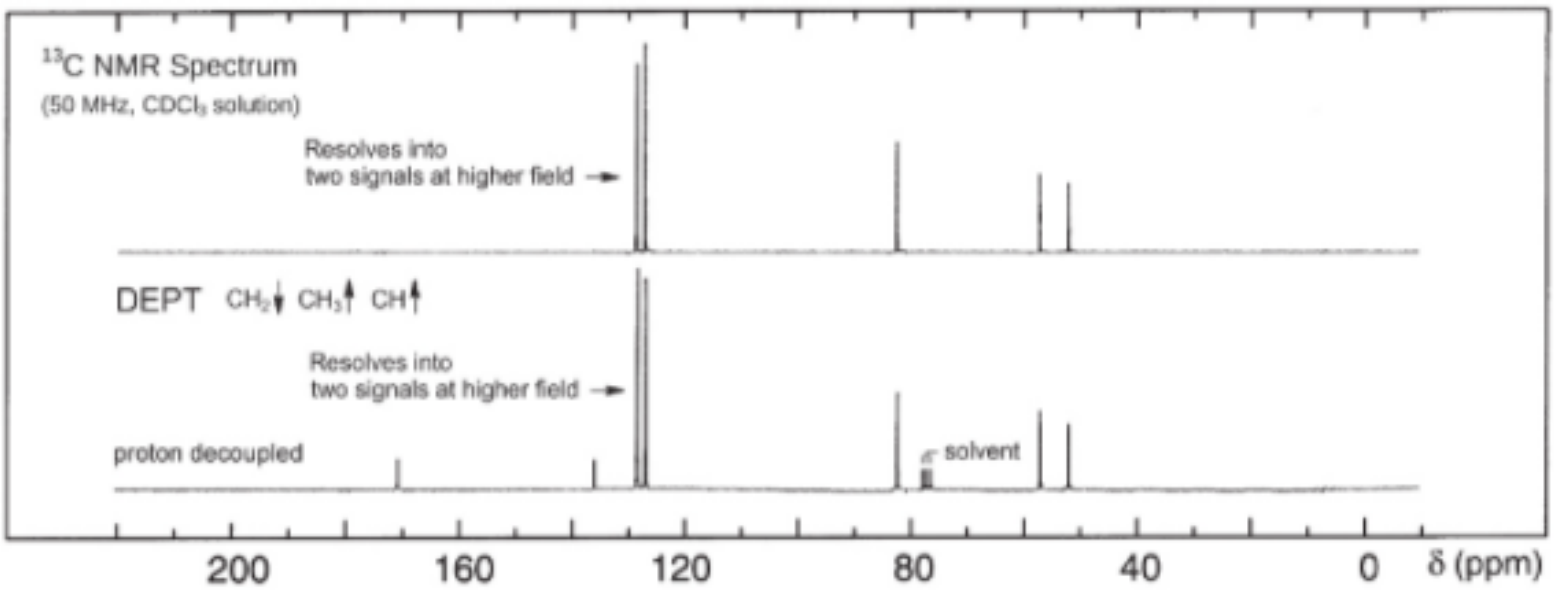


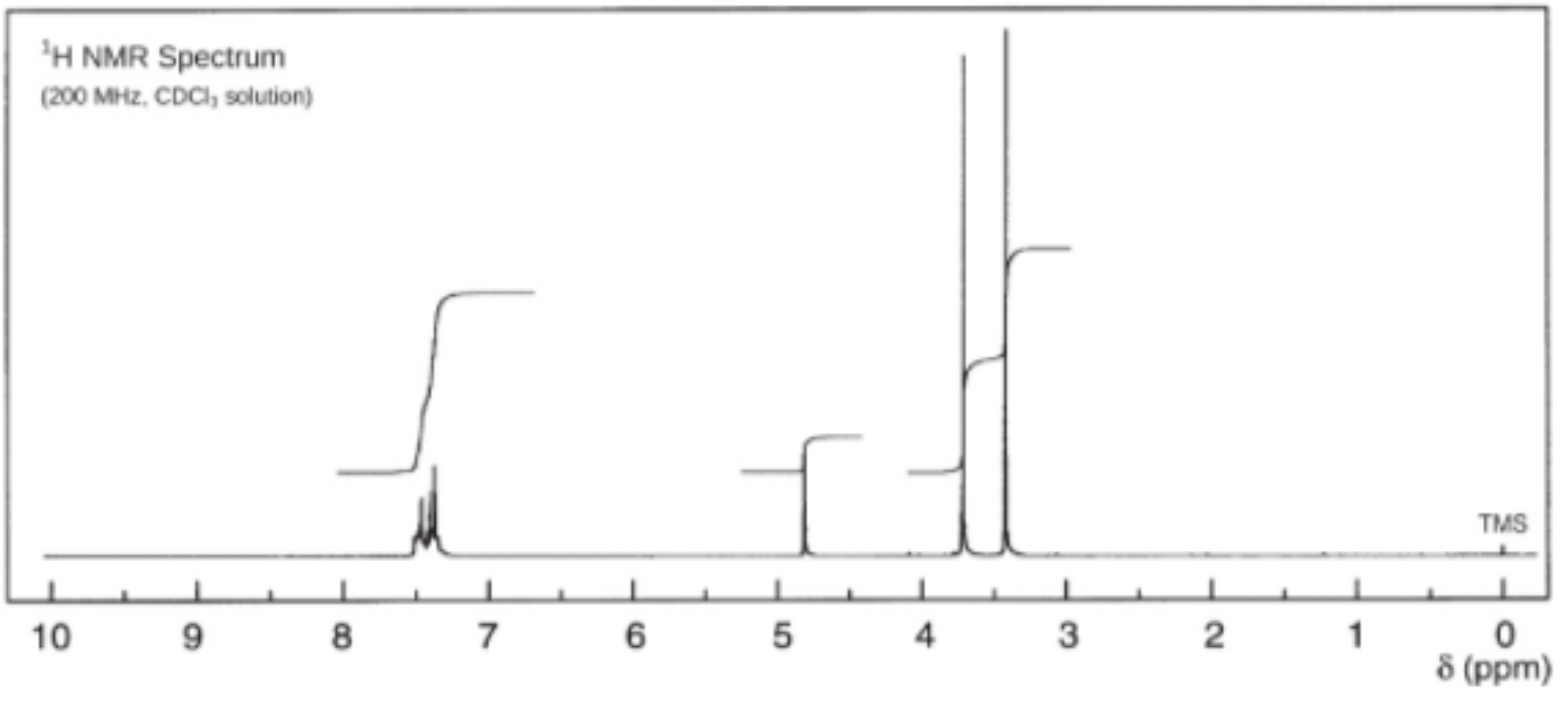
Problem 153


IR Spectrum
(liquid film)
1750
4000
3000
2000
1600
1200
800
ν (cm-1)

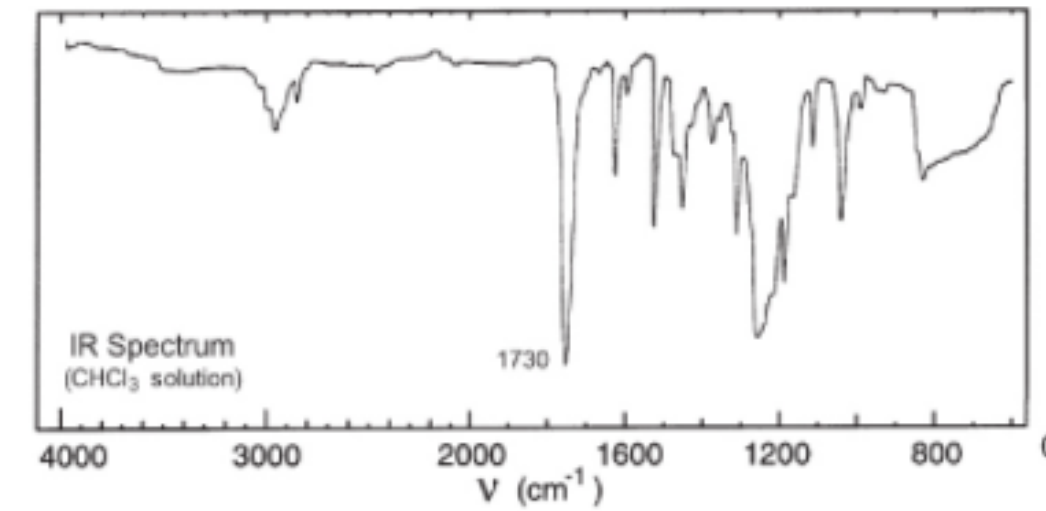

Mass Spectrum
% of base peak
100
80
60
40
20
121
77
M+·
180
C10H12O3
40
80
120
160
200
240
280
m/e

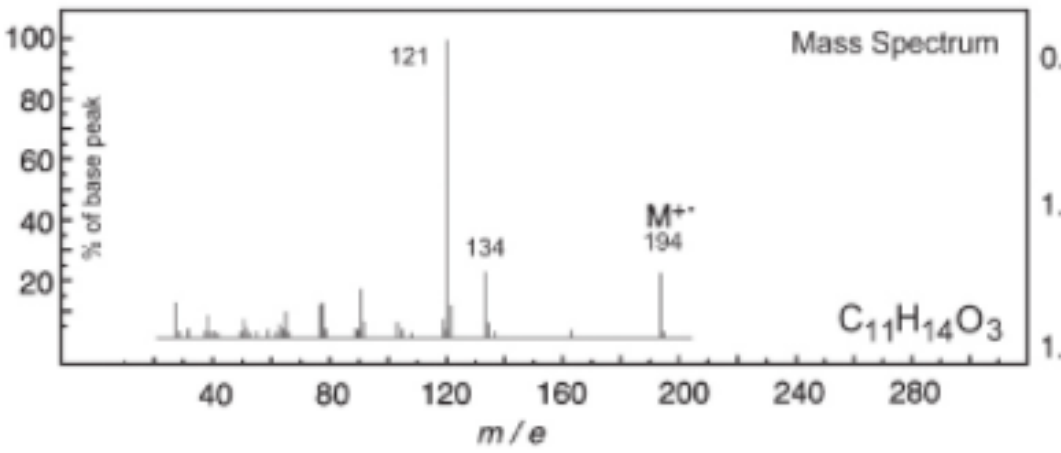

absorbance
0.0
0.5
1.0
1.5
UV spectrum
33.9 mg / 10 ml
path length : 0.2 cm
solvent : ethanol
200
250
300
350
λ (nm)

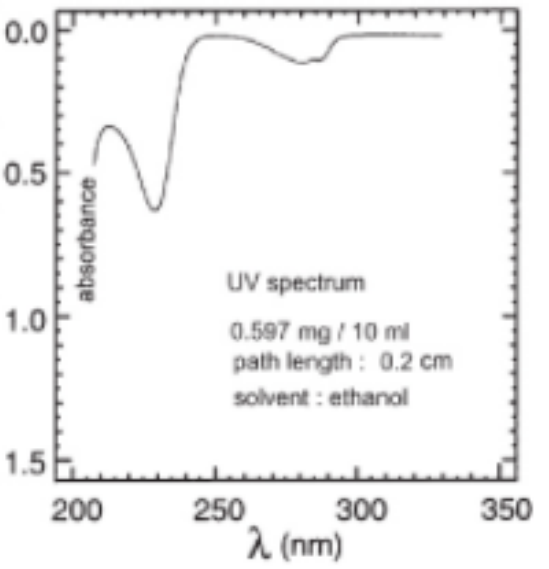

13C NMR Spectrum
(50 MHz, CDCl3 solution)
Resolves into
two signals at higher field
DEPT CH2 CH3 CH
Resolves into
two signals at higher field
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

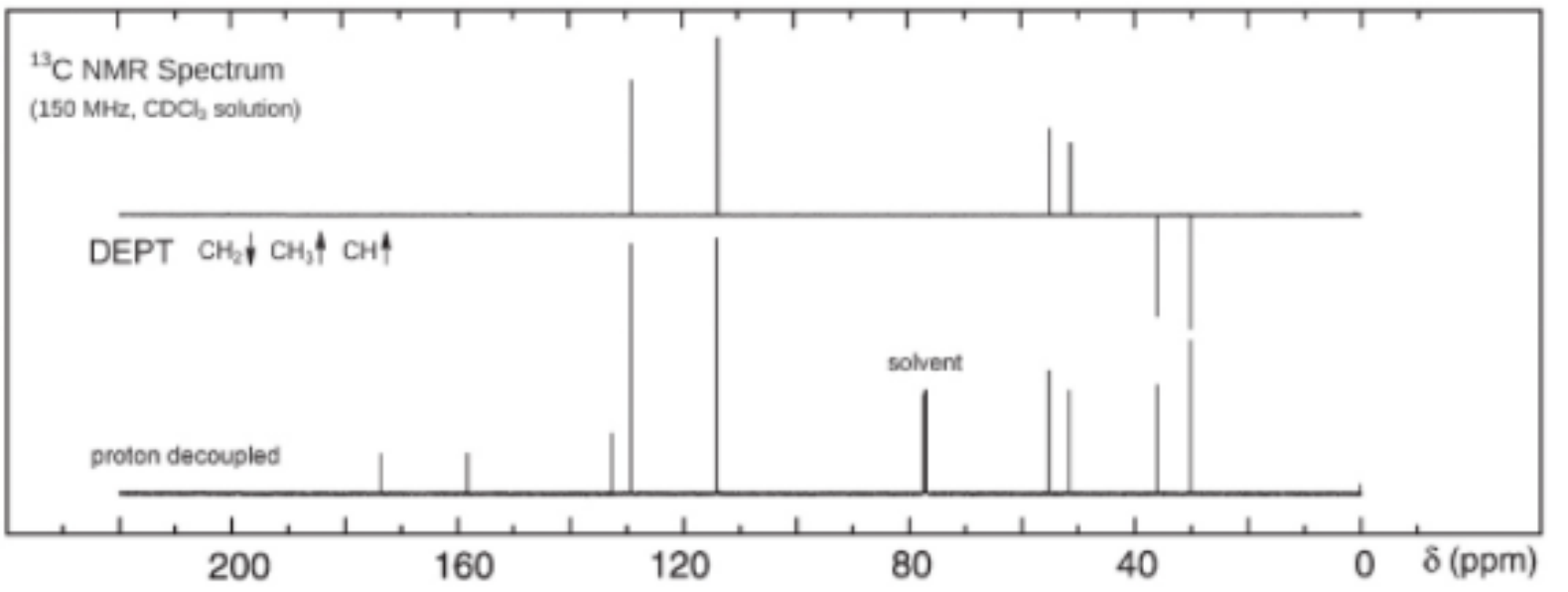

1H NMR Spectrum
(200 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

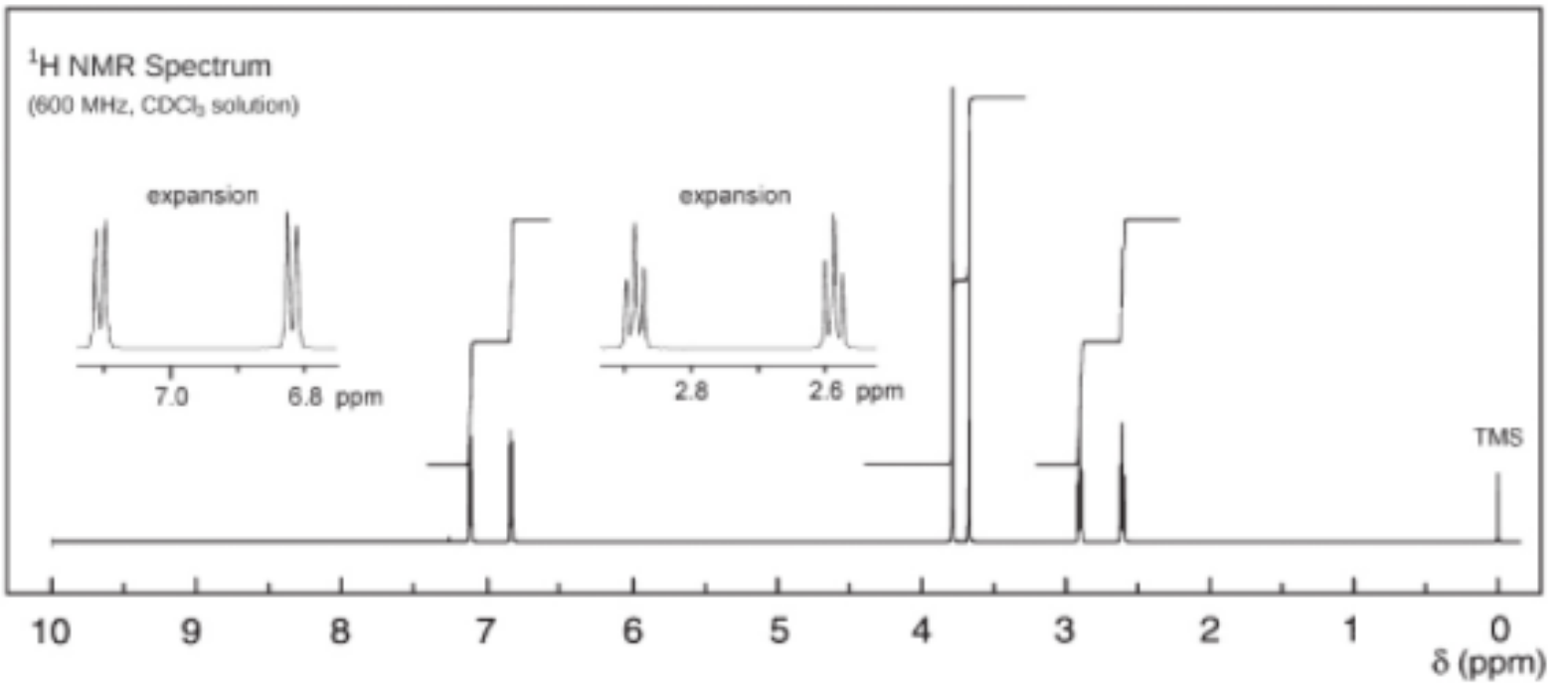
Problem 154

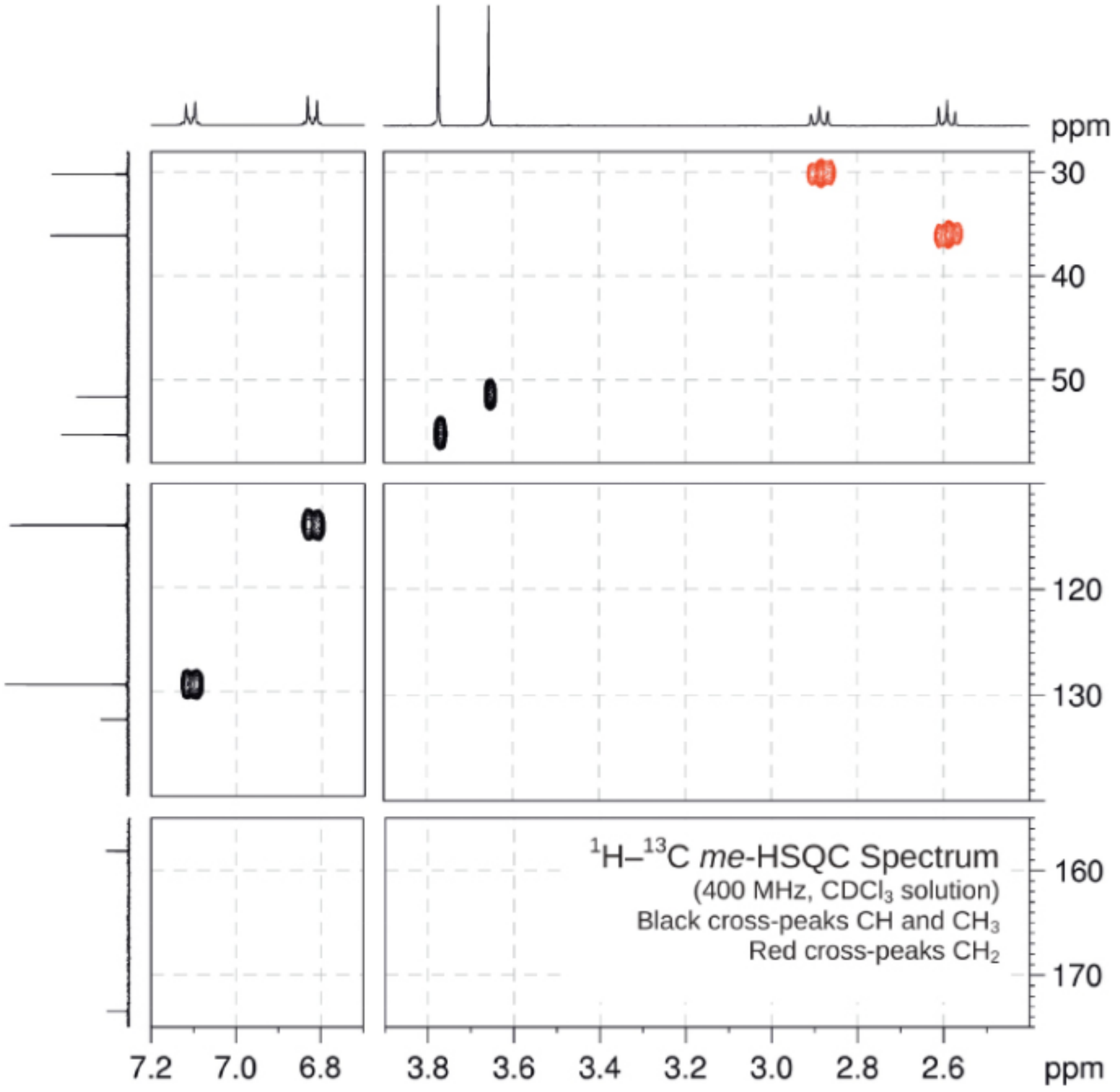

IR Spectrum
(CHCl3 solution)
1730
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
121
134
M+·
194
C11H14O3
40
80
120
160
200
240
280
m/e

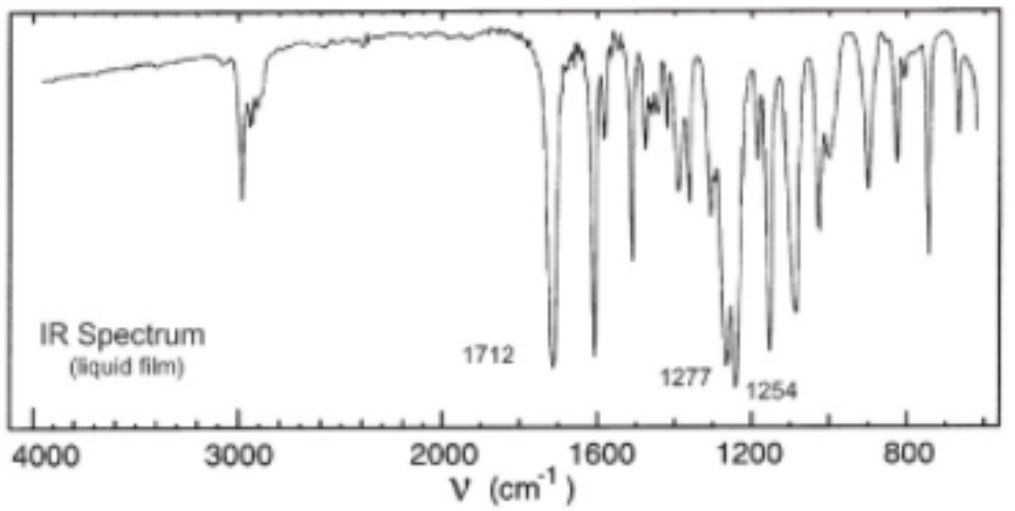

absorbance
UV spectrum
0.597 mg / 10 ml
path length : 0.2 cm
solvent : ethanol
200
250
300
350
λ (nm)

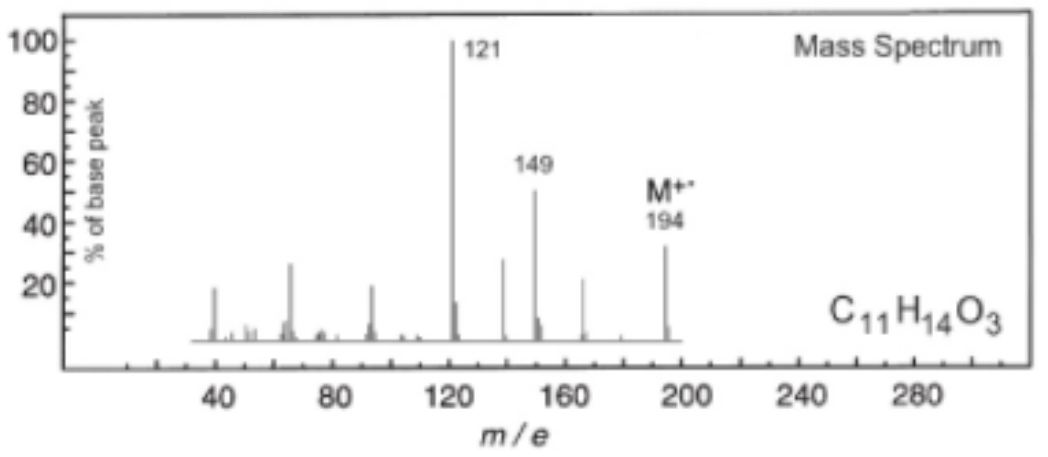

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion
7.0
6.8 ppm
expansion
2.8
2.6 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
30
40
50
120
130
160
170
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.2
7.0
6.8
3.8
3.6
3.4
3.2
3.0
2.8
2.6
ppm

Problem 155

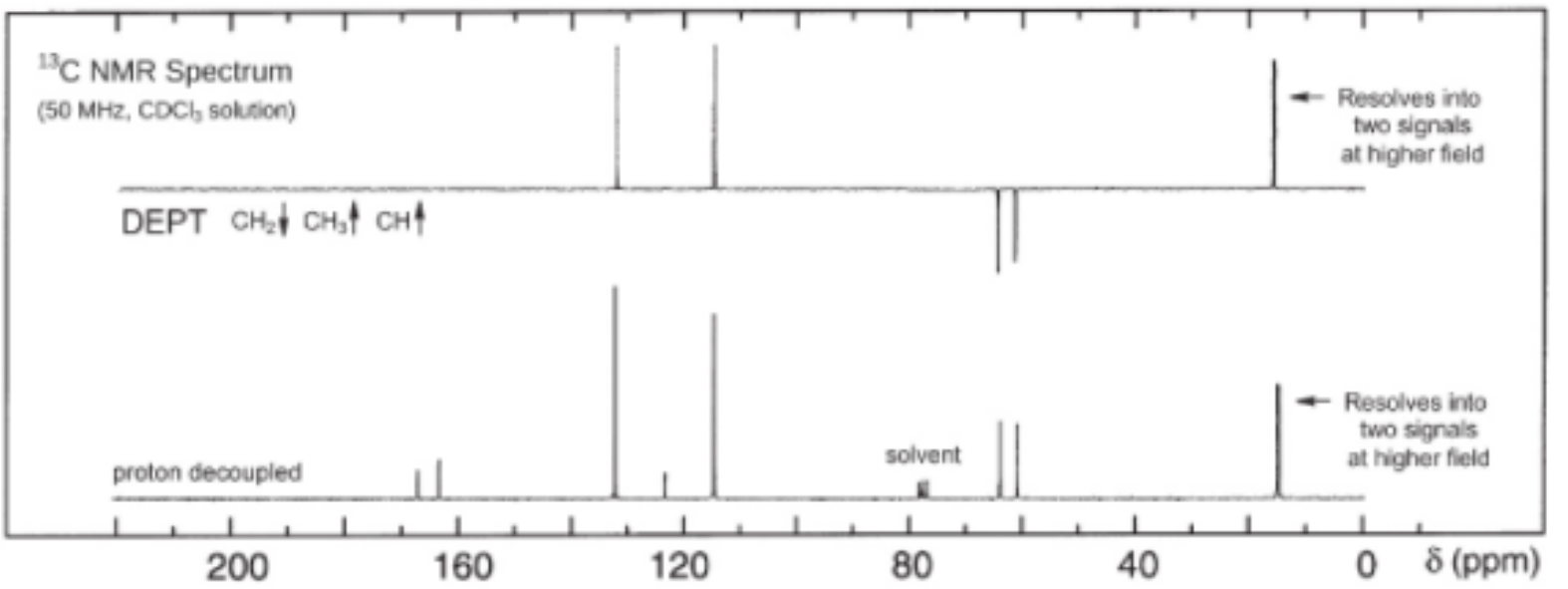


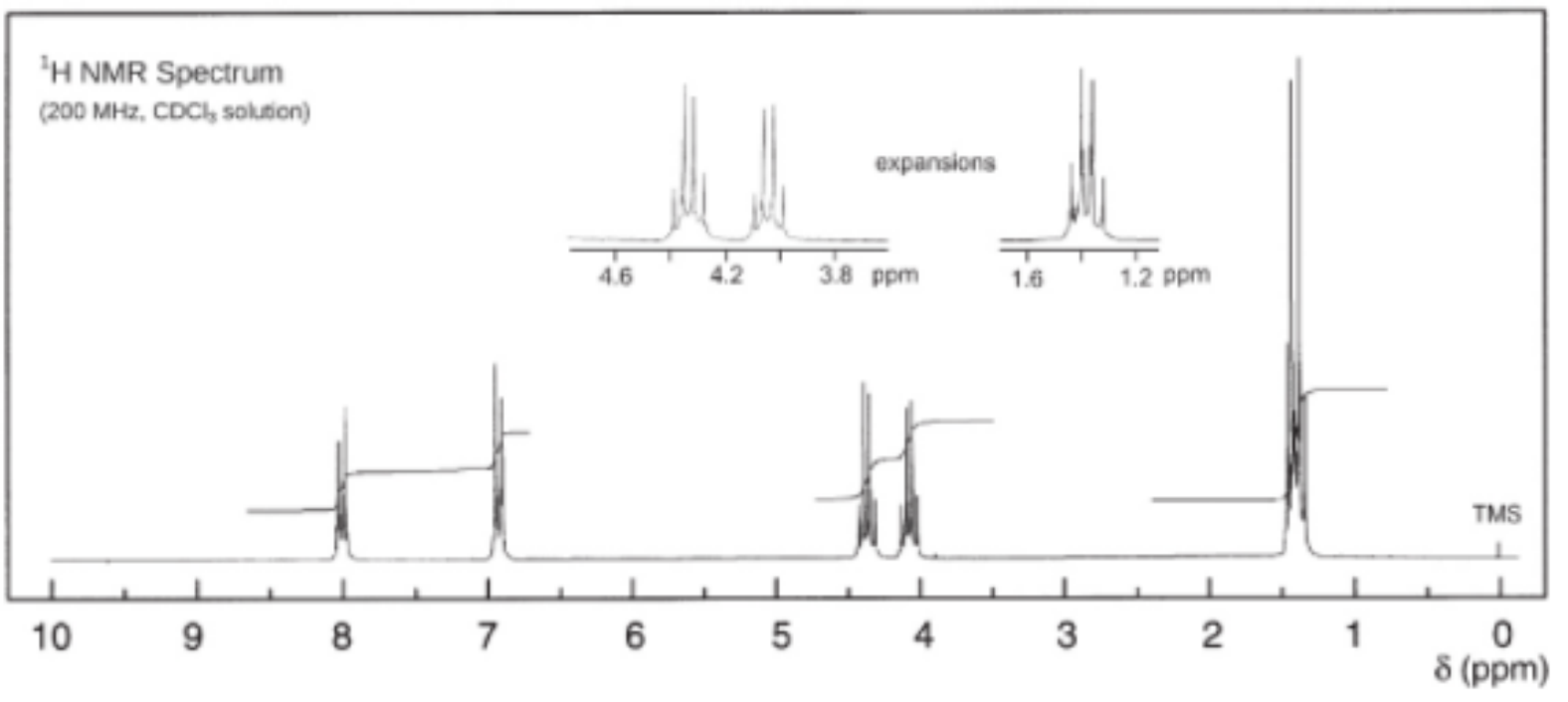


UV Spectrum

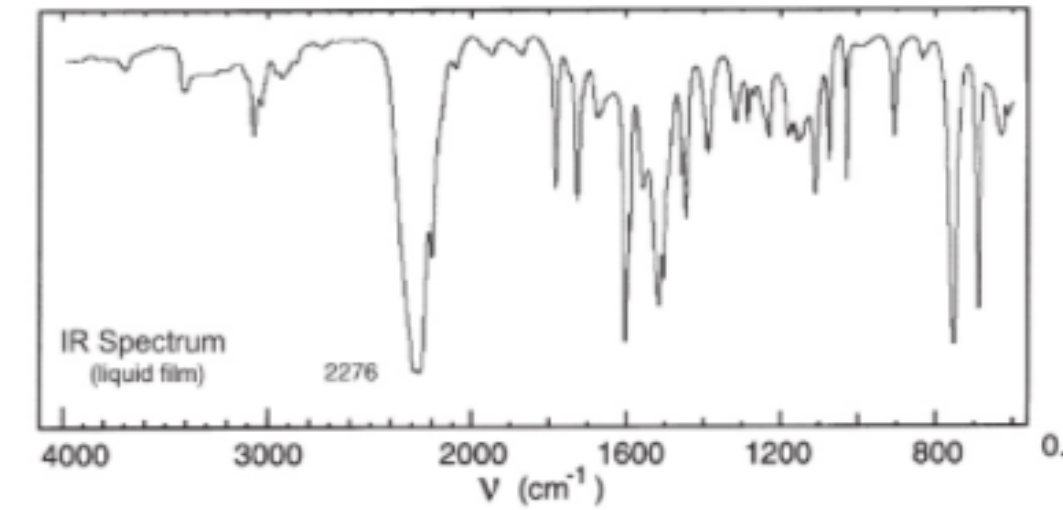
λ_{max} 257 nm ($\log_{10}\varepsilon$ 4.3)

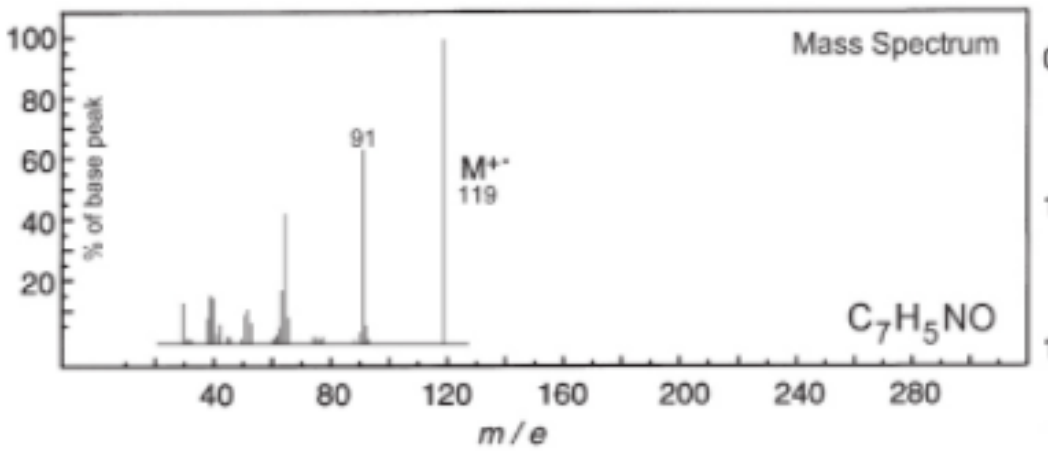
solvent : methanol

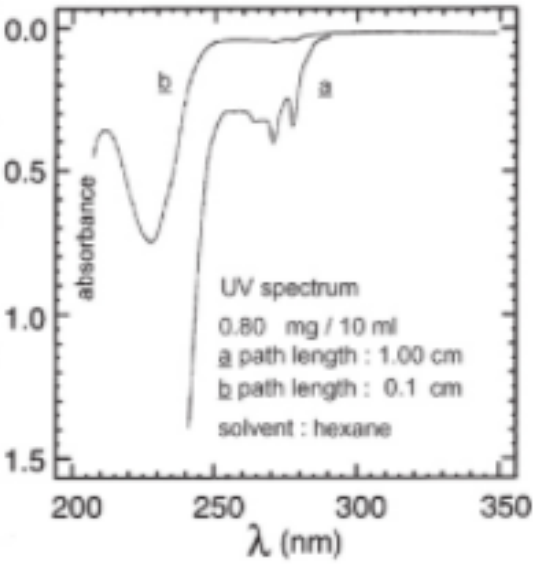


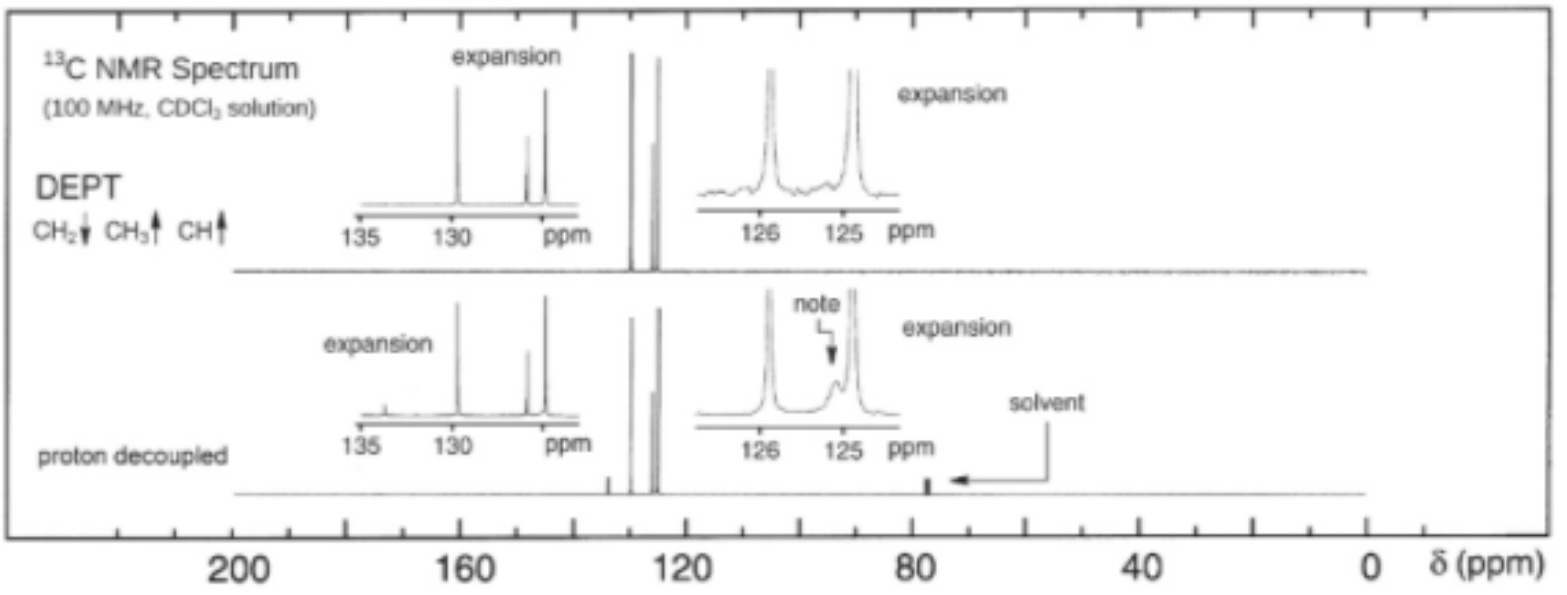


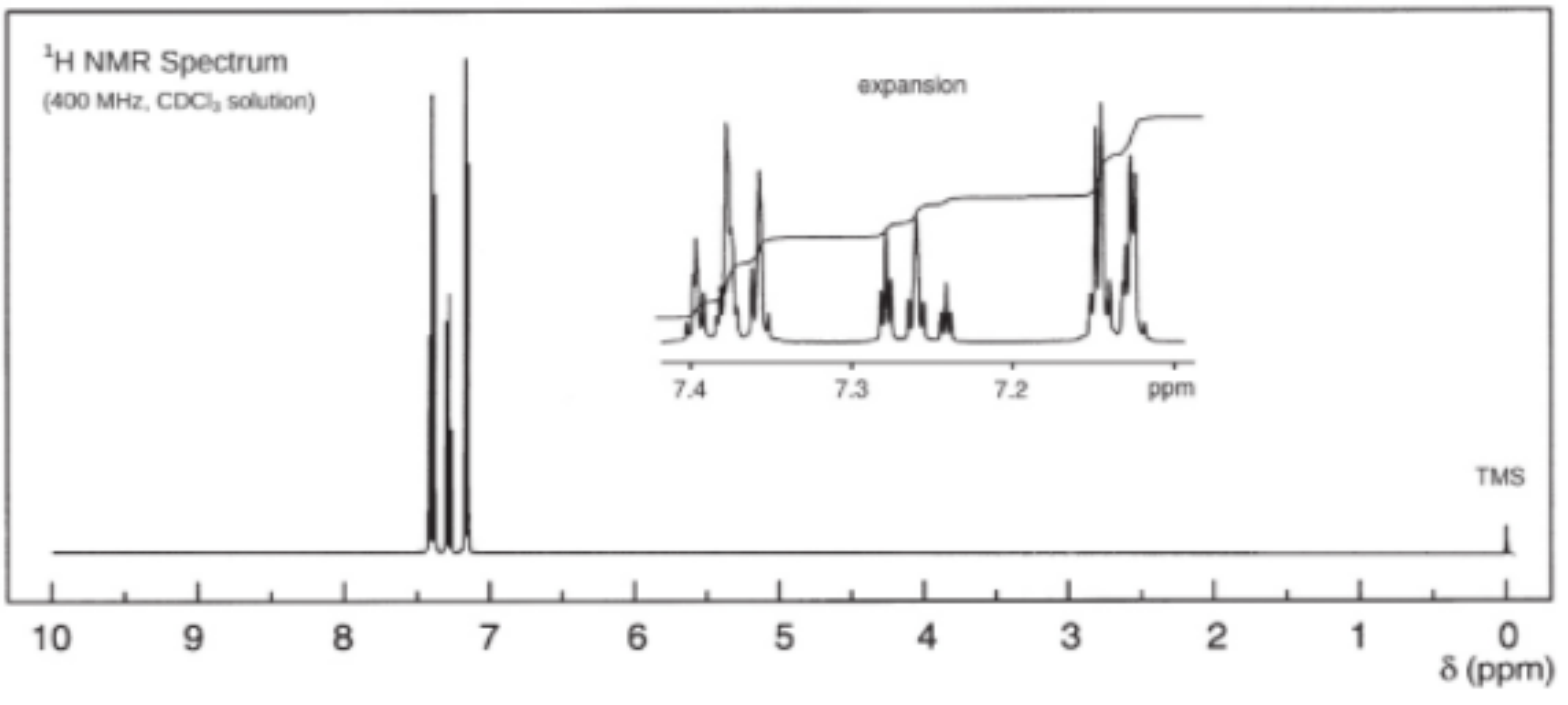
Problem 156


IR Spectrum
(liquid film)
2276
4000
3000
2000
1600
1200
800
ν (cm-1)

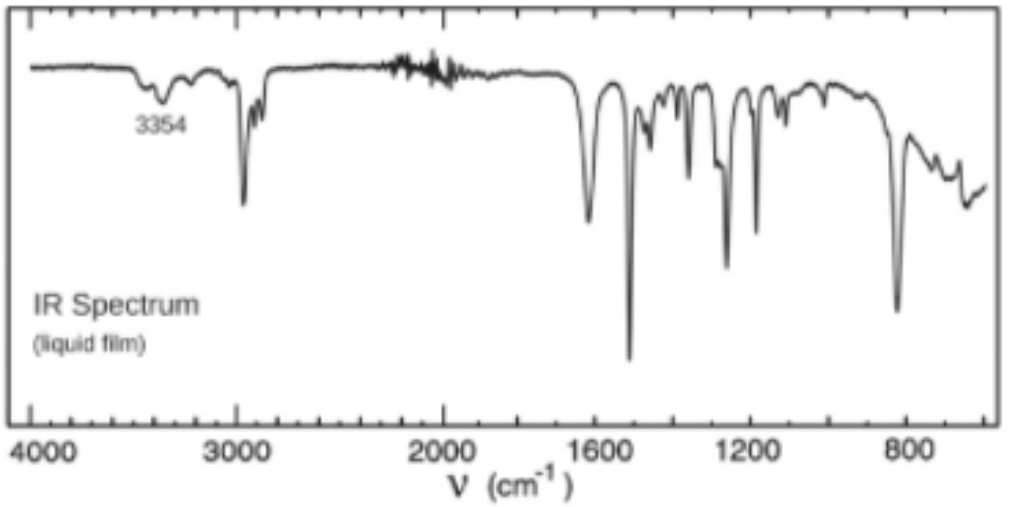

Mass Spectrum
% of base peak
100
80
60
40
20
91
M+·
119
C7H5NO
40
80
120
160
200
240
280
m/e

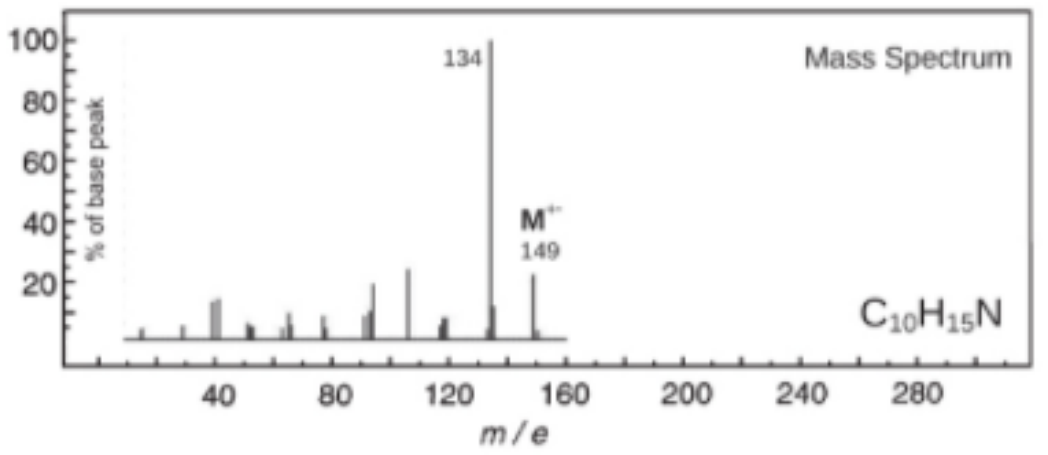

absorbance
0.0
0.5
1.0
1.5
b
a
UV spectrum
0.80 mg / 10 ml
a path length : 1.00 cm
b path length : 0.1 cm
solvent : hexane
200
250
300
350
λ (nm)

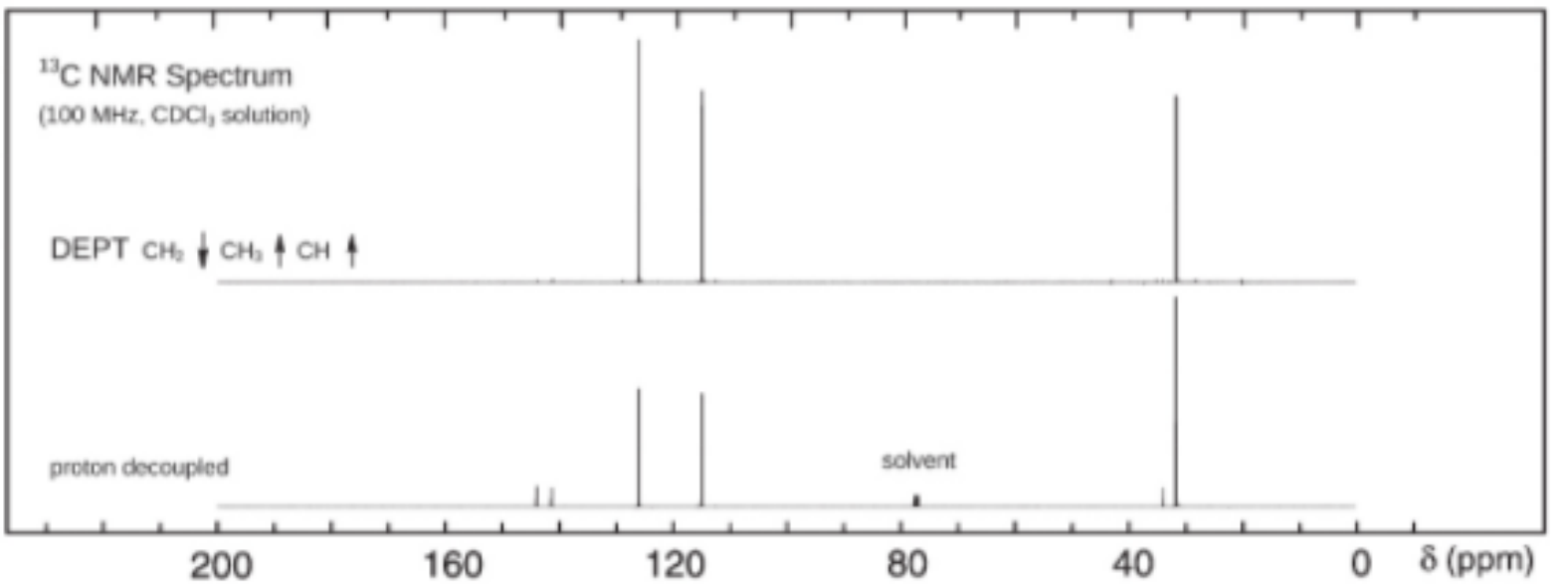

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT
CH2 CH3 CH
expansion
135
130
ppm
expansion
126
125
ppm
proton decoupled
expansion
note
expansion
solvent
200
160
120
80
40
0
δ (ppm)

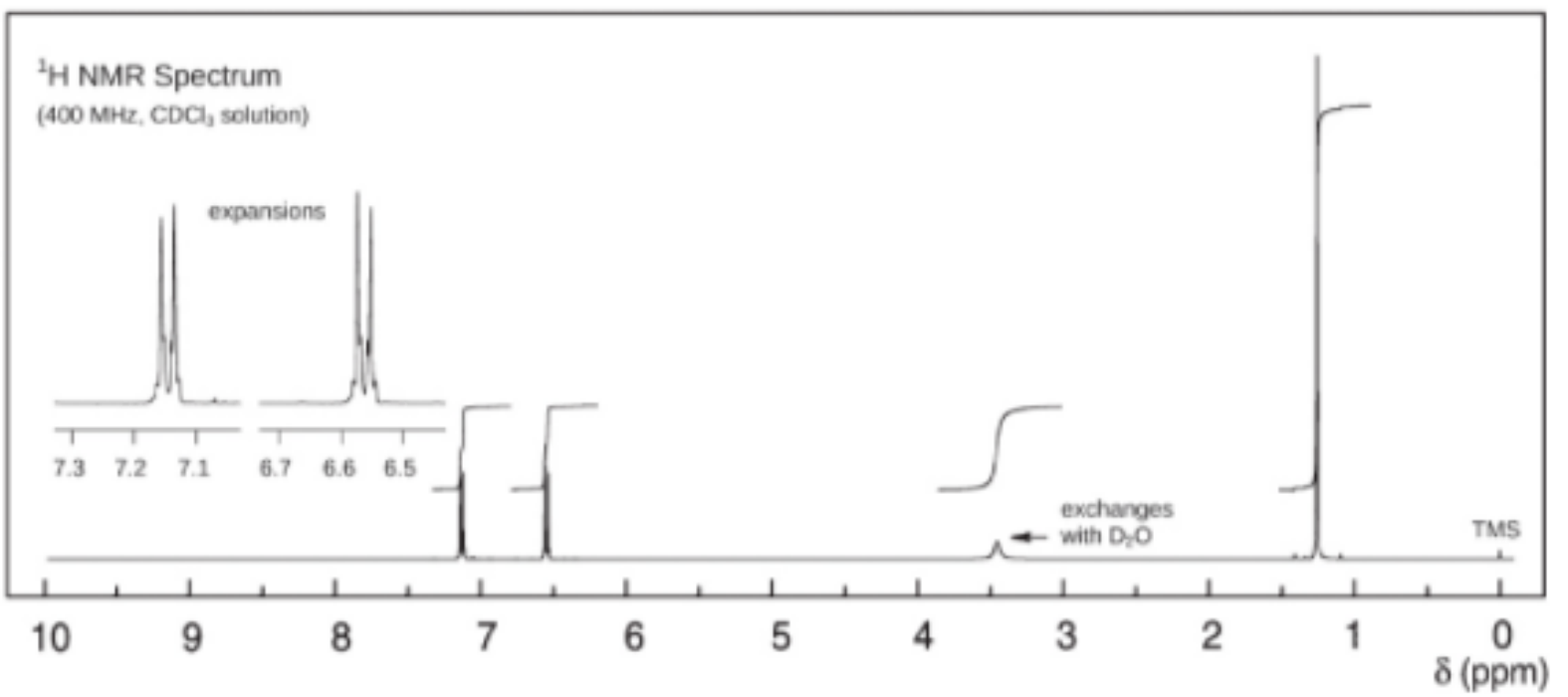

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.4
7.3
7.2
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 157

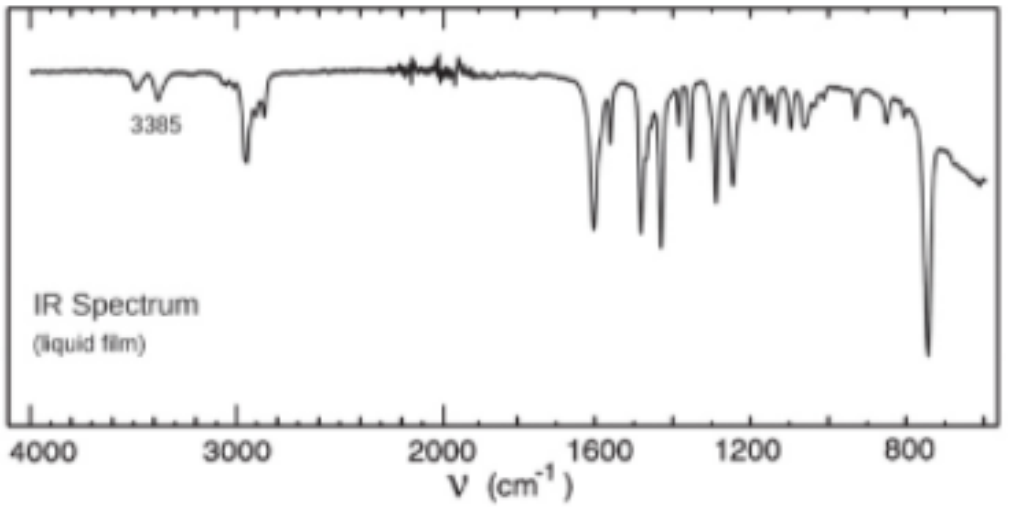

3354
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

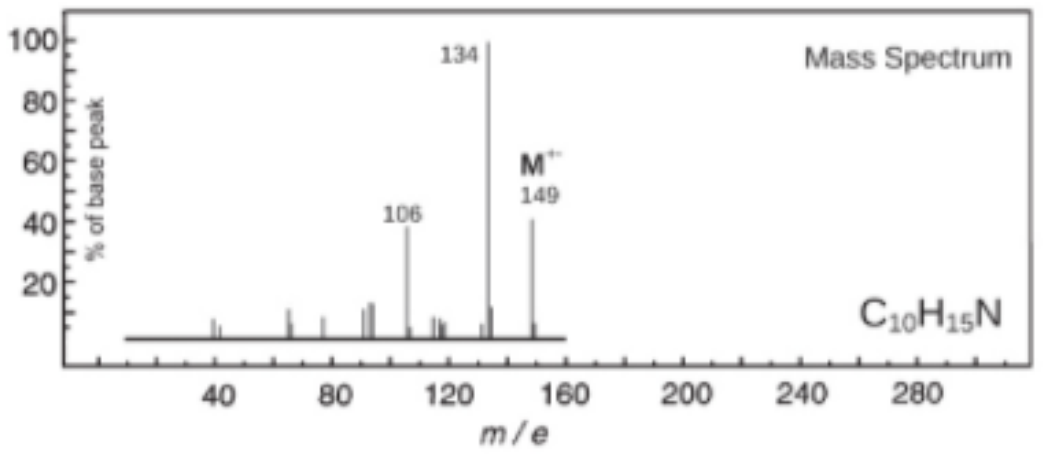

Mass Spectrum
134
M+·
149
% of base peak
100
80
60
40
20
C10H15N
40
80
120
160
200
240
280
m/e

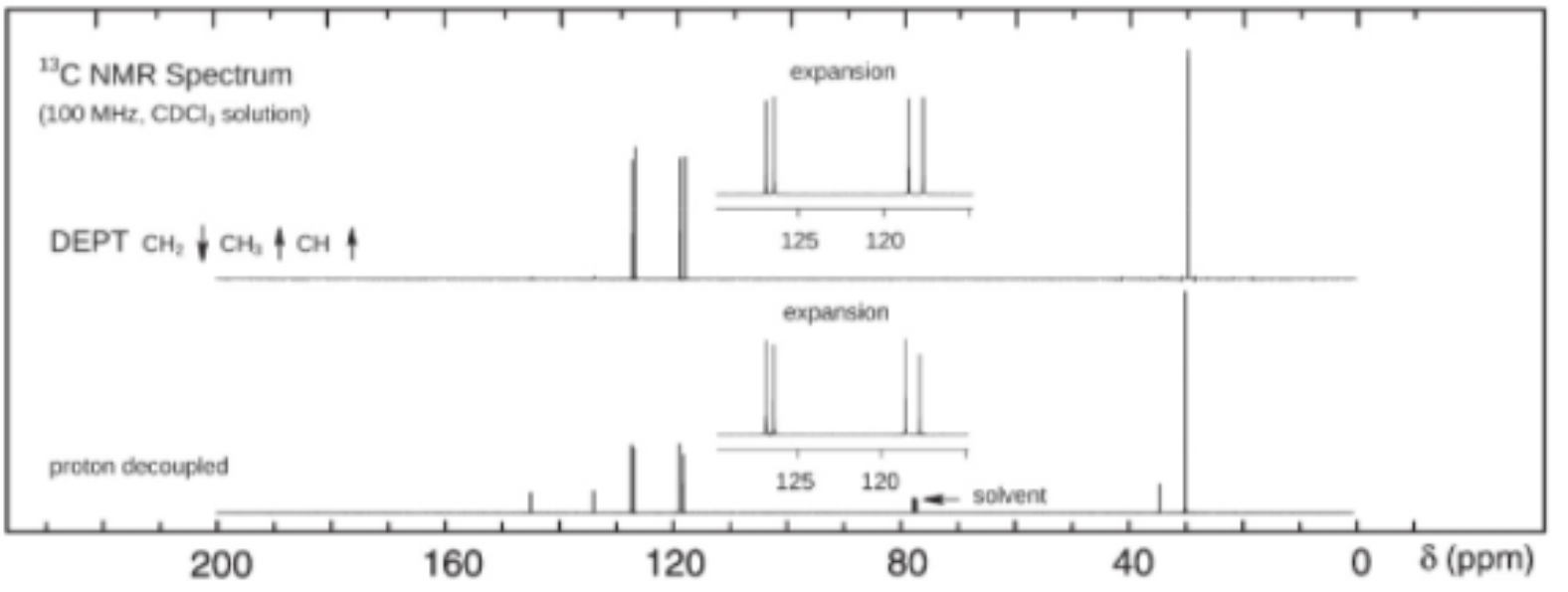

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

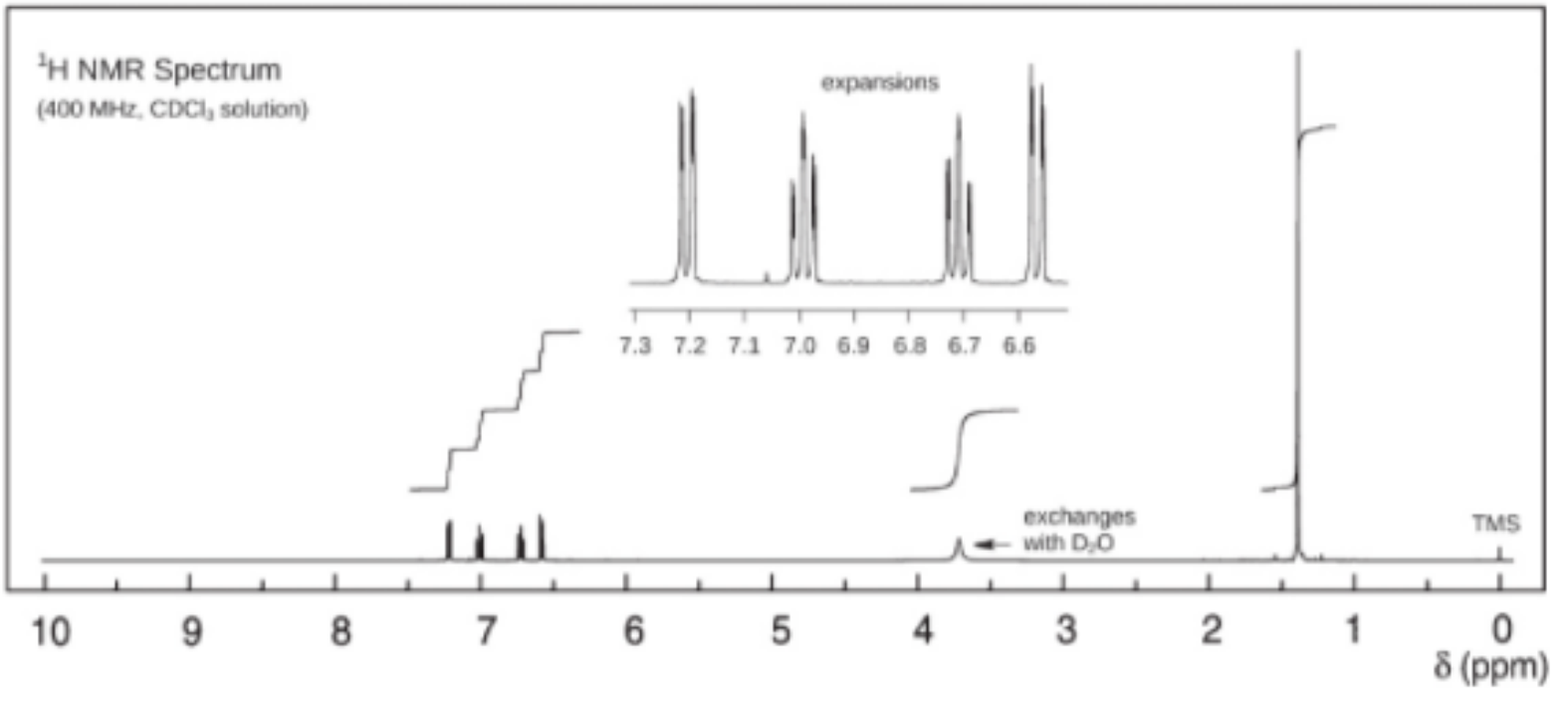

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
7.3
7.2
7.1
6.7
6.6
6.5
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 158

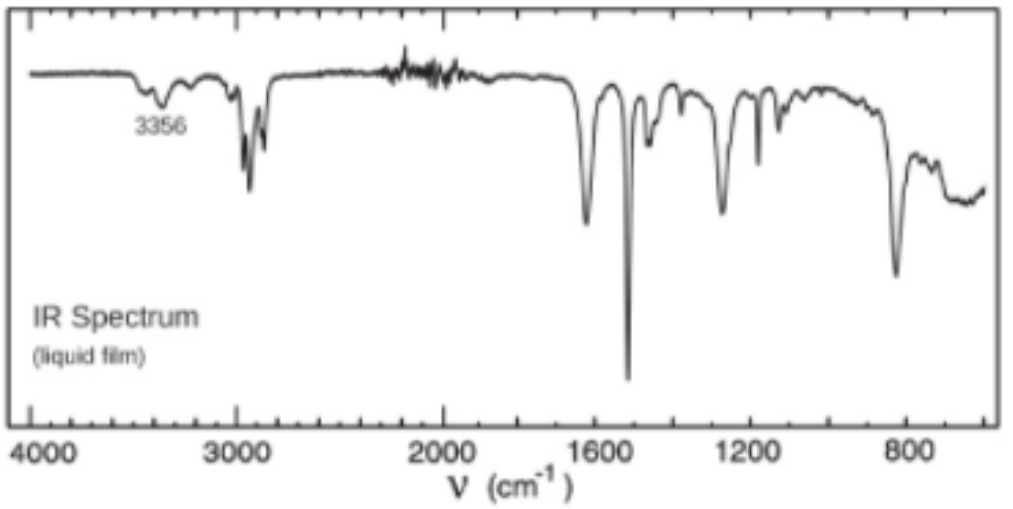

3385
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

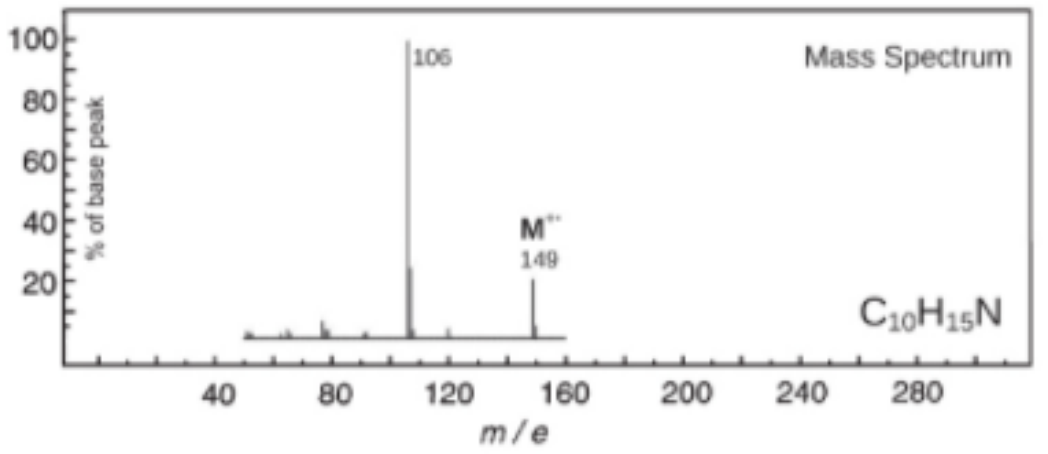

Mass Spectrum
134
106
M+·
149
% of base peak
100
80
60
40
20
C10H15N
40
80
120
160
200
240
280
m/e

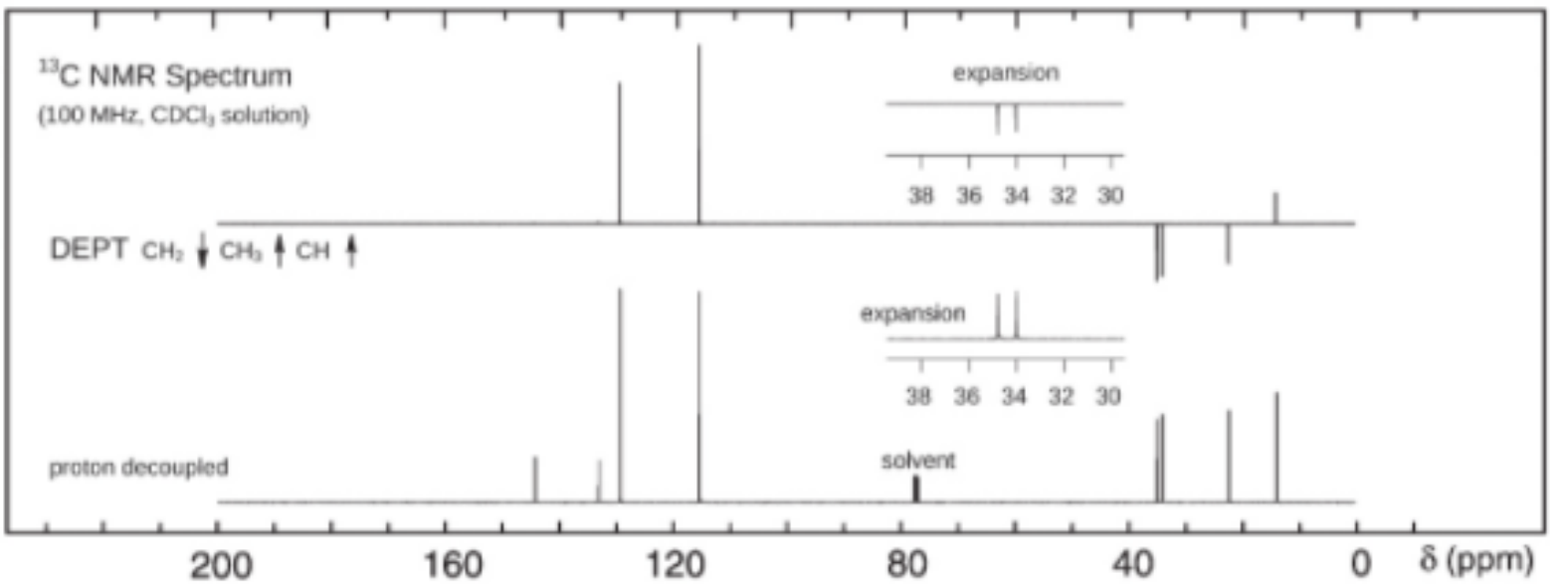

13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
125
120
DEPT CH2 CH3 CH
expansion
125
120
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

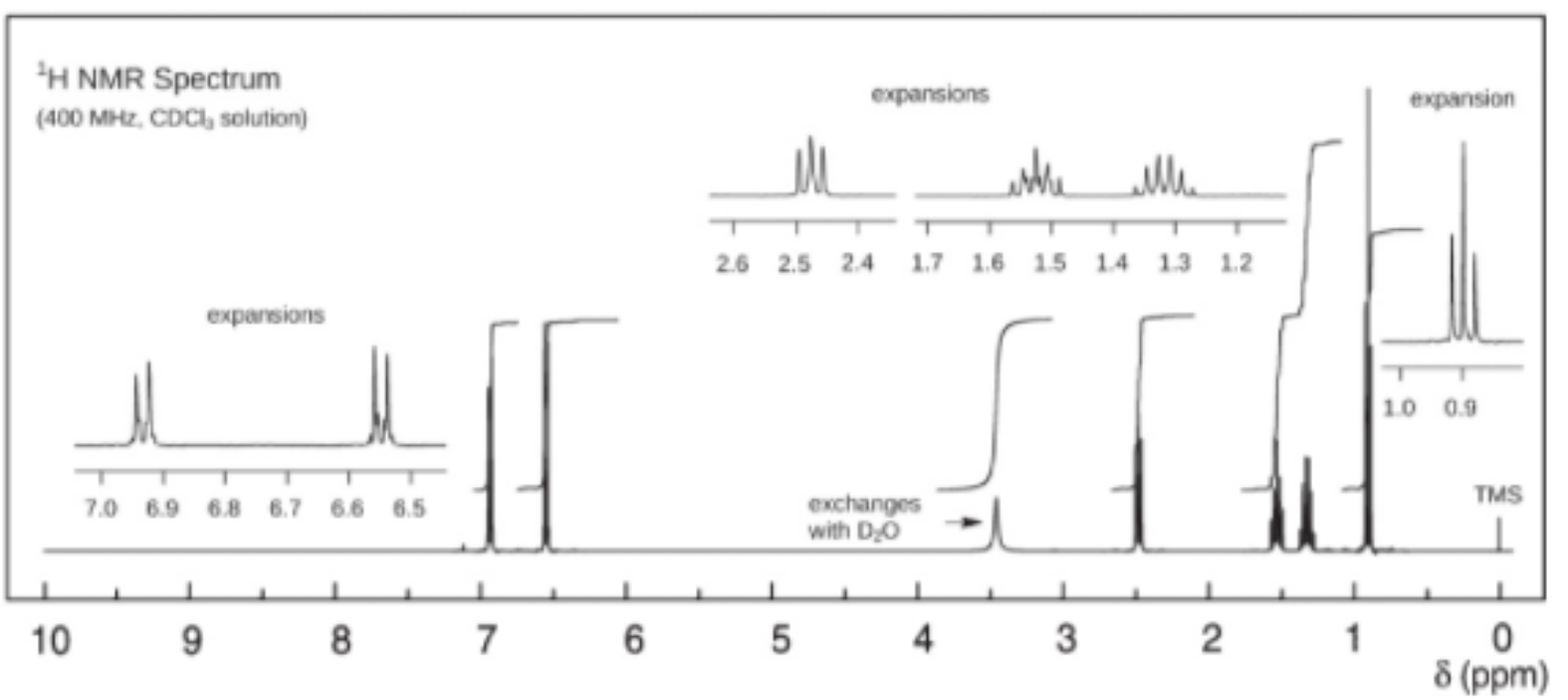

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

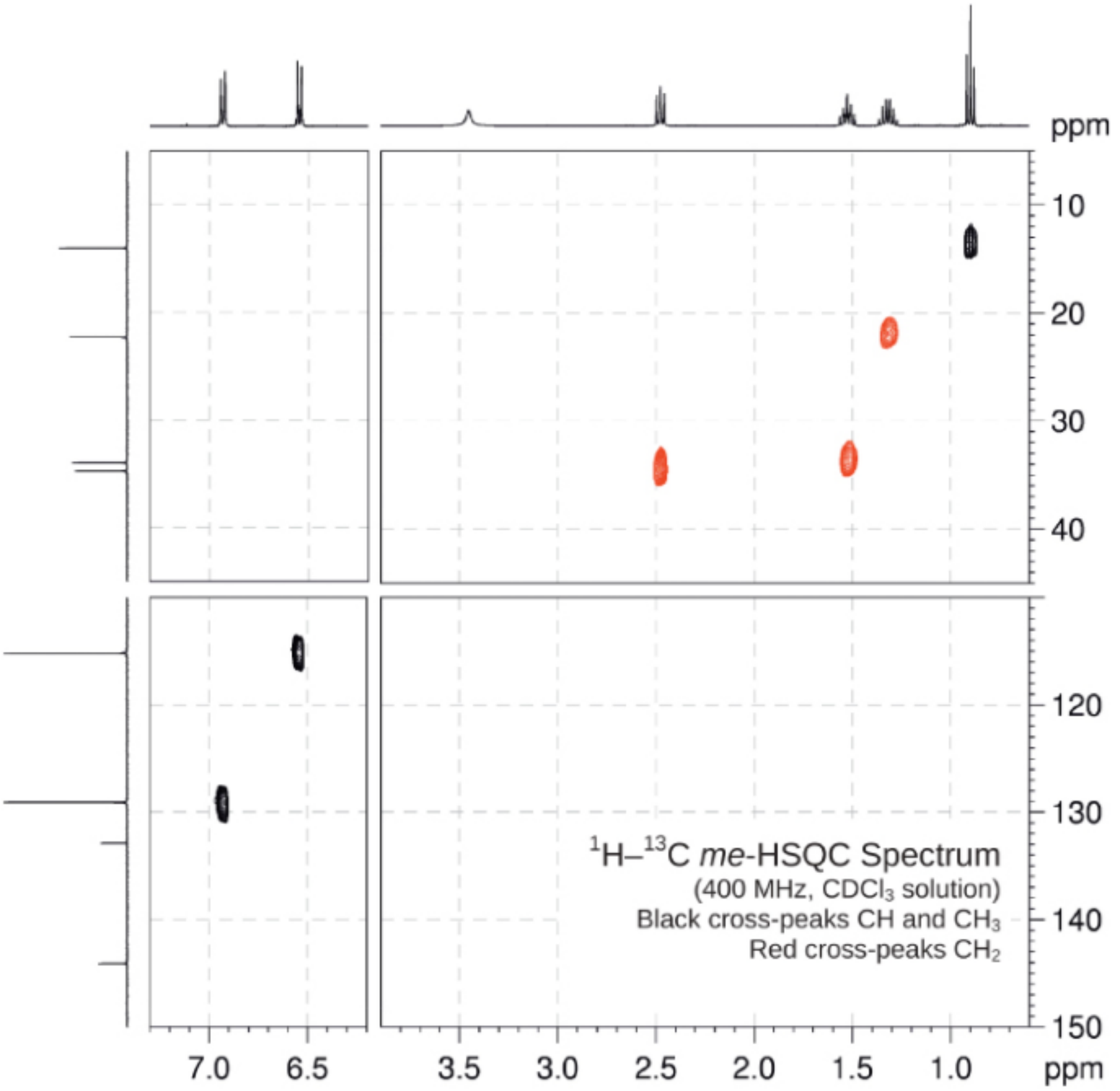
Problem 159


3356
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

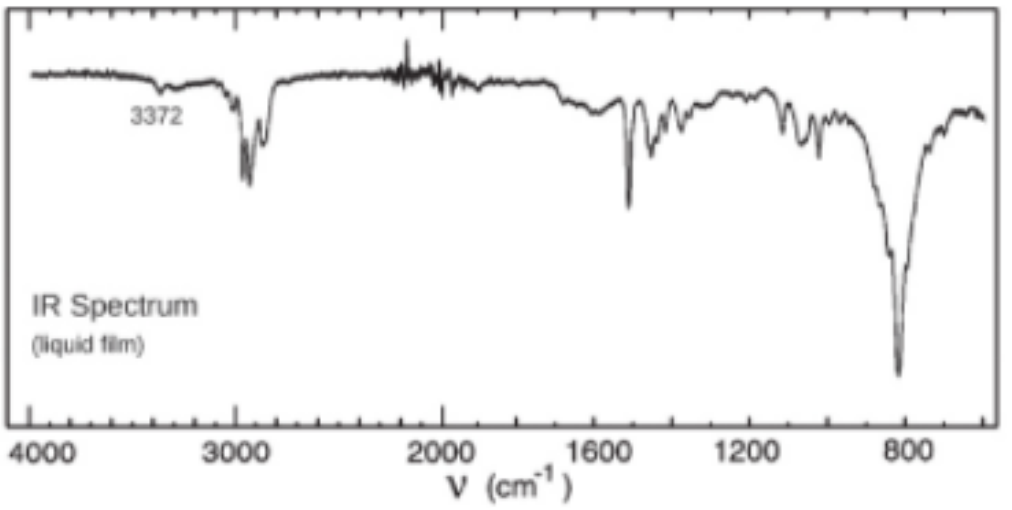

100
80
60
40
20
% of base peak
106
Mass Spectrum
M+·
149
C10H15N
40
80
120
160
200
240
280
m/e

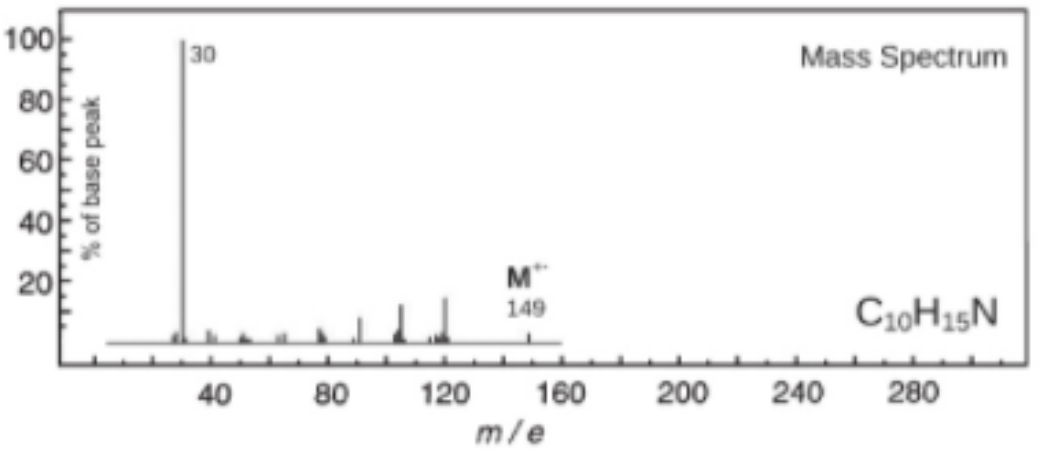

13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
38 36 34 32 30
DEPT CH2 CH3 CH
expansion
38 36 34 32 30
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

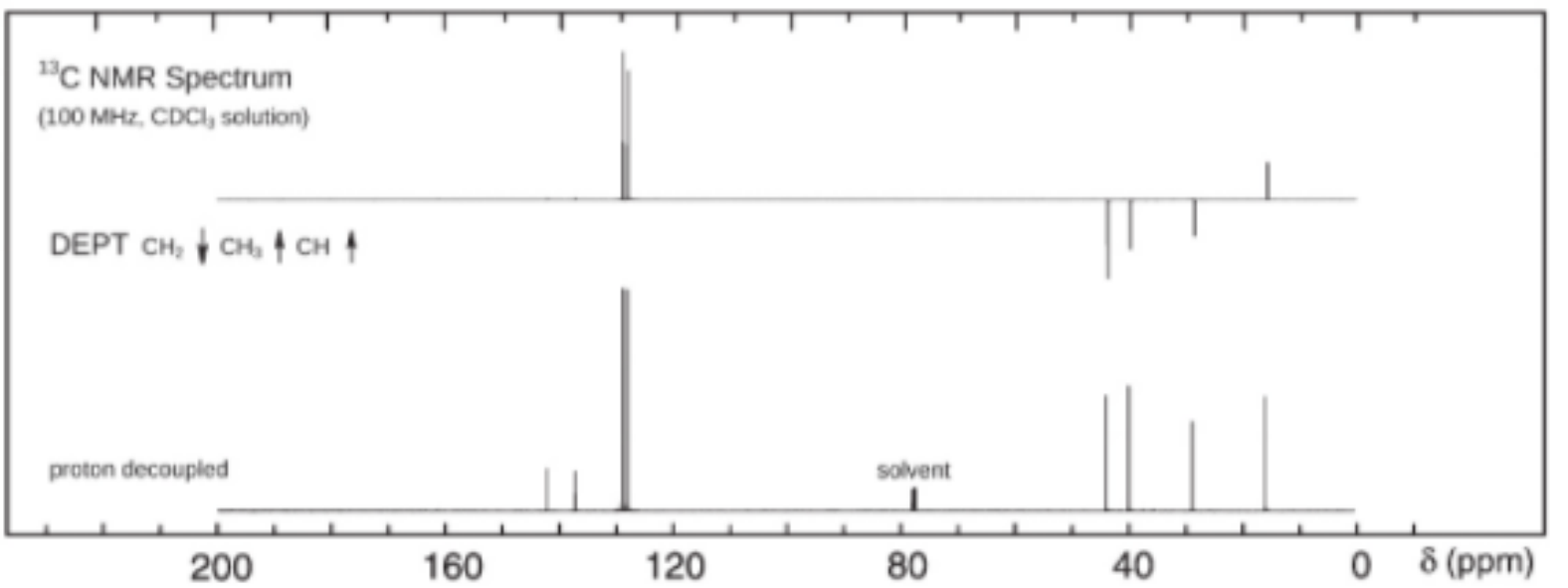

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
2.6 2.5 2.4
1.7 1.6 1.5 1.4 1.3 1.2
expansion
1.0 0.9
expansions
7.0 6.9 6.8 6.7 6.6 6.5
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

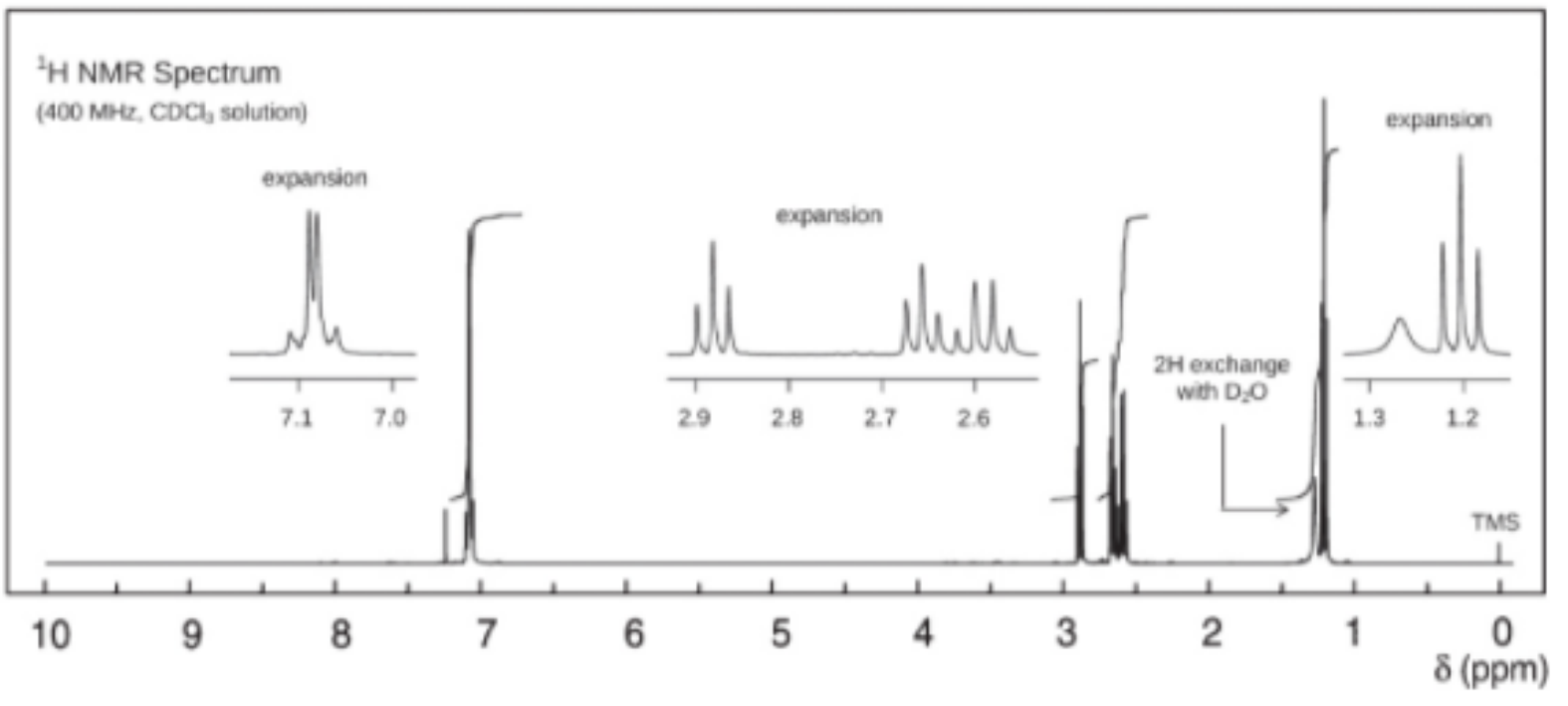

ppm
10
20
30
40
120
130
140
150
7.0
6.5
3.5
3.0
2.5
2.0
1.5
1.0
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

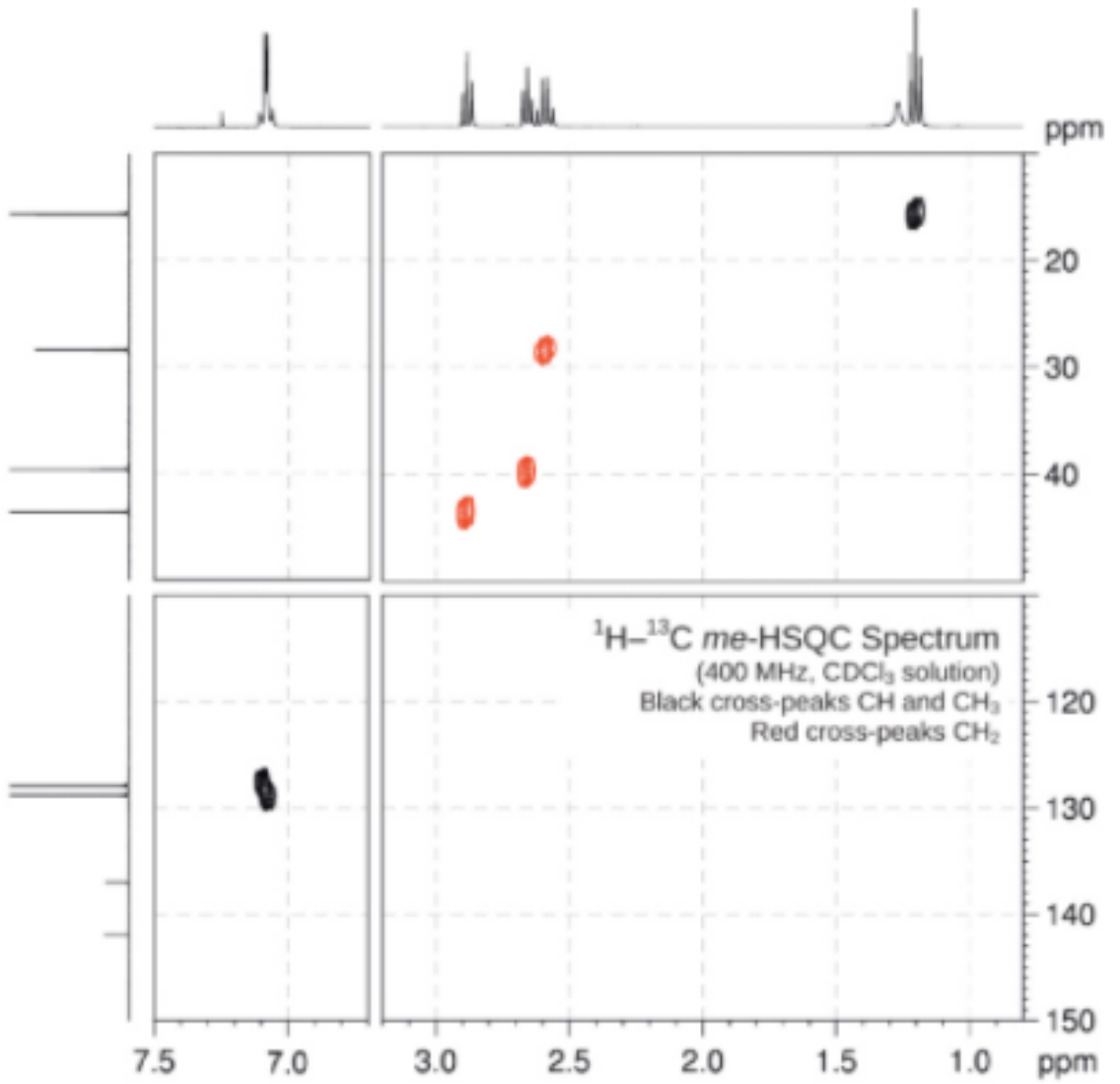
Problem 160

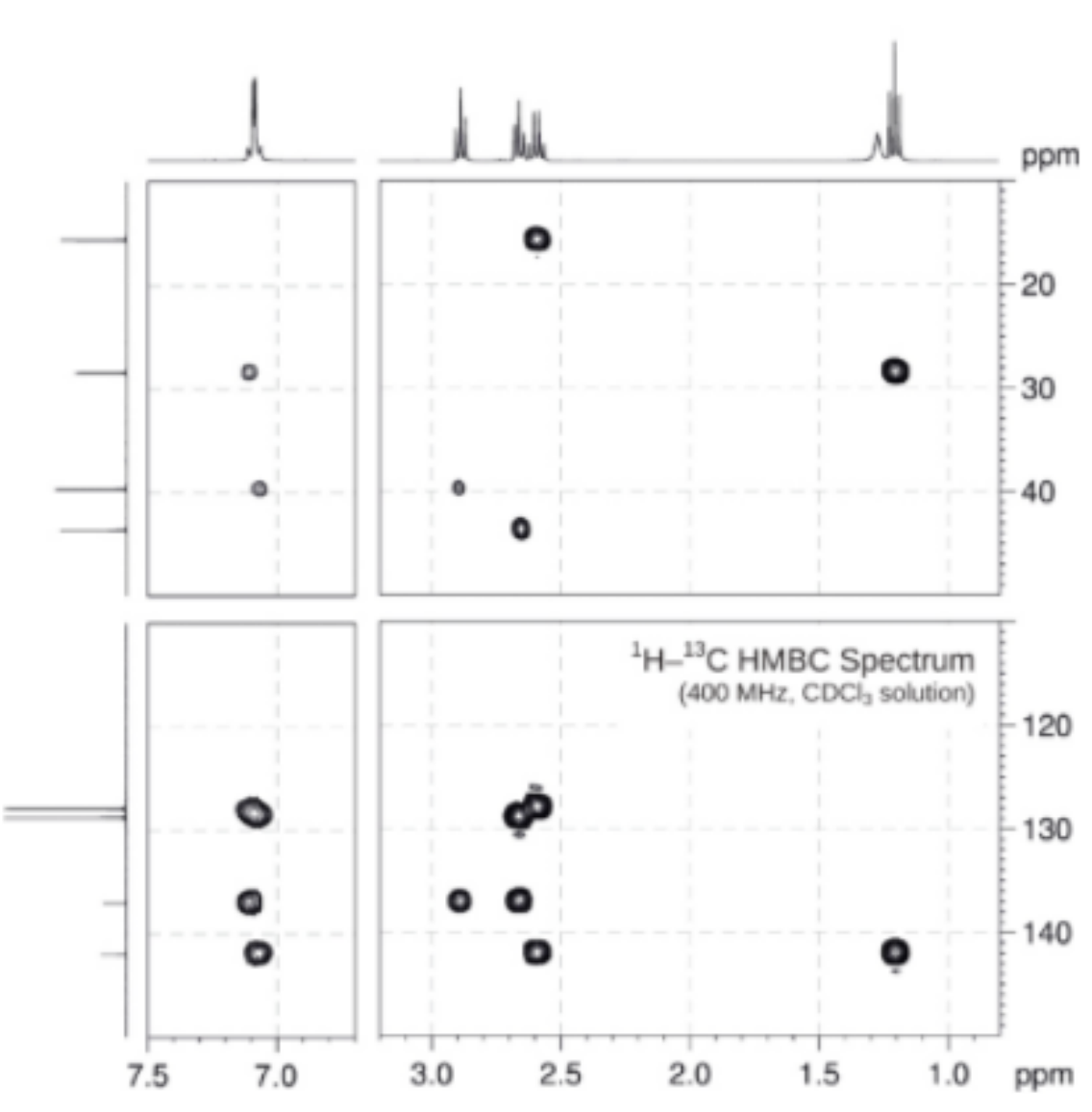

3372
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)


100
80
60
40
20
% of base peak
30
Mass Spectrum
M+·
149
C10H15N
40
80
120
160
200
240
280
m/e

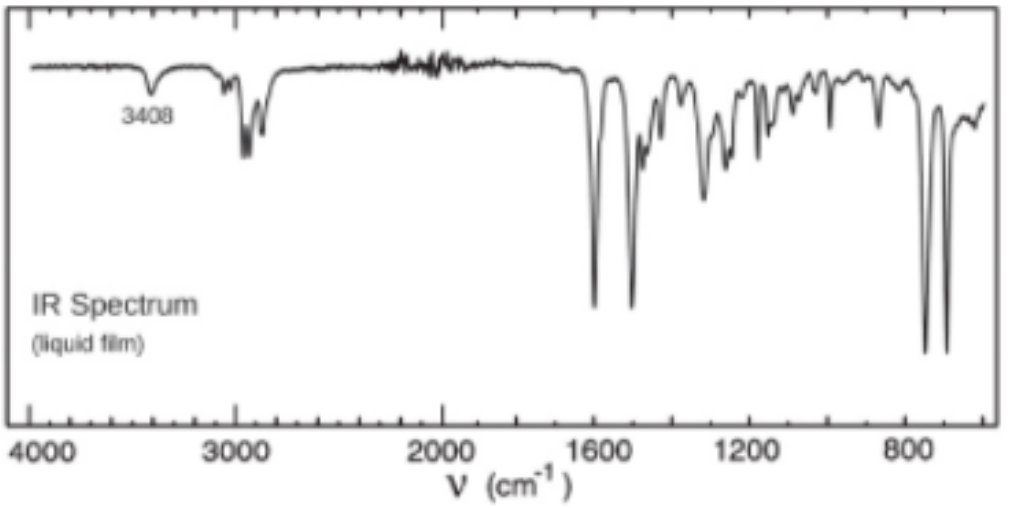

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

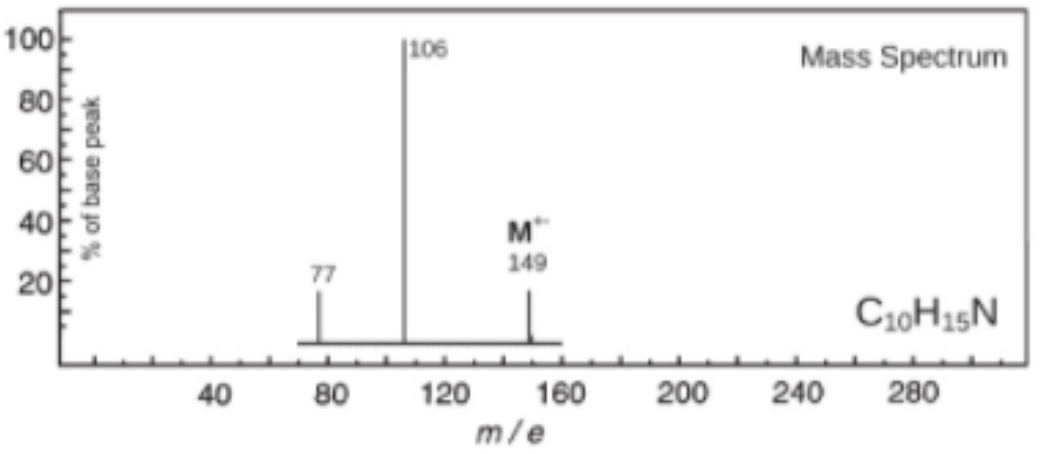

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.1
7.0
expansion
2.9
2.8
2.7
2.6
2H exchange
with D2O
expansion
1.3
1.2
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

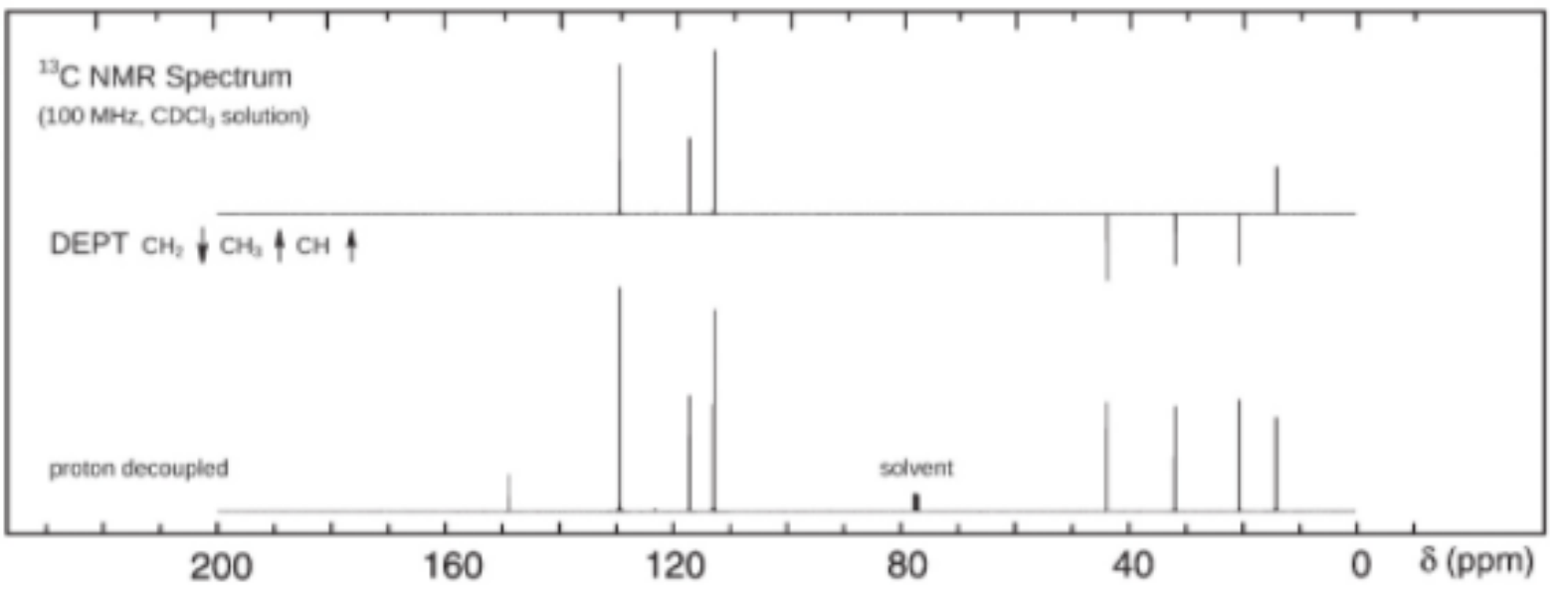

ppm
20
30
40
120
130
140
150
7.5
7.0
3.0
2.5
2.0
1.5
1.0
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

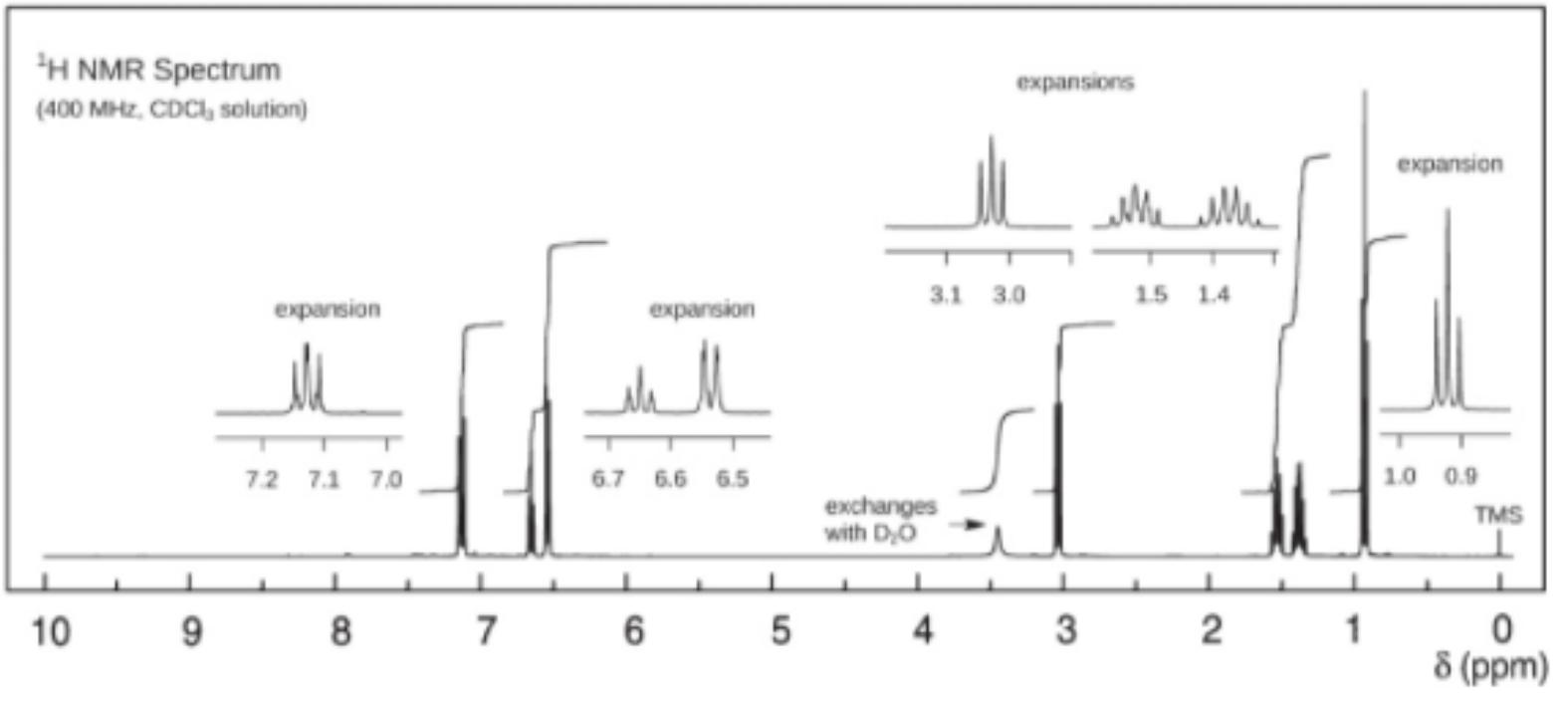

ppm
20
30
40
120
130
140
7.5
7.0
3.0
2.5
2.0
1.5
1.0
ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)

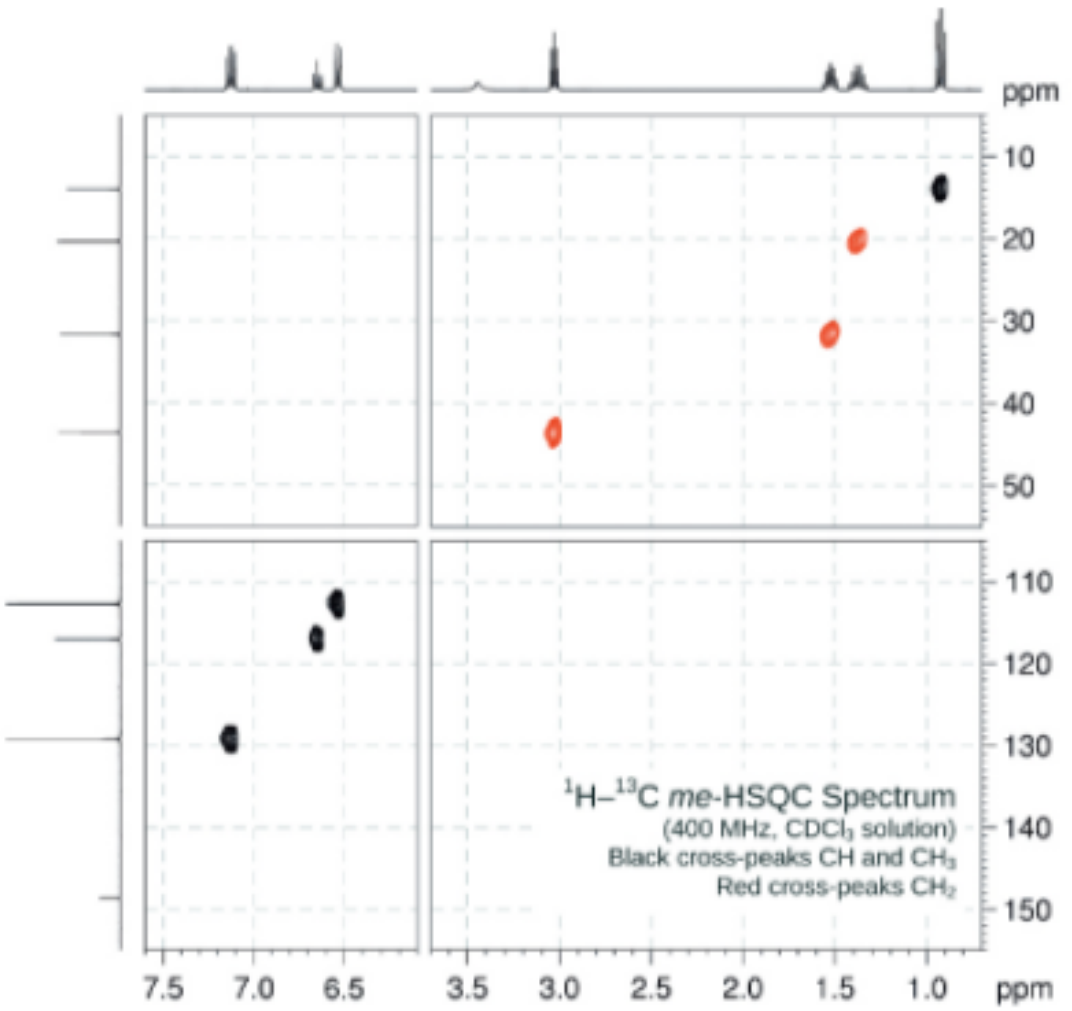
Problem 161

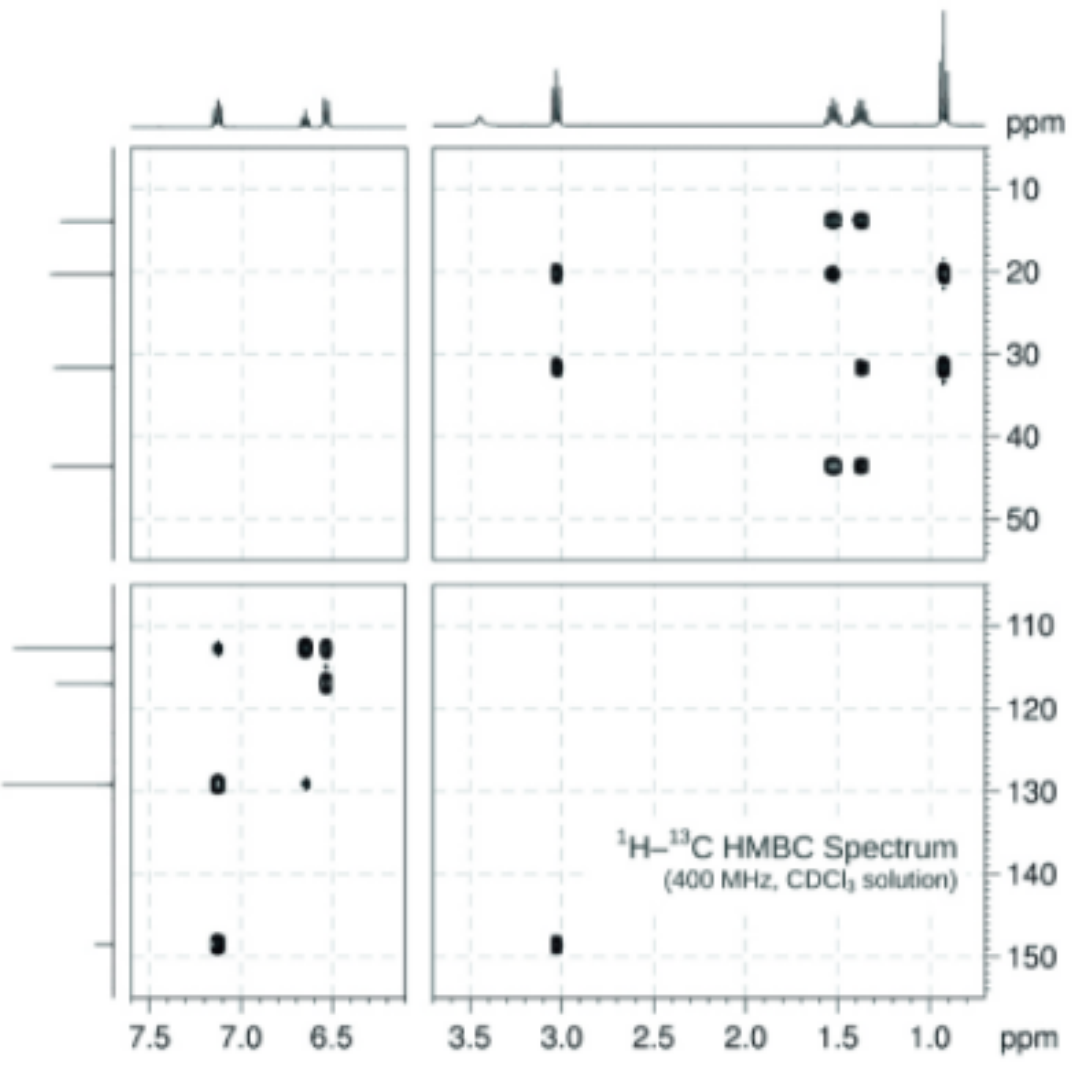

3408
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)


100
80
60
40
20
% of base peak
106
77
M+·
149
Mass Spectrum
C10H15N
40
80
120
160
200
240
280
m/e

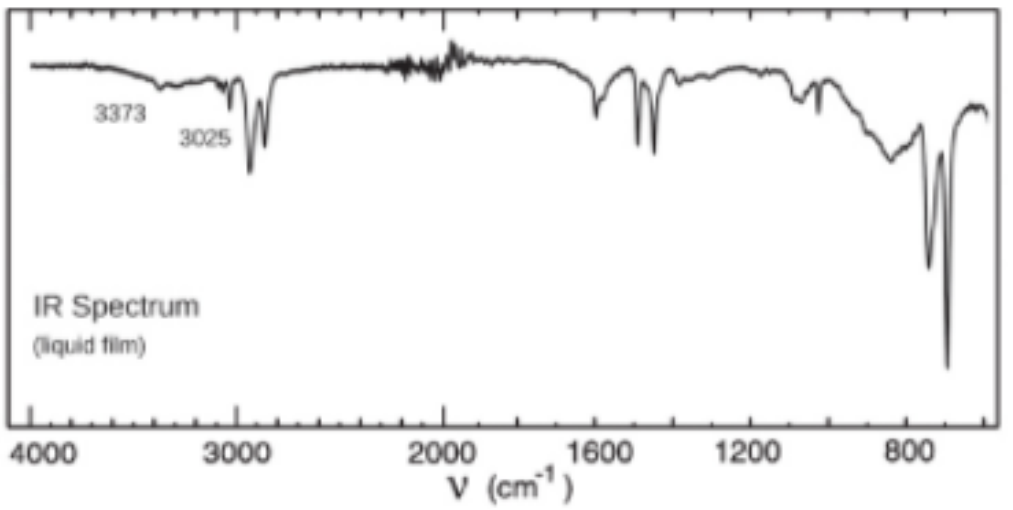

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

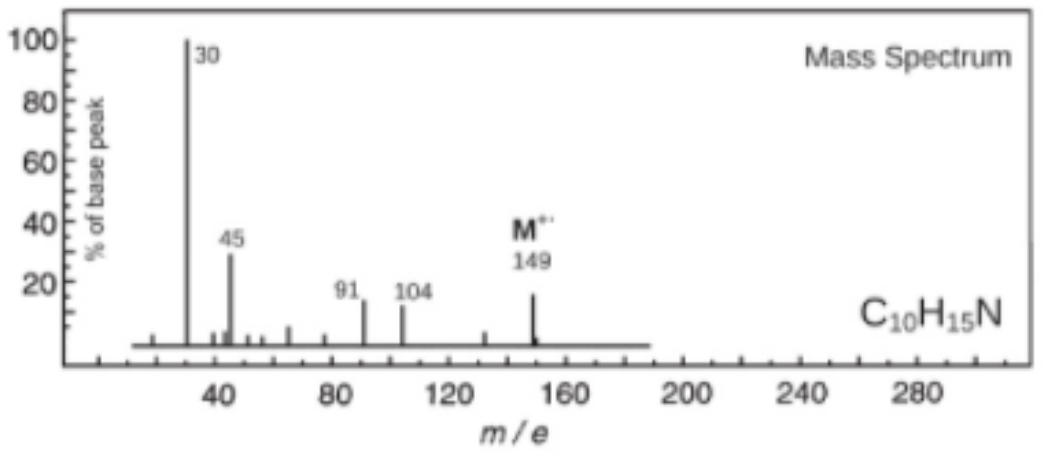

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
expansion
expansion
expansion
7.2
7.1
7.0
6.7
6.6
6.5
3.1
3.0
1.5
1.4
1.0
0.9
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

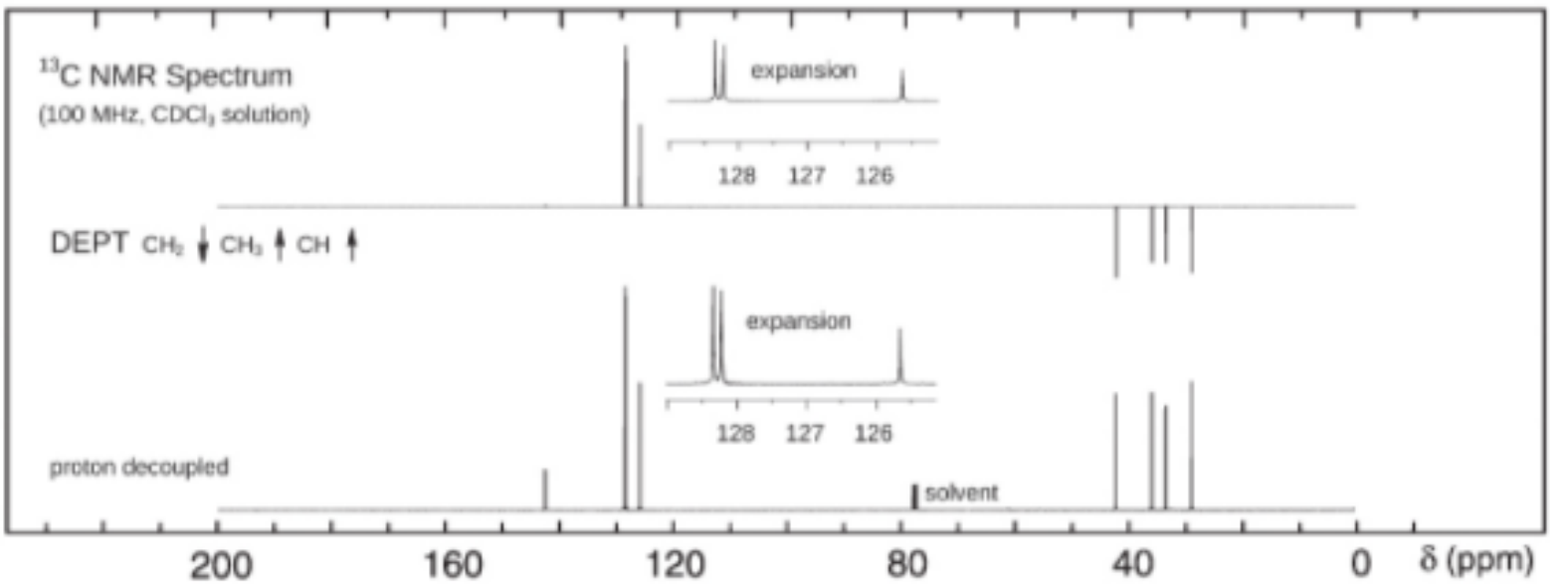

ppm
10
20
30
40
50
110
120
130
140
150
7.5
7.0
6.5
3.5
3.0
2.5
2.0
1.5
1.0
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

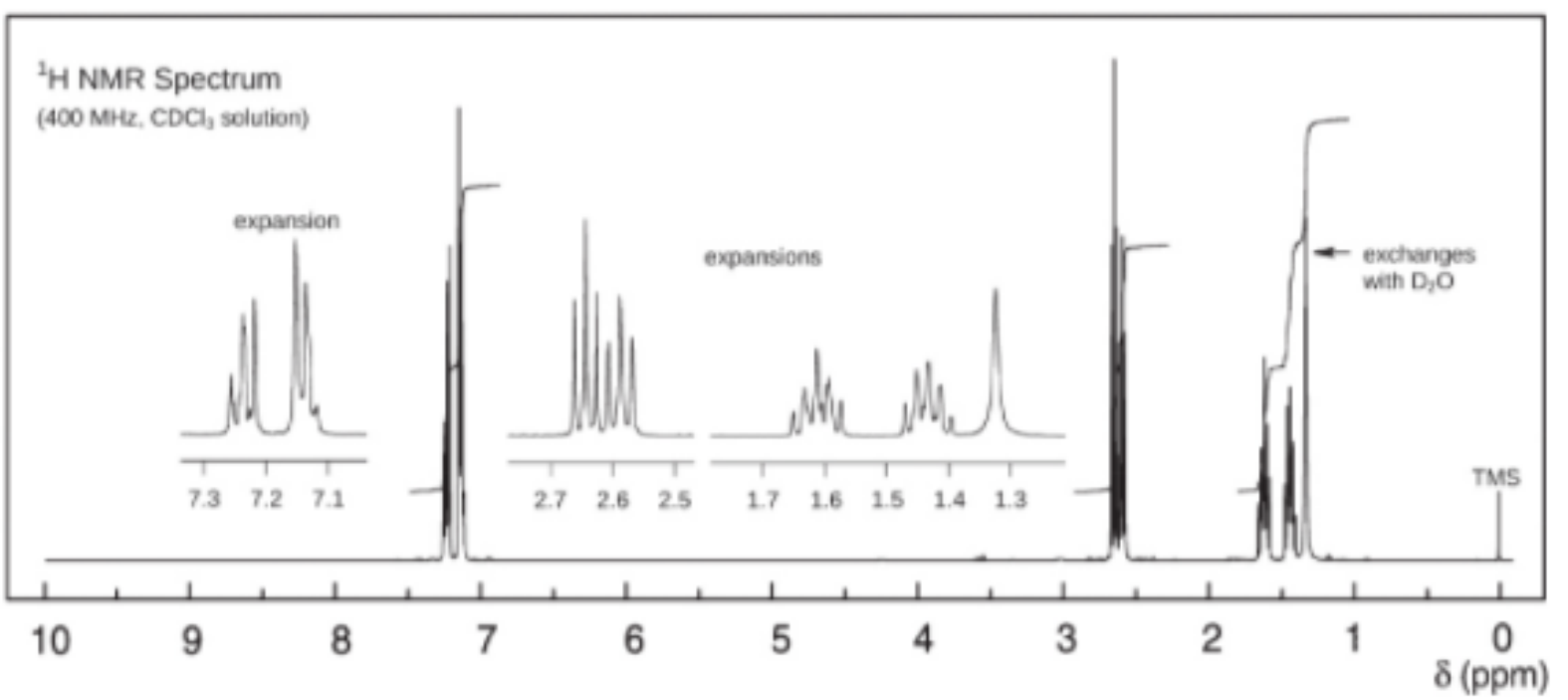

ppm
10
20
30
40
50
110
120
130
140
150
7.5
7.0
6.5
3.5
3.0
2.5
2.0
1.5
1.0
ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)

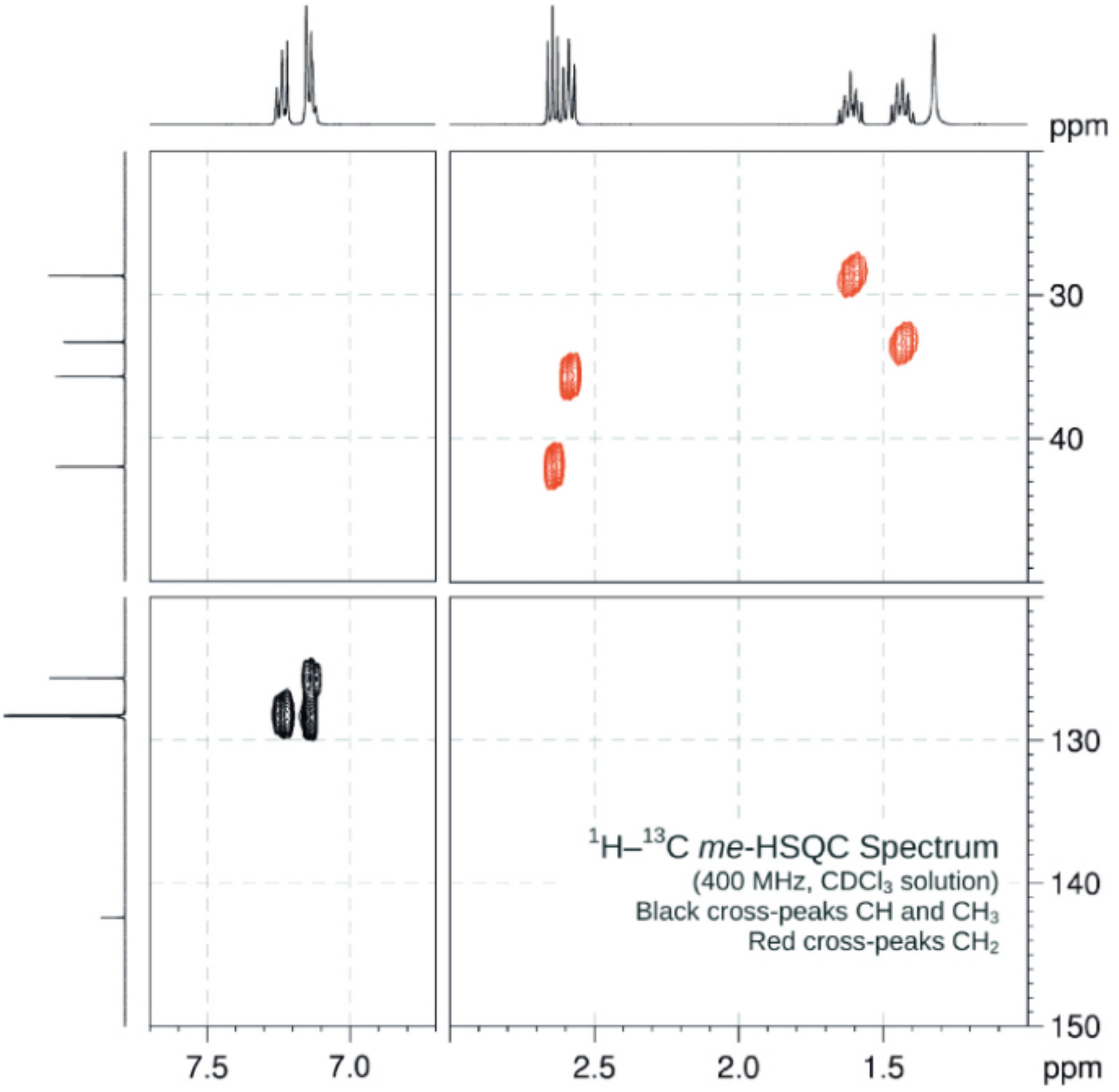
Problem 162


3373
3025
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

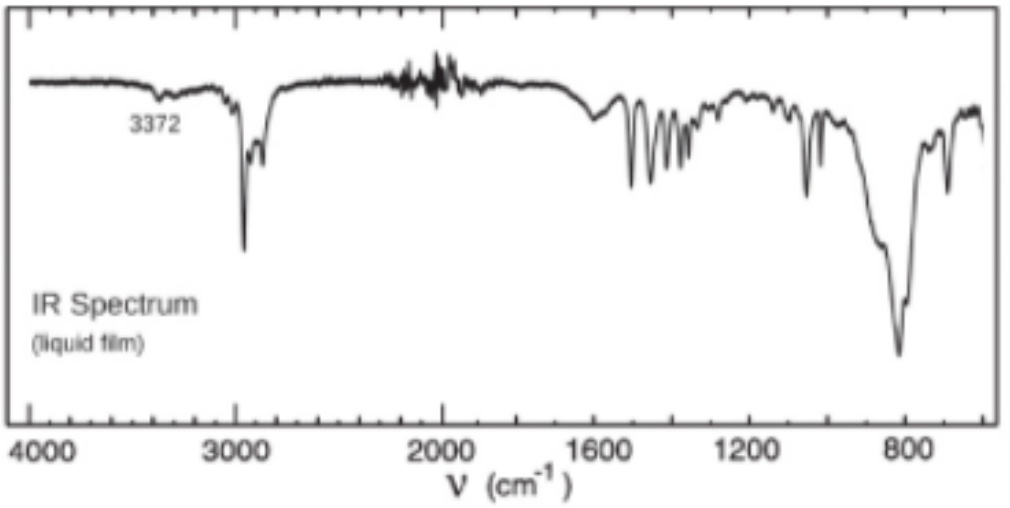

Mass Spectrum
% of base peak
100
80
60
40
20
30
45
91
104
M+·
149
C10H15N
40
80
120
160
200
240
280
m/e

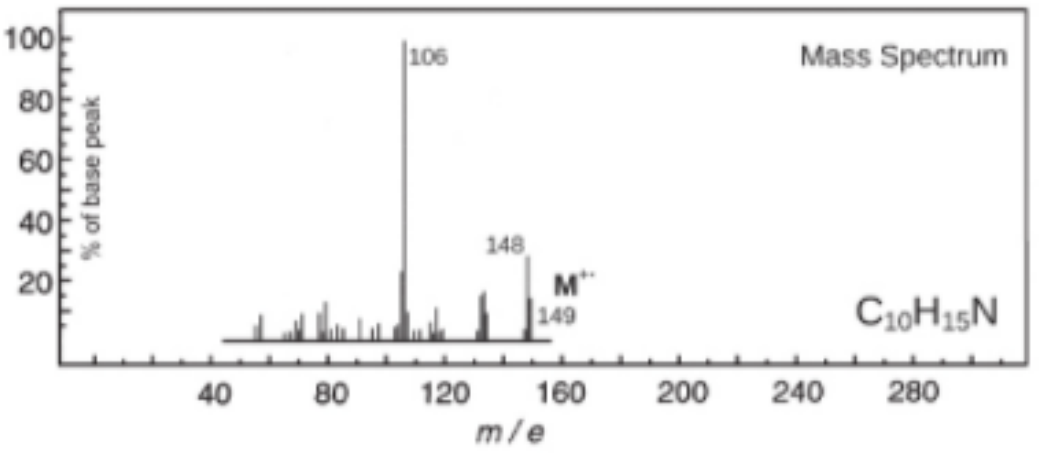

13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
128 127 126
DEPT CH2 CH3 CH
expansion
128 127 126
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

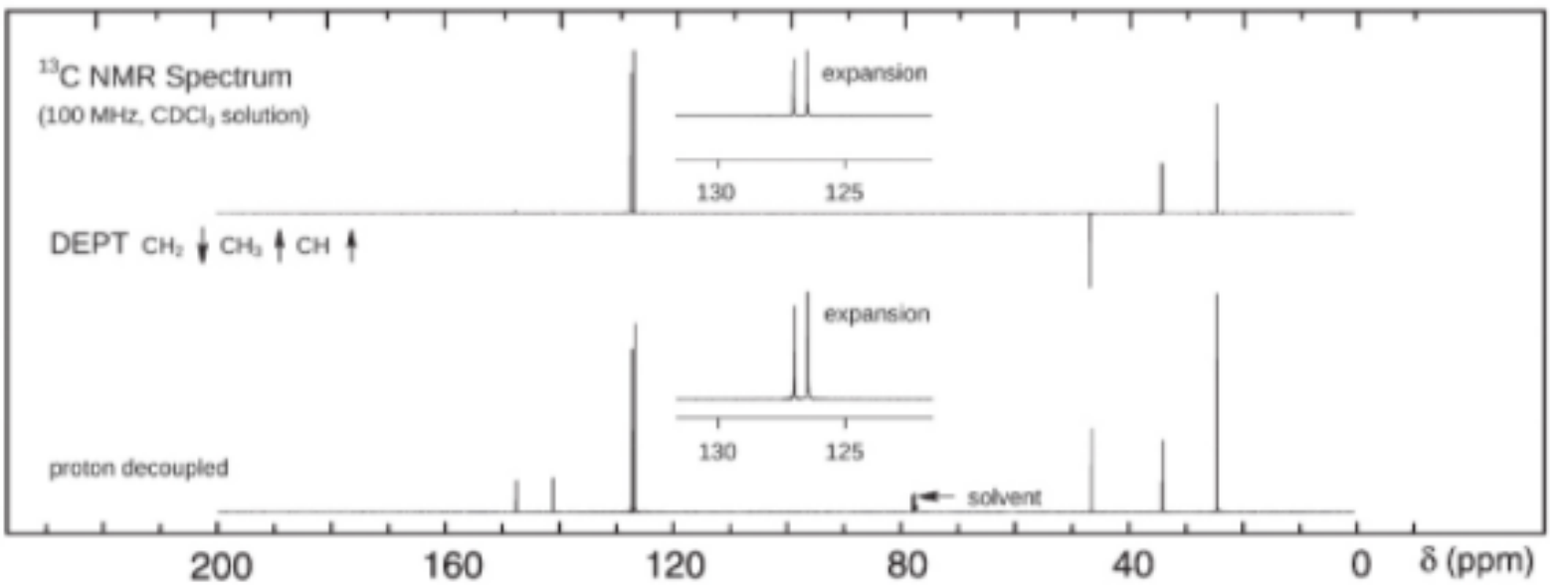

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.3 7.2 7.1
expansions
2.7 2.6 2.5
1.7 1.6 1.5 1.4 1.3
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

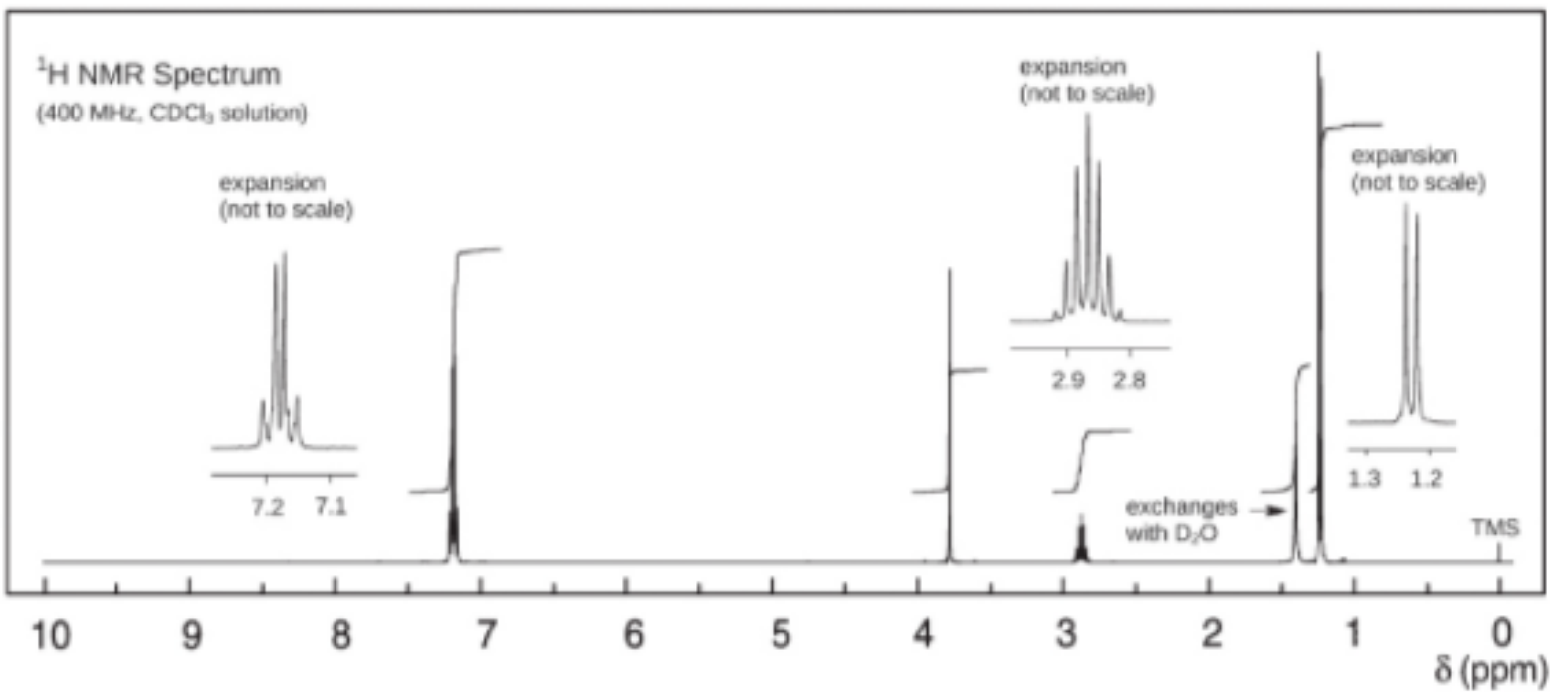

ppm
30
40
130
140
150
7.5
7.0
2.5
2.0
1.5
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

Problem 163

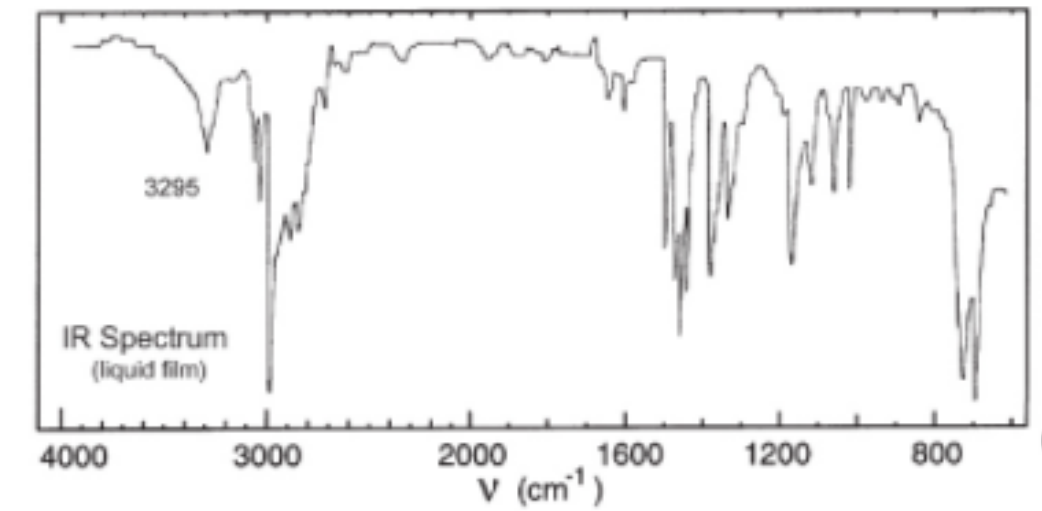

3372
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

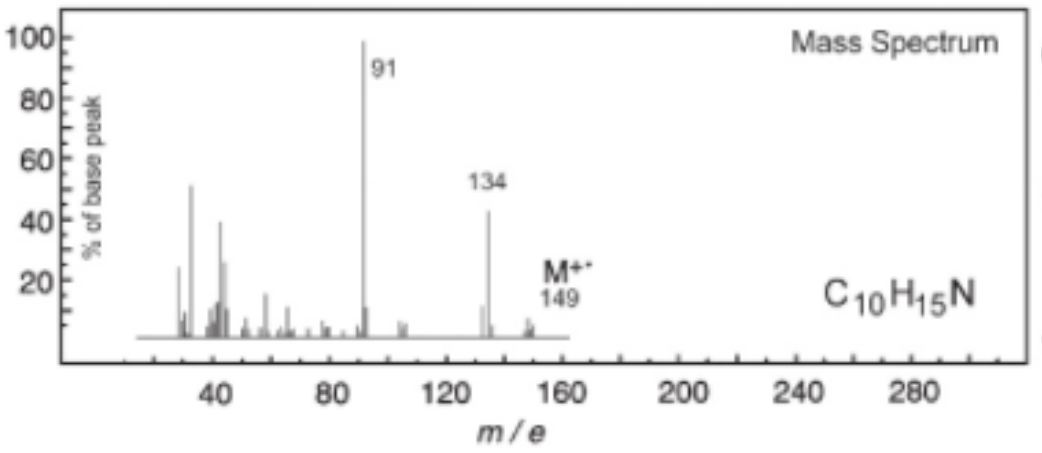

100
80
60
40
20
% of base peak
106
148
M+·
149
Mass Spectrum
C10H15N
40
80
120
160
200
240
280
m/e

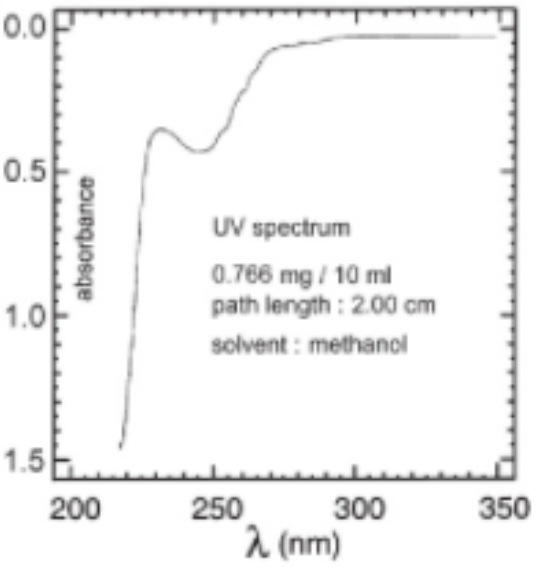

13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
130
125
DEPT CH2 CH3 CH
expansion
130
125
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

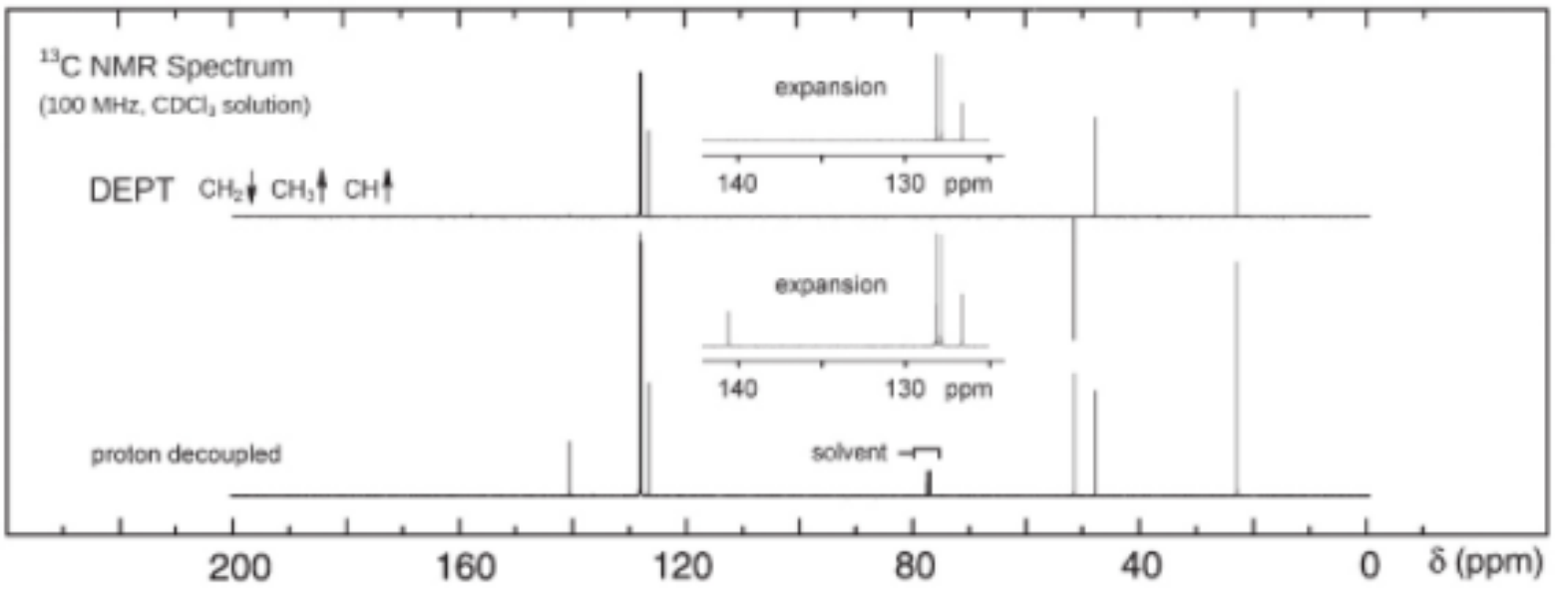

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
(not to scale)
7.2
7.1
expansion
(not to scale)
2.9
2.8
expansion
(not to scale)
1.3
1.2
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

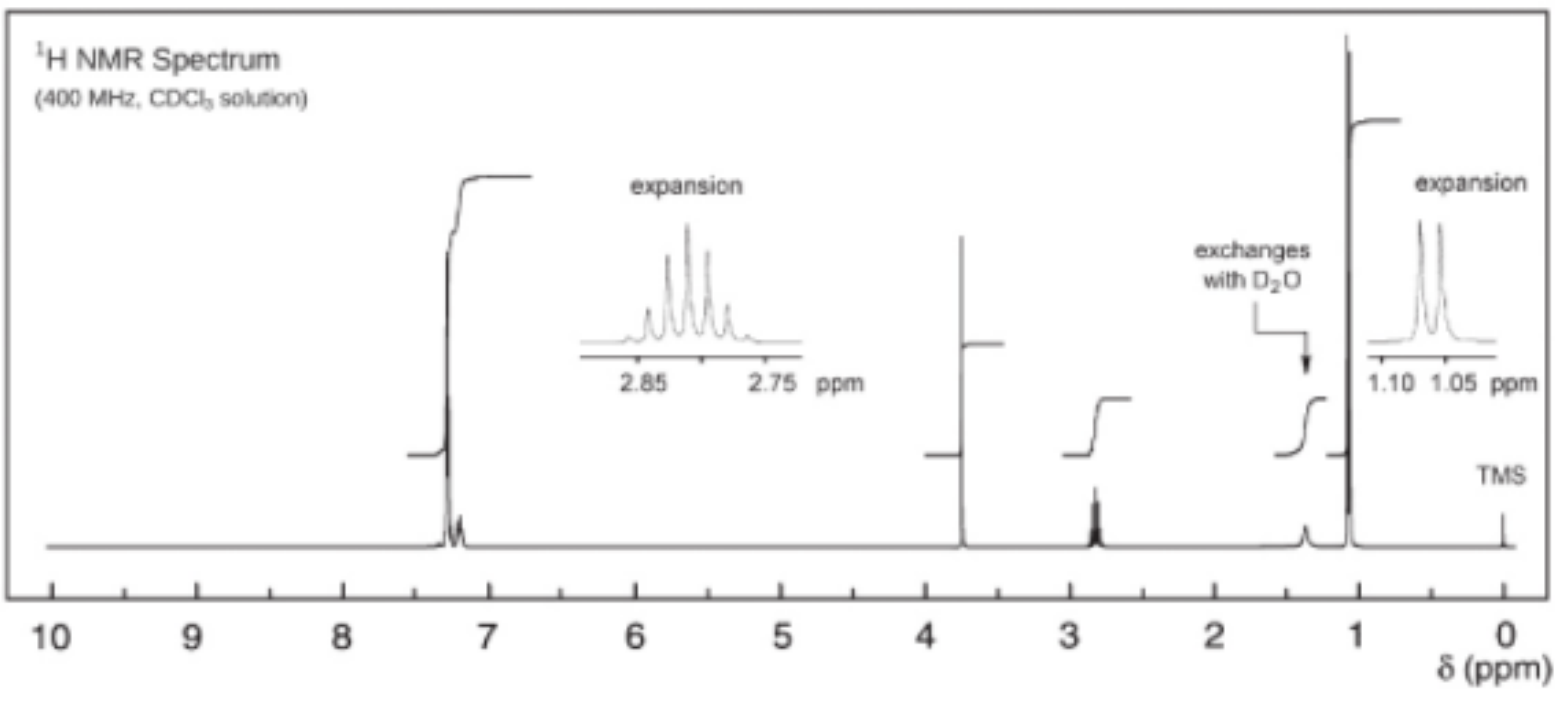
Problem 164


3295
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

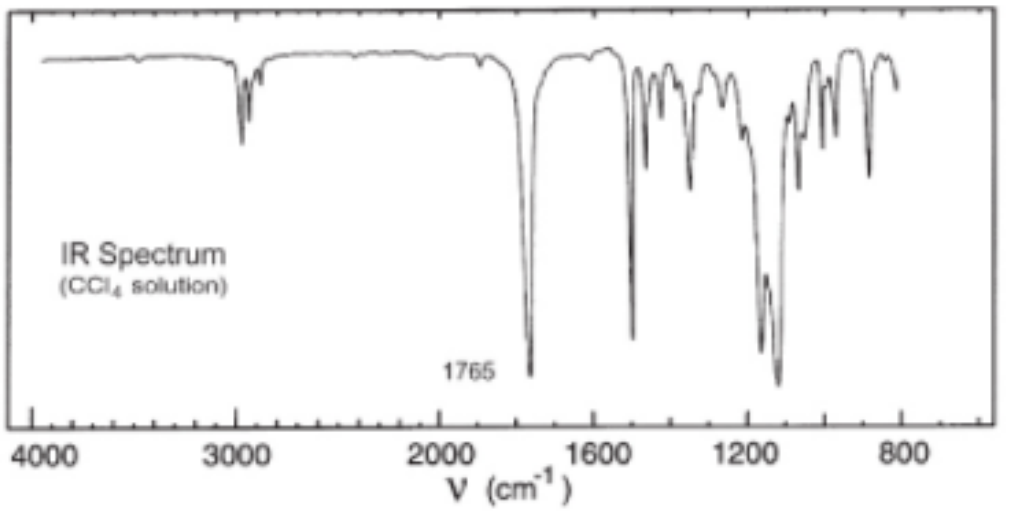

Mass Spectrum
% of base peak
100
80
60
40
20
91
134
M+·
149
C10H15N
40
80
120
160
200
240
280
m/e

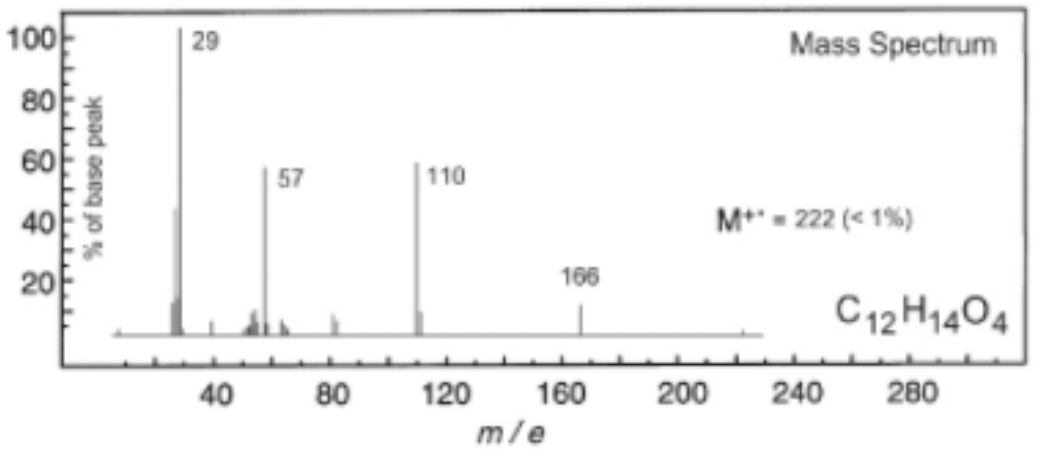

0.0
0.5
1.0
1.5
absorbance
UV spectrum
0.766 mg / 10 ml
path length : 2.00 cm
solvent : methanol
200
250
300
350
λ (nm)


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
expansion
140
130 ppm
expansion
140
130 ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
2.85
2.75 ppm
exchanges
with D2O
expansion
1.10
1.05 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 165



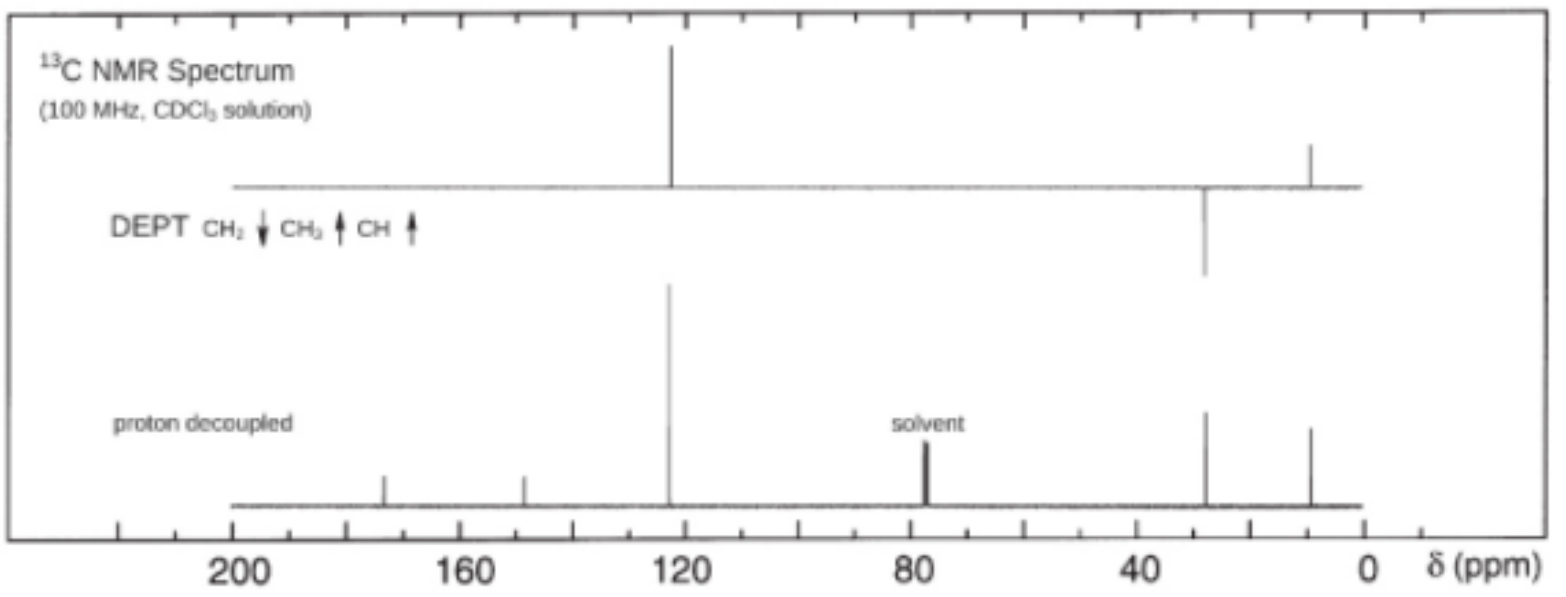


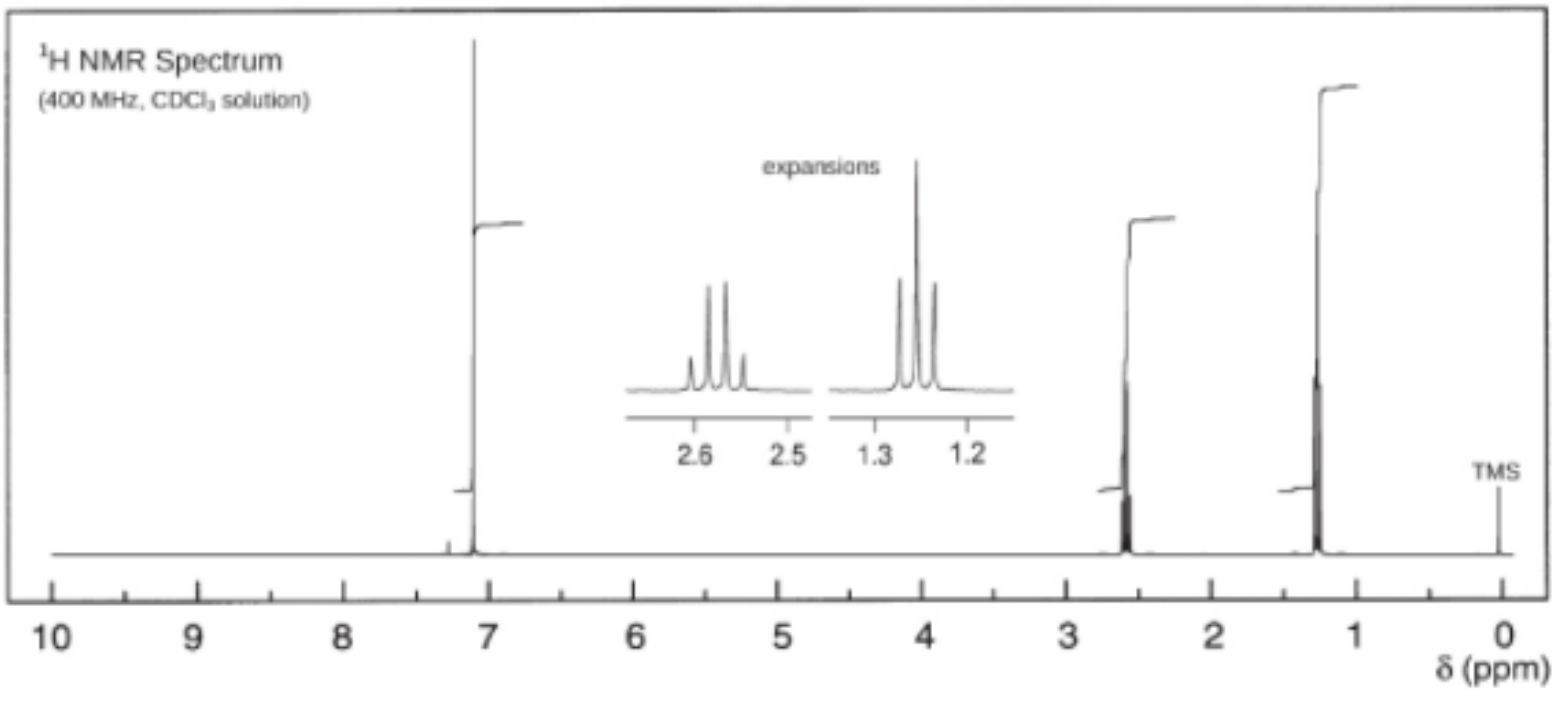
UV Spectrum

λ_{max} 269 nm ($\log_{10}\varepsilon$ 2.7)

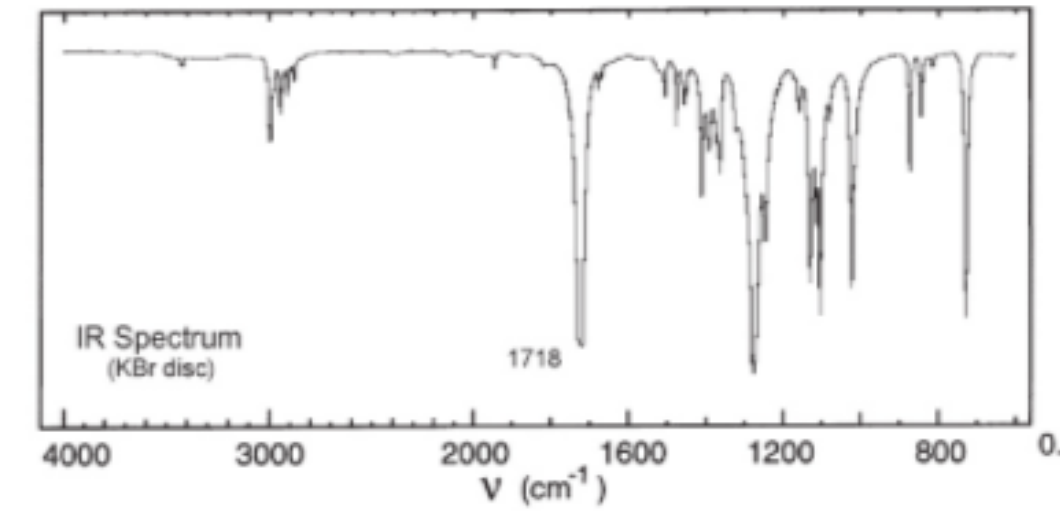
λ_{max} 263 nm ($\log_{10}\varepsilon$ 2.7)

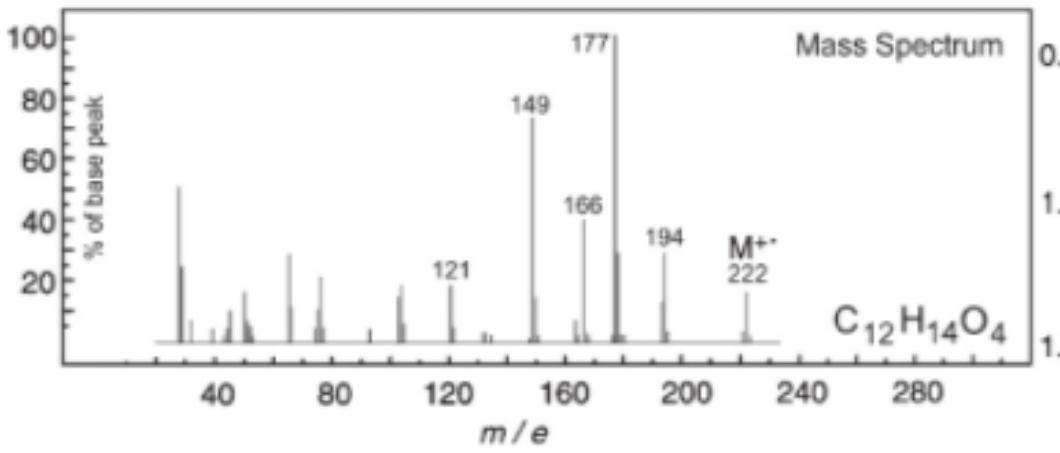
solvent : methanol

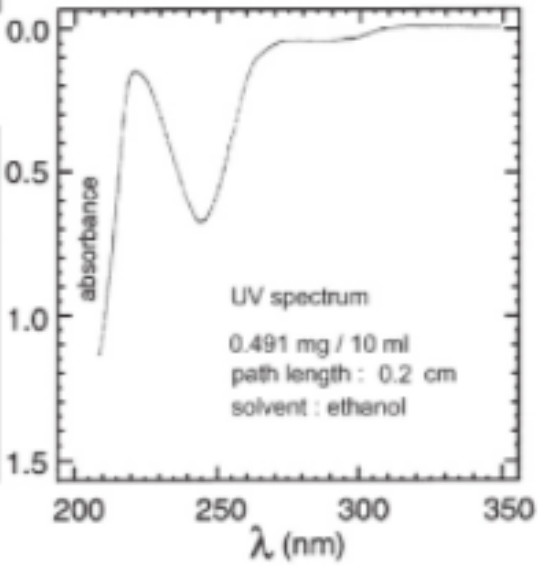


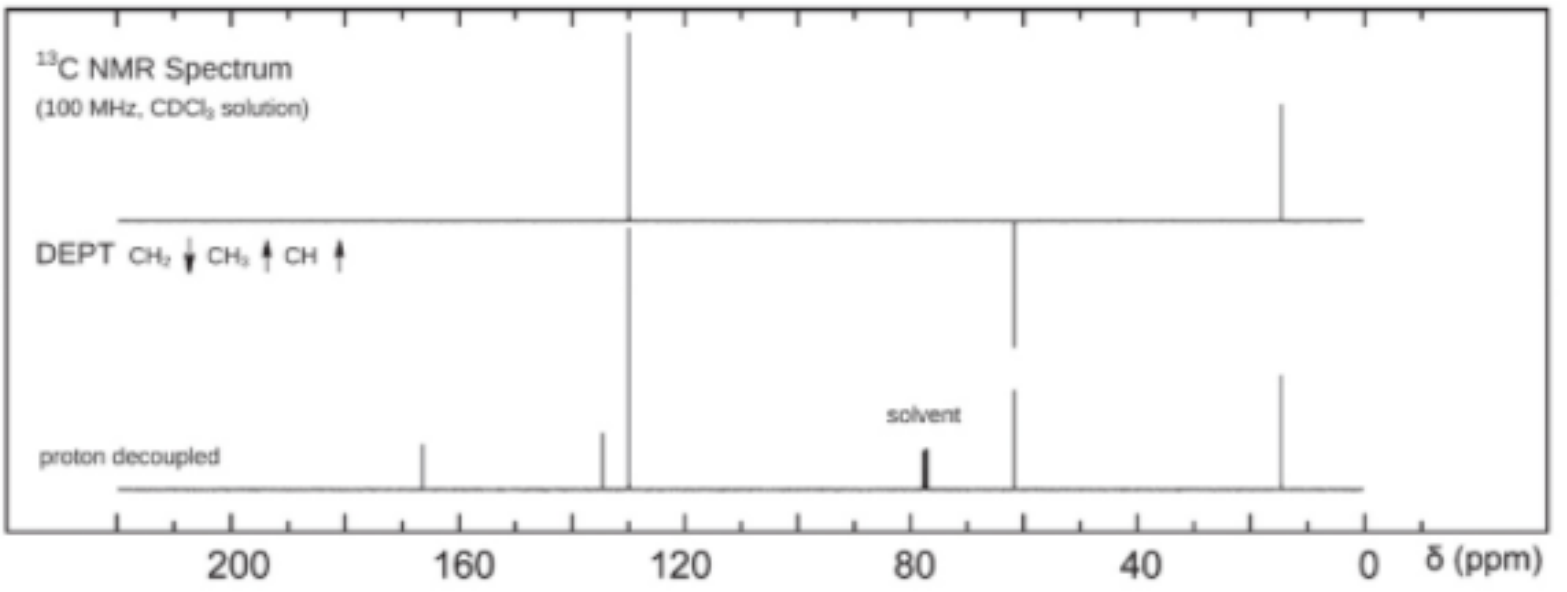


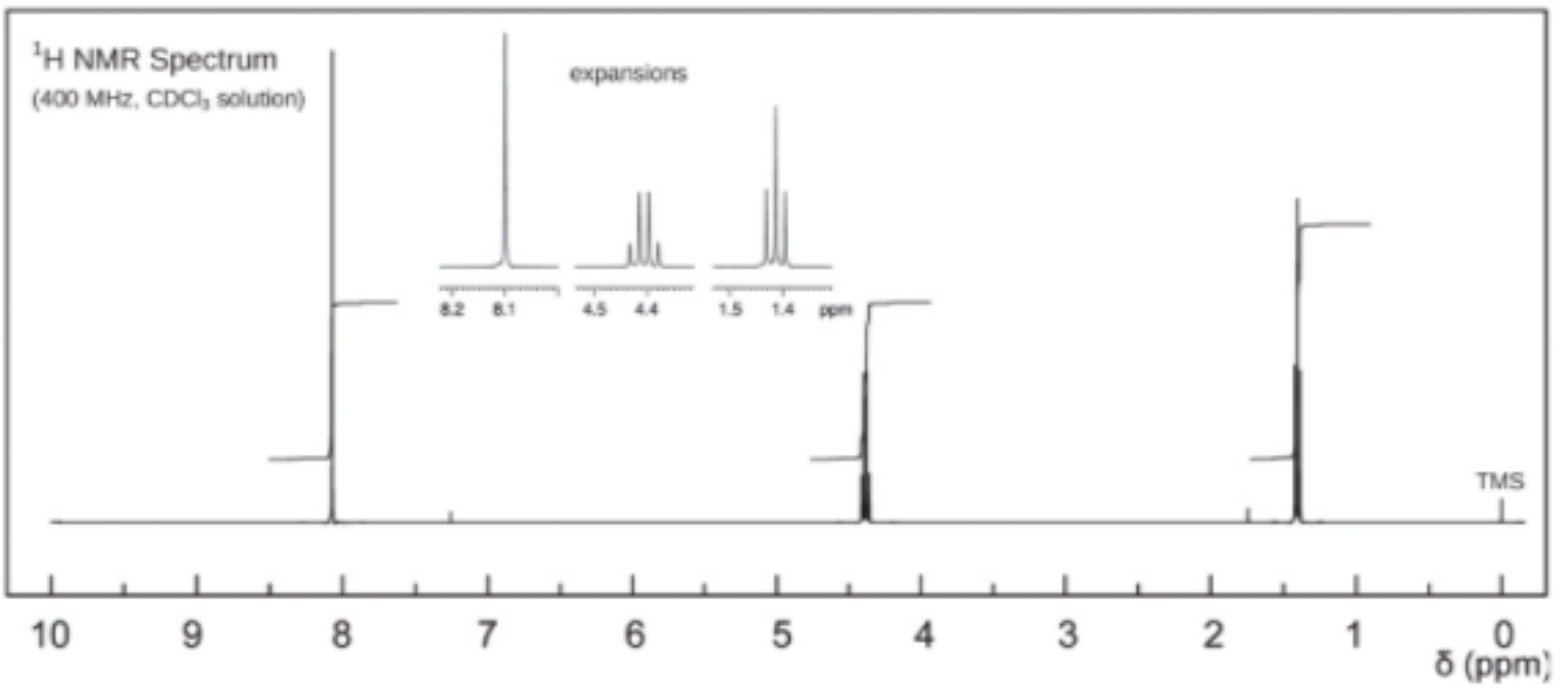
Problem 166


IR Spectrum
(KBr disc)
1718
4000
3000
2000
1600
1200
800
ν (cm-1)

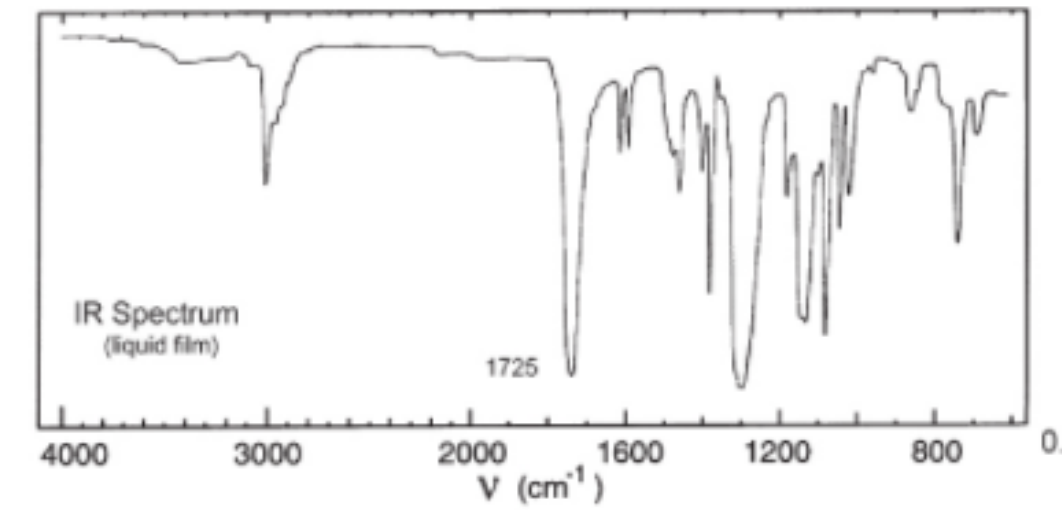

Mass Spectrum
% of base peak
100
80
60
40
20
177
149
166
194
121
M+·
222
C12H14O4
40
80
120
160
200
240
280
m/e

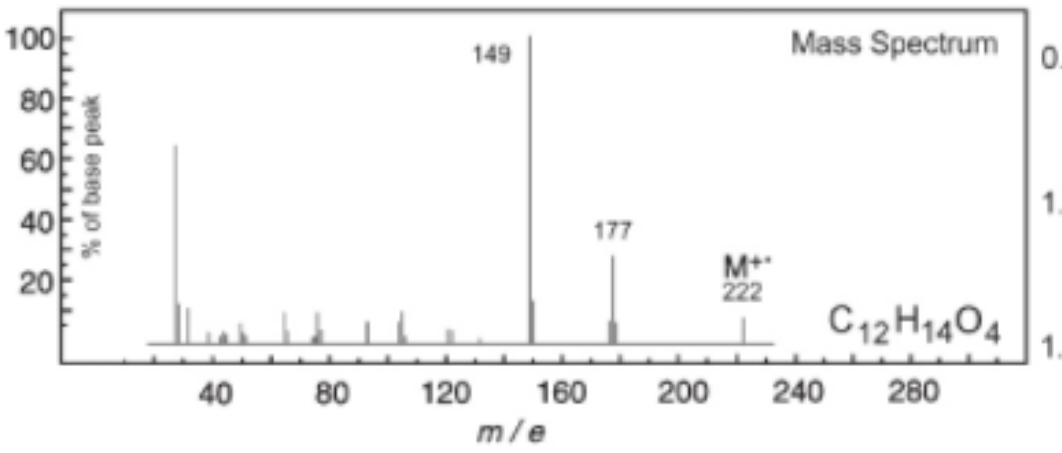

absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.491 mg / 10 ml
path length : 0.2 cm
solvent : ethanol
200
250
300
350
λ (nm)

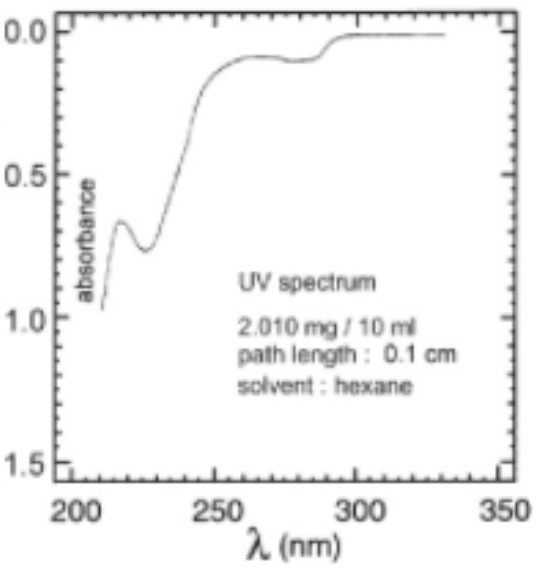

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

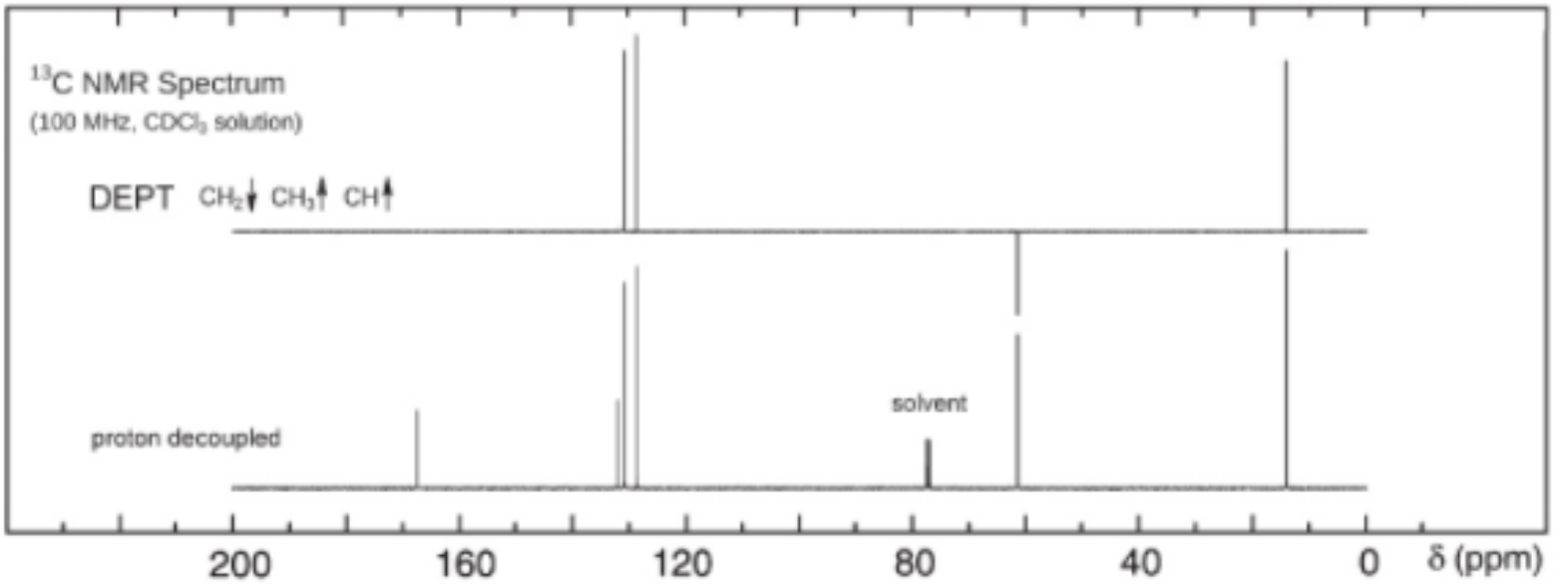

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
8.2
8.1
4.5
4.4
1.5
1.4
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

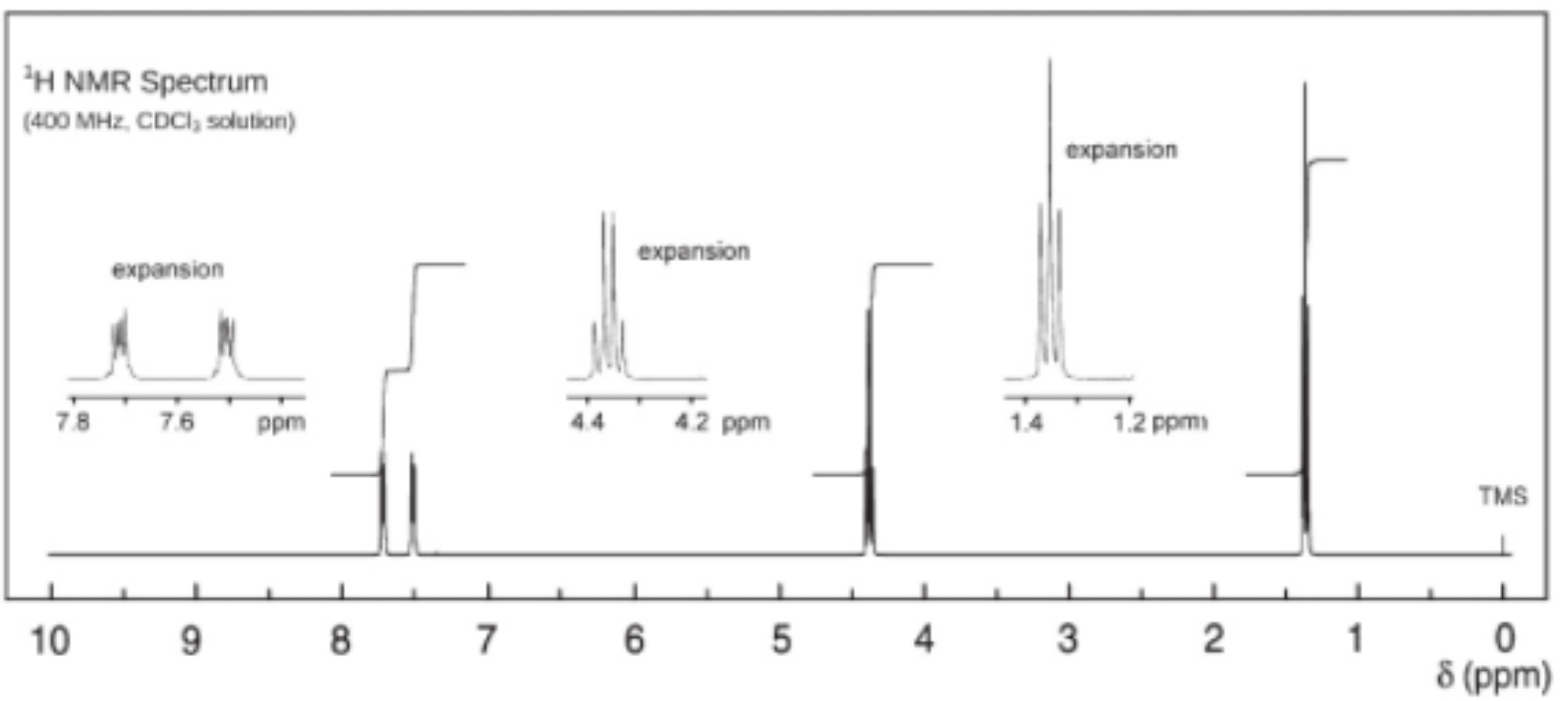
Problem 167


IR Spectrum
(liquid film)
1725
4000
3000
2000
1600
1200
800
V (cm-1)

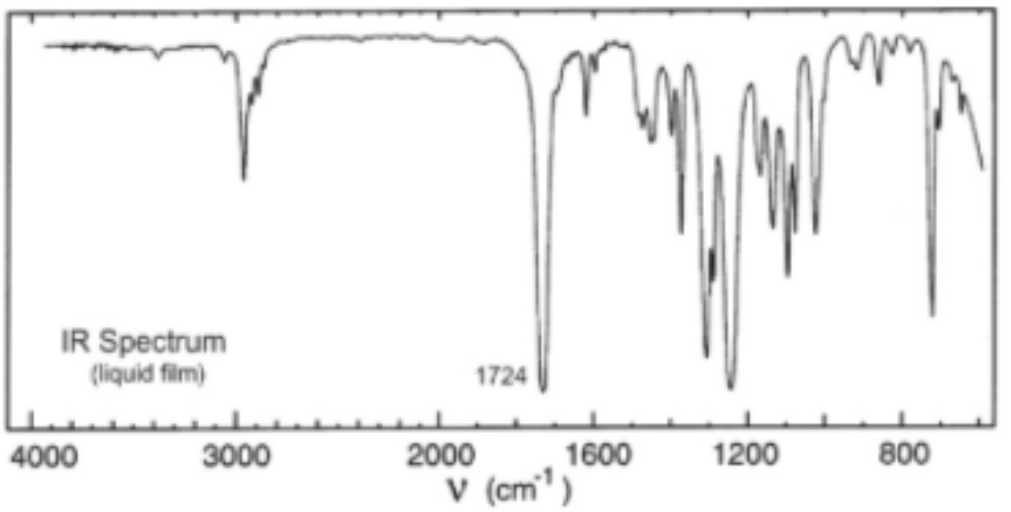

Mass Spectrum
149
177
M+·
222
C12H14O4
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m/e

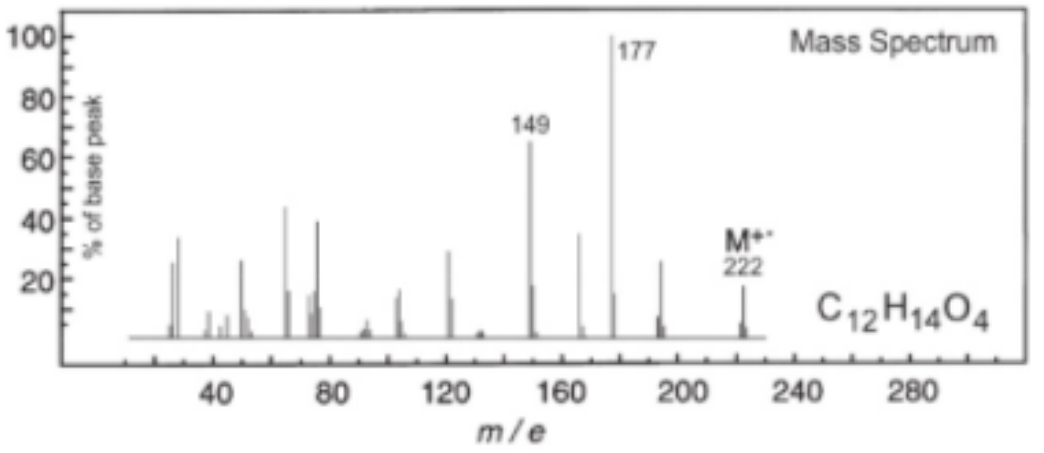

UV spectrum
2.010 mg / 10 ml
path length : 0.1 cm
solvent : hexane
absorbance
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)

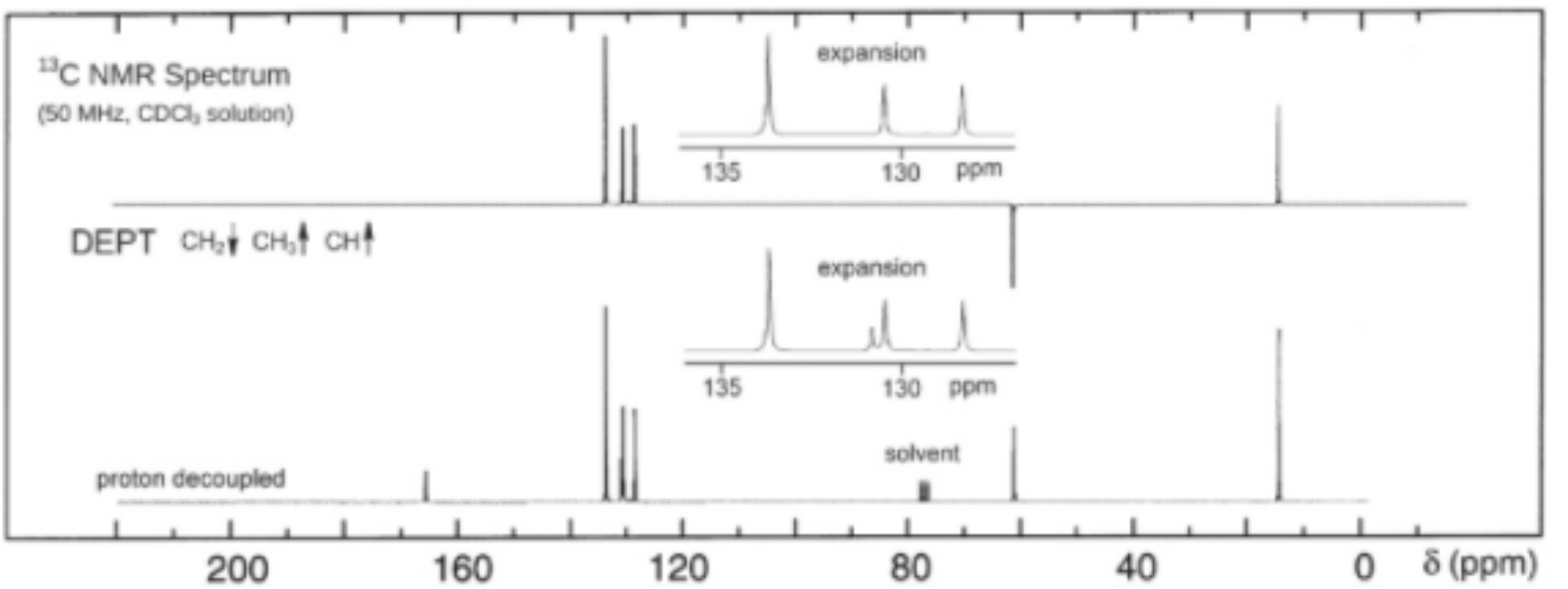

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

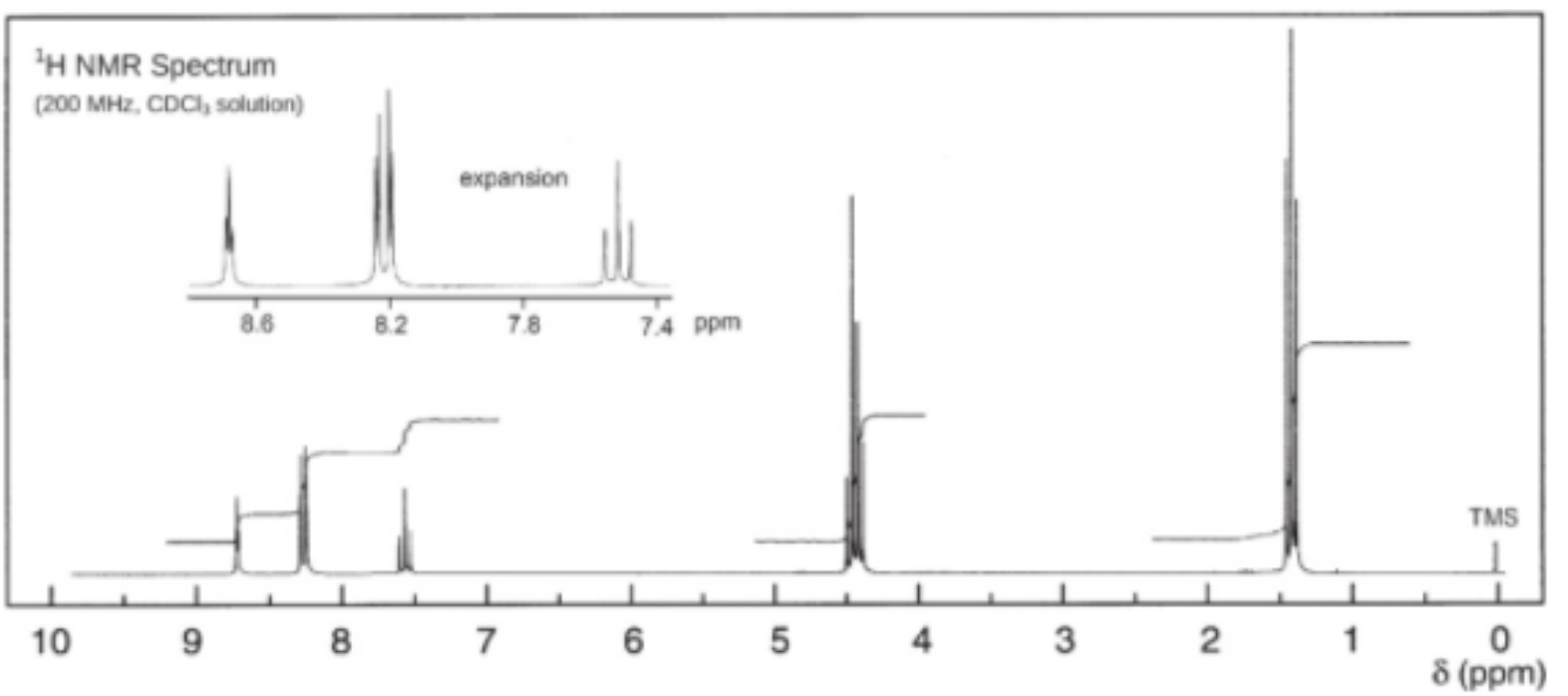

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.8
7.6
ppm
expansion
4.4
4.2 ppm
expansion
1.4
1.2 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 168

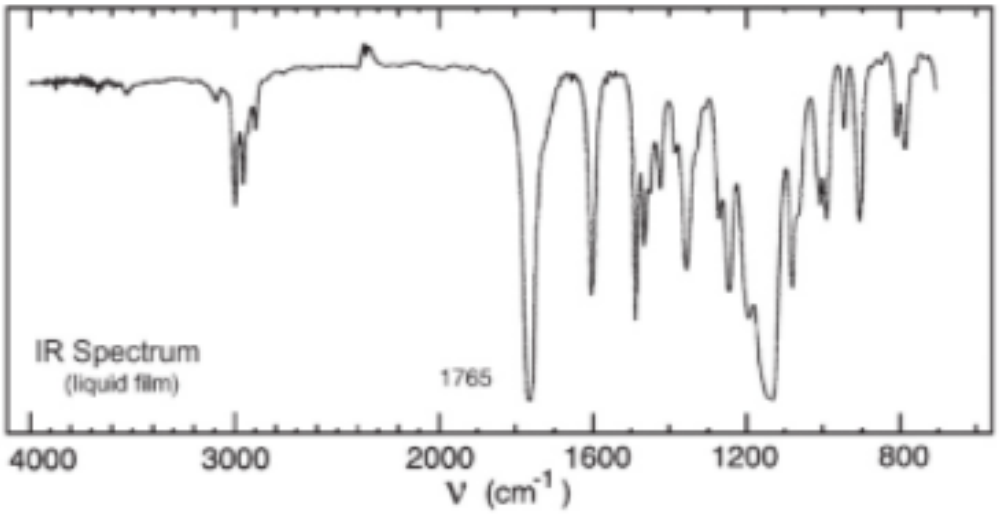

IR Spectrum
(liquid film)
1724
4000
3000
2000
1600
1200
800
ν (cm-1)

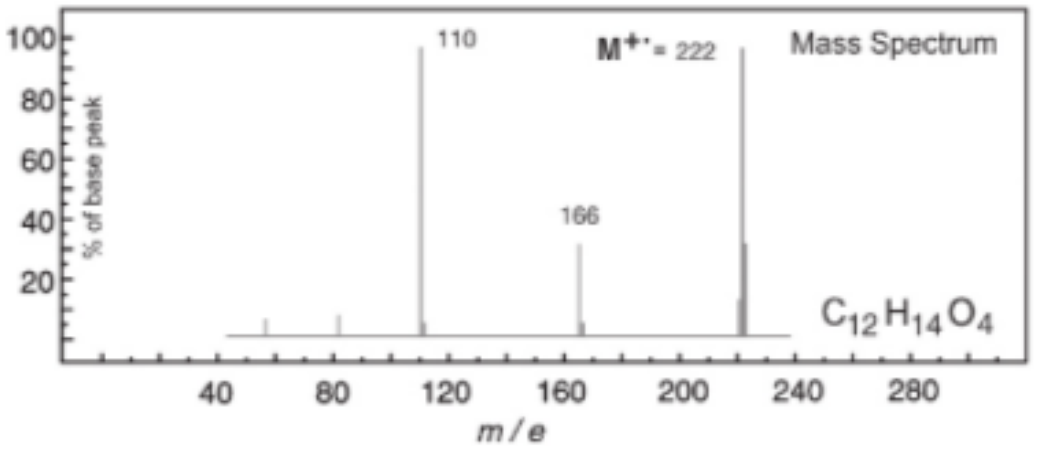

Mass Spectrum
% of base peak
100
80
60
40
20
177
149
M+·
222
C12H14O4
40
80
120
160
200
240
280
m/e


13C NMR Spectrum
(50 MHz, CDCl3 solution)
expansion
135
130
ppm
DEPT CH2 CH3 CH
expansion
135
130
ppm
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(200 MHz, CDCl3 solution)
expansion
8.6
8.2
7.8
7.4
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 169



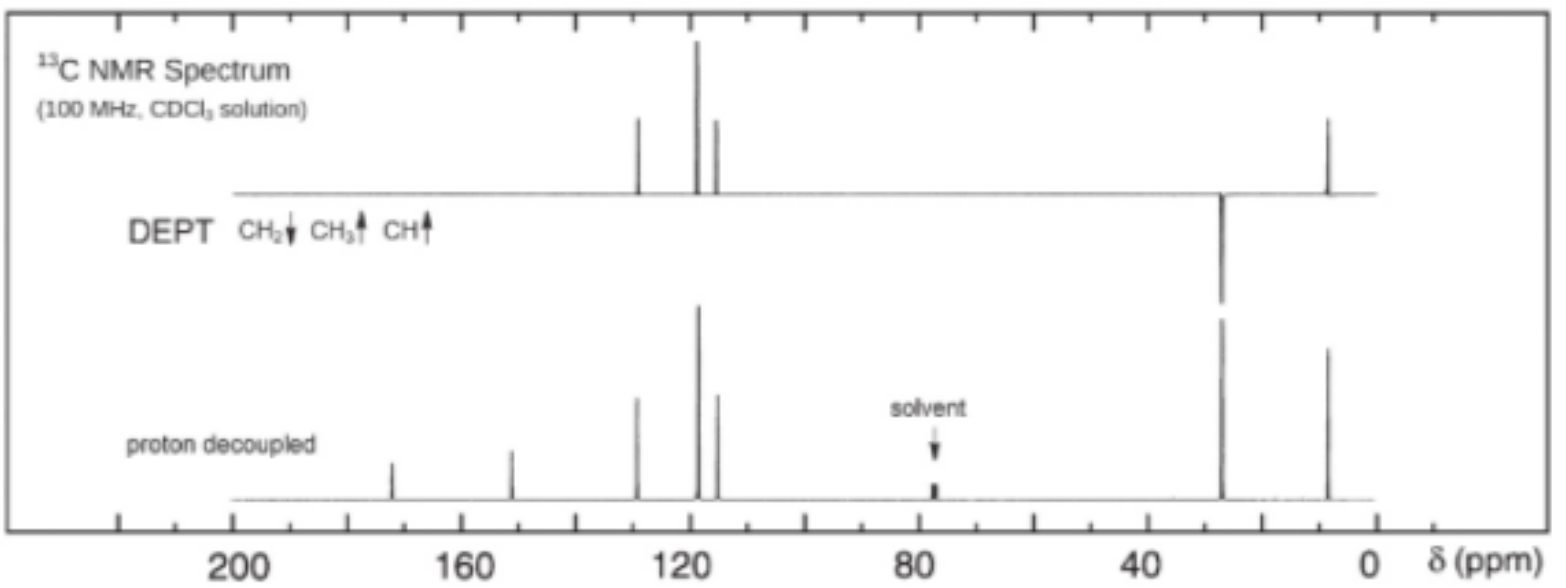


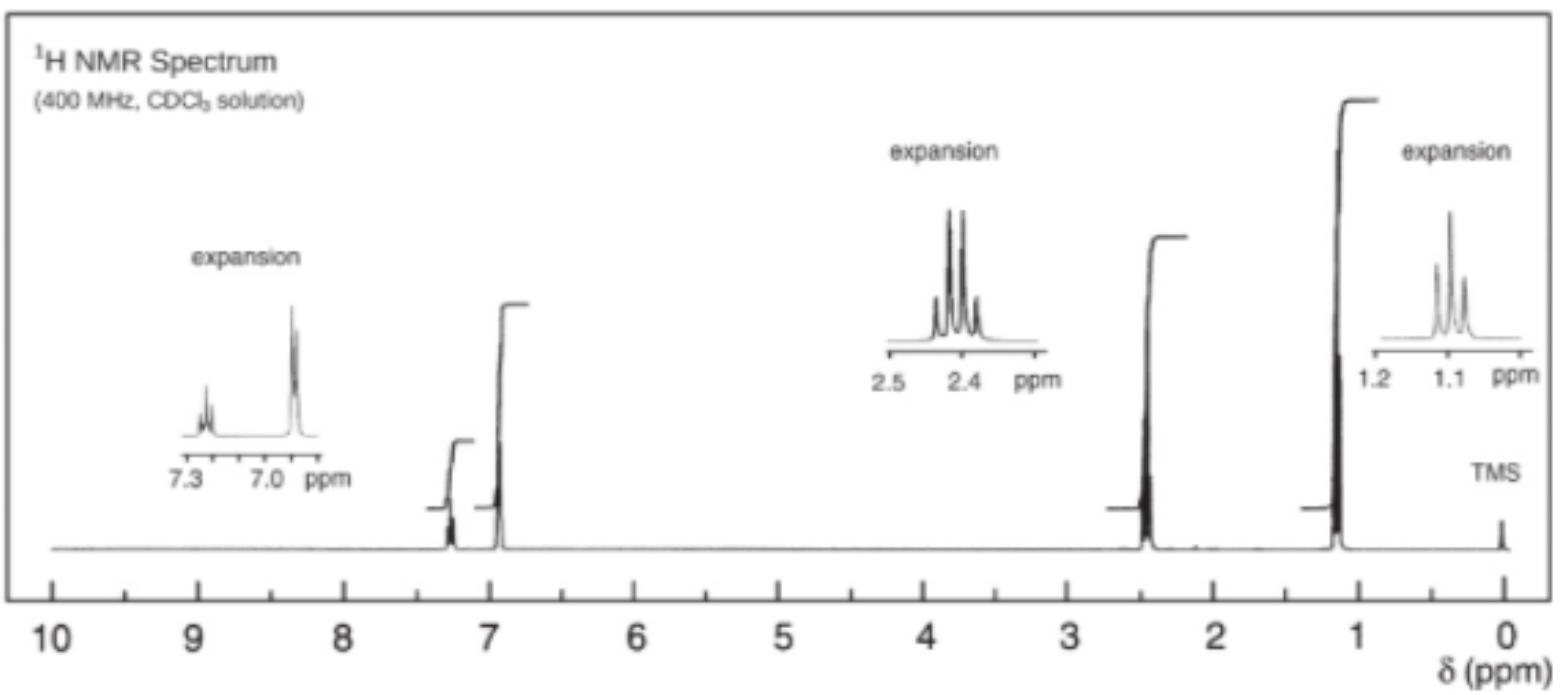
UV Spectrum

λ_{max} 220 nm ($\log_{10}\varepsilon$ 3.7)

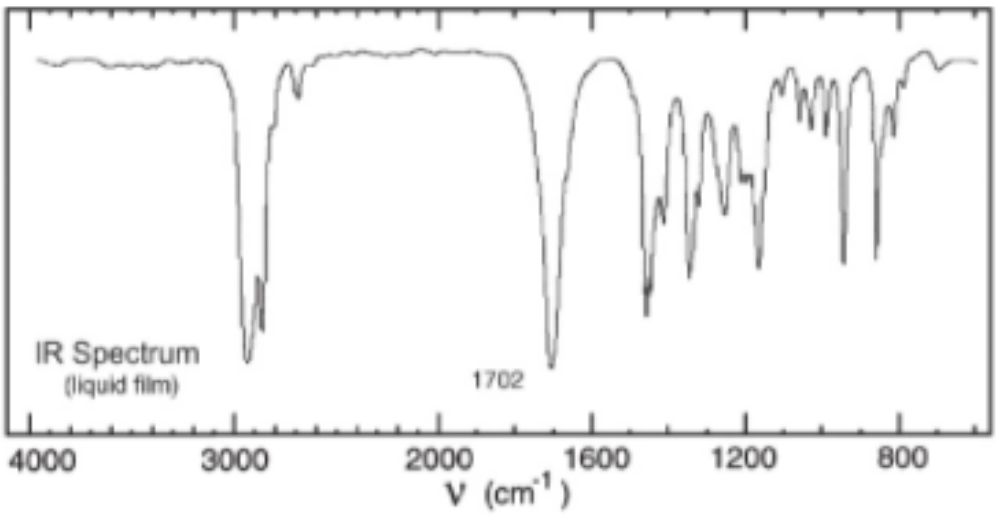
λ_{max} 274 nm ($\log_{10}\varepsilon$ 3.3)

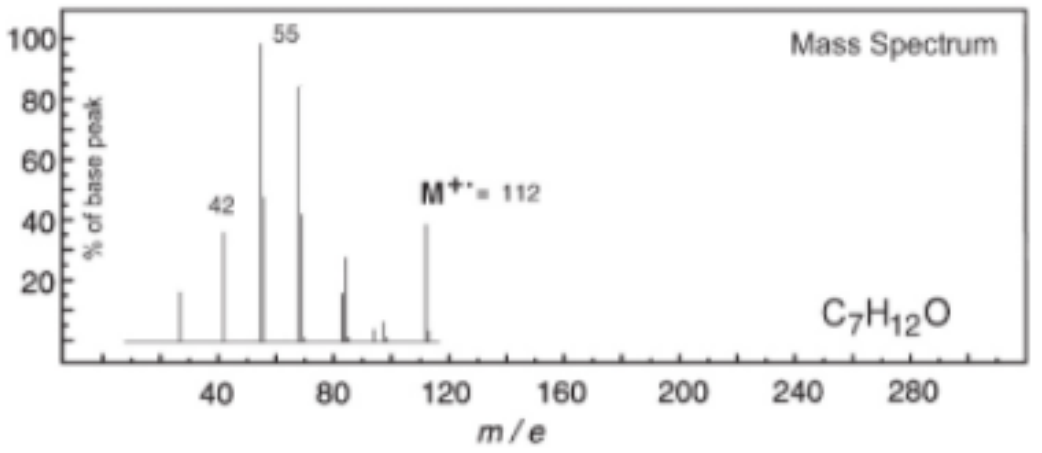
solvent : ethanol



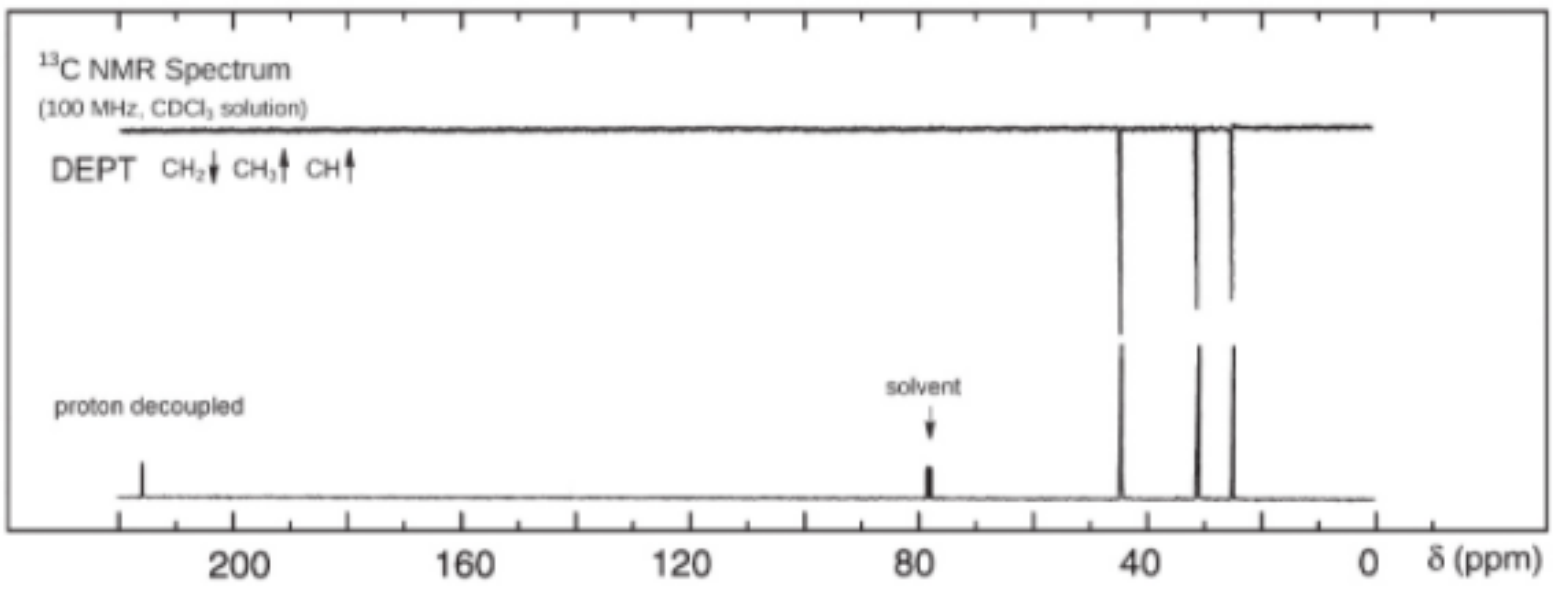


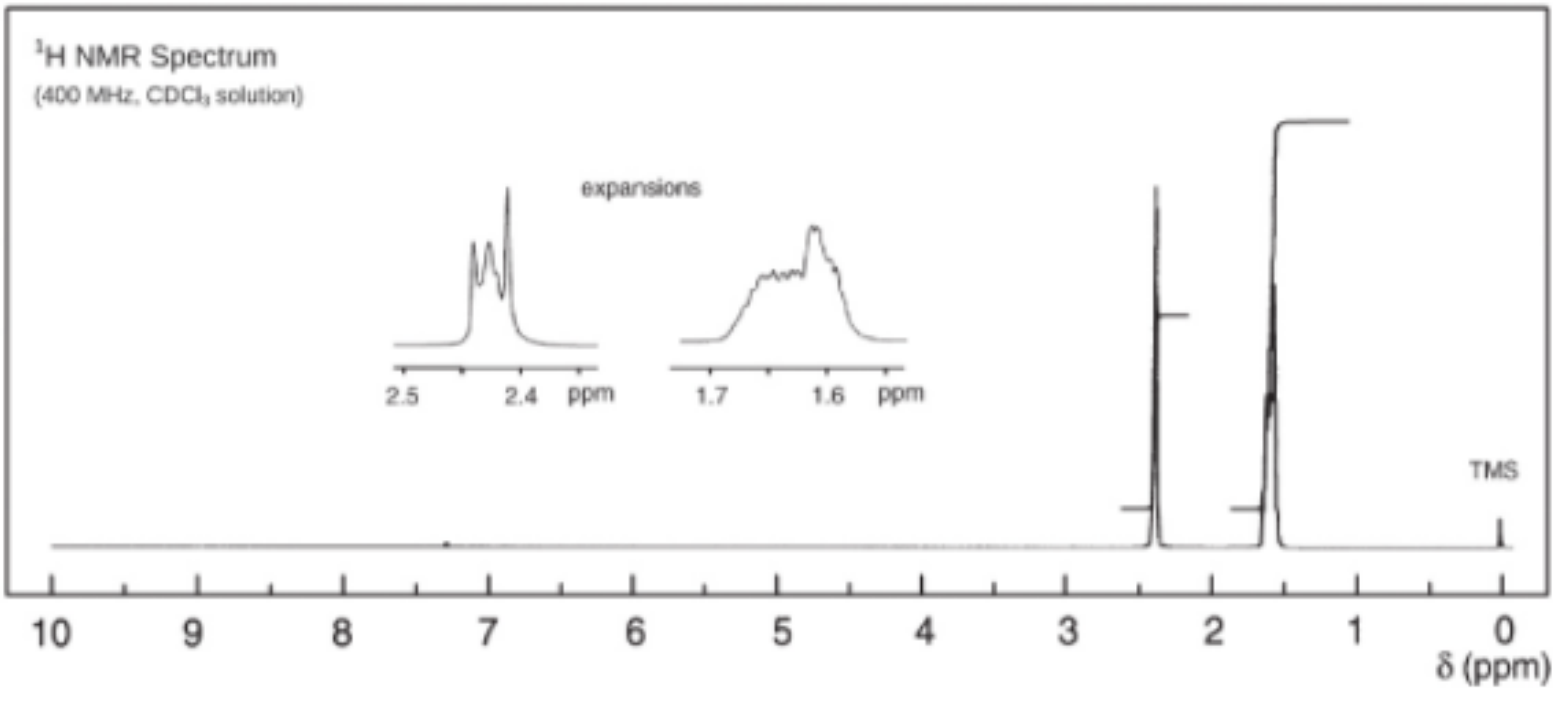
Problem 170



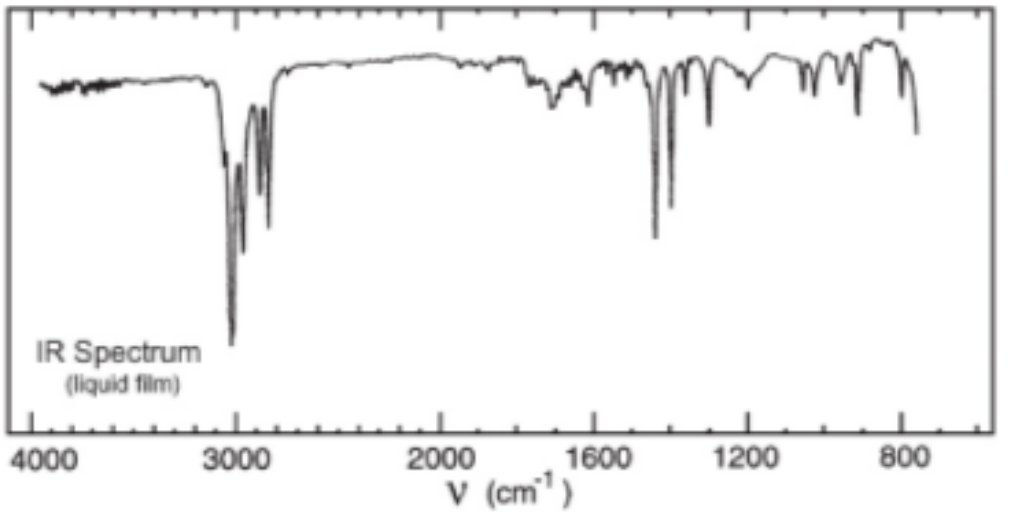


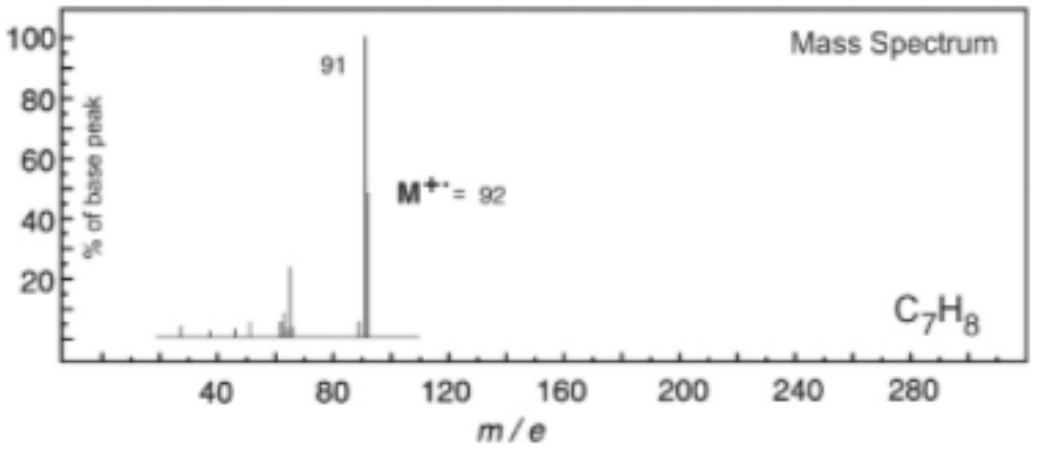
No significant UV absorption above 220 nm





Problem 171

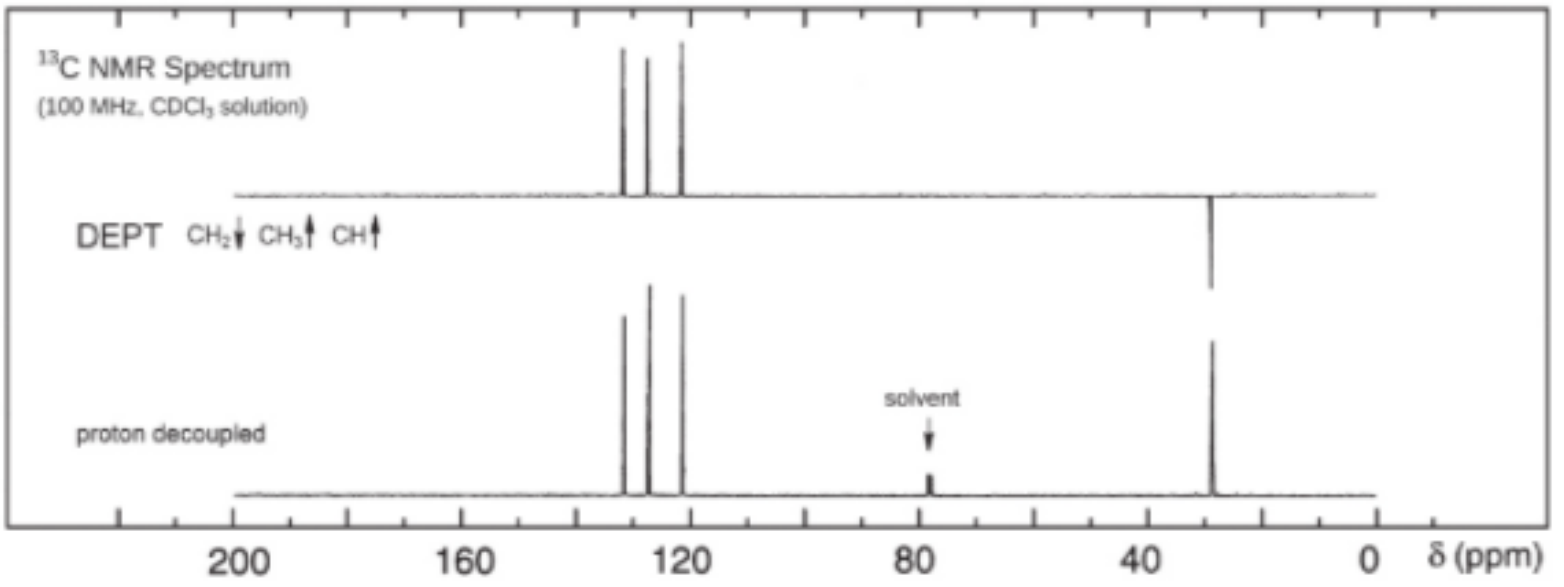


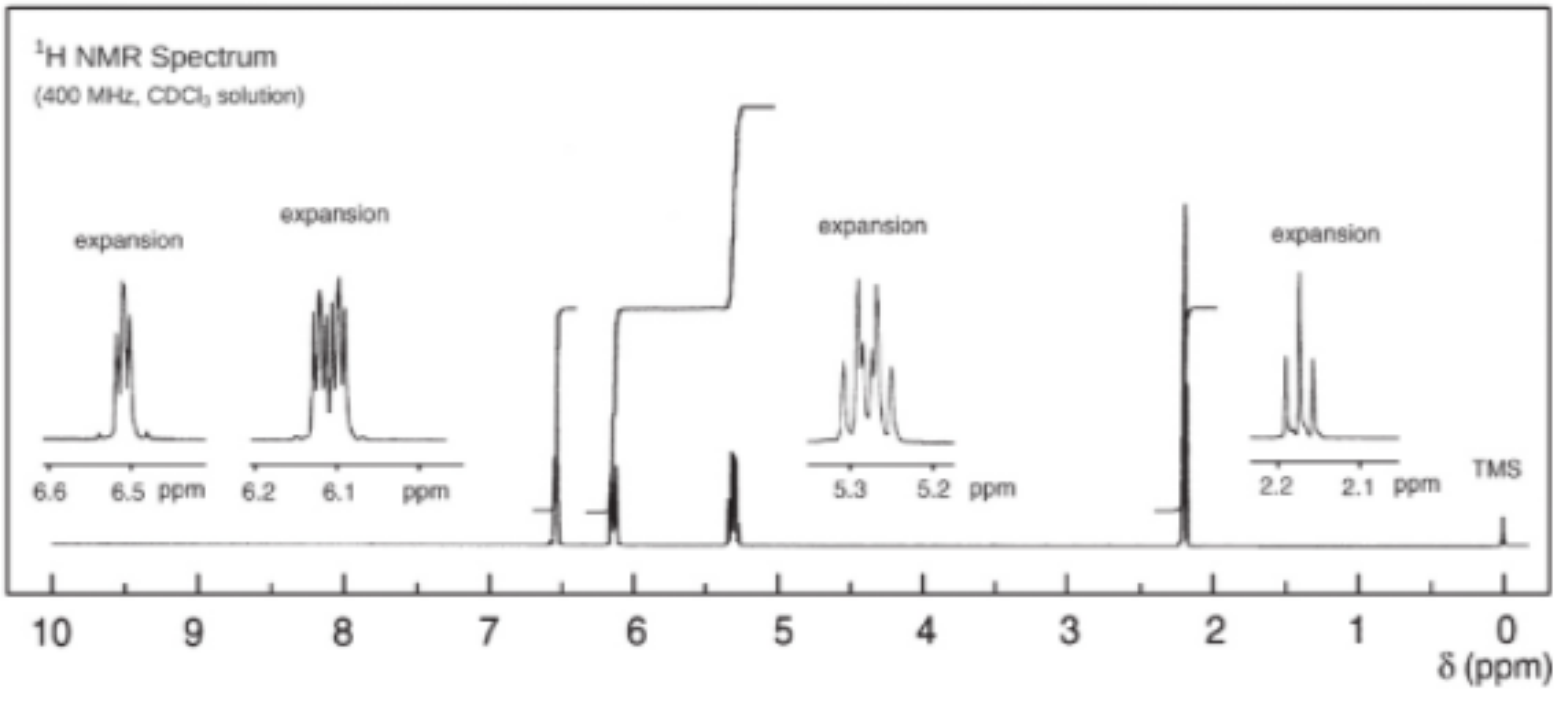


UV Spectrum

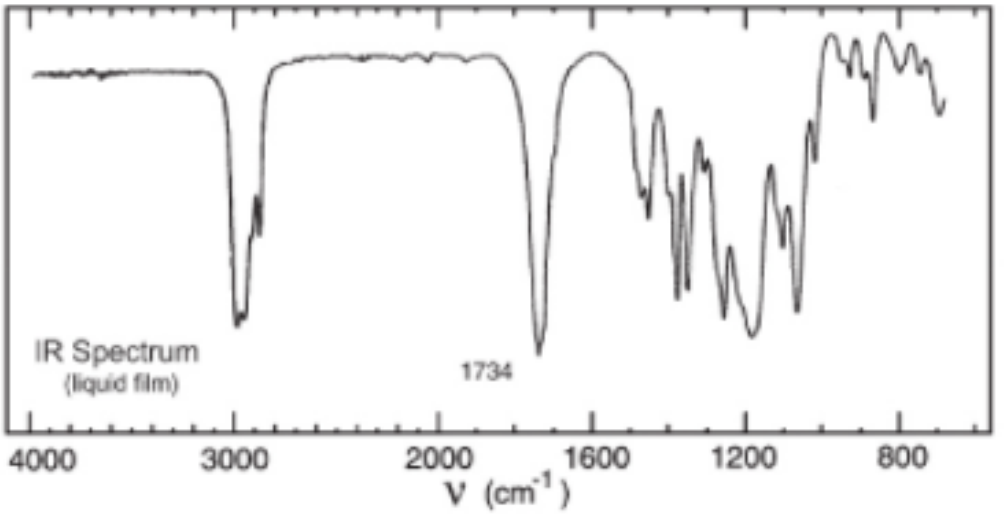
λ_{max} 261 nm ($\log_{10}\varepsilon$ 3.5)

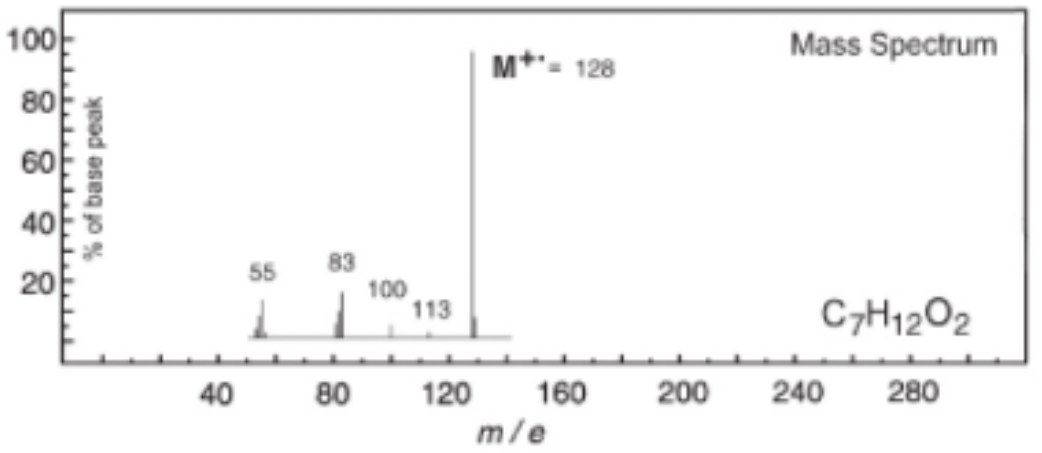
solvent : ethanol



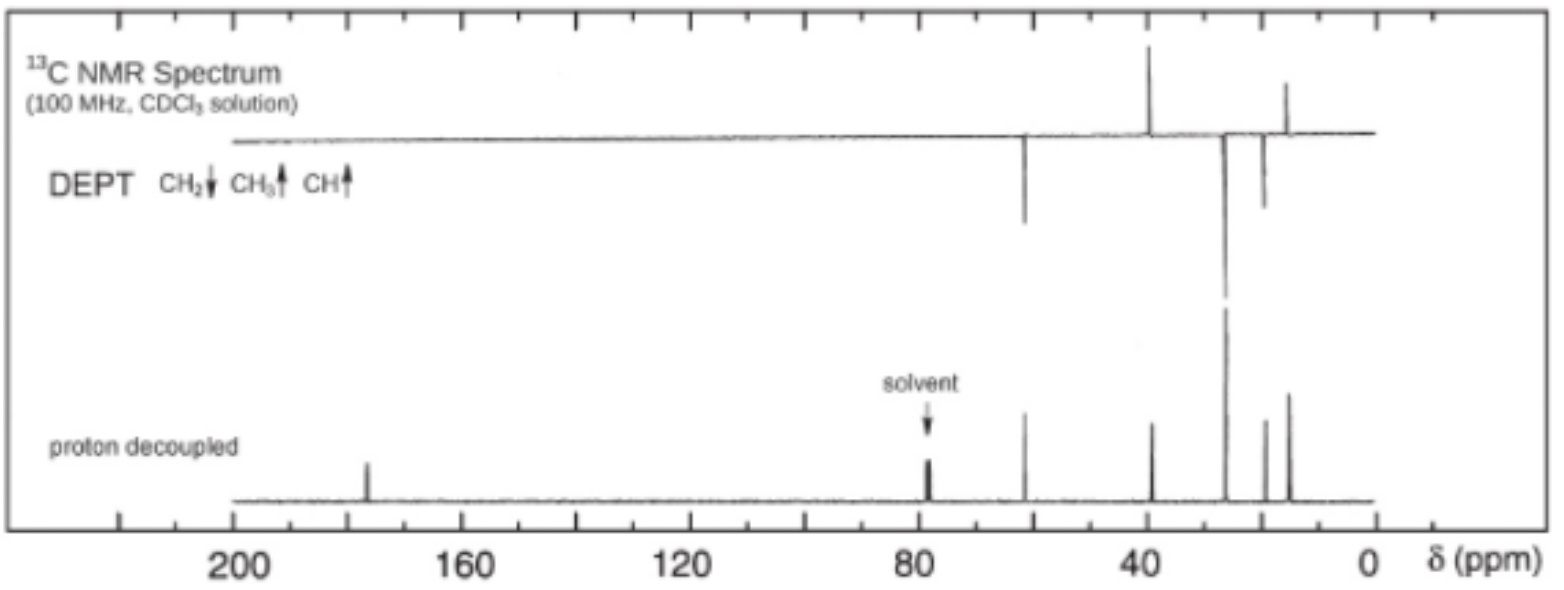


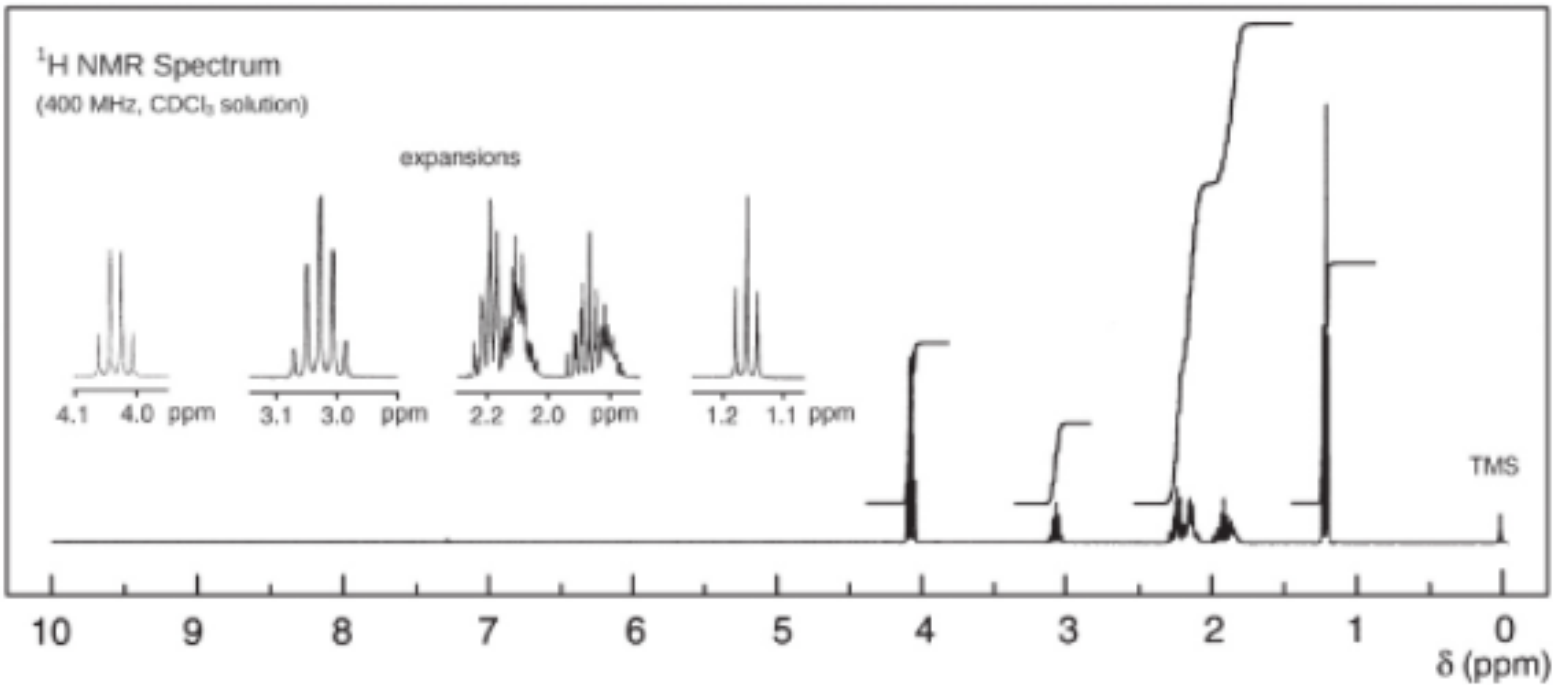
Problem 172



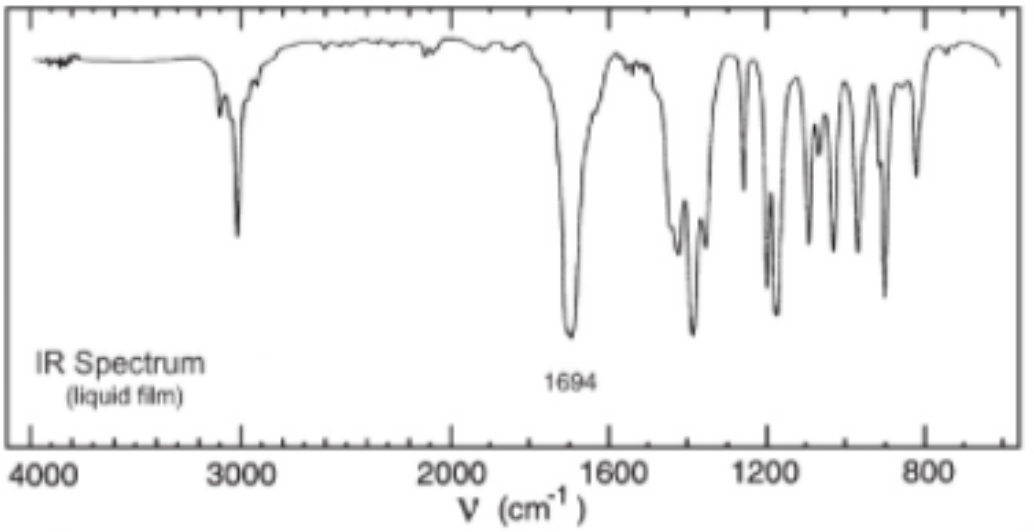


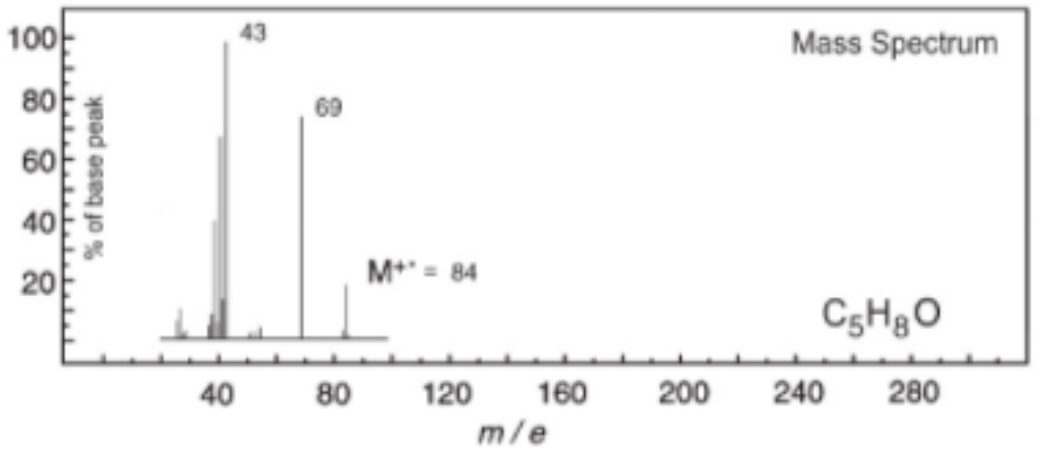
No significant UV absorption above 220 nm



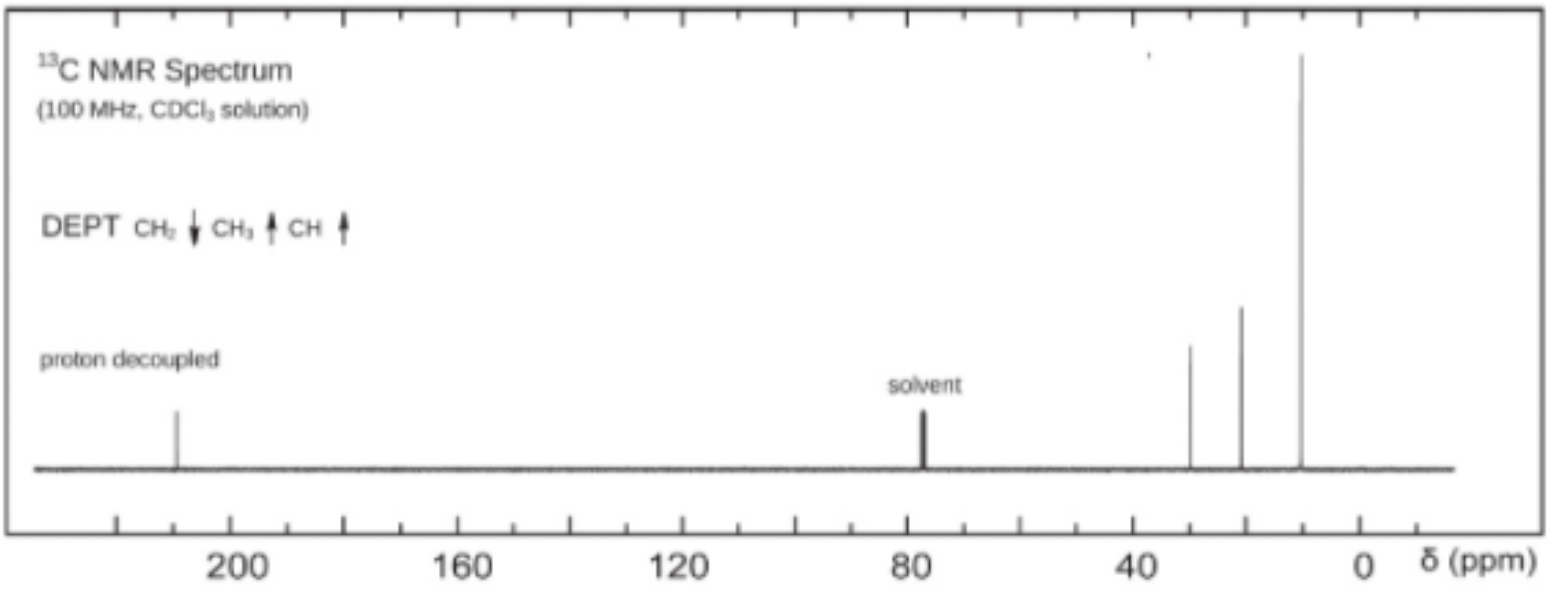


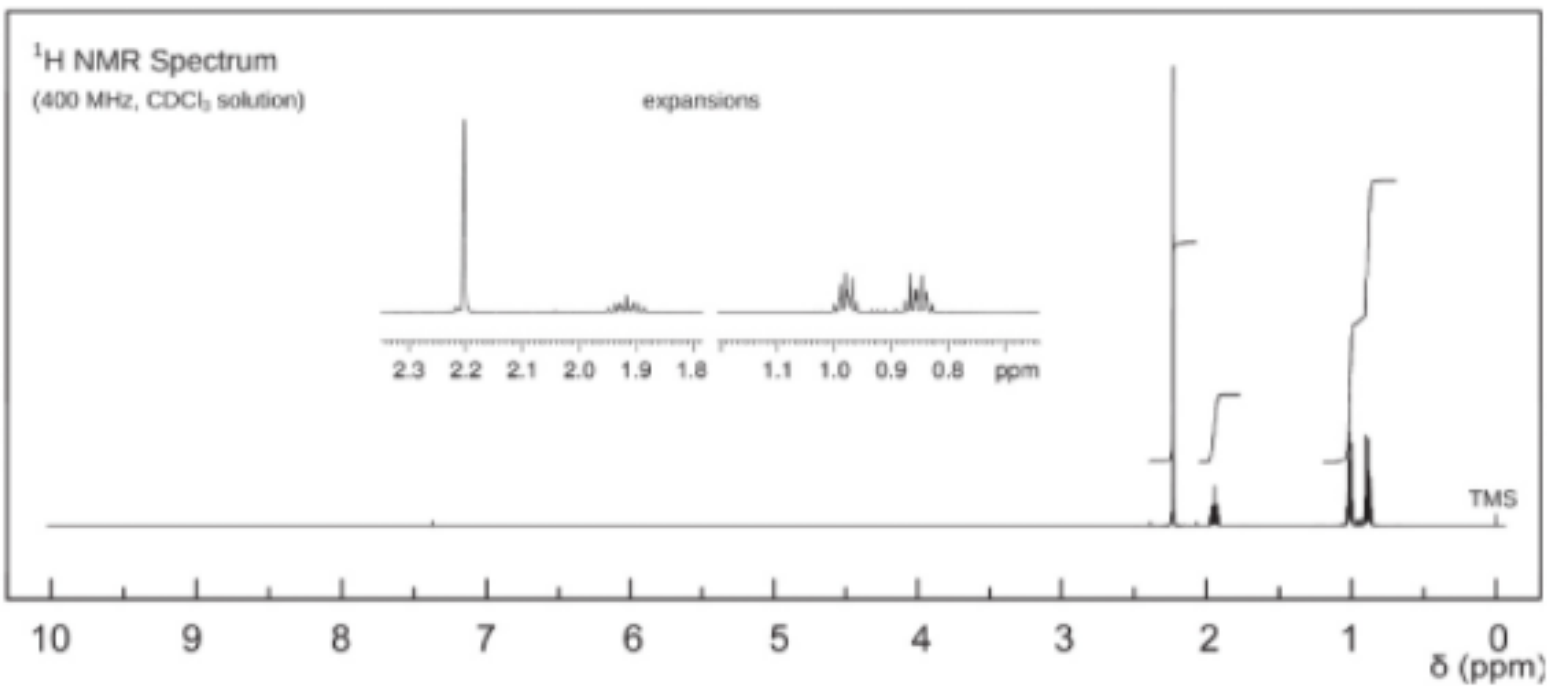
Problem 173

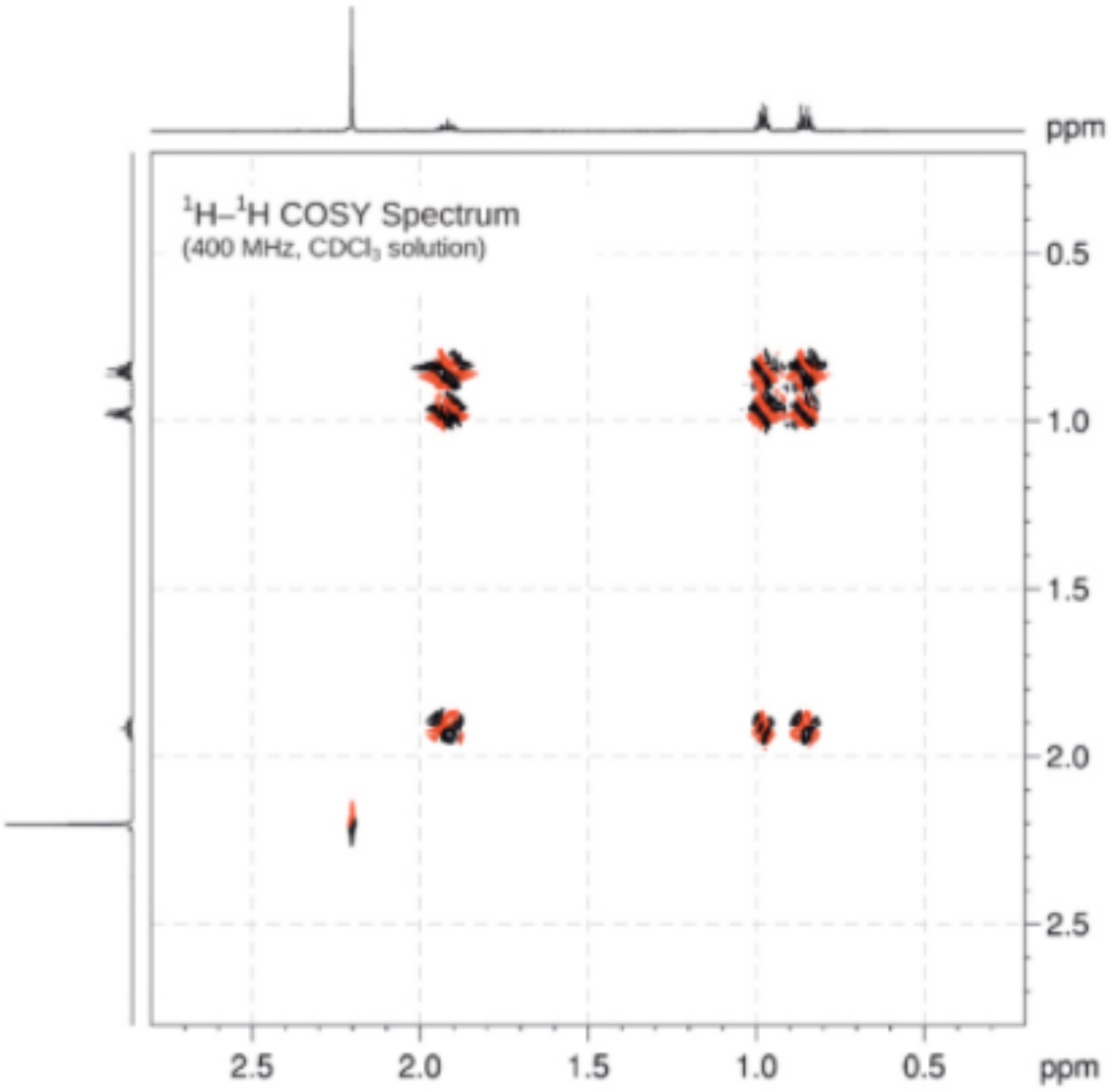


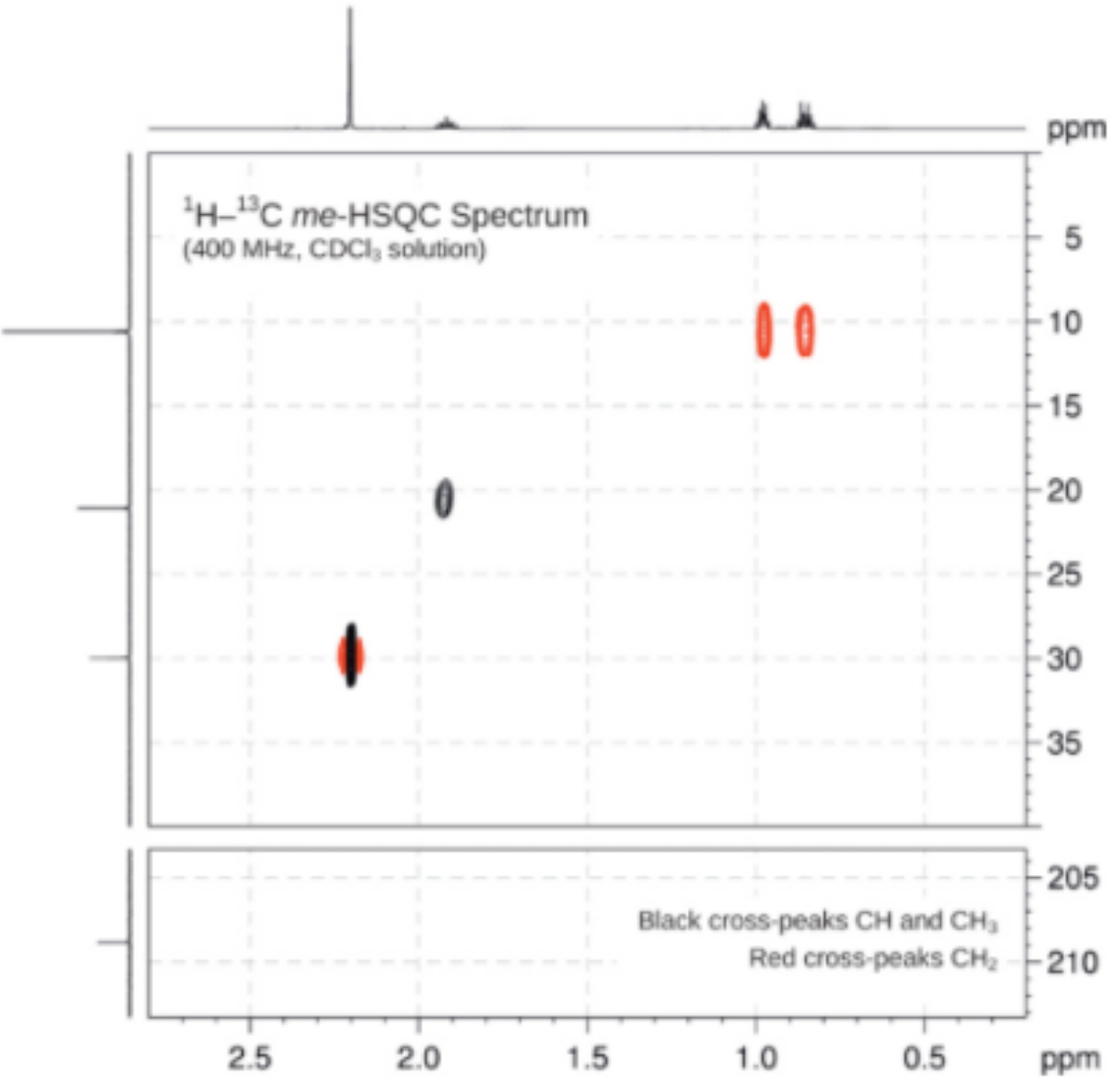


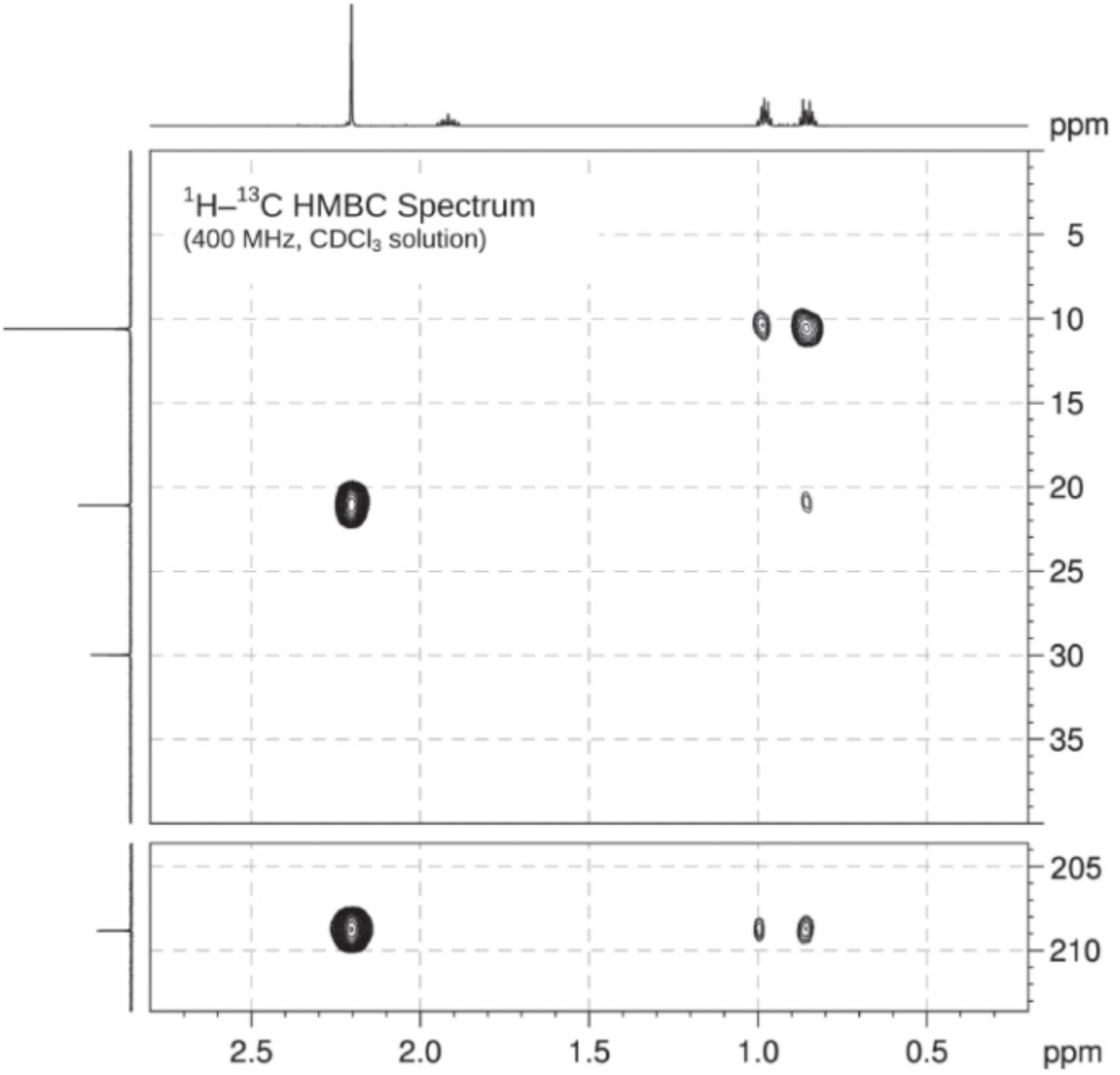
No significant UV absorption above 220 nm



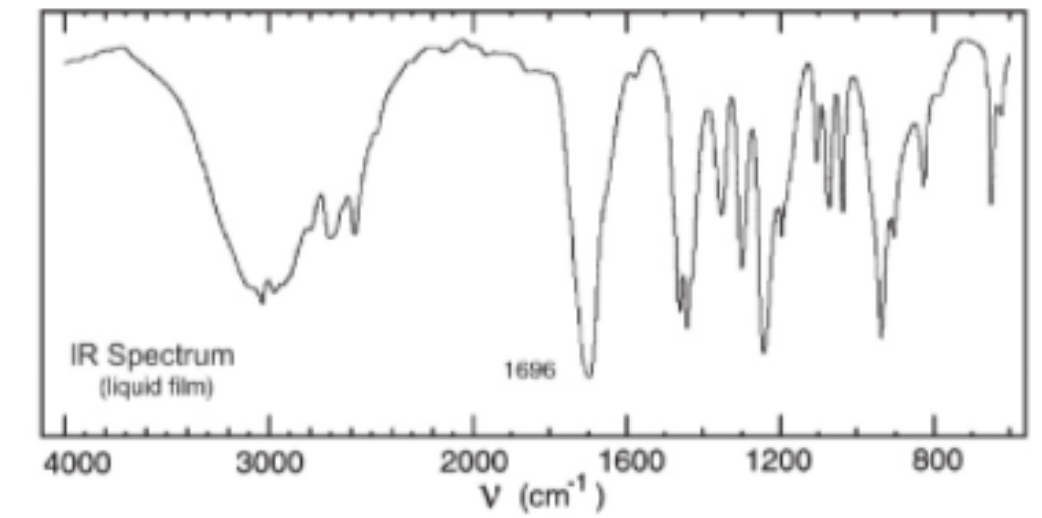


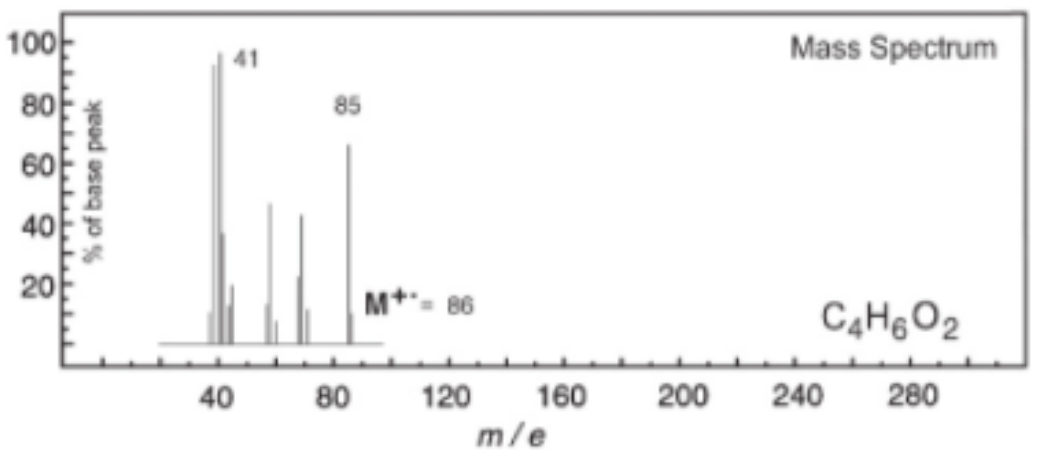

^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
ppm
0.5
1.0
1.5
2.0
2.5
2.5
2.0
1.5
1.0
0.5
ppm


^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
ppm
5
10
15
20
25
30
35
205
210
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
2.5
2.0
1.5
1.0
0.5
ppm

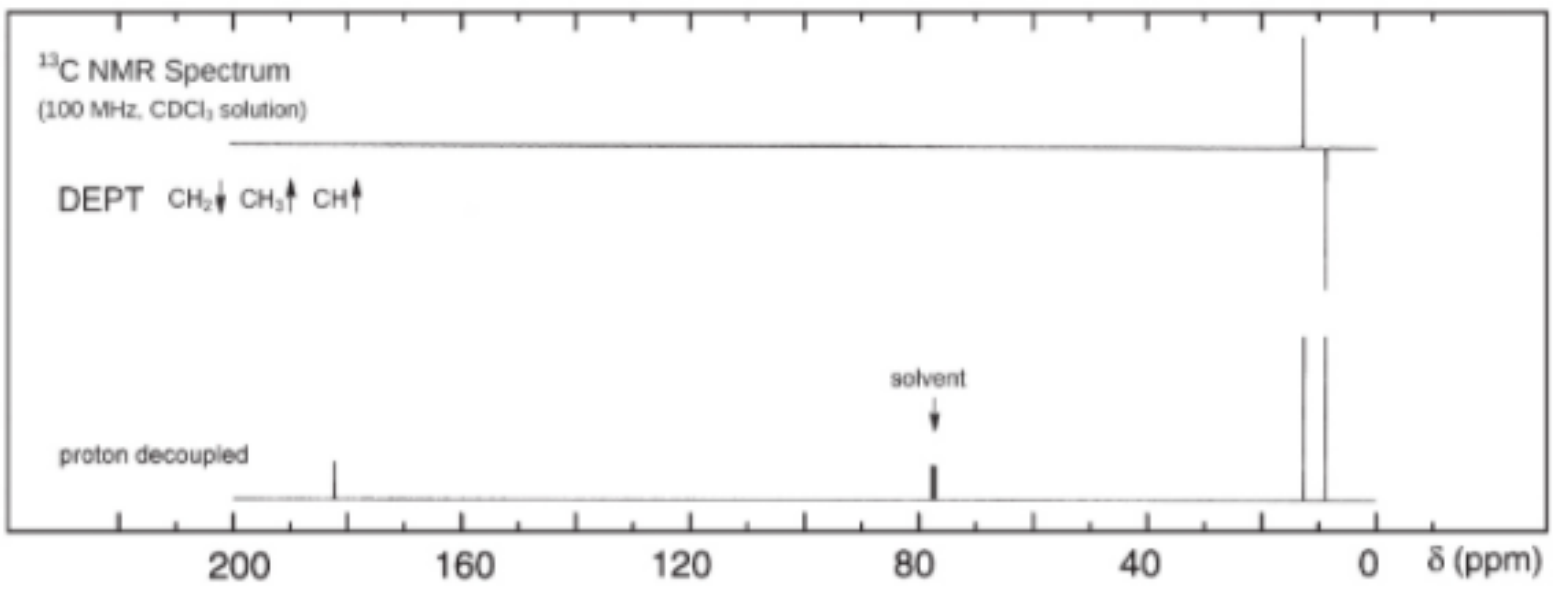

ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
5
10
15
20
25
30
35
205
210
2.5
2.0
1.5
1.0
0.5
ppm

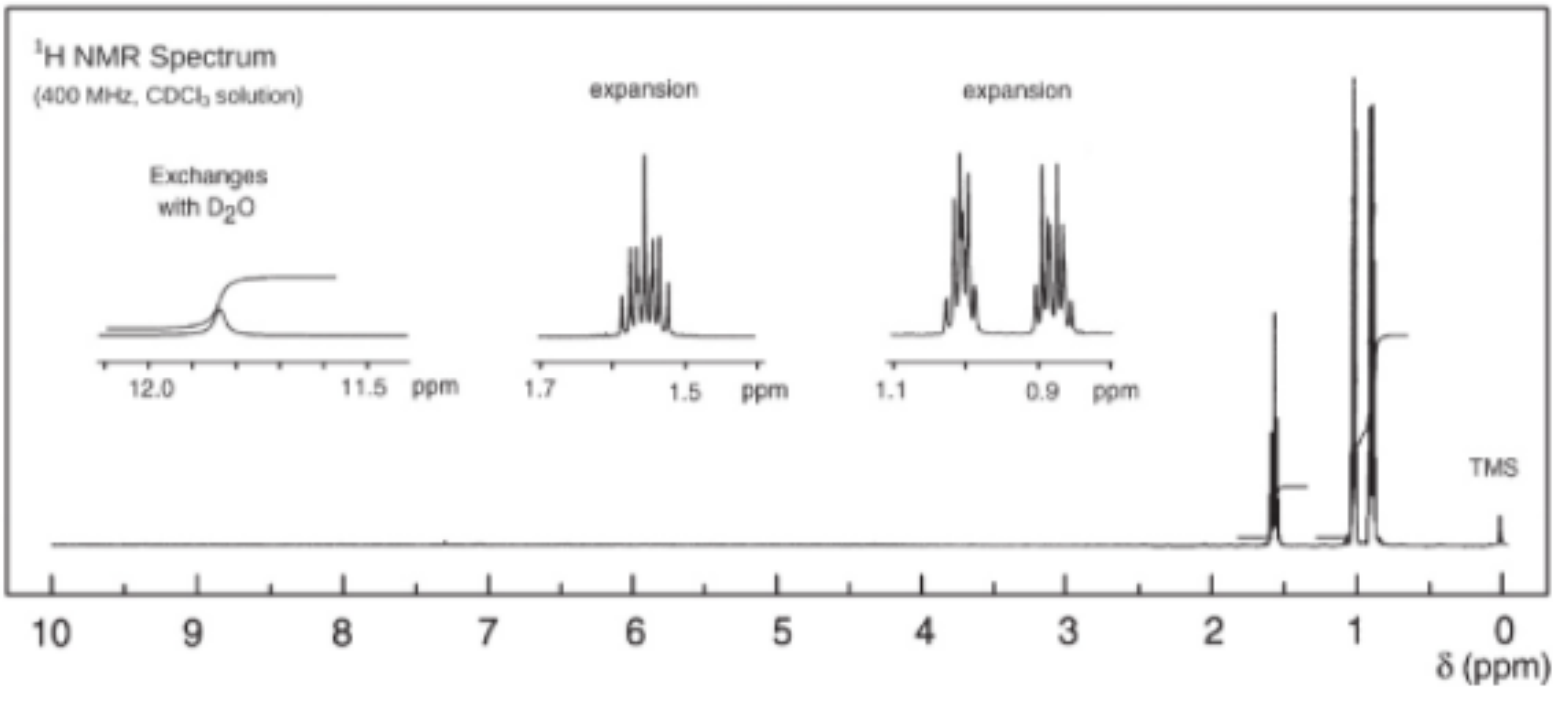
Problem 174



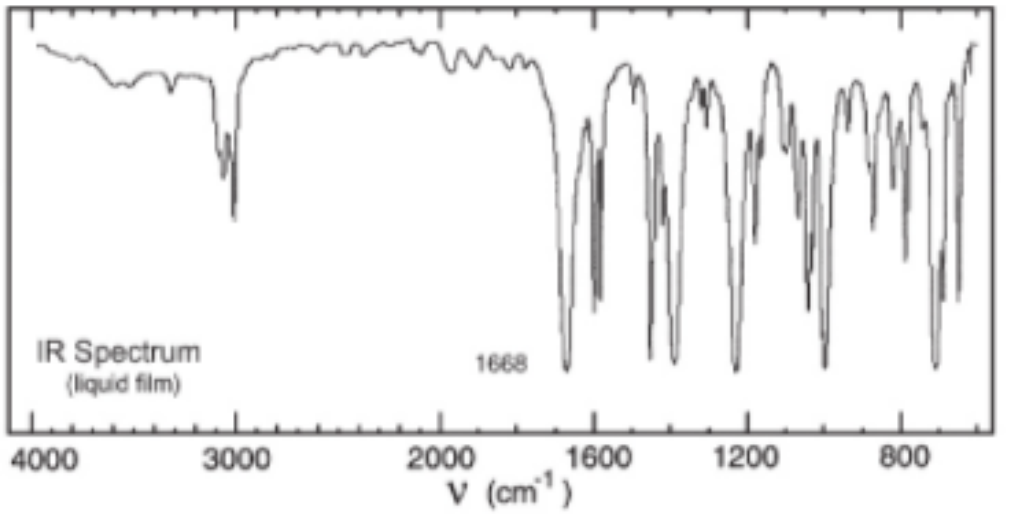


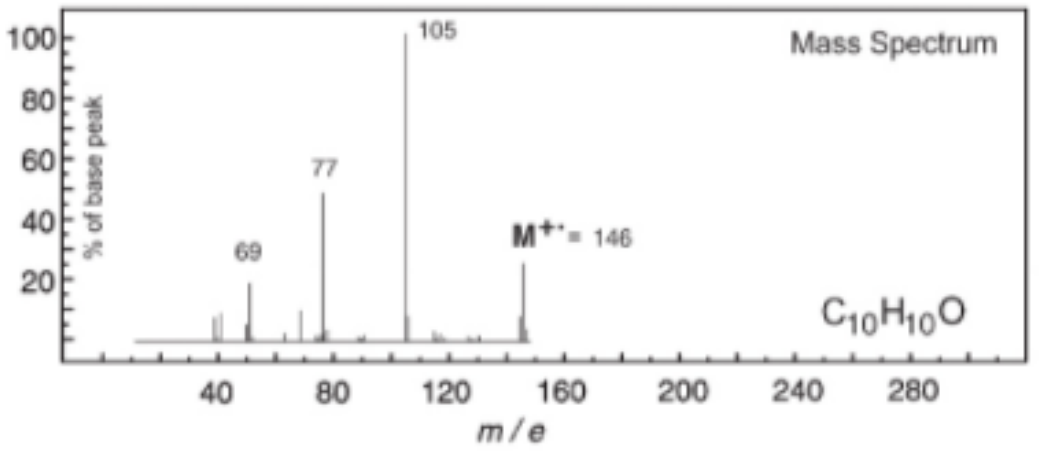
No significant UV absorption above 220 nm



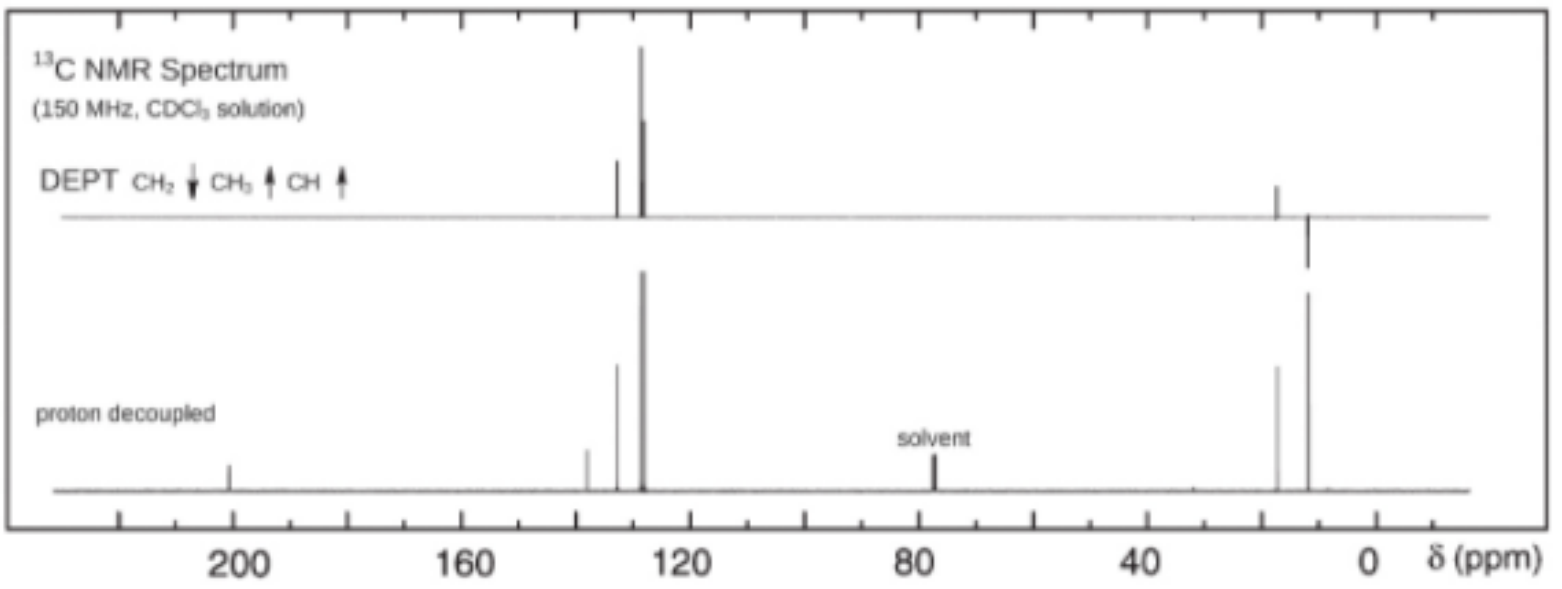


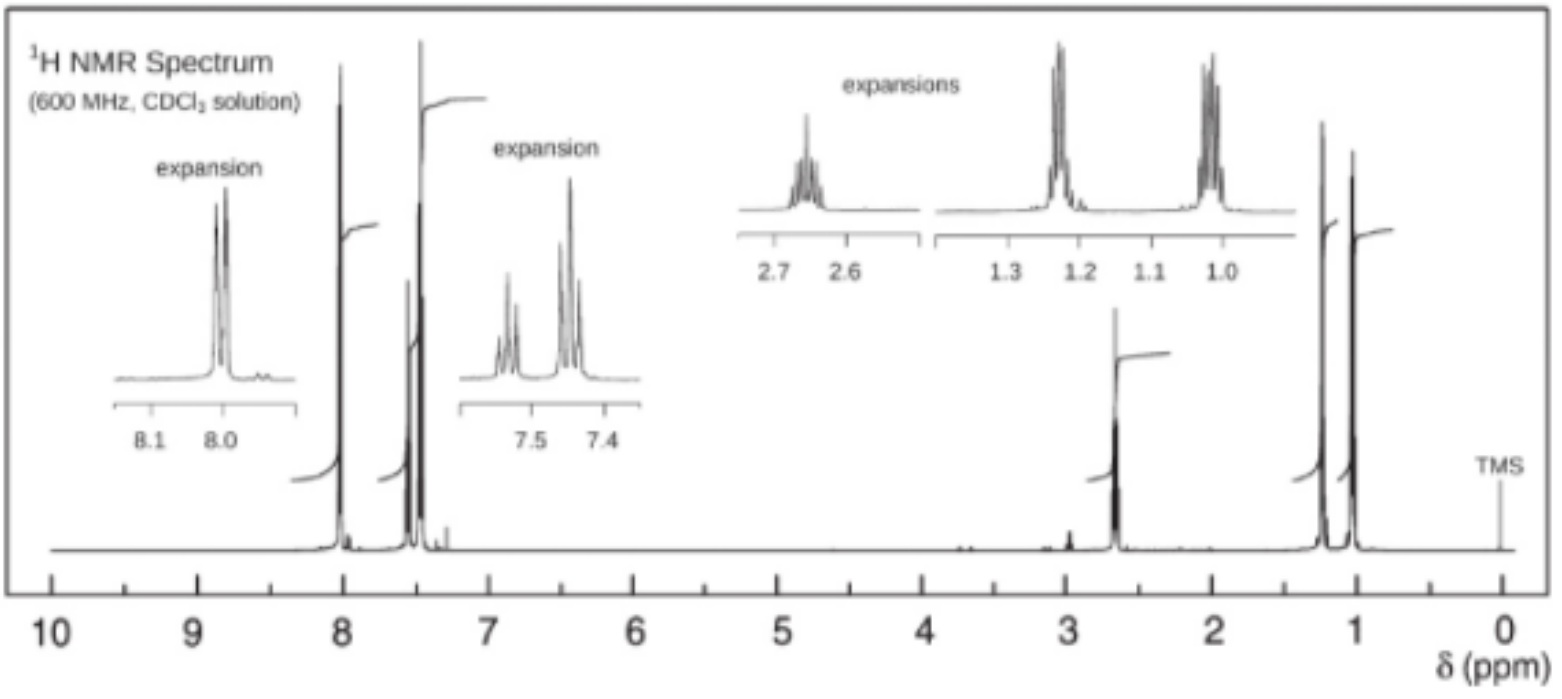
Problem 175

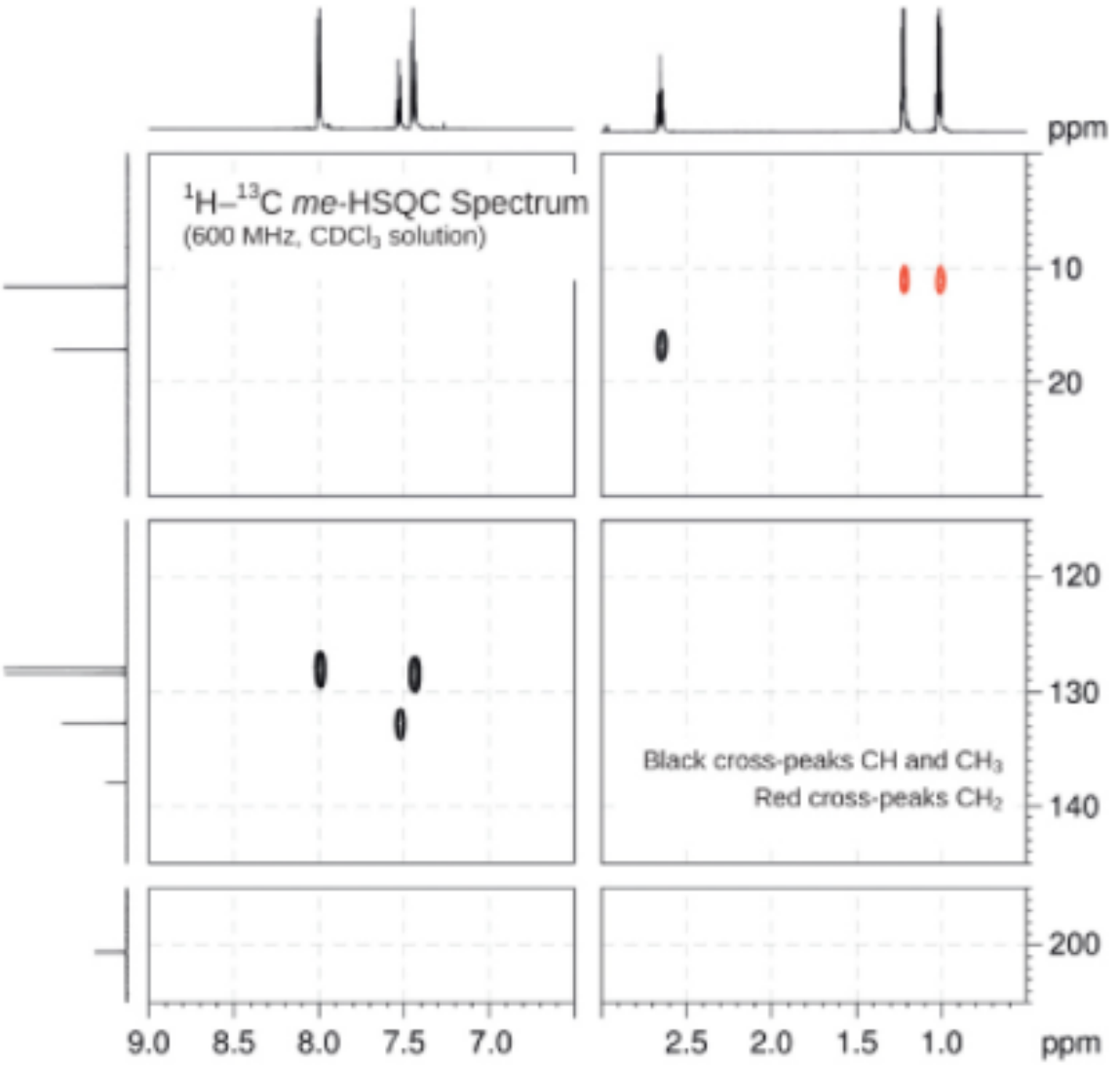


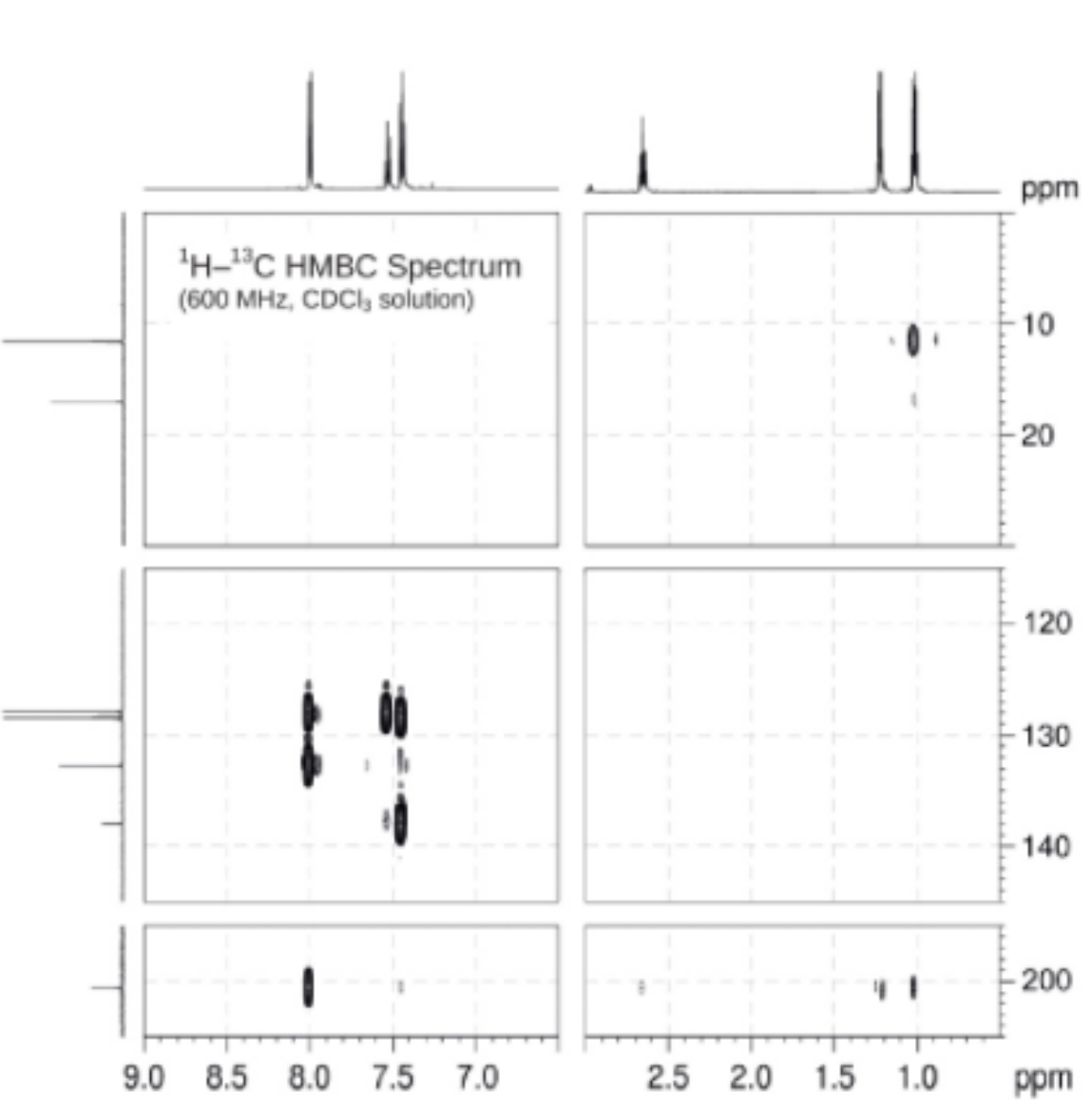


No significant UV absorption above 220 nm

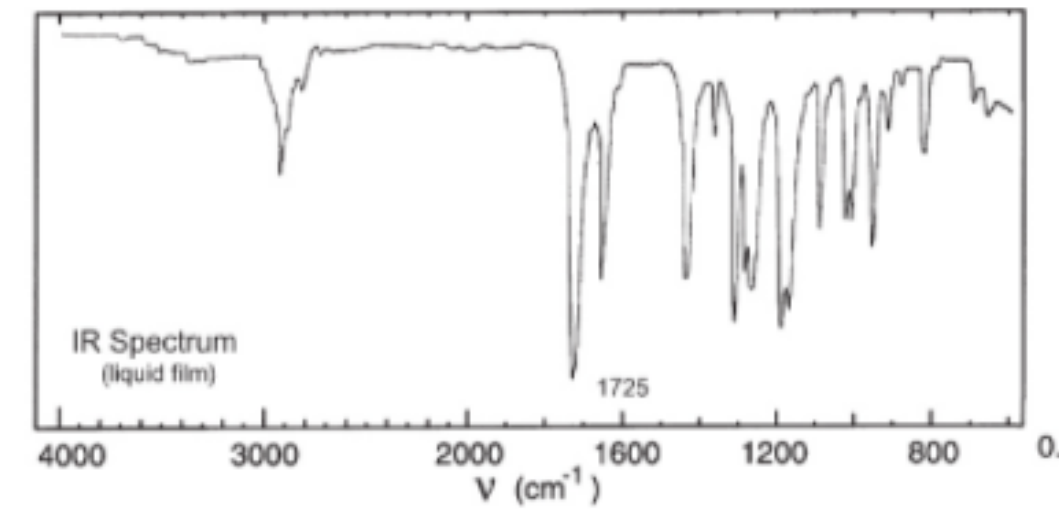


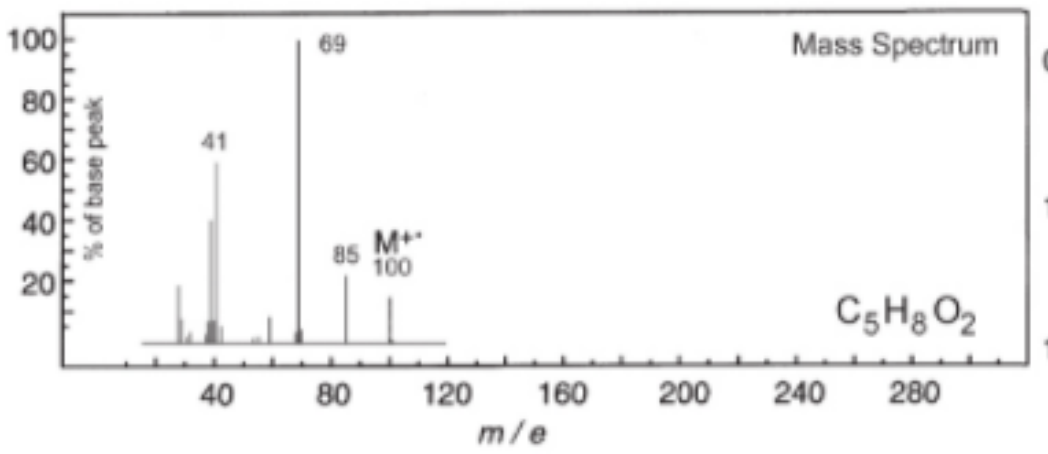


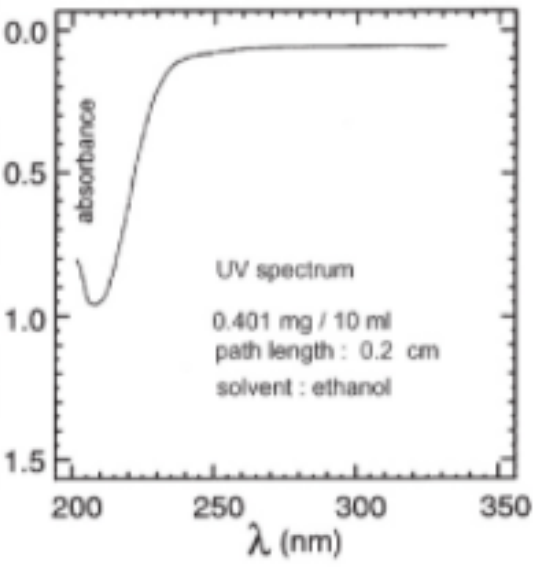

^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
ppm
10
20
120
130
140
200
9.0
8.5
8.0
7.5
7.0
2.5
2.0
1.5
1.0
ppm

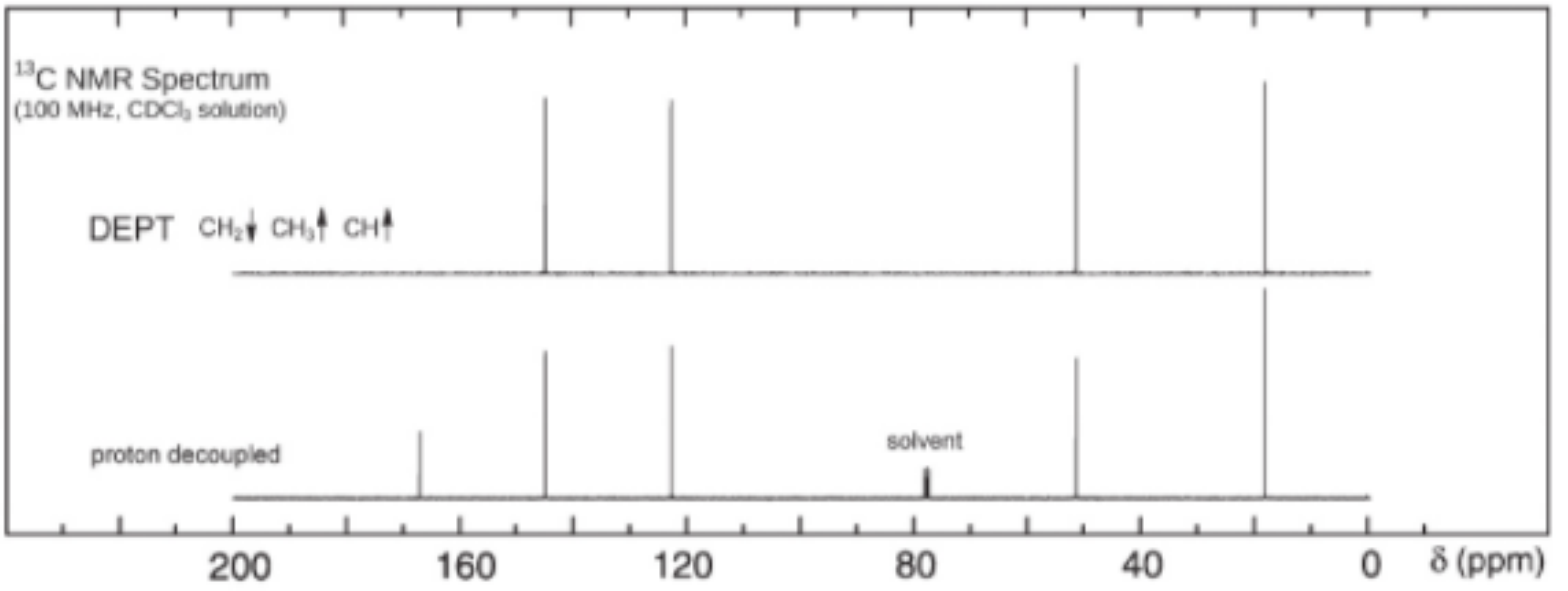

^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)
ppm
10
20
120
130
140
200
9.0
8.5
8.0
7.5
7.0
2.5
2.0
1.5
1.0
ppm

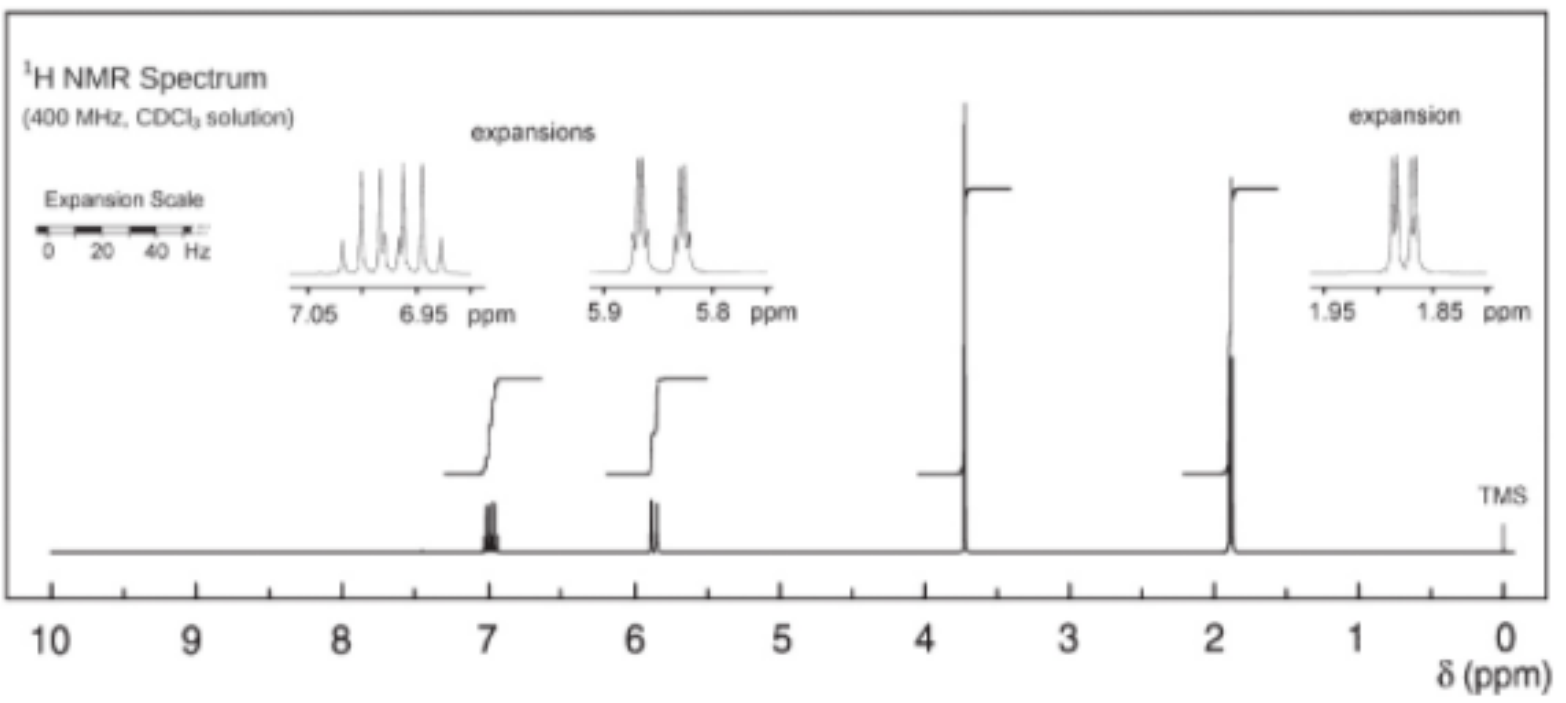
Problem 176

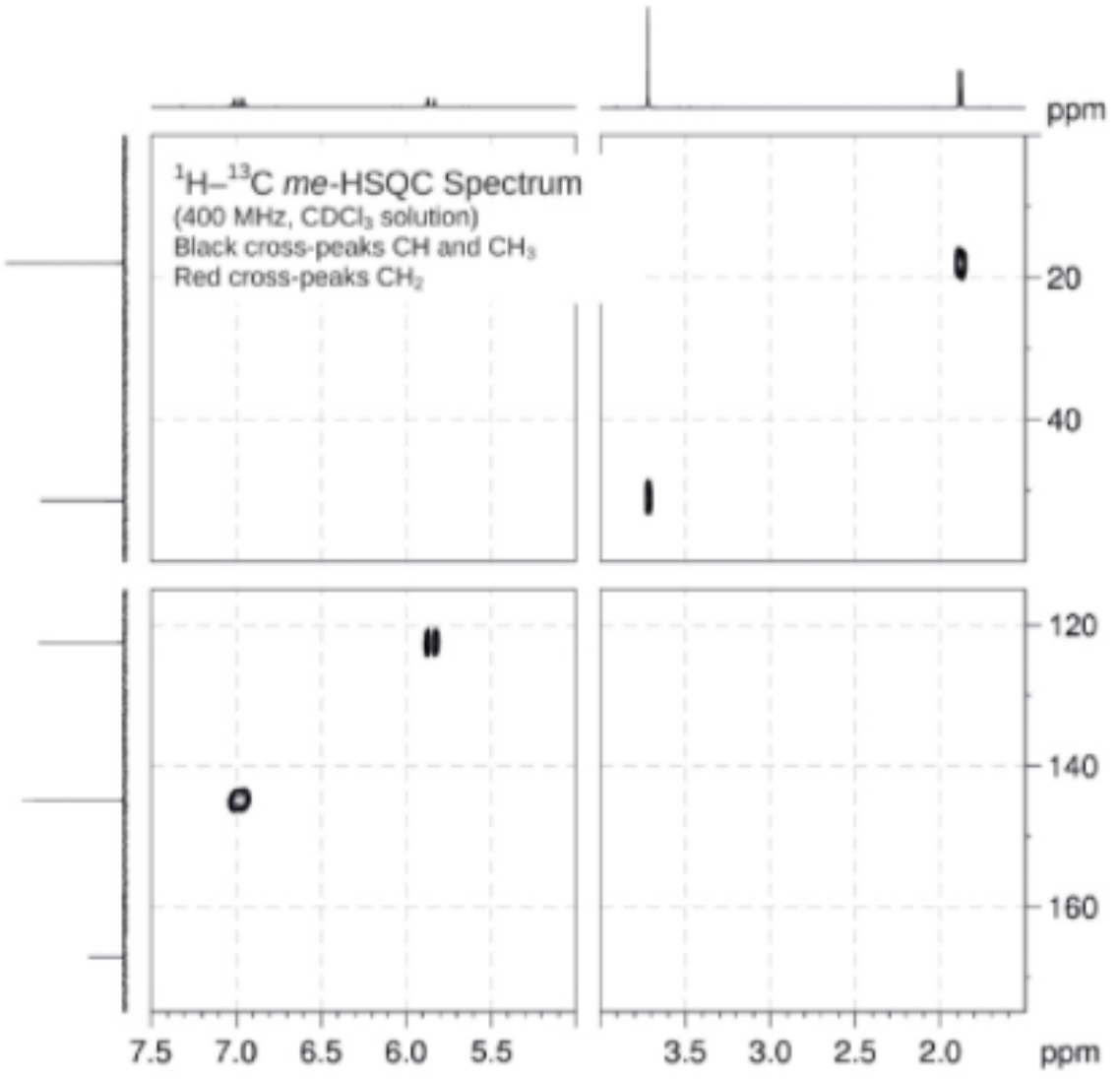

IR Spectrum
(liquid film)
1725
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
100
80
60
40
20
69
41
85
M+·
100
C5H8O2
40
80
120
160
200
240
280
m/e


absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.401 mg / 10 ml
path length : 0.2 cm
solvent : ethanol
200
250
300
350
λ (nm)

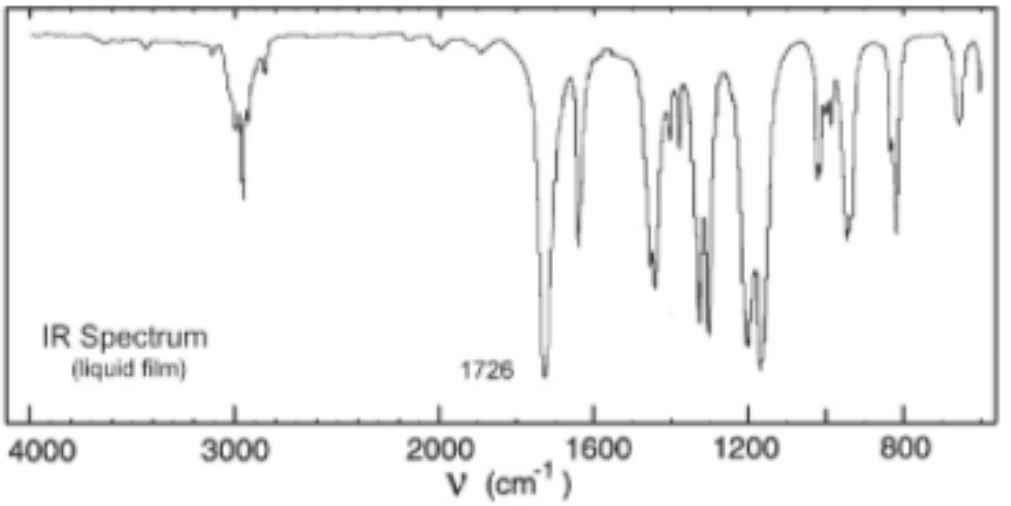

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

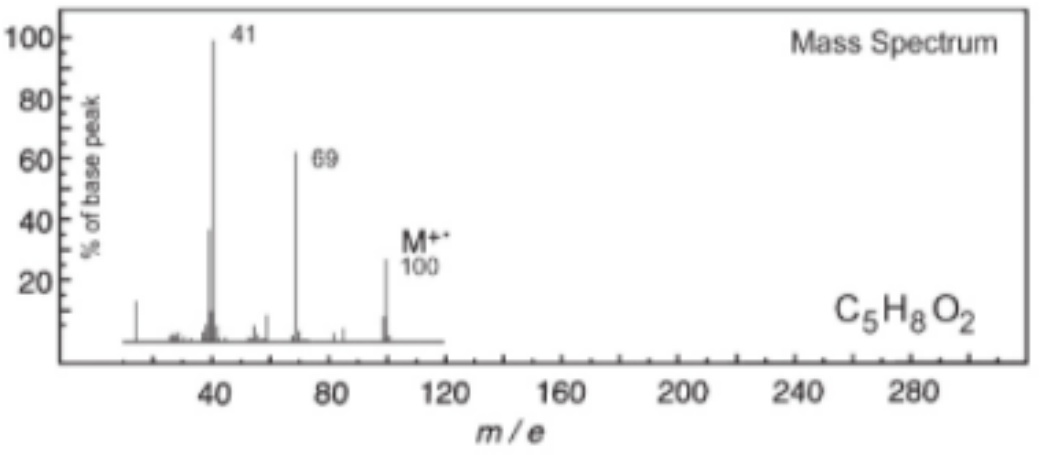

1H NMR Spectrum
(400 MHz, CDCl3 solution)
Expansion Scale
0 20 40 Hz
expansions
7.05
6.95 ppm
5.9
5.8 ppm
expansion
1.95
1.85 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
20
40
120
140
160
7.5
7.0
6.5
6.0
5.5
3.5
3.0
2.5
2.0
ppm

ppm
^{1}H–^{1}H NOESY Spectrum
(400 MHz, $CDCl_3$ solution)
2.0
2.5
3.0
3.5
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
3.5
3.0
2.5
2.0
ppm

Problem 177



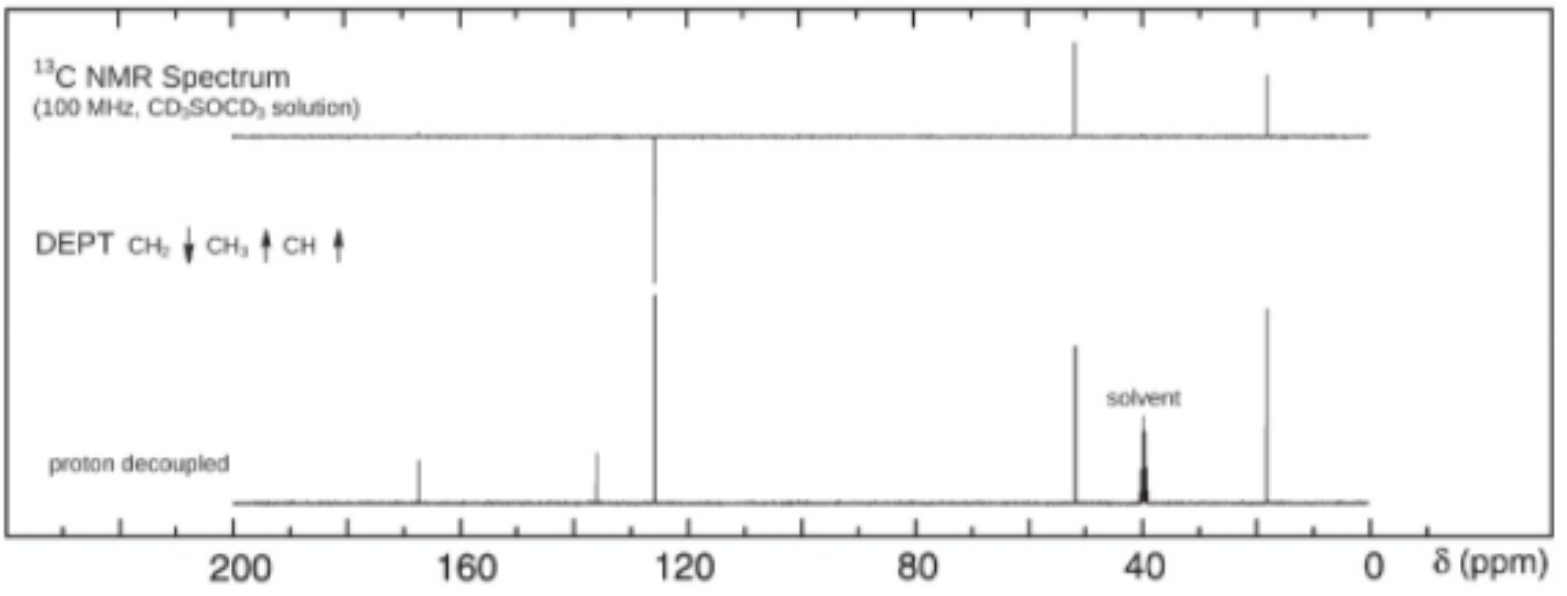


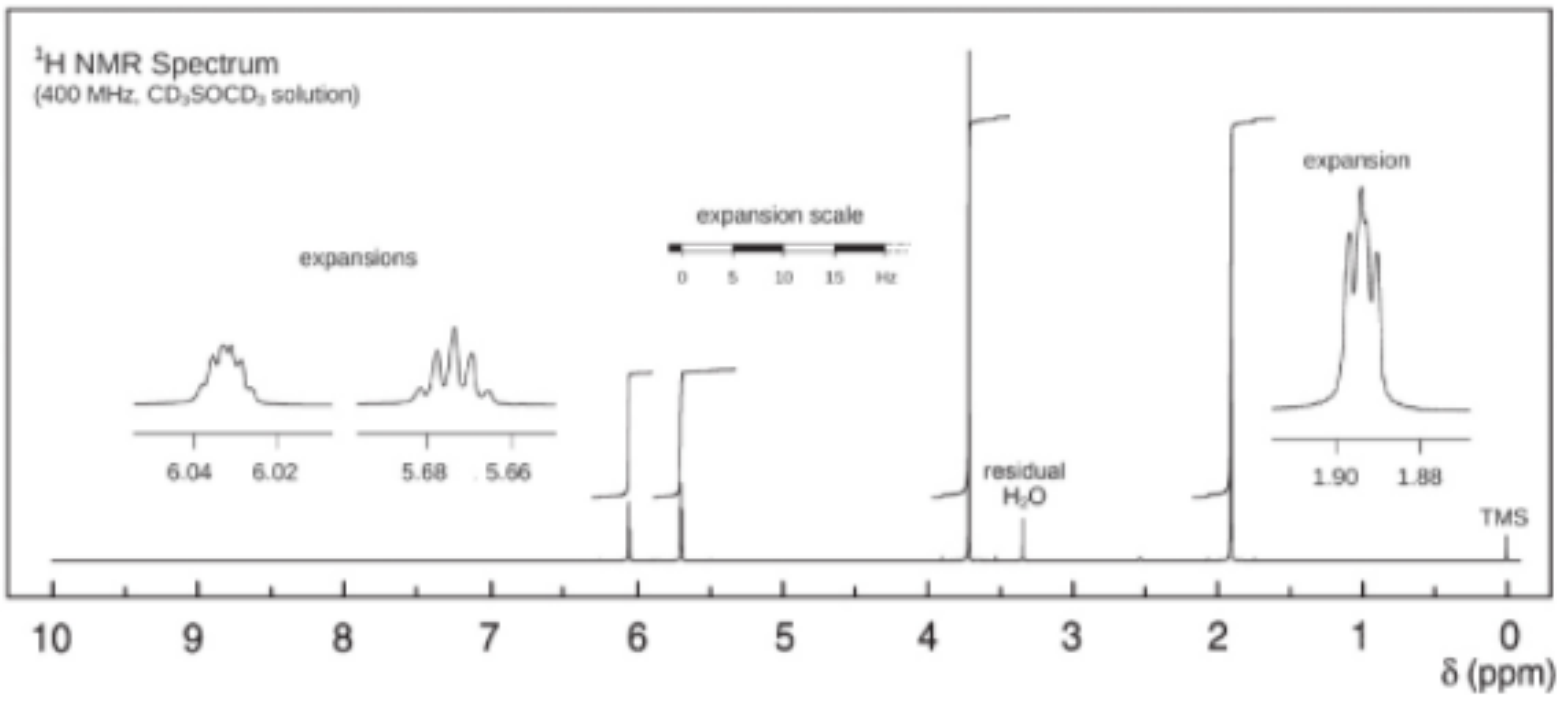
UV Spectrum

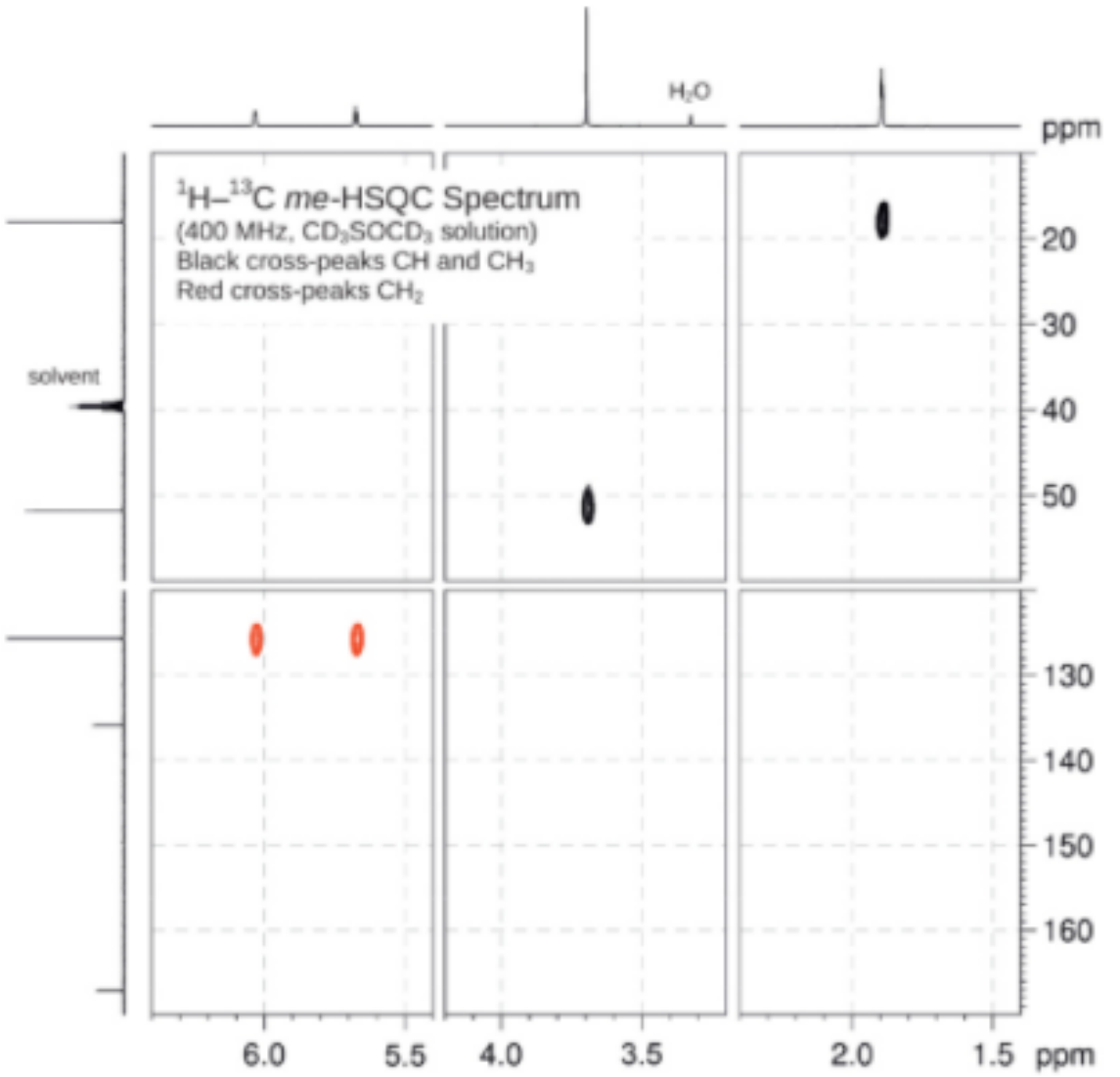
λ_{max} 198 nm ($\log_{10}\varepsilon$ 0.6)

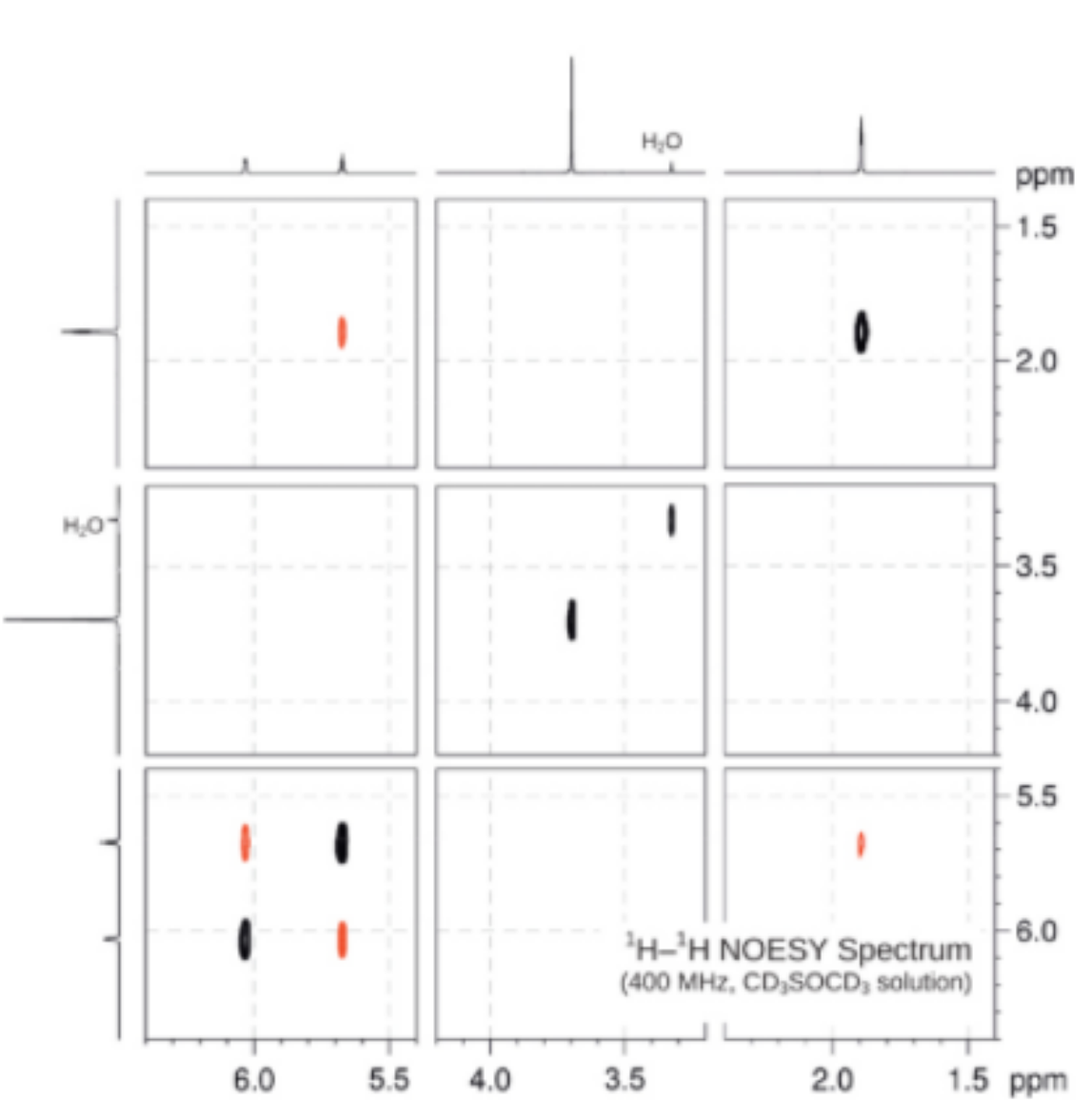
λ_{max} 233 nm ($\log_{10}\varepsilon$ 0.3)

λ_{max} 236 nm ($\log_{10}\varepsilon$ 0.3)

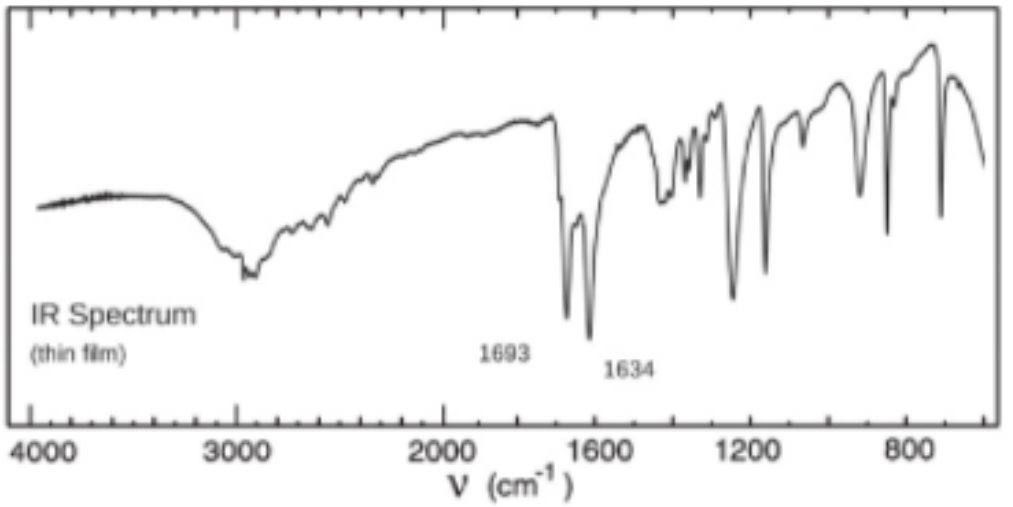


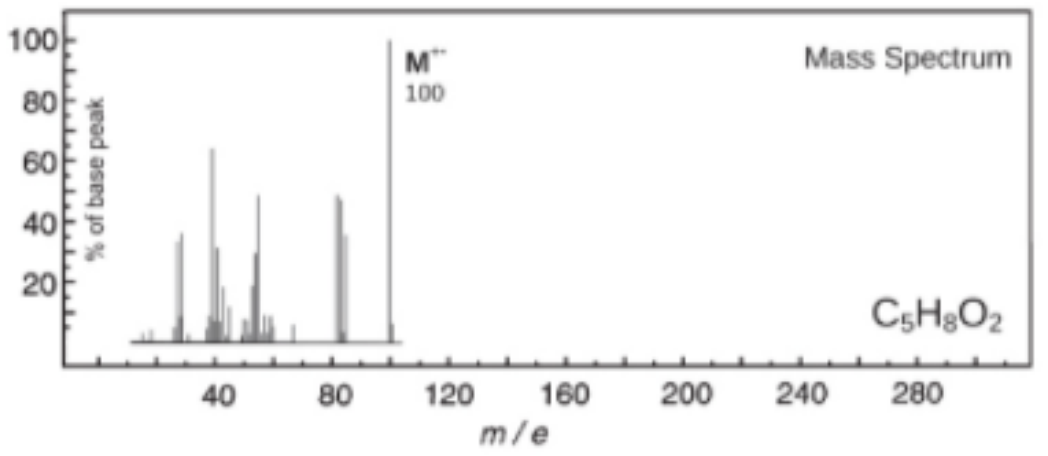


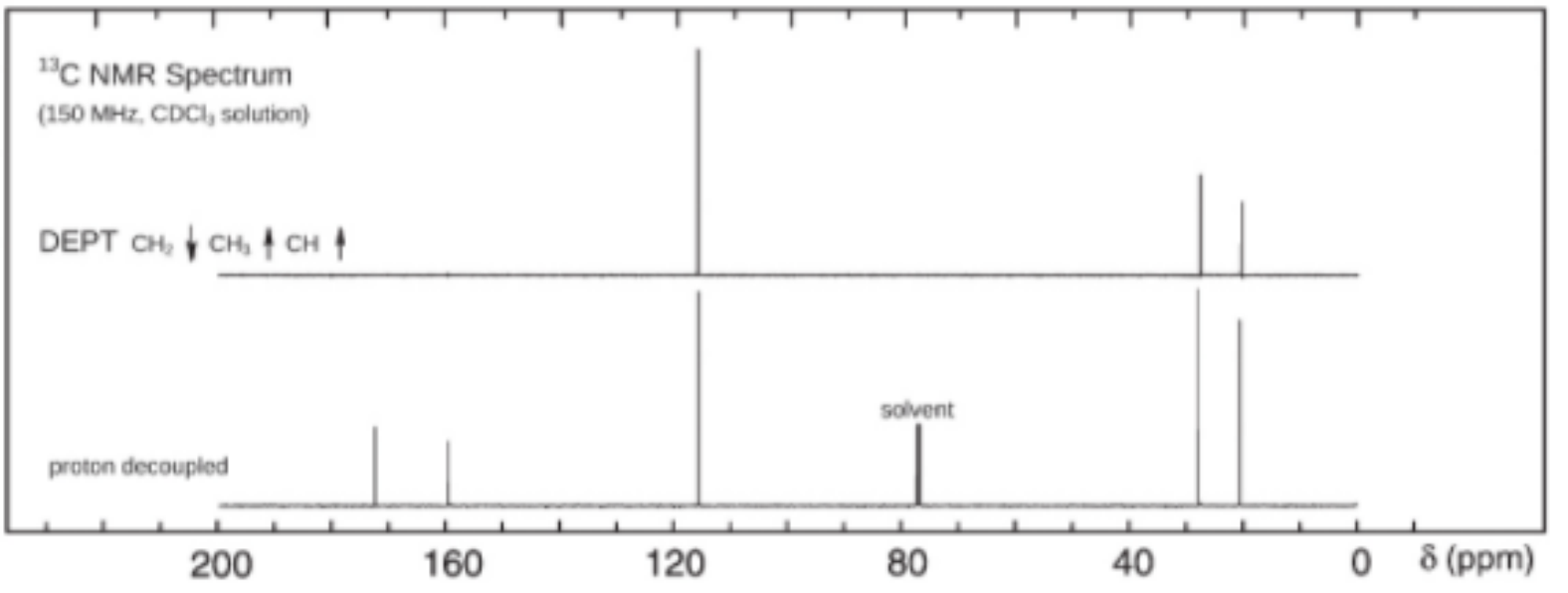

^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, CD_3SOCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
H_2O
solvent
ppm
20
30
40
50
130
140
150
160
6.0
5.5
4.0
3.5
2.0
1.5
ppm

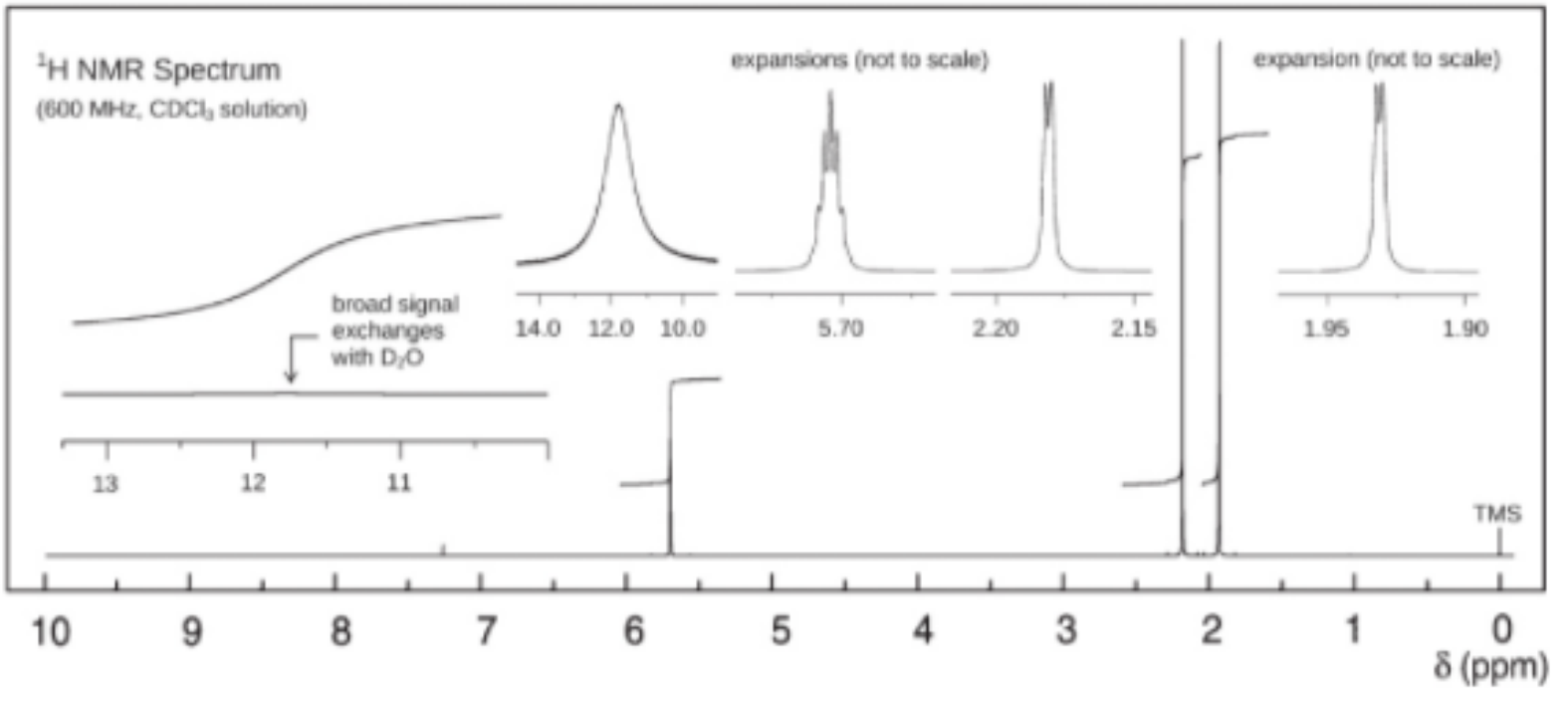

H_2O
ppm
1.5
2.0
H_2O
3.5
4.0
5.5
6.0
^{1}H–^{3}H NOESY Spectrum
(400 MHz, CD_3SOCD_3 solution)
6.0
5.5
4.0
3.5
2.0
1.5
ppm

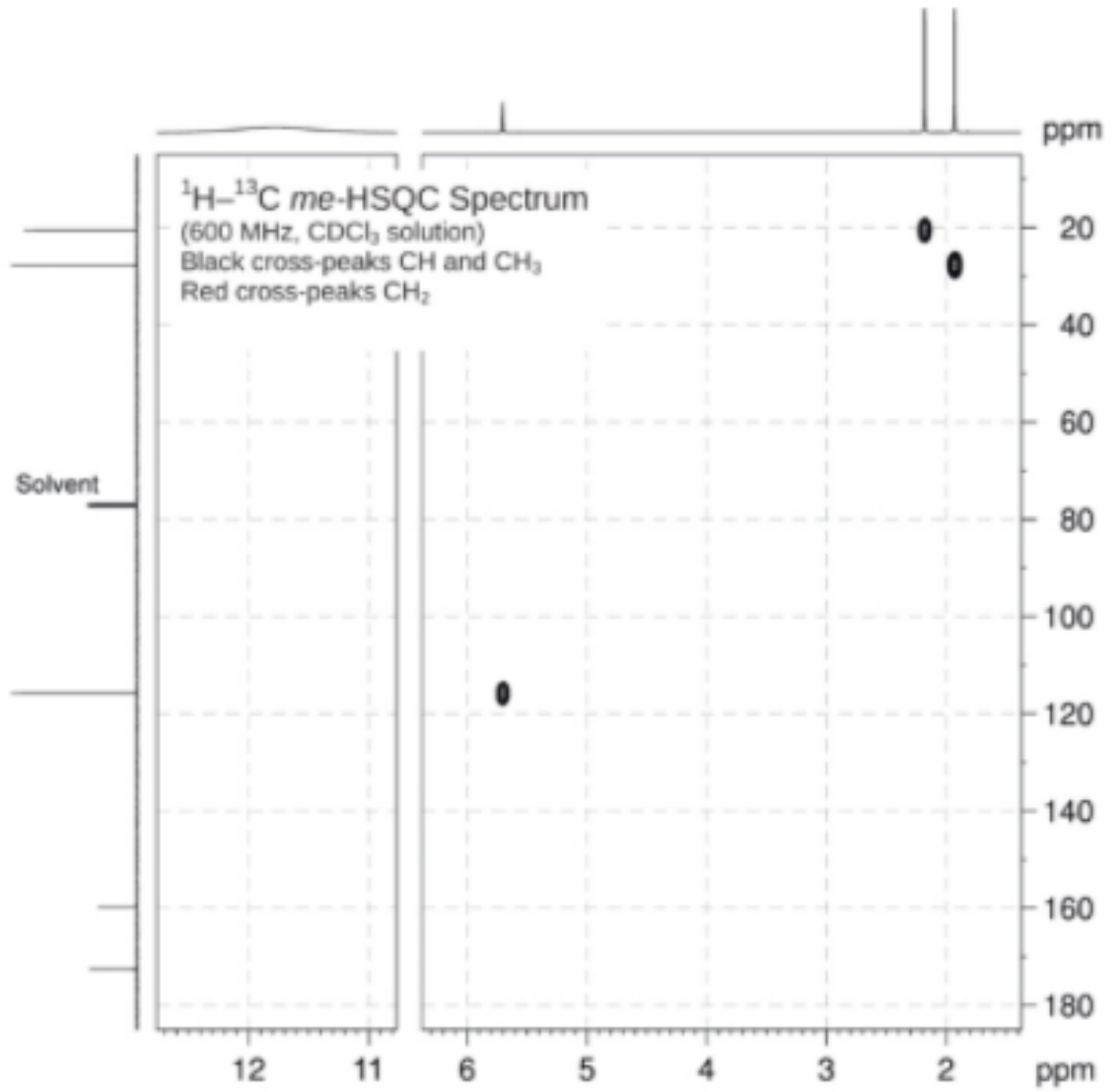
Problem 178


IR Spectrum
(thin film)
1693
1634
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
M+·
100
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m/e
C5H8O2

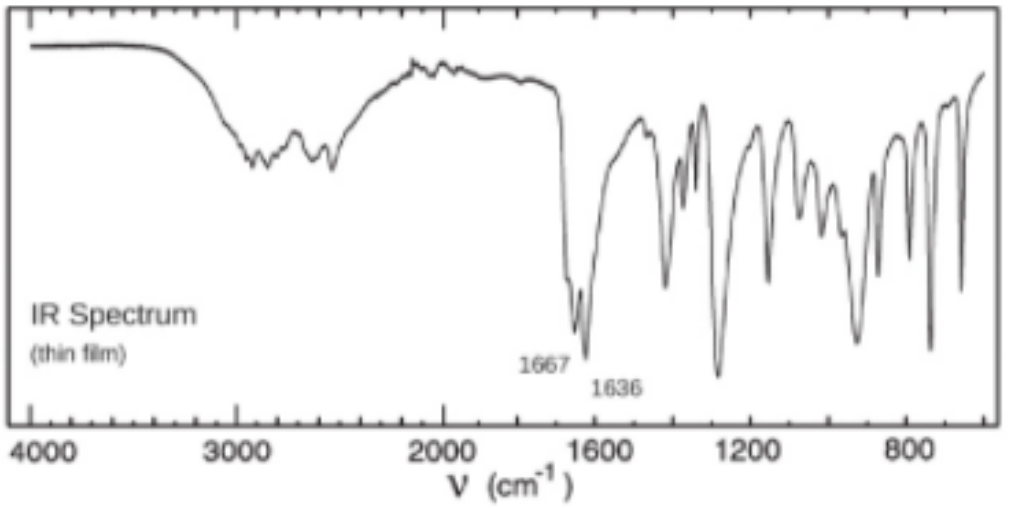

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

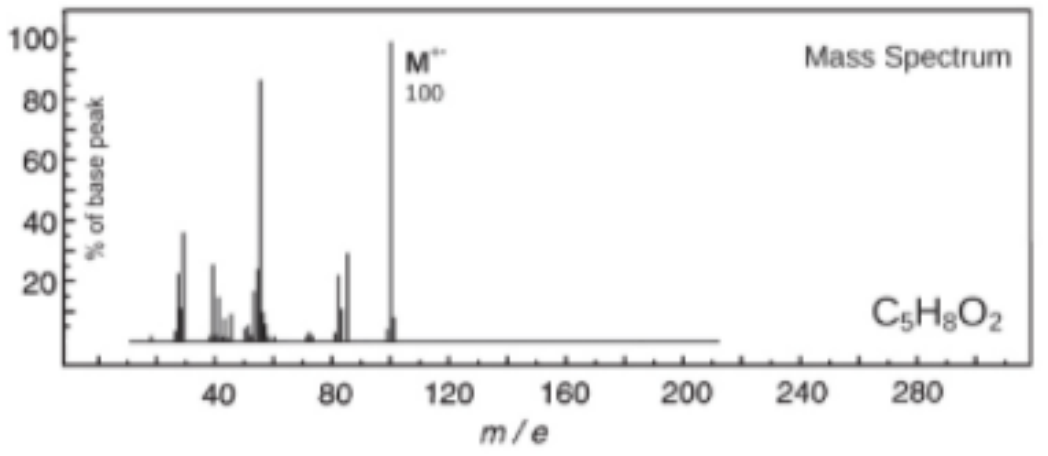

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansions (not to scale)
expansion (not to scale)
broad signal
exchanges
with D2O
14.0
12.0
10.0
5.70
2.20
2.15
1.95
1.90
13
12
11
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

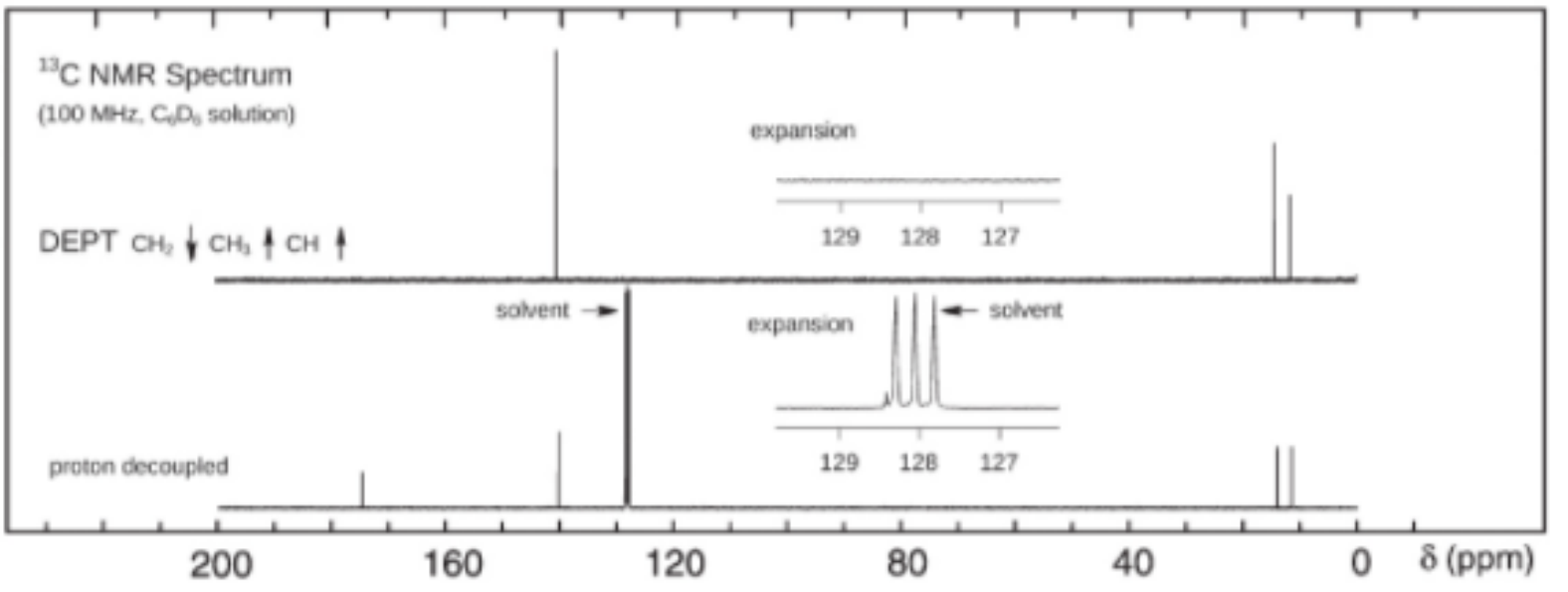

^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
Solvent
ppm
20
40
60
80
100
120
140
160
180
12
11
6
5
4
3
2
ppm

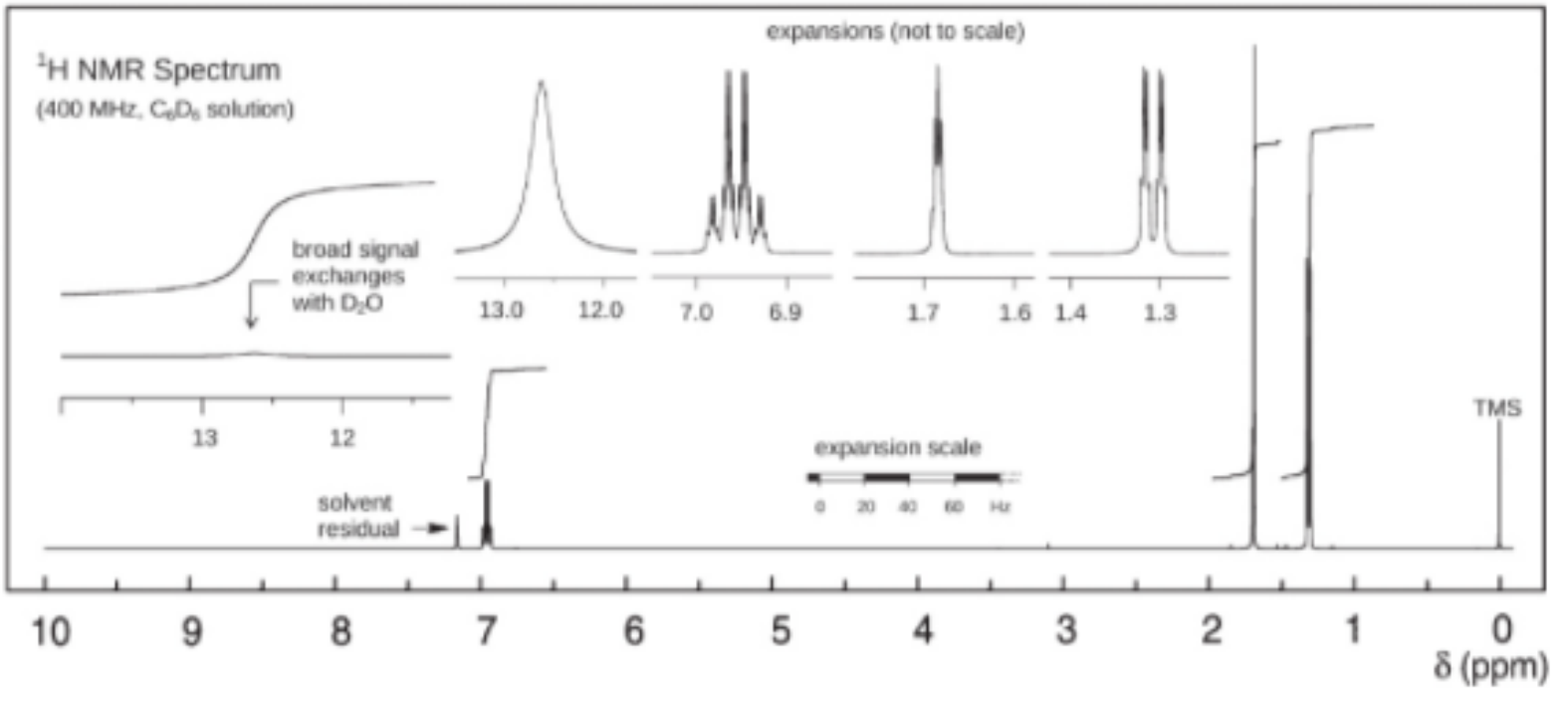
ppm
1.5
2.0
2.5
5.0
5.5
6.0
11.0
11.5
12.0
12.5
^{1}H–^{1}H NOESY Spectrum
(600 MHz, $CDCl_3$ solution)
12.5 12.0 11.5 11.0
6.0 5.5 5.0
2.5 2.0 1.5
ppm

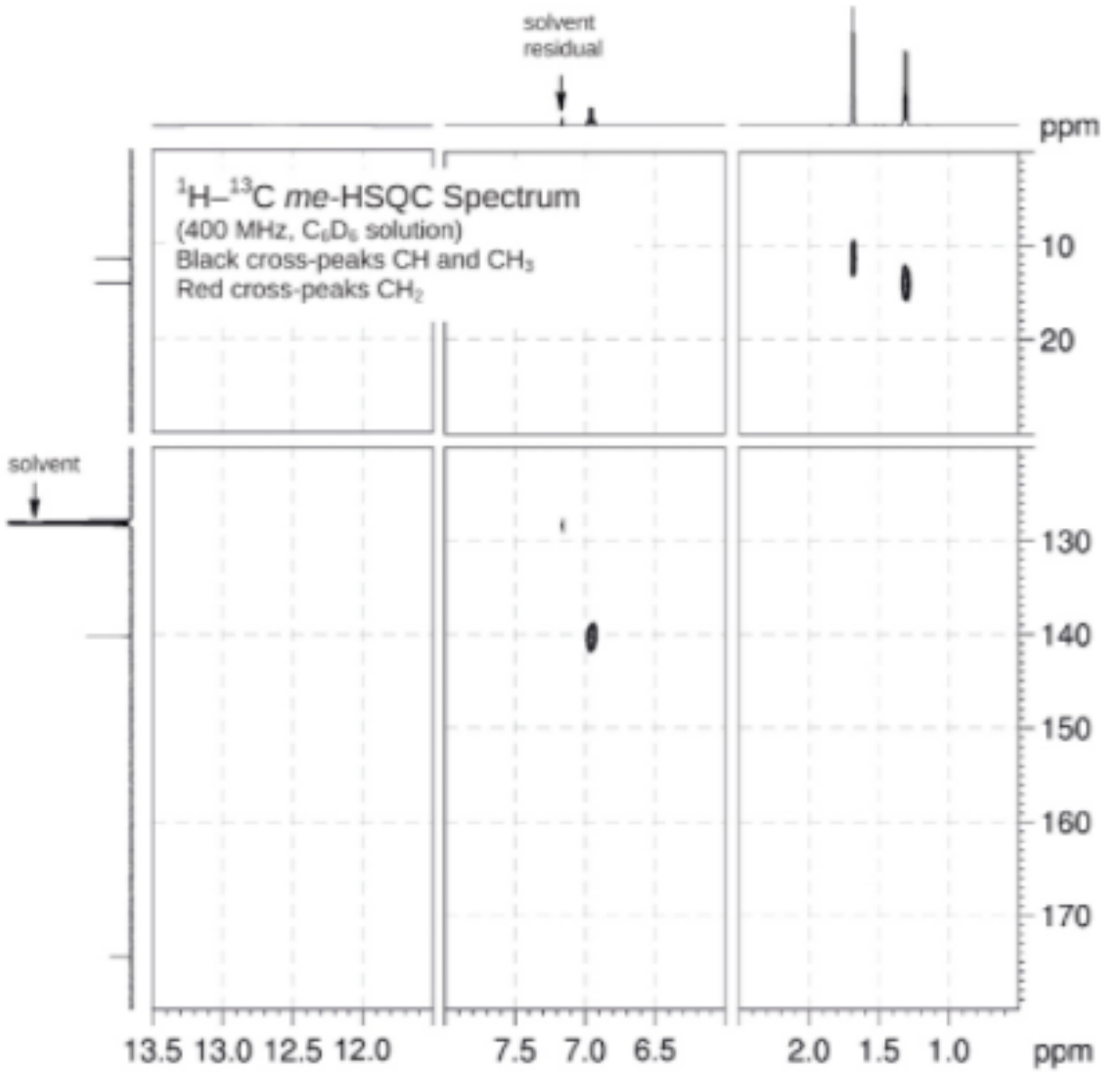
Problem 179


IR Spectrum
(thin film)
1667
1636
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
M+·
100
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m/e
C5H8O2

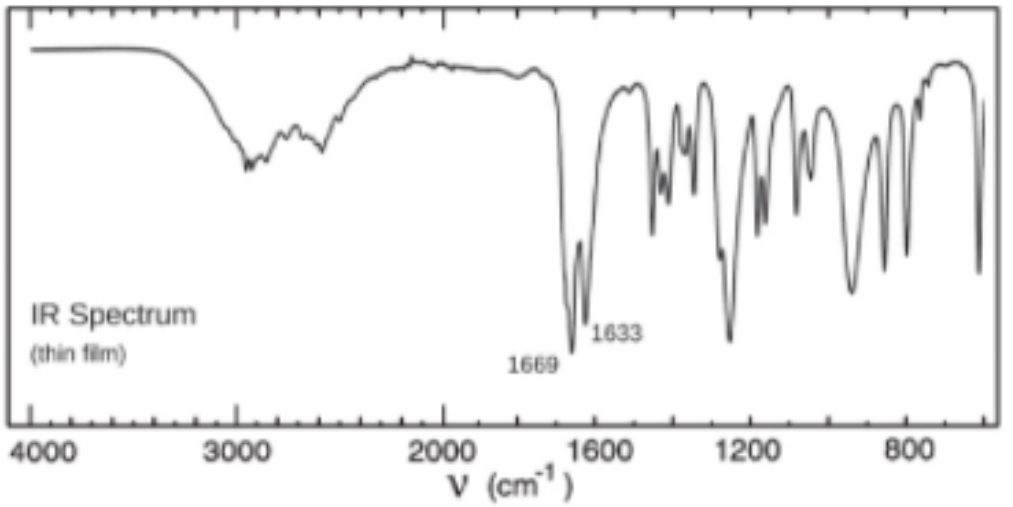

13C NMR Spectrum
(100 MHz, C6D6 solution)
expansion
129
128
127
DEPT CH2 CH3 CH
solvent
expansion
solvent
129
128
127
proton decoupled
200
160
120
80
40
0
δ (ppm)

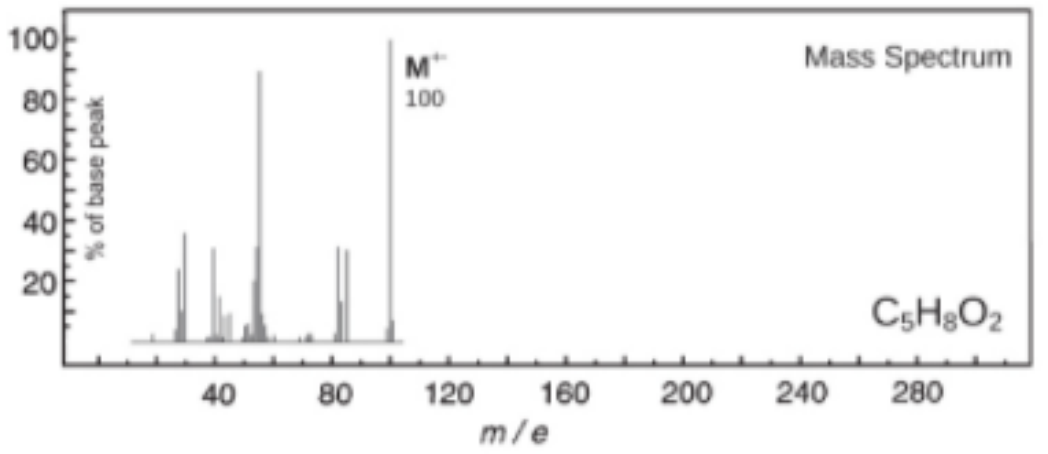

expansions (not to scale)
1H NMR Spectrum
(400 MHz, C6D6 solution)
broad signal
exchanges
with D2O
13.0
12.0
7.0
6.9
1.7
1.6
1.4
1.3
13
12
expansion scale
0
20
40
60
Hz
TMS
solvent
residual
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

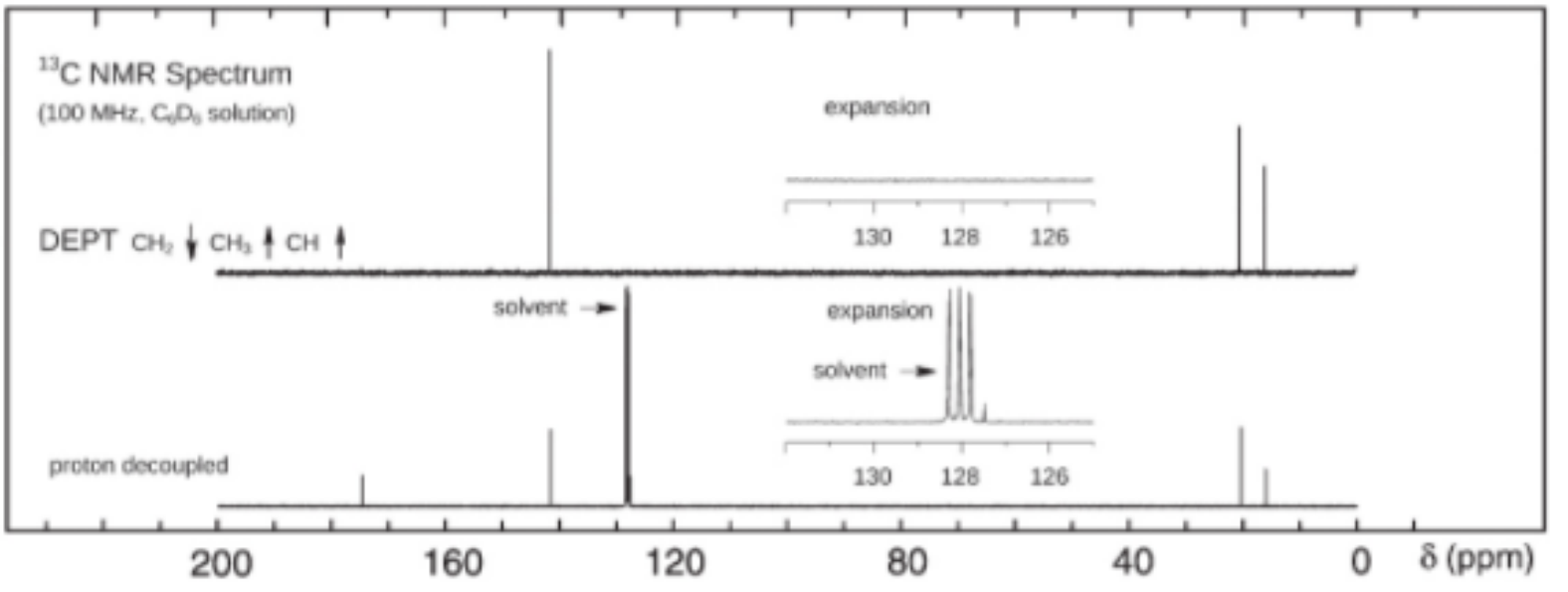

solvent
residual
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, C_6D_6 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
solvent
10
20
130
140
150
160
170
13.5 13.0 12.5 12.0
7.5 7.0 6.5
2.0 1.5 1.0
ppm

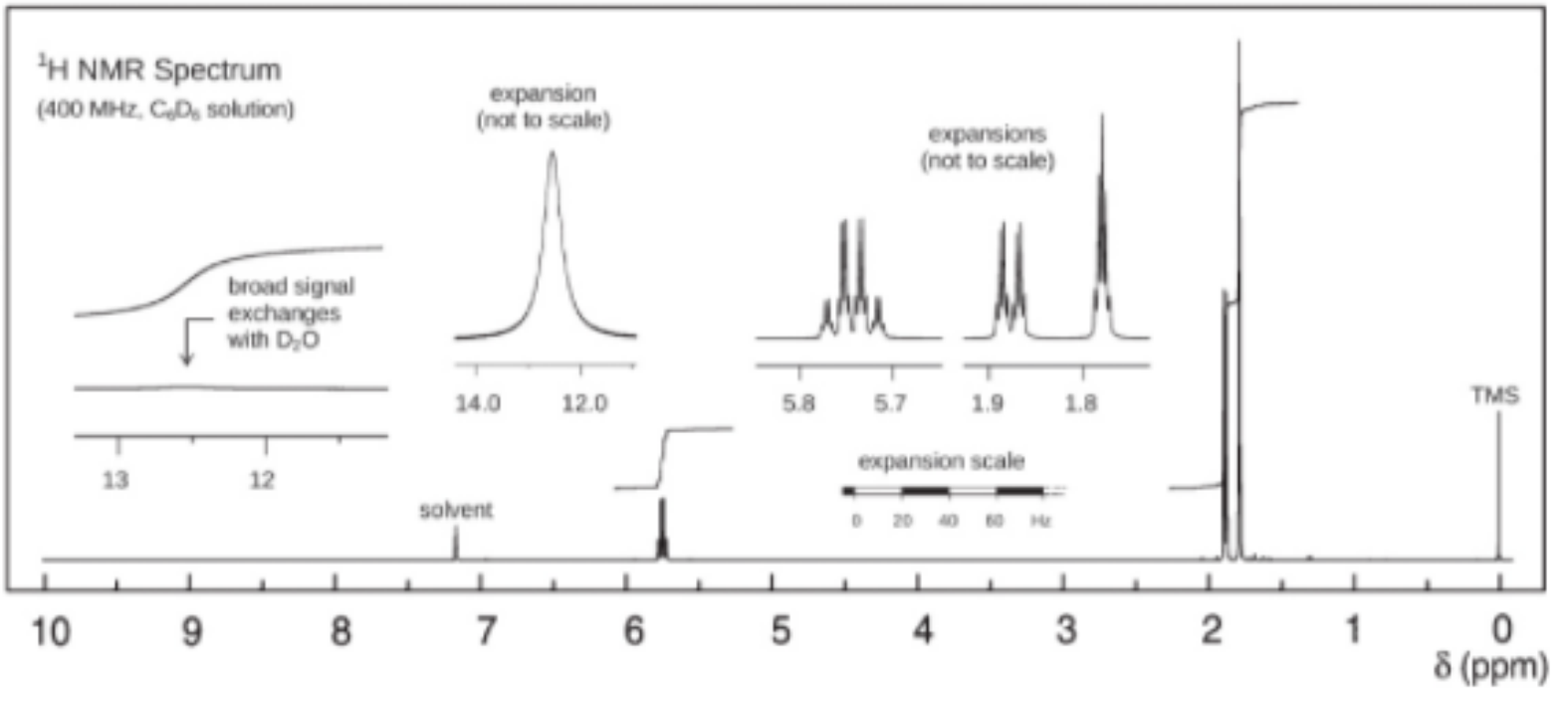
solvent
residual
ppm
1.0
1.5
2.0
6.5
7.0
7.5
solvent
residual
12.0
12.5
13.0
13.5
^{1}H–^{1}H NOESY Spectrum
(400 MHz, C_6D_6 solution)
13.5 13.0 12.5 12.0
7.5 7.0 6.5
2.0 1.5 1.0
ppm

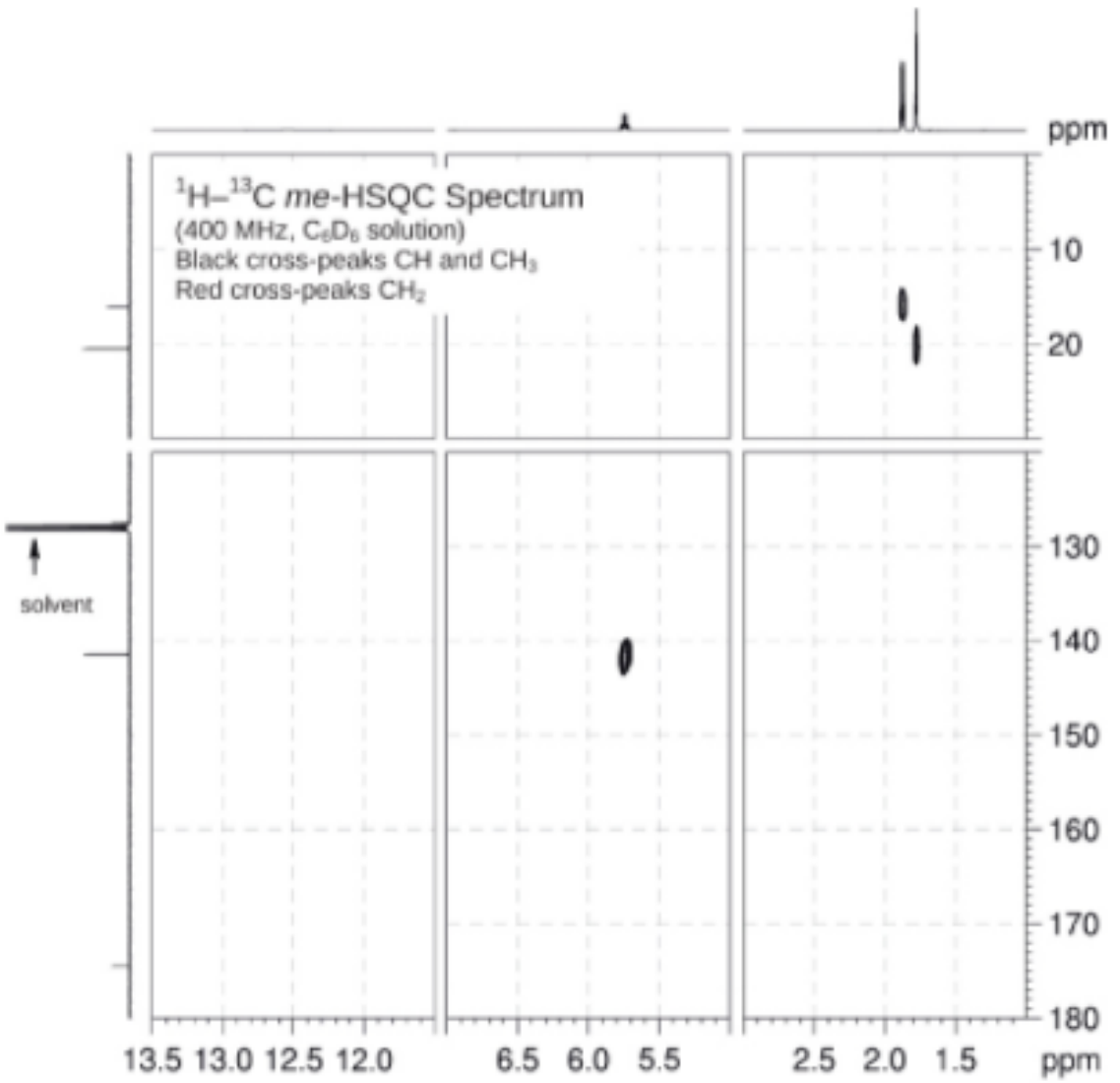
Problem 180


IR Spectrum
(thin film)
1669
1633
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
M+·
100
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m/e
C5H8O2

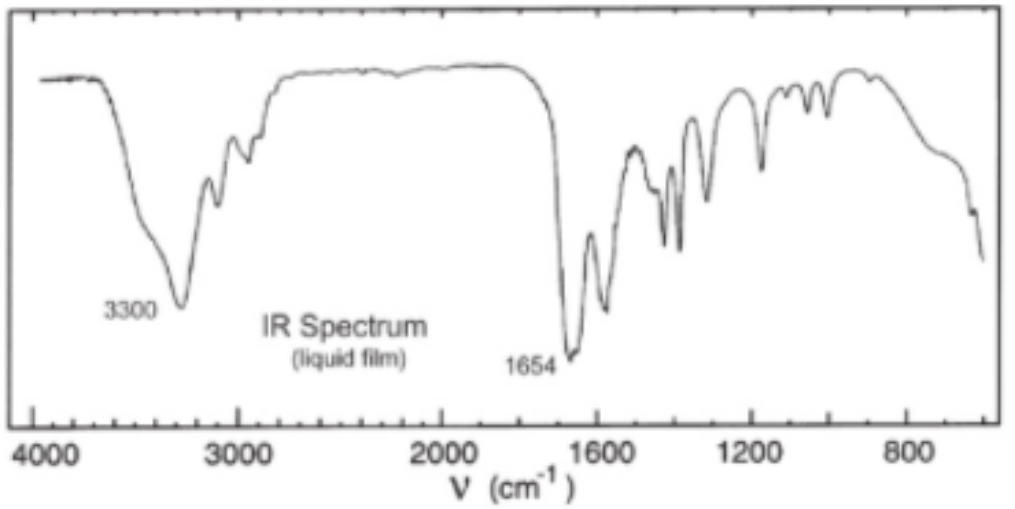

13C NMR Spectrum
(100 MHz, C6D6 solution)
expansion
130
128
126
DEPT CH2 CH3 CH
solvent
expansion
solvent
proton decoupled
130
128
126
200
160
120
80
40
0
δ (ppm)

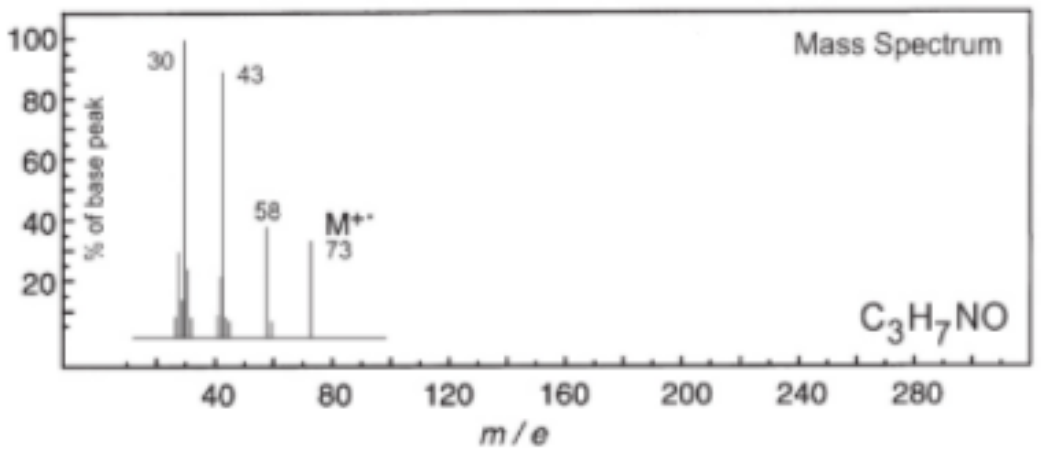

1H NMR Spectrum
(400 MHz, C6D6 solution)
expansion
(not to scale)
expansions
(not to scale)
broad signal
exchanges
with D2O
13
12
14.0
12.0
5.8
5.7
1.9
1.8
TMS
expansion scale
0 20 40 60 Hz
solvent
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, C_6D_6 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
solvent
ppm
10
20
130
140
150
160
170
180
13.5 13.0 12.5 12.0
6.5 6.0 5.5
2.5 2.0 1.5
ppm

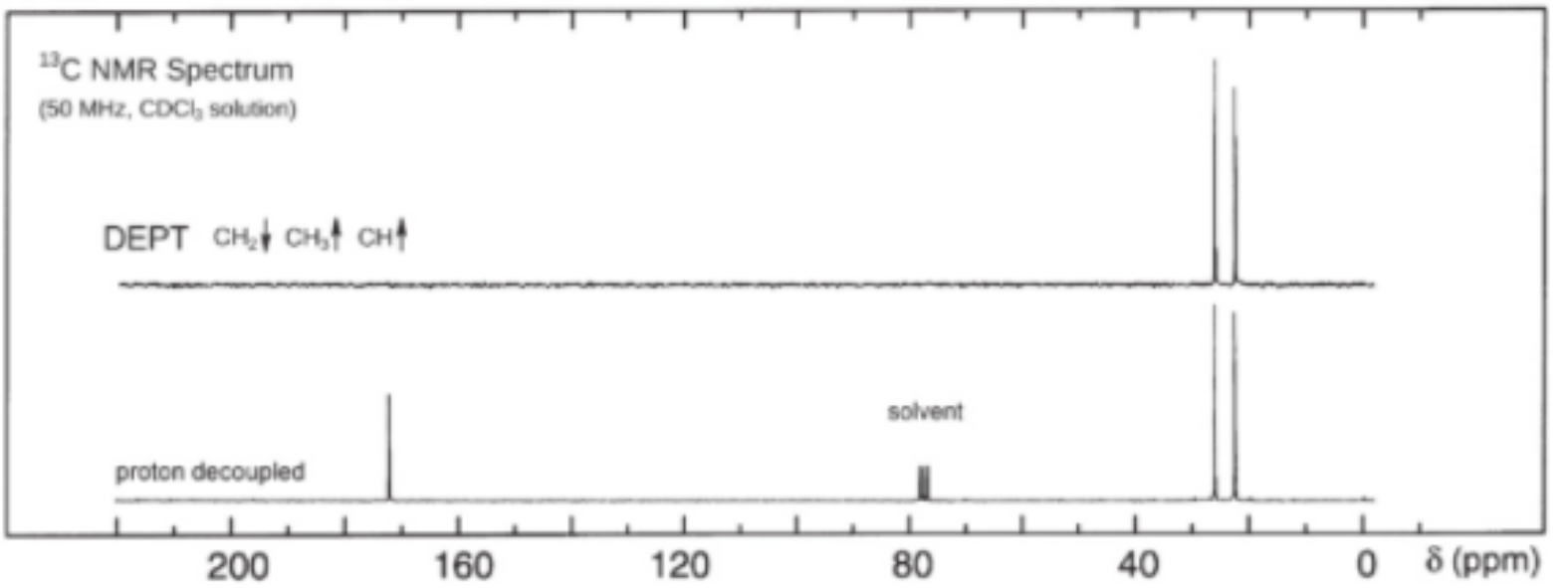
ppm
1.5
2.0
2.5
5.5
6.0
6.5
12.0
12.5
13.0
13.5
^{1}H–^{1}H NOESY Spectrum
(400 MHz, C_6D_6 solution)
13.5 13.0 12.5 12.0
6.5 6.0 5.5
2.5 2.0 1.5
ppm

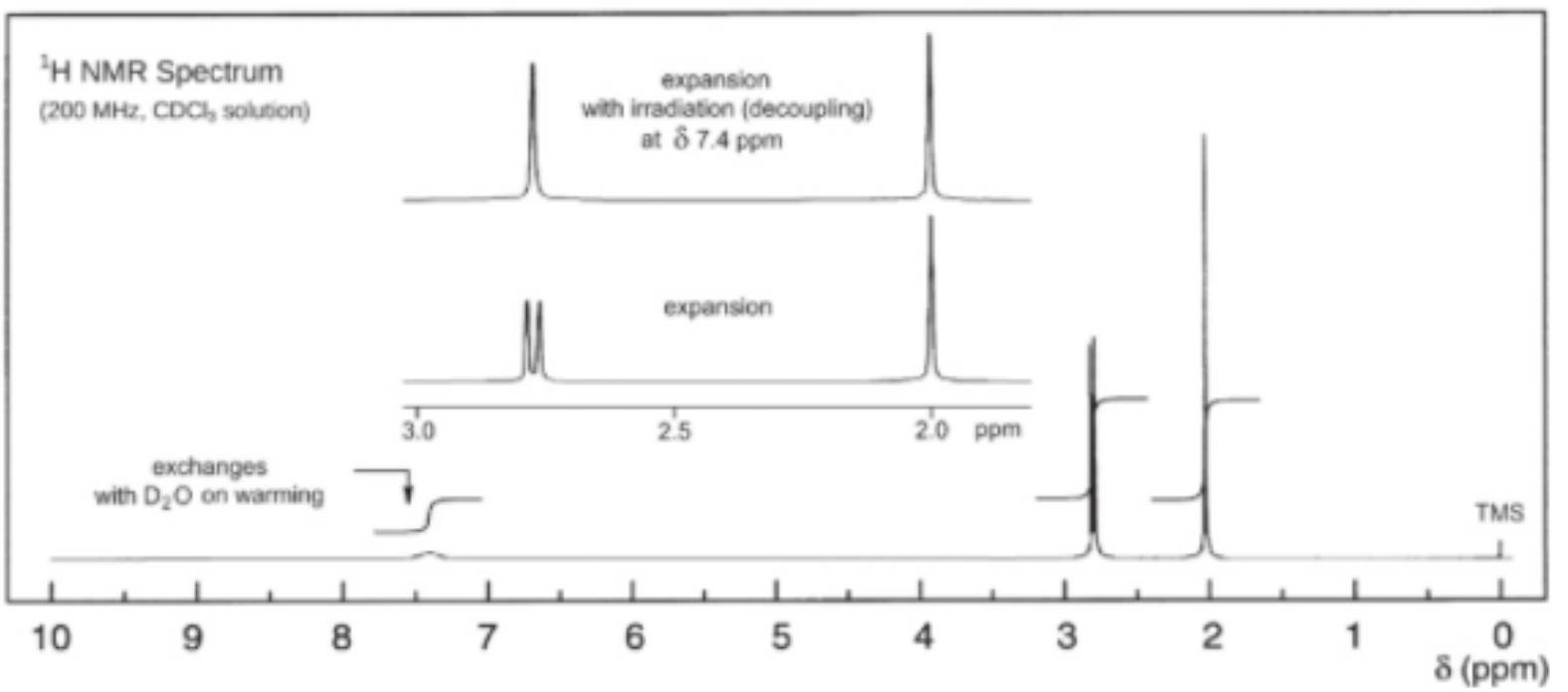
Problem 181



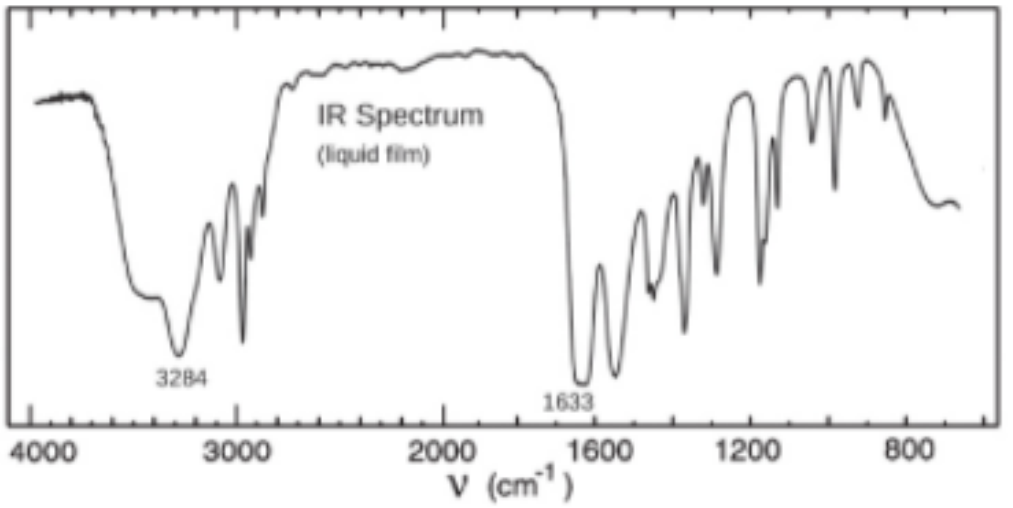


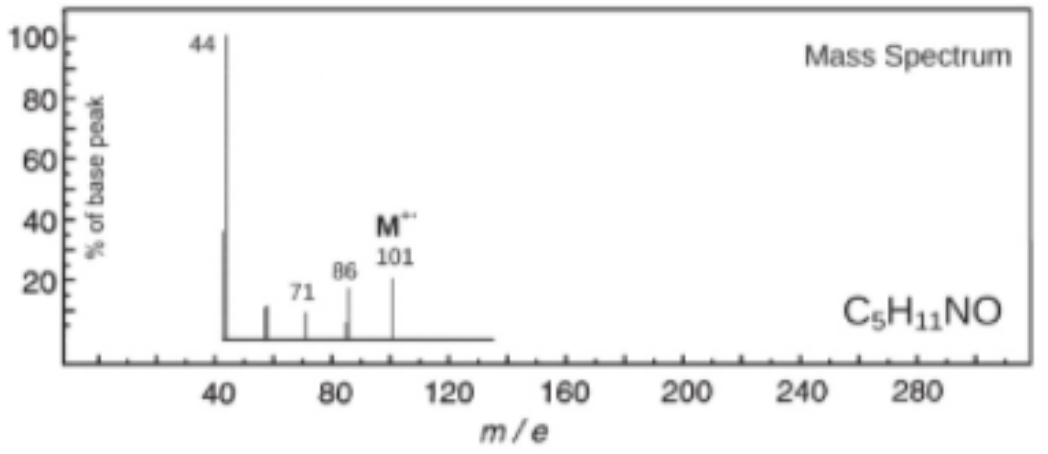
No significant UV
absorption above 220 nm

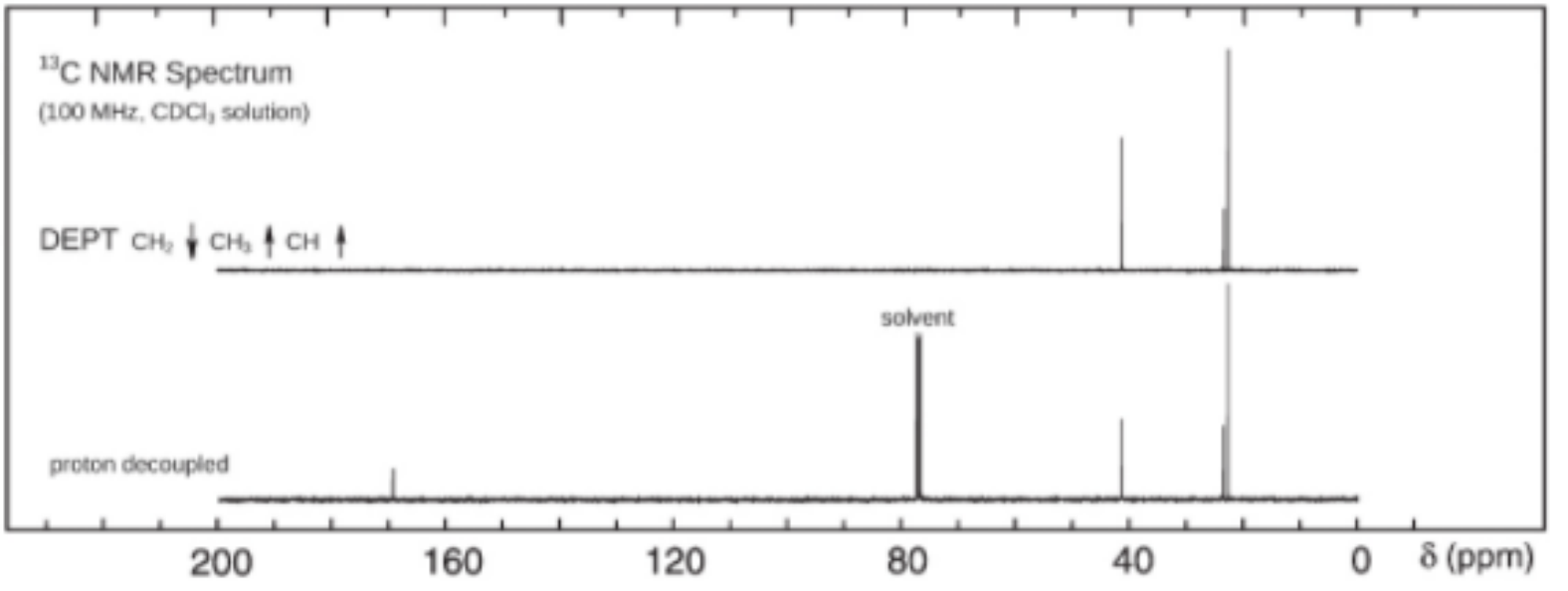


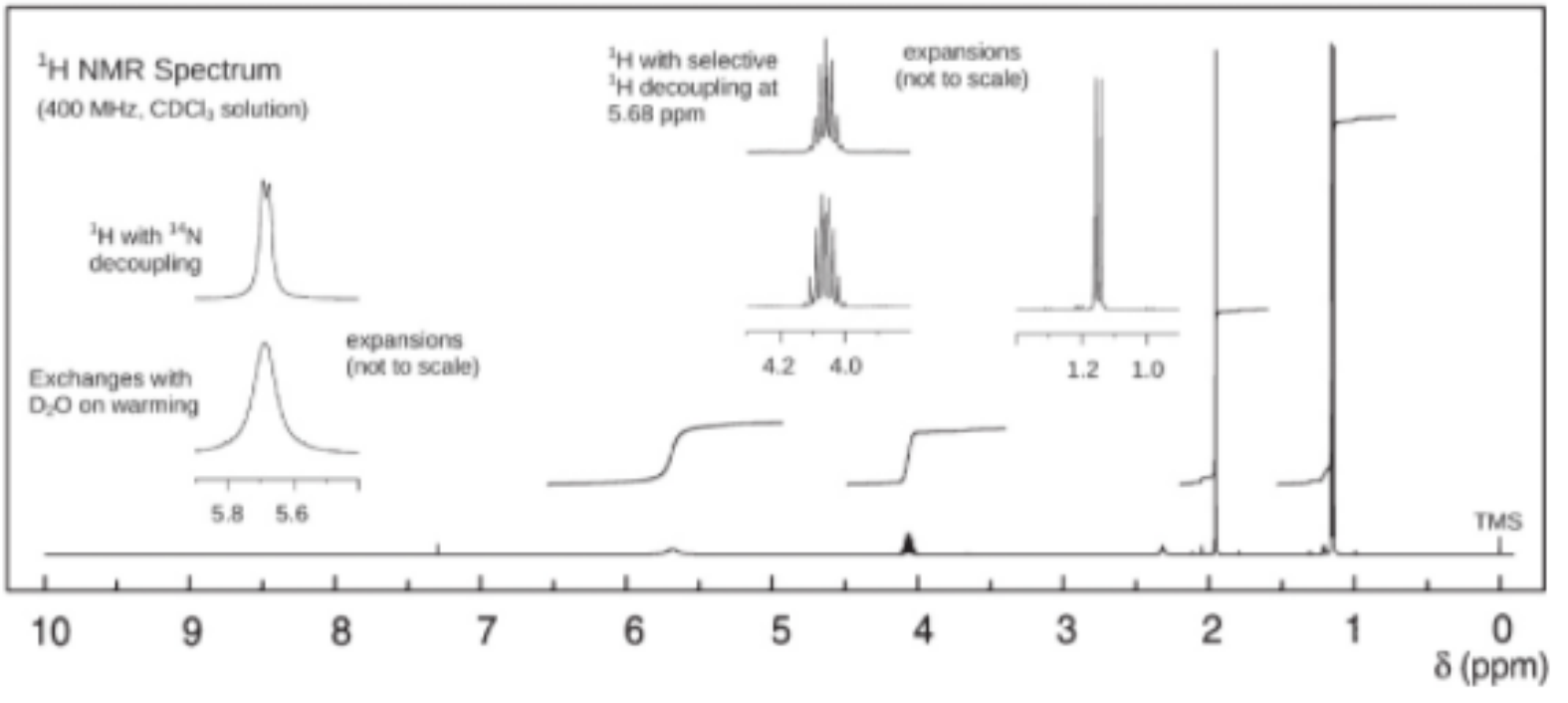


Problem 182

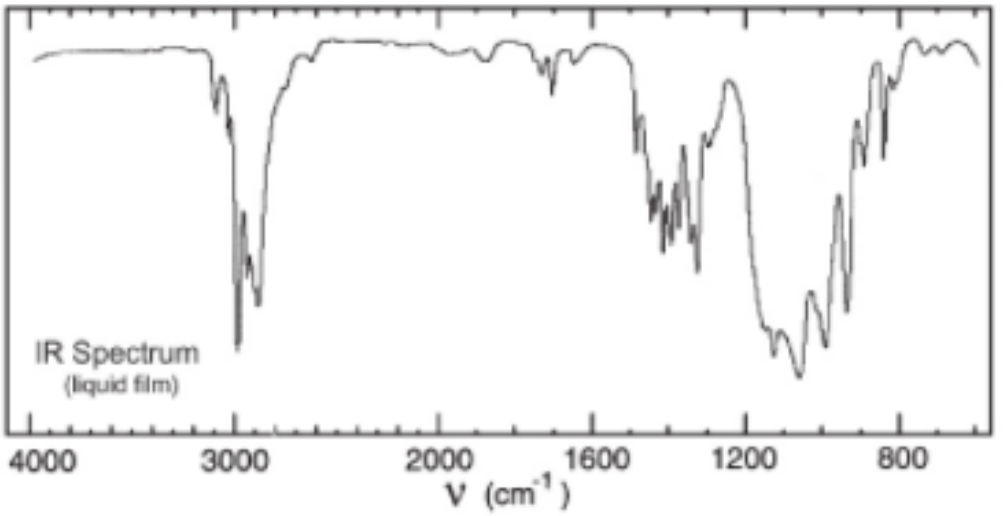

IR Spectrum
(liquid film)
3284
1633
4000
3000
2000
1600
1200
800
ν (cm-1)

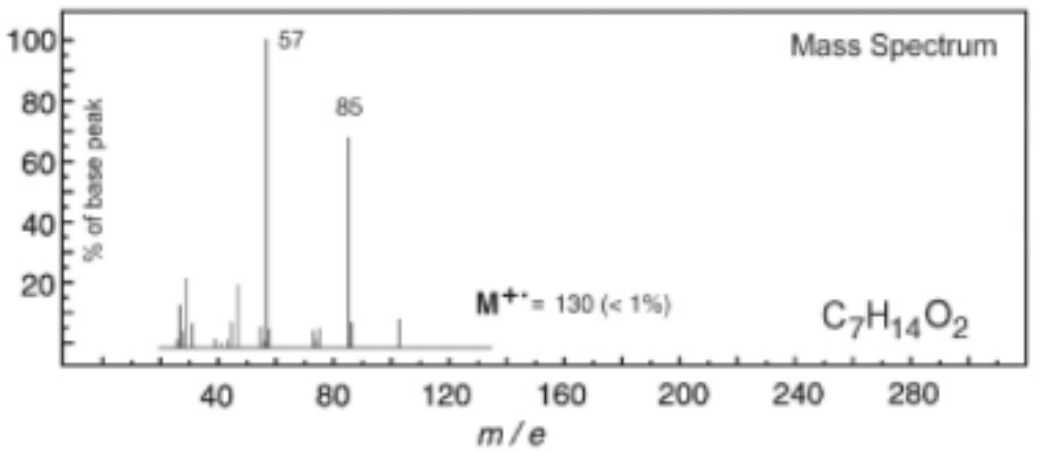

Mass Spectrum
% of base peak
100
80
60
40
20
44
M+·
101
86
71
C5H11NO
40
80
120
160
200
240
280
m/e


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

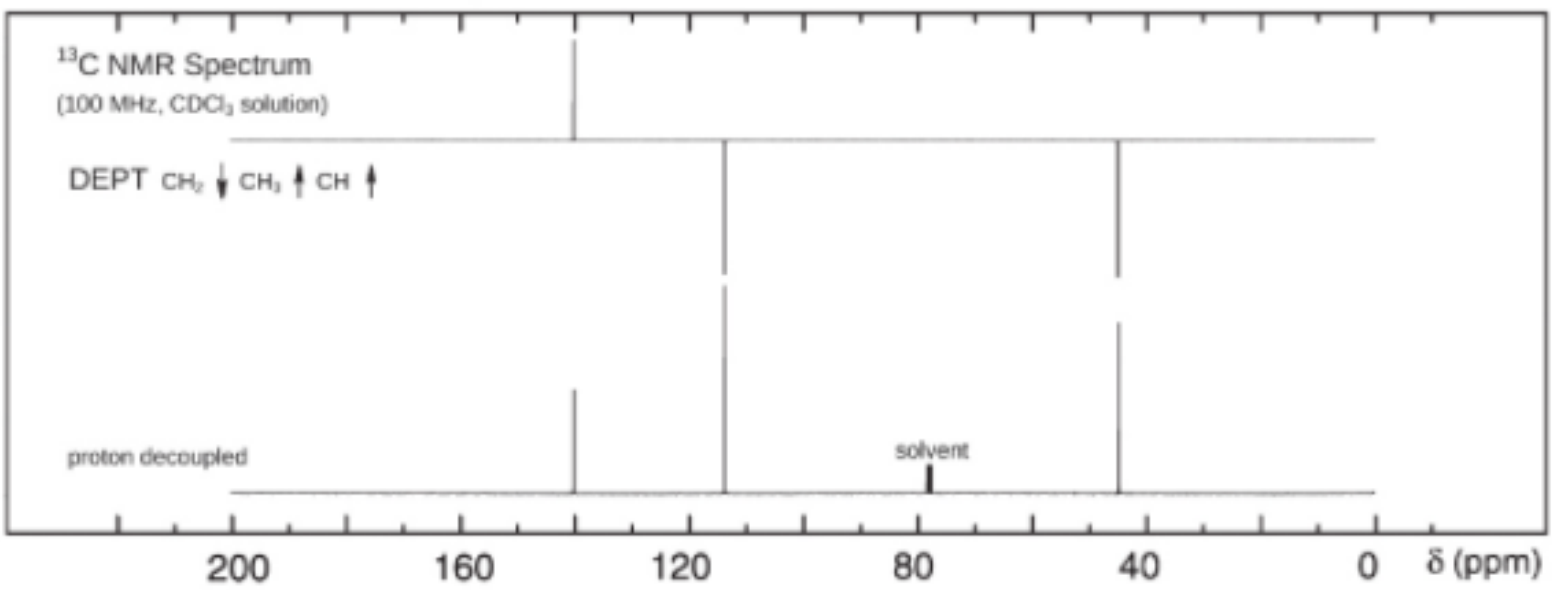

1H NMR Spectrum
(400 MHz, CDCl3 solution)
1H with 14N
decoupling
Exchanges with
D2O on warming
expansions
(not to scale)
5.8
5.6
1H with selective
1H decoupling at
5.68 ppm
expansions
(not to scale)
4.2
4.0
1.2
1.0
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

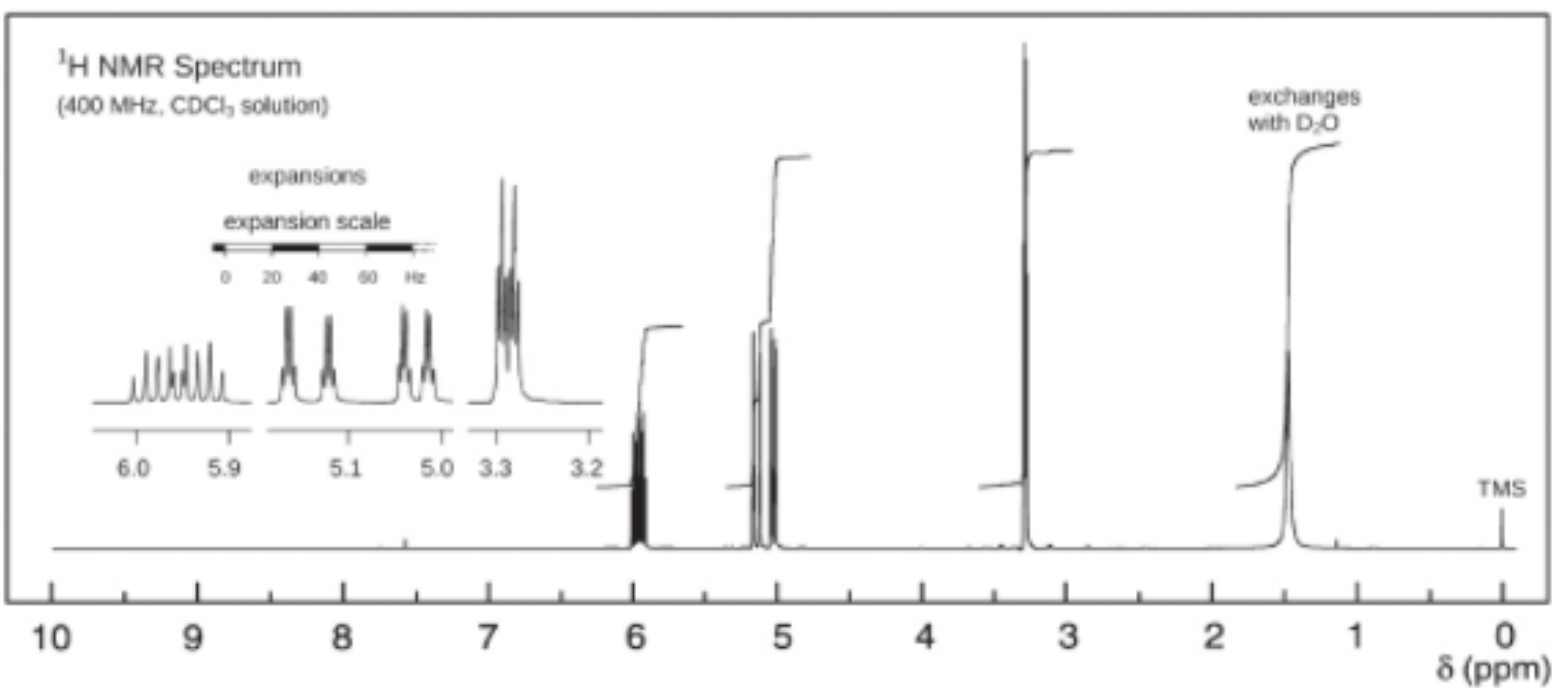
Problem 183

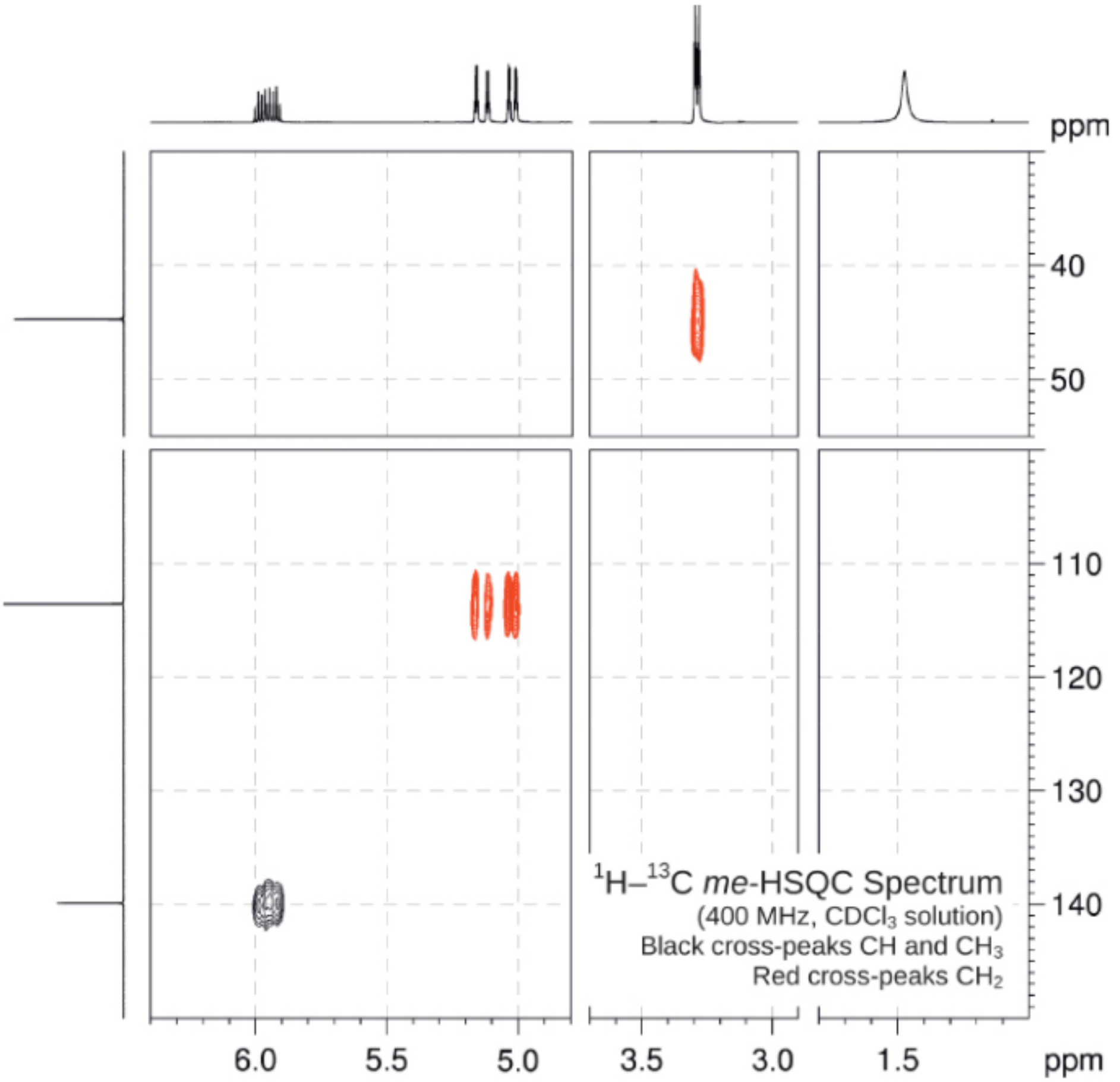




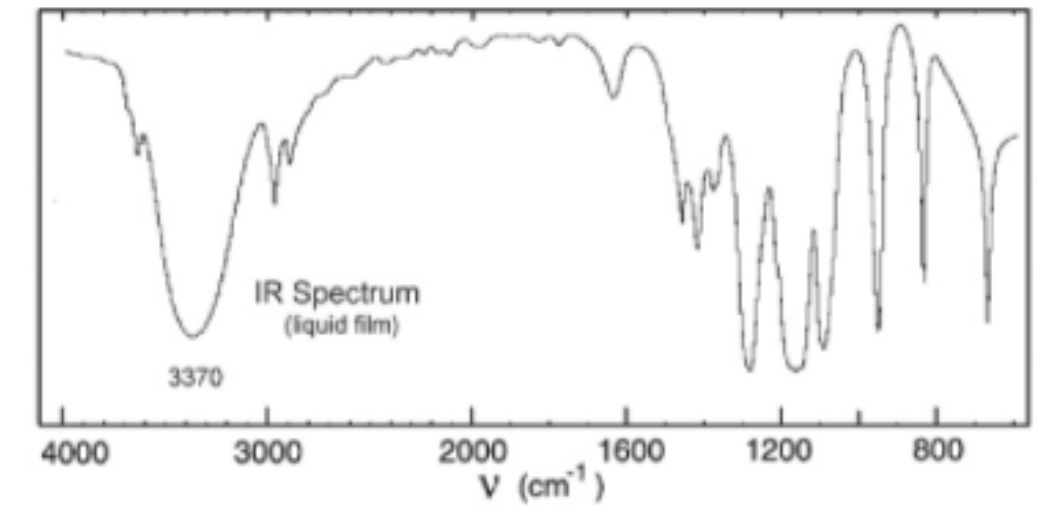
No significant UV absorption above 220 nm

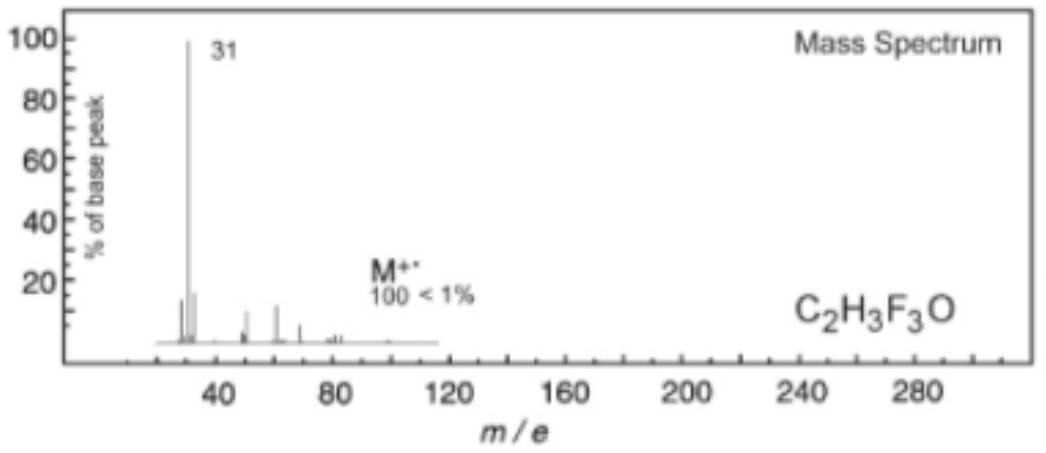




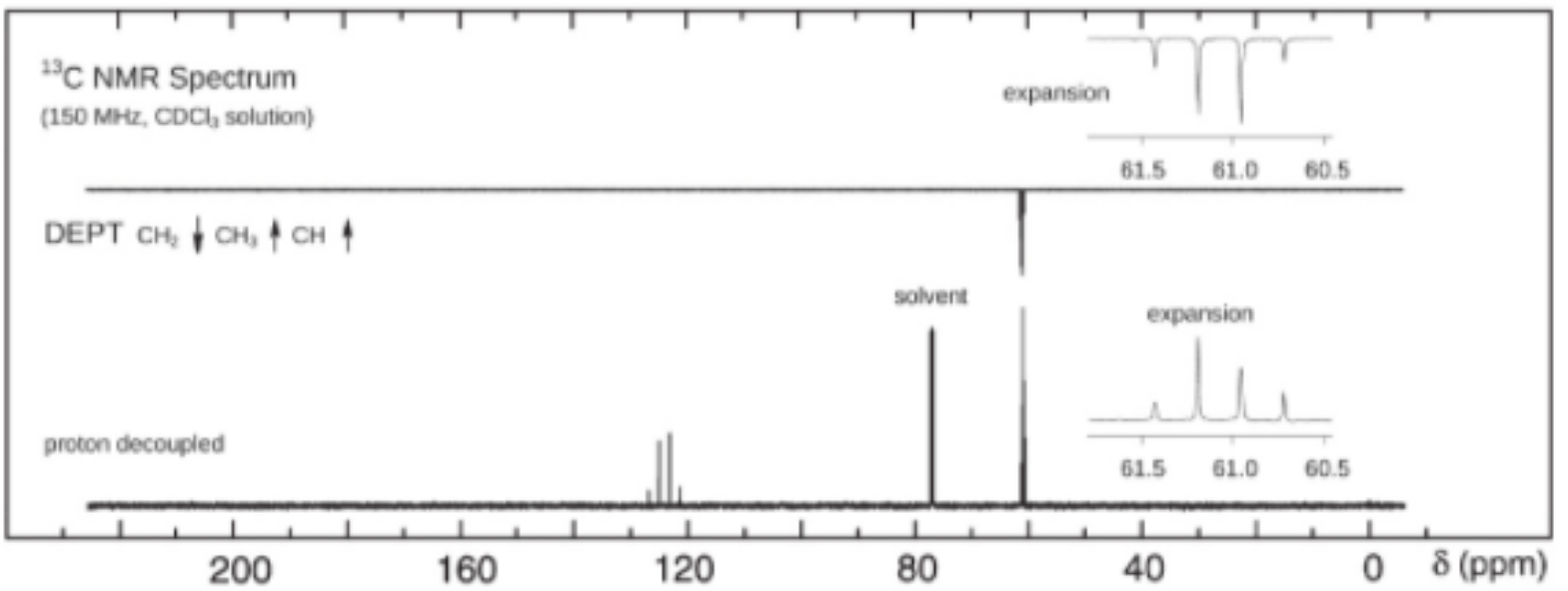

ppm
40
50
110
120
130
140
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
6.0
5.5
5.0
3.5
3.0
1.5
ppm

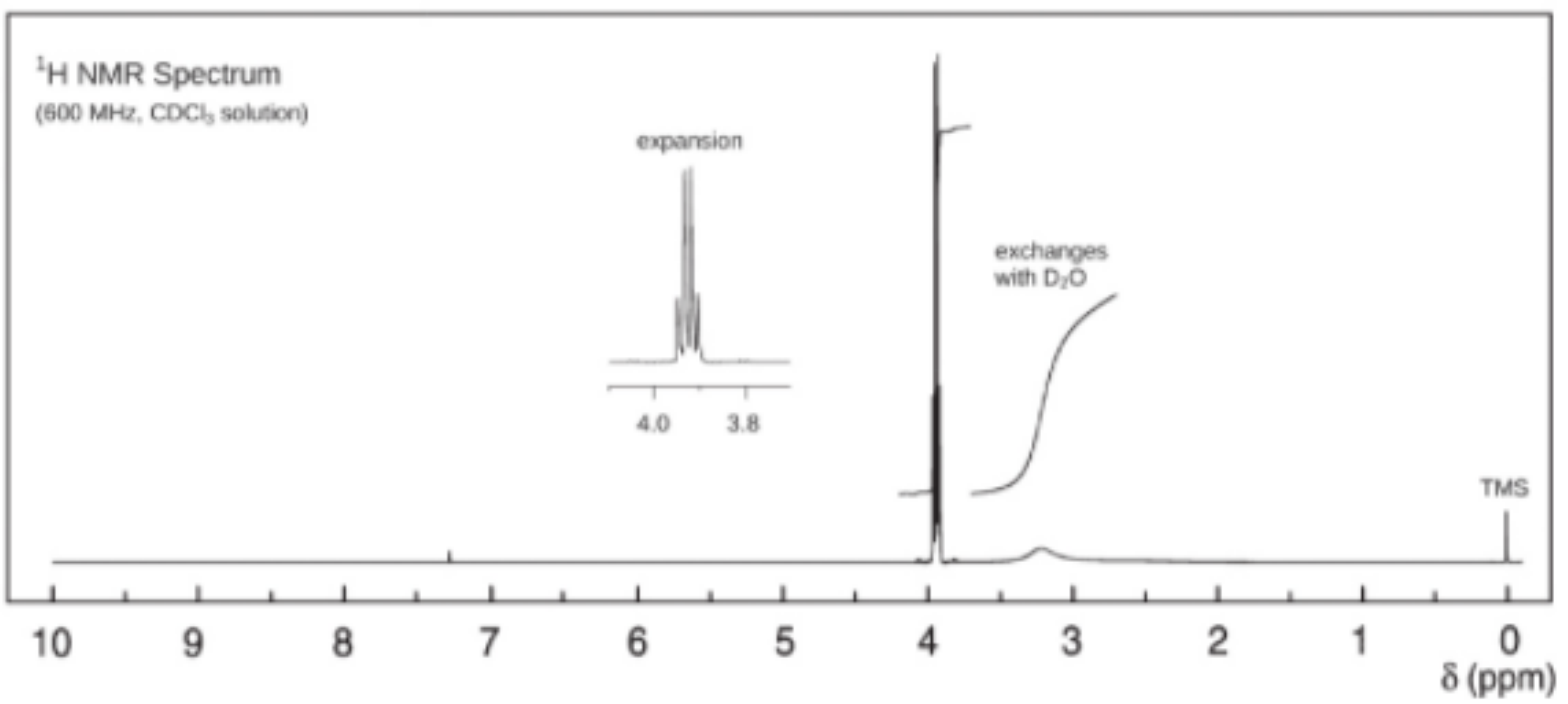
Problem 184

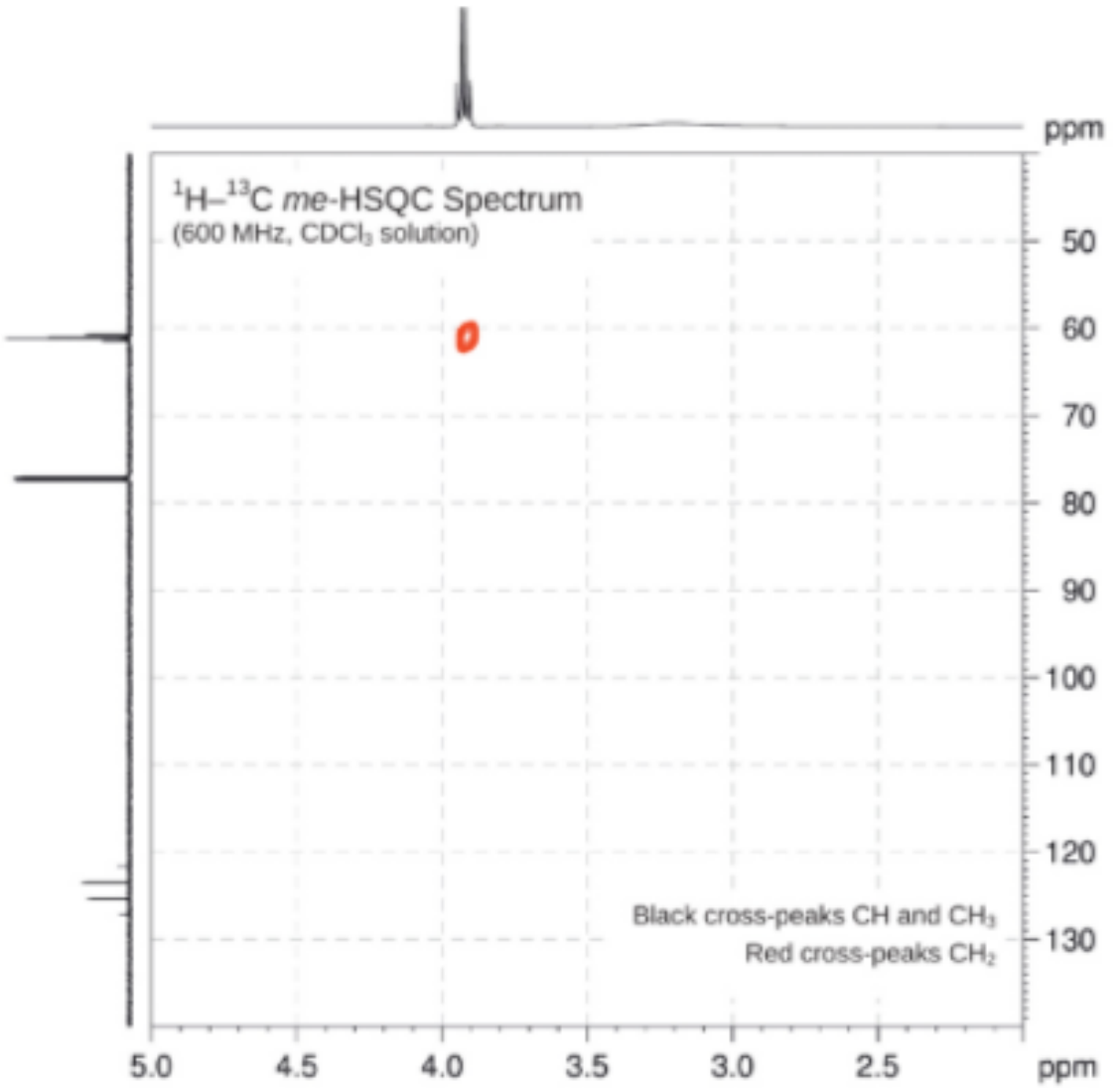


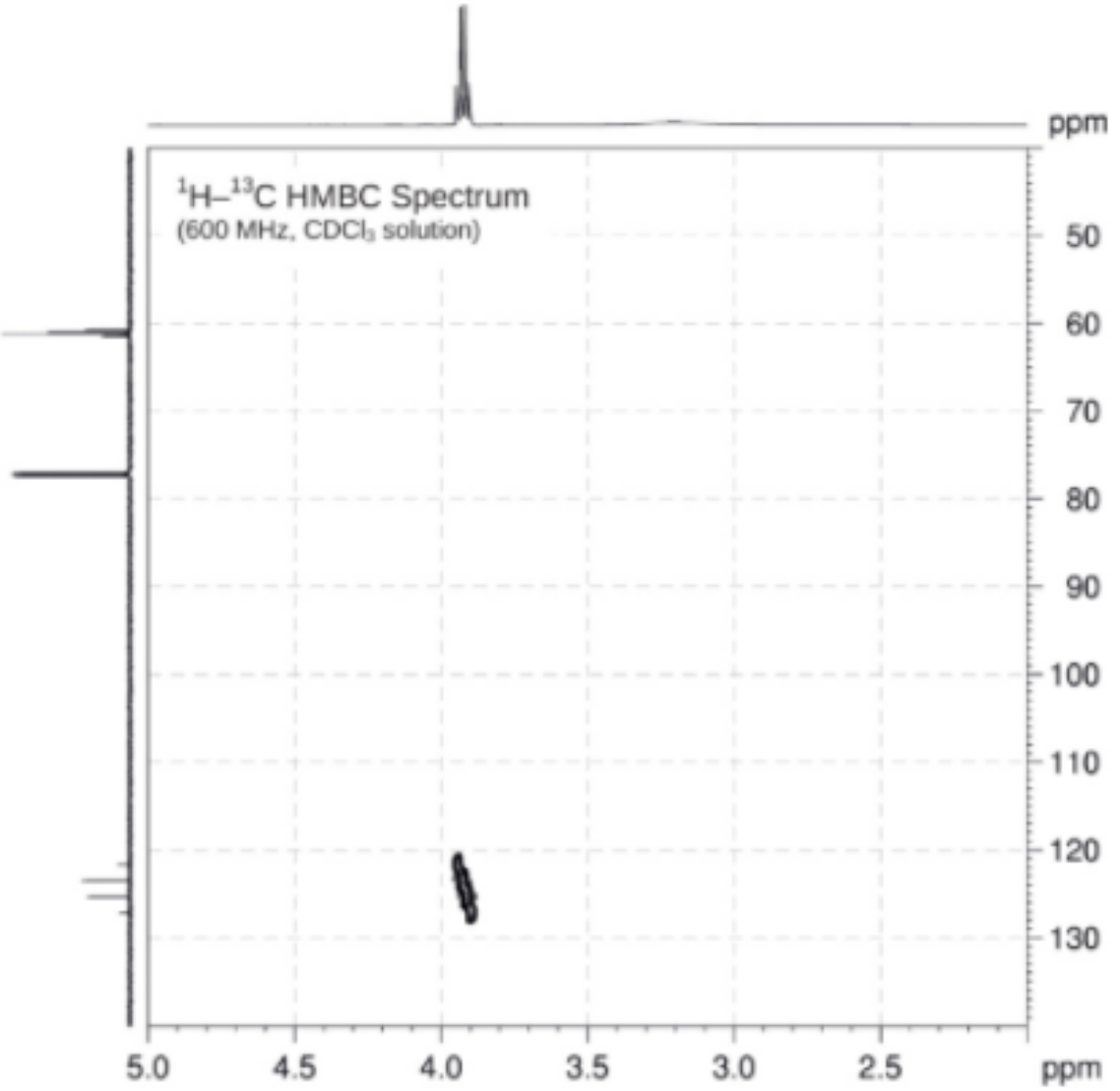


No significant UV
absorption above 220 nm

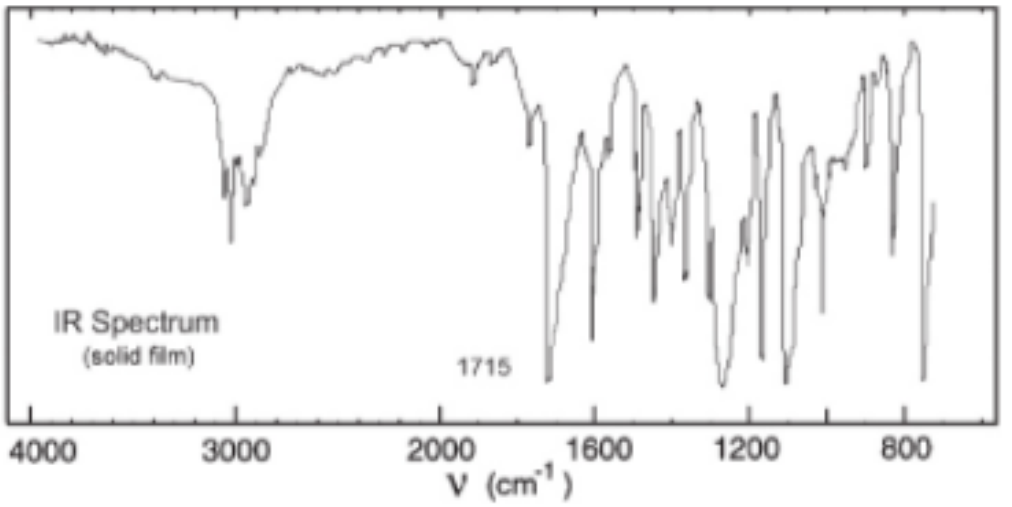


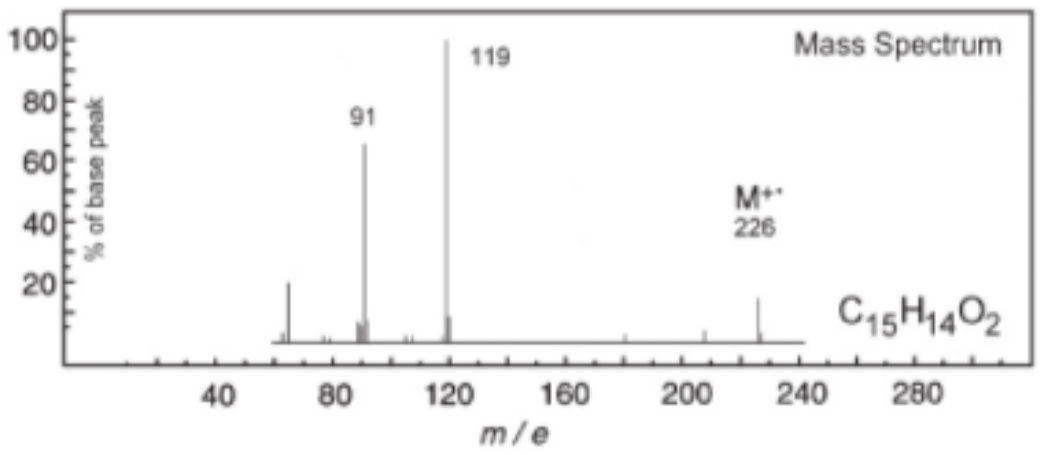



^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
ppm
50
60
70
80
90
100
110
120
130
5.0
4.5
4.0
3.5
3.0
2.5
ppm


^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)
ppm
50
60
70
80
90
100
110
120
130
5.0
4.5
4.0
3.5
3.0
2.5
ppm

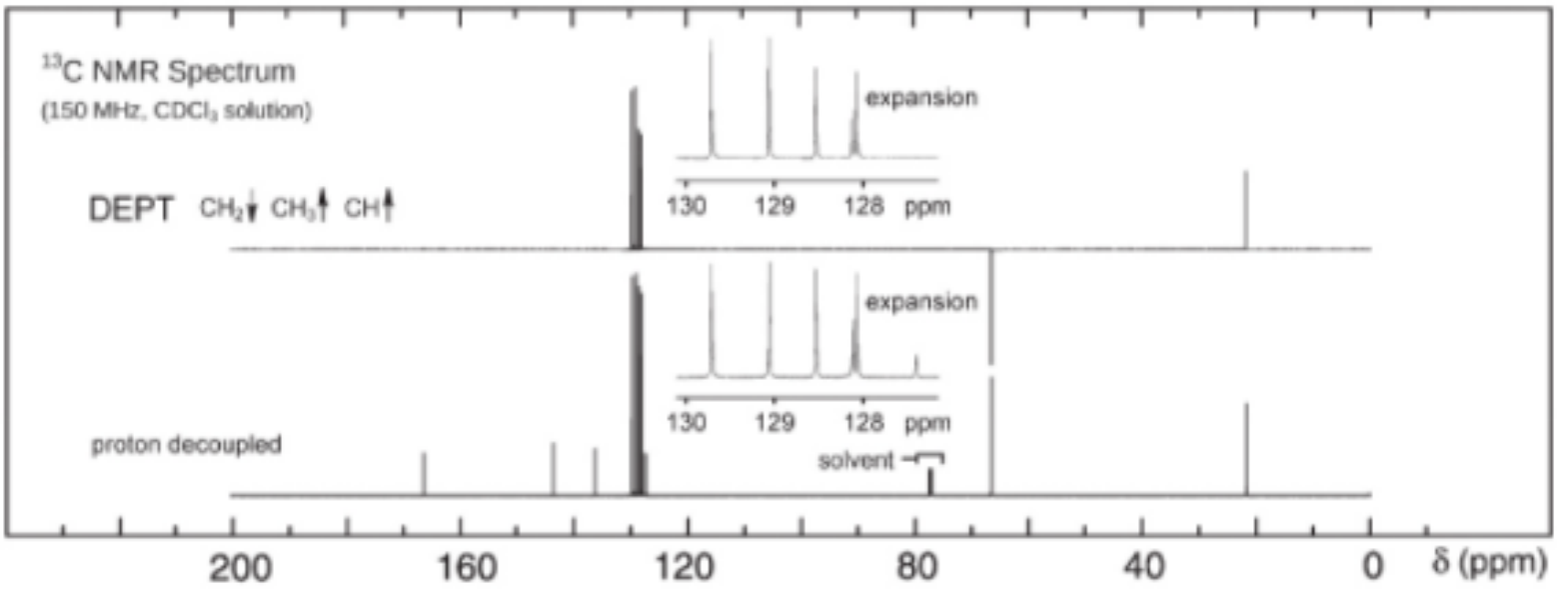
Problem 185

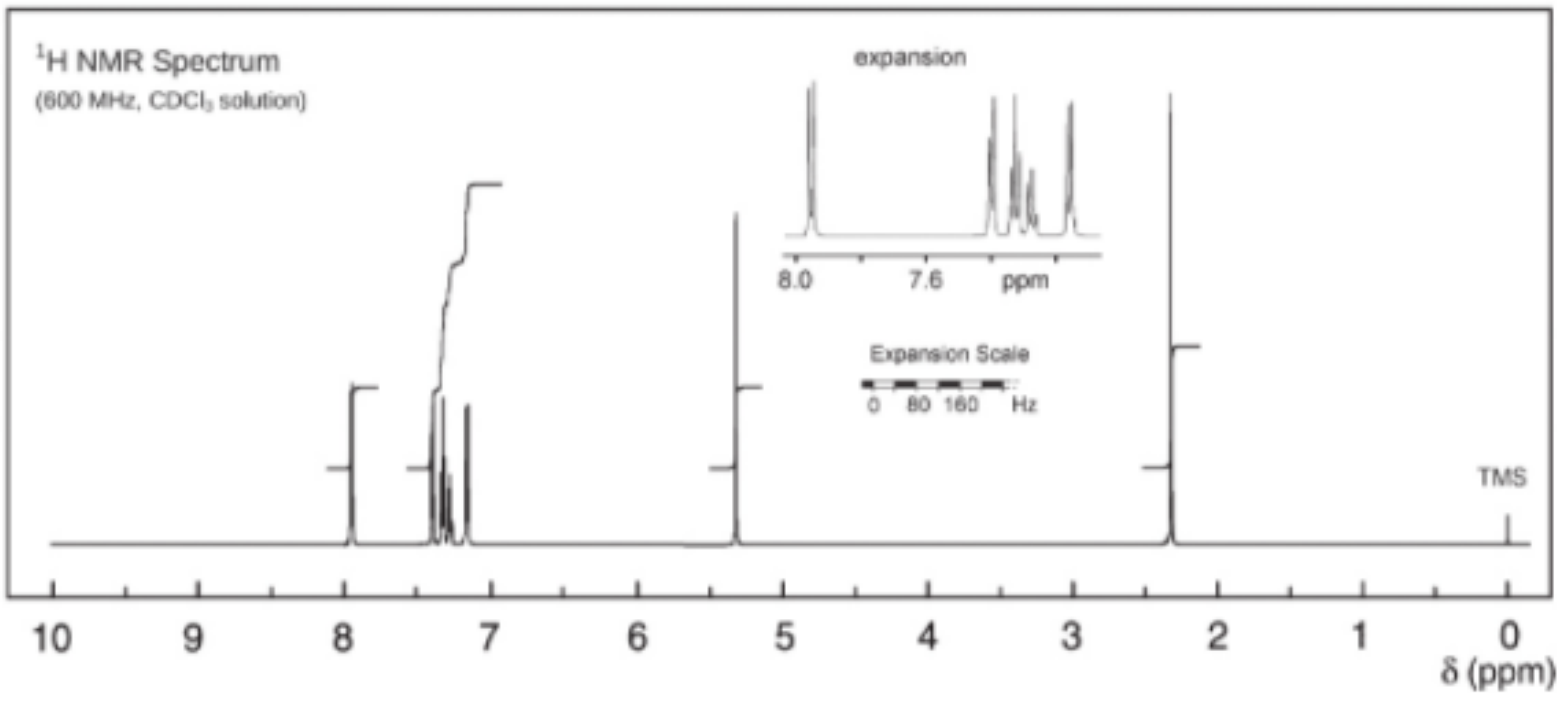




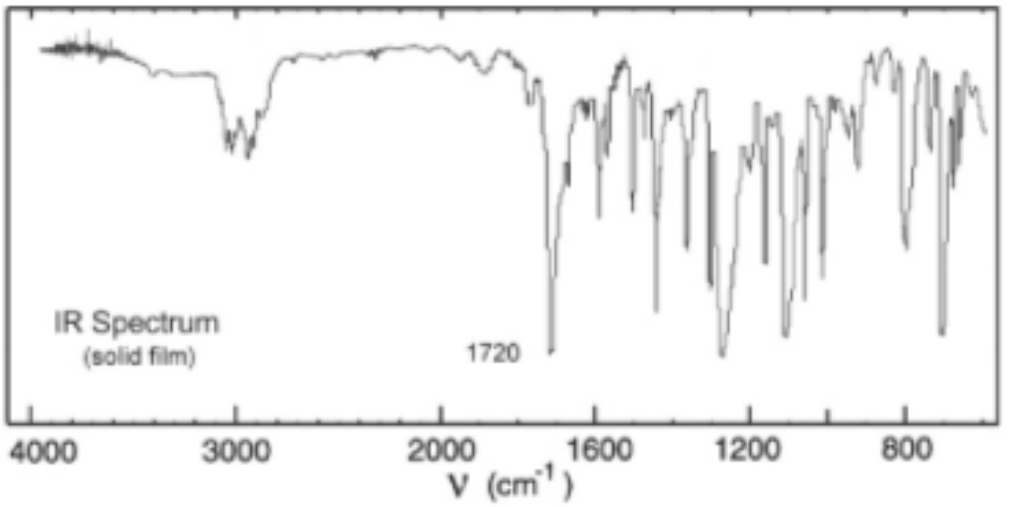
UV Spectrum

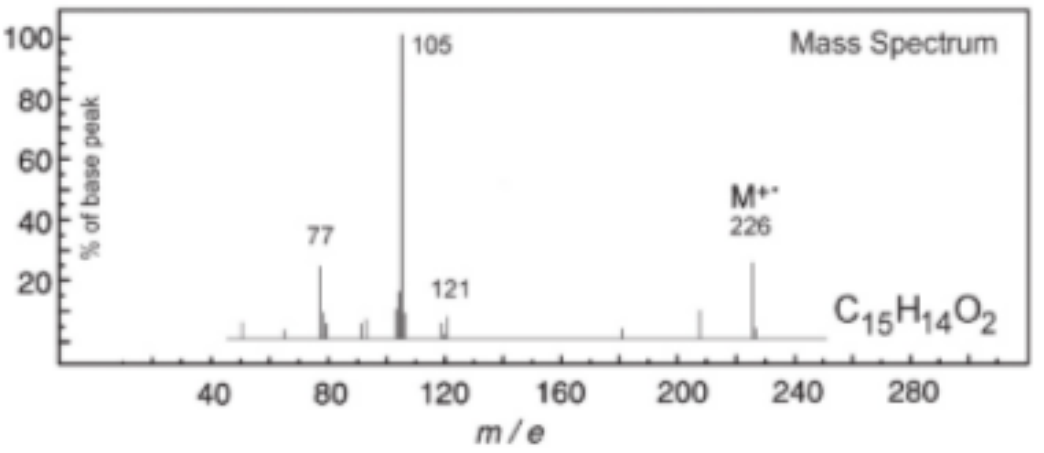
$\log_{10}\varepsilon > 5$





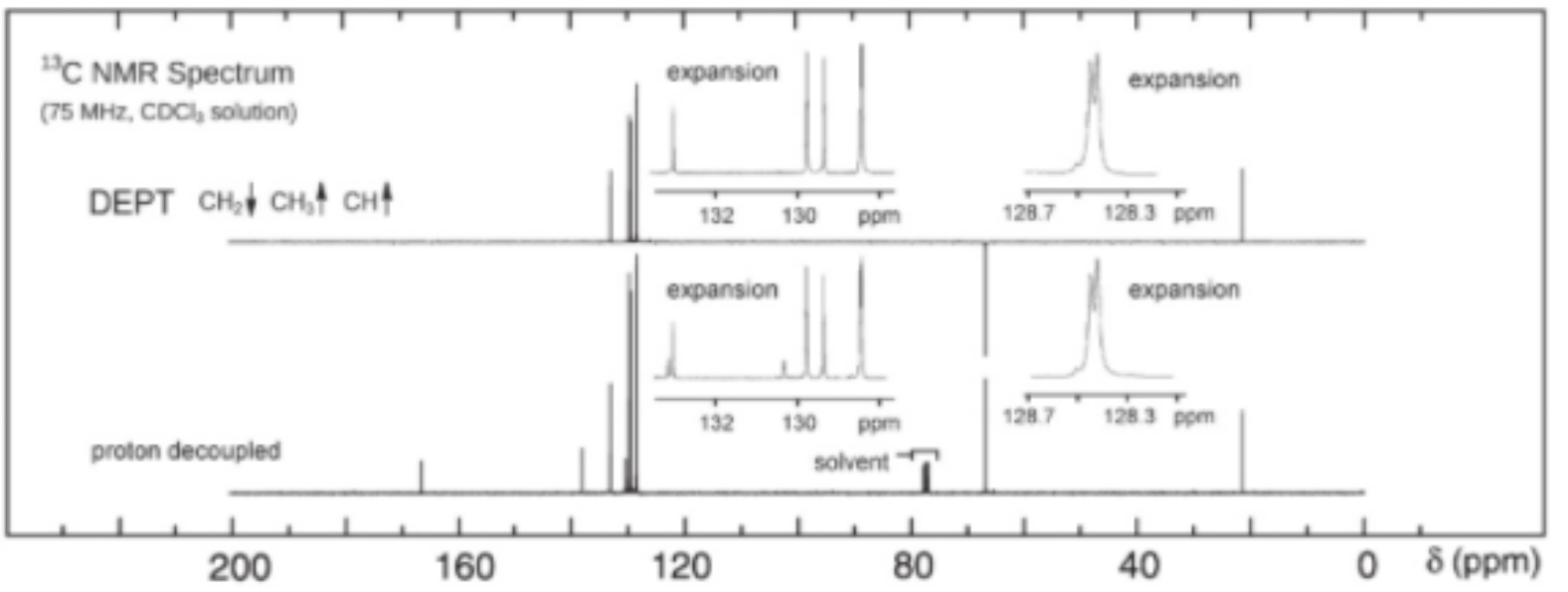
Problem 186

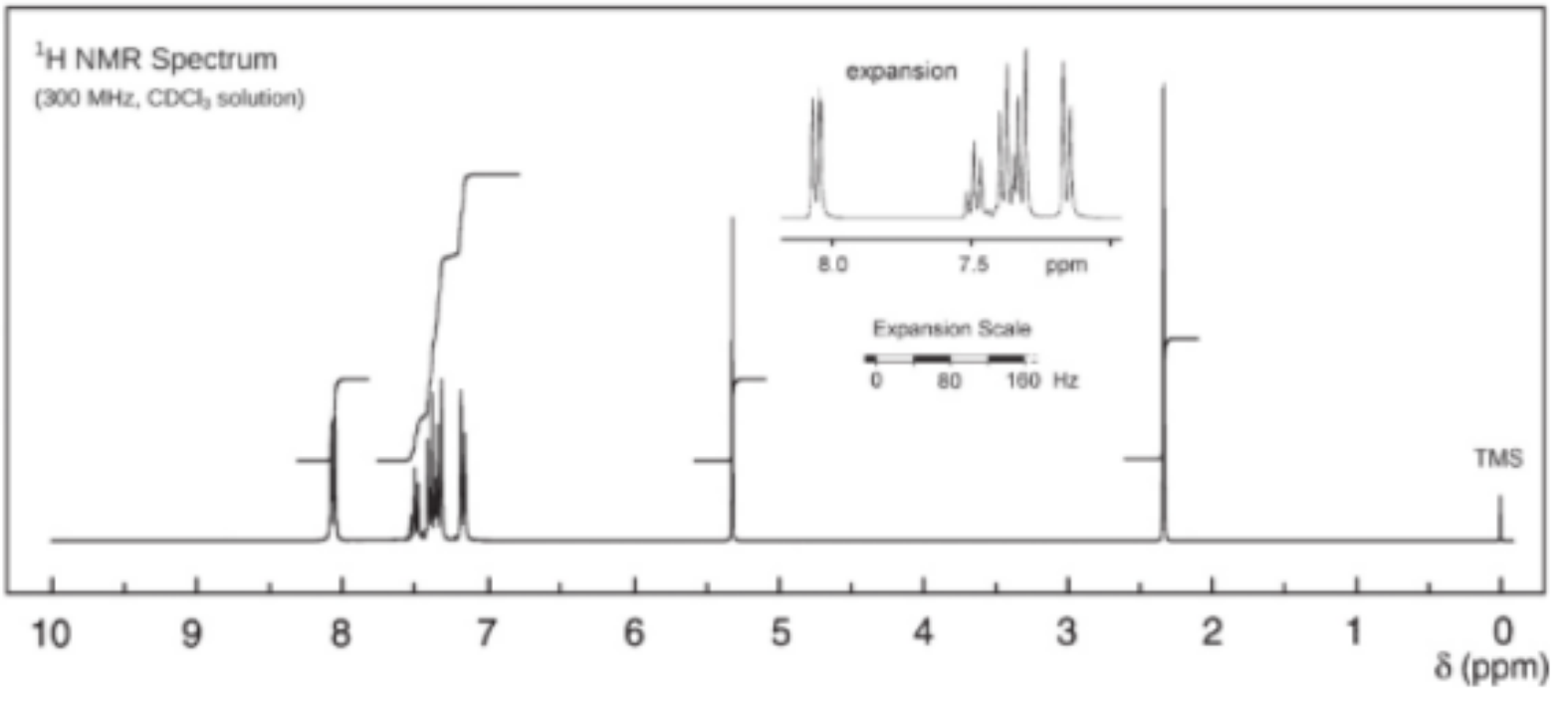




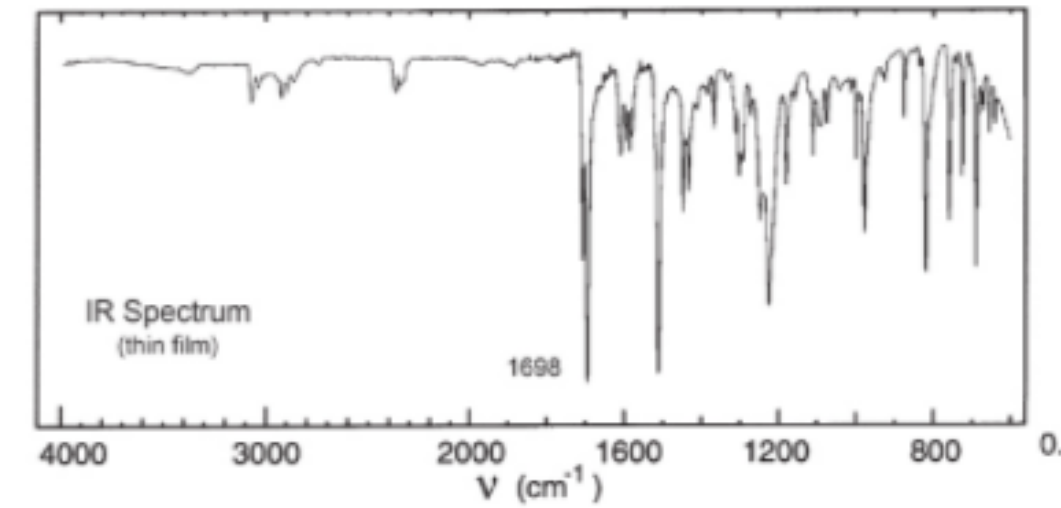
UV Spectrum

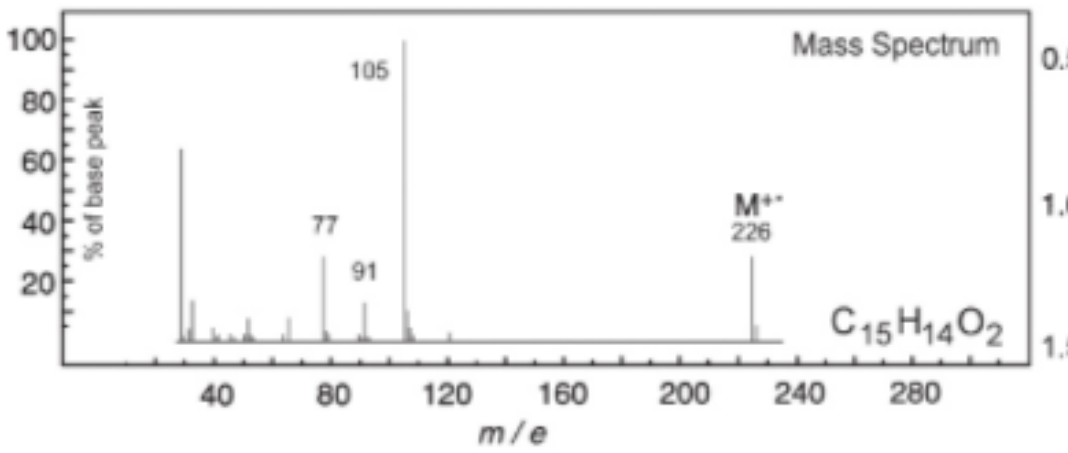
$\log_{10}\varepsilon > 5$

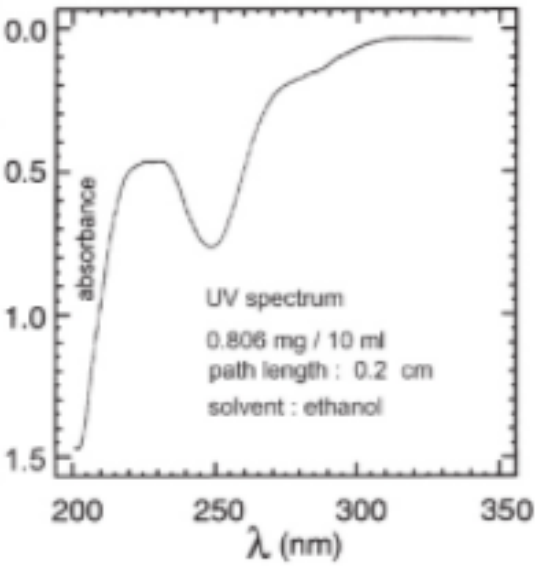


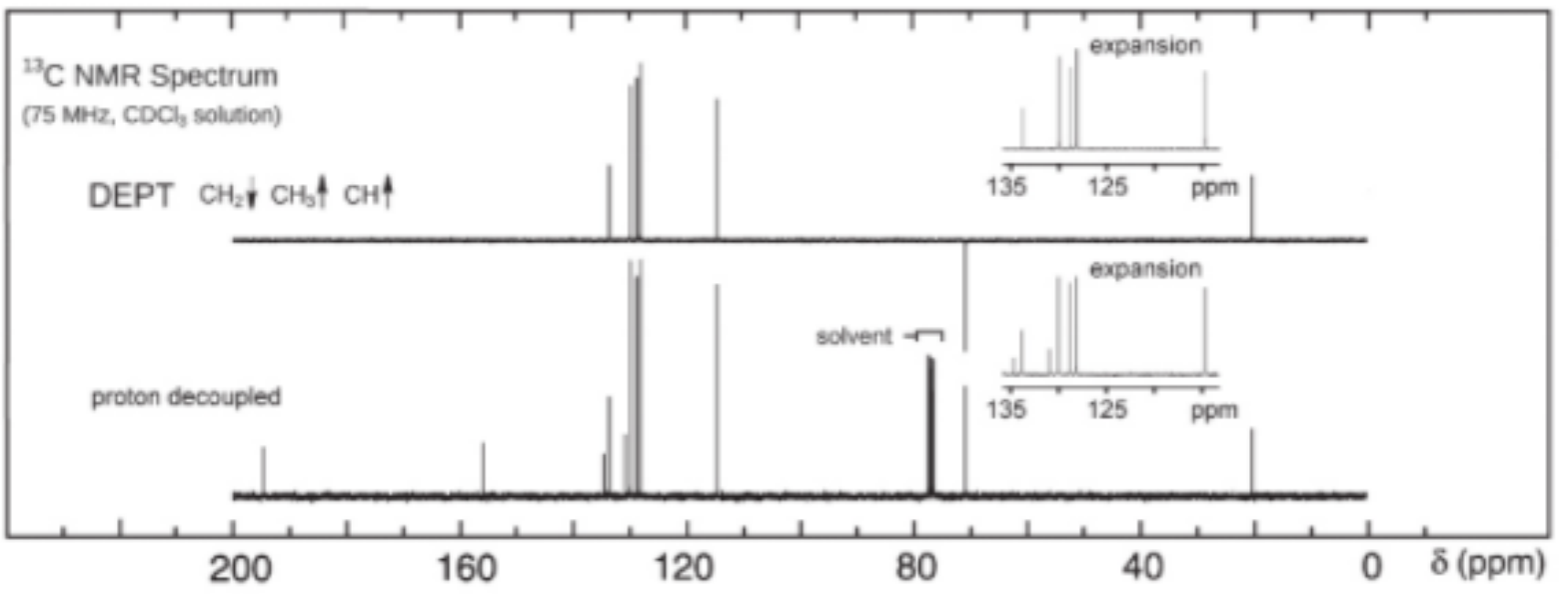


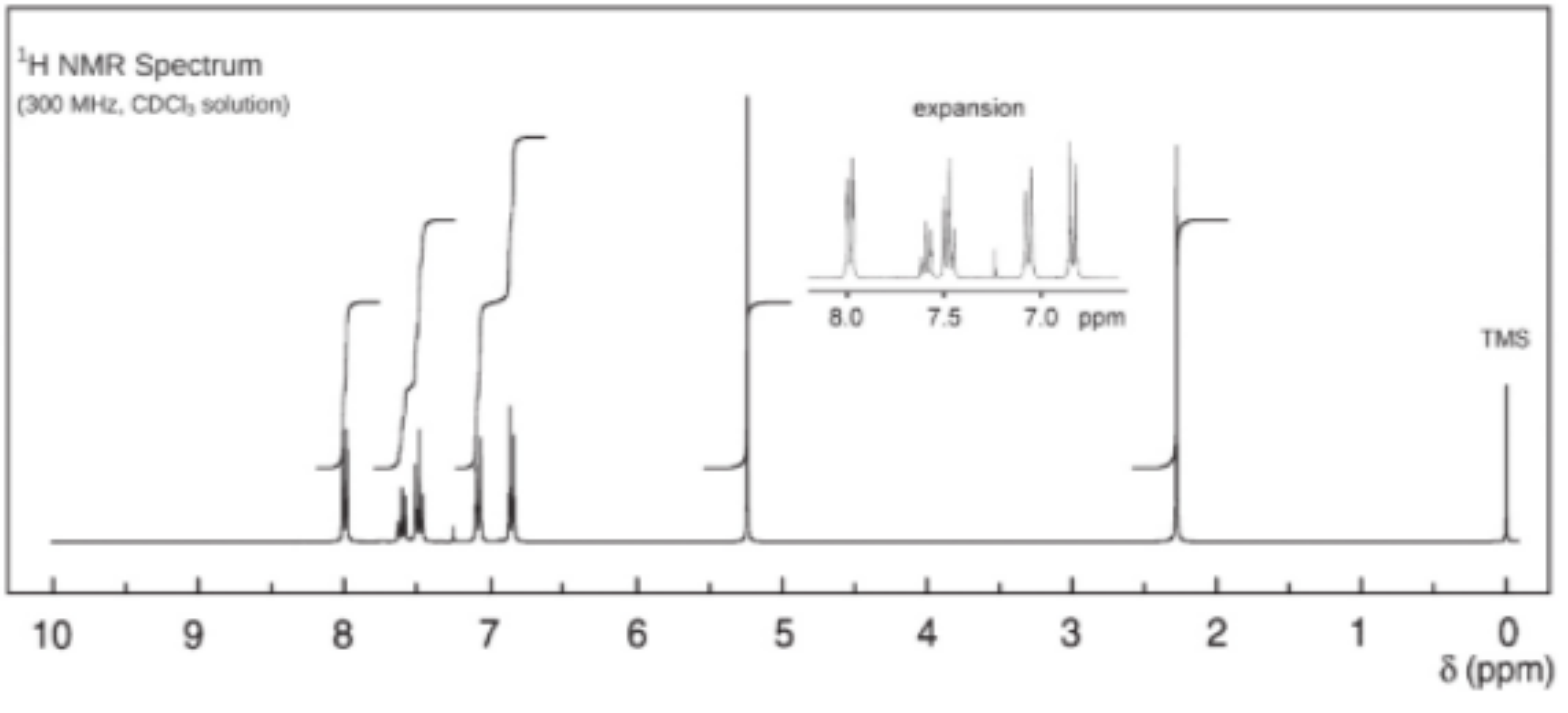
Problem 187


IR Spectrum
(thin film)
1698
4000
3000
2000
1600
1200
800
ν (cm-1)

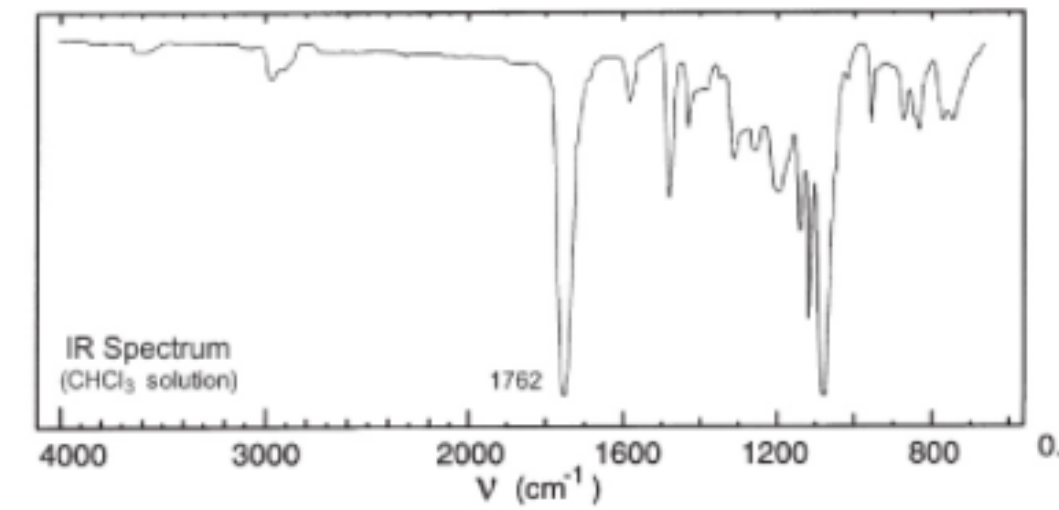

Mass Spectrum
105
77
91
M+·
226
% of base peak
C15H14O2
40
80
120
160
200
240
280
m/e

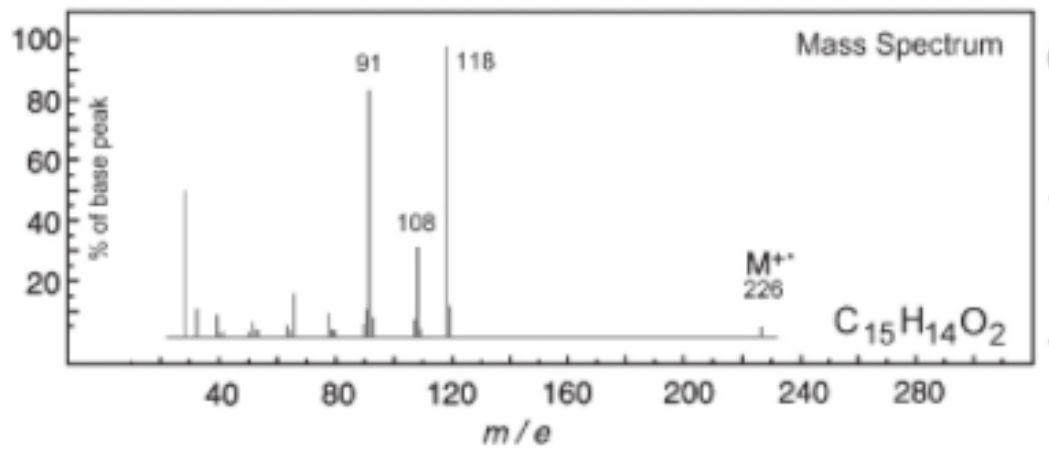

absorbance
UV spectrum
0.806 mg / 10 ml
path length : 0.2 cm
solvent : ethanol
200
250
300
350
λ (nm)

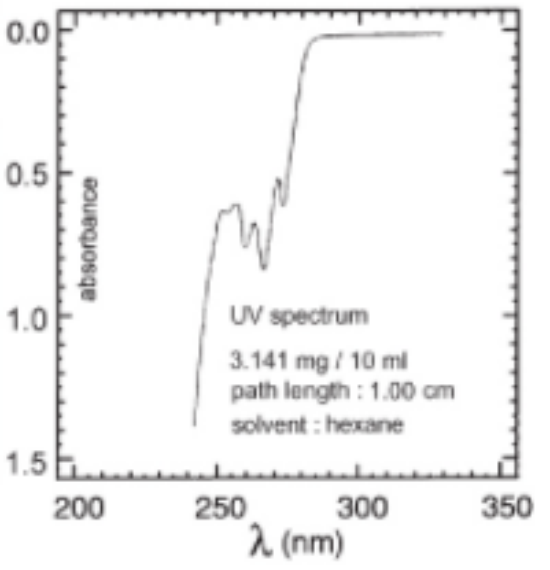

13C NMR Spectrum
(75 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
expansion
135
125
ppm
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

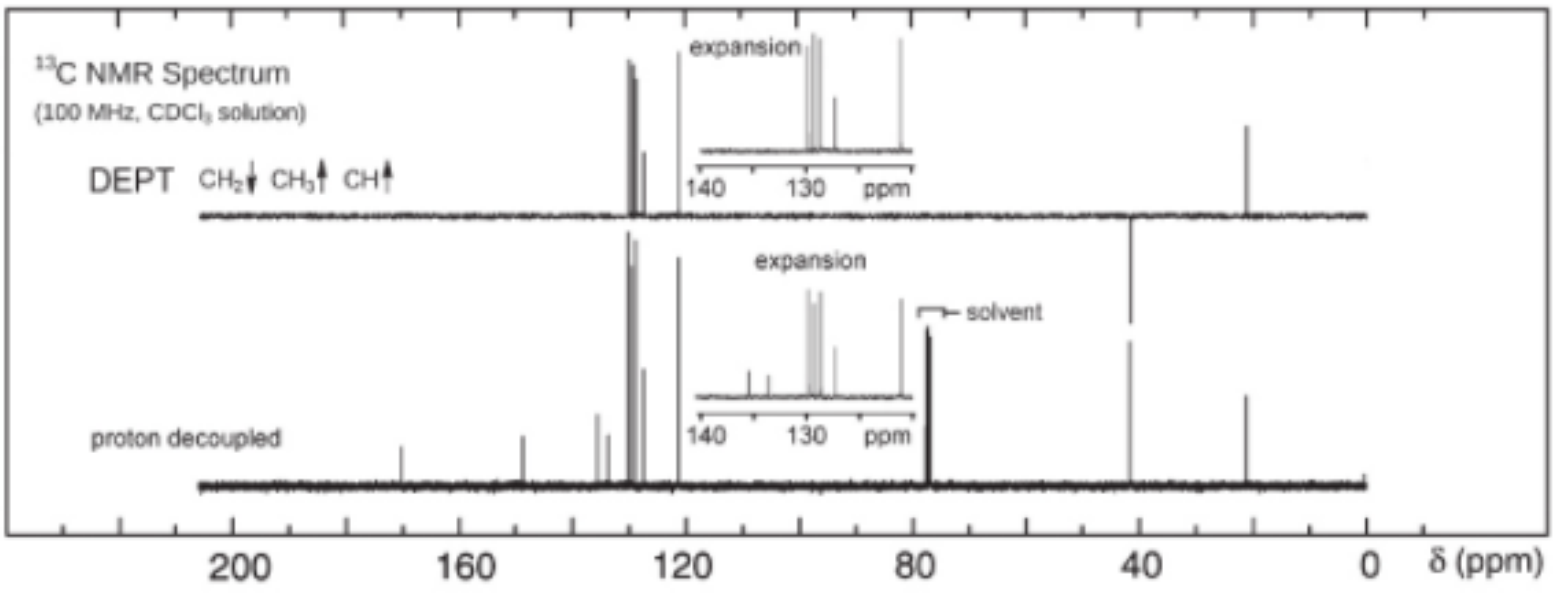

1H NMR Spectrum
(300 MHz, CDCl3 solution)
expansion
8.0
7.5
7.0
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

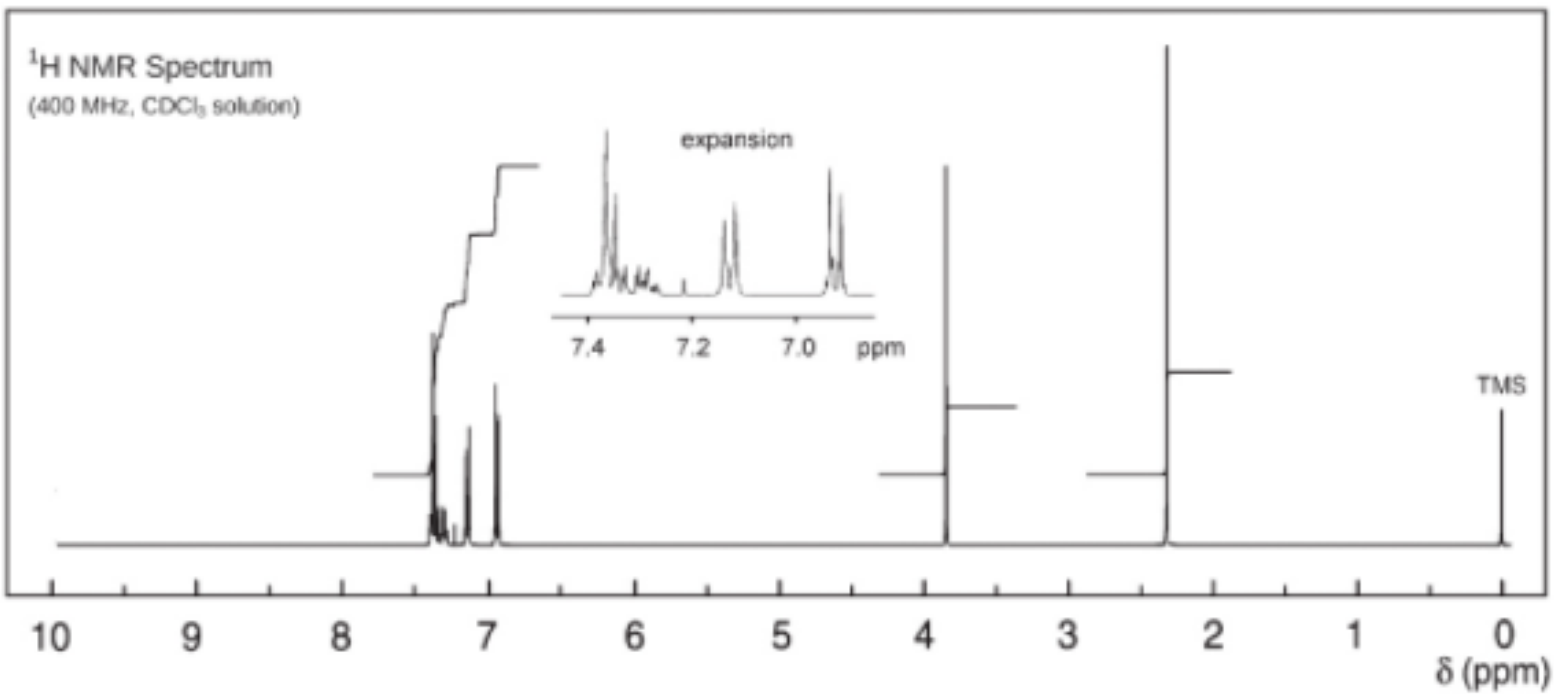
Problem 188


IR Spectrum
(CHCl3 solution)
1762
4000
3000
2000
1600
1200
800
ν (cm-1)

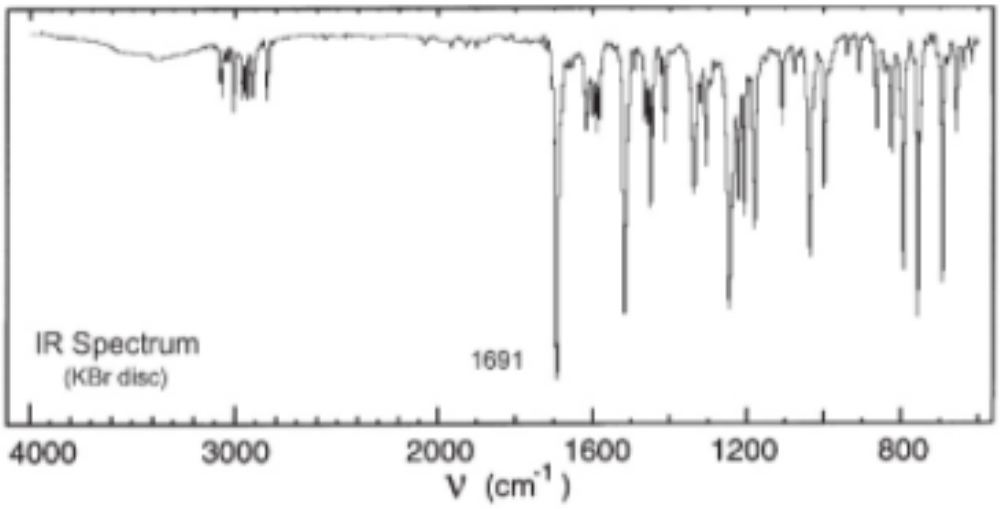

Mass Spectrum
% of base peak
91
118
108
M+·
226
C15H14O2
100
80
60
40
20
40
80
120
160
200
240
280
m/e

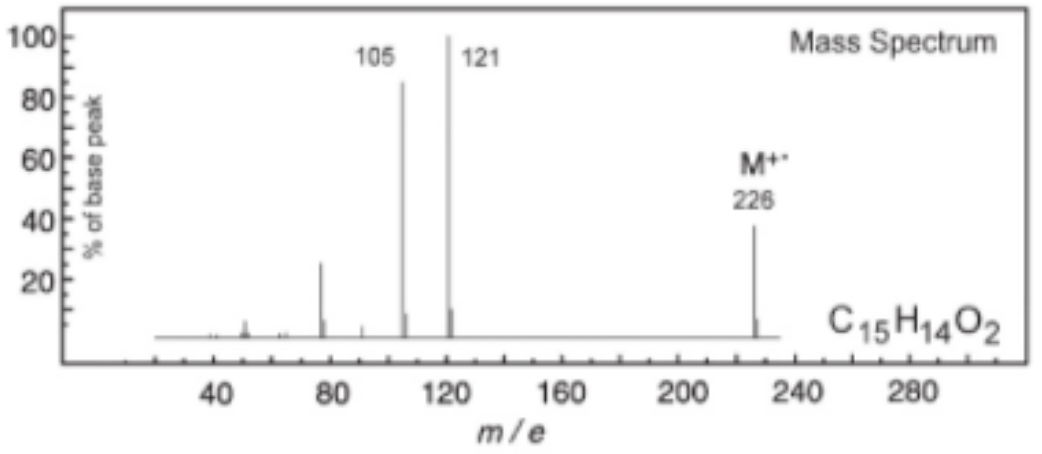

absorbance
UV spectrum
3.141 mg / 10 ml
path length : 1.00 cm
solvent : hexane
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
expansion
140
130
ppm
expansion
solvent
proton decoupled
140
130
ppm
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.4
7.2
7.0
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

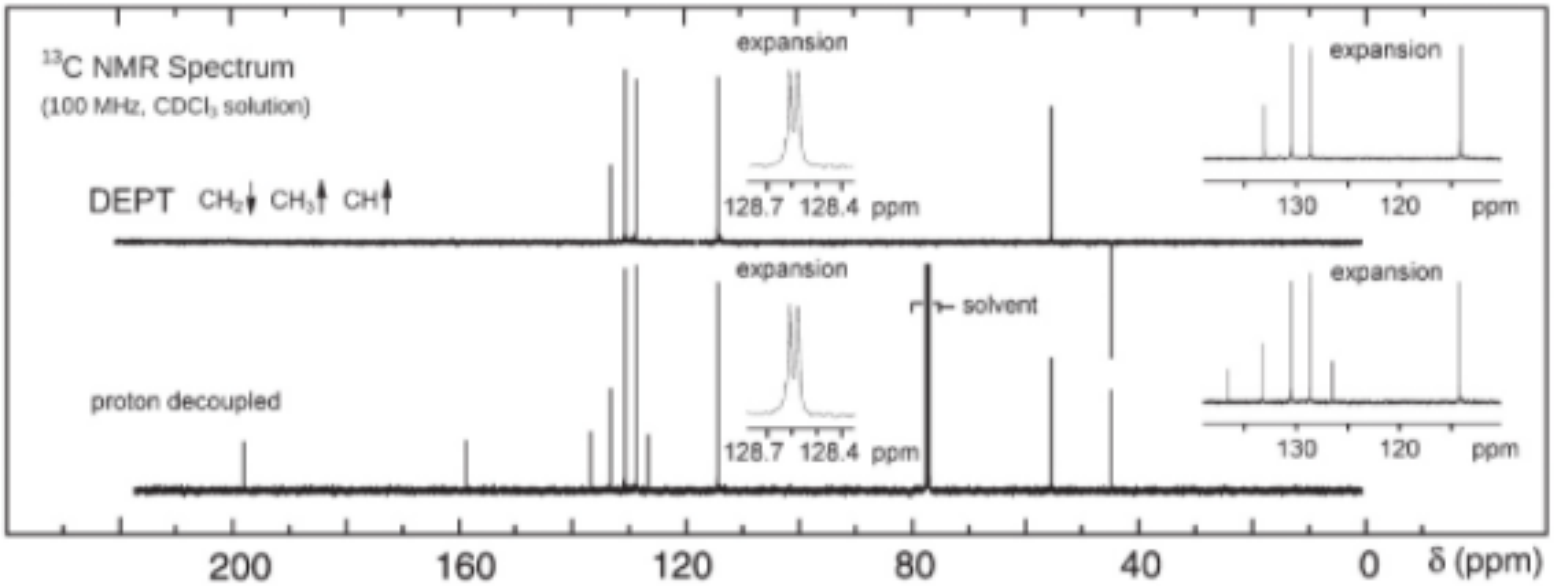
Problem 189

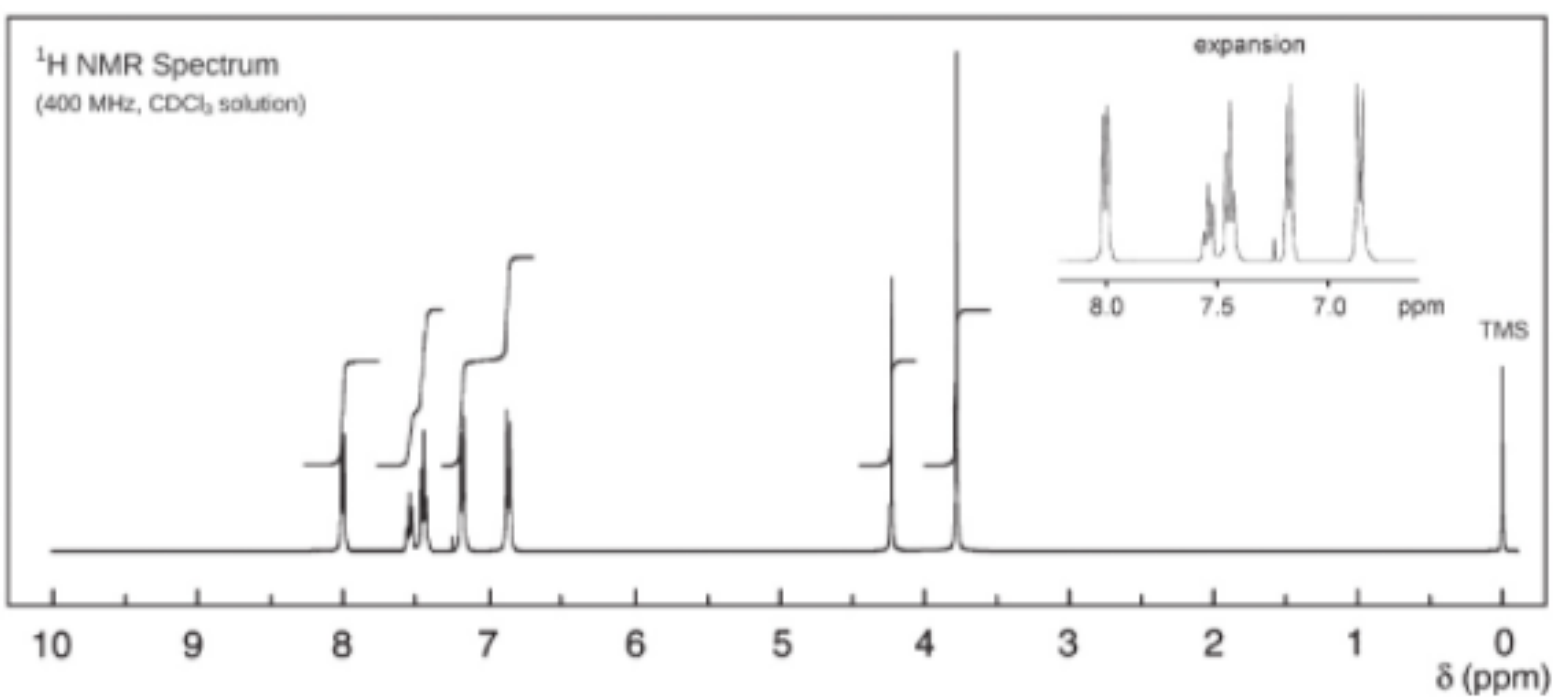




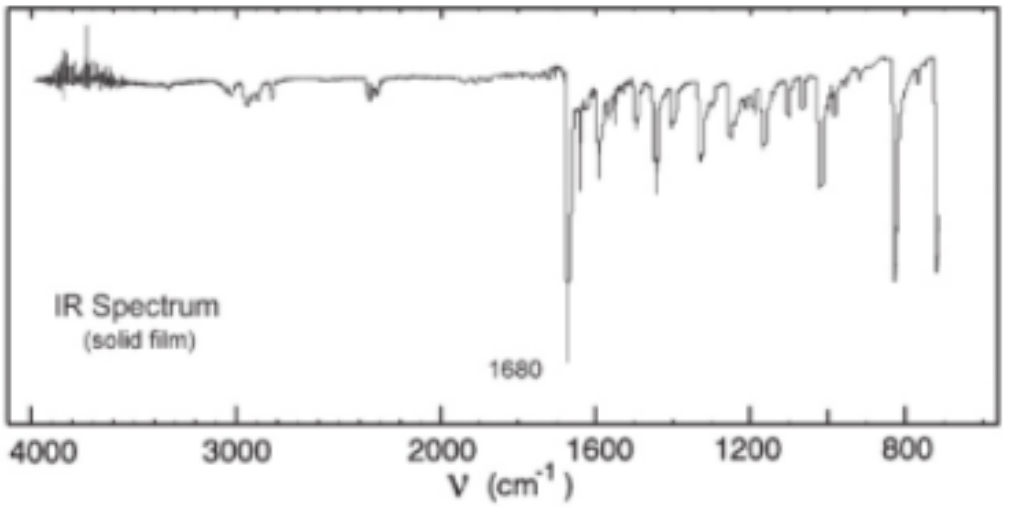
UV Spectrum

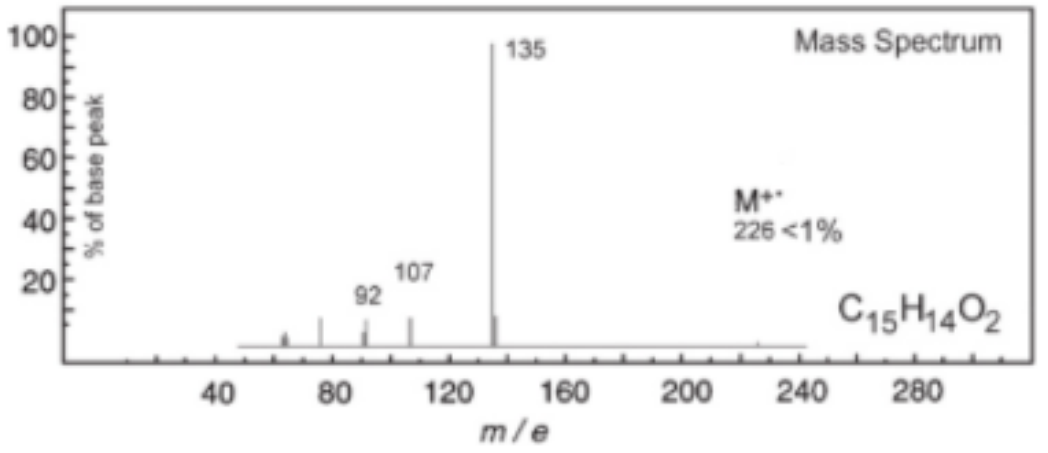
$\log_{10}\varepsilon > 4$





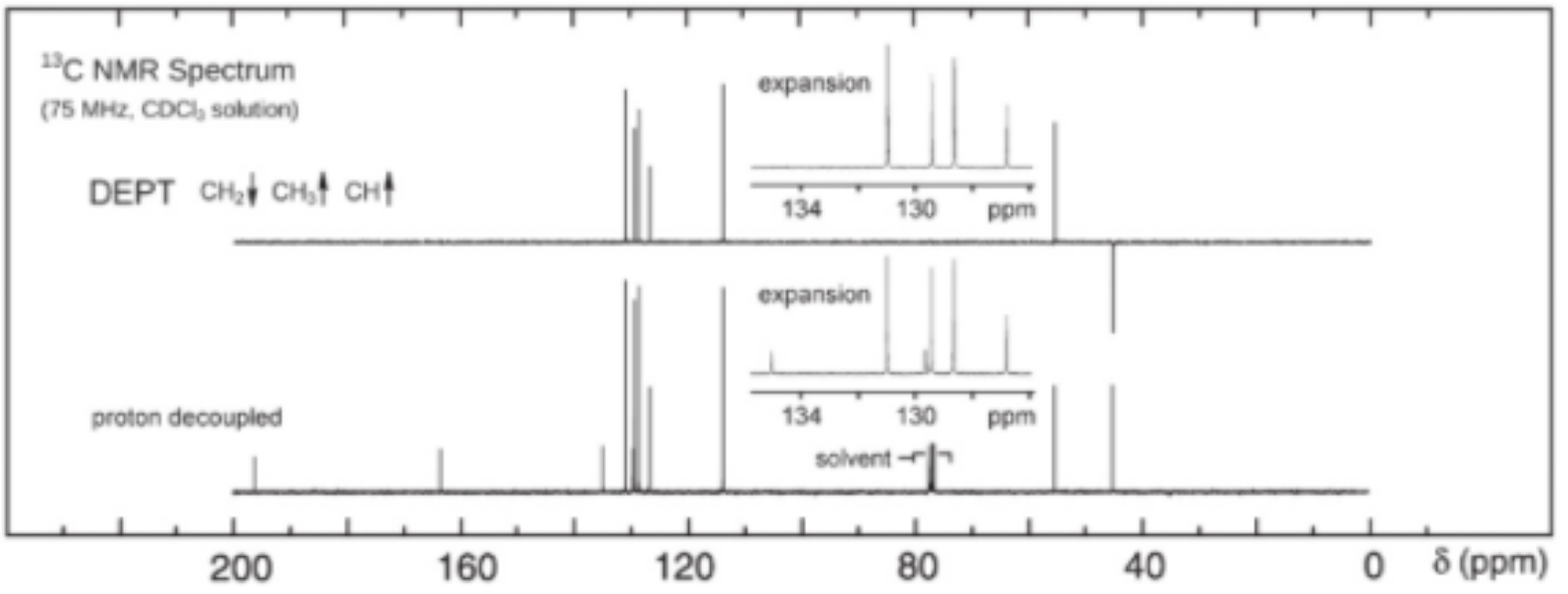
Problem 190

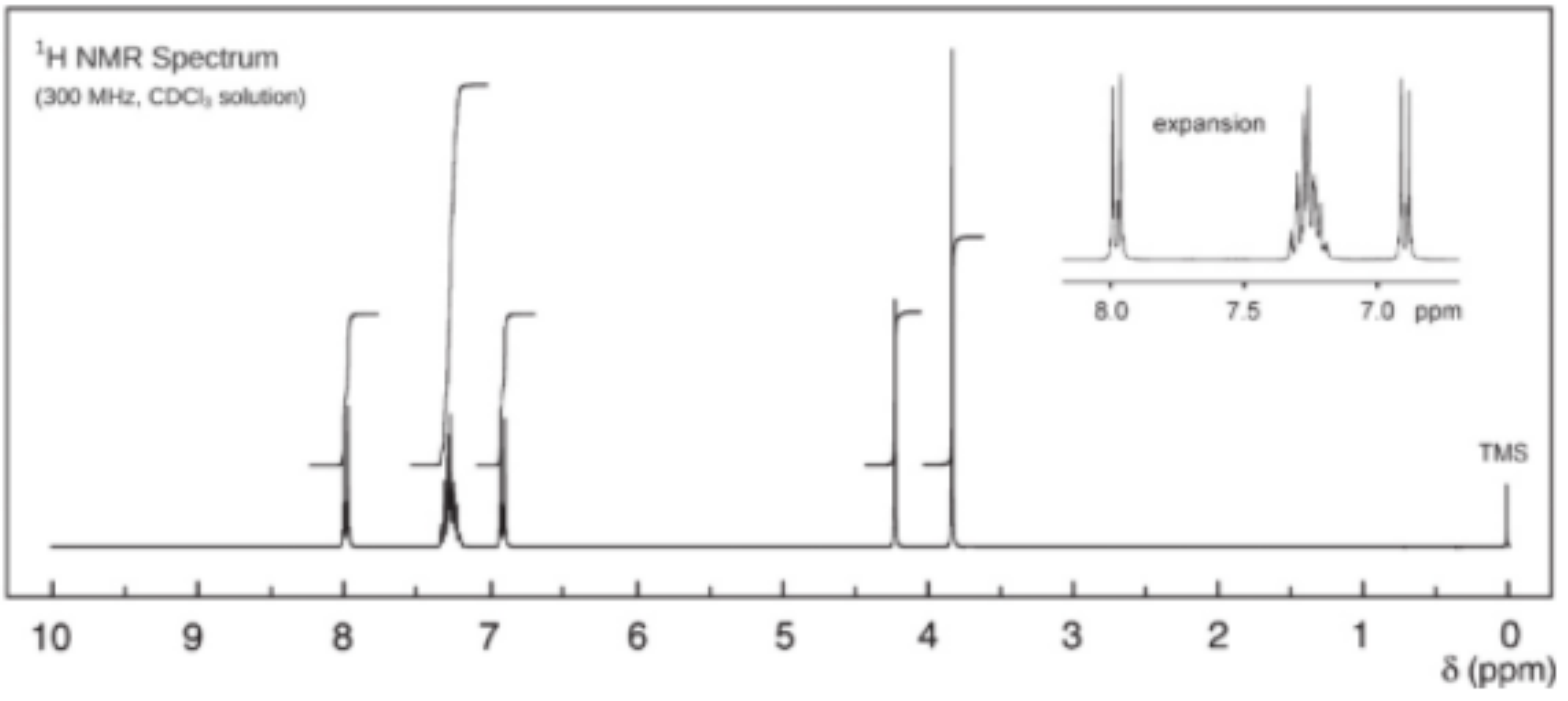




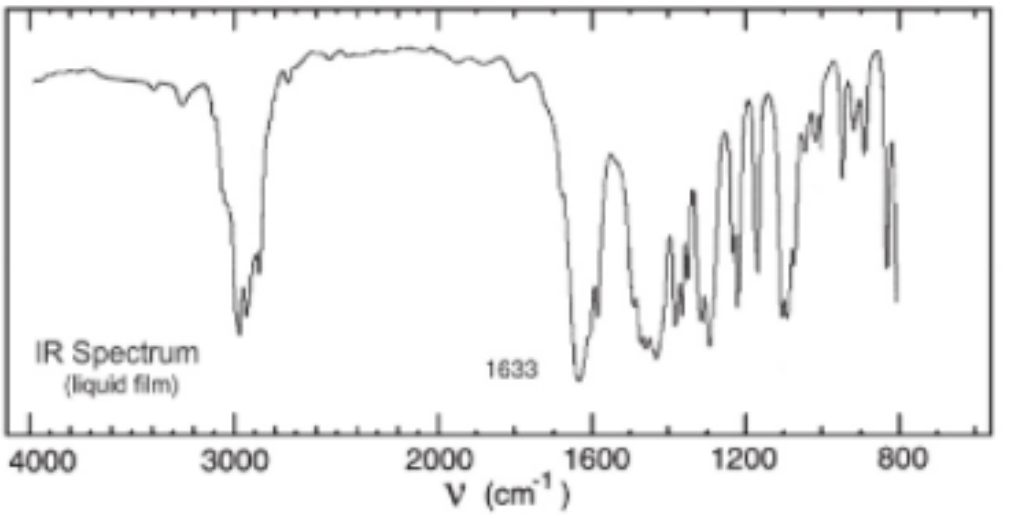
UV Spectrum

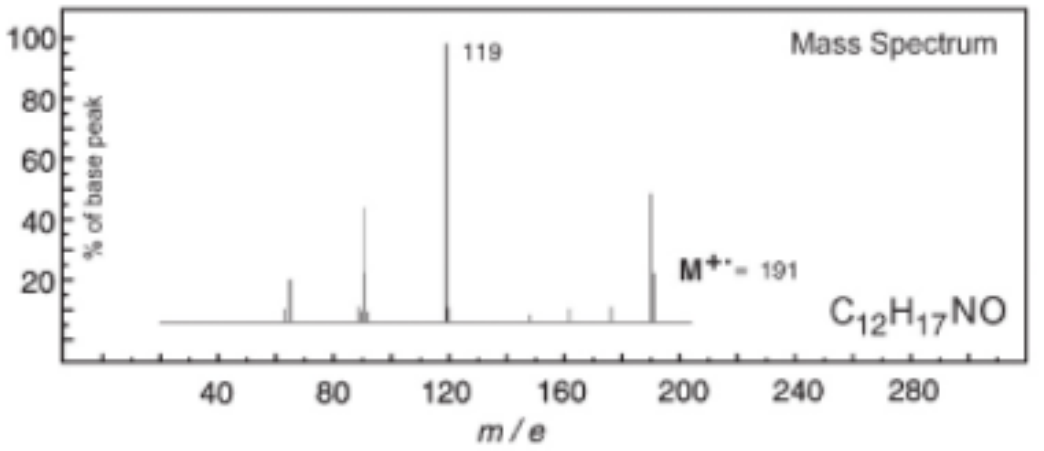
$\log_{10}\varepsilon > 4$





Problem 191



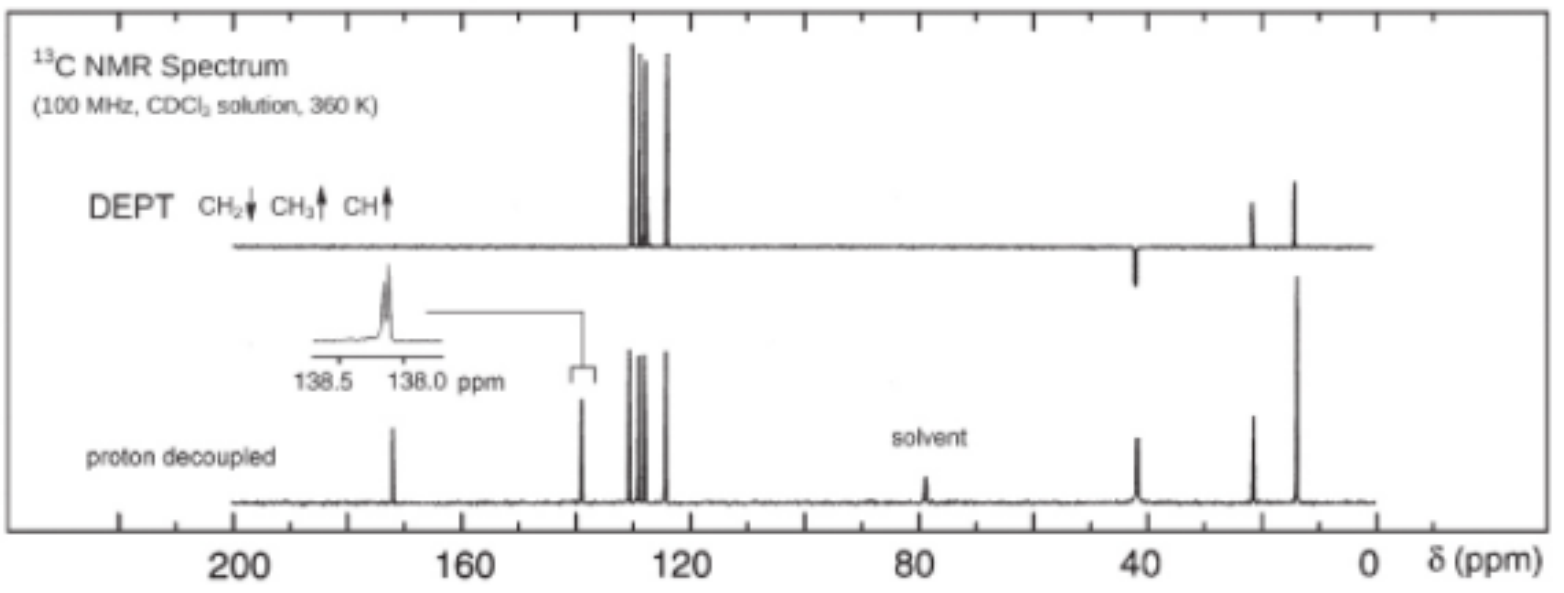


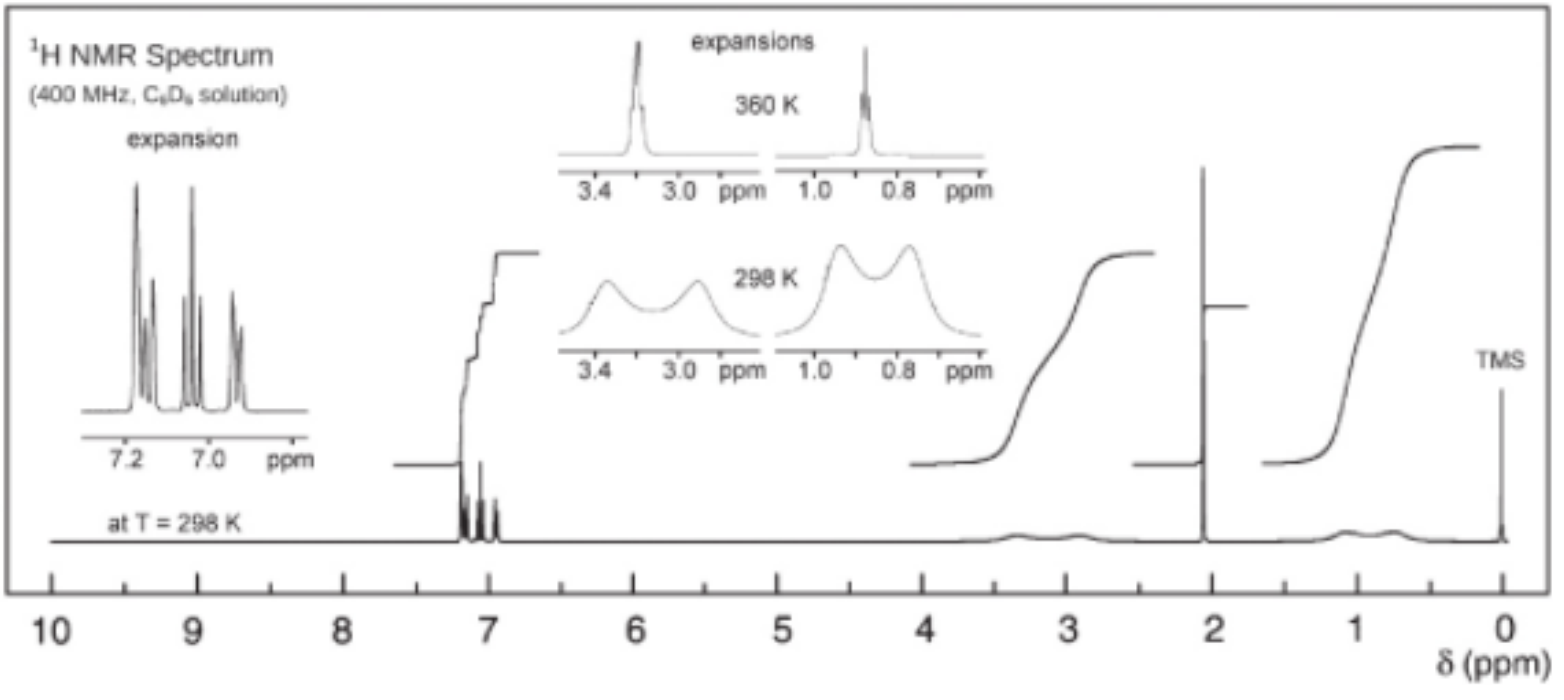
UV Spectrum

λ_{max} 246 nm ($\log_{10}\varepsilon$ 3.7)

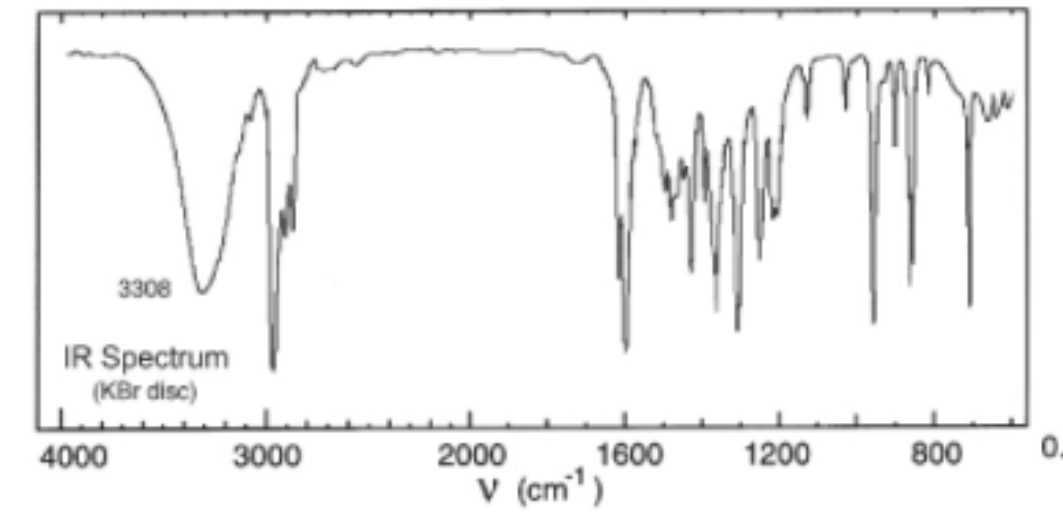
λ_{max} 273 nm ($\log_{10}\varepsilon$ 2.6)

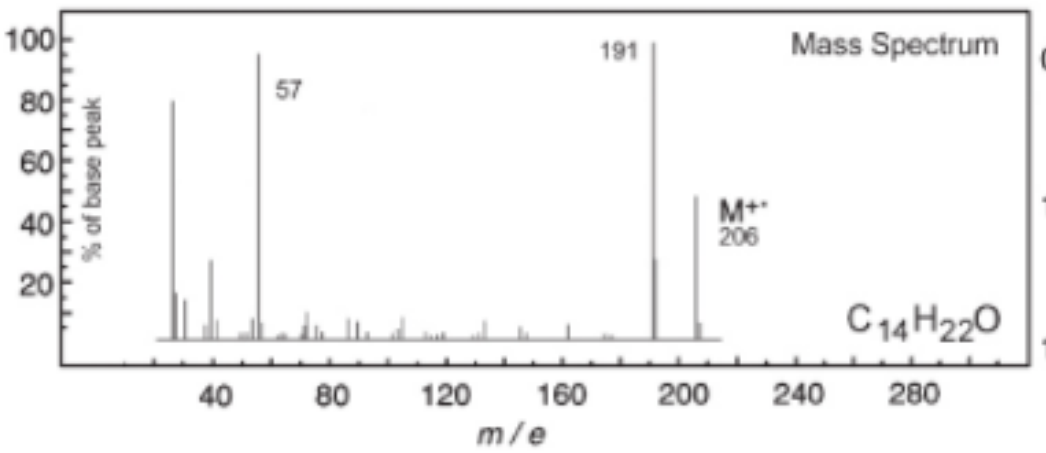
solvent : ethanol

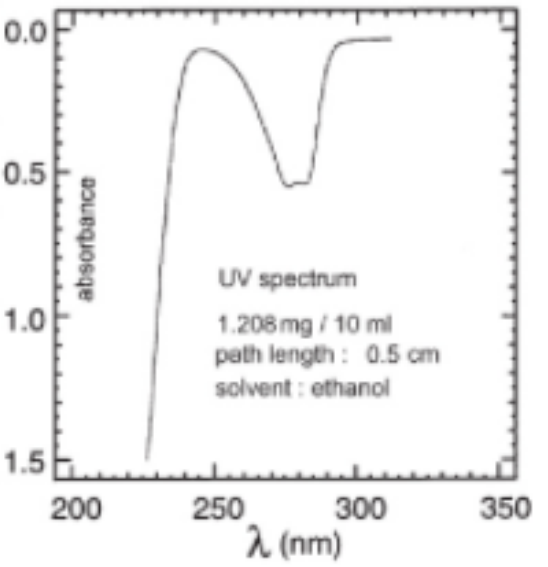


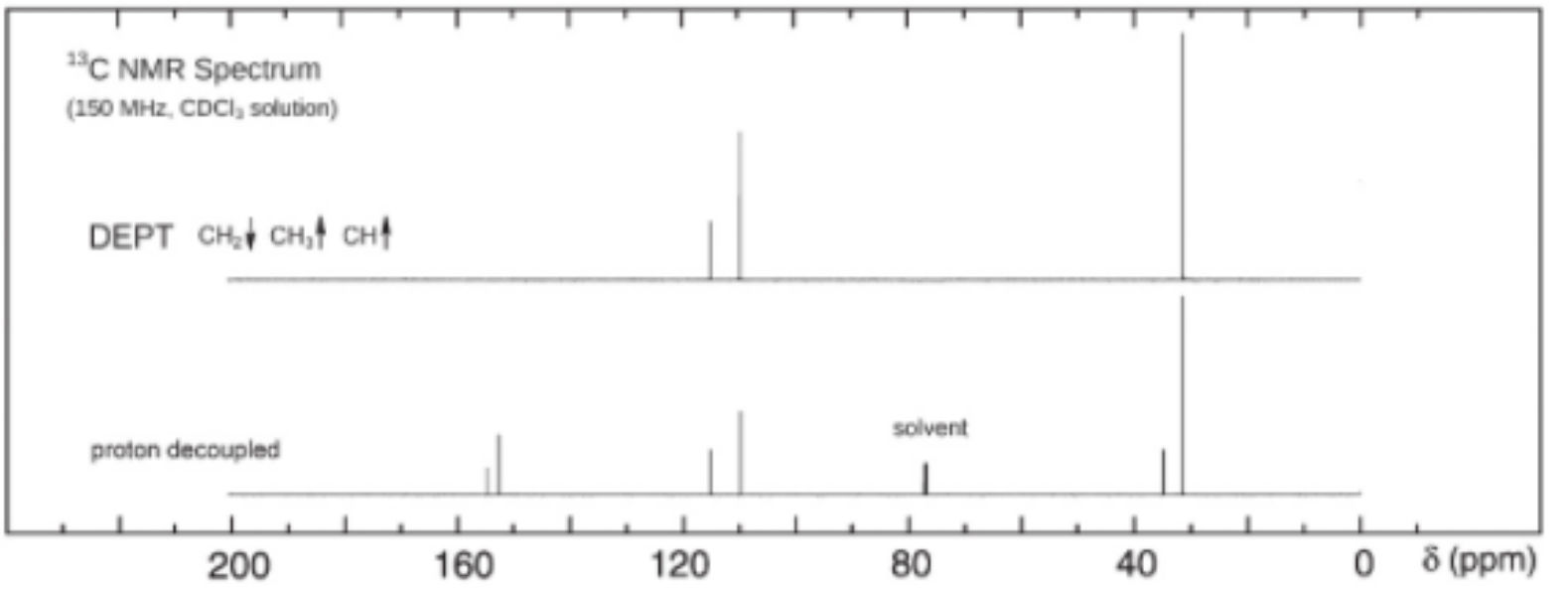


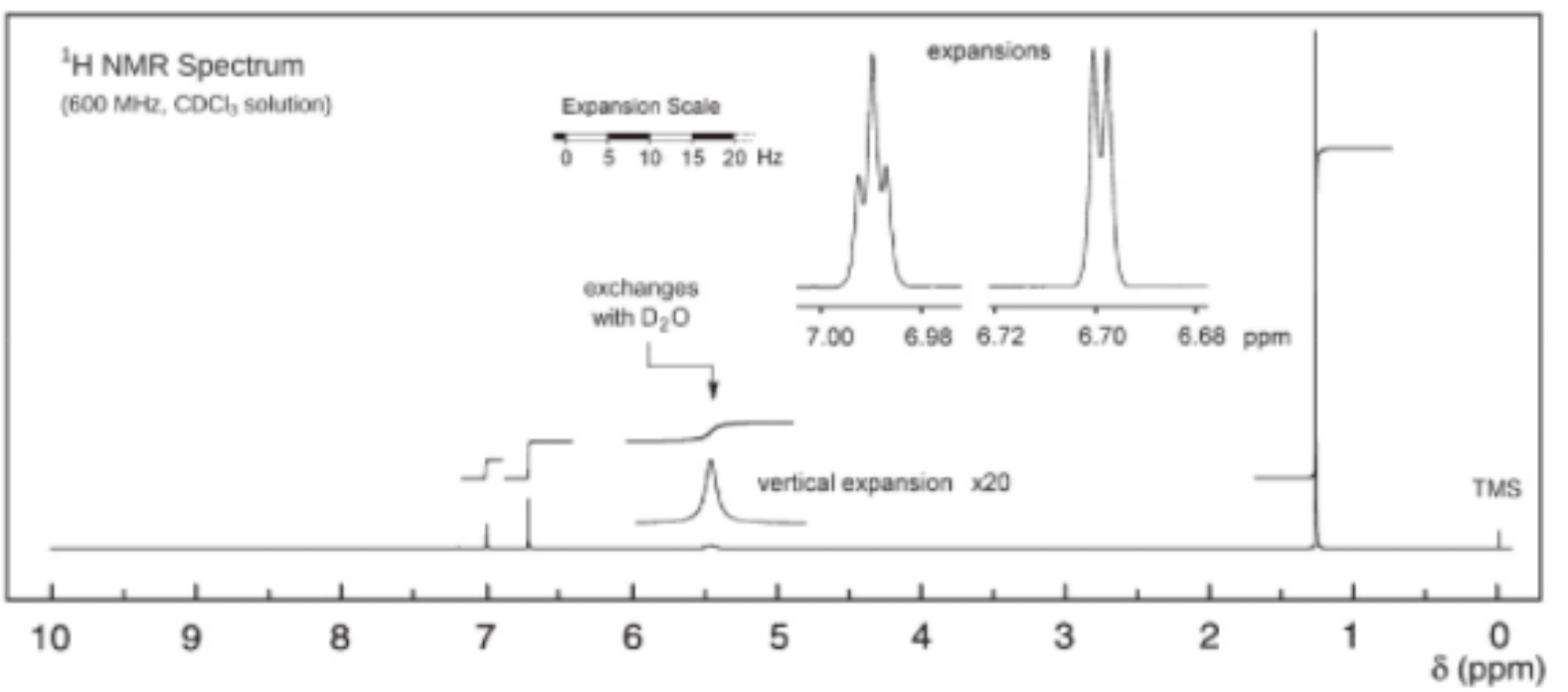
Problem 192


3308
IR Spectrum
(KBr disc)
4000
3000
2000
1600
1200
800
ν (cm-1)

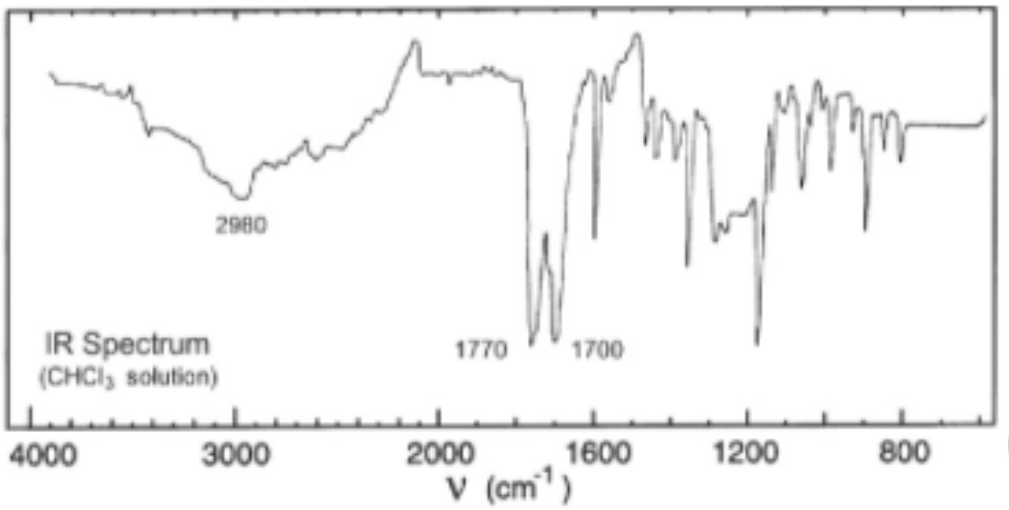

Mass Spectrum
% of base peak
100
80
60
40
20
57
191
M+·
206
C14H22O
40
80
120
160
200
240
280
m/e

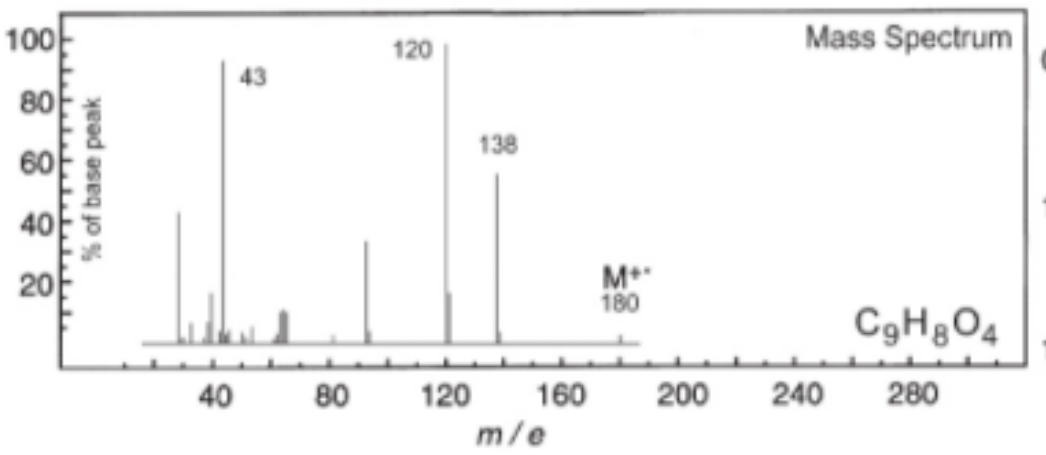

absorbance
0.0
0.5
1.0
1.5
UV spectrum
1.208 mg / 10 ml
path length : 0.5 cm
solvent : ethanol
200
250
300
350
λ (nm)

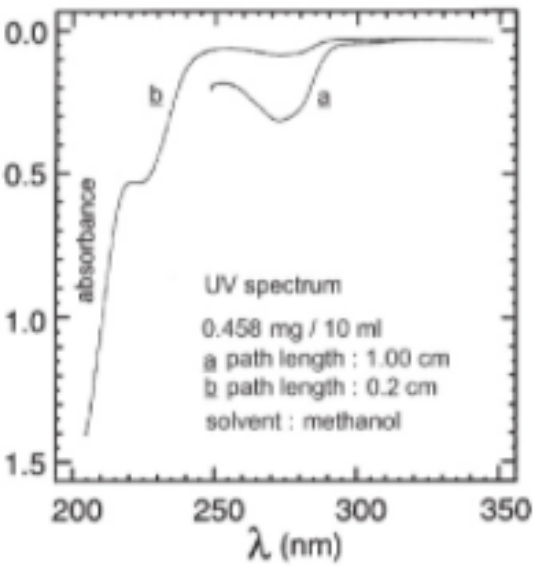

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

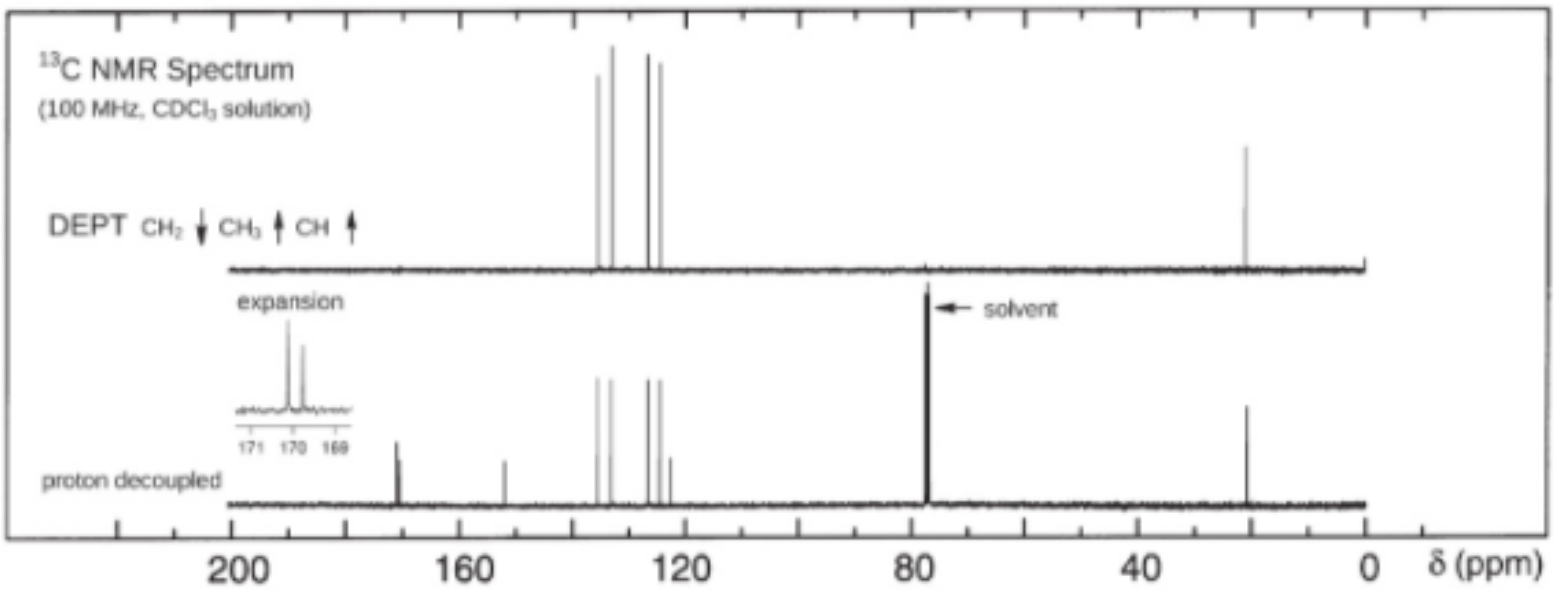

1H NMR Spectrum
(600 MHz, CDCl3 solution)
Expansion Scale
0 5 10 15 20 Hz
expansions
exchanges
with D2O
7.00
6.98
6.72
6.70
6.68
ppm
vertical expansion x20
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

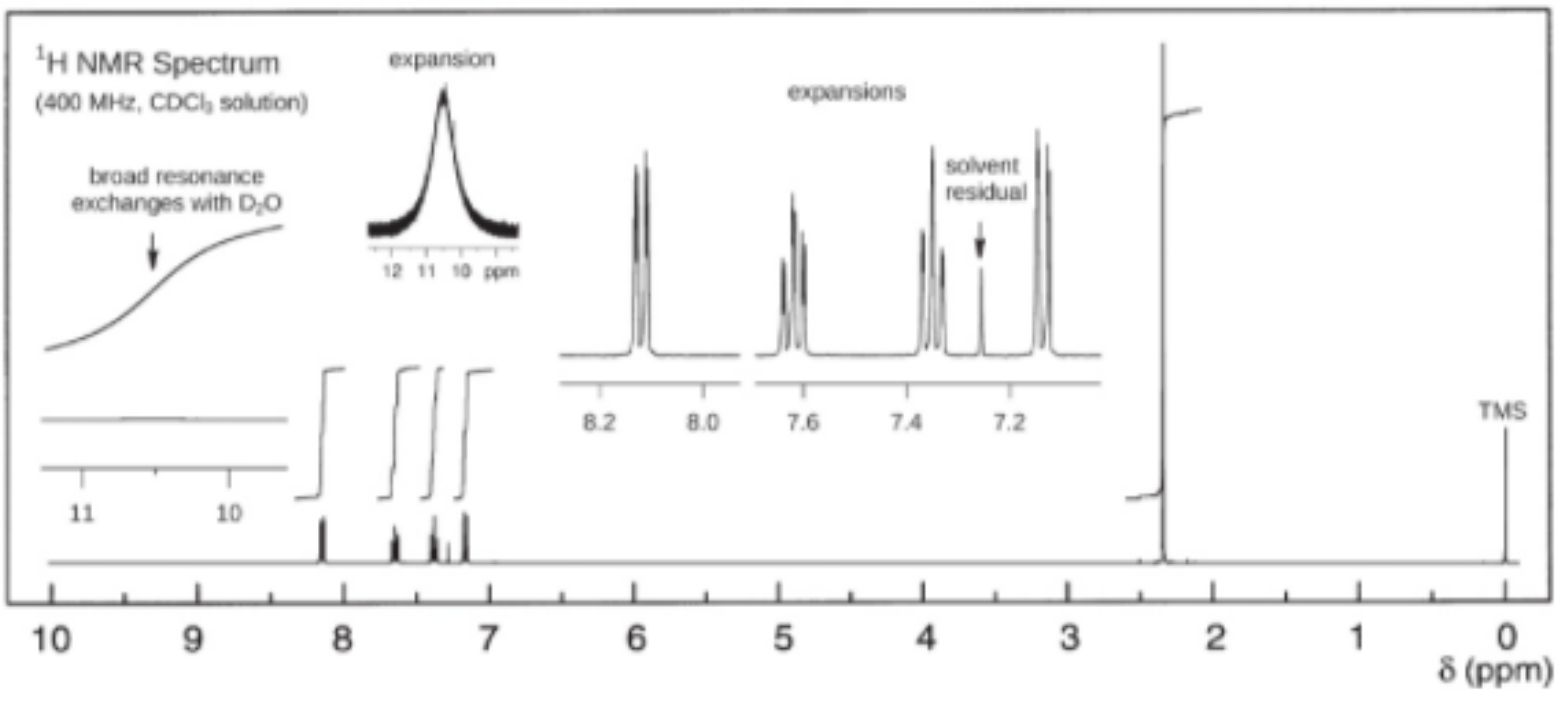
Problem 193


2980
IR Spectrum
($CHCl_3$ solution)
1770
1700
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

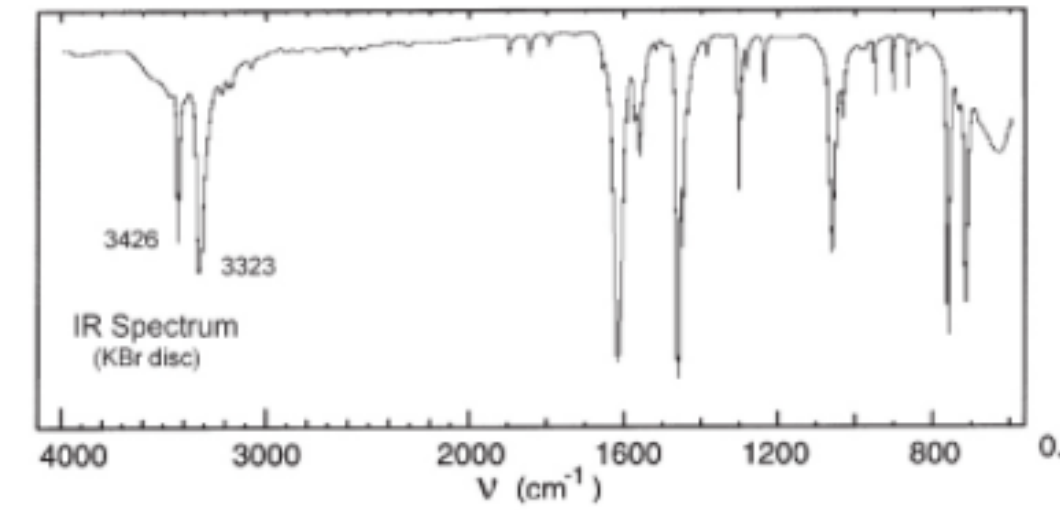

Mass Spectrum
% of base peak
100
80
60
40
20
43
120
138
M+·
180
$C_9H_8O_4$
40
80
120
160
200
240
280
m / e

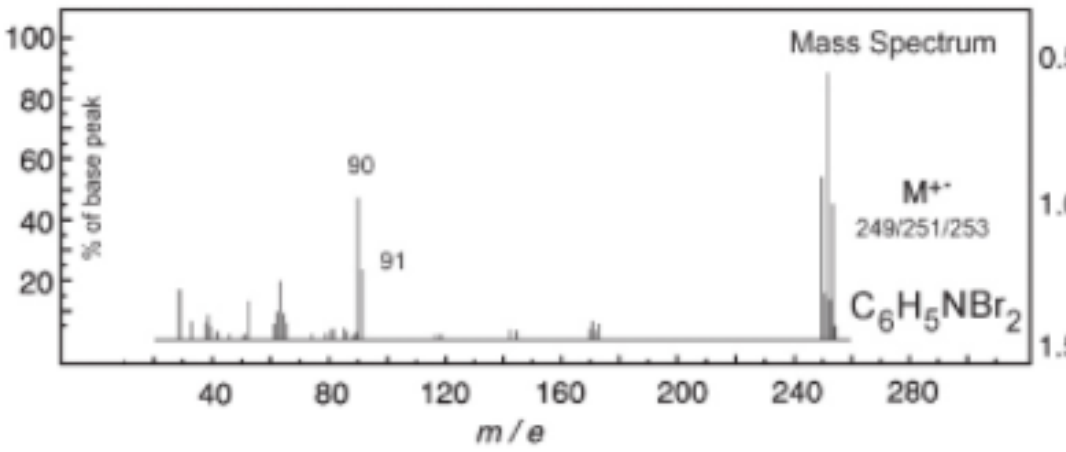

absorbance
0.0
0.5
1.0
1.5
b
a
UV spectrum
0.458 mg / 10 ml
a path length : 1.00 cm
b path length : 0.2 cm
solvent : methanol
200
250
300
350
λ (nm)

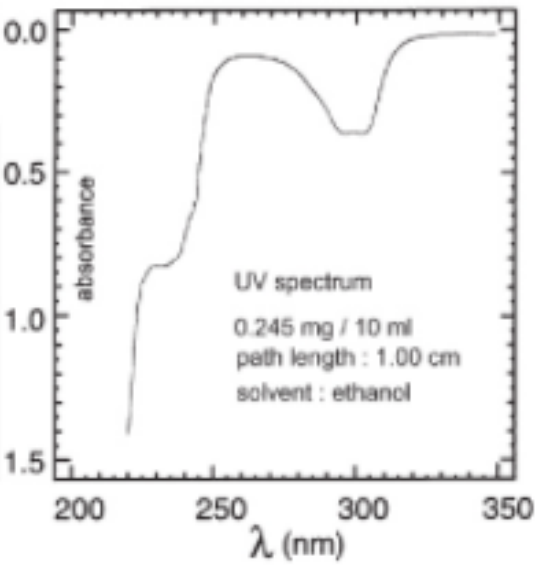

^{13}C NMR Spectrum
(100 MHz, $CDCl_3$ solution)
DEPT CH_2 ↓ CH_3 ↑ CH ↑
expansion
171 170 169
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

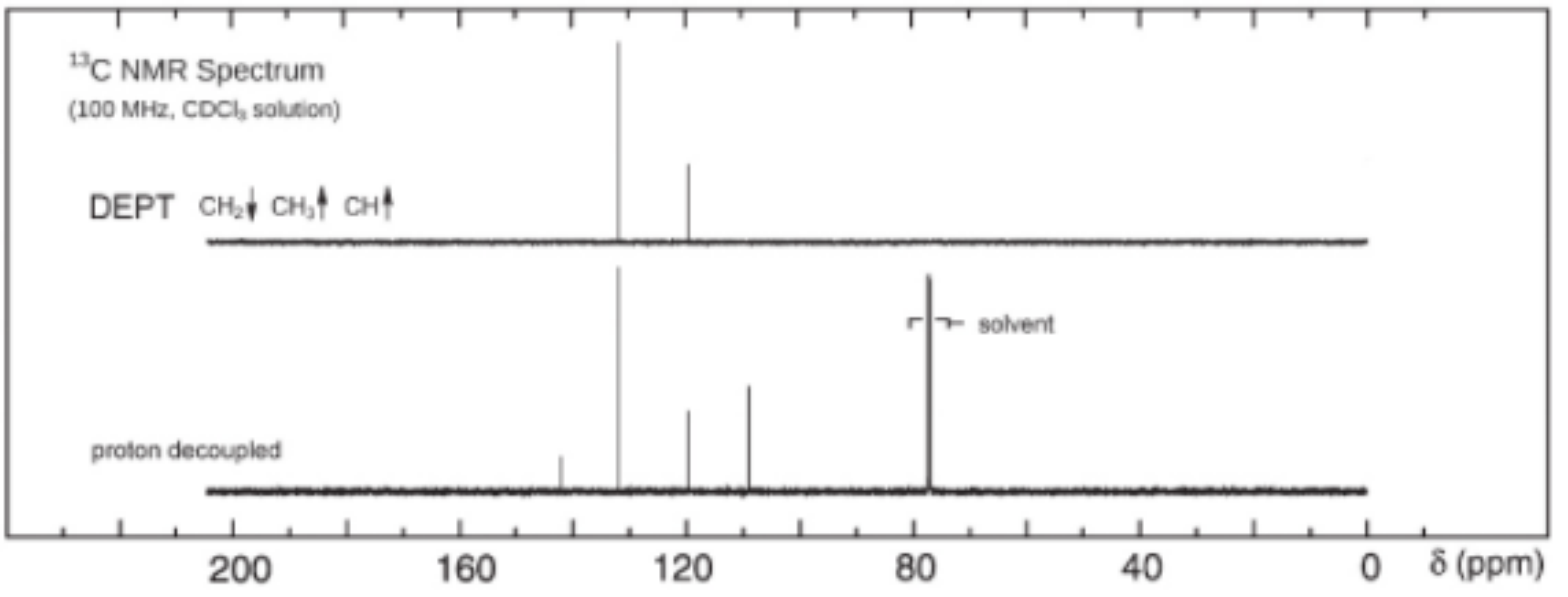

^{1}H NMR Spectrum
(400 MHz, $CDCl_3$ solution)
broad resonance
exchanges with D_2O
expansion
12 11 10 ppm
expansions
solvent
residual
8.2
8.0
7.6
7.4
7.2
11
10
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

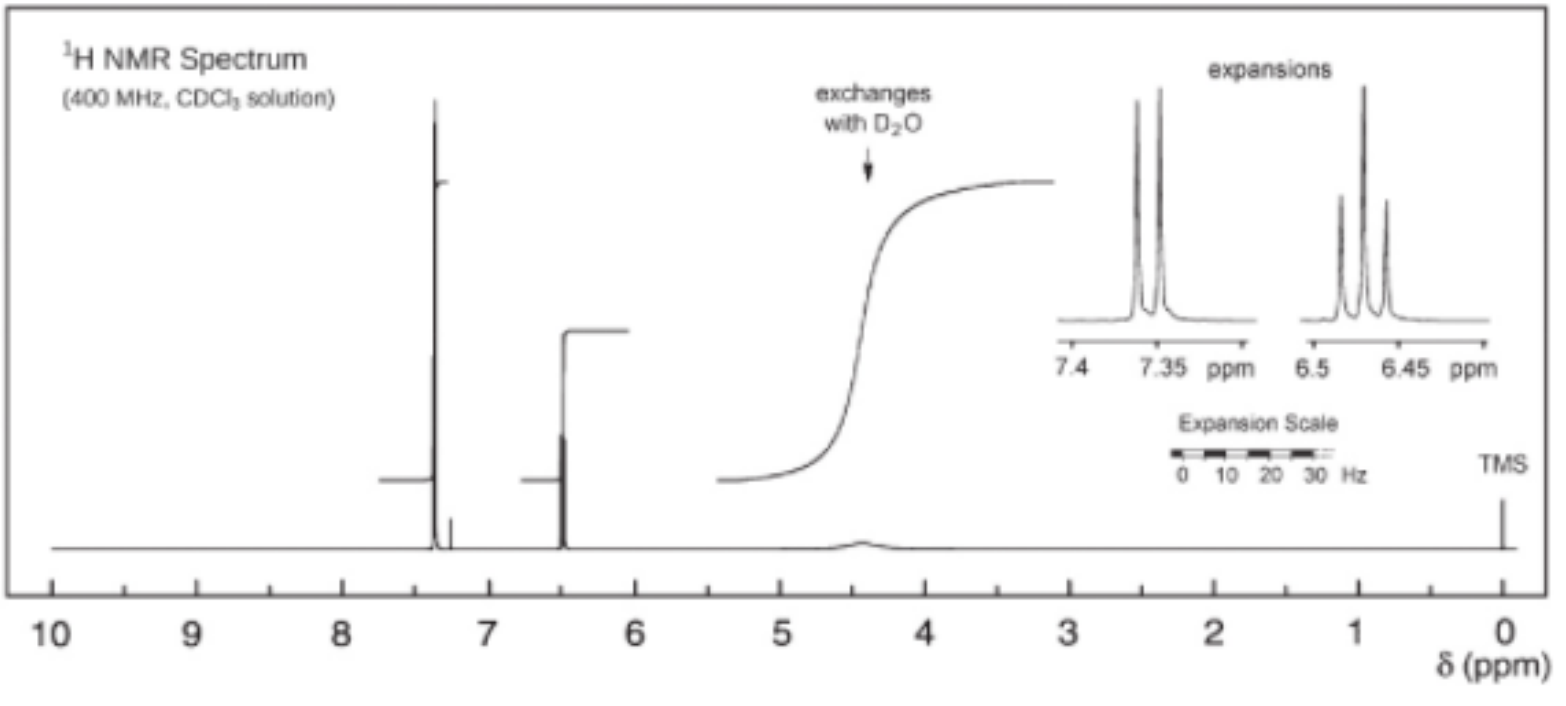
Problem 194


3426
3323
IR Spectrum
(KBr disc)
4000
3000
2000
1600
1200
800
ν (cm-1)

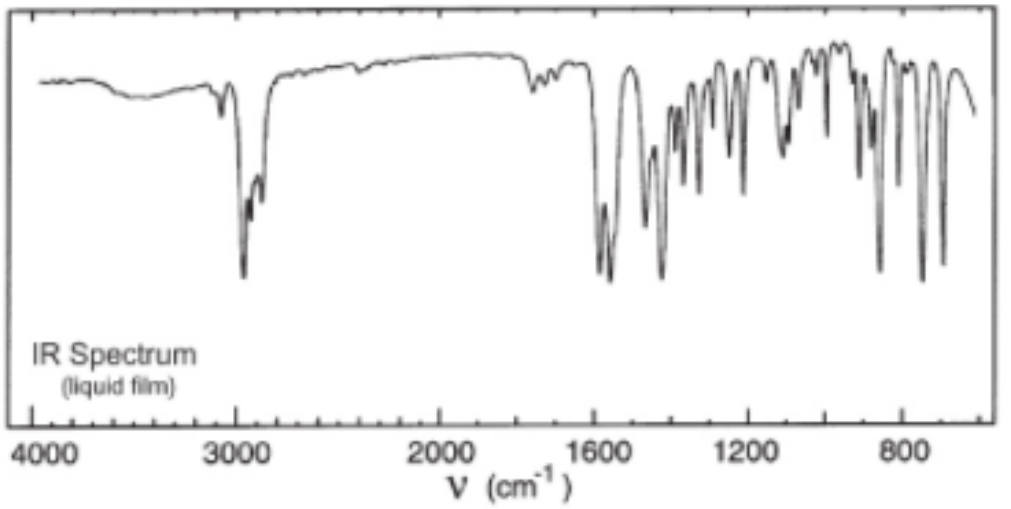

Mass Spectrum
% of base peak
100
80
60
40
20
90
91
M+·
249/251/253
C6H5NBr2
40
80
120
160
200
240
280
m / e

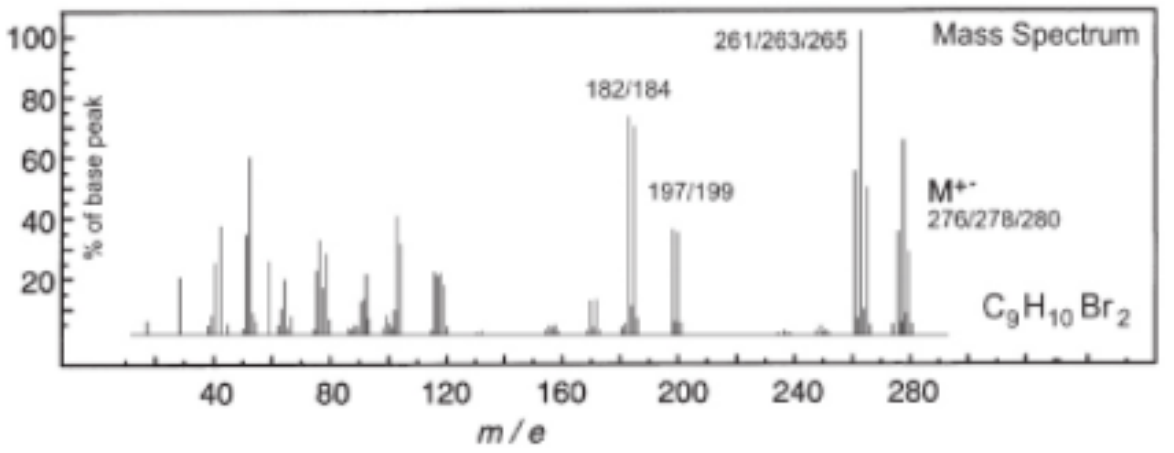

absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.245 mg / 10 ml
path length : 1.00 cm
solvent : ethanol
200
250
300
350
λ (nm)

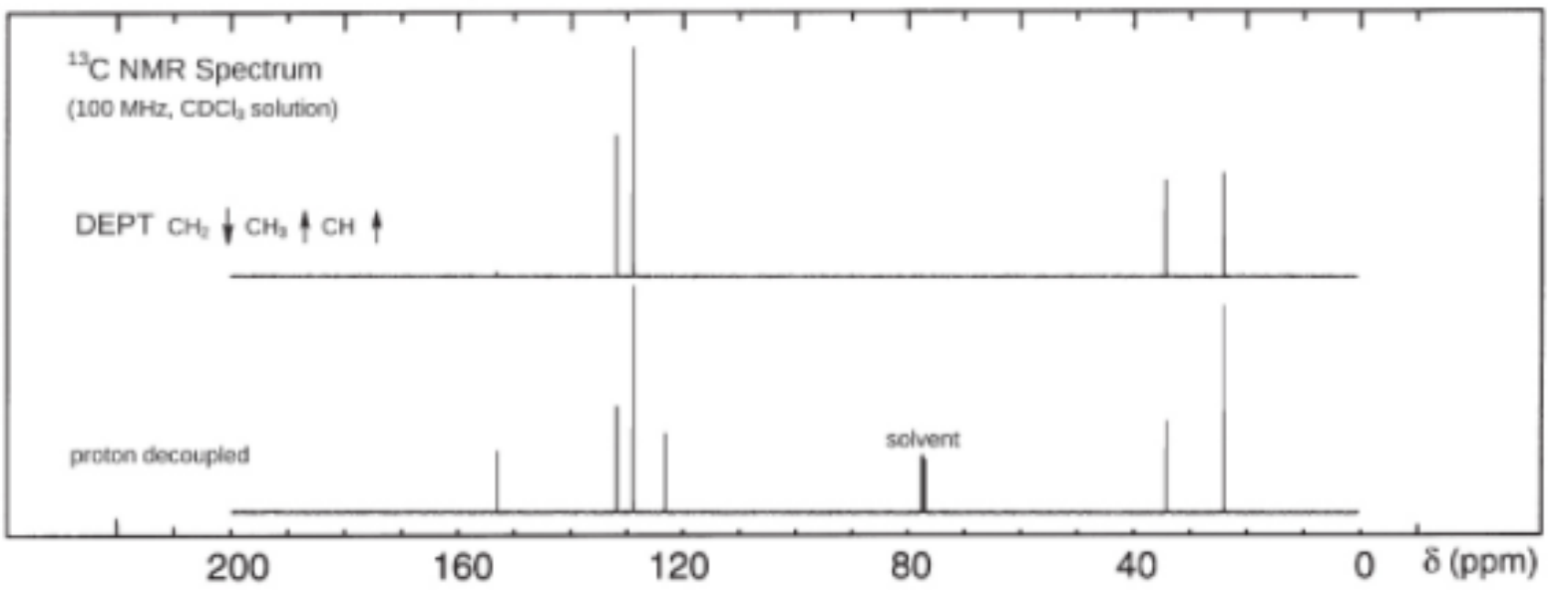

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

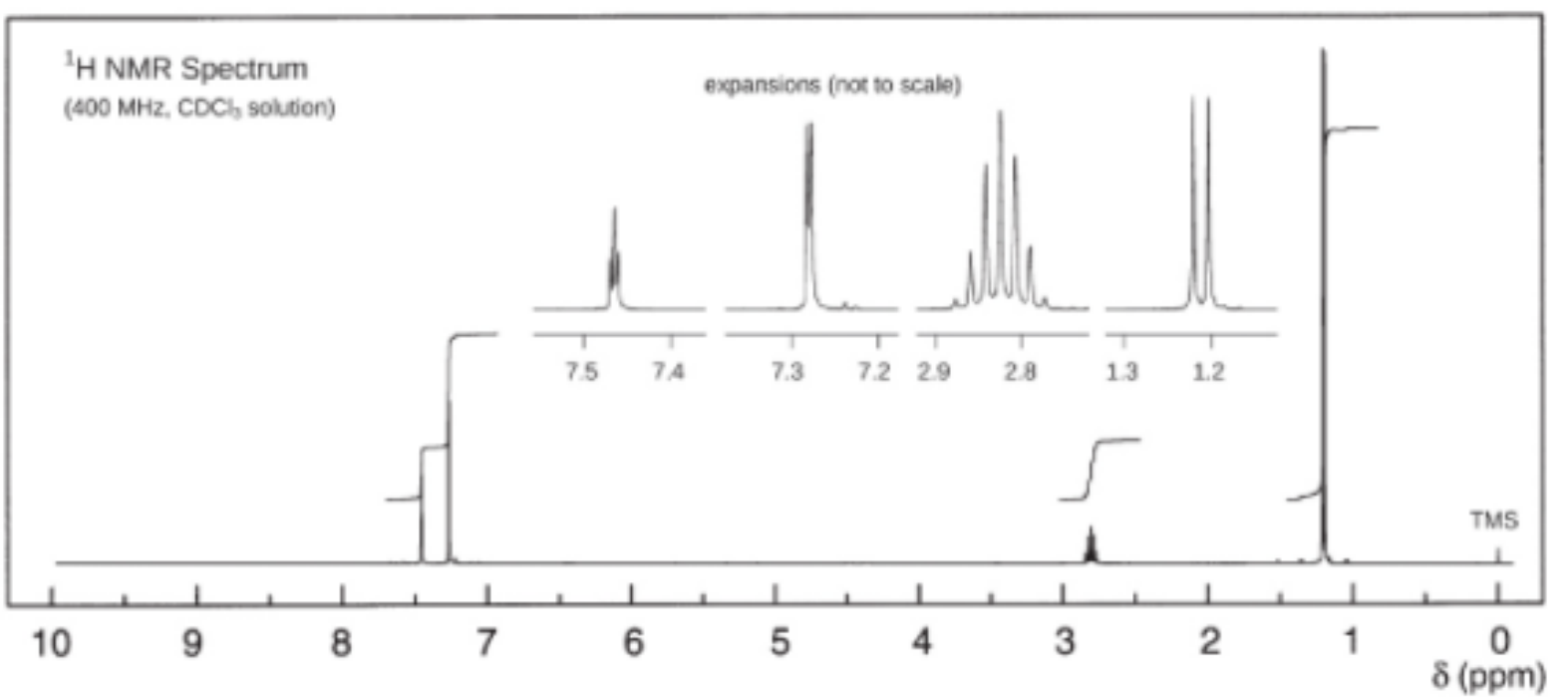

1H NMR Spectrum
(400 MHz, CDCl3 solution)
exchanges
with D2O
expansions
7.4
7.35 ppm
6.5
6.45 ppm
Expansion Scale
0 10 20 30 Hz
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

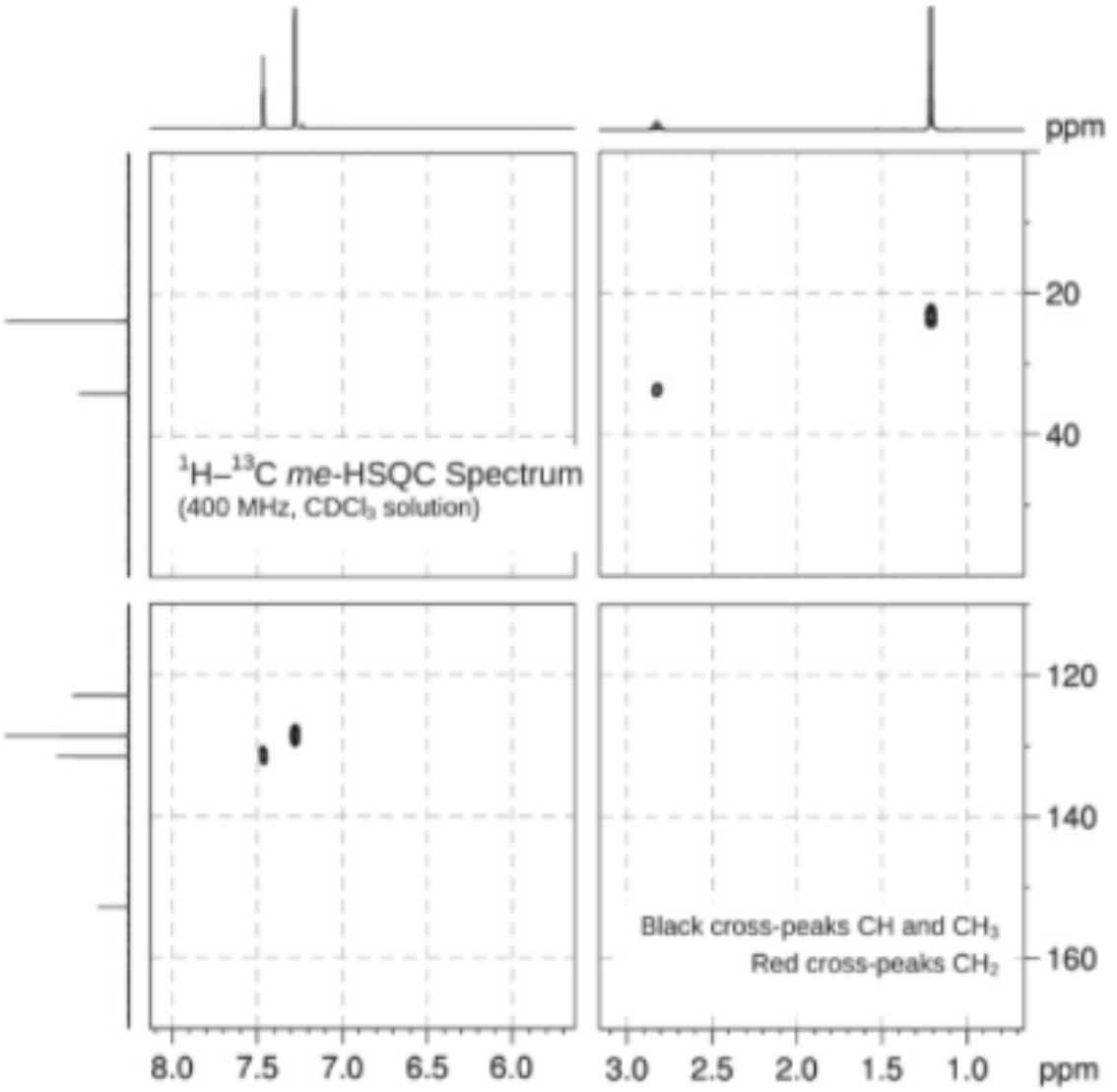
Problem 195


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
261/263/265
182/184
197/199
M+·
276/278/280
C9H10Br2
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m/e

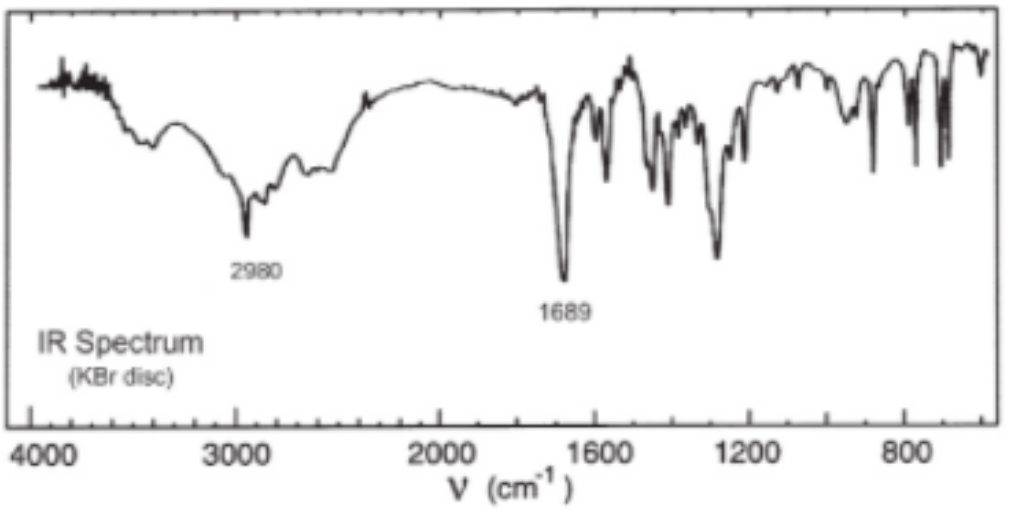

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

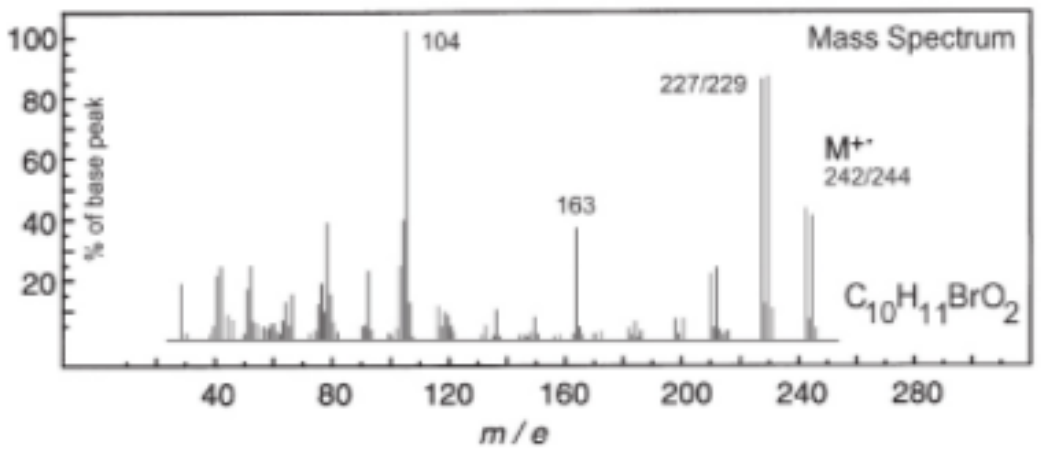

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions (not to scale)
7.5
7.4
7.3
7.2
2.9
2.8
1.3
1.2
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

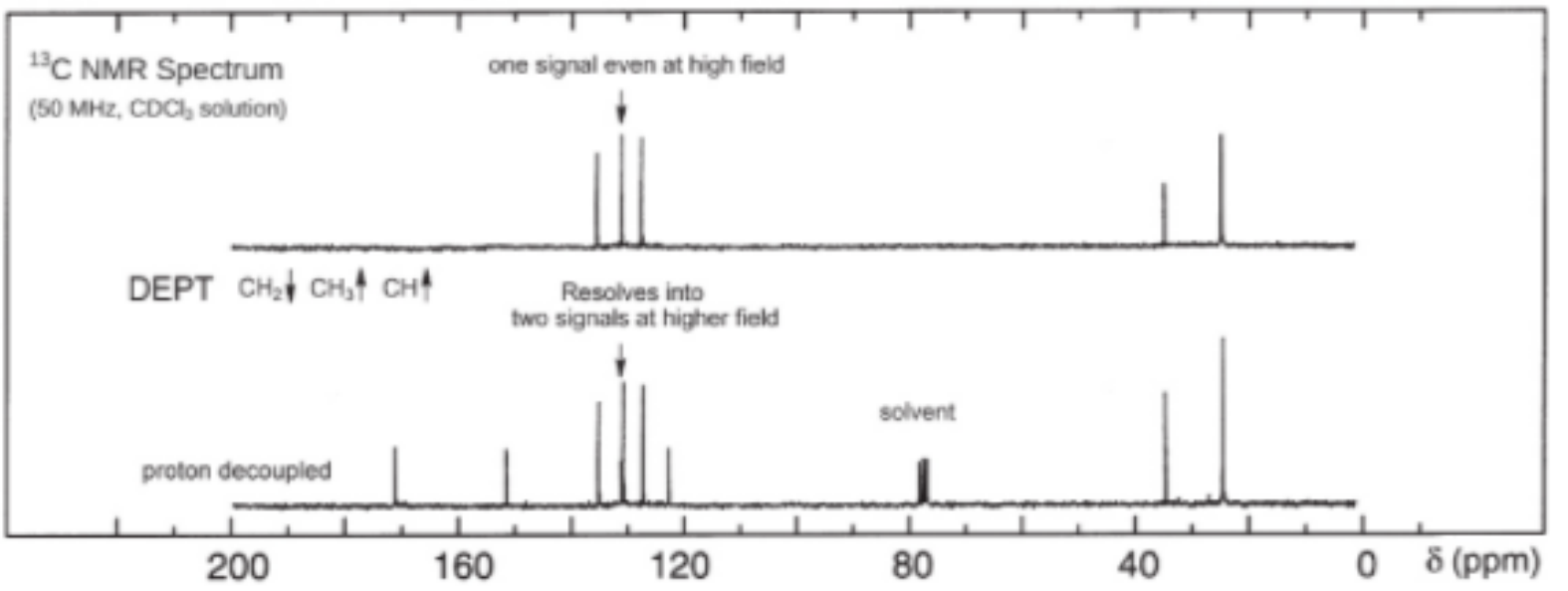

ppm
20
40
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
120
140
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
160
8.0
7.5
7.0
6.5
6.0
3.0
2.5
2.0
1.5
1.0
ppm

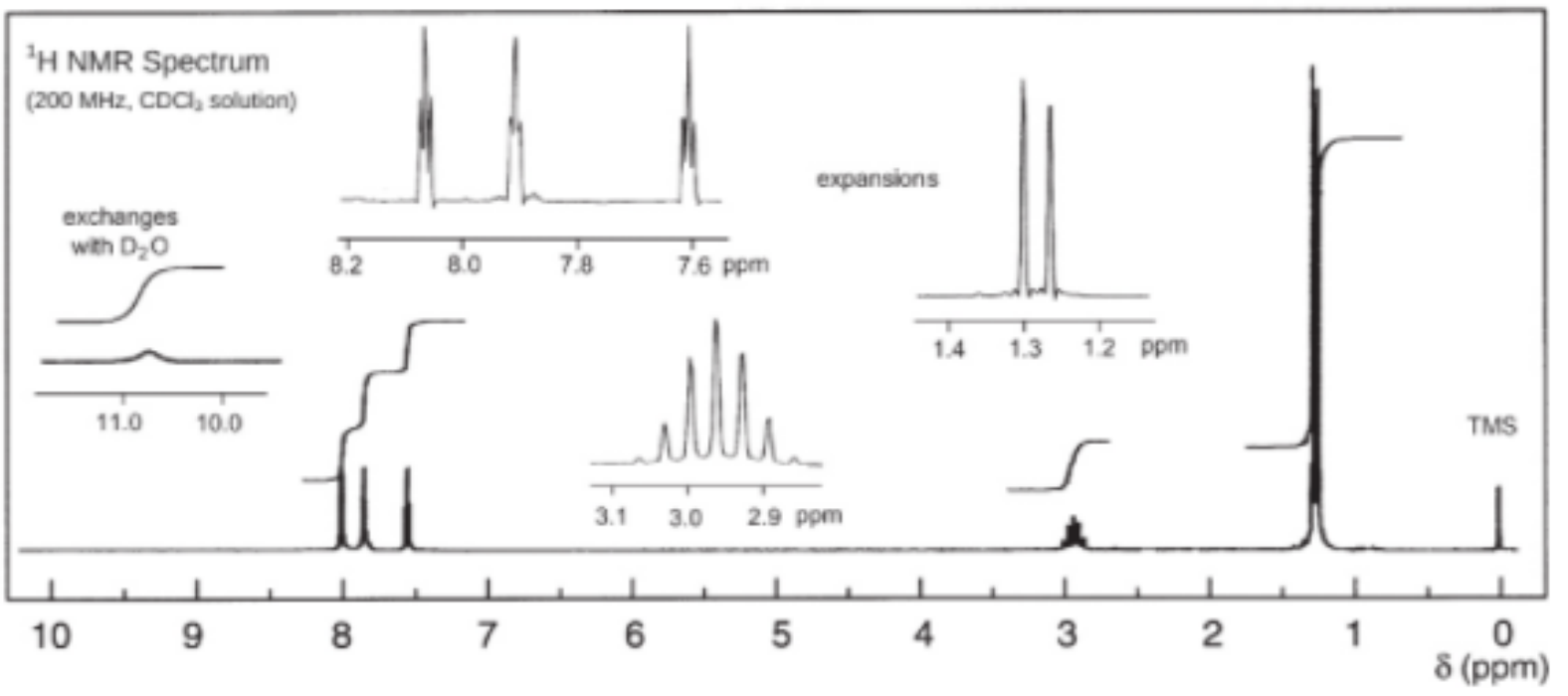
ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
20
40
120
140
160
8.0
7.5
7.0
6.5
6.0
3.0
2.5
2.0
1.5
1.0
ppm

Problem 196

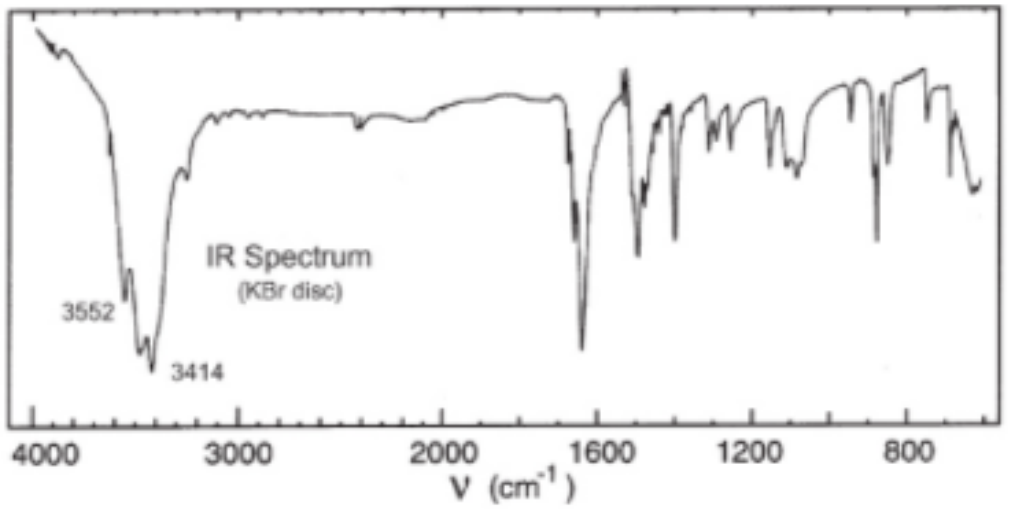

2980
1689
IR Spectrum
(KBr disc)
4000
3000
2000
1600
1200
800
ν (cm-1)

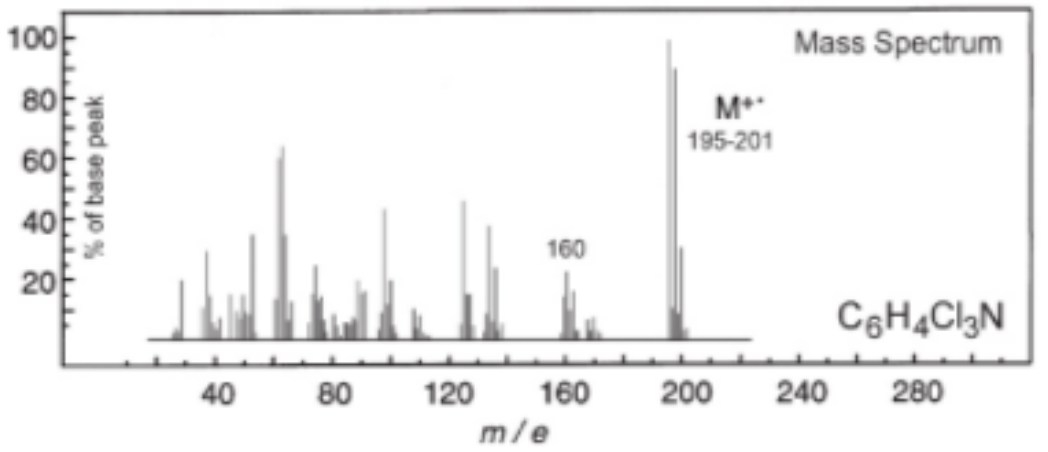

104
227/229
163
Mass Spectrum
M+·
242/244
C10H11BrO2
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m / e

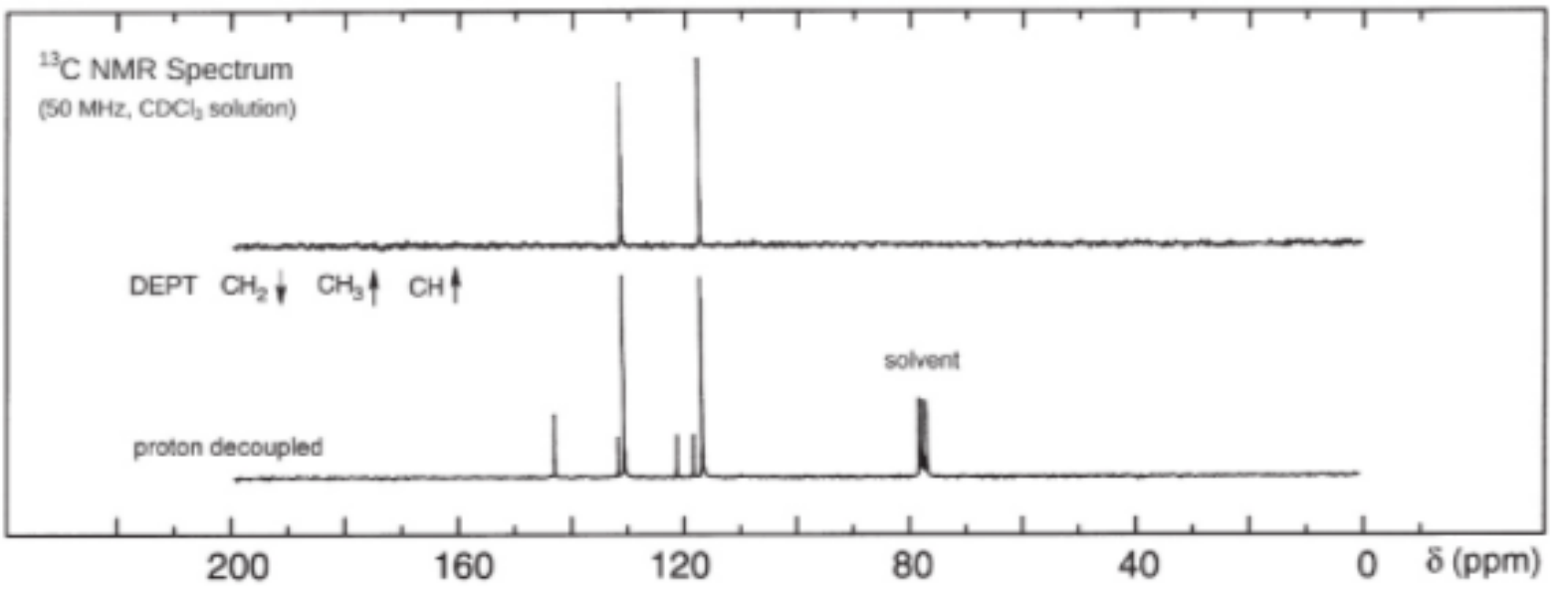

13C NMR Spectrum
(50 MHz, CDCl3 solution)
one signal even at high field
DEPT CH2 CH3 CH
Resolves into
two signals at higher field
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

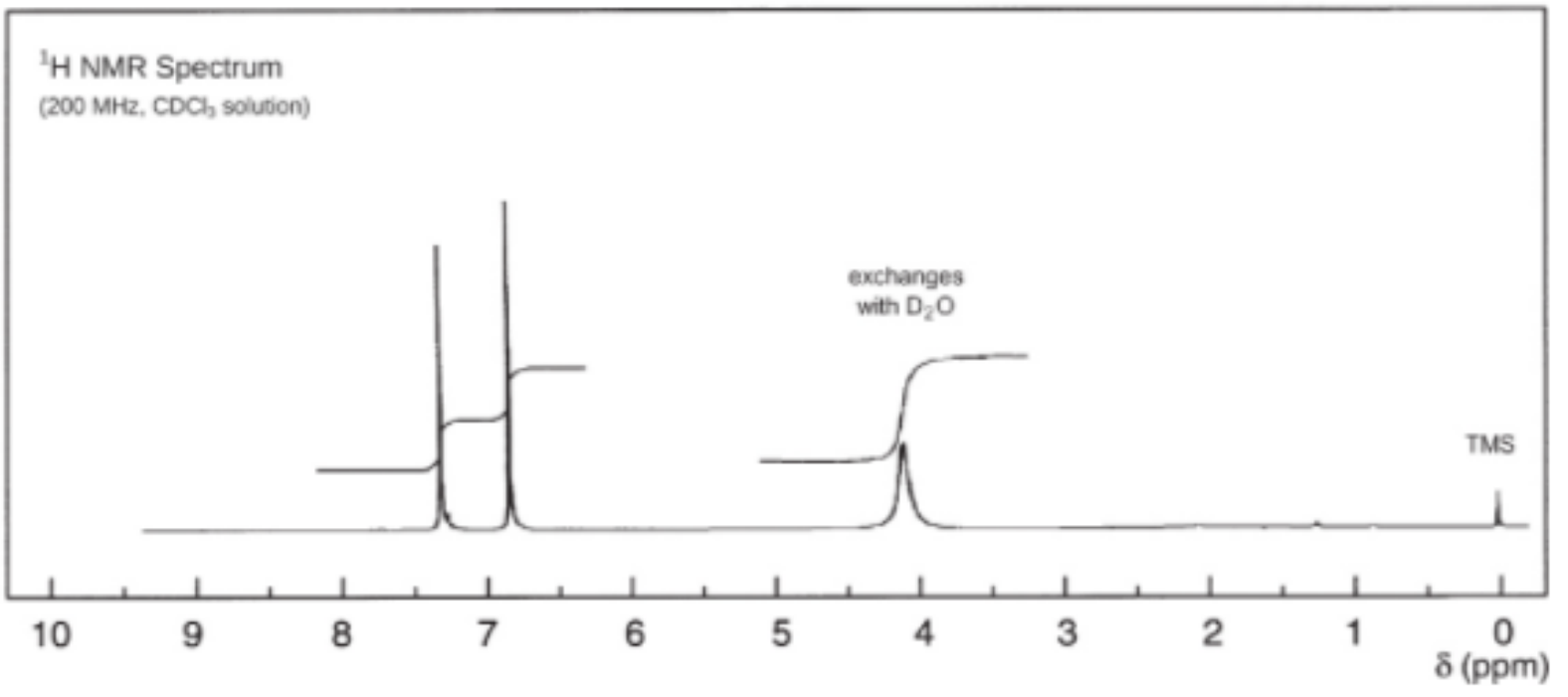

1H NMR Spectrum
(200 MHz, CDCl3 solution)
exchanges
with D2O
11.0
10.0
8.2
8.0
7.8
7.6 ppm
expansions
1.4
1.3
1.2 ppm
3.1
3.0
2.9 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 197

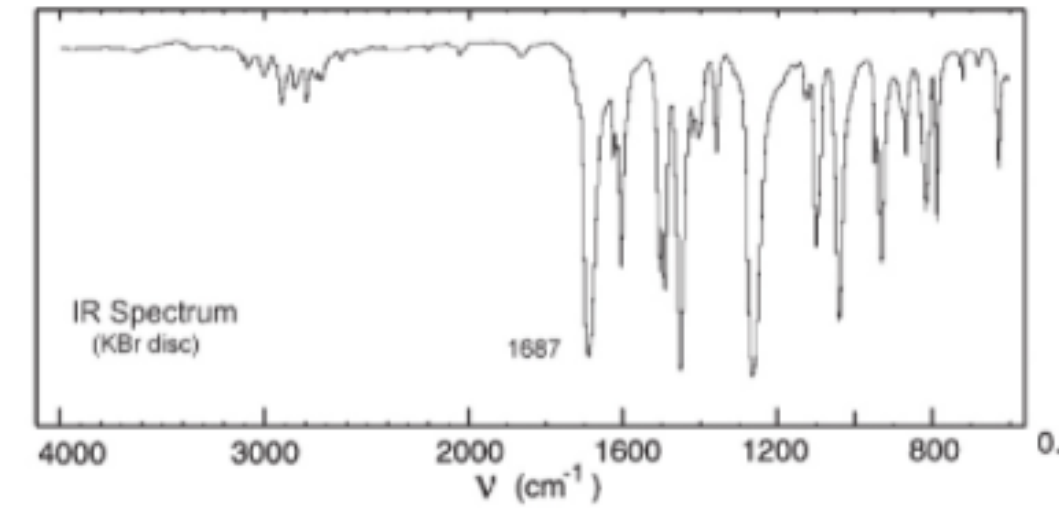

IR Spectrum
(KBr disc)
3552
3414
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

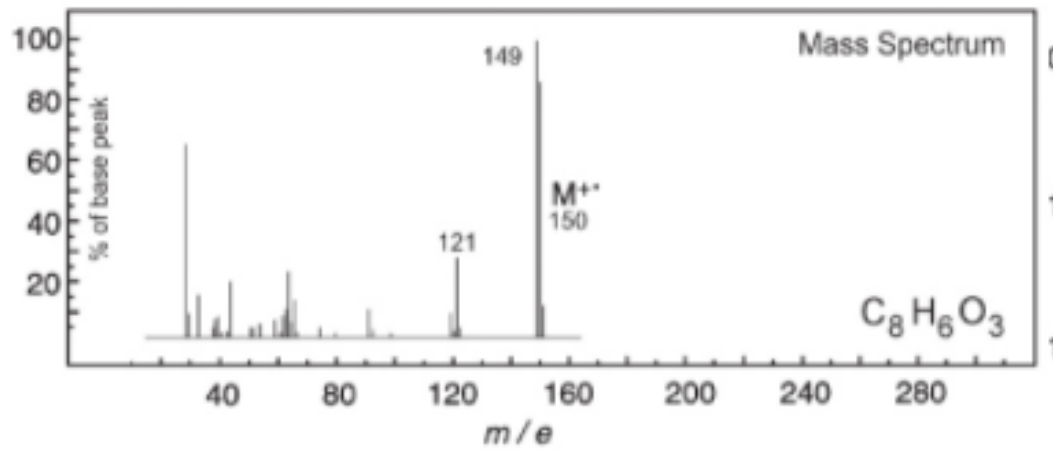

Mass Spectrum
M+·
195-201
160
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m/e
C6H4Cl3N

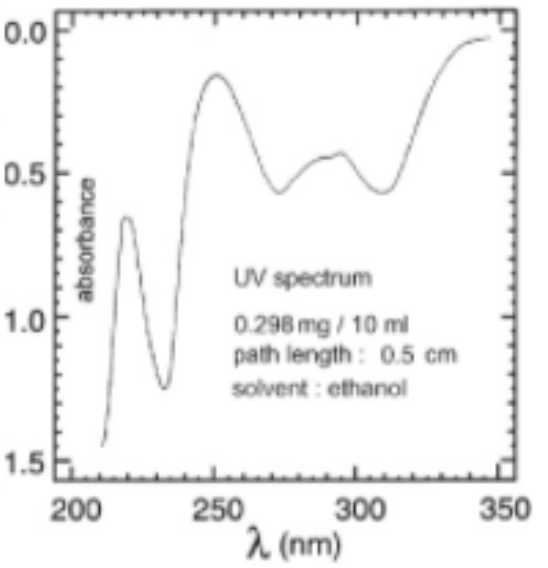

13C NMR Spectrum
(50 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

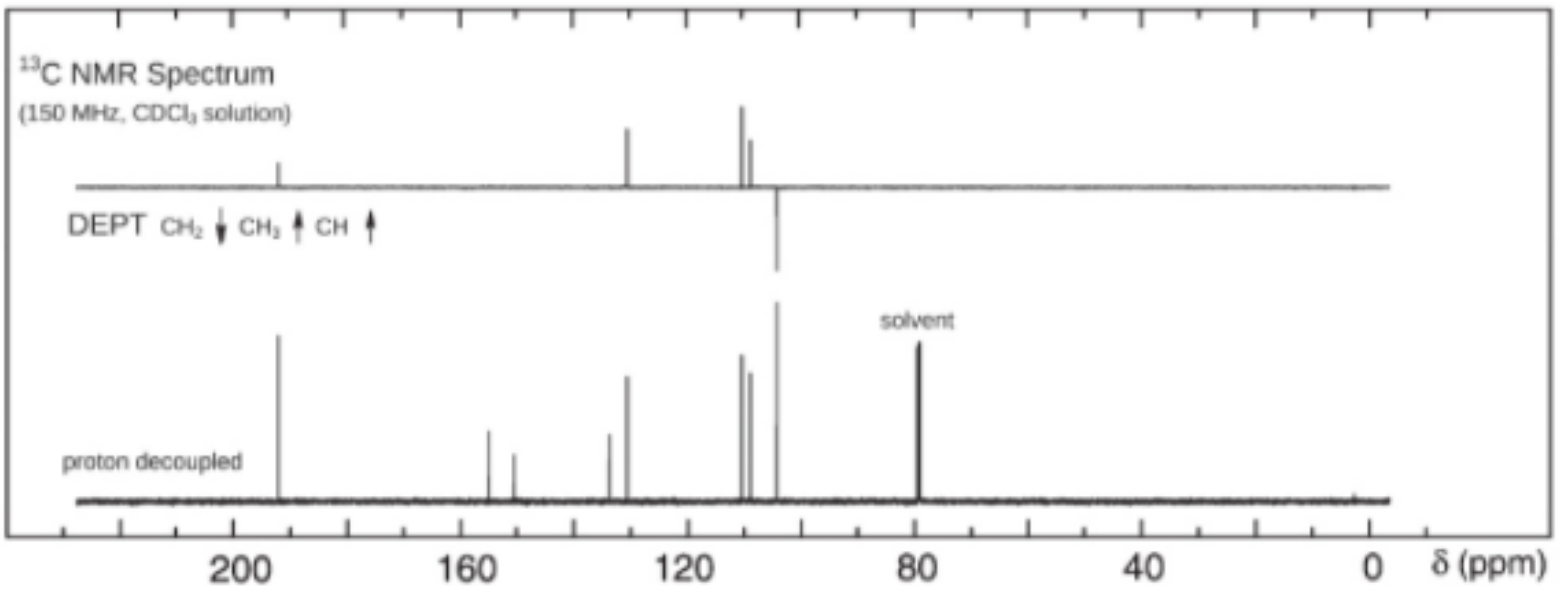

1H NMR Spectrum
(200 MHz, CDCl3 solution)
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

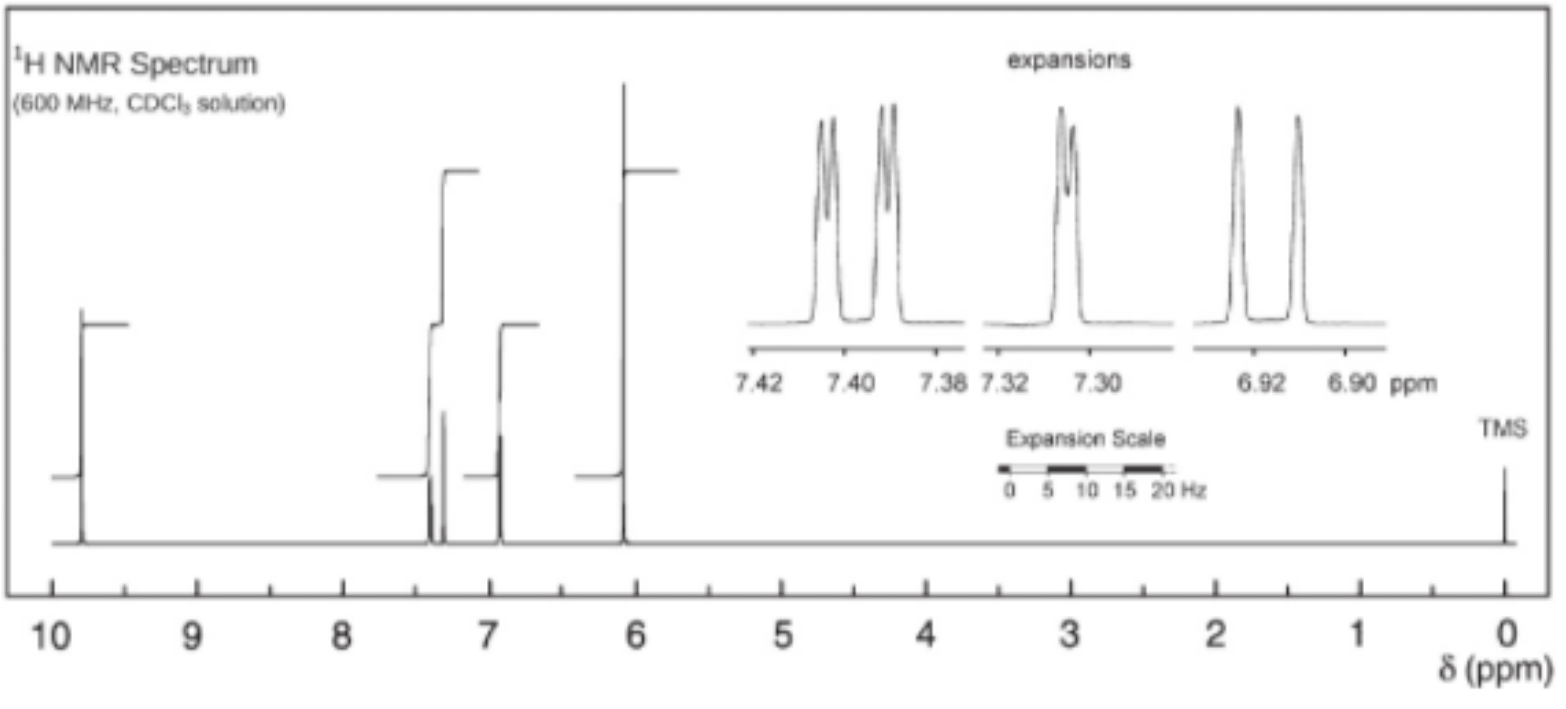
Problem 198

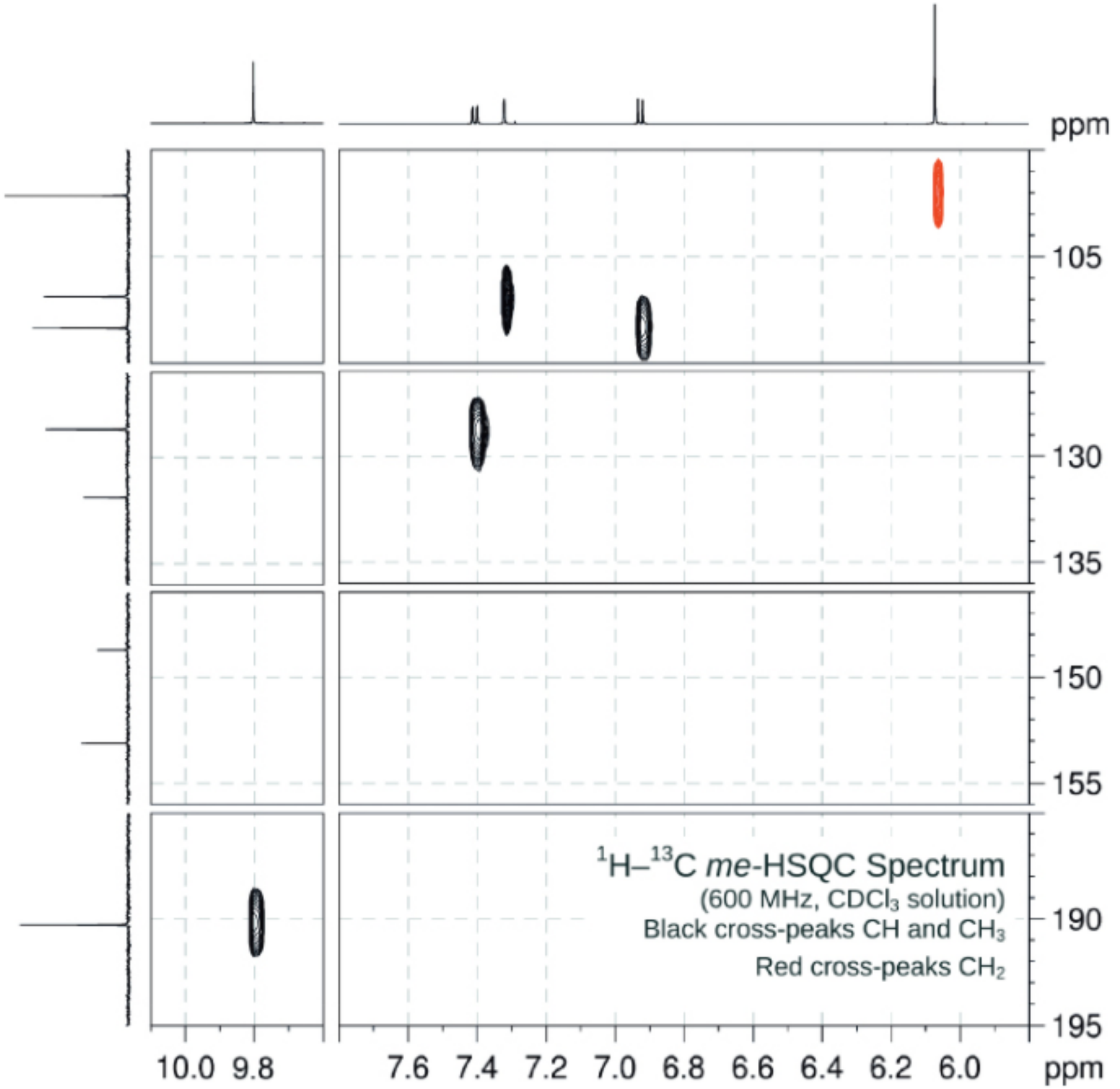

IR Spectrum
(KBr disc)
1687
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
149
M+·
150
121
C8H6O3
100
80
60
40
20
40
80
120
160
200
240
280
m/e

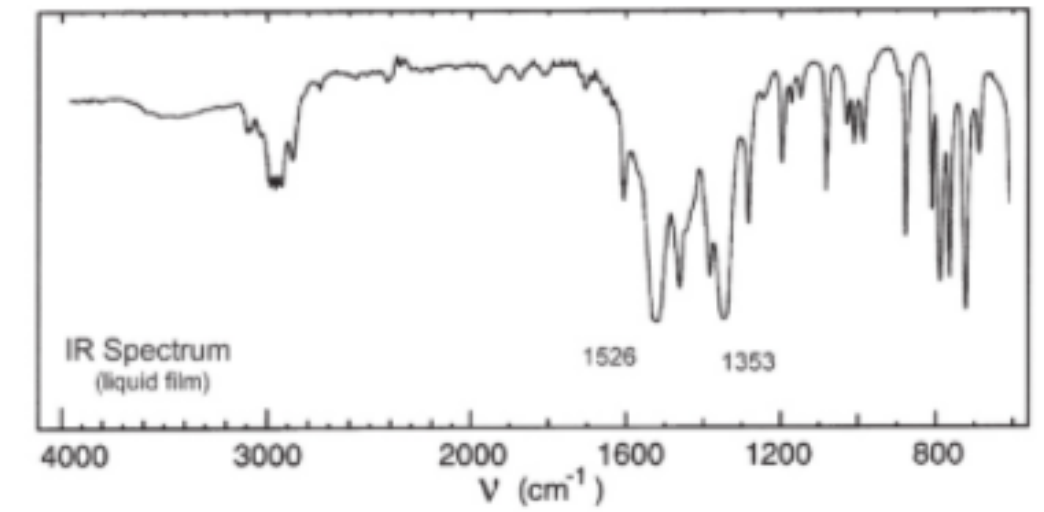

absorbance
UV spectrum
0.298 mg / 10 ml
path length : 0.5 cm
solvent : ethanol
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)

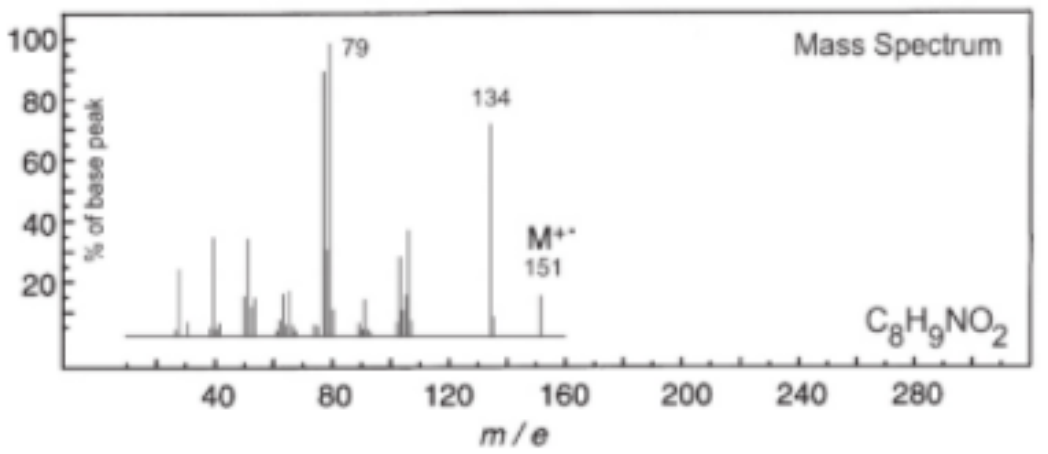

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

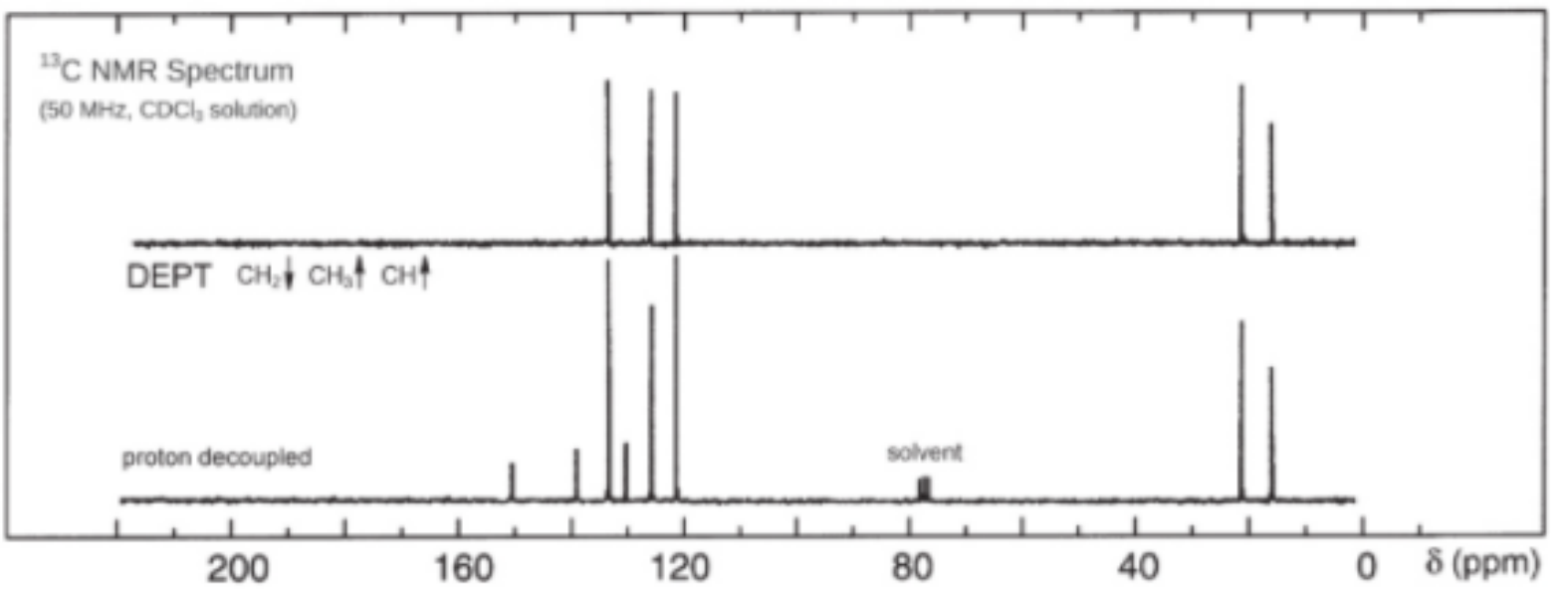

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansions
7.42
7.40
7.38
7.32
7.30
6.92
6.90
ppm
Expansion Scale
0 5 10 15 20 Hz
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

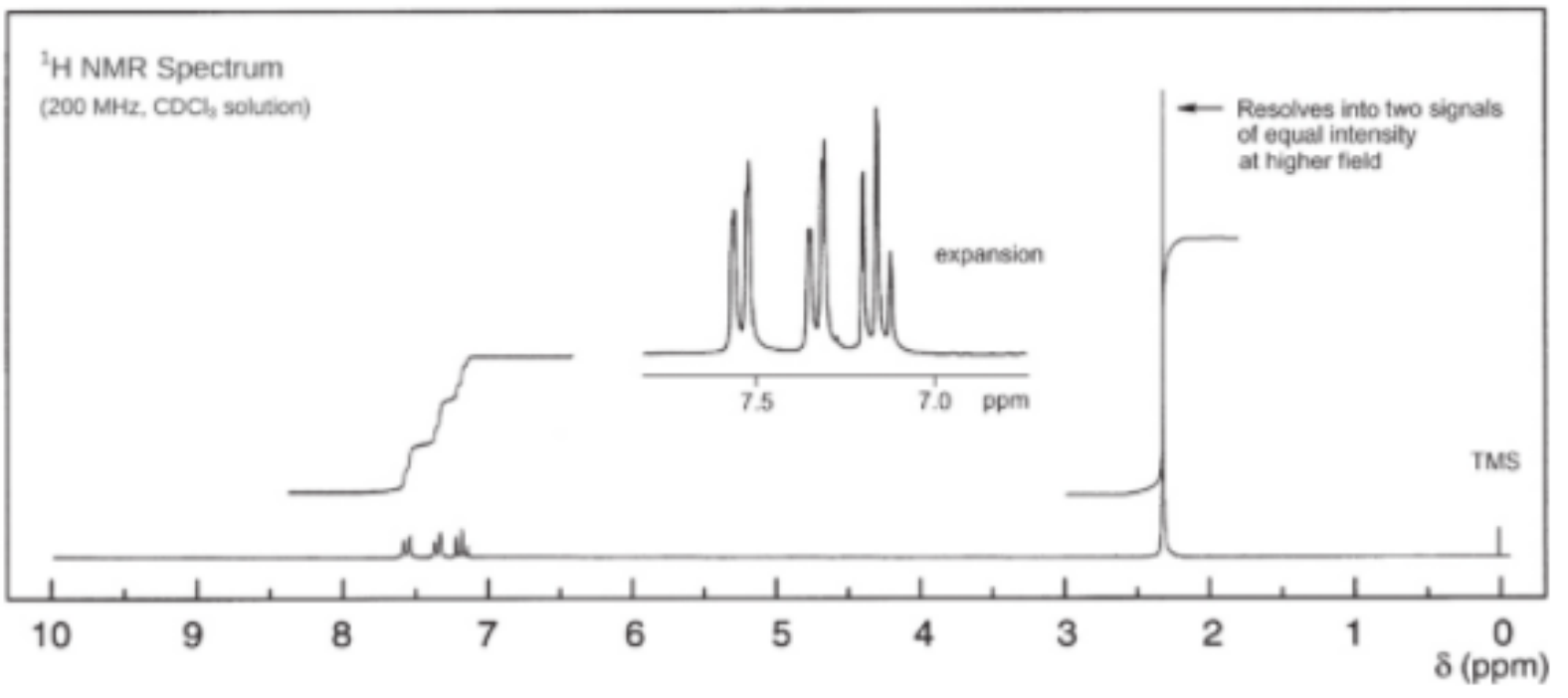

ppm
105
130
135
150
155
190
195
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
10.0 9.8
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0
ppm

Problem 199

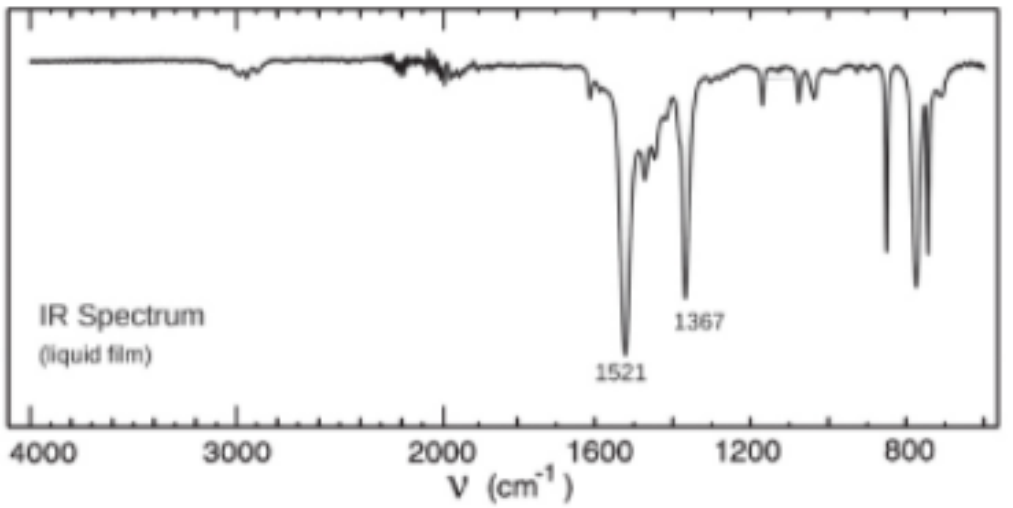

IR Spectrum
(liquid film)
1526
1353
4000
3000
2000
1600
1200
800
ν (cm-1)

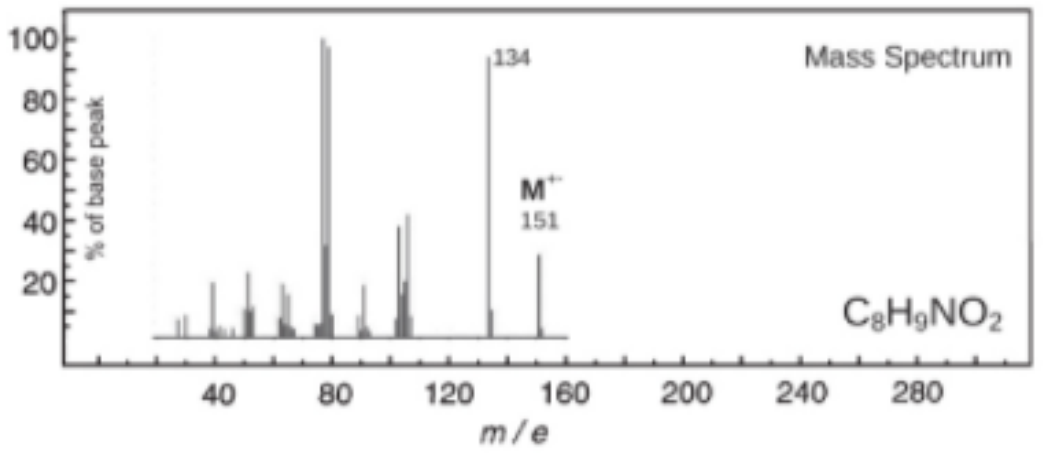

Mass Spectrum
% of base peak
100
80
60
40
20
79
134
M+·
151
C8H9NO2
40
80
120
160
200
240
280
m / e

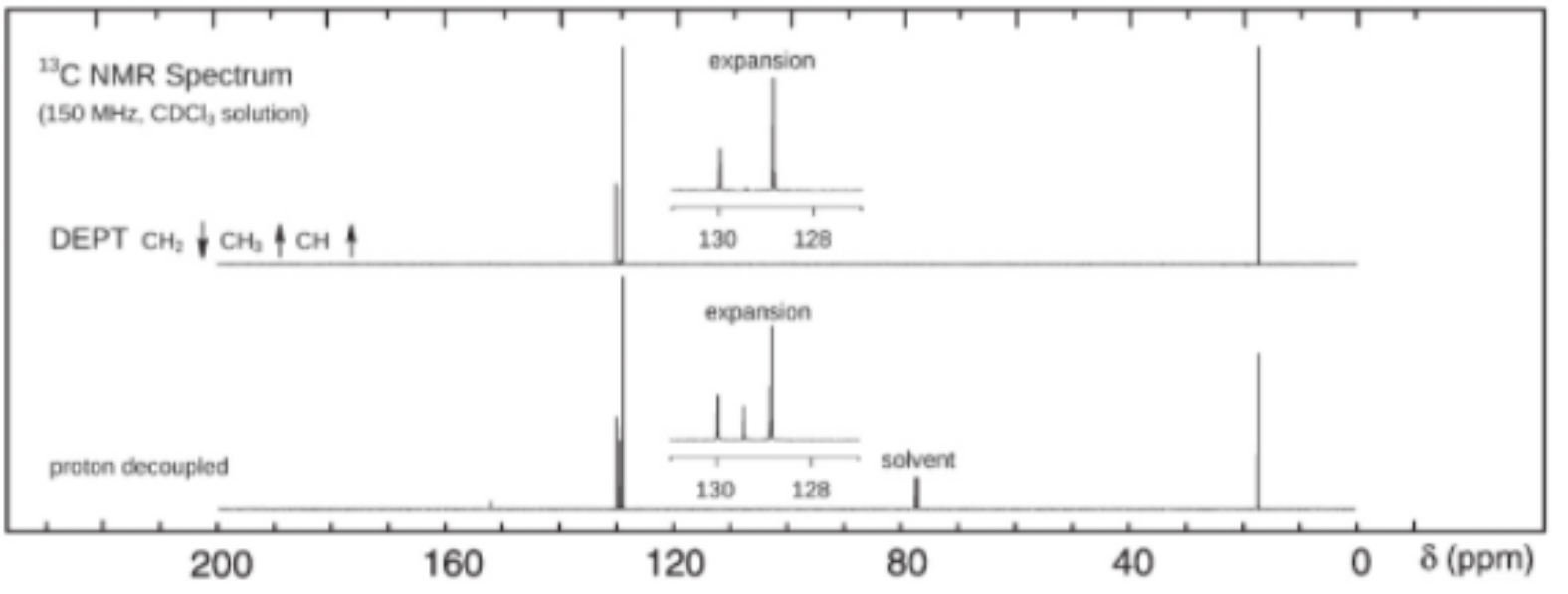

13C NMR Spectrum
(50 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

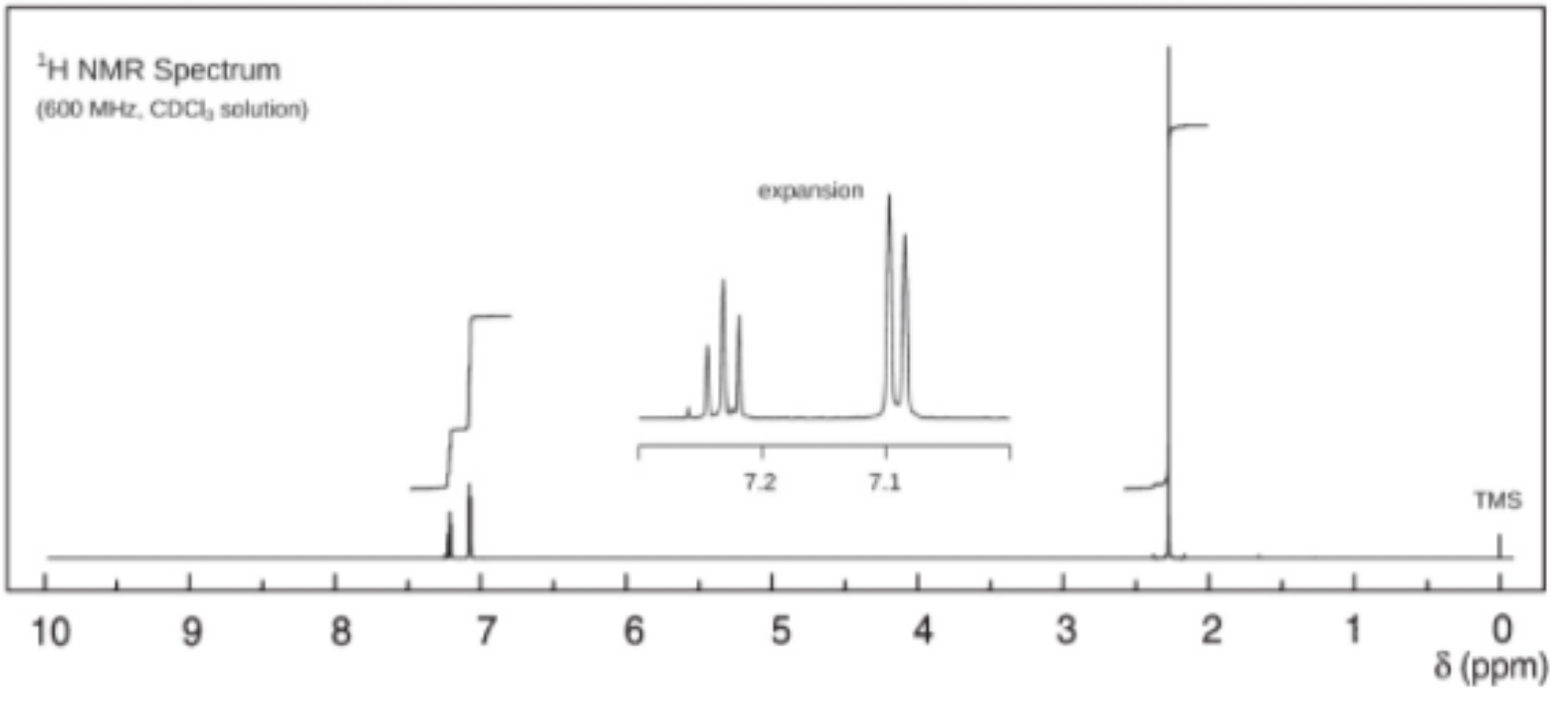

1H NMR Spectrum
(200 MHz, CDCl3 solution)
Resolves into two signals
of equal intensity
at higher field
expansion
7.5
7.0
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 200

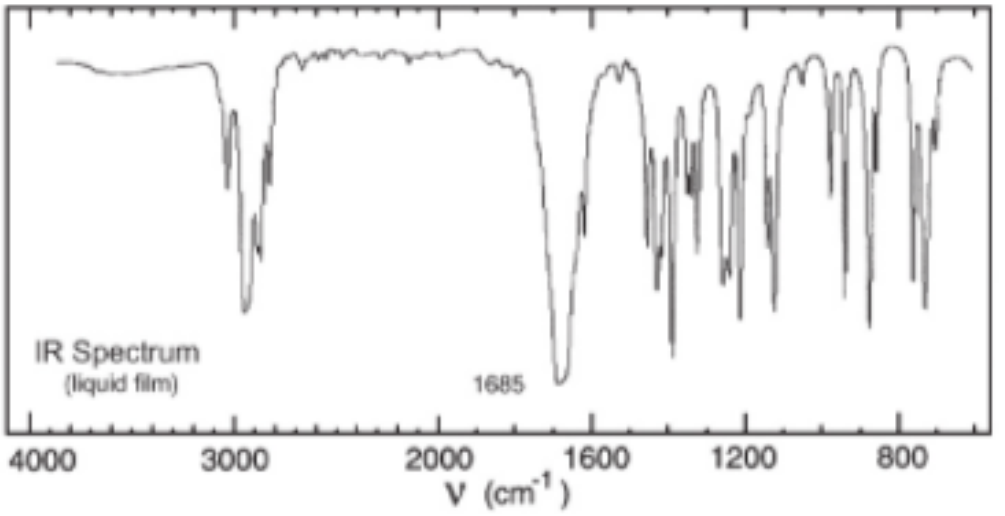

IR Spectrum
(liquid film)
1521
1367
4000
3000
2000
1600
1200
800
ν (cm-1)

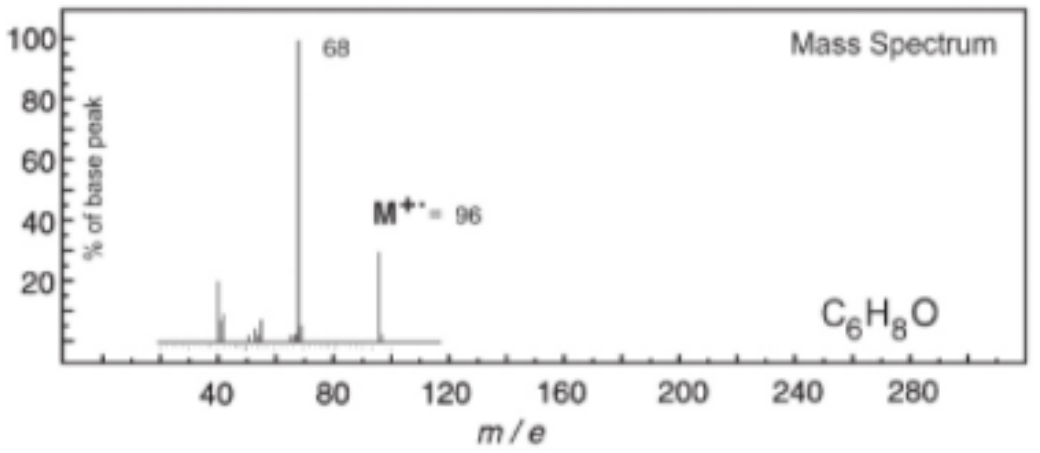

Mass Spectrum
% of base peak
134
M+·
151
C8H9NO2
100
80
60
40
20
40
80
120
160
200
240
280
m/e


13C NMR Spectrum
(150 MHz, CDCl3 solution)
expansion
130
128
DEPT CH2 CH3 CH
expansion
130
128
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion
7.2
7.1
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 201

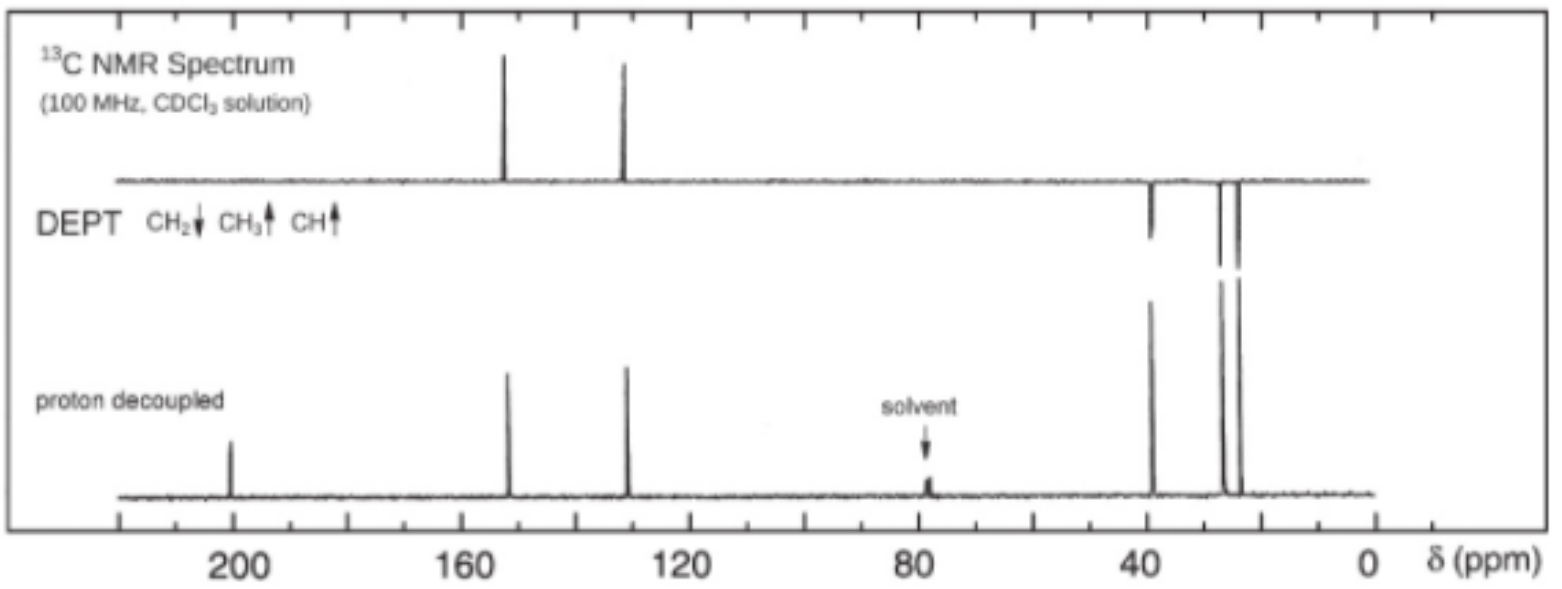


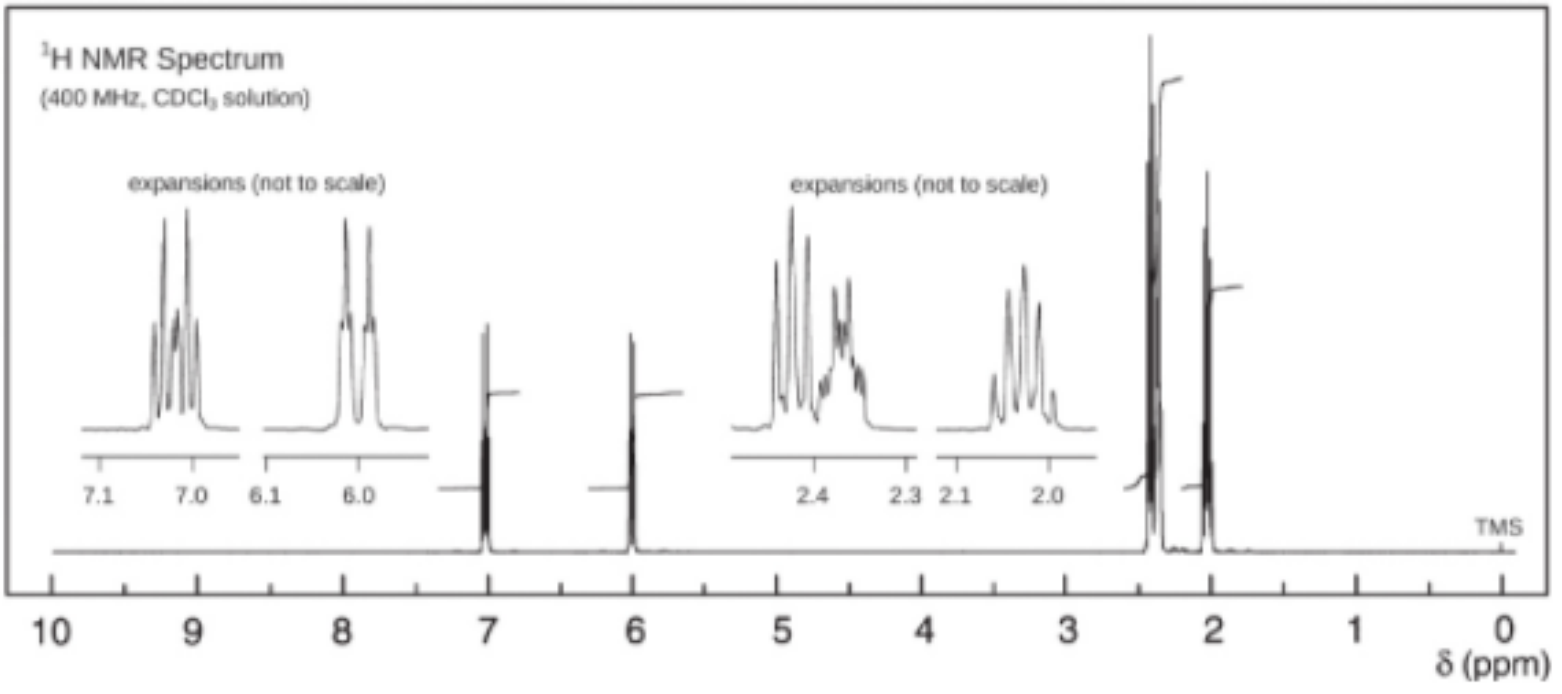


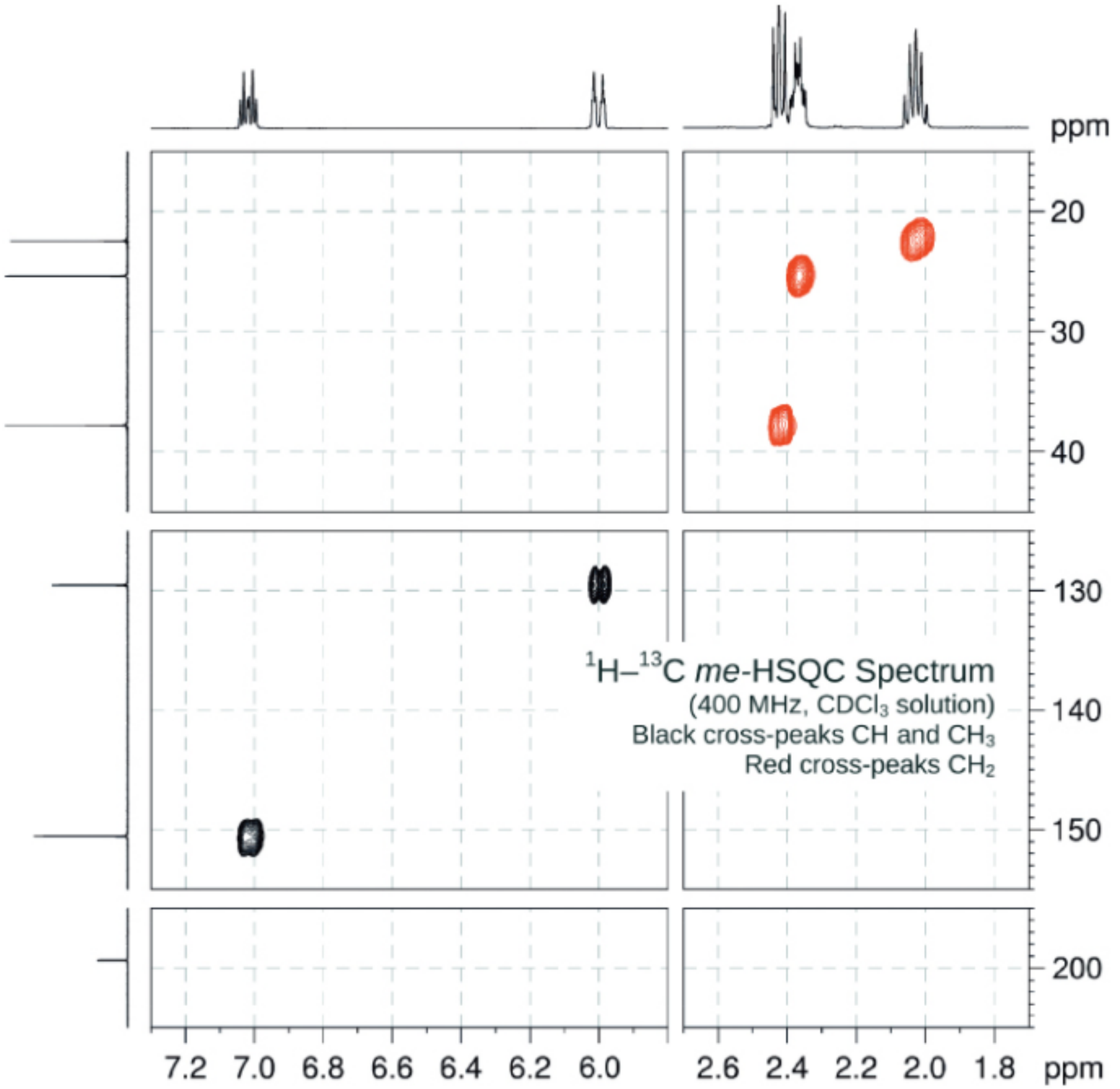
UV Spectrum

λ_{max} 225 nm ($\log_{10}\varepsilon$ 3.9)

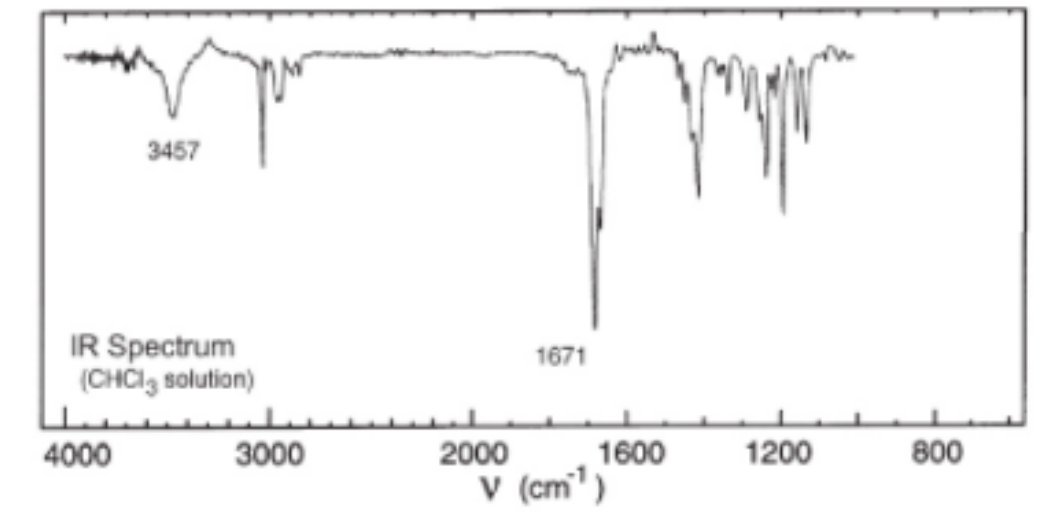
solvent : methanol

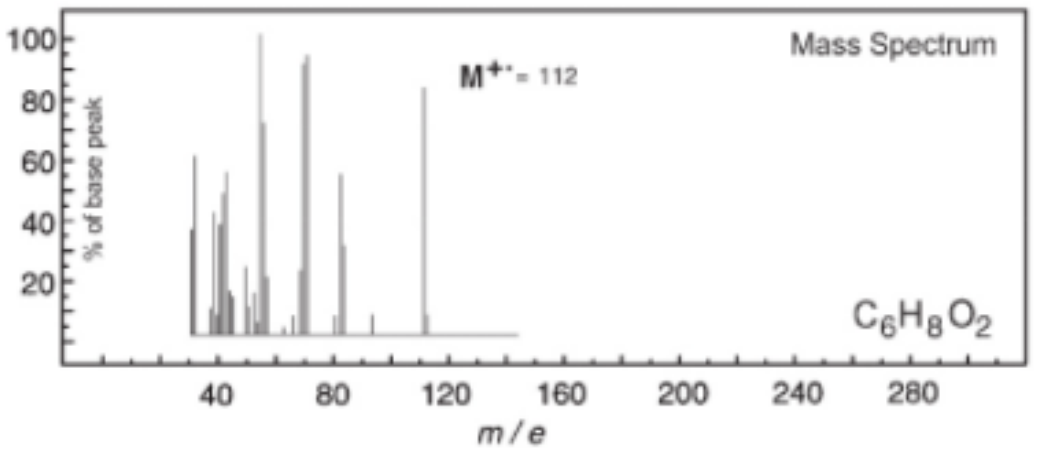





ppm
20
30
40
130
140
150
200
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.2 7.0 6.8 6.6 6.4 6.2 6.0
2.6 2.4 2.2 2.0 1.8 ppm

Problem 202



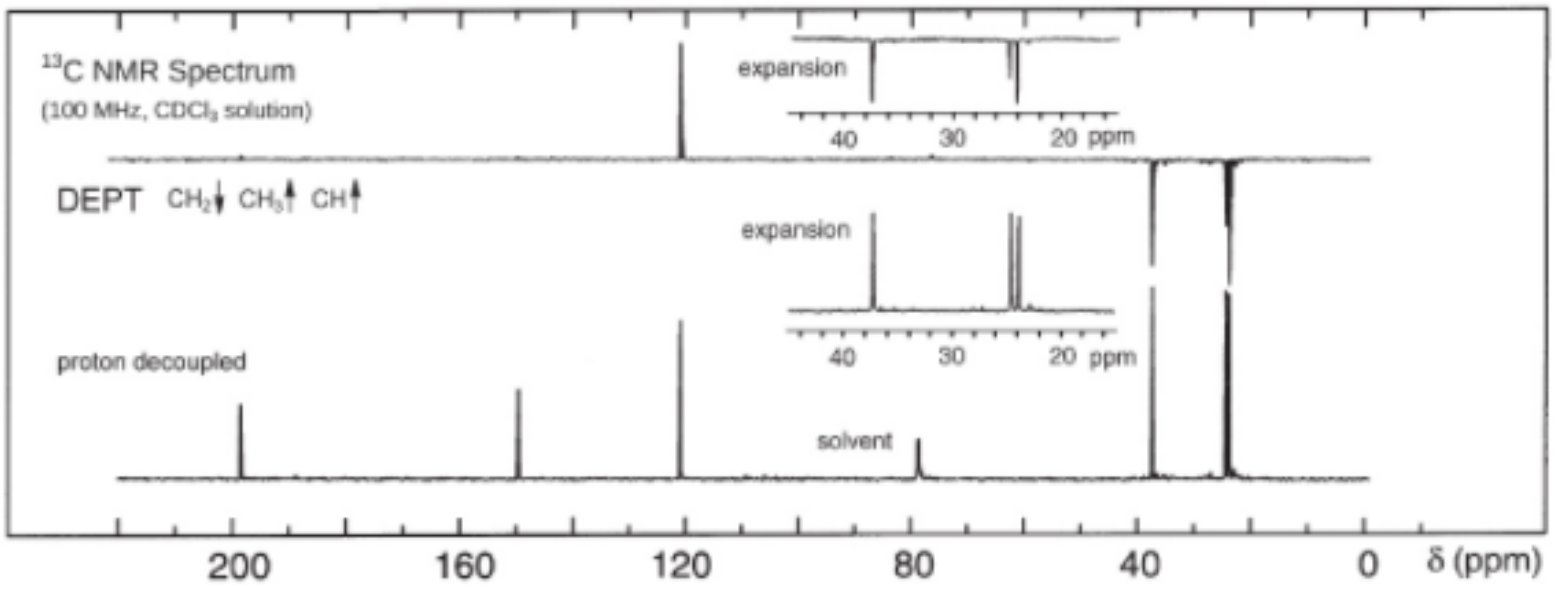


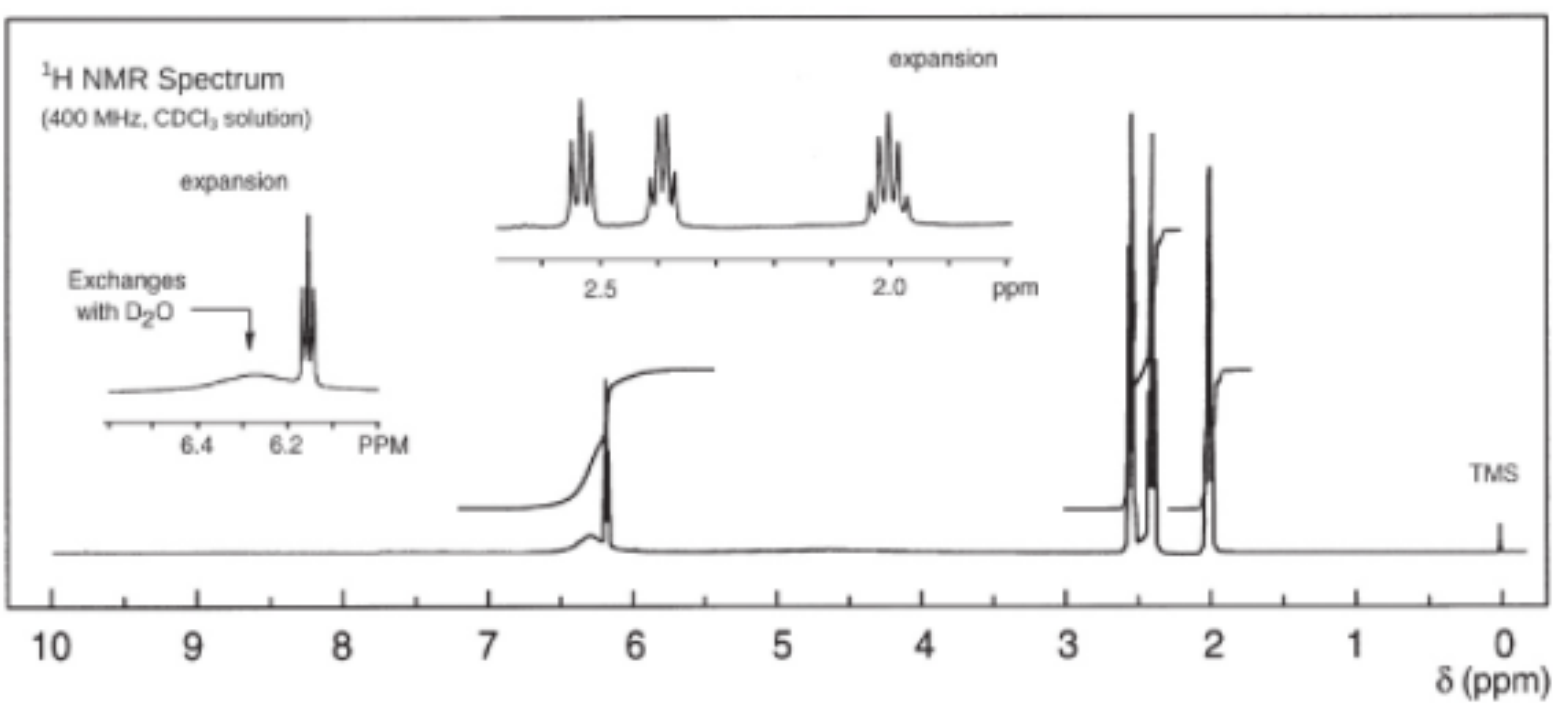
UV Spectrum

λ_{max} 263 nm ($\log_{10}\varepsilon$ 3.9)

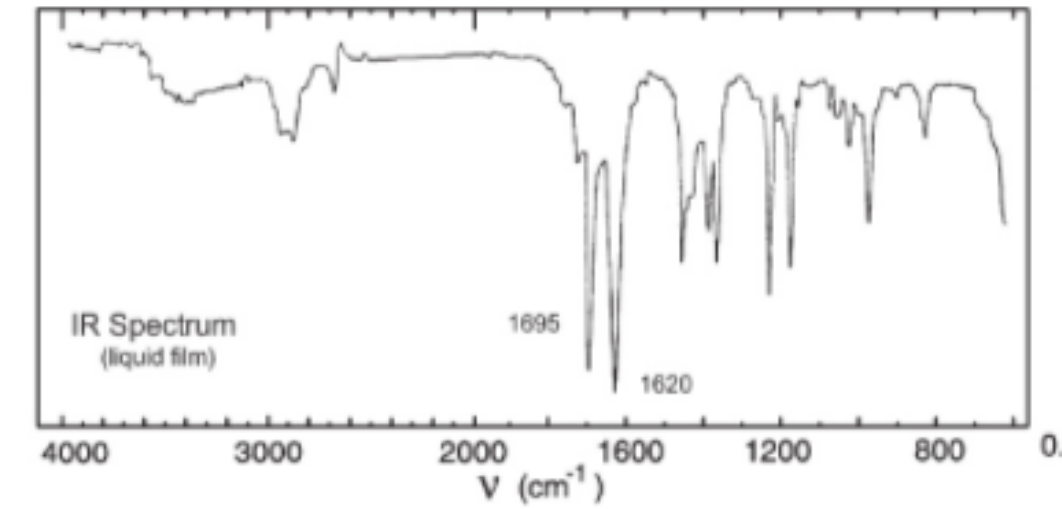
λ_{max} 305 nm ($\log_{10}\varepsilon$ 2.1)

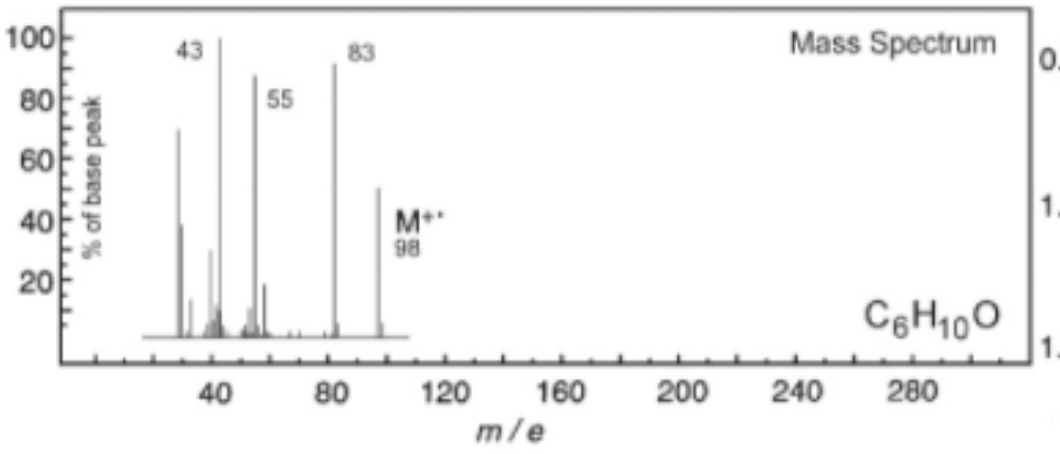
solvent : hexane

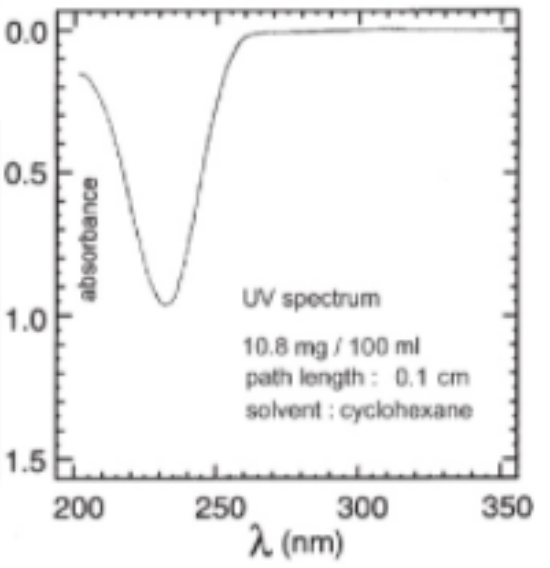


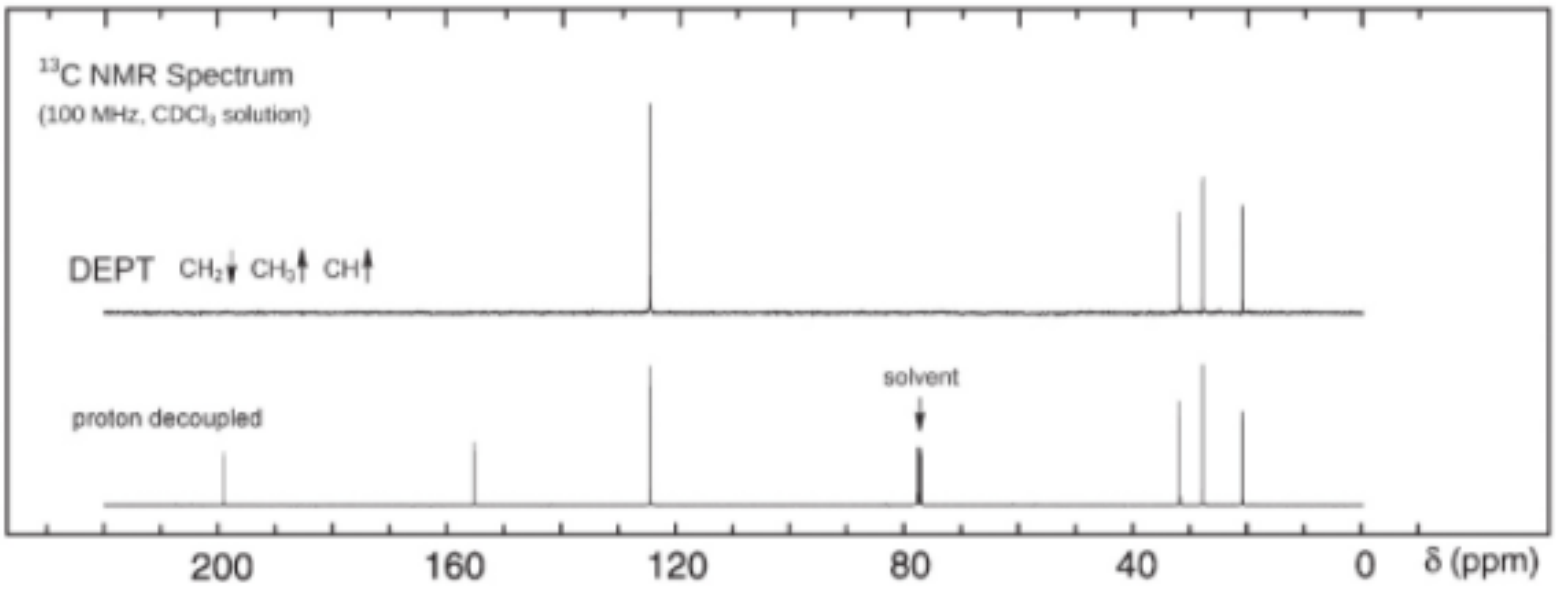


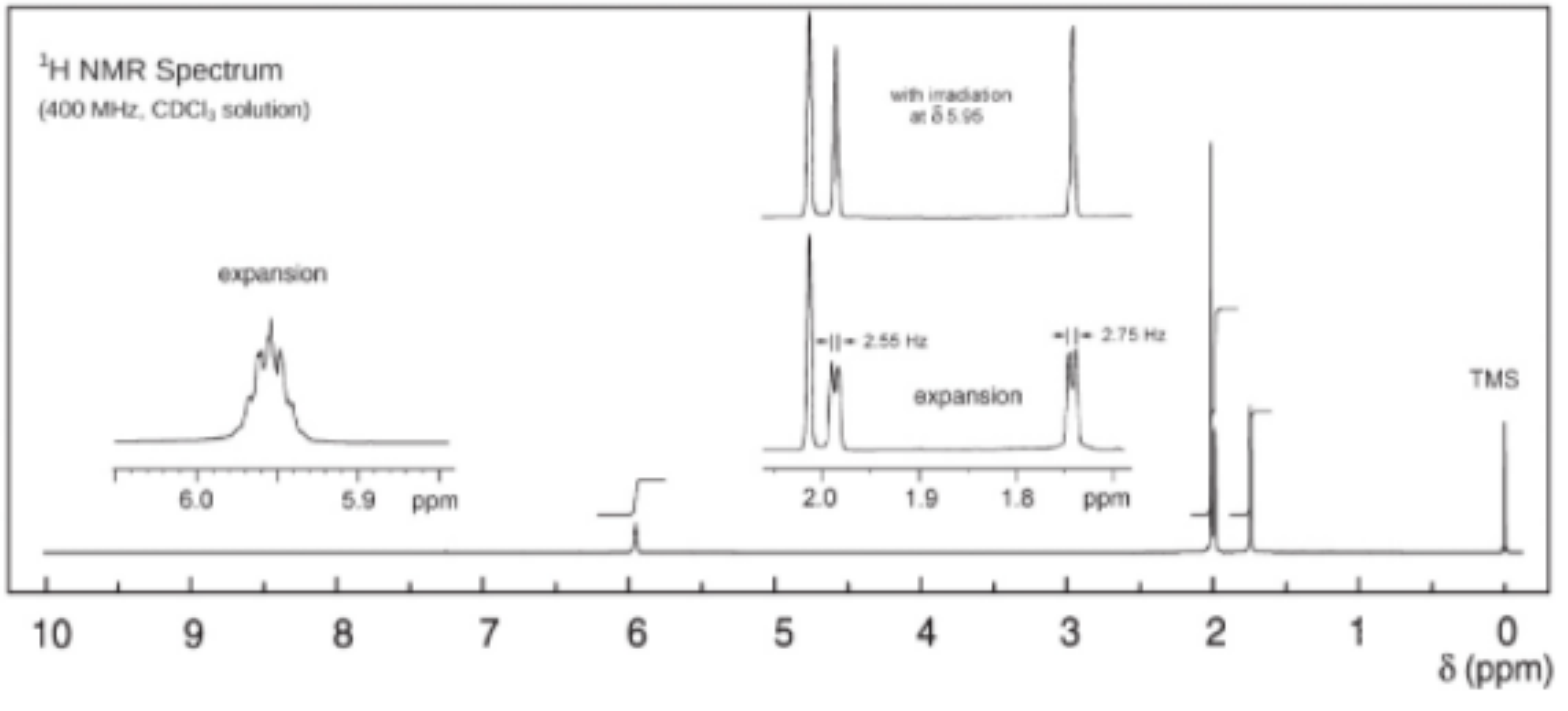
Problem 203


IR Spectrum
(liquid film)
1695
1620
4000
3000
2000
1600
1200
800
ν (cm-1)

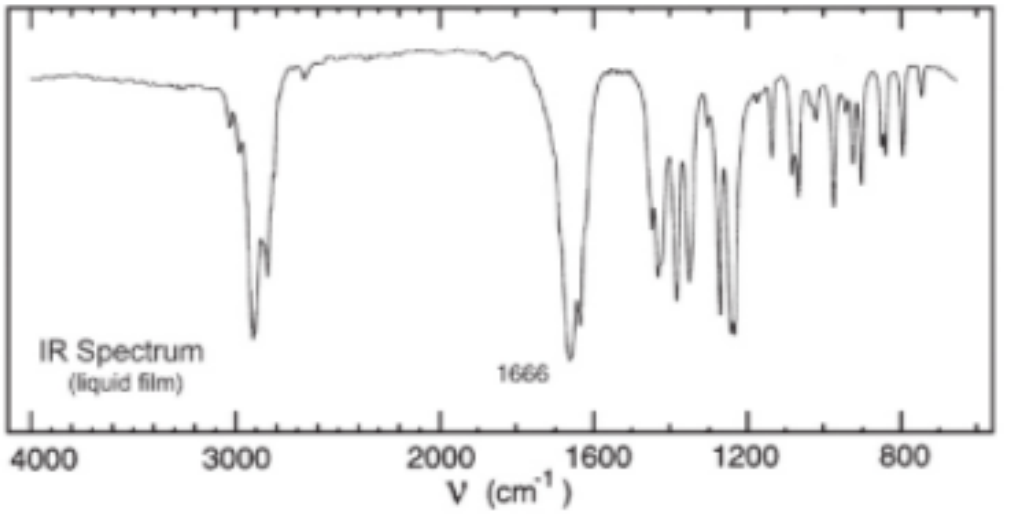

Mass Spectrum
% of base peak
100
80
60
40
20
43
55
83
M+·
98
C6H10O
40
80
120
160
200
240
280
m/e

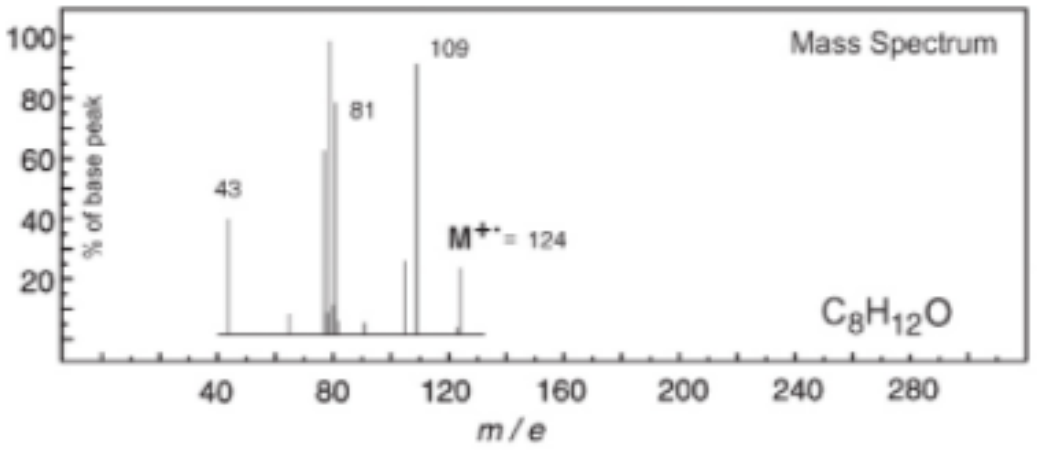

absorbance
0.0
0.5
1.0
1.5
UV spectrum
10.8 mg / 100 ml
path length : 0.1 cm
solvent : cyclohexane
200
250
300
350
λ (nm)


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
with irradiation at δ 5.95
expansion
6.0
5.9
ppm
2.55 Hz
2.75 Hz
expansion
2.0
1.9
1.8
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 204

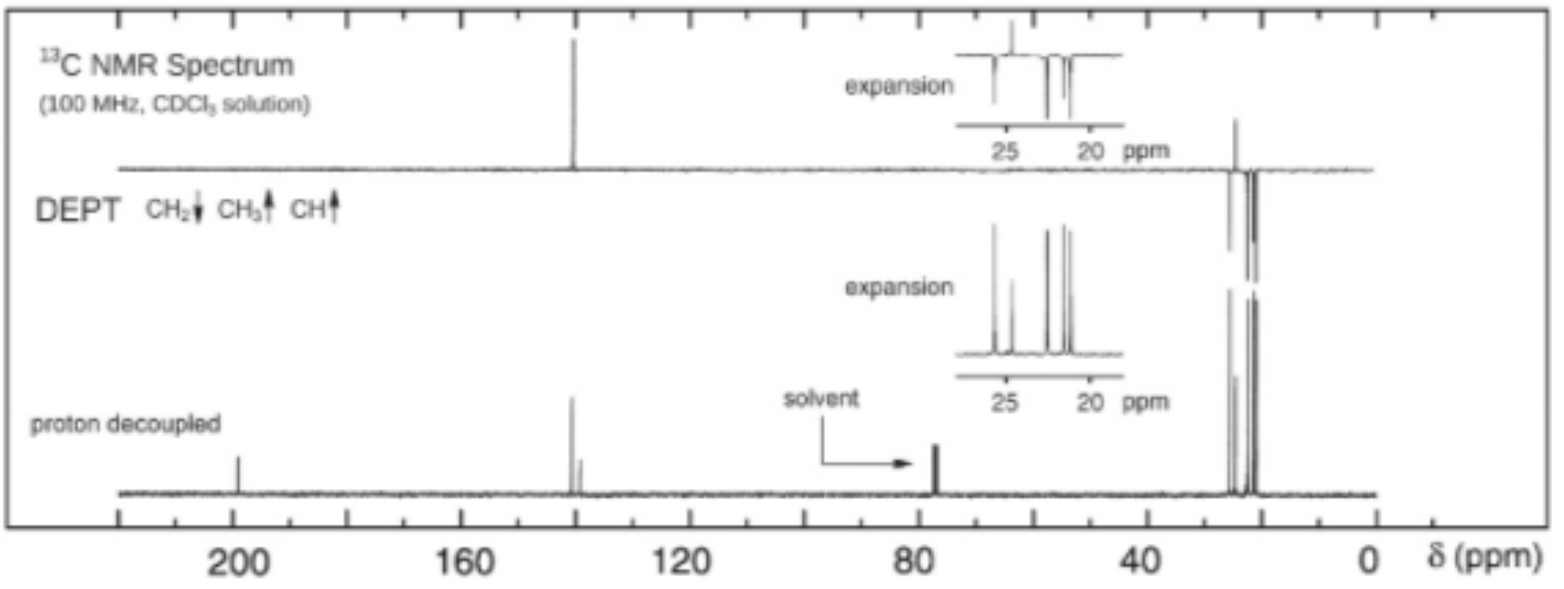


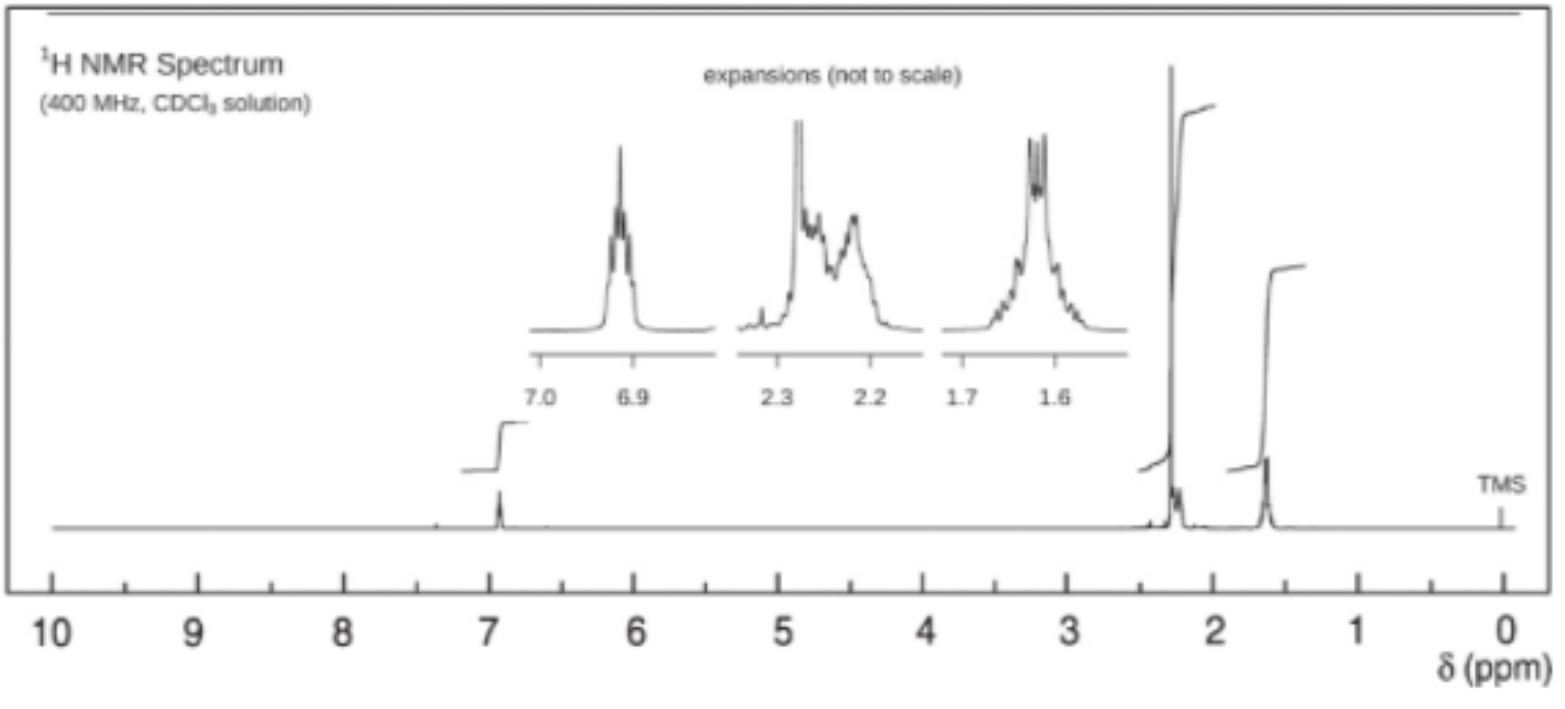


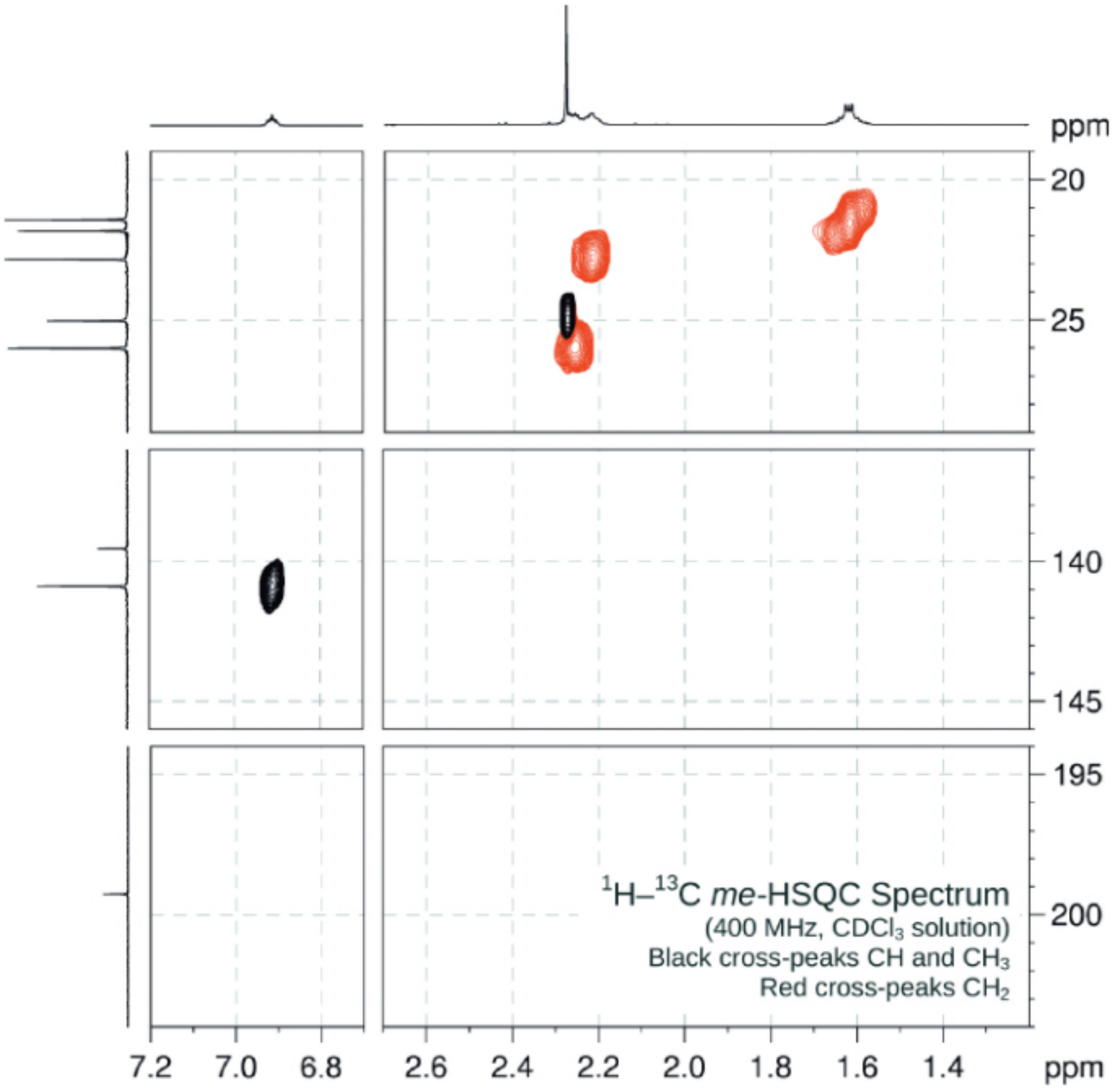
UV Spectrum

λ_{max} 234 nm ($\log_{10}\varepsilon$ 4.1)

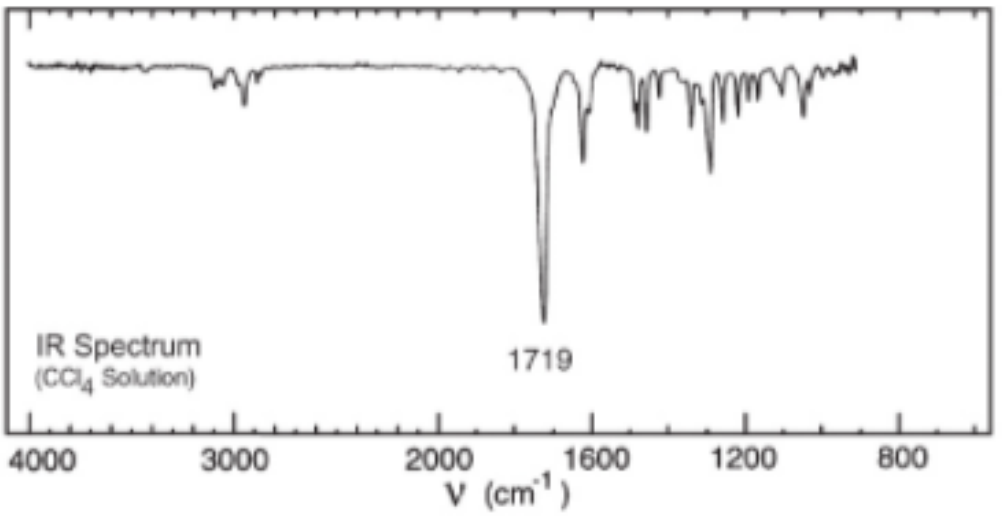
solvent : ethanol

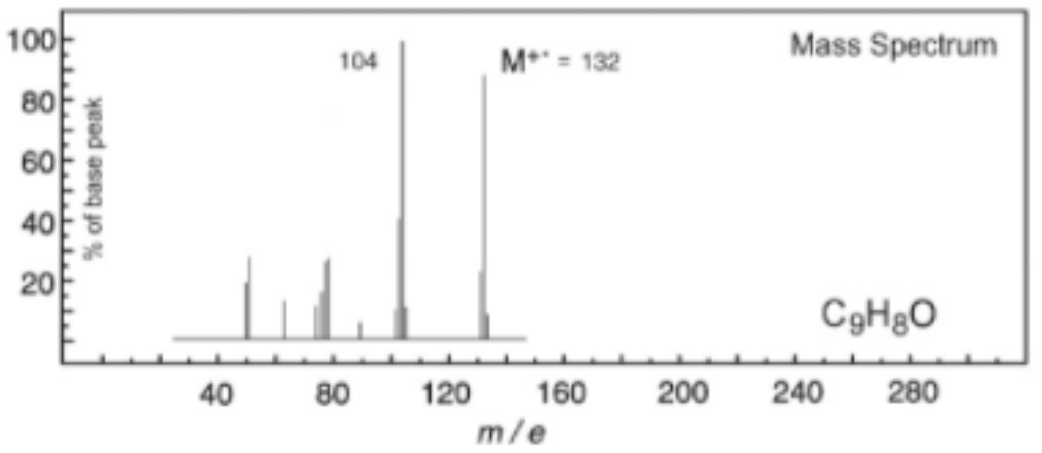





ppm
20
25
140
145
195
200
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.2
7.0
6.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
ppm

Problem 205



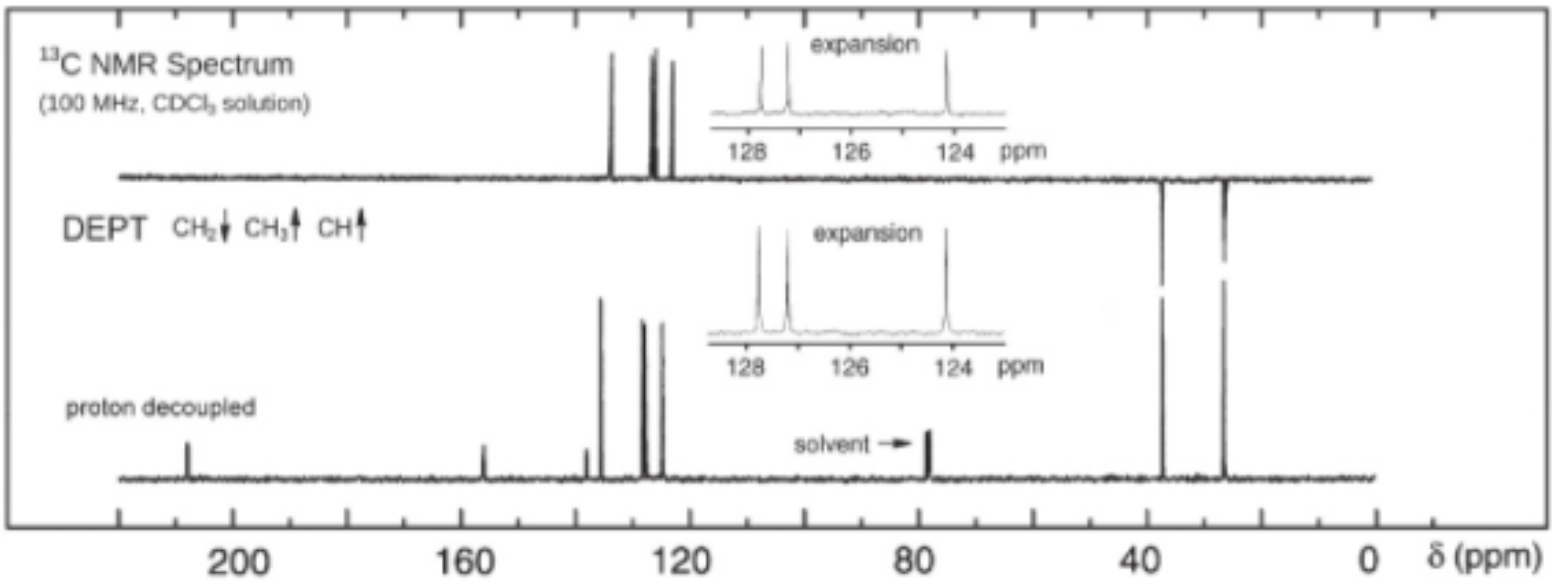


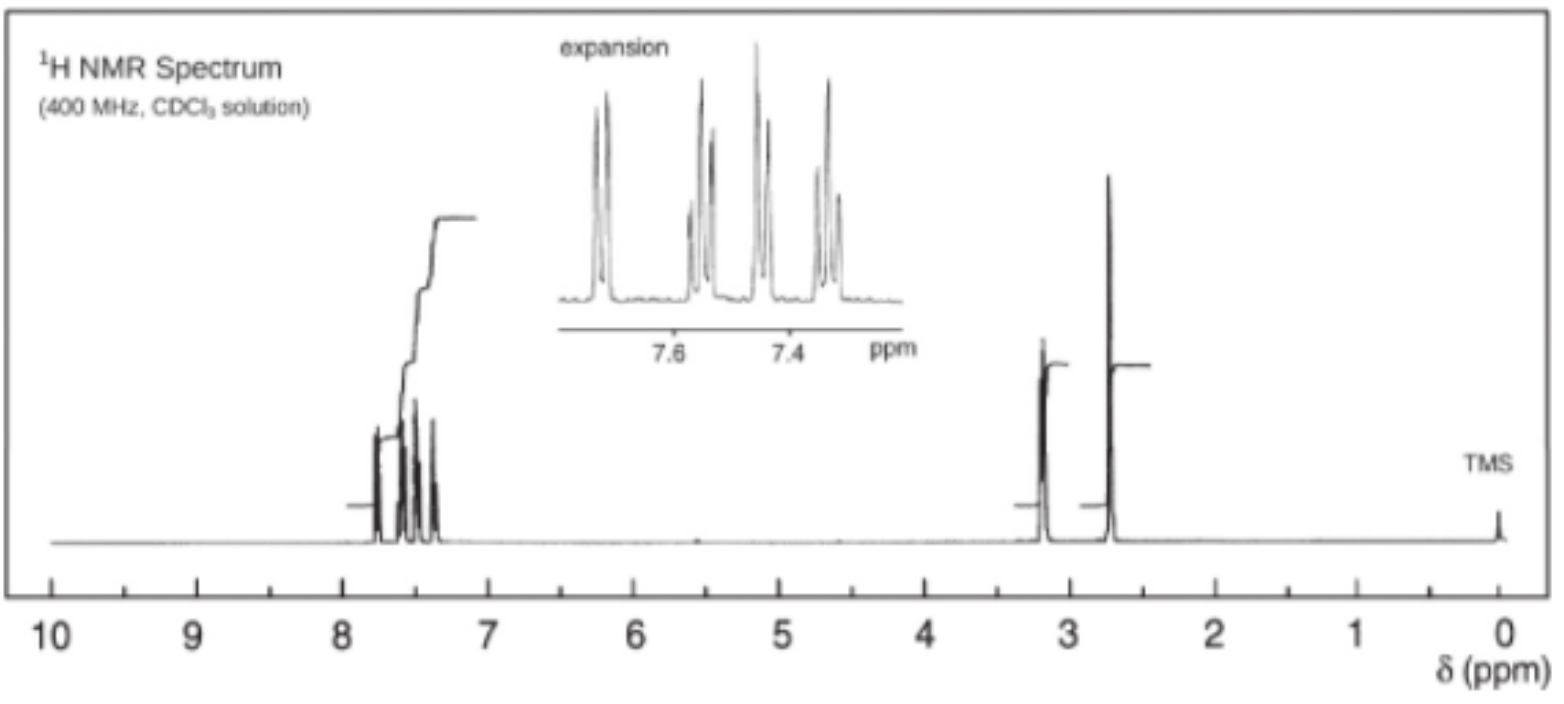
UV Spectrum

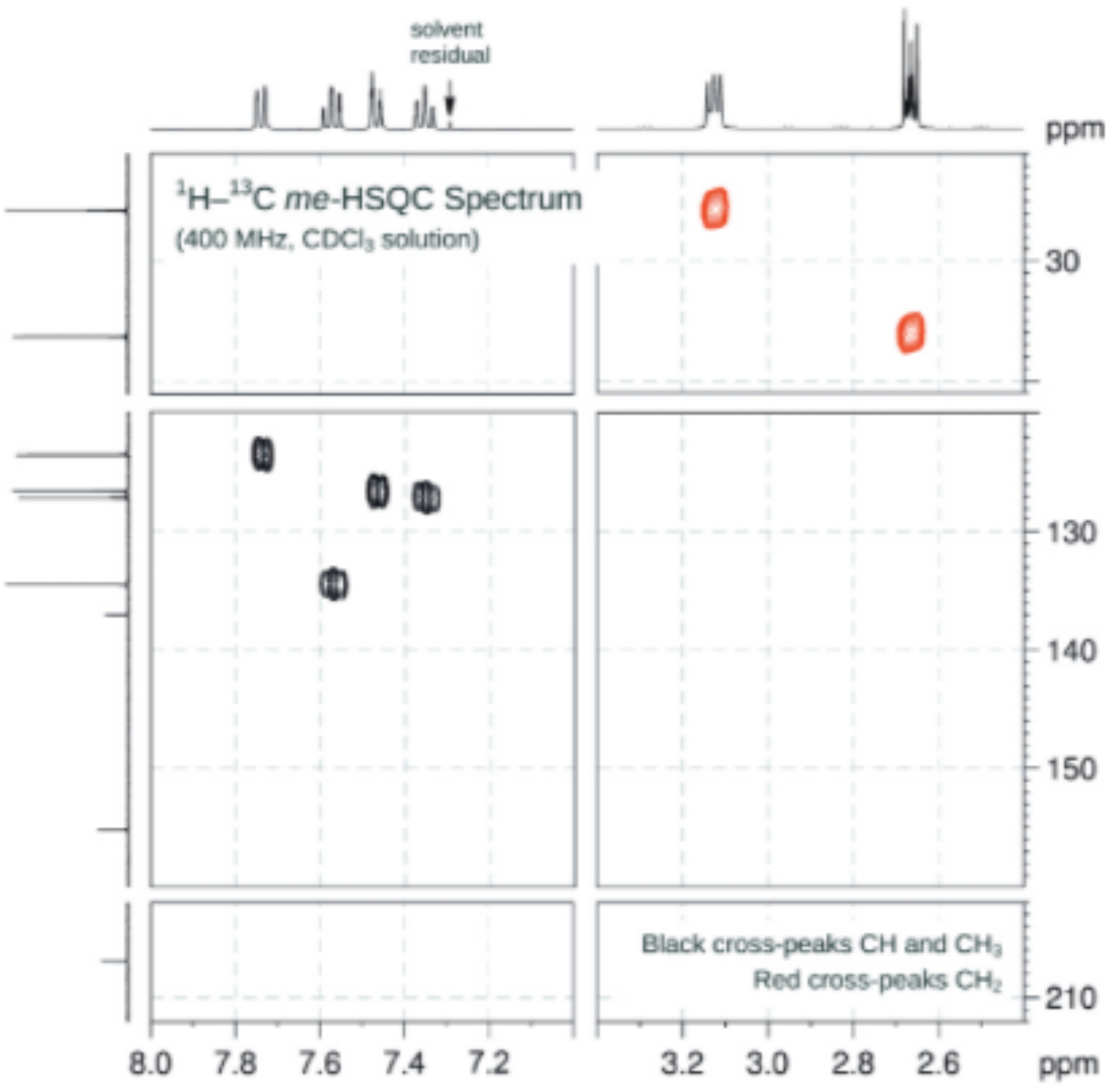
λ_{max} = 243 nm ($\log_{10}\varepsilon$ 4.1)

λ_{max} = 291 nm ($\log_{10}\varepsilon$ 3.4)

solvent : ethanol

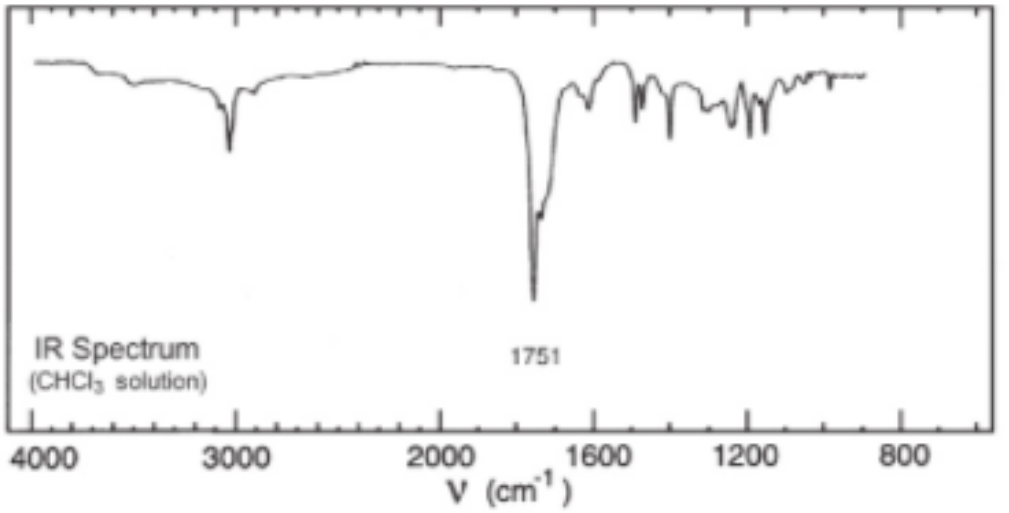


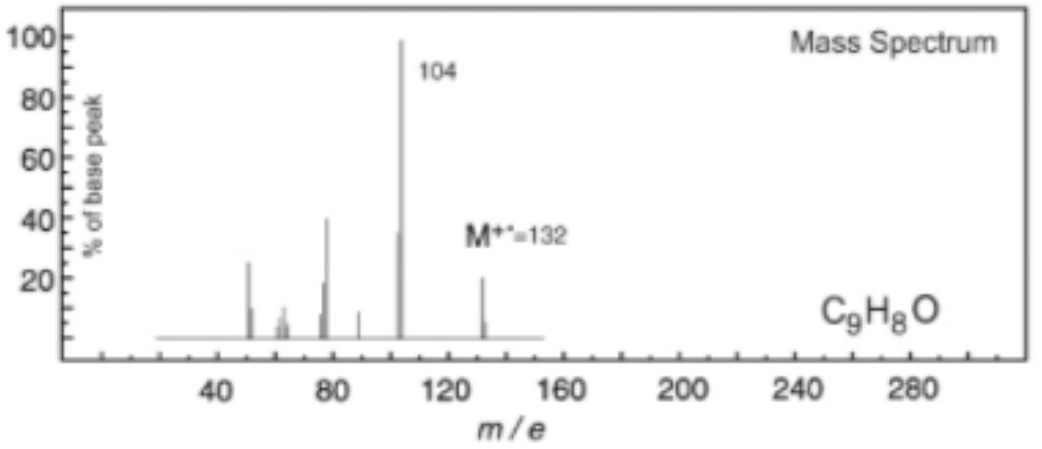



solvent
residual
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
30
130
140
150
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
210
8.0
7.8
7.6
7.4
7.2
3.2
3.0
2.8
2.6
ppm

ppm
30
130
140
150
210
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
8.0
7.8
7.6
7.4
7.2
3.2
3.0
2.8
2.6
ppm

Problem 206



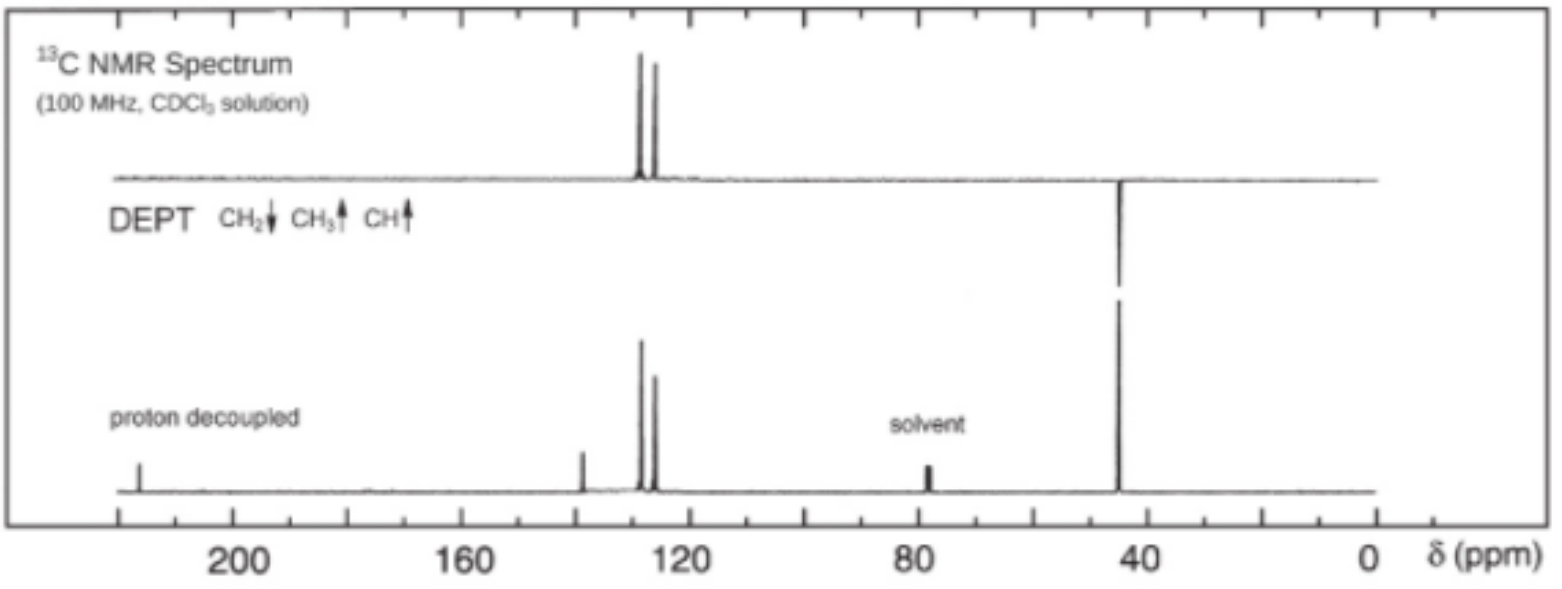


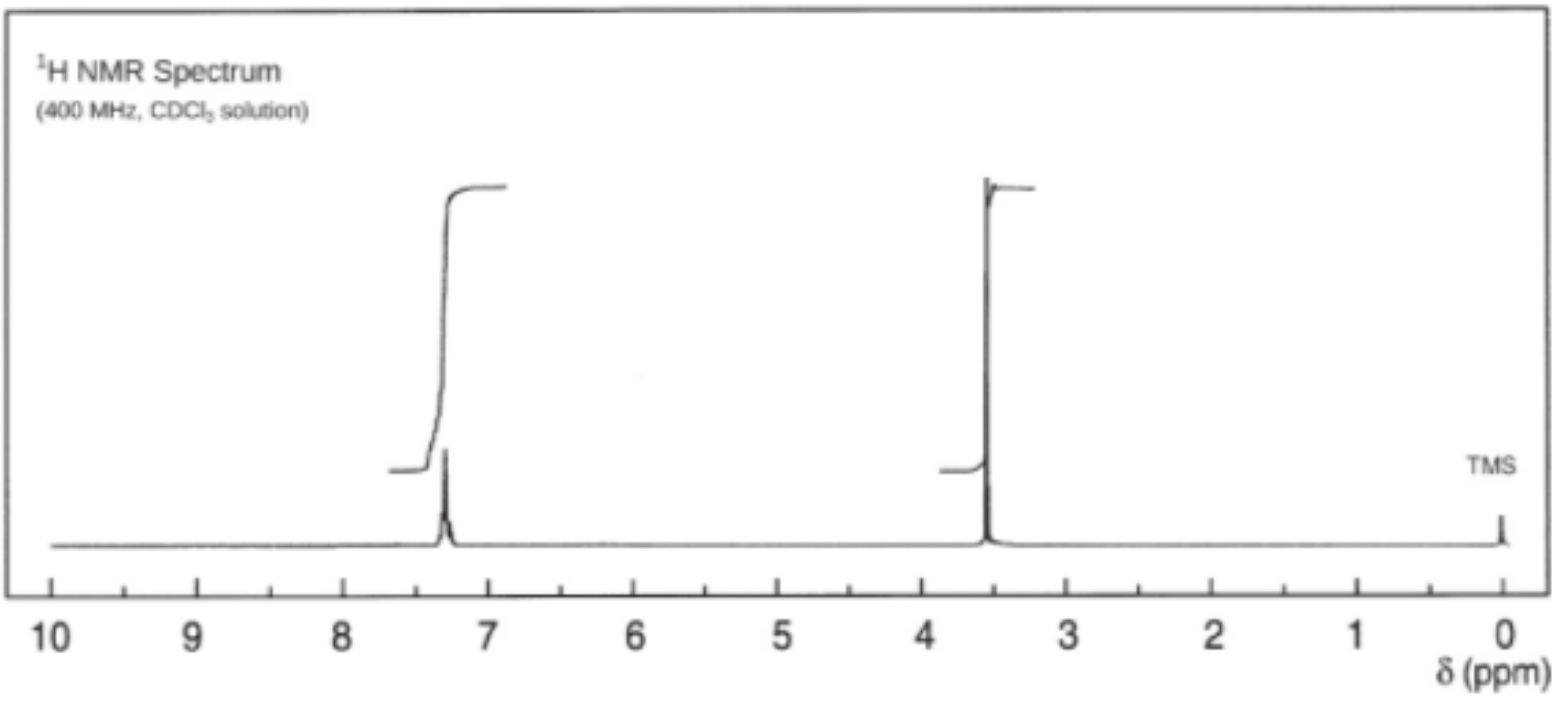
UV Spectrum

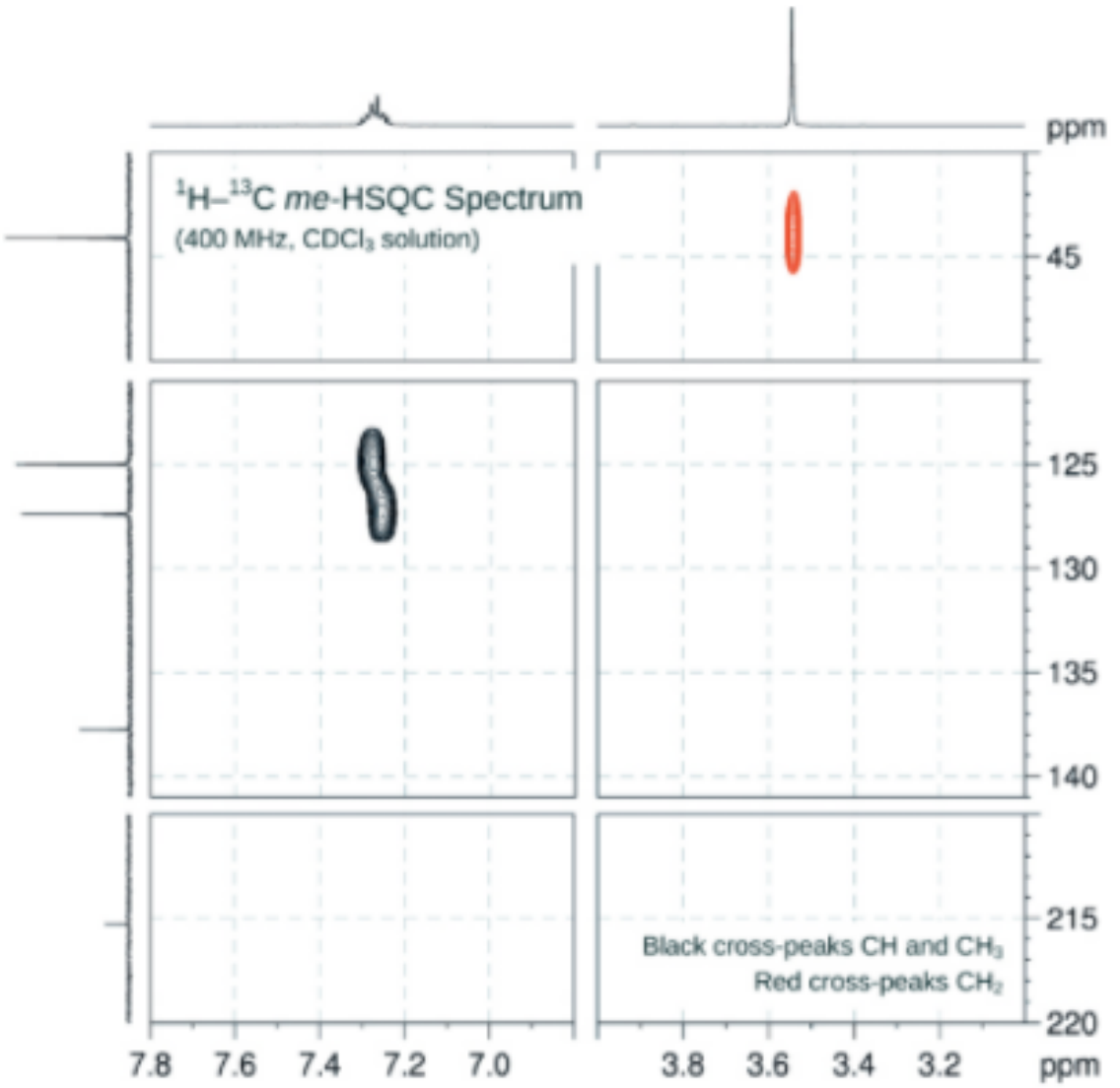
λ_{max} 268 nm ($\log_{10}\varepsilon$ 3.1)

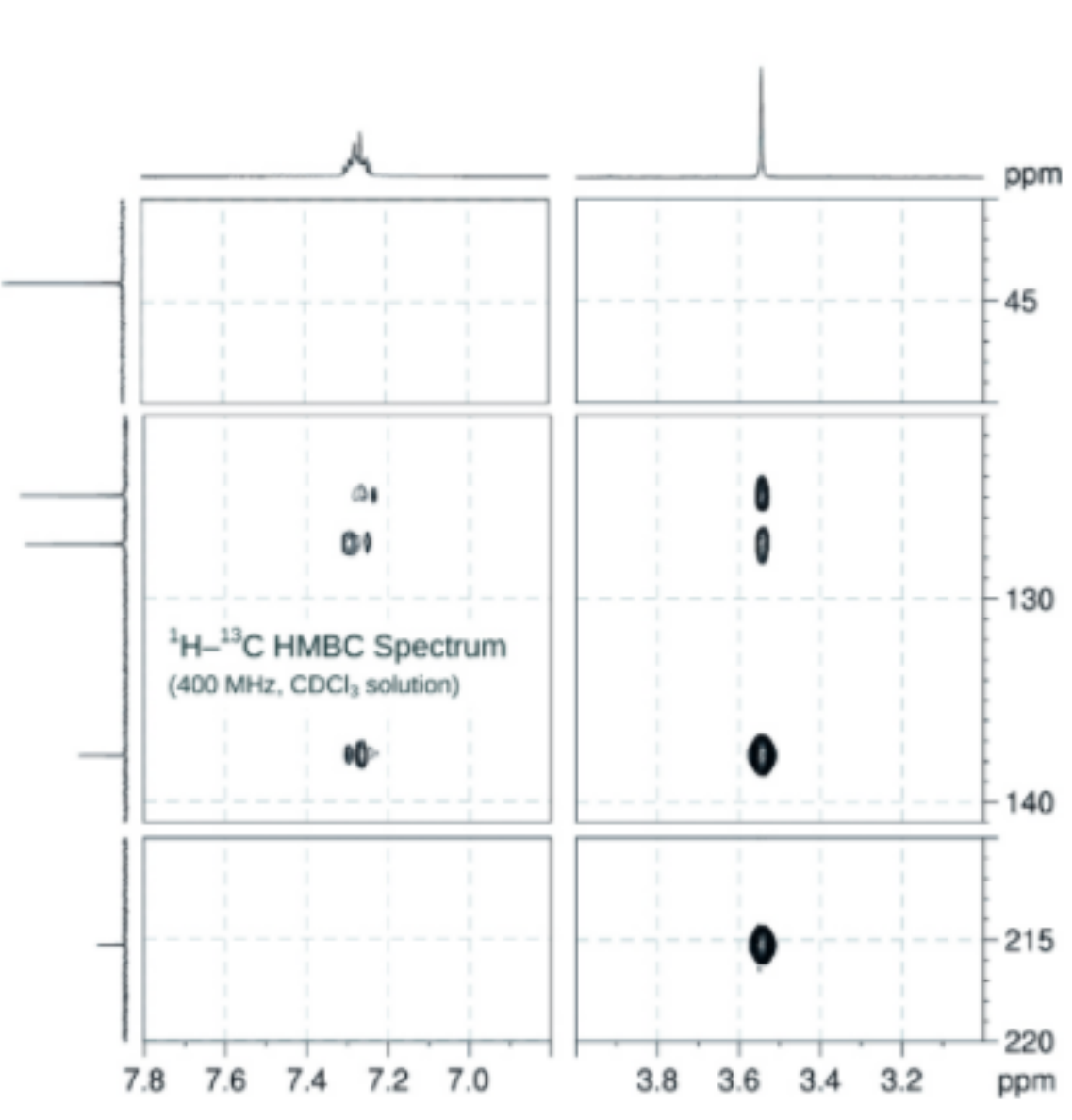
λ_{max} 275 nm ($\log_{10}\varepsilon$ 3.1)

solvent : ethanol

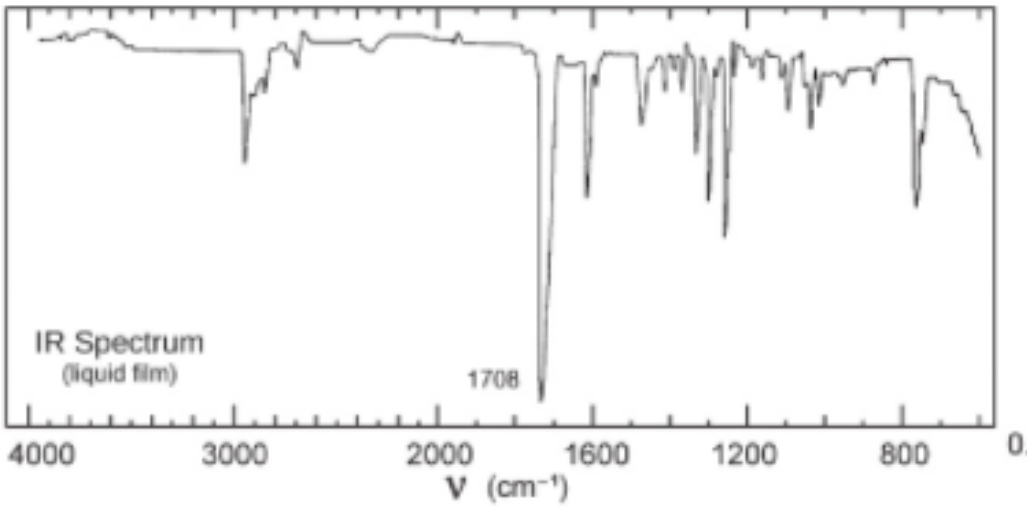


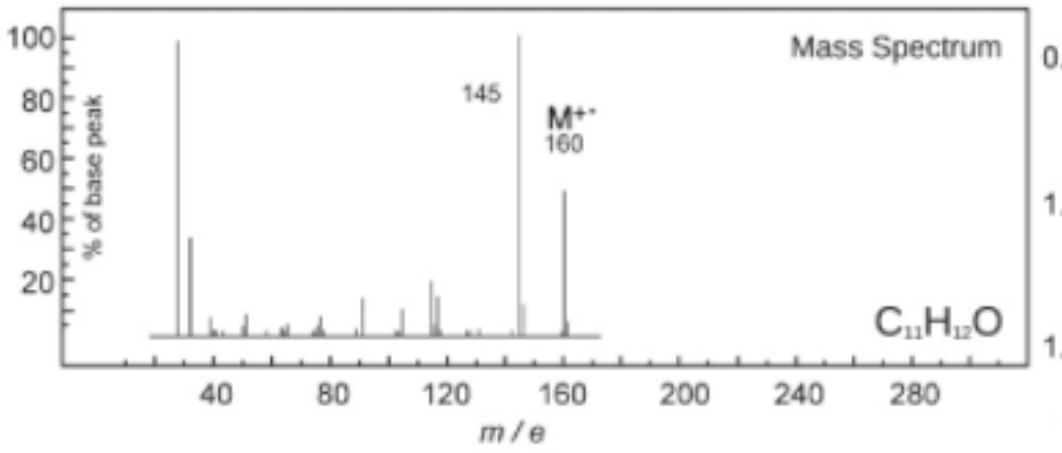


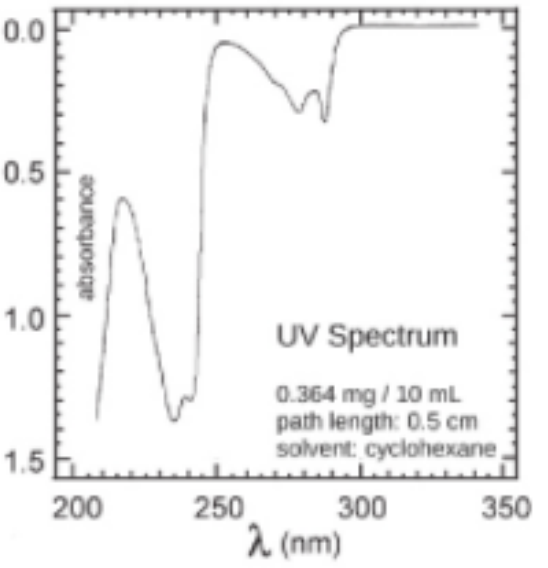

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
45
125
130
135
140
215
220
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.8
7.6
7.4
7.2
7.0
3.8
3.6
3.4
3.2
ppm

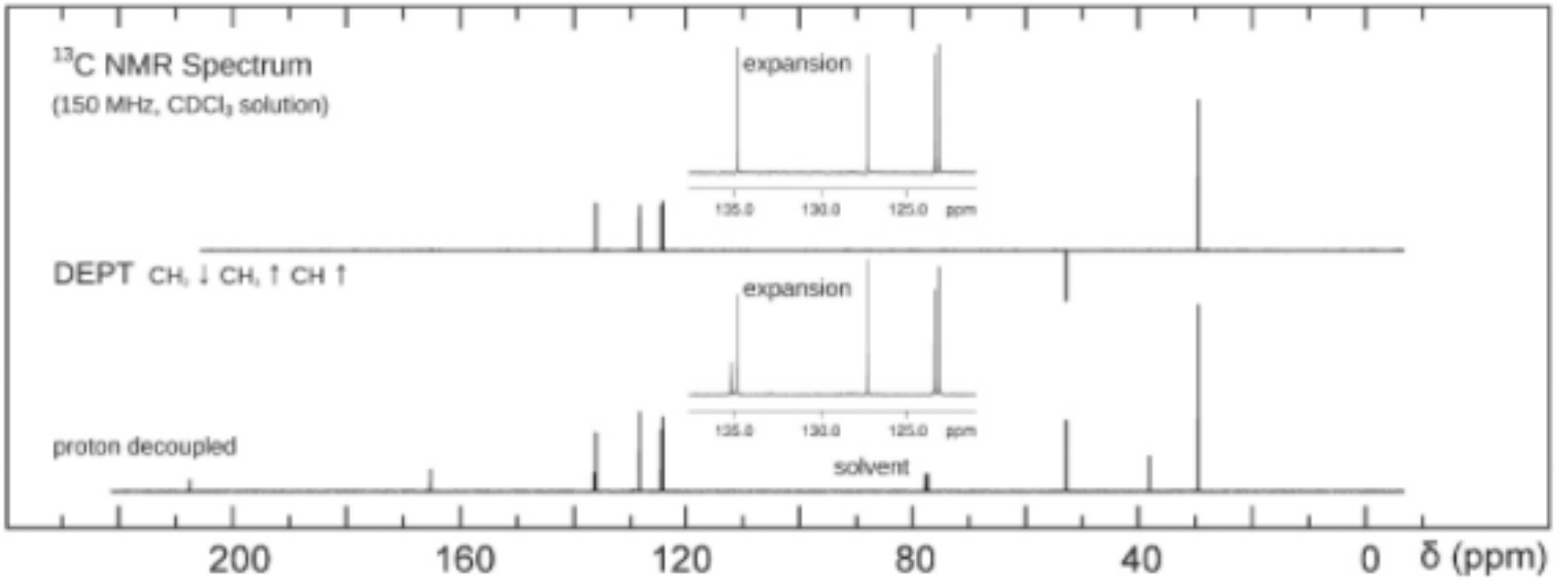

ppm
45
130
140
215
220
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
7.8
7.6
7.4
7.2
7.0
3.8
3.6
3.4
3.2
ppm

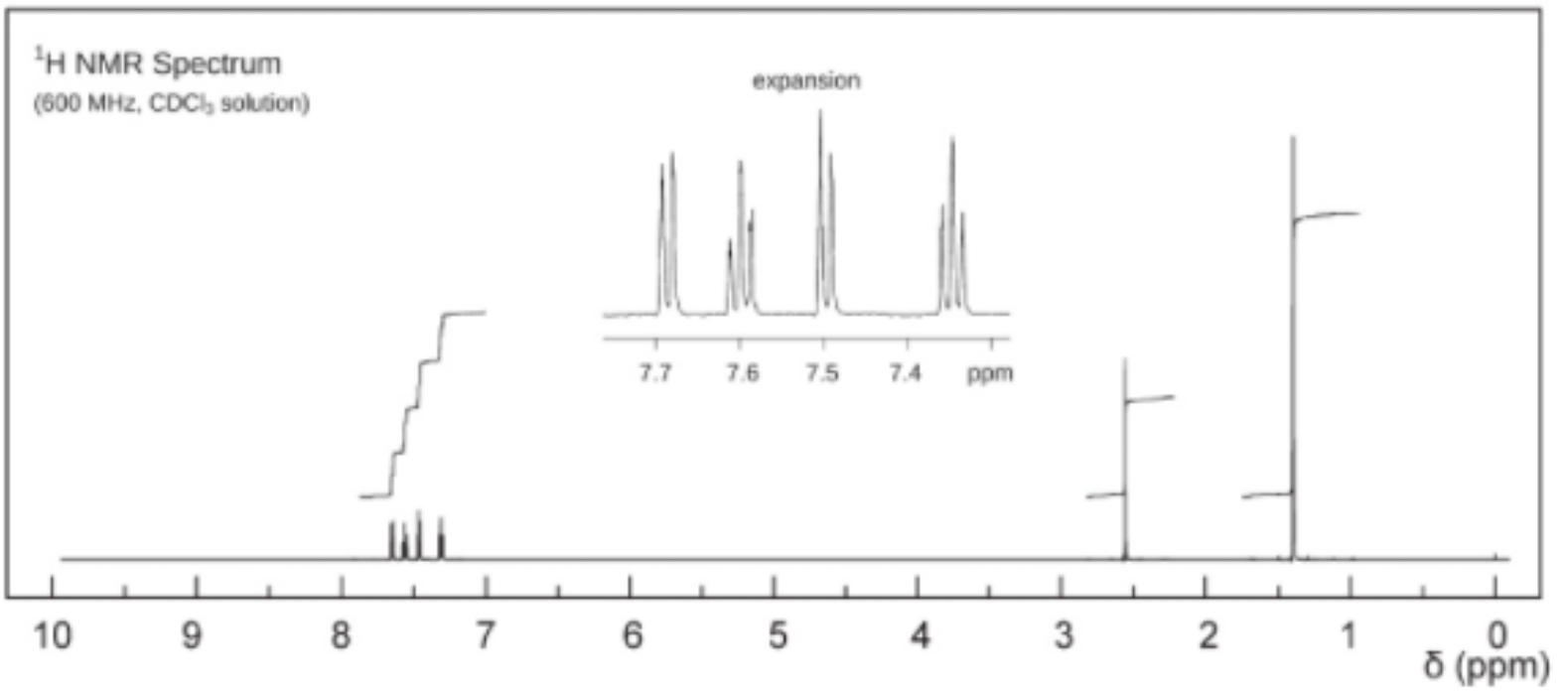
Problem 207

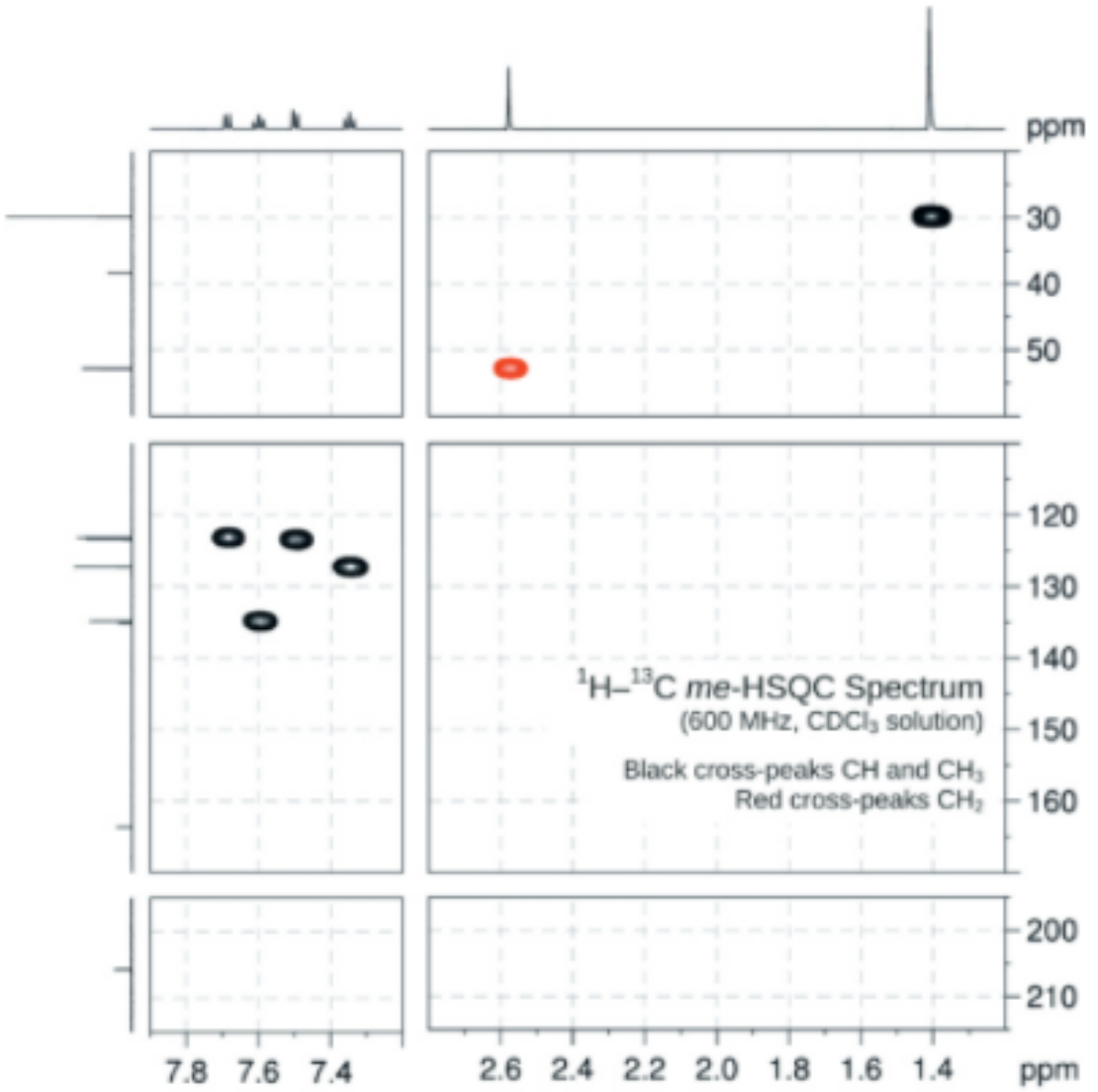

IR Spectrum
(liquid film)
1708
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

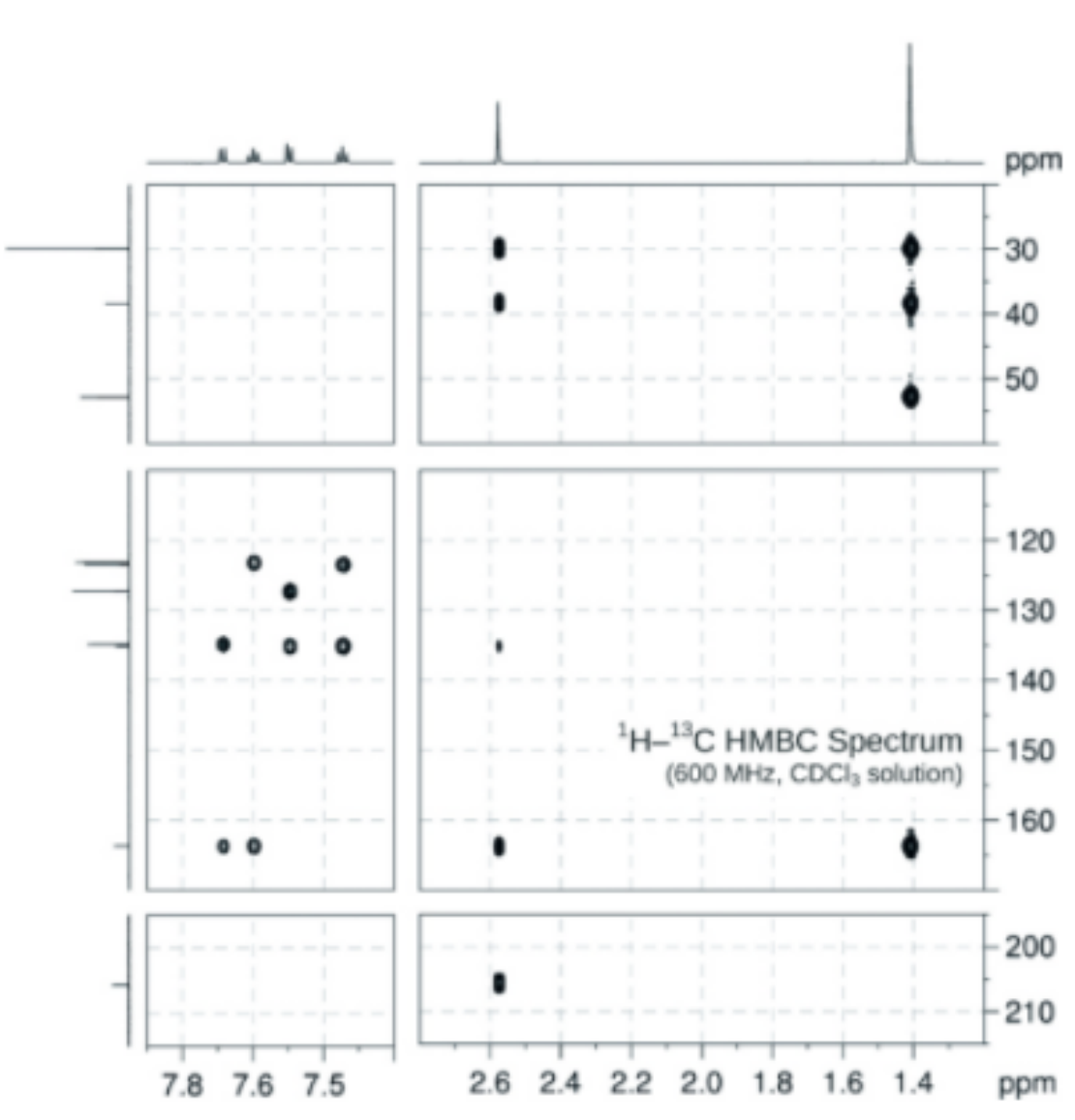

Mass Spectrum
% of base peak
100
80
60
40
20
145
M+·
160
C11H12O
40
80
120
160
200
240
280
m / e


absorbance
0.0
0.5
1.0
1.5
UV Spectrum
0.364 mg / 10 mL
path length: 0.5 cm
solvent: cyclohexane
200
250
300
350
λ (nm)

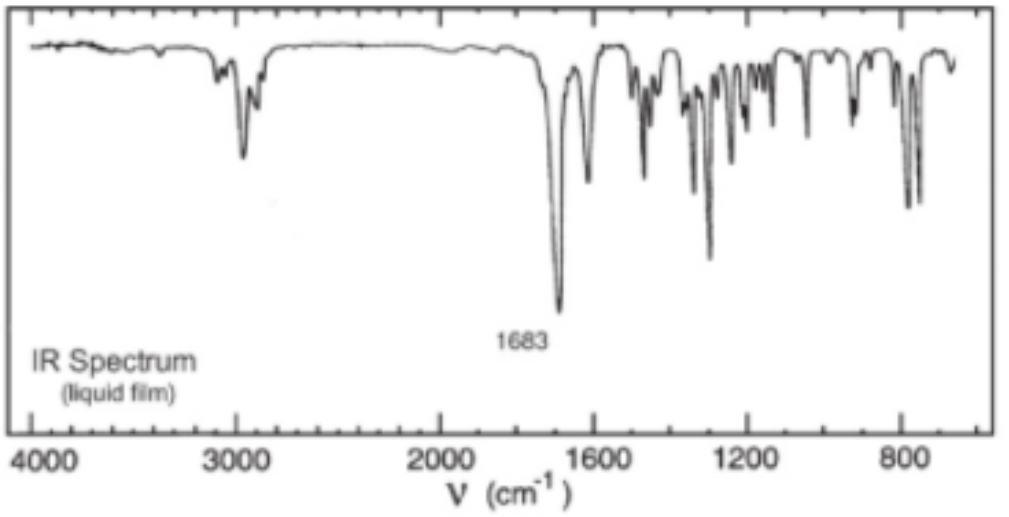

13C NMR Spectrum
(150 MHz, CDCl3 solution)
expansion
135.0
130.0
125.0
ppm
DEPT CH3 ↓ CH2 ↑ CH ↑
expansion
135.0
130.0
125.0
ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

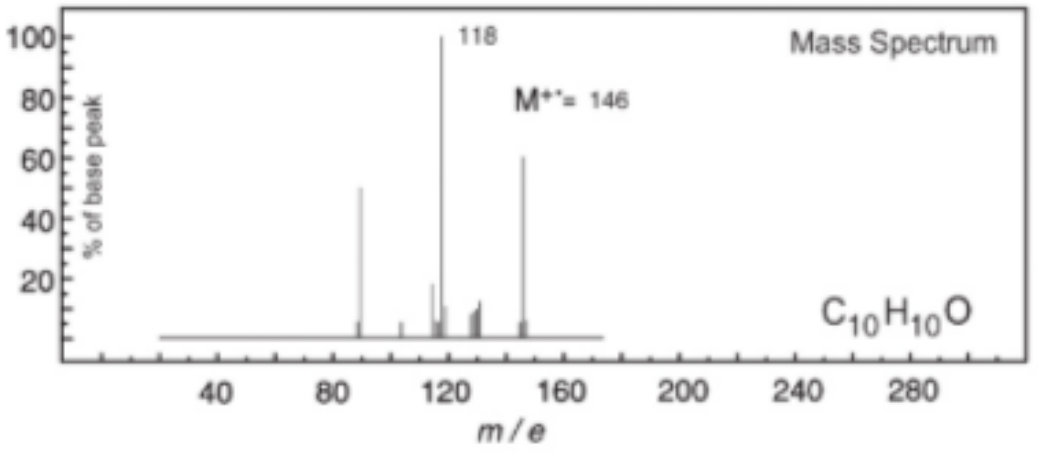

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion
7.7
7.6
7.5
7.4
ppm
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
30
40
50
120
130
140
150
160
200
210
7.8
7.6
7.4
2.6
2.4
2.2
2.0
1.8
1.6
1.4
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2


ppm
30
40
50
120
130
140
150
160
200
210
7.8
7.6
7.5
2.6
2.4
2.2
2.0
1.8
1.6
1.4
ppm
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)

Problem 208



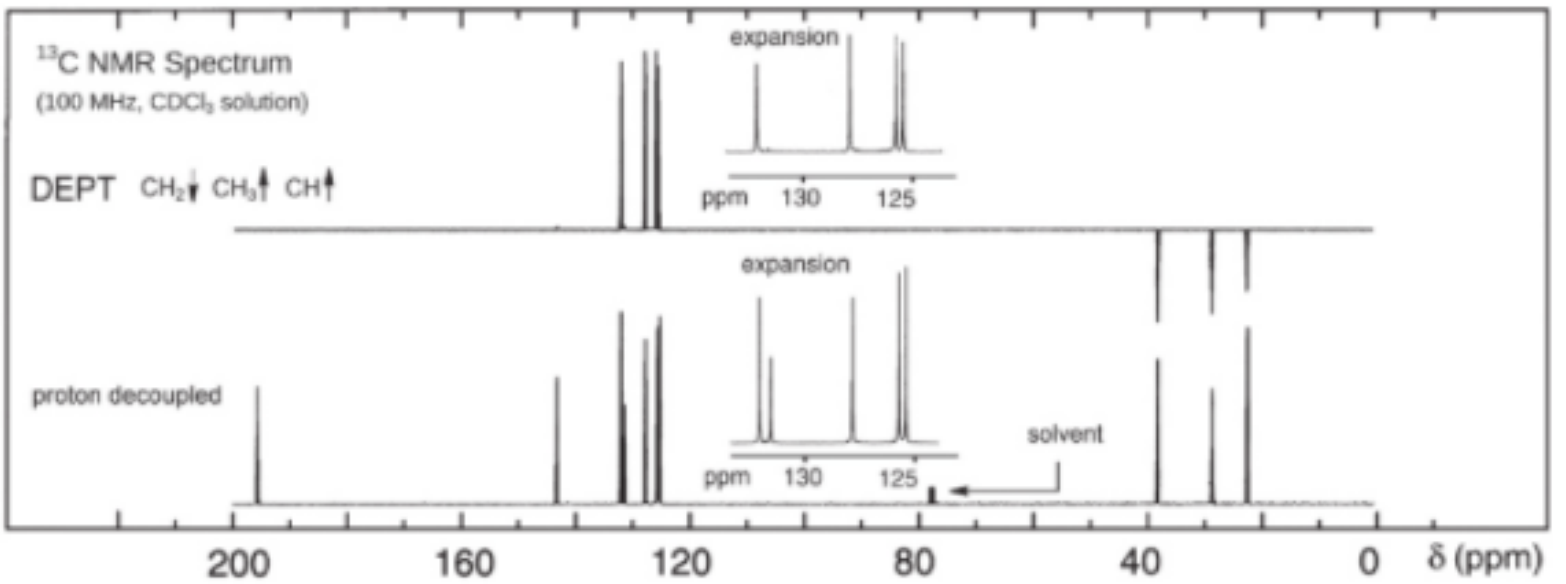


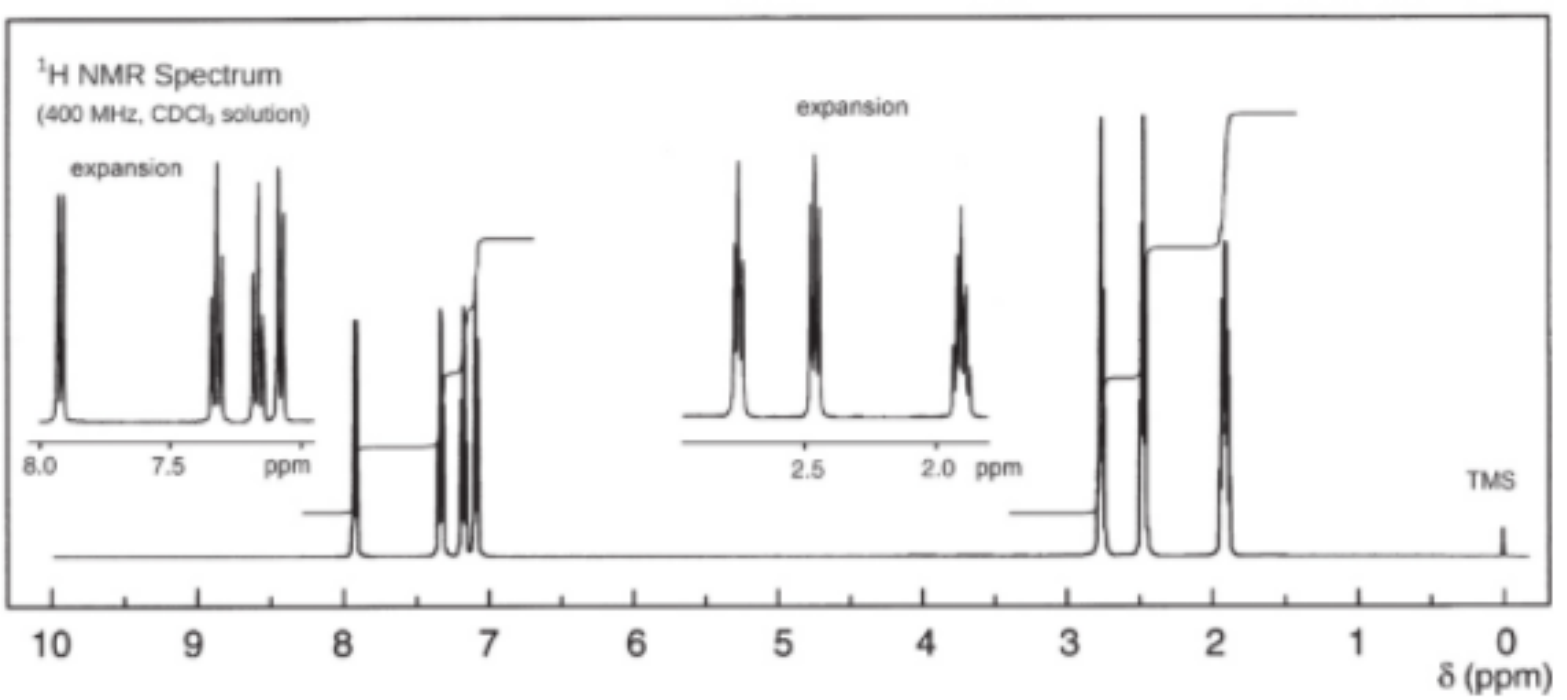
UV Spectrum

λ_{max} 249 nm ($\log_{10}\varepsilon$ 4.1)

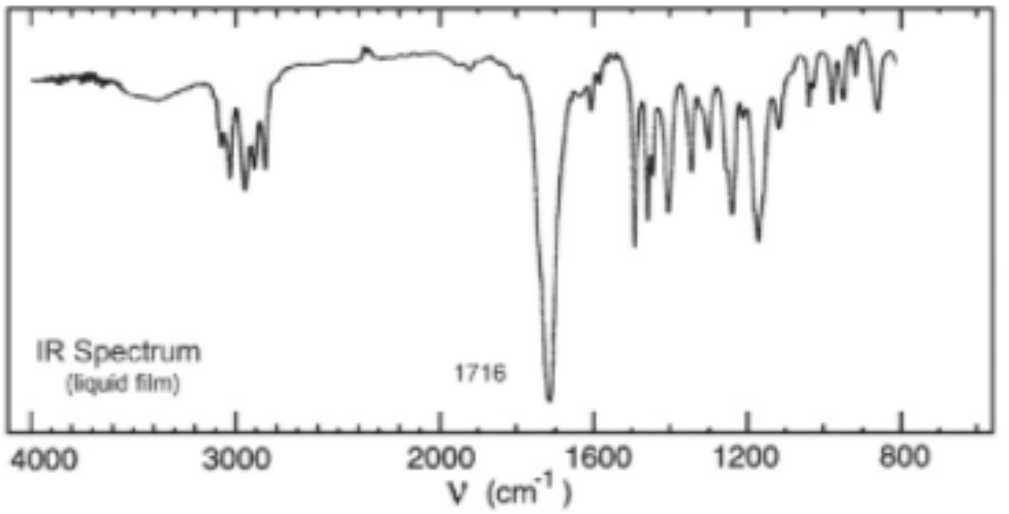
λ_{max} 292 nm ($\log_{10}\varepsilon$ 3.3)

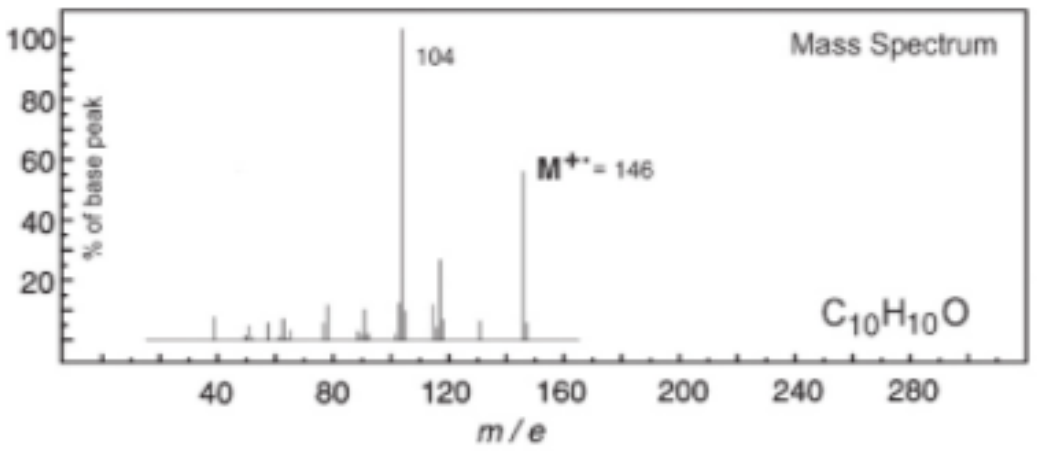
solvent : ethanol





Problem 209





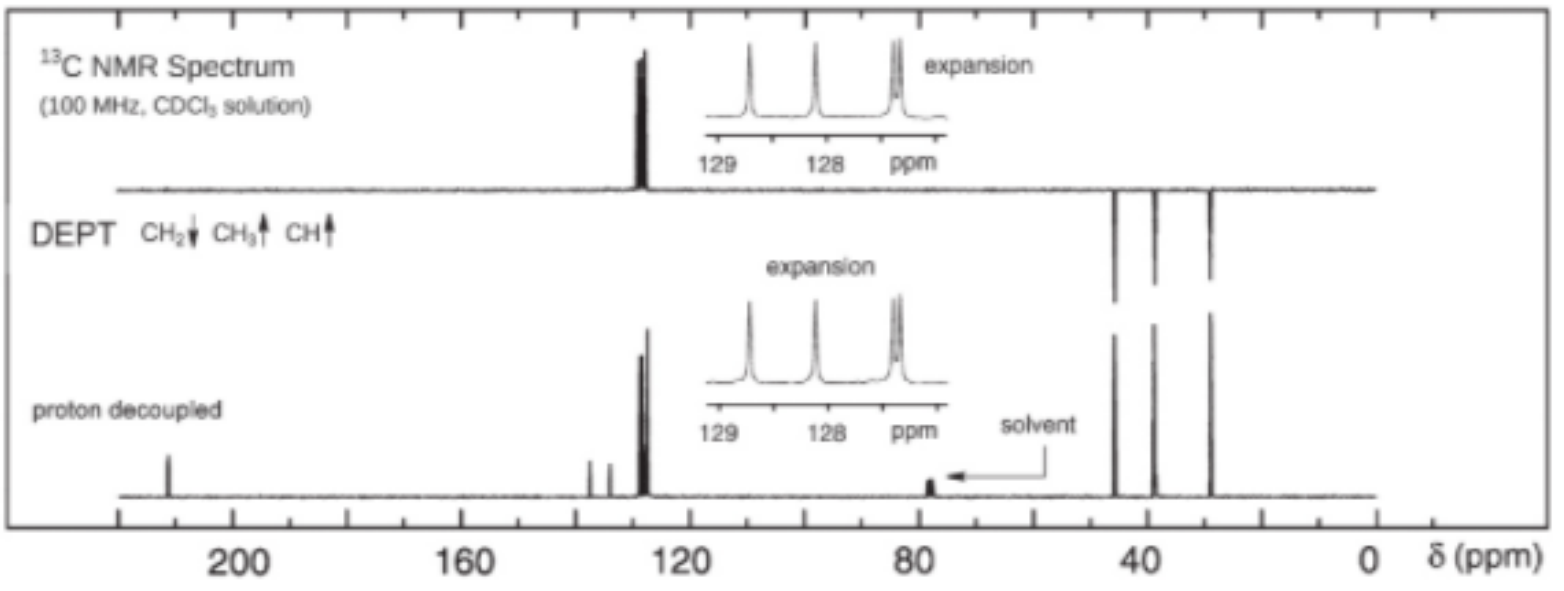
UV Spectrum

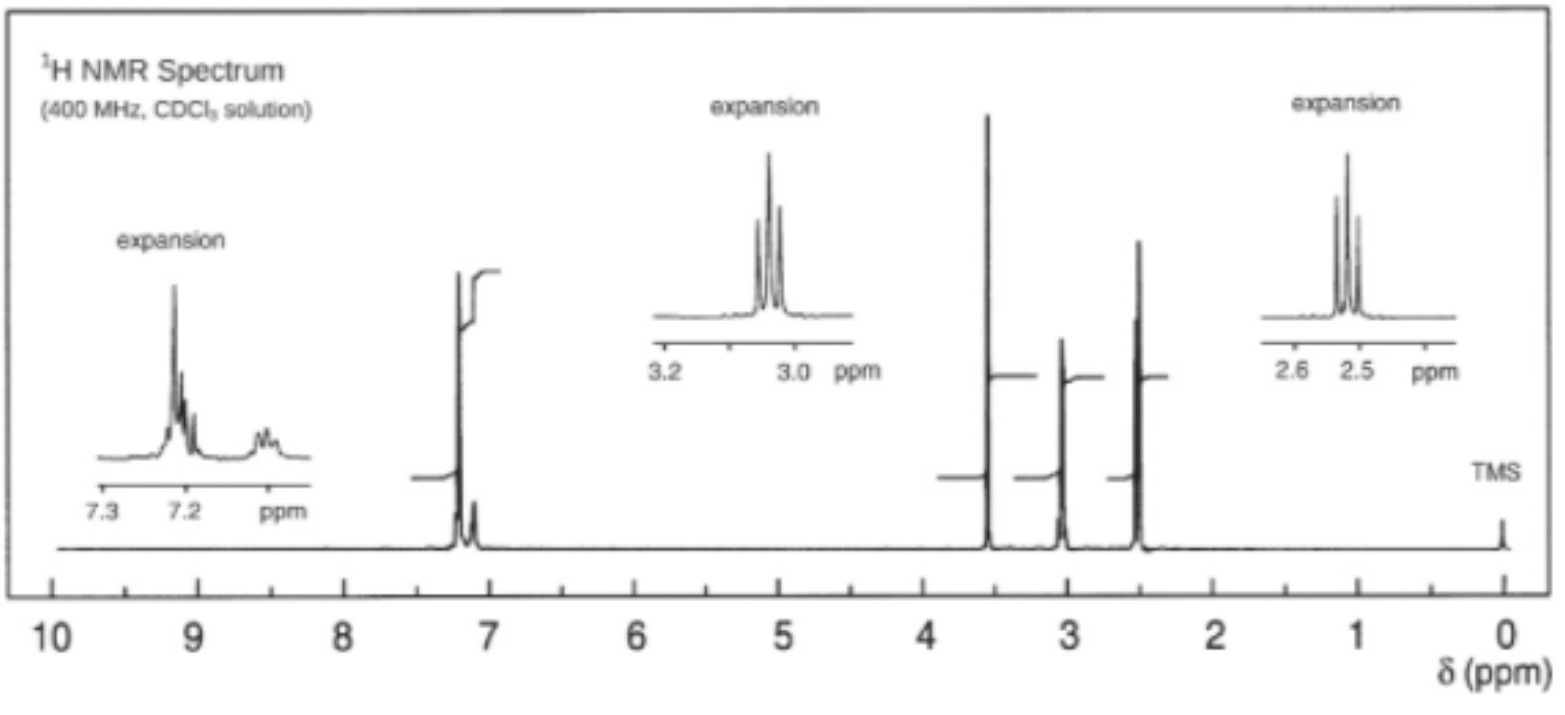
λ_{max} 265 nm ($\log_{10}\varepsilon$ 3.0)

λ_{max} 272 nm ($\log_{10}\varepsilon$ 3.1)

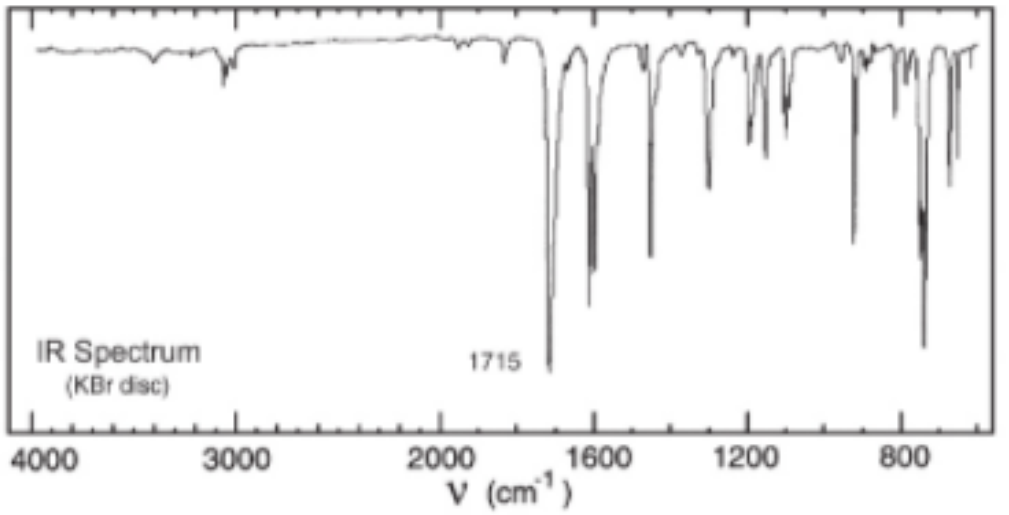
λ_{max} 294 nm ($\log_{10}\varepsilon$ 1.9)

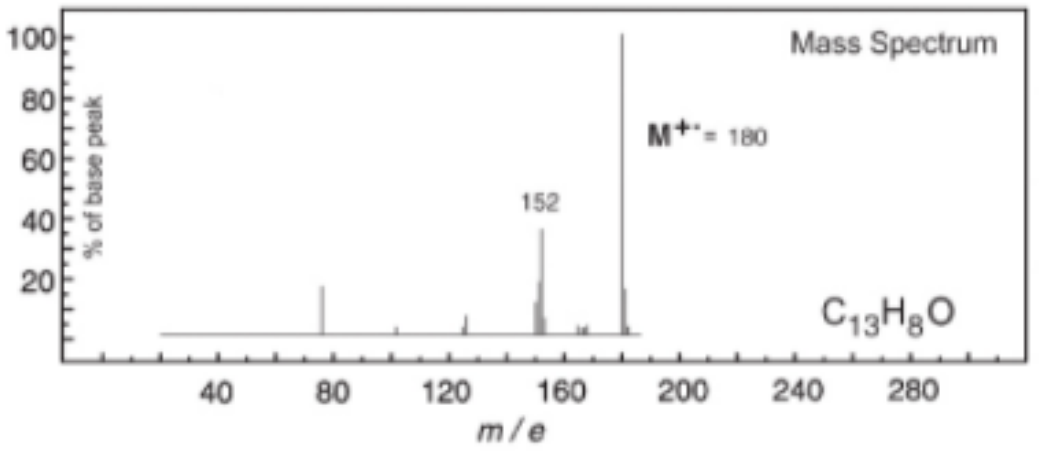
solvent : ethanol





Problem 210



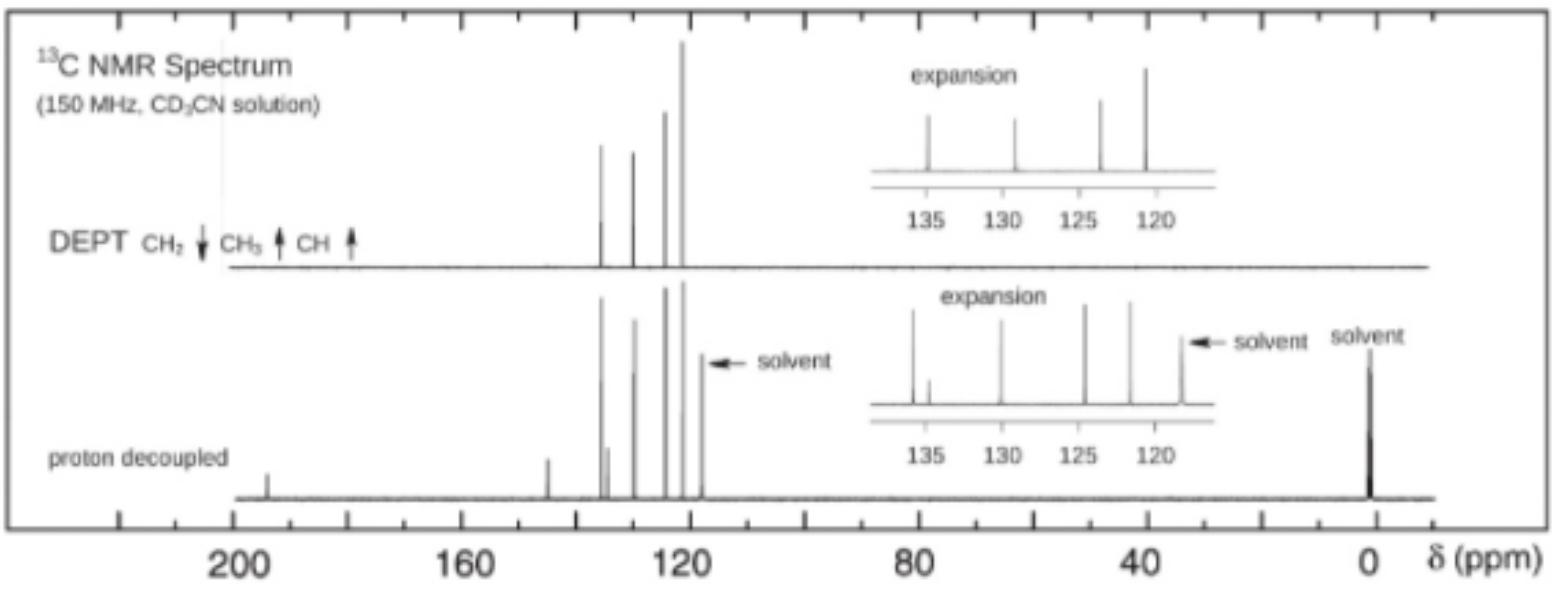


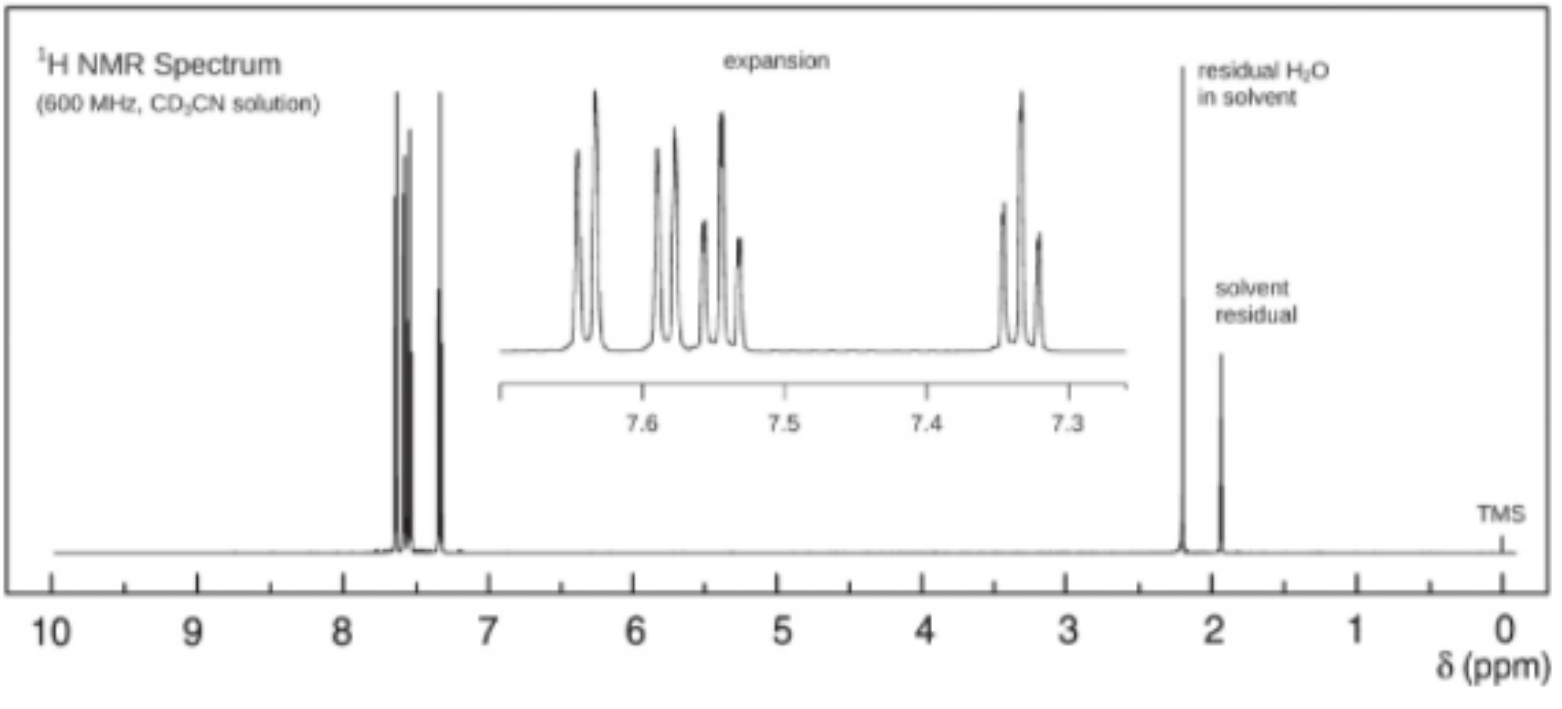
UV Spectrum

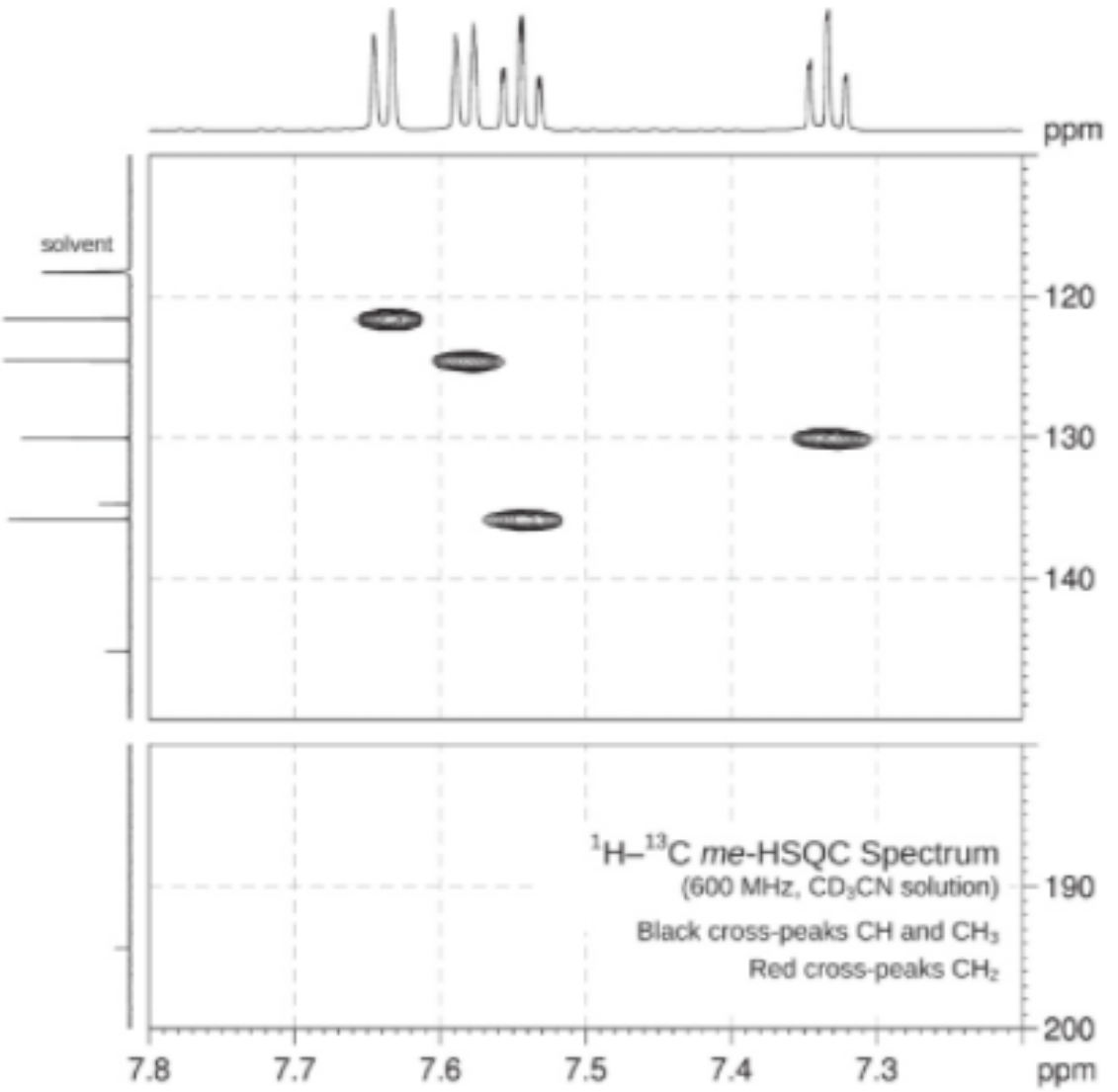
λ_{max} 265 nm ($\log_{10}\varepsilon$ 4.5)

λ_{max} 330 nm ($\log_{10}\varepsilon$ 4.2)

solvent : ethanol

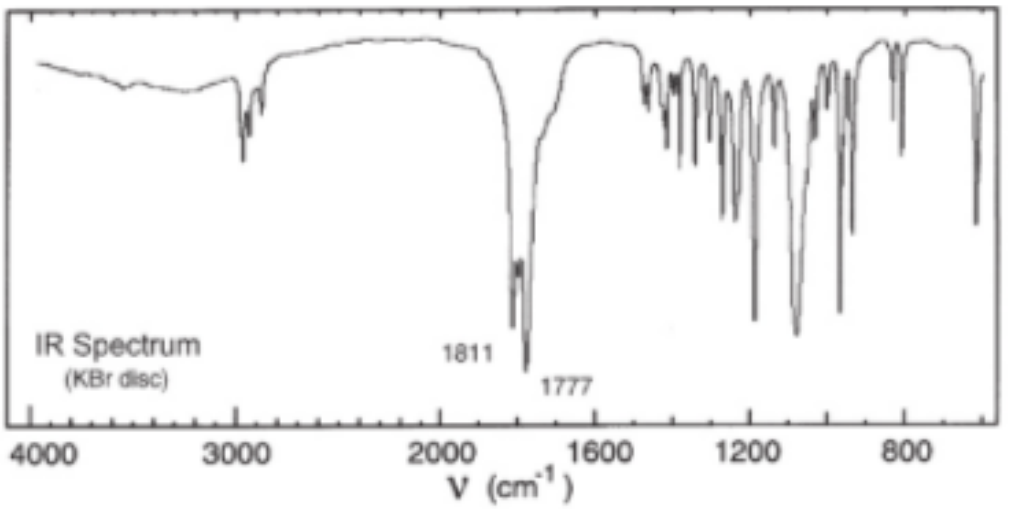


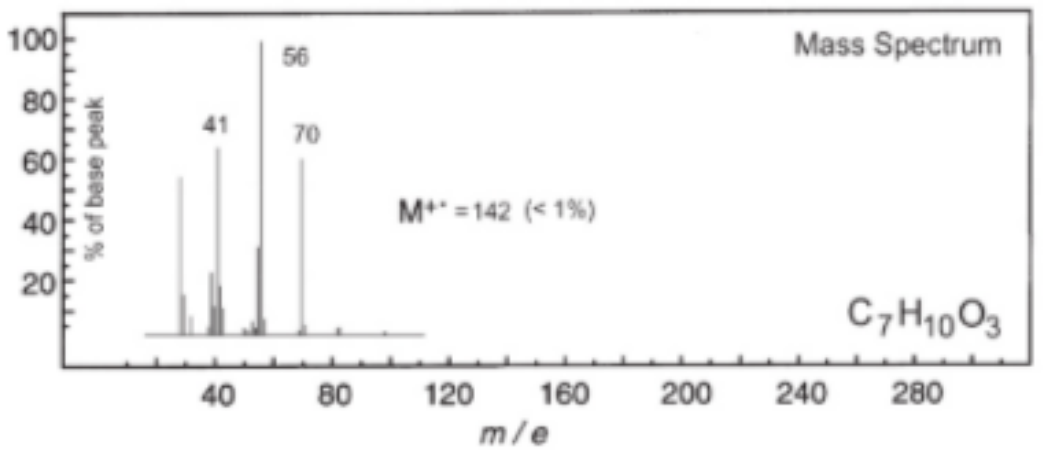



ppm
solvent
120
130
140
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, CD_3CN solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
190
200
7.8
7.7
7.6
7.5
7.4
7.3
ppm

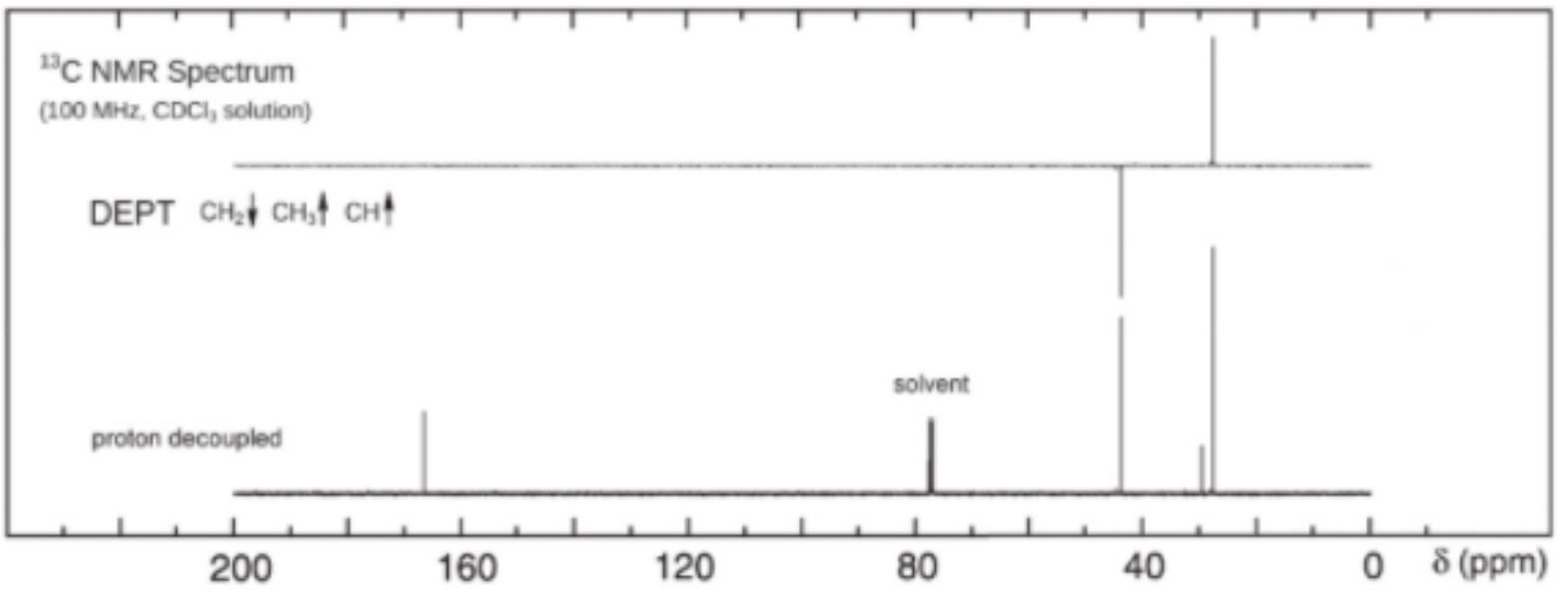
ppm
solvent
120
130
140
^{1}H–^{13}C HMBC Spectrum
(600 MHz, CD_3CN solution)
190
200
7.8
7.7
7.6
7.5
7.4
7.3
ppm

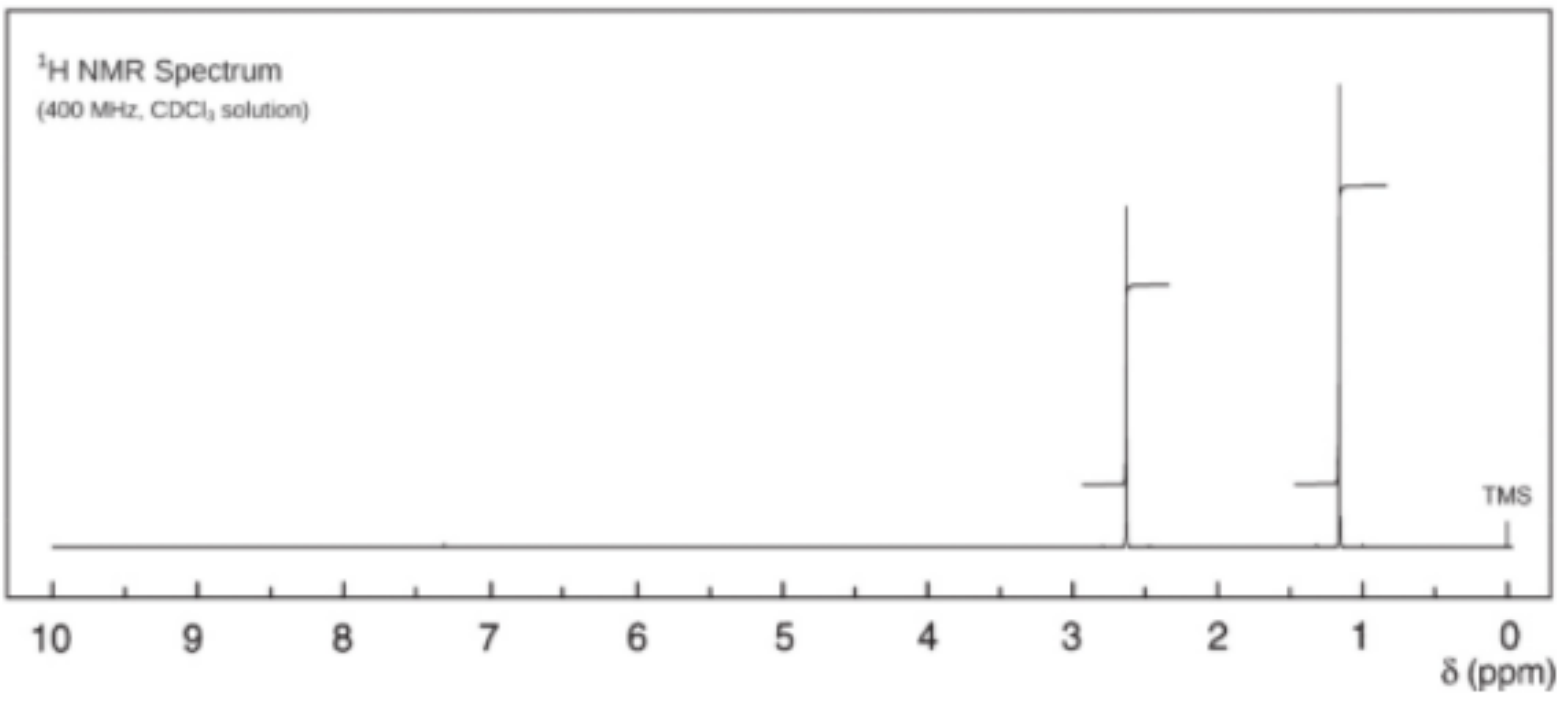
Problem 211



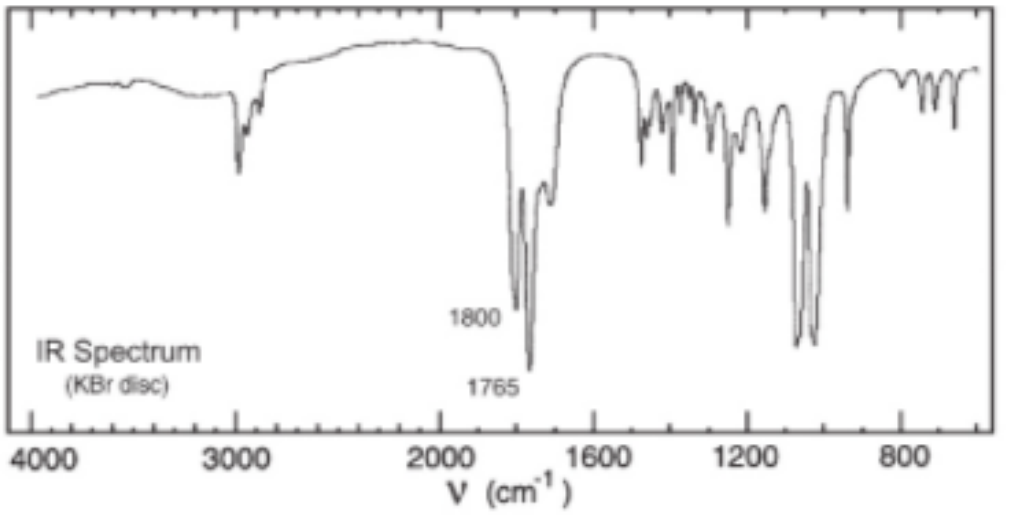


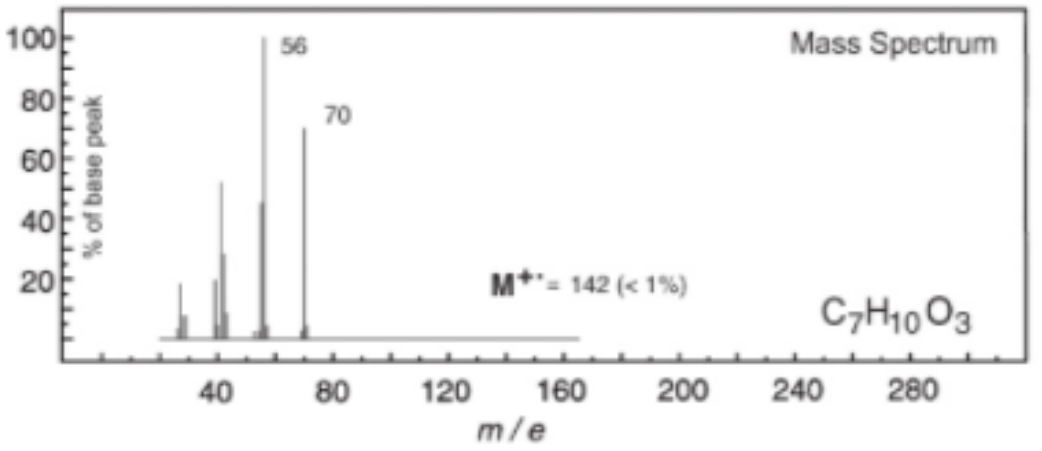
No significant UV absorption above 220 nm



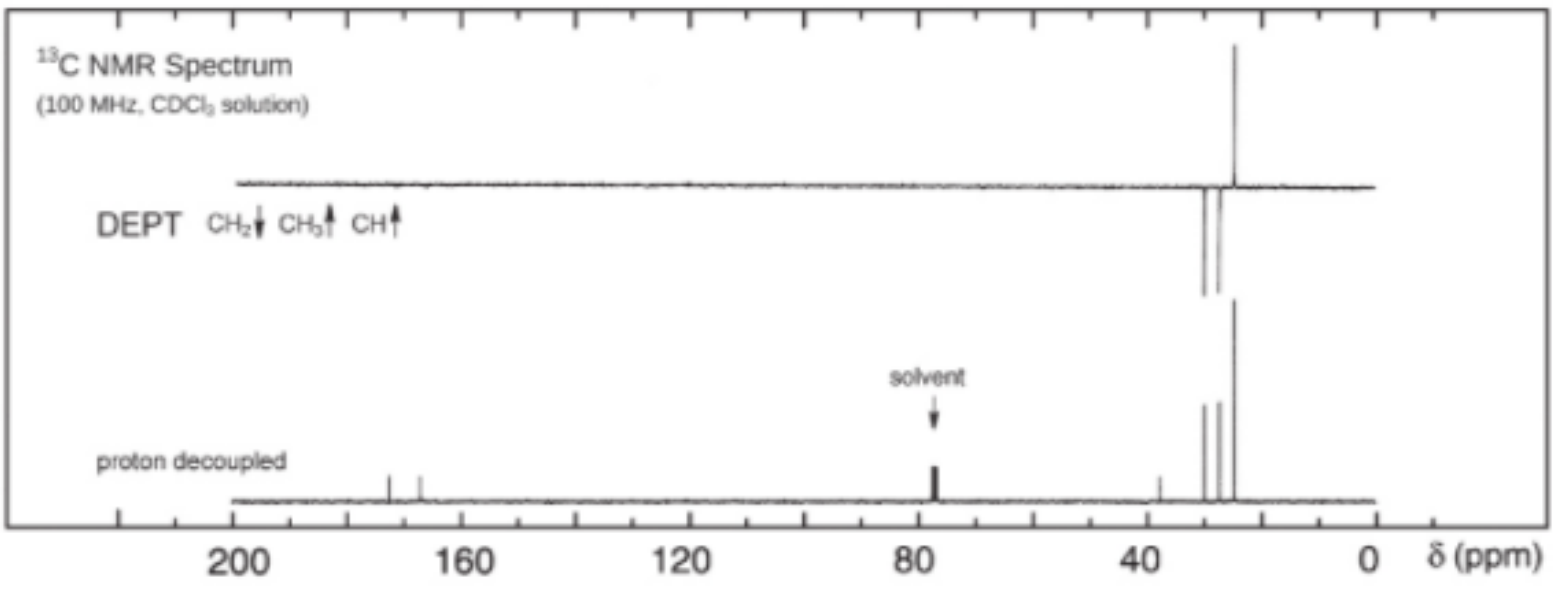


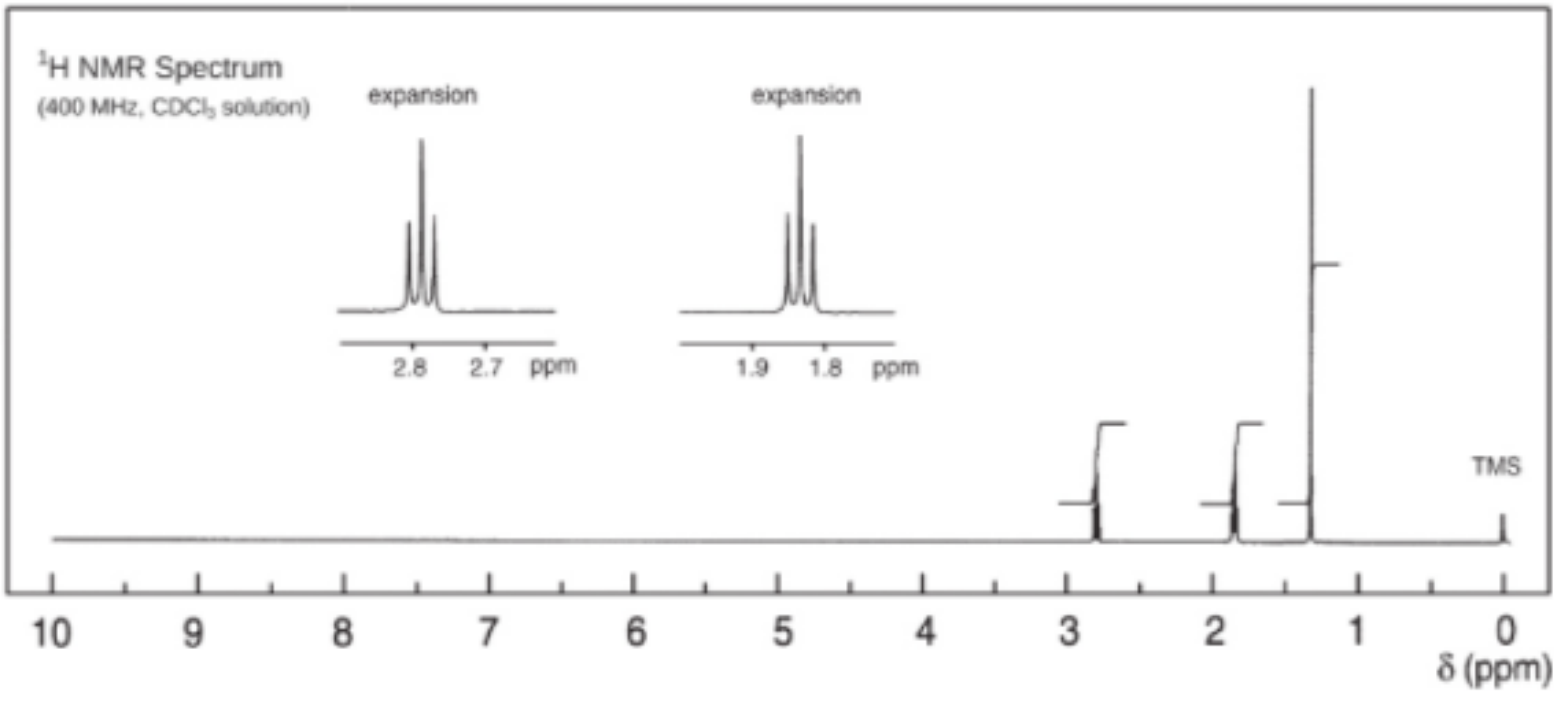
Problem 212



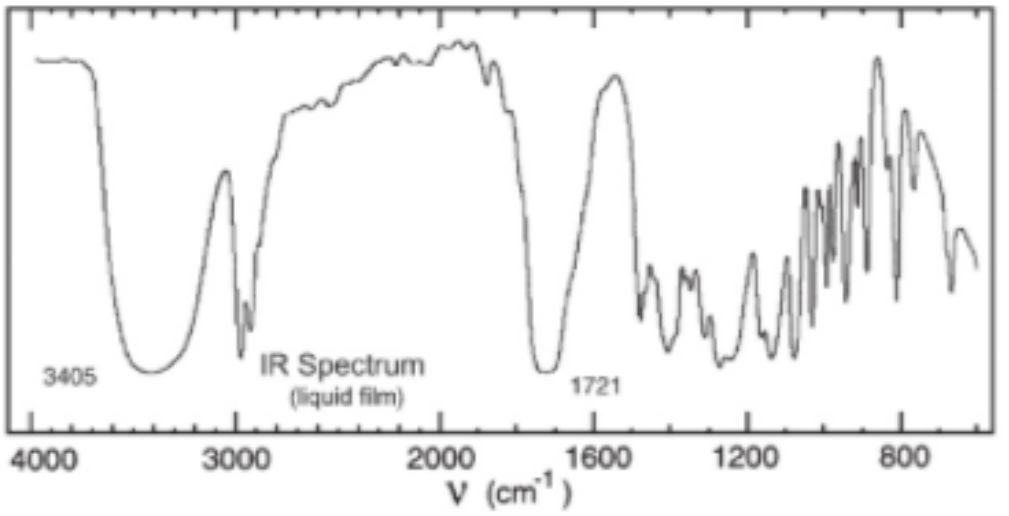


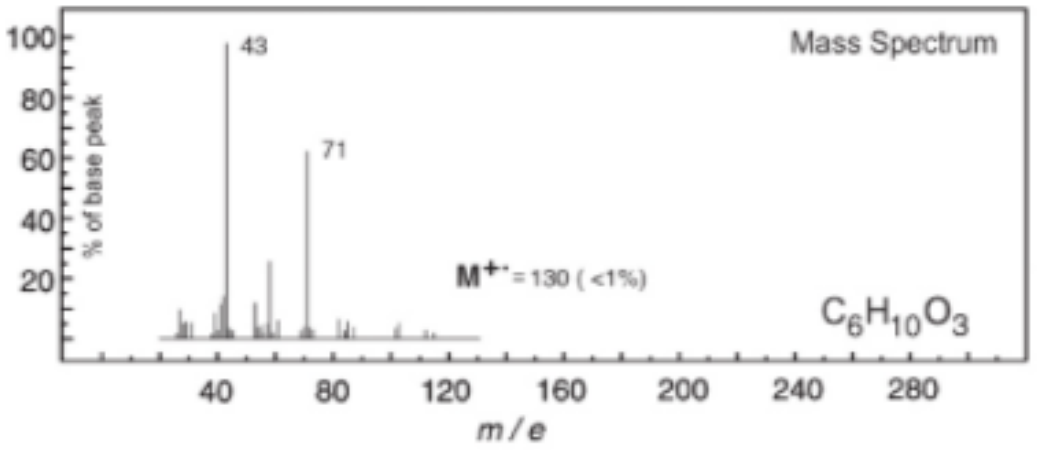
No significant UV absorption above 220 nm



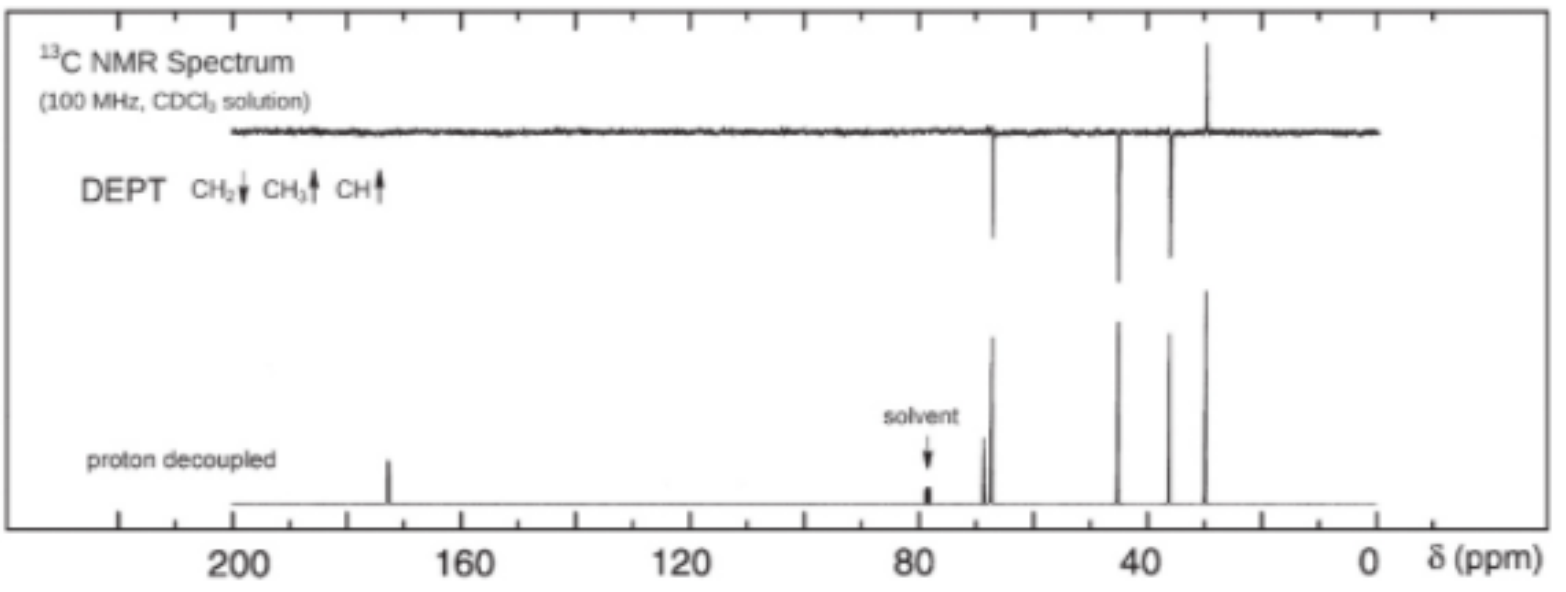


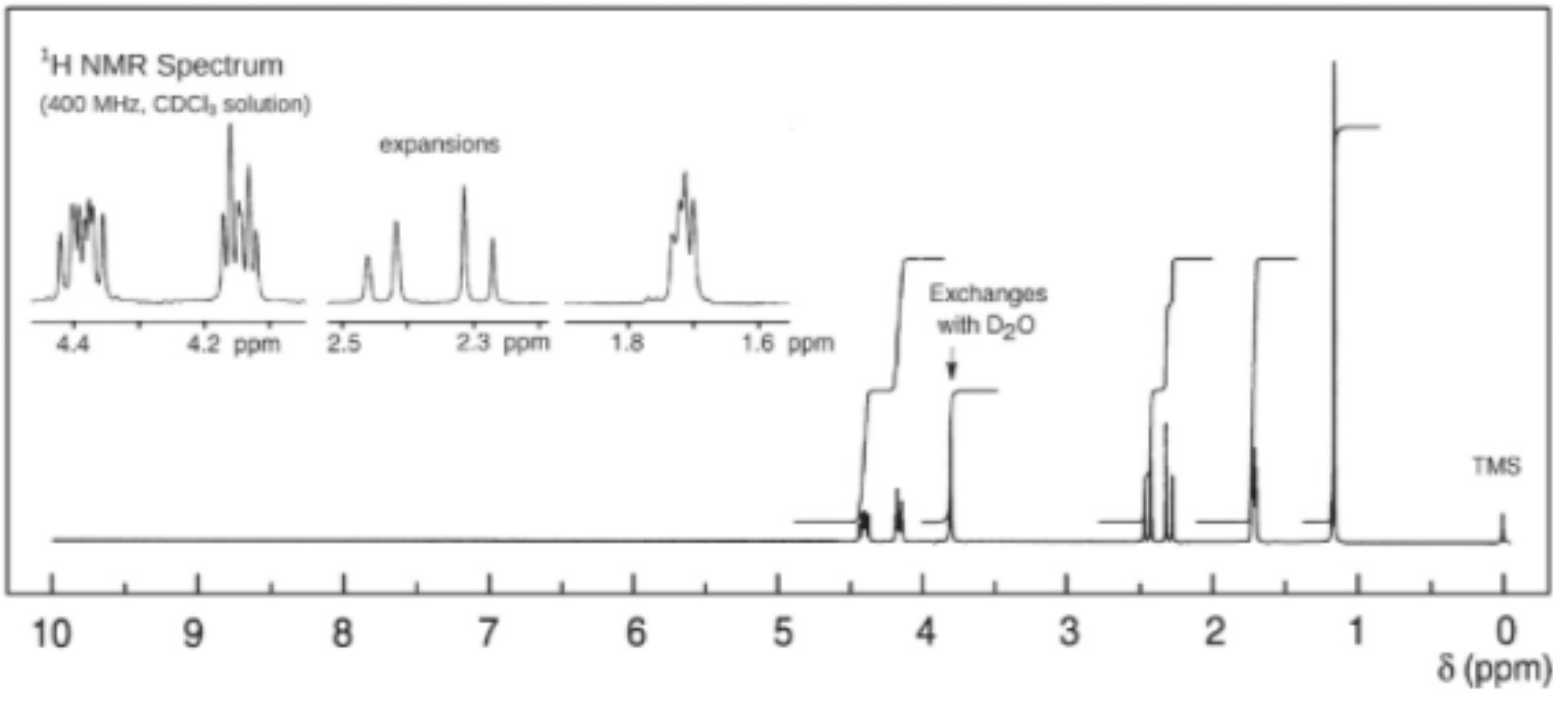
Problem 213



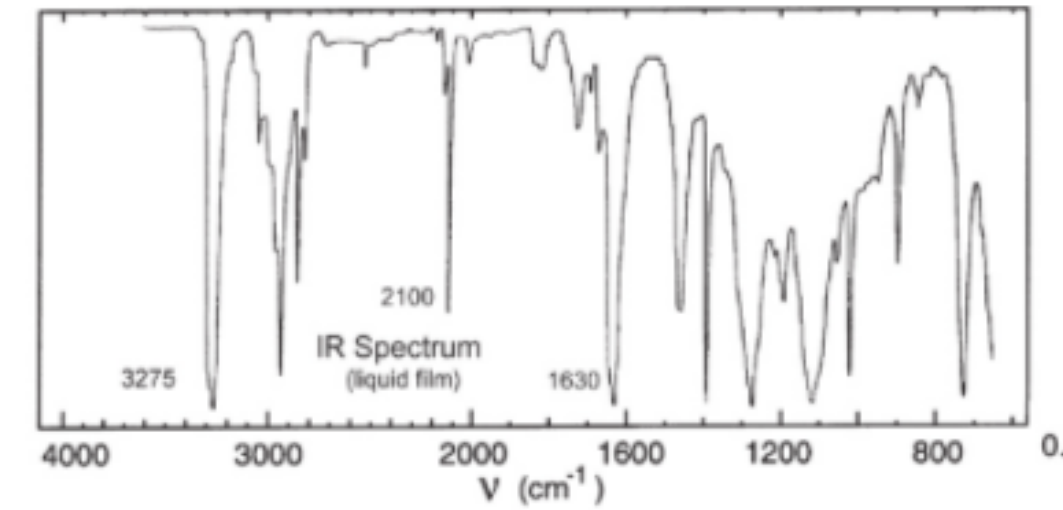


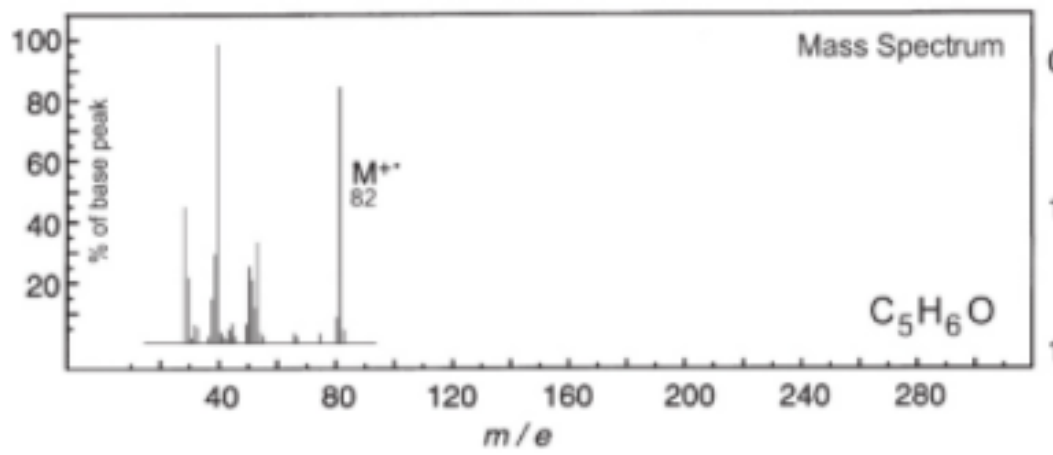
No significant UV absorption above 220 nm

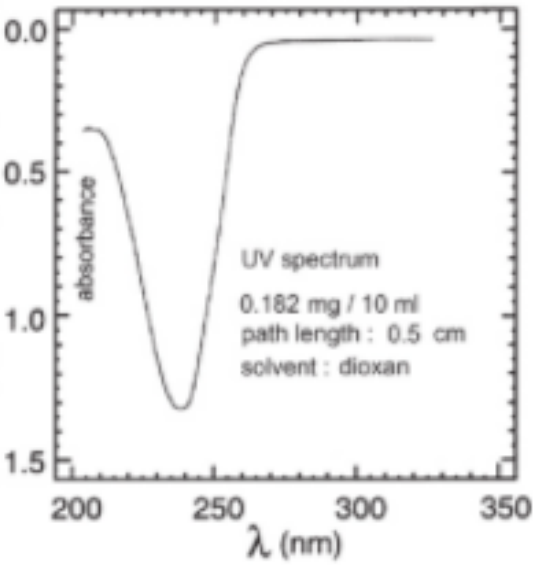


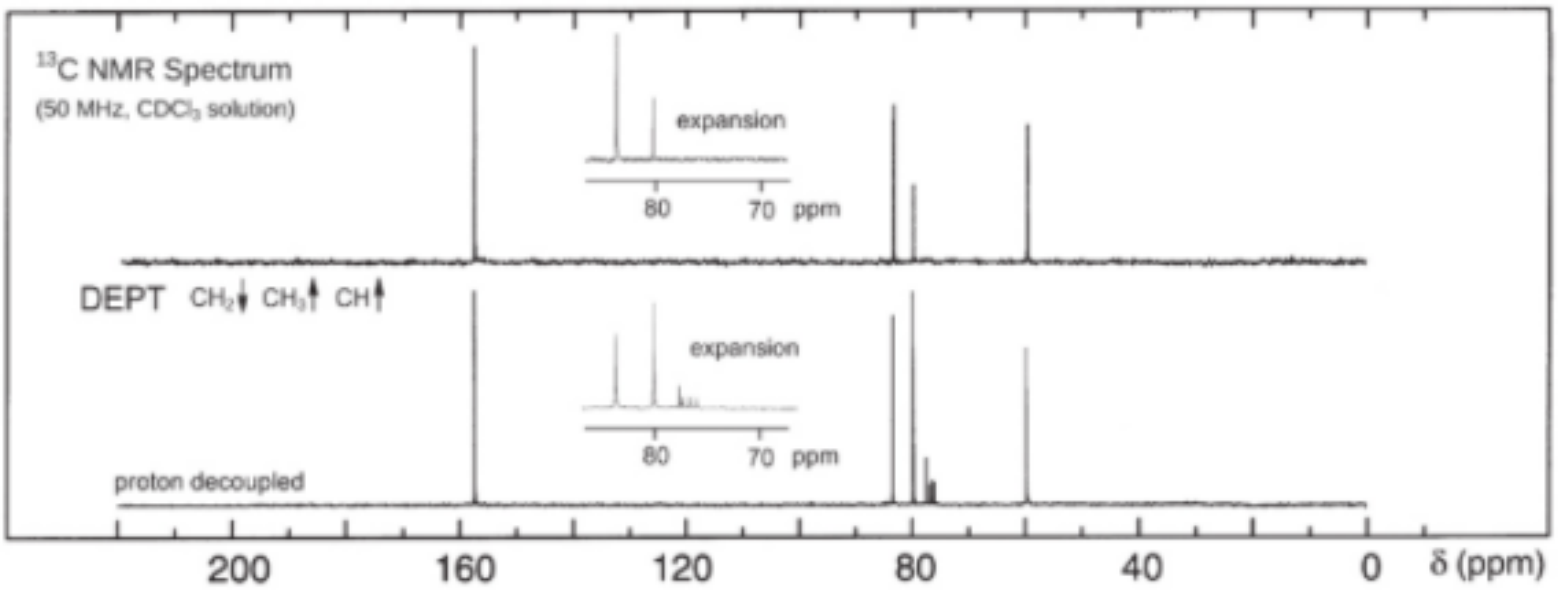


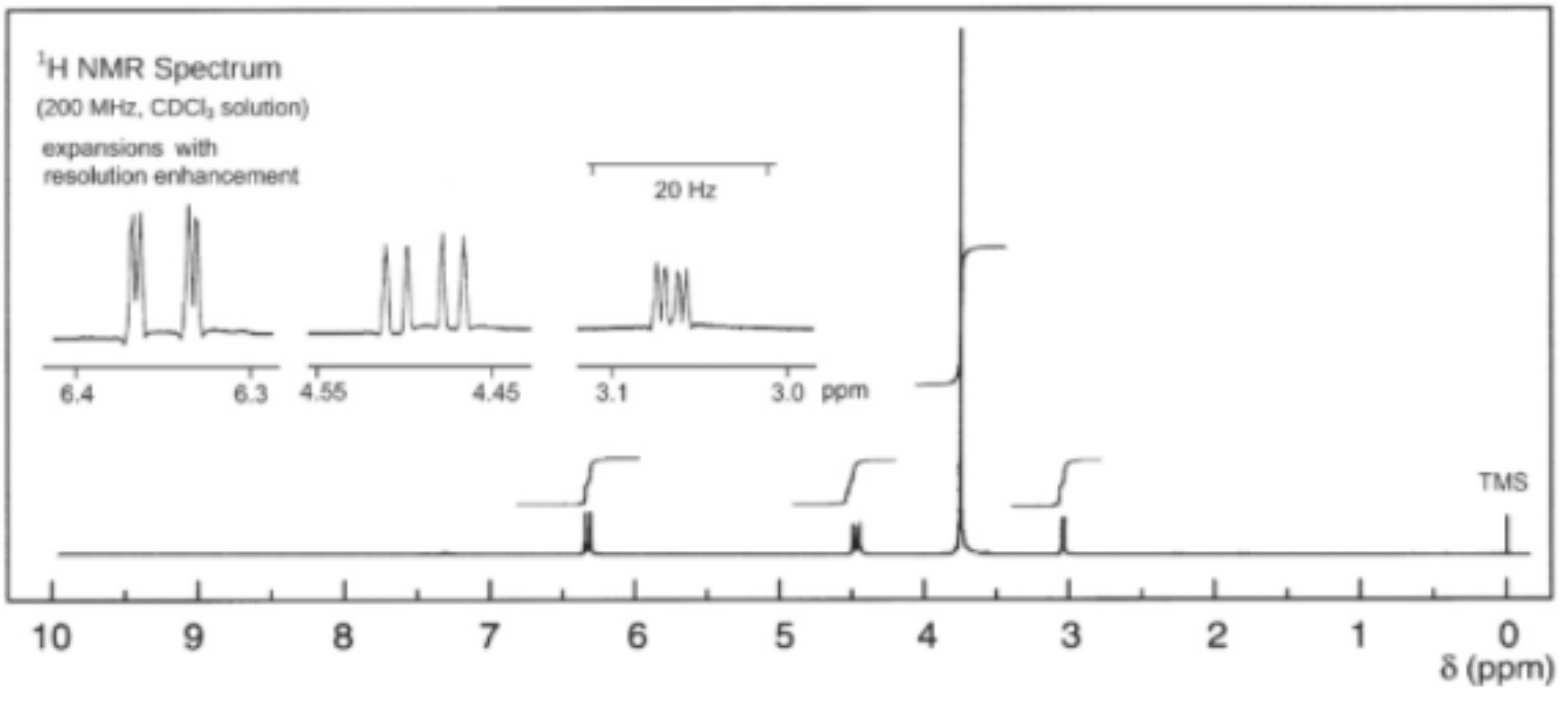
Problem 214


2100
IR Spectrum
(liquid film)
3275
1630
4000
3000
2000
1600
1200
800
ν (cm-1)

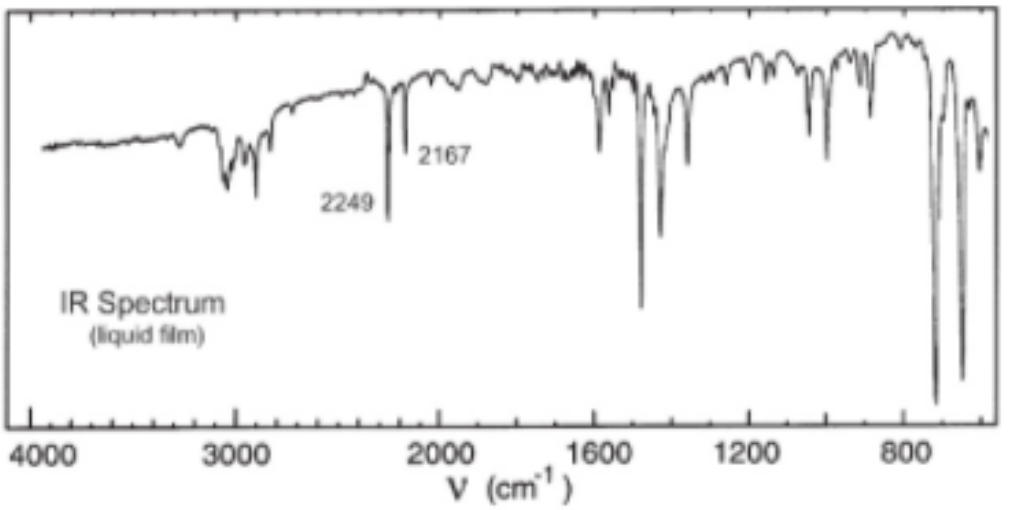

Mass Spectrum
% of base peak
M+·
82
C5H6O
100
80
60
40
20
40
80
120
160
200
240
280
m/e

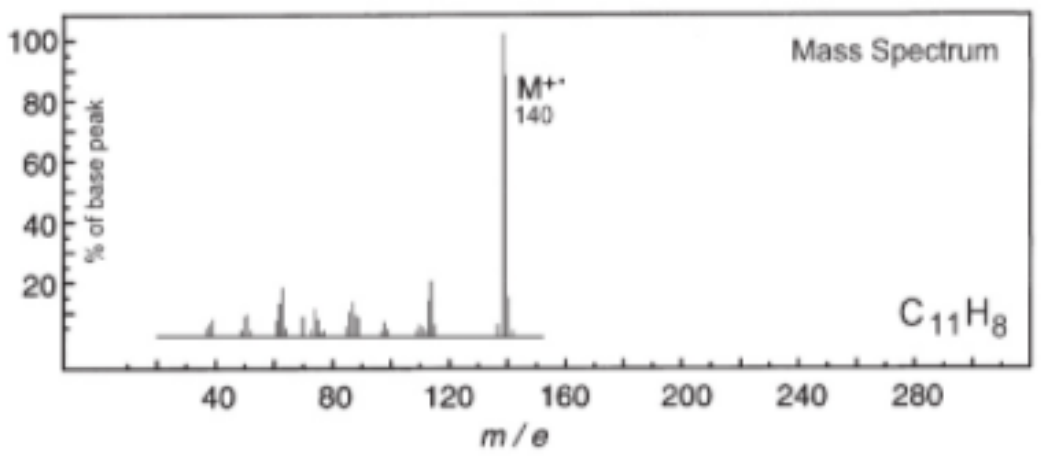

absorbance
UV spectrum
0.182 mg / 10 ml
path length : 0.5 cm
solvent : dioxan
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)


13C NMR Spectrum
(50 MHz, CDCl3 solution)
expansion
80
70 ppm
DEPT CH2 CH3 CH
expansion
80
70 ppm
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(200 MHz, CDCl3 solution)
expansions with
resolution enhancement
20 Hz
6.4
6.3
4.55
4.45
3.1
3.0 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

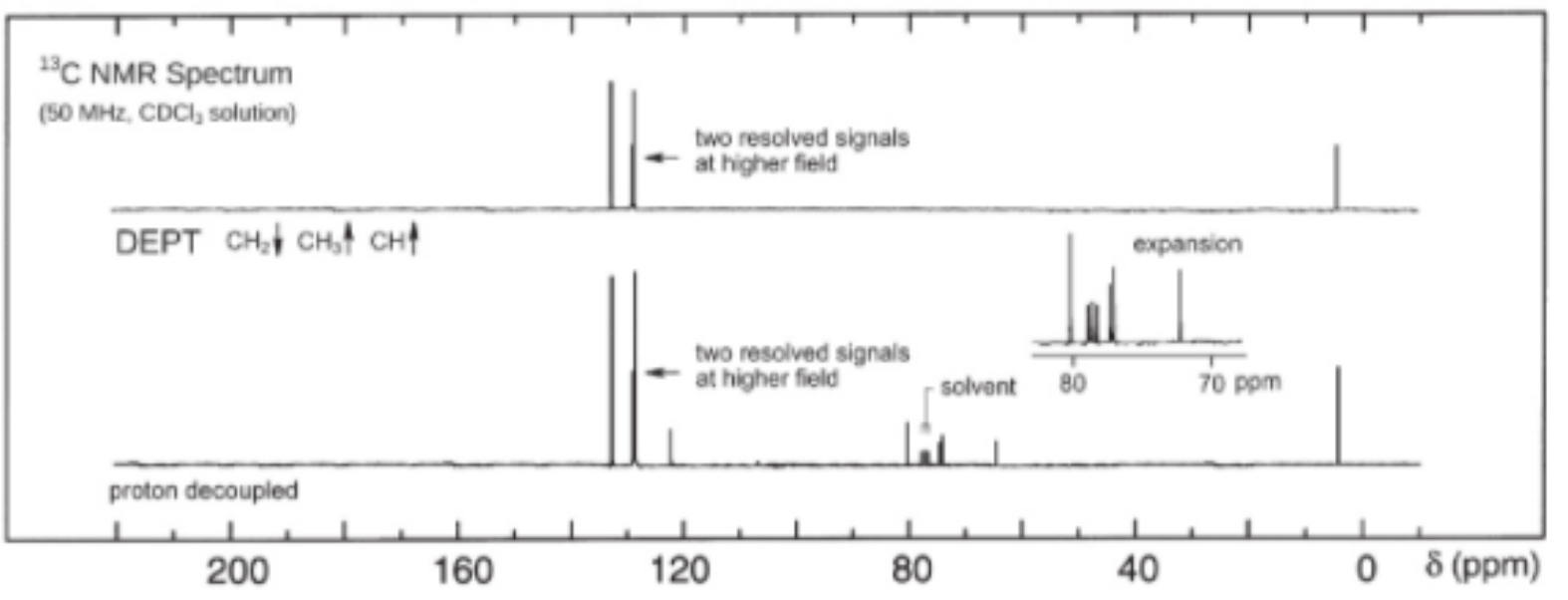
Problem 215

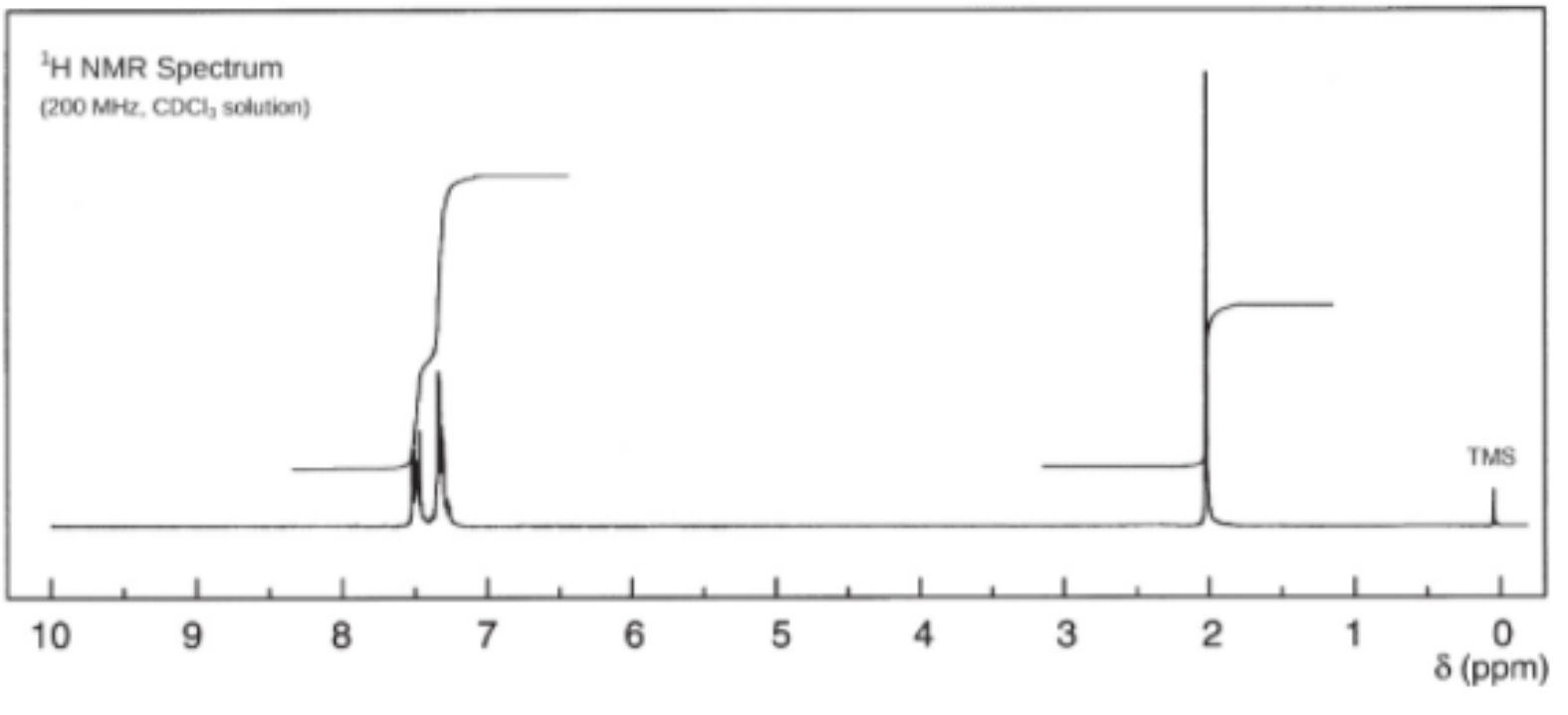




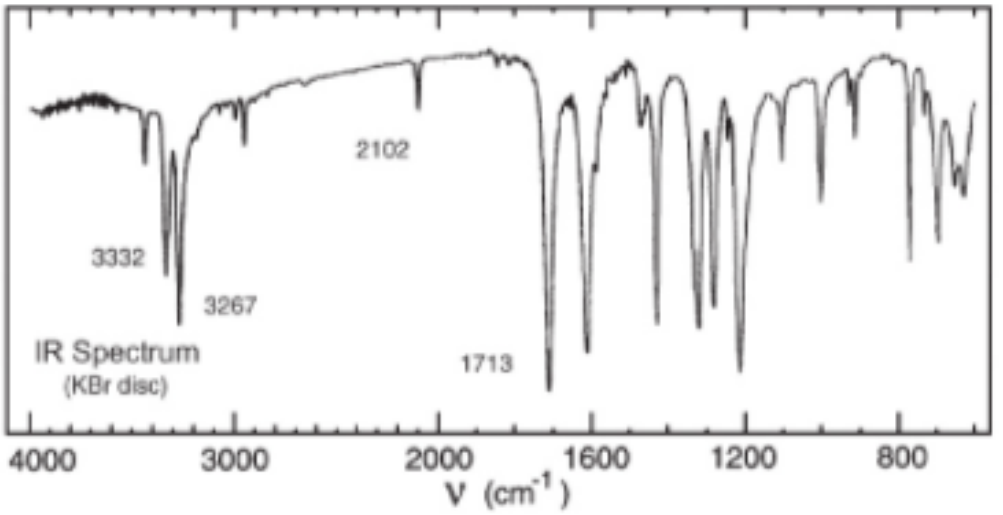
UV Spectrum

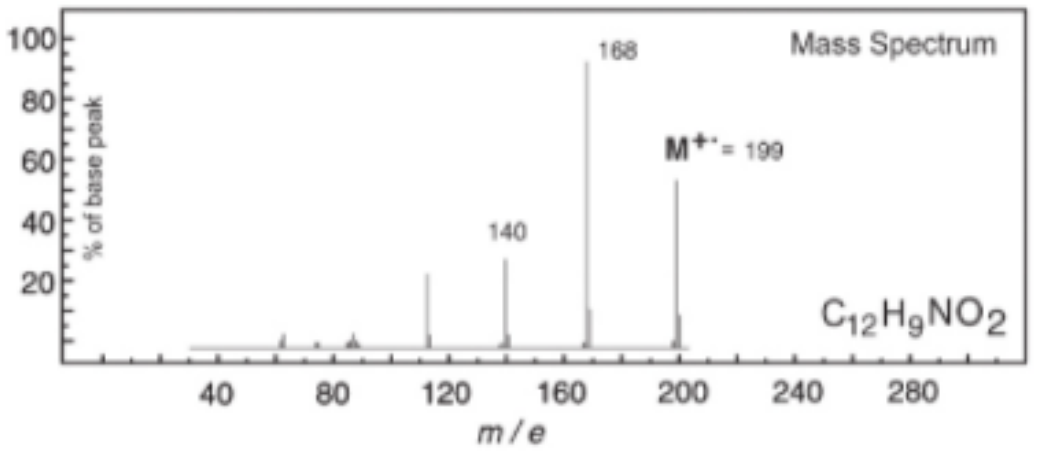
$\log_{10}\varepsilon > 4.0$





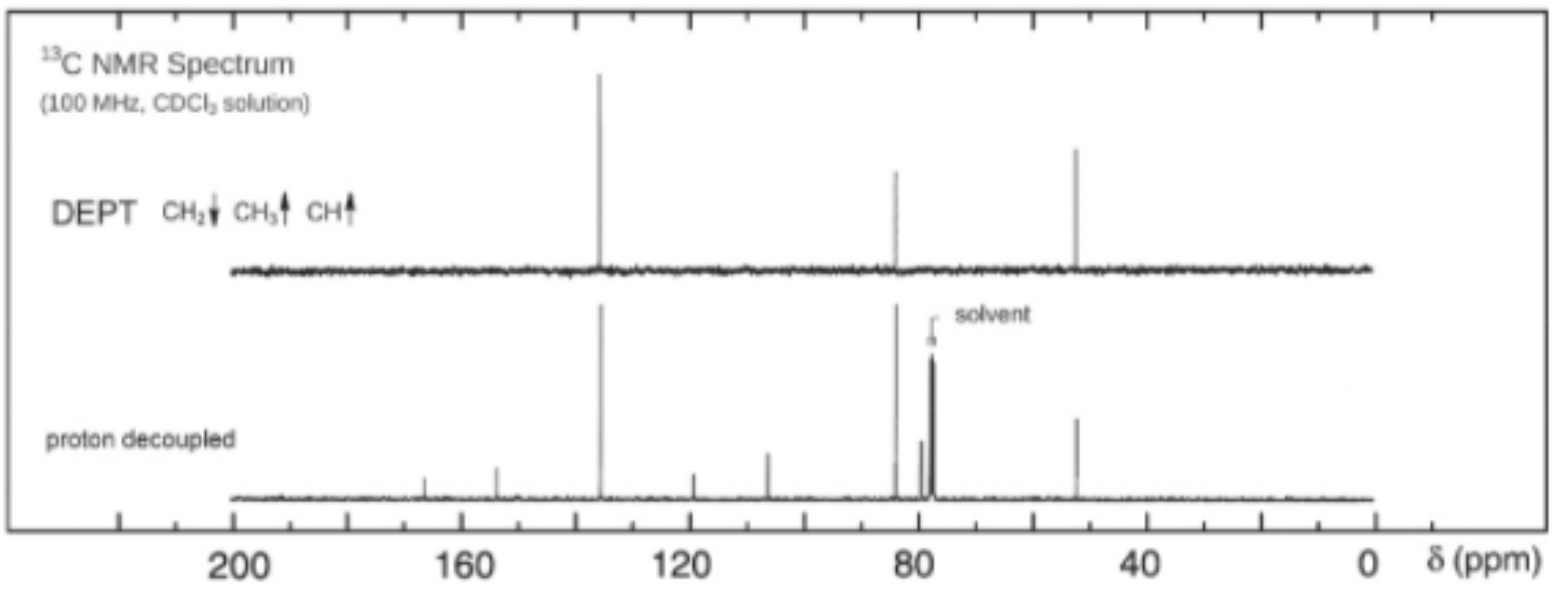
Problem 216

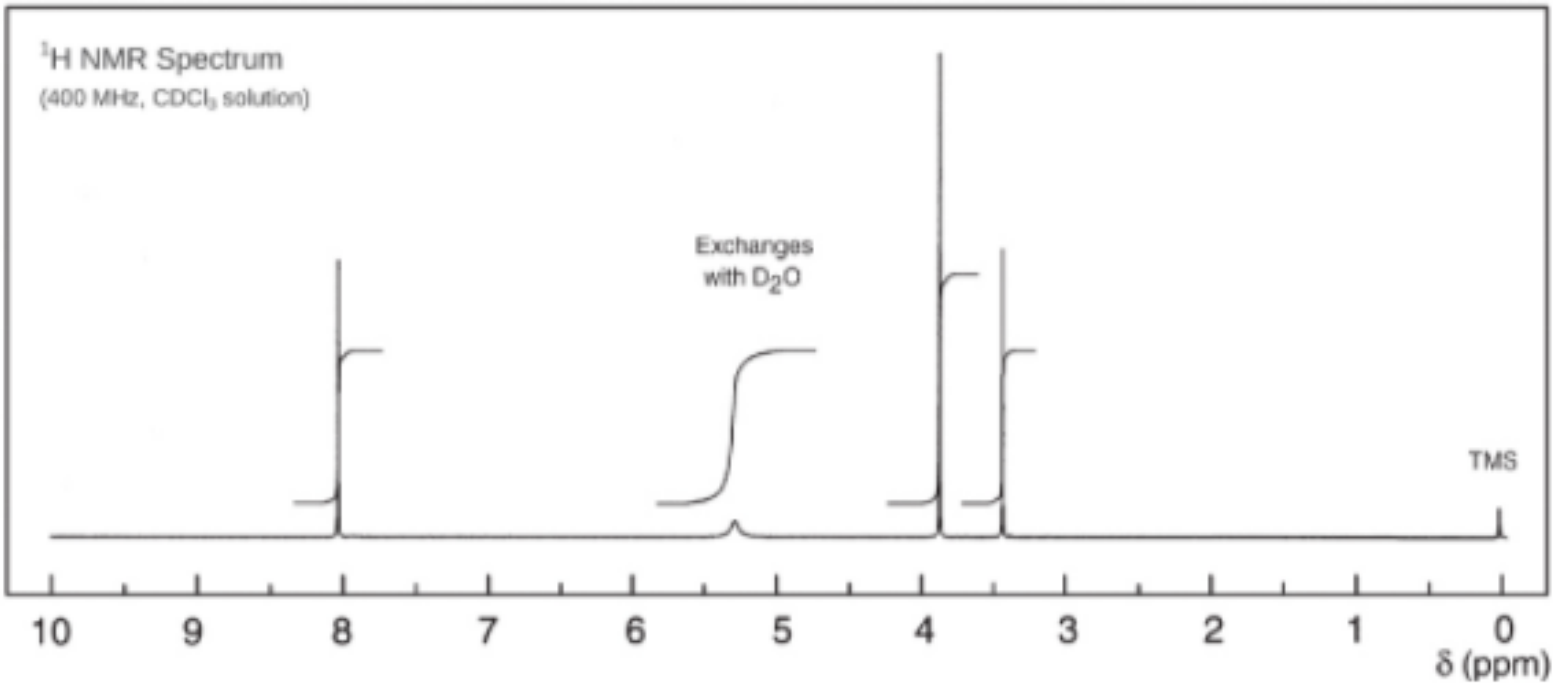




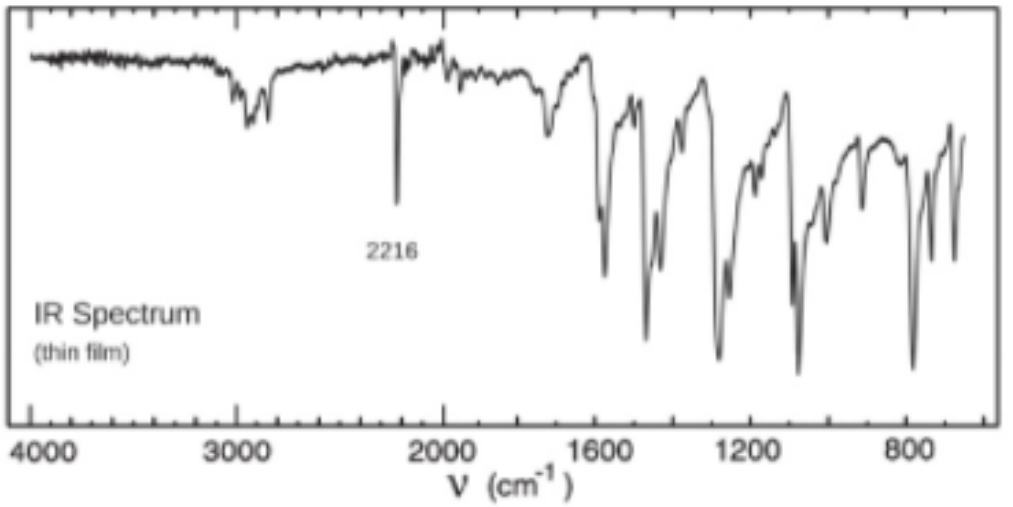
UV Spectrum

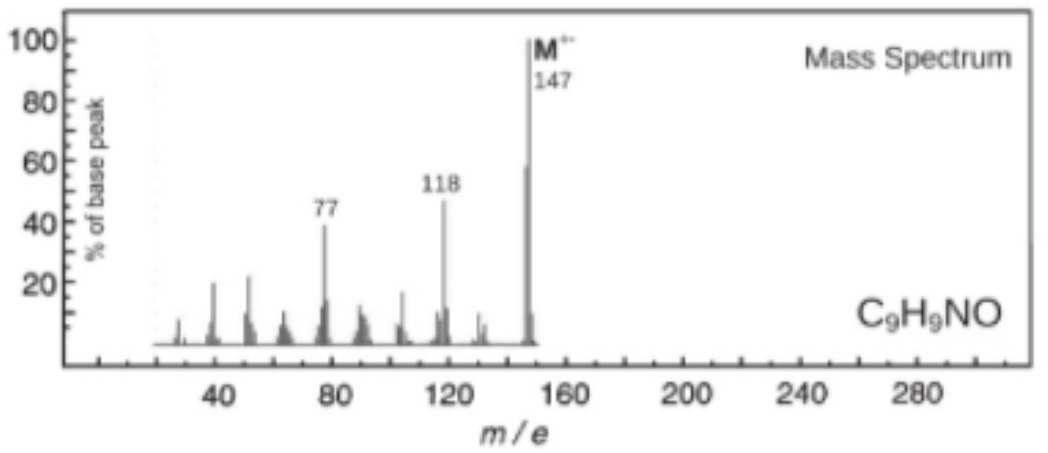
$\log_{10}\varepsilon > 4.0$

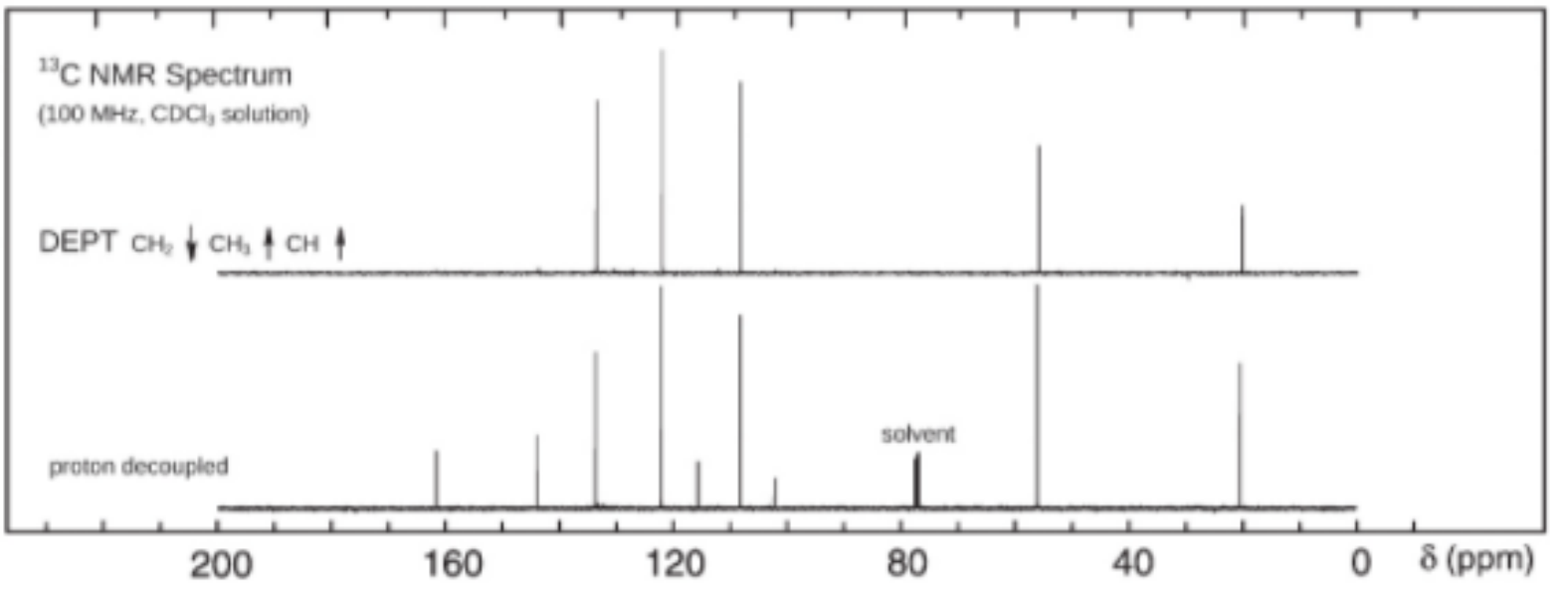


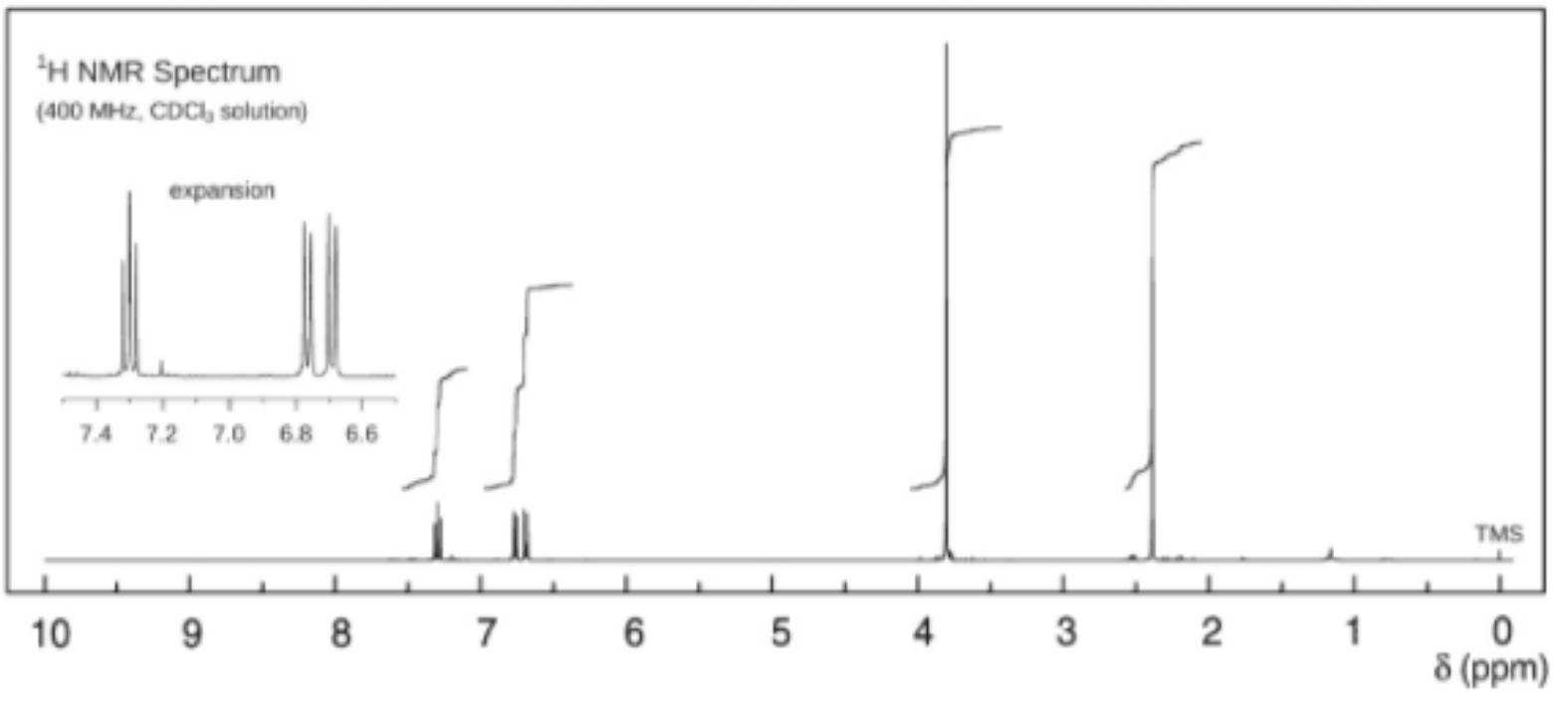


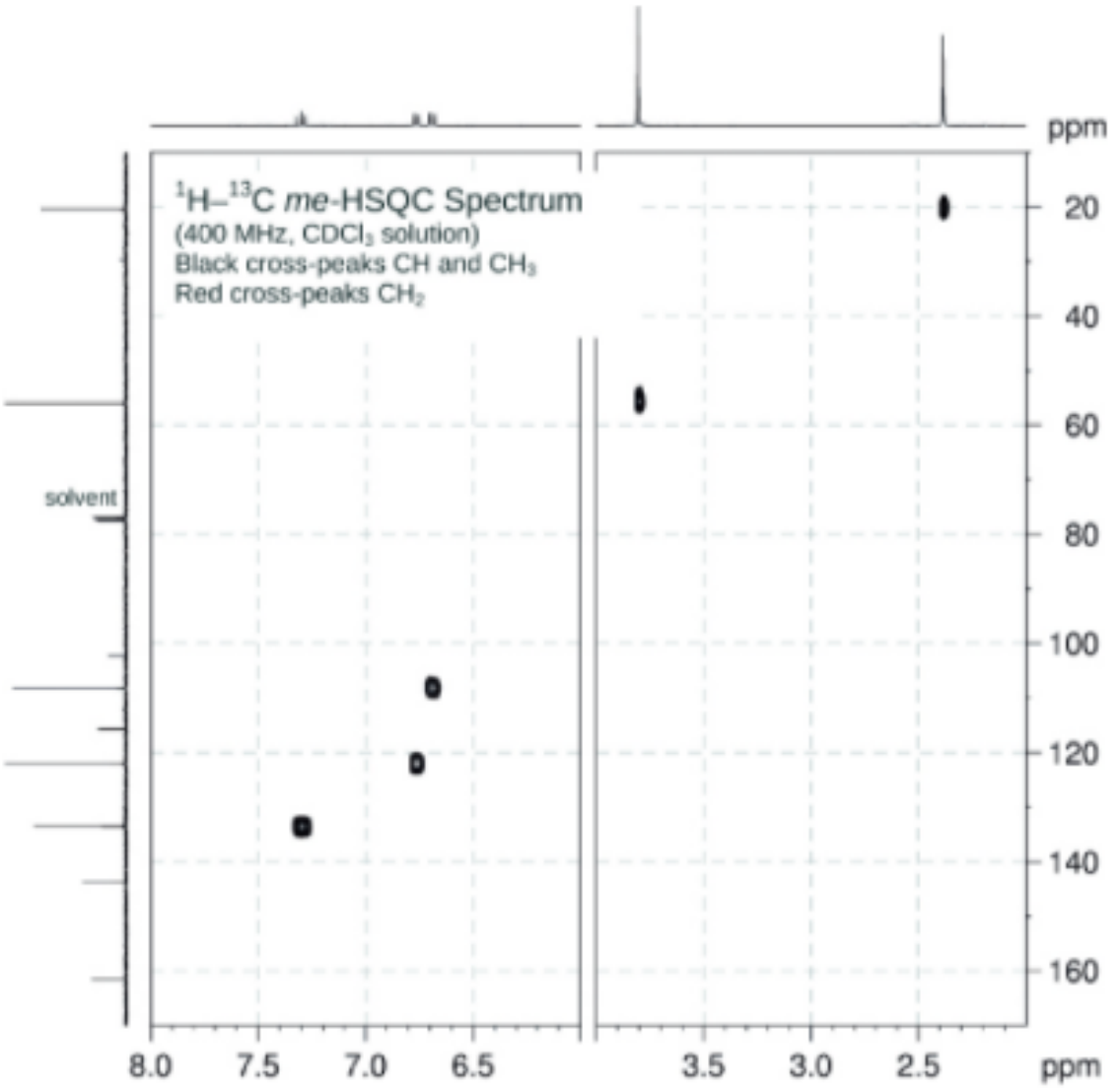
Problem 217

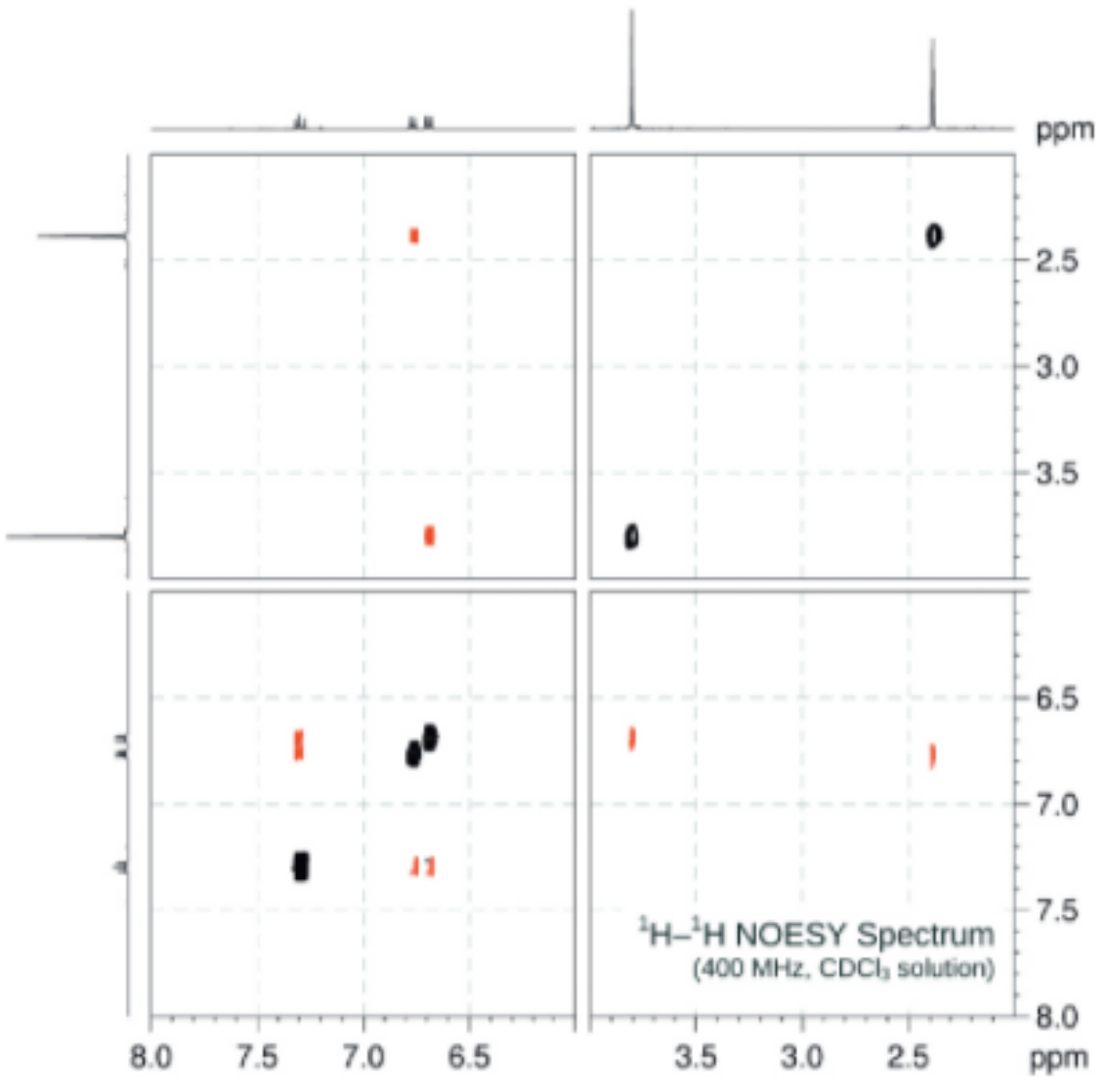

2216
IR Spectrum
(thin film)
4000
3000
2000
1600
1200
800
ν (cm-1)


100
80
60
40
20
% of base peak
M+·
147
77
118
Mass Spectrum
C9H9NO
40
80
120
160
200
240
280
m/e

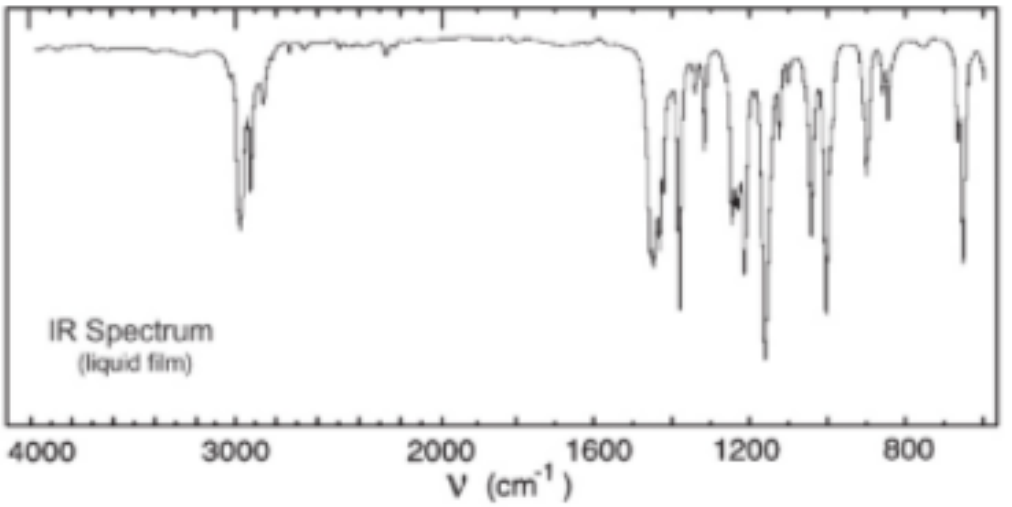

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

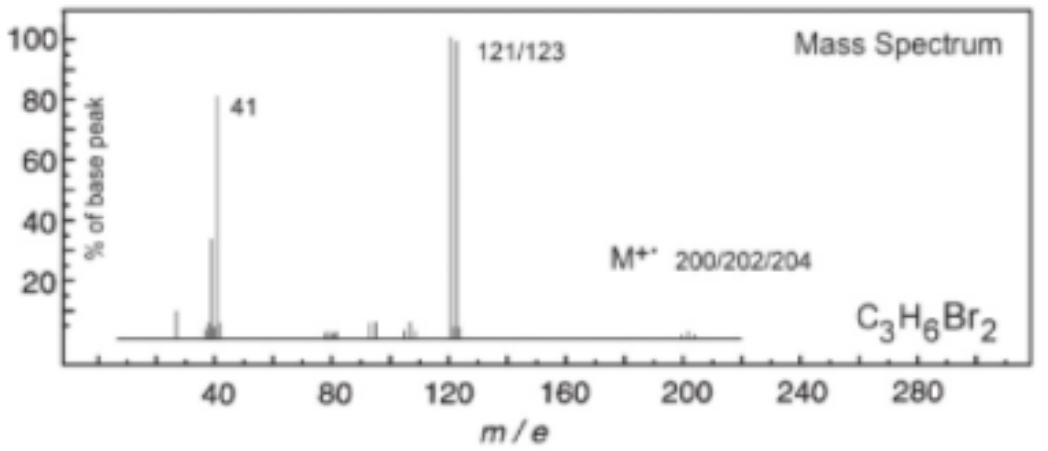

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.4
7.2
7.0
6.8
6.6
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
solvent
ppm
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
3.5
3.0
2.5
ppm

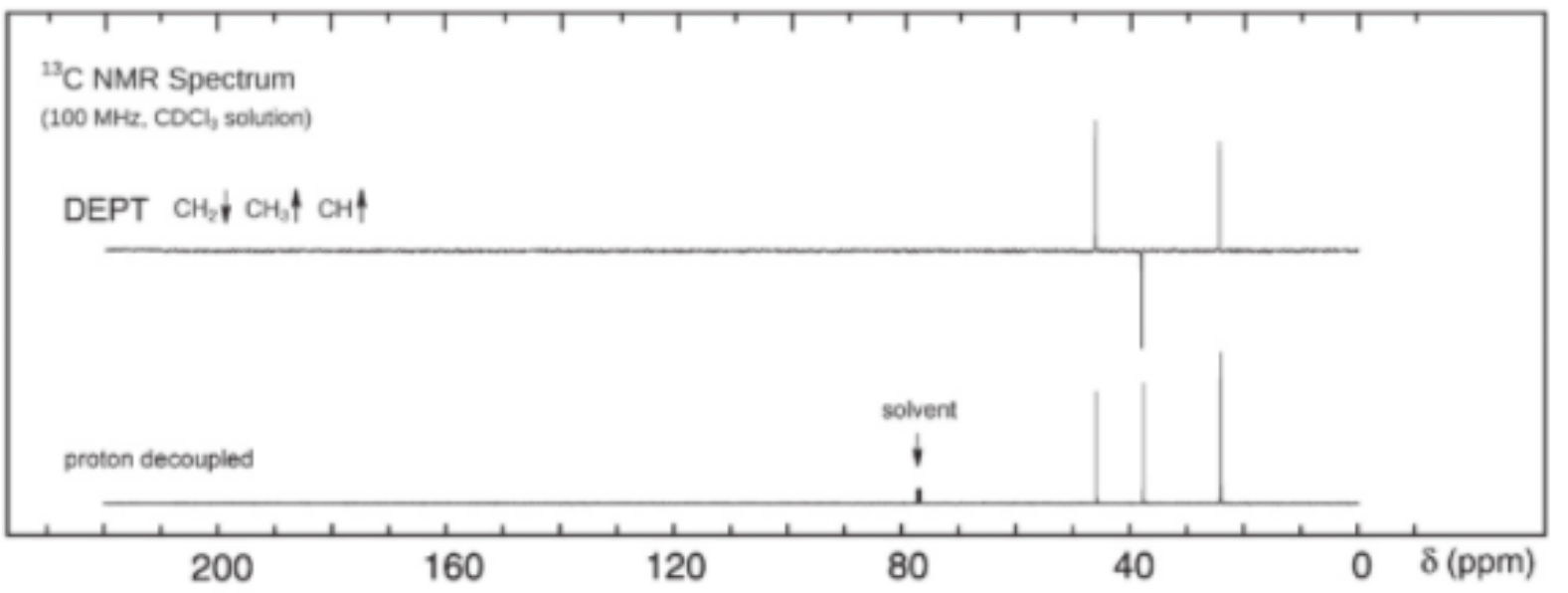

ppm
2.5
3.0
3.5
6.5
7.0
7.5
8.0
^{1}H–^{1}H NOESY Spectrum
(400 MHz, $CDCl_3$ solution)
8.0
7.5
7.0
6.5
3.5
3.0
2.5
ppm

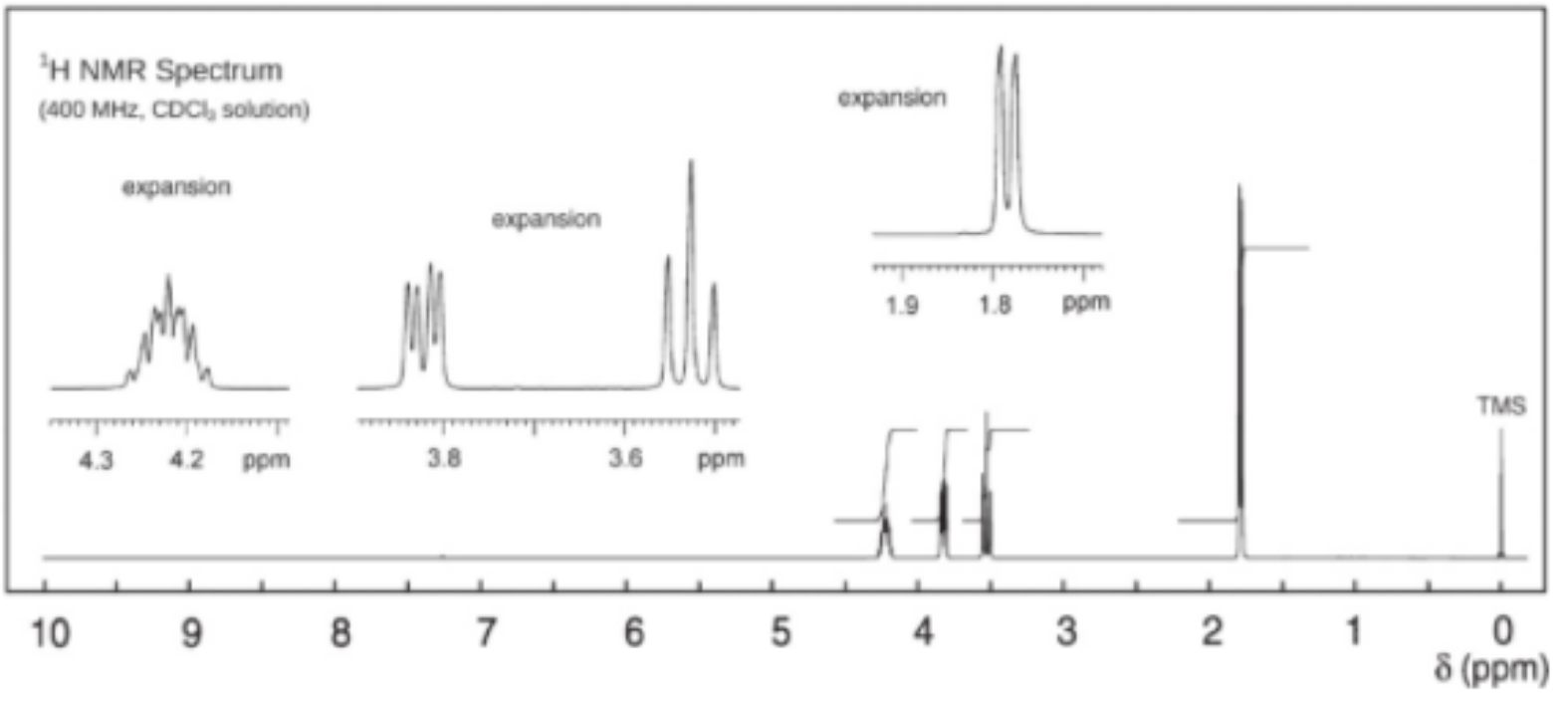
Problem 218

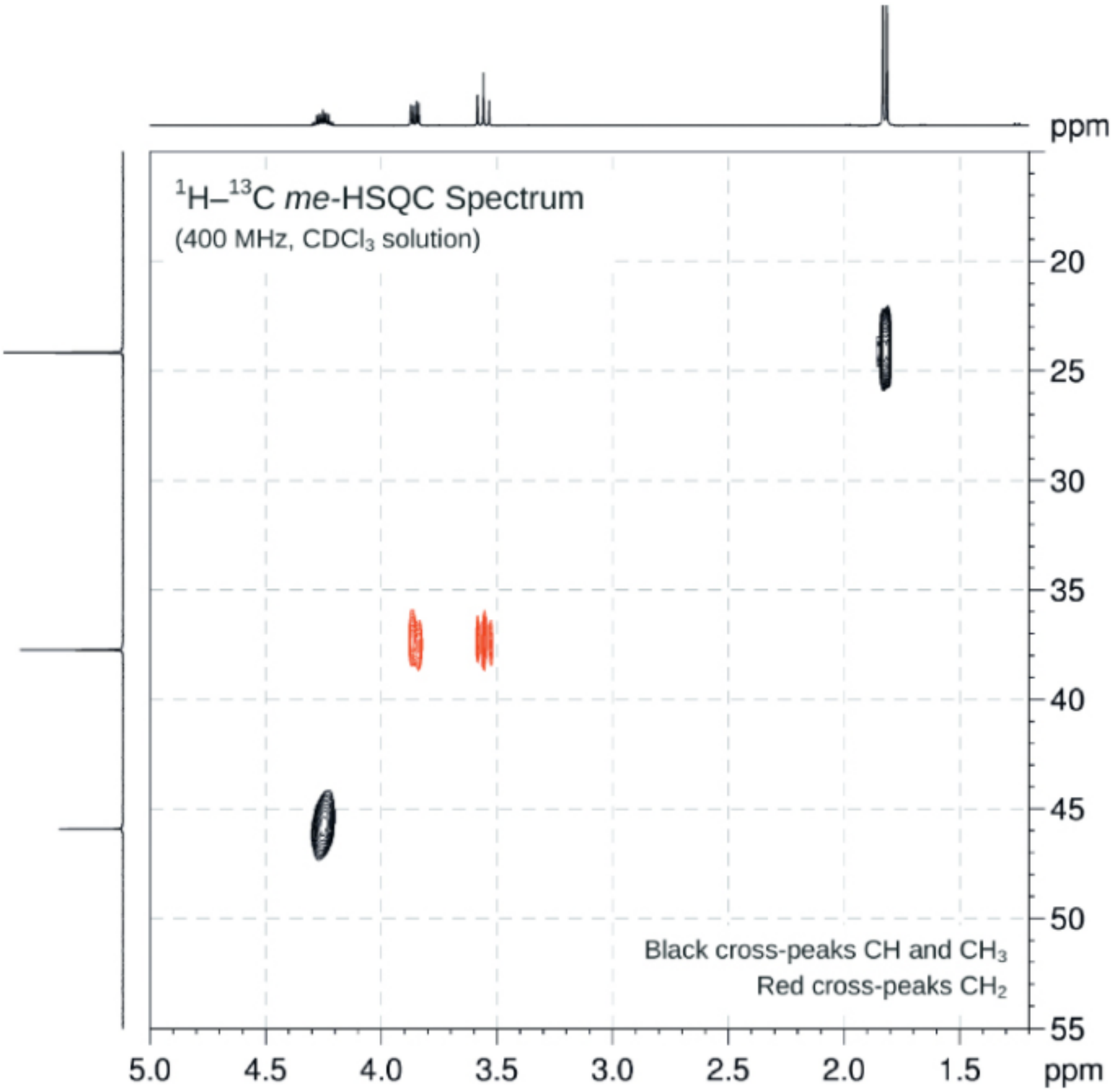




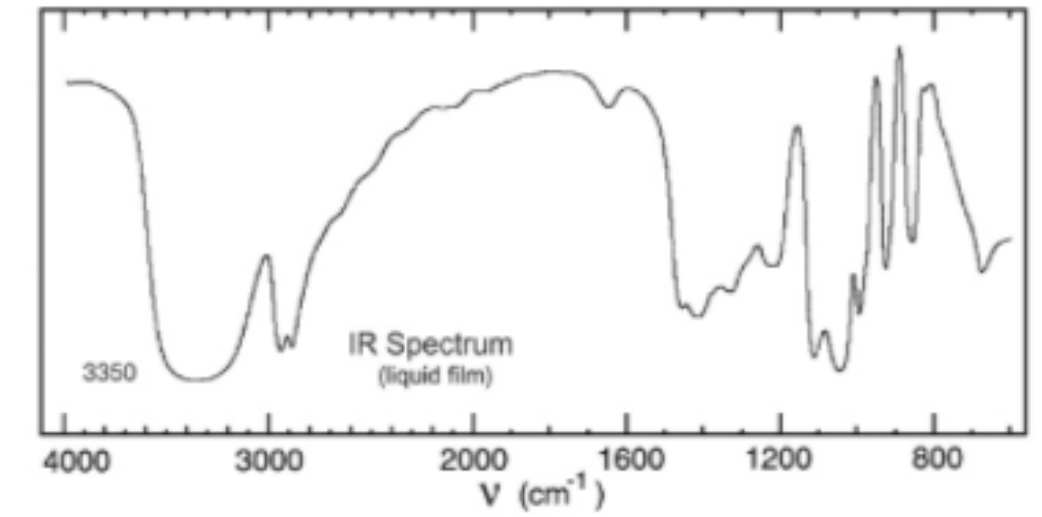
No significant UV absorption above 220 nm

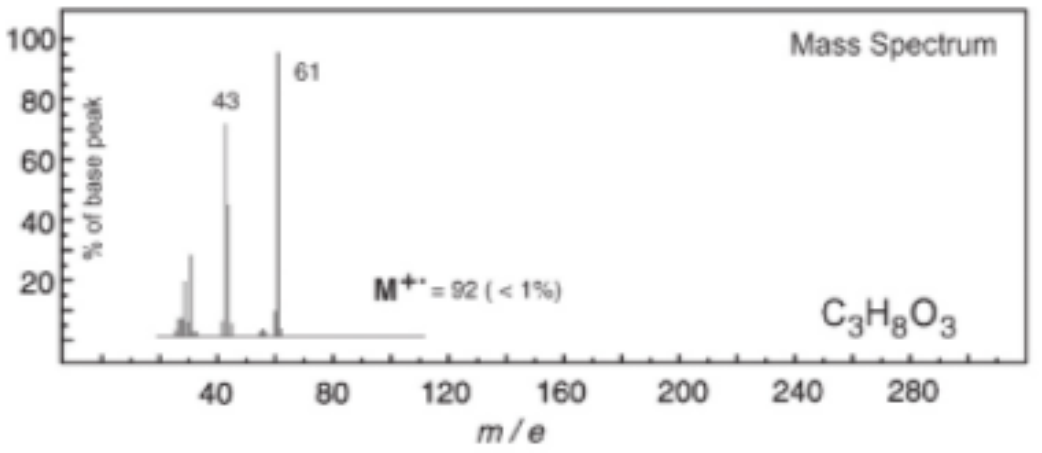




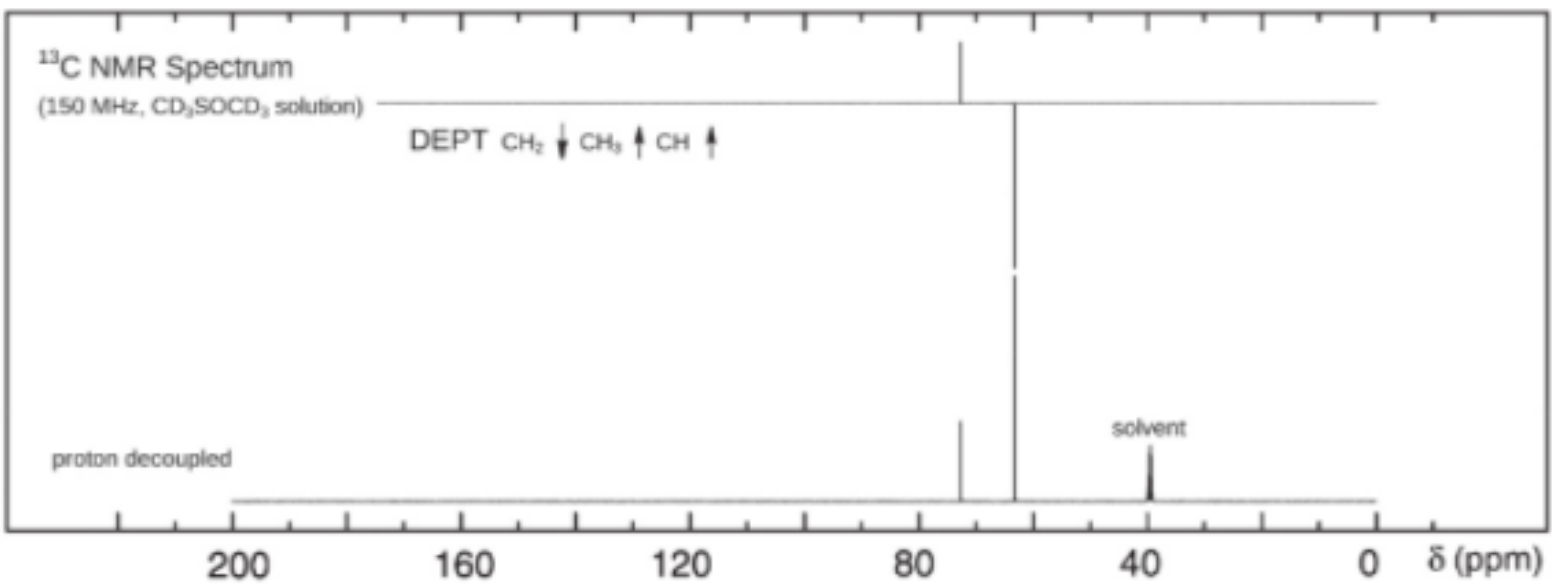

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
20
25
30
35
40
45
50
55
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

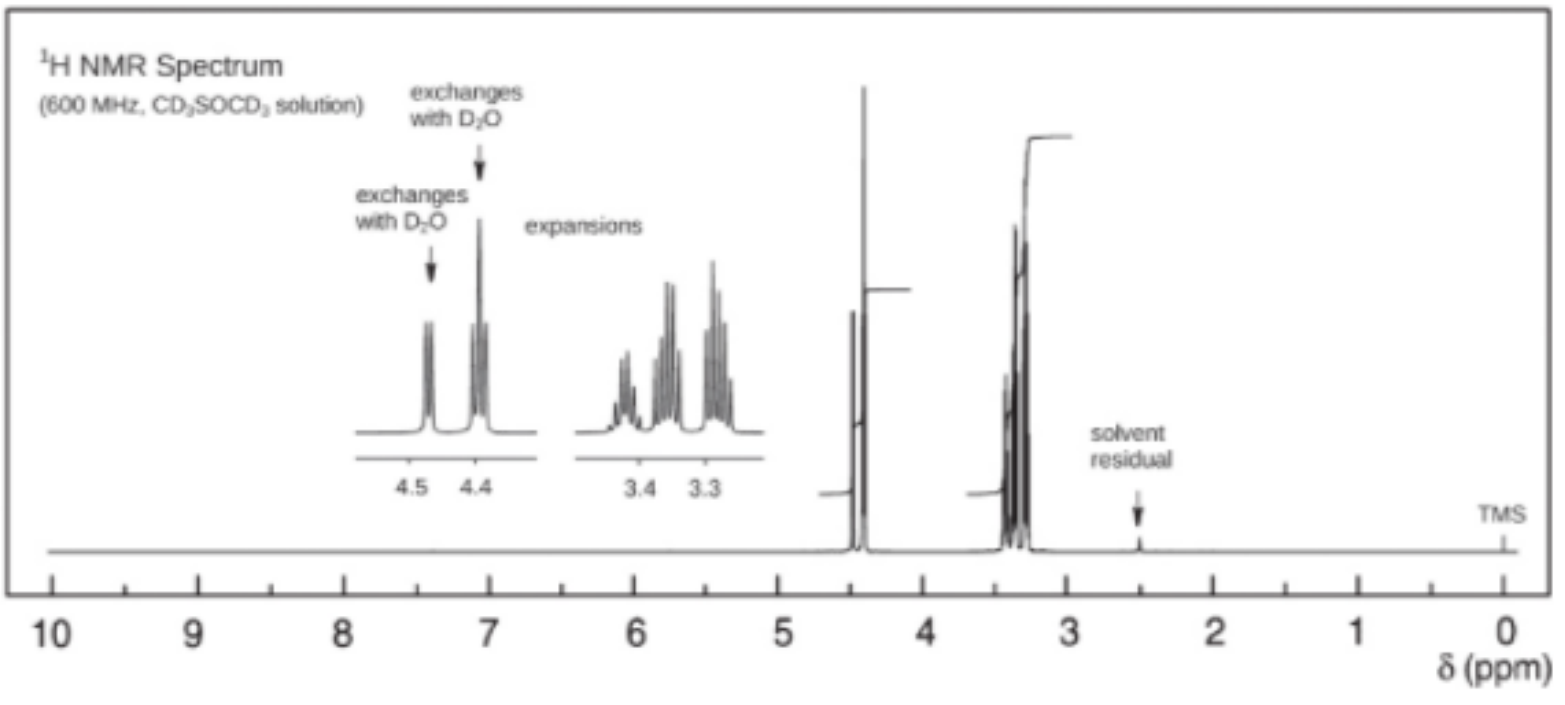
Problem 219

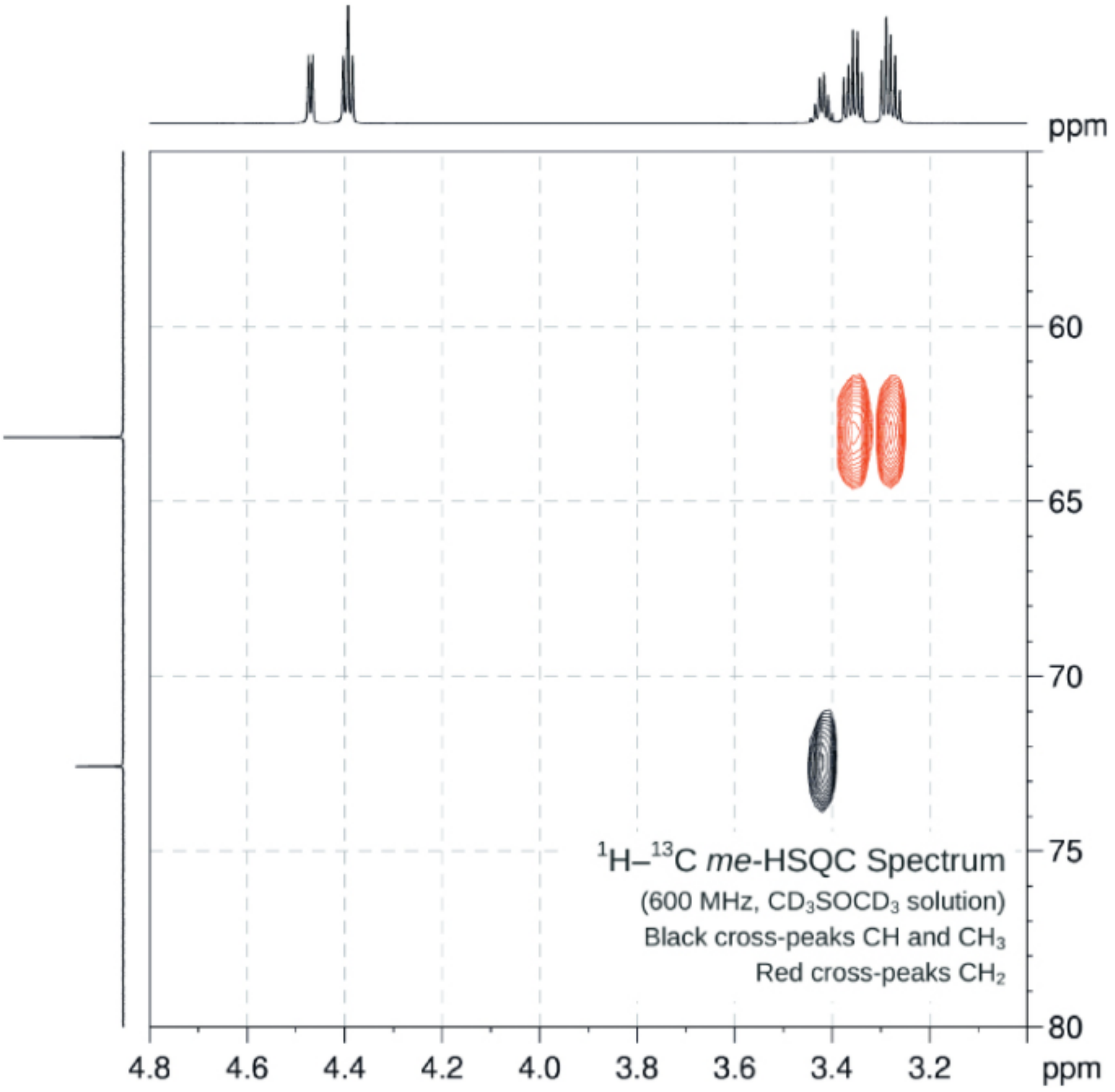




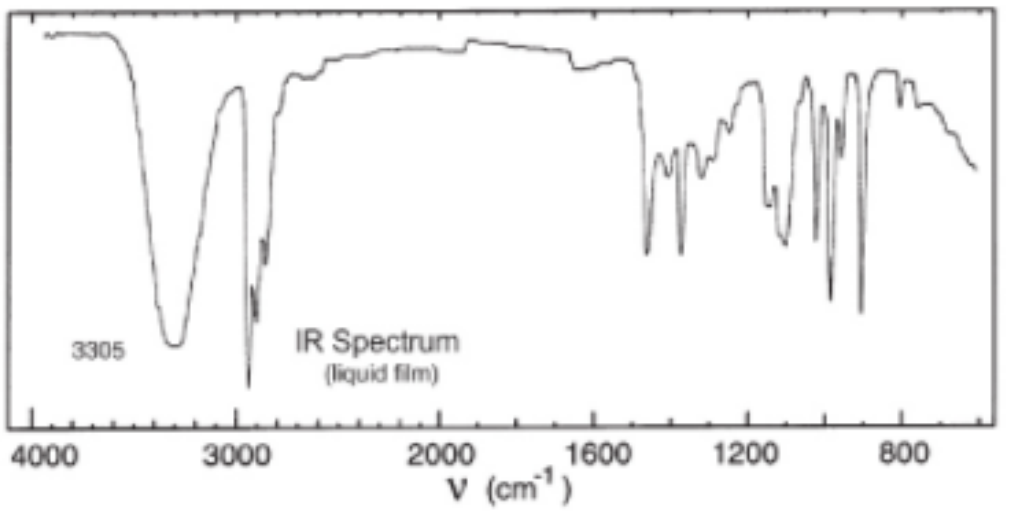
No significant UV absorption above 220 nm

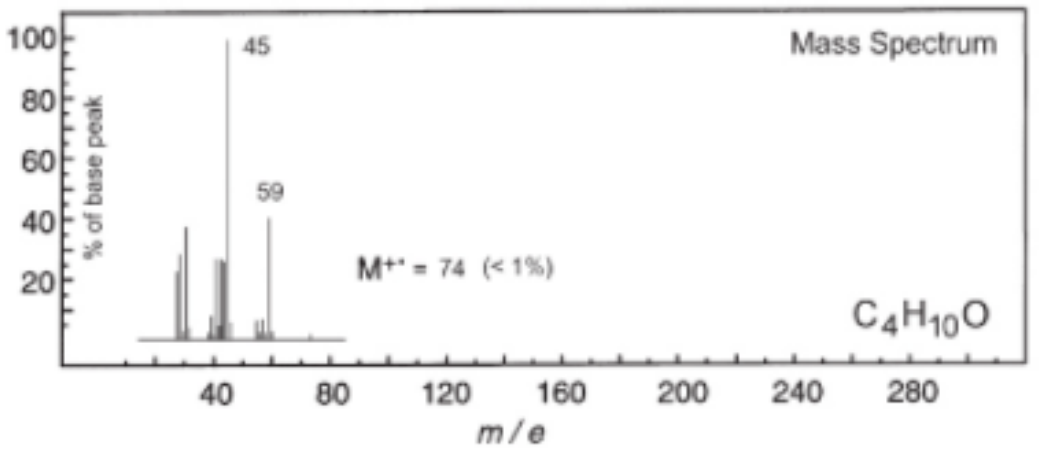




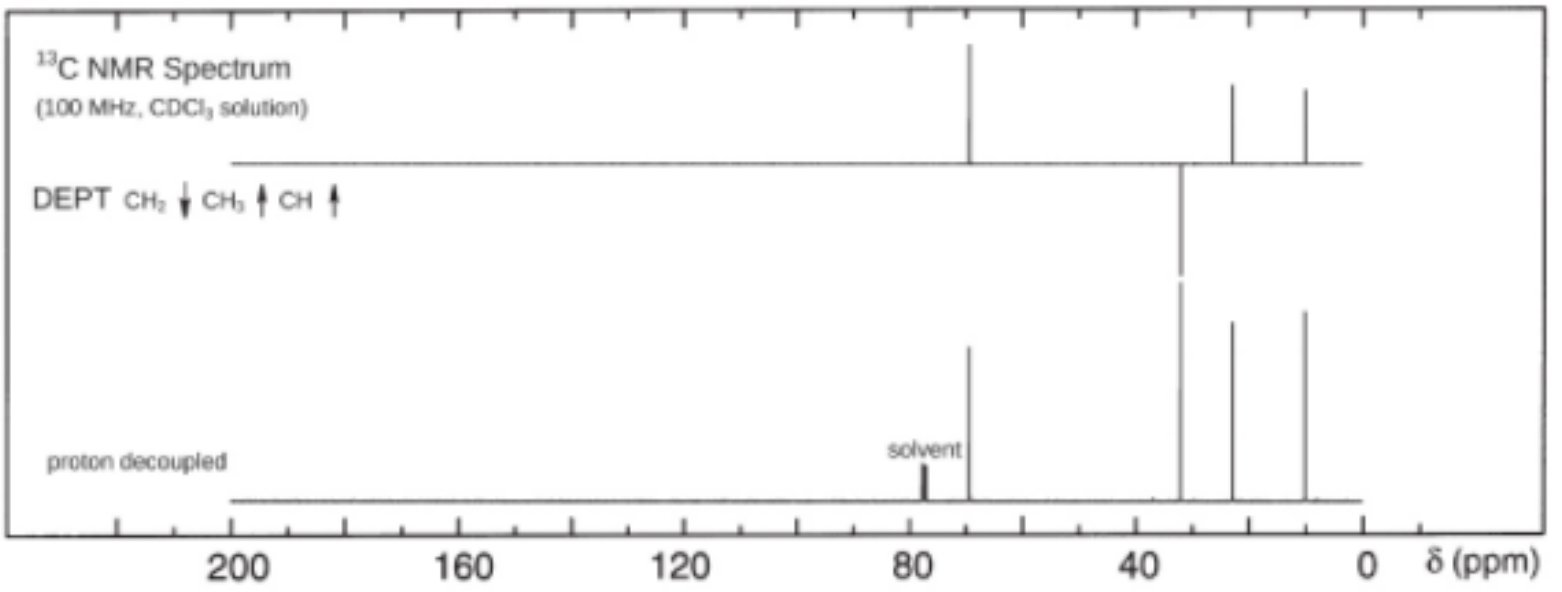

ppm
60
65
70
75
80
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(600 MHz, CD_3SOCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm

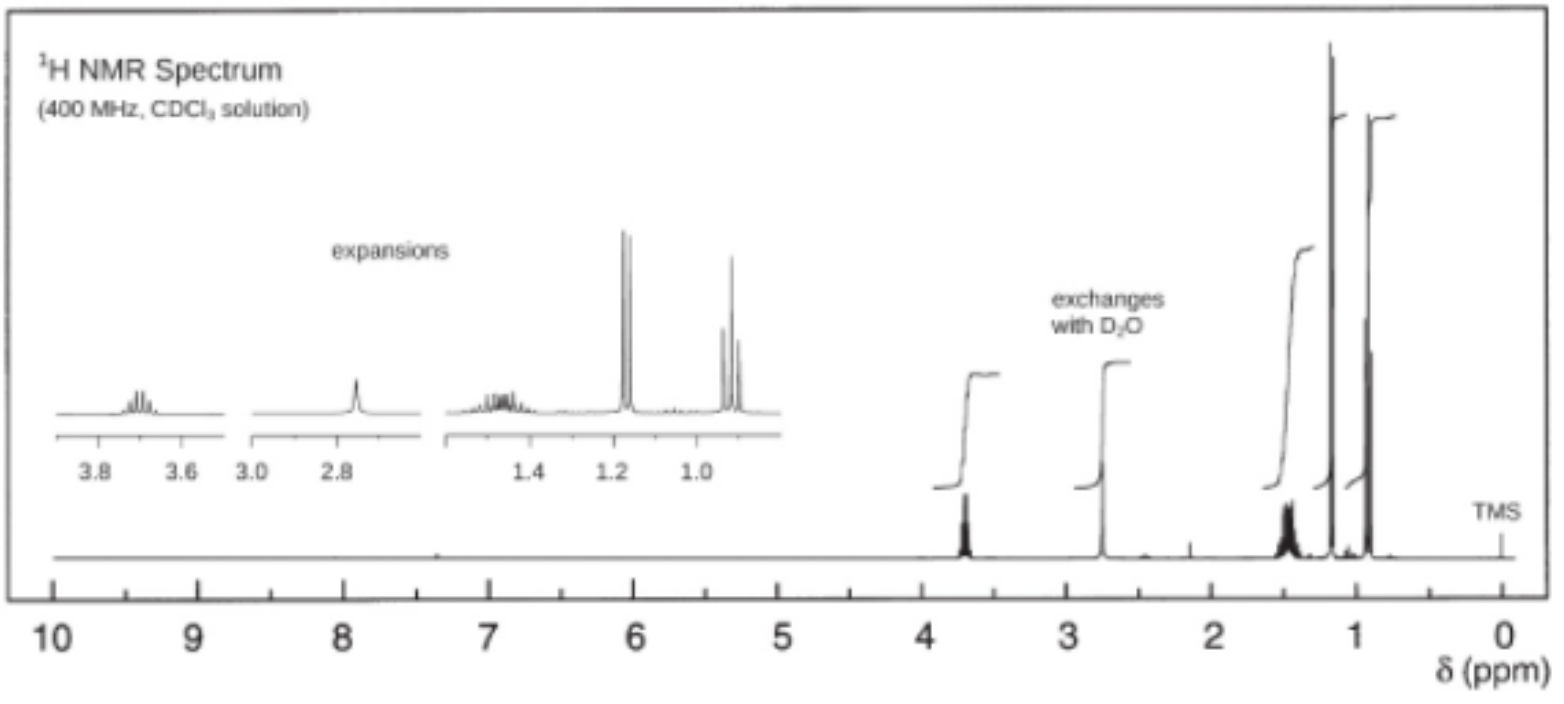
Problem 220

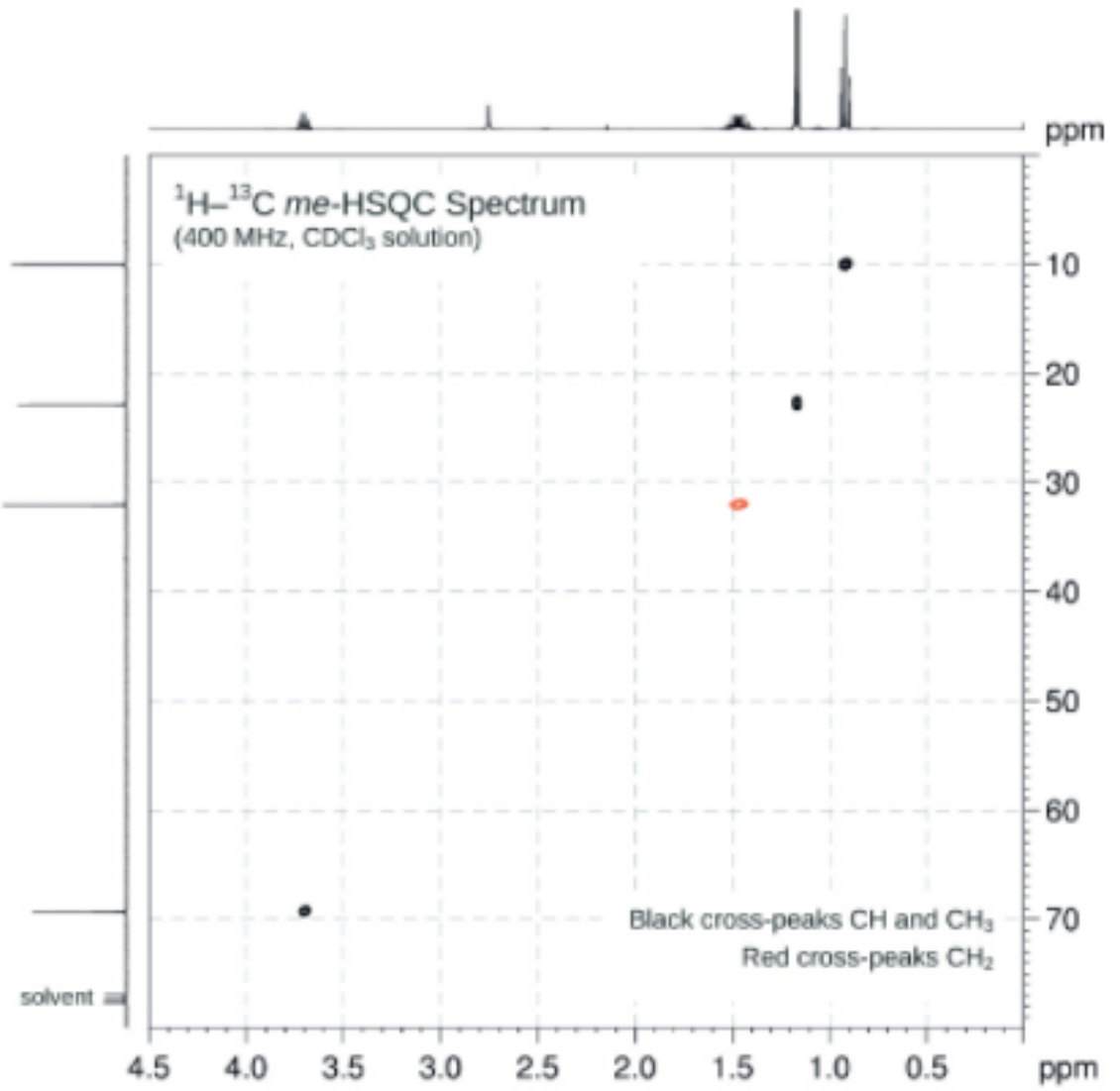


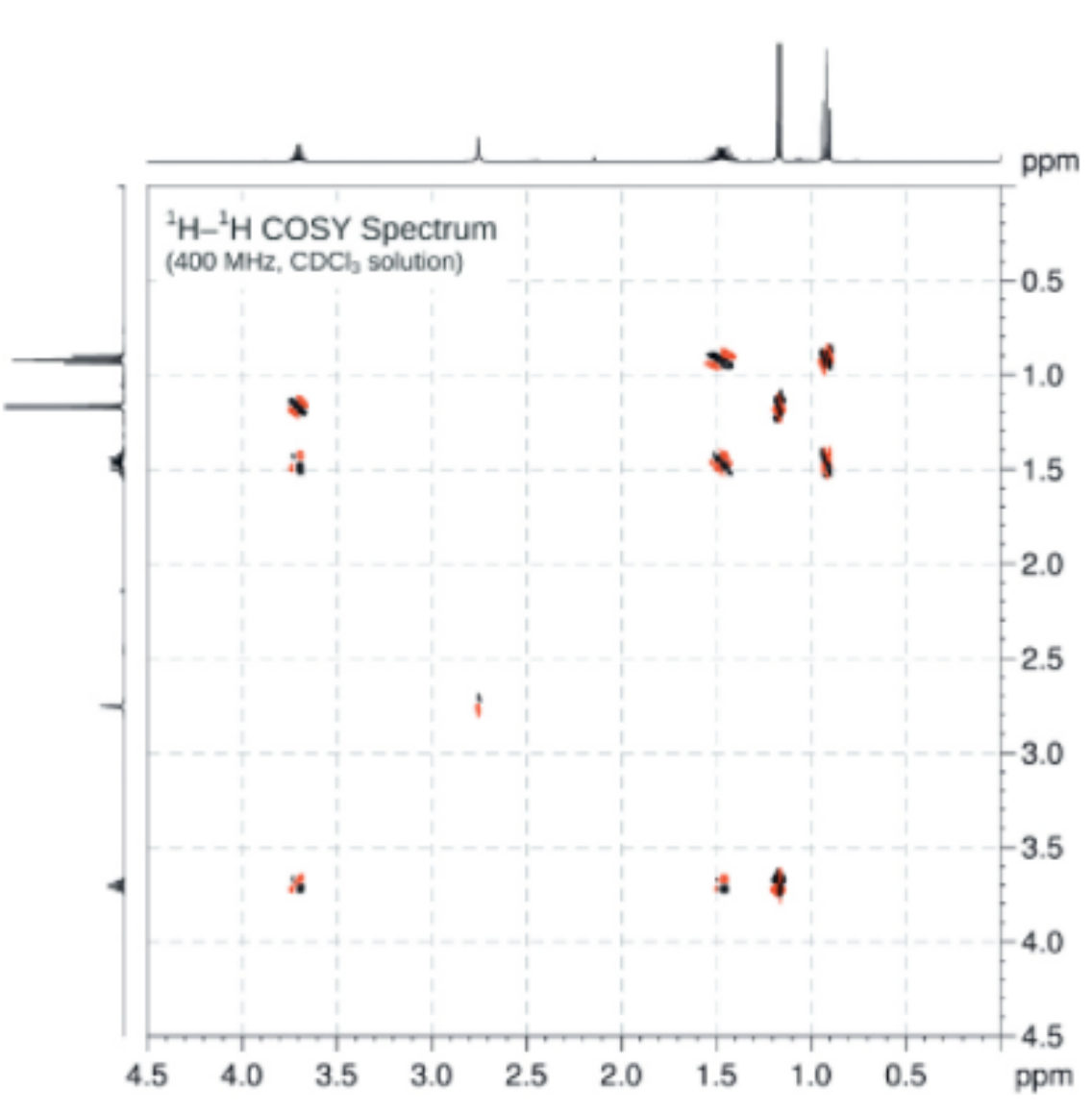


No significant UV
absorption above 220 nm

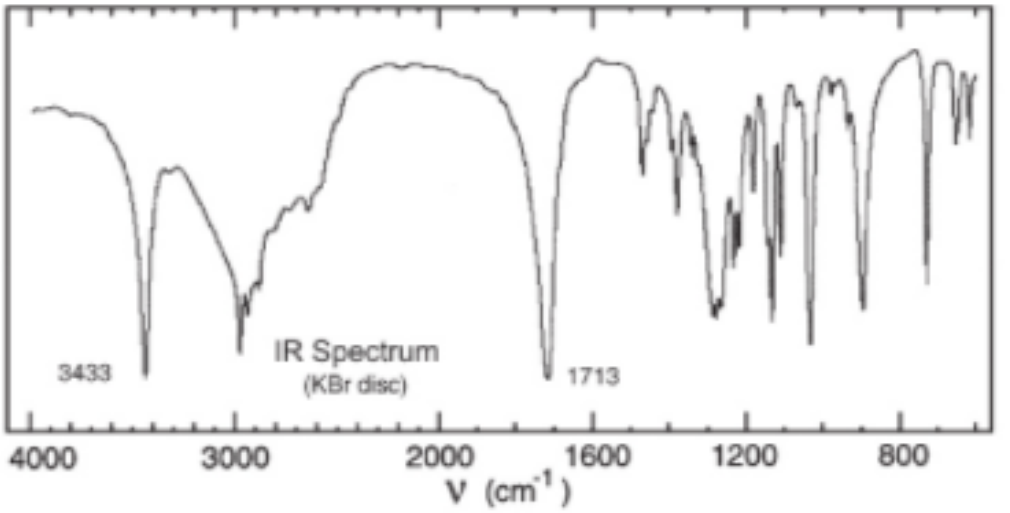


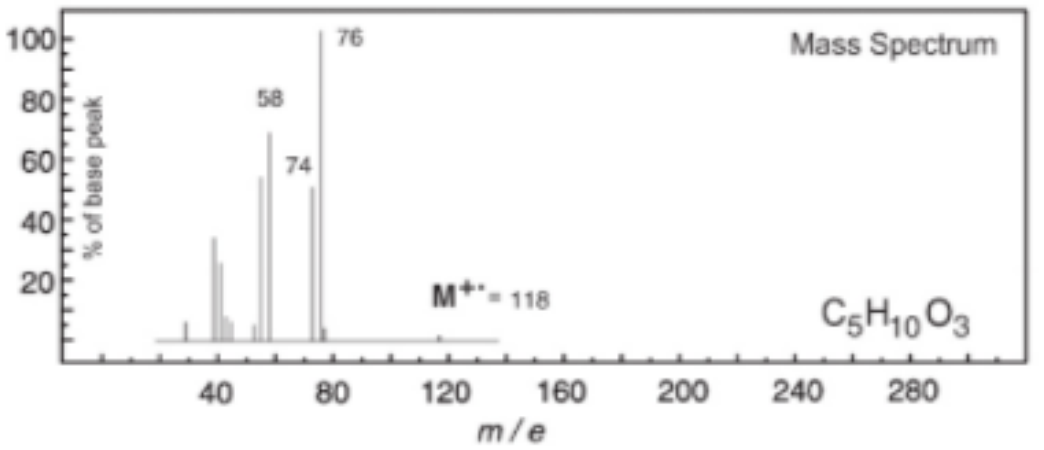



ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
10
20
30
40
50
60
70
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
solvent
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

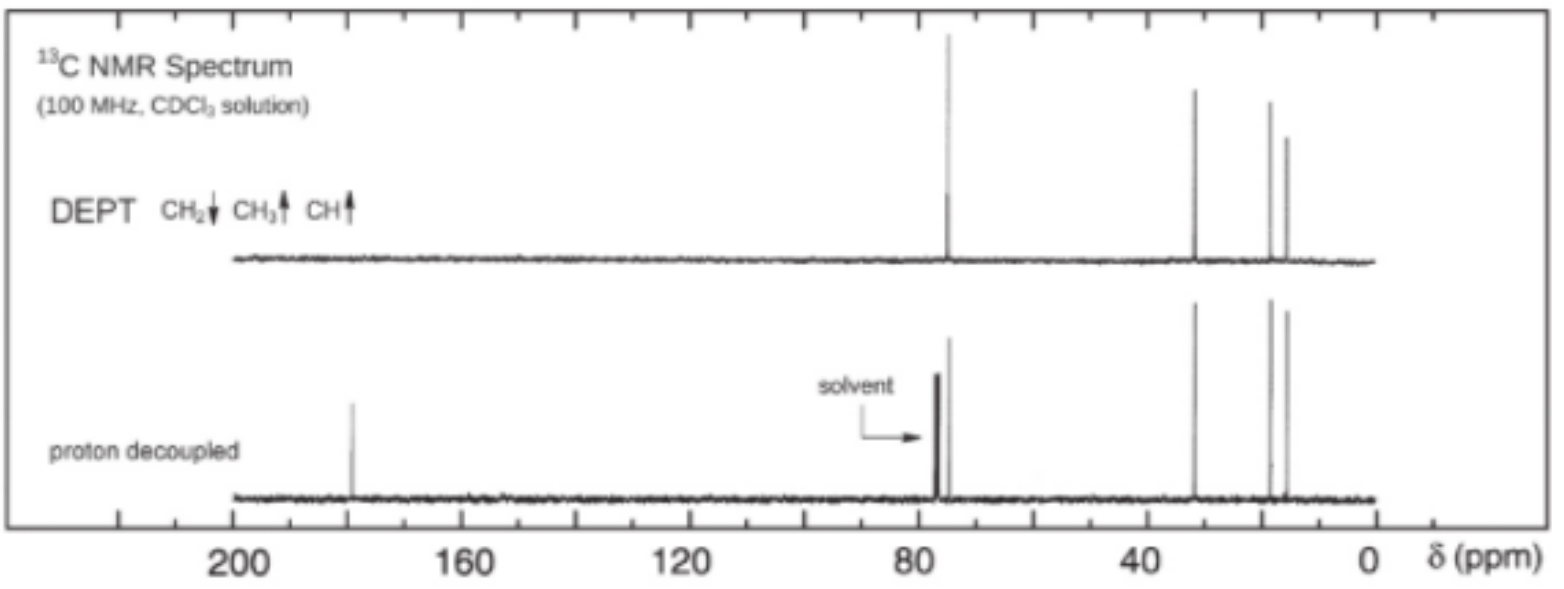

ppm
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

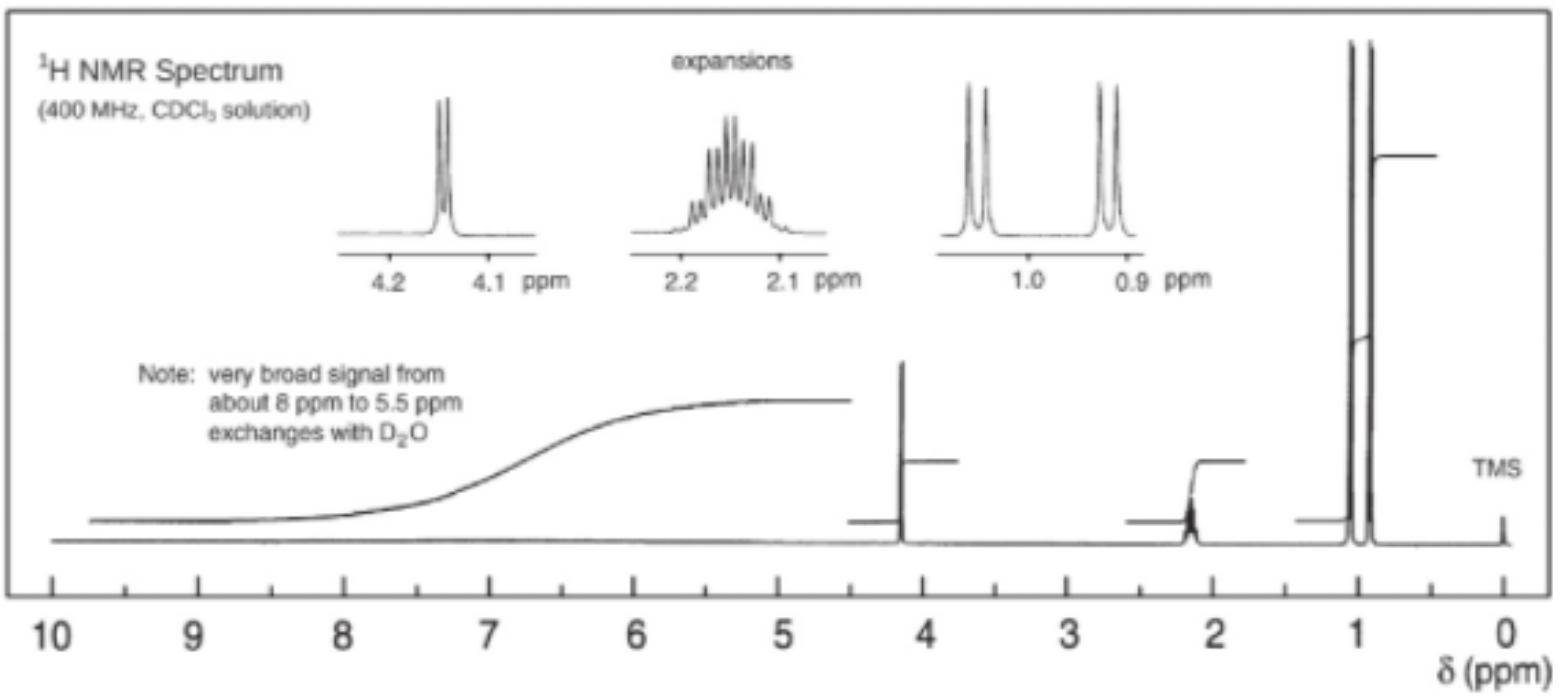
Problem 221



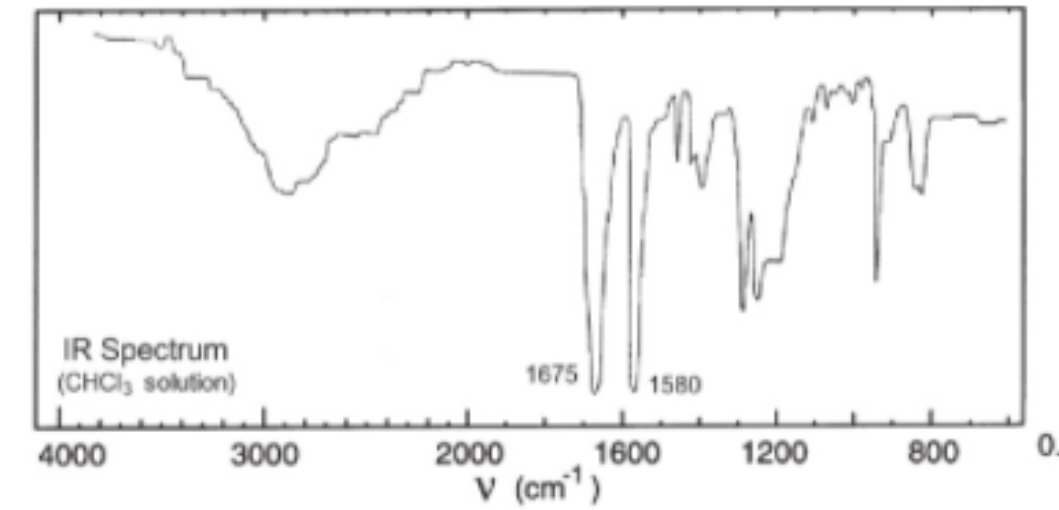


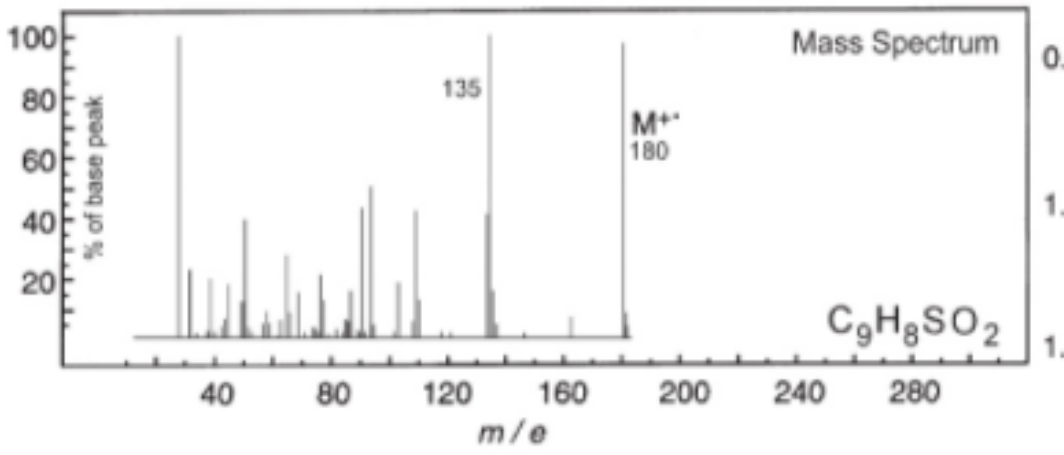
No significant UV absorption above 220 nm

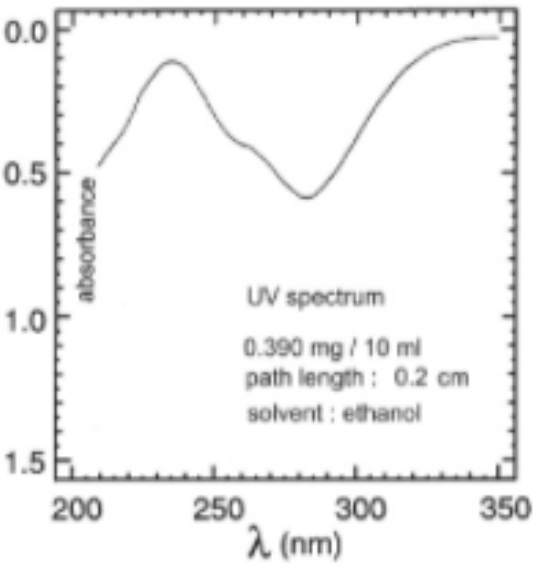


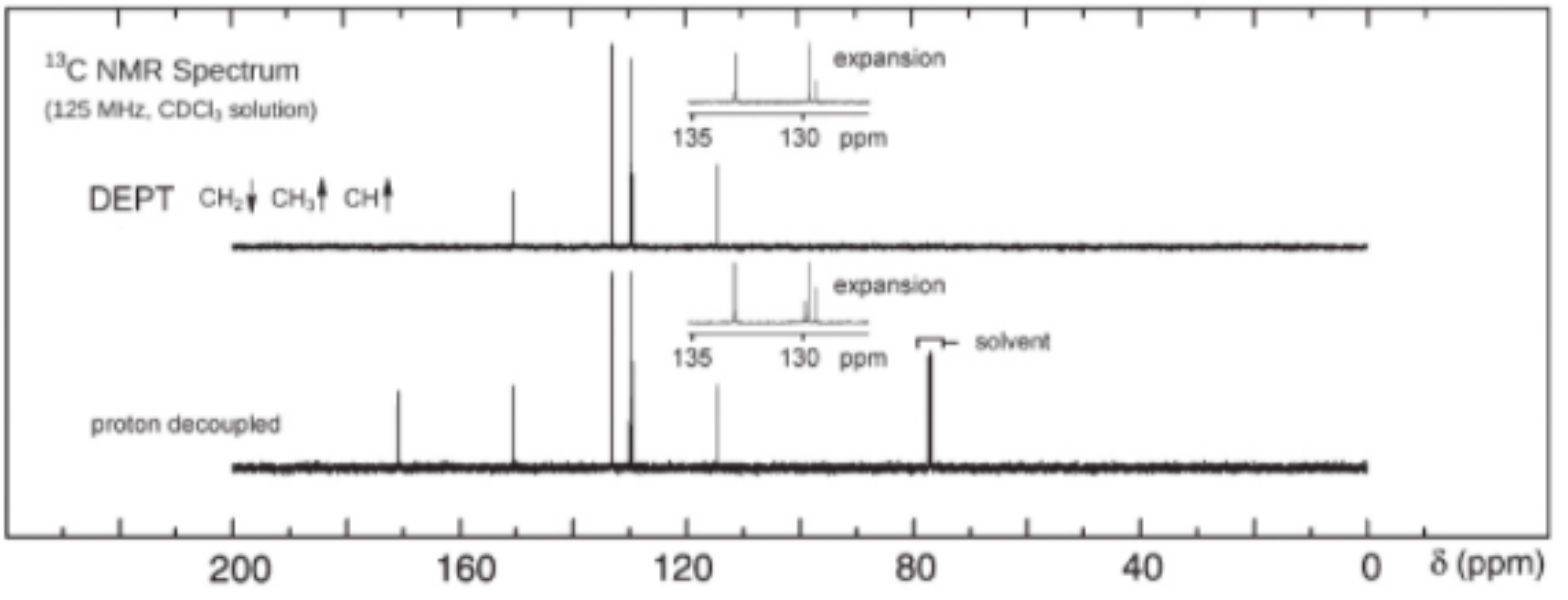


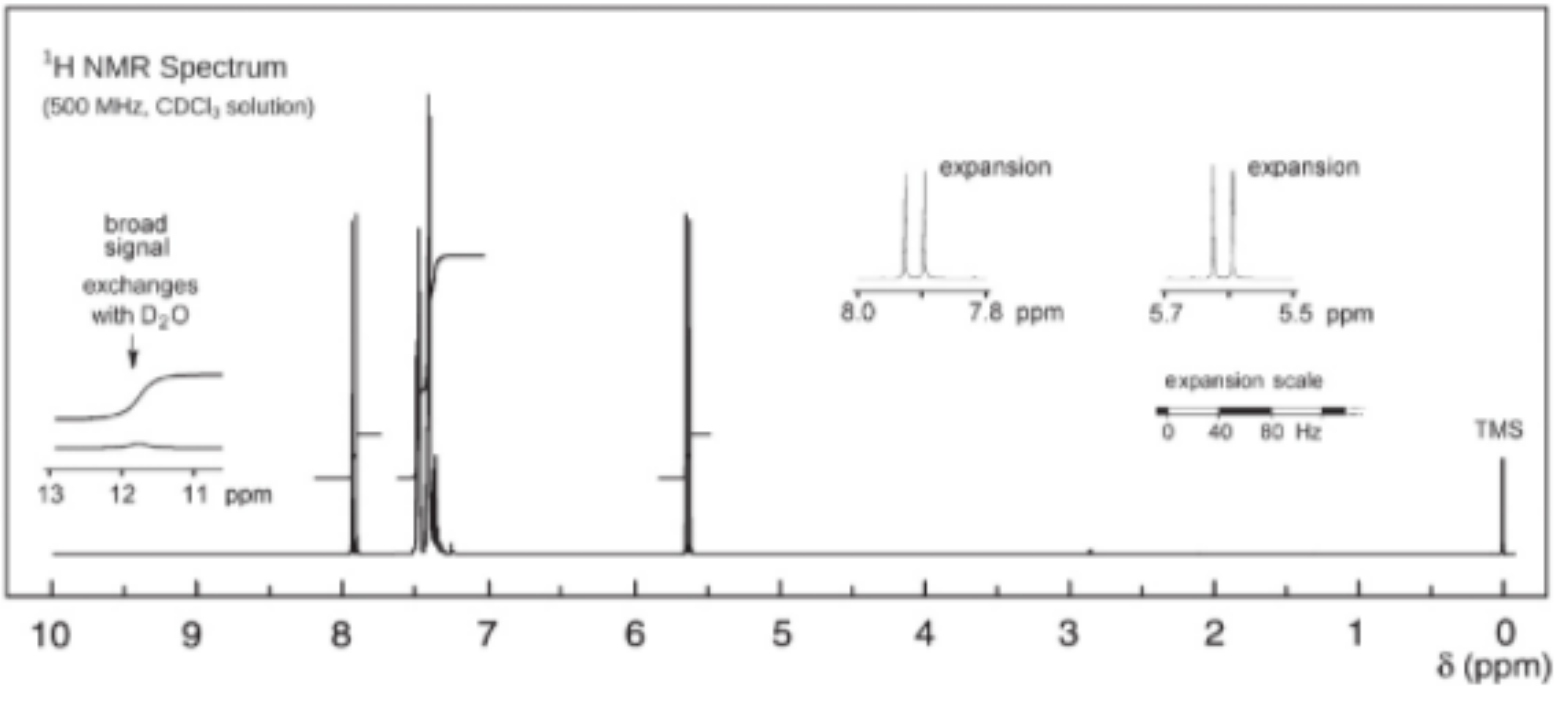
Problem 222


IR Spectrum
(CHCl3 solution)
1675
1580
4000
3000
2000
1600
1200
800
ν (cm-1)

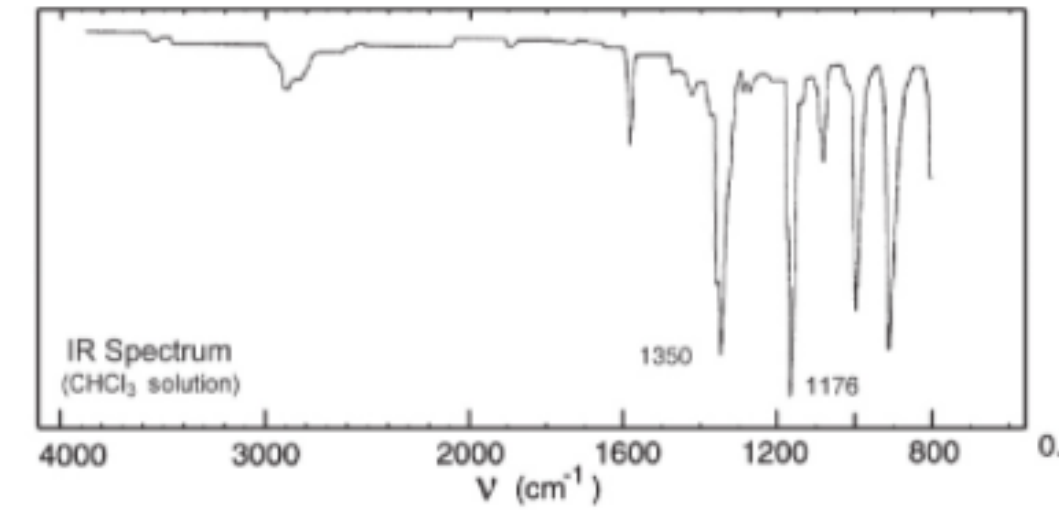

Mass Spectrum
% of base peak
135
M+·
180
C9H8SO2
100
80
60
40
20
40
80
120
160
200
240
280
m / e

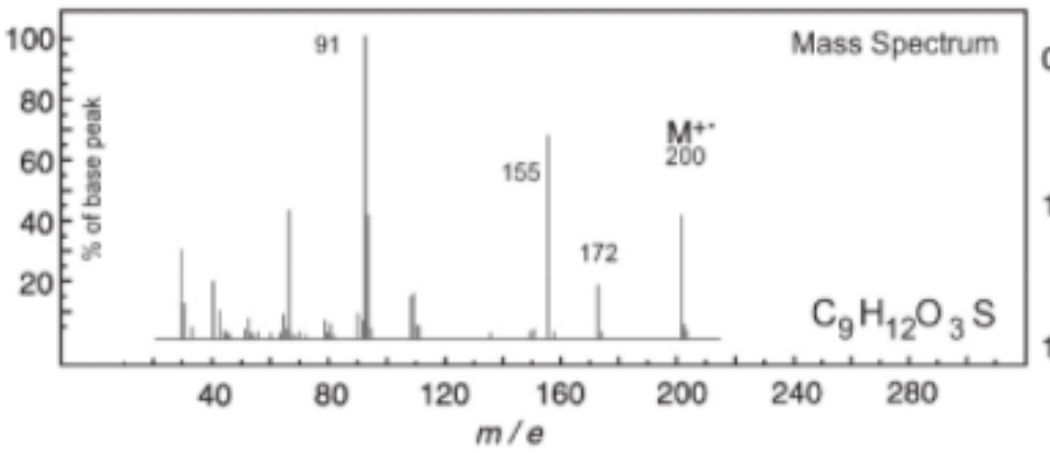

absorbance
UV spectrum
0.390 mg / 10 ml
path length : 0.2 cm
solvent : ethanol
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)

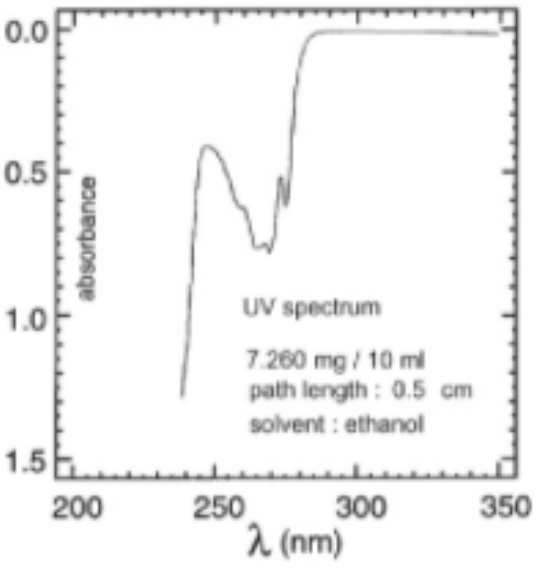

13C NMR Spectrum
(125 MHz, CDCl3 solution)
expansion
135
130 ppm
DEPT CH2 CH3 CH
expansion
135
130 ppm
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

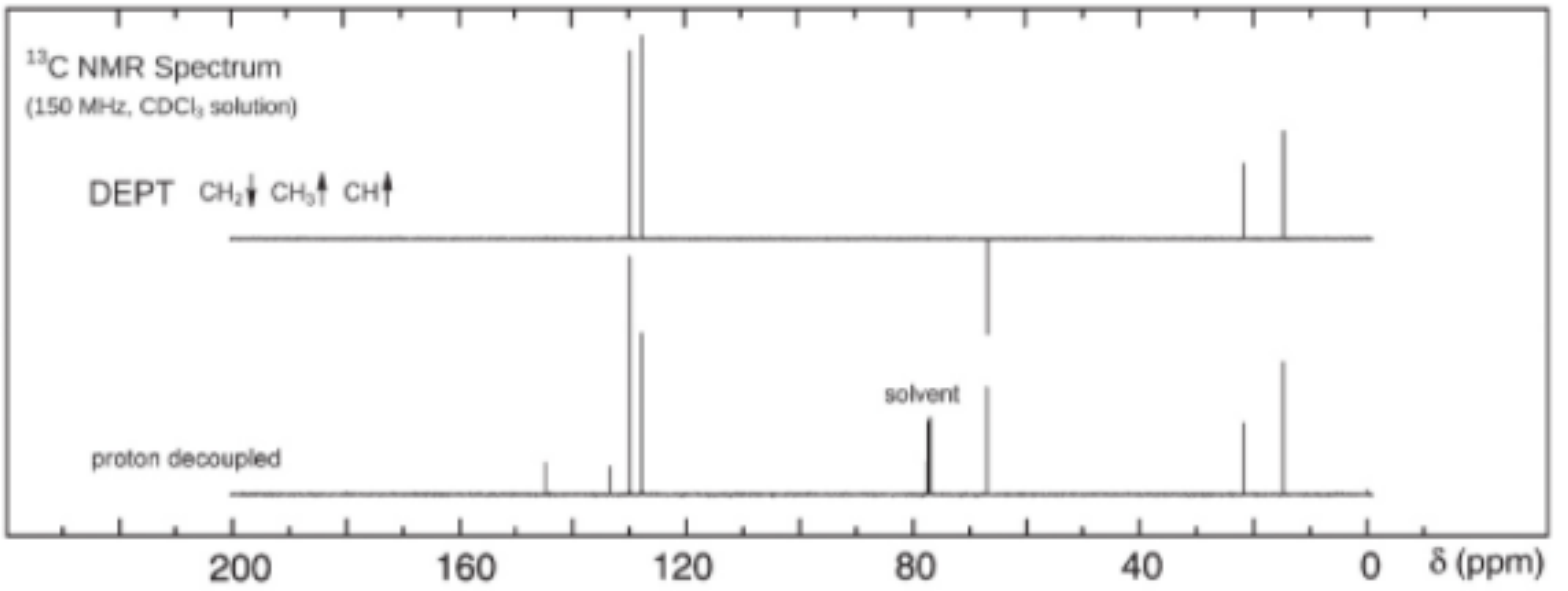

1H NMR Spectrum
(500 MHz, CDCl3 solution)
broad
signal
exchanges
with D2O
13
12
11 ppm
expansion
8.0
7.8 ppm
expansion
5.7
5.5 ppm
expansion scale
0
40
80 Hz
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

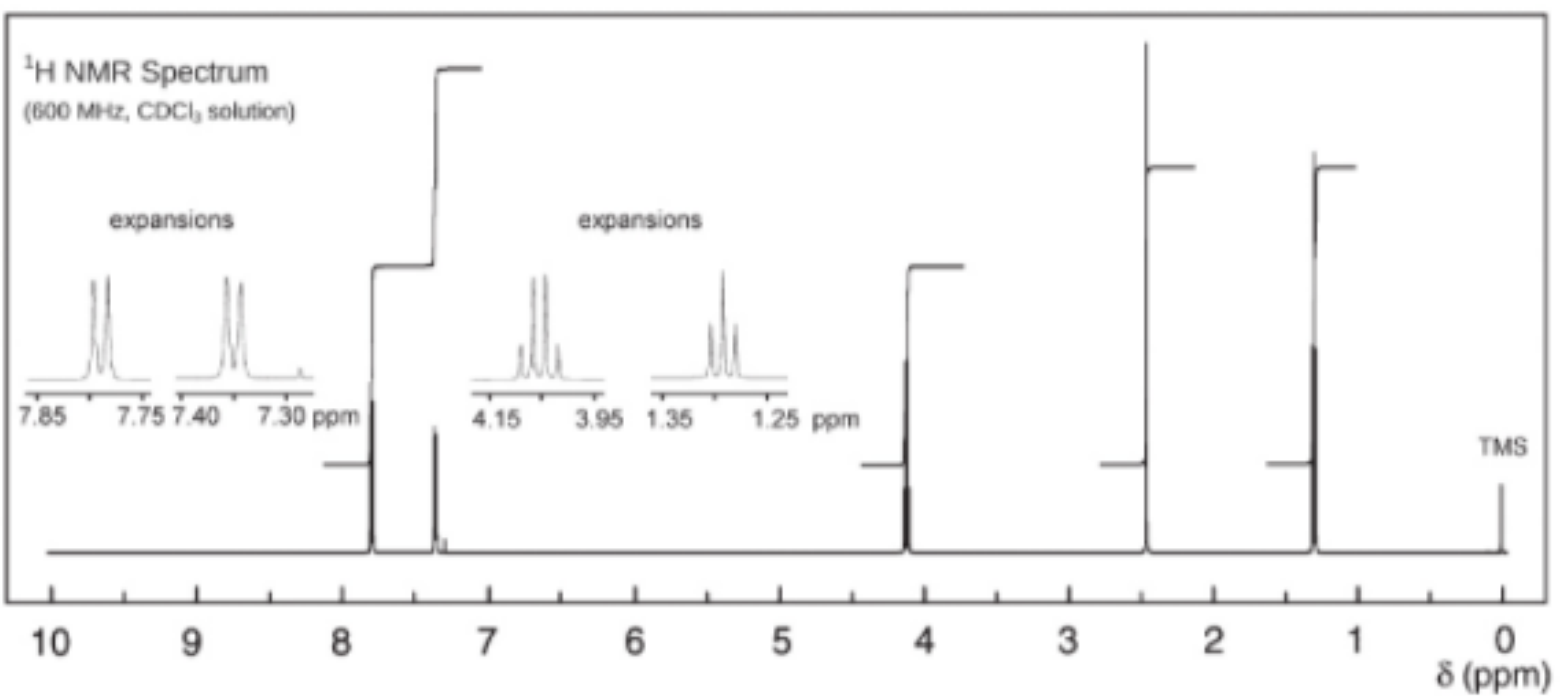
Problem 223


IR Spectrum
(CHCl3 solution)
1350
1176
4000
3000
2000
1600
1200
800
ν (cm-1)

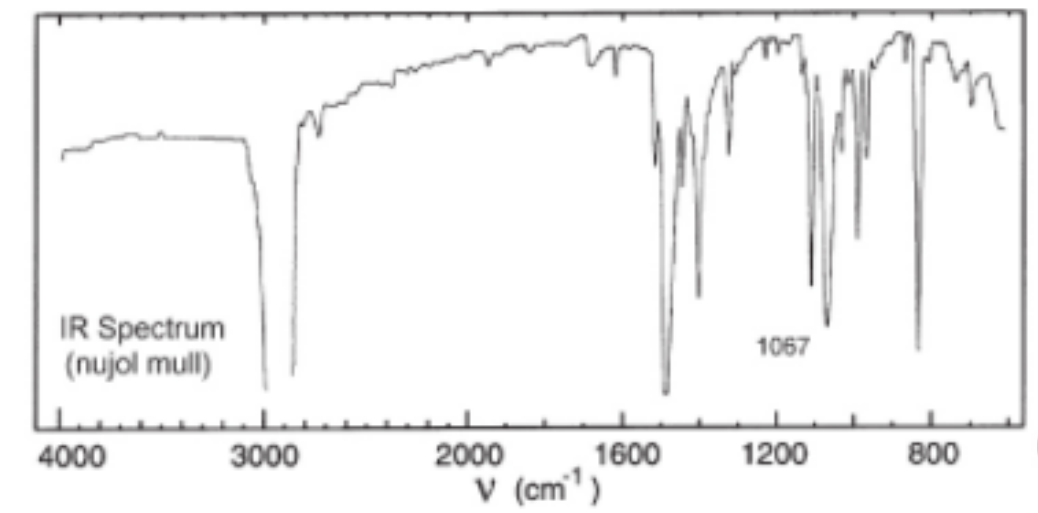

Mass Spectrum
91
155
172
M+·
200
% of base peak
100
80
60
40
20
C9H12O3S
40
80
120
160
200
240
280
m/e

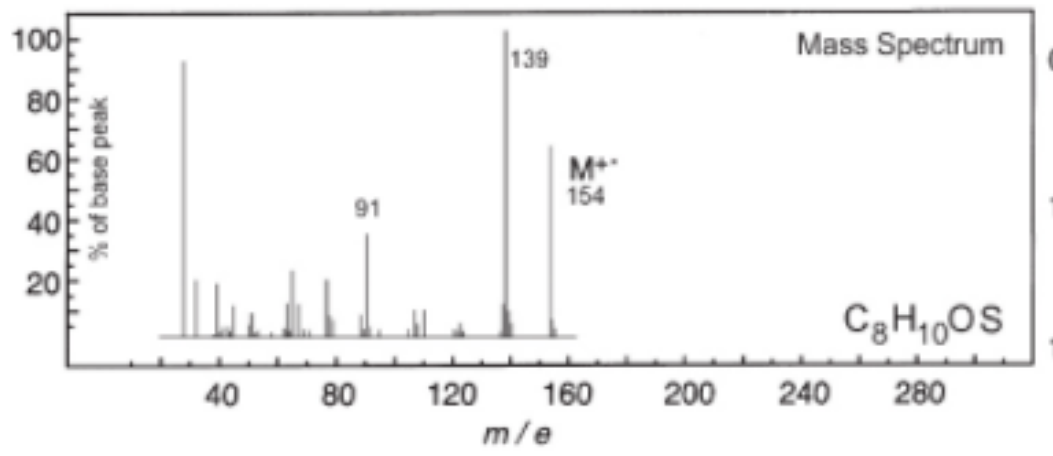

absorbance
0.0
0.5
1.0
1.5
UV spectrum
7.260 mg / 10 ml
path length : 0.5 cm
solvent : ethanol
200
250
300
350
λ (nm)

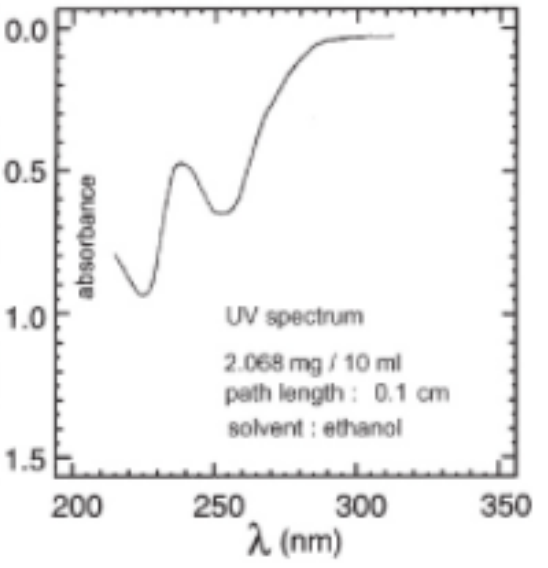

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

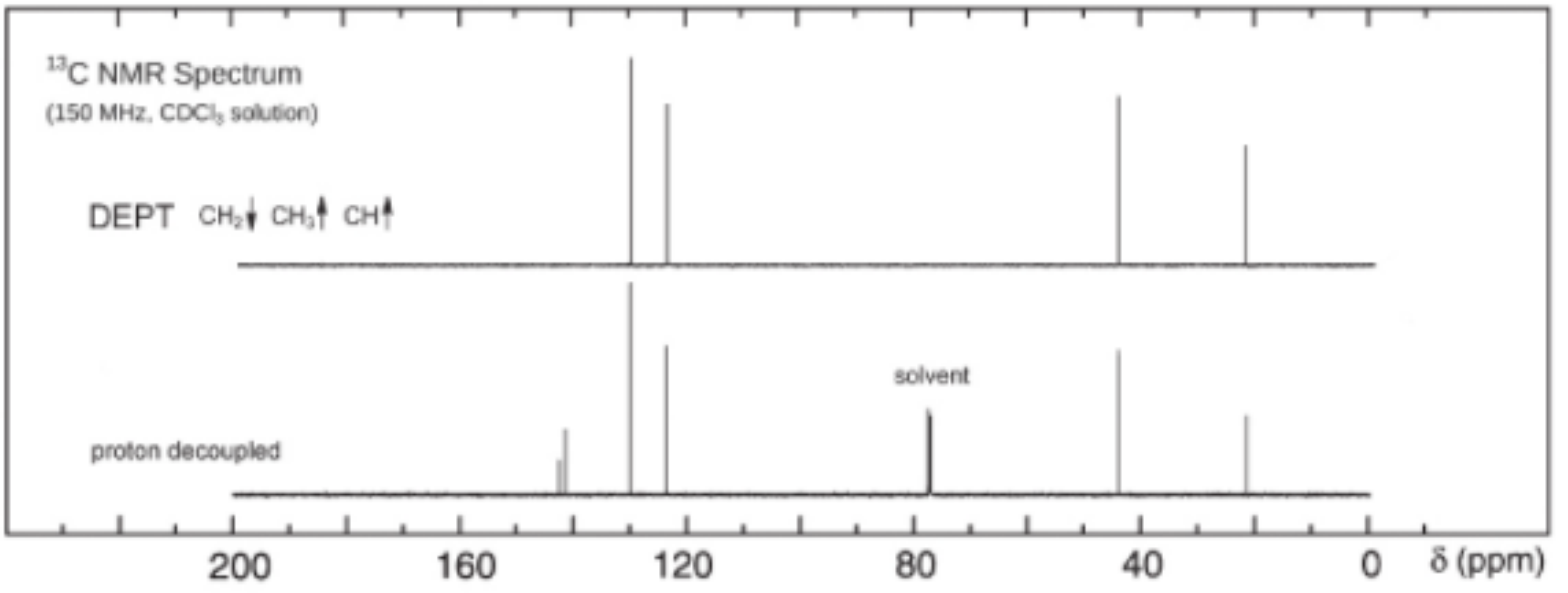

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansions
expansions
7.85
7.75
7.40
7.30 ppm
4.15
3.95
1.35
1.25 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

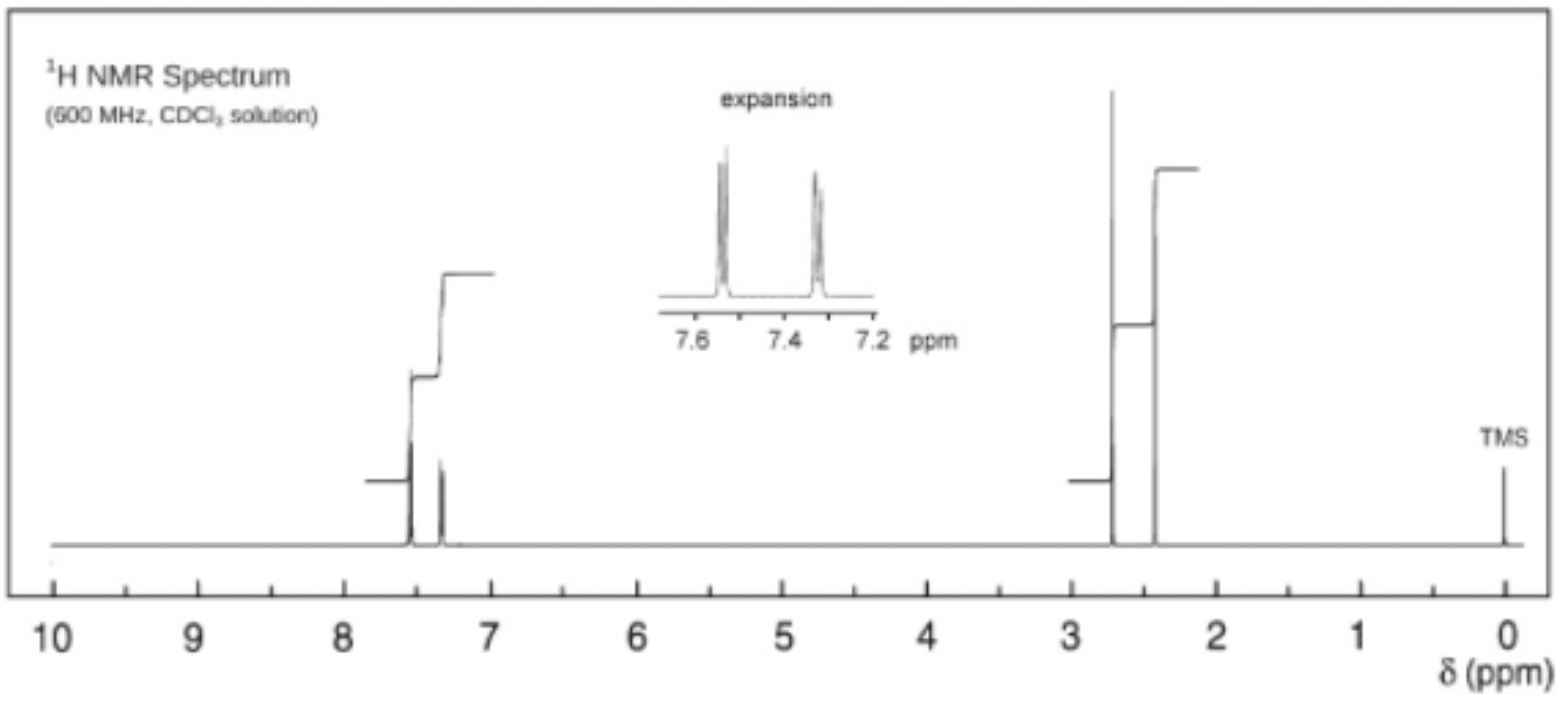
Problem 224


IR Spectrum
(nujol mull)
1067
4000
3000
2000
1600
1200
800
ν (cm-1)

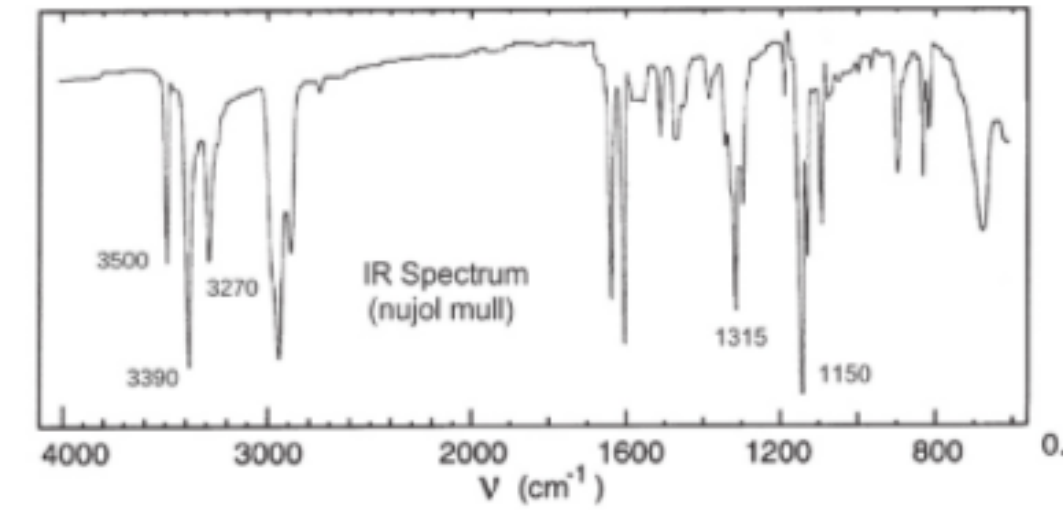

Mass Spectrum
% of base peak
100
80
60
40
20
139
M+·
154
91
C8H10OS
40
80
120
160
200
240
280
m/e

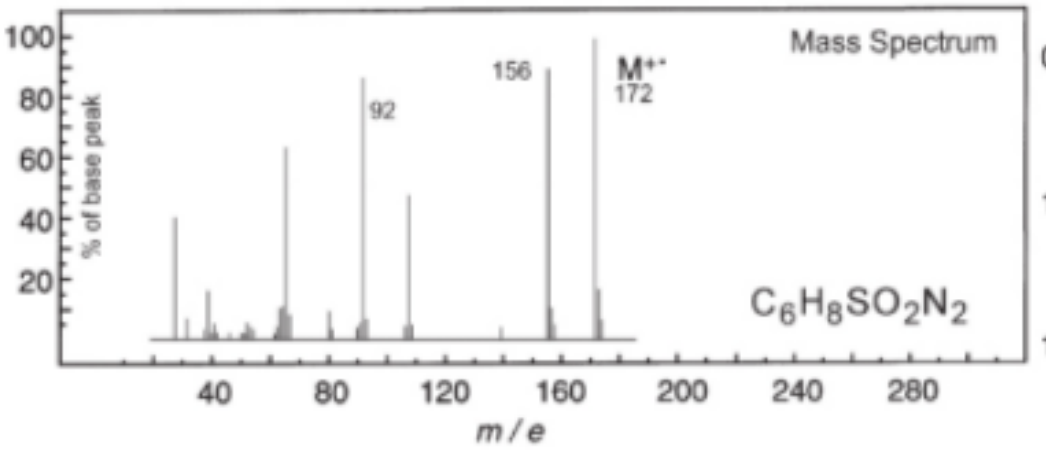

absorbance
0.0
0.5
1.0
1.5
UV spectrum
2.068 mg / 10 ml
path length : 0.1 cm
solvent : ethanol
200
250
300
350
λ (nm)

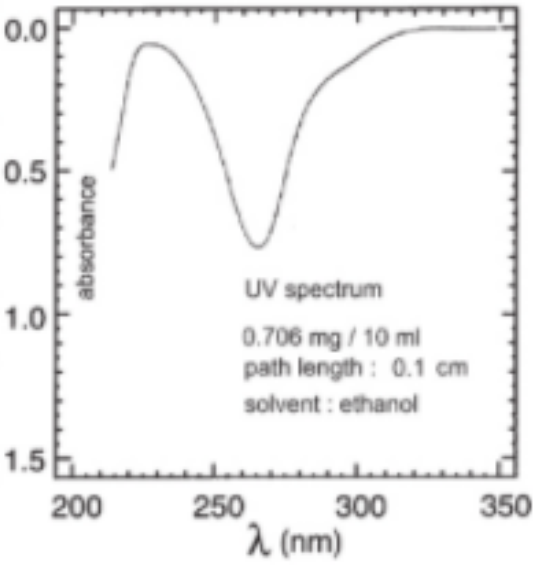

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

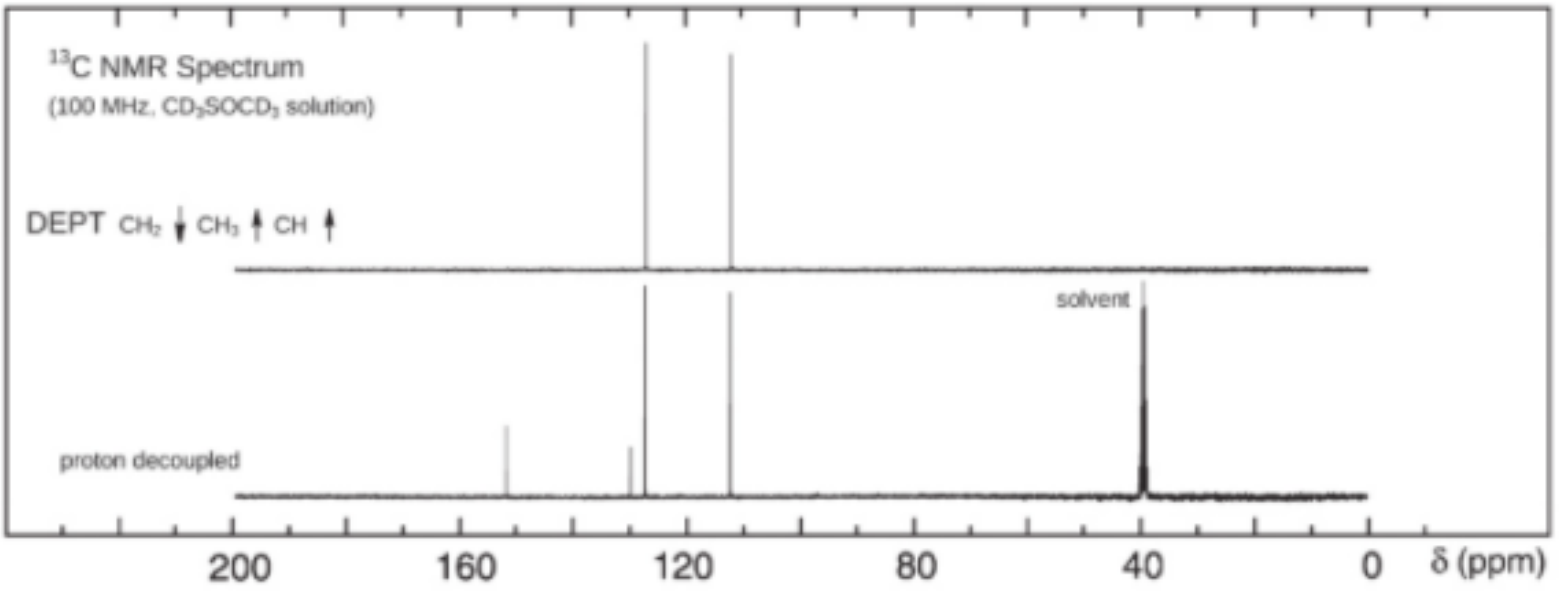

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion
7.6
7.4
7.2
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

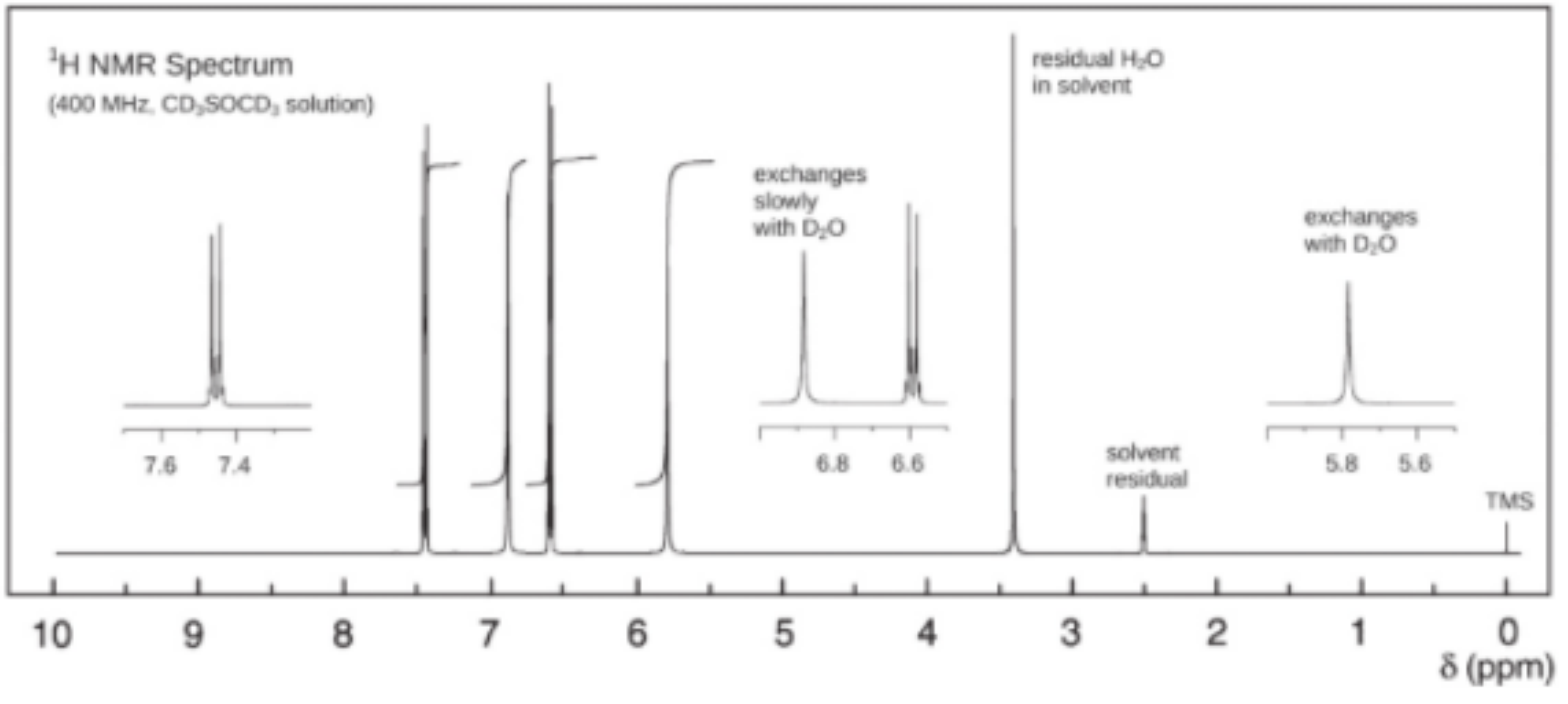
Problem 225


3500
3270
3390
IR Spectrum
(nujol mull)
1315
1150
4000
3000
2000
1600
1200
800
ν (cm-1)

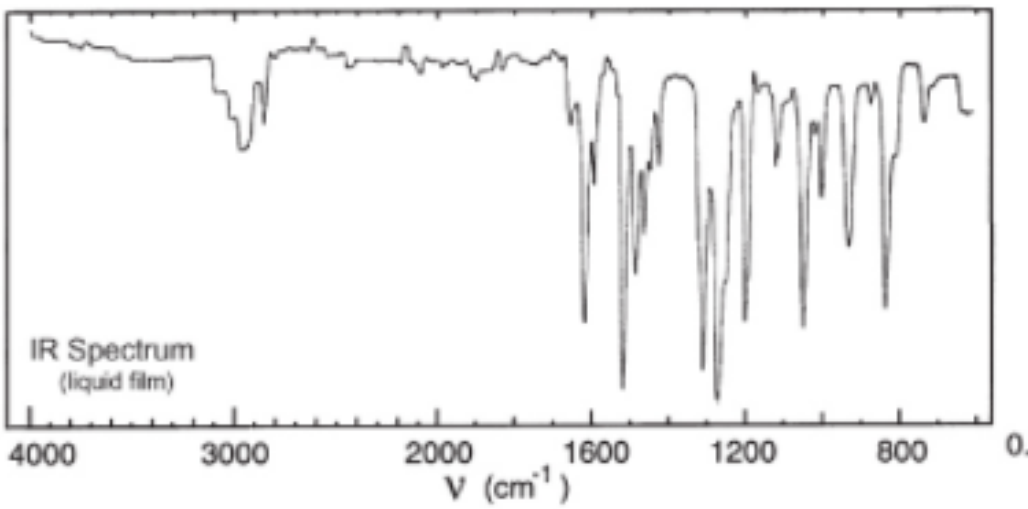

Mass Spectrum
% of base peak
100
80
60
40
20
92
156
M+·
172
C6H8SO2N2
40
80
120
160
200
240
280
m/e

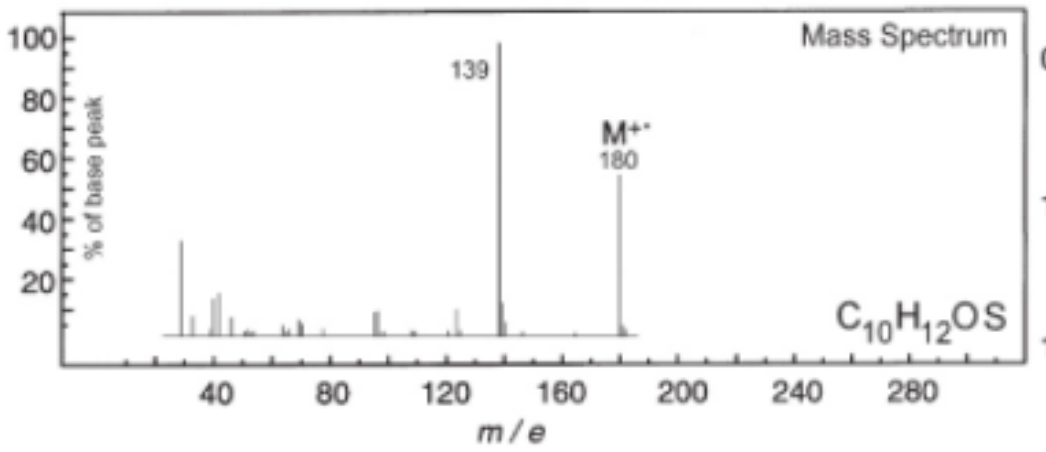

0.0
0.5
1.0
1.5
absorbance
UV spectrum
0.706 mg / 10 ml
path length : 0.1 cm
solvent : ethanol
200
250
300
350
λ (nm)

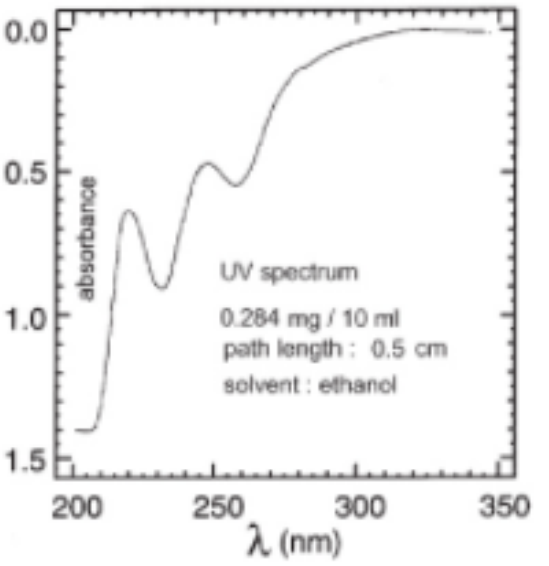

13C NMR Spectrum
(100 MHz, CD3SOCD3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

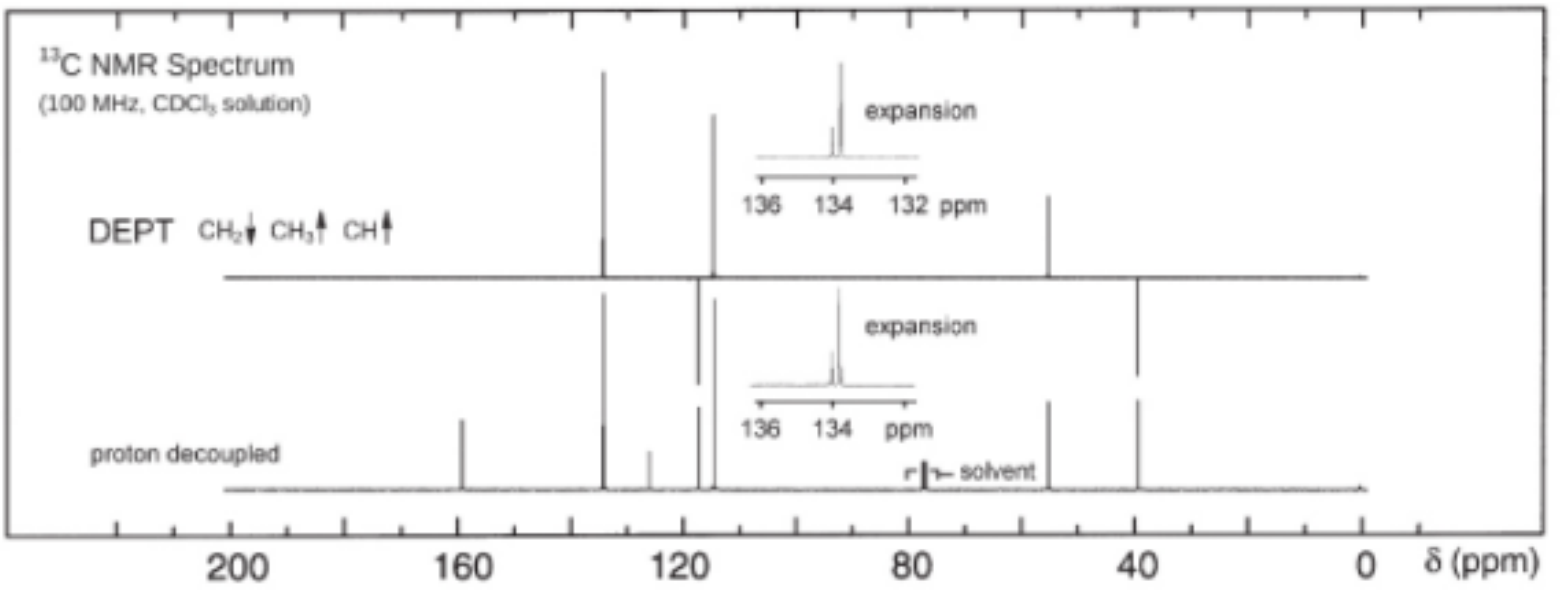

1H NMR Spectrum
(400 MHz, CD3SOCD3 solution)
residual H2O
in solvent
exchanges
slowly
with D2O
exchanges
with D2O
7.6
7.4
6.8
6.6
5.8
5.6
solvent
residual
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

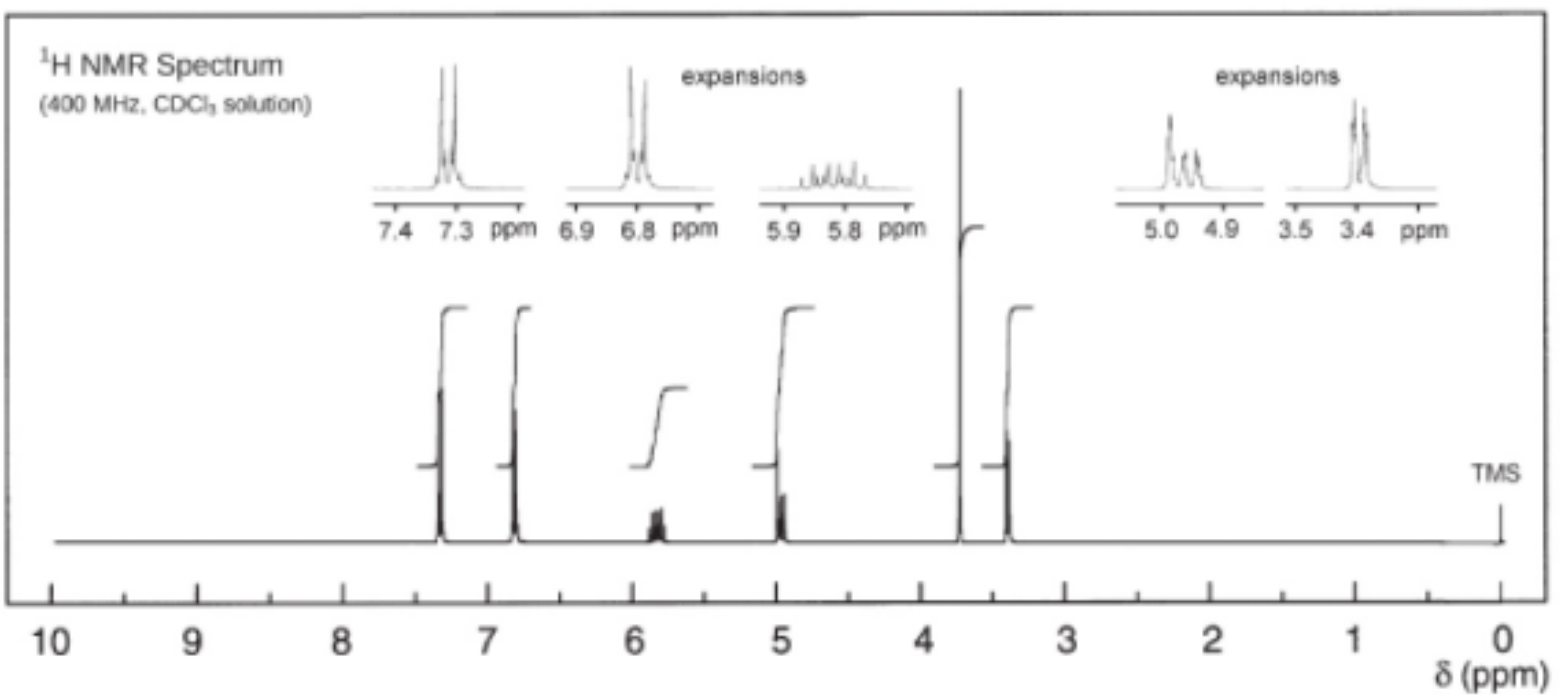
Problem 226


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

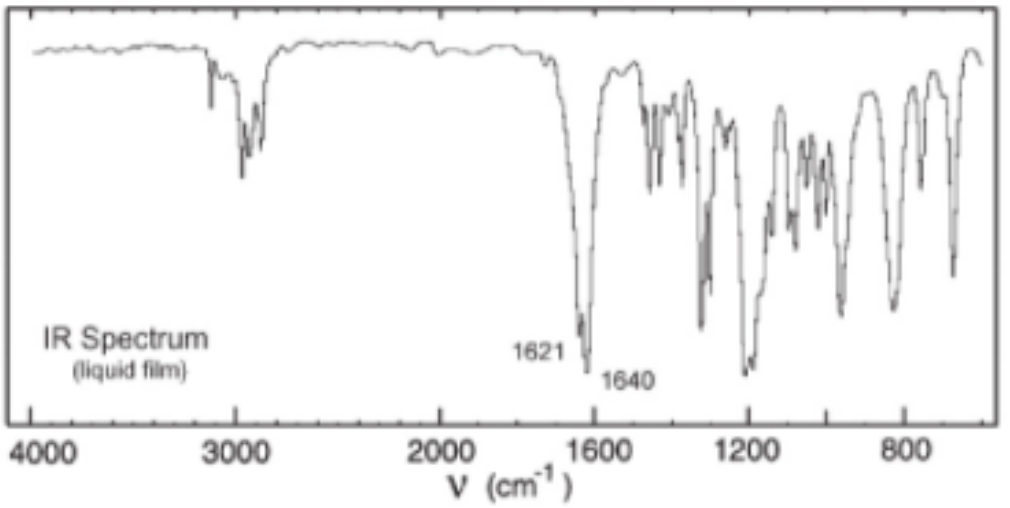

Mass Spectrum
% of base peak
139
M+·
180
C10H12OS
100
80
60
40
20
40
80
120
160
200
240
280
m/e

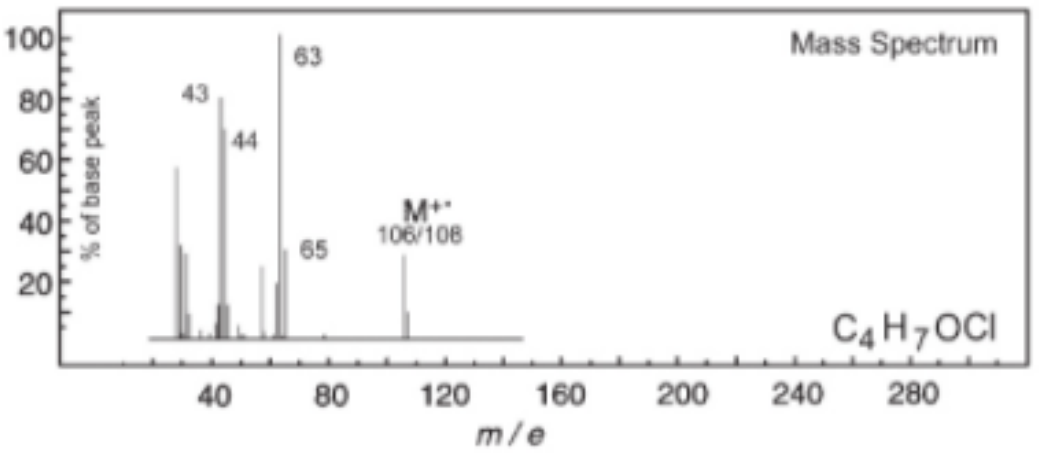

absorbance
UV spectrum
0.284 mg / 10 ml
path length : 0.5 cm
solvent : ethanol
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)


13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
136 134 132 ppm
DEPT CH2 CH3 CH
expansion
136 134 ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

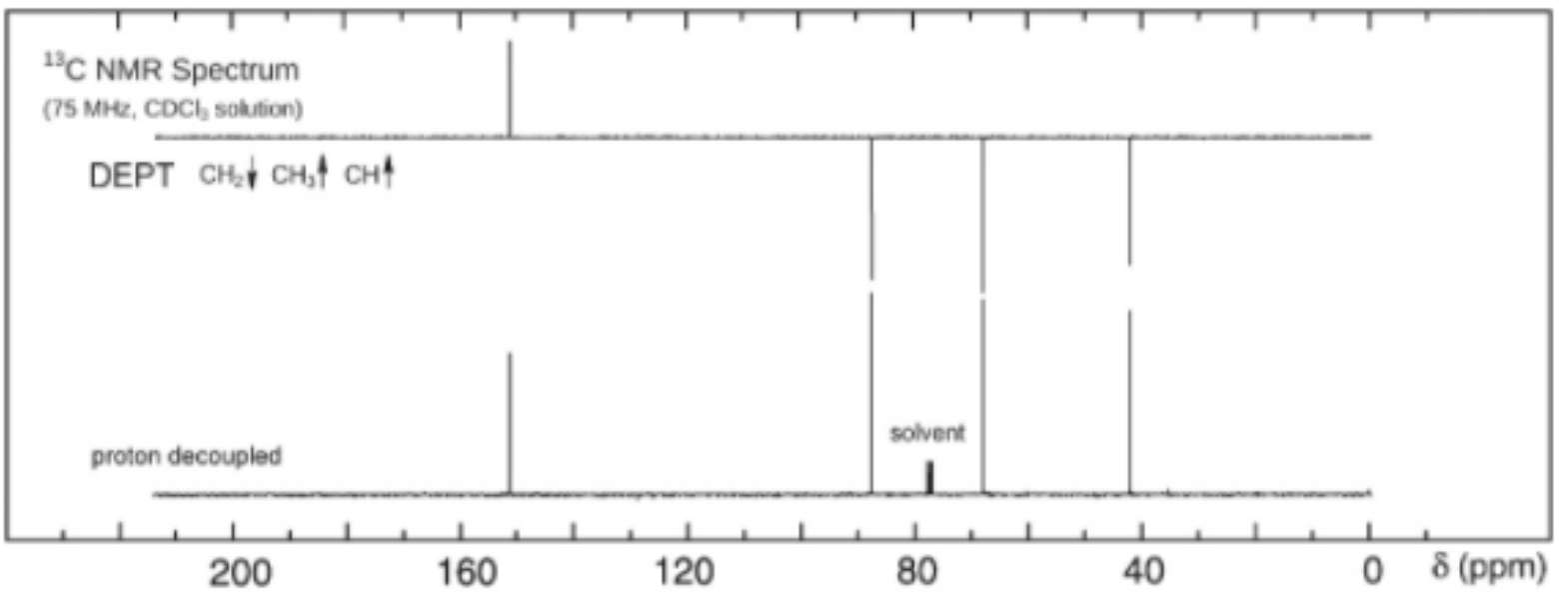

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
7.4 7.3 ppm
6.9 6.8 ppm
5.9 5.8 ppm
expansions
5.0 4.9
3.5 3.4 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

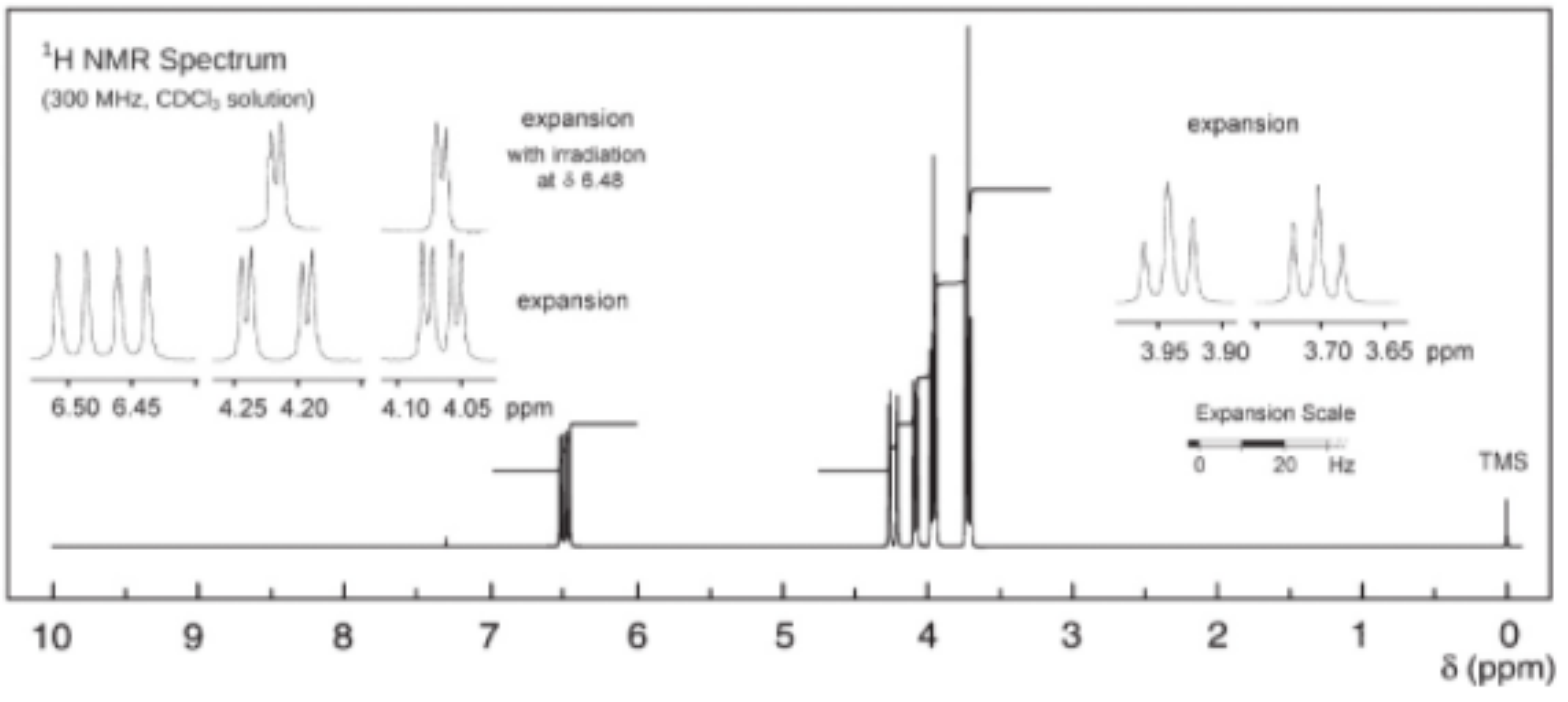
Problem 227

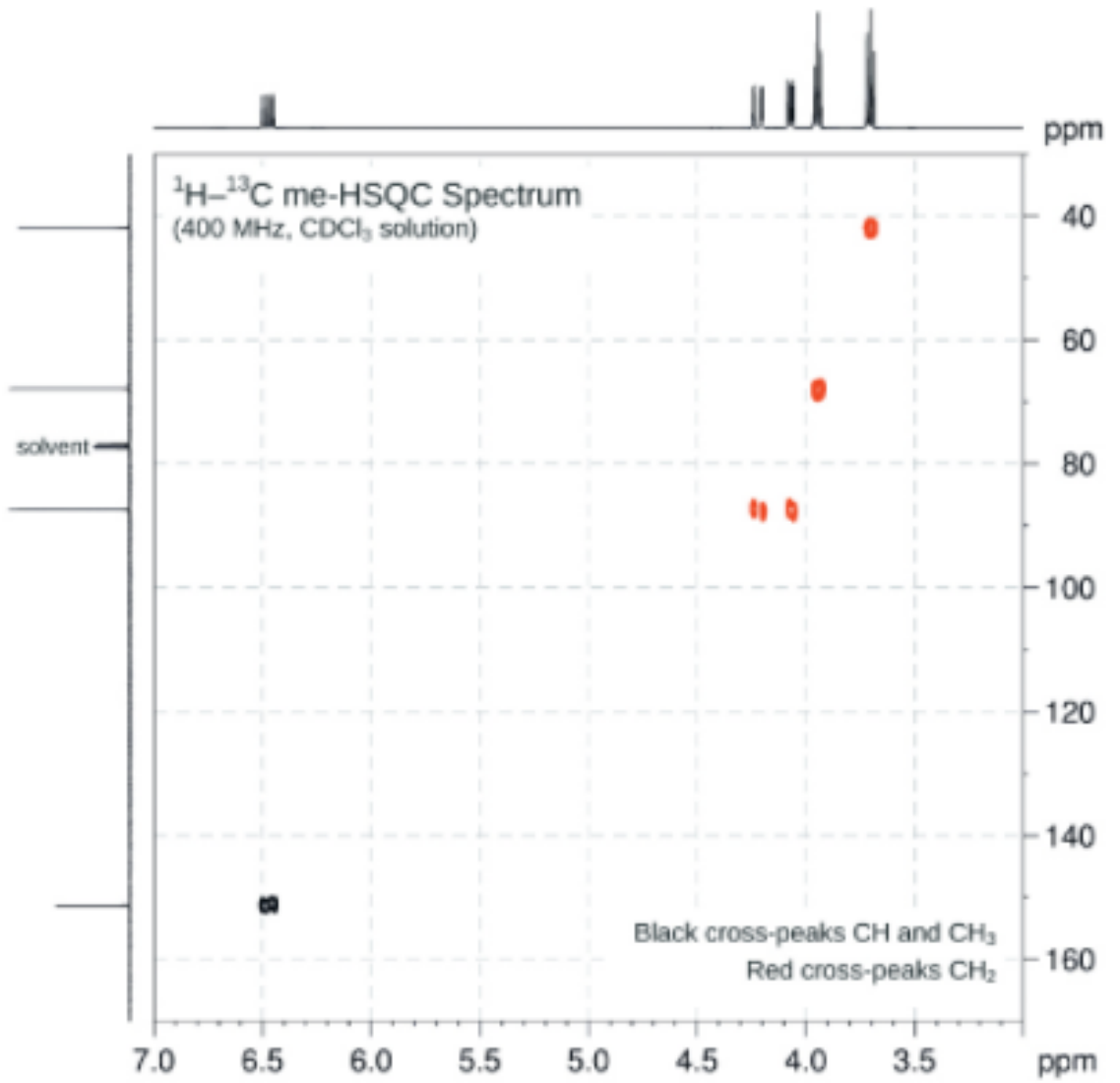




No significant UV absorption above 220 nm

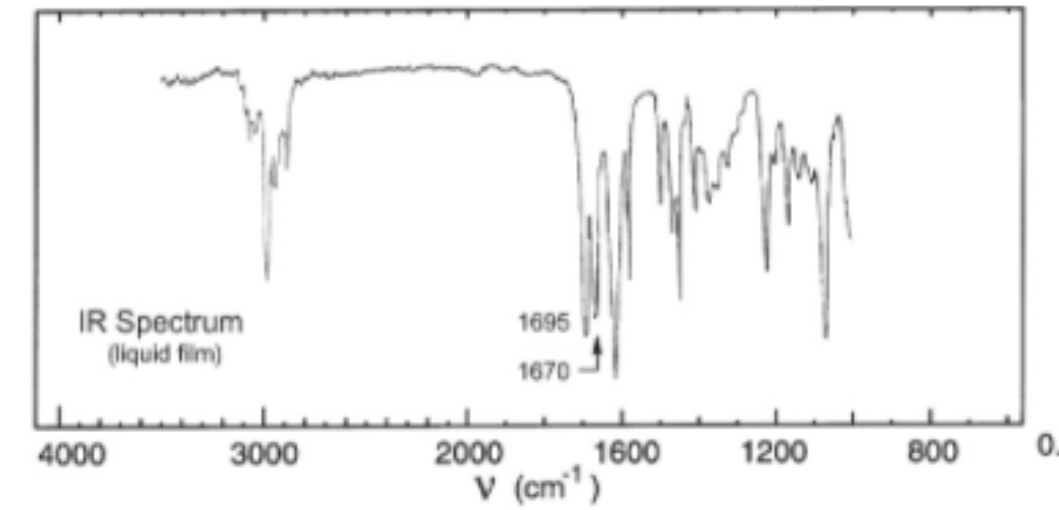


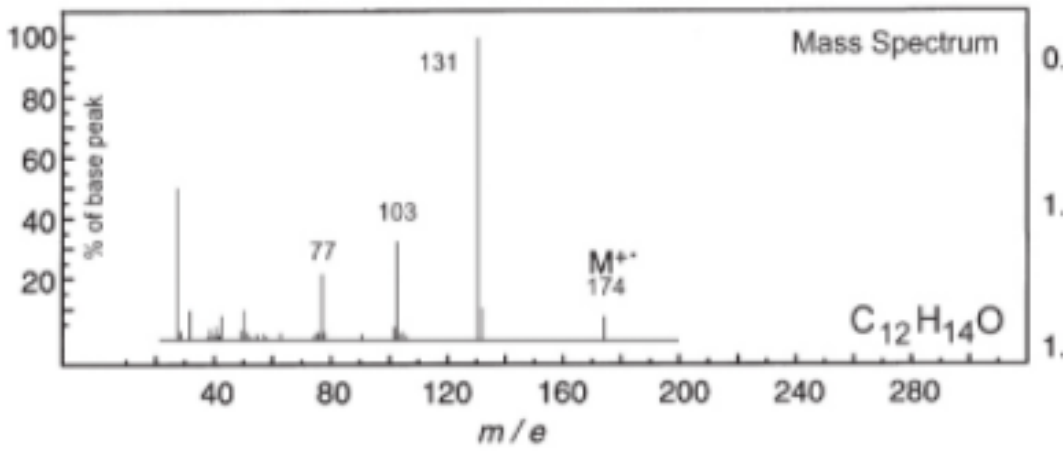


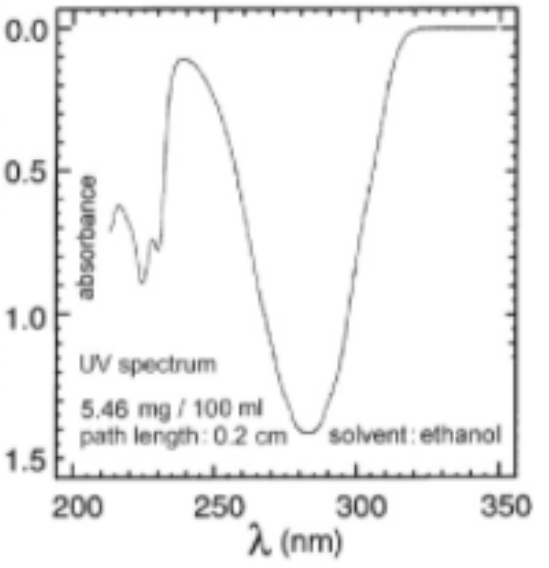

ppm
^{1}H–^{13}C me-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
solvent
40
60
80
100
120
140
160
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

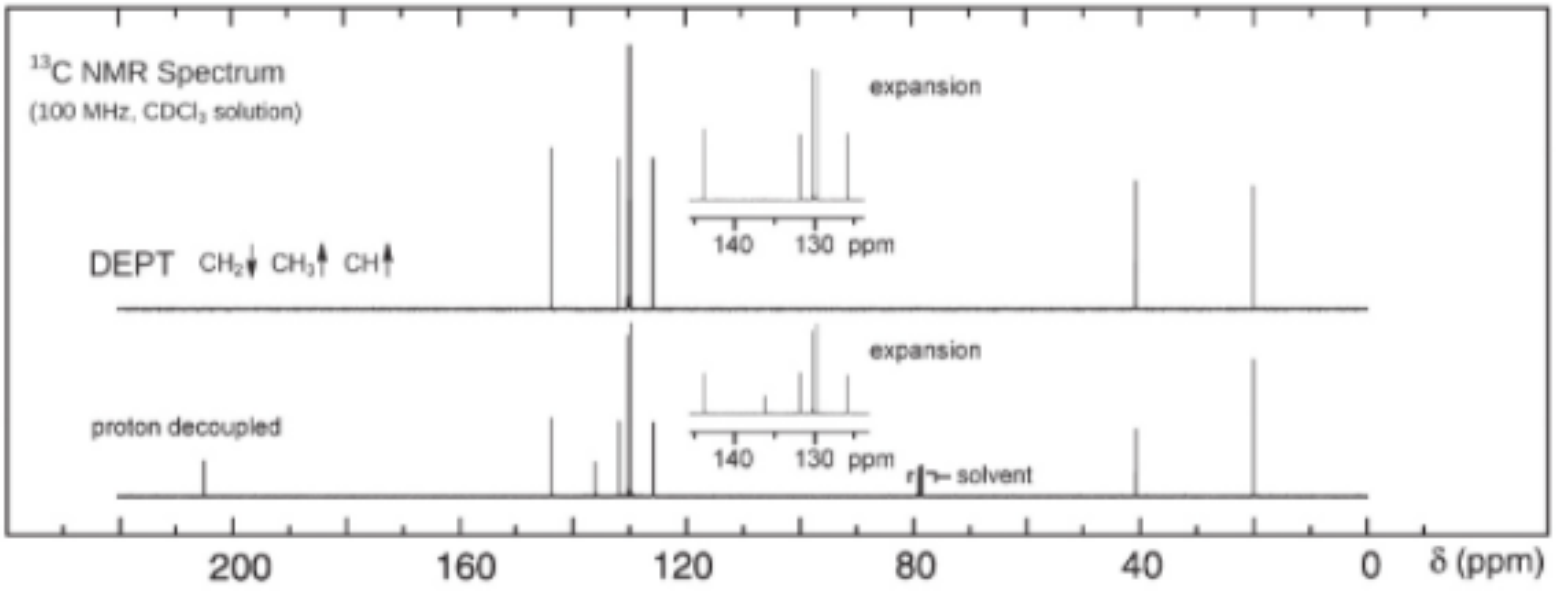
ppm
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

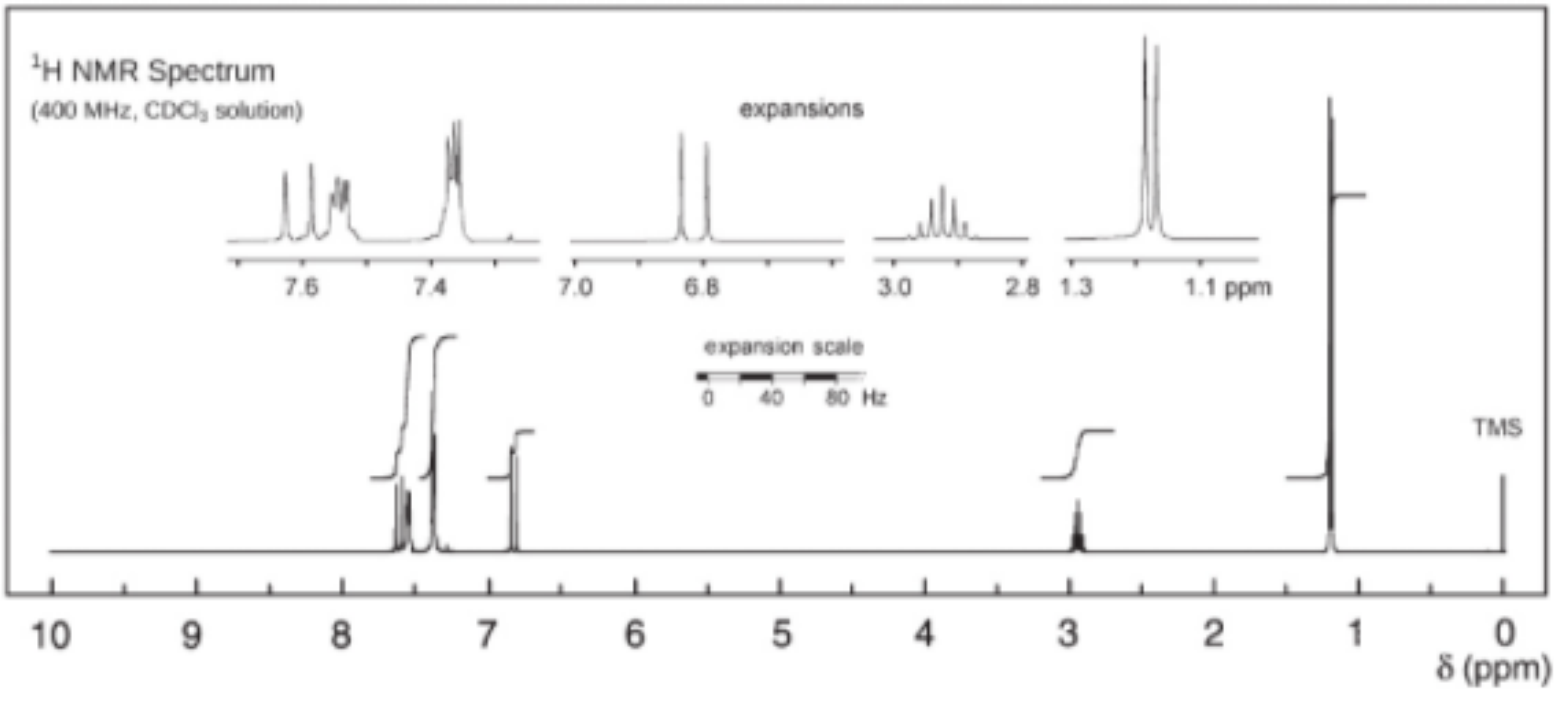
Problem 228


IR Spectrum
(liquid film)
1695
1670
4000
3000
2000
1600
1200
800
ν (cm-1)

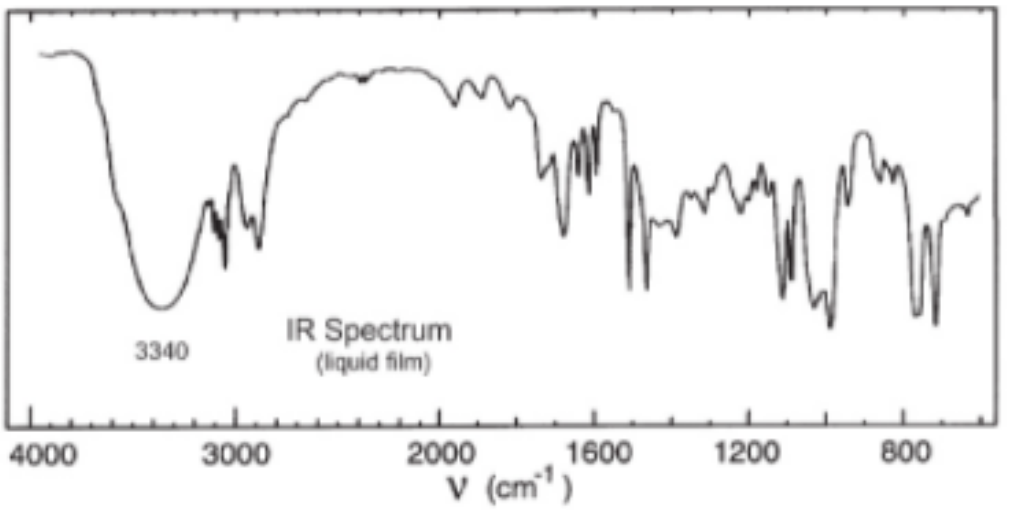

Mass Spectrum
% of base peak
100
80
60
40
20
131
103
77
M+·
174
C12H14O
40
80
120
160
200
240
280
m/e

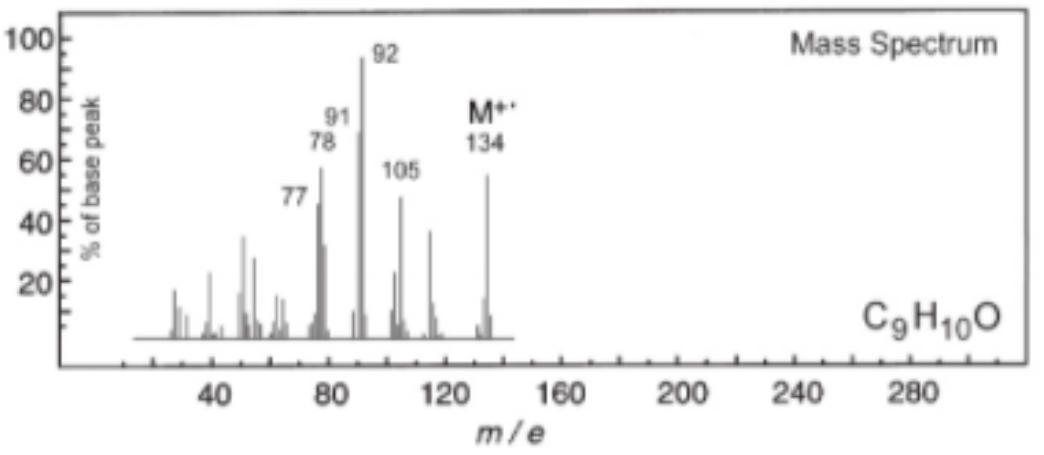

absorbance
0.0
0.5
1.0
1.5
UV spectrum
5.46 mg / 100 ml
path length: 0.2 cm
solvent: ethanol
200
250
300
350
λ (nm)


13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
140
130 ppm
DEPT CH2 CH3 CH
expansion
proton decoupled
140
130 ppm
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
7.6
7.4
7.0
6.8
3.0
2.8
1.3
1.1 ppm
expansion scale
0
40
80 Hz
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

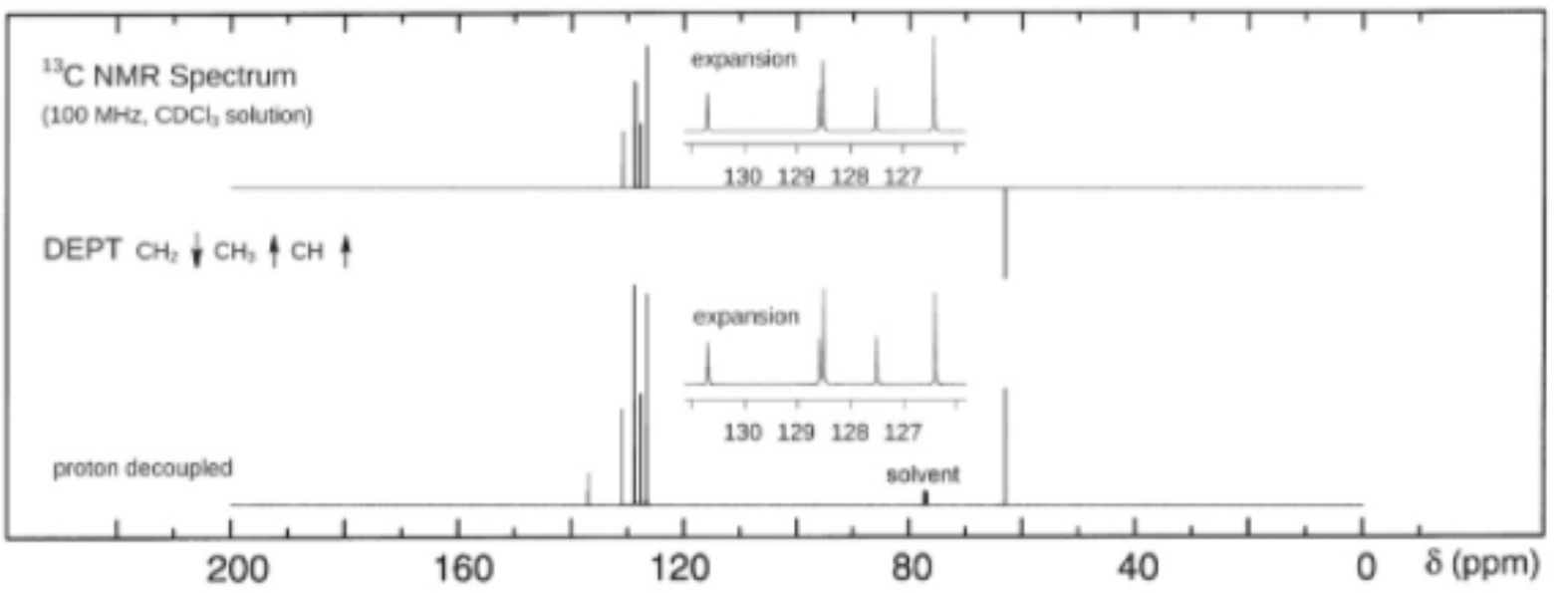
Problem 229

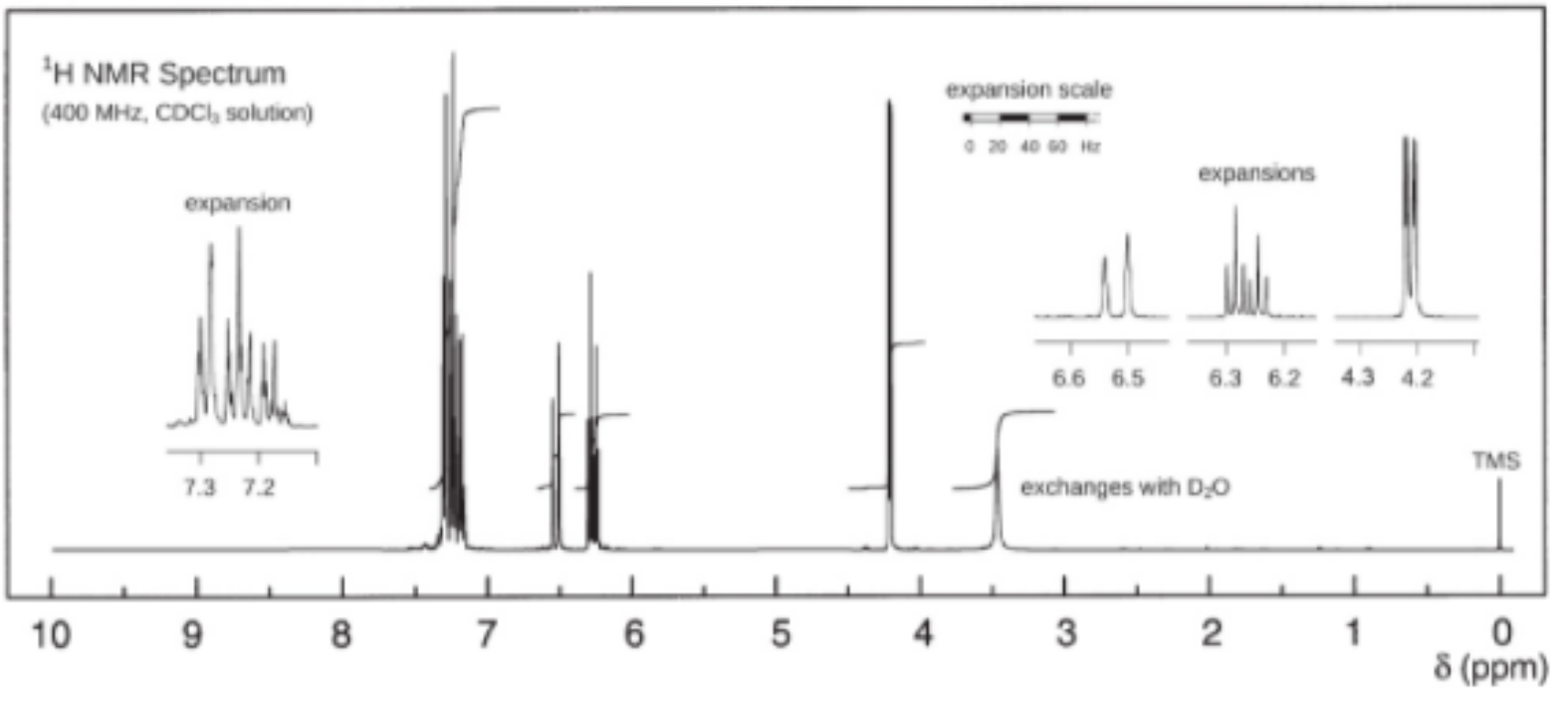




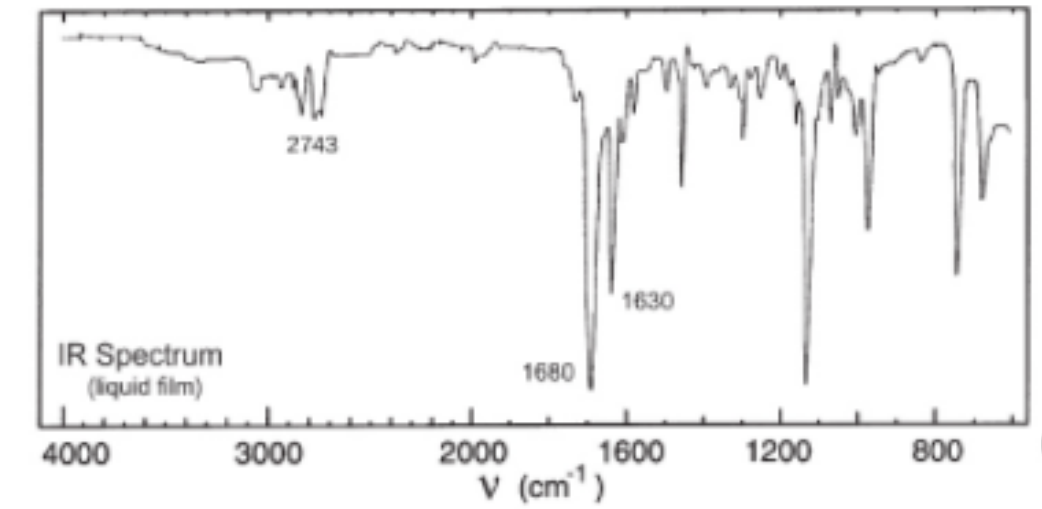
UV Spectrum

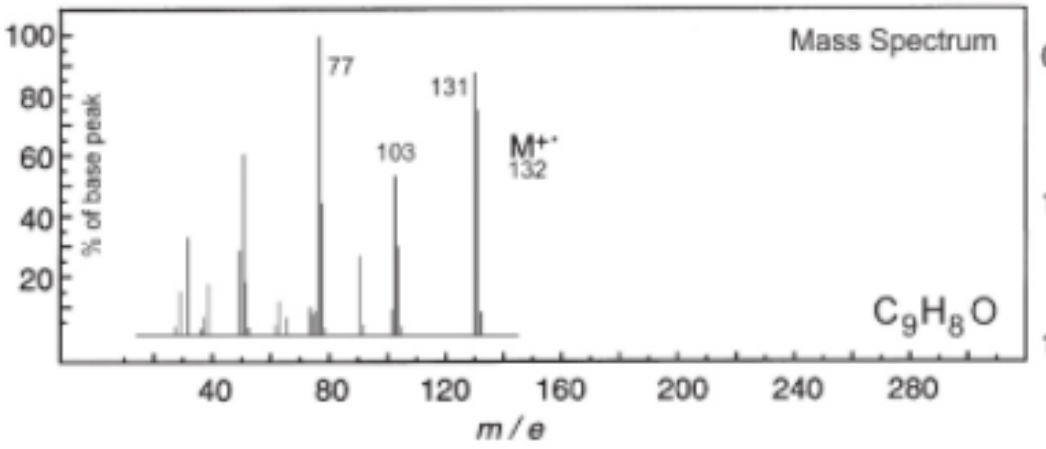
$\lambda_{max} \approx 250$ nm $(\log_{10}\varepsilon > 4.0)$

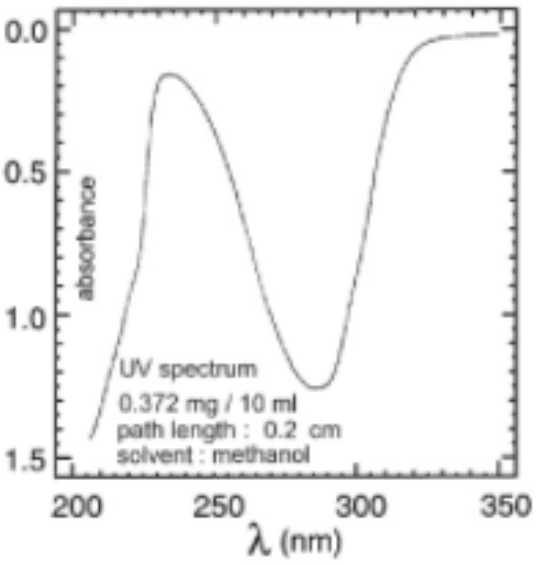


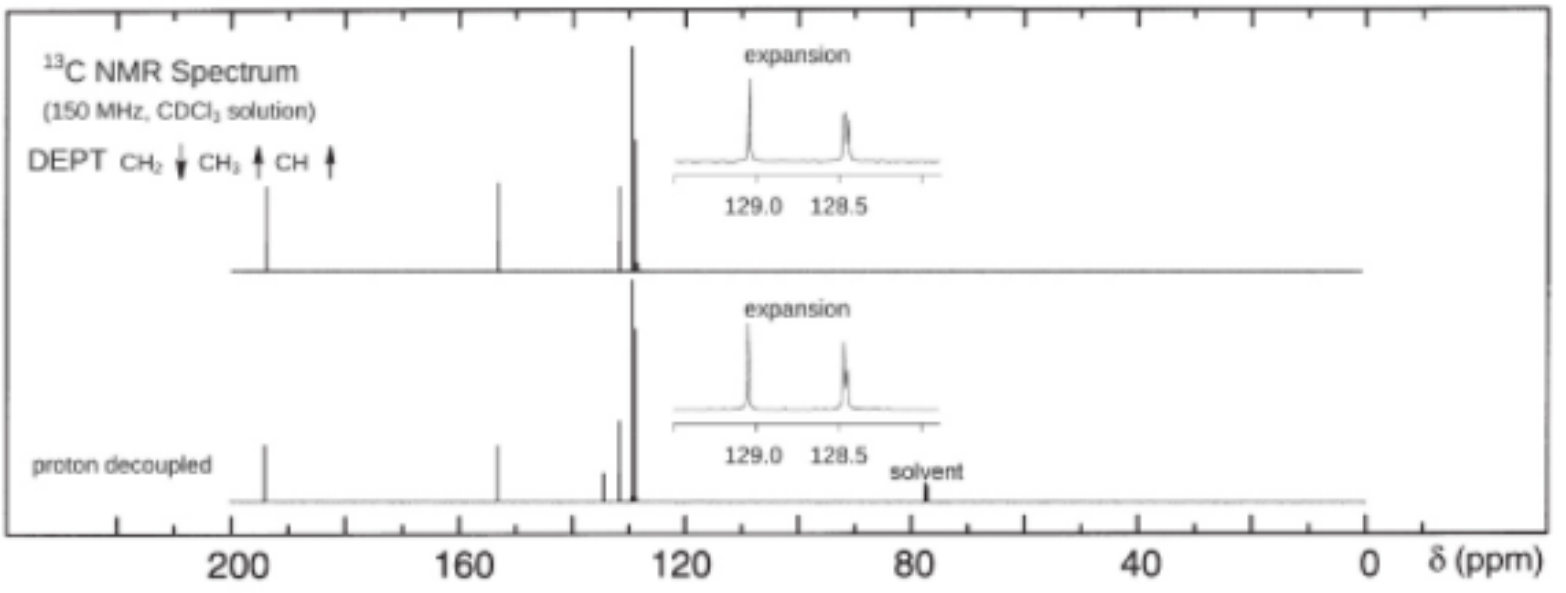


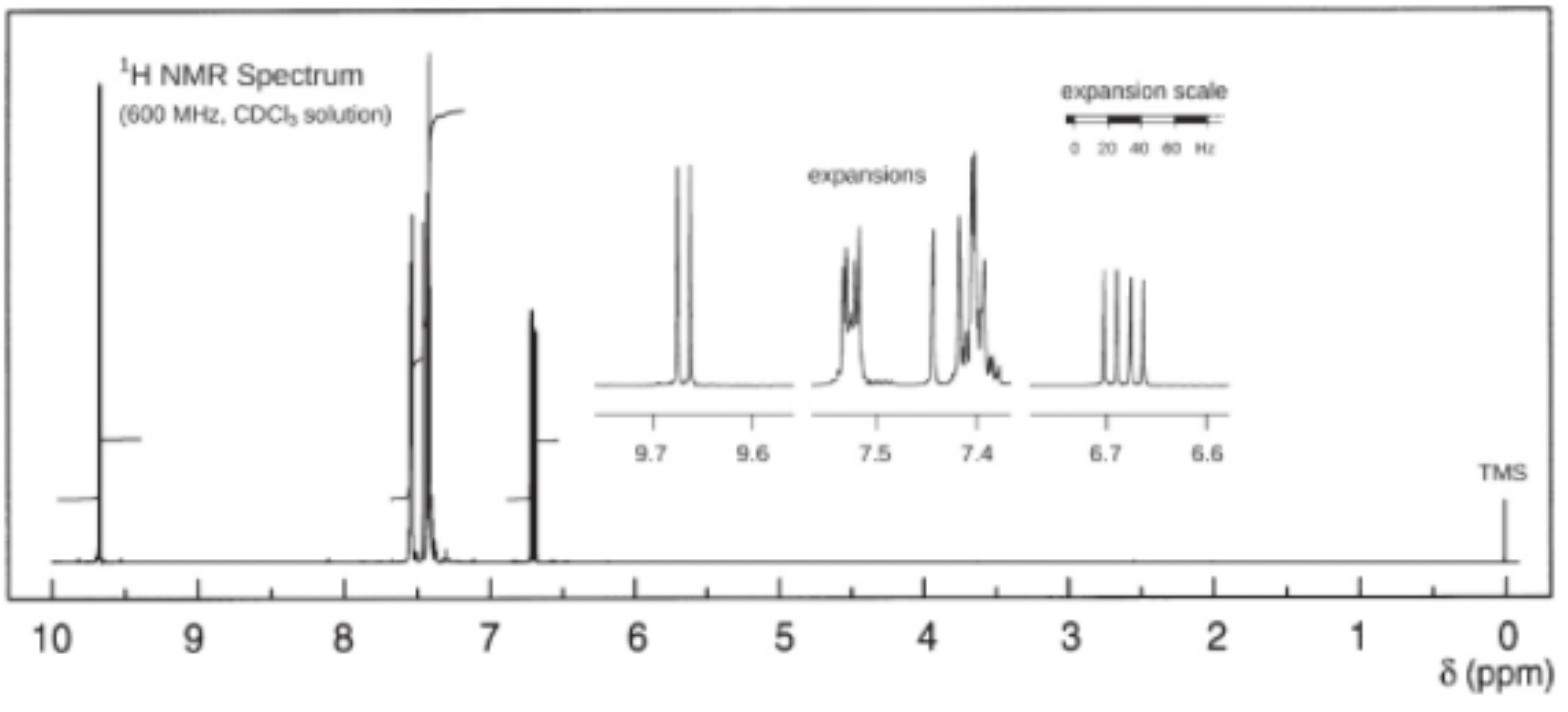
Problem 230

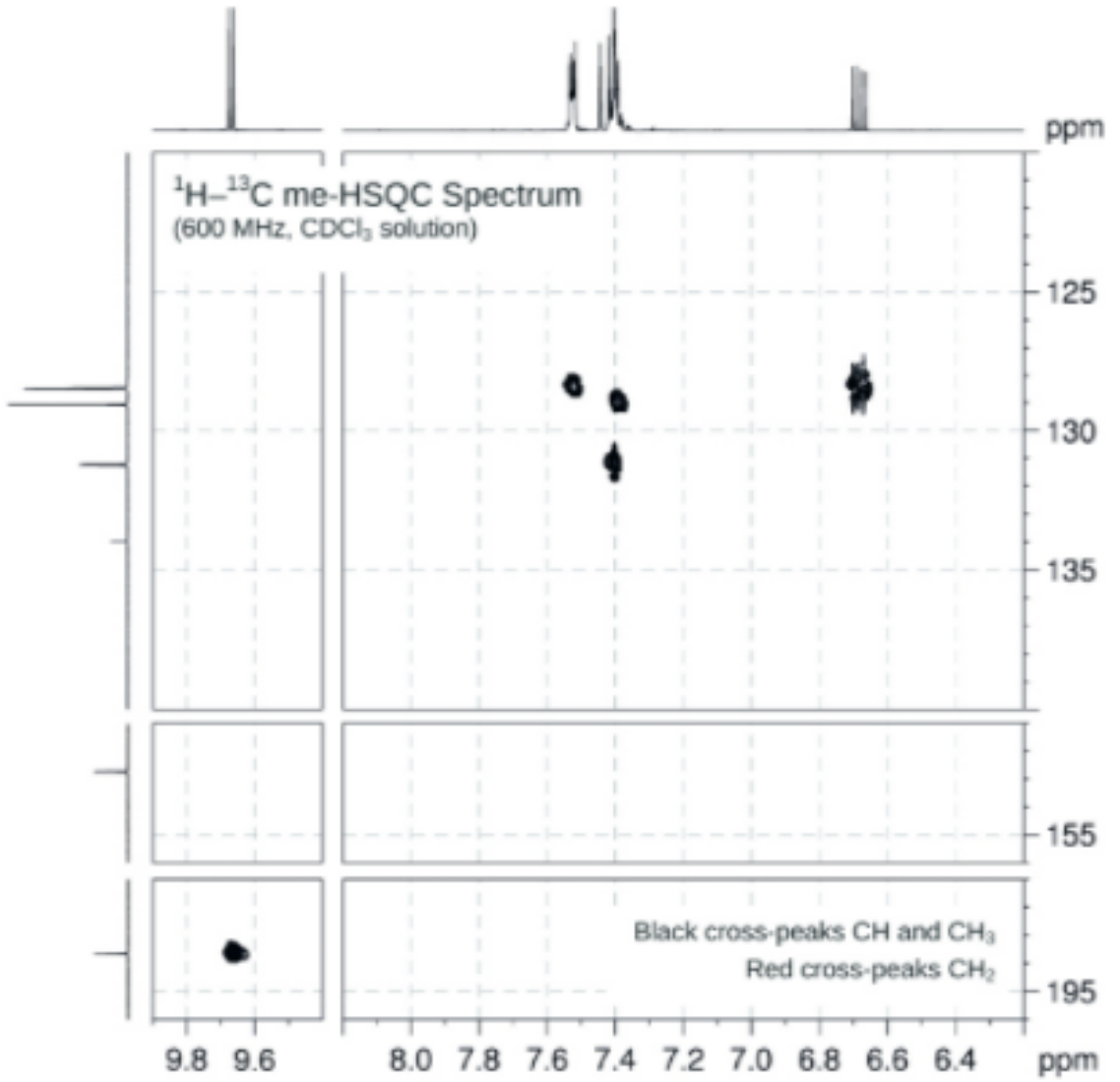

IR Spectrum
(liquid film)
2743
1680
1630
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

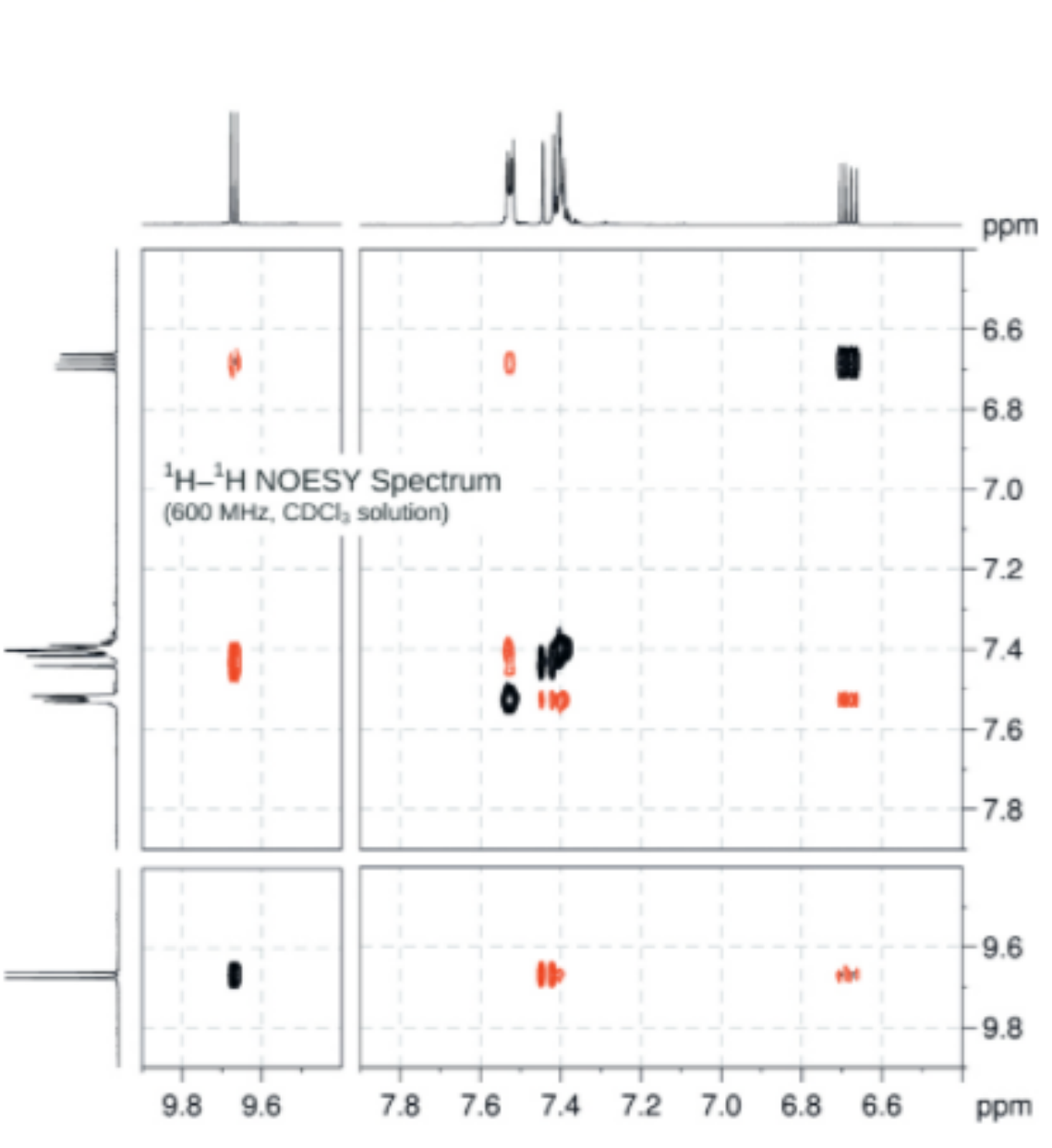

Mass Spectrum
% of base peak
100
80
60
40
20
77
131
103
M+·
132
C9H8O
40
80
120
160
200
240
280
m/e


absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.372 mg / 10 ml
path length : 0.2 cm
solvent : methanol
200
250
300
350
λ (nm)

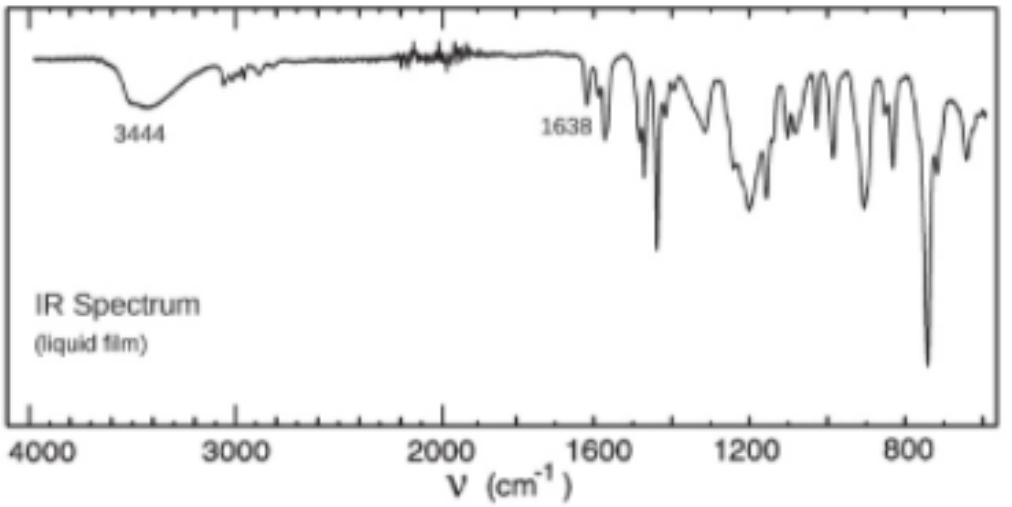

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 ↓ CH3 ↑ CH ↑
expansion
129.0 128.5
expansion
129.0 128.5
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

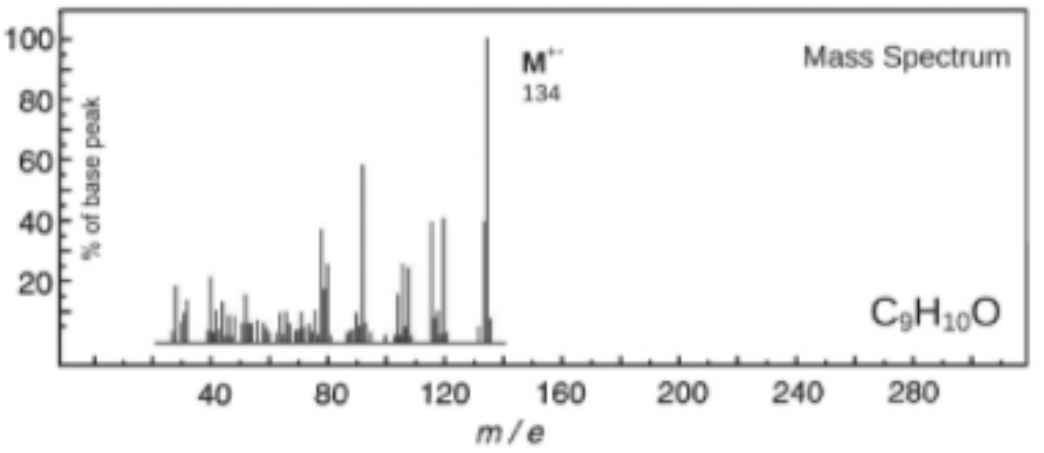

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion scale
0 20 40 60 Hz
expansions
9.7
9.6
7.5
7.4
6.7
6.6
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

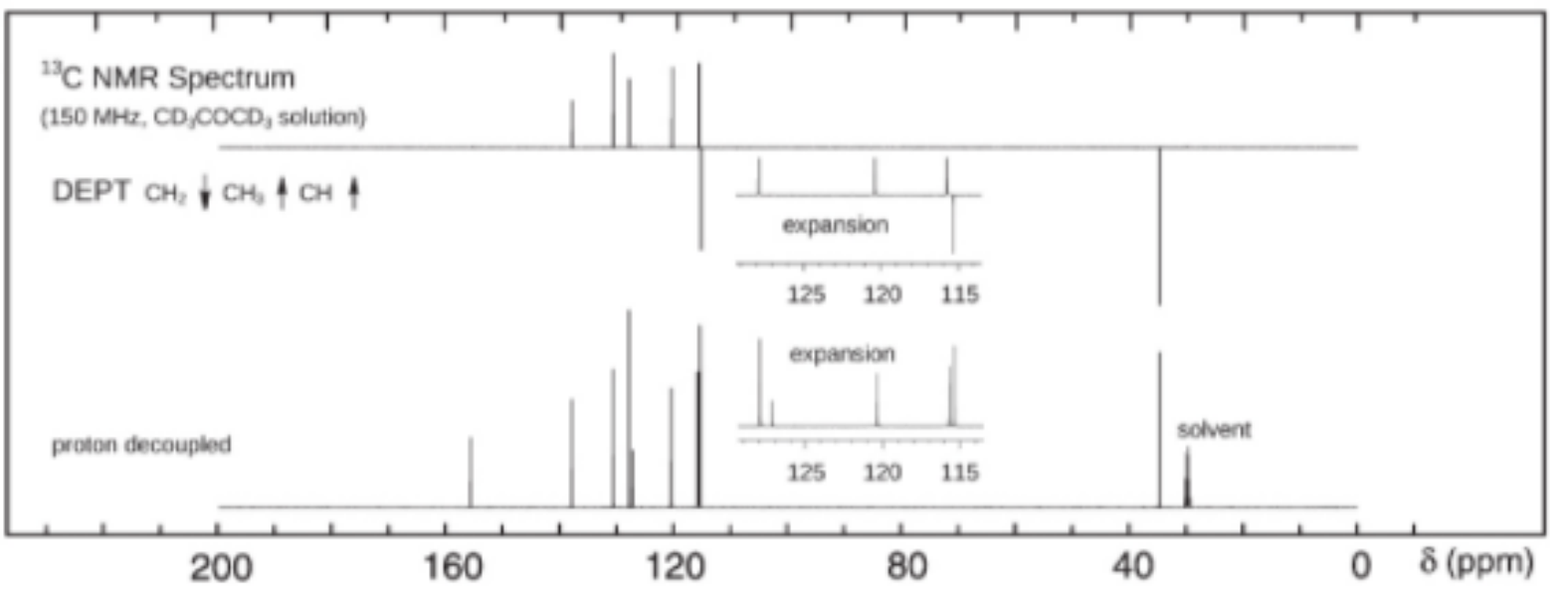

ppm
$^{1}H–^{13}C$ me-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
125
130
135
155
195
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
9.8 9.6
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
ppm

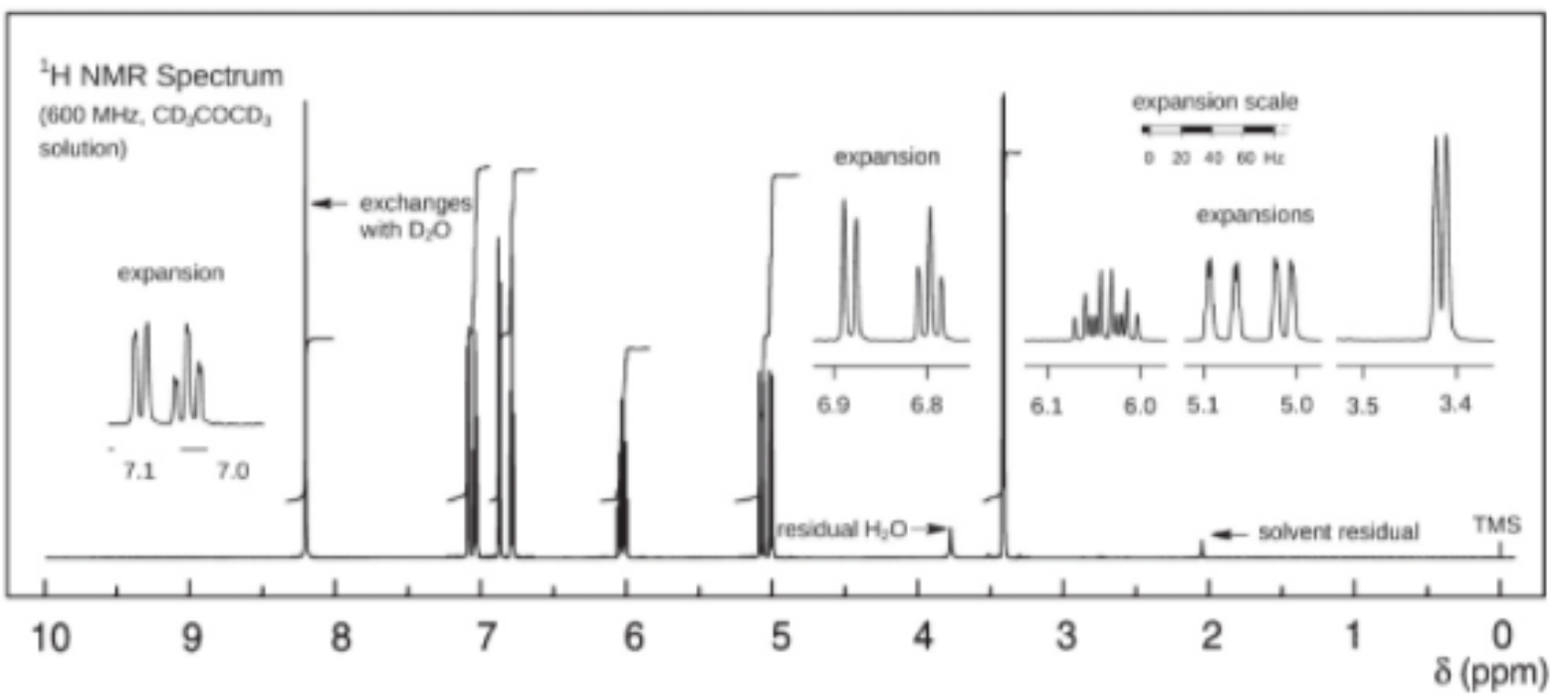

ppm
6.6
6.8
7.0
7.2
7.4
7.6
7.8
$^{1}H–^{1}H$ NOESY Spectrum
(600 MHz, $CDCl_3$ solution)
9.6
9.8
9.8 9.6
7.8 7.6 7.4 7.2 7.0 6.8 6.6
ppm

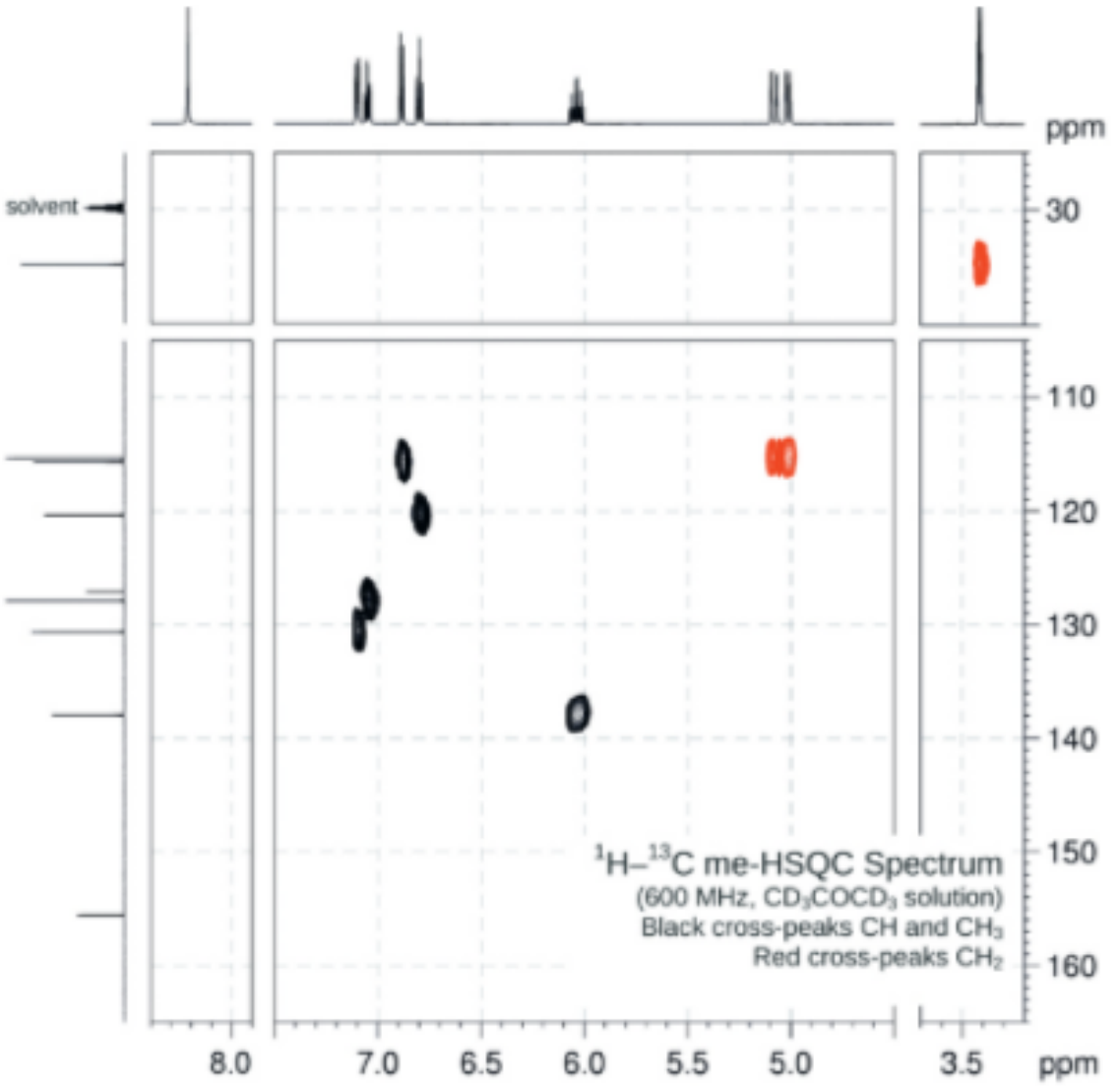
Problem 231

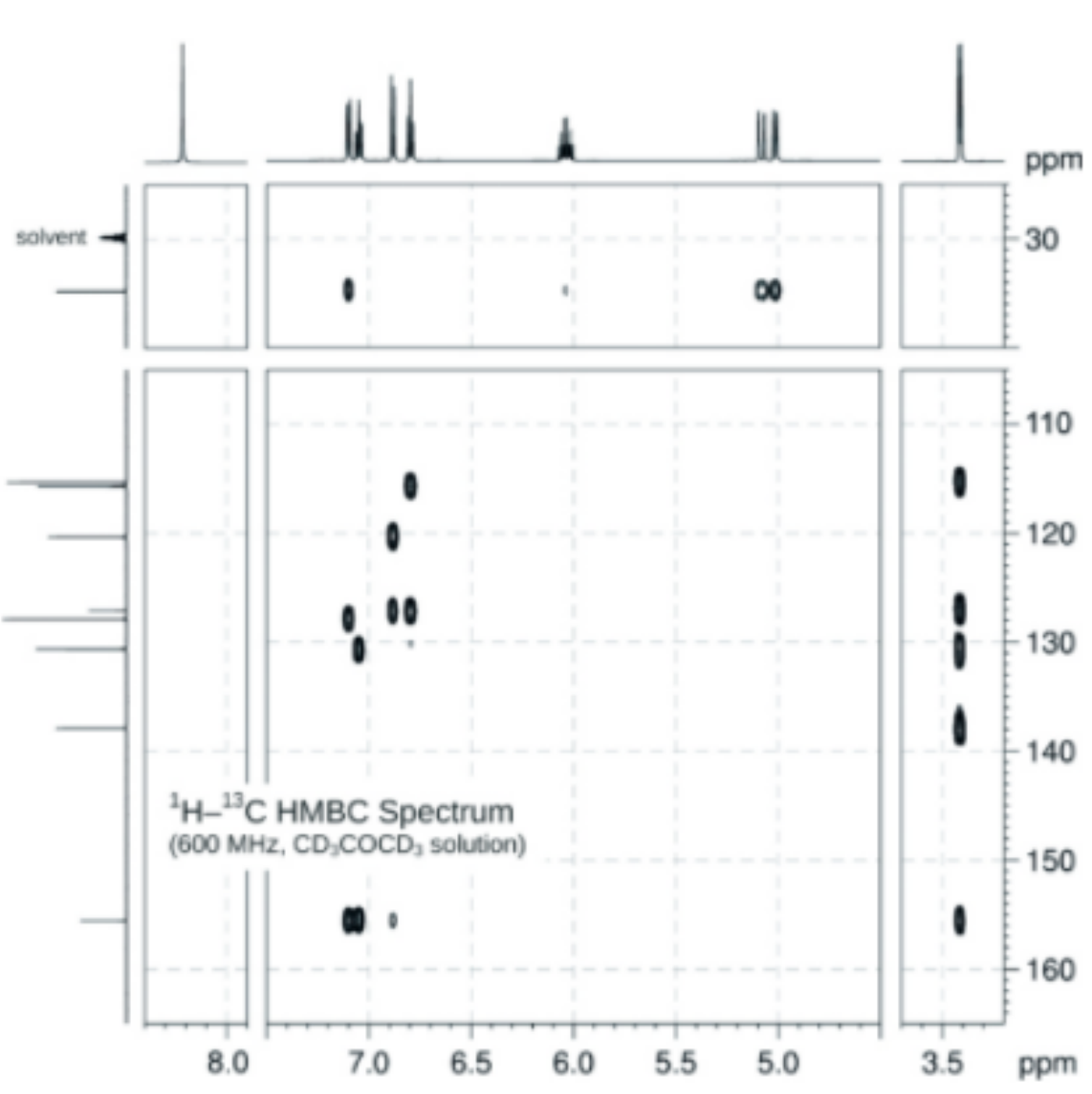

3444
1638
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)


100
80
60
40
20
% of base peak
M+·
134
Mass Spectrum
C9H10O
40
80
120
160
200
240
280
m/e

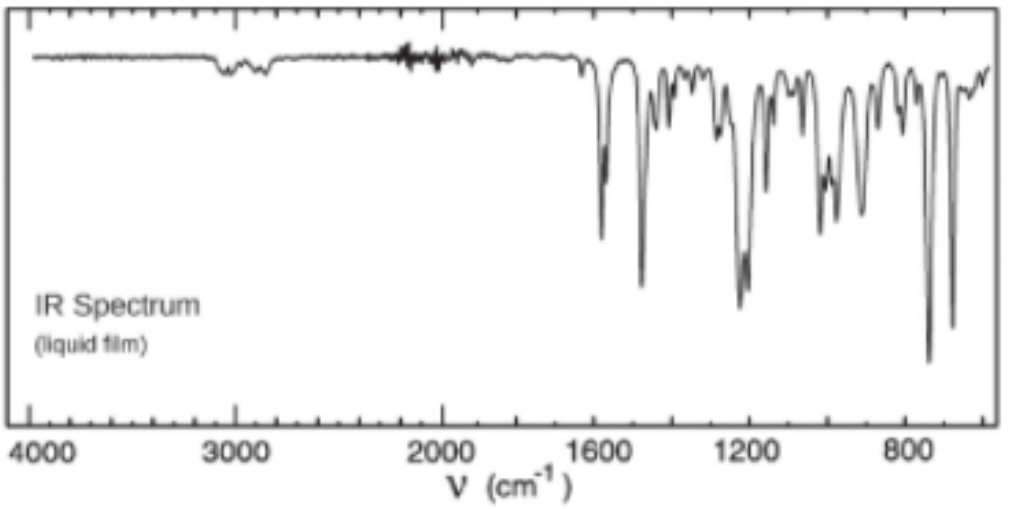

13C NMR Spectrum
(150 MHz, CD3COCD3 solution)
DEPT CH2 CH3 CH
expansion
125 120 115
expansion
125 120 115
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

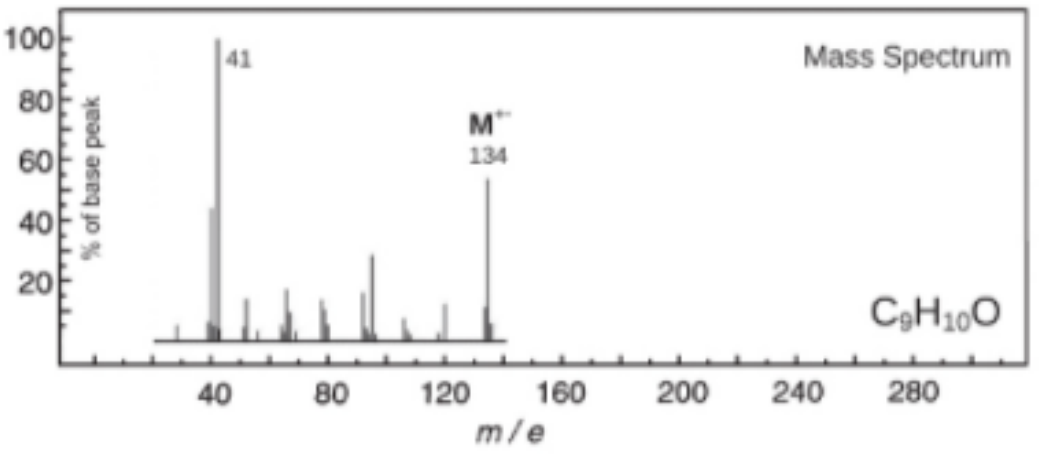

1H NMR Spectrum
(600 MHz, CD3COCD3 solution)
expansion
7.1
7.0
exchanges with D2O
expansion
6.9
6.8
expansion scale
0 20 40 60 Hz
expansions
6.1
6.0
5.1
5.0
3.5
3.4
residual H2O
solvent residual
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

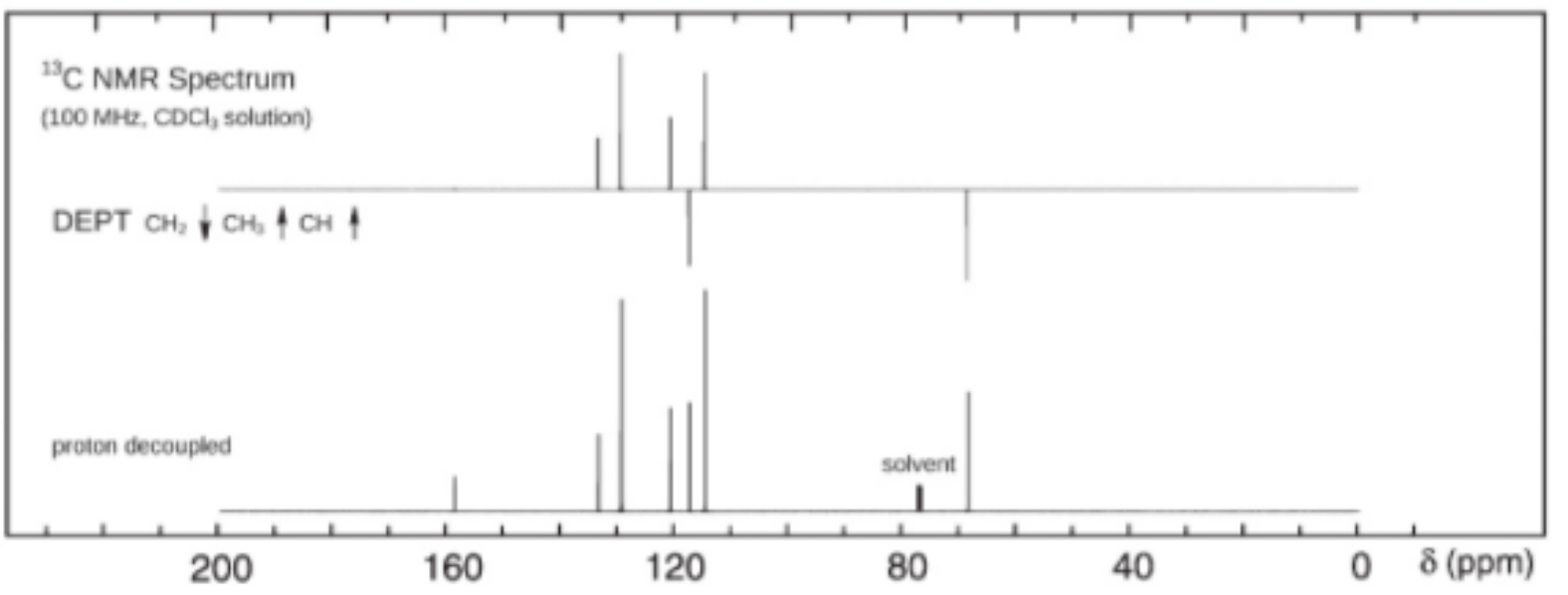

ppm
solvent
30
110
120
130
140
150
160
8.0
7.0
6.5
6.0
5.5
5.0
3.5
ppm
$^{1}H–^{13}C$ me-HSQC Spectrum
(600 MHz, CD_3COCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

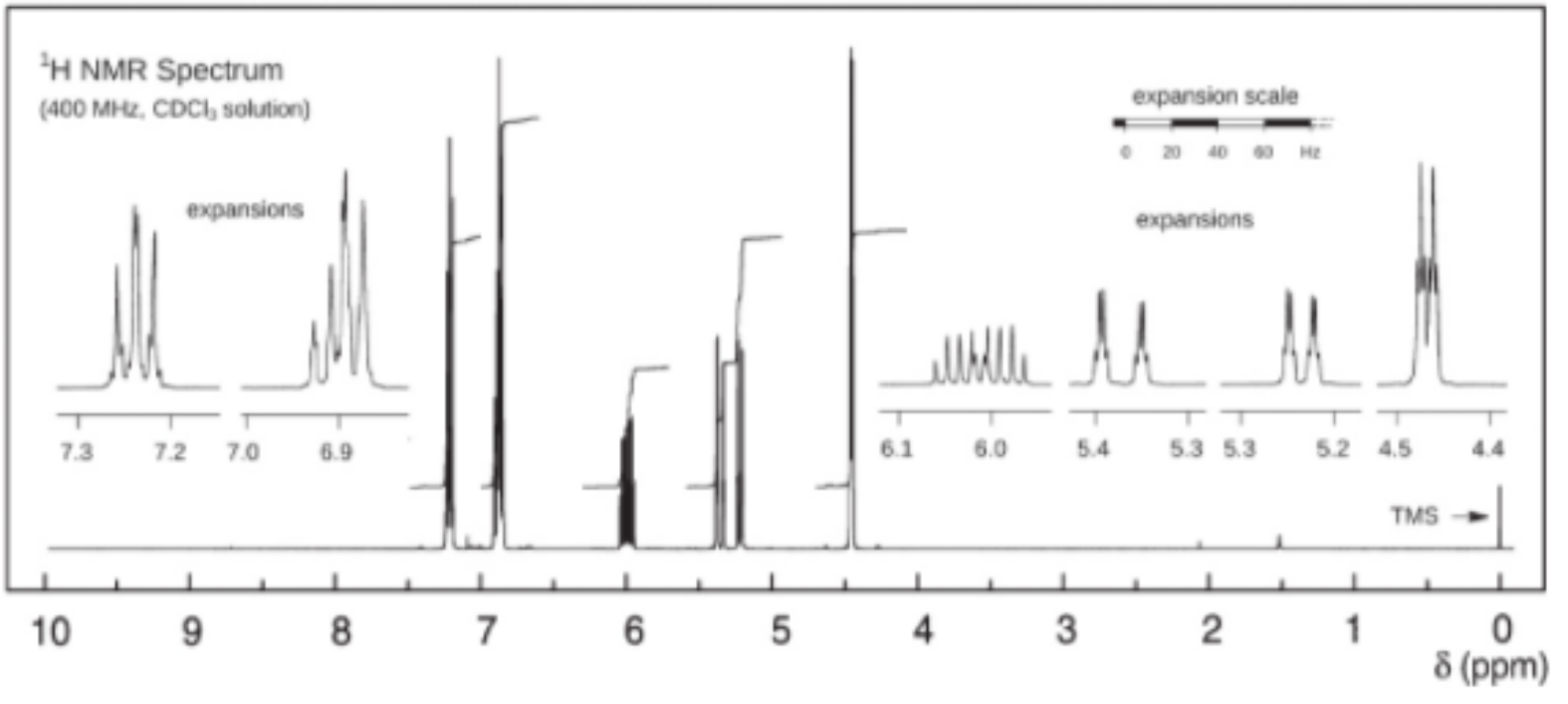

ppm
solvent
30
110
120
130
140
150
160
8.0
7.0
6.5
6.0
5.5
5.0
3.5
ppm
$^{1}H–^{13}C$ HMBC Spectrum
(600 MHz, CD_3COCD_3 solution)

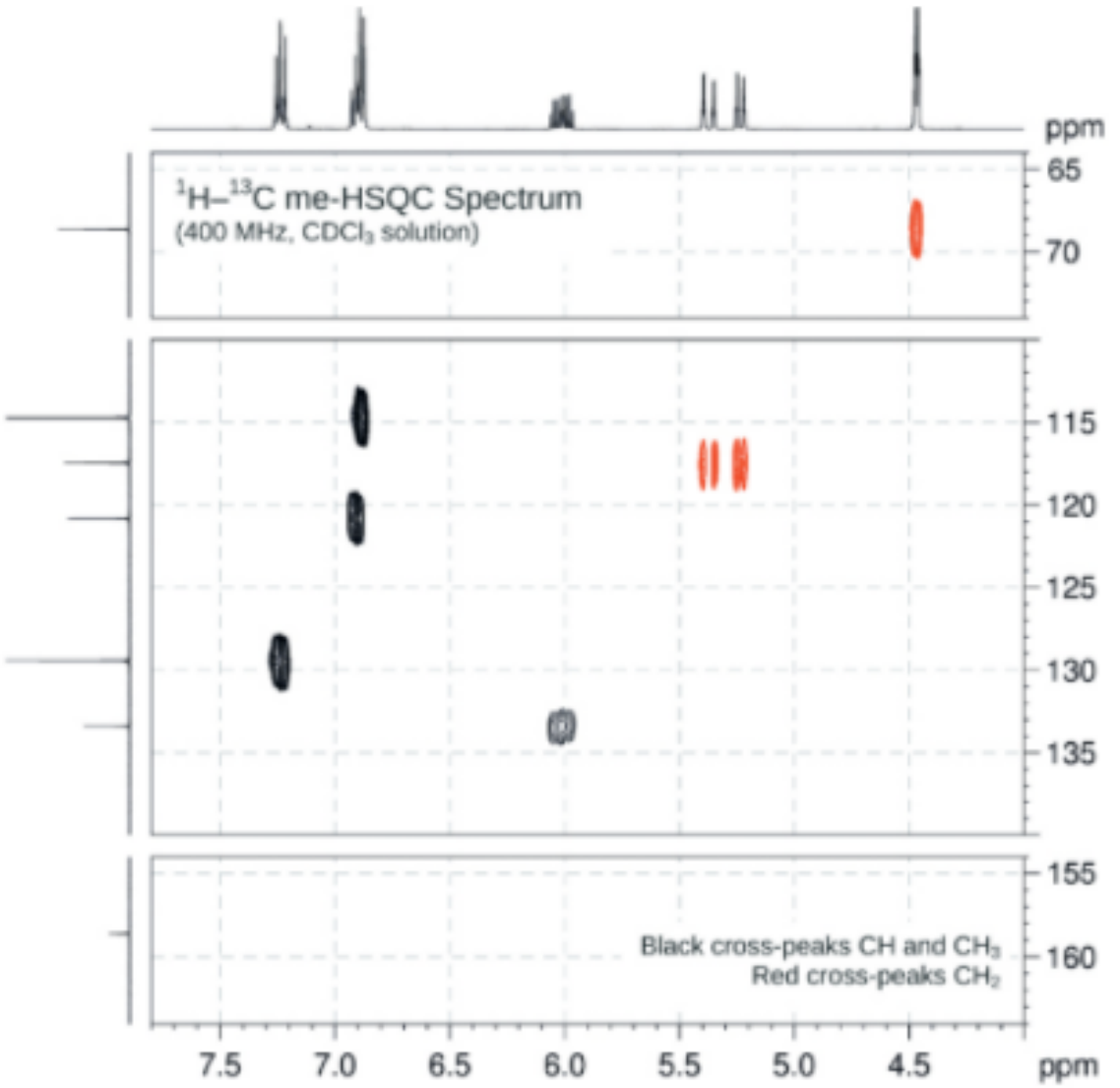
Problem 232

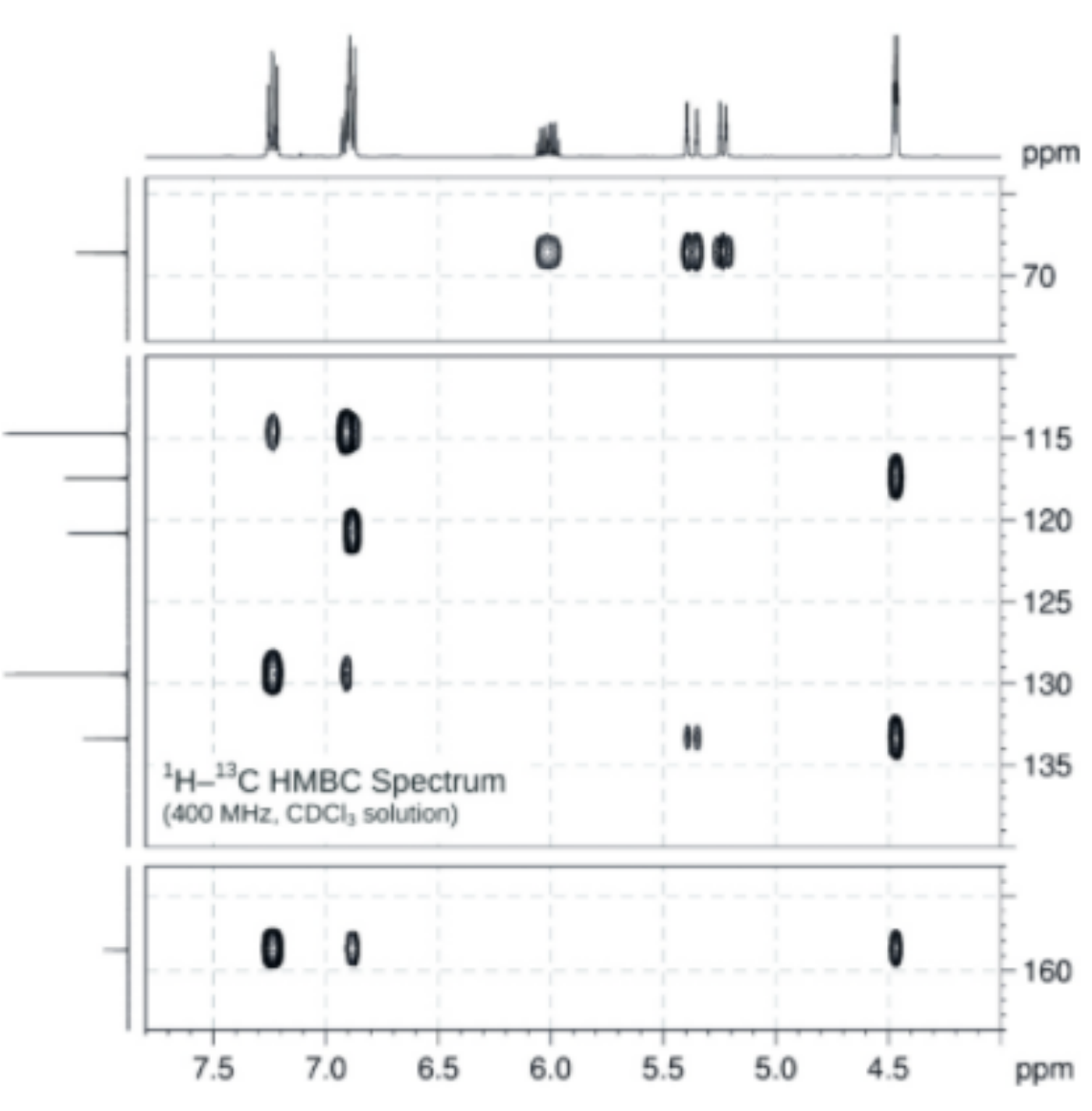

IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
100
80
60
40
20
41
M+·
134
C9H10O
40
80
120
160
200
240
280
m/e

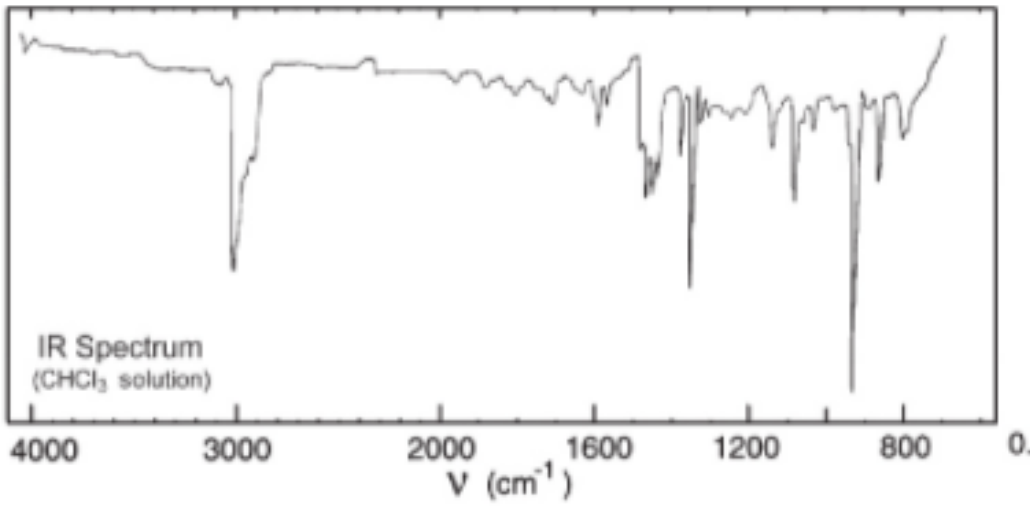

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

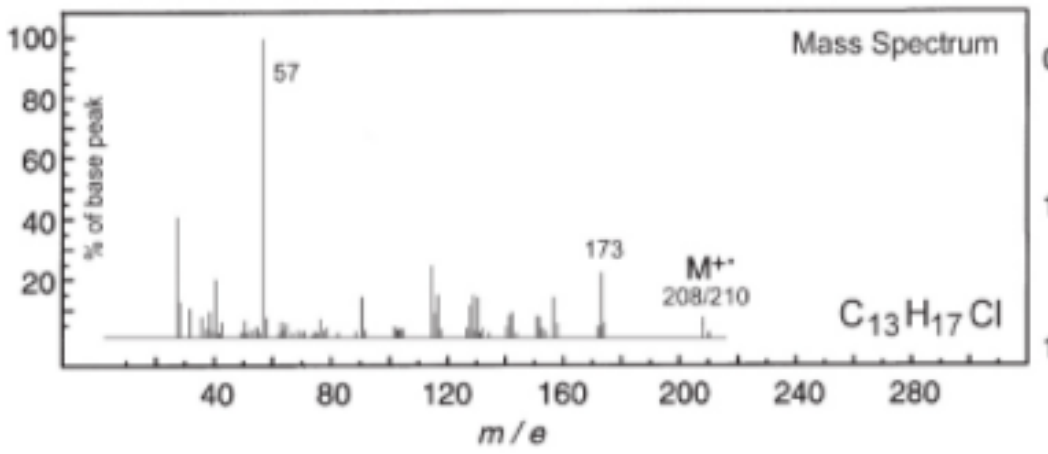

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansions
7.3
7.2
7.0
6.9
expansion scale
0
20
40
60
Hz
expansions
6.1
6.0
5.4
5.3
5.3
5.2
4.5
4.4
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

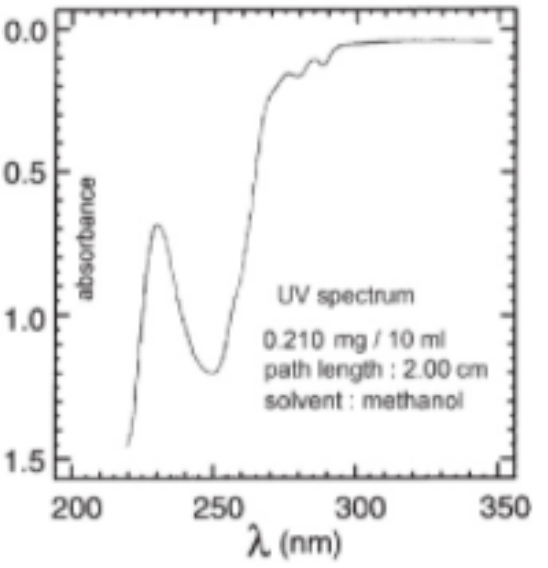

ppm
^{1}H–^{13}C me-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
65
70
115
120
125
130
135
155
160
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm

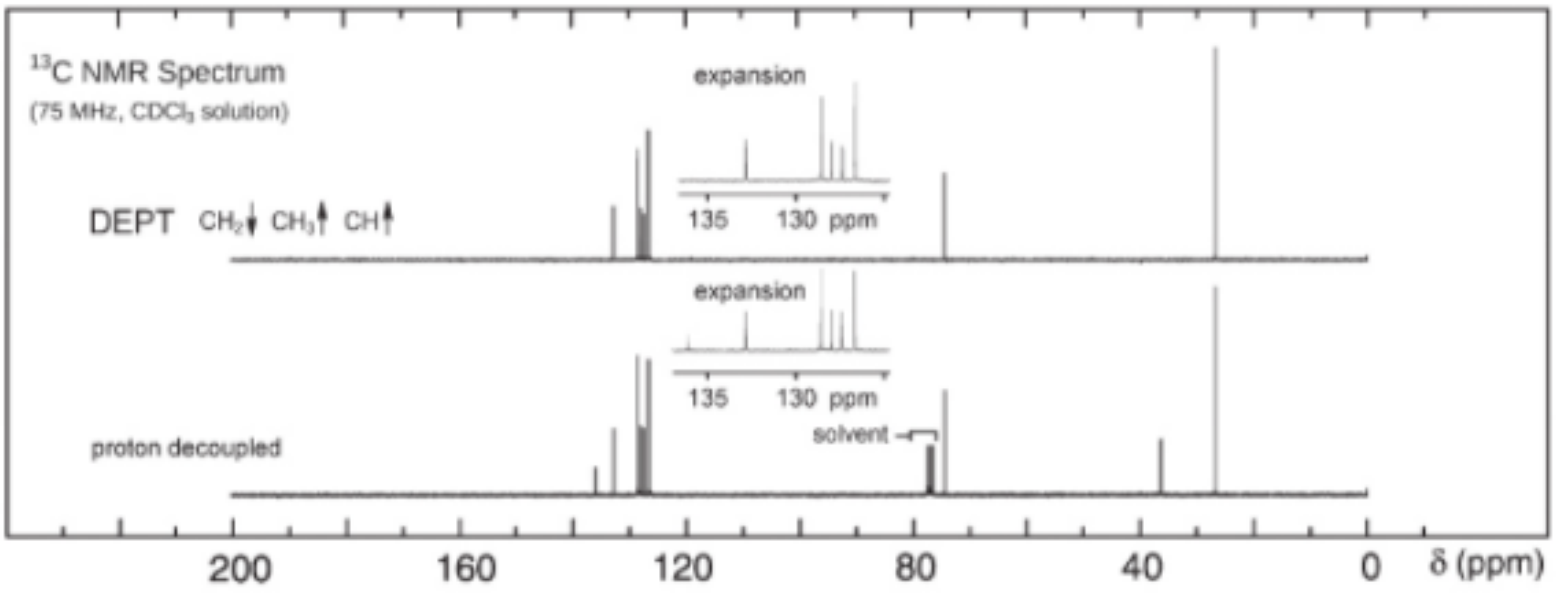

ppm
70
115
120
125
130
135
160
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm

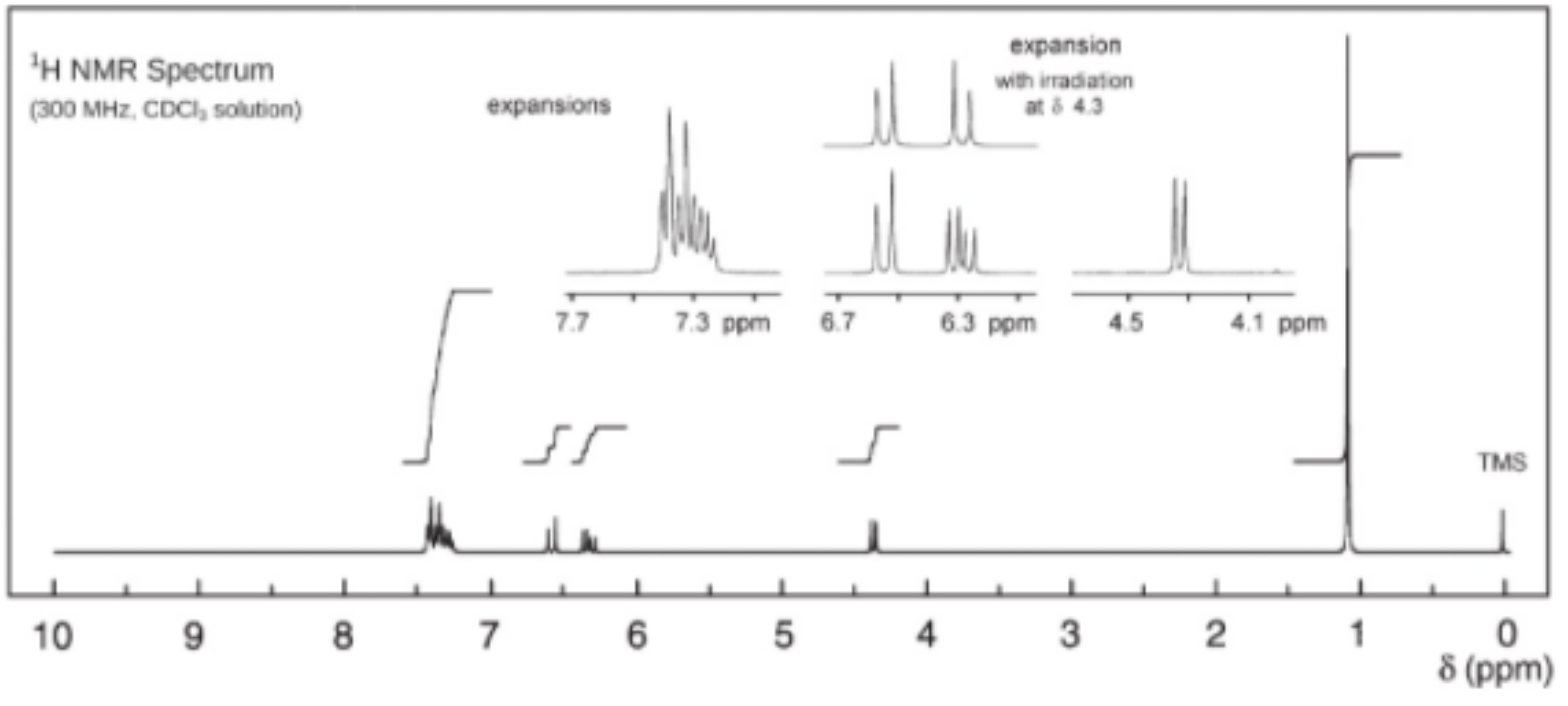
Problem 233


IR Spectrum
(CHCl3 solution)
4000
3000
2000
1600
1200
800
ν (cm-1)

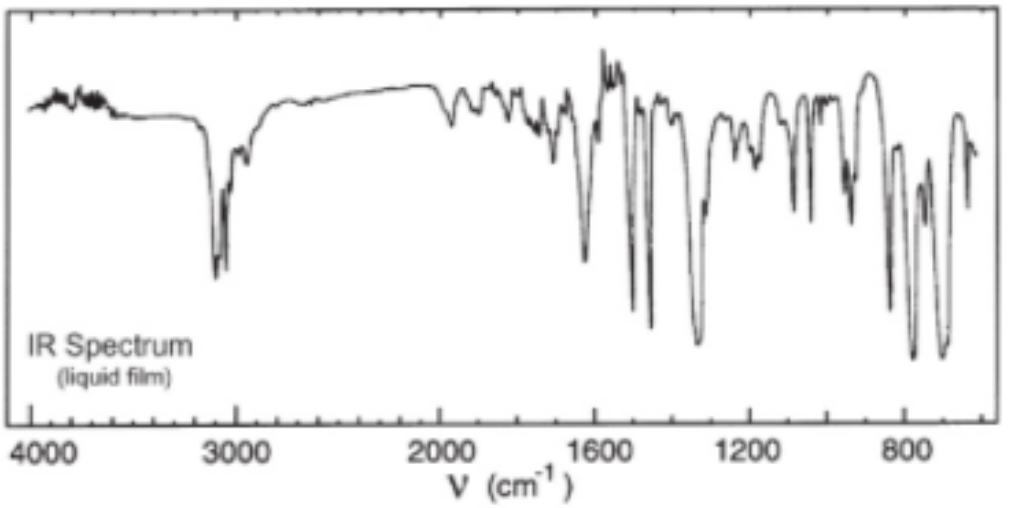

Mass Spectrum
% of base peak
100
80
60
40
20
57
173
M+·
208/210
C13H17Cl
40
80
120
160
200
240
280
m/e

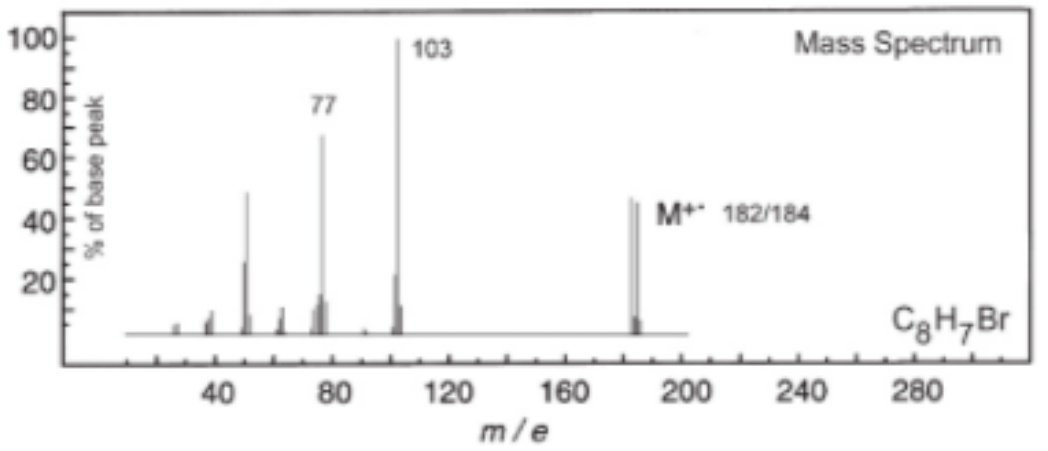

absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.210 mg / 10 ml
path length : 2.00 cm
solvent : methanol
200
250
300
350
λ (nm)


13C NMR Spectrum
(75 MHz, CDCl3 solution)
expansion
135
130 ppm
DEPT CH2 CH3 CH
expansion
135
130 ppm
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(300 MHz, CDCl3 solution)
expansions
expansion
with irradiation
at δ 4.3
7.7
7.3 ppm
6.7
6.3 ppm
4.5
4.1 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

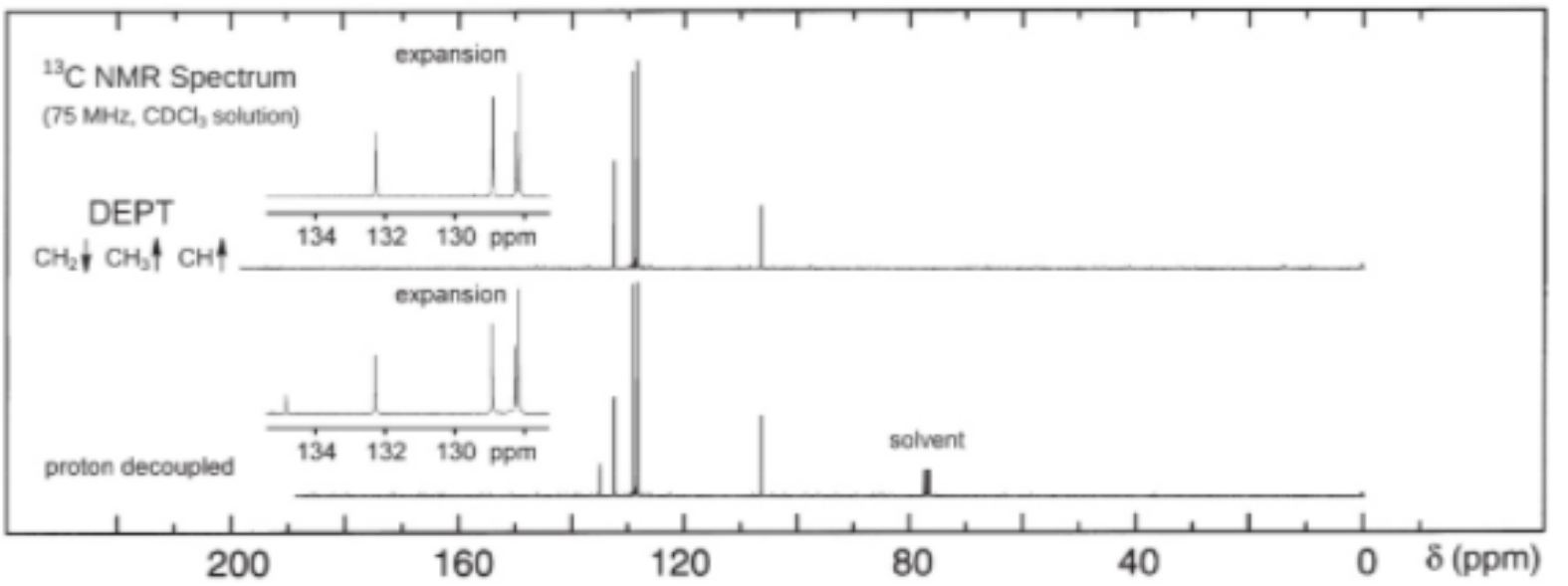
Problem 234

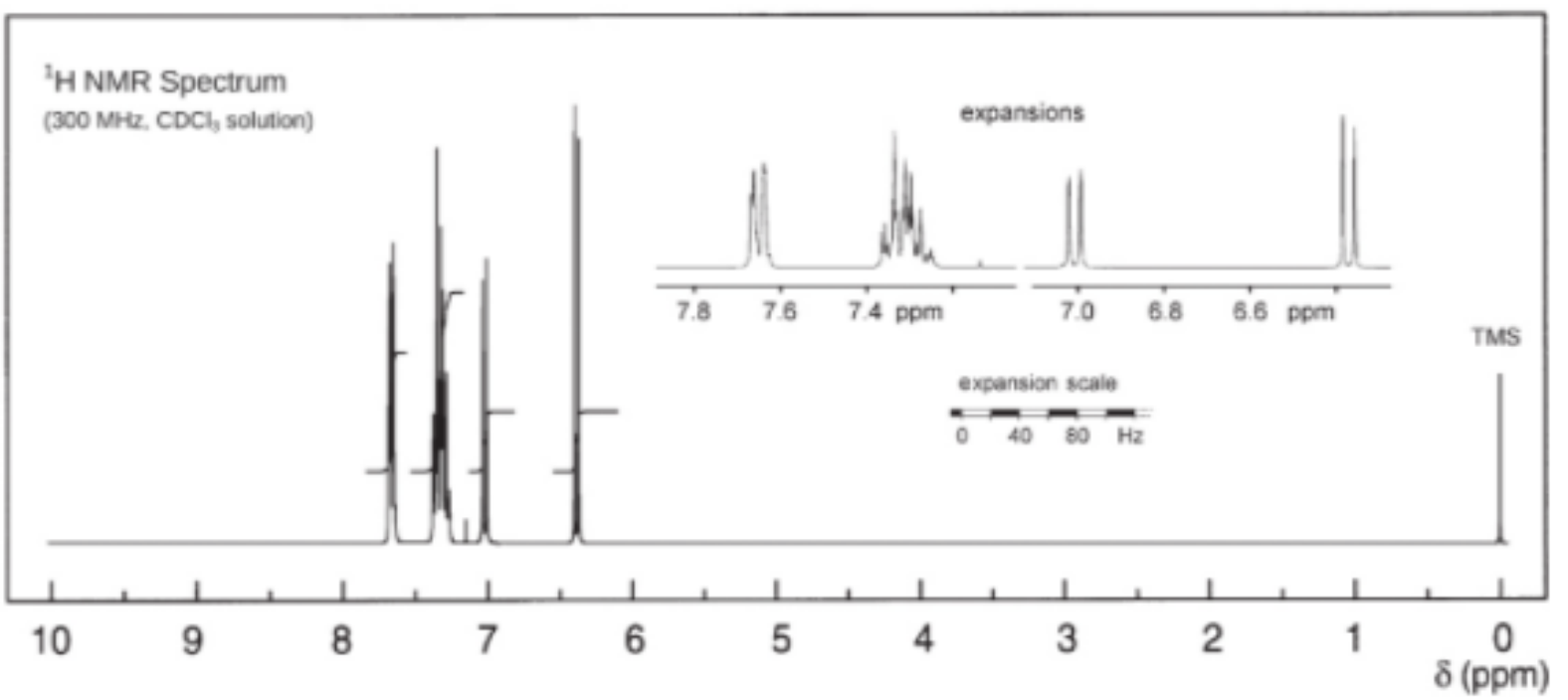




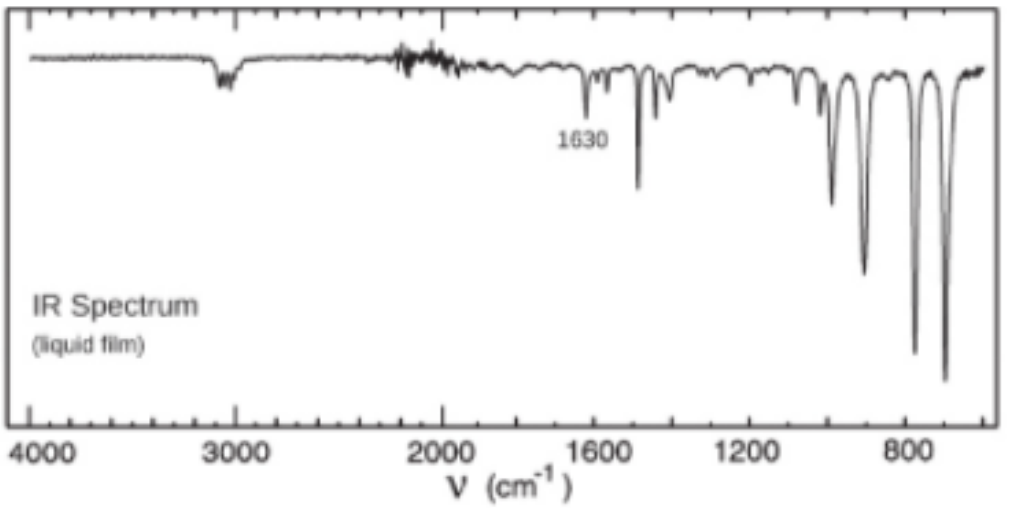
UV Spectrum

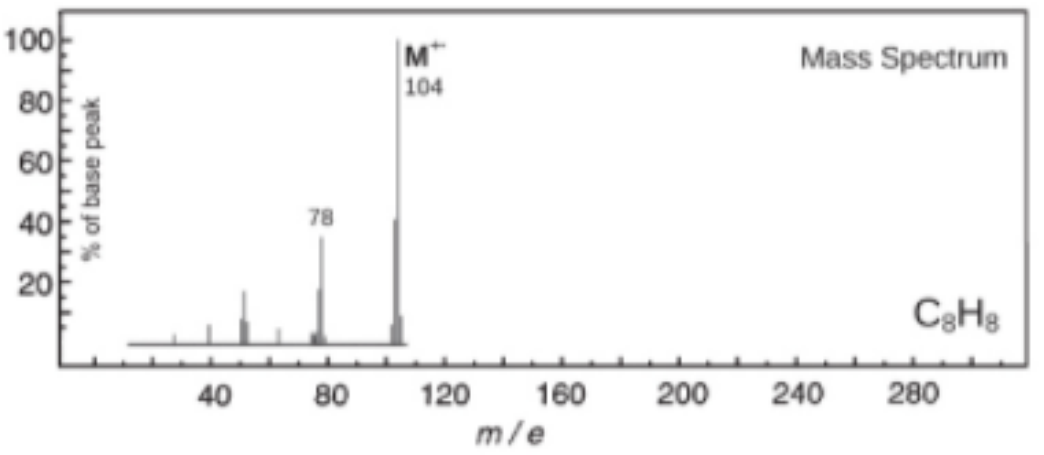
$\lambda_{max} \approx 250$ nm $(\log_{10}\varepsilon > 4.0)$

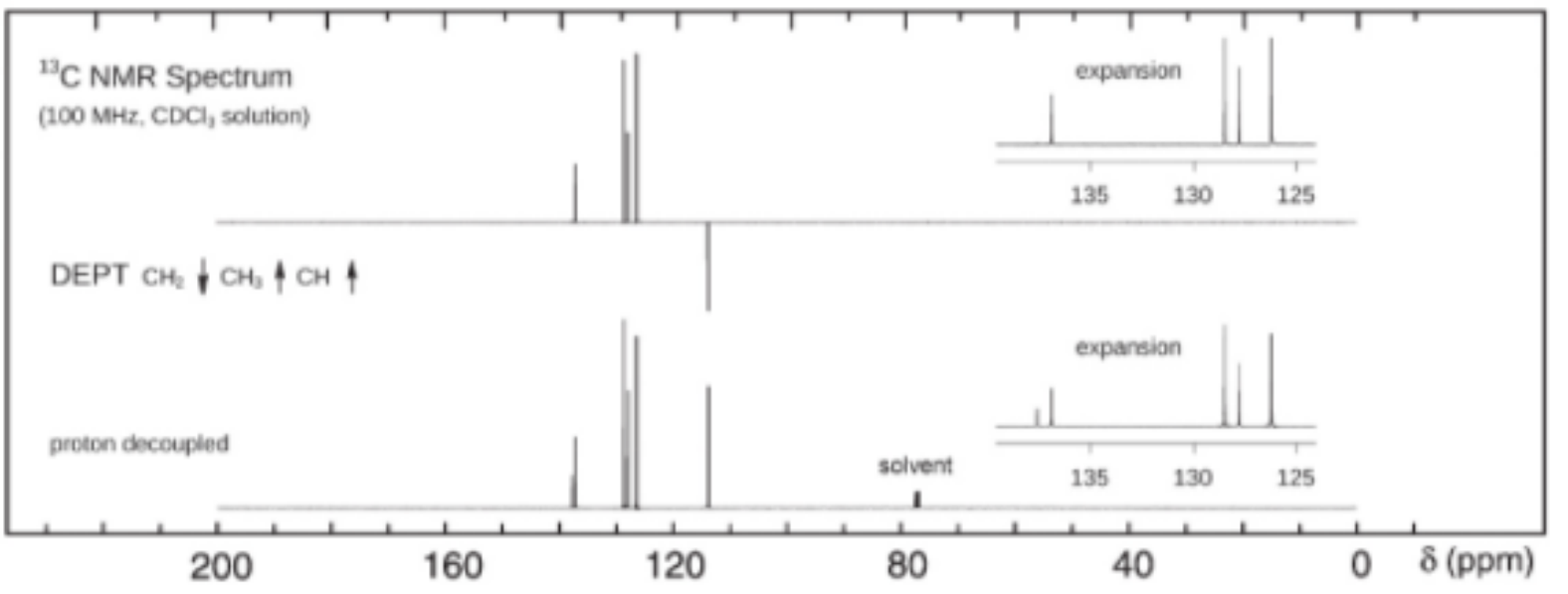


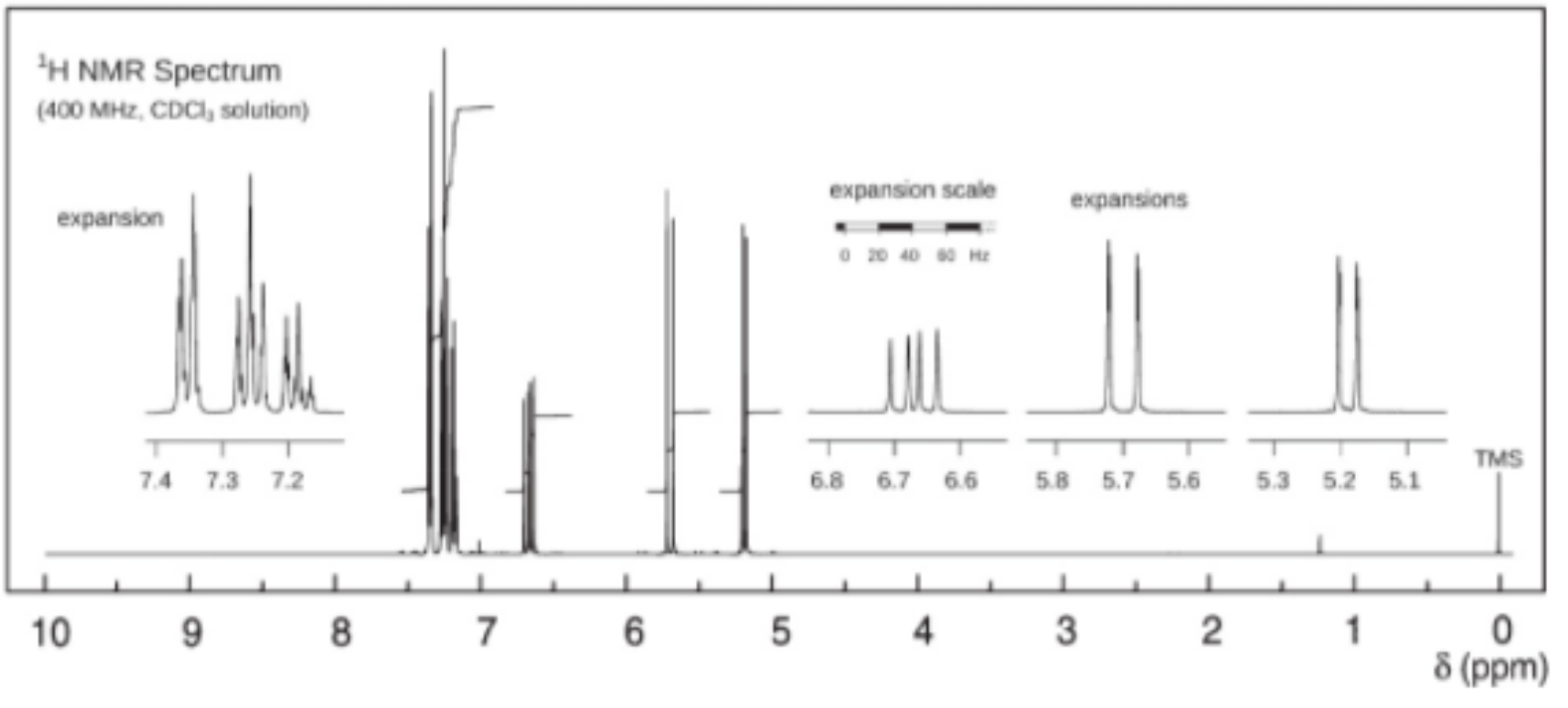


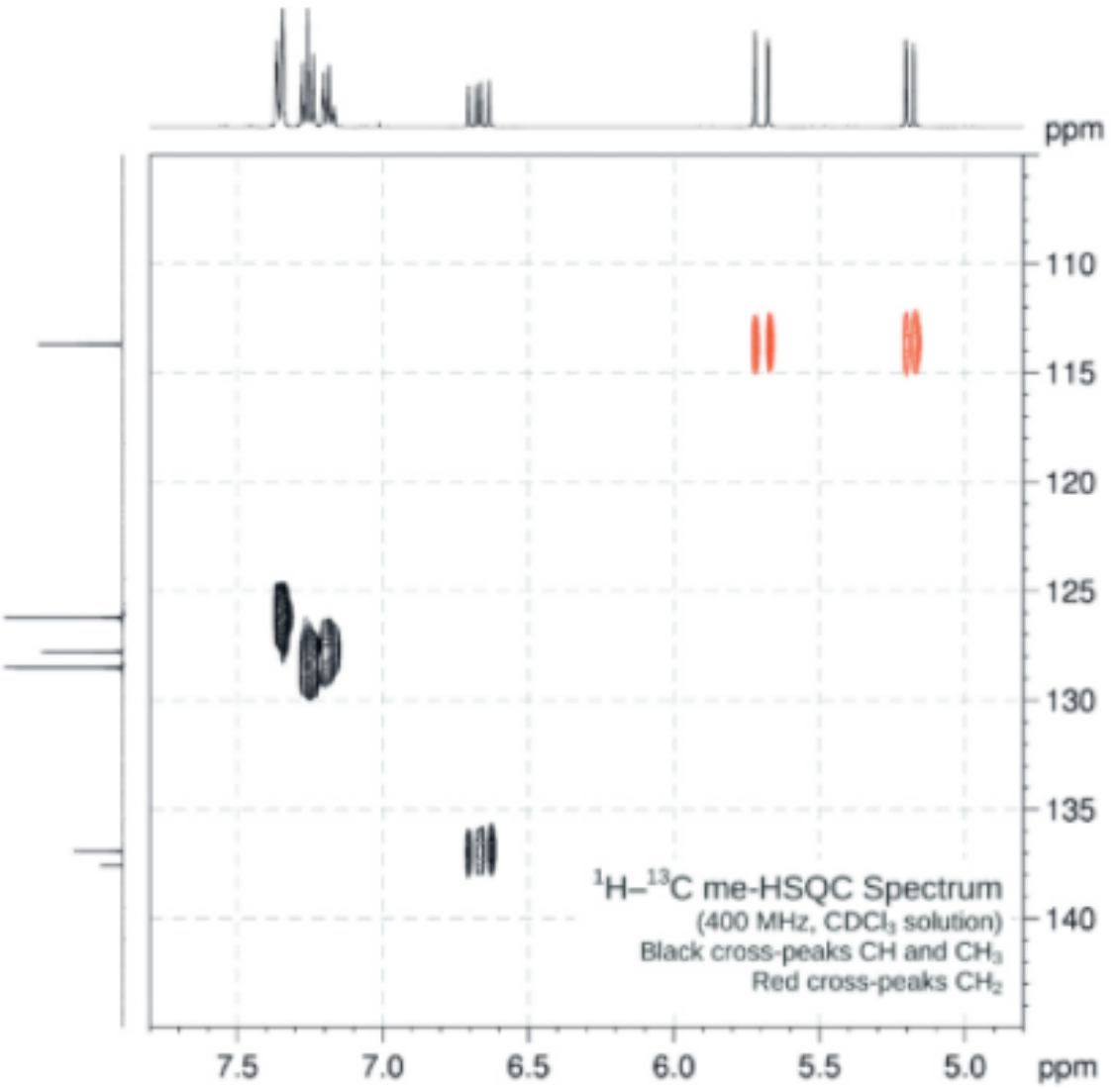
Problem 235

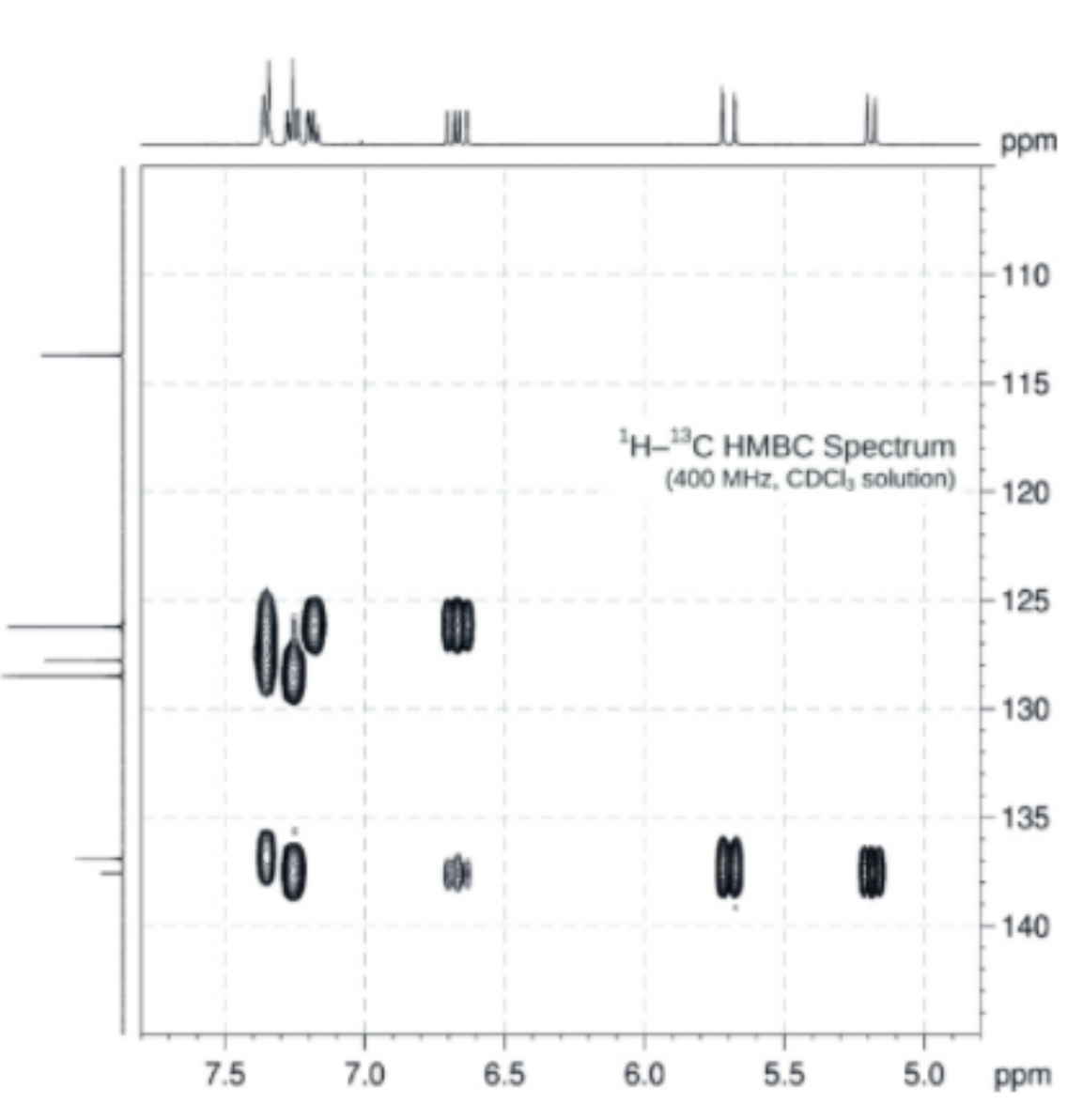

1630
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)


100
80
60
40
20
% of base peak
M+·
104
78
Mass Spectrum
C8H8
40
80
120
160
200
240
280
m/e

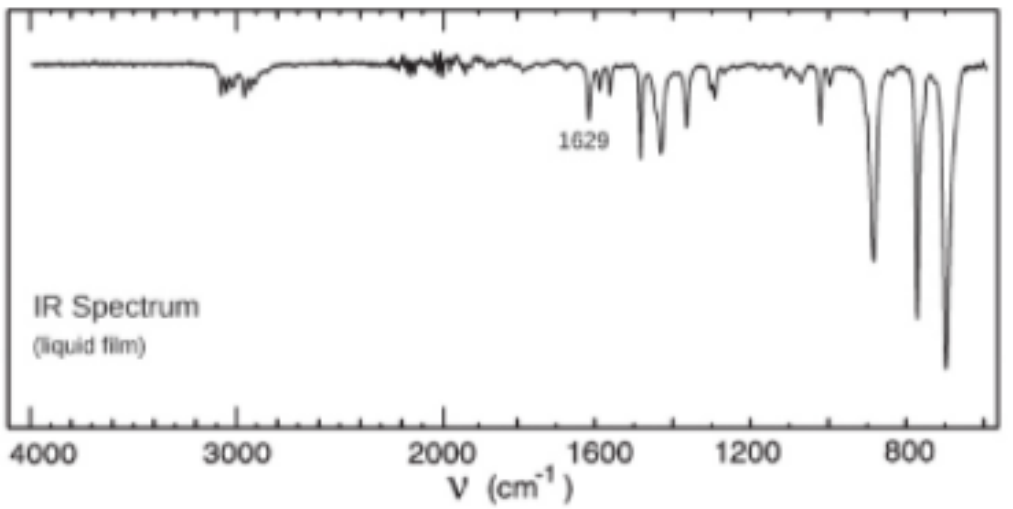

13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
135
130
125
DEPT CH2 CH3 CH
expansion
proton decoupled
solvent
135
130
125
200
160
120
80
40
0
δ (ppm)

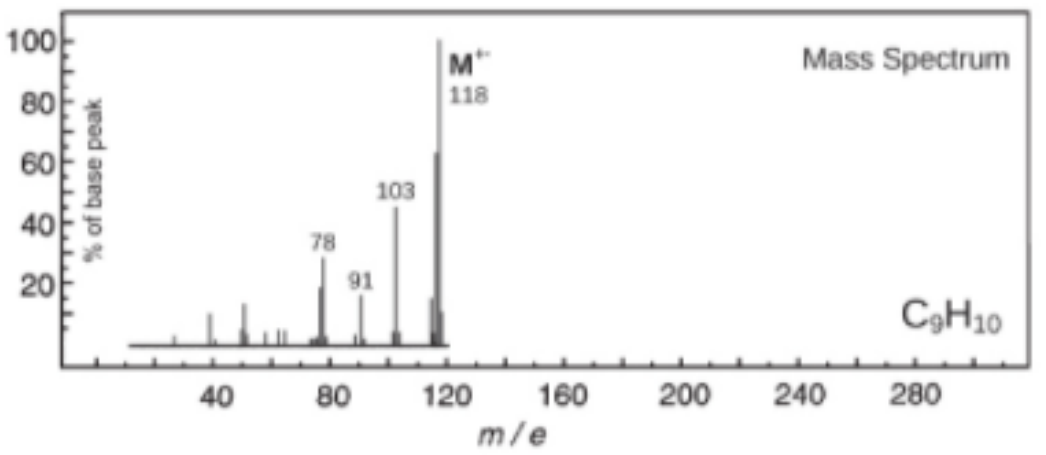

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion
7.4
7.3
7.2
expansion scale
0 20 40 60 Hz
6.8
6.7
6.6
expansions
5.8
5.7
5.6
5.3
5.2
5.1
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

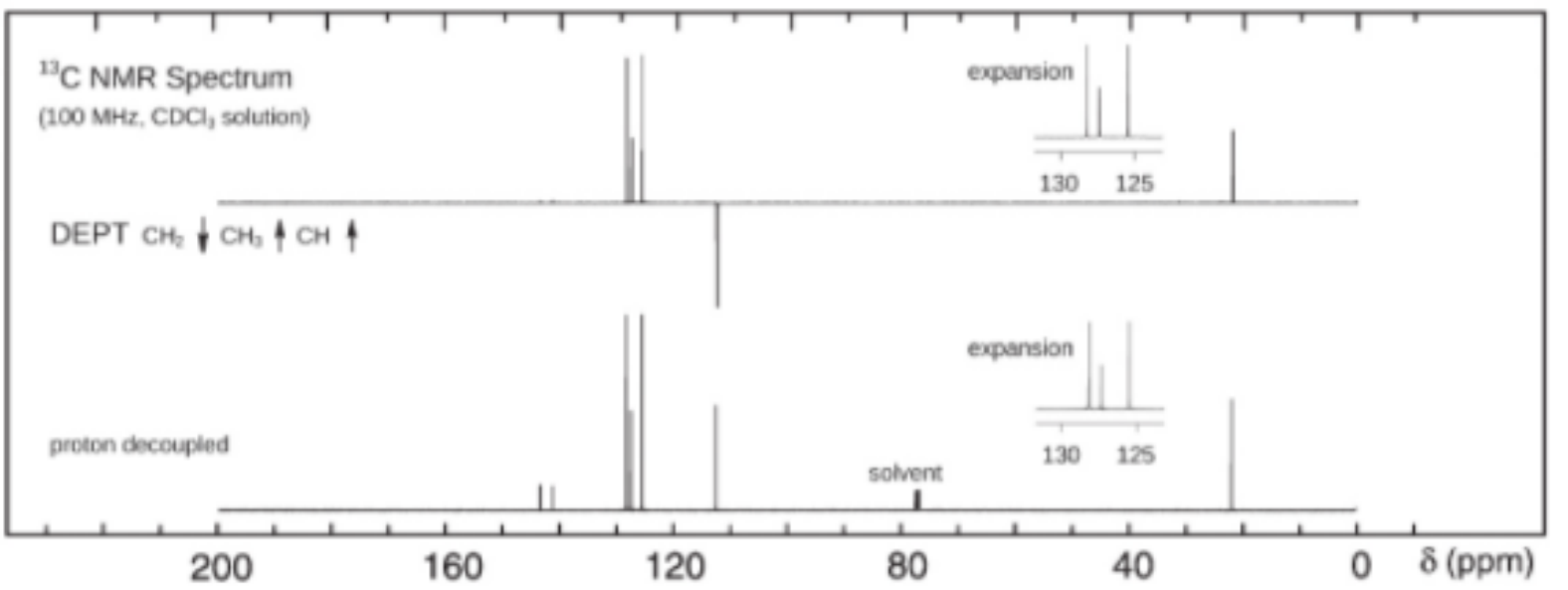

ppm
110
115
120
125
130
135
140
7.5
7.0
6.5
6.0
5.5
5.0
ppm
$^{1}H–^{13}C$ me-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

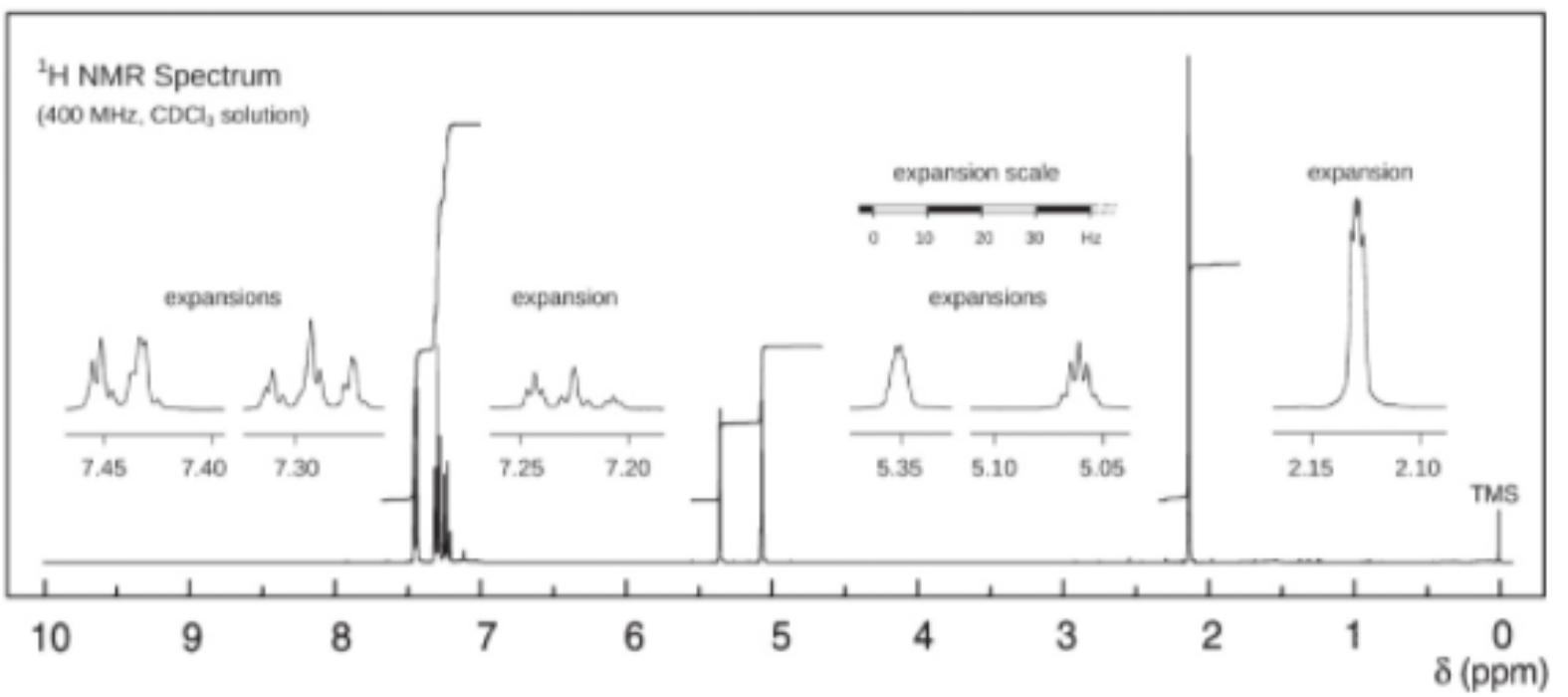

ppm
110
115
120
125
130
135
140
7.5
7.0
6.5
6.0
5.5
5.0
ppm
$^{1}H–^{13}C$ HMBC Spectrum
(400 MHz, $CDCl_3$ solution)

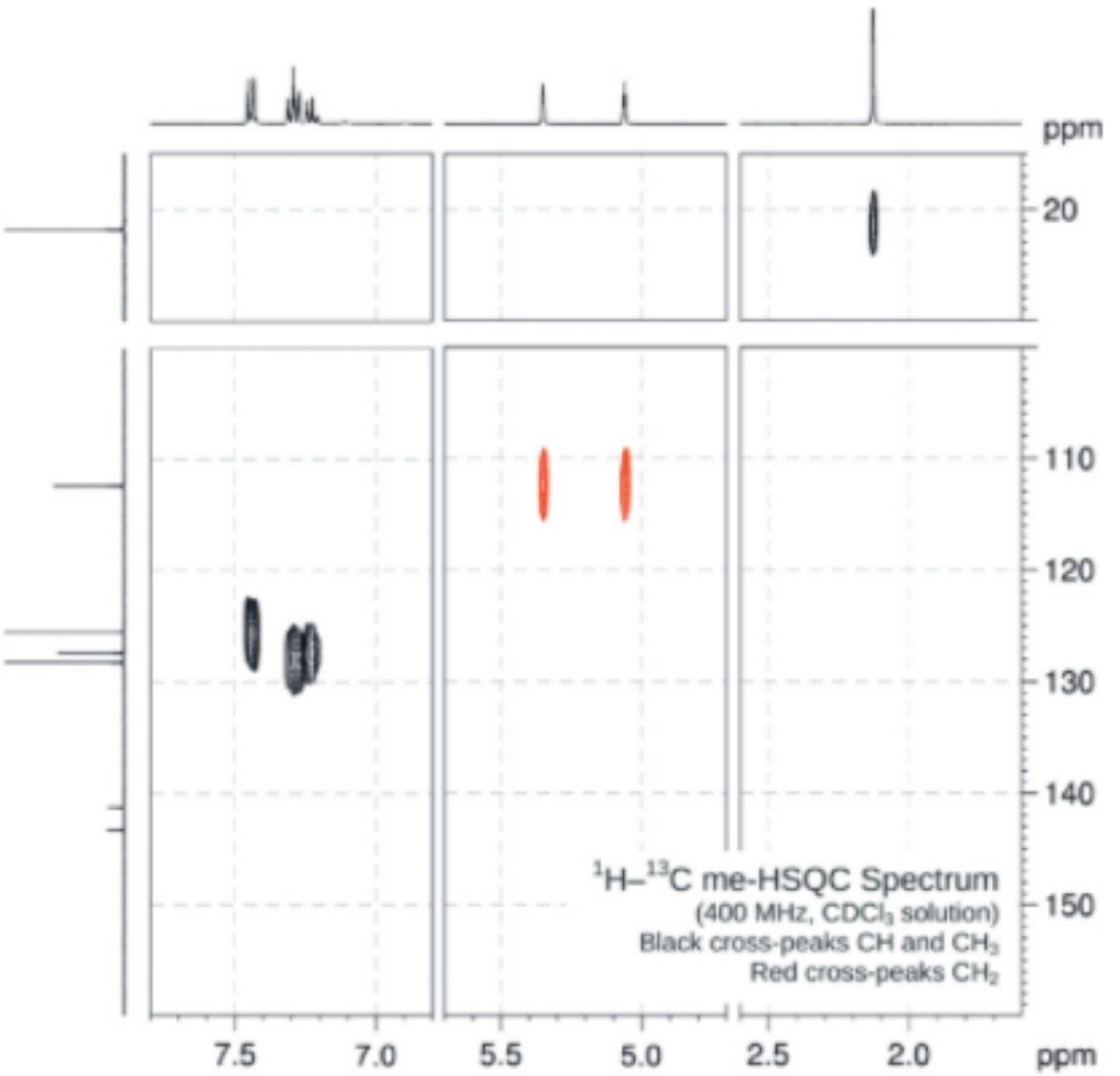
Problem 236


1629
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)


100
80
60
40
20
% of base peak
M+·
118
103
78
91
Mass Spectrum
C9H10
40
80
120
160
200
240
280
m/e

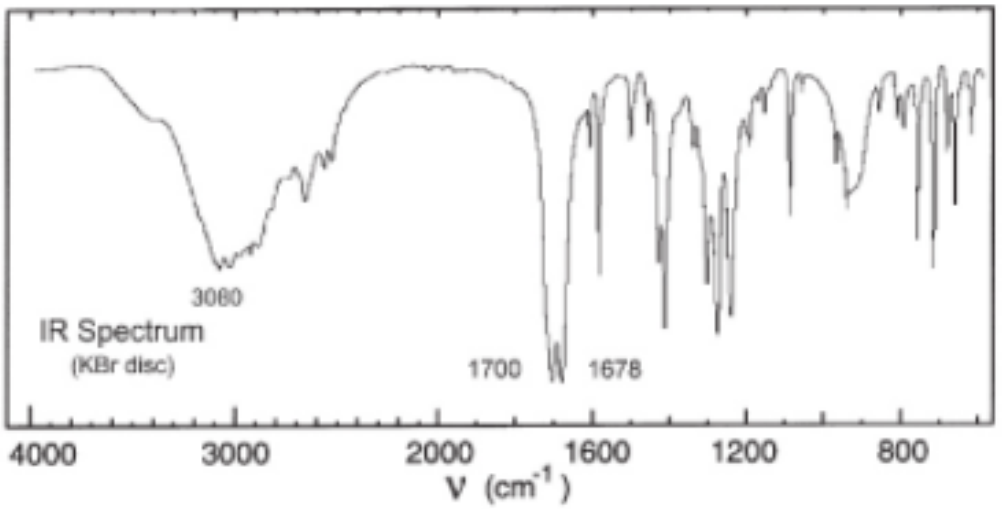

13C NMR Spectrum
(100 MHz, CDCl3 solution)
expansion
130
125
DEPT CH2 CH3 CH
expansion
130
125
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

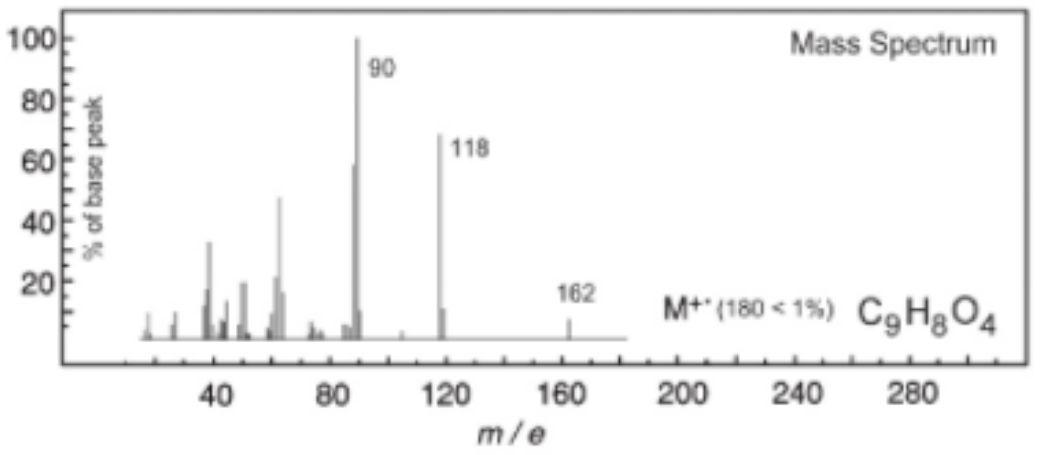

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion scale
0
10
20
30
Hz
expansion
expansions
expansion
expansions
7.45
7.40
7.30
7.25
7.20
5.35
5.10
5.05
2.15
2.10
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
20
110
120
130
140
150
$^{1}H–^{13}C$ me-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.5
7.0
5.5
5.0
2.5
2.0
ppm

ppm
$^{1}H–^{1}H$ NOESY Spectrum
(400 MHz, $CDCl_3$ solution)
2.0
2.5
5.0
5.5
7.0
7.5
solvent
7.5
7.0
5.5
5.0
2.5
2.0
ppm

Problem 237



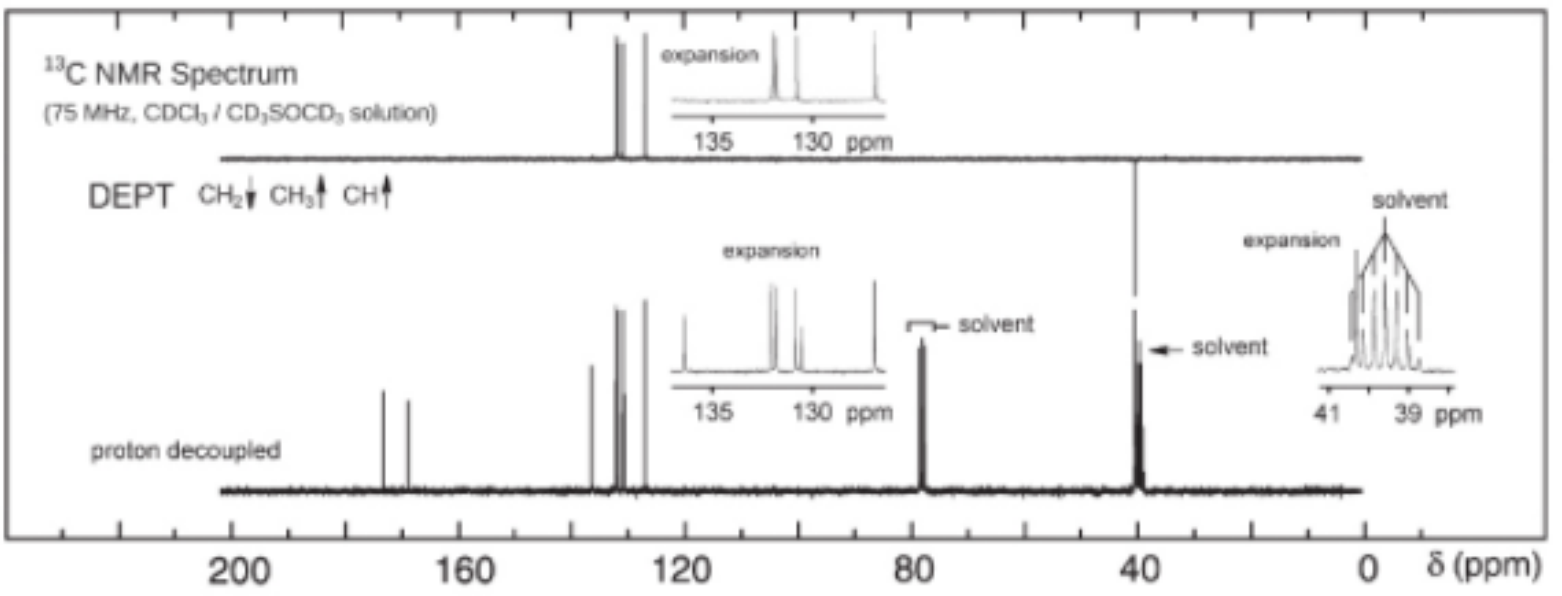


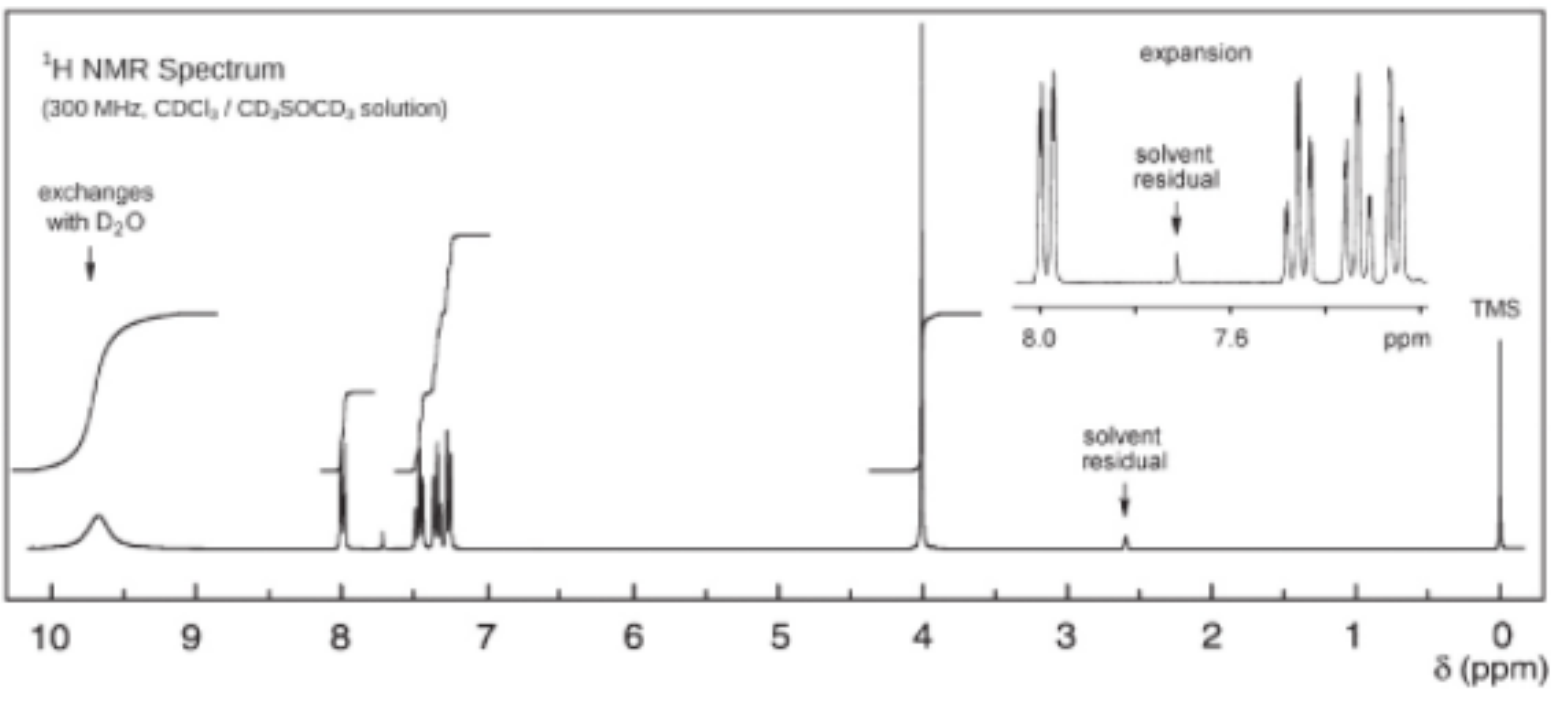
UV Spectrum

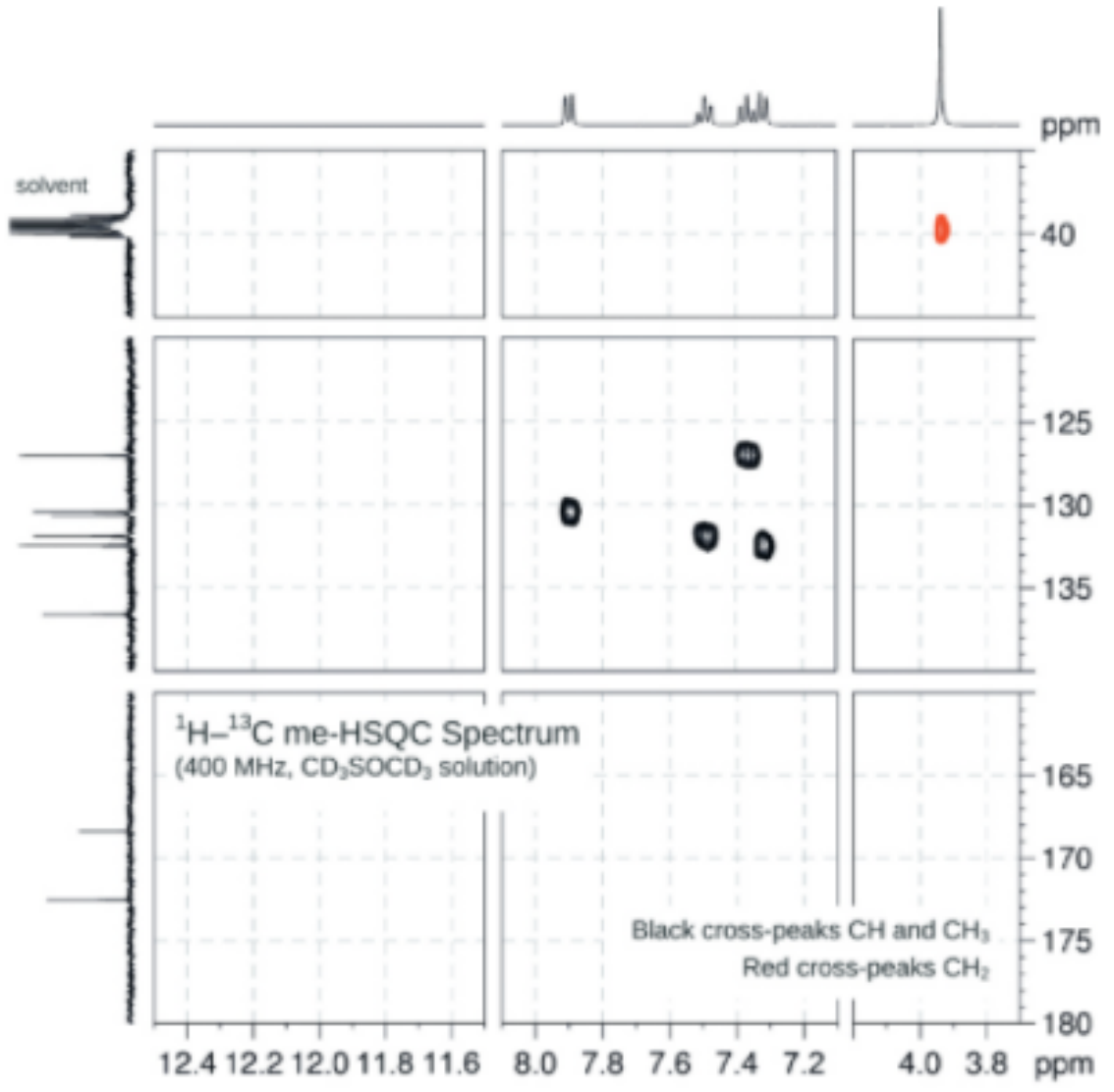
λ_{max} 276 nm ($\log_{10}\varepsilon$ 3.1)

λ_{max} 228 nm ($\log_{10}\varepsilon$ 3.9)

solvent : methanol

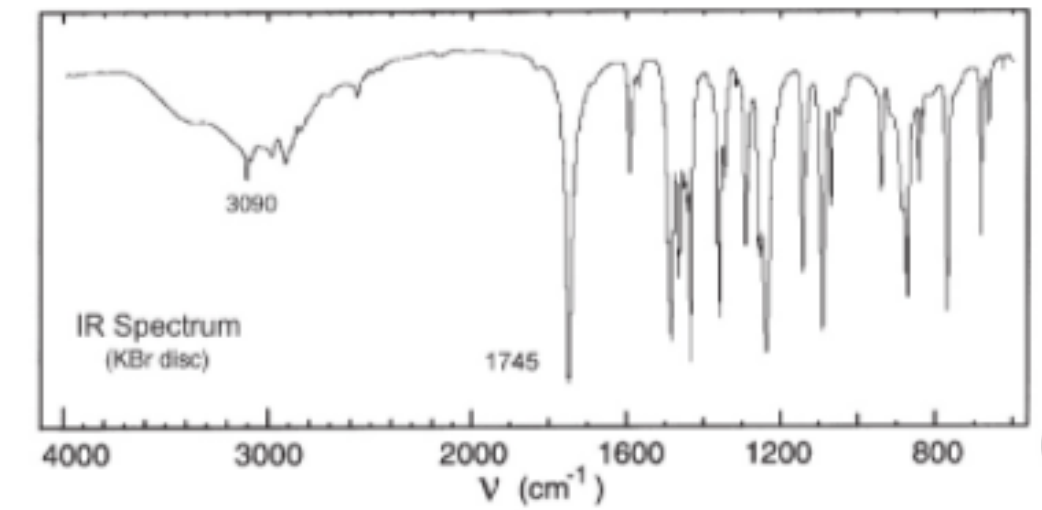


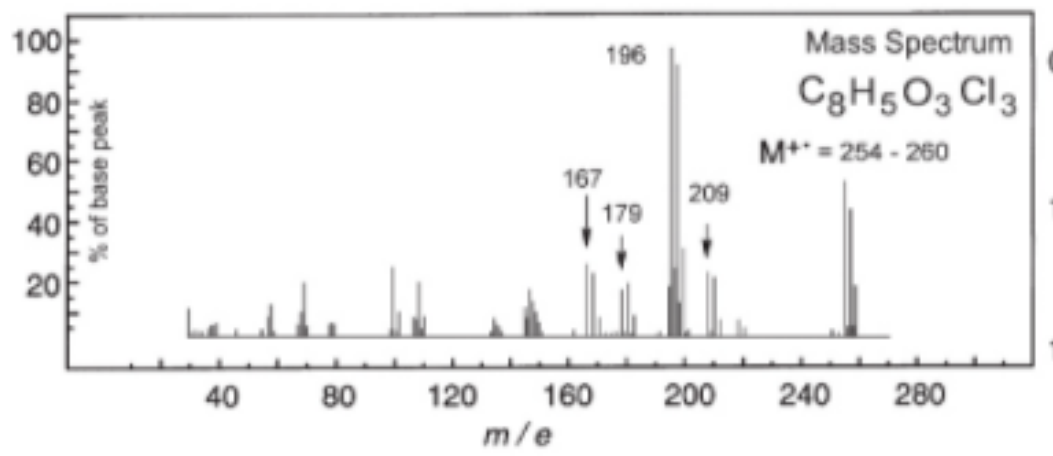


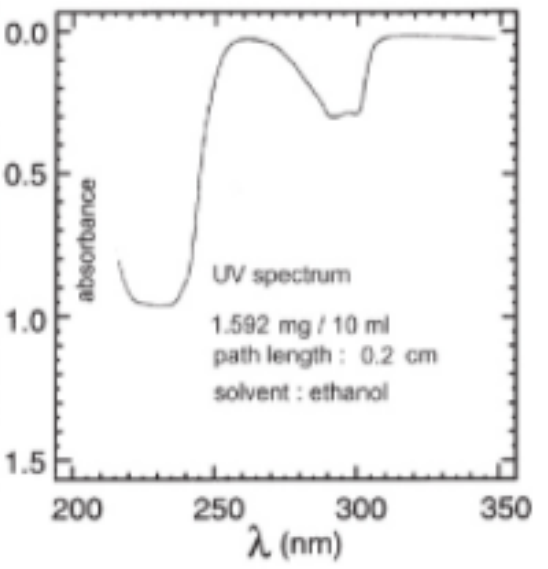

ppm
solvent
40
125
130
135
165
170
175
180
^{1}H–^{13}C me-HSQC Spectrum
(400 MHz, CD_3SOCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
12.4 12.2 12.0 11.8 11.6
8.0 7.8 7.6 7.4 7.2
4.0 3.8
ppm

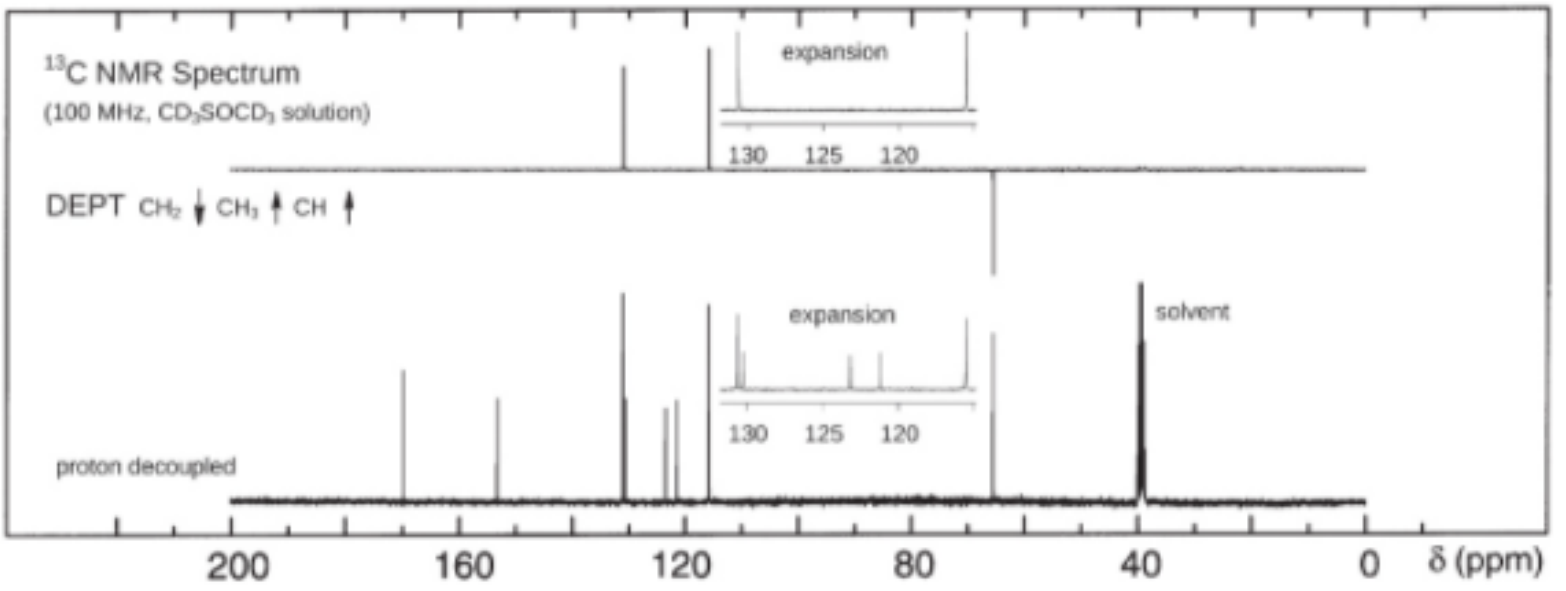
ppm
solvent
40
125
130
135
165
170
175
180
^{1}H–^{13}C HMBC Spectrum
(400 MHz, CD_3SOCD_3 solution)
12.4 12.2 12.0 11.8 11.6
8.0 7.8 7.6 7.4 7.2
4.0 3.8
ppm

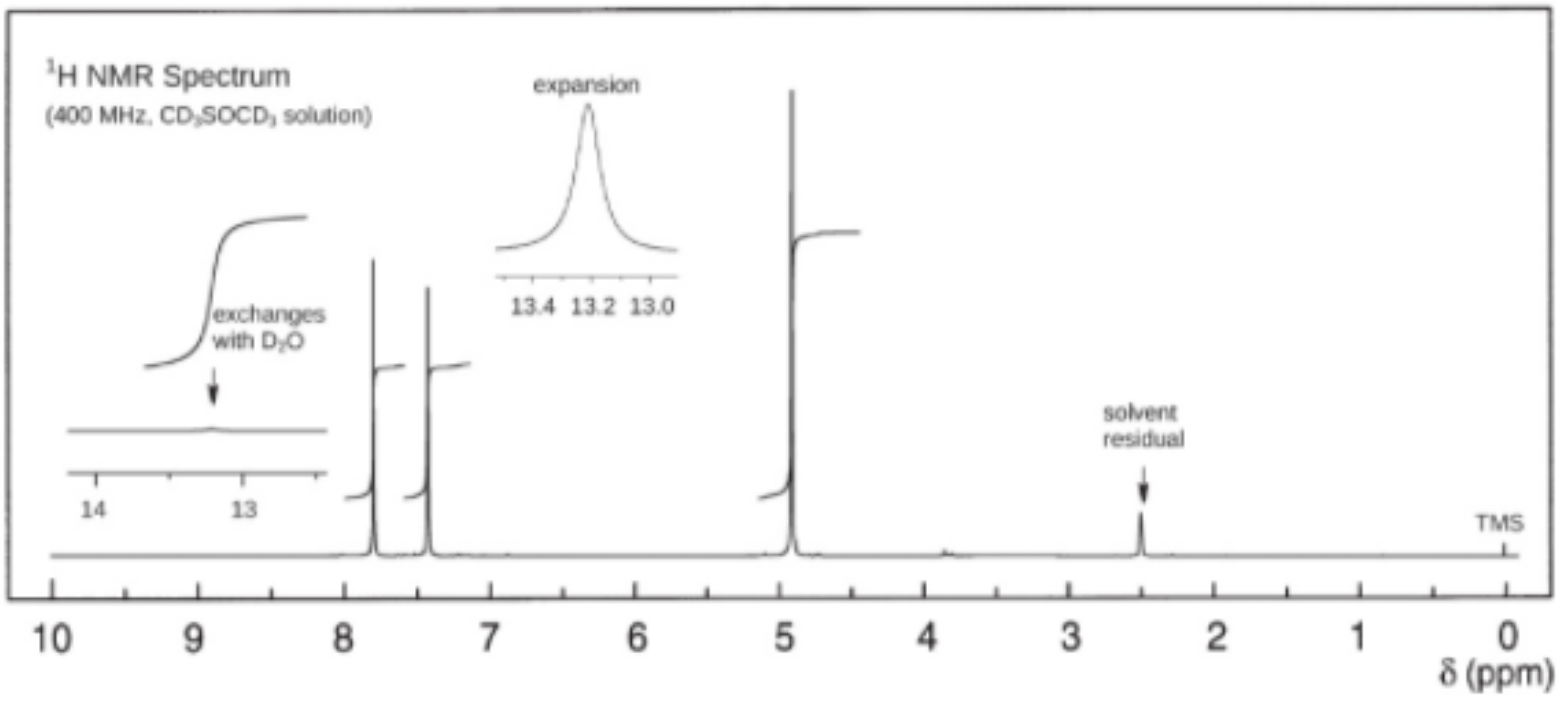
Problem 238


3090
IR Spectrum
(KBr disc)
1745
4000
3000
2000
1600
1200
800
ν (cm-1)

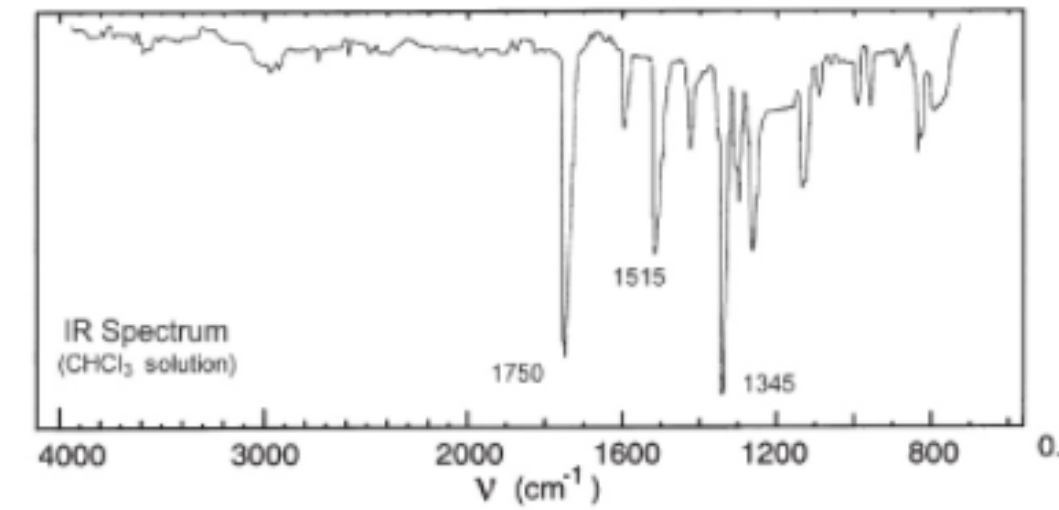

Mass Spectrum
C8H5O3Cl3
M+· = 254 - 260
196
167
179
209
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m/e

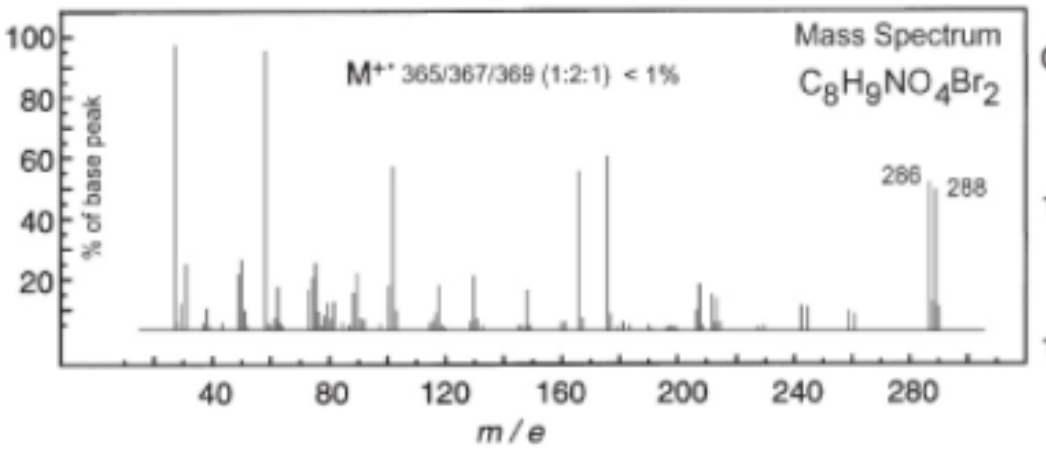

absorbance
UV spectrum
1.592 mg / 10 ml
path length : 0.2 cm
solvent : ethanol
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)

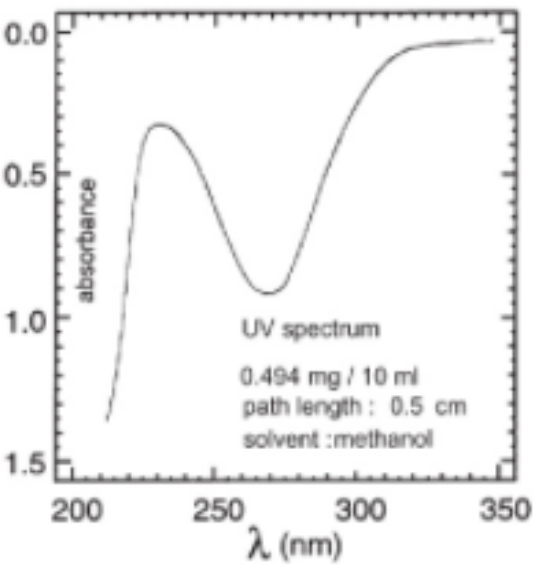

13C NMR Spectrum
(100 MHz, CD3SOCD3 solution)
expansion
130 125 120
DEPT CH2 CH3 CH
expansion
130 125 120
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

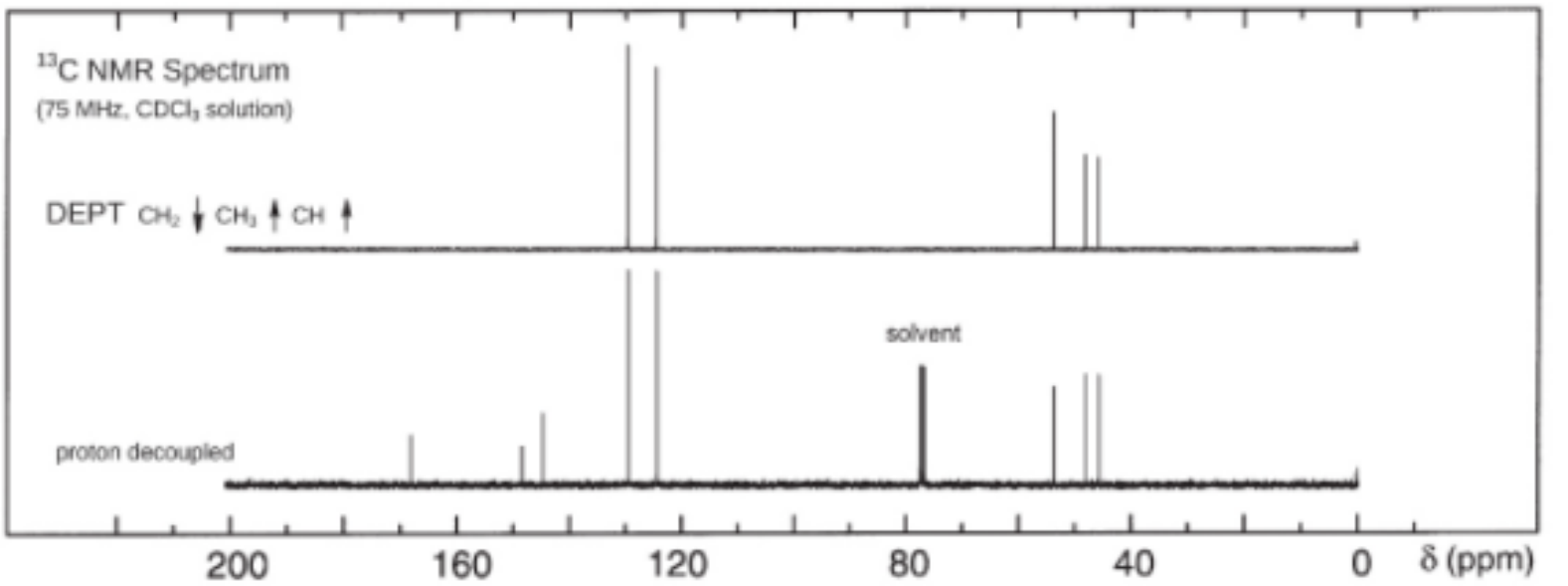

1H NMR Spectrum
(400 MHz, CD3SOCD3 solution)
expansion
13.4 13.2 13.0
exchanges
with D2O
14
13
solvent
residual
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

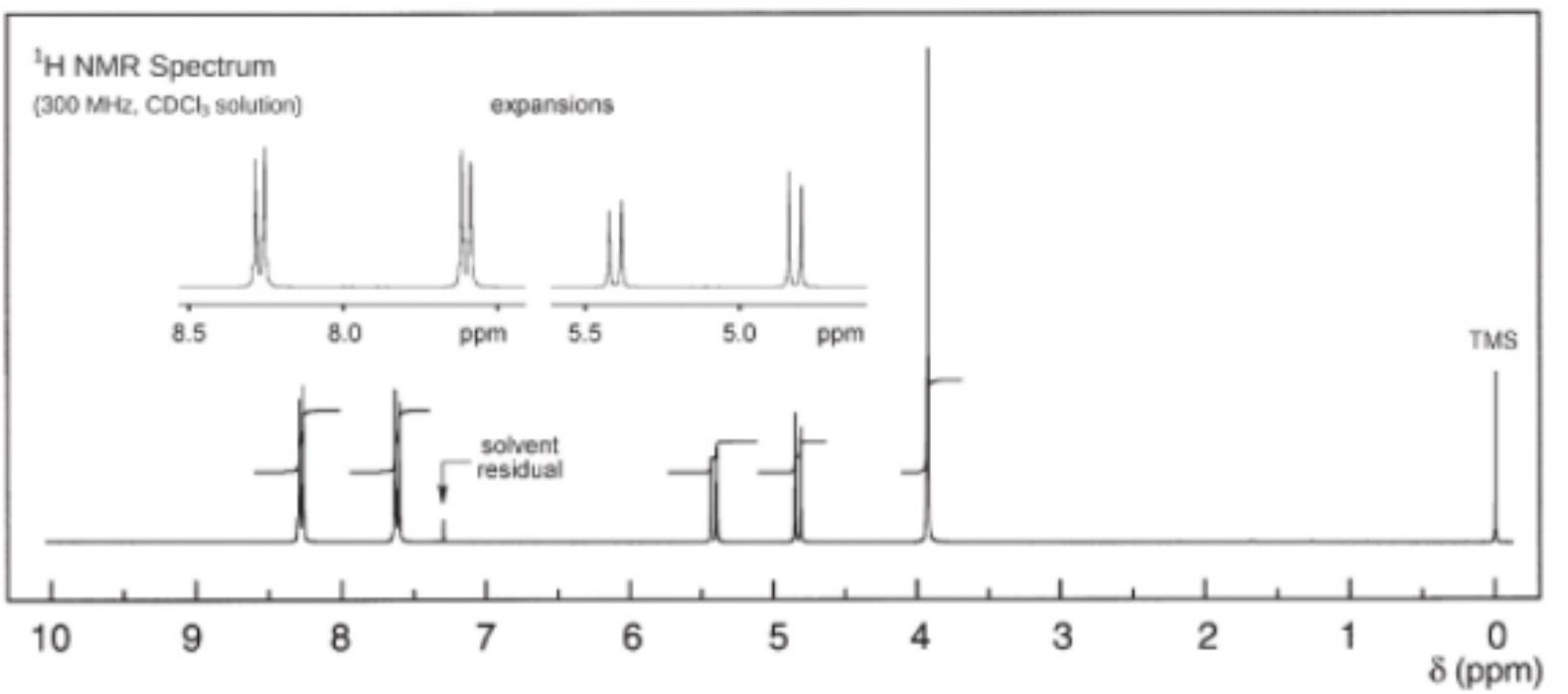
Problem 239


IR Spectrum
(CHCl3 solution)
1750
1515
1345
4000
3000
2000
1600
1200
800
ν (cm-1)

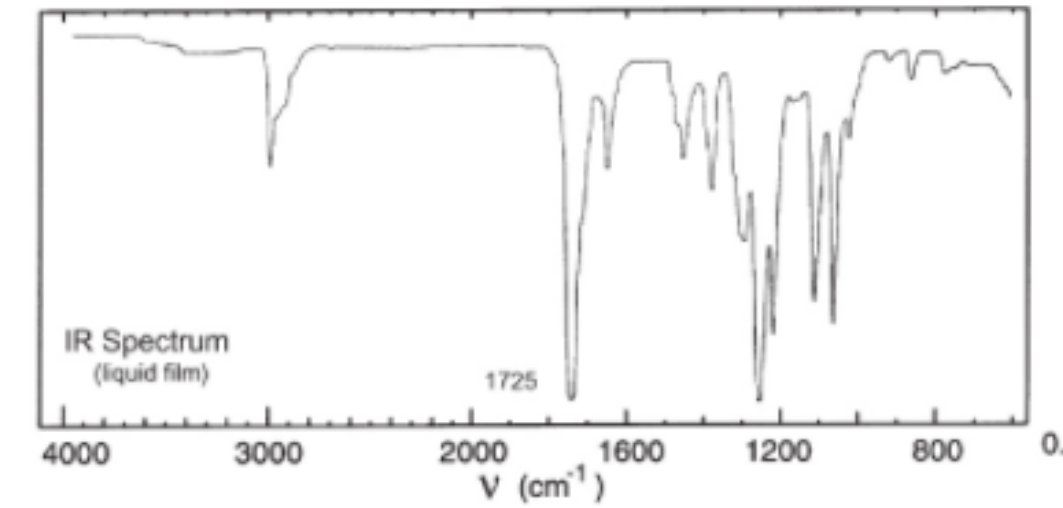

Mass Spectrum
M+· 365/367/369 (1:2:1) < 1%
C8H9NO4Br2
286
288
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m / e


absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.494 mg / 10 ml
path length : 0.5 cm
solvent :methanol
200
250
300
350
λ (nm)

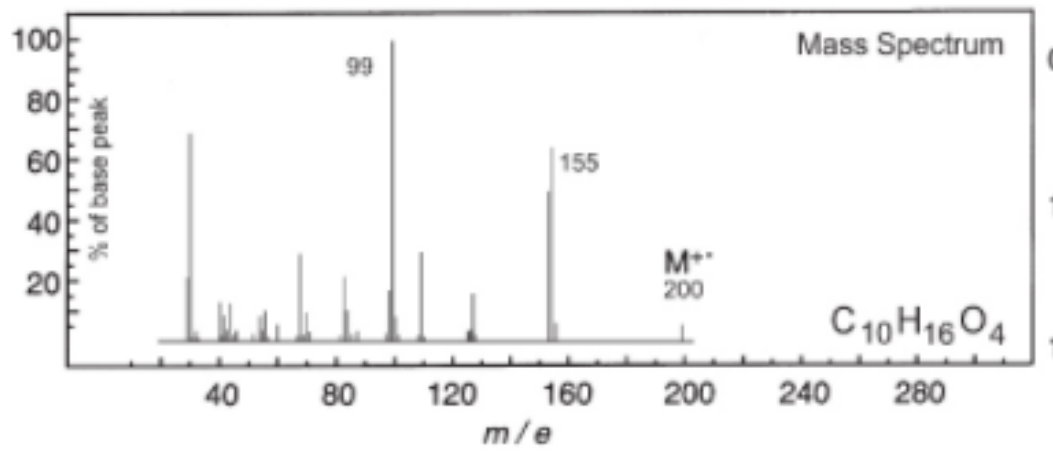

13C NMR Spectrum
(75 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

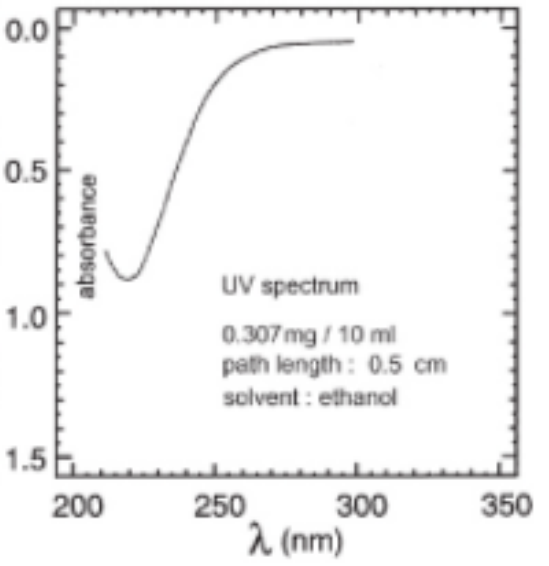

1H NMR Spectrum
(300 MHz, CDCl3 solution)
expansions
8.5
8.0
ppm
5.5
5.0
ppm
TMS
solvent
residual
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

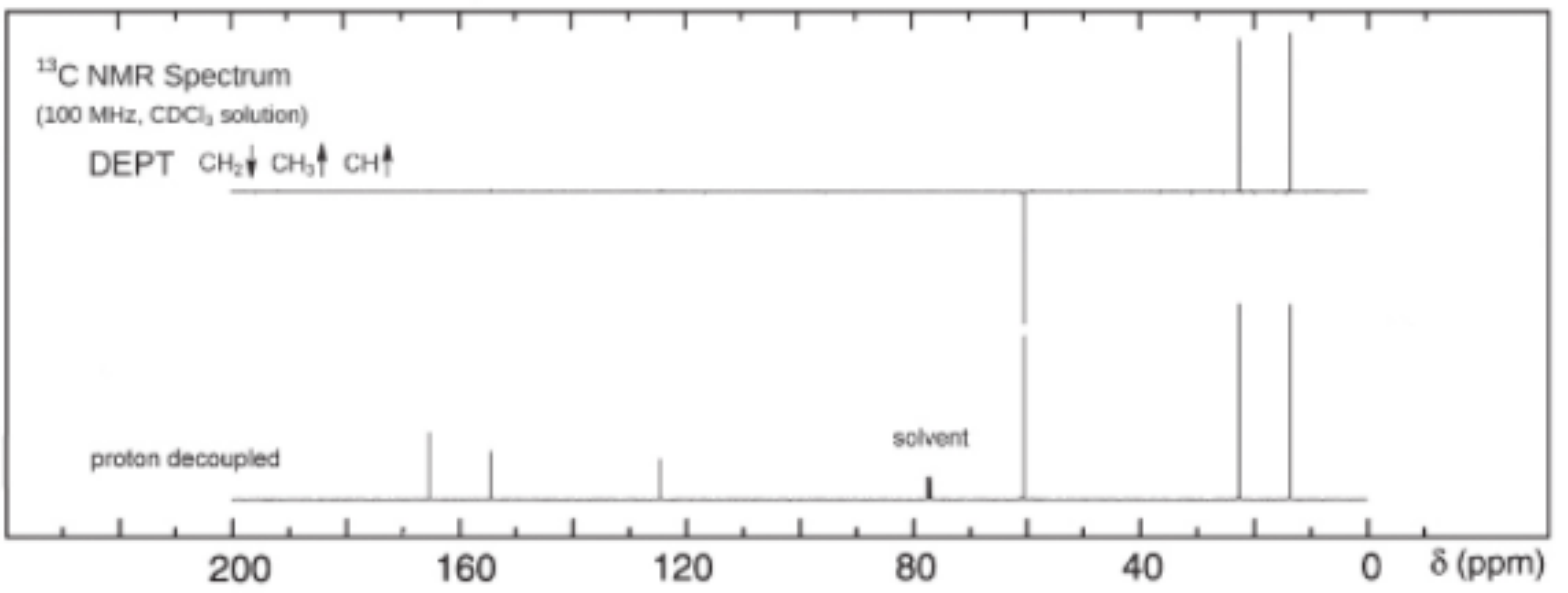
Problem 240

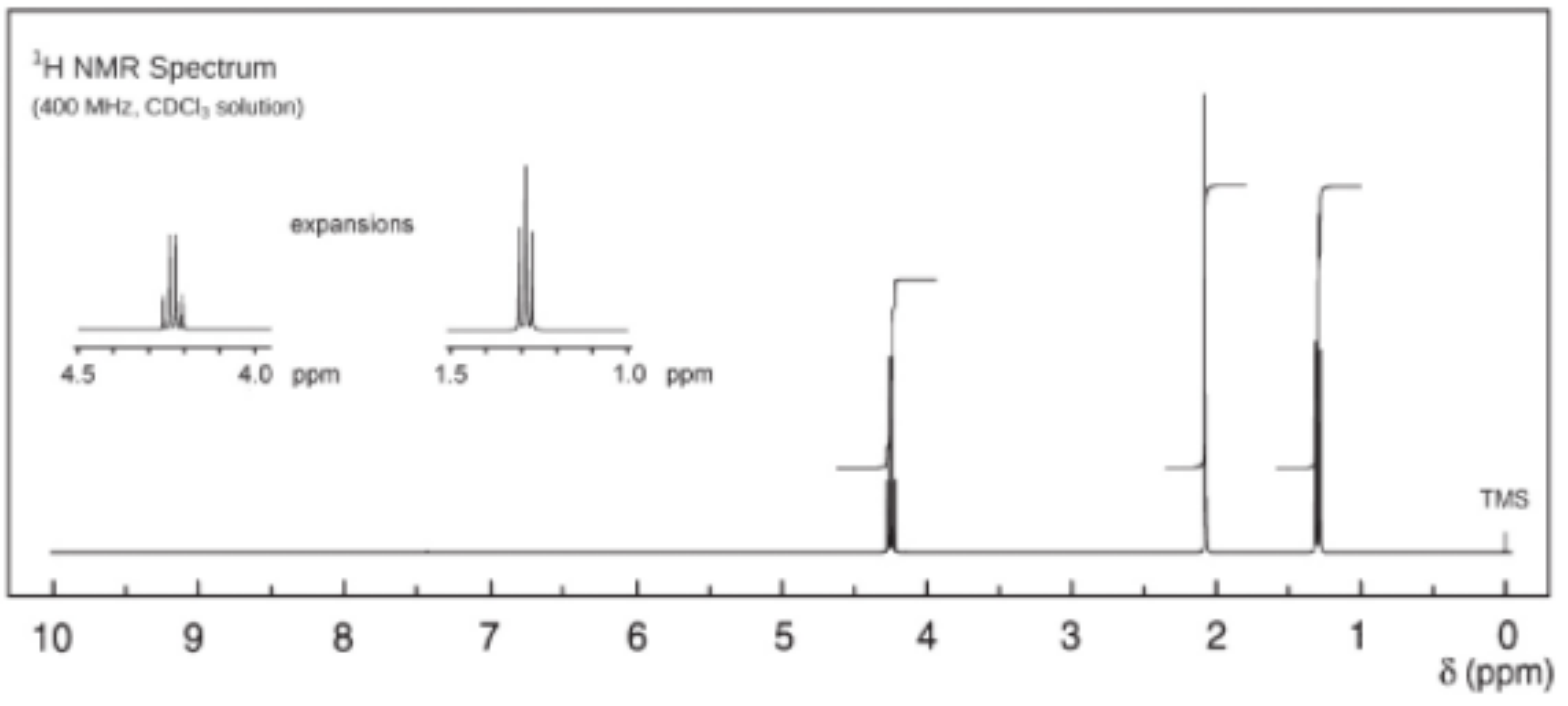


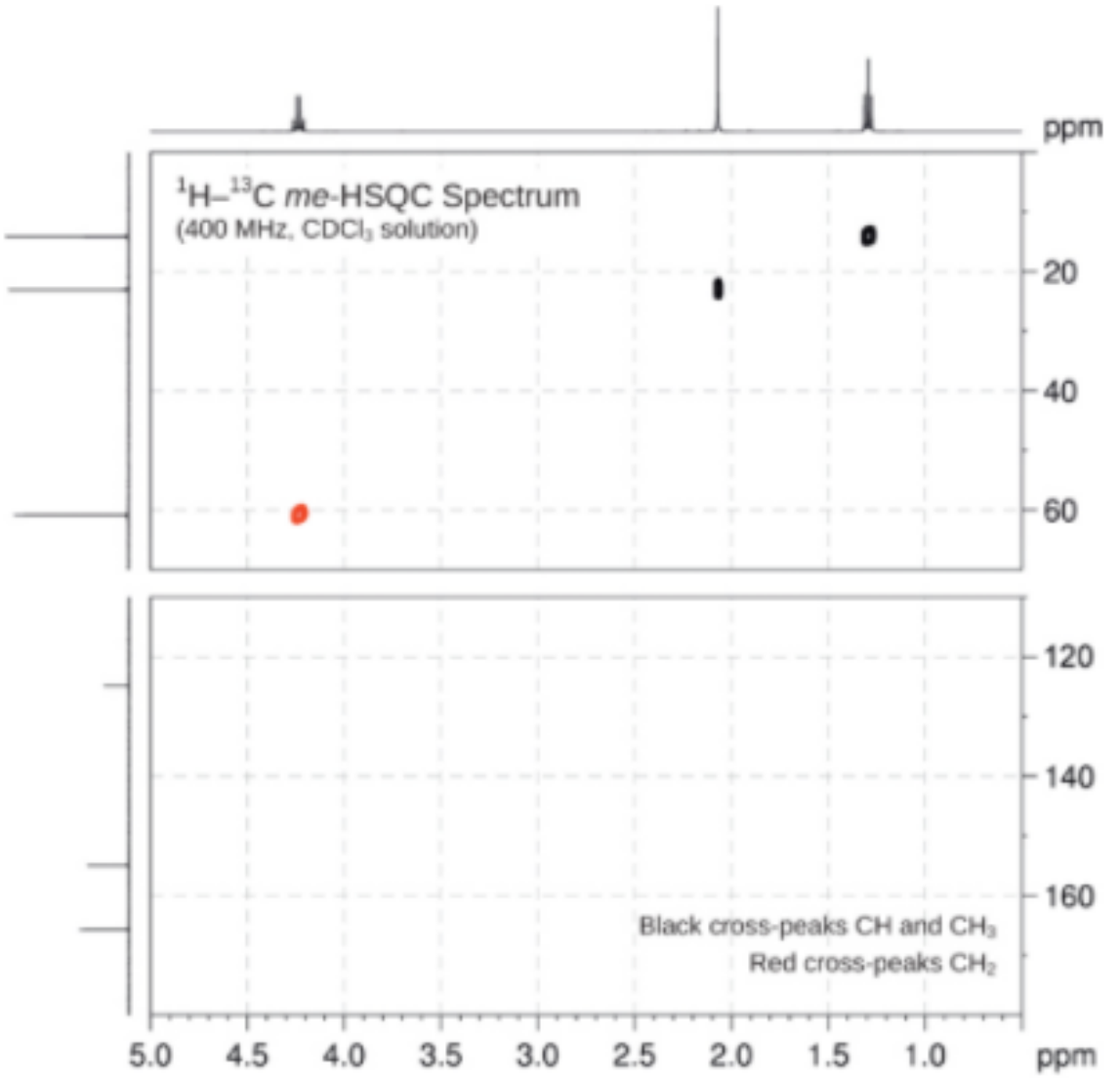
Note: ozonolysis of this compound affords acetone

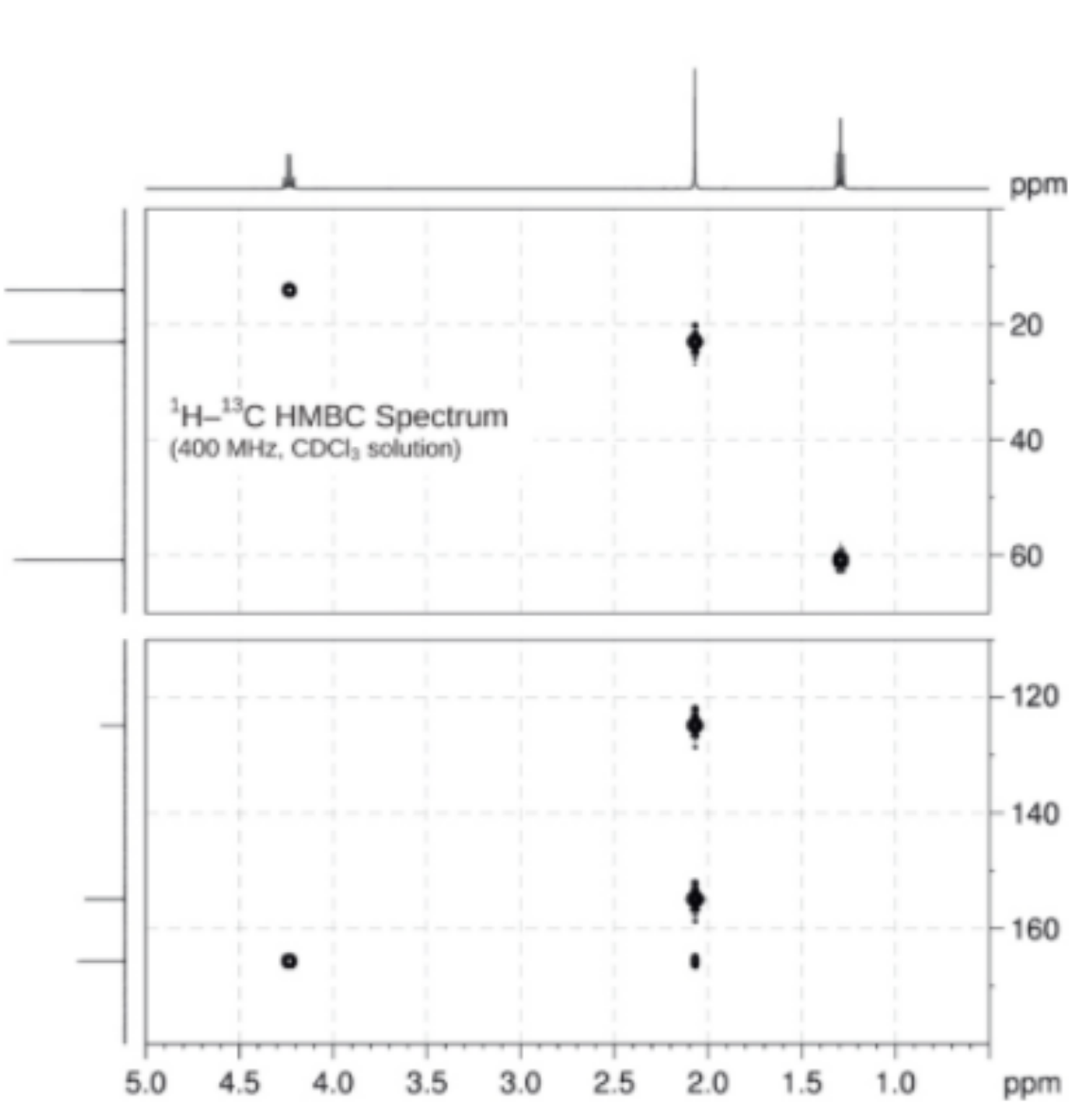




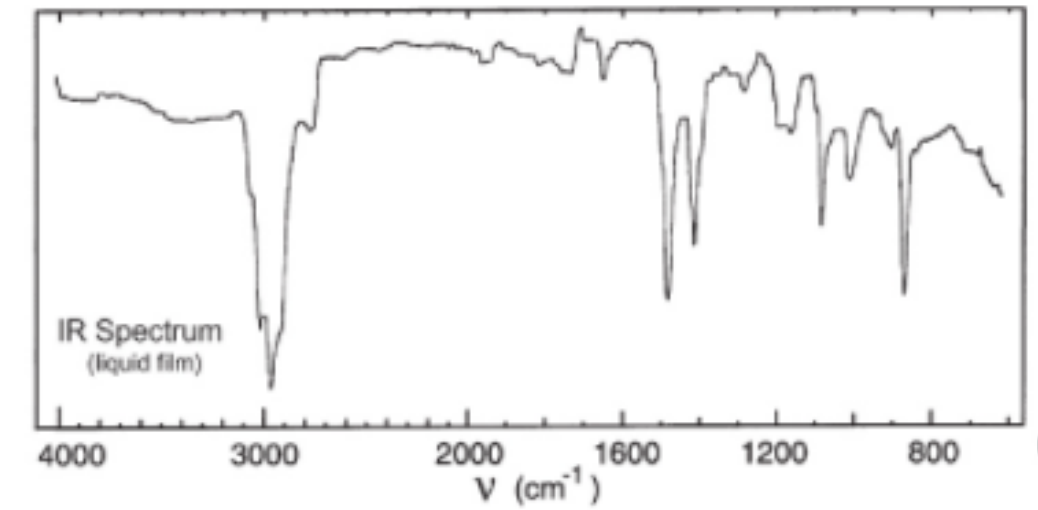


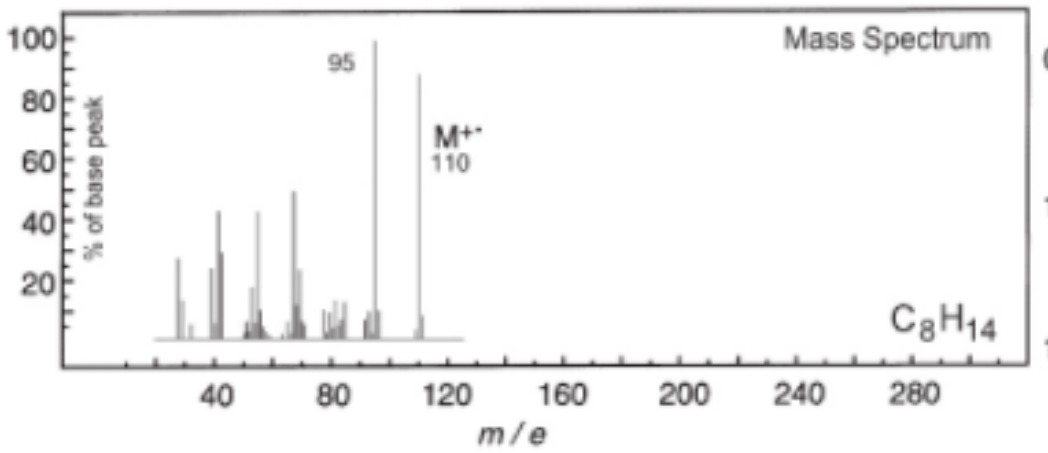


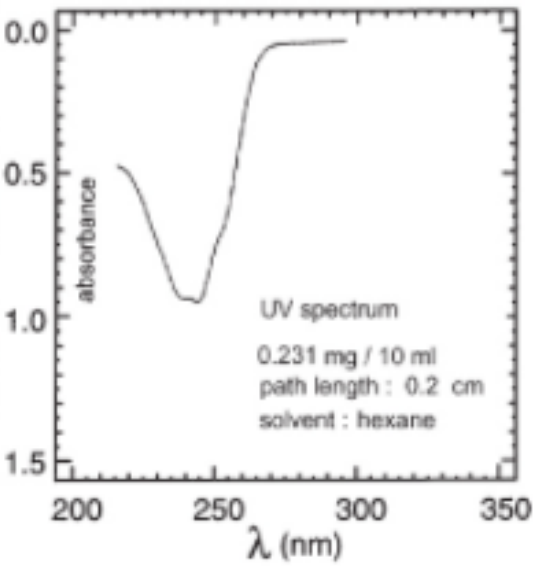

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
20
40
60
120
140
160
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

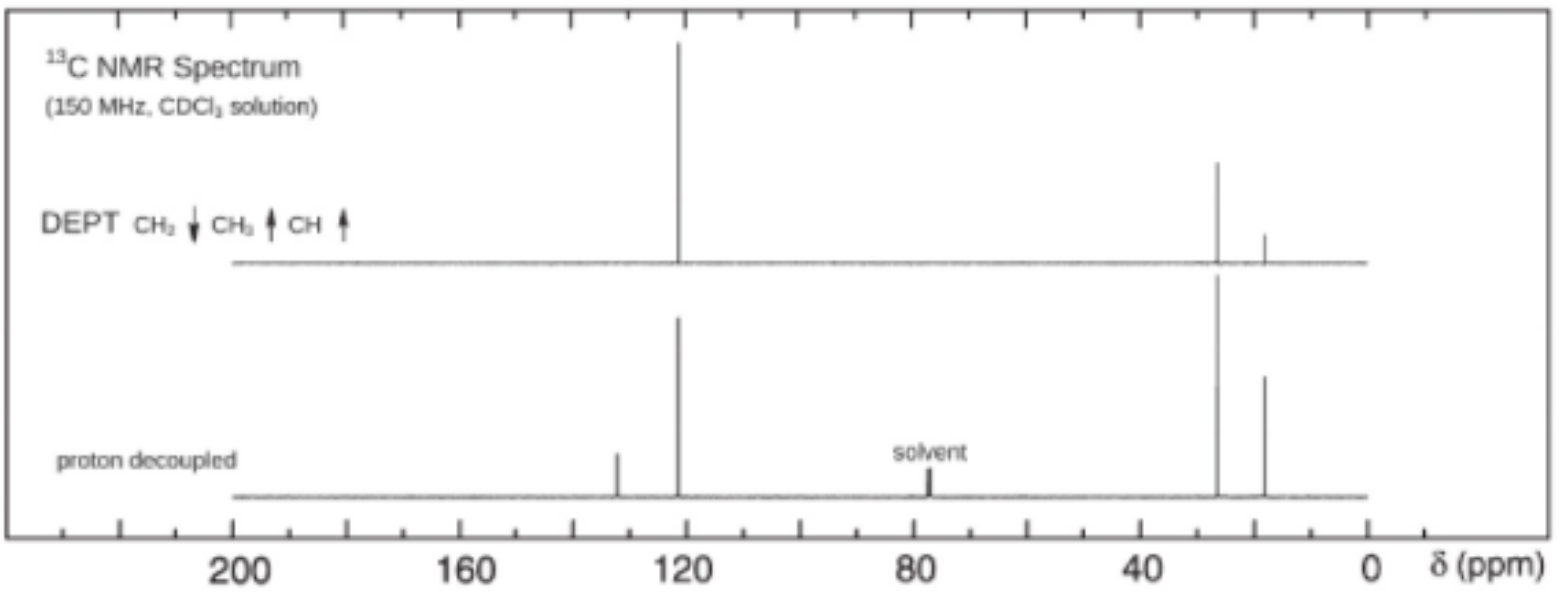

ppm
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
20
40
60
120
140
160
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

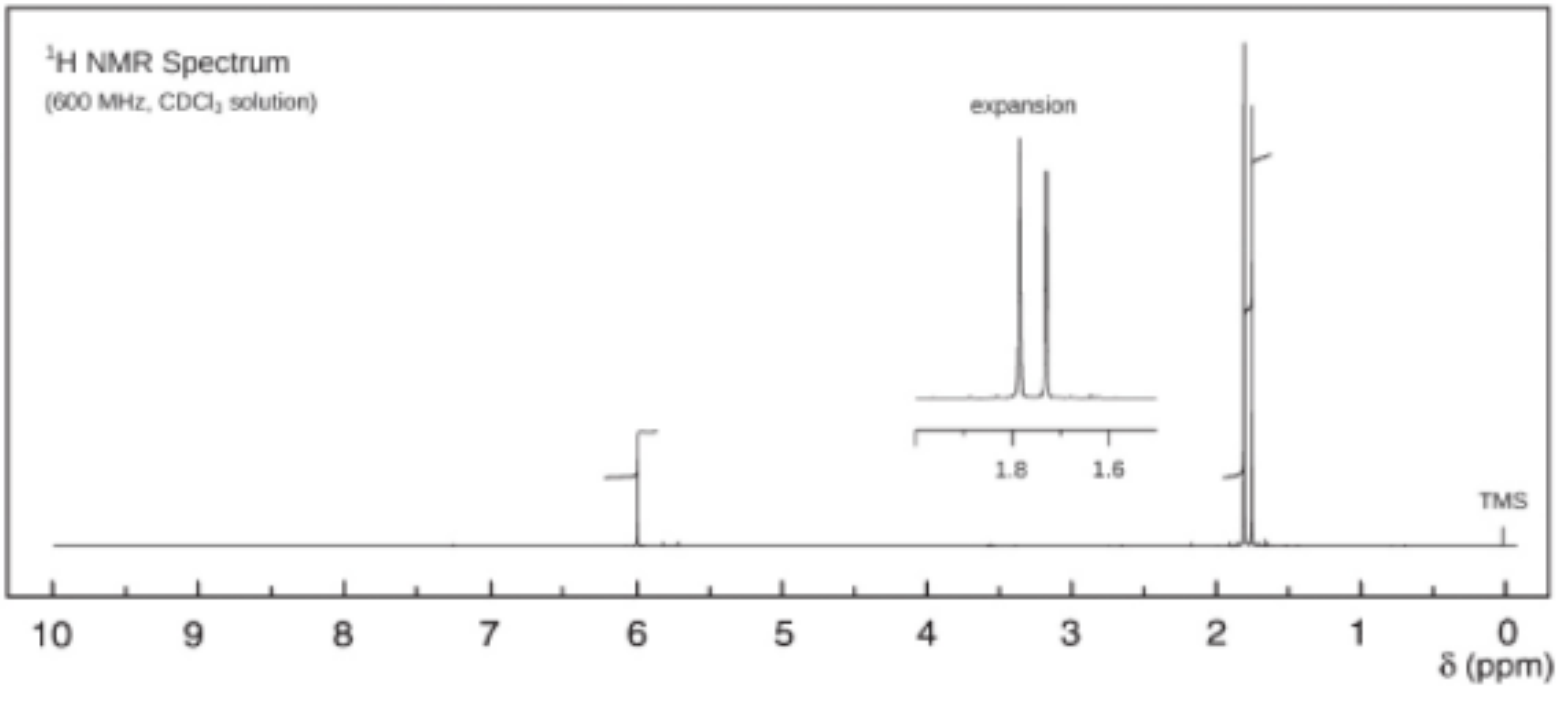
Problem 241

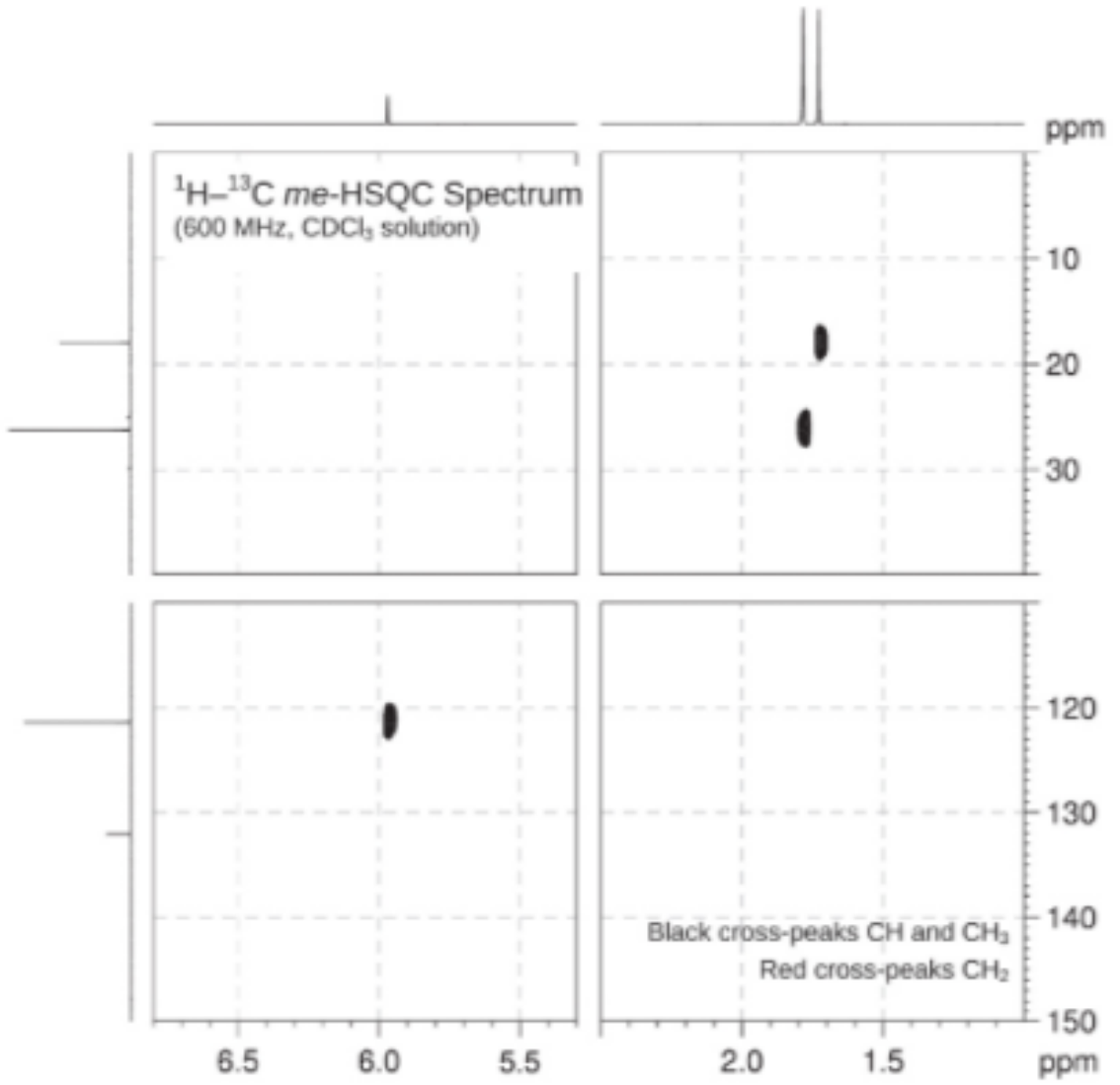

IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

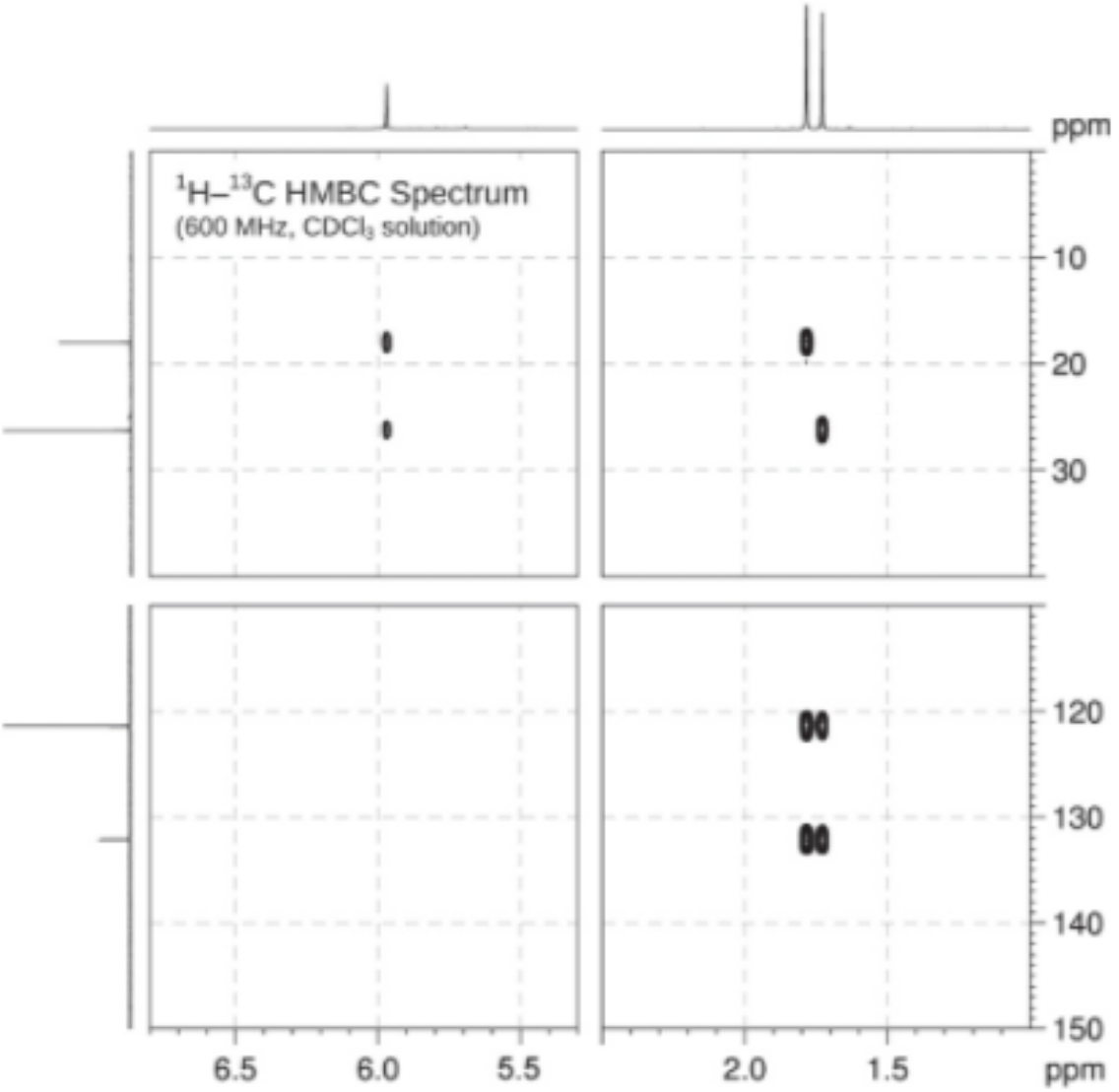

Mass Spectrum
95
M+·
110
% of base peak
100
80
60
40
20
C8H14
40
80
120
160
200
240
280
m / e


absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.231 mg / 10 ml
path length : 0.2 cm
solvent : hexane
200
250
300
350
λ (nm)

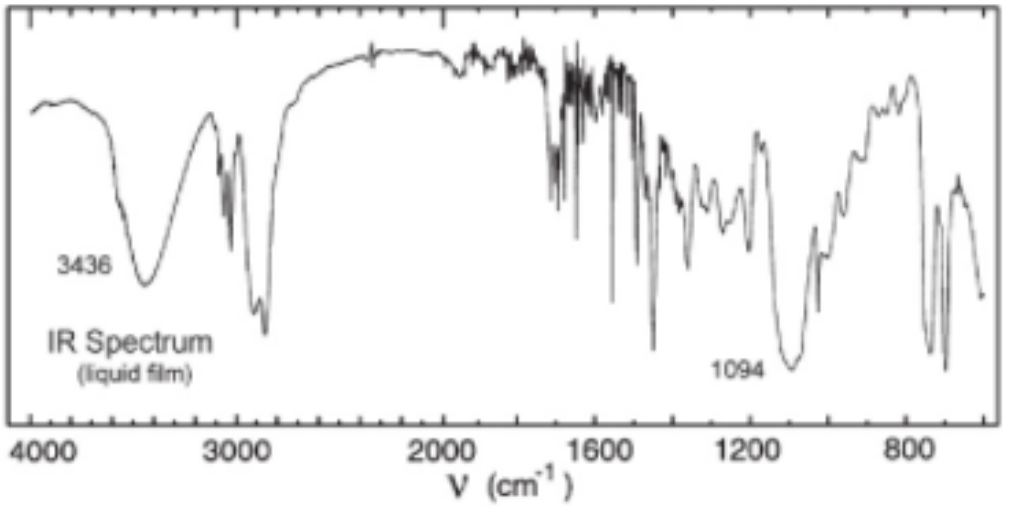

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

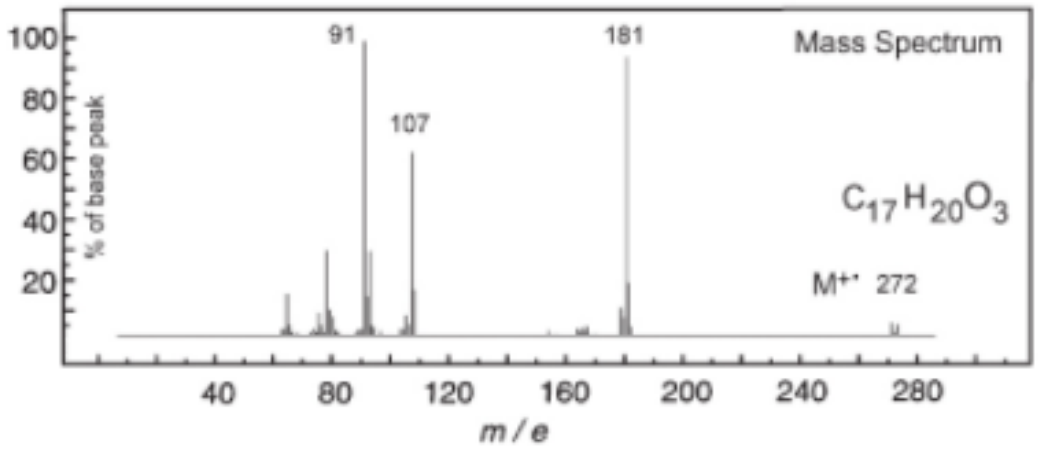

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion
1.8
1.6
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
10
20
30
120
130
140
150
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
6.5
6.0
5.5
2.0
1.5
ppm


ppm
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)
10
20
30
120
130
140
150
6.5
6.0
5.5
2.0
1.5
ppm

Problem 242

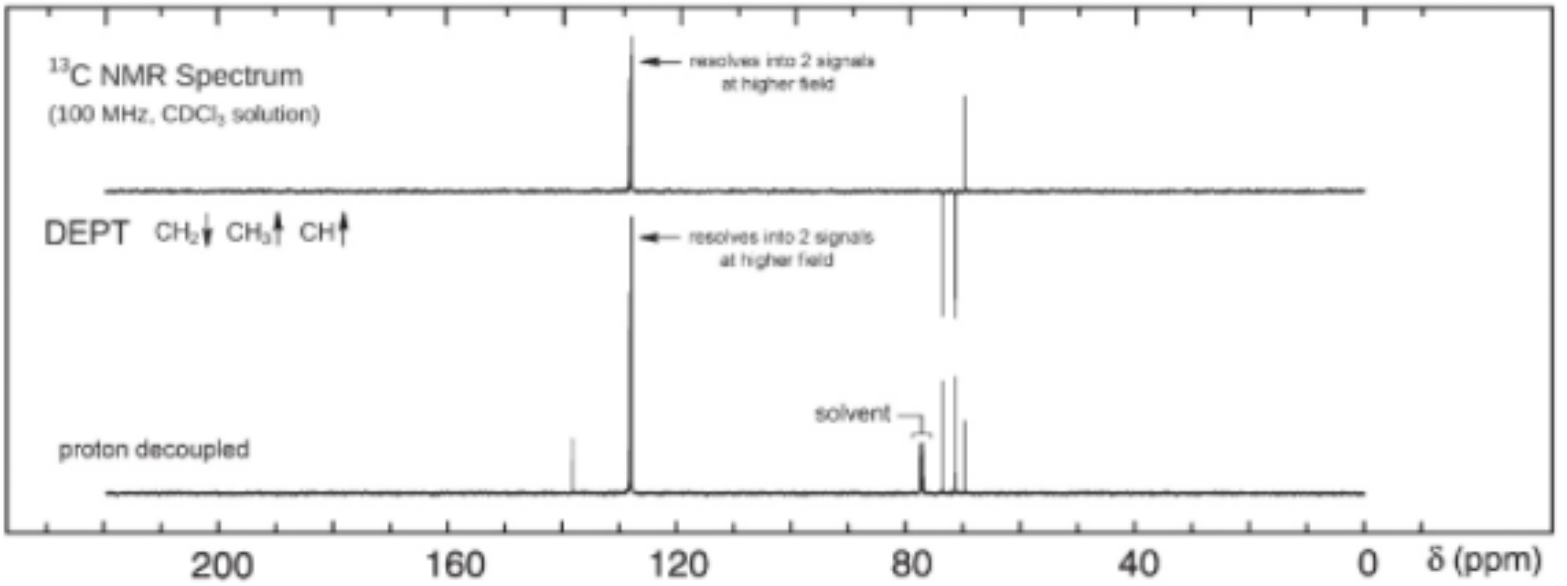


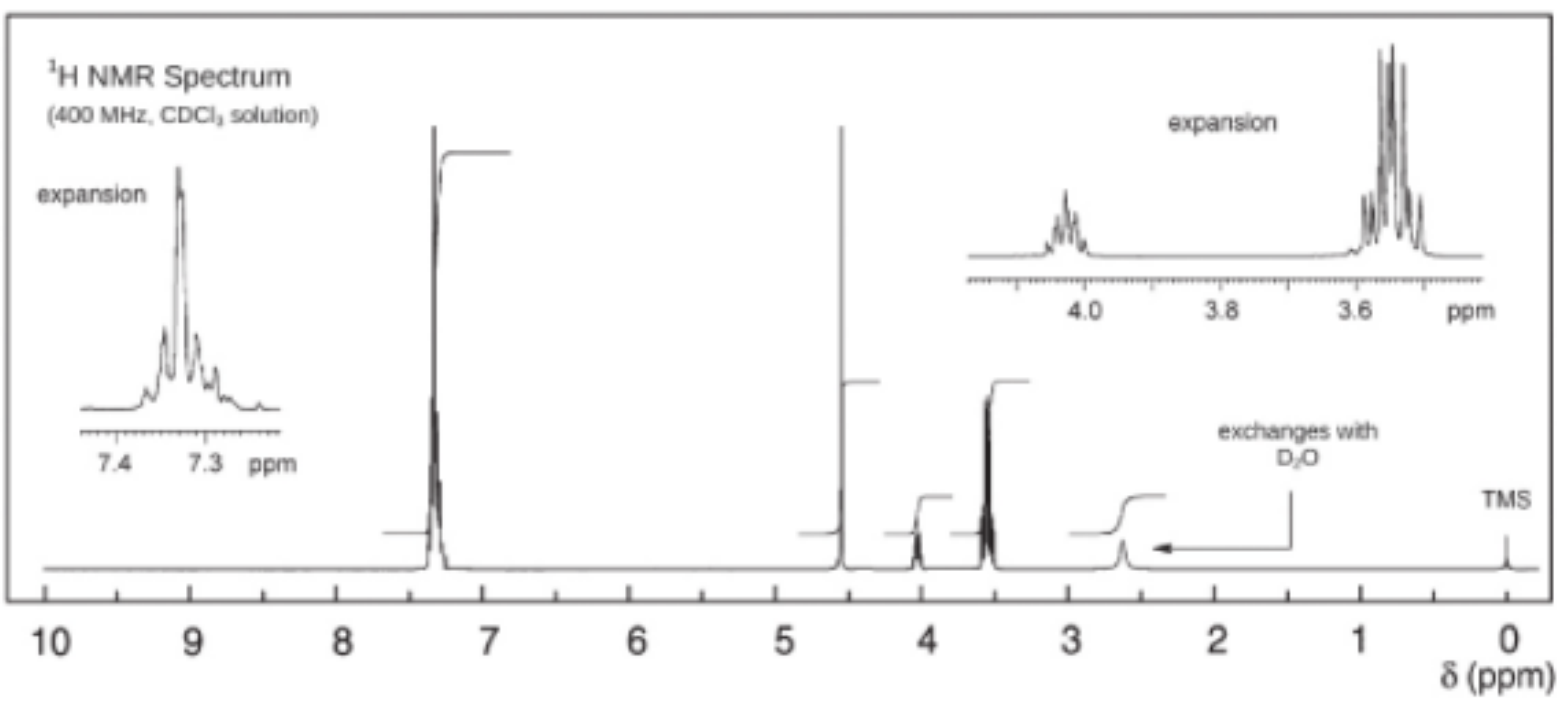


UV Spectrum

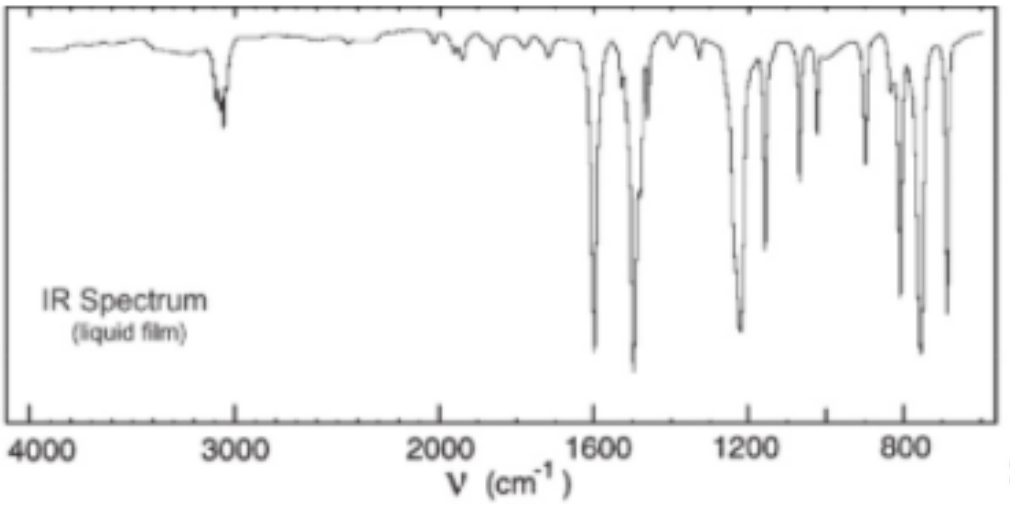
$\log_{10}\varepsilon$ between 2 and 3

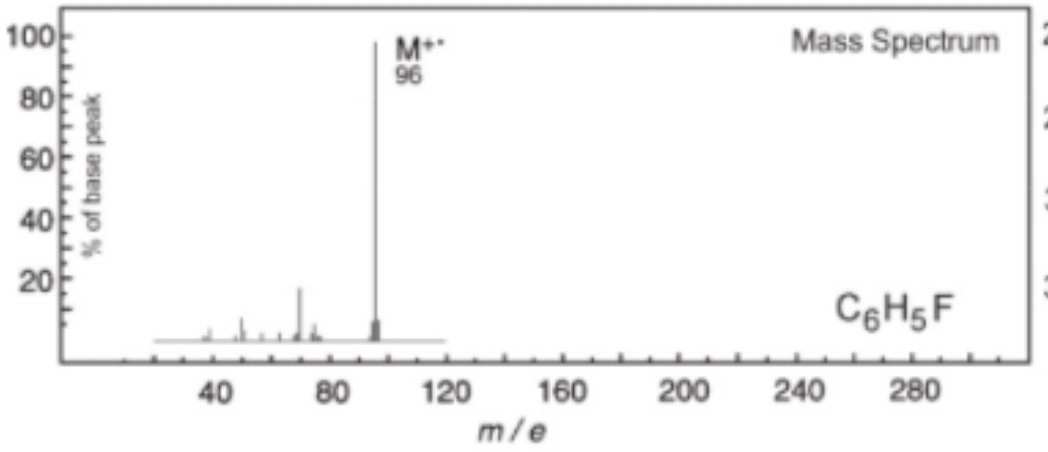
solvent : methanol

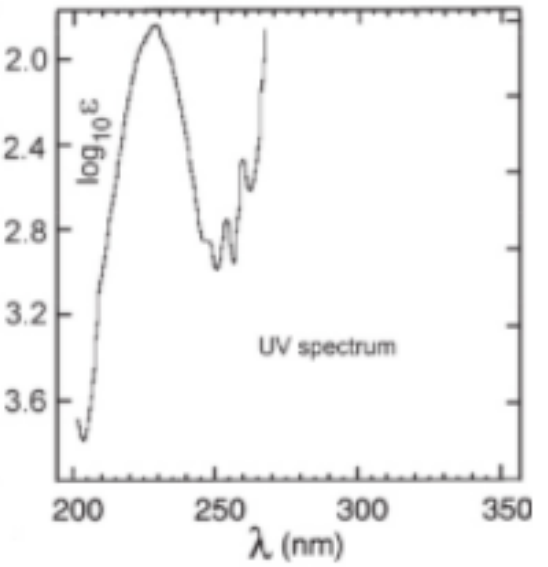


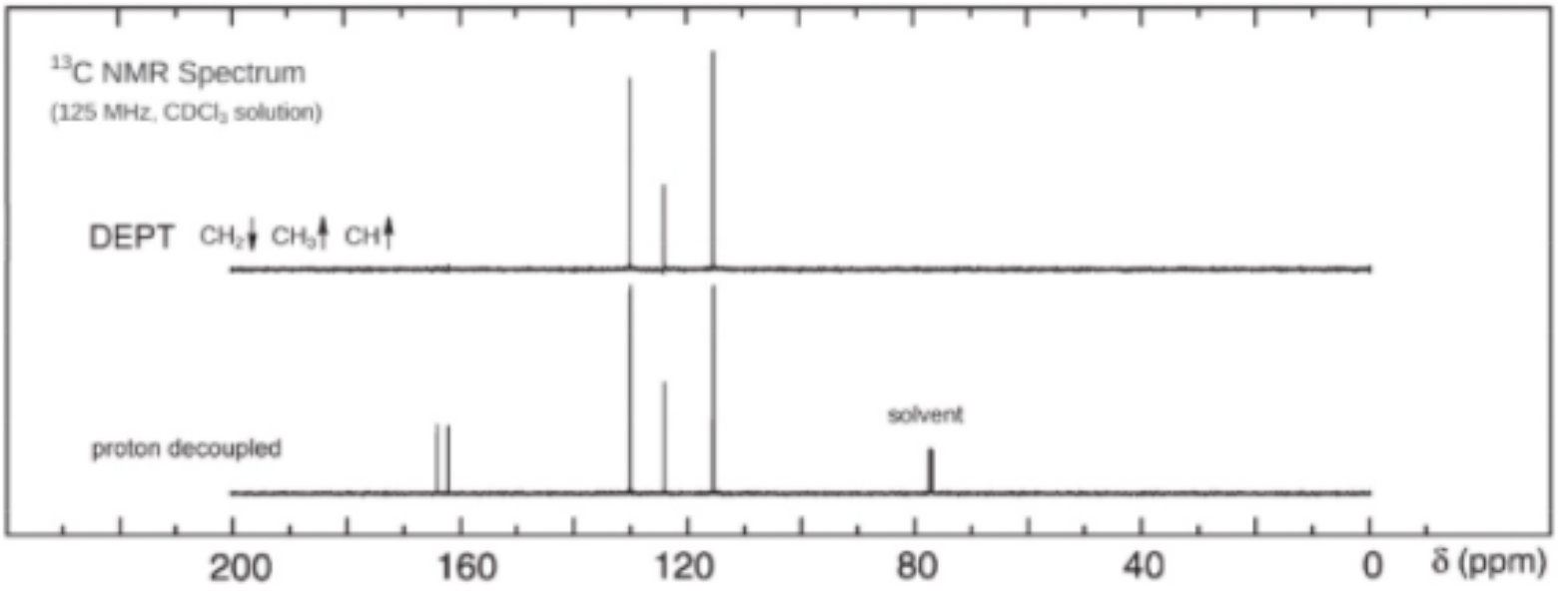


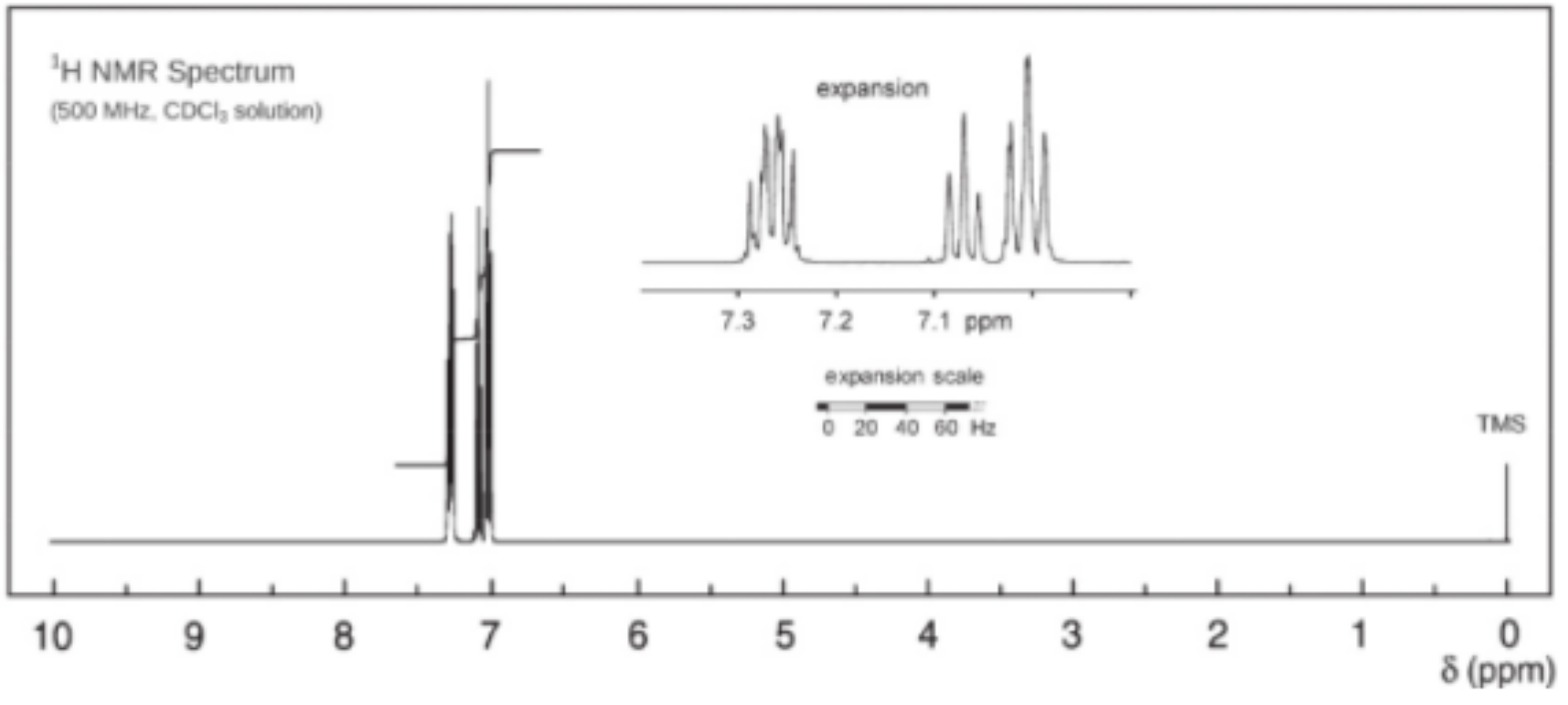
Problem 243


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

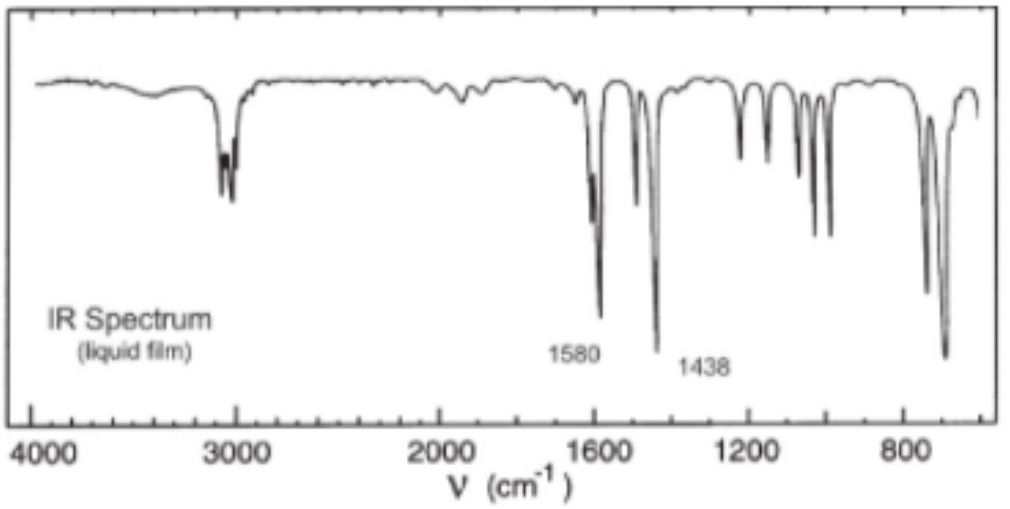

Mass Spectrum
M+·
96
% of base peak
100
80
60
40
20
C6H5F
40
80
120
160
200
240
280
m/e

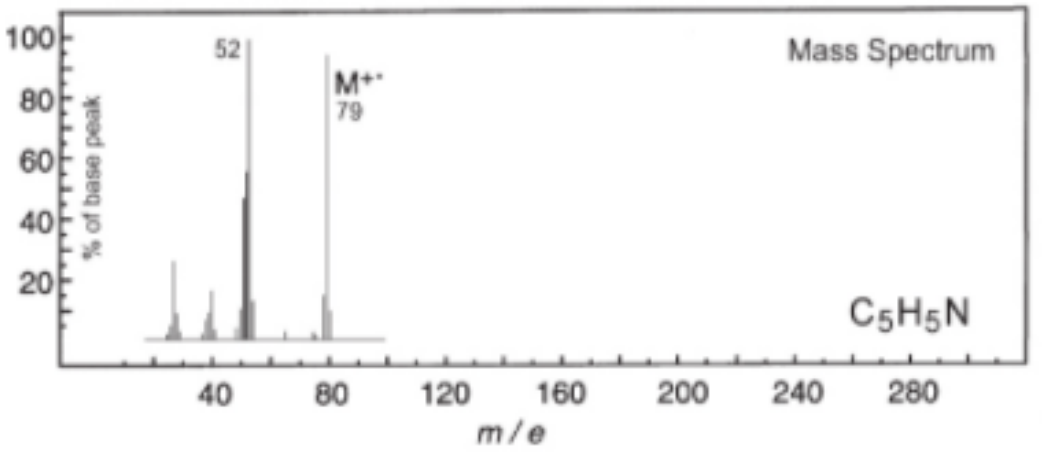

log10ε
2.0
2.4
2.8
3.2
3.6
UV spectrum
200
250
300
350
λ (nm)


13C NMR Spectrum
(125 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(500 MHz, CDCl3 solution)
expansion
7.3
7.2
7.1 ppm
expansion scale
0 20 40 60 Hz
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 244



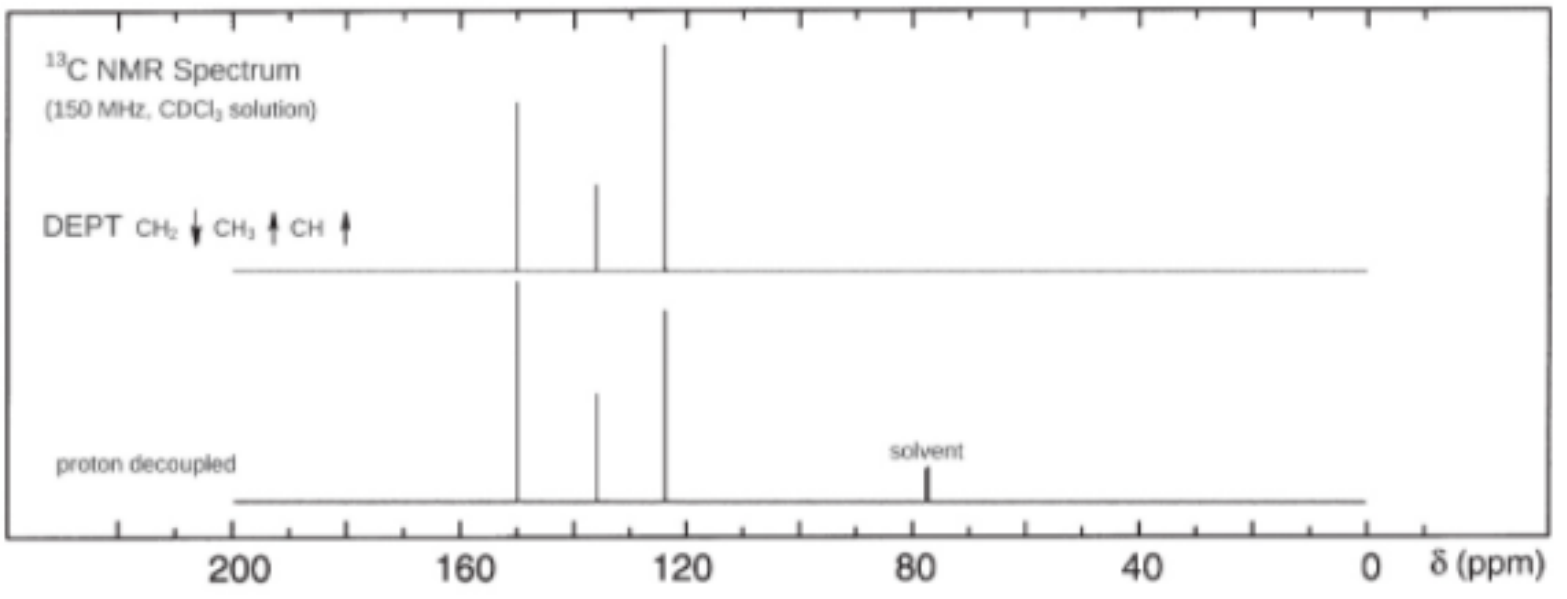


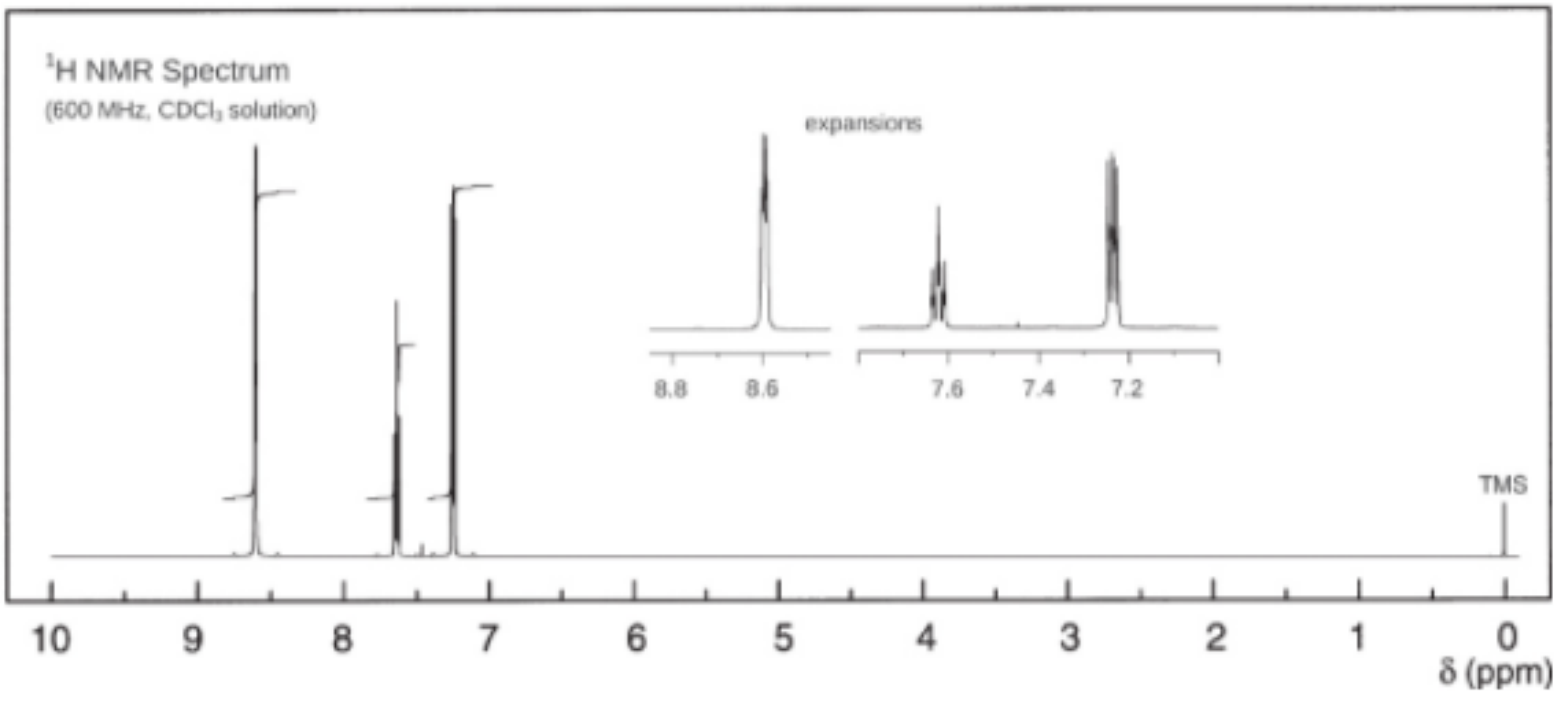
UV Spectrum

λ_{max} 257 nm ($\log_{10}\varepsilon$ 3.4)

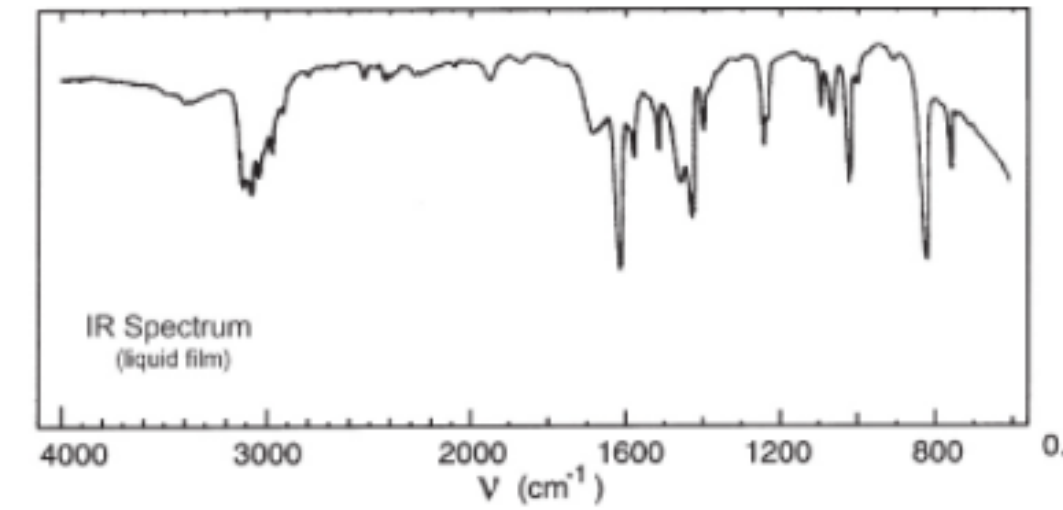
λ_{max} 270 nm ($\log_{10}\varepsilon$ 2.6)

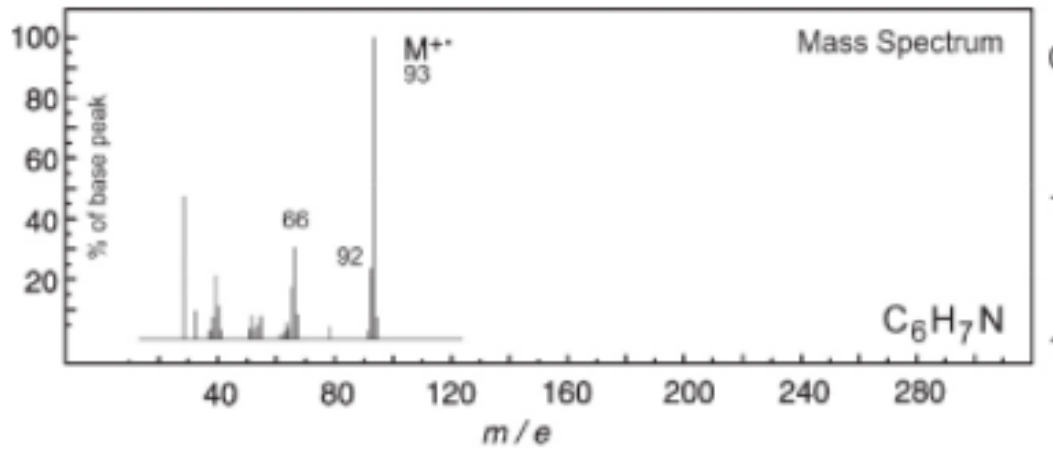
solvent : methanol

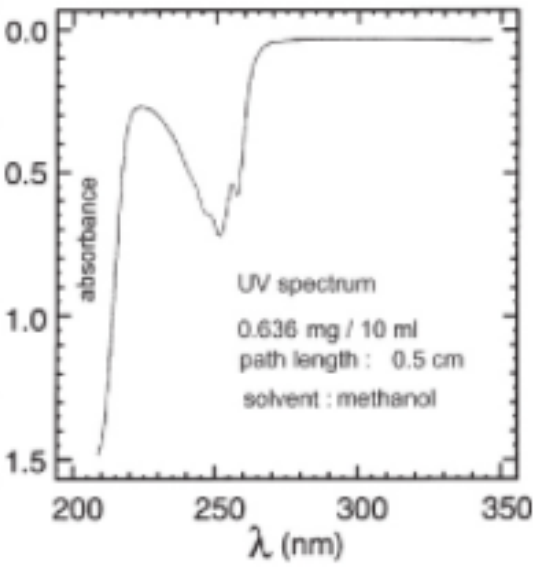


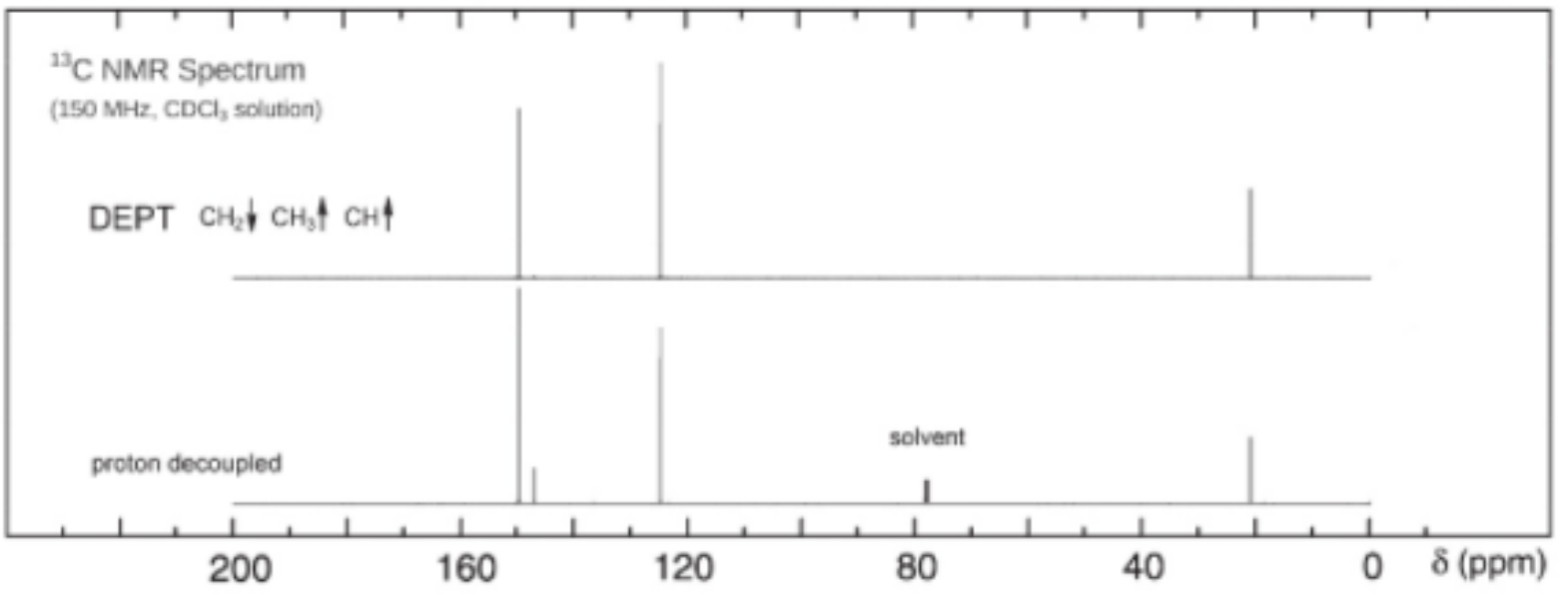


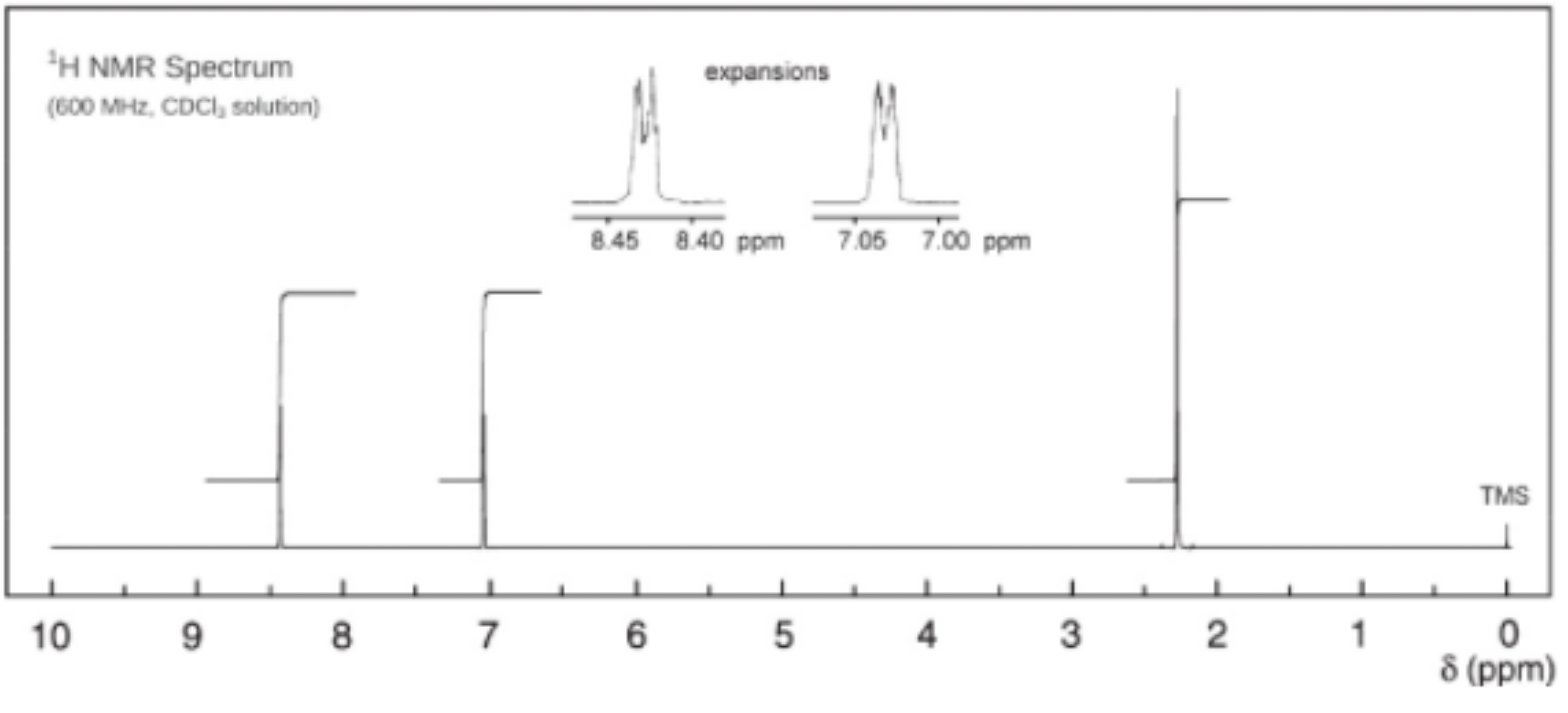
Problem 245


IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

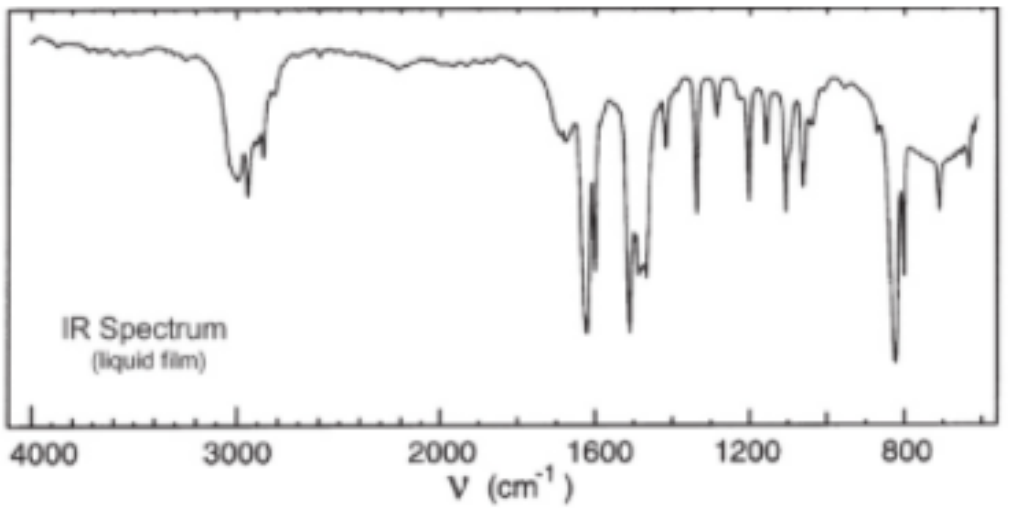

Mass Spectrum
M+·
93
66
92
% of base peak
100
80
60
40
20
C6H7N
40
80
120
160
200
240
280
m / e

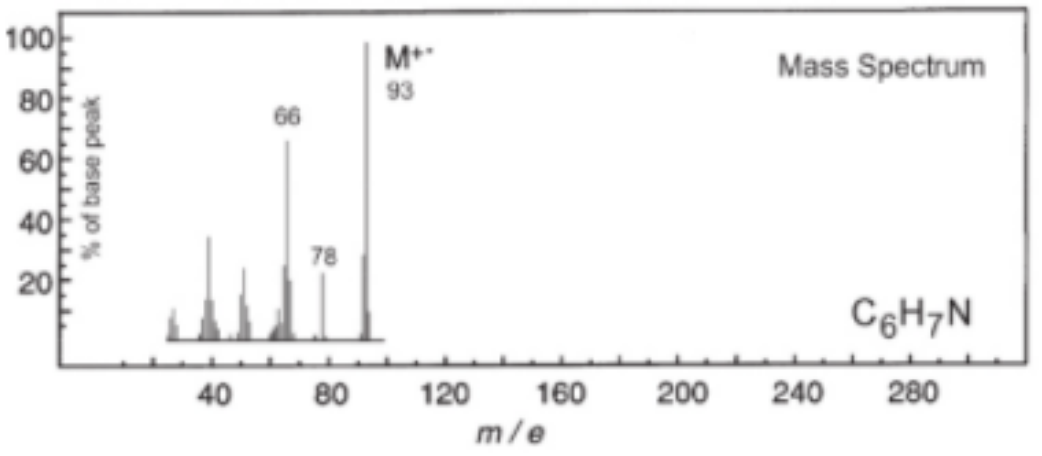

absorbance
0.0
0.5
1.0
1.5
UV spectrum
0.636 mg / 10 ml
path length : 0.5 cm
solvent : methanol
200
250
300
350
λ (nm)


13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansions
8.45
8.40 ppm
7.05
7.00 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 246

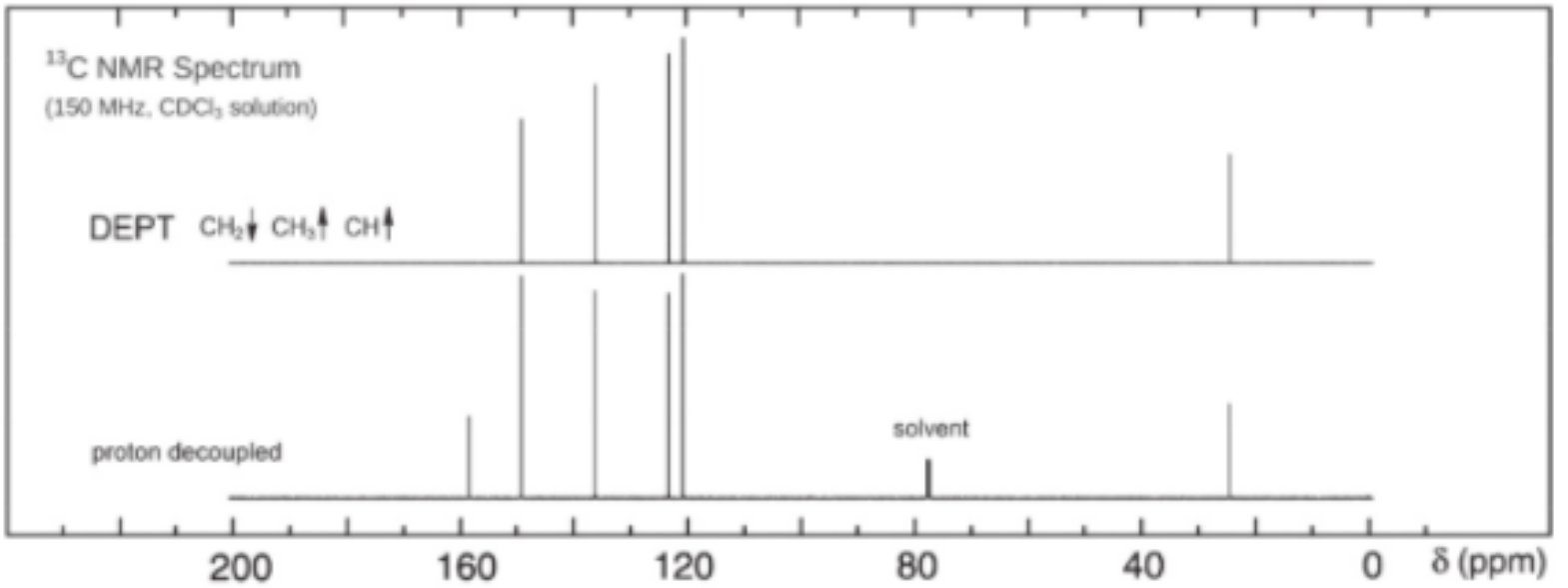


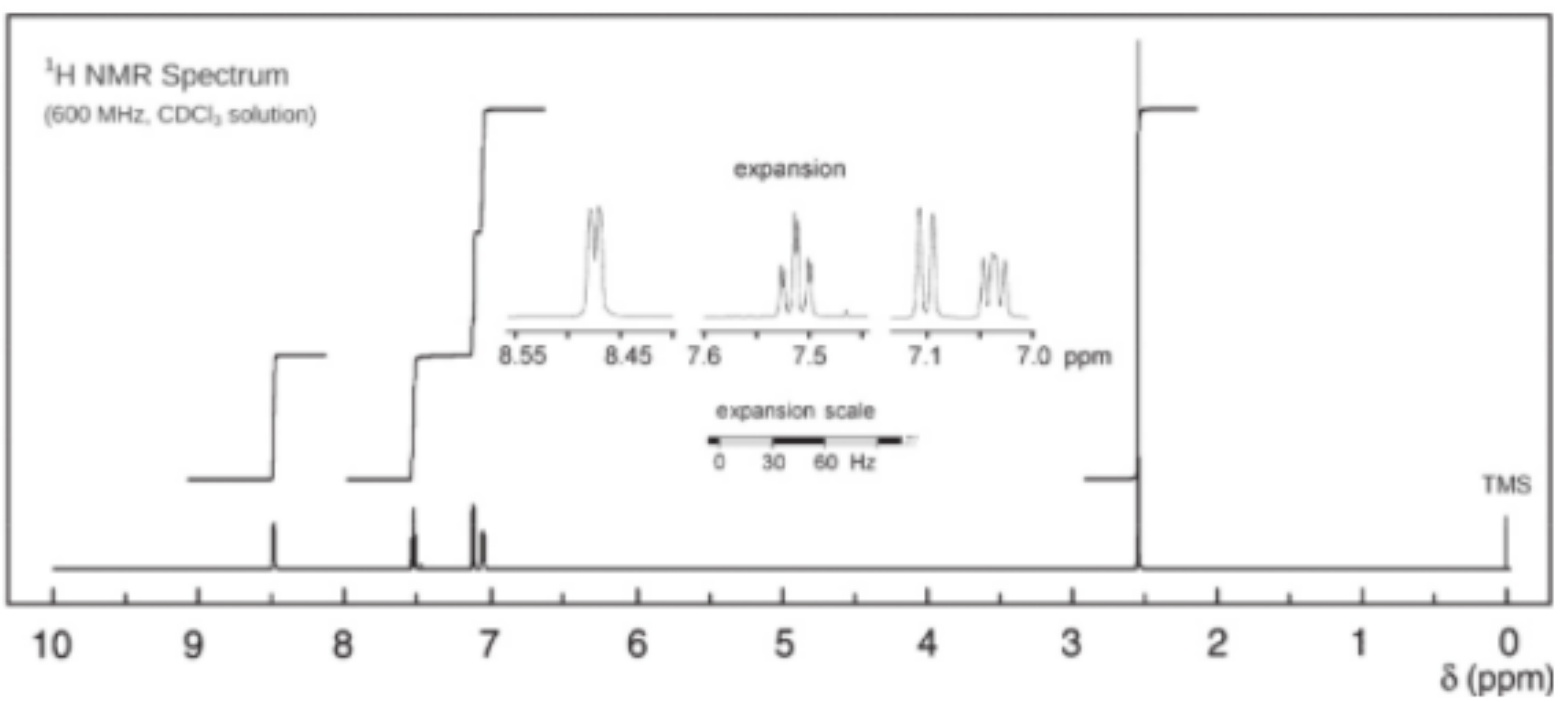


UV Spectrum

λ_{max} 262 nm ($\log_{10}\varepsilon$ 3.6)

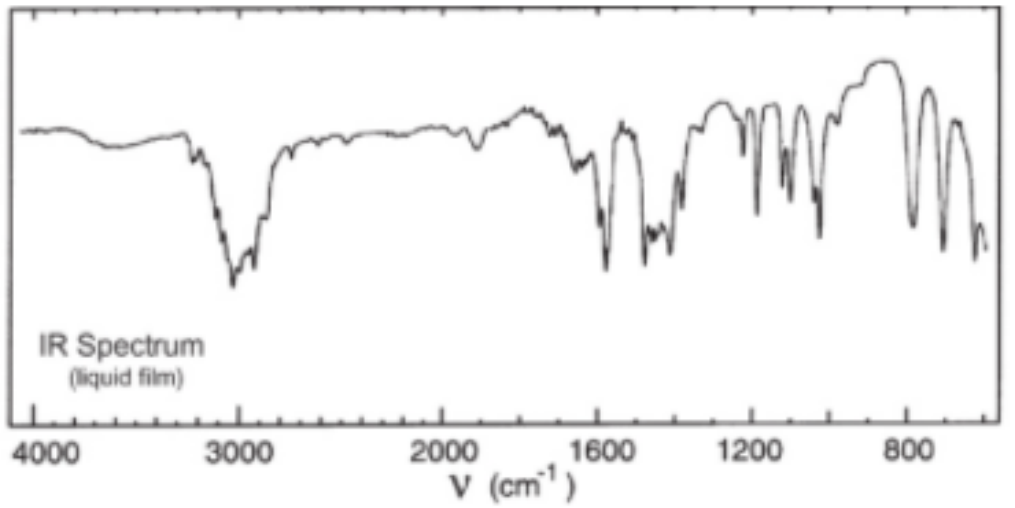
solvent : methanol

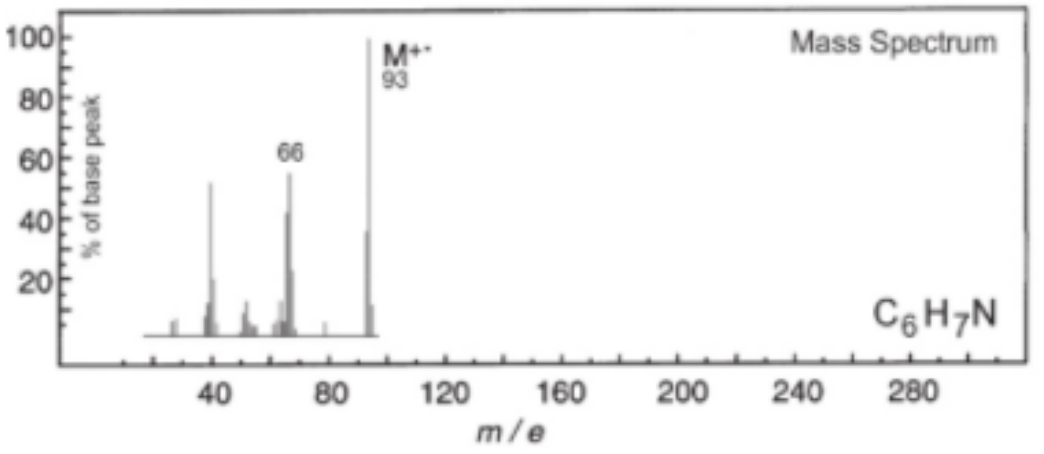




Problem 247

Problem 247

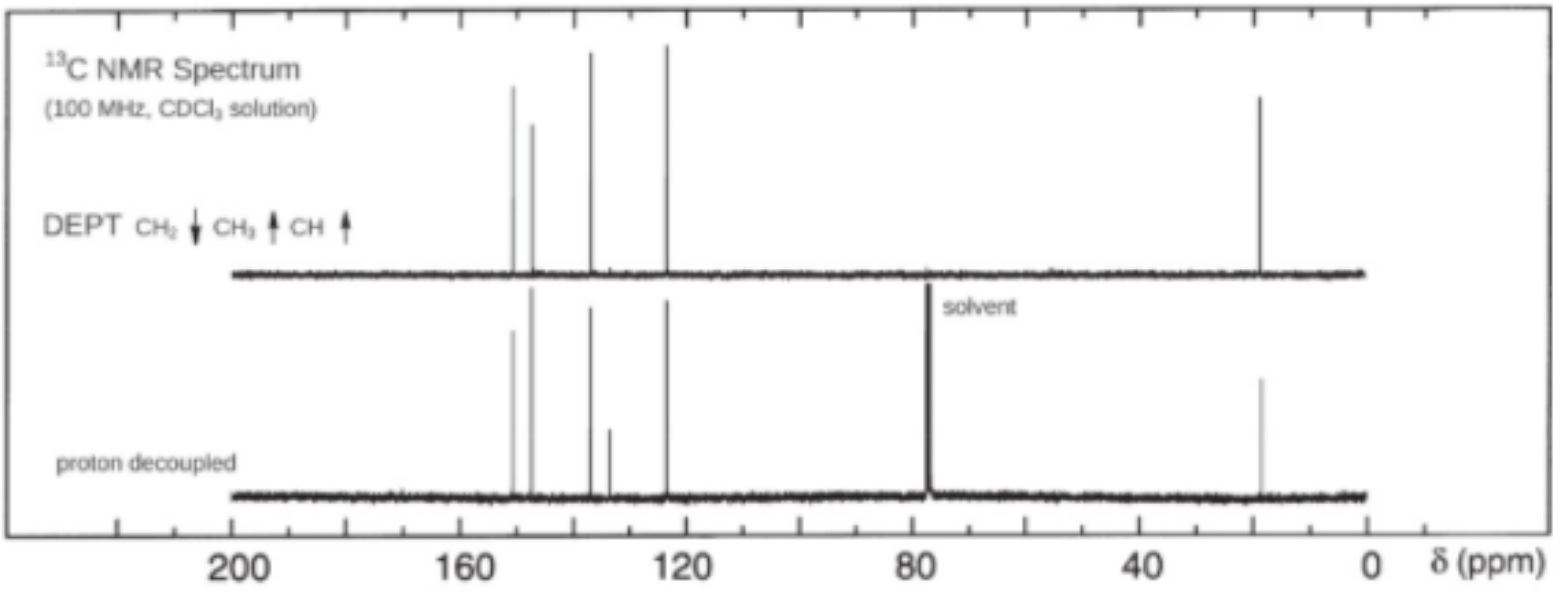


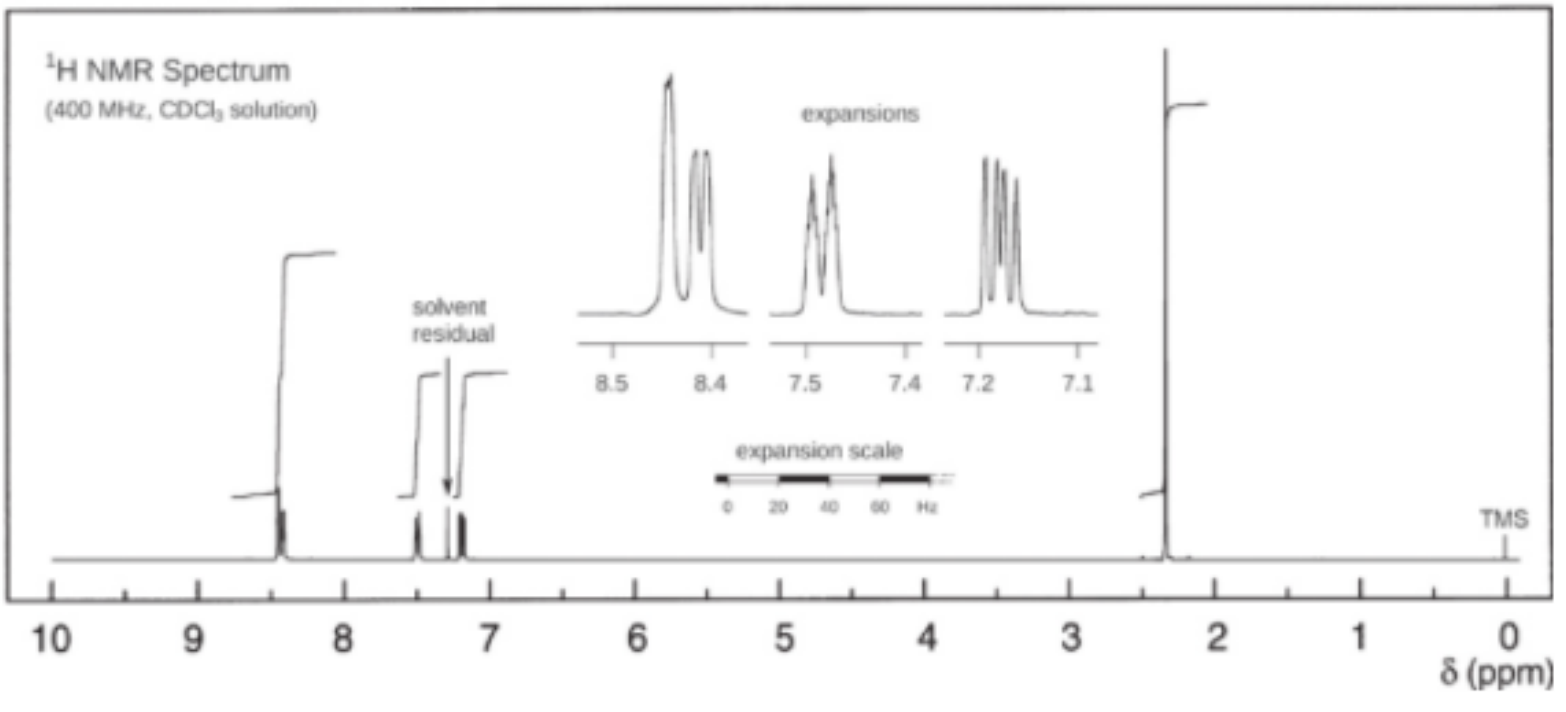


UV Spectrum

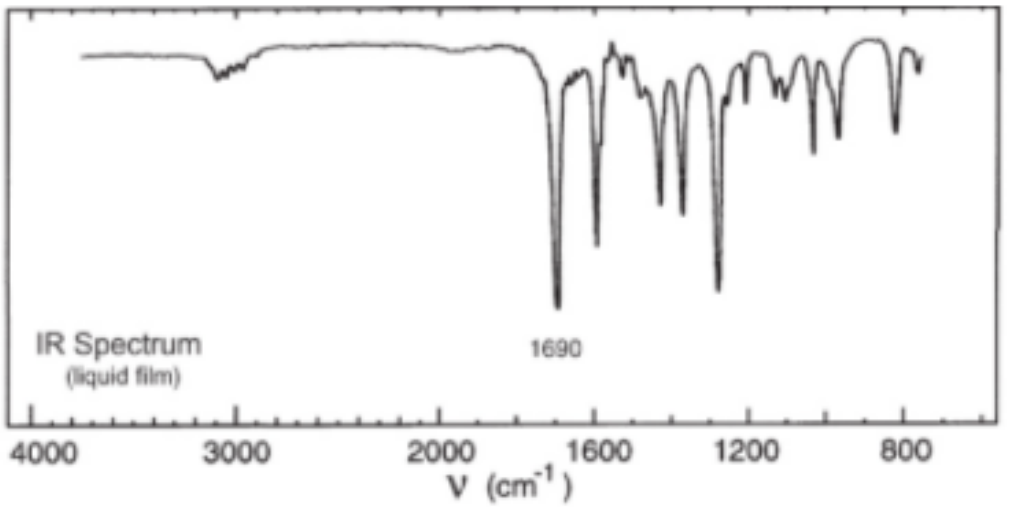
λ_{max} 263 nm ($\log_{10}\varepsilon$ 3.5)

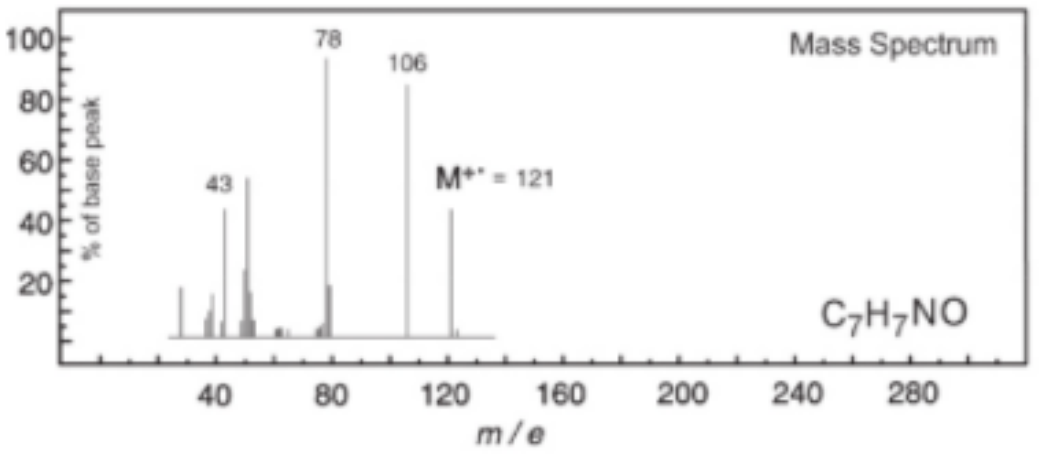
solvent : methanol





Problem 248



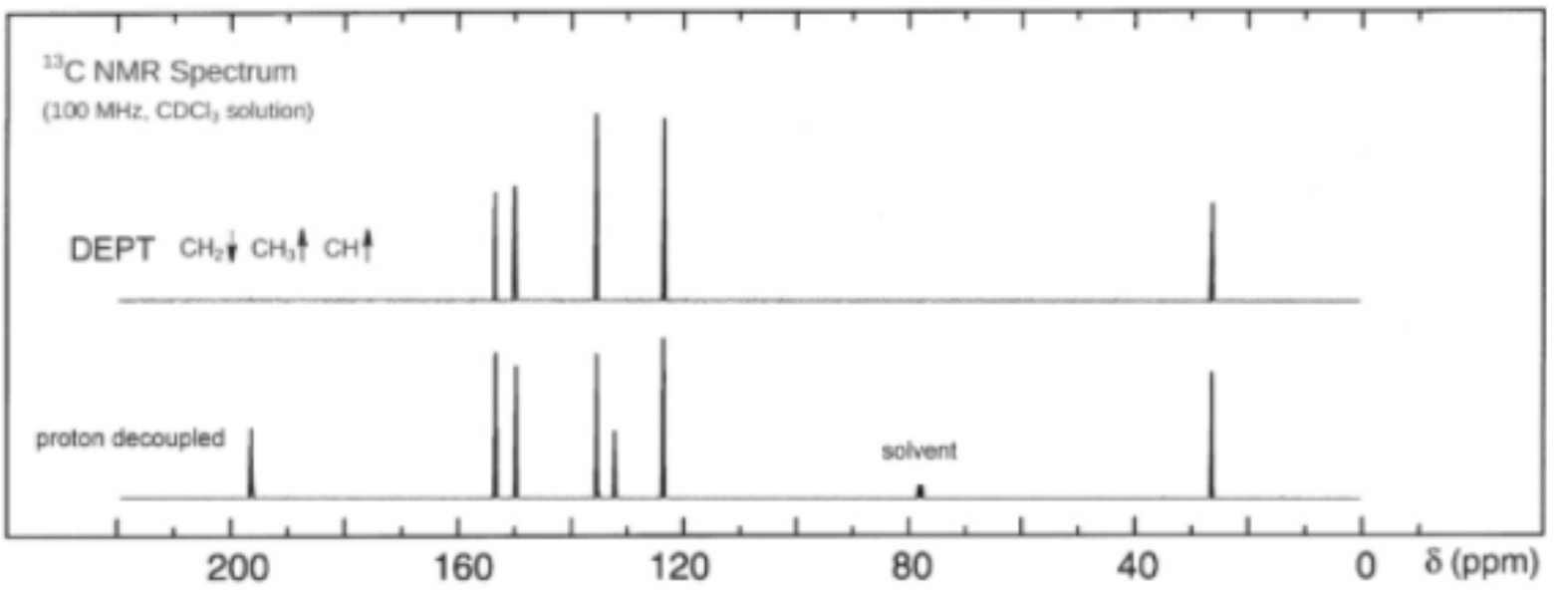


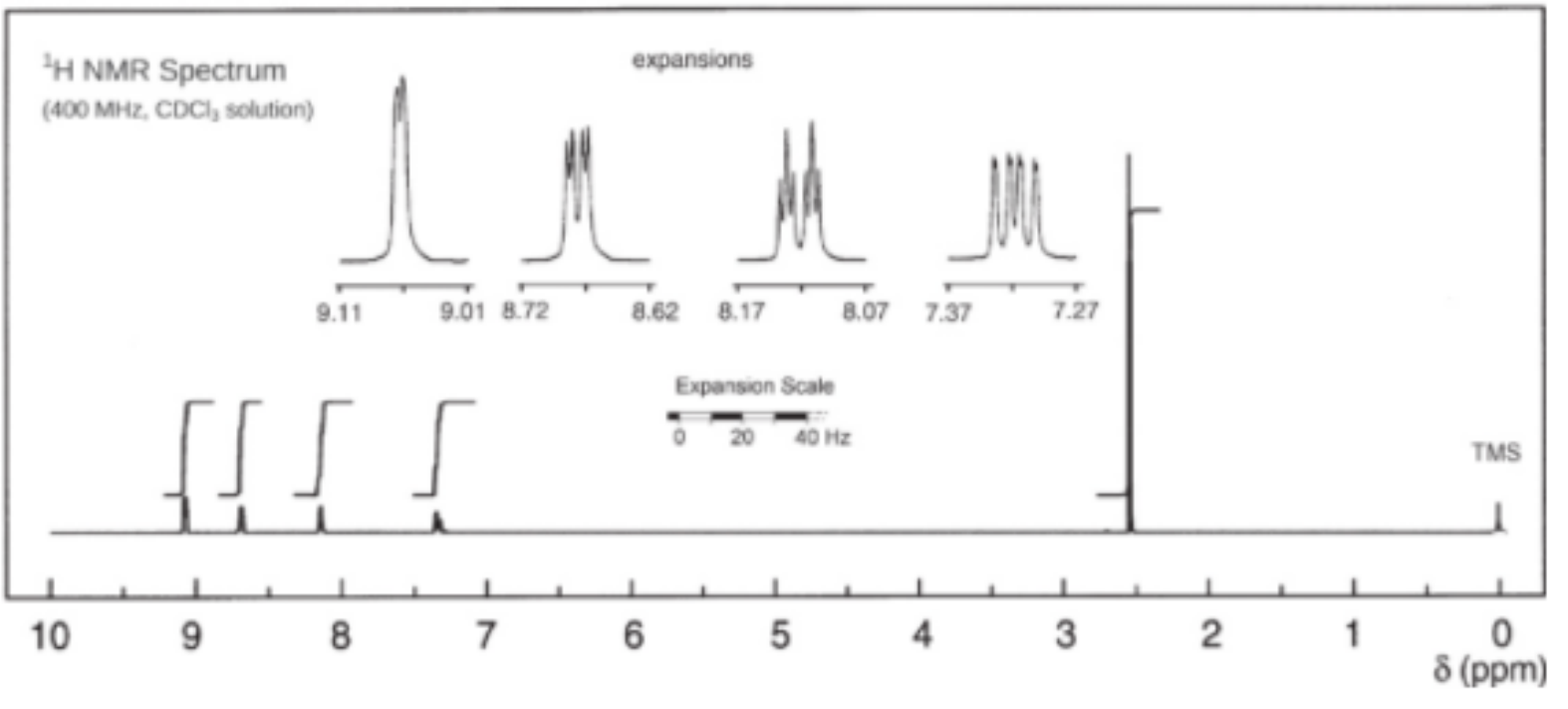
UV Spectrum

λ_{max} 228 nm ($\log_{10}\varepsilon$ 3.9)

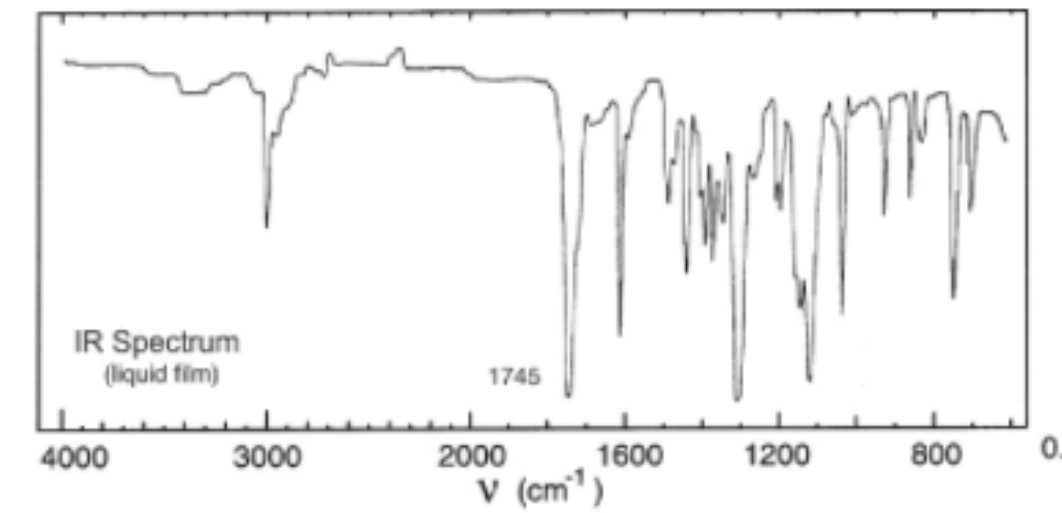
λ_{max} 267 nm ($\log_{10}\varepsilon$ 3.5)

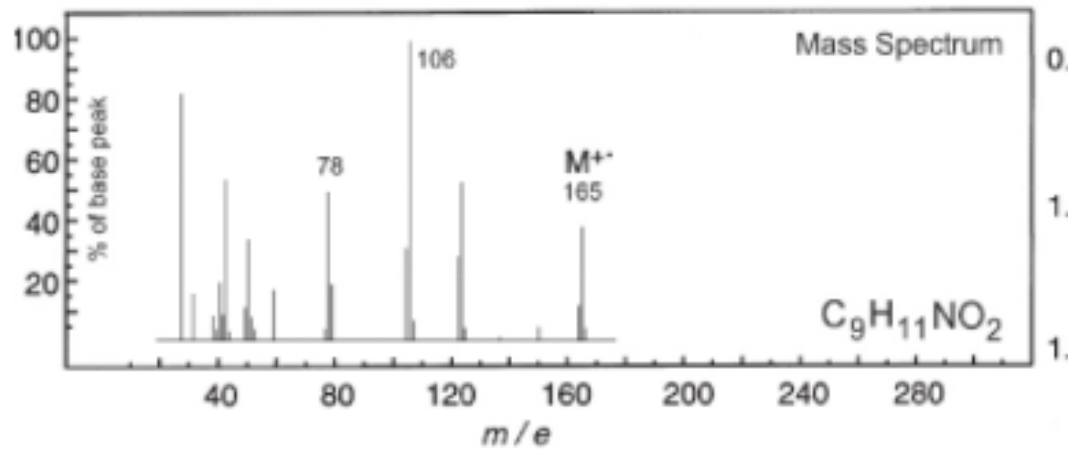
solvent : ethanol

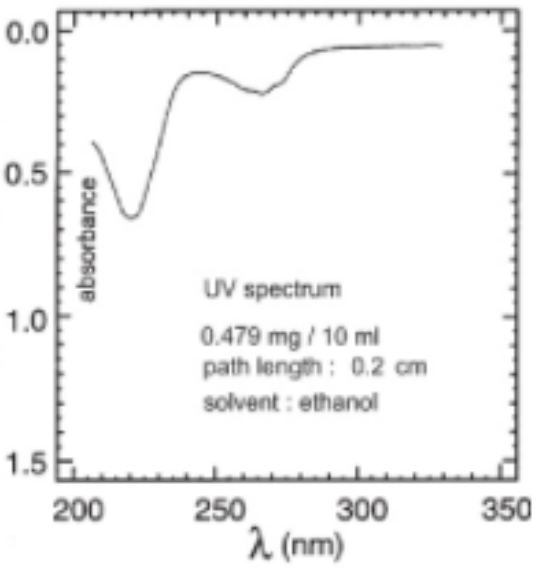


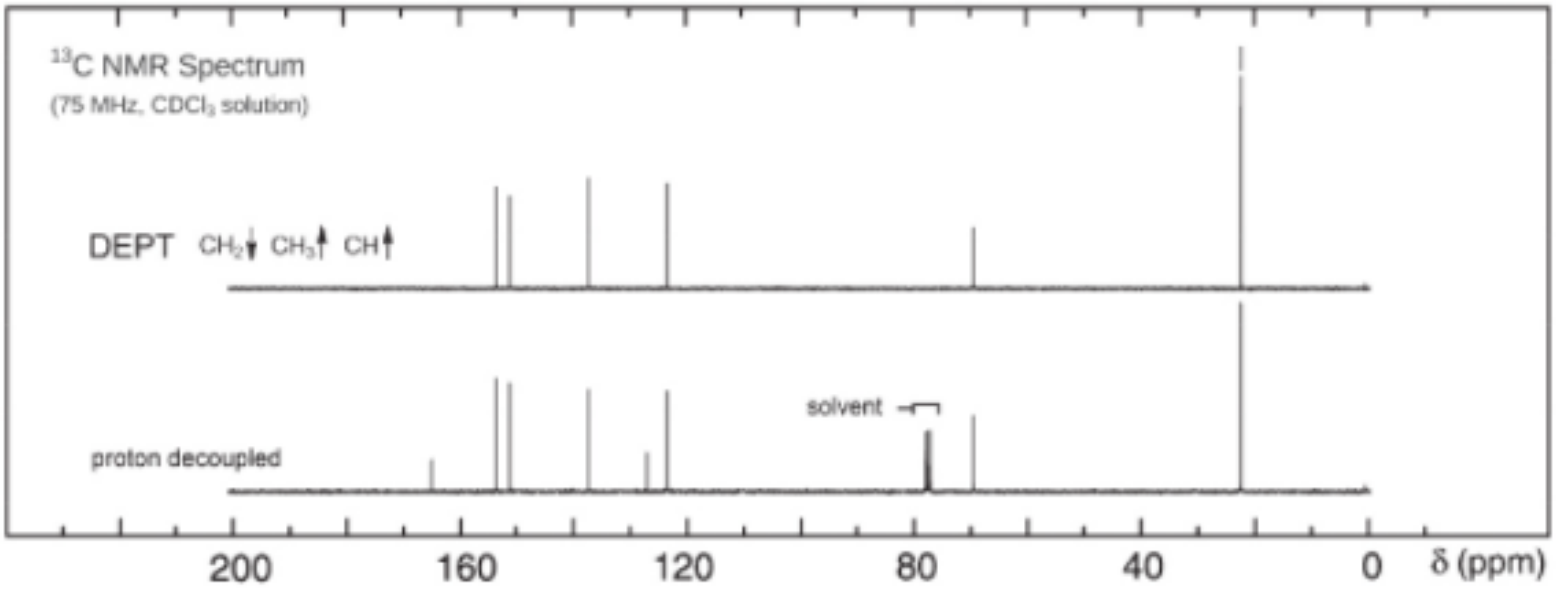


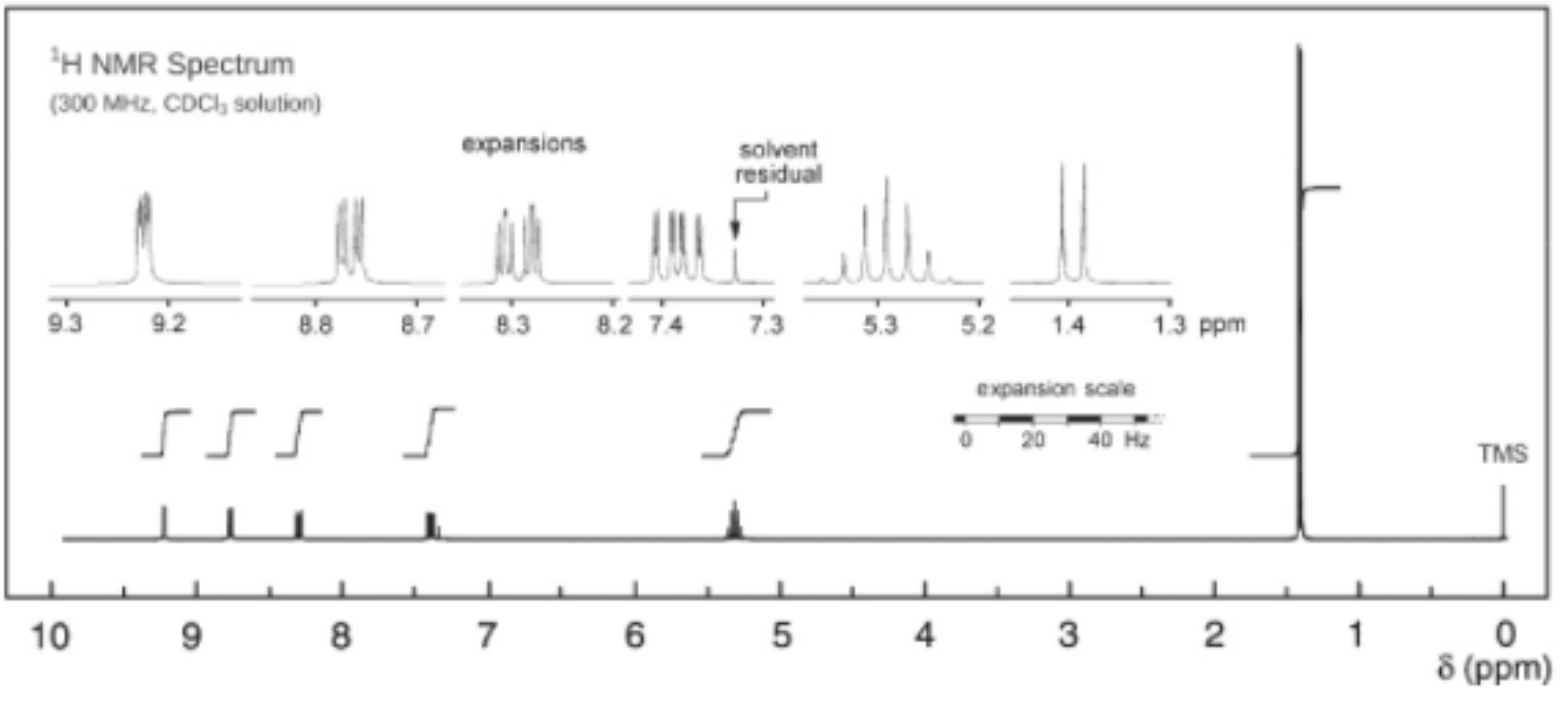
Problem 249


IR Spectrum
(liquid film)
1745
4000
3000
2000
1600
1200
800
ν (cm-1)

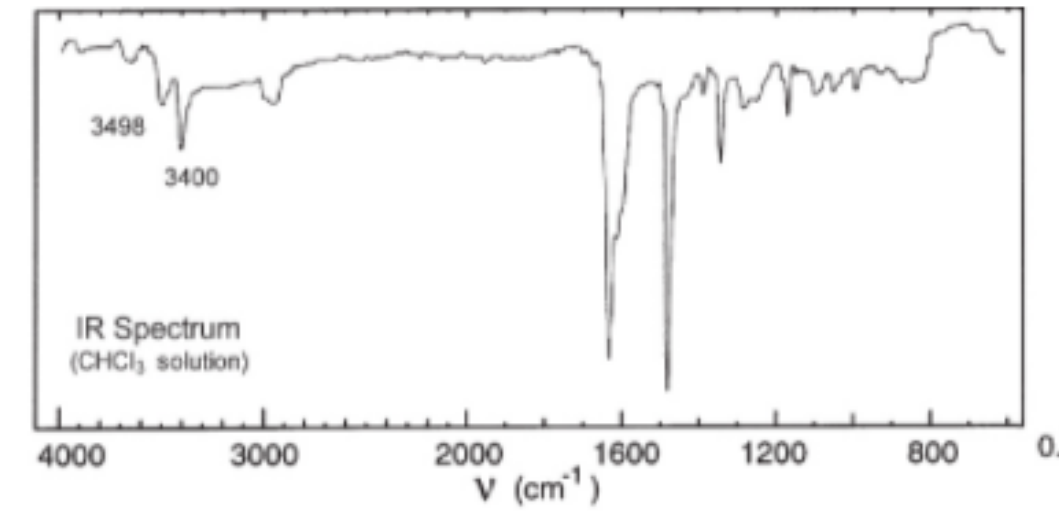

Mass Spectrum
% of base peak
106
78
M+·
165
C9H11NO2
40
80
120
160
200
240
280
m/e

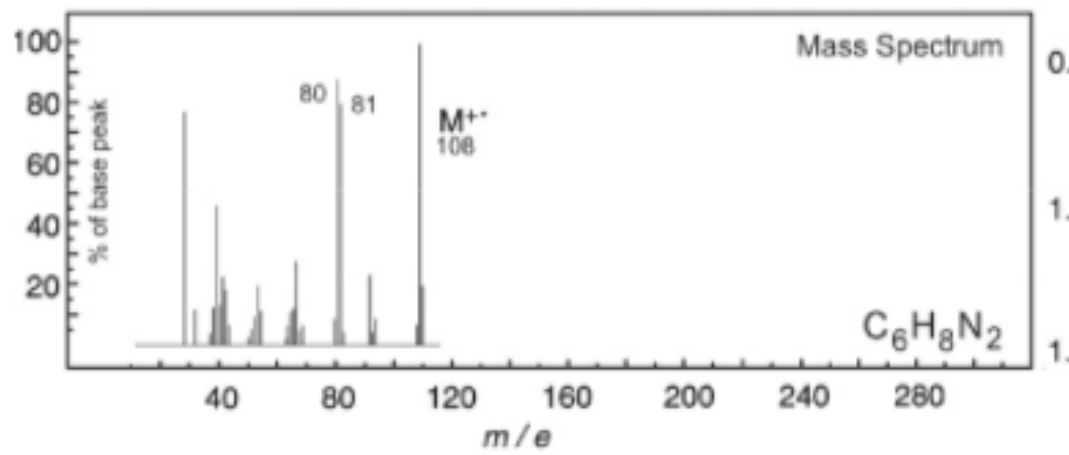

absorbance
UV spectrum
0.479 mg / 10 ml
path length : 0.2 cm
solvent : ethanol
200
250
300
350
λ (nm)

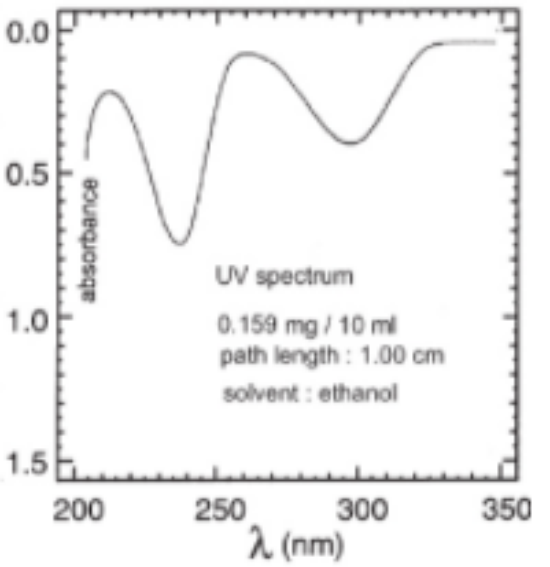

13C NMR Spectrum
(75 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

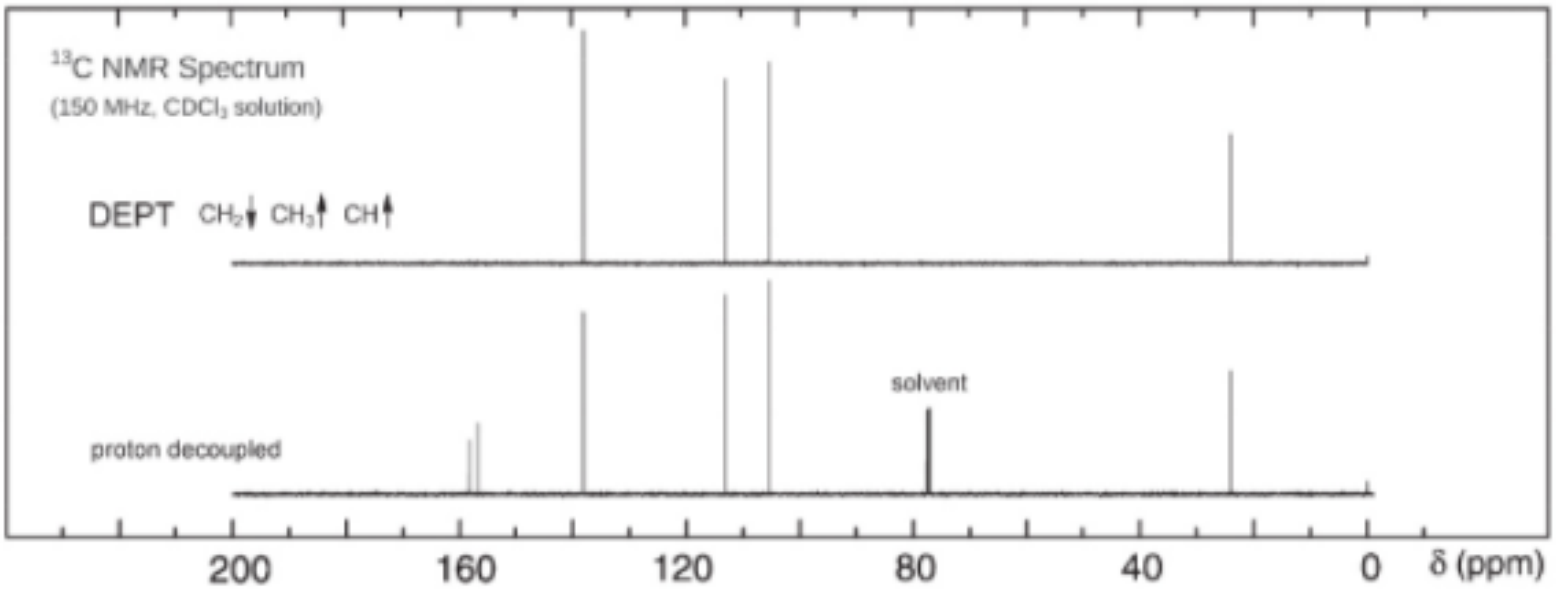

1H NMR Spectrum
(300 MHz, CDCl3 solution)
expansions
solvent residual
9.3
9.2
8.8
8.7
8.3
8.2
7.4
7.3
5.3
5.2
1.4
1.3 ppm
expansion scale
0
20
40 Hz
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

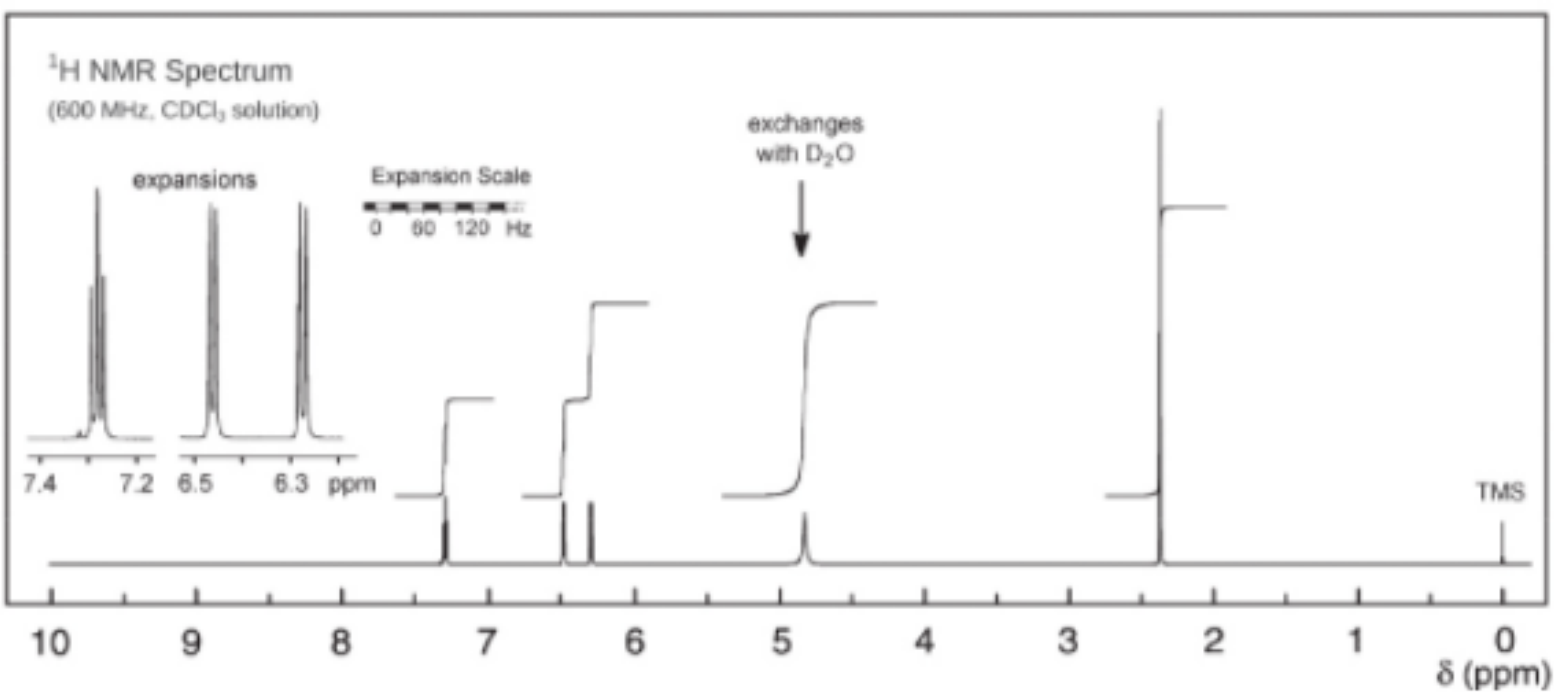
Problem 250


3498
3400
IR Spectrum
(CHCl3 solution)
4000
3000
2000
1600
1200
800
ν (cm-1)

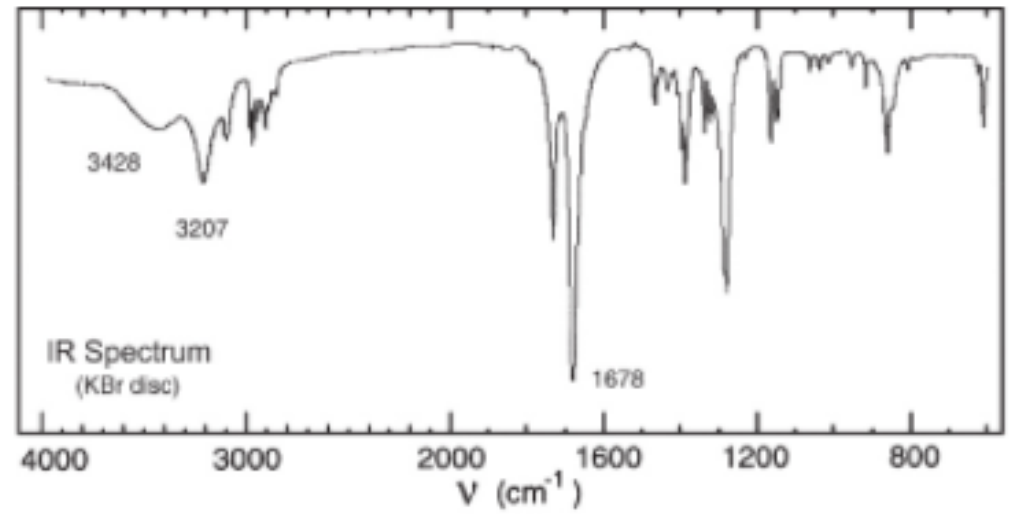

Mass Spectrum
% of base peak
80
81
M+·
108
C6H8N2
100
80
60
40
20
40
80
120
160
200
240
280
m/e

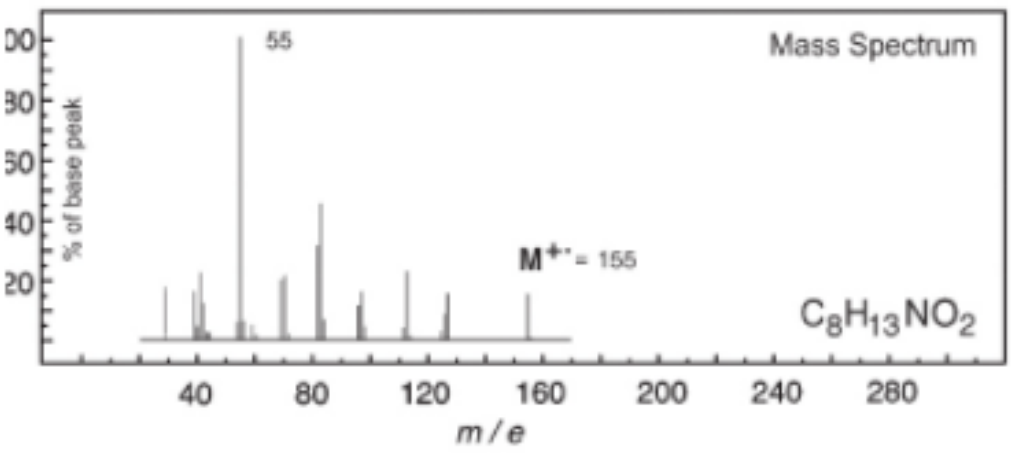

absorbance
UV spectrum
0.159 mg / 10 ml
path length : 1.00 cm
solvent : ethanol
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)


13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansions
Expansion Scale
0 60 120 Hz
exchanges
with D2O
7.4
7.2
6.5
6.3
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 251



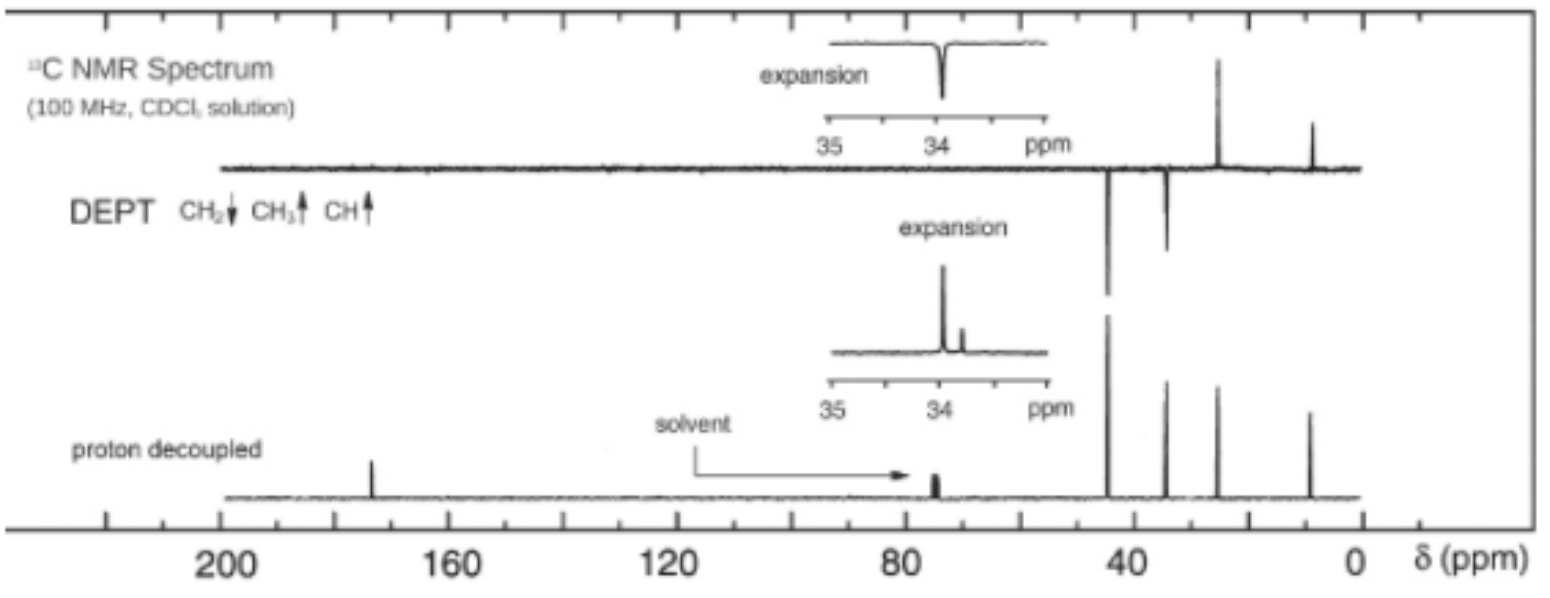


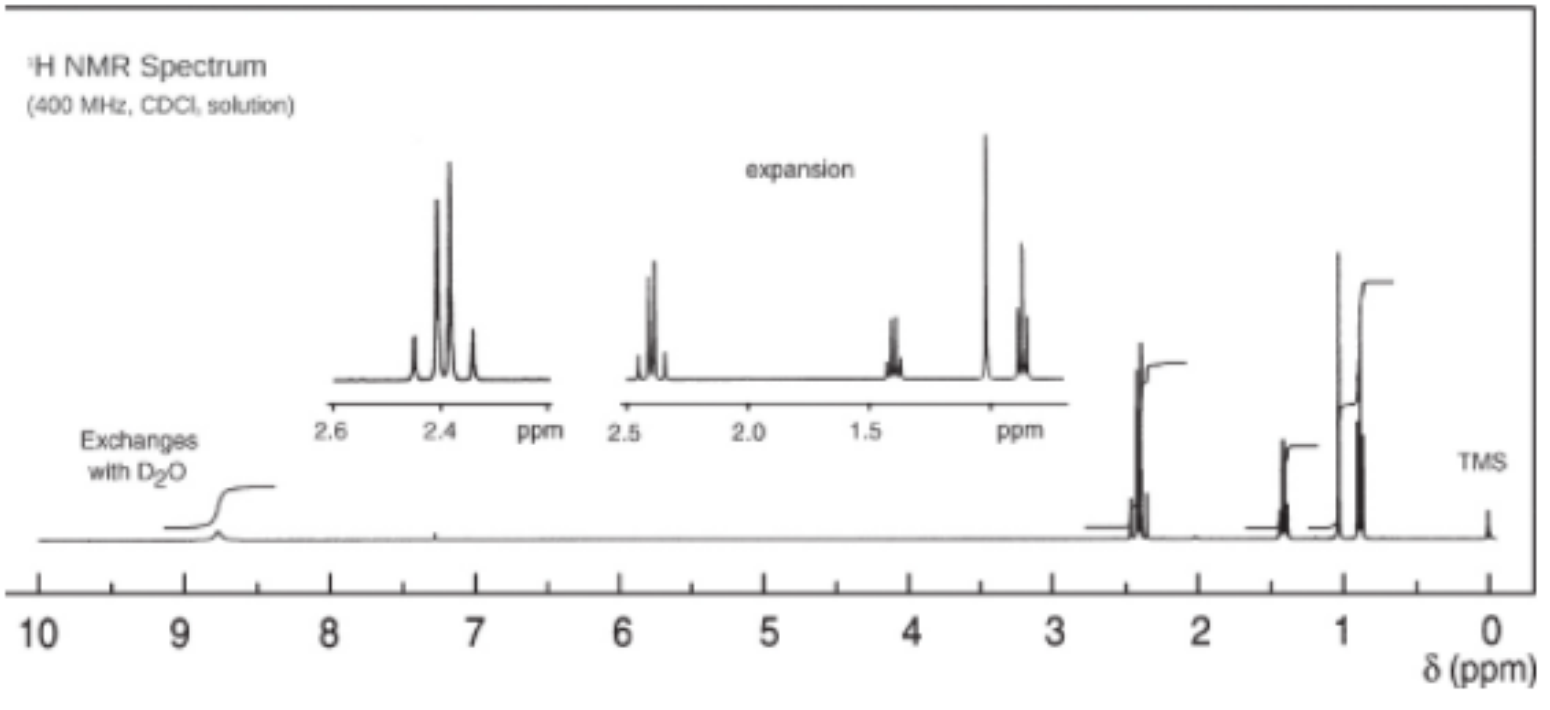
UV Spectrum

λ_{max} 230 nm ($\log_{10}\varepsilon$ 3.6) pH 11

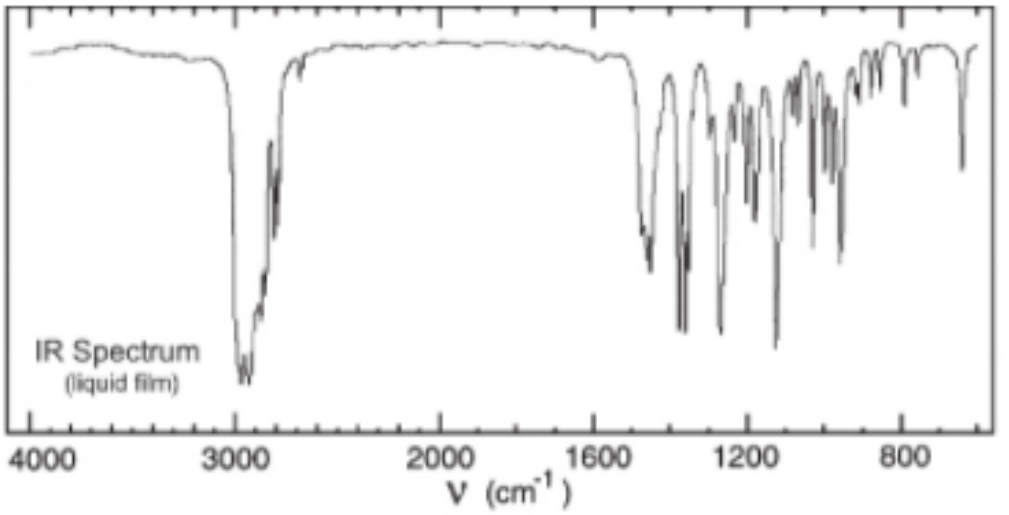
λ_{max} 230 nm ($\log_{10}\varepsilon$ 4.4) pH 13

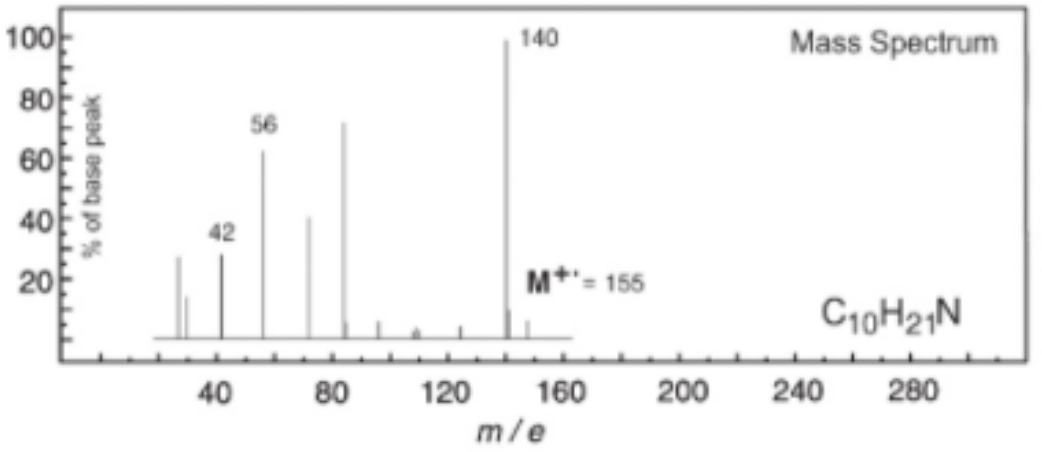
solvent : water



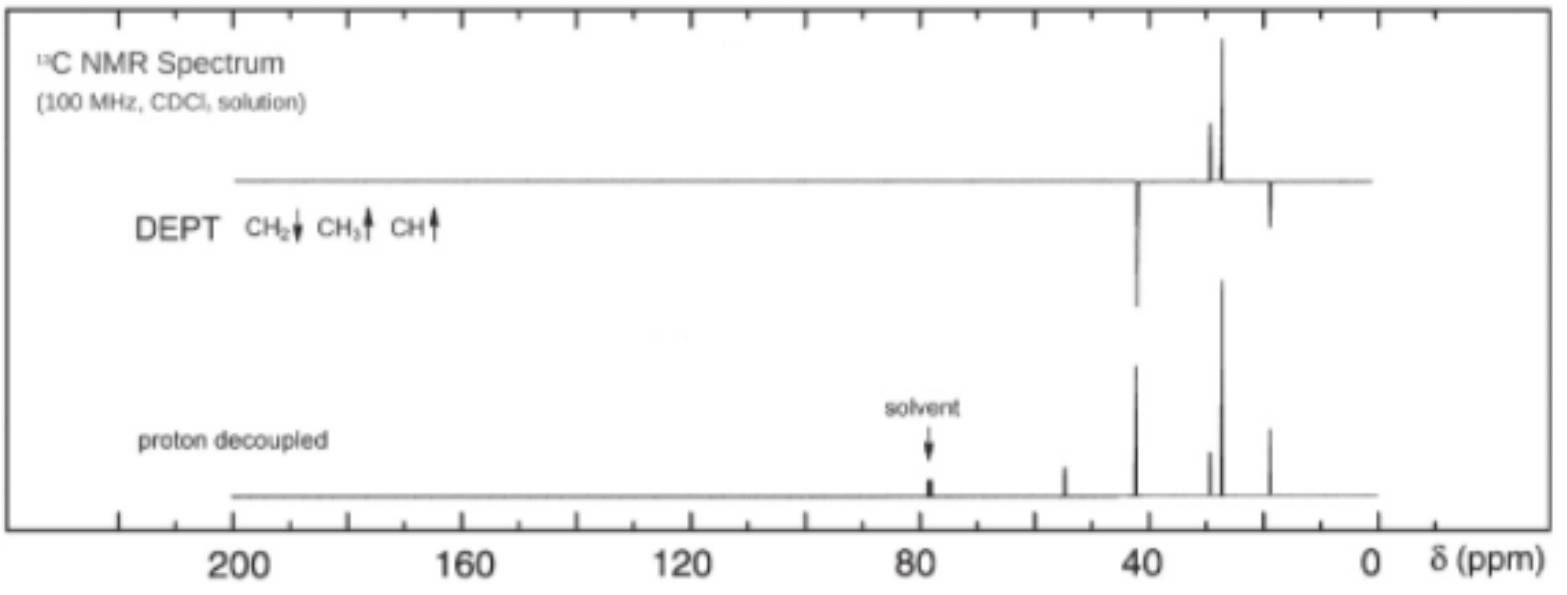


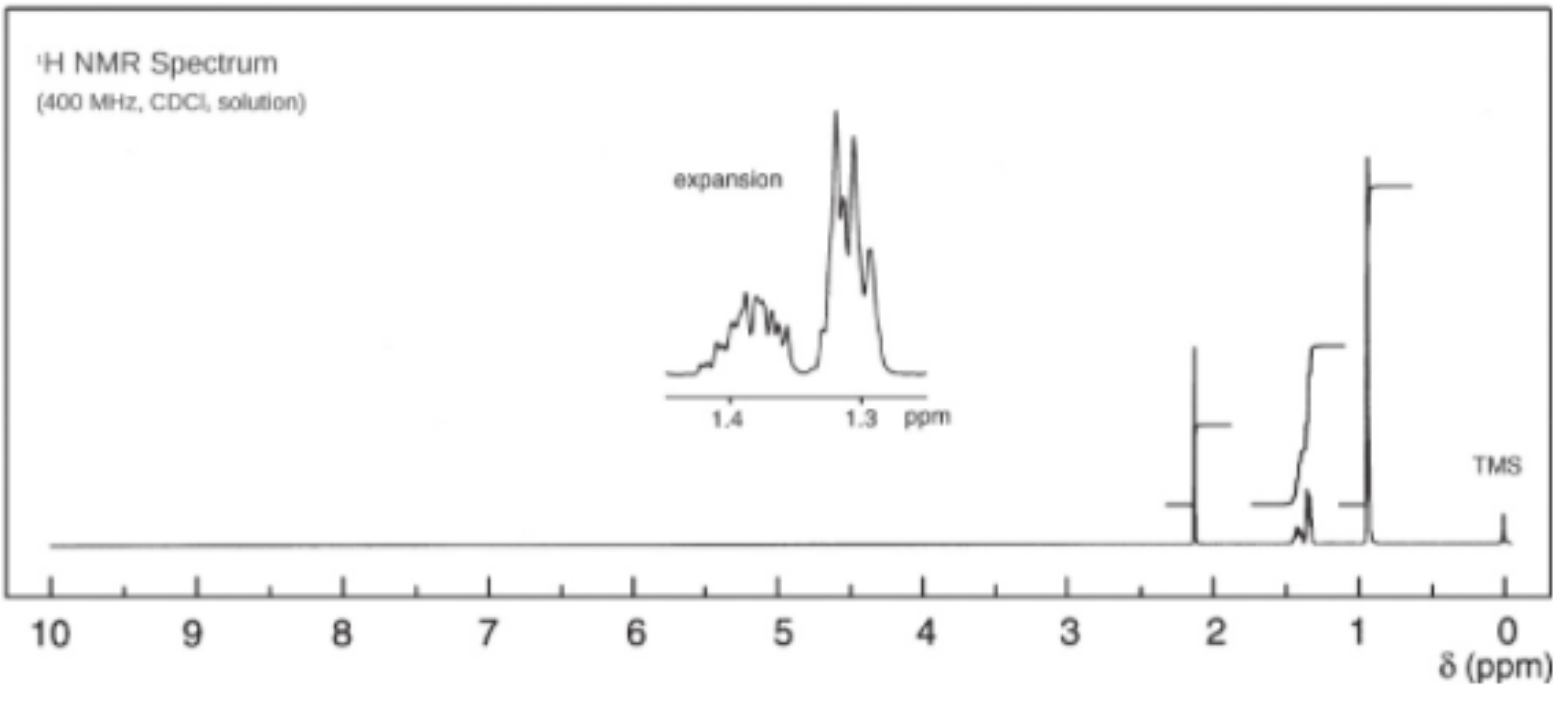
Problem 252

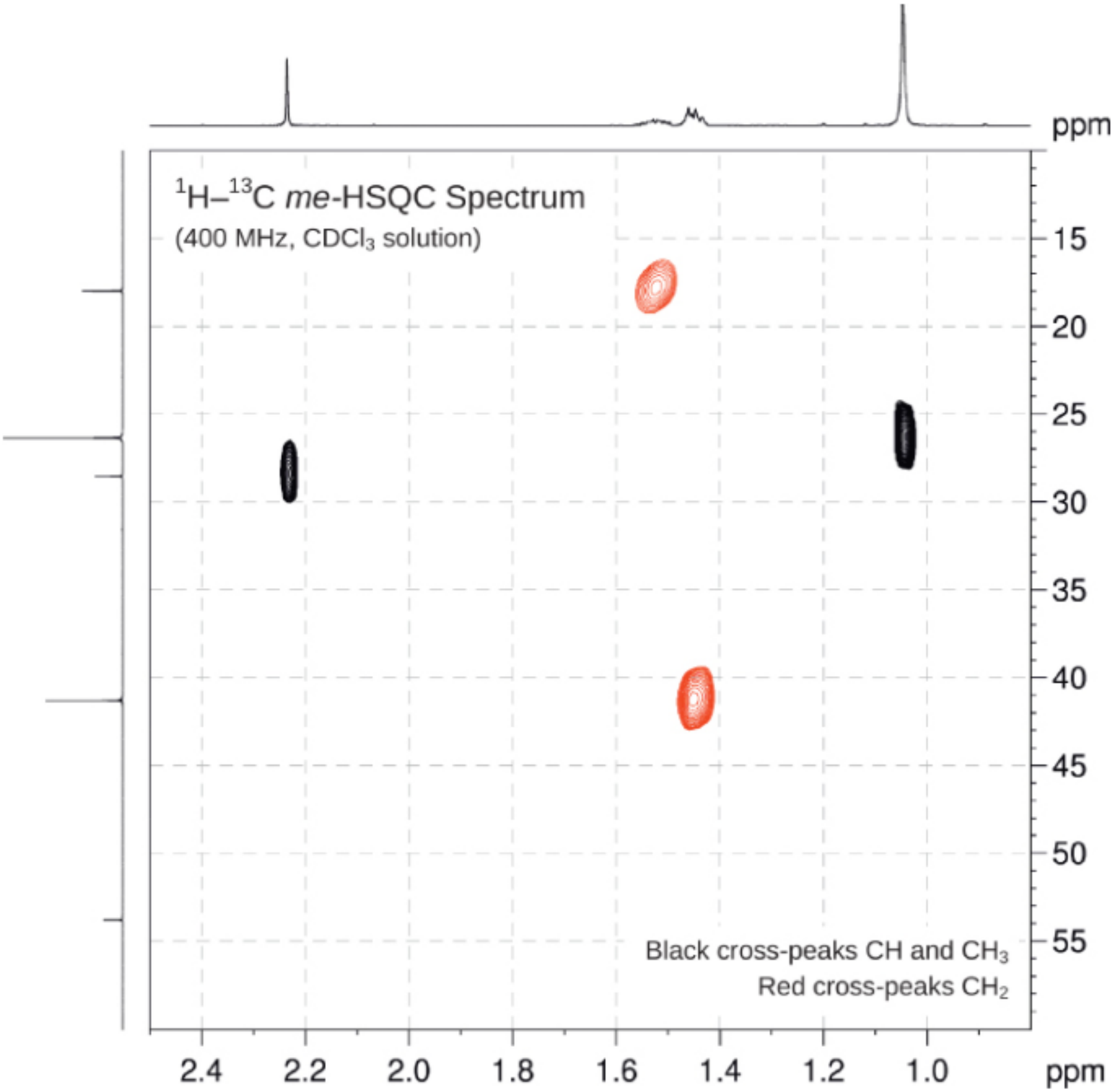




No significant UV absorption above 220 nm

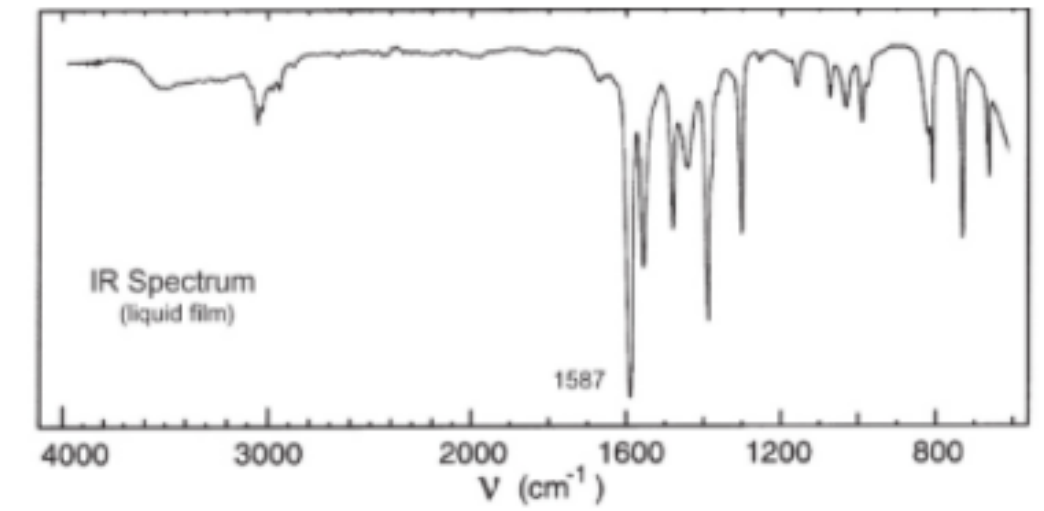


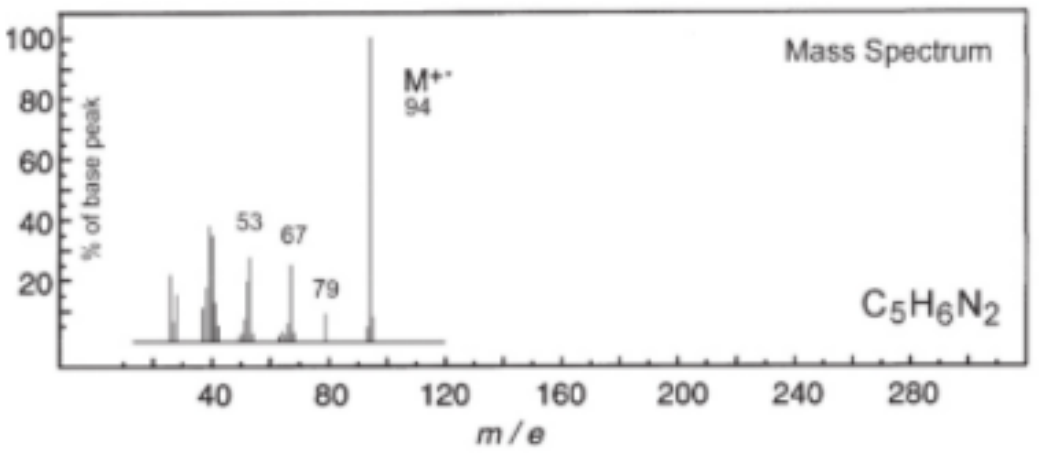



ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
15
20
25
30
35
40
45
50
55
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
ppm

Problem 253

Problem 253



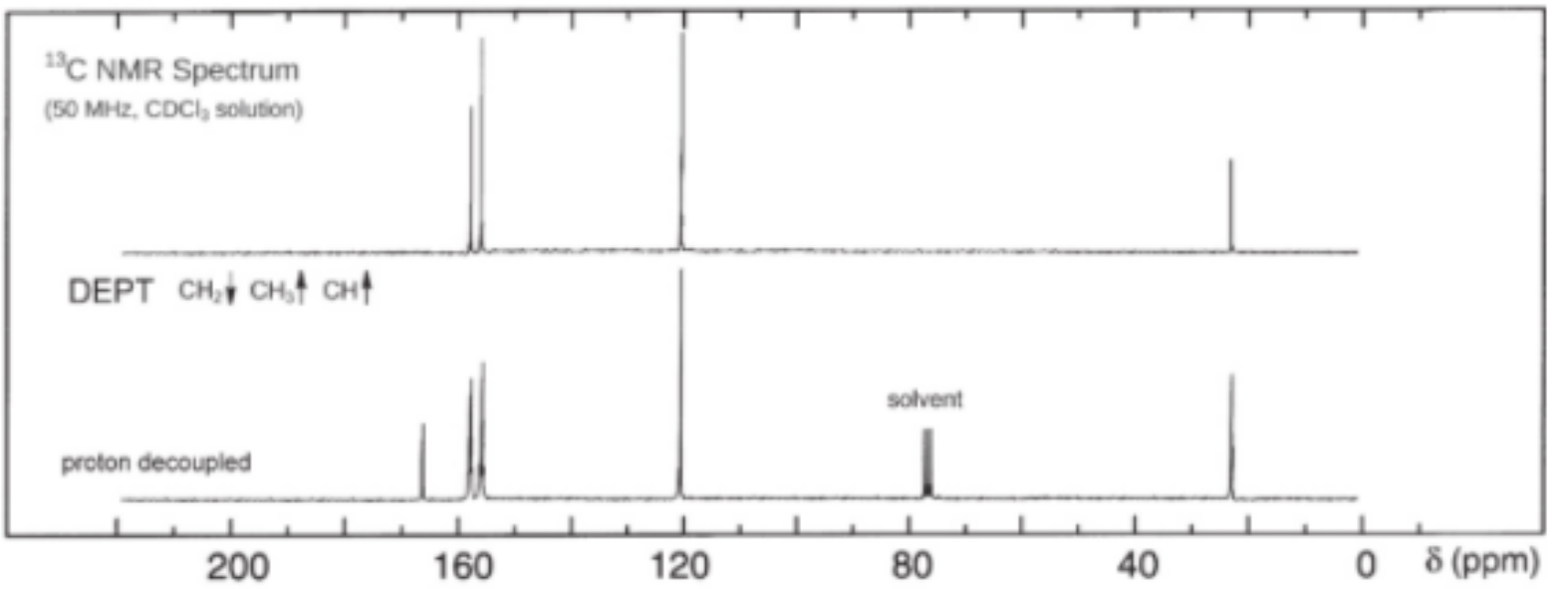


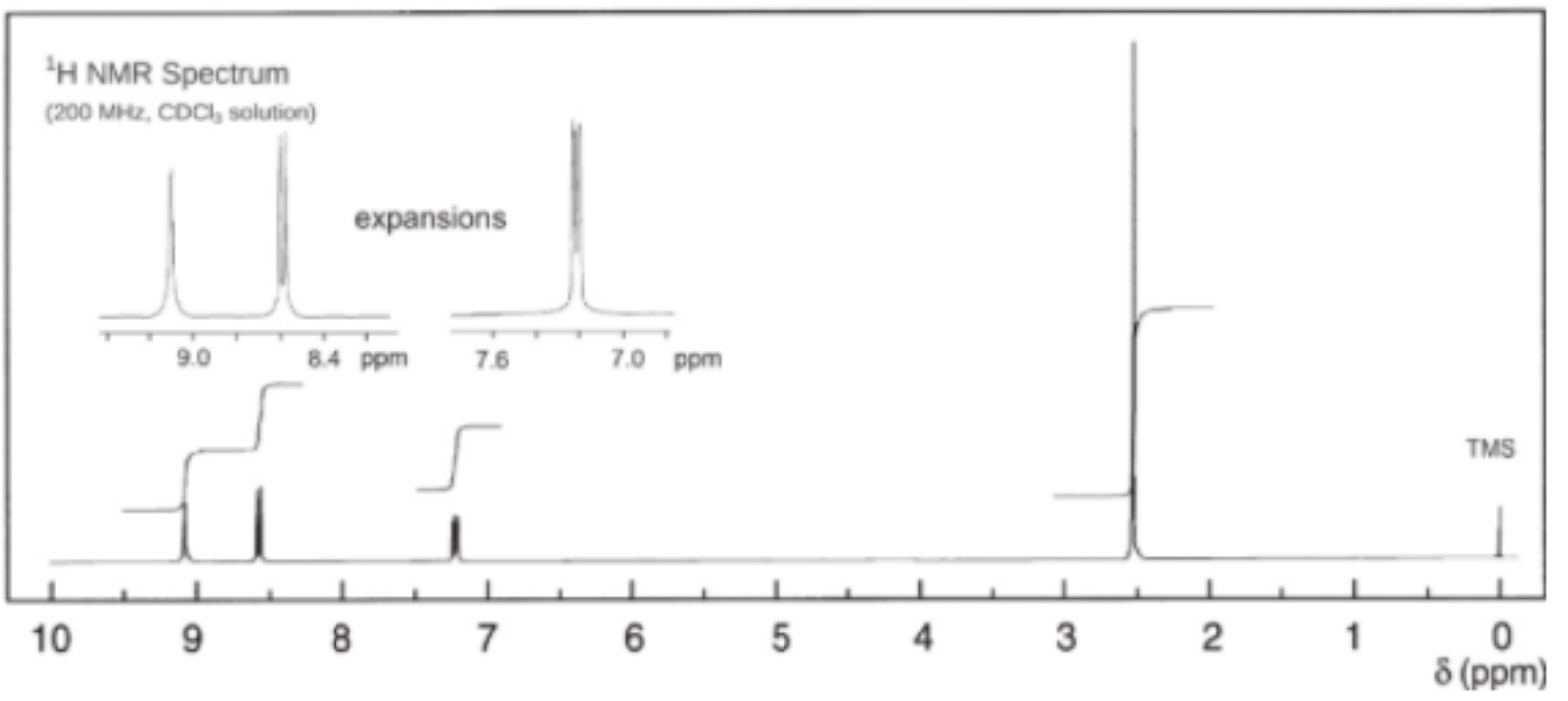
UV Spectrum

λ_{max} 270 nm ($\log_{10}\varepsilon$ 2.5)

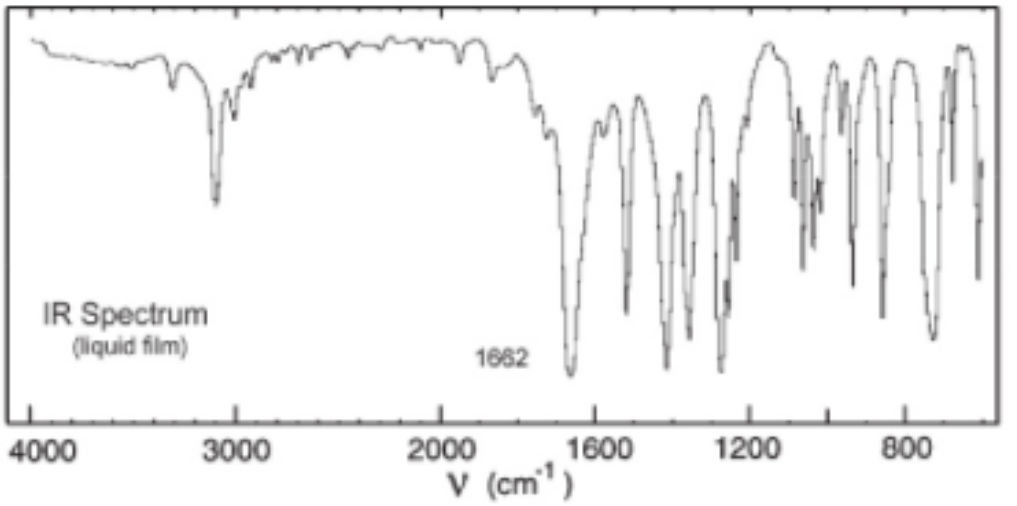
λ_{max} 240 nm ($\log_{10}\varepsilon$ 3.4)

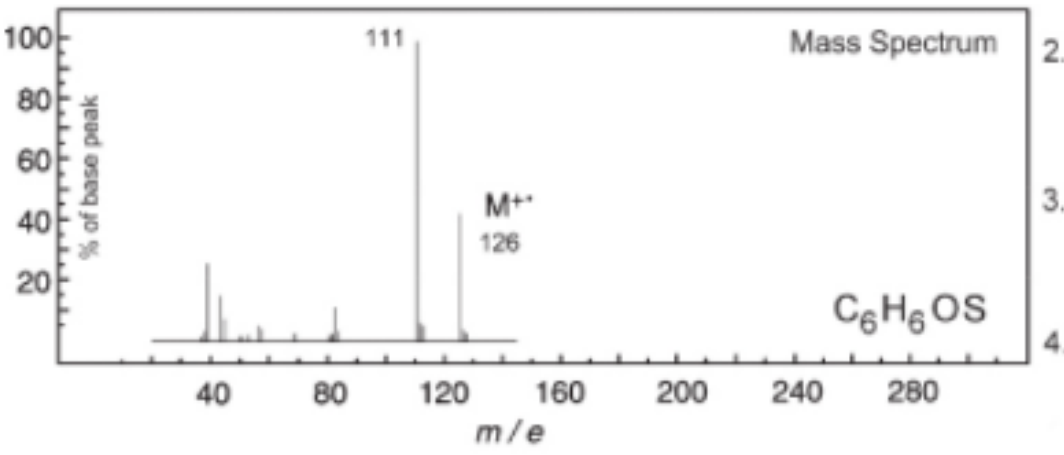
solvent : methanol

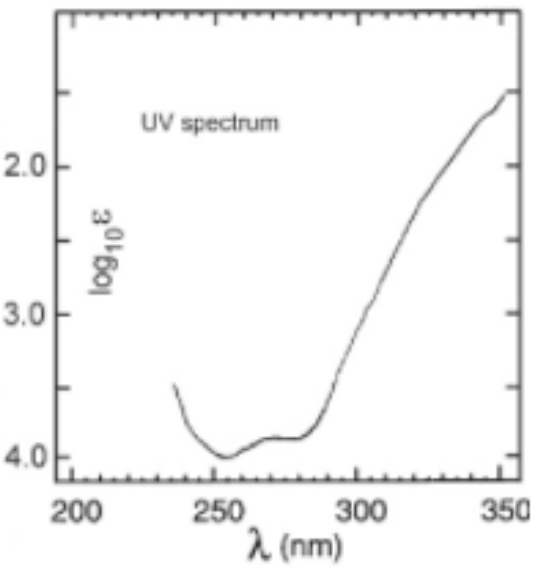


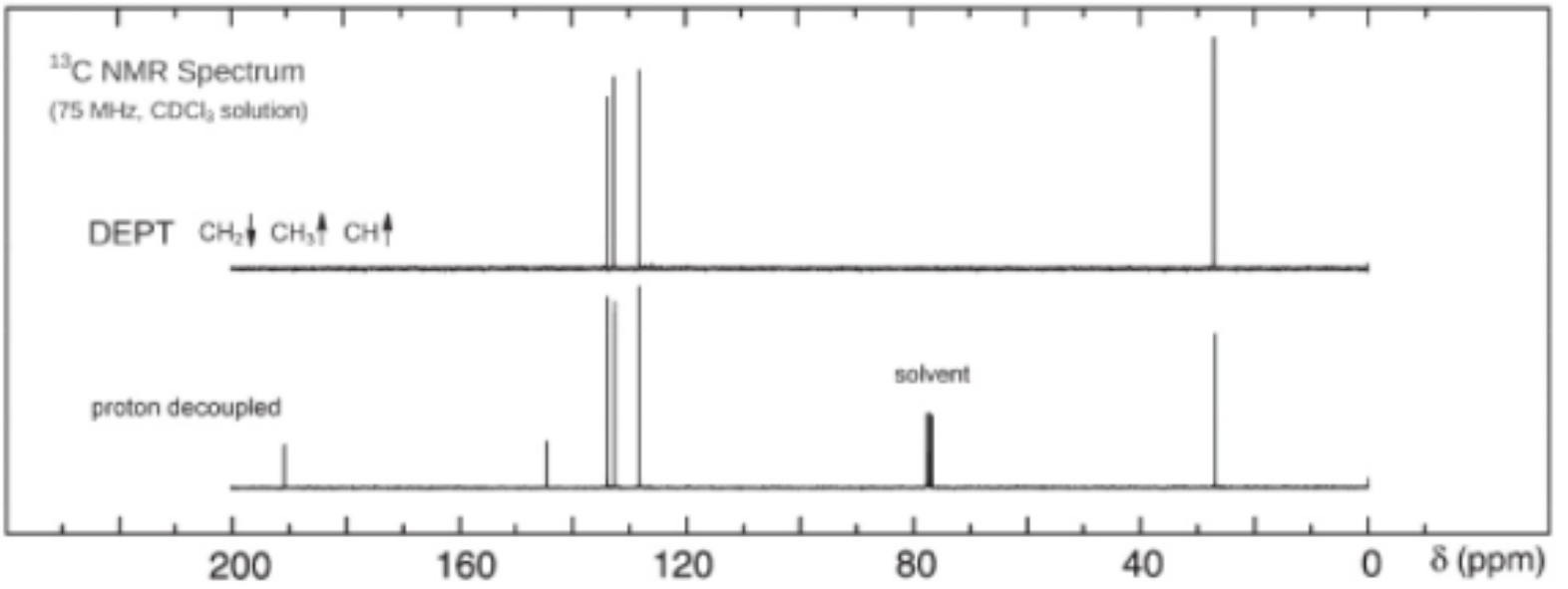


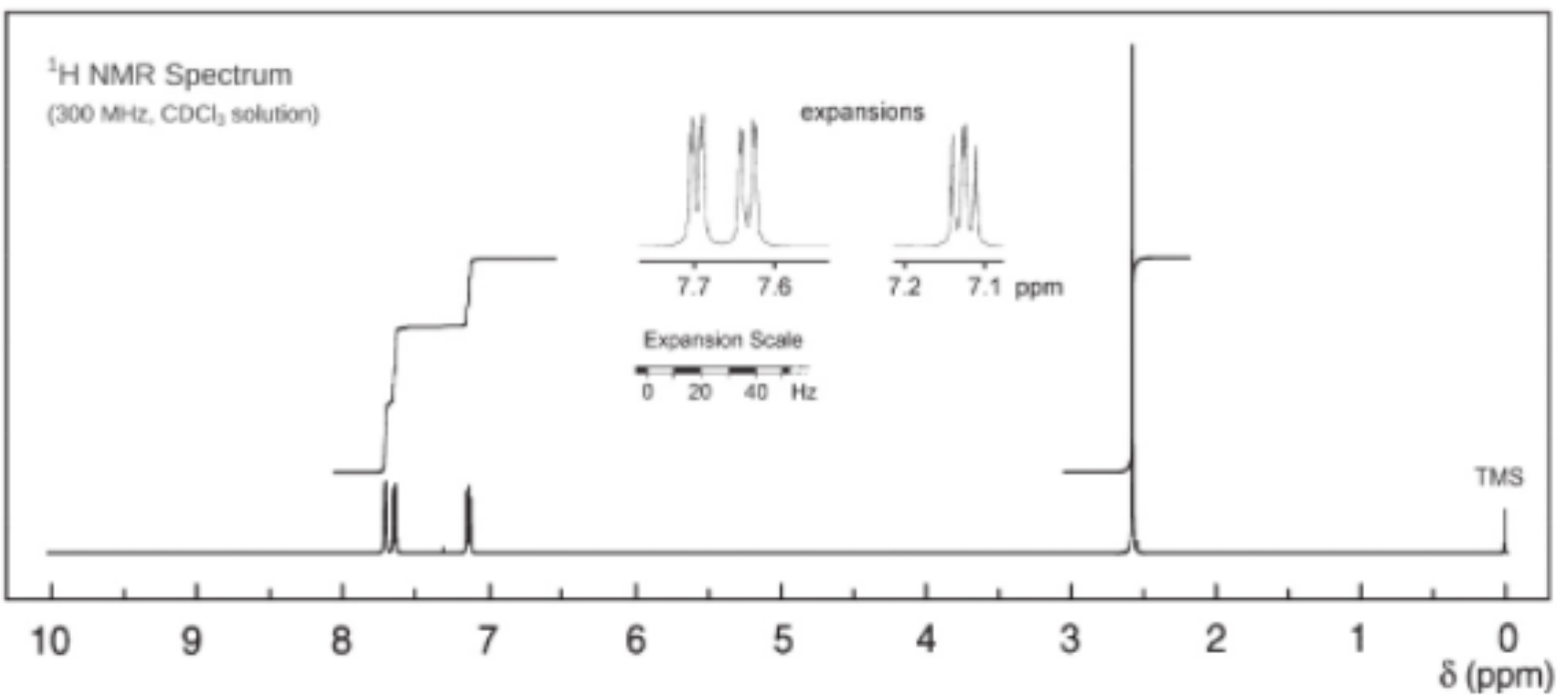
Problem 254


IR Spectrum
(liquid film)
1662
4000
3000
2000
1600
1200
800
V (cm-1)

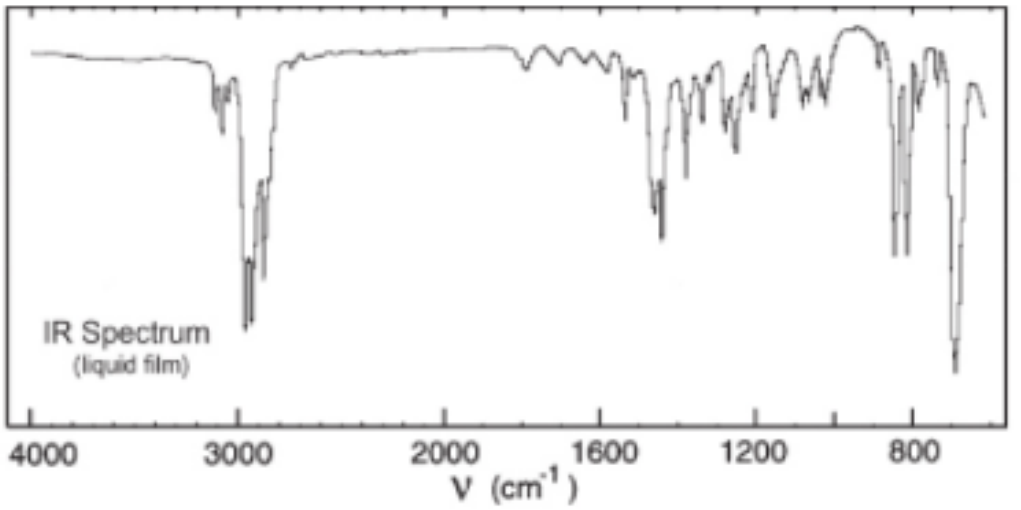

Mass Spectrum
111
M+·
126
% of base peak
100
80
60
40
20
C6H6OS
40
80
120
160
200
240
280
m/e

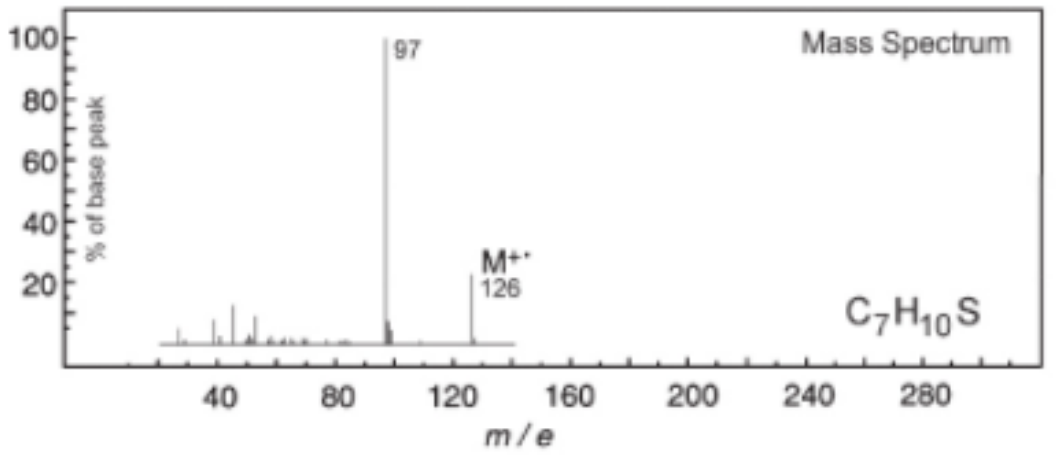

UV spectrum
log10ε
2.0
3.0
4.0
200
250
300
350
λ (nm)


13C NMR Spectrum
(75 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(300 MHz, CDCl3 solution)
expansions
7.7
7.6
7.2
7.1
ppm
Expansion Scale
0
20
40
Hz
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

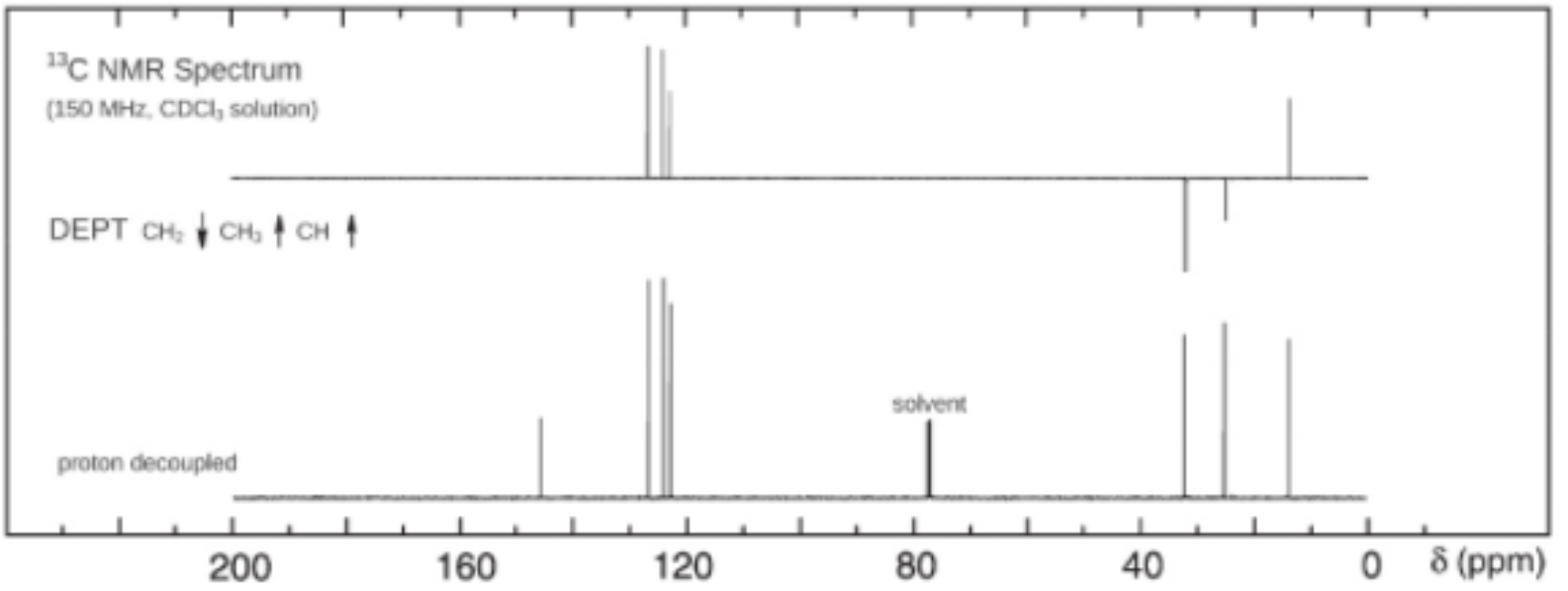
Problem 255

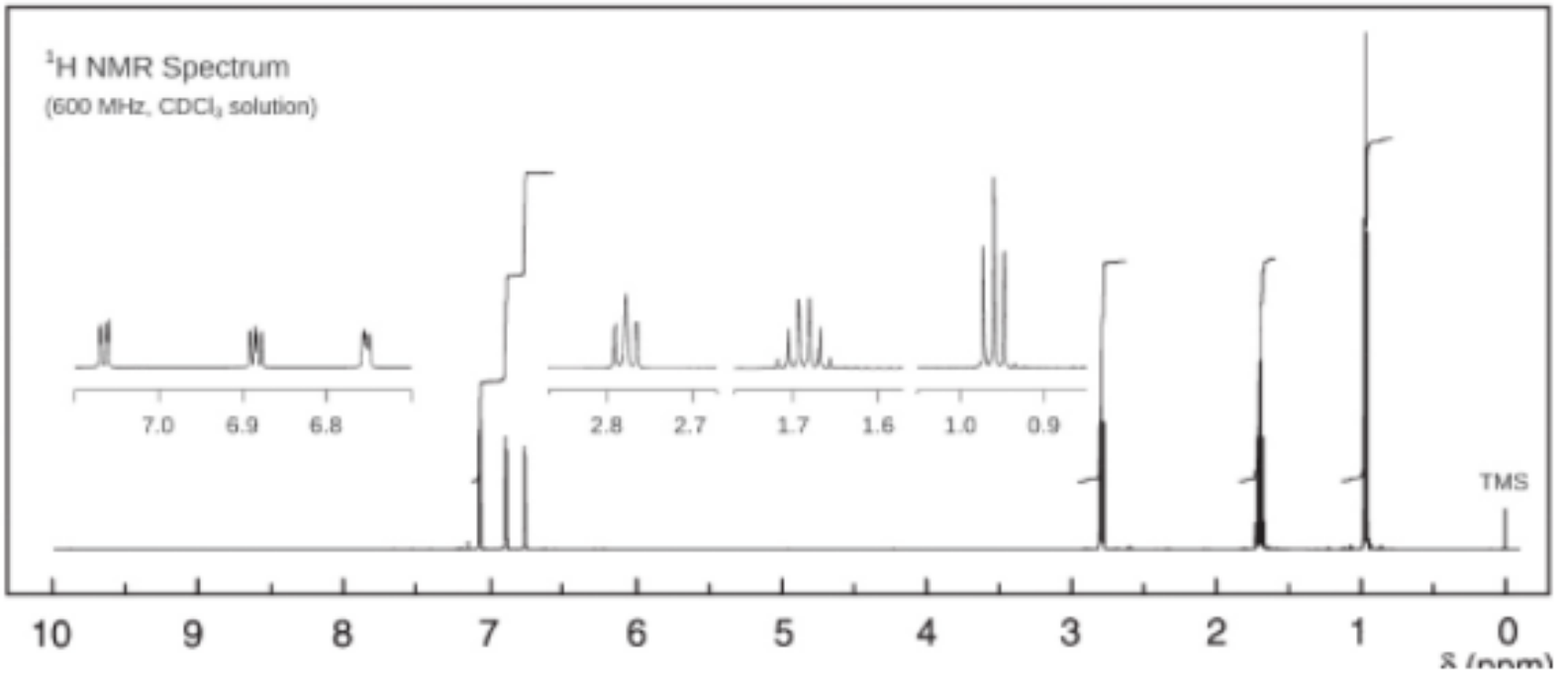


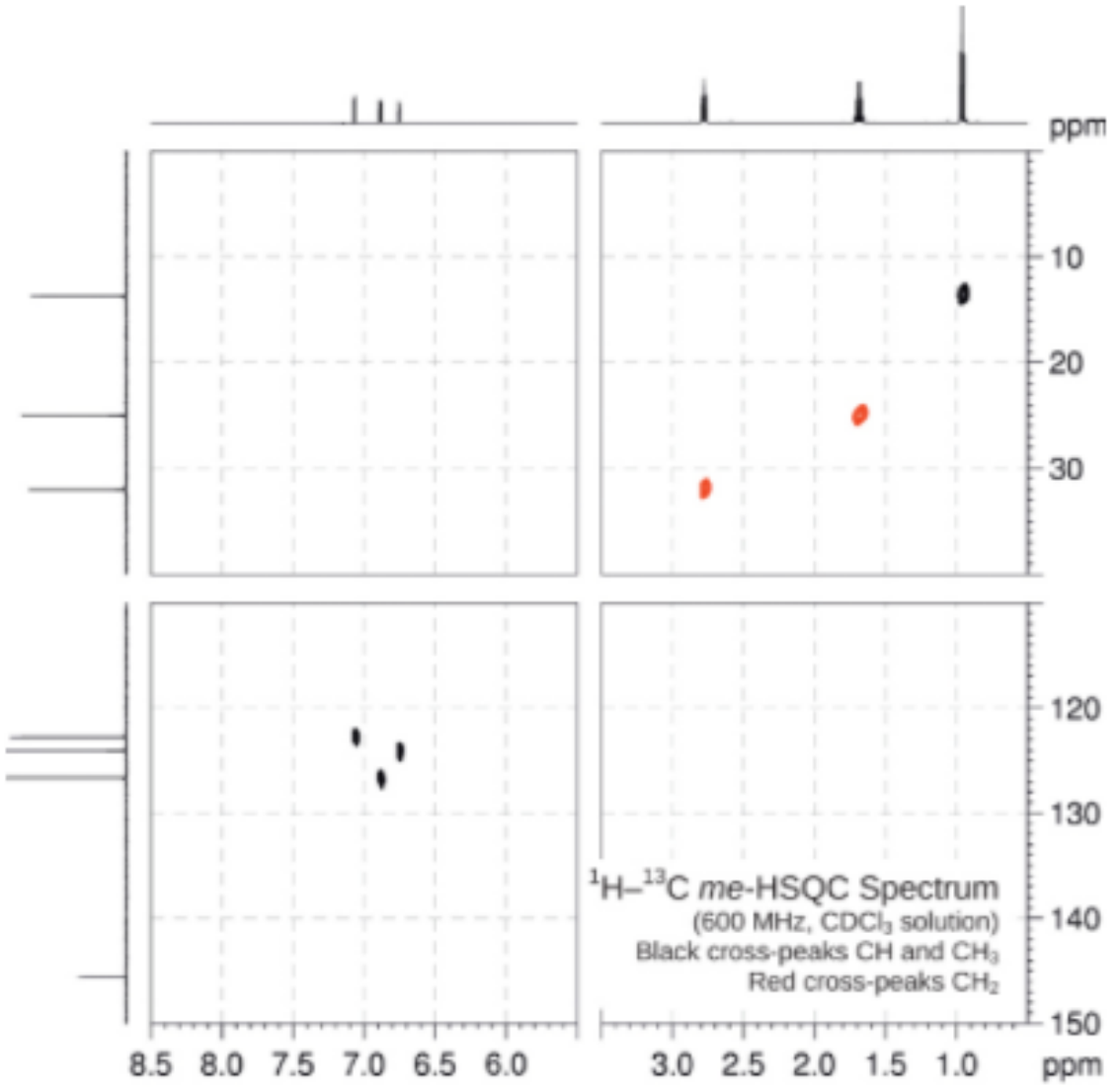


UV Spectrum

λ_{max} 237 nm ($\log_{10}\varepsilon$ 4.0)

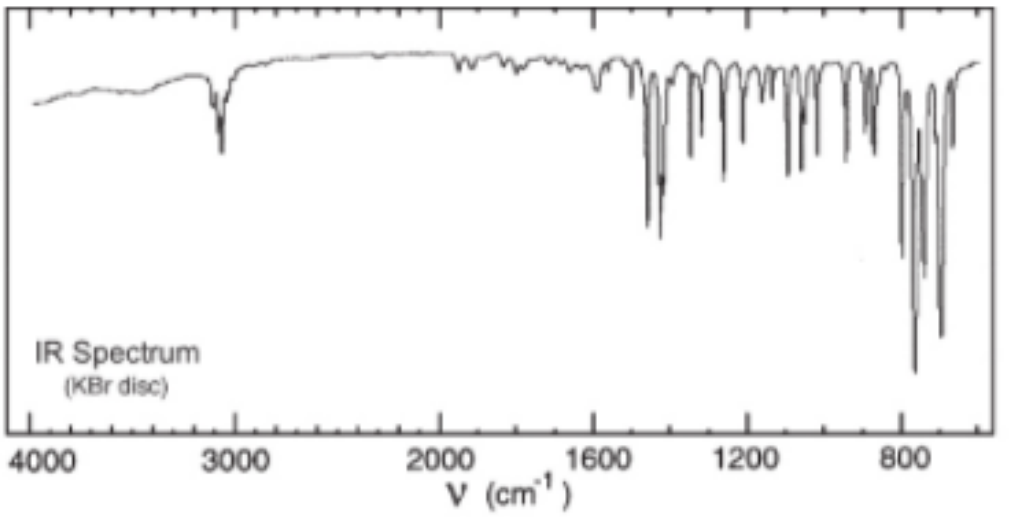


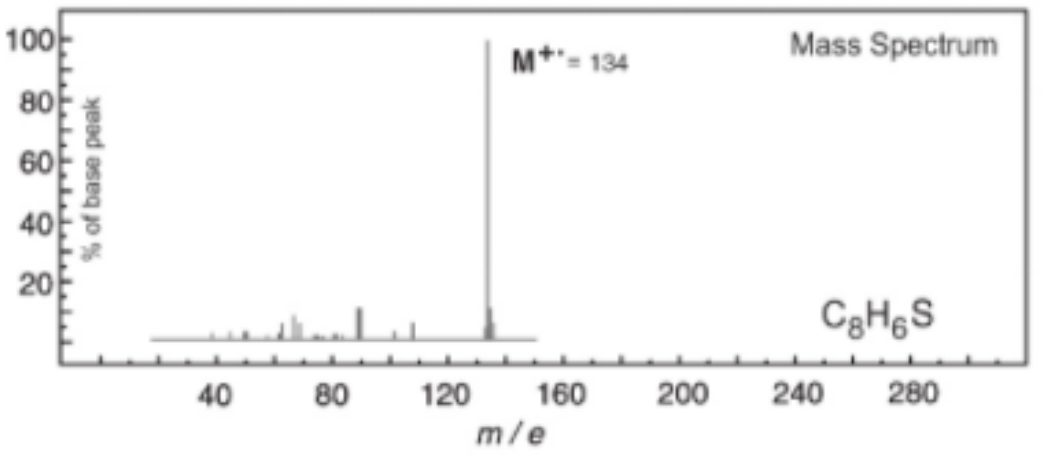



ppm
10
20
30
120
130
140
150
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
8.5 8.0 7.5 7.0 6.5 6.0
3.0 2.5 2.0 1.5 1.0
ppm

ppm
$^{1}H–^{1}H$ COSY Spectrum
(600 MHz, $CDCl_3$ solution)
1
2
3
6
7
8
8.5 8.0 7.5 7.0 6.5 6.0
3.0 2.5 2.0 1.5 1.0
ppm

Problem 256





UV Spectrum

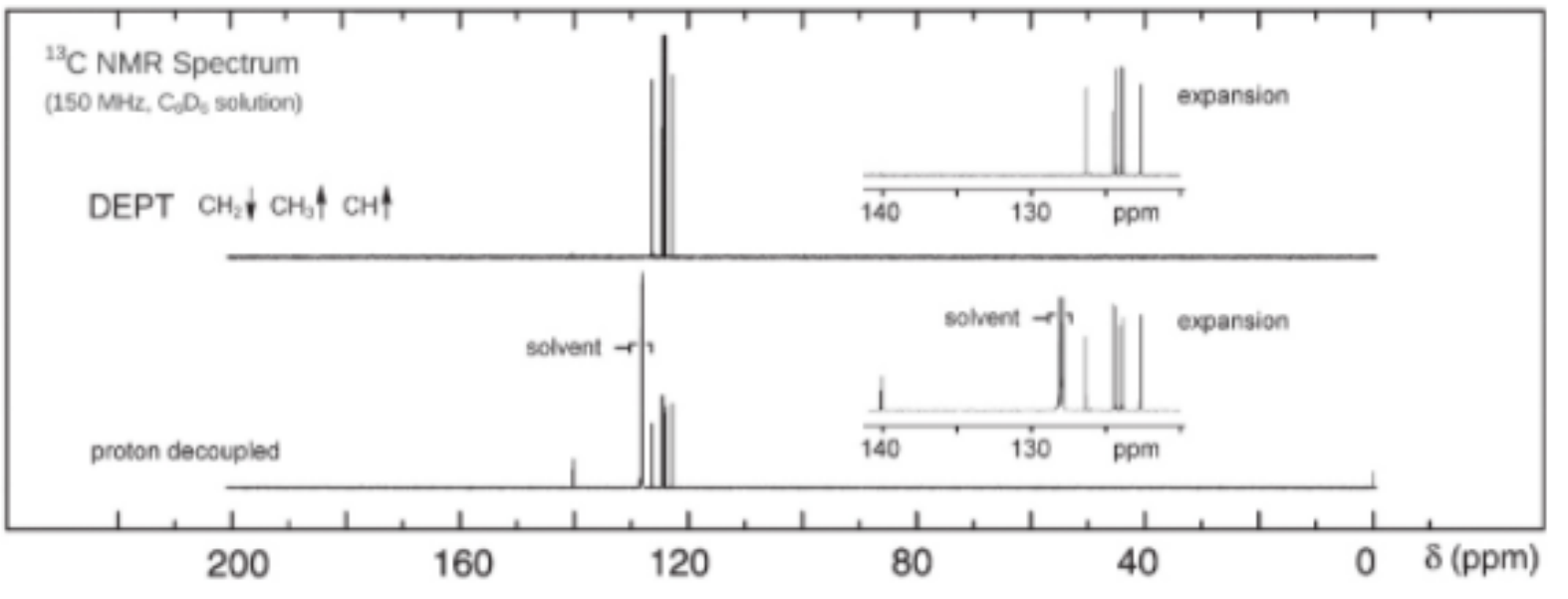
λ_{max} 226 nm ($\log_{10}\varepsilon$ 4.4)

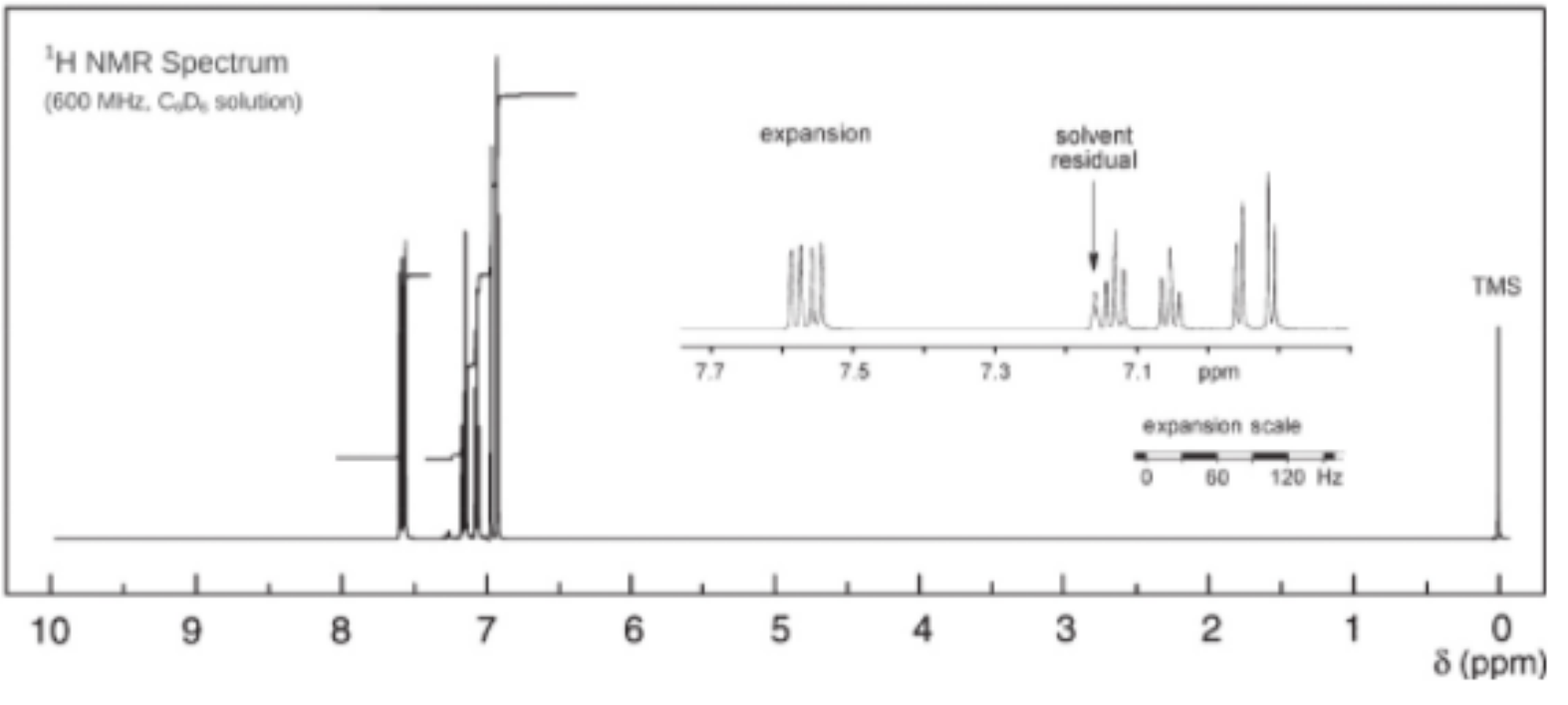
λ_{max} 256 nm ($\log_{10}\varepsilon$ 3.7)

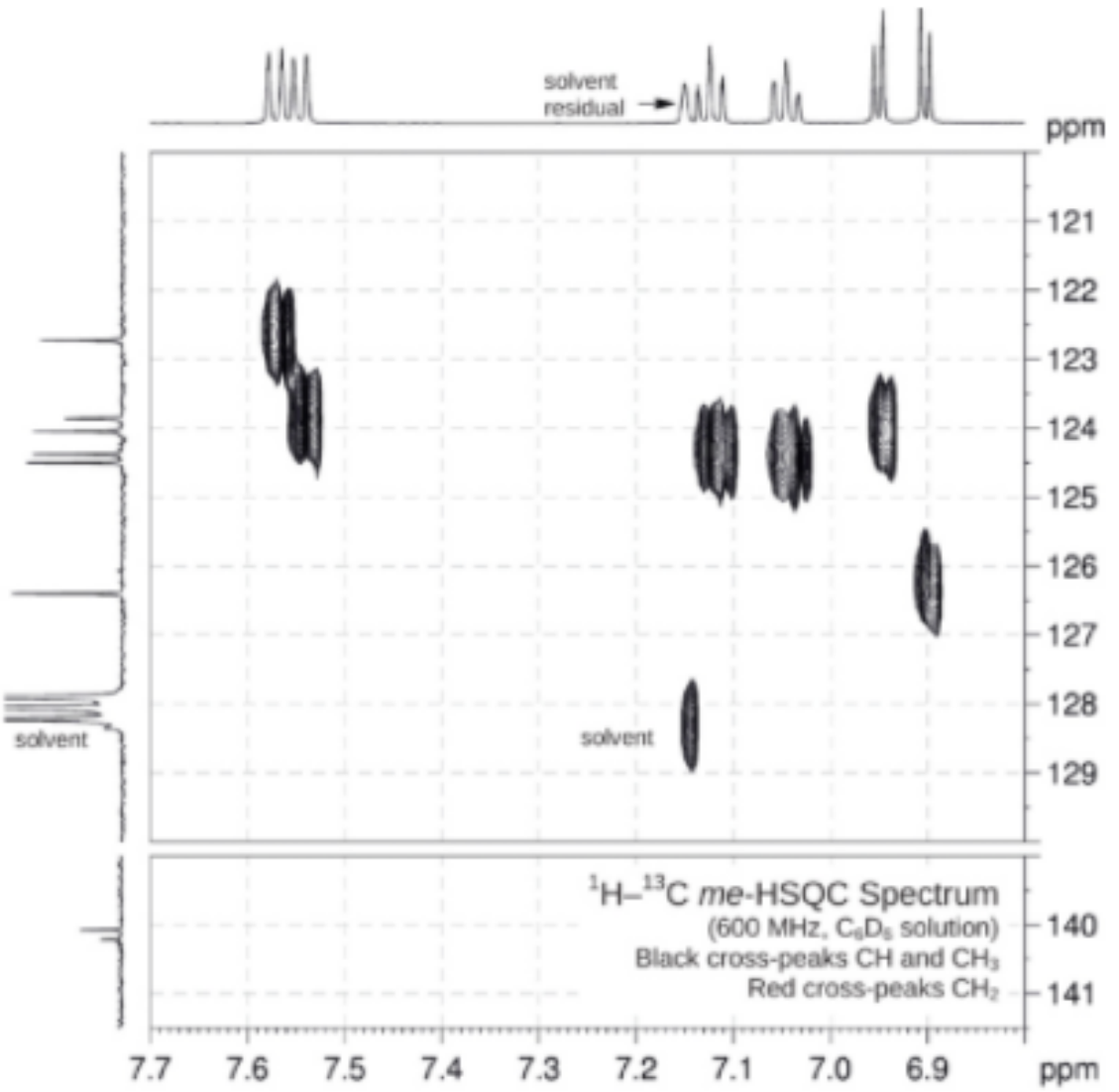
λ_{max} 288 nm ($\log_{10}\varepsilon$ 3.3)

λ_{max} 297 nm ($\log_{10}\varepsilon$ 3.5)

solvent : ethanol



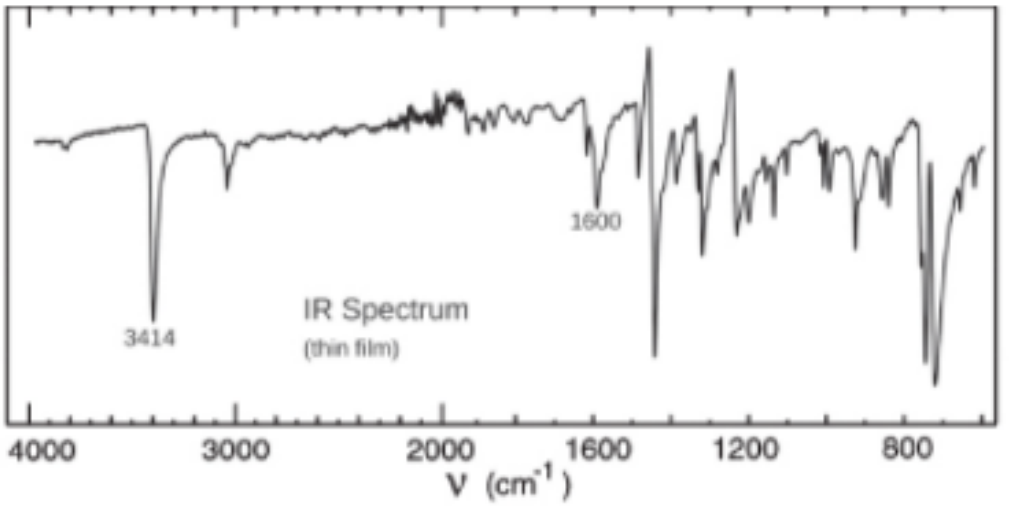


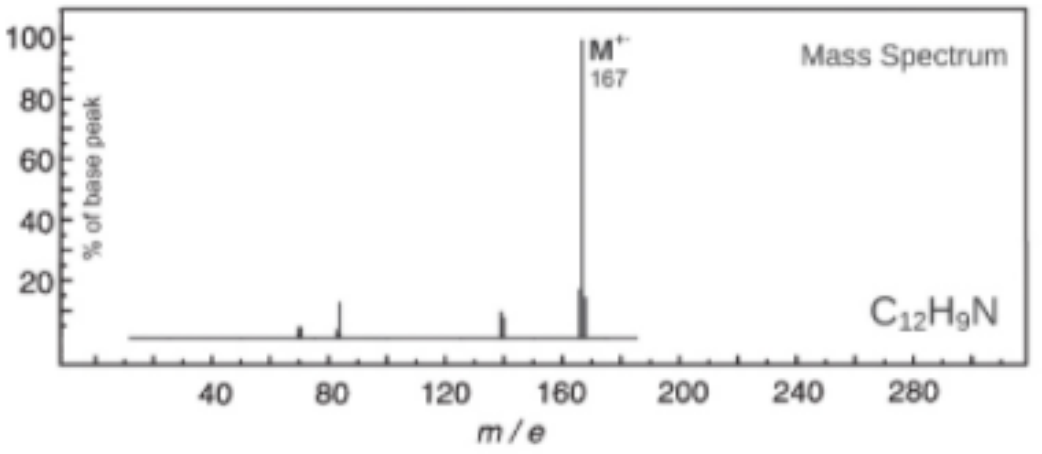

solvent
residual
ppm
121
122
123
124
125
126
127
128
129
solvent
solvent
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, C_6D_5 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
140
141
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm

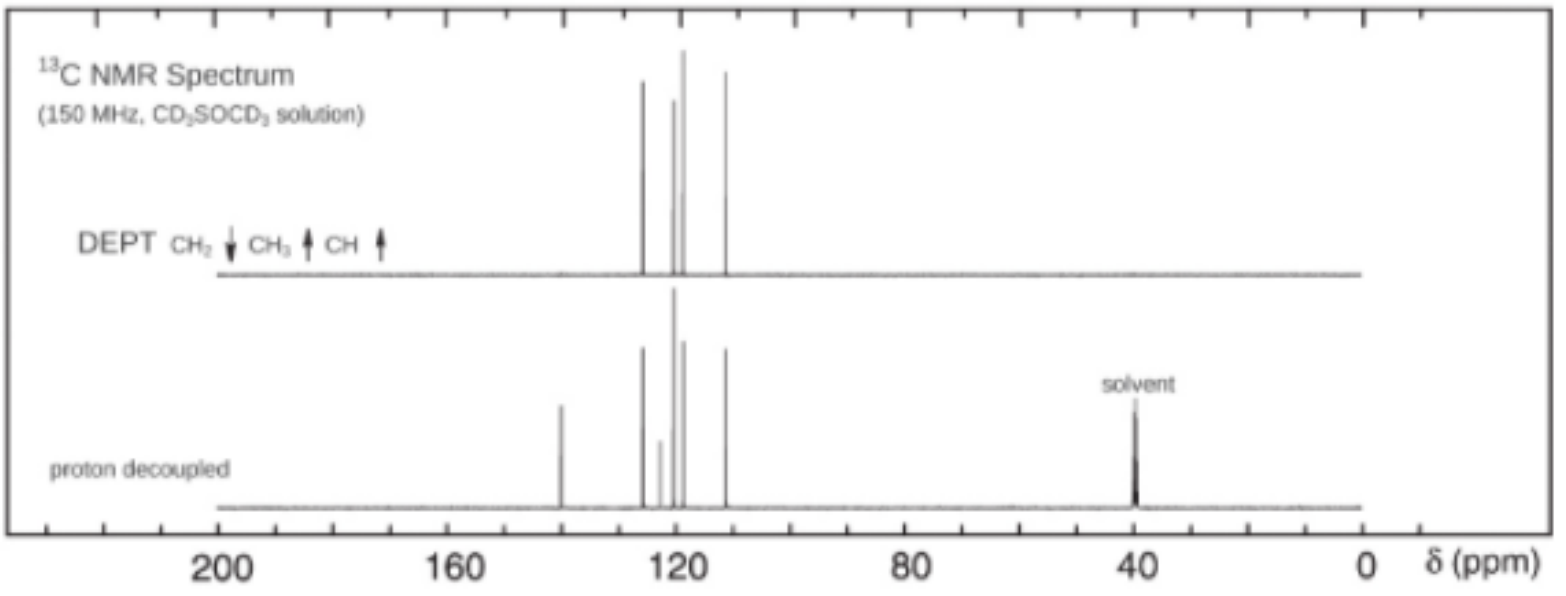
solvent
residual
ppm
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
solvent
residual
^{1}H–^{1}H COSY Spectrum
(600 MHz, C_6D_5 solution)
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm

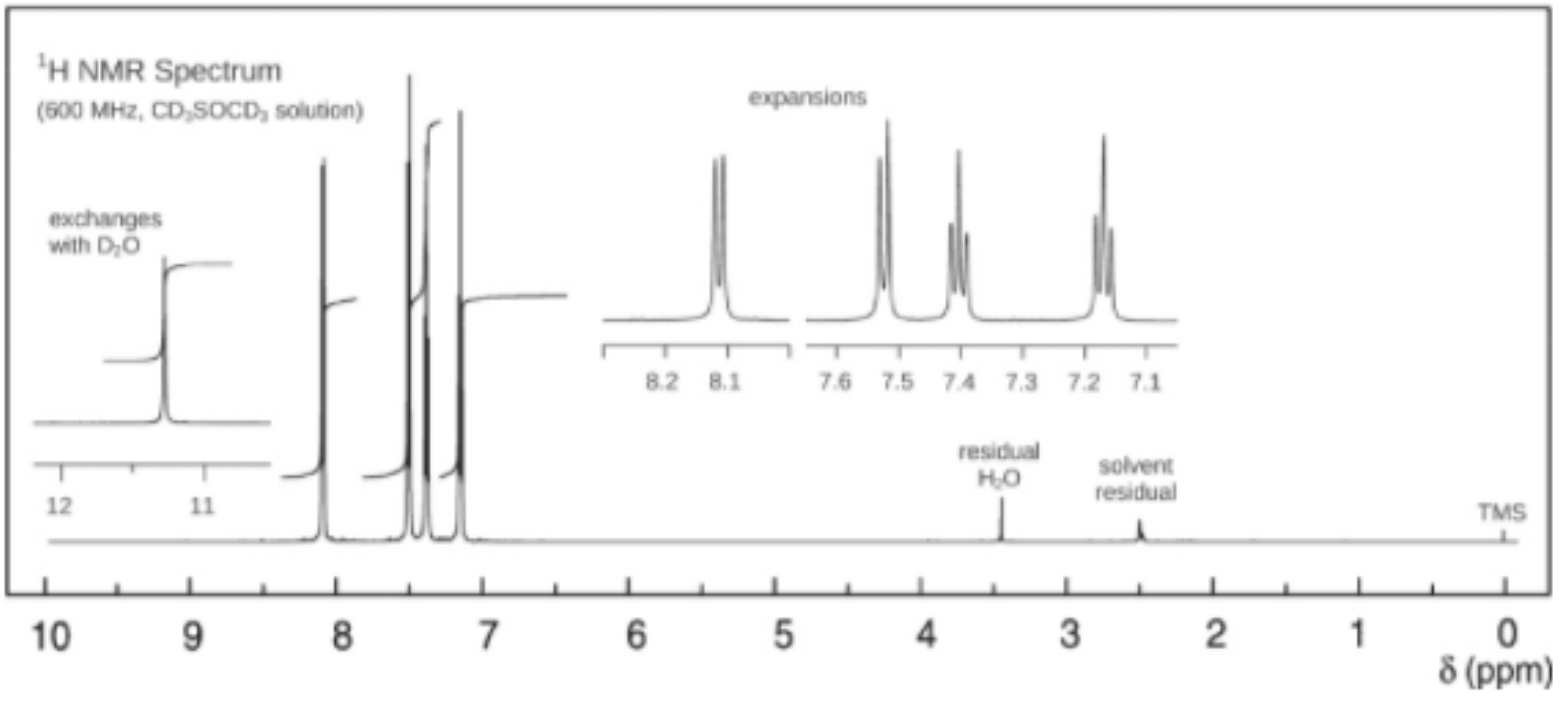
Problem 257

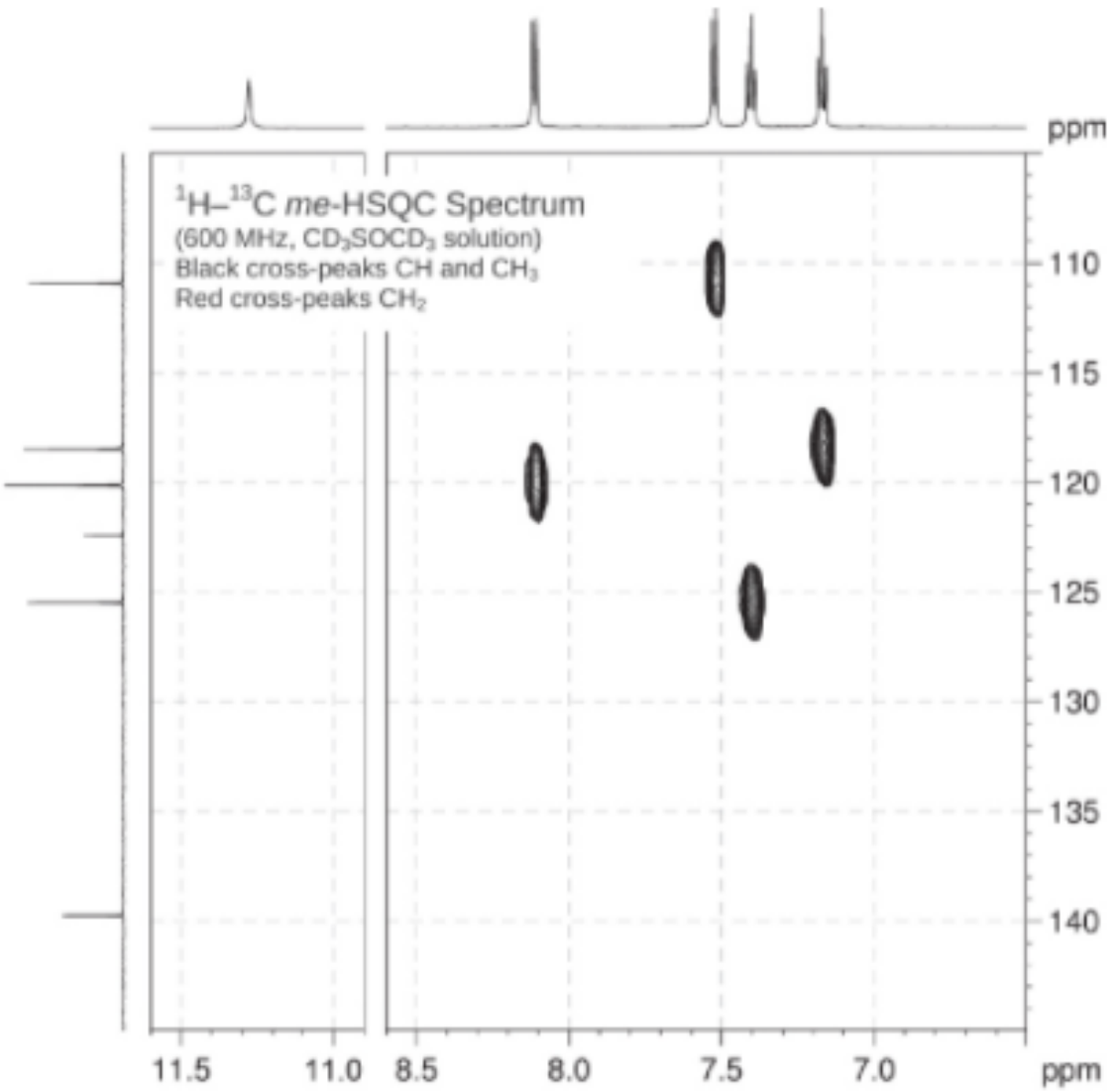
Problem 257

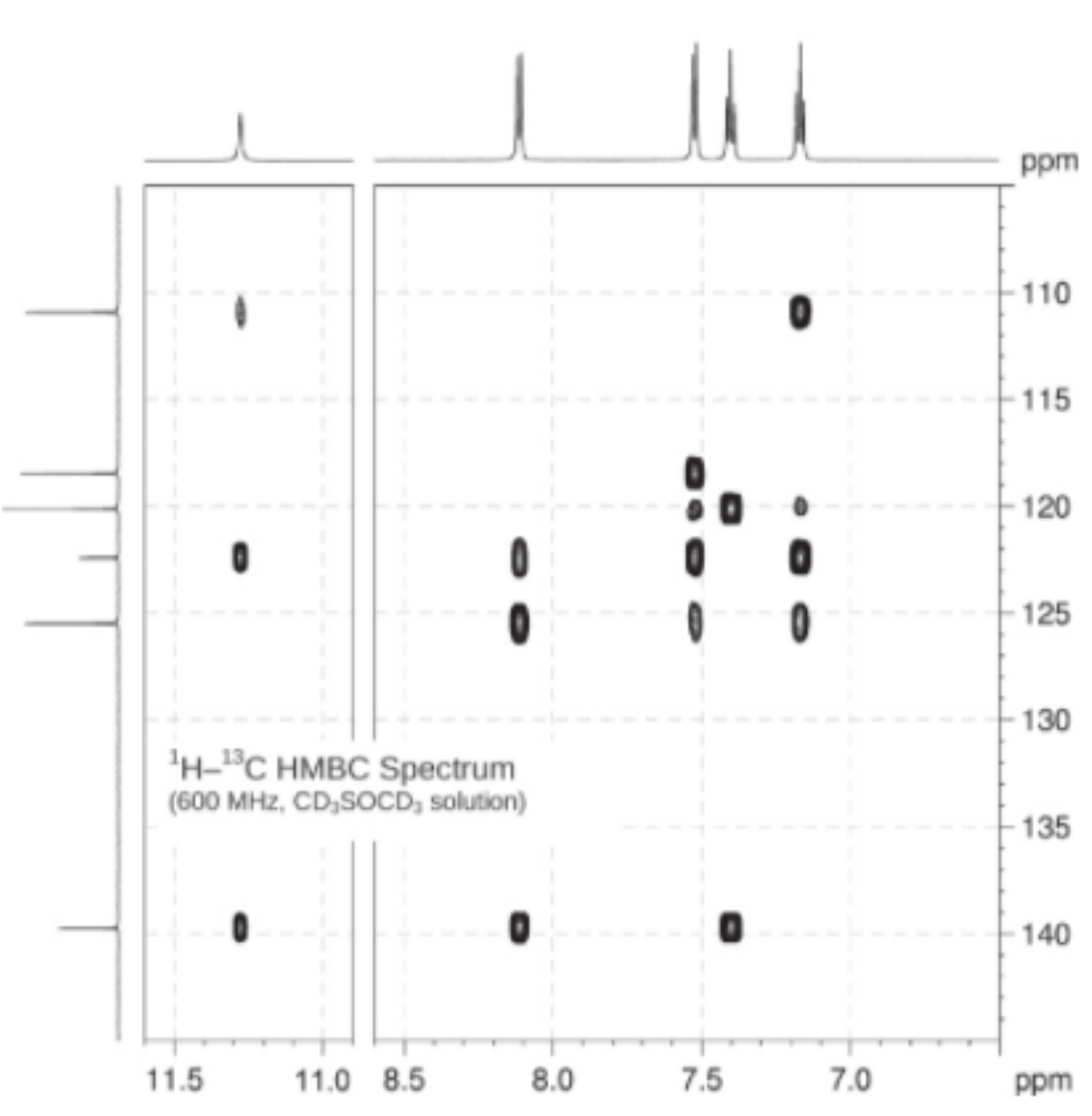




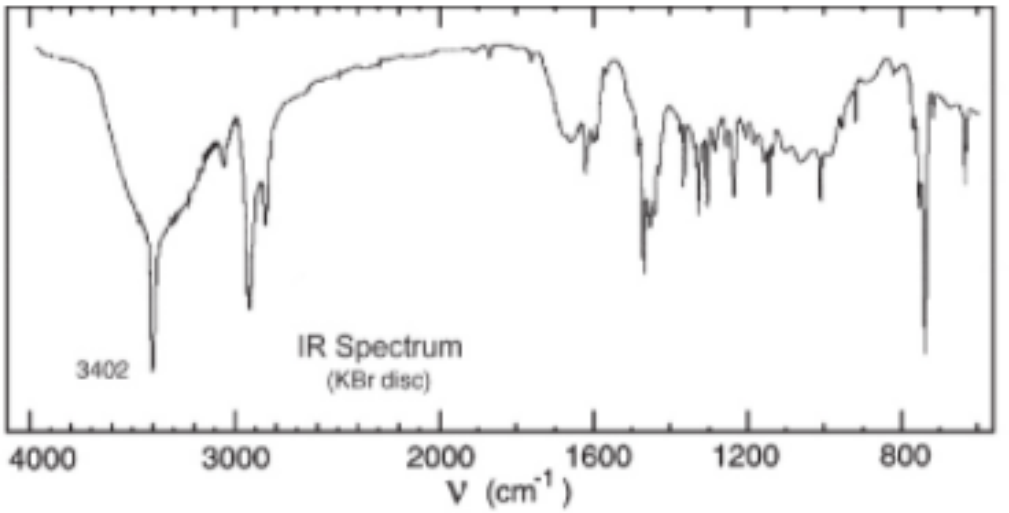


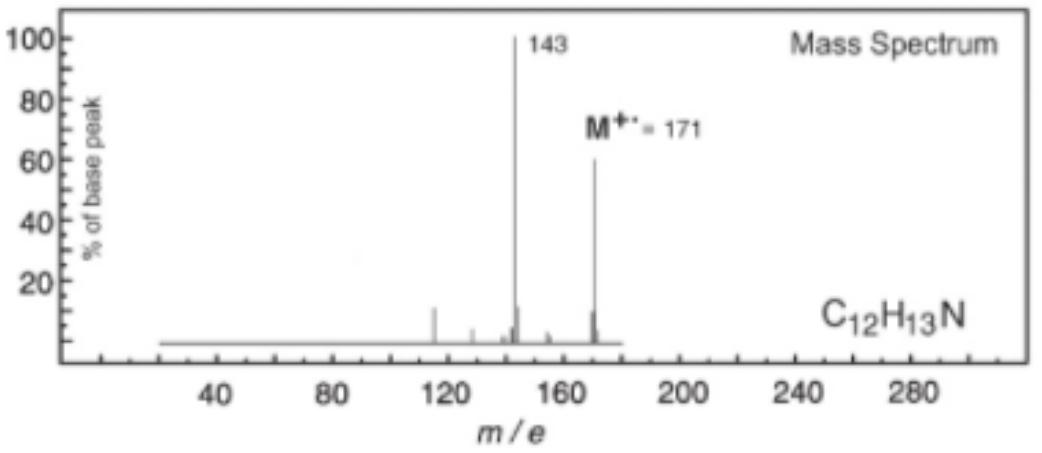



ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, CD_3SOCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
110
115
120
125
130
135
140
11.5
11.0
8.5
8.0
7.5
7.0
ppm


ppm
110
115
120
125
130
135
140
^{1}H–^{13}C HMBC Spectrum
(600 MHz, CD_3SOCD_3 solution)
11.5
11.0
8.5
8.0
7.5
7.0
ppm

Problem 258



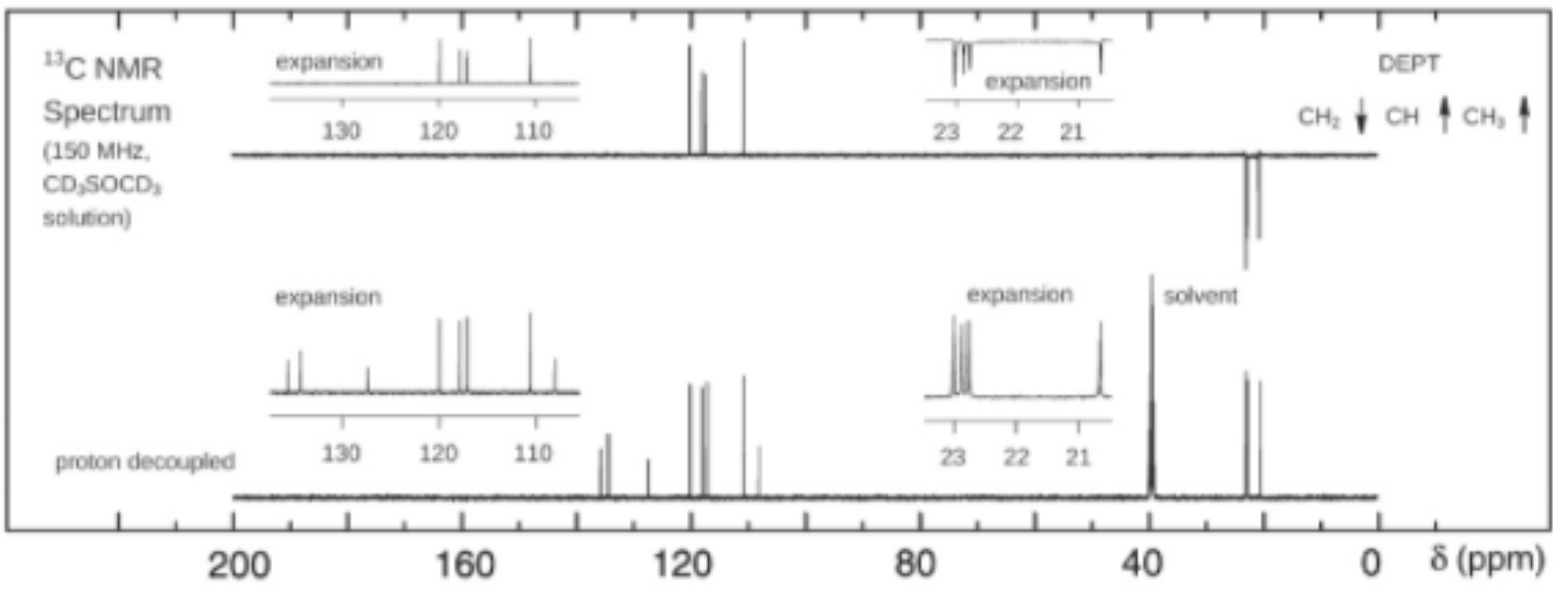


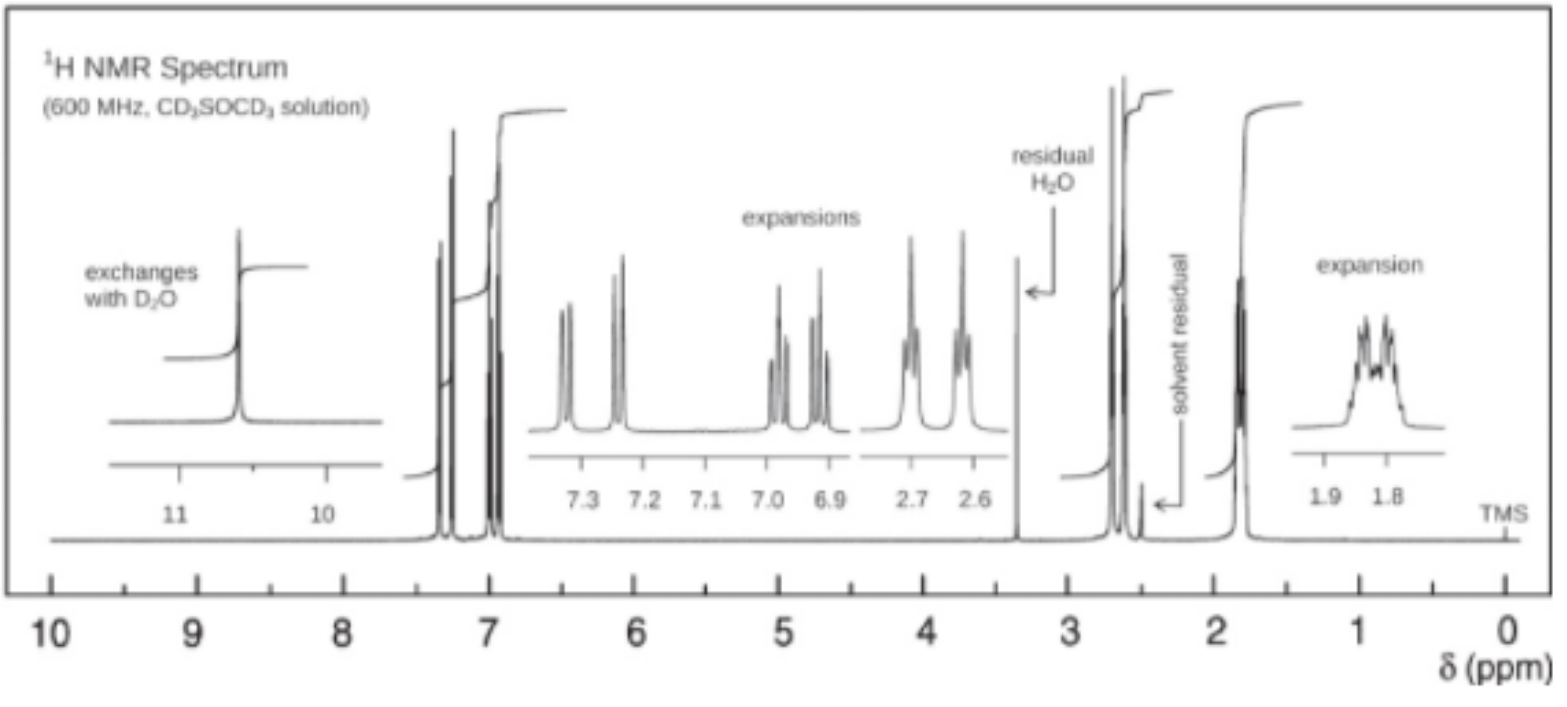
UV Spectrum

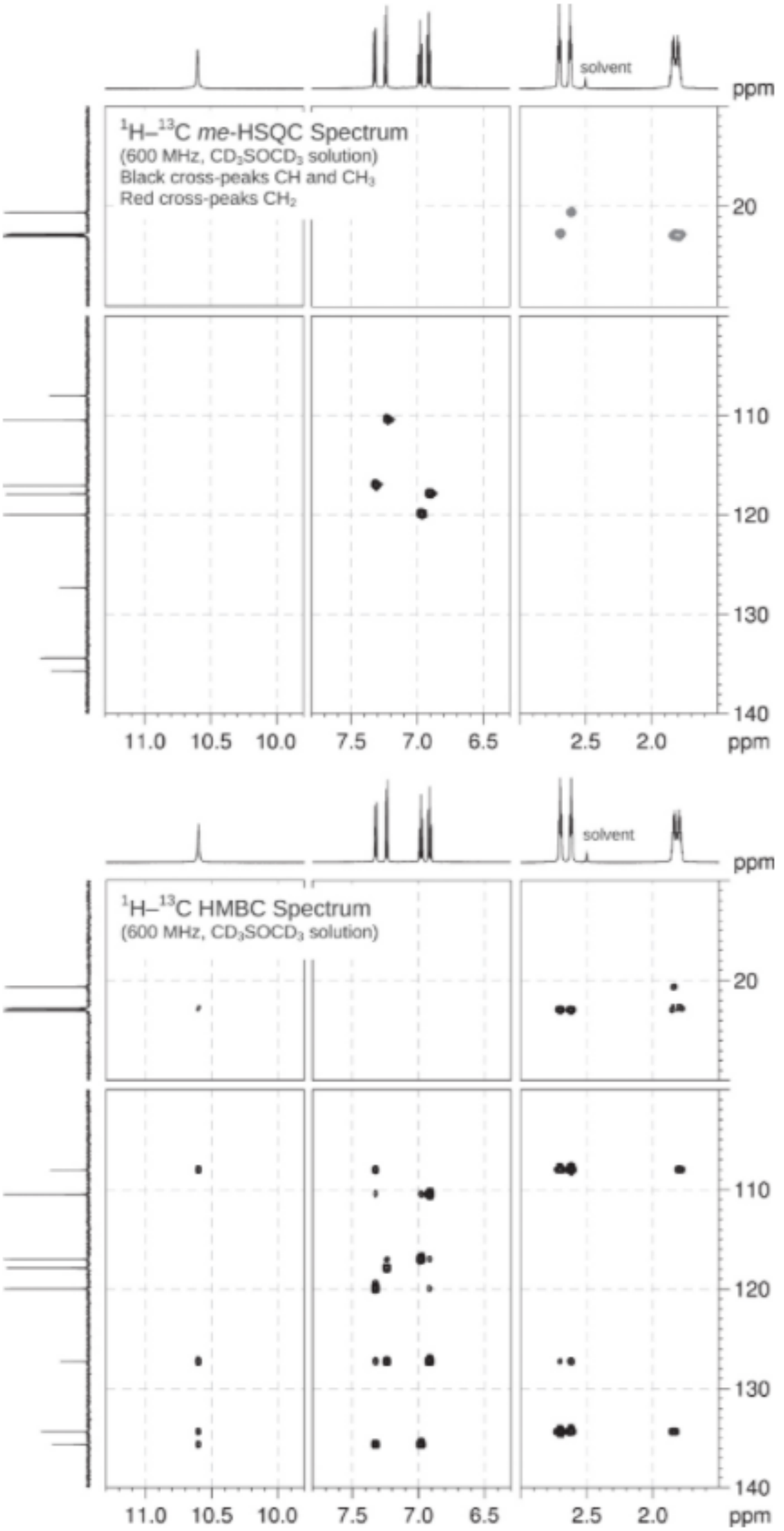
λ_{max} 229 nm ($\log_{10}\varepsilon$ 4.4)

λ_{max} 284 nm ($\log_{10}\varepsilon$ 3.8)

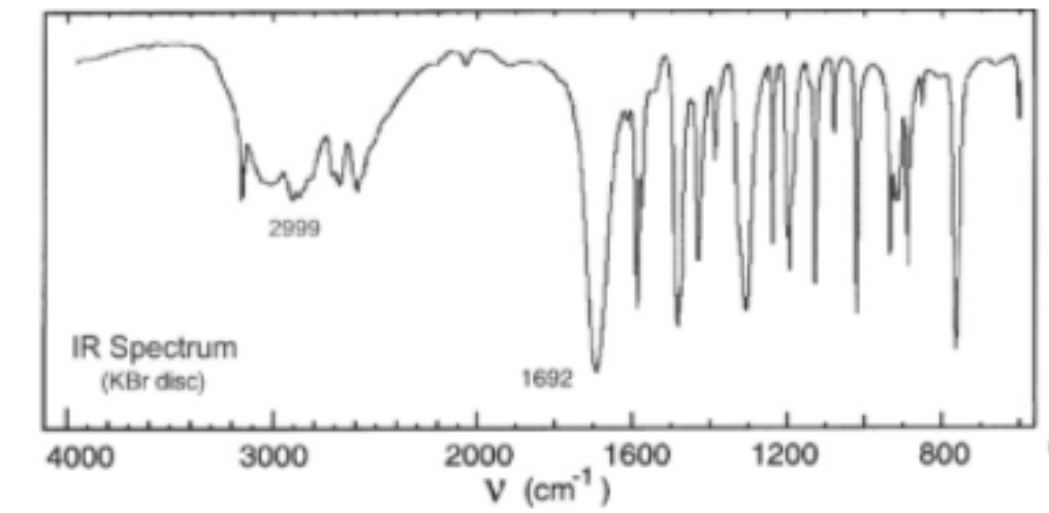
solvent : ethanol

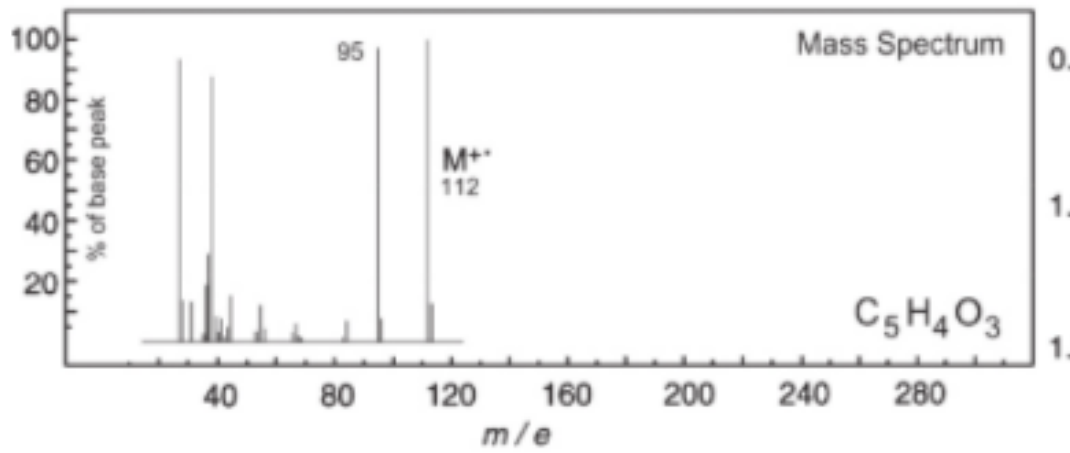


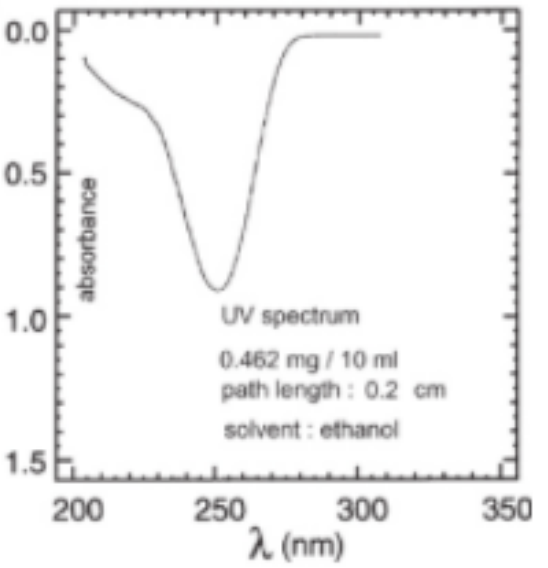


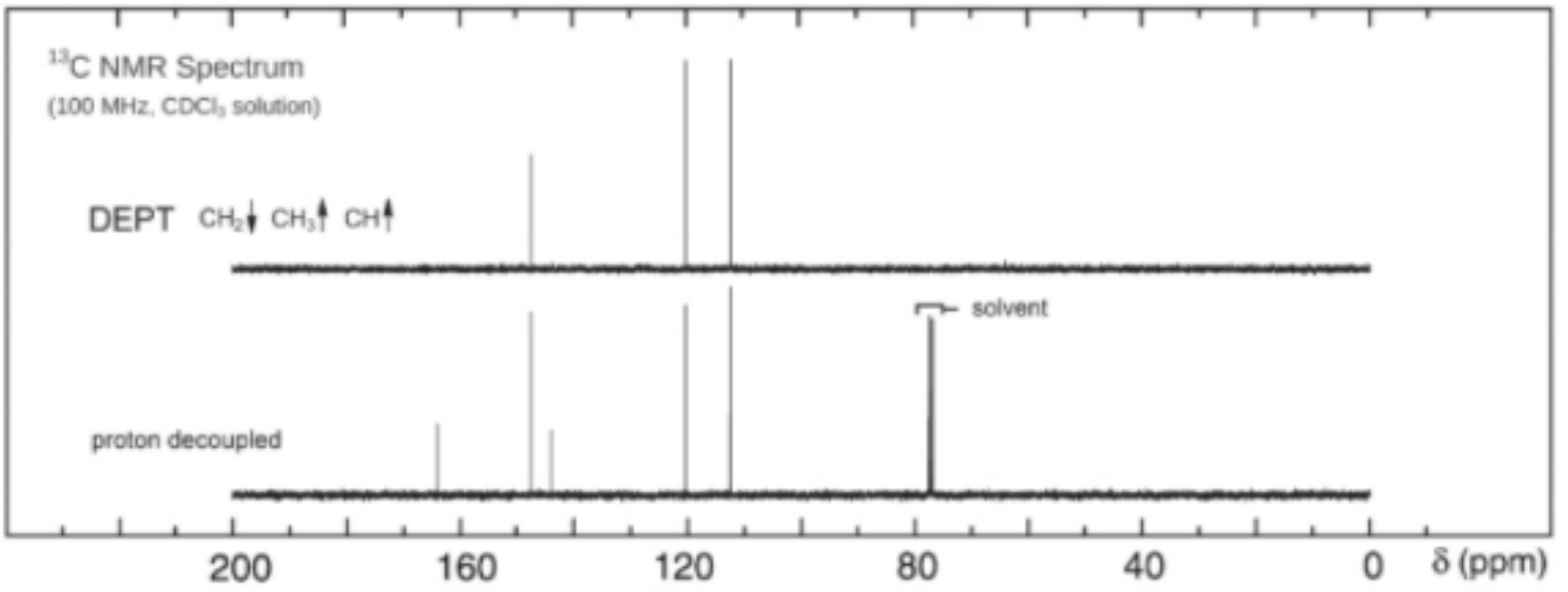

solvent
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, CD_3SOCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
20
110
120
130
140
11.0
10.5
10.0
7.5
7.0
6.5
2.5
2.0
ppm
solvent
ppm
^{1}H–^{13}C HMBC Spectrum
(600 MHz, CD_3SOCD_3 solution)
20
110
120
130
140
11.0
10.5
10.0
7.5
7.0
6.5
2.5
2.0
ppm

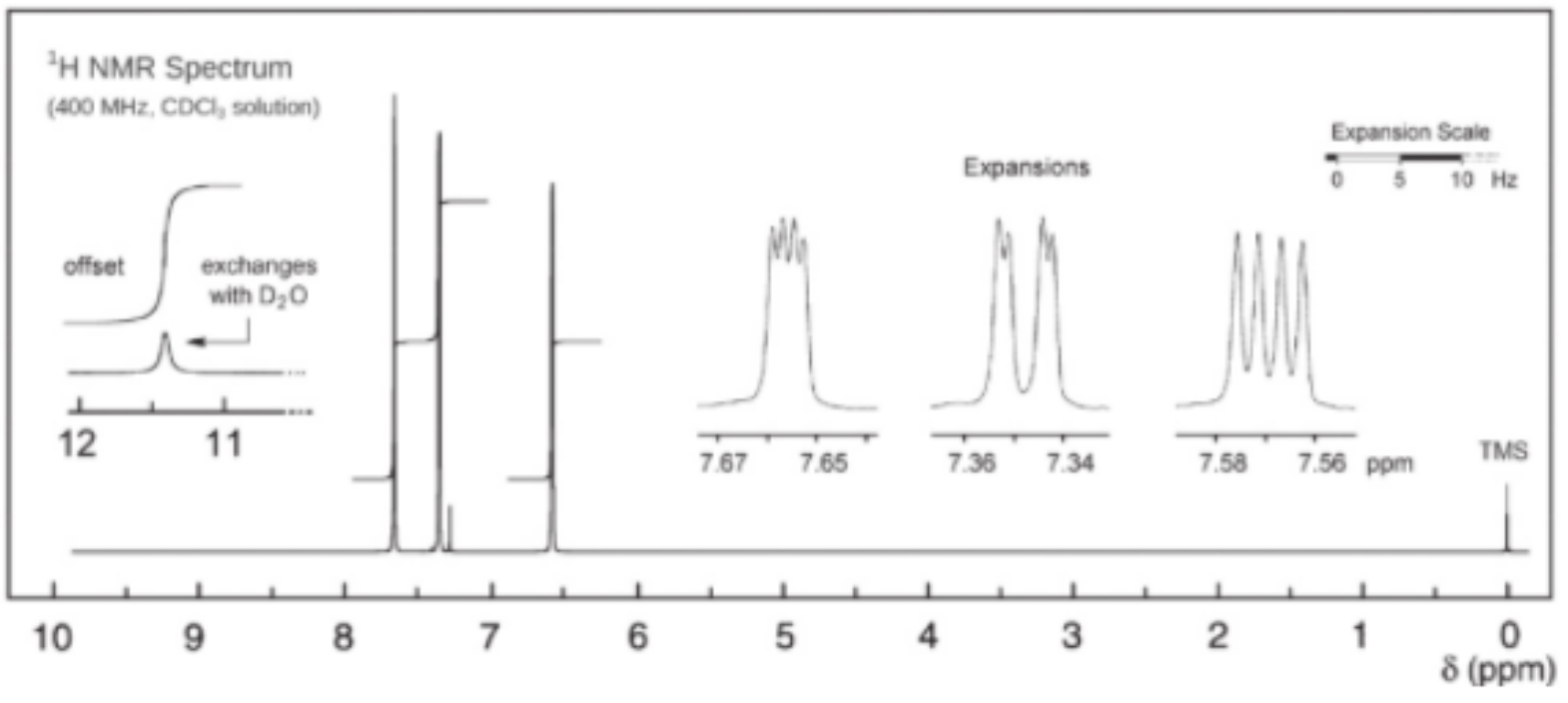
Problem 259

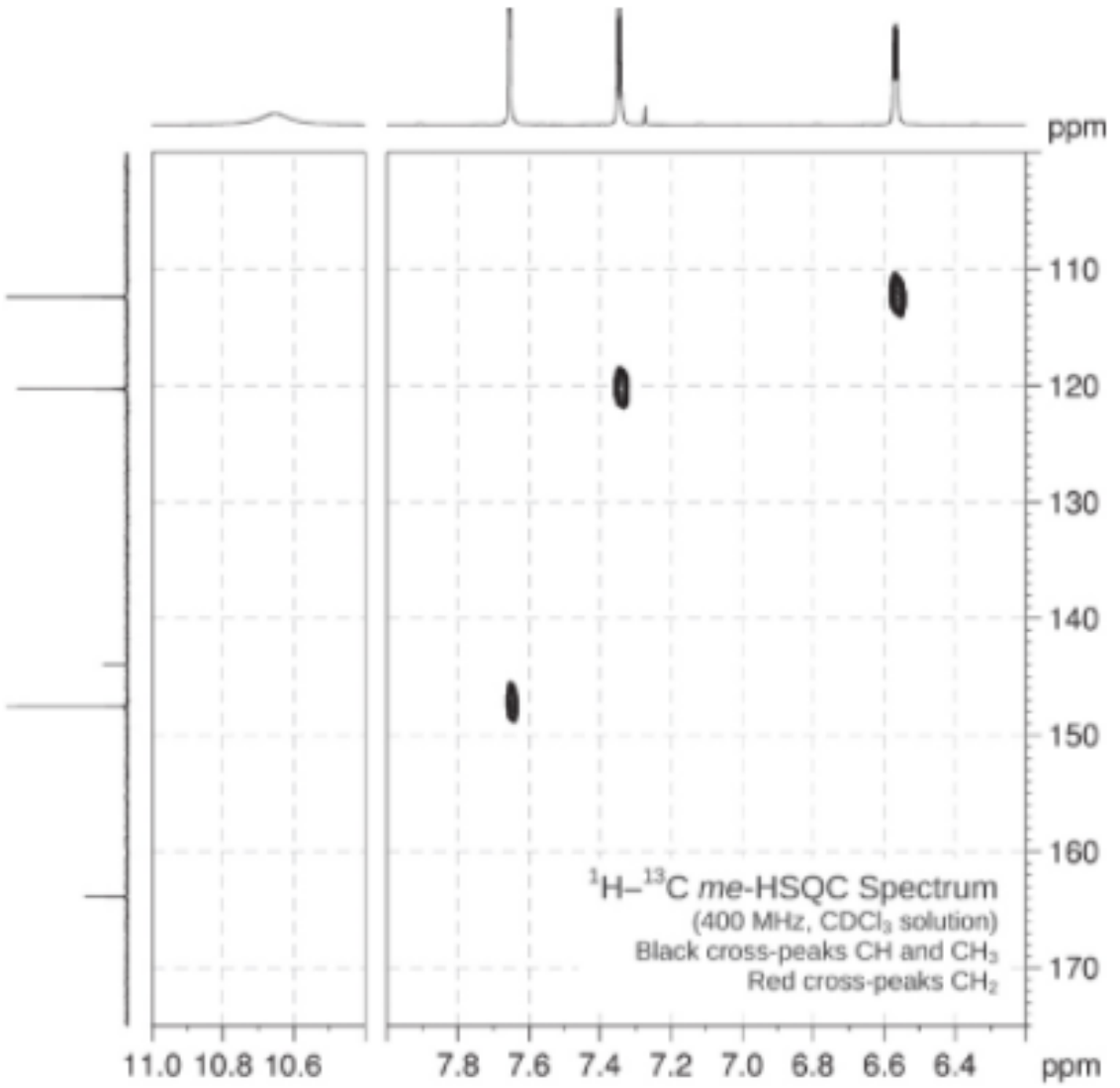

IR Spectrum
(KBr disc)
2999
1692
4000
3000
2000
1600
1200
800
ν (cm-1)

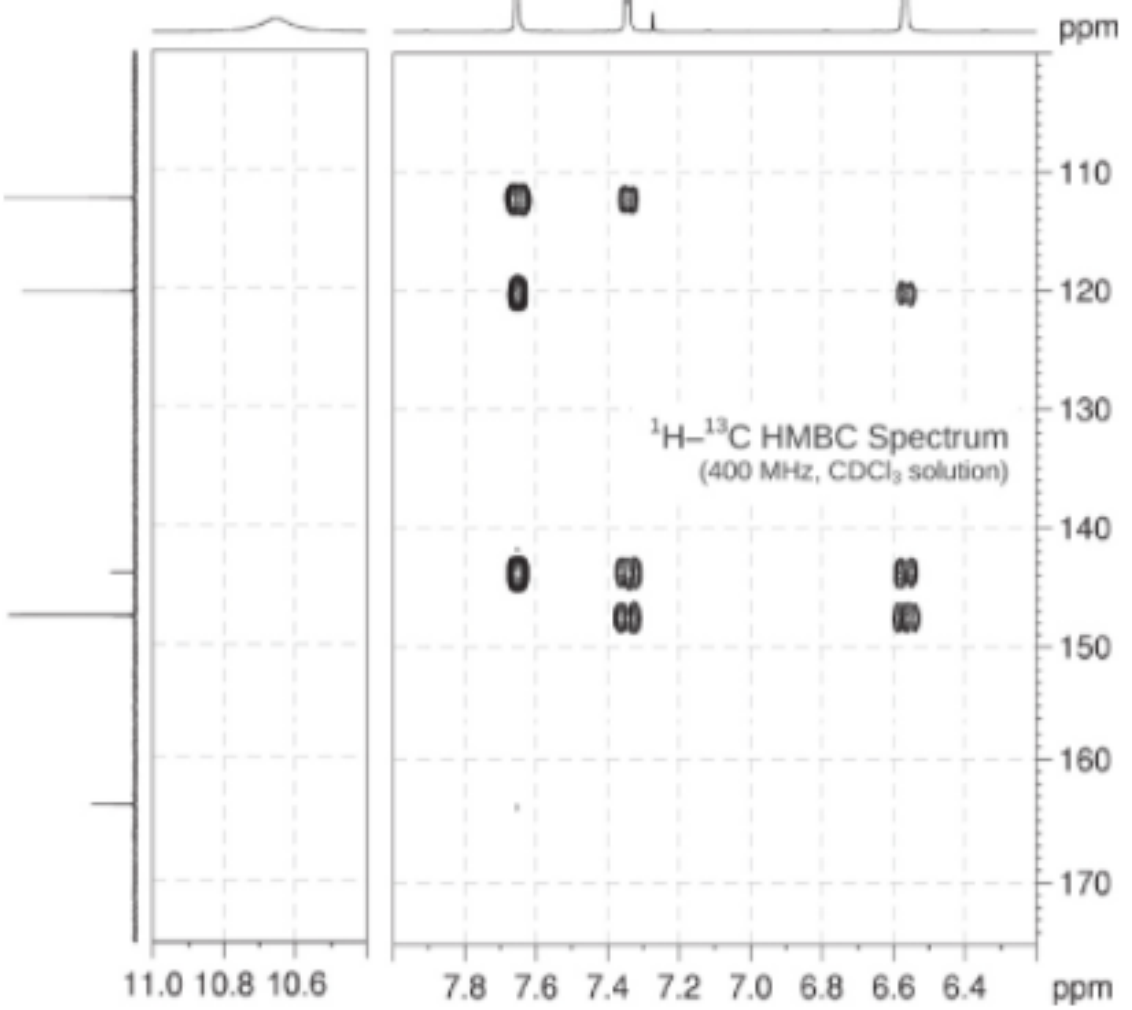

Mass Spectrum
95
M+·
112
% of base peak
C5H4O3
m/e


absorbance
UV spectrum
0.462 mg / 10 ml
path length : 0.2 cm
solvent : ethanol
λ (nm)

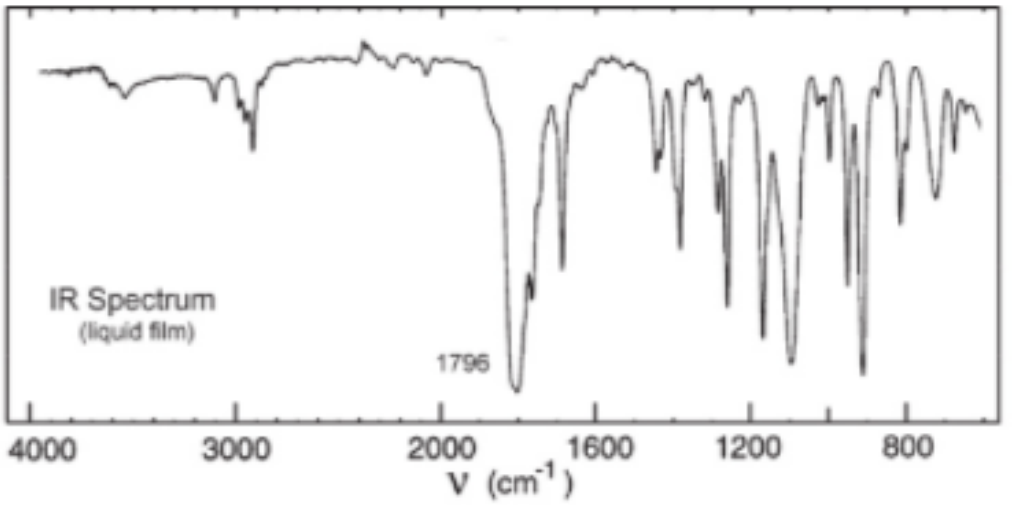

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
δ (ppm)

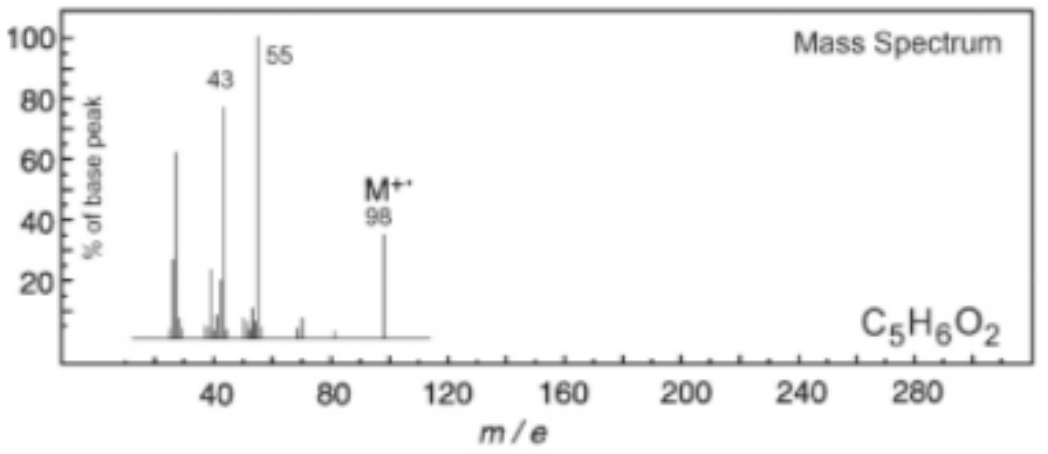

1H NMR Spectrum
(400 MHz, CDCl3 solution)
offset
exchanges with D2O
Expansions
Expansion Scale
0 5 10 Hz
7.67 7.65
7.36 7.34
7.58 7.56 ppm
TMS
δ (ppm)


ppm
110
120
130
140
150
160
170
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
11.0 10.8 10.6
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
ppm


ppm
110
120
130
140
150
160
170
^{1}H–^{13}C HMBC Spectrum
(400 MHz, $CDCl_3$ solution)
11.0 10.8 10.6
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
ppm

Problem 260

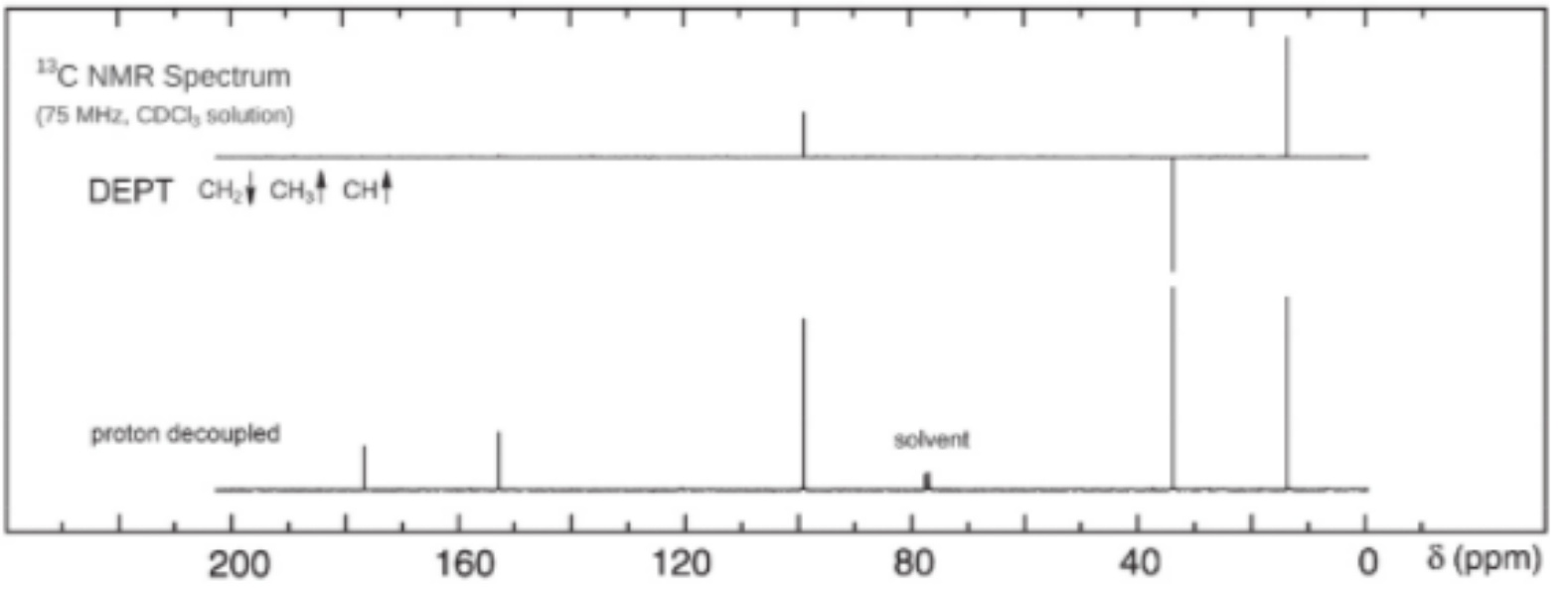


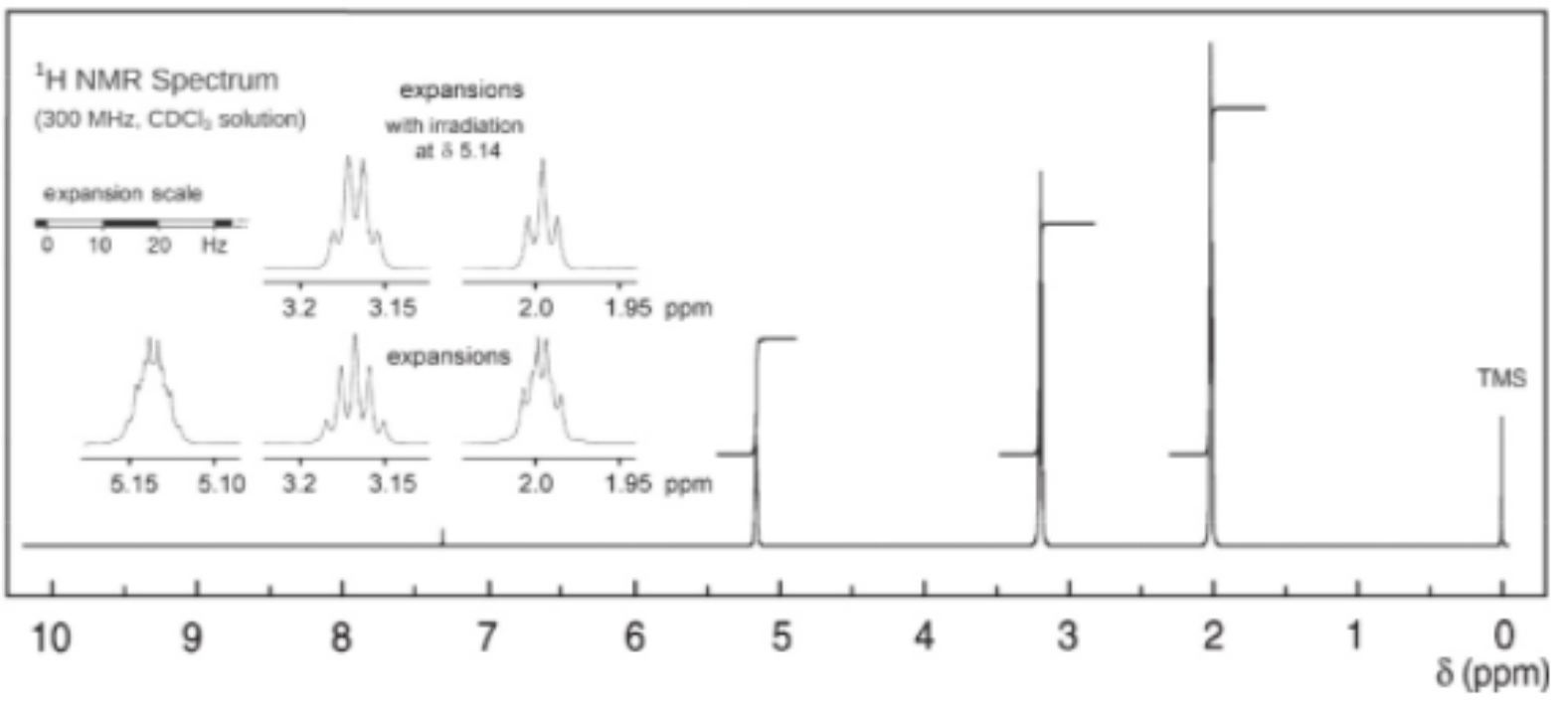


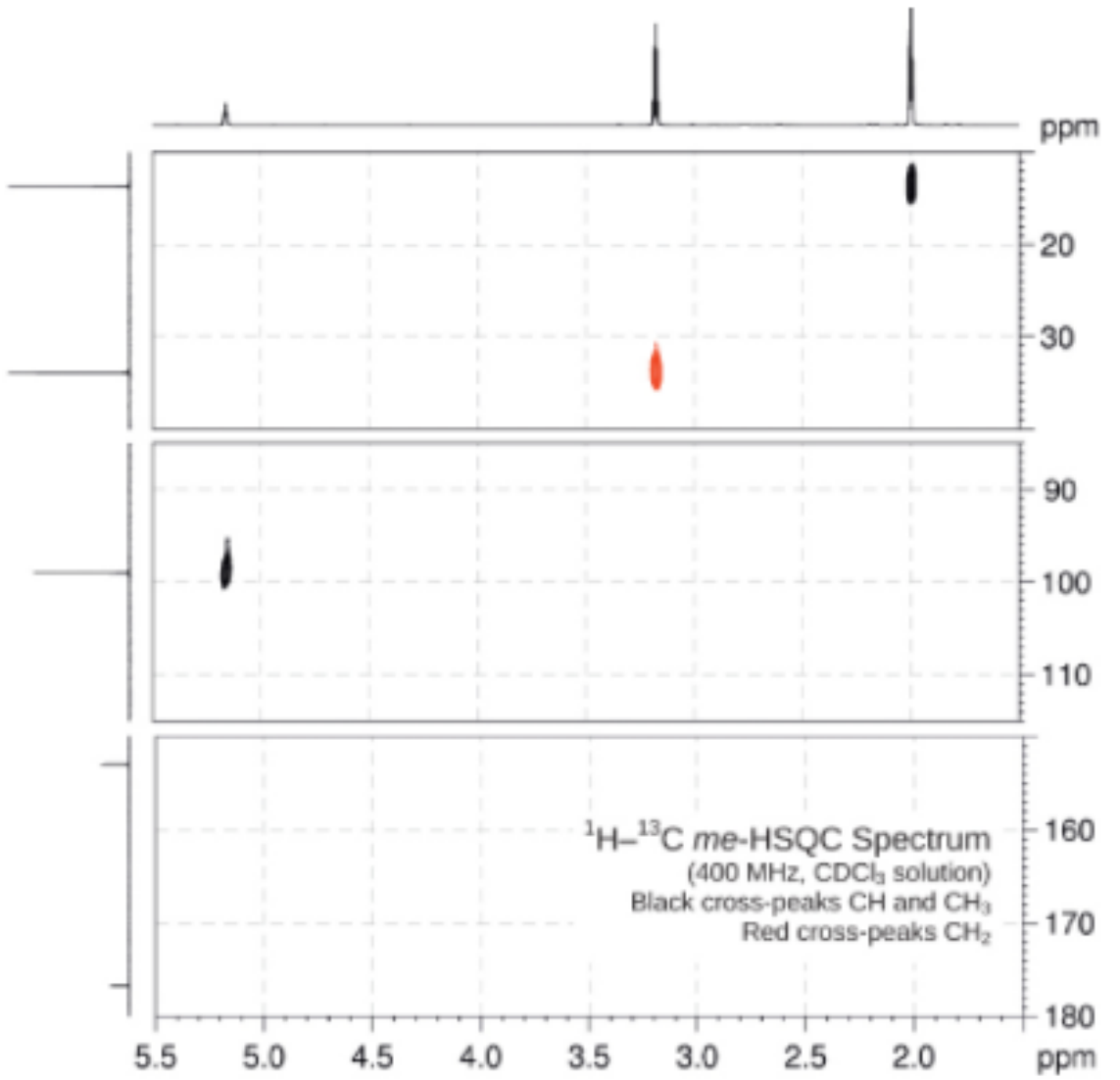
UV Spectrum

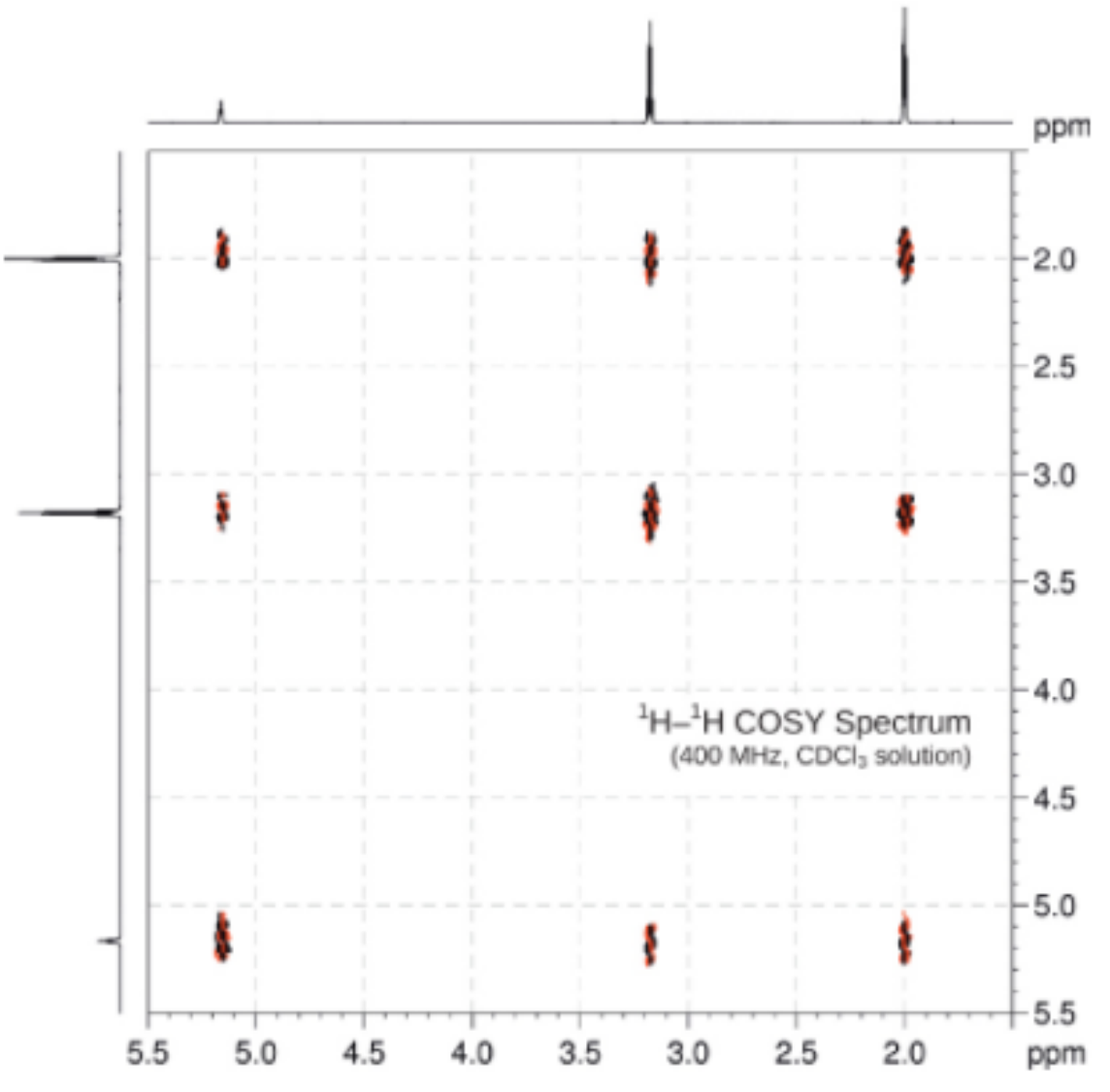
λ_{max} 217 nm ($\log_{10}\varepsilon$ 3.4)

solvent : ethanol

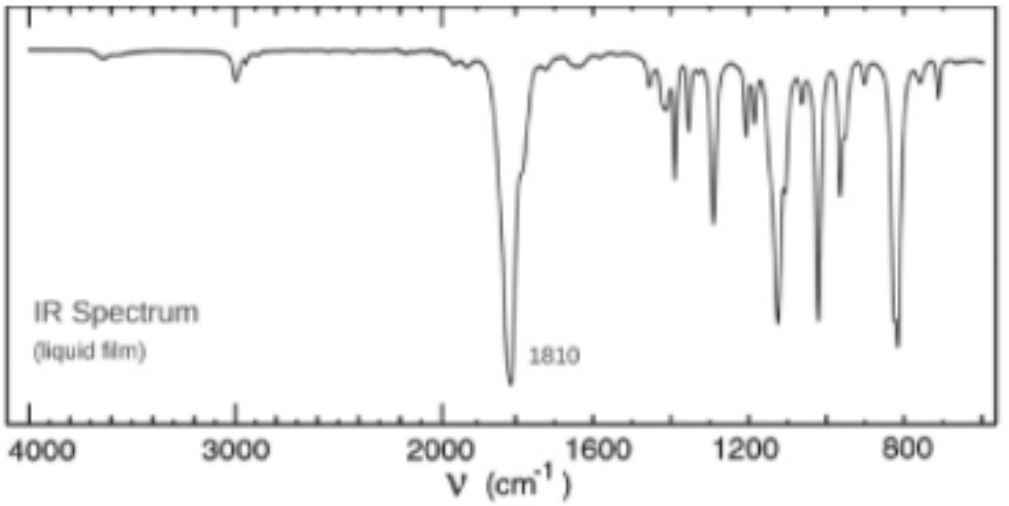


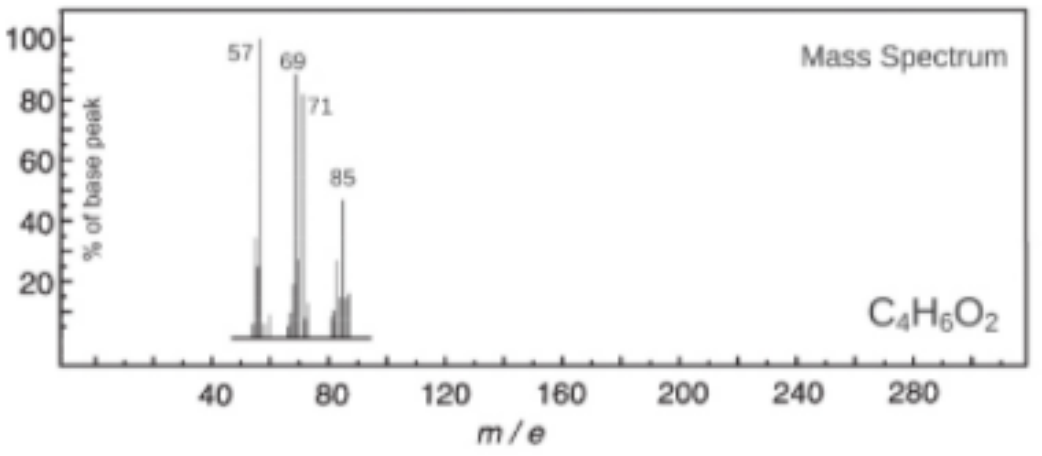


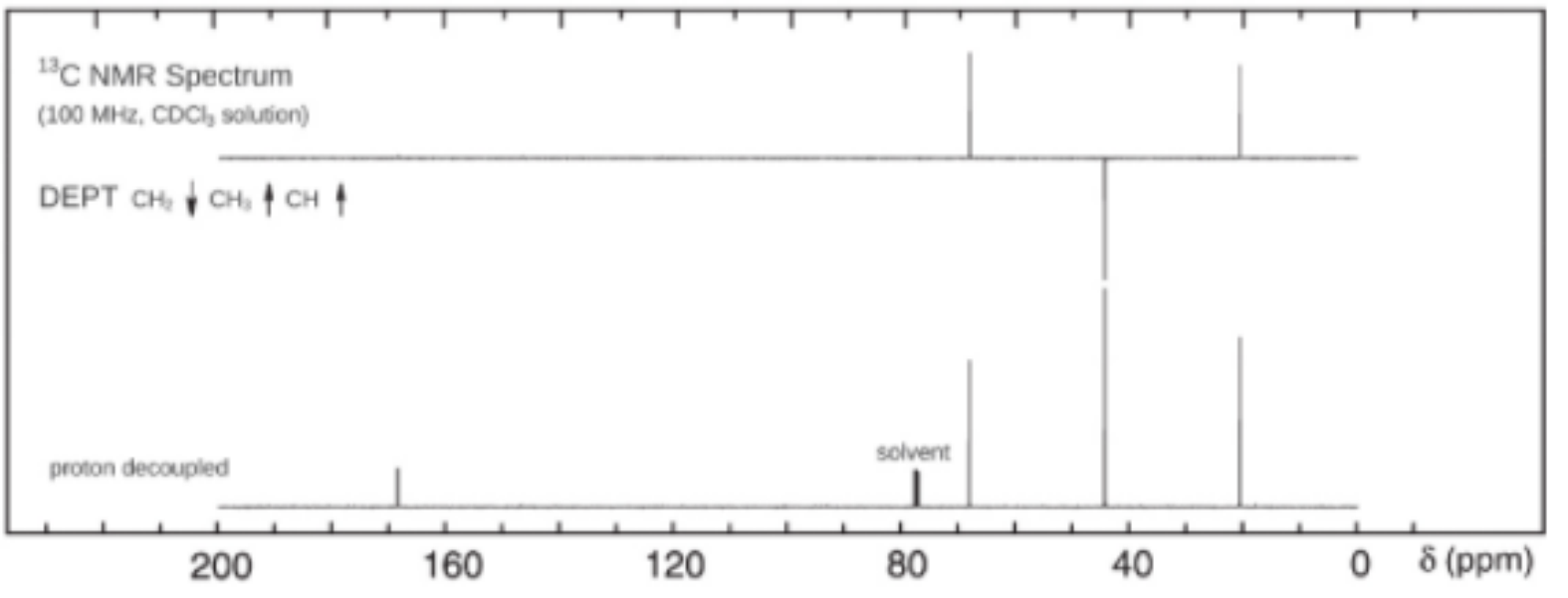

ppm
20
30
90
100
110
160
170
180
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

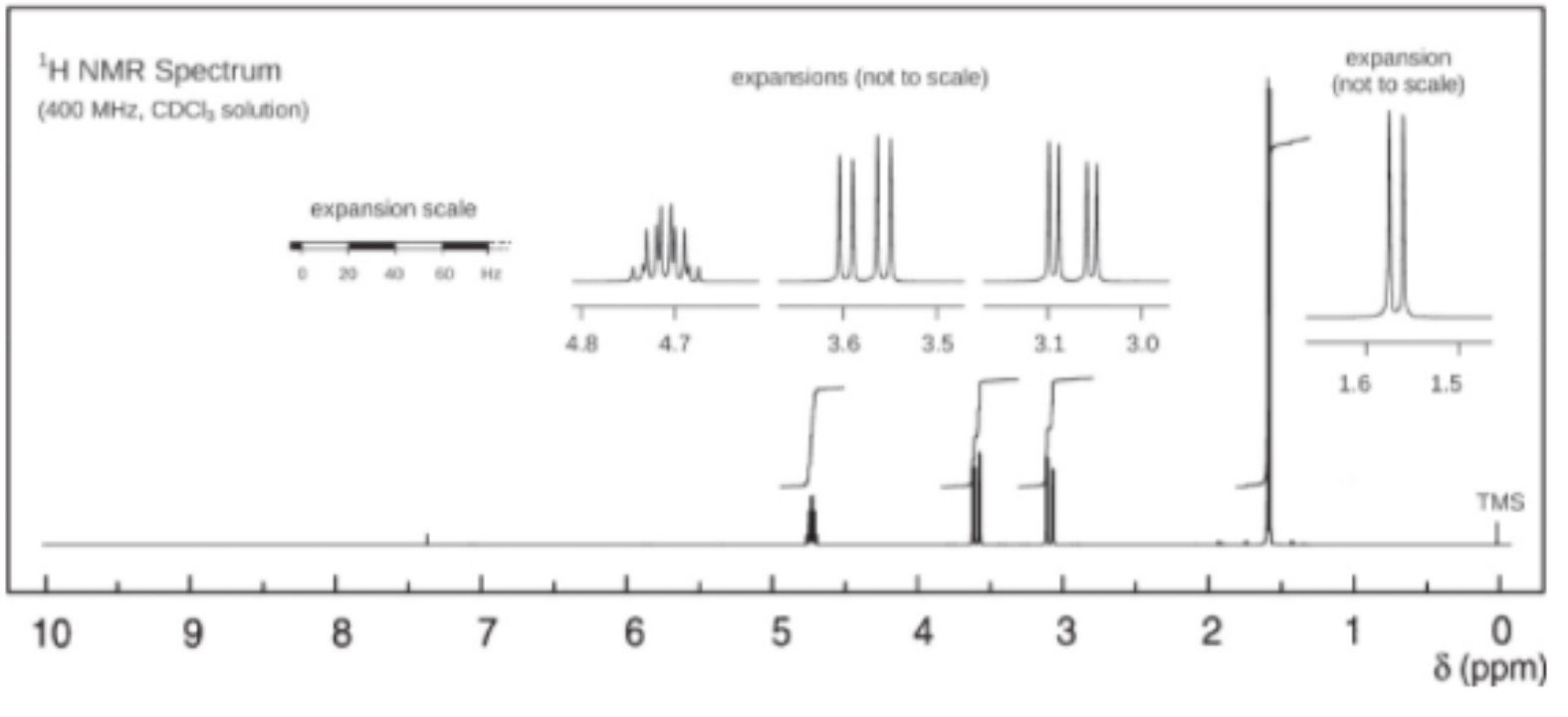

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
$^{1}H–^{1}H$ COSY Spectrum
(400 MHz, $CDCl_3$ solution)

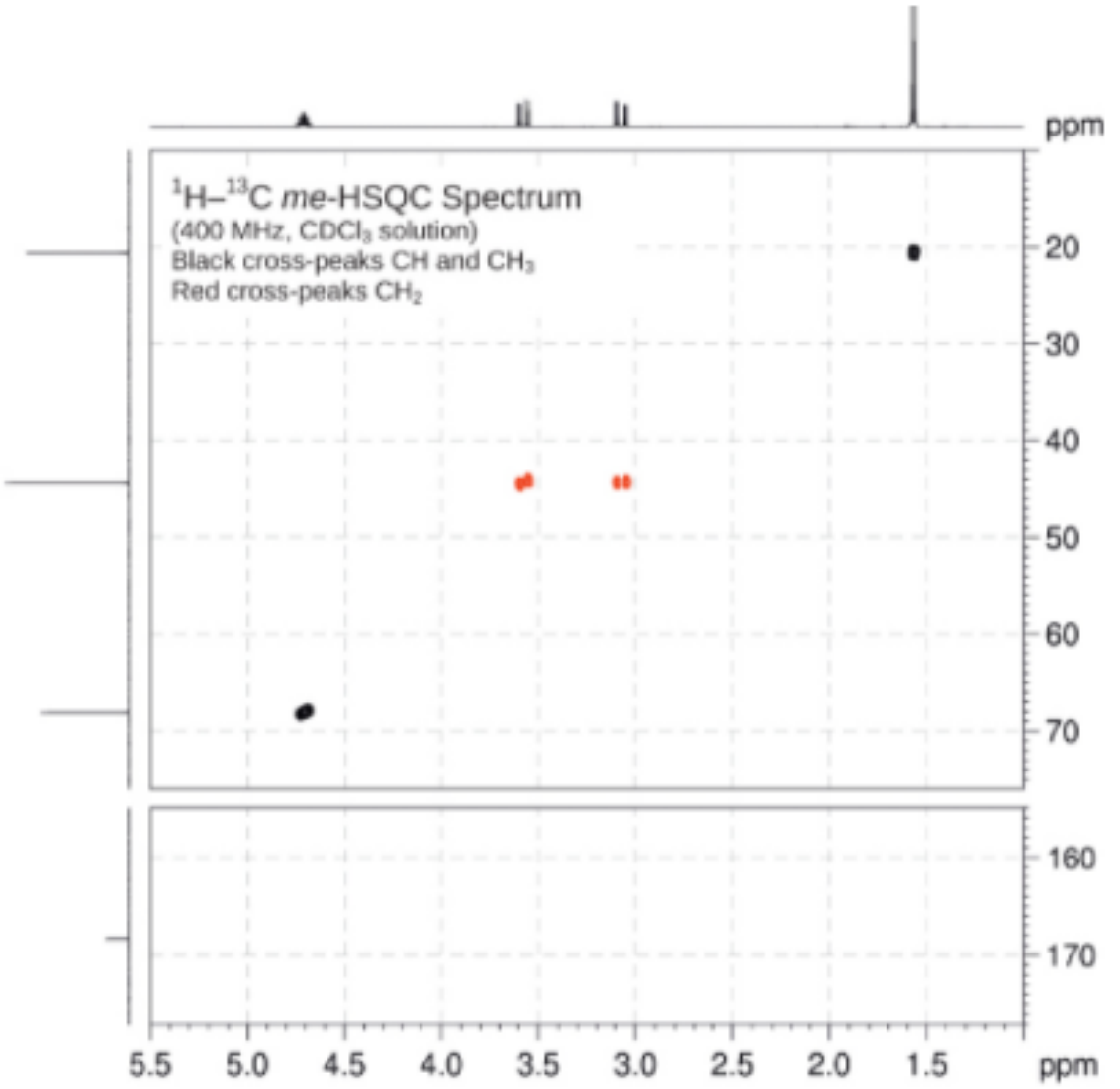
Problem 261


IR Spectrum
(liquid film)
1810
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
100
80
60
40
20
57
69
71
85
C4H6O2
40
80
120
160
200
240
280
m / e

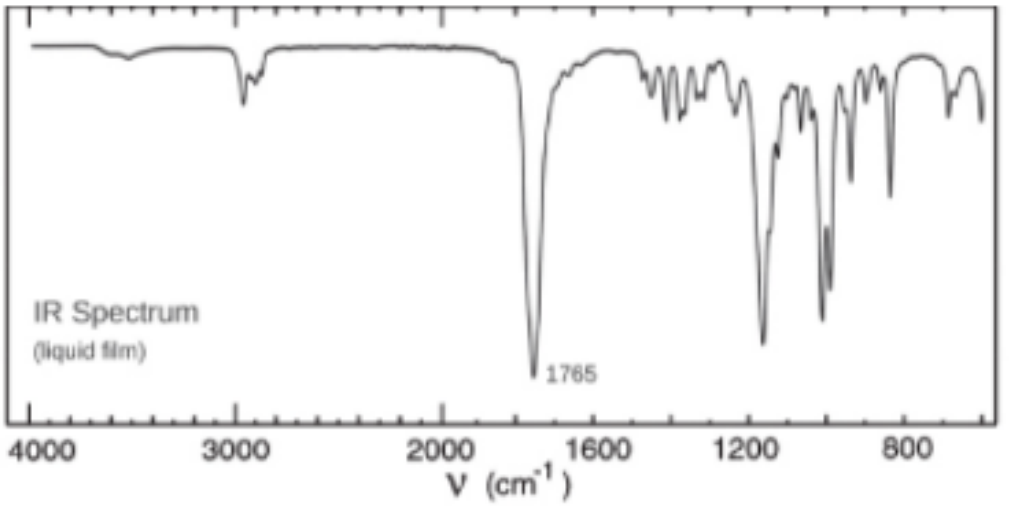

13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

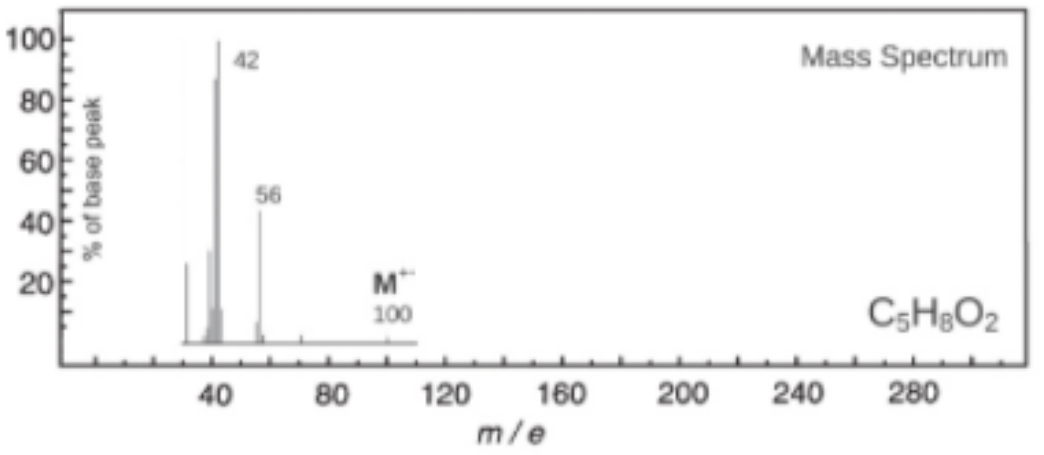

1H NMR Spectrum
(400 MHz, CDCl3 solution)
expansion scale
0 20 40 60 Hz
expansions (not to scale)
4.8
4.7
3.6
3.5
3.1
3.0
expansion
(not to scale)
1.6
1.5
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

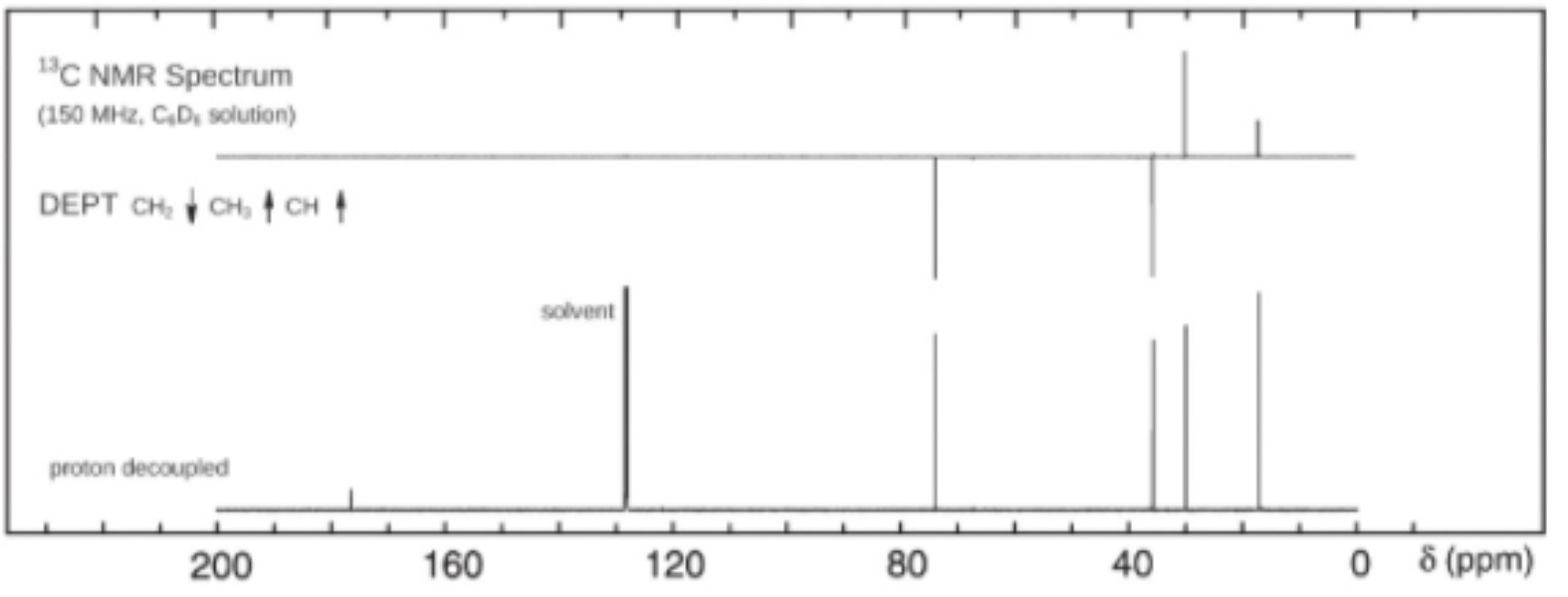

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
20
30
40
50
60
70
160
170
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

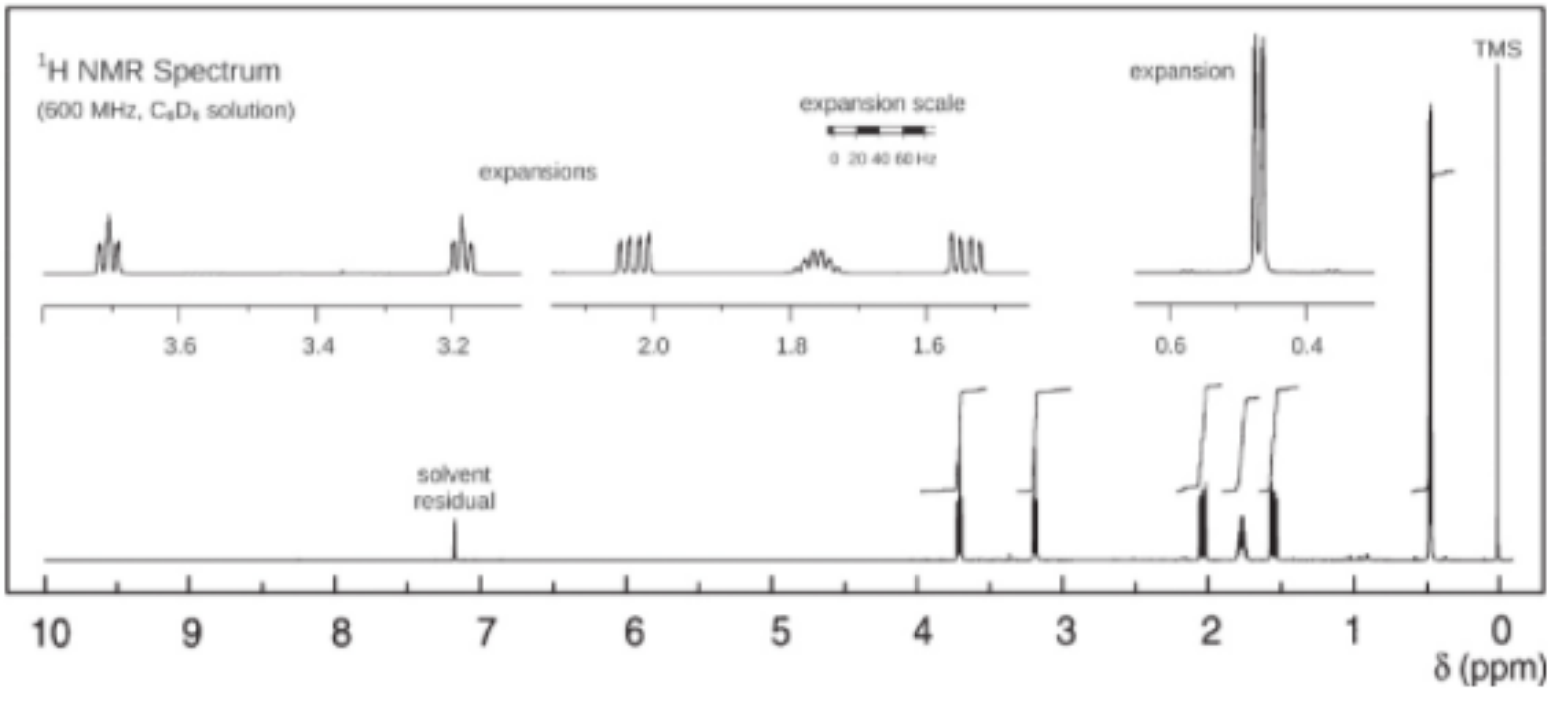
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

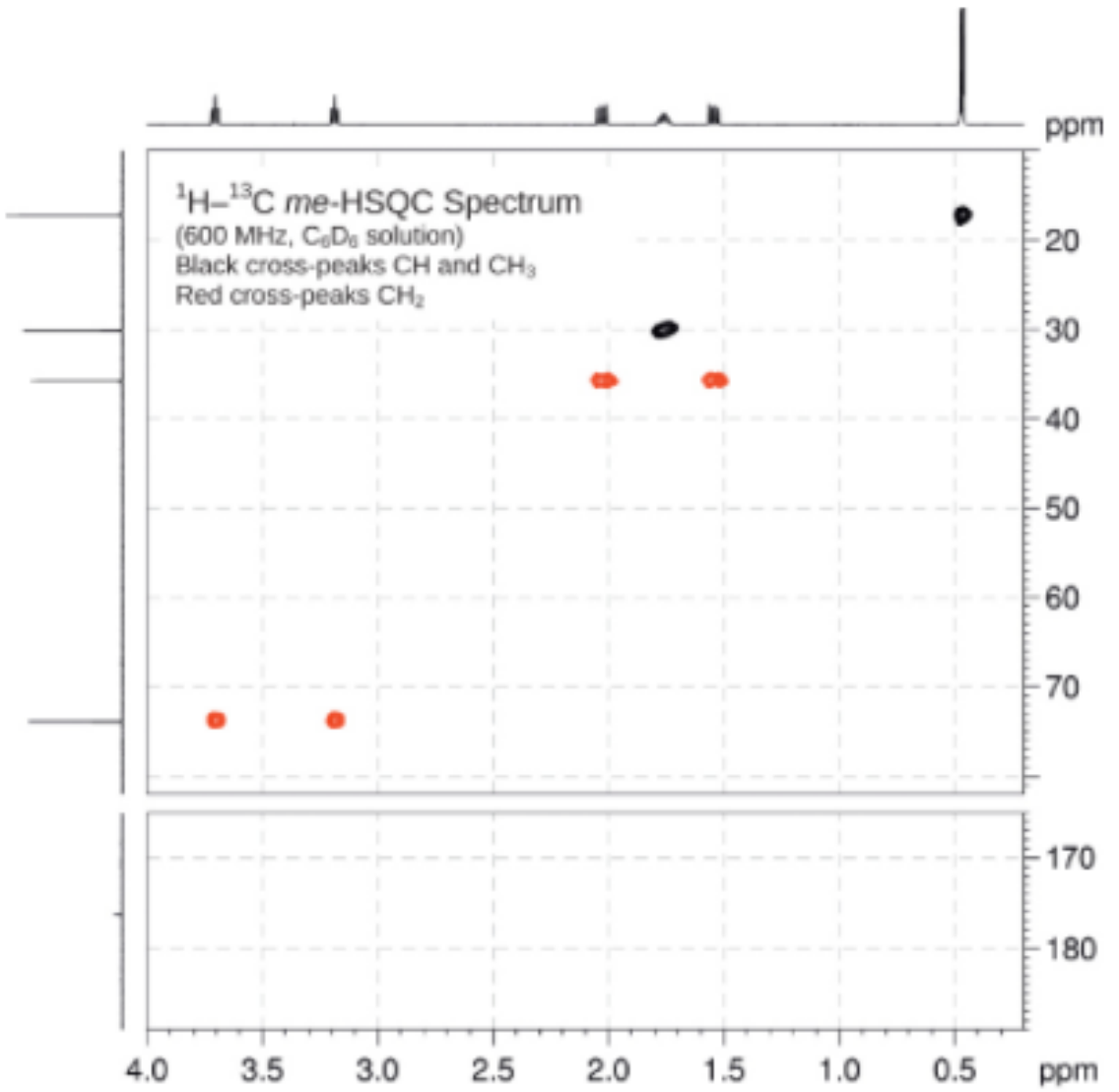
Problem 262

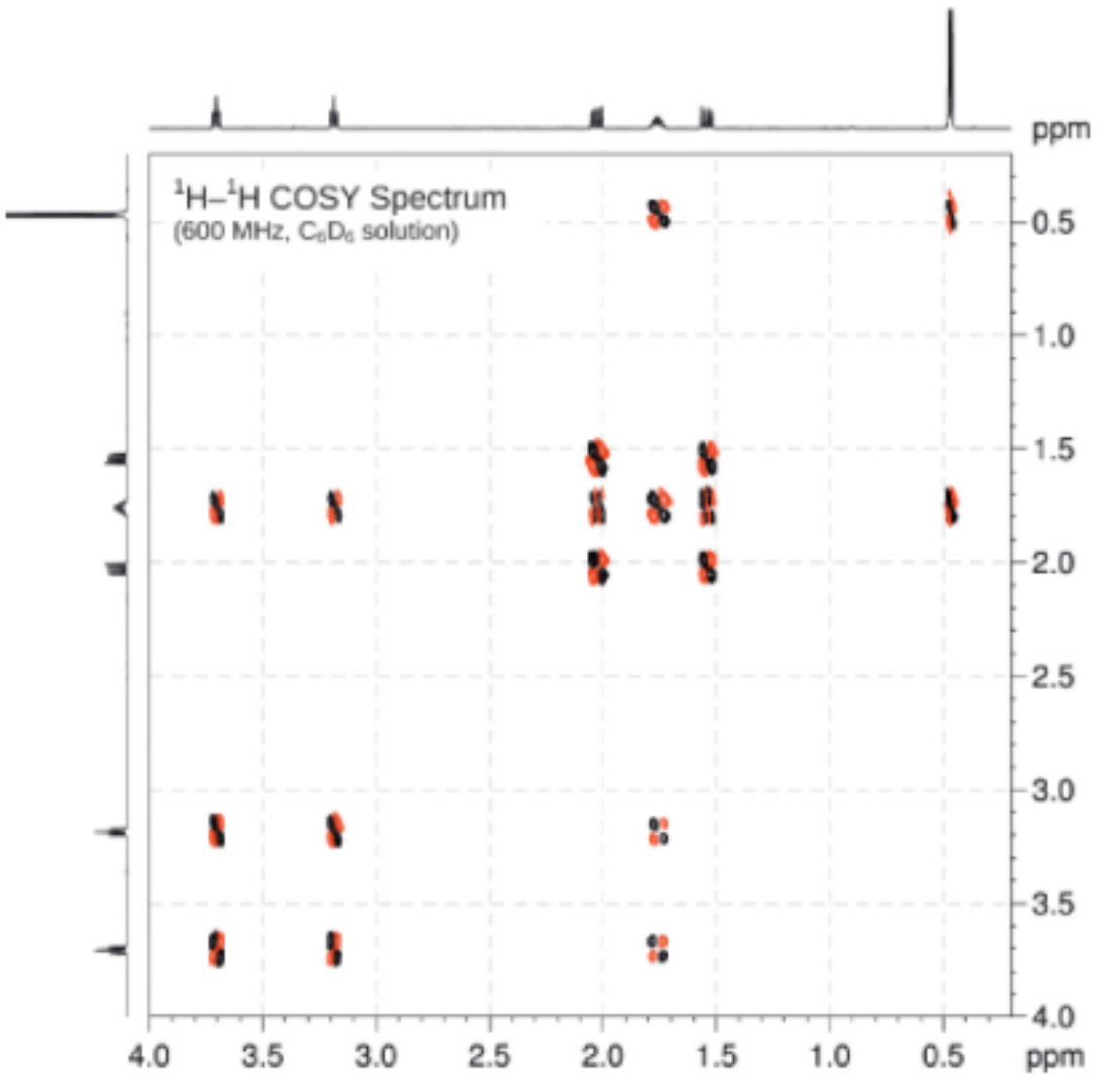

IR Spectrum
(liquid film)
1765
4000
3000
2000
1600
1200
800
ν (cm-1)

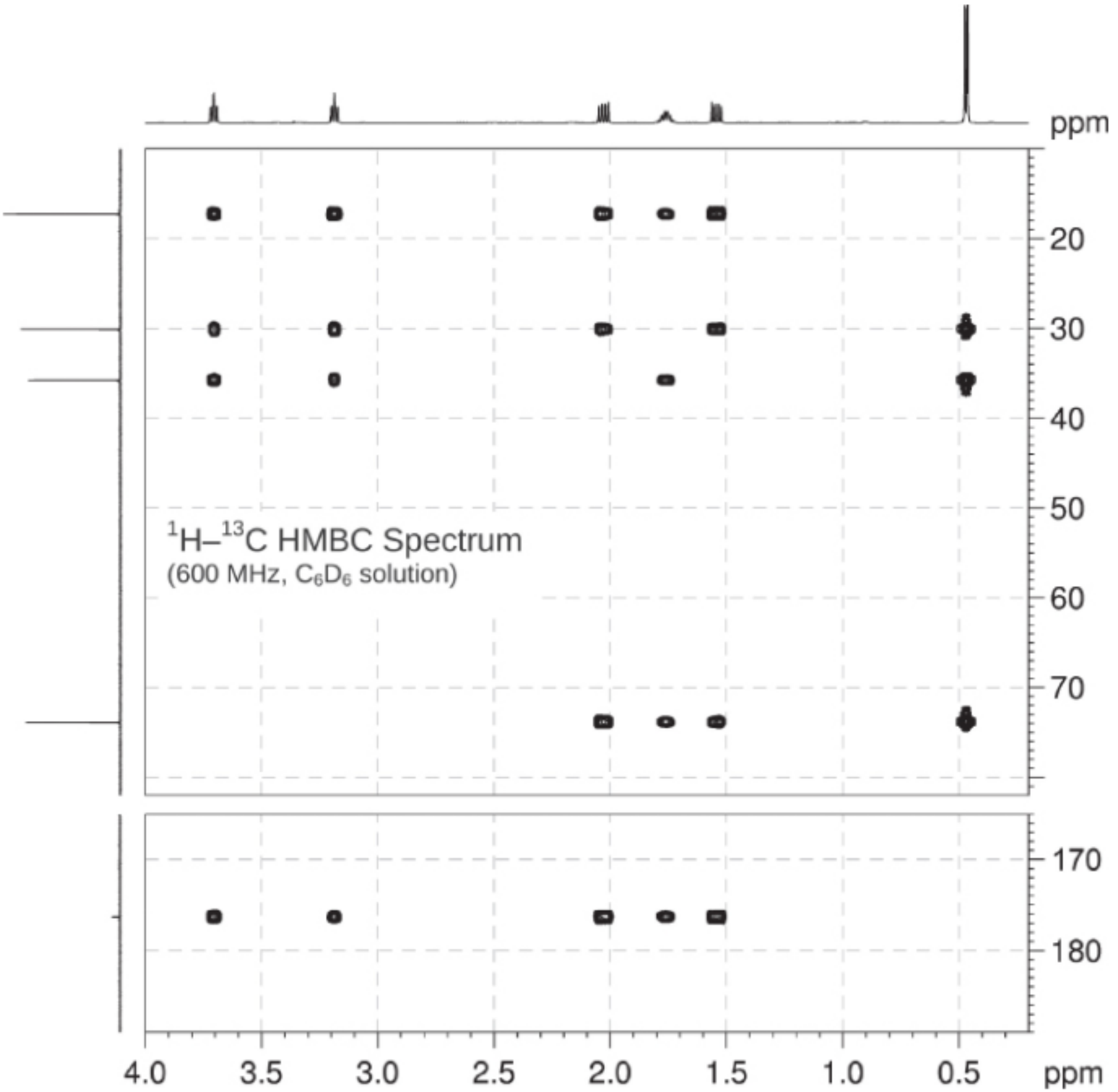

Mass Spectrum
% of base peak
100
80
60
40
20
42
56
M+·
100
C5H8O2
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(150 MHz, C6D6 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

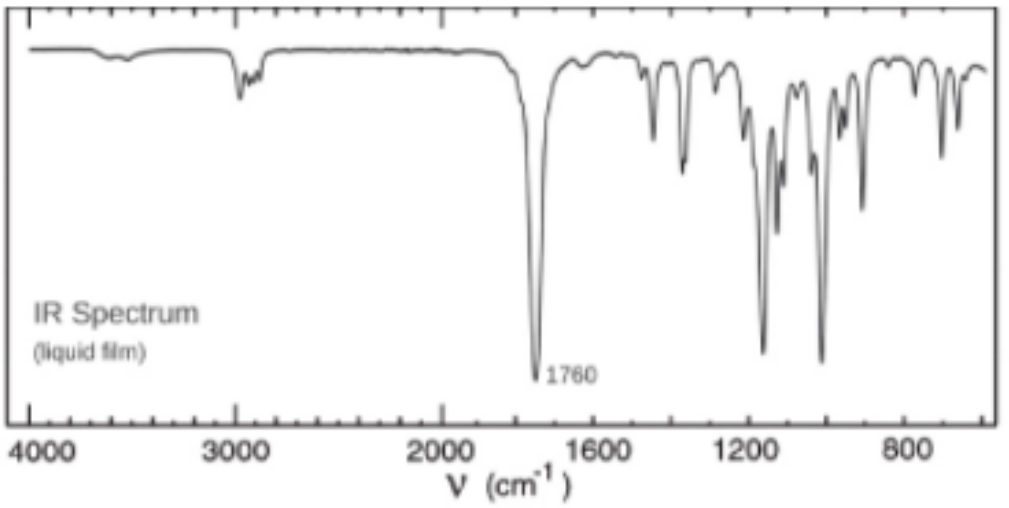

1H NMR Spectrum
(600 MHz, C6D6 solution)
expansions
expansion scale
0 20 40 60 Hz
expansion
TMS
3.6
3.4
3.2
2.0
1.8
1.6
0.6
0.4
solvent
residual
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

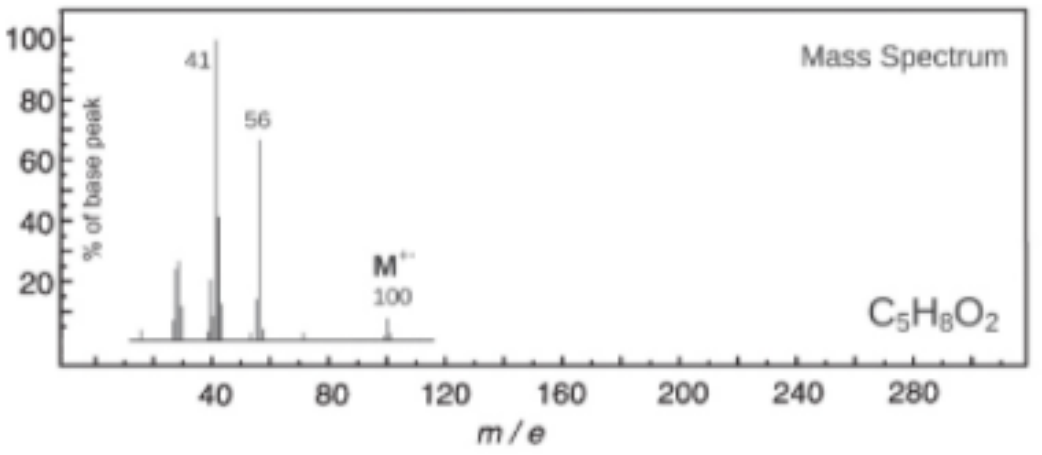

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, C_6D_6 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
20
30
40
50
60
70
170
180
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

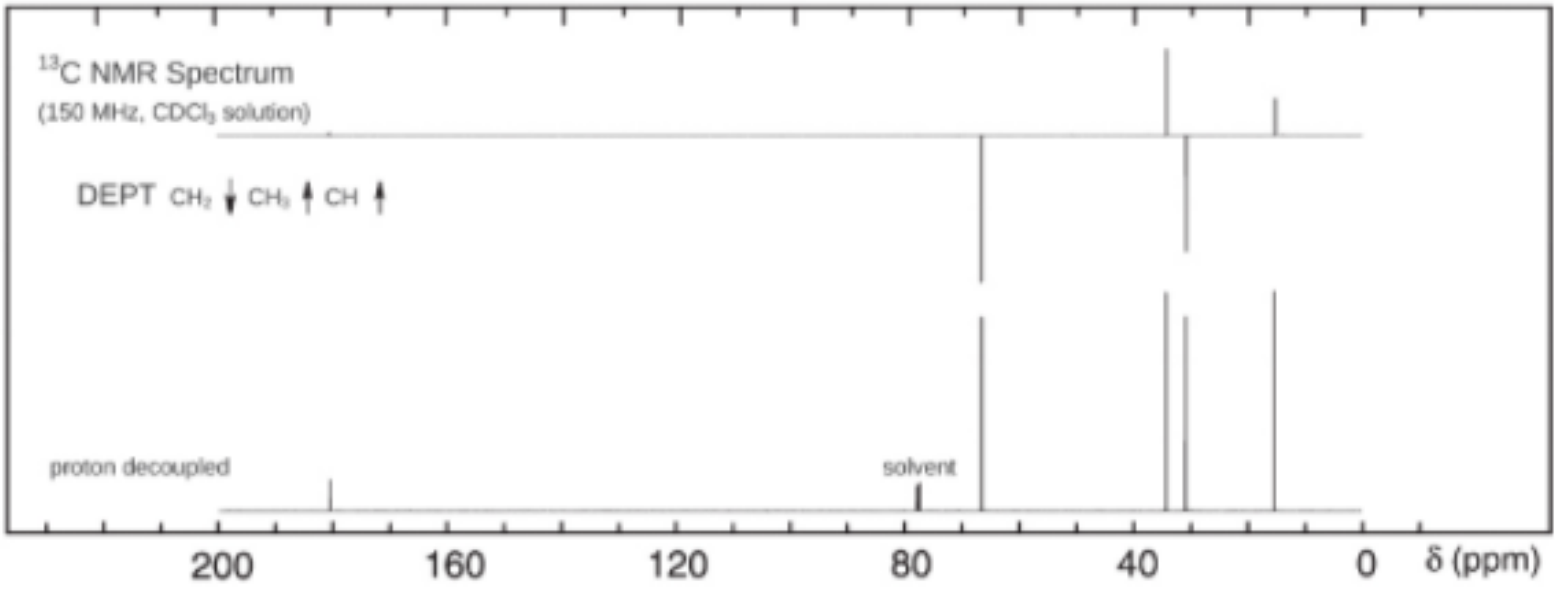

ppm
^{1}H–^{1}H COSY Spectrum
(600 MHz, C_6D_6 solution)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

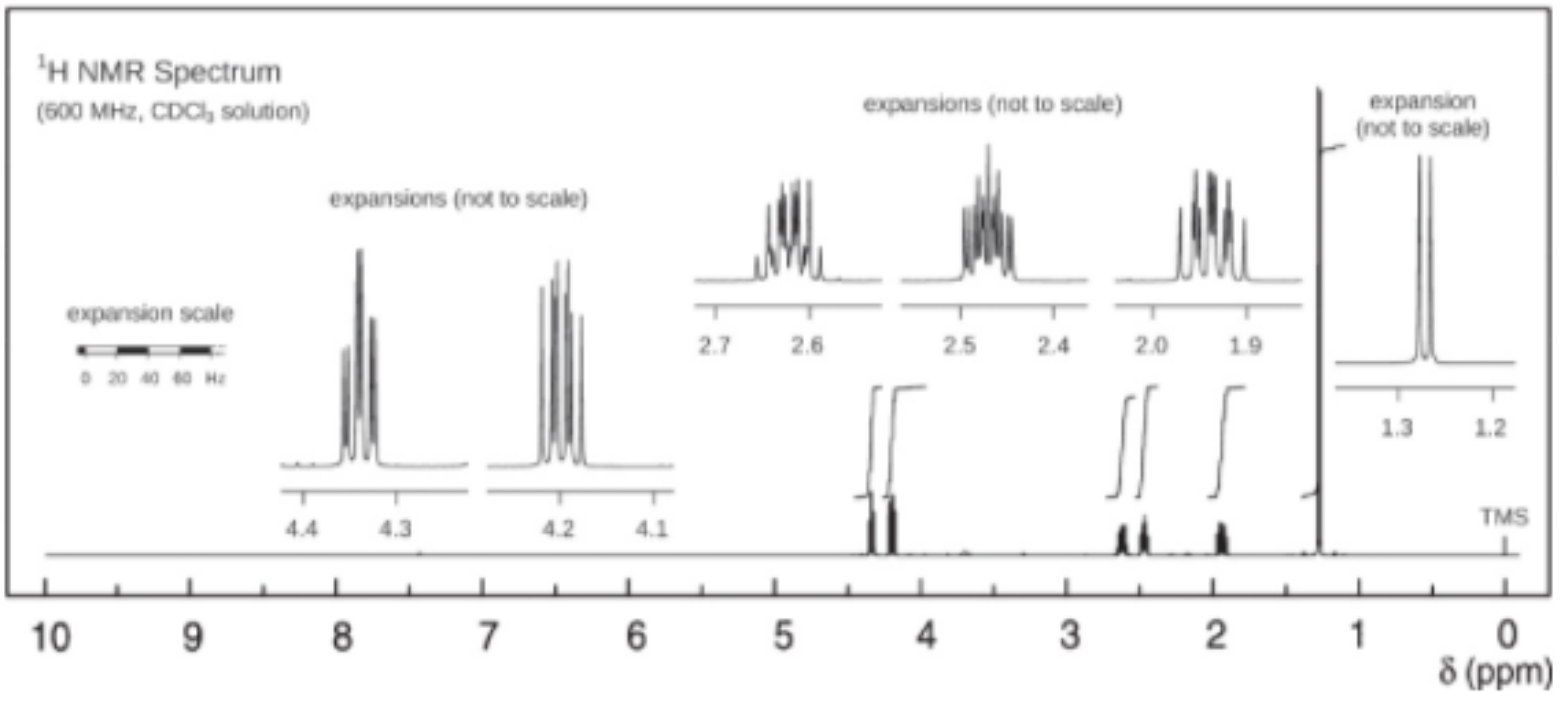

ppm
20
30
40
50
60
70
170
180
^{1}H–^{13}C HMBC Spectrum
(600 MHz, C_6D_6 solution)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

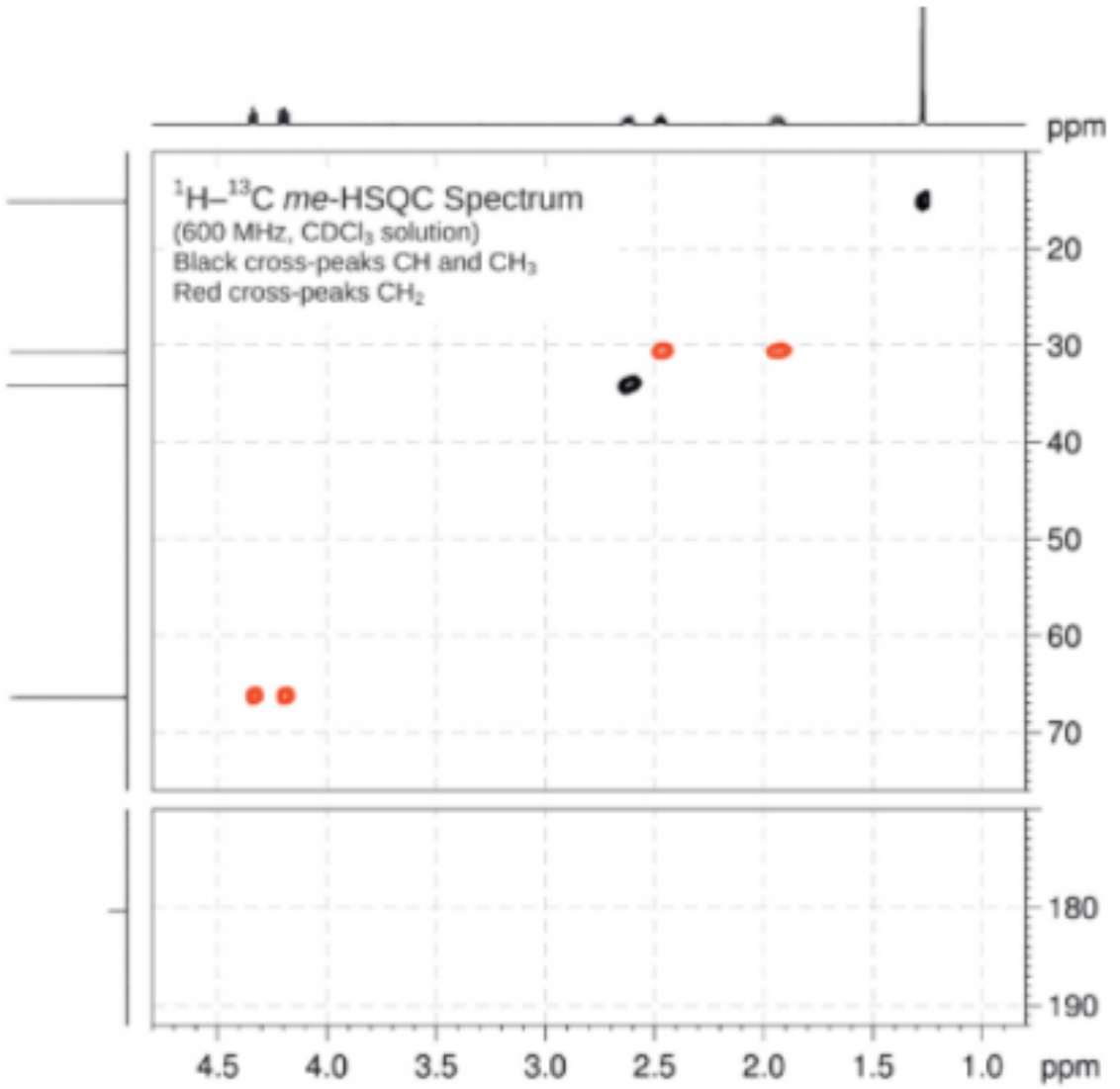
Problem 263


IR Spectrum
(liquid film)
1760
4000
3000
2000
1600
1200
800
ν (cm-1)

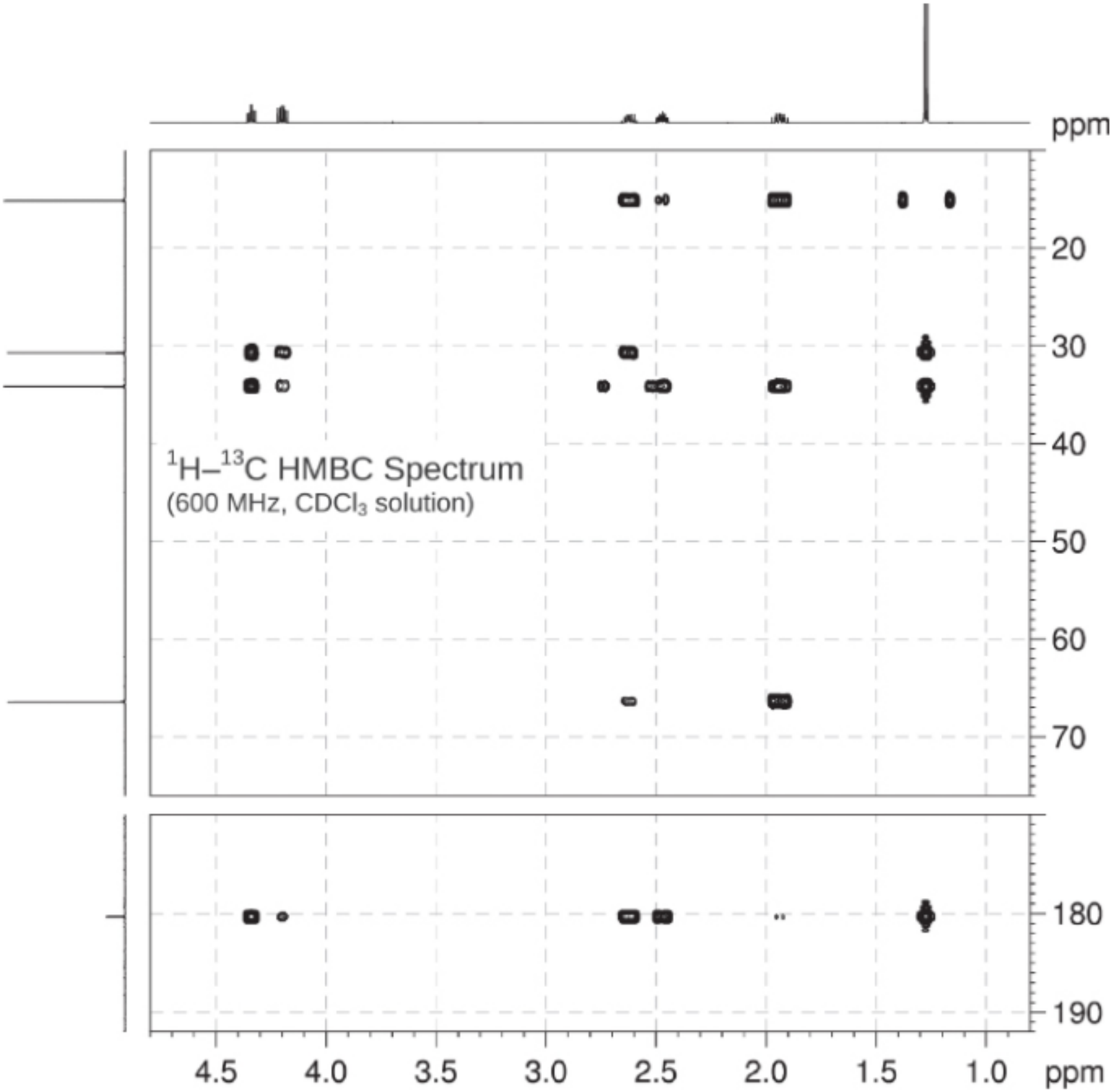

Mass Spectrum
% of base peak
100
80
60
40
20
41
56
M+·
100
C5H8O2
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

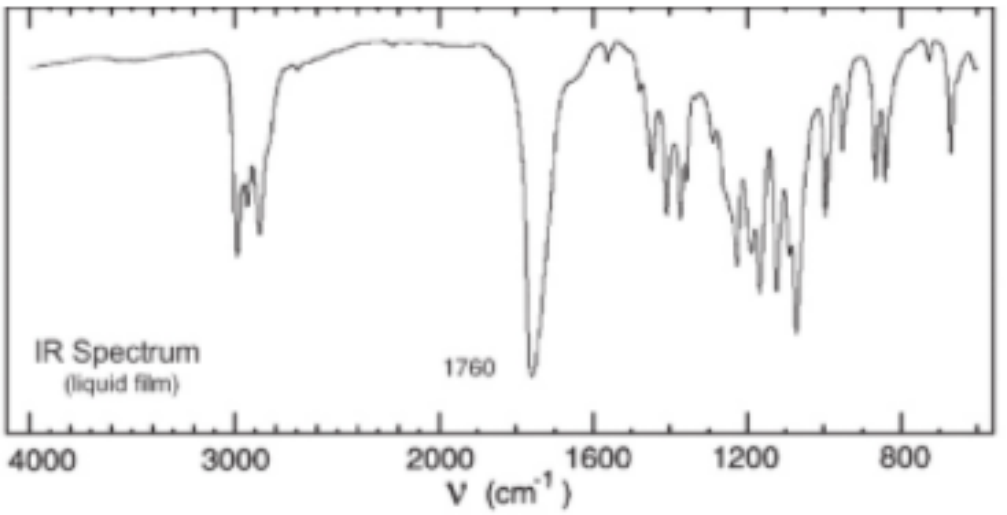

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion scale
0 20 40 60 Hz
expansions (not to scale)
4.4
4.3
4.2
4.1
expansions (not to scale)
2.7
2.6
2.5
2.4
2.0
1.9
expansion
(not to scale)
1.3
1.2
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

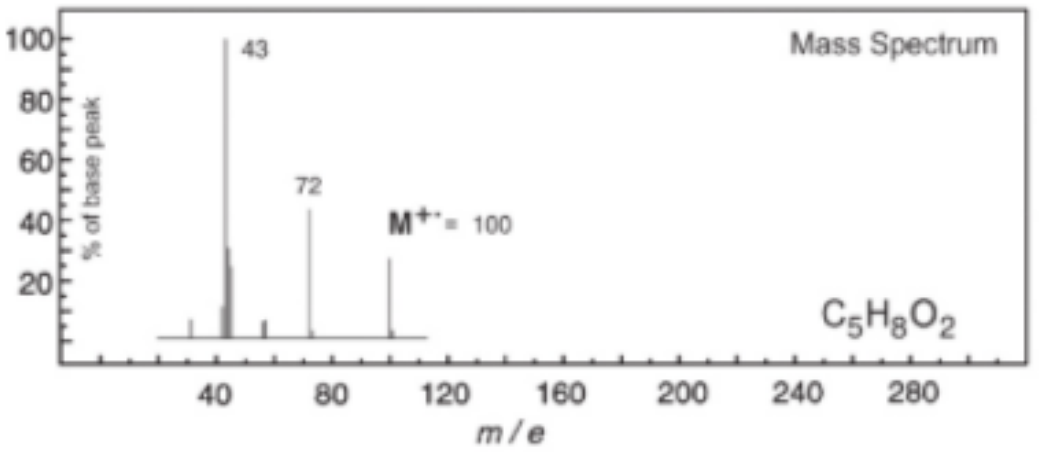

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
20
30
40
50
60
70
180
190
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

ppm
^{1}H–^{1}H COSY Spectrum
(600 MHz, $CDCl_3$ solution)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

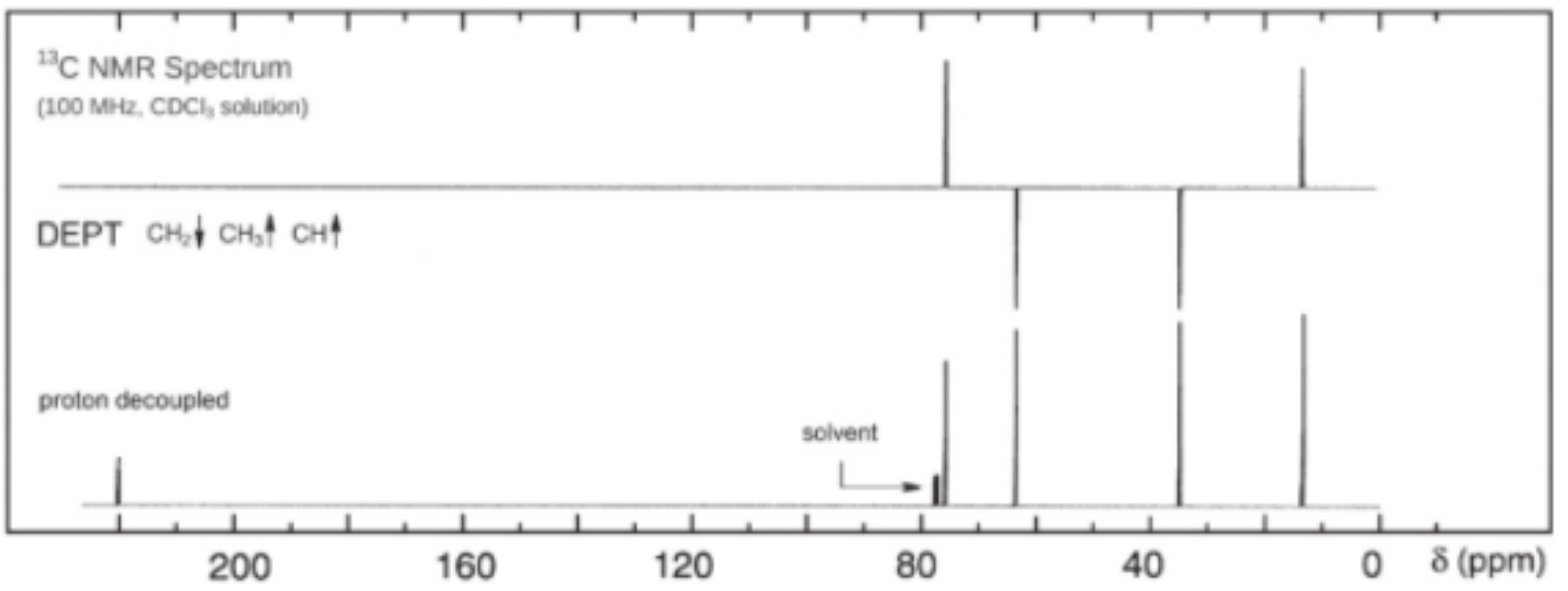

ppm
20
30
40
50
60
70
180
190
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

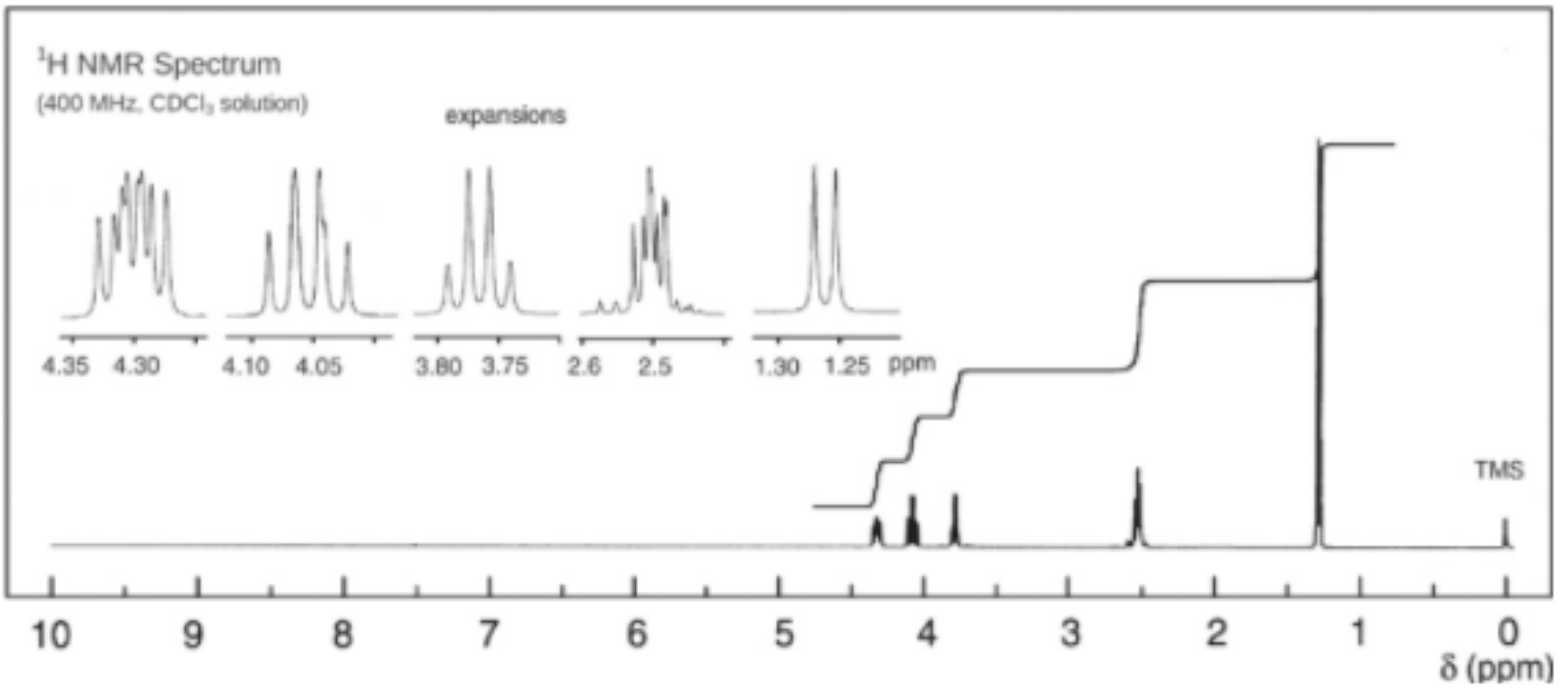
Problem 264



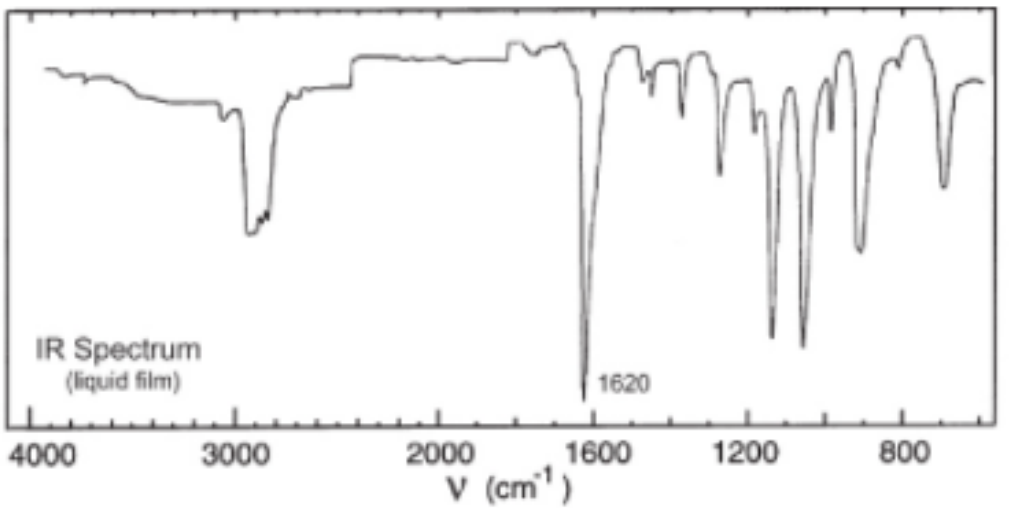


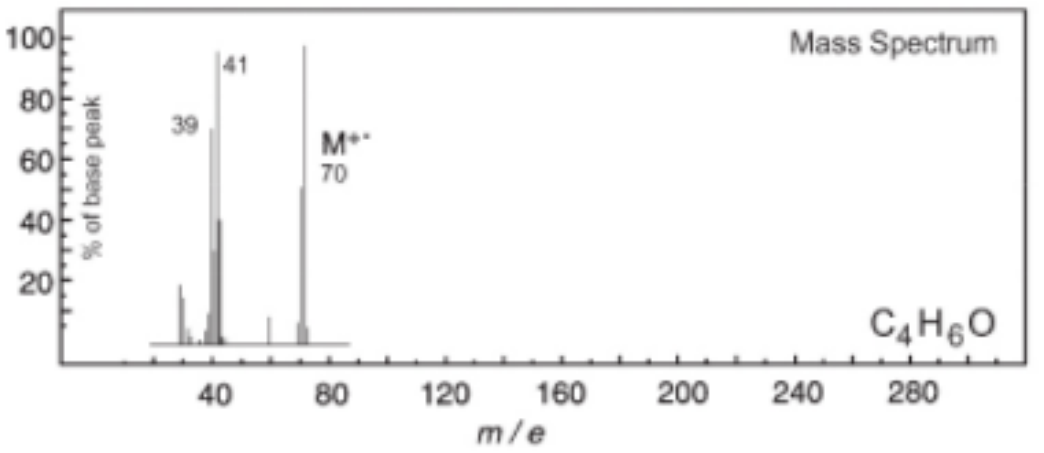
No significant UV
absorption above 220 nm



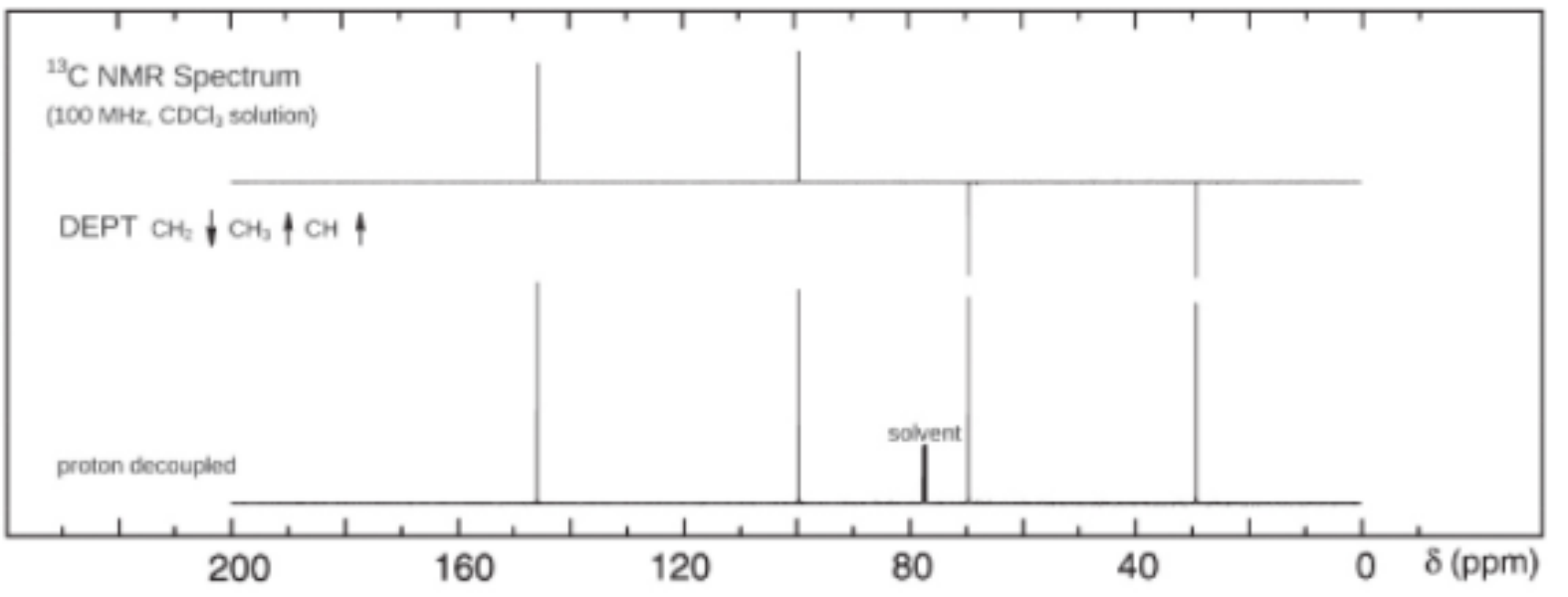


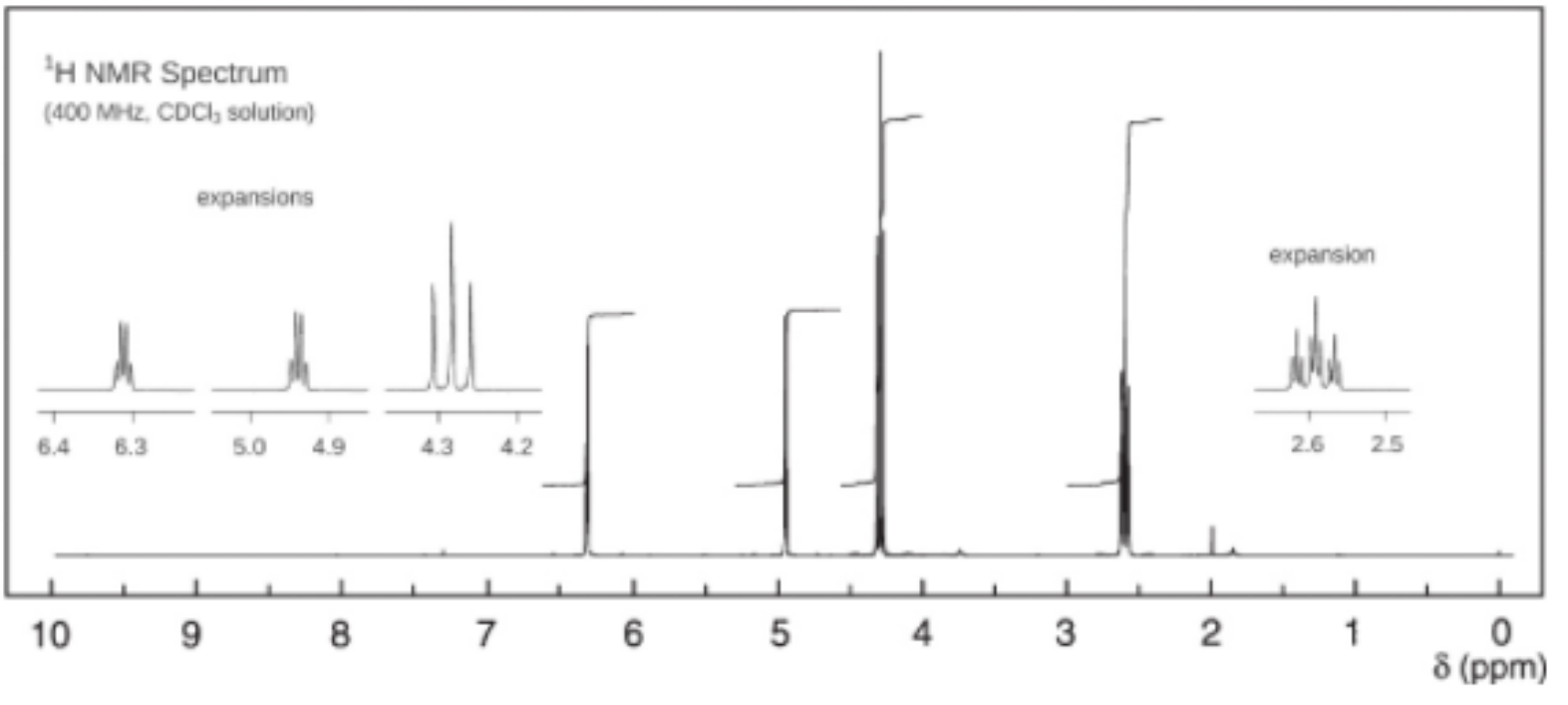
Problem 265



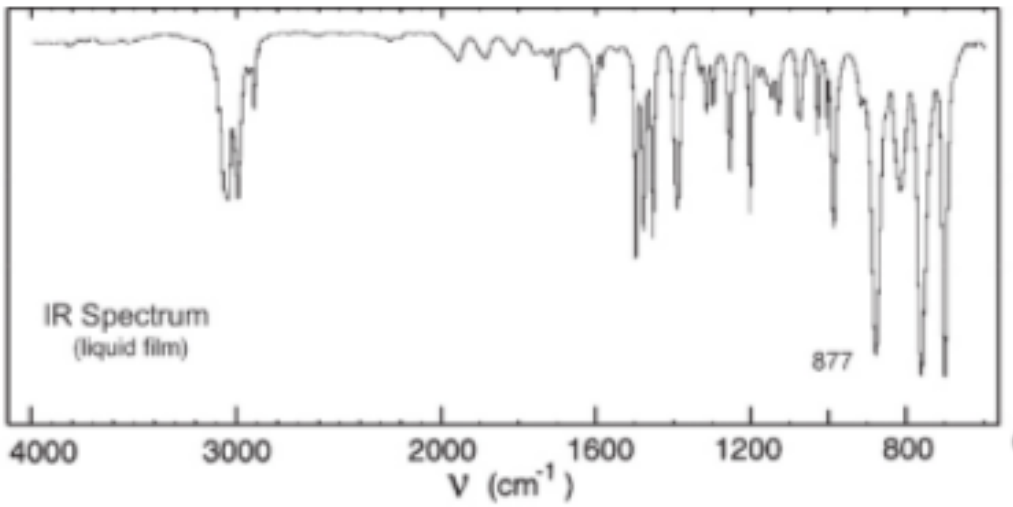


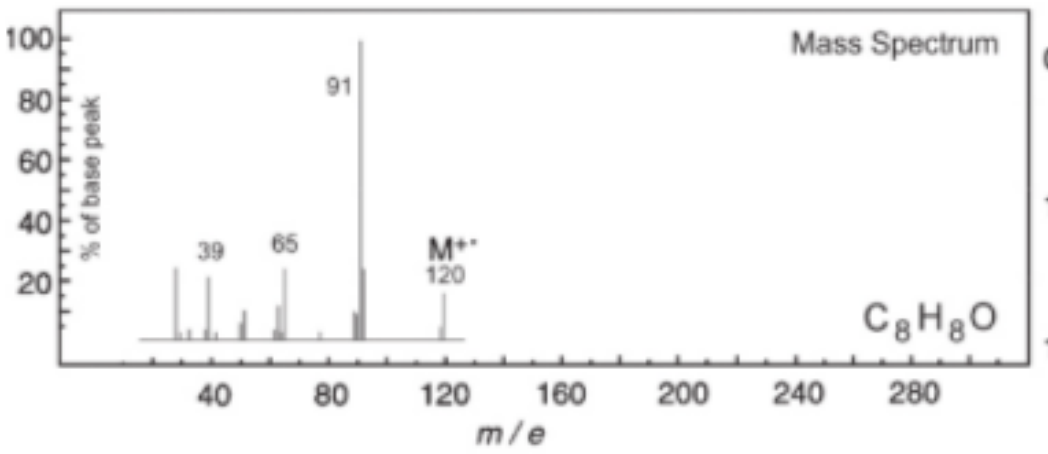
No significant UV absorption above 220 nm

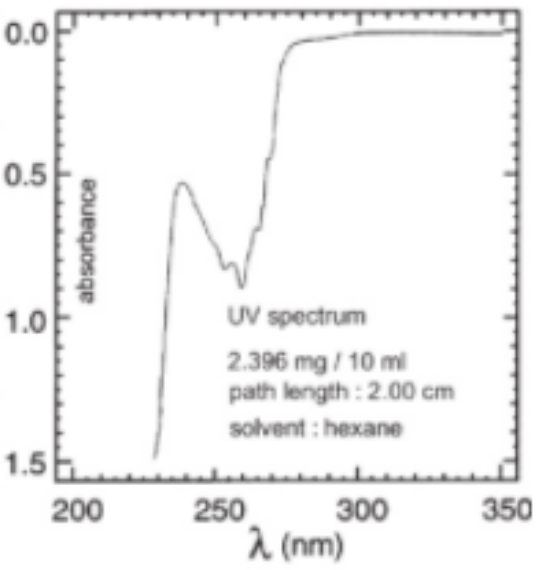


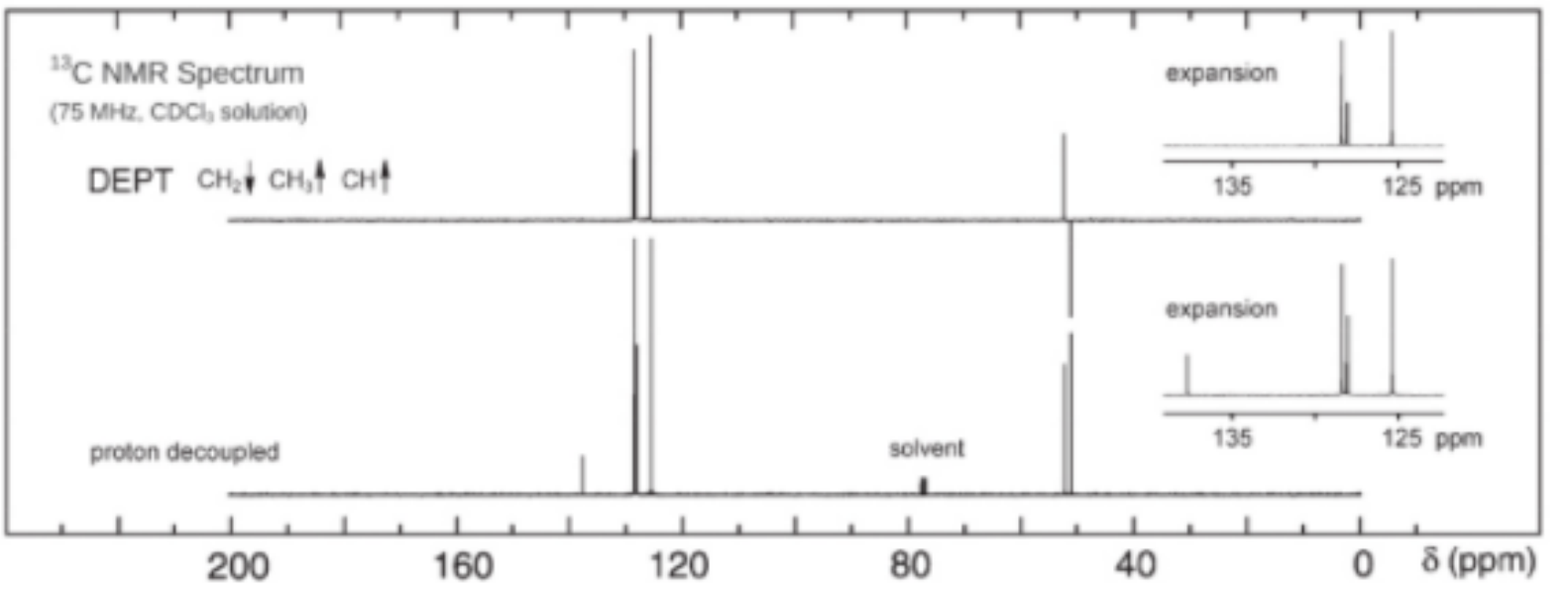


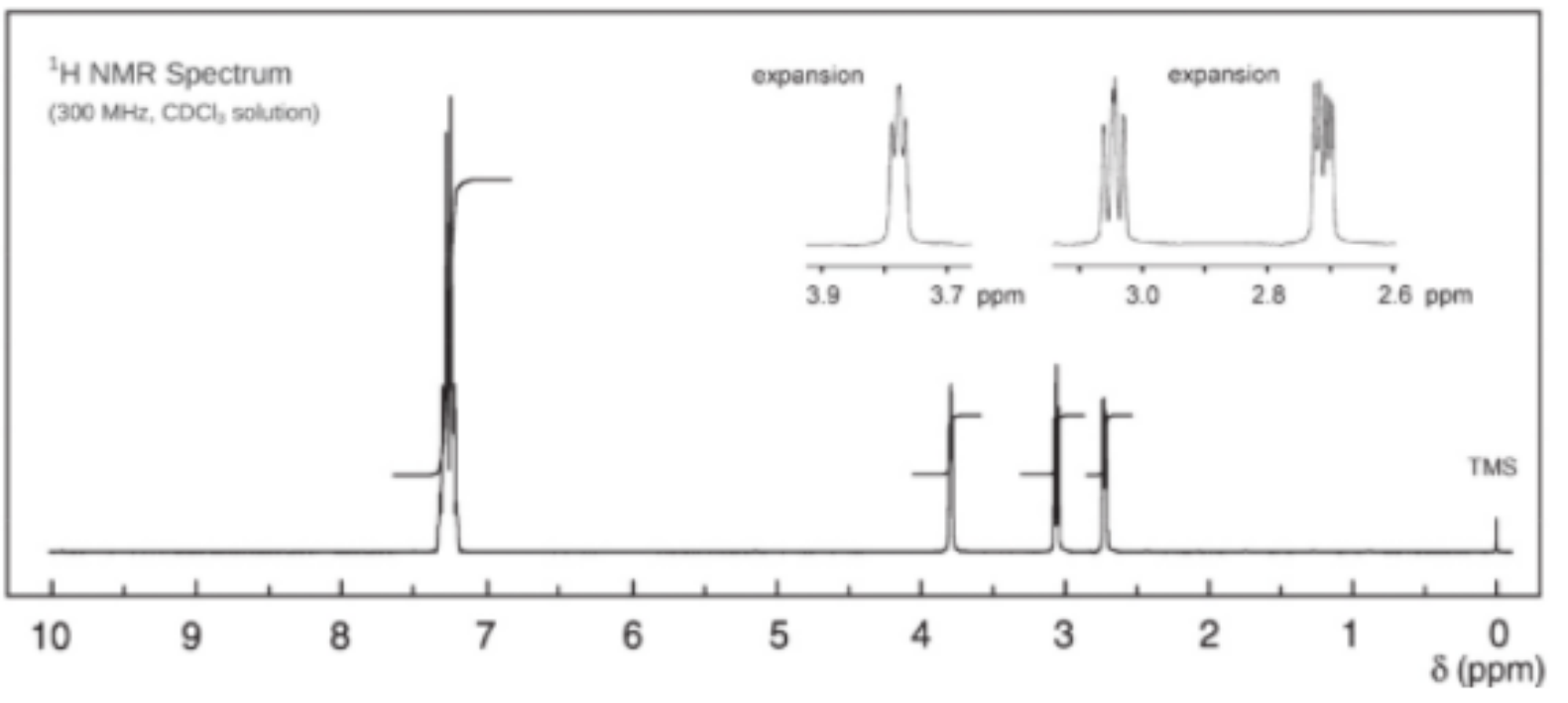
Problem 266

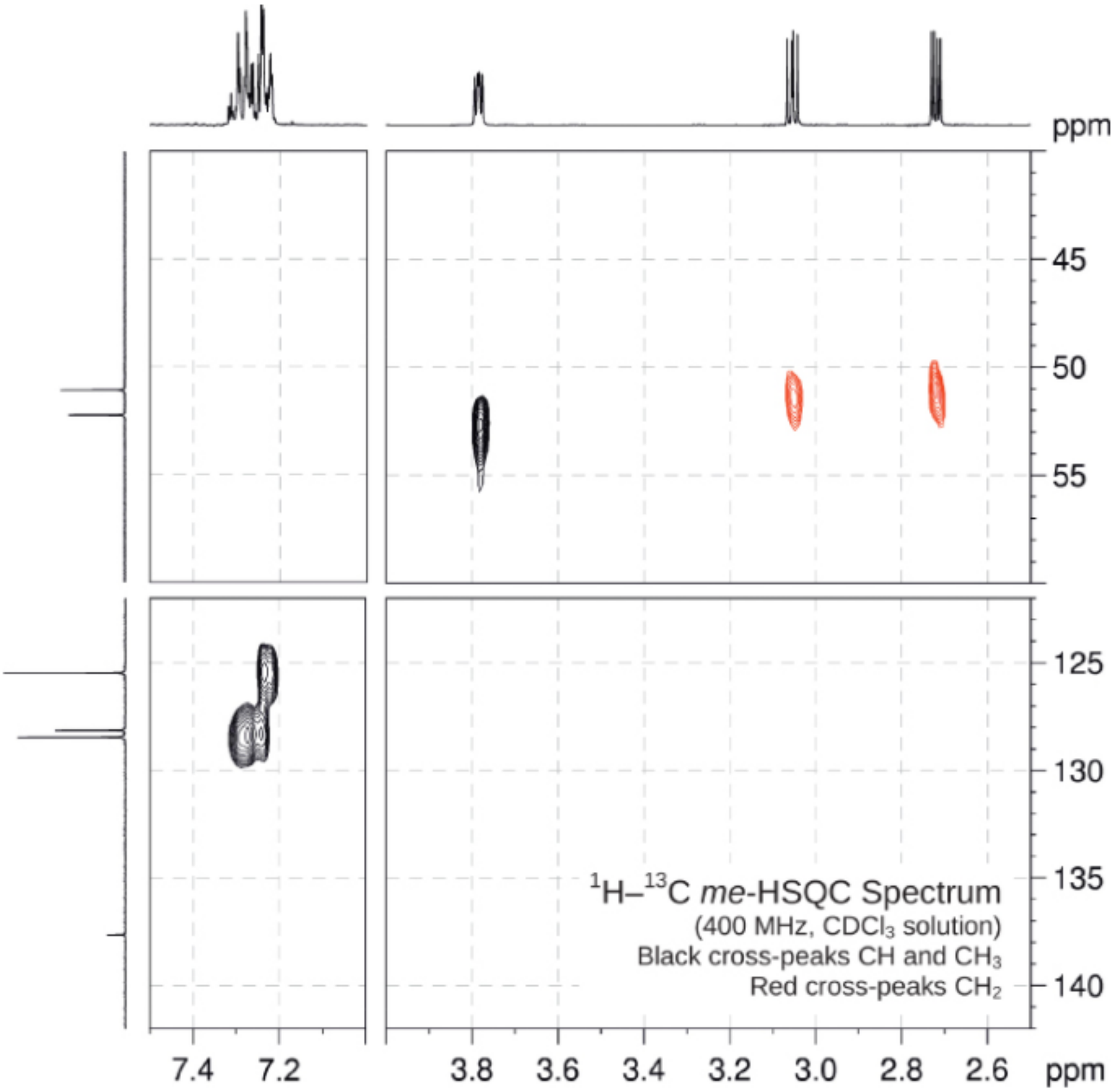

IR Spectrum
(liquid film)
877
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
% of base peak
100
80
60
40
20
91
39
65
M+·
120
C8H8O
40
80
120
160
200
240
280
m/e

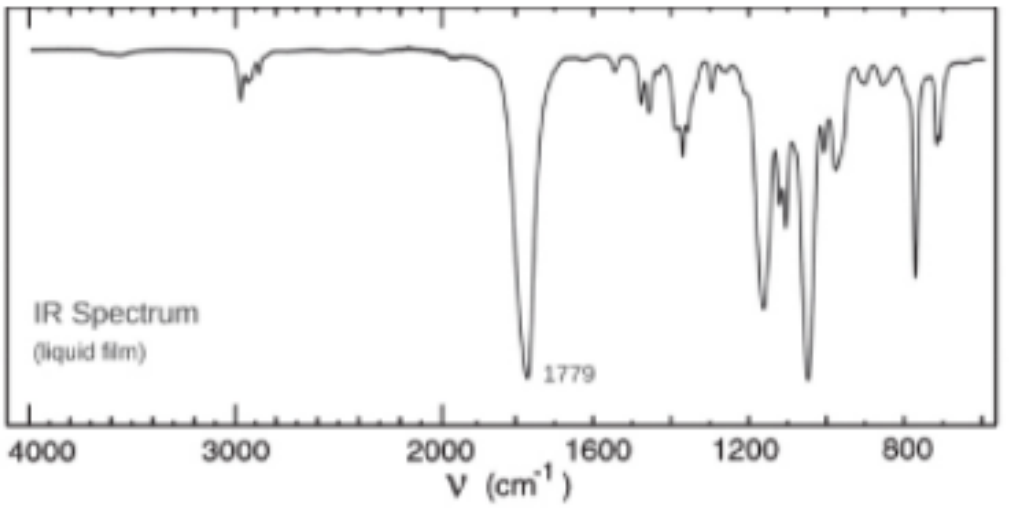

absorbance
0.0
0.5
1.0
1.5
UV spectrum
2.396 mg / 10 ml
path length : 2.00 cm
solvent : hexane
200
250
300
350
λ (nm)

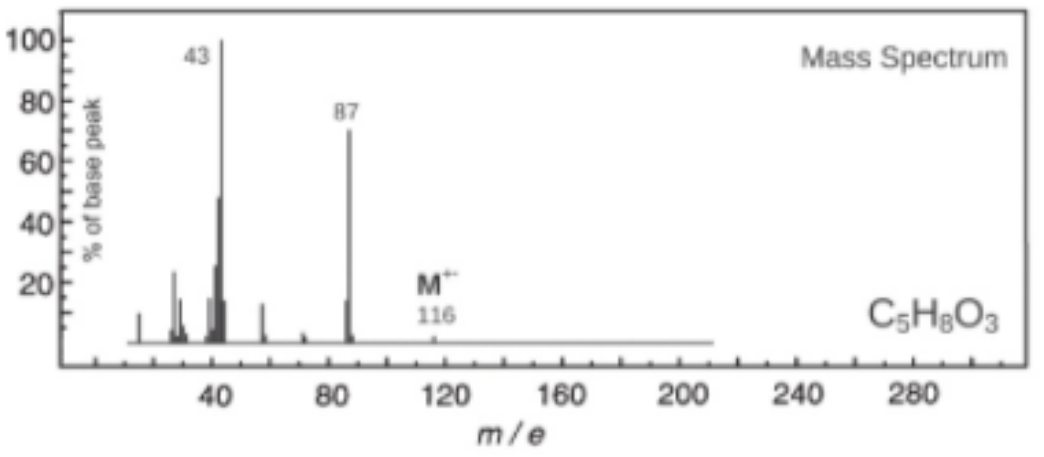

13C NMR Spectrum
(75 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
expansion
135
125 ppm
expansion
135
125 ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

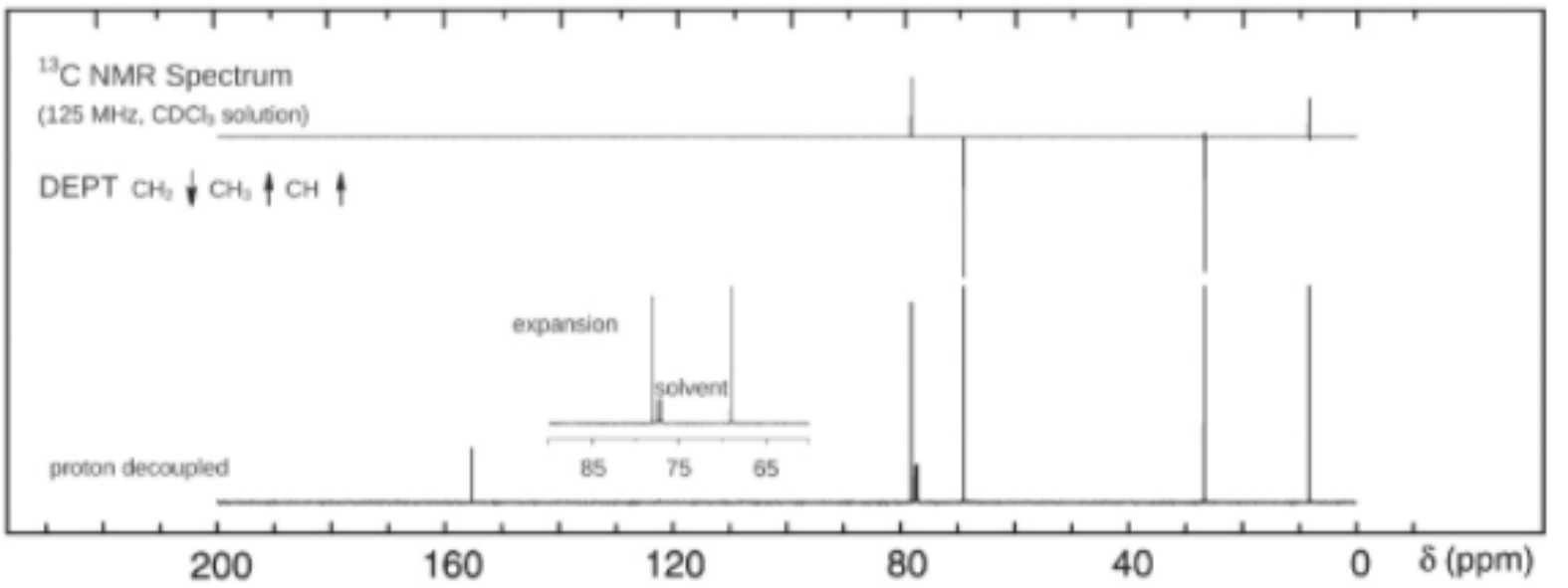

1H NMR Spectrum
(300 MHz, CDCl3 solution)
expansion
3.9
3.7 ppm
expansion
3.0
2.8
2.6 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

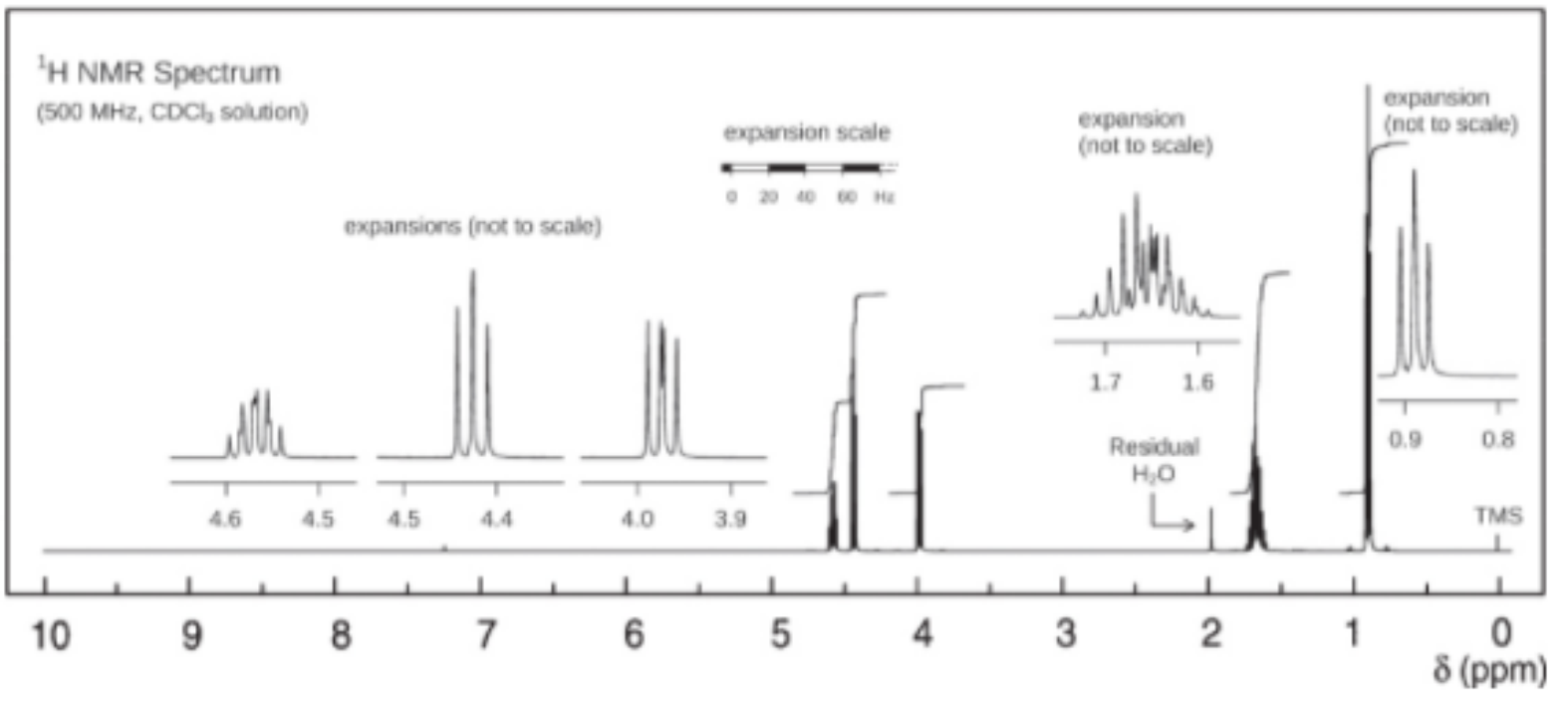

ppm
45
50
55
125
130
135
140
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.4
7.2
3.8
3.6
3.4
3.2
3.0
2.8
2.6
ppm

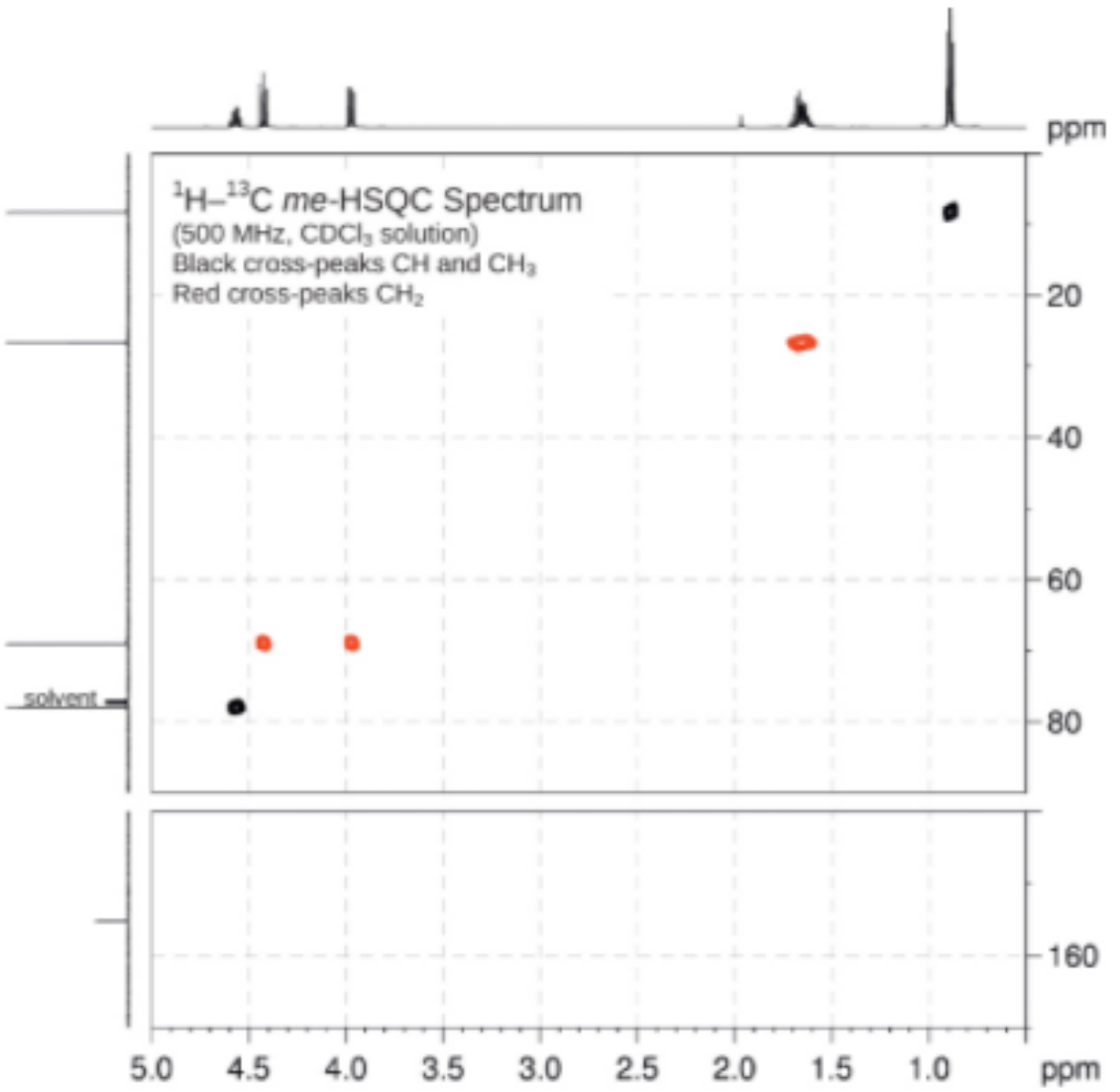
Problem 267

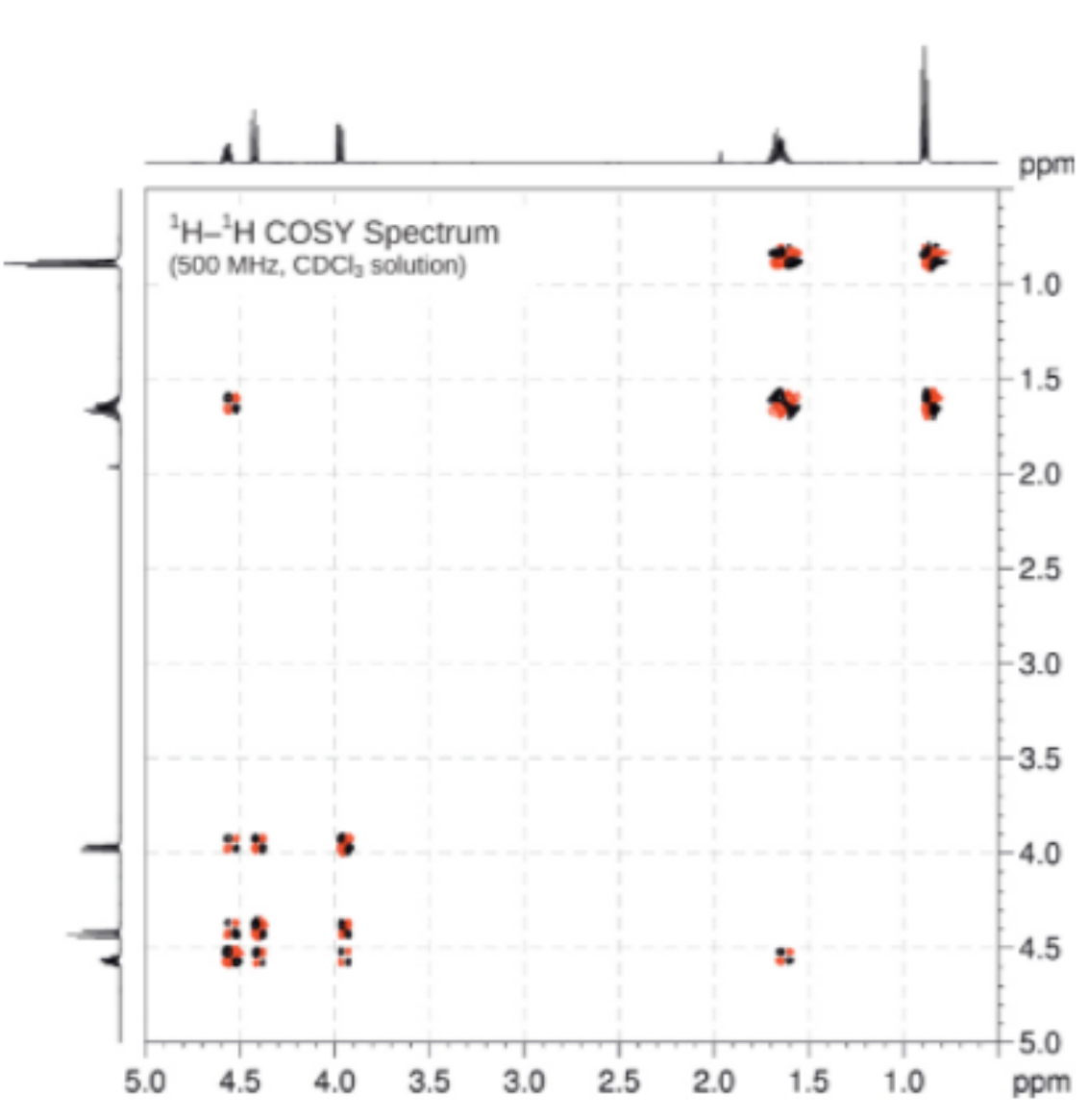

IR Spectrum
(liquid film)
1779
4000
3000
2000
1600
1200
800
ν (cm-1)

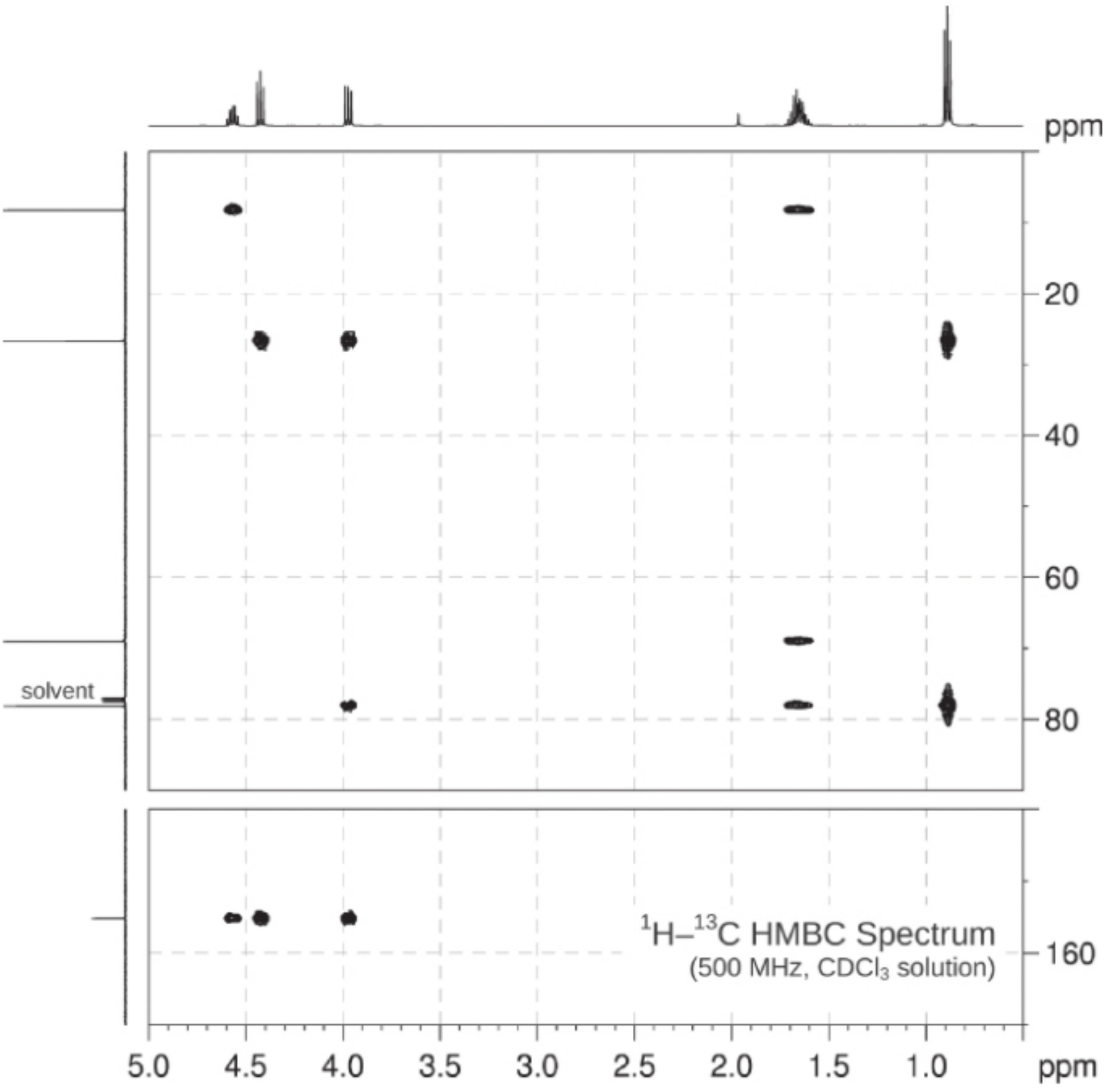

Mass Spectrum
% of base peak
100
80
60
40
20
43
87
M+·
116
C5H8O3
40
80
120
160
200
240
280
m/e


13C NMR Spectrum
(125 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
expansion
solvent
85
75
65
proton decoupled
200
160
120
80
40
0
δ (ppm)

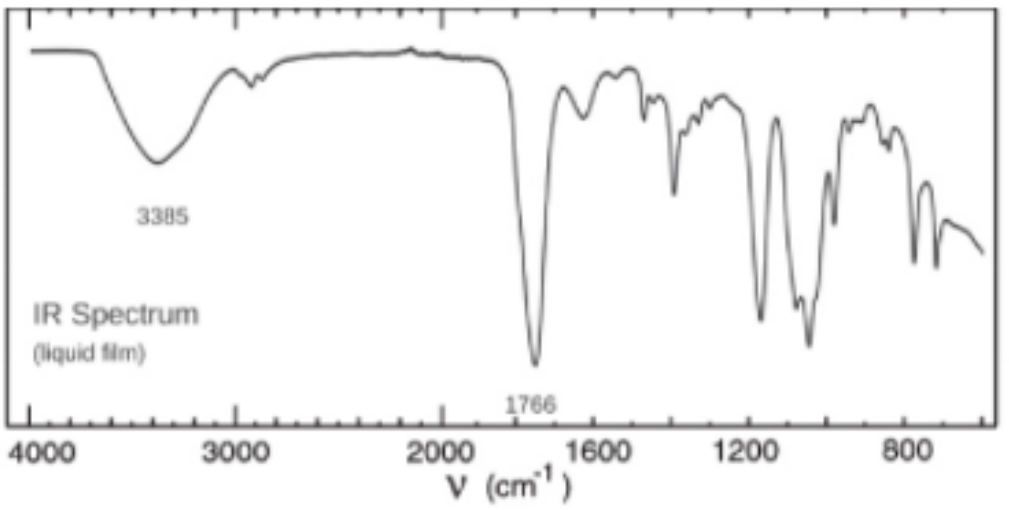

1H NMR Spectrum
(500 MHz, CDCl3 solution)
expansion scale
0 20 40 60 Hz
expansions (not to scale)
4.6
4.5
4.5
4.4
4.0
3.9
expansion
(not to scale)
1.7
1.6
Residual
H2O
expansion
(not to scale)
0.9
0.8
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

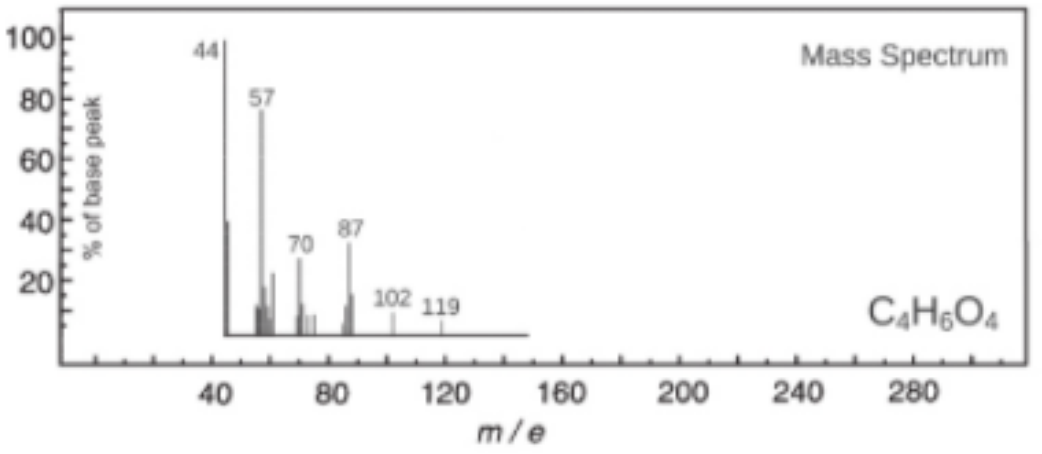

ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(500 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
20
40
60
80
solvent
160
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

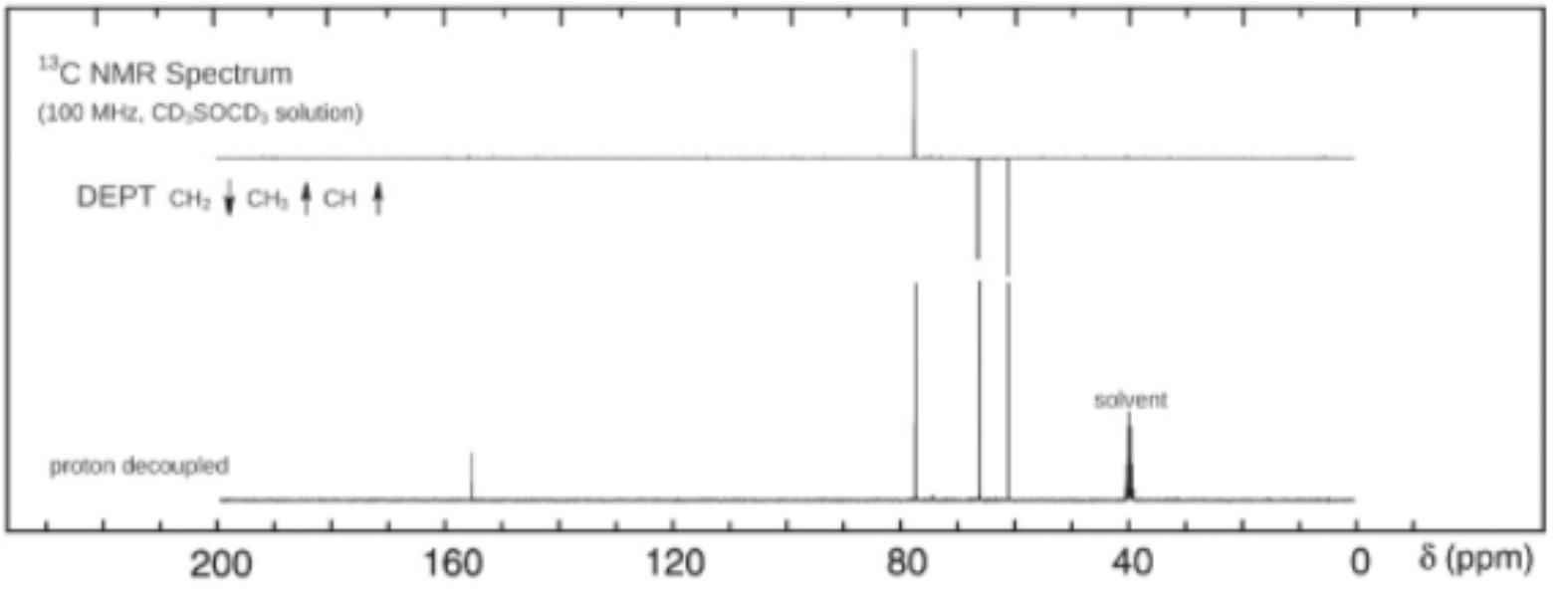

ppm
^{1}H–^{1}H COSY Spectrum
(500 MHz, $CDCl_3$ solution)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

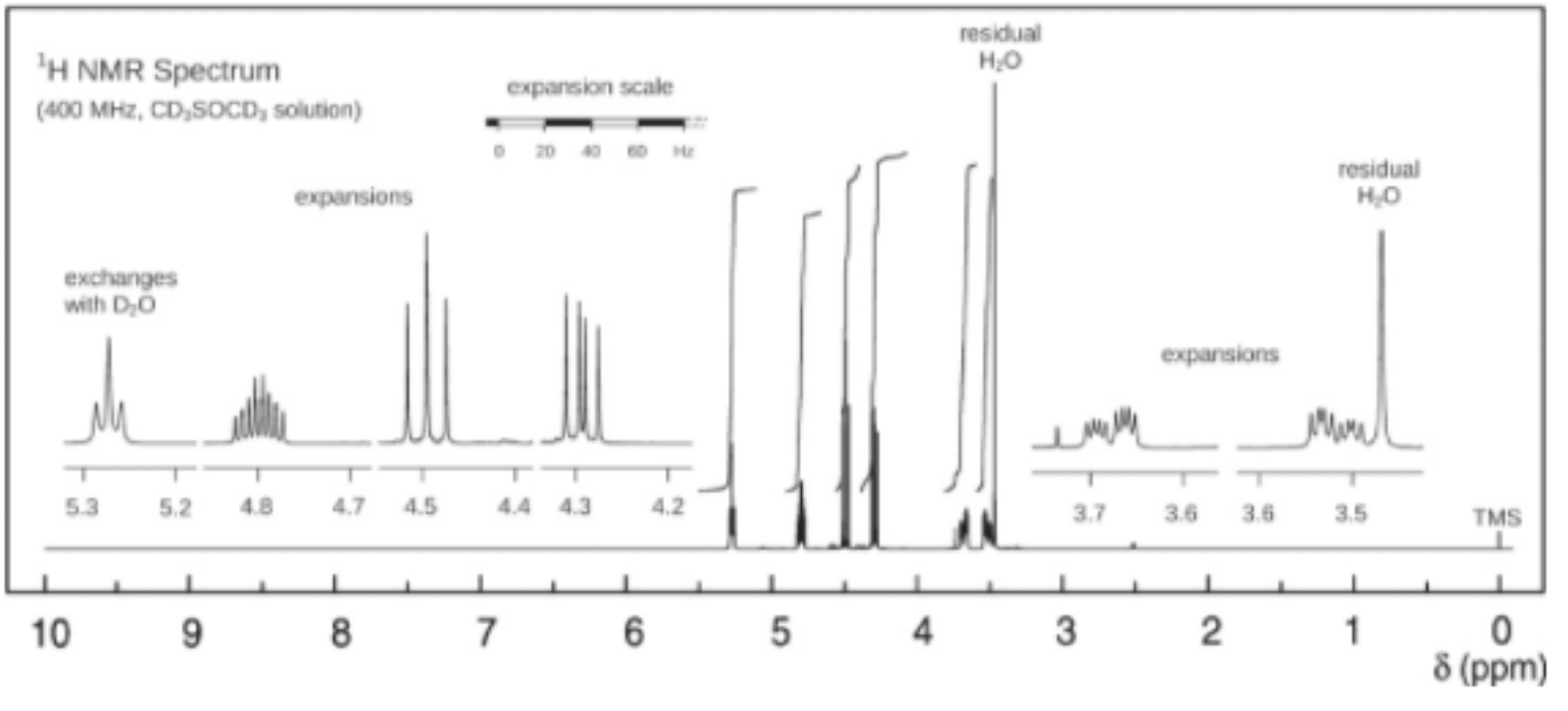

ppm
20
40
60
solvent
80
160
^{1}H–^{13}C HMBC Spectrum
(500 MHz, $CDCl_3$ solution)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

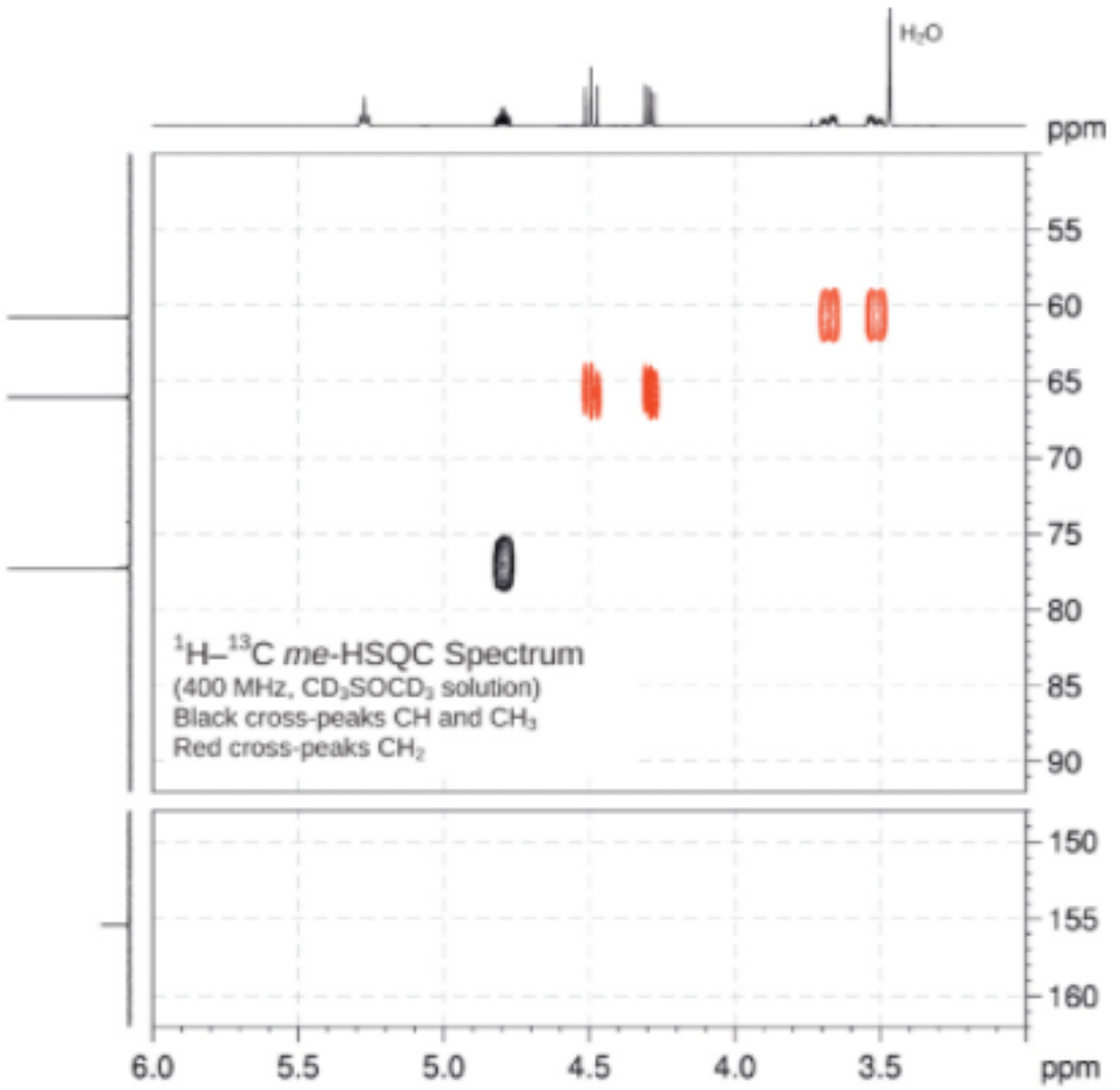
Problem 268


3385
IR Spectrum
(liquid film)
1766
4000
3000
2000
1600
1200
800
ν (cm-1)

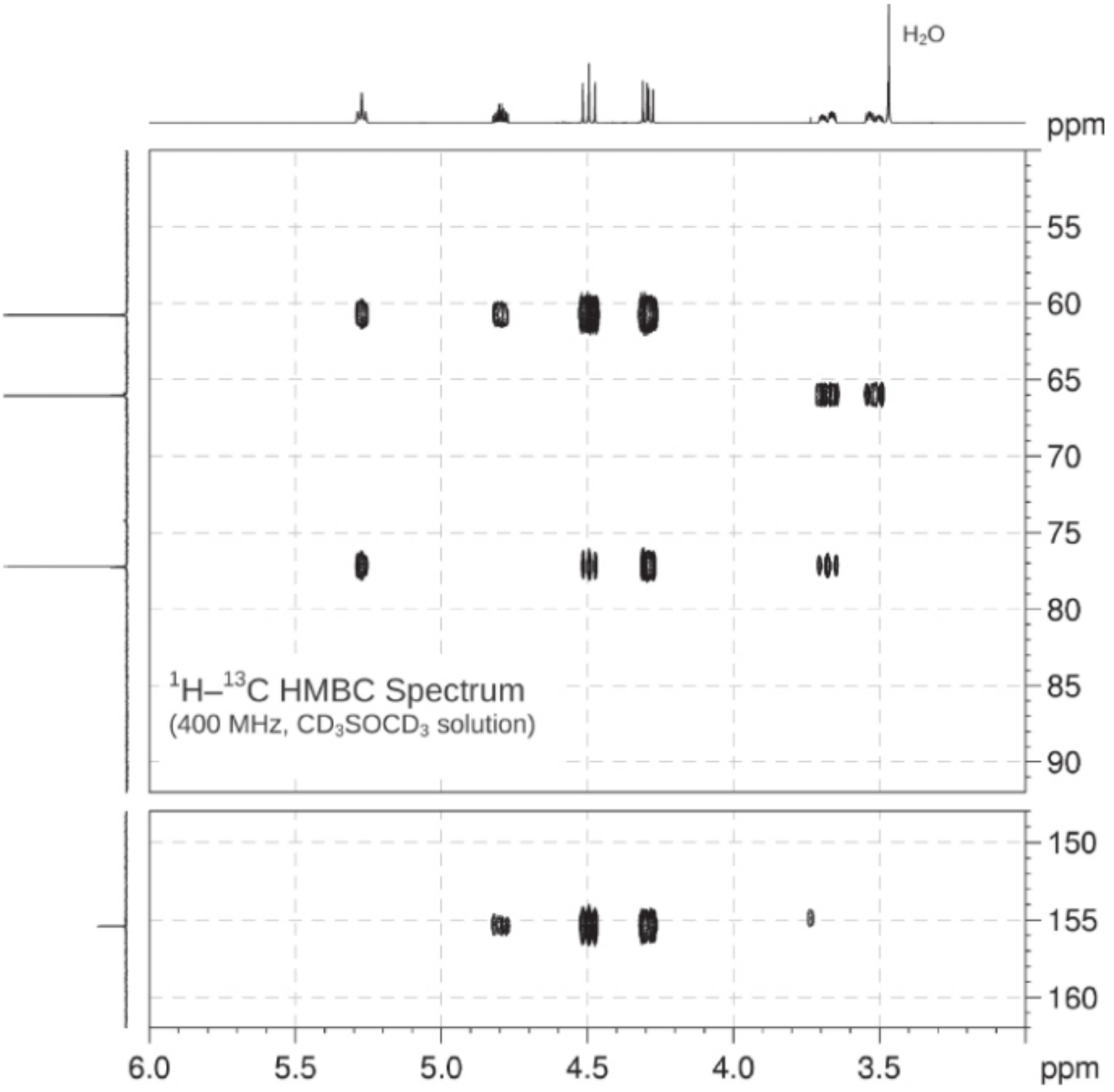

Mass Spectrum
% of base peak
100
80
60
40
20
44
57
70
87
102
119
C4H6O4
40
80
120
160
200
240
280
m / e


13C NMR Spectrum
(100 MHz, CD3SOCD3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

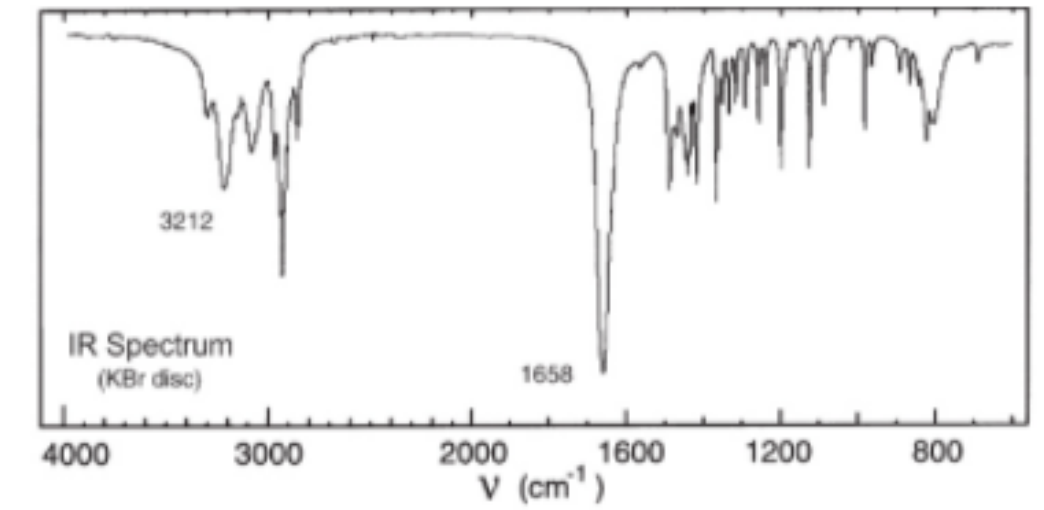

1H NMR Spectrum
(400 MHz, CD3SOCD3 solution)
expansion scale
0 20 40 60 Hz
residual H2O
expansions
exchanges with D2O
residual H2O
expansions
5.3
5.2
4.8
4.7
4.5
4.4
4.3
4.2
3.7
3.6
3.6
3.5
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

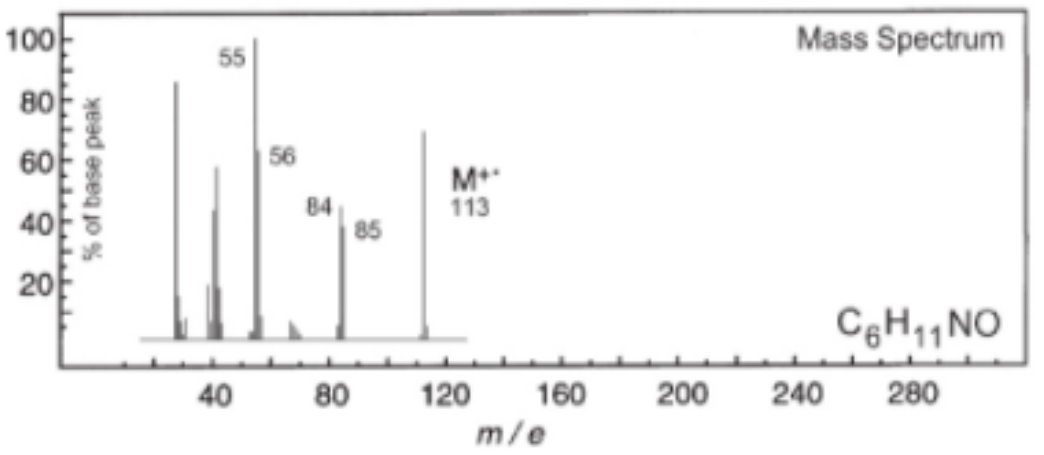

H2O
ppm
55
60
65
70
75
80
85
90
150
155
160
6.0
5.5
5.0
4.5
4.0
3.5
ppm
1H–13C me-HSQC Spectrum
(400 MHz, CD3SOCD3 solution)
Black cross-peaks CH and CH3
Red cross-peaks CH2

H2O
ppm
1H–1H COSY Spectrum
(400 MHz, CD3SOCD3 solution)
H2O
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
ppm

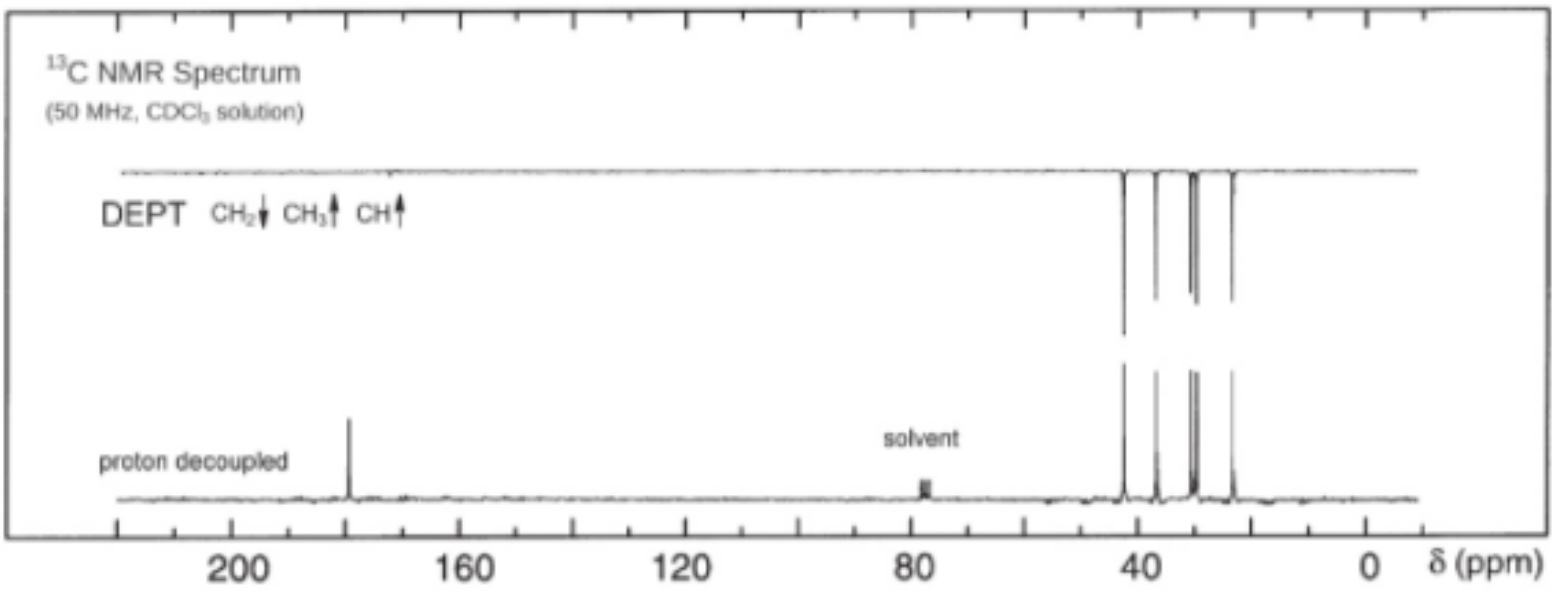

H2O
ppm
55
60
65
70
75
80
85
90
150
155
160
1H–13C HMBC Spectrum
(400 MHz, CD3SOCD3 solution)
6.0
5.5
5.0
4.5
4.0
3.5
ppm

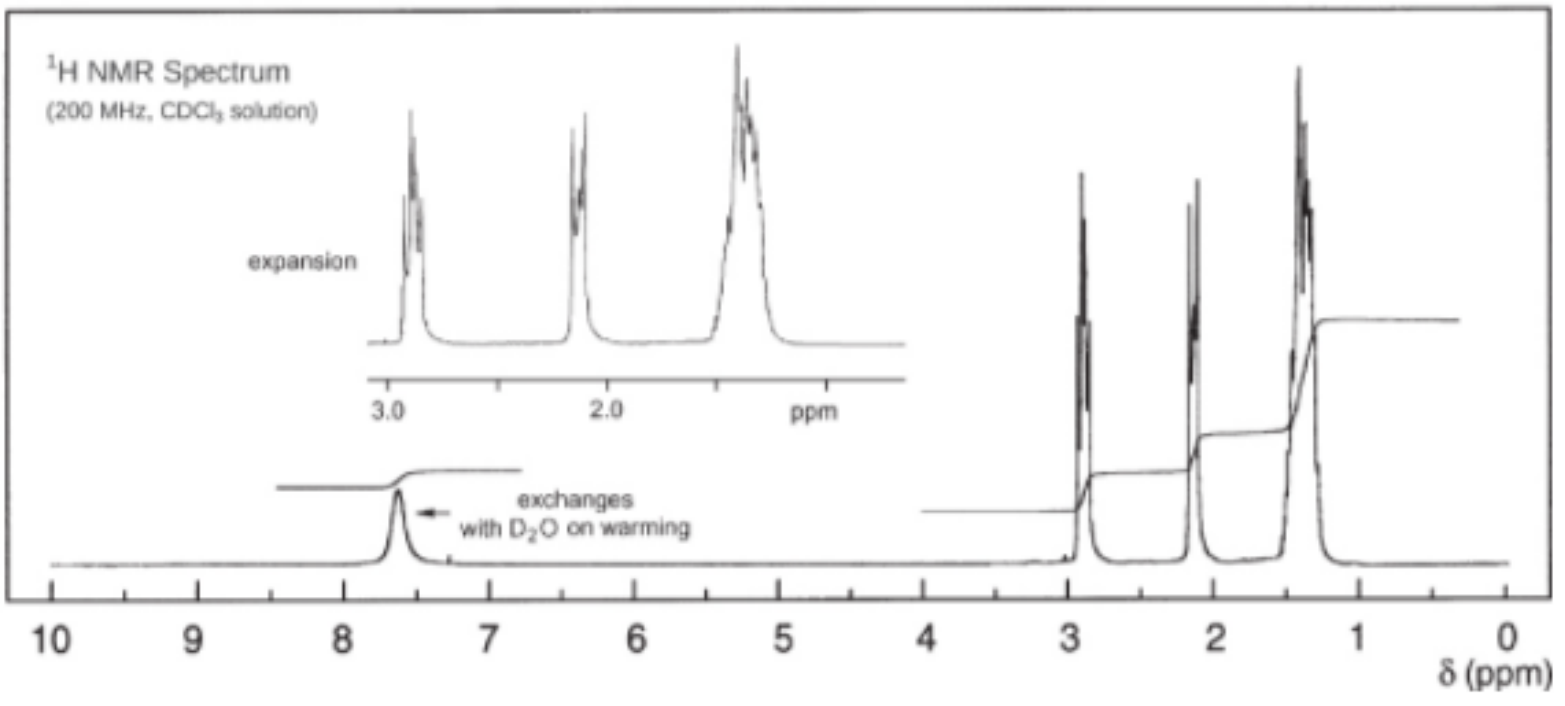
Problem 269



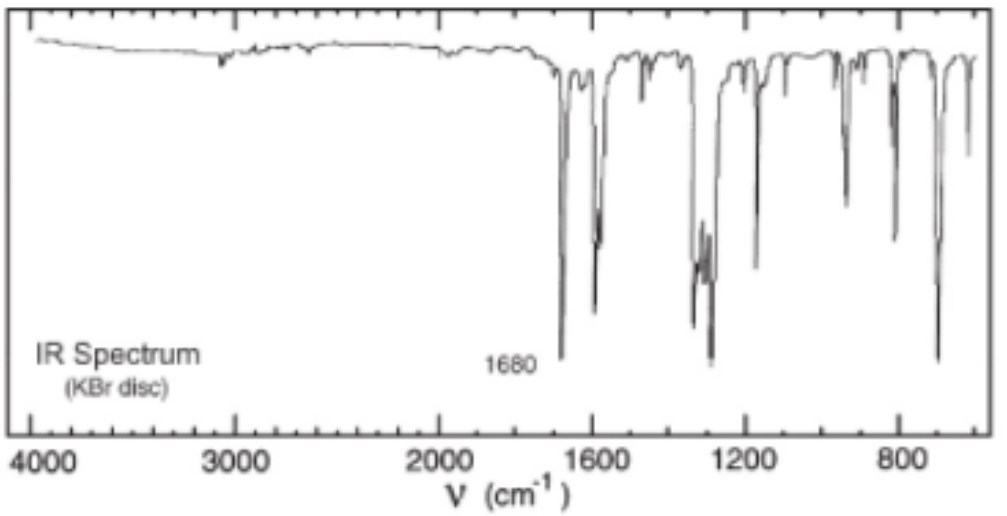


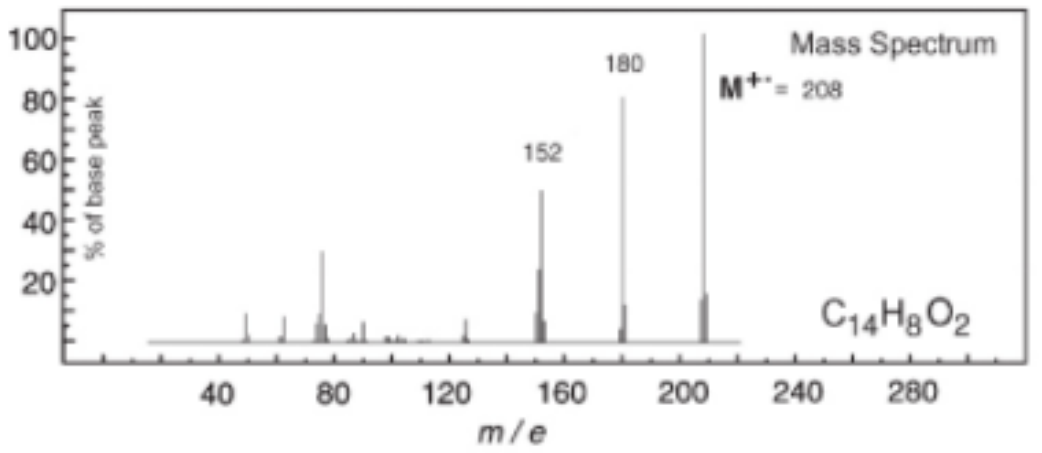
No significant UV absorption above 220 nm





Problem 270





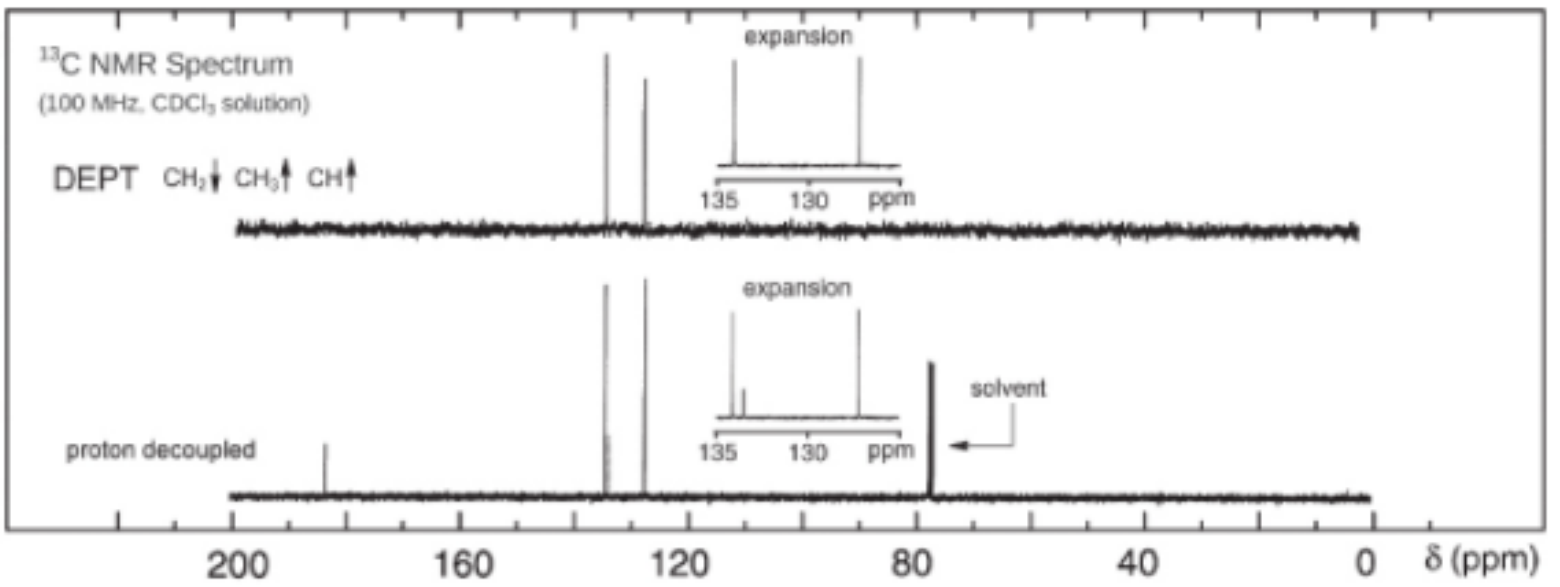
UV Spectrum

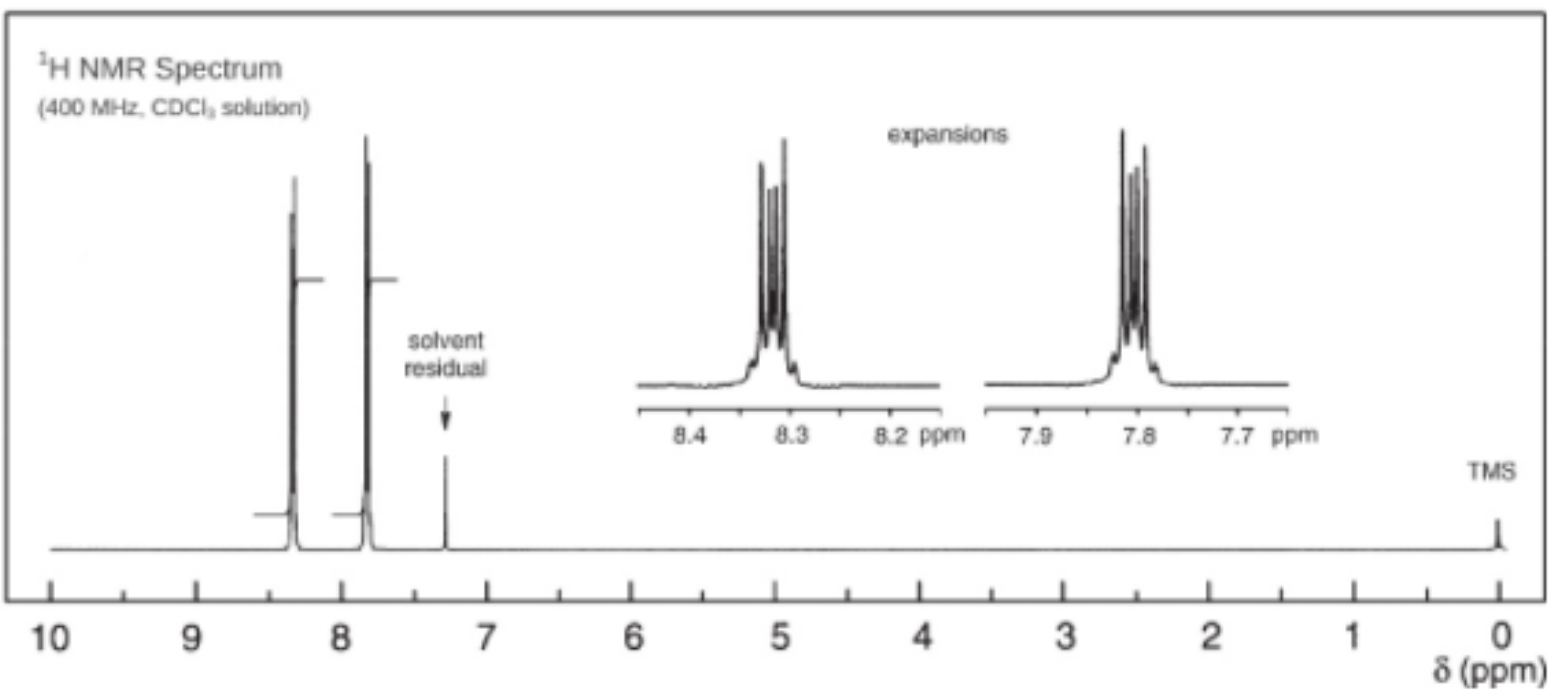
λ_{max} 255 nm ($\log_{10}\varepsilon$ 4.7)

λ_{max} 275 nm ($\log_{10}\varepsilon$ 4.3)

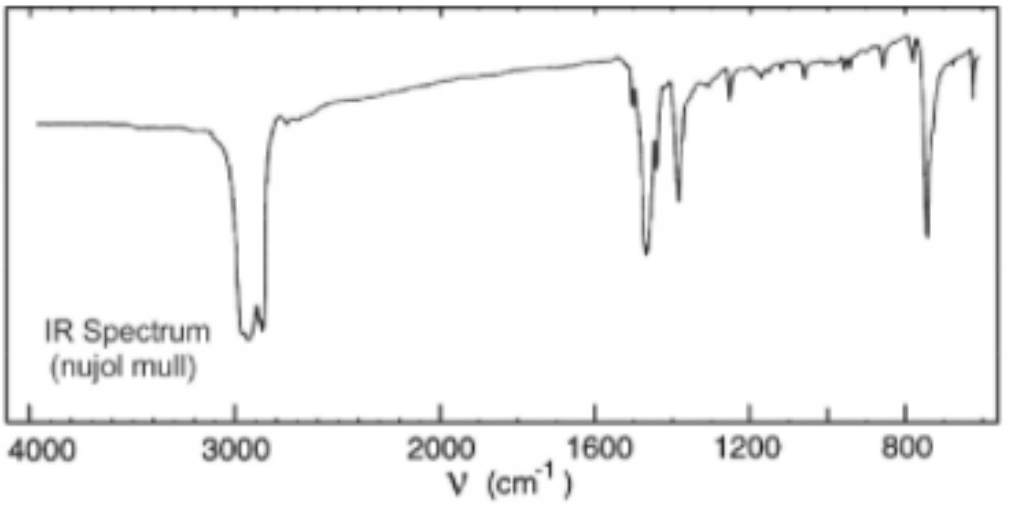
λ_{max} 330 nm ($\log_{10}\varepsilon$ 3.8)

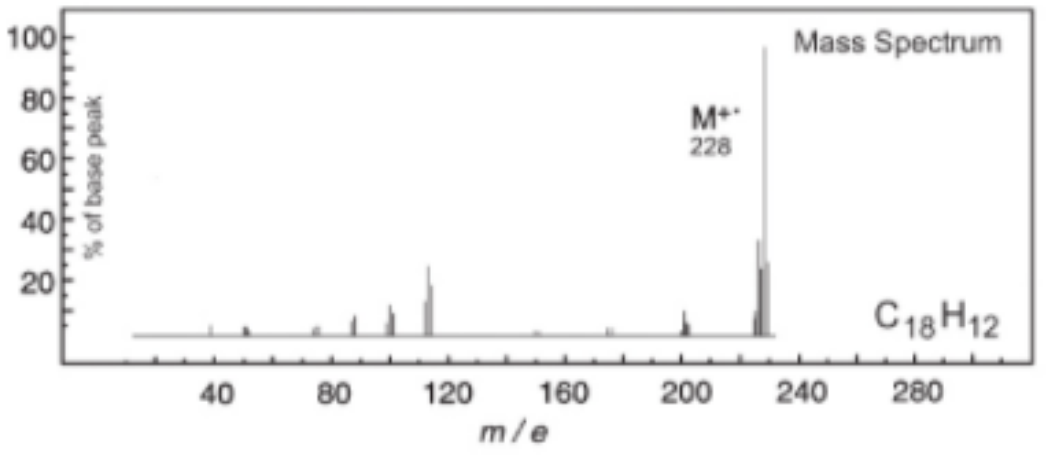
solvent : ethanol





Problem 271





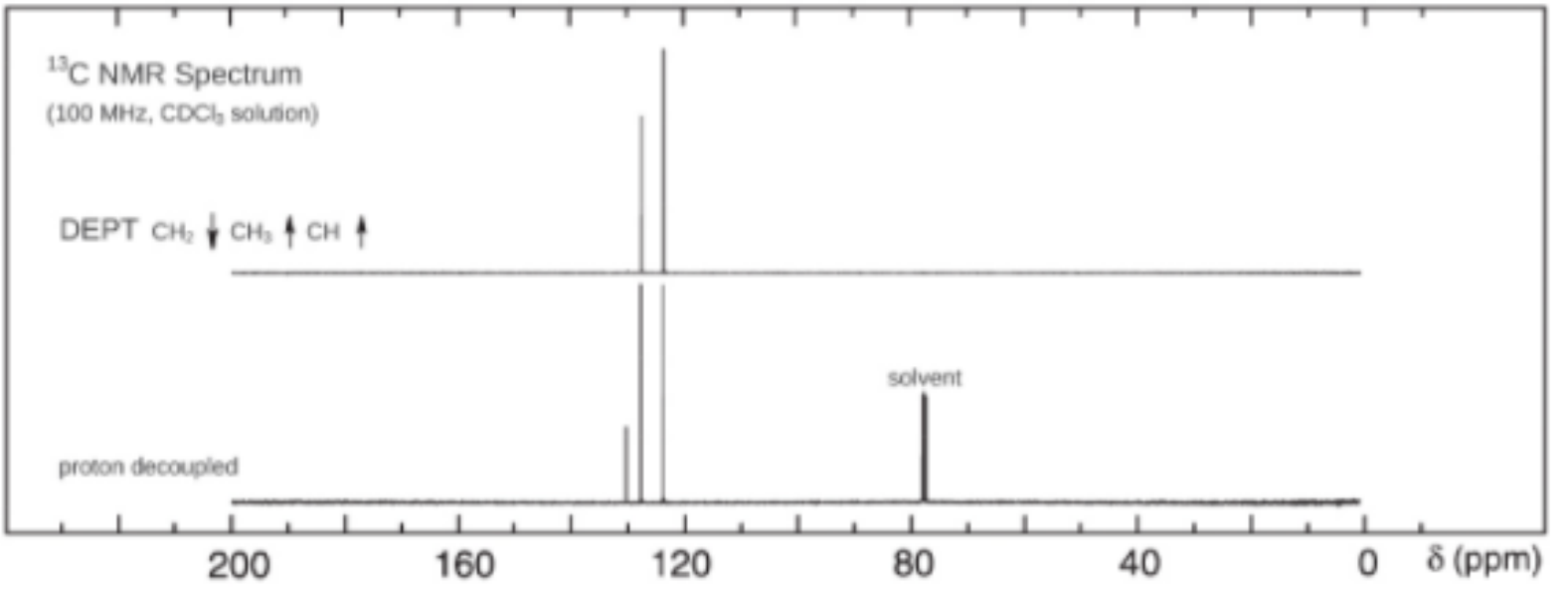
UV Spectrum

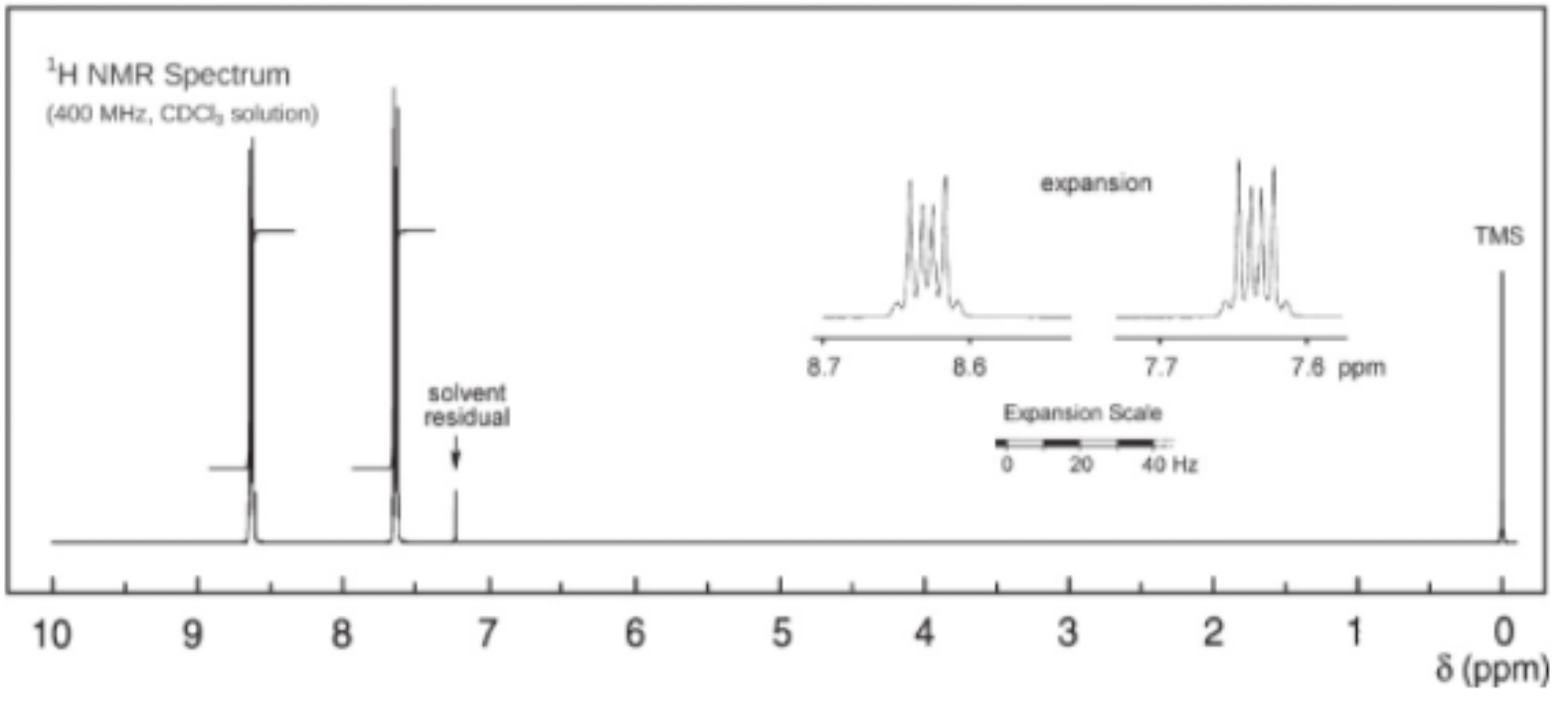
λ_{max} 249 nm ($\log_{10}\varepsilon$ 5.0)

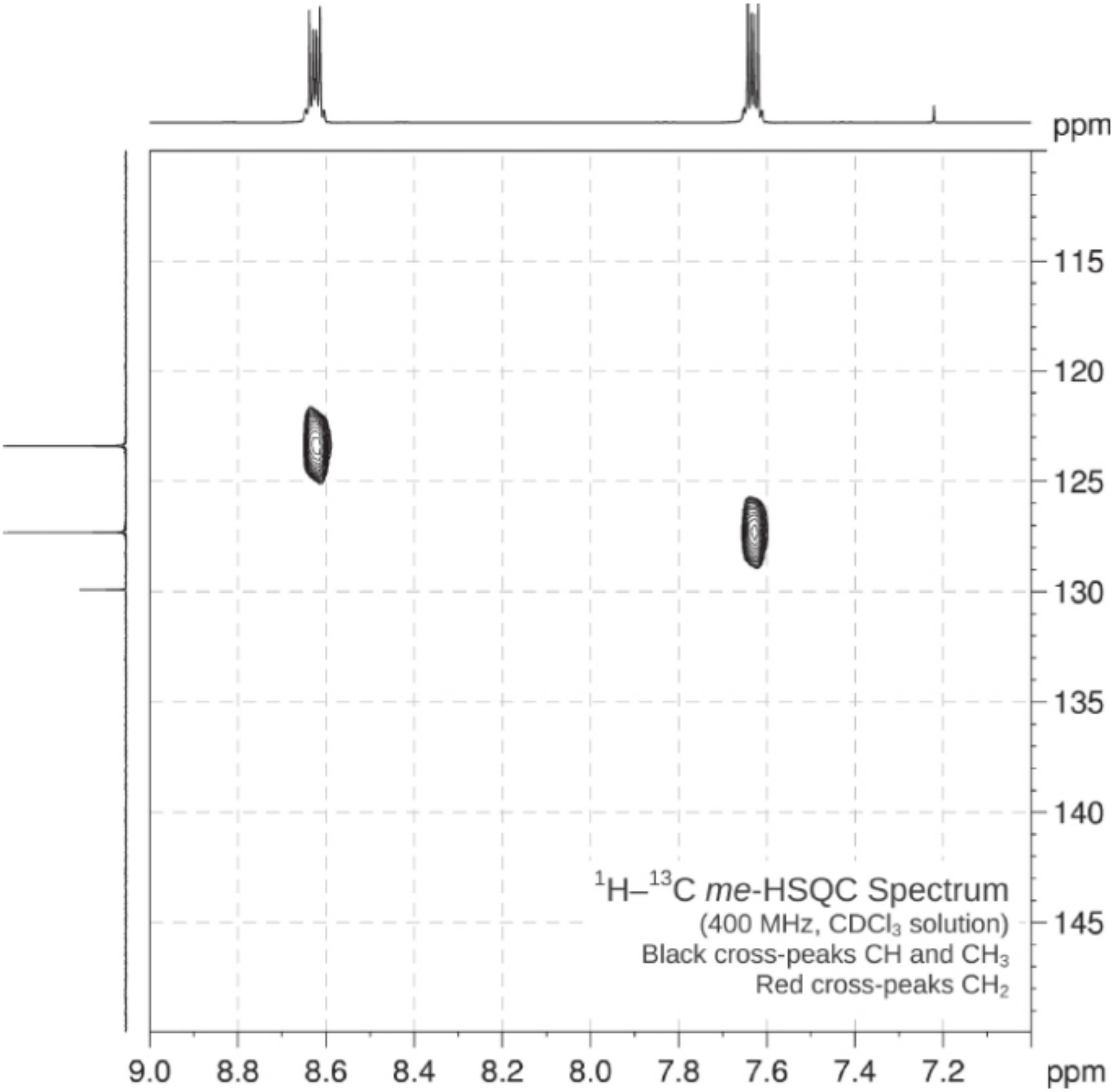
λ_{max} 257 nm ($\log_{10}\varepsilon$ 5.2)

λ_{max} 273 nm ($\log_{10}\varepsilon$ 4.4)

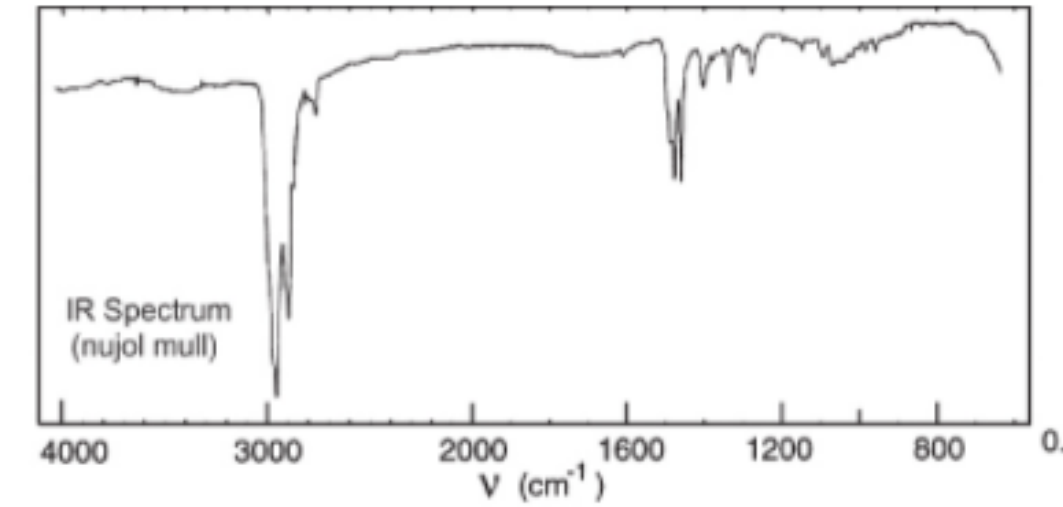
solvent : ethanol

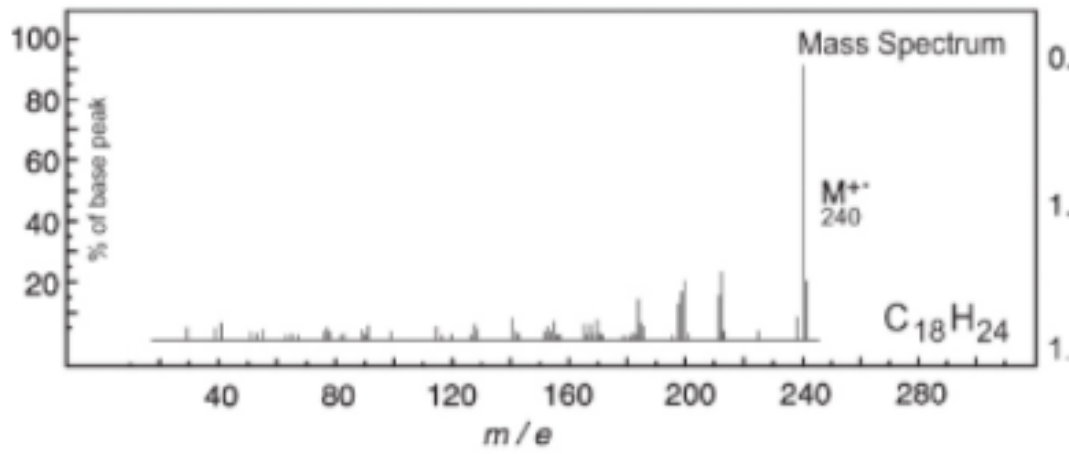


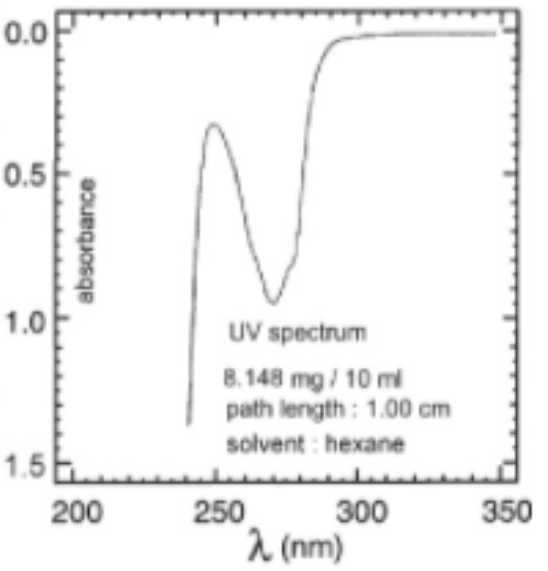


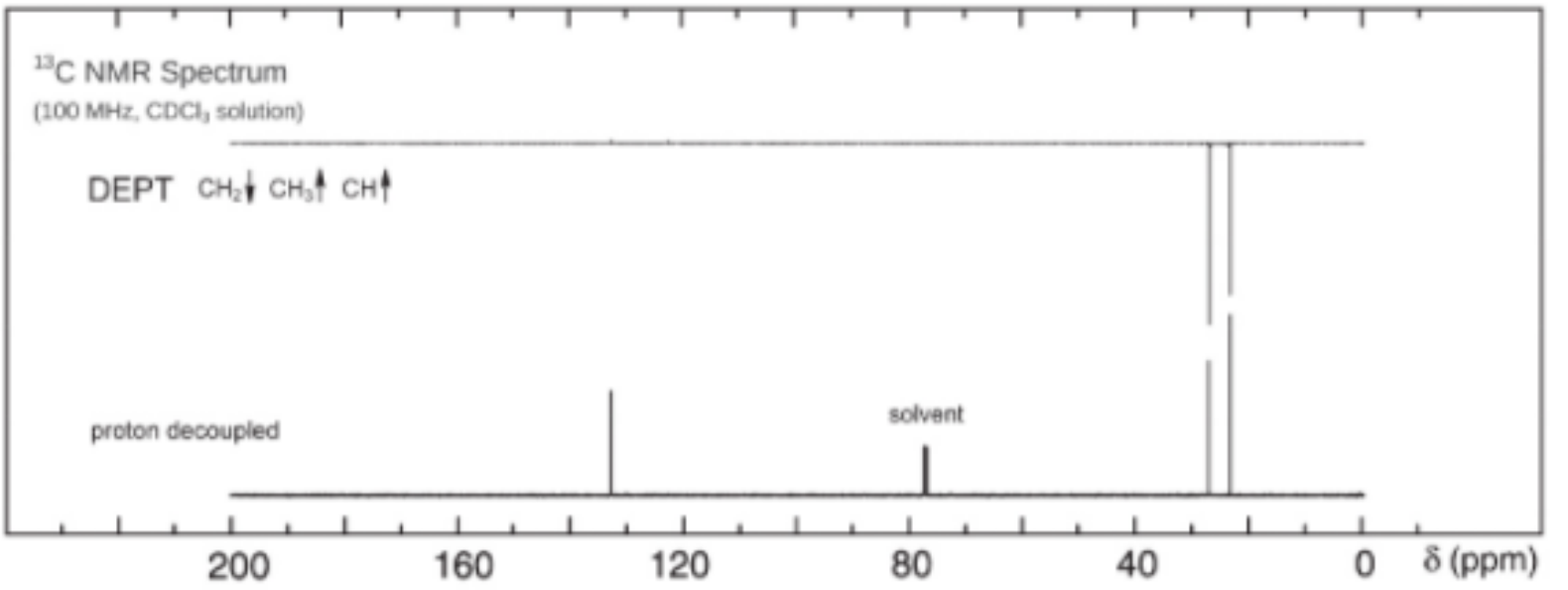

ppm
115
120
125
130
135
140
145
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm

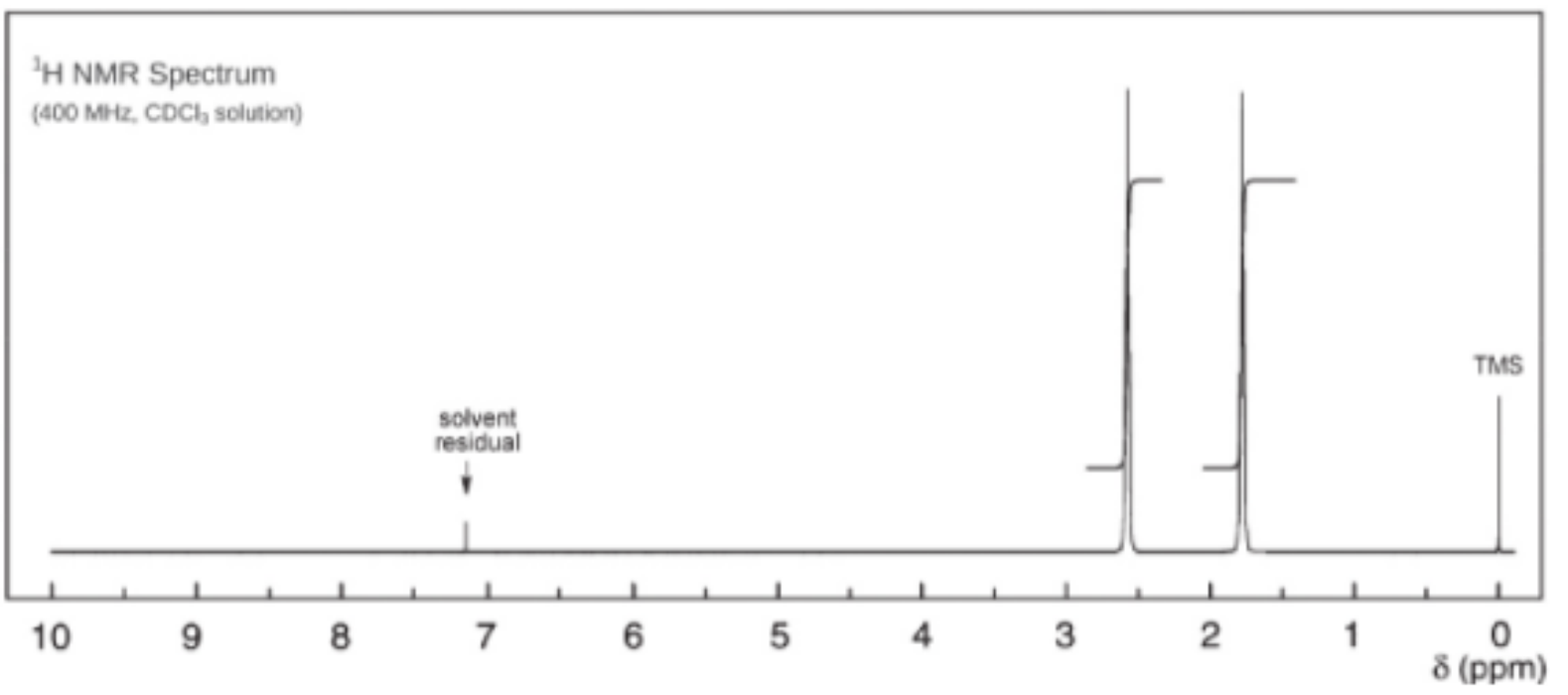
Problem 272


IR Spectrum
(nujol mull)
4000
3000
2000
1600
1200
800
ν (cm-1)

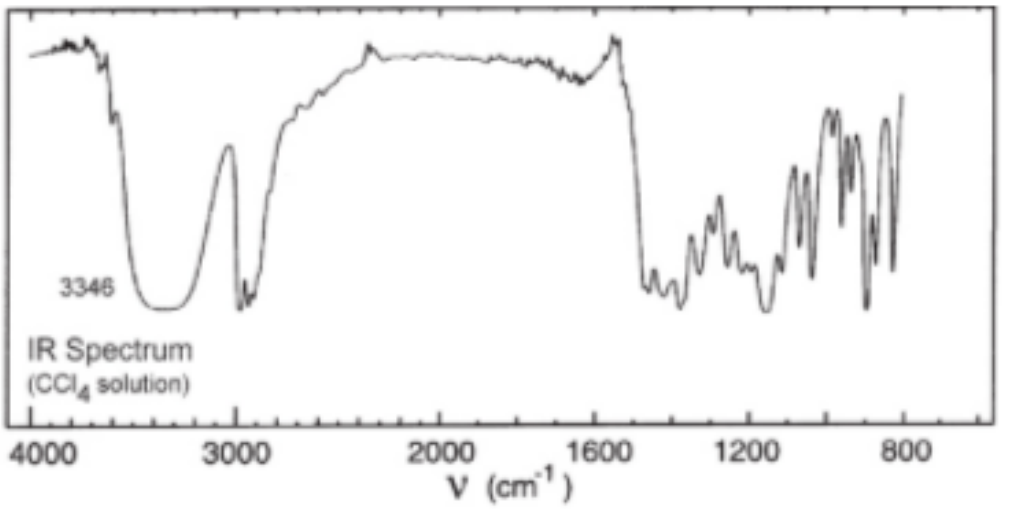

Mass Spectrum
% of base peak
100
80
60
40
20
M+·
240
C18H24
40
80
120
160
200
240
280
m / e

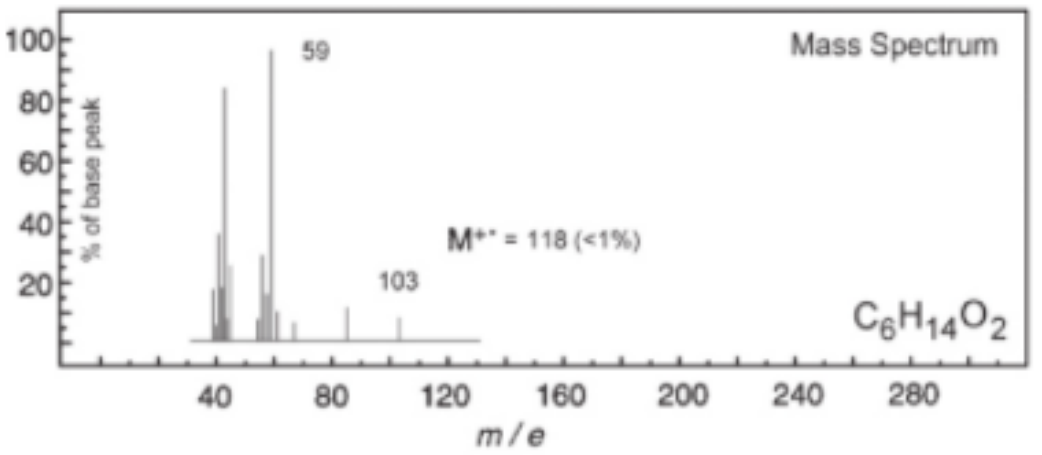

0.0
0.5
1.0
1.5
absorbance
UV spectrum
8.148 mg / 10 ml
path length : 1.00 cm
solvent : hexane
200
250
300
350
λ (nm)


13C NMR Spectrum
(100 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

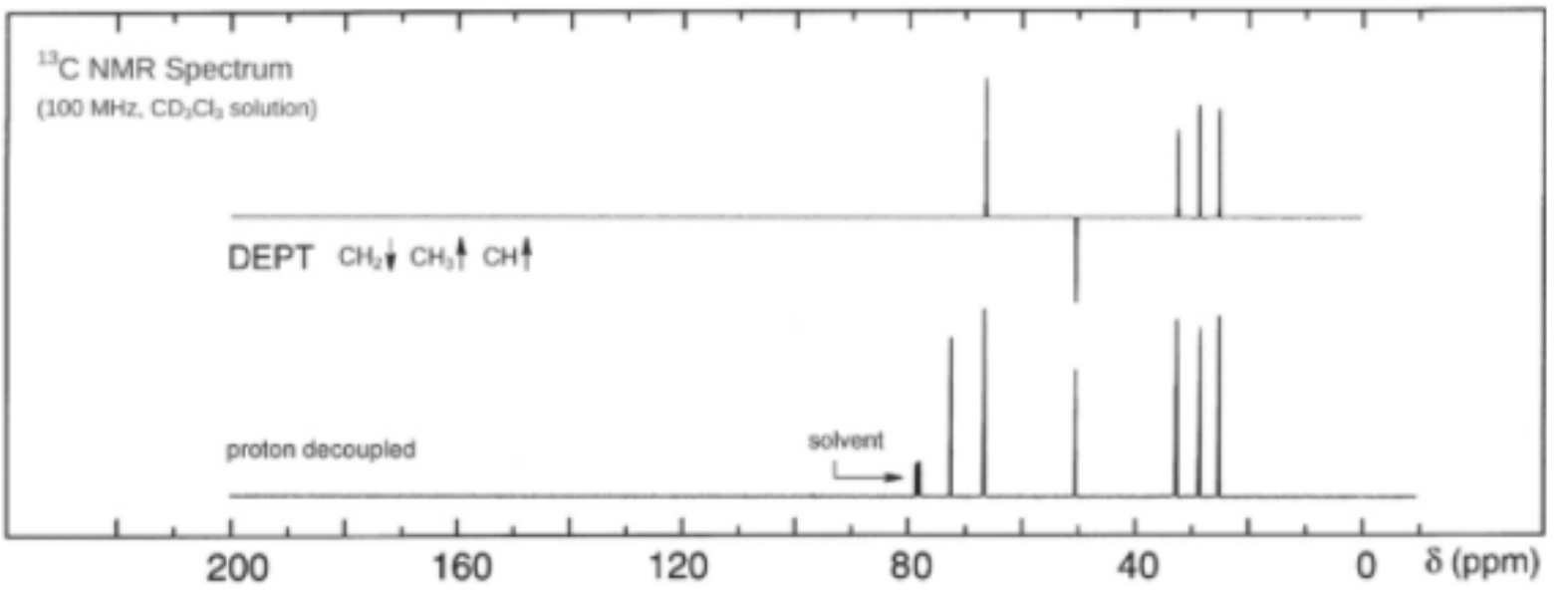

1H NMR Spectrum
(400 MHz, CDCl3 solution)
solvent
residual
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

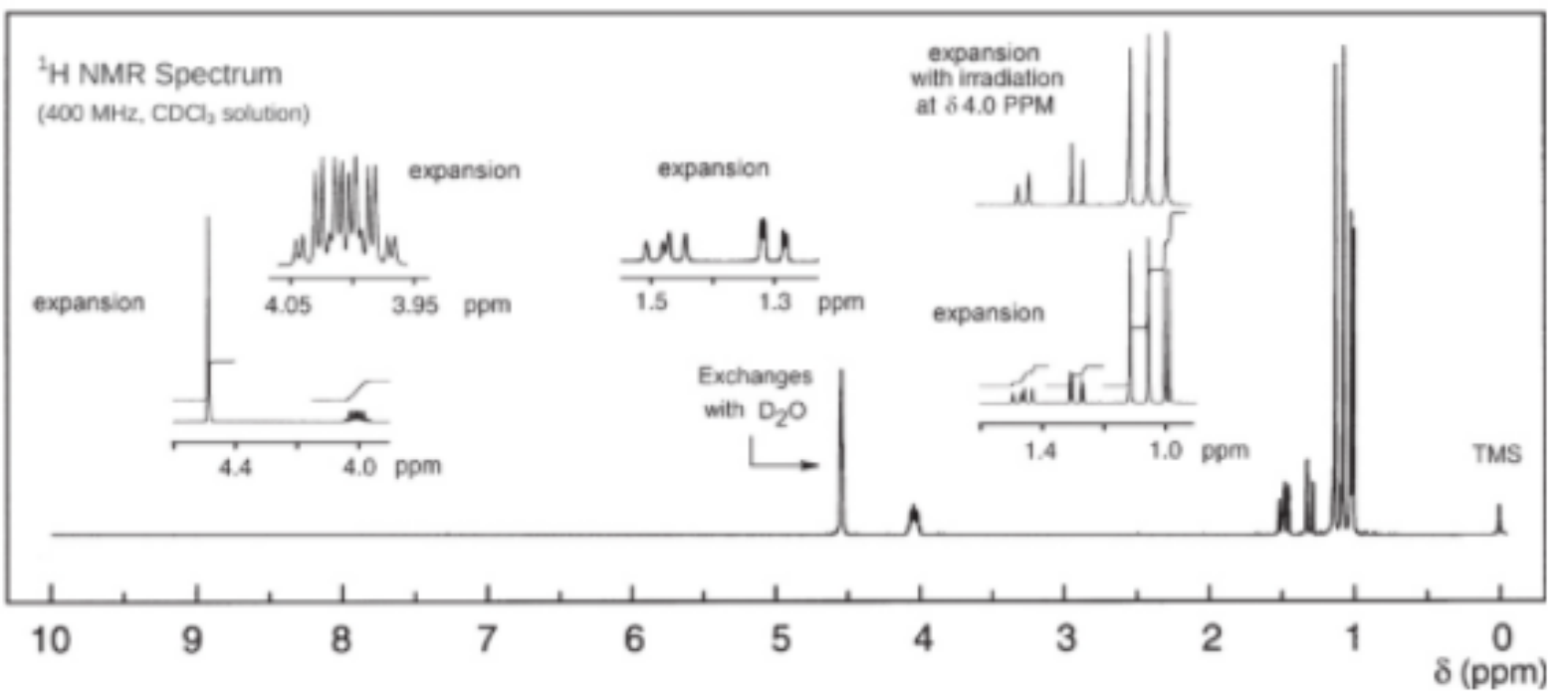
Problem 273



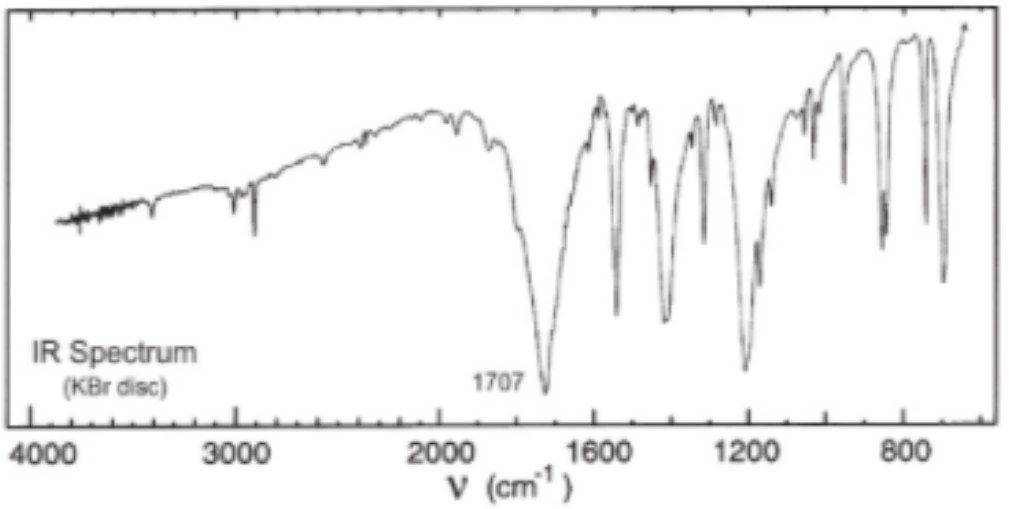


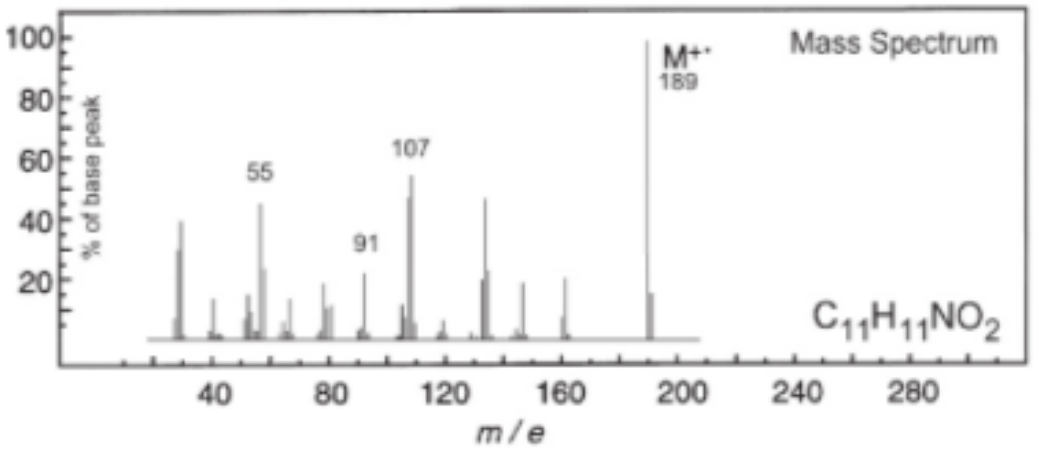
No significant UV absorption above 220 nm

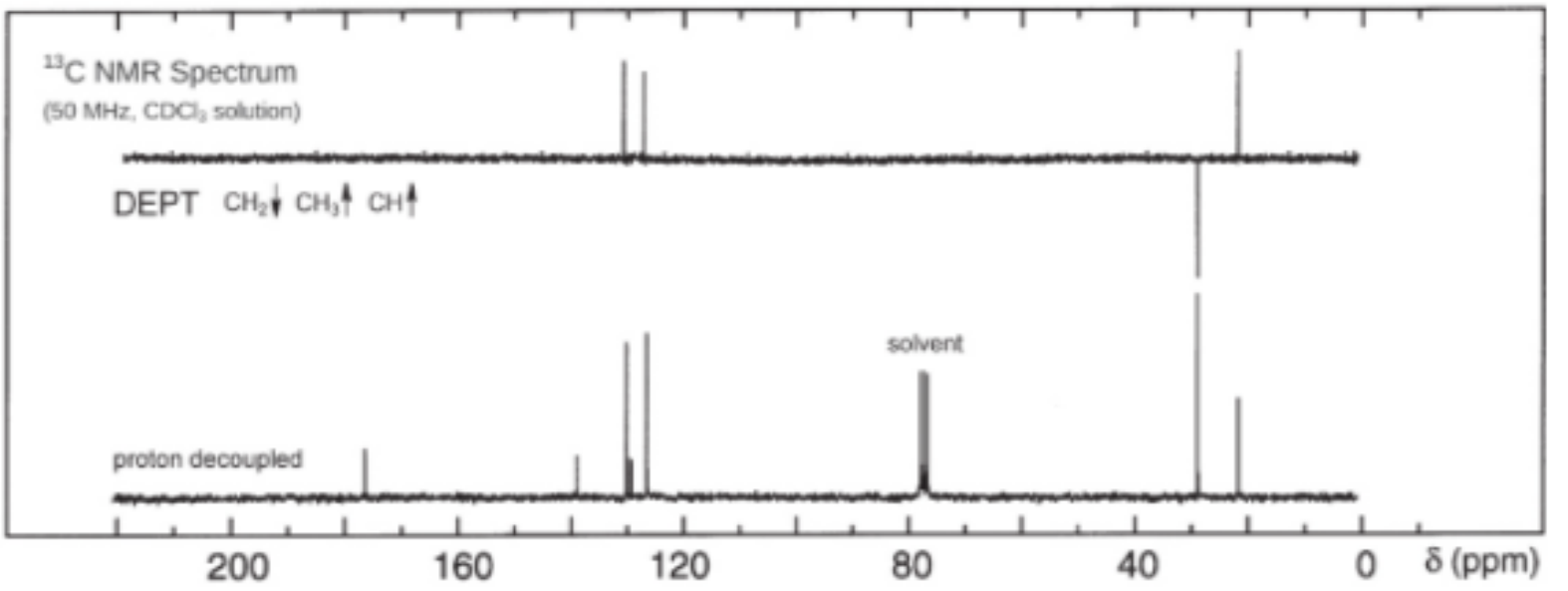


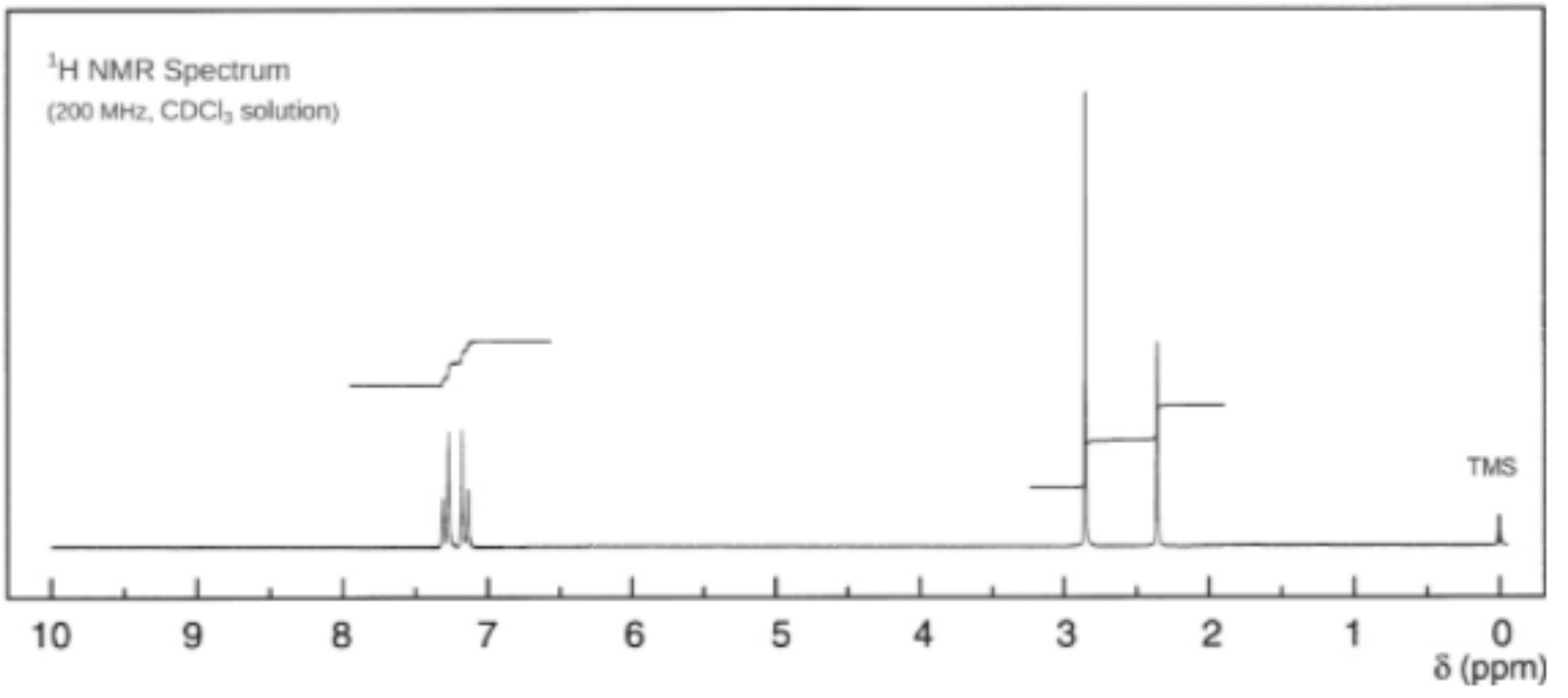


Problem 274

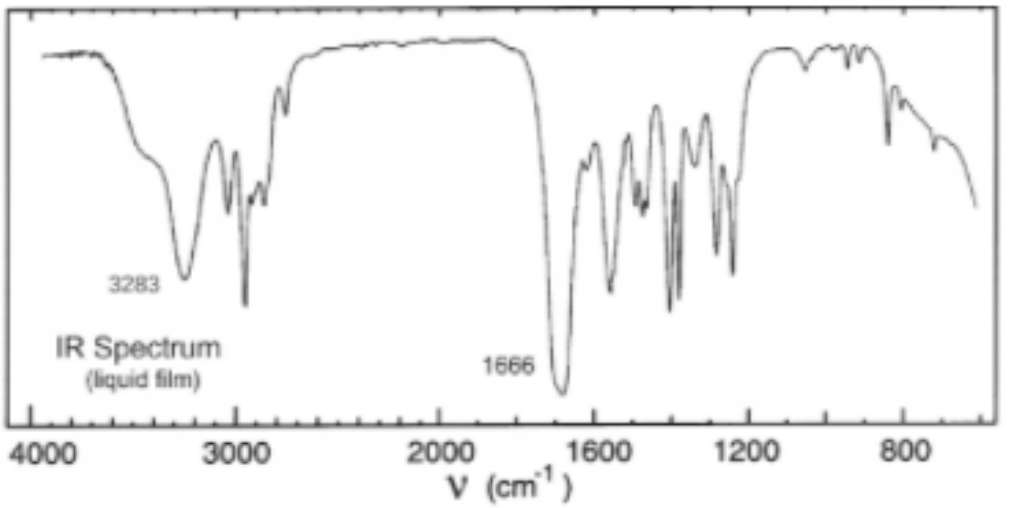

IR Spectrum
(KBr disc)
1707
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
M+·
189
107
55
91
% of base peak
100
80
60
40
20
C11H11NO2
40
80
120
160
200
240
280
m / e

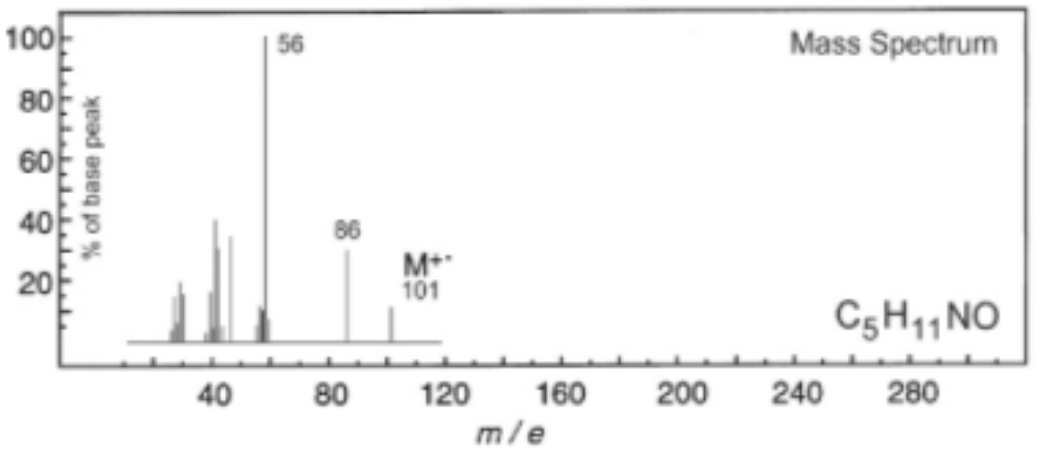

13C NMR Spectrum
(50 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(200 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

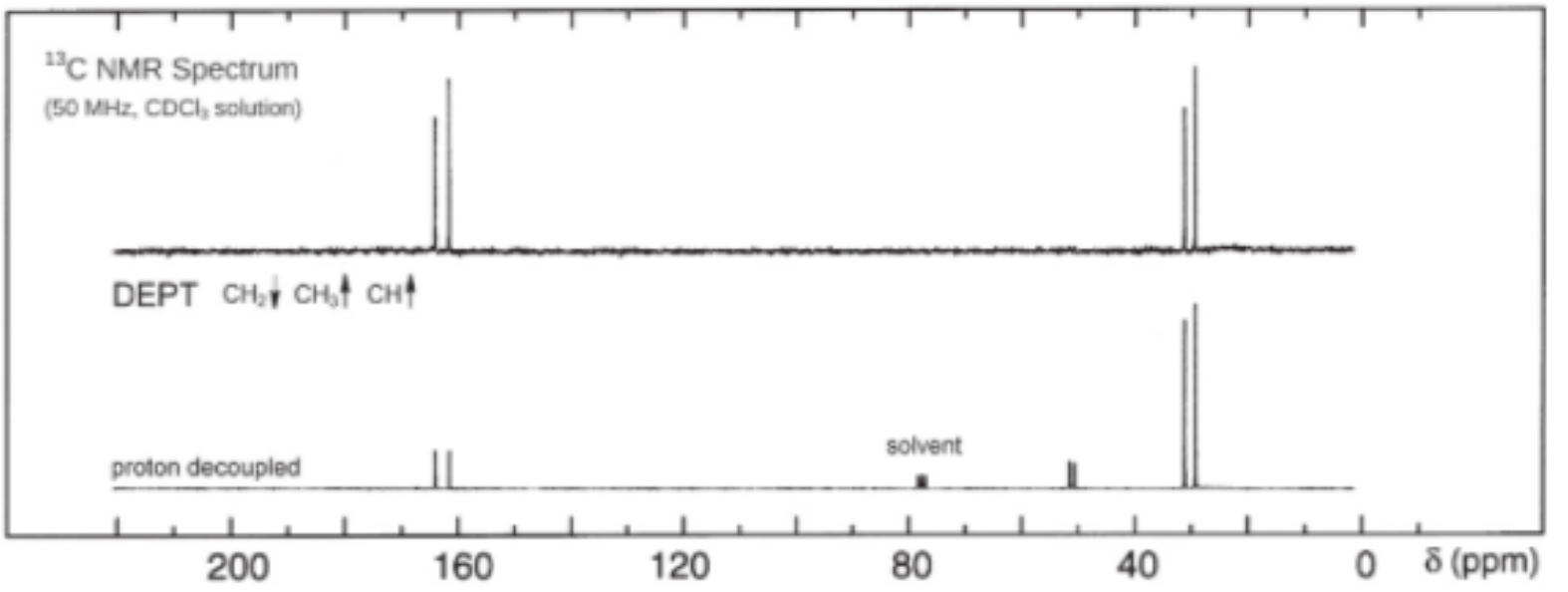
Problem 275

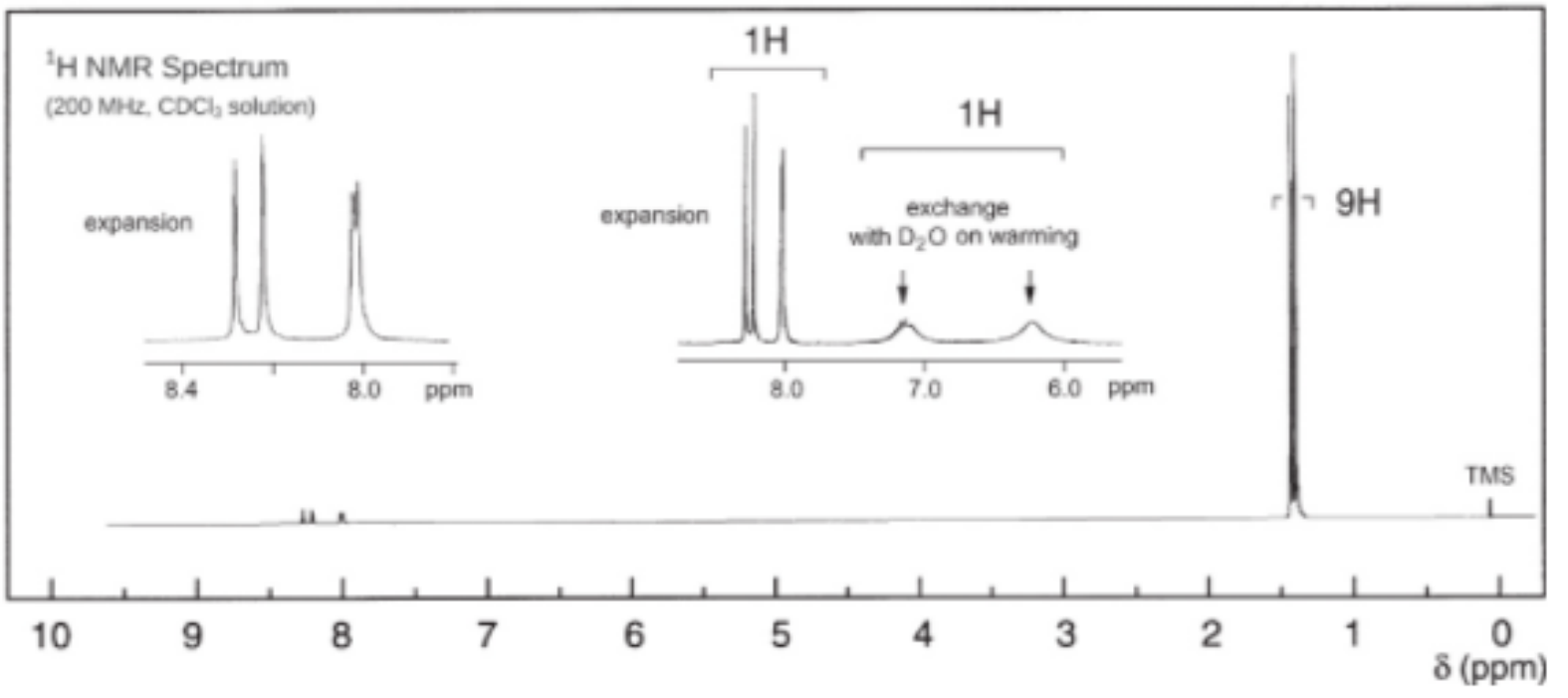


HINT: This compound is a mixture of two isomers

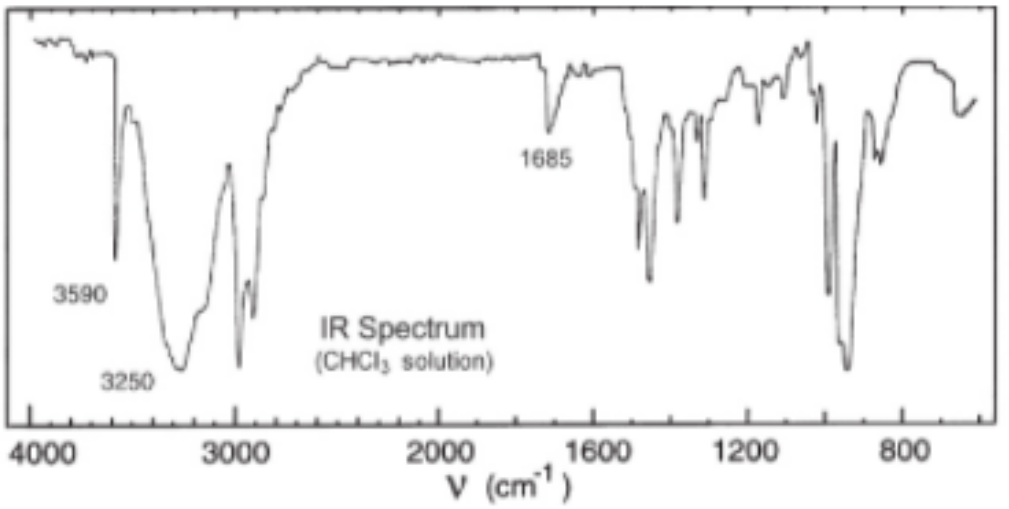


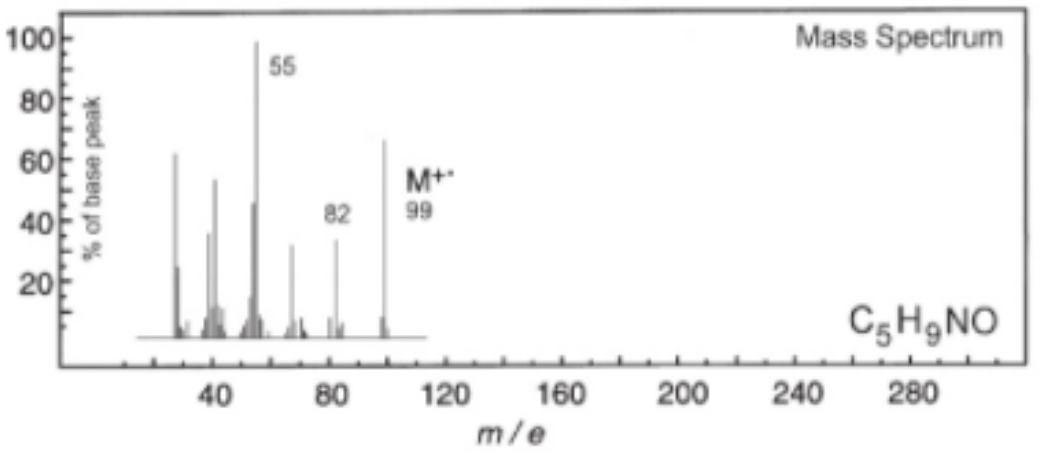
No significant UV absorption above 220 nm



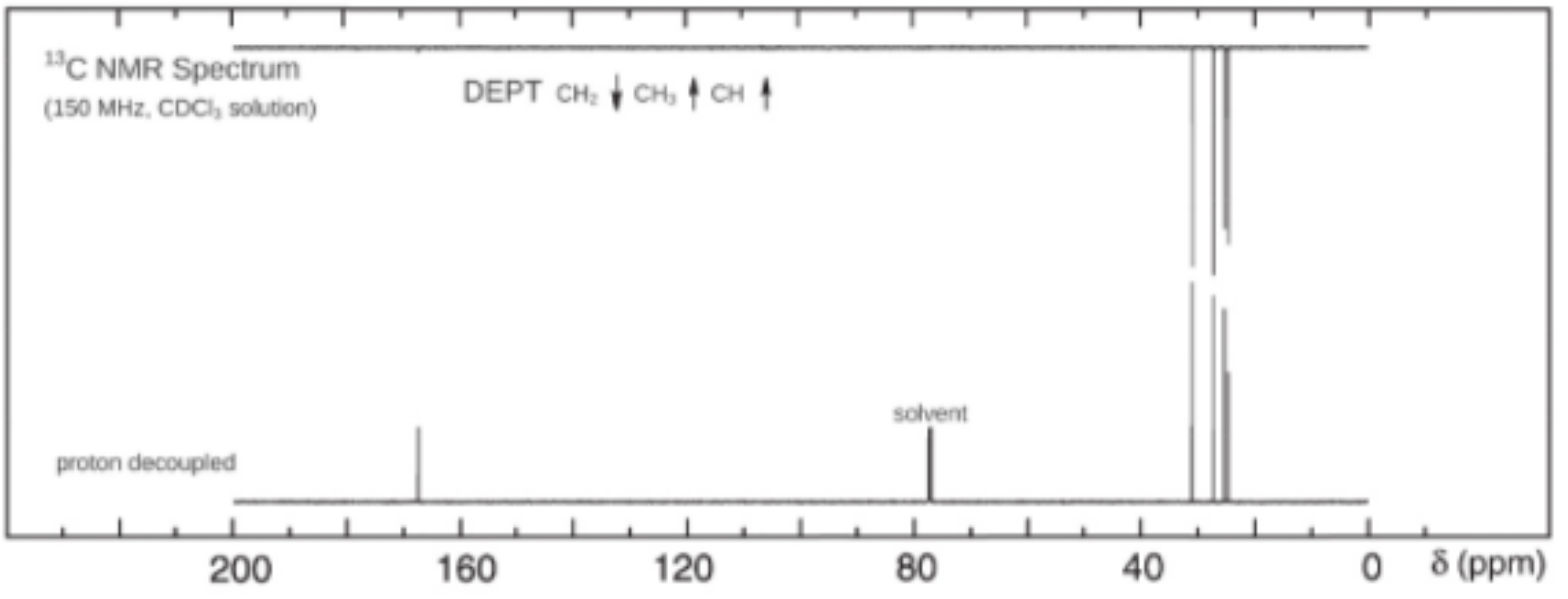


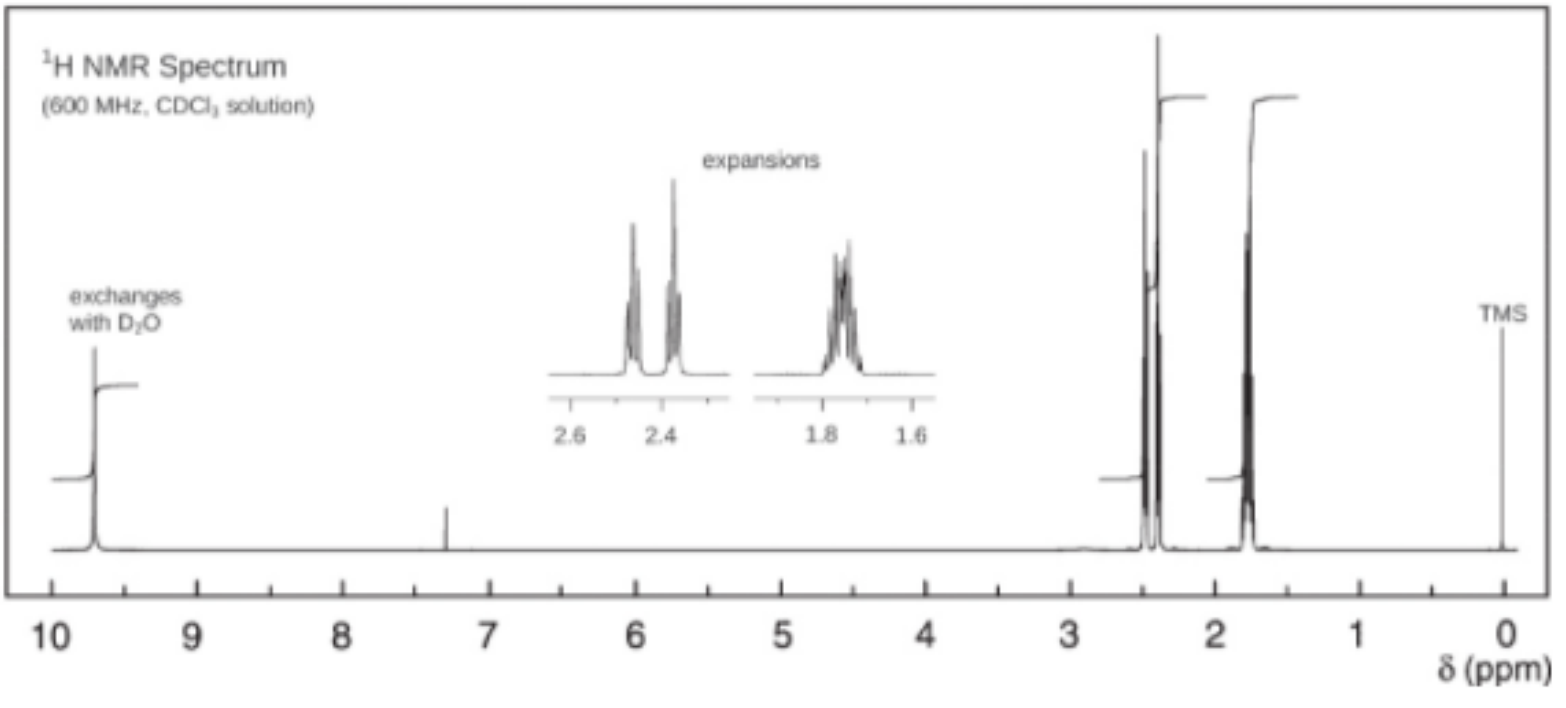
Problem 276

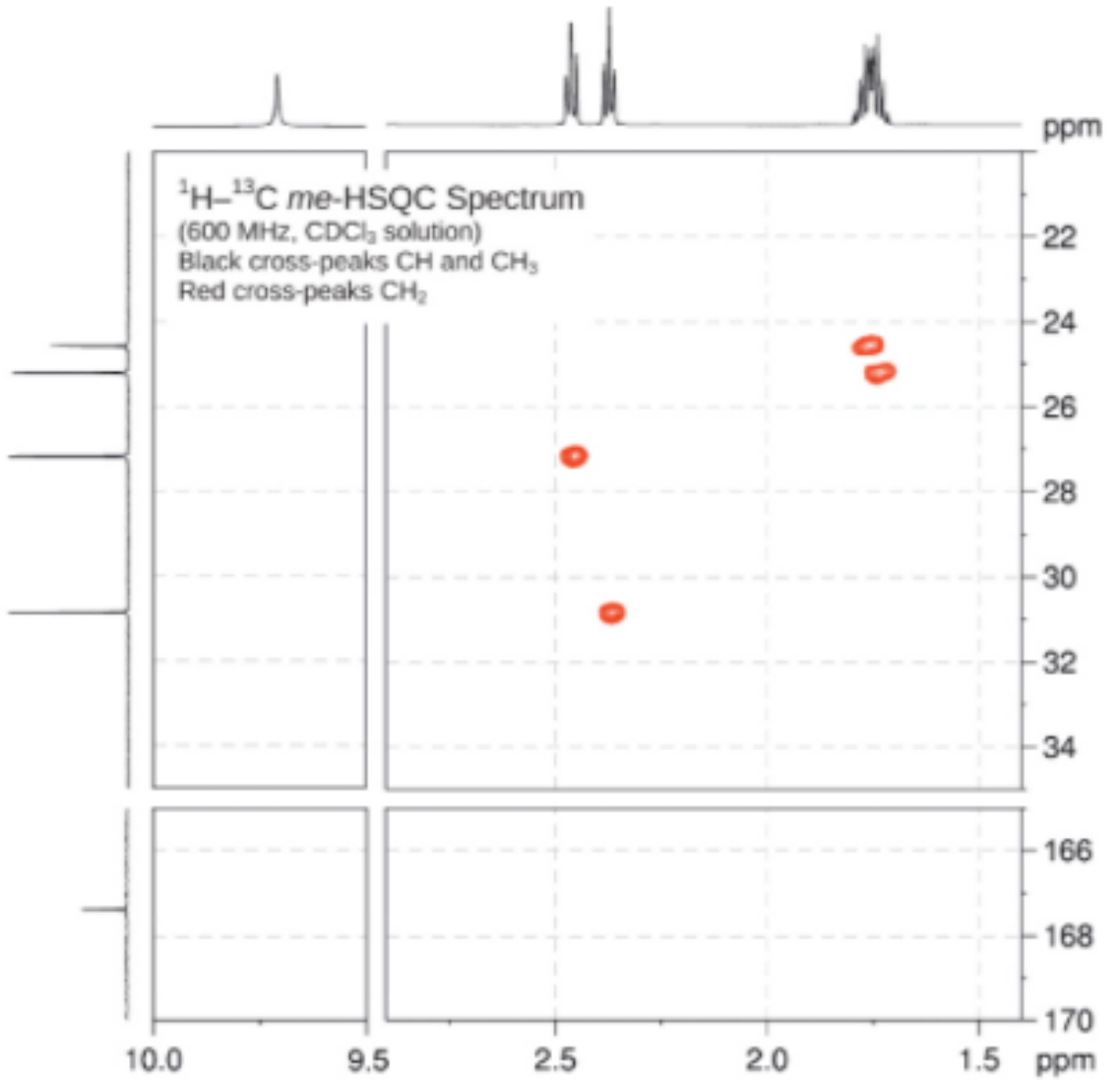


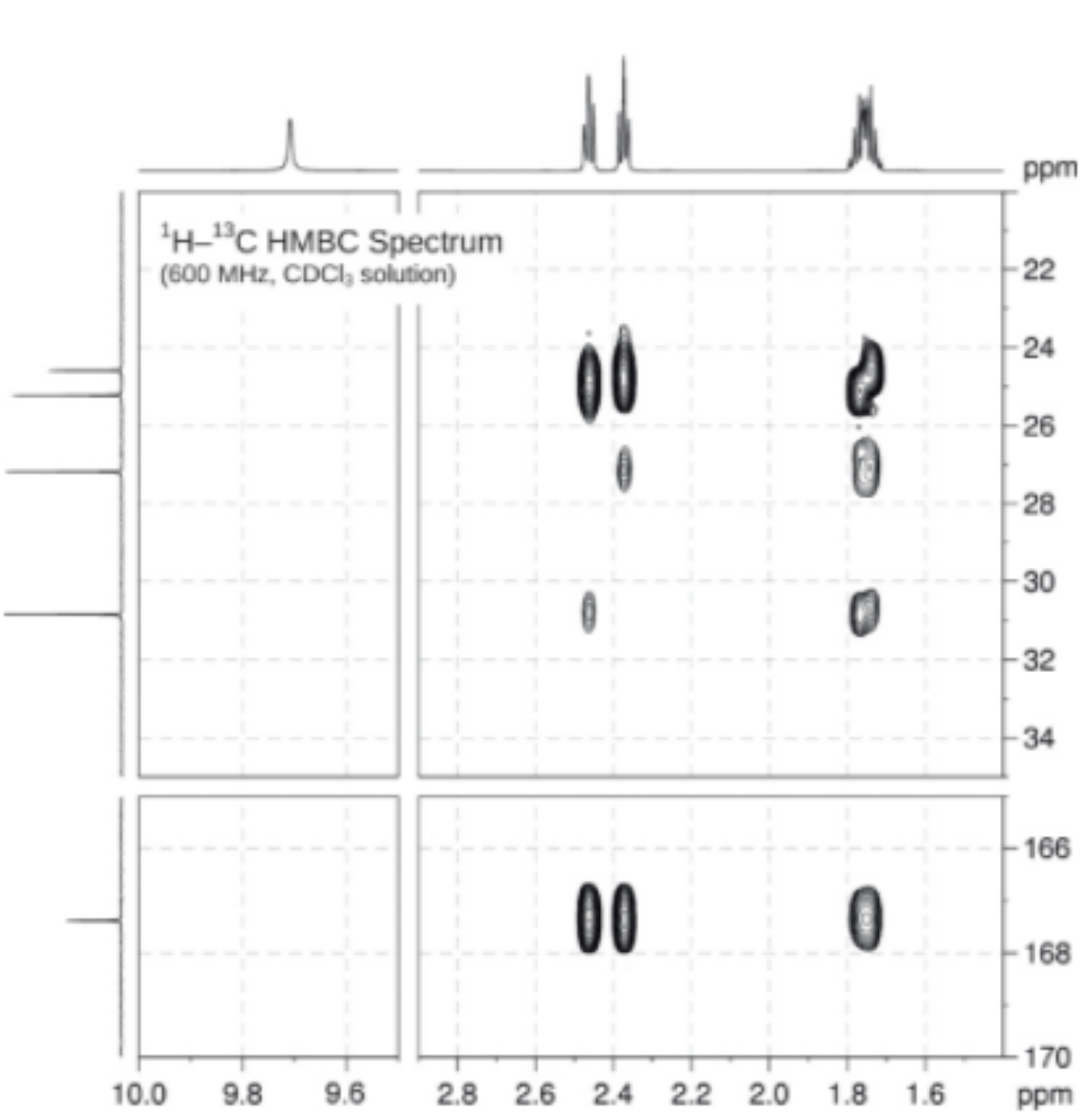


No significant UV absorption above 220 nm

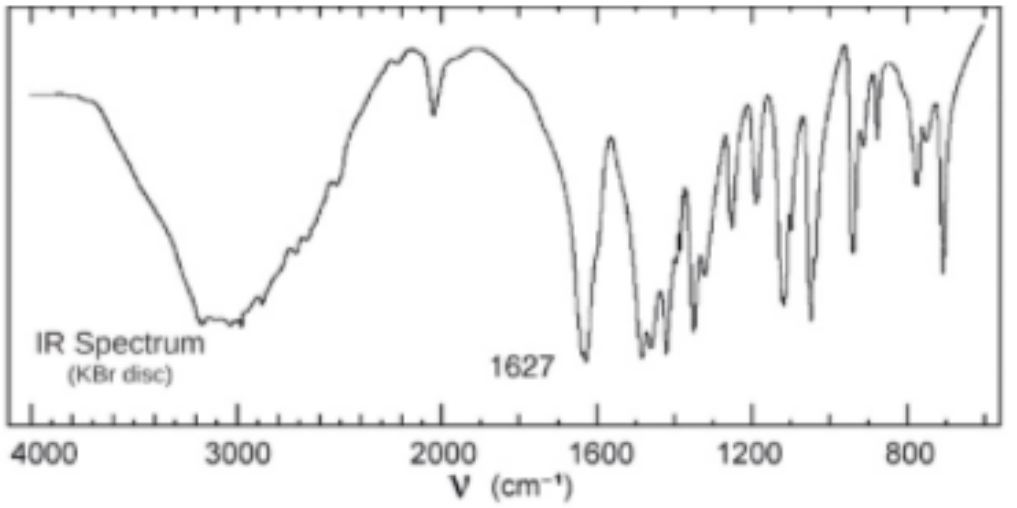


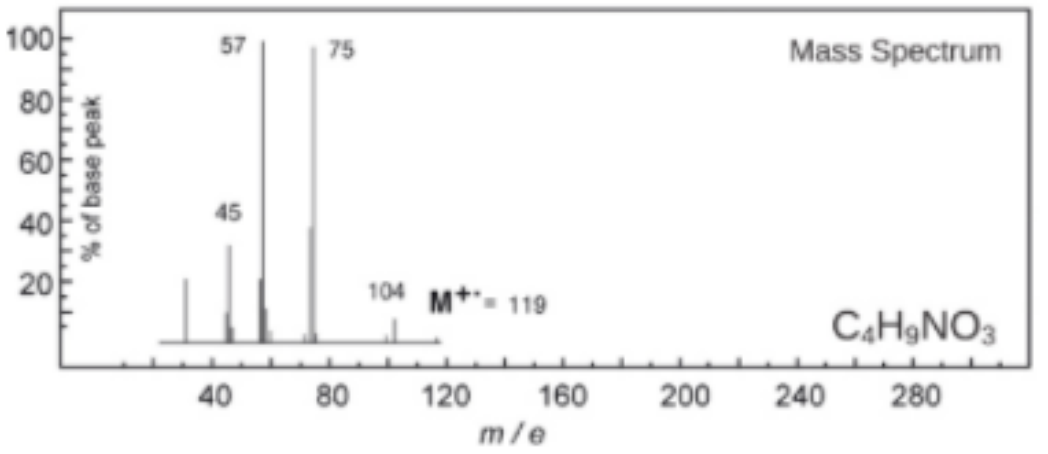



ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
22
24
26
28
30
32
34
166
168
170
10.0
9.5
2.5
2.0
1.5
ppm

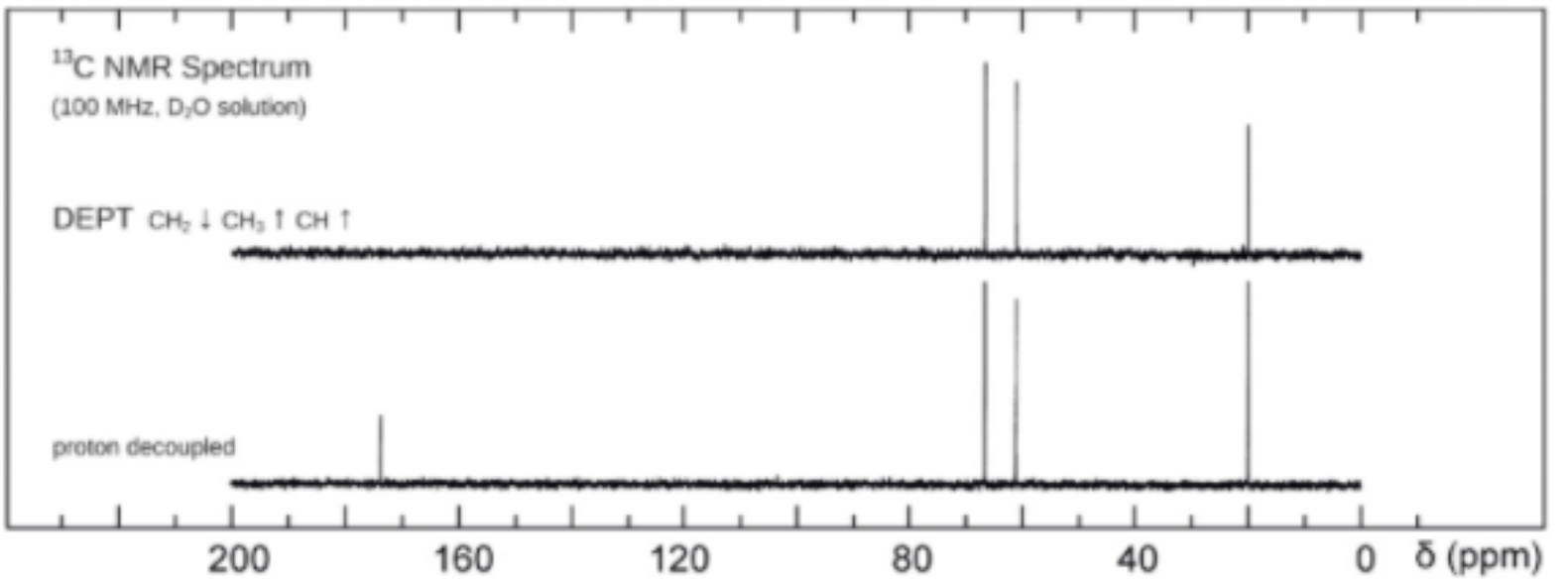

ppm
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)
22
24
26
28
30
32
34
166
168
170
10.0
9.8
9.6
2.8
2.6
2.4
2.2
2.0
1.8
1.6
ppm

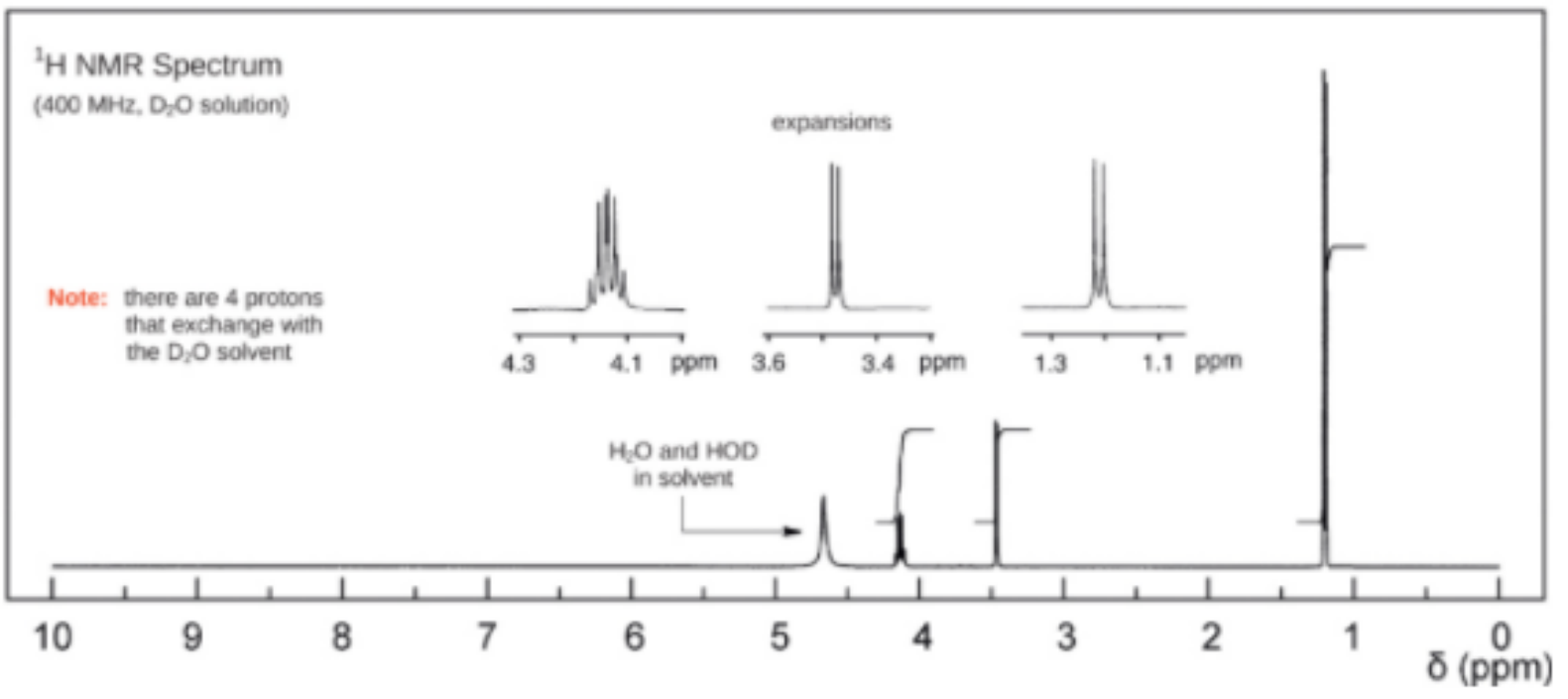
Problem 277



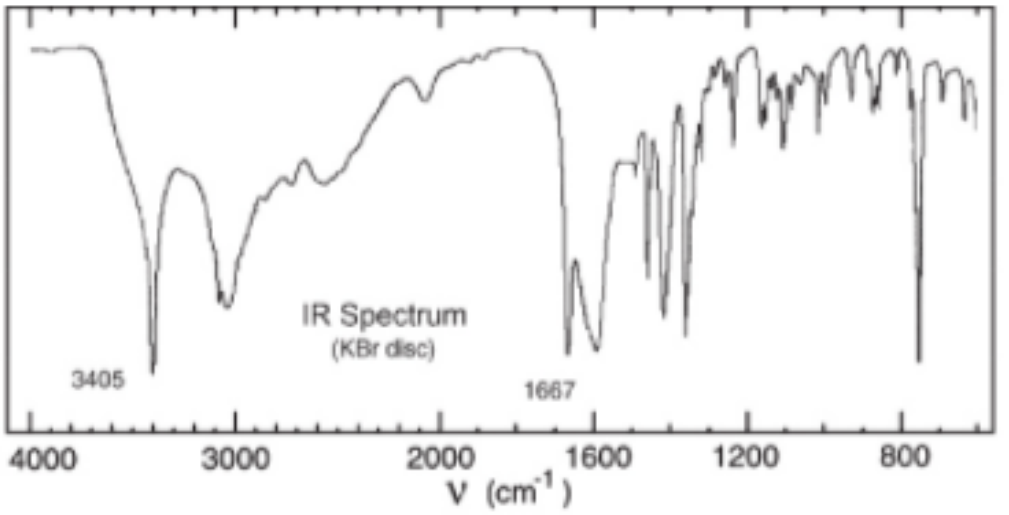


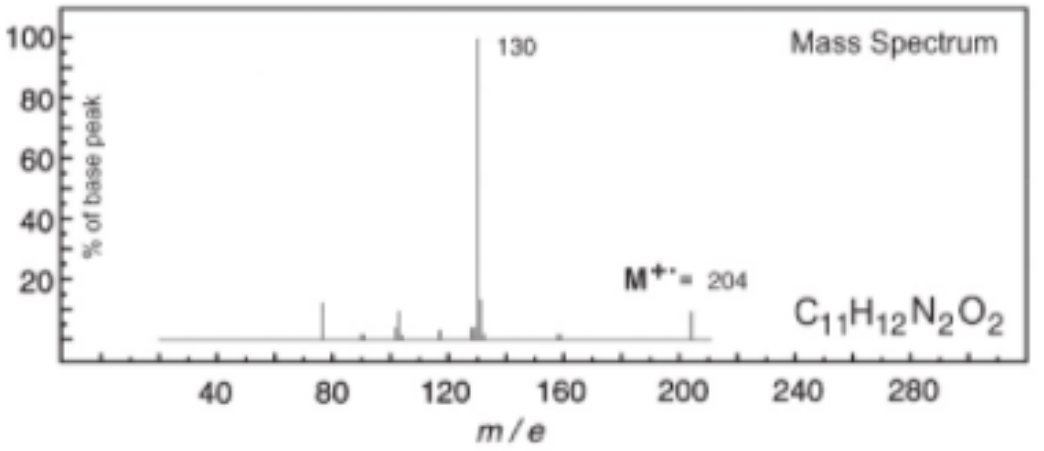
No significant UV absorption above 220 nm





Problem 278





UV Spectrum

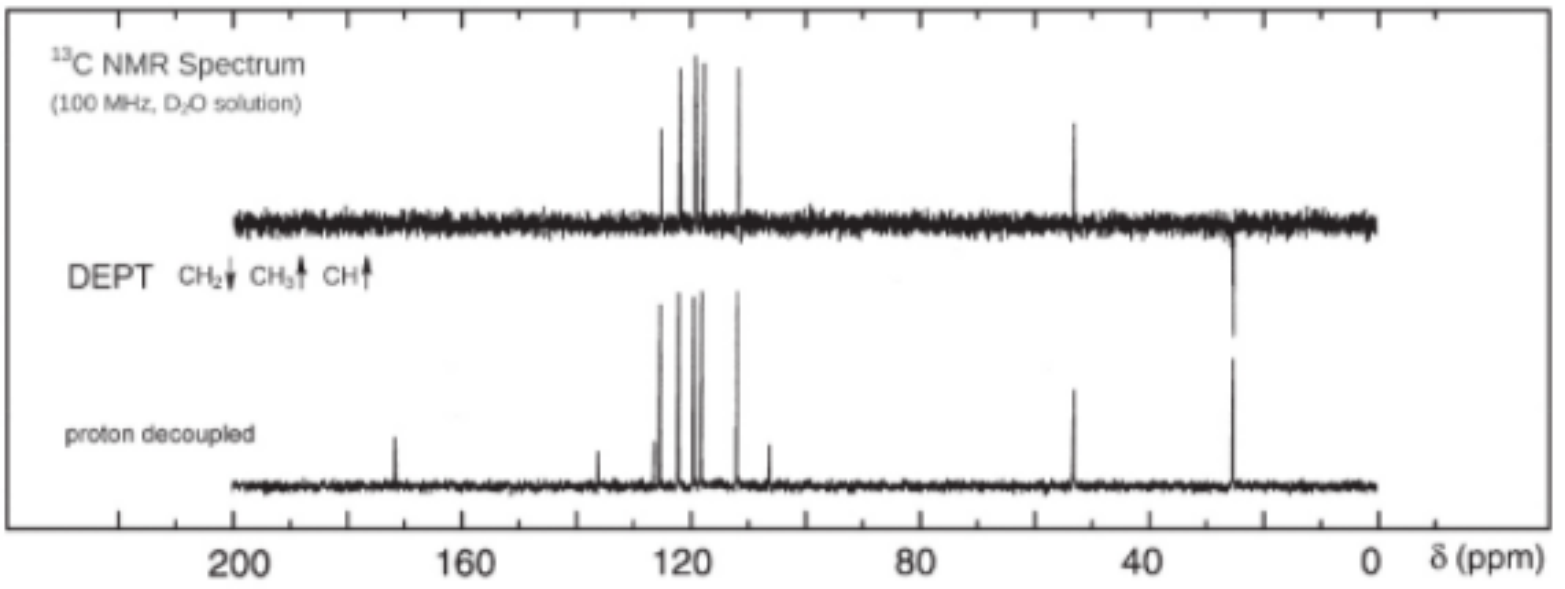
λ_{max} 220 nm ($\log_{10}\varepsilon$ 4.6)

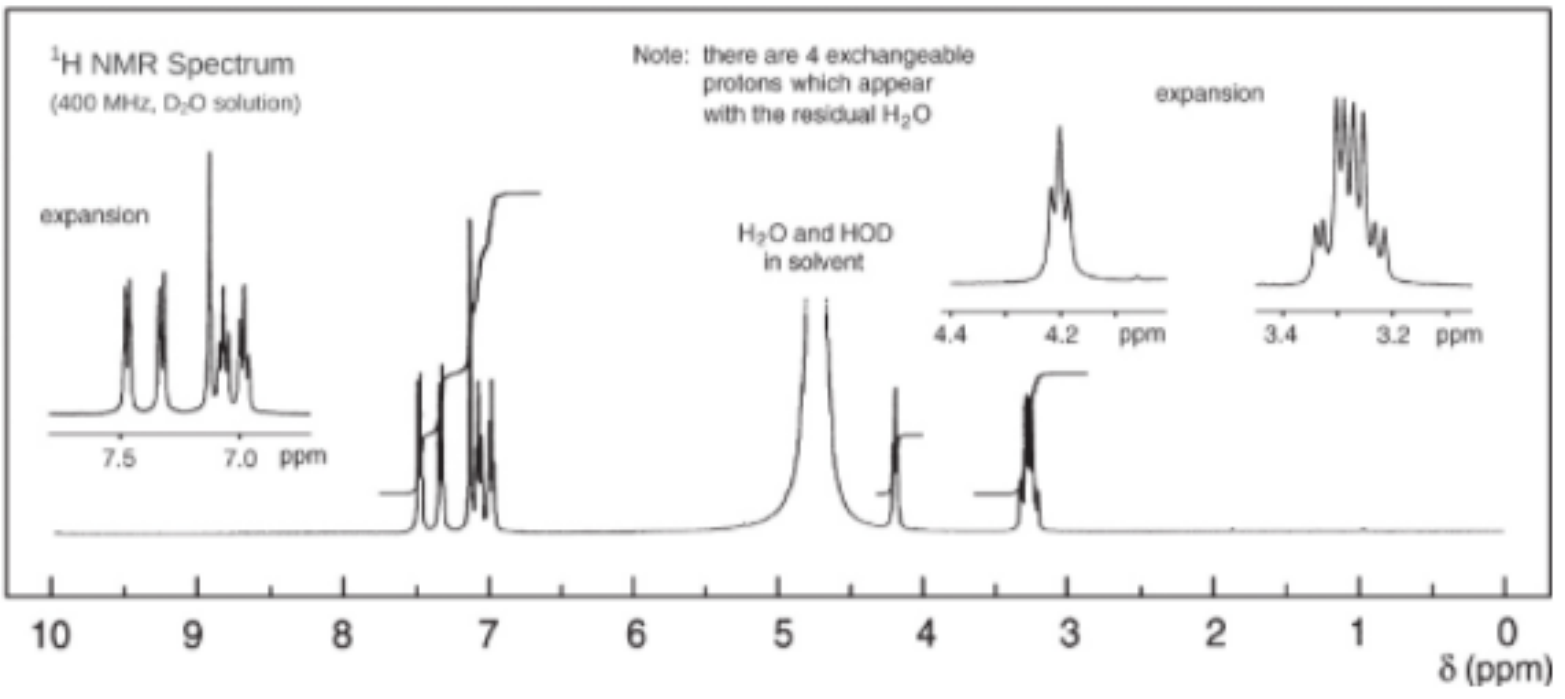
λ_{max} 273 nm ($\log_{10}\varepsilon$ 3.8)

λ_{max} 280 nm ($\log_{10}\varepsilon$ 3.8)

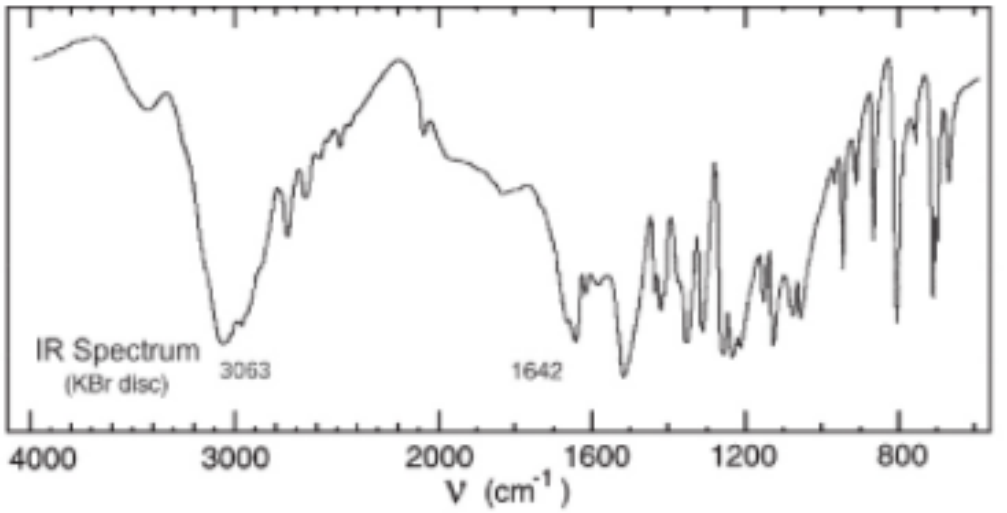
λ_{max} 289 nm ($\log_{10}\varepsilon$ 3.7)

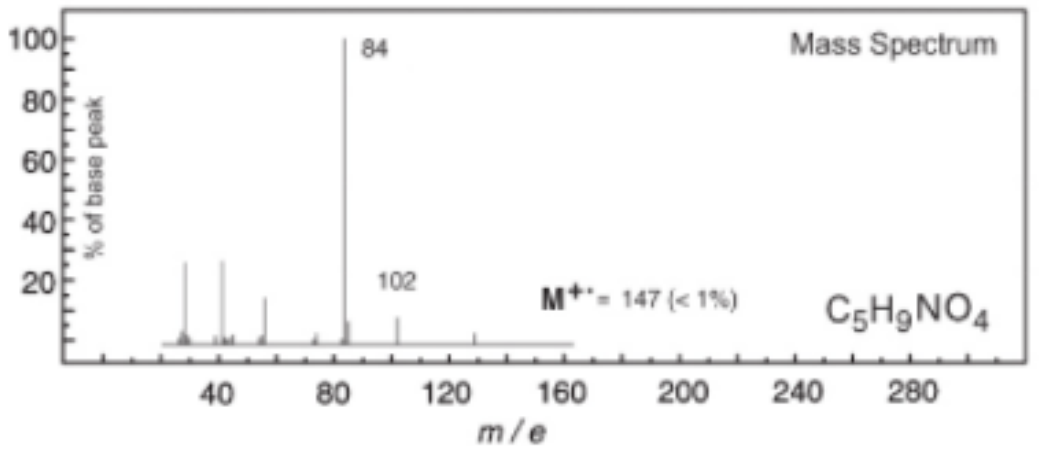
solvent : methanol



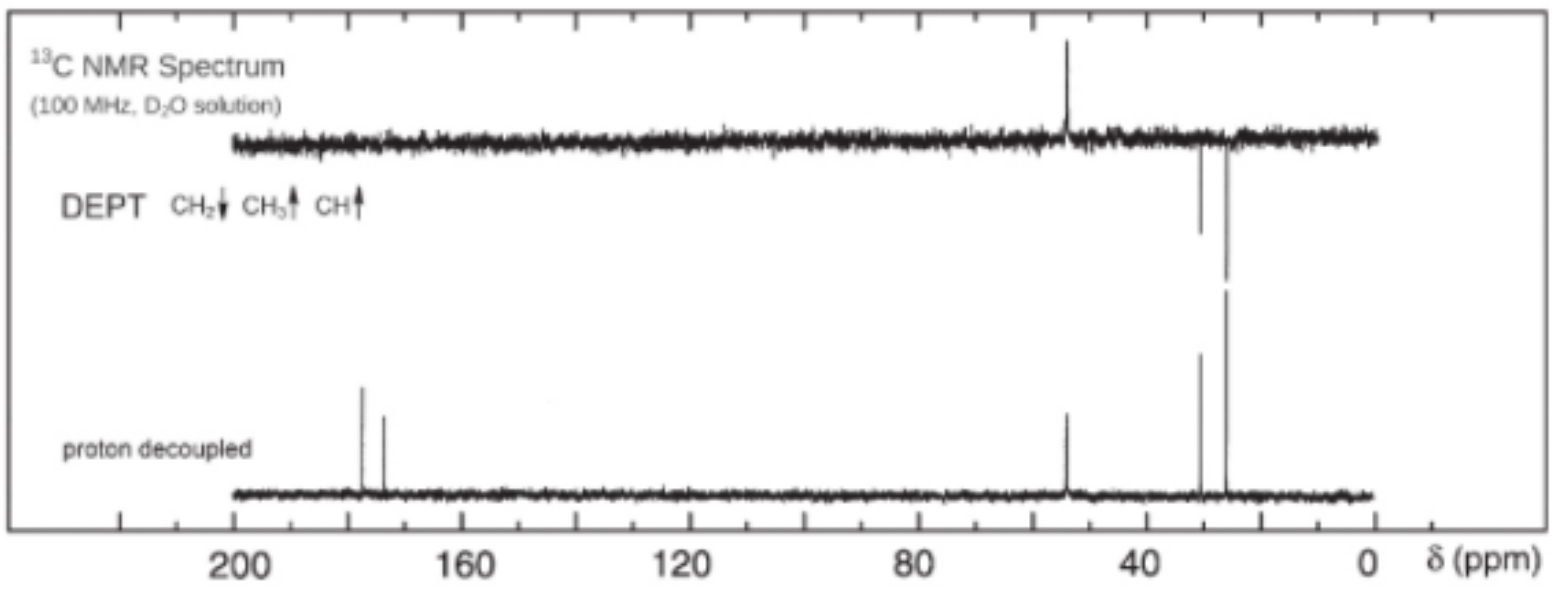


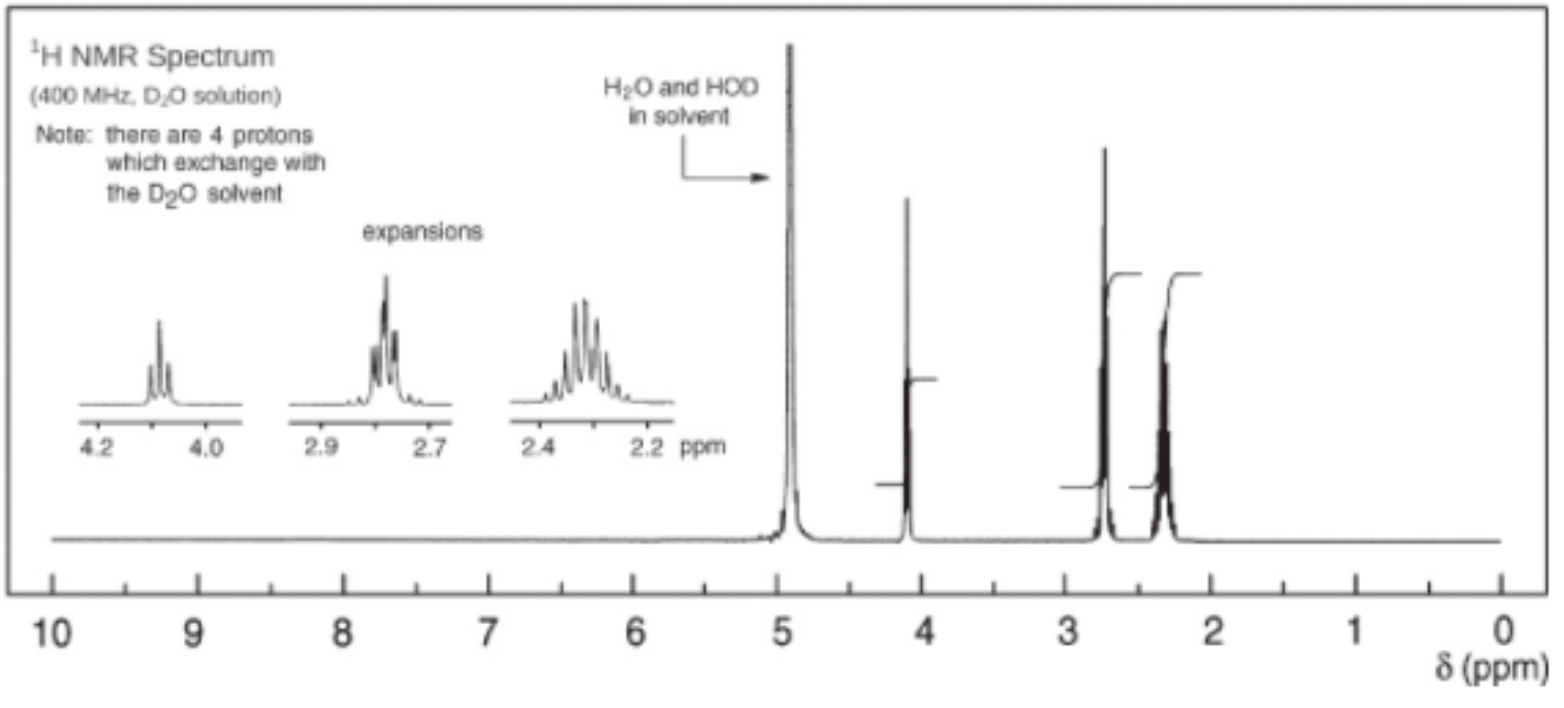
Problem 279

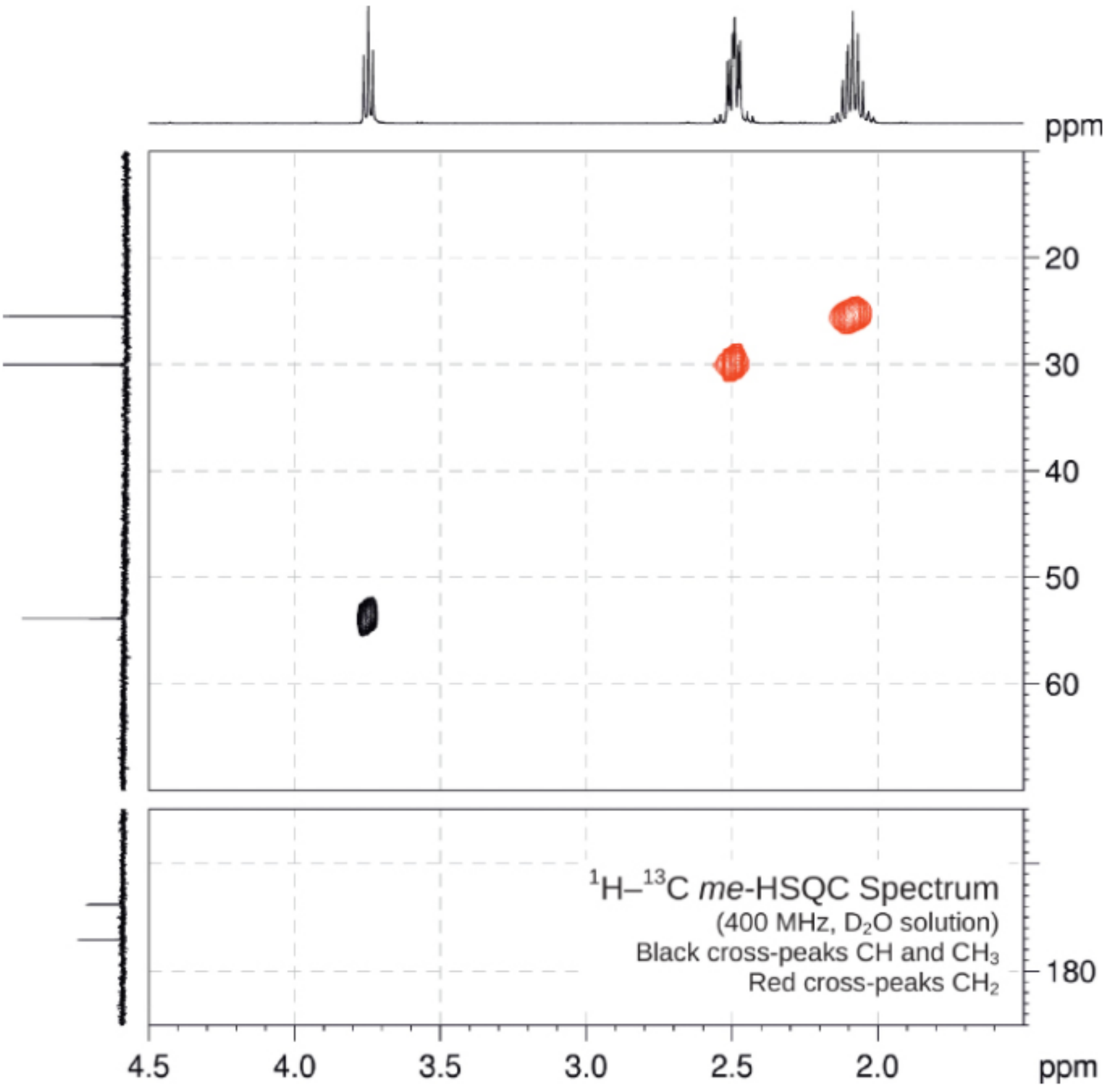




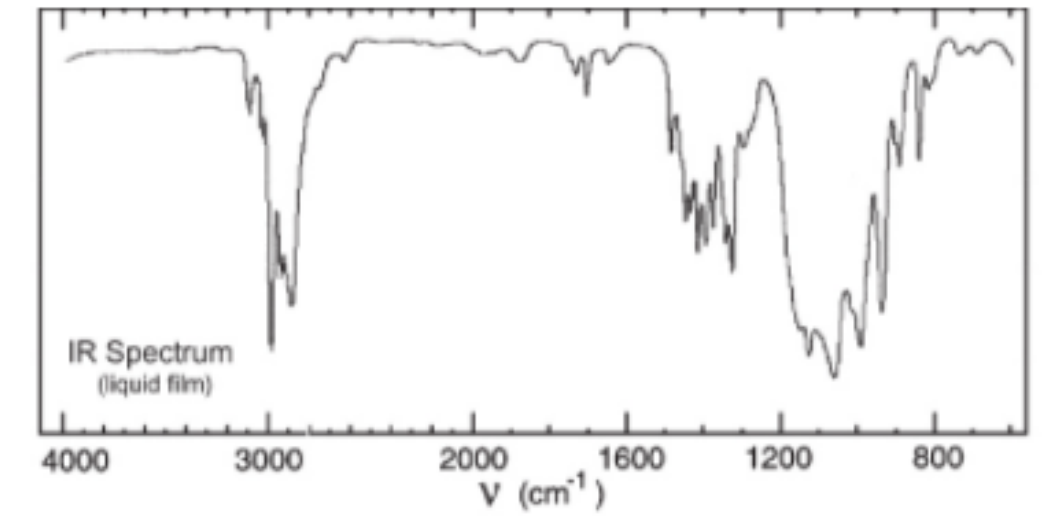
No significant UV absorption above 220 nm

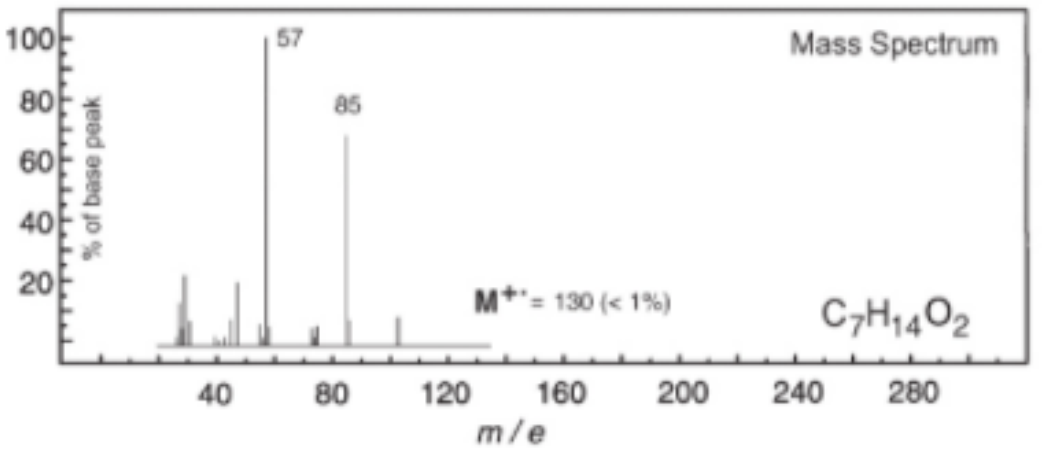




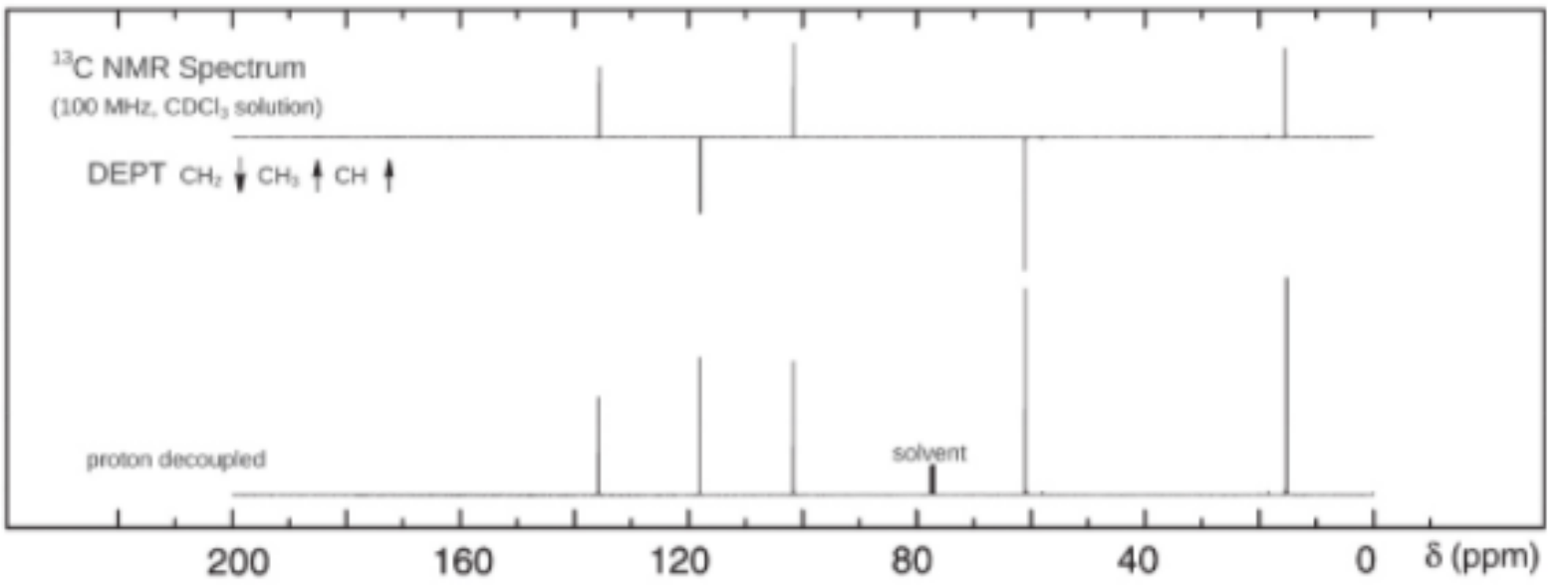

ppm
20
30
40
50
60
180
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(400 MHz, D_2O solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
4.5
4.0
3.5
3.0
2.5
2.0
ppm

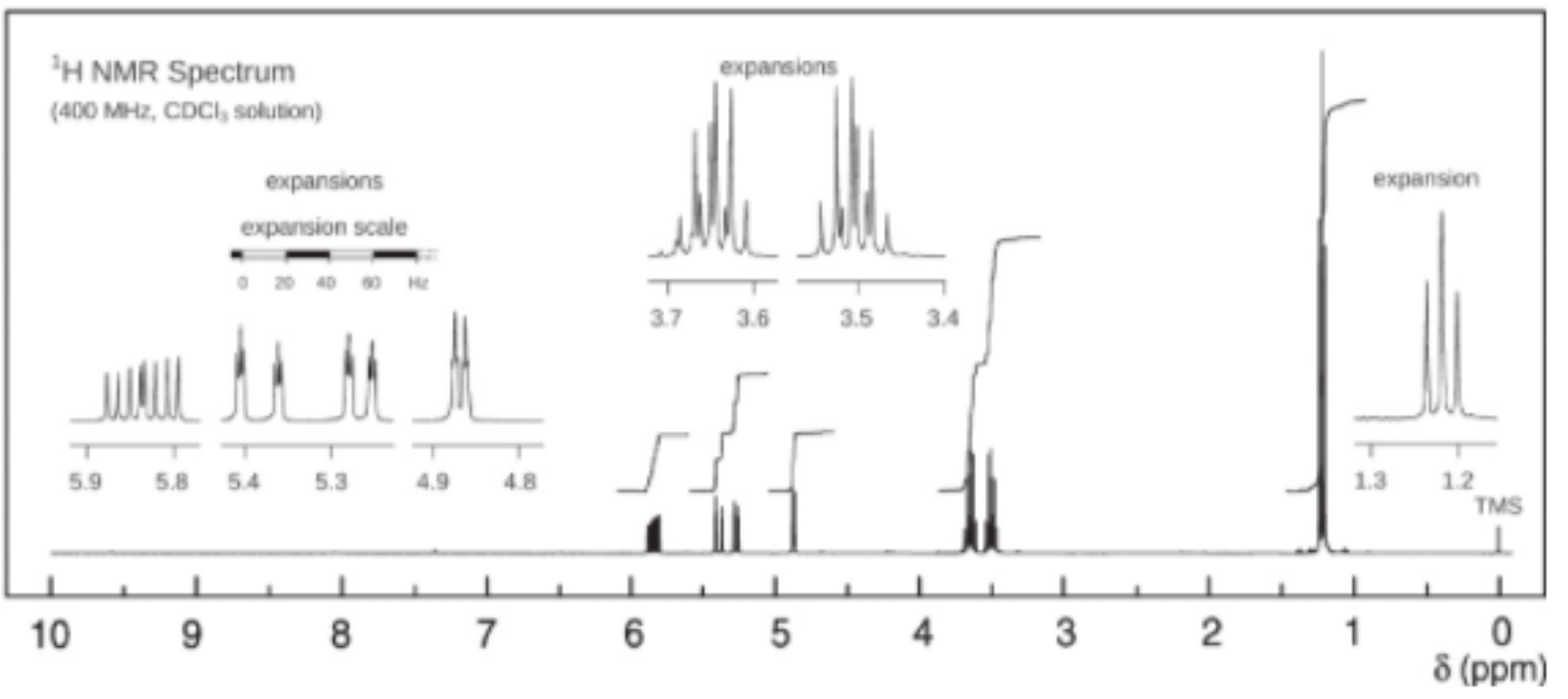
Problem 280

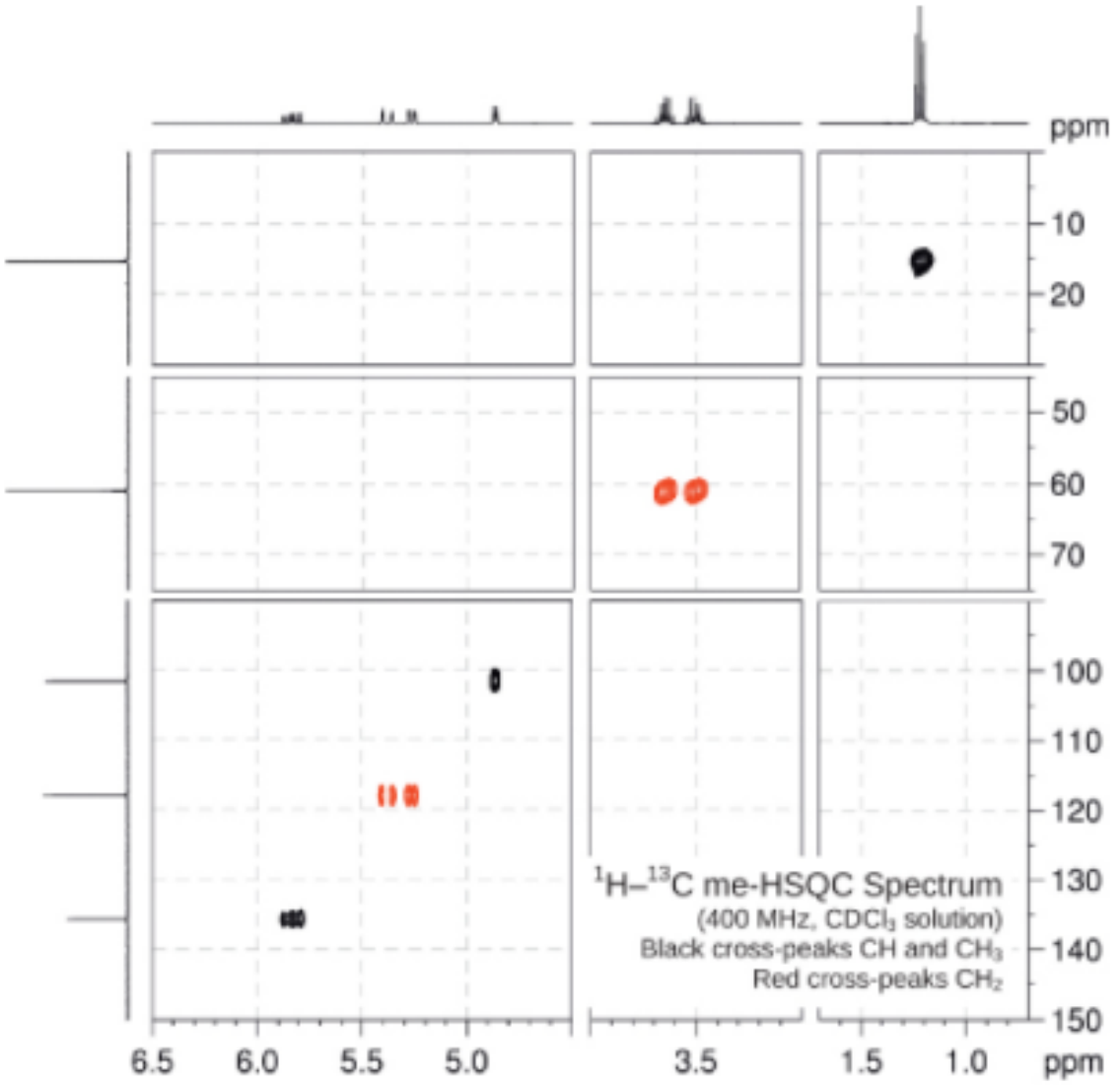




No significant UV absorption above 220 nm

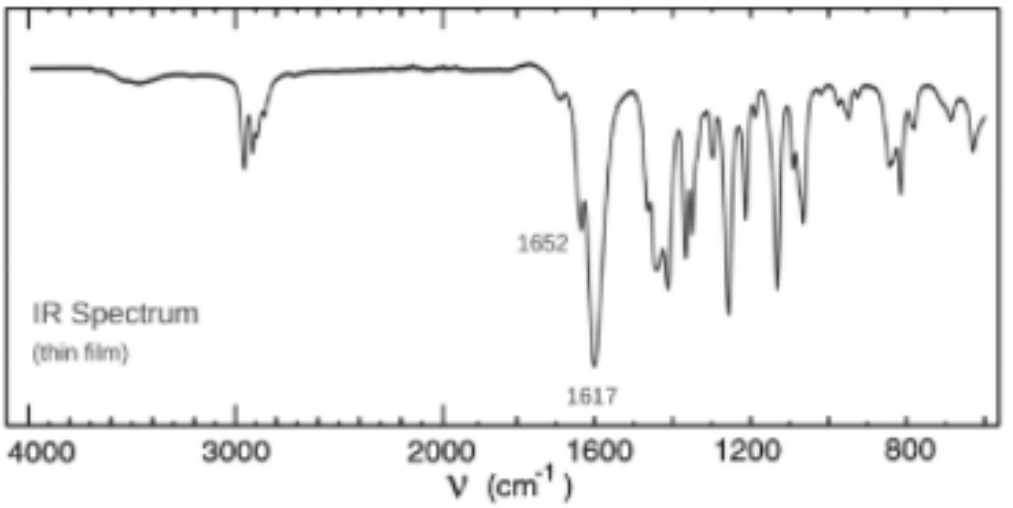


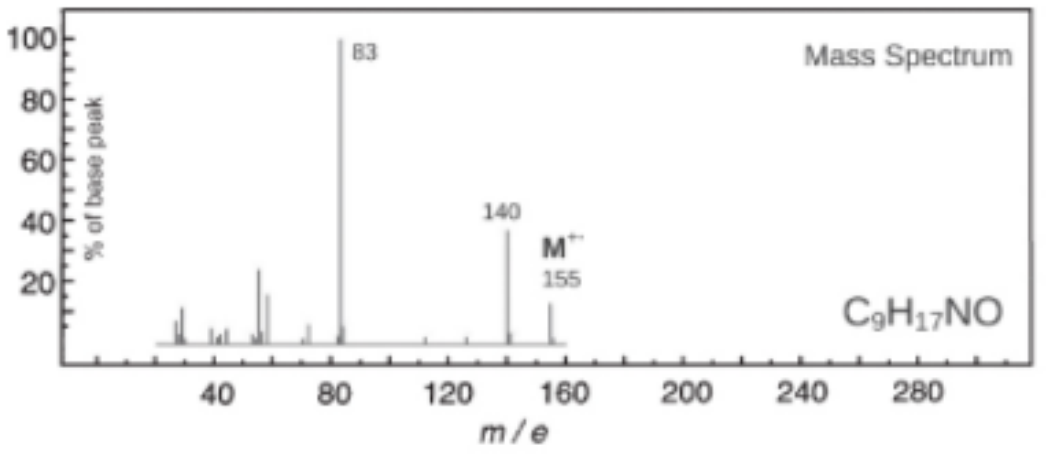


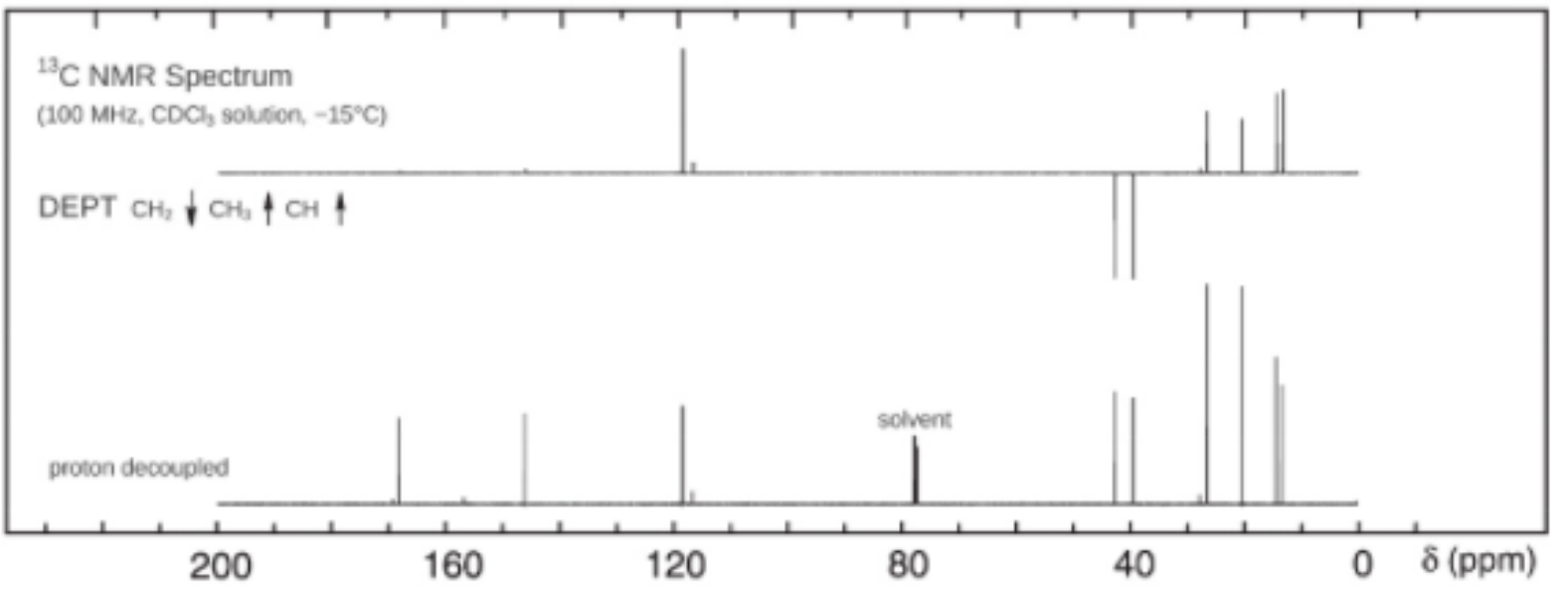

ppm
10
20
50
60
70
100
110
120
130
140
150
6.5
6.0
5.5
5.0
3.5
1.5
1.0
ppm
$^{1}H–^{13}C$ me-HSQC Spectrum
(400 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2

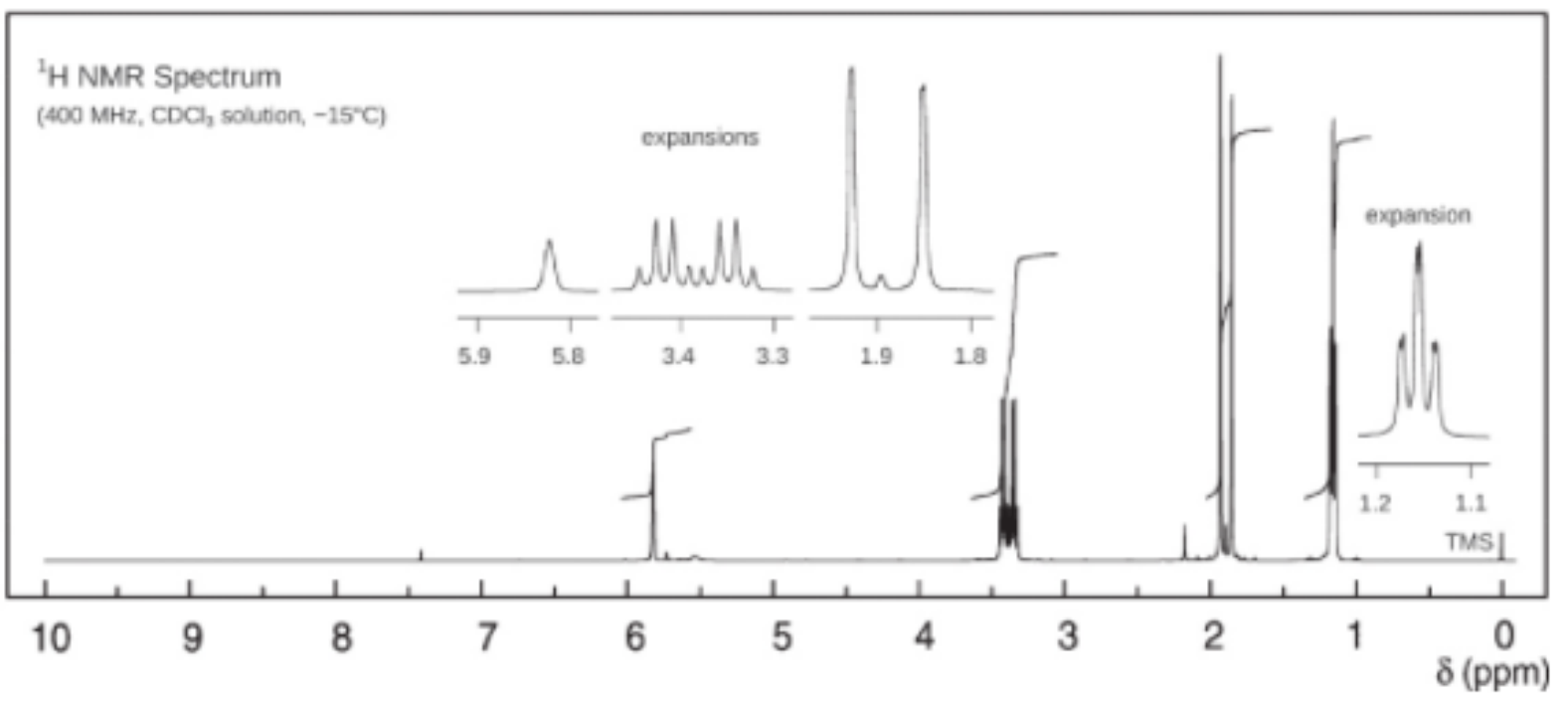
ppm
1.0
1.5
3.5
5.0
5.5
6.0
6.5
6.5
6.0
5.5
5.0
3.5
1.5
1.0
ppm
^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution)

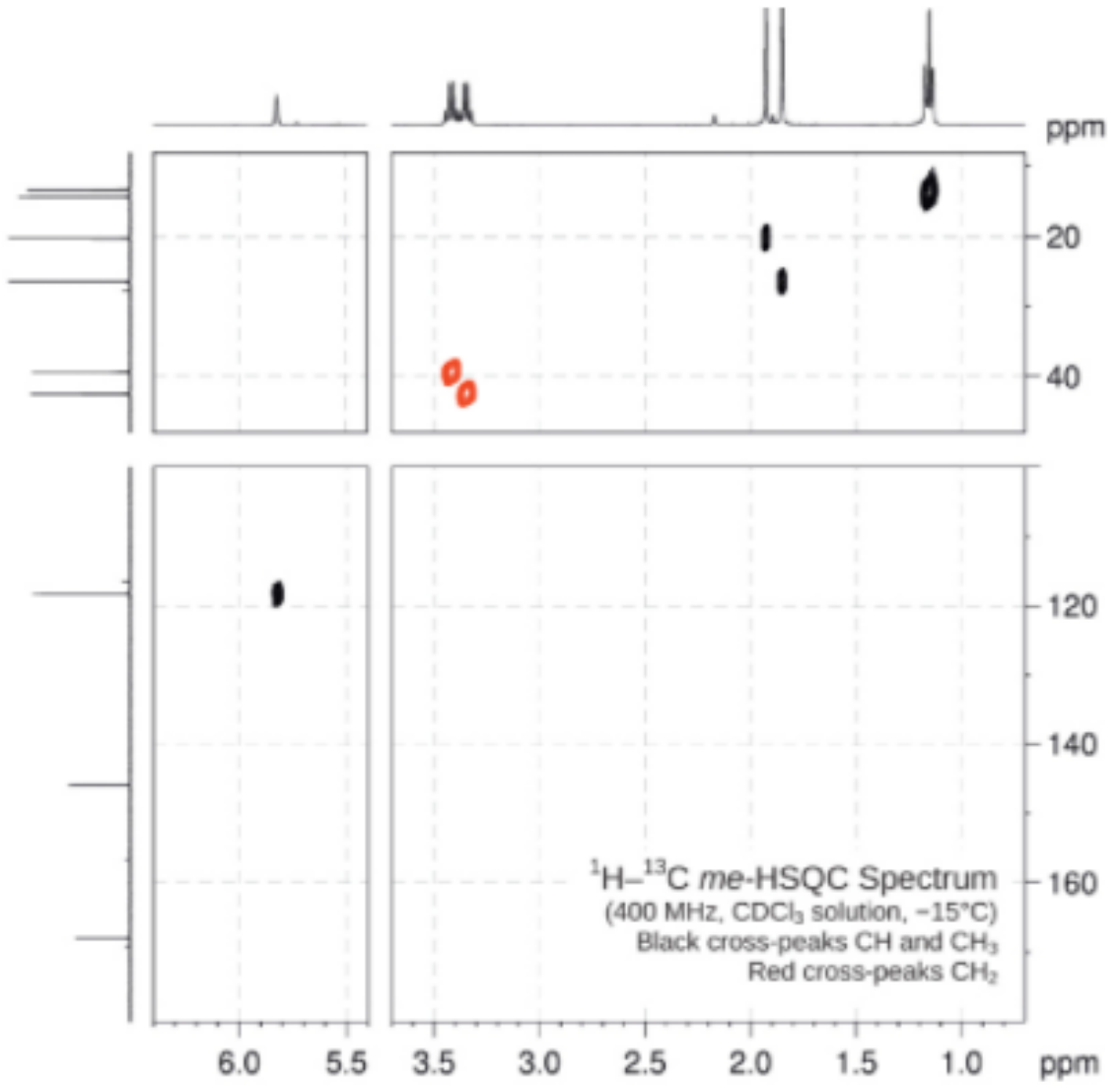
Problem 281

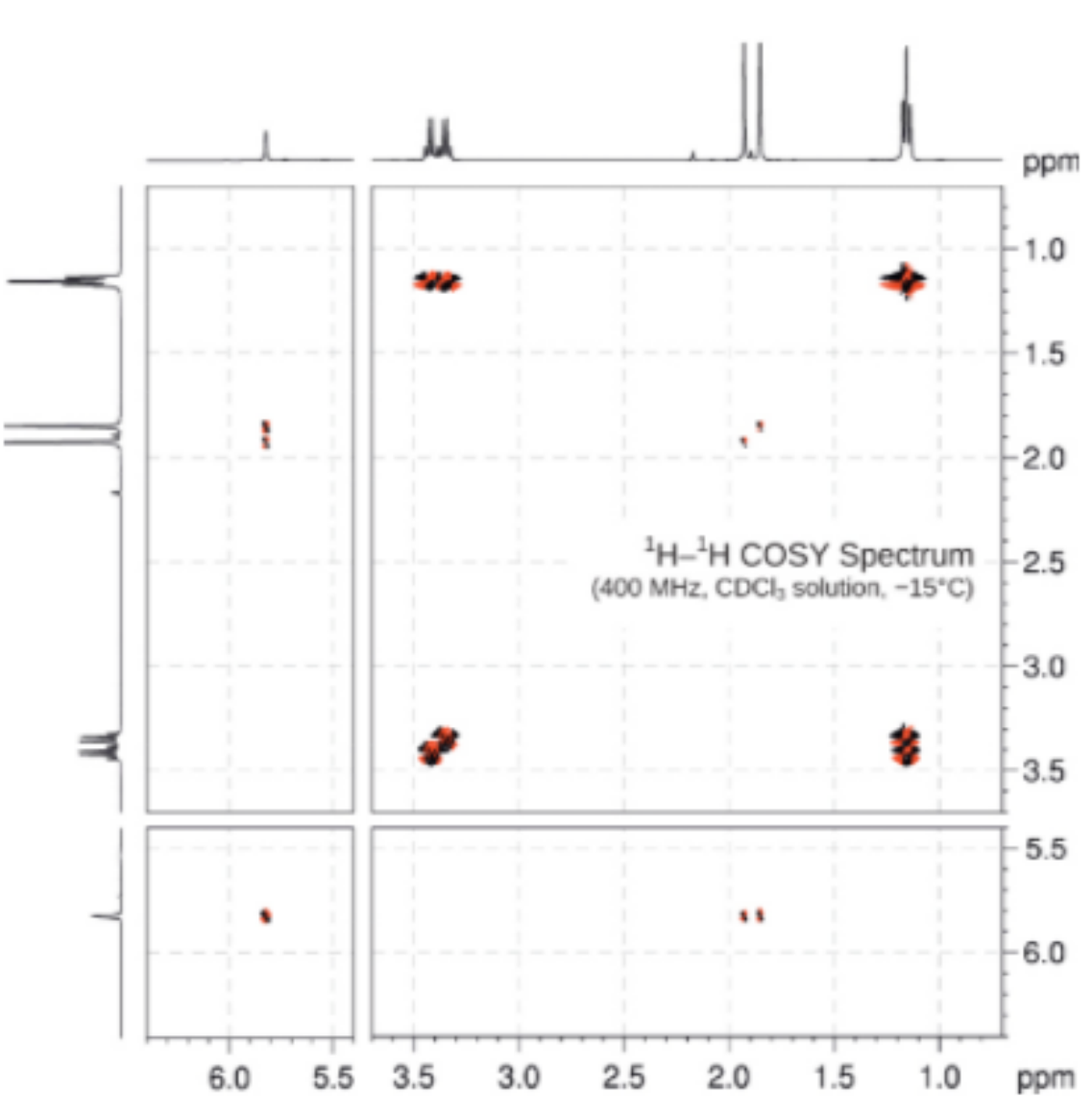

IR Spectrum
(thin film)
1652
1617
4000
3000
2000
1600
1200
800
ν (cm-1)

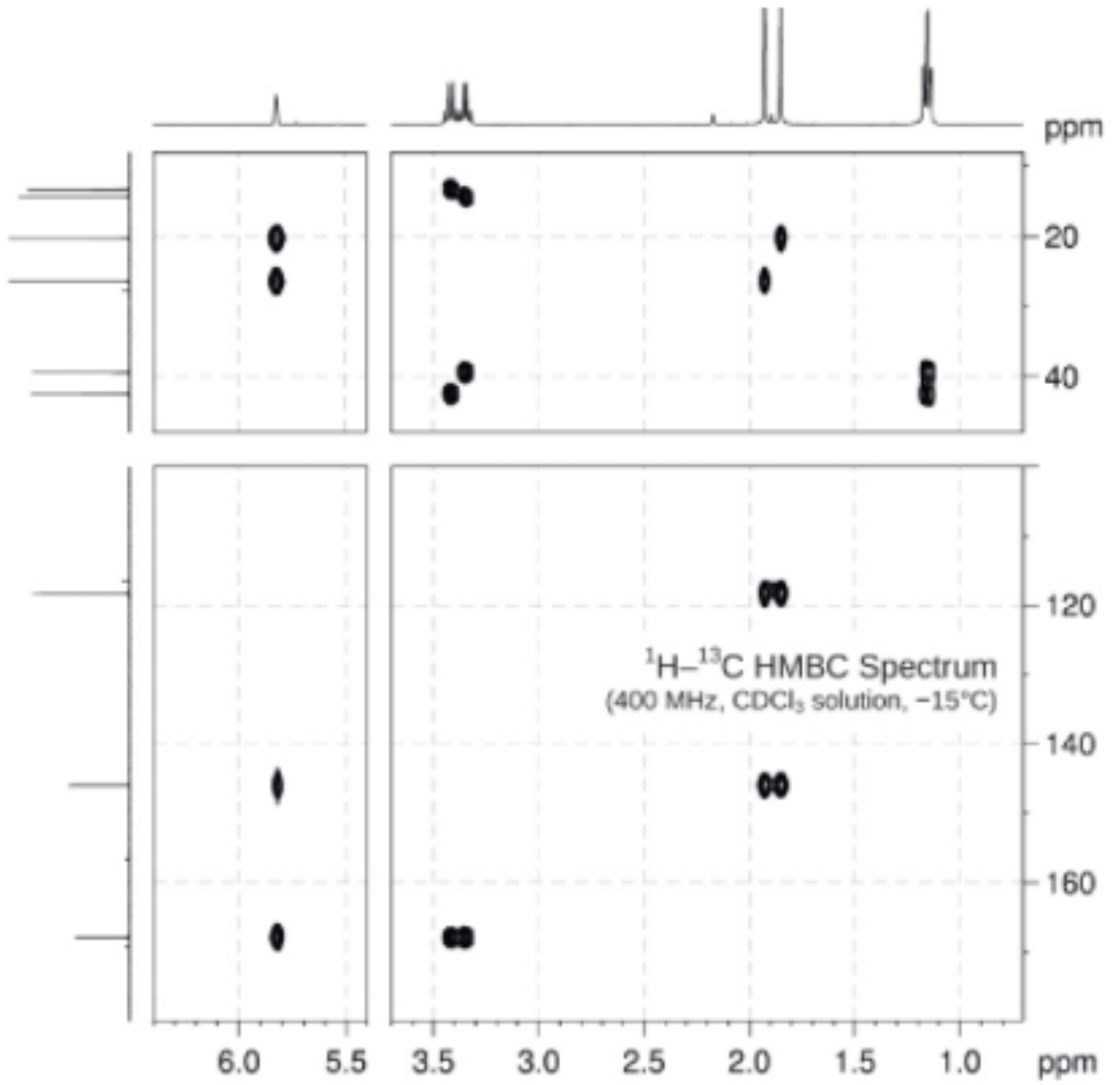

Mass Spectrum
% of base peak
100
80
60
40
20
83
140
M+·
155
C9H17NO
40
80
120
160
200
240
280
m/e

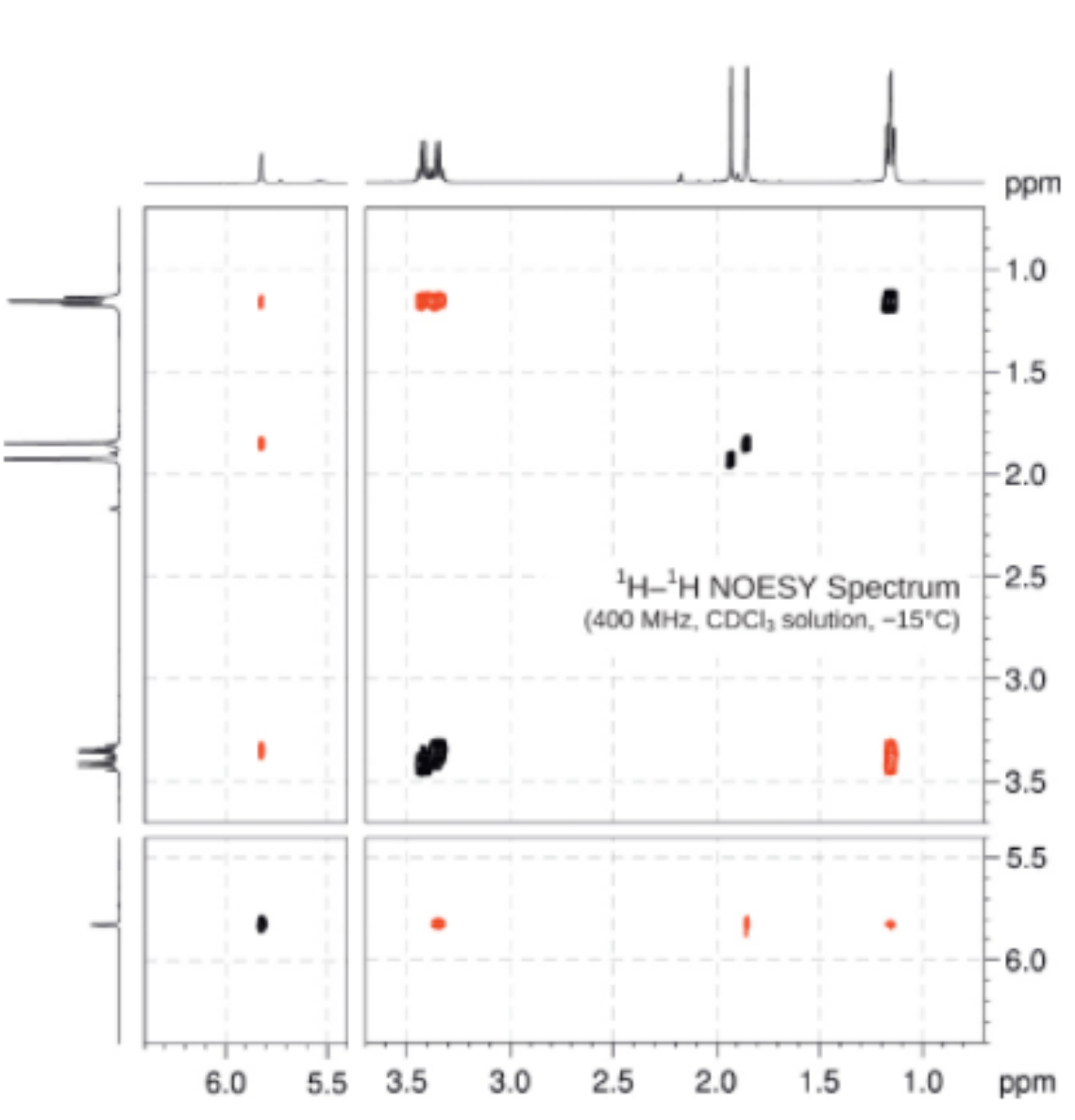

13C NMR Spectrum
(100 MHz, CDCl3 solution, −15°C)
DEPT CH2 CH3 CH
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(400 MHz, CDCl3 solution, −15°C)
expansions
5.9
5.8
3.4
3.3
1.9
1.8
expansion
1.2
1.1
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

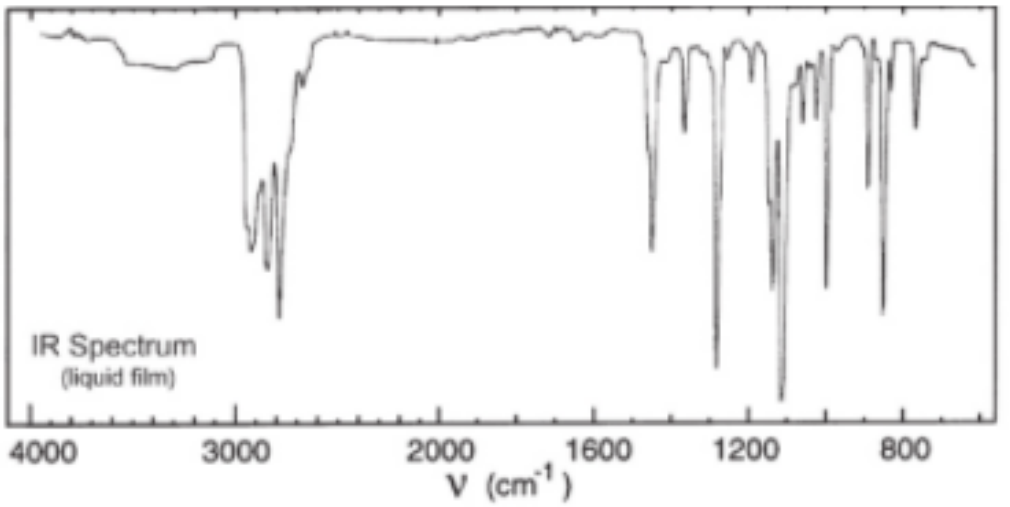

ppm
20
40
120
140
160
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ solution, −15°C)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
6.0
5.5
3.5
3.0
2.5
2.0
1.5
1.0
ppm

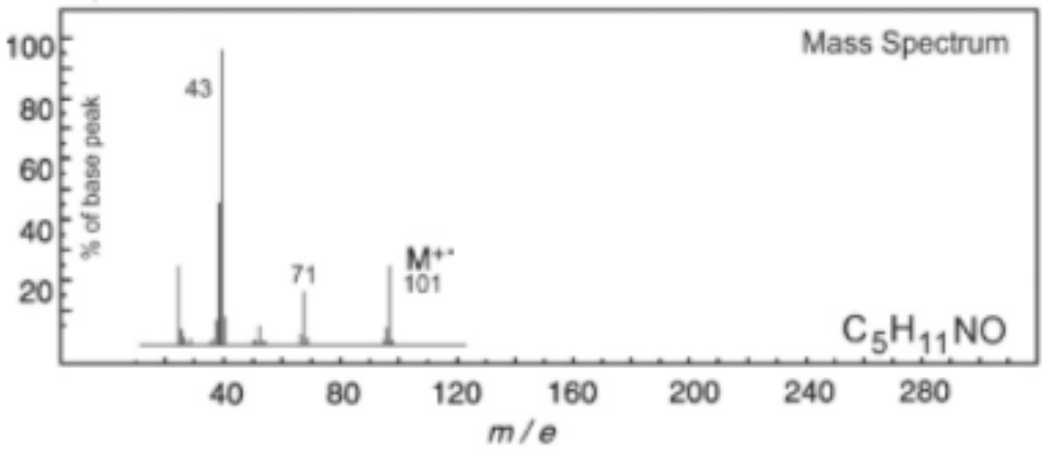

ppm
1.0
1.5
2.0
2.5
3.0
3.5
5.5
6.0
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ solution, −15°C)
6.0
5.5
3.5
3.0
2.5
2.0
1.5
1.0
ppm


ppm
20
40
120
140
160
$^{1}H–^{13}C$ HMBC Spectrum
(400 MHz, $CDCl_3$ solution, −15°C)
6.0
5.5
3.5
3.0
2.5
2.0
1.5
1.0
ppm

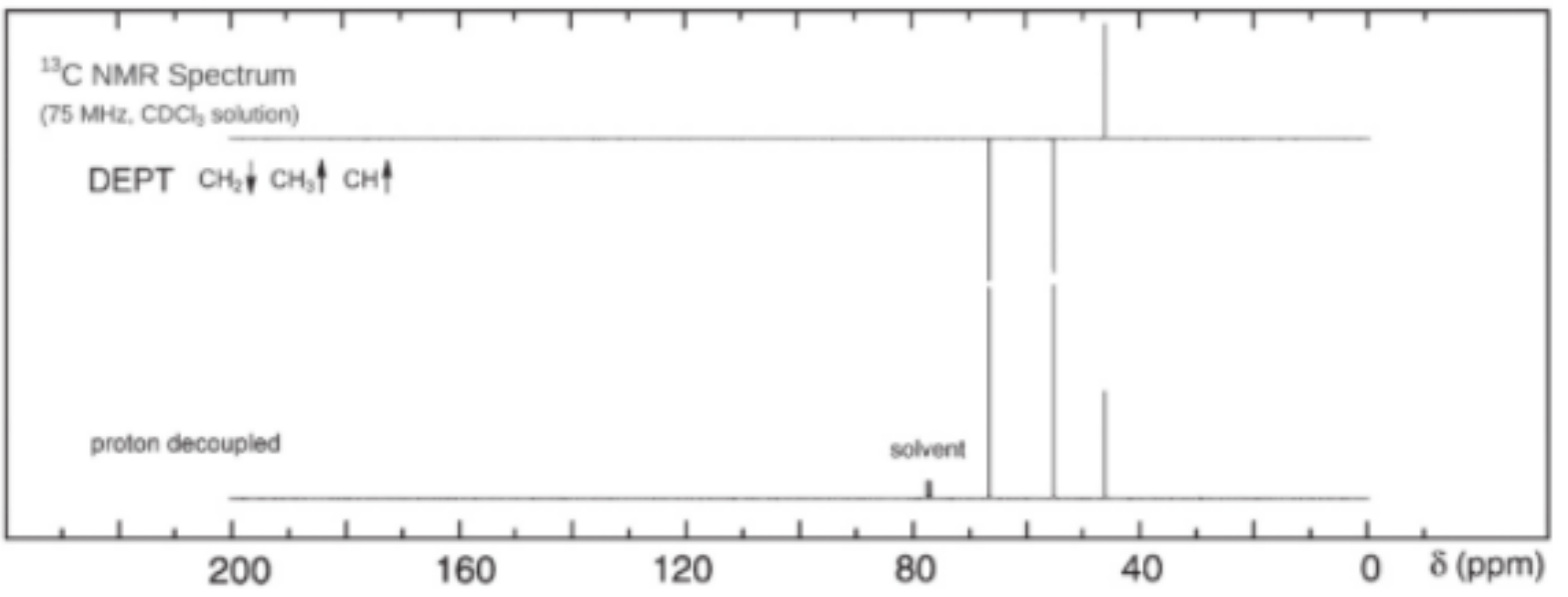

ppm
1.0
1.5
2.0
2.5
3.0
3.5
5.5
6.0
$^{1}H–^{1}H$ NOESY Spectrum
(400 MHz, $CDCl_3$ solution, −15°C)
6.0
5.5
3.5
3.0
2.5
2.0
1.5
1.0
ppm

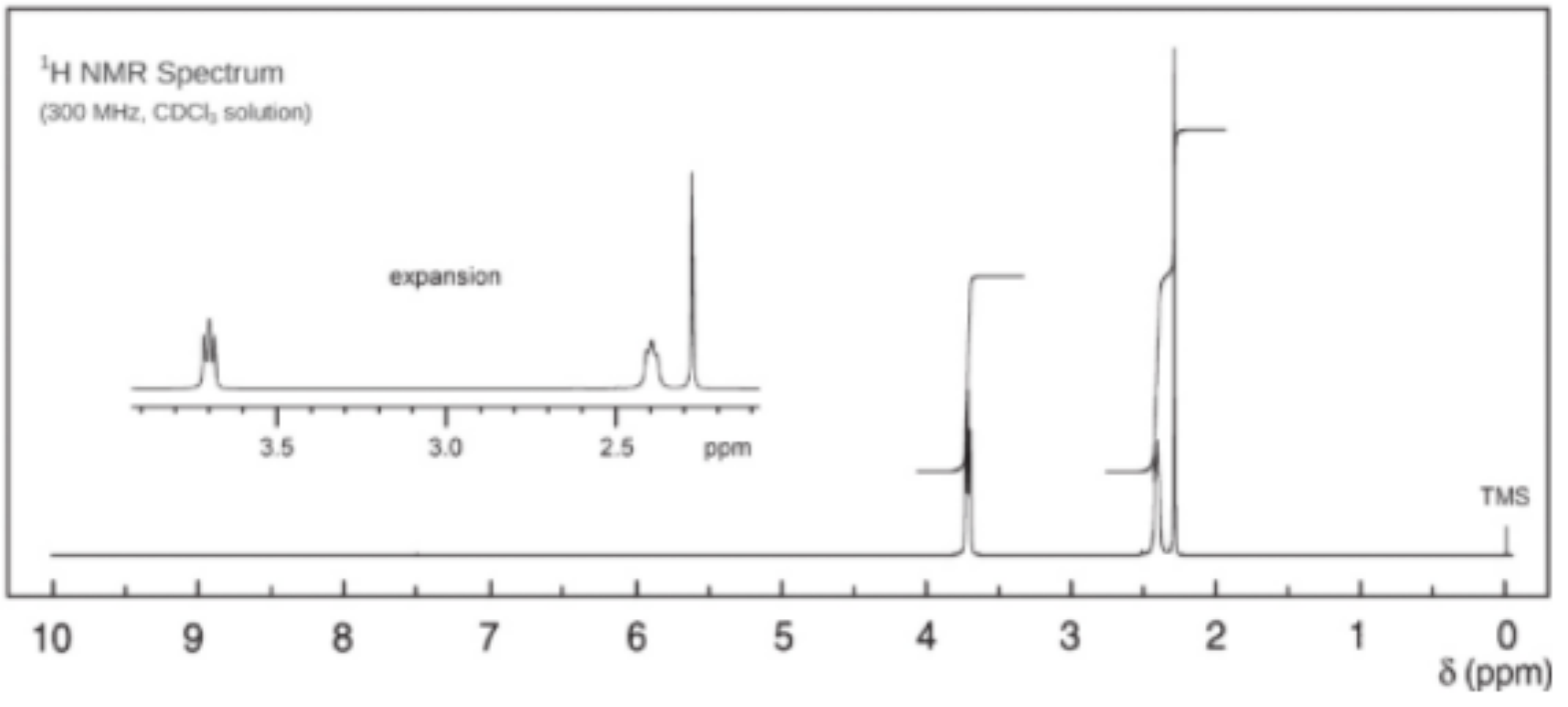
Problem 282



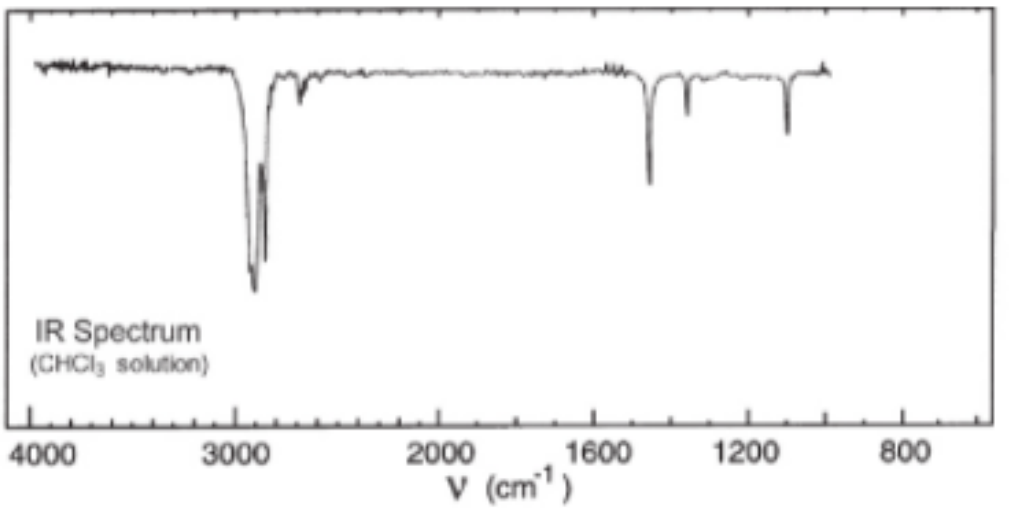


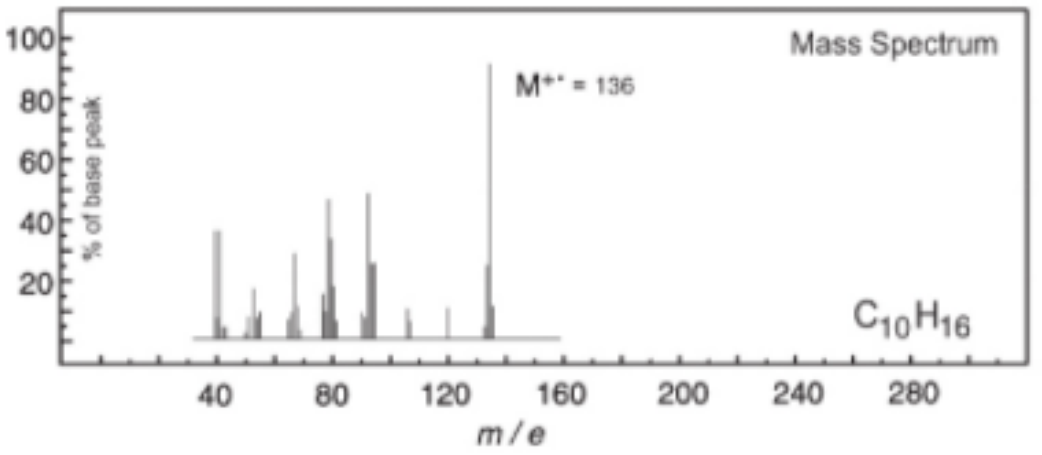
No significant UV absorption above 220 nm



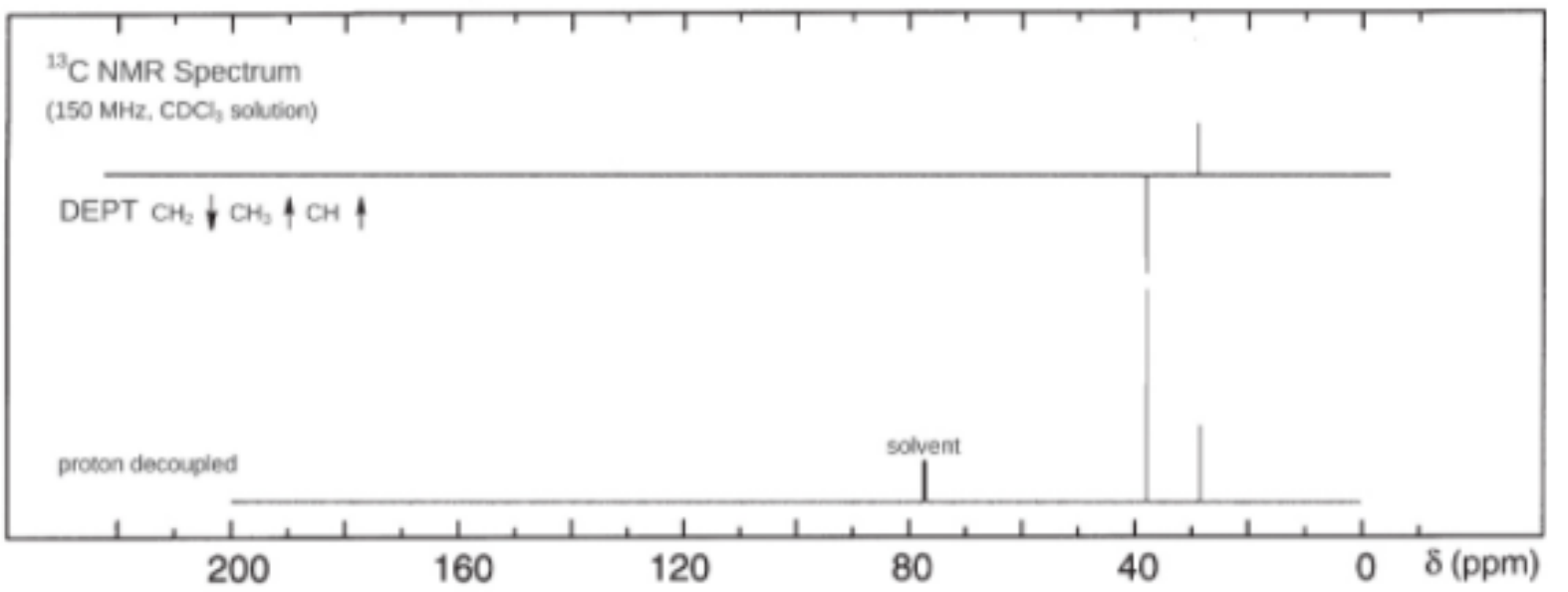


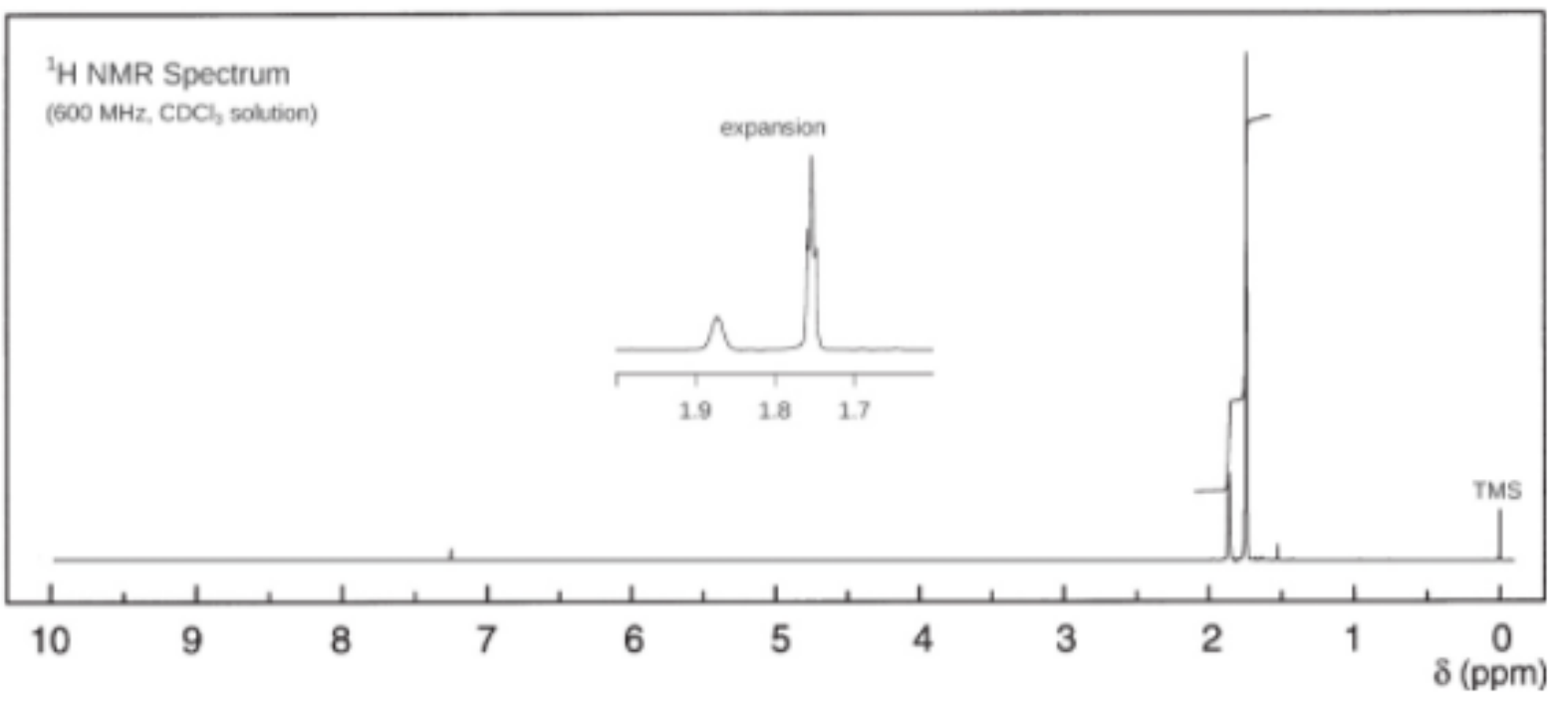
Problem 283

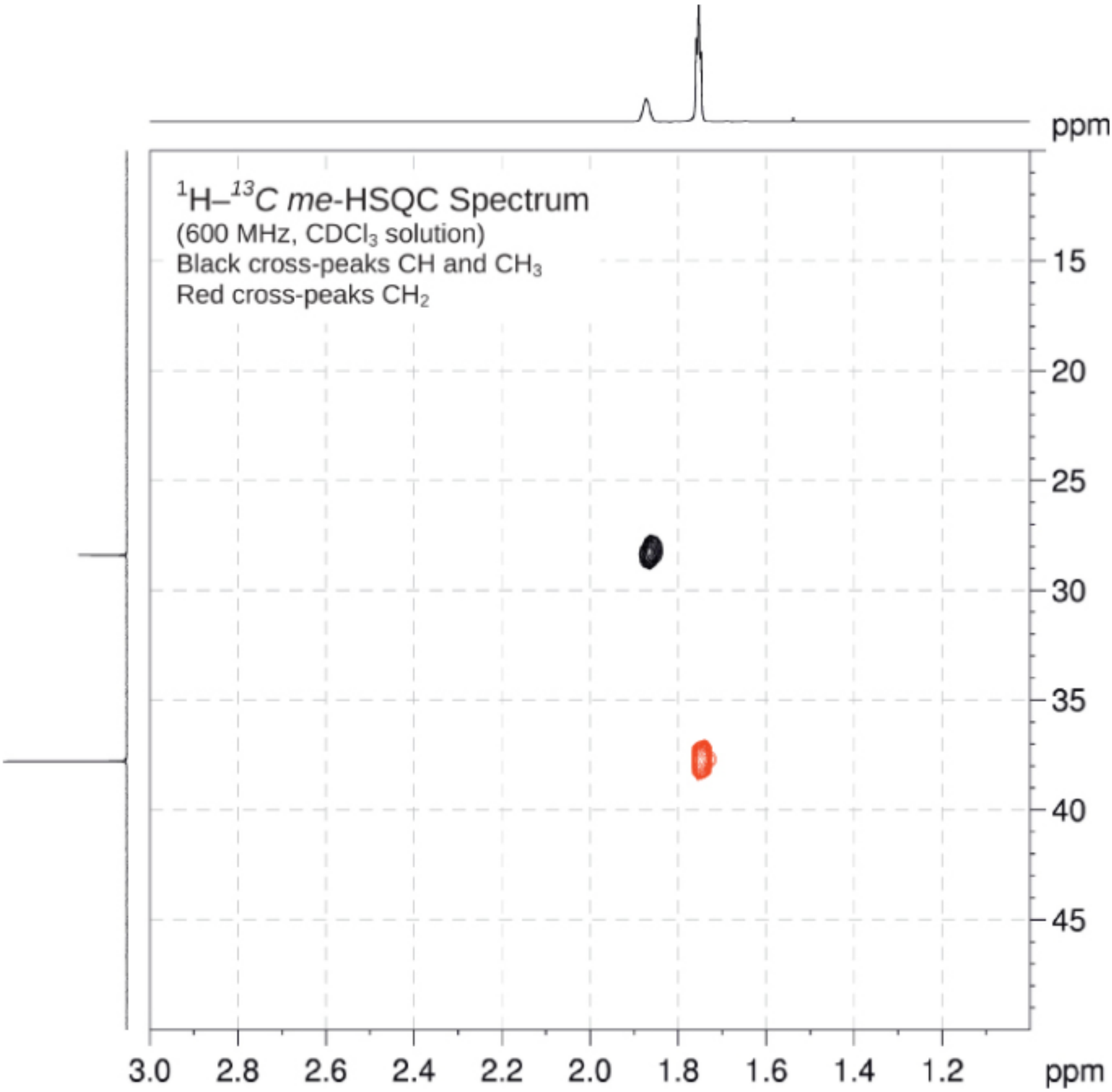




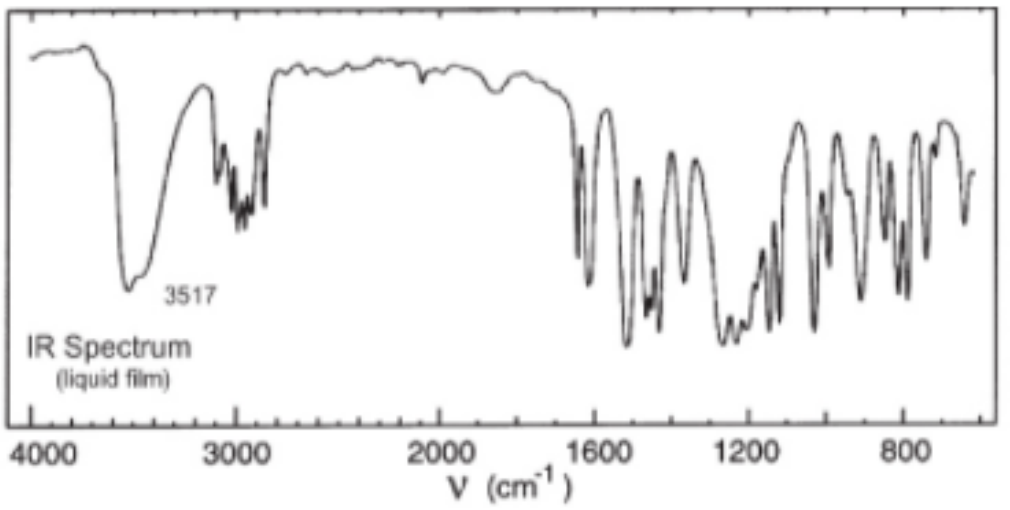
No significant UV absorption above 220 nm

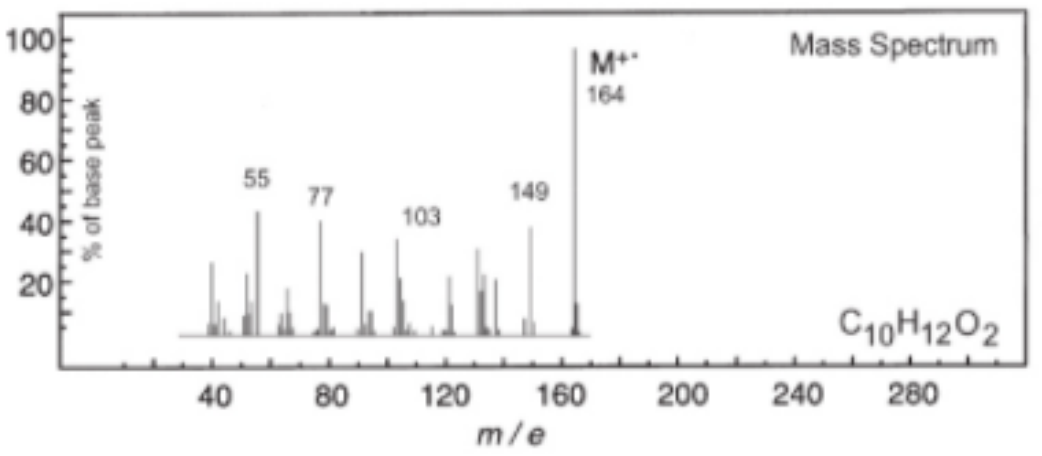





ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
15
20
25
30
35
40
45
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
ppm

Problem 284



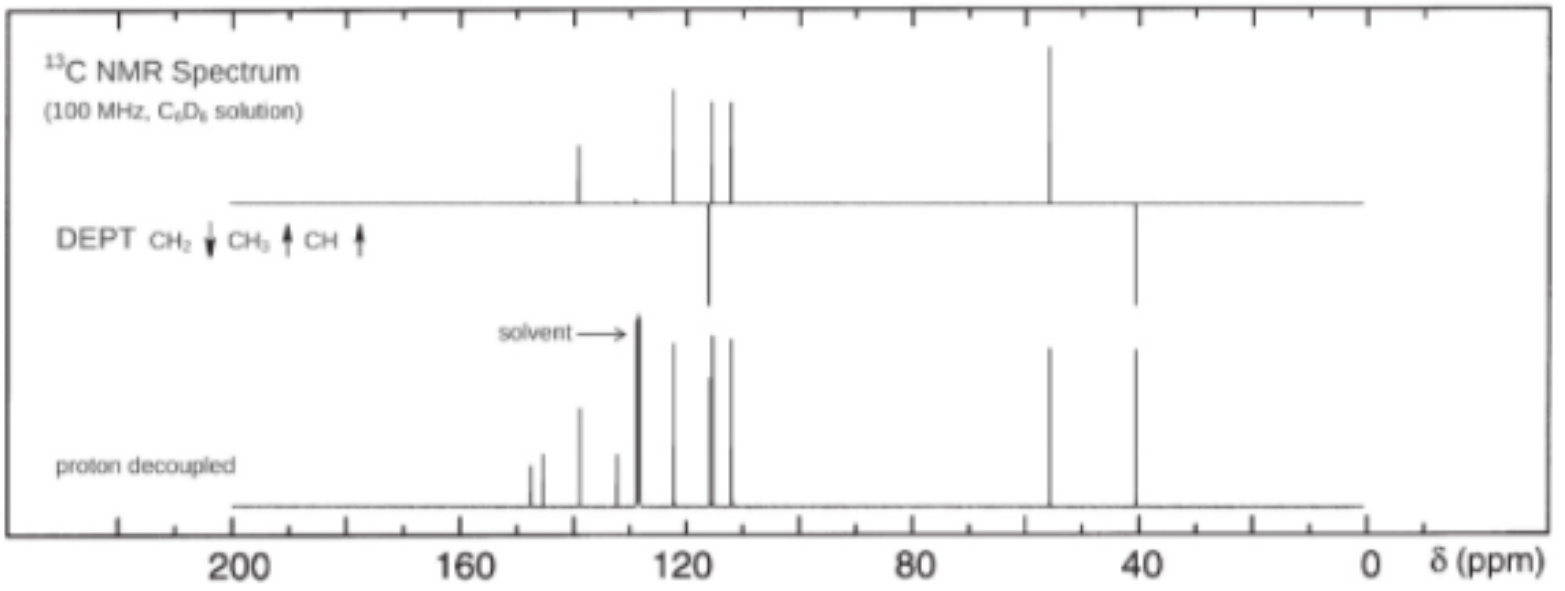


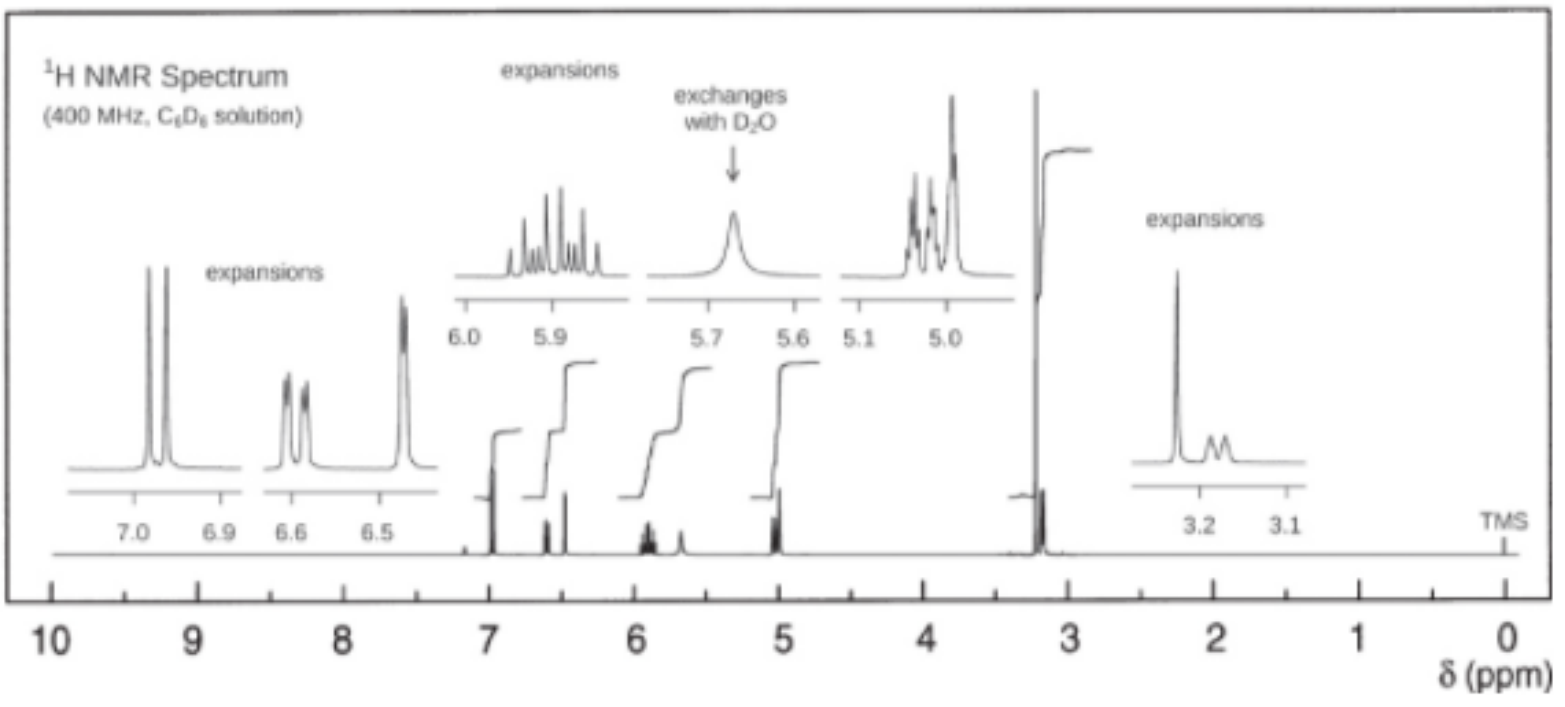
UV Spectrum

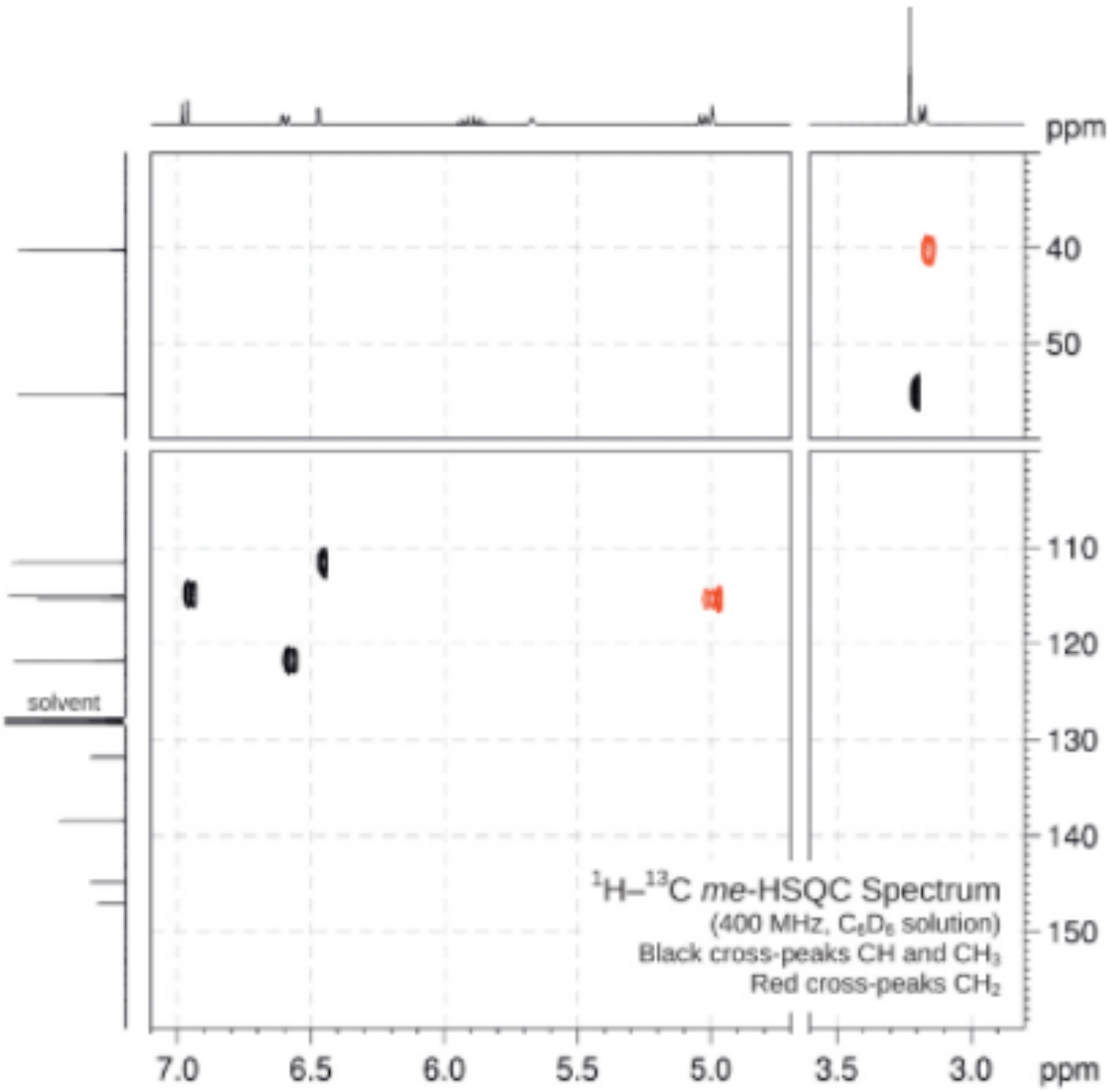
λ_{max} 281 nm ($\log_{10}\varepsilon$ 3.5)

λ_{max} 230 nm ($\log_{10}\varepsilon$ 3.6)

solvent : methanol

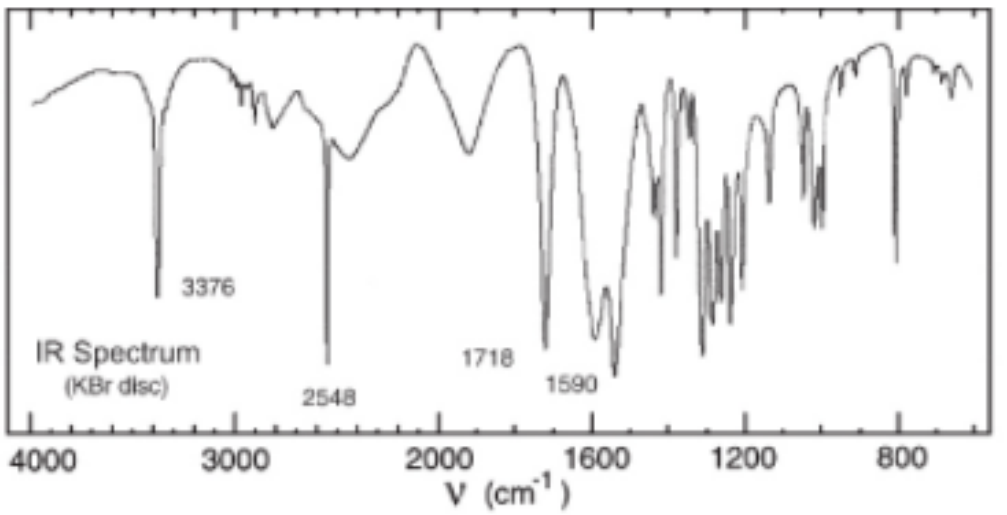


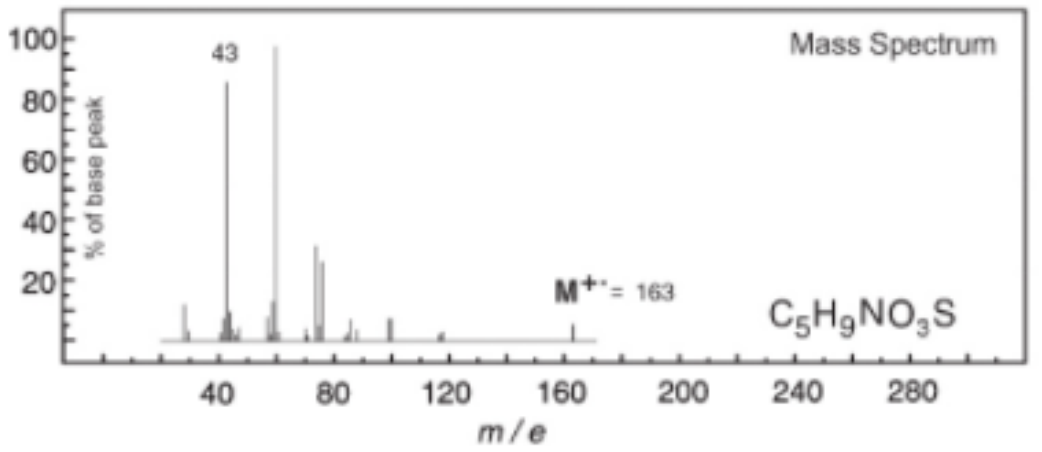



ppm
40
50
110
120
130
140
150
solvent
$^{1}H–^{13}C$ *me*-HSQC Spectrum
(400 MHz, C_6D_6 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.0
6.5
6.0
5.5
5.0
3.5
3.0
ppm

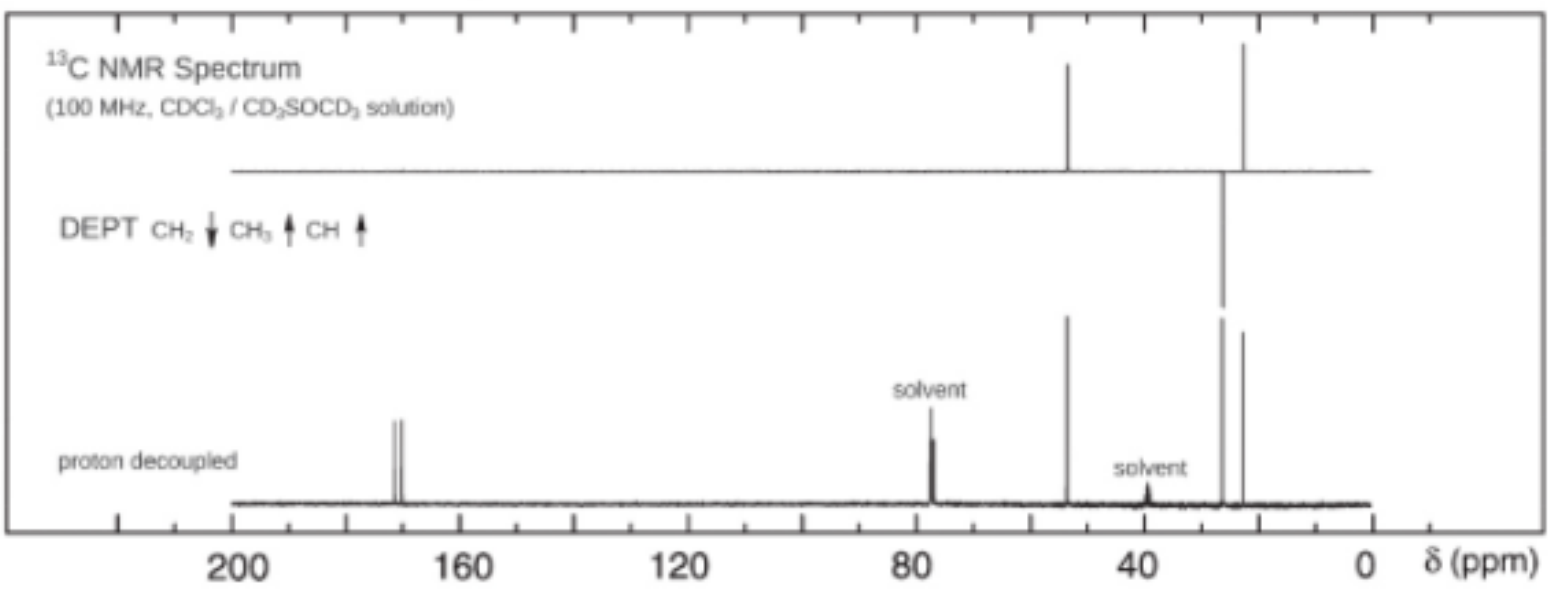
ppm
3.0
3.5
5.0
5.5
6.0
6.5
7.0
$^{1}H–^{1}H$ NOESY Spectrum
(400 MHz, C_6D_6 solution)
7.0
6.5
6.0
5.5
5.0
3.5
3.0
ppm

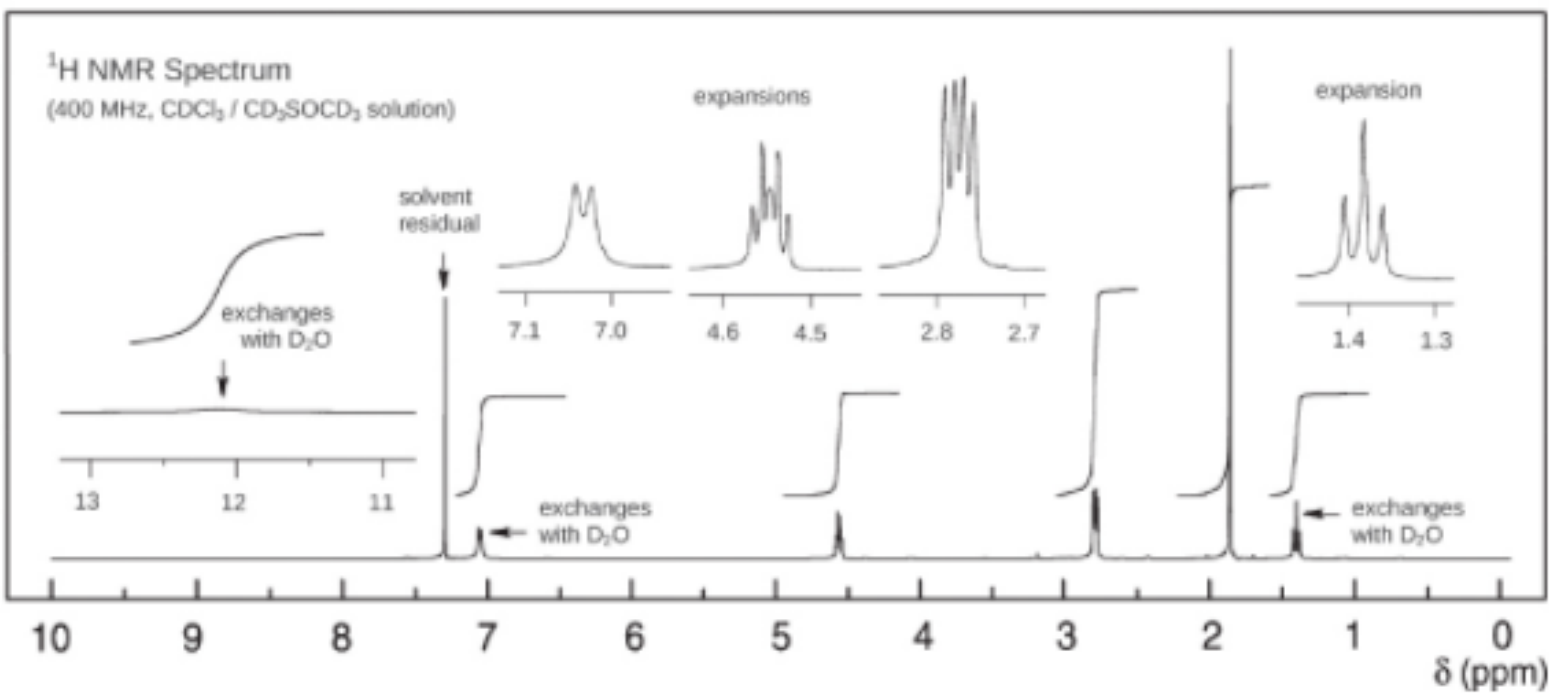
Problem 285

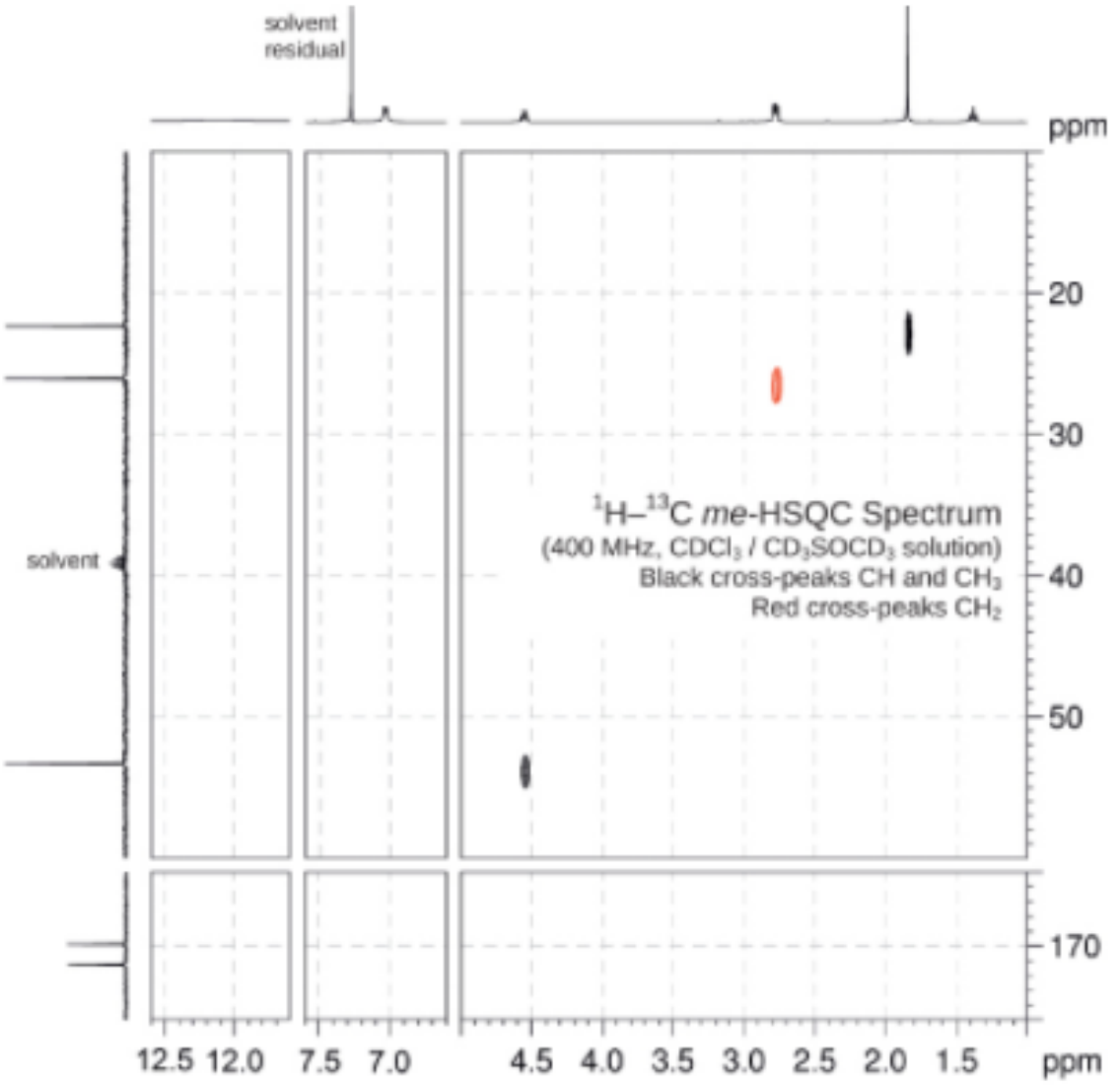




No significant UV absorption above 220 nm

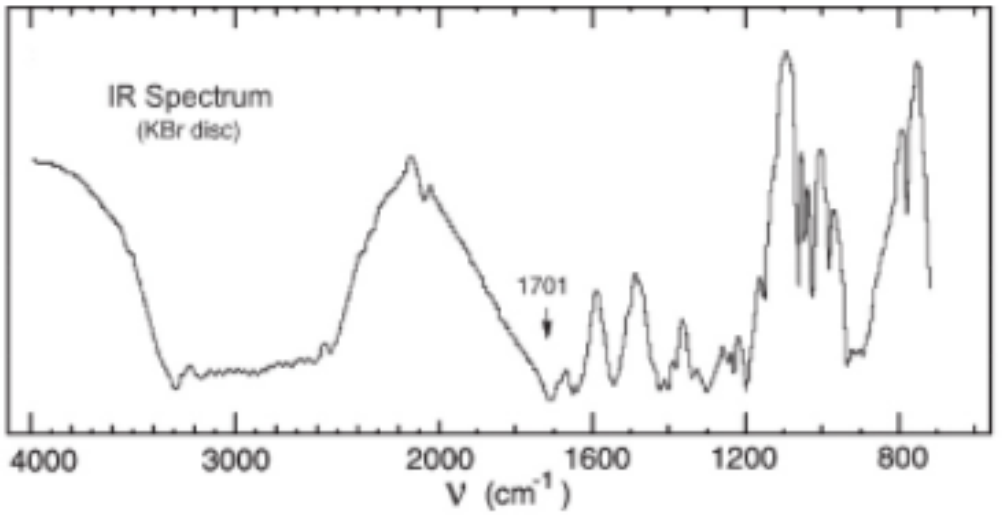


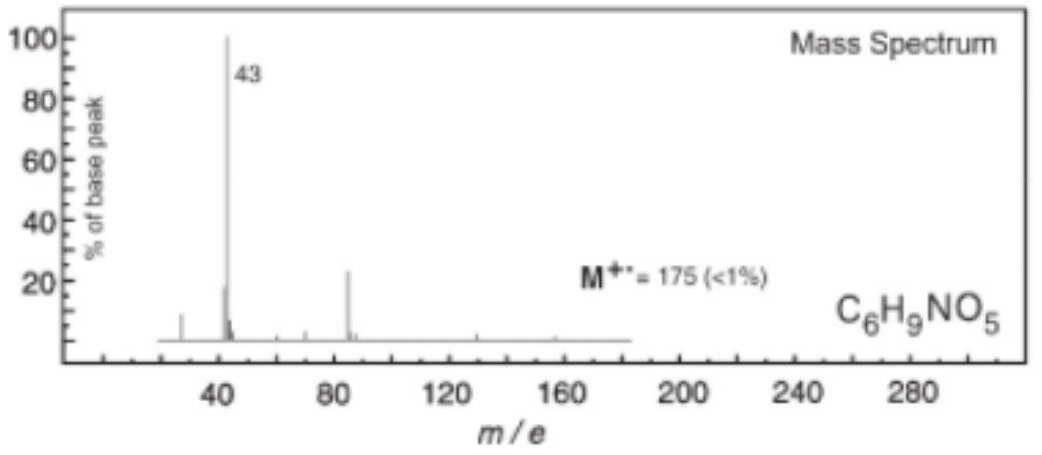



solvent
residual
ppm
20
30
40
50
170
solvent
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, $CDCl_3$ / CD_3SOCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
12.5 12.0 7.5 7.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
ppm

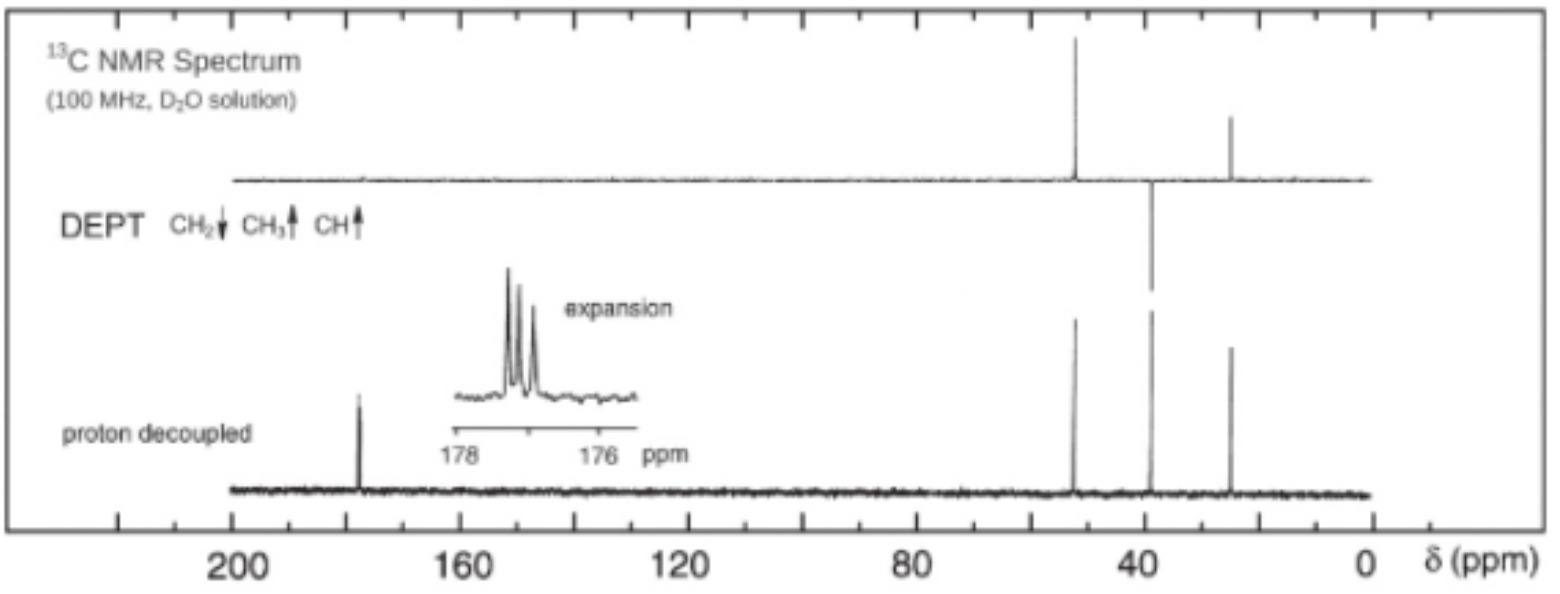
solvent
ppm
2.0
3.0
4.0
7.0
12.0
solvent
^{1}H–^{1}H COSY Spectrum
(400 MHz, $CDCl_3$ / CD_3SOCD_3 solution)
12.0 7.0 4.0 3.0 2.0
ppm

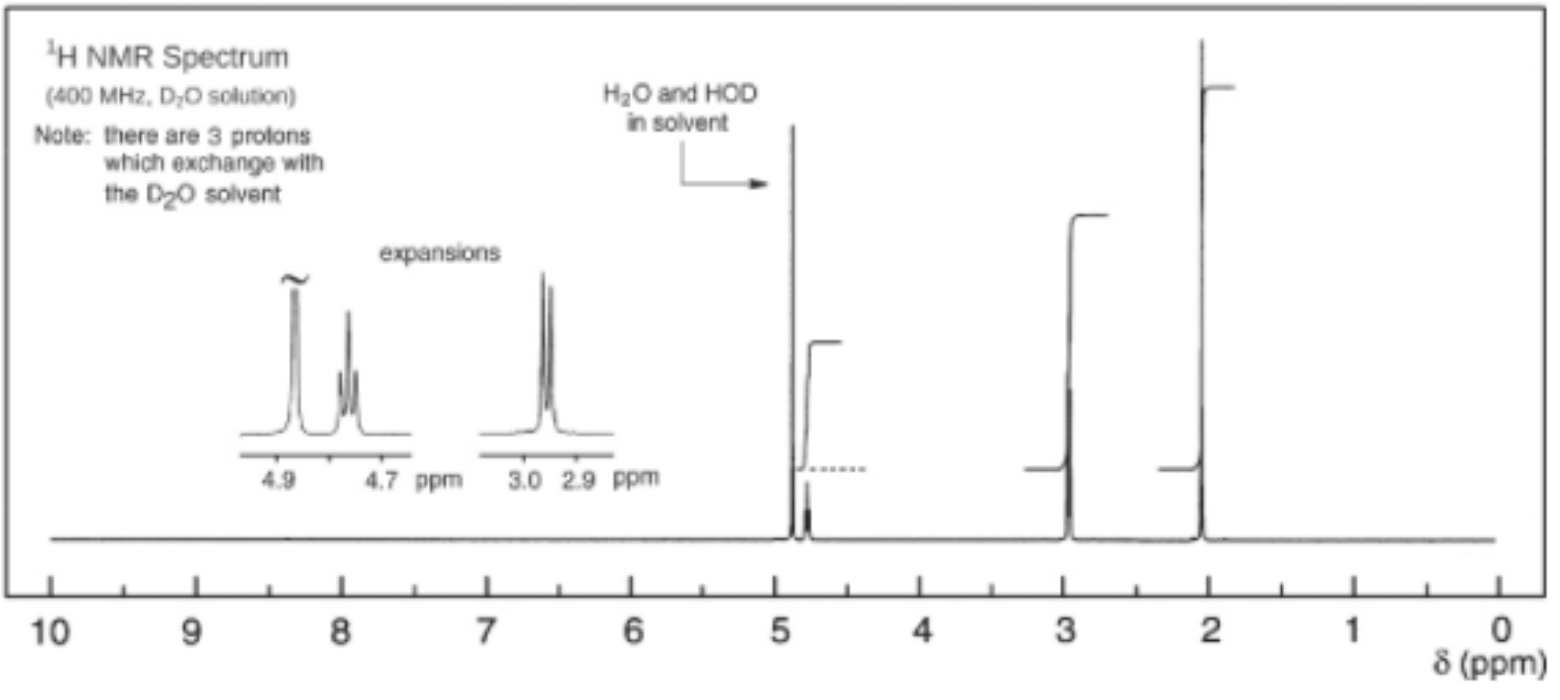
Problem 286



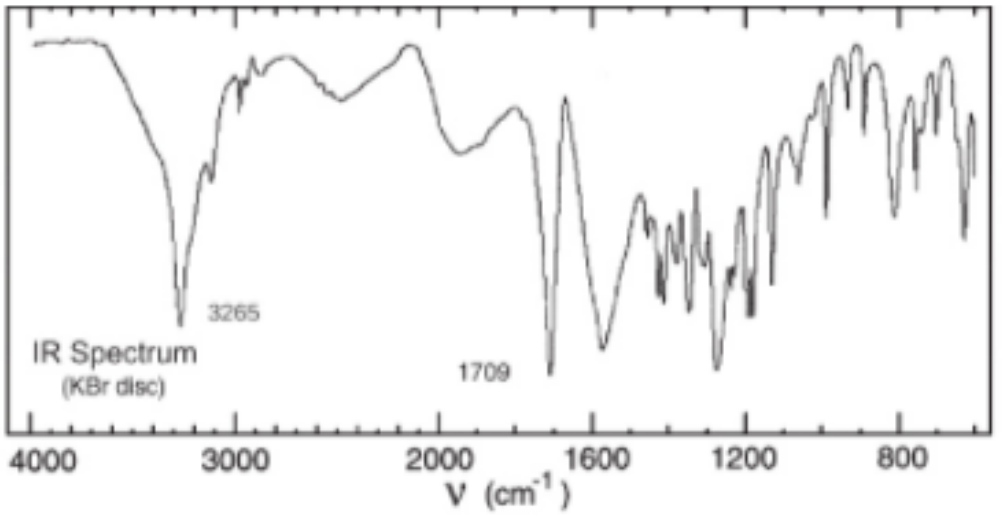


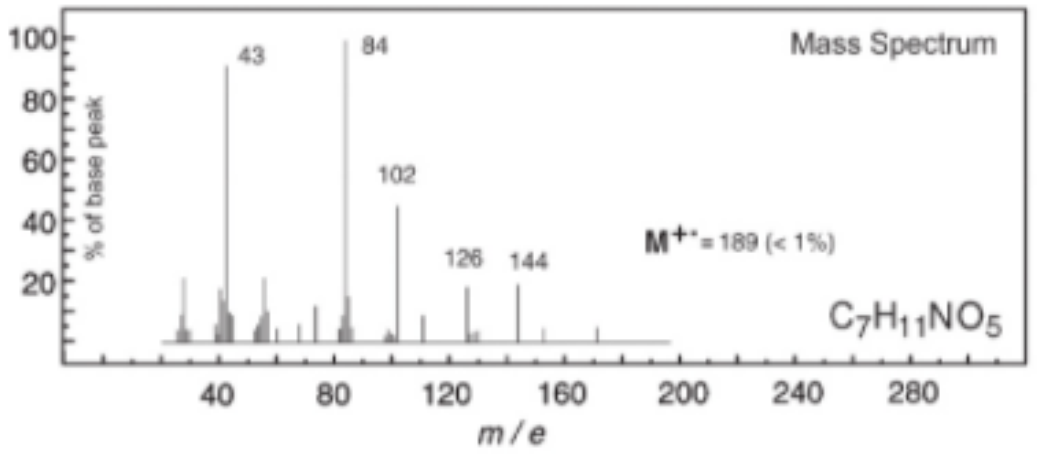
No significant UV absorption above 220 nm



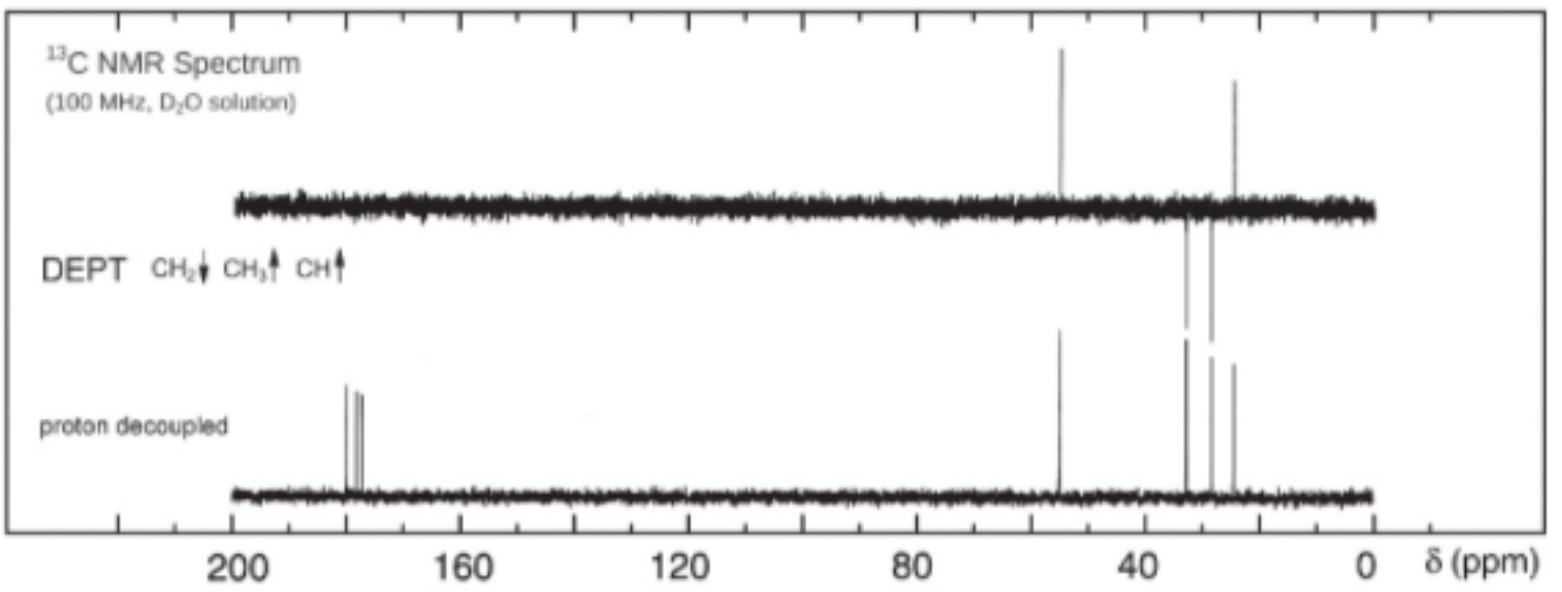


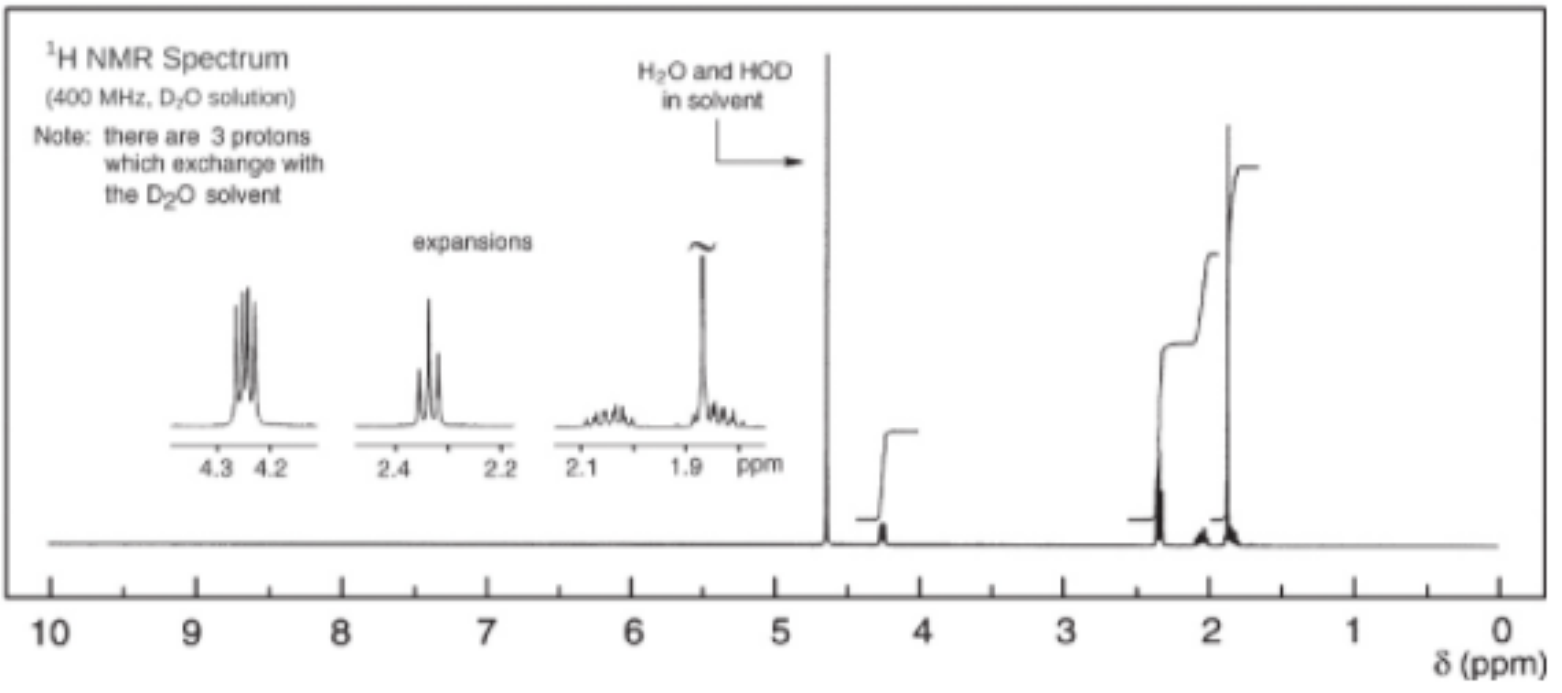
Problem 287



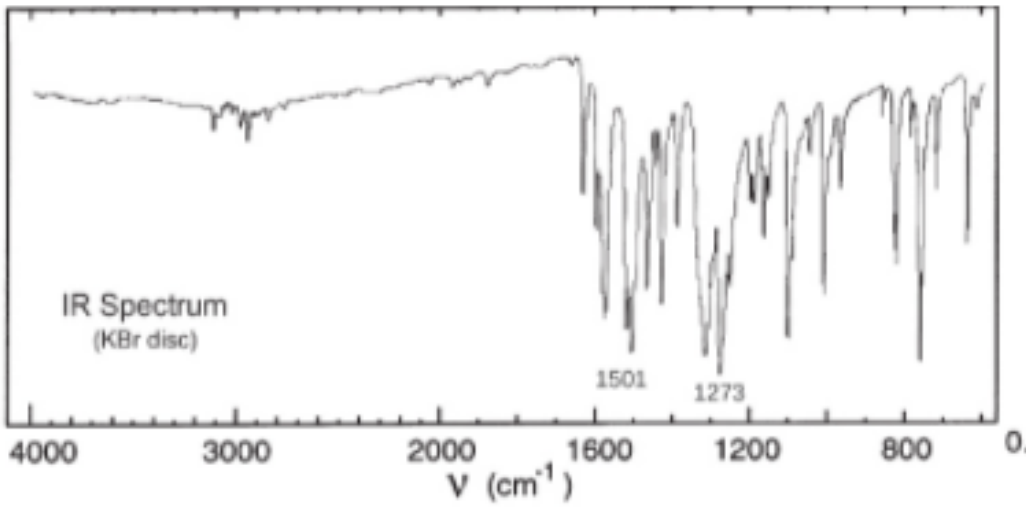


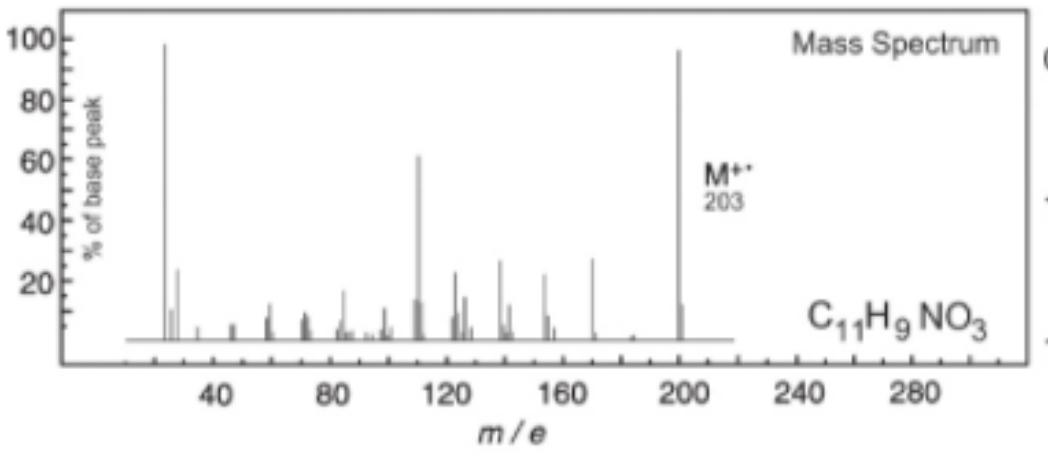
No significant UV absorption above 220 nm

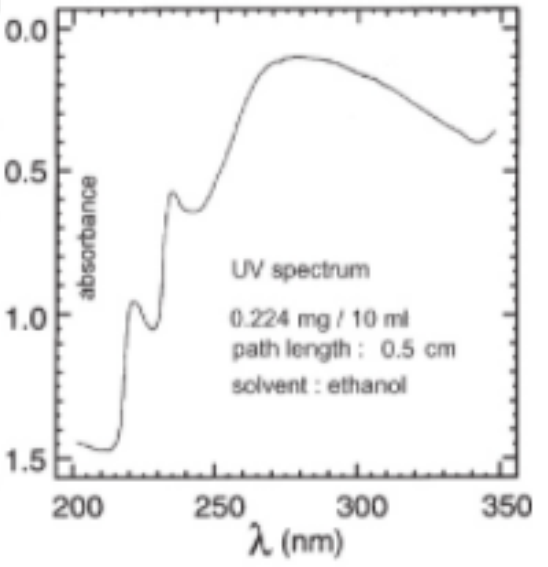


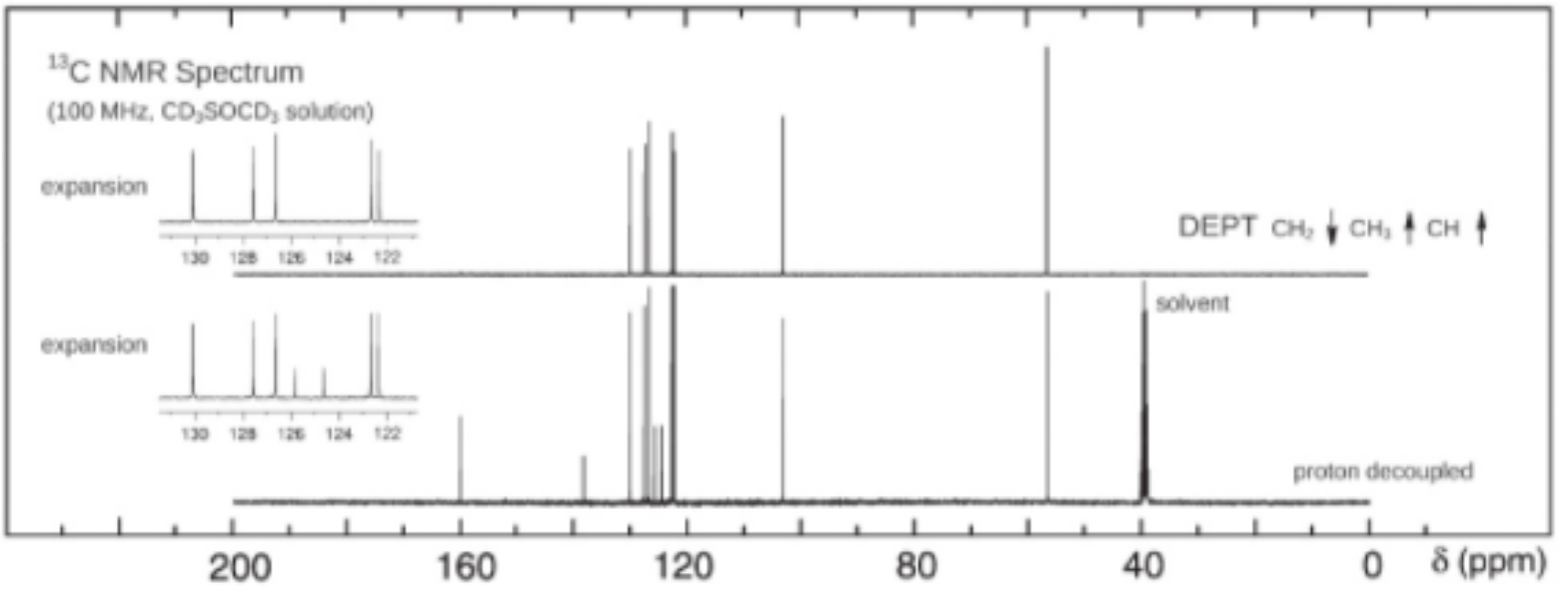


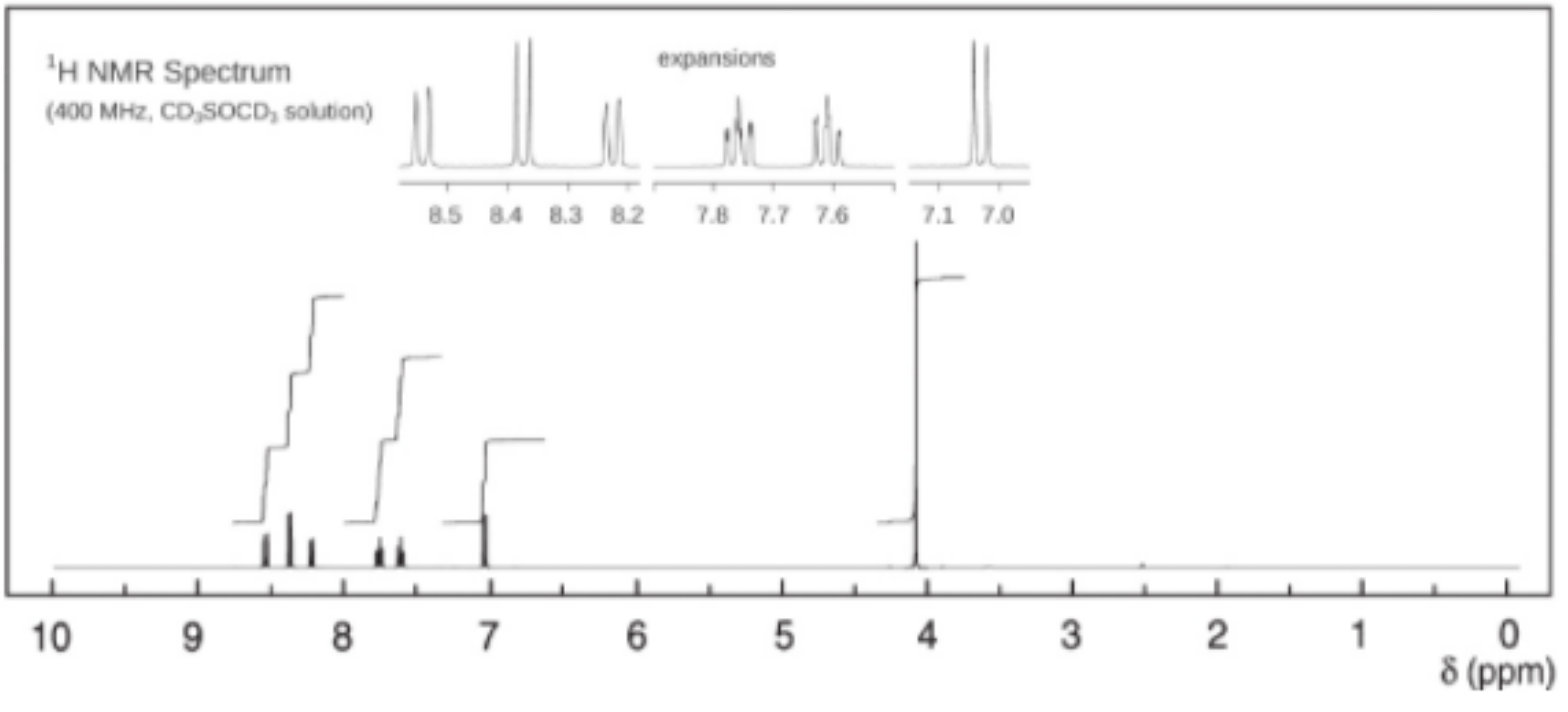
Problem 288

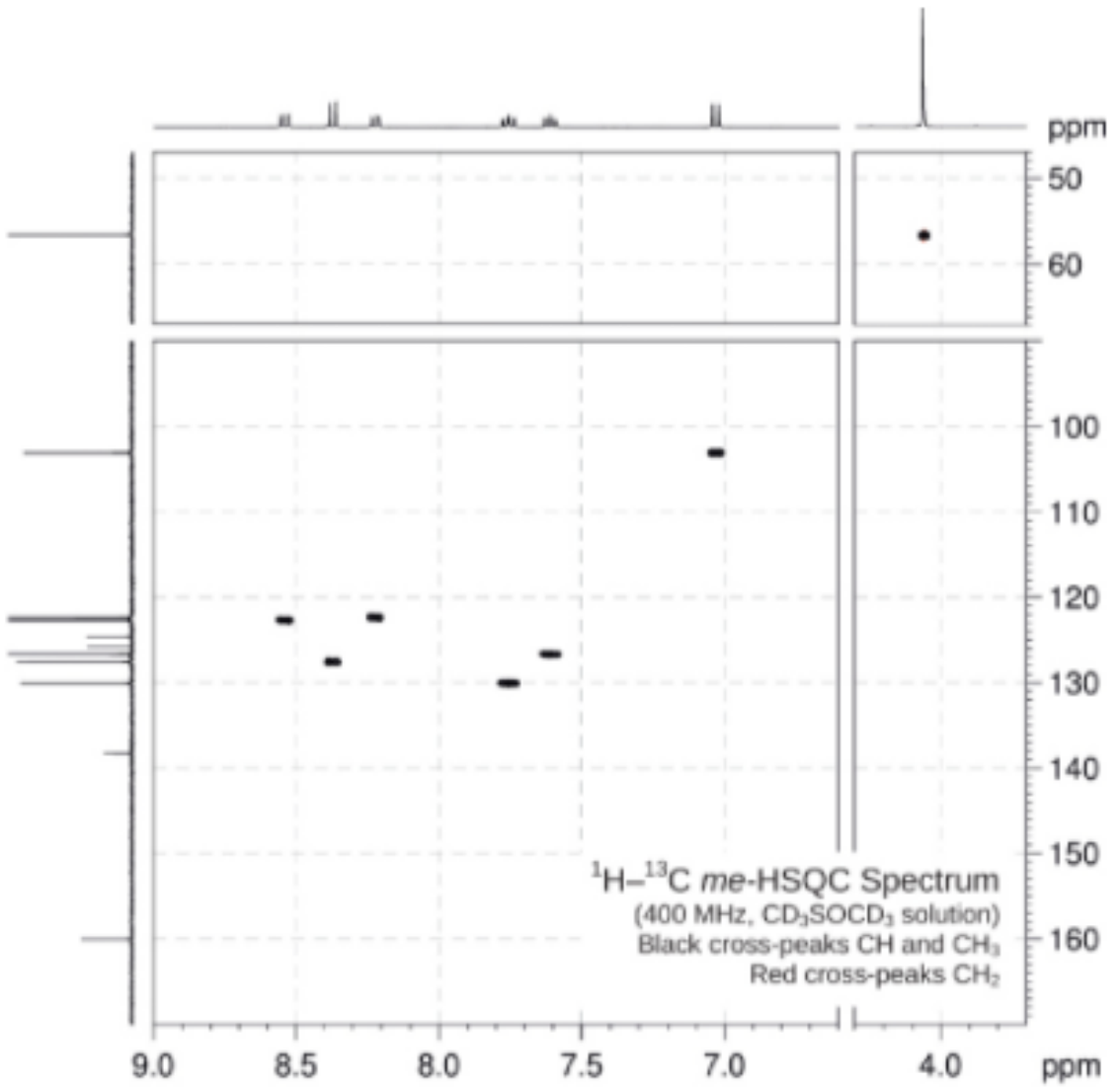

IR Spectrum
(KBr disc)
1501
1273
4000
3000
2000
1600
1200
800
ν (cm-1)

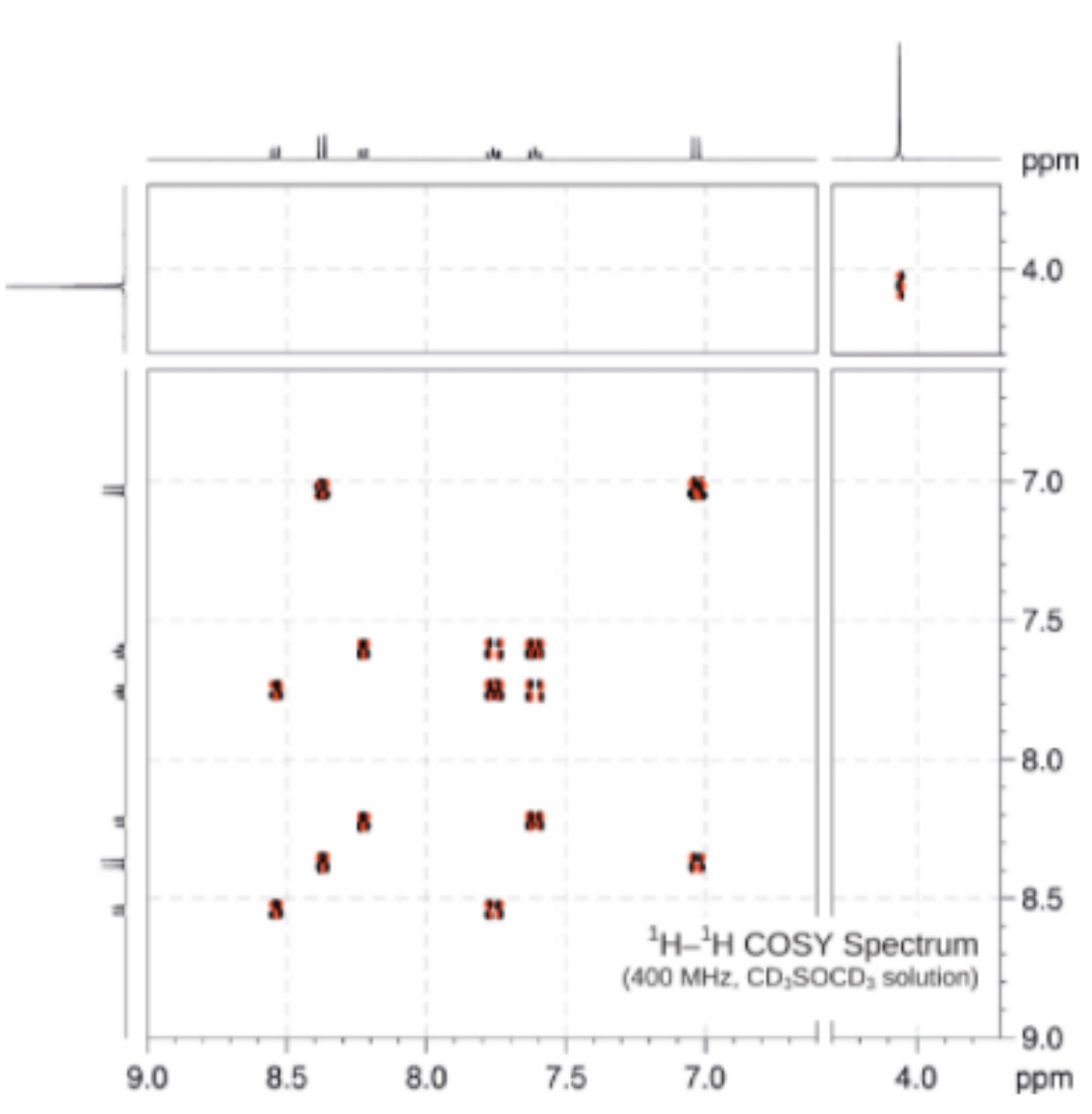

Mass Spectrum
% of base peak
M+·
203
C11H9NO3
100
80
60
40
20
40
80
120
160
200
240
280
m/e


absorbance
UV spectrum
0.224 mg / 10 ml
path length : 0.5 cm
solvent : ethanol
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)

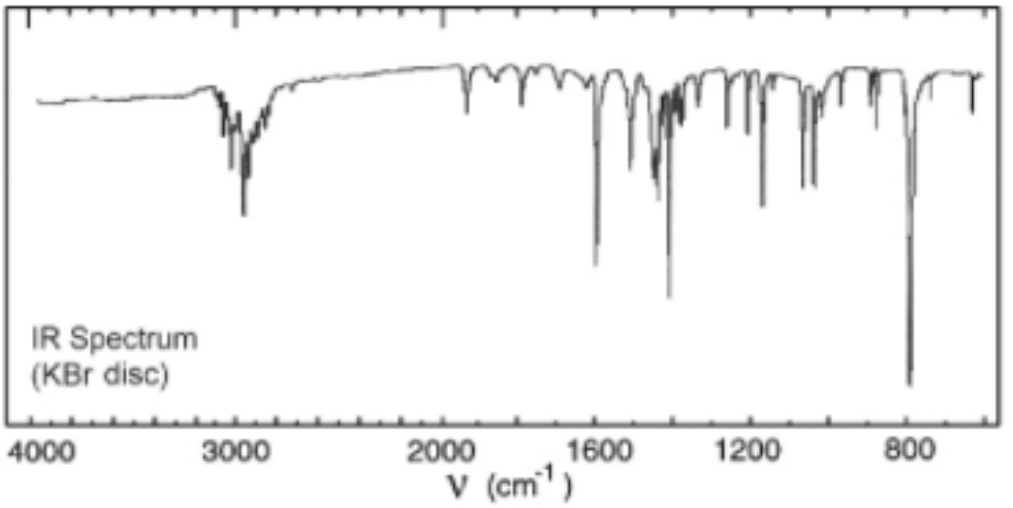

13C NMR Spectrum
(100 MHz, CD3SOCD3 solution)
expansion
130
128
126
124
122
DEPT CH2 CH3 CH
expansion
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)

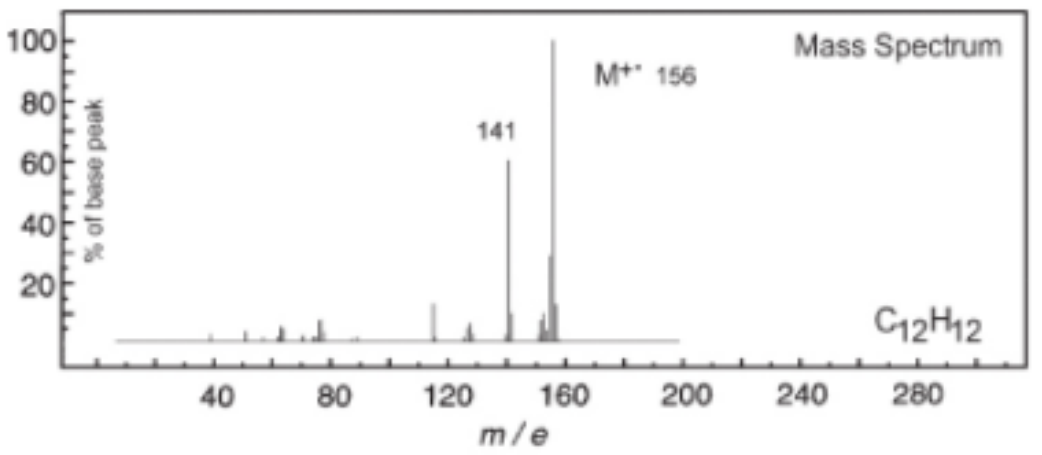

1H NMR Spectrum
(400 MHz, CD3SOCD3 solution)
expansions
8.5
8.4
8.3
8.2
7.8
7.7
7.6
7.1
7.0
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
50
60
100
110
120
130
140
150
160
9.0
8.5
8.0
7.5
7.0
4.0
ppm
^{1}H–^{13}C *me*-HSQC Spectrum
(400 MHz, CD_3SOCD_3 solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2


ppm
4.0
7.0
7.5
8.0
8.5
9.0
9.0
8.5
8.0
7.5
7.0
4.0
ppm
^{1}H–^{1}H COSY Spectrum
(400 MHz, CD_3SOCD_3 solution)

Problem 289

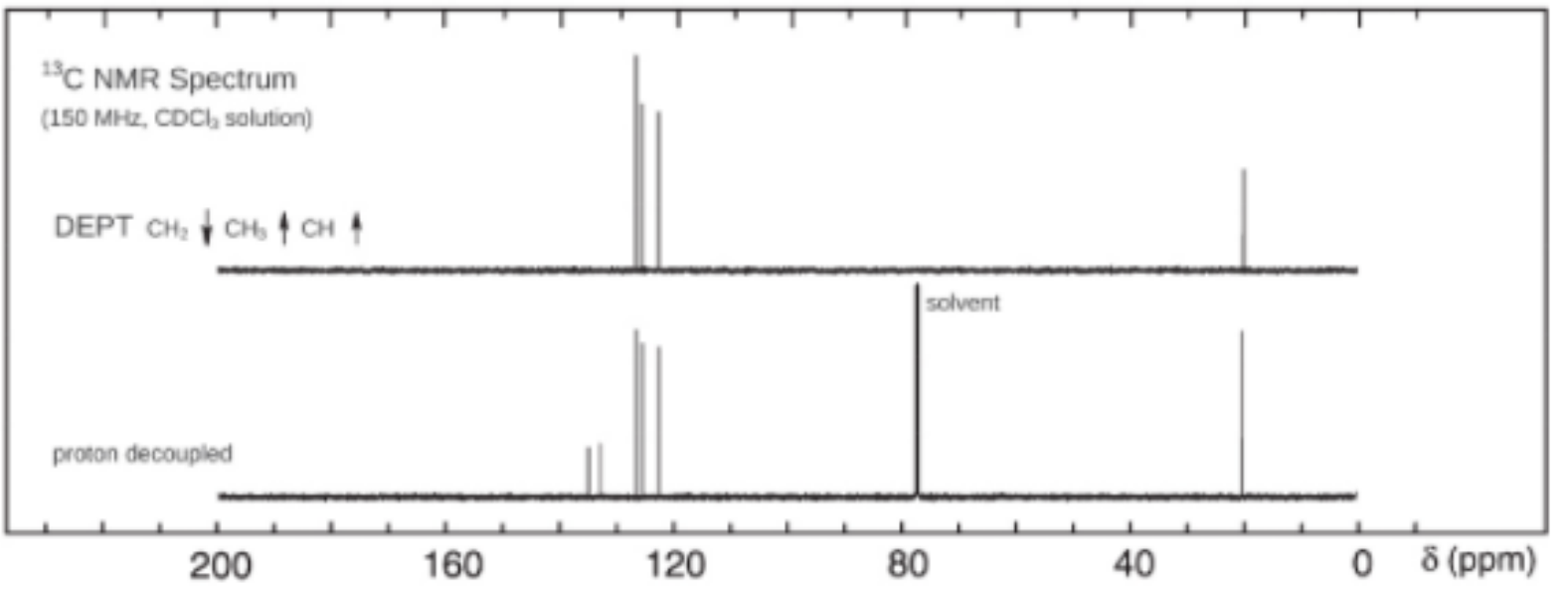


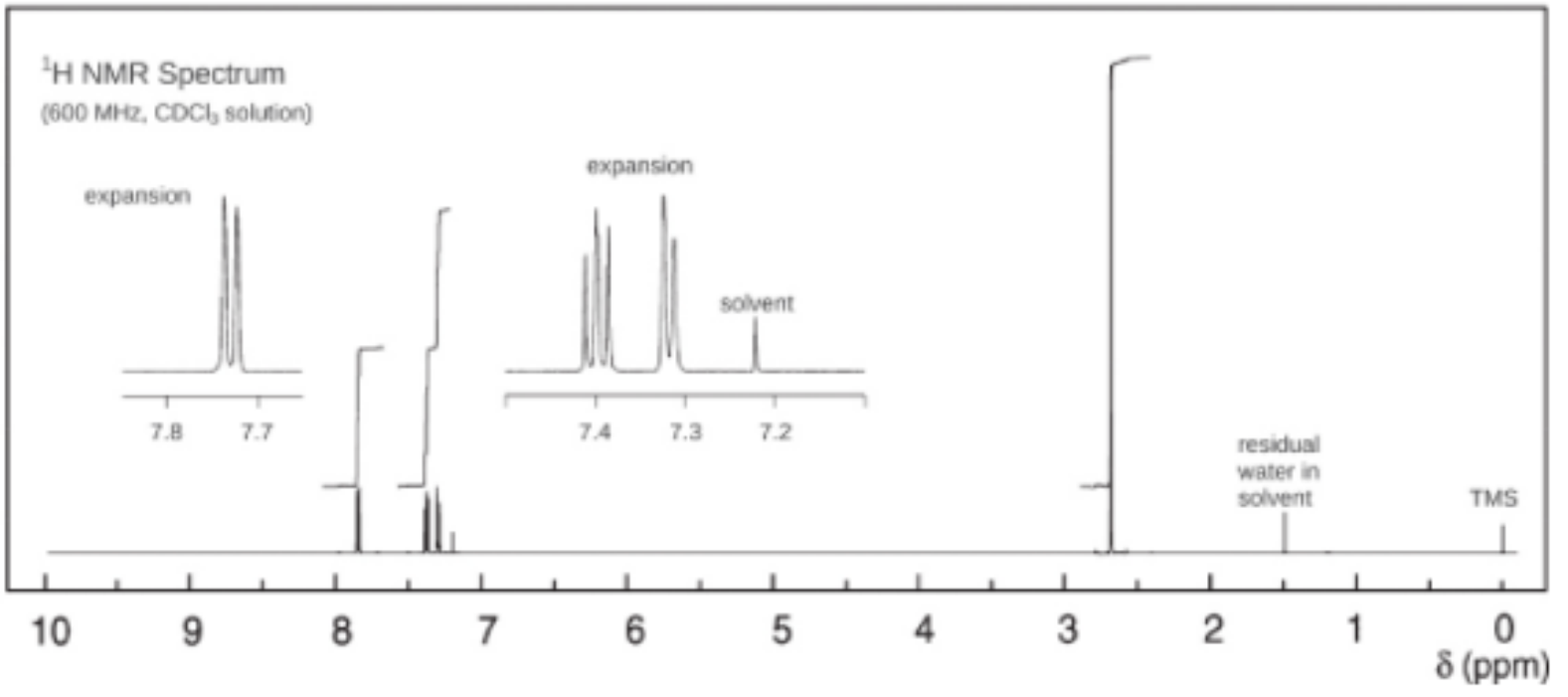


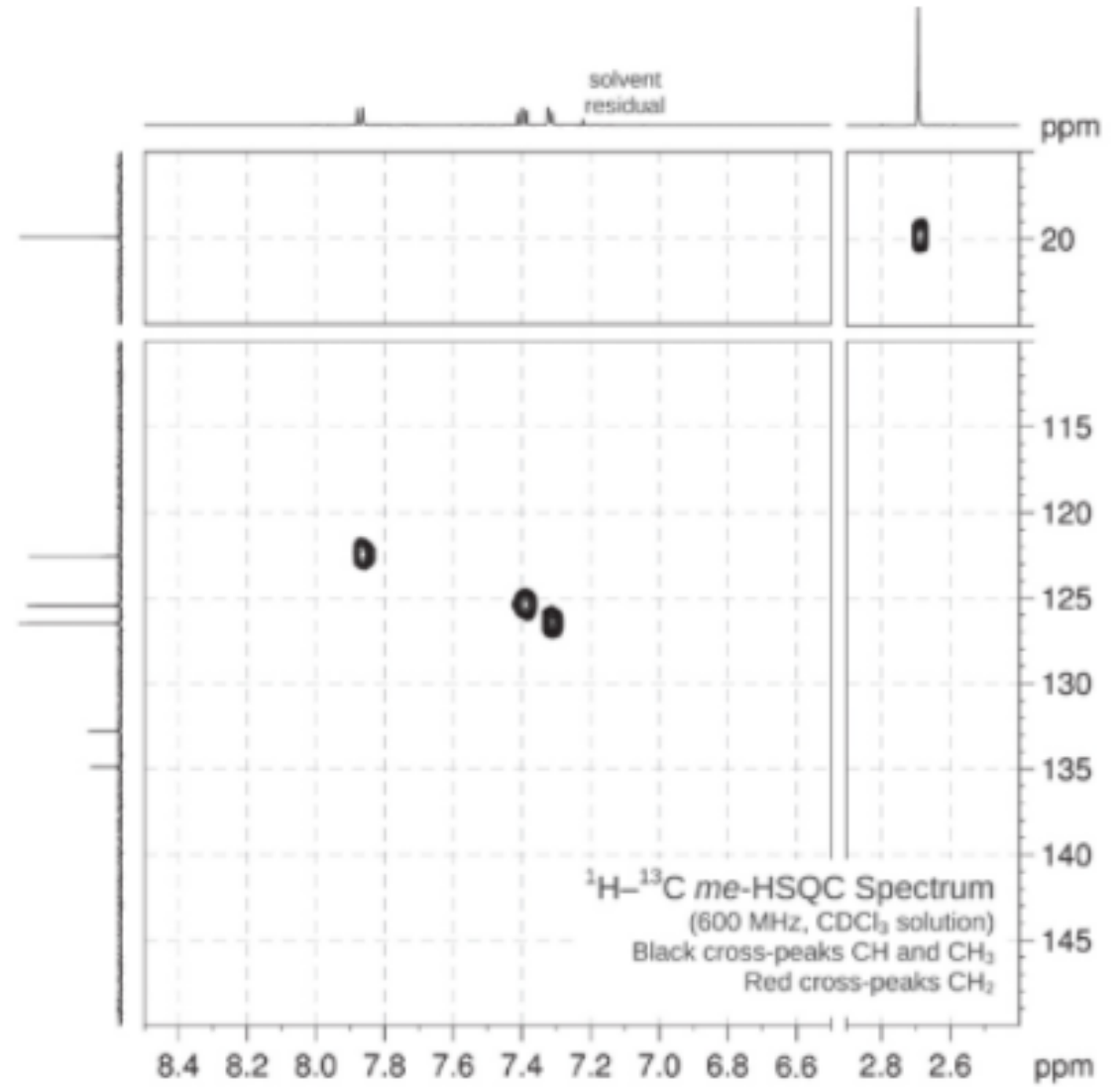
UV Spectrum

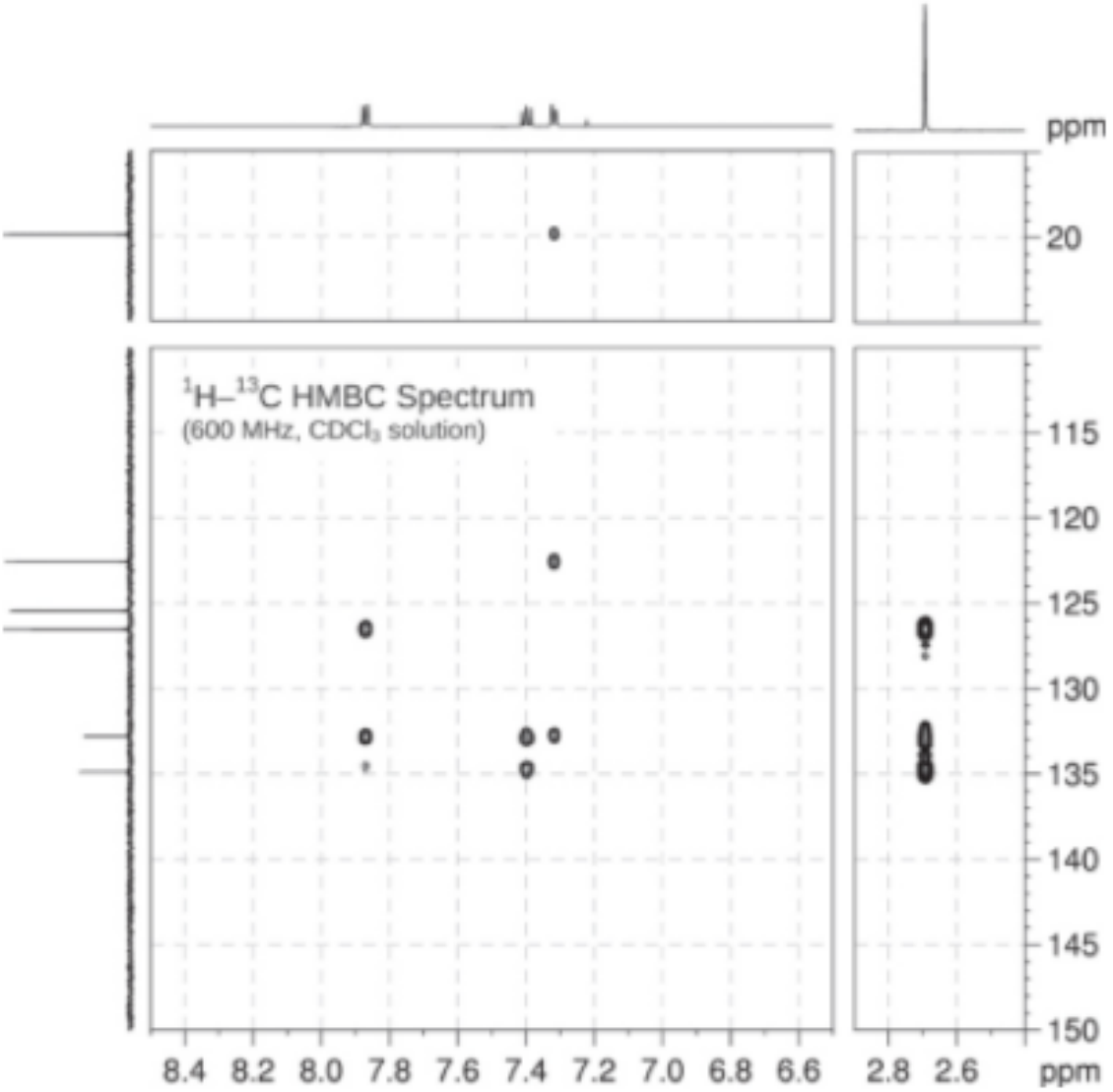
λ_{max} 225 nm ($\log_{10}\varepsilon$ 5.2)
λ_{max} 266 nm ($\log_{10}\varepsilon$ 3.6)
λ_{max} 276 nm ($\log_{10}\varepsilon$ 3.9)
λ_{max} 285 nm ($\log_{10}\varepsilon$ 4.0)
λ_{max} 297 nm ($\log_{10}\varepsilon$ 3.8)

solvent : methanol

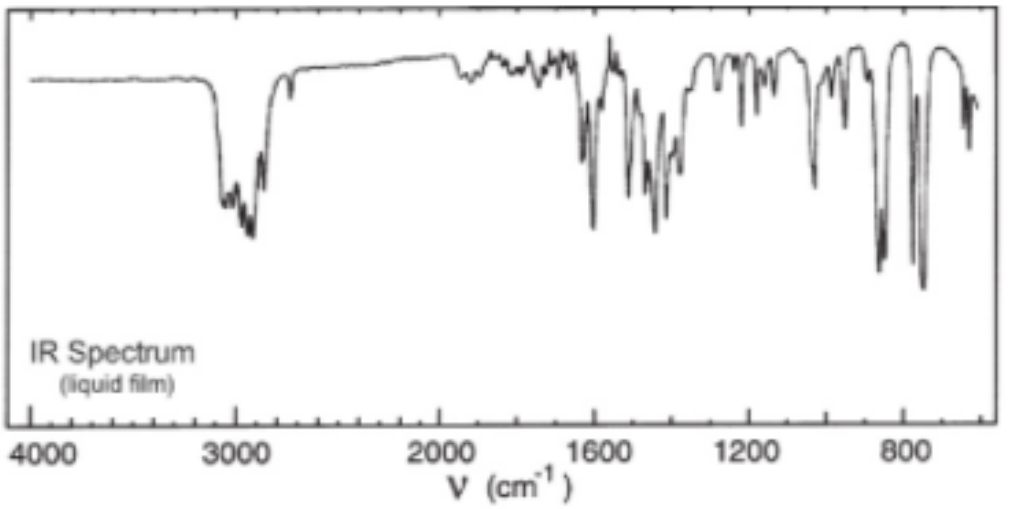


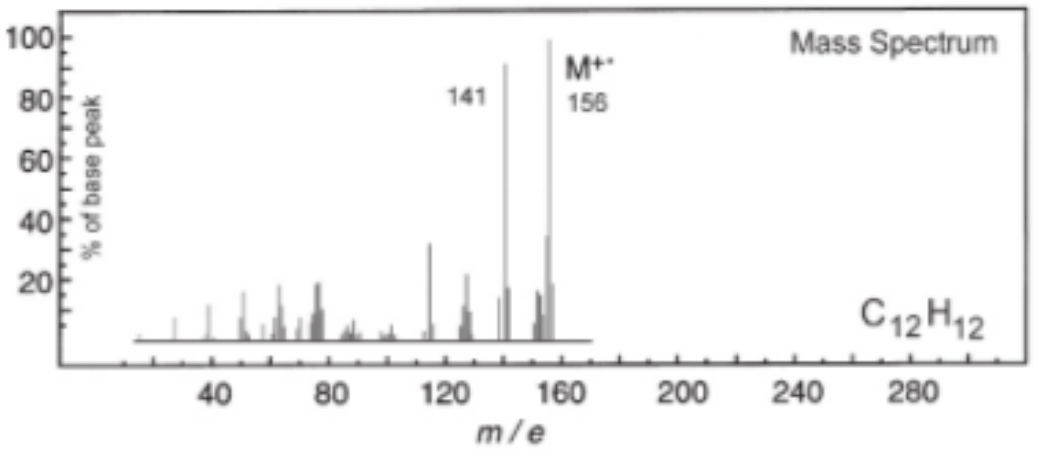



solvent
residual
ppm
20
115
120
125
130
135
140
145
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
2.8 2.6
ppm


ppm
20
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)
115
120
125
130
135
140
145
150
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
2.8 2.6
ppm

Problem 290



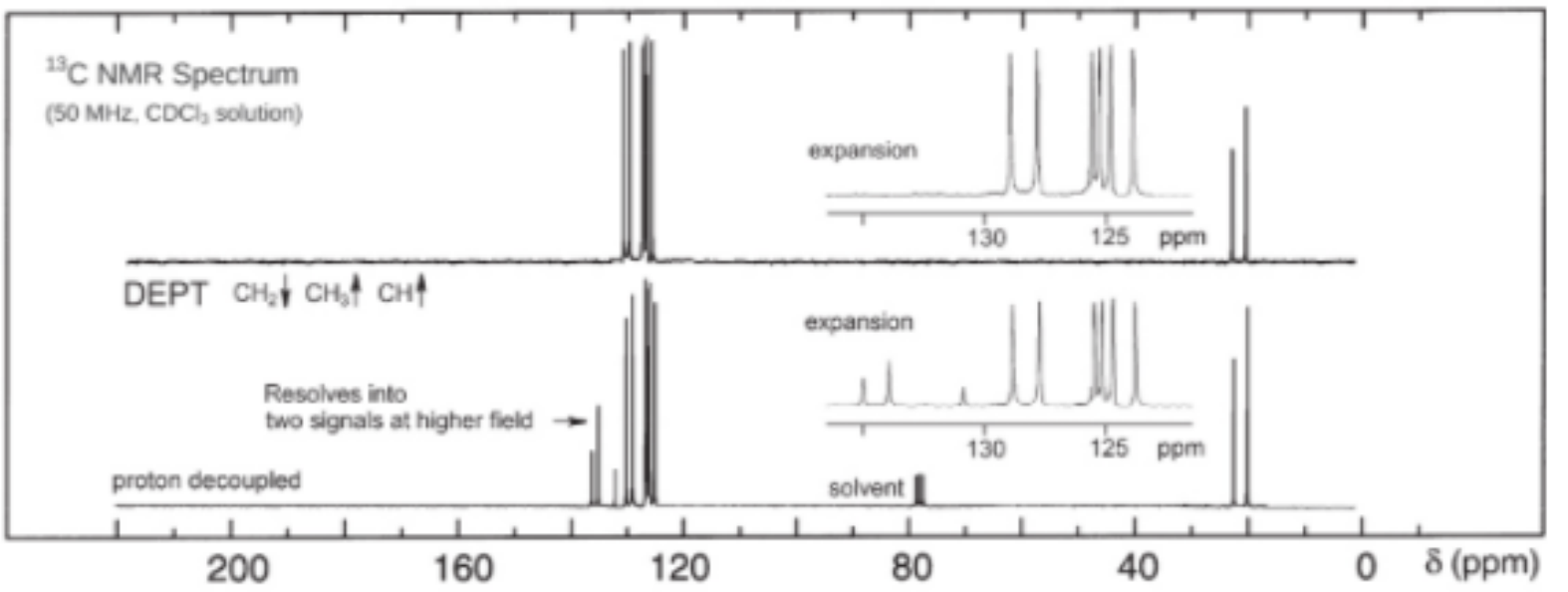


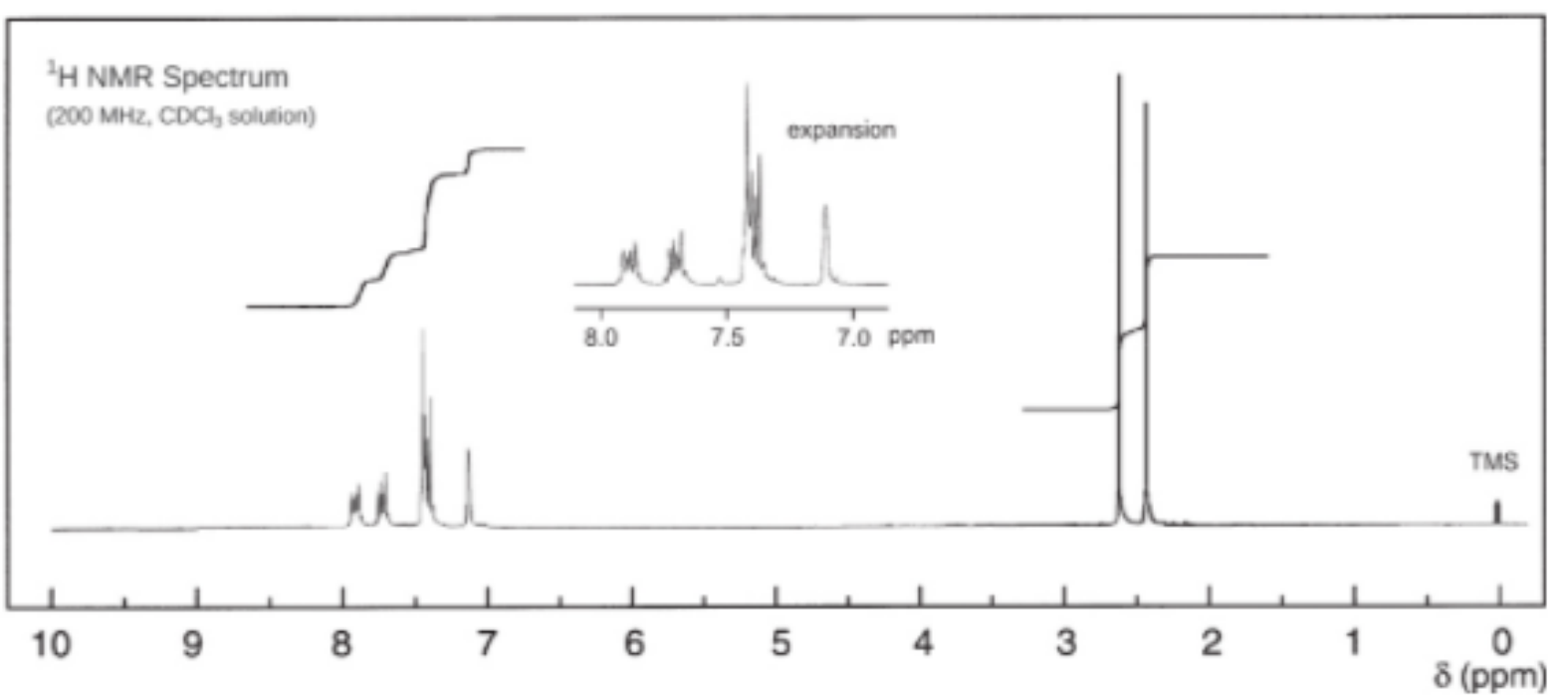
UV Spectrum

λ_{max} 321 nm ($\log_{10}\varepsilon$ 2.6)

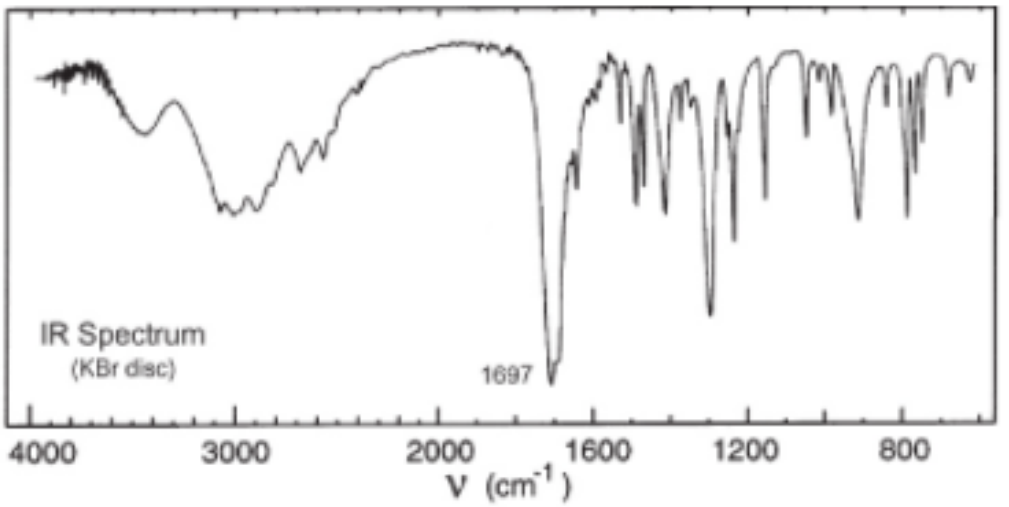
λ_{max} 281 nm ($\log_{10}\varepsilon$ 3.7)

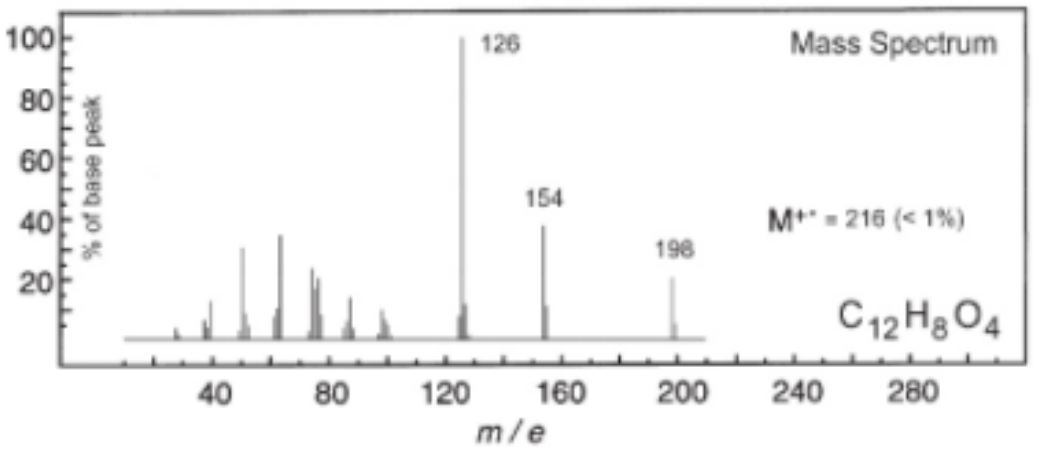
solvent : ethanol





Problem 291

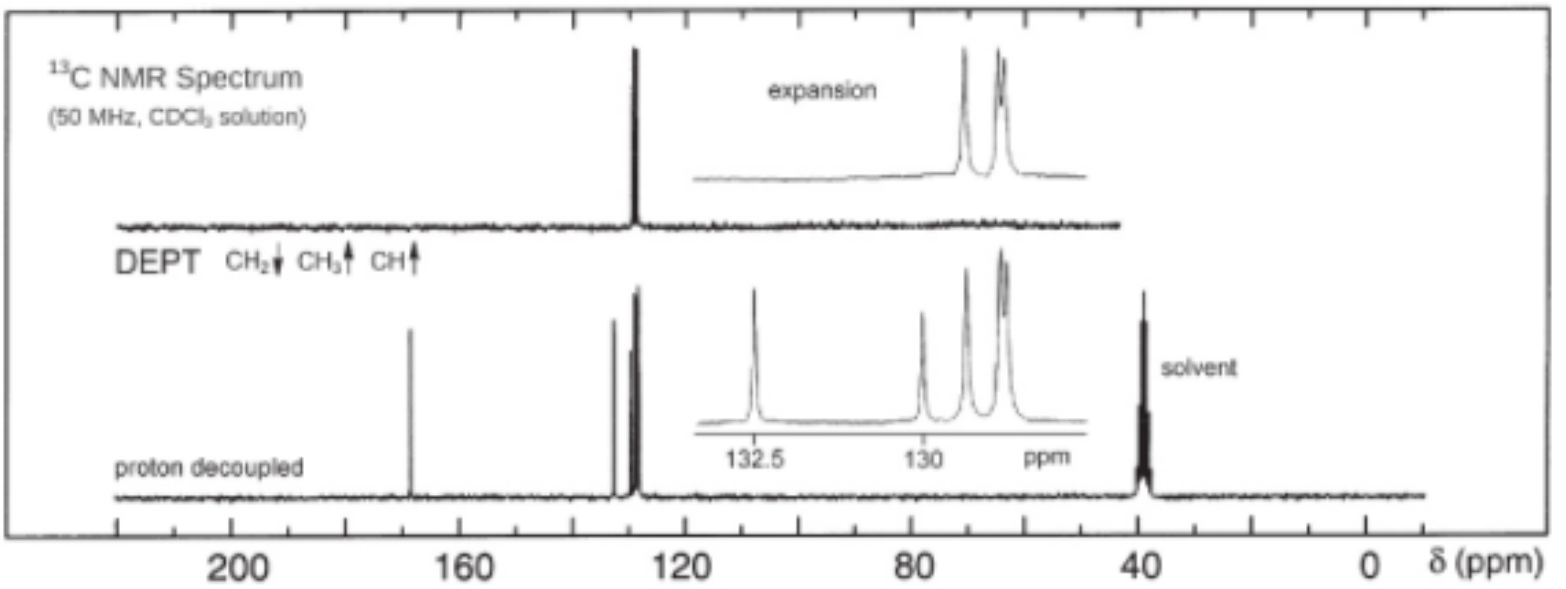


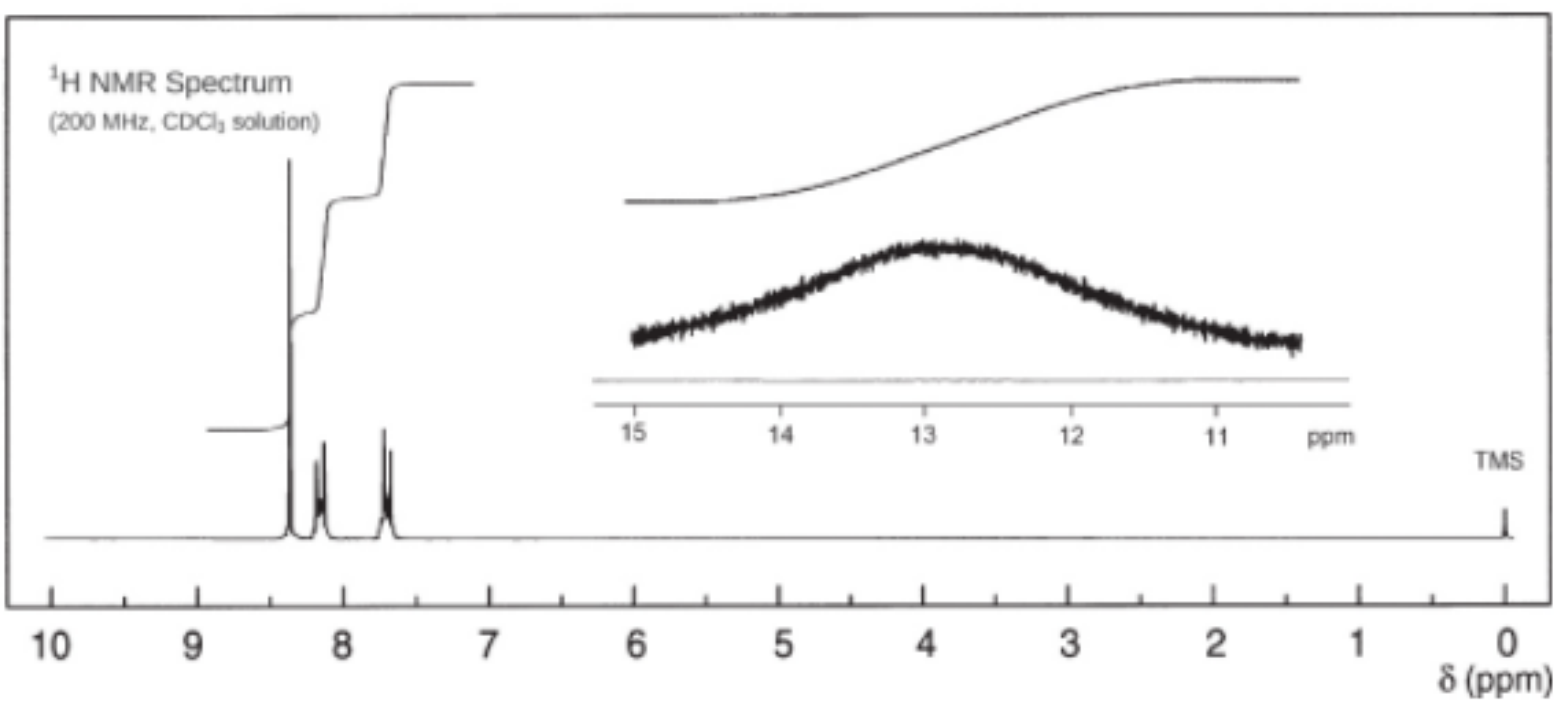


UV Spectrum

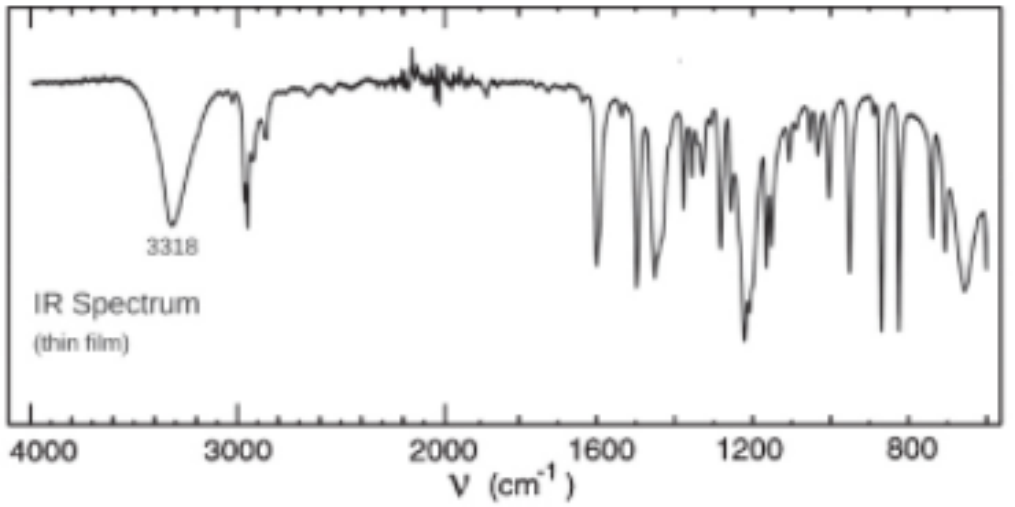
λ_{max} 334 nm ($\log_{10}\varepsilon$ 3.2)
λ_{max} 279 nm ($\log_{10}\varepsilon$ 3.7)
λ_{max} 270 nm ($\log_{10}\varepsilon$ 3.7)
λ_{max} 236 nm ($\log_{10}\varepsilon$ 4.8)

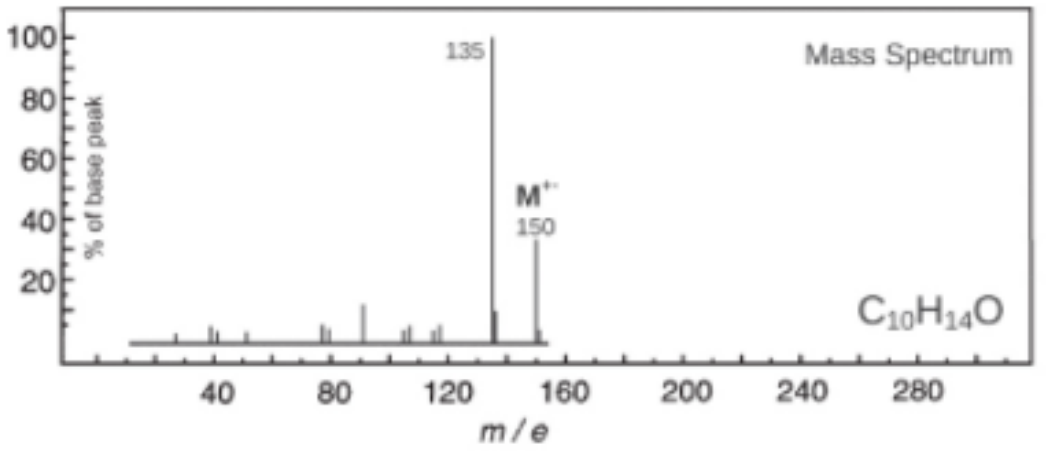
solvent : methanol

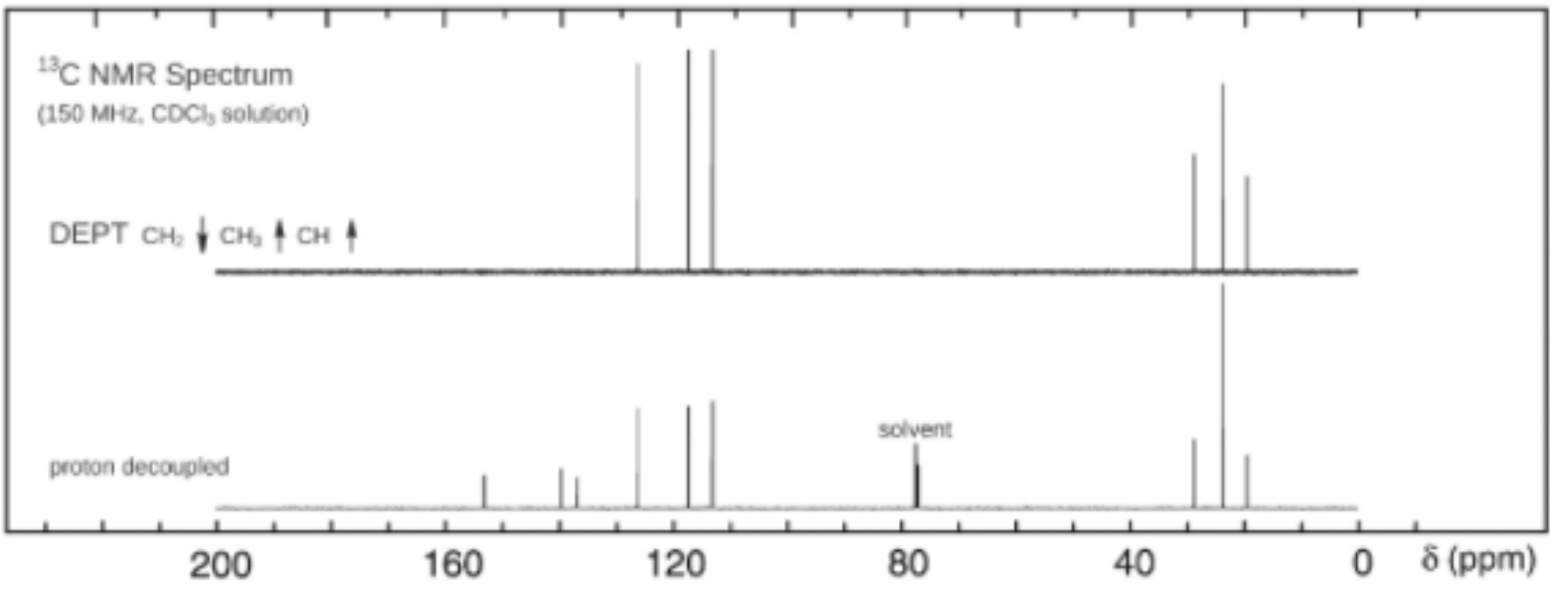


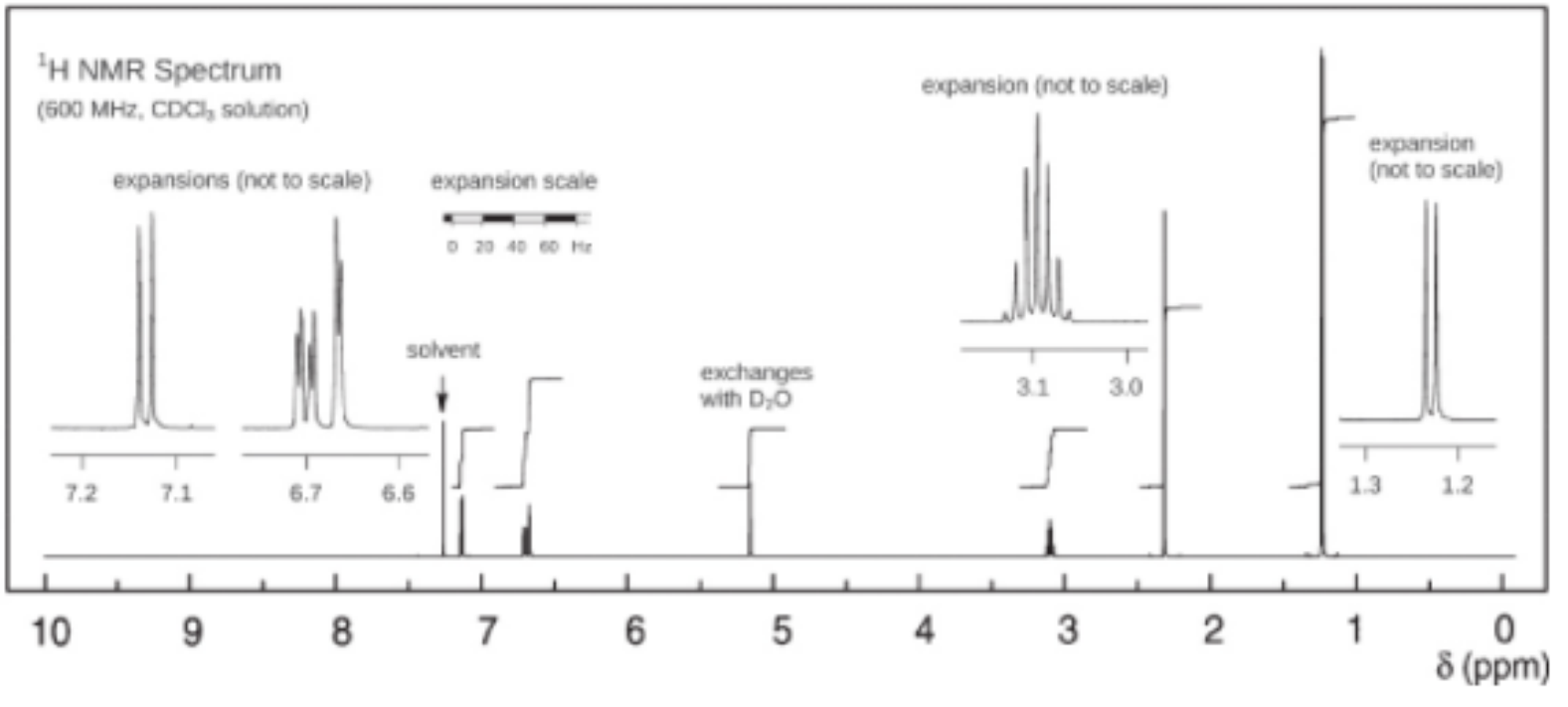


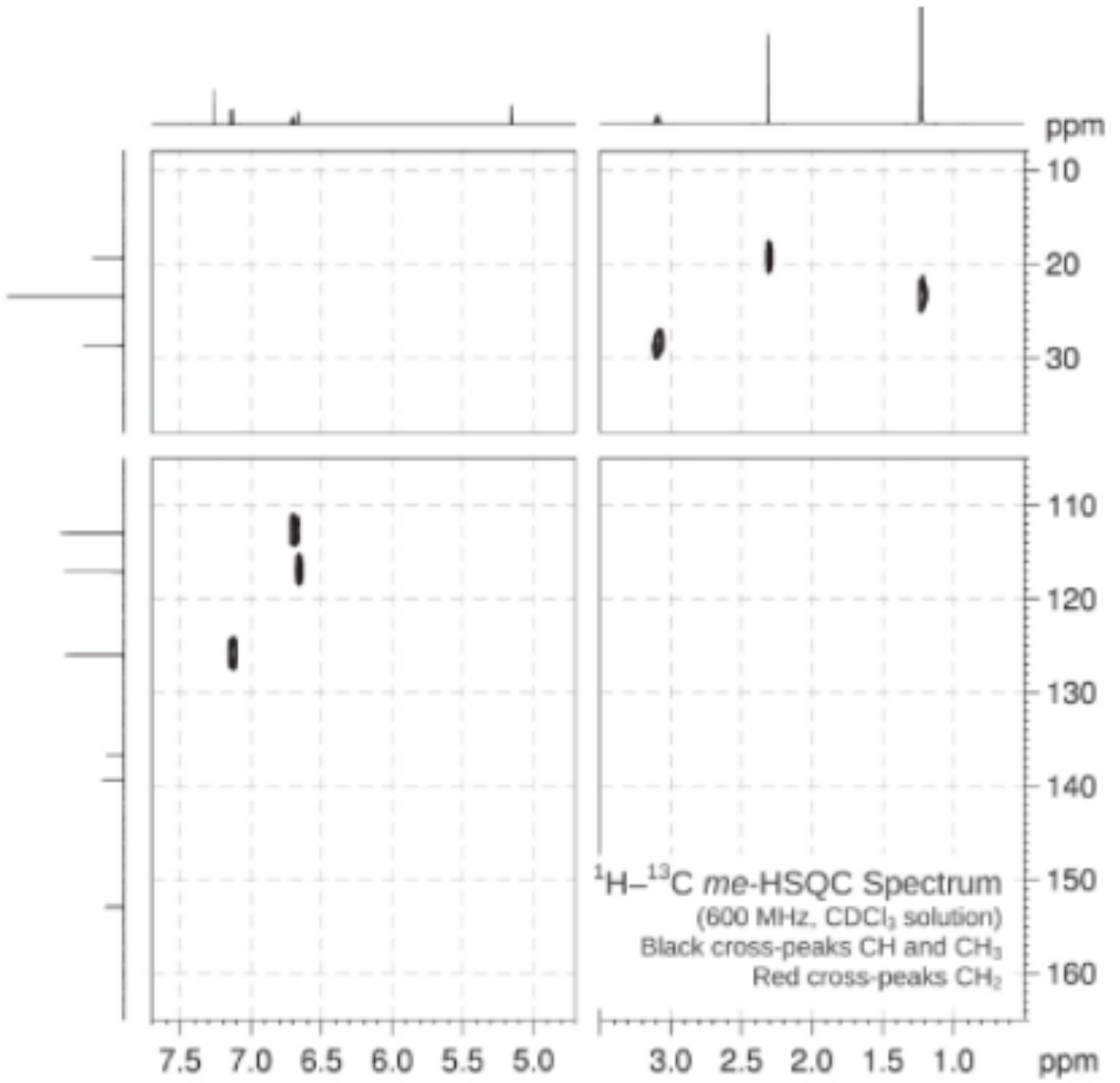
Problem 292


3318
IR Spectrum
(thin film)
4000
3000
2000
1600
1200
800
ν (cm-1)


100
80
60
40
20
% of base peak
135
M+·
150
Mass Spectrum
C10H14O
40
80
120
160
200
240
280
m/e

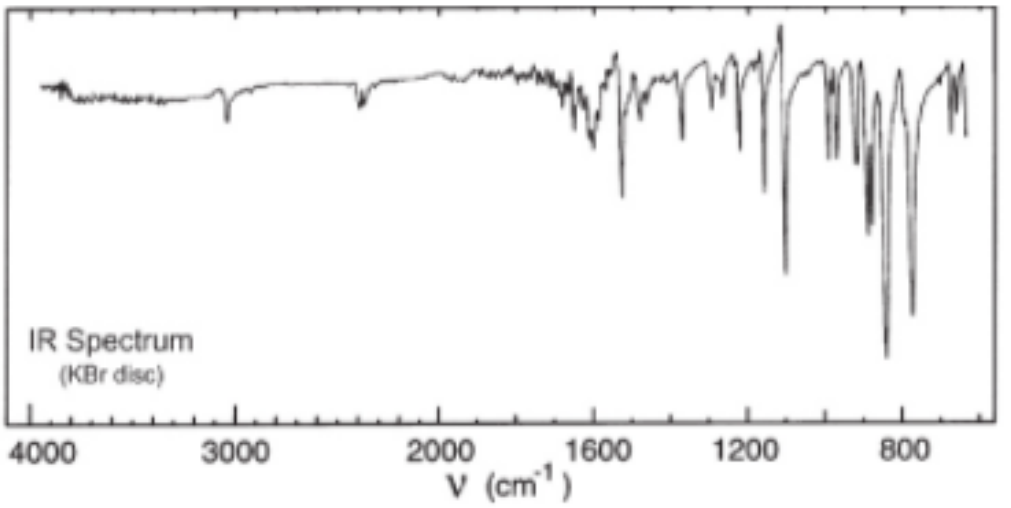

13C NMR Spectrum
(150 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

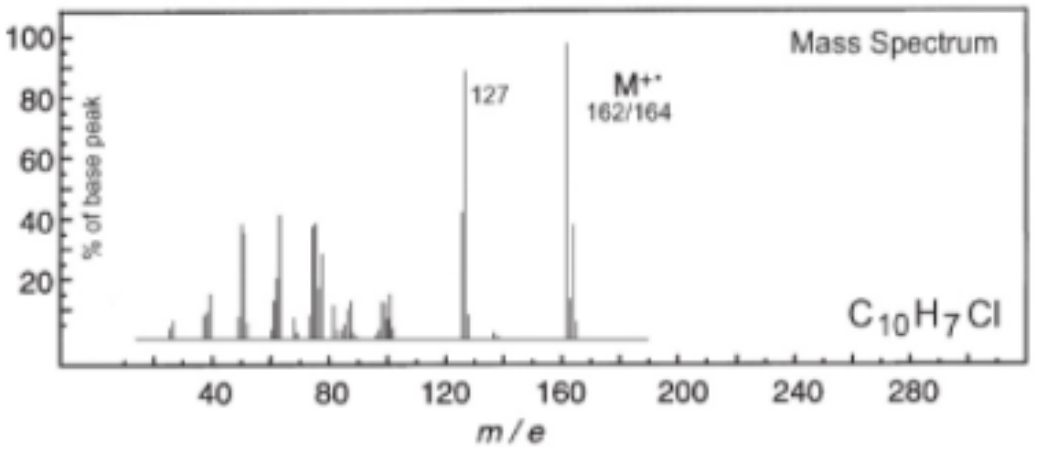

1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansions (not to scale)
expansion scale
0 20 40 60 Hz
solvent
exchanges with D2O
expansion (not to scale)
3.1
3.0
expansion (not to scale)
1.3
1.2
7.2
7.1
6.7
6.6
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)


ppm
10
20
30
110
120
130
140
150
160
^{1}H–^{13}C *me*-HSQC Spectrum
(600 MHz, $CDCl_3$ solution)
Black cross-peaks CH and CH_3
Red cross-peaks CH_2
7.5 7.0 6.5 6.0 5.5 5.0
3.0 2.5 2.0 1.5 1.0
ppm

ppm
10
20
30
110
120
130
140
150
160
^{1}H–^{13}C HMBC Spectrum
(600 MHz, $CDCl_3$ solution)
7.5 7.0 6.5 6.0 5.5 5.0
3.0 2.5 2.0 1.5 1.0
ppm

Problem 293





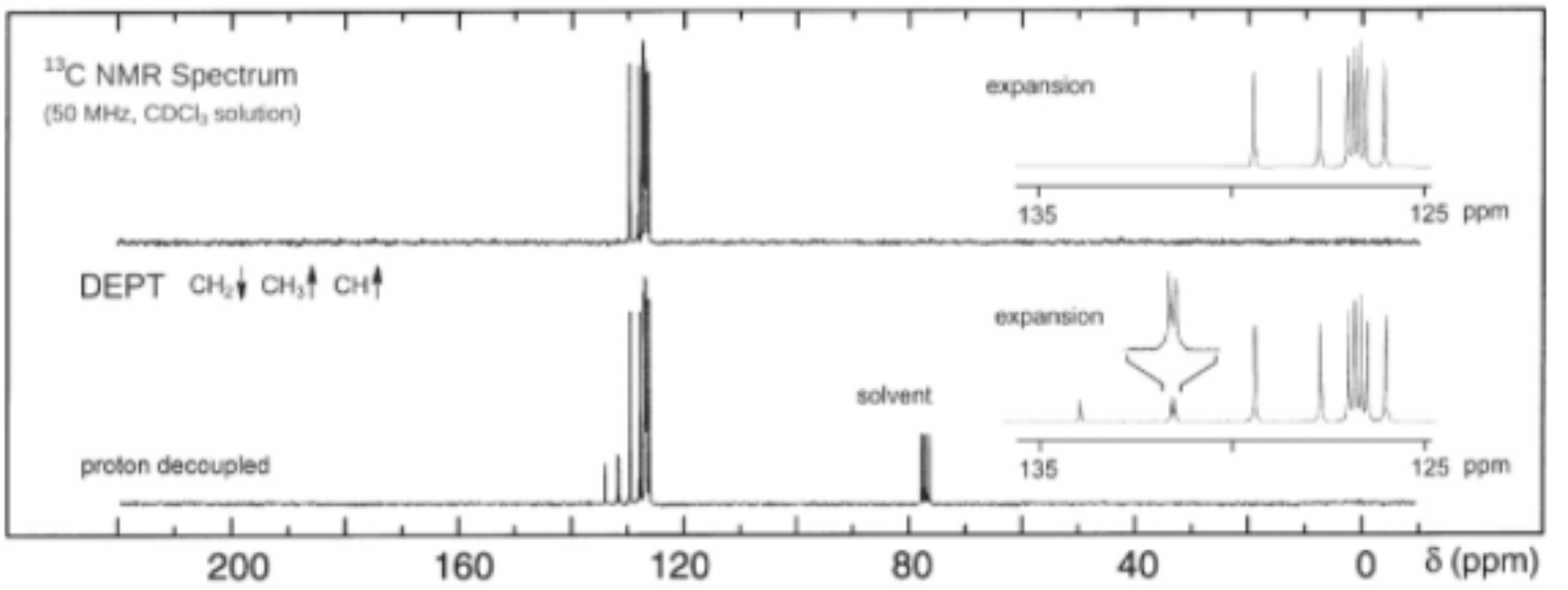
UV Spectrum

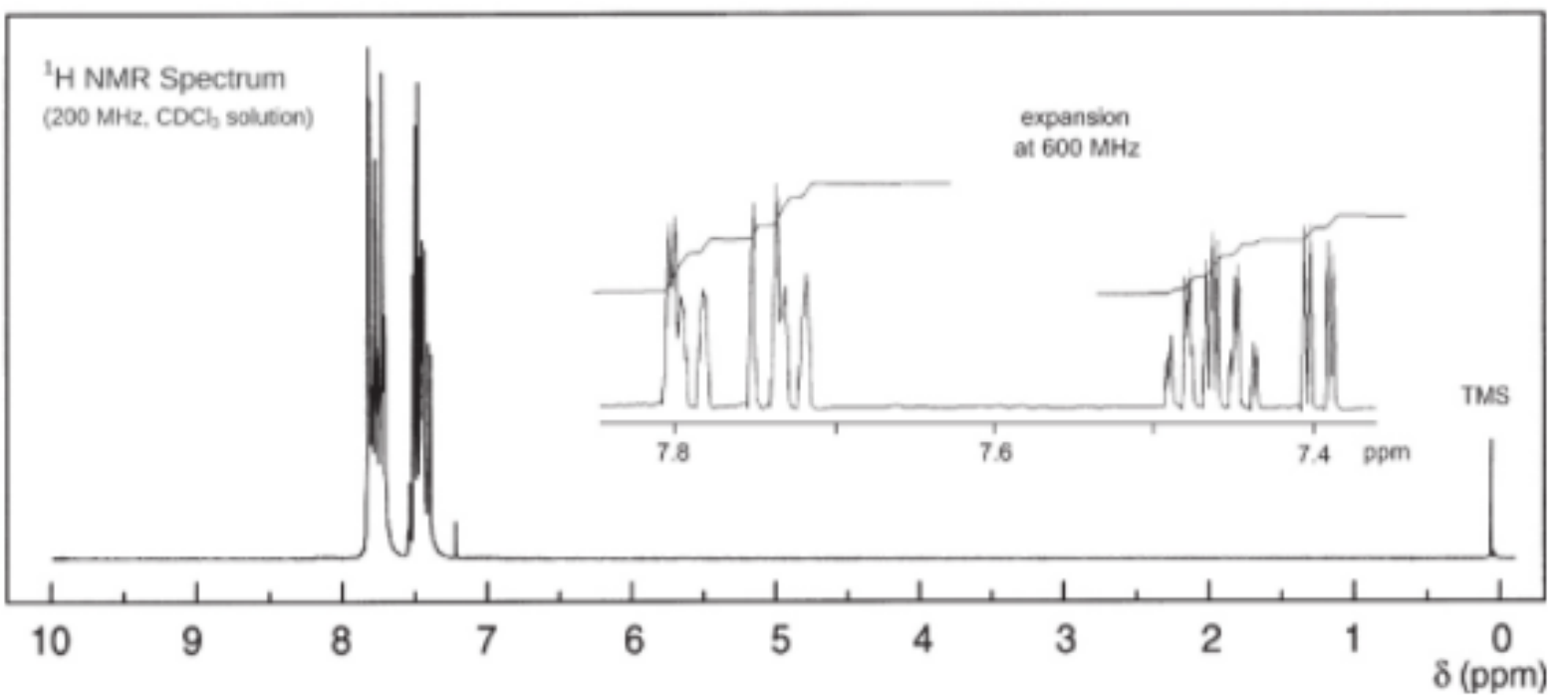
λ_{max} 311 nm ($\log_{10}\varepsilon$ 2.6)

λ_{max} 289 nm ($\log_{10}\varepsilon$ 3.7)

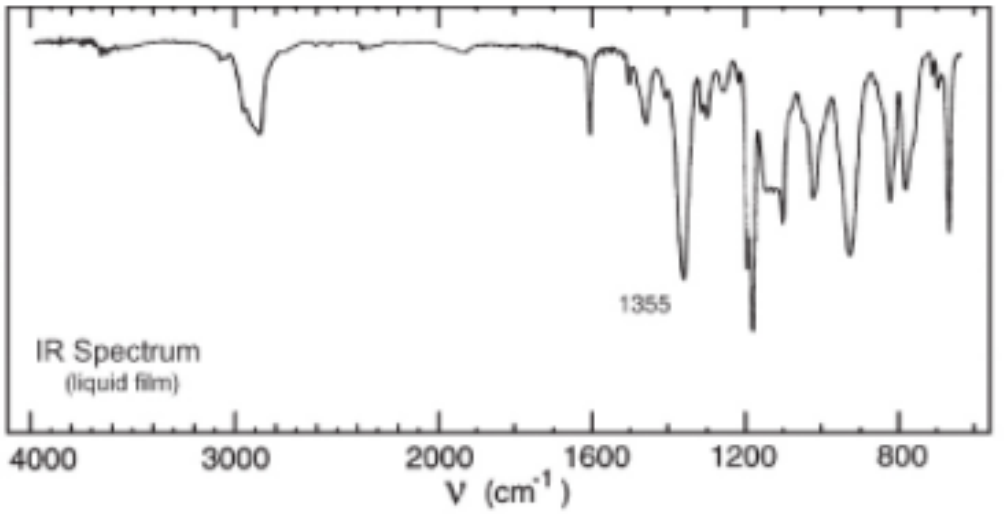
λ_{max} 225 nm ($\log_{10}\varepsilon$ 5.0)

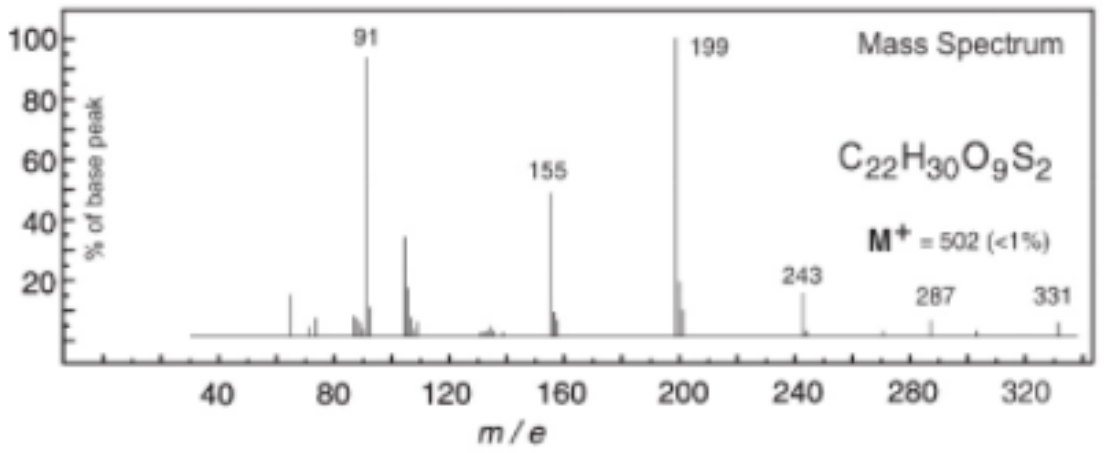
solvent : methanol





Problem 294





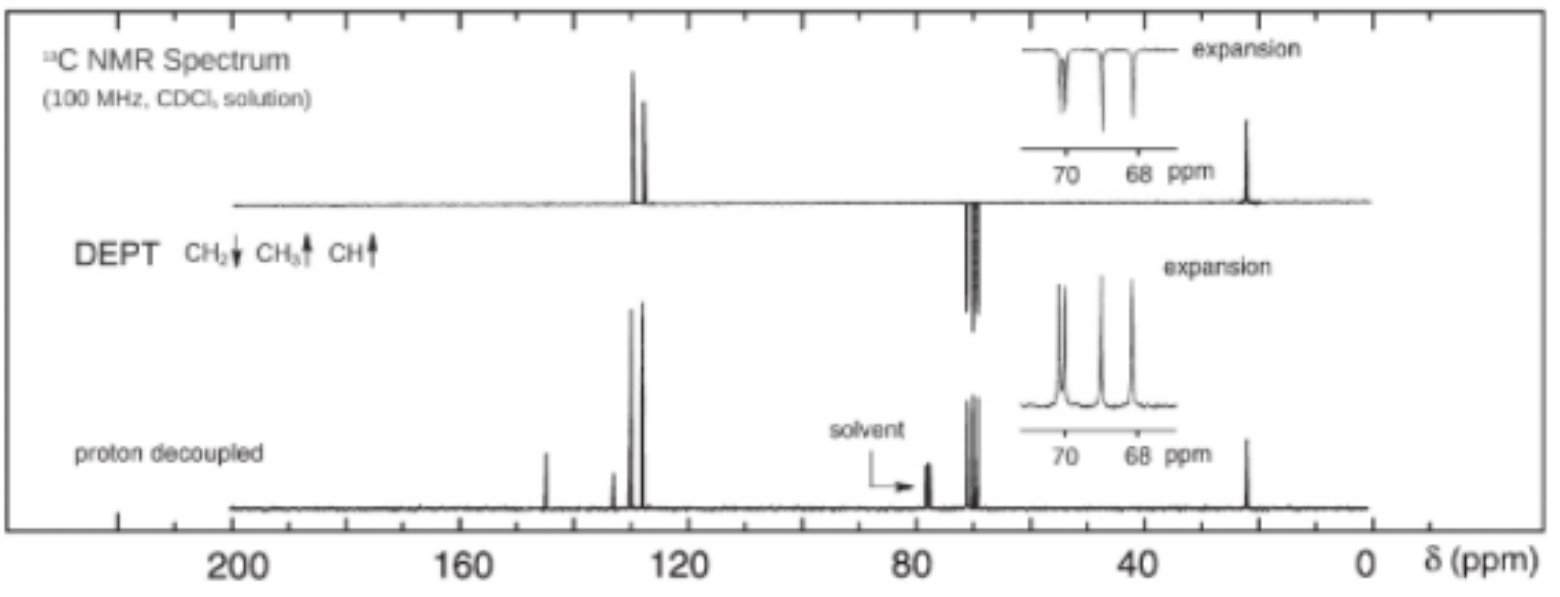
UV Spectrum

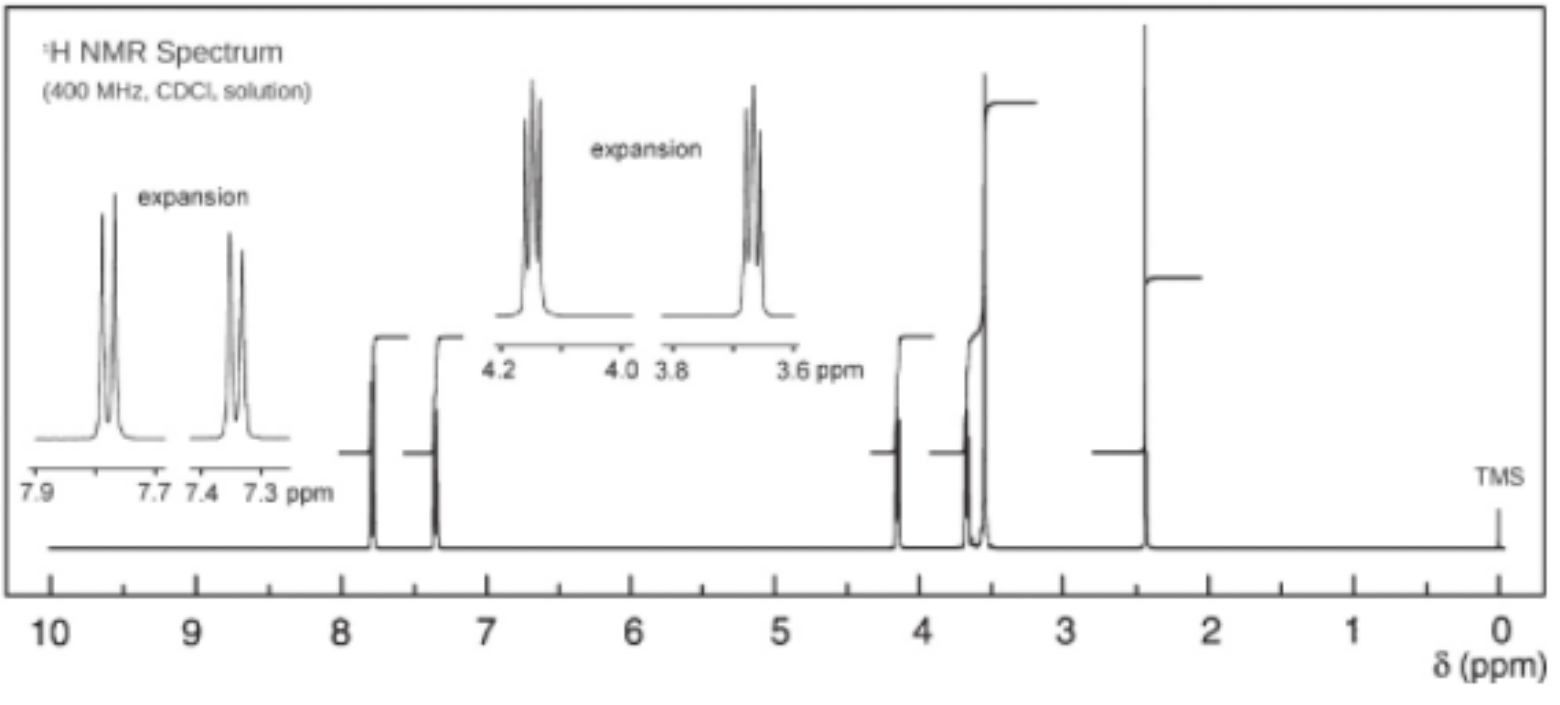
λ_{max} 225 nm ($\log_{10}\varepsilon$ 4.6)

λ_{max} 260 nm ($\log_{10}\varepsilon$ 3.3)

λ_{max} 272 nm ($\log_{10}\varepsilon$ 3.1)

solvent : methanol





Problem 295

An organic compound has the molecular formula $C_{10}H_{14}$. Identify the compound using the spectroscopic data given below.

ν_{max} (liquid film): no significant features in the infrared spectrum. λ_{max}: 265 (log ε: 2.3) nm. ^{1}H NMR ($CDCl_3$ solution): δ 7.1, m, 5H; 2.5, apparent sextet, *J* 7 Hz, 1H; 1.6, apparent quintet, *J* 7 Hz, 2H; 1.22, d, *J* 7 Hz, 3H; 0.81, t, *J* 7 Hz, 3H ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$ solution): δ 148.4 (C), 129.3, 127.9, 126.1, 42.3 (CH), 31.7 (CH_2), 22.2, 12.2 (CH_3) ppm. Mass spectrum: *m/e* 134 ($M^{+\cdot}$, 20), 119(8), 105(100), 77(10).

Problem 296

An organic compound has the molecular formula $C_{12}H_{17}NO$. Identify the compound using the spectroscopic data given below.

ν_{max} (KBr disc): 3296m, 1642s cm^{-1}. ^{1}H NMR ($CDCl_3$ solution): δ 7.23–7.42, m, 5H; 5.74, br s, exch. D_2O, 1H; 5.14, q, *J* 6.7 Hz, 1H; 2.15, t, *J* 7.1 Hz, 2H; 1.66, m, 2H; 1.48, d, *J* 6.7 Hz, 3H; 0.93, t, *J* 7.3 Hz, 3H ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$ solution): δ 172.0 (C), 143.3 (C), 128.6, 127.3, 126.1, 48.5 (CH), 38.8 (CH_2), 21.7 (CH_3), 19.1 (CH_2), 13.7 (CH_3) ppm. Mass spectrum: *m/e* 191($M^{+\cdot}$, 40), 120(33), 105(58), 104(100), 77(18), 43(46).

Problem 297

An organic compound has the molecular formula $C_{16}H_{30}O_4$. Identify the compound using the spectroscopic data given below.

ν_{max} ($CHCl_3$ solution): 1733 cm^{-1}. ^{1}H NMR ($CDCl_3$ solution): δ 4.19, q, *J* 7.2 Hz, 4H; 3.35, s, 1H; 1.20, t, *J* 7.2 Hz, 6H; 1.25–1.29, m, 10H; 1.10, s, 6H; 0.88, t, *J* 6.8 Hz, 3H ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$ solution): δ 168.5 (C), 60.8 (CH_2), 59.6 (CH), 41.1 (CH_2), 36.3 (C), 31.8 (CH_2), 29.9 (CH_2), 25.1 (CH_3), 23.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3), 14.0 (CH_3) ppm. Mass spectrum: *m/e* 286 ($M^{+\cdot}$, 70), 241(25), 201(38), 160(100), 115(53).

Problem 298

An organic compound has the molecular formula $C_8H_{13}NO_3$. Identify the compound using the spectroscopic data given below.

ν_{max} (nujol mull): 1690–1725s cm^{-1}. λ_{max}: no significant features in the ultraviolet spectrum. ^{1}H NMR ($CDCl_3$ solution): δ 4.25, q, *J* 6.7 Hz, 2H; 3.8, t, *J* 7 Hz, 4H; 2.45, t, *J* 7 Hz, 4H; 1.3, t, *J* 6.7 Hz, 3H ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$ solution): δ 207 (C); 155 (C); 62 (CH_2); 43 (CH_2); 41 (CH_2); 15 (CH_3) ppm. Mass spectrum: *m/e* 171 ($M^{+\cdot}$,15), 142(25), 56(68), 42(100).

Problem 299

An organic compound has the molecular formula $C_{12}H_{13}NO_3$. Identify the compound using the spectroscopic data given below.

ν_{max} (nujol mull): 3338, 1715, 1592 cm^{-1}. λ_{max}: 254 (log ε: 4.3) nm. ^{1}H NMR (DMSO–d_6 solution): δ 12.7, broad s, exch. D_2O, 1H; 8.42, d, *J* 6.1 Hz, 1H; 7.45–7.25, m, 5H; 6.63 dd, *J* 15.9, 1.2 Hz, 1H; 6.30, dd, *J* 15.9, 6.7 Hz, 1H; 4.93 ddd, *J* 6.7, 6.1, 1.2 Hz, 1H; 1.90, s, 3H ppm. $^{13}C\{^{1}H\}$ NMR (DMSO–d_6 solution): δ 171.9 (C), 169.0 (C), 135.9

(C), 131.7 (CH), 128.7 (CH), 127.9 (CH), 126.3 (CH), 124.6 (CH), 54.4 (CH), 22.3 (CH_3) ppm. Mass spectrum: *m/e* 219 ($M^{+\cdot}$, 25), 175(10), 132(100), 131(94), 103(35), 77(46), 43(83).

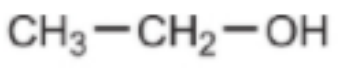
Problem 300

An organic compound has the molecular formula $C_{13}H_{16}O_4$. Identify the compound using the spectroscopic data given below.

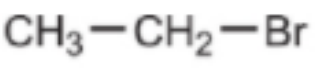
ν_{max} (KBr disc): 3479s, 1670s cm^{-1}. λ_{max}: 250 (log ε: 4) nm. ^1H NMR ($CDCl_3$ solution): 1.40, s, 3H; 2.00, bs exch., 1H; 2.71, d, *J* 15.7 Hz, 1H; 2.77, d, *J* 15.7 Hz, 1H; 2.91, d, *J* 17.8 Hz, 1H; 3.14, d, *J* 17.8 Hz, 1H; 3.79, s, 3H; 3.84, s, 3H; 6.80, d, *J* 9.0 Hz, 1H; 6.98, d, *J* 9.0 Hz, 1H ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution) : δ 196.0 (C); 154.0 (C); 157.7 (C); 131.5 (C); 122.0 (C); 116.0 (CH); 110.5 (CH); 70.8 (C); 56.3 (CH_3); 55.9 (CH_3); 54.1 (CH_2); 37.7 (CH_2); 29.2 (CH_3) ppm. Mass spectrum: *m/e* 236 ($M^{+\cdot}$, 87), 218(33), 178(100), 163(65).

Problem 301

A 400 MHz ^1H NMR spectrum of a mixture of ethanol (C^2H_6O) δ 1.24, δ 1.78, δ 3.72 and bromoethane (C^2H_5Br) δ 1.68 and δ 3.44 is given below. Estimate the relative proportions (mole %) of the 2 components from the integrals in the spectrum.

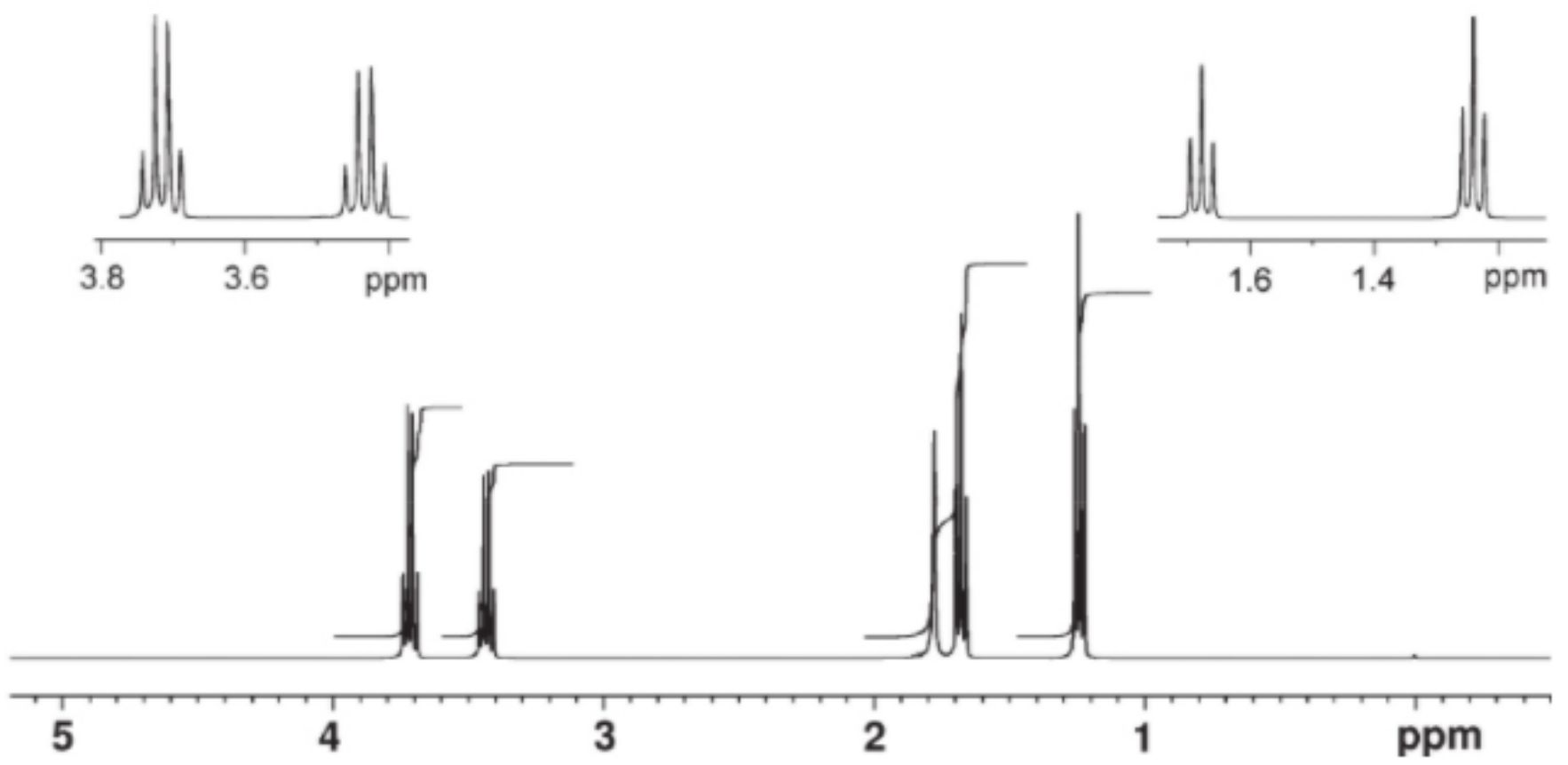


ethanol



bromoethane

^1H NMR Spectrum
(400 MHz, $CDCl_3$ solution)

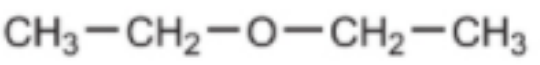


Compound	Mole %
ethanol	
bromoethane	

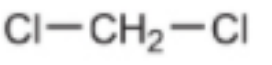
Problem 302

A 400 MHz ^{1}H NMR spectrum of a mixture of common organic solvents consisting of benzene (C_6H_6) δ 7.37; diethyl ether ($C_4H_{10}O$) δ 3.49 and δ 1.22; and dichloromethane (CH_2Cl_2) δ 5.30 is given below. Estimate the relative proportions (mole %) of the 3 components from the integrals in the spectrum.

benzene

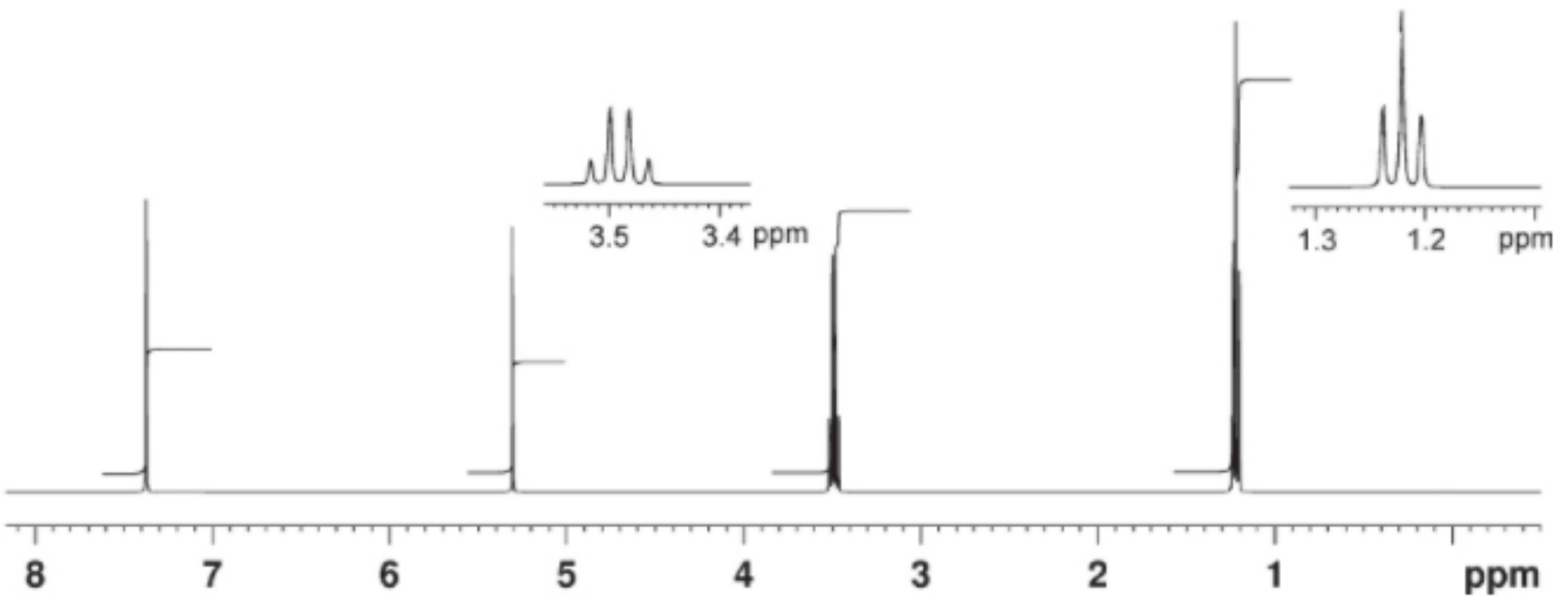


diethyl ether



dichloromethane

^{1}H NMR Spectrum
(400 MHz, $CDCl_3$ solution)

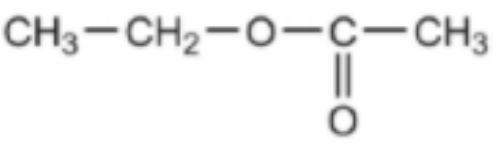


Compound	Mole %
benzene	
diethyl ether	
dichloromethane	

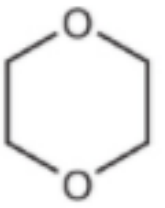
Problem 303

A 400 MHz ^{1}H NMR spectrum of a mixture of benzene (C_6H_6) δ 7.37, ethyl acetate ($C_4H_8O_2$) δ 4.13, δ 2.05, δ 1.26 and dioxane ($C_4H_8O_2$) δ 3.70 is given below. Estimate the relative proportions (mole %) of the 3 components from the integrals in the spectrum.

benzene

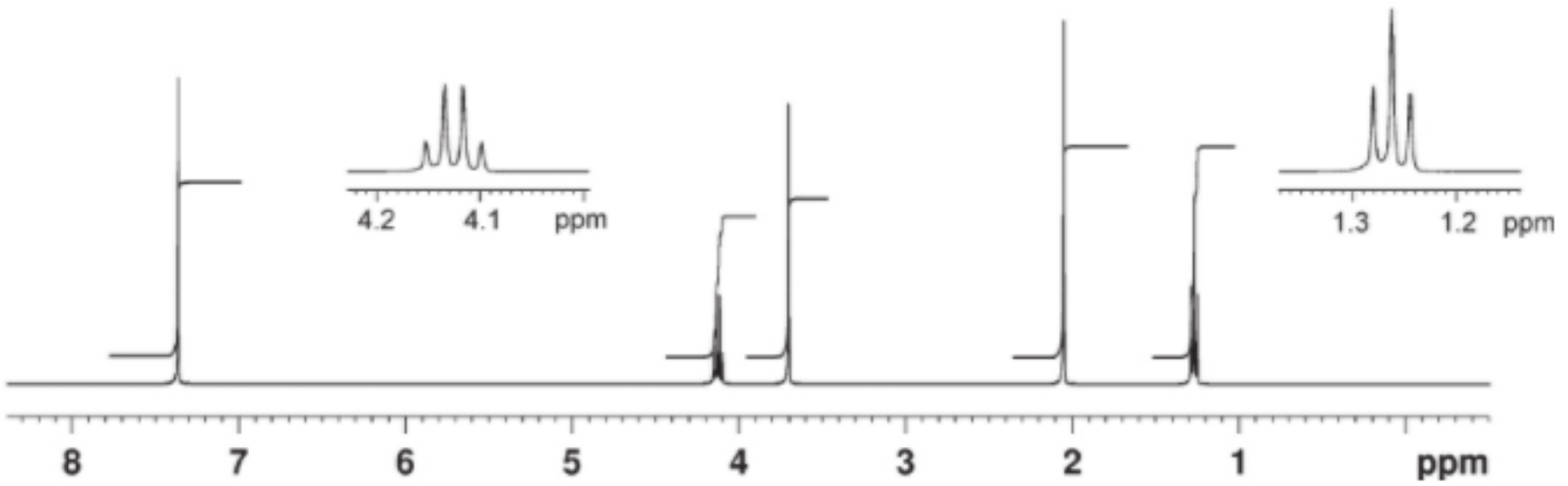


ethyl acetate



dioxane

^{1}H NMR Spectrum
(400 MHz, $CDCl_3$ solution)

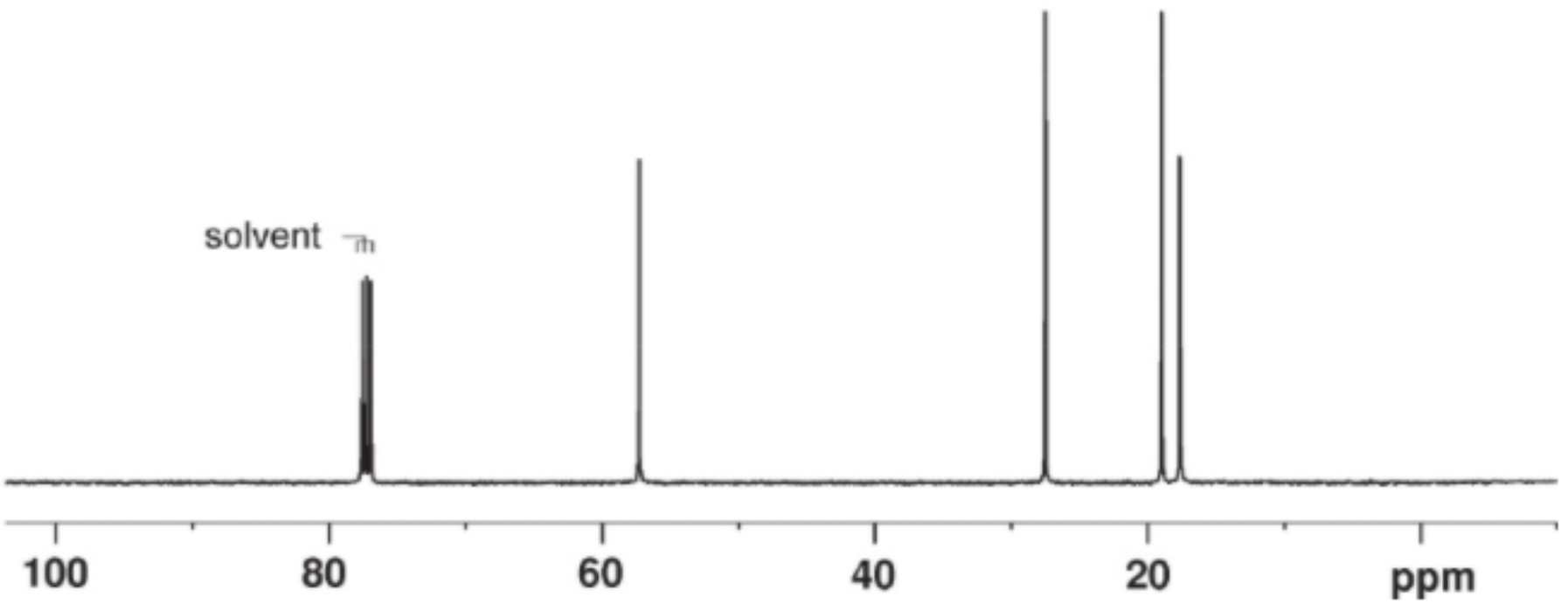


Compound	Mole %
benzene	
ethyl acetate	
dioxane	

Problem 304

A 100 MHz ^{13}C NMR spectrum of a mixture of ethanol (C^2H_6O) δ 18.3 (CH_3), δ 57.8 (CH_2) and bromoethane (C^2H_5Br) δ 19.5 (CH_3) and δ 27.9 (CH_2) in $CDCl_3$ solution is given below. The spectrum was recorded with a long relaxation delay (300 seconds) between acquisitions and with the NOE suppressed. Estimate the relative proportions (mole %) of the 2 components from the peak intensities in the spectrum.

^{13}C NMR Spectrum
(100 MHz, $CDCl_3$ solution)



Compound	Mole %
ethanol	
bromoethane	

Problem 305

A 100 MHz ^{13}C NMR spectrum of a mixture of benzene (C_6H_6) δ 128.7 (CH), diethyl ether ($C_4H_{10}O$) δ 67.4 (CH_2) and δ 17.1 (CH_3) and dichloromethane (CH_2Cl_2) δ 53.7 in $CDCl_3$ solution is given below. The spectrum was recorded with a long relaxation delay (300 seconds) between acquisitions and with the NOE suppressed. Estimate the relative proportions (mole %) of the 3 components from the peak intensities in the spectrum.

benzene

$CH_3-CH_2-O-CH_2-CH_3$

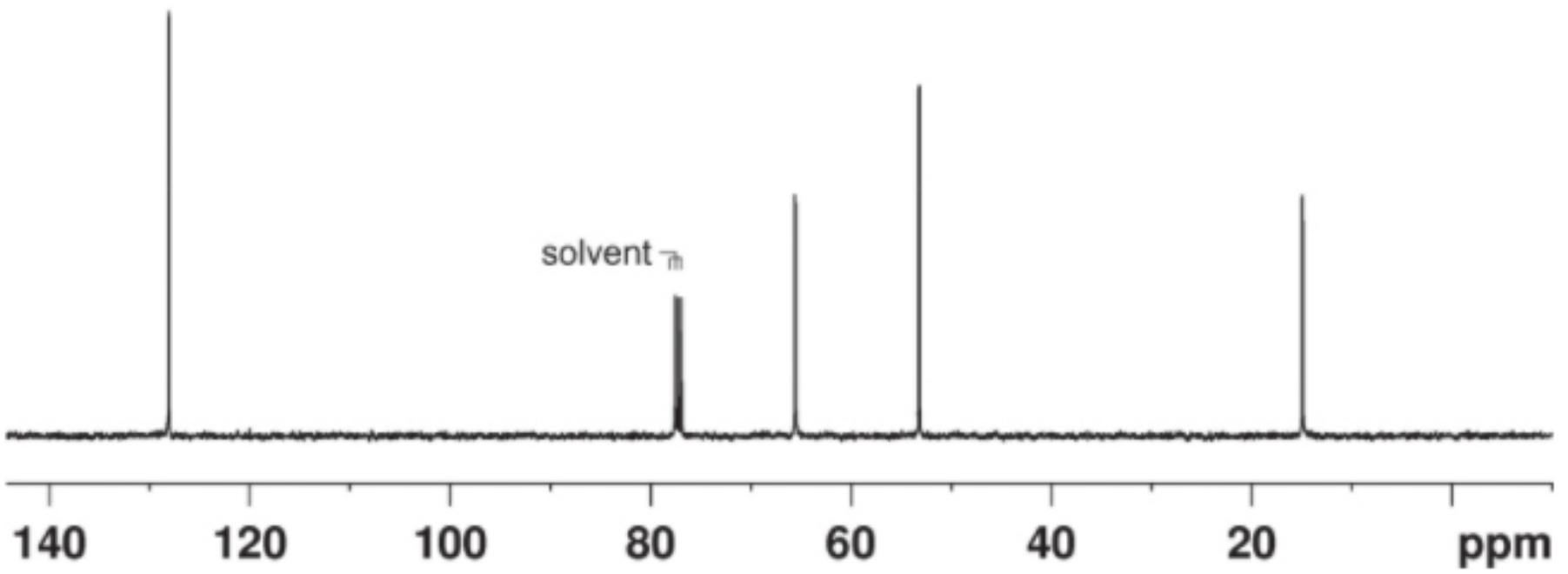
diethyl ether

$Cl-CH_2-Cl$

dichloromethane

^{13}C NMR Spectrum

(100 MHz, $CDCl_3$ solution)

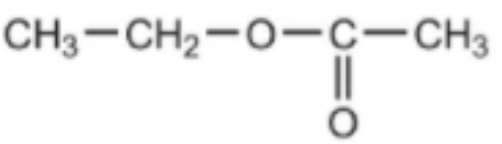


Compound	Mole %
benzene	
diethyl ether	
dichloromethane	

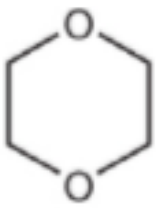
Problem 306

A 100 MHz ^{13}C NMR spectrum of a mixture of benzene (C_6H_6) δ 128.7 (CH), ethyl acetate ($CH_3CH_2OCOCH_3$) δ 170.4 (C=O), δ 60.1 (CH_2), δ 20.1 (CH_3), δ 14.3 (CH_3) and dioxane ($C_4H_8O_2$) δ 66.3 (CH_2) in $CDCl_3$ solution is given below. The spectrum was recorded with a long relaxation delay (300 seconds) between acquisitions and with the NOE suppressed. Estimate the relative proportions (mole %) of the 3 components from the peak intensities in the spectrum.

benzene

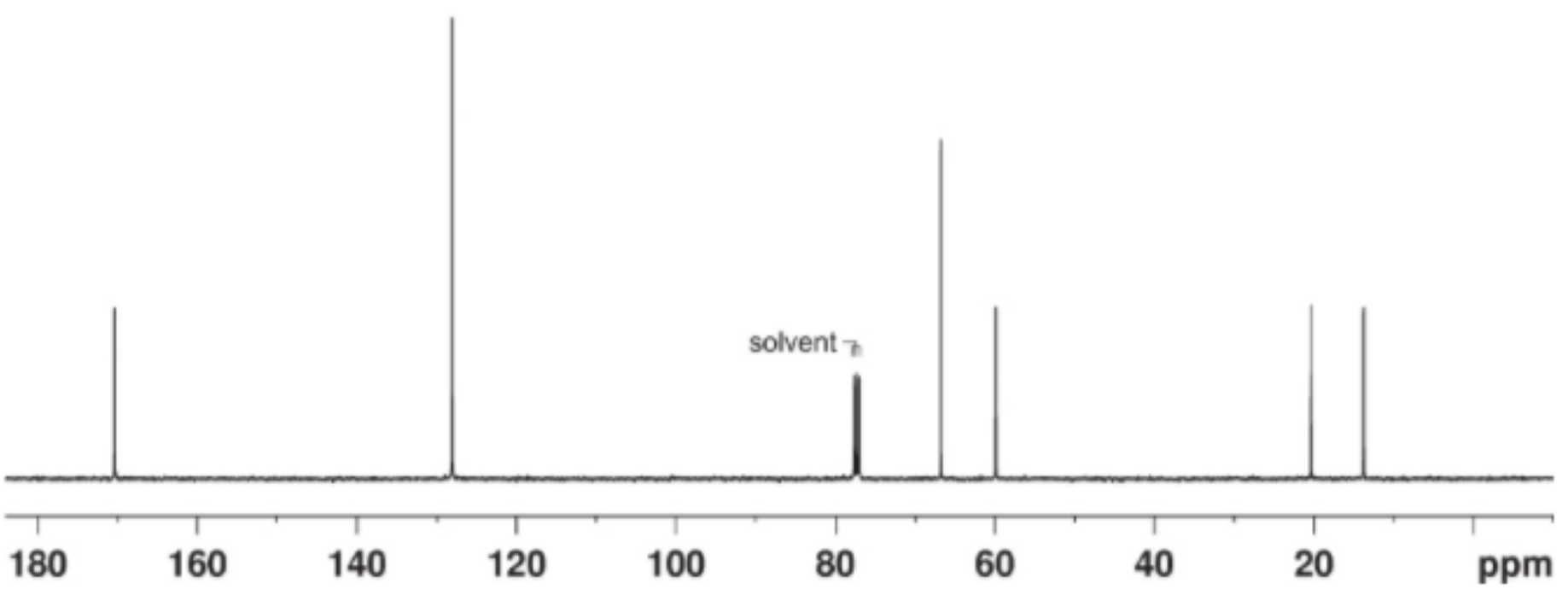


ethyl acetate



dioxane

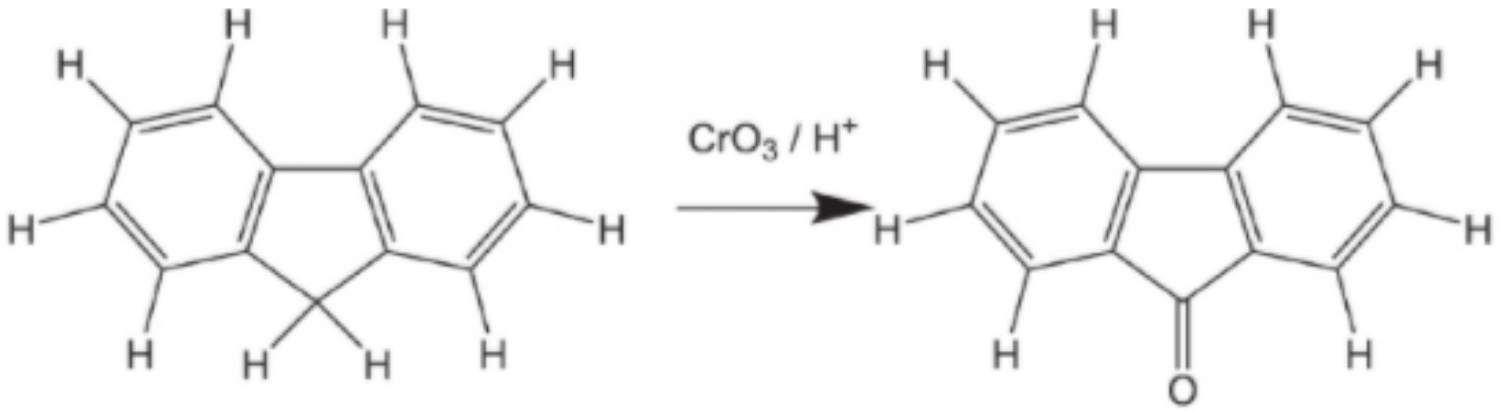
^{13}C NMR Spectrum
(100 MHz, $CDCl_3$ solution)



Compound	Mole %
benzene	
ethyl acetate	
dioxane	

Problem 307

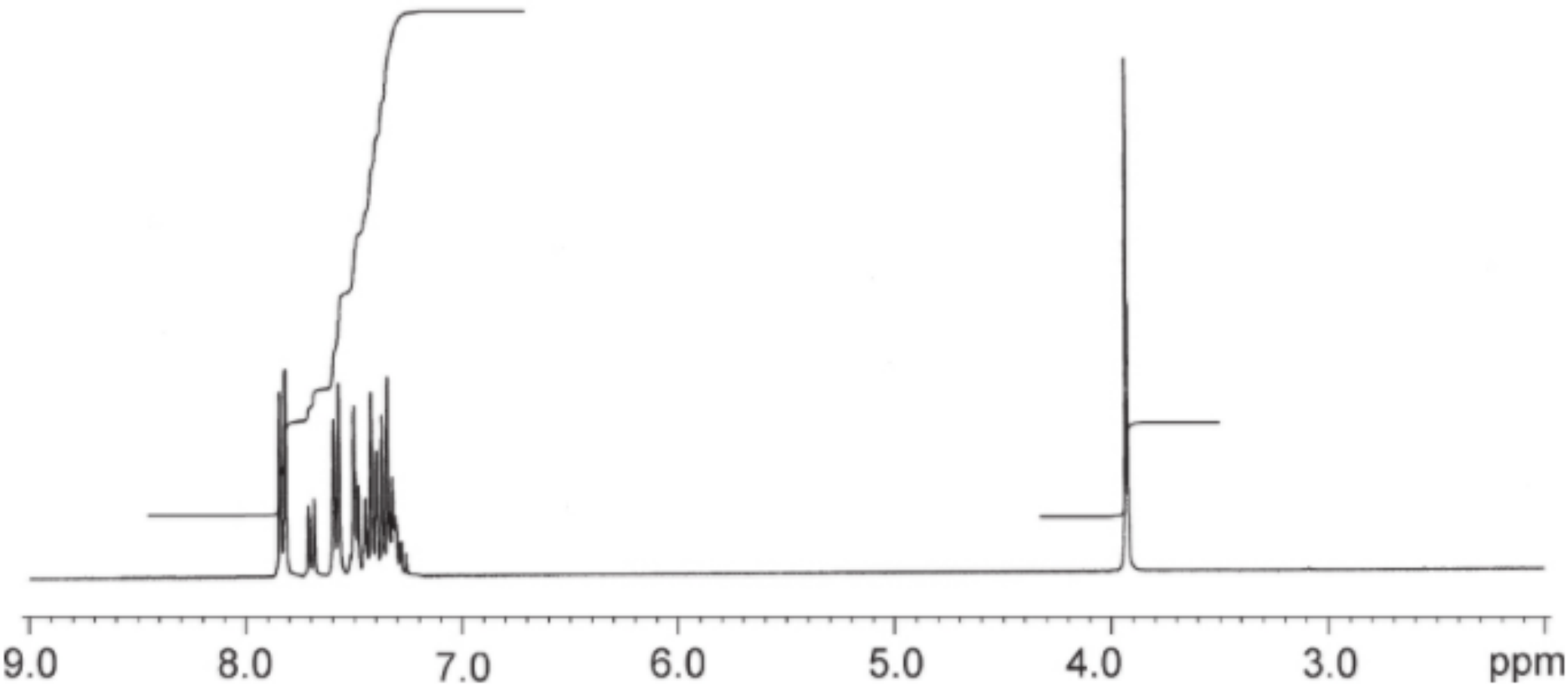
Oxidation of fluorene ($C_{13}H_{10}$) with chromic acid gives fluorenone ($C_{13}H_8O$). If the reaction does not go to completion, then a mixture of the starting material and the product is usually obtained. The ^{1}H NMR spectrum below is from a partially oxidised sample of fluorene so it contains a mixture of fluorene and fluorenone. Determine the relative amounts (mole %) of fluorene and fluorenone in the mixture.



fluorene

fluorenone

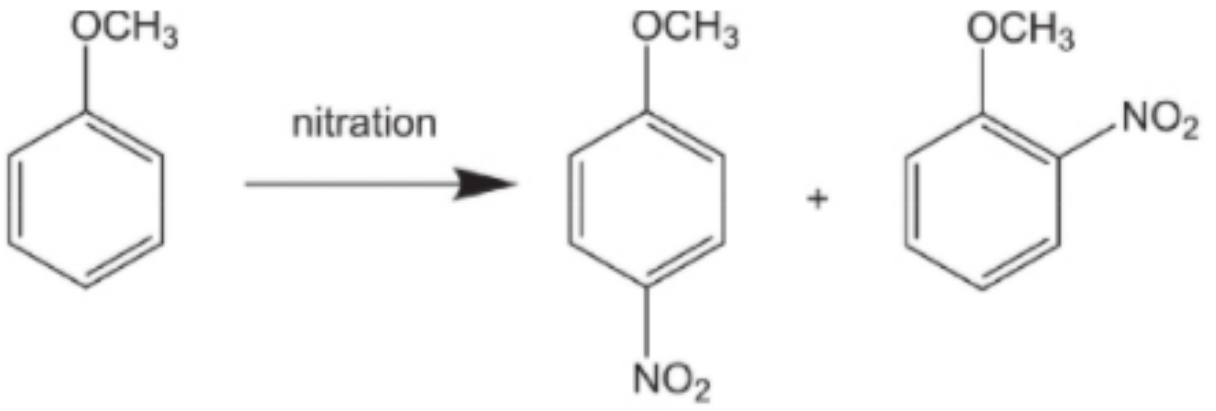
^1H NMR Spectrum
(300 MHz, $CDCl_3$ solution)



Compound	Mole %
fluorene	
fluorenone	

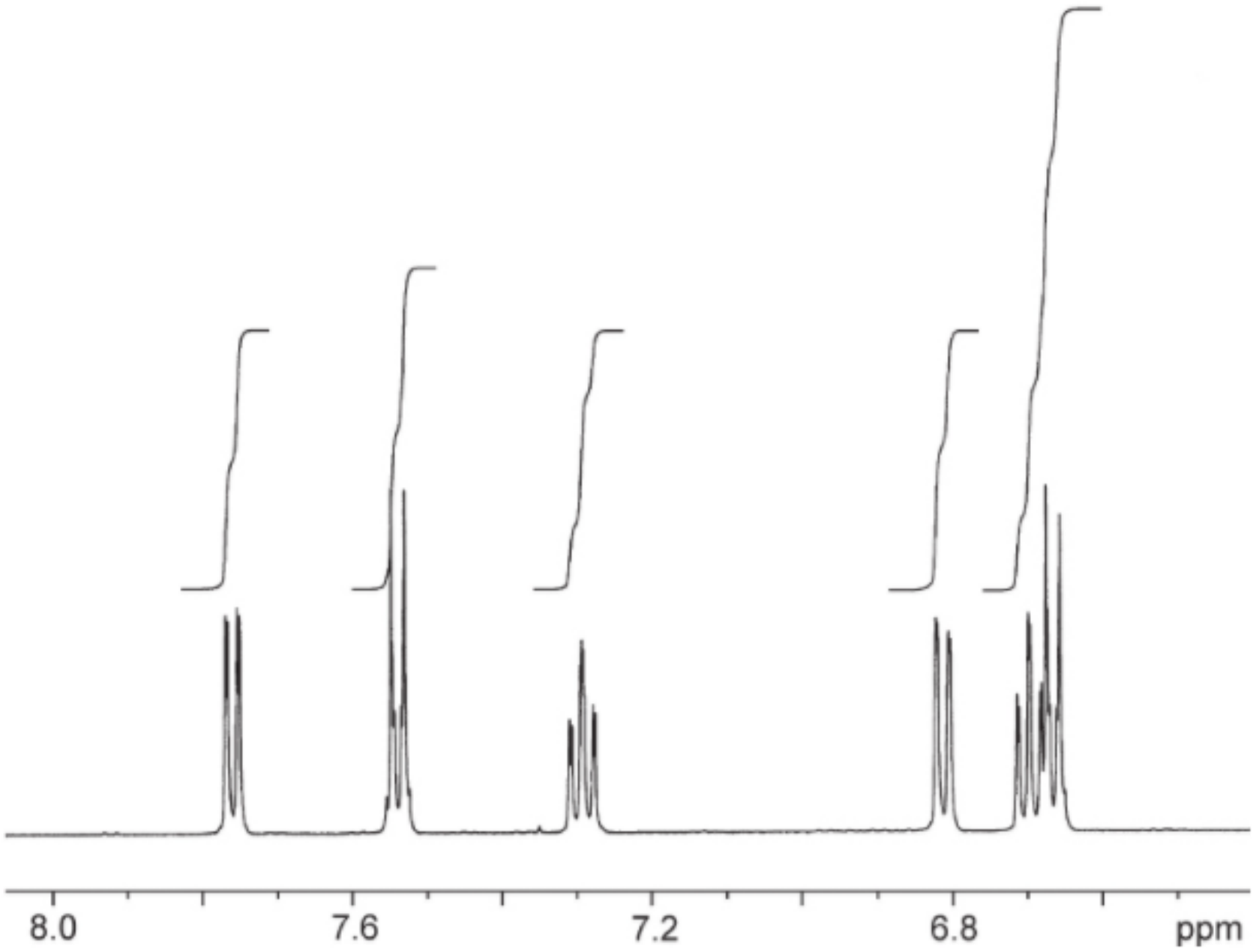
Problem 308

Careful nitration of anisole ($CH_3OC_6H_5$) with a new nitrating reagent gives a mixture of 4-nitroanisole and 2-nitroanisole. The section of the ^1H NMR spectrum below is from the aromatic region of the crude reaction mixture which is a mixture of the 4- and 2-nitroanisoles. Determine the relative amounts of the two products in the reaction mixture from the integrals in the spectrum.



^{1}H NMR Spectrum

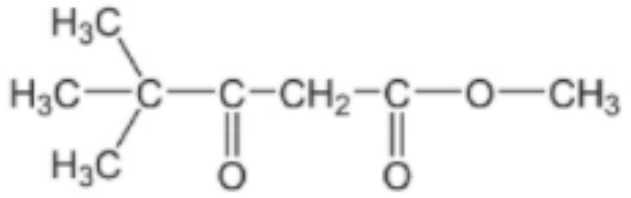
(500 MHz, $CDCl_3$ solution)



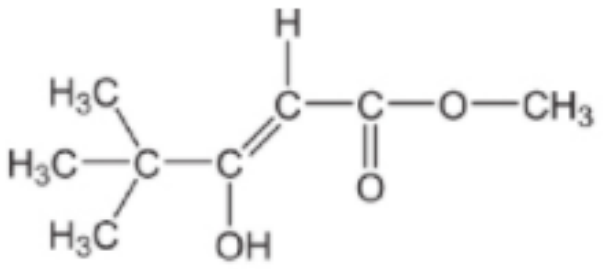
Compound	Mole %
4-nitroanisole	
2-nitroanisole	

Problem 309

A 400 MHz ^{1}H NMR spectrum of a mixture of methyl pivaloylacetate ($C_8H_{14}O_3$) δ 3.377, δ 3.19, δ 0.86 and its enol tautomer δ 12.84, δ 5.08, δ 3.378, δ 1.00 is given below. Estimate the relative proportions (mole %) of the 2 components from the integrals in the spectrum.



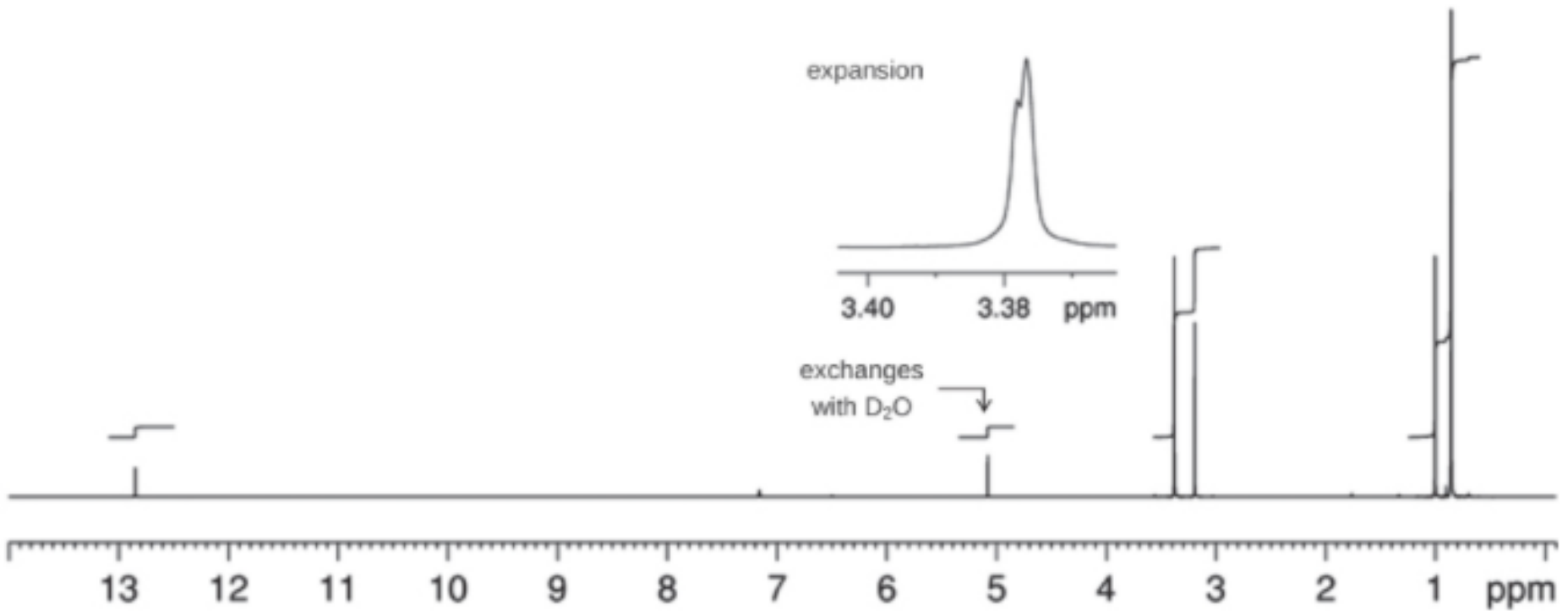
Methyl pivaloylacetate



Enol tautomer

^{1}H NMR Spectrum

(400 MHz, C_6D_6 solution)



Compound	Mole %
Methyl pivaloylacetate	
Enol tautomer	

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Key: ^{13}C NMR = Carbon 13 nuclear magnetic resonance spectrometry

^{1}H NMR = Proton nuclear magnetic resonance spectrometry

2D NMR = 2-dimensional NMR

IR = Infrared spectroscopy

MS = Mass spectrometry

UV = Ultraviolet spectroscopy