

**SILVERSTEIN, BASSLER AND MORRILL**

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**SPECTROMETRIC  
IDENTIFICATION  
OF ORGANIC  
COMPOUNDS**

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**F O U R T H   E D I T I O N**

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The rapid development of  $^{13}\text{C}$  NMR spectrometry has necessitated a new edition of this invaluable text. The 4th edition will serve as an introduction to the determination of structures of organic compounds through the integrated use of five different spectrometric techniques: mass, infrared, proton and carbon magnetic resonance, and ultraviolet spectrometry. The book provides examples for the procedures to interrelate the information from these five spectral classes and puts the student through the logical steps necessary to solve structure determination problems.

The thoroughly revised and updated 4th edition includes these new features:

- problems at the end of each chapter
- a complete new chapter on  $^{13}\text{C}$  NMR spectrometry
- $^{13}\text{C}$  NMR spectra included in many of the problems in the last two chapters
- a large number of new problems in the last chapter
- better organization of reference tables and charts

Other features include readable information on magnetic and chemical shift equivalence, detailed characterization of all infrared spectra as to band-structure correlations, a discussion of the use of lanthanide shift reagents for NMR spectral simplification, and infrared and NMR spectra of many common laboratory compounds.









# SPECTROMETRIC IDENTIFICATION OF ORGANIC COMPOUNDS





# SPECTROMETRIC IDENTIFICATION OF ORGANIC COMPOUNDS

FOURTH EDITION

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# PREFACE

For those whose primary concerns are teaching and research, the writing or revising of a textbook is largely an extracurricular activity, and the burden of compensating for such preoccupation devolves on the author's wife. Our wives have our deepest appreciation.

R.M. Silverstein

T.C. Morrill

The major impetus for the preparation of the fourth edition was the rapid development of  $^{13}\text{C}$  NMR spectrometry, which was treated in a few paragraphs in the third edition but which now constitutes a full chapter. Many of the "problem sets" now consist of 5 spectra — the  $^{13}\text{C}$  spectrum having been added to the mass, infrared, proton NMR, and UV spectra of the earlier editions.

Other chapters have been revised, resulting in some expansion and, we hope, in some clarification. The revision has also prompted reorganization of reference material.

We include one paragraph from the preface to the third edition:

"In the first edition (1963) we referred to "methods now available and used in research but *not systematically taught* in universities. . . ." The concept behind the first edition was that organic structures could be elucidated from the complementary information available from mass, infrared, NMR, and UV spectrometry. Since that time, several excellent books have appeared, organized similarly to this text, and brief treatments of the four areas of spectrometry are a part of almost every elementary organic textbook. In the first and second editions we stated: "In one form or another, such material [i.e., spectrometric interpretation] should soon become part of the training of every organic chemist." We are now constrained to change "should soon" to "has." One of us (T.C.M.) has a unique perspective. He can look back over the past decade to his first contact with spectrometry in a graduate course at San Jose State College in 1962. The instructors were R.M. Silverstein and G.C. Bassler, whose lecture notes were the basis for the first edition of this text."

Several of the revisions are results of stimulating and enjoyable discussions with our colleagues, Dr. Robert R. LaLonde, Dr. Conrad Schuerch, and Dr. Alan Harvey (SUNY College of Environmental Science and Forestry), and Dr. Craig Van Antwerp (Rochester Institute of Technology). The comments of several reviewers were most helpful.





# PREFACE TO FIRST EDITION

endured, they also encouraged, assisted, and inspired.

R. M. Silverstein  
G. C. Bassler

*Menlo Park, California  
April 1963*

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During the past several years, we have been engaged in isolating small amounts of organic compounds from complex mixtures and identifying these compounds spectrometrically.

At the suggestion of Dr. A. J. Castro of San Jose State College, we developed a one unit course entitled "Spectrometric Identification of Organic Compounds," and presented it to a class of graduate students and industrial chemists during the 1962 spring semester. This book has evolved largely from the material gathered for the course and bears the same title as the course.

We should first like to acknowledge the financial support we received from two sources: The Perkin-Elmer Corporation and Stanford Research Institute.

A large debt of gratitude is owed to our colleagues at Stanford Research Institute. We have taken advantage of the generosity of too many of them to list them individually, but we should like to thank Dr. S. A. Fuqua, in particular, for many helpful discussions of NMR spectrometry. We wish to acknowledge also the cooperation at the management level, of Dr. C. M. Himel, chairman of the Organic Research Department, and Dr. D. M. Coulson, chairman of the Analytical Research Department.

Varian Associates contributed the time and talents of its NMR Applications Laboratory. We are indebted to Mr. N. S. Bhacca, Mr. L. F. Johnson, and Dr. J. N. Shoolery for the NMR spectra and for their generous help with points of interpretation.

The invitation to teach at San Jose State College was extended by Dr. Bert M. Morris, head of the Department of Chemistry, who kindly arranged the administrative details.

The bulk of the manuscript was read by DR. R. H. Eastman of the Stanford University whose comments were most helpful and are deeply appreciated.

Finally, we want to thank our wives. As a test of a wife's patience, there are few things to compare with an author in the throes of composition. Our wives not only





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# SPECTROMETRIC IDENTIFICATION OF ORGANIC COMPOUNDS





## introduction

Our purpose in writing this book is to teach the organic chemist how to identify organic compounds from the complementary information afforded by four spectra: mass, infrared, nuclear magnetic resonance, and ultraviolet. Essentially, the molecule in question is subjected to four energy probes, and the molecule's responses are recorded as spectra.

The small amounts of pure compounds that can be isolated from complex mixtures by chromatography present a challenge to the chemist concerned with identification and structure elucidation of organic compounds. These techniques have two characteristics: they are rapid, and they are most effective in milligram and microgram quantities. There is neither enough time nor enough material to accommodate the classical manipulations involving sodium fusion, boiling point, refractive index, solubility tests, functional group tests, derivative preparation, mixture melting point, combustion analysis, molecular weight, and degradation with similar manipulations of the degradation products.

Our goal in this book is a rather modest level of sophistication and expertise in each of the four areas of spectrometry. Even this level will permit solution of a gratifying number of identification problems with *no history and no other chemical or physical data*. Of course, in practice other information is usually available: the sample source, details of isolation, a synthesis sequence, or information on analogous material. Often complex molecules can be identified because partial structures are known, and specific questions can be formulated; the process is more confirmation than identification. In practice, however, difficulties arise in physical handling of minute amounts of compound: trapping, elution from adsorbents, solvent removal, prevention of contamination, and decomposition of unstable compounds. Water, air, stopcock greases, solvent impurities, and plasticizers have frustrated many investigations. The quality of

spectra obtained in practice is usually inferior to that presented here.

For pedagogical reasons, we deal only with pure organic compounds. *Pure* in this context is a relative term, and all we can say is: the purer, the better. A good criterion of purity (for a sufficiently volatile compound) is gas chromatographic homogeneity on both polar and nonpolar substrate capillary columns. Various forms of liquid-phase chromatography (adsorption and liquid-liquid columns, paper, thin layer) are applicable to many compounds. The spectra presented in this book were obtained on purified samples.

In many cases, identification can be made on a fraction of a milligram, or even on several micrograms, of sample. Identification on the milligram scale is routine. Of course, not all molecules yield so easily. Chemical manipulations may be necessary but the information obtained from the four spectra will permit intelligent selection of chemical treatment, and the energy probe methodology can be applied to the resulting products.

There are limitations to the methodology we espouse. A mass spectrum is dependent on a degree of volatility and thermal stability. However, mass spectra have been obtained on many high molecular weight compounds—steroids, terpenoids, peptides, polysaccharides, and alkaloids—by obtaining positive ions by special techniques. Solubility is a limiting factor in nuclear magnetic resonance spectrometry. However, the availability of many deuterated solvents and the development of microsample tubes, and Fourier transform NMR make it possible to obtain good spectra from many kinds of compounds.

The problem of cost of necessary instrumentation is raised and answered by pointing to the amazing evolution of commercial instruments. The time saved, the smaller samples required, and the information made available far outweigh the cost. Identifications are frequently made on the basis of several hours of a student's, technician's, or analyst's time. Under a classical regime, much larger samples and several days or even weeks of a skilled analyst's time would probably be necessary. Infrared and ultraviolet spectrometers have been developed beyond the stage of reliable instruments in the hands of a trained technician. They are now cheap, rugged, and simple enough to be used as bench tools by the organic chemist. Certain types of simple nuclear magnetic resonance spectrometers are now available to even the more modest institutions; these are essentially as easy to run as infrared instruments. More sophisticated magnetic resonance spectrometers, especially those with computer facets, require skilled technicians.

Almost from its inception, the utility of nuclear magnetic resonance spectrometry to the organic chemist has been evident. Mass spectrometry, however, has had a somewhat different history. Developed by the physicist and utilized extensively by the petroleum chemist, it has been ignored until recently by the organic chemist concerned

with identification and structure determination. Mass spectrometers have become available to a wide range of institutions.

We spend very little time on instrumentation, *per se*, for three reasons: it is not requisite to our goal; we are not qualified; and excellent treatises on the subject are available. The five chapters on spectrometry are designed to give the analyst an appreciation of the potentialities of each technique as applied to the identification of organic compounds. The rest of the book consists of selected spectra. These mass, infrared, nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$ ), and ultraviolet spectra are presented as sets, each set repre-

senting a compound. These are translated, as exercises, into the chemical structure (Chapter 7), identified by a Beilstein reference, or presented without identification (Chapter 8). Aside from practical applications, the considerations involved in translating spectra into organic compounds lead to an appreciation of modern concepts of structural organic chemistry.

If we have been judicious in our selection of spectra, they should serve as useful references for teachers and for chemists in industry. In one form or another such material has become part of the training of every organic chemist.



## mass spectrometry

## I. INTRODUCTION

A mass spectrometer bombards the substance under investigation with an electron beam and quantitatively records the result as a spectrum of positive ion fragments. This record is a mass spectrum. Separation of the positive ion fragments is on the basis of mass (strictly, mass/charge, but the majority of ions are singly charged). How this is accomplished will be sketched in sufficient detail to impart some appreciation for the potentialities of mass spectrometry as applied to compound identification to the organic chemist.

A number of good texts are available for the broad field of mass spectrometry;<sup>1-36</sup> these include general<sup>1-15, 34-36</sup> and specialized<sup>30-33</sup> monographs. Journals include *Organic Mass Spectrometry*, the *Journal of Mass Spectrometry* and *Ion Physics*, and *Biomedical Mass Spectrometry*. Compilations of data and spectra are available;<sup>16-29</sup> references include Appendix I (organized by compound class) of Hamming and Foster,<sup>7</sup> the *Atlas of Mass Spectral Data*<sup>28</sup>, the CRC collection,<sup>22</sup> and the NIH-CIS collection.<sup>27</sup> Chapter 7 of Middleditch<sup>11</sup> contains an extensive listing of other compilations. Indexes to mass spectral information include the *ASTM index*,<sup>16, 17</sup> and the chemical compound index of the journal *Org. Mass Spec.*

Mass spectrometers are still characterized by high cost and the need for skilled technicians for operation and maintenance. Mass spectral data, however, are routinely reported in professional journals. In addition, mass spectral discussions are commonplace in organic chemistry textbooks and problem manuals for structure determination.

## II. INSTRUMENTATION

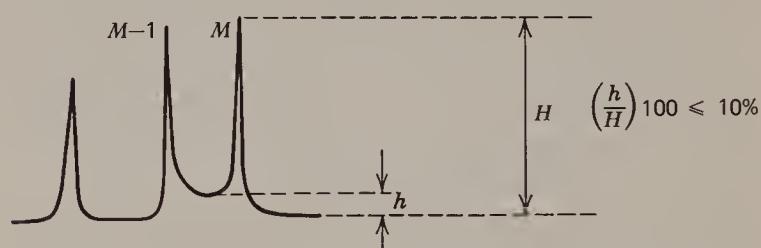
In this section we describe the electron impact method for obtaining mass spectra.

Mass spectrometers for structure elucidation can be classified according to the method of separating the charged particles:

- A. Magnetic Field Deflection (Direction Focusing)
  1. Magnetic field only (unit resolution)
  2. Double focusing (electrostatic field before magnetic field, high resolution)
- B. Time of Flight
- C. Quadrupole

The minimum instrumental requirement for the organic chemist is the ability to record the molecular weight of the compound under examination to the nearest whole number. Thus, the recording should show a peak at, say, mass 400, which is distinguishable from a peak at mass 399 or at mass 401. In order to select possible molecular formulas by measuring isotope peak intensities (see Section IV), adjacent peaks must be quite cleanly separated. Arbitrarily, a valley between two adjacent peaks should not be more than about 10% of the height of the larger peak. This latter degree of resolution is termed "unit" resolution and can be obtained up to about mass 500 on several single-focusing (magnetic-focusing) instruments.

To determine the resolution of an instrument, consider two adjacent peaks of approximately equal intensity. These



peaks should be chosen so that the height of the valley between the peaks is about 10% of the intensity of the peaks. The resolution ( $R$ ) is

$$R = \frac{M}{\Delta M}$$

where  $M$  is the higher mass number of the two peaks, and  $\Delta M$  is the difference between the two mass numbers.

There are two important categories of magnetic-deflection mass spectrometers: low resolution and high resolution. Low-resolution instruments can be defined arbitrarily as the instruments that separate unit masses up to  $m/e$  2000 [ $R = 2000/(2000-1999) = 2000$ ]. Unit mass (or low-resolution) spectra are obtained from these instruments. An instrument is generally considered high resolution if it can separate two ions differing in mass by at least one part in ten thousand to fifteen thousand ( $R = 10,000-15,000$ ). An instrument with 10,000 resolution can separate an ion of mass 500.00 from one of mass 499.95 ( $R = 500/0.05 = 10,000$ ). This important class of mass spectrometers can measure the mass of an ion with sufficient accuracy to

determine its atomic composition. High-resolution mass spectrometry will be discussed only briefly, since the instruments are not available in most laboratories.

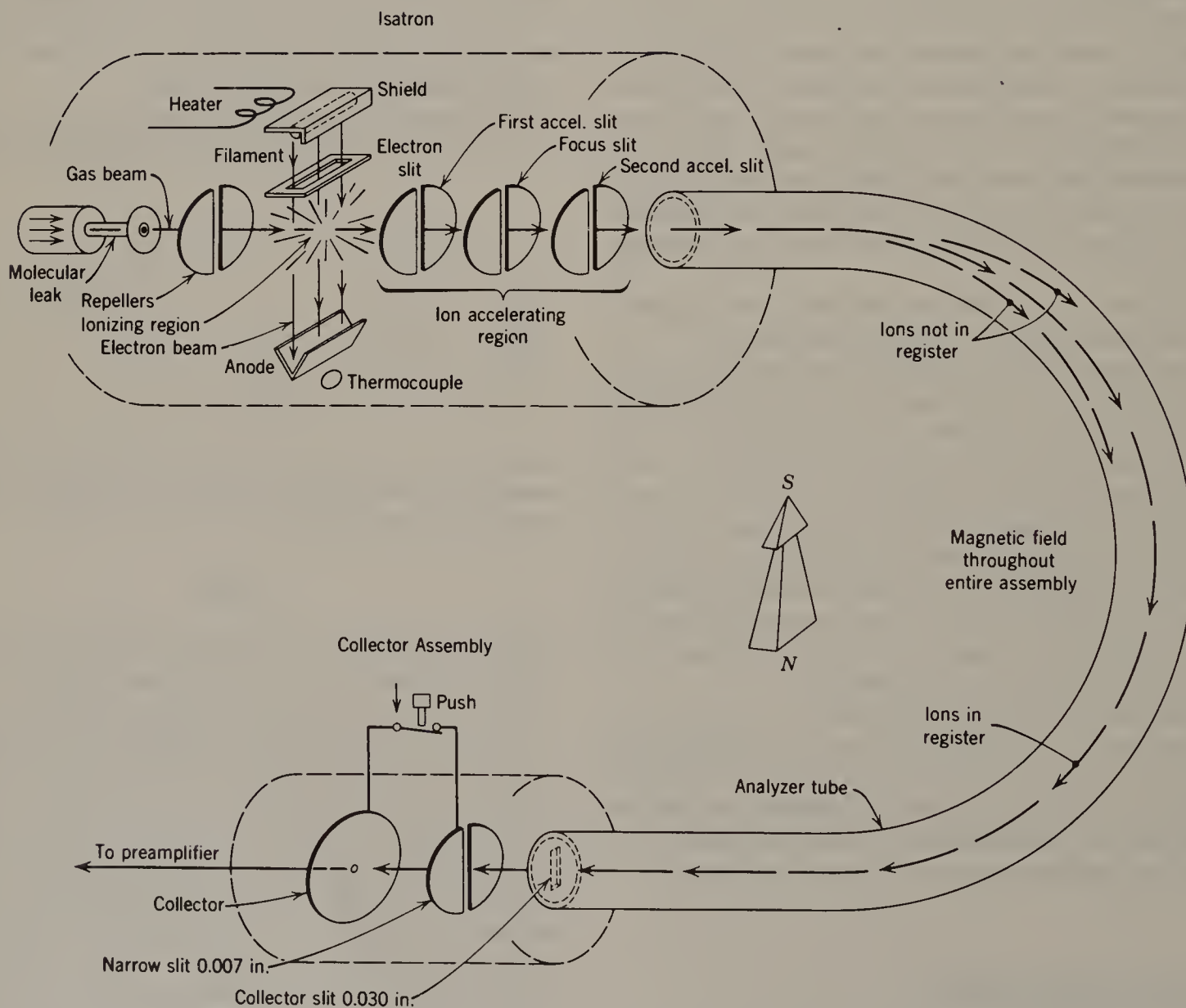
A schematic diagram of a typical  $180^\circ$  single-focusing mass spectrometer is shown in Figure 1. There are five component parts in this low-resolution system.

**1. SAMPLE HANDLING SYSTEM.** This consists of a device for introducing the sample, a micromanometer for determining the amount of sample introduced, a device (molecular leak) for metering the sample to the ionization chamber, and a pumping system. Introduction of gases is usually a simple matter of transfer from a gas bulb into the metering volume, thence to the ionizing chamber. Liquids are introduced by touching a micropipette to a sintered glass disc or an orifice under mercury or gallium, or simply by hypodermic needle injection through a serum cap. A bulb containing the sample may be pumped out under dry ice, then warmed to vaporize the sample into the inlet system. Heated inlet systems are used for less volatile

liquids and for solids. Insertion of the sample directly into the ionization chamber further reduces the limitations imposed by lack of volatility and of thermal stability.

This direct-insertion technique decreases the degree of volatility necessary for analysis. Since ionization must take place in the vapor state, some degree of volatility and thermal stability is still required. Reproducible breakdown patterns have been obtained on high molecular weight terpenoids, steroids, polysaccharides, peptides, and alkaloids. Even with these special techniques, a compound must be stable at a temperature at which its vapor pressure is of the order of  $10^{-7}$  to  $10^{-6}$  Torr. For routine work, using a molecular leak, a vapor pressure of about  $10^{-1}$  to  $10^{-3}$  Torr is desired. Sample sizes for liquids and solids range from several milligrams to less than a microgram, depending on the method of introduction and the detector.

**2. IONIZATION AND ACCELERATING CHAMBERS.** The gas stream from the molecular leak enters the ionization chamber (operated at a pressure of about  $10^{-6}$  to



**Figure 1.** Schematic diagram of CEC model 21-103 Mass Spectrometer, a single-focusing,  $180^\circ$  sector mass analyzer. The magnetic field is perpendicular to the page.



$10^{-5}$  Torr) in which it is bombarded at right angles by an electron beam emitted from a hot filament. Positive ions produced by interaction with the electron beam are forced through the first accelerating slit by a small electrostatic field between the repellers and the first accelerating slit. A strong electrostatic field between the first and second accelerating slits accelerates the ions to their final velocities. Additional focusing of the ion beam is provided between the accelerating slits. To obtain a spectrum, either the magnetic field applied to the analyzer tube (Figure 1) or the accelerating voltage between the first and second ion slits is varied. Thus, the ions are successively focused at the collector slit as a function of mass (strictly, mass/charge). In most instruments, a scan from mass 12 to mass 500 may be performed in 1 to 4 minutes. However, scan speeds of a few seconds have been used to obtain spectra of gas chromatography fractions (see below).

3. ANALYZER TUBE AND MAGNET. The analyzer tube is an evacuated ( $10^{-7}$  to  $10^{-8}$  Torr), curved (in Figure 1, a  $180^\circ$  curve), metal tube through which the ion beam passes from ion source to collector. The magnetic pole pieces (electromagnets are usually used for the larger instruments) are mounted perpendicular to the plane of the diagram (Figure 1). The main requirement is a uniform, stable magnetic field.

4. ION COLLECTOR AND AMPLIFIER. A typical ion collector consists of one or more collimating slits and a Faraday cylinder; the ion beam impinges axially into the collector, and the signal is amplified by an electron multiplier.

5. RECORDER. A widely used recorder employs five separate galvanometers that record simultaneously. Figure 2a presents a spectrum traced by a five-element galvanometer system at sensitivity levels decreasing from top to bottom in the ratios of 1:3:10:30:100. Peak heights from the base line are read on the most sensitive trace remaining on scale and are multiplied by the appropriate sensitivity factor. Peak heights are proportional to the number of ions of each mass. The recorder trace can be presented as a table or as a graph (Figures 2b and 2c).

Throughout this book, and in most published work, a peak is reported as a value of mass divided by charge ( $m/e$ ). Since we are usually dealing with singly charged ions (i.e.,  $e = 1$ ), such a value is the mass ( $m$ ) of the ion corresponding to that peak. That multiple ionization does occur is indicated by the peaks at half-mass units (e.g.,  $m/e$  43.5) in the tracing; these represent odd-numbered masses that carry a double charge. A broad, weak, "metastable" peak (see below) can be seen between  $m/e$  90 and 91 (Figure 2a).\*

Assignment of mass to the peaks of the recorder tracing can be a problem at the high mass end of the scan. The

common practice is to start at the low mass end of the scan, which can be accurately set, and count the peaks to the last recorded peak. This is often feasible because the most sensitive galvanometer will record a slight ion current at each mass unit. Sometimes the peaks at the high end of the spectrum may be widely spaced, and the background trace indistinct; in this case, a calibration compound may be added to the sample. Some instruments are equipped with automatic mass markers, but often these are not reliable where they are most needed—at the high mass end of the spectrum. A mass digitizer that prints out the mass number and relative intensities is a valuable auxiliary piece of equipment. However, a slight maladjustment may result in loss or gain of a full mass unit in a scan; this can be disastrous. It is well to check the digitizer printout against the galvanometer trace.

A mass analyzer using four electric poles (a "quadrupole") and no magnetic field has been developed (Figure 3). Ions entering from the top travel with constant velocity in the direction parallel to the poles ( $z$  direction), but acquire oscillations in the  $x$  and  $y$  directions. This is accomplished by application of both a dc voltage and a radio frequency voltage to the poles. There is a "stable oscillation" that allows an ion to pass from one end of the quadrupole to the other without striking the poles; this oscillation is dependent on the mass-to-charge ratio of an ion. Therefore, ions of only a single  $m/e$  value will traverse the entire length of the analyzer. All other ions will have unstable oscillations and will strike the poles. Mass scanning is carried out by varying each of the dc and radio frequencies while keeping their ratios constant. Resolutions as high as  $R = 10,000$  have been achieved with this type of analyzer.

The introduction of an electrostatic field ahead of the magnetic field (double focusing) permits high resolution so that the mass of a particle can be obtained to three or four decimal places. Figure 4 shows an example of such a double-focusing instrument. A positive ion in an electric field experiences a force in the direction of the field; the path of an ion moving through the field is thus curved. In a radial electric field (always perpendicular to the direction of flight of the ions) the radius of curvature,  $r_e$ , of the ion path is dependent on the energy of the ion and the strength of the electric field. The electric field is an energy analyzer, instead of a mass analyzer, and serves to limit the energy spread of the ion beam before it enters the magnetic field. The energy spread is one of the major factors in decreasing the resolution of the simple magnetic deflection analyzers. Proper choice of the angle of deflection in the electric field also results in directional focusing of an ion beam. The Nier-Johnson double-focusing mass analyzer incorporates  $90^\circ$  electrostatic and  $90^\circ$  magnetic analyzers (Figure 4). The multimass ion beam is uniform in energy as it leaves the electrostatic analyzer, and the magnetic field produces the desired mass dispersion while focusing each unimass ion beam to the same point. Another common double-focusing arrangement, the Mattauch-Herzog mass analyzer,

\*The symbol  $z$  has been recommended as a substitute for  $e$ .

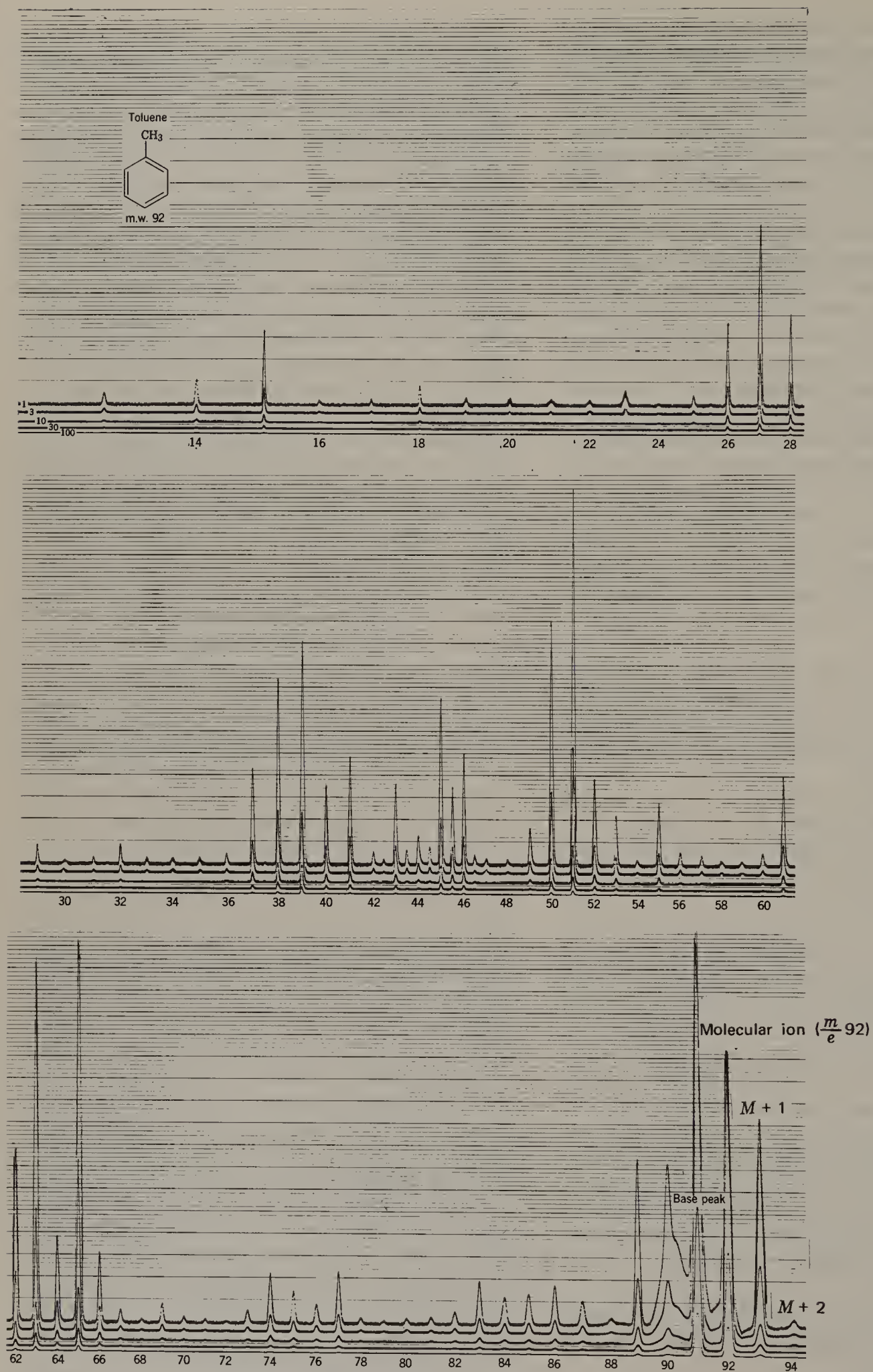
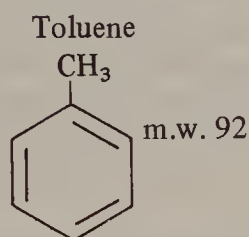


Figure 2a. Mass Spectrum traced by a five-element galvanometer. Note the metastable peak at  $m^* = (91)^2/(92) = \text{ca. } 90$ . The relative peak intensities decrease from top to bottom trace, by 1:3:10:30:100.



has electric and magnetic sectors of  $90^\circ$  and  $31^\circ 50'$  respectively, and the ions are focused at different points in the detector.

Resolutions on the order of 40,000 are routinely obtainable with the high-resolution commercial instruments available (either geometry) when relatively monoenergetic ions are produced; both geometries have been used extensively for accurate measurement of the masses of ions in organic structure determinations. However, the high cost and complexity make this instrument available to relatively few laboratories.



|       |                         | Isotope Abundances |          |
|-------|-------------------------|--------------------|----------|
| $m/e$ | % of Base Peak          | $m/e$              | % of $M$ |
| 38    | 4.4                     | 92 ( $M$ )         | 100      |
| 39    | 5.3                     | 93 ( $M + 1$ )     | 7.23     |
| 45    | 3.9                     | 94 ( $M + 2$ )     | 0.29     |
| 50    | 6.3                     |                    |          |
| 51    | 9.1                     |                    |          |
| 62    | 4.1                     |                    |          |
| 63    | 8.6                     |                    |          |
| 65    | 11                      |                    |          |
| 91    | 100 (Base)              |                    |          |
| 92    | 68 (Molecular Ion Peak) |                    |          |
| 93    | 4.9 ( $M + 1$ )         |                    |          |
| 94    | 0.21 ( $M + 2$ )        |                    |          |

Figure 2b. Tabular presentation of Figure 2a.

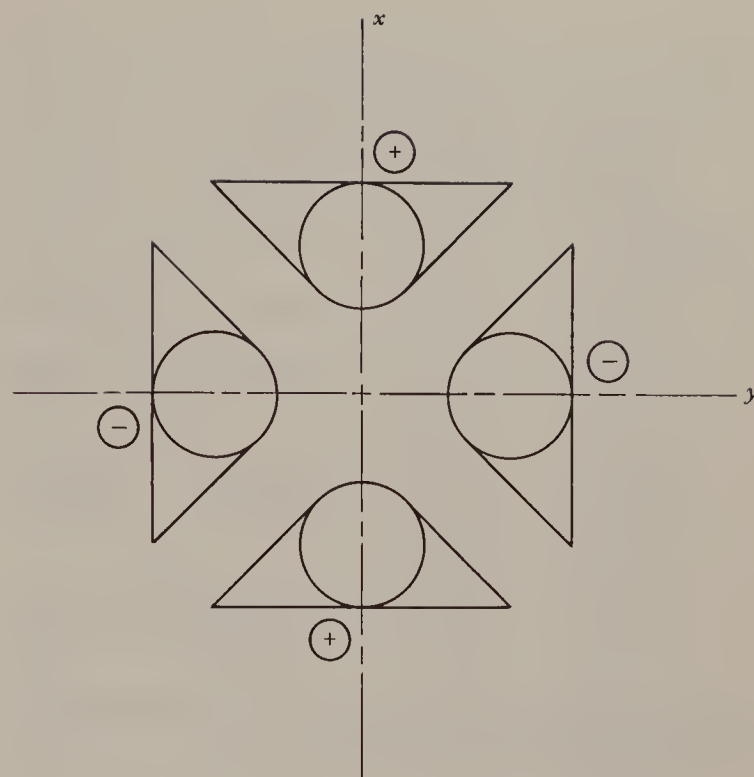


Figure 3. Quadrupole arrangement.

Several firms offer a gas chromatographic instrument coupled to a mass spectrometer through an interface that enriches the concentration of the sample in the carrier gas by taking advantage of the higher diffusivity of the carrier gas, (Figure 5). Scan times are rapid enough so that several mass spectra can be obtained during the elution of a single peak from the gas chromatographic unit. The enrichment device decreases the pressure of gas emitted from the gas chromatograph to a pressure suitable for the spectrometer detector.

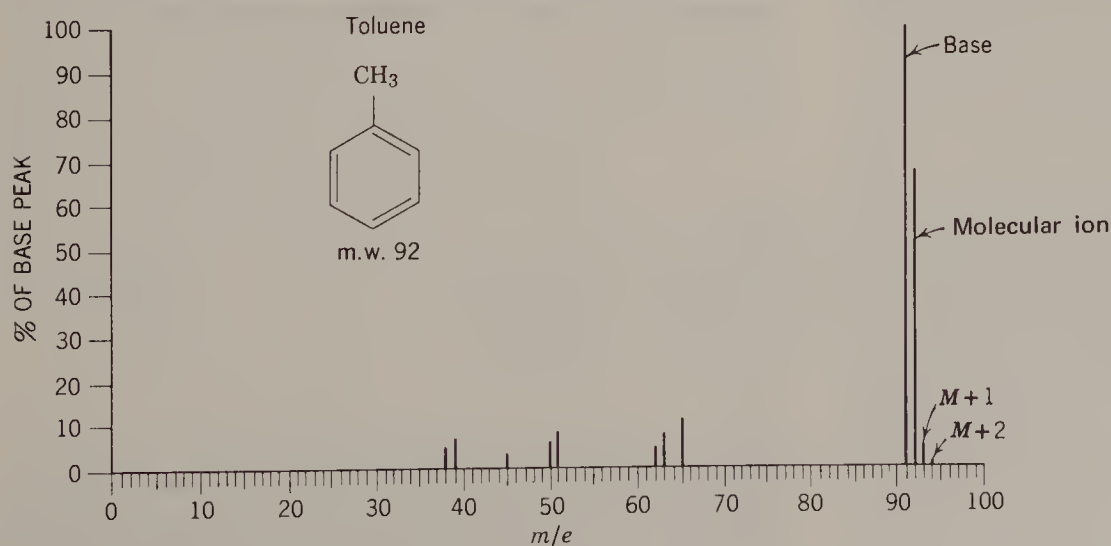


Figure 2c. Graphical presentation of Figure 2a.



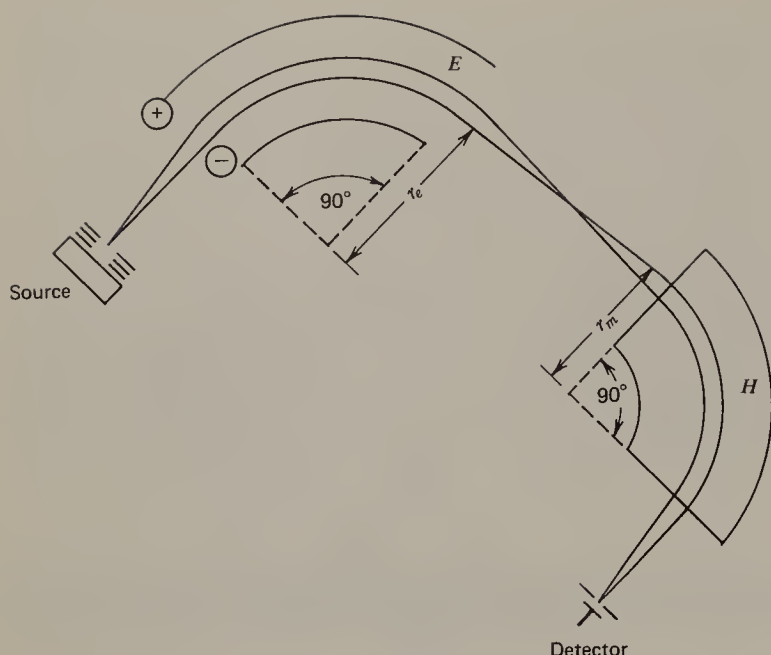


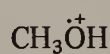
Figure 4. Nier-Johnson double-focusing mass analyzer.  $E$  = electric field.  $H$  = magnetic field.

### III. THE MASS SPECTRUM

Mass spectra are routinely obtained at an electron beam energy of 70 electron volts. The simplest event that occurs is the removal of a single electron from the molecule in the gas phase by an electron of the electron beam to form a molecular ion, which is a radical cation ( $M^+$ ). For example, methanol forms a molecular ion:

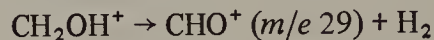
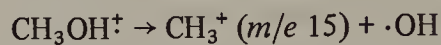
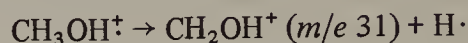


When the charge can be localized on one particular atom, the charge is shown on that atom:



The single dot represents the odd electron. Many of these molecular ions disintegrate in  $10^{-10}$  to  $10^{-3}$  second to give,

in the simplest case, a positively charged fragment and a radical. A number of fragment ions are thus formed, and each of these can cleave to yield smaller fragments. Again, illustrating with methanol:



If some of the molecular (parent) ions remain intact long enough (about  $10^{-6}$  seconds) to reach the detector, we see a molecular ion peak. It is important to recognize the molecular ion peak because this gives the molecular weight of the compound. With unit resolution, this molecular weight is the molecular weight to the nearest whole number, and not merely the approximation obtained by all other molecular weight determinations familiar to the organic chemist.

A mass spectrum is a presentation of the masses of the positively charged fragments (including the molecular ion) versus their relative concentrations. The most intense peak in the spectrum, called the base peak, is assigned a value of 100%, and the intensities (height  $\times$  sensitivity factor) of the other peaks, including the molecular ion peak, are reported as percentages of the base peak. Of course, the molecular ion peak may sometimes be the base peak. In Figure 2a, the molecular ion peak is  $m/e\ 92$ , and the base peak is  $m/e\ 91$ .

A tabular or graphic presentation of a spectrum may be used. A graph has the advantage of presenting patterns that, with experience, can be quickly recognized. However, a graph must be drawn so that there is no difficulty in distinguishing mass units. Mistaking a peak at, say,  $m/e\ 79$  for  $m/e\ 80$  can result in total confusion. Unfortunately, many of the graphs presented in the journals are illegible. Computer programs are available for printing out good line graphs. The grid that we use permits ready recognition of individual mass units as well as patterns. Except for isotope peaks and molecular ion peaks, peaks of less than 3%

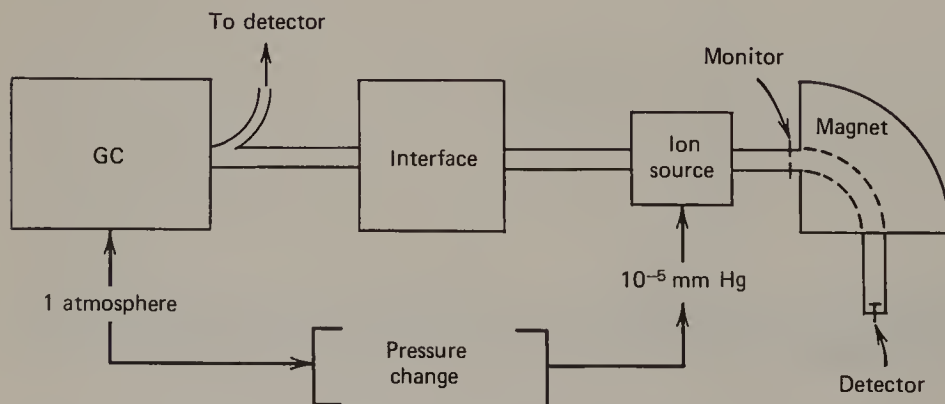


Figure 5. Gas Chromatograph-mass spectrometer combination.

intensity are not shown unless they have special significance.

The molecular ion peak is usually the peak of highest mass number except for the isotope peaks. These isotope peaks are present because a certain number of molecules contain heavier isotopes than the common isotopes. We shall show how the intensities of the isotope peaks relative to the parent peak can lead to the determination of a molecular formula. In a separate table accompanying the mass spectral graphs in the problems in Chapters 7 and 8, the molecular ion peak is given an intensity of 100%, and the isotope peak intensities are given relative to the molecular ion peak intensity (Figure 2b).

If an ion ( $m_1$ ) fragments after acceleration but before entering the magnetic field, it will have been accelerated as mass  $m_1$  but dispersed in the magnetic field as  $m_2$ . The resulting ion current will be recorded as a low-intensity, broad peak at apparent mass  $m^*$ . The numerical value of  $m^*$  is given by

$$m^* = \frac{(m_2)^2}{m_1}$$

The peak caused by the ion current corresponding to mass  $m^*$  is called a *metastable peak*. Measurement of the mass of the metastable peak affords information that  $m_2$  is derived directly from  $m_1$  by loss of a neutral fragment. An example of a metastable peak is the broad peak at about  $m/e$  90 in Figure 2a. The  $m_1$  peak is the molecular ion ( $m/e$  92) and the  $m_2$  peak is at  $m/e$  91. Although this technique is useful in interpretations of spectra, it will not be used in this book. Its use is discussed in References 1, 4, and 5.

#### IV. DETERMINATION OF A MOLECULAR FORMULA

A unique molecular formula (or fragment formula) can often be derived from a sufficiently accurate mass measurement alone (high-resolution mass spectrometry). This is possible because the atomic masses are not integers (see Table I). For example, we can distinguish at a nominal mass of 28 among CO, N<sub>2</sub>, CH<sub>2</sub>N, and C<sub>2</sub>H<sub>4</sub>:

|                 |         |                              |         |                             |         |                              |         |
|-----------------|---------|------------------------------|---------|-----------------------------|---------|------------------------------|---------|
| <sup>12</sup> C | 12.0000 | <sup>14</sup> N <sub>2</sub> | 28.0062 | <sup>12</sup> C             | 12.0000 | <sup>12</sup> C <sub>2</sub> | 24.0000 |
| <sup>16</sup> O | 15.9949 |                              |         | <sup>1</sup> H <sub>2</sub> | 2.0156  | <sup>1</sup> H <sub>4</sub>  | 4.0312  |
|                 | 27.9949 |                              |         | <sup>14</sup> N             | 14.0031 |                              | 28.0312 |
|                 |         |                              |         |                             | 28.0187 |                              |         |

Thus, the mass observed for the molecular ion of CO is the sum of the exact masses of the most abundant isotope of carbon and of oxygen. This differs from a molecular weight of CO based on atomic weights that are the average of weights of all natural isotopes of an element (e.g., C =

Table I. Exact Masses of Isotopes

| Element    | Atomic Weight | Nuclide             | Mass           |
|------------|---------------|---------------------|----------------|
| Hydrogen   | 1.00797       | <sup>1</sup> H      | 1.00783        |
|            |               | D ( <sup>2</sup> H) | 2.01410        |
| Carbon     | 12.01115      | <sup>12</sup> C     | 12.00000 (std) |
|            |               | <sup>13</sup> C     | 13.00336       |
| Nitrogen   | 14.0067       | <sup>14</sup> N     | 14.0031        |
|            |               | <sup>15</sup> N     | 15.0001        |
| Oxygen     | 15.9994       | <sup>16</sup> O     | 15.9949        |
|            |               | <sup>17</sup> O     | 16.9991        |
|            |               | <sup>18</sup> O     | 17.9992        |
| Fluorine   | 18.9984       | <sup>19</sup> F     | 18.9984        |
| Silicon    | 28.086        | <sup>28</sup> Si    | 27.9769        |
|            |               | <sup>29</sup> Si    | 28.9765        |
|            |               | <sup>30</sup> Si    | 29.9738        |
| Phosphorus | 30.974        | <sup>31</sup> P     | 30.9738        |
| Sulfur     | 32.064        | <sup>32</sup> S     | 31.9721        |
|            |               | <sup>33</sup> S     | 32.9715        |
|            |               | <sup>34</sup> S     | 33.9679        |
|            |               | <sup>35</sup> S     | 35.9671        |
| Chlorine   | 35.453        | <sup>35</sup> Cl    | 34.9689        |
|            |               | <sup>37</sup> Cl    | 36.9659        |
| Bromine    | 79.909        | <sup>79</sup> Br    | 78.9183        |
|            |               | <sup>81</sup> Br    | 80.9163        |
| Iodine     | 126.904       | <sup>127</sup> I    | 126.9045       |

12.01, O = 15.999). It is a tedious task to find a molecular formula by arithmetic trial and error from the output of a high-resolution mass spectrometer. Tables (Appendix A), algorithms, and computer programs have been assembled for this purpose.<sup>13,18,21,23,24</sup> We will use unit mass resolution results and intensities of isotope peaks to arrive at possible molecular formulas, since most laboratories have limited access to high-resolution spectrometers. Determination of a possible molecular formula from the isotope peak intensities is limited to the cases in which the molecular ion peak is relatively intense so that the isotope peaks are large enough to be measured accurately. In a high-resolution spectrum, the position of even a very weak molecular ion peak can be accurately measured.

Table II lists the principal stable isotopes of the common elements and their relative abundance calculated on the basis of 100 molecules containing the most common isotope. Note that this presentation differs from many isotope abundance tables in which the sum of all the isotopes of an element adds up to 100%.

Suppose that a compound contains 1 carbon atom. Then for every 100 molecules containing a <sup>12</sup>C atom, about 1.08 "molecules" contain a <sup>13</sup>C atom, and these molecules will produce an  $M + 1$  peak of about 1.08% the intensity of the molecular ion peak; the <sup>2</sup>H atoms present will make an additional very small contribution to the  $M + 1$  peak. If a compound contains one sulfur atom, the  $M + 2$  peak will be about 4.4% of the parent peak. The  $M + 1$  and  $M + 2$  peaks are so designated in Figure 2.



Selection of likely molecular formulas appropriate to particular mass and isotope abundance measurements is greatly facilitated by the table constructed by Beynon.\* This table, which had later been extended<sup>18</sup> to mass 500, can be used for high resolution mass spectrometry. Beyond about mass 250, use of the isotopes to determine a molecular formula loses its effectiveness. A reduced, modified version of Beynon's table is presented as Appendix A. Its use will become more evident as we work through the spectra in this book. In practice, the measured isotope peaks are usually slightly higher than the calculated contributions because of incomplete resolution, bimolecular collisions (see below), or a contribution from the coincident peak of an impurity. The table is limited to compounds containing C, H, O, and N. The presence of S, Cl, or Br is usually readily apparent because of a large isotope contribution to  $M + 2$ . We shall see that the number of sulfur, chlorine, and bromine atoms can be determined. Iodine, fluorine, and phosphorus are monoisotopic. Their presence can usually be deduced from a suspiciously small  $M + 1$  peak relative to the molecular weight, from the fragmentation pattern, from the other spectra with which we are concerned, or from the history of the compound.

If only C, H, N, O, F, P, I are present, the approximate expected % ( $M + 1$ ) and % ( $M + 2$ ) data can be calculated by use of the following formulas:

$$\begin{aligned} \% (M + 1) &= 100 \left\{ \frac{[M + 1]}{[M]} \right\} \\ &\simeq 1.1 \times \text{number of C atoms} \\ &\quad + 0.36 \times \text{number of N atoms}^\dagger \\ \% (M + 2) &= 100 \left\{ \frac{[M + 2]}{[M]} \right\} \\ &\simeq \frac{(1.1 \times \text{number of C atoms})^2}{200} \\ &\quad + 0.20 \times \text{number of O atoms}^\dagger \end{aligned}$$

These equations are useful for cases in which one has a preconceived notion about the molecular formula for the compound of interest.

It is difficult to overemphasize the importance of locating the molecular ion peak. It will be stressed again that this gives an exact numerical molecular weight. Even in cases in which the molecular ion peak is very small (and therefore an accurate determination of  $M + 1$  and  $M + 2$  is impossible), only a little extra information can often lead to identification. This information may be available from

\*Beynon's first table is based on O = 16.000000. His expanded table is based on the currently accepted standard, C = 12.000000.

† $[M + 1]$  is the intensity of the  $M + 1$  peak, and  $[M]$  is the intensity of the  $M$  peak.

Table II. Relative Isotope Abundances of Common Elements

| Elements   | Abundance        |     |                  |       |
|------------|------------------|-----|------------------|-------|
| Carbon     | <sup>12</sup> C  | 100 | <sup>13</sup> C  | 1.08  |
| Hydrogen   | <sup>1</sup> H   | 100 | <sup>2</sup> H   | 0.016 |
| Nitrogen   | <sup>14</sup> N  | 100 | <sup>15</sup> N  | 0.38  |
| Oxygen     | <sup>16</sup> O  | 100 | <sup>17</sup> O  | 0.04  |
| Fluorine   | <sup>19</sup> F  | 100 |                  |       |
| Silicon    | <sup>28</sup> Si | 100 | <sup>29</sup> Si | 5.10  |
| Phosphorus | <sup>31</sup> P  | 100 |                  |       |
| Sulfur     | <sup>32</sup> S  | 100 | <sup>33</sup> S  | 0.78  |
| Chlorine   | <sup>35</sup> Cl | 100 | <sup>37</sup> Cl | 32.5  |
| Bromine    | <sup>79</sup> Br | 100 | <sup>81</sup> Br | 98.0  |
| Iodine     | <sup>127</sup> I | 100 |                  |       |

the source and history of the sample, from the fragmentation pattern, and from other spectra. Let us work through the selection of a molecular formula from the isotope abundance data obtained on an organic compound. We are given the following information:

| $m/e$           | %    |
|-----------------|------|
| 150 ( $M$ )     | 100  |
| 151 ( $M + 1$ ) | 10.2 |
| 152 ( $M + 2$ ) | 0.88 |

The molecular ion peak is mass 150; thus we have the molecular weight. The  $M + 2$  peak obviously does not allow for the presence of sulfur or halogen atoms. We look in Appendix A under mass 150. Our  $M + 1$  peak is 10.2% of the parent peak. We list the formulas whose calculated isotope contribution to the  $M + 1$  peak falls—to be arbitrary—between 9.0 and 11.0; we also list the calculated  $M + 2$  values:

| Formula   | $M + 1$ | $M + 2$ |
|---|---------|---------|
| C <sub>7</sub> H <sub>10</sub> N <sub>4</sub>   | 9.25    | 0.38    |
| C <sub>8</sub> H <sub>8</sub> NO <sub>2</sub>   | 9.23    | 0.78    |
| C <sub>8</sub> H <sub>10</sub> N <sub>2</sub> O | 9.61    | 0.61    |
| C <sub>8</sub> H <sub>12</sub> N <sub>3</sub>   | 9.98    | 0.45    |
| C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>   | 9.96    | 0.84    |
| C <sub>9</sub> H <sub>12</sub> NO               | 10.34   | 0.68    |
| C <sub>9</sub> H <sub>14</sub> N <sub>2</sub>   | 10.71   | 0.52    |

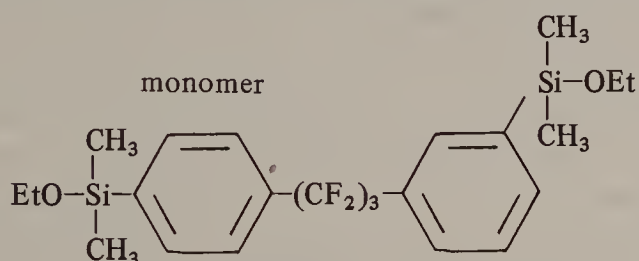
On the basis of the "nitrogen rule" (see Section V), we immediately eliminate three of these formulas because they contain an odd number of nitrogen atoms. Our  $M + 2$  peak is 0.88% of the parent. This best fits C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>. However, C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O cannot be ruled out without additional evidence.



Note that mass 150 is the sum of the masses of the common isotopes of these molecular formulas; the isotope masses used are whole numbers (12 for carbon, 14 for nitrogen, etc.).

When elements other than C, H, O, and N are present, their kind and number must be determined (see the discussion under the appropriate chemical class) and their mass subtracted from the molecular weight. The composition of the remainder of the molecule is then determined from Appendix A.

Quite often the organic chemist must identify a by-product or an unexpected main product from a reaction. Under these circumstances, even rather complex molecules can be handled expeditiously. Since the compound has a history, an intelligent guess can be made as to what elements are present. The following example may be instructive. In the course of polymerizing the fluorinated silicon-containing monomer, a crystalline sublimate was



obtained as a by-product. The parent peak of the mass spectrum of the sublimate was  $m/e$  434, and the base peak,  $m/e$  419 (i.e.,  $M - 15$ ). The  $M + 1$  peak was 31.2% of the molecular ion peak, and the  $M + 2$  peak, 10.4%. On the assumption that the compound contained six fluorine and two silicon atoms, the molecular formula  $C_{19}H_{20}F_6OSi_2$  was written. The intensities of the  $M + 1$  and  $M + 2$  peaks for this formula were calculated as follows:

| Contributor               | $M + 1$ | $M + 2$ | Source      |
|---------------------------|---------|---------|-------------|
| $C_{19}H_{20}$ (mass 248) | 20.85   | 2.06    | Appendix A* |
| O                         | 0.04    | 0.20    | Table II    |
| $F_6$                     | —       | —       | Table II    |
| $Si_2$                    | 10.20†  | 6.70†   | Table II    |
| Sum:                      | 31.09   | 8.96    |             |

\*The C, H, and O content could have been obtained directly from Beynon's extended tables.<sup>4</sup> An alternative method for obtaining C, H, and O contributions is the use of the equations given earlier, thus:

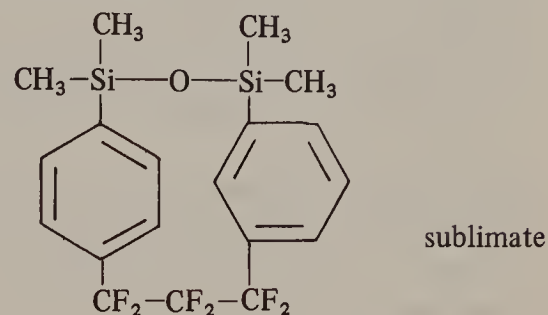
$$\%(M + 1) = (1.1)(19) + (0.36)(0) = 20.9\% \text{ of parent}$$

$$\%(M + 2) = [(1.1)(19)]^2/200 + 0.20(1) = 2.38\% \text{ of parent}$$

†  $2 \times$  (contribution to  $M + 1$  or  $M + 2$  per Si atom).

The good agreement between the calculated and the determined values provided strong support for the molecular formula written. This information combined with the

fragmentation pattern and the infrared and NMR spectra led to the following structure.



The foregoing is a good example of both the possibilities and limitations of spectrometric identification without any chemical manipulation on the compound. It is doubtful that even an experienced mass spectrometrists would have derived a molecular formula without some indication that silicon and fluorine were present. Confirmation is certainly easier than diagnosis.

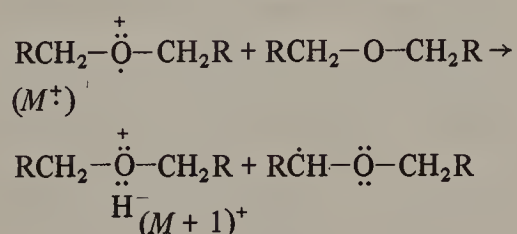
A reasonable amount of caution must be used in developing a molecular formula from the relative intensities of the  $M$ ,  $M + 1$ , and  $M + 2$  peaks. Clearly, if these peaks are small, the error associated with their relative measurements will be large. Several spectra should be obtained to determine the reproducibility of these measurements on a specific instrument. As we shall see in Chapter 5, a  $^{13}C$  NMR spectrum is a powerful aid in establishing the molecular formula.

## V. RECOGNITION OF THE MOLECULAR ION PEAK

There are two situations in which identification of the molecular ion peak may be difficult.

1. The molecular ion does not appear or is very weak. The obvious remedy in most cases is to run the spectrum at maximum sensitivity (and accept the resulting loss in resolution) and to use a larger sample. (Sometimes a large sample exaggerates the  $M + 1$  peak. See below.) Still the molecular ion may not be evident, and other sources of information may be useful. The type of compound may be known, and the molecular mass may be deduced from the breakdown pattern. For example, alcohols usually give a very weak parent molecular ion peak but often show a pronounced peak resulting from loss of water ( $M - 18$ ). A combustion analysis together with consideration of the fragmentation pattern may help us to arrive at the parent mass. Preparation of a suitable derivative is another device.
2. The molecular ion is present but is one of several peaks which may be as prominent or even more prominent. In this situation, the first question is that of purity. If the compound can be assumed to be pure, the usual problem is to distinguish the molecular ion peak from a more

prominent  $M - 1$  peak. One good test is to reduce the energy of the bombarding electron beam to near the appearance potential. This will reduce the intensities of all peaks, but will increase the intensity of the molecular ion relative to other peaks, including fragmentation peaks (but not molecular ion peaks) of impurities. Another test frequently used is to increase the size of the sample, or increase the time the sample spends in the ionization chamber by decreasing the ion repeller voltage. In either case, the net effect is to increase the opportunity for bimolecular collisions to occur in the ion chamber. The most common result of a bimolecular collision of a molecular ion containing a heteroatom (O, N, or S) is a contribution to the  $M + 1$  peak (i.e., the net effect is the transfer of a hydrogen atom from a neutral molecule to the molecular ion).



Thus, an increase in peak size relative to other peaks, as sample size is increased or the repeller voltage is decreased, designates that peak as the  $M + 1$  peak and affords an indirect identification of the molecular ion. Of course, the dependence of the  $M + 1$  peak on sample size must be kept in mind when this peak is used to establish a molecular formula of a compound containing a heteroatom.

Many peaks can be ruled out as possible molecular ions simply on grounds of reasonable structure requirements. The "nitrogen rule" is often helpful in this regard. It states that a molecule of even-numbered molecular weight must contain no nitrogen or an even number of nitrogen atoms; an odd-numbered molecular weight requires an odd number of nitrogen atoms. This rule holds for all compounds containing carbon, hydrogen, oxygen, nitrogen, sulfur, and the halogens, as well as many of the less usual atoms such as phosphorus, boron, silicon, arsenic, and the alkaline earths. A useful corollary states that fragmentation at a single bond gives an odd-numbered ion fragment from an even-numbered molecular ion, and an even-numbered ion fragment from an odd-numbered molecular ion. For this corollary to hold, the ion fragment must contain all of the nitrogen (if any) of the molecular ion. Consideration of the breakdown pattern coupled with other information will also assist in identifying molecular ions. It should be kept in mind that Appendix A contains fragment formulas as well as molecular formulas. Some of the formulas may be regarded as trivial when used in attempts to solve practical problems.

The presence of appreciable amounts of impurities that give rise to prominent peaks near the molecular ion can be troublesome. Here again, the expediency of reducing the

energy of the electron beam will cause a relative increase in the intensity of the molecular ion peak (and also of the molecular ion peak of an impurity). The fragmentation pattern will often furnish clues.

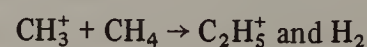
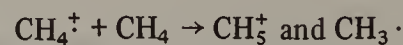
Another useful technique for detection of impurities is microeffusiometry. A fixed volume of sample is allowed to flow through a molecular leak, and the logarithms of the intensities of the peaks in question are plotted as a function of time. All peaks belonging to the same molecule will give lines of the same slope. Those due to other components of different volatility will give lines of different slopes. In essence, a fractionation is effected.

The intensity of the molecular ion peak depends on the stability of the molecular ion. The most stable molecular ions are those of purely aromatic systems. If substituents that have favorable modes of cleavage are present, the molecular ion peak will be less intense, and the fragment peaks relatively more intense. In general, the following group of compounds will, in order of decreasing ability, give prominent molecular ion peaks: aromatic compounds > conjugated alkenes > cyclic compounds > organic sulfides > short, normal alkanes > mercaptans. Recognizable molecular ions are usually produced for these compound in order of decreasing ability: ketones > amines > esters > ethers > carboxylic acids ~ aldehydes ~ amides ~ halides. The molecular ion is frequently not detectable in aliphatic alcohols, nitrites, nitrates, nitro compounds, nitriles, and in highly branched compounds.

The presence of an  $M - 15$  peak (loss of  $\text{CH}_3$ ) or an  $M - 18$  peak (loss of  $\text{H}_2\text{O}$ ) or an  $M - 31$  peak (loss of  $\text{OCH}_3$  from methyl esters), etc., is taken as confirmation of a molecular ion peak. An  $M - 1$  peak is common, and occasionally an  $M - 2$  peak (loss of  $\text{H}_2$  by either fragmentation or thermolysis), or even a rare  $M - 3$  peak (from alcohols) is reasonable. Peaks in the range of  $M - 3$  to  $M - 14$ , however, indicate that contaminants may be present or that the presumed molecular ion peak is actually a fragment ion peak. Losses of fragments of masses 19 to 25 are also unlikely (except for loss of  $F = 19$  or  $\text{HF} = 20$  from fluorinated compounds). Loss of 16 (O), 17 (OH), or 18 ( $\text{H}_2\text{O}$ ) are likely only if an oxygen atom is in the molecule.

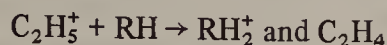
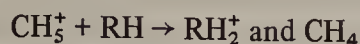
In addition to the electron impact (EI) method described above, several promising techniques have been developed for obtaining and locating the molecular ion peak for compounds that give very weak or nonexistent molecular ions.

In chemical ionization (CI) the sample is introduced near atmospheric pressure with a carrier gas, such as methane. The methane is ionized by electron impact to the primary ions:  $\text{CH}_4^+ + \text{CH}_3^+$ , etc. These react with the excess methane to give secondary ions:

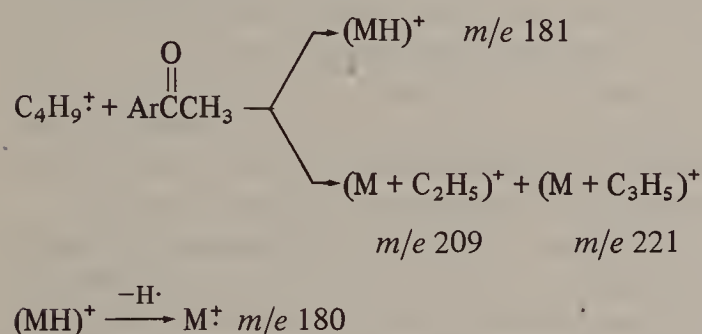




The secondary ions react with the sample (RH):



These  $M + 1$  ions (*quasi-molecular ions*) are often prominent. They can fragment (loss of  $\text{H}_2$ ) to give prominent  $M - 1$  ions. Since the  $M + 1$  ions that are chemically produced do not have the great excess of energy associated with ionization by electron impact, they undergo less fragmentation. For example, the EI spectrum of 3,4-dimethoxyacetophenone shows, in addition to the molecular ion at  $m/e$  180, 49 fragment peaks in the range of  $m/e$  40-167; these include the base peak at  $m/e$  165 and prominent peaks at  $m/e$  137 and  $m/e$  77. The CI spectrum shows the quasi-molecular ion ( $\text{MH}^+$ ,  $m/e$  181) as the base peak (100%) and virtually the only other peaks, each of just a few % intensity, are the molecular ion peak,  $m/e$  180, and  $m/e$  209 and 221 peaks due to the transfer of carbocations from the protonated carrier gas (butane) to the ketone.



Field ionization (FI) is a technique that, like CI and EI techniques, requires a reasonable concentration of the sample in the gas phase. In FI spectrometry, gaseous sample molecules approach a sharp metal surface that has a high positive potential ( $10^8$  volts/cm), which causes an electron to "tunnel" from the sample molecule to the metal surface. This process occurs without exciting the sample molecules, and, since the molecular ion is quickly accelerated, the time scale for analysis is much shorter than for EI spectrometry. Thus, there is less fragmentation with a more intense molecular ion peak.

Molecular ions can be obtained from samples of very low volatility by the field desorption (FD) technique. Here the solid sample is placed directly on the field ion emitter. The ion source is operated only slightly above room temperature, and the ions produced thus have little or no internal energy. Since the internal energy necessary for fragmentation is not present, predominantly molecular ions are formed. These ions are desorbed from the solid by a strong electric field. Related techniques include plasma desorption (PD) mass spectrometry, in which  $^{252}\text{Cf}$  fission fragments provide short energy pulses that vaporize the solid samples. The vaporized sample particle quickly forms molecular or quasi-molecular ions, and these ions are

immediately accelerated. Ionization takes place quickly and little energy is converted to vibrational motion. Most of the ion's energy is used for translational motion. Thus, molecular ions or quasi-molecular ions of substantial intensity are produced. Similar procedures in which the short pulse of energy is provided by a laser have been developed.

Applications and comparisons of EI, CI, FI, and FD techniques are illustrated in the portion on natural products. (See Figures 17-19 and related text.)

## VI. USE OF THE MOLECULAR FORMULA

If an organic chemist had to choose a single item of information above all others that are usually available to him from spectra or from chemical manipulations, he would certainly choose the molecular formula.

In addition to the kinds and numbers of atoms, the molecular formula gives the index of hydrogen deficiency. The index of hydrogen deficiency is the number of *pairs* of hydrogen atoms that must be removed from the "saturated" formula (e.g.,  $\text{C}_n\text{H}_{2n+2}$  for alkanes) to produce the molecular formula of the compound of interest. The index of hydrogen deficiency has also been called the number of "sites (or degrees) of unsaturation"; this description is unsatisfactory since hydrogen deficiency can be due to cyclic structure features as well as to multiple bonds. The index is thus the sum of the number of rings, the number of double bonds, and twice the number of triple bonds.

The index of hydrogen deficiency can be calculated for compounds containing carbon, hydrogen, nitrogen, halogen, oxygen, and sulfur from the formula

$$\text{Index} = \text{carbons} - \frac{\text{hydrogens}}{2} - \frac{\text{halogens}}{2} + \frac{\text{nitrogens}}{2} + 1$$

Thus, the compound  $\text{C}_7\text{H}_7\text{NO}$  has an index of  $7 - 3.5 - 0.5 + 1 = 4$ . Note that divalent atoms (oxygen and sulfur) are not counted in the formula.

For the generalized molecular formula  $\alpha_I\beta_{II}\gamma_{III}\delta_{IV}$ , the index =  $\text{IV} - \text{I}/2 + \text{III}/2 + 1$ , where

$\alpha$  is H,D or halogen (i.e., any monovalent atom)

$\beta$  is O,S or any other bivalent atom

$\gamma$  is N,P or any other trivalent atom.

$\delta$  is C,Si or any other tetravalent atom

I,II,III, and IV designate the numbers of the mono-, di-, tri-, and tetravalent atoms, respectively.

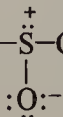
For simple molecular formulas, we can arrive at the index by comparison of the formula of interest with the molecular formula of the corresponding saturated com-



pound. Compare  $C_6H_6$  and  $C_6H_{14}$ ; the index is 4 for the former and 0 for the latter.

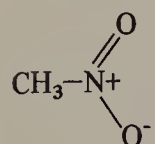
Polar structures must be used for compounds containing an atom in a higher valence state, such as sulfur or phosphorus. Thus, if we treat sulfur in dimethyl sulfoxide formally as a divalent atom, the calculated index, zero, is

compatible with the structure  $CH_3-\overset{+}{S}-CH_3$ . We must use



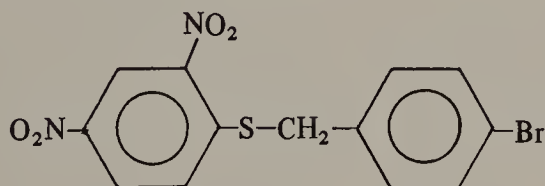
only formulas with filled valence shells; that is, the Lewis octet rule must be obeyed.

Similarly, if we treat the nitrogen in nitromethane as a trivalent atom, the index is 1, which is compatible with



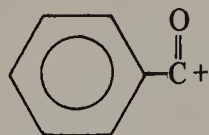
. If we treat phosphorus in triphenylphosphine

oxide as trivalent, the index is 12, which fits  $(C_6H_5)_3P^+-O^-$ . As an example, consider the molecular formula  $C_{13}H_9N_2O_4BrS$ . The index of hydrogen deficiency would be  $13 - 10/2 + 2/2 + 1 = 10$  and a consistent structure would be:



(Index of hydrogen deficiency = 4 per benzene ring and 1 per  $NO_2$  group.)

The formula above for the index can be applied to fragment ions as well as to the molecular ion. When it is applied to even-electron (all electrons paired) ions, the result is always an odd multiple of 0.5. As an example, consider  $C_7H_5O^+$  with an index of 5.5. A reasonable structure is



since  $5\frac{1}{2}$  pairs of hydrogens would be necessary to obtain the corresponding saturated formula  $C_7H_{16}O(C_nH_{2n+2}O)$ . Odd-electron fragment ions will always give integer values of the index.

Terpenes often present a choice between a double bond and a ring structure. This question can readily be resolved on a microgram scale by catalytically hydrogenating the compound and rerunning the mass spectrum. If no other easily reducible groups are present, the increase in the mass of the molecular peak is a measure of the number of double

bonds; and other "unsaturated sites" must be rings.

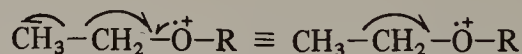
Such simple considerations give the chemist very ready information about structure. As another example, a compound containing a single oxygen atom may quickly be determined to be an ether or a carbonyl compound simply by counting "unsaturated sites."

## VII. FRAGMENTATION

As a first impression, fragmenting a molecule with a huge excess of energy would seem a brute-force approach to molecular structure. The rationalizations used to correlate spectral patterns with structure, however, can only be described as elegant. The insight of such pioneers as McLafferty, Beynon, Stenhagen, Ryhage, and Meyerson have led to a number of rational mechanisms for fragmentation. These have been masterfully summarized and elaborated by Biemann.

Generally, the tendency has been to represent the molecular ion with a delocalized charge. Djerassi's approach has been to localize the positive charge on either a  $\pi$  bond (except in conjugated systems), or on a heteroatom. Whether or not this concept is totally rigorous, it is at the least a *pedagogic tour de force*. We shall use such locally charged molecular ions in this book.

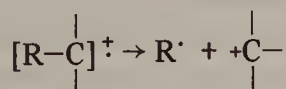
A single-barbed fishhook ( $\curvearrowright$ ) designates the shift of a single electron. Cleavage of a bond requires the movement of two electrons. However, to prevent clutter, only one of a pair of fishhooks will be drawn. This practice can be illustrated for cleavage of a C—C bond next to a heteroatom:



The probability of cleavage of a particular bond is related to the bond strength, to the possibility of low-energy transitions, and to the stability of the fragments both charged and uncharged formed in the fragmentation process. Our knowledge of pyrolytic cleavages can be used, to some extent, to predict likely modes of cleavage of the molecular ion. Because of the extremely low vapor pressure in the mass spectrometer, there are very few fragment collisions; we are dealing largely with unimolecular decompositions. This assumption, backed by a file of reference spectra, is the basis for the vast amount of information available from the fragmentation pattern of a molecule. Whereas conventional organic chemistry deals with reactions initiated by chemical reagents, by thermal energy, or by light, mass spectrometry is concerned with the consequences suffered by an organic molecule struck by an ionizing electronic beam at a vapor pressure of about  $10^{-5}$  mm Hg.

A number of general rules for predicting prominent peaks in electron impact spectra can be written and rationalized by using standard concepts of physical organic chemistry:

1. The relative height of the molecular ion peak is greatest for the straight-chain compound and decreases as the degree of branching increases. (See Rule 3.)
2. The relative height of the molecular ion peak usually decreases with increasing molecular weight in a homologous series. Fatty esters appear to be an exception.
3. Cleavage is favored at alkyl substituted carbons; the more substituted, the more likely is cleavage. This is a consequence of the increased stability of a tertiary carbocation over a secondary, which in turn is more stable than a primary.

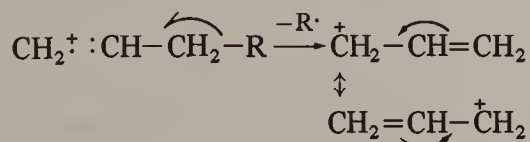


Cation stability order:

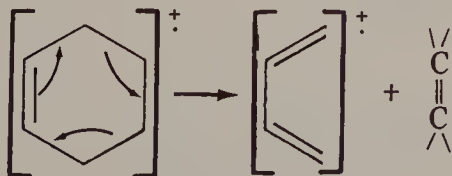


Generally, the largest substituent at a branch is eliminated most readily as a radical, presumably because a long-chain radical can achieve some stability by delocalization of the lone electron.

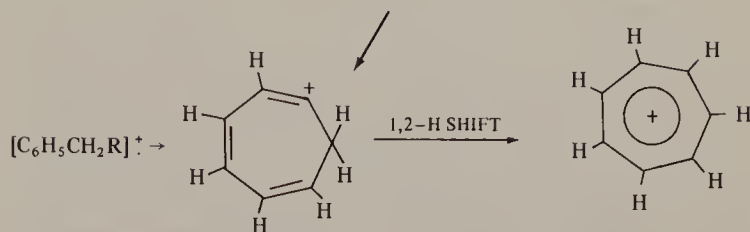
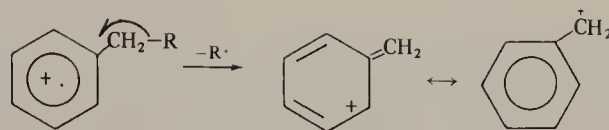
4. Double bonds, cyclic structures, and especially aromatic (or heteroaromatic) rings stabilize the molecular ion, and thus increase the probability of its appearance.
5. Double bonds favor allylic cleavage and give the resonance-stabilized allylic carbonium ion.



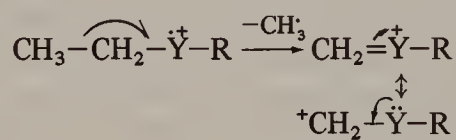
6. Saturated rings tend to lose side chains at the  $\alpha$ -bond. This is merely a special case of branching (Rule 3). The positive charge tends to stay with the ring fragment. Unsaturated rings can undergo a *retro*-Diels-Alder reaction:



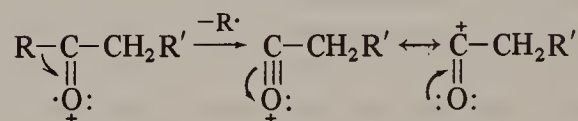
7. In alkyl-substituted aromatic compounds, cleavage is very probable at the bond beta to the ring, giving the resonance-stabilized benzyl ion or, more likely, the tropylium ion:



8. C—C bonds next to a heteroatom are frequently cleaved, leaving the charge on the fragment containing the heteroatom whose nonbonding electrons provide resonance stabilization.



Y = O, N, or S



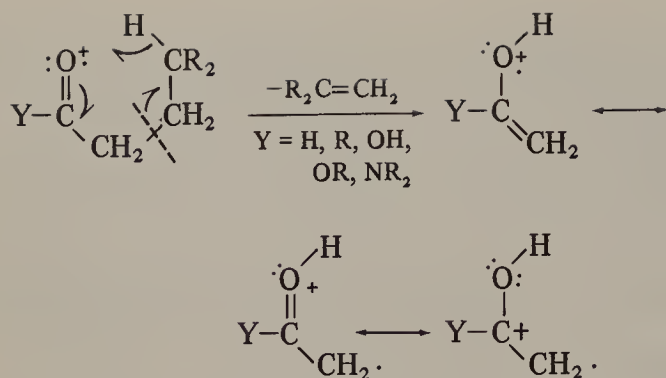
9. Cleavage is often associated with elimination of small stable neutral molecules, such as carbon monoxide, olefins, water, ammonia, hydrogen sulfide, hydrogen cyanide, mercaptans, ketene, or alcohols.

It should be kept in mind that the fragmentation rules above apply to EI mass spectrometry. Since other ionizing (CI, etc.) techniques often produce molecular ions with much lower energy or quasi-molecular ions with very different fragmentation patterns, different rules govern the fragmentation of these molecular ions.

## VIII. REARRANGEMENTS

Rearrangement ions are fragments whose origin cannot be described by simple cleavage of bonds in the molecular ion, but are a result of intramolecular atomic rearrangement during fragmentation. Rearrangements involving migration of hydrogen atoms in molecules that contain a heteroatom are especially common. One important example is the so-called McLafferty rearrangement:



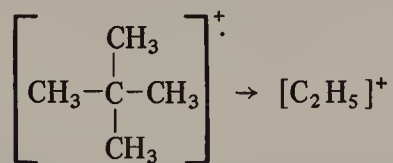


To undergo a McLafferty rearrangement, a molecule must possess: an appropriately located heteroatom (e.g., O), a  $\pi$ -system (usually a double bond) and an abstractable hydrogen  $\gamma$  to the C=O system.

Such rearrangements often account for prominent characteristic peaks and are consequently very useful for our purpose. They can frequently be rationalized on the basis of low-energy transitions and increased stability of the products. Rearrangements resulting in elimination of a stable neutral molecule are common (e.g., the olefin product in the McLafferty rearrangement) and will be encountered in the discussion of mass spectra of chemical classes.

Rearrangement peaks can be recognized by considering the mass ( $m/e$ ) number for fragment ions and for their corresponding molecular ions. A simple (no rearrangement) cleavage of an even-numbered molecular ion gives an odd-numbered fragment ion and simple cleavage of an odd-numbered molecular ion gives an even-numbered fragment. Observation of a fragment ion mass different by 1 unit from that expected for a fragment resulting from simple cleavage (e.g., an even-numbered fragment mass from an even-numbered molecular ion mass) indicates rearrangement of hydrogen has accompanied fragmentation. Rearrangement peaks may be recognized by considering the corollary to the "nitrogen rule" (Section V). Thus, an even-numbered peak derived from an even-numbered molecular ion is a result of two cleavages, which may involve a rearrangement.

"Random" rearrangements of hydrocarbons were noted by the early mass spectrometrists in the petroleum industry. For example:



These rearrangements defy straightforward explanations based on ground-state theory.

## IX. DERIVATIVES

If a compound has low volatility or if the parent mass cannot be determined, it may be possible to prepare a

suitable derivative. The derivative selected should provide enhanced volatility, a predictable mode of cleavage, a simplified fragmentation pattern, or an increased stability of the parent ion.

Compounds containing several polar groups may have very low volatility (e.g., sugars, peptides, and dibasic carboxylic acids). Acetylation of hydroxyl and amino groups and methylation of free acids are obvious and effective choices to increase volatility and give characteristic peaks. Perhaps less immediately obvious is the use of trimethylsilyl derivatives of hydroxyl, amino, sulfhydryl, and carboxylic acid groups. Trimethylsilyl derivatives of sugars and of amino acids are volatile enough to pass through gas chromatographic columns. The molecular ion peak of trimethylsilyl derivatives may not always be present, but the  $M - 15$  peak due to cleavage of one of the Si-CH<sub>3</sub> bonds is always prominent.

Reduction of ketones to hydrocarbons has been used to elucidate the carbon skeleton of the ketone molecule. Polypeptides have been reduced with LiAlH<sub>4</sub> to give polyamino alcohols that are volatile with predictable fragmentation patterns. Methylation and trifluoroacylation of tri- and tetrapeptides have been used to obtain mass spectra.

## X. MASS SPECTRA OF SOME CHEMICAL CLASSES

Mass spectra of a number of chemical classes are briefly described in this section in terms of the most useful generalizations for identification. For more details, the references cited (in particular, the thorough treatment by Budzikiewicz, Djerassi, and Williams)<sup>1-3</sup> should be consulted. The references are selective rather than comprehensive. A table of frequently encountered fragment ions is given in Appendix B. A table of fragments (uncharged) that are commonly eliminated is presented in Appendix C. More exhaustive listings of common fragment ions have been compiled in the books by Hamming and Foster and by McLafferty. The cleavage patterns described here in Section X are for EI spectra, unless stated otherwise.

### HYDROCARBONS

#### *Saturated Hydrocarbons*

Most of the work in mass spectrometry has been done on hydrocarbons of interest to the petroleum industry. Rules 1 to 3 (p. 15) apply quite generally; rearrangement peaks, though common, are not usually intense (random rearrangements), and numerous reference spectra are available.



The molecular ion peak ( $M$ ) of a straight-chain, saturated hydrocarbon is always present, though of low intensity for long-chain compounds. The fragmentation pattern is characterized by clusters of peaks, and the corresponding peaks of each cluster are 14 ( $\text{CH}_2$ ) mass units apart. The largest peak in each cluster represents a  $\text{C}_n\text{H}_{2n+1}$  fragment; this is accompanied by  $\text{C}_n\text{H}_{2n}$  and  $\text{C}_n\text{H}_{2n-1}$  fragments. The most abundant fragments are at  $\text{C}_3$  and  $\text{C}_4$ , and the fragment abundances decrease in a smooth curve down to  $\text{M}-\text{C}_2\text{H}_5$ ; the  $\text{M}-\text{CH}_3$  peak is characteristically very weak or missing. Compounds containing more than 8 carbon atoms show fairly similar spectra; identification then depends on the molecular ion peak.

Spectra of branched saturated hydrocarbons are grossly similar to those of straight-chain compounds, but the smooth curve of decreasing intensities is broken by preferred fragmentation at each branch. The smooth curve for the  $n$ -alkane in Figure 6a is in contrast to the discontinuity at  $\text{C}_{10}$  for the branched alkane (Figure 6b). This discontinuity indicates that the longest branch of 5-methylpentadecane has 10 carbons.

In Figure 6b, the peaks at  $m/e$  169 and 85 represent cleavage on either side of the branch with charge retention on the substituted carbon atom. Subtraction of the molecular weight from the sum of these fragments accounts for

the fragment  $-\text{CH}-\text{CH}_3$ . Again we appreciate the absence of a  $\text{C}_{11}$  unit, which cannot form by a single cleavage. Finally, the presence of a distinct  $\text{M}-15$  peak also indicates a methyl branch. The fragment resulting from cleavage at a branch tends to lose a single hydrogen atom so that the resulting  $\text{C}_n\text{H}_{2n}$  peak is prominent and sometimes more intense than the corresponding  $\text{C}_n\text{H}_{2n+1}$  peak. Random rearrangements are common, and the use of reference compounds for final identification is good practice.

A saturated ring in a hydrocarbon increases the relative intensity of the molecular ion peak, and favors cleavage at the bond connecting the ring to the rest of the molecule (Rule 6, p. 15). Fragmentation of the ring is usually characterized by loss of two carbon atoms as  $\text{C}_2\text{H}_4$  (28) and  $\text{C}_2\text{H}_5$  (29). This tendency to lose even numbered fragments, such as  $\text{C}_2\text{H}_4$ , gives a spectrum that contains a greater proportion of even-numbered mass ions than the spectrum of an acyclic hydrocarbon. As in branched hydrocarbons, C-C cleavage is accompanied by loss of a hydrogen atom. The characteristic peaks are therefore in the  $\text{C}_n\text{H}_{2n-1}$  and  $\text{C}_n\text{H}_{2n-2}$  series.

The mass spectrum of cyclohexane (Figure 6c) shows a much more intense molecular ion than those of acyclic compounds, since fragmentation requires the cleavage of two carbon-carbon bonds. This spectrum has its base peak

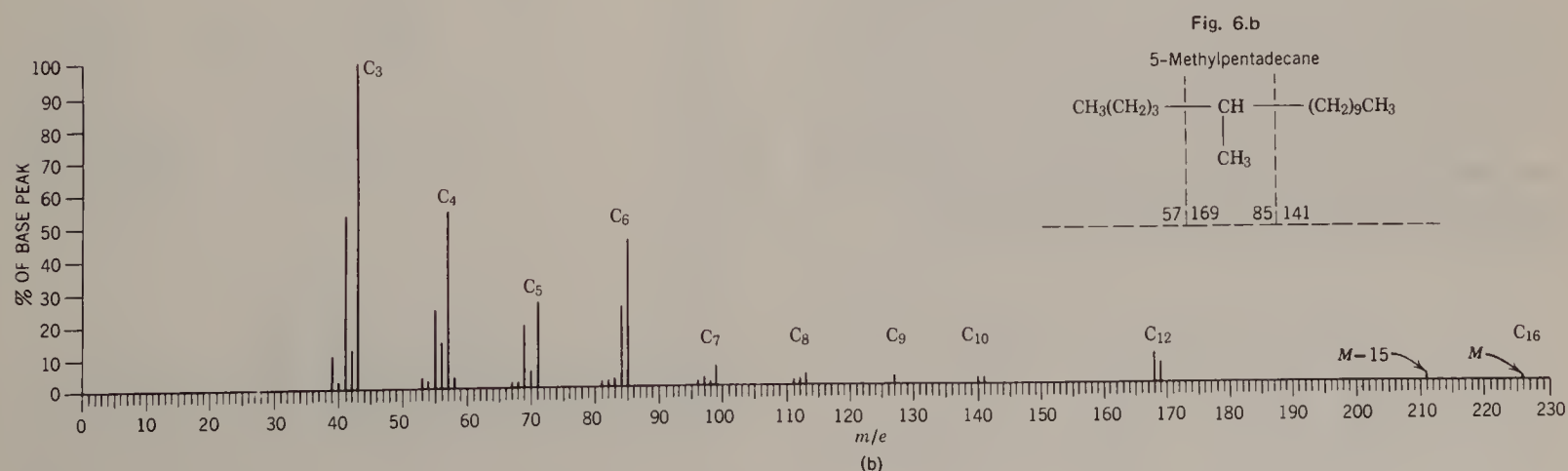
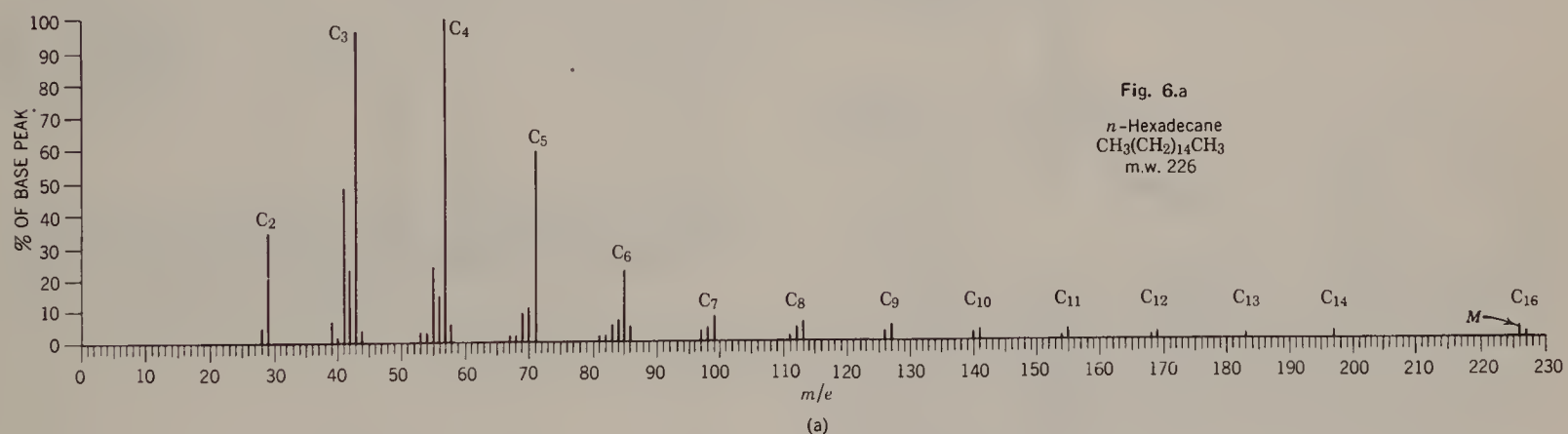


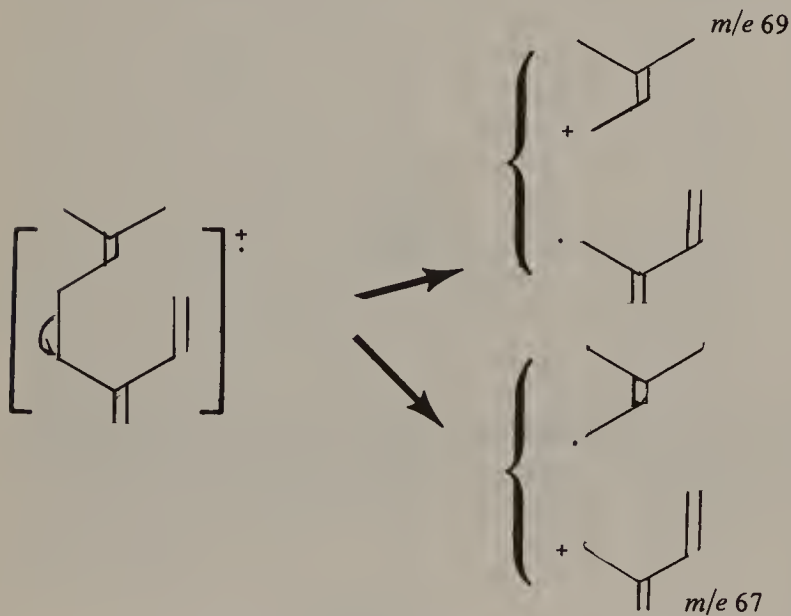
Figure 6 a and b. Isomeric  $\text{C}_{16}$  hydrocarbons.

at  $m/e$  56 (due to loss of  $C_2H_4$ ) and a large peak at  $m/e$  41, which is a fragment in the  $C_nH_{2n-1}$  series with  $n = 3$ .

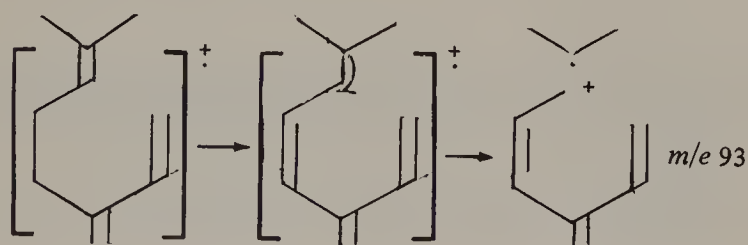
### Olefins

The molecular ion peak of olefins, especially polyolefins, is usually distinct. Location of the double bond in acyclic olefins is difficult because of its facile migration in the fragments. In cyclic (especially polycyclic) olefins, location of the double bond is frequently evident as a result of a strong tendency for allylic cleavage without much double bond migration (Rule 5, p. 15). Conjugation with a carbonyl group also fixes the position of the double bond. As with saturated hydrocarbons, acyclic olefins are characterized by clusters of peaks at intervals of 14 units. In these clusters the  $C_nH_{2n-1}$  and  $C_nH_{2n}$  peaks are more intense than the  $C_nH_{2n+1}$  peaks.

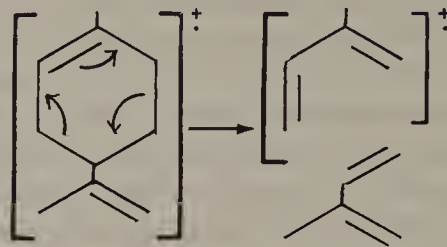
The mass spectrum of  $\beta$ -myrcene, a terpene, is shown in Figure 7. The peaks at  $m/e$  41, 55, and 69 correspond to the formula  $C_nH_{2n-1}$  with  $n = 3, 4$ , and 5, respectively. Formation of the  $m/e$  41 peak must involve rearrangement. The peaks at  $m/e$  67 and 69 are the fragments from cleavage of a bi-allylic bond.



The peak at  $m/e$  93 may be rationalized as a structure of formula  $C_7H_9^+$  formed by isomerization (resulting in increased conjugation), followed by allylic cleavage.



Cyclic olefins usually show a distinct molecular ion peak. A unique mode of cleavage is a type of homolytic *retro*-Diels-Alder reaction as shown by limonene.



### Aromatic and Aralkyl Hydrocarbons

An aromatic ring in a molecule stabilizes the molecular ion peak (Rule 4, p. 15), which is usually sufficiently large that accurate measurements can be made on the  $M+1$  and  $M+2$  peaks.

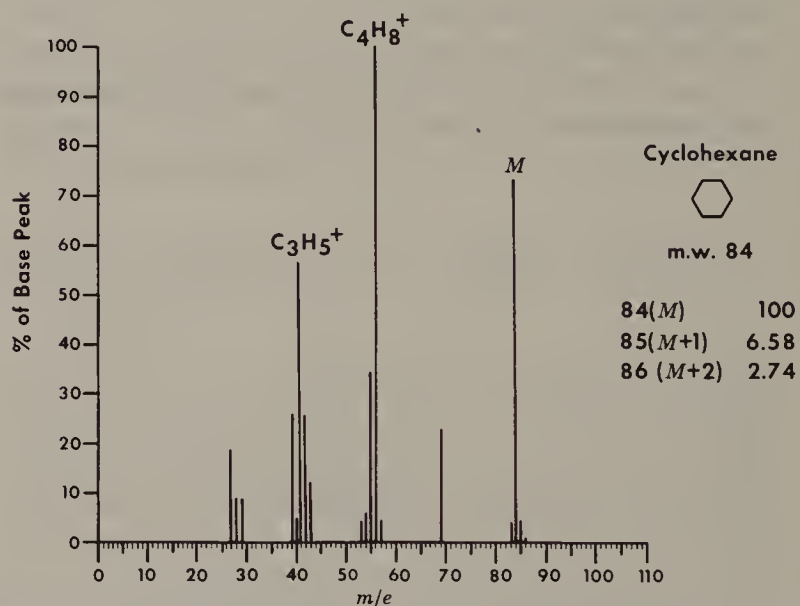


Figure 6c. Cyclohexane.

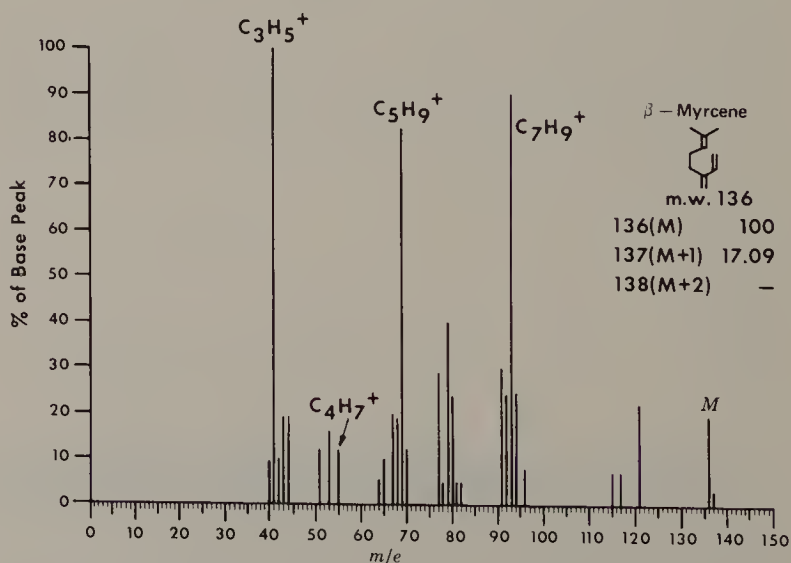
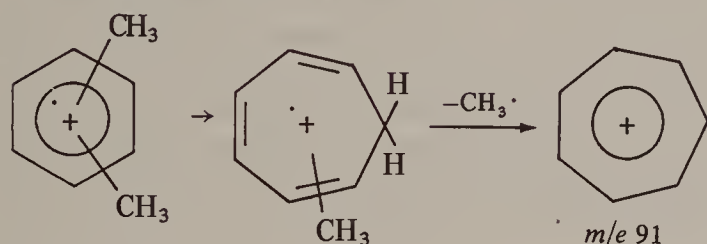


Figure 7.  $\beta$ -Myrcene.

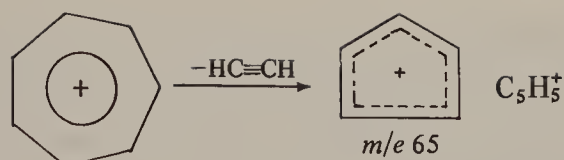
Figure 8 is the mass spectrum of naphthalene. The molecular ion peak is also the base peak, and the largest fragment peak,  $m/e$  51, is only 12.5% as intense as the molecular ion peak.

A prominent peak (often the base peak) at  $m/e$  91 ( $C_6H_5CH_2^+$ ) is indicative of an alkyl substituted benzene ring. Branching at the  $\alpha$ -carbon leads to masses higher than 91 by increments of 14, the largest substituent being eliminated most readily (Rule 3, p. 15). The mere presence of a peak at mass 91, however, does not preclude branching at the  $\alpha$ -carbon because this highly stabilized fragment may result from rearrangements. A distinct and sometimes prominent  $M - 1$  peak results from similar benzylic cleavage of a C-H bond.

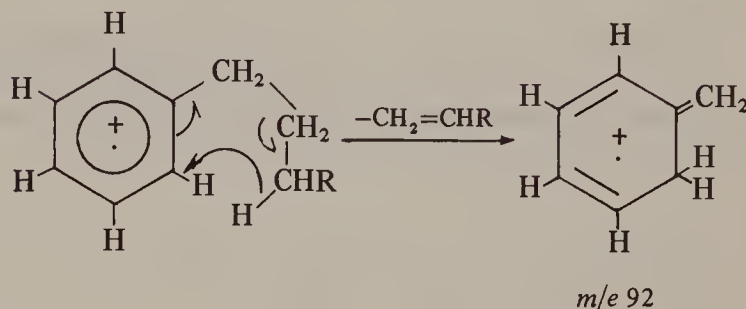
It has been shown that, in most cases, the ion of mass 91 is a tropylium rather than a benzylic cation. This explains the ready loss of a methyl group from xylenes although toluene does not easily lose a methyl group. The incipient molecular ion rearranges to the parent tropylium radical ion, which then cleaves to the simple tropylium ion ( $C_7H_7^+$ ):



The frequently observed peak at  $m/e$  65 results from elimination of a neutral acetylene molecule from the tropylium ion:



Hydrogen migration with elimination of a neutral olefin molecule accounts for the peak at  $m/e$  92 observed when the alkyl group is longer than  $C_2$ .



A characteristic cluster of ions due to  $\alpha$ -cleavage and hydrogen migration in monalkylbenzenes appears at  $m/e$  77 ( $C_6H_5^+$ ), 78 ( $C_6H_6^+$ ), and 79 ( $C_6H_7^+$ ).

Alkylated polyphenyls and alkylated polycyclic aromatic hydrocarbons exhibit the same  $\beta$ -cleavage as alkylbenzene compounds.

## HYDROXY COMPOUNDS

### Alcohols

The molecular ion peak of a primary or secondary alcohol is quite small and for a tertiary alcohol is undetectable. The molecular ion of 1-pentanol is extremely weak compared with its near homologs. The expedients mentioned above may be used to obtain the molecular weight.

Cleavage of the C-C bond next to the oxygen atom is of general occurrence (Rule 8, p. 15). Thus, primary alcohols show a prominent peak due to  $CH_2=\ddot{O}H$  ( $m/e$  31). Secondary and tertiary alcohols cleave analogously to give a prominent

peak due to  $\begin{matrix} R \\ | \\ R' - C = \ddot{O}H \\ | \\ R'' \end{matrix}$  ( $m/e$  45, 59, 73, etc.), and  $\begin{matrix} R \\ | \\ R' - C = \ddot{O}H \\ | \\ R'' \end{matrix}$  ( $m/e$  59, 73, 87, etc.), respectively. The largest substituent is expelled most readily (Rule 3).

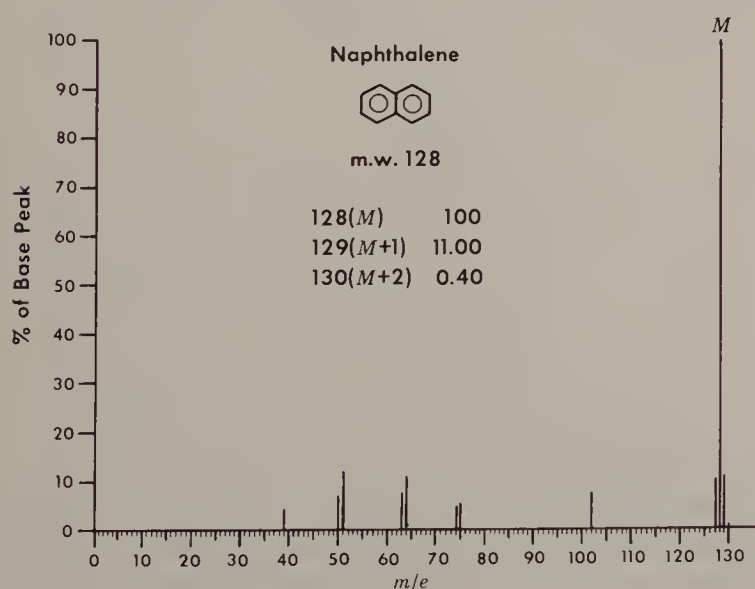
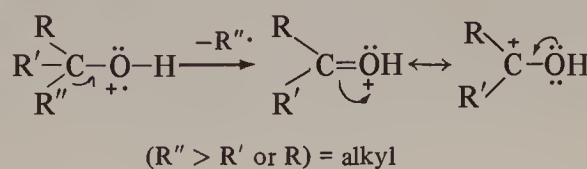


Figure 8. Naphthalene.

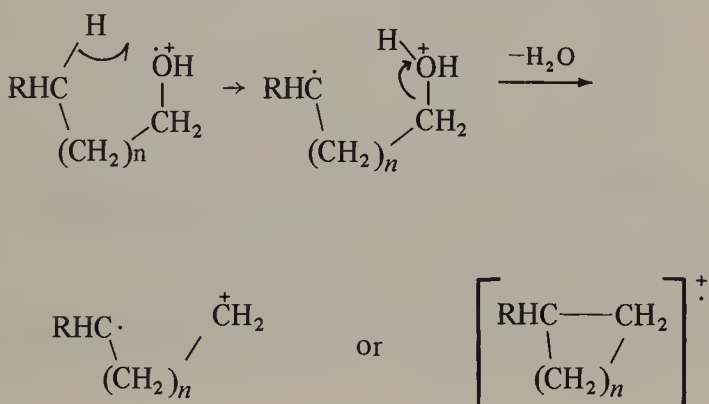


When R and/or R' = H, an  $M - 1$  peak can usually be seen.

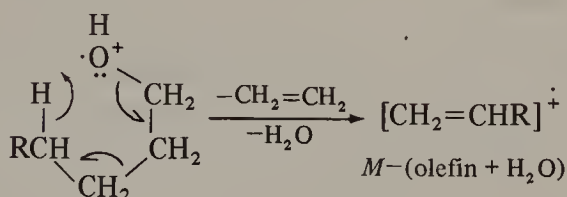
Primary alcohols, in addition to the principal C-C cleavage next to the oxygen atom, show a homologous series of peaks of progressively decreasing intensity resulting from cleavage at C-C bonds successively removed from the oxygen atom. In long-chain ( $> C_6$ ) alcohols, the fragmentation becomes dominated by the hydrocarbon pattern; in fact, the spectrum resembles that of the corresponding olefin.

The spectrum in the vicinity of the very weak or missing molecular ion peak of a primary alcohol is sometimes complicated by weak  $M - 2$  ( $R-CH=\ddot{O}^+$ ) and  $M - 3$  ( $R-C\equiv O^+$ ) peaks.

A distinct and sometimes prominent peak can usually be found at  $M - 18$  from loss of water. This peak is most noticeable in spectra of primary alcohols. This elimination by electron impact has been rationalized as follows:



This pathway is consistent with the loss of the OH and  $\gamma$ -hydrogen ( $n = 1$ ) or  $\delta$ -hydrogen ( $n = 2$ ); the ring structure is not proven by the observations and is merely one possible structure for the product radical cation. The  $M - 18$  peak is frequently exaggerated by thermal decomposition of higher alcohols on hot inlet surfaces. Elimination of water, together with elimination of an olefin from primary alcohols, accounts for the presence of a peak at  $M - (\text{olefin} + H_2O)$ , that is, a peak at  $M - 46$ ,  $M - 74$ ,  $M - 102$ , ...



The olefinic ion then decomposes by successive eliminations of ethylene.

Alcohols containing branched methyl groups (e.g., terpene alcohols) frequently show a fairly strong peak at  $M - 33$  resulting from loss of  $CH_3$  and  $H_2O$ .

Cyclic alcohols undergo fragmentation by complicated

pathways; for example, cyclohexanol ( $M = m/e$  100) forms  $C_6H_{11}O^+$  by simple loss of the  $\alpha$ -hydrogen, loses  $H_2O$  to form  $C_6H_{10}^+$  (which appears to have more than one possible bridged bicyclic structure), and forms  $C_3H_5O^+$  ( $m/e$  57) by a complex ring cleavage pathway.

A peak at  $m/e$  31 (see above) is quite diagnostic for a primary alcohol provided it is more intense than peaks at  $m/e$  45, 59, 73, ... However, the first-formed ion of a secondary alcohol can decompose further to give a moderately intense  $m/e$  31 ion.

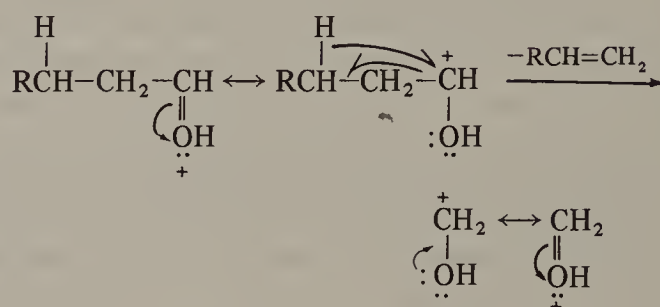
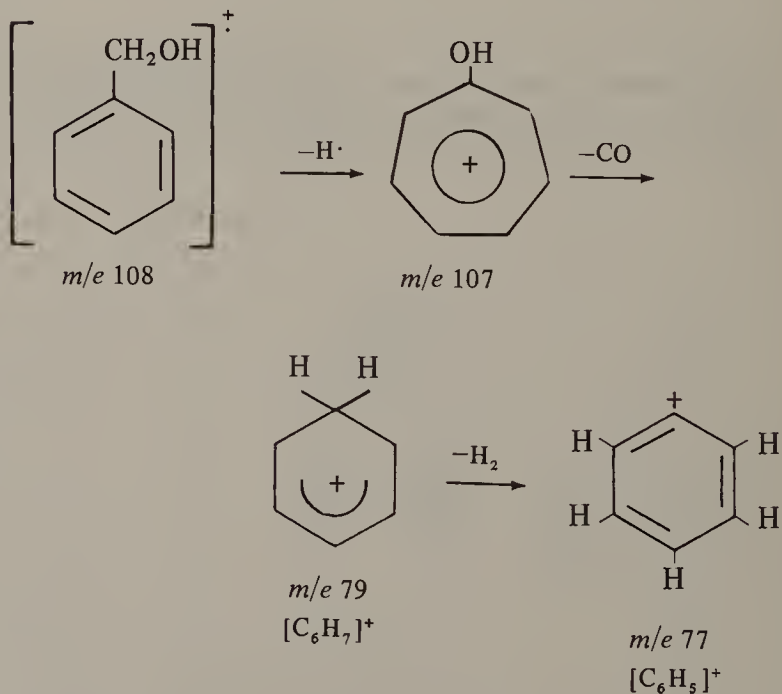


Figure 9 gives the characteristic spectra of isomeric primary, secondary, and tertiary  $C_5$  alcohols.

Benzyl alcohols and their substituted homologs and analogs constitute a distinct class. Generally the parent peak is strong. A moderate benzylic peak ( $M - OH$ ) is present as expected from cleavage beta to the ring. A complicated sequence leads to prominent  $M - 1$ ,  $M - 2$ , and  $M - 3$  peaks. Benzyl alcohol itself fragments to give sequentially the  $M - 1$  ion, the  $C_6H_7$  ion by loss of CO, and the  $C_6H_5$  ion by loss of  $H_2$ :



Loss of  $H_2O$  to give a distinct  $M - 18$  peak is a common feature, especially pronounced and mechanistically straightforward in some ortho-substituted benzyl alcohols.

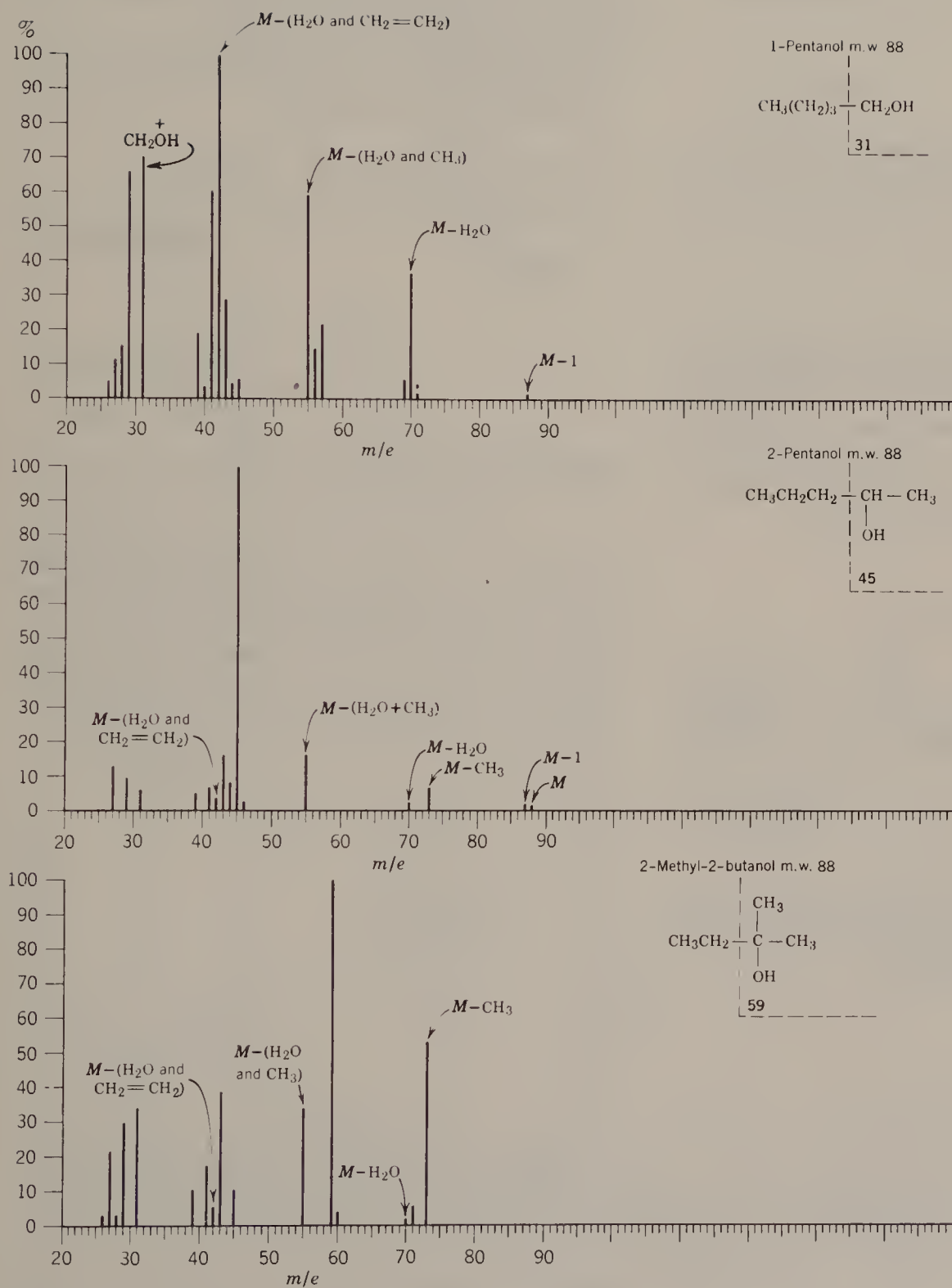
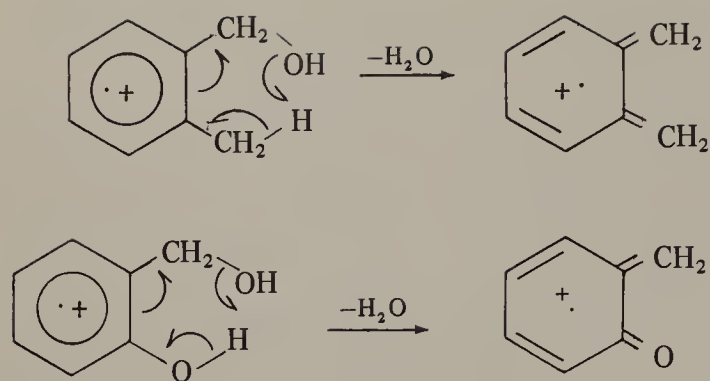


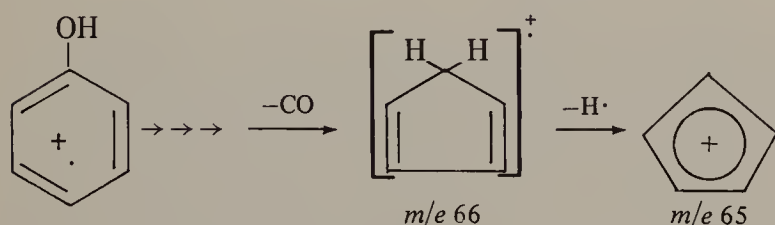
Figure 9. Isomeric pentanols.



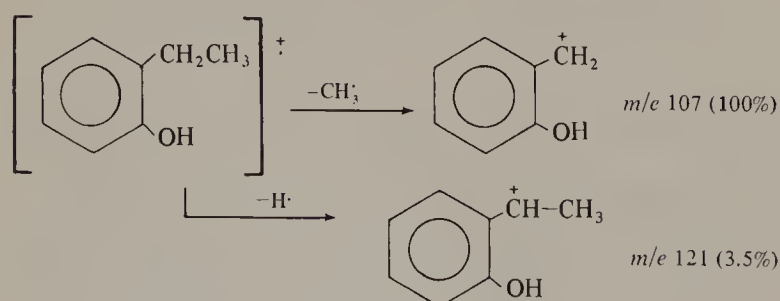
The aromatic cluster at  $m/e$  77, 78, and 79 resulting from complex degradation is prominent here also.

### Phenols

A conspicuous molecular ion peak facilitates identification of phenols. In phenol itself, the molecular ion peak is the base peak, and the  $M - 1$  peak is small. In cresols, the  $M - 1$  peak is larger than the parent peak as a result of a facile benzylic C-H cleavage. A rearrangement peak at  $m/e$  77 and peaks resulting from loss of CO ( $M - 28$ ) and CHO ( $M - 29$ ) are usually found in phenols:



The mass spectrum of a typical phenol is shown in Figure 10. This spectrum shows that a methyl group is lost much more readily than an  $\alpha$ -hydrogen.



## ETHERS

### Aliphatic Ethers

The molecular ion peak (two mass units larger than that of an analogous hydrocarbon) is small, but larger sample size usually will make the molecular ion peak or the  $M + 1$  peak obvious ( $H\cdot$  transfer during ion-molecule collision, see part 2, Section V).

The presence of an oxygen atom can be deduced from strong peaks at  $m/e$  31, 45, 59, 73, .... These peaks represent the  $RO^+$  and  $ROCH_2^+$  fragments.

Fragmentation occurs in two principal ways:

- Cleavage of the C-C bond next to the oxygen atom ( $\alpha$ - $\beta$  bond, Rule 8, Section VII)

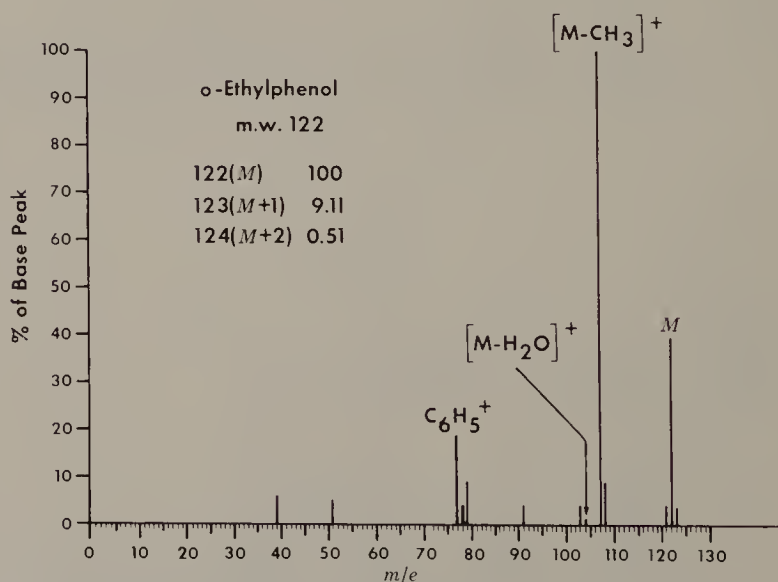
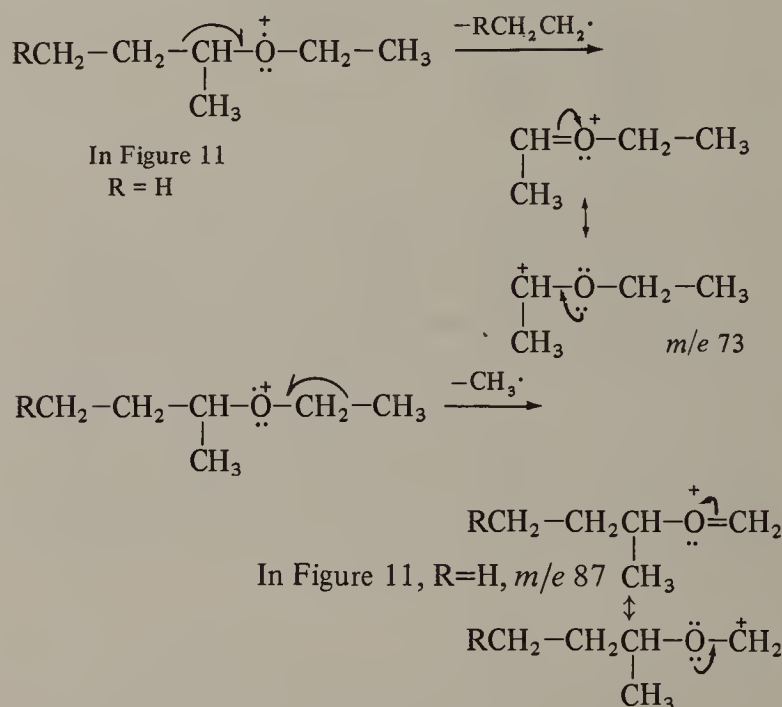
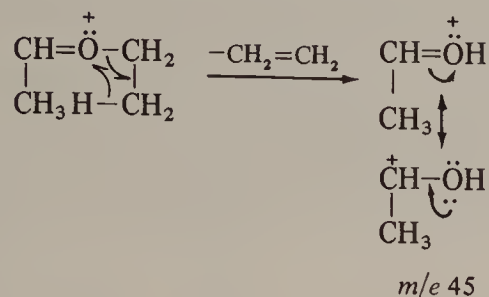


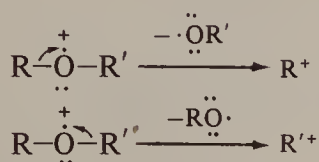
Figure 10. *o*-Ethylphenol.



One or the other of these oxygen-containing ions may account for the base peak. In the case shown, the first cleavage (i.e., at the branch positions to lose the larger fragment) is preferred. However, the first-formed fragment decomposes further by the following process, often to give the base peak (Figure 11); the decomposition is important when the  $\alpha$ -C is substituted.



- b. C-O bond cleavage with the charge remaining on the alkyl fragment.

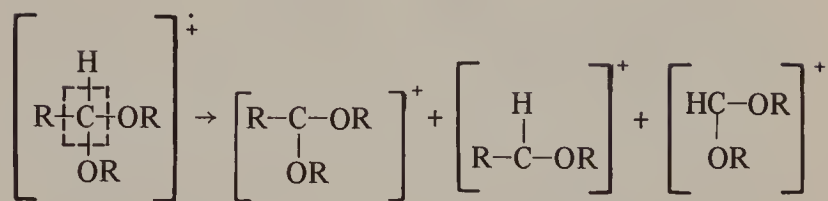


(Rule 8, Section VII)

As expected, the spectrum of long-chain ethers becomes dominated by the hydrocarbon pattern.

Acetals are a special class of ethers. Their mass spectra are characterized by an extremely weak molecular ion peak, by the prominent peaks at  $M$  minus R, and  $M$  minus OR, and a weak peak at  $M$  minus H. Each of these cleavages is mediated by an oxygen atom and thus facile. As usual elimination of the largest group is preferred. As with aliphatic ethers, the first-formed oxygen-con-

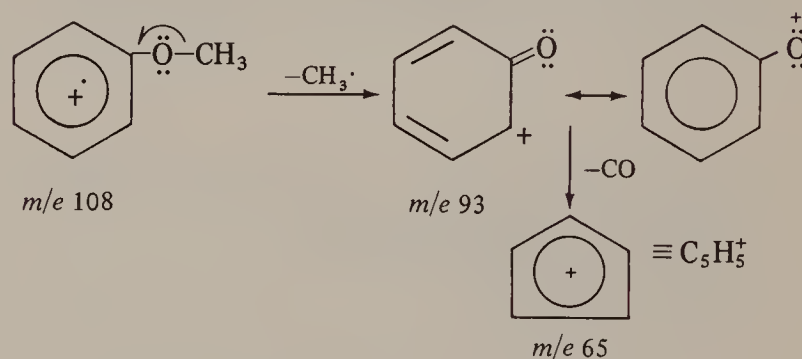
taining fragments can decompose further with hydrogen migration and olefin elimination.



Ketals behave similarly.

### Aromatic Ethers

The molecular ion peak of aromatic ethers is prominent. Primary cleavage occurs at the bond beta to the ring, and the first-formed ion can decompose further. Thus anisole, m.w. 108, gives ions of  $m/e$  93 and 65.



The characteristic aromatic peaks at  $m/e$  78 and 77 may arise from anisole as follows.

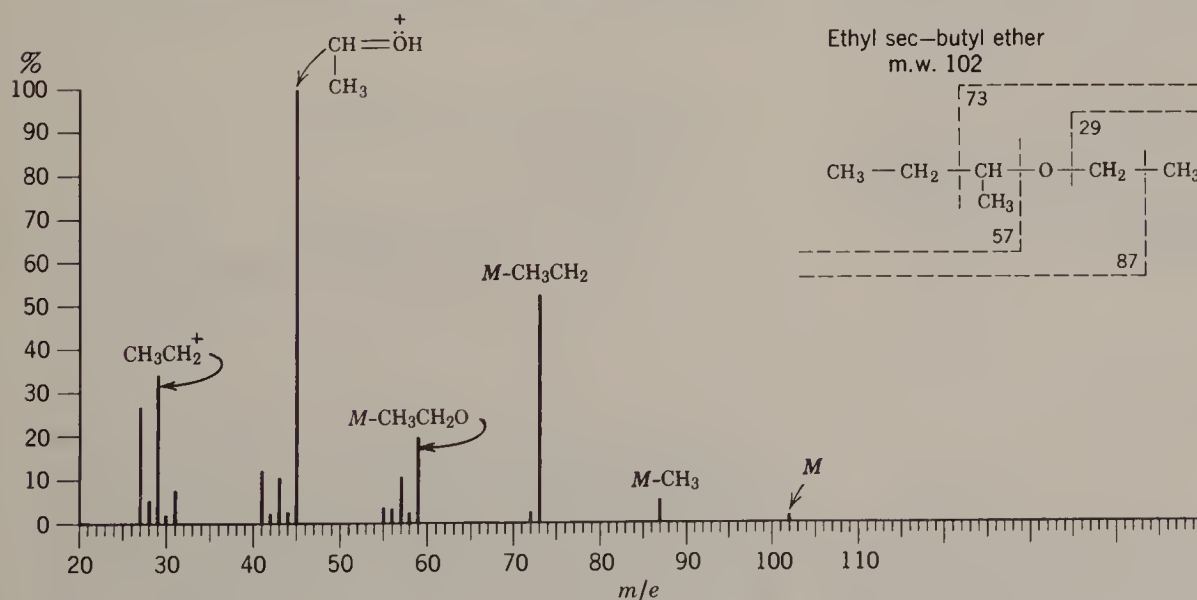
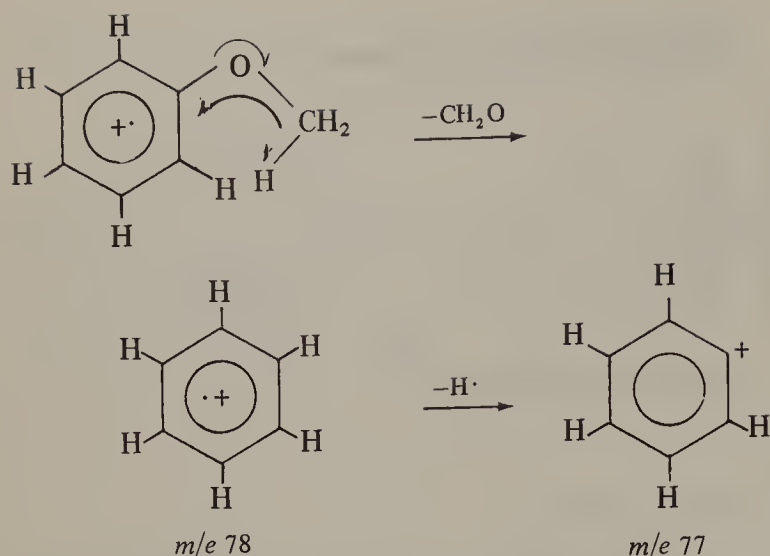
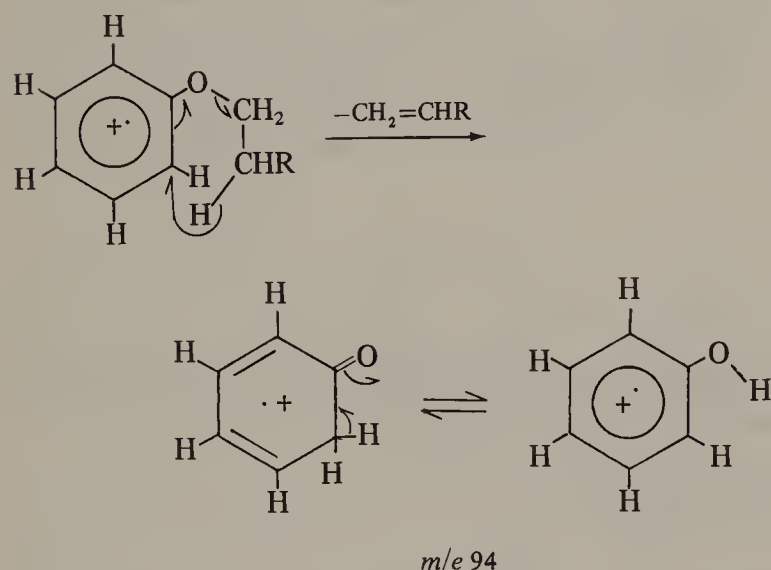


Figure 11. Ethyl sec-butyl ether.



When the alkyl portion of an aromatic alkyl ether is  $C_2$  or larger, cleavage beta to the ring is accompanied by hydrogen migration as noted above for alkylbenzenes. Clearly, cleavage is mediated by the ring rather than by the oxygen atom; C-C cleavage next to the oxygen atom is insignificant.

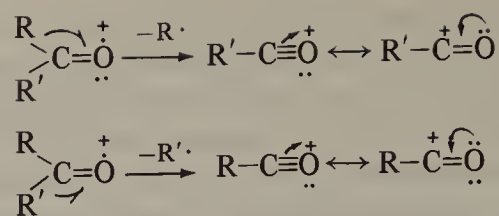


Diphenyl ethers show peaks at  $M - H$ ,  $M - CO$ , and  $M - CHO$  by complex rearrangements.

## KETONES

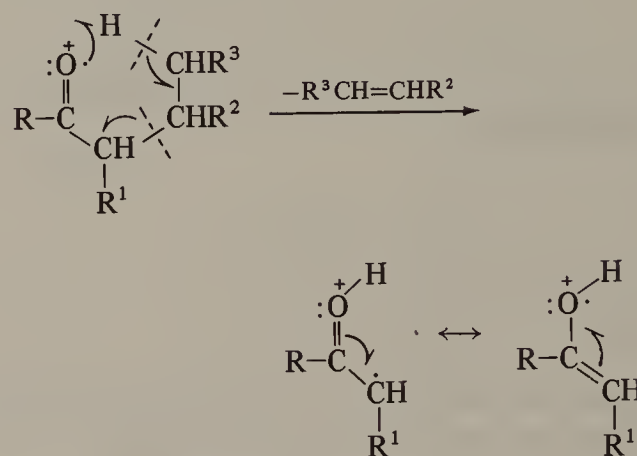
### Aliphatic Ketones

The molecular ion peak of ketones is usually quite pronounced. Major fragmentation peaks of aliphatic ketones result from cleavage at the C-C bonds adjacent to the oxygen atom, the charge remaining with the oxygenated fragment. Thus, as with alcohols and ethers, cleavage is again at the C-C bond next to the oxygen atom.



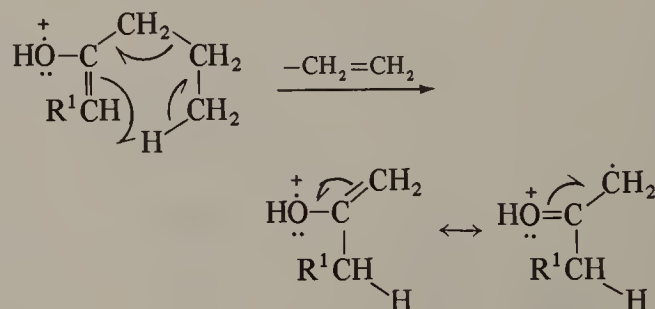
This cleavage gives rise to a peak at  $m/e\ 43$  or  $57$  or  $71$ . . . . The base peak very often results from loss of the larger alkyl group.

When one of the alkyl chains attached to the  $C=O$  group is  $C_3$  or longer, cleavage of the C-C bond once removed ( $\alpha\beta$  bond) from the  $C=O$  group occurs with hydrogen migration to give a major peak (McLafferty rearrangement):



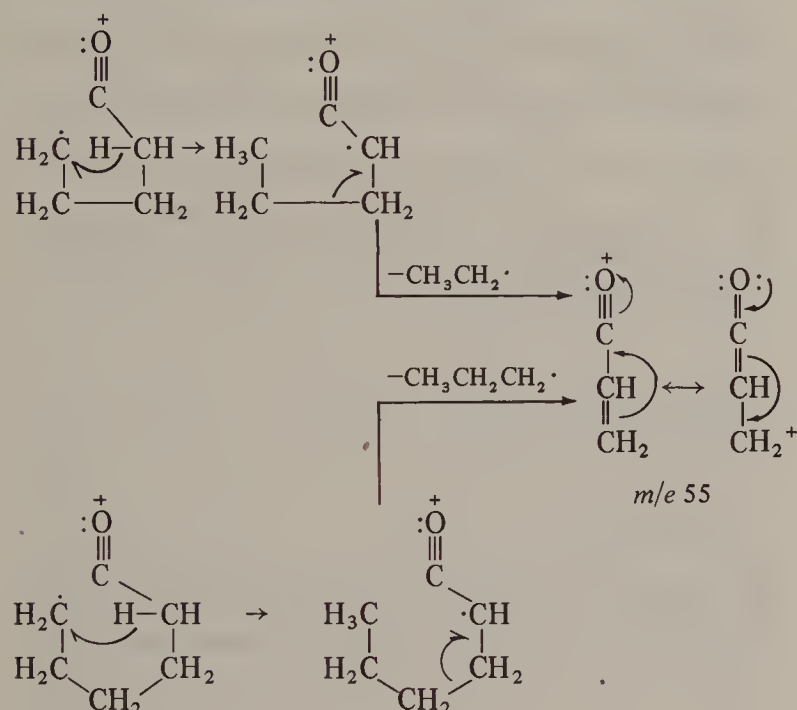
Simple cleavage of the  $\alpha\beta$  bond, which does not occur to any extent, would give an ion of low stability with two adjacent positive centers  $\text{R}-\overset{\delta+}{\text{C}}-\overset{+}{\text{C}}\text{H}_2$ . When R is  $C_3$  or longer, the first-

formed ion can cleave again with hydrogen migration:

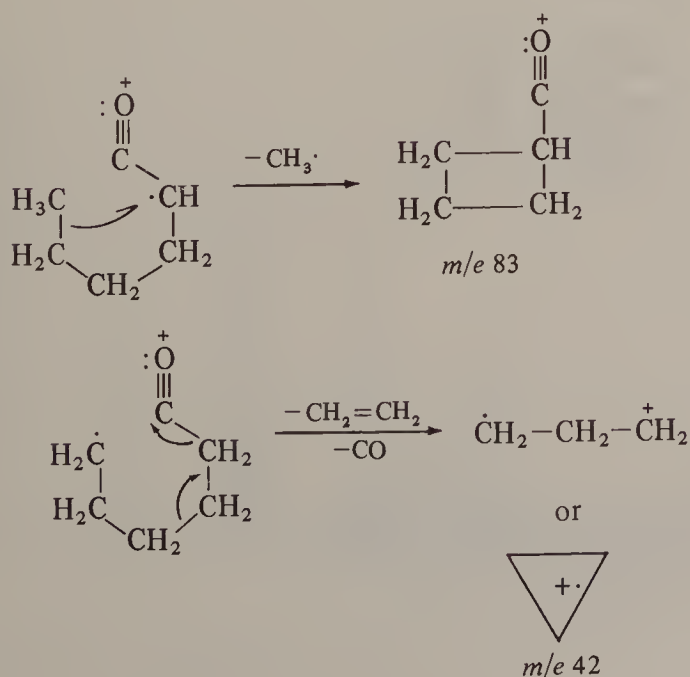


Note that in long-chain ketones the hydrocarbon peaks are indistinguishable (without the aid of high-resolution techniques) from the acyl peaks, since the mass of the CO unit ( $C=O$ , 28) is the same as two methylene units. The multiple cleavage modes in ketones sometimes make difficult the determination of the carbon chain configuration. Reduction of the carbonyl group to a methylene group yields the corresponding hydrocarbon whose fragmentation pattern leads to the carbon skeleton.

The molecular ion peak in cyclic ketones is prominent. As with aliphatic ketones, the primary cleavage of cyclic ketones is adjacent to the C=O group, but the ion thus formed must undergo further cleavage in order to produce a fragment. The base peak in the spectrum of cyclopentanone and of cyclohexanone is  $m/e$  55. The mechanism is similar in both cases: hydrogen shift to convert a primary radical to a conjugated secondary radical followed by formation of the resonance-stable ion,  $m/e$  55.

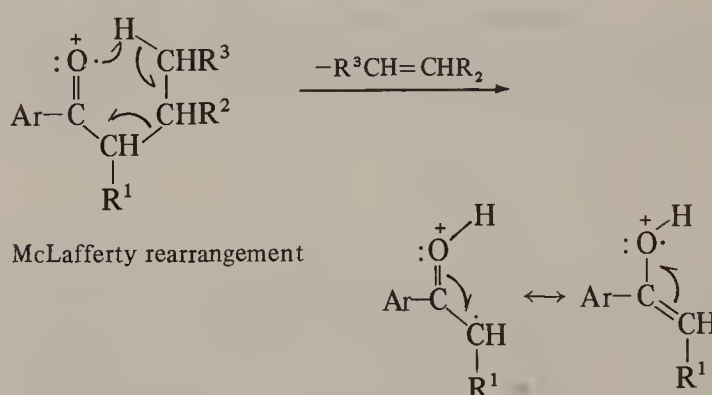


The other distinctive peaks at  $m/e$  83 and 42 in the spectrum of cyclohexanone have been rationalized as follows.



The molecular ion peak of aromatic ketones is prominent. Cleavage of aryl alkyl ketones occurs at the bond beta to the ring, leaving a characteristic  $\text{ArC}\equiv\ddot{\text{O}}\cdot$  fragment which usually accounts for the base peak. Loss of CO from this fragment gives the "aryl" ion ( $m/e$  77 in the case of acetophenone). Cleavage of the bond adjacent to the ring to form a  $\text{RC}\equiv\ddot{\text{O}}\cdot$  fragment is less important though somewhat enhanced by electron-withdrawing groups (and diminished by electron-donating groups) in the *para* position of the Ar group.

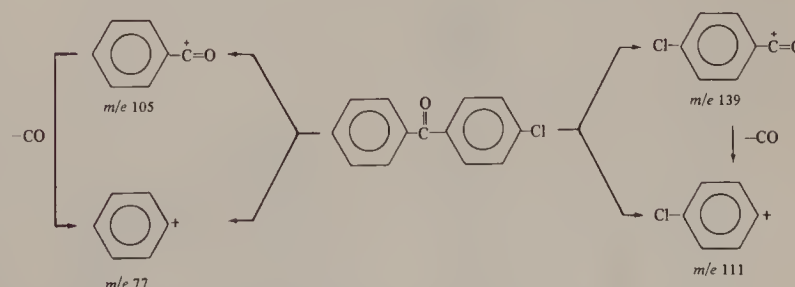
When the alkyl chain is  $\text{C}_3$  or longer, cleavage of the C-C bond once-removed from the C=O group occurs with hydrogen migration. This is the same cleavage noted for aliphatic ketones that proceeds through a cyclic transition state and results in elimination of an olefin and formation of a stable ion.



The mass spectrum of an unsymmetrical diaryl ketone, *p*-chlorobenzophenone, is displayed in Figure 12. The molecular ion peak ( $m/e$  216) is prominent and the intensity (33.99%) of the  $M + 2$  peak (relative to the molecular ion peak) demonstrates that chlorine is in the structure (see the discussion of Table III and Figure 18 below).

Since the intensity of the  $m/e$  141 peak is about  $\frac{1}{3}$  the intensity of the  $m/e$  139 peak, these peaks correspond to fragments containing 1 chlorine each. The same can be said about the fragments producing the  $m/e$  111 and 113 peaks.

The major peaks in Figure 12 arise as follows.



The observed peak intensities make it clear that formation of a  $\text{ArCO}^+$  fragment occurs more readily than does  $\text{Ar}^+$  formation. In addition, for either of these two types of fragments, the structure bearing the chlorine is less favored



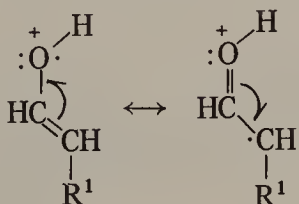
than that bearing no chlorine because the electron-withdrawal effect of the chlorine destabilizes a positively charged fragment.

## ALDEHYDES

### Aliphatic Aldehydes

The molecular ion peak of aliphatic aldehydes is usually discernible. Cleavage of the C-H and C-C bonds next to the oxygen atom results in an  $M - 1$  peak and in an  $M - R$  peak ( $m/e$  29,  $\text{CHO}^+$ ). The  $M - 1$  peak is a good diagnostic peak even for long-chain aldehydes, but the  $m/e$  29 peak present in  $\text{C}_4$  and higher aldehydes is due to the hydrocarbon  $\text{C}_2\text{H}_5^+$  ion.

In the  $\text{C}_4$  and higher aldehydes, McLafferty cleavage of the  $\alpha\beta$  C-C bond occurs to give a major peak at  $m/e$  44, 58, or 72, . . . , depending on the  $\alpha$ -substituents. This is the resonance-stabilized ion formed through the cyclic transition state as shown above for aliphatic ketones ( $\text{R} = \text{H}$ ):



In straight-chain aldehydes, the other unique, diagnostic peaks are at  $M - 18$  (loss of water),  $M - 28$  (loss of ethylene),  $M - 43$  (loss of  $\text{CH}_2=\text{CH}-\text{O}^\cdot$ ), and  $M - 44$  (loss of  $\text{CH}_2=\text{CH}-\text{OH}$ ). The rearrangements leading to these peaks have been rationalized (see Reference 2). As the chain lengthens, the hydrocarbon pattern ( $m/e$  29, 43, 57, 71, . . .) becomes dominant. These features are evident in the spectrum of nonanal (Figure 13).

### Aromatic Aldehydes

Aromatic aldehydes are characterized by a large molecular ion peak and by an  $M - 1$  peak ( $\text{Ar}-\text{C}\equiv\text{O}^+$ ) that is always large and may be larger than the molecular ion peak. The  $M - 1$  ion  $\text{C}_6\text{H}_5\text{C}\equiv\text{O}^+$  eliminates CO to give the phenyl ion ( $m/e$  77), which in turn eliminates  $\text{HC}\equiv\text{CH}$  to give the  $\text{C}_4\text{H}_3^+$  ion ( $m/e$  51).

## CARBOXYLIC ACIDS

### Aliphatic Acids

The molecular ion peak of a straight-chain monocarboxylic acid is weak but usually discernible. The most characteristic

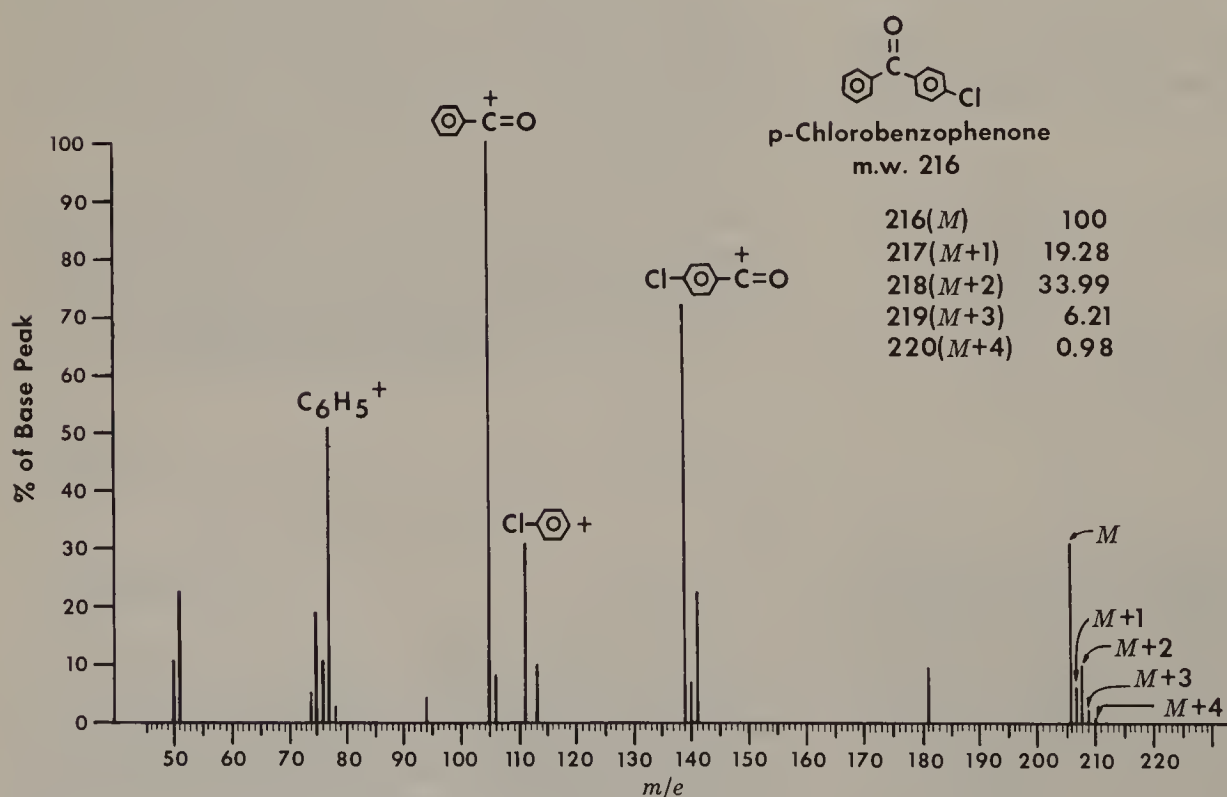
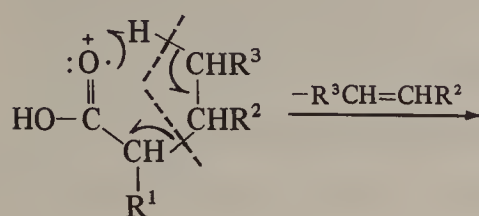
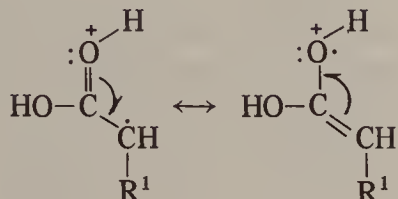


Figure 12. *p*-Chlorobenzophenone.

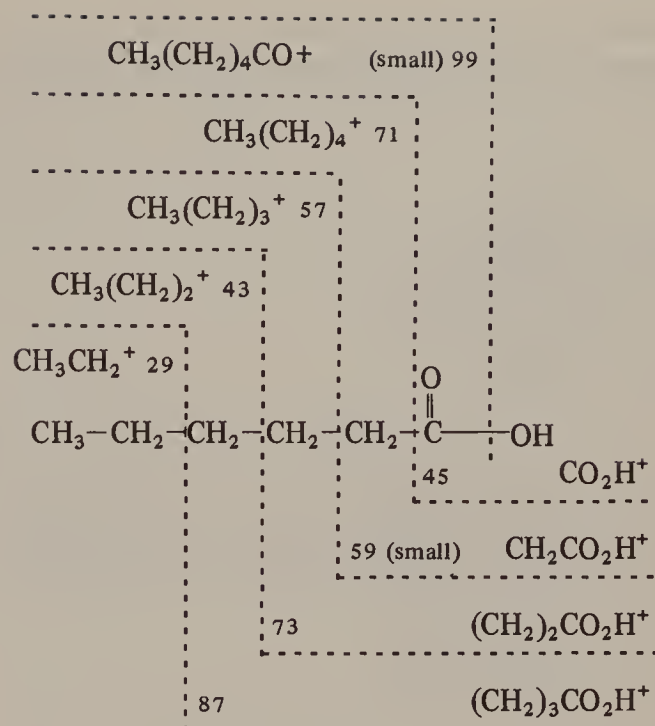
(sometimes the base) peak is  $m/e$  60 due to the McLafferty rearrangement. Branching at the  $\alpha$ -carbon enhances this cleavage.



McLafferty rearrangement



In short-chain acids, peaks at  $M - OH$  and  $M - COOH$  are prominent; these represent cleavage of bonds next to  $C=O$ . In long-chain acids, the spectrum consists of two series of peaks resulting from cleavage at each  $C-C$  bond with retention of charge either on the oxygen-containing fragment ( $m/e$  45, 59, 73, 87, ...) or on the alkyl fragment ( $m/e$  29, 43, 57, 71, 85, ...). As previously discussed, the hydrocarbon pattern also shows peaks at  $m/e$  27, 28; 41, 42; 55, 56; 69, 70; .... In summary, besides the McLafferty rearrangement peak, the spectrum of a long-chain acid resembles the series of "hydrocarbon" clusters at interval of 14 mass units. In each cluster, however, is a prominent peak at  $C_nH_{2n-1}O_2$ . Hexanoic acid (m.w. 116) for example, cleaves as follows:



Dibasic acids are usually converted to esters to increase volatility.

### Aromatic Acids

The molecular ion peak of aromatic acids is large. The other prominent peaks are formed by loss of  $OH$  ( $M - 17$ ) and of  $COOH$  ( $M - 45$ ). Loss of  $H_2O$  ( $M - 18$ ) is noted if a hydrogen-bearing ortho group is available. This is one example of the general "ortho effect" noted when the

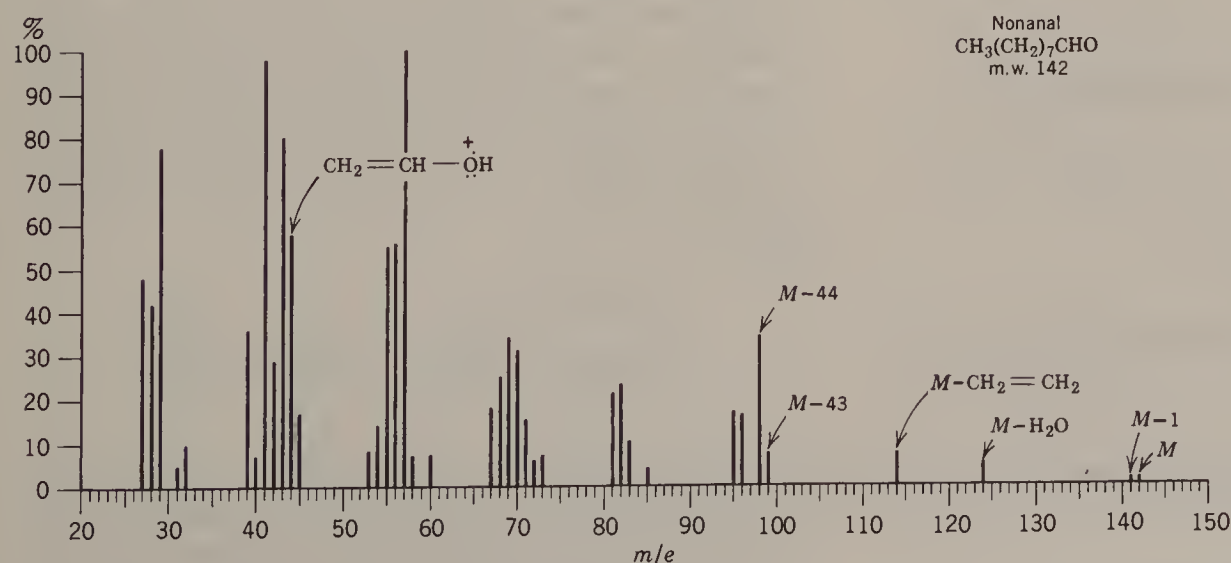
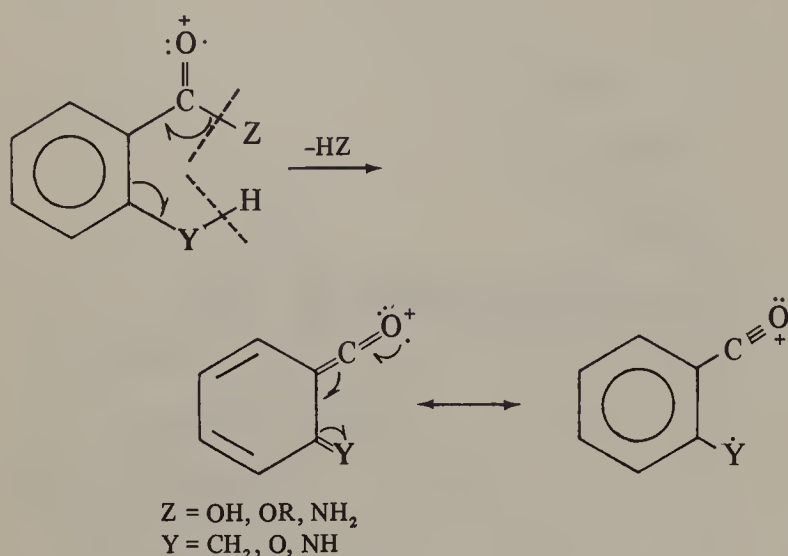


Figure 13. Nonanal.

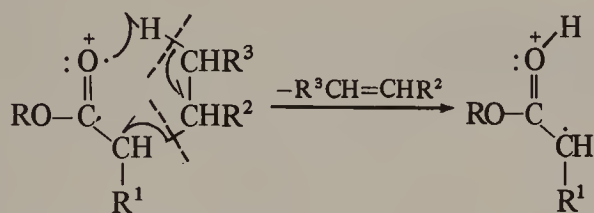
substituents can be in a 6-membered transition state to facilitate loss of a neutral molecule of  $\text{H}_2\text{O}$ ,  $\text{ROH}$ , or  $\text{NH}_3$ .



## CARBOXYLIC ESTERS

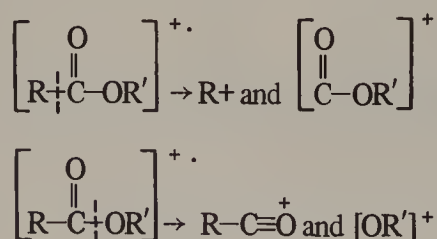
### Aliphatic Esters

The molecular ion peak of a methyl ester of a straight-chain aliphatic acid is usually distinct. Even waxes usually show a discernible molecular ion peak. The molecular ion peak is weak in the range  $m/e$  130 to about 200, but becomes somewhat more intense beyond this range. The most characteristic peak is due to the familiar McLafferty rearrangement and cleavage one bond removed from the  $\text{C}=\text{O}$  group. Thus a methyl ester of an aliphatic acid unbranched at the  $\alpha$ -carbon gives a strong peak at  $m/e$  74, which, in fact, is the base peak in straight-chain methyl esters from  $\text{C}_6$  to  $\text{C}_{26}$ . The alcohol moiety and/or the  $\alpha$ -substituent can often be deduced by the location of the peak resulting from this cleavage.



McLafferty rearrangement

Four ions can result from bond cleavage next to  $\text{C}=\text{O}$ .

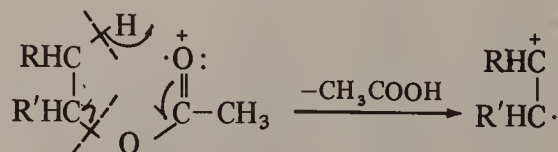


The ion  $\text{R}^+$  is prominent in the short chain esters, but diminishes rapidly with increasing chain length and is barely perceptible in methyl hexanoate. The ion  $\text{R}-\text{C}\equiv\text{O}^+$  gives an excellent diagnostic peak for esters. In methyl esters it occurs at  $M - 31$ . It is the base peak in methyl acetate, and is still 4% of the base peak in the  $\text{C}_{26}$  methyl ester. The ions  $[\text{OR}']^+$  and  $\left[ \begin{array}{c} \text{O} \\ \parallel \\ \text{COR}' \end{array} \right]^+$  are usually of little importance. The latter is discernible when  $\text{R}' = \text{CH}_3$  (see  $m/e$  59 peak of Figure 14).

Consider, first, esters in which the acid portion is the predominant portion of the molecule. The fragmentation pattern for methyl esters of straight-chain acids can be described in the same terms used for the pattern of the free acid. Cleavage at each  $\text{C}-\text{C}$  bond gives an alkyl ion ( $m/e$  29, 43, 57, ...) and an oxygen-containing ion,  $\text{C}_n\text{H}_{2n-1}\text{O}_2^+$  (59, 73, 87, ...). Thus, there are hydrocarbon clusters at intervals of 14 mass units; in each cluster is a prominent peak at  $\text{C}_n\text{H}_{2n-1}\text{O}_2$ . The peak ( $m/e$  87) representing the ion  $[\text{CH}_2\text{CH}_2\text{COOCH}_3]^+$  is always more intense than its homologs, but the reason is not immediately obvious. However, it seems clear that the  $\text{C}_n\text{H}_{2n-1}\text{O}_2$  ions do not at all arise from simple cleavage.

The spectrum of methyl octanoate is presented as Figure 14. This spectrum illustrates one difficulty previously mentioned (Section V, part 2) in using the  $M + 1$  peak to arrive at a molecular formula. The measured value for the  $M + 1$  peak is 12.9%. The calculated value (Appendix A) is 10.0%. The measured value is high due to an ion-molecule reaction because a relatively large sample was used in order to see the weak molecular ion peak. The utility of the 5-galvanometer recorder is implied by this spectrum; thus, the  $M + 1$  peak can be measured accurately even though its intensity is only 0.11% of that of the base peak. The accuracy of the  $M + 2$  peak measurement is marginal.

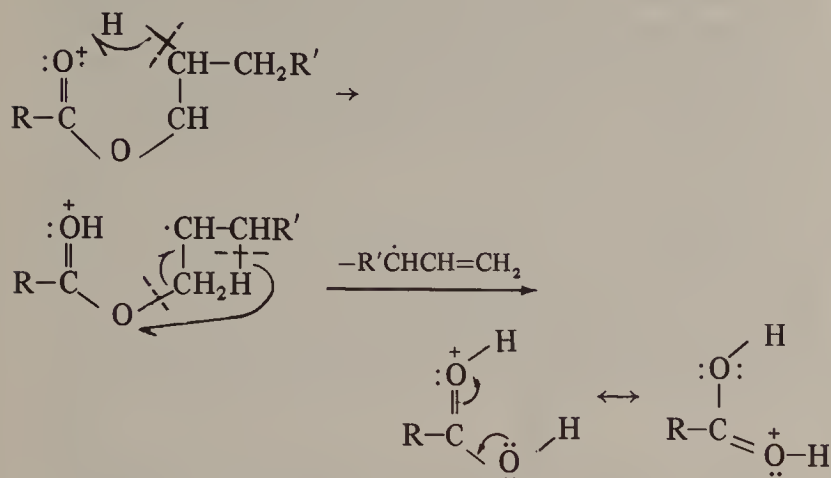
Now let us consider esters in which the alcohol portion is the predominant portion of the molecule. Esters of fatty alcohols (except methyl esters) eliminate a molecule of acid in the same manner that alcohols eliminate water. A scheme similar to that described earlier for alcohols, involving a single hydrogen transfer to the alcohol oxygen of the ester, can be written. An alternative mechanism involves a hydride transfer to the carbonyl oxygen (McLafferty rearrangement):



The preceding loss of acetic acid is so facile in steroidal acetates that they frequently show no detectable molecular ion peak. Steroidal systems also seem unusual in that they often display significant molecular ions as alcohols, even when the corresponding acetates do not.



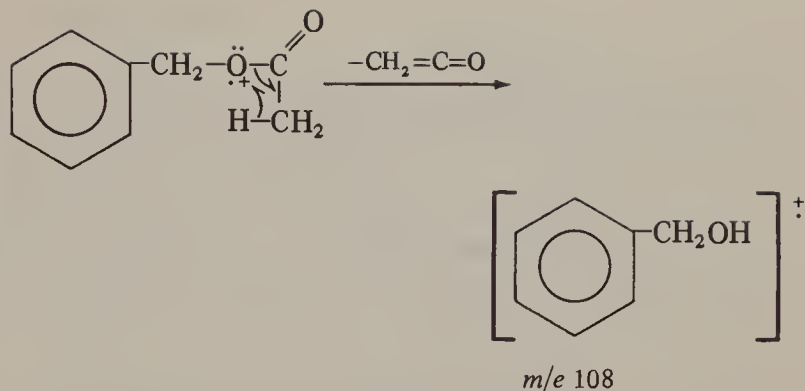
Esters of long-chain alcohols show a diagnostic peak at  $m/e$  61, 75, or 89, . . . from elimination of the alkyl moiety and transfer of *two* hydrogen atoms to the fragment containing the oxygen atoms.



Esters of dibasic acids  $\text{ROC}(\text{CH}_2)_n\text{COR}$ , in general, give recognizable molecular ion peaks. Intense peaks are found at  $(\text{ROC}(\text{CH}_2)_n\text{C})^+$  and at  $(\text{ROC}(\text{CH}_2)_n)^+$ .

#### Benzyl and Phenyl Esters

Benzyl acetate (also furfuryl acetate and other similar acetates) and phenyl acetate eliminate the neutral molecule ketene; frequently this gives rise to the base peak.



Of course, the  $m/e$  43 peak ( $\text{CH}_3\text{C}\equiv\text{O}^+$ ) and  $m/e$  91 ( $\text{C}_7\text{H}_7^+$ ) peaks are prominent for benzyl acetate.

#### Esters of Aromatic Acids

The molecular ion peak of methyl esters of aromatic acids is prominent. As the size of the alcohol moiety increases, the intensity of the molecular ion peak decreases rapidly to practically zero at  $\text{C}_5$ . The base peak results from elimination of  $\cdot\text{OR}$ , and elimination of  $\cdot\text{COOR}$  accounts for another prominent peak. In methyl esters, these peaks are at  $M - 31$ , and  $M - 59$ , respectively.

As the alkyl moiety increases in length, three modes of cleavage become important: (1) McLafferty rearrangement, (2) rearrangement of two hydrogen atoms with elimination of an allylic radical, and (3) retention of the positive charge by the alkyl group.

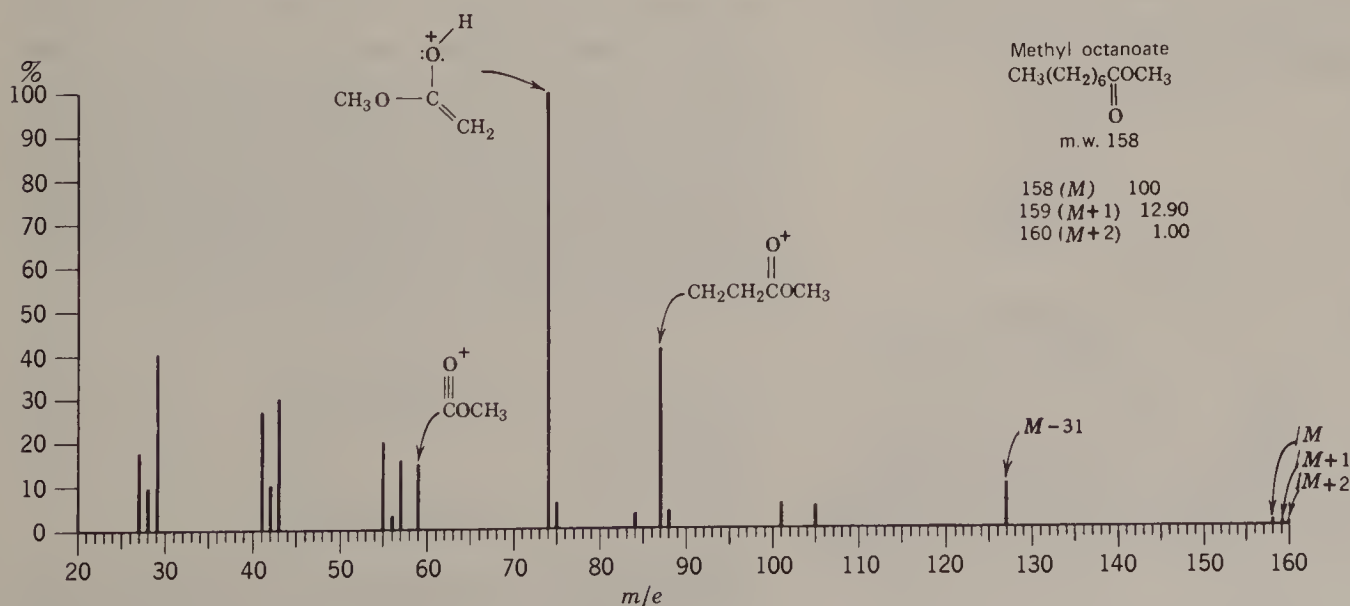
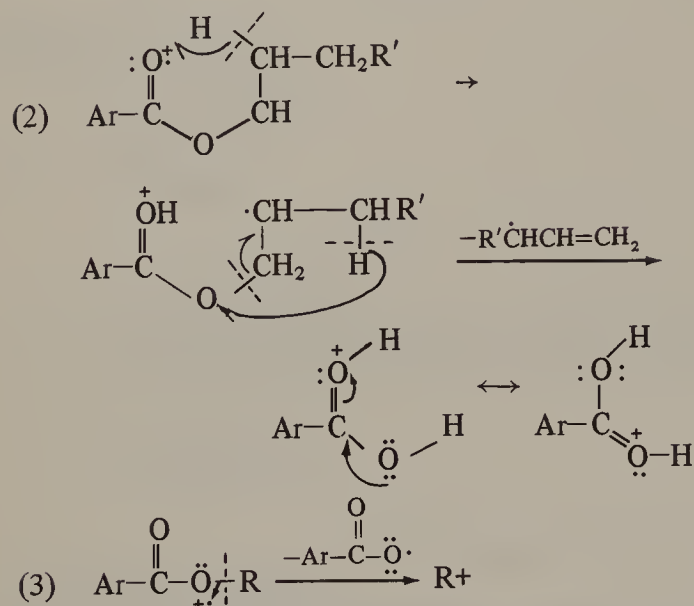
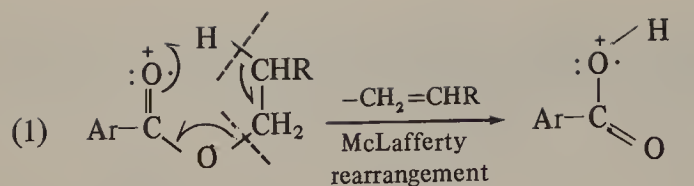
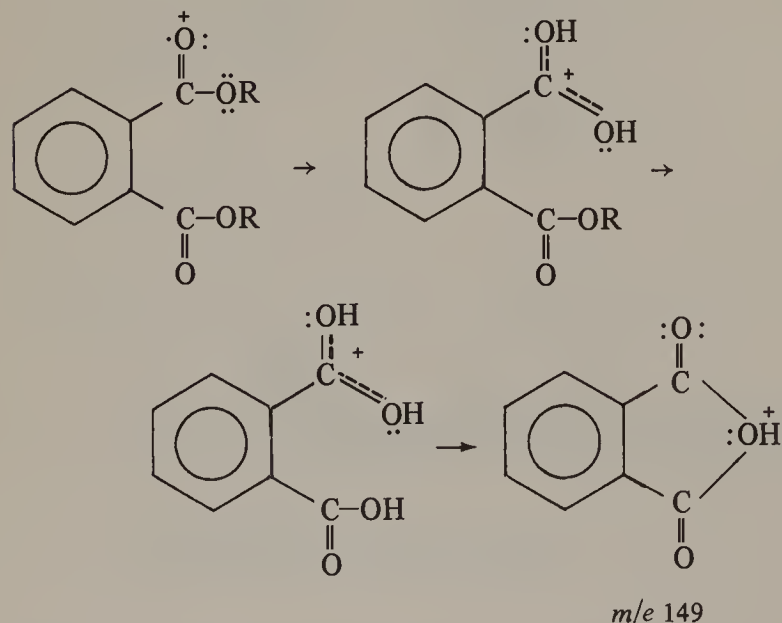


Figure 14. Methyl octanoate.



Appropriately, ortho-substituted benzoates eliminate ROH through the general "ortho" effect described above under aromatic acids. Thus, the base peak in the spectrum of methyl salicylate is  $m/e$  120; this ion eliminates carbon monoxide to give a strong peak at  $m/e$  92.

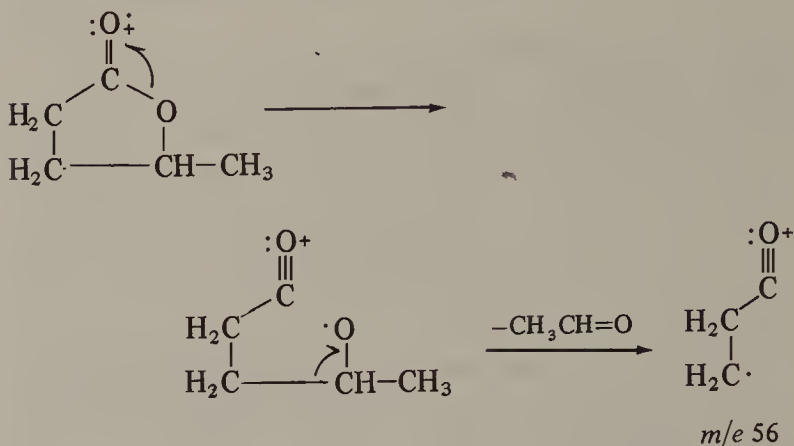
A strong characteristic peak at mass 149 is found in the spectra of all esters of phthalic acid, starting with the diethyl ester. This peak is not significant in the dimethyl or methyl ethyl ester of phthalic acid, nor in esters of isophthalic or terephthalic acids, all of which give the expected peaks at  $M - R$ ,  $M - 2R$ ,  $M - COOR$ , and  $M - 2COOR$ . Since long-chain phthalate esters are widely used as plasticizers and in oil diffusion pumps (often in the diffusion pump of the mass spectrometer inlet), a strong peak at  $m/e$  149 may indicate contamination. The  $m/e$  149 fragment is probably formed by two ester cleavages involving the shift of two hydrogen atoms and then another hydrogen atom, followed by elimination of  $H_2O$ :



## LACTONES

The molecular ion peak of 5-membered ring lactones is distinct but is weaker when an alkyl substituent is present at  $C_4$ . Facile cleavage of the side chain at  $C_4$  (Rules 3 and 8, p. 15) gives a strong peak at  $M$  minus alkyl.

The base peak ( $m/e$  56) of  $\gamma$ -valerolactone and the same strong peak of butyrolactone probably arise as follows.

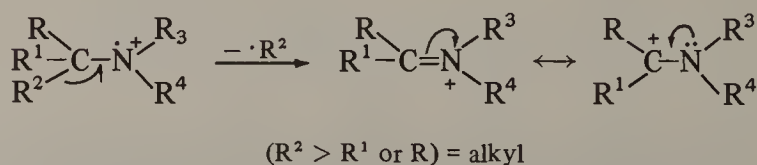


Labeling experiments indicate that some of the  $m/e$  56 peak in  $\gamma$ -valerolactone arises from the  $C_4H_8^+$  ion. The other intense peaks in  $\gamma$ -valerolactone are at  $m/e$  27 ( $C_2H_3^+$ ), 28 ( $C_2H_4^+$ ), 29 ( $C_2H_5^+$ ), 41 ( $C_3H_5^+$ ), and 43 ( $C_3H_7^+$ ), and 85 ( $C_4H_5O_2^+$ , loss of the methyl group). In butyrolactone, there are strong peaks at  $m/e$  27, 28, 29, 41, and 42 ( $C_3H_6^+$ ).

## AMINES

### Aliphatic Amines

The molecular ion peak of an aliphatic monoamine is an odd number, but it is usually quite weak and, in long-chain or highly branched amines, undetectable. The base peak frequently results from C-C cleavage next ( $\alpha\beta$ ) to the nitrogen atom (Rule 8, p. 15); for primary amines unbranched at the  $\alpha$ -carbon, this is  $m/e$  30 ( $CH_2NH_2^+$ ). This cleavage accounts for the base peak in all primary amines and secondary and tertiary amines that are not branched at the  $\alpha$ -carbon. Loss of the largest branch from the  $\alpha$ -C atom is preferred.

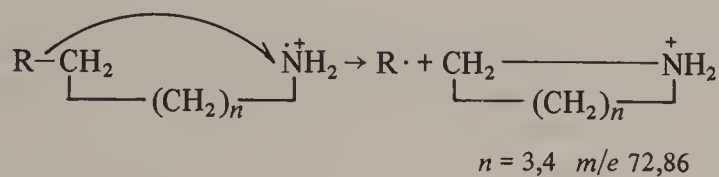


When  $R$  and/or  $R^1 = H$ , an  $M - 1$  peak is usually visible. This is the same type of cleavage noted above for alcohols. The effect is more pronounced in amines because of the better resonance stabilization of the ion fragment by the

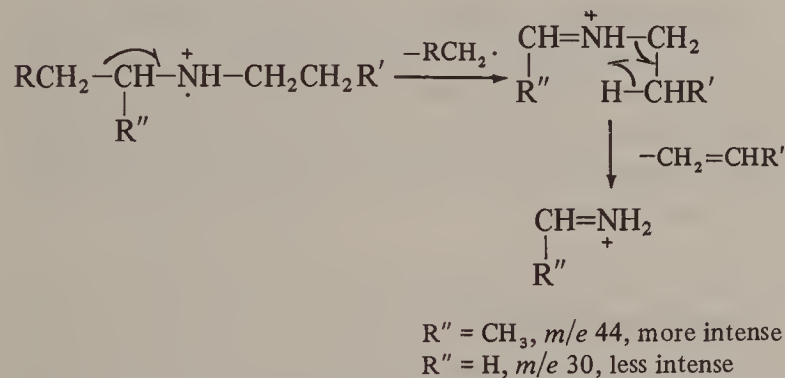
less electronegative N atom compared with the O atom.

Primary straight-chain amines show a homologous series of peaks of progressively decreasing intensity (the cleavage at the  $\epsilon$  bond is slightly more important than at the neighboring bonds) at  $m/e$  30, 44, 58, . . . resulting from cleavage at C—C bonds successively removed from the nitrogen atom with retention of the charge on the N-containing fragment. These peaks are accompanied by the hydrocarbon pattern of  $C_nH_{2n+1}$ ,  $C_nH_{2n}$ , and  $C_nH_{2n-1}$  ions. Thus, we note characteristic clusters at intervals of 14 mass units, each cluster containing a peak due to a  $C_nH_{2n+2}N$  ion. Because of the very facile cleavage to form the base peak, the fragmentation pattern in the high mass region becomes extremely weak.

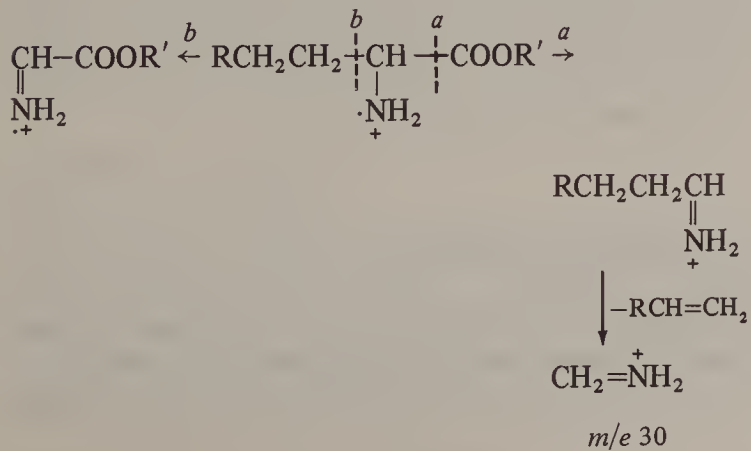
Cyclic fragments apparently occur during the fragmentation of longer chain amines:



A peak at  $m/e$  30 is good though not conclusive evidence for a straight-chain primary amine. Further decomposition of the first-formed ion from a secondary or tertiary amine leads to a peak at  $m/e$  30, 44, 58, 72, . . . . This is a process similar to that described for aliphatic alcohols and ethers above, and similarly is enhanced by branching at one of the  $\alpha$ -carbon atoms:



Cleavage of amino acid esters occurs at both C—C bonds (*a*, *b*, below) next to the nitrogen atom, loss of the carbalkoxy group being preferred (*a*). The aliphatic amine fragment decomposes further to give a peak at *m/e* 30.



## Cyclic Amines

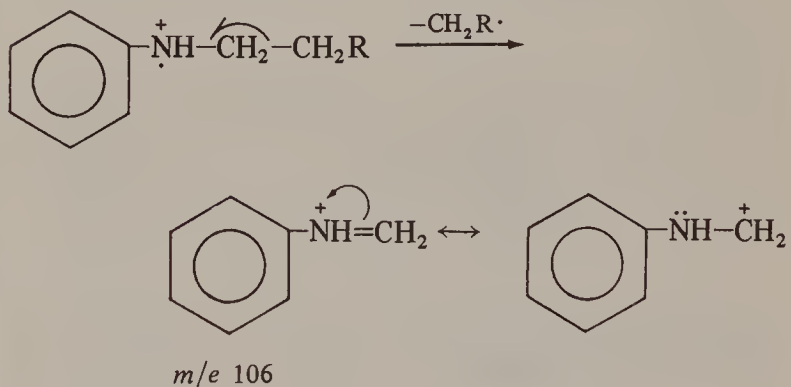
In contrast to acyclic amines, the molecular ion peaks of cyclic amines are usually intense; e.g., the molecular ion peak of pyrrolidine is strong. Primary cleavage at the bonds next to the N atom leads either to loss of an  $\alpha$ -H atom to give a strong  $M - 1$  peak or to opening of the ring; the latter event is followed by elimination of ethylene to give  $\cdot\text{CH}_2\dot{\text{N}}\text{H}=\text{CH}_2$  ( $m/e$  43, base peak), thence by loss of a hydrogen atom to give  $\text{CH}_2=\dot{\text{N}}=\text{CH}_2$  ( $m/e$  42). *N*-Methylpyrrolidine also gives a  $\text{C}_2\text{H}_4\text{N}^+$  ( $m/e$  42) peak, apparently by more than one pathway.

Piperidine likewise shows a strong molecular ion and  $M - 1$  (base) peak. Ring opening followed by several available sequences leads to characteristic peaks at  $m/e$  70, 57, 56, 44, 43, 42, 30, 29, and 28. Substituents are cleaved from the ring (Rule 6, p. 15).

## Anilines

The molecular ion peak (odd number) of an aromatic monoamine is intense. Loss of one of the amino H atoms of aniline gives a moderately intense  $M - 1$  peak; loss of a neutral molecule of HCN followed by loss of a hydrogen atom gives prominent peaks at  $m/e$  66 and 65, respectively.

It was noted above that cleavage of alkyl aryl ethers occurs with rearrangement involving cleavage of the ArO-R bond; that is, cleavage was controlled by the ring rather than by the oxygen atom. In the case of alkylaryl amines, cleavage of the C-C bond next to the nitrogen atom is dominant; i.e., the heteroatom controls cleavage:

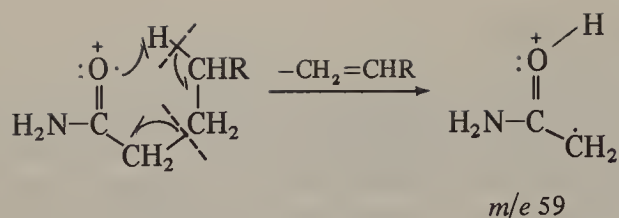


## ALIPHATIC AMIDES

The molecular ion peak of straight-chain monoamides is usually discernible. The dominant modes of cleavage depend on the length of the acyl moiety, and on the lengths and number of the alkyl groups attached to the nitrogen atom.

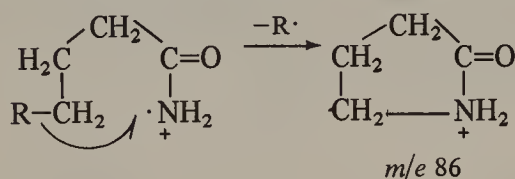
The base peak in all straight-chain primary amides higher than propionamide results from the familiar McLafferty rearrangement:



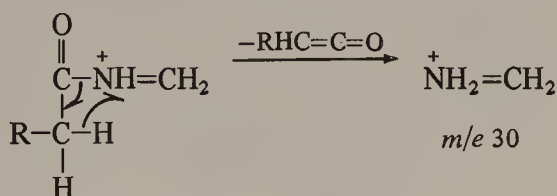
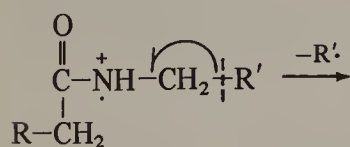


Branching at the  $\alpha$ -carbon ( $\text{CH}_3$ , etc.) gives a homologous peak at  $m/e\ 73$  or  $87$ , ...

Primary amides give a strong peak at  $m/e\ 44$  from cleavage of the  $\text{R}-\text{CONH}_2$  bond: ( $\text{O}^+=\text{C}-\ddot{\text{N}}\text{H}_2 \leftrightarrow \ddot{\text{O}}=\text{C}=\text{NH}_2^+$ ); this is the base peak in  $\text{C}_1$ – $\text{C}_3$  primary amides and in isobutyramide. A moderate peak at  $m/e\ 86$  results from  $\gamma\delta$  C–C cleavage, possibly accompanied by cyclization:



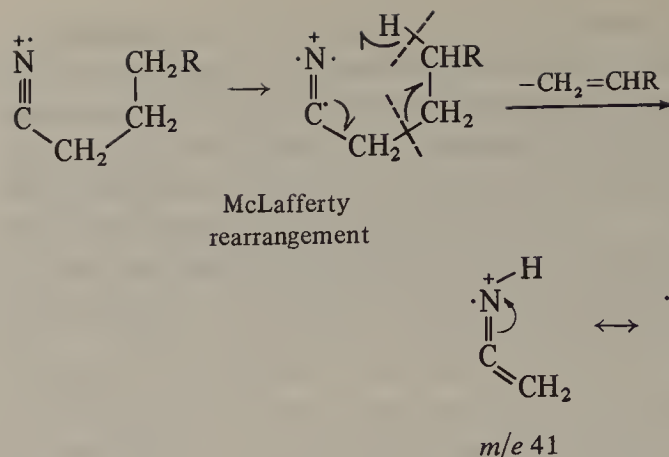
Secondary and tertiary amides with an available hydrogen on the  $\gamma$ -carbon of the acyl moiety and methyl groups on the N atom show the dominant peak resulting from the McLafferty rearrangement. When the N-alkyl groups are  $\text{C}_2$  or longer and the acyl moiety is shorter than  $\text{C}_3$ , another mode of cleavage predominates. This is cleavage of the N-alkyl group beta to the N atom, and cleavage of the carbonyl C–N bond with migration of an  $\alpha$ -H atom of the acyl moiety:



## ALIPHATIC NITRILES

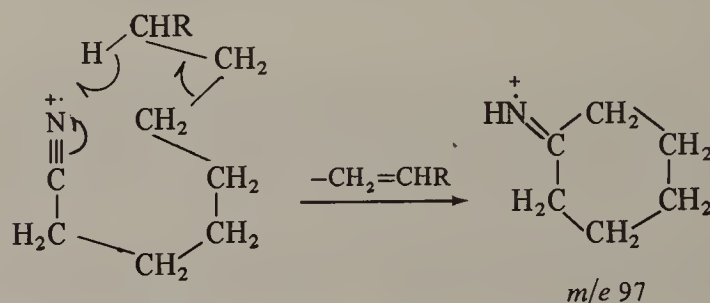
The molecular ion peaks of aliphatic nitriles (except for acetonitrile and propionitrile) are weak or absent, but the  $M+1$  peak can usually be located by its behavior on increasing inlet pressure or decreasing repeller voltage (Section V, part 2). A weak but diagnostically useful  $M-1$  peak is formed by loss of an  $\alpha$ -hydrogen to form the stable ion:  $\text{R}\dot{\text{C}}\text{H}-\text{C}\equiv\text{N}^+ \leftrightarrow \text{RCH}=\text{C}=\dot{\text{N}}^+$

The base peak of straight-chain nitriles between  $\text{C}_4$  and  $\text{C}_9$  is  $m/e\ 41$ . This peak is the ion resulting from hydrogen rearrangement in a 6-membered transition state:



However, this peak lacks diagnostic value because of the presence of the  $\text{C}_3\text{H}_5$  ( $m/e\ 41$ ) for all molecules containing a hydrocarbon chain.

A peak at  $m/e\ 97$  is characteristic and intense (sometimes the base peak) in straight-chain nitriles  $\text{C}_8$  and higher. The following mechanism has been depicted:



Simple cleavage at each C–C bond (except the one next to the N atom) gives a characteristic series of homologous peaks of even mass number down the entire length of the chain ( $m/e\ 40, 54, 68, 82, \dots$ ) due to the  $(\text{CH}_2)_n\text{C}\equiv\text{N}^+$  ions. Accompanying these peaks are the usual peaks of the hydrocarbon pattern.

## NITRO COMPOUNDS

### Aliphatic Nitro Compounds

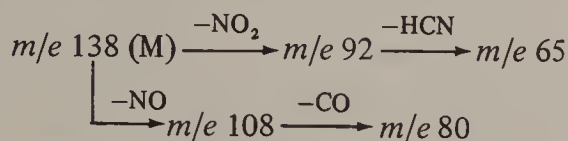
The molecular ion peak (odd number) of an aliphatic mononitro compound is weak or absent (except in the lower homologs). The main peaks are attributable to the hydrocarbon fragments up to  $M - \text{NO}_2$ . Presence of a nitro group is indicated by an appreciable peak at  $m/e\ 30$  ( $\text{NO}^+$ ) and a smaller peak at mass 46 ( $\text{NO}_2^+$ ).

### Aromatic Nitro Compounds

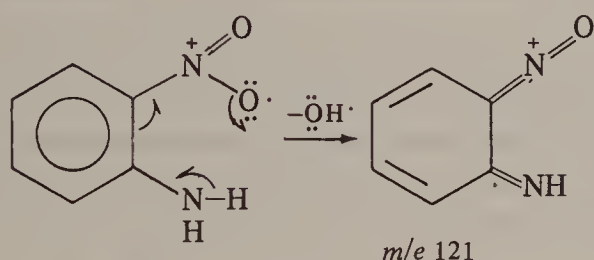
The molecular ion peak of aromatic nitro compounds (odd number for one N atom) is strong. Prominent peaks result from elimination of an  $\text{NO}_2$  radical ( $M - 46$ , the base peak

in nitrobenzene), and of a neutral NO molecule with rearrangement to form the phenoxy cation ( $M - 30$ ); both are good diagnostic peaks. Loss of  $\text{HC}\equiv\text{CH}$  from the  $M - 46$  ion accounts for a strong peak at  $M - 72$ ; loss of CO from the  $M - 30$  ion gives a peak at  $M - 58$ . A diagnostic peak at  $m/e$  30 results from the  $\text{NO}^+$  ion.

The isomeric *o*-, *m*-, and *p*-nitroanilines each give a strong molecular ion (even number). They all give prominent peaks resulting from two sequences:



Aside from differences in intensities, the three isomers give very similar spectra. The *m*- and *p*-compounds give a small peak at  $m/e$  122 from loss of an O atom, whereas the *o*-compound eliminates  $\cdot\ddot{\text{O}}\text{H}$  as follows to give a small peak at  $m/e$  121.

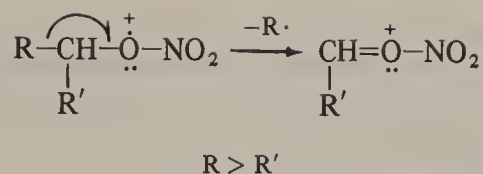


## ALIPHATIC NITRITES

The molecular ion peak (odd number) of aliphatic nitrites (1 N present) is weak or absent. The peak at  $m/e$  30 ( $\text{NO}^+$ ) is always large and is often the base peak. There is a large peak at  $m/e$  60 ( $\text{CH}_2=\ddot{\text{O}}\text{NO}^+$ ) in all nitrites unbranched at the  $\alpha$ -carbon; this represents cleavage of the C-C bond next to the ONO group. An  $\alpha$ -branch can be identified by a peak at  $m/e$  74, 88, or 102, . . . Absence of a large peak at  $m/e$  46 permits differentiation from nitro compounds. Hydrocarbon peaks are prominent, and their distribution and intensities describe the arrangement of the carbon chain.

## ALIPHATIC NITRATES

The molecular ion peak (odd number) of aliphatic nitrates (1 N present) is weak or absent. A prominent (frequently the base) peak is formed by cleavage of the C-C bond next to the  $\text{ONO}_2$  group with loss of the heaviest alkyl group attached to the  $\alpha$ -carbon.



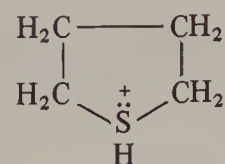
The  $\text{NO}_2^+$  peak at  $m/e$  46 is also prominent. As in the case of aliphatic nitrites, the hydrocarbon fragment ions are distinct.

## SULFUR COMPOUNDS

The contribution (4.4%, see Table II) of the  $^{34}\text{S}$  isotope to the  $M + 2$  peak, and often to a [fragment + 2] peak, affords ready recognition of sulfur-containing compounds. A homologous series of sulfur-containing fragments is four mass units higher than the hydrocarbon fragment series. The number of sulfur atoms can be determined from the size of the contribution of the  $^{34}\text{S}$  isotope to the  $M + 2$  peak. The mass of the sulfur atom(s) present is subtracted from the molecular weight. The formula of the rest of the molecule is now determined from the  $M + 1$  peak after subtracting the contribution of the  $^{33}\text{S}$  isotope. The large correction applied to the  $M + 2$  peak makes this peak unreliable for use in Appendix A. In di-isopentyl disulfide, for example, the molecular weight is 206, and the molecule contains two sulfur atoms. The formula for the rest of the molecule is therefore found under mass 142, that is, 206 minus  $(2 \times 32)$ . The corrected intensity for the  $M + 1$  peak is 12.5 minus  $(2 \times 0.78)$  which gives 10.9.

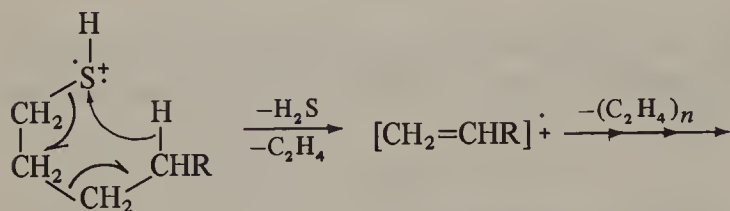
### Aliphatic Mercaptans

The molecular ion peak of aliphatic mercaptans, except for higher tertiary mercaptans, is usually strong enough so that the  $M + 2$  peak can be accurately measured. In general, the cleavage modes resemble those of alcohols. Cleavage of the C-C bond ( $\alpha\beta$  bond) next to the SH group gives the characteristic ion  $\text{CH}_2=\ddot{\text{S}}\text{H}^+ \leftrightarrow \text{CH}_2^+-\ddot{\text{S}}\text{H}$  ( $m/e$  47). Sulfur is poorer than nitrogen, but better than oxygen, at stabilizing such a fragment. Cleavage at the  $\beta\gamma$  bond gives a peak at  $m/e$  61 of about one-half the intensity of the  $m/e$  47 peak. Cleavage at the  $\gamma\delta$  bond gives a small peak at  $m/e$  75, and cleavage at the  $\delta\epsilon$  bond gives a peak at  $m/e$  89 that is more intense than the peak at  $m/e$  75; presumably the  $m/e$  89 ion is stabilized by cyclization:





Again analogous to alcohols, primary mercaptans split out  $\text{H}_2\text{S}$  to give a strong  $M - 34$  peak, the resulting ion then eliminating ethylene; thus the homologous series  $M - \text{H}_2\text{S} - (\text{CH}_2=\text{CH}_2)_n$  arises:

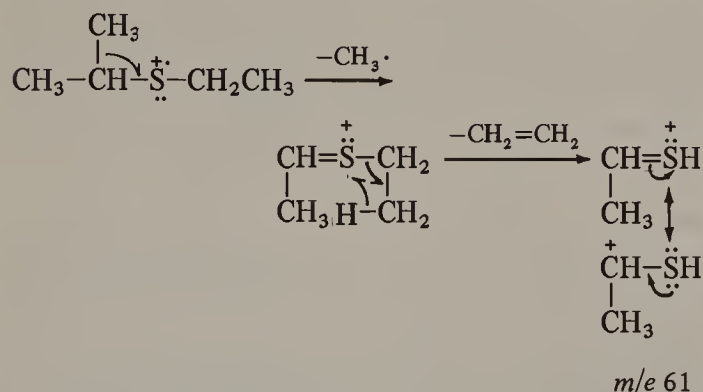


Secondary and tertiary mercaptans cleave at the  $\alpha$ -C with loss of the largest group to give a prominent peak  $M - \text{CH}_3$ ,  $M - \text{C}_2\text{H}_5$ ,  $M - \text{C}_3\text{H}_7$ , . . . However, a peak at  $m/e$  47 may also appear as a rearrangement peak of secondary and tertiary mercaptans. A peak at  $M - 33$  (loss of HS) is usually present for secondary mercaptans.

In long-chain mercaptans, the hydrocarbon pattern is superimposed on the mercaptan pattern. As for alcohols, the alkenyl peaks (i.e.,  $m/e$  41, 55, 69, . . .) are as large or larger than the alkyl peaks ( $m/e$  43, 57, 71, . . .).

### Aliphatic Sulfides

The molecular ion peak of aliphatic sulfides is usually intense enough so that the  $M + 2$  peak can be accurately measured. The cleavage modes generally resemble those of ethers. Cleavage of one or the other of the  $\alpha\beta$  C-C bonds occurs, with loss of the largest group being favored. These first-formed ions decompose further with hydrogen transfer and elimination of an olefin. The steps for aliphatic ethers also occur for sulfides; the end result is the ion  $\text{RCH}=\text{S}^+\text{H}$  (see p. 35 for an example.)

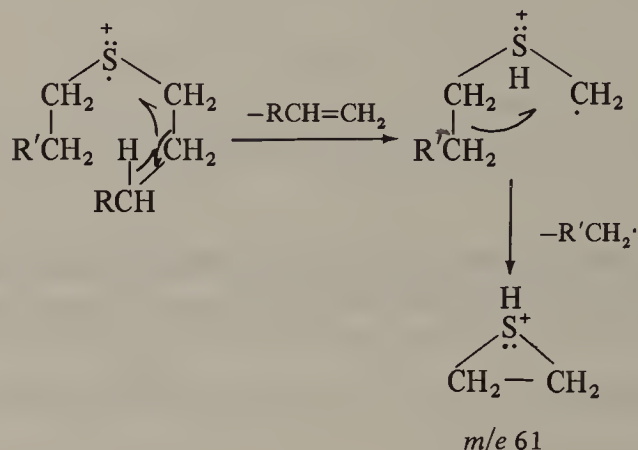


For a sulfide unbranched at either  $\alpha$ -C, this ion is  $\text{CH}_2=\text{S}^+\text{H}$  ( $m/e$  47), and its intensity may lead to confusion with the same ion derived from a mercaptan. However, the absence of  $M - \text{H}_2\text{S}$  or  $M - \text{SH}$  peaks in sulfide spectra makes the distinction.

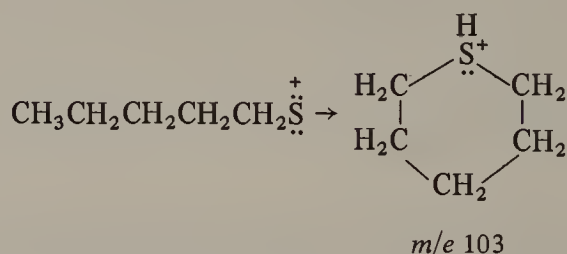
A moderate to strong peak at  $m/e$  61 is present (see

alkyl sulfide cleavage above) in the spectrum of all except tertiary sulfides. When an  $\alpha$ -methyl substituent is present,  $m/e$  61 is the ion  $\text{CH}_3\text{CH}=\text{S}^+\text{H}$  resulting from the double cleavage described above. Methyl primary sulfides cleave at the  $\alpha\beta$  bond to give the  $m/e$  61 ion,  $\text{CH}_3-\text{S}^+=\text{CH}_2$ .

However, a strong  $m/e$  61 peak in the spectrum of a completely straight-chain sulfide calls for a different explanation. The following rationalization is offered



Sulfides give a characteristic ion by cleavage of the C-S bond with retention of charge on sulfur. The resulting  $\text{RS}^+$  ion gives a peak at  $m/e$  32 +  $\text{CH}_3$ , 32 +  $\text{C}_2\text{H}_5$ , 32 +  $\text{C}_3\text{H}_7$ , . . . The ion of  $m/e$  103 seems especially favored possibly because of formation of a rearranged cyclic ion:



These features are illustrated by the spectrum of di-*n*-pentyl sulfide (Figure 15).

As with long-chain ethers, the hydrocarbon pattern may dominate the spectrum of long-chain sulfides; the  $\text{C}_n\text{H}_{2n}$  peaks seem especially prominent. In branched-chain sulfides, cleavage at the branch may reduce the relative intensity of the characteristic sulfide peaks.

### Aliphatic Disulfides

The molecular ion peak, at least up to  $\text{C}_{10}$  disulfides, is strong (Chapter 8. Compound No. 8-29).

A major peak results from cleavage of one of the C-S bonds with retention of the charge on the alkyl fragment. Another major peak results from the same cleavage with shift of a hydrogen atom to form the RSSH fragment which



retains the charge. Other peaks apparently result from cleavage between the sulfur atoms without rearrangement, and with migration of one or two hydrogen atoms to give, respectively,  $RS^+$ ,  $RS - 1$ , and  $RS - 2$ .

## HALOGEN COMPOUNDS

A compound that contains 1 chlorine atom will have an  $M + 2$  peak approximately one-third the intensity of the molecular ion peak because of the presence of a molecular ion containing the  $^{37}\text{Cl}$  isotope (see Table II). A compound that contains one bromine atom will have an  $M + 2$  peak almost equal in intensity to the molecular ion because of the presence of a molecular ion containing the  $^{81}\text{Br}$  isotope. A compound that contains two chlorines, or two bromines, or one chlorine and one bromine, will show a distinct  $M + 4$  peak, in addition to the  $M + 2$  peak, because of the presence of a molecular ion containing 2 atoms of the heavy isotope. In general, the number of chlorine and/or bromine atoms in a molecule can be ascertained by the number of alternate peaks beyond the molecular ion peak. Thus, 3 Cl atoms in a molecule will give peaks at  $M + 2$ ,  $M + 4$ , and  $M + 6$ ; in polychloro compounds, the peak of highest mass may be so weak as to escape notice.

The relative abundances of the peaks (molecular ion,  $M + 2$ ,  $M + 4$ , and so forth,) have been calculated by Beynon for compounds containing chlorine and bromine (atoms other than chlorine and bromine were ignored). A portion of these results is presented here, somewhat modified, as Table III. We can now tell what combination of chlorine and bromine atoms is present. It should be noted that Table III presents the isotope contributions in terms of percent of the molecular ion peak.

As required by Table III, the  $M + 2$  peak in the spec-

Table III. Intensities of Isotope Peaks (Relative to the Molecular Ion) for Combinations of Bromine and Chlorine

| Halogen Present    | % $M + 2$ | % $M + 4$ | % $M + 6$ | % $M + 8$ | % $M + 10$ | % $M + 12$ |
|--------------------|-----------|-----------|-----------|-----------|------------|------------|
| Br                 | 97.9      |           |           |           |            |            |
| Br <sub>2</sub>    | 195.0     | 95.5      |           |           |            |            |
| Br <sub>3</sub>    | 293.0     | 286.0     | 93.4      |           |            |            |
| Cl                 | 32.6      |           |           |           |            |            |
| Cl <sub>2</sub>    | 65.3      | 10.6      |           |           |            |            |
| Cl <sub>3</sub>    | 97.8      | 31.9      | 3.47      |           |            |            |
| Cl <sub>4</sub>    | 131.0     | 63.9      | 14.0      | 1.15      |            |            |
| Cl <sub>5</sub>    | 163.0     | 106.0     | 34.7      | 5.66      | 0.37       |            |
| Cl <sub>6</sub>    | 196.0     | 161.0     | 69.4      | 17.0      | 2.23       | 0.11       |
| BrCl               | 130.0     | 31.9      |           |           |            |            |
| Br <sub>2</sub> Cl | 228.0     | 159.0     | 31.2      |           |            |            |
| Cl <sub>2</sub> Br | 163.0     | 74.4      | 10.4      |           |            |            |

trum of *p*-chlorobenzophenone (Figure 12) is about one-third the intensity of the molecular ion peak ( $m/e$  218). As mentioned earlier, the chlorine-containing fragments ( $m/e$  141 and 113) show [fragment + 2] peaks of the proper intensity.

The  $M + 1$  peak is still useful for arriving at a molecular formula by use of Appendix A, after we subtract the masses of the appropriate number of chlorine and bromine atoms.

Unfortunately, the application of isotope contributions, though generally useful for aromatic halogen compounds, is limited by the weak molecular ion peak of many aliphatic halogen compounds of more than about six carbon atoms for a straight chain, or fewer for a branched chain. However, the halogen-containing fragments are recognizable by the ratio of the [fragment + 2] peaks to fragment peaks in monochlorides or monobromides. In polychloro- or bromo-

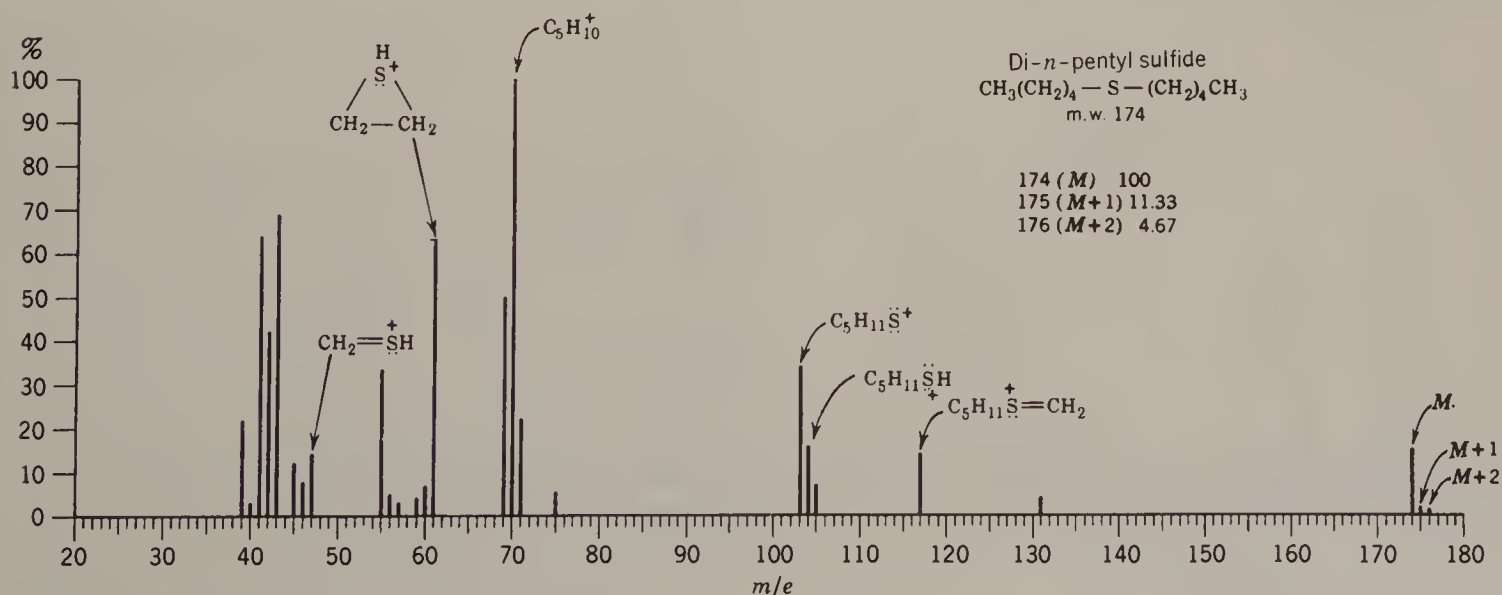


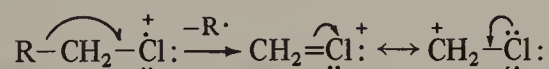
Figure 15. Di-n-pentyl sulfide.

compounds, these [fragment + isotope] peaks form a distinctive series of multiplets (Figure 16). Coincidence of fragment ion with one of the isotope fragments, with another disruption of the characteristic ratios, must always be kept in mind.

Neither fluorine nor iodine has a heavier isotope.

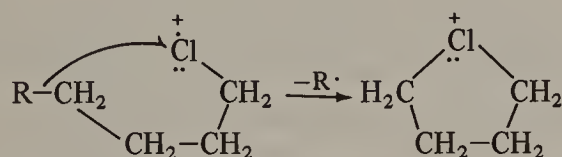
### Aliphatic Chlorides

The molecular ion peak is detectable only in the lower monochlorides. Fragmentation of the molecular ion is mediated by the chlorine atom but to a much lesser degree than is the case in oxygen-, nitrogen-, or sulfur-containing compounds. Thus, cleavage of a straight-chain monochloride at the C—C bond adjacent to the chlorine atom accounts for a small peak at  $m/e$  49 (and, of course, the isotope peak at  $m/e$  51).



Cleavage of the C-Cl bond leads to a small  $\text{Cl}^+$  peak and to a  $\text{R}^+$  peak which is prominent in the lower chlorides, but quite small when the chain is longer than about  $\text{C}_5$ .

Straight-chain chlorides longer than  $C_6$  give  $C_3H_6^+Cl$ ,  $C_4H_8^+Cl$ , and  $C_5H_{10}^+Cl$  ions. Of these the  $C_4H_8^+Cl$  ion forms the most intense (sometimes the base) peak; a five-membered cyclic structure may explain its stability.



Loss of HCl occurs, possibly by 1,2-elimination, to give a peak (weak or moderate) at  $M - 36$ .

In general, the spectrum of an aliphatic monochloride is dominated by the hydrocarbon pattern to a greater extent than that of a corresponding alcohol, amine, or mercaptan.

### Aliphatic Bromides

The remarks under aliphatic chlorides apply quite generally to the corresponding bromides.

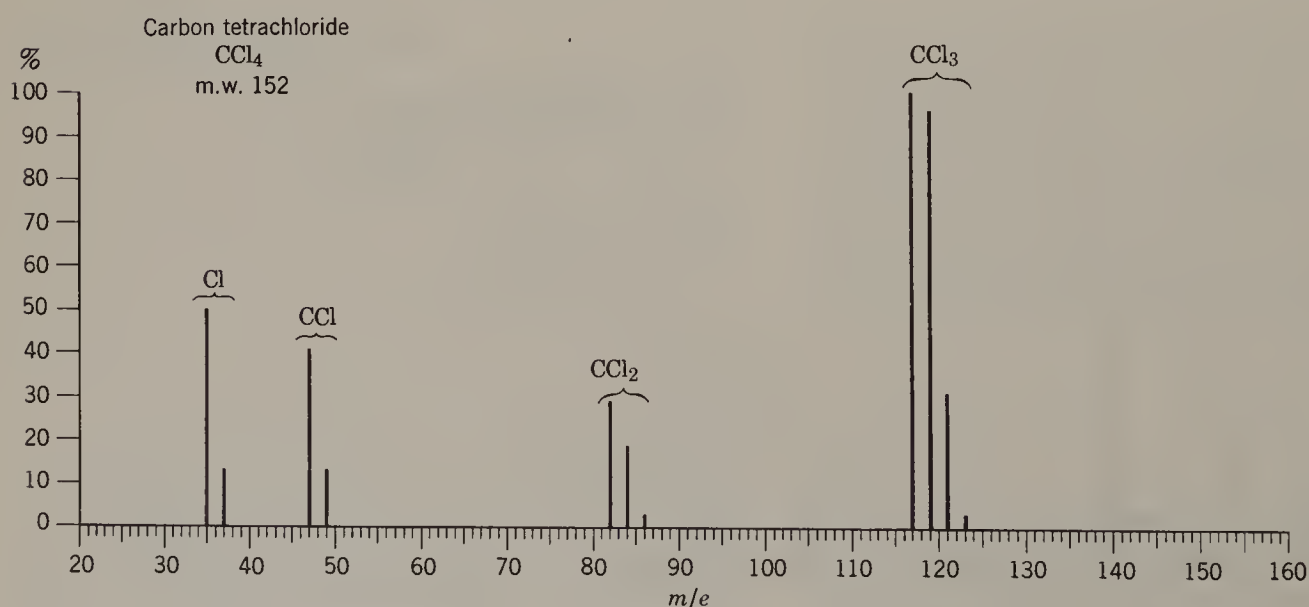
### Aliphatic Iodides

Aliphatic iodides give the strongest molecular ion peak of the aliphatic halides. Since iodine is monoisotopic, there is no distinctive isotope peak. The presence of an iodine atom can sometimes be deduced from isotope peaks that are suspiciously low in relation to the molecular weight, and from several distinctive peaks; in polyiodo compounds, the large interval between major peaks is characteristic.

Iodides cleave much as do chlorides and bromides, but the  $C_4H_8I^+$  ion is not as evident as the corresponding chloride and bromide ions.

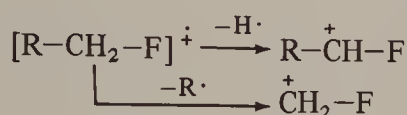
## Aliphatic Fluorides

Aliphatic fluorides give the weakest molecular ion peak of the aliphatic halides. Fluorine is monoisotopic, and its detection in polyfluoro compounds depends on suspiciously small isotopic peaks relative to the molecular ion, on the intervals between peaks, and on characteristic peaks. Of



**Figure 16.** *Carbon tetrachloride.*

these, the most characteristic is  $m/e$  69 due to the ion  $\text{CF}_3^+$ , which is the base peak in all perfluorocarbons. Prominent peaks are noted at  $m/e$  119, 169, 219...; these are increments of  $\text{CF}_2$ . The stable ions  $\text{C}_3\text{F}_5^+$  and  $\text{C}_4\text{F}_7^+$  give large peaks at  $m/e$  131 and 181. The  $M - \text{F}$  peak is frequently visible in perfluorinated compounds. In monofluorides, cleavage of the  $\alpha\beta$  C—C bond is less important than in the other monohalides, but cleavage of a C—H bond on the  $\alpha$ -C is more important. This reversal is a consequence of the high electronegativity of the F atom, and is rationalized by placing the positive charge on the  $\alpha$ -carbon. The secondary carbonium ion thus depicted by a loss of a hydrogen atom is more stable than the primary carbonium ion resulting from loss of an alkyl radical.



### Benzyl Halides

The molecular ion peak of benzyl halides is usually detectable. The benzyl (or tropylium) ion from loss of the halide (Section VII, Rule 8) is favored even over  $\beta$ -bond cleavage of an alkyl substituent. A substituted phenyl ion ( $\alpha$ -bond cleavage) is prominent when the ring is polysubstituted.

## Aromatic Halides

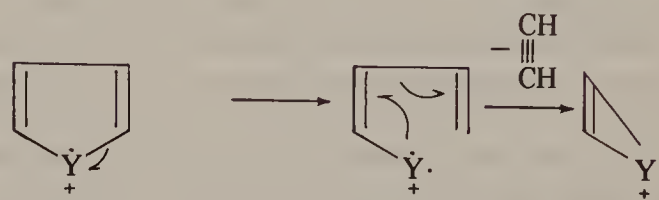
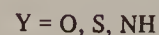
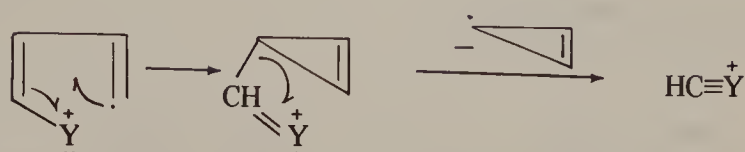
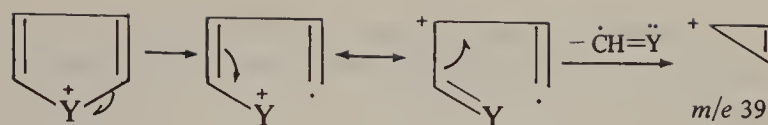
The molecular ion peak of an aryl halide is readily apparent. The  $M-X$  peak is large for all compounds in which  $X$  is attached directly to the ring.

## HETEROAROMATIC COMPOUNDS

The molecular ion peak of heteroaromatics and alkylated heteroaromatics is intense. Cleavage of the bond beta to the ring, as in alkylbenzenes, is the general rule; in pyridine, the position of substitution determines the ease of cleavage of the beta bond (see below).

Localizing the charge of the molecular ion on the heteroatom, rather than in the ring  $\pi$  structure, provides a satisfactory rationale for the observed mode of cleavage. The present treatment follows that used by Djerassi.<sup>2</sup>

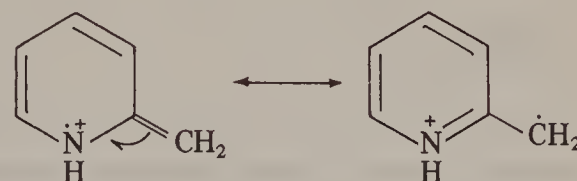
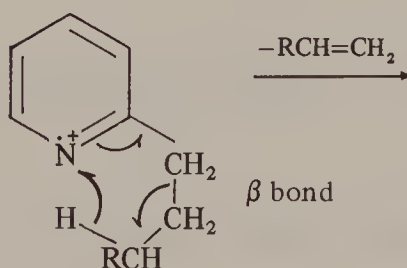
The five-membered ring heteroaromatics (furan, thiophene, and pyrrole) show very similar ring cleavage patterns. The first step in each case is cleavage of the carbon-heteroatom bond.



Thus furan exhibits two principal peaks:  $\text{C}_3\text{H}_3^+$  ( $m/e$  39) and  $\text{HC}\equiv\ddot{\text{O}}^+$  ( $m/e$  29). For thiophene, there are three:  $\text{C}_3\text{H}_3^+$  ( $m/e$  39),  $\text{HC}\equiv\ddot{\text{S}}^+$  ( $m/e$  45), and  $\text{C}_2\text{H}_2\ddot{\text{S}}^+$  ( $m/e$  58). And for pyrrole, there are three:  $\text{C}_3\text{H}_3^+$  ( $m/e$  39),  $\text{HC}\equiv\ddot{\text{N}}\text{H}^+$  ( $m/e$  28) and  $\text{C}_2\text{H}_2\ddot{\text{N}}\text{H}^+$  ( $m/e$  41). Pyrrole also eliminates a neutral molecule of HCN to give an intense peak at  $m/e$  40.

The base peak of 2,5-dimethylfuran is  $m/e$  43 ( $\text{CH}_3\text{C}\equiv\text{O}^+$ ).

Cleavage of the  $\beta$  C—C bond in alkylpyridines depends on the position of the ring substitution, being more pronounced when the alkyl group is in the 3-position. An alkyl group of more than 3 carbon atoms in the 2 position can undergo migration of a hydrogen atom to the ring nitrogen.





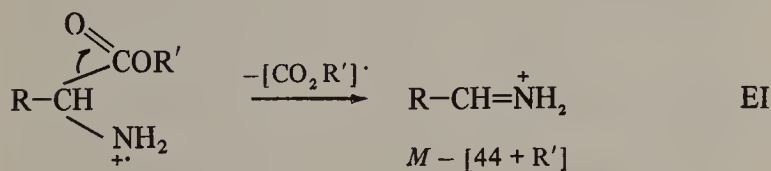
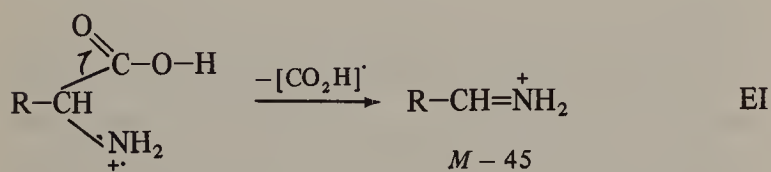
A similar cleavage is found in pyrazines since all ring substituents are necessarily ortho to one of the nitrogen atoms.

## NATURAL PRODUCTS

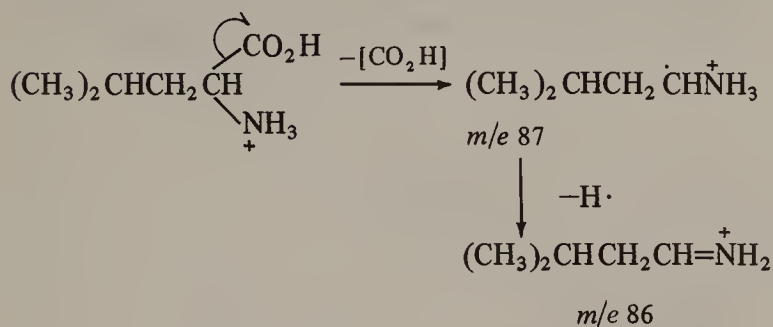
### Amino Acids

Detection of the molecular ion peaks of amino acids can be difficult. If we examine the mass spectra of amino acids, as well as of steroids and triglycerides, by a variety of ionization techniques, we can appreciate their relative merits.

The EI spectra of amino acids (Figure 17a) or their esters give weak or nonexistent molecular ion peaks, but CI and FI (Figure 17b, c) give either molecular or quasi-molecular ion peaks. The weak molecular ions in the EI spectra arise since amino acids easily lose their carboxyl group and the esters easily lose their carboalkoxyl group upon electron impact.



The FI and FD fragmentation patterns for leucine are similar. An ion-molecule reaction produces an  $\text{MH}^+$  ( $m/e$  132) ion, which readily loses a carboxyl group to form the



$m/e$  87 ion, which in turn loses a hydrogen atom to form the  $m/e$  86 ion.

## STERIODS

Polyhydroxy steroids (e.g., the tetrol for which spectra are shown in Figure 18) give EI spectra that often show weak or nonexistent molecular ion peaks. For this tetrol facile

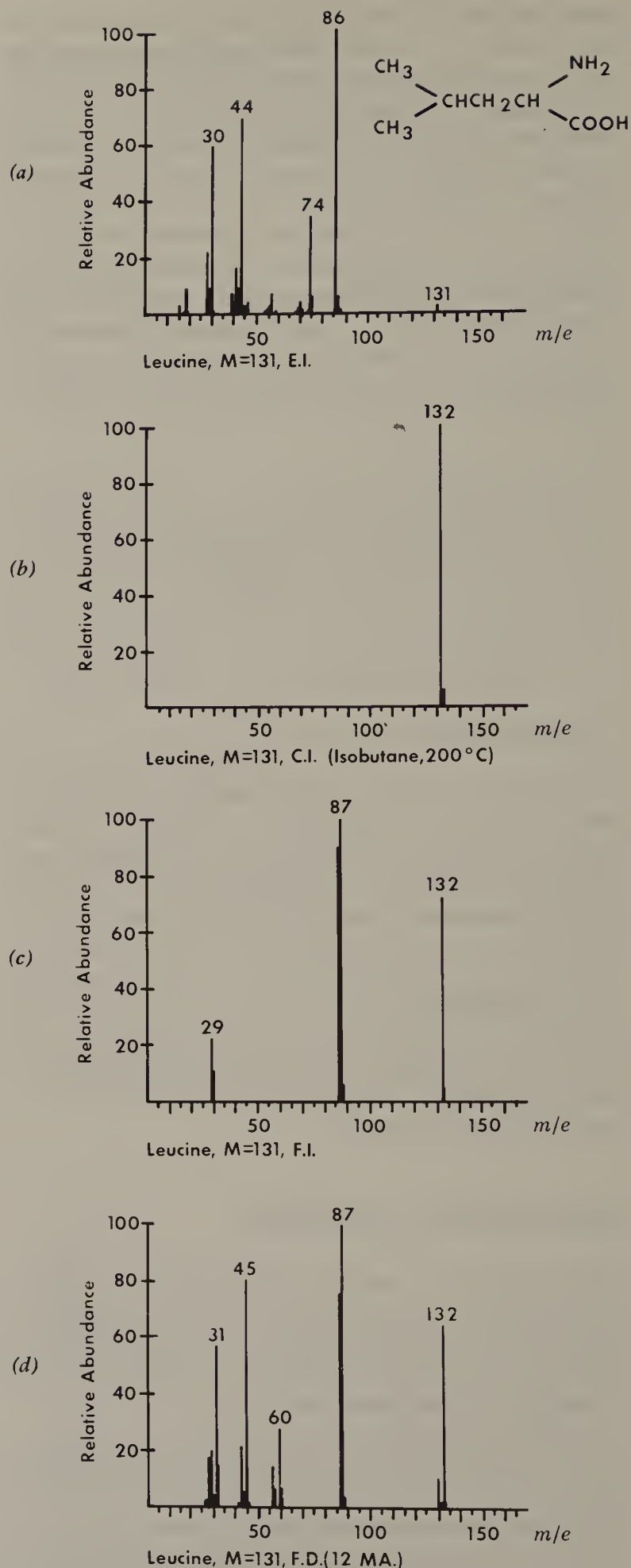
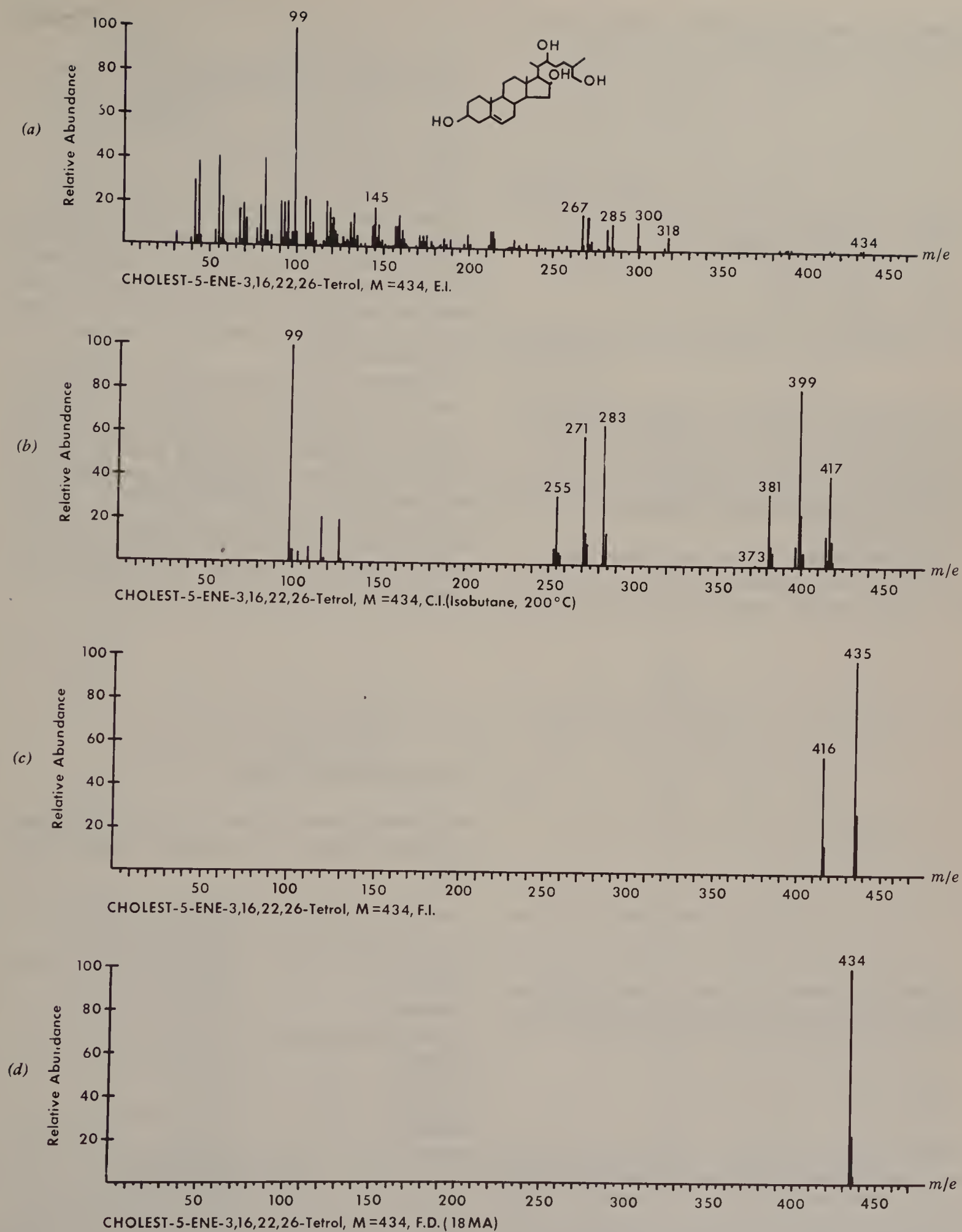
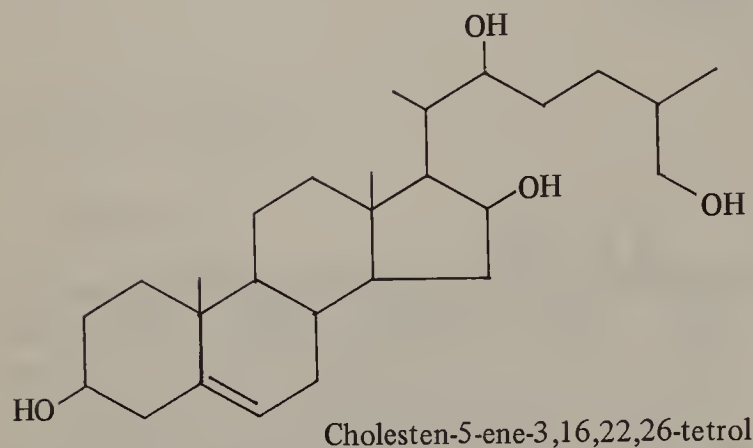


Figure 17. Mass spectra of leucine. (a) Electron impact (EI). (b) Chemical ionization (CI). (c) Field ionization (FI). (d) Field desorption (FD). See reference a, Table IV.



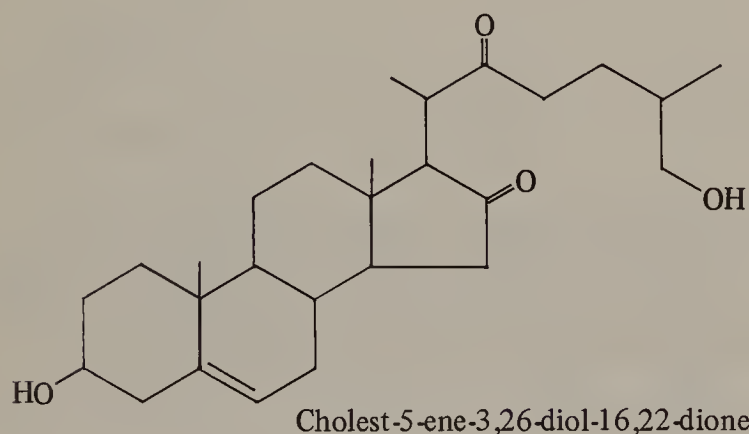
**Figure 18.** Mass spectra of cholest-5-ene-3,16,22,26-tetrol. (a) Electron Impact (EI) (b) Chemical Ionization (CI). (c) Field Ionization (FI). (d) Field Desorption (FD). See reference a, Table IV.

dehydration is not entirely thermally induced since the



FI spectrum (Figure 18c) shows an intense  $M + H$  peak. CI (Figure 18b) is not useful since the protonated molecular ion also readily dehydrates. Dehydration is, however, a secondary path in FI (Figure 18c) and is not observed at all in the FD spectrum (Figure 18d) which shows only a molecular ion peak.

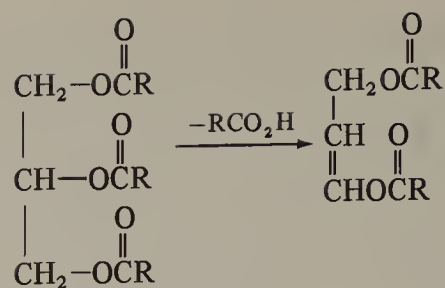
Generalizations about steroids are not easily made since the following steroidal diol dione behaves quite differently. Here the FD spectrum shows the  $M - H_2O$  peak as the



base peak, accompanied by a reasonably intense molecular ion peak. The FI spectrum is very similar, whereas neither the CI nor EI spectrum shows molecular ion peaks.

### Triglycerides

Naturally occurring triglycerides, which have high molecular weights and low volatility, give weak or nonexistent molecular ion (or  $MH^+$ ) peaks by EI, CI, and FI techniques. These triester samples require high source temperatures, and this leads to pyrolytic elimination of the elements of carboxylic acid.



Thus, the EI spectrum of trilaurin (Figure 19a) shows a modest molecular ion peak ( $m/e$  638) but a much more intense  $M - RCO_2H$  peak ( $m/e$  439). In the CI and FI spectra (Figure 19), the molecular ion peaks (or  $MH^+$  peaks) are not visible, and the  $m/e$  439 peak is the base peak. The FD spectrum provides an  $MH^+$  peak ( $m/e$  639), which is the base peak.

In summary, it is clear that no simple instructions can be set forth for choosing the best method of producing molecular ions. EI analyses are useful for those instances in which the samples are sufficiently thermally stable and have reasonable vapor pressure. EI instrumentation is also widely available as are a substantial number of published spectra, and data compilations are available for comparison. Table IV provides guidelines for selecting an appropriate ionization technique. CI, FI and FD techniques can be valuable alternatives when EI is not successful.

### MISCELLANEOUS CLASSES

The following classes of organic compounds are discussed in Biemann's book (B)<sup>1</sup>, or in Djerassi's books (D<sup>2</sup>, DI<sup>3</sup>, DII<sup>3</sup>).

|                            |  |
|----------------------------|--|
| Alkaloids                  | D, Chapter 5; DI; DII, Chapter 17; B, p. 305 |
| Amino Acids & Peptides     | DII, Chapter 26; B, Chapter 7                |
| Antibiotics                | DII, p. 172                                  |
| Carbohydrates              | DII, Chapter 27                              |
| Cyanides & Isothiocyanates | D, Chapter 11                                |
| Estrogens                  | DII, Chapter 19                              |
| Glycerides                 | B, p. 255                                    |
| Sapogenins                 | DII, Chapter 22                              |
| Silicones                  | B, p. 172                                    |
| Steroids                   | B, Chapter 9; DII, Chapters 17, 20, 21, 22   |
| Terpenes                   | B, p. 334; DII, Chapters 23, 24              |
| Thioketals                 | D, Chapter 7                                 |
| Tropone & Tropolones       | D, Chapter 18                                |



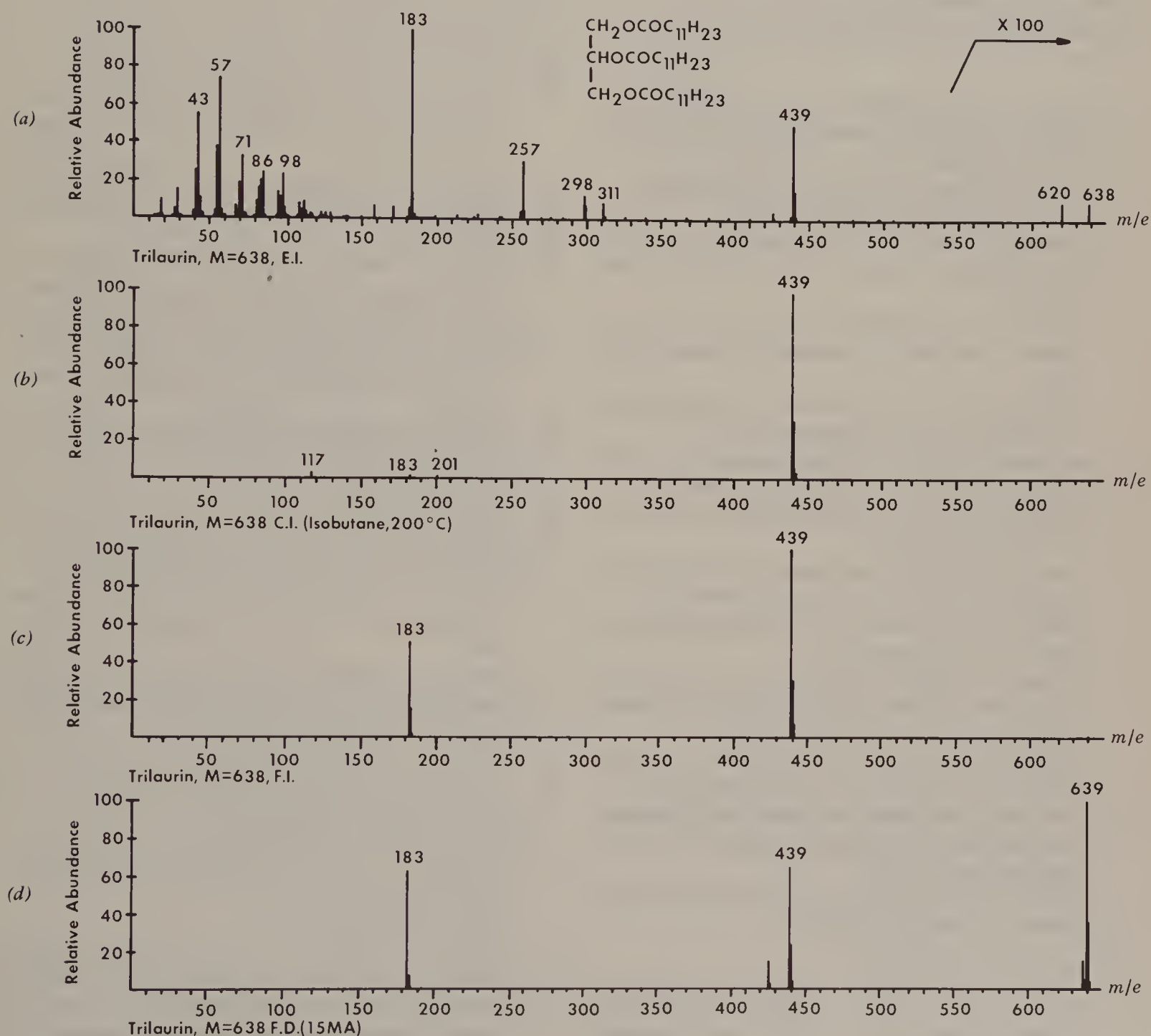
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2. Budzikiewicz, H., Djerassi, C., Williams, D. H. *Mass Spectrometry of Organic Compounds*. San Francisco: Holden-Day, 1967. This is the most complete general reference written for the organic chemist interested in employing mass spectrometry in structure determination.

3. Budzikiewicz, H., Djerassi, C., Williams, D. H. *Structure Elucidation of Natural Products by Mass Spectrometry*. San Francisco: Holden-Day, 1964, Vol. I, Vol. II.

## General Monographs

4. Beynon, J. H. *Mass Spectrometry and Its Application to Organic Chemistry*. Amsterdam: Elsevier, 1960.



**Figure 19.** Mass spectra of trilaurin: (a) Electron impact (EI). (b) Chemical ionization (CI). (c) Field ionization (FI). (d) Field desorption (FD). Note: that in a molecular ion peak ( $m/e$  638) would be 1% the intensity shown if it was at the same intensity as the peaks from  $m/e$  0 to 450. See Reference a, Table IV.

Table IV. Molecular Ion (or  $MH^+$ ) Peak and Fragmentation Characteristics for Four Compounds not Easily Analyzed by EI<sup>a</sup>

| Compound                | Class         | Volatility | Stability to Heat | EI                       |               | CI                        |                      | FI                        |               | FD                       |               |
|-------------------------|---------------|------------|-------------------|--------------------------|---------------|---------------------------|----------------------|---------------------------|---------------|--------------------------|---------------|
|                         |               |            |                   | M <sup>+</sup> Intensity | Fragmentation | MH <sup>+</sup> Intensity | Fragmentation        | MH <sup>+</sup> Intensity | Fragmentation | M <sup>+</sup> Intensity | Fragmentation |
| leucine                 | amino acid    | modest     | acceptable        | very weak                | extensive     | base peak                 | none                 | intense                   | moderate      | intense                  | extensive     |
| tetrol <sup>b</sup>     | steroid       | very low   | poor              | very weak                | extensive     | none                      | extensive            | base                      | minor         | base                     | none          |
| diol dione <sup>c</sup> | steroid       | very low   | poor              | none                     | extensive     | none                      | extensive            | base                      | minor         | base                     | none          |
| trilaurin               | triglycerides | very low   | high              | weak                     | extensive     | none                      | limited <sup>d</sup> | none                      | modest        | MH <sup>+</sup> base     | substantial   |

<sup>a</sup>Taken from H.M. Fales, et al., *Anal. Chem.*, 1975, 47, 207.

<sup>b</sup>For structure, see discussion in text, pp. 38-41.

<sup>c</sup>Cholest-5-ene-3, 26-diol-16, 22-dione.

<sup>d</sup>M - RCO<sub>2</sub>H only.

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Deduce the molecular formula for this compound.

- 2.2 The exact mass of a compound determined by high-resolution mass spectrometry is 70.0419. What is the molecular formula of the compound?
- 2.3 The low-resolution mass spectrum of 2-butenal shows a peak at  $m/e$  69 that is 28.9% as intense as the base peak. Propose at least one fragmentation route to account for this peak, and explain why this fragment would be reasonably stable.
- 2.4 The low-resolution mass spectrum of 3-butyne-2-ol shows the base peak at  $m/e$  55. Explain why the fragment giving rise to this peak would be very stable.
- 2.5 Consider the mass spectra (low resolution) of 2 isomers of molecular formula  $\text{C}_{10}\text{H}_{14}$ . Determine their structures and explain the major spectral features for each.
- 2.6 The mass spectrum of *o*-nitrotoluene shows a substantial peak at  $m/e$  120. Similar analysis of  $\alpha,\alpha,\alpha$ -trideutero-*o*-nitrotoluene does not give a peak at  $m/e$  120 but rather at  $m/e$  122. Explain.
- 2.7 Determine the structure for the mass spectrum shown.

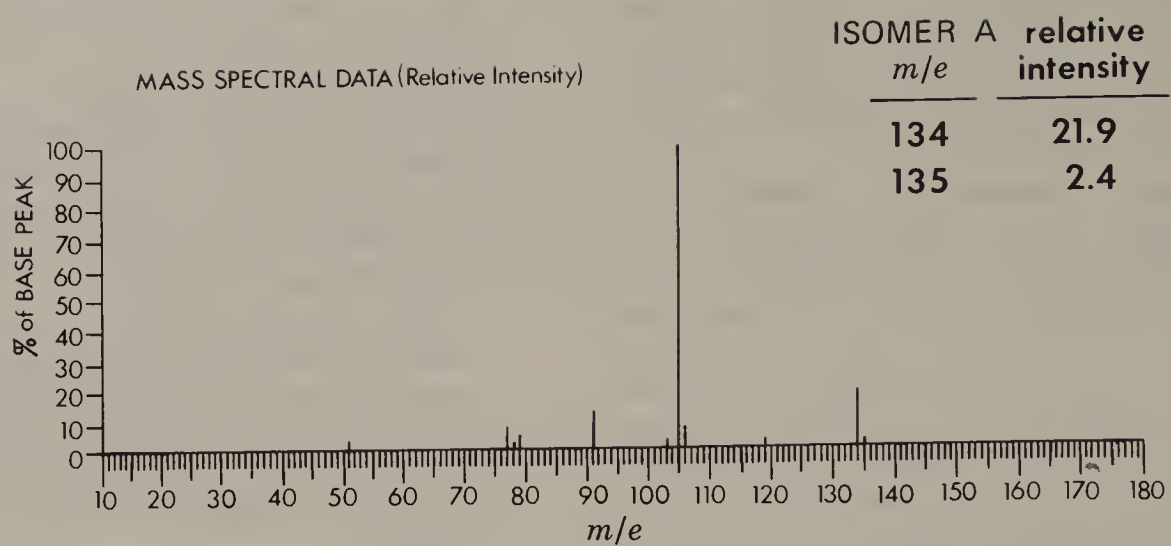
## PROBLEMS

- 2.1 A compound gives rise to the following intensities for peaks in the region of the molecular ion ( $M$ ):

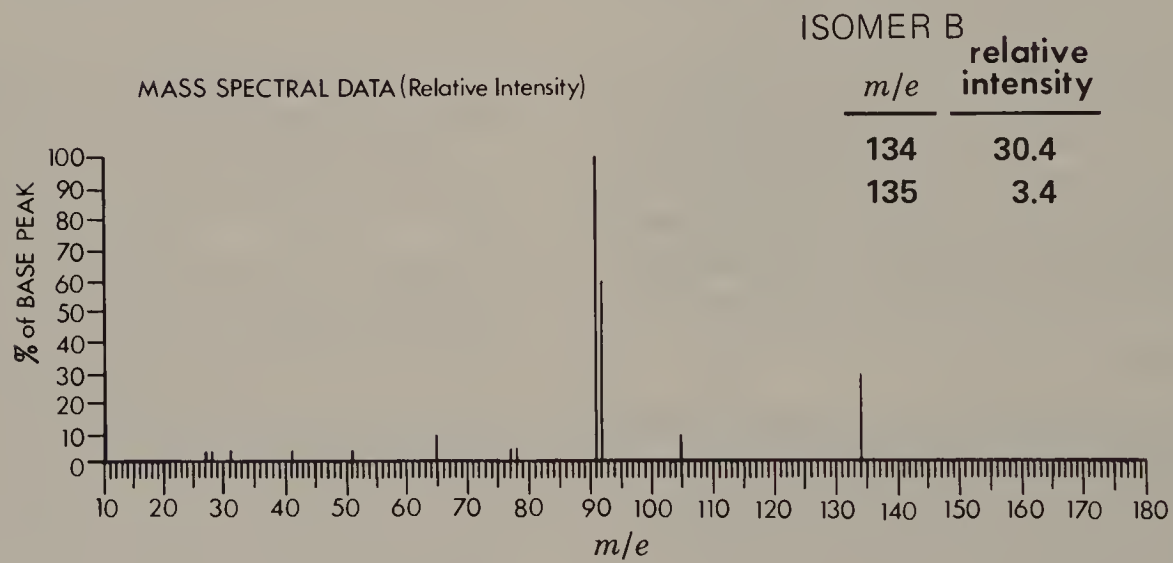
| $m/e$           | intensity |
|-----------------|-----------|
| 110 ( $M$ )     | 100       |
| 111 ( $M + 1$ ) | 6.96      |
| 112 ( $M + 2$ ) | 0.60      |



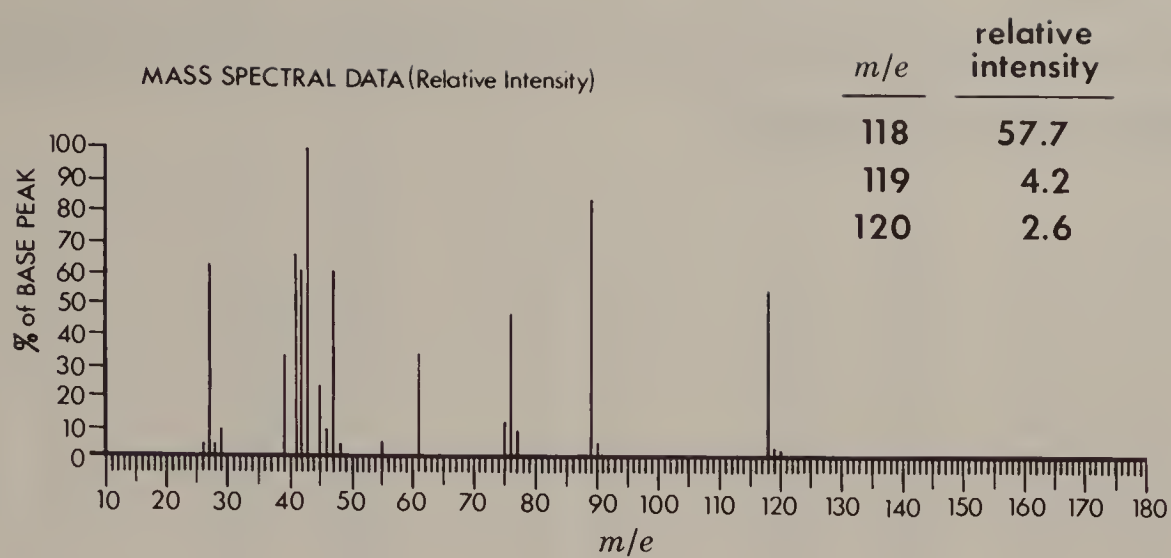
# Problem 2.5



# Problem 2.5



Problem 2.7



# appendix a masses and isotopic abundance ratios for various combinations of carbon, hydrogen, nitrogen and oxygen\*

|                               | M+1  | M+2  | MW      |                                     | M+1  | M+2  | MW      |                                 | M+1  | M+2  | MW      |
|-------------------------------|------|------|---------|-------------------------------------|------|------|---------|---------------------------------|------|------|---------|
| 12<br>C                       | 1.08 | 0.00 | 12.0000 | 31<br>HNO                           | 0.44 | 0.20 | 31.0058 | CH <sub>3</sub> N <sub>2</sub>  | 1.89 | 0.01 | 43.0297 |
| 13<br>CH                      | 1.10 | 0.00 | 13.0078 | H <sub>3</sub> N <sub>2</sub>       | 0.81 | 0.00 | 31.0297 | C <sub>2</sub> H <sub>3</sub> O | 2.25 | 0.21 | 43.0184 |
| 14<br>N                       | 0.38 | 0.00 | 14.0031 | CH <sub>3</sub> O                   | 1.17 | 0.20 | 31.0184 | C <sub>2</sub> H <sub>5</sub> N | 2.62 | 0.02 | 43.0422 |
| CH <sub>2</sub>               | 1.11 | 0.00 | 14.0157 | CH <sub>5</sub> N                   | 1.54 | 0.01 | 31.0422 | C <sub>3</sub> H <sub>7</sub>   | 3.35 | 0.04 | 43.0548 |
| 15<br>HN                      | 0.40 | 0.00 | 15.0109 | 32<br>O <sub>2</sub>                | 0.08 | 0.40 | 31.9898 | 44<br>N <sub>2</sub> O          | 0.80 | 0.20 | 44.0011 |
| CH <sub>3</sub>               | 1.13 | 0.00 | 15.0235 | H <sub>2</sub> NO                   | 0.45 | 0.20 | 32.0136 | H <sub>2</sub> N <sub>3</sub>   | 1.18 | 0.00 | 44.0249 |
| 16<br>O                       | 0.04 | 0.20 | 15.9949 | H <sub>4</sub> N <sub>2</sub>       | 0.83 | 0.00 | 32.0375 | CO <sub>2</sub>                 | 1.16 | 0.40 | 43.9898 |
| H <sub>2</sub> N              | 0.41 | 0.00 | 16.0187 | CH <sub>4</sub> O                   | 1.18 | 0.20 | 32.0262 | CH <sub>2</sub> NO              | 1.53 | 0.21 | 44.0136 |
| CH <sub>4</sub>               | 1.14 | 0.00 | 16.0313 | 33<br>HO <sub>2</sub>               | 0.09 | 0.40 | 32.9976 | CH <sub>4</sub> N <sub>2</sub>  | 1.91 | 0.01 | 44.0375 |
| 17<br>HO                      | 0.06 | 0.20 | 17.0027 | H <sub>3</sub> NO                   | 0.47 | 0.20 | 33.0215 | C <sub>2</sub> H <sub>4</sub> O | 2.26 | 0.21 | 44.0262 |
| H <sub>3</sub> N              | 0.43 | 0.00 | 17.0266 | 34<br>H <sub>2</sub> O <sub>2</sub> | 0.11 | 0.40 | 34.0054 | C <sub>2</sub> H <sub>6</sub> N | 2.64 | 0.02 | 44.0501 |
| 18<br>H <sub>2</sub> O        | 0.07 | 0.20 | 18.0106 | 36<br>C <sub>3</sub>                | 3.24 | 0.04 | 36.0000 | C <sub>3</sub> H <sub>8</sub>   | 3.37 | 0.04 | 44.0626 |
| 24<br>C <sub>2</sub>          | 2.16 | 0.01 | 24.0000 | 37<br>C <sub>3</sub> H              | 3.26 | 0.04 | 37.0078 | 45<br>HN <sub>2</sub> O         | 0.82 | 0.20 | 45.0089 |
| 25<br>C <sub>2</sub> H        | 2.18 | 0.01 | 25.0078 | 38<br>C <sub>2</sub> N              | 2.54 | 0.02 | 38.0031 | H <sub>3</sub> N <sub>3</sub>   | 1.19 | 0.00 | 45.0328 |
| 26<br>CN                      | 1.46 | 0.00 | 26.0031 | C <sub>3</sub> H <sub>2</sub>       | 3.27 | 0.04 | 38.0157 | CH <sub>2</sub> O <sub>2</sub>  | 1.17 | 0.40 | 44.9976 |
| C <sub>2</sub> H <sub>2</sub> | 2.19 | 0.01 | 26.0157 | 39<br>C <sub>2</sub> HN             | 2.56 | 0.02 | 39.0109 | CH <sub>3</sub> NO              | 1.55 | 0.21 | 45.0215 |
| 27<br>CHN                     | 1.48 | 0.00 | 27.0109 | C <sub>3</sub> H <sub>3</sub>       | 3.29 | 0.04 | 39.0235 | CH <sub>5</sub> N <sub>2</sub>  | 1.92 | 0.01 | 45.0453 |
| C <sub>2</sub> H <sub>3</sub> | 2.21 | 0.01 | 27.0235 | 40<br>CN <sub>2</sub>               | 1.84 | 0.01 | 40.0062 | C <sub>2</sub> H <sub>5</sub> O | 2.28 | 0.21 | 45.0340 |
| 28<br>N <sub>2</sub>          | 0.76 | 0.00 | 28.0062 | C <sub>2</sub> O                    | 2.20 | 0.21 | 39.9949 | C <sub>2</sub> H <sub>7</sub> N | 2.65 | 0.02 | 45.0579 |
| CO                            | 1.12 | 0.20 | 27.9949 | C <sub>2</sub> H <sub>2</sub> N     | 2.57 | 0.02 | 40.0187 | 46<br>NO <sub>2</sub>           | 0.46 | 0.40 | 45.9929 |
| CH <sub>2</sub> N             | 1.49 | 0.00 | 28.0187 | C <sub>3</sub> H <sub>4</sub>       | 3.31 | 0.04 | 40.0313 | H <sub>2</sub> N <sub>2</sub> O | 0.83 | 0.20 | 46.0167 |
| C <sub>2</sub> H <sub>4</sub> | 2.23 | 0.01 | 28.0313 | 41<br>CHN <sub>2</sub>              | 1.86 | 0.01 | 41.0140 | H <sub>4</sub> N <sub>3</sub>   | 1.21 | 0.01 | 46.0406 |
| 29<br>HN <sub>2</sub>         | 0.78 | 0.00 | 29.0140 | C <sub>2</sub> HO                   | 2.22 | 0.21 | 41.0027 | CH <sub>2</sub> O <sub>2</sub>  | 1.19 | 0.40 | 46.0054 |
| CHO                           | 1.14 | 0.20 | 29.0027 | C <sub>2</sub> H <sub>3</sub> N     | 2.59 | 0.02 | 41.0266 | CH <sub>4</sub> NO              | 1.57 | 0.21 | 46.0293 |
| CH <sub>3</sub> N             | 1.51 | 0.00 | 29.0266 | C <sub>3</sub> H <sub>5</sub>       | 3.32 | 0.04 | 41.0391 | CH <sub>6</sub> N <sub>2</sub>  | 1.94 | 0.01 | 46.0532 |
| C <sub>2</sub> H <sub>5</sub> | 2.24 | 0.01 | 29.0391 | 42<br>N <sub>3</sub>                | 1.14 | 0.00 | 42.0093 | C <sub>2</sub> H <sub>6</sub> O | 2.30 | 0.22 | 46.0419 |
| 30<br>NO                      | 0.42 | 0.20 | 29.9980 | CNO                                 | 1.50 | 0.21 | 41.9980 | 47<br>HN <sub>2</sub> O         | 0.48 | 0.40 | 47.0007 |
| H <sub>2</sub> N <sub>2</sub> | 0.79 | 0.00 | 30.0218 | CH <sub>2</sub> N <sub>2</sub>      | 1.88 | 0.01 | 42.0218 | H <sub>3</sub> N <sub>2</sub> O | 0.85 | 0.20 | 47.0246 |
| CH <sub>2</sub> O             | 1.15 | 0.20 | 30.0106 | C <sub>2</sub> H <sub>2</sub> O     | 2.23 | 0.21 | 42.0106 | H <sub>5</sub> N <sub>3</sub>   | 1.22 | 0.01 | 47.0484 |
| CH <sub>4</sub> N             | 1.53 | 0.01 | 30.0344 | C <sub>2</sub> H <sub>4</sub> N     | 2.61 | 0.02 | 42.0344 | CH <sub>3</sub> O <sub>2</sub>  | 1.21 | 0.40 | 47.0133 |
| C <sub>2</sub> H <sub>6</sub> | 2.26 | 0.01 | 30.0470 | C <sub>3</sub> H <sub>6</sub>       | 3.34 | 0.04 | 42.0470 | CH <sub>5</sub> NO              | 1.58 | 0.21 | 47.0371 |
|                               |      |      |         | 43<br>HN <sub>3</sub>               | 1.16 | 0.00 | 43.0171 | 48<br>O <sub>3</sub>            | 0.12 | 0.60 | 47.9847 |
|                               |      |      |         | CHNO                                | 1.52 | 0.21 | 43.0058 | H <sub>2</sub> NO <sub>2</sub>  | 0.49 | 0.40 | 48.0085 |
|                               |      |      |         |                                     |      |      |         | H <sub>4</sub> N <sub>2</sub> O | 0.87 | 0.20 | 48.0324 |
|                               |      |      |         |                                     |      |      |         | CH <sub>4</sub> O <sub>2</sub>  | 1.22 | 0.40 | 48.0211 |
|                               |      |      |         |                                     |      |      |         | C <sub>4</sub>                  | 4.32 | 0.07 | 48.0000 |

The M+1 and M+2 data were taken, with permission, from J.H. Beynon, *Mass Spectrometry and its Application to Organic Chemistry*, Elsevier, Amsterdam, 1960. These data form a self-consistent set and can be used regardless of the mass standard.

The columns headed MW contain the molecular weights using the exact mass of the most abundant isotope of each element; these weights are based on the most abundant isotope of carbon having a mass of 12.0000.



|  | M+1  | M+2  | MW      |  | M+1  | M+2  | MW      |  | M+1  | M+2  | MW      |
|--|------|------|---------|--|------|------|---------|--|------|------|---------|
| 49<br>H <sub>2</sub> O <sub>3</sub>          | 0.13 | 0.60 | 48.9925 | H <sub>2</sub> N <sub>4</sub>                | 1.56 | 0.01 | 58.0280 | C <sub>4</sub> N                             | 4.70 | 0.09 | 62.0031 |
| H <sub>3</sub> N <sub>2</sub> O <sub>2</sub> | 0.51 | 0.40 | 49.0164 | CN <sub>2</sub> O <sub>2</sub>               | 1.54 | 0.41 | 57.9929 | C <sub>5</sub> H <sub>2</sub>                | 5.44 | 0.12 | 62.0157 |
| C <sub>4</sub> H                             | 4.34 | 0.07 | 49.0078 | CH <sub>2</sub> N <sub>2</sub> O             | 1.91 | 0.21 | 58.0167 | 63<br>HN <sub>2</sub> O <sub>3</sub>         | 0.51 | 0.60 | 62.9956 |
| 50<br>H <sub>2</sub> O <sub>3</sub>          | 0.15 | 0.60 | 50.0003 | CH <sub>4</sub> N <sub>3</sub>               | 2.29 | 0.02 | 58.0406 | H <sub>3</sub> N <sub>2</sub> O <sub>2</sub> | 0.89 | 0.40 | 63.0195 |
| C <sub>3</sub> N                             | 3.62 | 0.05 | 50.0031 | C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> | 2.27 | 0.42 | 58.0054 | H <sub>5</sub> N <sub>3</sub> O              | 1.26 | 0.21 | 63.0433 |
| C <sub>4</sub> H <sub>2</sub>                | 4.35 | 0.07 | 50.0157 | C <sub>2</sub> H <sub>4</sub> NO             | 2.65 | 0.22 | 58.0293 | CH <sub>3</sub> O <sub>3</sub>               | 1.25 | 0.60 | 63.0082 |
| 51<br>C <sub>3</sub> HN                      | 3.64 | 0.05 | 51.0109 | C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> | 3.02 | 0.03 | 58.0532 | CH <sub>5</sub> NO <sub>2</sub>              | 1.62 | 0.41 | 63.0320 |
| C <sub>4</sub> H <sub>3</sub>                | 4.37 | 0.07 | 51.0235 | C <sub>3</sub> H <sub>6</sub> O              | 3.38 | 0.24 | 58.0419 | C <sub>4</sub> HN                            | 4.72 | 0.09 | 63.0109 |
| 52<br>C <sub>2</sub> N <sub>2</sub>          | 2.92 | 0.03 | 52.0062 | C <sub>3</sub> H <sub>8</sub> N              | 3.75 | 0.05 | 58.0657 | C <sub>5</sub> H <sub>3</sub>                | 5.45 | 0.12 | 63.0235 |
| C <sub>3</sub> O                             | 3.28 | 0.24 | 51.9949 | C <sub>4</sub> H <sub>10</sub>               | 4.48 | 0.08 | 58.0783 | 64<br>O <sub>4</sub>                         | 0.16 | 0.80 | 63.9796 |
| C <sub>3</sub> H <sub>2</sub> N              | 3.66 | 0.05 | 52.0187 | 59<br>HN <sub>3</sub> O                      | 1.20 | 0.21 | 59.0120 | H <sub>2</sub> NO <sub>3</sub>               | 0.53 | 0.60 | 64.0034 |
| C <sub>4</sub> H <sub>4</sub>                | 4.39 | 0.07 | 52.0313 | H <sub>3</sub> N <sub>4</sub>                | 1.57 | 0.01 | 59.0359 | H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> | 0.91 | 0.40 | 64.0273 |
| 53<br>C <sub>2</sub> HN <sub>2</sub>         | 2.94 | 0.03 | 53.0140 | CHNO <sub>2</sub>                            | 1.56 | 0.41 | 59.0007 | CH <sub>4</sub> O <sub>3</sub>               | 1.26 | 0.60 | 64.0160 |
| C <sub>3</sub> HO                            | 3.30 | 0.24 | 53.0027 | CH <sub>3</sub> N <sub>2</sub> O             | 1.93 | 0.21 | 59.0246 | C <sub>3</sub> N <sub>2</sub>                | 4.00 | 0.06 | 64.0062 |
| C <sub>3</sub> H <sub>3</sub> N              | 3.67 | 0.05 | 53.0266 | CH <sub>5</sub> N <sub>3</sub>               | 2.30 | 0.02 | 59.0484 | C <sub>4</sub> O                             | 4.36 | 0.27 | 63.9949 |
| C <sub>4</sub> H <sub>5</sub>                | 4.40 | 0.07 | 53.0391 | C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> | 2.29 | 0.42 | 59.0133 | C <sub>4</sub> H <sub>2</sub> N              | 4.74 | 0.09 | 64.0187 |
| 54<br>CN <sub>3</sub>                        | 2.22 | 0.02 | 54.0093 | C <sub>2</sub> H <sub>5</sub> NO             | 2.66 | 0.22 | 59.0371 | C <sub>5</sub> H <sub>4</sub>                | 5.47 | 0.12 | 64.0313 |
| C <sub>2</sub> NO                            | 2.58 | 0.22 | 53.9980 | C <sub>2</sub> H <sub>7</sub> N <sub>2</sub> | 3.04 | 0.03 | 59.0610 | 65<br>HO <sub>4</sub>                        | 0.17 | 0.80 | 64.9874 |
| C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> | 2.96 | 0.03 | 54.0218 | C <sub>3</sub> H <sub>7</sub> O              | 3.39 | 0.24 | 59.0497 | H <sub>3</sub> NO <sub>3</sub>               | 0.55 | 0.60 | 65.0113 |
| C <sub>3</sub> H <sub>2</sub> O              | 3.31 | 0.24 | 54.0106 | C <sub>3</sub> H <sub>9</sub> N              | 3.77 | 0.05 | 59.0736 | C <sub>3</sub> HN <sub>2</sub>               | 4.02 | 0.06 | 65.0140 |
| C <sub>3</sub> H <sub>4</sub> N              | 3.69 | 0.05 | 54.0344 | 60<br>N <sub>2</sub> O <sub>2</sub>          | 0.84 | 0.40 | 59.9960 | C <sub>4</sub> HO                            | 4.38 | 0.27 | 65.0027 |
| C <sub>4</sub> H <sub>6</sub>                | 4.42 | 0.07 | 54.0470 | H <sub>2</sub> N <sub>3</sub> O              | 1.22 | 0.21 | 60.0198 | C <sub>4</sub> H <sub>3</sub> N              | 4.75 | 0.09 | 65.0266 |
| 55<br>CHN <sub>3</sub>                       | 2.24 | 0.02 | 55.0171 | H <sub>4</sub> N <sub>4</sub>                | 1.59 | 0.01 | 60.0437 | C <sub>5</sub> H <sub>5</sub>                | 5.48 | 0.12 | 65.0391 |
| C <sub>2</sub> HN <sub>2</sub>               | 2.60 | 0.22 | 55.0058 | CO <sub>3</sub>                              | 1.20 | 0.60 | 59.9847 | 66<br>H <sub>2</sub> O <sub>4</sub>          | 0.19 | 0.80 | 65.9953 |
| C <sub>2</sub> H <sub>3</sub> N <sub>2</sub> | 2.97 | 0.03 | 55.0297 | CH <sub>2</sub> NO <sub>2</sub>              | 1.57 | 0.41 | 60.0085 | C <sub>2</sub> N <sub>3</sub>                | 3.31 | 0.04 | 66.0093 |
| C <sub>3</sub> H <sub>3</sub> O              | 3.33 | 0.24 | 55.0184 | CH <sub>4</sub> N <sub>2</sub> O             | 1.95 | 0.21 | 60.0324 | C <sub>3</sub> NO                            | 3.66 | 0.25 | 65.9980 |
| C <sub>3</sub> H <sub>5</sub> N              | 3.70 | 0.05 | 55.0422 | CH <sub>5</sub> N <sub>3</sub>               | 2.32 | 0.02 | 60.0563 | C <sub>3</sub> H <sub>2</sub> N <sub>2</sub> | 4.04 | 0.06 | 66.0218 |
| C <sub>4</sub> H <sub>7</sub>                | 4.43 | 0.07 | 55.0548 | C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> | 2.30 | 0.42 | 60.0211 | C <sub>4</sub> H <sub>2</sub> O              | 4.39 | 0.27 | 66.0106 |
| 56<br>N <sub>4</sub>                         | 1.53 | 0.01 | 56.0124 | C <sub>2</sub> H <sub>6</sub> NO             | 2.68 | 0.22 | 60.0449 | C <sub>4</sub> H <sub>4</sub> N              | 4.77 | 0.09 | 66.0344 |
| CN <sub>2</sub> O                            | 1.88 | 0.21 | 56.0011 | C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> | 3.05 | 0.03 | 60.0688 | C <sub>5</sub> H <sub>6</sub>                | 5.50 | 0.12 | 66.0470 |
| CH <sub>2</sub> N <sub>3</sub>               | 2.26 | 0.02 | 56.0249 | C <sub>3</sub> H <sub>8</sub> O              | 3.41 | 0.24 | 60.0575 | 67<br>C <sub>2</sub> HN <sub>3</sub>         | 3.32 | 0.04 | 67.0171 |
| C <sub>2</sub> O <sub>2</sub>                | 2.24 | 0.41 | 55.9898 | C <sub>5</sub>                               | 5.40 | 0.12 | 60.0000 | C <sub>3</sub> HN <sub>2</sub>               | 3.68 | 0.25 | 67.0058 |
| C <sub>2</sub> H <sub>2</sub> NO             | 2.61 | 0.22 | 56.0136 | 61<br>HN <sub>2</sub> O <sub>2</sub>         | 0.86 | 0.40 | 61.0038 | C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> | 4.05 | 0.06 | 67.0297 |
| C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> | 2.99 | 0.03 | 56.0375 | H <sub>3</sub> N <sub>3</sub> O              | 1.23 | 0.21 | 61.0277 | C <sub>4</sub> H <sub>3</sub> O              | 4.41 | 0.27 | 67.0184 |
| C <sub>3</sub> H <sub>4</sub> O              | 3.34 | 0.24 | 56.0262 | H <sub>5</sub> N <sub>4</sub>                | 1.61 | 0.01 | 61.0515 | C <sub>4</sub> H <sub>5</sub> N              | 4.78 | 0.09 | 67.0422 |
| C <sub>3</sub> H <sub>6</sub> N              | 3.72 | 0.05 | 56.0501 | CH <sub>2</sub> O <sub>3</sub>               | 1.21 | 0.60 | 60.9925 | C <sub>5</sub> H <sub>7</sub>                | 5.52 | 0.12 | 67.0548 |
| C <sub>4</sub> H <sub>8</sub>                | 4.45 | 0.08 | 56.0626 | CH <sub>3</sub> NO <sub>2</sub>              | 1.59 | 0.41 | 61.0164 | 68<br>CN <sub>4</sub>                        | 2.61 | 0.03 | 68.0124 |
| 57<br>HN <sub>4</sub>                        | 1.54 | 0.01 | 57.0202 | CH <sub>5</sub> N <sub>2</sub> O             | 1.96 | 0.21 | 61.0402 | C <sub>2</sub> N <sub>2</sub> O              | 2.96 | 0.23 | 68.0011 |
| CHN <sub>2</sub> O                           | 1.90 | 0.21 | 57.0089 | CH <sub>7</sub> N <sub>3</sub>               | 2.34 | 0.02 | 61.0641 | C <sub>2</sub> H <sub>2</sub> N <sub>3</sub> | 3.34 | 0.04 | 68.0249 |
| CH <sub>3</sub> N <sub>3</sub>               | 2.27 | 0.02 | 57.0328 | C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> | 2.32 | 0.42 | 61.0289 | C <sub>3</sub> O <sub>2</sub>                | 3.32 | 0.44 | 67.9898 |
| C <sub>2</sub> HO <sub>2</sub>               | 2.26 | 0.41 | 56.9976 | C <sub>2</sub> H <sub>7</sub> NO             | 2.69 | 0.22 | 61.0528 | C <sub>3</sub> H <sub>2</sub> NO             | 3.69 | 0.25 | 68.0136 |
| C <sub>2</sub> H <sub>3</sub> NO             | 2.63 | 0.22 | 57.0215 | C <sub>5</sub> H                             | 5.42 | 0.12 | 61.0078 | C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> | 4.07 | 0.06 | 68.0375 |
| C <sub>2</sub> H <sub>5</sub> N <sub>2</sub> | 3.00 | 0.03 | 57.0453 | 62<br>NO <sub>3</sub>                        | 0.50 | 0.60 | 61.9878 | C <sub>4</sub> H <sub>4</sub> O              | 4.43 | 0.28 | 68.0262 |
| C <sub>3</sub> H <sub>5</sub> O              | 3.36 | 0.24 | 57.0340 | H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> | 0.87 | 0.40 | 62.0116 | C <sub>4</sub> H <sub>6</sub> N              | 4.80 | 0.09 | 68.0501 |
| C <sub>3</sub> H <sub>7</sub> N              | 3.74 | 0.05 | 57.0579 | H <sub>4</sub> N <sub>3</sub> O              | 1.25 | 0.21 | 62.0355 | C <sub>5</sub> H <sub>8</sub>                | 5.53 | 0.12 | 68.0626 |
| C <sub>4</sub> H <sub>9</sub>                | 4.47 | 0.08 | 57.0705 | H <sub>6</sub> N <sub>4</sub>                | 1.62 | 0.01 | 62.0594 | 69<br>CHN <sub>4</sub>                       | 2.62 | 0.03 | 69.0202 |
| 58<br>N <sub>3</sub> O                       | 1.18 | 0.21 | 58.0042 | CH <sub>2</sub> O <sub>3</sub>               | 1.23 | 0.60 | 62.0003 | C <sub>2</sub> HN <sub>2</sub> O             | 2.98 | 0.23 | 69.0089 |
|  |      |      |         | CH <sub>4</sub> NO <sub>2</sub>              | 1.60 | 0.41 | 62.0242 | C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> | 3.35 | 0.04 | 69.0328 |
|  |      |      |         | CH <sub>6</sub> N <sub>2</sub> O             | 1.98 | 0.21 | 62.0480 |  |      |      |         |
|  |      |      |         | C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> | 2.34 | 0.42 | 62.0368 |  |      |      |         |

|  | M+1  | M+2  | MW      |  | M+1  | M+2  | MW      |   | M+1  | M+2  | MW      |
|--|------|------|---------|--|------|------|---------|---|------|------|---------|
| C <sub>3</sub> H <sub>2</sub> O <sub>2</sub>   | 3.34 | 0.44 | 68.9976 | C <sub>2</sub> H <sub>7</sub> N <sub>3</sub>   | 3.42 | 0.04 | 73.0641 | C <sub>5</sub> H <sub>2</sub> N               | 5.82 | 0.14 | 76.0187 |
| C <sub>3</sub> H <sub>3</sub> NO               | 3.71 | 0.25 | 69.0215 | C <sub>3</sub> H <sub>5</sub> O <sub>2</sub>   | 3.40 | 0.44 | 73.0289 | C <sub>6</sub> H <sub>4</sub>                 | 6.55 | 0.18 | 76.0313 |
| C <sub>3</sub> H <sub>5</sub> N <sub>2</sub>   | 4.08 | 0.06 | 69.0453 | C <sub>3</sub> H <sub>7</sub> NO               | 3.77 | 0.25 | 73.0528 | 77  |      |      |         |
| C <sub>4</sub> H <sub>5</sub> O                | 4.44 | 0.28 | 69.0340 | C <sub>3</sub> H <sub>9</sub> N <sub>2</sub>   | 4.15 | 0.07 | 73.0767 | HN <sub>2</sub> O <sub>3</sub>                | 0.90 | 0.60 | 76.9987 |
| C <sub>4</sub> H <sub>7</sub> N                | 4.82 | 0.09 | 69.0579 | C <sub>4</sub> H <sub>9</sub> O                | 4.51 | 0.28 | 73.0653 | H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>  | 1.27 | 0.41 | 77.0226 |
| C <sub>5</sub> H <sub>9</sub>                  | 5.55 | 0.12 | 69.0705 | C <sub>4</sub> H <sub>11</sub> N               | 4.88 | 0.09 | 73.0892 | H <sub>5</sub> N <sub>4</sub> O               | 1.64 | 0.21 | 77.0464 |
| 70   |      |      |         | C <sub>6</sub> H                               | 6.50 | 0.18 | 73.0078 | CHO <sub>4</sub>                              | 1.25 | 0.80 | 76.9874 |
| CN <sub>3</sub> O                              | 2.26 | 0.22 | 70.0042 | 74   |      |      |         | CH <sub>3</sub> NO <sub>3</sub>               | 1.63 | 0.61 | 77.0113 |
| CH <sub>2</sub> N <sub>4</sub>                 | 2.64 | 0.03 | 70.0280 | N <sub>3</sub> O <sub>2</sub>                  | 1.22 | 0.41 | 73.9991 | CH <sub>5</sub> N <sub>2</sub> O <sub>2</sub> | 2.00 | 0.41 | 77.0351 |
| C <sub>2</sub> NO <sub>2</sub>                 | 2.62 | 0.42 | 69.9929 | H <sub>2</sub> N <sub>4</sub> O                | 1.60 | 0.21 | 74.0229 | CH <sub>7</sub> N <sub>3</sub> O              | 2.38 | 0.22 | 77.0590 |
| C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O | 3.00 | 0.23 | 70.0167 | CNO <sub>3</sub>                               | 1.58 | 0.61 | 73.9878 | C <sub>2</sub> H <sub>5</sub> O <sub>3</sub>  | 2.36 | 0.62 | 77.0238 |
| C <sub>2</sub> H <sub>4</sub> N <sub>3</sub>   | 3.37 | 0.04 | 70.0406 | CH <sub>2</sub> N <sub>2</sub> O <sub>2</sub>  | 1.95 | 0.41 | 74.0116 | C <sub>2</sub> H <sub>7</sub> NO <sub>2</sub> | 2.73 | 0.43 | 77.0477 |
| C <sub>3</sub> H <sub>2</sub> O <sub>2</sub>   | 3.35 | 0.44 | 70.0054 | CH <sub>4</sub> N <sub>3</sub> O               | 2.33 | 0.22 | 74.0355 | C <sub>4</sub> HN <sub>2</sub>                | 5.10 | 0.11 | 77.0140 |
| C <sub>3</sub> H <sub>4</sub> NO               | 3.73 | 0.25 | 70.0293 | CH <sub>6</sub> N <sub>4</sub>                 | 2.70 | 0.03 | 74.0594 | C <sub>5</sub> HO                             | 5.46 | 0.32 | 77.0027 |
| C <sub>3</sub> H <sub>6</sub> N <sub>2</sub>   | 4.10 | 0.07 | 70.0532 | C <sub>2</sub> H <sub>2</sub> O <sub>3</sub>   | 2.31 | 0.62 | 74.0003 | C <sub>5</sub> H <sub>3</sub> N               | 5.83 | 0.14 | 77.0266 |
| C <sub>4</sub> H <sub>6</sub> O                | 4.46 | 0.28 | 70.0419 | C <sub>2</sub> H <sub>4</sub> NO <sub>2</sub>  | 2.68 | 0.42 | 74.0242 | C <sub>6</sub> H <sub>5</sub>                 | 6.56 | 0.18 | 77.0391 |
| C <sub>4</sub> H <sub>8</sub> N                | 4.83 | 0.09 | 70.0657 | C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O | 3.06 | 0.23 | 74.0480 | 78  |      |      |         |
| C <sub>5</sub> H <sub>10</sub>                 | 5.56 | 0.13 | 70.0783 | C <sub>2</sub> H <sub>8</sub> N <sub>3</sub>   | 3.43 | 0.05 | 74.0719 | NO <sub>4</sub>                               | 0.54 | 0.80 | 77.9827 |
| 71   |      |      |         | C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>   | 3.42 | 0.44 | 74.0368 | H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>  | 0.91 | 0.60 | 78.0065 |
| CHN <sub>3</sub> O                             | 2.28 | 0.22 | 71.0120 | C <sub>3</sub> H <sub>8</sub> NO               | 3.79 | 0.25 | 74.0606 | H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>  | 1.29 | 0.41 | 78.0304 |
| CH <sub>3</sub> N <sub>4</sub>                 | 2.65 | 0.03 | 71.0359 | C <sub>3</sub> H <sub>10</sub> N <sub>2</sub>  | 4.16 | 0.07 | 74.0845 | H <sub>6</sub> N <sub>4</sub> O               | 1.66 | 0.21 | 78.0542 |
| C <sub>2</sub> HNO <sub>2</sub>                | 2.64 | 0.42 | 71.0007 | C <sub>4</sub> H <sub>10</sub> O               | 4.52 | 0.28 | 74.0732 | CH <sub>2</sub> O <sub>4</sub>                | 1.27 | 0.80 | 77.9953 |
| C <sub>2</sub> H <sub>3</sub> N <sub>2</sub> O | 3.01 | 0.23 | 71.0246 | C <sub>5</sub> N                               | 5.78 | 0.14 | 74.0031 | CH <sub>4</sub> NO <sub>3</sub>               | 1.64 | 0.61 | 78.0191 |
| C <sub>2</sub> H <sub>5</sub> N <sub>3</sub>   | 3.39 | 0.04 | 71.0484 | C <sub>6</sub> H <sub>2</sub>                  | 6.52 | 0.18 | 74.0157 | CH <sub>6</sub> N <sub>2</sub> O <sub>2</sub> | 2.02 | 0.41 | 78.0429 |
| C <sub>3</sub> H <sub>3</sub> O <sub>2</sub>   | 3.37 | 0.44 | 71.0133 | 75   |      |      |         | C <sub>2</sub> H <sub>6</sub> O <sub>3</sub>  | 2.37 | 0.62 | 78.0317 |
| C <sub>3</sub> H <sub>5</sub> NO               | 3.74 | 0.25 | 71.0371 | HN <sub>3</sub> O <sub>2</sub>                 | 1.24 | 0.41 | 75.0069 | C <sub>3</sub> N <sub>3</sub>                 | 4.39 | 0.08 | 78.0093 |
| C <sub>3</sub> H <sub>7</sub> N <sub>2</sub>   | 4.12 | 0.07 | 71.0610 | H <sub>3</sub> N <sub>4</sub> O                | 1.61 | 0.21 | 75.0308 | C <sub>4</sub> NO                             | 4.74 | 0.29 | 77.9980 |
| C <sub>4</sub> H <sub>7</sub> O                | 4.47 | 0.28 | 71.0497 | CHNO <sub>3</sub>                              | 1.60 | 0.61 | 74.9956 | C <sub>4</sub> H <sub>2</sub> N <sub>2</sub>  | 5.12 | 0.11 | 78.0218 |
|  |      |      |         | CH <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 1.97 | 0.41 | 75.0195 | C <sub>5</sub> H <sub>2</sub> O               | 5.47 | 0.32 | 78.0106 |
| C <sub>4</sub> H <sub>9</sub> N                | 4.85 | 0.09 | 71.0736 | CH <sub>5</sub> N <sub>3</sub> O               | 2.34 | 0.22 | 75.0433 | C <sub>5</sub> H <sub>4</sub> N               | 5.85 | 0.14 | 78.0344 |
| C <sub>5</sub> H <sub>11</sub>                 | 5.58 | 0.13 | 71.0861 | CH <sub>7</sub> N <sub>4</sub>                 | 2.72 | 0.03 | 75.0672 | C <sub>6</sub> H <sub>6</sub>                 | 6.58 | 0.18 | 78.0470 |
| 72   |      |      |         | C <sub>2</sub> H <sub>3</sub> O <sub>3</sub>   | 2.33 | 0.62 | 75.0082 | 79  |      |      |         |
| N <sub>4</sub> O                               | 1.56 | 0.21 | 72.0073 | C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>  | 2.70 | 0.43 | 75.0320 | HN <sub>2</sub> O <sub>4</sub>                | 0.55 | 0.80 | 78.9905 |
| CN <sub>2</sub> O <sub>2</sub>                 | 1.92 | 0.41 | 71.9960 | C <sub>2</sub> H <sub>7</sub> N <sub>2</sub> O | 3.08 | 0.23 | 75.0559 | H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 0.93 | 0.60 | 79.0144 |
| CH <sub>2</sub> N <sub>3</sub> O               | 2.30 | 0.22 | 72.0198 | C <sub>2</sub> H <sub>9</sub> N <sub>3</sub>   | 3.45 | 0.05 | 75.0798 | H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>  | 1.30 | 0.41 | 79.0382 |
| CH <sub>4</sub> N <sub>4</sub>                 | 2.67 | 0.03 | 72.0437 | C <sub>3</sub> H <sub>7</sub> O <sub>2</sub>   | 3.43 | 0.44 | 75.0446 | CH <sub>3</sub> O <sub>4</sub>                | 1.28 | 0.80 | 79.0031 |
| C <sub>2</sub> O <sub>3</sub>                  | 2.28 | 0.62 | 71.9847 | C <sub>3</sub> H <sub>9</sub> NO               | 3.81 | 0.25 | 75.0684 | CH <sub>5</sub> NO <sub>3</sub>               | 1.66 | 0.61 | 79.0269 |
| C <sub>2</sub> H <sub>2</sub> NO <sub>2</sub>  | 2.65 | 0.42 | 72.0085 | C <sub>5</sub> HN                              | 5.80 | 0.14 | 75.0109 | C <sub>3</sub> HN <sub>3</sub>                | 4.40 | 0.08 | 79.0171 |
| C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O | 3.03 | 0.23 | 72.0324 | C <sub>6</sub> H <sub>3</sub>                  | 6.53 | 0.18 | 75.0235 | C <sub>4</sub> HNO                            | 4.76 | 0.29 | 79.0058 |
| C <sub>2</sub> H <sub>6</sub> N <sub>3</sub>   | 3.40 | 0.04 | 72.0563 | 76   |      |      |         | C <sub>4</sub> H <sub>3</sub> N <sub>2</sub>  | 5.13 | 0.11 | 79.0297 |
| C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>   | 3.38 | 0.44 | 72.0211 | N <sub>2</sub> O <sub>3</sub>                  | 0.88 | 0.60 | 75.9909 | C <sub>5</sub> H <sub>3</sub> O               | 5.49 | 0.32 | 79.0184 |
| C <sub>3</sub> H <sub>6</sub> NO               | 3.76 | 0.25 | 72.0449 | H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>   | 1.25 | 0.41 | 76.0147 | C <sub>5</sub> H <sub>5</sub> N               | 5.86 | 0.14 | 79.0422 |
| C <sub>3</sub> H <sub>8</sub> N <sub>2</sub>   | 4.13 | 0.07 | 72.0688 | H <sub>4</sub> N <sub>4</sub> O                | 1.63 | 0.21 | 76.0386 | C <sub>6</sub> H <sub>7</sub>                 | 6.60 | 0.18 | 79.0548 |
| C <sub>4</sub> H <sub>8</sub> O                | 4.49 | 0.28 | 72.0575 | CO <sub>4</sub>                                | 1.24 | 0.80 | 75.9796 | 80  |      |      |         |
| C <sub>4</sub> H <sub>10</sub> N               | 4.86 | 0.09 | 72.0814 | CH <sub>2</sub> NO <sub>3</sub>                | 1.61 | 0.61 | 76.0034 | H <sub>2</sub> NO <sub>4</sub>                | 0.57 | 0.80 | 79.9983 |
| C <sub>5</sub> H <sub>12</sub>                 | 5.60 | 0.13 | 72.0939 | CH <sub>4</sub> N <sub>2</sub> O <sub>2</sub>  | 1.99 | 0.41 | 76.0273 | H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 0.94 | 0.60 | 80.0222 |
| C <sub>6</sub>                                 | 6.48 | 0.18 | 72.0000 | CH <sub>6</sub> N <sub>3</sub> O               | 2.36 | 0.22 | 76.0511 | CH <sub>4</sub> O <sub>4</sub>                | 1.30 | 0.80 | 80.0109 |
| 73   |      |      |         | CH <sub>8</sub> N <sub>4</sub>                 | 2.73 | 0.03 | 76.0750 | C <sub>2</sub> N <sub>4</sub>                 | 3.69 | 0.05 | 80.0124 |
| HN <sub>4</sub> O                              | 1.58 | 0.21 | 73.0151 | C <sub>2</sub> H <sub>4</sub> O <sub>3</sub>   | 2.34 | 0.62 | 76.0160 | C <sub>3</sub> N <sub>2</sub> O               | 4.04 | 0.26 | 80.0011 |
| CHN <sub>2</sub> O <sub>2</sub>                | 1.94 | 0.41 | 73.0038 | C <sub>2</sub> H <sub>6</sub> NO <sub>2</sub>  | 2.72 | 0.43 | 76.0399 | C <sub>3</sub> H <sub>2</sub> N <sub>3</sub>  | 4.42 | 0.08 | 80.0249 |
| CH <sub>3</sub> N <sub>3</sub> O               | 2.31 | 0.22 | 73.0277 | C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> O | 3.09 | 0.24 | 76.0637 | C <sub>4</sub> O <sub>2</sub>                 | 4.40 | 0.47 | 79.9898 |
| CH <sub>5</sub> N <sub>4</sub>                 | 2.69 | 0.03 | 73.0515 | C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>   | 3.45 | 0.44 | 76.0524 | C <sub>4</sub> H <sub>2</sub> NO              | 4.77 | 0.29 | 80.0136 |
| C <sub>2</sub> H <sub>2</sub> O <sub>3</sub>   | 2.29 | 0.62 | 72.9925 | C <sub>4</sub> N <sub>2</sub>                  | 5.09 | 0.10 | 76.0062 | C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>  | 5.15 | 0.11 | 80.0375 |
| C <sub>2</sub> H <sub>3</sub> NO <sub>2</sub>  | 2.67 | 0.42 | 73.0164 | C <sub>5</sub> O                               | 5.44 | 0.32 | 75.9949 | C <sub>5</sub> H <sub>4</sub> O               | 5.51 | 0.32 | 80.0262 |
| C <sub>2</sub> H <sub>5</sub> N <sub>2</sub> O | 3.04 | 0.23 | 73.0402 |  |      |      |         | C <sub>5</sub> H <sub>6</sub> N               | 5.88 | 0.14 | 80.0501 |

|   | M+1  | M+2  | MW      |   | M+1  | M+2  | MW      |   | M+1  | M+2  | MW      |
|---|------|------|---------|---|------|------|---------|---|------|------|---------|
| C <sub>6</sub> H <sub>8</sub>                               | 6.61 | 0.18 | 80.0626 | C <sub>2</sub> H <sub>5</sub> N <sub>4</sub>                | 3.77 | 0.06 | 85.0515 | C <sub>2</sub> H <sub>2</sub> N <sub>3</sub> O              | 2.69 | 0.63 | 88.0034 |
| 81  |      |      |         | C <sub>3</sub> H <sub>3</sub> O                             | 3.38 | 0.64 | 84.9925 | C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> | 3.07 | 0.43 | 88.0273 |
| H <sub>3</sub> N <sub>3</sub> O <sub>4</sub>                | 0.59 | 0.80 | 81.0062 | C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub> | 3.75 | 0.45 | 85.0164 | C <sub>2</sub> H <sub>6</sub> N <sub>3</sub> O              | 3.44 | 0.25 | 88.0511 |
| C <sub>2</sub> HN <sub>4</sub>                              | 3.70 | 0.05 | 81.0202 | C <sub>3</sub> H <sub>5</sub> N <sub>2</sub> O              | 4.12 | 0.27 | 85.0402 | C <sub>2</sub> H <sub>8</sub> N <sub>4</sub>                | 3.82 | 0.06 | 88.0750 |
| C <sub>3</sub> HN <sub>2</sub> O                            | 4.06 | 0.26 | 81.0089 | C <sub>3</sub> H <sub>7</sub> N <sub>3</sub>                | 4.50 | 0.08 | 85.0641 | C <sub>3</sub> H <sub>4</sub> O <sub>3</sub>                | 3.42 | 0.64 | 88.0160 |
| C <sub>3</sub> H <sub>3</sub> N <sub>3</sub>                | 4.43 | 0.08 | 81.0328 | C <sub>4</sub> H <sub>5</sub> O <sub>2</sub>                | 4.48 | 0.48 | 85.0289 | C <sub>3</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub> | 3.80 | 0.45 | 88.0399 |
| C <sub>4</sub> H <sub>3</sub> O <sub>2</sub>                | 4.42 | 0.48 | 80.9976 | C <sub>4</sub> H <sub>7</sub> N <sub>3</sub>                | 4.85 | 0.29 | 85.0528 | C <sub>3</sub> H <sub>8</sub> N <sub>2</sub> O              | 4.17 | 0.27 | 88.0637 |
| C <sub>4</sub> H <sub>3</sub> N <sub>3</sub> O              | 4.79 | 0.29 | 81.0215 | C <sub>4</sub> H <sub>9</sub> N <sub>2</sub>                | 5.23 | 0.11 | 85.0767 | C <sub>3</sub> H <sub>10</sub> N <sub>3</sub>               | 4.55 | 0.08 | 88.0876 |
| C <sub>4</sub> H <sub>5</sub> N <sub>2</sub>                | 5.17 | 0.11 | 81.0453 | C <sub>5</sub> H <sub>9</sub> O                             | 5.59 | 0.33 | 85.0653 | C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>                | 4.53 | 0.48 | 88.0524 |
| C <sub>5</sub> H <sub>5</sub> O                             | 5.52 | 0.32 | 81.0340 | C <sub>5</sub> H <sub>11</sub> N                            | 5.96 | 0.15 | 85.0892 | C <sub>4</sub> H <sub>10</sub> N <sub>3</sub> O             | 4.90 | 0.30 | 88.0763 |
| C <sub>5</sub> H <sub>7</sub> N                             | 5.90 | 0.14 | 81.0579 | C <sub>6</sub> H <sub>13</sub>                              | 6.69 | 0.19 | 85.1018 | C <sub>4</sub> H <sub>12</sub> N <sub>2</sub>               | 5.28 | 0.11 | 88.1001 |
| C <sub>6</sub> H <sub>9</sub>                               | 6.63 | 0.18 | 81.0705 | C <sub>7</sub> H  | 7.58 | 0.25 | 85.0078 | C <sub>5</sub> H <sub>12</sub> O                            | 5.63 | 0.33 | 88.0888 |
| 82  |      |      |         | 86  |      |      |         | C <sub>5</sub> N <sub>2</sub>                               | 6.17 | 0.16 | 88.0062 |
| C <sub>2</sub> N <sub>3</sub> O                             | 3.34 | 0.24 | 82.0042 | CN <sub>3</sub> O <sub>2</sub>                              | 2.30 | 0.42 | 85.9991 | C <sub>6</sub> O  | 6.52 | 0.38 | 87.9949 |
| C <sub>2</sub> H <sub>2</sub> N <sub>4</sub>                | 3.72 | 0.05 | 82.0280 | CH <sub>2</sub> N <sub>4</sub> O                            | 2.68 | 0.23 | 86.0229 | C <sub>6</sub> H <sub>2</sub> N                             | 6.90 | 0.20 | 88.0187 |
| C <sub>3</sub> N <sub>3</sub> O <sub>2</sub>                | 3.70 | 0.45 | 81.9929 | C <sub>2</sub> N <sub>3</sub> O <sub>3</sub>                | 2.66 | 0.62 | 85.9878 | C <sub>7</sub> H <sub>4</sub>                               | 7.63 | 0.25 | 88.0313 |
| C <sub>3</sub> H <sub>2</sub> N <sub>2</sub> O              | 4.08 | 0.26 | 82.0167 | C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> | 3.03 | 0.43 | 86.0116 | 89  |      |      |         |
| C <sub>3</sub> H <sub>4</sub> N <sub>3</sub>                | 4.45 | 0.08 | 82.0406 | C <sub>2</sub> H <sub>4</sub> N <sub>3</sub> O              | 3.41 | 0.24 | 86.0355 | HN <sub>4</sub> O <sub>2</sub>                              | 1.62 | 0.41 | 89.0100 |
| C <sub>4</sub> H <sub>2</sub> O <sub>2</sub>                | 4.43 | 0.48 | 82.0054 | C <sub>2</sub> H <sub>6</sub> N <sub>4</sub>                | 3.78 | 0.06 | 86.0594 | CHN <sub>2</sub> O <sub>3</sub>                             | 1.98 | 0.61 | 88.9987 |
| C <sub>4</sub> H <sub>4</sub> N <sub>3</sub> O              | 4.81 | 0.29 | 82.0293 | C <sub>3</sub> H <sub>2</sub> O <sub>3</sub>                | 3.39 | 0.64 | 86.0003 | CH <sub>3</sub> N <sub>3</sub> O <sub>2</sub>               | 2.35 | 0.42 | 89.0226 |
| C <sub>4</sub> H <sub>6</sub> N <sub>2</sub>                | 5.18 | 0.11 | 82.0532 | C <sub>3</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub> | 3.77 | 0.45 | 86.0242 | CH <sub>5</sub> N <sub>4</sub> O                            | 2.73 | 0.23 | 89.0464 |
| C <sub>5</sub> H <sub>6</sub> O                             | 5.54 | 0.32 | 82.0419 | C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> O              | 4.14 | 0.27 | 86.0480 | C <sub>2</sub> H <sub>4</sub> O <sub>4</sub>                | 2.33 | 0.82 | 88.9874 |
| C <sub>5</sub> H <sub>8</sub> N                             | 5.91 | 0.14 | 82.0657 | C <sub>3</sub> H <sub>8</sub> N <sub>3</sub>                | 4.51 | 0.08 | 86.0719 | C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub> | 2.71 | 0.63 | 89.0113 |
| C <sub>6</sub> H <sub>10</sub>                              | 6.64 | 0.19 | 82.0783 | C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>                | 4.50 | 0.48 | 86.0368 | C <sub>2</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> | 3.08 | 0.44 | 89.0351 |
| 83  |      |      |         | C <sub>4</sub> H <sub>8</sub> N <sub>3</sub> O              | 4.87 | 0.30 | 86.0606 | C <sub>2</sub> H <sub>7</sub> N <sub>3</sub> O              | 3.46 | 0.25 | 89.0590 |
| C <sub>2</sub> HN <sub>3</sub> O                            | 3.36 | 0.24 | 83.0120 | C <sub>4</sub> H <sub>10</sub> N <sub>2</sub>               | 5.25 | 0.11 | 86.0845 | C <sub>2</sub> H <sub>9</sub> N <sub>4</sub>                | 3.83 | 0.06 | 89.0829 |
| C <sub>2</sub> H <sub>3</sub> N <sub>4</sub>                | 3.74 | 0.06 | 83.0359 | C <sub>5</sub> H <sub>10</sub> O                            | 5.60 | 0.33 | 86.0732 | C <sub>3</sub> H <sub>5</sub> O <sub>3</sub>                | 3.44 | 0.64 | 89.0238 |
| C <sub>3</sub> HN <sub>3</sub> O <sub>2</sub>               | 3.72 | 0.45 | 83.0007 | C <sub>5</sub> H <sub>12</sub> N                            | 5.98 | 0.15 | 86.0970 | C <sub>3</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub> | 3.81 | 0.46 | 89.0477 |
| C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> O              | 4.09 | 0.27 | 83.0246 | C <sub>6</sub> H <sub>14</sub>                              | 6.71 | 0.19 | 86.1096 | C <sub>3</sub> H <sub>9</sub> N <sub>2</sub> O              | 4.19 | 0.27 | 89.0715 |
| C <sub>3</sub> H <sub>5</sub> N <sub>3</sub>                | 4.47 | 0.08 | 83.0484 | C <sub>6</sub> N  | 6.87 | 0.20 | 86.0031 | C <sub>3</sub> H <sub>11</sub> N <sub>3</sub>               | 4.56 | 0.08 | 89.0954 |
| C <sub>4</sub> H <sub>3</sub> O <sub>2</sub>                | 4.45 | 0.48 | 83.0133 | C <sub>7</sub> H <sub>2</sub>                               | 7.60 | 0.25 | 86.0157 | C <sub>4</sub> H <sub>9</sub> O <sub>2</sub>                | 4.54 | 0.48 | 89.0603 |
| C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O              | 4.82 | 0.29 | 83.0371 | 87  |      |      |         | C <sub>4</sub> H <sub>11</sub> N <sub>3</sub> O             | 4.92 | 0.30 | 89.0841 |
| C <sub>4</sub> H <sub>7</sub> N <sub>2</sub>                | 5.20 | 0.11 | 83.0610 | CHN <sub>3</sub> O <sub>2</sub>                             | 2.32 | 0.42 | 87.0069 | C <sub>5</sub> HN <sub>2</sub>                              | 6.18 | 0.16 | 89.0140 |
| C <sub>5</sub> H <sub>7</sub> O                             | 5.55 | 0.33 | 83.0497 | CH <sub>3</sub> N <sub>4</sub> O                            | 2.69 | 0.23 | 87.0308 | C <sub>6</sub> H <sub>3</sub> N                             | 6.54 | 0.38 | 89.0027 |
| C <sub>5</sub> H <sub>9</sub> N                             | 5.93 | 0.15 | 83.0736 | C <sub>2</sub> HN <sub>3</sub> O <sub>3</sub>               | 2.68 | 0.62 | 86.9956 | C <sub>7</sub> H <sub>5</sub>                               | 7.64 | 0.25 | 89.0391 |
| C <sub>6</sub> H <sub>11</sub>                              | 6.66 | 0.19 | 83.0861 | C <sub>2</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub> | 3.05 | 0.43 | 87.0195 | 90  |      |      |         |
| 84  |      |      |         | C <sub>2</sub> H <sub>5</sub> N <sub>3</sub> O              | 3.42 | 0.25 | 87.0433 | N <sub>3</sub> O <sub>3</sub>                               | 1.26 | 0.61 | 89.9940 |
| CN <sub>4</sub> O   | 2.65 | 0.23 | 84.0073 | C <sub>2</sub> H <sub>7</sub> N <sub>4</sub>                | 3.80 | 0.06 | 87.0672 | H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>                | 1.64 | 0.41 | 90.0178 |
| C <sub>2</sub> N <sub>2</sub> O <sub>2</sub>                | 3.00 | 0.43 | 83.9960 | C <sub>3</sub> H <sub>3</sub> O <sub>3</sub>                | 3.41 | 0.64 | 87.0082 | CN <sub>4</sub> O   | 1.62 | 0.81 | 89.9827 |
| C <sub>2</sub> H <sub>2</sub> N <sub>3</sub> O              | 3.38 | 0.24 | 84.0198 | C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub> | 3.78 | 0.45 | 87.0320 | CH <sub>2</sub> N <sub>2</sub> O <sub>3</sub>               | 1.99 | 0.61 | 90.0065 |
| C <sub>2</sub> H <sub>4</sub> N <sub>4</sub>                | 3.75 | 0.06 | 84.0437 | C <sub>3</sub> H <sub>7</sub> N <sub>2</sub> O              | 4.16 | 0.27 | 87.0559 | CH <sub>4</sub> N <sub>3</sub> O <sub>2</sub>               | 2.37 | 0.42 | 90.0304 |
| C <sub>3</sub> O <sub>3</sub>                               | 3.36 | 0.64 | 83.9847 | C <sub>3</sub> H <sub>9</sub> N <sub>3</sub>                | 4.53 | 0.08 | 87.0798 | CH <sub>6</sub> N <sub>4</sub> O                            | 2.74 | 0.23 | 90.0542 |
| C <sub>3</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub> | 3.73 | 0.45 | 84.0085 | C <sub>4</sub> H <sub>7</sub> O <sub>2</sub>                | 4.51 | 0.48 | 87.0446 | C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>                | 2.35 | 0.82 | 89.9953 |
| C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> O              | 4.11 | 0.27 | 84.0324 | C <sub>4</sub> H <sub>9</sub> N <sub>3</sub>                | 4.89 | 0.30 | 87.0684 | C <sub>2</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub> | 2.72 | 0.63 | 90.0191 |
| C <sub>3</sub> H <sub>6</sub> N <sub>3</sub>                | 4.48 | 0.08 | 84.0563 | C <sub>4</sub> H <sub>11</sub> N <sub>2</sub>               | 5.26 | 0.11 | 87.0923 | C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> | 3.10 | 0.44 | 90.0429 |
| C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>                | 4.46 | 0.48 | 84.0211 | C <sub>5</sub> H <sub>11</sub> O                            | 5.62 | 0.33 | 87.0810 | C <sub>2</sub> H <sub>8</sub> N <sub>3</sub> O              | 3.47 | 0.25 | 90.0668 |
| C <sub>4</sub> H <sub>6</sub> N <sub>3</sub> O              | 4.84 | 0.29 | 84.0449 | C <sub>5</sub> H <sub>13</sub> N                            | 5.99 | 0.15 | 87.1049 | C <sub>2</sub> H <sub>10</sub> N <sub>4</sub>               | 3.85 | 0.06 | 90.0907 |
| C <sub>4</sub> H <sub>8</sub> N <sub>2</sub>                | 5.21 | 0.11 | 84.0688 | C <sub>6</sub> HN   | 6.88 | 0.20 | 87.0109 | C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>                | 3.46 | 0.64 | 90.0317 |
| C <sub>5</sub> H <sub>8</sub> O                             | 5.57 | 0.33 | 84.0575 | C <sub>7</sub> H <sub>3</sub>                               | 7.61 | 0.25 | 87.0235 | C <sub>3</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub> | 3.83 | 0.46 | 90.0555 |
| C <sub>5</sub> H <sub>10</sub> N                            | 5.94 | 0.15 | 84.0814 | 88  |      |      |         | C <sub>3</sub> H <sub>10</sub> N <sub>2</sub> O             | 4.20 | 0.27 | 90.0794 |
| C <sub>6</sub> H <sub>12</sub>                              | 6.68 | 0.19 | 84.0939 | N <sub>4</sub> O <sub>2</sub>                               | 1.60 | 0.41 | 88.0022 | C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>               | 4.56 | 0.48 | 90.0681 |
| C <sub>7</sub>  | 7.56 | 0.25 | 84.0000 | CN <sub>2</sub> O <sub>3</sub>                              | 1.96 | 0.61 | 87.9909 | C <sub>4</sub> N <sub>3</sub>                               | 5.47 | 0.12 | 90.0093 |
| 85  |      |      |         | CH <sub>2</sub> N <sub>3</sub> O <sub>2</sub>               | 2.34 | 0.42 | 88.0147 | C <sub>5</sub> N <sub>3</sub>                               | 5.82 | 0.34 | 89.9980 |
| CHN <sub>4</sub> O  | 2.66 | 0.23 | 85.0151 | CH <sub>4</sub> N <sub>4</sub> O                            | 2.71 | 0.23 | 88.0386 | C <sub>5</sub> H <sub>2</sub> N <sub>2</sub>                | 6.20 | 0.16 | 90.0218 |
| C <sub>2</sub> HN <sub>2</sub> O <sub>2</sub>               | 3.02 | 0.43 | 85.0038 | C <sub>2</sub> O <sub>4</sub>                               | 2.32 | 0.82 | 87.9796 |   |      |      |         |
| C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> O              | 3.39 | 0.24 | 85.0277 |   |      |      |         |   |      |      |         |



|   | M+1  | M+2  | MW      |  | M+1  | M+2  | MW      |   | M+1  | M+2  | MW      |
|---|------|------|---------|--|------|------|---------|---|------|------|---------|
| C <sub>6</sub> H <sub>2</sub> O                             | 6.55 | 0.38 | 90.0106 | C <sub>4</sub> H <sub>3</sub> N <sub>3</sub>   | 5.51 | 0.13 | 93.0328 | C <sub>6</sub> H <sub>10</sub> N                            | 7.03 | 0.21 | 96.0814 |
| C <sub>6</sub> H <sub>4</sub> N                             | 6.93 | 0.20 | 90.0344 | C <sub>5</sub> H <sub>2</sub> O                | 5.50 | 0.52 | 92.9976 | C <sub>7</sub> H <sub>12</sub>                              | 7.76 | 0.26 | 96.0939 |
| C <sub>7</sub> H <sub>6</sub>                               | 7.66 | 0.25 | 90.0470 | C <sub>5</sub> H <sub>3</sub> NO               | 5.87 | 0.34 | 93.0215 | C <sub>8</sub>  | 8.64 | 0.33 | 96.0000 |
| 91  |      |      |         | C <sub>5</sub> H <sub>5</sub> N <sub>2</sub>   | 6.25 | 0.16 | 93.0453 | 97  |      |      |         |
| HN <sub>3</sub> O <sub>3</sub>                              | 1.28 | 0.61 | 91.0018 | C <sub>6</sub> H <sub>5</sub> O                | 6.60 | 0.38 | 93.0340 | C <sub>2</sub> HN <sub>4</sub> O                            | 3.74 | 0.26 | 97.0151 |
| H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>                | 1.65 | 0.41 | 91.0257 | C <sub>6</sub> H <sub>7</sub> N                | 6.98 | 0.21 | 93.0579 | C <sub>3</sub> HN <sub>2</sub> O <sub>2</sub>               | 4.10 | 0.47 | 97.0038 |
| CHNO <sub>4</sub>   | 1.63 | 0.81 | 90.9905 | C <sub>7</sub> H <sub>9</sub>                  | 7.71 | 0.26 | 93.0705 | C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> O              | 4.47 | 0.28 | 97.0277 |
| CH <sub>3</sub> N <sub>2</sub> O <sub>3</sub>               | 2.01 | 0.61 | 91.0144 | 94   |      |      |         | C <sub>3</sub> H <sub>5</sub> N <sub>4</sub>                | 4.85 | 0.10 | 97.0515 |
| CH <sub>5</sub> N <sub>3</sub> O <sub>2</sub>               | 2.38 | 0.42 | 91.0382 | H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>   | 0.95 | 0.80 | 94.0014 | C <sub>4</sub> H <sub>2</sub> O <sub>3</sub>                | 4.46 | 0.68 | 96.9925 |
| CH <sub>7</sub> N <sub>4</sub> O                            | 2.76 | 0.23 | 91.0621 | H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>   | 1.33 | 0.61 | 94.0253 | C <sub>4</sub> H <sub>3</sub> NO <sub>2</sub>               | 4.83 | 0.49 | 97.0164 |
| C <sub>2</sub> H <sub>3</sub> O <sub>4</sub>                | 2.37 | 0.82 | 91.0031 | H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>   | 1.70 | 0.41 | 94.0491 | C <sub>4</sub> H <sub>5</sub> N <sub>2</sub> O              | 5.20 | 0.31 | 97.0402 |
| C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>               | 2.74 | 0.63 | 91.0269 | CH <sub>4</sub> NO <sub>4</sub>                | 1.68 | 0.81 | 94.0140 | C <sub>4</sub> H <sub>7</sub> N <sub>3</sub>                | 5.58 | 0.13 | 97.0641 |
| C <sub>2</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> | 3.11 | 0.44 | 91.0508 | CH <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 2.06 | 0.62 | 94.0379 | C <sub>5</sub> H <sub>5</sub> O <sub>2</sub>                | 5.56 | 0.53 | 97.0289 |
| C <sub>2</sub> H <sub>9</sub> N <sub>3</sub> O              | 3.49 | 0.25 | 91.0746 | C <sub>2</sub> H <sub>6</sub> O <sub>4</sub>   | 2.41 | 0.82 | 94.0266 | C <sub>5</sub> H <sub>7</sub> NO                            | 5.94 | 0.35 | 97.0528 |
| C <sub>3</sub> H <sub>7</sub> O <sub>3</sub>                | 3.47 | 0.64 | 91.0395 | C <sub>3</sub> N <sub>3</sub> O                | 4.43 | 0.28 | 94.0042 | C <sub>5</sub> H <sub>9</sub> N <sub>2</sub>                | 6.31 | 0.17 | 97.0767 |
| C <sub>3</sub> H <sub>9</sub> NO <sub>2</sub>               | 3.85 | 0.46 | 91.0634 | C <sub>3</sub> H <sub>2</sub> N <sub>4</sub>   | 4.80 | 0.09 | 94.0280 | C <sub>6</sub> H <sub>9</sub> O                             | 6.67 | 0.39 | 97.0653 |
| C <sub>4</sub> HN <sub>3</sub>                              | 5.48 | 0.12 | 91.0171 | C <sub>4</sub> NO <sub>2</sub>                 | 4.78 | 0.49 | 93.9929 | C <sub>6</sub> H <sub>11</sub> N                            | 7.04 | 0.21 | 97.0892 |
| C <sub>5</sub> HN <sub>2</sub> O                            | 5.84 | 0.34 | 91.0058 | C <sub>4</sub> H <sub>2</sub> N <sub>2</sub> O | 5.16 | 0.31 | 94.0167 | C <sub>7</sub> H <sub>13</sub>                              | 7.77 | 0.26 | 97.1018 |
| C <sub>5</sub> H <sub>3</sub> N <sub>2</sub>                | 6.21 | 0.16 | 91.0297 | C <sub>4</sub> H <sub>4</sub> N <sub>3</sub>   | 5.53 | 0.13 | 94.0406 | C <sub>8</sub> H  | 8.66 | 0.33 | 97.0078 |
| C <sub>6</sub> H <sub>3</sub> O                             | 6.57 | 0.38 | 91.0184 | C <sub>5</sub> H <sub>2</sub> O <sub>2</sub>   | 5.51 | 0.52 | 94.0054 | 98  |      |      |         |
| C <sub>6</sub> H <sub>5</sub> N                             | 6.95 | 0.21 | 91.0422 | C <sub>5</sub> H <sub>4</sub> NO               | 5.89 | 0.34 | 94.0293 | C <sub>2</sub> N <sub>3</sub> O <sub>2</sub>                | 3.38 | 0.44 | 97.9991 |
| C <sub>7</sub> H <sub>7</sub>                               | 7.68 | 0.25 | 91.0548 | C <sub>5</sub> H <sub>6</sub> N <sub>2</sub>   | 6.26 | 0.17 | 94.0532 | C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O              | 3.76 | 0.26 | 98.0229 |
| 92  |      |      |         | C <sub>6</sub> H <sub>6</sub> O                | 6.62 | 0.38 | 94.0419 | C <sub>3</sub> NO <sub>3</sub>                              | 3.74 | 0.65 | 97.9878 |
| N <sub>2</sub> O <sub>4</sub>                               | 0.92 | 0.80 | 91.9858 | C <sub>6</sub> H <sub>8</sub> N                | 6.99 | 0.21 | 94.0657 | C <sub>3</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> | 4.11 | 0.47 | 98.0116 |
| H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>                | 1.29 | 0.61 | 92.0096 | C <sub>7</sub> H <sub>10</sub>                 | 7.72 | 0.26 | 94.0783 | C <sub>3</sub> H <sub>4</sub> N <sub>3</sub> O              | 4.49 | 0.28 | 98.0355 |
| H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>                | 1.67 | 0.41 | 92.0335 | 95   |      |      |         | C <sub>3</sub> H <sub>6</sub> N <sub>4</sub>                | 4.86 | 0.10 | 98.0594 |
| CH <sub>2</sub> NO <sub>4</sub>                             | 1.65 | 0.81 | 91.9983 | H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>   | 0.97 | 0.81 | 95.0093 | C <sub>4</sub> H <sub>2</sub> O <sub>3</sub>                | 4.47 | 0.68 | 98.0003 |
| CH <sub>4</sub> N <sub>2</sub> O <sub>3</sub>               | 2.02 | 0.61 | 92.0222 | H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>   | 1.34 | 0.61 | 95.0331 | C <sub>4</sub> H <sub>4</sub> NO <sub>2</sub>               | 4.85 | 0.49 | 98.0242 |
| CH <sub>6</sub> N <sub>3</sub> O <sub>2</sub>               | 2.40 | 0.42 | 92.0460 | CH <sub>5</sub> NO <sub>4</sub>                | 1.70 | 0.81 | 95.0218 | C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O              | 5.22 | 0.31 | 98.0480 |
| CH <sub>8</sub> N <sub>4</sub> O                            | 2.77 | 0.23 | 92.0699 | C <sub>3</sub> HN <sub>3</sub> O               | 4.44 | 0.28 | 95.0120 | C <sub>4</sub> H <sub>8</sub> N <sub>3</sub>                | 5.59 | 0.13 | 98.0719 |
| C <sub>2</sub> H <sub>4</sub> O <sub>4</sub>                | 2.38 | 0.82 | 92.0109 | C <sub>3</sub> H <sub>3</sub> N <sub>4</sub>   | 4.82 | 0.10 | 95.0359 | C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>                | 5.58 | 0.53 | 98.0368 |
| C <sub>2</sub> H <sub>6</sub> NO <sub>3</sub>               | 2.76 | 0.63 | 92.0348 | C <sub>4</sub> HN <sub>2</sub> O               | 4.80 | 0.49 | 95.0007 | C <sub>5</sub> H <sub>8</sub> NO                            | 5.95 | 0.35 | 98.0606 |
| C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> | 3.13 | 0.44 | 92.0586 | C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> O | 5.17 | 0.31 | 95.0246 | C <sub>5</sub> H <sub>10</sub> N <sub>2</sub>               | 6.33 | 0.17 | 98.0845 |
| C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>                | 3.49 | 0.64 | 92.0473 | C <sub>4</sub> H <sub>5</sub> N <sub>3</sub>   | 5.55 | 0.13 | 95.0484 | C <sub>6</sub> H <sub>10</sub> O                            | 6.68 | 0.39 | 98.0732 |
| C <sub>3</sub> N <sub>4</sub>                               | 4.77 | 0.09 | 92.0124 | C <sub>5</sub> H <sub>3</sub> O <sub>2</sub>   | 5.53 | 0.52 | 95.0133 | C <sub>6</sub> H <sub>12</sub> N                            | 7.06 | 0.21 | 98.0970 |
| C <sub>4</sub> N <sub>2</sub> O                             | 5.12 | 0.31 | 92.0011 | C <sub>5</sub> H <sub>5</sub> NO               | 5.90 | 0.34 | 95.0371 | C <sub>7</sub> H <sub>14</sub>                              | 7.79 | 0.26 | 98.1096 |
| C <sub>4</sub> H <sub>2</sub> N <sub>3</sub>                | 5.50 | 0.13 | 92.0249 | C <sub>5</sub> H <sub>7</sub> N <sub>2</sub>   | 6.28 | 0.17 | 95.0610 | C <sub>7</sub> N  | 7.95 | 0.27 | 98.0031 |
| C <sub>5</sub> O <sub>2</sub>                               | 5.48 | 0.52 | 91.9898 | C <sub>6</sub> H <sub>7</sub> O                | 6.63 | 0.39 | 95.0497 | C <sub>8</sub> H <sub>2</sub>                               | 8.68 | 0.33 | 98.0157 |
| C <sub>5</sub> H <sub>2</sub> NO                            | 5.86 | 0.34 | 92.0136 | C <sub>6</sub> H <sub>9</sub> N                | 7.01 | 0.21 | 95.0736 | 99  |      |      |         |
| C <sub>5</sub> H <sub>4</sub> N <sub>2</sub>                | 6.23 | 0.16 | 92.0375 | C <sub>7</sub> H <sub>11</sub>                 | 7.74 | 0.26 | 95.0861 | C <sub>2</sub> HN <sub>3</sub> O <sub>2</sub>               | 3.40 | 0.44 | 99.0069 |
| C <sub>6</sub> H <sub>4</sub> O                             | 6.59 | 0.38 | 92.0262 | 96   |      |      |         | C <sub>2</sub> H <sub>3</sub> N <sub>4</sub> O              | 3.77 | 0.26 | 99.0308 |
| C <sub>6</sub> H <sub>6</sub> N                             | 6.96 | 0.21 | 92.0501 | H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>   | 0.98 | 0.81 | 96.0171 | C <sub>3</sub> HN <sub>2</sub> O <sub>3</sub>               | 3.76 | 0.65 | 98.9956 |
| C <sub>7</sub> H <sub>8</sub>                               | 7.69 | 0.25 | 92.0626 | C <sub>2</sub> N <sub>4</sub> O                | 3.73 | 0.26 | 96.0073 | C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub> | 4.13 | 0.47 | 99.0195 |
| 93  |      |      |         | C <sub>3</sub> N <sub>2</sub> O <sub>2</sub>   | 4.08 | 0.47 | 95.9960 | C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> O              | 4.51 | 0.28 | 99.0433 |
| HN <sub>2</sub> O <sub>4</sub>                              | 0.94 | 0.80 | 92.9936 | C <sub>3</sub> H <sub>2</sub> N <sub>3</sub> O | 4.46 | 0.28 | 96.0198 | C <sub>3</sub> H <sub>7</sub> N <sub>4</sub>                | 4.88 | 0.10 | 99.0672 |
| H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>                | 1.31 | 0.61 | 93.0175 | C <sub>3</sub> H <sub>4</sub> N <sub>4</sub>   | 4.83 | 0.10 | 96.0437 | C <sub>4</sub> H <sub>3</sub> O <sub>3</sub>                | 4.49 | 0.68 | 99.0082 |
| H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>                | 1.68 | 0.41 | 93.0413 | C <sub>4</sub> O <sub>3</sub>                  | 4.44 | 0.68 | 95.9847 | C <sub>4</sub> H <sub>5</sub> NO <sub>2</sub>               | 4.86 | 0.50 | 99.0320 |
| CH <sub>3</sub> NO <sub>4</sub>                             | 1.67 | 0.81 | 93.0062 | C <sub>4</sub> H <sub>2</sub> NO <sub>2</sub>  | 4.81 | 0.49 | 96.0085 | C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> O              | 5.24 | 0.31 | 99.0559 |
| CH <sub>5</sub> N <sub>2</sub> O <sub>3</sub>               | 2.04 | 0.61 | 93.0300 | C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O | 5.19 | 0.31 | 96.0324 | C <sub>4</sub> H <sub>9</sub> N <sub>3</sub>                | 5.61 | 0.13 | 99.0798 |
| CH <sub>7</sub> N <sub>3</sub> O <sub>2</sub>               | 2.42 | 0.42 | 93.0539 | C <sub>4</sub> H <sub>6</sub> N <sub>3</sub>   | 5.56 | 0.13 | 96.0563 | C <sub>5</sub> H <sub>7</sub> O <sub>2</sub>                | 5.59 | 0.53 | 99.0446 |
| C <sub>2</sub> H <sub>5</sub> O <sub>4</sub>                | 2.40 | 0.82 | 93.0187 | C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>   | 5.55 | 0.53 | 96.0211 | C <sub>5</sub> H <sub>9</sub> NO                            | 5.97 | 0.35 | 99.0684 |
| C <sub>2</sub> H <sub>7</sub> NO <sub>3</sub>               | 2.77 | 0.63 | 93.0426 | C <sub>5</sub> H <sub>6</sub> NO               | 5.92 | 0.35 | 96.0449 | C <sub>5</sub> H <sub>11</sub> N <sub>2</sub>               | 6.34 | 0.17 | 99.0923 |
| C <sub>3</sub> HN <sub>4</sub>                              | 4.78 | 0.09 | 93.0202 | C <sub>5</sub> H <sub>8</sub> N <sub>2</sub>   | 6.29 | 0.17 | 96.0688 | C <sub>6</sub> H <sub>11</sub> O                            | 6.70 | 0.39 | 99.0810 |
| C <sub>4</sub> HN <sub>2</sub> O                            | 5.14 | 0.31 | 93.0089 | C <sub>6</sub> H <sub>8</sub> O                | 6.65 | 0.39 | 96.0575 | C <sub>6</sub> H <sub>13</sub> N                            | 7.07 | 0.21 | 99.1049 |

|   | M+1  | M+2  | MW       |   | M+1  | M+2  | MW       |  | M+1  | M+2  | MW       |
|---|------|------|----------|---|------|------|----------|--|------|------|----------|
| C <sub>7</sub> H <sub>15</sub>                              | 7.80 | 0.26 | 99.1174  | C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub> | 3.07 | 0.64 | 102.0065 | C <sub>2</sub> H <sub>8</sub> N <sub>4</sub> O               | 3.85 | 0.26 | 104.0699 |
| C <sub>7</sub> HN   | 7.96 | 0.28 | 99.0109  | C <sub>2</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub> | 3.45 | 0.45 | 102.0304 | C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>                 | 3.46 | 0.84 | 104.0109 |
| C <sub>8</sub> H <sub>3</sub>                               | 8.69 | 0.33 | 99.0235  | C <sub>2</sub> H <sub>6</sub> N <sub>4</sub> O              | 3.82 | 0.26 | 102.0542 | C <sub>3</sub> H <sub>6</sub> NO <sub>3</sub>                | 3.84 | 0.66 | 104.0348 |
| 100   |      |      |          | C <sub>3</sub> H <sub>2</sub> O <sub>4</sub>                | 3.43 | 0.84 | 101.9953 | C <sub>3</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 4.21 | 0.47 | 104.0586 |
| CN <sub>4</sub> O <sub>2</sub>                              | 2.68 | 0.43 | 100.0022 | C <sub>3</sub> H <sub>4</sub> NO <sub>3</sub>               | 3.80 | 0.66 | 102.0191 | C <sub>3</sub> H <sub>10</sub> N <sub>3</sub> O              | 4.59 | 0.29 | 104.0825 |
| C <sub>2</sub> N <sub>2</sub> O <sub>3</sub>                | 3.04 | 0.63 | 99.9909  | C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> | 4.18 | 0.47 | 102.0429 | C <sub>3</sub> H <sub>12</sub> N <sub>4</sub>                | 4.96 | 0.10 | 104.1063 |
| C <sub>2</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub> | 3.42 | 0.45 | 100.0147 | C <sub>3</sub> H <sub>8</sub> N <sub>3</sub> O              | 4.55 | 0.28 | 102.0668 | C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>                 | 4.57 | 0.68 | 104.0473 |
| C <sub>2</sub> H <sub>4</sub> N <sub>4</sub> O              | 3.79 | 0.26 | 100.0386 | C <sub>3</sub> H <sub>10</sub> N <sub>4</sub>               | 4.93 | 0.10 | 102.0907 | C <sub>4</sub> H <sub>10</sub> NO <sub>2</sub>               | 4.94 | 0.50 | 104.0712 |
| C <sub>3</sub> O <sub>4</sub>                               | 3.40 | 0.84 | 99.9796  | C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>                | 4.54 | 0.68 | 102.0317 | C <sub>4</sub> H <sub>12</sub> N <sub>2</sub> O              | 5.32 | 0.32 | 104.0950 |
| C <sub>3</sub> H <sub>2</sub> NO <sub>3</sub>               | 3.77 | 0.65 | 100.0034 | C <sub>4</sub> H <sub>8</sub> NO <sub>2</sub>               | 4.91 | 0.50 | 102.0555 | C <sub>4</sub> N <sub>4</sub>                                | 5.85 | 0.14 | 104.0124 |
| C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> | 4.15 | 0.47 | 100.0273 | C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O             | 5.28 | 0.32 | 102.0794 | C <sub>5</sub> H <sub>12</sub> O <sub>2</sub>                | 5.67 | 0.53 | 104.0837 |
| C <sub>3</sub> H <sub>6</sub> N <sub>3</sub> O              | 4.52 | 0.28 | 100.0511 | C <sub>4</sub> H <sub>12</sub> N <sub>3</sub>               | 5.66 | 0.13 | 102.1032 | C <sub>5</sub> N <sub>2</sub> O                              | 6.20 | 0.36 | 104.0011 |
| C <sub>3</sub> H <sub>8</sub> N <sub>4</sub>                | 4.90 | 0.10 | 100.0750 | C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>               | 5.64 | 0.53 | 102.0681 | C <sub>5</sub> H <sub>2</sub> N <sub>3</sub>                 | 6.58 | 0.19 | 104.0249 |
| C <sub>4</sub> H <sub>4</sub> O <sub>3</sub>                | 4.50 | 0.68 | 100.0160 | C <sub>5</sub> H <sub>12</sub> NO                           | 6.02 | 0.35 | 102.0919 | C <sub>6</sub> O <sub>2</sub>                                | 6.56 | 0.58 | 103.9898 |
| C <sub>4</sub> H <sub>6</sub> NO <sub>2</sub>               | 4.88 | 0.50 | 100.0399 | C <sub>5</sub> H <sub>14</sub> N <sub>2</sub>               | 6.39 | 0.17 | 102.1158 | C <sub>6</sub> H <sub>2</sub> NO                             | 6.94 | 0.41 | 104.0136 |
| C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O              | 5.25 | 0.31 | 100.0637 | C <sub>5</sub> N <sub>3</sub>                               | 6.55 | 0.18 | 102.0093 | C <sub>6</sub> H <sub>4</sub> N <sub>2</sub>                 | 7.31 | 0.23 | 104.0375 |
| C <sub>4</sub> H <sub>10</sub> N <sub>3</sub>               | 5.63 | 0.13 | 100.0876 | C <sub>6</sub> H <sub>14</sub> O                            | 6.75 | 0.39 | 102.1045 | C <sub>7</sub> H <sub>4</sub> O                              | 7.67 | 0.45 | 104.0262 |
| C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>                | 5.61 | 0.53 | 100.0524 | C <sub>6</sub> NO   | 6.90 | 0.40 | 101.9980 | C <sub>7</sub> H <sub>6</sub> N                              | 8.04 | 0.28 | 104.0501 |
| C <sub>5</sub> H <sub>10</sub> NO                           | 5.98 | 0.35 | 100.0763 | C <sub>6</sub> H <sub>2</sub> N <sub>2</sub>                | 7.28 | 0.23 | 102.0218 | C <sub>8</sub> H <sub>8</sub>                                | 8.77 | 0.34 | 104.0626 |
| C <sub>5</sub> H <sub>12</sub> N <sub>2</sub>               | 6.36 | 0.17 | 100.1001 | C <sub>7</sub> H <sub>2</sub> O                             | 7.64 | 0.45 | 102.0106 | 105  |      |      |          |
| C <sub>6</sub> H <sub>12</sub> O                            | 6.71 | 0.39 | 100.0888 | C <sub>7</sub> H <sub>4</sub> N                             | 8.01 | 0.28 | 102.0344 | CHN <sub>2</sub> O <sub>4</sub>                              | 2.02 | 0.81 | 104.9936 |
| C <sub>6</sub> H <sub>14</sub> N                            | 7.09 | 0.22 | 100.1127 | C <sub>8</sub> H <sub>6</sub>                               | 8.74 | 0.34 | 102.0470 | CH <sub>3</sub> N <sub>3</sub> O <sub>3</sub>                | 2.39 | 0.62 | 105.0175 |
| C <sub>6</sub> N <sub>2</sub>                               | 7.25 | 0.23 | 100.0062 | 103   |      |      |          | CH <sub>5</sub> N <sub>4</sub> O <sub>2</sub>                | 2.76 | 0.43 | 105.0413 |
| C <sub>7</sub> H <sub>16</sub>                              | 7.82 | 0.26 | 100.1253 | CHN <sub>3</sub> O <sub>3</sub>                             | 2.36 | 0.62 | 103.0018 | C <sub>2</sub> H <sub>3</sub> NO <sub>4</sub>                | 2.75 | 0.83 | 105.0062 |
| C <sub>7</sub> O  | 7.60 | 0.45 | 99.9949  | CH <sub>3</sub> N <sub>4</sub> O <sub>2</sub>               | 2.73 | 0.43 | 103.0257 | C <sub>2</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>  | 3.12 | 0.64 | 105.0300 |
| C <sub>7</sub> H <sub>2</sub> N                             | 7.98 | 0.28 | 100.0187 | C <sub>2</sub> HNO <sub>4</sub>                             | 2.72 | 0.83 | 102.9905 | C <sub>2</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>  | 3.50 | 0.45 | 105.0539 |
| C <sub>8</sub> H <sub>4</sub>                               | 8.71 | 0.33 | 100.0313 | C <sub>2</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub> | 3.09 | 0.64 | 103.0144 | C <sub>2</sub> H <sub>9</sub> N <sub>4</sub> O               | 3.87 | 0.26 | 105.0777 |
| 101   |      |      |          | C <sub>2</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub> | 3.46 | 0.45 | 103.0382 | C <sub>3</sub> H <sub>5</sub> O <sub>4</sub>                 | 3.48 | 0.84 | 105.0187 |
| CHN <sub>4</sub> O <sub>2</sub>                             | 2.70 | 0.43 | 101.0100 | C <sub>2</sub> H <sub>7</sub> N <sub>4</sub> O              | 3.84 | 0.26 | 103.0621 | C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>                | 3.85 | 0.66 | 105.0426 |
| C <sub>2</sub> HN <sub>2</sub> O <sub>3</sub>               | 3.06 | 0.64 | 100.9987 | C <sub>3</sub> H <sub>3</sub> O <sub>4</sub>                | 3.45 | 0.84 | 103.0031 | C <sub>3</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 4.23 | 0.47 | 105.0664 |
| C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub> | 3.43 | 0.45 | 101.0226 | C <sub>3</sub> H <sub>5</sub> NO <sub>3</sub>               | 3.82 | 0.66 | 103.0269 | C <sub>3</sub> H <sub>11</sub> N <sub>3</sub> O              | 4.60 | 0.29 | 105.0903 |
| C <sub>2</sub> H <sub>5</sub> N <sub>4</sub> O              | 3.81 | 0.26 | 101.0464 | C <sub>3</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> | 4.19 | 0.47 | 103.0508 | C <sub>4</sub> H <sub>9</sub> O <sub>3</sub>                 | 4.58 | 0.68 | 105.0552 |
| C <sub>3</sub> HO <sub>4</sub>                              | 3.41 | 0.84 | 100.9874 | C <sub>3</sub> H <sub>9</sub> N <sub>3</sub> O              | 4.57 | 0.29 | 103.0746 | C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub>               | 4.96 | 0.50 | 105.0790 |
| C <sub>3</sub> H <sub>3</sub> NO <sub>3</sub>               | 3.79 | 0.65 | 101.0113 | C <sub>3</sub> H <sub>11</sub> N <sub>4</sub>               | 4.94 | 0.10 | 103.0985 | C <sub>4</sub> HN <sub>4</sub>                               | 5.86 | 0.15 | 105.0202 |
| C <sub>3</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> | 4.16 | 0.47 | 101.0351 | C <sub>4</sub> H <sub>7</sub> O <sub>3</sub>                | 4.55 | 0.68 | 103.0395 | C <sub>5</sub> HN <sub>2</sub> O                             | 6.22 | 0.36 | 105.0089 |
| C <sub>3</sub> H <sub>7</sub> N <sub>3</sub> O              | 4.54 | 0.28 | 101.0590 | C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>               | 4.93 | 0.50 | 103.0634 | C <sub>5</sub> H <sub>3</sub> N <sub>3</sub>                 | 6.60 | 0.19 | 105.0328 |
| C <sub>3</sub> H <sub>9</sub> N <sub>4</sub>                | 4.91 | 0.10 | 101.0829 | C <sub>4</sub> H <sub>11</sub> N <sub>2</sub> O             | 5.30 | 0.32 | 103.0872 | C <sub>6</sub> HO <sub>2</sub>                               | 6.58 | 0.58 | 104.9976 |
| C <sub>4</sub> H <sub>5</sub> O <sub>3</sub>                | 4.52 | 0.68 | 101.0238 | C <sub>4</sub> H <sub>13</sub> N <sub>3</sub>               | 5.67 | 0.14 | 103.1111 | C <sub>6</sub> H <sub>3</sub> NO                             | 6.95 | 0.41 | 105.0215 |
| C <sub>4</sub> H <sub>7</sub> NO <sub>2</sub>               | 4.89 | 0.50 | 101.0477 | C <sub>5</sub> H <sub>11</sub> O <sub>2</sub>               | 5.66 | 0.53 | 103.0759 | C <sub>6</sub> H <sub>5</sub> N <sub>2</sub>                 | 7.33 | 0.23 | 105.0453 |
| C <sub>4</sub> H <sub>9</sub> N <sub>2</sub> O              | 5.27 | 0.31 | 101.0715 | C <sub>5</sub> H <sub>13</sub> NO                           | 6.03 | 0.35 | 103.0998 | C <sub>7</sub> H <sub>5</sub> O                              | 7.68 | 0.45 | 105.0340 |
| C <sub>4</sub> H <sub>11</sub> N <sub>3</sub>               | 5.64 | 0.13 | 101.0954 | C <sub>5</sub> HN <sub>3</sub>                              | 6.56 | 0.18 | 103.0171 | C <sub>7</sub> H <sub>7</sub> N                              | 8.06 | 0.28 | 105.0579 |
| C <sub>5</sub> H <sub>9</sub> O <sub>2</sub>                | 5.63 | 0.53 | 101.0603 | C <sub>6</sub> HN <sub>2</sub>                              | 6.92 | 0.40 | 103.0058 | C <sub>8</sub> H <sub>9</sub>                                | 8.79 | 0.34 | 105.0705 |
| C <sub>5</sub> H <sub>11</sub> NO                           | 6.00 | 0.35 | 101.0841 | C <sub>7</sub> H <sub>3</sub> O                             | 7.65 | 0.45 | 103.0184 | 106  |      |      |          |
| C <sub>5</sub> H <sub>13</sub> N <sub>2</sub>               | 6.37 | 0.17 | 101.1080 | C <sub>7</sub> H <sub>5</sub> N                             | 8.03 | 0.28 | 103.0422 | CH <sub>2</sub> N <sub>2</sub> O <sub>4</sub>                | 2.03 | 0.82 | 106.0014 |
| C <sub>6</sub> H <sub>13</sub> O                            | 6.73 | 0.39 | 101.0967 | C <sub>8</sub> H <sub>7</sub>                               | 8.76 | 0.34 | 103.0548 | CH <sub>4</sub> N <sub>3</sub> O <sub>3</sub>                | 2.41 | 0.62 | 106.0253 |
| C <sub>6</sub> H <sub>15</sub> N                            | 7.11 | 0.22 | 101.1205 | 104   |      |      |          | CH <sub>6</sub> N <sub>4</sub> O <sub>2</sub>                | 2.78 | 0.43 | 106.0491 |
| C <sub>6</sub> HN <sub>2</sub>                              | 7.26 | 0.23 | 101.0140 | CN <sub>2</sub> O <sub>4</sub>                              | 2.00 | 0.81 | 103.9858 | C <sub>2</sub> H <sub>4</sub> NO <sub>4</sub>                | 2.76 | 0.83 | 106.0140 |
| C <sub>7</sub> HO   | 7.62 | 0.45 | 101.0027 | CH <sub>2</sub> N <sub>3</sub> O <sub>3</sub>               | 2.37 | 0.62 | 104.0096 | C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 3.14 | 0.64 | 106.0379 |
| C <sub>7</sub> H <sub>3</sub> N                             | 7.99 | 0.28 | 101.0266 | CH <sub>4</sub> N <sub>4</sub> O <sub>2</sub>               | 2.75 | 0.43 | 104.0335 | C <sub>2</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 3.51 | 0.45 | 106.0617 |
| C <sub>8</sub> H <sub>5</sub>                               | 8.72 | 0.33 | 101.0391 | C <sub>2</sub> H <sub>2</sub> NO <sub>4</sub>               | 2.73 | 0.83 | 103.9983 | C <sub>2</sub> H <sub>10</sub> N <sub>4</sub> O              | 3.89 | 0.26 | 106.0856 |
| 102   |      |      |          | C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub> | 3.11 | 0.64 | 104.0222 | C <sub>3</sub> H <sub>6</sub> O <sub>4</sub>                 | 3.49 | 0.85 | 106.0266 |
| CN <sub>3</sub> O <sub>3</sub>                              | 2.34 | 0.62 | 101.9940 | C <sub>2</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub> | 3.48 | 0.45 | 104.0460 | C <sub>3</sub> H <sub>8</sub> NO <sub>3</sub>                | 3.87 | 0.66 | 106.0504 |
| CH <sub>2</sub> N <sub>4</sub> O <sub>2</sub>               | 2.72 | 0.43 | 102.0178 |   |      |      |          | C <sub>3</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 4.24 | 0.47 | 106.0743 |
| C <sub>2</sub> NO <sub>4</sub>                              | 2.70 | 0.83 | 101.9827 |   |      |      |          | C <sub>4</sub> H <sub>10</sub> O <sub>3</sub>                | 4.60 | 0.68 | 106.0630 |



|   | M+1  | M+2  | MW       |   | M+1  | M+2  | MW       |   | M+1  | M+2  | MW       |
|---|------|------|----------|---|------|------|----------|---|------|------|----------|
| C <sub>4</sub> N <sub>3</sub> O                             | 5.51 | 0.33 | 106.0042 | 109   |      |      |          | C <sub>7</sub> H <sub>13</sub> N                            | 8.15 | 0.29 | 111.1049 |
| C <sub>4</sub> H <sub>2</sub> N <sub>4</sub>                | 5.88 | 0.15 | 106.0280 | CH <sub>5</sub> N <sub>2</sub> O <sub>4</sub>               | 2.08 | 0.82 | 109.0249 | C <sub>8</sub> H <sub>15</sub>                              | 8.88 | 0.35 | 111.1174 |
| C <sub>5</sub> N <sub>2</sub> O                             | 5.86 | 0.54 | 105.9929 | CH <sub>7</sub> N <sub>3</sub> O <sub>3</sub>               | 2.45 | 0.62 | 109.0468 | C <sub>8</sub> HN   | 9.04 | 0.36 | 111.0109 |
| C <sub>5</sub> H <sub>2</sub> N <sub>2</sub> O              | 6.24 | 0.36 | 106.0167 | C <sub>2</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub> | 2.81 | 0.83 | 109.0375 | C <sub>9</sub> H <sub>3</sub>                               | 9.77 | 0.43 | 111.0235 |
| C <sub>5</sub> H <sub>4</sub> N <sub>3</sub>                | 6.61 | 0.19 | 106.0406 | C <sub>3</sub> HN <sub>4</sub> O                            | 4.82 | 0.30 | 109.0151 | 112   |      |      |          |
| C <sub>6</sub> H <sub>2</sub> O <sub>2</sub>                | 6.59 | 0.58 | 106.0054 | C <sub>4</sub> HN <sub>2</sub> O <sub>2</sub>               | 5.18 | 0.51 | 109.0038 | C <sub>2</sub> N <sub>4</sub> O <sub>2</sub>                | 3.77 | 0.46 | 112.0022 |
| C <sub>6</sub> H <sub>4</sub> NO                            | 6.97 | 0.41 | 106.0293 | C <sub>4</sub> H <sub>3</sub> N <sub>3</sub> O              | 5.55 | 0.33 | 109.0277 | C <sub>3</sub> N <sub>2</sub> O <sub>3</sub>                | 4.12 | 0.67 | 111.9909 |
| C <sub>6</sub> H <sub>6</sub> N <sub>2</sub>                | 7.34 | 0.23 | 106.0532 | C <sub>4</sub> H <sub>5</sub> N <sub>4</sub>                | 5.93 | 0.15 | 109.0515 | C <sub>3</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub> | 4.50 | 0.48 | 112.0147 |
| C <sub>7</sub> H <sub>6</sub> O                             | 7.70 | 0.46 | 106.0419 | C <sub>5</sub> HO <sub>3</sub>                              | 5.54 | 0.73 | 108.9925 | C <sub>3</sub> H <sub>4</sub> N <sub>4</sub> O              | 4.87 | 0.30 | 112.0386 |
| C <sub>7</sub> H <sub>8</sub> N                             | 8.07 | 0.28 | 106.0657 | C <sub>5</sub> H <sub>3</sub> N <sub>2</sub> O              | 5.91 | 0.55 | 109.0164 | C <sub>4</sub> O <sub>4</sub>                               | 4.48 | 0.88 | 111.9796 |
| C <sub>8</sub> H <sub>10</sub>                              | 8.80 | 0.34 | 106.0783 | C <sub>5</sub> H <sub>5</sub> N <sub>2</sub> O              | 6.29 | 0.37 | 109.0402 | C <sub>4</sub> H <sub>2</sub> NO <sub>3</sub>               | 4.85 | 0.70 | 112.0034 |
| 107   |      |      |          | C <sub>5</sub> H <sub>7</sub> N <sub>3</sub>                | 6.66 | 0.19 | 109.0641 | C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> | 5.23 | 0.51 | 112.0273 |
| CH <sub>3</sub> N <sub>2</sub> O <sub>4</sub>               | 2.05 | 0.82 | 107.0093 | C <sub>6</sub> H <sub>5</sub> O <sub>2</sub>                | 6.64 | 0.59 | 109.0289 | C <sub>4</sub> H <sub>6</sub> N <sub>3</sub> O              | 5.60 | 0.33 | 112.0511 |
| CH <sub>5</sub> N <sub>3</sub> O <sub>3</sub>               | 2.42 | 0.62 | 107.0331 | C <sub>6</sub> H <sub>7</sub> NO                            | 7.02 | 0.41 | 109.0528 | C <sub>4</sub> H <sub>8</sub> N <sub>4</sub>                | 5.98 | 0.15 | 112.0750 |
| CH <sub>7</sub> N <sub>4</sub> O <sub>2</sub>               | 2.80 | 0.43 | 107.0570 | C <sub>6</sub> H <sub>9</sub> N <sub>2</sub>                | 7.39 | 0.24 | 109.0767 | C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>                | 5.58 | 0.73 | 112.0160 |
| C <sub>2</sub> H <sub>5</sub> NO <sub>4</sub>               | 2.78 | 0.83 | 107.0218 | C <sub>7</sub> H <sub>9</sub> O                             | 7.75 | 0.46 | 109.0653 | C <sub>5</sub> H <sub>6</sub> NO <sub>2</sub>               | 5.96 | 0.55 | 112.0399 |
| C <sub>2</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub> | 3.15 | 0.64 | 107.0457 | C <sub>7</sub> H <sub>11</sub> N                            | 8.12 | 0.29 | 109.0892 | C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> O              | 6.33 | 0.37 | 112.0637 |
| C <sub>2</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub> | 3.53 | 0.45 | 107.0695 | C <sub>8</sub> H <sub>13</sub>                              | 8.85 | 0.35 | 109.1018 | C <sub>5</sub> H <sub>10</sub> N <sub>3</sub>               | 6.71 | 0.19 | 112.0876 |
| C <sub>3</sub> H <sub>7</sub> O <sub>4</sub>                | 3.51 | 0.85 | 107.0344 | C <sub>9</sub> H  | 9.74 | 0.42 | 109.0078 | C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>                | 6.69 | 0.59 | 112.0524 |
| C <sub>3</sub> H <sub>9</sub> NO <sub>3</sub>               | 3.88 | 0.66 | 107.0583 | 110   |      |      |          | C <sub>6</sub> H <sub>10</sub> NO                           | 7.06 | 0.41 | 112.0763 |
| C <sub>4</sub> HN <sub>3</sub> O                            | 5.52 | 0.33 | 107.0120 | CH <sub>6</sub> N <sub>2</sub> O <sub>4</sub>               | 2.10 | 0.82 | 110.0328 | C <sub>6</sub> H <sub>12</sub> N <sub>2</sub>               | 7.44 | 0.24 | 112.1001 |
| C <sub>4</sub> H <sub>3</sub> N <sub>4</sub>                | 5.90 | 0.15 | 107.0359 | C <sub>3</sub> N <sub>3</sub> O <sub>2</sub>                | 4.46 | 0.48 | 109.9991 | C <sub>7</sub> H <sub>12</sub> O                            | 7.80 | 0.46 | 112.0888 |
| C <sub>5</sub> HN <sub>2</sub> O                            | 5.88 | 0.54 | 107.0007 | C <sub>3</sub> H <sub>2</sub> N <sub>4</sub> O              | 4.84 | 0.30 | 110.0229 | C <sub>7</sub> H <sub>14</sub> N                            | 8.17 | 0.29 | 112.1127 |
| C <sub>5</sub> H <sub>3</sub> N <sub>2</sub> O              | 6.25 | 0.37 | 107.0246 | C <sub>4</sub> NO <sub>3</sub>                              | 4.82 | 0.69 | 109.9878 | C <sub>7</sub> N <sub>2</sub>                               | 8.33 | 0.30 | 112.0062 |
| C <sub>5</sub> H <sub>5</sub> N <sub>3</sub>                | 6.63 | 0.19 | 107.0484 | C <sub>4</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> | 5.20 | 0.51 | 110.0116 | C <sub>8</sub> H <sub>16</sub>                              | 8.90 | 0.35 | 112.1253 |
| C <sub>6</sub> H <sub>3</sub> O <sub>2</sub>                | 6.61 | 0.58 | 107.0133 | C <sub>4</sub> H <sub>4</sub> N <sub>3</sub> O              | 5.57 | 0.33 | 110.0355 | C <sub>8</sub> O  | 8.68 | 0.53 | 111.9949 |
| C <sub>6</sub> H <sub>5</sub> NO                            | 6.98 | 0.41 | 107.0371 | C <sub>4</sub> H <sub>6</sub> N <sub>4</sub>                | 5.94 | 0.15 | 110.0594 | C <sub>8</sub> H <sub>2</sub> N                             | 9.06 | 0.36 | 112.0187 |
| C <sub>6</sub> H <sub>7</sub> N <sub>2</sub>                | 7.36 | 0.23 | 107.0610 | C <sub>5</sub> H <sub>2</sub> O <sub>3</sub>                | 5.55 | 0.73 | 110.0003 | C <sub>9</sub> H <sub>4</sub>                               | 9.79 | 0.43 | 112.0313 |
| C <sub>7</sub> H <sub>7</sub> O                             | 7.72 | 0.46 | 107.0497 | C <sub>5</sub> H <sub>4</sub> NO <sub>2</sub>               | 5.93 | 0.55 | 110.0242 | 113   |      |      |          |
| C <sub>7</sub> H <sub>9</sub> N                             | 8.09 | 0.29 | 107.0736 | C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O              | 6.30 | 0.37 | 110.0480 | C <sub>2</sub> HN <sub>4</sub> O <sub>2</sub>               | 3.78 | 0.46 | 113.0100 |
| C <sub>8</sub> H <sub>11</sub>                              | 8.82 | 0.34 | 107.0861 | C <sub>5</sub> H <sub>8</sub> N <sub>3</sub>                | 6.68 | 0.19 | 110.0719 | C <sub>3</sub> HN <sub>2</sub> O <sub>3</sub>               | 4.14 | 0.67 | 112.9987 |
| 108   |      |      |          | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>                | 6.66 | 0.59 | 110.0368 | C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub> | 4.51 | 0.48 | 113.0226 |
| CH <sub>4</sub> N <sub>2</sub> O <sub>4</sub>               | 2.06 | 0.82 | 108.0171 | C <sub>6</sub> H <sub>8</sub> NO                            | 7.03 | 0.41 | 110.0606 | C <sub>3</sub> H <sub>5</sub> N <sub>4</sub> O              | 4.89 | 0.30 | 113.0464 |
| CH <sub>6</sub> N <sub>3</sub> O <sub>3</sub>               | 2.44 | 0.62 | 108.0410 | C <sub>6</sub> H <sub>10</sub> N <sub>2</sub>               | 7.41 | 0.24 | 110.0845 | C <sub>4</sub> HO <sub>4</sub>                              | 4.49 | 0.88 | 112.9874 |
| CH <sub>8</sub> N <sub>4</sub> O <sub>2</sub>               | 2.81 | 0.43 | 108.0648 | C <sub>7</sub> H <sub>10</sub> O                            | 7.76 | 0.46 | 110.0732 | C <sub>4</sub> H <sub>3</sub> NO <sub>3</sub>               | 4.87 | 0.70 | 113.0113 |
| C <sub>2</sub> H <sub>6</sub> NO <sub>4</sub>               | 2.80 | 0.83 | 108.0297 | C <sub>7</sub> H <sub>12</sub> N                            | 8.14 | 0.29 | 110.0970 | C <sub>4</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> | 5.24 | 0.51 | 113.0351 |
| C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub> | 3.17 | 0.64 | 108.0535 | C <sub>8</sub> H <sub>14</sub>                              | 8.87 | 0.35 | 110.1096 | C <sub>4</sub> H <sub>7</sub> N <sub>3</sub> O              | 5.62 | 0.33 | 113.0590 |
| C <sub>3</sub> H <sub>8</sub> O <sub>4</sub>                | 3.53 | 0.85 | 108.0422 | C <sub>8</sub> N  | 9.03 | 0.36 | 110.0031 | C <sub>4</sub> H <sub>9</sub> N <sub>4</sub>                | 5.99 | 0.15 | 113.0829 |
| C <sub>3</sub> N <sub>4</sub> O                             | 4.81 | 0.30 | 108.0073 | C <sub>9</sub> H <sub>2</sub>                               | 9.76 | 0.42 | 110.0157 | C <sub>5</sub> H <sub>5</sub> O <sub>3</sub>                | 5.60 | 0.73 | 113.0238 |
| C <sub>4</sub> N <sub>2</sub> O <sub>2</sub>                | 5.16 | 0.51 | 107.9960 | 111   |      |      |          | C <sub>5</sub> H <sub>7</sub> NO <sub>2</sub>               | 5.97 | 0.55 | 113.0477 |
| C <sub>4</sub> H <sub>2</sub> N <sub>3</sub> O              | 5.54 | 0.33 | 108.0198 | C <sub>3</sub> HN <sub>3</sub> O <sub>2</sub>               | 4.48 | 0.48 | 111.0069 | C <sub>5</sub> H <sub>9</sub> N <sub>2</sub> O              | 6.35 | 0.37 | 113.0715 |
| C <sub>4</sub> H <sub>4</sub> N <sub>4</sub>                | 5.91 | 0.15 | 108.0437 | C <sub>3</sub> H <sub>3</sub> N <sub>4</sub> O              | 4.85 | 0.30 | 111.0308 | C <sub>5</sub> H <sub>11</sub> N <sub>3</sub>               | 6.72 | 0.19 | 113.0954 |
| C <sub>5</sub> O <sub>3</sub>                               | 5.52 | 0.72 | 107.9847 | C <sub>4</sub> HN <sub>2</sub> O <sub>3</sub>               | 4.84 | 0.69 | 110.9956 | C <sub>6</sub> H <sub>9</sub> O <sub>2</sub>                | 6.71 | 0.59 | 113.0603 |
| C <sub>5</sub> H <sub>2</sub> NO <sub>2</sub>               | 5.89 | 0.54 | 108.0085 | C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub> | 5.21 | 0.51 | 111.0195 | C <sub>6</sub> H <sub>11</sub> NO                           | 7.08 | 0.42 | 113.0841 |
| C <sub>5</sub> H <sub>4</sub> N <sub>2</sub> O              | 6.27 | 0.37 | 108.0324 | C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O              | 5.59 | 0.33 | 111.0433 | C <sub>6</sub> H <sub>13</sub> N <sub>2</sub>               | 7.45 | 0.24 | 113.1080 |
| C <sub>5</sub> H <sub>6</sub> N <sub>3</sub>                | 6.64 | 0.19 | 108.0563 | C <sub>4</sub> H <sub>7</sub> N <sub>4</sub>                | 5.96 | 0.15 | 111.0672 | C <sub>7</sub> H <sub>13</sub> O                            | 7.81 | 0.46 | 113.0967 |
| C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>                | 6.63 | 0.59 | 108.0211 | C <sub>5</sub> H <sub>3</sub> O <sub>3</sub>                | 5.57 | 0.73 | 111.0082 | C <sub>7</sub> H <sub>15</sub> N                            | 8.19 | 0.29 | 113.1205 |
| C <sub>6</sub> H <sub>6</sub> NO                            | 7.00 | 0.41 | 108.0449 | C <sub>5</sub> H <sub>5</sub> NO <sub>2</sub>               | 5.94 | 0.55 | 111.0320 | C <sub>7</sub> HN <sub>2</sub>                              | 8.34 | 0.31 | 113.0140 |
| C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>                | 7.37 | 0.24 | 108.0688 | C <sub>5</sub> H <sub>7</sub> N <sub>2</sub> O              | 6.32 | 0.37 | 111.0559 | C <sub>8</sub> H <sub>17</sub>                              | 8.92 | 0.35 | 113.1331 |
| C <sub>7</sub> H <sub>8</sub> O                             | 7.73 | 0.46 | 108.0575 | C <sub>5</sub> H <sub>9</sub> N <sub>3</sub>                | 6.69 | 0.19 | 111.0798 | C <sub>8</sub> HO   | 8.70 | 0.53 | 113.0027 |
| C <sub>7</sub> H <sub>10</sub> N                            | 8.11 | 0.29 | 108.0814 | C <sub>6</sub> H <sub>7</sub> O <sub>2</sub>                | 6.67 | 0.59 | 111.0446 | C <sub>8</sub> H <sub>3</sub> N                             | 9.07 | 0.36 | 113.0266 |
| C <sub>8</sub> H <sub>12</sub>                              | 8.84 | 0.34 | 108.0939 | C <sub>6</sub> H <sub>9</sub> NO                            | 7.05 | 0.41 | 111.0684 | C <sub>9</sub> H <sub>5</sub>                               | 9.81 | 0.43 | 113.0391 |
| C <sub>9</sub>  | 9.73 | 0.42 | 108.0000 | C <sub>6</sub> H <sub>11</sub> N <sub>2</sub>               | 7.42 | 0.24 | 111.0923 | 114   |      |      |          |
|   |      |      |          | C <sub>7</sub> H <sub>11</sub> O                            | 7.78 | 0.46 | 111.0810 | C <sub>2</sub> N <sub>3</sub> O <sub>3</sub>                | 3.42 | 0.85 | 113.9940 |



|   | M+1  | M+2  | MW       |  | M+1  | M+2  | MW       |  | M+1  | M+2  | MW       |
|---|------|------|----------|--|------|------|----------|--|------|------|----------|
| C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub> | 3.80 | 0.46 | 114.0178 | 116  |      |      |          | C <sub>7</sub> H <sub>5</sub> N <sub>2</sub>                 | 8.41 | 0.31 | 117.0453 |
| C <sub>3</sub> N <sub>2</sub> O <sub>4</sub>                | 3.78 | 0.86 | 113.9827 | C <sub>2</sub> N <sub>2</sub> O <sub>4</sub>                 | 3.08 | 0.84 | 115.9858 | C <sub>8</sub> H <sub>5</sub> O                              | 8.76 | 0.54 | 117.0340 |
| C <sub>3</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub> | 4.15 | 0.67 | 114.0065 | C <sub>2</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>  | 3.45 | 0.65 | 116.0096 | C <sub>8</sub> H <sub>7</sub> N                              | 9.14 | 0.37 | 117.0579 |
| C <sub>3</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub> | 4.53 | 0.48 | 114.0304 | C <sub>2</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>  | 3.83 | 0.46 | 116.0335 | C <sub>9</sub> H <sub>9</sub>                                | 9.87 | 0.43 | 117.0705 |
| C <sub>3</sub> H <sub>6</sub> N <sub>4</sub> O              | 4.90 | 0.30 | 114.0542 | C <sub>3</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 3.81 | 0.86 | 115.9983 | 118  |      |      |          |
| C <sub>4</sub> H <sub>2</sub> O <sub>4</sub>                | 4.51 | 0.88 | 113.9953 | C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 4.19 | 0.67 | 116.0222 | C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 3.11 | 0.84 | 118.0014 |
| C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub> | 4.89 | 0.70 | 114.0191 | C <sub>3</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>  | 4.56 | 0.49 | 116.0460 | C <sub>2</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>  | 3.49 | 0.65 | 118.0253 |
| C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> | 5.26 | 0.51 | 114.0429 | C <sub>3</sub> H <sub>8</sub> N <sub>4</sub> O               | 4.93 | 0.30 | 116.0699 | C <sub>2</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 3.86 | 0.46 | 118.0491 |
| C <sub>4</sub> H <sub>8</sub> N <sub>3</sub> O              | 5.63 | 0.33 | 114.0668 | C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>                 | 4.54 | 0.88 | 116.0109 | C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>  | 3.84 | 0.86 | 118.0140 |
| C <sub>4</sub> H <sub>10</sub> N <sub>4</sub>               | 6.01 | 0.15 | 114.0907 | C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 4.92 | 0.70 | 116.0348 | C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 4.22 | 0.67 | 118.0379 |
| C <sub>5</sub> H <sub>6</sub> O <sub>3</sub>                | 5.62 | 0.73 | 114.0317 | C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 5.29 | 0.52 | 116.0586 | C <sub>3</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 4.59 | 0.49 | 118.0617 |
| C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> | 5.99 | 0.55 | 114.0555 | C <sub>4</sub> H <sub>10</sub> N <sub>3</sub> O              | 5.67 | 0.34 | 116.0825 | C <sub>3</sub> H <sub>10</sub> N <sub>4</sub> O              | 4.97 | 0.30 | 118.0856 |
| C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O             | 6.37 | 0.37 | 114.0794 | C <sub>4</sub> H <sub>12</sub> N <sub>4</sub>                | 6.04 | 0.16 | 116.1063 | C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>                 | 4.57 | 0.88 | 118.0266 |
| C <sub>5</sub> H <sub>12</sub> N <sub>3</sub>               | 6.74 | 0.20 | 114.1032 | C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>                 | 5.65 | 0.73 | 116.0473 | C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 4.95 | 0.70 | 118.0504 |
| C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>               | 6.72 | 0.59 | 114.0681 | C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 6.02 | 0.55 | 116.0712 | C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 5.32 | 0.52 | 118.0743 |
| C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> O             | 7.10 | 0.42 | 114.0919 | C <sub>5</sub> H <sub>12</sub> N <sub>2</sub> O              | 6.40 | 0.37 | 116.0950 | C <sub>4</sub> H <sub>12</sub> N <sub>3</sub> O              | 5.70 | 0.34 | 118.0981 |
| C <sub>6</sub> H <sub>14</sub> N <sub>2</sub>               | 7.47 | 0.24 | 114.1158 | C <sub>5</sub> H <sub>14</sub> N <sub>3</sub>                | 6.77 | 0.20 | 116.1189 | C <sub>4</sub> H <sub>14</sub> N <sub>4</sub>                | 6.07 | 0.16 | 118.1220 |
| C <sub>6</sub> N <sub>3</sub>                               | 7.63 | 0.25 | 114.0093 | C <sub>5</sub> N <sub>4</sub>                                | 6.93 | 0.21 | 116.0124 | C <sub>5</sub> H <sub>10</sub> O <sub>3</sub>                | 5.68 | 0.73 | 118.0630 |
| C <sub>7</sub> H <sub>14</sub> O                            | 7.83 | 0.47 | 114.1045 | C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>                | 6.75 | 0.59 | 116.0837 | C <sub>5</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | 6.05 | 0.55 | 118.0868 |
| C <sub>7</sub> H <sub>16</sub> N                            | 8.20 | 0.29 | 114.1284 | C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> O              | 7.13 | 0.42 | 116.1076 | C <sub>5</sub> H <sub>14</sub> N <sub>2</sub> O              | 6.43 | 0.38 | 118.1107 |
| C <sub>7</sub> N <sub>2</sub> O                             | 7.98 | 0.48 | 113.9980 | C <sub>6</sub> H <sub>16</sub> N <sub>2</sub>                | 7.50 | 0.24 | 116.1315 | C <sub>5</sub> N <sub>3</sub> O                              | 6.59 | 0.39 | 118.0042 |
| C <sub>7</sub> H <sub>2</sub> N <sub>2</sub>                | 8.36 | 0.31 | 114.0218 | C <sub>6</sub> N <sub>2</sub> O                              | 7.29 | 0.43 | 116.0011 | C <sub>5</sub> H <sub>2</sub> N <sub>4</sub>                 | 6.96 | 0.21 | 118.0280 |
| C <sub>8</sub> H <sub>18</sub>                              | 8.93 | 0.35 | 114.1409 | C <sub>6</sub> H <sub>2</sub> N <sub>3</sub>                 | 7.66 | 0.26 | 116.0249 | C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>                | 6.79 | 0.60 | 118.0994 |
| C <sub>8</sub> H <sub>2</sub> O                             | 8.72 | 0.53 | 114.0106 | C <sub>7</sub> H <sub>16</sub> O                             | 7.86 | 0.47 | 116.1202 | C <sub>6</sub> N <sub>2</sub> O                              | 6.94 | 0.61 | 117.9929 |
| C <sub>8</sub> H <sub>4</sub> N                             | 9.09 | 0.37 | 114.0344 | C <sub>7</sub> O <sub>2</sub>                                | 7.64 | 0.65 | 115.9898 | C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> O               | 7.32 | 0.43 | 118.0167 |
| C <sub>9</sub> H <sub>6</sub>                               | 9.82 | 0.43 | 114.0470 | C <sub>7</sub> H <sub>2</sub> N <sub>2</sub> O               | 8.02 | 0.48 | 116.0136 | C <sub>6</sub> H <sub>4</sub> N <sub>3</sub>                 | 7.69 | 0.26 | 118.0406 |
| 115   |      |      |          | C <sub>7</sub> H <sub>4</sub> N <sub>2</sub>                 | 8.39 | 0.31 | 116.0375 | C <sub>7</sub> H <sub>2</sub> O <sub>2</sub>                 | 7.67 | 0.65 | 118.0054 |
| C <sub>2</sub> HN <sub>3</sub> O <sub>3</sub>               | 3.44 | 0.65 | 115.0018 | C <sub>8</sub> H <sub>4</sub> O                              | 8.75 | 0.54 | 116.0262 | C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O               | 8.05 | 0.48 | 118.0293 |
| C <sub>2</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub> | 3.81 | 0.46 | 115.0257 | C <sub>8</sub> H <sub>6</sub> N                              | 9.12 | 0.37 | 116.0501 | C <sub>7</sub> H <sub>6</sub> N <sub>2</sub>                 | 8.42 | 0.31 | 118.0532 |
| C <sub>3</sub> HN <sub>2</sub> O <sub>4</sub>               | 3.80 | 0.86 | 114.9905 | C <sub>9</sub> H <sub>8</sub>                                | 9.85 | 0.43 | 116.0626 | C <sub>8</sub> H <sub>6</sub> O                              | 8.78 | 0.54 | 118.0419 |
| C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub> | 4.17 | 0.67 | 115.0144 | 117  |      |      |          | C <sub>8</sub> H <sub>8</sub> N                              | 9.15 | 0.37 | 118.0657 |
| C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub> | 4.54 | 0.48 | 115.0382 | C <sub>2</sub> HN <sub>2</sub> O <sub>4</sub>                | 3.10 | 0.84 | 116.9936 | C <sub>9</sub> H <sub>10</sub>                               | 9.89 | 0.44 | 118.0783 |
| C <sub>3</sub> H <sub>7</sub> N <sub>4</sub> O              | 4.92 | 0.30 | 115.0621 | C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>  | 3.47 | 0.65 | 117.0175 | 119  |      |      |          |
| C <sub>4</sub> H <sub>3</sub> O <sub>4</sub>                | 4.53 | 0.88 | 115.0031 | C <sub>2</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>  | 3.85 | 0.46 | 117.0413 | C <sub>2</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>  | 3.13 | 0.84 | 119.0093 |
| C <sub>4</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub> | 4.90 | 0.70 | 115.0269 | C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>  | 3.83 | 0.86 | 117.0062 | C <sub>2</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>  | 3.50 | 0.65 | 119.0331 |
| C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> | 5.28 | 0.52 | 115.0508 | C <sub>3</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>  | 4.20 | 0.67 | 117.0300 | C <sub>2</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>  | 3.88 | 0.46 | 119.0570 |
| C <sub>4</sub> H <sub>9</sub> N <sub>3</sub> O              | 5.65 | 0.33 | 115.0746 | C <sub>3</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>  | 4.58 | 0.49 | 117.0539 | C <sub>3</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>  | 3.86 | 0.86 | 119.0218 |
| C <sub>4</sub> H <sub>11</sub> N <sub>4</sub>               | 6.02 | 0.16 | 115.0985 | C <sub>3</sub> H <sub>9</sub> N <sub>4</sub> O               | 4.95 | 0.30 | 117.0777 | C <sub>3</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>  | 4.23 | 0.67 | 119.0457 |
| C <sub>5</sub> H <sub>7</sub> O <sub>3</sub>                | 5.63 | 0.73 | 115.0395 | C <sub>4</sub> H <sub>5</sub> O <sub>4</sub>                 | 4.56 | 0.88 | 117.0187 | C <sub>3</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>  | 4.61 | 0.49 | 119.0695 |
| C <sub>5</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub> | 6.01 | 0.55 | 115.0634 | C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>  | 4.93 | 0.70 | 117.0426 | C <sub>3</sub> H <sub>11</sub> N <sub>4</sub> O              | 4.98 | 0.30 | 119.0934 |
| C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> O             | 6.38 | 0.37 | 115.0872 | C <sub>4</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 5.31 | 0.52 | 117.0664 | C <sub>4</sub> H <sub>7</sub> O <sub>4</sub>                 | 4.59 | 0.88 | 119.0344 |
| C <sub>5</sub> H <sub>13</sub> N <sub>3</sub>               | 6.76 | 0.20 | 115.1111 | C <sub>4</sub> H <sub>11</sub> N <sub>3</sub> O              | 5.68 | 0.34 | 117.0903 | C <sub>4</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>  | 4.97 | 0.70 | 119.0583 |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub>               | 6.74 | 0.59 | 115.0759 | C <sub>4</sub> H <sub>13</sub> N <sub>4</sub>                | 6.06 | 0.16 | 117.1142 | C <sub>4</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 5.34 | 0.52 | 119.0821 |
| C <sub>6</sub> H <sub>13</sub> N <sub>2</sub> O             | 7.11 | 0.42 | 115.0998 | C <sub>5</sub> H <sub>9</sub> O <sub>3</sub>                 | 5.66 | 0.73 | 117.0552 | C <sub>4</sub> H <sub>13</sub> N <sub>3</sub> O              | 5.71 | 0.34 | 119.1060 |
| C <sub>6</sub> H <sub>15</sub> N <sub>2</sub>               | 7.49 | 0.24 | 115.1236 | C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 6.04 | 0.55 | 117.0790 | C <sub>5</sub> H <sub>11</sub> O <sub>3</sub>                | 5.70 | 0.73 | 119.0708 |
| C <sub>6</sub> HN <sub>3</sub>                              | 7.64 | 0.25 | 115.0171 | C <sub>5</sub> H <sub>13</sub> N <sub>2</sub> O              | 6.41 | 0.38 | 117.1029 | C <sub>5</sub> H <sub>13</sub> N <sub>2</sub> O              | 6.07 | 0.56 | 119.0947 |
| C <sub>7</sub> H <sub>15</sub> O                            | 7.84 | 0.47 | 115.1123 | C <sub>5</sub> H <sub>15</sub> N <sub>3</sub>                | 6.79 | 0.20 | 117.1267 | C <sub>5</sub> HN <sub>3</sub> O                             | 6.60 | 0.39 | 119.0120 |
| C <sub>7</sub> H <sub>17</sub> N                            | 8.22 | 0.30 | 115.1362 | C <sub>5</sub> HN <sub>4</sub>                               | 6.94 | 0.21 | 117.0202 | C <sub>5</sub> H <sub>3</sub> N <sub>4</sub>                 | 6.98 | 0.21 | 119.0359 |
| C <sub>7</sub> HN <sub>2</sub> O                            | 8.00 | 0.48 | 115.0058 | C <sub>6</sub> H <sub>13</sub> O <sub>2</sub>                | 6.77 | 0.60 | 117.0916 | C <sub>6</sub> HN <sub>2</sub> O                             | 6.96 | 0.61 | 119.0007 |
| C <sub>7</sub> H <sub>3</sub> N <sub>2</sub>                | 8.38 | 0.31 | 115.0297 | C <sub>6</sub> H <sub>15</sub> N <sub>2</sub> O              | 7.14 | 0.42 | 117.1154 | C <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O               | 7.33 | 0.43 | 119.0246 |
| C <sub>8</sub> H <sub>3</sub> O                             | 8.73 | 0.53 | 115.0184 | C <sub>6</sub> HN <sub>2</sub> O                             | 7.30 | 0.43 | 117.0089 | C <sub>6</sub> H <sub>5</sub> N <sub>3</sub>                 | 7.71 | 0.26 | 119.0484 |
| C <sub>8</sub> H <sub>5</sub> N                             | 9.11 | 0.37 | 115.0422 | C <sub>6</sub> H <sub>3</sub> N <sub>3</sub>                 | 7.68 | 0.26 | 117.0328 | C <sub>7</sub> H <sub>3</sub> O <sub>2</sub>                 | 7.69 | 0.66 | 119.0133 |
| C <sub>9</sub> H <sub>7</sub>                               | 9.84 | 0.43 | 115.0548 | C <sub>7</sub> H <sub>2</sub> O                              | 7.66 | 0.65 | 116.9976 | C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> O               | 8.06 | 0.48 | 119.0371 |
|   |      |      |          | C <sub>7</sub> H <sub>3</sub> N <sub>2</sub> O               | 8.03 | 0.48 | 117.0215 | C <sub>7</sub> H <sub>7</sub> N <sub>2</sub>                 | 8.44 | 0.31 | 119.0610 |

|                      | M+1   | M+2  | MW       |                      | M+1   | M+2  | MW       |                    | M+1   | M+2  | MW       |
|----------------------|-------|------|----------|----------------------|-------|------|----------|--------------------|-------|------|----------|
| $C_8H_7O$            | 8.80  | 0.54 | 119.0497 | $^{122}C_2H_6N_2O_4$ | 3.18  | 0.84 | 122.0328 | $C_5H_2NO_3$       | 5.93  | 0.75 | 124.0034 |
| $C_8H_9N$            | 9.17  | 0.37 | 119.0736 | $C_2H_8N_3O_3$       | 3.55  | 0.65 | 122.0566 | $C_5H_4N_2O_2$     | 6.31  | 0.57 | 124.0273 |
| $C_9H_{11}$          | 9.90  | 0.44 | 119.0861 | $C_2H_{10}N_4O_2$    | 3.93  | 0.46 | 122.0805 | $C_5H_6N_3O$       | 6.68  | 0.39 | 124.0511 |
| $^{120}C_2H_4N_2O_4$ | 3.14  | 0.84 | 120.0171 | $C_3H_8NO_4$         | 3.91  | 0.86 | 122.0453 | $C_5H_8N_4$        | 7.06  | 0.22 | 124.0750 |
| $C_2H_6N_3O_3$       | 3.52  | 0.65 | 120.0410 | $C_3H_{10}N_2O_3$    | 4.28  | 0.67 | 122.0692 | $C_6H_4O_3$        | 6.66  | 0.79 | 124.0160 |
| $C_2H_8N_4O_2$       | 3.89  | 0.46 | 120.0648 | $C_4H_{10}O_4$       | 4.64  | 0.89 | 122.0579 | $C_6H_6NO_2$       | 7.04  | 0.61 | 124.0399 |
| $C_3H_6NO_4$         | 3.88  | 0.86 | 120.0297 | $C_4N_3O_2$          | 5.54  | 0.53 | 121.9991 | $C_6H_8N_2O$       | 7.41  | 0.44 | 124.0637 |
| $C_3H_8N_2O_3$       | 4.25  | 0.67 | 120.0535 | $C_4H_2N_4O$         | 5.92  | 0.35 | 122.0229 | $C_6H_{10}N_3$     | 7.79  | 0.27 | 124.0876 |
| $C_3H_{10}N_3O_2$    | 4.62  | 0.49 | 120.0774 | $C_5NO_3$            | 5.90  | 0.75 | 121.9878 | $C_7H_8O_2$        | 7.77  | 0.66 | 124.0524 |
| $C_3H_{12}N_4O$      | 5.00  | 0.30 | 120.1012 | $C_5H_2N_2O_2$       | 6.28  | 0.57 | 122.0116 | $C_7H_{10}NO$      | 8.14  | 0.49 | 124.0763 |
| $C_4H_8O_4$          | 4.61  | 0.88 | 120.0422 | $C_5H_4N_3O$         | 6.65  | 0.39 | 122.0355 | $C_7H_{12}N_2$     | 8.52  | 0.32 | 124.1001 |
| $C_4H_{10}NO_3$      | 4.98  | 0.70 | 120.0661 | $C_5H_6N_4$          | 7.02  | 0.21 | 122.0594 | $C_8H_{12}O$       | 8.88  | 0.55 | 124.0888 |
| $C_4H_{12}N_2O_2$    | 5.36  | 0.52 | 120.0899 | $C_6H_2O_3$          | 6.63  | 0.79 | 122.0003 | $C_8H_{14}N$       | 9.25  | 0.38 | 124.1127 |
| $C_4N_4O$            | 5.89  | 0.35 | 120.0073 | $C_6H_4NO_2$         | 7.01  | 0.61 | 122.0242 | $C_8N_2$           | 9.41  | 0.39 | 124.0062 |
| $C_5H_{12}O_3$       | 5.71  | 0.74 | 120.0786 | $C_6H_6N_2O$         | 7.38  | 0.44 | 122.0480 | $C_9H_{16}$        | 9.98  | 0.45 | 124.1253 |
| $C_5N_2O_2$          | 6.24  | 0.57 | 119.9960 | $C_6H_8N_3$          | 7.76  | 0.26 | 122.0719 | $C_9O$             | 9.76  | 0.62 | 123.9949 |
| $C_5H_2N_3O$         | 6.62  | 0.39 | 120.0198 | $C_7H_6O_2$          | 7.74  | 0.66 | 122.0368 | $C_9H_2N$          | 10.14 | 0.46 | 124.0187 |
| $C_5H_4N_4$          | 6.99  | 0.21 | 120.0437 | $C_7H_8NO$           | 8.11  | 0.49 | 122.0606 | $C_{10}H_4$        | 10.87 | 0.53 | 124.0313 |
| $C_6O_3$             | 6.60  | 0.78 | 119.9847 | $C_7H_{10}N_2$       | 8.49  | 0.32 | 122.0845 | $^{125}C_3HN_4O_2$ | 4.86  | 0.50 | 125.0100 |
| $C_6H_2NO_2$         | 6.98  | 0.61 | 120.0085 | $C_8H_{10}O$         | 8.84  | 0.54 | 122.0732 | $C_4HN_2O_3$       | 5.22  | 0.71 | 124.9987 |
| $C_6H_4N_2O$         | 7.35  | 0.43 | 120.0324 | $C_8H_{12}N$         | 9.22  | 0.38 | 122.0970 | $C_4H_3N_3O_2$     | 5.59  | 0.53 | 125.0226 |
| $C_6H_6N_3$          | 7.72  | 0.26 | 120.0563 | $C_9H_{14}$          | 9.95  | 0.44 | 122.1096 | $C_4H_5N_4O$       | 5.97  | 0.35 | 125.0464 |
| $C_7H_4O_2$          | 7.71  | 0.66 | 120.0211 | $C_9N$               | 10.11 | 0.46 | 122.0031 | $C_5HO_4$          | 5.58  | 0.93 | 124.9874 |
| $C_7H_6NO$           | 8.08  | 0.49 | 120.0449 | $C_{10}H_2$          | 10.84 | 0.53 | 122.0157 | $C_5H_3NO_3$       | 5.95  | 0.75 | 125.0113 |
| $C_7H_8N_2$          | 8.46  | 0.32 | 120.0688 | $^{123}C_2H_7N_2O_4$ | 3.19  | 0.84 | 123.0406 | $C_5H_5N_2O_2$     | 6.32  | 0.57 | 125.0351 |
| $C_8H_8O$            | 8.81  | 0.54 | 120.0575 | $C_2H_9N_3O_3$       | 3.57  | 0.65 | 123.0644 | $C_5H_7N_3O$       | 6.70  | 0.39 | 125.0590 |
| $C_8H_{10}N$         | 9.19  | 0.37 | 120.0814 | $C_3H_9NO_4$         | 3.92  | 0.86 | 123.0532 | $C_5H_9N_4$        | 7.07  | 0.22 | 125.0829 |
| $C_9H_{12}$          | 9.92  | 0.44 | 120.0939 | $C_4HN_3O_2$         | 5.56  | 0.53 | 123.0069 | $C_6H_5O_3$        | 6.68  | 0.79 | 125.0238 |
| $C_{10}$             | 10.81 | 0.53 | 120.0000 | $C_4H_3N_4O$         | 5.94  | 0.35 | 123.0308 | $C_6H_7NO_2$       | 7.06  | 0.61 | 125.0477 |
| $^{121}C_2H_5N_2O_4$ | 3.16  | 0.84 | 121.0249 | $C_5HNO_3$           | 5.92  | 0.75 | 122.9956 | $C_6H_9N_2O$       | 7.43  | 0.44 | 125.0715 |
| $C_2H_7N_3O_3$       | 3.53  | 0.65 | 121.0488 | $C_5H_3N_2O_2$       | 6.29  | 0.57 | 123.0195 | $C_6H_{11}N_3$     | 7.80  | 0.27 | 125.0954 |
| $C_2H_9N_4O_2$       | 3.91  | 0.46 | 121.0726 | $C_5H_5N_3O$         | 6.67  | 0.39 | 123.0433 | $C_7H_9O_2$        | 7.79  | 0.66 | 125.0603 |
| $C_3H_7NO_4$         | 3.89  | 0.86 | 121.0375 | $C_5H_7N_4$          | 7.04  | 0.22 | 123.0672 | $C_7H_{11}NO$      | 8.16  | 0.49 | 125.0841 |
| $C_3H_9N_2O_3$       | 4.27  | 0.67 | 121.0614 | $C_6H_3O_3$          | 6.65  | 0.79 | 123.0082 | $C_7H_{13}N_2$     | 8.54  | 0.32 | 125.1080 |
| $C_3H_{11}N_3O_2$    | 4.64  | 0.49 | 121.0852 | $C_6H_5NO_2$         | 7.02  | 0.61 | 123.0320 | $C_8H_{13}O$       | 8.89  | 0.55 | 125.0967 |
| $C_4H_9O_4$          | 4.62  | 0.89 | 121.0501 | $C_6H_7N_2O$         | 7.40  | 0.44 | 123.0559 | $C_8H_{15}N$       | 9.27  | 0.38 | 125.1205 |
| $C_4H_{11}NO_3$      | 5.00  | 0.70 | 121.0739 | $C_6H_9N_3$          | 7.77  | 0.26 | 123.0798 | $C_8HN_2$          | 9.42  | 0.40 | 125.0140 |
| $C_4HN_4O$           | 5.90  | 0.35 | 121.0151 | $C_7H_7O_2$          | 7.75  | 0.66 | 123.0446 | $C_9H_{17}$        | 10.00 | 0.45 | 125.1331 |
| $C_5HN_2O_2$         | 6.26  | 0.57 | 121.0038 | $C_7H_9NO$           | 8.13  | 0.49 | 123.0684 | $C_9HO$            | 9.78  | 0.63 | 125.0027 |
| $C_5H_3N_3O$         | 6.63  | 0.39 | 121.0277 | $C_7H_{11}N_2$       | 8.50  | 0.32 | 123.0923 | $C_9H_3N$          | 10.15 | 0.46 | 125.0266 |
| $C_5H_5N_4$          | 7.01  | 0.21 | 121.0515 | $C_8H_{11}O$         | 8.86  | 0.55 | 123.0810 | $C_{10}H_5$        | 10.89 | 0.53 | 125.0391 |
| $C_6HO_3$            | 6.62  | 0.79 | 120.9925 | $C_8H_{13}N$         | 9.23  | 0.38 | 123.1049 | $^{126}C_3N_3O_3$  | 4.50  | 0.68 | 125.9940 |
| $C_6H_3NO_2$         | 6.99  | 0.61 | 121.0164 | $C_9H_{15}$          | 9.97  | 0.44 | 123.1174 | $C_3H_2N_4O_2$     | 4.88  | 0.50 | 126.0178 |
| $C_6H_5N_2O$         | 7.37  | 0.44 | 121.0402 | $C_9HN$              | 10.12 | 0.46 | 123.0109 | $C_4NO_4$          | 4.86  | 0.90 | 125.9827 |
| $C_6H_7N_3$          | 7.74  | 0.26 | 121.0641 | $C_{10}H_3$          | 10.85 | 0.53 | 123.0235 | $C_4H_2N_2O_3$     | 5.23  | 0.71 | 126.0065 |
| $C_7H_5O_2$          | 7.72  | 0.66 | 121.0289 | $^{124}C_2H_8N_2O_4$ | 3.21  | 0.84 | 124.0484 | $C_4H_4N_3O_2$     | 5.61  | 0.53 | 126.0304 |
| $C_7H_7NO$           | 8.10  | 0.49 | 121.0528 | $C_3N_4O_2$          | 4.85  | 0.50 | 124.0022 | $C_4H_6N_4O$       | 5.98  | 0.35 | 126.0542 |
| $C_7H_9N_2$          | 8.47  | 0.32 | 121.0767 | $C_4N_2O_3$          | 5.20  | 0.71 | 123.9909 | $C_5H_2O_4$        | 5.59  | 0.93 | 125.9953 |
| $C_8H_9O$            | 8.83  | 0.54 | 121.0653 | $C_4H_2N_3O_2$       | 5.58  | 0.53 | 124.0147 | $C_5H_4NO_3$       | 5.97  | 0.75 | 126.0191 |
| $C_8H_{11}N$         | 9.20  | 0.38 | 121.0892 | $C_4H_4N_4O$         | 5.95  | 0.35 | 124.0386 | $C_5H_6N_2O_2$     | 6.34  | 0.57 | 126.0429 |
| $C_9H_{13}$          | 9.93  | 0.44 | 121.1018 | $C_5O_4$             | 5.56  | 0.93 | 123.9796 | $C_5H_8N_3O$       | 6.71  | 0.39 | 126.0668 |
| $C_{10}H$            | 10.82 | 0.53 | 121.0078 |                      |       |      |          | $C_5H_{10}N_4$     | 7.09  | 0.22 | 126.0907 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|--|-------|------|----------|
| C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>                | 6.70  | 0.79 | 126.0317 | C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> | 6.37  | 0.57 | 128.0586 | 130  |       |      |          |
| C <sub>6</sub> H <sub>8</sub> NO <sub>2</sub>               | 7.07  | 0.62 | 126.0555 | C <sub>5</sub> H <sub>10</sub> N <sub>3</sub> O             | 6.75  | 0.40 | 128.0825 | C <sub>3</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 4.19  | 0.87 | 130.0014 |
| C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O             | 7.45  | 0.44 | 126.0794 | C <sub>5</sub> H <sub>12</sub> N <sub>4</sub>               | 7.12  | 0.22 | 128.1063 | C <sub>3</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>  | 4.57  | 0.69 | 130.0253 |
| C <sub>6</sub> H <sub>12</sub> N <sub>3</sub>               | 7.82  | 0.27 | 126.1032 | C <sub>6</sub> H <sub>8</sub> O <sub>3</sub>                | 6.73  | 0.79 | 128.0473 | C <sub>3</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 4.94  | 0.50 | 130.0491 |
| C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>               | 7.80  | 0.66 | 126.0681 | C <sub>6</sub> H <sub>10</sub> NO <sub>2</sub>              | 7.10  | 0.62 | 128.0712 | C <sub>4</sub> H <sub>4</sub> NO <sub>4</sub>                | 4.92  | 0.90 | 130.0140 |
| C <sub>7</sub> H <sub>12</sub> NO                           | 8.18  | 0.49 | 126.0919 | C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> O             | 7.48  | 0.44 | 128.0950 | C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 5.30  | 0.72 | 130.0379 |
| C <sub>7</sub> H <sub>14</sub> N <sub>2</sub>               | 8.55  | 0.32 | 126.1158 | C <sub>6</sub> H <sub>14</sub> N <sub>3</sub>               | 7.85  | 0.27 | 128.1189 | C <sub>4</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 5.67  | 0.54 | 130.0617 |
| C <sub>7</sub> N <sub>3</sub>                               | 8.71  | 0.34 | 126.0093 | C <sub>6</sub> N <sub>4</sub>                               | 8.01  | 0.28 | 128.0124 | C <sub>4</sub> H <sub>10</sub> N <sub>4</sub> O              | 6.05  | 0.36 | 130.0856 |
| C <sub>8</sub> H <sub>14</sub> O                            | 8.91  | 0.55 | 126.1045 | C <sub>7</sub> H <sub>12</sub> O <sub>2</sub>               | 7.83  | 0.67 | 128.0837 | C <sub>5</sub> H <sub>6</sub> O <sub>4</sub>                 | 5.66  | 0.93 | 130.0266 |
| C <sub>8</sub> H <sub>16</sub> N                            | 9.28  | 0.38 | 126.1284 | C <sub>7</sub> H <sub>14</sub> NO                           | 8.21  | 0.50 | 128.1076 | C <sub>5</sub> H <sub>8</sub> NO <sub>3</sub>                | 6.03  | 0.75 | 130.0504 |
| C <sub>8</sub> NO   | 9.07  | 0.56 | 125.9980 | C <sub>7</sub> H <sub>16</sub> N <sub>2</sub>               | 8.58  | 0.33 | 128.1315 | C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 6.40  | 0.58 | 130.0743 |
| C <sub>8</sub> H <sub>2</sub> N <sub>2</sub>                | 9.44  | 0.40 | 126.0218 | C <sub>7</sub> N <sub>2</sub> O                             | 8.37  | 0.51 | 128.0011 | C <sub>5</sub> H <sub>12</sub> N <sub>3</sub> O              | 6.78  | 0.40 | 130.0981 |
| C <sub>9</sub> H <sub>18</sub>                              | 10.01 | 0.45 | 126.1409 | C <sub>7</sub> H <sub>2</sub> N <sub>3</sub>                | 8.74  | 0.34 | 128.0249 | C <sub>5</sub> H <sub>14</sub> N <sub>4</sub>                | 7.15  | 0.22 | 130.1220 |
| C <sub>9</sub> H <sub>2</sub> O                             | 9.80  | 0.63 | 126.0106 | C <sub>8</sub> H <sub>16</sub> O                            | 8.94  | 0.55 | 128.1202 | C <sub>6</sub> H <sub>10</sub> O <sub>3</sub>                | 6.76  | 0.79 | 130.0630 |
| C <sub>9</sub> H <sub>4</sub> N                             | 10.17 | 0.46 | 126.0344 | C <sub>8</sub> O <sub>2</sub>                               | 8.72  | 0.73 | 127.9898 | C <sub>6</sub> H <sub>12</sub> NO <sub>2</sub>               | 7.14  | 0.62 | 130.0868 |
| C <sub>10</sub> H <sub>6</sub>                              | 10.90 | 0.54 | 126.0470 | C <sub>8</sub> H <sub>18</sub> N                            | 9.31  | 0.39 | 128.1440 | C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> O              | 7.51  | 0.45 | 130.1107 |
| 127   |       |      |          | C <sub>8</sub> H <sub>2</sub> NO                            | 9.10  | 0.57 | 128.0136 | C <sub>6</sub> H <sub>16</sub> N <sub>3</sub>                | 7.88  | 0.27 | 130.1346 |
| C <sub>3</sub> HN <sub>3</sub> O <sub>3</sub>               | 4.52  | 0.68 | 127.0018 | C <sub>8</sub> H <sub>4</sub> N <sub>2</sub>                | 9.47  | 0.40 | 128.0375 | C <sub>6</sub> N <sub>3</sub> O                              | 7.67  | 0.46 | 130.0042 |
| C <sub>3</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub> | 4.89  | 0.50 | 127.0257 | C <sub>9</sub> H <sub>20</sub>                              | 10.05 | 0.45 | 128.1566 | C <sub>6</sub> H <sub>2</sub> N <sub>4</sub>                 | 8.04  | 0.29 | 130.0280 |
| C <sub>4</sub> HN <sub>4</sub>                              | 4.88  | 0.90 | 126.9905 | C <sub>9</sub> H <sub>4</sub> O                             | 9.83  | 0.63 | 128.0262 | C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>                | 7.87  | 0.67 | 130.0994 |
| C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub> | 5.25  | 0.71 | 127.0144 | C <sub>9</sub> H <sub>6</sub> N                             | 10.20 | 0.47 | 128.0501 | C <sub>7</sub> H <sub>16</sub> NO                            | 8.24  | 0.50 | 130.1233 |
| C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub> | 5.62  | 0.53 | 127.0382 | C <sub>10</sub> H <sub>8</sub>                              | 10.93 | 0.54 | 128.0626 | C <sub>7</sub> NO <sub>2</sub>                               | 8.02  | 0.68 | 129.9929 |
| C <sub>4</sub> H <sub>7</sub> N <sub>4</sub> O              | 6.00  | 0.35 | 127.0621 | 129   |       |      |          | C <sub>7</sub> H <sub>18</sub> N <sub>2</sub>                | 8.62  | 0.33 | 130.1471 |
| C <sub>5</sub> H <sub>3</sub> O <sub>4</sub>                | 5.61  | 0.93 | 127.0031 | C <sub>3</sub> HN <sub>2</sub> O <sub>4</sub>               | 4.18  | 0.87 | 128.9936 | C <sub>7</sub> H <sub>2</sub> N <sub>2</sub> O               | 8.40  | 0.51 | 130.0167 |
| C <sub>5</sub> H <sub>5</sub> NO <sub>3</sub>               | 5.98  | 0.75 | 127.0269 | C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub> | 4.55  | 0.69 | 129.0175 | C <sub>7</sub> H <sub>4</sub> N <sub>3</sub>                 | 8.77  | 0.34 | 130.0406 |
| C <sub>5</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> | 6.36  | 0.57 | 127.0508 | C <sub>3</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub> | 4.93  | 0.50 | 129.0413 | C <sub>8</sub> H <sub>18</sub> O                             | 8.97  | 0.56 | 130.1358 |
| C <sub>5</sub> H <sub>9</sub> N <sub>3</sub> O              | 6.73  | 0.40 | 127.0746 | C <sub>4</sub> H <sub>3</sub> NO <sub>4</sub>               | 4.91  | 0.90 | 129.0062 | C <sub>8</sub> H <sub>2</sub> O <sub>2</sub>                 | 8.75  | 0.74 | 130.0054 |
| C <sub>5</sub> H <sub>11</sub> N <sub>4</sub>               | 7.10  | 0.22 | 127.0985 | C <sub>4</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub> | 5.28  | 0.72 | 129.0300 | C <sub>8</sub> H <sub>4</sub> NO                             | 9.13  | 0.57 | 130.0293 |
| C <sub>6</sub> H <sub>7</sub> O <sub>3</sub>                | 6.71  | 0.79 | 127.0395 | C <sub>4</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub> | 5.66  | 0.54 | 129.0539 | C <sub>8</sub> H <sub>6</sub> N <sub>2</sub>                 | 9.50  | 0.40 | 130.0532 |
| C <sub>6</sub> H <sub>9</sub> NO <sub>2</sub>               | 7.09  | 0.62 | 127.0634 | C <sub>4</sub> H <sub>9</sub> N <sub>4</sub> O              | 6.03  | 0.36 | 129.0777 | C <sub>9</sub> H <sub>6</sub> O                              | 9.86  | 0.63 | 130.0419 |
| C <sub>6</sub> H <sub>11</sub> N <sub>2</sub> O             | 7.46  | 0.44 | 127.0872 | C <sub>5</sub> H <sub>5</sub> O <sub>4</sub>                | 5.64  | 0.93 | 129.0187 | C <sub>9</sub> H <sub>8</sub> N                              | 10.23 | 0.47 | 130.0657 |
| C <sub>6</sub> H <sub>13</sub> N <sub>3</sub>               | 7.84  | 0.27 | 127.1111 | C <sub>5</sub> H <sub>7</sub> NO <sub>3</sub>               | 6.01  | 0.75 | 129.0426 | C <sub>10</sub> H <sub>10</sub>                              | 10.97 | 0.54 | 130.0783 |
| C <sub>7</sub> H <sub>11</sub> O <sub>2</sub>               | 7.82  | 0.67 | 127.0759 | C <sub>5</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub> | 6.39  | 0.57 | 129.0664 | 131  |       |      |          |
| C <sub>7</sub> H <sub>13</sub> NO                           | 8.19  | 0.49 | 127.0998 | C <sub>5</sub> H <sub>11</sub> N <sub>3</sub> O             | 6.76  | 0.40 | 129.0903 | C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>  | 4.21  | 0.87 | 131.0093 |
| C <sub>7</sub> H <sub>15</sub> N <sub>2</sub>               | 8.57  | 0.32 | 127.1236 | C <sub>5</sub> H <sub>13</sub> N <sub>4</sub>               | 7.14  | 0.22 | 129.1142 | C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>  | 4.58  | 0.69 | 131.0331 |
| C <sub>7</sub> HN <sub>3</sub>                              | 8.72  | 0.34 | 127.0171 | C <sub>6</sub> H <sub>9</sub> O <sub>3</sub>                | 6.74  | 0.79 | 129.0552 | C <sub>3</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>  | 4.96  | 0.50 | 131.0570 |
| C <sub>8</sub> H <sub>15</sub> O                            | 8.92  | 0.55 | 127.1123 | C <sub>6</sub> H <sub>11</sub> NO <sub>2</sub>              | 7.12  | 0.62 | 129.0790 | C <sub>4</sub> H <sub>5</sub> NO <sub>4</sub>                | 4.94  | 0.90 | 131.0218 |
| C <sub>8</sub> H <sub>17</sub> N                            | 9.30  | 0.38 | 127.1362 | C <sub>6</sub> H <sub>13</sub> N <sub>2</sub> O             | 7.49  | 0.44 | 129.1029 | C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>  | 5.31  | 0.72 | 131.0457 |
| C <sub>8</sub> HN <sub>4</sub>                              | 9.08  | 0.57 | 127.0058 | C <sub>6</sub> H <sub>15</sub> N <sub>3</sub>               | 7.87  | 0.27 | 129.1267 | C <sub>4</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>  | 5.69  | 0.54 | 131.0695 |
| C <sub>8</sub> H <sub>3</sub> N <sub>2</sub>                | 9.46  | 0.40 | 127.0297 | C <sub>6</sub> HN <sub>4</sub>                              | 8.03  | 0.28 | 129.0202 | C <sub>4</sub> H <sub>11</sub> N <sub>4</sub> O              | 6.06  | 0.36 | 131.0934 |
| C <sub>9</sub> H <sub>19</sub>                              | 10.03 | 0.45 | 127.1488 | C <sub>7</sub> H <sub>13</sub> O <sub>2</sub>               | 7.85  | 0.67 | 129.0916 | C <sub>5</sub> H <sub>7</sub> O <sub>4</sub>                 | 5.67  | 0.93 | 131.0344 |
| C <sub>9</sub> H <sub>3</sub> O                             | 9.81  | 0.63 | 127.0184 | C <sub>7</sub> H <sub>15</sub> NO                           | 8.22  | 0.50 | 129.1154 | C <sub>5</sub> H <sub>9</sub> NO <sub>3</sub>                | 6.05  | 0.75 | 131.0583 |
| C <sub>9</sub> H <sub>5</sub> N                             | 10.19 | 0.47 | 127.0422 | C <sub>7</sub> H <sub>17</sub> N <sub>2</sub>               | 8.60  | 0.33 | 129.1393 | C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 6.42  | 0.58 | 131.0821 |
| C <sub>10</sub> H <sub>7</sub>                              | 10.92 | 0.54 | 127.0548 | C <sub>7</sub> HN <sub>2</sub> O                            | 8.38  | 0.51 | 129.0089 | C <sub>5</sub> H <sub>13</sub> N <sub>3</sub> O              | 6.79  | 0.40 | 131.1060 |
| 128   |       |      |          | C <sub>7</sub> H <sub>3</sub> N <sub>3</sub>                | 8.76  | 0.34 | 129.0328 | C <sub>5</sub> H <sub>15</sub> N <sub>4</sub>                | 7.17  | 0.22 | 131.1298 |
| C <sub>3</sub> N <sub>2</sub> O <sub>4</sub>                | 4.16  | 0.87 | 127.9858 | C <sub>8</sub> H <sub>17</sub> O                            | 8.96  | 0.55 | 129.1280 | C <sub>6</sub> H <sub>11</sub> O <sub>3</sub>                | 6.78  | 0.80 | 131.0708 |
| C <sub>3</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub> | 4.54  | 0.68 | 128.0096 | C <sub>8</sub> HO <sub>2</sub>                              | 8.74  | 0.74 | 128.9976 | C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub>               | 7.15  | 0.62 | 131.0947 |
| C <sub>3</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub> | 4.91  | 0.50 | 128.0335 | C <sub>8</sub> H <sub>19</sub> N                            | 9.33  | 0.39 | 129.1519 | C <sub>6</sub> H <sub>15</sub> N <sub>2</sub> O              | 7.53  | 0.45 | 131.1185 |
| C <sub>4</sub> H <sub>2</sub> NO <sub>4</sub>               | 4.89  | 0.90 | 127.9983 | C <sub>8</sub> H <sub>3</sub> NO                            | 9.11  | 0.57 | 129.0215 | C <sub>6</sub> H <sub>17</sub> N <sub>3</sub>                | 7.90  | 0.27 | 131.1424 |
| C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub> | 5.27  | 0.72 | 128.0222 | C <sub>8</sub> H <sub>5</sub> N <sub>2</sub>                | 9.49  | 0.40 | 129.0453 | C <sub>6</sub> HN <sub>3</sub> O                             | 7.68  | 0.46 | 131.0120 |
| C <sub>4</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub> | 5.64  | 0.53 | 128.0460 | C <sub>9</sub> H <sub>5</sub> O                             | 9.84  | 0.63 | 129.0340 | C <sub>6</sub> H <sub>3</sub> N <sub>4</sub>                 | 8.06  | 0.29 | 131.0359 |
| C <sub>4</sub> H <sub>8</sub> N <sub>4</sub> O              | 6.02  | 0.36 | 128.0699 | C <sub>9</sub> H <sub>7</sub> N                             | 10.22 | 0.47 | 129.0579 | C <sub>7</sub> H <sub>15</sub> O <sub>2</sub>                | 7.88  | 0.67 | 131.1072 |
| C <sub>5</sub> H <sub>4</sub> O <sub>4</sub>                | 5.62  | 0.93 | 128.0109 | C <sub>10</sub> H <sub>9</sub>                              | 10.95 | 0.54 | 129.0705 | C <sub>7</sub> H <sub>17</sub> NO                            | 8.26  | 0.50 | 131.1311 |
| C <sub>5</sub> H <sub>6</sub> NO <sub>3</sub>               | 6.00  | 0.75 | 128.0348 |   |       |      |          | C <sub>7</sub> HN <sub>2</sub> O                             | 8.04  | 0.68 | 131.0007 |



|                   | M+1   | M+2  | MW       |                   | M+1   | M+2  | MW       |                   | M+1   | M+2  | MW       |
|-------------------|-------|------|----------|-------------------|-------|------|----------|-------------------|-------|------|----------|
| $C_7H_3N_2O$      | 8.41  | 0.51 | 131.0246 | $C_6H_{15}NO_2$   | 7.18  | 0.62 | 133.1103 | $C_5HN_3O_2$      | 6.64  | 0.59 | 135.0069 |
| $C_7H_5N_3$       | 8.79  | 0.34 | 131.0484 | $C_6HN_2O_2$      | 7.34  | 0.63 | 133.0038 | $C_5H_3N_4O$      | 7.02  | 0.41 | 135.0308 |
| $C_8H_3O_2$       | 8.77  | 0.74 | 131.0133 | $C_6H_3N_3O$      | 7.72  | 0.46 | 133.0277 | $C_6HNO_3$        | 7.00  | 0.81 | 134.9956 |
| $C_8H_5NO$        | 9.15  | 0.57 | 131.0371 | $C_6H_5N_4$       | 8.09  | 0.29 | 133.0515 | $C_6H_3N_2O_2$    | 7.37  | 0.64 | 135.0195 |
| $C_8H_7N_2$       | 9.52  | 0.40 | 131.0610 | $C_7HO_3$         | 7.70  | 0.86 | 132.9925 | $C_6H_5N_3O$      | 7.75  | 0.46 | 135.0433 |
| $C_9H_7O$         | 9.88  | 0.64 | 131.0497 | $C_7H_3NO_2$      | 8.07  | 0.69 | 133.0164 | $C_6H_7N_4$       | 8.12  | 0.29 | 135.0672 |
| $C_9H_9N$         | 10.25 | 0.47 | 131.0736 | $C_7H_5N_2O$      | 8.45  | 0.51 | 133.0402 | $C_7H_3O_3$       | 7.73  | 0.86 | 135.0082 |
| $C_{10}H_{11}$    | 10.98 | 0.54 | 131.0861 | $C_7H_7N_3$       | 8.82  | 0.35 | 133.0641 | $C_7H_5NO_2$      | 8.10  | 0.69 | 135.0320 |
| 132               |       |      |          | $C_8H_5O_2$       | 8.80  | 0.74 | 133.0289 | $C_7H_7N_2O$      | 8.48  | 0.52 | 135.0559 |
| $C_3H_4N_2O_4$    | 4.23  | 0.87 | 132.0171 | $C_8H_7NO$        | 9.18  | 0.57 | 133.0528 | $C_7H_9N_3$       | 8.85  | 0.35 | 135.0798 |
| $C_3H_6N_3O_3$    | 4.60  | 0.69 | 132.0410 | $C_8H_9N_2$       | 9.55  | 0.41 | 133.0767 | $C_8H_7O_2$       | 8.84  | 0.74 | 135.0446 |
| $C_3H_8N_4O_2$    | 4.97  | 0.50 | 132.0648 | $C_9H_9O$         | 9.91  | 0.64 | 133.0653 | $C_8H_9NO$        | 9.21  | 0.58 | 135.0684 |
| $C_4H_6NO_4$      | 4.96  | 0.90 | 132.0297 | $C_9H_{11}N$      | 10.28 | 0.48 | 133.0892 | $C_8H_{11}N_2$    | 9.58  | 0.41 | 135.0923 |
| $C_4H_8N_2O_3$    | 5.33  | 0.72 | 132.0535 | $C_{10}H_{13}$    | 11.01 | 0.55 | 133.1018 | $C_9H_{11}O$      | 9.94  | 0.64 | 135.0810 |
| $C_4H_{10}N_3O_2$ | 5.70  | 0.54 | 132.0774 | $C_{11}H$         | 11.90 | 0.64 | 133.0078 | $C_9H_{13}N$      | 10.31 | 0.48 | 135.1049 |
| $C_4H_{12}N_4O$   | 6.08  | 0.36 | 132.1012 | 134               |       |      |          | $C_{10}H_{15}$    | 11.05 | 0.55 | 135.1174 |
| $C_5H_8O_4$       | 5.69  | 0.93 | 132.0422 | $C_3H_6N_2O_4$    | 4.26  | 0.87 | 134.0328 | $C_{10}HN$        | 11.20 | 0.57 | 135.0109 |
| $C_5H_{10}NO_3$   | 6.06  | 0.76 | 132.0661 | $C_3H_8N_3O_3$    | 4.63  | 0.69 | 134.0566 | $C_{11}H_3$       | 11.93 | 0.65 | 135.0235 |
| $C_5H_{12}N_2O_2$ | 6.44  | 0.58 | 132.0899 | $C_3H_{10}N_4O_2$ | 5.01  | 0.51 | 134.0805 | 136               |       |      |          |
| $C_5H_{14}N_3O$   | 6.81  | 0.40 | 132.1138 | $C_4H_8NO_4$      | 4.99  | 0.90 | 134.0453 | $C_3H_8N_2O_4$    | 4.29  | 0.87 | 136.0484 |
| $C_5H_{16}N_4$    | 7.18  | 0.23 | 132.1377 | $C_4H_{10}N_2O_3$ | 5.36  | 0.72 | 134.0692 | $C_3H_{10}N_3O_3$ | 4.66  | 0.69 | 136.0723 |
| $C_5N_4O$         | 6.97  | 0.41 | 132.0073 | $C_4H_{12}N_3O_2$ | 5.74  | 0.54 | 134.0930 | $C_3H_{12}N_4O_2$ | 5.04  | 0.51 | 136.0961 |
| $C_6H_{12}O_3$    | 6.79  | 0.80 | 132.0786 | $C_4H_{14}N_4O$   | 6.11  | 0.36 | 134.1169 | $C_4H_{10}NO_4$   | 5.02  | 0.90 | 136.0610 |
| $C_6H_{14}NO_2$   | 7.17  | 0.62 | 132.1025 | $C_5H_{10}O_4$    | 5.72  | 0.94 | 134.0579 | $C_4H_{12}N_2O_3$ | 5.39  | 0.72 | 136.0848 |
| $C_6H_{16}N_2O$   | 7.54  | 0.45 | 132.1264 | $C_5H_{12}NO_3$   | 6.09  | 0.76 | 134.0817 | $C_4N_4O_2$       | 5.93  | 0.55 | 136.0022 |
| $C_6N_2O_2$       | 7.32  | 0.63 | 131.9960 | $C_5H_{14}N_2O_2$ | 6.47  | 0.58 | 134.1056 | $C_5H_{12}O_4$    | 5.75  | 0.94 | 136.0735 |
| $C_6H_2N_3O$      | 7.70  | 0.46 | 132.0198 | $C_5N_3O_2$       | 6.63  | 0.59 | 133.9991 | $C_5N_2O_3$       | 6.28  | 0.77 | 135.9909 |
| $C_6H_4N_4$       | 8.07  | 0.29 | 132.0437 | $C_5H_2N_4O$      | 7.00  | 0.41 | 134.0229 | $C_5H_2N_3O_2$    | 6.66  | 0.59 | 136.0147 |
| $C_7H_{16}O_2$    | 7.90  | 0.67 | 132.1151 | $C_6H_{14}O_3$    | 6.82  | 0.80 | 134.0943 | $C_5H_4N_4O$      | 7.03  | 0.42 | 136.0386 |
| $C_7O_3$          | 7.68  | 0.86 | 131.9847 | $C_6NO_3$         | 6.98  | 0.81 | 133.9878 | $C_6O_4$          | 6.64  | 0.99 | 135.9796 |
| $C_7H_2NO_2$      | 8.06  | 0.68 | 132.0085 | $C_6H_2N_2O_2$    | 7.36  | 0.64 | 134.0116 | $C_6H_2NO_3$      | 7.01  | 0.81 | 136.0034 |
| $C_7H_4N_2O$      | 8.43  | 0.51 | 132.0324 | $C_6H_4N_3O$      | 7.73  | 0.46 | 134.0355 | $C_6H_4N_2O_2$    | 7.39  | 0.64 | 136.0273 |
| $C_7H_6N_3$       | 8.80  | 0.34 | 132.0563 | $C_6H_6N_4$       | 8.11  | 0.29 | 134.0594 | $C_6H_6N_3O$      | 7.76  | 0.46 | 136.0511 |
| $C_8H_4O_2$       | 8.79  | 0.74 | 132.0211 | $C_7H_2O_3$       | 7.71  | 0.86 | 134.0003 | $C_6H_8N_4$       | 8.14  | 0.29 | 136.0750 |
| $C_8H_6NO$        | 9.16  | 0.57 | 132.0449 | $C_7H_4NO_2$      | 8.09  | 0.69 | 134.0242 | $C_7H_4O_3$       | 7.75  | 0.86 | 136.0160 |
| $C_8H_8N_2$       | 9.54  | 0.41 | 132.0688 | $C_7H_6N_2O$      | 8.46  | 0.52 | 134.0480 | $C_7H_6NO_2$      | 8.12  | 0.69 | 136.0399 |
| $C_9H_8O$         | 9.89  | 0.64 | 132.0575 | $C_7H_8N_3$       | 8.84  | 0.35 | 134.0719 | $C_7H_8N_2O$      | 8.49  | 0.52 | 136.0637 |
| $C_9H_{10}N$      | 10.27 | 0.47 | 132.0814 | $C_8H_6O_2$       | 8.82  | 0.74 | 134.0368 | $C_7H_{10}N_3$    | 8.87  | 0.35 | 136.0876 |
| $C_{10}H_{12}$    | 11.00 | 0.55 | 132.0939 | $C_8H_8NO$        | 9.19  | 0.58 | 134.0606 | $C_8H_8O_2$       | 8.85  | 0.75 | 136.0524 |
| $C_{11}$          | 11.89 | 0.64 | 132.0000 | $C_8H_{10}N_2$    | 9.57  | 0.41 | 134.0845 | $C_8H_{10}NO$     | 9.23  | 0.58 | 136.0763 |
| 133               |       |      |          | $C_9H_{10}O$      | 9.92  | 0.64 | 134.0732 | $C_8H_{12}N_2$    | 9.60  | 0.41 | 136.1001 |
| $C_3H_5N_2O_4$    | 4.24  | 0.87 | 133.0249 | $C_9H_{12}N$      | 10.30 | 0.48 | 134.0970 | $C_9H_{12}O$      | 9.96  | 0.64 | 136.0888 |
| $C_3H_7N_3O_3$    | 4.62  | 0.69 | 133.0488 | $C_{10}H_{14}$    | 11.03 | 0.55 | 134.1096 | $C_9H_{14}N$      | 10.33 | 0.48 | 136.1127 |
| $C_3H_9N_4O_2$    | 4.99  | 0.50 | 133.0726 | $C_{10}N$         | 11.19 | 0.57 | 134.0031 | $C_9N_2$          | 10.49 | 0.50 | 136.0062 |
| $C_4H_7NO_4$      | 4.97  | 0.90 | 133.0375 | $C_{11}H_2$       | 11.92 | 0.65 | 134.0157 | $C_{10}H_{16}$    | 11.06 | 0.55 | 136.1253 |
| $C_4H_9N_2O_3$    | 5.35  | 0.72 | 133.0614 | 135               |       |      |          | $C_{10}O$         | 10.85 | 0.73 | 135.9949 |
| $C_4H_{11}N_3O_2$ | 5.72  | 0.54 | 133.0852 | $C_3H_7N_2O_4$    | 4.27  | 0.87 | 135.0406 | $C_{10}H_2N$      | 11.22 | 0.57 | 136.0187 |
| $C_4H_{13}N_4O$   | 6.10  | 0.36 | 133.1091 | $C_3H_9N_3O_3$    | 4.65  | 0.69 | 135.0644 | $C_{11}H_4$       | 11.95 | 0.65 | 136.0313 |
| $C_5H_9O_4$       | 5.70  | 0.94 | 133.0501 | $C_3H_{11}N_4O_2$ | 5.02  | 0.51 | 135.0883 | 137               |       |      |          |
| $C_5H_{11}NO_3$   | 6.08  | 0.76 | 133.0739 | $C_4H_9NO_4$      | 5.00  | 0.90 | 135.0532 | $C_3H_9N_2O_4$    | 4.31  | 0.88 | 137.0563 |
| $C_5H_{13}N_2O_2$ | 6.45  | 0.58 | 133.0978 | $C_4H_{11}N_2O_3$ | 5.38  | 0.72 | 135.0770 | $C_3H_{11}N_3O_3$ | 4.68  | 0.69 | 137.0801 |
| $C_5H_{15}N_3O$   | 6.83  | 0.40 | 133.1216 | $C_4H_{13}N_3O_2$ | 5.75  | 0.54 | 135.1009 | $C_4H_{11}NO_4$   | 5.04  | 0.90 | 137.0688 |
| $C_5HN_4O$        | 6.98  | 0.41 | 133.0151 | $C_5H_{11}O_4$    | 5.74  | 0.94 | 135.0657 | $C_4HN_4O_2$      | 5.94  | 0.55 | 137.0100 |
| $C_6H_{13}O_3$    | 6.81  | 0.80 | 133.0865 | $C_5H_{13}NO_3$   | 6.11  | 0.76 | 135.0896 | $C_5HN_2O_3$      | 6.30  | 0.77 | 136.9987 |

|  | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|--|-------|------|----------|---|-------|------|----------|--|-------|------|----------|
| C <sub>5</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>  | 6.67  | 0.59 | 137.0226 | C <sub>5</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub> | 6.33  | 0.77 | 139.0144 | C <sub>10</sub> H <sub>4</sub> O                             | 10.91 | 0.74 | 140.0262 |
| C <sub>5</sub> H <sub>5</sub> N <sub>4</sub> O               | 7.05  | 0.42 | 137.0464 | C <sub>5</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub> | 6.71  | 0.59 | 139.0382 | C <sub>10</sub> H <sub>6</sub> N                             | 11.28 | 0.58 | 140.0501 |
| C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>                | 6.66  | 0.99 | 136.9874 | C <sub>5</sub> H <sub>7</sub> N <sub>4</sub> O              | 7.08  | 0.42 | 139.0621 | C <sub>11</sub> H <sub>8</sub>                               | 12.01 | 0.66 | 140.0626 |
| C <sub>6</sub> H <sub>3</sub> NO <sub>3</sub>                | 7.03  | 0.81 | 137.0113 | C <sub>6</sub> H <sub>3</sub> O <sub>4</sub>                | 6.69  | 0.99 | 139.0031 | 141  |       |      |          |
| C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>  | 7.40  | 0.64 | 137.0351 | C <sub>6</sub> H <sub>5</sub> NO <sub>3</sub>               | 7.06  | 0.82 | 139.0269 | C <sub>4</sub> HN <sub>2</sub> O <sub>4</sub>                | 5.26  | 0.92 | 140.9936 |
| C <sub>6</sub> H <sub>7</sub> N <sub>3</sub> O               | 7.78  | 0.47 | 137.0590 | C <sub>6</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> | 7.44  | 0.64 | 139.0508 | C <sub>4</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>  | 5.63  | 0.73 | 141.0175 |
| C <sub>6</sub> H <sub>9</sub> N <sub>4</sub>                 | 8.15  | 0.29 | 137.0829 | C <sub>6</sub> H <sub>9</sub> N <sub>3</sub> O              | 7.81  | 0.47 | 139.0746 | C <sub>4</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>  | 6.01  | 0.56 | 141.0413 |
| C <sub>7</sub> H <sub>5</sub> O <sub>3</sub>                 | 7.76  | 0.86 | 137.0238 | C <sub>6</sub> H <sub>11</sub> N <sub>4</sub>               | 8.19  | 0.30 | 139.0985 | C <sub>5</sub> H <sub>3</sub> NO <sub>4</sub>                | 5.99  | 0.95 | 141.0062 |
| C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>                | 8.14  | 0.69 | 137.0477 | C <sub>7</sub> H <sub>7</sub> O <sub>3</sub>                | 7.79  | 0.86 | 139.0395 | C <sub>5</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>  | 6.36  | 0.77 | 141.0300 |
| C <sub>7</sub> H <sub>9</sub> N <sub>2</sub> O               | 8.51  | 0.52 | 137.0715 | C <sub>7</sub> H <sub>9</sub> NO <sub>2</sub>               | 8.17  | 0.69 | 139.0634 | C <sub>5</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>  | 6.74  | 0.60 | 141.0539 |
| C <sub>7</sub> H <sub>11</sub> N <sub>3</sub>                | 8.88  | 0.35 | 137.0954 | C <sub>7</sub> H <sub>11</sub> N <sub>2</sub> O             | 8.54  | 0.52 | 139.0872 | C <sub>5</sub> H <sub>9</sub> N <sub>4</sub> O               | 7.11  | 0.42 | 141.0777 |
| C <sub>8</sub> H <sub>9</sub> O <sub>2</sub>                 | 8.87  | 0.75 | 137.0603 | C <sub>7</sub> H <sub>13</sub> N <sub>3</sub>               | 8.92  | 0.35 | 139.1111 | C <sub>6</sub> H <sub>5</sub> O <sub>4</sub>                 | 6.72  | 0.99 | 141.0187 |
| C <sub>8</sub> H <sub>11</sub> NO                            | 9.24  | 0.58 | 137.0841 | C <sub>8</sub> H <sub>11</sub> O <sub>2</sub>               | 8.90  | 0.75 | 139.0759 | C <sub>6</sub> H <sub>7</sub> NO <sub>3</sub>                | 7.09  | 0.82 | 141.0426 |
| C <sub>8</sub> H <sub>13</sub> N <sub>2</sub>                | 9.62  | 0.41 | 137.1080 | C <sub>8</sub> H <sub>13</sub> NO                           | 9.27  | 0.58 | 139.0998 | C <sub>6</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 7.47  | 0.64 | 141.0664 |
| C <sub>9</sub> H <sub>13</sub> O                             | 9.97  | 0.65 | 137.0967 | C <sub>8</sub> H <sub>15</sub> N <sub>2</sub>               | 9.65  | 0.42 | 139.1236 | C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> O              | 7.84  | 0.47 | 141.0903 |
| C <sub>9</sub> H <sub>15</sub> N                             | 10.35 | 0.48 | 137.1205 | C <sub>8</sub> HN <sub>3</sub>                              | 9.81  | 0.43 | 139.0171 | C <sub>6</sub> H <sub>13</sub> N <sub>4</sub>                | 8.22  | 0.30 | 141.1142 |
| C <sub>9</sub> HN <sub>2</sub>                               | 10.50 | 0.50 | 137.0140 | C <sub>9</sub> H <sub>15</sub> O                            | 10.00 | 0.65 | 139.1123 | C <sub>7</sub> H <sub>9</sub> O <sub>3</sub>                 | 7.83  | 0.87 | 141.0552 |
| C <sub>10</sub> H <sub>17</sub>                              | 11.08 | 0.56 | 137.1331 | C <sub>9</sub> H <sub>17</sub> N                            | 10.38 | 0.49 | 139.1362 | C <sub>7</sub> H <sub>11</sub> NO <sub>2</sub>               | 8.20  | 0.70 | 141.0790 |
| C <sub>10</sub> H <sub>10</sub>                              | 10.86 | 0.73 | 137.0027 | C <sub>9</sub> HN <sub>10</sub>                             | 10.16 | 0.66 | 139.0058 | C <sub>7</sub> H <sub>13</sub> N <sub>2</sub> O              | 8.57  | 0.53 | 141.1029 |
| C <sub>10</sub> H <sub>3</sub> N                             | 11.24 | 0.57 | 137.0266 | C <sub>9</sub> H <sub>3</sub> N <sub>2</sub>                | 10.54 | 0.50 | 139.0297 | C <sub>7</sub> H <sub>15</sub> N <sub>3</sub>                | 8.95  | 0.36 | 141.1267 |
| C <sub>11</sub> H <sub>5</sub>                               | 11.97 | 0.65 | 137.0391 | C <sub>10</sub> H <sub>19</sub>                             | 11.11 | 0.56 | 139.1488 | C <sub>7</sub> HN <sub>4</sub>                               | 9.11  | 0.37 | 141.0202 |
| 138  |       |      |          | C <sub>10</sub> H <sub>3</sub> O                            | 10.89 | 0.74 | 139.0184 | C <sub>8</sub> H <sub>13</sub> O <sub>2</sub>                | 8.93  | 0.75 | 141.0916 |
| C <sub>3</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> | 4.32  | 0.88 | 138.0641 | C <sub>10</sub> H <sub>5</sub> N                            | 11.27 | 0.58 | 139.0422 | C <sub>8</sub> H <sub>15</sub> NO                            | 9.31  | 0.59 | 141.1154 |
| C <sub>4</sub> N <sub>3</sub> O <sub>3</sub>                 | 5.58  | 0.73 | 137.9940 | C <sub>11</sub> H <sub>7</sub>                              | 12.00 | 0.66 | 139.0548 | C <sub>8</sub> H <sub>17</sub> N <sub>2</sub>                | 9.68  | 0.42 | 141.1393 |
| C <sub>4</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>  | 5.96  | 0.55 | 138.0178 | 140   |       |      |          | C <sub>8</sub> HN <sub>2</sub> O                             | 9.46  | 0.60 | 141.0089 |
| C <sub>5</sub> NO <sub>4</sub>                               | 5.94  | 0.95 | 137.9827 | C <sub>4</sub> N <sub>2</sub> O <sub>4</sub>                | 5.24  | 0.91 | 139.9858 | C <sub>8</sub> H <sub>3</sub> N <sub>3</sub>                 | 9.84  | 0.43 | 141.0328 |
| C <sub>5</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>  | 6.32  | 0.77 | 138.0065 | C <sub>4</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub> | 5.62  | 0.73 | 140.0096 | C <sub>9</sub> H <sub>17</sub> O                             | 10.04 | 0.65 | 141.1280 |
| C <sub>5</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>  | 6.69  | 0.59 | 138.0304 | C <sub>4</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub> | 5.99  | 0.55 | 140.0335 | C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>                | 9.82  | 0.83 | 140.9976 |
| C <sub>5</sub> H <sub>6</sub> N <sub>4</sub> O               | 7.06  | 0.42 | 138.0542 | C <sub>5</sub> H <sub>2</sub> NO <sub>4</sub>               | 5.97  | 0.95 | 139.9983 | C <sub>9</sub> H <sub>19</sub> N                             | 10.41 | 0.49 | 141.1519 |
| C <sub>6</sub> H <sub>2</sub> O <sub>4</sub>                 | 6.67  | 0.99 | 137.9953 | C <sub>5</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub> | 6.35  | 0.77 | 140.0222 | C <sub>9</sub> H <sub>3</sub> NO                             | 10.19 | 0.67 | 141.0215 |
| C <sub>6</sub> H <sub>4</sub> NO <sub>3</sub>                | 7.05  | 0.81 | 138.0191 | C <sub>5</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub> | 6.72  | 0.60 | 140.0460 | C <sub>9</sub> H <sub>5</sub> N <sub>2</sub>                 | 10.57 | 0.50 | 141.0453 |
| C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 7.42  | 0.64 | 138.0429 | C <sub>5</sub> H <sub>8</sub> N <sub>4</sub> O              | 7.10  | 0.42 | 140.0699 | C <sub>10</sub> H <sub>21</sub>                              | 11.14 | 0.56 | 141.1644 |
| C <sub>6</sub> H <sub>8</sub> N <sub>3</sub> O               | 7.80  | 0.47 | 138.0668 | C <sub>6</sub> H <sub>4</sub> O <sub>4</sub>                | 6.70  | 0.99 | 140.0109 | C <sub>10</sub> H <sub>5</sub> O                             | 10.93 | 0.74 | 141.0340 |
| C <sub>6</sub> H <sub>10</sub> N <sub>4</sub>                | 8.17  | 0.30 | 138.0907 | C <sub>6</sub> H <sub>6</sub> NO <sub>3</sub>               | 7.08  | 0.82 | 140.0348 | C <sub>10</sub> H <sub>7</sub> N                             | 11.30 | 0.58 | 141.0579 |
| C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>                 | 7.78  | 0.86 | 138.0317 | C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> | 7.45  | 0.64 | 140.0586 | C <sub>11</sub> H <sub>9</sub>                               | 12.03 | 0.66 | 141.0705 |
| C <sub>7</sub> H <sub>8</sub> NO <sub>2</sub>                | 8.15  | 0.69 | 138.0555 | C <sub>6</sub> H <sub>10</sub> N <sub>3</sub> O             | 7.83  | 0.47 | 140.0825 | 142  |       |      |          |
| C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O              | 8.53  | 0.52 | 138.0794 | C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>               | 8.20  | 0.30 | 140.1063 | C <sub>4</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 5.27  | 0.92 | 142.0014 |
| C <sub>7</sub> H <sub>12</sub> N <sub>3</sub>                | 8.90  | 0.35 | 138.1032 | C <sub>7</sub> H <sub>8</sub> O <sub>3</sub>                | 7.81  | 0.87 | 140.0473 | C <sub>4</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>  | 5.65  | 0.74 | 142.0253 |
| C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>                | 8.88  | 0.75 | 138.0681 | C <sub>7</sub> H <sub>10</sub> NO <sub>2</sub>              | 8.18  | 0.69 | 140.0712 | C <sub>4</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 6.02  | 0.56 | 142.0491 |
| C <sub>8</sub> H <sub>12</sub> NO                            | 9.26  | 0.58 | 138.0919 | C <sub>7</sub> H <sub>12</sub> N <sub>2</sub> O             | 8.56  | 0.52 | 140.0950 | C <sub>5</sub> H <sub>4</sub> NO <sub>4</sub>                | 6.00  | 0.95 | 142.0140 |
| C <sub>8</sub> H <sub>14</sub> N <sub>2</sub>                | 9.63  | 0.42 | 138.1158 | C <sub>7</sub> H <sub>14</sub> N <sub>3</sub>               | 8.93  | 0.36 | 140.1189 | C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 6.38  | 0.77 | 142.0379 |
| C <sub>8</sub> N <sub>3</sub>                                | 9.79  | 0.43 | 138.0093 | C <sub>7</sub> N <sub>4</sub>                               | 9.09  | 0.37 | 140.0124 | C <sub>5</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 6.75  | 0.60 | 142.0617 |
| C <sub>9</sub> H <sub>14</sub> O                             | 9.99  | 0.65 | 138.1045 | C <sub>8</sub> H <sub>12</sub> O <sub>2</sub>               | 8.92  | 0.75 | 140.0837 | C <sub>5</sub> H <sub>10</sub> N <sub>4</sub> O              | 7.13  | 0.42 | 142.0856 |
| C <sub>9</sub> H <sub>16</sub> N                             | 10.36 | 0.48 | 138.1284 | C <sub>8</sub> H <sub>14</sub> NO                           | 9.29  | 0.58 | 140.1076 | C <sub>6</sub> H <sub>6</sub> O <sub>4</sub>                 | 6.74  | 0.99 | 142.0266 |
| C <sub>9</sub> NO  | 10.15 | 0.66 | 137.9980 | C <sub>8</sub> H <sub>16</sub> N <sub>2</sub>               | 9.66  | 0.42 | 140.1315 | C <sub>6</sub> H <sub>8</sub> NO <sub>3</sub>                | 7.11  | 0.82 | 142.0504 |
| C <sub>9</sub> H <sub>2</sub> N <sub>2</sub>                 | 10.52 | 0.50 | 138.0218 | C <sub>8</sub> N <sub>2</sub> O                             | 9.45  | 0.60 | 140.0011 | C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 7.48  | 0.64 | 142.0743 |
| C <sub>10</sub> H <sub>18</sub>                              | 11.09 | 0.56 | 138.1409 | C <sub>8</sub> H <sub>2</sub> N <sub>3</sub>                | 9.82  | 0.43 | 140.0249 | C <sub>6</sub> H <sub>12</sub> N <sub>3</sub> O              | 7.86  | 0.47 | 142.0981 |
| C <sub>10</sub> H <sub>2</sub> O                             | 10.88 | 0.73 | 138.0106 | C <sub>9</sub> H <sub>16</sub> O                            | 10.02 | 0.65 | 140.1202 | C <sub>6</sub> H <sub>14</sub> N <sub>4</sub>                | 8.23  | 0.30 | 142.1220 |
| C <sub>10</sub> H <sub>4</sub> N                             | 11.25 | 0.57 | 138.0344 | C <sub>9</sub> O <sub>2</sub>                               | 9.80  | 0.83 | 139.9898 | C <sub>7</sub> H <sub>10</sub> O <sub>3</sub>                | 7.84  | 0.87 | 142.0630 |
| C <sub>11</sub> H <sub>6</sub>                               | 11.98 | 0.65 | 138.0470 | C <sub>9</sub> H <sub>18</sub> N                            | 10.39 | 0.49 | 140.1440 | C <sub>7</sub> H <sub>12</sub> NO <sub>2</sub>               | 8.22  | 0.70 | 142.0868 |
| 139  |       |      |          | C <sub>9</sub> H <sub>2</sub> NO                            | 10.18 | 0.67 | 140.0136 | C <sub>7</sub> H <sub>14</sub> N <sub>2</sub> O              | 8.59  | 0.53 | 142.1107 |
| C <sub>4</sub> HN <sub>3</sub> O <sub>3</sub>                | 5.60  | 0.73 | 139.0018 | C <sub>9</sub> H <sub>4</sub> N <sub>2</sub>                | 10.55 | 0.50 | 140.0375 | C <sub>7</sub> H <sub>16</sub> N <sub>3</sub>                | 8.96  | 0.36 | 142.1346 |
| C <sub>4</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>  | 5.97  | 0.55 | 139.0257 | C <sub>10</sub> H <sub>20</sub>                             | 11.13 | 0.56 | 140.1566 | C <sub>7</sub> N <sub>3</sub> O                              | 8.75  | 0.54 | 142.0042 |
| C <sub>5</sub> HN <sub>10</sub> O <sub>4</sub>               | 5.96  | 0.95 | 138.9905 |   |       |      |          | C <sub>7</sub> H <sub>2</sub> N <sub>4</sub>                 | 9.12  | 0.37 | 142.0280 |



|                   | M+1   | M+2  | MW       |                   | M+1   | M+2  | MW       |                   | M+1   | M+2  | MW       |
|-------------------|-------|------|----------|-------------------|-------|------|----------|-------------------|-------|------|----------|
| $C_8H_{14}O_2$    | 8.95  | 0.75 | 142.0994 | $C_5H_{10}N_3O_2$ | 6.79  | 0.60 | 144.0774 | $C_8H_{19}NO$     | 9.37  | 0.59 | 145.1467 |
| $C_8H_{16}NO$     | 9.32  | 0.59 | 142.1233 | $C_5H_{12}N_4O$   | 7.16  | 0.42 | 144.1012 | $C_8H_3NO_2$      | 9.15  | 0.77 | 145.0164 |
| $C_8NO_2$         | 9.10  | 0.77 | 141.9929 | $C_6H_8O_4$       | 6.77  | 1.00 | 144.0422 | $C_8H_5N_2O$      | 9.53  | 0.61 | 145.0402 |
| $C_8H_{18}N_2$    | 9.70  | 0.42 | 142.1471 | $C_6H_{10}NO_3$   | 7.14  | 0.82 | 144.0661 | $C_8H_7N_3$       | 9.90  | 0.44 | 145.0641 |
| $C_8H_2N_2O$      | 9.48  | 0.60 | 142.0167 | $C_6H_{12}N_2O_2$ | 7.52  | 0.65 | 144.0899 | $C_9H_5O_2$       | 9.88  | 0.84 | 145.0289 |
| $C_8H_4N_3$       | 9.85  | 0.44 | 142.0406 | $C_6H_{14}N_3O$   | 7.89  | 0.47 | 144.1138 | $C_9H_7NO$        | 10.26 | 0.67 | 145.0528 |
| $C_9H_{18}O$      | 10.05 | 0.65 | 142.1358 | $C_6H_{16}N_4$    | 8.27  | 0.30 | 144.1377 | $C_9H_9N_2$       | 10.63 | 0.51 | 145.0767 |
| $C_9H_2O_2$       | 9.84  | 0.83 | 142.0054 | $C_6N_4O$         | 8.05  | 0.49 | 144.0073 | $C_{10}H_9O$      | 10.99 | 0.75 | 145.0653 |
| $C_9H_{20}N$      | 10.43 | 0.49 | 142.1597 | $C_7H_{12}O_3$    | 7.87  | 0.87 | 144.0786 | $C_{10}H_{11}N$   | 11.36 | 0.59 | 145.0892 |
| $C_9H_4NO$        | 10.21 | 0.67 | 142.0293 | $C_7H_{14}NO_2$   | 8.25  | 0.70 | 144.1025 | $C_{11}H_{13}$    | 12.09 | 0.67 | 145.1018 |
| $C_9H_6N_2$       | 10.58 | 0.51 | 142.0532 | $C_7H_{16}N_2O$   | 8.62  | 0.53 | 144.1264 | $C_{12}H$         | 12.98 | 0.77 | 145.0078 |
| $C_{10}H_{22}$    | 11.16 | 0.56 | 142.1722 | $C_7N_2O_2$       | 8.41  | 0.71 | 143.9960 | $C_4H_6N_2O_4$    | 5.34  | 0.92 | 146.0328 |
| $C_{10}H_6O$      | 10.94 | 0.74 | 142.0419 | $C_7H_{18}N_3$    | 9.00  | 0.36 | 144.1502 | $C_4H_8N_3O_3$    | 5.71  | 0.74 | 146.0566 |
| $C_{10}H_8N$      | 11.32 | 0.58 | 142.0657 | $C_7H_2N_3O$      | 8.78  | 0.54 | 144.0198 | $C_4H_{10}N_4O_2$ | 6.09  | 0.56 | 146.0805 |
| $C_{11}H_{10}$    | 12.05 | 0.66 | 142.0783 | $C_7H_4N_4$       | 9.15  | 0.38 | 144.0437 | $C_5H_8NO_4$      | 6.07  | 0.96 | 146.0453 |
| $C_4H_3N_2O_4$    | 5.29  | 0.92 | 143.0093 | $C_8H_{16}O_2$    | 8.98  | 0.76 | 144.1151 | $C_5H_{10}N_2O_3$ | 6.44  | 0.78 | 146.0692 |
| $C_4H_5N_3O_3$    | 5.66  | 0.74 | 143.0331 | $C_8O_3$          | 8.76  | 0.94 | 143.9847 | $C_5H_{12}N_3O_2$ | 6.82  | 0.60 | 146.0930 |
| $C_4H_7N_4O_2$    | 6.04  | 0.56 | 143.0570 | $C_8H_{18}NO$     | 9.35  | 0.59 | 144.1389 | $C_5H_{14}N_4O$   | 7.19  | 0.43 | 146.1169 |
| $C_5H_5NO_4$      | 6.02  | 0.95 | 143.0218 | $C_8H_2NO_2$      | 9.14  | 0.77 | 144.0085 | $C_6H_{10}O_4$    | 6.80  | 1.00 | 146.0579 |
| $C_5H_7N_2O_3$    | 6.40  | 0.78 | 143.0457 | $C_8H_{20}N_2$    | 9.73  | 0.42 | 144.1628 | $C_6H_{12}NO_3$   | 7.17  | 0.82 | 146.0817 |
| $C_5H_9N_3O_2$    | 6.77  | 0.60 | 143.0695 | $C_8H_4N_2O$      | 9.51  | 0.60 | 144.0324 | $C_6H_{14}N_2O_2$ | 7.55  | 0.65 | 146.1056 |
| $C_5H_{11}N_4O$   | 7.14  | 0.42 | 143.0934 | $C_8H_6N_3$       | 9.89  | 0.44 | 144.0563 | $C_6H_{16}N_3O$   | 7.92  | 0.48 | 146.1295 |
| $C_6H_7O_4$       | 6.75  | 0.99 | 143.0344 | $C_9H_{20}O$      | 10.08 | 0.66 | 144.1515 | $C_6N_3O_2$       | 7.71  | 0.66 | 145.9991 |
| $C_6H_9NO_3$      | 7.13  | 0.82 | 143.0583 | $C_9H_4O_2$       | 9.87  | 0.84 | 144.0211 | $C_6H_{18}N_4$    | 8.30  | 0.31 | 146.1533 |
| $C_6H_{11}N_2O_2$ | 7.50  | 0.65 | 143.0821 | $C_9H_6NO$        | 10.24 | 0.67 | 144.0449 | $C_6H_2N_4O$      | 8.08  | 0.49 | 146.0229 |
| $C_6H_{13}N_3O$   | 7.88  | 0.47 | 143.1060 | $C_9H_8N_2$       | 10.62 | 0.51 | 144.0688 | $C_7H_{14}O_3$    | 7.91  | 0.87 | 146.0943 |
| $C_6H_{15}N_4$    | 8.25  | 0.30 | 143.1298 | $C_{10}H_8O$      | 10.97 | 0.74 | 144.0575 | $C_7H_{16}NO_2$   | 8.28  | 0.70 | 146.1182 |
| $C_7H_{11}O_3$    | 7.86  | 0.87 | 143.0708 | $C_{10}H_{10}N$   | 11.35 | 0.58 | 144.0814 | $C_7NO_3$         | 8.06  | 0.88 | 145.9878 |
| $C_7H_{13}NO_2$   | 8.23  | 0.70 | 143.0947 | $C_{11}H_{12}$    | 12.08 | 0.67 | 144.0939 | $C_7H_{18}N_2O$   | 8.65  | 0.53 | 146.1420 |
| $C_7H_{15}N_2O$   | 8.61  | 0.53 | 143.1185 | $C_{12}$          | 12.97 | 0.77 | 144.0000 | $C_7H_2N_2O_2$    | 8.44  | 0.71 | 146.0116 |
| $C_7H_{17}N_3$    | 8.98  | 0.36 | 143.1424 | $C_4H_5N_2O_4$    | 5.32  | 0.92 | 145.0249 | $C_7H_4N_3O$      | 8.81  | 0.55 | 146.0355 |
| $C_7HN_3O$        | 8.76  | 0.54 | 143.0120 | $C_4H_7N_3O_3$    | 5.70  | 0.74 | 145.0488 | $C_7H_6N_4$       | 9.19  | 0.38 | 146.0594 |
| $C_7H_3N_4$       | 9.14  | 0.37 | 143.0359 | $C_4H_9N_4O_2$    | 6.07  | 0.56 | 145.0726 | $C_8H_{18}O_2$    | 9.01  | 0.76 | 146.1307 |
| $C_8H_{15}O_2$    | 8.96  | 0.76 | 143.1072 | $C_5H_7NO_4$      | 6.05  | 0.96 | 145.0375 | $C_8H_2O_3$       | 8.79  | 0.94 | 146.0003 |
| $C_8H_{17}NO$     | 9.34  | 0.59 | 143.1311 | $C_5H_9N_2O_3$    | 6.43  | 0.78 | 145.0614 | $C_8H_4NO_2$      | 9.17  | 0.77 | 146.0242 |
| $C_8HNO_2$        | 9.12  | 0.77 | 143.0007 | $C_5H_{11}N_3O_2$ | 6.80  | 0.60 | 145.0852 | $C_8H_5N_2O$      | 9.54  | 0.61 | 146.0480 |
| $C_8H_{19}N_2$    | 9.71  | 0.42 | 143.1549 | $C_5H_{13}N_4O$   | 7.18  | 0.43 | 145.1091 | $C_8H_8N_3$       | 9.92  | 0.44 | 146.0719 |
| $C_8H_3N_2O$      | 9.49  | 0.60 | 143.0246 | $C_6H_9O_4$       | 6.78  | 1.00 | 145.0501 | $C_9H_6O_2$       | 9.90  | 0.84 | 146.0368 |
| $C_8H_5N_3$       | 9.87  | 0.44 | 143.0484 | $C_6H_{11}NO_3$   | 7.16  | 0.82 | 145.0739 | $C_9H_8NO$        | 10.27 | 0.67 | 146.0606 |
| $C_9H_{19}O$      | 10.07 | 0.65 | 143.1436 | $C_6H_{13}N_2O_2$ | 7.53  | 0.65 | 145.0978 | $C_9H_{10}N_2$    | 10.65 | 0.51 | 146.0845 |
| $C_9H_3O_2$       | 9.85  | 0.83 | 143.0133 | $C_6H_{15}N_3O$   | 7.91  | 0.48 | 145.1216 | $C_{10}H_{10}O$   | 11.01 | 0.75 | 146.0732 |
| $C_9H_{21}N$      | 10.44 | 0.49 | 143.1675 | $C_6H_{17}N_4$    | 8.28  | 0.30 | 145.1455 | $C_{10}H_{12}N$   | 11.38 | 0.59 | 146.0970 |
| $C_9H_5NO$        | 10.23 | 0.67 | 143.0371 | $C_6HN_4O$        | 8.06  | 0.49 | 145.0151 | $C_{11}H_{14}$    | 12.11 | 0.67 | 146.1096 |
| $C_9H_7N_2$       | 10.60 | 0.51 | 143.0610 | $C_7H_{13}O_3$    | 7.89  | 0.87 | 145.0865 | $C_{11}N$         | 12.27 | 0.69 | 146.0031 |
| $C_{10}H_7O$      | 10.96 | 0.74 | 143.0497 | $C_7H_{15}NO_2$   | 8.26  | 0.70 | 145.1103 | $C_{12}H_2$       | 13.00 | 0.77 | 146.0157 |
| $C_{10}H_9N$      | 11.33 | 0.58 | 143.0736 | $C_7H_{17}N_2O$   | 8.64  | 0.53 | 145.1342 | $C_4H_7N_2O_4$    | 5.35  | 0.92 | 147.0406 |
| $C_{11}H_{11}$    | 12.06 | 0.66 | 143.0861 | $C_7HN_2O_2$      | 8.42  | 0.71 | 145.0038 | $C_4H_9N_3O_3$    | 5.73  | 0.74 | 147.0644 |
| $C_4H_4N_2O_4$    | 5.31  | 0.92 | 144.0171 | $C_7H_{19}N_3$    | 9.01  | 0.36 | 145.1580 | $C_4H_{11}N_4O_2$ | 6.10  | 0.56 | 147.0883 |
| $C_4H_6N_3O_3$    | 5.68  | 0.74 | 144.0410 | $C_7H_3N_3O$      | 8.80  | 0.54 | 145.0277 | $C_5H_9NO_4$      | 6.08  | 0.96 | 147.0532 |
| $C_4H_8N_4O_2$    | 6.05  | 0.56 | 144.0648 | $C_7H_5N_4$       | 9.17  | 0.38 | 145.0515 | $C_5H_{11}N_2O_3$ | 6.46  | 0.78 | 147.0770 |
| $C_5H_6NO_4$      | 6.04  | 0.95 | 144.0297 | $C_8H_{17}O_2$    | 9.00  | 0.76 | 145.1229 | $C_5H_{13}N_3O_2$ | 6.83  | 0.60 | 147.1009 |
| $C_5H_8N_2O_3$    | 6.41  | 0.78 | 144.0535 | $C_8HO_3$         | 8.78  | 0.94 | 144.9925 | $C_5H_{15}N_4O$   | 7.21  | 0.43 | 147.1247 |



|  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|--|-------|------|----------|--|-------|------|----------|--|-------|------|----------|
| C <sub>6</sub> H <sub>11</sub> O <sub>4</sub>                | 6.82  | 1.00 | 147.0657 | C <sub>10</sub> H <sub>14</sub> N                            | 11.41 | 0.59 | 148.1127 | C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O               | 8.88  | 0.55 | 150.0668 |
| C <sub>6</sub> H <sub>13</sub> NO <sub>3</sub>               | 7.19  | 0.82 | 147.0896 | C <sub>10</sub> N <sub>2</sub>                               | 11.57 | 0.61 | 148.0062 | C <sub>7</sub> H <sub>10</sub> N <sub>4</sub>                | 9.25  | 0.38 | 150.0907 |
| C <sub>6</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> | 7.56  | 0.65 | 147.1134 | C <sub>11</sub> H <sub>16</sub>                              | 12.14 | 0.67 | 148.1253 | C <sub>8</sub> H <sub>6</sub> O <sub>3</sub>                 | 8.86  | 0.95 | 150.0317 |
| C <sub>6</sub> H <sub>17</sub> N <sub>3</sub> O              | 7.94  | 0.48 | 147.1373 | C <sub>11</sub> O  | 11.93 | 0.85 | 147.9949 | C <sub>8</sub> H <sub>8</sub> NO <sub>2</sub>                | 9.23  | 0.78 | 150.0555 |
| C <sub>6</sub> HN <sub>3</sub> O <sub>2</sub>                | 7.72  | 0.66 | 147.0069 | C <sub>11</sub> H <sub>2</sub> N                             | 12.30 | 0.69 | 148.0187 | C <sub>8</sub> H <sub>10</sub> N <sub>2</sub> O              | 9.61  | 0.61 | 150.0794 |
| C <sub>6</sub> H <sub>3</sub> N <sub>4</sub> O               | 8.10  | 0.49 | 147.0308 | C <sub>12</sub> H <sub>4</sub>                               | 13.03 | 0.78 | 148.0313 | C <sub>8</sub> H <sub>12</sub> N <sub>3</sub>                | 9.98  | 0.45 | 150.1032 |
| C <sub>7</sub> H <sub>15</sub> O <sub>3</sub>                | 7.92  | 0.87 | 147.1021 | 149  |       |      |          | C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>                | 9.96  | 0.84 | 150.0681 |
| C <sub>7</sub> H <sub>17</sub> NO <sub>2</sub>               | 8.30  | 0.70 | 147.1260 | C <sub>4</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>  | 5.39  | 0.92 | 149.0563 | C <sub>9</sub> H <sub>12</sub> NO                            | 10.34 | 0.68 | 150.0919 |
| C <sub>7</sub> HNO <sub>3</sub>                              | 8.08  | 0.89 | 146.9956 | C <sub>4</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> | 5.76  | 0.74 | 149.0801 | C <sub>9</sub> H <sub>14</sub> N <sub>2</sub>                | 10.71 | 0.52 | 150.1158 |
| C <sub>7</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 8.45  | 0.72 | 147.0195 | C <sub>4</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> | 6.13  | 0.56 | 149.1040 | C <sub>9</sub> N <sub>3</sub>                                | 10.87 | 0.54 | 150.0093 |
| C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O               | 8.83  | 0.55 | 147.0433 | C <sub>5</sub> H <sub>11</sub> NO <sub>4</sub>               | 6.12  | 0.96 | 149.0688 | C <sub>10</sub> H <sub>14</sub> O                            | 11.07 | 0.75 | 150.1045 |
| C <sub>7</sub> H <sub>7</sub> N <sub>4</sub>                 | 9.20  | 0.38 | 147.0672 | C <sub>5</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> | 6.49  | 0.78 | 149.0927 | C <sub>10</sub> H <sub>16</sub> N                            | 11.44 | 0.60 | 150.1284 |
| C <sub>8</sub> H <sub>3</sub> O <sub>3</sub>                 | 8.81  | 0.94 | 147.0082 | C <sub>5</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> | 6.87  | 0.61 | 149.1165 | C <sub>10</sub> NO   | 11.23 | 0.77 | 149.9980 |
| C <sub>8</sub> H <sub>5</sub> NO <sub>2</sub>                | 9.18  | 0.78 | 147.0320 | C <sub>5</sub> HN <sub>4</sub> O <sub>2</sub>                | 7.02  | 0.62 | 149.0100 | C <sub>10</sub> H <sub>2</sub> N <sub>2</sub>                | 11.60 | 0.61 | 150.0218 |
| C <sub>8</sub> H <sub>7</sub> N <sub>2</sub> O               | 9.56  | 0.61 | 147.0559 | C <sub>6</sub> H <sub>13</sub> O <sub>4</sub>                | 6.85  | 1.00 | 149.0814 | C <sub>11</sub> H <sub>18</sub>                              | 12.17 | 0.68 | 150.1409 |
| C <sub>8</sub> H <sub>9</sub> N <sub>3</sub>                 | 9.93  | 0.44 | 147.0798 | C <sub>6</sub> H <sub>15</sub> NO <sub>3</sub>               | 7.22  | 0.83 | 149.1052 | C <sub>11</sub> H <sub>2</sub> O                             | 11.96 | 0.85 | 150.0106 |
| C <sub>9</sub> H <sub>7</sub> O <sub>2</sub>                 | 9.92  | 0.84 | 147.0446 | C <sub>6</sub> HN <sub>2</sub> O <sub>3</sub>                | 7.38  | 0.84 | 148.9987 | C <sub>11</sub> H <sub>4</sub> N                             | 12.33 | 0.70 | 150.0344 |
| C <sub>9</sub> H <sub>9</sub> NO                             | 10.29 | 0.68 | 147.0684 | C <sub>6</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>  | 7.75  | 0.66 | 149.0226 | C <sub>12</sub> H <sub>6</sub>                               | 13.06 | 0.78 | 150.0470 |
| C <sub>9</sub> H <sub>11</sub> N <sub>2</sub>                | 10.66 | 0.51 | 147.0923 | C <sub>6</sub> H <sub>5</sub> N <sub>4</sub> O               | 8.13  | 0.49 | 149.0464 | 151  |       |      |          |
| C <sub>10</sub> H <sub>11</sub> O                            | 11.02 | 0.75 | 147.0810 | C <sub>7</sub> H <sub>9</sub> O <sub>4</sub>                 | 7.74  | 1.06 | 148.9874 | C <sub>4</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> | 5.42  | 0.92 | 151.0719 |
| C <sub>10</sub> H <sub>13</sub> N                            | 11.40 | 0.59 | 147.1049 | C <sub>7</sub> H <sub>3</sub> NO <sub>3</sub>                | 8.11  | 0.89 | 149.0113 | C <sub>4</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> | 5.79  | 0.74 | 151.0958 |
| C <sub>11</sub> H <sub>15</sub>                              | 12.13 | 0.67 | 147.1174 | C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>  | 8.49  | 0.72 | 149.0351 | C <sub>5</sub> H <sub>13</sub> NO <sub>4</sub>               | 6.15  | 0.96 | 151.0845 |
| C <sub>11</sub> HN   | 12.28 | 0.69 | 147.0109 | C <sub>7</sub> H <sub>7</sub> N <sub>3</sub> O               | 8.86  | 0.55 | 149.0590 | C <sub>5</sub> HN <sub>3</sub> O <sub>3</sub>                | 6.68  | 0.79 | 151.0018 |
| C <sub>12</sub> H <sub>3</sub>                               | 13.02 | 0.78 | 147.0235 | C <sub>7</sub> H <sub>9</sub> N <sub>4</sub>                 | 9.23  | 0.38 | 149.0829 | C <sub>5</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>  | 7.05  | 0.62 | 151.0257 |
| 148  |       |      |          | C <sub>8</sub> H <sub>5</sub> O <sub>3</sub>                 | 8.84  | 0.95 | 149.0238 | C <sub>6</sub> HNO <sub>4</sub>                              | 7.04  | 1.01 | 150.9905 |
| C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>  | 5.37  | 0.92 | 148.0484 | C <sub>8</sub> H <sub>7</sub> NO <sub>2</sub>                | 9.22  | 0.78 | 149.0477 | C <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 7.41  | 0.84 | 151.0144 |
| C <sub>4</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> | 5.74  | 0.74 | 148.0723 | C <sub>8</sub> H <sub>9</sub> N <sub>2</sub> O               | 9.59  | 0.61 | 149.0715 | C <sub>6</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>  | 7.79  | 0.67 | 151.0382 |
| C <sub>4</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> | 6.12  | 0.56 | 148.0961 | C <sub>8</sub> H <sub>11</sub> N <sub>3</sub>                | 9.97  | 0.45 | 149.0954 | C <sub>6</sub> H <sub>7</sub> N <sub>4</sub> O               | 8.16  | 0.50 | 151.0621 |
| C <sub>5</sub> H <sub>10</sub> NO <sub>4</sub>               | 6.10  | 0.96 | 148.0610 | C <sub>9</sub> H <sub>9</sub> O <sub>2</sub>                 | 9.95  | 0.84 | 149.0603 | C <sub>7</sub> H <sub>3</sub> O <sub>4</sub>                 | 7.77  | 1.06 | 151.0031 |
| C <sub>5</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> | 6.48  | 0.78 | 148.0848 | C <sub>9</sub> H <sub>11</sub> NO                            | 10.32 | 0.68 | 149.0841 | C <sub>7</sub> H <sub>5</sub> NO <sub>3</sub>                | 8.14  | 0.89 | 151.0269 |
| C <sub>5</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> | 6.85  | 0.60 | 148.1087 | C <sub>9</sub> H <sub>13</sub> N <sub>2</sub>                | 10.70 | 0.52 | 149.1080 | C <sub>7</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>  | 8.52  | 0.72 | 151.0508 |
| C <sub>5</sub> H <sub>16</sub> N <sub>4</sub> O              | 7.22  | 0.43 | 148.1325 | C <sub>10</sub> H <sub>13</sub> O                            | 11.05 | 0.75 | 149.0967 | C <sub>7</sub> H <sub>9</sub> N <sub>3</sub> O               | 8.89  | 0.55 | 151.0746 |
| C <sub>5</sub> N <sub>4</sub> O <sub>2</sub>                 | 7.01  | 0.61 | 148.0022 | C <sub>10</sub> H <sub>15</sub> N                            | 11.43 | 0.59 | 149.1205 | C <sub>7</sub> H <sub>11</sub> N <sub>4</sub>                | 9.27  | 0.39 | 151.0985 |
| C <sub>6</sub> H <sub>12</sub> O <sub>4</sub>                | 6.83  | 1.00 | 148.0735 | C <sub>10</sub> HN <sub>2</sub>                              | 11.58 | 0.61 | 149.0140 | C <sub>8</sub> H <sub>7</sub> O <sub>3</sub>                 | 8.87  | 0.95 | 151.0395 |
| C <sub>6</sub> H <sub>14</sub> NO <sub>3</sub>               | 7.21  | 0.83 | 148.0974 | C <sub>11</sub> H <sub>17</sub>                              | 12.16 | 0.67 | 149.1331 | C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub>                | 9.25  | 0.78 | 151.0634 |
| C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> | 7.58  | 0.65 | 148.1213 | C <sub>11</sub> HO   | 11.94 | 0.85 | 149.0027 | C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> O              | 9.62  | 0.62 | 151.0872 |
| C <sub>6</sub> N <sub>2</sub> O <sub>3</sub>                 | 7.36  | 0.84 | 147.9909 | C <sub>11</sub> H <sub>3</sub> N                             | 12.32 | 0.69 | 149.0266 | C <sub>8</sub> H <sub>13</sub> N <sub>3</sub>                | 10.00 | 0.45 | 151.1111 |
| C <sub>6</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>  | 7.74  | 0.66 | 148.0147 | C <sub>12</sub> H <sub>5</sub>                               | 13.05 | 0.78 | 149.0391 | C <sub>9</sub> H <sub>11</sub> O <sub>2</sub>                | 9.98  | 0.85 | 151.0759 |
| C <sub>6</sub> H <sub>4</sub> N <sub>4</sub> O               | 8.11  | 0.49 | 148.0386 | 150  |       |      |          | C <sub>9</sub> H <sub>13</sub> NO                            | 10.35 | 0.68 | 151.0998 |
| C <sub>7</sub> H <sub>16</sub> O <sub>3</sub>                | 7.94  | 0.88 | 148.1100 | C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> | 5.40  | 0.92 | 150.0641 | C <sub>9</sub> H <sub>15</sub> N <sub>2</sub>                | 10.73 | 0.52 | 151.1236 |
| C <sub>7</sub> O <sub>4</sub>                                | 7.72  | 1.06 | 147.9796 | C <sub>4</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> | 5.78  | 0.74 | 150.0879 | C <sub>9</sub> HN <sub>3</sub>                               | 10.89 | 0.54 | 151.0171 |
| C <sub>7</sub> H <sub>2</sub> NO <sub>3</sub>                | 8.09  | 0.89 | 148.0034 | C <sub>4</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> | 6.15  | 0.56 | 150.1118 | C <sub>10</sub> H <sub>15</sub> O                            | 11.09 | 0.76 | 151.1123 |
| C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>  | 8.47  | 0.72 | 148.0273 | C <sub>5</sub> H <sub>12</sub> NO <sub>4</sub>               | 6.13  | 0.96 | 150.0766 | C <sub>10</sub> H <sub>17</sub> N                            | 11.46 | 0.60 | 151.1362 |
| C <sub>7</sub> H <sub>6</sub> N <sub>3</sub> O               | 8.84  | 0.55 | 148.0511 | C <sub>5</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> | 6.51  | 0.78 | 150.1005 | C <sub>10</sub> HN <sub>2</sub>                              | 11.24 | 0.77 | 151.0058 |
| C <sub>7</sub> H <sub>8</sub> N <sub>4</sub>                 | 9.22  | 0.38 | 148.0750 | C <sub>5</sub> N <sub>3</sub> O <sub>3</sub>                 | 6.66  | 0.79 | 149.9940 | C <sub>10</sub> H <sub>3</sub> N <sub>2</sub>                | 11.62 | 0.61 | 151.0297 |
| C <sub>8</sub> H <sub>4</sub> O <sub>3</sub>                 | 8.83  | 0.94 | 148.0160 | C <sub>5</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>  | 7.04  | 0.62 | 150.0178 | C <sub>11</sub> H <sub>19</sub>                              | 12.19 | 0.68 | 151.1488 |
| C <sub>8</sub> H <sub>6</sub> NO <sub>2</sub>                | 9.20  | 0.78 | 148.0399 | C <sub>6</sub> H <sub>14</sub> O <sub>4</sub>                | 6.86  | 1.00 | 150.0892 | C <sub>11</sub> H <sub>3</sub> O                             | 11.97 | 0.85 | 151.0184 |
| C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> O               | 9.57  | 0.61 | 148.0637 | C <sub>6</sub> NO <sub>4</sub>                               | 7.02  | 1.01 | 149.9827 | C <sub>11</sub> H <sub>5</sub> N                             | 12.35 | 0.70 | 151.0422 |
| C <sub>8</sub> H <sub>10</sub> N <sub>3</sub>                | 9.95  | 0.45 | 148.0876 | C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>  | 7.40  | 0.84 | 150.0065 | C <sub>12</sub> H <sub>7</sub>                               | 13.08 | 0.79 | 151.0548 |
| C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>                 | 9.93  | 0.84 | 148.0524 | C <sub>6</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>  | 7.77  | 0.67 | 150.0304 | 152  |       |      |          |
| C <sub>9</sub> H <sub>10</sub> NO                            | 10.31 | 0.68 | 148.0763 | C <sub>6</sub> H <sub>6</sub> N <sub>4</sub> O               | 8.14  | 0.49 | 150.0542 | C <sub>4</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> | 5.43  | 0.92 | 152.0797 |
| C <sub>9</sub> H <sub>12</sub> N <sub>2</sub>                | 10.68 | 0.52 | 148.1001 | C <sub>7</sub> H <sub>2</sub> O <sub>4</sub>                 | 7.75  | 1.06 | 149.9953 | C <sub>5</sub> N <sub>2</sub> O <sub>4</sub>                 | 6.32  | 0.97 | 151.9858 |
| C <sub>10</sub> H <sub>12</sub> O                            | 11.04 | 0.75 | 148.0888 | C <sub>7</sub> H <sub>4</sub> NO <sub>3</sub>                | 8.13  | 0.89 | 150.0191 | C <sub>5</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>  | 6.70  | 0.79 | 152.0096 |
|  |       |      |          | C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 8.50  | 0.72 | 150.0429 | C <sub>5</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>  | 7.07  | 0.62 | 152.0335 |

|  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|--|-------|------|----------|--|-------|------|----------|--|-------|------|----------|
| C <sub>6</sub> H <sub>2</sub> N <sub>0</sub> O <sub>4</sub>  | 7.05  | 1.01 | 151.9983 | C <sub>10</sub> H <sub>19</sub> N                            | 11.49 | 0.60 | 153.1519 | C <sub>8</sub> H <sub>11</sub> O <sub>3</sub>                | 8.94  | 0.95 | 155.0708 |
| C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 7.43  | 0.84 | 152.0222 | C <sub>10</sub> H <sub>3</sub> N <sub>0</sub>                | 11.27 | 0.78 | 153.0215 | C <sub>8</sub> H <sub>13</sub> N <sub>0</sub> O <sub>2</sub> | 9.31  | 0.79 | 155.0947 |
| C <sub>6</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>  | 7.80  | 0.67 | 152.0460 | C <sub>10</sub> H <sub>5</sub> N <sub>2</sub>                | 11.65 | 0.62 | 153.0453 | C <sub>8</sub> H <sub>15</sub> N <sub>2</sub> O              | 9.69  | 0.62 | 155.1185 |
| C <sub>6</sub> H <sub>8</sub> N <sub>4</sub> O               | 8.18  | 0.50 | 152.0699 | C <sub>11</sub> H <sub>21</sub>                              | 12.22 | 0.68 | 153.1644 | C <sub>8</sub> H <sub>17</sub> N <sub>3</sub>                | 10.06 | 0.46 | 155.1424 |
| C <sub>7</sub> H <sub>4</sub> O <sub>4</sub>                 | 7.78  | 1.06 | 152.0109 | C <sub>11</sub> H <sub>5</sub> O                             | 12.01 | 0.86 | 153.0340 | C <sub>8</sub> HN <sub>3</sub> O                             | 9.84  | 0.64 | 155.0120 |
| C <sub>7</sub> H <sub>6</sub> N <sub>0</sub> O <sub>3</sub>  | 8.16  | 0.89 | 152.0348 | C <sub>11</sub> H <sub>7</sub> N                             | 12.38 | 0.70 | 153.0579 | C <sub>8</sub> H <sub>3</sub> N <sub>4</sub>                 | 10.22 | 0.47 | 155.0359 |
| C <sub>7</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 8.53  | 0.72 | 152.0586 | C <sub>12</sub> H <sub>9</sub>                               | 13.11 | 0.79 | 153.0705 | C <sub>9</sub> H <sub>15</sub> O <sub>2</sub>                | 10.04 | 0.85 | 155.1072 |
| C <sub>7</sub> H <sub>10</sub> N <sub>3</sub> O              | 8.91  | 0.55 | 152.0825 | 154  |       |      |          | C <sub>9</sub> H <sub>17</sub> N <sub>0</sub>                | 10.42 | 0.69 | 155.1311 |
| C <sub>7</sub> H <sub>12</sub> N <sub>4</sub>                | 9.28  | 0.39 | 152.1063 | C <sub>5</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 6.35  | 0.97 | 154.0014 | C <sub>9</sub> HN <sub>0</sub> O <sub>2</sub>                | 10.20 | 0.87 | 155.0007 |
| C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>                 | 8.89  | 0.95 | 152.0473 | C <sub>5</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>  | 6.73  | 0.80 | 154.0253 | C <sub>9</sub> H <sub>19</sub> N <sub>2</sub>                | 10.79 | 0.53 | 155.1549 |
| C <sub>8</sub> H <sub>10</sub> N <sub>0</sub> O <sub>2</sub> | 9.26  | 0.78 | 152.0712 | C <sub>5</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 7.10  | 0.62 | 154.0491 | C <sub>9</sub> H <sub>3</sub> N <sub>2</sub> O               | 10.58 | 0.71 | 155.0246 |
| C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O              | 9.64  | 0.62 | 152.0950 | C <sub>6</sub> H <sub>4</sub> N <sub>0</sub> O <sub>4</sub>  | 7.09  | 1.02 | 154.0140 | C <sub>9</sub> H <sub>5</sub> N <sub>3</sub>                 | 10.95 | 0.54 | 155.0484 |
| C <sub>8</sub> H <sub>14</sub> N <sub>3</sub>                | 10.01 | 0.45 | 152.1189 | C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 7.46  | 0.84 | 154.0379 | C <sub>10</sub> H <sub>19</sub> O                            | 11.15 | 0.76 | 155.1436 |
| C <sub>8</sub> N <sub>4</sub>                                | 10.17 | 0.47 | 152.0124 | C <sub>6</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 7.83  | 0.67 | 154.0617 | C <sub>10</sub> H <sub>3</sub> O <sub>2</sub>                | 10.93 | 0.94 | 155.0133 |
| C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>                | 10.00 | 0.85 | 152.0837 | C <sub>6</sub> H <sub>10</sub> N <sub>4</sub> O              | 8.21  | 0.50 | 154.0856 | C <sub>10</sub> H <sub>21</sub> N                            | 11.52 | 0.60 | 155.1675 |
| C <sub>9</sub> H <sub>14</sub> N <sub>0</sub>                | 10.37 | 0.68 | 152.1076 | C <sub>7</sub> H <sub>6</sub> O <sub>4</sub>                 | 7.82  | 1.07 | 154.0266 | C <sub>10</sub> H <sub>5</sub> N <sub>0</sub>                | 11.31 | 0.78 | 155.0371 |
| C <sub>9</sub> H <sub>16</sub> N <sub>2</sub>                | 10.74 | 0.52 | 152.1315 | C <sub>7</sub> H <sub>8</sub> N <sub>0</sub> O <sub>3</sub>  | 8.19  | 0.90 | 154.0504 | C <sub>10</sub> H <sub>7</sub> N <sub>2</sub>                | 11.68 | 0.62 | 155.0610 |
| C <sub>9</sub> N <sub>2</sub> O                              | 10.53 | 0.70 | 152.0011 | C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 8.57  | 0.73 | 154.0743 | C <sub>11</sub> H <sub>23</sub>                              | 12.25 | 0.69 | 155.1801 |
| C <sub>9</sub> H <sub>2</sub> N <sub>3</sub>                 | 10.90 | 0.54 | 152.0249 | C <sub>7</sub> H <sub>12</sub> N <sub>3</sub> O              | 8.94  | 0.56 | 154.0981 | C <sub>11</sub> H <sub>7</sub> O                             | 12.04 | 0.86 | 155.0497 |
| C <sub>10</sub> H <sub>16</sub> O                            | 11.10 | 0.76 | 152.1202 | C <sub>7</sub> H <sub>14</sub> N <sub>4</sub>                | 9.31  | 0.39 | 154.1220 | C <sub>11</sub> H <sub>9</sub> N                             | 12.41 | 0.71 | 155.0736 |
| C <sub>10</sub> O <sub>2</sub>                               | 10.88 | 0.93 | 151.9898 | C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>                | 8.92  | 0.95 | 154.0630 | C <sub>12</sub> H <sub>11</sub>                              | 13.14 | 0.79 | 155.0861 |
| C <sub>10</sub> H <sub>18</sub> N                            | 11.48 | 0.60 | 152.1440 | C <sub>8</sub> H <sub>12</sub> N <sub>0</sub> O <sub>2</sub> | 9.30  | 0.79 | 154.0868 | 156  |       |      |          |
| C <sub>10</sub> H <sub>2</sub> N <sub>0</sub>                | 11.26 | 0.78 | 152.0136 | C <sub>8</sub> H <sub>14</sub> N <sub>2</sub> O              | 9.67  | 0.62 | 154.1107 | C <sub>5</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>  | 6.39  | 0.98 | 156.0171 |
| C <sub>10</sub> H <sub>4</sub> N <sub>2</sub>                | 11.63 | 0.62 | 152.0375 | C <sub>8</sub> H <sub>16</sub> N <sub>3</sub>                | 10.05 | 0.46 | 154.1346 | C <sub>5</sub> H <sub>6</sub> N <sub>3</sub> O <sub>3</sub>  | 6.76  | 0.80 | 156.0410 |
| C <sub>11</sub> H <sub>20</sub>                              | 12.21 | 0.68 | 152.1566 | C <sub>8</sub> N <sub>3</sub> O                              | 9.83  | 0.63 | 154.0042 | C <sub>5</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>  | 7.14  | 0.62 | 156.0648 |
| C <sub>11</sub> H <sub>4</sub> O                             | 11.99 | 0.86 | 152.0262 | C <sub>8</sub> H <sub>2</sub> N <sub>4</sub>                 | 10.20 | 0.47 | 154.0280 | C <sub>6</sub> H <sub>6</sub> N <sub>0</sub> O <sub>4</sub>  | 7.12  | 1.02 | 156.0297 |
| C <sub>11</sub> H <sub>6</sub> N                             | 12.36 | 0.70 | 152.0501 | C <sub>9</sub> H <sub>14</sub> O <sub>2</sub>                | 10.03 | 0.85 | 154.0994 | C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 7.49  | 0.85 | 156.0535 |
| C <sub>12</sub> H <sub>8</sub>                               | 13.10 | 0.79 | 152.0626 | C <sub>9</sub> H <sub>16</sub> N <sub>0</sub>                | 10.40 | 0.69 | 154.1233 | C <sub>6</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub> | 7.87  | 0.67 | 156.0774 |
| 153  |       |      |          | C <sub>9</sub> N <sub>0</sub> O <sub>2</sub>                 | 10.19 | 0.87 | 153.9929 | C <sub>6</sub> H <sub>12</sub> N <sub>4</sub> O              | 8.24  | 0.50 | 156.1012 |
| C <sub>5</sub> HN <sub>2</sub> O <sub>4</sub>                | 6.34  | 0.97 | 152.9936 | C <sub>9</sub> H <sub>18</sub> N <sub>2</sub>                | 10.78 | 0.53 | 154.1471 | C <sub>7</sub> H <sub>8</sub> O <sub>4</sub>                 | 7.85  | 1.07 | 156.0422 |
| C <sub>5</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>  | 6.71  | 0.80 | 153.0175 | C <sub>9</sub> H <sub>2</sub> N <sub>2</sub> O               | 10.56 | 0.70 | 154.0167 | C <sub>7</sub> H <sub>10</sub> N <sub>0</sub> O <sub>3</sub> | 8.22  | 0.90 | 156.0661 |
| C <sub>5</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>  | 7.09  | 0.62 | 153.0413 | C <sub>9</sub> H <sub>4</sub> N <sub>3</sub>                 | 10.93 | 0.54 | 154.0406 | C <sub>7</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | 8.60  | 0.73 | 156.0899 |
| C <sub>6</sub> H <sub>3</sub> N <sub>0</sub> O <sub>4</sub>  | 7.07  | 1.02 | 153.0062 | C <sub>10</sub> H <sub>18</sub> O                            | 11.13 | 0.76 | 154.1358 | C <sub>7</sub> H <sub>14</sub> N <sub>3</sub> O              | 8.97  | 0.56 | 156.1138 |
| C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>  | 7.44  | 0.84 | 153.0300 | C <sub>10</sub> H <sub>2</sub> O <sub>2</sub>                | 10.92 | 0.94 | 154.0054 | C <sub>7</sub> H <sub>16</sub> N <sub>4</sub>                | 9.35  | 0.39 | 156.1377 |
| C <sub>6</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>  | 7.82  | 0.67 | 153.0539 | C <sub>10</sub> H <sub>20</sub> N                            | 11.51 | 0.60 | 154.1597 | C <sub>7</sub> N <sub>4</sub> O                              | 9.13  | 0.57 | 156.0073 |
| C <sub>6</sub> H <sub>9</sub> N <sub>4</sub> O               | 8.19  | 0.50 | 153.0777 | C <sub>10</sub> H <sub>4</sub> N <sub>0</sub>                | 11.29 | 0.78 | 154.0293 | C <sub>8</sub> H <sub>12</sub> O <sub>3</sub>                | 8.95  | 0.96 | 156.0786 |
| C <sub>7</sub> H <sub>5</sub> O <sub>4</sub>                 | 7.80  | 1.07 | 153.0187 | C <sub>10</sub> H <sub>6</sub> N <sub>2</sub>                | 11.66 | 0.62 | 154.0532 | C <sub>8</sub> H <sub>14</sub> N <sub>0</sub> O <sub>2</sub> | 9.33  | 0.79 | 156.1025 |
| C <sub>7</sub> H <sub>7</sub> N <sub>0</sub> O <sub>3</sub>  | 8.17  | 0.89 | 153.0426 | C <sub>11</sub> H <sub>22</sub>                              | 12.24 | 0.68 | 154.1722 | C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> O              | 9.70  | 0.62 | 156.1264 |
| C <sub>7</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 8.55  | 0.72 | 153.0664 | C <sub>11</sub> H <sub>6</sub> O                             | 12.02 | 0.86 | 154.0419 | C <sub>8</sub> N <sub>2</sub> O <sub>2</sub>                 | 9.49  | 0.80 | 155.9960 |
| C <sub>7</sub> H <sub>11</sub> N <sub>3</sub> O              | 8.92  | 0.56 | 153.0903 | C <sub>11</sub> H <sub>8</sub> N                             | 12.40 | 0.70 | 154.0657 | C <sub>8</sub> H <sub>18</sub> N <sub>3</sub>                | 10.08 | 0.46 | 156.1502 |
| C <sub>7</sub> H <sub>13</sub> N <sub>4</sub>                | 9.30  | 0.39 | 153.1142 | C <sub>12</sub> H <sub>10</sub>                              | 13.13 | 0.79 | 154.0783 | C <sub>8</sub> H <sub>2</sub> N <sub>3</sub> O               | 9.86  | 0.64 | 156.0198 |
| C <sub>8</sub> H <sub>9</sub> O <sub>3</sub>                 | 8.91  | 0.95 | 153.0552 | 155  |       |      |          | C <sub>8</sub> H <sub>4</sub> N <sub>4</sub>                 | 10.23 | 0.47 | 156.0437 |
| C <sub>8</sub> H <sub>11</sub> N <sub>0</sub> O <sub>2</sub> | 9.28  | 0.78 | 153.0790 | C <sub>5</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>  | 6.37  | 0.97 | 155.0093 | C <sub>9</sub> H <sub>16</sub> O <sub>2</sub>                | 10.06 | 0.85 | 156.1151 |
| C <sub>8</sub> H <sub>13</sub> N <sub>2</sub> O              | 9.65  | 0.62 | 153.1029 | C <sub>5</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>  | 6.74  | 0.80 | 155.0331 | C <sub>9</sub> O <sub>3</sub>                                | 9.84  | 1.03 | 155.9847 |
| C <sub>8</sub> H <sub>15</sub> N <sub>3</sub>                | 10.03 | 0.45 | 153.1267 | C <sub>5</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>  | 7.12  | 0.62 | 155.0570 | C <sub>9</sub> H <sub>18</sub> N <sub>0</sub>                | 10.43 | 0.69 | 156.1389 |
| C <sub>8</sub> HN <sub>4</sub>                               | 10.19 | 0.47 | 153.0202 | C <sub>6</sub> H <sub>5</sub> N <sub>0</sub> O <sub>4</sub>  | 7.10  | 1.02 | 155.0218 | C <sub>9</sub> H <sub>2</sub> N <sub>0</sub> O <sub>2</sub>  | 10.22 | 0.87 | 156.0085 |
| C <sub>9</sub> H <sub>13</sub> O <sub>2</sub>                | 10.01 | 0.85 | 153.0916 | C <sub>6</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>  | 7.48  | 0.84 | 155.0457 | C <sub>9</sub> H <sub>20</sub> N <sub>2</sub>                | 10.81 | 0.53 | 156.1628 |
| C <sub>9</sub> H <sub>15</sub> N <sub>0</sub>                | 10.39 | 0.69 | 153.1154 | C <sub>6</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>  | 7.85  | 0.67 | 155.0695 | C <sub>9</sub> H <sub>4</sub> N <sub>2</sub> O               | 10.59 | 0.71 | 156.0324 |
| C <sub>9</sub> H <sub>17</sub> N <sub>2</sub>                | 10.76 | 0.52 | 153.1393 | C <sub>6</sub> H <sub>11</sub> N <sub>4</sub> O              | 8.22  | 0.50 | 155.0934 | C <sub>9</sub> H <sub>6</sub> N <sub>3</sub>                 | 10.97 | 0.55 | 156.0563 |
| C <sub>9</sub> HN <sub>2</sub> O                             | 10.54 | 0.70 | 153.0089 | C <sub>7</sub> H <sub>7</sub> O <sub>4</sub>                 | 7.83  | 1.07 | 155.0344 | C <sub>10</sub> H <sub>20</sub> O                            | 11.17 | 0.77 | 156.1515 |
| C <sub>9</sub> H <sub>3</sub> N <sub>3</sub>                 | 10.92 | 0.54 | 153.0328 | C <sub>7</sub> H <sub>9</sub> N <sub>0</sub> O <sub>3</sub>  | 8.21  | 0.90 | 155.0583 | C <sub>10</sub> H <sub>4</sub> O <sub>2</sub>                | 10.95 | 0.94 | 156.0211 |
| C <sub>10</sub> H <sub>17</sub> O                            | 11.12 | 0.76 | 153.1280 | C <sub>7</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 8.58  | 0.73 | 155.0821 | C <sub>10</sub> H <sub>22</sub> N                            | 11.54 | 0.61 | 156.1753 |
| C <sub>10</sub> HO <sub>2</sub>                              | 10.90 | 0.94 | 152.9976 | C <sub>7</sub> H <sub>13</sub> N <sub>3</sub> O              | 8.96  | 0.56 | 155.1060 | C <sub>10</sub> H <sub>6</sub> N <sub>0</sub>                | 11.32 | 0.78 | 156.0449 |
|  |       |      |          | C <sub>7</sub> H <sub>15</sub> N <sub>4</sub>                | 9.33  | 0.39 | 155.1298 |  |       |      |          |



|  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|--|-------|------|----------|--|-------|------|----------|--|-------|------|----------|
| C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>                | 11.70 | 0.62 | 156.0688 | C <sub>7</sub> H <sub>16</sub> N <sub>3</sub> O              | 9.00  | 0.56 | 158.1295 | C <sub>9</sub> H <sub>21</sub> NO                            | 10.48 | 0.70 | 159.1624 |
| C <sub>11</sub> H <sub>24</sub>                              | 12.27 | 0.69 | 156.1879 | C <sub>7</sub> N <sub>3</sub> O <sub>2</sub>                 | 8.79  | 0.74 | 157.9991 | C <sub>9</sub> H <sub>5</sub> NO <sub>2</sub>                | 10.27 | 0.87 | 159.0320 |
| C <sub>11</sub> H <sub>8</sub> O                             | 12.05 | 0.86 | 156.0575 | C <sub>7</sub> H <sub>18</sub> N <sub>4</sub>                | 9.38  | 0.40 | 158.1533 | C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> O               | 10.64 | 0.71 | 159.0559 |
| C <sub>11</sub> H <sub>10</sub> N                            | 12.43 | 0.71 | 156.0814 | C <sub>7</sub> H <sub>2</sub> N <sub>4</sub> O               | 9.16  | 0.58 | 158.0229 | C <sub>9</sub> H <sub>9</sub> N <sub>3</sub>                 | 11.01 | 0.55 | 159.0798 |
| C <sub>12</sub> H <sub>12</sub>                              | 13.16 | 0.80 | 156.0939 | C <sub>8</sub> H <sub>14</sub> O <sub>3</sub>                | 8.99  | 0.96 | 158.0943 | C <sub>10</sub> H <sub>7</sub> O <sub>2</sub>                | 11.00 | 0.95 | 159.0446 |
| C <sub>13</sub>  | 14.05 | 0.91 | 156.0000 | C <sub>8</sub> H <sub>16</sub> NO <sub>2</sub>               | 9.36  | 0.79 | 158.1182 | C <sub>10</sub> H <sub>9</sub> NO                            | 11.37 | 0.79 | 159.0684 |
| 157  |       |      |          | C <sub>8</sub> NO <sub>3</sub>                               | 9.14  | 0.97 | 157.9878 | C <sub>10</sub> H <sub>11</sub> N <sub>2</sub>               | 11.74 | 0.63 | 159.0923 |
| C <sub>5</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>  | 6.40  | 0.98 | 157.0249 | C <sub>8</sub> H <sub>18</sub> N <sub>2</sub> O              | 9.73  | 0.63 | 158.1420 | C <sub>11</sub> H <sub>11</sub> O                            | 12.10 | 0.87 | 159.0810 |
| C <sub>5</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>  | 6.78  | 0.80 | 157.0488 | C <sub>8</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>  | 9.52  | 0.81 | 158.0116 | C <sub>11</sub> H <sub>13</sub> N                            | 12.48 | 0.71 | 159.1049 |
| C <sub>5</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>  | 7.15  | 0.62 | 157.0726 | C <sub>8</sub> H <sub>20</sub> N <sub>3</sub>                | 10.11 | 0.46 | 158.1659 | C <sub>12</sub> H <sub>15</sub>                              | 13.21 | 0.80 | 159.1174 |
| C <sub>6</sub> H <sub>7</sub> NO <sub>4</sub>                | 7.13  | 1.02 | 157.0375 | C <sub>8</sub> H <sub>4</sub> N <sub>3</sub> O               | 9.89  | 0.64 | 158.0355 | C <sub>12</sub> HN   | 13.36 | 0.82 | 159.0109 |
| C <sub>6</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>  | 7.51  | 0.85 | 157.0614 | C <sub>8</sub> H <sub>6</sub> N <sub>4</sub>                 | 10.27 | 0.48 | 158.0594 | C <sub>13</sub> H <sub>3</sub>                               | 14.10 | 0.92 | 159.0235 |
| C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> | 7.88  | 0.67 | 157.0852 | C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>                | 10.09 | 0.86 | 158.1307 | 160  |       |      |          |
| C <sub>6</sub> H <sub>13</sub> N <sub>4</sub> O              | 8.26  | 0.50 | 157.1091 | C <sub>9</sub> H <sub>2</sub> O <sub>3</sub>                 | 9.87  | 1.04 | 158.0003 | C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>  | 6.45  | 0.98 | 160.0484 |
| C <sub>7</sub> H <sub>9</sub> O <sub>4</sub>                 | 7.86  | 1.07 | 157.0501 | C <sub>9</sub> H <sub>20</sub> NO                            | 10.47 | 0.69 | 158.1546 | C <sub>5</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> | 6.82  | 0.80 | 160.0723 |
| C <sub>7</sub> H <sub>11</sub> NO <sub>3</sub>               | 8.24  | 0.90 | 157.0739 | C <sub>9</sub> H <sub>4</sub> NO <sub>2</sub>                | 10.25 | 0.87 | 158.0242 | C <sub>5</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> | 7.20  | 0.63 | 160.0961 |
| C <sub>7</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> | 8.61  | 0.73 | 157.0978 | C <sub>9</sub> H <sub>22</sub> N <sub>2</sub>                | 10.84 | 0.53 | 158.1784 | C <sub>6</sub> H <sub>10</sub> NO <sub>4</sub>               | 7.18  | 1.02 | 160.0610 |
| C <sub>7</sub> H <sub>15</sub> N <sub>3</sub> O              | 8.99  | 0.56 | 157.1216 | C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O               | 10.62 | 0.71 | 158.0480 | C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> | 7.56  | 0.85 | 160.0848 |
| C <sub>7</sub> H <sub>17</sub> N <sub>4</sub>                | 9.36  | 0.39 | 157.1455 | C <sub>9</sub> H <sub>8</sub> N <sub>3</sub>                 | 11.00 | 0.55 | 158.0719 | C <sub>6</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> | 7.93  | 0.68 | 160.1087 |
| C <sub>7</sub> HN <sub>4</sub> O                             | 9.15  | 0.57 | 157.0151 | C <sub>10</sub> H <sub>22</sub> O                            | 11.20 | 0.77 | 158.1671 | C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> O              | 8.30  | 0.51 | 160.1325 |
| C <sub>8</sub> H <sub>13</sub> O <sub>3</sub>                | 8.97  | 0.96 | 157.0865 | C <sub>10</sub> H <sub>6</sub> O <sub>2</sub>                | 10.98 | 0.95 | 158.0368 | C <sub>6</sub> N <sub>4</sub> O <sub>2</sub>                 | 8.09  | 0.69 | 160.0022 |
| C <sub>8</sub> H <sub>15</sub> NO <sub>2</sub>               | 9.34  | 0.79 | 157.1103 | C <sub>10</sub> H <sub>8</sub> NO                            | 11.35 | 0.79 | 158.0606 | C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>                | 7.91  | 1.07 | 160.0735 |
| C <sub>8</sub> H <sub>17</sub> N <sub>2</sub> O              | 9.72  | 0.62 | 157.1342 | C <sub>10</sub> H <sub>10</sub> N <sub>2</sub>               | 11.73 | 0.63 | 158.0845 | C <sub>7</sub> H <sub>14</sub> NO <sub>3</sub>               | 8.29  | 0.90 | 160.0974 |
| C <sub>8</sub> HN <sub>2</sub> O <sub>2</sub>                | 9.50  | 0.80 | 157.0038 | C <sub>11</sub> H <sub>10</sub> O                            | 12.09 | 0.87 | 158.0732 | C <sub>7</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> | 8.66  | 0.73 | 160.1213 |
| C <sub>8</sub> H <sub>19</sub> N <sub>3</sub>                | 10.09 | 0.46 | 157.1580 | C <sub>11</sub> H <sub>12</sub> N                            | 12.46 | 0.71 | 158.0970 | C <sub>7</sub> N <sub>2</sub> O <sub>3</sub>                 | 8.44  | 0.92 | 159.9909 |
| C <sub>8</sub> H <sub>3</sub> N <sub>3</sub> O               | 9.88  | 0.64 | 157.0277 | C <sub>12</sub> H <sub>14</sub>                              | 13.19 | 0.80 | 158.1096 | C <sub>7</sub> H <sub>18</sub> N <sub>3</sub> O              | 9.04  | 0.57 | 160.1451 |
| C <sub>8</sub> H <sub>5</sub> N <sub>4</sub>                 | 10.25 | 0.48 | 157.0515 | C <sub>12</sub> N  | 13.35 | 0.82 | 158.0031 | C <sub>7</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>  | 8.82  | 0.75 | 160.0147 |
| C <sub>9</sub> H <sub>17</sub> O <sub>2</sub>                | 10.08 | 0.86 | 157.1229 | C <sub>13</sub> H <sub>2</sub>                               | 14.08 | 0.92 | 158.0157 | C <sub>7</sub> H <sub>20</sub> N <sub>4</sub>                | 9.41  | 0.40 | 160.1690 |
| C <sub>9</sub> HO <sub>3</sub>                               | 9.86  | 1.03 | 156.9925 | 159  |       |      |          | C <sub>7</sub> H <sub>4</sub> N <sub>4</sub> O               | 9.19  | 0.58 | 160.0386 |
| C <sub>9</sub> H <sub>19</sub> NO                            | 10.45 | 0.69 | 157.1467 | C <sub>5</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub>  | 6.43  | 0.98 | 159.0406 | C <sub>8</sub> H <sub>16</sub> O <sub>3</sub>                | 9.02  | 0.96 | 160.1100 |
| C <sub>9</sub> H <sub>3</sub> NO <sub>2</sub>                | 10.23 | 0.87 | 157.0164 | C <sub>5</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>  | 6.81  | 0.80 | 159.0644 | C <sub>8</sub> O <sub>4</sub>                                | 8.80  | 1.14 | 159.9796 |
| C <sub>9</sub> H <sub>21</sub> N <sub>2</sub>                | 10.82 | 0.53 | 157.1706 | C <sub>5</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> | 7.18  | 0.63 | 159.0883 | C <sub>8</sub> H <sub>18</sub> NO <sub>2</sub>               | 9.39  | 0.79 | 160.1338 |
| C <sub>9</sub> H <sub>5</sub> N <sub>2</sub> O               | 10.61 | 0.71 | 157.0402 | C <sub>6</sub> H <sub>9</sub> NO <sub>4</sub>                | 7.17  | 1.02 | 159.0532 | C <sub>8</sub> H <sub>2</sub> NO <sub>3</sub>                | 9.18  | 0.97 | 160.0034 |
| C <sub>9</sub> H <sub>7</sub> N <sub>3</sub>                 | 10.98 | 0.55 | 157.0641 | C <sub>6</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> | 7.54  | 0.85 | 159.0770 | C <sub>8</sub> H <sub>20</sub> N <sub>2</sub> O              | 9.77  | 0.63 | 160.1577 |
| C <sub>10</sub> H <sub>21</sub> O                            | 11.18 | 0.77 | 157.1593 | C <sub>6</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> | 7.91  | 0.68 | 159.1009 | C <sub>8</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>  | 9.55  | 0.81 | 160.0273 |
| C <sub>10</sub> H <sub>5</sub> O <sub>2</sub>                | 10.96 | 0.94 | 157.0289 | C <sub>6</sub> H <sub>15</sub> N <sub>4</sub> O              | 8.29  | 0.51 | 159.1247 | C <sub>8</sub> H <sub>6</sub> N <sub>3</sub> O               | 9.92  | 0.64 | 160.0511 |
| C <sub>10</sub> H <sub>23</sub> N                            | 11.56 | 0.61 | 157.1832 | C <sub>7</sub> H <sub>11</sub> O <sub>4</sub>                | 7.90  | 1.07 | 159.0657 | C <sub>8</sub> H <sub>8</sub> N <sub>4</sub>                 | 10.30 | 0.48 | 160.0750 |
| C <sub>10</sub> H <sub>7</sub> NO                            | 11.34 | 0.78 | 157.0528 | C <sub>7</sub> H <sub>13</sub> NO <sub>3</sub>               | 8.27  | 0.90 | 159.0896 | C <sub>9</sub> H <sub>20</sub> O <sub>2</sub>                | 10.12 | 0.86 | 160.1464 |
| C <sub>10</sub> H <sub>9</sub> N <sub>2</sub>                | 11.71 | 0.63 | 157.0767 | C <sub>7</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> | 8.65  | 0.73 | 159.1134 | C <sub>9</sub> H <sub>4</sub> O <sub>3</sub>                 | 9.91  | 1.04 | 160.0160 |
| C <sub>11</sub> H <sub>9</sub> O                             | 12.07 | 0.86 | 157.0653 | C <sub>7</sub> H <sub>17</sub> N <sub>3</sub> O              | 9.02  | 0.56 | 159.1373 | C <sub>9</sub> H <sub>6</sub> NO <sub>2</sub>                | 10.28 | 0.88 | 160.0399 |
| C <sub>11</sub> H <sub>11</sub> N                            | 12.44 | 0.71 | 157.0892 | C <sub>7</sub> HN <sub>3</sub> O <sub>2</sub>                | 8.80  | 0.75 | 159.0069 | C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O               | 10.66 | 0.71 | 160.0637 |
| C <sub>12</sub> H <sub>13</sub>                              | 13.18 | 0.80 | 157.1018 | C <sub>7</sub> H <sub>19</sub> N <sub>4</sub>                | 9.39  | 0.40 | 159.1611 | C <sub>9</sub> H <sub>10</sub> N <sub>3</sub>                | 11.03 | 0.55 | 160.0876 |
| C <sub>13</sub> H  | 14.06 | 0.91 | 157.0078 | C <sub>7</sub> H <sub>3</sub> N <sub>4</sub> O               | 9.18  | 0.58 | 159.0308 | C <sub>10</sub> H <sub>8</sub> O <sub>2</sub>                | 11.01 | 0.95 | 160.0524 |
| 158  |       |      |          | C <sub>8</sub> H <sub>15</sub> O <sub>3</sub>                | 9.00  | 0.96 | 159.1021 | C <sub>10</sub> H <sub>10</sub> NO                           | 11.39 | 0.79 | 160.0763 |
| C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>  | 6.42  | 0.98 | 158.0328 | C <sub>8</sub> H <sub>17</sub> NO <sub>2</sub>               | 9.38  | 0.79 | 159.1260 | C <sub>10</sub> H <sub>12</sub> N <sub>2</sub>               | 11.76 | 0.63 | 160.1001 |
| C <sub>5</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>  | 6.79  | 0.80 | 158.0566 | C <sub>8</sub> HN <sub>3</sub> O                             | 9.16  | 0.97 | 158.9956 | C <sub>11</sub> H <sub>12</sub> O                            | 12.12 | 0.87 | 160.0888 |
| C <sub>5</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> | 7.17  | 0.63 | 158.0805 | C <sub>8</sub> H <sub>19</sub> N <sub>2</sub> O              | 9.75  | 0.63 | 159.1498 | C <sub>11</sub> H <sub>14</sub> N                            | 12.49 | 0.72 | 160.1127 |
| C <sub>6</sub> H <sub>8</sub> NO <sub>4</sub>                | 7.15  | 1.02 | 158.0453 | C <sub>8</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 9.53  | 0.81 | 159.0195 | C <sub>11</sub> N <sub>2</sub>                               | 12.65 | 0.73 | 160.0062 |
| C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 7.52  | 0.85 | 158.0692 | C <sub>8</sub> H <sub>21</sub> N <sub>3</sub>                | 10.13 | 0.46 | 159.1737 | C <sub>12</sub> H <sub>16</sub>                              | 13.22 | 0.80 | 160.1253 |
| C <sub>6</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> | 7.90  | 0.68 | 158.0930 | C <sub>8</sub> H <sub>5</sub> N <sub>3</sub> O               | 9.91  | 0.64 | 159.0433 | C <sub>12</sub> O  | 13.01 | 0.98 | 159.9949 |
| C <sub>6</sub> H <sub>14</sub> N <sub>4</sub> O              | 8.27  | 0.50 | 158.1169 | C <sub>8</sub> H <sub>7</sub> N <sub>4</sub>                 | 10.28 | 0.48 | 159.0672 | C <sub>12</sub> H <sub>2</sub> N                             | 13.38 | 0.82 | 160.0187 |
| C <sub>7</sub> H <sub>10</sub> O <sub>4</sub>                | 7.88  | 1.07 | 158.0579 | C <sub>9</sub> H <sub>19</sub> O <sub>2</sub>                | 10.11 | 0.86 | 159.1385 | C <sub>13</sub> H <sub>4</sub>                               | 14.11 | 0.92 | 160.0313 |
| C <sub>7</sub> H <sub>12</sub> NO <sub>3</sub>               | 8.25  | 0.90 | 158.0817 | C <sub>9</sub> H <sub>3</sub> O <sub>3</sub>                 | 9.89  | 1.04 | 159.0082 | 161  |       |      |          |
| C <sub>7</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> | 8.63  | 0.73 | 158.1056 |  |       |      |          | C <sub>5</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>  | 6.47  | 0.98 | 161.0563 |



|                   | M+1   | M+2  | MW       |                   | M+1   | M+2  | MW       |                   | M+1   | M+2  | MW       |
|-------------------|-------|------|----------|-------------------|-------|------|----------|-------------------|-------|------|----------|
| $C_5H_{11}N_3O_3$ | 6.84  | 0.80 | 161.0801 | $C_8H_2O_4$       | 8.83  | 1.15 | 161.9953 | $C_{12}H_{19}$    | 13.27 | 0.81 | 163.1488 |
| $C_5H_{13}N_4O_2$ | 7.22  | 0.63 | 161.1040 | $C_8H_4NO_3$      | 9.21  | 0.98 | 162.0191 | $C_{12}H_3O$      | 13.05 | 0.98 | 163.0184 |
| $C_6H_{11}NO_4$   | 7.20  | 1.03 | 161.0688 | $C_8H_6N_2O_2$    | 9.58  | 0.81 | 162.0429 | $C_{12}H_5N$      | 13.43 | 0.83 | 163.0422 |
| $C_6H_{13}N_2O_3$ | 7.57  | 0.85 | 161.0927 | $C_8H_8N_3O$      | 9.96  | 0.65 | 162.0668 | $C_{13}H_7$       | 14.16 | 0.93 | 163.0548 |
| $C_6H_{15}N_3O_2$ | 7.95  | 0.68 | 161.1165 | $C_8H_{10}N_4$    | 10.33 | 0.48 | 162.0907 | 164               |       |      |          |
| $C_6H_{17}N_4O$   | 8.32  | 0.51 | 161.1404 | $C_9H_6O_3$       | 9.94  | 1.04 | 162.0317 | $C_5H_{12}N_2O_4$ | 6.51  | 0.98 | 164.0797 |
| $C_6HN_4O_2$      | 8.10  | 0.69 | 161.0100 | $C_9H_8NO_2$      | 10.31 | 0.88 | 162.0555 | $C_5H_{14}N_3O_3$ | 6.89  | 0.81 | 164.1036 |
| $C_7H_{13}O_4$    | 7.93  | 1.08 | 161.0814 | $C_9H_{10}N_2O$   | 10.69 | 0.72 | 162.0794 | $C_5H_{16}N_4O_2$ | 7.26  | 0.63 | 164.1275 |
| $C_7H_{15}NO_3$   | 8.30  | 0.90 | 161.1052 | $C_9H_{12}N_3$    | 11.06 | 0.56 | 162.1032 | $C_6H_{14}NO_4$   | 7.25  | 1.03 | 164.0923 |
| $C_7H_{17}N_2O_2$ | 8.68  | 0.74 | 161.1291 | $C_{10}H_{10}O_2$ | 11.04 | 0.95 | 162.0681 | $C_6H_{16}N_2O_3$ | 7.62  | 0.86 | 164.1162 |
| $C_7HN_2O_3$      | 8.46  | 0.92 | 160.9987 | $C_{10}H_{12}NO$  | 11.42 | 0.79 | 162.0919 | $C_6N_2O_4$       | 7.40  | 1.04 | 163.9858 |
| $C_7H_{19}N_3O$   | 9.05  | 0.57 | 161.1529 | $C_{10}H_{14}N_2$ | 11.79 | 0.64 | 162.1158 | $C_6H_2N_3O_3$    | 7.78  | 0.87 | 164.0096 |
| $C_7H_3N_3O_2$    | 8.83  | 0.75 | 161.0226 | $C_{10}N_3$       | 11.95 | 0.65 | 162.0093 | $C_6H_4N_4O_2$    | 8.15  | 0.70 | 164.0335 |
| $C_7H_5N_4O$      | 9.21  | 0.58 | 161.0464 | $C_{11}H_{14}O$   | 12.15 | 0.87 | 162.1045 | $C_7H_{16}O_4$    | 7.98  | 1.08 | 164.1049 |
| $C_8H_{17}O_3$    | 9.03  | 0.96 | 161.1178 | $C_{11}H_{16}N$   | 12.52 | 0.72 | 162.1284 | $C_7H_2NO_4$      | 8.13  | 1.09 | 163.9983 |
| $C_8HO_4$         | 8.82  | 1.14 | 160.9874 | $C_{11}NO$        | 12.31 | 0.89 | 161.9980 | $C_7H_4N_2O_3$    | 8.51  | 0.92 | 164.0222 |
| $C_8H_{19}NO_2$   | 9.41  | 0.80 | 161.1416 | $C_{11}H_2N_2$    | 12.68 | 0.74 | 162.0218 | $C_7H_6N_3O_2$    | 8.88  | 0.75 | 164.0460 |
| $C_8H_3NO_3$      | 9.19  | 0.98 | 161.0113 | $C_{12}H_{18}$    | 13.26 | 0.81 | 162.1409 | $C_7H_8N_4O$      | 9.26  | 0.59 | 164.0699 |
| $C_8H_5N_2O_2$    | 9.57  | 0.81 | 161.0351 | $C_{12}H_2O$      | 13.04 | 0.98 | 162.0106 | $C_8H_4O_4$       | 8.87  | 1.15 | 164.0109 |
| $C_8H_7N_3O$      | 9.94  | 0.65 | 161.0590 | $C_{12}H_4N$      | 13.41 | 0.83 | 162.0344 | $C_8H_6NO_3$      | 9.24  | 0.98 | 164.0348 |
| $C_8H_9N_4$       | 10.31 | 0.48 | 161.0829 | $C_{13}H_6$       | 14.14 | 0.92 | 162.0470 | $C_8H_8N_2O_2$    | 9.61  | 0.81 | 164.0586 |
| $C_9H_5O_3$       | 9.92  | 1.04 | 161.0238 | 163               |       |      |          | $C_8H_{10}N_3O$   | 9.99  | 0.65 | 164.0825 |
| $C_9H_7NO_2$      | 10.30 | 0.88 | 161.0477 | $C_5H_{11}N_2O_4$ | 6.50  | 0.98 | 163.0719 | $C_8H_{12}N_4$    | 10.36 | 0.49 | 164.1063 |
| $C_9H_9N_2O$      | 10.67 | 0.72 | 161.0715 | $C_5H_{13}N_3O_3$ | 6.87  | 0.81 | 163.0958 | $C_9H_8O_3$       | 9.97  | 1.05 | 164.0473 |
| $C_9H_{11}N_3$    | 11.05 | 0.56 | 161.0954 | $C_5H_{15}N_4O_2$ | 7.25  | 0.63 | 163.1196 | $C_9H_{10}NO_2$   | 10.35 | 0.88 | 164.0712 |
| $C_{10}H_9O_2$    | 11.03 | 0.95 | 161.0603 | $C_6H_{13}NO_4$   | 7.23  | 1.03 | 163.0845 | $C_9H_{12}N_2O$   | 10.72 | 0.72 | 164.0950 |
| $C_{10}H_{11}NO$  | 11.40 | 0.79 | 161.0841 | $C_6H_{15}N_2O_3$ | 7.60  | 0.85 | 163.1083 | $C_9H_{14}N_3$    | 11.09 | 0.56 | 164.1189 |
| $C_{10}H_{13}N_2$ | 11.78 | 0.63 | 161.1080 | $C_6H_{17}N_3O_2$ | 7.98  | 0.68 | 163.1322 | $C_9N_4$          | 11.25 | 0.58 | 164.0124 |
| $C_{11}H_{13}O$   | 12.13 | 0.87 | 161.0967 | $C_6HN_3O_3$      | 7.76  | 0.87 | 163.0018 | $C_{10}H_{12}O_2$ | 11.08 | 0.96 | 164.0837 |
| $C_{11}H_{15}N$   | 12.51 | 0.72 | 161.1205 | $C_6H_3N_4O_2$    | 8.14  | 0.69 | 163.0257 | $C_{10}H_{14}NO$  | 11.45 | 0.80 | 164.1076 |
| $C_{11}HN_2$      | 12.67 | 0.74 | 161.0140 | $C_7H_{15}O_4$    | 7.96  | 1.08 | 163.0970 | $C_{10}H_{16}N_2$ | 11.82 | 0.64 | 164.1315 |
| $C_{12}H_{17}$    | 13.24 | 0.81 | 161.1331 | $C_7H_{17}NO_3$   | 8.33  | 0.91 | 163.1209 | $C_{10}N_2O$      | 11.61 | 0.81 | 164.0011 |
| $C_{12}HO$        | 13.02 | 0.98 | 161.0027 | $C_7HNO_4$        | 8.12  | 1.09 | 162.9905 | $C_{10}H_2N_3$    | 11.98 | 0.66 | 164.0249 |
| $C_{12}H_3N$      | 13.40 | 0.83 | 161.0266 | $C_7H_3N_2O_3$    | 8.49  | 0.92 | 163.0144 | $C_{11}H_{16}O$   | 12.18 | 0.88 | 164.1202 |
| $C_{13}H_5$       | 14.13 | 0.92 | 161.0391 | $C_7H_5N_3O_2$    | 8.87  | 0.75 | 163.0382 | $C_{11}O_2$       | 11.96 | 1.05 | 163.9898 |
| 162               |       |      |          | $C_7H_7N_4O$      | 9.24  | 0.58 | 163.0621 | $C_{11}H_{18}N$   | 12.56 | 0.72 | 164.1440 |
| $C_5H_{10}N_2O_4$ | 6.48  | 0.98 | 162.0641 | $C_8H_3O_4$       | 8.85  | 1.15 | 163.0031 | $C_{11}H_2NO$     | 12.34 | 0.90 | 164.0136 |
| $C_5H_{12}N_3O_3$ | 6.86  | 0.81 | 162.0879 | $C_8H_5NO_3$      | 9.22  | 0.98 | 163.0269 | $C_{11}H_4N_2$    | 12.71 | 0.74 | 164.0375 |
| $C_5H_{14}N_4O_2$ | 7.23  | 0.63 | 162.1118 | $C_8H_7N_2O_2$    | 9.60  | 0.81 | 163.0508 | $C_{12}H_{20}$    | 13.29 | 0.81 | 164.1566 |
| $C_6H_{12}NO_4$   | 7.21  | 1.03 | 162.0766 | $C_8H_9N_3O$      | 9.97  | 0.65 | 163.0746 | $C_{12}H_4O$      | 13.07 | 0.98 | 164.0262 |
| $C_6H_{14}N_2O_3$ | 7.59  | 0.85 | 162.1005 | $C_8H_{11}N_4$    | 10.35 | 0.49 | 163.0985 | $C_{12}H_6N$      | 13.44 | 0.83 | 164.0501 |
| $C_6H_{16}N_3O_2$ | 7.96  | 0.68 | 162.1244 | $C_9H_7O_3$       | 9.95  | 1.04 | 163.0395 | $C_{13}H_8$       | 14.18 | 0.93 | 164.0626 |
| $C_6N_3O_3$       | 7.75  | 0.86 | 161.9940 | $C_9H_9NO_2$      | 10.33 | 0.88 | 163.0634 | 165               |       |      |          |
| $C_6H_{18}N_4O$   | 8.34  | 0.51 | 162.1482 | $C_9H_{11}N_2O$   | 10.70 | 0.72 | 163.0872 | $C_5H_{13}N_2O_4$ | 6.53  | 0.98 | 165.0876 |
| $C_6H_2N_4O_2$    | 8.12  | 0.69 | 162.0178 | $C_9H_{13}N_3$    | 11.08 | 0.56 | 163.1111 | $C_5H_{15}N_3O_3$ | 6.90  | 0.81 | 165.1114 |
| $C_7H_{14}O_4$    | 7.94  | 1.08 | 162.0892 | $C_{10}H_{11}O_2$ | 11.06 | 0.95 | 163.0759 | $C_6H_{15}NO_4$   | 7.26  | 1.03 | 165.1001 |
| $C_7H_{16}NO_3$   | 8.32  | 0.91 | 162.1131 | $C_{10}H_{13}NO$  | 11.43 | 0.80 | 163.0998 | $C_6HN_2O_4$      | 7.42  | 1.04 | 164.9936 |
| $C_7NO_4$         | 8.10  | 1.09 | 161.9827 | $C_{10}H_{15}N_2$ | 11.81 | 0.64 | 163.1236 | $C_6H_3N_3O_3$    | 7.79  | 0.87 | 165.0175 |
| $C_7H_{18}N_2O_2$ | 8.69  | 0.74 | 162.1369 | $C_{10}HN_3$      | 11.97 | 0.66 | 163.0171 | $C_6H_5N_4O_2$    | 8.17  | 0.70 | 165.0413 |
| $C_7H_2N_2O_3$    | 8.48  | 0.92 | 162.0065 | $C_{11}H_{15}O$   | 12.17 | 0.88 | 163.1123 | $C_7H_3NO_4$      | 8.15  | 1.09 | 165.0062 |
| $C_7H_4N_3O_2$    | 8.85  | 0.75 | 162.0304 | $C_{11}H_{17}N$   | 12.54 | 0.72 | 163.1362 | $C_7H_5N_2O_3$    | 8.52  | 0.92 | 165.0300 |
| $C_7H_6N_4O$      | 9.23  | 0.58 | 162.0542 | $C_{11}HNO$       | 12.32 | 0.89 | 163.0058 | $C_7H_7N_3O_2$    | 8.90  | 0.75 | 165.0539 |
| $C_8H_{18}O_3$    | 9.05  | 0.96 | 162.1256 | $C_{11}H_3N_2$    | 12.70 | 0.74 | 163.0297 | $C_7H_9N_4O$      | 9.27  | 0.59 | 165.0777 |
|                   |       |      |          |                   |       |      |          | $C_8H_5O_4$       | 8.88  | 1.15 | 165.0187 |

|  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|--|-------|------|----------|--|-------|------|----------|--|-------|------|----------|
| C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>  | 9.26  | 0.98 | 165.0426 | C <sub>11</sub> H <sub>6</sub> N <sub>2</sub>                | 12.75 | 0.75 | 166.0532 | C <sub>9</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> | 10.41 | 0.89 | 168.1025 |
| C <sub>8</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 9.63  | 0.82 | 165.0664 | C <sub>12</sub> H <sub>22</sub>                              | 13.32 | 0.82 | 166.1722 | C <sub>9</sub> H <sub>16</sub> N <sub>2</sub> O              | 10.78 | 0.73 | 168.1264 |
| C <sub>8</sub> H <sub>11</sub> N <sub>3</sub> O              | 10.00 | 0.65 | 165.0903 | C <sub>12</sub> H <sub>6</sub> O                             | 13.10 | 0.99 | 166.0419 | C <sub>9</sub> N <sub>2</sub> O <sub>2</sub>                 | 10.57 | 0.51 | 167.9960 |
| C <sub>8</sub> H <sub>13</sub> N <sub>4</sub>                | 10.38 | 0.49 | 165.1142 | C <sub>12</sub> H <sub>8</sub> N                             | 13.48 | 0.84 | 166.0657 | C <sub>9</sub> H <sub>18</sub> N <sub>3</sub>                | 11.16 | 0.57 | 168.1502 |
| C <sub>9</sub> H <sub>9</sub> O <sub>3</sub>                 | 9.99  | 1.05 | 165.0552 | C <sub>13</sub> H <sub>10</sub>                              | 14.21 | 0.93 | 166.0783 | C <sub>9</sub> H <sub>2</sub> N <sub>3</sub> O               | 10.94 | 0.74 | 168.0198 |
| C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O              | 10.36 | 0.88 | 165.0790 | 167  |       |      |          | C <sub>9</sub> H <sub>4</sub> N <sub>4</sub>                 | 11.32 | 0.58 | 168.0437 |
| C <sub>9</sub> H <sub>13</sub> N <sub>2</sub> O              | 10.74 | 0.72 | 165.1029 | C <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>  | 7.45  | 1.04 | 167.0093 | C <sub>10</sub> H <sub>16</sub> O <sub>2</sub>               | 11.14 | 0.96 | 168.1151 |
| C <sub>9</sub> H <sub>15</sub> N <sub>3</sub>                | 11.11 | 0.56 | 165.1267 | C <sub>6</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>  | 7.83  | 0.87 | 167.0331 | C <sub>10</sub> O <sub>3</sub>                               | 10.92 | 1.14 | 167.9847 |
| C <sub>9</sub> HN <sub>4</sub>                               | 11.27 | 0.58 | 165.0202 | C <sub>6</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>  | 8.20  | 0.70 | 167.0570 | C <sub>10</sub> H <sub>18</sub> NO                           | 11.51 | 0.80 | 168.1389 |
| C <sub>10</sub> H <sub>13</sub> O <sub>2</sub>               | 11.09 | 0.96 | 165.0916 | C <sub>7</sub> H <sub>5</sub> NO <sub>4</sub>                | 8.18  | 1.10 | 167.0218 | C <sub>10</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> | 11.30 | 0.98 | 168.0085 |
| C <sub>10</sub> H <sub>15</sub> NO                           | 11.47 | 0.80 | 165.1154 | C <sub>7</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>  | 8.56  | 0.93 | 167.0457 | C <sub>10</sub> H <sub>20</sub> N <sub>2</sub>               | 11.89 | 0.65 | 168.1628 |
| C <sub>10</sub> H <sub>17</sub> N <sub>2</sub>               | 11.84 | 0.64 | 165.1393 | C <sub>7</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>  | 8.93  | 0.76 | 167.0695 | C <sub>10</sub> H <sub>4</sub> N <sub>2</sub> O              | 11.67 | 0.82 | 168.0324 |
| C <sub>10</sub> HN <sub>2</sub> O                            | 11.62 | 0.82 | 165.0089 | C <sub>7</sub> H <sub>11</sub> N <sub>4</sub> O              | 9.31  | 0.59 | 167.0934 | C <sub>10</sub> H <sub>6</sub> N <sub>3</sub>                | 12.05 | 0.67 | 168.0563 |
| C <sub>10</sub> H <sub>3</sub> N <sub>3</sub>                | 12.00 | 0.66 | 165.0328 | C <sub>8</sub> H <sub>7</sub> O <sub>4</sub>                 | 8.91  | 1.15 | 167.0344 | C <sub>11</sub> H <sub>20</sub> O                            | 12.25 | 0.89 | 168.1515 |
| C <sub>11</sub> H <sub>17</sub> O                            | 12.20 | 0.88 | 165.1280 | C <sub>8</sub> H <sub>9</sub> NO <sub>3</sub>                | 9.29  | 0.99 | 167.0583 | C <sub>11</sub> H <sub>4</sub> O <sub>2</sub>                | 12.03 | 1.06 | 168.0211 |
| C <sub>11</sub> HO <sub>2</sub>                              | 11.98 | 1.05 | 164.9976 | C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 9.66  | 0.82 | 167.0821 | C <sub>11</sub> H <sub>22</sub> N                            | 12.62 | 0.73 | 168.1753 |
| C <sub>11</sub> H <sub>19</sub> N                            | 12.57 | 0.73 | 165.1519 | C <sub>8</sub> H <sub>13</sub> N <sub>3</sub> O              | 10.04 | 0.66 | 167.1060 | C <sub>11</sub> H <sub>6</sub> NO                            | 12.40 | 0.90 | 168.0449 |
| C <sub>11</sub> H <sub>3</sub> NO                            | 12.36 | 0.90 | 165.0215 | C <sub>8</sub> H <sub>15</sub> N <sub>4</sub>                | 10.41 | 0.49 | 167.1298 | C <sub>11</sub> H <sub>8</sub> N <sub>2</sub>                | 12.78 | 0.75 | 168.0688 |
| C <sub>11</sub> H <sub>5</sub> N <sub>2</sub>                | 12.73 | 0.74 | 165.0453 | C <sub>9</sub> H <sub>11</sub> O <sub>3</sub>                | 10.02 | 1.05 | 167.0708 | C <sub>12</sub> H <sub>24</sub>                              | 13.35 | 0.82 | 168.1879 |
| C <sub>12</sub> H <sub>21</sub>                              | 13.30 | 0.81 | 165.1644 | C <sub>9</sub> H <sub>13</sub> NO <sub>2</sub>               | 10.39 | 0.89 | 167.0947 | C <sub>12</sub> H <sub>8</sub> O                             | 13.13 | 0.99 | 168.0575 |
| C <sub>12</sub> H <sub>5</sub> O                             | 13.09 | 0.99 | 165.0340 | C <sub>9</sub> H <sub>15</sub> N <sub>2</sub> O              | 10.77 | 0.73 | 167.1185 | C <sub>12</sub> H <sub>10</sub> N                            | 13.51 | 0.84 | 168.0814 |
| C <sub>12</sub> H <sub>7</sub> N                             | 13.46 | 0.84 | 165.0579 | C <sub>9</sub> H <sub>17</sub> N <sub>3</sub>                | 11.14 | 0.57 | 167.1424 | C <sub>13</sub> H <sub>12</sub>                              | 14.24 | 0.94 | 168.0939 |
| C <sub>13</sub> H <sub>9</sub>                               | 14.19 | 0.93 | 165.0705 | C <sub>9</sub> HN <sub>3</sub> O                             | 10.92 | 0.74 | 167.0120 | C <sub>14</sub>  | 15.13 | 1.06 | 168.0000 |
| 166  |       |      |          | C <sub>9</sub> H <sub>3</sub> N <sub>4</sub>                 | 11.30 | 0.58 | 167.0359 | 169  |       |      |          |
| C <sub>5</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> | 6.55  | 0.99 | 166.0954 | C <sub>10</sub> H <sub>15</sub> O <sub>2</sub>               | 11.12 | 0.96 | 167.1072 | C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>  | 7.48  | 1.05 | 169.0249 |
| C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 7.43  | 1.04 | 166.0014 | C <sub>10</sub> H <sub>17</sub> NO                           | 11.50 | 0.80 | 167.1311 | C <sub>6</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>  | 7.86  | 0.87 | 169.0488 |
| C <sub>6</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>  | 7.81  | 0.87 | 166.0253 | C <sub>10</sub> HN <sub>2</sub> O                            | 11.28 | 0.98 | 167.0007 | C <sub>6</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>  | 8.23  | 0.70 | 169.0726 |
| C <sub>6</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 8.18  | 0.70 | 166.0491 | C <sub>10</sub> H <sub>19</sub> N <sub>2</sub>               | 11.87 | 0.64 | 167.1549 | C <sub>7</sub> H <sub>7</sub> NO <sub>4</sub>                | 8.21  | 1.10 | 169.0375 |
| C <sub>7</sub> H <sub>4</sub> NO <sub>4</sub>                | 8.17  | 1.09 | 166.0140 | C <sub>10</sub> H <sub>3</sub> N <sub>2</sub> O              | 11.66 | 0.82 | 167.0246 | C <sub>7</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>  | 8.59  | 0.93 | 169.0614 |
| C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 8.54  | 0.92 | 166.0379 | C <sub>10</sub> H <sub>5</sub> N <sub>3</sub>                | 12.03 | 0.66 | 167.0484 | C <sub>7</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> | 8.96  | 0.76 | 169.0852 |
| C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 8.91  | 0.76 | 166.0617 | C <sub>11</sub> H <sub>19</sub> O                            | 12.23 | 0.88 | 167.1436 | C <sub>7</sub> H <sub>13</sub> N <sub>4</sub> O              | 9.34  | 0.59 | 169.1091 |
| C <sub>7</sub> H <sub>10</sub> N <sub>4</sub> O              | 9.29  | 0.59 | 166.0856 | C <sub>11</sub> H <sub>3</sub> O <sub>2</sub>                | 12.01 | 1.06 | 167.0133 | C <sub>8</sub> H <sub>9</sub> O <sub>4</sub>                 | 8.95  | 1.16 | 169.0501 |
| C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>                 | 8.90  | 1.15 | 166.0266 | C <sub>11</sub> H <sub>21</sub> N                            | 12.60 | 0.73 | 167.1675 | C <sub>8</sub> H <sub>11</sub> NO <sub>3</sub>               | 9.32  | 0.99 | 169.0739 |
| C <sub>8</sub> H <sub>8</sub> NO <sub>3</sub>                | 9.27  | 0.98 | 166.0504 | C <sub>11</sub> H <sub>5</sub> NO                            | 12.39 | 0.90 | 167.0371 | C <sub>8</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> | 9.69  | 0.82 | 169.0978 |
| C <sub>8</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 9.65  | 0.82 | 166.0743 | C <sub>11</sub> H <sub>7</sub> N <sub>2</sub>                | 12.76 | 0.75 | 167.0610 | C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> O              | 10.07 | 0.66 | 169.1216 |
| C <sub>8</sub> H <sub>12</sub> N <sub>3</sub> O              | 10.02 | 0.65 | 166.0981 | C <sub>12</sub> H <sub>23</sub>                              | 13.34 | 0.82 | 167.1801 | C <sub>8</sub> H <sub>17</sub> N <sub>4</sub>                | 10.44 | 0.50 | 169.1455 |
| C <sub>8</sub> H <sub>14</sub> N <sub>4</sub>                | 10.39 | 0.49 | 166.1220 | C <sub>12</sub> H <sub>7</sub> O                             | 13.12 | 0.99 | 167.0497 | C <sub>8</sub> HN <sub>4</sub> O                             | 10.23 | 0.67 | 169.0151 |
| C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>                | 10.00 | 1.05 | 166.0630 | C <sub>12</sub> H <sub>9</sub> N                             | 13.49 | 0.84 | 167.0736 | C <sub>9</sub> H <sub>13</sub> O <sub>3</sub>                | 10.05 | 1.05 | 169.0865 |
| C <sub>9</sub> H <sub>12</sub> NO <sub>2</sub>               | 10.38 | 0.89 | 166.0868 | C <sub>13</sub> H <sub>11</sub>                              | 14.22 | 0.94 | 167.0861 | C <sub>9</sub> H <sub>15</sub> NO <sub>2</sub>               | 10.43 | 0.89 | 169.1103 |
| C <sub>9</sub> H <sub>14</sub> N <sub>2</sub> O              | 10.75 | 0.72 | 166.1107 | 168  |       |      |          | C <sub>9</sub> H <sub>17</sub> N <sub>2</sub> O              | 10.80 | 0.73 | 169.1342 |
| C <sub>9</sub> H <sub>16</sub> N <sub>3</sub>                | 11.13 | 0.56 | 166.1346 | C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>  | 7.47  | 1.04 | 168.0171 | C <sub>9</sub> HN <sub>2</sub> O <sub>2</sub>                | 10.58 | 0.91 | 169.0038 |
| C <sub>9</sub> N <sub>3</sub> O                              | 10.91 | 0.74 | 166.0042 | C <sub>6</sub> H <sub>6</sub> N <sub>3</sub> O <sub>3</sub>  | 7.84  | 0.87 | 168.0410 | C <sub>9</sub> H <sub>19</sub> N <sub>3</sub>                | 11.17 | 0.57 | 169.1580 |
| C <sub>9</sub> H <sub>2</sub> N <sub>4</sub>                 | 11.28 | 0.58 | 166.0280 | C <sub>6</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>  | 8.22  | 0.70 | 168.0648 | C <sub>9</sub> H <sub>3</sub> N <sub>3</sub> O               | 10.96 | 0.75 | 169.0277 |
| C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>               | 11.11 | 0.96 | 166.0994 | C <sub>7</sub> H <sub>6</sub> NO <sub>4</sub>                | 8.20  | 1.10 | 168.0297 | C <sub>9</sub> H <sub>5</sub> N <sub>4</sub>                 | 11.33 | 0.59 | 169.0515 |
| C <sub>10</sub> H <sub>16</sub> NO                           | 11.48 | 0.80 | 166.1233 | C <sub>7</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 8.57  | 0.93 | 168.0535 | C <sub>10</sub> H <sub>17</sub> O <sub>2</sub>               | 11.16 | 0.96 | 169.1229 |
| C <sub>10</sub> NO <sub>2</sub>                              | 11.27 | 0.98 | 165.9929 | C <sub>7</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub> | 8.95  | 0.76 | 168.0774 | C <sub>10</sub> HO <sub>3</sub>                              | 10.94 | 1.14 | 168.9925 |
| C <sub>10</sub> H <sub>18</sub> N <sub>2</sub>               | 11.86 | 0.64 | 166.1471 | C <sub>7</sub> H <sub>12</sub> N <sub>4</sub> O              | 9.32  | 0.59 | 168.1012 | C <sub>10</sub> H <sub>19</sub> NO                           | 11.53 | 0.81 | 169.1467 |
| C <sub>10</sub> H <sub>2</sub> N <sub>2</sub> O              | 11.64 | 0.82 | 166.0167 | C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>                 | 8.93  | 1.15 | 168.0422 | C <sub>10</sub> H <sub>3</sub> NO <sub>2</sub>               | 11.31 | 0.98 | 169.0164 |
| C <sub>10</sub> H <sub>4</sub> N <sub>3</sub>                | 12.01 | 0.66 | 166.0406 | C <sub>8</sub> H <sub>10</sub> NO <sub>3</sub>               | 9.30  | 0.99 | 168.0661 | C <sub>10</sub> H <sub>21</sub> N <sub>2</sub>               | 11.90 | 0.65 | 169.1706 |
| C <sub>11</sub> H <sub>18</sub> O                            | 12.21 | 0.88 | 166.1358 | C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | 9.68  | 0.82 | 168.0899 | C <sub>10</sub> H <sub>5</sub> N <sub>2</sub> O              | 11.69 | 0.82 | 169.0402 |
| C <sub>11</sub> H <sub>2</sub> O <sub>2</sub>                | 12.00 | 1.06 | 166.0054 | C <sub>8</sub> H <sub>14</sub> N <sub>3</sub> O              | 10.05 | 0.66 | 168.1138 | C <sub>10</sub> H <sub>7</sub> N <sub>3</sub>                | 12.06 | 0.67 | 169.0641 |
| C <sub>11</sub> H <sub>20</sub> N                            | 12.59 | 0.73 | 166.1597 | C <sub>8</sub> H <sub>16</sub> N <sub>4</sub>                | 10.43 | 0.49 | 168.1377 | C <sub>11</sub> H <sub>21</sub> O                            | 12.26 | 0.89 | 169.1593 |
| C <sub>11</sub> H <sub>4</sub> NO                            | 12.37 | 0.90 | 166.0293 | C <sub>8</sub> N <sub>4</sub> O                              | 10.21 | 0.67 | 168.0073 | C <sub>11</sub> H <sub>5</sub> O <sub>2</sub>                | 12.04 | 1.06 | 169.0289 |
|  |       |      |          | C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>                | 10.03 | 1.05 | 168.0786 |  |       |      |          |



|  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|--|-------|------|----------|--|-------|------|----------|--|-------|------|----------|
| C <sub>11</sub> H <sub>23</sub> N                            | 12.64 | 0.73 | 169.1832 | C <sub>7</sub> H <sub>9</sub> N <sub>3</sub> O <sub>4</sub>  | 8.25  | 1.10 | 171.0532 | C <sub>9</sub> H <sub>16</sub> O <sub>3</sub>                | 10.10 | 1.06 | 172.1100 |
| C <sub>11</sub> H <sub>7</sub> N <sub>3</sub> O              | 12.42 | 0.91 | 169.0528 | C <sub>7</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> | 8.62  | 0.93 | 171.0770 | C <sub>9</sub> O <sub>4</sub>                                | 9.88  | 1.24 | 171.9796 |
| C <sub>11</sub> H <sub>9</sub> N <sub>2</sub>                | 12.79 | 0.75 | 169.0767 | C <sub>7</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> | 8.99  | 0.76 | 171.1009 | C <sub>9</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> | 10.47 | 0.90 | 172.1338 |
| C <sub>12</sub> H <sub>25</sub>                              | 13.37 | 0.82 | 169.1957 | C <sub>7</sub> H <sub>15</sub> N <sub>4</sub> O              | 9.37  | 0.60 | 171.1247 | C <sub>9</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>  | 10.26 | 1.07 | 172.0034 |
| C <sub>12</sub> H <sub>9</sub> O                             | 13.15 | 1.00 | 169.0653 | C <sub>8</sub> H <sub>11</sub> O <sub>4</sub>                | 8.98  | 1.16 | 171.0657 | C <sub>9</sub> H <sub>20</sub> N <sub>2</sub> O              | 10.85 | 0.73 | 172.1577 |
| C <sub>12</sub> H <sub>11</sub> N                            | 13.52 | 0.84 | 169.0892 | C <sub>8</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> | 9.35  | 0.99 | 171.0896 | C <sub>9</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>  | 10.63 | 0.91 | 172.0273 |
| C <sub>13</sub> H <sub>13</sub>                              | 14.26 | 0.94 | 169.1018 | C <sub>8</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> | 9.73  | 0.83 | 171.1134 | C <sub>9</sub> H <sub>22</sub> N <sub>3</sub>                | 11.22 | 0.57 | 172.1815 |
| C <sub>14</sub> H  | 15.14 | 1.07 | 169.0078 | C <sub>8</sub> H <sub>17</sub> N <sub>3</sub> O              | 10.10 | 0.66 | 171.1373 | C <sub>9</sub> H <sub>6</sub> N <sub>3</sub> O               | 11.00 | 0.75 | 172.0511 |
| 170  |       |      |          | C <sub>8</sub> HN <sub>3</sub> O <sub>2</sub>                | 9.88  | 0.84 | 171.0069 | C <sub>9</sub> H <sub>8</sub> N <sub>4</sub>                 | 11.38 | 0.59 | 172.0750 |
| C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>  | 7.50  | 1.05 | 170.0328 | C <sub>8</sub> H <sub>19</sub> N <sub>4</sub>                | 10.47 | 0.50 | 171.1611 | C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>               | 11.20 | 0.97 | 172.1464 |
| C <sub>6</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>  | 7.87  | 0.87 | 170.0566 | C <sub>8</sub> H <sub>3</sub> N <sub>4</sub> O               | 10.26 | 0.68 | 171.0308 | C <sub>10</sub> H <sub>4</sub> O <sub>3</sub>                | 10.99 | 1.15 | 172.0160 |
| C <sub>6</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> | 8.25  | 0.70 | 170.0805 | C <sub>9</sub> H <sub>15</sub> O <sub>3</sub>                | 10.08 | 1.06 | 171.1021 | C <sub>10</sub> H <sub>22</sub> N <sub>3</sub> O             | 11.58 | 0.81 | 172.1702 |
| C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>4</sub>  | 8.23  | 1.10 | 170.0453 | C <sub>9</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> | 10.46 | 0.89 | 171.1260 | C <sub>10</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub> | 11.36 | 0.99 | 172.0399 |
| C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 8.60  | 0.93 | 170.0692 | C <sub>9</sub> HN <sub>3</sub> O <sub>3</sub>                | 10.24 | 1.07 | 170.9956 | C <sub>10</sub> H <sub>24</sub> N <sub>2</sub>               | 11.95 | 0.65 | 172.1941 |
| C <sub>7</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> | 8.98  | 0.76 | 170.0930 | C <sub>9</sub> H <sub>19</sub> N <sub>2</sub> O              | 10.83 | 0.73 | 171.1498 | C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> O              | 11.74 | 0.83 | 172.0637 |
| C <sub>7</sub> H <sub>14</sub> N <sub>4</sub> O              | 9.35  | 0.59 | 170.1169 | C <sub>9</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 10.61 | 0.91 | 171.0195 | C <sub>10</sub> H <sub>10</sub> N <sub>3</sub>               | 12.11 | 0.67 | 172.0876 |
| C <sub>8</sub> H <sub>10</sub> O <sub>4</sub>                | 8.96  | 1.16 | 170.0579 | C <sub>9</sub> H <sub>21</sub> N <sub>3</sub>                | 11.21 | 0.57 | 171.1737 | C <sub>11</sub> H <sub>24</sub> O                            | 12.31 | 0.89 | 172.1828 |
| C <sub>8</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> | 9.34  | 0.99 | 170.0817 | C <sub>9</sub> H <sub>5</sub> N <sub>3</sub> O               | 10.99 | 0.75 | 171.0433 | C <sub>11</sub> H <sub>8</sub> O <sub>2</sub>                | 12.09 | 1.07 | 172.0524 |
| C <sub>8</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> | 9.71  | 0.82 | 170.1056 | C <sub>9</sub> H <sub>7</sub> N <sub>4</sub>                 | 11.36 | 0.59 | 171.0672 | C <sub>11</sub> H <sub>10</sub> N <sub>3</sub> O             | 12.47 | 0.91 | 172.0763 |
| C <sub>8</sub> H <sub>16</sub> N <sub>3</sub> O              | 10.08 | 0.66 | 170.1295 | C <sub>10</sub> H <sub>19</sub> O <sub>2</sub>               | 11.19 | 0.97 | 171.1385 | C <sub>11</sub> H <sub>12</sub> N <sub>2</sub>               | 12.84 | 0.76 | 172.1001 |
| C <sub>8</sub> N <sub>3</sub> O <sub>2</sub>                 | 9.87  | 0.84 | 169.9991 | C <sub>10</sub> H <sub>3</sub> O <sub>3</sub>                | 10.97 | 1.14 | 171.0082 | C <sub>12</sub> H <sub>12</sub> O                            | 13.20 | 1.00 | 172.0888 |
| C <sub>8</sub> H <sub>18</sub> N <sub>4</sub>                | 10.46 | 0.50 | 170.1533 | C <sub>10</sub> H <sub>21</sub> N <sub>3</sub> O             | 11.56 | 0.81 | 171.1624 | C <sub>12</sub> H <sub>14</sub> N                            | 13.57 | 0.85 | 172.1127 |
| C <sub>8</sub> H <sub>2</sub> N <sub>4</sub> O               | 10.24 | 0.68 | 170.0229 | C <sub>10</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub> | 11.35 | 0.99 | 171.0320 | C <sub>12</sub> N <sub>2</sub>                               | 13.73 | 0.87 | 172.0062 |
| C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>                | 10.07 | 1.06 | 170.0943 | C <sub>10</sub> H <sub>23</sub> N <sub>2</sub>               | 11.94 | 0.65 | 171.1863 | C <sub>13</sub> H <sub>16</sub>                              | 14.30 | 0.95 | 172.1253 |
| C <sub>9</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub> | 10.44 | 0.89 | 170.1182 | C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> O              | 11.72 | 0.83 | 171.0559 | C <sub>13</sub> O  | 14.09 | 1.12 | 171.9949 |
| C <sub>9</sub> N <sub>3</sub> O <sub>3</sub>                 | 10.22 | 1.07 | 169.9878 | C <sub>10</sub> H <sub>9</sub> N <sub>3</sub>                | 12.09 | 0.67 | 171.0798 | C <sub>13</sub> H <sub>2</sub> N                             | 14.46 | 0.97 | 172.0187 |
| C <sub>9</sub> H <sub>18</sub> N <sub>2</sub> O              | 10.82 | 0.73 | 170.1420 | C <sub>11</sub> H <sub>23</sub> O                            | 12.29 | 0.89 | 171.1750 | C <sub>14</sub> H <sub>4</sub>                               | 15.19 | 1.07 | 172.0313 |
| C <sub>9</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>  | 10.60 | 0.91 | 170.0116 | C <sub>11</sub> H <sub>7</sub> O <sub>2</sub>                | 12.08 | 1.07 | 171.0446 | 173  |       |      |          |
| C <sub>9</sub> H <sub>20</sub> N <sub>3</sub>                | 11.19 | 0.57 | 170.1659 | C <sub>11</sub> H <sub>25</sub> N                            | 12.67 | 0.74 | 171.1988 | C <sub>6</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>  | 7.55  | 1.05 | 173.0563 |
| C <sub>9</sub> H <sub>4</sub> N <sub>3</sub> O               | 10.97 | 0.75 | 170.0355 | C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O              | 12.45 | 0.91 | 171.0684 | C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> | 7.92  | 0.88 | 173.0801 |
| C <sub>9</sub> H <sub>6</sub> N <sub>4</sub>                 | 11.35 | 0.59 | 170.0594 | C <sub>11</sub> H <sub>11</sub> N <sub>2</sub>               | 12.83 | 0.76 | 171.0923 | C <sub>6</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> | 8.30  | 0.71 | 173.1040 |
| C <sub>10</sub> H <sub>18</sub> O <sub>2</sub>               | 11.17 | 0.97 | 170.1307 | C <sub>12</sub> H <sub>11</sub> O                            | 13.18 | 1.00 | 171.0810 | C <sub>7</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub> | 8.28  | 1.10 | 173.0688 |
| C <sub>10</sub> H <sub>2</sub> O <sub>3</sub>                | 10.96 | 1.14 | 170.0003 | C <sub>12</sub> H <sub>13</sub> N                            | 13.56 | 0.85 | 171.1049 | C <sub>7</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> | 8.65  | 0.93 | 173.0927 |
| C <sub>10</sub> H <sub>20</sub> N <sub>3</sub> O             | 11.55 | 0.81 | 170.1546 | C <sub>13</sub> H <sub>15</sub>                              | 14.29 | 0.94 | 171.1174 | C <sub>7</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> | 9.03  | 0.77 | 173.1165 |
| C <sub>10</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub> | 11.33 | 0.98 | 170.0242 | C <sub>13</sub> HN   | 14.45 | 0.97 | 171.0109 | C <sub>7</sub> H <sub>17</sub> N <sub>4</sub> O              | 9.40  | 0.60 | 173.1404 |
| C <sub>10</sub> H <sub>22</sub> N <sub>2</sub>               | 11.92 | 0.65 | 170.1784 | C <sub>14</sub> H <sub>3</sub>                               | 15.18 | 1.07 | 171.0235 | C <sub>7</sub> HN <sub>4</sub> O <sub>2</sub>                | 9.18  | 0.78 | 173.0100 |
| C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O              | 11.70 | 0.83 | 170.0480 | 172  |       |      |          | C <sub>8</sub> H <sub>13</sub> O <sub>4</sub>                | 9.01  | 1.16 | 173.0814 |
| C <sub>10</sub> H <sub>8</sub> N <sub>3</sub>                | 12.08 | 0.67 | 170.0719 | C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>  | 7.53  | 1.05 | 172.0484 | C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> O              | 9.38  | 0.99 | 173.1052 |
| C <sub>11</sub> H <sub>22</sub> O                            | 12.28 | 0.89 | 170.1671 | C <sub>6</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> | 7.91  | 0.88 | 172.0723 | C <sub>8</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> | 9.76  | 0.83 | 173.1291 |
| C <sub>11</sub> H <sub>6</sub> O <sub>2</sub>                | 12.06 | 1.06 | 170.0368 | C <sub>6</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> | 8.28  | 0.71 | 172.0961 | C <sub>8</sub> HN <sub>2</sub> O <sub>3</sub>                | 9.54  | 1.01 | 172.9987 |
| C <sub>11</sub> H <sub>24</sub> N                            | 12.65 | 0.74 | 170.1910 | C <sub>7</sub> H <sub>10</sub> N <sub>3</sub> O <sub>4</sub> | 8.26  | 1.10 | 172.0610 | C <sub>8</sub> H <sub>19</sub> N <sub>3</sub> O              | 10.13 | 0.66 | 173.1529 |
| C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O              | 12.44 | 0.91 | 170.0606 | C <sub>7</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> | 8.64  | 0.93 | 172.0848 | C <sub>8</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>  | 9.92  | 0.84 | 173.0226 |
| C <sub>11</sub> H <sub>10</sub> N <sub>2</sub>               | 12.81 | 0.75 | 170.0845 | C <sub>7</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> | 9.01  | 0.76 | 172.1087 | C <sub>8</sub> H <sub>21</sub> N <sub>4</sub>                | 10.51 | 0.50 | 173.1768 |
| C <sub>12</sub> H <sub>26</sub>                              | 13.38 | 0.83 | 170.2036 | C <sub>7</sub> H <sub>16</sub> N <sub>4</sub> O              | 9.39  | 0.60 | 172.1325 | C <sub>8</sub> H <sub>5</sub> N <sub>4</sub> O               | 10.29 | 0.68 | 173.0464 |
| C <sub>12</sub> H <sub>10</sub> O                            | 13.17 | 1.00 | 170.0732 | C <sub>7</sub> N <sub>4</sub> O <sub>2</sub>                 | 9.17  | 0.78 | 172.0022 | C <sub>9</sub> H <sub>17</sub> O <sub>3</sub>                | 10.11 | 1.06 | 173.1178 |
| C <sub>12</sub> H <sub>12</sub> N                            | 13.54 | 0.85 | 170.0970 | C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>                | 8.99  | 1.16 | 172.0735 | C <sub>9</sub> H <sub>3</sub> O <sub>4</sub>                 | 9.90  | 1.24 | 172.9874 |
| C <sub>13</sub> H <sub>14</sub>                              | 14.27 | 0.94 | 170.1095 | C <sub>8</sub> H <sub>14</sub> N <sub>3</sub> O              | 9.37  | 0.99 | 172.0974 | C <sub>9</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> | 10.49 | 0.90 | 173.1416 |
| C <sub>13</sub> N  | 14.43 | 0.96 | 170.0031 | C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> | 9.74  | 0.83 | 172.1213 | C <sub>9</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>  | 10.27 | 1.08 | 173.0113 |
| C <sub>14</sub> H <sub>2</sub>                               | 15.16 | 1.07 | 170.0157 | C <sub>8</sub> N <sub>2</sub> O <sub>3</sub>                 | 9.52  | 1.01 | 171.9909 | C <sub>9</sub> H <sub>21</sub> N <sub>2</sub> O              | 10.86 | 0.74 | 173.1655 |
| 171  |       |      |          | C <sub>8</sub> H <sub>18</sub> N <sub>3</sub> O              | 10.12 | 0.66 | 172.1451 | C <sub>9</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>  | 10.65 | 0.91 | 173.0351 |
| C <sub>6</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub>  | 7.51  | 1.05 | 171.0406 | C <sub>8</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>  | 9.90  | 0.84 | 172.0147 | C <sub>9</sub> H <sub>23</sub> N <sub>3</sub>                | 11.24 | 0.58 | 173.1894 |
| C <sub>6</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>  | 7.89  | 0.88 | 171.0644 | C <sub>8</sub> H <sub>20</sub> N <sub>4</sub>                | 10.49 | 0.50 | 172.1690 | C <sub>9</sub> H <sub>7</sub> N <sub>3</sub> O               | 11.02 | 0.75 | 173.0590 |
| C <sub>6</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> | 8.26  | 0.70 | 171.0883 | C <sub>8</sub> H <sub>4</sub> N <sub>4</sub> O               | 10.27 | 0.58 | 172.0386 | C <sub>9</sub> H <sub>9</sub> N <sub>4</sub>                 | 11.40 | 0.59 | 173.0829 |



|  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|--|-------|------|----------|--|-------|------|----------|--|-------|------|----------|
| C <sub>10</sub> H <sub>21</sub> O <sub>2</sub>               | 11.22 | 0.97 | 173.1542 | C <sub>12</sub> H <sub>16</sub> N                            | 13.60 | 0.85 | 174.1284 | C <sub>7</sub> N <sub>2</sub> O <sub>4</sub>                 | 8.48  | 1.12 | 175.9858 |
| C <sub>10</sub> H <sub>5</sub> O <sub>3</sub>                | 11.00 | 1.15 | 173.0238 | C <sub>12</sub> NO   | 13.39 | 1.03 | 173.9980 | C <sub>7</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> | 9.07  | 0.77 | 176.1400 |
| C <sub>10</sub> H <sub>23</sub> NO                           | 11.59 | 0.81 | 173.1781 | C <sub>12</sub> H <sub>2</sub> N <sub>2</sub>                | 13.76 | 0.88 | 174.0218 | C <sub>7</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>  | 8.86  | 0.95 | 176.0096 |
| C <sub>10</sub> H <sub>7</sub> NO <sub>2</sub>               | 11.38 | 0.99 | 173.0477 | C <sub>13</sub> H <sub>18</sub>                              | 14.34 | 0.95 | 174.1409 | C <sub>7</sub> H <sub>20</sub> N <sub>4</sub> O              | 9.45  | 0.60 | 176.1639 |
| C <sub>10</sub> H <sub>9</sub> N <sub>2</sub> O              | 11.75 | 0.83 | 173.0715 | C <sub>13</sub> H <sub>2</sub> O                             | 14.12 | 1.12 | 174.0106 | C <sub>7</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>  | 9.23  | 0.78 | 176.0335 |
| C <sub>10</sub> H <sub>11</sub> N <sub>3</sub>               | 12.13 | 0.67 | 173.0954 | C <sub>13</sub> H <sub>4</sub> N                             | 14.49 | 0.97 | 174.0344 | C <sub>8</sub> H <sub>16</sub> O <sub>4</sub>                | 9.06  | 1.17 | 176.1049 |
| C <sub>11</sub> H <sub>9</sub> O <sub>2</sub>                | 12.11 | 1.07 | 173.0603 | C <sub>14</sub> H <sub>6</sub>                               | 15.22 | 1.08 | 174.0470 | C <sub>8</sub> H <sub>18</sub> NO <sub>3</sub>               | 9.43  | 1.00 | 176.1287 |
| C <sub>11</sub> H <sub>11</sub> NO                           | 12.48 | 0.91 | 173.0841 | 175  |       |      |          | C <sub>8</sub> H <sub>2</sub> NO <sub>4</sub>                | 9.21  | 1.18 | 175.9983 |
| C <sub>11</sub> H <sub>13</sub> N <sub>2</sub>               | 12.86 | 0.76 | 173.1080 | C <sub>6</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> | 7.58  | 1.05 | 175.0719 | C <sub>8</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> | 9.81  | 0.83 | 176.1526 |
| C <sub>12</sub> H <sub>13</sub> O                            | 13.21 | 1.00 | 173.0967 | C <sub>6</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> | 7.95  | 0.88 | 175.0958 | C <sub>8</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 9.59  | 1.01 | 176.0222 |
| C <sub>12</sub> H <sub>15</sub> N                            | 13.59 | 0.85 | 173.1205 | C <sub>6</sub> H <sub>15</sub> N <sub>4</sub> O <sub>2</sub> | 8.33  | 0.71 | 175.1196 | C <sub>8</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>  | 9.96  | 0.85 | 176.0460 |
| C <sub>12</sub> HN <sub>2</sub>                              | 13.75 | 0.87 | 173.0140 | C <sub>7</sub> H <sub>13</sub> NO <sub>4</sub>               | 8.31  | 1.11 | 175.0845 | C <sub>8</sub> H <sub>8</sub> N <sub>4</sub> O               | 10.34 | 0.69 | 176.0699 |
| C <sub>13</sub> H <sub>17</sub>                              | 14.32 | 0.95 | 173.1331 | C <sub>7</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub> | 8.68  | 0.94 | 175.1083 | C <sub>9</sub> H <sub>20</sub> O <sub>3</sub>                | 10.16 | 1.07 | 176.1413 |
| C <sub>13</sub> HO   | 14.10 | 1.12 | 173.0027 | C <sub>7</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> | 9.06  | 0.77 | 175.1322 | C <sub>9</sub> H <sub>4</sub> O <sub>4</sub>                 | 9.95  | 1.24 | 176.0109 |
| C <sub>13</sub> H <sub>3</sub> N                             | 14.48 | 0.97 | 173.0266 | C <sub>7</sub> HN <sub>3</sub> O <sub>3</sub>                | 8.84  | 0.95 | 175.0018 | C <sub>9</sub> H <sub>6</sub> NO <sub>3</sub>                | 10.32 | 1.08 | 176.0348 |
| C <sub>14</sub> H <sub>5</sub>                               | 15.21 | 1.07 | 173.0391 | C <sub>7</sub> H <sub>19</sub> N <sub>4</sub> O              | 9.43  | 0.60 | 175.1560 | C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 10.69 | 0.92 | 176.0586 |
| 174  |       |      |          | C <sub>7</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>  | 9.22  | 0.78 | 175.0257 | C <sub>9</sub> H <sub>10</sub> N <sub>3</sub> O              | 11.07 | 0.76 | 176.0825 |
| C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> | 7.56  | 1.05 | 174.0641 | C <sub>8</sub> H <sub>15</sub> O <sub>4</sub>                | 9.04  | 1.16 | 175.0970 | C <sub>9</sub> H <sub>12</sub> N <sub>4</sub>                | 11.44 | 0.60 | 176.1063 |
| C <sub>6</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> | 7.94  | 0.88 | 174.0879 | C <sub>8</sub> H <sub>17</sub> NO <sub>3</sub>               | 9.42  | 1.00 | 175.1209 | C <sub>10</sub> H <sub>8</sub> O <sub>3</sub>                | 11.05 | 1.15 | 176.0473 |
| C <sub>6</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> | 8.31  | 0.71 | 174.1118 | C <sub>8</sub> HN <sub>4</sub> O <sub>4</sub>                | 9.20  | 1.18 | 174.9905 | C <sub>10</sub> H <sub>10</sub> NO <sub>2</sub>              | 11.43 | 0.99 | 176.0712 |
| C <sub>7</sub> H <sub>12</sub> NO <sub>4</sub>               | 8.29  | 1.10 | 174.0766 | C <sub>8</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub> | 9.79  | 0.83 | 175.1447 | C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O             | 11.80 | 0.84 | 176.0950 |
| C <sub>7</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> | 8.67  | 0.93 | 174.1005 | C <sub>8</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 9.57  | 1.01 | 175.0144 | C <sub>10</sub> H <sub>14</sub> N <sub>3</sub>               | 12.17 | 0.68 | 176.1189 |
| C <sub>7</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub> | 9.04  | 0.77 | 174.1244 | C <sub>8</sub> H <sub>21</sub> N <sub>3</sub> O              | 10.16 | 0.67 | 175.1686 | C <sub>10</sub> N <sub>4</sub>                               | 12.33 | 0.70 | 176.0124 |
| C <sub>7</sub> N <sub>3</sub> O <sub>3</sub>                 | 8.83  | 0.95 | 173.9940 | C <sub>8</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>  | 9.95  | 0.85 | 175.0382 | C <sub>11</sub> H <sub>12</sub> O <sub>2</sub>               | 12.16 | 1.08 | 176.0837 |
| C <sub>7</sub> H <sub>18</sub> N <sub>4</sub> O              | 9.42  | 0.60 | 174.1482 | C <sub>8</sub> H <sub>7</sub> N <sub>4</sub> O               | 10.32 | 0.68 | 175.0621 | C <sub>11</sub> H <sub>14</sub> NO                           | 12.53 | 0.92 | 176.1076 |
| C <sub>7</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>  | 9.20  | 0.78 | 174.0178 | C <sub>9</sub> H <sub>19</sub> O <sub>3</sub>                | 10.15 | 1.06 | 175.1334 | C <sub>11</sub> H <sub>16</sub> N <sub>2</sub>               | 12.91 | 0.77 | 176.1315 |
| C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>                | 9.03  | 1.16 | 174.0892 | C <sub>9</sub> H <sub>3</sub> O <sub>4</sub>                 | 9.93  | 1.24 | 175.0031 | C <sub>11</sub> N <sub>2</sub> O                             | 12.69 | 0.94 | 176.0011 |
| C <sub>8</sub> H <sub>16</sub> NO <sub>3</sub>               | 9.40  | 1.00 | 174.1131 | C <sub>9</sub> H <sub>21</sub> NO <sub>2</sub>               | 10.52 | 0.90 | 175.1573 | C <sub>11</sub> H <sub>2</sub> N <sub>3</sub>                | 13.06 | 0.79 | 176.0249 |
| C <sub>8</sub> NO <sub>4</sub>                               | 9.18  | 1.18 | 173.9827 | C <sub>9</sub> H <sub>5</sub> NO <sub>3</sub>                | 10.30 | 1.08 | 175.0269 | C <sub>12</sub> H <sub>16</sub> O                            | 13.26 | 1.01 | 176.1202 |
| C <sub>8</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> | 9.77  | 0.83 | 174.1369 | C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>  | 10.68 | 0.92 | 175.0508 | C <sub>12</sub> O <sub>2</sub>                               | 13.05 | 1.18 | 175.9898 |
| C <sub>8</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>  | 9.56  | 1.01 | 174.0065 | C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> O               | 11.05 | 0.76 | 175.0746 | C <sub>12</sub> H <sub>18</sub> N                            | 13.64 | 0.86 | 176.1440 |
| C <sub>8</sub> H <sub>20</sub> N <sub>3</sub> O              | 10.15 | 0.67 | 174.1608 | C <sub>9</sub> H <sub>11</sub> N <sub>4</sub>                | 11.43 | 0.60 | 175.0985 | C <sub>12</sub> H <sub>2</sub> NO                            | 13.42 | 1.03 | 176.0136 |
| C <sub>8</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>  | 9.93  | 0.85 | 174.0304 | C <sub>10</sub> H <sub>7</sub> O <sub>3</sub>                | 11.04 | 1.15 | 175.0395 | C <sub>12</sub> H <sub>4</sub> N <sub>2</sub>                | 13.79 | 0.88 | 176.0375 |
| C <sub>8</sub> H <sub>22</sub> N <sub>4</sub>                | 10.52 | 0.50 | 174.1846 | C <sub>10</sub> H <sub>9</sub> NO <sub>2</sub>               | 11.41 | 0.99 | 175.0634 | C <sub>13</sub> H <sub>20</sub>                              | 14.37 | 0.96 | 176.1566 |
| C <sub>8</sub> H <sub>6</sub> N <sub>4</sub> O               | 10.31 | 0.68 | 174.0542 | C <sub>10</sub> H <sub>11</sub> N <sub>2</sub> O             | 11.78 | 0.83 | 175.0872 | C <sub>13</sub> H <sub>4</sub> O                             | 14.15 | 1.13 | 176.0262 |
| C <sub>9</sub> H <sub>18</sub> O <sub>3</sub>                | 10.13 | 1.06 | 174.1256 | C <sub>10</sub> H <sub>13</sub> N <sub>3</sub>               | 12.16 | 0.68 | 175.1111 | C <sub>13</sub> H <sub>6</sub> N                             | 14.53 | 0.98 | 176.0501 |
| C <sub>9</sub> H <sub>2</sub> O <sub>4</sub>                 | 9.91  | 1.24 | 173.9953 | C <sub>11</sub> H <sub>11</sub> O <sub>2</sub>               | 12.14 | 1.07 | 175.0759 | C <sub>14</sub> H <sub>8</sub>                               | 15.26 | 1.08 | 176.0626 |
| C <sub>9</sub> H <sub>20</sub> NO <sub>2</sub>               | 10.51 | 0.90 | 174.1495 | C <sub>11</sub> H <sub>13</sub> NO                           | 12.52 | 0.92 | 175.0998 | 177  |       |      |          |
| C <sub>9</sub> H <sub>4</sub> NO <sub>3</sub>                | 10.29 | 1.08 | 174.0191 | C <sub>11</sub> H <sub>15</sub> N <sub>2</sub>               | 12.89 | 0.77 | 175.1236 | C <sub>6</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> | 7.61  | 1.06 | 177.0876 |
| C <sub>9</sub> H <sub>22</sub> N <sub>2</sub> O              | 10.88 | 0.74 | 174.1733 | C <sub>11</sub> HN <sub>3</sub>                              | 13.05 | 0.78 | 175.0171 | C <sub>6</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> | 7.99  | 0.88 | 177.1114 |
| C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 10.66 | 0.92 | 174.0429 | C <sub>12</sub> H <sub>15</sub> O                            | 13.25 | 1.01 | 175.1123 | C <sub>6</sub> H <sub>17</sub> N <sub>4</sub> O <sub>2</sub> | 8.36  | 0.71 | 177.1353 |
| C <sub>9</sub> H <sub>8</sub> N <sub>3</sub> O               | 11.04 | 0.75 | 174.0668 | C <sub>12</sub> H <sub>17</sub> N                            | 13.62 | 0.86 | 175.1362 | C <sub>7</sub> H <sub>15</sub> NO <sub>4</sub>               | 8.34  | 1.11 | 177.1001 |
| C <sub>9</sub> H <sub>10</sub> N <sub>4</sub>                | 11.41 | 0.60 | 174.0907 | C <sub>12</sub> HN <sub>4</sub> O                            | 13.40 | 1.03 | 175.0058 | C <sub>7</sub> H <sub>17</sub> N <sub>2</sub> O <sub>3</sub> | 8.72  | 0.94 | 177.1240 |
| C <sub>10</sub> H <sub>22</sub> O <sub>2</sub>               | 11.24 | 0.97 | 174.1620 | C <sub>12</sub> H <sub>3</sub> N <sub>2</sub>                | 13.78 | 0.88 | 175.0297 | C <sub>7</sub> HN <sub>2</sub> O <sub>4</sub>                | 8.50  | 1.12 | 176.9936 |
| C <sub>10</sub> H <sub>6</sub> O <sub>3</sub>                | 11.02 | 1.15 | 174.0317 | C <sub>13</sub> H <sub>19</sub>                              | 14.35 | 0.95 | 175.1488 | C <sub>7</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> | 9.09  | 0.77 | 177.1478 |
| C <sub>10</sub> H <sub>8</sub> NO <sub>2</sub>               | 11.39 | 0.99 | 174.0555 | C <sub>13</sub> H <sub>3</sub> O                             | 14.13 | 1.12 | 175.0184 | C <sub>7</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>  | 8.87  | 0.95 | 177.0175 |
| C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O             | 11.77 | 0.83 | 174.0794 | C <sub>13</sub> H <sub>5</sub> N                             | 14.51 | 0.98 | 175.0422 | C <sub>7</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>  | 9.25  | 0.78 | 177.0413 |
| C <sub>10</sub> H <sub>12</sub> N <sub>3</sub>               | 12.14 | 0.68 | 174.1032 | C <sub>14</sub> H <sub>7</sub>                               | 15.24 | 1.08 | 175.0548 | C <sub>8</sub> H <sub>17</sub> O <sub>4</sub>                | 9.07  | 1.17 | 177.1127 |
| C <sub>11</sub> H <sub>10</sub> O <sub>2</sub>               | 12.12 | 1.07 | 174.0681 | 176  |       |      |          | C <sub>8</sub> H <sub>19</sub> NO <sub>3</sub>               | 9.45  | 1.00 | 177.1365 |
| C <sub>11</sub> H <sub>12</sub> NO                           | 12.50 | 0.92 | 174.0919 | C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> | 7.59  | 1.05 | 176.0797 | C <sub>8</sub> H <sub>3</sub> NO <sub>4</sub>                | 9.23  | 1.18 | 177.0062 |
| C <sub>11</sub> H <sub>14</sub> N <sub>2</sub>               | 12.87 | 0.76 | 174.1158 | C <sub>6</sub> H <sub>14</sub> N <sub>3</sub> O <sub>3</sub> | 7.97  | 0.88 | 176.1036 | C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>  | 9.60  | 1.01 | 177.0300 |
| C <sub>11</sub> N <sub>3</sub>                               | 13.03 | 0.78 | 174.0093 | C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> | 8.34  | 0.71 | 176.1275 | C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>  | 9.98  | 0.85 | 177.0539 |
| C <sub>12</sub> H <sub>14</sub> O                            | 13.23 | 1.01 | 174.1045 | C <sub>7</sub> H <sub>14</sub> NO <sub>4</sub>               | 8.33  | 1.11 | 176.0923 | C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O               | 10.35 | 0.69 | 177.0777 |
|  |       |      |          | C <sub>7</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> | 8.70  | 0.94 | 176.1162 |  |       |      |          |

|  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|--|-------|------|----------|--|-------|------|----------|--|-------|------|----------|
| C <sub>9</sub> H <sub>5</sub> O <sub>4</sub>                 | 9.96  | 1.25 | 177.0187 | C <sub>11</sub> H <sub>2</sub> N <sub>2</sub> O              | 12.72 | 0.94 | 178.0167 | C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 9.65  | 1.02 | 180.0535 |
| C <sub>9</sub> H <sub>7</sub> NO <sub>3</sub>                | 10.34 | 1.08 | 177.0426 | C <sub>11</sub> H <sub>4</sub> N <sub>3</sub>                | 13.09 | 0.79 | 178.0406 | C <sub>8</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub> | 10.03 | 0.85 | 180.0774 |
| C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 10.71 | 0.92 | 177.0664 | C <sub>12</sub> H <sub>18</sub> O                            | 13.29 | 1.01 | 178.1358 | C <sub>8</sub> H <sub>12</sub> N <sub>4</sub> O              | 10.40 | 0.69 | 180.1012 |
| C <sub>9</sub> H <sub>11</sub> N <sub>3</sub> O              | 11.08 | 0.76 | 177.0903 | C <sub>12</sub> H <sub>2</sub> O <sub>2</sub>                | 13.08 | 1.19 | 178.0054 | C <sub>9</sub> H <sub>8</sub> O <sub>4</sub>                 | 10.01 | 1.25 | 180.0422 |
| C <sub>9</sub> H <sub>13</sub> N <sub>4</sub>                | 11.46 | 0.60 | 177.1142 | C <sub>12</sub> H <sub>20</sub> N                            | 13.67 | 0.86 | 178.1597 | C <sub>9</sub> H <sub>10</sub> NO <sub>3</sub>               | 10.38 | 1.09 | 180.0661 |
| C <sub>10</sub> H <sub>9</sub> O <sub>3</sub>                | 11.07 | 1.16 | 177.0552 | C <sub>12</sub> H <sub>4</sub> NO                            | 13.45 | 1.03 | 178.0293 | C <sub>9</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | 10.76 | 0.93 | 180.0899 |
| C <sub>10</sub> H <sub>11</sub> NO <sub>2</sub>              | 11.44 | 1.00 | 177.0790 | C <sub>12</sub> H <sub>6</sub> N <sub>2</sub>                | 13.83 | 0.88 | 178.0532 | C <sub>9</sub> H <sub>14</sub> N <sub>3</sub> O              | 11.13 | 0.77 | 180.1138 |
| C <sub>10</sub> H <sub>13</sub> N <sub>2</sub> O             | 11.82 | 0.84 | 177.1029 | C <sub>13</sub> H <sub>22</sub>                              | 14.40 | 0.96 | 178.1722 | C <sub>9</sub> H <sub>16</sub> N <sub>4</sub>                | 11.51 | 0.61 | 180.1377 |
| C <sub>10</sub> H <sub>15</sub> N <sub>3</sub>               | 12.19 | 0.68 | 177.1267 | C <sub>13</sub> H <sub>6</sub> O                             | 14.18 | 1.13 | 178.0419 | C <sub>9</sub> N <sub>4</sub> O                              | 11.29 | 0.78 | 180.0073 |
| C <sub>10</sub> HN <sub>4</sub>                              | 12.35 | 0.70 | 177.0202 | C <sub>13</sub> H <sub>8</sub> N                             | 14.56 | 0.98 | 178.0657 | C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>               | 11.12 | 1.16 | 180.0786 |
| C <sub>11</sub> H <sub>13</sub> O <sub>2</sub>               | 12.17 | 1.08 | 177.0916 | C <sub>14</sub> H <sub>10</sub>                              | 15.29 | 1.09 | 178.0783 | C <sub>10</sub> H <sub>14</sub> NO <sub>2</sub>              | 11.49 | 1.00 | 180.1025 |
| C <sub>11</sub> H <sub>15</sub> NO                           | 12.55 | 0.92 | 177.1154 | 179  |       |      |          | C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O             | 11.86 | 0.84 | 180.1264 |
| C <sub>11</sub> H <sub>17</sub> N <sub>2</sub>               | 12.92 | 0.77 | 177.1393 | C <sub>6</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub> | 7.64  | 1.06 | 179.1032 | C <sub>10</sub> N <sub>2</sub> O <sub>2</sub>                | 11.65 | 1.02 | 179.9960 |
| C <sub>11</sub> HN <sub>2</sub> O                            | 12.70 | 0.94 | 177.0089 | C <sub>6</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> | 8.02  | 0.89 | 179.1271 | C <sub>10</sub> H <sub>18</sub> N <sub>3</sub>               | 12.24 | 0.69 | 180.1502 |
| C <sub>11</sub> H <sub>3</sub> N <sub>3</sub>                | 13.08 | 0.79 | 177.0328 | C <sub>7</sub> H <sub>17</sub> NO <sub>4</sub>               | 8.37  | 1.11 | 179.1158 | C <sub>10</sub> H <sub>2</sub> N <sub>3</sub> O              | 12.02 | 0.86 | 180.0198 |
| C <sub>12</sub> H <sub>17</sub> O                            | 13.28 | 1.01 | 177.1280 | C <sub>7</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>  | 8.53  | 1.12 | 179.0093 | C <sub>10</sub> H <sub>4</sub> N <sub>4</sub>                | 12.40 | 0.71 | 180.0437 |
| C <sub>12</sub> HO <sub>2</sub>                              | 13.06 | 1.18 | 176.9976 | C <sub>7</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>  | 8.91  | 0.95 | 179.0331 | C <sub>11</sub> H <sub>16</sub> O <sub>2</sub>               | 12.22 | 1.08 | 180.1151 |
| C <sub>12</sub> H <sub>19</sub> N                            | 13.65 | 0.86 | 177.1519 | C <sub>7</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>  | 9.28  | 0.79 | 179.0570 | C <sub>11</sub> O <sub>3</sub>                               | 12.00 | 1.26 | 179.9847 |
| C <sub>12</sub> H <sub>3</sub> NO                            | 13.44 | 1.03 | 177.0215 | C <sub>8</sub> H <sub>5</sub> NO <sub>4</sub>                | 9.26  | 1.18 | 179.0218 | C <sub>11</sub> H <sub>18</sub> NO                           | 12.60 | 0.93 | 180.1389 |
| C <sub>12</sub> H <sub>5</sub> N <sub>2</sub>                | 13.81 | 0.88 | 177.0453 | C <sub>8</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>  | 9.64  | 1.02 | 179.0457 | C <sub>11</sub> H <sub>2</sub> NO <sub>2</sub>               | 12.38 | 1.10 | 180.0085 |
| C <sub>13</sub> H <sub>21</sub>                              | 14.38 | 0.96 | 177.1644 | C <sub>8</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>  | 10.01 | 0.85 | 179.0695 | C <sub>11</sub> H <sub>20</sub> N <sub>2</sub>               | 12.97 | 0.78 | 180.1628 |
| C <sub>13</sub> H <sub>5</sub> O                             | 14.17 | 1.13 | 177.0340 | C <sub>8</sub> H <sub>11</sub> N <sub>4</sub> O              | 10.39 | 0.69 | 179.0934 | C <sub>11</sub> H <sub>4</sub> N <sub>2</sub> O              | 12.75 | 0.95 | 180.0324 |
| C <sub>13</sub> H <sub>7</sub> N                             | 14.54 | 0.98 | 177.0579 | C <sub>9</sub> H <sub>7</sub> O <sub>4</sub>                 | 9.99  | 1.25 | 179.0344 | C <sub>11</sub> H <sub>6</sub> N <sub>3</sub>                | 13.13 | 0.80 | 180.0563 |
| C <sub>14</sub> H <sub>9</sub>                               | 15.27 | 1.08 | 177.0705 | C <sub>9</sub> H <sub>9</sub> NO <sub>3</sub>                | 10.37 | 1.09 | 179.0583 | C <sub>12</sub> H <sub>20</sub> O                            | 13.33 | 1.02 | 180.1515 |
| 178  |       |      |          | C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 10.74 | 0.92 | 179.0821 | C <sub>12</sub> H <sub>4</sub> O <sub>2</sub>                | 13.11 | 1.19 | 180.0211 |
| C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> | 7.63  | 1.06 | 178.0954 | C <sub>9</sub> H <sub>13</sub> N <sub>3</sub> O              | 11.12 | 0.76 | 179.1060 | C <sub>12</sub> H <sub>22</sub> N                            | 13.70 | 0.87 | 180.1753 |
| C <sub>6</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> | 8.00  | 0.88 | 178.1193 | C <sub>9</sub> H <sub>15</sub> N <sub>4</sub>                | 11.49 | 0.60 | 179.1298 | C <sub>12</sub> H <sub>6</sub> NO                            | 13.48 | 1.04 | 180.0449 |
| C <sub>6</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> | 8.38  | 0.71 | 178.1431 | C <sub>10</sub> H <sub>11</sub> O <sub>3</sub>               | 11.10 | 1.16 | 179.0708 | C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>                | 13.86 | 0.89 | 180.0688 |
| C <sub>7</sub> H <sub>16</sub> NO <sub>4</sub>               | 8.36  | 1.11 | 178.1080 | C <sub>10</sub> H <sub>13</sub> NO <sub>2</sub>              | 11.47 | 1.00 | 179.0947 | C <sub>13</sub> H <sub>24</sub>                              | 14.43 | 0.97 | 180.1879 |
| C <sub>7</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> | 8.73  | 0.94 | 178.1318 | C <sub>10</sub> H <sub>15</sub> N <sub>2</sub> O             | 11.85 | 0.84 | 179.1185 | C <sub>13</sub> H <sub>8</sub> O                             | 14.21 | 1.13 | 180.0575 |
| C <sub>7</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 8.52  | 1.12 | 178.0014 | C <sub>10</sub> H <sub>17</sub> N <sub>3</sub>               | 12.22 | 0.69 | 179.1424 | C <sub>13</sub> H <sub>10</sub> N                            | 14.59 | 0.99 | 180.0814 |
| C <sub>7</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>  | 8.89  | 0.95 | 178.0253 | C <sub>10</sub> HN <sub>3</sub> O                            | 12.01 | 0.86 | 179.0120 | C <sub>14</sub> H <sub>12</sub>                              | 15.32 | 1.09 | 180.0939 |
| C <sub>7</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 9.26  | 0.79 | 178.0491 | C <sub>10</sub> H <sub>3</sub> N <sub>4</sub>                | 12.38 | 0.71 | 179.0359 | C <sub>15</sub>  | 16.21 | 1.23 | 180.0000 |
| C <sub>8</sub> H <sub>18</sub> O <sub>4</sub>                | 9.09  | 1.17 | 178.1205 | C <sub>11</sub> H <sub>15</sub> O <sub>2</sub>               | 12.20 | 1.08 | 179.1072 | 181  |       |      |          |
| C <sub>8</sub> H <sub>4</sub> NO <sub>4</sub>                | 9.25  | 1.18 | 178.0140 | C <sub>11</sub> H <sub>17</sub> NO                           | 12.58 | 0.93 | 179.1311 | C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>  | 8.56  | 1.13 | 181.0249 |
| C <sub>8</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 9.62  | 1.02 | 178.0379 | C <sub>11</sub> HN <sub>2</sub> O                            | 12.36 | 1.10 | 179.0007 | C <sub>7</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>  | 8.94  | 0.96 | 181.0488 |
| C <sub>8</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 10.00 | 0.85 | 178.0617 | C <sub>11</sub> H <sub>19</sub> N <sub>2</sub>               | 12.95 | 0.77 | 179.1549 | C <sub>7</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>  | 9.31  | 0.79 | 181.0726 |
| C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O              | 10.37 | 0.69 | 178.0856 | C <sub>11</sub> H <sub>3</sub> N <sub>2</sub> O              | 12.74 | 0.95 | 179.0246 | C <sub>8</sub> H <sub>7</sub> NO <sub>4</sub>                | 9.29  | 1.19 | 181.0375 |
| C <sub>9</sub> H <sub>6</sub> O <sub>4</sub>                 | 9.98  | 1.25 | 178.0266 | C <sub>11</sub> H <sub>5</sub> N <sub>3</sub>                | 13.11 | 0.79 | 179.0484 | C <sub>8</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>  | 9.67  | 1.02 | 181.0614 |
| C <sub>9</sub> H <sub>8</sub> NO <sub>3</sub>                | 10.35 | 1.08 | 178.0504 | C <sub>12</sub> H <sub>19</sub> O                            | 13.31 | 1.02 | 179.1436 | C <sub>8</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> | 10.04 | 0.86 | 181.0852 |
| C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 10.73 | 0.92 | 178.0743 | C <sub>12</sub> H <sub>3</sub> O <sub>2</sub>                | 13.09 | 1.19 | 179.0133 | C <sub>8</sub> H <sub>13</sub> N <sub>4</sub> O              | 10.42 | 0.69 | 181.1091 |
| C <sub>9</sub> H <sub>12</sub> N <sub>3</sub> O              | 11.10 | 0.76 | 178.0981 | C <sub>12</sub> H <sub>21</sub> N                            | 13.68 | 0.87 | 179.1675 | C <sub>9</sub> H <sub>9</sub> O <sub>4</sub>                 | 10.03 | 1.25 | 181.0501 |
| C <sub>9</sub> H <sub>14</sub> N <sub>4</sub>                | 11.48 | 0.60 | 178.1220 | C <sub>12</sub> H <sub>5</sub> NO                            | 13.47 | 1.04 | 179.0371 | C <sub>9</sub> H <sub>11</sub> NO <sub>3</sub>               | 10.40 | 1.09 | 181.0739 |
| C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>               | 11.08 | 1.16 | 178.0630 | C <sub>12</sub> H <sub>7</sub> N <sub>2</sub>                | 13.84 | 0.89 | 179.0610 | C <sub>9</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> | 10.77 | 0.93 | 181.0978 |
| C <sub>10</sub> H <sub>12</sub> NO <sub>2</sub>              | 11.46 | 1.00 | 178.0868 | C <sub>13</sub> H <sub>23</sub>                              | 14.42 | 0.96 | 179.1801 | C <sub>9</sub> H <sub>15</sub> N <sub>3</sub> O              | 11.15 | 0.77 | 181.1216 |
| C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O             | 11.83 | 0.84 | 178.1107 | C <sub>13</sub> H <sub>7</sub> O                             | 14.20 | 1.13 | 179.0497 | C <sub>9</sub> H <sub>17</sub> N <sub>4</sub>                | 11.52 | 0.61 | 181.1455 |
| C <sub>10</sub> H <sub>16</sub> N <sub>3</sub>               | 12.21 | 0.68 | 178.1346 | C <sub>13</sub> H <sub>9</sub> N                             | 14.57 | 0.99 | 179.0736 | C <sub>9</sub> HN <sub>4</sub> O                             | 11.31 | 0.78 | 181.0151 |
| C <sub>10</sub> N <sub>3</sub> O                             | 11.99 | 0.86 | 178.0042 | C <sub>14</sub> H <sub>11</sub>                              | 15.30 | 1.09 | 179.0861 | C <sub>10</sub> H <sub>13</sub> O <sub>3</sub>               | 11.13 | 1.16 | 181.0865 |
| C <sub>10</sub> H <sub>2</sub> N <sub>4</sub>                | 12.36 | 0.70 | 178.0280 | 180  |       |      |          | C <sub>10</sub> H <sub>15</sub> NO <sub>2</sub>              | 11.51 | 1.00 | 181.1103 |
| C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>               | 12.19 | 1.08 | 178.0994 | C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> | 7.66  | 1.06 | 180.1111 | C <sub>10</sub> H <sub>17</sub> N <sub>2</sub> O             | 11.88 | 0.85 | 181.1342 |
| C <sub>11</sub> H <sub>16</sub> NO                           | 12.56 | 0.92 | 178.1233 | C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>  | 8.55  | 1.12 | 180.0171 | C <sub>10</sub> HN <sub>2</sub> O <sub>2</sub>               | 11.66 | 1.02 | 181.0038 |
| C <sub>11</sub> NO <sub>2</sub>                              | 12.35 | 1.10 | 177.9929 | C <sub>7</sub> H <sub>6</sub> N <sub>3</sub> O <sub>3</sub>  | 8.92  | 0.96 | 180.0410 | C <sub>10</sub> H <sub>19</sub> N <sub>3</sub>               | 12.25 | 0.69 | 181.1580 |
| C <sub>11</sub> H <sub>18</sub> N <sub>2</sub>               | 12.94 | 0.77 | 178.1471 | C <sub>7</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>  | 9.30  | 0.79 | 180.0648 | C <sub>10</sub> H <sub>3</sub> N <sub>3</sub> O              | 12.04 | 0.86 | 181.0277 |
|  |       |      |          | C <sub>8</sub> H <sub>6</sub> NO <sub>4</sub>                | 9.28  | 1.18 | 180.0297 |  |       |      |          |



|  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|--|-------|------|----------|--|-------|------|----------|--|-------|------|----------|
| C <sub>10</sub> H <sub>5</sub> N <sub>4</sub>                | 12.41 | 0.71 | 181.0515 | C <sub>13</sub> H <sub>26</sub>                              | 14.46 | 0.97 | 182.2036 | C <sub>8</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> | 10.09 | 0.86 | 184.1087 |
| C <sub>11</sub> H <sub>17</sub> O <sub>2</sub>               | 12.24 | 1.09 | 181.1229 | C <sub>13</sub> H <sub>10</sub> O                            | 14.25 | 1.14 | 182.0732 | C <sub>8</sub> H <sub>16</sub> N <sub>4</sub> O              | 10.47 | 0.70 | 184.1325 |
| C <sub>11</sub> H <sub>19</sub> NO                           | 12.02 | 1.26 | 180.9925 | C <sub>13</sub> H <sub>12</sub> N                            | 14.62 | 0.99 | 182.0970 | C <sub>8</sub> N <sub>4</sub> O <sub>2</sub>                 | 10.25 | 0.88 | 184.0022 |
| C <sub>11</sub> H <sub>3</sub> N <sub>2</sub> O              | 12.61 | 0.93 | 181.1467 | C <sub>14</sub> H <sub>14</sub>                              | 15.35 | 1.10 | 182.1096 | C <sub>9</sub> H <sub>12</sub> O <sub>4</sub>                | 10.07 | 1.26 | 184.0735 |
| C <sub>11</sub> H <sub>21</sub> N <sub>2</sub>               | 12.39 | 1.10 | 181.0164 | C <sub>14</sub> N  | 15.51 | 1.12 | 182.0031 | C <sub>9</sub> H <sub>14</sub> N <sub>3</sub> O              | 10.45 | 1.09 | 184.0974 |
| C <sub>11</sub> H <sub>5</sub> N <sub>2</sub> O              | 12.99 | 0.78 | 181.1706 | C <sub>15</sub> H <sub>2</sub>                               | 16.24 | 1.23 | 182.0157 | C <sub>9</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> | 10.82 | 0.93 | 184.1213 |
| C <sub>11</sub> H <sub>7</sub> N <sub>3</sub>                | 12.77 | 0.95 | 181.0402 | 183  |       |      |          | C <sub>9</sub> N <sub>2</sub> O <sub>3</sub>                 | 10.61 | 1.11 | 183.9909 |
| C <sub>12</sub> H <sub>21</sub> O                            | 13.14 | 0.80 | 181.0641 | C <sub>7</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub>  | 8.60  | 1.13 | 183.0406 | C <sub>9</sub> H <sub>18</sub> N <sub>3</sub> O              | 11.20 | 0.77 | 184.1451 |
| C <sub>12</sub> H <sub>5</sub> O <sub>2</sub>                | 13.34 | 1.02 | 181.1593 | C <sub>7</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>  | 8.97  | 0.96 | 183.0644 | C <sub>9</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>  | 10.98 | 0.95 | 184.0147 |
| C <sub>12</sub> H <sub>23</sub> N                            | 13.13 | 1.19 | 181.0289 | C <sub>7</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> | 9.34  | 0.79 | 183.0883 | C <sub>9</sub> H <sub>20</sub> N <sub>4</sub>                | 11.57 | 0.61 | 184.1690 |
| C <sub>12</sub> H <sub>7</sub> NO                            | 13.72 | 0.87 | 181.1832 | C <sub>8</sub> H <sub>9</sub> NO <sub>4</sub>                | 9.33  | 1.19 | 183.0532 | C <sub>9</sub> H <sub>4</sub> N <sub>4</sub> O               | 11.35 | 0.79 | 184.0386 |
| C <sub>12</sub> H <sub>9</sub> N <sub>2</sub>                | 13.50 | 1.04 | 181.0528 | C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> | 9.70  | 1.02 | 183.0770 | C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>               | 11.18 | 1.17 | 184.1100 |
| C <sub>13</sub> H <sub>25</sub>                              | 13.87 | 0.89 | 181.0767 | C <sub>8</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> | 10.08 | 0.86 | 183.1009 | C <sub>10</sub> O <sub>4</sub>                               | 10.96 | 1.34 | 183.9796 |
| C <sub>13</sub> H <sub>9</sub> O                             | 14.45 | 0.97 | 181.1957 | C <sub>8</sub> H <sub>15</sub> N <sub>4</sub> O              | 10.45 | 0.70 | 183.1247 | C <sub>10</sub> H <sub>18</sub> NO <sub>2</sub>              | 11.55 | 1.01 | 184.1338 |
| C <sub>13</sub> H <sub>11</sub> N                            | 14.23 | 1.14 | 181.0653 | C <sub>9</sub> H <sub>11</sub> O <sub>4</sub>                | 10.06 | 1.26 | 183.0657 | C <sub>10</sub> H <sub>2</sub> NO <sub>3</sub>               | 11.34 | 1.18 | 184.0034 |
| C <sub>14</sub> H <sub>13</sub>                              | 14.61 | 0.99 | 181.0892 | C <sub>9</sub> H <sub>13</sub> NO <sub>3</sub>               | 10.43 | 1.09 | 183.0896 | C <sub>10</sub> H <sub>20</sub> N <sub>2</sub> O             | 11.93 | 0.85 | 184.1577 |
| C <sub>15</sub> H  | 15.34 | 1.09 | 181.1018 | C <sub>9</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> | 10.81 | 0.93 | 183.1134 | C <sub>10</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> | 11.71 | 1.03 | 184.0273 |
| 182  | 16.22 | 1.23 | 181.0078 | C <sub>9</sub> H <sub>17</sub> N <sub>3</sub> O              | 11.18 | 0.77 | 183.1373 | C <sub>10</sub> H <sub>22</sub> N <sub>3</sub>               | 12.30 | 0.70 | 184.1815 |
| C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>  |       |      |          | C <sub>9</sub> HN <sub>3</sub> O <sub>2</sub>                | 10.96 | 0.95 | 183.0069 | C <sub>10</sub> H <sub>6</sub> N <sub>3</sub> O              | 12.09 | 0.87 | 184.0511 |
| C <sub>7</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>  | 8.58  | 1.13 | 182.0328 | C <sub>9</sub> H <sub>19</sub> N <sub>4</sub>                | 11.56 | 0.61 | 183.1611 | C <sub>10</sub> H <sub>8</sub> N <sub>4</sub>                | 12.46 | 0.71 | 184.0750 |
| C <sub>7</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> | 8.95  | 0.96 | 182.0566 | C <sub>9</sub> H <sub>3</sub> N <sub>4</sub> O               | 11.34 | 0.79 | 183.0308 | C <sub>11</sub> H <sub>20</sub> O <sub>2</sub>               | 12.28 | 1.09 | 184.1464 |
| C <sub>8</sub> H <sub>8</sub> NO <sub>4</sub>                | 9.33  | 0.79 | 182.0805 | C <sub>10</sub> H <sub>15</sub> O <sub>3</sub>               | 11.16 | 1.17 | 183.1021 | C <sub>11</sub> H <sub>4</sub> O <sub>3</sub>                | 12.07 | 1.27 | 184.0160 |
| C <sub>8</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 9.31  | 1.19 | 182.0453 | C <sub>10</sub> H <sub>17</sub> NO <sub>2</sub>              | 11.54 | 1.01 | 183.1260 | C <sub>11</sub> H <sub>22</sub> NO                           | 12.66 | 0.94 | 184.1702 |
| C <sub>8</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> | 9.69  | 1.02 | 182.0692 | C <sub>10</sub> HN <sub>3</sub> O                            | 11.32 | 1.18 | 182.9956 | C <sub>11</sub> H <sub>6</sub> NO <sub>2</sub>               | 12.44 | 1.11 | 184.0399 |
| C <sub>8</sub> H <sub>14</sub> N <sub>4</sub> O              | 10.06 | 0.86 | 182.0930 | C <sub>10</sub> H <sub>19</sub> N <sub>2</sub> O             | 11.91 | 0.85 | 183.1498 | C <sub>11</sub> H <sub>24</sub> N <sub>2</sub>               | 13.03 | 0.78 | 184.1941 |
| C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>                | 10.43 | 0.70 | 182.1169 | C <sub>10</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub> | 11.70 | 1.02 | 183.0195 | C <sub>11</sub> H <sub>8</sub> N <sub>2</sub> O              | 12.82 | 0.96 | 184.0637 |
| C <sub>9</sub> H <sub>12</sub> NO <sub>3</sub>               | 10.04 | 1.25 | 182.0579 | C <sub>10</sub> H <sub>21</sub> N <sub>3</sub>               | 12.29 | 0.69 | 183.1737 | C <sub>11</sub> H <sub>10</sub> N <sub>3</sub>               | 13.19 | 0.80 | 184.0876 |
| C <sub>9</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> | 10.42 | 1.09 | 182.0817 | C <sub>10</sub> H <sub>5</sub> N <sub>3</sub> O              | 12.07 | 0.87 | 183.0433 | C <sub>12</sub> H <sub>24</sub> O                            | 13.39 | 1.03 | 184.1828 |
| C <sub>9</sub> H <sub>16</sub> N <sub>3</sub> O              | 10.79 | 0.93 | 182.1056 | C <sub>10</sub> H <sub>7</sub> N <sub>4</sub>                | 12.44 | 0.71 | 183.0672 | C <sub>12</sub> H <sub>8</sub> O <sub>2</sub>                | 13.17 | 1.20 | 184.0524 |
| C <sub>9</sub> N <sub>3</sub> O <sub>2</sub>                 | 11.16 | 0.77 | 182.1295 | C <sub>11</sub> H <sub>19</sub> O <sub>2</sub>               | 12.27 | 1.09 | 183.1385 | C <sub>12</sub> H <sub>26</sub> N                            | 13.76 | 0.88 | 184.2067 |
| C <sub>9</sub> H <sub>18</sub> N <sub>4</sub>                | 10.95 | 0.95 | 181.9991 | C <sub>11</sub> H <sub>3</sub> O <sub>3</sub>                | 12.05 | 1.26 | 183.0082 | C <sub>12</sub> H <sub>10</sub> NO                           | 13.55 | 1.05 | 184.0763 |
| C <sub>9</sub> H <sub>2</sub> N <sub>4</sub> O               | 11.54 | 0.61 | 182.1533 | C <sub>11</sub> H <sub>21</sub> NO                           | 12.64 | 0.93 | 183.1624 | C <sub>12</sub> H <sub>12</sub> N <sub>2</sub>               | 13.92 | 0.90 | 184.1001 |
| C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>               | 11.32 | 0.79 | 182.0229 | C <sub>11</sub> H <sub>5</sub> NO <sub>2</sub>               | 12.43 | 1.11 | 183.0320 | C <sub>13</sub> H <sub>28</sub>                              | 14.50 | 0.97 | 184.2192 |
| C <sub>10</sub> H <sub>16</sub> NO <sub>2</sub>              | 11.15 | 1.16 | 182.0943 | C <sub>11</sub> H <sub>23</sub> N <sub>2</sub>               | 13.02 | 0.78 | 183.1863 | C <sub>13</sub> H <sub>12</sub> O                            | 14.28 | 1.14 | 184.0888 |
| C <sub>10</sub> NO <sub>3</sub>                              | 11.52 | 1.01 | 182.1182 | C <sub>11</sub> H <sub>7</sub> N <sub>2</sub> O              | 12.80 | 0.95 | 183.0559 | C <sub>13</sub> H <sub>14</sub> N                            | 14.65 | 1.00 | 184.1127 |
| C <sub>10</sub> H <sub>18</sub> N <sub>2</sub> O             | 11.30 | 1.18 | 181.9878 | C <sub>11</sub> H <sub>9</sub> N <sub>3</sub>                | 13.17 | 0.80 | 183.0798 | C <sub>13</sub> N <sub>2</sub>                               | 14.81 | 1.02 | 184.0062 |
| C <sub>10</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> | 11.90 | 0.85 | 182.1420 | C <sub>12</sub> H <sub>23</sub> O                            | 13.37 | 1.02 | 183.1750 | C <sub>14</sub> H <sub>16</sub>                              | 15.38 | 1.10 | 184.1253 |
| C <sub>10</sub> H <sub>4</sub> N <sub>3</sub> O              | 11.68 | 1.02 | 182.0116 | C <sub>12</sub> H <sub>7</sub> O <sub>2</sub>                | 13.16 | 1.20 | 183.0446 | C <sub>14</sub> O  | 15.17 | 1.27 | 183.9949 |
| C <sub>10</sub> H <sub>6</sub> N <sub>4</sub>                | 12.27 | 0.69 | 182.1659 | C <sub>12</sub> H <sub>25</sub> N                            | 13.75 | 0.87 | 183.1988 | C <sub>14</sub> H <sub>2</sub> N                             | 15.54 | 1.13 | 184.0187 |
| C <sub>11</sub> H <sub>18</sub> O <sub>2</sub>               | 12.05 | 0.87 | 182.0355 | C <sub>12</sub> H <sub>9</sub> NO                            | 13.53 | 1.05 | 183.0684 | C <sub>15</sub> H <sub>4</sub>                               | 16.27 | 1.24 | 184.0313 |
| C <sub>11</sub> H <sub>2</sub> O <sub>3</sub>                | 12.43 | 0.71 | 182.0594 | C <sub>12</sub> H <sub>11</sub> N <sub>2</sub>               | 13.91 | 0.90 | 183.0923 | 185  |       |      |          |
| C <sub>11</sub> H <sub>4</sub> NO <sub>2</sub>               | 12.25 | 1.09 | 182.1307 | C <sub>13</sub> H <sub>27</sub>                              | 14.48 | 0.97 | 183.2114 | C <sub>7</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>  | 8.63  | 1.13 | 185.0563 |
| C <sub>11</sub> H <sub>20</sub> NO                           | 12.04 | 1.26 | 182.0003 | C <sub>13</sub> H <sub>11</sub> O                            | 14.26 | 1.14 | 183.0810 | C <sub>7</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> | 9.00  | 0.96 | 185.0801 |
| C <sub>11</sub> H <sub>22</sub> N <sub>2</sub>               | 12.63 | 0.93 | 182.1546 | C <sub>13</sub> H <sub>13</sub> N                            | 14.64 | 0.99 | 183.1049 | C <sub>7</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> | 9.38  | 0.80 | 185.1040 |
| C <sub>11</sub> H <sub>6</sub> N <sub>2</sub> O              | 12.41 | 1.11 | 182.0242 | C <sub>14</sub> H <sub>15</sub>                              | 15.37 | 1.10 | 183.1174 | C <sub>8</sub> H <sub>11</sub> NO <sub>4</sub>               | 9.36  | 1.19 | 185.0688 |
| C <sub>12</sub> H <sub>22</sub> O                            | 13.00 | 0.78 | 182.1784 | C <sub>14</sub> HN   | 15.53 | 1.12 | 183.0109 | C <sub>8</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> | 9.73  | 1.03 | 185.0927 |
| C <sub>12</sub> H <sub>5</sub> O <sub>2</sub>                | 12.78 | 0.95 | 182.0480 | C <sub>15</sub> H <sub>3</sub>                               | 16.26 | 1.23 | 183.0235 | C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> | 10.11 | 0.86 | 185.1165 |
| C <sub>12</sub> H <sub>7</sub> NO                            | 13.16 | 0.80 | 182.0719 | 184  |       |      |          | C <sub>8</sub> H <sub>17</sub> N <sub>4</sub> O              | 10.48 | 0.70 | 185.1404 |
| C <sub>12</sub> H <sub>9</sub> NO                            | 13.36 | 1.02 | 182.1671 | C <sub>7</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>  | 8.61  | 1.13 | 184.0484 | C <sub>8</sub> HN <sub>4</sub> O <sub>2</sub>                | 10.26 | 0.88 | 185.0100 |
| C <sub>12</sub> H <sub>24</sub> N                            | 13.14 | 1.19 | 182.0368 | C <sub>7</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> | 8.99  | 0.96 | 184.0723 | C <sub>9</sub> H <sub>13</sub> O <sub>4</sub>                | 10.09 | 1.26 | 185.0814 |
| C <sub>12</sub> H <sub>8</sub> NO                            | 13.73 | 0.87 | 182.1910 | C <sub>7</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> | 9.36  | 0.80 | 184.0961 | C <sub>9</sub> H <sub>15</sub> NO <sub>3</sub>               | 10.46 | 1.10 | 185.1052 |
| C <sub>12</sub> H <sub>10</sub> N <sub>2</sub>               | 13.52 | 1.04 | 182.0606 | C <sub>8</sub> H <sub>10</sub> NO <sub>4</sub>               | 9.34  | 1.19 | 184.0610 | C <sub>9</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> | 10.84 | 0.93 | 185.1291 |
|  | 13.89 | 0.89 | 182.0845 | C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> | 9.72  | 1.03 | 184.0848 | C <sub>9</sub> HN <sub>2</sub> O <sub>3</sub>                | 10.62 | 1.11 | 184.9987 |



|   | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|---|-------|------|----------|--|-------|------|----------|--|-------|------|----------|
| C <sub>9</sub> H <sub>19</sub> N <sub>3</sub> O               | 11.21 | 0.77 | 185.1529 | C <sub>10</sub> H <sub>20</sub> N <sub>2</sub> O             | 11.59 | 1.01 | 186.1495 | C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> O              | 12.13 | 0.88 | 187.0746 |
| C <sub>9</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>   | 11.00 | 0.95 | 185.0226 | C <sub>10</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub> | 11.37 | 1.19 | 186.0191 | C <sub>10</sub> H <sub>11</sub> N <sub>4</sub>               | 12.51 | 0.72 | 187.0985 |
| C <sub>9</sub> H <sub>21</sub> N <sub>4</sub>                 | 11.59 | 0.62 | 185.1768 | C <sub>10</sub> H <sub>22</sub> N <sub>2</sub> O             | 11.96 | 0.86 | 186.1733 | C <sub>11</sub> H <sub>23</sub> O <sub>2</sub>               | 12.33 | 1.10 | 187.1699 |
| C <sub>9</sub> H <sub>5</sub> N <sub>4</sub> O                | 11.37 | 0.79 | 185.0464 | C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> | 11.74 | 1.03 | 186.0429 | C <sub>11</sub> H <sub>7</sub> O <sub>3</sub>                | 12.12 | 1.27 | 187.0395 |
| C <sub>10</sub> H <sub>17</sub> O <sub>3</sub>                | 11.20 | 1.17 | 185.1178 | C <sub>10</sub> H <sub>24</sub> N <sub>3</sub>               | 12.33 | 0.70 | 186.1972 | C <sub>11</sub> H <sub>25</sub> N <sub>2</sub> O             | 12.71 | 0.94 | 187.1937 |
| C <sub>10</sub> H <sub>2</sub> O <sub>4</sub>                 | 10.98 | 1.35 | 184.9874 | C <sub>10</sub> H <sub>8</sub> N <sub>3</sub> O              | 12.12 | 0.87 | 186.0668 | C <sub>11</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub> | 12.49 | 1.12 | 187.0634 |
| C <sub>10</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub> | 11.57 | 1.01 | 185.1416 | C <sub>10</sub> H <sub>10</sub> N <sub>4</sub>               | 12.49 | 0.72 | 186.0907 | C <sub>11</sub> H <sub>11</sub> N <sub>2</sub> O             | 12.86 | 0.96 | 187.0872 |
| C <sub>10</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 11.35 | 1.19 | 185.0113 | C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>               | 12.32 | 1.10 | 186.1620 | C <sub>11</sub> H <sub>13</sub> N <sub>3</sub>               | 13.24 | 0.81 | 187.1111 |
| C <sub>10</sub> H <sub>21</sub> N <sub>2</sub> O              | 11.94 | 0.85 | 185.1655 | C <sub>11</sub> H <sub>6</sub> O <sub>3</sub>                | 12.10 | 1.27 | 186.0317 | C <sub>12</sub> H <sub>11</sub> O <sub>2</sub>               | 13.22 | 1.20 | 187.0759 |
| C <sub>10</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>  | 11.73 | 1.03 | 185.0351 | C <sub>11</sub> H <sub>24</sub> N <sub>2</sub> O             | 12.69 | 0.94 | 186.1859 | C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O             | 13.60 | 1.05 | 187.0998 |
| C <sub>10</sub> H <sub>23</sub> N <sub>3</sub>                | 12.32 | 0.70 | 185.1894 | C <sub>11</sub> H <sub>8</sub> N <sub>2</sub> O              | 12.47 | 1.11 | 186.0555 | C <sub>12</sub> H <sub>15</sub> N <sub>2</sub>               | 13.97 | 0.90 | 187.1236 |
| C <sub>10</sub> H <sub>7</sub> N <sub>3</sub> O               | 12.10 | 0.87 | 185.0590 | C <sub>11</sub> H <sub>26</sub> N <sub>2</sub>               | 13.07 | 0.79 | 186.2098 | C <sub>12</sub> HN <sub>3</sub>                              | 14.13 | 0.93 | 187.0171 |
| C <sub>10</sub> H <sub>9</sub> N <sub>4</sub>                 | 12.48 | 0.72 | 185.0829 | C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O             | 12.85 | 0.96 | 186.0794 | C <sub>13</sub> H <sub>15</sub> O                            | 14.33 | 1.15 | 187.1123 |
| C <sub>11</sub> H <sub>21</sub> O <sub>2</sub>                | 12.30 | 1.09 | 185.1542 | C <sub>11</sub> H <sub>12</sub> N <sub>3</sub>               | 13.22 | 0.81 | 186.1032 | C <sub>13</sub> H <sub>17</sub> N                            | 14.70 | 1.00 | 187.1362 |
| C <sub>11</sub> H <sub>5</sub> O <sub>3</sub>                 | 12.08 | 1.27 | 185.0238 | C <sub>12</sub> H <sub>26</sub> O                            | 13.42 | 1.03 | 186.1985 | C <sub>13</sub> HN <sub>2</sub> O                            | 14.48 | 1.17 | 187.0058 |
| C <sub>11</sub> H <sub>23</sub> N <sub>2</sub> O              | 12.68 | 0.94 | 185.1781 | C <sub>12</sub> H <sub>10</sub> O <sub>2</sub>               | 13.21 | 1.20 | 186.0681 | C <sub>13</sub> H <sub>3</sub> N <sub>2</sub>                | 14.86 | 1.03 | 187.0297 |
| C <sub>11</sub> H <sub>7</sub> N <sub>2</sub> O               | 12.46 | 1.11 | 185.0477 | C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O             | 13.58 | 1.05 | 186.0919 | C <sub>14</sub> H <sub>19</sub>                              | 15.43 | 1.11 | 187.1488 |
| C <sub>11</sub> H <sub>25</sub> N <sub>2</sub>                | 13.05 | 0.79 | 185.2019 | C <sub>12</sub> H <sub>14</sub> N <sub>2</sub>               | 13.95 | 0.90 | 186.1158 | C <sub>14</sub> H <sub>3</sub> O                             | 15.22 | 1.28 | 187.0184 |
| C <sub>11</sub> H <sub>9</sub> N <sub>2</sub> O               | 12.83 | 0.96 | 185.0715 | C <sub>12</sub> N <sub>3</sub>                               | 14.11 | 0.92 | 186.0093 | C <sub>14</sub> H <sub>5</sub> N                             | 15.59 | 1.13 | 187.0422 |
| C <sub>11</sub> H <sub>11</sub> N <sub>3</sub>                | 13.21 | 0.81 | 185.0954 | C <sub>13</sub> H <sub>14</sub> O                            | 14.31 | 1.15 | 186.1045 | C <sub>15</sub> H <sub>7</sub>                               | 16.32 | 1.24 | 187.0548 |
| C <sub>12</sub> H <sub>25</sub> O                             | 13.41 | 1.03 | 185.1906 | C <sub>13</sub> H <sub>16</sub> N                            | 14.69 | 1.00 | 186.1284 |  |       |      |          |
| C <sub>12</sub> H <sub>9</sub> O <sub>2</sub>                 | 13.19 | 1.20 | 185.0603 | C <sub>13</sub> N <sub>2</sub> O                             | 14.47 | 1.17 | 185.9980 | C <sub>7</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> | 8.68  | 1.14 | 188.0797 |
| C <sub>12</sub> H <sub>27</sub> N                             | 13.78 | 0.88 | 185.2145 | C <sub>13</sub> H <sub>2</sub> N <sub>2</sub>                | 14.84 | 1.02 | 186.0218 | C <sub>7</sub> H <sub>14</sub> N <sub>3</sub> O <sub>3</sub> | 9.05  | 0.97 | 188.1036 |
| C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O              | 13.56 | 1.05 | 185.0841 | C <sub>14</sub> H <sub>18</sub>                              | 15.42 | 1.11 | 186.1409 | C <sub>7</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> | 9.42  | 0.80 | 188.1275 |
| C <sub>12</sub> H <sub>13</sub> N <sub>2</sub>                | 13.94 | 0.90 | 185.1080 | C <sub>14</sub> H <sub>2</sub> O                             | 15.20 | 1.27 | 186.0106 | C <sub>8</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> | 9.41  | 1.20 | 188.0923 |
| C <sub>13</sub> H <sub>13</sub> O                             | 14.29 | 1.15 | 185.0967 | C <sub>14</sub> H <sub>4</sub> N                             | 15.57 | 1.13 | 186.0344 | C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> | 9.78  | 1.03 | 188.1162 |
| C <sub>13</sub> H <sub>15</sub> N                             | 14.67 | 1.00 | 185.1205 | C <sub>15</sub> H <sub>6</sub>                               | 16.30 | 1.24 | 186.0470 | C <sub>8</sub> N <sub>2</sub> O <sub>4</sub>                 | 9.56  | 1.21 | 187.9858 |
| C <sub>13</sub> HN <sub>2</sub>                               | 14.83 | 1.02 | 185.0140 |  |       |      |          | C <sub>8</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> | 10.16 | 0.87 | 188.1400 |
| C <sub>14</sub> H <sub>17</sub>                               | 15.40 | 1.10 | 185.1331 | 187  |       |      |          | C <sub>8</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>  | 9.94  | 1.05 | 188.0096 |
| C <sub>14</sub> HO  | 15.18 | 1.27 | 185.0027 | C <sub>7</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> | 8.66  | 1.13 | 187.0719 | C <sub>8</sub> H <sub>20</sub> N <sub>4</sub> O              | 10.53 | 0.71 | 188.1639 |
| C <sub>14</sub> H <sub>3</sub> N                              | 15.56 | 1.13 | 185.0266 | C <sub>7</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> | 9.03  | 0.97 | 187.0958 | C <sub>8</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>  | 10.31 | 0.88 | 188.0335 |
| C <sub>15</sub> H <sub>5</sub>                                | 16.29 | 1.24 | 185.0391 | C <sub>7</sub> H <sub>15</sub> N <sub>4</sub> O <sub>2</sub> | 9.41  | 0.80 | 187.1196 | C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>                | 10.14 | 1.26 | 188.1049 |
|   |       |      |          | C <sub>8</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> | 9.39  | 1.20 | 187.0845 | C <sub>9</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> | 10.51 | 1.10 | 188.1287 |
| 186   |       |      |          | C <sub>8</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub> | 9.77  | 1.03 | 187.1083 | C <sub>9</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 10.30 | 1.28 | 187.9983 |
| C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub>  | 8.64  | 1.13 | 186.0641 | C <sub>8</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> | 10.14 | 0.87 | 187.1322 | C <sub>9</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> | 10.89 | 0.94 | 188.1526 |
| C <sub>7</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub>  | 9.02  | 0.96 | 186.0879 | C <sub>8</sub> HN <sub>3</sub> O <sub>3</sub>                | 9.92  | 1.04 | 187.0018 | C <sub>9</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 10.67 | 1.12 | 188.0222 |
| C <sub>7</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>  | 9.39  | 0.80 | 186.1118 | C <sub>8</sub> H <sub>19</sub> N <sub>4</sub> O              | 10.51 | 0.70 | 187.1560 | C <sub>9</sub> H <sub>22</sub> N <sub>3</sub> O              | 11.26 | 0.78 | 188.1764 |
| C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>  | 9.37  | 1.19 | 186.0766 | C <sub>8</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>  | 10.30 | 0.88 | 187.0257 | C <sub>9</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>  | 11.04 | 0.96 | 188.0460 |
| C <sub>8</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>  | 9.75  | 1.03 | 186.1005 | C <sub>9</sub> H <sub>15</sub> O <sub>4</sub>                | 10.12 | 1.26 | 187.0970 | C <sub>9</sub> H <sub>24</sub> N <sub>4</sub>                | 11.64 | 0.62 | 188.2003 |
| C <sub>8</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub>  | 10.12 | 0.86 | 186.1244 | C <sub>9</sub> H <sub>17</sub> N <sub>2</sub> O <sub>3</sub> | 10.50 | 1.10 | 187.1209 | C <sub>9</sub> H <sub>8</sub> N <sub>4</sub> O               | 11.42 | 0.80 | 188.0699 |
| C <sub>8</sub> N <sub>3</sub> O <sub>3</sub>                  | 9.91  | 1.04 | 185.9940 | C <sub>9</sub> HN <sub>2</sub> O <sub>4</sub>                | 10.28 | 1.28 | 186.9905 | C <sub>10</sub> H <sub>20</sub> O <sub>3</sub>               | 11.24 | 1.18 | 188.1413 |
| C <sub>8</sub> H <sub>18</sub> N <sub>4</sub> O               | 10.50 | 0.70 | 186.1482 | C <sub>9</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub> | 10.87 | 0.94 | 187.1447 | C <sub>10</sub> H <sub>4</sub> O <sub>4</sub>                | 11.03 | 1.35 | 188.0109 |
| C <sub>8</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>   | 10.28 | 0.88 | 186.0178 | C <sub>9</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 10.65 | 1.11 | 187.0144 | C <sub>10</sub> H <sub>12</sub> N <sub>4</sub>               | 12.52 | 0.72 | 188.1063 |
| C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>                 | 10.11 | 1.26 | 186.0892 | C <sub>9</sub> H <sub>21</sub> N <sub>3</sub> O              | 11.24 | 0.78 | 187.1686 | C <sub>11</sub> H <sub>24</sub> O <sub>2</sub>               | 12.35 | 1.10 | 188.1777 |
| C <sub>9</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>  | 10.48 | 1.10 | 186.1131 | C <sub>9</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>  | 11.03 | 0.95 | 187.0382 | C <sub>11</sub> H <sub>6</sub> O <sub>3</sub>                | 12.13 | 1.27 | 188.0473 |
| C <sub>9</sub> N <sub>2</sub> O <sub>4</sub>                  | 10.26 | 1.28 | 185.9827 | C <sub>9</sub> H <sub>23</sub> N <sub>4</sub>                | 11.62 | 0.62 | 187.1925 | C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O             | 12.51 | 1.12 | 188.0712 |
| C <sub>9</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>  | 10.85 | 0.94 | 186.1369 | C <sub>9</sub> H <sub>7</sub> N <sub>4</sub> O               | 11.40 | 0.80 | 187.0621 | C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O             | 12.88 | 0.96 | 188.0950 |
| C <sub>9</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>   | 10.64 | 1.11 | 186.0065 | C <sub>10</sub> H <sub>19</sub> O <sub>3</sub>               | 11.23 | 1.17 | 187.1334 | C <sub>11</sub> H <sub>14</sub> N <sub>3</sub>               | 13.25 | 0.81 | 188.1189 |
| C <sub>9</sub> H <sub>20</sub> N <sub>3</sub> O               | 11.23 | 0.78 | 186.1608 | C <sub>10</sub> H <sub>3</sub> O <sub>4</sub>                | 11.01 | 1.35 | 187.0031 |  |       |      |          |
| C <sub>9</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>   | 11.01 | 0.95 | 186.0304 | C <sub>10</sub> H <sub>21</sub> N <sub>2</sub> O             | 11.60 | 1.01 | 187.1573 |  |       |      |          |
| C <sub>9</sub> H <sub>22</sub> N <sub>4</sub>                 | 11.60 | 0.62 | 186.1846 | C <sub>10</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub> | 11.38 | 1.19 | 187.0269 |  |       |      |          |
| C <sub>9</sub> H <sub>6</sub> N <sub>4</sub> O                | 11.39 | 0.79 | 186.0542 | C <sub>10</sub> H <sub>23</sub> N <sub>2</sub> O             | 11.98 | 0.86 | 187.1811 |  |       |      |          |
| C <sub>10</sub> H <sub>18</sub> O <sub>3</sub>                | 11.21 | 1.17 | 186.1256 | C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> | 11.76 | 1.03 | 187.0508 |  |       |      |          |
| C <sub>10</sub> H <sub>2</sub> O <sub>4</sub>                 | 10.99 | 1.35 | 185.9953 | C <sub>10</sub> H <sub>25</sub> N <sub>3</sub>               | 12.35 | 0.70 | 187.2050 |  |       |      |          |

|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>11</sub> N <sub>4</sub>                                | 13.41 | 0.83 | 188.0124 | C <sub>13</sub> H <sub>19</sub> N                             | 14.73 | 1.01 | 189.1519 | C <sub>7</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub>  | 9.10  | 0.97 | 191.1271 |
| C <sub>12</sub> H <sub>12</sub> O <sub>2</sub>                | 13.24 | 1.21 | 188.0837 | C <sub>13</sub> H <sub>3</sub> N <sub>3</sub> O               | 14.52 | 1.18 | 189.0215 | C <sub>7</sub> H <sub>19</sub> N <sub>4</sub> O <sub>2</sub>  | 9.47  | 0.81 | 191.1509 |
| C <sub>12</sub> H <sub>14</sub> N <sub>3</sub> O              | 13.61 | 1.06 | 188.1076 | C <sub>13</sub> H <sub>5</sub> N <sub>2</sub>                 | 14.89 | 1.03 | 189.0453 | C <sub>8</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub>  | 9.45  | 1.20 | 191.1158 |
| C <sub>12</sub> H <sub>16</sub> N <sub>2</sub>                | 13.99 | 0.91 | 188.1315 | C <sub>14</sub> H <sub>21</sub>                               | 15.46 | 1.11 | 189.1644 | C <sub>8</sub> H <sub>19</sub> N <sub>2</sub> O <sub>3</sub>  | 9.83  | 1.04 | 191.1396 |
| C <sub>12</sub> N <sub>2</sub> O                              | 13.77 | 1.08 | 188.0011 | C <sub>14</sub> H <sub>5</sub> O                              | 15.25 | 1.28 | 189.0340 | C <sub>8</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>   | 9.61  | 1.22 | 191.0093 |
| C <sub>12</sub> H <sub>2</sub> N <sub>3</sub>                 | 14.14 | 0.93 | 188.0249 | C <sub>14</sub> H <sub>7</sub> N                              | 15.62 | 1.14 | 189.0579 | C <sub>8</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub>  | 10.20 | 0.87 | 191.1635 |
| C <sub>13</sub> H <sub>16</sub> O                             | 14.34 | 1.15 | 188.1202 | C <sub>15</sub> H <sub>9</sub>                                | 16.35 | 1.25 | 189.0705 | C <sub>8</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>   | 9.99  | 1.05 | 191.0331 |
| C <sub>13</sub> O <sub>2</sub>                                | 14.13 | 1.32 | 187.9896 | 190   |       |      |          | C <sub>8</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>   | 10.36 | 0.89 | 191.0570 |
| C <sub>13</sub> H <sub>18</sub> N                             | 14.72 | 1.01 | 188.1440 | C <sub>7</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>  | 8.71  | 1.14 | 190.0954 | C <sub>9</sub> H <sub>19</sub> O <sub>4</sub>                 | 10.19 | 1.27 | 191.1284 |
| C <sub>13</sub> H <sub>2</sub> N <sub>3</sub> O               | 14.50 | 1.18 | 188.0136 | C <sub>7</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub>  | 9.08  | 0.97 | 190.1193 | C <sub>9</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub>  | 10.56 | 1.11 | 191.1522 |
| C <sub>13</sub> H <sub>4</sub> N <sub>2</sub>                 | 14.87 | 1.03 | 188.0375 | C <sub>7</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>  | 9.46  | 0.80 | 190.1431 | C <sub>9</sub> H <sub>5</sub> N <sub>3</sub> O <sub>4</sub>   | 10.34 | 1.28 | 191.0218 |
| C <sub>14</sub> H <sub>20</sub>                               | 15.45 | 1.11 | 188.1566 | C <sub>8</sub> H <sub>16</sub> N <sub>3</sub> O <sub>4</sub>  | 9.44  | 1.20 | 190.1080 | C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>   | 10.72 | 1.12 | 191.0457 |
| C <sub>14</sub> H <sub>4</sub> O                              | 15.23 | 1.28 | 188.0262 | C <sub>8</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>  | 9.81  | 1.03 | 190.1318 | C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>   | 11.09 | 0.96 | 191.0695 |
| C <sub>14</sub> H <sub>6</sub> N                              | 15.61 | 1.14 | 188.0501 | C <sub>8</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>   | 9.60  | 1.21 | 190.0014 | C <sub>9</sub> H <sub>11</sub> N <sub>4</sub> O               | 11.47 | 0.80 | 191.0934 |
| C <sub>15</sub> H <sub>8</sub>                                | 16.34 | 1.25 | 188.0626 | C <sub>8</sub> H <sub>20</sub> N <sub>3</sub> O <sub>2</sub>  | 10.19 | 0.87 | 190.1557 | C <sub>10</sub> H <sub>7</sub> O <sub>4</sub>                 | 11.07 | 1.36 | 191.0344 |
| 189   |       |      |          | C <sub>8</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>   | 9.97  | 1.05 | 190.0253 | C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> O               | 11.45 | 1.20 | 191.0583 |
| C <sub>7</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub>  | 8.69  | 1.14 | 189.0876 | C <sub>8</sub> H <sub>22</sub> N <sub>4</sub> O               | 10.56 | 0.71 | 190.1795 | C <sub>10</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 11.82 | 1.04 | 191.0821 |
| C <sub>7</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub>  | 9.07  | 0.97 | 189.1114 | C <sub>8</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>   | 10.34 | 0.89 | 190.0491 | C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O              | 12.20 | 0.88 | 191.1060 |
| C <sub>7</sub> H <sub>17</sub> N <sub>4</sub> O <sub>2</sub>  | 9.44  | 0.80 | 189.1353 | C <sub>9</sub> H <sub>18</sub> O <sub>4</sub>                 | 10.17 | 1.27 | 190.1205 | C <sub>10</sub> H <sub>15</sub> N <sub>4</sub>                | 12.57 | 0.73 | 191.1298 |
| C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub>  | 9.42  | 1.20 | 189.1001 | C <sub>9</sub> H <sub>20</sub> N <sub>3</sub> O               | 10.54 | 1.10 | 190.1444 | C <sub>11</sub> H <sub>11</sub> O <sub>3</sub>                | 12.18 | 1.28 | 191.0708 |
| C <sub>8</sub> H <sub>17</sub> N <sub>2</sub> O <sub>3</sub>  | 9.80  | 1.03 | 189.1240 | C <sub>9</sub> H <sub>4</sub> N <sub>3</sub> O <sub>4</sub>   | 10.33 | 1.28 | 190.0140 | C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> | 12.55 | 1.12 | 191.0947 |
| C <sub>8</sub> HN <sub>2</sub> O <sub>4</sub>                 | 9.58  | 1.21 | 188.9936 | C <sub>9</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>  | 10.92 | 0.94 | 190.1682 | C <sub>11</sub> H <sub>15</sub> N <sub>2</sub> O              | 12.93 | 0.97 | 191.1185 |
| C <sub>8</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub>  | 10.17 | 0.87 | 189.1478 | C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>   | 10.70 | 1.12 | 190.0379 | C <sub>11</sub> H <sub>17</sub> N <sub>3</sub>                | 13.30 | 0.82 | 191.1424 |
| C <sub>8</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>   | 9.95  | 1.05 | 189.0175 | C <sub>9</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>   | 11.08 | 0.96 | 190.0617 | C <sub>11</sub> HN <sub>3</sub> O                             | 13.09 | 0.99 | 191.0120 |
| C <sub>8</sub> H <sub>21</sub> N <sub>4</sub> O               | 10.55 | 0.71 | 189.1717 | C <sub>9</sub> H <sub>10</sub> N <sub>4</sub> O               | 11.45 | 0.80 | 190.0856 | C <sub>11</sub> H <sub>3</sub> N <sub>4</sub>                 | 13.46 | 0.84 | 191.0359 |
| C <sub>8</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>   | 10.33 | 0.88 | 189.0413 | C <sub>10</sub> H <sub>22</sub> O <sub>3</sub>                | 11.28 | 1.18 | 190.1569 | C <sub>12</sub> H <sub>15</sub> O <sub>2</sub>                | 13.29 | 1.21 | 191.1072 |
| C <sub>9</sub> H <sub>17</sub> O <sub>4</sub>                 | 10.15 | 1.26 | 189.1127 | C <sub>10</sub> H <sub>6</sub> O <sub>4</sub>                 | 11.06 | 1.35 | 190.0266 | C <sub>12</sub> H <sub>17</sub> N <sub>3</sub> O              | 13.66 | 1.06 | 191.1311 |
| C <sub>9</sub> H <sub>19</sub> N <sub>3</sub> O               | 10.53 | 1.10 | 189.1365 | C <sub>10</sub> H <sub>8</sub> N <sub>3</sub> O               | 11.43 | 1.20 | 190.0504 | C <sub>12</sub> HN <sub>3</sub> O <sub>2</sub>                | 13.44 | 1.23 | 191.0007 |
| C <sub>9</sub> H <sub>3</sub> N <sub>3</sub> O <sub>4</sub>   | 10.31 | 1.28 | 189.0062 | C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 11.81 | 1.04 | 190.0743 | C <sub>12</sub> H <sub>19</sub> N <sub>2</sub>                | 14.03 | 0.91 | 191.1549 |
| C <sub>9</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub>  | 10.90 | 0.94 | 189.1604 | C <sub>10</sub> H <sub>12</sub> N <sub>3</sub> O              | 12.18 | 0.88 | 190.0981 | C <sub>12</sub> H <sub>3</sub> N <sub>2</sub> O               | 13.82 | 1.08 | 191.0246 |
| C <sub>9</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>   | 10.69 | 1.12 | 189.0300 | C <sub>10</sub> H <sub>14</sub> N <sub>4</sub>                | 12.56 | 0.73 | 190.1220 | C <sub>12</sub> H <sub>5</sub> N <sub>3</sub>                 | 14.19 | 0.93 | 191.0484 |
| C <sub>9</sub> H <sub>23</sub> N <sub>3</sub> O               | 11.28 | 0.78 | 189.1842 | C <sub>11</sub> H <sub>10</sub> O <sub>3</sub>                | 12.16 | 1.28 | 190.0630 | C <sub>13</sub> H <sub>19</sub> O                             | 14.39 | 1.16 | 191.1436 |
| C <sub>9</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>   | 11.06 | 0.96 | 189.0539 | C <sub>11</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> | 12.54 | 1.12 | 190.0868 | C <sub>13</sub> H <sub>3</sub> O <sub>2</sub>                 | 14.17 | 1.33 | 191.0133 |
| C <sub>9</sub> H <sub>9</sub> N <sub>4</sub> O                | 11.43 | 0.80 | 189.0777 | C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O              | 12.91 | 0.97 | 190.1107 | C <sub>13</sub> H <sub>21</sub> N                             | 14.77 | 1.01 | 191.1675 |
| C <sub>10</sub> H <sub>21</sub> O <sub>3</sub>                | 11.26 | 1.18 | 189.1491 | C <sub>11</sub> H <sub>16</sub> N <sub>3</sub>                | 13.29 | 0.82 | 190.1346 | C <sub>13</sub> H <sub>5</sub> N <sub>3</sub> O               | 14.55 | 1.18 | 191.0371 |
| C <sub>10</sub> H <sub>5</sub> O <sub>4</sub>                 | 11.04 | 1.35 | 189.0187 | C <sub>11</sub> N <sub>3</sub> O                              | 13.07 | 0.99 | 190.0042 | C <sub>13</sub> H <sub>7</sub> N <sub>2</sub>                 | 14.92 | 1.04 | 191.0610 |
| C <sub>10</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub> | 11.63 | 1.02 | 189.1730 | C <sub>11</sub> H <sub>2</sub> N <sub>4</sub>                 | 13.44 | 0.84 | 190.0280 | C <sub>14</sub> H <sub>23</sub>                               | 15.50 | 1.12 | 191.1801 |
| C <sub>10</sub> H <sub>7</sub> N <sub>3</sub> O               | 11.42 | 1.19 | 189.0426 | C <sub>12</sub> H <sub>14</sub> O <sub>2</sub>                | 13.27 | 1.21 | 190.0994 | C <sub>14</sub> H <sub>7</sub> O                              | 15.28 | 1.29 | 191.0497 |
| C <sub>10</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 11.79 | 1.04 | 189.0664 | C <sub>12</sub> H <sub>16</sub> N <sub>3</sub> O              | 13.64 | 1.06 | 190.1233 | C <sub>14</sub> H <sub>9</sub> N                              | 15.65 | 1.14 | 191.0736 |
| C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O              | 12.17 | 0.88 | 189.0903 | C <sub>12</sub> N <sub>3</sub> O <sub>2</sub>                 | 13.43 | 1.23 | 189.9929 | C <sub>15</sub> H <sub>11</sub>                               | 16.39 | 1.25 | 191.0861 |
| C <sub>10</sub> H <sub>13</sub> N <sub>4</sub>                | 12.54 | 0.72 | 189.1142 | C <sub>12</sub> H <sub>18</sub> N <sub>2</sub>                | 14.02 | 0.91 | 190.1471 | 192   |       |      |          |
| C <sub>11</sub> H <sub>9</sub> O <sub>3</sub>                 | 12.15 | 1.28 | 189.0552 | C <sub>12</sub> H <sub>2</sub> N <sub>2</sub> O               | 13.80 | 1.08 | 190.0167 | C <sub>7</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>  | 8.74  | 1.14 | 192.1111 |
| C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> | 12.52 | 1.12 | 189.0790 | C <sub>12</sub> H <sub>4</sub> N <sub>3</sub>                 | 14.18 | 0.93 | 190.0406 | C <sub>7</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub>  | 9.11  | 0.97 | 192.1349 |
| C <sub>11</sub> H <sub>13</sub> N <sub>2</sub> O              | 12.90 | 0.97 | 189.1029 | C <sub>13</sub> H <sub>18</sub> O                             | 14.37 | 1.16 | 190.1358 | C <sub>7</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>  | 9.49  | 0.81 | 192.1588 |
| C <sub>11</sub> H <sub>15</sub> N <sub>3</sub>                | 13.27 | 0.81 | 189.1267 | C <sub>13</sub> H <sub>2</sub> O <sub>2</sub>                 | 14.16 | 1.33 | 190.0054 | C <sub>8</sub> H <sub>18</sub> N <sub>3</sub> O <sub>4</sub>  | 9.47  | 1.20 | 192.1236 |
| C <sub>11</sub> HN <sub>4</sub>                               | 13.43 | 0.83 | 189.0202 | C <sub>13</sub> H <sub>20</sub> N                             | 14.75 | 1.01 | 190.1597 | C <sub>8</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>  | 9.85  | 1.04 | 192.1475 |
| C <sub>12</sub> H <sub>13</sub> O <sub>2</sub>                | 13.25 | 1.21 | 189.0916 | C <sub>13</sub> H <sub>4</sub> N <sub>3</sub> O               | 14.53 | 1.18 | 190.0293 | C <sub>8</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>   | 9.63  | 1.22 | 192.0171 |
| C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O              | 13.63 | 1.06 | 189.1154 | C <sub>13</sub> H <sub>6</sub> N <sub>2</sub>                 | 14.91 | 1.03 | 190.0532 | C <sub>8</sub> H <sub>6</sub> N <sub>3</sub> O <sub>3</sub>   | 10.00 | 1.05 | 192.0410 |
| C <sub>12</sub> H <sub>17</sub> N <sub>2</sub>                | 14.00 | 0.91 | 189.1393 | C <sub>14</sub> H <sub>22</sub>                               | 15.48 | 1.12 | 190.1722 | C <sub>8</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>   | 10.38 | 0.89 | 192.0648 |
| C <sub>12</sub> HN <sub>2</sub> O                             | 13.79 | 1.08 | 189.0089 | C <sub>14</sub> H <sub>6</sub> O                              | 15.26 | 1.28 | 190.0419 | C <sub>9</sub> H <sub>20</sub> O <sub>4</sub>                 | 10.20 | 1.27 | 192.1362 |
| C <sub>12</sub> H <sub>3</sub> N <sub>3</sub>                 | 14.16 | 0.93 | 189.0328 | C <sub>14</sub> H <sub>8</sub> N                              | 15.64 | 1.14 | 190.0657 | C <sub>9</sub> H <sub>6</sub> N <sub>3</sub> O <sub>4</sub>   | 10.36 | 1.29 | 192.0297 |
| C <sub>13</sub> H <sub>17</sub> O                             | 14.36 | 1.16 | 189.1280 | C <sub>15</sub> H <sub>10</sub>                               | 16.37 | 1.25 | 190.0783 | C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>   | 10.73 | 1.12 | 192.0535 |
| C <sub>13</sub> H <sub>3</sub> O <sub>2</sub>                 | 14.14 | 1.33 | 188.9976 | 191   |       |      |          | C <sub>9</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub>  | 11.11 | 0.96 | 192.0774 |
|   |       |      |          | C <sub>7</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub>  | 8.72  | 1.14 | 191.1032 |   |       |      |          |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |  | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|--|-------|------|----------|
| C <sub>9</sub> H <sub>12</sub> N <sub>4</sub> O                             | 11.48 | 0.80 | 192.1012 | C <sub>11</sub> H <sub>3</sub> N <sub>3</sub> O                             | 13.12 | 0.99 | 193.0277 | C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O                            | 14.60 | 1.19 | 194.0606 |
| C <sub>10</sub> H <sub>8</sub> O <sub>4</sub>                               | 11.09 | 1.36 | 192.0422 | C <sub>11</sub> H <sub>5</sub> N <sub>4</sub>                               | 13.49 | 0.84 | 193.0515 | C <sub>13</sub> H <sub>10</sub> N <sub>2</sub>                             | 14.97 | 1.04 | 194.0845 |
| C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>               | 11.46 | 1.20 | 192.0661 | C <sub>12</sub> H <sub>17</sub> O <sub>2</sub>                              | 13.32 | 1.22 | 193.1229 | C <sub>14</sub> H <sub>26</sub>  | 15.54 | 1.13 | 194.2036 |
| C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>               | 11.84 | 1.04 | 192.0899 | C <sub>12</sub> H <sub>17</sub> O <sub>3</sub>                              | 13.10 | 1.39 | 192.9925 | C <sub>14</sub> H <sub>10</sub> O  | 15.33 | 1.29 | 194.0732 |
| C <sub>10</sub> H <sub>14</sub> N <sub>3</sub> O                            | 12.21 | 0.89 | 192.1138 | C <sub>12</sub> H <sub>19</sub> N <sub>2</sub> O                            | 13.69 | 1.07 | 193.1467 | C <sub>14</sub> H <sub>12</sub> N  | 15.70 | 1.15 | 194.0970 |
| C <sub>10</sub> H <sub>16</sub> N <sub>4</sub>                              | 12.59 | 0.73 | 192.1377 | C <sub>12</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>                | 13.47 | 1.24 | 193.0164 | C <sub>15</sub> H <sub>14</sub>  | 16.43 | 1.26 | 194.1096 |
| C <sub>10</sub> N <sub>4</sub> O  | 12.37 | 0.90 | 192.0073 | C <sub>12</sub> H <sub>21</sub> N <sub>2</sub>                              | 14.07 | 0.92 | 193.1706 | C <sub>15</sub> N  | 16.59 | 1.29 | 194.0031 |
| C <sub>11</sub> H <sub>12</sub> O <sub>3</sub>                              | 12.20 | 1.28 | 192.0786 | C <sub>12</sub> H <sub>5</sub> N <sub>2</sub> O                             | 13.85 | 1.09 | 193.0402 | C <sub>16</sub> H <sub>2</sub>   | 17.32 | 1.41 | 194.0157 |
| C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>               | 12.57 | 1.13 | 192.1025 | C <sub>12</sub> H <sub>7</sub> N <sub>3</sub>                               | 14.22 | 0.94 | 193.0641 | <sup>195</sup> C <sub>8</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub> | 9.68  | 1.22 | 195.0406 |
| C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O                            | 12.94 | 0.97 | 192.1264 | C <sub>13</sub> H <sub>21</sub> O   | 14.42 | 1.16 | 193.1593 | C <sub>8</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>                | 10.05 | 1.06 | 195.0644 |
| C <sub>11</sub> N <sub>2</sub> O <sub>2</sub>                               | 12.73 | 1.15 | 191.9960 | C <sub>13</sub> H <sub>5</sub> O <sub>2</sub>                               | 14.21 | 1.33 | 193.0289 | C <sub>8</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub>               | 10.42 | 0.89 | 195.0883 |
| C <sub>11</sub> H <sub>18</sub> N <sub>3</sub>                              | 13.32 | 0.82 | 192.1502 | C <sub>13</sub> H <sub>23</sub> N   | 14.80 | 1.02 | 193.1832 | C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>                | 10.44 | 1.29 | 195.0532 |
| C <sub>11</sub> H <sub>2</sub> N <sub>3</sub> O                             | 13.10 | 0.99 | 192.0198 | C <sub>13</sub> H <sub>7</sub> N <sub>2</sub> O                             | 14.58 | 1.19 | 193.0528 | C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub>               | 10.78 | 1.13 | 195.0770 |
| C <sub>11</sub> H <sub>4</sub> N <sub>4</sub>                               | 13.48 | 0.84 | 192.0437 | C <sub>13</sub> H <sub>9</sub> N <sub>2</sub>                               | 14.95 | 1.04 | 193.0767 | C <sub>9</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>               | 11.16 | 0.97 | 195.1009 |
| C <sub>12</sub> H <sub>16</sub> O <sub>2</sub>                              | 13.30 | 1.22 | 192.1151 | C <sub>14</sub> H <sub>25</sub>   | 15.53 | 1.12 | 193.1957 | C <sub>9</sub> H <sub>15</sub> N <sub>4</sub> O                            | 11.53 | 0.81 | 195.1247 |
| C <sub>12</sub> O <sub>3</sub>  | 13.08 | 1.39 | 191.9847 | C <sub>14</sub> H <sub>9</sub> O  | 15.31 | 1.29 | 193.0653 | C <sub>10</sub> H <sub>11</sub> O <sub>4</sub>                             | 11.14 | 1.36 | 195.0657 |
| C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O                            | 13.68 | 1.06 | 192.1389 | C <sub>14</sub> H <sub>11</sub> N   | 15.69 | 1.15 | 193.0892 | C <sub>10</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub>              | 11.51 | 1.21 | 195.0896 |
| C <sub>12</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>                | 13.46 | 1.24 | 192.0085 | C <sub>15</sub> H <sub>13</sub>   | 16.42 | 1.26 | 193.1018 | C <sub>10</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub>              | 11.89 | 1.05 | 195.1134 |
| C <sub>12</sub> H <sub>20</sub> N <sub>2</sub>                              | 14.05 | 0.92 | 192.1628 | C <sub>16</sub> H   | 17.31 | 1.40 | 193.0078 | C <sub>10</sub> H <sub>17</sub> N <sub>3</sub> O                           | 12.26 | 0.89 | 195.1373 |
| C <sub>12</sub> H <sub>4</sub> N <sub>2</sub> O                             | 13.83 | 1.09 | 192.0324 | <sup>194</sup> C <sub>7</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> | 8.77  | 1.14 | 194.1267 | C <sub>10</sub> HN <sub>3</sub> O <sub>2</sub>                             | 12.04 | 1.07 | 195.0069 |
| C <sub>12</sub> H <sub>6</sub> N <sub>3</sub>                               | 14.21 | 0.94 | 192.0563 | C <sub>8</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>                 | 9.66  | 1.22 | 194.0328 | C <sub>10</sub> H <sub>19</sub> N <sub>4</sub>                             | 12.64 | 0.74 | 195.1611 |
| C <sub>13</sub> H <sub>20</sub> O   | 14.41 | 1.16 | 192.1515 | C <sub>8</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>                 | 10.03 | 1.06 | 194.0566 | C <sub>10</sub> H <sub>3</sub> N <sub>4</sub> O                            | 12.42 | 0.91 | 195.0308 |
| C <sub>13</sub> H <sub>4</sub> O <sub>2</sub>                               | 14.19 | 1.33 | 192.0211 | C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>                | 10.41 | 0.89 | 194.0805 | C <sub>11</sub> H <sub>15</sub> O <sub>3</sub>                             | 12.24 | 1.29 | 195.1021 |
| C <sub>13</sub> H <sub>22</sub> N   | 14.78 | 1.02 | 192.1753 | C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>                 | 10.39 | 1.29 | 194.0453 | C <sub>11</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub>              | 12.62 | 1.13 | 195.1260 |
| C <sub>13</sub> H <sub>6</sub> N <sub>2</sub> O                             | 14.56 | 1.18 | 192.0449 | C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>                | 10.77 | 1.13 | 194.0692 | C <sub>11</sub> HN <sub>2</sub> O <sub>3</sub>                             | 12.40 | 1.31 | 194.9956 |
| C <sub>13</sub> H <sub>8</sub> N <sub>2</sub>                               | 14.94 | 1.04 | 192.0688 | C <sub>9</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub>                | 11.14 | 0.97 | 194.0930 | C <sub>11</sub> H <sub>19</sub> N <sub>2</sub> O                           | 12.99 | 0.98 | 195.1498 |
| C <sub>14</sub> H <sub>24</sub>   | 15.51 | 1.12 | 192.1879 | C <sub>9</sub> H <sub>14</sub> N <sub>4</sub> O                             | 11.51 | 0.81 | 194.1169 | C <sub>11</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>               | 12.78 | 1.15 | 195.0195 |
| C <sub>14</sub> H <sub>8</sub> O  | 15.30 | 1.29 | 192.0575 | C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>                              | 11.12 | 1.36 | 194.0579 | C <sub>11</sub> H <sub>21</sub> N <sub>3</sub>                             | 13.37 | 0.83 | 195.1737 |
| C <sub>14</sub> H <sub>10</sub> N   | 15.67 | 1.15 | 192.0814 | C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>               | 11.50 | 1.20 | 194.0817 | C <sub>11</sub> H <sub>5</sub> N <sub>3</sub> O                            | 13.15 | 1.00 | 195.0433 |
| C <sub>15</sub> H <sub>12</sub>   | 16.40 | 1.26 | 192.0939 | C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>               | 11.87 | 1.05 | 194.1056 | C <sub>11</sub> H <sub>7</sub> N <sub>4</sub>                              | 13.52 | 0.85 | 195.0672 |
| C <sub>16</sub>   | 17.29 | 1.40 | 192.0000 | C <sub>10</sub> H <sub>16</sub> N <sub>3</sub> O                            | 12.25 | 0.89 | 194.1295 | C <sub>12</sub> H <sub>19</sub> O <sub>2</sub>                             | 13.35 | 1.22 | 195.1385 |
| <sup>193</sup> C <sub>7</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub> | 8.76  | 1.14 | 193.1189 | C <sub>10</sub> N <sub>3</sub> O <sub>2</sub>                               | 12.03 | 1.06 | 193.9991 | C <sub>12</sub> H <sub>3</sub> O <sub>3</sub>                              | 13.13 | 1.39 | 195.0082 |
| C <sub>7</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub>                | 9.13  | 0.98 | 193.1427 | C <sub>10</sub> H <sub>18</sub> N <sub>4</sub>                              | 12.62 | 0.73 | 194.1533 | C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O                           | 13.72 | 1.07 | 195.1624 |
| C <sub>8</sub> H <sub>19</sub> N <sub>2</sub> O <sub>4</sub>                | 9.49  | 1.20 | 193.1315 | C <sub>10</sub> H <sub>2</sub> N <sub>4</sub> O                             | 12.40 | 0.91 | 194.0229 | C <sub>12</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>               | 13.51 | 1.24 | 195.0320 |
| C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>                 | 9.64  | 1.22 | 193.0249 | C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>                              | 12.23 | 1.28 | 194.0943 | C <sub>12</sub> H <sub>23</sub> N <sub>2</sub>                             | 14.10 | 0.92 | 195.1863 |
| C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>                 | 10.02 | 1.05 | 193.0488 | C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>               | 12.60 | 1.13 | 194.1182 | C <sub>12</sub> H <sub>7</sub> N <sub>2</sub> O                            | 13.88 | 1.09 | 195.0559 |
| C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>                 | 10.39 | 0.89 | 193.0726 | C <sub>11</sub> N <sub>2</sub> O <sub>3</sub>                               | 12.39 | 1.30 | 193.9878 | C <sub>12</sub> H <sub>9</sub> N <sub>3</sub>                              | 14.26 | 0.94 | 195.0798 |
| C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub>                 | 10.38 | 1.29 | 193.0375 | C <sub>11</sub> H <sub>18</sub> N <sub>2</sub> O                            | 12.98 | 0.98 | 194.1420 | C <sub>13</sub> H <sub>23</sub> O  | 14.45 | 1.17 | 195.1750 |
| C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>                 | 10.75 | 1.13 | 193.0614 | C <sub>11</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>                | 12.76 | 1.15 | 194.0116 | C <sub>13</sub> H <sub>7</sub> O <sub>2</sub>                              | 14.24 | 1.34 | 195.0446 |
| C <sub>9</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub>                | 11.12 | 0.96 | 193.0852 | C <sub>11</sub> H <sub>20</sub> N <sub>3</sub>                              | 13.35 | 0.82 | 194.1659 | C <sub>13</sub> H <sub>25</sub> N  | 14.83 | 1.02 | 195.1988 |
| C <sub>9</sub> H <sub>13</sub> N <sub>4</sub> O                             | 11.50 | 0.81 | 193.1091 | C <sub>11</sub> H <sub>4</sub> N <sub>3</sub> O                             | 13.13 | 1.00 | 194.0355 | C <sub>13</sub> H <sub>9</sub> N <sub>2</sub> O                            | 14.61 | 1.19 | 195.0684 |
| C <sub>10</sub> H <sub>9</sub> O <sub>4</sub>                               | 11.11 | 1.36 | 193.0501 | C <sub>11</sub> H <sub>6</sub> N <sub>4</sub>                               | 13.51 | 0.85 | 194.0594 | C <sub>13</sub> H <sub>11</sub> N <sub>2</sub>                             | 14.99 | 1.05 | 195.0923 |
| C <sub>10</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub>               | 11.48 | 1.20 | 193.0739 | C <sub>12</sub> H <sub>18</sub> O <sub>2</sub>                              | 13.33 | 1.22 | 194.1307 | C <sub>14</sub> H <sub>27</sub>  | 15.56 | 1.13 | 195.2114 |
| C <sub>10</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub>               | 11.86 | 1.04 | 193.0978 | C <sub>12</sub> H <sub>2</sub> O <sub>3</sub>                               | 13.12 | 1.39 | 194.0003 | C <sub>14</sub> H <sub>11</sub> O  | 15.34 | 1.30 | 195.0810 |
| C <sub>10</sub> H <sub>15</sub> N <sub>3</sub> O                            | 12.23 | 0.89 | 193.1216 | C <sub>12</sub> H <sub>20</sub> N <sub>2</sub> O                            | 13.71 | 1.07 | 194.1546 | C <sub>14</sub> H <sub>13</sub> N  | 15.72 | 1.15 | 195.1049 |
| C <sub>10</sub> H <sub>17</sub> N <sub>4</sub>                              | 12.60 | 0.73 | 193.1455 | C <sub>12</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>                | 13.49 | 1.24 | 194.0242 | C <sub>15</sub> H <sub>15</sub>  | 16.45 | 1.27 | 195.1174 |
| C <sub>10</sub> HN <sub>4</sub> O   | 12.39 | 0.91 | 193.0151 | C <sub>12</sub> H <sub>22</sub> N <sub>2</sub>                              | 14.08 | 0.92 | 194.1784 | C <sub>15</sub> HN   | 16.61 | 1.29 | 195.0109 |
| C <sub>11</sub> H <sub>13</sub> O <sub>3</sub>                              | 12.21 | 1.28 | 193.0865 | C <sub>12</sub> H <sub>6</sub> N <sub>2</sub> O                             | 13.87 | 1.09 | 194.0480 | C <sub>16</sub> H <sub>3</sub>   | 17.34 | 1.41 | 195.0235 |
| C <sub>11</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub>               | 12.59 | 1.13 | 193.1103 | C <sub>12</sub> H <sub>8</sub> N <sub>3</sub>                               | 14.24 | 0.94 | 194.0719 | <sup>196</sup> C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> | 9.69  | 1.22 | 196.0484 |
| C <sub>11</sub> H <sub>17</sub> N <sub>2</sub> O                            | 12.96 | 0.97 | 193.1342 | C <sub>13</sub> H <sub>22</sub> O   | 14.44 | 1.17 | 194.1671 | C <sub>8</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub>               | 10.07 | 1.06 | 196.0723 |
| C <sub>11</sub> HN <sub>2</sub> O <sub>2</sub>                              | 12.74 | 1.15 | 193.0038 | C <sub>13</sub> H <sub>6</sub> O <sub>2</sub>                               | 14.22 | 1.34 | 194.0368 | C <sub>8</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub>               | 10.44 | 0.90 | 196.0961 |
| C <sub>11</sub> H <sub>19</sub> N <sub>3</sub>                              | 13.34 | 0.82 | 193.1580 | C <sub>13</sub> H <sub>24</sub> N   | 14.81 | 1.02 | 194.1910 |  |       |      |          |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>9</sub> H <sub>10</sub> N <sub>0</sub> O <sub>4</sub>  | 10.42 | 1.29 | 196.0610 | C <sub>10</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> | 11.92 | 1.05 | 197.1291 | C <sub>10</sub> H <sub>6</sub> N <sub>4</sub> O               | 12.47 | 0.92 | 198.0542 |
| C <sub>9</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>  | 10.80 | 1.13 | 196.0848 | C <sub>10</sub> HN <sub>2</sub> O <sub>3</sub>                | 11.70 | 1.23 | 196.9987 | C <sub>11</sub> H <sub>18</sub> O <sub>3</sub>                | 12.29 | 1.29 | 198.1256 |
| C <sub>9</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub>  | 11.17 | 0.97 | 196.1087 | C <sub>10</sub> H <sub>19</sub> N <sub>3</sub> O              | 12.29 | 0.90 | 197.1529 | C <sub>11</sub> H <sub>2</sub> O <sub>4</sub>                 | 12.07 | 1.47 | 197.9953 |
| C <sub>9</sub> H <sub>16</sub> N <sub>4</sub> O               | 11.55 | 0.81 | 196.1325 | C <sub>10</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>  | 12.08 | 1.07 | 197.0226 | C <sub>11</sub> H <sub>20</sub> N <sub>0</sub> O <sub>2</sub> | 12.67 | 1.14 | 198.1495 |
| C <sub>9</sub> N <sub>4</sub> O <sub>2</sub>                  | 11.33 | 0.99 | 196.0022 | C <sub>10</sub> H <sub>21</sub> N <sub>4</sub>                | 12.67 | 0.74 | 197.1768 | C <sub>11</sub> H <sub>4</sub> N <sub>0</sub> O <sub>3</sub>  | 12.45 | 1.31 | 198.0191 |
| C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>                | 11.15 | 1.37 | 196.0735 | C <sub>10</sub> H <sub>5</sub> N <sub>4</sub> O               | 12.45 | 0.91 | 197.0464 | C <sub>11</sub> H <sub>22</sub> N <sub>2</sub> O              | 13.04 | 0.99 | 198.1733 |
| C <sub>10</sub> H <sub>14</sub> N <sub>0</sub> O <sub>3</sub> | 11.53 | 1.21 | 196.0974 | C <sub>11</sub> H <sub>17</sub> O <sub>3</sub>                | 12.28 | 1.29 | 197.1178 | C <sub>11</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 12.82 | 1.16 | 198.0429 |
| C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> | 11.90 | 1.05 | 196.1213 | C <sub>11</sub> HO <sub>4</sub>                               | 12.06 | 1.46 | 196.9874 | C <sub>11</sub> H <sub>24</sub> N <sub>3</sub>                | 13.42 | 0.83 | 198.1972 |
| C <sub>10</sub> N <sub>2</sub> O <sub>3</sub>                 | 11.69 | 1.22 | 195.9909 | C <sub>11</sub> H <sub>19</sub> N <sub>0</sub> O <sub>2</sub> | 12.65 | 1.14 | 197.1416 | C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O               | 13.20 | 1.01 | 198.0668 |
| C <sub>10</sub> H <sub>18</sub> N <sub>3</sub> O              | 12.28 | 0.89 | 196.1451 | C <sub>11</sub> H <sub>3</sub> N <sub>0</sub> O <sub>3</sub>  | 12.43 | 1.31 | 197.0113 | C <sub>11</sub> H <sub>10</sub> N <sub>4</sub>                | 13.57 | 0.85 | 198.0907 |
| C <sub>10</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>  | 12.06 | 1.07 | 196.0147 | C <sub>11</sub> H <sub>21</sub> N <sub>2</sub> O              | 13.02 | 0.98 | 197.1655 | C <sub>12</sub> H <sub>22</sub> O <sub>2</sub>                | 13.40 | 1.23 | 198.1620 |
| C <sub>10</sub> H <sub>20</sub> N <sub>4</sub>                | 12.65 | 0.74 | 196.1690 | C <sub>11</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>  | 12.81 | 1.16 | 197.0351 | C <sub>12</sub> H <sub>6</sub> O <sub>3</sub>                 | 13.18 | 1.40 | 198.0317 |
| C <sub>10</sub> H <sub>4</sub> N <sub>4</sub> O               | 12.43 | 0.91 | 196.0386 | C <sub>11</sub> H <sub>23</sub> N <sub>3</sub>                | 13.40 | 0.83 | 197.1894 | C <sub>12</sub> H <sub>24</sub> N <sub>0</sub>                | 13.77 | 1.08 | 198.1859 |
| C <sub>11</sub> H <sub>16</sub> O <sub>3</sub>                | 12.26 | 1.29 | 196.1100 | C <sub>11</sub> H <sub>7</sub> N <sub>3</sub> O               | 13.18 | 1.00 | 197.0590 | C <sub>12</sub> H <sub>8</sub> N <sub>0</sub> O <sub>2</sub>  | 13.55 | 1.25 | 198.0555 |
| C <sub>11</sub> O <sub>4</sub>                                | 12.04 | 1.46 | 195.9796 | C <sub>11</sub> H <sub>9</sub> N <sub>4</sub>                 | 13.56 | 0.85 | 197.0829 | C <sub>12</sub> H <sub>26</sub> N <sub>2</sub>                | 14.15 | 0.93 | 198.2098 |
| C <sub>11</sub> H <sub>18</sub> N <sub>0</sub> O <sub>2</sub> | 12.63 | 1.13 | 196.1338 | C <sub>12</sub> H <sub>21</sub> O <sub>2</sub>                | 13.38 | 1.23 | 197.1542 | C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O              | 13.93 | 1.10 | 198.0794 |
| C <sub>11</sub> H <sub>2</sub> N <sub>0</sub> O <sub>3</sub>  | 12.42 | 1.31 | 196.0034 | C <sub>12</sub> H <sub>5</sub> O <sub>3</sub>                 | 13.16 | 1.40 | 197.0238 | C <sub>12</sub> H <sub>12</sub> N <sub>3</sub>                | 14.30 | 0.95 | 198.1032 |
| C <sub>11</sub> H <sub>20</sub> N <sub>2</sub> O              | 13.01 | 0.98 | 196.1577 | C <sub>12</sub> H <sub>23</sub> N <sub>0</sub>                | 13.76 | 1.08 | 197.1781 | C <sub>13</sub> H <sub>26</sub> O                             | 14.50 | 1.18 | 198.1985 |
| C <sub>11</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>  | 12.79 | 1.15 | 196.0273 | C <sub>12</sub> H <sub>7</sub> N <sub>0</sub> O <sub>2</sub>  | 13.54 | 1.25 | 197.0477 | C <sub>13</sub> H <sub>10</sub> O <sub>2</sub>                | 14.29 | 1.35 | 198.0681 |
| C <sub>11</sub> H <sub>22</sub> N <sub>3</sub>                | 13.38 | 0.83 | 196.1815 | C <sub>12</sub> H <sub>25</sub> N <sub>2</sub>                | 14.13 | 0.93 | 197.2019 | C <sub>13</sub> H <sub>28</sub> N                             | 14.88 | 1.03 | 198.2223 |
| C <sub>11</sub> H <sub>6</sub> N <sub>3</sub> O               | 13.17 | 1.00 | 196.0511 | C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O               | 13.91 | 1.10 | 197.0715 | C <sub>13</sub> H <sub>12</sub> N <sub>0</sub>                | 14.66 | 1.20 | 198.0919 |
| C <sub>11</sub> H <sub>8</sub> N <sub>4</sub>                 | 13.54 | 0.85 | 196.0750 | C <sub>12</sub> H <sub>11</sub> N <sub>3</sub>                | 14.29 | 0.95 | 197.0954 | C <sub>13</sub> H <sub>14</sub> N <sub>2</sub>                | 15.03 | 1.05 | 198.1158 |
| C <sub>12</sub> H <sub>20</sub> O <sub>2</sub>                | 13.37 | 1.22 | 196.1464 | C <sub>13</sub> H <sub>25</sub> O                             | 14.49 | 1.17 | 197.1906 | C <sub>13</sub> N <sub>3</sub>                                | 15.19 | 1.08 | 198.0093 |
| C <sub>12</sub> H <sub>4</sub> O <sub>3</sub>                 | 13.15 | 1.40 | 196.0160 | C <sub>13</sub> H <sub>9</sub> O <sub>2</sub>                 | 14.27 | 1.34 | 197.0603 | C <sub>14</sub> H <sub>30</sub>                               | 15.61 | 1.14 | 198.2349 |
| C <sub>12</sub> H <sub>22</sub> N <sub>0</sub>                | 13.74 | 1.07 | 196.1702 | C <sub>13</sub> H <sub>27</sub> N                             | 14.86 | 1.03 | 197.2145 | C <sub>14</sub> H <sub>14</sub> O                             | 15.39 | 1.30 | 198.1045 |
| C <sub>12</sub> H <sub>6</sub> N <sub>0</sub> O <sub>2</sub>  | 13.52 | 1.24 | 196.0399 | C <sub>13</sub> H <sub>11</sub> N <sub>0</sub>                | 14.64 | 1.20 | 197.0841 | C <sub>14</sub> H <sub>16</sub> N                             | 15.77 | 1.16 | 198.1284 |
| C <sub>12</sub> H <sub>24</sub> N <sub>2</sub>                | 14.11 | 0.92 | 196.1941 | C <sub>13</sub> H <sub>13</sub> N <sub>2</sub>                | 15.02 | 1.05 | 197.1080 | C <sub>14</sub> N <sub>0</sub>                                | 15.55 | 1.33 | 197.9980 |
| C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O               | 13.90 | 1.09 | 196.0637 | C <sub>14</sub> H <sub>29</sub>                               | 15.59 | 1.13 | 197.2270 | C <sub>14</sub> H <sub>2</sub> N <sub>2</sub>                 | 15.92 | 1.18 | 198.0218 |
| C <sub>12</sub> H <sub>10</sub> N <sub>3</sub>                | 14.27 | 0.95 | 196.0876 | C <sub>14</sub> H <sub>13</sub> O                             | 15.38 | 1.30 | 197.0967 | C <sub>15</sub> H <sub>18</sub>                               | 16.50 | 1.27 | 198.1409 |
| C <sub>13</sub> H <sub>24</sub> O                             | 14.47 | 1.17 | 196.1828 | C <sub>14</sub> H <sub>15</sub> N                             | 15.75 | 1.16 | 197.1205 | C <sub>15</sub> H <sub>2</sub> O                              | 16.28 | 1.44 | 198.0106 |
| C <sub>13</sub> H <sub>8</sub> O <sub>2</sub>                 | 14.25 | 1.34 | 196.0524 | C <sub>14</sub> HN <sub>2</sub>                               | 15.91 | 1.18 | 197.0140 | C <sub>15</sub> H <sub>4</sub> N                              | 16.65 | 1.30 | 198.0344 |
| C <sub>13</sub> H <sub>26</sub> N                             | 14.85 | 1.03 | 196.2067 | C <sub>15</sub> H <sub>17</sub>                               | 16.48 | 1.27 | 197.1331 | C <sub>16</sub> H <sub>6</sub>                                | 17.39 | 1.42 | 198.0470 |
| C <sub>13</sub> H <sub>10</sub> N <sub>0</sub>                | 14.63 | 1.19 | 196.0763 | C <sub>15</sub> HO  | 16.26 | 1.44 | 197.0027 |   |       |      |          |
| C <sub>13</sub> H <sub>12</sub> N <sub>2</sub>                | 15.00 | 1.05 | 196.1001 | C <sub>15</sub> H <sub>3</sub> N                              | 16.64 | 1.30 | 197.0266 | 199   |       |      |          |
| C <sub>14</sub> H <sub>28</sub>                               | 15.58 | 1.13 | 196.2192 | C <sub>16</sub> H <sub>5</sub>                                | 17.37 | 1.42 | 197.0391 | C <sub>8</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub>  | 9.74  | 1.23 | 199.0719 |
| C <sub>14</sub> H <sub>12</sub> O                             | 15.36 | 1.30 | 196.0888 |   |       |      |          | C <sub>8</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>  | 10.11 | 1.06 | 199.0958 |
| C <sub>14</sub> H <sub>14</sub> N                             | 15.73 | 1.16 | 196.1127 | 198   |       |      |          | C <sub>8</sub> H <sub>15</sub> N <sub>4</sub> O <sub>2</sub>  | 10.49 | 0.90 | 199.1196 |
| C <sub>14</sub> N <sub>2</sub>                                | 15.89 | 1.18 | 196.0062 | C <sub>8</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub>  | 9.72  | 1.23 | 198.0641 | C <sub>9</sub> H <sub>13</sub> N <sub>0</sub> O <sub>4</sub>  | 10.47 | 1.30 | 199.0845 |
| C <sub>15</sub> H <sub>16</sub>                               | 16.47 | 1.27 | 196.1253 | C <sub>8</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub>  | 10.10 | 1.06 | 198.0879 | C <sub>9</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub>  | 10.85 | 1.14 | 199.1083 |
| C <sub>15</sub> O   | 16.25 | 1.43 | 195.9949 | C <sub>8</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>  | 10.47 | 0.90 | 198.1118 | C <sub>9</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub>  | 11.22 | 0.98 | 199.1322 |
| C <sub>15</sub> H <sub>2</sub> N                              | 16.62 | 1.29 | 196.0187 | C <sub>9</sub> H <sub>12</sub> N <sub>0</sub> O <sub>4</sub>  | 10.46 | 1.30 | 198.0766 | C <sub>9</sub> HN <sub>3</sub> O <sub>3</sub>                 | 11.00 | 1.15 | 199.0018 |
| C <sub>16</sub> H <sub>4</sub>                                | 17.35 | 1.41 | 196.0313 | C <sub>9</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>  | 10.83 | 1.13 | 198.1005 | C <sub>9</sub> H <sub>19</sub> N <sub>4</sub> O               | 11.59 | 0.82 | 199.1560 |
|   |       |      |          | C <sub>9</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub>  | 11.20 | 0.97 | 198.1244 | C <sub>9</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>   | 11.38 | 0.99 | 199.0257 |
|   |       |      |          | C <sub>9</sub> N <sub>3</sub> O <sub>3</sub>                  | 10.99 | 1.15 | 197.9940 | C <sub>10</sub> H <sub>15</sub> O <sub>4</sub>                | 11.20 | 1.37 | 199.0970 |
| 197   |       |      |          | C <sub>9</sub> H <sub>18</sub> N <sub>4</sub> O               | 11.58 | 0.82 | 198.1482 | C <sub>10</sub> H <sub>17</sub> N <sub>0</sub> O <sub>3</sub> | 11.58 | 1.21 | 199.1209 |
| C <sub>8</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>   | 9.71  | 1.22 | 197.0563 | C <sub>9</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>   | 11.36 | 0.99 | 198.0178 | C <sub>10</sub> HN <sub>0</sub> O <sub>4</sub>                | 11.36 | 1.39 | 198.9905 |
| C <sub>8</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub>  | 10.08 | 1.06 | 197.0801 | C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>                | 11.19 | 1.37 | 198.0892 | C <sub>10</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub> | 11.95 | 1.06 | 199.1447 |
| C <sub>8</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub>  | 10.46 | 0.90 | 197.1040 | C <sub>10</sub> H <sub>16</sub> N <sub>0</sub> O <sub>3</sub> | 11.56 | 1.21 | 198.1131 | C <sub>10</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 11.73 | 1.23 | 199.0144 |
| C <sub>9</sub> H <sub>11</sub> N <sub>0</sub> O <sub>4</sub>  | 10.44 | 1.29 | 197.0688 | C <sub>10</sub> N <sub>0</sub> O <sub>4</sub>                 | 11.34 | 1.39 | 197.9827 | C <sub>10</sub> H <sub>21</sub> N <sub>3</sub> O              | 12.33 | 0.90 | 199.1686 |
| C <sub>9</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub>  | 10.81 | 1.13 | 197.0927 | C <sub>10</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> | 11.94 | 1.05 | 198.1369 | C <sub>10</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>  | 12.11 | 1.07 | 199.0382 |
| C <sub>9</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>  | 11.19 | 0.97 | 197.1165 | C <sub>10</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>  | 11.72 | 1.23 | 198.0065 | C <sub>10</sub> H <sub>23</sub> N <sub>4</sub>                | 12.70 | 0.75 | 199.1925 |
| C <sub>9</sub> H <sub>17</sub> N <sub>4</sub> O               | 11.56 | 0.81 | 197.1404 | C <sub>10</sub> H <sub>20</sub> N <sub>3</sub> O              | 12.31 | 0.90 | 198.1608 | C <sub>10</sub> H <sub>7</sub> N <sub>4</sub> O               | 12.48 | 0.92 | 199.0621 |
| C <sub>9</sub> HN <sub>4</sub> O <sub>2</sub>                 | 11.35 | 0.99 | 197.0100 | C <sub>10</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>  | 12.09 | 1.07 | 198.0304 | C <sub>11</sub> H <sub>19</sub> O <sub>3</sub>                | 12.31 | 1.29 | 199.1334 |
| C <sub>10</sub> H <sub>13</sub> O <sub>4</sub>                | 11.17 | 1.37 | 197.0814 | C <sub>10</sub> H <sub>22</sub> N <sub>4</sub>                | 12.68 | 0.74 | 198.1846 | C <sub>11</sub> H <sub>3</sub> O <sub>4</sub>                 | 12.09 | 1.47 | 199.0031 |
| C <sub>10</sub> H <sub>15</sub> N <sub>0</sub> O <sub>3</sub> | 11.54 | 1.21 | 197.1052 |   |       |      |          |   |       |      |          |

|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>11</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub> | 12.68 | 1.14 | 199.1573 | C <sub>11</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 12.86 | 1.16 | 200.0586 | C <sub>11</sub> H <sub>27</sub> N <sub>3</sub>                | 13.46 | 0.84 | 201.2207 |
| C <sub>11</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>  | 12.47 | 1.31 | 199.0269 | C <sub>11</sub> H <sub>26</sub> N <sub>3</sub>                | 13.45 | 0.84 | 200.2129 | C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O              | 13.25 | 1.01 | 201.0903 |
| C <sub>11</sub> H <sub>23</sub> N <sub>2</sub> O              | 13.06 | 0.99 | 199.1811 | C <sub>11</sub> H <sub>10</sub> N <sub>3</sub> O              | 13.23 | 1.01 | 200.0825 | C <sub>11</sub> H <sub>13</sub> N <sub>4</sub>                | 13.62 | 0.86 | 201.1142 |
| C <sub>11</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>  | 12.84 | 1.16 | 199.0518 | C <sub>11</sub> H <sub>12</sub> N <sub>4</sub>                | 13.60 | 0.86 | 200.1063 | C <sub>12</sub> H <sub>25</sub> O <sub>2</sub>                | 13.45 | 1.23 | 201.1855 |
| C <sub>11</sub> H <sub>25</sub> N <sub>3</sub>                | 13.43 | 0.84 | 199.2050 | C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>                | 13.43 | 1.23 | 200.1777 | C <sub>12</sub> H <sub>9</sub> O <sub>3</sub>                 | 13.23 | 1.41 | 201.0552 |
| C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O               | 13.21 | 1.01 | 199.0746 | C <sub>12</sub> H <sub>8</sub> O <sub>3</sub>                 | 13.21 | 1.40 | 200.0473 | C <sub>12</sub> H <sub>27</sub> NO                            | 13.82 | 1.08 | 201.2094 |
| C <sub>11</sub> H <sub>11</sub> N <sub>4</sub>                | 13.59 | 0.86 | 199.0985 | C <sub>12</sub> H <sub>26</sub> NO                            | 13.80 | 1.08 | 200.2015 | C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 13.60 | 1.26 | 201.0790 |
| C <sub>12</sub> H <sub>23</sub> O <sub>2</sub>                | 13.41 | 1.23 | 199.1699 | C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 13.59 | 1.25 | 200.0712 | C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O              | 13.98 | 1.11 | 201.1029 |
| C <sub>12</sub> H <sub>7</sub> O <sub>3</sub>                 | 13.20 | 1.40 | 199.0395 | C <sub>12</sub> H <sub>28</sub> N <sub>2</sub>                | 14.18 | 0.93 | 200.2254 | C <sub>12</sub> H <sub>15</sub> N <sub>3</sub>                | 14.35 | 0.96 | 201.1267 |
| C <sub>12</sub> H <sub>25</sub> NO                            | 13.79 | 1.08 | 199.1937 | C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O              | 13.96 | 1.10 | 200.0950 | C <sub>12</sub> HN <sub>4</sub>                               | 14.51 | 0.98 | 201.0202 |
| C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 13.57 | 1.25 | 199.0634 | C <sub>12</sub> H <sub>14</sub> N <sub>3</sub>                | 14.34 | 0.96 | 200.1189 | C <sub>13</sub> H <sub>13</sub> O <sub>2</sub>                | 14.33 | 1.35 | 201.0916 |
| C <sub>12</sub> H <sub>27</sub> N <sub>2</sub>                | 14.16 | 0.93 | 199.2176 | C <sub>12</sub> N <sub>4</sub>                                | 14.49 | 0.98 | 200.0124 | C <sub>13</sub> H <sub>15</sub> NO                            | 14.71 | 1.21 | 201.1154 |
| C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O              | 13.95 | 1.10 | 199.0872 | C <sub>13</sub> H <sub>28</sub> O                             | 14.53 | 1.18 | 200.2141 | C <sub>13</sub> H <sub>17</sub> N <sub>2</sub>                | 15.08 | 1.06 | 201.1393 |
| C <sub>12</sub> H <sub>13</sub> N <sub>3</sub>                | 14.32 | 0.95 | 199.1111 | C <sub>13</sub> H <sub>12</sub> O <sub>2</sub>                | 14.32 | 1.35 | 200.0837 | C <sub>13</sub> HN <sub>2</sub> O                             | 14.87 | 1.23 | 201.0089 |
| C <sub>13</sub> H <sub>27</sub> O                             | 14.52 | 1.18 | 199.2063 | C <sub>13</sub> H <sub>14</sub> NO                            | 14.69 | 1.20 | 200.1076 | C <sub>13</sub> H <sub>3</sub> N <sub>3</sub>                 | 15.24 | 1.08 | 201.0328 |
| C <sub>13</sub> H <sub>11</sub> O <sub>2</sub>                | 14.30 | 1.35 | 199.0759 | C <sub>13</sub> H <sub>16</sub> N <sub>2</sub>                | 15.07 | 1.06 | 200.1315 | C <sub>14</sub> H <sub>17</sub> O                             | 15.44 | 1.31 | 201.1280 |
| C <sub>13</sub> H <sub>29</sub> N                             | 14.89 | 1.03 | 199.2301 | C <sub>13</sub> N <sub>2</sub> O                              | 14.85 | 1.23 | 200.0011 | C <sub>14</sub> H <sub>2</sub> O <sub>2</sub>                 | 15.22 | 1.48 | 200.9976 |
| C <sub>13</sub> H <sub>13</sub> NO                            | 14.68 | 1.20 | 199.0998 | C <sub>13</sub> H <sub>2</sub> N <sub>3</sub>                 | 15.22 | 1.08 | 200.0249 | C <sub>14</sub> H <sub>19</sub> N                             | 15.81 | 1.17 | 201.1519 |
| C <sub>13</sub> H <sub>15</sub> N <sub>2</sub>                | 15.05 | 1.06 | 199.1236 | C <sub>14</sub> H <sub>16</sub> O                             | 15.42 | 1.31 | 200.1202 | C <sub>14</sub> H <sub>3</sub> NO                             | 15.60 | 1.33 | 201.0215 |
| C <sub>13</sub> HN <sub>3</sub>                               | 15.21 | 1.08 | 199.0171 | C <sub>14</sub> O <sub>2</sub>                                | 15.21 | 1.48 | 199.9898 | C <sub>14</sub> H <sub>5</sub> N <sub>2</sub>                 | 15.97 | 1.19 | 201.0453 |
| C <sub>14</sub> H <sub>15</sub> O                             | 15.41 | 1.31 | 199.1123 | C <sub>14</sub> H <sub>18</sub> N                             | 15.80 | 1.17 | 200.1440 | C <sub>15</sub> H <sub>21</sub>                               | 16.55 | 1.28 | 201.1644 |
| C <sub>14</sub> H <sub>17</sub> N                             | 15.78 | 1.16 | 199.1362 | C <sub>14</sub> H <sub>2</sub> NO                             | 15.58 | 1.33 | 200.0136 | C <sub>15</sub> H <sub>5</sub> O                              | 16.33 | 1.45 | 201.0340 |
| C <sub>14</sub> HN <sub>2</sub> O                             | 15.56 | 1.33 | 199.0058 | C <sub>14</sub> H <sub>4</sub> N <sub>2</sub>                 | 15.96 | 1.19 | 200.0375 | C <sub>15</sub> H <sub>7</sub> N                              | 16.70 | 1.31 | 201.0579 |
| C <sub>14</sub> H <sub>3</sub> N <sub>2</sub>                 | 15.94 | 1.19 | 199.0297 | C <sub>15</sub> H <sub>20</sub>                               | 16.53 | 1.28 | 200.1566 | C <sub>16</sub> H <sub>9</sub>                                | 17.43 | 1.43 | 201.0705 |
| C <sub>15</sub> H <sub>19</sub>                               | 16.51 | 1.28 | 199.1488 | C <sub>15</sub> H <sub>4</sub> O                              | 16.31 | 1.44 | 200.0262 | 202   |       |      |          |
| C <sub>15</sub> H <sub>3</sub> O                              | 16.30 | 1.44 | 199.0184 | C <sub>15</sub> H <sub>6</sub> N                              | 16.69 | 1.30 | 200.0501 | C <sub>8</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>  | 9.79  | 1.23 | 202.0954 |
| C <sub>15</sub> H <sub>5</sub> N                              | 16.67 | 1.30 | 199.0422 | C <sub>16</sub> H <sub>8</sub>                                | 17.42 | 1.42 | 200.0626 | C <sub>8</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub>  | 10.16 | 1.07 | 202.1193 |
| C <sub>16</sub> H <sub>7</sub>                                | 17.40 | 1.42 | 199.0548 | 201   |       |      |          | C <sub>8</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>  | 10.54 | 0.91 | 202.1431 |
|   |       |      |          | C <sub>8</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub>  | 9.77  | 1.23 | 201.0876 | C <sub>9</sub> H <sub>16</sub> NO <sub>4</sub>                | 10.52 | 1.30 | 202.1080 |
| 200   |       |      |          | C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub>  | 10.15 | 1.07 | 201.1114 | C <sub>9</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>  | 10.89 | 1.14 | 202.1318 |
| C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>  | 9.76  | 1.23 | 200.0797 | C <sub>8</sub> H <sub>17</sub> N <sub>4</sub> O <sub>2</sub>  | 10.52 | 0.90 | 201.1353 | C <sub>9</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>   | 10.68 | 1.32 | 202.0014 |
| C <sub>8</sub> H <sub>14</sub> N <sub>3</sub> O <sub>3</sub>  | 10.13 | 1.07 | 200.1036 | C <sub>9</sub> H <sub>15</sub> NO <sub>4</sub>                | 10.50 | 1.30 | 201.1001 | C <sub>9</sub> H <sub>20</sub> N <sub>3</sub> O <sub>2</sub>  | 11.27 | 0.98 | 202.1557 |
| C <sub>8</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub>  | 10.50 | 0.90 | 200.1275 | C <sub>9</sub> H <sub>17</sub> N <sub>2</sub> O <sub>3</sub>  | 10.88 | 1.14 | 201.1240 | C <sub>9</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>   | 11.05 | 1.16 | 202.0253 |
| C <sub>9</sub> H <sub>14</sub> NO <sub>4</sub>                | 10.49 | 1.30 | 200.0923 | C <sub>9</sub> HN <sub>2</sub> O <sub>4</sub>                 | 10.66 | 1.32 | 200.9936 | C <sub>9</sub> H <sub>22</sub> N <sub>4</sub> O               | 11.64 | 0.82 | 202.1795 |
| C <sub>9</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>  | 10.86 | 1.14 | 200.1162 | C <sub>9</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub>  | 11.25 | 0.98 | 201.1478 | C <sub>9</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>   | 11.43 | 1.00 | 202.0491 |
| C <sub>9</sub> N <sub>2</sub> O <sub>4</sub>                  | 10.64 | 1.31 | 199.9858 | C <sub>9</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>   | 11.04 | 1.16 | 201.0175 | C <sub>10</sub> H <sub>18</sub> O <sub>4</sub>                | 11.25 | 1.38 | 202.1205 |
| C <sub>9</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub>  | 11.24 | 0.98 | 200.1400 | C <sub>9</sub> H <sub>21</sub> N <sub>4</sub> O               | 11.63 | 0.82 | 201.1717 | C <sub>10</sub> H <sub>20</sub> NO <sub>3</sub>               | 11.62 | 1.22 | 202.1444 |
| C <sub>9</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>   | 11.02 | 1.15 | 200.0096 | C <sub>9</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>   | 11.41 | 1.00 | 201.0413 | C <sub>10</sub> H <sub>4</sub> NO <sub>4</sub>                | 11.41 | 1.39 | 202.0140 |
| C <sub>9</sub> H <sub>20</sub> N <sub>4</sub> O               | 11.61 | 0.82 | 200.1639 | C <sub>10</sub> H <sub>17</sub> O <sub>4</sub>                | 11.23 | 1.37 | 201.1127 | C <sub>10</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> | 12.00 | 1.06 | 202.1682 |
| C <sub>9</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>   | 11.39 | 0.99 | 200.0335 | C <sub>10</sub> H <sub>19</sub> NO <sub>3</sub>               | 11.61 | 1.22 | 201.1365 | C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 11.78 | 1.24 | 202.0379 |
| C <sub>10</sub> H <sub>16</sub> O <sub>4</sub>                | 11.22 | 1.37 | 200.1049 | C <sub>10</sub> H <sub>3</sub> NO <sub>4</sub>                | 11.39 | 1.39 | 201.0062 | C <sub>10</sub> H <sub>24</sub> N <sub>3</sub> O              | 12.37 | 0.91 | 202.1921 |
| C <sub>10</sub> H <sub>18</sub> NO <sub>3</sub>               | 11.59 | 1.21 | 200.1287 | C <sub>10</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub> | 11.98 | 1.06 | 201.1604 | C <sub>10</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 12.16 | 1.08 | 202.0617 |
| C <sub>10</sub> H <sub>2</sub> NO <sub>4</sub>                | 11.38 | 1.39 | 199.9983 | C <sub>10</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>  | 11.77 | 1.23 | 201.0300 | C <sub>10</sub> H <sub>26</sub> N <sub>4</sub>                | 12.75 | 0.75 | 202.2160 |
| C <sub>10</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> | 11.97 | 1.06 | 200.1526 | C <sub>10</sub> H <sub>23</sub> N <sub>3</sub> O              | 12.36 | 0.90 | 201.1842 | C <sub>10</sub> H <sub>10</sub> N <sub>4</sub> O              | 12.53 | 0.92 | 202.0856 |
| C <sub>10</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 11.75 | 1.23 | 200.0222 | C <sub>10</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>  | 12.14 | 1.08 | 201.0539 | C <sub>11</sub> H <sub>22</sub> O <sub>3</sub>                | 12.33 | 1.30 | 202.1569 |
| C <sub>10</sub> H <sub>22</sub> N <sub>3</sub> O              | 12.34 | 0.90 | 200.1764 | C <sub>10</sub> H <sub>25</sub> N <sub>4</sub>                | 12.73 | 0.75 | 201.2081 | C <sub>11</sub> H <sub>6</sub> O <sub>4</sub>                 | 12.14 | 1.47 | 202.0266 |
| C <sub>10</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>  | 12.12 | 1.08 | 200.0460 | C <sub>11</sub> H <sub>21</sub> O <sub>3</sub>                | 12.34 | 1.30 | 201.0777 | C <sub>11</sub> H <sub>24</sub> NO <sub>2</sub>               | 12.73 | 1.15 | 202.1809 |
| C <sub>10</sub> H <sub>24</sub> N <sub>4</sub>                | 12.72 | 0.75 | 200.2003 | C <sub>11</sub> H <sub>5</sub> O <sub>4</sub>                 | 12.12 | 1.47 | 201.0187 | C <sub>11</sub> H <sub>3</sub> NO <sub>3</sub>                | 12.51 | 1.32 | 202.0504 |
| C <sub>10</sub> H <sub>8</sub> N <sub>4</sub> O               | 12.50 | 0.92 | 200.0699 | C <sub>11</sub> H <sub>23</sub> NO <sub>2</sub>               | 12.71 | 1.14 | 201.1730 | C <sub>11</sub> H <sub>26</sub> N <sub>2</sub> O              | 13.10 | 0.99 | 202.2046 |
| C <sub>11</sub> H <sub>20</sub> O <sub>3</sub>                | 12.32 | 1.30 | 200.1413 | C <sub>11</sub> H <sub>7</sub> NO <sub>3</sub>                | 12.50 | 1.32 | 201.0426 | C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 12.89 | 1.17 | 202.0743 |
| C <sub>11</sub> H <sub>4</sub> O <sub>4</sub>                 | 12.11 | 1.47 | 200.0109 | C <sub>11</sub> H <sub>25</sub> N <sub>2</sub> O              | 13.09 | 0.99 | 201.1968 | C <sub>11</sub> H <sub>12</sub> N <sub>3</sub> O              | 13.26 | 1.01 | 202.0991 |
| C <sub>11</sub> H <sub>22</sub> NO <sub>2</sub>               | 12.70 | 1.14 | 200.1651 | C <sub>11</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 12.87 | 1.16 | 201.0664 | C <sub>11</sub> H <sub>14</sub> N <sub>4</sub>                | 13.64 | 0.86 | 202.1220 |
| C <sub>11</sub> H <sub>6</sub> NO <sub>3</sub>                | 12.48 | 1.32 | 200.0348 |   |       |      |          | C <sub>12</sub> H <sub>26</sub> O <sub>2</sub>                | 13.46 | 1.24 | 202.1934 |
| C <sub>11</sub> H <sub>24</sub> N <sub>2</sub> O              | 13.07 | 0.99 | 200.1890 |   |       |      |          | C <sub>12</sub> H <sub>10</sub> O <sub>3</sub>                | 13.24 | 1.41 | 202.0630 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | 13.62 | 1.26 | 202.0868 | C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O              | 14.74 | 1.21 | 203.1311 | C <sub>14</sub> H <sub>4</sub> O <sub>2</sub>                 | 15.27 | 1.49 | 204.0211 |
| C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O              | 13.99 | 1.11 | 202.1107 | C <sub>13</sub> HN <sub>2</sub> O <sub>2</sub>                | 14.52 | 1.38 | 203.0007 | C <sub>14</sub> H <sub>22</sub> N                             | 15.86 | 1.18 | 204.1753 |
| C <sub>12</sub> H <sub>16</sub> N <sub>3</sub>                | 14.37 | 0.96 | 202.1346 | C <sub>13</sub> H <sub>19</sub> N <sub>2</sub>                | 15.11 | 1.06 | 203.1549 | C <sub>14</sub> H <sub>6</sub> N <sub>2</sub> O               | 15.64 | 1.34 | 204.0449 |
| C <sub>12</sub> N <sub>3</sub> O                              | 14.15 | 1.13 | 202.0042 | C <sub>13</sub> H <sub>3</sub> N <sub>2</sub> O               | 14.90 | 1.23 | 203.0246 | C <sub>14</sub> H <sub>8</sub> N <sub>2</sub>                 | 16.02 | 1.20 | 204.0688 |
| C <sub>12</sub> H <sub>2</sub> N <sub>4</sub>                 | 14.53 | 0.98 | 202.0280 | C <sub>13</sub> H <sub>5</sub> N <sub>3</sub>                 | 15.27 | 1.09 | 203.0484 | C <sub>15</sub> H <sub>24</sub>                               | 16.59 | 1.29 | 204.1879 |
| C <sub>13</sub> H <sub>14</sub> O <sub>2</sub>                | 14.35 | 1.35 | 202.0994 | C <sub>14</sub> H <sub>19</sub> O                             | 15.47 | 1.32 | 203.1436 | C <sub>15</sub> H <sub>8</sub> O                              | 16.38 | 1.45 | 204.0575 |
| C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O              | 14.72 | 1.21 | 202.1233 | C <sub>14</sub> H <sub>3</sub> O <sub>2</sub>                 | 15.25 | 1.48 | 203.0133 | C <sub>15</sub> H <sub>10</sub> N                             | 16.75 | 1.31 | 204.0814 |
| C <sub>13</sub> N <sub>2</sub> O <sub>2</sub>                 | 14.51 | 1.38 | 201.9929 | C <sub>14</sub> H <sub>21</sub> N                             | 15.85 | 1.17 | 203.1675 | C <sub>16</sub> H <sub>12</sub>                               | 17.48 | 1.43 | 204.0939 |
| C <sub>13</sub> H <sub>18</sub> N <sub>2</sub>                | 15.10 | 1.06 | 202.1471 | C <sub>14</sub> H <sub>5</sub> N <sub>2</sub> O               | 15.63 | 1.34 | 203.0371 | C <sub>17</sub>   | 18.37 | 1.59 | 204.0000 |
| C <sub>13</sub> H <sub>2</sub> N <sub>2</sub> O               | 14.88 | 1.23 | 202.0167 | C <sub>14</sub> H <sub>7</sub> N <sub>2</sub>                 | 16.00 | 1.20 | 203.0610 | 205   |       |      |          |
| C <sub>13</sub> H <sub>4</sub> N <sub>3</sub>                 | 15.26 | 1.09 | 202.0406 | C <sub>15</sub> H <sub>23</sub>                               | 16.58 | 1.29 | 203.1801 | C <sub>8</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub>  | 9.84  | 1.24 | 205.1189 |
| C <sub>14</sub> H <sub>18</sub> O                             | 15.46 | 1.31 | 202.1358 | C <sub>15</sub> H <sub>7</sub> O                              | 16.36 | 1.45 | 203.0497 | C <sub>8</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub>  | 10.21 | 1.07 | 205.1427 |
| C <sub>14</sub> H <sub>2</sub> O <sub>2</sub>                 | 15.24 | 1.48 | 202.0054 | C <sub>15</sub> H <sub>9</sub> N                              | 16.73 | 1.31 | 203.0736 | C <sub>8</sub> H <sub>21</sub> N <sub>4</sub> O <sub>2</sub>  | 10.58 | 0.91 | 205.1666 |
| C <sub>14</sub> H <sub>20</sub> N                             | 15.83 | 1.17 | 202.1597 | C <sub>16</sub> H <sub>11</sub>                               | 17.47 | 1.43 | 203.0861 | C <sub>9</sub> H <sub>19</sub> N <sub>2</sub> O <sub>4</sub>  | 10.57 | 1.31 | 205.1315 |
| C <sub>14</sub> H <sub>4</sub> N <sub>2</sub> O               | 15.61 | 1.34 | 202.0293 | 204   |       |      |          | C <sub>9</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub>  | 10.94 | 1.15 | 205.1553 |
| C <sub>14</sub> H <sub>6</sub> N <sub>2</sub>                 | 15.99 | 1.19 | 202.0532 | C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>  | 9.82  | 1.24 | 204.1111 | C <sub>9</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>   | 10.72 | 1.32 | 205.0249 |
| C <sub>15</sub> H <sub>22</sub>                               | 16.56 | 1.28 | 202.1722 | C <sub>8</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub>  | 10.19 | 1.07 | 204.1349 | C <sub>9</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub>  | 11.32 | 0.99 | 205.1791 |
| C <sub>15</sub> H <sub>6</sub> O                              | 16.34 | 1.45 | 202.0419 | C <sub>8</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>  | 10.57 | 0.91 | 204.1588 | C <sub>9</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>   | 11.10 | 1.16 | 205.0488 |
| C <sub>15</sub> H <sub>8</sub> N                              | 16.72 | 1.31 | 202.0657 | C <sub>9</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>  | 10.55 | 1.31 | 204.1236 | C <sub>9</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>   | 11.47 | 1.00 | 205.0726 |
| C <sub>16</sub> H <sub>10</sub>                               | 17.45 | 1.43 | 202.0783 | C <sub>9</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>  | 10.93 | 1.14 | 204.1475 | C <sub>10</sub> H <sub>21</sub> O <sub>4</sub>                | 11.30 | 1.38 | 205.1440 |
|   |       |      |          | C <sub>9</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>   | 10.71 | 1.32 | 204.0171 | C <sub>10</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub> | 11.67 | 1.22 | 205.1679 |
| 203   |       |      |          | C <sub>9</sub> H <sub>22</sub> N <sub>3</sub> O <sub>2</sub>  | 11.30 | 0.98 | 204.1713 | C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub>  | 11.46 | 1.40 | 205.0375 |
| C <sub>8</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub>  | 9.80  | 1.23 | 203.1032 | C <sub>9</sub> H <sub>6</sub> N <sub>3</sub> O <sub>3</sub>   | 11.08 | 1.16 | 204.0410 | C <sub>10</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>  | 11.83 | 1.24 | 205.0614 |
| C <sub>8</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub>  | 10.18 | 1.07 | 203.1271 | C <sub>9</sub> H <sub>24</sub> N <sub>4</sub> O               | 11.67 | 0.83 | 204.1952 | C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> | 12.20 | 1.09 | 205.0852 |
| C <sub>8</sub> H <sub>19</sub> N <sub>4</sub> O <sub>2</sub>  | 10.55 | 0.91 | 203.1509 | C <sub>9</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>   | 11.46 | 1.00 | 204.0648 | C <sub>10</sub> H <sub>13</sub> N <sub>4</sub> O              | 12.58 | 0.93 | 205.1091 |
| C <sub>9</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub>  | 10.54 | 1.30 | 203.1158 | C <sub>10</sub> H <sub>20</sub> O <sub>4</sub>                | 11.28 | 1.38 | 204.1362 | C <sub>11</sub> H <sub>9</sub> O <sub>4</sub>                 | 12.19 | 1.48 | 205.0501 |
| C <sub>9</sub> H <sub>19</sub> N <sub>2</sub> O <sub>3</sub>  | 10.91 | 1.14 | 203.1396 | C <sub>10</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> | 11.66 | 1.22 | 204.1600 | C <sub>11</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> | 12.56 | 1.33 | 205.0739 |
| C <sub>9</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>   | 10.69 | 1.32 | 203.0093 | C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>  | 11.44 | 1.40 | 204.0297 | C <sub>11</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> | 12.94 | 1.17 | 205.0978 |
| C <sub>9</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub>  | 11.28 | 0.98 | 203.1635 | C <sub>10</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> | 12.03 | 1.06 | 204.1839 | C <sub>11</sub> H <sub>15</sub> N <sub>3</sub> O              | 13.31 | 1.02 | 205.1216 |
| C <sub>9</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>   | 11.07 | 1.16 | 203.0331 | C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 11.81 | 1.24 | 204.0535 | C <sub>11</sub> H <sub>17</sub> N <sub>4</sub>                | 13.68 | 0.87 | 205.1455 |
| C <sub>9</sub> H <sub>23</sub> N <sub>4</sub> O               | 11.66 | 0.82 | 203.1873 | C <sub>10</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub> | 12.19 | 1.08 | 204.0774 | C <sub>11</sub> HN <sub>4</sub> O                             | 13.47 | 1.04 | 205.0151 |
| C <sub>9</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>   | 11.44 | 1.00 | 203.0570 | C <sub>10</sub> H <sub>12</sub> N <sub>4</sub> O              | 12.56 | 0.93 | 204.1012 | C <sub>12</sub> H <sub>13</sub> O <sub>3</sub>                | 13.29 | 1.41 | 205.0865 |
| C <sub>10</sub> H <sub>19</sub> O <sub>4</sub>                | 11.27 | 1.38 | 203.1284 | C <sub>11</sub> H <sub>24</sub> O <sub>3</sub>                | 12.39 | 1.30 | 204.1726 | C <sub>12</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> | 13.67 | 1.26 | 205.1103 |
| C <sub>10</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> | 11.64 | 1.22 | 203.1522 | C <sub>11</sub> H <sub>8</sub> O <sub>4</sub>                 | 12.17 | 1.48 | 204.0422 | C <sub>12</sub> H <sub>17</sub> N <sub>2</sub> O              | 14.04 | 1.11 | 205.1342 |
| C <sub>10</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>  | 11.42 | 1.40 | 203.0218 | C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 12.55 | 1.32 | 204.0661 | C <sub>12</sub> HN <sub>2</sub> O <sub>2</sub>                | 13.82 | 1.28 | 205.0038 |
| C <sub>10</sub> H <sub>23</sub> N <sub>2</sub> O <sub>2</sub> | 12.02 | 1.06 | 203.1761 | C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | 12.92 | 1.17 | 204.0899 | C <sub>12</sub> H <sub>19</sub> N <sub>3</sub>                | 14.42 | 0.97 | 205.1580 |
| C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>  | 11.80 | 1.24 | 203.0457 | C <sub>11</sub> H <sub>14</sub> N <sub>3</sub> O              | 13.29 | 1.02 | 204.1138 | C <sub>12</sub> H <sub>3</sub> N <sub>3</sub> O               | 14.20 | 1.14 | 205.0277 |
| C <sub>10</sub> H <sub>25</sub> N <sub>3</sub> O              | 12.39 | 0.91 | 203.1999 | C <sub>11</sub> H <sub>16</sub> N <sub>4</sub>                | 13.67 | 0.87 | 204.1377 | C <sub>12</sub> H <sub>5</sub> N <sub>4</sub>                 | 14.57 | 0.99 | 205.0515 |
| C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>  | 12.17 | 1.08 | 203.0695 | C <sub>11</sub> N <sub>4</sub> O                              | 13.45 | 1.04 | 204.0073 | C <sub>13</sub> H <sub>17</sub> O <sub>2</sub>                | 14.40 | 1.36 | 205.1229 |
| C <sub>10</sub> H <sub>11</sub> N <sub>4</sub> O              | 12.55 | 0.93 | 203.0934 | C <sub>12</sub> H <sub>12</sub> O <sub>3</sub>                | 13.28 | 1.41 | 204.0786 | C <sub>13</sub> HO <sub>3</sub>                               | 14.18 | 1.53 | 204.9925 |
| C <sub>11</sub> H <sub>23</sub> O <sub>3</sub>                | 12.37 | 1.30 | 203.1648 | C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> | 13.65 | 1.26 | 204.1025 | C <sub>13</sub> H <sub>19</sub> N <sub>2</sub> O              | 14.77 | 1.21 | 205.1467 |
| C <sub>11</sub> H <sub>7</sub> O <sub>4</sub>                 | 12.15 | 1.48 | 203.0344 | C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O              | 14.03 | 1.11 | 204.1264 | C <sub>13</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 14.56 | 1.38 | 205.0164 |
| C <sub>11</sub> H <sub>25</sub> N <sub>2</sub> O <sub>2</sub> | 12.75 | 1.15 | 203.1886 | C <sub>12</sub> N <sub>2</sub> O <sub>2</sub>                 | 13.81 | 1.28 | 203.9960 | C <sub>13</sub> H <sub>21</sub> N <sub>2</sub>                | 15.15 | 1.07 | 205.1706 |
| C <sub>11</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>  | 12.53 | 1.32 | 203.0583 | C <sub>12</sub> H <sub>18</sub> N <sub>3</sub>                | 14.40 | 0.96 | 204.1502 | C <sub>13</sub> H <sub>5</sub> N <sub>2</sub> O               | 14.93 | 1.24 | 205.0402 |
| C <sub>11</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 12.90 | 1.17 | 203.0821 | C <sub>12</sub> H <sub>2</sub> N <sub>3</sub> O               | 14.18 | 1.13 | 204.0198 | C <sub>13</sub> H <sub>7</sub> N <sub>3</sub>                 | 15.30 | 1.09 | 205.0641 |
| C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O              | 13.28 | 1.02 | 203.1060 | C <sub>12</sub> H <sub>4</sub> N <sub>4</sub>                 | 14.56 | 0.99 | 204.0437 | C <sub>14</sub> H <sub>21</sub> O                             | 15.50 | 1.32 | 205.1593 |
| C <sub>11</sub> H <sub>15</sub> N <sub>4</sub>                | 13.65 | 0.86 | 203.1298 | C <sub>13</sub> H <sub>16</sub> O <sub>2</sub>                | 14.38 | 1.36 | 204.1151 | C <sub>14</sub> H <sub>5</sub> O <sub>2</sub>                 | 15.29 | 1.49 | 205.0289 |
| C <sub>12</sub> H <sub>11</sub> O <sub>3</sub>                | 13.26 | 1.41 | 203.0708 | C <sub>13</sub> O <sub>3</sub>                                | 14.17 | 1.53 | 203.9847 | C <sub>14</sub> H <sub>23</sub> N                             | 15.88 | 1.18 | 205.1832 |
| C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> | 13.63 | 1.26 | 203.0947 | C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O              | 14.76 | 1.21 | 204.1389 | C <sub>14</sub> H <sub>7</sub> N <sub>2</sub> O               | 15.66 | 1.34 | 205.0528 |
| C <sub>12</sub> H <sub>15</sub> N <sub>2</sub> O              | 14.01 | 1.11 | 203.1185 | C <sub>13</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>  | 14.54 | 1.38 | 204.0085 | C <sub>14</sub> H <sub>9</sub> N <sub>2</sub>                 | 16.04 | 1.20 | 205.0767 |
| C <sub>12</sub> H <sub>17</sub> N <sub>3</sub>                | 14.38 | 0.96 | 203.1424 | C <sub>13</sub> H <sub>20</sub> N <sub>2</sub>                | 15.13 | 1.07 | 204.1628 | C <sub>15</sub> H <sub>25</sub>                               | 16.61 | 1.29 | 205.1957 |
| C <sub>12</sub> HN <sub>3</sub> O                             | 14.17 | 1.13 | 203.0120 | C <sub>13</sub> H <sub>4</sub> N <sub>2</sub> O               | 14.91 | 1.24 | 204.0324 | C <sub>15</sub> H <sub>9</sub> O                              | 16.39 | 1.46 | 205.0653 |
| C <sub>12</sub> H <sub>3</sub> N <sub>4</sub>                 | 14.54 | 0.98 | 203.0359 | C <sub>13</sub> H <sub>6</sub> N <sub>3</sub>                 | 15.29 | 1.09 | 204.0563 | C <sub>15</sub> H <sub>11</sub> N                             | 16.77 | 1.32 | 205.0892 |
| C <sub>13</sub> H <sub>15</sub> O <sub>2</sub>                | 14.37 | 1.36 | 203.1072 | C <sub>14</sub> H <sub>20</sub> O                             | 15.49 | 1.32 | 204.1515 | C <sub>16</sub> H <sub>13</sub>                               | 17.50 | 1.44 | 205.1018 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>17</sub> H   | 18.39 | 1.59 | 205.0078 | C <sub>9</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub>  | 11.51 | 1.01 | 207.0883 | C <sub>11</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>  | 13.14 | 1.20 | 208.0147 |
| 206   |       |      |          | C <sub>10</sub> H <sub>9</sub> N <sub>4</sub> O <sub>4</sub>  | 11.49 | 1.40 | 207.0532 | C <sub>11</sub> H <sub>20</sub> N <sub>4</sub>                | 13.73 | 0.88 | 208.1690 |
| C <sub>8</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>  | 9.85  | 1.24 | 206.1267 | C <sub>10</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> | 11.86 | 1.25 | 207.0770 | C <sub>11</sub> H <sub>4</sub> N <sub>4</sub> O               | 13.52 | 1.05 | 208.0386 |
| C <sub>8</sub> H <sub>20</sub> N <sub>3</sub> O <sub>3</sub>  | 10.23 | 1.08 | 206.1506 | C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> | 12.24 | 1.09 | 207.1009 | C <sub>12</sub> H <sub>16</sub> O <sub>3</sub>                | 13.34 | 1.42 | 208.1100 |
| C <sub>8</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub>  | 10.60 | 0.91 | 206.1744 | C <sub>10</sub> H <sub>15</sub> N <sub>4</sub> O              | 12.61 | 0.93 | 207.1247 | C <sub>12</sub> O <sub>4</sub>                                | 13.12 | 1.59 | 207.9796 |
| C <sub>9</sub> H <sub>20</sub> N <sub>4</sub> O               | 10.58 | 1.31 | 206.1393 | C <sub>11</sub> H <sub>11</sub> O <sub>4</sub>                | 12.22 | 1.48 | 207.0657 | C <sub>12</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> | 13.71 | 1.27 | 208.1338 |
| C <sub>9</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub>  | 10.96 | 1.15 | 206.1631 | C <sub>11</sub> H <sub>13</sub> N <sub>4</sub> O <sub>3</sub> | 12.59 | 1.33 | 207.0896 | C <sub>12</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>  | 13.50 | 1.44 | 208.0034 |
| C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>   | 10.74 | 1.32 | 206.0328 | C <sub>11</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> | 12.97 | 1.18 | 207.1134 | C <sub>12</sub> H <sub>20</sub> N <sub>2</sub> O              | 14.09 | 1.12 | 208.1577 |
| C <sub>9</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>   | 11.12 | 1.16 | 206.0566 | C <sub>11</sub> H <sub>17</sub> N <sub>3</sub> O              | 13.34 | 1.02 | 207.1373 | C <sub>12</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>  | 13.87 | 1.29 | 208.0273 |
| C <sub>9</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>  | 11.49 | 1.01 | 206.0805 | C <sub>11</sub> HN <sub>3</sub> O <sub>2</sub>                | 13.13 | 1.20 | 207.0069 | C <sub>12</sub> H <sub>22</sub> N <sub>3</sub>                | 14.46 | 0.97 | 208.1815 |
| C <sub>10</sub> H <sub>22</sub> O <sub>4</sub>                | 11.31 | 1.38 | 206.1518 | C <sub>11</sub> H <sub>19</sub> N <sub>4</sub>                | 13.72 | 0.87 | 207.1611 | C <sub>12</sub> H <sub>6</sub> N <sub>3</sub> O               | 14.25 | 1.14 | 208.0511 |
| C <sub>10</sub> H <sub>8</sub> N <sub>4</sub> O               | 11.47 | 1.40 | 206.0453 | C <sub>11</sub> H <sub>3</sub> N <sub>4</sub> O               | 13.50 | 1.04 | 207.0308 | C <sub>12</sub> H <sub>8</sub> N <sub>4</sub>                 | 14.62 | 1.00 | 208.0750 |
| C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 11.85 | 1.24 | 206.0692 | C <sub>12</sub> H <sub>15</sub> O <sub>3</sub>                | 13.32 | 1.42 | 207.1021 | C <sub>13</sub> H <sub>20</sub> O <sub>2</sub>                | 14.45 | 1.37 | 208.1464 |
| C <sub>10</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> | 12.22 | 1.09 | 206.0930 | C <sub>12</sub> H <sub>17</sub> N <sub>4</sub> O <sub>2</sub> | 13.70 | 1.27 | 207.1260 | C <sub>13</sub> H <sub>4</sub> O <sub>3</sub>                 | 14.23 | 1.54 | 208.0160 |
| C <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O              | 12.59 | 0.93 | 206.1169 | C <sub>12</sub> HN <sub>4</sub> O <sub>3</sub>                | 13.48 | 1.44 | 206.9956 | C <sub>13</sub> H <sub>22</sub> N <sub>4</sub> O              | 14.82 | 1.22 | 208.1702 |
| C <sub>11</sub> H <sub>10</sub> O <sub>4</sub>                | 12.20 | 1.48 | 206.0579 | C <sub>12</sub> H <sub>19</sub> N <sub>2</sub> O              | 14.07 | 1.12 | 207.1498 | C <sub>13</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 14.60 | 1.39 | 208.0399 |
| C <sub>11</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub> | 12.58 | 1.33 | 206.0817 | C <sub>12</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 13.86 | 1.29 | 207.0195 | C <sub>13</sub> H <sub>24</sub> N <sub>2</sub>                | 15.19 | 1.08 | 208.1941 |
| C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> | 12.95 | 1.17 | 206.1056 | C <sub>12</sub> H <sub>21</sub> N <sub>3</sub>                | 14.45 | 0.97 | 207.1737 | C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O               | 14.98 | 1.24 | 208.0637 |
| C <sub>11</sub> H <sub>16</sub> N <sub>3</sub> O              | 13.33 | 1.02 | 206.1295 | C <sub>12</sub> H <sub>5</sub> N <sub>3</sub> O               | 14.23 | 1.14 | 207.0433 | C <sub>13</sub> H <sub>10</sub> N <sub>3</sub>                | 15.35 | 1.10 | 208.0876 |
| C <sub>11</sub> N <sub>3</sub> O <sub>2</sub>                 | 13.11 | 1.19 | 205.9991 | C <sub>12</sub> H <sub>7</sub> N <sub>4</sub>                 | 14.61 | 0.99 | 207.0672 | C <sub>14</sub> H <sub>24</sub> O                             | 15.55 | 1.33 | 208.1828 |
| C <sub>11</sub> H <sub>18</sub> N <sub>4</sub>                | 13.70 | 0.87 | 206.1533 | C <sub>13</sub> H <sub>19</sub> O <sub>2</sub>                | 14.43 | 1.37 | 207.1385 | C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>                 | 15.33 | 1.49 | 208.0524 |
| C <sub>11</sub> H <sub>2</sub> N <sub>4</sub> O               | 13.48 | 1.04 | 206.0229 | C <sub>13</sub> H <sub>3</sub> O <sub>3</sub>                 | 14.21 | 1.54 | 207.0082 | C <sub>14</sub> H <sub>26</sub> N                             | 15.93 | 1.19 | 208.2067 |
| C <sub>12</sub> H <sub>14</sub> O <sub>3</sub>                | 13.31 | 1.42 | 206.0943 | C <sub>13</sub> H <sub>21</sub> N <sub>4</sub> O              | 14.80 | 1.22 | 207.1624 | C <sub>14</sub> H <sub>10</sub> N <sub>4</sub> O              | 15.71 | 1.35 | 208.0763 |
| C <sub>12</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> | 13.68 | 1.27 | 206.1182 | C <sub>13</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>  | 14.59 | 1.39 | 207.0320 | C <sub>14</sub> H <sub>12</sub> N <sub>2</sub>                | 16.08 | 1.21 | 208.1001 |
| C <sub>12</sub> N <sub>4</sub> O <sub>3</sub>                 | 13.47 | 1.44 | 205.9878 | C <sub>13</sub> H <sub>23</sub> N <sub>2</sub>                | 15.18 | 1.07 | 207.1863 | C <sub>15</sub> H <sub>28</sub>                               | 16.66 | 1.30 | 208.2192 |
| C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O              | 14.06 | 1.12 | 206.1420 | C <sub>13</sub> H <sub>7</sub> N <sub>2</sub> O               | 14.96 | 1.24 | 207.0559 | C <sub>15</sub> H <sub>12</sub> O                             | 16.44 | 1.46 | 208.0888 |
| C <sub>12</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>  | 13.84 | 1.29 | 206.0116 | C <sub>13</sub> H <sub>9</sub> N <sub>3</sub>                 | 15.34 | 1.10 | 207.0798 | C <sub>15</sub> H <sub>14</sub> N                             | 16.81 | 1.33 | 208.1127 |
| C <sub>12</sub> H <sub>20</sub> N <sub>3</sub>                | 14.43 | 0.97 | 206.1659 | C <sub>14</sub> H <sub>23</sub> O                             | 15.54 | 1.33 | 207.1750 | C <sub>15</sub> N <sub>2</sub>                                | 16.97 | 1.35 | 208.0062 |
| C <sub>12</sub> H <sub>4</sub> N <sub>3</sub> O               | 14.21 | 1.14 | 206.0355 | C <sub>14</sub> H <sub>7</sub> O <sub>2</sub>                 | 15.32 | 1.49 | 207.0446 | C <sub>16</sub> H <sub>16</sub>                               | 17.55 | 1.45 | 208.1253 |
| C <sub>12</sub> H <sub>6</sub> N <sub>4</sub>                 | 14.59 | 0.99 | 206.0594 | C <sub>14</sub> H <sub>25</sub> N                             | 15.91 | 1.18 | 207.1988 | C <sub>16</sub> O   | 17.33 | 1.61 | 207.9949 |
| C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>                | 14.41 | 1.36 | 206.1307 | C <sub>14</sub> H <sub>9</sub> N <sub>4</sub> O               | 15.69 | 1.35 | 207.0684 | C <sub>16</sub> H <sub>2</sub> N                              | 17.70 | 1.47 | 208.0187 |
| C <sub>13</sub> H <sub>2</sub> O <sub>3</sub>                 | 14.20 | 1.53 | 206.0003 | C <sub>14</sub> H <sub>11</sub> N <sub>2</sub>                | 16.07 | 1.21 | 207.0923 | C <sub>17</sub> H <sub>4</sub>                                | 18.43 | 1.60 | 208.0313 |
| C <sub>13</sub> H <sub>20</sub> N <sub>4</sub> O              | 14.79 | 1.22 | 206.1546 | C <sub>15</sub> H <sub>27</sub>                               | 16.64 | 1.30 | 207.2114 |   |       |      |          |
| C <sub>13</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>  | 14.57 | 1.39 | 206.0242 | C <sub>15</sub> H <sub>11</sub> O                             | 16.42 | 1.46 | 207.0810 |   |       |      |          |
| C <sub>13</sub> H <sub>22</sub> N <sub>2</sub>                | 15.16 | 1.07 | 206.1784 | C <sub>15</sub> H <sub>13</sub> N                             | 16.80 | 1.32 | 207.1049 | 209   |       |      |          |
| C <sub>13</sub> H <sub>6</sub> N <sub>2</sub> O               | 14.95 | 1.24 | 206.0480 | C <sub>16</sub> H <sub>15</sub>                               | 17.53 | 1.44 | 207.1174 | C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>   | 10.79 | 1.33 | 209.0563 |
| C <sub>13</sub> H <sub>8</sub> N <sub>3</sub>                 | 15.32 | 1.10 | 206.0719 | C <sub>16</sub> HN  | 17.69 | 1.47 | 207.0109 | C <sub>9</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub>  | 11.16 | 1.17 | 209.0801 |
| C <sub>14</sub> H <sub>22</sub> O                             | 15.52 | 1.32 | 206.1671 | C <sub>17</sub> H <sub>3</sub>                                | 18.42 | 1.60 | 207.0235 | C <sub>9</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub>  | 11.54 | 1.01 | 209.1040 |
| C <sub>14</sub> H <sub>6</sub> O <sub>2</sub>                 | 15.30 | 1.49 | 206.0368 |   |       |      |          | C <sub>10</sub> H <sub>11</sub> N <sub>4</sub> O <sub>4</sub> | 11.52 | 1.41 | 209.0688 |
| C <sub>14</sub> H <sub>24</sub> N                             | 15.89 | 1.18 | 206.1910 | 208   |       |      |          | C <sub>10</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> | 11.89 | 1.25 | 209.0927 |
| C <sub>14</sub> H <sub>8</sub> N <sub>4</sub> O               | 15.68 | 1.35 | 206.0606 | C <sub>8</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>  | 9.88  | 1.24 | 208.1424 | C <sub>10</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> | 12.27 | 1.09 | 209.1165 |
| C <sub>14</sub> H <sub>10</sub> N <sub>2</sub>                | 16.05 | 1.21 | 206.0845 | C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>   | 10.77 | 1.33 | 208.0484 | C <sub>10</sub> H <sub>17</sub> N <sub>4</sub> O              | 12.64 | 0.94 | 209.1404 |
| C <sub>15</sub> H <sub>26</sub>                               | 16.63 | 1.29 | 206.2036 | C <sub>9</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub>  | 11.15 | 1.17 | 208.0723 | C <sub>10</sub> HN <sub>4</sub> O <sub>2</sub>                | 12.43 | 1.11 | 209.0100 |
| C <sub>15</sub> H <sub>10</sub> O                             | 16.41 | 1.46 | 206.0732 | C <sub>9</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub>  | 11.52 | 1.01 | 208.0961 | C <sub>11</sub> H <sub>13</sub> O <sub>4</sub>                | 12.25 | 1.49 | 209.0814 |
| C <sub>15</sub> H <sub>12</sub> N                             | 16.78 | 1.32 | 206.0970 | C <sub>10</sub> H <sub>10</sub> N <sub>4</sub> O              | 11.50 | 1.40 | 208.0610 | C <sub>11</sub> H <sub>15</sub> N <sub>4</sub> O <sub>3</sub> | 12.63 | 1.33 | 209.1052 |
| C <sub>16</sub> H <sub>14</sub>                               | 17.51 | 1.44 | 206.1096 | C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> | 11.88 | 1.25 | 208.0848 | C <sub>11</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> | 13.00 | 1.18 | 209.1291 |
| C <sub>16</sub> N   | 17.67 | 1.47 | 206.0031 | C <sub>10</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> | 12.25 | 1.09 | 208.1087 | C <sub>11</sub> HN <sub>2</sub> O <sub>3</sub>                | 12.78 | 1.35 | 208.9987 |
| C <sub>17</sub> H <sub>2</sub>                                | 18.40 | 1.59 | 206.0157 | C <sub>10</sub> H <sub>16</sub> N <sub>4</sub> O              | 12.63 | 0.94 | 208.1325 | C <sub>11</sub> H <sub>19</sub> N <sub>3</sub> O              | 13.37 | 1.03 | 209.1529 |
| 207   |       |      |          | C <sub>10</sub> N <sub>4</sub> O <sub>2</sub>                 | 12.41 | 1.11 | 208.0022 | C <sub>11</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>  | 13.16 | 1.20 | 209.0226 |
| C <sub>8</sub> H <sub>19</sub> N <sub>2</sub> O <sub>4</sub>  | 9.87  | 1.24 | 207.1345 | C <sub>11</sub> H <sub>12</sub> O <sub>4</sub>                | 12.24 | 1.49 | 208.0735 | C <sub>11</sub> H <sub>21</sub> N <sub>4</sub>                | 13.75 | 0.88 | 209.1768 |
| C <sub>8</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub>  | 10.24 | 1.08 | 207.1584 | C <sub>11</sub> H <sub>14</sub> N <sub>4</sub> O <sub>3</sub> | 12.61 | 1.33 | 208.0974 | C <sub>11</sub> H <sub>5</sub> N <sub>4</sub> O               | 13.53 | 1.05 | 209.0464 |
| C <sub>9</sub> H <sub>21</sub> N <sub>4</sub> O               | 10.60 | 1.31 | 207.1471 | C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> | 12.98 | 1.18 | 208.1213 | C <sub>12</sub> H <sub>17</sub> O <sub>3</sub>                | 13.36 | 1.42 | 209.1176 |
| C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub>   | 10.76 | 1.33 | 207.0406 | C <sub>11</sub> N <sub>2</sub> O <sub>3</sub>                 | 12.77 | 1.35 | 207.9909 | C <sub>12</sub> H <sub>4</sub> O                              | 13.14 | 1.60 | 208.9874 |
| C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>   | 11.13 | 1.17 | 207.0644 | C <sub>11</sub> H <sub>18</sub> N <sub>3</sub> O              | 13.36 | 1.03 | 208.1451 | C <sub>12</sub> H <sub>19</sub> N <sub>4</sub> O <sub>2</sub> | 13.73 | 1.27 | 209.1416 |

|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>12</sub> H <sub>3</sub> NC <sub>3</sub>                | 13.51 | 1.44 | 209.0113 | C <sub>12</sub> H <sub>10</sub> N <sub>4</sub>                | 14.65 | 1.00 | 210.0907 | C <sub>13</sub> H <sub>25</sub> NC                            | 14.87 | 1.23 | 211.1937 |
| C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O              | 14.11 | 1.12 | 209.1555 | C <sub>13</sub> H <sub>22</sub> O <sub>2</sub>                | 14.48 | 1.37 | 210.1620 | C <sub>13</sub> H <sub>9</sub> NO <sub>2</sub>                | 14.65 | 1.40 | 211.0634 |
| C <sub>12</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>  | 13.89 | 1.29 | 209.0351 | C <sub>13</sub> H <sub>6</sub> O <sub>3</sub>                 | 14.26 | 1.54 | 210.0317 | C <sub>13</sub> H <sub>27</sub> N <sub>2</sub>                | 15.24 | 1.08 | 211.2176 |
| C <sub>12</sub> H <sub>23</sub> N <sub>3</sub>                | 14.48 | 0.98 | 209.1894 | C <sub>13</sub> H <sub>24</sub> NO                            | 14.85 | 1.23 | 210.1859 | C <sub>13</sub> H <sub>11</sub> N <sub>2</sub> O              | 15.03 | 1.25 | 211.0872 |
| C <sub>12</sub> H <sub>7</sub> N <sub>3</sub> O               | 14.26 | 1.15 | 209.0590 | C <sub>13</sub> H <sub>8</sub> NO <sub>2</sub>                | 14.64 | 1.40 | 210.0555 | C <sub>13</sub> H <sub>13</sub> N <sub>3</sub>                | 15.40 | 1.11 | 211.1111 |
| C <sub>12</sub> H <sub>9</sub> N <sub>4</sub>                 | 14.64 | 1.00 | 209.0829 | C <sub>13</sub> H <sub>26</sub> N <sub>2</sub>                | 15.23 | 1.08 | 210.2098 | C <sub>14</sub> H <sub>27</sub> O                             | 15.60 | 1.34 | 211.2063 |
| C <sub>13</sub> H <sub>21</sub> O <sub>2</sub>                | 14.46 | 1.37 | 209.1542 | C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O              | 15.01 | 1.25 | 210.0794 | C <sub>14</sub> H <sub>11</sub> O <sub>2</sub>                | 15.38 | 1.50 | 211.0759 |
| C <sub>13</sub> H <sub>5</sub> O <sub>3</sub>                 | 14.25 | 1.54 | 209.0238 | C <sub>13</sub> H <sub>12</sub> N <sub>3</sub>                | 15.38 | 1.11 | 210.1032 | C <sub>14</sub> H <sub>29</sub> N                             | 15.97 | 1.19 | 211.2301 |
| C <sub>13</sub> H <sub>23</sub> NO                            | 14.84 | 1.22 | 209.1781 | C <sub>14</sub> H <sub>26</sub> O                             | 15.58 | 1.33 | 210.1985 | C <sub>14</sub> H <sub>13</sub> NO                            | 15.76 | 1.36 | 211.0998 |
| C <sub>13</sub> H <sub>7</sub> NO <sub>2</sub>                | 14.62 | 1.39 | 209.0477 | C <sub>14</sub> H <sub>10</sub> O <sub>2</sub>                | 15.37 | 1.50 | 210.0681 | C <sub>14</sub> H <sub>15</sub> N <sub>2</sub>                | 16.13 | 1.22 | 211.1236 |
| C <sub>13</sub> H <sub>25</sub> N <sub>2</sub>                | 15.21 | 1.08 | 209.2019 | C <sub>14</sub> H <sub>28</sub> N                             | 15.96 | 1.19 | 210.2223 | C <sub>14</sub> HN <sub>3</sub>                               | 16.29 | 1.24 | 211.0171 |
| C <sub>13</sub> H <sub>9</sub> N <sub>2</sub> O               | 14.99 | 1.25 | 209.0715 | C <sub>14</sub> H <sub>12</sub> NO                            | 15.74 | 1.36 | 210.0919 | C <sub>15</sub> H <sub>31</sub>                               | 16.71 | 1.31 | 211.2427 |
| C <sub>13</sub> H <sub>11</sub> N <sub>3</sub>                | 15.37 | 1.10 | 209.0954 | C <sub>14</sub> H <sub>14</sub> N <sub>2</sub>                | 16.12 | 1.22 | 210.1158 | C <sub>15</sub> H <sub>15</sub> O                             | 16.49 | 1.47 | 211.1123 |
| C <sub>14</sub> H <sub>25</sub> O                             | 15.57 | 1.33 | 209.1906 | C <sub>14</sub> N <sub>3</sub>                                | 16.27 | 1.24 | 210.0093 | C <sub>15</sub> H <sub>17</sub> N                             | 16.86 | 1.33 | 211.1362 |
| C <sub>14</sub> H <sub>9</sub> O <sub>2</sub>                 | 15.35 | 1.50 | 209.0603 | C <sub>15</sub> H <sub>30</sub>                               | 16.69 | 1.31 | 210.2349 | C <sub>15</sub> HNO   | 16.65 | 1.50 | 211.0058 |
| C <sub>14</sub> H <sub>27</sub> N                             | 15.94 | 1.19 | 209.2145 | C <sub>15</sub> H <sub>14</sub> O                             | 16.47 | 1.47 | 210.1045 | C <sub>15</sub> H <sub>3</sub> N <sub>2</sub>                 | 17.02 | 1.36 | 211.0297 |
| C <sub>14</sub> H <sub>11</sub> NO                            | 15.72 | 1.35 | 209.0841 | C <sub>15</sub> H <sub>16</sub> N                             | 16.85 | 1.33 | 210.1284 | C <sub>16</sub> H <sub>19</sub>                               | 17.59 | 1.45 | 211.1488 |
| C <sub>14</sub> H <sub>13</sub> N <sub>2</sub>                | 16.10 | 1.21 | 209.1080 | C <sub>15</sub> NO  | 16.63 | 1.49 | 209.9980 | C <sub>16</sub> H <sub>3</sub> O                              | 17.38 | 1.62 | 211.0184 |
| C <sub>15</sub> H <sub>29</sub>                               | 16.67 | 1.30 | 209.2270 | C <sub>15</sub> H <sub>2</sub> N <sub>2</sub>                 | 17.00 | 1.36 | 210.0218 | C <sub>16</sub> H <sub>5</sub> N                              | 17.75 | 1.48 | 211.0422 |
| C <sub>15</sub> H <sub>13</sub> O                             | 16.46 | 1.47 | 209.0967 | C <sub>16</sub> H <sub>18</sub>                               | 17.58 | 1.45 | 210.1409 | C <sub>17</sub> H <sub>7</sub>                                | 18.48 | 1.61 | 211.0548 |
| C <sub>15</sub> H <sub>15</sub> N                             | 16.83 | 1.33 | 209.1205 | C <sub>16</sub> H <sub>2</sub> O                              | 17.36 | 1.61 | 210.0106 | 212   |       |      |          |
| C <sub>15</sub> HN <sub>2</sub>                               | 16.99 | 1.35 | 209.0140 | C <sub>16</sub> H <sub>4</sub> N                              | 17.74 | 1.48 | 210.0344 | C <sub>9</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>  | 10.84 | 1.34 | 212.0797 |
| C <sub>16</sub> H <sub>17</sub>                               | 17.56 | 1.45 | 209.1331 | C <sub>17</sub> H <sub>6</sub>                                | 18.47 | 1.61 | 210.0470 | C <sub>9</sub> H <sub>14</sub> N <sub>3</sub> O <sub>3</sub>  | 11.21 | 1.18 | 212.1036 |
| C <sub>16</sub> HO  | 17.34 | 1.61 | 209.0027 |   |       |      |          | C <sub>9</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub>  | 11.59 | 1.02 | 212.1275 |
| C <sub>16</sub> H <sub>3</sub> N                              | 17.72 | 1.48 | 209.0266 | 211   |       |      |          | C <sub>10</sub> H <sub>14</sub> NO <sub>4</sub>               | 11.57 | 1.41 | 212.0923 |
| C <sub>17</sub> H <sub>5</sub>                                | 18.45 | 1.60 | 209.0391 | C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub>  | 10.82 | 1.33 | 211.0719 | C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> | 11.94 | 1.25 | 212.1162 |
| 210   |       |      |          | C <sub>9</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>  | 11.20 | 1.17 | 211.0958 | C <sub>10</sub> N <sub>2</sub> O <sub>4</sub>                 | 11.73 | 1.43 | 211.9858 |
| C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub>  | 10.80 | 1.33 | 210.0641 | C <sub>9</sub> H <sub>15</sub> N <sub>4</sub> O <sub>2</sub>  | 11.57 | 1.01 | 211.1196 | C <sub>10</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> | 12.32 | 1.10 | 212.1400 |
| C <sub>9</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub>  | 11.18 | 1.17 | 210.0879 | C <sub>10</sub> H <sub>13</sub> NO <sub>4</sub>               | 11.55 | 1.41 | 211.0845 | C <sub>10</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>  | 12.10 | 1.27 | 212.0096 |
| C <sub>9</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>  | 11.55 | 1.01 | 210.1118 | C <sub>10</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub> | 11.93 | 1.25 | 211.1083 | C <sub>10</sub> H <sub>20</sub> N <sub>4</sub> O              | 12.69 | 0.94 | 212.1639 |
| C <sub>10</sub> H <sub>12</sub> NO <sub>4</sub>               | 11.54 | 1.41 | 210.0766 | C <sub>10</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> | 12.30 | 1.10 | 211.1322 | C <sub>10</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>  | 12.47 | 1.12 | 212.0335 |
| C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> | 11.91 | 1.25 | 210.1005 | C <sub>10</sub> HN <sub>3</sub> O <sub>3</sub>                | 12.08 | 1.27 | 211.0018 | C <sub>11</sub> H <sub>16</sub> O <sub>4</sub>                | 12.30 | 1.49 | 212.1049 |
| C <sub>10</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub> | 12.28 | 1.09 | 210.1244 | C <sub>10</sub> H <sub>19</sub> N <sub>4</sub> O              | 12.67 | 0.94 | 211.1560 | C <sub>11</sub> H <sub>18</sub> NO <sub>3</sub>               | 12.67 | 1.34 | 212.1287 |
| C <sub>10</sub> N <sub>3</sub> O <sub>3</sub>                 | 12.07 | 1.27 | 209.9940 | C <sub>10</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>  | 12.46 | 1.12 | 211.0257 | C <sub>11</sub> H <sub>2</sub> NO <sub>4</sub>                | 12.46 | 1.51 | 211.9983 |
| C <sub>10</sub> H <sub>18</sub> N <sub>4</sub> O              | 12.66 | 0.94 | 210.1482 | C <sub>11</sub> H <sub>15</sub> O <sub>4</sub>                | 12.28 | 1.49 | 211.0970 | C <sub>11</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> | 13.05 | 1.19 | 212.1526 |
| C <sub>10</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>  | 12.44 | 1.11 | 210.0178 | C <sub>11</sub> H <sub>17</sub> NO <sub>3</sub>               | 12.66 | 1.34 | 211.1209 | C <sub>11</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 12.83 | 1.36 | 212.0222 |
| C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>                | 12.27 | 1.49 | 210.0892 | C <sub>11</sub> HNO <sub>4</sub>                              | 12.44 | 1.51 | 210.9905 | C <sub>11</sub> H <sub>22</sub> N <sub>3</sub> O              | 13.42 | 1.03 | 212.1764 |
| C <sub>11</sub> H <sub>16</sub> NO <sub>3</sub>               | 12.64 | 1.34 | 210.1131 | C <sub>11</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub> | 13.03 | 1.18 | 211.1447 | C <sub>11</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>  | 13.21 | 1.21 | 212.0460 |
| C <sub>11</sub> NO <sub>4</sub>                               | 12.42 | 1.51 | 209.9827 | C <sub>11</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 12.81 | 1.36 | 211.0144 | C <sub>11</sub> H <sub>24</sub> N <sub>4</sub>                | 13.80 | 0.88 | 212.2003 |
| C <sub>11</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> | 13.02 | 1.18 | 210.1369 | C <sub>11</sub> H <sub>21</sub> N <sub>3</sub> O              | 13.41 | 1.03 | 211.1686 | C <sub>11</sub> H <sub>8</sub> N <sub>4</sub> O               | 13.58 | 1.06 | 212.0699 |
| C <sub>11</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>  | 12.80 | 1.35 | 210.0065 | C <sub>11</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>  | 13.19 | 1.20 | 211.0382 | C <sub>12</sub> H <sub>20</sub> O <sub>3</sub>                | 13.40 | 1.43 | 212.1413 |
| C <sub>11</sub> H <sub>20</sub> N <sub>3</sub> O              | 13.39 | 1.03 | 210.1608 | C <sub>11</sub> H <sub>23</sub> N <sub>4</sub>                | 13.78 | 0.88 | 211.1925 | C <sub>12</sub> H <sub>4</sub> O <sub>4</sub>                 | 13.19 | 1.60 | 212.0109 |
| C <sub>11</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>  | 13.17 | 1.20 | 210.0304 | C <sub>11</sub> H <sub>7</sub> N <sub>4</sub> O               | 13.56 | 1.05 | 211.0621 | C <sub>12</sub> H <sub>22</sub> NO <sub>2</sub>               | 13.78 | 1.28 | 212.1651 |
| C <sub>11</sub> H <sub>22</sub> N <sub>4</sub>                | 13.76 | 0.88 | 210.1846 | C <sub>12</sub> H <sub>19</sub> O <sub>3</sub>                | 13.39 | 1.43 | 211.1334 | C <sub>12</sub> H <sub>6</sub> NO <sub>3</sub>                | 13.56 | 1.45 | 212.0348 |
| C <sub>11</sub> H <sub>6</sub> N <sub>4</sub> O               | 13.55 | 1.05 | 210.0542 | C <sub>12</sub> H <sub>3</sub> O <sub>4</sub>                 | 13.17 | 1.60 | 211.0031 | C <sub>12</sub> H <sub>24</sub> N <sub>2</sub> O              | 14.15 | 1.13 | 212.1890 |
| C <sub>12</sub> H <sub>18</sub> O <sub>3</sub>                | 13.37 | 1.43 | 210.1256 | C <sub>12</sub> H <sub>21</sub> NO <sub>2</sub>               | 13.76 | 1.28 | 211.1573 | C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 13.94 | 1.30 | 212.0586 |
| C <sub>12</sub> H <sub>2</sub> O <sub>4</sub>                 | 13.16 | 1.60 | 209.9953 | C <sub>12</sub> H <sub>5</sub> NO <sub>3</sub>                | 13.55 | 1.45 | 211.0269 | C <sub>12</sub> H <sub>26</sub> N <sub>3</sub>                | 14.53 | 0.98 | 212.2129 |
| C <sub>12</sub> H <sub>20</sub> NO <sub>2</sub>               | 13.75 | 1.28 | 210.1495 | C <sub>12</sub> H <sub>23</sub> N <sub>2</sub> O              | 14.14 | 1.13 | 211.1811 | C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> O              | 14.31 | 1.15 | 212.0825 |
| C <sub>12</sub> H <sub>4</sub> NO <sub>3</sub>                | 13.53 | 1.45 | 210.0191 | C <sub>12</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>  | 13.92 | 1.30 | 211.0508 | C <sub>12</sub> H <sub>12</sub> N <sub>4</sub>                | 14.69 | 1.01 | 212.1063 |
| C <sub>12</sub> H <sub>22</sub> N <sub>2</sub> O              | 14.12 | 1.13 | 210.1733 | C <sub>12</sub> H <sub>25</sub> N <sub>3</sub>                | 14.51 | 0.98 | 211.2050 | C <sub>13</sub> H <sub>24</sub> O <sub>2</sub>                | 14.51 | 1.38 | 212.1777 |
| C <sub>12</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 13.90 | 1.30 | 210.0429 | C <sub>12</sub> H <sub>9</sub> N <sub>3</sub> O               | 14.29 | 1.15 | 211.0746 | C <sub>13</sub> H <sub>8</sub> O <sub>3</sub>                 | 14.29 | 1.55 | 212.0473 |
| C <sub>12</sub> H <sub>24</sub> N <sub>3</sub>                | 14.50 | 0.98 | 210.1972 | C <sub>12</sub> H <sub>11</sub> N <sub>4</sub>                | 14.67 | 1.00 | 211.0985 | C <sub>13</sub> H <sub>26</sub> NO                            | 14.88 | 1.23 | 212.2015 |
| C <sub>12</sub> H <sub>8</sub> N <sub>3</sub> O               | 14.28 | 1.15 | 210.0668 | C <sub>13</sub> H <sub>23</sub> O <sub>2</sub>                | 14.49 | 1.38 | 211.1699 | C <sub>13</sub> H <sub>10</sub> NO <sub>2</sub>               | 14.67 | 1.40 | 212.0712 |
|   |       |      |          | C <sub>13</sub> H <sub>7</sub> O <sub>3</sub>                 | 14.28 | 1.54 | 211.0395 |   |       |      |          |



|                      | M+1   | M+2  | MW       |                      | M+1   | M+2  | MW       |                      | M+1   | M+2  | MW       |
|----------------------|-------|------|----------|----------------------|-------|------|----------|----------------------|-------|------|----------|
| $C_{13}H_{28}N_2$    | 15.26 | 1.09 | 212.2254 | $C_{13}H_{11}NO_2$   | 14.68 | 1.40 | 213.0790 | $C_{13}H_{12}NO_2$   | 14.70 | 1.40 | 214.0868 |
| $C_{13}H_{12}N_2O$   | 15.04 | 1.25 | 212.0950 | $C_{13}H_{29}N_2$    | 15.27 | 1.09 | 213.2332 | $C_{13}H_{30}N_2$    | 15.29 | 1.09 | 214.2411 |
| $C_{13}H_{14}N_3$    | 15.42 | 1.11 | 212.1189 | $C_{13}H_{13}N_2O$   | 15.06 | 1.26 | 213.1029 | $C_{13}H_{14}N_2O$   | 15.07 | 1.26 | 214.1107 |
| $C_{13}N_4$          | 15.57 | 1.13 | 212.0124 | $C_{13}H_{15}N_3$    | 15.43 | 1.11 | 213.1267 | $C_{13}H_{16}N_3$    | 15.45 | 1.12 | 214.1346 |
| $C_{14}H_{28}O$      | 15.62 | 1.34 | 212.2141 | $C_{13}HN_4$         | 15.59 | 1.14 | 213.0202 | $C_{13}N_3O$         | 15.23 | 1.28 | 214.0042 |
| $C_{14}H_{12}O_2$    | 15.40 | 1.50 | 212.0837 | $C_{14}H_{29}O$      | 15.63 | 1.34 | 213.2219 | $C_{13}H_2N_4$       | 15.61 | 1.14 | 214.0280 |
| $C_{14}H_{30}N$      | 15.99 | 1.20 | 212.2380 | $C_{14}H_{13}O_2$    | 15.41 | 1.51 | 213.0916 | $C_{14}H_{30}O$      | 15.65 | 1.34 | 214.2298 |
| $C_{14}H_{14}NO$     | 15.77 | 1.36 | 212.1076 | $C_{14}H_{31}N$      | 16.01 | 1.20 | 213.2458 | $C_{14}H_{14}O_2$    | 15.43 | 1.51 | 214.0994 |
| $C_{14}H_{16}N_2$    | 16.15 | 1.22 | 212.1315 | $C_{14}H_{15}NO$     | 15.79 | 1.36 | 213.1154 | $C_{14}H_{16}NO$     | 15.80 | 1.37 | 214.1233 |
| $C_{14}N_2O$         | 15.93 | 1.39 | 212.0011 | $C_{14}H_{17}N_2$    | 16.16 | 1.22 | 213.1393 | $C_{14}NO_2$         | 15.59 | 1.53 | 213.9929 |
| $C_{14}H_2N_3$       | 16.30 | 1.25 | 212.0249 | $C_{14}HN_2O$        | 15.95 | 1.39 | 213.0089 | $C_{14}H_{18}N_2$    | 16.18 | 1.23 | 214.1471 |
| $C_{15}H_{32}$       | 16.72 | 1.31 | 212.2505 | $C_{14}H_3N_3$       | 16.32 | 1.25 | 213.0328 | $C_{14}H_2N_2O$      | 15.96 | 1.39 | 214.0167 |
| $C_{15}H_{16}O$      | 16.50 | 1.47 | 212.1202 | $C_{15}H_{17}O$      | 16.52 | 1.48 | 213.1280 | $C_{14}H_4N_3$       | 16.34 | 1.25 | 214.0406 |
| $C_{15}O_2$          | 16.29 | 1.64 | 211.9898 | $C_{15}HO_2$         | 16.30 | 1.64 | 212.9976 | $C_{15}H_{18}O$      | 16.54 | 1.48 | 214.1358 |
| $C_{15}H_{18}N$      | 16.88 | 1.34 | 212.1440 | $C_{15}H_{19}N$      | 16.89 | 1.34 | 213.1519 | $C_{15}H_2O_2$       | 16.32 | 1.64 | 214.0054 |
| $C_{15}H_2NO$        | 16.66 | 1.50 | 212.0136 | $C_{15}H_3NO$        | 16.68 | 1.50 | 213.0215 | $C_{15}H_{20}N$      | 16.91 | 1.34 | 214.1597 |
| $C_{15}H_4N_2$       | 17.04 | 1.36 | 212.0375 | $C_{15}H_5N_2$       | 17.05 | 1.36 | 213.0453 | $C_{15}H_4NO$        | 16.69 | 1.51 | 214.0293 |
| $C_{16}H_{20}$       | 17.61 | 1.46 | 212.1566 | $C_{16}H_{21}$       | 17.63 | 1.46 | 213.1644 | $C_{15}H_6N_2$       | 17.07 | 1.37 | 214.0532 |
| $C_{16}H_4O$         | 17.39 | 1.62 | 212.0262 | $C_{16}H_5O$         | 17.41 | 1.62 | 213.0340 | $C_{16}H_{22}$       | 17.64 | 1.46 | 214.1722 |
| $C_{16}H_6N$         | 17.77 | 1.48 | 212.0501 | $C_{16}H_7N$         | 17.78 | 1.49 | 213.0579 | $C_{16}H_6O$         | 17.42 | 1.63 | 214.0419 |
| $C_{17}H_8$          | 18.50 | 1.61 | 212.0626 | $C_{17}H_9$          | 18.51 | 1.61 | 213.0705 | $C_{16}H_8N$         | 17.80 | 1.49 | 214.0657 |
|                      |       |      |          |                      |       |      |          | $C_{17}H_{10}$       | 18.53 | 1.62 | 214.0783 |
| 213                  |       |      |          | 214                  |       |      |          | 215                  |       |      |          |
| $C_9H_{13}N_2O_4$    | 10.85 | 1.34 | 213.0876 | $C_9H_{14}N_2O_4$    | 10.87 | 1.34 | 214.0954 | $C_9H_{15}N_2O_4$    | 10.88 | 1.34 | 215.1032 |
| $C_9H_{15}N_3O_3$    | 11.23 | 1.18 | 213.1114 | $C_9H_{16}N_3O_3$    | 11.24 | 1.18 | 214.1193 | $C_9H_{17}N_3O_3$    | 11.26 | 1.18 | 215.1271 |
| $C_9H_{17}N_4O_2$    | 11.60 | 1.02 | 213.1353 | $C_9H_{18}N_4O_2$    | 11.62 | 1.02 | 214.1431 | $C_9H_{19}N_4O_2$    | 11.63 | 1.02 | 215.1509 |
| $C_{10}H_{15}NO_4$   | 11.58 | 1.41 | 213.1001 | $C_{10}H_{16}NO_4$   | 11.60 | 1.42 | 214.1080 | $C_{10}H_{17}NO_4$   | 11.62 | 1.42 | 215.1158 |
| $C_{10}H_{17}N_2O_3$ | 11.96 | 1.26 | 213.1240 | $C_{10}H_{18}N_2O_3$ | 11.97 | 1.26 | 214.1318 | $C_{10}H_{19}N_2O_3$ | 11.99 | 1.26 | 215.1396 |
| $C_{10}HN_2O_4$      | 11.74 | 1.43 | 212.9936 | $C_{10}H_2N_2O_4$    | 11.76 | 1.43 | 214.0014 | $C_{10}H_3N_2O_4$    | 11.77 | 1.44 | 215.0093 |
| $C_{10}H_{19}N_3O_2$ | 12.33 | 1.10 | 213.1478 | $C_{10}H_{20}N_3O_2$ | 12.35 | 1.10 | 214.1557 | $C_{10}H_{21}N_3O_2$ | 12.36 | 1.10 | 215.1635 |
| $C_{10}H_3N_3O_3$    | 12.12 | 1.27 | 213.0175 | $C_{10}H_4N_3O_3$    | 12.13 | 1.28 | 214.0253 | $C_{10}H_5N_3O_3$    | 12.15 | 1.28 | 215.0331 |
| $C_{10}H_{21}N_4O$   | 12.71 | 0.95 | 213.1717 | $C_{10}H_{22}N_4O$   | 12.72 | 0.95 | 214.1795 | $C_{10}H_{23}N_4O$   | 12.74 | 0.95 | 215.1873 |
| $C_{10}H_5N_4O_2$    | 12.49 | 1.12 | 213.0413 | $C_{10}H_6N_4O_2$    | 12.51 | 1.12 | 214.0491 | $C_{10}H_7N_4O_2$    | 12.52 | 1.12 | 215.0570 |
| $C_{11}H_{17}O_4$    | 12.32 | 1.50 | 213.1127 | $C_{11}H_{18}O_4$    | 12.33 | 1.50 | 214.1205 | $C_{11}H_{19}O_4$    | 12.35 | 1.50 | 215.1284 |
| $C_{11}H_{19}NO_3$   | 12.69 | 1.34 | 213.1365 | $C_{11}H_{20}NO_3$   | 12.71 | 1.34 | 214.1444 | $C_{11}H_{21}NO_3$   | 12.72 | 1.35 | 215.1522 |
| $C_{11}H_3NO_4$      | 12.47 | 1.51 | 213.0062 | $C_{11}H_4NO_4$      | 12.49 | 1.52 | 214.0140 | $C_{11}H_5NO_4$      | 12.50 | 1.52 | 215.0218 |
| $C_{11}H_{21}N_2O_2$ | 13.06 | 1.19 | 213.1604 | $C_{11}H_{22}N_2O_2$ | 13.08 | 1.19 | 214.1682 | $C_{11}H_{23}N_2O_2$ | 13.10 | 1.19 | 215.1761 |
| $C_{11}H_5N_2O_3$    | 12.85 | 1.36 | 213.0300 | $C_{11}H_6N_2O_3$    | 12.86 | 1.36 | 214.0379 | $C_{11}H_7N_2O_3$    | 12.88 | 1.37 | 215.0457 |
| $C_{11}H_{23}N_3O$   | 13.44 | 1.04 | 213.1842 | $C_{11}H_{24}N_3O$   | 13.45 | 1.04 | 214.1921 | $C_{11}H_{25}N_3O$   | 13.47 | 1.04 | 215.1999 |
| $C_{11}H_7N_3O_2$    | 13.22 | 1.21 | 213.0539 | $C_{11}H_8N_3O_2$    | 13.24 | 1.21 | 214.0617 | $C_{11}H_9N_3O_2$    | 13.25 | 1.21 | 215.0695 |
| $C_{11}H_{25}N_4$    | 13.81 | 0.89 | 213.2081 | $C_{11}H_{26}N_4$    | 13.83 | 0.89 | 214.2160 | $C_{11}H_{27}N_4$    | 13.84 | 0.89 | 215.2238 |
| $C_{11}H_9N_4O$      | 13.60 | 1.06 | 213.0777 | $C_{11}H_{10}N_4O$   | 13.61 | 1.06 | 214.0856 | $C_{11}H_{11}N_4O$   | 13.63 | 1.06 | 215.0934 |
| $C_{12}H_{21}O_3$    | 13.42 | 1.43 | 213.1491 | $C_{12}H_{22}O_3$    | 13.44 | 1.43 | 214.1569 | $C_{12}H_{23}O_3$    | 13.45 | 1.44 | 215.1648 |
| $C_{12}H_5O_4$       | 13.20 | 1.60 | 213.0187 | $C_{12}H_6O_4$       | 13.22 | 1.61 | 214.0266 | $C_{12}H_7O_4$       | 13.24 | 1.61 | 215.0344 |
| $C_{12}H_{23}NO_2$   | 13.79 | 1.28 | 213.1730 | $C_{12}H_{24}NO_2$   | 13.81 | 1.28 | 214.1808 | $C_{12}H_{25}NO_2$   | 13.83 | 1.29 | 215.1886 |
| $C_{12}H_7NO_3$      | 13.58 | 1.45 | 213.0426 | $C_{12}H_8NO_3$      | 13.59 | 1.45 | 214.0504 | $C_{12}H_9NO_3$      | 13.61 | 1.46 | 215.0583 |
| $C_{12}H_{25}N_2O$   | 14.17 | 1.13 | 213.1968 | $C_{12}H_{26}N_2O$   | 14.19 | 1.14 | 214.2046 | $C_{12}H_{27}N_2O$   | 14.20 | 1.14 | 215.2125 |
| $C_{12}H_9N_2O_2$    | 13.95 | 1.30 | 213.0664 | $C_{12}H_{10}N_2O_2$ | 13.97 | 1.30 | 214.0743 | $C_{12}H_{11}N_2O_2$ | 13.98 | 1.31 | 215.0821 |
| $C_{12}H_{27}N_3$    | 14.54 | 0.99 | 213.2207 | $C_{12}H_{28}N_3$    | 14.56 | 0.99 | 214.2285 | $C_{12}H_{29}N_3$    | 14.58 | 0.99 | 215.2363 |
| $C_{12}H_{11}N_3O$   | 14.33 | 1.15 | 213.0903 | $C_{12}H_{12}N_3O$   | 14.34 | 1.16 | 214.0981 | $C_{12}H_{13}N_3O$   | 14.36 | 1.16 | 215.1060 |
| $C_{12}H_{13}N_4$    | 14.70 | 1.01 | 213.1142 | $C_{12}H_{14}N_4$    | 14.72 | 1.01 | 214.1220 | $C_{12}H_{15}N_4$    | 14.73 | 1.01 | 215.1298 |
| $C_{13}H_{25}O_2$    | 14.53 | 1.38 | 213.1855 | $C_{13}H_{26}O_2$    | 14.54 | 1.38 | 214.1934 | $C_{13}H_{27}O_2$    | 14.56 | 1.38 | 215.2012 |
| $C_{13}H_9O_3$       | 14.31 | 1.55 | 213.0552 | $C_{13}H_{10}O_3$    | 14.33 | 1.55 | 214.0630 | $C_{13}H_{11}O_3$    | 14.34 | 1.55 | 215.0708 |
| $C_{13}H_{27}NO$     | 14.90 | 1.23 | 213.2094 | $C_{13}H_{28}NO$     | 14.92 | 1.24 | 214.2172 | $C_{13}H_{29}NO$     | 14.93 | 1.24 | 215.2250 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> | 14.72 | 1.41 | 215.0947 | C <sub>13</sub> N <sub>2</sub> O <sub>2</sub>                 | 14.89 | 1.43 | 215.9960 | C <sub>13</sub> H <sub>3</sub> N <sub>3</sub> O               | 15.28 | 1.29 | 217.0277 |
| C <sub>13</sub> H <sub>15</sub> N <sub>2</sub> O              | 15.09 | 1.26 | 215.1185 | C <sub>13</sub> H <sub>18</sub> N <sub>3</sub>                | 15.48 | 1.12 | 216.1502 | C <sub>13</sub> H <sub>5</sub> N <sub>4</sub>                 | 15.65 | 1.15 | 217.0515 |
| C <sub>13</sub> H <sub>17</sub> N <sub>3</sub>                | 15.46 | 1.12 | 215.1424 | C <sub>13</sub> H <sub>2</sub> N <sub>3</sub> O               | 15.26 | 1.29 | 216.0198 | C <sub>14</sub> H <sub>17</sub> O <sub>2</sub>                | 15.48 | 1.52 | 217.1229 |
| C <sub>13</sub> HN <sub>3</sub> O                             | 15.25 | 1.28 | 215.0120 | C <sub>13</sub> H <sub>4</sub> N <sub>4</sub>                 | 15.64 | 1.14 | 216.0437 | C <sub>14</sub> H <sub>3</sub> O <sub>3</sub>                 | 15.26 | 1.68 | 216.9925 |
| C <sub>13</sub> H <sub>3</sub> N <sub>4</sub>                 | 15.62 | 1.14 | 215.0359 | C <sub>14</sub> H <sub>16</sub> O <sub>2</sub>                | 15.46 | 1.51 | 216.1151 | C <sub>14</sub> H <sub>19</sub> NO                            | 15.85 | 1.37 | 217.1467 |
| C <sub>14</sub> H <sub>15</sub> O <sub>2</sub>                | 15.45 | 1.51 | 215.1072 | C <sub>14</sub> O <sub>3</sub>                                | 15.25 | 1.68 | 215.9847 | C <sub>14</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 15.64 | 1.54 | 217.0164 |
| C <sub>14</sub> H <sub>17</sub> NO                            | 15.82 | 1.37 | 215.1311 | C <sub>14</sub> H <sub>18</sub> NO                            | 15.84 | 1.37 | 216.1389 | C <sub>14</sub> H <sub>21</sub> N <sub>2</sub>                | 16.23 | 1.23 | 217.1706 |
| C <sub>14</sub> HN <sub>2</sub> O <sub>2</sub>                | 15.60 | 1.54 | 215.0007 | C <sub>14</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>  | 15.62 | 1.54 | 216.0085 | C <sub>14</sub> H <sub>5</sub> N <sub>2</sub> O               | 16.01 | 1.40 | 217.0402 |
| C <sub>14</sub> H <sub>19</sub> N <sub>2</sub>                | 16.20 | 1.23 | 215.1549 | C <sub>14</sub> H <sub>20</sub> N <sub>2</sub>                | 16.21 | 1.23 | 216.1628 | C <sub>14</sub> H <sub>7</sub> N <sub>3</sub>                 | 16.38 | 1.26 | 217.0641 |
| C <sub>14</sub> H <sub>3</sub> N <sub>2</sub> O               | 15.98 | 1.39 | 215.0246 | C <sub>14</sub> H <sub>4</sub> N <sub>2</sub> O               | 15.99 | 1.40 | 216.0324 | C <sub>15</sub> H <sub>21</sub> O                             | 16.58 | 1.49 | 217.1593 |
| C <sub>14</sub> H <sub>5</sub> N <sub>3</sub>                 | 16.35 | 1.25 | 215.0484 | C <sub>14</sub> H <sub>6</sub> N <sub>3</sub>                 | 16.37 | 1.26 | 216.0563 | C <sub>15</sub> H <sub>5</sub> O <sub>2</sub>                 | 16.37 | 1.65 | 217.0289 |
| C <sub>15</sub> H <sub>19</sub> O                             | 16.55 | 1.48 | 215.1436 | C <sub>15</sub> H <sub>20</sub> O                             | 16.57 | 1.49 | 216.1515 | C <sub>15</sub> H <sub>23</sub> N                             | 16.96 | 1.35 | 217.1832 |
| C <sub>15</sub> H <sub>3</sub> O <sub>2</sub>                 | 16.34 | 1.65 | 215.0133 | C <sub>15</sub> H <sub>4</sub> O <sub>2</sub>                 | 16.35 | 1.65 | 216.0211 | C <sub>15</sub> H <sub>7</sub> NO                             | 16.74 | 1.51 | 217.0528 |
| C <sub>15</sub> H <sub>21</sub> N                             | 16.93 | 1.34 | 215.1675 | C <sub>15</sub> H <sub>22</sub> N                             | 16.94 | 1.35 | 216.1753 | C <sub>15</sub> H <sub>9</sub> N <sub>2</sub>                 | 17.12 | 1.38 | 217.0767 |
| C <sub>15</sub> H <sub>5</sub> NO                             | 16.71 | 1.51 | 215.0371 | C <sub>15</sub> H <sub>6</sub> NO                             | 16.73 | 1.51 | 216.0449 | C <sub>16</sub> H <sub>25</sub>                               | 17.69 | 1.47 | 217.1957 |
| C <sub>15</sub> H <sub>7</sub> N <sub>2</sub>                 | 17.08 | 1.37 | 215.0610 | C <sub>15</sub> H <sub>8</sub> N <sub>2</sub>                 | 17.10 | 1.37 | 216.0688 | C <sub>16</sub> H <sub>9</sub> O                              | 17.47 | 1.63 | 217.0653 |
| C <sub>16</sub> H <sub>23</sub>                               | 17.66 | 1.47 | 215.1801 | C <sub>16</sub> H <sub>24</sub>                               | 17.67 | 1.47 | 216.1879 | C <sub>16</sub> H <sub>11</sub> N                             | 17.85 | 1.50 | 217.0892 |
| C <sub>16</sub> H <sub>7</sub> O                              | 17.44 | 1.63 | 215.0497 | C <sub>16</sub> H <sub>8</sub> O                              | 17.46 | 1.63 | 216.0575 | C <sub>17</sub> H <sub>13</sub>                               | 18.58 | 1.63 | 217.1018 |
| C <sub>16</sub> H <sub>9</sub> N                              | 17.82 | 1.49 | 215.0736 | C <sub>16</sub> H <sub>10</sub> N                             | 17.83 | 1.50 | 216.0814 | C <sub>18</sub> H   | 19.47 | 1.79 | 217.0078 |
| C <sub>17</sub> H <sub>11</sub>                               | 18.55 | 1.62 | 215.0861 | C <sub>17</sub> H <sub>12</sub>                               | 18.56 | 1.62 | 216.0939 | 218   |       |      |          |
|   |       |      |          | C <sub>18</sub>   | 19.45 | 1.79 | 216.0000 | C <sub>9</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>  | 10.93 | 1.35 | 218.1267 |
| 216   |       |      |          | 217   |       |      |          | C <sub>9</sub> H <sub>20</sub> N <sub>3</sub> O <sub>3</sub>  | 11.31 | 1.19 | 218.1506 |
| C <sub>9</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>  | 10.90 | 1.34 | 216.1111 |   |       |      |          | C <sub>9</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub>  | 11.68 | 1.03 | 218.1744 |
| C <sub>9</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub>  | 11.28 | 1.18 | 216.1349 | C <sub>9</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub>  | 10.92 | 1.34 | 217.1189 | C <sub>10</sub> H <sub>20</sub> NO <sub>4</sub>               | 11.66 | 1.42 | 218.1393 |
| C <sub>9</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>  | 11.65 | 1.02 | 216.1588 | C <sub>9</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub>  | 11.29 | 1.18 | 217.1427 | C <sub>10</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> | 12.04 | 1.27 | 218.1631 |
| C <sub>10</sub> H <sub>18</sub> NO <sub>4</sub>               | 11.63 | 1.42 | 216.1236 | C <sub>9</sub> H <sub>21</sub> N <sub>4</sub> O <sub>2</sub>  | 11.67 | 1.03 | 217.1666 | C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>  | 11.82 | 1.44 | 218.0328 |
| C <sub>10</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> | 12.01 | 1.26 | 216.1475 | C <sub>10</sub> H <sub>19</sub> NO <sub>4</sub>               | 11.65 | 1.42 | 217.1315 | C <sub>10</sub> H <sub>24</sub> N <sub>3</sub> O <sub>2</sub> | 12.41 | 1.11 | 218.1870 |
| C <sub>10</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>  | 11.79 | 1.44 | 216.0171 | C <sub>10</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> | 12.02 | 1.26 | 217.1553 | C <sub>10</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>  | 12.20 | 1.28 | 218.0566 |
| C <sub>10</sub> H <sub>22</sub> N <sub>3</sub> O <sub>2</sub> | 12.38 | 1.11 | 216.1713 | C <sub>10</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>  | 11.81 | 1.44 | 217.0249 | C <sub>10</sub> H <sub>26</sub> N <sub>4</sub> O              | 12.79 | 0.96 | 218.2108 |
| C <sub>10</sub> H <sub>6</sub> N <sub>3</sub> O <sub>3</sub>  | 12.16 | 1.28 | 216.0410 | C <sub>10</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub> | 12.40 | 1.11 | 217.1791 | C <sub>10</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> | 12.57 | 1.13 | 218.0805 |
| C <sub>10</sub> H <sub>24</sub> N <sub>4</sub> O              | 12.75 | 0.95 | 216.1952 | C <sub>10</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>  | 12.18 | 1.28 | 217.0488 | C <sub>11</sub> H <sub>22</sub> O <sub>4</sub>                | 12.40 | 1.51 | 218.1518 |
| C <sub>10</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>  | 12.54 | 1.13 | 216.0648 | C <sub>10</sub> H <sub>25</sub> N <sub>4</sub> O              | 12.77 | 0.95 | 217.2030 | C <sub>11</sub> H <sub>24</sub> NO <sub>3</sub>               | 12.77 | 1.35 | 218.1757 |
| C <sub>11</sub> H <sub>20</sub> O <sub>4</sub>                | 12.36 | 1.50 | 216.1362 | C <sub>10</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>  | 12.55 | 1.13 | 217.0726 | C <sub>11</sub> H <sub>8</sub> NO <sub>4</sub>                | 12.55 | 1.52 | 218.0453 |
| C <sub>11</sub> H <sub>22</sub> NO <sub>3</sub>               | 12.74 | 1.35 | 216.1600 | C <sub>11</sub> H <sub>21</sub> O <sub>4</sub>                | 12.38 | 1.50 | 217.1440 | C <sub>11</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> | 13.14 | 1.20 | 218.1996 |
| C <sub>11</sub> H <sub>6</sub> NO <sub>4</sub>                | 12.52 | 1.52 | 216.0297 | C <sub>11</sub> H <sub>23</sub> NO <sub>3</sub>               | 12.75 | 1.35 | 217.1679 | C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 12.93 | 1.37 | 218.0692 |
| C <sub>11</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> | 13.11 | 1.19 | 216.1839 | C <sub>11</sub> H <sub>7</sub> NO <sub>4</sub>                | 12.54 | 1.52 | 217.0375 | C <sub>11</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> | 13.30 | 1.22 | 218.0930 |
| C <sub>11</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 12.89 | 1.37 | 216.0535 | C <sub>11</sub> H <sub>25</sub> N <sub>2</sub> O <sub>2</sub> | 13.13 | 1.20 | 217.1917 | C <sub>11</sub> H <sub>14</sub> N <sub>4</sub> O              | 13.68 | 1.07 | 218.1169 |
| C <sub>11</sub> H <sub>26</sub> N <sub>3</sub> O              | 13.49 | 1.04 | 216.2077 | C <sub>11</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>  | 12.91 | 1.37 | 217.0614 | C <sub>12</sub> H <sub>26</sub> O <sub>3</sub>                | 13.50 | 1.44 | 218.1883 |
| C <sub>11</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub> | 13.27 | 1.21 | 216.0774 | C <sub>11</sub> H <sub>27</sub> N <sub>3</sub> O              | 13.50 | 1.05 | 217.2156 | C <sub>12</sub> H <sub>10</sub> O <sub>4</sub>                | 13.28 | 1.61 | 218.0579 |
| C <sub>11</sub> H <sub>28</sub> N <sub>4</sub>                | 13.86 | 0.89 | 216.2316 | C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> | 13.29 | 1.22 | 217.0852 | C <sub>12</sub> H <sub>12</sub> NO <sub>3</sub>               | 13.66 | 1.46 | 218.0817 |
| C <sub>11</sub> H <sub>12</sub> N <sub>4</sub> O              | 13.64 | 1.06 | 216.1012 | C <sub>11</sub> H <sub>13</sub> N <sub>4</sub> O              | 13.66 | 1.07 | 217.1091 | C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> | 14.03 | 1.31 | 218.1056 |
| C <sub>12</sub> H <sub>24</sub> O <sub>3</sub>                | 13.47 | 1.44 | 216.1726 | C <sub>12</sub> H <sub>25</sub> O <sub>3</sub>                | 13.48 | 1.44 | 217.1804 | C <sub>12</sub> H <sub>16</sub> N <sub>3</sub> O              | 14.41 | 1.17 | 218.1295 |
| C <sub>12</sub> H <sub>8</sub> O <sub>4</sub>                 | 13.25 | 1.61 | 216.0422 | C <sub>12</sub> H <sub>9</sub> O <sub>4</sub>                 | 13.27 | 1.61 | 217.0501 | C <sub>12</sub> N <sub>3</sub> O <sub>2</sub>                 | 14.19 | 1.34 | 217.9991 |
| C <sub>12</sub> H <sub>26</sub> NO <sub>2</sub>               | 13.84 | 1.29 | 216.1965 | C <sub>12</sub> H <sub>27</sub> NO <sub>2</sub>               | 13.86 | 1.29 | 217.2043 | C <sub>12</sub> H <sub>18</sub> N <sub>4</sub>                | 14.78 | 1.02 | 218.1533 |
| C <sub>12</sub> H <sub>10</sub> NO <sub>3</sub>               | 13.63 | 1.46 | 216.0661 | C <sub>12</sub> H <sub>11</sub> NO <sub>3</sub>               | 13.64 | 1.46 | 217.0739 | C <sub>12</sub> H <sub>2</sub> N <sub>4</sub> O               | 14.56 | 1.19 | 218.0229 |
| C <sub>12</sub> H <sub>28</sub> N <sub>2</sub> O              | 14.22 | 1.14 | 216.2203 | C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> | 14.02 | 1.31 | 217.0978 | C <sub>13</sub> H <sub>14</sub> O <sub>3</sub>                | 14.39 | 1.56 | 218.0943 |
| C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | 14.00 | 1.31 | 216.0899 | C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O              | 14.39 | 1.16 | 217.1216 | C <sub>13</sub> H <sub>16</sub> NO <sub>2</sub>               | 14.76 | 1.41 | 218.1182 |
| C <sub>12</sub> H <sub>14</sub> N <sub>3</sub> O              | 14.37 | 1.16 | 216.1138 | C <sub>12</sub> H <sub>17</sub> N <sub>4</sub>                | 14.77 | 1.02 | 217.1455 | C <sub>13</sub> NO <sub>3</sub>                               | 14.55 | 1.58 | 217.9878 |
| C <sub>12</sub> H <sub>16</sub> N <sub>4</sub>                | 14.75 | 1.01 | 216.1377 | C <sub>12</sub> HN <sub>4</sub> O                             | 14.55 | 1.19 | 217.0151 | C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O              | 15.14 | 1.27 | 218.1420 |
| C <sub>12</sub> N <sub>4</sub> O                              | 14.53 | 1.18 | 216.0073 | C <sub>13</sub> H <sub>13</sub> O <sub>3</sub>                | 14.37 | 1.56 | 217.0865 | C <sub>13</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>  | 14.92 | 1.44 | 218.0116 |
| C <sub>13</sub> H <sub>28</sub> O <sub>2</sub>                | 14.57 | 1.39 | 216.2090 | C <sub>13</sub> H <sub>15</sub> NO <sub>2</sub>               | 14.75 | 1.41 | 217.1103 | C <sub>13</sub> H <sub>20</sub> N <sub>3</sub>                | 15.51 | 1.13 | 218.1659 |
| C <sub>13</sub> H <sub>12</sub> O <sub>3</sub>                | 14.36 | 1.56 | 216.0786 | C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O              | 15.12 | 1.27 | 217.1342 | C <sub>13</sub> H <sub>4</sub> N <sub>3</sub> O               | 15.30 | 1.29 | 218.0355 |
| C <sub>13</sub> H <sub>14</sub> NO <sub>2</sub>               | 14.73 | 1.41 | 216.1025 | C <sub>13</sub> HN <sub>2</sub> O <sub>2</sub>                | 14.90 | 1.43 | 217.0038 | C <sub>13</sub> H <sub>6</sub> N <sub>4</sub>                 | 15.67 | 1.15 | 218.0594 |
| C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O              | 15.11 | 1.26 | 216.1264 | C <sub>13</sub> H <sub>19</sub> N <sub>3</sub>                | 15.50 | 1.12 | 217.1580 | C <sub>14</sub> H <sub>18</sub> O <sub>2</sub>                | 15.49 | 1.52 | 218.1307 |

|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>14</sub> H <sub>2</sub> O <sub>3</sub>                 | 15.28 | 1.69 | 218.0003 | C <sub>14</sub> H <sub>7</sub> N <sub>2</sub> O               | 16.04 | 1.40 | 219.0559 | C <sub>15</sub> H <sub>8</sub> O <sub>2</sub>                 | 16.42 | 1.66 | 220.0524 |
| C <sub>14</sub> H <sub>20</sub> NO                            | 15.87 | 1.38 | 218.1546 | C <sub>14</sub> H <sub>9</sub> N <sub>3</sub>                 | 16.42 | 1.26 | 219.0798 | C <sub>15</sub> H <sub>26</sub> N                             | 17.01 | 1.36 | 220.2067 |
| C <sub>14</sub> H <sub>4</sub> NO <sub>2</sub>                | 15.65 | 1.54 | 218.0242 | C <sub>15</sub> H <sub>23</sub> O                             | 16.62 | 1.49 | 219.1750 | C <sub>15</sub> H <sub>10</sub> NO                            | 16.79 | 1.52 | 220.0763 |
| C <sub>14</sub> H <sub>22</sub> N <sub>2</sub>                | 16.24 | 1.24 | 218.1784 | C <sub>15</sub> H <sub>7</sub> O <sub>2</sub>                 | 16.40 | 1.66 | 219.0446 | C <sub>15</sub> H <sub>12</sub> N <sub>2</sub>                | 17.16 | 1.38 | 220.1001 |
| C <sub>14</sub> H <sub>6</sub> N <sub>2</sub> O               | 16.03 | 1.40 | 218.0480 | C <sub>15</sub> H <sub>25</sub> N                             | 16.99 | 1.36 | 219.1988 | C <sub>16</sub> H <sub>28</sub>                               | 17.74 | 1.48 | 220.2192 |
| C <sub>14</sub> H <sub>8</sub> N <sub>3</sub>                 | 16.40 | 1.26 | 218.0719 | C <sub>15</sub> H <sub>9</sub> NO                             | 16.77 | 1.52 | 219.0684 | C <sub>16</sub> H <sub>12</sub> O                             | 17.52 | 1.64 | 220.0888 |
| C <sub>15</sub> H <sub>22</sub> O                             | 16.60 | 1.49 | 218.1671 | C <sub>15</sub> H <sub>11</sub> N <sub>2</sub>                | 17.15 | 1.38 | 219.0923 | C <sub>16</sub> H <sub>14</sub> N                             | 17.90 | 1.51 | 220.1127 |
| C <sub>15</sub> H <sub>6</sub> O <sub>2</sub>                 | 16.38 | 1.66 | 218.0368 | C <sub>16</sub> H <sub>27</sub>                               | 17.72 | 1.48 | 219.2114 | C <sub>16</sub> N <sub>2</sub>                                | 18.05 | 1.53 | 220.0062 |
| C <sub>15</sub> H <sub>24</sub> N                             | 16.97 | 1.35 | 218.1910 | C <sub>16</sub> H <sub>11</sub> O                             | 17.50 | 1.64 | 219.0810 | C <sub>17</sub> H <sub>16</sub>                               | 18.63 | 1.64 | 220.1253 |
| C <sub>15</sub> H <sub>8</sub> NO                             | 16.76 | 1.52 | 218.0606 | C <sub>16</sub> H <sub>13</sub> N                             | 17.88 | 1.50 | 219.1049 | C <sub>17</sub> O   | 18.41 | 1.80 | 219.9949 |
| C <sub>15</sub> H <sub>10</sub> N <sub>2</sub>                | 17.13 | 1.38 | 218.0845 | C <sub>17</sub> H <sub>15</sub>                               | 18.61 | 1.63 | 219.1174 | C <sub>17</sub> H <sub>2</sub> N                              | 18.78 | 1.66 | 220.0187 |
| C <sub>16</sub> H <sub>26</sub>                               | 17.71 | 1.47 | 218.2036 | C <sub>17</sub> HN  | 18.77 | 1.66 | 219.0109 | C <sub>18</sub> H <sub>4</sub>                                | 19.51 | 1.80 | 220.0313 |
| C <sub>16</sub> H <sub>10</sub> O                             | 17.49 | 1.64 | 218.0732 | C <sub>18</sub> H <sub>3</sub>                                | 19.50 | 1.80 | 219.0235 |   |       |      |          |
| C <sub>16</sub> H <sub>12</sub> N                             | 17.86 | 1.50 | 218.0970 | 220   |       |      |          | 221   |       |      |          |
| C <sub>17</sub> H <sub>14</sub>                               | 18.59 | 1.63 | 218.1096 | C <sub>9</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>  | 10.96 | 1.35 | 220.1424 | C <sub>9</sub> H <sub>21</sub> N <sub>2</sub> O <sub>4</sub>  | 10.98 | 1.35 | 221.1502 |
| C <sub>17</sub> N   | 18.75 | 1.66 | 218.0031 | C <sub>9</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub>  | 11.34 | 1.19 | 220.1662 | C <sub>9</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub>  | 11.36 | 1.19 | 221.1741 |
| C <sub>18</sub> H <sub>2</sub>                                | 19.48 | 1.79 | 218.0157 | C <sub>9</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub>  | 11.71 | 1.03 | 220.1901 | C <sub>10</sub> H <sub>23</sub> NO <sub>4</sub>               | 11.71 | 1.43 | 221.1628 |
|   |       |      |          | C <sub>10</sub> H <sub>22</sub> NO <sub>4</sub>               | 11.70 | 1.43 | 220.1549 | C <sub>10</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>  | 11.87 | 1.45 | 221.0563 |
| 219   |       |      |          | C <sub>10</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub> | 12.07 | 1.27 | 220.1788 | C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> | 12.24 | 1.29 | 221.0801 |
| C <sub>9</sub> H <sub>19</sub> N <sub>2</sub> O <sub>4</sub>  | 10.95 | 1.35 | 219.1345 | C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>  | 11.85 | 1.44 | 220.0484 | C <sub>10</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> | 12.62 | 1.14 | 221.1040 |
| C <sub>9</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub>  | 11.32 | 1.19 | 219.1584 | C <sub>10</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> | 12.23 | 1.29 | 220.0723 | C <sub>11</sub> H <sub>11</sub> NO <sub>4</sub>               | 12.60 | 1.53 | 221.0688 |
| C <sub>9</sub> H <sub>23</sub> N <sub>4</sub> O <sub>2</sub>  | 11.70 | 1.03 | 219.1822 | C <sub>10</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> | 12.60 | 1.13 | 220.0961 | C <sub>11</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> | 12.97 | 1.38 | 221.0927 |
| C <sub>10</sub> H <sub>21</sub> NO <sub>4</sub>               | 11.68 | 1.42 | 219.1471 | C <sub>11</sub> H <sub>24</sub> O <sub>4</sub>                | 12.43 | 1.51 | 220.1675 | C <sub>11</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> | 13.35 | 1.23 | 221.1165 |
| C <sub>10</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub> | 12.05 | 1.27 | 219.1710 | C <sub>11</sub> H <sub>10</sub> NO <sub>4</sub>               | 12.58 | 1.53 | 220.0610 | C <sub>11</sub> H <sub>17</sub> N <sub>4</sub> O              | 13.72 | 1.07 | 221.1404 |
| C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub>  | 11.84 | 1.44 | 219.0406 | C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> | 12.96 | 1.38 | 220.0848 | C <sub>11</sub> HN <sub>4</sub> O <sub>2</sub>                | 13.51 | 1.25 | 221.0100 |
| C <sub>10</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub> | 12.43 | 1.11 | 219.1948 | C <sub>11</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> | 13.33 | 1.22 | 220.1087 | C <sub>12</sub> H <sub>13</sub> O <sub>4</sub>                | 13.33 | 1.62 | 221.0814 |
| C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>  | 12.21 | 1.29 | 219.0644 | C <sub>11</sub> H <sub>16</sub> N <sub>4</sub> O              | 13.71 | 1.07 | 220.1325 | C <sub>12</sub> H <sub>15</sub> NO <sub>3</sub>               | 13.71 | 1.47 | 221.1052 |
| C <sub>10</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> | 12.59 | 1.13 | 219.0883 | C <sub>11</sub> N <sub>4</sub> O <sub>2</sub>                 | 13.49 | 1.24 | 220.0022 | C <sub>12</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> | 14.08 | 1.32 | 221.1291 |
| C <sub>11</sub> H <sub>23</sub> O <sub>4</sub>                | 12.41 | 1.51 | 219.1597 | C <sub>12</sub> H <sub>12</sub> O <sub>4</sub>                | 13.32 | 1.62 | 220.0735 | C <sub>12</sub> HN <sub>2</sub> O <sub>3</sub>                | 13.86 | 1.49 | 220.9987 |
| C <sub>11</sub> H <sub>25</sub> NO <sub>3</sub>               | 12.79 | 1.35 | 219.1835 | C <sub>12</sub> H <sub>14</sub> NO <sub>3</sub>               | 13.69 | 1.47 | 220.0974 | C <sub>12</sub> H <sub>19</sub> N <sub>3</sub> O              | 14.45 | 1.17 | 221.1529 |
| C <sub>11</sub> H <sub>9</sub> NO <sub>4</sub>                | 12.57 | 1.53 | 219.0532 | C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> | 14.06 | 1.32 | 220.1213 | C <sub>12</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>  | 14.24 | 1.34 | 221.0226 |
| C <sub>11</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> | 12.94 | 1.37 | 219.0770 | C <sub>12</sub> N <sub>2</sub> O <sub>3</sub>                 | 13.85 | 1.49 | 219.9909 | C <sub>12</sub> H <sub>21</sub> N <sub>4</sub>                | 14.83 | 1.03 | 221.1768 |
| C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> | 13.32 | 1.22 | 219.1009 | C <sub>12</sub> H <sub>18</sub> N <sub>3</sub> O              | 14.44 | 1.17 | 220.1451 | C <sub>12</sub> H <sub>5</sub> N <sub>4</sub> O               | 14.61 | 1.20 | 221.0464 |
| C <sub>11</sub> H <sub>15</sub> N <sub>4</sub> O              | 13.69 | 1.07 | 219.1247 | C <sub>12</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>  | 14.22 | 1.34 | 220.0147 | C <sub>13</sub> H <sub>17</sub> O <sub>3</sub>                | 14.44 | 1.57 | 221.1178 |
| C <sub>12</sub> H <sub>11</sub> O <sub>4</sub>                | 13.30 | 1.62 | 219.0657 | C <sub>12</sub> H <sub>20</sub> N <sub>4</sub>                | 14.81 | 1.02 | 220.1690 | C <sub>13</sub> HO <sub>4</sub>                               | 14.22 | 1.74 | 220.9874 |
| C <sub>12</sub> H <sub>13</sub> NO <sub>3</sub>               | 13.67 | 1.47 | 219.0896 | C <sub>12</sub> H <sub>4</sub> N <sub>4</sub> O               | 14.60 | 1.19 | 220.0386 | C <sub>13</sub> H <sub>19</sub> NO <sub>2</sub>               | 14.81 | 1.42 | 221.1416 |
| C <sub>12</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> | 14.05 | 1.32 | 219.1134 | C <sub>13</sub> H <sub>16</sub> O <sub>3</sub>                | 14.42 | 1.57 | 220.1100 | C <sub>13</sub> H <sub>3</sub> NO <sub>3</sub>                | 14.59 | 1.59 | 221.0113 |
| C <sub>12</sub> H <sub>17</sub> N <sub>3</sub> O              | 14.42 | 1.17 | 219.1373 | C <sub>13</sub> O <sub>4</sub>                                | 14.20 | 1.73 | 219.9796 | C <sub>13</sub> H <sub>21</sub> N <sub>2</sub> O              | 15.19 | 1.28 | 221.1655 |
| C <sub>12</sub> HN <sub>3</sub> O <sub>2</sub>                | 14.21 | 1.34 | 219.0069 | C <sub>13</sub> H <sub>18</sub> NO <sub>2</sub>               | 14.80 | 1.42 | 220.1338 | C <sub>13</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>  | 14.97 | 1.44 | 221.0351 |
| C <sub>12</sub> H <sub>19</sub> N <sub>4</sub>                | 14.80 | 1.02 | 219.1611 | C <sub>13</sub> H <sub>2</sub> NO <sub>3</sub>                | 14.58 | 1.59 | 220.0034 | C <sub>13</sub> H <sub>23</sub> N <sub>3</sub>                | 15.56 | 1.13 | 221.1894 |
| C <sub>12</sub> H <sub>3</sub> N <sub>4</sub> O               | 14.58 | 1.19 | 219.0308 | C <sub>13</sub> H <sub>20</sub> N <sub>2</sub> O              | 15.17 | 1.27 | 220.1577 | C <sub>13</sub> H <sub>7</sub> N <sub>3</sub> O               | 15.34 | 1.30 | 221.0590 |
| C <sub>13</sub> H <sub>15</sub> O <sub>3</sub>                | 14.41 | 1.56 | 219.1021 | C <sub>13</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>  | 14.95 | 1.44 | 220.0273 | C <sub>13</sub> H <sub>9</sub> N <sub>4</sub>                 | 15.72 | 1.16 | 221.0829 |
| C <sub>13</sub> H <sub>17</sub> NO <sub>2</sub>               | 14.78 | 1.42 | 219.1260 | C <sub>13</sub> H <sub>22</sub> N <sub>3</sub>                | 15.54 | 1.13 | 220.1815 | C <sub>14</sub> H <sub>21</sub> O <sub>2</sub>                | 15.54 | 1.53 | 221.1542 |
| C <sub>13</sub> HNO <sub>3</sub>                              | 14.56 | 1.59 | 218.9956 | C <sub>13</sub> H <sub>6</sub> N <sub>3</sub> O               | 15.33 | 1.30 | 220.0511 | C <sub>14</sub> H <sub>5</sub> O <sub>3</sub>                 | 15.33 | 1.69 | 221.0238 |
| C <sub>13</sub> H <sub>19</sub> N <sub>2</sub> O              | 15.15 | 1.27 | 219.1498 | C <sub>13</sub> H <sub>8</sub> N <sub>4</sub>                 | 15.70 | 1.15 | 220.0750 | C <sub>14</sub> H <sub>23</sub> NO                            | 15.92 | 1.38 | 221.1781 |
| C <sub>13</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 14.94 | 1.44 | 219.0195 | C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>                | 15.53 | 1.52 | 220.1464 | C <sub>14</sub> H <sub>7</sub> NO <sub>2</sub>                | 15.70 | 1.55 | 221.0477 |
| C <sub>13</sub> H <sub>21</sub> N <sub>3</sub>                | 15.53 | 1.13 | 219.1737 | C <sub>14</sub> H <sub>4</sub> O <sub>3</sub>                 | 15.31 | 1.69 | 220.0160 | C <sub>14</sub> H <sub>25</sub> N <sub>2</sub>                | 16.29 | 1.24 | 221.2019 |
| C <sub>13</sub> H <sub>5</sub> N <sub>3</sub> O               | 15.31 | 1.29 | 219.0433 | C <sub>14</sub> H <sub>22</sub> NO                            | 15.90 | 1.38 | 220.1702 | C <sub>14</sub> H <sub>9</sub> N <sub>2</sub> O               | 16.07 | 1.41 | 221.0715 |
| C <sub>13</sub> H <sub>7</sub> N <sub>4</sub>                 | 15.69 | 1.15 | 219.0672 | C <sub>14</sub> H <sub>6</sub> NO <sub>2</sub>                | 15.68 | 1.55 | 220.0399 | C <sub>14</sub> H <sub>11</sub> N <sub>3</sub>                | 16.45 | 1.27 | 221.0954 |
| C <sub>14</sub> H <sub>19</sub> O <sub>2</sub>                | 15.51 | 1.52 | 219.1385 | C <sub>14</sub> H <sub>24</sub> N <sub>2</sub>                | 16.28 | 1.24 | 220.1941 | C <sub>15</sub> H <sub>25</sub> O                             | 16.65 | 1.50 | 221.1906 |
| C <sub>14</sub> H <sub>3</sub> O <sub>3</sub>                 | 15.29 | 1.69 | 219.0082 | C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O               | 16.06 | 1.41 | 220.0637 | C <sub>15</sub> H <sub>9</sub> O <sub>2</sub>                 | 16.43 | 1.66 | 221.0603 |
| C <sub>14</sub> H <sub>21</sub> NO                            | 15.89 | 1.38 | 219.1624 | C <sub>14</sub> H <sub>10</sub> N <sub>3</sub>                | 16.43 | 1.27 | 220.0876 | C <sub>15</sub> H <sub>27</sub> N                             | 17.02 | 1.36 | 221.2145 |
| C <sub>14</sub> H <sub>5</sub> NO <sub>2</sub>                | 15.67 | 1.55 | 219.0320 | C <sub>15</sub> H <sub>24</sub> O                             | 16.63 | 1.50 | 220.1828 | C <sub>15</sub> H <sub>11</sub> NO                            | 16.81 | 1.52 | 221.0841 |
| C <sub>14</sub> H <sub>23</sub> N <sub>2</sub>                | 16.26 | 1.24 | 219.1863 |   |       |      |          | C <sub>15</sub> H <sub>13</sub> N <sub>2</sub>                | 17.18 | 1.39 | 221.1080 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>16</sub> H <sub>29</sub>                               | 17.75 | 1.48 | 221.2270 | C <sub>16</sub> H <sub>2</sub> N <sub>2</sub>                 | 18.08 | 1.54 | 222.0218 | C <sub>17</sub> H <sub>5</sub> N                              | 18.83 | 1.67 | 223.0422 |
| C <sub>16</sub> H <sub>13</sub> O                             | 17.54 | 1.64 | 221.0967 | C <sub>17</sub> H <sub>18</sub>                               | 18.66 | 1.64 | 222.1409 | C <sub>18</sub> H <sub>7</sub>                                | 19.56 | 1.81 | 223.0548 |
| C <sub>16</sub> H <sub>15</sub> N                             | 17.91 | 1.51 | 221.1205 | C <sub>17</sub> H <sub>2</sub> O                              | 18.44 | 1.80 | 222.0106 | 224   |       |      |          |
| C <sub>16</sub> HN <sub>2</sub>                               | 18.07 | 1.54 | 221.0140 | C <sub>17</sub> H <sub>4</sub> N                              | 18.82 | 1.67 | 222.0344 | C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> | 11.92 | 1.45 | 224.0797 |
| C <sub>17</sub> H <sub>17</sub>                               | 18.64 | 1.64 | 221.1331 | C <sub>18</sub> H <sub>6</sub>                                | 19.55 | 1.81 | 222.0470 | C <sub>10</sub> H <sub>14</sub> N <sub>3</sub> O <sub>3</sub> | 12.29 | 1.30 | 224.1036 |
| C <sub>17</sub> HO  | 18.43 | 1.80 | 221.0027 | 223   |       |      |          | C <sub>10</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> | 12.67 | 1.14 | 224.1275 |
| C <sub>17</sub> H <sub>3</sub> N                              | 18.80 | 1.67 | 221.0266 | C <sub>10</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> | 11.90 | 1.45 | 223.0719 | C <sub>11</sub> H <sub>14</sub> NO <sub>4</sub>               | 12.65 | 1.54 | 224.0923 |
| C <sub>18</sub> H <sub>5</sub>                                | 19.53 | 1.80 | 221.0391 | C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> | 12.28 | 1.29 | 223.0958 | C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> | 13.02 | 1.38 | 224.1162 |
| 222   |       |      |          | C <sub>10</sub> H <sub>15</sub> N <sub>4</sub> O <sub>2</sub> | 12.65 | 1.14 | 223.1196 | C <sub>11</sub> N <sub>2</sub> O <sub>4</sub>                 | 12.81 | 1.56 | 223.9858 |
| C <sub>9</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub>  | 11.00 | 1.35 | 222.1580 | C <sub>11</sub> H <sub>13</sub> NO <sub>4</sub>               | 12.63 | 1.53 | 223.0845 | C <sub>11</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> | 13.40 | 1.23 | 224.1400 |
| C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> | 11.89 | 1.45 | 222.0641 | C <sub>11</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub> | 13.01 | 1.38 | 223.1083 | C <sub>11</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>  | 13.18 | 1.40 | 224.0096 |
| C <sub>10</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> | 12.26 | 1.29 | 222.0879 | C <sub>11</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> | 13.38 | 1.23 | 223.1322 | C <sub>11</sub> H <sub>20</sub> N <sub>4</sub> O              | 13.77 | 1.08 | 224.1639 |
| C <sub>10</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> | 12.63 | 1.14 | 222.1118 | C <sub>11</sub> HN <sub>3</sub> O <sub>3</sub>                | 13.16 | 1.40 | 223.0018 | C <sub>11</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>  | 13.55 | 1.25 | 224.0335 |
| C <sub>11</sub> H <sub>12</sub> NO <sub>4</sub>               | 12.62 | 1.53 | 222.0766 | C <sub>11</sub> H <sub>19</sub> N <sub>4</sub> O              | 13.76 | 1.08 | 223.1560 | C <sub>12</sub> H <sub>16</sub> O <sub>4</sub>                | 13.38 | 1.63 | 224.1049 |
| C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> | 12.99 | 1.38 | 222.1005 | C <sub>11</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>  | 13.54 | 1.25 | 223.0257 | C <sub>12</sub> H <sub>18</sub> NO <sub>3</sub>               | 13.75 | 1.48 | 224.1287 |
| C <sub>11</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub> | 13.37 | 1.23 | 222.1244 | C <sub>12</sub> H <sub>15</sub> O <sub>4</sub>                | 13.36 | 1.62 | 223.0970 | C <sub>12</sub> H <sub>2</sub> NO <sub>4</sub>                | 13.54 | 1.65 | 223.9983 |
| C <sub>11</sub> N <sub>3</sub> O <sub>3</sub>                 | 13.15 | 1.40 | 221.9940 | C <sub>12</sub> H <sub>17</sub> NO <sub>3</sub>               | 13.74 | 1.47 | 223.1209 | C <sub>12</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> | 14.13 | 1.33 | 224.1526 |
| C <sub>11</sub> H <sub>18</sub> N <sub>4</sub> O              | 13.74 | 1.08 | 222.1482 | C <sub>12</sub> HN <sub>3</sub> O <sub>4</sub>                | 13.52 | 1.65 | 222.9905 | C <sub>12</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 13.91 | 1.50 | 224.0222 |
| C <sub>11</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>  | 13.52 | 1.25 | 222.0178 | C <sub>12</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub> | 14.11 | 1.33 | 223.1447 | C <sub>12</sub> H <sub>22</sub> N <sub>3</sub> O              | 14.50 | 1.18 | 224.1764 |
| C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>                | 13.35 | 1.62 | 222.0892 | C <sub>12</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 13.90 | 1.50 | 223.0144 | C <sub>12</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>  | 14.29 | 1.35 | 224.0460 |
| C <sub>12</sub> H <sub>16</sub> NO <sub>3</sub>               | 13.72 | 1.47 | 222.1131 | C <sub>12</sub> H <sub>21</sub> N <sub>3</sub> O              | 14.49 | 1.18 | 223.1686 | C <sub>12</sub> H <sub>24</sub> N <sub>4</sub>                | 14.88 | 1.03 | 224.2003 |
| C <sub>12</sub> NO <sub>4</sub>                               | 13.51 | 1.64 | 221.9827 | C <sub>12</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>  | 14.27 | 1.35 | 223.0382 | C <sub>12</sub> H <sub>8</sub> N <sub>4</sub> O               | 14.66 | 1.20 | 224.0699 |
| C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> | 14.10 | 1.32 | 222.1369 | C <sub>12</sub> H <sub>23</sub> N <sub>4</sub>                | 14.86 | 1.03 | 223.1925 | C <sub>13</sub> H <sub>20</sub> O <sub>3</sub>                | 14.49 | 1.57 | 224.1413 |
| C <sub>12</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>  | 13.88 | 1.49 | 222.0065 | C <sub>12</sub> H <sub>7</sub> N <sub>4</sub> O               | 14.64 | 1.20 | 223.0621 | C <sub>13</sub> H <sub>4</sub> O <sub>4</sub>                 | 14.27 | 1.74 | 224.0109 |
| C <sub>12</sub> H <sub>20</sub> N <sub>3</sub> O              | 14.47 | 1.18 | 222.1608 | C <sub>13</sub> H <sub>19</sub> O <sub>3</sub>                | 14.47 | 1.57 | 223.1334 | C <sub>13</sub> H <sub>22</sub> NO <sub>2</sub>               | 14.86 | 1.43 | 224.1651 |
| C <sub>12</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>  | 14.25 | 1.34 | 222.0304 | C <sub>13</sub> H <sub>3</sub> O <sub>4</sub>                 | 14.25 | 1.74 | 223.0031 | C <sub>13</sub> H <sub>6</sub> NO <sub>3</sub>                | 14.64 | 1.60 | 224.0348 |
| C <sub>12</sub> H <sub>22</sub> N <sub>4</sub>                | 14.85 | 1.03 | 222.1846 | C <sub>13</sub> H <sub>21</sub> NO <sub>2</sub>               | 14.84 | 1.43 | 223.1573 | C <sub>13</sub> H <sub>24</sub> N <sub>2</sub> O              | 15.23 | 1.28 | 224.1890 |
| C <sub>12</sub> H <sub>6</sub> N <sub>4</sub> O               | 14.63 | 1.20 | 222.0542 | C <sub>13</sub> H <sub>5</sub> NO <sub>3</sub>                | 14.63 | 1.59 | 223.0269 | C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 15.02 | 1.45 | 224.0586 |
| C <sub>13</sub> H <sub>18</sub> O <sub>3</sub>                | 14.45 | 1.57 | 222.1256 | C <sub>13</sub> H <sub>23</sub> N <sub>2</sub> O              | 15.22 | 1.28 | 223.1811 | C <sub>13</sub> H <sub>26</sub> N <sub>3</sub>                | 15.61 | 1.14 | 224.2129 |
| C <sub>13</sub> H <sub>2</sub> O <sub>4</sub>                 | 14.24 | 1.74 | 221.9953 | C <sub>13</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>  | 15.00 | 1.45 | 223.0508 | C <sub>13</sub> H <sub>10</sub> N <sub>3</sub> O              | 15.39 | 1.31 | 224.0825 |
| C <sub>13</sub> H <sub>20</sub> NO <sub>2</sub>               | 14.83 | 1.42 | 222.1495 | C <sub>13</sub> H <sub>25</sub> N <sub>3</sub>                | 15.59 | 1.14 | 223.2050 | C <sub>13</sub> H <sub>12</sub> N <sub>4</sub>                | 15.77 | 1.16 | 224.1063 |
| C <sub>13</sub> H <sub>4</sub> NO <sub>3</sub>                | 14.61 | 1.59 | 222.0191 | C <sub>13</sub> H <sub>9</sub> N <sub>3</sub> O               | 15.38 | 1.30 | 223.0746 | C <sub>14</sub> H <sub>24</sub> O <sub>2</sub>                | 15.59 | 1.53 | 224.1777 |
| C <sub>13</sub> H <sub>22</sub> N <sub>2</sub> O              | 15.20 | 1.28 | 222.1733 | C <sub>13</sub> H <sub>11</sub> N <sub>4</sub>                | 15.75 | 1.16 | 223.0985 | C <sub>14</sub> H <sub>8</sub> O <sub>3</sub>                 | 15.37 | 1.70 | 224.0473 |
| C <sub>13</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 14.98 | 1.45 | 222.0429 | C <sub>14</sub> H <sub>23</sub> O <sub>2</sub>                | 15.57 | 1.53 | 223.1699 | C <sub>14</sub> H <sub>26</sub> NO                            | 15.97 | 1.39 | 224.2015 |
| C <sub>13</sub> H <sub>24</sub> N <sub>3</sub>                | 15.58 | 1.13 | 222.1972 | C <sub>14</sub> H <sub>7</sub> O <sub>3</sub>                 | 15.36 | 1.70 | 223.0395 | C <sub>14</sub> H <sub>10</sub> NO <sub>2</sub>               | 15.75 | 1.56 | 224.0712 |
| C <sub>13</sub> H <sub>8</sub> N <sub>3</sub> O               | 15.36 | 1.30 | 222.0668 | C <sub>14</sub> H <sub>25</sub> NO                            | 15.95 | 1.39 | 223.1937 | C <sub>14</sub> H <sub>28</sub> N <sub>2</sub>                | 16.34 | 1.25 | 224.2254 |
| C <sub>13</sub> H <sub>10</sub> N <sub>4</sub>                | 15.73 | 1.16 | 222.0907 | C <sub>14</sub> H <sub>9</sub> NO <sub>2</sub>                | 15.73 | 1.56 | 223.0634 | C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O              | 16.12 | 1.42 | 224.0950 |
| C <sub>14</sub> H <sub>22</sub> O <sub>2</sub>                | 15.56 | 1.53 | 222.1620 | C <sub>14</sub> H <sub>27</sub> N <sub>2</sub>                | 16.32 | 1.25 | 223.2176 | C <sub>14</sub> H <sub>14</sub> N <sub>3</sub>                | 16.50 | 1.28 | 224.1189 |
| C <sub>14</sub> H <sub>6</sub> O <sub>3</sub>                 | 15.34 | 1.70 | 222.0317 | C <sub>14</sub> H <sub>11</sub> N <sub>2</sub> O              | 16.11 | 1.41 | 223.0872 | C <sub>14</sub> N <sub>4</sub>                                | 16.65 | 1.30 | 224.0124 |
| C <sub>14</sub> H <sub>24</sub> NO                            | 15.93 | 1.39 | 222.1859 | C <sub>14</sub> H <sub>13</sub> N <sub>3</sub>                | 16.48 | 1.27 | 223.1111 | C <sub>15</sub> H <sub>28</sub> O                             | 16.70 | 1.51 | 224.2141 |
| C <sub>14</sub> H <sub>8</sub> NO <sub>2</sub>                | 15.72 | 1.55 | 222.0555 | C <sub>15</sub> H <sub>27</sub> O                             | 16.68 | 1.50 | 223.2063 | C <sub>15</sub> H <sub>12</sub> O <sub>2</sub>                | 16.48 | 1.67 | 224.0837 |
| C <sub>14</sub> H <sub>26</sub> N <sub>2</sub>                | 16.31 | 1.25 | 222.2098 | C <sub>15</sub> H <sub>11</sub> O <sub>2</sub>                | 16.46 | 1.67 | 223.0759 | C <sub>15</sub> H <sub>30</sub> N                             | 17.07 | 1.37 | 224.2380 |
| C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O              | 16.09 | 1.41 | 222.0794 | C <sub>15</sub> H <sub>29</sub> N                             | 17.05 | 1.37 | 223.2301 | C <sub>15</sub> H <sub>14</sub> NO                            | 16.85 | 1.53 | 224.1076 |
| C <sub>14</sub> H <sub>12</sub> N <sub>3</sub>                | 16.46 | 1.27 | 222.1032 | C <sub>15</sub> H <sub>13</sub> NO                            | 16.84 | 1.53 | 223.0998 | C <sub>15</sub> H <sub>16</sub> N <sub>2</sub>                | 17.23 | 1.39 | 224.1315 |
| C <sub>15</sub> H <sub>26</sub> O                             | 16.66 | 1.50 | 222.1985 | C <sub>15</sub> H <sub>15</sub> N <sub>2</sub>                | 17.21 | 1.39 | 223.1236 | C <sub>15</sub> N <sub>2</sub> O                              | 17.01 | 1.56 | 224.0011 |
| C <sub>15</sub> H <sub>10</sub> O <sub>2</sub>                | 16.45 | 1.67 | 222.0681 | C <sub>15</sub> HN <sub>3</sub>                               | 17.37 | 1.42 | 223.0171 | C <sub>15</sub> H <sub>2</sub> N <sub>3</sub>                 | 17.39 | 1.42 | 224.0249 |
| C <sub>15</sub> H <sub>28</sub> N                             | 17.04 | 1.36 | 222.2223 | C <sub>16</sub> H <sub>31</sub>                               | 17.79 | 1.49 | 223.2427 | C <sub>16</sub> H <sub>32</sub>                               | 17.80 | 1.49 | 224.2505 |
| C <sub>15</sub> H <sub>12</sub> NO                            | 16.82 | 1.53 | 222.0919 | C <sub>16</sub> H <sub>15</sub> O                             | 17.57 | 1.65 | 223.1123 | C <sub>16</sub> H <sub>16</sub> O                             | 17.58 | 1.65 | 224.1202 |
| C <sub>15</sub> H <sub>14</sub> N <sub>2</sub>                | 17.20 | 1.39 | 222.1158 | C <sub>16</sub> H <sub>17</sub> N                             | 17.94 | 1.52 | 223.1362 | C <sub>16</sub> O <sub>2</sub>                                | 17.37 | 1.82 | 223.9898 |
| C <sub>15</sub> N <sub>3</sub>                                | 17.35 | 1.42 | 222.0093 | C <sub>16</sub> HN <sub>3</sub>                               | 17.73 | 1.68 | 223.0058 | C <sub>16</sub> H <sub>18</sub> N                             | 17.96 | 1.52 | 224.1440 |
| C <sub>16</sub> H <sub>30</sub>                               | 17.77 | 1.49 | 222.2349 | C <sub>16</sub> H <sub>3</sub> N <sub>2</sub>                 | 18.10 | 1.54 | 223.0297 | C <sub>16</sub> H <sub>2</sub> NO                             | 17.74 | 1.68 | 224.0136 |
| C <sub>16</sub> H <sub>14</sub> O                             | 17.55 | 1.65 | 222.1045 | C <sub>17</sub> H <sub>19</sub>                               | 18.67 | 1.64 | 223.1488 | C <sub>16</sub> H <sub>4</sub> N <sub>2</sub>                 | 18.12 | 1.55 | 224.0375 |
| C <sub>16</sub> H <sub>16</sub> N                             | 17.93 | 1.51 | 222.1284 | C <sub>17</sub> H <sub>3</sub> O                              | 18.46 | 1.80 | 223.0184 | C <sub>17</sub> H <sub>20</sub>                               | 18.69 | 1.65 | 224.1566 |
| C <sub>16</sub> NO  | 17.71 | 1.67 | 221.9980 |   |       |      |          | C <sub>17</sub> H <sub>4</sub> O                              | 18.47 | 1.81 | 224.0262 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>17</sub> H <sub>6</sub> N                              | 18.85 | 1.68 | 224.0501 | C <sub>17</sub> H <sub>5</sub> O                              | 18.49 | 1.81 | 225.0340 | C <sub>16</sub> H <sub>4</sub> NO                             | 17.77 | 1.69 | 226.0293 |
| C <sub>18</sub> H <sub>8</sub>                                | 19.58 | 1.81 | 224.0626 | C <sub>17</sub> H <sub>7</sub> N                              | 18.86 | 1.68 | 225.0579 | C <sub>16</sub> H <sub>6</sub> N <sub>2</sub>                 | 18.15 | 1.55 | 226.0532 |
| 225   |       |      |          | C <sub>18</sub> H <sub>9</sub>                                | 19.59 | 1.81 | 225.0705 | C <sub>17</sub> H <sub>22</sub>                               | 18.72 | 1.65 | 226.1722 |
| C <sub>10</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> | 11.93 | 1.45 | 225.0876 |   |       |      |          | C <sub>17</sub> H <sub>6</sub> O                              | 18.51 | 1.81 | 226.0419 |
| C <sub>10</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> | 12.31 | 1.30 | 225.1114 | 226   |       |      |          | C <sub>17</sub> H <sub>8</sub> N                              | 18.88 | 1.68 | 226.0657 |
| C <sub>10</sub> H <sub>17</sub> N <sub>4</sub> O <sub>2</sub> | 12.68 | 1.14 | 225.1353 | C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> | 11.95 | 1.46 | 226.0954 | C <sub>18</sub> H <sub>10</sub>                               | 19.61 | 1.82 | 226.0783 |
| C <sub>11</sub> H <sub>15</sub> NO <sub>4</sub>               | 12.66 | 1.54 | 225.1001 | C <sub>10</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> | 12.32 | 1.30 | 226.1193 |   |       |      |          |
| C <sub>11</sub> H <sub>17</sub> N <sub>2</sub> O <sub>3</sub> | 13.04 | 1.39 | 225.1240 | C <sub>10</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> | 12.70 | 1.15 | 226.1431 | 227   |       |      |          |
| C <sub>11</sub> HN <sub>2</sub> O <sub>4</sub>                | 12.82 | 1.56 | 224.9936 | C <sub>11</sub> H <sub>16</sub> NO <sub>4</sub>               | 12.68 | 1.54 | 226.1080 | C <sub>10</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub> | 11.97 | 1.46 | 227.1032 |
| C <sub>11</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> | 13.41 | 1.23 | 225.1478 | C <sub>11</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> | 13.05 | 1.39 | 226.1318 | C <sub>10</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> | 12.34 | 1.30 | 227.1271 |
| C <sub>11</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>  | 13.20 | 1.41 | 225.0175 | C <sub>11</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 12.84 | 1.56 | 226.0014 | C <sub>10</sub> H <sub>19</sub> N <sub>4</sub> O <sub>2</sub> | 12.71 | 1.15 | 227.1509 |
| C <sub>11</sub> H <sub>21</sub> N <sub>4</sub> O              | 13.79 | 1.08 | 225.1717 | C <sub>11</sub> H <sub>20</sub> N <sub>3</sub> O <sub>2</sub> | 13.43 | 1.24 | 226.1557 | C <sub>11</sub> H <sub>17</sub> NO <sub>4</sub>               | 12.70 | 1.54 | 227.1158 |
| C <sub>11</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>  | 13.57 | 1.25 | 225.0413 | C <sub>11</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>  | 13.21 | 1.41 | 226.0253 | C <sub>11</sub> H <sub>19</sub> N <sub>2</sub> O <sub>3</sub> | 13.07 | 1.39 | 227.1396 |
| C <sub>12</sub> H <sub>17</sub> O <sub>4</sub>                | 13.40 | 1.63 | 225.1127 | C <sub>11</sub> H <sub>22</sub> N <sub>4</sub> O              | 13.80 | 1.09 | 226.1795 | C <sub>11</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>  | 12.85 | 1.56 | 227.0093 |
| C <sub>12</sub> H <sub>19</sub> NO <sub>3</sub>               | 13.77 | 1.48 | 225.1365 | C <sub>11</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 13.59 | 1.26 | 226.0491 | C <sub>11</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> | 13.45 | 1.24 | 227.1635 |
| C <sub>12</sub> H <sub>3</sub> NO <sub>4</sub>                | 13.55 | 1.65 | 225.0062 | C <sub>12</sub> H <sub>18</sub> O <sub>4</sub>                | 13.41 | 1.63 | 226.1205 | C <sub>11</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>  | 13.23 | 1.41 | 227.0331 |
| C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub> | 14.14 | 1.33 | 225.1604 | C <sub>12</sub> H <sub>20</sub> NO <sub>3</sub>               | 13.79 | 1.48 | 226.1444 | C <sub>11</sub> H <sub>23</sub> N <sub>4</sub> O              | 13.82 | 1.09 | 227.1873 |
| C <sub>12</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>  | 13.93 | 1.50 | 225.0300 | C <sub>12</sub> H <sub>4</sub> NO <sub>4</sub>                | 13.57 | 1.65 | 226.0140 | C <sub>11</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>  | 13.60 | 1.26 | 227.0570 |
| C <sub>12</sub> H <sub>23</sub> N <sub>3</sub> O              | 14.52 | 1.18 | 225.1842 | C <sub>12</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> | 14.16 | 1.33 | 226.1682 | C <sub>12</sub> H <sub>19</sub> O <sub>4</sub>                | 13.43 | 1.63 | 227.1284 |
| C <sub>12</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>  | 14.30 | 1.35 | 225.0539 | C <sub>12</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 13.94 | 1.50 | 226.0379 | C <sub>12</sub> H <sub>21</sub> NO <sub>3</sub>               | 13.80 | 1.48 | 227.1522 |
| C <sub>12</sub> H <sub>25</sub> N <sub>4</sub>                | 14.89 | 1.04 | 225.2081 | C <sub>12</sub> H <sub>24</sub> N <sub>3</sub> O              | 14.53 | 1.18 | 226.1921 | C <sub>12</sub> H <sub>5</sub> NO <sub>4</sub>                | 13.59 | 1.65 | 227.0218 |
| C <sub>12</sub> H <sub>9</sub> N <sub>4</sub> O               | 14.68 | 1.20 | 225.0777 | C <sub>12</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 14.32 | 1.35 | 226.0617 | C <sub>12</sub> H <sub>23</sub> N <sub>2</sub> O <sub>2</sub> | 14.18 | 1.33 | 227.1761 |
| C <sub>13</sub> H <sub>21</sub> O <sub>3</sub>                | 14.50 | 1.58 | 225.1491 | C <sub>12</sub> H <sub>26</sub> N <sub>4</sub>                | 14.91 | 1.04 | 226.2160 | C <sub>12</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>  | 13.96 | 1.50 | 227.0457 |
| C <sub>13</sub> H <sub>5</sub> O <sub>4</sub>                 | 14.28 | 1.75 | 225.0187 | C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> O              | 14.69 | 1.21 | 226.0856 | C <sub>12</sub> H <sub>25</sub> N <sub>3</sub> O              | 14.55 | 1.19 | 227.1999 |
| C <sub>13</sub> H <sub>23</sub> NO <sub>2</sub>               | 14.88 | 1.43 | 225.1730 | C <sub>13</sub> H <sub>22</sub> O <sub>3</sub>                | 14.52 | 1.58 | 226.1569 | C <sub>12</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>  | 14.33 | 1.36 | 227.0695 |
| C <sub>13</sub> H <sub>7</sub> NO <sub>3</sub>                | 14.66 | 1.60 | 225.0426 | C <sub>13</sub> H <sub>6</sub> O <sub>4</sub>                 | 14.30 | 1.75 | 226.0266 | C <sub>12</sub> H <sub>27</sub> N <sub>4</sub>                | 14.93 | 1.04 | 227.2238 |
| C <sub>13</sub> H <sub>25</sub> N <sub>2</sub> O              | 15.25 | 1.29 | 225.1968 | C <sub>13</sub> H <sub>24</sub> NO <sub>2</sub>               | 14.89 | 1.43 | 226.1808 | C <sub>12</sub> H <sub>11</sub> N <sub>4</sub> O              | 14.71 | 1.21 | 227.0934 |
| C <sub>13</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 15.03 | 1.45 | 225.0664 | C <sub>13</sub> H <sub>8</sub> NO <sub>3</sub>                | 14.67 | 1.60 | 226.0504 | C <sub>13</sub> H <sub>23</sub> O <sub>3</sub>                | 14.53 | 1.58 | 227.1648 |
| C <sub>13</sub> H <sub>27</sub> N <sub>3</sub>                | 15.62 | 1.14 | 225.2207 | C <sub>13</sub> H <sub>26</sub> N <sub>2</sub> O              | 15.27 | 1.29 | 226.2046 | C <sub>13</sub> H <sub>7</sub> O <sub>4</sub>                 | 14.32 | 1.75 | 227.0344 |
| C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> O              | 15.41 | 1.31 | 225.0903 | C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 15.05 | 1.46 | 226.0743 | C <sub>13</sub> H <sub>25</sub> NO <sub>2</sub>               | 14.91 | 1.44 | 227.1886 |
| C <sub>13</sub> H <sub>13</sub> N <sub>4</sub>                | 15.78 | 1.17 | 225.1142 | C <sub>13</sub> H <sub>28</sub> N <sub>3</sub>                | 15.64 | 1.14 | 226.2285 | C <sub>13</sub> H <sub>9</sub> NO <sub>3</sub>                | 14.69 | 1.60 | 227.0583 |
| C <sub>14</sub> H <sub>25</sub> O <sub>2</sub>                | 15.61 | 1.54 | 225.1855 | C <sub>13</sub> H <sub>12</sub> N <sub>3</sub> O              | 15.42 | 1.31 | 226.0981 | C <sub>13</sub> H <sub>27</sub> N <sub>2</sub> O              | 15.28 | 1.29 | 227.2125 |
| C <sub>14</sub> H <sub>9</sub> O <sub>3</sub>                 | 15.39 | 1.70 | 225.0552 | C <sub>13</sub> H <sub>14</sub> N <sub>4</sub>                | 15.80 | 1.17 | 226.1220 | C <sub>13</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 15.06 | 1.46 | 227.0821 |
| C <sub>14</sub> H <sub>27</sub> NO                            | 15.98 | 1.39 | 225.2094 | C <sub>14</sub> H <sub>26</sub> O <sub>2</sub>                | 15.62 | 1.54 | 226.1934 | C <sub>13</sub> H <sub>29</sub> N <sub>3</sub>                | 15.66 | 1.15 | 227.2363 |
| C <sub>14</sub> H <sub>11</sub> NO <sub>2</sub>               | 15.76 | 1.56 | 225.0790 | C <sub>14</sub> H <sub>10</sub> O <sub>3</sub>                | 15.41 | 1.71 | 226.0630 | C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O              | 15.44 | 1.31 | 227.1060 |
| C <sub>14</sub> H <sub>29</sub> N <sub>2</sub>                | 16.36 | 1.25 | 225.2332 | C <sub>14</sub> H <sub>28</sub> NO                            | 16.00 | 1.40 | 226.2172 | C <sub>13</sub> H <sub>15</sub> N <sub>4</sub>                | 15.81 | 1.17 | 227.1298 |
| C <sub>14</sub> H <sub>13</sub> N <sub>2</sub> O              | 16.14 | 1.42 | 225.1029 | C <sub>14</sub> H <sub>12</sub> NO <sub>2</sub>               | 15.78 | 1.56 | 226.0868 | C <sub>14</sub> H <sub>27</sub> O <sub>2</sub>                | 15.64 | 1.54 | 227.2012 |
| C <sub>14</sub> H <sub>15</sub> N <sub>3</sub>                | 16.51 | 1.28 | 225.1267 | C <sub>14</sub> H <sub>30</sub> N <sub>2</sub>                | 16.37 | 1.26 | 226.2411 | C <sub>14</sub> H <sub>11</sub> O <sub>3</sub>                | 15.42 | 1.71 | 227.0708 |
| C <sub>14</sub> HN <sub>4</sub>                               | 16.67 | 1.30 | 225.0202 | C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O              | 16.15 | 1.42 | 226.1107 | C <sub>14</sub> H <sub>29</sub> NO                            | 16.01 | 1.40 | 227.2250 |
| C <sub>15</sub> H <sub>29</sub> O                             | 16.71 | 1.51 | 225.2219 | C <sub>14</sub> H <sub>16</sub> N <sub>3</sub>                | 16.53 | 1.28 | 226.1346 | C <sub>14</sub> H <sub>13</sub> NO <sub>2</sub>               | 15.80 | 1.57 | 227.0947 |
| C <sub>15</sub> H <sub>13</sub> O <sub>2</sub>                | 16.50 | 1.67 | 225.0916 | C <sub>14</sub> N <sub>3</sub> O                              | 16.31 | 1.45 | 226.0042 | C <sub>14</sub> H <sub>31</sub> N <sub>2</sub>                | 16.39 | 1.26 | 227.2489 |
| C <sub>15</sub> H <sub>31</sub> N                             | 17.09 | 1.37 | 225.2458 | C <sub>14</sub> H <sub>2</sub> N <sub>4</sub>                 | 16.69 | 1.31 | 226.0280 | C <sub>14</sub> H <sub>15</sub> N <sub>2</sub> O              | 16.17 | 1.42 | 227.1185 |
| C <sub>15</sub> H <sub>15</sub> NO                            | 16.87 | 1.54 | 225.1154 | C <sub>15</sub> H <sub>30</sub> O                             | 16.73 | 1.51 | 226.2298 | C <sub>14</sub> H <sub>17</sub> N <sub>3</sub>                | 16.54 | 1.28 | 227.1424 |
| C <sub>15</sub> H <sub>17</sub> N <sub>2</sub>                | 17.24 | 1.40 | 225.1393 | C <sub>15</sub> H <sub>14</sub> O <sub>2</sub>                | 16.51 | 1.68 | 226.0994 | C <sub>14</sub> HN <sub>3</sub> O                             | 16.33 | 1.45 | 227.0120 |
| C <sub>15</sub> HN <sub>2</sub> O                             | 17.03 | 1.56 | 225.0089 | C <sub>15</sub> H <sub>32</sub> N                             | 17.10 | 1.37 | 226.2536 | C <sub>14</sub> H <sub>3</sub> N <sub>4</sub>                 | 16.70 | 1.31 | 227.0359 |
| C <sub>15</sub> H <sub>3</sub> N <sub>3</sub>                 | 17.40 | 1.42 | 225.0328 | C <sub>15</sub> H <sub>16</sub> NO                            | 16.89 | 1.54 | 226.1233 | C <sub>15</sub> H <sub>31</sub> O                             | 16.74 | 1.51 | 227.2376 |
| C <sub>16</sub> H <sub>33</sub>                               | 17.82 | 1.49 | 225.2584 | C <sub>15</sub> NO <sub>2</sub>                               | 16.67 | 1.70 | 225.9929 | C <sub>15</sub> H <sub>15</sub> O <sub>2</sub>                | 16.53 | 1.68 | 227.1072 |
| C <sub>16</sub> H <sub>17</sub> O                             | 17.60 | 1.66 | 225.1280 | C <sub>15</sub> H <sub>18</sub> N <sub>2</sub>                | 17.26 | 1.40 | 226.1471 | C <sub>15</sub> H <sub>33</sub> N                             | 17.12 | 1.38 | 227.2615 |
| C <sub>16</sub> HO <sub>2</sub>                               | 17.38 | 1.82 | 224.9976 | C <sub>15</sub> H <sub>2</sub> N <sub>2</sub> O               | 17.04 | 1.56 | 226.0167 | C <sub>15</sub> H <sub>17</sub> NO                            | 16.90 | 1.54 | 227.1311 |
| C <sub>16</sub> H <sub>19</sub> N                             | 17.98 | 1.52 | 225.1519 | C <sub>15</sub> H <sub>4</sub> N <sub>3</sub>                 | 17.42 | 1.43 | 226.0406 | C <sub>15</sub> HN <sub>2</sub> O <sub>2</sub>                | 16.68 | 1.70 | 227.0007 |
| C <sub>16</sub> H <sub>3</sub> NO                             | 17.76 | 1.68 | 225.0215 | C <sub>16</sub> H <sub>34</sub>                               | 17.83 | 1.50 | 226.2662 | C <sub>15</sub> H <sub>19</sub> N <sub>2</sub>                | 17.28 | 1.40 | 227.1549 |
| C <sub>16</sub> H <sub>5</sub> N <sub>2</sub>                 | 18.13 | 1.55 | 225.0453 | C <sub>16</sub> H <sub>18</sub> O                             | 17.62 | 1.66 | 226.1358 | C <sub>15</sub> H <sub>3</sub> N <sub>2</sub> O               | 17.06 | 1.57 | 227.0246 |
| C <sub>17</sub> H <sub>21</sub>                               | 18.71 | 1.65 | 225.1644 | C <sub>16</sub> H <sub>2</sub> O <sub>2</sub>                 | 17.40 | 1.82 | 226.0054 | C <sub>15</sub> H <sub>5</sub> N <sub>3</sub>                 | 17.43 | 1.43 | 227.0484 |
|   |       |      |          | C <sub>16</sub> H <sub>20</sub> N                             | 17.99 | 1.52 | 226.1597 | C <sub>16</sub> H <sub>19</sub> O                             | 17.63 | 1.66 | 227.1436 |

|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>16</sub> H <sub>3</sub> O <sub>2</sub>                 | 17.42 | 1.82 | 227.0133 | C <sub>15</sub> H <sub>20</sub> N <sub>2</sub>                | 17.29 | 1.41 | 228.1628 | C <sub>15</sub> H <sub>3</sub> O <sub>3</sub>                 | 16.34 | 1.85 | 228.9925 |
| C <sub>16</sub> H <sub>21</sub> N                             | 18.01 | 1.53 | 227.1675 | C <sub>15</sub> H <sub>4</sub> N <sub>2</sub> O               | 17.07 | 1.57 | 228.0324 | C <sub>15</sub> H <sub>19</sub> NO                            | 16.93 | 1.55 | 229.1467 |
| C <sub>16</sub> H <sub>5</sub> NO                             | 17.79 | 1.69 | 227.0371 | C <sub>15</sub> H <sub>6</sub> N <sub>3</sub>                 | 17.45 | 1.43 | 228.0563 | C <sub>15</sub> H <sub>3</sub> NO <sub>2</sub>                | 16.72 | 1.71 | 229.0164 |
| C <sub>16</sub> H <sub>7</sub> N <sub>2</sub>                 | 18.16 | 1.55 | 227.0610 | C <sub>16</sub> H <sub>20</sub> O                             | 17.65 | 1.66 | 228.1515 | C <sub>15</sub> H <sub>21</sub> N <sub>2</sub>                | 17.31 | 1.41 | 229.1706 |
| C <sub>17</sub> H <sub>23</sub>                               | 18.74 | 1.66 | 227.1801 | C <sub>16</sub> H <sub>4</sub> O <sub>2</sub>                 | 17.43 | 1.83 | 228.0211 | C <sub>15</sub> H <sub>5</sub> N <sub>2</sub> O               | 17.09 | 1.57 | 229.0402 |
| C <sub>17</sub> H <sub>7</sub> O                              | 18.52 | 1.82 | 227.0497 | C <sub>16</sub> H <sub>22</sub> N                             | 18.02 | 1.53 | 228.1753 | C <sub>15</sub> H <sub>7</sub> N <sub>3</sub>                 | 17.47 | 1.44 | 229.0641 |
| C <sub>17</sub> H <sub>9</sub> N                              | 18.90 | 1.69 | 227.0736 | C <sub>16</sub> H <sub>6</sub> NO                             | 17.81 | 1.69 | 228.0449 | C <sub>16</sub> H <sub>21</sub> O                             | 17.66 | 1.67 | 229.1593 |
| C <sub>18</sub> H <sub>11</sub>                               | 19.63 | 1.82 | 227.0861 | C <sub>16</sub> H <sub>8</sub> N <sub>2</sub>                 | 18.18 | 1.56 | 228.0688 | C <sub>16</sub> H <sub>5</sub> O <sub>2</sub>                 | 17.45 | 1.83 | 229.0289 |
|   |       |      |          | C <sub>17</sub> H <sub>24</sub>                               | 18.75 | 1.66 | 228.1879 | C <sub>16</sub> H <sub>23</sub> N                             | 18.04 | 1.53 | 229.1832 |
| 228   |       |      |          | C <sub>17</sub> H <sub>8</sub> O                              | 18.54 | 1.82 | 228.0575 | C <sub>16</sub> H <sub>7</sub> NO                             | 17.82 | 1.69 | 229.0528 |
| C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> | 11.98 | 1.46 | 228.1111 | C <sub>17</sub> H <sub>10</sub> N                             | 18.91 | 1.69 | 228.0814 | C <sub>16</sub> H <sub>9</sub> N <sub>2</sub>                 | 18.20 | 1.56 | 229.0767 |
| C <sub>10</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> | 12.36 | 1.30 | 228.1349 | C <sub>18</sub> H <sub>12</sub>                               | 19.64 | 1.82 | 228.0939 | C <sub>17</sub> H <sub>25</sub>                               | 18.77 | 1.66 | 229.1957 |
| C <sub>10</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub> | 12.73 | 1.15 | 228.1588 | C <sub>19</sub>   | 20.53 | 2.00 | 228.0000 | C <sub>17</sub> H <sub>9</sub> O                              | 18.55 | 1.82 | 229.0653 |
| C <sub>11</sub> H <sub>18</sub> NO <sub>4</sub>               | 12.71 | 1.54 | 228.1236 |   |       |      |          | C <sub>17</sub> H <sub>11</sub> N                             | 18.93 | 1.69 | 229.0892 |
| C <sub>11</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> | 13.09 | 1.39 | 228.1475 | 229   |       |      |          | C <sub>18</sub> H <sub>13</sub>                               | 19.66 | 1.83 | 229.1018 |
| C <sub>11</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>  | 12.87 | 1.56 | 228.0171 | C <sub>10</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub> | 12.00 | 1.46 | 229.1189 | C <sub>19</sub> H   | 20.55 | 2.00 | 229.0078 |
| C <sub>11</sub> H <sub>22</sub> N <sub>3</sub> O <sub>2</sub> | 13.46 | 1.24 | 228.1713 | C <sub>10</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub> | 12.37 | 1.31 | 229.1427 |   |       |      |          |
| C <sub>11</sub> H <sub>6</sub> N <sub>3</sub> O <sub>3</sub>  | 13.24 | 1.41 | 228.0410 | C <sub>10</sub> H <sub>21</sub> N <sub>4</sub> O <sub>2</sub> | 12.75 | 1.15 | 229.1666 | 230   |       |      |          |
| C <sub>11</sub> H <sub>24</sub> N <sub>4</sub> O              | 13.84 | 1.09 | 228.1952 | C <sub>11</sub> H <sub>19</sub> NO <sub>4</sub>               | 12.73 | 1.55 | 229.1315 | C <sub>10</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> | 12.01 | 1.46 | 230.1267 |
| C <sub>11</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>  | 13.62 | 1.26 | 228.0648 | C <sub>11</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> | 13.10 | 1.39 | 229.1553 | C <sub>10</sub> H <sub>20</sub> N <sub>3</sub> O <sub>3</sub> | 12.39 | 1.31 | 230.1506 |
| C <sub>12</sub> H <sub>20</sub> O <sub>4</sub>                | 13.44 | 1.64 | 228.1362 | C <sub>11</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>  | 12.89 | 1.57 | 229.0249 | C <sub>10</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub> | 12.76 | 1.15 | 230.1744 |
| C <sub>12</sub> H <sub>22</sub> NO <sub>3</sub>               | 13.82 | 1.49 | 228.1600 | C <sub>11</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub> | 13.48 | 1.24 | 229.1791 | C <sub>11</sub> H <sub>20</sub> NO <sub>4</sub>               | 12.74 | 1.55 | 230.1393 |
| C <sub>12</sub> H <sub>6</sub> NO <sub>4</sub>                | 13.60 | 1.66 | 228.0297 | C <sub>11</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>  | 13.26 | 1.41 | 229.0488 | C <sub>11</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> | 13.12 | 1.40 | 230.1631 |
| C <sub>12</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> | 14.19 | 1.34 | 228.1839 | C <sub>11</sub> H <sub>25</sub> N <sub>4</sub> O              | 13.85 | 1.09 | 229.2030 | C <sub>11</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>  | 12.90 | 1.57 | 230.0328 |
| C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 13.98 | 1.51 | 228.0535 | C <sub>11</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>  | 13.63 | 1.26 | 229.0726 | C <sub>11</sub> H <sub>24</sub> N <sub>3</sub> O <sub>2</sub> | 13.49 | 1.24 | 230.1870 |
| C <sub>12</sub> H <sub>26</sub> N <sub>3</sub> O              | 14.57 | 1.19 | 228.2077 | C <sub>12</sub> H <sub>21</sub> O <sub>4</sub>                | 13.46 | 1.64 | 229.1440 | C <sub>11</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>  | 13.28 | 1.42 | 230.0566 |
| C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub> | 14.35 | 1.36 | 228.0774 | C <sub>12</sub> H <sub>23</sub> NO <sub>3</sub>               | 13.83 | 1.49 | 229.1679 | C <sub>11</sub> H <sub>26</sub> N <sub>4</sub> O              | 13.87 | 1.09 | 230.2108 |
| C <sub>12</sub> H <sub>28</sub> N <sub>4</sub>                | 14.94 | 1.04 | 228.2316 | C <sub>12</sub> H <sub>7</sub> NO <sub>4</sub>                | 13.62 | 1.66 | 229.0375 | C <sub>11</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> | 13.65 | 1.27 | 230.0805 |
| C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> O              | 14.72 | 1.21 | 228.1012 | C <sub>12</sub> H <sub>25</sub> N <sub>2</sub> O <sub>2</sub> | 14.21 | 1.34 | 229.1917 | C <sub>12</sub> H <sub>22</sub> O <sub>4</sub>                | 13.48 | 1.64 | 230.1518 |
| C <sub>13</sub> H <sub>24</sub> O <sub>3</sub>                | 14.55 | 1.58 | 228.1726 | C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>  | 13.99 | 1.51 | 229.0614 | C <sub>12</sub> H <sub>24</sub> NO <sub>3</sub>               | 13.85 | 1.49 | 230.1757 |
| C <sub>13</sub> H <sub>8</sub> O <sub>4</sub>                 | 14.33 | 1.75 | 228.0422 | C <sub>12</sub> H <sub>27</sub> N <sub>3</sub> O              | 14.58 | 1.19 | 229.2156 | C <sub>12</sub> H <sub>8</sub> NO <sub>4</sub>                | 13.63 | 1.66 | 230.0453 |
| C <sub>13</sub> H <sub>26</sub> NO <sub>2</sub>               | 14.92 | 1.44 | 228.1965 | C <sub>12</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> | 14.37 | 1.36 | 229.0852 | C <sub>12</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> | 14.22 | 1.34 | 230.1996 |
| C <sub>13</sub> H <sub>10</sub> NO <sub>3</sub>               | 14.71 | 1.61 | 228.0661 | C <sub>12</sub> H <sub>29</sub> N <sub>4</sub>                | 14.96 | 1.05 | 229.2394 | C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 14.01 | 1.51 | 230.0692 |
| C <sub>13</sub> H <sub>28</sub> N <sub>2</sub> O              | 15.30 | 1.29 | 228.2203 | C <sub>12</sub> H <sub>13</sub> N <sub>4</sub> O              | 14.74 | 1.21 | 229.1091 | C <sub>12</sub> H <sub>28</sub> N <sub>3</sub> O              | 14.60 | 1.19 | 230.2234 |
| C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | 15.08 | 1.46 | 228.0899 | C <sub>13</sub> H <sub>25</sub> O <sub>3</sub>                | 14.57 | 1.59 | 229.1804 | C <sub>12</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> | 14.38 | 1.36 | 230.0930 |
| C <sub>13</sub> H <sub>30</sub> N <sub>3</sub>                | 15.67 | 1.15 | 228.2442 | C <sub>13</sub> H <sub>9</sub> O <sub>4</sub>                 | 14.35 | 1.76 | 229.0501 | C <sub>12</sub> H <sub>30</sub> N <sub>4</sub>                | 14.97 | 1.05 | 230.2473 |
| C <sub>13</sub> H <sub>14</sub> N <sub>3</sub> O              | 15.46 | 1.32 | 228.1138 | C <sub>13</sub> H <sub>27</sub> NO <sub>2</sub>               | 14.94 | 1.44 | 229.2043 | C <sub>12</sub> H <sub>14</sub> N <sub>4</sub> O              | 14.76 | 1.22 | 230.1169 |
| C <sub>13</sub> H <sub>16</sub> N <sub>4</sub>                | 15.83 | 1.17 | 228.1377 | C <sub>13</sub> H <sub>11</sub> NO <sub>3</sub>               | 14.72 | 1.61 | 229.0739 | C <sub>13</sub> H <sub>26</sub> O <sub>3</sub>                | 14.58 | 1.59 | 230.1883 |
| C <sub>13</sub> N <sub>4</sub> O                              | 15.61 | 1.34 | 228.0073 | C <sub>13</sub> H <sub>29</sub> N <sub>2</sub> O              | 15.31 | 1.30 | 229.2281 | C <sub>13</sub> H <sub>10</sub> O <sub>4</sub>                | 14.36 | 1.76 | 230.0579 |
| C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>                | 15.65 | 1.54 | 228.2090 | C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> | 15.10 | 1.46 | 229.0978 | C <sub>13</sub> H <sub>28</sub> NO <sub>2</sub>               | 14.96 | 1.44 | 230.2121 |
| C <sub>14</sub> H <sub>12</sub> O <sub>3</sub>                | 15.44 | 1.71 | 228.0786 | C <sub>13</sub> H <sub>31</sub> N <sub>3</sub>                | 15.69 | 1.15 | 229.2520 | C <sub>13</sub> H <sub>12</sub> NO <sub>3</sub>               | 14.74 | 1.61 | 230.0817 |
| C <sub>14</sub> H <sub>30</sub> NO                            | 16.03 | 1.40 | 228.2329 | C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> O              | 15.47 | 1.32 | 229.1216 | C <sub>13</sub> H <sub>30</sub> N <sub>2</sub> O              | 15.33 | 1.30 | 230.2360 |
| C <sub>14</sub> H <sub>14</sub> NO <sub>2</sub>               | 15.81 | 1.57 | 228.1025 | C <sub>13</sub> H <sub>17</sub> N <sub>4</sub>                | 15.85 | 1.18 | 229.1455 | C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> | 15.11 | 1.47 | 230.1056 |
| C <sub>14</sub> H <sub>32</sub> N <sub>2</sub>                | 16.40 | 1.26 | 228.2567 | C <sub>13</sub> HN <sub>4</sub> O                             | 15.63 | 1.34 | 229.0151 | C <sub>13</sub> H <sub>16</sub> N <sub>3</sub> O              | 15.49 | 1.32 | 230.1295 |
| C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O              | 16.19 | 1.43 | 228.1264 | C <sub>14</sub> H <sub>29</sub> O <sub>2</sub>                | 15.67 | 1.55 | 229.2168 | C <sub>13</sub> N <sub>3</sub> O <sub>2</sub>                 | 15.27 | 1.49 | 229.9991 |
| C <sub>14</sub> N <sub>2</sub> O <sub>2</sub>                 | 15.97 | 1.59 | 227.9960 | C <sub>14</sub> H <sub>13</sub> O <sub>3</sub>                | 15.45 | 1.71 | 229.0865 | C <sub>13</sub> H <sub>18</sub> N <sub>4</sub>                | 15.86 | 1.18 | 230.1533 |
| C <sub>14</sub> H <sub>18</sub> N <sub>3</sub>                | 16.56 | 1.29 | 228.1502 | C <sub>14</sub> H <sub>31</sub> NO                            | 16.05 | 1.41 | 229.2407 | C <sub>13</sub> H <sub>2</sub> N <sub>4</sub> O               | 15.64 | 1.35 | 230.0229 |
| C <sub>14</sub> H <sub>2</sub> N <sub>3</sub> O               | 16.34 | 1.45 | 228.0198 | C <sub>14</sub> H <sub>15</sub> NO <sub>2</sub>               | 15.83 | 1.57 | 229.1103 | C <sub>14</sub> H <sub>30</sub> O <sub>2</sub>                | 15.69 | 1.55 | 230.2247 |
| C <sub>14</sub> H <sub>4</sub> N <sub>4</sub>                 | 16.72 | 1.31 | 228.0437 | C <sub>14</sub> H <sub>17</sub> N <sub>2</sub> O              | 16.20 | 1.43 | 229.1342 | C <sub>14</sub> H <sub>14</sub> O <sub>3</sub>                | 15.47 | 1.72 | 230.0943 |
| C <sub>15</sub> H <sub>32</sub> O                             | 16.76 | 1.52 | 228.2454 | C <sub>14</sub> HN <sub>2</sub> O <sub>2</sub>                | 15.99 | 1.60 | 229.0038 | C <sub>14</sub> H <sub>16</sub> NO <sub>2</sub>               | 15.84 | 1.57 | 230.1182 |
| C <sub>15</sub> H <sub>16</sub> O <sub>2</sub>                | 16.54 | 1.68 | 228.1151 | C <sub>14</sub> H <sub>19</sub> N <sub>3</sub>                | 16.58 | 1.29 | 229.1580 | C <sub>14</sub> NO <sub>3</sub>                               | 15.63 | 1.74 | 229.9878 |
| C <sub>15</sub> O <sub>3</sub>                                | 16.33 | 1.85 | 227.9847 | C <sub>14</sub> H <sub>3</sub> N <sub>3</sub> O               | 16.36 | 1.45 | 229.0277 | C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O              | 16.22 | 1.43 | 230.1420 |
| C <sub>15</sub> H <sub>18</sub> NO                            | 16.92 | 1.54 | 228.1389 | C <sub>14</sub> H <sub>5</sub> N <sub>4</sub>                 | 16.73 | 1.32 | 229.0515 | C <sub>14</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>  | 16.00 | 1.60 | 230.0116 |
| C <sub>15</sub> H <sub>2</sub> NO <sub>2</sub>                | 16.70 | 1.71 | 228.0085 | C <sub>15</sub> H <sub>17</sub> O <sub>2</sub>                | 16.56 | 1.68 | 229.1229 | C <sub>14</sub> H <sub>20</sub> N <sub>3</sub>                | 16.59 | 1.29 | 230.1659 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>14</sub> H <sub>4</sub> N <sub>3</sub> O               | 16.38 | 1.46 | 230.0355 | C <sub>14</sub> H <sub>21</sub> N <sub>3</sub>                | 16.61 | 1.30 | 231.1737 | C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O              | 16.25 | 1.44 | 232.1577 |
| C <sub>14</sub> H <sub>6</sub> N <sub>4</sub>                 | 16.75 | 1.32 | 230.0594 | C <sub>14</sub> H <sub>5</sub> N <sub>3</sub> O               | 16.39 | 1.46 | 231.0433 | C <sub>14</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>  | 16.03 | 1.60 | 232.0273 |
| C <sub>15</sub> H <sub>18</sub> O <sub>2</sub>                | 16.58 | 1.69 | 230.1307 | C <sub>14</sub> H <sub>7</sub> N <sub>4</sub>                 | 16.77 | 1.32 | 231.0672 | C <sub>14</sub> H <sub>22</sub> N <sub>3</sub>                | 16.62 | 1.30 | 232.1815 |
| C <sub>15</sub> H <sub>2</sub> O <sub>3</sub>                 | 16.36 | 1.85 | 230.0003 | C <sub>15</sub> H <sub>19</sub> O <sub>2</sub>                | 16.59 | 1.69 | 231.1385 | C <sub>14</sub> H <sub>6</sub> N <sub>3</sub> O               | 16.41 | 1.46 | 232.0511 |
| C <sub>15</sub> H <sub>20</sub> NO                            | 16.95 | 1.55 | 230.1546 | C <sub>15</sub> H <sub>3</sub> O <sub>3</sub>                 | 16.37 | 1.85 | 231.0082 | C <sub>14</sub> H <sub>8</sub> N <sub>4</sub>                 | 16.78 | 1.32 | 232.0750 |
| C <sub>15</sub> H <sub>4</sub> NO <sub>2</sub>                | 16.73 | 1.71 | 230.0242 | C <sub>15</sub> H <sub>21</sub> NO                            | 16.97 | 1.55 | 231.1624 | C <sub>15</sub> H <sub>20</sub> O <sub>2</sub>                | 16.61 | 1.69 | 232.1464 |
| C <sub>15</sub> H <sub>22</sub> N <sub>2</sub>                | 17.32 | 1.41 | 230.1784 | C <sub>15</sub> H <sub>5</sub> NO <sub>2</sub>                | 16.75 | 1.72 | 231.0320 | C <sub>15</sub> H <sub>4</sub> O <sub>3</sub>                 | 16.39 | 1.86 | 232.0160 |
| C <sub>15</sub> H <sub>6</sub> N <sub>2</sub> O               | 17.11 | 1.57 | 230.0480 | C <sub>15</sub> H <sub>23</sub> N <sub>2</sub>                | 17.34 | 1.41 | 231.1863 | C <sub>15</sub> H <sub>22</sub> NO                            | 16.98 | 1.55 | 232.1702 |
| C <sub>15</sub> H <sub>8</sub> N <sub>3</sub>                 | 17.48 | 1.44 | 230.0719 | C <sub>15</sub> H <sub>7</sub> N <sub>2</sub> O               | 17.12 | 1.58 | 231.0559 | C <sub>15</sub> H <sub>6</sub> NO <sub>2</sub>                | 16.76 | 1.72 | 232.0399 |
| C <sub>16</sub> H <sub>22</sub> O                             | 17.68 | 1.67 | 230.1671 | C <sub>15</sub> H <sub>9</sub> N <sub>3</sub>                 | 17.50 | 1.44 | 231.0798 | C <sub>15</sub> H <sub>24</sub> N <sub>2</sub>                | 17.36 | 1.42 | 232.1941 |
| C <sub>16</sub> H <sub>6</sub> O <sub>2</sub>                 | 17.46 | 1.83 | 230.0368 | C <sub>16</sub> H <sub>23</sub> O                             | 17.70 | 1.67 | 231.1750 | C <sub>15</sub> H <sub>8</sub> N <sub>2</sub> O               | 17.14 | 1.58 | 232.0637 |
| C <sub>16</sub> H <sub>24</sub> N                             | 18.06 | 1.54 | 230.1910 | C <sub>16</sub> H <sub>7</sub> O <sub>2</sub>                 | 17.48 | 1.84 | 231.0446 | C <sub>15</sub> H <sub>10</sub> N <sub>3</sub>                | 17.51 | 1.44 | 232.0876 |
| C <sub>16</sub> H <sub>8</sub> NO                             | 17.84 | 1.70 | 230.0606 | C <sub>16</sub> H <sub>25</sub> N                             | 18.07 | 1.54 | 231.1988 | C <sub>16</sub> H <sub>24</sub> O                             | 17.71 | 1.68 | 232.1828 |
| C <sub>16</sub> H <sub>10</sub> N <sub>2</sub>                | 18.21 | 1.56 | 230.0845 | C <sub>16</sub> H <sub>9</sub> NO                             | 17.85 | 1.70 | 231.0684 | C <sub>16</sub> H <sub>8</sub> O <sub>2</sub>                 | 17.50 | 1.84 | 232.0524 |
| C <sub>17</sub> H <sub>26</sub>                               | 18.79 | 1.67 | 230.2036 | C <sub>16</sub> H <sub>11</sub> N <sub>2</sub>                | 18.23 | 1.57 | 231.0923 | C <sub>16</sub> H <sub>26</sub> N                             | 18.09 | 1.54 | 232.2067 |
| C <sub>17</sub> H <sub>10</sub> O                             | 18.57 | 1.83 | 230.0732 | C <sub>17</sub> H <sub>27</sub>                               | 18.80 | 1.67 | 231.2114 | C <sub>16</sub> H <sub>10</sub> NO                            | 17.87 | 1.70 | 232.0768 |
| C <sub>17</sub> H <sub>12</sub> N                             | 18.94 | 1.69 | 230.0970 | C <sub>17</sub> H <sub>11</sub> O                             | 18.59 | 1.83 | 231.0810 | C <sub>16</sub> H <sub>12</sub> N <sub>2</sub>                | 18.24 | 1.57 | 232.1001 |
| C <sub>18</sub> H <sub>14</sub>                               | 19.67 | 1.83 | 230.1096 | C <sub>17</sub> H <sub>13</sub> N                             | 18.96 | 1.70 | 231.1049 | C <sub>17</sub> H <sub>28</sub>                               | 18.82 | 1.67 | 232.2192 |
| C <sub>18</sub> N   | 19.83 | 1.86 | 230.0031 | C <sub>18</sub> H <sub>15</sub>                               | 19.69 | 1.83 | 231.1174 | C <sub>17</sub> H <sub>12</sub> O                             | 18.60 | 1.83 | 232.0888 |
| C <sub>19</sub> H <sub>2</sub>                                | 20.56 | 2.00 | 230.0157 | C <sub>18</sub> HN  | 19.85 | 1.86 | 231.0109 | C <sub>17</sub> H <sub>14</sub> N                             | 18.98 | 1.70 | 232.1127 |
|   |       |      |          | C <sub>19</sub> H <sub>3</sub>                                | 20.58 | 2.01 | 231.0235 | C <sub>17</sub> N <sub>2</sub>                                | 19.13 | 1.73 | 232.0062 |
| 231   |       |      |          |   |       |      |          | C <sub>18</sub> H <sub>16</sub>                               | 19.71 | 1.84 | 232.1253 |
| C <sub>10</sub> H <sub>19</sub> N <sub>2</sub> O <sub>4</sub> | 12.03 | 1.47 | 231.1345 | 232   |       |      |          | C <sub>18</sub> O   | 19.49 | 1.99 | 231.9949 |
| C <sub>10</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub> | 12.40 | 1.31 | 231.1584 | C <sub>10</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> | 12.05 | 1.47 | 232.1424 | C <sub>18</sub> H <sub>2</sub> N                              | 19.86 | 1.87 | 232.0187 |
| C <sub>10</sub> H <sub>23</sub> N <sub>4</sub> O <sub>2</sub> | 12.78 | 1.16 | 231.1822 | C <sub>10</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub> | 12.42 | 1.31 | 232.1662 | C <sub>19</sub> H <sub>4</sub>                                | 20.60 | 2.01 | 232.0313 |
| C <sub>11</sub> H <sub>21</sub> NO <sub>4</sub>               | 12.76 | 1.55 | 231.1471 | C <sub>10</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> | 12.79 | 1.16 | 232.1901 | 233   |       |      |          |
| C <sub>11</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub> | 13.13 | 1.40 | 231.1710 | C <sub>11</sub> H <sub>22</sub> NO <sub>4</sub>               | 12.78 | 1.55 | 232.1549 | C <sub>10</sub> H <sub>21</sub> N <sub>2</sub> O <sub>4</sub> | 12.06 | 1.47 | 233.1502 |
| C <sub>11</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub>  | 12.92 | 1.57 | 231.0406 | C <sub>11</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub> | 13.15 | 1.40 | 232.1788 | C <sub>10</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub> | 12.44 | 1.31 | 233.1741 |
| C <sub>11</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub> | 13.51 | 1.25 | 231.1948 | C <sub>11</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>  | 12.93 | 1.57 | 232.0484 | C <sub>10</sub> H <sub>25</sub> N <sub>4</sub> O <sub>2</sub> | 12.81 | 1.16 | 233.1979 |
| C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>  | 13.29 | 1.42 | 231.0644 | C <sub>11</sub> H <sub>26</sub> N <sub>3</sub> O <sub>2</sub> | 13.53 | 1.25 | 232.2026 | C <sub>11</sub> H <sub>23</sub> NO <sub>4</sub>               | 12.79 | 1.56 | 233.1628 |
| C <sub>11</sub> H <sub>27</sub> N <sub>4</sub> O              | 13.88 | 1.10 | 231.2187 | C <sub>11</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> | 13.31 | 1.42 | 232.0723 | C <sub>11</sub> H <sub>25</sub> N <sub>2</sub> O <sub>3</sub> | 13.17 | 1.40 | 233.1866 |
| C <sub>11</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> | 13.67 | 1.27 | 231.0883 | C <sub>11</sub> H <sub>28</sub> N <sub>4</sub> O              | 13.90 | 1.10 | 232.2265 | C <sub>11</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>  | 12.95 | 1.57 | 233.0563 |
| C <sub>12</sub> H <sub>23</sub> O <sub>4</sub>                | 13.49 | 1.64 | 231.1597 | C <sub>11</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> | 13.68 | 1.27 | 232.0961 | C <sub>11</sub> H <sub>27</sub> N <sub>3</sub> O <sub>2</sub> | 13.54 | 1.25 | 233.2105 |
| C <sub>12</sub> H <sub>25</sub> NO <sub>3</sub>               | 13.87 | 1.49 | 231.1835 | C <sub>12</sub> H <sub>24</sub> O <sub>4</sub>                | 13.51 | 1.64 | 232.1675 | C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> | 13.32 | 1.42 | 233.0801 |
| C <sub>12</sub> H <sub>9</sub> NO <sub>4</sub>                | 13.65 | 1.66 | 231.0532 | C <sub>12</sub> H <sub>26</sub> NO <sub>3</sub>               | 13.88 | 1.49 | 232.1914 | C <sub>11</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> | 13.70 | 1.27 | 233.1040 |
| C <sub>12</sub> H <sub>27</sub> N <sub>2</sub> O <sub>2</sub> | 14.24 | 1.34 | 231.2074 | C <sub>12</sub> H <sub>10</sub> NO <sub>4</sub>               | 13.67 | 1.66 | 232.0610 | C <sub>12</sub> H <sub>25</sub> O <sub>4</sub>                | 13.52 | 1.65 | 233.1753 |
| C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> | 14.02 | 1.51 | 231.0770 | C <sub>12</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> | 14.26 | 1.35 | 232.2152 | C <sub>12</sub> H <sub>27</sub> NO <sub>3</sub>               | 13.90 | 1.50 | 233.1992 |
| C <sub>12</sub> H <sub>29</sub> N <sub>3</sub> O              | 14.61 | 1.20 | 231.2312 | C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> | 14.04 | 1.52 | 232.0848 | C <sub>12</sub> H <sub>11</sub> NO <sub>4</sub>               | 13.68 | 1.67 | 233.0688 |
| C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> | 14.40 | 1.37 | 231.1009 | C <sub>12</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> | 14.41 | 1.37 | 232.1087 | C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> | 14.06 | 1.52 | 233.0927 |
| C <sub>12</sub> H <sub>15</sub> N <sub>4</sub> O              | 14.77 | 1.22 | 231.1247 | C <sub>12</sub> H <sub>16</sub> N <sub>4</sub> O              | 14.79 | 1.22 | 232.1325 | C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> | 14.43 | 1.37 | 233.1165 |
| C <sub>13</sub> H <sub>27</sub> O <sub>3</sub>                | 14.60 | 1.59 | 231.1961 | C <sub>12</sub> N <sub>4</sub> O <sub>2</sub>                 | 14.57 | 1.39 | 232.0022 | C <sub>12</sub> H <sub>17</sub> N <sub>4</sub> O              | 14.80 | 1.22 | 233.1404 |
| C <sub>13</sub> H <sub>11</sub> O <sub>4</sub>                | 14.38 | 1.76 | 231.0657 | C <sub>13</sub> H <sub>28</sub> O <sub>3</sub>                | 14.61 | 1.59 | 232.2039 | C <sub>12</sub> HN <sub>4</sub> O <sub>2</sub>                | 14.59 | 1.39 | 233.0100 |
| C <sub>13</sub> H <sub>29</sub> NO <sub>2</sub>               | 14.97 | 1.45 | 231.2199 | C <sub>13</sub> H <sub>12</sub> O <sub>4</sub>                | 14.40 | 1.76 | 232.0735 | C <sub>13</sub> H <sub>13</sub> O <sub>4</sub>                | 14.41 | 1.76 | 233.0814 |
| C <sub>13</sub> H <sub>13</sub> NO <sub>3</sub>               | 14.75 | 1.61 | 231.0896 | C <sub>13</sub> H <sub>14</sub> NO <sub>3</sub>               | 14.77 | 1.62 | 232.0974 | C <sub>13</sub> H <sub>15</sub> NO <sub>3</sub>               | 14.79 | 1.62 | 233.1052 |
| C <sub>13</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> | 15.13 | 1.47 | 231.1134 | C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> | 15.14 | 1.47 | 232.1213 | C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> | 15.16 | 1.47 | 233.1291 |
| C <sub>13</sub> H <sub>17</sub> N <sub>3</sub> O              | 15.50 | 1.32 | 231.1373 | C <sub>13</sub> N <sub>2</sub> O <sub>3</sub>                 | 14.93 | 1.64 | 231.9909 | C <sub>13</sub> HN <sub>2</sub> O <sub>3</sub>                | 14.94 | 1.64 | 232.9987 |
| C <sub>13</sub> HN <sub>3</sub> O <sub>2</sub>                | 15.29 | 1.49 | 231.0069 | C <sub>13</sub> H <sub>18</sub> N <sub>3</sub> O              | 15.52 | 1.33 | 232.1451 | C <sub>13</sub> H <sub>19</sub> N <sub>3</sub> O              | 15.54 | 1.33 | 233.1529 |
| C <sub>13</sub> H <sub>19</sub> N <sub>4</sub>                | 15.88 | 1.18 | 231.1611 | C <sub>13</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>  | 15.30 | 1.49 | 232.0147 | C <sub>13</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>  | 15.32 | 1.50 | 233.0226 |
| C <sub>13</sub> H <sub>3</sub> N <sub>4</sub> O               | 15.66 | 1.35 | 231.0308 | C <sub>13</sub> H <sub>20</sub> N <sub>4</sub>                | 15.89 | 1.18 | 232.1690 | C <sub>13</sub> H <sub>21</sub> N <sub>4</sub>                | 15.91 | 1.19 | 233.1768 |
| C <sub>14</sub> H <sub>15</sub> O <sub>3</sub>                | 15.49 | 1.72 | 231.1021 | C <sub>13</sub> H <sub>4</sub> N <sub>4</sub> O               | 15.68 | 1.35 | 232.0386 | C <sub>13</sub> H <sub>5</sub> N <sub>4</sub> O               | 15.69 | 1.35 | 233.0464 |
| C <sub>14</sub> H <sub>17</sub> NO <sub>2</sub>               | 15.86 | 1.58 | 231.1260 | C <sub>14</sub> H <sub>16</sub> O <sub>3</sub>                | 15.50 | 1.72 | 232.1100 | C <sub>14</sub> H <sub>17</sub> O <sub>3</sub>                | 15.52 | 1.72 | 233.1178 |
| C <sub>14</sub> HN <sub>3</sub> O <sub>3</sub>                | 15.64 | 1.74 | 230.9956 | C <sub>14</sub> O <sub>4</sub>                                | 15.28 | 1.89 | 231.9796 | C <sub>14</sub> HO <sub>4</sub>                               | 15.30 | 1.89 | 232.9874 |
| C <sub>14</sub> H <sub>19</sub> N <sub>2</sub> O              | 16.23 | 1.44 | 231.1498 | C <sub>14</sub> H <sub>18</sub> NO <sub>2</sub>               | 15.88 | 1.58 | 232.1338 | C <sub>14</sub> H <sub>19</sub> NO <sub>2</sub>               | 15.89 | 1.58 | 233.1416 |
| C <sub>14</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 16.02 | 1.60 | 231.0195 | C <sub>14</sub> H <sub>2</sub> NO <sub>3</sub>                | 15.66 | 1.74 | 232.0034 | C <sub>14</sub> H <sub>3</sub> NO <sub>3</sub>                | 15.68 | 1.75 | 233.0113 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>14</sub> H <sub>21</sub> N <sub>2</sub> O              | 16.27 | 1.44 | 233.1655 | C <sub>14</sub> H <sub>4</sub> N <sub>3</sub> O               | 15.69 | 1.75 | 234.0191 | C <sub>14</sub> H <sub>23</sub> N <sub>2</sub> O              | 16.30 | 1.45 | 235.1811 |
| C <sub>14</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>  | 16.05 | 1.61 | 233.0351 | C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O              | 16.28 | 1.44 | 234.1733 | C <sub>14</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>  | 16.08 | 1.61 | 235.0508 |
| C <sub>14</sub> H <sub>23</sub> N <sub>3</sub>                | 16.64 | 1.30 | 233.1894 | C <sub>14</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 16.07 | 1.61 | 234.0429 | C <sub>14</sub> H <sub>25</sub> N <sub>3</sub>                | 16.67 | 1.31 | 235.2050 |
| C <sub>14</sub> H <sub>7</sub> N <sub>3</sub> O               | 16.42 | 1.47 | 233.0590 | C <sub>14</sub> H <sub>24</sub> N <sub>3</sub>                | 16.66 | 1.30 | 234.1972 | C <sub>14</sub> H <sub>9</sub> N <sub>3</sub> O               | 16.46 | 1.47 | 235.0746 |
| C <sub>14</sub> H <sub>9</sub> N <sub>4</sub>                 | 16.80 | 1.33 | 233.0829 | C <sub>14</sub> H <sub>8</sub> N <sub>3</sub> O               | 16.44 | 1.47 | 234.0668 | C <sub>14</sub> H <sub>11</sub> N <sub>4</sub>                | 16.83 | 1.33 | 235.0985 |
| C <sub>15</sub> H <sub>21</sub> O <sub>2</sub>                | 16.62 | 1.70 | 233.1542 | C <sub>14</sub> H <sub>10</sub> N <sub>4</sub>                | 16.81 | 1.33 | 234.0907 | C <sub>15</sub> H <sub>23</sub> O <sub>2</sub>                | 16.66 | 1.70 | 235.1699 |
| C <sub>15</sub> H <sub>5</sub> O <sub>3</sub>                 | 16.41 | 1.86 | 233.0238 | C <sub>15</sub> H <sub>22</sub> O <sub>2</sub>                | 16.64 | 1.70 | 234.1620 | C <sub>15</sub> H <sub>7</sub> O <sub>3</sub>                 | 16.44 | 1.86 | 235.0395 |
| C <sub>15</sub> H <sub>23</sub> NO                            | 17.00 | 1.56 | 233.1781 | C <sub>15</sub> H <sub>6</sub> O <sub>3</sub>                 | 16.42 | 1.86 | 234.0317 | C <sub>15</sub> H <sub>25</sub> NO                            | 17.03 | 1.56 | 235.1937 |
| C <sub>15</sub> H <sub>7</sub> NO <sub>2</sub>                | 16.78 | 1.72 | 233.0477 | C <sub>15</sub> H <sub>24</sub> NO                            | 17.01 | 1.56 | 234.1859 | C <sub>15</sub> H <sub>9</sub> NO <sub>2</sub>                | 16.81 | 1.73 | 235.0634 |
| C <sub>15</sub> H <sub>25</sub> N <sub>2</sub>                | 17.37 | 1.42 | 233.2019 | C <sub>15</sub> H <sub>8</sub> NO <sub>2</sub>                | 16.80 | 1.72 | 234.0555 | C <sub>15</sub> H <sub>27</sub> N <sub>2</sub>                | 17.40 | 1.43 | 235.2176 |
| C <sub>15</sub> H <sub>9</sub> N <sub>2</sub> O               | 17.16 | 1.58 | 233.0715 | C <sub>15</sub> H <sub>26</sub> N <sub>2</sub>                | 17.39 | 1.42 | 234.2098 | C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O              | 17.19 | 1.59 | 235.0872 |
| C <sub>15</sub> H <sub>11</sub> N <sub>3</sub>                | 17.53 | 1.45 | 233.0954 | C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O              | 17.17 | 1.59 | 234.0794 | C <sub>15</sub> H <sub>13</sub> N <sub>3</sub>                | 17.56 | 1.45 | 235.1111 |
| C <sub>16</sub> H <sub>25</sub> O                             | 17.73 | 1.68 | 233.1906 | C <sub>15</sub> H <sub>12</sub> N <sub>3</sub>                | 17.55 | 1.45 | 234.1032 | C <sub>16</sub> H <sub>27</sub> O                             | 17.76 | 1.68 | 235.2063 |
| C <sub>16</sub> H <sub>9</sub> O <sub>2</sub>                 | 17.51 | 1.84 | 233.0603 | C <sub>16</sub> H <sub>26</sub> O                             | 17.74 | 1.68 | 234.1985 | C <sub>16</sub> H <sub>11</sub> O <sub>2</sub>                | 17.54 | 1.85 | 235.0759 |
| C <sub>16</sub> H <sub>27</sub> N                             | 18.10 | 1.54 | 233.2145 | C <sub>16</sub> H <sub>10</sub> O <sub>2</sub>                | 17.53 | 1.84 | 234.0681 | C <sub>16</sub> H <sub>29</sub> N                             | 18.14 | 1.55 | 235.2301 |
| C <sub>16</sub> H <sub>11</sub> NO                            | 17.89 | 1.71 | 233.0841 | C <sub>16</sub> H <sub>28</sub> N                             | 18.12 | 1.55 | 234.2223 | C <sub>16</sub> H <sub>13</sub> NO                            | 17.92 | 1.71 | 235.0998 |
| C <sub>16</sub> H <sub>13</sub> N <sub>2</sub>                | 18.26 | 1.57 | 233.1080 | C <sub>16</sub> H <sub>12</sub> NO                            | 17.90 | 1.71 | 234.0919 | C <sub>16</sub> H <sub>15</sub> N <sub>2</sub>                | 18.29 | 1.58 | 235.1236 |
| C <sub>17</sub> H <sub>29</sub>                               | 18.83 | 1.67 | 233.2270 | C <sub>16</sub> H <sub>14</sub> N <sub>2</sub>                | 18.28 | 1.58 | 234.1158 | C <sub>16</sub> HN <sub>3</sub>                               | 18.45 | 1.61 | 235.0171 |
| C <sub>17</sub> H <sub>13</sub> O                             | 18.62 | 1.83 | 233.0967 | C <sub>16</sub> N <sub>3</sub>                                | 18.43 | 1.60 | 234.0093 | C <sub>17</sub> H <sub>31</sub>                               | 18.87 | 1.68 | 235.2427 |
| C <sub>17</sub> H <sub>15</sub> N                             | 18.99 | 1.70 | 233.1205 | C <sub>17</sub> H <sub>30</sub>                               | 18.85 | 1.68 | 234.2349 | C <sub>17</sub> H <sub>15</sub> O                             | 18.65 | 1.84 | 235.1123 |
| C <sub>17</sub> HN <sub>2</sub>                               | 19.15 | 1.73 | 233.0140 | C <sub>17</sub> H <sub>14</sub> O                             | 18.63 | 1.84 | 234.1045 | C <sub>17</sub> H <sub>17</sub> N                             | 19.02 | 1.71 | 235.1362 |
| C <sub>18</sub> H <sub>17</sub>                               | 19.72 | 1.84 | 233.1331 | C <sub>17</sub> H <sub>16</sub> N                             | 19.01 | 1.71 | 234.1284 | C <sub>17</sub> HN <sub>3</sub>                               | 18.81 | 1.87 | 235.0058 |
| C <sub>18</sub> HO  | 19.51 | 2.00 | 233.0027 | C <sub>17</sub> NO  | 18.79 | 1.87 | 233.9980 | C <sub>17</sub> H <sub>3</sub> N <sub>2</sub>                 | 19.18 | 1.74 | 235.0297 |
| C <sub>18</sub> H <sub>3</sub> N                              | 19.88 | 1.87 | 233.0266 | C <sub>17</sub> H <sub>2</sub> N <sub>2</sub>                 | 19.17 | 1.74 | 234.0218 | C <sub>18</sub> H <sub>19</sub>                               | 19.75 | 1.85 | 235.1488 |
| C <sub>19</sub> H <sub>5</sub>                                | 20.61 | 2.01 | 233.0391 | C <sub>18</sub> H <sub>18</sub>                               | 19.74 | 1.84 | 234.1409 | C <sub>18</sub> H <sub>3</sub> O                              | 19.54 | 2.00 | 235.0184 |
|   |       |      |          | C <sub>18</sub> H <sub>2</sub> O                              | 19.52 | 2.00 | 234.0106 | C <sub>18</sub> H <sub>5</sub> N                              | 19.91 | 1.88 | 235.0422 |
| 234   |       |      |          | C <sub>18</sub> H <sub>4</sub> N                              | 19.90 | 1.87 | 234.0344 | C <sub>19</sub> H <sub>7</sub>                                | 20.64 | 2.02 | 235.0548 |
| C <sub>10</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> | 12.08 | 1.47 | 234.1580 | C <sub>19</sub> H <sub>6</sub>                                | 20.63 | 2.02 | 234.0470 |   |       |      |          |
| C <sub>10</sub> H <sub>24</sub> N <sub>3</sub> O <sub>3</sub> | 12.45 | 1.32 | 234.1819 | 235   |       |      |          | 236   |       |      |          |
| C <sub>10</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub> | 12.83 | 1.16 | 234.2057 | C <sub>10</sub> H <sub>23</sub> N <sub>2</sub> O <sub>4</sub> | 12.09 | 1.47 | 235.1659 | C <sub>10</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> | 12.11 | 1.48 | 236.1737 |
| C <sub>11</sub> H <sub>24</sub> NO <sub>4</sub>               | 12.81 | 1.56 | 234.1706 | C <sub>10</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub> | 12.47 | 1.32 | 235.1897 | C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> | 13.00 | 1.58 | 236.0797 |
| C <sub>11</sub> H <sub>26</sub> N <sub>2</sub> O <sub>3</sub> | 13.18 | 1.40 | 234.1945 | C <sub>11</sub> H <sub>25</sub> NO <sub>4</sub>               | 12.82 | 1.56 | 235.1784 | C <sub>11</sub> H <sub>14</sub> N <sub>3</sub> O <sub>3</sub> | 13.37 | 1.43 | 236.1036 |
| C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> | 12.97 | 1.58 | 234.0641 | C <sub>11</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> | 12.98 | 1.58 | 235.0719 | C <sub>11</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> | 13.75 | 1.28 | 236.1275 |
| C <sub>11</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> | 13.34 | 1.42 | 234.0879 | C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> | 13.36 | 1.43 | 235.0958 | C <sub>12</sub> H <sub>14</sub> NO <sub>4</sub>               | 13.73 | 1.67 | 236.0923 |
| C <sub>11</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> | 13.71 | 1.27 | 234.1118 | C <sub>11</sub> H <sub>15</sub> N <sub>4</sub> O <sub>2</sub> | 13.73 | 1.28 | 235.1196 | C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> | 14.10 | 1.52 | 236.1162 |
| C <sub>12</sub> H <sub>26</sub> O <sub>4</sub>                | 13.54 | 1.65 | 234.1832 | C <sub>12</sub> H <sub>13</sub> NO <sub>4</sub>               | 13.71 | 1.67 | 235.0845 | C <sub>12</sub> N <sub>2</sub> O <sub>4</sub>                 | 13.89 | 1.69 | 235.9858 |
| C <sub>12</sub> H <sub>12</sub> NO <sub>4</sub>               | 13.70 | 1.67 | 234.0766 | C <sub>12</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub> | 14.09 | 1.52 | 235.1083 | C <sub>12</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> | 14.48 | 1.38 | 236.1400 |
| C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> | 14.07 | 1.52 | 234.1005 | C <sub>12</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> | 14.46 | 1.37 | 235.1322 | C <sub>12</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>  | 14.26 | 1.55 | 236.0096 |
| C <sub>12</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub> | 14.45 | 1.37 | 234.1244 | C <sub>12</sub> HN <sub>3</sub> O <sub>3</sub>                | 14.24 | 1.54 | 235.0018 | C <sub>12</sub> H <sub>20</sub> N <sub>4</sub> O              | 14.85 | 1.23 | 236.1639 |
| C <sub>12</sub> N <sub>3</sub> O <sub>3</sub>                 | 14.23 | 1.54 | 233.9940 | C <sub>12</sub> H <sub>19</sub> N <sub>4</sub> O              | 14.84 | 1.23 | 235.1560 | C <sub>12</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>  | 14.64 | 1.40 | 236.0335 |
| C <sub>12</sub> H <sub>18</sub> N <sub>4</sub> O              | 14.82 | 1.23 | 234.1482 | C <sub>12</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>  | 14.62 | 1.40 | 235.0257 | C <sub>13</sub> H <sub>16</sub> O <sub>4</sub>                | 14.46 | 1.77 | 236.1049 |
| C <sub>12</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>  | 14.60 | 1.39 | 234.0178 | C <sub>13</sub> H <sub>15</sub> O <sub>4</sub>                | 14.44 | 1.77 | 235.0970 | C <sub>13</sub> H <sub>18</sub> NO <sub>3</sub>               | 14.83 | 1.63 | 236.1287 |
| C <sub>13</sub> H <sub>14</sub> O <sub>4</sub>                | 14.43 | 1.77 | 234.0892 | C <sub>13</sub> H <sub>17</sub> NO <sub>3</sub>               | 14.82 | 1.62 | 235.1209 | C <sub>13</sub> H <sub>2</sub> NO <sub>4</sub>                | 14.62 | 1.79 | 235.9983 |
| C <sub>13</sub> H <sub>16</sub> NO <sub>3</sub>               | 14.80 | 1.62 | 234.1131 | C <sub>13</sub> HN <sub>3</sub> O <sub>4</sub>                | 14.60 | 1.79 | 234.9905 | C <sub>13</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> | 15.21 | 1.48 | 236.1526 |
| C <sub>13</sub> NO <sub>4</sub>                               | 14.59 | 1.79 | 233.9827 | C <sub>13</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub> | 15.19 | 1.48 | 235.1447 | C <sub>13</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 14.99 | 1.65 | 236.0222 |
| C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> | 15.18 | 1.48 | 234.1369 | C <sub>13</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 14.98 | 1.65 | 235.0144 | C <sub>13</sub> H <sub>22</sub> N <sub>3</sub> O              | 15.58 | 1.34 | 236.1764 |
| C <sub>13</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>  | 14.96 | 1.64 | 234.0065 | C <sub>13</sub> H <sub>21</sub> N <sub>3</sub> O              | 15.57 | 1.33 | 235.1686 | C <sub>13</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>  | 15.37 | 1.50 | 236.0460 |
| C <sub>13</sub> H <sub>20</sub> N <sub>3</sub> O              | 15.55 | 1.33 | 234.1608 | C <sub>13</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>  | 15.35 | 1.50 | 235.0382 | C <sub>13</sub> H <sub>24</sub> N <sub>4</sub>                | 15.96 | 1.19 | 236.2003 |
| C <sub>13</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>  | 15.33 | 1.50 | 234.0304 | C <sub>13</sub> H <sub>23</sub> N <sub>4</sub>                | 15.94 | 1.19 | 235.1925 | C <sub>13</sub> H <sub>8</sub> N <sub>4</sub> O               | 15.74 | 1.36 | 236.0699 |
| C <sub>13</sub> H <sub>22</sub> N <sub>4</sub>                | 15.93 | 1.19 | 234.1846 | C <sub>13</sub> H <sub>7</sub> N <sub>4</sub> O               | 15.72 | 1.36 | 235.0621 | C <sub>14</sub> H <sub>20</sub> O <sub>3</sub>                | 15.57 | 1.73 | 236.1413 |
| C <sub>13</sub> H <sub>6</sub> N <sub>4</sub> O               | 15.71 | 1.36 | 234.0542 | C <sub>14</sub> H <sub>19</sub> O <sub>3</sub>                | 15.55 | 1.73 | 235.1334 | C <sub>14</sub> H <sub>4</sub> O <sub>4</sub>                 | 15.35 | 1.90 | 236.0109 |
| C <sub>14</sub> H <sub>18</sub> O <sub>3</sub>                | 15.53 | 1.73 | 234.1256 | C <sub>14</sub> H <sub>3</sub> O <sub>4</sub>                 | 15.33 | 1.90 | 235.0031 | C <sub>14</sub> H <sub>22</sub> NO <sub>2</sub>               | 15.94 | 1.59 | 236.1651 |
| C <sub>14</sub> H <sub>2</sub> O <sub>4</sub>                 | 15.32 | 1.89 | 233.9953 | C <sub>14</sub> H <sub>21</sub> NO <sub>2</sub>               | 15.92 | 1.59 | 235.1573 | C <sub>14</sub> H <sub>6</sub> NO <sub>3</sub>                | 15.72 | 1.76 | 236.0348 |
| C <sub>14</sub> H <sub>20</sub> NO <sub>2</sub>               | 15.91 | 1.58 | 234.1495 | C <sub>14</sub> H <sub>5</sub> NO <sub>3</sub>                | 15.71 | 1.75 | 235.0269 | C <sub>14</sub> H <sub>24</sub> N <sub>2</sub> O              | 16.31 | 1.45 | 236.1890 |

|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 16.10 | 1.61 | 236.0586 | C <sub>14</sub> H <sub>25</sub> N <sub>2</sub> O              | 16.33 | 1.45 | 237.1968 | C <sub>14</sub> H <sub>26</sub> N <sub>2</sub> O              | 16.35 | 1.45 | 238.2046 |
| C <sub>14</sub> H <sub>26</sub> N <sub>3</sub>                | 16.69 | 1.31 | 236.2129 | C <sub>14</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 16.11 | 1.62 | 237.0664 | C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 16.13 | 1.62 | 238.0743 |
| C <sub>14</sub> H <sub>10</sub> N <sub>3</sub> O              | 16.47 | 1.47 | 236.0825 | C <sub>14</sub> H <sub>27</sub> N <sub>3</sub>                | 16.70 | 1.31 | 237.2207 | C <sub>14</sub> H <sub>28</sub> N <sub>3</sub>                | 16.72 | 1.31 | 238.2285 |
| C <sub>14</sub> H <sub>12</sub> N <sub>4</sub>                | 16.85 | 1.33 | 236.1063 | C <sub>14</sub> H <sub>11</sub> N <sub>3</sub> O              | 16.49 | 1.48 | 237.0903 | C <sub>14</sub> H <sub>12</sub> N <sub>3</sub> O              | 16.50 | 1.48 | 238.0981 |
| C <sub>15</sub> H <sub>24</sub> O <sub>2</sub>                | 16.67 | 1.70 | 236.1777 | C <sub>14</sub> H <sub>13</sub> N <sub>4</sub>                | 16.86 | 1.34 | 237.1142 | C <sub>14</sub> H <sub>14</sub> N <sub>4</sub>                | 16.88 | 1.34 | 238.1220 |
| C <sub>15</sub> H <sub>8</sub> O <sub>3</sub>                 | 16.45 | 1.87 | 236.0473 | C <sub>15</sub> H <sub>25</sub> O <sub>2</sub>                | 16.69 | 1.71 | 237.1855 | C <sub>15</sub> H <sub>26</sub> O <sub>2</sub>                | 16.70 | 1.71 | 238.1934 |
| C <sub>15</sub> H <sub>26</sub> NO                            | 17.05 | 1.56 | 236.2015 | C <sub>15</sub> H <sub>9</sub> O <sub>3</sub>                 | 16.47 | 1.87 | 237.0552 | C <sub>15</sub> H <sub>10</sub> O <sub>3</sub>                | 16.49 | 1.87 | 238.0630 |
| C <sub>15</sub> H <sub>10</sub> NO <sub>2</sub>               | 16.83 | 1.73 | 236.0712 | C <sub>15</sub> H <sub>27</sub> NO                            | 17.06 | 1.57 | 237.2094 | C <sub>15</sub> H <sub>28</sub> NO                            | 17.08 | 1.57 | 238.2172 |
| C <sub>15</sub> H <sub>28</sub> N <sub>2</sub>                | 17.42 | 1.43 | 236.2254 | C <sub>15</sub> H <sub>11</sub> NO <sub>2</sub>               | 16.84 | 1.73 | 237.0790 | C <sub>15</sub> H <sub>12</sub> NO <sub>2</sub>               | 16.86 | 1.73 | 238.0868 |
| C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O              | 17.20 | 1.59 | 236.0950 | C <sub>15</sub> H <sub>29</sub> N <sub>2</sub>                | 17.44 | 1.43 | 237.2332 | C <sub>15</sub> H <sub>30</sub> N <sub>2</sub>                | 17.45 | 1.43 | 238.2411 |
| C <sub>15</sub> H <sub>14</sub> N <sub>3</sub>                | 17.58 | 1.46 | 236.1189 | C <sub>15</sub> H <sub>13</sub> N <sub>2</sub> O              | 17.22 | 1.59 | 237.1029 | C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O              | 17.24 | 1.60 | 238.1107 |
| C <sub>15</sub> N <sub>4</sub>                                | 17.73 | 1.48 | 236.0124 | C <sub>15</sub> H <sub>15</sub> N <sub>3</sub>                | 17.59 | 1.46 | 237.1267 | C <sub>15</sub> H <sub>16</sub> N <sub>3</sub>                | 17.61 | 1.46 | 238.1346 |
| C <sub>16</sub> H <sub>28</sub> O                             | 17.78 | 1.69 | 236.2141 | C <sub>15</sub> HN <sub>4</sub>                               | 17.75 | 1.48 | 237.0202 | C <sub>15</sub> N <sub>3</sub> O                              | 17.39 | 1.62 | 238.0042 |
| C <sub>16</sub> H <sub>12</sub> O <sub>2</sub>                | 17.56 | 1.85 | 236.0837 | C <sub>16</sub> H <sub>29</sub> O                             | 17.79 | 1.69 | 237.2219 | C <sub>15</sub> H <sub>2</sub> N <sub>4</sub>                 | 17.77 | 1.49 | 238.0280 |
| C <sub>16</sub> H <sub>30</sub> N                             | 18.15 | 1.55 | 236.2380 | C <sub>16</sub> H <sub>13</sub> O <sub>2</sub>                | 17.58 | 1.85 | 237.0916 | C <sub>16</sub> H <sub>30</sub> O                             | 17.81 | 1.69 | 238.2298 |
| C <sub>16</sub> H <sub>14</sub> NO                            | 17.93 | 1.71 | 236.1076 | C <sub>16</sub> H <sub>31</sub> N                             | 18.17 | 1.56 | 237.2458 | C <sub>16</sub> H <sub>14</sub> O <sub>2</sub>                | 17.59 | 1.85 | 238.0994 |
| C <sub>16</sub> H <sub>16</sub> N <sub>2</sub>                | 18.31 | 1.58 | 236.1315 | C <sub>16</sub> H <sub>15</sub> NO                            | 17.95 | 1.72 | 237.1154 | C <sub>16</sub> H <sub>32</sub> N                             | 18.18 | 1.56 | 238.2536 |
| C <sub>16</sub> N <sub>2</sub> O                              | 18.09 | 1.74 | 236.0011 | C <sub>16</sub> H <sub>17</sub> N <sub>2</sub>                | 18.32 | 1.58 | 237.1393 | C <sub>16</sub> H <sub>16</sub> NO                            | 17.97 | 1.72 | 238.1233 |
| C <sub>16</sub> H <sub>2</sub> N <sub>3</sub>                 | 18.47 | 1.61 | 236.0249 | C <sub>16</sub> HN <sub>2</sub> O                             | 18.11 | 1.75 | 237.0089 | C <sub>16</sub> NO <sub>2</sub>                               | 17.75 | 1.88 | 237.9929 |
| C <sub>17</sub> H <sub>32</sub>                               | 18.88 | 1.68 | 236.2505 | C <sub>16</sub> H <sub>3</sub> N <sub>3</sub>                 | 18.48 | 1.61 | 237.0328 | C <sub>16</sub> H <sub>18</sub> N <sub>2</sub>                | 18.34 | 1.59 | 238.1471 |
| C <sub>17</sub> H <sub>16</sub> O                             | 18.67 | 1.84 | 236.1202 | C <sub>17</sub> H <sub>33</sub>                               | 18.90 | 1.69 | 237.2584 | C <sub>16</sub> H <sub>2</sub> N <sub>2</sub> O               | 18.12 | 1.75 | 238.0167 |
| C <sub>17</sub> O <sub>2</sub>                                | 18.45 | 2.00 | 235.9898 | C <sub>17</sub> H <sub>17</sub> O                             | 18.68 | 1.85 | 237.1280 | C <sub>16</sub> H <sub>4</sub> N <sub>3</sub>                 | 18.50 | 1.62 | 238.0406 |
| C <sub>17</sub> H <sub>18</sub> N                             | 19.04 | 1.71 | 236.1440 | C <sub>17</sub> HO <sub>2</sub>                               | 18.46 | 2.01 | 236.9976 | C <sub>17</sub> H <sub>34</sub>                               | 18.91 | 1.69 | 238.2662 |
| C <sub>17</sub> H <sub>2</sub> NO                             | 18.82 | 1.87 | 236.0136 | C <sub>17</sub> H <sub>19</sub> N                             | 19.06 | 1.72 | 237.1519 | C <sub>17</sub> H <sub>18</sub> O                             | 18.70 | 1.85 | 238.1358 |
| C <sub>17</sub> H <sub>4</sub> N <sub>2</sub>                 | 19.20 | 1.74 | 236.0375 | C <sub>17</sub> H <sub>3</sub> NO                             | 18.84 | 1.87 | 237.0215 | C <sub>17</sub> H <sub>2</sub> O <sub>2</sub>                 | 18.48 | 2.01 | 238.0054 |
| C <sub>18</sub> H <sub>20</sub>                               | 19.77 | 1.85 | 236.1566 | C <sub>17</sub> H <sub>5</sub> N <sub>2</sub>                 | 19.21 | 1.75 | 237.0453 | C <sub>17</sub> H <sub>20</sub> N                             | 19.07 | 1.72 | 238.1597 |
| C <sub>18</sub> H <sub>4</sub> O                              | 19.55 | 2.01 | 236.0262 | C <sub>18</sub> H <sub>21</sub>                               | 19.79 | 1.85 | 237.1644 | C <sub>17</sub> H <sub>4</sub> NO                             | 18.85 | 1.88 | 238.0293 |
| C <sub>18</sub> H <sub>6</sub> N                              | 19.93 | 1.88 | 236.0501 | C <sub>18</sub> H <sub>5</sub> O                              | 19.57 | 2.01 | 237.0340 | C <sub>17</sub> H <sub>6</sub> N <sub>2</sub>                 | 19.23 | 1.75 | 238.0532 |
| C <sub>19</sub> H <sub>8</sub>                                | 20.66 | 2.02 | 236.0626 | C <sub>18</sub> H <sub>7</sub> N                              | 19.94 | 1.88 | 237.0579 | C <sub>18</sub> H <sub>22</sub>                               | 19.80 | 1.86 | 238.1722 |
|   |       |      |          | C <sub>19</sub> H <sub>9</sub>                                | 20.68 | 2.03 | 237.0705 | C <sub>18</sub> H <sub>6</sub> O                              | 19.59 | 2.01 | 238.0419 |
| 237   |       |      |          | 238   |       |      |          | C <sub>18</sub> H <sub>8</sub> N                              | 19.96 | 1.89 | 238.0657 |
| C <sub>11</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> | 13.01 | 1.58 | 237.0876 | C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> | 13.03 | 1.59 | 238.0954 | C <sub>19</sub> H <sub>10</sub>                               | 20.69 | 2.03 | 238.0783 |
| C <sub>11</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> | 13.39 | 1.43 | 237.1114 | C <sub>11</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> | 13.40 | 1.43 | 238.1193 |   |       |      |          |
| C <sub>11</sub> H <sub>17</sub> N <sub>4</sub> O <sub>2</sub> | 13.76 | 1.28 | 237.1353 | C <sub>11</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> | 13.78 | 1.28 | 238.1431 | 239   |       |      |          |
| C <sub>12</sub> H <sub>15</sub> NO <sub>4</sub>               | 13.75 | 1.68 | 237.1001 | C <sub>12</sub> H <sub>16</sub> NO <sub>4</sub>               | 13.76 | 1.68 | 238.1080 | C <sub>11</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub> | 13.05 | 1.59 | 239.1032 |
| C <sub>12</sub> H <sub>17</sub> N <sub>2</sub> O <sub>3</sub> | 14.12 | 1.53 | 237.1240 | C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> | 14.14 | 1.53 | 238.1318 | C <sub>11</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> | 13.42 | 1.44 | 239.1271 |
| C <sub>12</sub> HN <sub>2</sub> O <sub>4</sub>                | 13.90 | 1.70 | 236.9936 | C <sub>12</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 13.92 | 1.70 | 238.0014 | C <sub>11</sub> H <sub>19</sub> N <sub>4</sub> O <sub>2</sub> | 13.79 | 1.29 | 239.1509 |
| C <sub>12</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> | 14.49 | 1.38 | 237.1478 | C <sub>12</sub> H <sub>20</sub> N <sub>3</sub> O <sub>2</sub> | 14.51 | 1.38 | 238.1557 | C <sub>12</sub> H <sub>17</sub> NO <sub>4</sub>               | 13.78 | 1.68 | 239.1158 |
| C <sub>12</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>  | 14.28 | 1.55 | 237.0175 | C <sub>12</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>  | 14.29 | 1.55 | 238.0253 | C <sub>12</sub> H <sub>19</sub> N <sub>2</sub> O <sub>3</sub> | 14.15 | 1.53 | 239.1396 |
| C <sub>12</sub> H <sub>21</sub> N <sub>4</sub> O              | 14.87 | 1.23 | 237.1717 | C <sub>12</sub> H <sub>22</sub> N <sub>4</sub> O              | 14.88 | 1.24 | 238.1795 | C <sub>12</sub> H <sub>3</sub> N <sub>2</sub> O <sub>4</sub>  | 13.93 | 1.70 | 239.0093 |
| C <sub>12</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>  | 14.65 | 1.40 | 237.0413 | C <sub>12</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 14.67 | 1.40 | 238.0491 | C <sub>12</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> | 14.53 | 1.38 | 239.1635 |
| C <sub>13</sub> H <sub>17</sub> O <sub>4</sub>                | 14.48 | 1.77 | 237.1127 | C <sub>13</sub> H <sub>18</sub> O <sub>4</sub>                | 14.49 | 1.78 | 238.1205 | C <sub>12</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub>  | 14.31 | 1.55 | 239.0331 |
| C <sub>13</sub> H <sub>19</sub> NO <sub>3</sub>               | 14.85 | 1.63 | 237.1365 | C <sub>13</sub> H <sub>20</sub> NO <sub>3</sub>               | 14.87 | 1.63 | 238.1444 | C <sub>12</sub> H <sub>23</sub> N <sub>4</sub> O              | 14.90 | 1.24 | 239.1873 |
| C <sub>13</sub> H <sub>3</sub> NO <sub>4</sub>                | 14.63 | 1.80 | 237.0062 | C <sub>13</sub> H <sub>4</sub> NO <sub>4</sub>                | 14.65 | 1.80 | 238.0140 | C <sub>12</sub> H <sub>7</sub> N <sub>4</sub> O <sub>2</sub>  | 14.68 | 1.41 | 239.0570 |
| C <sub>13</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub> | 15.22 | 1.48 | 237.1604 | C <sub>13</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> | 15.24 | 1.48 | 238.1682 | C <sub>13</sub> H <sub>19</sub> O <sub>4</sub>                | 14.51 | 1.78 | 239.1284 |
| C <sub>13</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>  | 15.01 | 1.65 | 237.0300 | C <sub>13</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 15.02 | 1.65 | 238.0379 | C <sub>13</sub> H <sub>21</sub> NO <sub>3</sub>               | 14.88 | 1.63 | 239.1522 |
| C <sub>13</sub> H <sub>23</sub> N <sub>3</sub> O              | 15.60 | 1.34 | 237.1842 | C <sub>13</sub> H <sub>24</sub> N <sub>3</sub> O              | 15.62 | 1.34 | 238.1921 | C <sub>13</sub> H <sub>5</sub> NO <sub>4</sub>                | 14.67 | 1.80 | 239.0218 |
| C <sub>13</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>  | 15.38 | 1.51 | 237.0539 | C <sub>13</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 15.40 | 1.51 | 238.0617 | C <sub>13</sub> H <sub>23</sub> N <sub>2</sub> O <sub>2</sub> | 15.26 | 1.49 | 239.1761 |
| C <sub>13</sub> H <sub>25</sub> N <sub>4</sub>                | 15.97 | 1.20 | 237.2081 | C <sub>13</sub> H <sub>26</sub> N <sub>4</sub>                | 15.99 | 1.20 | 238.2160 | C <sub>13</sub> H <sub>7</sub> N <sub>2</sub> O <sub>3</sub>  | 15.04 | 1.66 | 239.0457 |
| C <sub>13</sub> H <sub>9</sub> N <sub>4</sub> O               | 15.76 | 1.36 | 237.0777 | C <sub>13</sub> H <sub>10</sub> N <sub>4</sub> O              | 15.77 | 1.37 | 238.0856 | C <sub>13</sub> H <sub>25</sub> N <sub>3</sub> O              | 15.63 | 1.34 | 239.1999 |
| C <sub>14</sub> H <sub>21</sub> O <sub>3</sub>                | 15.58 | 1.73 | 237.1491 | C <sub>14</sub> H <sub>22</sub> O <sub>3</sub>                | 15.60 | 1.74 | 238.1569 | C <sub>13</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>  | 15.41 | 1.51 | 239.0695 |
| C <sub>14</sub> H <sub>5</sub> O <sub>4</sub>                 | 15.36 | 1.90 | 237.0187 | C <sub>14</sub> H <sub>6</sub> O <sub>4</sub>                 | 15.38 | 1.90 | 238.0266 | C <sub>13</sub> H <sub>27</sub> N <sub>4</sub>                | 16.01 | 1.20 | 239.2238 |
| C <sub>14</sub> H <sub>23</sub> NO <sub>2</sub>               | 15.96 | 1.59 | 237.1730 | C <sub>14</sub> H <sub>24</sub> NO <sub>2</sub>               | 15.97 | 1.59 | 238.1808 | C <sub>13</sub> H <sub>11</sub> N <sub>4</sub> O              | 15.79 | 1.37 | 239.0934 |
| C <sub>14</sub> H <sub>7</sub> NO <sub>3</sub>                | 15.74 | 1.76 | 237.0426 | C <sub>14</sub> H <sub>8</sub> NO <sub>3</sub>                | 15.76 | 1.76 | 238.0504 | C <sub>14</sub> H <sub>23</sub> O <sub>3</sub>                | 15.61 | 1.74 | 239.1648 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>14</sub> H <sub>7</sub> O <sub>4</sub>                 | 15.40 | 1.91 | 239.0344 | C <sub>13</sub> H <sub>28</sub> N <sub>4</sub>                | 16.02 | 1.20 | 240.2316 | C <sub>13</sub> H <sub>21</sub> O <sub>4</sub>                | 14.54 | 1.78 | 241.1440 |
| C <sub>14</sub> H <sub>25</sub> NO <sub>2</sub>               | 15.99 | 1.60 | 239.1886 | C <sub>13</sub> H <sub>12</sub> N <sub>4</sub> O              | 15.80 | 1.37 | 240.1012 | C <sub>13</sub> H <sub>23</sub> NO <sub>3</sub>               | 14.91 | 1.64 | 241.1679 |
| C <sub>14</sub> H <sub>9</sub> NO <sub>3</sub>                | 15.77 | 1.76 | 239.0583 | C <sub>14</sub> H <sub>24</sub> O <sub>3</sub>                | 15.63 | 1.74 | 240.1726 | C <sub>13</sub> H <sub>7</sub> NO <sub>4</sub>                | 14.70 | 1.81 | 241.0375 |
| C <sub>14</sub> H <sub>27</sub> N <sub>2</sub> O              | 16.36 | 1.46 | 239.2125 | C <sub>14</sub> H <sub>8</sub> O <sub>4</sub>                 | 15.41 | 1.91 | 240.0422 | C <sub>13</sub> H <sub>25</sub> N <sub>2</sub> O <sub>2</sub> | 15.29 | 1.49 | 241.1917 |
| C <sub>14</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> | 16.15 | 1.62 | 239.0821 | C <sub>14</sub> H <sub>26</sub> NO <sub>2</sub>               | 16.00 | 1.60 | 240.1965 | C <sub>13</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub>  | 15.07 | 1.66 | 241.0614 |
| C <sub>14</sub> H <sub>29</sub> N <sub>3</sub>                | 16.74 | 1.32 | 239.2363 | C <sub>14</sub> H <sub>10</sub> NO <sub>3</sub>               | 15.79 | 1.77 | 240.0661 | C <sub>13</sub> H <sub>27</sub> N <sub>3</sub> O              | 15.66 | 1.35 | 241.2156 |
| C <sub>14</sub> H <sub>13</sub> N <sub>3</sub> O              | 16.52 | 1.48 | 239.1060 | C <sub>14</sub> H <sub>28</sub> N <sub>2</sub> O              | 16.38 | 1.46 | 240.2203 | C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> | 15.45 | 1.52 | 241.0852 |
| C <sub>14</sub> H <sub>15</sub> N <sub>4</sub>                | 16.89 | 1.34 | 239.1298 | C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | 16.16 | 1.62 | 240.0899 | C <sub>13</sub> H <sub>29</sub> N <sub>4</sub>                | 16.04 | 1.21 | 241.2394 |
| C <sub>15</sub> H <sub>27</sub> O <sub>2</sub>                | 16.72 | 1.71 | 239.2012 | C <sub>14</sub> H <sub>30</sub> N <sub>3</sub>                | 16.75 | 1.32 | 240.2442 | C <sub>13</sub> H <sub>13</sub> N <sub>4</sub> O              | 15.82 | 1.37 | 241.1091 |
| C <sub>15</sub> H <sub>11</sub> O <sub>3</sub>                | 16.50 | 1.88 | 239.0708 | C <sub>14</sub> H <sub>14</sub> N <sub>3</sub> O              | 16.54 | 1.48 | 240.1138 | C <sub>14</sub> H <sub>25</sub> O <sub>3</sub>                | 15.65 | 1.74 | 241.1804 |
| C <sub>15</sub> H <sub>29</sub> NO                            | 17.09 | 1.57 | 239.2250 | C <sub>14</sub> H <sub>16</sub> N <sub>4</sub>                | 16.91 | 1.35 | 240.1377 | C <sub>14</sub> H <sub>9</sub> O <sub>4</sub>                 | 15.43 | 1.91 | 241.0501 |
| C <sub>15</sub> H <sub>13</sub> NO <sub>2</sub>               | 16.88 | 1.74 | 239.0947 | C <sub>14</sub> N <sub>4</sub> O                              | 16.69 | 1.51 | 240.0073 | C <sub>14</sub> H <sub>27</sub> NO <sub>2</sub>               | 16.02 | 1.60 | 241.2043 |
| C <sub>15</sub> H <sub>31</sub> N <sub>2</sub>                | 17.47 | 1.44 | 239.2489 | C <sub>15</sub> H <sub>28</sub> O <sub>2</sub>                | 16.74 | 1.71 | 240.2090 | C <sub>14</sub> H <sub>11</sub> NO <sub>3</sub>               | 15.80 | 1.77 | 241.0739 |
| C <sub>15</sub> H <sub>15</sub> N <sub>2</sub> O              | 17.25 | 1.60 | 239.1185 | C <sub>15</sub> H <sub>12</sub> O <sub>3</sub>                | 16.52 | 1.88 | 240.0786 | C <sub>14</sub> H <sub>29</sub> N <sub>2</sub> O              | 16.39 | 1.46 | 241.2281 |
| C <sub>15</sub> H <sub>17</sub> N <sub>3</sub>                | 17.63 | 1.46 | 239.1424 | C <sub>15</sub> H <sub>30</sub> NO                            | 17.11 | 1.58 | 240.2329 | C <sub>14</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> | 16.18 | 1.63 | 241.0978 |
| C <sub>15</sub> HN <sub>3</sub> O                             | 17.41 | 1.63 | 239.0120 | C <sub>15</sub> H <sub>14</sub> NO <sub>2</sub>               | 16.89 | 1.74 | 240.1025 | C <sub>14</sub> H <sub>31</sub> N <sub>3</sub>                | 16.77 | 1.32 | 241.2520 |
| C <sub>15</sub> H <sub>3</sub> N <sub>4</sub>                 | 17.78 | 1.49 | 239.0359 | C <sub>15</sub> H <sub>32</sub> N <sub>2</sub>                | 17.48 | 1.44 | 240.2567 | C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O              | 16.55 | 1.49 | 241.1216 |
| C <sub>16</sub> H <sub>31</sub> O                             | 17.82 | 1.70 | 239.2376 | C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O              | 17.27 | 1.60 | 240.1264 | C <sub>14</sub> H <sub>17</sub> N <sub>4</sub>                | 16.93 | 1.35 | 241.1455 |
| C <sub>16</sub> H <sub>15</sub> O <sub>2</sub>                | 17.61 | 1.86 | 239.1072 | C <sub>15</sub> N <sub>2</sub> O <sub>2</sub>                 | 17.05 | 1.77 | 239.9960 | C <sub>14</sub> HN <sub>4</sub> O                             | 16.71 | 1.51 | 241.0151 |
| C <sub>16</sub> H <sub>33</sub> N                             | 18.20 | 1.56 | 239.2615 | C <sub>15</sub> H <sub>18</sub> N <sub>3</sub>                | 17.64 | 1.47 | 240.1502 | C <sub>15</sub> H <sub>29</sub> O <sub>2</sub>                | 16.75 | 1.72 | 241.2168 |
| C <sub>16</sub> H <sub>17</sub> NO                            | 17.98 | 1.72 | 239.1311 | C <sub>15</sub> H <sub>2</sub> N <sub>3</sub> O               | 17.42 | 1.63 | 240.0198 | C <sub>15</sub> H <sub>13</sub> O <sub>3</sub>                | 16.53 | 1.88 | 241.0865 |
| C <sub>16</sub> HN <sub>2</sub> O                             | 17.77 | 1.88 | 239.0007 | C <sub>15</sub> H <sub>4</sub> N <sub>4</sub>                 | 17.80 | 1.49 | 240.0437 | C <sub>15</sub> H <sub>31</sub> NO                            | 17.13 | 1.58 | 241.2407 |
| C <sub>16</sub> H <sub>19</sub> N <sub>2</sub>                | 18.36 | 1.59 | 239.1549 | C <sub>16</sub> H <sub>32</sub> O                             | 17.84 | 1.70 | 240.2454 | C <sub>15</sub> H <sub>15</sub> NO <sub>2</sub>               | 16.91 | 1.74 | 241.1103 |
| C <sub>16</sub> H <sub>3</sub> N <sub>2</sub> O               | 18.14 | 1.75 | 239.0246 | C <sub>16</sub> H <sub>16</sub> O <sub>2</sub>                | 17.62 | 1.86 | 240.1151 | C <sub>15</sub> H <sub>33</sub> N <sub>2</sub>                | 17.50 | 1.44 | 241.2646 |
| C <sub>16</sub> H <sub>5</sub> N <sub>3</sub>                 | 18.51 | 1.62 | 239.0484 | C <sub>16</sub> O <sub>3</sub>                                | 17.41 | 2.02 | 239.9847 | C <sub>15</sub> H <sub>17</sub> N <sub>2</sub> O              | 17.28 | 1.60 | 241.1342 |
| C <sub>17</sub> H <sub>35</sub>                               | 18.93 | 1.69 | 239.2740 | C <sub>16</sub> H <sub>34</sub> N                             | 18.22 | 1.56 | 240.2693 | C <sub>15</sub> HN <sub>2</sub> O <sub>2</sub>                | 17.07 | 1.77 | 241.0038 |
| C <sub>17</sub> H <sub>19</sub> O                             | 18.71 | 1.85 | 239.1436 | C <sub>16</sub> H <sub>18</sub> NO                            | 18.00 | 1.73 | 240.1389 | C <sub>15</sub> H <sub>19</sub> N <sub>3</sub>                | 17.66 | 1.47 | 241.1580 |
| C <sub>17</sub> H <sub>3</sub> O <sub>2</sub>                 | 18.50 | 2.01 | 239.0133 | C <sub>16</sub> H <sub>2</sub> NO <sub>2</sub>                | 17.78 | 1.89 | 240.0085 | C <sub>15</sub> H <sub>3</sub> N <sub>3</sub> O               | 17.44 | 1.63 | 241.0277 |
| C <sub>17</sub> H <sub>21</sub> N                             | 19.09 | 1.72 | 239.1675 | C <sub>16</sub> H <sub>20</sub> N <sub>2</sub>                | 18.37 | 1.59 | 240.1628 | C <sub>15</sub> H <sub>5</sub> N <sub>4</sub>                 | 17.81 | 1.50 | 241.0515 |
| C <sub>17</sub> H <sub>5</sub> NO                             | 18.87 | 1.88 | 239.0371 | C <sub>16</sub> H <sub>4</sub> N <sub>2</sub> O               | 18.16 | 1.75 | 240.0324 | C <sub>16</sub> H <sub>33</sub> O                             | 17.86 | 1.70 | 241.2533 |
| C <sub>17</sub> H <sub>7</sub> N <sub>2</sub>                 | 19.25 | 1.75 | 239.0610 | C <sub>16</sub> H <sub>6</sub> N <sub>3</sub>                 | 18.53 | 1.62 | 240.0563 | C <sub>16</sub> H <sub>17</sub> O <sub>2</sub>                | 17.64 | 1.86 | 241.1229 |
| C <sub>18</sub> H <sub>23</sub>                               | 19.82 | 1.86 | 239.1801 | C <sub>17</sub> H <sub>36</sub>                               | 18.95 | 1.70 | 240.2819 | C <sub>16</sub> HO <sub>3</sub>                               | 17.42 | 2.03 | 240.9925 |
| C <sub>18</sub> H <sub>7</sub> O                              | 19.60 | 2.02 | 239.0497 | C <sub>17</sub> H <sub>20</sub> O                             | 18.73 | 1.86 | 240.1515 | C <sub>16</sub> H <sub>35</sub> N                             | 18.23 | 1.57 | 241.2771 |
| C <sub>18</sub> H <sub>9</sub> N                              | 19.98 | 1.89 | 239.0736 | C <sub>17</sub> H <sub>4</sub> O <sub>2</sub>                 | 18.51 | 2.02 | 240.0211 | C <sub>16</sub> H <sub>19</sub> NO                            | 18.01 | 1.73 | 241.1467 |
| C <sub>19</sub> H <sub>11</sub>                               | 20.71 | 2.03 | 239.0861 | C <sub>17</sub> H <sub>22</sub> N                             | 19.10 | 1.72 | 240.1753 | C <sub>16</sub> H <sub>3</sub> NO <sub>2</sub>                | 17.80 | 1.89 | 241.0164 |
|   |       |      |          | C <sub>17</sub> H <sub>6</sub> NO                             | 18.89 | 1.88 | 240.0449 | C <sub>16</sub> H <sub>21</sub> N <sub>2</sub>                | 18.39 | 1.60 | 241.1706 |
| 240   |       |      |          | C <sub>17</sub> H <sub>8</sub> N <sub>2</sub>                 | 19.26 | 1.75 | 240.0688 | C <sub>16</sub> H <sub>5</sub> N <sub>2</sub> O               | 18.17 | 1.76 | 241.0402 |
| C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> | 13.06 | 1.59 | 240.1111 | C <sub>18</sub> H <sub>24</sub>                               | 19.83 | 1.86 | 240.1879 | C <sub>16</sub> H <sub>7</sub> N <sub>3</sub>                 | 18.55 | 1.62 | 241.0641 |
| C <sub>11</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> | 13.44 | 1.44 | 240.1349 | C <sub>18</sub> H <sub>8</sub> O                              | 19.62 | 2.02 | 240.0575 | C <sub>17</sub> H <sub>21</sub> O                             | 18.75 | 1.86 | 241.1593 |
| C <sub>11</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub> | 13.81 | 1.29 | 240.1588 | C <sub>18</sub> H <sub>10</sub> N                             | 19.99 | 1.89 | 240.0814 | C <sub>17</sub> H <sub>5</sub> O <sub>2</sub>                 | 18.53 | 2.02 | 241.0289 |
| C <sub>12</sub> H <sub>18</sub> NO <sub>4</sub>               | 13.79 | 1.68 | 240.1236 | C <sub>19</sub> H <sub>12</sub>                               | 20.72 | 2.04 | 240.0939 | C <sub>17</sub> H <sub>23</sub> N                             | 19.12 | 1.73 | 241.1832 |
| C <sub>12</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> | 14.17 | 1.53 | 240.1475 | C <sub>20</sub>   | 21.61 | 2.22 | 240.0000 | C <sub>17</sub> H <sub>7</sub> NO                             | 18.90 | 1.89 | 241.0528 |
| C <sub>12</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>  | 13.95 | 1.70 | 240.0171 |   |       |      |          | C <sub>17</sub> H <sub>9</sub> N <sub>2</sub>                 | 19.28 | 1.76 | 241.0767 |
| C <sub>12</sub> H <sub>22</sub> N <sub>3</sub> O <sub>2</sub> | 14.54 | 1.39 | 240.1713 | 241   |       |      |          | C <sub>18</sub> H <sub>25</sub>                               | 19.85 | 1.87 | 241.1957 |
| C <sub>12</sub> H <sub>6</sub> N <sub>3</sub> O <sub>3</sub>  | 14.32 | 1.56 | 240.0410 | C <sub>11</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub> | 13.08 | 1.59 | 241.1189 | C <sub>18</sub> H <sub>9</sub> O                              | 19.63 | 2.02 | 241.0653 |
| C <sub>12</sub> H <sub>24</sub> N <sub>4</sub> O              | 14.92 | 1.24 | 240.1952 | C <sub>11</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub> | 13.45 | 1.44 | 241.1427 | C <sub>18</sub> H <sub>11</sub> N                             | 20.01 | 1.90 | 241.0892 |
| C <sub>12</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>  | 14.70 | 1.41 | 240.0648 | C <sub>11</sub> H <sub>21</sub> N <sub>4</sub> O <sub>2</sub> | 13.83 | 1.29 | 241.1666 | C <sub>19</sub> H <sub>13</sub>                               | 20.74 | 2.04 | 241.1018 |
| C <sub>13</sub> H <sub>20</sub> O <sub>4</sub>                | 14.52 | 1.78 | 240.1362 | C <sub>12</sub> H <sub>19</sub> NO <sub>4</sub>               | 13.81 | 1.68 | 241.1315 | C <sub>20</sub> H   | 21.63 | 2.22 | 241.0078 |
| C <sub>13</sub> H <sub>22</sub> NO <sub>3</sub>               | 14.90 | 1.63 | 240.1600 | C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> | 14.18 | 1.54 | 241.1553 |   |       |      |          |
| C <sub>13</sub> H <sub>6</sub> NO <sub>4</sub>                | 14.68 | 1.80 | 240.0297 | C <sub>12</sub> H <sub>5</sub> N <sub>2</sub> O <sub>4</sub>  | 13.97 | 1.71 | 241.0249 |   |       |      |          |
| C <sub>13</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> | 15.27 | 1.49 | 240.1839 | C <sub>12</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub> | 14.56 | 1.39 | 241.1791 | 242   |       |      |          |
| C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 15.06 | 1.66 | 240.0535 | C <sub>12</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub>  | 14.34 | 1.56 | 241.0488 | C <sub>11</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> | 13.09 | 1.59 | 242.1267 |
| C <sub>13</sub> H <sub>26</sub> N <sub>3</sub> O              | 15.65 | 1.35 | 240.2077 | C <sub>12</sub> H <sub>25</sub> N <sub>4</sub> O              | 14.93 | 1.24 | 241.2030 | C <sub>11</sub> H <sub>20</sub> N <sub>3</sub> O <sub>3</sub> | 13.47 | 1.44 | 242.1506 |
| C <sub>13</sub> H <sub>10</sub> N <sub>3</sub> O <sub>2</sub> | 15.43 | 1.51 | 240.0774 | C <sub>12</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub>  | 14.72 | 1.41 | 241.0726 | C <sub>11</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub> | 13.84 | 1.29 | 242.1744 |
|   |       |      |          |   |       |      |          | C <sub>12</sub> H <sub>20</sub> NO <sub>4</sub>               | 13.83 | 1.69 | 242.1393 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>12</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> | 14.20 | 1.54 | 242.1631 | C <sub>19</sub> H <sub>14</sub>                               | 20.76 | 2.04 | 242.1096 | C <sub>17</sub> H <sub>25</sub> N                             | 19.15 | 1.73 | 243.1988 |
| C <sub>12</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>  | 13.98 | 1.71 | 242.0328 | C <sub>19</sub> N   | 20.91 | 2.08 | 242.0031 | C <sub>17</sub> H <sub>9</sub> NO                             | 18.93 | 1.89 | 243.0684 |
| C <sub>12</sub> H <sub>24</sub> N <sub>3</sub> O <sub>2</sub> | 14.57 | 1.39 | 242.1870 | C <sub>20</sub> H <sub>2</sub>                                | 21.64 | 2.23 | 242.0157 | C <sub>17</sub> H <sub>11</sub> N <sub>2</sub>                | 19.31 | 1.76 | 243.0923 |
| C <sub>12</sub> H <sub>8</sub> N <sub>3</sub> O <sub>3</sub>  | 14.36 | 1.56 | 242.0566 | 243   |       |      |          | C <sub>18</sub> H <sub>27</sub>                               | 19.88 | 1.87 | 243.2114 |
| C <sub>12</sub> H <sub>26</sub> N <sub>4</sub> O              | 14.95 | 1.24 | 242.2108 | C <sub>11</sub> H <sub>19</sub> N <sub>2</sub> O <sub>4</sub> | 13.11 | 1.60 | 243.1345 | C <sub>18</sub> H <sub>11</sub> O                             | 19.67 | 2.03 | 243.0810 |
| C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub> | 14.73 | 1.41 | 242.0805 | C <sub>11</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub> | 13.48 | 1.44 | 243.1584 | C <sub>18</sub> H <sub>13</sub> N                             | 20.04 | 1.90 | 243.1049 |
| C <sub>13</sub> H <sub>22</sub> O <sub>4</sub>                | 14.56 | 1.79 | 242.1518 | C <sub>11</sub> H <sub>23</sub> N <sub>4</sub> O <sub>2</sub> | 13.86 | 1.29 | 243.1822 | C <sub>19</sub> H <sub>15</sub>                               | 20.77 | 2.05 | 243.1174 |
| C <sub>13</sub> H <sub>24</sub> NO <sub>3</sub>               | 14.93 | 1.64 | 242.1757 | C <sub>12</sub> H <sub>21</sub> NO <sub>4</sub>               | 13.84 | 1.69 | 243.1471 | C <sub>19</sub> HN  | 20.93 | 2.08 | 243.0109 |
| C <sub>13</sub> H <sub>8</sub> NO <sub>4</sub>                | 14.71 | 1.81 | 242.0453 | C <sub>12</sub> H <sub>23</sub> N <sub>2</sub> O <sub>3</sub> | 14.22 | 1.54 | 243.1710 | C <sub>20</sub> H <sub>3</sub>                                | 21.66 | 2.23 | 243.0235 |
| C <sub>13</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> | 15.30 | 1.49 | 242.1996 | C <sub>12</sub> H <sub>7</sub> N <sub>2</sub> O <sub>4</sub>  | 14.00 | 1.71 | 243.0406 | 244   |       |      |          |
| C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 15.09 | 1.66 | 242.0692 | C <sub>12</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub> | 14.59 | 1.39 | 243.1948 | C <sub>11</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> | 13.13 | 1.60 | 244.1424 |
| C <sub>13</sub> H <sub>28</sub> N <sub>3</sub> O              | 15.68 | 1.35 | 242.2234 | C <sub>12</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>  | 14.37 | 1.56 | 243.0644 | C <sub>11</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub> | 13.50 | 1.45 | 244.1662 |
| C <sub>13</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> | 15.46 | 1.52 | 242.0930 | C <sub>12</sub> H <sub>27</sub> N <sub>4</sub> O              | 14.96 | 1.25 | 243.2187 | C <sub>11</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> | 13.87 | 1.30 | 244.1901 |
| C <sub>13</sub> H <sub>30</sub> N <sub>4</sub>                | 16.05 | 1.21 | 242.2473 | C <sub>12</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub> | 14.75 | 1.42 | 243.0883 | C <sub>12</sub> H <sub>22</sub> NO <sub>4</sub>               | 13.86 | 1.69 | 244.1549 |
| C <sub>13</sub> H <sub>14</sub> N <sub>4</sub> O              | 15.84 | 1.38 | 242.1169 | C <sub>13</sub> H <sub>23</sub> O <sub>4</sub>                | 14.57 | 1.79 | 243.1597 | C <sub>12</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub> | 14.23 | 1.54 | 244.1788 |
| C <sub>14</sub> H <sub>26</sub> O <sub>3</sub>                | 15.66 | 1.75 | 242.1883 | C <sub>13</sub> H <sub>25</sub> NO <sub>3</sub>               | 14.95 | 1.64 | 243.1835 | C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>  | 14.01 | 1.71 | 244.0484 |
| C <sub>14</sub> H <sub>10</sub> O <sub>4</sub>                | 15.44 | 1.91 | 242.0579 | C <sub>13</sub> H <sub>9</sub> NO <sub>4</sub>                | 14.73 | 1.81 | 243.0532 | C <sub>12</sub> H <sub>26</sub> N <sub>3</sub> O <sub>2</sub> | 14.61 | 1.40 | 244.2026 |
| C <sub>14</sub> H <sub>28</sub> NO <sub>2</sub>               | 16.04 | 1.60 | 242.2121 | C <sub>13</sub> H <sub>27</sub> N <sub>2</sub> O <sub>2</sub> | 15.32 | 1.50 | 243.2074 | C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> | 14.39 | 1.56 | 244.0723 |
| C <sub>14</sub> H <sub>12</sub> NO <sub>3</sub>               | 15.82 | 1.77 | 242.0817 | C <sub>13</sub> H <sub>11</sub> N <sub>2</sub> O <sub>3</sub> | 15.10 | 1.66 | 243.0770 | C <sub>12</sub> H <sub>28</sub> N <sub>4</sub> O              | 14.98 | 1.25 | 244.2265 |
| C <sub>14</sub> H <sub>30</sub> N <sub>2</sub> O              | 16.41 | 1.46 | 242.2360 | C <sub>13</sub> H <sub>29</sub> N <sub>3</sub> O              | 15.70 | 1.35 | 243.2312 | C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub> | 14.76 | 1.42 | 244.0961 |
| C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> | 16.19 | 1.63 | 242.1056 | C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> | 15.48 | 1.52 | 243.1009 | C <sub>13</sub> H <sub>24</sub> O <sub>4</sub>                | 14.59 | 1.79 | 244.1675 |
| C <sub>14</sub> H <sub>32</sub> N <sub>3</sub>                | 16.78 | 1.32 | 242.2598 | C <sub>13</sub> H <sub>31</sub> N <sub>4</sub>                | 16.07 | 1.21 | 243.2551 | C <sub>13</sub> H <sub>26</sub> NO <sub>3</sub>               | 14.96 | 1.64 | 244.1914 |
| C <sub>14</sub> H <sub>16</sub> N <sub>3</sub> O              | 16.57 | 1.49 | 242.1295 | C <sub>13</sub> H <sub>15</sub> N <sub>4</sub> O              | 15.85 | 1.38 | 243.1247 | C <sub>13</sub> H <sub>10</sub> NO <sub>4</sub>               | 14.75 | 1.81 | 244.0610 |
| C <sub>14</sub> N <sub>3</sub> O <sub>2</sub>                 | 16.35 | 1.65 | 241.9991 | C <sub>14</sub> H <sub>27</sub> O <sub>3</sub>                | 15.68 | 1.75 | 243.1961 | C <sub>13</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> | 15.34 | 1.50 | 244.2152 |
| C <sub>14</sub> H <sub>18</sub> N <sub>4</sub>                | 16.94 | 1.35 | 242.1533 | C <sub>14</sub> H <sub>11</sub> O <sub>4</sub>                | 15.46 | 1.92 | 243.0657 | C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> | 15.12 | 1.67 | 244.0848 |
| C <sub>14</sub> H <sub>2</sub> N <sub>4</sub> O               | 16.73 | 1.51 | 242.0229 | C <sub>14</sub> H <sub>29</sub> NO <sub>2</sub>               | 16.05 | 1.61 | 243.2199 | C <sub>13</sub> H <sub>30</sub> N <sub>3</sub> O              | 15.71 | 1.36 | 244.2391 |
| C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>                | 16.77 | 1.72 | 242.2247 | C <sub>14</sub> H <sub>13</sub> NO <sub>3</sub>               | 15.84 | 1.77 | 243.0896 | C <sub>13</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> | 15.49 | 1.52 | 244.1087 |
| C <sub>15</sub> H <sub>14</sub> O <sub>3</sub>                | 16.55 | 1.88 | 242.0943 | C <sub>14</sub> H <sub>31</sub> N <sub>2</sub> O              | 16.43 | 1.47 | 243.2438 | C <sub>13</sub> H <sub>32</sub> N <sub>4</sub>                | 16.09 | 1.21 | 244.2629 |
| C <sub>15</sub> H <sub>32</sub> NO                            | 17.14 | 1.58 | 242.2485 | C <sub>14</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub> | 16.21 | 1.63 | 243.1134 | C <sub>13</sub> H <sub>16</sub> N <sub>4</sub> O              | 15.87 | 1.38 | 244.1325 |
| C <sub>15</sub> H <sub>16</sub> NO <sub>2</sub>               | 16.92 | 1.74 | 242.1182 | C <sub>14</sub> H <sub>33</sub> N <sub>3</sub>                | 16.80 | 1.33 | 243.2677 | C <sub>13</sub> N <sub>4</sub> O <sub>2</sub>                 | 15.65 | 1.55 | 244.0022 |
| C <sub>15</sub> NO <sub>3</sub>                               | 16.71 | 1.91 | 241.9878 | C <sub>14</sub> H <sub>17</sub> N <sub>3</sub> O              | 16.58 | 1.49 | 243.1373 | C <sub>14</sub> H <sub>28</sub> O <sub>3</sub>                | 15.69 | 1.75 | 244.2039 |
| C <sub>15</sub> H <sub>34</sub> N <sub>2</sub>                | 17.52 | 1.44 | 242.2724 | C <sub>14</sub> HN <sub>3</sub> O <sub>2</sub>                | 16.37 | 1.66 | 243.0069 | C <sub>14</sub> H <sub>12</sub> O <sub>4</sub>                | 15.48 | 1.92 | 244.0735 |
| C <sub>15</sub> H <sub>18</sub> N <sub>2</sub> O              | 17.30 | 1.61 | 242.1420 | C <sub>14</sub> H <sub>19</sub> N <sub>4</sub>                | 16.96 | 1.35 | 243.1611 | C <sub>14</sub> H <sub>30</sub> NO <sub>2</sub>               | 16.07 | 1.61 | 244.2278 |
| C <sub>15</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>  | 17.08 | 1.77 | 242.0116 | C <sub>14</sub> H <sub>3</sub> N <sub>4</sub> O               | 16.74 | 1.52 | 243.0308 | C <sub>14</sub> H <sub>14</sub> NO <sub>3</sub>               | 15.85 | 1.78 | 244.0974 |
| C <sub>15</sub> H <sub>20</sub> N <sub>3</sub>                | 17.67 | 1.47 | 242.1659 | C <sub>15</sub> H <sub>31</sub> O <sub>2</sub>                | 16.78 | 1.72 | 243.2325 | C <sub>14</sub> H <sub>32</sub> N <sub>2</sub> O              | 16.44 | 1.47 | 244.2516 |
| C <sub>15</sub> H <sub>4</sub> N <sub>3</sub> O               | 17.46 | 1.63 | 242.0355 | C <sub>15</sub> H <sub>15</sub> O <sub>3</sub>                | 16.57 | 1.89 | 243.1021 | C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> | 16.23 | 1.63 | 244.1213 |
| C <sub>15</sub> H <sub>6</sub> N <sub>4</sub>                 | 17.83 | 1.50 | 242.0594 | C <sub>15</sub> H <sub>33</sub> NO                            | 17.16 | 1.58 | 243.2564 | C <sub>14</sub> N <sub>2</sub> O <sub>3</sub>                 | 16.01 | 1.80 | 243.9909 |
| C <sub>16</sub> H <sub>34</sub> O                             | 17.87 | 1.70 | 242.2611 | C <sub>15</sub> H <sub>17</sub> NO <sub>2</sub>               | 16.94 | 1.75 | 243.1260 | C <sub>14</sub> H <sub>18</sub> N <sub>3</sub> O              | 16.60 | 1.49 | 244.1451 |
| C <sub>16</sub> H <sub>18</sub> O <sub>2</sub>                | 17.66 | 1.87 | 242.1307 | C <sub>15</sub> HN <sub>3</sub> O <sub>3</sub>                | 16.72 | 1.91 | 242.9956 | C <sub>14</sub> H <sub>2</sub> N <sub>3</sub> O <sub>2</sub>  | 16.38 | 1.66 | 244.0147 |
| C <sub>16</sub> H <sub>2</sub> O <sub>3</sub>                 | 17.44 | 2.03 | 242.0003 | C <sub>15</sub> H <sub>19</sub> N <sub>2</sub> O              | 17.32 | 1.61 | 243.1498 | C <sub>14</sub> H <sub>20</sub> N <sub>4</sub>                | 16.97 | 1.36 | 244.1690 |
| C <sub>16</sub> H <sub>20</sub> NO                            | 18.03 | 1.73 | 242.1546 | C <sub>15</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>  | 17.10 | 1.77 | 243.0195 | C <sub>14</sub> H <sub>4</sub> N <sub>4</sub> O               | 16.76 | 1.52 | 244.0386 |
| C <sub>16</sub> H <sub>4</sub> NO <sub>2</sub>                | 17.81 | 1.89 | 242.0242 | C <sub>15</sub> H <sub>21</sub> N <sub>3</sub>                | 17.69 | 1.47 | 243.1737 | C <sub>15</sub> H <sub>32</sub> O <sub>2</sub>                | 16.80 | 1.72 | 244.2403 |
| C <sub>16</sub> H <sub>22</sub> N <sub>2</sub>                | 18.40 | 1.60 | 242.1784 | C <sub>15</sub> H <sub>5</sub> N <sub>3</sub> O               | 17.47 | 1.64 | 243.0433 | C <sub>15</sub> H <sub>16</sub> O <sub>3</sub>                | 16.58 | 1.89 | 244.1100 |
| C <sub>16</sub> H <sub>6</sub> N <sub>2</sub> O               | 18.19 | 1.76 | 242.0480 | C <sub>15</sub> H <sub>7</sub> N <sub>4</sub>                 | 17.85 | 1.50 | 243.0672 | C <sub>15</sub> O <sub>4</sub>                                | 16.37 | 2.05 | 243.9796 |
| C <sub>16</sub> H <sub>8</sub> N <sub>3</sub>                 | 18.56 | 1.63 | 242.0719 | C <sub>16</sub> H <sub>19</sub> O <sub>2</sub>                | 17.67 | 1.87 | 243.1385 | C <sub>15</sub> H <sub>18</sub> NO <sub>2</sub>               | 16.96 | 1.75 | 244.1338 |
| C <sub>17</sub> H <sub>22</sub> O                             | 18.76 | 1.86 | 242.1671 | C <sub>16</sub> H <sub>3</sub> O <sub>3</sub>                 | 17.45 | 2.03 | 243.0082 | C <sub>15</sub> H <sub>2</sub> NO <sub>3</sub>                | 16.74 | 1.91 | 244.0034 |
| C <sub>17</sub> H <sub>6</sub> O <sub>2</sub>                 | 18.54 | 2.02 | 242.0368 | C <sub>16</sub> H <sub>21</sub> NO                            | 18.05 | 1.73 | 243.1624 | C <sub>15</sub> H <sub>20</sub> N <sub>2</sub> O              | 17.33 | 1.61 | 244.1577 |
| C <sub>17</sub> H <sub>24</sub> N                             | 19.14 | 1.73 | 242.1910 | C <sub>16</sub> H <sub>5</sub> NO <sub>2</sub>                | 17.83 | 1.90 | 243.0320 | C <sub>15</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>  | 17.11 | 1.78 | 244.0273 |
| C <sub>17</sub> H <sub>8</sub> NO                             | 18.92 | 1.89 | 242.0606 | C <sub>16</sub> H <sub>23</sub> N <sub>2</sub>                | 18.42 | 1.60 | 243.1863 | C <sub>15</sub> H <sub>22</sub> N <sub>3</sub>                | 17.71 | 1.48 | 244.1815 |
| C <sub>17</sub> H <sub>10</sub> N <sub>2</sub>                | 19.29 | 1.76 | 242.0845 | C <sub>16</sub> H <sub>7</sub> N <sub>2</sub> O               | 18.20 | 1.76 | 243.0559 | C <sub>15</sub> H <sub>6</sub> N <sub>3</sub> O               | 17.49 | 1.64 | 244.0511 |
| C <sub>18</sub> H <sub>26</sub>                               | 19.87 | 1.87 | 242.2036 | C <sub>16</sub> H <sub>9</sub> N <sub>3</sub>                 | 18.58 | 1.63 | 243.0798 | C <sub>15</sub> H <sub>8</sub> N <sub>4</sub>                 | 17.86 | 1.50 | 244.0750 |
| C <sub>18</sub> H <sub>10</sub> O                             | 19.65 | 2.03 | 242.0732 | C <sub>17</sub> H <sub>23</sub> O                             | 18.78 | 1.86 | 243.1750 | C <sub>16</sub> H <sub>20</sub> O <sub>2</sub>                | 17.69 | 1.87 | 244.1464 |
| C <sub>18</sub> H <sub>12</sub> N                             | 20.02 | 1.90 | 242.0970 | C <sub>17</sub> H <sub>7</sub> O <sub>2</sub>                 | 18.56 | 2.02 | 243.0446 | C <sub>16</sub> H <sub>4</sub> O <sub>3</sub>                 | 17.47 | 2.03 | 244.0160 |

|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>16</sub> H <sub>22</sub> N <sub>0</sub>                | 18.06 | 1.74 | 244.1702 | C <sub>15</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub>  | 17.13 | 1.78 | 245.0351 | C <sub>14</sub> H <sub>6</sub> N <sub>4</sub> O               | 16.79 | 1.53 | 246.0542 |
| C <sub>16</sub> H <sub>6</sub> N <sub>0</sub> O <sub>2</sub>  | 17.85 | 1.90 | 244.0399 | C <sub>15</sub> H <sub>23</sub> N <sub>3</sub>                | 17.72 | 1.48 | 245.1894 | C <sub>15</sub> H <sub>18</sub> O <sub>3</sub>                | 16.61 | 1.89 | 246.1256 |
| C <sub>16</sub> H <sub>24</sub> N <sub>2</sub>                | 18.44 | 1.60 | 244.1941 | C <sub>15</sub> H <sub>7</sub> N <sub>3</sub> O               | 17.50 | 1.64 | 245.0590 | C <sub>15</sub> H <sub>2</sub> O <sub>4</sub>                 | 16.40 | 2.06 | 245.9953 |
| C <sub>16</sub> H <sub>8</sub> N <sub>2</sub> O               | 18.22 | 1.77 | 244.0637 | C <sub>15</sub> H <sub>9</sub> N <sub>4</sub>                 | 17.88 | 1.51 | 245.0829 | C <sub>15</sub> H <sub>20</sub> N <sub>0</sub> O <sub>2</sub> | 16.99 | 1.76 | 246.1495 |
| C <sub>16</sub> H <sub>10</sub> N <sub>3</sub>                | 18.59 | 1.63 | 244.0876 | C <sub>16</sub> H <sub>21</sub> O <sub>2</sub>                | 17.70 | 1.87 | 245.1542 | C <sub>15</sub> H <sub>4</sub> N <sub>0</sub> O <sub>3</sub>  | 16.77 | 1.92 | 246.0191 |
| C <sub>17</sub> H <sub>24</sub> O                             | 18.79 | 1.87 | 244.1828 | C <sub>16</sub> H <sub>5</sub> O <sub>3</sub>                 | 17.49 | 2.04 | 245.0238 | C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O              | 17.36 | 1.62 | 246.1733 |
| C <sub>17</sub> H <sub>8</sub> O <sub>2</sub>                 | 18.58 | 2.03 | 244.0524 | C <sub>16</sub> H <sub>23</sub> N <sub>0</sub>                | 18.08 | 1.74 | 245.1781 | C <sub>15</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 17.15 | 1.78 | 246.0429 |
| C <sub>17</sub> H <sub>26</sub> N                             | 19.17 | 1.74 | 244.2067 | C <sub>16</sub> H <sub>7</sub> N <sub>0</sub> O <sub>2</sub>  | 17.86 | 1.90 | 245.0477 | C <sub>15</sub> H <sub>24</sub> N <sub>3</sub>                | 17.74 | 1.48 | 246.1972 |
| C <sub>17</sub> H <sub>10</sub> N <sub>0</sub>                | 18.95 | 1.90 | 244.0763 | C <sub>16</sub> H <sub>25</sub> N <sub>2</sub>                | 18.45 | 1.61 | 245.2019 | C <sub>15</sub> H <sub>8</sub> N <sub>3</sub> O               | 17.52 | 1.65 | 246.0668 |
| C <sub>17</sub> H <sub>12</sub> N <sub>2</sub>                | 19.33 | 1.77 | 244.1001 | C <sub>16</sub> H <sub>9</sub> N <sub>2</sub> O               | 18.24 | 1.77 | 245.0715 | C <sub>15</sub> H <sub>10</sub> N <sub>4</sub>                | 17.89 | 1.51 | 246.0907 |
| C <sub>18</sub> H <sub>28</sub>                               | 19.90 | 1.87 | 244.2192 | C <sub>16</sub> H <sub>11</sub> N <sub>3</sub>                | 18.61 | 1.64 | 245.0954 | C <sub>16</sub> H <sub>22</sub> O <sub>2</sub>                | 17.72 | 1.88 | 246.1620 |
| C <sub>18</sub> H <sub>12</sub> O                             | 19.68 | 2.03 | 244.0888 | C <sub>17</sub> H <sub>25</sub> O                             | 18.81 | 1.87 | 245.1906 | C <sub>16</sub> H <sub>6</sub> O <sub>3</sub>                 | 17.50 | 2.04 | 246.0317 |
| C <sub>18</sub> H <sub>14</sub> N                             | 20.06 | 1.91 | 244.1127 | C <sub>17</sub> H <sub>9</sub> O <sub>2</sub>                 | 18.59 | 2.03 | 245.0603 | C <sub>16</sub> H <sub>24</sub> N <sub>0</sub>                | 18.09 | 1.74 | 246.1859 |
| C <sub>18</sub> N <sub>2</sub>                                | 20.21 | 1.94 | 244.0062 | C <sub>17</sub> H <sub>27</sub> N                             | 19.18 | 1.74 | 245.2145 | C <sub>16</sub> H <sub>8</sub> N <sub>0</sub> O <sub>2</sub>  | 17.88 | 1.90 | 246.0555 |
| C <sub>19</sub> H <sub>16</sub>                               | 20.79 | 2.05 | 244.1253 | C <sub>17</sub> H <sub>11</sub> N <sub>0</sub>                | 18.97 | 1.90 | 245.0841 | C <sub>16</sub> H <sub>26</sub> N <sub>2</sub>                | 18.47 | 1.61 | 246.2098 |
| C <sub>19</sub> O   | 20.57 | 2.21 | 243.9949 | C <sub>17</sub> H <sub>13</sub> N <sub>2</sub>                | 19.34 | 1.77 | 245.1080 | C <sub>16</sub> H <sub>10</sub> N <sub>2</sub> O              | 18.25 | 1.77 | 246.0794 |
| C <sub>19</sub> H <sub>2</sub> N                              | 20.94 | 2.08 | 244.0187 | C <sub>18</sub> H <sub>29</sub>                               | 19.91 | 1.88 | 245.2270 | C <sub>16</sub> H <sub>12</sub> N <sub>3</sub>                | 18.63 | 1.64 | 246.1032 |
| C <sub>20</sub> H <sub>4</sub>                                | 21.68 | 2.23 | 244.0313 | C <sub>18</sub> H <sub>13</sub> O                             | 19.70 | 2.04 | 245.0967 | C <sub>17</sub> H <sub>26</sub> O                             | 18.83 | 1.87 | 246.1985 |
|   |       |      |          | C <sub>18</sub> H <sub>15</sub> N                             | 20.07 | 1.91 | 245.1205 | C <sub>17</sub> H <sub>10</sub> O <sub>2</sub>                | 18.61 | 2.03 | 246.0681 |
| 245   |       |      |          | C <sub>18</sub> HN <sub>2</sub>                               | 20.23 | 1.94 | 245.0140 | C <sub>17</sub> H <sub>28</sub> N                             | 19.20 | 1.74 | 246.2223 |
| C <sub>11</sub> H <sub>21</sub> N <sub>2</sub> O <sub>4</sub> | 13.14 | 1.60 | 245.1502 | C <sub>19</sub> H <sub>17</sub>                               | 20.80 | 2.05 | 245.1331 | C <sub>17</sub> H <sub>12</sub> N <sub>0</sub>                | 18.98 | 1.90 | 246.0919 |
| C <sub>11</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub> | 13.52 | 1.45 | 245.1741 | C <sub>19</sub> H <sub>0</sub>                                | 20.59 | 2.21 | 245.0027 | C <sub>17</sub> H <sub>14</sub> N <sub>2</sub>                | 19.36 | 1.77 | 246.1158 |
| C <sub>11</sub> H <sub>25</sub> N <sub>4</sub> O <sub>2</sub> | 13.89 | 1.30 | 245.1979 | C <sub>19</sub> H <sub>3</sub> N                              | 20.96 | 2.09 | 245.0266 | C <sub>17</sub> N <sub>3</sub>                                | 19.51 | 1.80 | 246.0093 |
| C <sub>12</sub> H <sub>23</sub> N <sub>0</sub> O <sub>4</sub> | 13.87 | 1.69 | 245.1628 | C <sub>20</sub> H <sub>5</sub>                                | 21.69 | 2.24 | 245.0391 | C <sub>18</sub> H <sub>30</sub>                               | 19.93 | 1.88 | 246.2349 |
| C <sub>12</sub> H <sub>25</sub> N <sub>2</sub> O <sub>3</sub> | 14.25 | 1.54 | 245.1866 |   |       |      |          | C <sub>18</sub> H <sub>14</sub> O                             | 19.71 | 2.04 | 246.1045 |
| C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub>  | 14.03 | 1.71 | 245.0563 | 246   |       |      |          | C <sub>18</sub> H <sub>16</sub> N                             | 20.09 | 1.91 | 246.1284 |
| C <sub>12</sub> H <sub>27</sub> N <sub>3</sub> O <sub>2</sub> | 14.62 | 1.40 | 245.2105 | C <sub>11</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> | 13.16 | 1.60 | 246.1580 | C <sub>18</sub> N <sub>0</sub>                                | 19.87 | 2.07 | 245.9980 |
| C <sub>12</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> | 14.40 | 1.57 | 245.0801 | C <sub>11</sub> H <sub>24</sub> N <sub>3</sub> O <sub>3</sub> | 13.53 | 1.45 | 246.1819 | C <sub>18</sub> H <sub>2</sub> N <sub>2</sub>                 | 20.25 | 1.94 | 246.0218 |
| C <sub>12</sub> H <sub>29</sub> N <sub>4</sub> O              | 15.00 | 1.25 | 245.2343 | C <sub>11</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub> | 13.91 | 1.30 | 246.2057 | C <sub>19</sub> H <sub>18</sub>                               | 20.82 | 2.06 | 246.1409 |
| C <sub>12</sub> H <sub>13</sub> N <sub>4</sub> O <sub>2</sub> | 14.78 | 1.42 | 245.1040 | C <sub>12</sub> H <sub>24</sub> N <sub>0</sub> O <sub>4</sub> | 13.89 | 1.70 | 246.1706 | C <sub>19</sub> H <sub>2</sub> O                              | 20.60 | 2.21 | 246.0106 |
| C <sub>13</sub> H <sub>25</sub> O <sub>4</sub>                | 14.60 | 1.79 | 245.1753 | C <sub>12</sub> H <sub>26</sub> N <sub>2</sub> O <sub>3</sub> | 14.26 | 1.55 | 246.1945 | C <sub>19</sub> H <sub>4</sub> N                              | 20.98 | 2.09 | 246.0344 |
| C <sub>13</sub> H <sub>27</sub> N <sub>0</sub> O <sub>3</sub> | 14.98 | 1.65 | 245.1992 | C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> | 14.05 | 1.72 | 246.0641 | C <sub>20</sub> H <sub>6</sub>                                | 21.71 | 2.24 | 246.0470 |
| C <sub>13</sub> H <sub>11</sub> N <sub>0</sub> O <sub>4</sub> | 14.76 | 1.81 | 245.0688 | C <sub>12</sub> H <sub>28</sub> N <sub>3</sub> O <sub>2</sub> | 14.64 | 1.40 | 246.2183 | 247   |       |      |          |
| C <sub>13</sub> H <sub>29</sub> N <sub>2</sub> O <sub>2</sub> | 15.35 | 1.50 | 245.2230 | C <sub>12</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> | 14.42 | 1.57 | 246.0879 | C <sub>11</sub> H <sub>23</sub> N <sub>2</sub> O <sub>4</sub> | 13.17 | 1.60 | 247.1659 |
| C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> | 15.14 | 1.67 | 245.0927 | C <sub>12</sub> H <sub>30</sub> N <sub>4</sub> O              | 15.01 | 1.25 | 246.2422 | C <sub>11</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub> | 13.55 | 1.45 | 247.1897 |
| C <sub>13</sub> H <sub>31</sub> N <sub>3</sub> O              | 15.73 | 1.36 | 245.2469 | C <sub>12</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> | 14.80 | 1.42 | 246.1118 | C <sub>11</sub> H <sub>27</sub> N <sub>4</sub> O <sub>2</sub> | 13.92 | 1.30 | 247.2136 |
| C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> | 15.51 | 1.53 | 245.1165 | C <sub>13</sub> H <sub>26</sub> O <sub>4</sub>                | 14.62 | 1.79 | 246.1832 | C <sub>12</sub> H <sub>25</sub> N <sub>0</sub> O <sub>4</sub> | 13.91 | 1.70 | 247.1784 |
| C <sub>13</sub> H <sub>17</sub> N <sub>4</sub> O              | 15.88 | 1.38 | 245.1404 | C <sub>13</sub> H <sub>28</sub> N <sub>0</sub> O <sub>3</sub> | 14.99 | 1.65 | 246.2070 | C <sub>12</sub> H <sub>27</sub> N <sub>2</sub> O <sub>3</sub> | 14.28 | 1.55 | 247.2023 |
| C <sub>13</sub> HN <sub>4</sub> O <sub>2</sub>                | 15.67 | 1.55 | 245.0100 | C <sub>13</sub> H <sub>12</sub> N <sub>0</sub> O <sub>4</sub> | 14.78 | 1.82 | 246.0766 | C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> | 14.06 | 1.72 | 247.0719 |
| C <sub>14</sub> H <sub>29</sub> O <sub>3</sub>                | 15.71 | 1.75 | 245.2117 | C <sub>13</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub> | 15.37 | 1.50 | 246.2309 | C <sub>12</sub> H <sub>29</sub> N <sub>3</sub> O <sub>2</sub> | 14.65 | 1.40 | 247.2261 |
| C <sub>14</sub> H <sub>13</sub> O <sub>4</sub>                | 15.49 | 1.92 | 245.0814 | C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub> | 15.15 | 1.67 | 246.1005 | C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> | 14.44 | 1.57 | 247.0958 |
| C <sub>14</sub> H <sub>31</sub> N <sub>0</sub> O <sub>2</sub> | 16.08 | 1.61 | 245.2356 | C <sub>13</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub> | 15.53 | 1.53 | 246.1244 | C <sub>12</sub> H <sub>15</sub> N <sub>4</sub> O <sub>2</sub> | 14.81 | 1.42 | 247.1196 |
| C <sub>14</sub> H <sub>15</sub> N <sub>0</sub> O <sub>3</sub> | 15.87 | 1.78 | 245.1052 | C <sub>13</sub> N <sub>3</sub> O <sub>3</sub>                 | 15.31 | 1.70 | 245.9940 | C <sub>13</sub> H <sub>27</sub> O <sub>4</sub>                | 14.64 | 1.80 | 247.1910 |
| C <sub>14</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> | 16.24 | 1.64 | 245.1291 | C <sub>13</sub> H <sub>18</sub> N <sub>4</sub> O              | 15.90 | 1.39 | 246.1482 | C <sub>13</sub> H <sub>29</sub> N <sub>0</sub> O <sub>3</sub> | 15.01 | 1.65 | 247.2148 |
| C <sub>14</sub> HN <sub>2</sub> O <sub>3</sub>                | 16.02 | 1.80 | 244.9987 | C <sub>13</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>  | 15.68 | 1.55 | 246.0178 | C <sub>13</sub> H <sub>13</sub> N <sub>0</sub> O <sub>4</sub> | 14.79 | 1.82 | 247.0845 |
| C <sub>14</sub> H <sub>19</sub> N <sub>3</sub> O              | 16.62 | 1.50 | 245.1529 | C <sub>14</sub> H <sub>30</sub> O <sub>3</sub>                | 15.73 | 1.76 | 246.2196 | C <sub>13</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub> | 15.17 | 1.67 | 247.1083 |
| C <sub>14</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub>  | 16.40 | 1.66 | 245.0226 | C <sub>14</sub> H <sub>14</sub> O <sub>4</sub>                | 15.51 | 1.92 | 246.0892 | C <sub>13</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> | 15.54 | 1.53 | 247.1322 |
| C <sub>14</sub> H <sub>21</sub> N <sub>4</sub>                | 16.99 | 1.36 | 245.1768 | C <sub>14</sub> H <sub>16</sub> N <sub>0</sub> O <sub>3</sub> | 15.88 | 1.78 | 246.1131 | C <sub>13</sub> HN <sub>3</sub> O <sub>3</sub>                | 15.33 | 1.70 | 247.0018 |
| C <sub>14</sub> H <sub>5</sub> N <sub>4</sub> O               | 16.77 | 1.52 | 245.0464 | C <sub>14</sub> N <sub>0</sub> O <sub>4</sub>                 | 15.67 | 1.95 | 245.9827 | C <sub>13</sub> H <sub>19</sub> N <sub>4</sub> O              | 15.92 | 1.39 | 247.1560 |
| C <sub>15</sub> H <sub>17</sub> O <sub>3</sub>                | 16.60 | 1.89 | 245.1178 | C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> | 16.26 | 1.64 | 246.1369 | C <sub>13</sub> H <sub>3</sub> N <sub>4</sub> O <sub>2</sub>  | 15.70 | 1.55 | 247.0257 |
| C <sub>15</sub> HO <sub>4</sub>                               | 16.38 | 2.06 | 244.9874 | C <sub>14</sub> H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>  | 16.04 | 1.80 | 246.0065 | C <sub>14</sub> H <sub>15</sub> O <sub>4</sub>                | 15.52 | 1.93 | 247.0970 |
| C <sub>15</sub> H <sub>19</sub> N <sub>0</sub> O <sub>2</sub> | 16.97 | 1.75 | 245.1416 | C <sub>14</sub> H <sub>20</sub> N <sub>3</sub> O              | 16.63 | 1.50 | 246.1608 | C <sub>14</sub> H <sub>17</sub> N <sub>0</sub> O <sub>3</sub> | 15.90 | 1.78 | 247.1209 |
| C <sub>15</sub> H <sub>3</sub> N <sub>0</sub> O <sub>3</sub>  | 16.76 | 1.92 | 245.0113 | C <sub>14</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>  | 16.41 | 1.66 | 246.0304 | C <sub>14</sub> HN <sub>0</sub> O <sub>4</sub>                | 15.68 | 1.95 | 246.9905 |
| C <sub>15</sub> H <sub>21</sub> N <sub>2</sub> O              | 17.35 | 1.62 | 245.1655 | C <sub>14</sub> H <sub>22</sub> N <sub>4</sub>                | 17.01 | 1.36 | 246.1846 | C <sub>14</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub> | 16.27 | 1.64 | 247.1447 |



|   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |   | M+1   | M+2  | MW       |
|---|-------|------|----------|---|-------|------|----------|---|-------|------|----------|
| C <sub>14</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub>  | 16.06 | 1.81 | 247.0144 | C <sub>14</sub> H <sub>16</sub> O <sub>4</sub>                | 15.54 | 1.93 | 248.1049 | C <sub>13</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>  | 15.36 | 1.70 | 249.0175 |
| C <sub>14</sub> H <sub>21</sub> N <sub>3</sub> O              | 16.65 | 1.50 | 247.1686 | C <sub>14</sub> H <sub>18</sub> NO <sub>3</sub>               | 15.92 | 1.79 | 248.1287 | C <sub>13</sub> H <sub>21</sub> N <sub>4</sub> O              | 15.95 | 1.39 | 249.1717 |
| C <sub>14</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>  | 16.43 | 1.67 | 247.0382 | C <sub>14</sub> H <sub>2</sub> NO <sub>4</sub>                | 15.70 | 1.95 | 247.9983 | C <sub>13</sub> H <sub>5</sub> N <sub>4</sub> O <sub>2</sub>  | 15.73 | 1.56 | 249.0413 |
| C <sub>14</sub> H <sub>23</sub> N <sub>4</sub>                | 17.02 | 1.36 | 247.1925 | C <sub>14</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> | 16.29 | 1.64 | 248.1526 | C <sub>14</sub> H <sub>17</sub> O <sub>4</sub>                | 15.56 | 1.93 | 249.1127 |
| C <sub>14</sub> H <sub>7</sub> N <sub>4</sub> O               | 16.81 | 1.53 | 247.0621 | C <sub>14</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub>  | 16.07 | 1.81 | 248.0222 | C <sub>14</sub> H <sub>19</sub> NO <sub>3</sub>               | 15.93 | 1.79 | 249.1365 |
| C <sub>15</sub> H <sub>19</sub> O <sub>3</sub>                | 16.63 | 1.90 | 247.1334 | C <sub>14</sub> H <sub>22</sub> N <sub>3</sub> O              | 16.66 | 1.50 | 248.1764 | C <sub>14</sub> H <sub>3</sub> NO <sub>4</sub>                | 15.71 | 1.95 | 249.0062 |
| C <sub>15</sub> H <sub>3</sub> O <sub>4</sub>                 | 16.41 | 2.06 | 247.0031 | C <sub>14</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>  | 16.45 | 1.67 | 248.0460 | C <sub>14</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub> | 16.31 | 1.65 | 249.1604 |
| C <sub>15</sub> H <sub>21</sub> NO <sub>2</sub>               | 17.00 | 1.76 | 247.1573 | C <sub>14</sub> H <sub>24</sub> N <sub>4</sub>                | 17.04 | 1.37 | 248.2003 | C <sub>14</sub> H <sub>5</sub> N <sub>2</sub> O <sub>3</sub>  | 16.09 | 1.81 | 249.0300 |
| C <sub>15</sub> H <sub>5</sub> NO <sub>3</sub>                | 16.79 | 1.92 | 247.0269 | C <sub>14</sub> H <sub>8</sub> N <sub>4</sub> O               | 16.82 | 1.53 | 248.0699 | C <sub>14</sub> H <sub>23</sub> N <sub>3</sub> O              | 16.68 | 1.51 | 249.1842 |
| C <sub>15</sub> H <sub>23</sub> N <sub>2</sub> O              | 17.38 | 1.62 | 247.1811 | C <sub>15</sub> H <sub>20</sub> O <sub>3</sub>                | 16.65 | 1.90 | 248.1413 | C <sub>14</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub>  | 16.46 | 1.67 | 249.0539 |
| C <sub>15</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>  | 17.16 | 1.78 | 247.0508 | C <sub>15</sub> H <sub>4</sub> O <sub>4</sub>                 | 16.43 | 2.06 | 248.0109 | C <sub>14</sub> H <sub>25</sub> N <sub>4</sub>                | 17.05 | 1.37 | 249.2081 |
| C <sub>15</sub> H <sub>25</sub> N <sub>3</sub>                | 17.75 | 1.49 | 247.2050 | C <sub>15</sub> H <sub>22</sub> NO <sub>2</sub>               | 17.02 | 1.76 | 248.1651 | C <sub>14</sub> H <sub>9</sub> N <sub>4</sub> O               | 16.84 | 1.53 | 249.0777 |
| C <sub>15</sub> H <sub>9</sub> N <sub>3</sub> O               | 17.54 | 1.65 | 247.0746 | C <sub>15</sub> H <sub>6</sub> NO <sub>3</sub>                | 16.80 | 1.92 | 248.0348 | C <sub>15</sub> H <sub>21</sub> O <sub>3</sub>                | 16.66 | 1.90 | 249.1491 |
| C <sub>15</sub> H <sub>11</sub> N <sub>4</sub>                | 17.91 | 1.51 | 247.0985 | C <sub>15</sub> H <sub>24</sub> N <sub>2</sub> O              | 17.40 | 1.62 | 248.1890 | C <sub>15</sub> H <sub>5</sub> O <sub>4</sub>                 | 16.45 | 2.07 | 249.0187 |
| C <sub>16</sub> H <sub>23</sub> O <sub>2</sub>                | 17.74 | 1.88 | 247.1699 | C <sub>15</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 17.18 | 1.79 | 248.0586 | C <sub>15</sub> H <sub>23</sub> NO <sub>2</sub>               | 17.04 | 1.76 | 249.1730 |
| C <sub>16</sub> H <sub>7</sub> O <sub>3</sub>                 | 17.52 | 2.04 | 247.0395 | C <sub>15</sub> H <sub>26</sub> N <sub>3</sub>                | 17.77 | 1.49 | 248.2129 | C <sub>15</sub> H <sub>7</sub> NO <sub>3</sub>                | 16.82 | 1.93 | 249.0426 |
| C <sub>16</sub> H <sub>25</sub> NO                            | 18.11 | 1.75 | 247.1937 | C <sub>15</sub> H <sub>10</sub> N <sub>3</sub> O              | 17.55 | 1.65 | 248.0825 | C <sub>15</sub> H <sub>25</sub> N <sub>2</sub> O              | 17.41 | 1.63 | 249.1968 |
| C <sub>16</sub> H <sub>9</sub> NO <sub>2</sub>                | 17.89 | 1.91 | 247.0634 | C <sub>15</sub> H <sub>12</sub> N <sub>4</sub>                | 17.93 | 1.52 | 248.1063 | C <sub>15</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>  | 17.19 | 1.79 | 249.0664 |
| C <sub>16</sub> H <sub>27</sub> N <sub>2</sub>                | 18.48 | 1.61 | 247.2176 | C <sub>16</sub> H <sub>24</sub> O <sub>2</sub>                | 17.75 | 1.88 | 248.1777 | C <sub>15</sub> H <sub>27</sub> N <sub>3</sub>                | 17.79 | 1.49 | 249.2207 |
| C <sub>16</sub> H <sub>11</sub> N <sub>2</sub> O              | 18.27 | 1.77 | 247.0872 | C <sub>16</sub> H <sub>8</sub> O <sub>3</sub>                 | 17.53 | 2.05 | 248.0473 | C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> O              | 17.57 | 1.65 | 249.0903 |
| C <sub>16</sub> H <sub>13</sub> N <sub>3</sub>                | 18.64 | 1.64 | 247.1111 | C <sub>16</sub> H <sub>26</sub> NO                            | 18.13 | 1.75 | 248.2015 | C <sub>15</sub> H <sub>13</sub> N <sub>4</sub>                | 17.94 | 1.52 | 249.1142 |
| C <sub>17</sub> H <sub>27</sub> O                             | 18.84 | 1.88 | 247.2063 | C <sub>16</sub> H <sub>10</sub> NO <sub>2</sub>               | 17.91 | 1.91 | 248.0712 | C <sub>16</sub> H <sub>25</sub> O <sub>2</sub>                | 17.77 | 1.89 | 249.1855 |
| C <sub>17</sub> H <sub>11</sub> O <sub>2</sub>                | 18.62 | 2.04 | 247.0759 | C <sub>16</sub> H <sub>28</sub> N <sub>2</sub>                | 18.50 | 1.62 | 248.2254 | C <sub>16</sub> H <sub>9</sub> O <sub>3</sub>                 | 17.55 | 2.05 | 249.0552 |
| C <sub>17</sub> H <sub>29</sub> N                             | 19.22 | 1.75 | 247.2301 | C <sub>16</sub> H <sub>12</sub> N <sub>2</sub> O              | 18.28 | 1.78 | 248.0950 | C <sub>16</sub> H <sub>27</sub> NO                            | 18.14 | 1.75 | 249.2094 |
| C <sub>17</sub> H <sub>13</sub> NO                            | 19.00 | 1.91 | 247.0998 | C <sub>16</sub> H <sub>14</sub> N <sub>3</sub>                | 18.66 | 1.64 | 248.1189 | C <sub>16</sub> H <sub>11</sub> NO <sub>2</sub>               | 17.93 | 1.91 | 249.0790 |
| C <sub>17</sub> H <sub>15</sub> N <sub>2</sub>                | 19.37 | 1.78 | 247.1236 | C <sub>16</sub> N <sub>4</sub>                                | 18.82 | 1.67 | 248.0124 | C <sub>16</sub> H <sub>29</sub> N <sub>2</sub>                | 18.52 | 1.62 | 249.2332 |
| C <sub>17</sub> HN <sub>3</sub>                               | 19.53 | 1.81 | 247.0171 | C <sub>17</sub> H <sub>28</sub> O                             | 18.86 | 1.88 | 248.2141 | C <sub>16</sub> H <sub>13</sub> N <sub>2</sub> O              | 18.30 | 1.78 | 249.1029 |
| C <sub>18</sub> H <sub>31</sub>                               | 19.95 | 1.88 | 247.2427 | C <sub>17</sub> H <sub>12</sub> O <sub>2</sub>                | 18.64 | 2.04 | 248.0837 | C <sub>16</sub> H <sub>15</sub> N <sub>3</sub>                | 18.67 | 1.65 | 249.1267 |
| C <sub>18</sub> H <sub>15</sub> O                             | 19.73 | 2.04 | 247.1123 | C <sub>17</sub> H <sub>30</sub> N                             | 19.23 | 1.75 | 248.2380 | C <sub>16</sub> HN <sub>4</sub>                               | 18.83 | 1.68 | 249.0202 |
| C <sub>18</sub> H <sub>17</sub> N                             | 20.10 | 1.92 | 247.1362 | C <sub>17</sub> H <sub>14</sub> NO                            | 19.01 | 1.91 | 248.1076 | C <sub>17</sub> H <sub>29</sub> O                             | 18.87 | 1.88 | 249.2219 |
| C <sub>18</sub> HN <sub>2</sub> O                             | 19.89 | 2.07 | 247.0058 | C <sub>17</sub> H <sub>16</sub> N <sub>2</sub>                | 19.39 | 1.78 | 248.1315 | C <sub>17</sub> H <sub>13</sub> O <sub>2</sub>                | 18.66 | 2.04 | 249.0916 |
| C <sub>18</sub> H <sub>3</sub> N <sub>2</sub>                 | 20.26 | 1.95 | 247.0297 | C <sub>17</sub> N <sub>2</sub> O                              | 19.17 | 1.94 | 248.0011 | C <sub>17</sub> H <sub>31</sub> N                             | 19.25 | 1.75 | 249.2458 |
| C <sub>19</sub> H <sub>19</sub>                               | 20.84 | 2.06 | 247.1488 | C <sub>17</sub> H <sub>2</sub> N <sub>3</sub>                 | 19.55 | 1.81 | 248.0249 | C <sub>17</sub> H <sub>15</sub> NO                            | 19.03 | 1.91 | 249.1154 |
| C <sub>19</sub> H <sub>3</sub> O                              | 20.62 | 2.22 | 247.0184 | C <sub>18</sub> H <sub>32</sub>                               | 19.96 | 1.89 | 248.2505 | C <sub>17</sub> H <sub>17</sub> N <sub>2</sub>                | 19.41 | 1.78 | 249.1393 |
| C <sub>19</sub> H <sub>5</sub> N                              | 20.99 | 2.09 | 247.0422 | C <sub>18</sub> H <sub>16</sub> O                             | 19.75 | 2.04 | 248.1202 | C <sub>17</sub> HN <sub>2</sub> O                             | 19.19 | 1.94 | 249.0089 |
| C <sub>20</sub> H <sub>7</sub>                                | 21.72 | 2.24 | 247.0548 | C <sub>18</sub> O <sub>2</sub>                                | 19.53 | 2.20 | 247.9898 | C <sub>17</sub> H <sub>3</sub> N <sub>3</sub>                 | 19.56 | 1.81 | 249.0328 |
|   |       |      |          | C <sub>18</sub> H <sub>18</sub> N                             | 20.12 | 1.92 | 248.1440 | C <sub>18</sub> H <sub>33</sub>                               | 19.98 | 1.89 | 249.2584 |
| 248   |       |      |          | C <sub>18</sub> H <sub>2</sub> NO                             | 19.90 | 2.08 | 248.0136 | C <sub>18</sub> H <sub>17</sub> O                             | 19.76 | 2.05 | 249.1280 |
| C <sub>11</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> | 13.19 | 1.61 | 248.1737 | C <sub>18</sub> H <sub>4</sub> N <sub>2</sub>                 | 20.28 | 1.95 | 248.0375 | C <sub>18</sub> HO <sub>2</sub>                               | 19.54 | 2.21 | 248.9976 |
| C <sub>11</sub> H <sub>26</sub> N <sub>3</sub> O <sub>3</sub> | 13.56 | 1.45 | 248.1976 | C <sub>19</sub> H <sub>20</sub>                               | 20.85 | 2.06 | 248.1566 | C <sub>18</sub> H <sub>19</sub> N                             | 20.14 | 1.92 | 249.1519 |
| C <sub>11</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> | 13.94 | 1.31 | 248.2214 | C <sub>19</sub> H <sub>4</sub> O                              | 20.63 | 2.22 | 248.0262 | C <sub>18</sub> H <sub>3</sub> NO                             | 19.92 | 2.08 | 249.0215 |
| C <sub>12</sub> H <sub>26</sub> NO <sub>4</sub>               | 13.92 | 1.70 | 248.1863 | C <sub>19</sub> H <sub>6</sub> N                              | 21.01 | 2.10 | 248.0501 | C <sub>18</sub> H <sub>5</sub> N <sub>2</sub>                 | 20.29 | 1.95 | 249.0453 |
| C <sub>12</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub> | 14.30 | 1.55 | 248.2101 | C <sub>20</sub> H <sub>8</sub>                                | 21.74 | 2.25 | 248.0626 | C <sub>19</sub> H <sub>21</sub>                               | 20.87 | 2.07 | 249.1644 |
| C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> | 14.08 | 1.72 | 248.0797 | 249   |       |      |          | C <sub>19</sub> H <sub>5</sub> O                              | 20.65 | 2.22 | 249.0340 |
| C <sub>12</sub> H <sub>14</sub> N <sub>3</sub> O <sub>3</sub> | 14.45 | 1.57 | 248.1036 | C <sub>11</sub> H <sub>25</sub> N <sub>2</sub> O <sub>4</sub> | 13.21 | 1.61 | 249.1815 | C <sub>19</sub> H <sub>7</sub> N                              | 21.02 | 2.10 | 249.0579 |
| C <sub>12</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> | 14.83 | 1.43 | 248.1275 | C <sub>11</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> | 13.58 | 1.46 | 249.2054 | C <sub>20</sub> H <sub>9</sub>                                | 21.76 | 2.25 | 249.0705 |
| C <sub>13</sub> H <sub>28</sub> O <sub>4</sub>                | 14.65 | 1.80 | 248.1988 | C <sub>12</sub> H <sub>27</sub> NO <sub>4</sub>               | 13.94 | 1.70 | 249.1941 |   |       |      |          |
| C <sub>13</sub> H <sub>14</sub> NO <sub>4</sub>               | 14.81 | 1.82 | 248.0923 | C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> | 14.09 | 1.72 | 249.0876 | 250   |       |      |          |
| C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> | 15.18 | 1.68 | 248.1162 | C <sub>12</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> | 14.47 | 1.58 | 249.1114 | C <sub>11</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> | 13.22 | 1.61 | 250.1894 |
| C <sub>13</sub> N <sub>2</sub> O <sub>4</sub>                 | 14.97 | 1.84 | 247.9858 | C <sub>12</sub> H <sub>17</sub> N <sub>4</sub> O <sub>2</sub> | 14.84 | 1.43 | 249.1353 | C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> | 14.11 | 1.73 | 250.0954 |
| C <sub>13</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> | 15.56 | 1.53 | 248.1400 | C <sub>13</sub> H <sub>15</sub> NO <sub>4</sub>               | 14.83 | 1.82 | 249.1001 | C <sub>12</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> | 14.48 | 1.58 | 250.1193 |
| C <sub>13</sub> H <sub>2</sub> N <sub>3</sub> O <sub>3</sub>  | 15.34 | 1.70 | 248.0096 | C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O <sub>3</sub> | 15.20 | 1.68 | 249.1240 | C <sub>12</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> | 14.86 | 1.43 | 250.1431 |
| C <sub>13</sub> H <sub>20</sub> N <sub>4</sub> O              | 15.93 | 1.39 | 248.1639 | C <sub>13</sub> HN <sub>2</sub> O <sub>4</sub>                | 14.98 | 1.85 | 248.9936 | C <sub>13</sub> H <sub>16</sub> NO <sub>4</sub>               | 14.84 | 1.83 | 250.1080 |
| C <sub>13</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>  | 15.72 | 1.56 | 248.0335 | C <sub>13</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> | 15.57 | 1.54 | 249.1478 | C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> | 15.22 | 1.68 | 250.1318 |





|   | M+1   | M+2  | MW       |
|---|-------|------|----------|
| C <sub>13</sub> H <sub>2</sub> N <sub>2</sub> O <sub>4</sub>  | 15.00 | 1.85 | 250.0014 |
| C <sub>13</sub> H <sub>20</sub> N <sub>3</sub> O <sub>2</sub> | 15.59 | 1.54 | 250.1557 |
| C <sub>13</sub> H <sub>4</sub> N <sub>3</sub> O <sub>3</sub>  | 15.37 | 1.71 | 250.0253 |
| C <sub>13</sub> H <sub>22</sub> N <sub>4</sub> O              | 15.96 | 1.40 | 250.1795 |
| C <sub>13</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>  | 15.75 | 1.56 | 250.0491 |
| C <sub>14</sub> H <sub>18</sub> O <sub>4</sub>                | 15.57 | 1.93 | 250.1205 |
| C <sub>14</sub> H <sub>20</sub> NO <sub>3</sub>               | 15.95 | 1.79 | 250.1444 |
| C <sub>14</sub> H <sub>4</sub> NO <sub>4</sub>                | 15.73 | 1.96 | 250.0140 |
| C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> | 16.32 | 1.65 | 250.1682 |
| C <sub>14</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 16.10 | 1.82 | 250.0379 |
| C <sub>14</sub> H <sub>24</sub> N <sub>3</sub> O              | 16.70 | 1.51 | 250.1921 |
| C <sub>14</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>  | 16.48 | 1.67 | 250.0617 |
| C <sub>14</sub> H <sub>26</sub> N <sub>4</sub>                | 17.07 | 1.37 | 250.2160 |
| C <sub>14</sub> H <sub>10</sub> N <sub>4</sub> O              | 16.85 | 1.54 | 250.0856 |
| C <sub>15</sub> H <sub>22</sub> O <sub>3</sub>                | 16.68 | 1.90 | 250.1569 |
| C <sub>15</sub> H <sub>6</sub> O <sub>4</sub>                 | 16.46 | 2.07 | 250.0266 |
| C <sub>15</sub> H <sub>24</sub> NO <sub>2</sub>               | 17.05 | 1.77 | 250.1808 |
| C <sub>15</sub> H <sub>8</sub> NO <sub>3</sub>                | 16.84 | 1.93 | 250.0504 |
| C <sub>15</sub> H <sub>26</sub> N <sub>2</sub> O              | 17.43 | 1.63 | 250.2046 |
| C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 17.21 | 1.79 | 250.0743 |
| C <sub>15</sub> H <sub>28</sub> N <sub>3</sub>                | 17.80 | 1.49 | 250.2285 |
| C <sub>15</sub> H <sub>12</sub> N <sub>3</sub> O              | 17.58 | 1.66 | 250.0981 |
| C <sub>15</sub> H <sub>14</sub> N <sub>4</sub>                | 17.96 | 1.52 | 250.1220 |
| C <sub>16</sub> H <sub>26</sub> O <sub>2</sub>                | 17.78 | 1.89 | 250.1934 |
| C <sub>16</sub> H <sub>10</sub> O <sub>3</sub>                | 17.57 | 2.05 | 250.0630 |
| C <sub>16</sub> H <sub>28</sub> NO                            | 18.16 | 1.75 | 250.2172 |
| C <sub>16</sub> H <sub>12</sub> NO <sub>2</sub>               | 17.94 | 1.92 | 250.0868 |
| C <sub>16</sub> H <sub>30</sub> N <sub>2</sub>                | 18.53 | 1.62 | 250.2411 |
| C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O              | 18.32 | 1.78 | 250.1107 |
| C <sub>16</sub> H <sub>16</sub> N <sub>3</sub>                | 18.69 | 1.65 | 250.1346 |
| C <sub>16</sub> N <sub>3</sub> O                              | 18.47 | 1.81 | 250.0042 |
| C <sub>16</sub> H <sub>2</sub> N <sub>4</sub>                 | 18.85 | 1.68 | 250.0280 |
| C <sub>17</sub> H <sub>30</sub> O                             | 18.89 | 1.89 | 250.2298 |
| C <sub>17</sub> H <sub>14</sub> O <sub>2</sub>                | 18.67 | 2.04 | 250.0994 |
| C <sub>17</sub> H <sub>32</sub> N                             | 19.26 | 1.76 | 250.2536 |
| C <sub>17</sub> H <sub>16</sub> NO                            | 19.05 | 1.91 | 250.1233 |
| C <sub>17</sub> NO <sub>2</sub>                               | 18.83 | 2.07 | 249.9929 |
| C <sub>17</sub> H <sub>18</sub> N <sub>2</sub>                | 19.42 | 1.79 | 250.1471 |
| C <sub>17</sub> H <sub>2</sub> N <sub>2</sub> O               | 19.20 | 1.94 | 250.0167 |
| C <sub>17</sub> H <sub>4</sub> N <sub>3</sub>                 | 19.58 | 1.82 | 250.0406 |
| C <sub>18</sub> H <sub>34</sub>                               | 19.99 | 1.89 | 250.2662 |
| C <sub>18</sub> H <sub>18</sub> O                             | 19.78 | 2.05 | 250.1358 |
| C <sub>18</sub> H <sub>2</sub> O <sub>2</sub>                 | 19.56 | 2.21 | 250.0054 |
| C <sub>18</sub> H <sub>20</sub> N                             | 20.15 | 1.92 | 250.1597 |
| C <sub>18</sub> H <sub>4</sub> NO                             | 19.94 | 2.08 | 250.0293 |
| C <sub>18</sub> H <sub>6</sub> N <sub>2</sub>                 | 20.31 | 1.96 | 250.0532 |
| C <sub>19</sub> H <sub>22</sub>                               | 20.88 | 2.07 | 250.1722 |
| C <sub>19</sub> H <sub>6</sub> O                              | 20.67 | 2.23 | 250.0419 |
| C <sub>19</sub> H <sub>8</sub> N                              | 21.04 | 2.10 | 250.0657 |
| C <sub>20</sub> H <sub>10</sub>                               | 21.77 | 2.25 | 250.0783 |

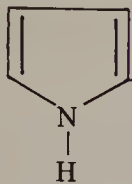
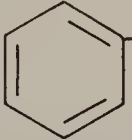
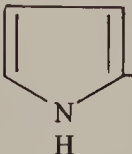
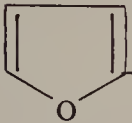
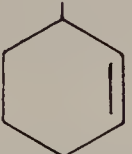
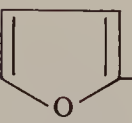

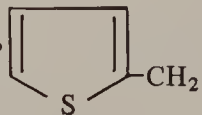



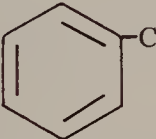
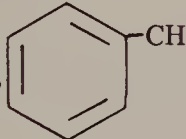
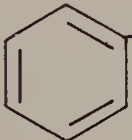
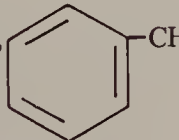
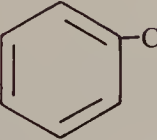
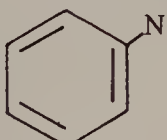
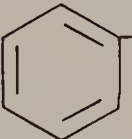
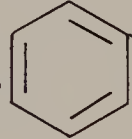
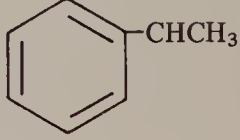
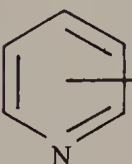
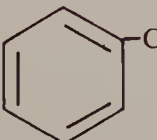
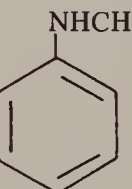
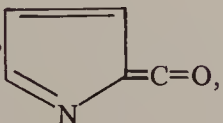
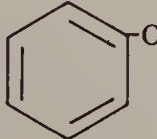
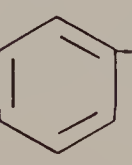
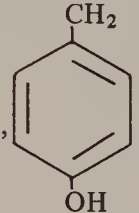
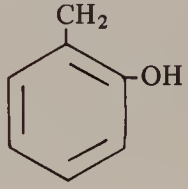
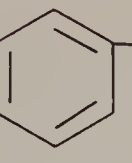
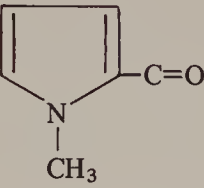
# appendix b

## COMMON FRAGMENT IONS

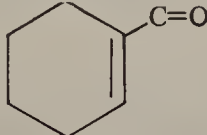
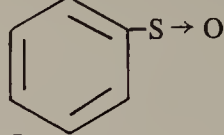
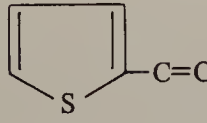
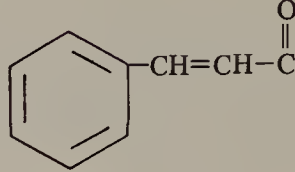
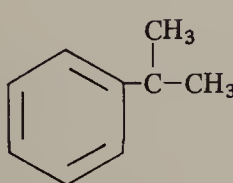
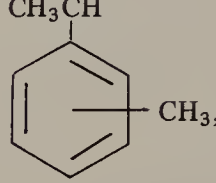
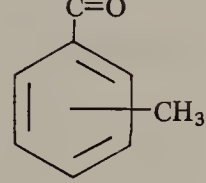
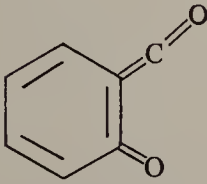
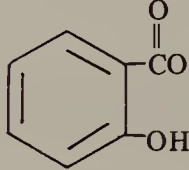
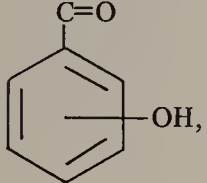
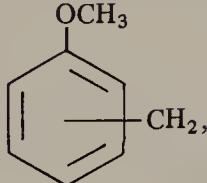
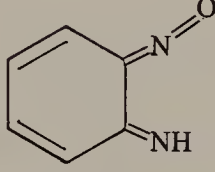
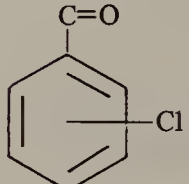
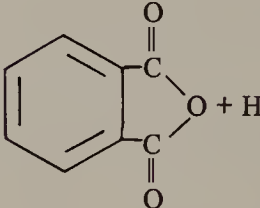
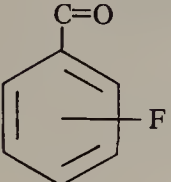
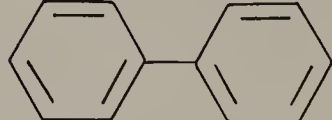
Not all members of homologous and isomeric series are given. The list is meant to be suggestive rather than exhaustive. Appendix II of Hamming and Foster,<sup>7</sup> Table A-7 of McLafferty's Interpretative book,<sup>9</sup> and the high-resolution ion data of McLafferty are recommended as supplements.

| <i>m/e</i> | Ions*   | <i>m/e</i> | Ions  |
|------------|---|------------|---|
| 14         | CH <sub>2</sub>   | 59         | (CH <sub>3</sub> ) <sub>2</sub> COH, CH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub> , $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OCH}_3, \text{NH}_2\text{C}=\text{O} + \text{H}, \\   \\ \text{CH}_2 \end{array}$ |
| 15         | CH <sub>3</sub>   |            | CH <sub>3</sub> OCHCH <sub>3</sub> , CH <sub>3</sub> CHCH <sub>2</sub> OH   |
| 16         | O   | 60         | $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2\text{C}^+ + \text{H}, \text{CH}_2\text{ONO} \\   \\ \text{OH} \end{array}$   |
| 17         | OH  | 61         | $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OCH}_3 + 2\text{H}, \text{CH}_2\text{CH}_2\text{SH}, \text{CH}_2\text{SCH}_3 \end{array}$   |
| 18         | H <sub>2</sub> O, NH <sub>4</sub>   | 65         |  ≡ C <sub>5</sub> H <sub>5</sub>  |
| 19         | F, H <sub>3</sub> O   | 66         |  ≡ C <sub>5</sub> H <sub>6</sub>  |
| 26         | C≡N   | 67         | C <sub>5</sub> H <sub>7</sub>   |
| 27         | C <sub>2</sub> H <sub>3</sub>   | 68         | CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C≡N   |
| 28         | C <sub>2</sub> H <sub>4</sub> , CO, N <sub>2</sub> (air), CH=NH   | 69         | C <sub>5</sub> H <sub>9</sub> , CF <sub>3</sub> , CH <sub>3</sub> CH=CHC=O, CH <sub>2</sub> =C(CH <sub>3</sub> )C=O   |
| 29         | C <sub>2</sub> H <sub>5</sub> , CHO   | 70         | C <sub>5</sub> H <sub>10</sub>  |
| 30         | CH <sub>2</sub> NH <sub>2</sub> , NO  | 71         | C <sub>5</sub> H <sub>11</sub> , C <sub>3</sub> H <sub>7</sub> C=O  |
| 31         | CH <sub>2</sub> OH, OCH <sub>3</sub>  | 72         | $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{C}^+ + \text{H}, \text{C}_3\text{H}_7\text{CHNH}_2, (\text{CH}_3)_2\text{N}=\text{C}=\text{O}, \\   \\ \text{CH}_2 \end{array}$                              |
| 32         | O <sub>2</sub> (Air)  |            | C <sub>2</sub> H <sub>5</sub> NHCHCH <sub>3</sub> , and isomers   |
| 33         | SH, CH <sub>2</sub> F   | 73         | Homologs of 59  |
| 34         | H <sub>2</sub> S  | 74         | $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2-\text{C}-\text{OCH}_3 + \text{H} \\   \\ \text{O} \end{array}$   |
| 35         | Cl  | 75         | $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OC}_2\text{H}_5 + 2\text{H}, \text{CH}_2\text{SC}_2\text{H}_5, (\text{CH}_3)_2\text{CSH}, (\text{CH}_3\text{O})_2\text{CH} \end{array}$                                 |
| 36         | HCl   | 77         | C <sub>6</sub> H <sub>5</sub>   |
| 39         | C <sub>3</sub> H <sub>3</sub>   | 78         | C <sub>6</sub> H <sub>5</sub> + H   |
| 40         | CH <sub>2</sub> C=N, Ar(Air)  | 79         | C <sub>6</sub> H <sub>5</sub> + 2H, Br  |
| 41         | C <sub>3</sub> H <sub>5</sub> , CH <sub>2</sub> C=N + H, C <sub>2</sub> H <sub>2</sub> NH   |            |   |
| 42         | C <sub>3</sub> H <sub>6</sub>   |            |   |
| 43         | C <sub>3</sub> H <sub>7</sub> , CH <sub>3</sub> C=O, C <sub>2</sub> H <sub>5</sub> N  |            |   |
| 44         | $\begin{array}{c} \text{H} \\   \\ \text{CH}_3\text{C}=\text{O} + \text{H}, \text{CH}_3\text{CHNH}_2, \text{CO}_2, \text{NH}_2\text{C}=\text{O}, (\text{CH}_3)_2\text{N} \\   \\ \text{CH}_3 \end{array}$   |            |   |
| 45         | CHOH, CH <sub>2</sub> CH <sub>2</sub> OH, CH <sub>2</sub> OCH <sub>3</sub> , $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{OH}, \text{CH}_3\text{CH}-\text{O} + \text{H} \end{array}$   |            |   |
| 46         | NO <sub>2</sub>   |            |   |
| 47         | CH <sub>2</sub> SH, CH <sub>3</sub> S   |            |   |
| 48         | CH <sub>3</sub> S + H   |            |   |
| 49         | CH <sub>2</sub> Cl  |            |   |
| 51         | CHF <sub>2</sub>  |            |   |
| 53         | C <sub>4</sub> H <sub>5</sub>   |            |   |
| 54         | CH <sub>2</sub> CH <sub>2</sub> C≡N   |            |   |
| 55         | C <sub>4</sub> H <sub>7</sub> , CH <sub>2</sub> =CHC=O  |            |   |
| 56         | C <sub>4</sub> H <sub>8</sub>   |            |   |
| 57         | C <sub>4</sub> H <sub>9</sub> , C <sub>2</sub> H <sub>5</sub> C=O   |            |   |
| 58         | $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}^+ + \text{H}, \text{C}_2\text{H}_5\text{CHNH}_2, (\text{CH}_3)_2\text{NCH}_2, \\   \\ \text{CH}_2 \end{array}$<br>C <sub>2</sub> H <sub>5</sub> NHCH <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> S |            |   |

\*Ions indicated as a fragment + nH (n = 1, 2, 3, ...) are ions that arise via rearrangement involving hydrogen transfer.

| <i>m/e</i> | Ions   | <i>m/e</i> | Ions  |
|------------|--|------------|---|
| 80         |  $\text{CH}_2, \text{CH}_3\text{SS} + \text{H}$   | 94         |  + H,   |
| 81         |  $\text{CH}_2, \text{C}_6\text{H}_9,$    | 95         |    |
| 82         | $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{N}, \text{CCl}_2, \text{C}_6\text{H}_{10}$  | 96         | $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{N}$   |
| 83         | $\text{C}_6\text{H}_{11}, \text{CHCl}_2,$   | 97         | $\text{C}_7\text{H}_{13},$   |
| 85         | $\text{C}_6\text{H}_{13}, \text{C}_4\text{H}_9\text{C}=\text{O}, \text{CClF}_2$  | 98         |  + H   |
| 86         | $\text{C}_3\text{H}_7\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{CH}_2 \end{smallmatrix} + \text{H}, \text{C}_4\text{H}_9\text{CHNH}_2, \text{ and isomers.}$  | 99         | $\text{C}_7\text{H}_{15}, \text{C}_6\text{H}_{11}\text{O}$  |
| 87         | $\text{C}_3\text{H}_7\text{CO},$ homologs of 73, $\text{CH}_2\text{CH}_2\text{COCH}_3$    | 100        | $\text{C}_4\text{H}_9\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{CH}_2 \end{smallmatrix} + \text{H}, \text{C}_5\text{H}_{11}\text{CHNH}_2$  |
| 88         | $\text{CH}_2-\text{C} \begin{smallmatrix} \text{O} \\ \parallel \end{smallmatrix}-\text{OC}_2\text{H}_5 + \text{H}$  | 101        | $\text{C}-\text{OC}_4\text{H}_9$   |
| 89         | $\text{C}-\text{OC}_3\text{H}_7 + 2\text{H},$   | 102        | $\text{CH}_2\text{C} \begin{smallmatrix} \text{O} \\ \parallel \end{smallmatrix}-\text{OC}_3\text{H}_7 + \text{H}$  |
| 90         | $\text{CH}_3\text{CHONO}_2,$    | 103        | $\text{C}-\text{OC}_4\text{H}_9 + 2\text{H}, \text{C}_5\text{H}_{11}\text{S}, \text{CH}(\text{OCH}_2\text{CH}_3)_2$   |
| 91         |  $\text{CH}_2,$  + H,  + 2H,      | 104        | $\text{C}_2\text{H}_5\text{CHONO}_2$  |
|            | $(\text{CH}_2)_4\text{Cl},$   | 105        |  $\text{C}=\text{O},$  $\text{CH}_2\text{CH}_2,$   |
| 92         |  $\text{CH}_2,$  + H,  | 106        |    |
| 93         | $\text{CH}_2\text{Br},$ $\text{C}_7\text{H}_9,$  $\text{C}=\text{O},$  $\text{O},$ $\text{C}_7\text{H}_9$ (terpenes) | 107        |  $\text{CH}_2\text{O},$  $\text{CH}_2, \text{OH}$  |
|            |  | 108        |  $\text{CH}_2\text{O},$ + H,    |







| <i>m/e</i> | Ions  | <i>m/e</i> | Ions  |
|------------|---|------------|---|
| 109        |    | 125        |                                  |
| 111        |    | 127        | I   |
| 119        | CF <sub>3</sub> CF <sub>2</sub> ,   | 131        | C <sub>3</sub> F <sub>5</sub> ,  |
|            |          | 135        | (CH <sub>2</sub> ) <sub>4</sub> Br  |
| 120        |    | 138        |  + H                             |
| 121        |    | 139        |                                 |
|            | C <sub>9</sub> H <sub>13</sub> (terpenes)   | 149        |  + H                           |
| 123        |    | 154        |                                |

# appendix c

## COMMON FRAGMENTS LOST

This list is suggestive rather than comprehensive. It should be used in conjunction with Appendix B. Table 5-19 of Hamming and Foster<sup>7</sup> and Table A-5 of McLafferty<sup>9</sup> are recommended as supplements. All of these are lost as neutral species.

| Molecular Ion Minus | Fragment Lost  | Molecular Ion Minus | Fragment Lost   |
|---------------------|--|---------------------|---|
| 1                   | H·   | 53                  | C <sub>4</sub> H <sub>5</sub>   |
| 15                  | CH <sub>3</sub> ·  | 54                  | CH <sub>2</sub> =CH-CH=CH <sub>2</sub>  |
| 17                  | HO·  | 55                  | CH <sub>2</sub> =CHCHCH <sub>3</sub>  |
| 18                  | H <sub>2</sub> O   | 56                  | CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> CH=CHCH <sub>3</sub> , 2CO   |
| 19                  | F·   | 57                  | C <sub>4</sub> H <sub>9</sub> ·   |
| 20                  | HF   | 58                  | ·NCS, (NO + CO), CH <sub>3</sub> COCH <sub>3</sub>  |
| 26                  | CH≡CH, ·C≡N  |                     |   |
| 27                  | CH <sub>2</sub> =CH·, HC≡N   |                     |   |
| 28                  | CH <sub>2</sub> =CH <sub>2</sub> , CO, (HCN + H)   |                     |   |
| 29                  | CH <sub>3</sub> CH <sub>2</sub> ·, ·CHO  | 59                  | CH <sub>3</sub> OC·, CH <sub>3</sub> CNH <sub>2</sub> ,  |
| 30                  | NH <sub>2</sub> CH <sub>2</sub> ·, CH <sub>2</sub> O, NO   | 60                  | C <sub>3</sub> H <sub>7</sub> OH  |
| 31                  | ·OCH <sub>3</sub> , ·CH <sub>2</sub> OH, CH <sub>3</sub> NH <sub>2</sub>   |                     |   |
| 32                  | CH <sub>3</sub> OH, S  |                     |   |
| 33                  | HS·, (·CH <sub>3</sub> and H <sub>2</sub> O)   | 61                  | CH <sub>3</sub> CH <sub>2</sub> S·,                     |
| 34                  | H <sub>2</sub> S   | 62                  | [H <sub>2</sub> S and CH <sub>2</sub> =CH <sub>2</sub> ]  |
| 35                  | Cl·  | 63                  | ·CH <sub>2</sub> CH <sub>2</sub> Cl   |
| 36                  | HCl, 2H <sub>2</sub> O   | 64                  | C <sub>5</sub> H <sub>4</sub> , S <sub>2</sub> , SO <sub>2</sub>  |
| 37                  | H <sub>2</sub> Cl (or HCl + H)   |                     |   |
| 38                  | C <sub>3</sub> H <sub>2</sub> ·, C <sub>2</sub> N, F <sub>2</sub>  |                     |   |
| 39                  | C <sub>3</sub> H <sub>3</sub> , HC <sub>2</sub> N  |                     |   |
| 40                  | CH <sub>3</sub> C≡CH   |                     |   |
| 41                  | CH <sub>2</sub> =CHCH <sub>2</sub> ·   | 68                  |  CH <sub>2</sub>   |
| 42                  | CH <sub>2</sub> =CHCH <sub>3</sub> , CH <sub>2</sub> =C=O, CH <sub>2</sub> -CH <sub>2</sub> , NCO, NCNH <sub>2</sub>                         | 69                  | CF <sub>3</sub> ·, C <sub>5</sub> H <sub>9</sub> ·  |
| 43                  | C <sub>3</sub> H <sub>7</sub> ·, CH <sub>3</sub> C·, CH <sub>2</sub> =CH-O·, [CH <sub>3</sub> · and CH <sub>2</sub> =CH <sub>2</sub> ], HCNO | 71                  | C <sub>5</sub> H <sub>11</sub> ·  |
| 44                  | CH <sub>2</sub> =CHOH, CO <sub>2</sub> , N <sub>2</sub> O, CONH <sub>2</sub> , NHCH <sub>2</sub> CH <sub>3</sub>                             |                     |   |
| 45                  | CH <sub>3</sub> CHOH, CH <sub>3</sub> CH <sub>2</sub> O·, CO <sub>2</sub> H, CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>                 | 73                  |  O   |
| 46                  | [H <sub>2</sub> O and CH <sub>2</sub> =CH <sub>2</sub> ], CH <sub>3</sub> CH <sub>2</sub> OH, ·NO <sub>2</sub>                               | 74                  | CH <sub>3</sub> CH <sub>2</sub> OC·   |
| 47                  | CH <sub>3</sub> S·   | 75                  | C <sub>4</sub> H <sub>9</sub> OH  |
| 48                  | CH <sub>3</sub> SH, SO, O <sub>3</sub>   | 76                  | C <sub>6</sub> H <sub>3</sub>   |
| 49                  | ·CH <sub>2</sub> Cl  | 77                  | C <sub>6</sub> H <sub>4</sub> , CS <sub>2</sub>   |
| 51                  | ·CHF <sub>2</sub>  | 78                  | C <sub>6</sub> H <sub>5</sub> , CS <sub>2</sub> H   |
| 52                  | C <sub>4</sub> H <sub>4</sub> , C <sub>2</sub> N <sub>2</sub>  | 79                  | C <sub>6</sub> H <sub>6</sub> , CS <sub>2</sub> H <sub>2</sub> , C <sub>5</sub> H <sub>4</sub> N  |
|                     |  | 80                  | Br·, C <sub>5</sub> H <sub>5</sub> N  |
|                     |  | 85                  | HBr   |
|                     |  | 100                 | ·CClF <sub>2</sub>  |
|                     |  | 119                 | CF <sub>2</sub> =CF <sub>2</sub>  |
|                     |  | 122                 | CF <sub>3</sub> -CF <sub>2</sub> ·  |
|                     |  | 127                 | C <sub>6</sub> H <sub>5</sub> COOH  |
|                     |  | 128                 | I·  |
|                     |  |                     | HI  |





The importance of infrared spectrometry as a tool of the practicing organic chemist is readily apparent from the number of books devoted wholly or in part to discussions of applications of infrared spectrometry (see References<sup>1-31</sup> at the end of the chapter.)

The text by Colthup, Daly, and Wiberley<sup>3</sup> is a thorough up-to-date discourse on infrared and Raman spectroscopy covering theory, practice, and structure correlations. Bellamy's books<sup>8,9</sup> include extensive discussions of infrared correlations from the literature and many tables of data. The book by Conley<sup>1</sup> is an introduction to theory, spectral determination, and spectral interpretation at an elementary level. There are many compilations of spectra as well as indices to spectral collections and to the literature.<sup>7-25</sup> Among the more commonly used compilations are those by Sadtler<sup>25</sup> and by Aldrich.<sup>7</sup>

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## I. INTRODUCTION

Infrared radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. Of greatest practical use to the organic chemist is the limited portion between  $4000\text{ cm}^{-1}$  and  $666\text{ cm}^{-1}$  ( $2.5\text{-}15.0\text{ }\mu\text{m}$ ). Recently there has been some interest in the near infrared region,  $14,290\text{-}4000\text{ cm}^{-1}$  ( $0.7\text{-}2.5\text{ }\mu\text{m}$ ) and the far infrared region,  $700\text{-}200\text{ cm}^{-1}$  ( $14.3\text{-}50\text{ }\mu\text{m}$ ).

From the brief theoretical discussion that follows, it is clear that even a very simple molecule can give an extremely complex spectrum. The organic chemist takes advantage of this complexity when he matches the spectrum of an unknown compound against that of an authentic sample. A peak-by-peak correlation is excellent evidence for identity. It is unlikely that any two compounds, except enantiomers, give the same infrared spectrum.

Although the infrared spectrum is characteristic of the entire molecule, it is true that certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule. It is the persistence of these characteristic bands that permits the chemist to obtain useful structural information by simple inspection and reference to generalized charts of characteristic group frequencies. We shall rely heavily on these characteristic group frequencies.

Since we are not solely dependent on infrared spectra for identification, a detailed analysis of the spectrum will not be required. Following our general plan, we shall present only sufficient theory to accomplish our purpose: utilization of infrared spectra in conjunction with other spectral data to determine molecular structure.

Because most academic and industrial laboratories make infrared spectrometers available as bench tools for the organic chemist, we shall describe instrumentation and sample preparation in somewhat more detail than is given in the other chapters.

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## II. THEORY

Infrared radiation of frequencies less than about  $100\text{ cm}^{-1}$  (wavelengths longer than  $100\text{ }\mu\text{m}$ ) is absorbed and converted by an organic molecule into energy of molecular rotation. This absorption is quantized; thus a molecular rotation spectrum consists of discrete lines.

Infrared radiation in the range from about  $10,000\text{-}100\text{ cm}^{-1}$  ( $1\text{-}100\text{ }\mu\text{m}$ ) is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption is also quantized, but vibrational spectra appear as bands rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes. It is with these vibrational-rotational bands, particularly those occurring between  $4000\text{ cm}^{-1}$  and  $666\text{ cm}^{-1}$  ( $2.5\text{-}15\text{ }\mu\text{m}$ ), that we shall be concerned. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms.

Band positions in infrared spectra are presented either as wavenumbers or wavelengths. The wavenumber unit ( $\text{cm}^{-1}$ , reciprocal centimeters) is used most often since it is directly proportional to the energy of the vibration and since most modern instruments are linear in the  $\text{cm}^{-1}$  scale. Wavelength is reported in micrometers ( $\mu\text{m}$ ,  $10^{-6}$  meters) although the older literature refers to this quantity as the micron ( $\mu$ ). Wavenumbers are reciprocally related to wavelength as follows:

$$\text{cm}^{-1} = \frac{1}{\mu\text{m}} \times 10^4$$

Specific absorptions and absorption ranges will be given in  $\text{cm}^{-1}$ , with the corresponding  $\mu\text{m}$  data adjoining (usually in parentheses).

Notice also that the wavenumbers ( $\bar{\nu}$ ) are often called "frequencies"; this is not rigorously correct, since wave-

numbers are  $1/\lambda$  and frequency ( $\nu$ ) is  $c/\lambda$ . Such “frequency” for  $\nu$  terminology is quite common and is probably not a serious error if the missing speed-of-light term ( $c$ ) is remembered. Spectra linear in  $\mu\text{m}$  and in  $\text{cm}^{-1}$  are used in this book. A spectrum linear in wavenumbers has a very different appearance from one linear in wavelength, as shown later (Figure 7, p. 105).

Band intensities are expressed either as transmittance ( $T$ ) or absorbance ( $A$ ). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm, to the base 10, of the reciprocal of the transmittance;  $A = \log_{10} (1/T)$ .

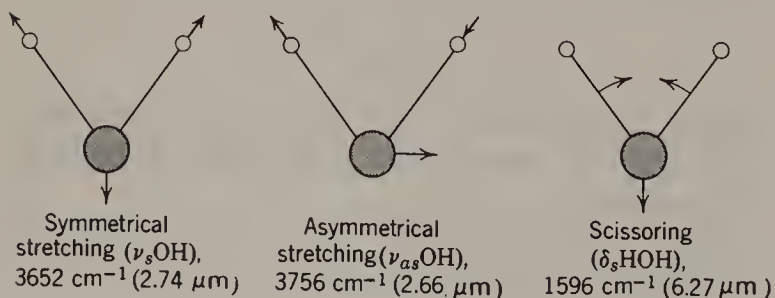
There are two types of molecular vibrations: stretching and bending. A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. A bending vibration may consist of a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another. For example, twisting, rocking, and torsional vibrations involve a change in bond angles with reference to a set of coordinates arbitrarily set up within the molecule.

Only those vibrations that result in a rhythmical change in the dipole moment of the molecule are observed in the infrared. The alternating electric field, produced by the changing charge distribution accompanying a vibration, couples the molecular vibration with the oscillating electric field of the electromagnetic radiation.

A molecule has as many degrees of freedom as the total degrees of freedom of its individual atoms. Each atom has 3 degrees of freedom corresponding to the Cartesian coordinates ( $x, y, z$ ) necessary to describe its position relative to other atoms in the molecule. A molecule of  $n$  atoms therefore has  $3n$  degrees of freedom. For nonlinear molecules, 3 degrees of freedom describe rotation and 3 describe translation; the remaining  $3n - 6$  degrees of freedom are vibrational degrees of freedom or fundamental vibrations. Linear molecules have  $3n - 5$  vibrational degrees of freedom, for only two degrees of freedom are required to describe rotation.

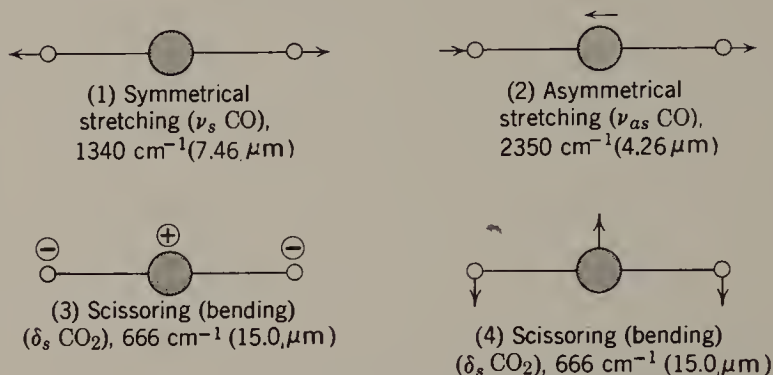
Fundamental vibrations involve no change in the center of gravity of the molecule.

The three fundamental vibrations of the nonlinear, triatomic water molecule can be depicted as follows:



Note the very close spacing of the interacting (“coupled”) asymmetric and symmetric stretching above compared with the far removed scissoring mode. This will be shown to be useful later in classification of absorptions and application to structure determination.

The  $\text{CO}_2$  molecule is linear and contains three atoms; therefore it has four fundamental vibrations ( $(3 \times 3) - 5$ ):



$\oplus$  and  $\ominus$  indicate movement perpendicular to the plane of the page.

The symmetrical stretching vibration (1) is inactive in the infrared since it produces no change in the dipole moment of the molecule. The bending vibrations (3) and (4) are equivalent, and are the resolved components of bending motion oriented at any angle to the internuclear axis; they have the same frequency and are said to be doubly degenerate.

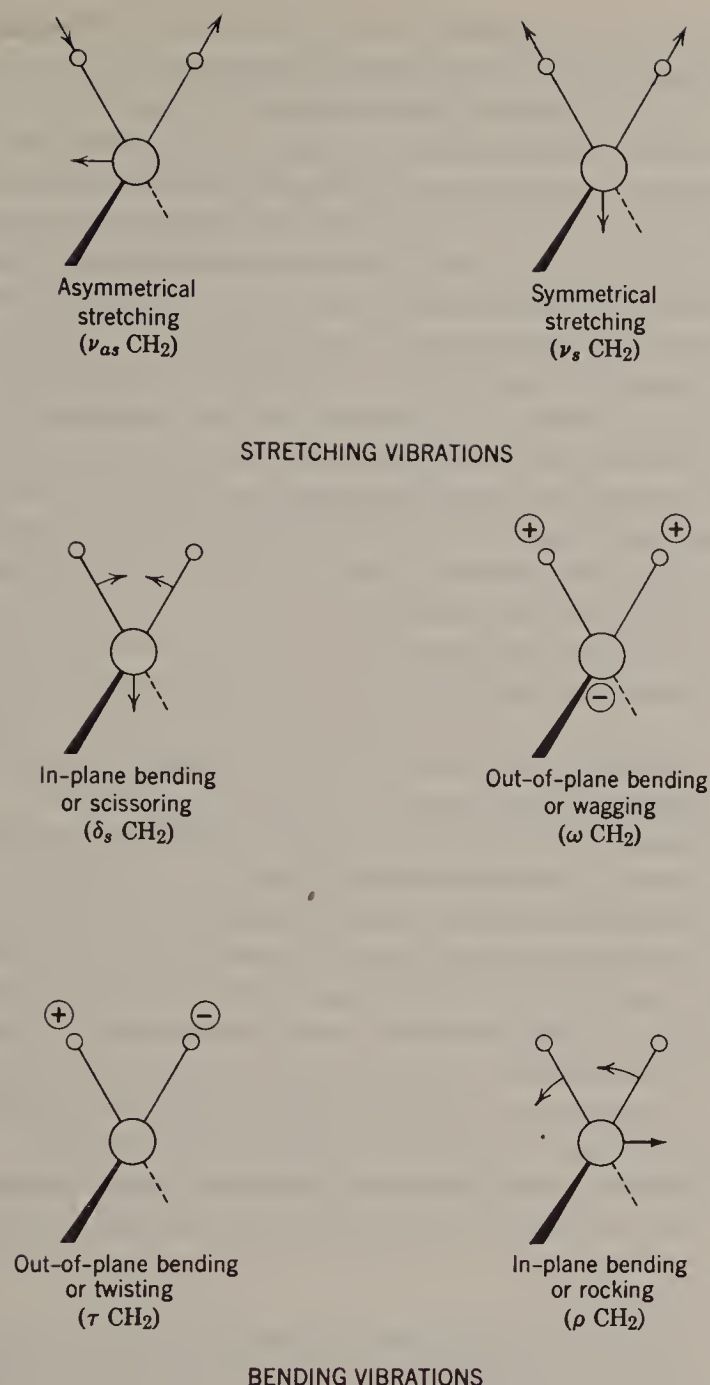
The various stretching and bending modes for an  $\text{AX}_2$  group appearing as a portion of a molecule, for example, the  $\text{CH}_2$  group in a hydrocarbon molecule, are shown in Figure 1. The  $3n - 6$  rule does not apply since the  $\text{CH}_2$  represents only a portion of a molecule.

The theoretical number of fundamental vibrations (absorption frequencies) will seldom be observed because overtones (multiples of a given frequency) and combination tones (sum of two other vibrations) increase the number of bands, whereas other phenomena reduce the number of bands. The following will reduce the theoretical number of bands:

1. Fundamental frequencies that fall outside of the 2.5-15  $\mu\text{m}$  region.
2. Fundamental bands that are too weak to be observed.
3. Fundamental vibrations that are so close that they coalesce.
4. The occurrence of a degenerate band from several absorptions of the same frequency in highly symmetrical molecules.
5. The failure of certain fundamental vibrations to appear in the infrared because of lack of required change in dipole character of the molecule.

Assignments for stretching frequencies can be approximated by the application of Hooke's law. In the application





**Figure 1.** *Vibrational modes for a CH<sub>2</sub> group. (⊕ and ⊖ indicate movement perpendicular to the plane of the page.)*

of the law, 2 atoms and their connecting bond are treated as a simple harmonic oscillator composed of 2 masses joined by a spring. The following equation, derived from Hooke's law, states the relationship between frequency of oscillation, atomic masses, and the force constant of the bond.

$$\nu = \frac{1}{2\pi c} \left( \frac{f}{\frac{M_x M_y}{M_x + M_y}} \right)^{1/2}$$

where  $\nu$  = the vibrational frequency ( $\text{cm}^{-1}$ )  
 $c$  = velocity of light ( $\text{cm/sec}$ )  
 $f$  = force constant of bond ( $\text{dynes/cm}$ )

$M_x$  and  $M_y$  = mass (g) of atom  $x$  and atom  $y$ , respectively.

The value of  $f$  is approximately  $5 \times 10^5$  dynes per cm for single bonds and approximately 2 and 3 times this value for double bonds and triple bonds, respectively.

Application of the formula to C-H stretching using  $19.8 \times 10^{-24}$  g and  $1.64 \times 10^{-24}$  g as mass values for C and H, respectively, places the frequency of the C-H bond vibration at  $3040 \text{ cm}^{-1}$  ( $3.30 \mu\text{m}$ ). Actually, C-H stretching vibrations, associated with methyl and methylene groups, are generally observed in the region between  $2960\text{--}2850 \text{ cm}^{-1}$  ( $3.38\text{--}3.51 \mu\text{m}$ ). The calculation is not precise because effects arising from the environment of the C-H within a molecule have been ignored. The frequency of infrared absorption is commonly used to calculate the force constants of bonds.

The shift in absorption frequency following deuteration is often employed in the assignment of C-H stretching frequencies. The above equation can be used to estimate the change in stretching frequency as the result of deuteration. The term  $M_x M_y / (M_x + M_y)$  will be equal to  $MCMH / (MC + MH)$  for the C-H compound. Since  $MC \gg MH$ , this term is approximately equal to  $MCMH / MC$  or to  $MH$ . Thus, for the C-D compound the term is equal to  $MD$ , and the frequency by Hooke's law application is inversely proportional to the square root of the mass of the isotope of hydrogen, and the ratio of the C-H to C-D stretching frequencies should equal  $\sqrt{2}$ . If the ratio of the frequencies, following deuteration, is much less than  $\sqrt{2}$ , we can assume that the vibration is not simply a C-H stretching vibration, but rather a mixed vibration involving interaction (coupling) with another vibration.

Calculations place the stretching frequencies of the following bonds in the general absorption regions indicated.

|                    |  |
|--------------------|--|
| C-C, C-O, C-N      | 1300-800 $\text{cm}^{-1}$ ( $7.7\text{--}12.5 \mu\text{m}$ ) |
| C=C, C=O, C=N, N=O | 1900-1500 $\text{cm}^{-1}$ ( $5.3\text{--}6.7 \mu\text{m}$ ) |
| C≡C, C≡N           | 2300-2000 $\text{cm}^{-1}$ ( $4.4\text{--}5.0 \mu\text{m}$ ) |
| C-H, O-H, N-H      | 3800-2700 $\text{cm}^{-1}$ ( $2.6\text{--}3.7 \mu\text{m}$ ) |

To approximate the vibrational frequencies of bond stretching by Hooke's law, the relative contributions of bond strengths and atomic masses must be considered. For example, a superficial comparison of the C-H group with the F-H group, on the basis of atomic masses, might lead to the conclusion that the stretching frequency of the F-H bond should occur at a lower frequency than that for the C-H bond. However, the increase in the force constant from left to right across the first two rows of the periodic table has a greater effect than the mass increase. Thus, the F-H group absorbs at a higher frequency ( $4138 \text{ cm}^{-1}$ ,  $2.42 \mu\text{m}$ ) than the C-H group ( $3040 \text{ cm}^{-1}$ ,  $3.30 \mu\text{m}$ ).



In general, functional groups that have a strong dipole give rise to strong absorptions in the infrared.

## COUPLED INTERACTIONS

When two bond oscillators share a common atom, they seldom behave as individual oscillators unless the individual oscillation frequencies are widely different. This is because there is mechanical coupling interaction between the oscillators. For example, the carbon dioxide molecule, which consists of two C=O bonds with a common carbon atom, has two fundamental stretching vibrations: an asymmetrical and a symmetrical stretching mode. The symmetrical stretching mode consists of an in-phase stretching or contracting of the C to O bonds, and absorption occurs at a wavelength longer than that observed for the carbonyl group in an aliphatic ketone. The symmetrical stretching mode produces no change in the dipole moment of the molecule and is therefore "inactive" in the infrared, but is easily observed in the Raman spectrum\* near  $1340\text{ cm}^{-1}$  ( $7.46\text{ }\mu\text{m}$ ). In the asymmetrical stretching mode, the two C to O bonds stretch out of phase; one C=O bond stretches as the other contracts. The asymmetrical stretching mode, since it produces a change in the dipole moment, is infrared active; the absorption ( $2350\text{ cm}^{-1}$ ,  $4.26\text{ }\mu\text{m}$ ) is at a shorter wavelength (higher frequency) than observed for a carbonyl group in aliphatic ketones.

This difference in carbonyl absorption frequencies displayed by the carbon dioxide molecule results from strong mechanical coupling or interaction. In contrast, 2 ketonic carbonyl groups separated by 1 or more carbon atoms show normal carbonyl absorption near  $1715\text{ cm}^{-1}$  ( $4.83\text{ }\mu\text{m}$ ) because appreciable coupling is apparently prevented by the intervening carbon atom(s).

Coupling accounts for the two N-H stretching bands in the  $3497\text{--}3077\text{ cm}^{-1}$  ( $2.86\text{--}3.25\text{ }\mu\text{m}$ ) region in primary amine and primary amide spectra, for the two C=O stretching bands in the  $1818\text{--}1720\text{ cm}^{-1}$  ( $5.50\text{--}5.81\text{ }\mu\text{m}$ ) region in carboxylic anhydride and imide spectra, and for the two C-H stretching bands in the  $3000\text{--}2760\text{ cm}^{-1}$  ( $3.33\text{--}3.62\text{ }\mu\text{m}$ ) region for both methylene and methyl groups.

Useful characteristic group frequency bands often involve coupled vibrations. The spectra of alcohols have a strong band in the region between  $1212\text{ to }1000\text{ cm}^{-1}$  ( $8.25\text{--}10.00\text{ }\mu\text{m}$ ), which is usually designated as the "C-O stretching band." In the spectrum of methanol this band is at  $1034\text{ cm}^{-1}$  ( $9.67\text{ }\mu\text{m}$ ); in the spectrum of ethanol it occurs at  $1053\text{ cm}^{-1}$  ( $9.50\text{ }\mu\text{m}$ ). Branching and unsaturation produce absorption characteristic of these structures (see alcohols). It is evident that we are not dealing with an

isolated C-O stretching vibration, but rather a coupled asymmetric vibration involving C-C-O stretching.

Vibrations resulting from bond angle changes frequently couple in a manner similar to stretching vibrations. Thus, the ring C-H out-of-plane bending frequencies of aromatic molecules depend on the number of adjacent hydrogen atoms on the ring; coupling between the hydrogen atoms is affected by the bending of the C-C bond in the ring to which the hydrogen atoms are attached.

Interaction arising from coupling of stretching and bending vibrations is illustrated by the absorption of secondary acyclic amides. Secondary acyclic amides, which exist predominantly in the *trans* conformation, show strong absorption in the  $1563\text{--}1515\text{ cm}^{-1}$  ( $6.40\text{--}6.60\text{ }\mu\text{m}$ ) region; this absorption involves coupling of the N-H bending and C-N stretching vibrations.

The requirements for effective coupling interaction may be summarized as follows:

1. The vibrations must be of the same symmetry species if interaction is to occur.
2. Strong coupling between stretching vibrations requires a common atom between the groups.
3. Interaction is greatest when the coupled groups absorb, individually, near the same frequency.
4. Coupling between bending and stretching vibrations can occur if the stretching bond forms one side of the changing angle.
5. A common bond is required for coupling of bending vibrations.
6. Coupling is negligible when groups are separated by one or more carbon atoms and the vibrations are mutually perpendicular.

**HYDROGEN BONDING.** Hydrogen bonding can occur in any system containing a proton donor group (X-H) and a proton acceptor (Y) if the *s* orbital of the proton can effectively overlap the *p* or  $\pi$  orbital of the acceptor group. Atoms X and Y are electronegative with Y possessing lone pair electrons. The common proton donor groups in organic molecules are carboxyl, hydroxyl, amine, or amide groups. Common proton acceptor atoms are oxygen, nitrogen, and the halogens. Unsaturated groups, such as the ethylenic linkage, can also act as proton acceptors.

The strength of the hydrogen bond is at a maximum when the proton donor group and the axis of the lone pair orbital are collinear. The strength of the bond is inversely proportional to the distance between X and Y.

Hydrogen bonding alters the force constant of both groups; thus, the frequencies of both stretching and bending vibrations are altered. The X-H stretching bands move to lower frequencies (longer wavelengths) usually with increased intensity and band widening. The stretching frequency of the acceptor group, for example, C=O, is also reduced but to a lesser degree than the proton donor

\*Band intensity in Raman spectra depends upon bond polarizability rather than molecular dipole changes.

group. The H–X bending vibration usually shifts to a shorter wavelength when bonding occurs; this shift is less pronounced than that of the stretching frequency.

Intermolecular hydrogen bonding involves association of two or more molecules of the same or different compounds. Intermolecular bonding may result in dimer molecules (as observed for carboxylic acids) or in polymer molecules, which exist in neat samples or concentrated solutions of monohydroxy alcohols. Intramolecular hydrogen bonds are formed when the proton donor and acceptor are present in a single molecule under spatial conditions that allow the required overlap of orbitals, for example, the formation of a 5- or 6-membered ring. The extent of both inter- and intra-molecular bonding is temperature dependent. The effect of concentration on intermolecular and intramolecular hydrogen bonding is markedly different. The bands that result from intermolecular bonding generally disappear at low concentrations (less than about 0.01 *M* in nonpolar solvents). Intramolecular hydrogen bonding is an internal effect and persists at very low concentrations.

The change in frequency between “free” OH absorption and bonded OH absorption is a measure of the strength of the hydrogen bond. Ring strain, molecular geometry, and the relative acidity and basicity of the proton donor and acceptor groups affect the strength of bonding. Intramolecular bonding involving the same bonding groups is stronger when a 6-membered ring is formed than when a smaller ring results from bonding. Hydrogen bonding is strongest when the bonded structure is stabilized by resonance.

The effects of hydrogen bonding on the stretching frequencies of hydroxyl and carbonyl groups are summarized in Table I.

An important aspect of hydrogen bonding involves interaction between functional groups of solvent and solute. If the solute is polar, then it is important to note the solvent used and the solute concentration.

**FERMI RESONANCE.** As we have seen in our discussion of interaction, coupling of two fundamental vibrational modes will produce two new modes of vibration, with frequencies higher and lower than that observed when interaction is absent. Interaction can also occur between fundamental vibrations and overtones or combination-tone vibrations. Such interaction is known as Fermi resonance. One example of Fermi resonance is afforded by the absorption pattern of carbon dioxide. In our discussion of interaction, we indicated that the symmetrical stretching band of CO<sub>2</sub> appears in the Raman spectrum near 1340 cm<sup>−1</sup> (7.46 μm). Actually two bands are observed; one at 1286 cm<sup>−1</sup> (7.78 μm), one at 1388 cm<sup>−1</sup> (7.20 μm). The splitting results from coupling between the fundamental C=O stretching vibration, near 1340 cm<sup>−1</sup> (7.46 μm), and the first overtone of the bending vibration. The fundamental bending vibration occurs near 666 cm<sup>−1</sup> (15.00 μm), the first overtone near 1334 cm<sup>−1</sup> (7.55 μm).

Fermi resonance is a common phenomenon in infrared and Raman spectra. It requires that the vibrational levels be of the same symmetry species and that the interacting groups be located in the molecule so that mechanical coupling is appreciable.

An example of Fermi resonance in an organic structure is the “doublet” appearance of the C=O stretch of cyclopentanone under sufficient resolution conditions. Figure 2 shows the appearance of the spectrum of cyclopentanone under the usual conditions. With adequate resolution (Fig-

**Table I. Stretching Frequencies in Hydrogen Bonding**

| X–H ··· Y<br>Strength | Intermolecular Bonding                                  |                   |   | Intramolecular Bonding                                  |                   |  |
|-----------------------|---|-------------------|---|---|-------------------|--|
|                       | Frequency Reduction<br>(cm <sup>−1</sup> ) <sup>a</sup> |                   |   | Frequency Reduction<br>(cm <sup>−1</sup> ) <sup>a</sup> |                   |  |
|                       | νOH   | νC=O <sup>b</sup> | Compound Class  | νOH   | νC=O <sup>b</sup> | Compound Class   |
| Weak                  | 300   | 15                | Alcohols, phenols, and<br>intermolecular hydroxyl<br>to carbonyl bonding. | < 100   | 10                | 1,2-diols; α- and most β-<br>hydroxy ketones; o-chloro<br>and o-alkoxy phenols                         |
| Medium                |   |                   |   | 100-300   | 50                | 1,3-diols; some β-hydroxy<br>ketones; β-hydroxy amino<br>compounds; β-hydroxy<br>nitro compounds       |
| Strong                | > 500   | 50                | RCOOH dimers  | > 300   | 100               | o-hydroxy aryl ketones;<br>o-hydroxy aryl acids;<br>o-hydroxy aryl esters;<br>β-diketones; tropolones. |

<sup>a</sup>Frequency shift relative to “free” stretching frequencies.

<sup>b</sup>Carbonyl stretching only where applicable.



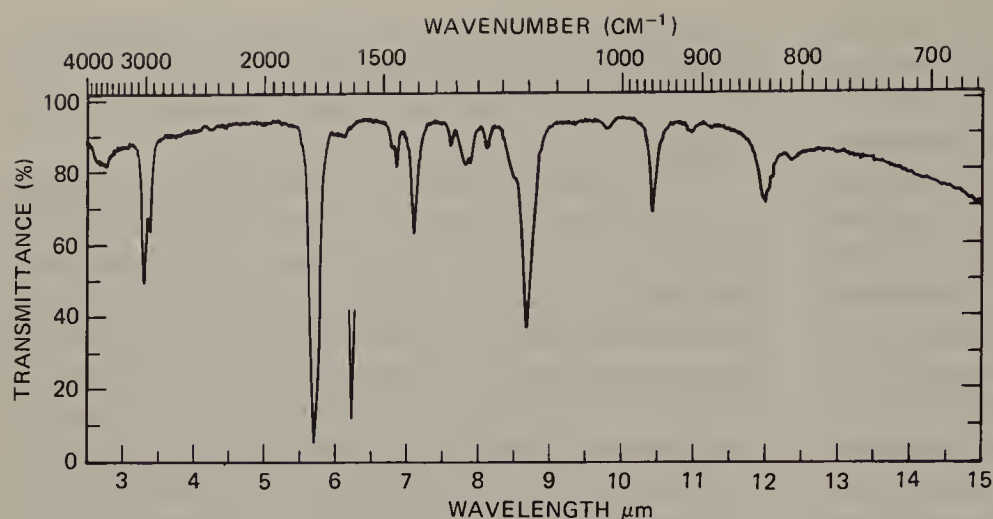


Figure 2. Cyclopentanone, liquid film.

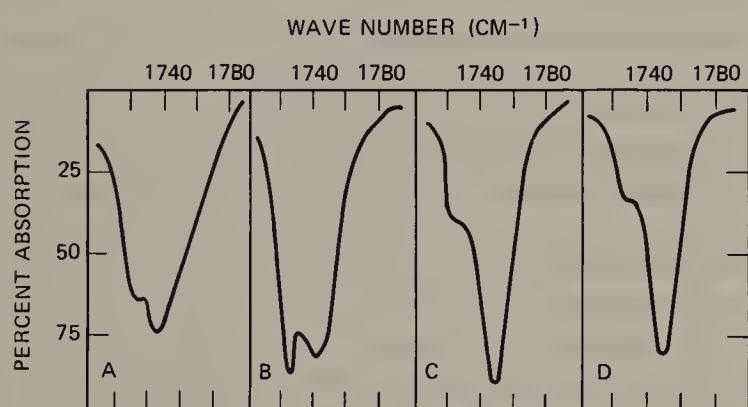


Figure 3. Infrared spectrum of cyclopentanone in various media. A. Carbon tetrachloride solution (0.15 molar). B. Carbon disulfide solution (0.023 molar). C. Chloroform solution (0.025 molar). D. Liquid state (thin films). (Computed spectral slit width  $2\text{ cm}^{-1}$ .)

ure 3), Fermi resonance with an overtone or combination band of an  $\alpha$ -methylene group shows two absorptions in the carbonyl stretch region.

### III. INSTRUMENTATION

The modern double-beam infrared spectrophotometer consists of five principal sections: source (radiation), sampling area, photometer, grating (monochromator), and detector (thermocouple). A diagram of the optical system of a double-beam infrared spectrophotometer is shown in Figure 4.

**RADIATION SOURCE.** Infrared radiation is produced by electrically heating a source, often a Nernst filament or

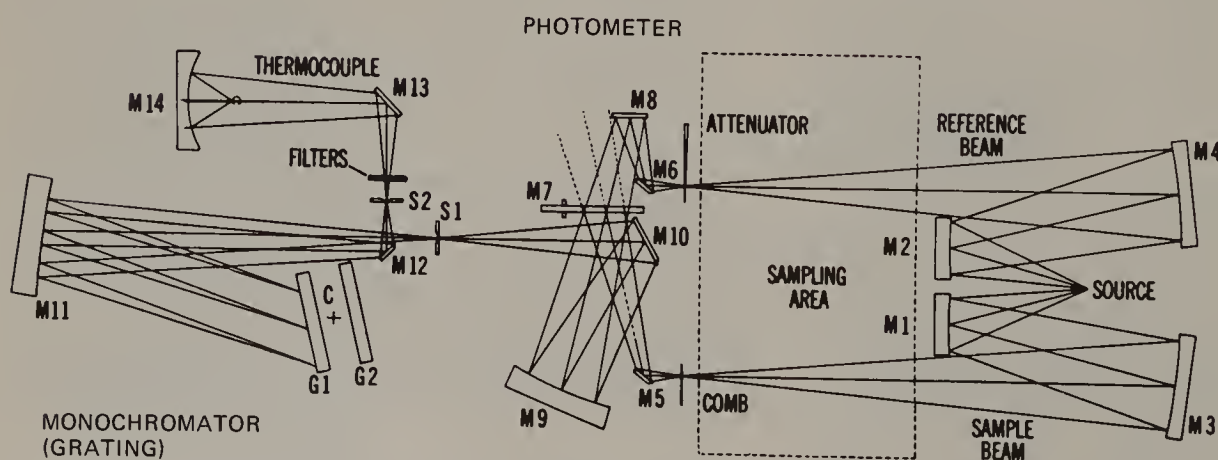


Figure 4. Optical system of double-beam infrared spectrophotometer.



a Globar, to 1000-1800°C. The Nernst filament is fabricated from a binder and oxides of zirconium, thorium, and cerium. The Globar is a small rod of silicon carbide. The image of the source must be wider than the maximum width of the slits (see Reference 1). The maximum radiation for the Globar occurs in the 5500-5000  $\text{cm}^{-1}$  (1.8-2.0  $\mu\text{m}$ ) region and drops off by a factor of about 600 as the 600  $\text{cm}^{-1}$  (16.7  $\mu\text{m}$ ) region is approached. The Nernst filament furnishes maximum radiation energy at about 7100  $\text{cm}^{-1}$  (1.4  $\mu\text{m}$ ) and drops by a factor of about 1000 as the lower frequency region is approached.

The radiation from the source is divided into two beams by mirrors *M1* and *M2*. The two beams, reference beam and sample beam, are focused in to the sample area by mirrors *M3* and *M4*.

**SAMPLING AREA.** Reference and sample beams enter the sampling area and pass through the reference cell and sampling cell, respectively. Opaque shutters, mounted on the source housing, permit blocking of either beam independently. The sampling area of a precision spectrophotometer accommodates a wide variety of sampling accessories varying from gas cells of 40 m effective path to microcells.

**PHOTOMETER.** The reference beam passes through the attenuator (see below) and is reflected by mirrors *M6* and *M8* to the rotating sector mirror *M7*, which alternately reflects the reference beam out of the optical system and transmits the beam to mirror *M9*. The reference beam is now an intermittent beam with a "frequency" of from 8 to 13 cycles per second depending on the particular instrument. This beam is focused by mirror *M10* on the slit *S1*. The sample beam passes through the comb (see below) and is reflected by mirror *M5* to the rotating sector mirror *M7*, which alternately transmits the beam out of the optical system and reflects it to mirror *M9*, thence to mirror *M10* and slit *S1*.

At any given moment, the beam focused on slit *S1* is either the reference beam, which was transmitted by the rotating sector mirror *M7*, or the sample beam, which was reflected by *M7*. In other words, the reference beam and the sample beam have been combined into a single beam of alternating segments; this establishes a switching frequency at the detector equal to the speed of rotation of *M7*.

When the beams are of equal intensity, the instrument is at an optical null. The comb in the sample beam permits balancing the beams. The recording pen is then at 100% transmittance when no sample is present.

The attenuator is driven in and out of the reference beam in response to the signal created at the detector by the sample beam. Thus, when the sample beam is absorbed by the sample, the attenuator is driven into the reference beam until its intensity matches that of the sample beam.

**MONOCHROMATOR.** The combined beam passes through the monochromator entrance slit *S1* to the mirror *M11*, which reflects it to the diffraction grating *G1*. This

beam is dispersed into various frequencies; this beam is reflected back to mirror *M11*, subsequently to mirror *M12*. *M12* focuses the beam on exit slit *S2*. The width of the frequency range focused on slit *S2* is determined by the width of entrance slit *S1* and the dispersing power of the grating. The frequency band of one dispersed beam focused on slit *S2* at any moment is determined by the angle of grating *G1* at that moment. Rotation of grating *G1* produces a scan of frequency bands at exit slit *S2* and thus at the detector. Filters are automatically inserted into the radiation path at the exit slit in a sequence during scanning to eliminate all unwanted radiation; this unwanted radiation corresponds to harmonic multiples of the frequency to be measured.

Maximum resolution is obtained by using gratings only in the range of greatest dispersing effectiveness. Therefore, often in a high-resolution instrument, two or more gratings are used (*G1* and *G2* of Figure 4).

The narrower the slit width, the greater is the resolution. Here again, some compromise is necessary because of the decreased energy output of the source at lower frequencies (longer wavelengths). On most instruments, the slit width is programmed to increase as the emitted source energy decreases, so that constant reference beam energy enters the monochromator.

**DETECTOR (THERMOCOUPLE).** After leaving the exit slit of the monochromator, the beam is reflected by a flat mirror *M13* to an ellipsoidal mirror *M14*. The foci of the ellipsoidal mirror are the exit slit *S2* and the detector.

The detector is a device that measures radiant energy by means of its heating effect. Two common types of detectors are the thermocouple and bolometer. In the thermocouple detector, the radiant energy heats one of two bimetallic junctions, and an emf is produced between the two junctions proportional to the degree of heating. The bolometer changes its resistance upon heating. It serves as one arm of a bridge so that a change in temperature will cause an unbalanced signal across the circuit. The unbalanced signal can be amplified and recorded or used to activate a servo-mechanism to re-establish a balance.

Since the detector sees alternately the reference and the sample beam at a switching frequency determined by the rotation of the sector mirror, any change in the intensity of the radiation due to absorption is detected as an off-null signal.

The amplified off-null signal of the detector is used to position the optical attenuator so that the radiation from the reference and sample beams are kept at equal intensity. The amount of attenuation required is a direct measure of the absorption by the sample. The movement of the attenuator is recorded by the recording chart pen.

In recent years Fourier Transform instruments have become available. FT IR allows analysis of very small samples.

## IV. SAMPLE HANDLING

Infrared spectra may be obtained for gases, liquids, or solids.

1. The spectra of gases or low-boiling liquids may be obtained by expansion of the sample into an evacuated cell. Cells equipped with freeze-out tips are used for sample concentration and cell evacuation prior to expansion of the sample into the cell. Gas cells are available in lengths of a few centimeters to 40 meters. The sampling area of a standard infrared spectrophotometer will not accommodate cells much longer than 10 cm; long paths are achieved by multiple reflection optics.

The vapor phase technique is limited because of the relatively large percentage of compounds that do not have sufficiently high vapor pressures to produce a useful absorption spectrum. However, the usefulness of the technique can be extended by heating the cell.

2. Liquids may be examined neat or in solution. Neat liquids are examined between salt plates usually without a spacer. Pressing a liquid sample between flat plates produces a film of 0.01 mm or less in thickness, the plates being held together by capillarity. Samples of 1-10 mg are required. Thick samples of neat liquids usually absorb too strongly to produce a satisfactory spectrum. Volatile liquids are examined in sealed cells with very thin spacers. Silver chloride or KRS-5 plates may be used for samples that dissolve sodium chloride plates.

Solutions are handled in cells of 0.1-1 mm thickness. Volumes of 0.1-1 ml of 0.05-10% solutions are required for readily available cells (Figure 5). A compensating cell, containing pure solvent, is placed in the reference beam. The spectrum thus obtained is that of the solute except in those regions in which the solvent absorbs strongly. For example, thick samples of carbon tetrachloride absorb strongly near  $800\text{ cm}^{-1}$  ( $12.50\text{ }\mu\text{m}$ ); compensation for this band is ineffective since strong absorption prevents any radiation from reaching the detector.

The solvent selected must be dry and reasonably transparent in the region of interest. When the entire spectrum is of interest, several solvents must be used. A common pair of solvents is carbon tetrachloride and carbon disulfide. Carbon tetrachloride is relatively free of absorption at frequencies above  $1333\text{ cm}^{-1}$  (shorter than  $7.50\text{ }\mu\text{m}$ ) whereas carbon disulfide shows little absorption below  $1333\text{ cm}^{-1}$  (longer than  $7.50\text{ }\mu\text{m}$ ). Solvent and solute combinations that react must be avoided. For example, carbon disulfide cannot be used as a solvent for primary or secondary amines. Amino alcohols react slowly with carbon disulfide and carbon tetrachloride.

When only very small samples are available, ultramicro cavity cells are used in conjunction with a beam condenser. The smallest commercially available cell has a path length of approximately 0.05 mm and a capacity of about 0.8 microliter.\* A spectrum can thus be obtained on a few micrograms of sample in solution. When volatility permits, the solute can be recovered for examination by other spectrometric techniques.

The absorption patterns of selected solvents and mulling oils are presented in Appendix A.

3. Solids are usually examined as a mull, a pressed disc, or as a deposited glassy film.

Mulls are prepared by thoroughly grinding 2-5 mg of a solid in a smooth agate mortar.\* Grinding is continued after the addition of 1 or 2 drops of the mulling oil. The suspended particles must be less than  $2\text{ }\mu\text{m}$  to avoid excessive scattering of radiation. The mull is examined as a thin film between flat salt plates. Nujol (a high-boiling petroleum oil) is commonly used as a mulling agent. When hydrocarbon bands interfere with the spectrum, Fluorolube (a completely halogenated polymer containing F and Cl) or hexachlorobutadiene may be used. The use of both Nujol and Fluorolube mulls makes possible a scan, essentially free of interfering

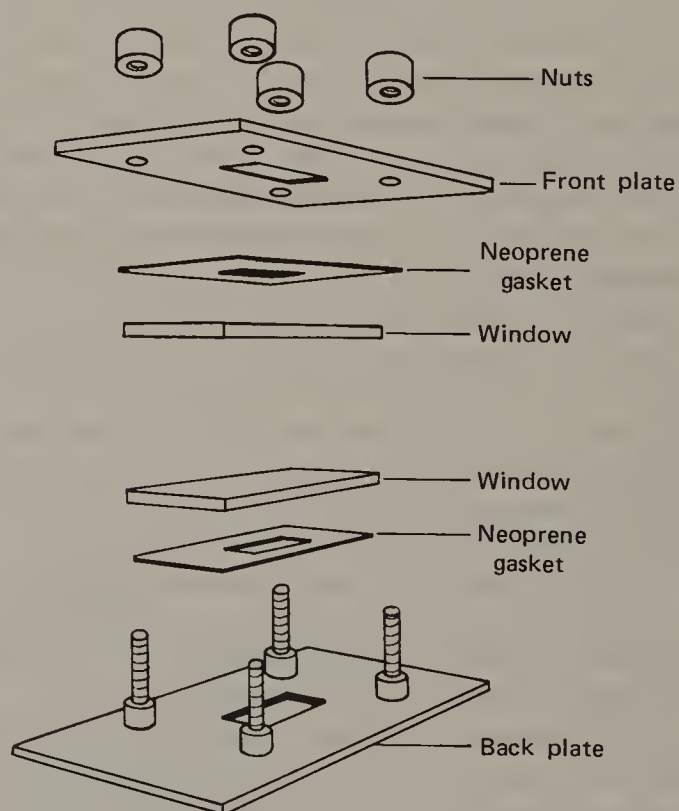


Figure 5. Infrared salt plate assembly.

\*Barnes Engineering Co., Instrument Division, Stamford, Conn.



bands, over the  $4000\text{ cm}^{-1}$ - $250\text{ cm}^{-1}$  ( $2.5$ - $40.0\text{ }\mu\text{m}$ ) region.

The pressed-disc technique depends upon the fact that dry, powdered potassium bromide (or other alkali metal halides) can be pressed under pressure *in vacuo* to form transparent discs. The sample ( $0.5$ - $1.0\text{ mg}$ ) is intimately mixed with approximately  $100\text{ mg}$  of dry, powdered potassium bromide. Mixing can be effected by thorough grinding in a smooth agate mortar or, more efficiently, with a small vibrating ball mill, or by lyophilization. The mixture is pressed with special dies under a pressure of  $10,000$ - $15,000$  pounds per square inch into a transparent disc. The quality of the spectrum depends on the intimacy of mixing and the reduction of the suspended particles to  $2\text{ }\mu\text{m}$  or less. Micro-discs,  $0.5$  to  $1.5\text{ mm}$  in diameter, can be used with a beam condenser. The micro-disc technique permits examination of samples as small as  $1$  microgram. Bands near  $3448\text{ cm}^{-1}$  and  $1639\text{ cm}^{-1}$  ( $2.9$  and  $6.1\text{ }\mu\text{m}$ ), due to moisture, frequently appear in spectra obtained by the pressed disc technique (see  $\text{H}_2\text{O}$  spectrum in Appendix B).

The use of KBr discs or pellets has often been avoided because of the demanding task of making good pellets. Such KBr techniques can be less formidable through the Mini-Press (Figure 6) that affords a simple procedure; the KBr-sample mixture is placed in the nut portion of the assembly with one bolt in place. The second bolt is introduced, and pressure is applied by tightening the bolts. Removal of the bolts leaves a pellet in the nut that now serves as a cell.

Deposited films are useful only when the material can be deposited from solution or cooled from a melt as micro-crystals or as a glassy film. Crystalline films generally lead to excessive light scattering. Specific crystal orientation may lead to spectra differing from those observed for randomly oriented particles such as exist in a mull or halide disc. The deposited film technique is particularly useful for obtaining spectra of resins and plastics. Care must be taken to free the sample of solvent by vacuum treatment or gentle heating.

A technique known as attenuated total reflection or internal reflection spectroscopy is now available for obtaining qualitative spectra of solids regardless of thickness. The technique depends on the fact that a beam of light that is internally reflected from the surface of a transmitting medium passes a short distance beyond the reflecting boundary and returns to the transmitting medium as a part of the process of reflection. If a material (i.e., the sample) of lower refractive index than the transmitting medium is brought in contact with the reflecting surface, the light passes through the material to the depth of a few  $\mu\text{m}$ , producing an absorption spectrum. An extension of the

technique provides for multiple internal reflections along the surface of the sample. The multiple internal reflection technique results in spectra with intensities comparable to transmission spectra.

In general, a dilute solution in a nonpolar solvent furnishes the best (i.e., least distorted) spectrum. Nonpolar compounds give essentially the same spectra in the con-



Figure 6. Mini-press and operation. (a) Cell holder. (b) Nut = cell. (c) Bolts.



condensed phase (i.e., neat liquid, a mull, a KBr disc, or a film) as they give in nonpolar solvents. Polar compounds, however, often show hydrogen bonding effects in the condensed phase. Unfortunately, polar compounds are frequently insoluble in nonpolar solvents, and the spectrum must be obtained either in a condensed phase or in a polar solvent; the latter introduces the possibility of solute-solvent hydrogen bonding.

Reasonable care must be taken in handling salt cells and plates. Moisture-free samples should be used. Fingers should not come in contact with the optical surfaces. Care should be taken to prevent contamination with silicones, which are hard to remove and have strong absorption patterns.

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## V. INTERPRETATION OF SPECTRA

There are no rigid rules for interpreting an infrared spectrum. Certain requirements, however, must be met before an attempt is made to interpret a spectrum.

1. The spectrum must be adequately resolved and of adequate intensity.
2. The spectrum should be that of a reasonably pure compound.
3. The spectrophotometer should be calibrated so that the bands are observed at their proper frequencies or wavelengths. Proper calibration can be made with reliable standards, such as polystyrene film.
4. The method of sample handling must be specified. If a solvent is employed, the solvent, concentration, and the cell thickness should be indicated.

A precise treatment of the vibrations of a complex molecule is not feasible; thus, the infrared spectrum must be interpreted from empirical comparison of spectra, and extrapolation of studies of simpler molecules. Many questions arising in the interpretation of an infrared spectrum can be answered by data obtained from the mass, ultraviolet, and NMR spectra.

Infrared absorption of organic molecules is summarized in the chart of characteristic group frequencies in Appendix C. Many of the group frequencies vary over a wide range because the bands arise from complex interacting vibrations within the molecule. Absorption bands may, however, represent predominantly a single vibrational mode. Certain absorption bands, for example, those arising from the C—H, O—H, and C=O stretching modes, remain within fairly narrow regions of the spectrum. Important details of structure may be revealed by the exact position of an absorption band within these narrow regions. Shifts in absorption position and changes in band contours, accompanying changes in molecular environment, may also suggest important structural details.

The two important areas for a preliminary examination of a spectrum are the region  $4000\text{--}1300\text{ cm}^{-1}$  ( $2.5\text{--}7.7\text{ }\mu\text{m}$ ) and the  $909\text{--}650\text{ cm}^{-1}$  ( $11.0\text{--}15.4\text{ }\mu\text{m}$ ) region. The high frequency portion of the spectrum is called the functional group region. The characteristic stretching frequencies for important functional groups such as OH, NH, and C=O occur in this portion of the spectrum. The absence of absorption in the assigned ranges for the various functional groups can usually be used as evidence for the absence of such groups in the molecule. Care must be exercised, however, in such interpretations since certain structural characteristics may cause a band to become extremely broad so that it may go unnoticed. For example, intramolecular hydrogen bonding in the enolic form of acetylacetone results in a broad OH band, which may be overlooked. The absence of absorption in the  $1850\text{--}1540\text{ cm}^{-1}$  ( $5.40\text{--}6.50\text{ }\mu\text{m}$ ) region excludes a structure containing a carbonyl group. Weak bands in the high frequency region, resulting from the fundamental absorption of functional groups, such as S—H and C $\equiv$ C, are extremely valuable in the determination of structure. Such weak bands would be of little value in the more complicated regions of the spectrum. Overtones and combination tones of lower frequency bands frequently appear in the high frequency region of the spectrum. Overtone- and combination-tone bands are characteristically weak except when Fermi resonance occurs. Strong skeletal bands for aromatics and heteroaromatics fall in the  $1600\text{--}1300\text{ cm}^{-1}$  ( $6.25\text{--}7.70\text{ }\mu\text{m}$ ) region of the spectrum.

The lack of strong absorption bands in the  $909\text{--}650\text{ cm}^{-1}$  ( $11.0\text{--}15.4\text{ }\mu\text{m}$ ) region generally indicates a nonaromatic structure. Aromatic and heteroaromatic compounds display strong out-of-plane C—H bending and ring bending absorption bands in this region that can frequently be correlated with the substitution pattern. Broad, moderately intense absorption in the low frequency region suggests the presence of carboxylic acid dimers, amines, or amides, all of which show out-of-plane bending in this region. If the region is extended to  $1,000\text{ cm}^{-1}$  ( $10.0\text{ }\mu\text{m}$ ) absorption bands characteristic of olefinic structures are included.

The intermediate portion of the spectrum,  $1300\text{--}909\text{ cm}^{-1}$  ( $7.7\text{--}11.0\text{ }\mu\text{m}$ ), is usually referred to as the "fingerprint" region. The absorption pattern in this region is frequently complex, with the bands originating in interacting vibrational modes. This portion of the spectrum is extremely valuable when examined in reference to the other regions. For example, if alcoholic or phenolic O—H stretching absorption appears in the high frequency region of the spectrum, the position of the C—C—O absorption band in the  $1260\text{--}1000\text{ cm}^{-1}$  ( $7.93\text{--}10.00\text{ }\mu\text{m}$ ) region frequently makes it possible to assign the O—H absorption to alcohols and phenols with highly specific structures. Absorption in this intermediate region is probably unique for every molecular species.

Any conclusions reached after examination of a particu-



lar band should be confirmed where possible by examination of other portions of the spectrum. For example, the assignment of a carbonyl band to an aldehyde should be confirmed by the appearance of a band or a pair of bands in the  $2900\text{--}2695\text{ cm}^{-1}$  ( $3.45\text{--}3.71\text{ }\mu\text{m}$ ) region of the spectrum, arising from the C—H stretching vibrations of the aldehyde group. Similarly, the assignment of a carbonyl band to an ester should be confirmed by observation of a strong band in the C—O stretching region,  $1300\text{--}1100\text{ cm}^{-1}$  ( $7.6\text{--}9.1\text{ }\mu\text{m}$ ).

Finally, in a “fingerprint” comparison of spectra, or any other situation in which the *shapes* of peaks are important,

we should anticipate the substantial change in the general appearance of the spectrum in changing from a spectrum that is linear in wavenumber to one that is linear in wavelength (Figure 7).

## VI. CHARACTERISTIC GROUP FREQUENCIES OF ORGANIC MOLECULES

A table of characteristic group frequencies is presented as Appendix C. The ranges presented for group frequencies

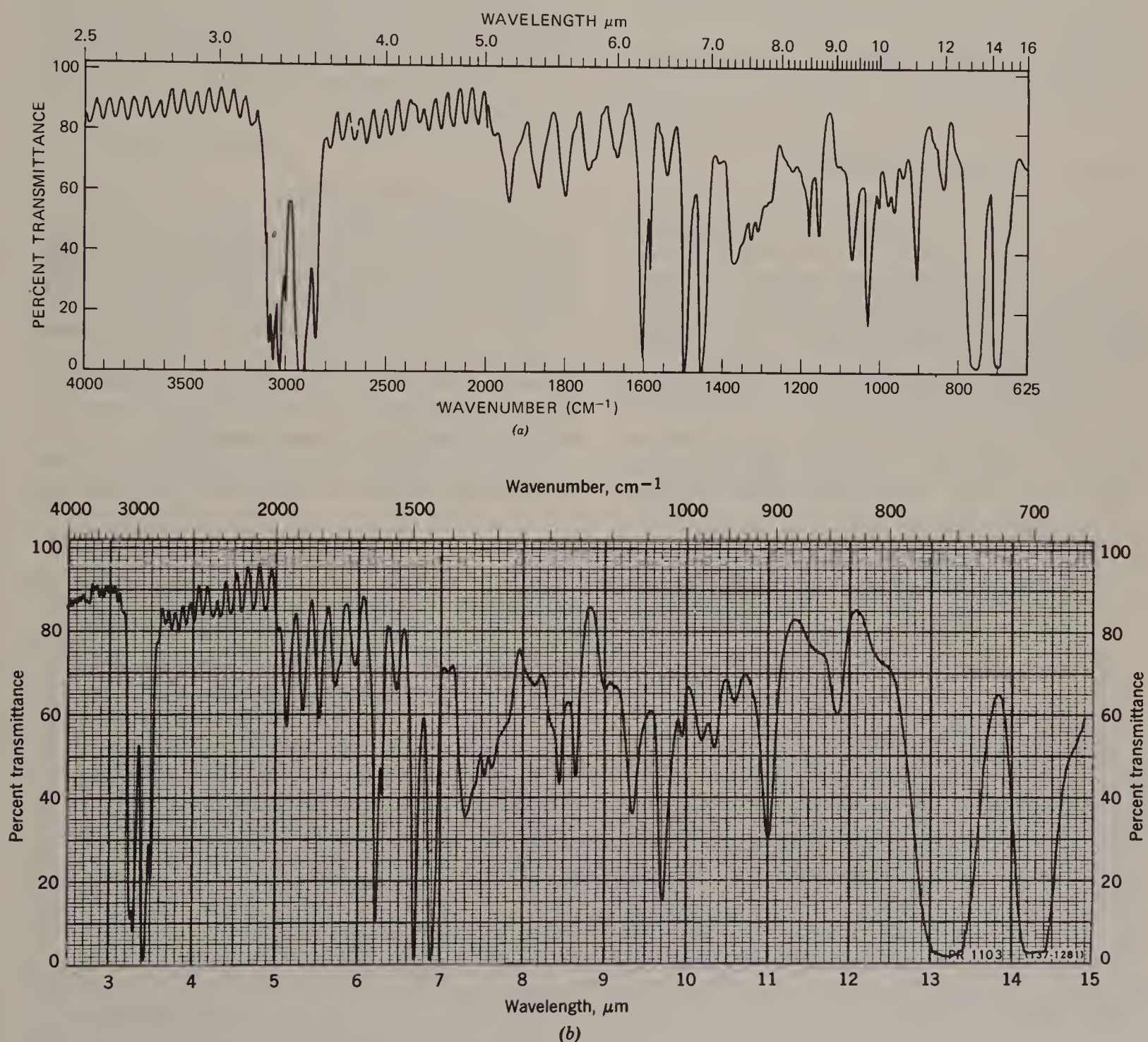


Figure 7. Polystyrene, same sample for both a and b. a, Linear in wavenumber ( $\text{cm}^{-1}$ ); b, Linear in wavelength ( $\mu\text{m}$ ).

have been assigned following the examination of many compounds in which the groups occur. Although the ranges are quite well defined, the precise frequency or wavelength at which a specific group absorbs is dependent on its environment within the molecule and on its physical state.

This section of the chapter is concerned with a comprehensive look at these characteristic group frequencies and their relationship to molecular structure. As a major type or class of molecule or functional group is introduced in the succeeding sections, an example of an infrared spectrum with the important peak assignments will be given. Spectra of common laboratory substances, representing many of the chemical classes listed below, are shown in Appendix B. Characteristic group absorptions are found in Appendix C.

References that serve to supplement this section have been cited.<sup>1-3, 7-25</sup>

## NORMAL ALKANES (PARAFFINS)

The spectra of normal paraffins can be interpreted in terms of 4 vibrations, namely the stretching and bending of C-H and C-C bonds. Detailed analysis of the spectra of the lower members of the alkane series has made detailed assignments of the spectral positions of specific vibrational modes possible.

Not all of the possible absorption frequencies of the paraffin molecule are of equal value in the assignment of structure. The C-C bending vibrations occur at very low frequencies (below  $500\text{ cm}^{-1}$ , longer than  $20\text{ }\mu\text{m}$ ) and therefore do not appear in our spectra. The bands assigned

to C-C stretching vibrations are weak and appear in the broad region of  $1200\text{--}800\text{ cm}^{-1}$  ( $8.3\text{--}12.5\text{ }\mu\text{m}$ ); they are generally of little value for identification.

The most characteristic vibrations are those arising from C-H stretching and bending. Of these vibrations, those arising from methylene twisting and wagging are usually of limited diagnostic value because of their weakness and instability. This instability is a result of strong coupling to the remainder of the molecule.

The vibrational modes of alkanes are common to many organic molecules. Although the positions of C-H stretching and bending frequencies of methyl and methylene groups remain nearly constant in hydrocarbons, the attachment of  $\text{CH}_3$  or  $\text{CH}_2$  to atoms other than carbon, or to a carbonyl group or aromatic ring, may result in appreciable shifts of the C-H stretching and bending frequencies. These shifts are summarized in Tables I and II of Appendix D.

The spectrum of dodecane, Figure 8, is that of a typical straight-chain hydrocarbon.

### C-H Stretching Vibrations

Absorption arising from C-H stretching in the alkanes occurs in the general region of  $3,000\text{--}2,840\text{ cm}^{-1}$  ( $3.3\text{--}3.5\text{ }\mu\text{m}$ ). The positions of the C-H stretching vibrations are among the most stable in the spectrum. When a spectrum is obtained with an instrument using a sodium chloride prism, the bands in this region are frequently unresolved (as in Figure 7b). Resolution (Figure 7a) is achieved through the use of a fluoride prism or a grating instrument.

**METHYL GROUPS.** An examination of a large number of saturated hydrocarbons containing methyl groups

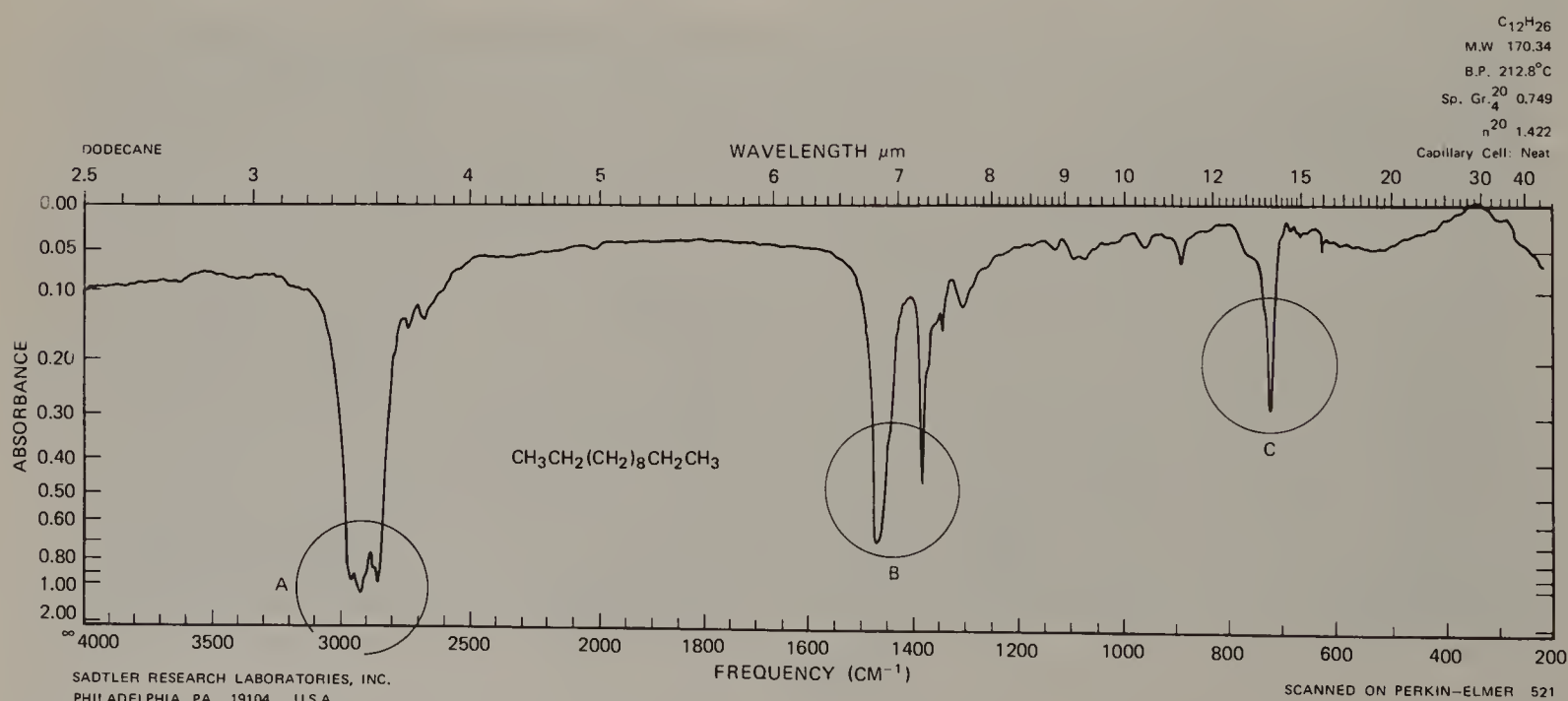


Figure 8. A. C-H stretch:  $2962\text{ cm}^{-1}$  ( $3.38\text{ }\mu\text{m}$ )  $\nu_{as}\text{ CH}_3$ ,  $2872\text{ cm}^{-1}$  ( $3.48\text{ }\mu\text{m}$ )  $\nu_s\text{ CH}_3$ ,  $2926\text{ cm}^{-1}$  ( $3.43\text{ }\mu\text{m}$ )  $\nu_{as}\text{ CH}_2$ ,  $2853\text{ cm}^{-1}$  ( $3.51\text{ }\mu\text{m}$ )  $\nu_s\text{ CH}_2$ . B. C-H bend:  $1465\text{ cm}^{-1}$  ( $6.83\text{ }\mu\text{m}$ )  $\delta_s\text{ CH}_2$ ,  $1450\text{ cm}^{-1}$  ( $6.90\text{ }\mu\text{m}$ )  $\delta_{as}\text{ CH}_3$ ,  $1375\text{ cm}^{-1}$  ( $7.28\text{ }\mu\text{m}$ )  $\delta_s\text{ CH}_3$ . C.  $\text{CH}_2$  rock:  $722\text{ cm}^{-1}$  ( $13.9\text{ }\mu\text{m}$ )  $\rho\text{ CH}_2$ .

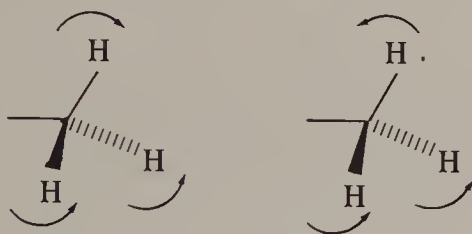


showed, in all cases, 2 distinct bands occurring at  $2962\text{ cm}^{-1}$  ( $3.38\text{ }\mu\text{m}$ ) and at  $2872\text{ cm}^{-1}$  ( $3.48\text{ }\mu\text{m}$ ). The first of these results from the asymmetrical stretching mode in which 2 C—H bonds of the methyl group are extending while the third one is contracting ( $\nu_{\text{as}}\text{CH}_3$ ). The second arises from symmetrical stretching ( $\nu_{\text{s}}\text{CH}_3$ ) in which all 3 of the C—H bonds extend and contract in phase. The presence of several methyl groups in a molecule results in strong absorption at these positions.

**METHYLENE GROUPS.** The asymmetrical stretching ( $\nu_{\text{as}}\text{CH}_2$ ) and symmetrical stretching ( $\nu_{\text{s}}\text{CH}_2$ ) occur, respectively, near  $2926\text{ cm}^{-1}$  ( $3.43\text{ }\mu\text{m}$ ) and  $2853\text{ cm}^{-1}$  ( $3.51\text{ }\mu\text{m}$ ). The positions of these bands do not vary more than  $\pm 10\text{ cm}^{-1}$  in the aliphatic and nonstrained cyclic hydrocarbons. The frequency of methylene stretching is increased when the methylene group is part of a strained ring.

### C—H Bending Vibrations

**METHYL GROUPS.** Two bending vibrations can occur within a methyl group. The first of these, the symmetrical bending vibration, involves the in-phase bending of the C—H bonds (I). The second, the asymmetrical bending vibration, involves out-of-phase bending of the C—H bonds (II).



In I, the C—H bonds are moving like the closing petals of a flower; in II, one petal opens as two petals close.

The symmetrical bending vibration ( $\delta_{\text{s}}\text{CH}_3$ ) occurs near  $1375\text{ cm}^{-1}$  ( $7.28\text{ }\mu\text{m}$ ), the asymmetrical bending vibration ( $\delta_{\text{as}}\text{CH}_3$ ) near  $1450\text{ cm}^{-1}$  ( $6.90\text{ }\mu\text{m}$ ).

The asymmetrical vibration generally overlaps the scissoring vibration of the methylene groups (see below). Two distinct bands are observed, however, in compounds such as diethyl ketone, in which the methylene scissoring band has been shifted to a lower frequency,  $1439\text{--}1399\text{ cm}^{-1}$  ( $6.95\text{--}7.15\text{ }\mu\text{m}$ ) and increased in intensity because of its proximity to the carbonyl group.

The absorption band near  $1375\text{ cm}^{-1}$  ( $7.28\text{ }\mu\text{m}$ ), arising from the symmetrical bending of the methyl C—H bonds, is very stable in position when the methyl group is attached to another carbon atom. The intensity of this band is greater for each methyl group in the compound than that for the asymmetrical methyl bending vibration or the methylene scissoring vibration.

**METHYLENE GROUPS.** The bending vibrations of the

C—H bonds in the methylene group have been shown schematically in Figure 1. The four bending vibrations are referred to as *scissoring*, *rocking*, *wagging*, and *twisting*.

The scissoring band ( $\delta_{\text{s}}\text{CH}_2$ ) in the spectra of hydrocarbons occurs at a nearly constant position near  $1465\text{ cm}^{-1}$  ( $6.83\text{ }\mu\text{m}$ ).

The band resulting from the methylene rocking vibration ( $\rho\text{CH}_2$ ), in which all of the methylene groups rock in phase, appears near  $720\text{ cm}^{-1}$  ( $13.9\text{ }\mu\text{m}$ ) for straight-chain alkanes of seven or more carbons. This band may appear as a doublet in the spectra of solid samples. In the lower members of the *n*-alkane series, the band appears at somewhat higher frequencies.

Absorption of hydrocarbons, due to methylene twisting and wagging vibrations, is observed in the  $1350\text{--}1150\text{ cm}^{-1}$  ( $7.4\text{--}8.7\text{ }\mu\text{m}$ ) region. These bands are generally appreciably weaker than those resulting from methylene scissoring. A series of bands in this region, arising from the methylene group, is characteristic of the spectra of solid samples of long-chain acids, amides, and esters.

## BRANCHED-CHAIN ALKANES

In general, the changes brought about in the spectrum of a hydrocarbon by branching result from changes in skeletal stretching vibrations and methyl bending vibrations; these occur below  $1500\text{ cm}^{-1}$  (longer than  $6.7\text{ }\mu\text{m}$ ). The spectrum of Figure 9 is that of a typical branched alkane.

### C—H Stretching Vibrations

**TERTIARY C—H GROUPS.** Absorption resulting from this vibrational mode is very weak and is usually lost in other aliphatic C—H absorption. Absorption in hydrocarbons occurs near  $2890\text{ cm}^{-1}$  ( $3.46\text{ }\mu\text{m}$ ).

### C—H Bending Vibrations

**GEM-DIMETHYL GROUPS.** Configurations in which 2 methyl groups are attached to the same carbon atom exhibit distinctive absorption in the C—H bending region. The isopropyl group shows a strong doublet, with peaks of almost equal intensity at  $1385\text{--}1380\text{ cm}^{-1}$  ( $7.22\text{--}7.25\text{ }\mu\text{m}$ ) and at  $1370\text{--}1365\text{ cm}^{-1}$  ( $7.30\text{--}7.33\text{ }\mu\text{m}$ ). The tertiary butyl group gives rise to 2 C—H bending bands, 1 in the  $1395\text{--}1385\text{ cm}^{-1}$  ( $7.17\text{--}7.22\text{ }\mu\text{m}$ ) region and 1 near  $1370\text{ cm}^{-1}$  ( $7.30\text{ }\mu\text{m}$ ). In the *t*-butyl doublet, the long wavelength band is more intense. When the gem-dimethyl group occurs at an internal position, a doublet is observed in essentially the same region where absorption occurs for the isopropyl and *t*-butyl groups. Doublets are observed for gem-dimethyl groups because of interaction between the in-phase and out-of-phase symmetrical  $\text{CH}_3$

bending of the 2 methyl groups attached to a common carbon atom.

Weak bands result from methyl rocking vibrations in isopropyl and *t*-butyl groups. These vibrations are sensitive to mass and interaction with skeletal stretching modes and are generally less reliable than the C–H bending vibrations. The following assignments have been made: isopropyl group, 922-919  $\text{cm}^{-1}$  (10.85-10.88  $\mu\text{m}$ ), and *t*-butyl group, 932-926  $\text{cm}^{-1}$  (10.73-10.80  $\mu\text{m}$ ).

## CYCLIC ALKANES

### C–H Stretching Vibrations

The methylene stretching vibrations of unstrained cyclic polymethylene structures are much the same as those observed for acyclic paraffins. Increasing ring strain moves the C–H stretching bands progressively to high frequencies. The ring  $\text{CH}_2$  and CH groups in a monoalkylcyclopropane ring absorb in the region of 3100-2990  $\text{cm}^{-1}$  (3.23-3.34  $\mu\text{m}$ ).

### C–H Bending Vibrations

Cyclization decreases the frequency of the  $\text{CH}_2$  scissoring vibration. Cyclohexane absorbs at 1452  $\text{cm}^{-1}$  (6.89  $\mu\text{m}$ ), whereas *n*-hexane absorbs at 1468  $\text{cm}^{-1}$  (6.81  $\mu\text{m}$ ). Cyclopentane absorbs at 1455  $\text{cm}^{-1}$  (6.87  $\mu\text{m}$ ), cyclopropane at 1442  $\text{cm}^{-1}$  (6.94  $\mu\text{m}$ ). This shift frequently makes it possible to observe distinct bands for methylene and methyl absorption in this region. Spectra of other saturated

hydrocarbons appear in Appendix B: hexane-no. 1, nujol-no. 2 and cyclohexane-no. 3.

## OLEFINIC HYDROCARBONS (ALKENES)

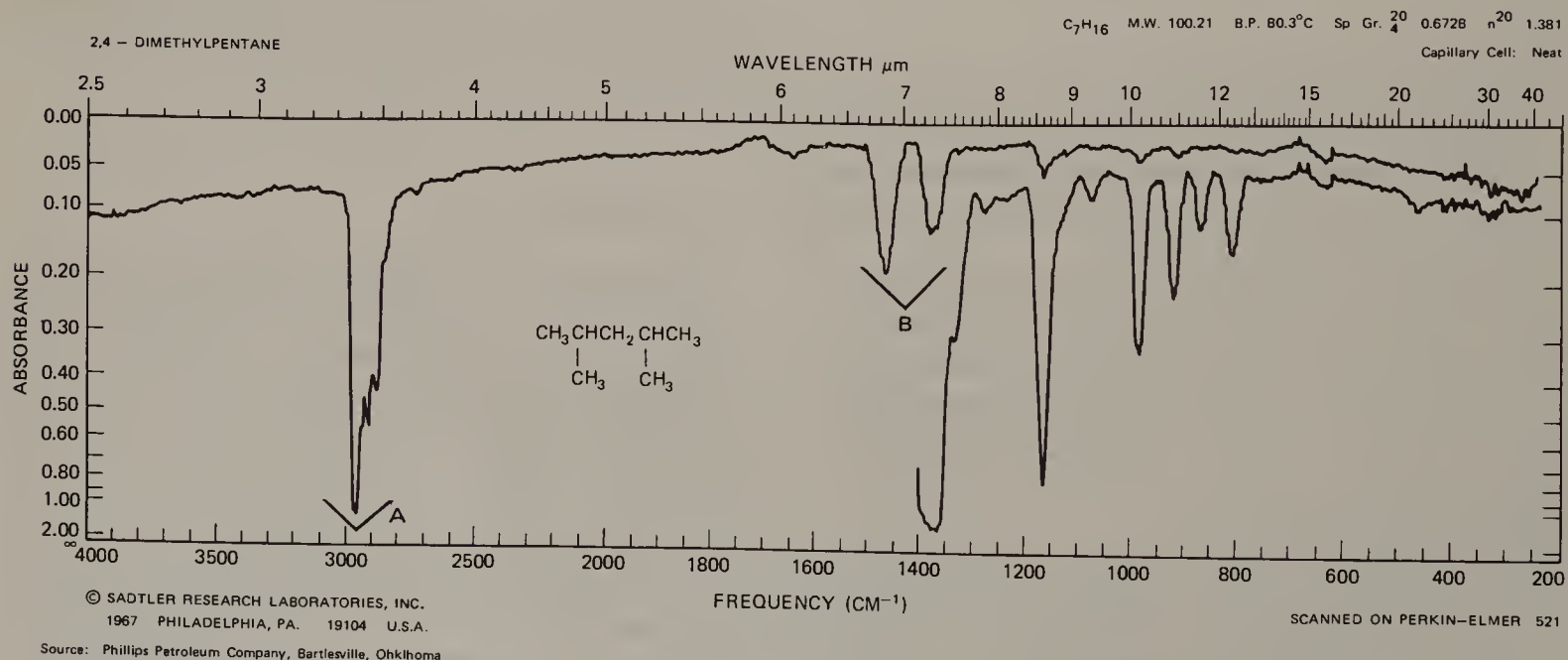
Olefinic structure introduces several new modes of vibration into a hydrocarbon molecule: a C=C stretching vibration, C–H stretching vibrations in which the carbon atom is present in the olefinic linkage, and in-plane and out-of-plane bending of the olefinic C–H bond. The spectrum of Figure 10 is that of a typical terminal olefin.

### C=C Stretching Vibrations

**UNCONJUGATED LINEAR OLEFINS.** The C=C stretching mode of unconjugated olefins usually shows moderate to weak absorption at 1667-1640  $\text{cm}^{-1}$  (6.00-6.10  $\mu\text{m}$ ). Monosubstituted olefins, that is, vinyl groups, absorb near 1640  $\text{cm}^{-1}$  (6.10  $\mu\text{m}$ ) with moderate intensity. Disubstituted *trans*-olefins, tri-, and tetra-alkyl substituted olefins absorb at or near 1670  $\text{cm}^{-1}$  (5.99  $\mu\text{m}$ ); disubstituted *cis*-olefins and vinylidene olefins absorb near 1650  $\text{cm}^{-1}$  (6.06  $\mu\text{m}$ ).

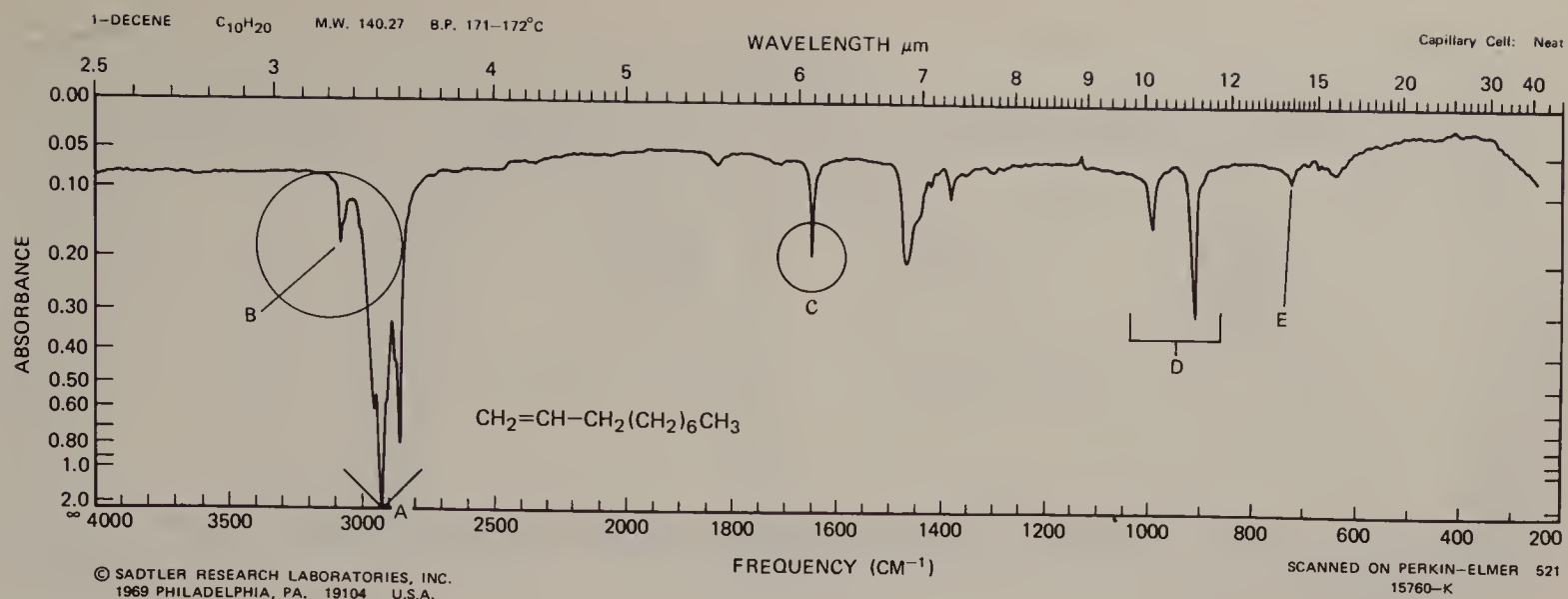
The absorption of symmetrical disubstituted *trans*-olefins or tetrasubstituted olefins may be extremely weak or absent. *Cis*-olefins, which lack the symmetry of the *trans* structure, absorb more strongly than *trans*-olefins. Internal double bonds generally absorb more weakly than terminal double bonds because of pseudosymmetry.

Abnormally high absorption frequency is observed for  $-\text{CH}=\text{CF}_2$  and  $-\text{CF}=\text{CF}_2$  groups. The former absorbs



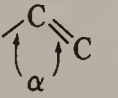
**Figure 9.** A. C–H stretch (see Figure 8). B. C–H bend (see Figure 8). There is an unresolved gem-dimethyl band from 1385-1395  $\text{cm}^{-1}$ . Compare the weak methylene rocking band(s) (800-1000  $\text{cm}^{-1}$ ) to that for Figure 8. (Also see absorption C in Figure 16.)





**Figure 10.** A. C-H stretch (see Figure 8). Note olefinic C-H stretch (B) at  $3049\text{ cm}^{-1}$  ( $3.28\text{ }\mu\text{m}$ ). C. C=C stretch,  $1645\text{ cm}^{-1}$  ( $6.08\text{ }\mu\text{m}$ ), see Table III of Appendix D. D. Out-of-plane C-H bend:  $986\text{ cm}^{-1}$  ( $10.14\text{ }\mu\text{m}$ ), (olefinic)  $907\text{ cm}^{-1}$  ( $11.03\text{ }\mu\text{m}$ ). E. (methylene rock:  $720\text{ cm}^{-1}$  ( $13.88\text{ }\mu\text{m}$ )).

near  $1754\text{ cm}^{-1}$  ( $5.70\text{ }\mu\text{m}$ ), the latter near  $1786\text{ cm}^{-1}$  ( $5.60\text{ }\mu\text{m}$ ). In contrast, the absorption frequency is reduced by the attachment of chlorine, bromine, or iodine.

**CYCLOOLEFINS.** Absorption of the internal double bond in the unstrained cyclohexene system is essentially the same as that of a *cis* isomer in an acyclic system. The C=C stretch vibration is coupled with the C-C stretching of the adjacent bonds. As the angle  $\alpha$   becomes smaller

the interaction becomes less until it is at a minimum at  $90^\circ$  in cyclobutene ( $1566\text{ cm}^{-1}$ ,  $6.39\text{ }\mu\text{m}$ ). In the cyclopropene structure, interaction again becomes appreciable, and the absorption frequency increases ( $1641\text{ cm}^{-1}$ ,  $6.09\text{ }\mu\text{m}$ ).

The substitution of alkyl groups for an  $\alpha$ -hydrogen atom in strained ring systems serves to increase the frequency of C=C absorption. Cyclobutene absorbs at  $1566\text{ cm}^{-1}$  ( $6.39\text{ }\mu\text{m}$ ), 1-methylcyclobutene at  $1641\text{ cm}^{-1}$  ( $6.09\text{ }\mu\text{m}$ ).

The absorption frequency of external exocyclic-olefinic bonds increases with decreasing ring size. Methylenecyclohexane absorbs at  $1650\text{ cm}^{-1}$  ( $6.06\text{ }\mu\text{m}$ ), methylenecyclopropane at  $1781\text{ cm}^{-1}$  ( $5.62\text{ }\mu\text{m}$ ).

**CONJUGATED SYSTEMS.** The olefinic bond stretching vibrations in conjugated dienes without a center of symmetry interact to produce two C=C stretching bands. The spectrum of an unsymmetrical conjugated diene, such as 1,3-pentadiene, shows absorption near  $1650\text{ cm}^{-1}$  ( $6.06\text{ }\mu\text{m}$ ) and near  $1600\text{ cm}^{-1}$  ( $6.25\text{ }\mu\text{m}$ ). The symmetrical molecule 1,3-butadiene shows only one band near  $1600\text{ cm}^{-1}$  ( $6.25\text{ }\mu\text{m}$ ), resulting from asymmetric stretching; the symmetrical stretching band is inactive in the infrared. The infrared spectrum of isoprene (Figure 11) illustrates many of these features.

Conjugation of an olefinic double bond with an aromatic ring produces enhanced olefinic absorption near  $1625\text{ cm}^{-1}$  ( $6.15\text{ }\mu\text{m}$ ).

The absorption frequency of the olefinic bond in conjugation with a carbonyl group is lowered by about  $30\text{ cm}^{-1}$  (ca  $0.11\text{ }\mu\text{m}$ ); the intensity of absorption is increased. In *s-cis* structures, the olefinic absorption may be as intense as that of the carbonyl group. *s-Trans* structures absorb more weakly than *s-cis* structures.

**CUMULATED OLEFINS.** A cumulated double bond system, as occurs in the allenes ( $>\text{C}=\text{C}=\text{CH}_2$ ), absorbs near  $2000\text{--}1900\text{ cm}^{-1}$  ( $5.00\text{--}5.26\text{ }\mu\text{m}$ ). The absorption results from asymmetric C=C=C stretching. The absorption may be considered an extreme case of exocyclic C=C absorption.

#### Olefinic C-H Stretching Vibrations

In general, any C-H stretching bands above  $3000\text{ cm}^{-1}$  (below  $3.33\text{ }\mu\text{m}$ ) result from aromatic, heteroaromatic, acetylenic, or olefinic C-H stretching. Also found in the same region are the C-H stretching in small rings, such as cyclopropane, and the C-H in halogenated alkyl groups. The frequency and intensity of olefinic C-H stretching absorption are influenced by the pattern of substitution. With proper resolution, multiple bands are observed for structures in which stretching interaction may occur. For example, the vinyl group produces three closely spaced C-H stretching bands. Two of these result from symmetrical and asymmetrical stretching of the terminal C-H groups, and the third from the stretching of the remaining single C-H.



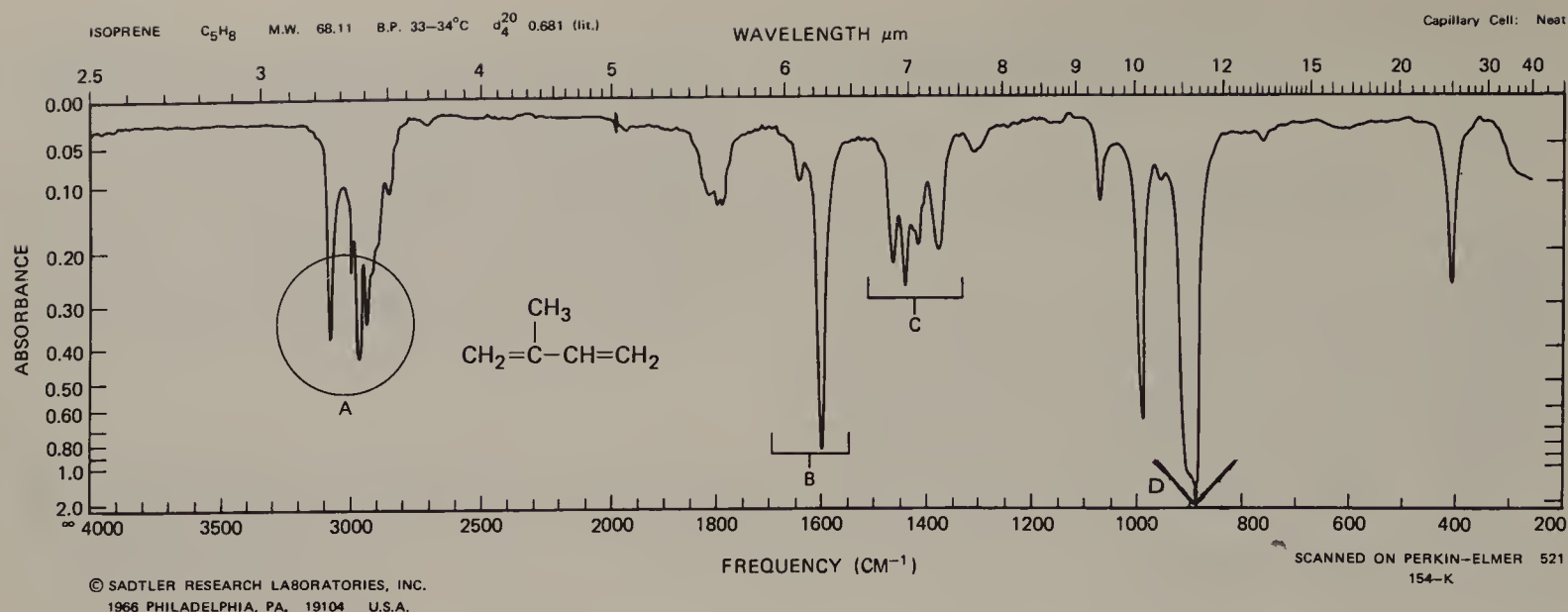


Figure 11. A. C-H stretch:  $\text{=C-H } 3078 \text{ cm}^{-1} (3.25 \text{ }\mu\text{m})$ . B. Coupled  $\text{C=C-C=C}$  stretch: symmetric  $1640 \text{ cm}^{-1} (6.10 \text{ }\mu\text{m})$  (weak), asymmetric  $1598 \text{ cm}^{-1} (6.26 \text{ }\mu\text{m})$  (strong). C. C-H bend (saturated, olefinic in-plane). D. C-H out-of-plane bend:  $980 \text{ cm}^{-1} (10.20 \text{ }\mu\text{m})$ ,  $880 \text{ cm}^{-1} (11.36 \text{ }\mu\text{m})$  (see vinyl, Table III, Appendix D).

### Olefinic C-H Bending Vibrations

Olefinic C-H bonds can undergo bending either in the same plane as the C=C bond or perpendicular to it; the bending vibrations can be either in-phase or out-of-phase with respect to each other.

Assignments have been made for a few of the more prominent and reliable in-plane bending vibrations. The vinyl group absorbs near  $1416 \text{ cm}^{-1} (7.06 \text{ }\mu\text{m})$  due to a scissoring vibration of the terminal methylene. The C-H rocking vibration of a *cis*-disubstituted olefin occurs in the same general region.

The most characteristic vibrational modes of olefins are the out-of-plane C-H bending vibrations between  $1000$  and  $650 \text{ cm}^{-1} (10.0 \text{ and } 15.4 \text{ }\mu\text{m})$ . These bands are usually the strongest in the spectra of olefins. The most reliable bands are those of the vinyl group, the vinylidene group, and the *trans* disubstituted olefins. Olefinic absorption is summarized in Tables III to V of Appendix D.

In allene structures, strong absorption is observed near  $850 \text{ cm}^{-1} (11.76 \text{ }\mu\text{m})$ , arising from  $\text{=CH}_2$  wagging. The first overtone of this band may also be seen. Some spectra showing olefinic features are shown in Appendix B: trichloroethylene-no. 12 and tetrachloroethylene-no. 13.

## ACETYLENIC HYDROCARBONS (ALKYNES)

The two stretching vibrations in acetylenic molecules involve  $\text{C}\equiv\text{C}$  and  $\text{C-C}$  stretching. Absorption due to C-H bending is characteristic of acetylene and monosubstituted alkynes. The spectrum of Figure 12 is that of a typical terminal alkyne.

### $\text{C}\equiv\text{C}$ Stretching Vibrations

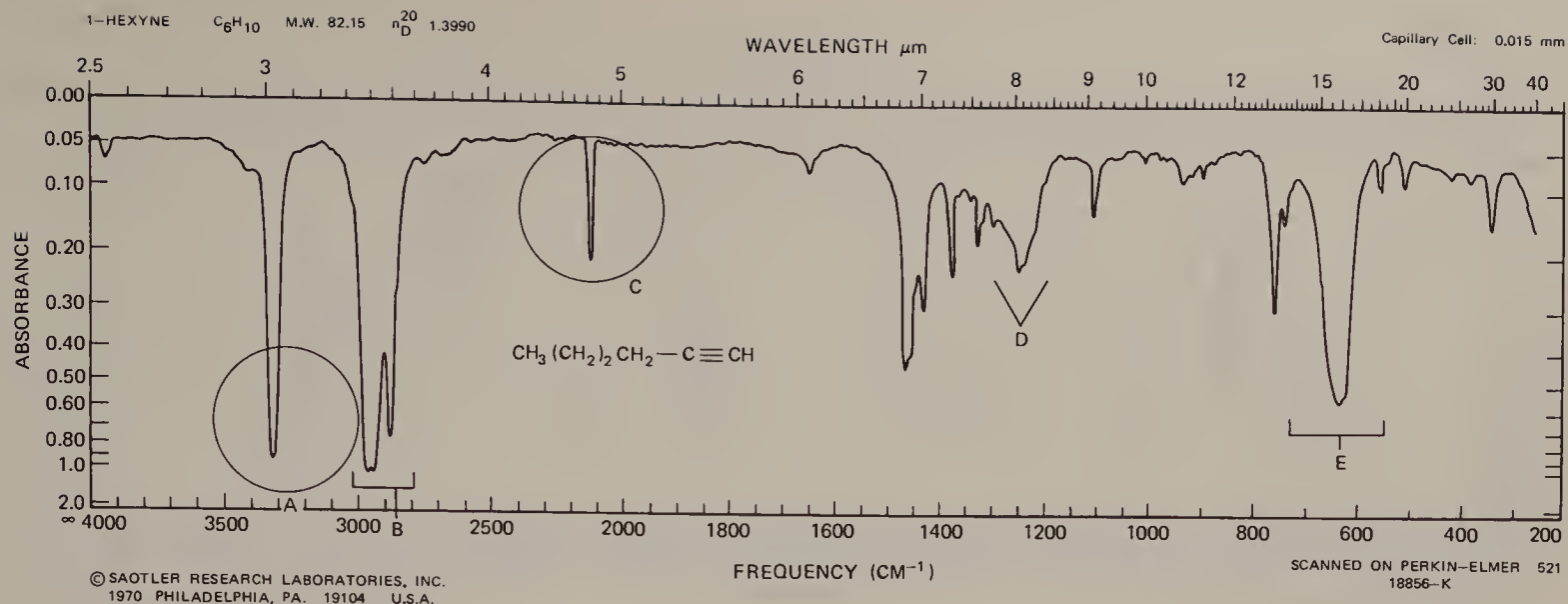
The weak  $\text{C}\equiv\text{C}$  stretching band of acetylenic molecules occurs in the region of  $2260\text{--}2100 \text{ cm}^{-1} (4.43\text{--}4.76 \text{ }\mu\text{m})$ . Because of symmetry, no  $\text{C}\equiv\text{C}$  band is observed in the infrared for acetylene and symmetrically substituted acetylenes. In the infrared spectra of monosubstituted acetylenes, the band appears at  $2140\text{--}2100 \text{ cm}^{-1} (4.67\text{--}4.76 \text{ }\mu\text{m})$ . Disubstituted acetylenes, in which the substituents are different, absorb near  $2260\text{--}2190 \text{ cm}^{-1} (4.43\text{--}4.57 \text{ }\mu\text{m})$ . When the substituents are similar in mass, or produce similar inductive and resonance effects, the band may be so weak as to be unobserved in the infrared spectrum. For reasons of symmetry, a terminal  $\text{C}\equiv\text{C}$  produces a stronger band than an internal  $\text{C}\equiv\text{C}$  (pseudosymmetry). The intensity of the  $\text{C}\equiv\text{C}$  stretching band is increased by conjugation with a carbonyl group.

### C-H Stretching Vibrations

The C-H stretching band of monosubstituted acetylenes occurs in the general region of  $3333\text{--}3267 \text{ cm}^{-1} (3.00\text{--}3.06 \text{ }\mu\text{m})$ . This is a strong band and is narrower than the hydrogen-bonded OH and NH bands occurring in the same region.

### C-H Bending Vibrations

The C-H bending vibration of acetylene or monosubstituted acetylenes leads to strong, broad absorption in the  $700\text{--}610 \text{ cm}^{-1} (14.29\text{--}16.39 \text{ }\mu\text{m})$  region. The first overtone



**Figure 12.** A.  $\equiv\text{C}-\text{H}$  stretch,  $3268\text{ cm}^{-1}$  ( $3.06\text{ }\mu\text{m}$ ). B. Normal  $\text{C}-\text{H}$  stretch (see Figure 8),  $2857\text{--}2941\text{ cm}^{-1}$  ( $3.4\text{--}3.5\text{ }\mu\text{m}$ ). C.  $\text{C}\equiv\text{C}$  stretch,  $2110\text{ cm}^{-1}$  ( $4.74\text{ }\mu\text{m}$ ). D.  $\equiv\text{C}-\text{H}$  bend overtone,  $1247\text{ cm}^{-1}$  ( $8.02\text{ }\mu\text{m}$ ). E.  $\equiv\text{C}-\text{H}$  bend fundamental,  $630\text{ cm}^{-1}$  ( $15.87\text{ }\mu\text{m}$ ).

of the  $\text{C}-\text{H}$  bending vibration appears as a weak, broad band in the  $1370\text{--}1220\text{ cm}^{-1}$  ( $7.30\text{--}8.20\text{ }\mu\text{m}$ ) region.

## MONONUCLEAR AROMATIC HYDROCARBONS

The most prominent and most informative bands in the spectra of aromatic compounds occur in the low-frequency range between  $900\text{--}675\text{ cm}^{-1}$  ( $11.11$  and  $14.82\text{ }\mu\text{m}$ ). These strong absorption bands result from the out-of-plane bending of the ring  $\text{C}-\text{H}$  bonds. In-plane bending bands appear in the  $1300\text{--}1000\text{ cm}^{-1}$  ( $7.70\text{--}10.00\text{ }\mu\text{m}$ ) region. Skeletal vibrations, involving carbon to carbon stretching within the ring, absorb in the  $1600\text{--}1585\text{ cm}^{-1}$  ( $6.25\text{--}6.31\text{ }\mu\text{m}$ ) and in the  $1500\text{--}1400\text{ cm}^{-1}$  ( $6.67\text{--}7.14\text{ }\mu\text{m}$ ) regions. The skeletal bands frequently appear as doublets, depending upon the nature of the ring substituents.

Aromatic  $\text{C}-\text{H}$  stretching bands occur between  $3100$  and  $3000\text{ cm}^{-1}$  ( $3.23\text{--}3.33\text{ }\mu\text{m}$ ).

Weak combination and overtone bands appear in the  $2000\text{--}1650\text{ cm}^{-1}$  ( $5.00\text{--}6.06\text{ }\mu\text{m}$ ) region. The pattern of the overtone bands is characteristic of the substitution pattern of the ring. Because they are weak, the overtone and combination bands are most readily observed in spectra obtained from thick samples. The spectrum of Figure 13 is that of a typical aromatic (benzenoid) compound.

### Out-of-Plane $\text{C}-\text{H}$ Bending Vibrations

The in-phase, out-of-plane bending of a ring hydrogen atom is strongly coupled to adjacent hydrogen atoms. The position of absorption of the out-of-plane bending bands is,

therefore, characteristic of the number of adjacent hydrogen atoms on the ring. The bands are frequently intense, and may be used for the quantitative determination of the relative concentrations of isomers in mixtures.

Assignments for  $\text{C}-\text{H}$  out-of-plane bending bands in the spectra of substituted benzenes appear in the chart of characteristic group frequencies (Appendix C). These assignments are usually reliable for alky-substituted benzenes, but caution must be observed in the interpretation of spectra when polar groups are attached directly to the ring, for example, in nitrobenzenes, aromatic acids, and esters or amides of aromatic acids.

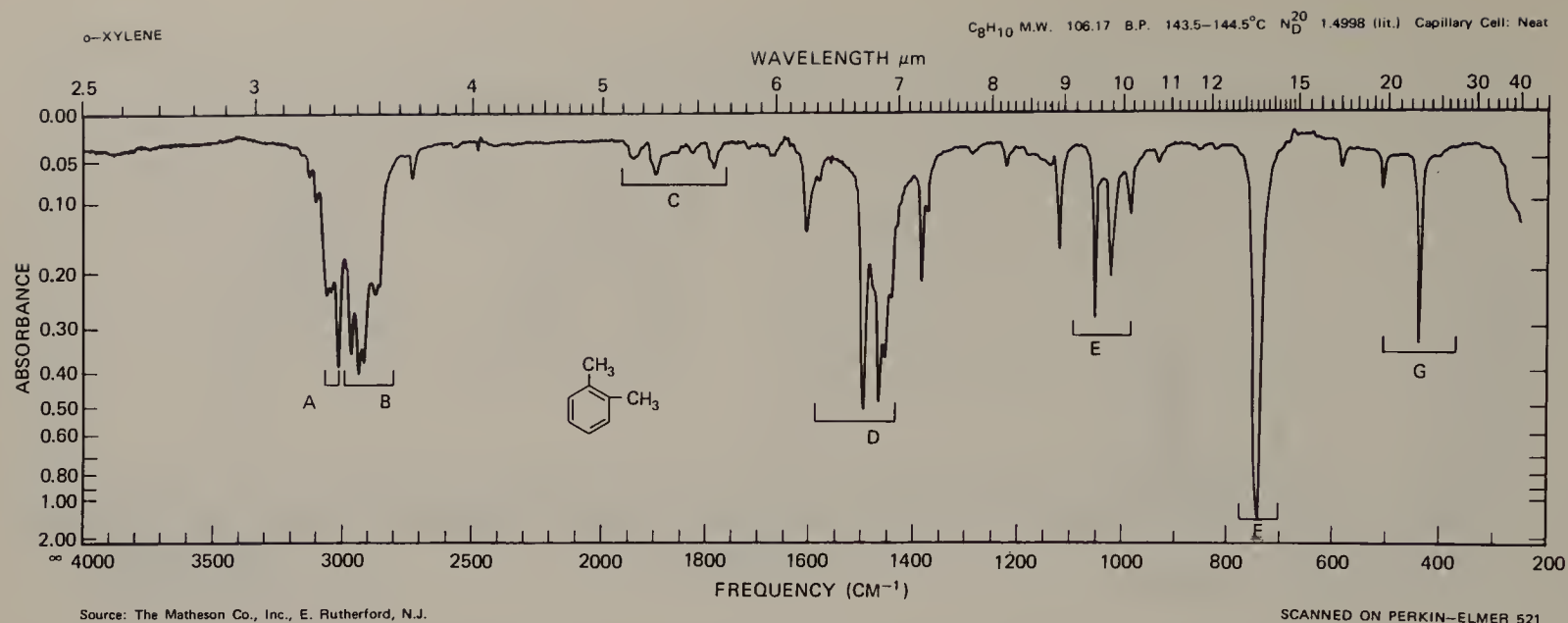
The absorption band that frequently appears in the spectra of substituted benzenes near  $710\text{--}675\text{ cm}^{-1}$  ( $14.08\text{--}14.81\text{ }\mu\text{m}$ ) is attributed to out-of-plane ring bending. Some spectra showing typical aromatic absorption are shown in Appendix B: benzene-no.4, indene-no.8, diethyl phthalate-no.21, and *m*-xylene-no.6.

## POLYNUCLEAR AROMATIC COMPOUNDS

Polynuclear aromatic compounds, like the mononuclear aromatics, show characteristic absorption in 3 regions of the spectrum.

The aromatic  $\text{C}-\text{H}$  stretching and the skeletal vibrations absorb in the same regions as observed for the mononuclear aromatics. The most characteristic absorption of polynuclear aromatics results from  $\text{C}-\text{H}$  out-of-plane bending in the  $900\text{--}675\text{ cm}^{-1}$  ( $11.11\text{--}14.81\text{ }\mu\text{m}$ ) region. These bands can be correlated with the number of adjacent hydrogen atoms on the rings. Most  $\beta$ -substituted naphthalenes, for example, show three absorption bands due to out-of-plane





**Figure 13.** A. Aromatic C–H stretch,  $3008\text{ cm}^{-1}$  ( $3.32\text{ }\mu\text{m}$ ). B. Methyl C–H stretch,  $2965, 2938, 2918, 2875\text{ cm}^{-1}$  ( $3.37, 3.40, 3.43, 3.48\text{ }\mu\text{m}$ ) (see Figure 8). C. Overtone or combination bands,  $2000\text{--}1667\text{ cm}^{-1}$  ( $5.0\text{--}6.0\text{ }\mu\text{m}$ ) (see Figure 14.) D. C≡C ring stretch,  $1605, 1495, 1466\text{ cm}^{-1}$  ( $6.23, 6.69, 6.82\text{ }\mu\text{m}$ ). E. In-plane C–H bend,  $1052, 1022\text{ cm}^{-1}$  ( $9.51, 9.78\text{ }\mu\text{m}$ ). F. Out-of-plane C–H bend,  $742\text{ cm}^{-1}$  ( $13.48\text{ }\mu\text{m}$ ). G. Out-of-plane ring C≡C bend,  $438\text{ cm}^{-1}$  ( $22.83\text{ }\mu\text{m}$ ).

C–H bending; these correspond to an isolated hydrogen atom and 2 adjacent hydrogen atoms on one ring and 4 adjacent hydrogen atoms on the other ring.

#### C–H Out-of-Plane Bending Vibrations of a $\beta$ -Substituted Naphthalene

|                      |   |
|----------------------|---|
| Isolated hydrogen    | $862\text{--}835\text{ cm}^{-1}$ ( $11.60\text{--}11.98\text{ }\mu\text{m}$ ) |
| 2 Adjacent hydrogens | $835\text{--}805\text{ cm}^{-1}$ ( $11.98\text{--}12.42\text{ }\mu\text{m}$ ) |
| 4 Adjacent hydrogens | $760\text{--}735\text{ cm}^{-1}$ ( $13.16\text{--}13.61\text{ }\mu\text{m}$ ) |

In the spectra of  $\alpha$ -substituted naphthalenes the bands for the isolated hydrogen and the two adjacent hydrogens of  $\beta$ -naphthalenes are replaced by a band for three adjacent hydrogens. This band is near  $810\text{--}785\text{ cm}^{-1}$  ( $12.34\text{--}12.74\text{ }\mu\text{m}$ ).

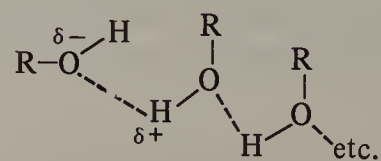
Additional bands may appear due to ring bending vibrations. The position of absorption bands for more highly substituted naphthalenes and other polynuclear aromatics are summarized by Colthup<sup>3</sup> and by Conley.<sup>1</sup>

## ALCOHOLS AND PHENOLS

The characteristic bands observed in the spectra of alcohols and phenols result from O–H stretching and C–O stretching. These vibrations are sensitive to hydrogen bonding. The C–O stretching and O–H bending modes are not independent vibrational modes because they couple with the vibrations of adjacent groups. Some typical spectra of alcohols and a phenol are shown in Figures 14 to 16.

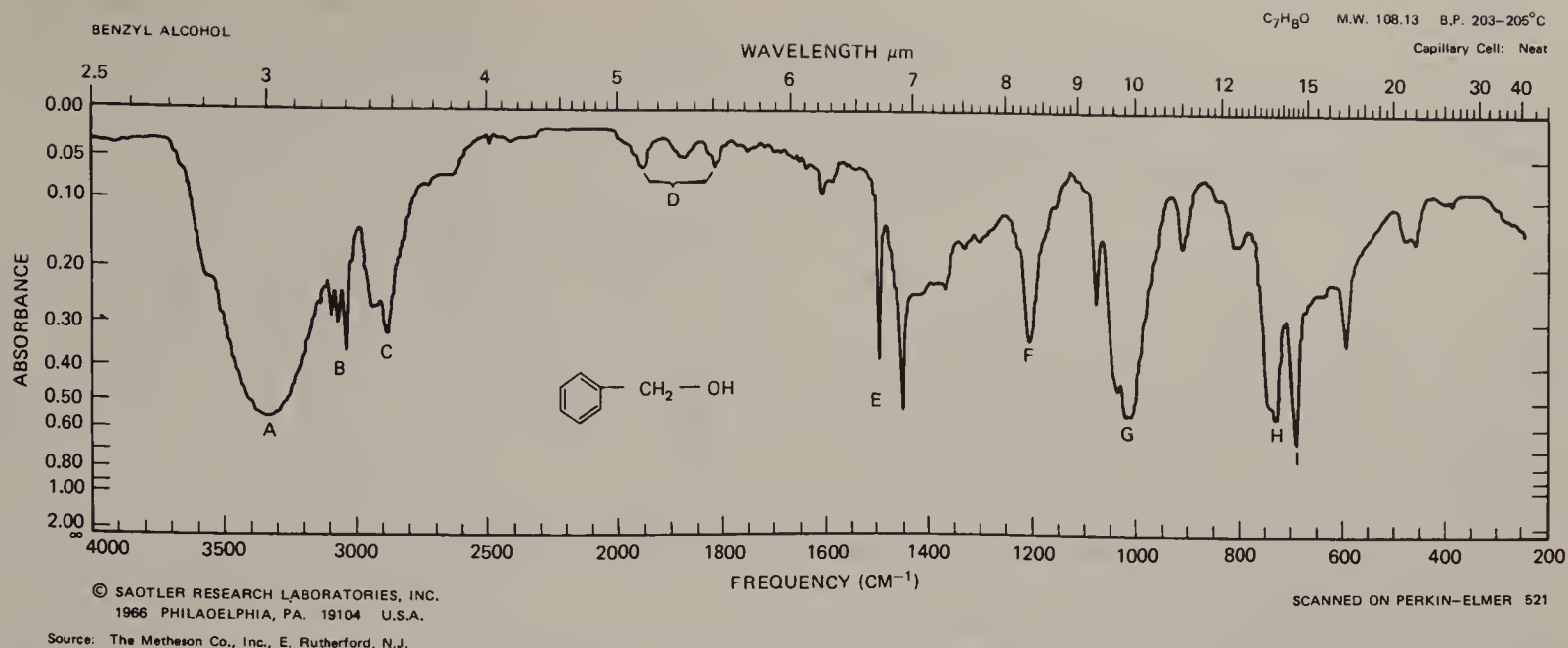
### O–H Stretching Vibrations

The unbonded or “free” hydroxyl group of alcohols and phenols absorbs strongly in the  $3650\text{--}3584\text{ cm}^{-1}$  ( $2.74\text{--}2.79\text{ }\mu\text{m}$ ) region. Sharp, “free” hydroxyl bands are observed only in the vapor phase or in very dilute solution in nonpolar solvents. Intermolecular hydrogen bonding increases as the concentration of the solution increases, and additional bands start to appear at lower frequencies,  $3550\text{--}3200\text{ cm}^{-1}$  ( $2.82\text{--}3.13\text{ }\mu\text{m}$ ), at the expense of the “free” hydroxyl band. This effect is illustrated in Figure 17 in which the absorption bands in the O–H stretching region are shown for two different concentrations of cyclohexylcarbinol in carbon tetrachloride. For comparisons of this type, the path length of the cell must be altered with changing concentration, so that the same number of absorbing molecules will be present in the infrared beam at each concentration. The band at  $3623\text{ cm}^{-1}$  ( $2.76\text{ }\mu\text{m}$ ) results from the monomer, whereas the broad absorption near  $3333\text{ cm}^{-1}$  ( $3.00\text{ }\mu\text{m}$ ) arises from “polymeric” structures.

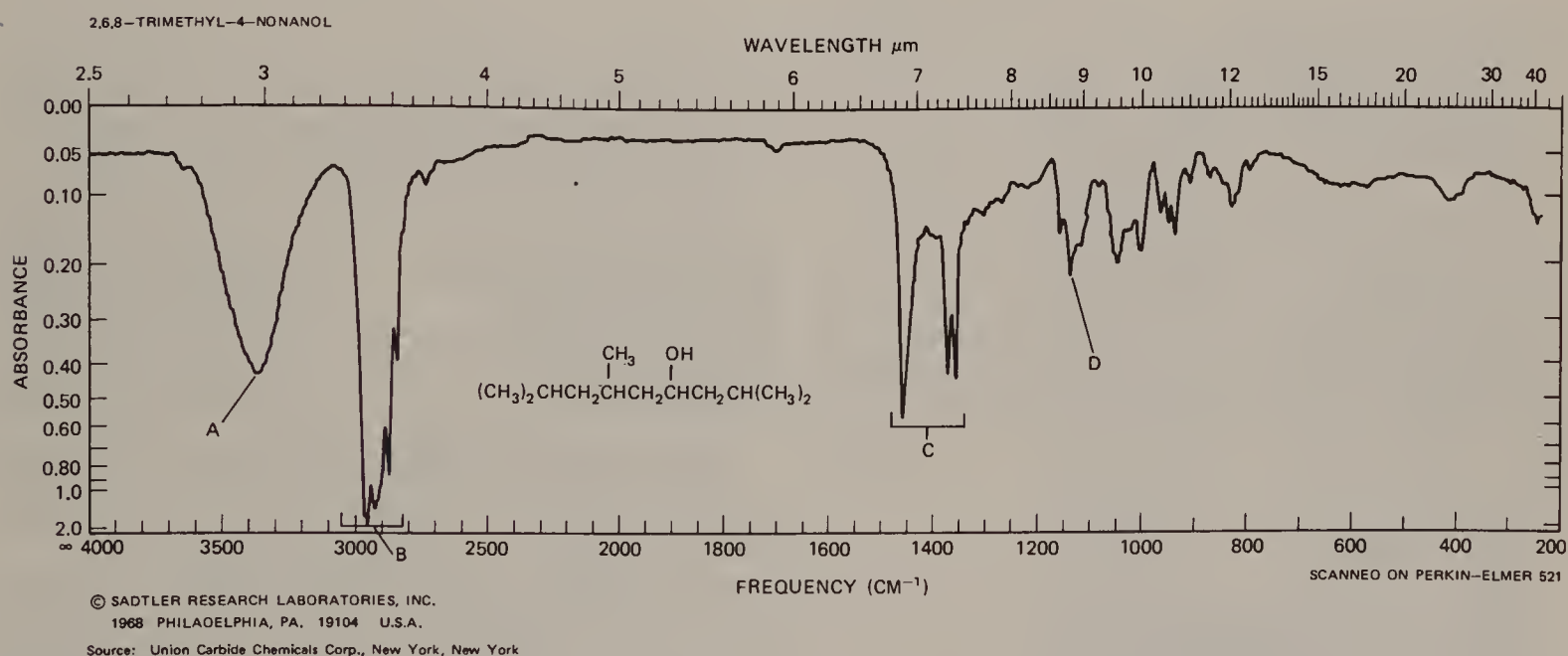


Strong intramolecular hydrogen bonding occurs in *o*-hydroxyacetophenone. The resulting absorption at  $3077\text{ cm}^{-1}$  ( $3.25\text{ }\mu\text{m}$ ) is broad, shallow, and independent of concentration (Figure 18).



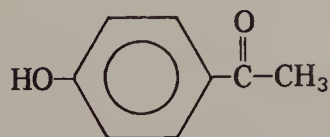


**Figure 14.** A. O–H stretch: intermolecular hydrogen bonded,  $3300\text{ cm}^{-1}$  ( $3.03\text{ }\mu\text{m}$ ). B. C–H stretch: aromatic  $3100\text{--}3000\text{ cm}^{-1}$  ( $3.22\text{--}3.33\text{ }\mu\text{m}$ ). C. C–H stretch: methylene,  $2980\text{--}2840\text{ cm}^{-1}$  ( $3.36\text{--}3.52\text{ }\mu\text{m}$ ). D. Overtone or combination bands,  $2000\text{--}1667\text{ cm}^{-1}$  ( $5.0\text{--}6.0\text{ }\mu\text{m}$ ). E. C=C ring stretch,  $1497, 1453\text{ cm}^{-1}$  ( $6.68, 6.88\text{ }\mu\text{m}$ ), overlapped by CH<sub>2</sub> scissoring, ca.  $1471\text{ cm}^{-1}$  (ca.  $6.8\text{ }\mu\text{m}$ ). F. O–H bend, possibly augmented by C–H in plane bend,  $1208\text{ cm}^{-1}$  ( $8.28\text{ }\mu\text{m}$ ). G. C–O stretch, primary alcohol (see Table II)  $1017\text{ cm}^{-1}$  ( $9.83\text{ }\mu\text{m}$ ). H. Out-of-plane aromatic C–H bend,  $735\text{ cm}^{-1}$  ( $13.60\text{ }\mu\text{m}$ ). I. Ring C=C bend,  $697\text{ cm}^{-1}$  ( $14.35\text{ }\mu\text{m}$ ).



**Figure 15.** A. O–H stretch, intermolecular hydrogen bonding  $3355\text{ cm}^{-1}$  ( $2.98\text{ }\mu\text{m}$ ). B. C–H stretch (see Figure 8),  $3000\text{--}2800\text{ cm}^{-1}$  ( $3.33\text{--}3.57\text{ }\mu\text{m}$ ). C. C–H bend (see Figure 8). Note the pair of bands for the gem di-methyl groups at  $1373$  and  $1355\text{ cm}^{-1}$  ( $7.28$  and  $7.39\text{ }\mu\text{m}$ ). D. C–O stretch  $1138\text{ cm}^{-1}$ , ( $8.79\text{ }\mu\text{m}$ ). This appears to be weak only because the C–H bands are very intense due to the large number of C–H bonds in the molecule.

In contrast, *p*-hydroxyacetophenone

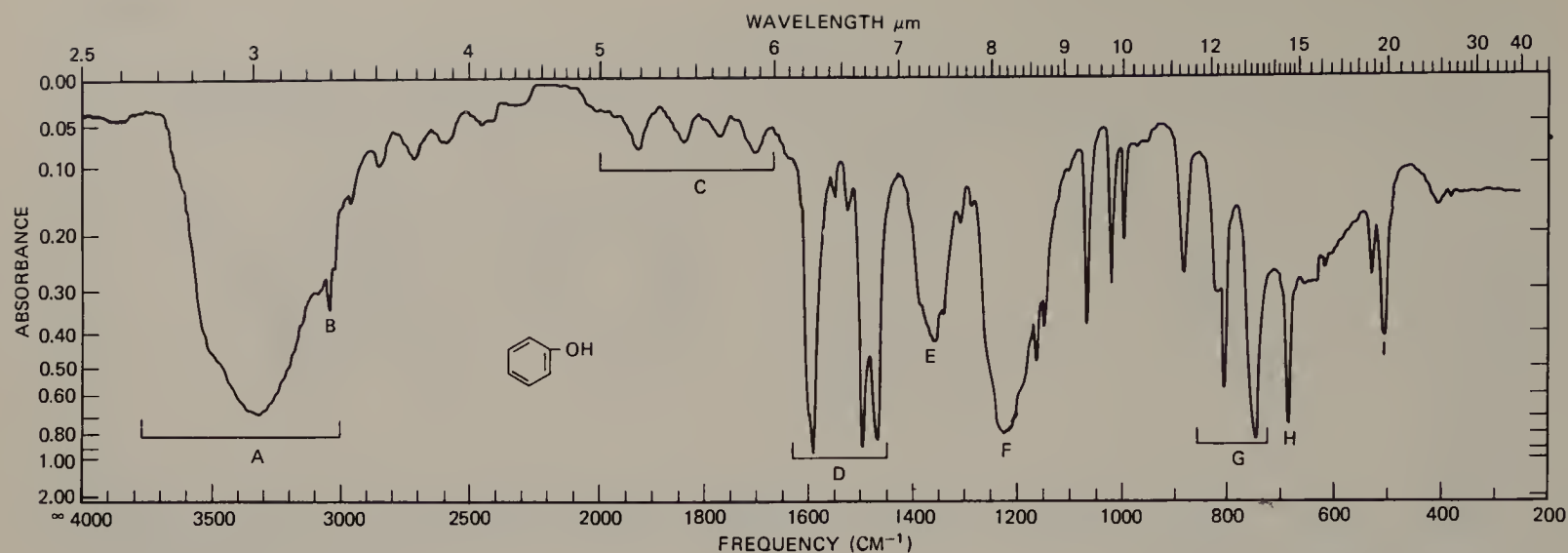


shows a sharp “free” hydroxyl peak at  $3600\text{ cm}^{-1}$  ( $2.78\text{ }\mu\text{m}$ ) in dilute CCl<sub>4</sub> solution as well as a broad strong intermolecular peak at  $3100\text{ cm}^{-1}$  ( $3.20\text{ }\mu\text{m}$ ) in the spectrum of a neat sample.

In structures, such as 2,6-di-*t*-butylphenol, in which steric hindrance prevents hydrogen bonding, no bonded hydroxyl band is observed, not even in spectra of neat samples.

#### C–O Stretching Vibrations

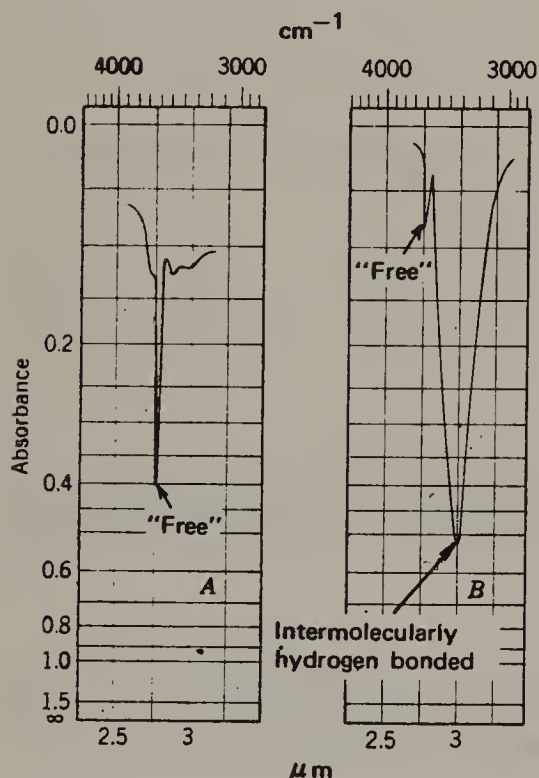
The C–O stretching vibrations in alcohols and phenols produce a strong band in the  $1260\text{--}1000\text{ cm}^{-1}$  ( $7.93\text{--}$



Source: Allied Chemical Corp., Plastics Div., Morristown, N.J.

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**Figure 16.** A. Broad, intermolecular hydrogen bonded, O-H stretch,  $3333\text{ cm}^{-1}$  ( $3.0\text{ }\mu\text{m}$ ). B. Aromatic C-H stretch,  $3045\text{ cm}^{-1}$  ( $3.28\text{ }\mu\text{m}$ ). C. Overtone or combination bands (see Figure 14),  $2000\text{--}1667\text{ cm}^{-1}$  ( $5.0\text{--}6.0\text{ }\mu\text{m}$ ). D. C=C ring stretch,  $1580, 1495, 1468\text{ cm}^{-1}$  ( $6.33, 6.69, 6.81\text{ }\mu\text{m}$ ). E. In plane O-H bend,  $1359\text{ cm}^{-1}$  ( $7.36\text{ }\mu\text{m}$ ). F. C-O stretch,  $1223\text{ cm}^{-1}$  ( $8.18\text{ }\mu\text{m}$ ). G. Out-of-plane C-H bend,  $805, 745\text{ cm}^{-1}$  ( $12.40, 13.43\text{ }\mu\text{m}$ ). H. Out-of-plane ring C=C bend,  $685\text{ cm}^{-1}$  ( $14.60\text{ }\mu\text{m}$ ). I. (Broad) hydrogen bonded, out-of-plane O-H bend,  $\text{ca. } 650\text{ cm}^{-1}$  ( $\text{ca. } 15.0\text{ }\mu\text{m}$ ).



**Figure 17.** Infrared spectrum of the O-H stretching region of cyclohexylcarbinol in CCl<sub>4</sub>. A.  $0.03\text{ M}$  ( $0.406\text{ mm}$  cell); B.  $1.00\text{ M}$  ( $0.014\text{ mm}$  cell).

$10.00\text{ }\mu\text{m}$ ) region of the spectrum. The C-O stretching mode is coupled with the adjacent C-C stretching vibration; thus in primary alcohols the vibration might better

be described as an asymmetric C-C-O stretching vibration. The vibrational mode is further complicated by branching and  $\alpha,\beta$ -unsaturation. These effects are summarized as follows for a series of secondary alcohols (neat samples):

|                         |   |
|-------------------------|---|
| Methylethylcarbinol     | $1105\text{ cm}^{-1}$ ( $9.05\text{ }\mu\text{m}$ ) |
| Methylisopropylcarbinol | $1091\text{ cm}^{-1}$ ( $9.17\text{ }\mu\text{m}$ ) |
| Methylphenylcarbinol    | $1073\text{ cm}^{-1}$ ( $9.32\text{ }\mu\text{m}$ ) |
| Methylvinylcarbinol     | $1058\text{ cm}^{-1}$ ( $9.45\text{ }\mu\text{m}$ ) |
| Diphenylcarbinol        | $1014\text{ cm}^{-1}$ ( $9.86\text{ }\mu\text{m}$ ) |

The absorption ranges of the various types of alcohols appear in Table II, p. 115. These values are for neat samples of the alcohols.

Mulls, pellets or melts of phenols absorb at  $1390\text{--}1330\text{ cm}^{-1}$  ( $7.20\text{--}7.52\text{ }\mu\text{m}$ ) and  $1260\text{--}1180\text{ cm}^{-1}$  ( $7.93\text{--}8.48\text{ }\mu\text{m}$ ). These bands apparently result from interaction between O-H bending and C-O stretching. The long wavelength band is the stronger and both bands appear at longer wavelengths in spectra observed in solution. The spectrum of Figure 16 was determined on a melt, to show a high degree of association.

#### O-H Bending Vibrations

The O-H in-plane bending vibration occurs in the general region of  $1420\text{--}1330\text{ cm}^{-1}$  ( $7.04\text{--}7.52\text{ }\mu\text{m}$ ). In primary and secondary alcohols, the O-H in-plane bending couples with the C-H wagging vibrations to produce 2 bands; the

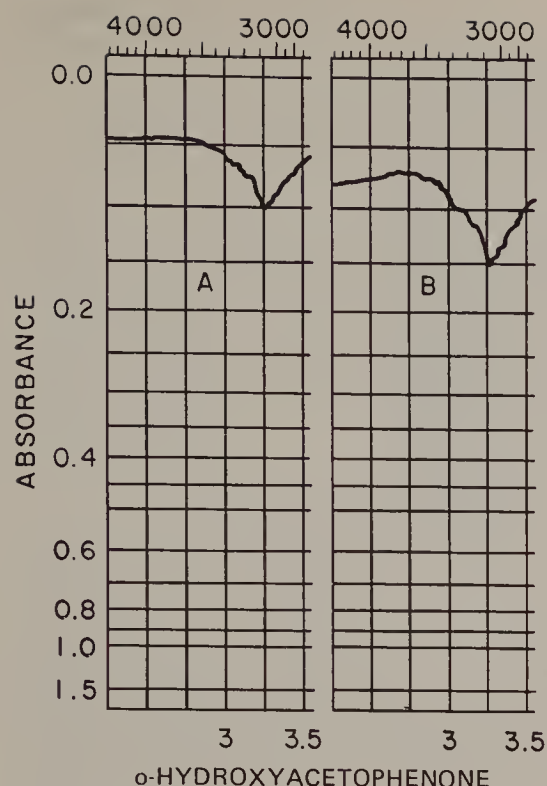


Figure 18. A portion of the infrared spectra of *o*-hydroxyacetophenone. A. 0.03 M, cell thickness: 0.41 mm. B. 1.0 M, cell thickness: 0.015 mm.

first near  $1420\text{ cm}^{-1}$  ( $7.04\text{ }\mu\text{m}$ ), the second near  $1330\text{ cm}^{-1}$  ( $7.52\text{ }\mu\text{m}$ ). These bands are of little diagnostic value. Tertiary alcohols, in which no coupling can occur, show a single band in this region, the position depending on the degree of hydrogen bonding.

The spectra of alcohols and phenols determined in the liquid state, show a broad absorption band in the  $769\text{--}650\text{ cm}^{-1}$  ( $13.00\text{--}15.40\text{ }\mu\text{m}$ ) region because of out-of-plane bending of the bonded O—H group. Some spectra showing

typical alcoholic absorptions are shown in Appendix B: ethyl alcohol-no.16 and methanol-no.15.

## ETHERS, EPOXIDES, AND PEROXIDES

### *C—O Stretching Vibrations*

The characteristic response of ethers in the infrared is associated with the stretching vibration of the C—O—C system. Since the vibrational characteristics of this system would not be expected to differ greatly from the C—C—C system, it is not surprising to find the response to C—O—C stretching in the same general region. However, since vibrations involving oxygen atoms result in greater dipole moment changes than those involving carbon atoms, more intense infrared bands are observed for ethers. The C—O—C stretching bands of ethers, as is the case with the C—O stretching bands of alcohols, involve coupling with other vibrations within the molecule. The spectrum of Figure 19 is that of a typical aryl alkyl ether. In addition, the spectra of ethyl ether-no.22 and *p*-dioxane (a cyclic diether, no.23) are shown in Appendix B.

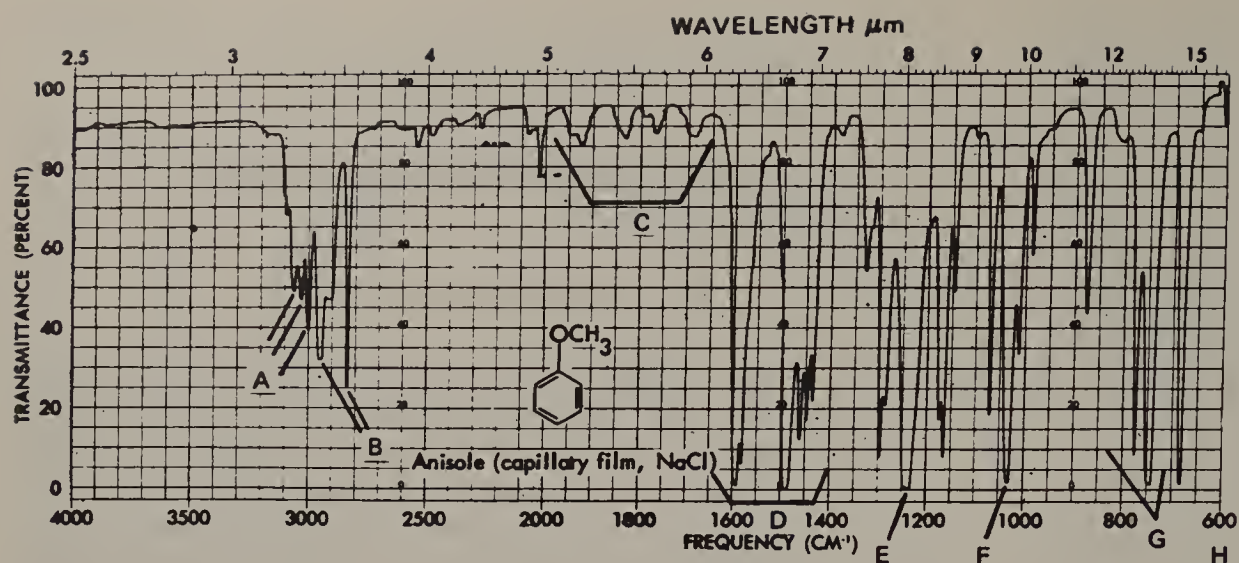
In the spectra of aliphatic ethers, the most characteristic absorption is a strong band in the  $1150\text{--}1085\text{ cm}^{-1}$  ( $8.70\text{--}9.23\text{ }\mu\text{m}$ ) region because of asymmetrical C—O—C stretching; this band usually occurs near  $1125\text{ cm}^{-1}$  ( $8.89\text{ }\mu\text{m}$ ). The symmetrical stretching band is usually weak and is more readily observed in the Raman spectrum.

The C—O—C group in a 6-membered ring absorbs at the same frequency as in an acyclic ether. As the ring becomes smaller, the asymmetrical C—O—C stretching vibration moves progressively to lower wavenumbers (longer wavelengths), whereas the symmetrical C—O—C stretching vibration (ring breathing frequency) moves to higher wavenumbers.

Table II. Alcoholic C—O Absorption

| Alcohol Type  | Absorption Range  |
|---|---|
| (1) Saturated tertiary<br>(2) Secondary, highly symmetrical }   | $1205\text{--}1124\text{ cm}^{-1}$ ( $8.30\text{--}8.90\text{ }\mu\text{m}$ ) |
| (1) Saturated secondary<br>(2) $\alpha$ -Unsaturated or cyclic tert. }  | $1124\text{--}1087\text{ cm}^{-1}$ ( $8.90\text{--}9.20\text{ }\mu\text{m}$ ) |
| (1) Secondary, $\alpha$ -unsaturated<br>(2) Secondary, alicyclic 5- or 6-membered ring<br>(3) Saturated primary }   | $1085\text{--}1050\text{ cm}^{-1}$ ( $9.22\text{--}9.52\text{ }\mu\text{m}$ ) |
| (1) Tertiary, highly $\alpha$ -unsaturated<br>(2) Secondary, di- $\alpha$ -unsaturated<br>(3) Secondary, $\alpha$ -unsaturated and $\alpha$ -branched<br>(4) Secondary, alicyclic 7- or 8-membered ring<br>(5) Primary, $\alpha$ -unsaturated and/or $\alpha$ -branched } | $< 1050\text{ cm}^{-1}$ ( $> 9.52\text{ }\mu\text{m}$ )                       |





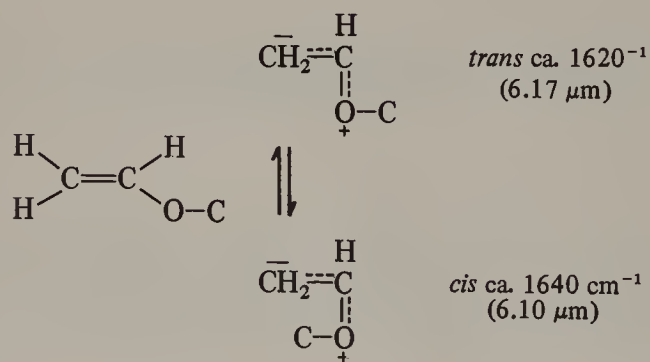
Anisole. (Source: Daniel J. Pasto and Carl R. Johnson, *Organic Structure Determination*, copyright 1969, p. 372. Reprinted by permission of Prentice-Hall, Inc., Englewood Cliffs, N.J.)

Figure 19. A. Aromatic C—H stretch, 3060, 3030, 3000  $\text{cm}^{-1}$  (3.27, 3.30, 3.33  $\mu\text{m}$ ). B. Methyl C—H stretch, 2950, 2835  $\text{cm}^{-1}$  (3.39, 3.53  $\mu\text{m}$ ). C. Overtone or combination region, 2000–1650  $\text{cm}^{-1}$  (5.0–6.0  $\mu\text{m}$ ), see Figure 13). D. C $\equiv$ C ring stretch, 1590, 1480  $\text{cm}^{-1}$  (6.29, 6.76  $\mu\text{m}$ ). E. Asymmetric C—O—C stretch, 1245  $\text{cm}^{-1}$  (8.03  $\mu\text{m}$ ). F. Symmetric C—O—C stretch, 1030  $\text{cm}^{-1}$  (9.71  $\mu\text{m}$ ). G. Out-of-plane C—H bend, 800–740  $\text{cm}^{-1}$  (12.6–13.5  $\mu\text{m}$ ). H. Out-of-plane ring C $\equiv$ C bend, 680  $\text{cm}^{-1}$  (14.7  $\mu\text{m}$ ).

Branching on the carbon atoms adjacent to the oxygen usually leads to splitting of the C—O—C band. Isopropyl ether shows a triplet structure in the 1170–1114  $\text{cm}^{-1}$  (8.55–8.98  $\mu\text{m}$ ) region, the principal band occurring at 1114  $\text{cm}^{-1}$  (8.98  $\mu\text{m}$ ).

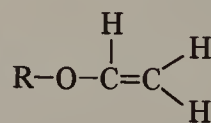
Spectra of aryl alkyl ethers display an asymmetrical C—O—C stretching band at 1275–1200  $\text{cm}^{-1}$  (7.84–8.33  $\mu\text{m}$ ) with symmetrical stretching near 1075–1020  $\text{cm}^{-1}$  (9.30–9.80  $\mu\text{m}$ ). Strong absorption due to asymmetrical C—O—C stretching in vinyl ethers occurs in the 1225–1200  $\text{cm}^{-1}$  (8.16–8.33  $\mu\text{m}$ ) region with a strong symmetrical band at 1075–1020  $\text{cm}^{-1}$  (9.30–9.80  $\mu\text{m}$ ). Resonance, which results in strengthening of the C—O bond, is responsible for the shift in the asymmetric absorption band of aryl alkyl and vinyl ethers.

The C=C stretching band of vinyl ethers occurs in the 1660–1610  $\text{cm}^{-1}$  (6.02–6.21  $\mu\text{m}$ ) region. This olefinic band is characterized by its higher intensity compared with the C=C stretching band in olefinic hydrocarbons. This band frequently appears as a doublet resulting from absorption of rotational isomers.



Coplanarity in the *trans* isomer allows maximum resonance, thus more effectively reducing the double-bond character of the olefinic linkage. Steric hindrance reduces resonance in the *cis* isomer.

The 2 bands arising from =C—H wagging in terminal olefins occur near 1000  $\text{cm}^{-1}$  (10.00  $\mu\text{m}$ ) and near 909  $\text{cm}^{-1}$  (11.00  $\mu\text{m}$ ). In the spectra of vinyl ethers, these bands are shifted to longer wavelengths because of resonance.



terminal CH<sub>2</sub> wag, 813  $\text{cm}^{-1}$  (12.30  $\mu\text{m}$ )  
*trans* CH wag, 960  $\text{cm}^{-1}$  (10.42  $\mu\text{m}$ )

Alkyl and aryl peroxides display C—C—O absorption in the 1198–1176  $\text{cm}^{-1}$  (8.35–8.50  $\mu\text{m}$ ) region. Acyl and aroyl peroxides display two carbonyl absorption bands in the 1818–1754  $\text{cm}^{-1}$  (5.50–5.70  $\mu\text{m}$ ) region. Two bands are observed because of mechanical interaction between the stretching modes of the two carbonyl groups.

The symmetrical stretching, or ring breathing frequency, of the epoxy ring, all ring bonds stretching and contracting in phase, occurs near 1250  $\text{cm}^{-1}$  (8.00  $\mu\text{m}$ ). Another band appears in the 950–810  $\text{cm}^{-1}$  (10.53–12.35  $\mu\text{m}$ ) region attributed to asymmetrical ring stretching in which the C—C bond is stretching during contraction of the C—O bond. A third band, referred to as the “12  $\mu$  band,” appears in the 840–750  $\text{cm}^{-1}$  (11.90–13.33  $\mu\text{m}$ ) region. The C—H stretching vibrations of epoxy rings occur in the 3050–2990  $\text{cm}^{-1}$  (3.28–3.34  $\mu\text{m}$ ) region of the spectrum.

## KETONES

### C=O Stretching Vibrations

Ketones, aldehydes, carboxylic acids, carboxylic esters, lactones, acid halides, anhydrides, amides, and lactams show a strong C=O stretching absorption band in the region of 1870-1540  $\text{cm}^{-1}$  (5.35-6.50  $\mu\text{m}$ ). Its relatively constant position, high intensity, and relative freedom from interfering bands make this one of the easiest bands to recognize in infrared spectra.

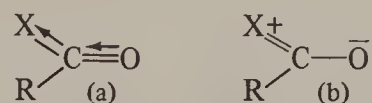
Within its given range, the position of the C=O stretching band is determined by the following factors: (1) the physical state, (2) electronic and mass effects of neighboring substituents, (3) conjugation, (4) hydrogen bonding (intermolecular and intramolecular), and (5) ring strain. Consideration of these factors leads to a considerable amount of information about the environment of the C=O group.

In a discussion of these effects, it is customary to refer to the absorption frequency of a neat sample of a saturated aliphatic ketone, 1715  $\text{cm}^{-1}$  (5.83  $\mu\text{m}$ ), as "normal." Changes in the environment of the carbonyl can either lower or raise the absorption frequency from this "normal" value. A typical ketone spectrum is displayed in Figure 20.

The absorption frequency observed for a neat sample is increased when absorption is observed in non-polar solvents. Polar solvents reduce the frequency of absorption. The overall range of solvent effects doesn't exceed 25  $\text{cm}^{-1}$ .

Replacement of an alkyl group of a saturated aliphatic ketone by a heteroatom (X) shifts the carbonyl absorption.

The direction of the shift depends on whether the inductive effect (a) or resonance effect (b) predominates:



The inductive effect reduces the length of the C=O bond and thus increases its force constant and the frequency of absorption. The resonance effect increases the C=O bond length and reduces the frequency of absorption.

The absorptions of several carbonyl compound classes are summarized in Table III.

Conjugation with a C=C bond results in delocalization of the  $\pi$  electrons of both unsaturated groups. Delocalization of the  $\pi$  electrons of the C=O group reduces the double bond character of the C to O bond, causing absorption at lower wavenumbers (longer wavelengths). Conjugation with an olefinic or phenyl group causes absorption in the 1685-1666  $\text{cm}^{-1}$  (5.93-6.00  $\mu\text{m}$ ) region. Additional conjugation may cause a slight further reduction in frequency. This effect of conjugation is illustrated in Figure 21.

Steric effects which reduce the coplanarity of the conjugated system reduce the effect of conjugation. In the absence of steric hindrance, a conjugated system will tend toward a planar conformation. Thus,  $\alpha,\beta$ -unsaturated ketones may exist in *s-cis* and *s-trans* conformations. When both forms are present, absorption for each of the forms is observed. The absorption of benzalacetone in carbon

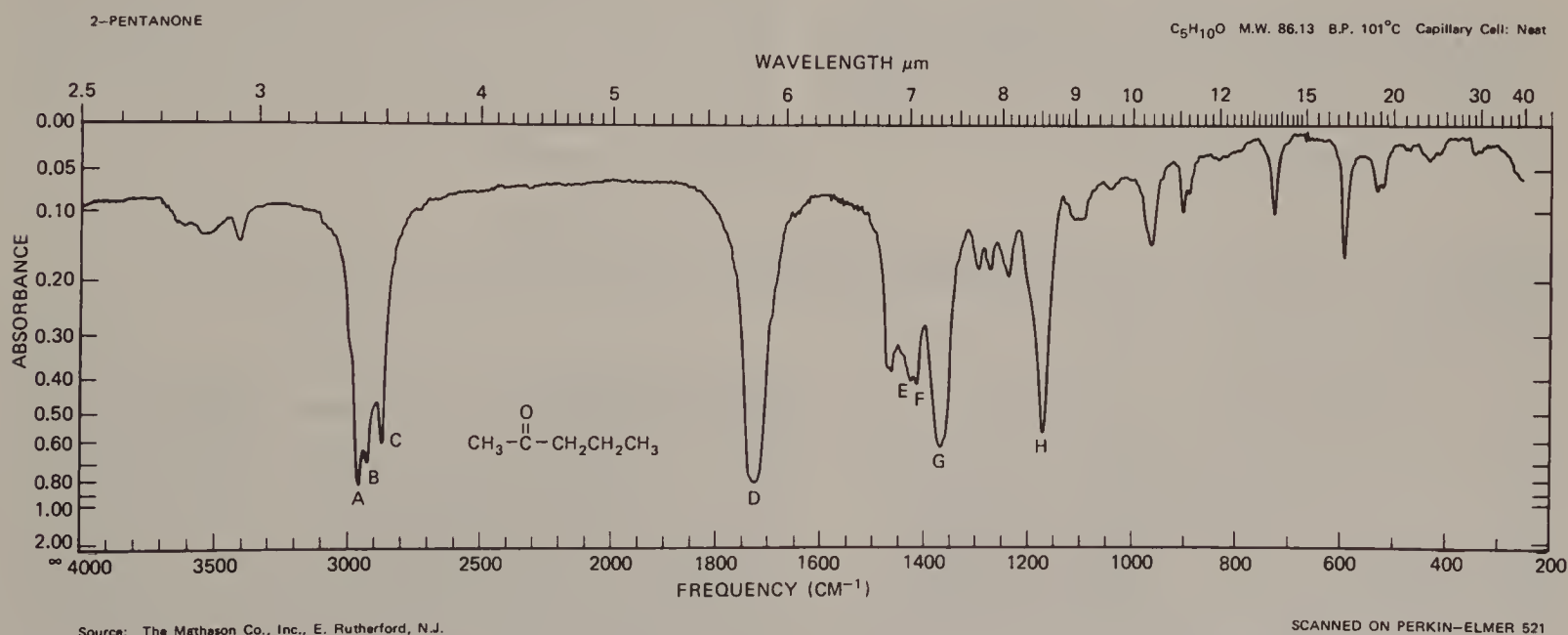


Figure 20. A.  $\nu_{\text{as}}$ , methyl, 2955  $\text{cm}^{-1}$  (3.39  $\mu\text{m}$ ). B.  $\nu_{\text{as}}$ , methylene, 2930  $\text{cm}^{-1}$  (3.41  $\mu\text{m}$ ). C.  $\nu_{\text{s}}$ , methyl, 2866  $\text{cm}^{-1}$  (3.49  $\mu\text{m}$ ). D. Normal\* C=O stretch, 1725  $\text{cm}^{-1}$  (5.80  $\mu\text{m}$ ). E.  $\delta_{\text{as}}$ , CH<sub>3</sub>, ca. 1430  $\text{cm}^{-1}$  (ca. 7.0  $\mu\text{m}$ ), see Table I, Appendix D. F.  $\delta_{\text{s}}$ , CH<sub>2</sub>, ca. 1430  $\text{cm}^{-1}$  (ca. 7.0  $\mu\text{m}$ ), see Table II, Appendix D. G.  $\delta_{\text{s}}$ , CH<sub>3</sub> of CH<sub>3</sub>CO unit, 1370  $\text{cm}^{-1}$  (7.30  $\mu\text{m}$ ), see Table I, Appendix D. H. C-CO-C stretch and bend, 1172  $\text{cm}^{-1}$  (8.53  $\mu\text{m}$ ).

\*See above for a definition of normal.



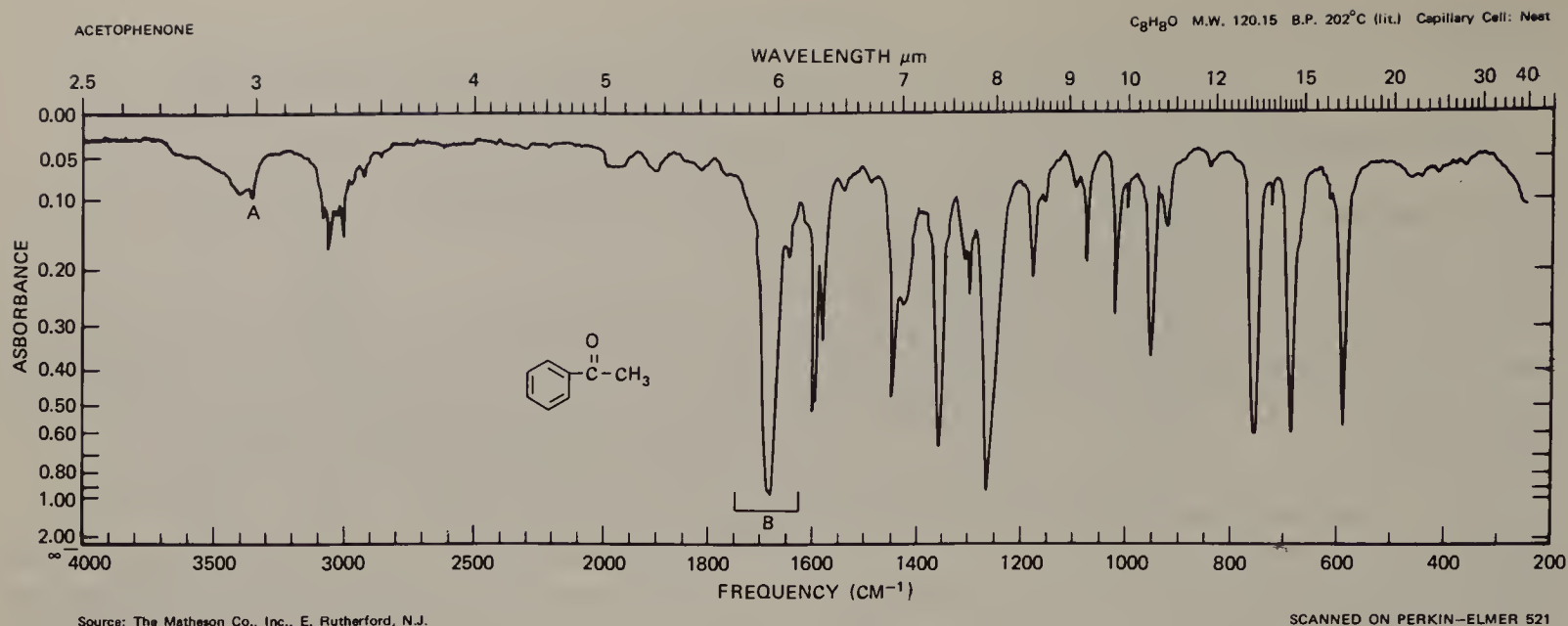
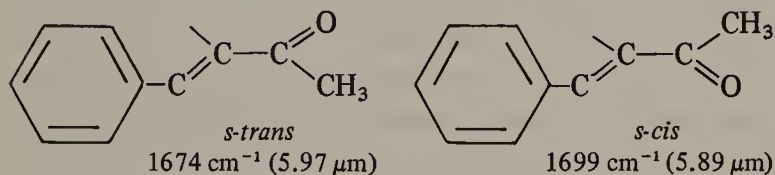


Figure 21. A. Overtone of C=O stretch,  $3350\text{ cm}^{-1}$  ( $2.98\text{ }\mu\text{m}$ ); frequency twice that of C=O stretch. B. C=O stretch,  $1683\text{ cm}^{-1}$  ( $5.94\text{ }\mu\text{m}$ ), lower frequency (longer wavelength) than observed in Figure 20 because of the conjugation with the phenyl group.

disulfide serves as an example; both the *s-cis* and *s-trans* forms are present at room temperature.



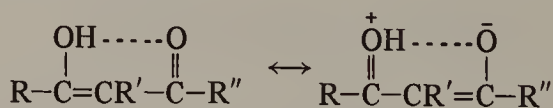
The absorption of the olefinic bond in conjugation with the carbonyl group occurs at a lower frequency than that of an isolated C=C bond; the intensity of the conjugated double bond absorption, when in an *s-cis* system, is greater than that of an isolated double bond.

Table III. The Carbonyl Absorption of Various  $\text{RCX}$  Compounds

| X Effect Predominantly Inductive<br>$\nu_{\text{C=O}}$ |   |
|--|---|
| X  |   |
| Cl   | $1815\text{--}1785\text{ cm}^{-1}$ ( $5.51\text{--}5.60\text{ }\mu\text{m}$ ) |
| F  | ca. $1869\text{ cm}^{-1}$ ( $5.35\text{ }\mu\text{m}$ )                       |
| Br   | $1812\text{ cm}^{-1}$ ( $5.52\text{ }\mu\text{m}$ )                           |
| OH (monomer)   | $1760\text{ cm}^{-1}$ ( $5.68\text{ }\mu\text{m}$ )                           |
| OR   | $1750\text{--}1735\text{ cm}^{-1}$ ( $5.71\text{--}5.76\text{ }\mu\text{m}$ ) |
| X Effect Predominantly Resonance<br>$\nu_{\text{C=O}}$ |   |
| X  |   |
| NH <sub>2</sub>  | $1695\text{--}1650\text{ cm}^{-1}$ ( $5.90\text{--}6.06\text{ }\mu\text{m}$ ) |
| SR   | $1720\text{--}1690\text{ cm}^{-1}$ ( $5.82\text{--}5.92\text{ }\mu\text{m}$ ) |

Intermolecular hydrogen bonding between a ketone and a hydroxylic solvent such as methyl alcohol causes a slight decrease in the absorption frequency of the carbonyl group. For example, a neat sample of methyl ethyl ketone absorbs at  $1715\text{ cm}^{-1}$  ( $5.83\text{ }\mu\text{m}$ ), whereas a 10% solution of the ketone in methanol absorbs at  $1706\text{ cm}^{-1}$  ( $5.86\text{ }\mu\text{m}$ ).

$\beta$ -Diketones usually exist as mixtures of tautomeric keto and enol forms. The enolic form does not show the normal absorption of conjugated ketones. Instead, a broad band appears in the  $1640\text{--}1580\text{ cm}^{-1}$  ( $6.10\text{--}6.33\text{ }\mu\text{m}$ ) region, many times more intense than normal carbonyl absorption. The intense and displaced absorption results from intramolecular hydrogen bonding, the bonded structure being stabilized by resonance.



Acetylacetone as a liquid at  $40^\circ\text{C}$  exists to the extent of 64% in the enolic form that absorbs at  $1613\text{ cm}^{-1}$  ( $6.20\text{ }\mu\text{m}$ ). The keto form and a small amount of unbonded enolic form may be responsible for 2 bands centering near  $1725\text{ cm}^{-1}$  ( $5.80\text{ }\mu\text{m}$ ). Interaction between the 2 carbonyl groups in the keto form has also been suggested as a cause for this doublet. The enolic O—H stretching absorption is seen as a broad shallow band at  $3000\text{--}2700\text{ cm}^{-1}$  ( $3.33\text{--}3.70\text{ }\mu\text{m}$ ).

$\alpha$ -Diketones, in which carbonyl groups exist in formal conjugation, show a single absorption band near the frequency observed for the corresponding monoketone. Biacetyl absorbs at  $1718\text{ cm}^{-1}$  ( $5.82\text{ }\mu\text{m}$ ), benzil at



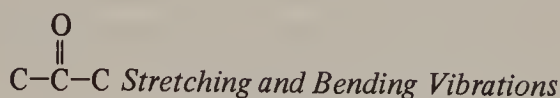
1681  $\text{cm}^{-1}$  (5.92  $\mu\text{m}$ ). Conjugation is ineffective for  $\alpha$ -diketones and the C=O groups of these diketones do not couple as do, for example, the corresponding groups in acid anhydrides (see below).

Quinones, which have both carbonyl groups in the same ring, absorb in the 1690-1655  $\text{cm}^{-1}$  (5.92-6.04  $\mu\text{m}$ ) region. With extended conjugation, in which the carbonyl groups appear in different rings, the absorption shifts to the 1655-1635  $\text{cm}^{-1}$  (6.04-6.12  $\mu\text{m}$ ) region.

Acyclic  $\alpha$ -chloro ketones absorb at 2 frequencies due to rotational isomerism. When the chlorine atom is near the oxygen, its negative field repels the nonbonding electrons of the oxygen atom, thus increasing the force constant of the C=O bond. This conformation absorbs at a higher frequency (1745  $\text{cm}^{-1}$ , 5.73  $\mu\text{m}$ ) than that in which the carbonyl oxygen and chlorine atom are widely separated (1725  $\text{cm}^{-1}$ , 5.80  $\mu\text{m}$ ). In rigid molecules such as the monoketo-steroids,  $\alpha$ -halogenation results in equatorial or axial substitution. In the equatorial orientation, the halogen atom is near the carbonyl group and the "field effect" causes an increase in the C=O stretching frequency. In the isomer in which the halogen atom is axial to the ring, and distant from the C=O, no shift is observed.

In cyclic ketones, the bond angle of the  $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C}=\text{O} \end{array}$  group influences the absorption frequency of the carbonyl group. The C=O stretching undoubtedly is affected by adjacent C—C stretching. In noncyclic ketones and in ketones with a 6-membered ring, the angle is near 120°. In strained rings in which the angle is less than 120°, interaction with C—C bond stretching increases the energy required to produce C=O stretching and thus increases the stretching frequency. Cyclohexanone absorbs at 1715  $\text{cm}^{-1}$  (5.83  $\mu\text{m}$ ), cyclo-

pentanone absorbs at 1751  $\text{cm}^{-1}$  (5.71  $\mu\text{m}$ ), and cyclobutanone absorbs at 1775  $\text{cm}^{-1}$  (5.63  $\mu\text{m}$ ).



Ketones show moderate absorption in the 1300-1100  $\text{cm}^{-1}$  (7.70-9.09  $\mu\text{m}$ ) region as a result of C—C—C stretching and

bending in the  $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C}-\text{C} \end{array}$  group. The absorption may consist of multiple bands. Aliphatic ketones absorb in the 1230-1100  $\text{cm}^{-1}$  (8.13-9.09  $\mu\text{m}$ ) region; aromatic ketones absorb at the higher frequency end of the general absorption region.

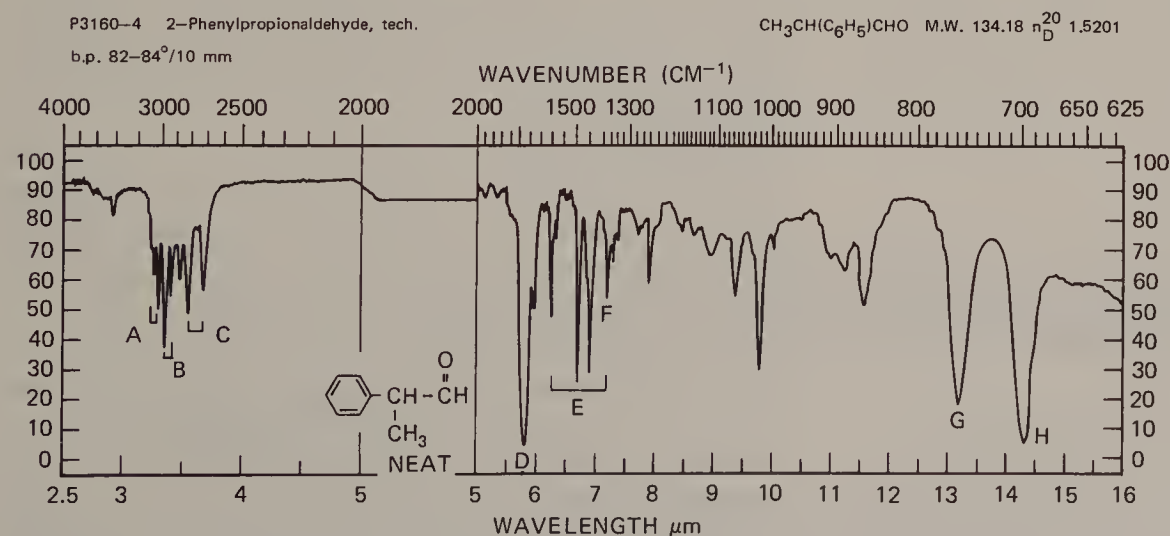
The spectra of 2-butanone (methyl ethyl ketone-no. 18), acetone-no. 17, and cyclohexanone-no. 19 in Appendix B illustrate ketonic absorptions.

## ALDEHYDES

The spectrum of 2-phenylpropionaldehyde, illustrating typical aldehydic absorption characteristics, is shown in Figure 22.

### C=O Stretching Vibrations

The carbonyl groups of aldehydes absorb at slightly higher frequencies than that of the corresponding methyl ketones. Aliphatic aldehydes absorb near 1740-1720  $\text{cm}^{-1}$  (5.75-5.82  $\mu\text{m}$ ). Aldehydic carbonyl absorption responds to structural changes in the same manner as ketones. Electro-



**Figure 22.** 2-Phenylpropionaldehyde. \* A. Aromatic, 3077, 3040  $\text{cm}^{-1}$  (3.25, 3.29  $\mu\text{m}$ ) (see Figure 13). B. Aliphatic, 2985, 2941, 2874  $\text{cm}^{-1}$  (3.35, 3.40, 3.48  $\mu\text{m}$ ) (see Figures 8 and 13). C. Aldehydic C—H stretch, 2825, 2717  $\text{cm}^{-1}$  (3.54, 3.68  $\mu\text{m}$ ). Doublet due to Fermi resonance with overtone of band at F. D. Normal aldehydic C=O stretch, 1730  $\text{cm}^{-1}$  (5.78  $\mu\text{m}$ ). Conjugated C=O stretch would be ca. 1700  $\text{cm}^{-1}$ ,

(5.89  $\mu\text{m}$ ), for example, in  $\text{C}_6\text{H}_5\text{CHO}$ . E. Ring C=C stretch, 1600, 1497, 1453  $\text{cm}^{-1}$  (6.25, 6.68, 6.88  $\mu\text{m}$ ). F. Aldehydic C—H bend, 1389  $\text{cm}^{-1}$  (7.20  $\mu\text{m}$ ). G. Out-of-plane C—H bend, 749  $\text{cm}^{-1}$  (13.35  $\mu\text{m}$ ). H. Out-of-plane C—C bend, 699  $\text{cm}^{-1}$  (14.30  $\mu\text{m}$ ).

\*A through C are C—H stretch absorptions.  
Courtesy of Aldrich Chemical Company.

negative substitution on the  $\alpha$ -carbon increases the frequency of carbonyl absorption. Acetaldehyde absorbs at  $1730\text{ cm}^{-1}$  ( $5.78\text{ }\mu\text{m}$ ), trichloroacetaldehyde absorbs at  $1768\text{ cm}^{-1}$  ( $5.65\text{ }\mu\text{m}$ ). Conjugate unsaturation, as in  $\alpha,\beta$ -unsaturated aldehydes and benzaldehydes, reduces the frequency of carbonyl absorption.  $\alpha,\beta$ -Unsaturated aldehydes and benzaldehydes absorb in the region of  $1710\text{--}1685\text{ cm}^{-1}$  ( $5.85\text{--}5.94\text{ }\mu\text{m}$ ). Internal hydrogen bonding, such as occurs in salicylaldehyde, shifts the absorption ( $1666\text{ cm}^{-1}$ ,  $6.00\text{ }\mu\text{m}$ , for salicylaldehyde) to lower wavenumbers (longer wavelengths). Glyoxal, like the  $\alpha$ -diketones, shows only one carbonyl absorption peak with no shift from the normal absorption position of mono-aldehydic absorption.

### C–H Stretching Vibrations

The majority of aldehydes show aldehydic C–H stretching absorption in the  $2830\text{--}2695\text{ cm}^{-1}$  ( $3.53\text{--}3.71\text{ }\mu\text{m}$ ) region. Two moderately intense bands are frequently observed in this region. The appearance of two bands is attributed to Fermi resonance between the fundamental aldehydic C–H stretch and the first overtone of the aldehydic C–H bending vibration that usually appears near  $1390\text{ cm}^{-1}$  ( $7.20\text{ }\mu\text{m}$ ). Only one C–H stretching band is observed for aldehydes whose C–H bending band has been shifted appreciably from  $1390\text{ cm}^{-1}$  ( $7.20\text{ }\mu\text{m}$ ).

Some aromatic aldehydes with strongly electronegative groups in the ortho position may absorb as high as  $2900\text{ cm}^{-1}$  ( $3.45\text{ }\mu\text{m}$ ).

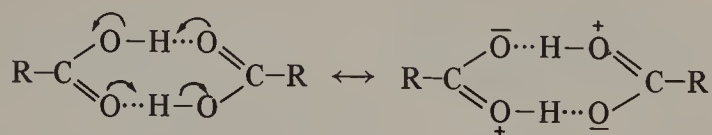
Medium intense absorption near  $2720\text{ cm}^{-1}$  ( $3.68\text{ }\mu\text{m}$ ), accompanied by a carbonyl absorption band is good evidence for the presence of an aldehyde group.

The absorption frequencies of methyl and methylene groups attached to a carbonyl are summarized in Tables I and II of Appendix D.

## CARBOXYLIC ACIDS

### O–H Stretching Vibrations

In the liquid or solid state, and in carbon tetrachloride solution at concentrations much over  $0.01\text{ M}$ , carboxylic acids exist as dimers due to strong hydrogen bonding.



The exceptional strength of the hydrogen bonding is explained on the basis of the large contribution of the ionic resonance structure. Because of the strong bonding, a free

hydroxyl stretching vibration (near  $3520\text{ cm}^{-1}$ ,  $2.84\text{ }\mu\text{m}$ ) is observed only in very dilute solution in nonpolar solvents or in the vapor phase. In each case, however, there is a mixture of monomer and dimer.

Carboxylic acid dimers display very broad, intense O–H stretching absorption in the region of  $3300\text{--}2500\text{ cm}^{-1}$  ( $3.03\text{--}4.00\text{ }\mu\text{m}$ ). The band usually centers near  $3000\text{ cm}^{-1}$  ( $3.33\text{ }\mu\text{m}$ ). The weaker C–H stretching bands are generally seen superimposed upon the broad O–H band. Fine structure observed on the long-wavelength side of the broad O–H band represents overtones and combination tones of fundamental bands occurring at longer wavelengths. The spectrum of a typical aliphatic carboxylic acid is displayed in Figure 23.

Other structures with strong hydrogen bonding, such as  $\beta$ -diketones, also absorb in the  $3300\text{--}2500\text{ cm}^{-1}$  ( $3.03\text{--}4.00\text{ }\mu\text{m}$ ) region, but the absorption is usually less intense. Also, the C=O stretching vibrations of structures such as  $\beta$ -diketones are shifted to lower frequencies than those observed for carboxylic acids.

Carboxylic acids can bond intermolecularly with ethers, such as dioxane and tetrahydrofuran, or with other solvents that can act as proton acceptors. Spectra determined in such solvents show bonded O–H absorption near  $3100\text{ cm}^{-1}$  ( $3.23\text{ }\mu\text{m}$ ).

### C=O Stretching Vibrations

The C=O stretching bands of acids are considerably more intense than ketonic C=O stretching bands. The monomers of saturated aliphatic acids absorb near  $1760\text{ cm}^{-1}$  ( $5.68\text{ }\mu\text{m}$ ).

The carboxylic dimer has a center of symmetry; only the asymmetrical C=O stretching mode absorbs in the infrared. Hydrogen bonding and resonance weaken the C=O bond, resulting in absorption at a lower frequency than the monomer. The C=O group in dimerized saturated aliphatic acids absorbs in the region of  $1720\text{--}1706\text{ cm}^{-1}$  ( $5.81\text{--}5.86\text{ }\mu\text{m}$ ).

Internal hydrogen bonding reduces the frequency of the carbonyl stretching absorption to a greater degree than does intermolecular hydrogen bonding. For example, salicylic acid absorbs at  $1665\text{ cm}^{-1}$  ( $6.01\text{ }\mu\text{m}$ ), whereas *p*-hydroxybenzoic acid absorbs at  $1680\text{ cm}^{-1}$  ( $5.95\text{ }\mu\text{m}$ ).

Unsaturation in conjugation with the carboxylic carbonyl group decreases the frequency (increases the wavelength) of absorption of both the monomer and dimer forms only slightly. In general,  $\alpha,\beta$ -unsaturated and aryl conjugated acids show absorption for the dimer in the  $1710\text{--}1680\text{ cm}^{-1}$  ( $5.85\text{--}5.95\text{ }\mu\text{m}$ ) region. Extension of conjugation beyond the  $\alpha,\beta$ -position results in very little additional shifting of the C=O absorption.

Substitution in the  $\alpha$ -position with electronegative groups, such as the halogens, brings about a slight increase



in the C=O absorption frequency (10-20  $\text{cm}^{-1}$ , 0.03-0.07  $\mu\text{m}$ ). The spectra of acids with halogens in the  $\alpha$ -position, determined in the liquid state or in solution, show dual carbonyl bands due to rotational isomerism (field effect). The higher frequency (shorter wavelength) band corresponds to the conformation in which the halogen is in proximity to the carbonyl group.

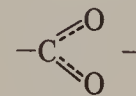
### C-O Stretching and O-H Bending Vibrations

Two bands arising from C-O stretching and O-H bending appear in the spectra of carboxylic acids near 1320-1210  $\text{cm}^{-1}$  (7.58-8.26  $\mu\text{m}$ ) and near 1440-1395  $\text{cm}^{-1}$  (6.94-7.17  $\mu\text{m}$ ), respectively. Both of these bands involve some interaction between C-O stretching and in-plane C-O-H bending. The more intense band, near 1315-1280  $\text{cm}^{-1}$  (7.60-7.81  $\mu\text{m}$ ) for dimers, is generally referred to as the C-O stretching band and usually appears as a doublet in the spectra of long-chain fatty acids. The C-O-H bending band near 1440-1395  $\text{cm}^{-1}$  (6.94-7.17  $\mu\text{m}$ ) is of moderate intensity and occurs in the same region as the  $\text{CH}_2$  scissoring vibration of the  $\text{CH}_2$  group adjacent to the carbonyl.

One of the characteristic bands in the spectra of dimeric carboxylic acids results from the out-of-plane bending of the bonded O-H. The band appears near 920  $\text{cm}^{-1}$  (10.87  $\mu\text{m}$ ) and is characteristically broad with medium intensity.

### CARBOXYLATE ANION

The carboxylate anion has two strongly coupled carbon to oxygen bonds with bond strengths intermediate between C=O and C-O.

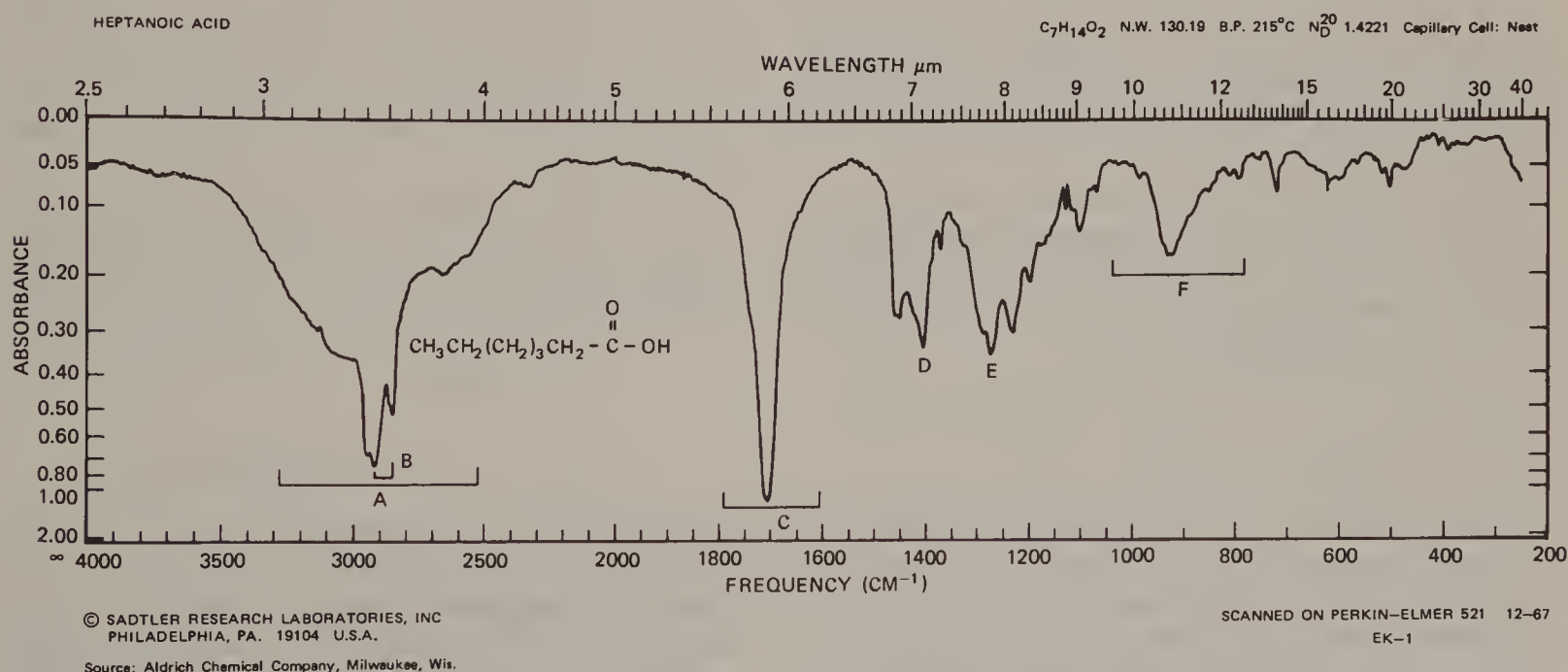


The carboxylate ion gives rise to 2 bands: a strong asymmetrical stretching band near 1650-1550  $\text{cm}^{-1}$  (6.06-6.45  $\mu\text{m}$ ), and a weaker, symmetrical stretching band near 1400  $\text{cm}^{-1}$  (7.15  $\mu\text{m}$ ).

The conversion of a carboxylic acid to a salt can serve as confirmation of the acid structure. This is conveniently done by the addition of a tertiary, aliphatic amine, such as triethylamine, to a solution of the carboxylic acid in chloroform (no reaction occurs in carbon tetrachloride). The carboxylate ion, thus formed, shows the two characteristic carbonyl absorption bands in addition to an "ammonium" band in the 2700-2200  $\text{cm}^{-1}$  (3.70-4.55  $\mu\text{m}$ ) region. The O-H stretching band, of course, disappears. The spectrum of ammonium benzoate, Figure 24, demonstrates most of these features.

### ESTERS AND LACTONES

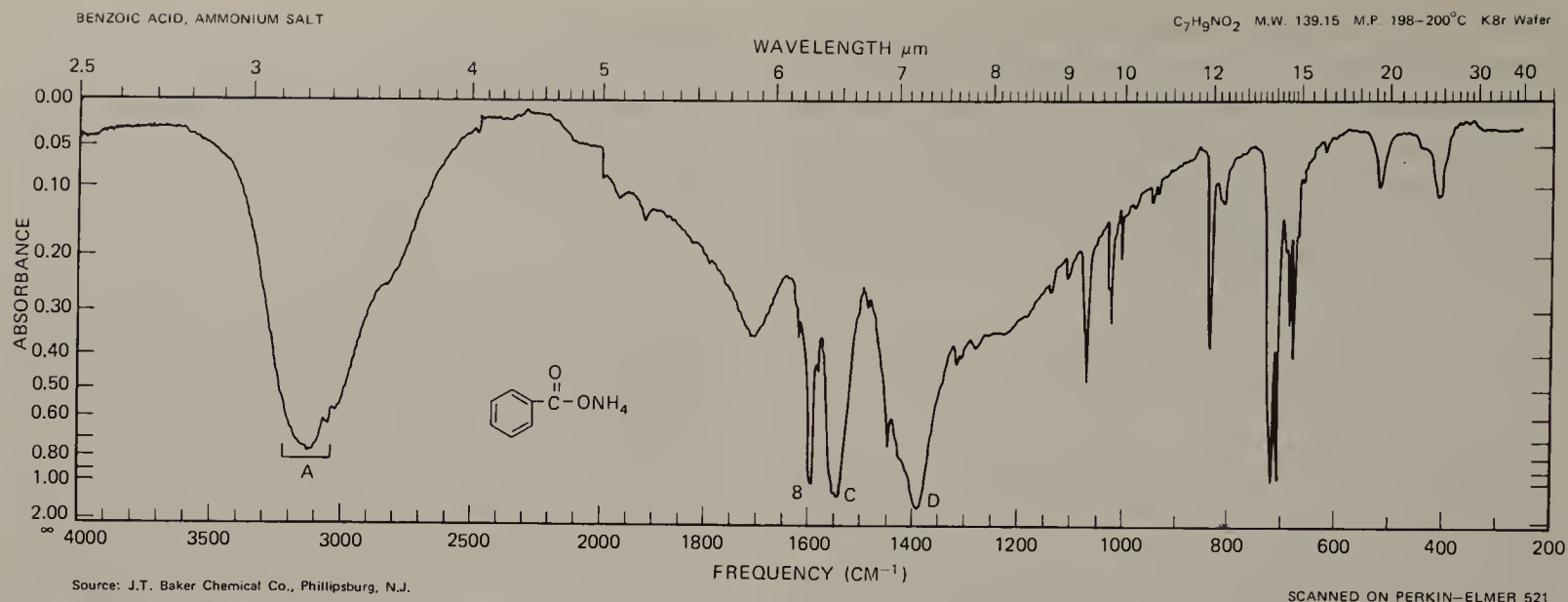
Esters and lactones have two characteristically strong absorption bands arising from C=O and C-O stretching.



**Figure 23.** A. Broad O-H stretch, 3300-2500  $\text{cm}^{-1}$  (3.03-4.00  $\mu\text{m}$ ). B. C-H stretch, (see Figure 8) 2950, 2920, 2850  $\text{cm}^{-1}$  (3.39, 3.43, 3.51  $\mu\text{m}$ ). (Superimposed upon O-H stretch. C. Normal, dimeric carboxylic C=O stretch, 1715  $\text{cm}^{-1}$  (5.83  $\mu\text{m}$ ). D. C-O-H in-plane bend,\* 1408  $\text{cm}^{-1}$  (7.10  $\mu\text{m}$ ). E. C-O stretch,\* dimer, 1280  $\text{cm}^{-1}$  (7.81  $\mu\text{m}$ ). F. O-H out-of-plane bend, 930  $\text{cm}^{-1}$  (10.75  $\mu\text{m}$ ).

\*Bands at D and E involve C-O-H interaction.





**Figure 24.** A. N–H and C–H stretch,  $3600\text{--}2500\text{ cm}^{-1}$  ( $2.78\text{--}4.00\text{ }\mu\text{m}$ ). B. Ring C=C stretch,  $1550\text{ cm}^{-1}$  ( $6.45\text{ }\mu\text{m}$ ). C. Asymmetric carboxylate anion  $\text{C}(\text{=O})_2^-$  stretch,  $1600\text{ cm}^{-1}$  ( $6.25\text{ }\mu\text{m}$ ). D. Symmetric carboxylate anion  $\text{C}(\text{=O})_2^-$  stretch,  $1385\text{ cm}^{-1}$  ( $7.22\text{ }\mu\text{m}$ ).

The intense C=O stretching vibration occurs at higher frequencies (shorter wavelength) than that of normal ketones. The force constant of the carbonyl bond is increased by the electron attracting nature of the adjacent oxygen atom (inductive effect). Overlapping occurs between esters in which the carbonyl frequency is lowered, and ketones in which the normal ketone frequency is raised. A distinguishing feature of esters and lactones, however, is the strong C–O stretching band in the region where a weaker band occurs for ketones. There is overlapping in the C=O frequency of esters or lactones and acids, but the OH stretching and bending vibrations and the possibility of salt formation distinguish the acids.

The frequency of the ester carbonyl responds to environmental changes in the vicinity of the carbonyl group in much the same manner as ketones. The spectrum of phenyl acetate, Figure 25, illustrates most of the important absorption characteristics for esters.

### C=O Stretching Vibrations

The C=O absorption band of saturated aliphatic esters (except formates) is in the  $1750\text{--}1735\text{ cm}^{-1}$  ( $5.71\text{--}5.76\text{ }\mu\text{m}$ ) region. The C=O absorption bands of formates,  $\alpha,\beta$ -unsaturated, and benzoate esters are in the region of  $1730\text{--}1715\text{ cm}^{-1}$  ( $5.78\text{--}5.83\text{ }\mu\text{m}$ ). Further conjugation has little or no additional effect upon the frequency of the carbonyl absorption.

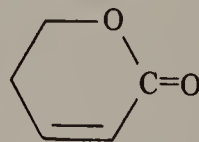
In the spectra of vinyl or phenyl esters, with unsaturation adjacent to the C–O– group, a marked rise in the carbonyl frequency is observed along with a lowering of the C–O frequency. Vinyl acetate has a carbonyl band at

$1776\text{ cm}^{-1}$  ( $5.63\text{ }\mu\text{m}$ ); phenyl acetate absorbs at  $1770\text{ cm}^{-1}$  ( $5.65\text{ }\mu\text{m}$ ).

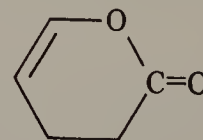
$\alpha$ -Halogen substitution results in a rise in the C=O stretching frequency. Ethyl trichloroacetate absorbs at  $1770\text{ cm}^{-1}$  ( $5.65\text{ }\mu\text{m}$ ).

In oxalates and  $\alpha$ -keto esters, as in  $\alpha$ -diketones, there appears to be little or no interaction between the two carbonyl groups so that normal absorption occurs in the region of  $1755\text{--}1740\text{ cm}^{-1}$  ( $5.70\text{--}5.75\text{ }\mu\text{m}$ ). In the spectra of  $\beta$ -keto esters, however, where enolization can occur, a band is observed near  $1650\text{ cm}^{-1}$  ( $6.06\text{ }\mu\text{m}$ ) that results from bonding between the ester C=O and the enolic hydroxyl group.

The carbonyl absorption of saturated  $\delta$ -lactones (6-membered ring) occurs in the same region as straight-chain, unconjugated esters. Unsaturation  $\alpha$  to the C=O reduces



$1720\text{ cm}^{-1}$  ( $5.81\text{ }\mu\text{m}$ )

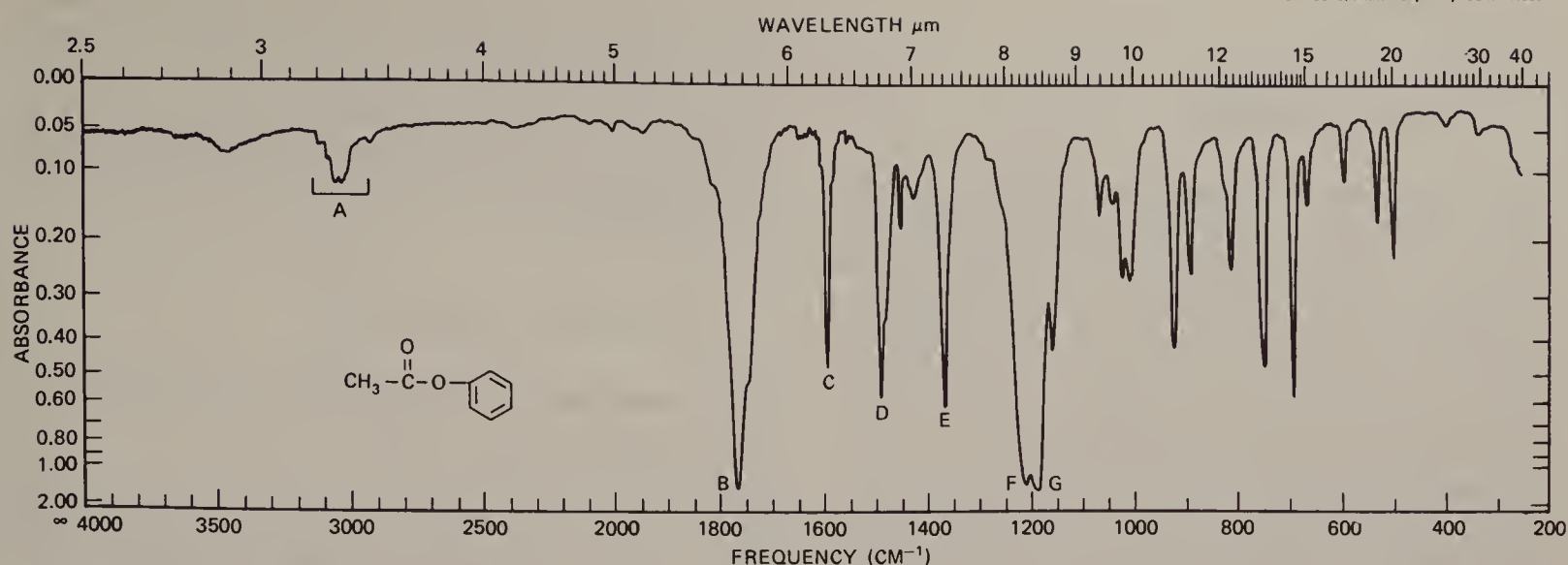


$1760\text{ cm}^{-1}$  ( $5.68\text{ }\mu\text{m}$ )

the C=O absorption frequency. Unsaturation  $\alpha$  to the –O– group increases it.

$\alpha$ -Pyrones frequently display 2 carbonyl absorption bands in the  $1775\text{--}1715\text{ cm}^{-1}$  ( $5.63\text{--}5.83\text{ }\mu\text{m}$ ) region, probably due to Fermi resonance.

Saturated  $\gamma$ -lactones (5-membered ring) absorb at shorter wavelengths than esters or  $\delta$ -lactones:  $1795\text{--}1760\text{ cm}^{-1}$  ( $5.57\text{--}5.68\text{ }\mu\text{m}$ );  $\gamma$ -valerolactone absorbs at  $1770\text{ cm}^{-1}$  ( $5.65\text{ }\mu\text{m}$ ). Unsaturation in the  $\gamma$ -lactone molecule affects the carbonyl absorption in the same manner as unsaturation in  $\delta$ -lactones.

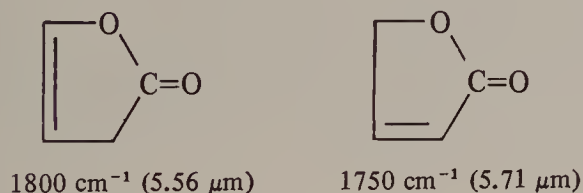
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Philadelphia, PA. 19104 U.S.A.

SCANNED ON PERKIN-ELMER 521 12-67

Source: The Matheson Company, Inc., East Rutherford, New Jersey

**Figure 25.** A. Aromatic C–H stretch,  $3070, 3040\text{ cm}^{-1}$  ( $3.26, 3.29\text{ }\mu\text{m}$ ). B. C=O stretch,  $1770\text{ cm}^{-1}$  ( $5.65\text{ }\mu\text{m}$ ); this is higher frequency than that due to normal ester C=O stretch (ca.  $1740\text{ cm}^{-1}$ ,  $5.75\text{ }\mu\text{m}$ , see Table III), due to phenyl conjugation with alcohol oxygen; conjugation of an aryl group or other unsaturation with the carbonyl group causes this C=O stretch to be at lower than normal frequency (e.g., benzoates absorb at ca.  $1724\text{ cm}^{-1}$ , ca.  $5.80\text{ }\mu\text{m}$ ). C. Ring C=C stretch,  $1593\text{ cm}^{-1}$  ( $6.28\text{ }\mu\text{m}$ ). D.  $\delta_{as}$ ,  $\text{CH}_3$ ,  $1493\text{ cm}^{-1}$  ( $6.70\text{ }\mu\text{m}$ ). \* E.  $\delta_s$ ,  $\text{CH}_3$ ,  $1360\text{ cm}^{-1}$  ( $7.35\text{ }\mu\text{m}$ ). \* F. Acetate  $\text{CC}(=\text{O})\text{--O}$  stretch,  $1205\text{ cm}^{-1}$  ( $8.30\text{ }\mu\text{m}$ ). G.  $\text{O--C}\equiv\text{C}$  asym. stretch,  $1183\text{ cm}^{-1}$  ( $8.45\text{ }\mu\text{m}$ ).

\*See Table I, Appendix D.



In unsaturated lactones, when the double bond is adjacent to the  $\text{--O--}$ , a strong  $\text{C}=\text{C}$  absorption is observed in the  $1685\text{--}1660\text{ cm}^{-1}$  ( $5.94\text{--}6.02\text{ }\mu\text{m}$ ) region.

### C–O Stretching Vibrations

The “C–O stretching vibrations” of esters actually consists of 2 asymmetric coupled vibrations:  $\text{C--C}(=\text{O})\text{--O}$  and  $\text{O--C--C}$ , the former being more important. These bands occur in the region of  $1300\text{--}1000\text{ cm}^{-1}$  ( $7.70\text{--}10.00\text{ }\mu\text{m}$ ). The corresponding symmetric vibrations are of little importance. The C–O stretch correlations are less reliable than the  $\text{C}=\text{O}$  stretch correlations.

The  $\text{C--C}(=\text{O})\text{--O}$  band of saturated esters, except for acetates, shows strongly in the  $1210\text{--}1163\text{ cm}^{-1}$  ( $8.26\text{--}8.60\text{ }\mu\text{m}$ ) region. It is often broader and stronger than the  $\text{C}=\text{O}$  stretch absorption. Acetates of saturated alcohols

display this band at  $1240\text{ cm}^{-1}$  ( $8.07\text{ }\mu\text{m}$ ). Vinyl and phenyl acetates absorb at a somewhat lower frequency,  $1190\text{--}1140\text{ cm}^{-1}$  ( $8.40\text{--}8.77\text{ }\mu\text{m}$ ); for example, see Figure 25. The  $\text{C--C}(=\text{O})\text{--O}$  stretch of esters of  $\alpha,\beta$ -unsaturated acids results in multiple bands in the  $1300\text{--}1160\text{ cm}^{-1}$  ( $7.69\text{--}8.62\text{ }\mu\text{m}$ ) region. Esters of aromatic acids absorb strongly in the  $1310\text{--}1250\text{ cm}^{-1}$  ( $7.63\text{--}8.00\text{ }\mu\text{m}$ ) region. The analogous type of stretch in lactones is observed in the  $1250\text{--}1111\text{ cm}^{-1}$  ( $8.00\text{--}9.00\text{ }\mu\text{m}$ ) region.

The  $\text{O--C--C}$  band of esters (“alcohol” carbon-oxygen stretch) of primary alcohols occurs at about  $1064\text{--}1031\text{ cm}^{-1}$  ( $9.40\text{--}9.70\text{ }\mu\text{m}$ ) and that of esters of secondary alcohols occurs at about  $1100\text{ cm}^{-1}$  ( $9.09\text{ }\mu\text{m}$ ). Aromatic esters of primary alcohols show this absorption near  $1111\text{ cm}^{-1}$  ( $9.00\text{ }\mu\text{m}$ ).

Methyl esters of long-chain fatty acids present a 3 band pattern with bands near  $1250\text{ cm}^{-1}$  ( $8.00\text{ }\mu\text{m}$ ),  $1205\text{ cm}^{-1}$  ( $8.30\text{ }\mu\text{m}$ ), and  $1175\text{ cm}^{-1}$  ( $8.51\text{ }\mu\text{m}$ ). The band near  $1175\text{ cm}^{-1}$  ( $8.51\text{ }\mu\text{m}$ ) is the strongest.

The influence of the  $\text{--C}(=\text{O})\text{--O}$  group upon adjacent  $\text{CH}_2$  and  $\text{CH}_3$  groups is summarized in Appendix C, Tables I and II. Some spectra showing typical ester absorptions are shown in Appendix B: ethyl acetate-no.20 and diethyl phthalate-no.21.

## ACID HALIDES

### *C=O Stretching Vibrations*

Acid halides show strong absorption in the C=O stretching region. Unconjugated acid chlorides absorb in the 1815-1785  $\text{cm}^{-1}$  (5.51-5.60  $\mu\text{m}$ ) region. Acetyl fluoride in the gas phase absorbs near 1869  $\text{cm}^{-1}$  (5.35  $\mu\text{m}$ ). Conjugated acid halides absorb at a slightly lower frequency because resonance reduces the force constant of the C=O bond; aromatic acid chlorides absorb strongly at 1800-1770  $\text{cm}^{-1}$  (5.56-5.65  $\mu\text{m}$ ). A weak band near 1750-1735  $\text{cm}^{-1}$  (5.71-5.76  $\mu\text{m}$ ) appearing in the spectra of aroyl chlorides probably results from Fermi resonance between the C=O band and the overtone of a longer wavelength band near 875  $\text{cm}^{-1}$  (11.43  $\mu\text{m}$ ). The annotated spectrum of benzoyl chloride is given in Figure 26.

## CARBOXYLIC ACID ANHYDRIDES

### *C=O Stretching Vibrations*

Anhydrides display 2 stretching bands in the carbonyl region. The 2 bands result from asymmetrical and symmetrical C=O stretching modes. Saturated noncyclic anhydrides absorb near 1818  $\text{cm}^{-1}$  (5.50  $\mu\text{m}$ ) and near 1750  $\text{cm}^{-1}$  (5.71  $\mu\text{m}$ ). Conjugated noncyclic anhydrides show absorption near 1775  $\text{cm}^{-1}$  (5.63  $\mu\text{m}$ ) and near 1720  $\text{cm}^{-1}$  (5.81  $\mu\text{m}$ ); the decrease in the frequency of absorption is due to resonance. The higher frequency band is the more intense.

Cyclic anhydrides with 5-membered rings show absorption at higher frequencies (lower wavelengths) than noncyclic anhydrides because of ring strain; succinic anhydride absorbs at 1865  $\text{cm}^{-1}$  (5.37  $\mu\text{m}$ ) and at 1782  $\text{cm}^{-1}$  (5.62  $\mu\text{m}$ ); The lower frequency (longer wavelength) C=O band is the stronger of the 2 carbonyl bands in 5-membered-ring cyclic anhydrides.

### *C-O Stretching Vibrations*

Other strong bands appear in the spectra of anhydrides as a

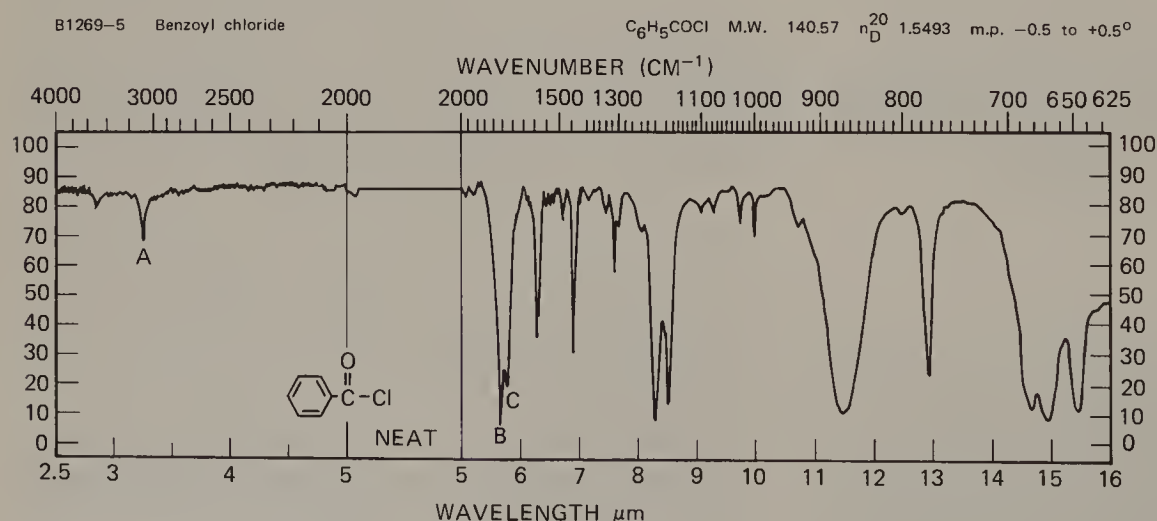
result of  $\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}$  stretching vibrations. Unconjugated straight chain anhydrides absorb near 1047  $\text{cm}^{-1}$  (9.55  $\mu\text{m}$ ). Cyclic anhydrides display bands near 952-909  $\text{cm}^{-1}$  (10.50-11.00  $\mu\text{m}$ ), and near 1299-1176  $\text{cm}^{-1}$  (7.70-8.50  $\mu\text{m}$ ). The C-O stretching band for acetic anhydride is at 1125  $\text{cm}^{-1}$  (8.89  $\mu\text{m}$ ).

The spectrum of Figure 27 is that of a typical aliphatic anhydride.

## AMIDES

All amides show a carbonyl absorption band known as the Amide I band. Its position depends on the degree of hydrogen bonding and, thus, on the physical state of the compound.

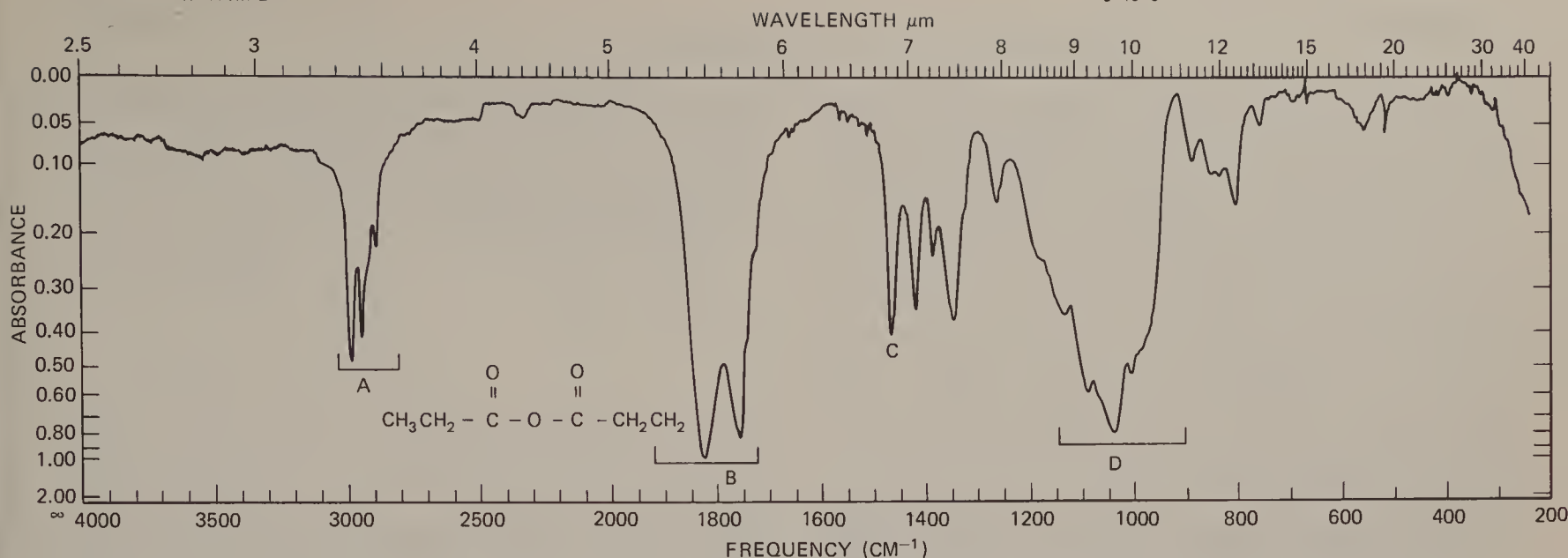
Primary amides show 2 N-H stretching bands resulting from symmetrical and asymmetrical N-H stretching. Secondary amides and lactams show only 1 N-H stretching band. As in the case of O-H stretching, the frequency of the N-H stretching is reduced by hydrogen bonding,



**Figure 26.** A. Aromatic C-H stretch, 3080  $\text{cm}^{-1}$  (3.25  $\mu\text{m}$ ). B. C=O stretch, 1790  $\text{cm}^{-1}$  (5.58  $\mu\text{m}$  see Table III p. 118). (Acid chloride C=O stretch position shows very small dependence upon conjugation; aroyl chlorides identified by band such as at C.) C. Fermi resonance band (of C=O stretch and overtone of 875  $\text{cm}^{-1}$  band), 1745  $\text{cm}^{-1}$  (5.73  $\mu\text{m}$ ).

Source: Courtesy of Aldrich Chemical Co.





**Figure 27.** A. C–H stretch, 2990, 2950, 2880  $\text{cm}^{-1}$  (3.34, 3.39, 3.47  $\mu\text{m}$ ). B. Asymmetric and symmetric C=O coupled stretching, respectively: 1825, 1758  $\text{cm}^{-1}$  (5.48, 5.69  $\mu\text{m}$ ). See Table III, p. 118. C.  $\delta_s$  CH<sub>2</sub> (scissoring), 1465  $\text{cm}^{-1}$  (6.83  $\mu\text{m}$ ), See Table II, Appendix D. D. C–CO–O–CO–C stretch, 1040  $\text{cm}^{-1}$  (9.62  $\mu\text{m}$ ).

though to a lesser degree. Overlapping occurs in the observed position of N–H and O–H stretching frequencies so that an unequivocal differentiation in structure is sometimes impossible.

Primary amides and secondary amides, and a few lactams, display a band or bands in the region of 1650–1515  $\text{cm}^{-1}$  (6.06–6.60  $\mu\text{m}$ ) due primarily to NH<sub>2</sub> or NH bending: the amide II band. This absorption involves coupling between N–H bending and other fundamental vibrations and requires a *trans* geometry.

Out-of-plane NH wagging is responsible for a broad band of medium intensity in the 800–666  $\text{cm}^{-1}$  (12.5–15.0  $\mu\text{m}$ ) region.

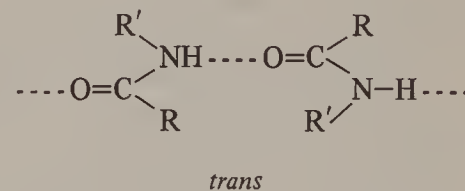
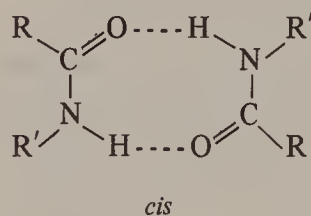
The spectrum of Figure 28 is that of a typical primary amide of an aliphatic acid. The spectrum of DMF (*N,N*-dimethylformamide, Appendix B, no. 28) displays typical amide absorptions.

### N–H Stretching Vibrations

In dilute solution in nonpolar solvents, primary amides show two moderately intense NH stretching frequencies corresponding to the asymmetrical and symmetrical NH stretching vibrations. These bands occur near 3520  $\text{cm}^{-1}$  (2.84  $\mu\text{m}$ ) and 3400  $\text{cm}^{-1}$  (2.94  $\mu\text{m}$ ), respectively. In the spectra of solid samples, these bands are observed near 3350  $\text{cm}^{-1}$  (2.99  $\mu\text{m}$ ) and 3180  $\text{cm}^{-1}$  (3.15  $\mu\text{m}$ ) because of hydrogen bonding.

In infrared spectra of secondary amides, which exist mainly in the *trans* conformation, the free NH stretching vibration observed in dilute solutions occurs near 3500–

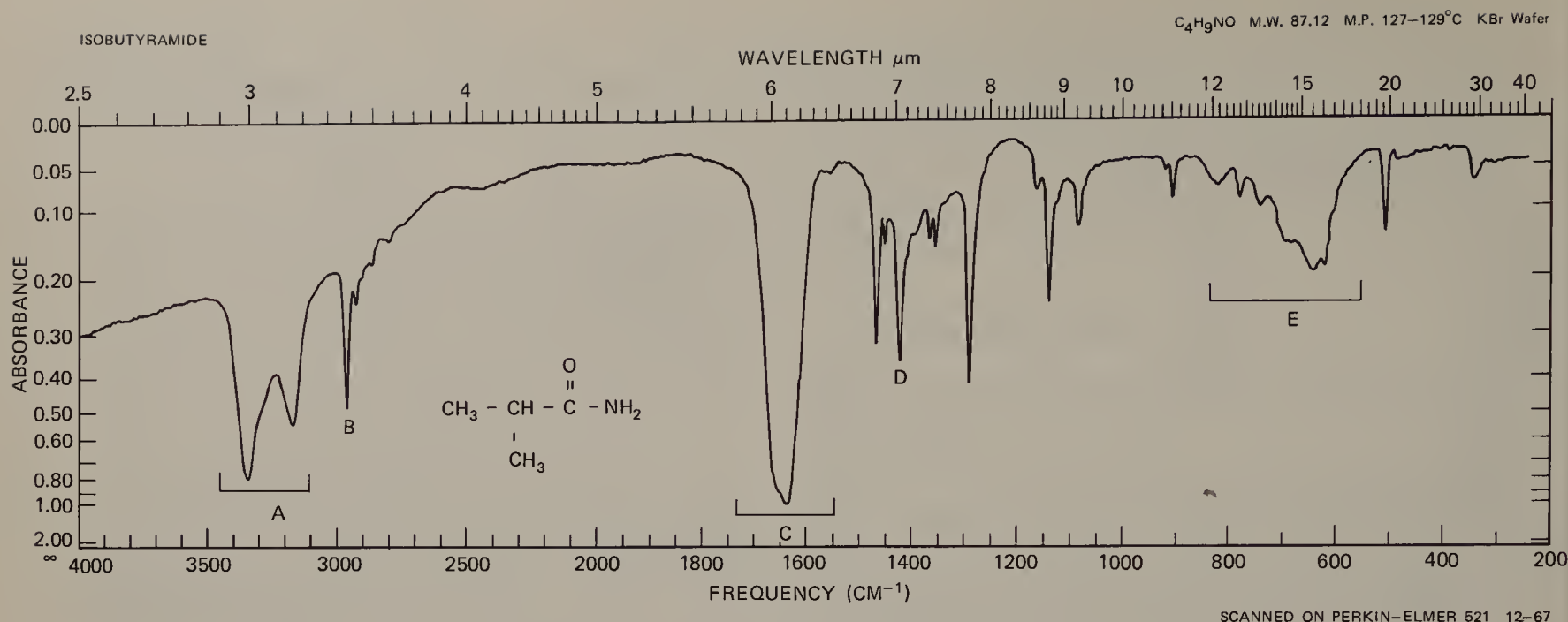
3400  $\text{cm}^{-1}$  (2.86–2.94  $\mu\text{m}$ ). In more concentrated solutions and in solid samples, the free NH band is replaced by multiple bands in the 3330–3060  $\text{cm}^{-1}$  (3.00–3.27  $\mu\text{m}$ ) region. Multiple bands are observed since the amide group can bond to produce dimers, with a *cis* conformation, and polymers, with a *trans* conformation.



### C=O Stretching Vibrations (Amide I Band)

The C=O absorption of amides occurs at longer wavelengths than “normal” carbonyl absorption due to the resonance effect (see p. 118). The position of absorption depends on the same environmental factors as the carbonyl absorption of other compounds.

Primary amides (except acetamide, whose C=O bond absorbs at 1694  $\text{cm}^{-1}$ , 5.90  $\mu\text{m}$ ) have a strong amide I band in the region of 1650  $\text{cm}^{-1}$  (6.06  $\mu\text{m}$ ) when examined in the solid phase. When the amide is examined in dilute solution, the absorption is observed at a higher frequency,



Source: Aldrich Chemical Company, Milwaukee, Wis.

**Figure 28.** A. N–H stretch, coupled, primary amide, hydrogen bonded. Asymmetric, 3350  $\text{cm}^{-1}$  (2.99  $\mu\text{m}$ ). Symmetric, 3170  $\text{cm}^{-1}$  (3.15  $\mu\text{m}$ ). B. Aliphatic C–H stretch, 2960  $\text{cm}^{-1}$  (3.15  $\mu\text{m}$ ). C. Overlap C=O stretch, Amide I band, 1640  $\text{cm}^{-1}$  (6.10  $\mu\text{m}$ ), see Table III. N–H bend, 1640  $\text{cm}^{-1}$  (6.10  $\mu\text{m}$ ), Amide II band. D. C–N stretch, 1425  $\text{cm}^{-1}$  (7.02  $\mu\text{m}$ ). E. Broad N–H out-of-plane bend, 700–600  $\text{cm}^{-1}$  (14.28–16.67  $\mu\text{m}$ ).

near 1690  $\text{cm}^{-1}$  (5.92  $\mu\text{m}$ ). In more concentrated solutions, the C=O frequency is observed at some intermediate value, depending on the degree of hydrogen bonding.

Simple, open-chain, secondary amides absorb near 1640  $\text{cm}^{-1}$  (6.10  $\mu\text{m}$ ) when examined in the solid state. In dilute solution, the frequency of the amide I band may be raised to 1680  $\text{cm}^{-1}$  (5.95  $\mu\text{m}$ ) and even to 1700  $\text{cm}^{-1}$  (5.88  $\mu\text{m}$ ) in the case of the anilides. In the anilide structure there is competition between the ring and the C=O for the non-bonded electron pair of the nitrogen.

The carbonyl frequency of tertiary amides is independent of the physical state since hydrogen bonding with another tertiary amide group is impossible. The C=O absorption occurs in the range of 1680–1630  $\text{cm}^{-1}$  (5.95–6.13  $\mu\text{m}$ ). The absorption range of tertiary amides in solution is influenced by hydrogen bonding with the solvent. *N,N*-Diethylacetamide absorbs at 1647  $\text{cm}^{-1}$  (6.07  $\mu\text{m}$ ) in dioxane and at 1615  $\text{cm}^{-1}$  (6.20  $\mu\text{m}$ ) in methanol.

Electron-attracting groups attached to the nitrogen increase the frequency of absorption since they effectively compete with the carbonyl oxygen for the electrons of the nitrogen, thus increasing the force constant of the C=O bond.

#### N–H Bending Vibrations (Amide II Band)

All primary amides show a sharp absorption band in dilute solution (amide II band) resulting from NH<sub>2</sub> bending at a

somewhat lower frequency than the C=O band. This band has an intensity of one-half to one-third of the C=O absorption band. In mulls and pellets the band occurs near 1655–1620  $\text{cm}^{-1}$  (6.04–6.17  $\mu\text{m}$ ) and is usually under the envelope of the amide I band. In dilute solutions, the band appears at lower frequency, 1620–1590  $\text{cm}^{-1}$  (6.17–6.29  $\mu\text{m}$ ), and normally is separated from the amide I band. Multiple bands may appear in the spectra of concentrated solutions, arising from the free and associated states. The nature of the R group ( $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ ) has little effect upon the amide II band.

Secondary acyclic amides in the solid state display an amide II band in the region of 1570–1515  $\text{cm}^{-1}$  (6.37–6.60  $\mu\text{m}$ ). In dilute solution, the band occurs in the 1550–1510  $\text{cm}^{-1}$  (6.45–6.62  $\mu\text{m}$ ) region. This band results from interaction between the N–H bending and the C–N stretching of the C–N–H group. A second, weaker band near 1250  $\text{cm}^{-1}$  (8.00  $\mu\text{m}$ ) also results from interaction between the N–H bending and C–N stretching.

#### Other Vibration Bands

The C–N stretching band of primary amides occurs near 1400  $\text{cm}^{-1}$  (7.14  $\mu\text{m}$ ). A broad, medium band in the 800–666  $\text{cm}^{-1}$  (12.5–15.0  $\mu\text{m}$ ) region in the spectra of primary and secondary amides results from out-of-plane N–H wagging.

## LACTAMS

In lactams of medium ring size, the amide group is forced into the *cis* conformation. Solid lactams absorb strongly near  $3200\text{ cm}^{-1}$  ( $3.12\text{ }\mu\text{m}$ ) because of the N—H stretching vibration. This band does not shift appreciably with dilution since the *cis* form remains associated at relatively low concentrations.

### C=O Stretching Vibrations

The C=O absorption of lactams with 6-membered rings or larger is near  $1650\text{ cm}^{-1}$  ( $6.06\text{ }\mu\text{m}$ ). Five-membered ring ( $\gamma$ ) lactams absorb in the  $1750\text{--}1700\text{ cm}^{-1}$  ( $5.71\text{--}5.88\text{ }\mu\text{m}$ ) region. Four-membered-ring ( $\beta$ ) lactams, unfused, absorb at  $1760\text{--}1730\text{ cm}^{-1}$  ( $5.68\text{--}5.78\text{ }\mu\text{m}$ ). Fusion of the lactam ring to another ring generally increases the frequency by  $20\text{--}50\text{ cm}^{-1}$  ( $0.07\text{--}0.17\text{ }\mu\text{m}$ ).

Most lactams do not show a band near  $1550\text{ cm}^{-1}$  ( $6.45\text{ }\mu\text{m}$ ) that is characteristic of *trans* noncyclic secondary amides. The N—H out-of-plane wagging in lactams causes broad absorption in the  $800\text{--}700\text{ cm}^{-1}$  ( $12.5\text{--}14.3\text{ }\mu\text{m}$ ) region.

## N—H Stretching Vibrations

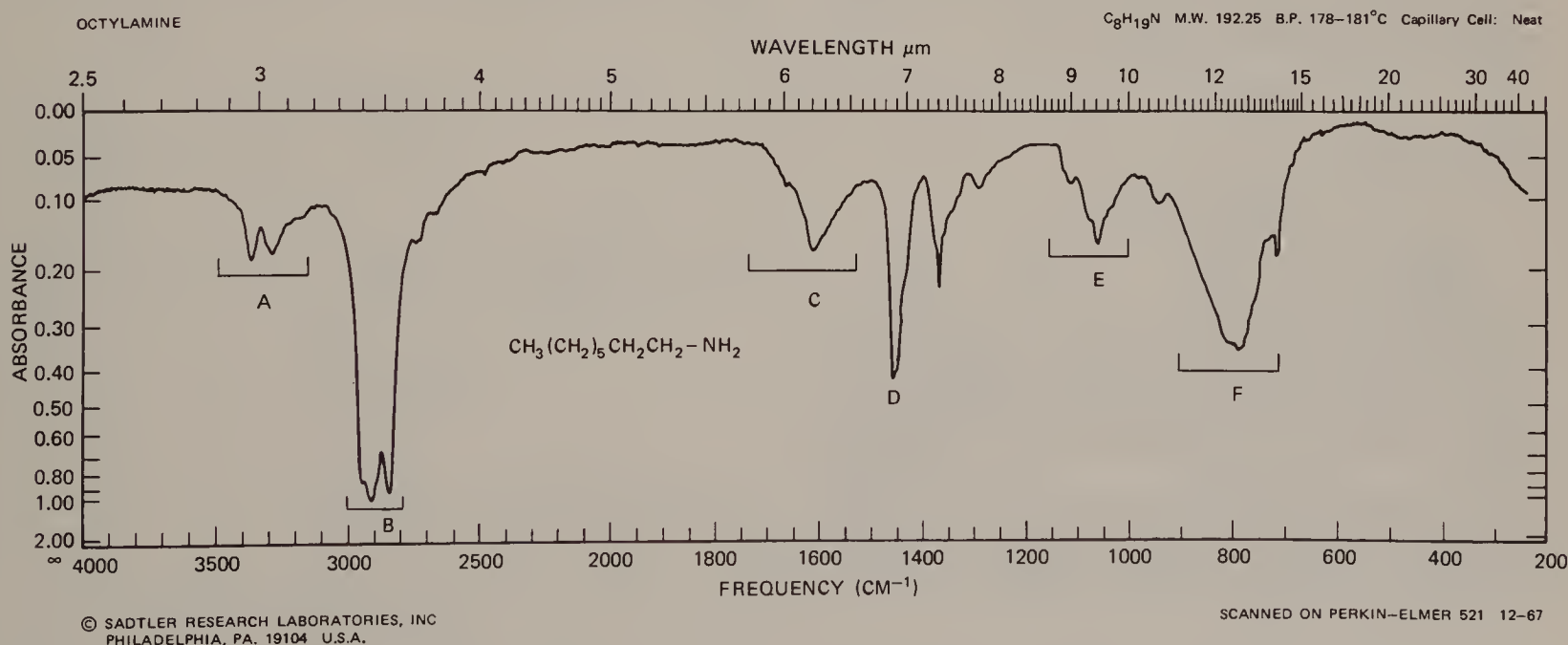
Primary amines, examined in dilute solution, display two weak absorption bands: one near  $3500\text{ cm}^{-1}$  ( $2.86\text{ }\mu\text{m}$ ), the other near  $3400\text{ cm}^{-1}$  ( $2.94\text{ }\mu\text{m}$ ). These bands represent, respectively, the “free” asymmetrical and symmetrical N—H stretching modes. Secondary amines show a single weak band in the  $3350\text{--}3310\text{ cm}^{-1}$  ( $2.98\text{--}3.02\text{ }\mu\text{m}$ ) region. These bands are shifted to longer wavelengths by hydrogen bonding. The associated N—H bands are weaker and frequently sharper than the corresponding O—H bands. Aliphatic primary amines (neat) absorb at  $3400\text{--}3330\text{ cm}^{-1}$  ( $2.94\text{--}3.00\text{ }\mu\text{m}$ ) and at  $3330\text{--}3250\text{ cm}^{-1}$  ( $3.00\text{--}3.08\text{ }\mu\text{m}$ ). Aromatic primary amines absorb at slightly higher frequencies (shorter wavelengths). In the spectra of liquid primary and secondary amines, a shoulder usually appears on the low-frequency (long-wavelength) side of the N—H stretching band, arising from the overtone of the NH bending band intensified by Fermi resonance. Tertiary amines do not absorb in this region of the spectrum.

## N—H Bending Vibrations

The N—H bending (scissoring) vibration of primary amines is observed in the  $1650\text{--}1580\text{ cm}^{-1}$  ( $6.06\text{--}6.33\text{ }\mu\text{m}$ ) region of the spectrum. The band is medium to strong in intensity and is moved to slightly higher frequencies when the compound is associated. The N—H bending band is seldom

## AMINES

The spectrum of a typical primary, aliphatic amine appears in Figure 29.



Source: The Matheson Company, Inc., East Rutherford, N.J.

**Figure 29.** A. N—H stretch, hydrogen bonded, primary amine coupled doublet: Asymmetric,  $3365\text{ cm}^{-1}$  ( $2.97\text{ }\mu\text{m}$ ). Symmetric,  $3290\text{ cm}^{-1}$  ( $3.04\text{ }\mu\text{m}$ ). (Shoulder at ca.  $3200\text{ cm}^{-1}$ , ca.  $3.12\text{ }\mu\text{m}$ , Fermi resonance band with overtone of band at C.) B. Aliphatic C—H stretch,  $2910, 2850\text{ cm}^{-1}$  ( $3.44, 3.51\text{ }\mu\text{m}$ );  $\nu_s$ ,  $\text{CH}_2$ ,  $2817\text{ cm}^{-1}$  ( $3.55\text{ }\mu\text{m}$ ), see Table II, Appendix C. C. N—H bend (scissoring),  $1620\text{ cm}^{-1}$  ( $6.17\text{ }\mu\text{m}$ ). D.  $\delta_s$ ,  $\text{CH}_2$  (scissoring),  $1458\text{ cm}^{-1}$  ( $6.86\text{ }\mu\text{m}$ ), see Table II, Appendix D. E. C—N stretch,  $1063\text{ cm}^{-1}$  ( $9.41\text{ }\mu\text{m}$ ). F. N—H wag (neat sample),  $909\text{--}666\text{ cm}^{-1}$  ( $11.00\text{--}15.00\text{ }\mu\text{m}$ ).



detectable in the spectra of aliphatic secondary amines, whereas secondary aromatic amines absorb near  $1515\text{ cm}^{-1}$  ( $6.60\text{ }\mu\text{m}$ ).

Liquid samples of primary and secondary amines display medium-to-strong broad absorption in the  $909\text{--}666\text{ cm}^{-1}$  ( $11.00\text{--}15.00\text{ }\mu\text{m}$ ) region of the spectrum arising from NH wagging. The position of this band depends on the degree of hydrogen bonding.

### *C–N Stretching Vibrations*

Medium-to-weak absorption bands for the unconjugated C–N linkage in primary, secondary, and tertiary aliphatic amines appear in the region of  $1250\text{--}1020\text{ cm}^{-1}$  ( $8.00\text{--}9.80\text{ }\mu\text{m}$ ). The vibrations responsible for these bands involve C–N stretching coupled with the stretching of adjacent bonds in the molecule. The position of absorption in this region depends on the class of the amine and the pattern of substitution on the  $\alpha$ -carbon.

Aromatic amines display strong C–N stretching absorption in the  $1342\text{--}1266\text{ cm}^{-1}$  ( $7.45\text{--}7.90\text{ }\mu\text{m}$ ) region. The absorption appears at higher frequencies (shorter wavelengths) than the corresponding absorption of aliphatic amines because the force constant of the C–N bond is increased by resonance with the ring.

Characteristic strong C–N stretching bands in the spectra of aromatic amines have been assigned as in Table IV.

The absorption frequencies of methyl and methylene groups attached to the nitrogen atom of an amine are summarized in Tables I and II of Appendix D.

## AMINE SALTS

### *N–H Stretching Vibrations*

The ammonium ion displays strong, broad absorption in the  $3300\text{--}3030\text{ cm}^{-1}$  ( $3.03\text{--}3.30\text{ }\mu\text{m}$ ) region because of N–H stretching vibrations (see Figure 24). There is also a combination band in the  $2000\text{--}1709\text{ cm}^{-1}$  ( $5.00\text{--}5.85\text{ }\mu\text{m}$ ) region.

Salts of primary amines show strong, broad absorption between  $3000\text{--}2800\text{ cm}^{-1}$  ( $3.33\text{--}3.57\text{ }\mu\text{m}$ ) arising from asymmetrical and symmetrical stretching in the  $\text{NH}_3^+$

Table IV. C–N Stretch of Primary, Secondary, and Tertiary Aromatic Amines

|           |   |
|-----------|---|
| Primary   | $1340\text{--}1250\text{ cm}^{-1}$ ( $7.46\text{--}8.00\text{ }\mu\text{m}$ ) |
| Secondary | $1350\text{--}1280\text{ cm}^{-1}$ ( $7.41\text{--}7.81\text{ }\mu\text{m}$ ) |
| Tertiary  | $1360\text{--}1310\text{ cm}^{-1}$ ( $7.35\text{--}7.63\text{ }\mu\text{m}$ ) |

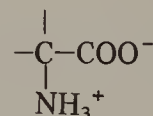
group. In addition, multiple combination bands of medium intensity occur in the  $2800\text{--}2000\text{ cm}^{-1}$  ( $3.57\text{--}5.00\text{ }\mu\text{m}$ ) region, the most prominent being the band near  $2000\text{ cm}^{-1}$  ( $5.00\text{ }\mu\text{m}$ ). Salts of secondary amines absorb strongly in the  $3000\text{--}2700\text{ cm}^{-1}$  ( $3.33\text{--}3.70\text{ }\mu\text{m}$ ) region with multiple bands extending to  $2273\text{ cm}^{-1}$  ( $4.00\text{ }\mu\text{m}$ ). A medium band near  $2000\text{ cm}^{-1}$  ( $5.00\text{ }\mu\text{m}$ ) may be observed. Tertiary amine salts absorb at longer wavelengths than the salts of primary and secondary amines;  $2700\text{--}2250\text{ cm}^{-1}$  ( $3.70\text{--}4.44\text{ }\mu\text{m}$ ). Quaternary ammonium salts can have no N–H stretching vibrations.

### *N–H Bending Vibrations*

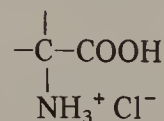
The ammonium ion displays a strong, broad  $\text{NH}_4^+$  bending band near  $1429\text{ cm}^{-1}$  ( $7.00\text{ }\mu\text{m}$ ). The  $\text{NH}_3^+$  group of the salt of a primary amine absorbs near  $1600\text{--}1575\text{ cm}^{-1}$  ( $6.25\text{--}6.35\text{ }\mu\text{m}$ ) and near  $1550\text{--}1504\text{ cm}^{-1}$  ( $6.45\text{--}6.65\text{ }\mu\text{m}$ ). These bands originate in asymmetrical and symmetrical  $\text{NH}_3^+$  bending, analogous to the corresponding bands of the  $\text{CH}_3$  group. Salts of secondary amines absorb near  $1620\text{--}1560\text{ cm}^{-1}$  ( $6.17\text{--}6.41\text{ }\mu\text{m}$ ). The N–H bending band of the salts of tertiary amines is weak and of no practical value.

## AMINO ACIDS AND SALTS OF AMINO ACIDS

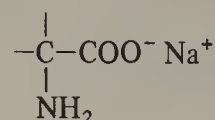
Amino acids are encountered in three forms: the free amino acid (zwitterion),



the hydrochloride (or other salt),



and the sodium (or other cation) salt,



Free primary amino acids are characterized by the following absorptions (most of the work has been done with  $\alpha$ -amino acids, but the relative positions of the amino and carboxyl groups seem to have little effect):

1. A broad, strong  $\text{NH}_3^+$  stretching band in the  $3100\text{--}2600\text{ cm}^{-1}$  ( $3.23\text{--}3.85\text{ }\mu\text{m}$ ) region. Multiple combination and overtone bands extend the absorption to about  $2000\text{ cm}^{-1}$  ( $5.00\text{ }\mu\text{m}$ ). This overtone region usually contains a prominent band near  $2222\text{--}2000\text{ cm}^{-1}$  ( $4.50\text{--}5.00\text{ }\mu\text{m}$ ) assigned to a combination of the asymmetrical  $\text{NH}_3^+$  bending vibration and the torsional oscillation of the  $\text{NH}_3^+$  group. The torsional oscillation occurs near  $500\text{ cm}^{-1}$  ( $20.00\text{ }\mu\text{m}$ ). The  $2000\text{ cm}^{-1}$  ( $5.00\text{ }\mu\text{m}$ ) band is absent if the nitrogen atom of the amino acid is substituted.
2. A weak asymmetric  $\text{NH}_3^+$  bending band near  $1660\text{--}1610\text{ cm}^{-1}$  ( $6.03\text{--}6.21\text{ }\mu\text{m}$ ); a fairly strong symmetrical bending band near  $1550\text{--}1485\text{ cm}^{-1}$  ( $6.45\text{--}6.73\text{ }\mu\text{m}$ ).
3. The carboxylate ion group  $\left(\text{--}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{--}\right)$  absorbs strongly near  $1600\text{--}1590\text{ cm}^{-1}$  ( $6.25\text{--}6.29\text{ }\mu\text{m}$ ) and more weakly near  $1400\text{ cm}^{-1}$  ( $7.14\text{ }\mu\text{m}$ ). These bands result, respectively, from asymmetrical and symmetrical  $\text{C}(\equiv\text{O})_2$  stretching.

The spectrum of the amino acid leucine, including assignments corresponding to the preceding three categories, is shown in Figure 30.

Hydrochlorides of amino acids present the following patterns:

1. Broad strong absorption in the  $3333\text{--}2380\text{ cm}^{-1}$  ( $3.00\text{--}4.20\text{ }\mu\text{m}$ ) region resulting from superimposed O—H

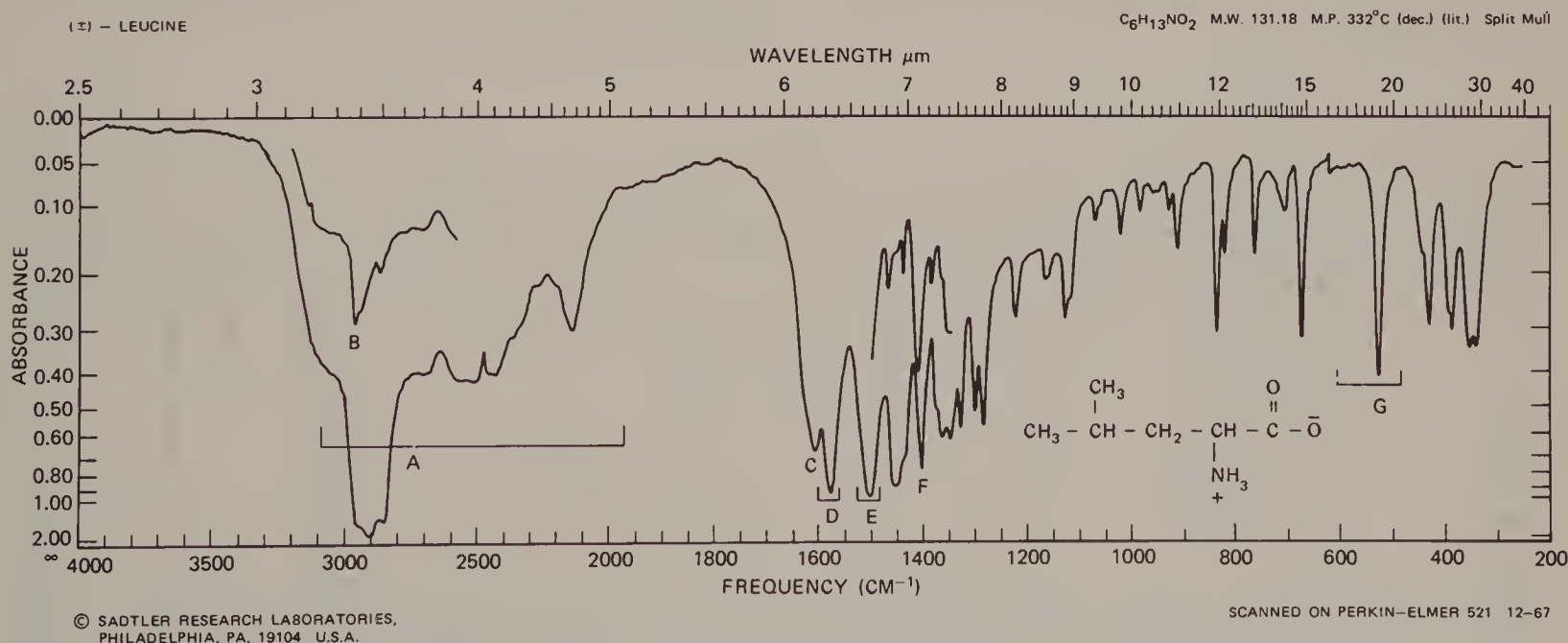
and  $\text{NH}_3^+$  stretching bands. Absorption in this region is characterized by multiple fine structure on the long wavelength side of the band.

2. A weak, asymmetrical  $\text{NH}_3^+$  bending band near  $1610\text{--}1590\text{ cm}^{-1}$  ( $6.21\text{--}6.29\text{ }\mu\text{m}$ ); a relatively strong, symmetrical  $\text{NH}_3^+$  bending band at  $1550\text{--}1481\text{ cm}^{-1}$  ( $6.45\text{--}6.75\text{ }\mu\text{m}$ ).
3. A strong band at  $1220\text{--}1190\text{ cm}^{-1}$  ( $8.20\text{--}8.40\text{ }\mu\text{m}$ ) arising from  $\text{C}\overset{\text{O}}{\parallel}\text{--}\text{C}\text{--}\text{O}$  stretching.
4. Strong carbonyl absorption at  $1755\text{--}1730\text{ cm}^{-1}$  ( $5.70\text{--}5.78\text{ }\mu\text{m}$ ) for  $\alpha$ -amino acid hydrochlorides, and at  $1730\text{--}1700\text{ cm}^{-1}$  ( $5.78\text{--}5.88\text{ }\mu\text{m}$ ) for other amino acid hydrochlorides.

Sodium salts of amino acids show the normal N—H stretching vibrations at  $3400\text{--}3200\text{ cm}^{-1}$  ( $2.94\text{--}3.13\text{ }\mu\text{m}$ ) common to other amines. The characteristic carboxylate ion bands appear near  $1600\text{--}1590\text{ cm}^{-1}$  ( $6.25\text{--}6.29\text{ }\mu\text{m}$ ) and near  $1400\text{ cm}^{-1}$  ( $7.14\text{ }\mu\text{m}$ ).

## NITRILES

The spectra of nitriles ( $\text{R--C}\equiv\text{N}$ ) are characterized by weak to medium absorption in the triple-bond stretching region of the spectrum. Aliphatic nitriles absorb near  $2260\text{--}2240\text{ cm}^{-1}$  ( $4.42\text{--}4.46\text{ }\mu\text{m}$ ). Electron attracting atoms, such as



Source: The Matheson Company, Inc., E. Rutherford, N.J.

**Figure 30.** A. Broad ( $\text{--NH}_3^+$ ) N—H stretch,  $3100\text{--}2000\text{ cm}^{-1}$  ( $3.25\text{--}5.00\text{ }\mu\text{m}$ ), extended by combination band at  $2140\text{ cm}^{-1}$  ( $4.67\text{ }\mu\text{m}$ ), and other combination-overtone bands. B. Aliphatic C—H stretch (superimposed on N—H stretch),  $2967\text{ cm}^{-1}$  ( $3.37\text{ }\mu\text{m}$ ). C. Asymmetric ( $\text{--NH}_3^+$ ) N—H bend,  $1610\text{ cm}^{-1}$  ( $6.21\text{ }\mu\text{m}$ ). D. Asymmetric carboxylate ( $\text{C}(\equiv\text{O})_2$ ) stretch,  $1580\text{ cm}^{-1}$  ( $6.33\text{ }\mu\text{m}$ ). E. Symmetric ( $\text{--NH}_3^+$ ) N—H bend,  $1505\text{ cm}^{-1}$  ( $6.65\text{ }\mu\text{m}$ ). F. Symmetric carboxylate ( $\text{C}(\equiv\text{O})_2$ ) stretch,  $1405\text{ cm}^{-1}$  ( $7.12\text{ }\mu\text{m}$ ). G. Torsional ( $\text{--NH}_3^+$ ) N—H oscillation,  $525\text{ cm}^{-1}$  ( $19.0\text{ }\mu\text{m}$ ).



oxygen or chlorine, attached to the carbon atom alpha to the  $\text{C}\equiv\text{N}$  group reduce the intensity of absorption. Conjugation, such as occurs in aromatic nitriles, reduces the frequency of absorption to  $2240\text{--}2222\text{ cm}^{-1}$  ( $4.46$  to  $4.50\text{ }\mu\text{m}$ ) and enhances the intensity. The spectrum of a typical nitrile, with an aryl group in conjugation with the cyano function, is shown in Figure 31.

#### COMPOUNDS CONTAINING $\text{C}\equiv\text{N}$ , $\text{C}=\text{N}$ , $-\text{N}=\text{C}=\text{O}$ AND $-\text{N}=\text{C}=\text{S}$ GROUPS

Isocyanides (isonitriles), isocyanates, thiocyanates, and isothiocyanates all show  $\text{C}\equiv\text{N}$  stretch or cumulated double bond ( $-\text{Y}=\text{C}=\text{X}$ ;  $\text{X}, \text{Y} = \text{N}, \text{S}$  or  $\text{O}$ ) stretch in the  $2273\text{--}2000\text{ cm}^{-1}$  ( $4.40\text{--}5.00\text{ }\mu\text{m}$ ) region (Appendix C). Schiff's bases ( $\text{RCH}=\text{NR}$ , imines), oximes, thiazoles, iminocarbonates, guanidines, etc., show the  $\text{C}=\text{N}$  stretch in the  $1689\text{--}1471\text{ cm}^{-1}$  ( $5.92\text{--}6.80\text{ }\mu\text{m}$ ) region. Although the intensity of the  $\text{C}=\text{N}$  stretch is variable, it is usually more intense than the  $\text{C}=\text{C}$  stretch.

#### COMPOUNDS CONTAINING $-\text{N}=\text{N}-$ GROUP

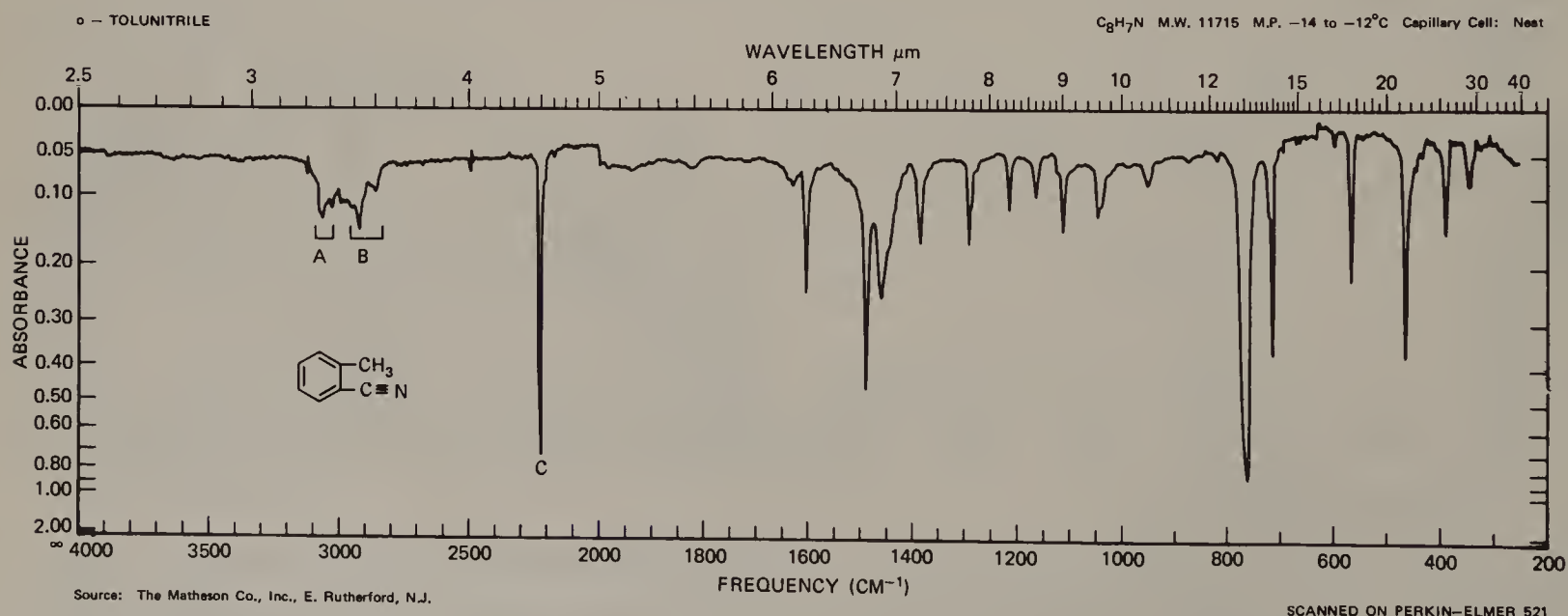
The  $\text{N}=\text{N}$  stretching vibration of a symmetrical *trans* azo compound is forbidden in the infrared but absorbs in the  $1576\text{ cm}^{-1}$  ( $6.35\text{ }\mu\text{m}$ ) region of the Raman spectrum. Unsymmetrical para-substituted azobenzenes in which the substituent is an electron donating group absorb near  $1429\text{ cm}^{-1}$  ( $7.00\text{ }\mu\text{m}$ ). The bands are weak because of the non-polar nature of the bond.

#### COVALENT COMPOUNDS CONTAINING NITROGEN-OXYGEN BONDS

Nitro compounds, nitrates, and nitramines contain an  $\text{NO}_2$  group. Each of these classes shows absorption due to asymmetrical and symmetrical stretching of the  $\text{NO}_2$  group. Asymmetrical absorption results in a strong band in the  $1661\text{--}1499\text{ cm}^{-1}$  ( $6.02\text{--}6.67\text{ }\mu\text{m}$ ) region; symmetrical absorption occurs in the region between  $1389\text{--}1259\text{ cm}^{-1}$  ( $7.20\text{--}7.94\text{ }\mu\text{m}$ ). The exact position of the bands is dependent on substitution and unsaturation in the vicinity of the  $\text{NO}_2$  group.

**NITRO COMPOUNDS.** In the nitro-alkanes, the bands occur near  $1550\text{ cm}^{-1}$  ( $6.45\text{ }\mu\text{m}$ ) and near  $1372\text{ cm}^{-1}$  ( $7.29\text{ }\mu\text{m}$ ). Conjugation lowers the frequency of both bands, resulting in absorption near  $1550\text{--}1500\text{ cm}^{-1}$  ( $6.45\text{--}6.67\text{ }\mu\text{m}$ ) and near  $1360\text{--}1290\text{ cm}^{-1}$  ( $7.36\text{--}7.75\text{ }\mu\text{m}$ ). Attachment of electronegative groups to the  $\alpha$ -carbon of a nitro compound causes an increase in the frequency of the asymmetrical  $\text{NO}_2$  band and a reduction in the frequency of the symmetrical band; chloropicrin,  $\text{Cl}_3\text{CNO}_2$ , absorbs at  $1610\text{ cm}^{-1}$  ( $6.21\text{ }\mu\text{m}$ ) and at  $1307\text{ cm}^{-1}$  ( $7.65\text{ }\mu\text{m}$ ).

Aromatic nitro groups absorb near the same frequencies as observed for conjugated aliphatic nitro compounds. Interaction between the  $\text{NO}_2$  out-of-plane bending and ring  $\text{C}-\text{H}$  out-of-plane bending frequencies destroys the reliability of the substitution pattern observed for nitro-aromatics in the long wavelength region of the spectrum. Nitro-aromatic compounds show a  $\text{C}-\text{N}$  stretching vibration near  $870\text{ cm}^{-1}$  ( $11.49\text{ }\mu\text{m}$ ). The spectrum of nitrobenzene, with assignments corresponding to the preceding discussion, is shown in Figure 32.



Source: The Matheson Co., Inc., E. Rutherford, N.J.

**Figure 31.** A. Aromatic  $\text{C}-\text{H}$  stretch,  $3070\text{ cm}^{-1}$ ,  $3025\text{ cm}^{-1}$  ( $3.26$ ,  $3.31\text{ }\mu\text{m}$ ). B. Aliphatic  $\text{C}-\text{H}$  stretch,  $2910$ ,  $2860\text{ cm}^{-1}$  ( $3.44$ ,  $3.50\text{ }\mu\text{m}$ ). C.  $\text{C}\equiv\text{N}$  stretch,  $2210\text{ cm}^{-1}$  ( $4.53\text{ }\mu\text{m}$ )(intensified by aryl conjugation); aliphatic nitriles absorb at higher frequency (shorter wavelength).



Because of strong resonance in aromatic systems containing NO<sub>2</sub> groups and electron-donating groups such as the amino group, ortho or para to one another, the symmetrical NO<sub>2</sub> vibration is shifted to lower frequencies and increases in intensity. *p*-Nitroaniline absorbs at 1475 cm<sup>-1</sup> (6.78 μm) and 1310 cm<sup>-1</sup> (7.64 μm).

The positions of asymmetric and symmetric NO<sub>2</sub> stretching bands of nitramines ( $\text{>N-NO}_2$ ) and the NO stretch of nitrosoamines are given in Appendix C.

**NITRATES.** Organic nitrates show absorption for N—O stretching vibrations of the NO<sub>2</sub> group and for the O—N linkage. Asymmetrical stretching in the NO<sub>2</sub> group results in strong absorption in the 1660-1625 cm<sup>-1</sup> (6.02-6.15 μm) region; the symmetrical vibration absorbs strongly near 1300-1255 cm<sup>-1</sup> (7.69-7.97 μm). Stretching of the π bonds of the N—O linkage produces absorption near 870-833 cm<sup>-1</sup> (11.50-12.00 μm). Absorption observed at longer wavelengths, near 763-690 cm<sup>-1</sup> (13.10-14.50 μm), likely results from NO<sub>2</sub> bending vibrations.

**NITRITES.** Nitrites display two strong N=O stretching bands. The band near 1680-1650 cm<sup>-1</sup> (5.95-6.06 μm) is attributed to the *trans* isomer; the *cis* isomer absorbs in the 1625-1610 cm<sup>-1</sup> (6.16-6.21 μm) region. The N—O stretching band appears in the region between 850-750 cm<sup>-1</sup> (11.76-13.33 μm). The nitrite absorption bands are among the strongest observed in infrared spectra.

**NITROSO COMPOUNDS.** Primary and secondary aliphatic C-nitroso compounds are usually unstable and re-

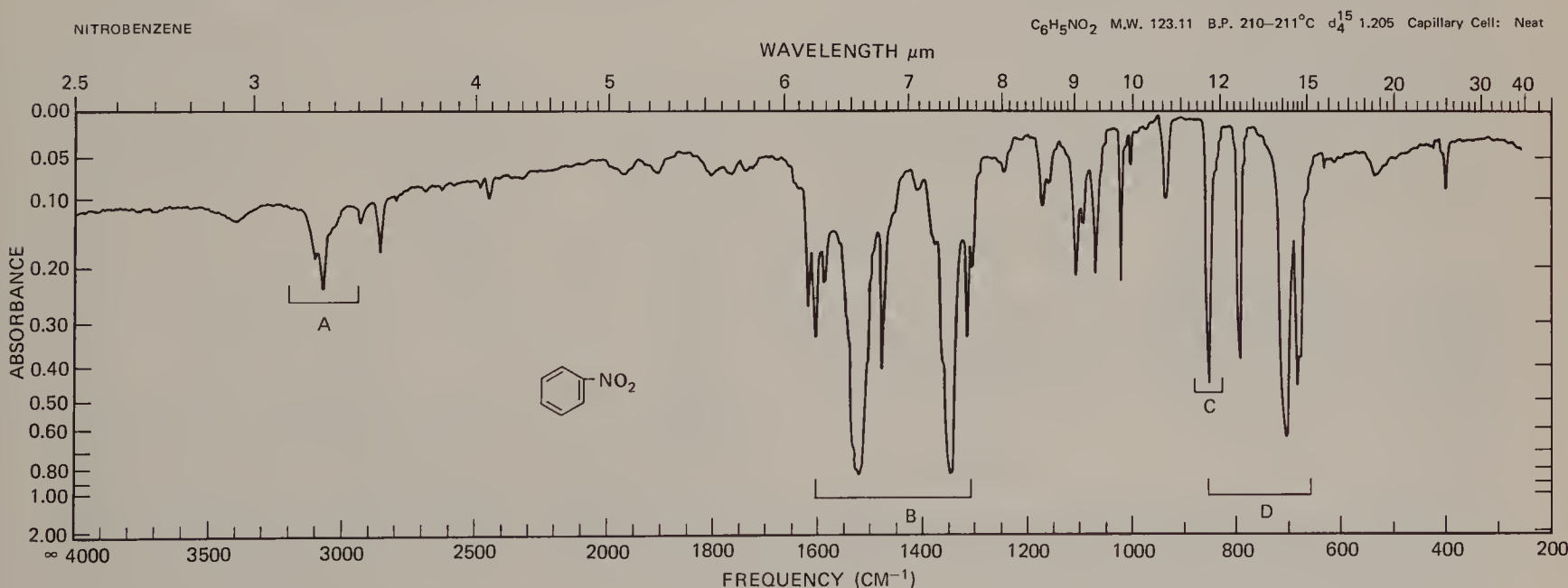
arrange to oximes or dimerize. Tertiary and aromatic nitroso compounds are reasonably stable, existing as monomers in the gaseous phase or in dilute solution and as dimers in neat samples. Monomeric, tertiary, aliphatic nitroso compounds show N=O absorption in the 1585-1539 cm<sup>-1</sup> (6.31-6.50 μm) region; aromatic monomers absorb between 1511-1495 cm<sup>-1</sup> (6.62-6.69 μm).

The N→O stretching absorption of dimeric nitroso compounds are categorized in Appendix C as to *cis* vs. *trans* and aliphatic vs. aromatic. Nitrosoamine absorptions are given in Appendix C.

## ORGANIC SULFUR COMPOUNDS

**MERCAPTANS.** Aliphatic mercaptans and thiophenols, as liquids or in solution, show S—H stretching absorption in the range of 2600-2550 cm<sup>-1</sup> (3.85-3.92 μm). The S—H stretching band is characteristically weak and may go undetected in the spectra of dilute solutions or thin films. However, since few other groups show absorption in this region, it is useful in detecting S—H groups. The spectrum of benzyl mercaptan in Figure 33 is that of a mercaptan with a detectable S—H stretch band. The band may be obscured by strong carboxyl absorption in the same region. Hydrogen bonding is much weaker for S—H groups than for O—H and N—H groups.

The S—H group of thiol acids absorbs in the same region as mercaptans and thiophenols.



Source: J.T. Baker Chemical Co., Phillipsburg, N.J.

**Figure 32.** A. Aromatic C—H stretch, 3100, 3080 cm<sup>-1</sup> (3.23, 3.25 μm). B. Asymmetric (ArNO<sub>2</sub>) N=O stretch, 1520 cm<sup>-1</sup> (6.58 μm). Symmetric (ArNO<sub>2</sub>) N=O stretch 1345 cm<sup>-1</sup> (7.44 μm). C. ArNO<sub>2</sub> C—N stretch, 850 cm<sup>-1</sup> (11.76 μm). D. Low frequency bands are of little use in determining the nature of ring substitution since these absorption patterns are due to interaction of NO<sub>2</sub> and C—H out-of-plane bending frequencies.

**SULFIDES.** The stretching vibrations assigned to the C—S linkage occur in the region of 700-600  $\text{cm}^{-1}$  (14.3-16.7  $\mu\text{m}$ ). The weakness of absorption and variability of position make this band of little value in structural determination.

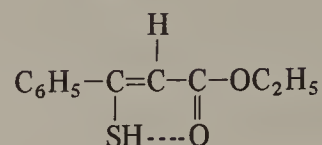
**DISULFIDES.** The S—S stretching vibration is very weak and falls between 500-400  $\text{cm}^{-1}$  (20-25  $\mu\text{m}$ ), outside the range of sodium chloride optics. The characteristic absorptions of methyl and methylene groups attached to sulfur are summarized in Tables I and II in Appendix D.

**THIOCARBONYL COMPOUNDS.** Aliphatic thials or thiones exist as trimeric, cyclic sulfides. Aralkyl thiones may exist either as monomers or trimers, whereas diaryl thiones, such as thiobenzophenone, exist only as monomers. The C=S group is less polar than the C=O group and has a considerably weaker bond. In consequence, the band is not intense, and it falls at lower frequencies, where it is much more susceptible to coupling effects. Identification is therefore difficult and uncertain.

Compounds that contain a thiocarbonyl group show absorption in the 1250-1020  $\text{cm}^{-1}$  (8.00-9.70  $\mu\text{m}$ ) region. Thiobenzophenone and its derivatives absorb moderately in the 1224-1207  $\text{cm}^{-1}$  (8.17-8.29  $\mu\text{m}$ ) region. Since the absorption occurs in the same general region as C—O and C—N stretching, considerable interaction can occur between these vibrations within a single molecule.

Spectra of compounds in which the C=S group is attached to a nitrogen atom show an absorption band in the general C=S stretching region. In addition, several other bands in the broad region of 1563-700  $\text{cm}^{-1}$  (6.40-14.30  $\mu\text{m}$ ) can be attributed to vibrations involving interaction between C=S stretching and C—N stretching.

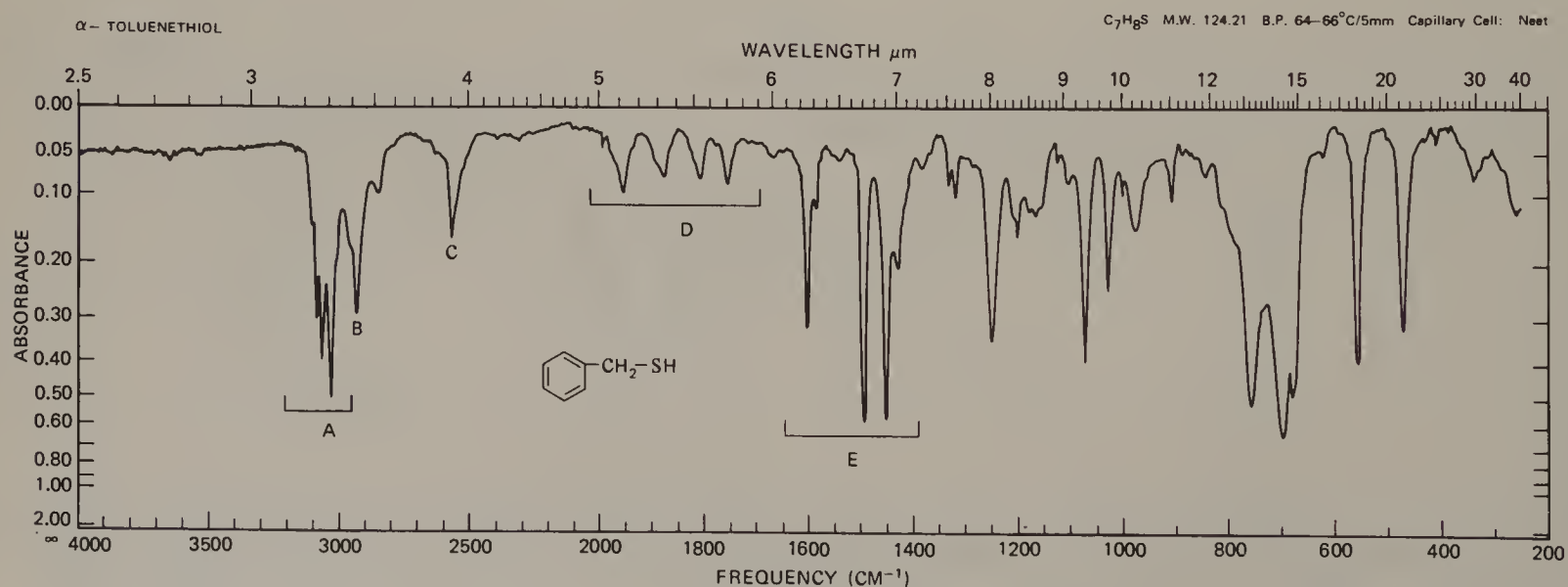
Thioketo compounds that can undergo enolization exist as thioketo-thioenol tautomeric systems; such systems show S—H stretching absorption. The thioenol tautomer of ethyl thiobenzoylacetate,



absorbs broadly at 2415  $\text{cm}^{-1}$  (4.14  $\mu\text{m}$ ) due to bonded S—H stretching absorption.

## COMPOUNDS CONTAINING SULFUR—OXYGEN BONDS

**SULFOXIDES.** Alkyl and aryl sulfoxides as liquids or in solution show strong absorption in the 1070-1030  $\text{cm}^{-1}$  (9.35-9.71  $\mu\text{m}$ ) region. This absorption occurs at 1050  $\text{cm}^{-1}$  (9.52  $\mu\text{m}$ ) for dimethyl sulfoxide (DMSO, methyl sulfoxide) as may be seen in Appendix B, spectrum 26. Conjugation brings about a small change (10-20  $\text{cm}^{-1}$ ) in the observed frequency in contrast to the marked reduction in frequency of the C=O bond accompanying conjugation. Diallyl sulfoxide absorbs at 1047  $\text{cm}^{-1}$  (9.55  $\mu\text{m}$ ). Phenyl methyl sulfoxide and cyclohexyl methyl sulfoxide absorb at 1055  $\text{cm}^{-1}$  (9.48  $\mu\text{m}$ ) in dilute solution in carbon tetrachloride. The sulfoxide group is susceptible to hydrogen bonding, the absorption shifting to slightly lower frequencies from dilute solution to the liquid phase. The frequency



**Figure 33.** A. Aromatic C—H stretch, 3085, 3060, 3030  $\text{cm}^{-1}$  (3.24, 3.27, 3.30  $\mu\text{m}$ ). B. Aliphatic C—H stretch, 2930  $\text{cm}^{-1}$  (3.41  $\mu\text{m}$ ). C. Moderately weak S—H stretch, 2565  $\text{cm}^{-1}$  (3.90  $\mu\text{m}$ ). D. Overtone or combination band pattern indicative of monosubstituted aromatic (see Figure 14), 2000-1667  $\text{cm}^{-1}$  (5.0-6.0  $\mu\text{m}$ ). E. C=C ring stretch, 1600, 1495, 1455  $\text{cm}^{-1}$  (6.25, 6.69, 6.87  $\mu\text{m}$ ).



of S=O absorption is increased by electronegative substitution.

**SULFONES.** Spectra of sulfones show strong absorption bands at 1350-1300  $\text{cm}^{-1}$  (7.41-7.70  $\mu\text{m}$ ) and at 1160-1120  $\text{cm}^{-1}$  (8.62-8.93  $\mu\text{m}$ ). These bands arise from asymmetric and symmetric  $\text{SO}_2$  stretching, respectively. Hydrogen bonding results in absorption near 1300  $\text{cm}^{-1}$  (7.70  $\mu\text{m}$ ) and near 1125  $\text{cm}^{-1}$  (8.90  $\mu\text{m}$ ). Splitting of the high frequency band often occurs in carbon tetrachloride solution or in the solid state.

**SULFONYL CHLORIDES.** Sulfonyl chlorides absorb strongly in the regions of 1410-1380  $\text{cm}^{-1}$  (7.09-7.25  $\mu\text{m}$ ) and 1204-1177  $\text{cm}^{-1}$  (8.31-8.49  $\mu\text{m}$ ). This increase in frequency, compared with the sulfones, results from the electronegativity of the chlorine atom.

**SULFONAMIDES.** Solutions of sulfonamides absorb strongly at 1370-1335  $\text{cm}^{-1}$  (7.30-7.49  $\mu\text{m}$ ) and at 1170-1155  $\text{cm}^{-1}$  (8.55-8.66  $\mu\text{m}$ ). In the solid phase, these frequencies are lowered by 10-20  $\text{cm}^{-1}$ . In solid samples, the high frequency band is broadened and several submaxima usually appear.

Primary sulfonamides show strong N-H stretching bands at 3390-3330  $\text{cm}^{-1}$  (2.95-3.00  $\mu\text{m}$ ) and 3300-3247  $\text{cm}^{-1}$  (3.03-3.08  $\mu\text{m}$ ) in the solid state; secondary sulfonamides absorb near 3265  $\text{cm}^{-1}$  (3.06  $\mu\text{m}$ ).

**SULFONATES, SULFATES, AND SULFONIC ACIDS.** The asymmetric (higher frequency, shorter wavelength) and symmetric S=O stretching frequency ranges for these compounds are as follows:

| Class                 | $\text{cm}^{-1}$ | $\mu\text{m}$ |
|-----------------------|------------------|---------------|
| Sulfonates (covalent) | 1372-1335,       | 7.29-7.49,    |
|                       | 1195-1168        | 8.37-8.56     |
| Sulfates (organic)    | 1415-1380,       | 7.06-7.24,    |
|                       | 1200-1185        | 8.33-8.44     |
| Sulfonic acids        | 1350-1342,       | 7.41-7.45,    |
|                       | 1165-1150        | 8.58-8.69     |
| Sulfonate salts       | ca. 1175         | ca. 8.5       |
|                       | ca. 1055         | ca. 9.5       |

The spectrum of a typical alkyl arenesulfonate is given in Figure 34. In virtually all sulfonates, the asymmetric stretch occurs as a doublet. Alkyl and aryl sulfonates show negligible differences; electron donating groups in the para position of arenesulfonates cause higher frequency absorption.

Sulfonic acids are listed in narrow ranges above; these apply only to anhydrous forms. Such acids hydrate readily to give bands that are probably a result of the formation of hydronium sulfonate salts, in the 1230-1120  $\text{cm}^{-1}$  (8.13-8.93  $\mu\text{m}$ ) range.

## ORGANIC HALOGEN COMPOUNDS

The strong absorption of halogenated hydrocarbons arises from the stretching vibrations of the carbon to halogen bond.

Aliphatic C-Cl absorption is observed in the broad region between 850 and 550  $\text{cm}^{-1}$  (11.76-18.18  $\mu\text{m}$ ). When several chlorine atoms are attached to one carbon atom, the band is usually more intense and at the high frequency end of the assigned limits. Carbon tetrachloride (see Appendix B, spectrum 10) shows an intense band at 797  $\text{cm}^{-1}$  (12.55  $\mu\text{m}$ ). The first overtones of the intense fundamental bands are frequently observed. Spectra of typical chlorinated hydrocarbons are shown in Appendix B: nos. 10, 11, 12, and 13. Brominated compounds absorb in the 690-515  $\text{cm}^{-1}$  (14.49-19.42  $\mu\text{m}$ ) region, iodo-compounds in the 600-500  $\text{cm}^{-1}$  (16.67-20.00  $\mu\text{m}$ ) region. A strong  $\text{CH}_2$  wagging band is observed for the  $\text{CH}_2\text{X}$  (X = Cl, Br, I) group in the 1300-1150  $\text{cm}^{-1}$  (7.69-8.70  $\mu\text{m}$ ) region.

Fluorine-containing compounds absorb strongly over a wide range between 1400-730  $\text{cm}^{-1}$  (7.14-13.70  $\mu\text{m}$ ) due to C-F stretching modes. A monofluoroalkane shows a strong band in the 1100-1000  $\text{cm}^{-1}$  (9.09-10.00  $\mu\text{m}$ ) region. As the number of fluorine atoms in an aliphatic molecule increases, the band pattern becomes more complex, with multiple strong bands appearing over the broad region of C-F absorption. The  $\text{CF}_3$  and  $\text{CF}_2$  groups absorb strongly in the 1350-1120  $\text{cm}^{-1}$  (7.41-8.93  $\mu\text{m}$ ) region. The spectrum of Fluorolube®, Appendix B, spectrum 14, illustrates many of the preceding absorption characteristics.

Chlorobenzenes absorb in the 1096-1089  $\text{cm}^{-1}$  (9.12-9.18  $\mu\text{m}$ ) region. The position within this region depends on the substitution pattern. Aryl fluorides absorb in the 1250-110  $\text{cm}^{-1}$  (8.00-9.10  $\mu\text{m}$ ) region of the spectrum. A monofluorinated benzene ring displays a strong, narrow absorption band near 1230  $\text{cm}^{-1}$  (8.13  $\mu\text{m}$ ).

## SILICON COMPOUNDS

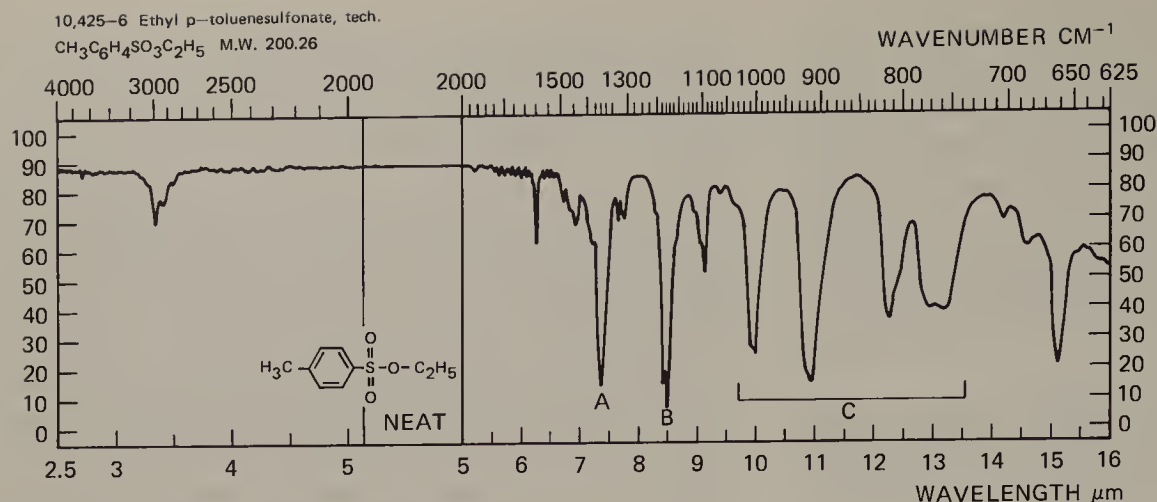
Tables of characteristic absorptions of silicon compounds are found in Appendix E. Special features related to these tables are discussed below.

### *Si-H Vibrations*

Vibrations for the Si-H bond are listed in Appendix E, Table I. The Si-H stretching frequencies are increased by the attachment of an electronegative group to the silicon.

The absorption bands of methylene and methyl groups attached to silicon are summarized in Appendix D, Tables I and II.





Courtesy of Aldrich Chemical Co.

**Figure 34.** A. Asymmetric  $\text{S}(=\text{O})_2$  stretch,  $1351\text{ cm}^{-1}$  ( $7.40\text{ }\mu\text{m}$ ). B. Symmetric  $\text{S}(=\text{O})_2$  stretch,  $1176\text{ cm}^{-1}$  ( $8.50\text{ }\mu\text{m}$ ). C. Various strong  $\text{S}-\text{O}-\text{C}$  stretching,  $1000\text{--}769\text{ cm}^{-1}$  ( $10.0\text{--}13.0\text{ }\mu\text{m}$ ).

### Si-O Stretching Vibration

The Si-O stretching vibrations are summarized in Appendix E, Table II.

The OH stretching vibrations of the SiOH group absorb in the same region as the alcohols,  $3700\text{--}3200\text{ cm}^{-1}$  ( $2.70\text{--}3.12\text{ }\mu\text{m}$ ). As in alcohols, the absorption characteristics depend on the degree of hydrogen bonding.

### Silicon-Halogen Stretching Vibrations

The absorption of groups containing Si-F bonds is summarized in Appendix E, Table III.

Bands resulting from Si-Cl stretching occur at frequencies below  $666\text{ cm}^{-1}$  (wavelengths longer than  $15\text{ }\mu\text{m}$ ).

The spectrum of silicone lubricant, Appendix B-no.27, illustrates some of the preceding absorptions.

## PHOSPHORUS COMPOUNDS

### P-H Stretching

The P-H group absorbs in the regions described in Appendix E, Table IV.

### P=O Stretching Vibrations

Such absorptions are listed in Appendix E, Table IV.

### P-O Stretching Vibrations

Absorption characteristics of P-O stretching vibrations are summarized in Appendix E, Table V.

The absorptions of methylene and methyl groups attached to a phosphorus atom are summarized in Appendix D, Tables I and II.

## HETEROAROMATIC COMPOUNDS

The spectra of heteroaromatic compounds result primarily from the same vibrational modes as observed for the aromatics.

### C-H Stretching Vibrations

Heteroaromatics, such as pyridines, pyrazines, pyrroles, furans, and thiophenes, show C-H stretching bands in the  $3077\text{--}3003\text{ cm}^{-1}$  ( $3.25\text{--}3.33\text{ }\mu\text{m}$ ) region.

### N-H Stretching Frequencies

Heteroaromatics containing an N-H group show N-H stretching absorption in the region of  $3500\text{--}3220\text{ cm}^{-1}$  ( $2.86\text{--}3.11\text{ }\mu\text{m}$ ). The position of absorption within this general region depends upon the degree of hydrogen bonding, and hence upon the physical state of the sample or the polarity of the solvent. Pyrrole and indole in dilute solution in nonpolar solvents show a sharp band near  $3495\text{ cm}^{-1}$ .

$\text{cm}^{-1}$  ( $2.86\ \mu\text{m}$ ); concentrated solutions show a widened band near  $3400\ \text{cm}^{-1}$  ( $2.94\ \mu\text{m}$ ). Both bands may be seen at intermediate concentrations.

### Ring-Stretching Vibrations (Skeletal Bands)

Ring stretching vibrations occur in the general region between  $1600\text{--}1300\ \text{cm}^{-1}$  ( $6.25\text{--}7.69\ \mu\text{m}$ ). The absorption involves stretching and contraction of all of the bonds in the ring and interaction between these stretching modes. The band pattern and the relative intensities depend on the substitution pattern and the nature of the substituents.

Pyridine (Figure 35) shows four bands in this region and, in this respect, closely resembles a monosubstituted benzene. Furans, pyrroles, and thiophenes display 2 to 4 bands in this region.

### C-H Out-of-Plane Bending

The C-H out-of-plane bending ( $\gamma\text{CH}$ ) absorption pattern of the heteroaromatics is determined by the number of adjacent hydrogen atoms bending in phase. The C-H out-of-plane and ring bending ( $\beta$  ring) absorption of the alkylpyridines are summarized in Table VI, Appendix E.

Absorption data for the out-of-phase C-H bending ( $\gamma\text{CH}$ ) and ring bending ( $\beta$  ring) modes of 3 common 5-membered heteroaromatic rings are presented in Table VII, Appendix E. The ranges in Table VII (p. 182) include polar as well as nonpolar substituents on the ring.

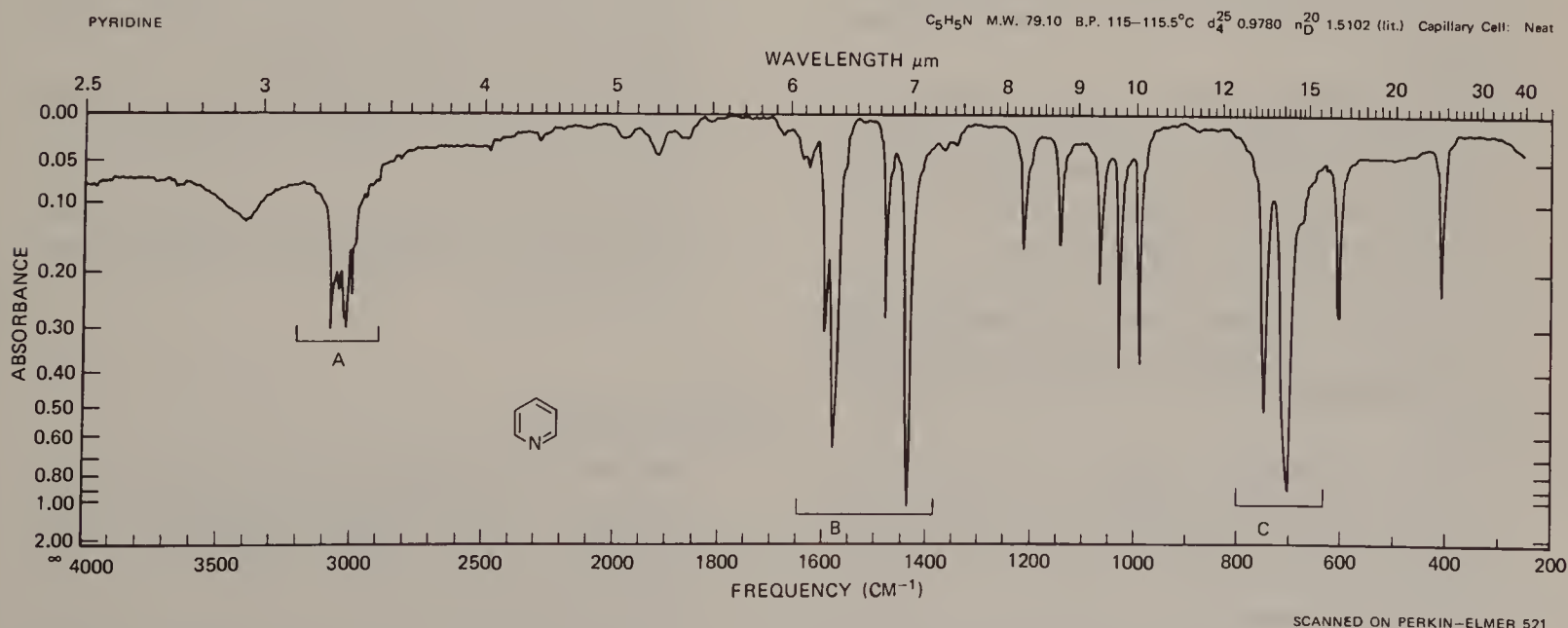
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Source: The Matheson Co., Inc. E. Rutherford, N.J.

**Figure 35.** A. Aromatic C-H stretch,  $3080\text{--}3010\ \text{cm}^{-1}$  ( $3.25\text{--}3.32\ \mu\text{m}$ ). B. C $\equiv$ C, C $\equiv$ N ring stretching (skeletal bands),  $1600\text{--}1430\ \text{cm}^{-1}$  ( $6.25\text{--}7.00\ \mu\text{m}$ ). C. C-H out-of-plane bending,  $748, 703\ \text{cm}^{-1}$  ( $13.37, 14.22\ \mu\text{m}$ ). See Appendix E, Table VII, for patterns in region C for substituted pyridines.



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3.1 *Spectra A-D*  
 1,3-cyclohexadiene  
 diphenylacetylene  
 1-octene  
 2-pentene

3.2 *Spectra E-I*  
*n*-butyl acetate  
 butyramide  
 isobutylamine  
 lauric acid  
 sodium propionate

3.3 *Spectra J-M*  
 allyl phenyl ether  
 benzaldehyde  
*o*-cresol  
*m*-toluic acid

3.4 *Spectra N-R*  
 aniline  
 azobenzene  
 benzophenone oxime  
 benzylamine  
 dimethylamine hydrochloride

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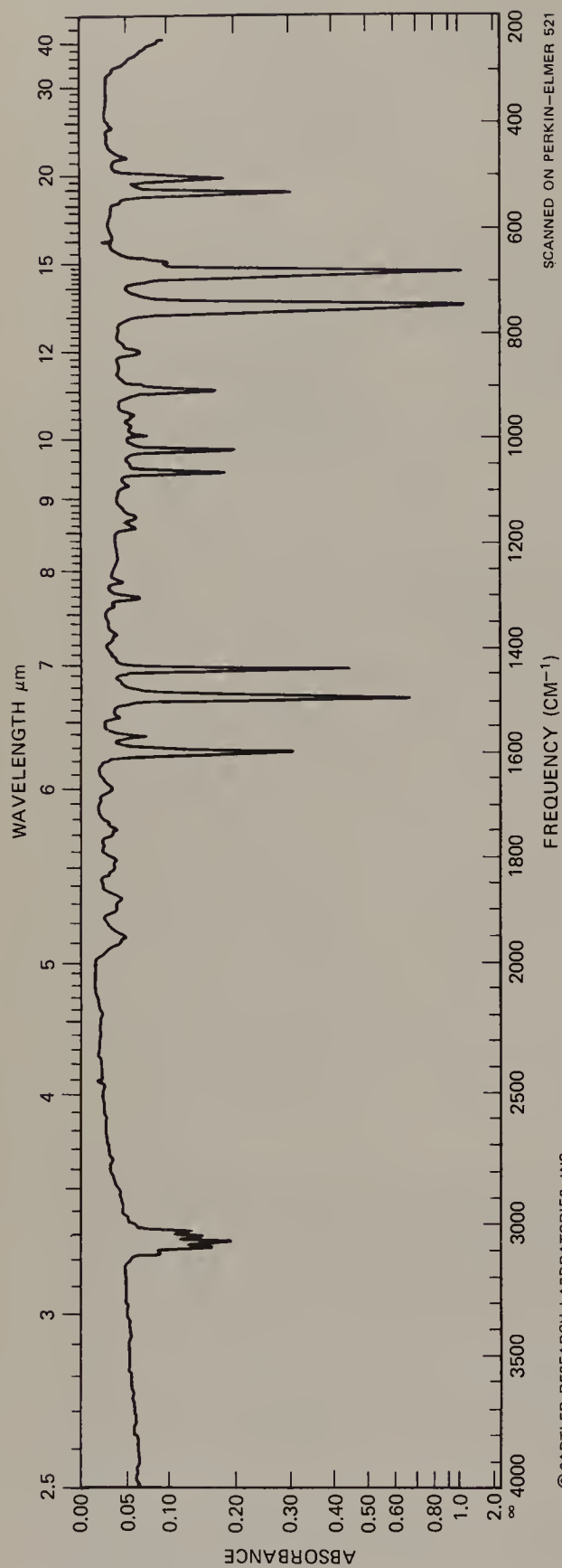
## PROBLEMS

For problems 3.1-3.5, match the name from each list to the proper infrared spectrum. Identify the diagnostic bands in each spectrum. These spectra are on pp. 138-148.

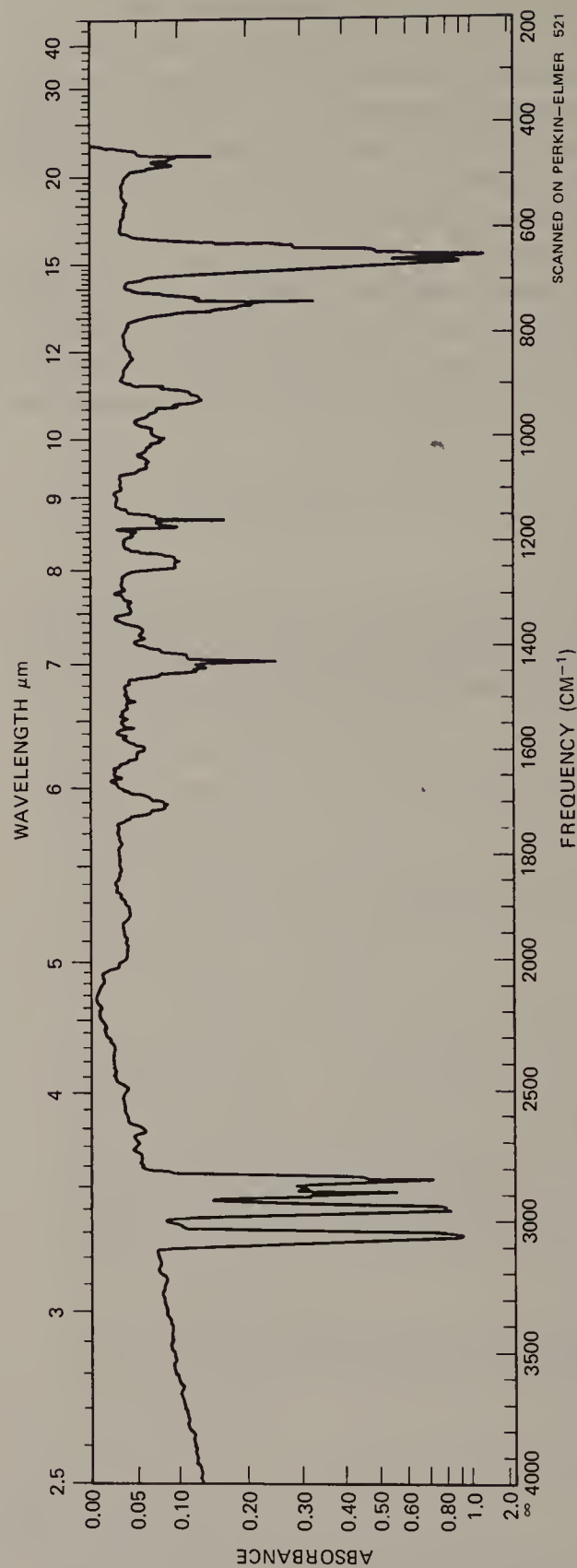
3.5 *Spectra S-U*

1,5-dichloropentane  
 epichlorohydrin  
 4-hydroxy-4-methyl-2-pentanone

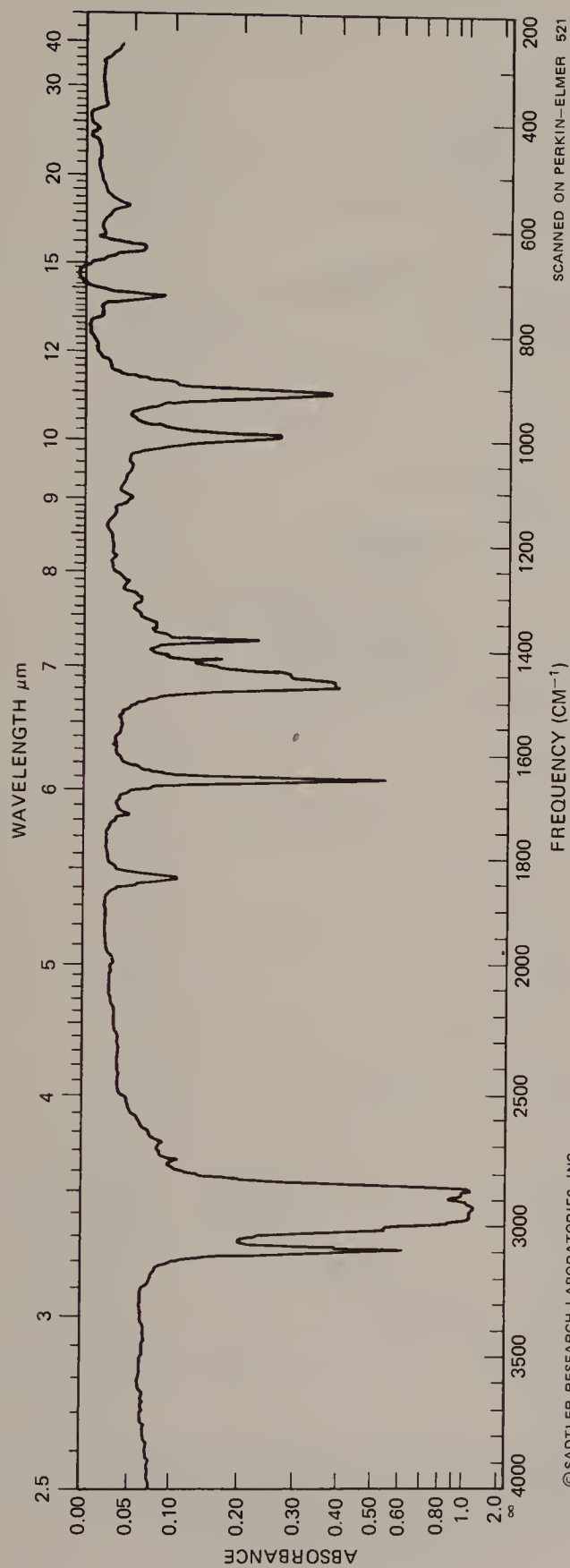
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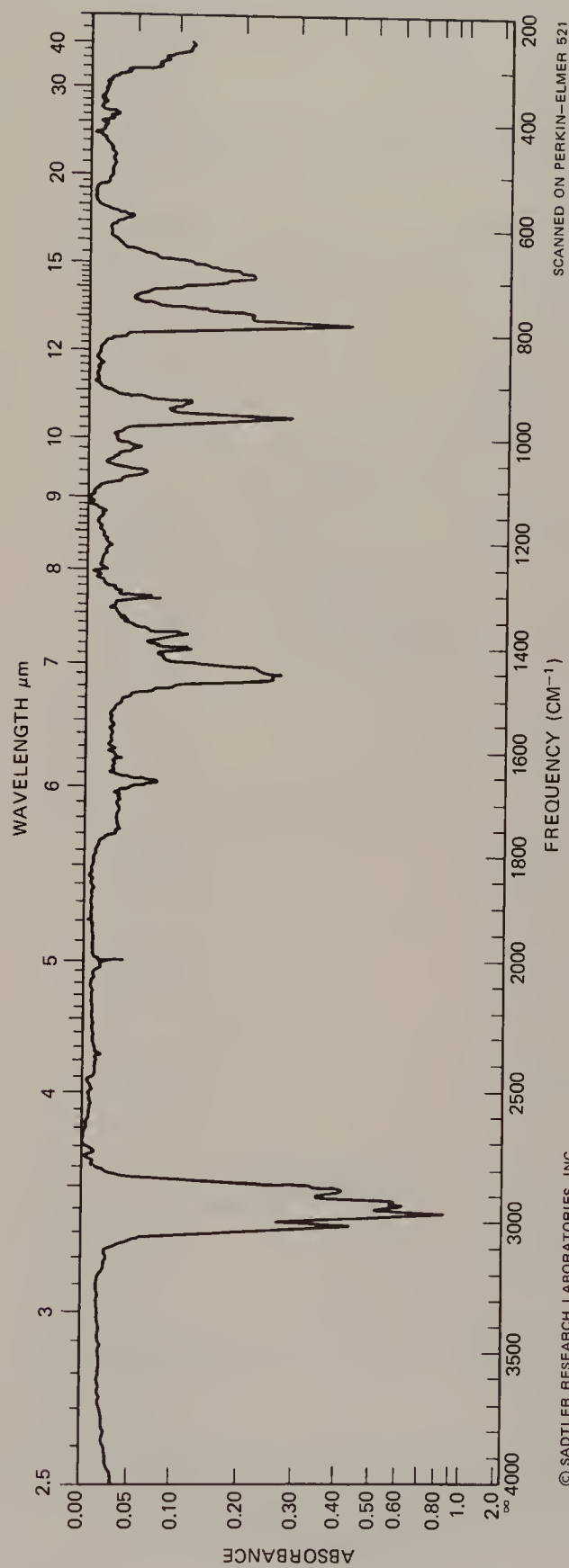
# PROB. 3.1 SPECTRUM B



# PROB. 3.1 SPECTRUM C

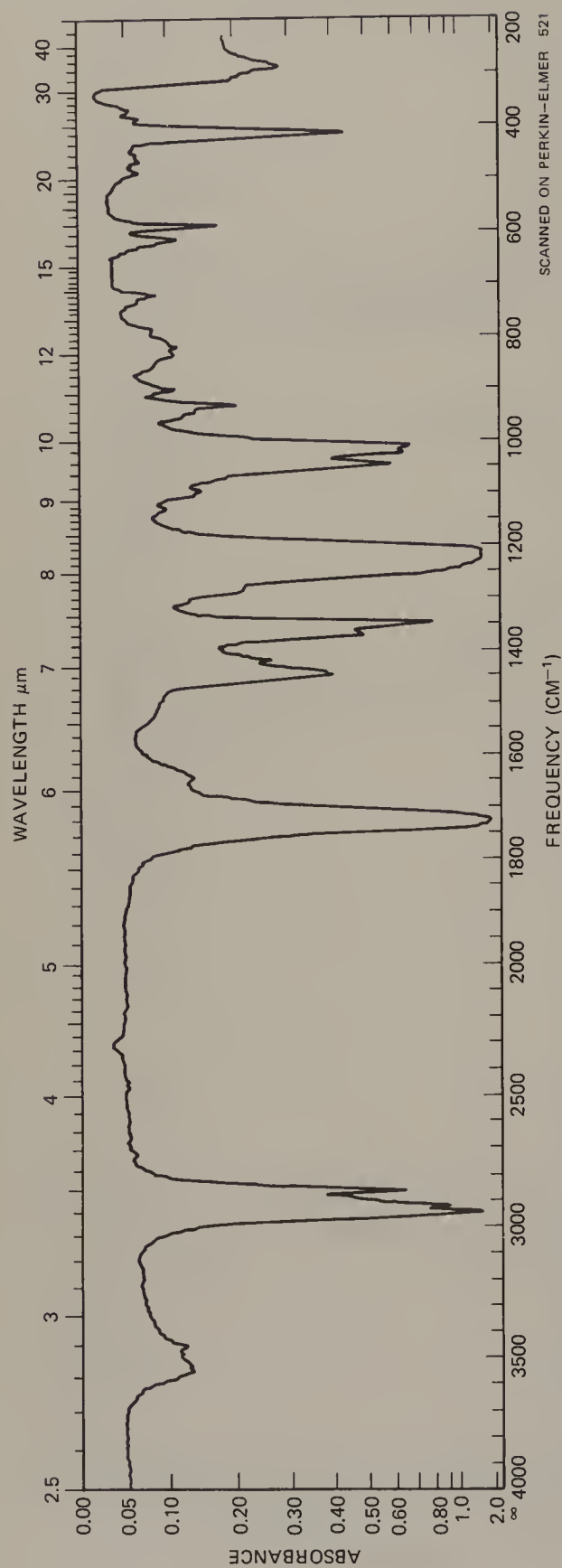


# PROB. 3.1 SPECTRUM D





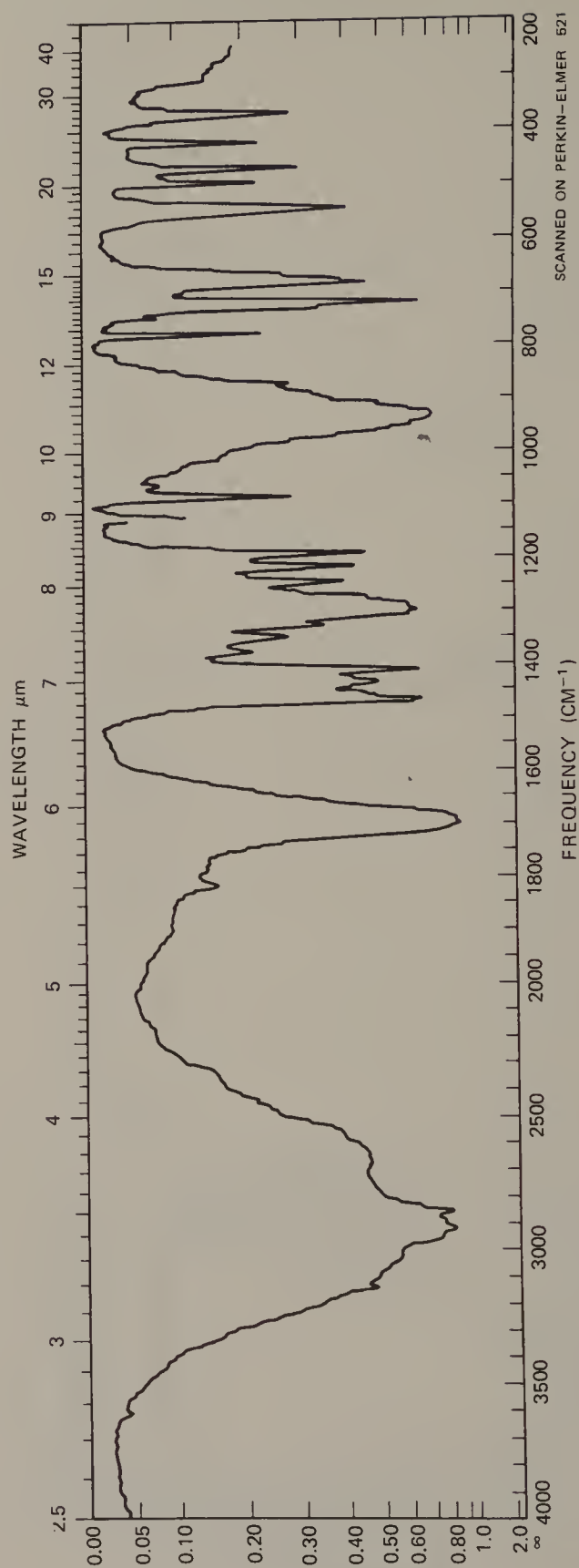
# PROB. 3.2 SPECTRUM E



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Source: Commercial Solvents Corp., New York, N.Y.

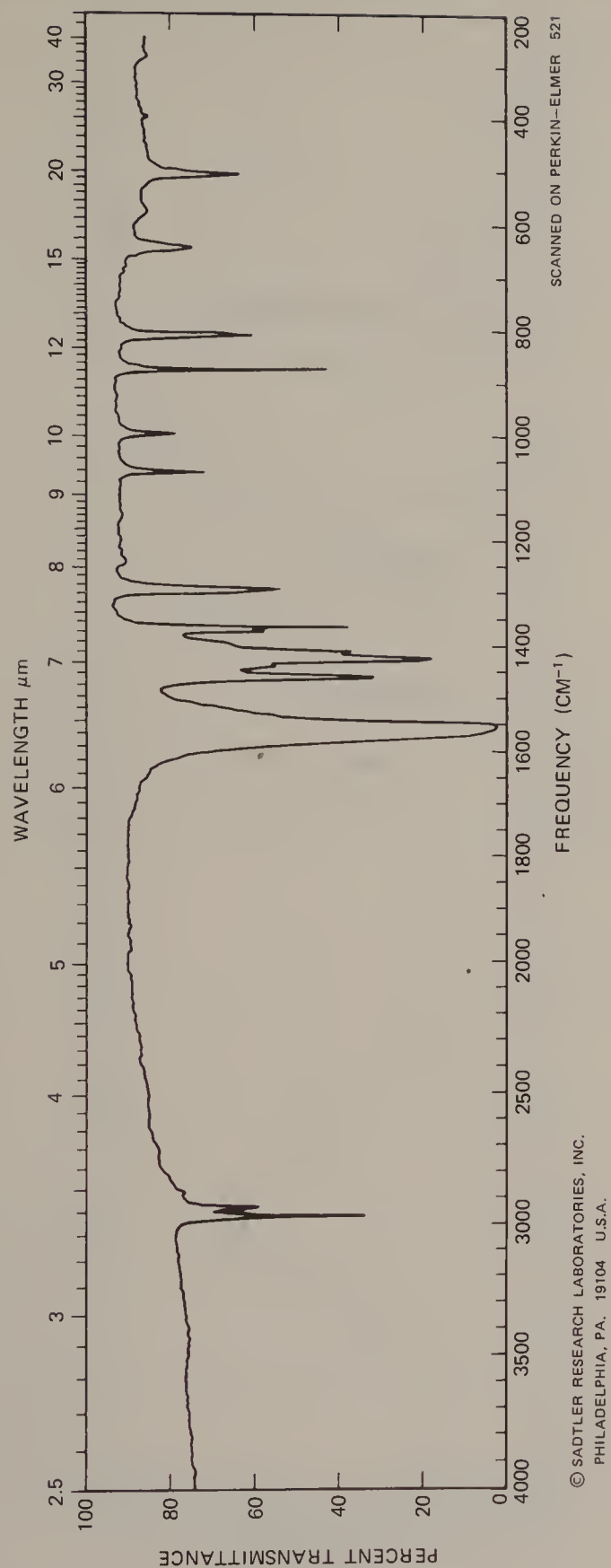
# PROB. 3.2 SPECTRUM F



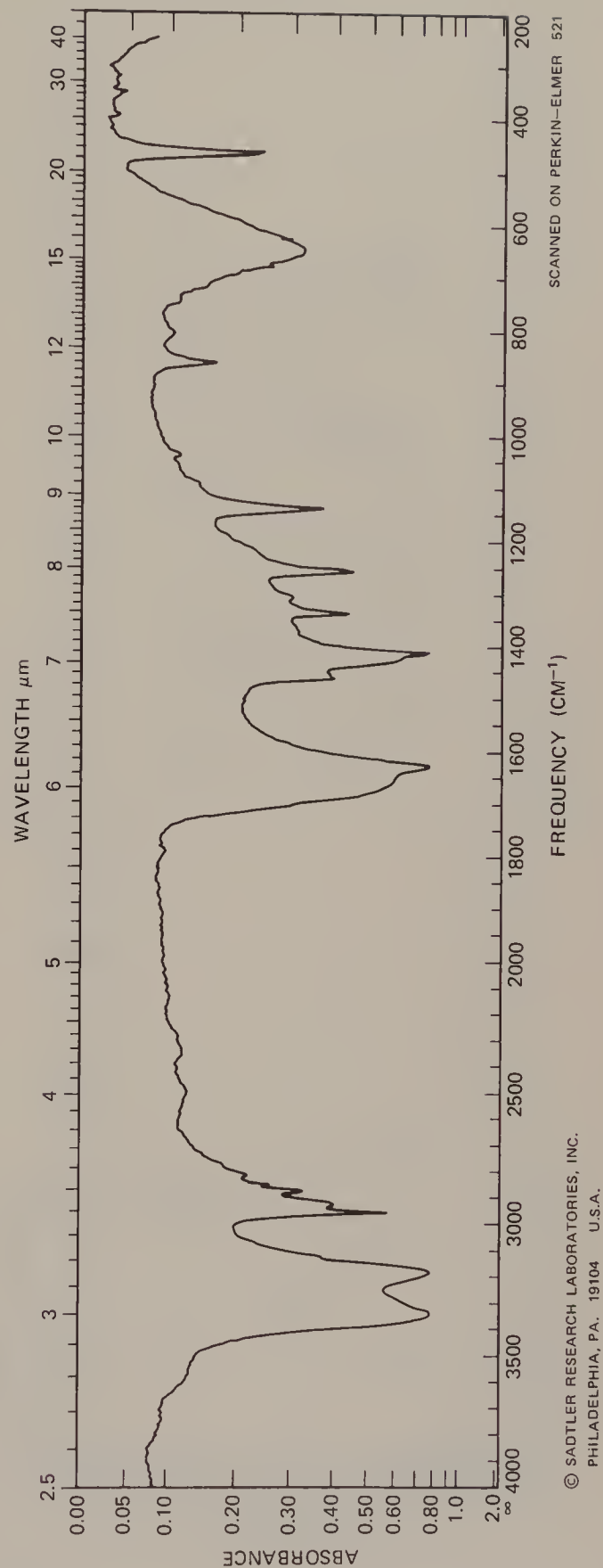
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Source: The Matheson Co., Inc., E. Rutherford, N.J.

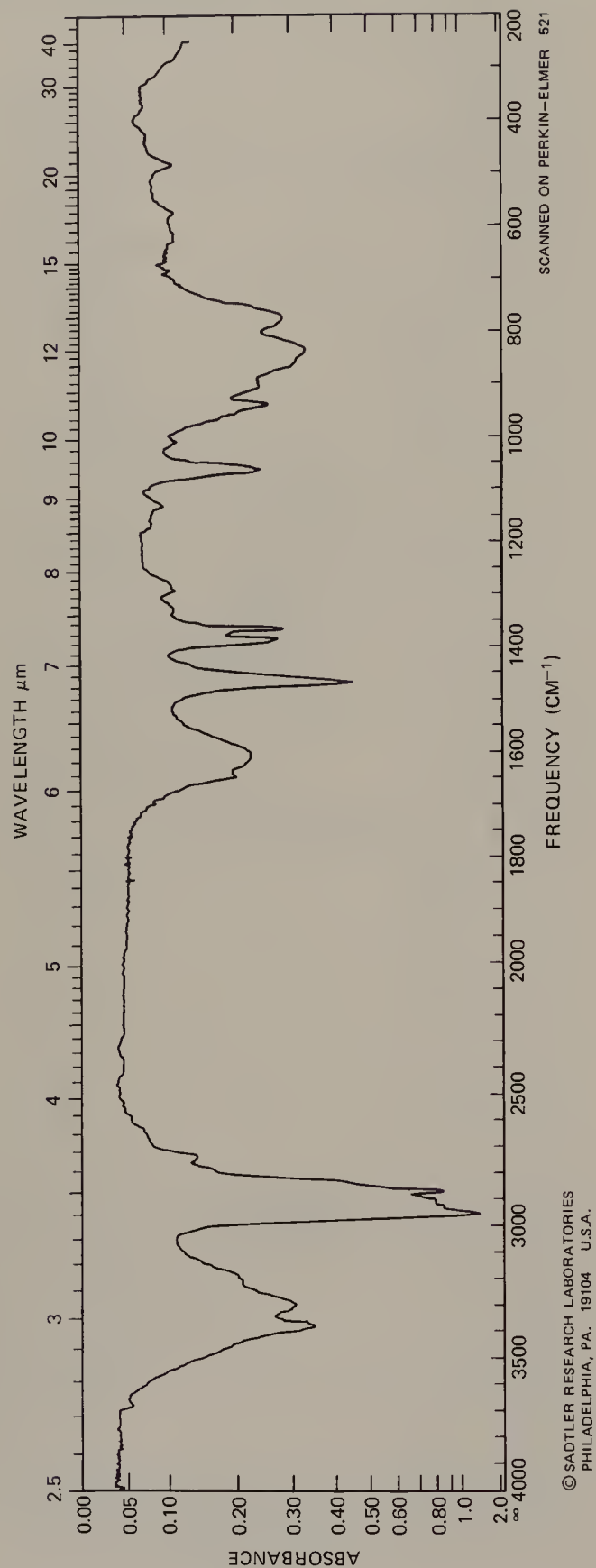
# PROB. 3.2 SPECTRUM G



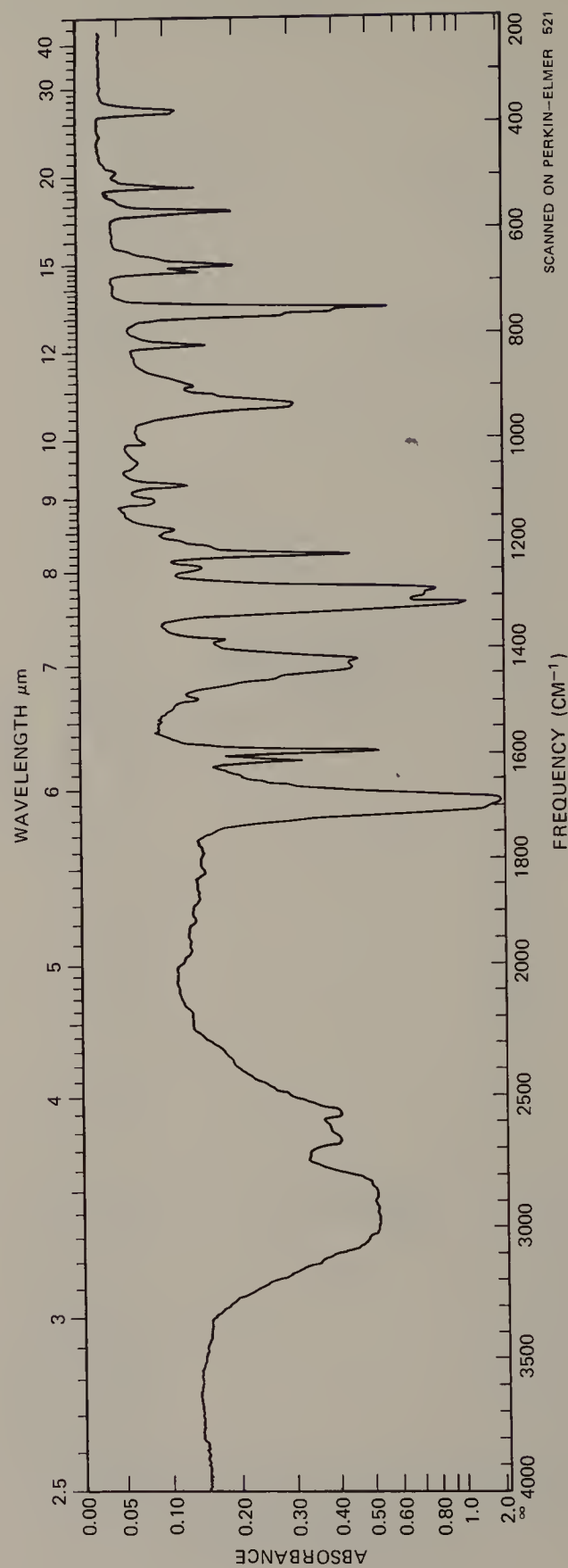
# PROB. 3.3 SPECTRUM H



# PROB. 3.2 SPECTRUM I

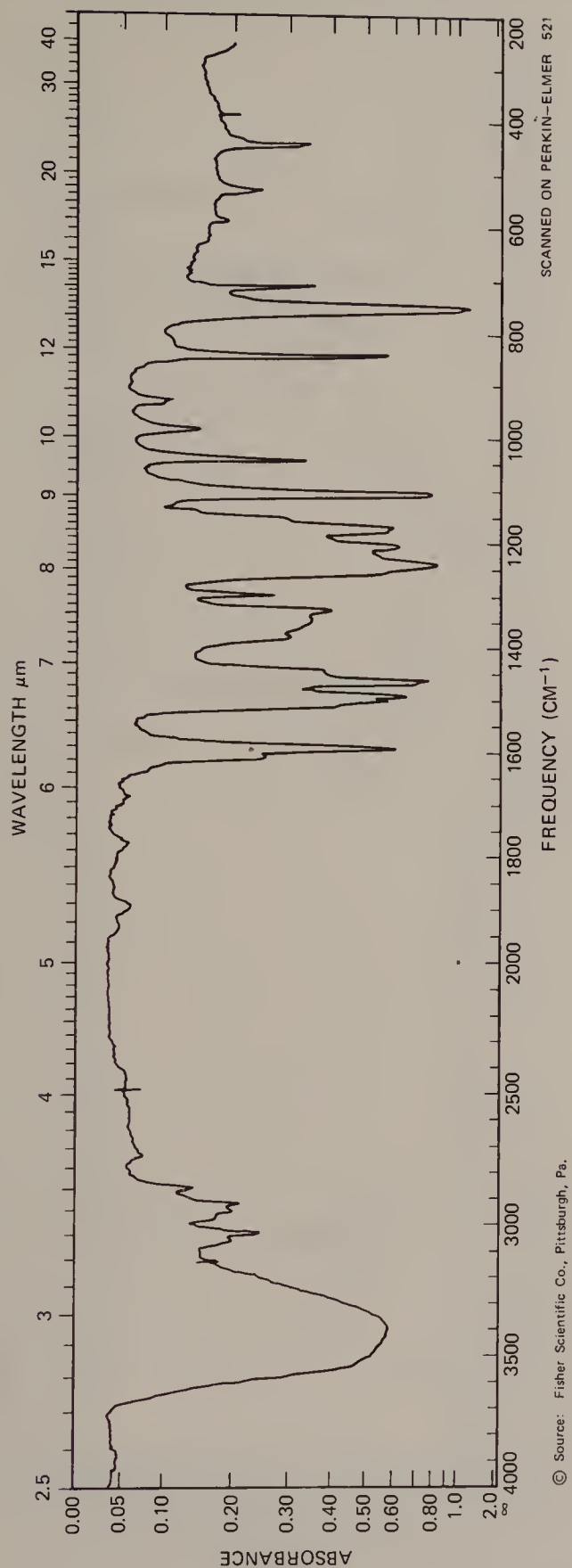


# PROB. 3.3 SPECTRUM J

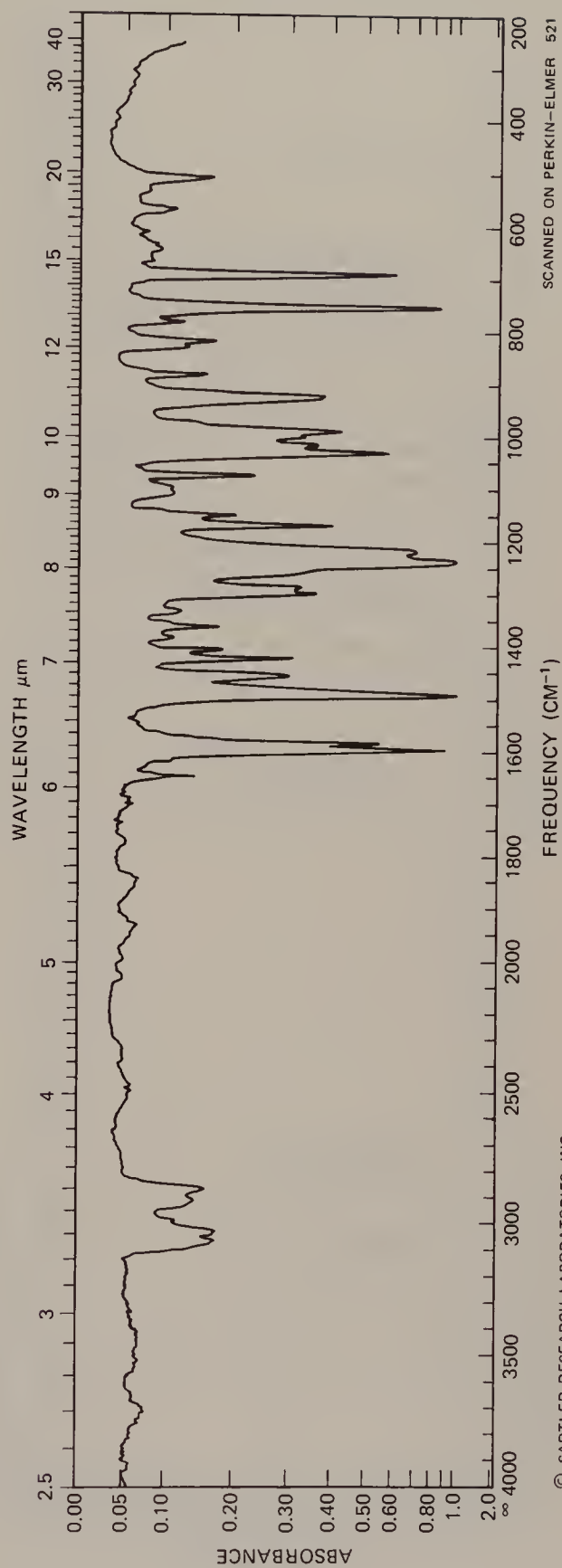




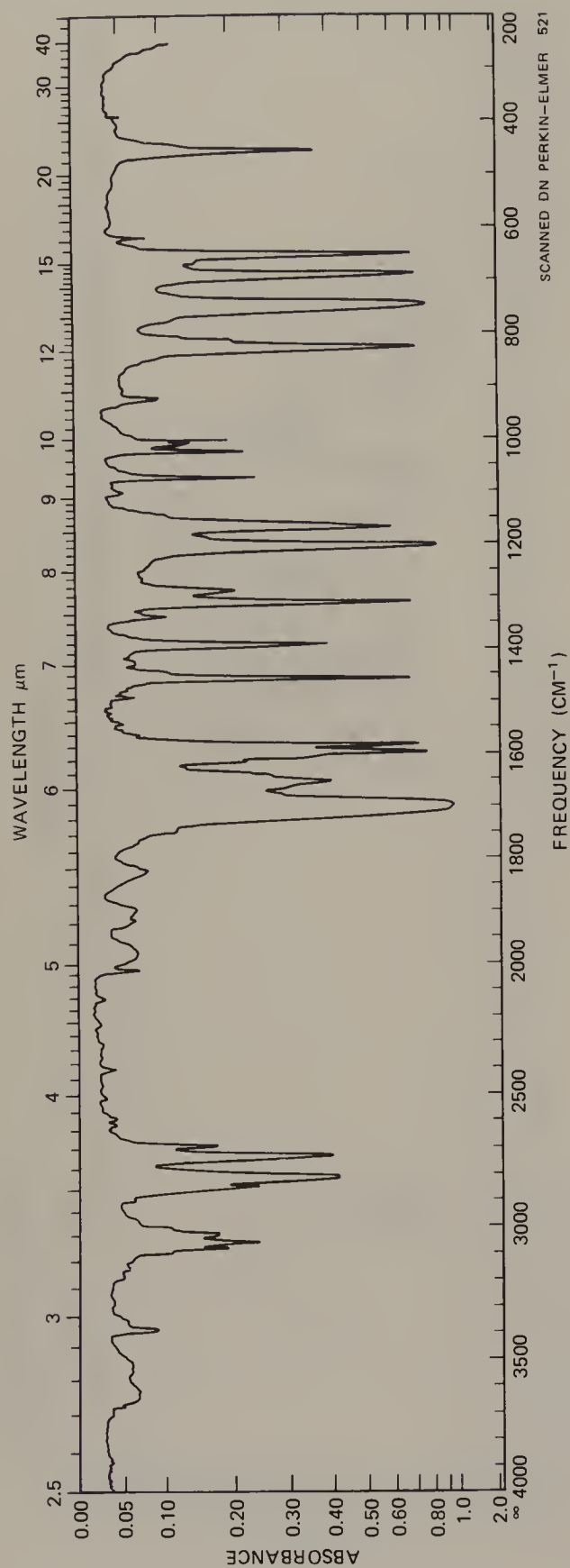
# PROB. 3.3 SPECTRUM K



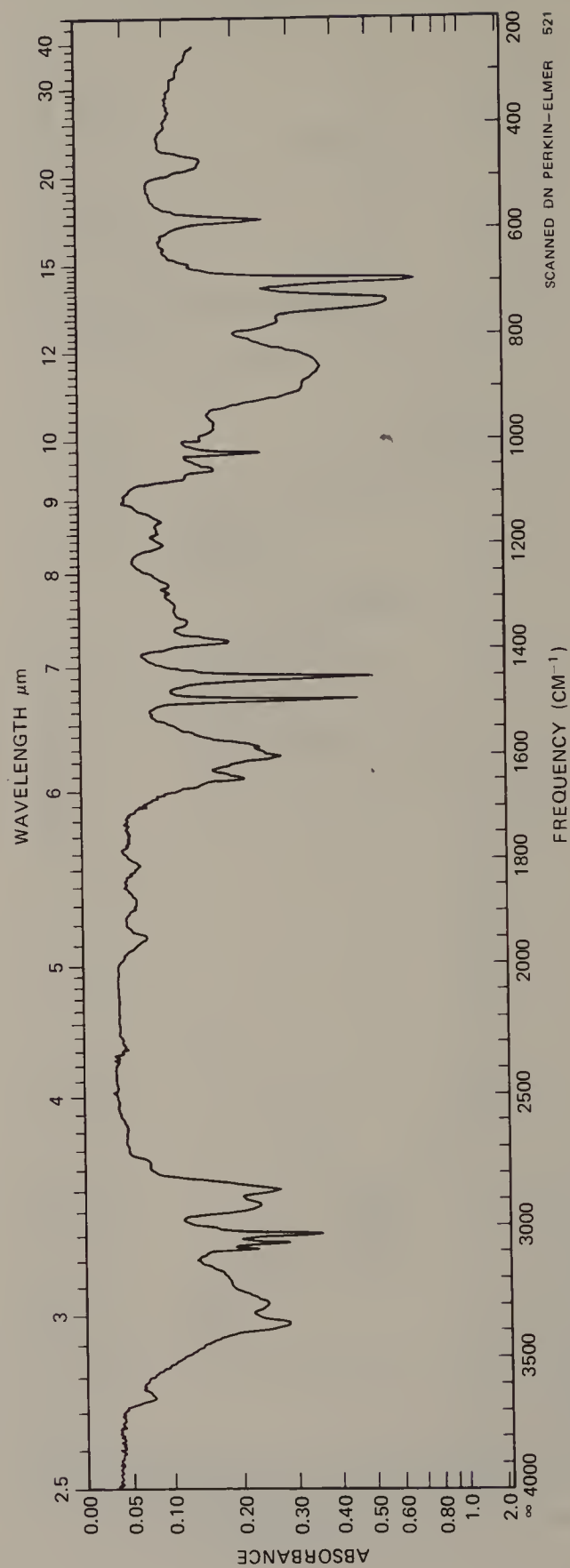
# PROB. 3.3 SPECTRUM L



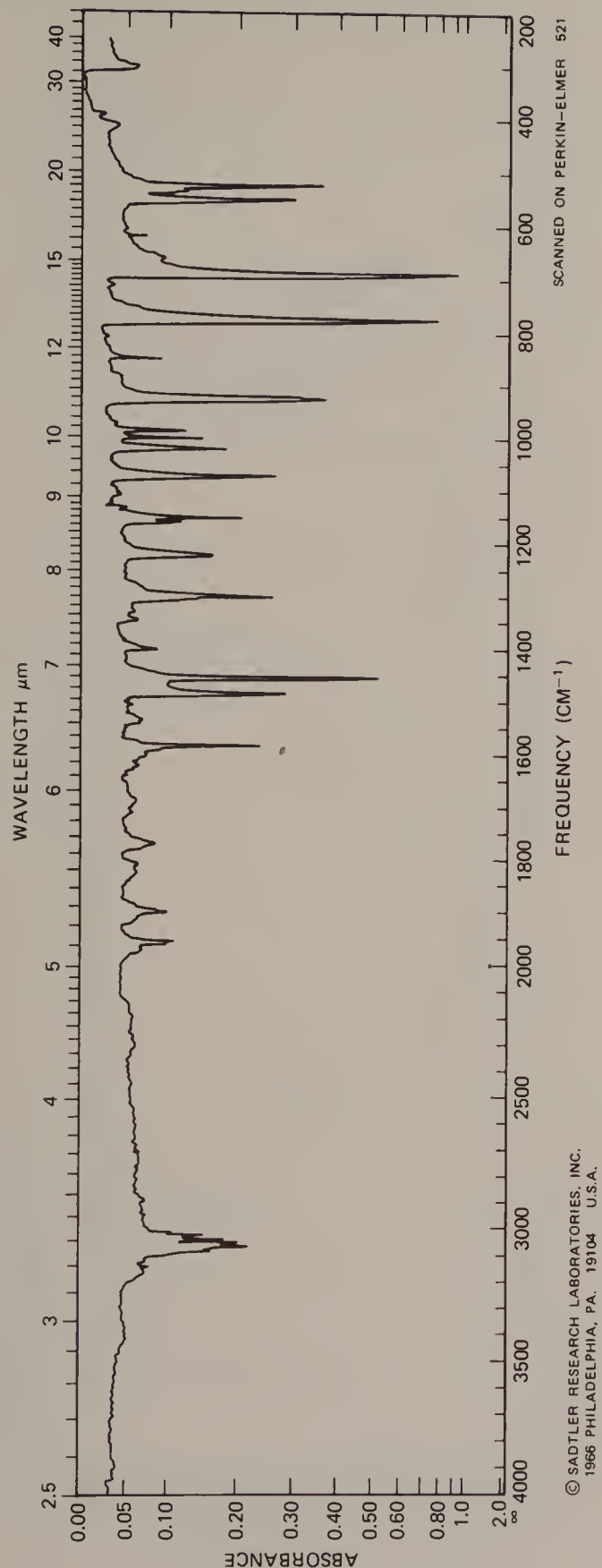
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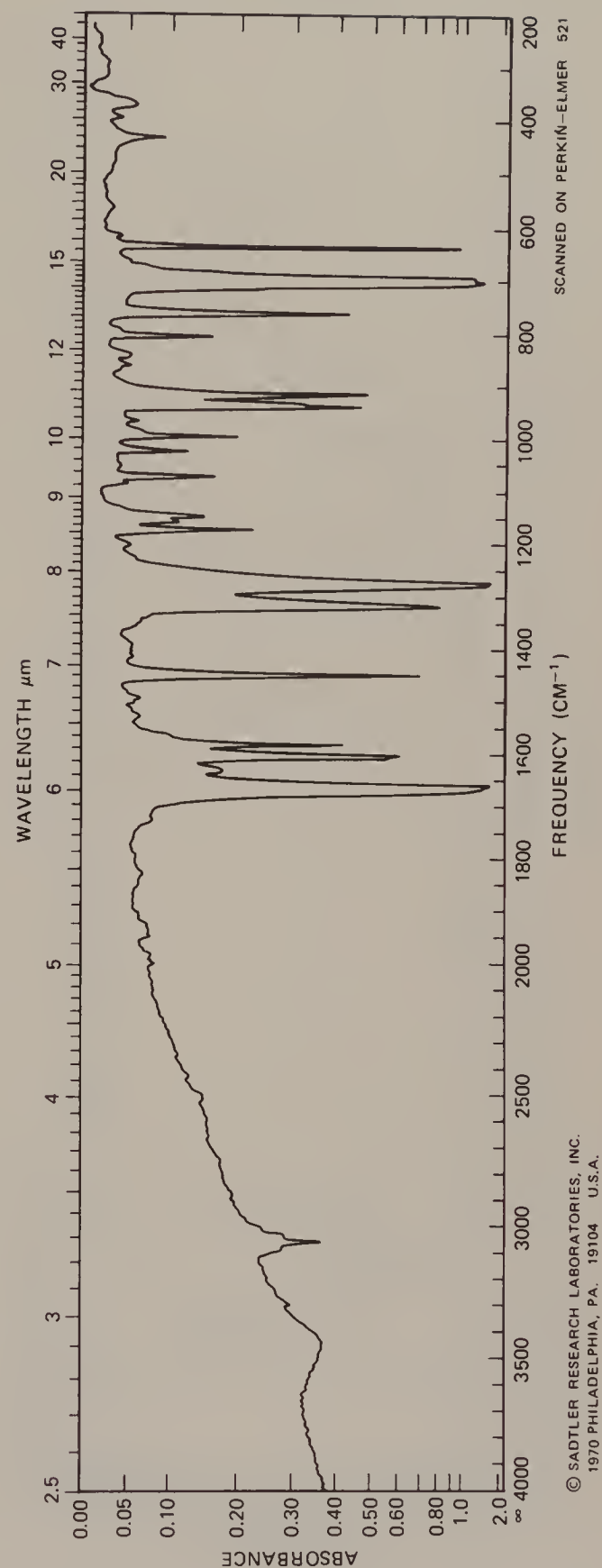
# PROB. 3.4 SPECTRUM N



PROB. 3.4 SPECTRUM O

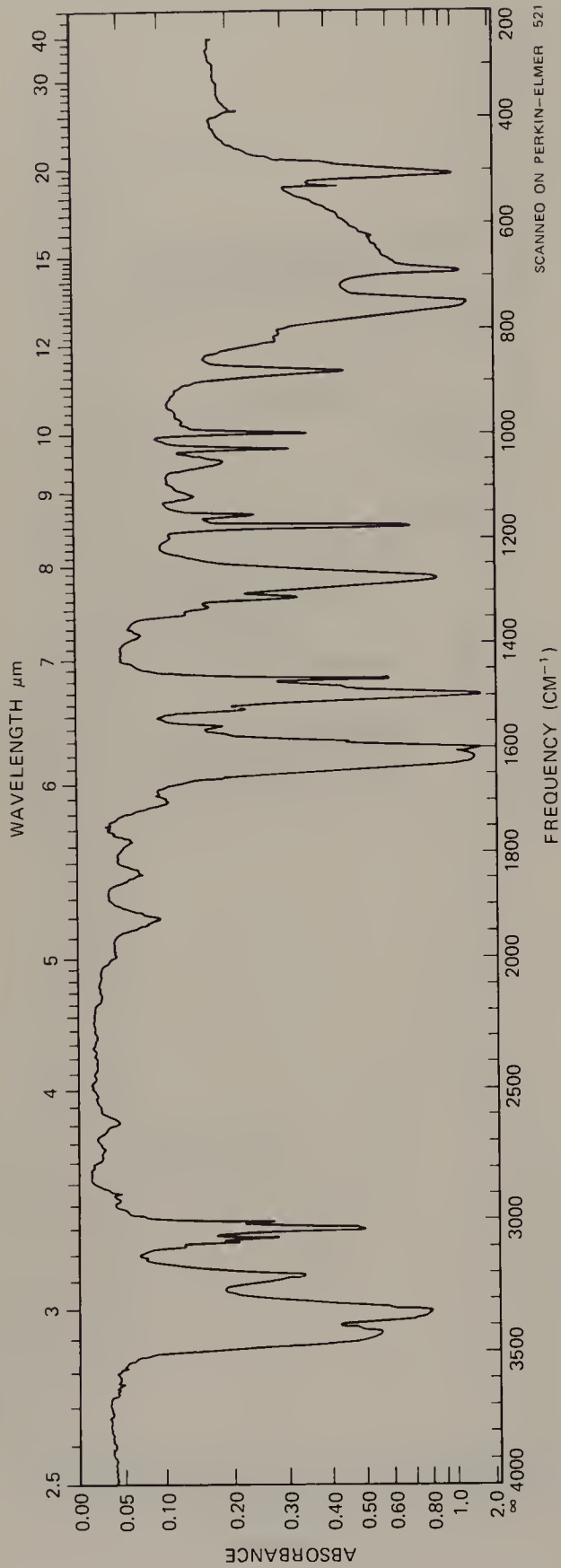


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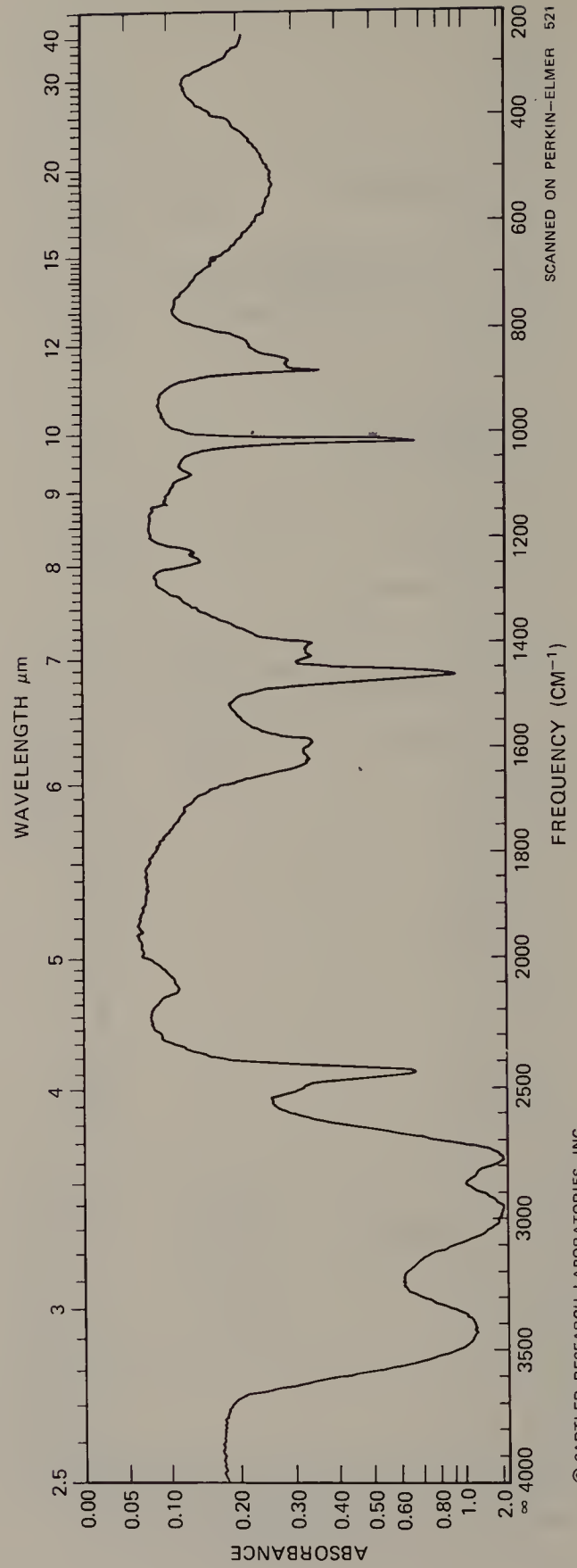




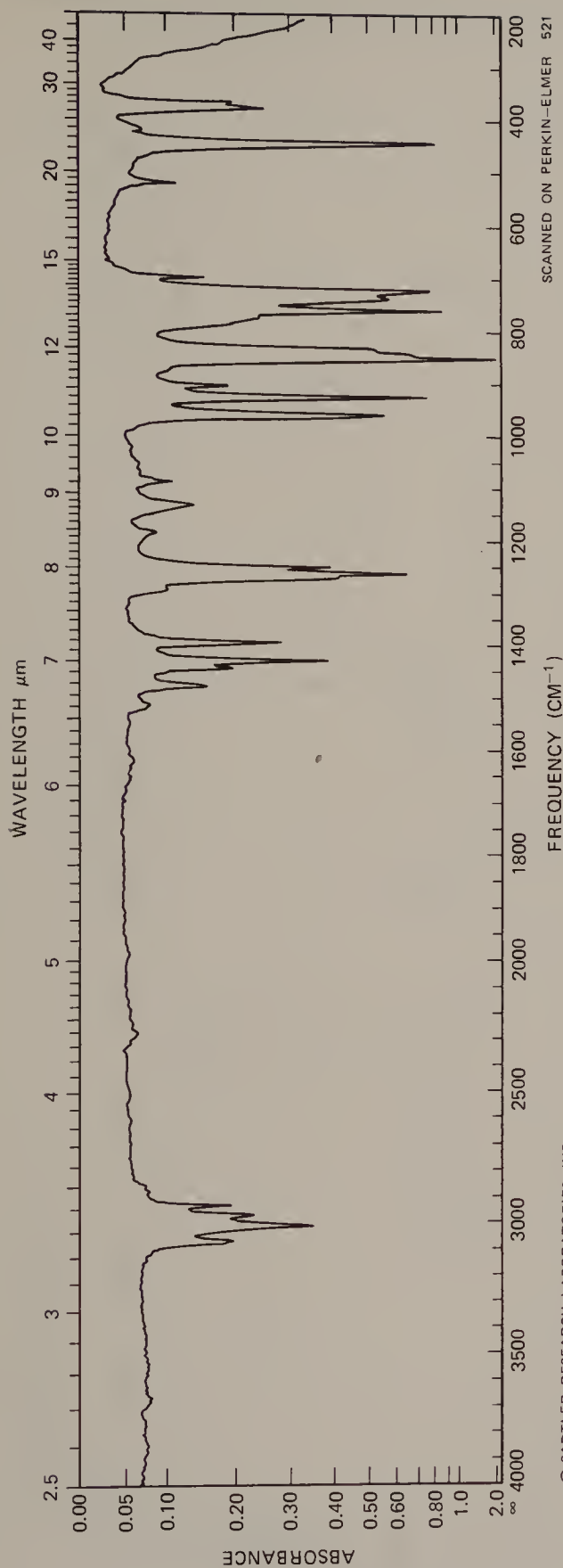
PROB. 3.4 SPECTRUM Q



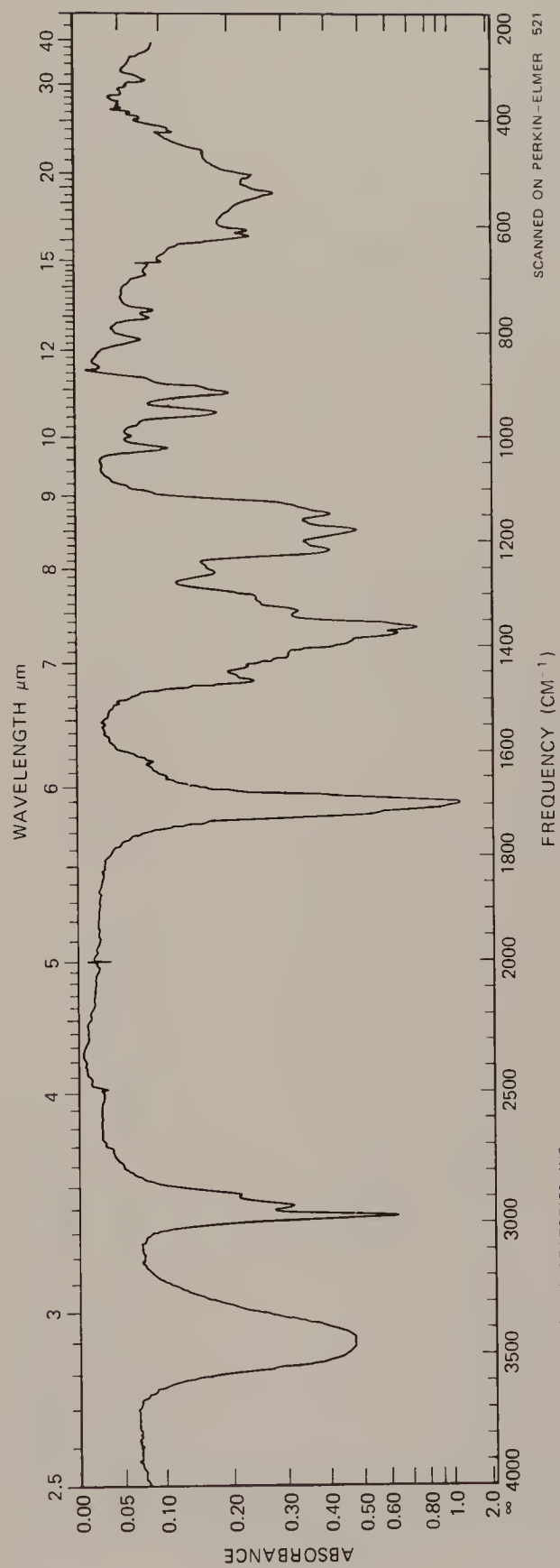
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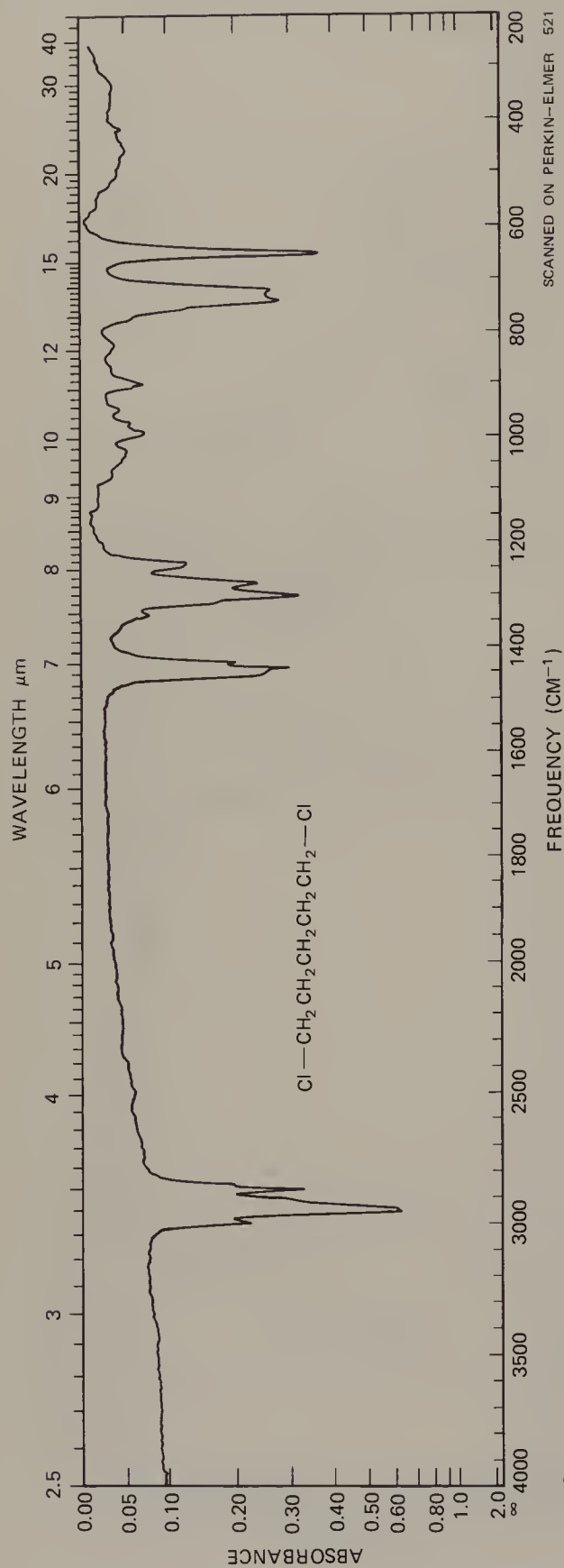
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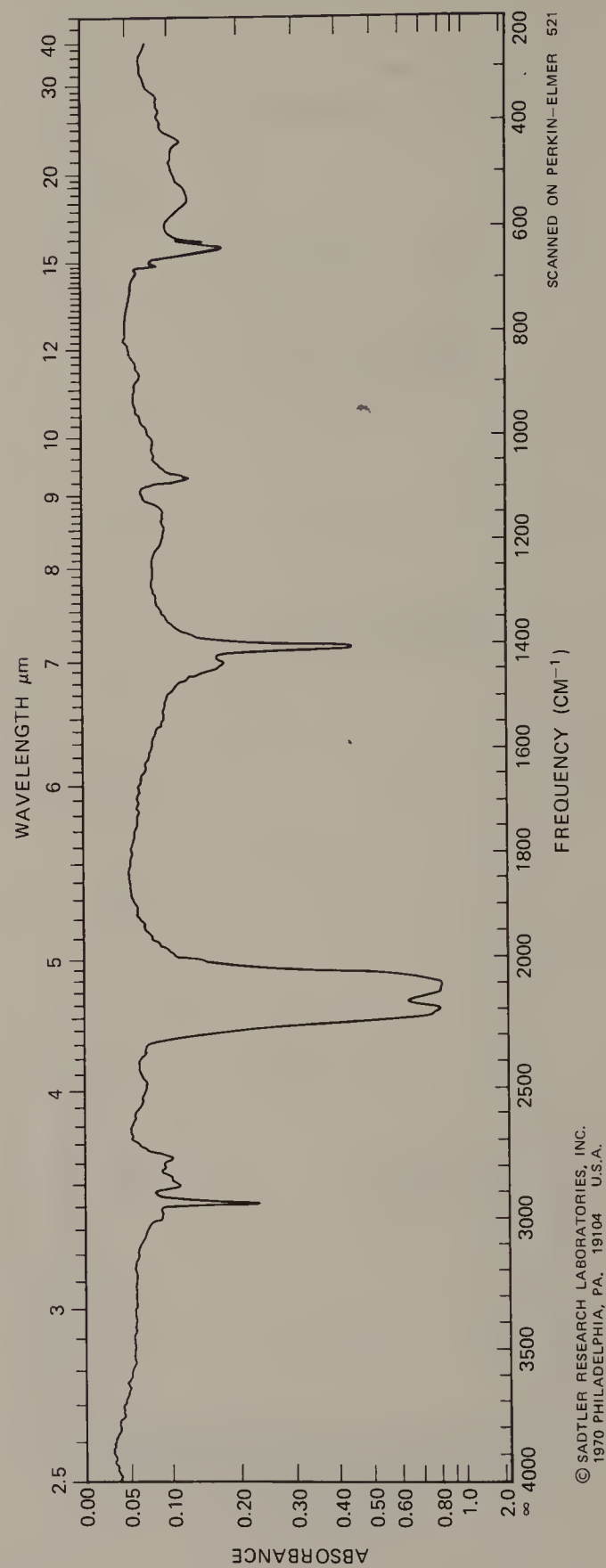
# PROB. 3.6 SPECTRUM T



# PROB. 3.5 SPECTRUM U

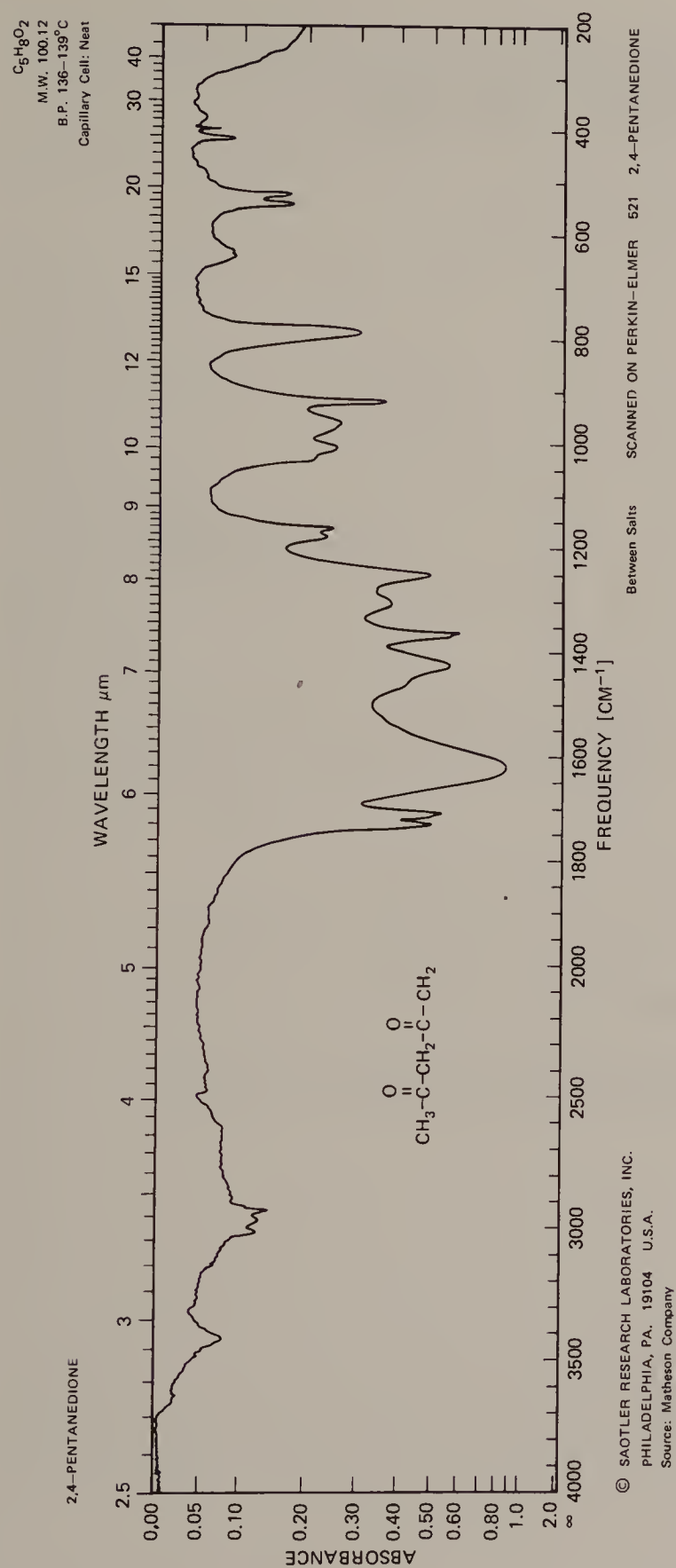


3.6 Deduce the structure of a compound whose formula is  $\text{C}_2\text{H}_3\text{NS}$  from the following spectrum.





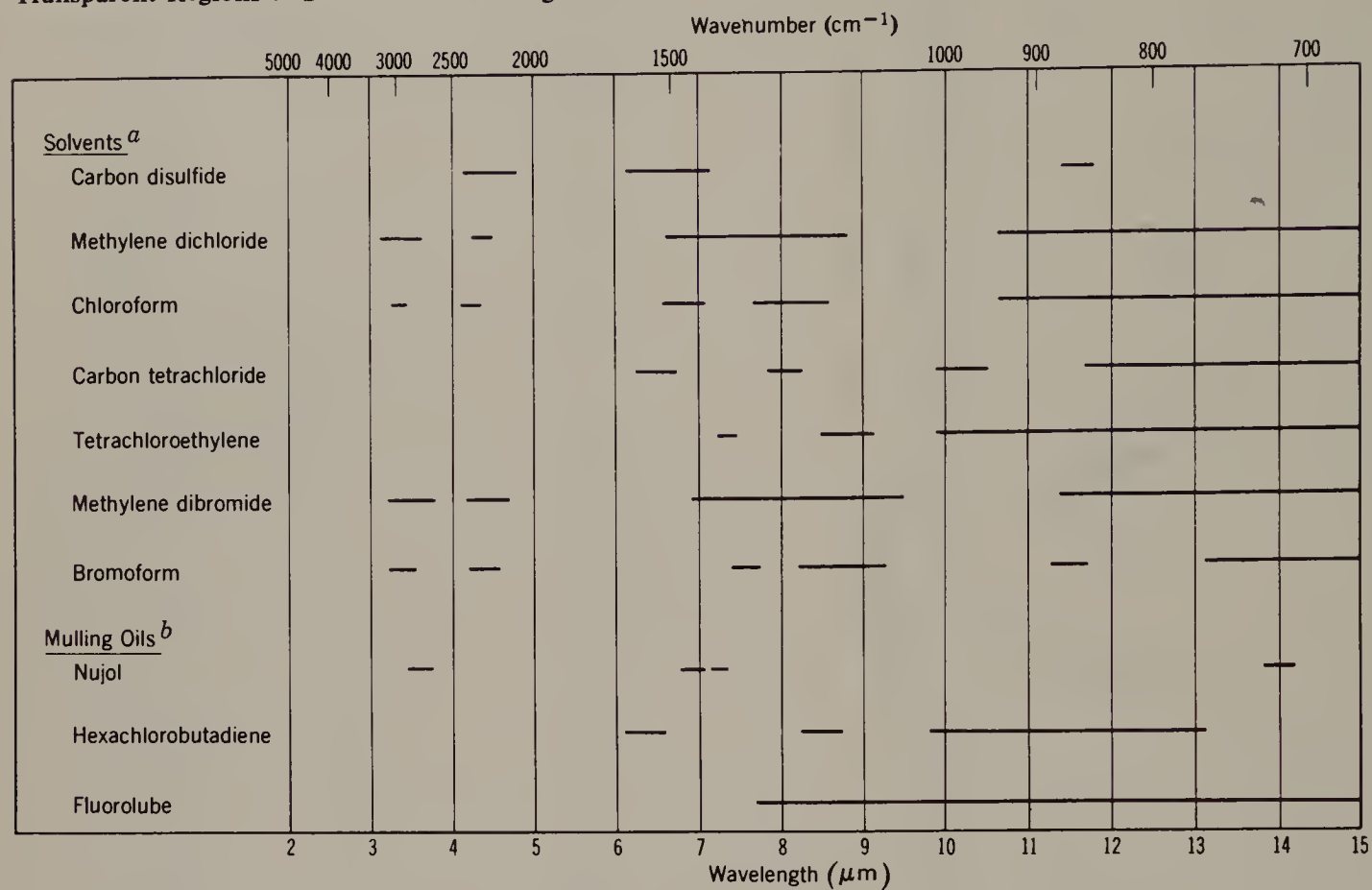
- 3.7 Point out evidence for enol formation in the infrared spectrum of 2,4-pentanedione (The band at  $3400\text{ cm}^{-1}$  is due to water).



# appendix a

## CHART AND SPECTRAL PRESENTATIONS OF ORGANIC SOLVENTS, MULLING OILS, AND OTHER COMMON LABORATORY SUBSTANCES

### Transparent Regions of Solvents and Mulling Oils.



Transparent regions of solvents and mulling oils. <sup>a</sup> The open regions are those in which the solvent transmits more than 25% of the incident light at 1 mm thickness. <sup>b</sup> The open regions for mulling oils indicate transparency of thin films.

# appendix b

## SPECTRA OF COMMON LABORATORY SUBSTANCES\*

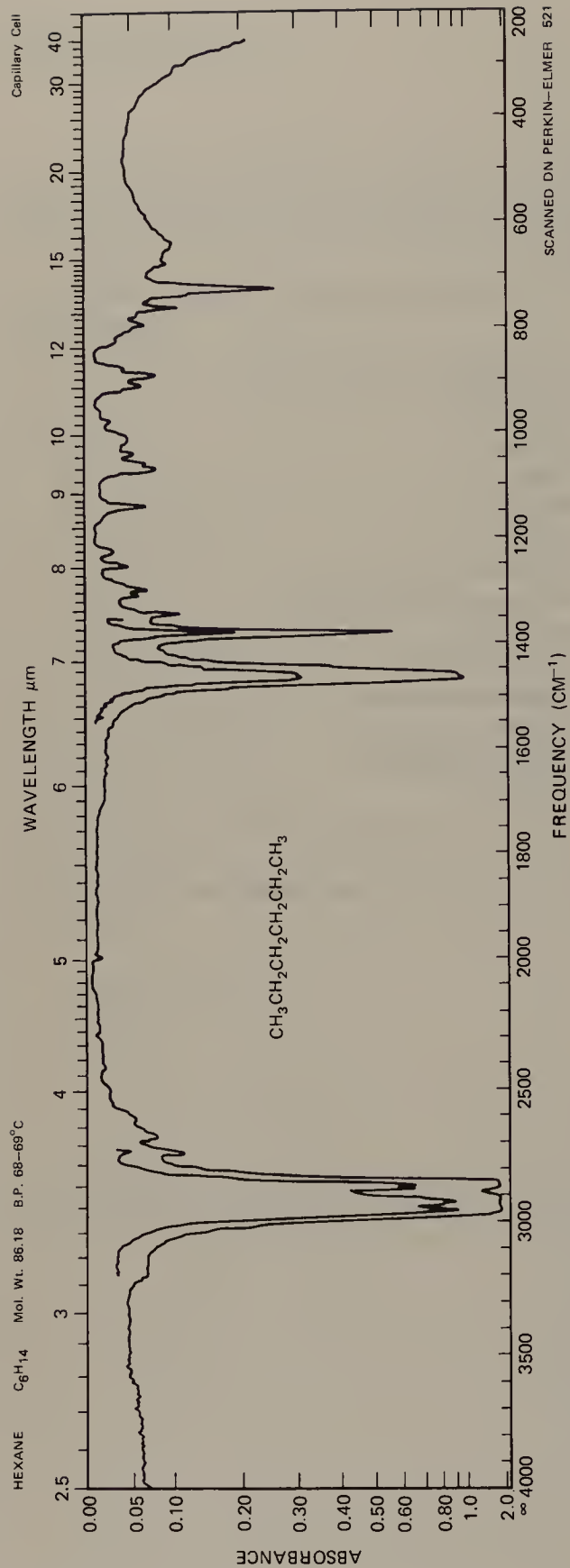
Alphabetical Listing of Spectra Shown on Succeeding Pages (pp. 152-165).

|                                     | Spectrum No. |                              | Spectrum No. |
|-------------------------------------|--------------|------------------------------|--------------|
| Acetone                             | 17           | Ethyl ether                  | 22           |
| Benzene                             | 4            | Fluorolube®                  | 14           |
| 2-Butanone                          | 18           | Hexane                       | 1            |
| Carbon disulfide                    | 25           | Indene                       | 8            |
| Carbon tetrachloride                | 10           | Methanol                     | 15           |
| Chloroform                          | 9            | Nujol®                       | 2            |
| Cyclohexane                         | 3            | Petroleum ether              | 24           |
| Cyclohexanone                       | 19           | Phthalic acid, diethyl ester | 21           |
| 1,2-Dichloroethane                  | 11           | Polystyrene                  | 7            |
| <i>N,N</i> -Dimethylformamide (DMF) | 28           | Silicone lubricant           | 27           |
| Dimethyl sulfoxide (DMSO)           | 26           | Tetrachloroethylene          | 13           |
| <i>p</i> -Dioxane                   | 23           | Toluene                      | 5            |
| Ethyl acetate                       | 20           | Trichloroethylene            | 12           |
| Ethyl alcohol                       | 16           | <i>m</i> -Xylene             | 6            |

*Spectra courtesy of Sadtler Laboratories and Aldrich Chemical Co.*

\*Carbon dioxide (Sadtler Prism Spectrum No. 1924) has bands in the  $3700\text{--}3550\text{ cm}^{-1}$  ( $2.70\text{--}2.82\text{ }\mu\text{m}$ ) and  $2380\text{--}2222\text{ cm}^{-1}$  ( $4.20\text{--}4.50\text{ }\mu\text{m}$ ) regions and at *ca.*  $720\text{ cm}^{-1}$  ( $13.9\text{ }\mu\text{m}$ ).

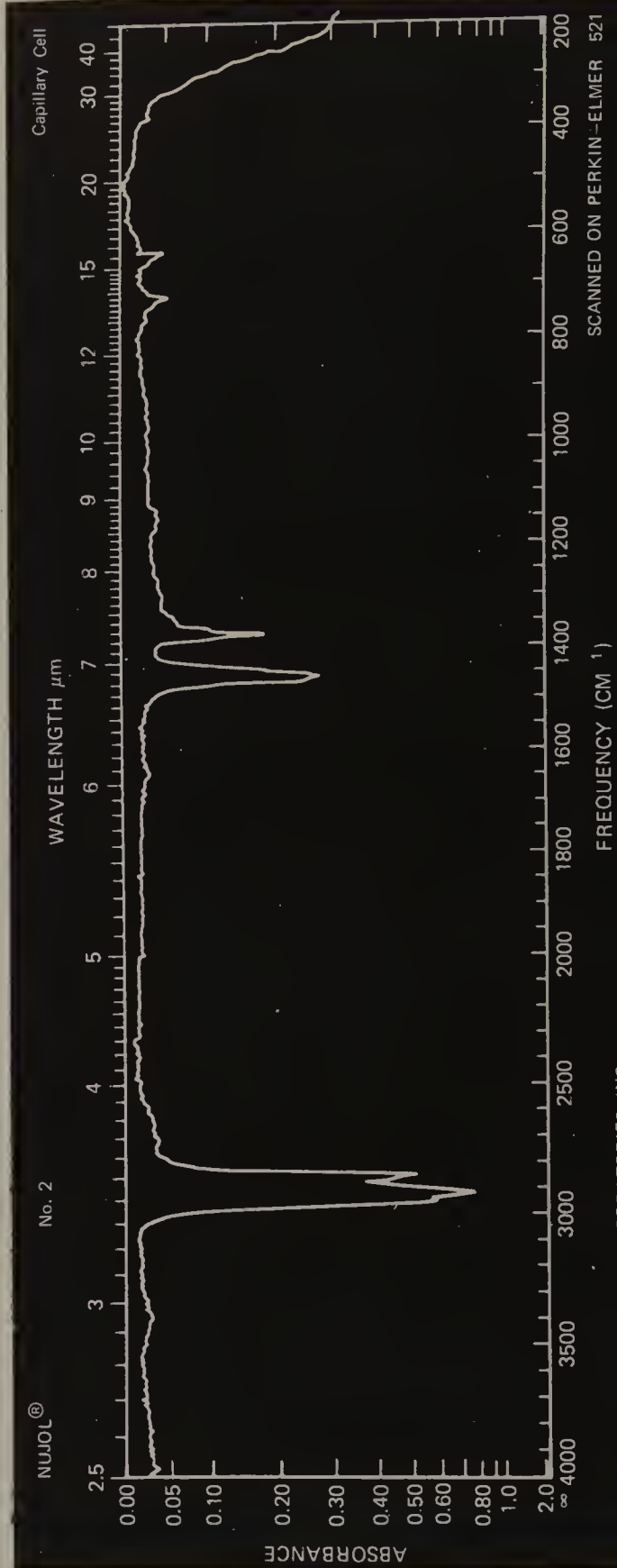




No. 1

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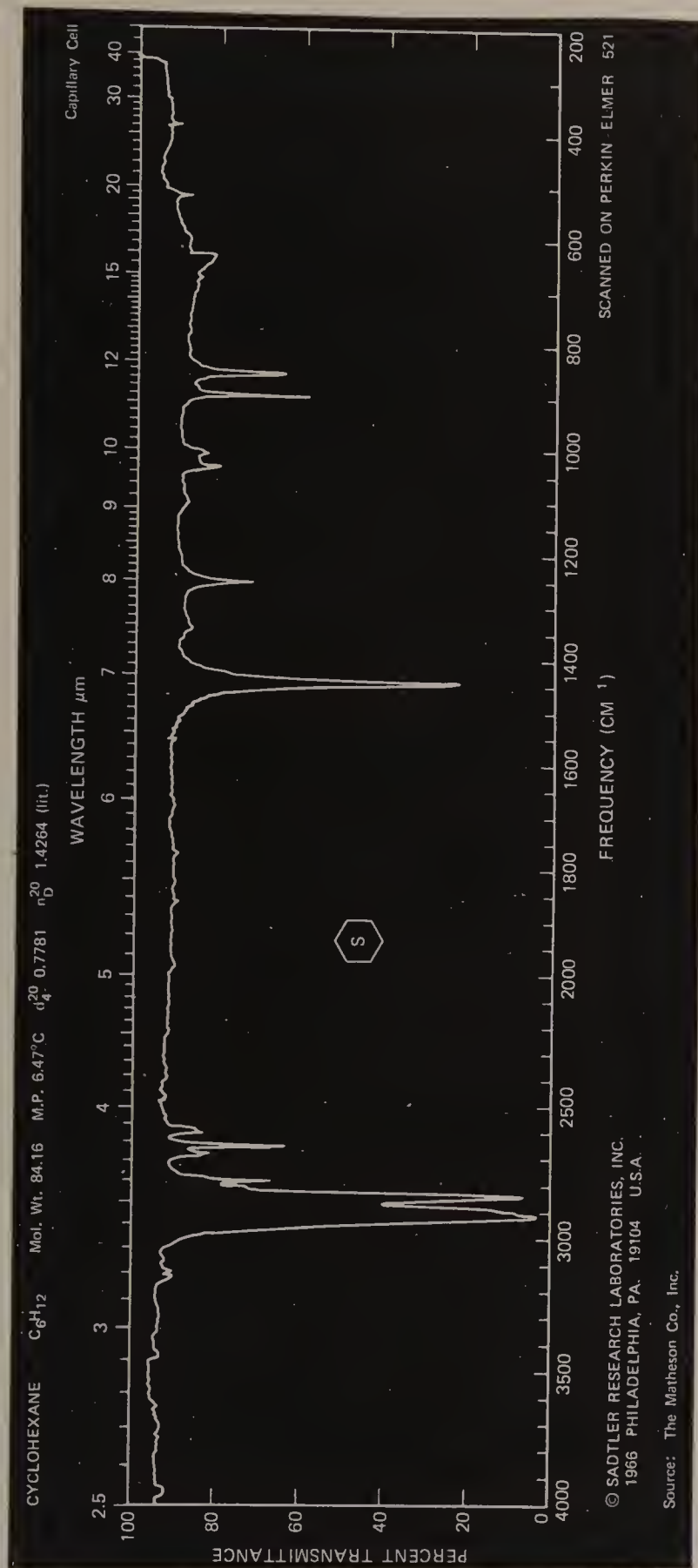
Source: Phillips Petroleum Co.



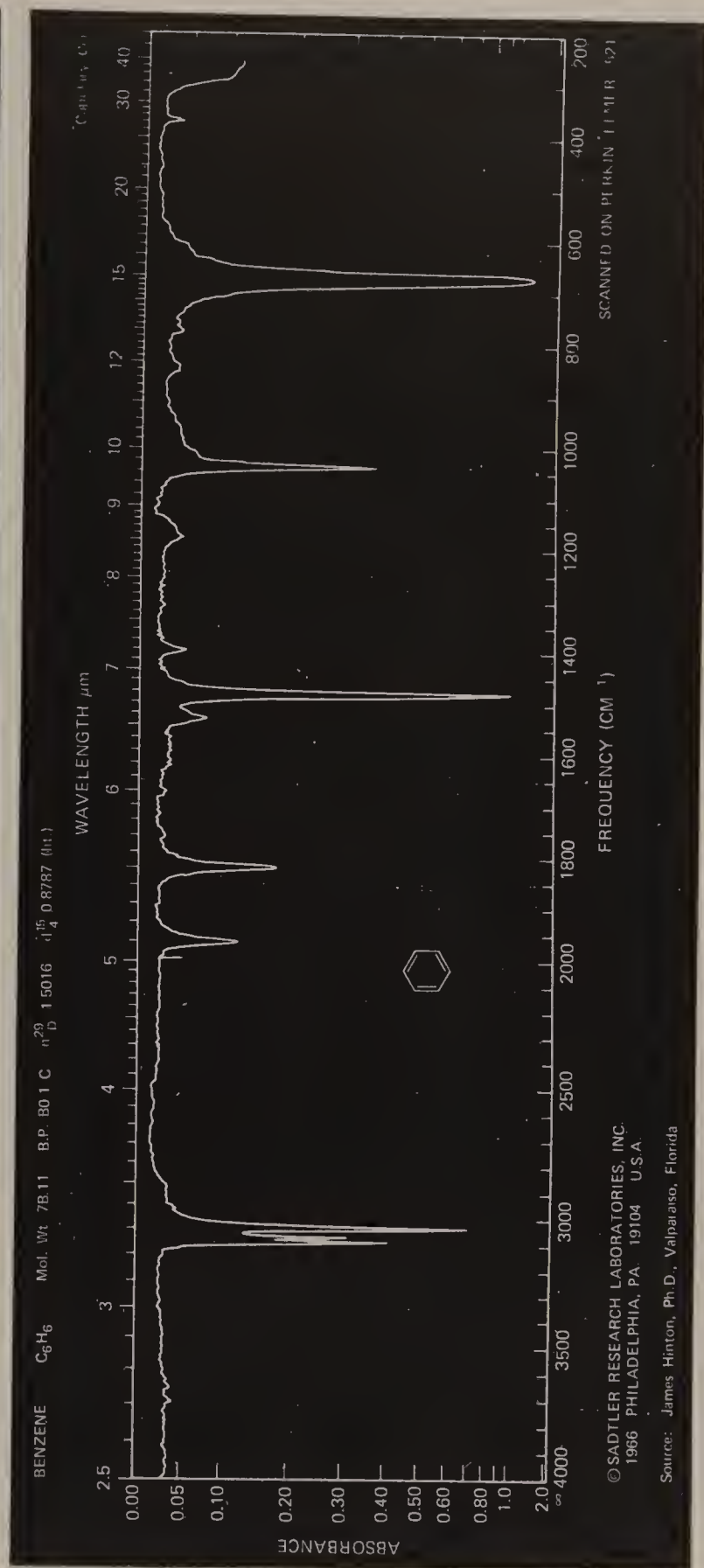
© SADTLER RESEARCH LABORATORIES, INC.  
1966 PHILADELPHIA, PA. 19104 U.S.A.

Source: Plough, Inc.

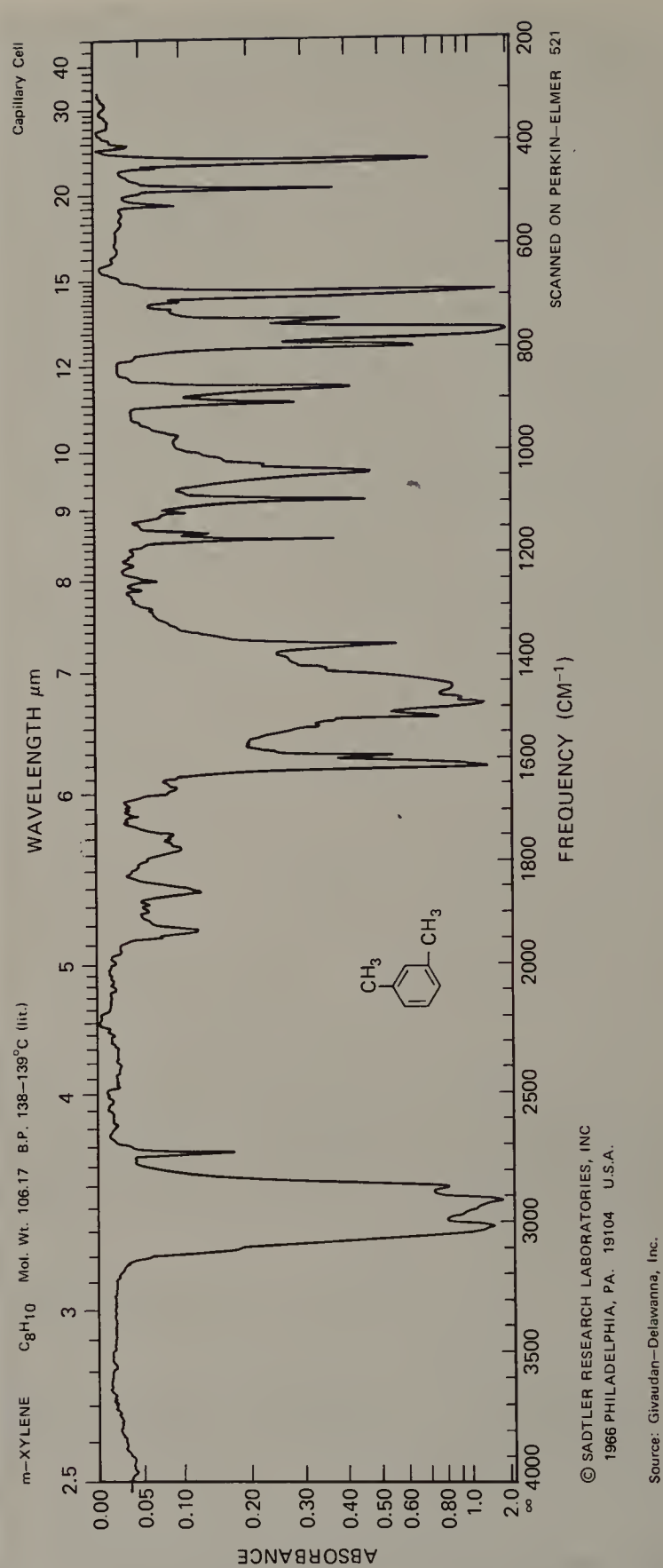
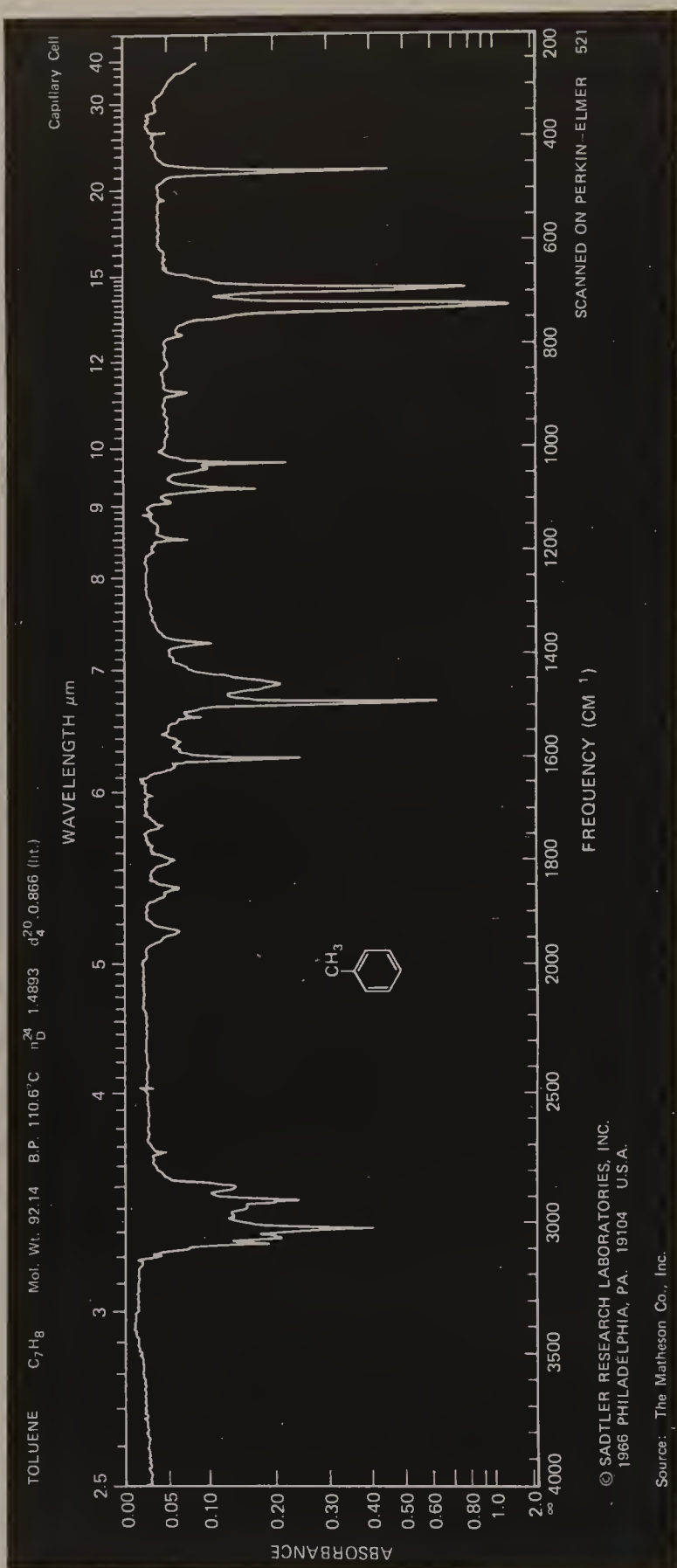
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No. 3

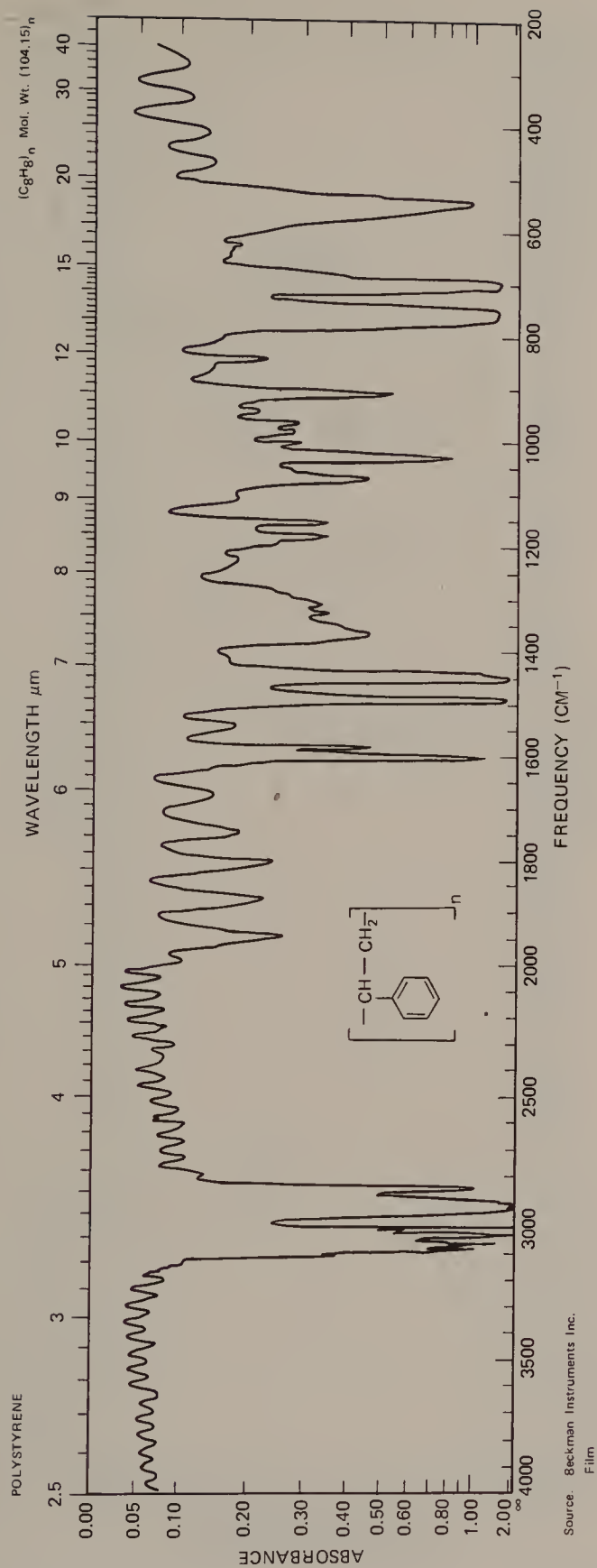


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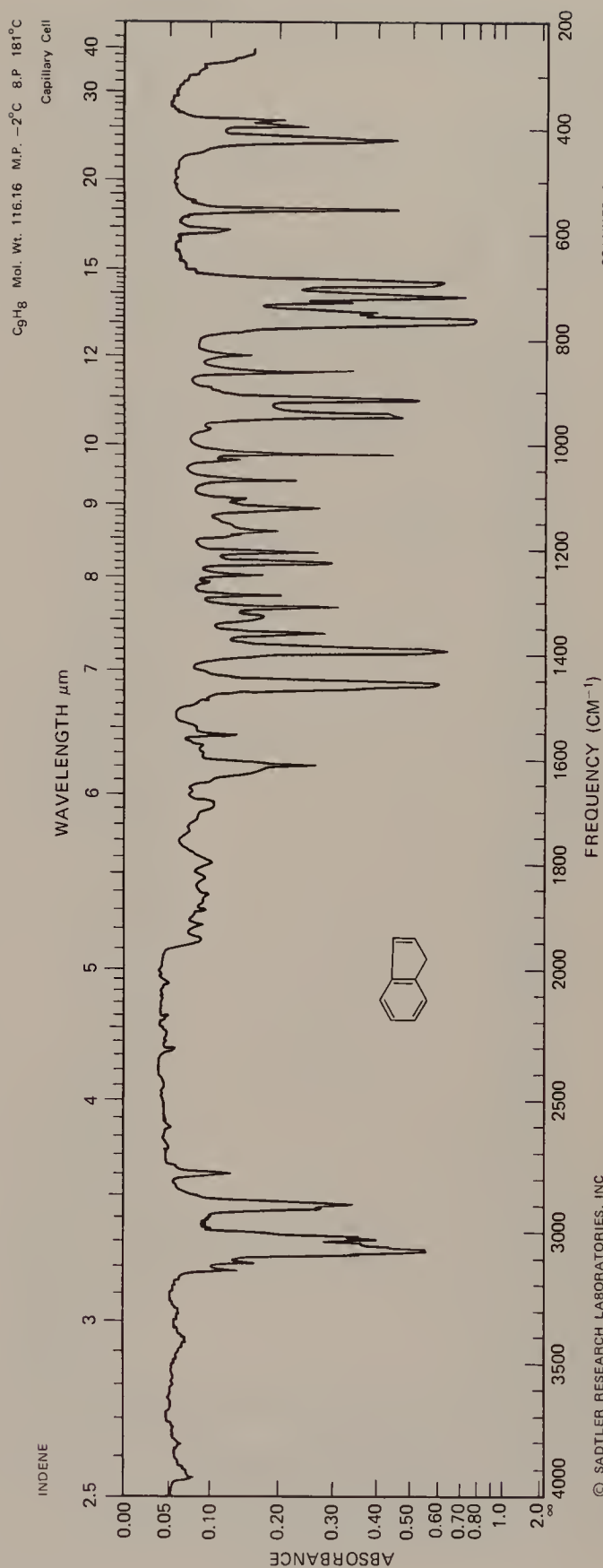




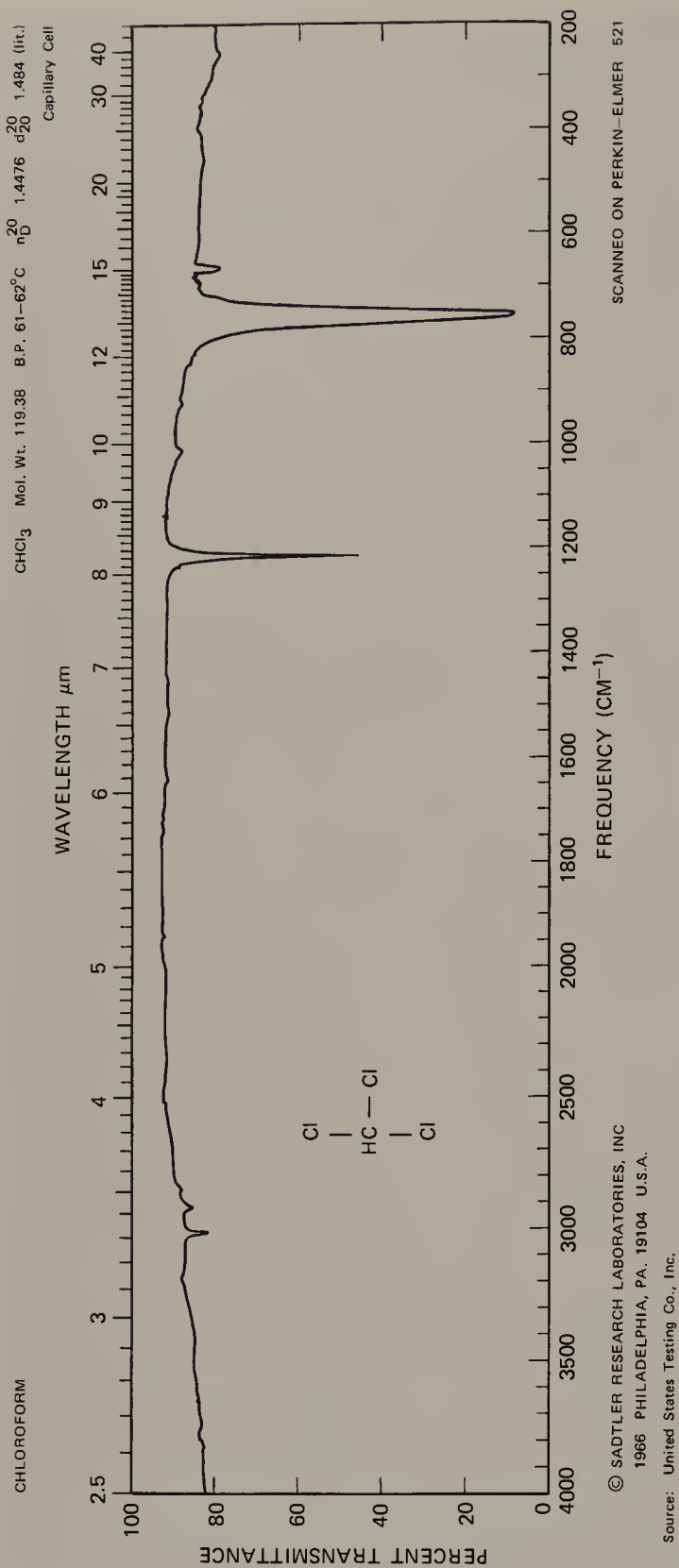
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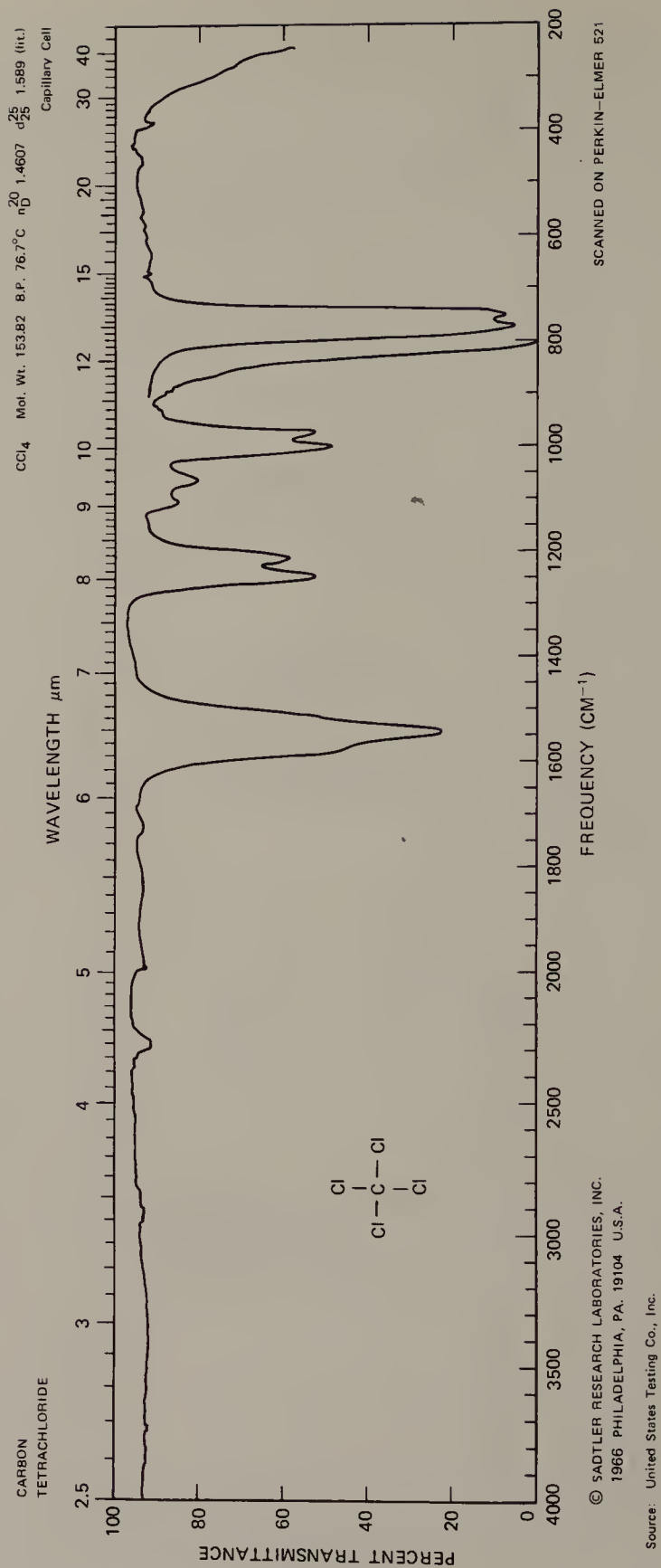
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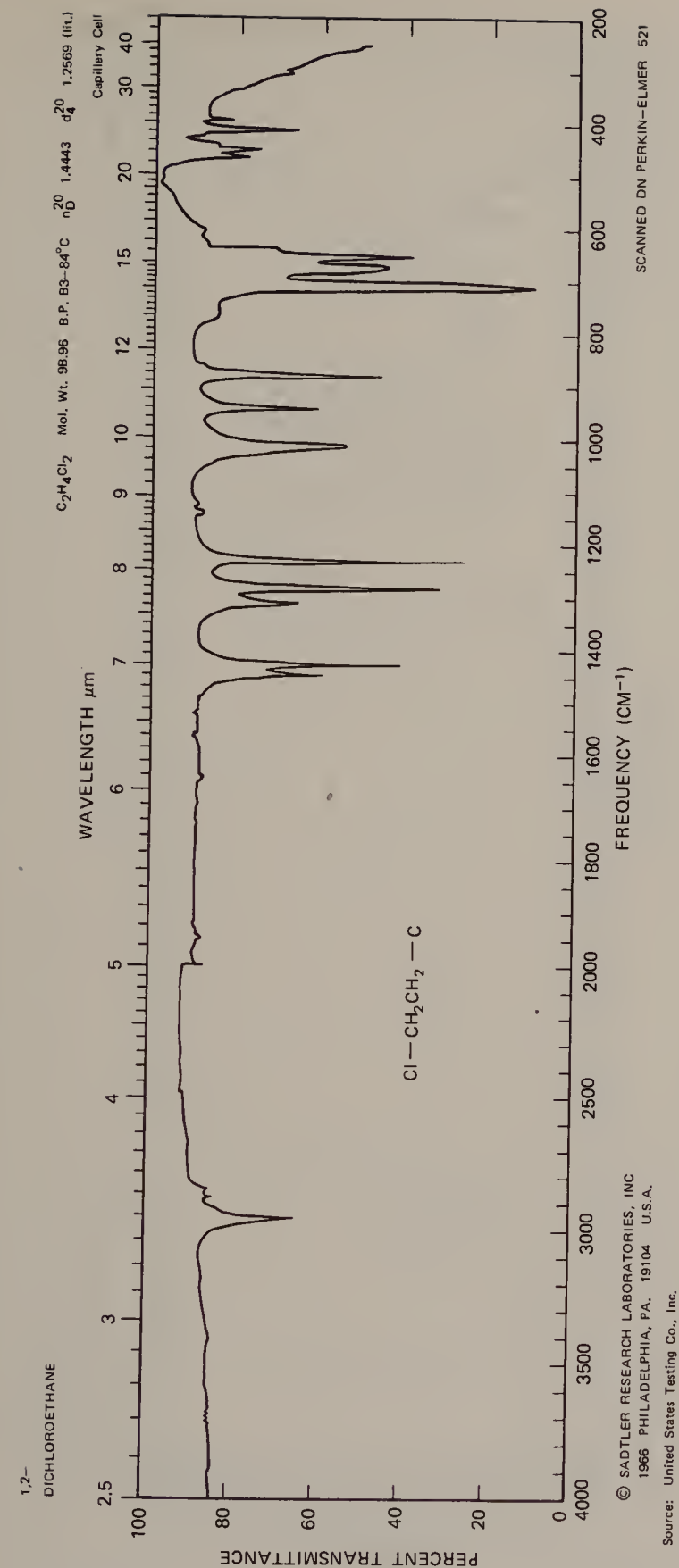


No. 9

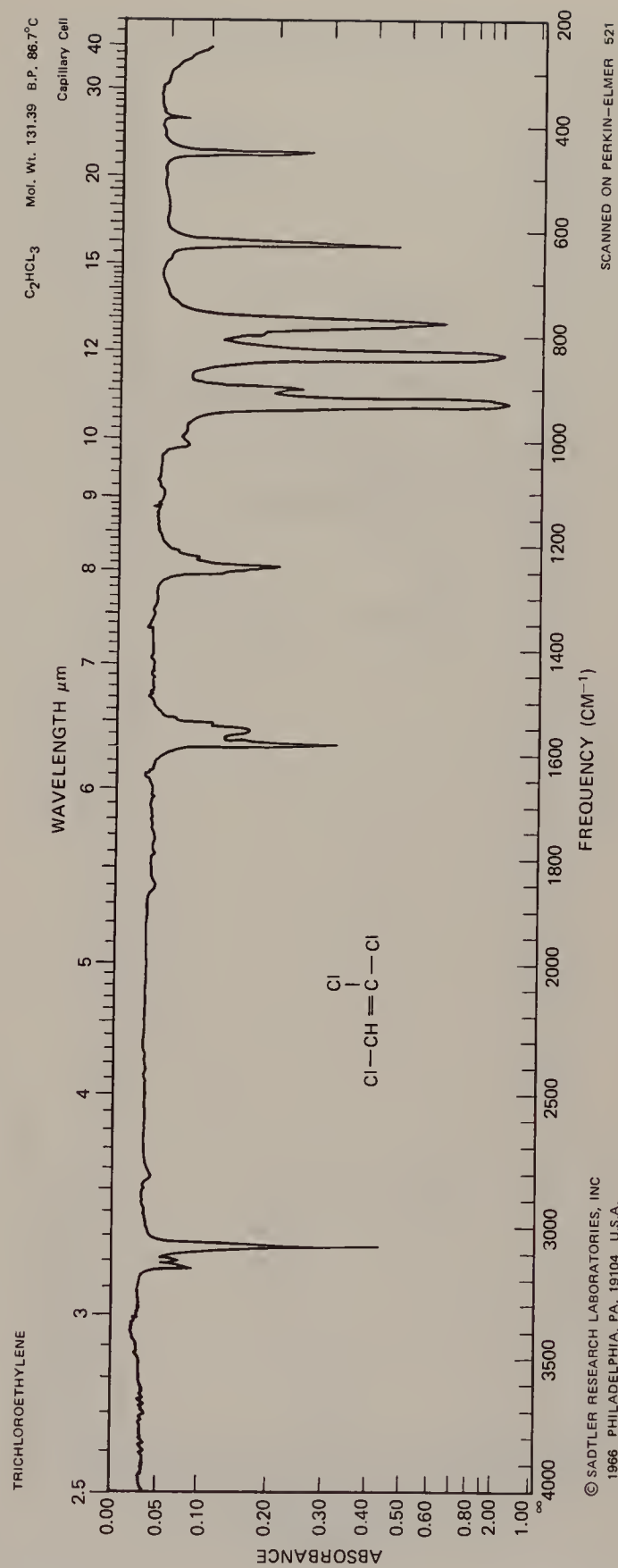


No. 10





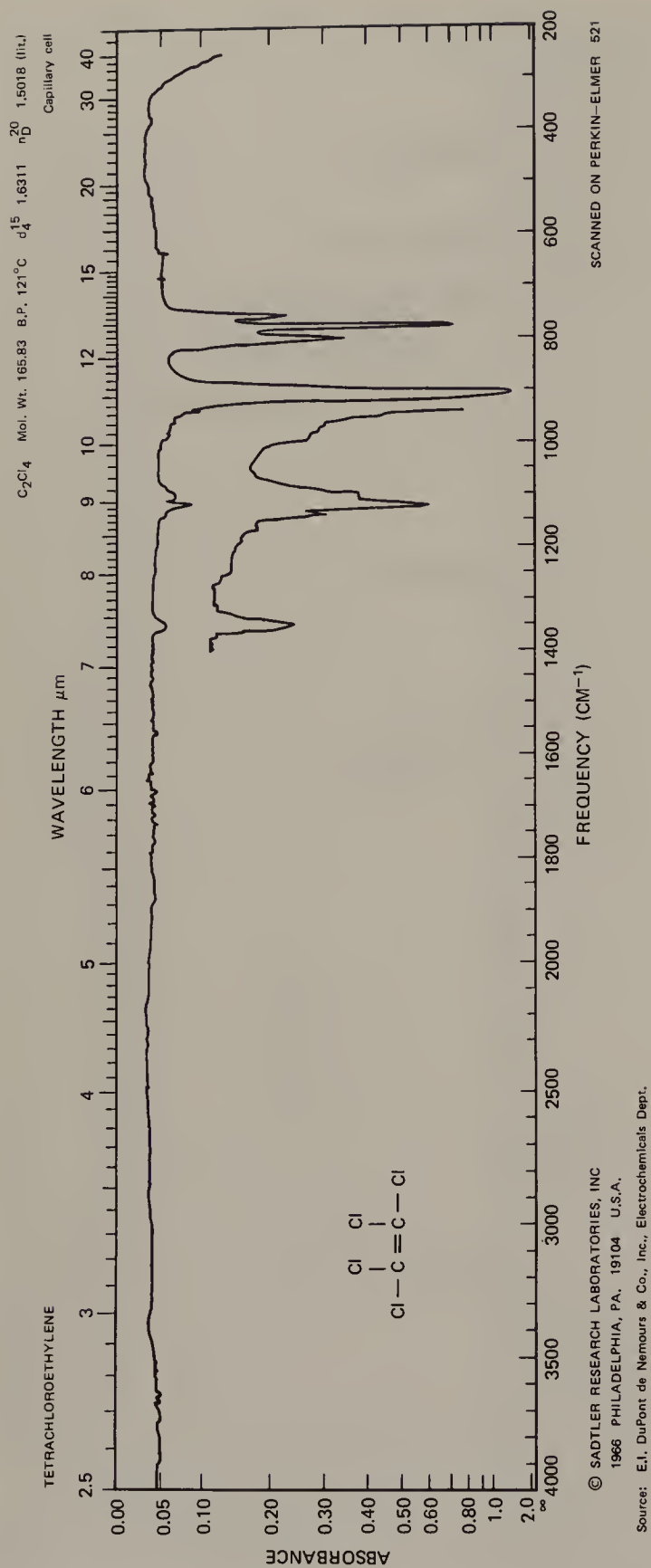
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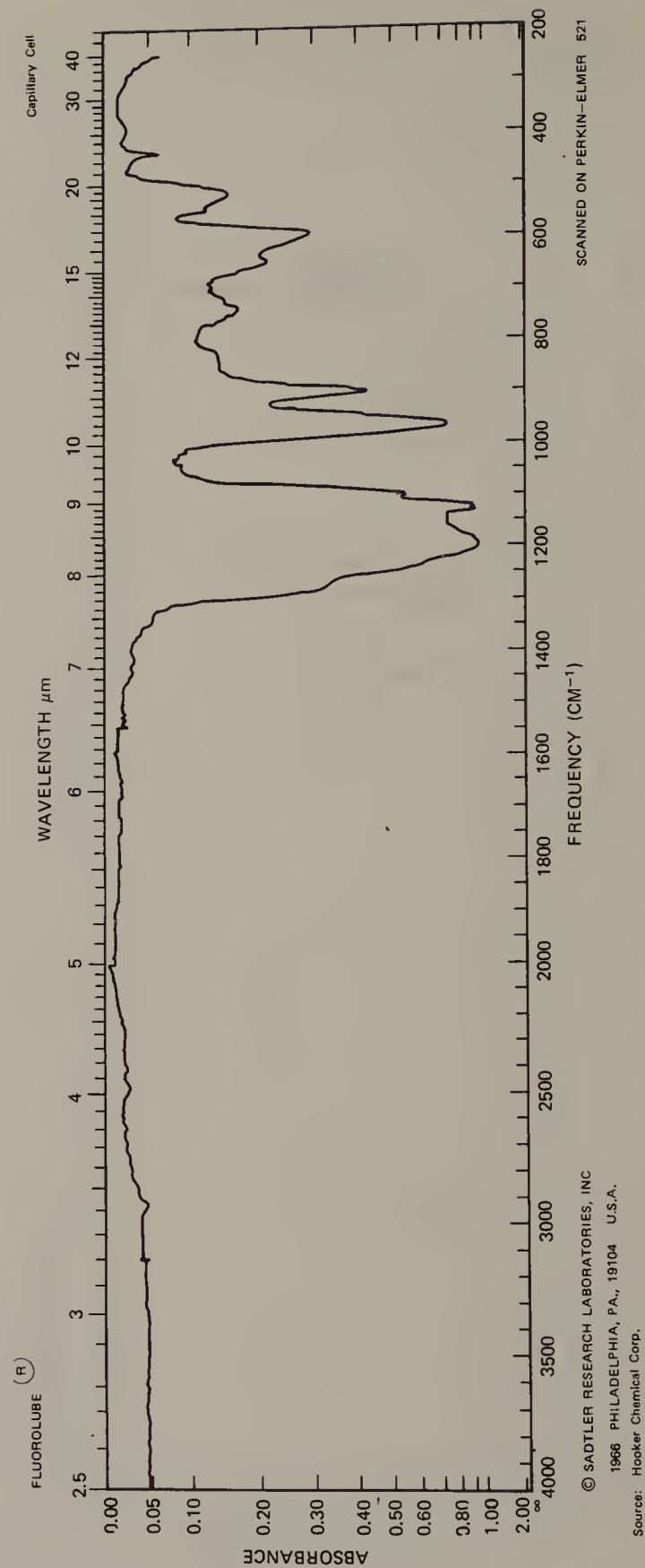
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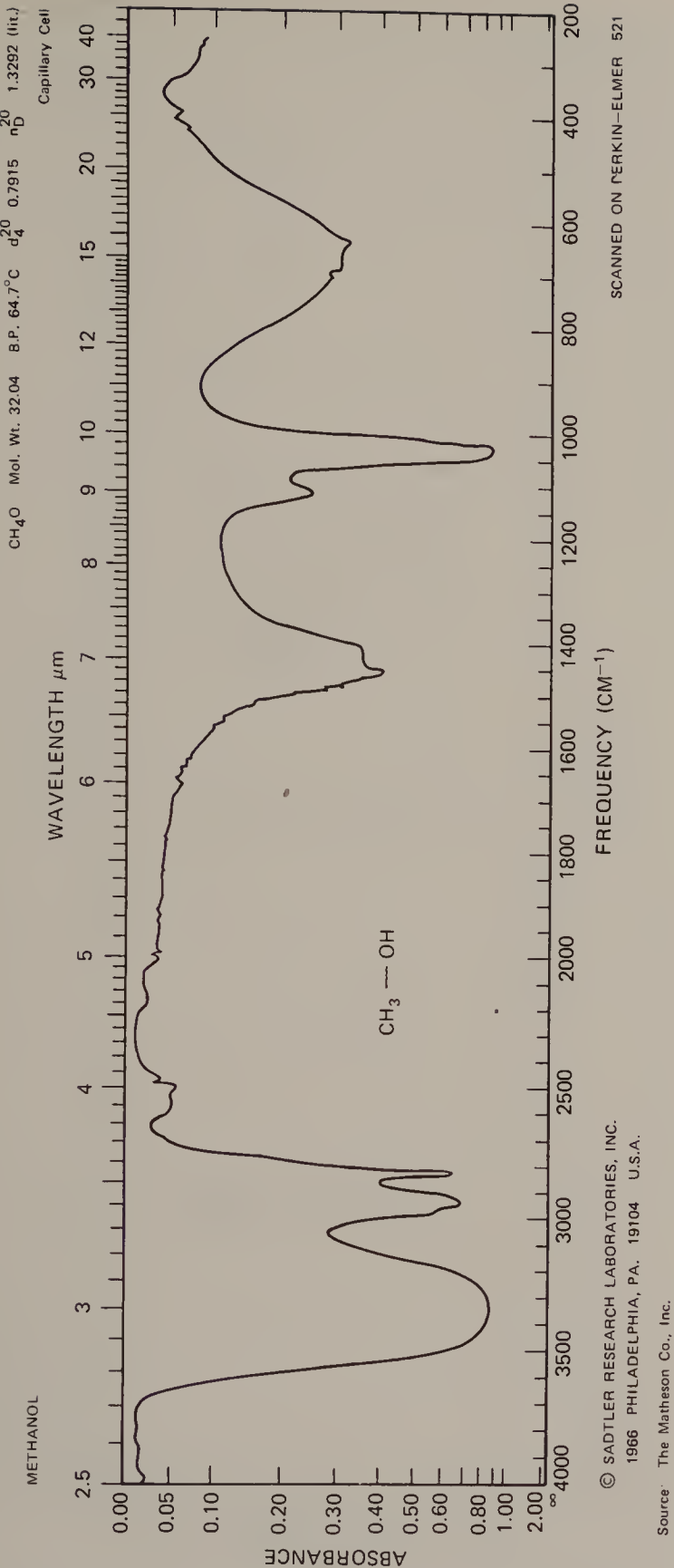


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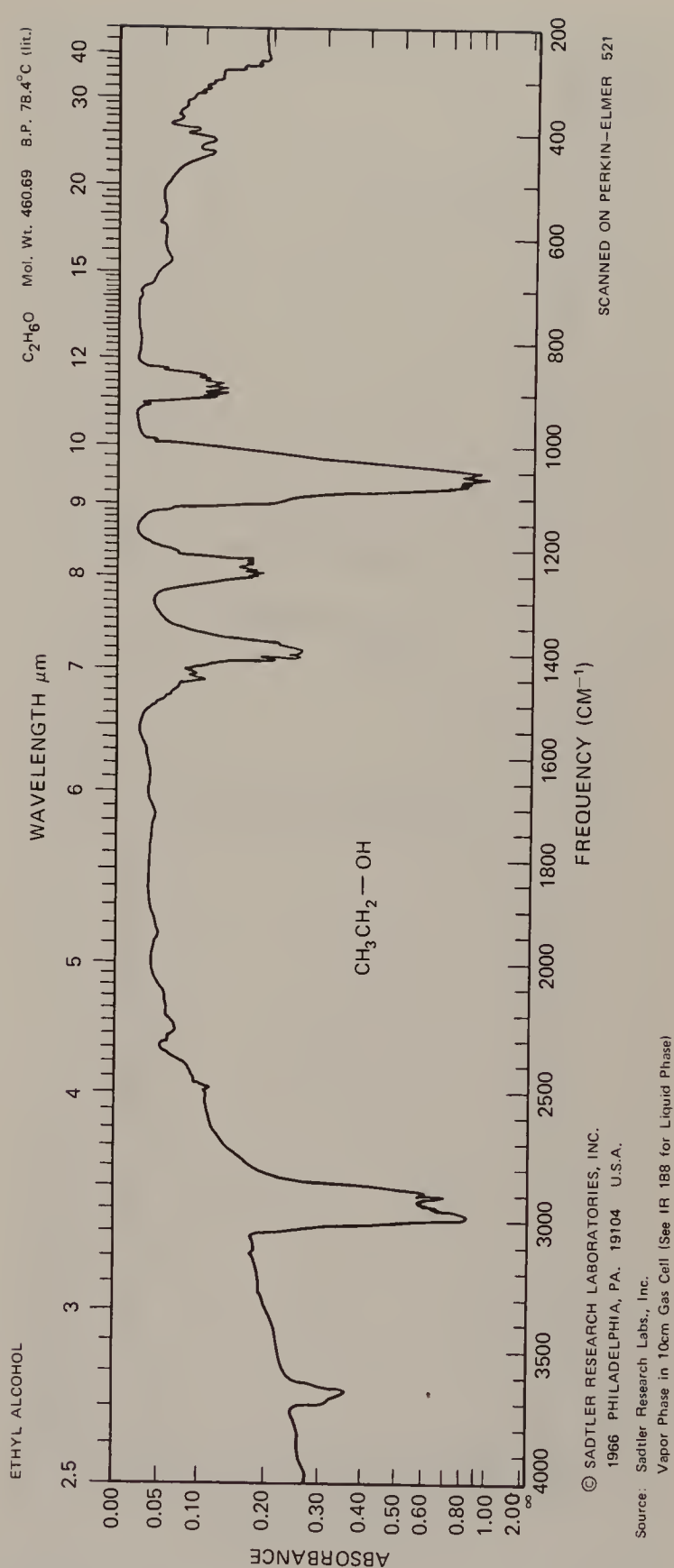


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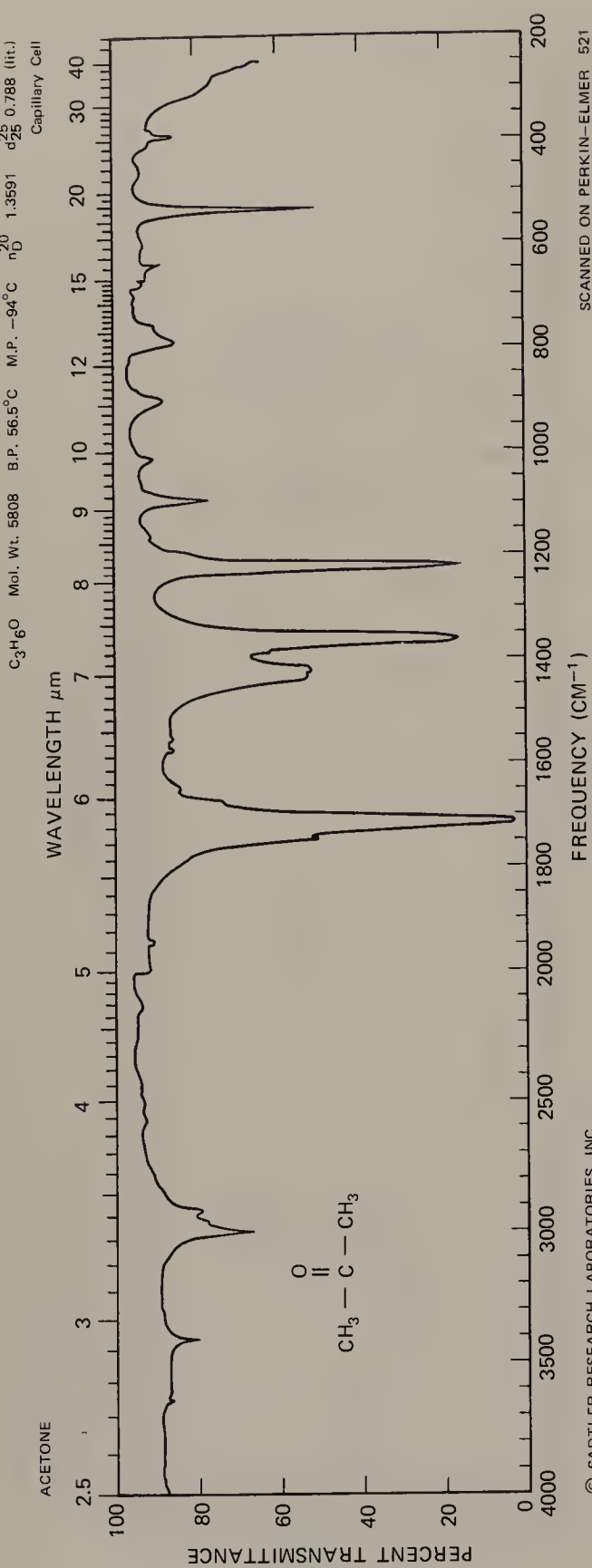




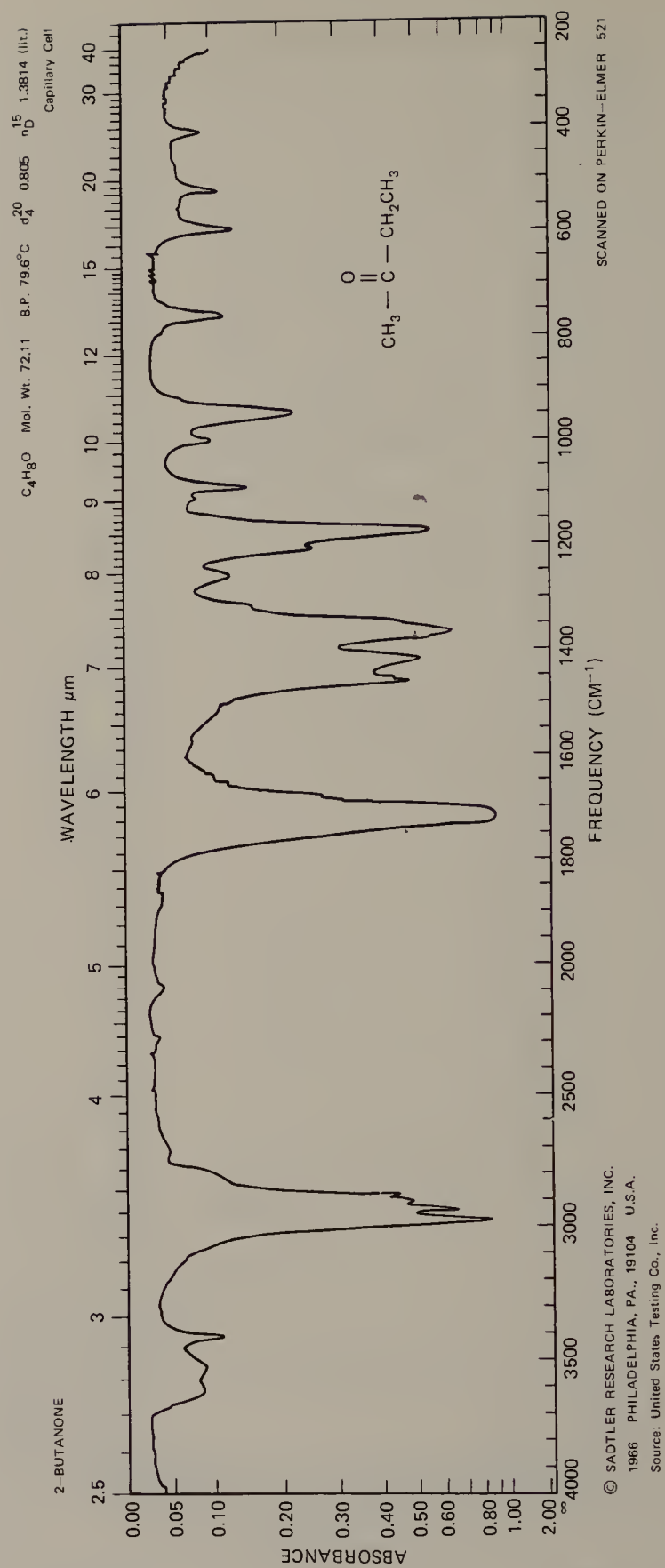
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No. 16



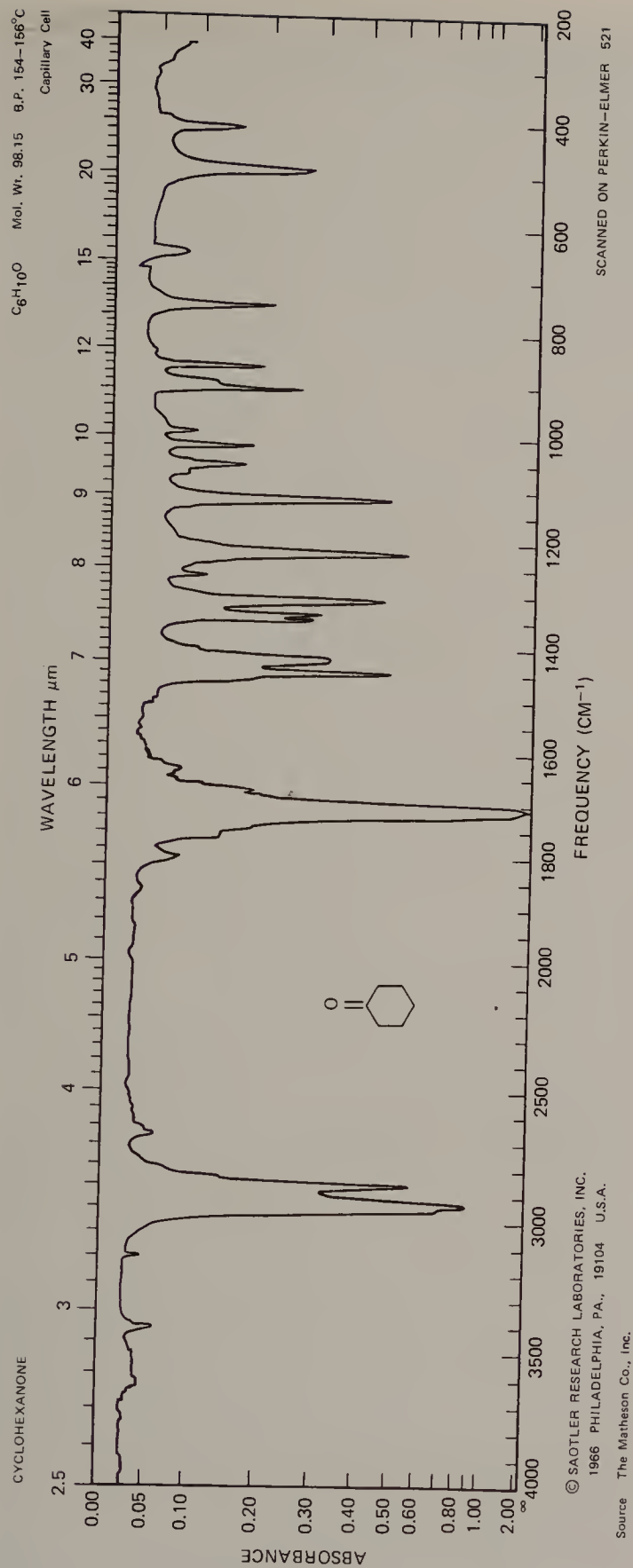
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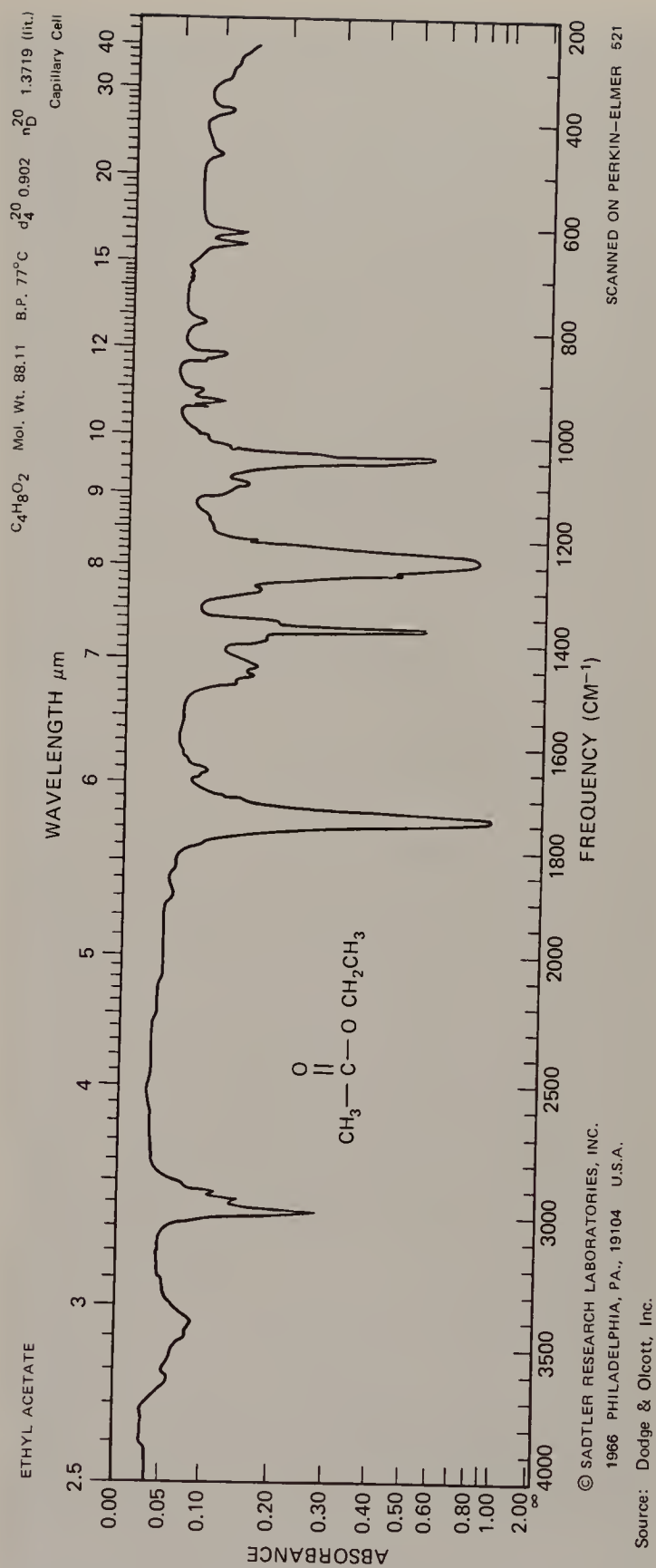
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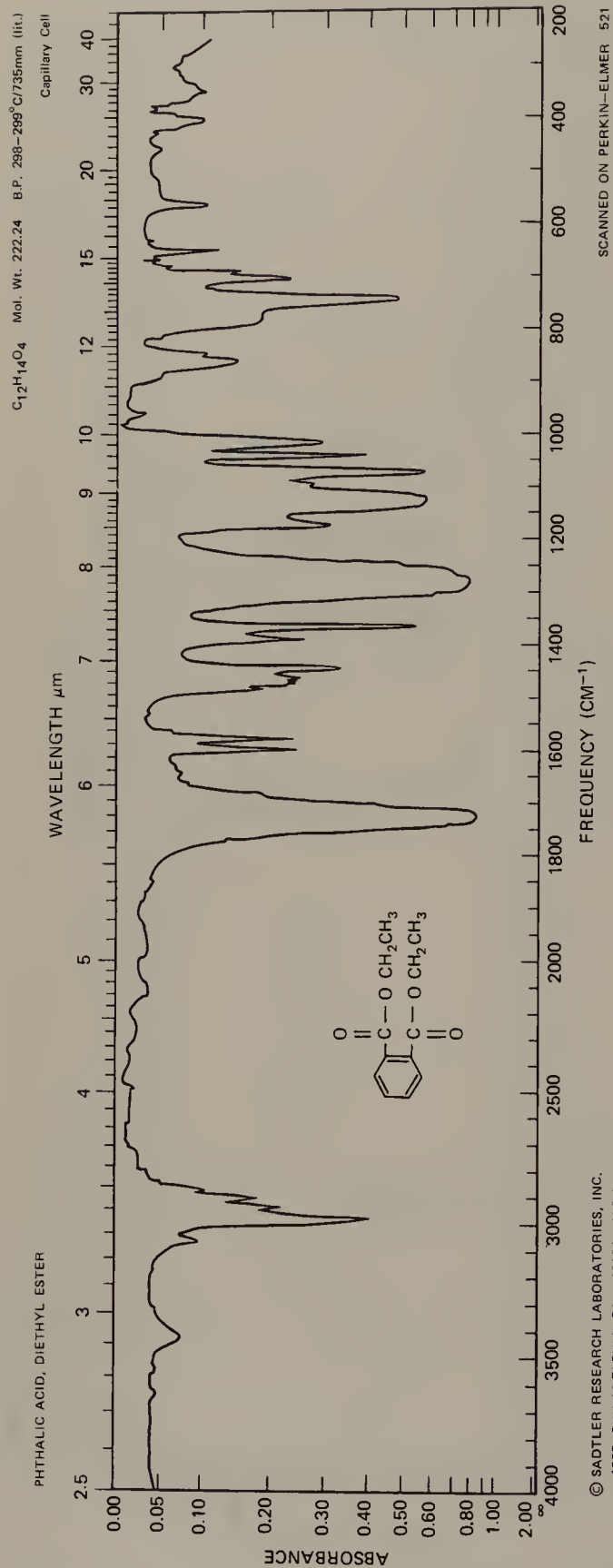
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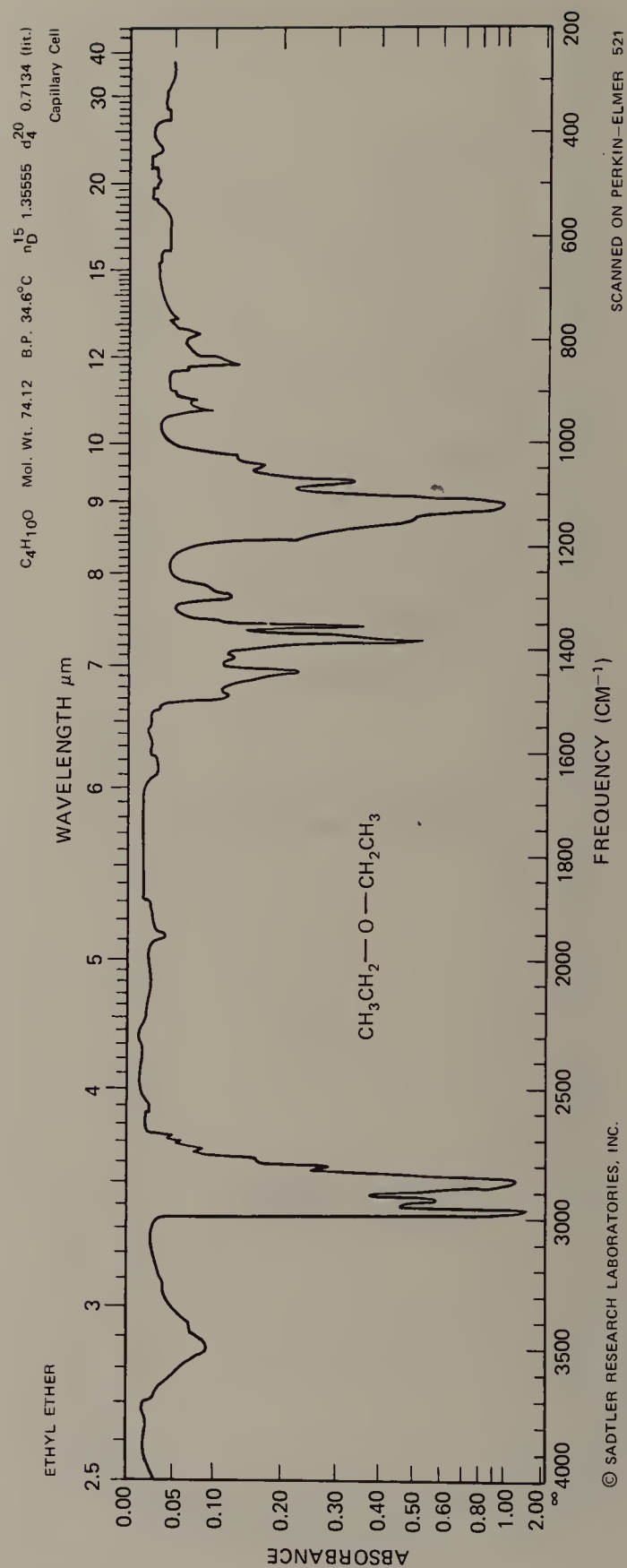
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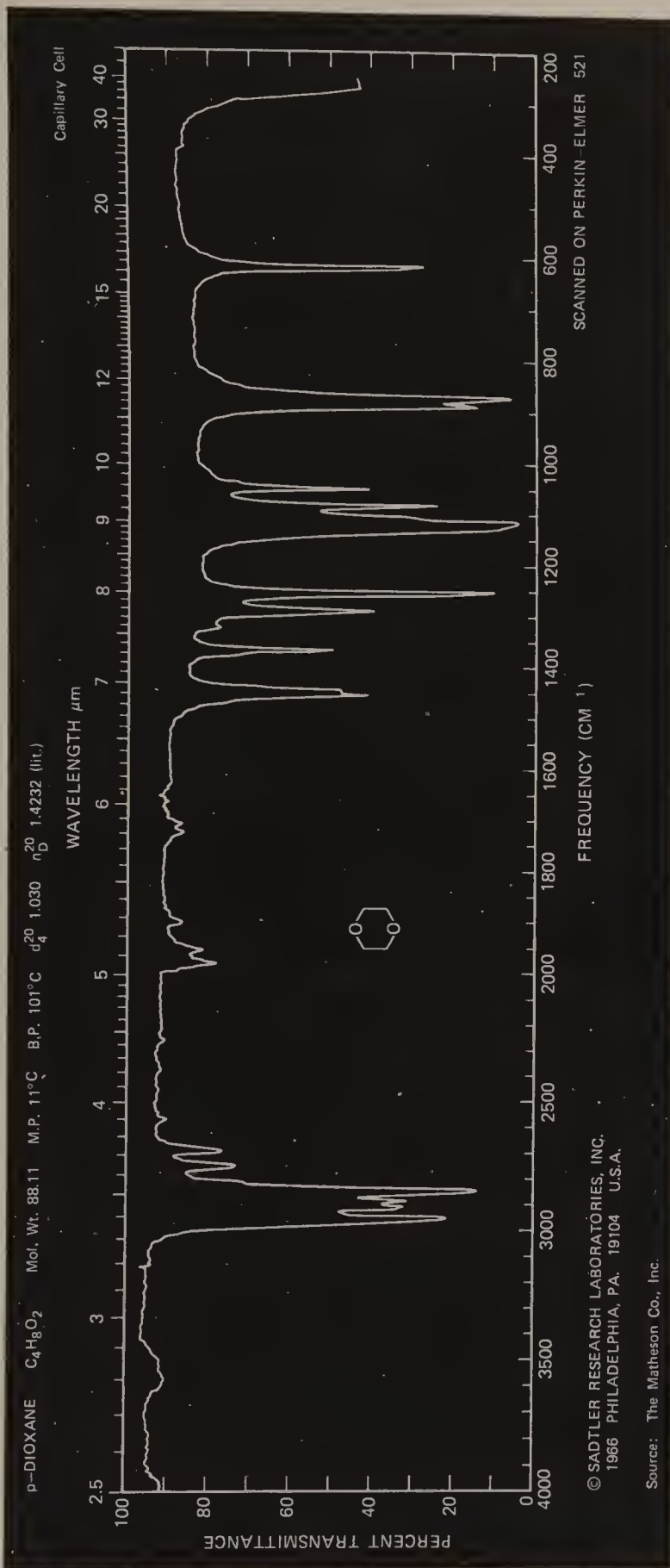


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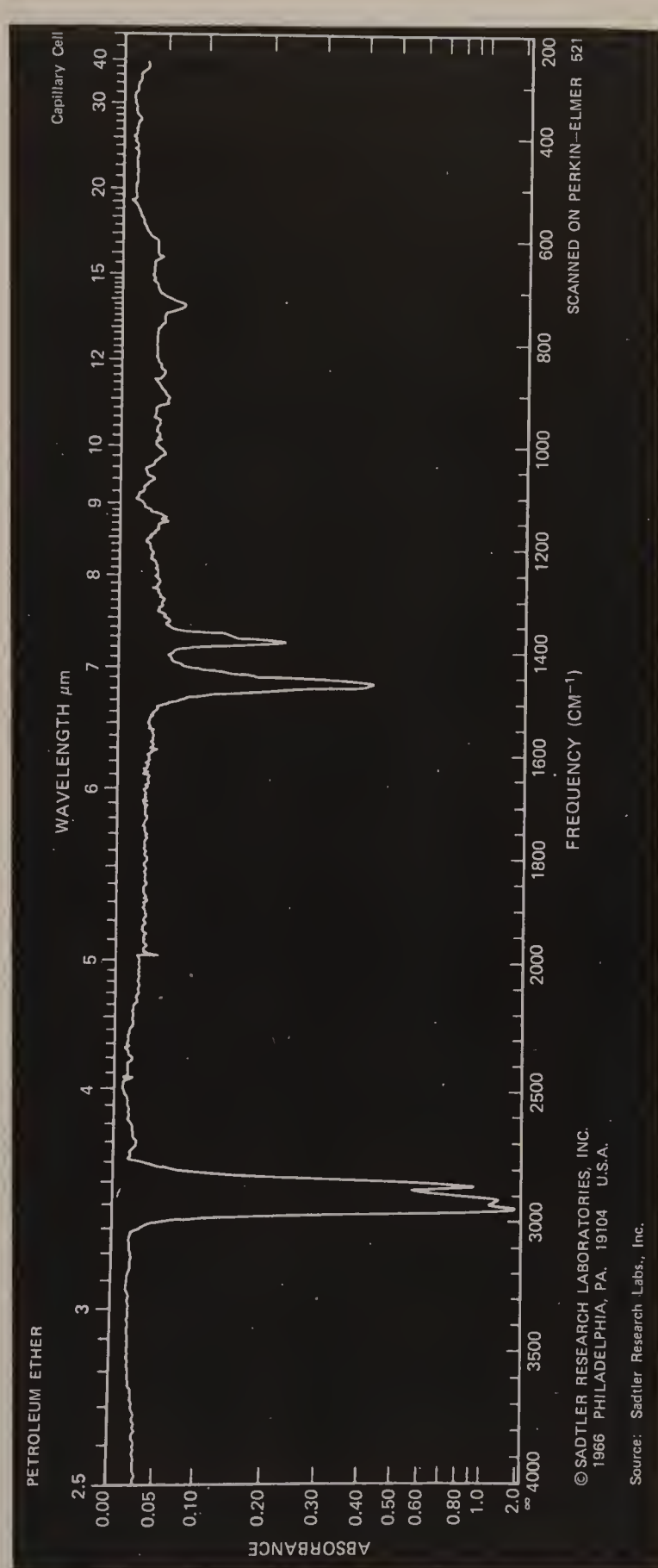


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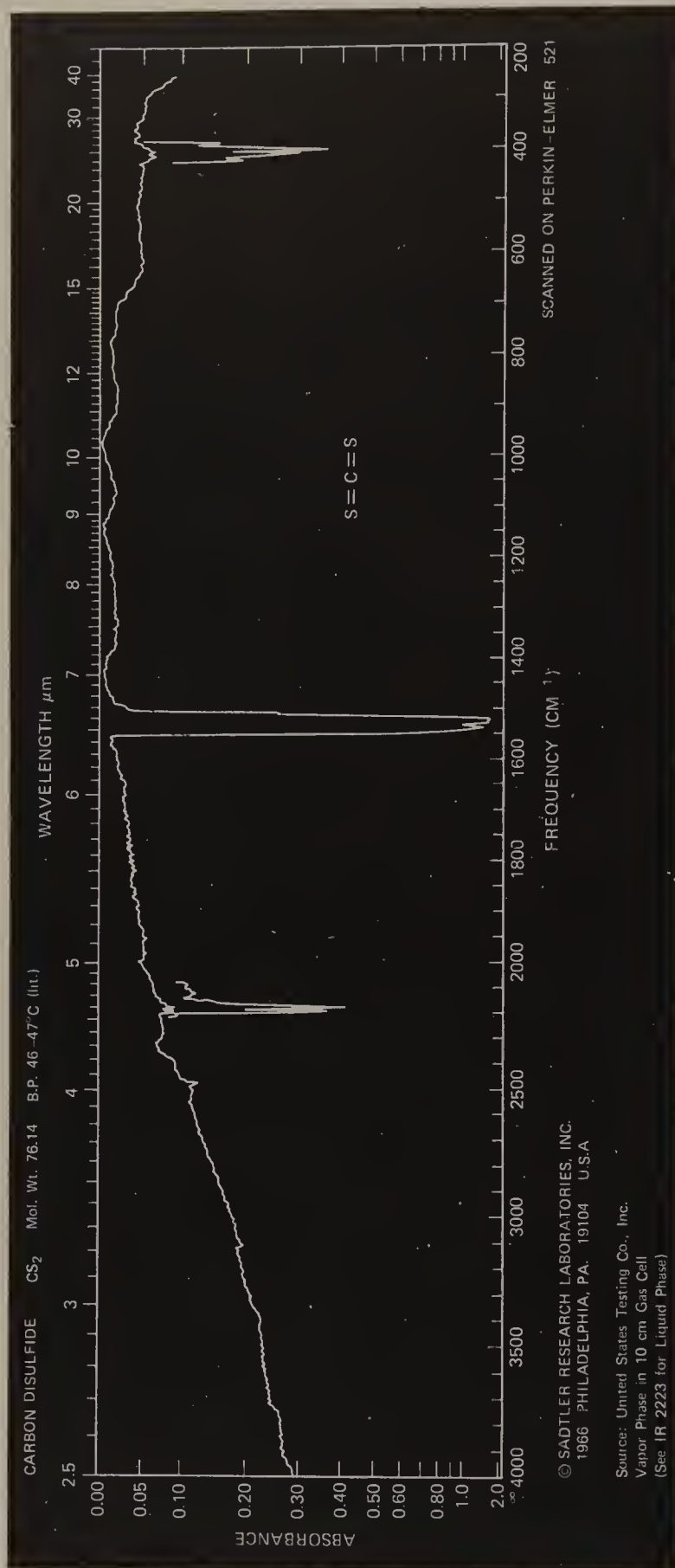
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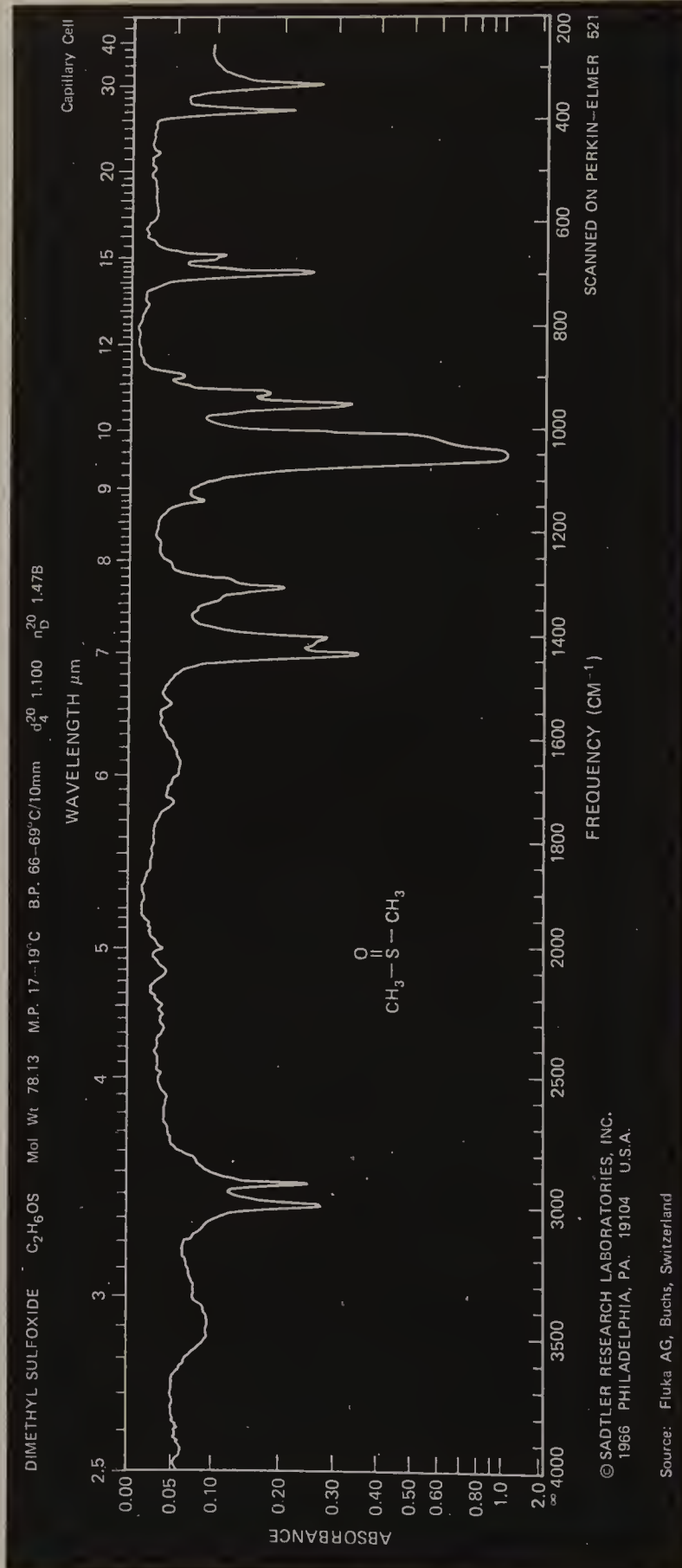
No. 24



No. 25



No. 26



Capillary Cell

SCANNED ON PERKIN-ELMER 521

WAVELENGTH  $\mu\text{m}$

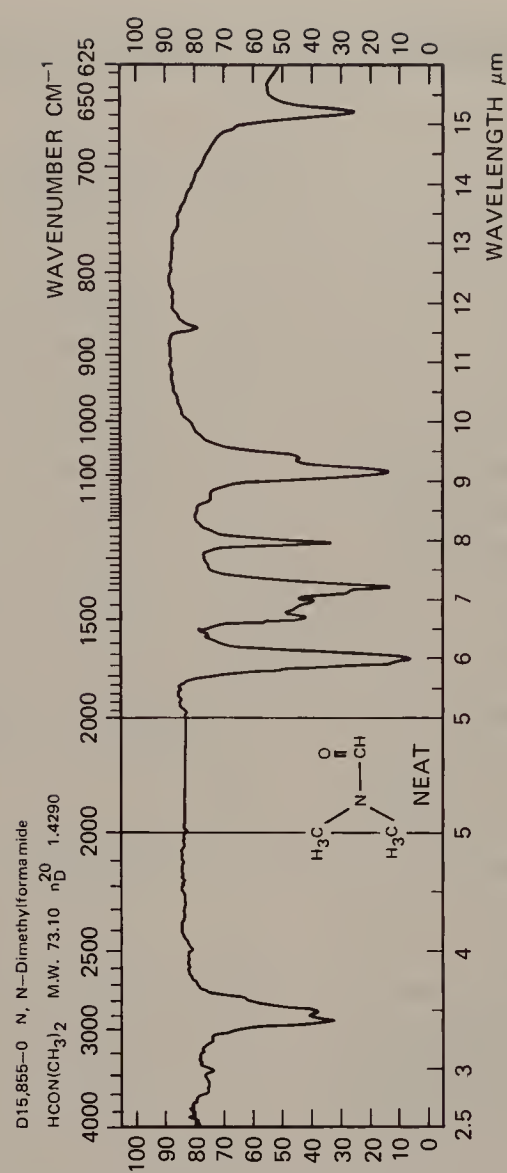
FREQUENCY  $\text{CM}^{-1}$

SILICONE LUBRICANT

ABSORBANCE

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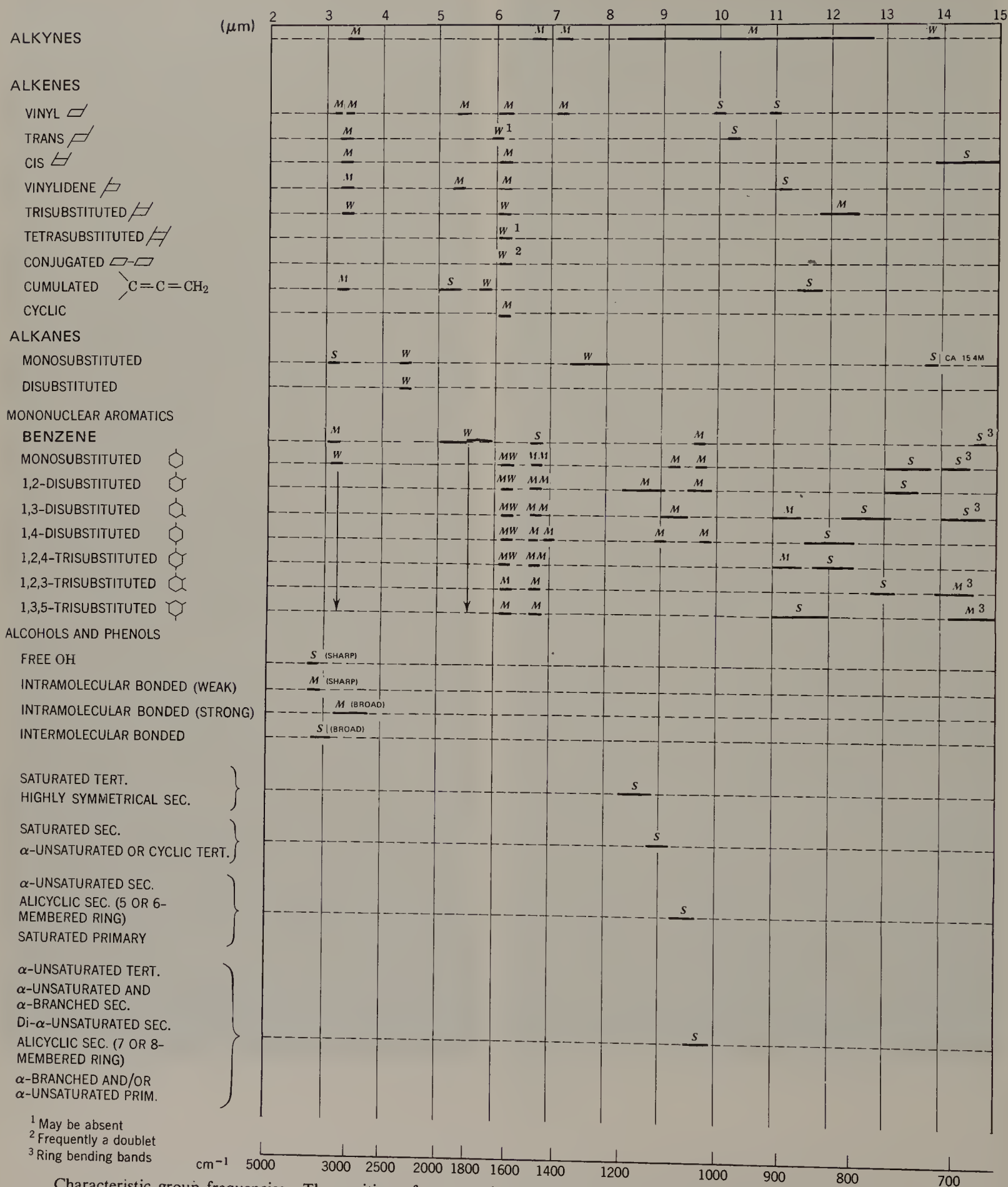
Source: Dow Corning Corp.



## No. 28

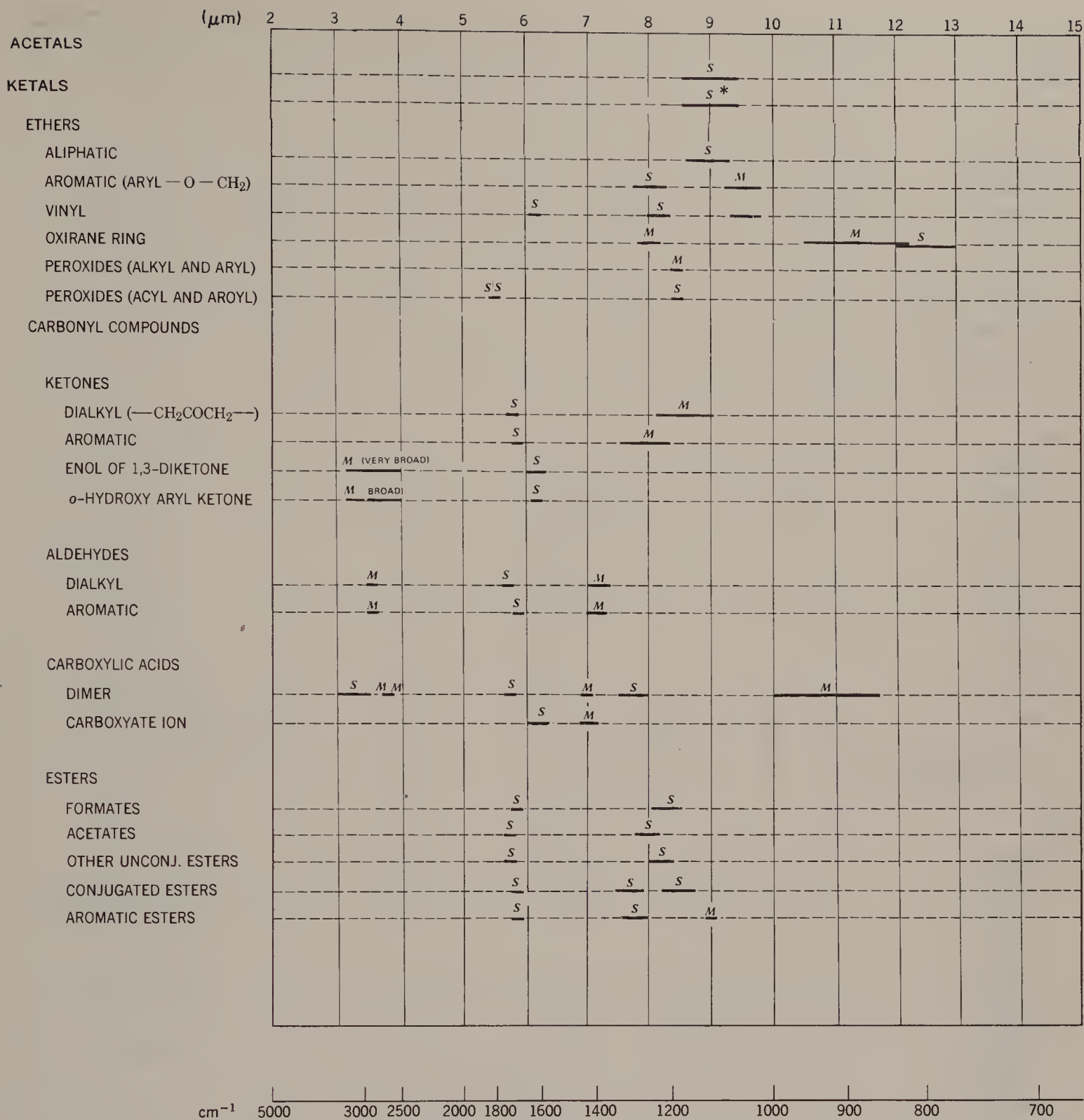
# appendix c

## CHARACTERISTIC GROUP ABSORPTIONS

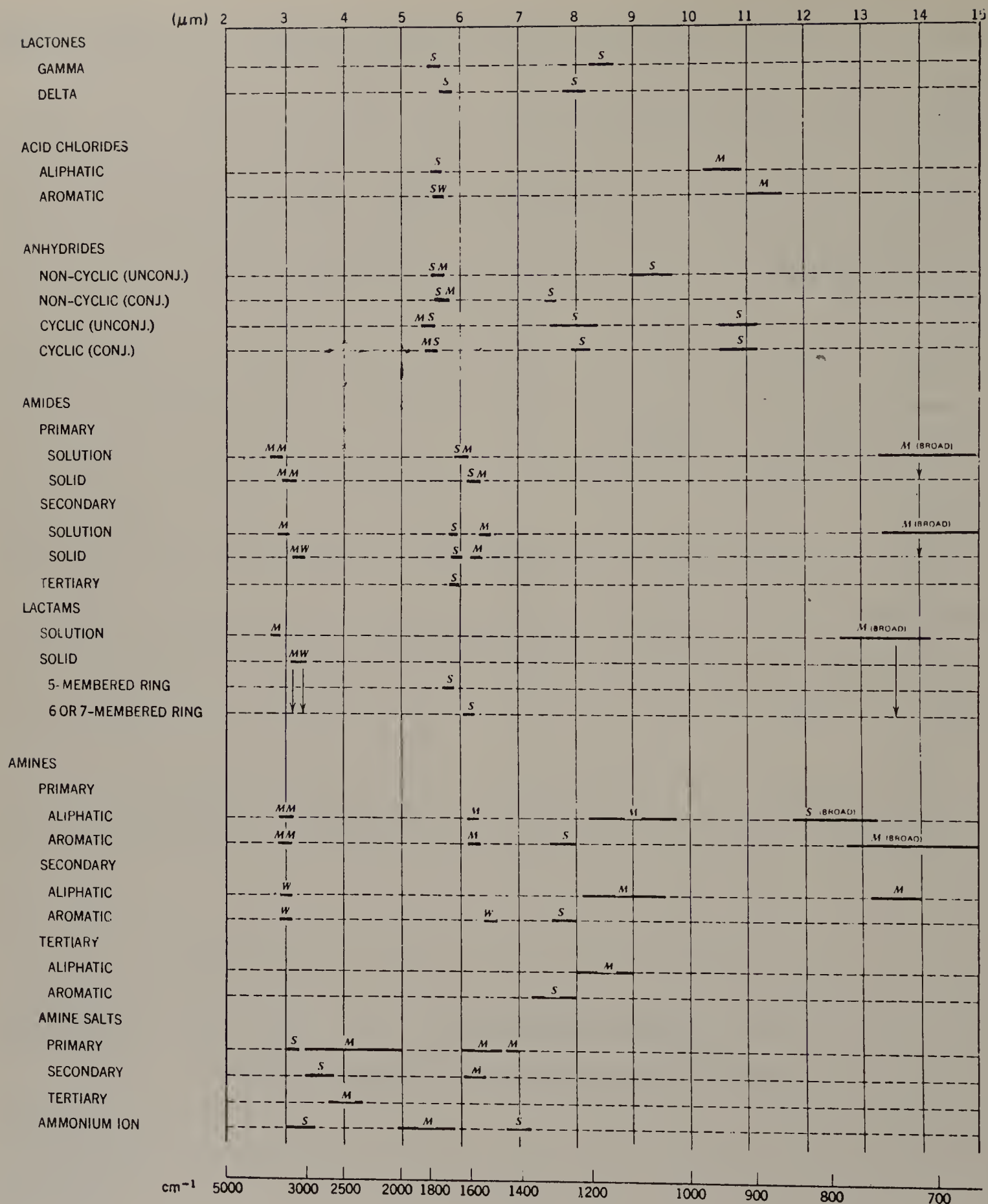


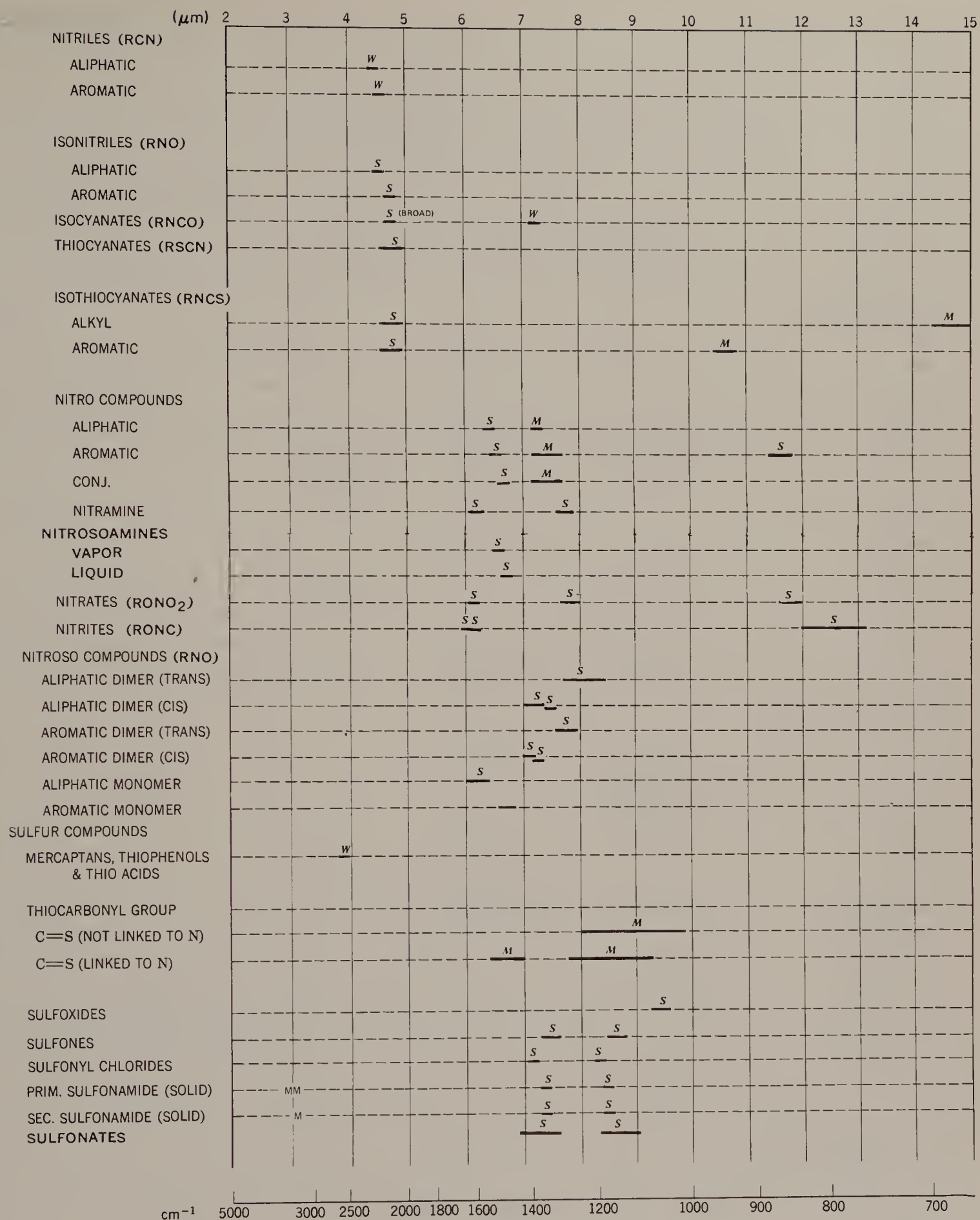
Characteristic group frequencies. The position of narrow absorption ranges is covered by a single letter indicating an average intensity. Broader absorption regions are indicated by a heavy bar. For example, a monosubstituted mononuclear aromatic may have four bands between 6 and 7  $\mu\text{m}$ , three of medium intensity, and one weak.



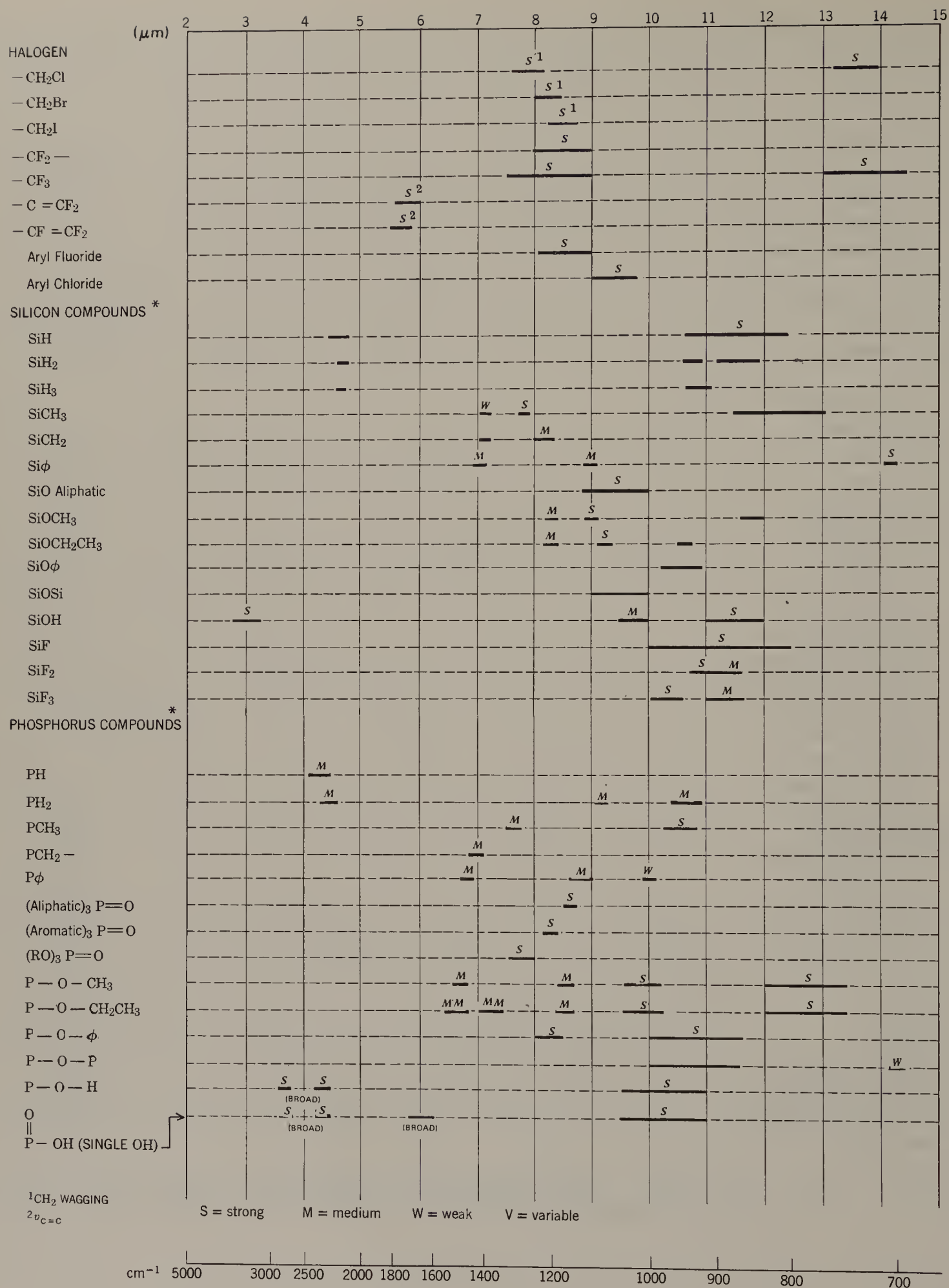


\*Three bands, sometimes a fourth band for ketals and a fifth band for acetals.









\*Tables relating to these absorptions are found in Appendix E.

# appendix d

## TABLES AND CHARTS OF SPECIFIC GROUP FREQUENCIES<sup>a</sup>

Table I. CH<sub>3</sub> Group Absorption

| Structure  | $\nu_s\text{CH}_3$                    | $\delta_{as}\text{CH}_3$ | $\delta_s\text{CH}_3$    |
|--|---------------------------------------|--------------------------|--------------------------|
|  | cm <sup>-1</sup> (μm)                 | cm <sup>-1</sup> (μm)    | cm <sup>-1</sup> (μm)    |
| $\text{CH}_3-\text{C}$<br> <br>                    | 2872<br>(3.48)                        | 1450<br>(6.90)           | 1375<br>(7.28)           |
| $\text{CH}_3-\text{C}(=\text{O})-$ (ketone)        | 3000-2900 <sup>aw</sup>               | 1450-1400<br>(6.90-7.15) | 1375-1350<br>(7.28-7.41) |
| $\text{CH}_3-\text{O}-\text{R}$                    | 2832-2815 <sup>b</sup><br>(3.53-3.55) | 1470-1440<br>(6.80-6.95) | 1470-1440<br>(6.80-6.95) |
| $\text{CH}_3-\text{C}(=\text{O})-\text{O}-$        | —                                     | 1450-1400<br>(6.90-7.15) | 1400-1340<br>(7.15-7.46) |
| $\text{CH}_3-\text{N}$ (amines and imines)         | 2820-2760<br>(3.55-3.62)              | —                        | 1440-1390<br>(6.95-7.20) |
| $\text{CH}_3-\text{NC}(=\text{O})-$ (amides)       | —                                     | 1500-1450<br>(6.67-6.90) | 1420-1405<br>(7.04-7.11) |
| $\text{CH}_3-\text{O}-\text{C}(=\text{O})\text{R}$ | —                                     | ca. 1440<br>(ca. 6.95)   | ca. 1360<br>(ca. 7.35)   |
| $\text{CH}_3-\text{X}$ (X = halogen)               | —                                     | —                        | 1500-1250<br>(6.67-8.00) |
| $\text{CH}_3-\text{S}-$                            | —                                     | 1440-1415<br>(6.95-7.07) | 1330-1290<br>(7.52-7.75) |
| $\text{CH}_3-\text{Si}$                            | —                                     | 1429-1389<br>(7.00-7.20) | 1280-1255<br>(7.81-7.97) |
| $\text{CH}_3-\text{P}$                             | —                                     | —                        | 1330-1290<br>(7.52-7.81) |

<sup>a</sup>w = weak; m = medium; s = strong.

<sup>b</sup>Overtone of CH<sub>3</sub> bending band.

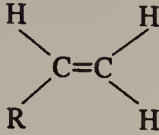
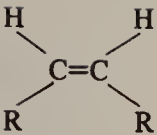
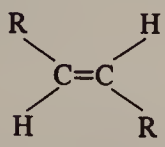
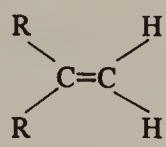
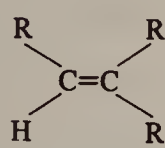
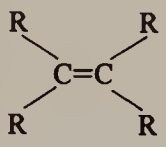
Table II. CH<sub>2</sub> Group Absorption

| Structure  | $\nu_s\text{CH}_2$                 | $\delta_s\text{CH}_2$<br>(scissoring) | $\omega\text{CH}_2$<br>(wagging)   |
|--|------------------------------------|---------------------------------------|------------------------------------|
|  | $\text{cm}^{-1}$ ( $\mu\text{m}$ ) | $\text{cm}^{-1}$ ( $\mu\text{m}$ )    | $\text{cm}^{-1}$ ( $\mu\text{m}$ ) |
| $-\text{CH}_2-\text{R}$  | —                                  | —                                     | —                                  |
| $-\text{CH}_2-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-$ (acyclic)        | —                                  | 1435-1405<br>(6.97-7.11)              | —                                  |
| $-\text{CH}_2-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-$ (small ring)     | —                                  | 1475-1425 <sup>a</sup><br>(6.78-7.02) | —                                  |
| $-\text{CH}_2-\text{O}-$ (acyclic)   | —                                  | 1470-1435<br>(6.80-6.97)              | —                                  |
| $-\text{CH}_2-\text{O}-$ (small ring)  | —                                  | 1500-1470 <sup>a</sup><br>(6.67-6.80) | —                                  |
| $-\text{CH}_2-\text{N}-$ (sec. and tert. amines)                                   | 2820-2760<br>(3.55-3.62)           | 1475-1445<br>(6.78-6.92)              | —                                  |
| $-\text{CH}_2-\overset{\overset{\text{O}}{\parallel}}{\text{N}}\text{C}-$ (amides) | —                                  | 1450-1405<br>(6.89-7.11)              | —                                  |
| $-\text{CH}_2-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-$         | —                                  | 1475-1460<br>(6.78-6.85)              | —                                  |
| $-\text{CH}_2-\text{S}-$   | —                                  | 1440-1415<br>(6.94-7.06)              | —                                  |
| $-\text{CH}_2-\text{halogen}$  | —                                  | 1460-1430<br>(6.85-7.00)              | 1275-1170<br>(7.85-8.55)           |
| $-\text{CH}_2\text{NO}_2$  | —                                  | 1425-1415<br>(7.02-7.06)              | —                                  |
| $-\text{CH}_2-\text{CN}$   | —                                  | 1425<br>(7.02)                        | —                                  |
| $-\text{CH}_2-\text{N}=\text{C}=\text{S}$  | —                                  | —                                     | 1351-1316<br>(7.40-7.60)           |
| $-\overset{\overset{ }{\text{Si}}}{\text{—}}-\text{CH}_2-$                         | —                                  | near 1410<br>(7.09)                   | 1250-1200<br>(8.00-8.33)           |
| $-\text{CH}_2-\text{P}<$   | —                                  | 1445-1405<br>(6.92-7.22)              | —                                  |

<sup>a</sup>Multiple bands.



Table III. Olefinic Absorption

|  |   |
|--|---|
|  <p>vinyl</p> <p>1648-1638 <math>\text{cm}^{-1}</math> (6.07-6.10 <math>\mu\text{m}</math>)<br/>           995-985 <math>\text{cm}^{-1}</math> (10.05-10.15 <math>\mu\text{m}</math>) (s)<sup>a</sup><br/>           915-905 <math>\text{cm}^{-1}</math> (10.93-11.05 <math>\mu\text{m}</math>) (s)</p> |  <p><i>cis</i></p> <p>1662-1626 <math>\text{cm}^{-1}</math> (6.02-6.15 <math>\mu\text{m}</math>) (v)<br/>           730-665 <math>\text{cm}^{-1}</math> (13.70-15.04 <math>\mu\text{m}</math>) (s)</p> |
|  <p><i>trans</i></p> <p>1678-1668 <math>\text{cm}^{-1}</math> (5.96-6.00 <math>\mu\text{m}</math>) (v)<br/>           980-960 <math>\text{cm}^{-1}</math> (10.20-10.42 <math>\mu\text{m}</math>) (s)<sup>b</sup></p>  |  <p>vinylidene</p> <p>1658-1648 <math>\text{cm}^{-1}</math> (6.03-6.07 <math>\mu\text{m}</math>) (m)<br/>           895-885 <math>\text{cm}^{-1}</math> (11.17-11.30 <math>\mu\text{m}</math>) (s)</p> |
|  <p>trisubstituted</p> <p>1675-1665 <math>\text{cm}^{-1}</math> (5.97-6.01 <math>\mu\text{m}</math>) (w)<br/>           840-790 <math>\text{cm}^{-1}</math> (11.91-12.66 <math>\mu\text{m}</math>) (m)</p>   |  <p>tetrasubstituted</p> <p>1675-1665 <math>\text{cm}^{-1}</math> (5.97-6.01 <math>\mu\text{m}</math>) very weak or absent.</p>  |

<sup>a</sup>This band also shows a strong overtone band.<sup>b</sup>This band occurs near 1000  $\text{cm}^{-1}$  (10.00  $\mu\text{m}$ ) in conjugated *trans-trans* systems such as the esters of sorbic acid.

s = strong; m = medium; w = weak; v = variable.

Table IV. C=C Stretching Frequencies in Acyclic Systems

| R <sub>1</sub>   | CH <sub>2</sub> =CHR <sub>1</sub> | CH <sub>2</sub> =C(R <sub>1</sub> ) <sub>2</sub> | R <sub>1</sub> -CH=CH-R <sub>1</sub>               | CHCH <sub>3</sub> =C(R <sub>1</sub> ) <sub>2</sub> |
|------------------|-----------------------------------|--|--|--|
| H                | 1623 <sup>a</sup> (6.16)          | 1623 <sup>a</sup> (6.16)                         | 1623 <sup>a</sup> (6.16)                           | 1648 (6.07)  |
| D                | —                                 | —  | —  | —  |
| F                | 1650 (6.06)                       | 1728 (5.79)                                      | —  | —  |
| Cl               | 1610 (6.21)                       | 1620 (6.17)                                      | <i>cis</i> 1590 (5.79)<br><i>trans</i> 1653 (6.05) | —  |
| Br               | 1605 (6.23)                       | 1593 (6.28)                                      | —  | —  |
| I                | 1593 (6.28)                       | —  | —  | —  |
| CH <sub>3</sub>  | 1648 (6.07)                       | 1661 (6.07)                                      | <i>cis</i> 1661 (6.02)<br><i>trans</i> 1676 (5.97) | 1681 (5.95)  |
| CF <sub>3</sub>  | —                                 | —  | 1700 ( <i>cis</i> ) (5.88)                         | —  |
| OCH <sub>3</sub> | 1618 (6.18)                       | 1639 (6.10)                                      | —  | 1675 (5.97)  |
| SCH <sub>3</sub> | 1586 (6.30)                       | —  | —  | 1605 (6.23)  |

<sup>a</sup>Raman value.

Table V. C=C Stretching Frequencies and Ring Strain,  $\text{cm}^{-1}$  ( $\mu\text{m}$ )

| Ring or Chain       | $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{C} & & \text{C} \end{array}$ | $\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{C} & & \text{C} \end{array}$ | $\begin{array}{c} \text{CH}_3 & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{C} & & \text{C} \end{array}$ | $\begin{array}{c} \text{C} \\ \diagdown \\ \text{C}=\text{CH}_2 \end{array}$ |
|---------------------|--|---|--|--|
| Chain <i>cis</i>    | 1661 (6.02)  |   | 1672 (5.98)  | 1661 (6.02)  |
| Chain <i>trans</i>  | 1676 (5.97)  | 1681 (5.95)   |  |  |
| Three-membered ring | 1641 (6.10)  |   | 1890 (5.29)  | 1780 (5.62)  |
| Four-membered ring  | 1566 (6.33)  |   | 1685 (5.94)  | 1678 (5.96)  |
| Five-membered ring  | 1611 (6.21)  | 1658  | 1686 (5.93)  | 1657 (6.03)  |
| Six-membered ring   | 1649 (6.06)  | 1678  | 1685 (5.93)  | 1651 (6.06)  |
| Seven-membered ring | 1651 (6.06)  | 1673  | —  |  |
| Eight-membered ring | 1653 (6.05)  | —   | —  |  |

Table I Si-H IR Absorptions

| Mode  | Position $\text{cm}^{-1}$ ( $\mu\text{m}$ ) intensity |
|---|---|
| Si-H stretch                                      | 2250-2100 (4.44-4.76) m-s                             |
| $\text{SiH}_2$ bend (scissoring)                  | 942-923 (10.62-10.83)                                 |
| $\text{SiH}_3$ , two bands<br>sym. and asym. bend | 959-900 (10.43-11.11)                                 |
| $\text{SiH}_2$ wag                                | 900-840 (11.11-11.90)                                 |
| $\text{R}_3\text{SiH}$ bend                       | 950-800 (10.53-12.50)                                 |

Table II Si-O Stretching Vibrations

| Group              | $\nu_{\text{Si-O}}$ Bands                               |
|--------------------|---|
| Si-O-R (aliphatic) | 1110-1000 $\text{cm}^{-1}$ (9.01-10.00 $\mu\text{m}$ )s |
| Si-O-Si            | 1110-1000 $\text{cm}^{-1}$ (9.01-10.00 $\mu\text{m}$ )s |
| Si-O-R (aromatic)  | 970-920 $\text{cm}^{-1}$ (10.31-10.87 $\mu\text{m}$ )s  |
| Si-OH              | 910-830 $\text{cm}^{-1}$ (11.00-12.05 $\mu\text{m}$ )s  |

s = strong.

Table III Absorption of Si-F Bonds

| Group   | $\nu_{\text{Si-F}}$ Bands   |
|---|---|
| $\begin{array}{c} \diagup \\ \text{SiF} \\ \diagdown \end{array}$   | 1000-800 $\text{cm}^{-1}$ (10.00-12.50 $\mu\text{m}$ )  |
| $\begin{array}{c} \diagup \\ \text{SiF}_2 \\ \diagdown \end{array}$ | 943-910 $\text{cm}^{-1}$ (10.60-11.00 $\mu\text{m}$ )s 910-870 $\text{cm}^{-1}$ (11.00-11.50 $\mu\text{m}$ )m |
| $-\text{SiF}_3$   | 980-945 $\text{cm}^{-1}$ (10.20-10.58 $\mu\text{m}$ )s 910-860 $\text{cm}^{-1}$ (11.00-11.63 $\mu\text{m}$ )m |

s = strong; m = medium.



Table IV PH, PO IR Absorptions

| Mode                          | Position $\text{cm}^{-1}$ ( $\mu\text{m}$ ) intensity |
|-------------------------------|---|
| P-H stretch                   | 2440-2275 (4.10-4.40)m                                |
| alkyl, aryl, P-H stretch      | 2326-2275 (4.30-4.40)                                 |
| PH <sub>2</sub> bend          |   |
| scissoring                    | 1090-1080 (9.19-9.26)m                                |
| wagging                       | 940-909 (10.64-11.00)                                 |
| P=O stretch                   |   |
| phosphine oxides              |   |
| aliphatic                     | ca. 1150 (8.70)                                       |
| aromatic                      | ca. 1190 (8.40)                                       |
| phosphate esters <sup>a</sup> | 1299-1250 (7.70-8.00)                                 |

<sup>a</sup>The increase in P = O stretching frequency of the ester, relative to the oxides, results from the electronegativity of the attached alkoxy groups.

Table V P-O Stretching Vibrations

| Group          | $\nu_{\text{P-O}}$ Bands  |
|----------------|---|
| P-OH           | 1040-910 $\text{cm}^{-1}$ (9.62-11.00 $\mu$ )s  |
| P-O-P          | 1000-870 $\text{cm}^{-1}$ (10.00-11.50 $\mu$ )s    ca. 700 $\text{cm}^{-1}$ (14.30 $\mu$ )w                             |
| P-O-C (aliph.) | 1050-970 $\text{cm}^{-1}$ (9.52-10.30 $\mu$ )s <sup>a</sup> 830-740 $\text{cm}^{-1}$ (12.05-13.51 $\mu$ )s <sup>b</sup> |
| P-O-C (arom.)  | 1260-1160 $\text{cm}^{-1}$ (7.94-8.62 $\mu$ )s    994-855 $\text{cm}^{-1}$ (10.06-11.70 $\mu$ )s                        |

<sup>a</sup>May be a doublet.

<sup>b</sup>May be absent.

s = strong; w = weak.

| Substitution | Number<br>Adjacent H's | $\gamma\text{CH}$                                 | $\beta$ Ring                                      |
|--------------|------------------------|---|---|
| 2-           | 4                      | 781-740 $\text{cm}^{-1}$<br>(12.80-13.50 $\mu$ m) | 752-746 $\text{cm}^{-1}$<br>(13.30-13.40 $\mu$ m) |
| 3-           | 3                      | 810-789 $\text{cm}^{-1}$<br>(12.35-12.67 $\mu$ m) | 715-712 $\text{cm}^{-1}$<br>(13.99-14.04 $\mu$ m) |
| 4-           | 2                      | 820-794 $\text{cm}^{-1}$<br>(12.19-12.60 $\mu$ m) | 775-709 $\text{cm}^{-1}$<br>(12.90-14.10 $\mu$ m) |

Table VII. Characteristic  $\gamma$ CH or  $\beta$  Ring Bands of Furans, Thiophenes, and Pyrroles

| Nucleus   | Position of Substitution | Phase           | $\gamma$ CH or $\beta$ Ring Modes     |                                       |                                       |                                       |
|-----------|--------------------------|-----------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
|           |                          |                 | $\text{cm}^{-1}$<br>( $\mu\text{m}$ ) | $\text{cm}^{-1}$<br>( $\mu\text{m}$ ) | $\text{cm}^{-1}$<br>( $\mu\text{m}$ ) | $\text{cm}^{-1}$<br>( $\mu\text{m}$ ) |
| Furan     | 2-                       | $\text{CHCl}_3$ | ca. 925<br>(10.8)                     | ca. 884<br>(11.3)                     | 835-780<br>(12.0-12.8)                |                                       |
|           | 2-                       | liq.            | 960-915<br>(10.4-10.9)                | 890-875<br>(11.2-11.4)                |                                       | 780-725<br>(12.8-13.8)                |
|           | 2-                       | Solid           | 955-906<br>(10.5-11.0)                | 887-860<br>(11.3-11.6)                | 821-793<br>(12.2-12.6)                | 750-723<br>(13.3-13.8)                |
|           | 3-                       | liq.            |                                       | 885-870<br>(11.3-11.5)                | 741<br>(13.5)                         |                                       |
| Thiophene | 2-                       | $\text{CHCl}_3$ | ca. 925<br>(10.8)                     | ca. 853<br>(11.7)                     | 843-803<br>(11.9-12.5)                |                                       |
|           | 3-                       | liq.            |                                       |                                       |                                       | 755<br>(13.2)                         |
| Pyrrole   | 2-Acyl                   | Solid           |                                       |                                       | 774-740<br>(12.9-13.5)                | ca. 755<br>(13.2)                     |

# appendix f

WAVELENGTH–WAVE NUMBER CONVERSION TABLE

|                 |     | Wave number (cm <sup>-1</sup> ) |      |      |      |      |      |      |      |      |      |
|-----------------|-----|---------------------------------|------|------|------|------|------|------|------|------|------|
|                 |     | 0                               | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
| wavelength (μm) | 2.0 | 5000                            | 4975 | 4950 | 4926 | 4902 | 4878 | 4854 | 4831 | 4808 | 4785 |
|                 | 2.1 | 4762                            | 4739 | 4717 | 4695 | 4673 | 4651 | 4630 | 4608 | 4587 | 4566 |
|                 | 2.2 | 4545                            | 4525 | 4505 | 4484 | 4464 | 4444 | 4425 | 4405 | 4386 | 4367 |
|                 | 2.3 | 4348                            | 4329 | 4310 | 4292 | 4274 | 4255 | 4237 | 4219 | 4202 | 4184 |
|                 | 2.4 | 4167                            | 4149 | 4232 | 4115 | 4098 | 4082 | 4065 | 4049 | 4032 | 4016 |
|                 | 2.5 | 4000                            | 3984 | 3968 | 4953 | 3937 | 3922 | 3006 | 3891 | 3876 | 3861 |
|                 | 2.6 | 3846                            | 3831 | 3817 | 3802 | 3788 | 3774 | 3759 | 3745 | 3731 | 3717 |
|                 | 2.7 | 3704                            | 3690 | 3676 | 3663 | 3650 | 3636 | 3623 | 3610 | 3597 | 3584 |
|                 | 2.8 | 3571                            | 3559 | 3546 | 3534 | 3521 | 3509 | 3497 | 3484 | 3472 | 3460 |
|                 | 2.9 | 3448                            | 3436 | 3425 | 3413 | 3401 | 3390 | 3378 | 3367 | 3356 | 3344 |
|                 | 3.0 | 3333                            | 3322 | 3311 | 3300 | 3289 | 3279 | 3268 | 3257 | 3247 | 3236 |
|                 | 3.1 | 3226                            | 3215 | 3205 | 3195 | 3185 | 3175 | 3165 | 3155 | 3145 | 3135 |
|                 | 3.2 | 3125                            | 3115 | 3106 | 3096 | 3086 | 3077 | 3067 | 3058 | 3049 | 3040 |
|                 | 3.3 | 3030                            | 3021 | 3012 | 3003 | 2994 | 2985 | 2976 | 2967 | 2959 | 2950 |
|                 | 3.4 | 2941                            | 2933 | 2924 | 2915 | 2907 | 2899 | 2890 | 2882 | 2874 | 2865 |
|                 | 3.5 | 2857                            | 2849 | 2841 | 2833 | 2825 | 2817 | 2809 | 2801 | 2793 | 2786 |
|                 | 3.6 | 2778                            | 2770 | 2762 | 2755 | 2747 | 2740 | 2732 | 2725 | 2717 | 2710 |
|                 | 3.7 | 2703                            | 2695 | 2688 | 2681 | 2674 | 2667 | 2660 | 2653 | 2646 | 2639 |
|                 | 3.8 | 2632                            | 2625 | 2618 | 2611 | 2604 | 2597 | 2591 | 2584 | 2577 | 2571 |
|                 | 3.9 | 2654                            | 2558 | 2551 | 2545 | 2538 | 2532 | 2525 | 2519 | 2513 | 2506 |
|                 | 4.0 | 2500                            | 2494 | 2488 | 2481 | 2475 | 2469 | 2463 | 2457 | 2451 | 2445 |
|                 | 4.1 | 2439                            | 2433 | 2427 | 2421 | 2415 | 2410 | 2404 | 2398 | 2387 | 2387 |
|                 | 4.2 | 2381                            | 2375 | 2370 | 2364 | 2358 | 2353 | 2347 | 2342 | 2336 | 2331 |
|                 | 4.3 | 2326                            | 2320 | 2315 | 2309 | 2304 | 2299 | 2294 | 2288 | 2283 | 2278 |
|                 | 4.4 | 2273                            | 2268 | 2262 | 2257 | 2252 | 2247 | 2242 | 2237 | 2232 | 2227 |
|                 | 4.5 | 2222                            | 2217 | 2212 | 2208 | 2203 | 2198 | 2193 | 2188 | 2183 | 2179 |
|                 | 4.6 | 2174                            | 2169 | 2165 | 2160 | 2155 | 2151 | 2146 | 2141 | 2137 | 2132 |
|                 | 4.7 | 2128                            | 2123 | 2119 | 2114 | 2110 | 2105 | 2101 | 2096 | 2092 | 2088 |
|                 | 4.8 | 2083                            | 2079 | 2075 | 2070 | 2066 | 2062 | 2058 | 2053 | 2049 | 2045 |
|                 | 4.9 | 2041                            | 2037 | 2033 | 2028 | 2024 | 2020 | 2016 | 2012 | 2008 | 2004 |
|                 | 5.0 | 2000                            | 1996 | 1992 | 1988 | 1984 | 1980 | 1976 | 1972 | 1969 | 1965 |
|                 | 5.1 | 1961                            | 1957 | 1953 | 1949 | 1946 | 1942 | 1938 | 1934 | 1931 | 1927 |
|                 | 5.2 | 1923                            | 1919 | 1916 | 1912 | 1908 | 1905 | 1901 | 1898 | 1894 | 1890 |
|                 | 5.3 | 1887                            | 1883 | 1880 | 1876 | 1873 | 1869 | 1866 | 1862 | 1859 | 1855 |
|                 |     | 0                               | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |



|      | Wave number (cm <sup>-1</sup> ) |      |      |      |      |      |      |      |      |      |
|------|---------------------------------|------|------|------|------|------|------|------|------|------|
|      | 0                               | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
| 5.4  | 1852                            | 1848 | 1845 | 1842 | 1838 | 1835 | 1832 | 1828 | 1825 | 1821 |
| 5.5  | 1818                            | 1815 | 1812 | 1808 | 1805 | 1802 | 1799 | 1795 | 1792 | 1788 |
| 5.6  | 1786                            | 1783 | 1779 | 1776 | 1773 | 1770 | 1767 | 1764 | 1761 | 1757 |
| 5.7  | 1754                            | 1751 | 1748 | 1745 | 1742 | 1739 | 1736 | 1733 | 1730 | 1727 |
| 5.8  | 1724                            | 1721 | 1718 | 1715 | 1712 | 1709 | 1706 | 1704 | 1701 | 1698 |
| 5.9  | 1695                            | 1692 | 1689 | 1686 | 1684 | 1681 | 1678 | 1675 | 1672 | 1669 |
| 6.0  | 1667                            | 1664 | 1661 | 1658 | 1656 | 1653 | 1650 | 1647 | 1645 | 1642 |
| 6.1  | 1639                            | 1637 | 1634 | 1631 | 1629 | 1626 | 1623 | 1621 | 1618 | 1616 |
| 6.2  | 1613                            | 1610 | 1608 | 1605 | 1603 | 1600 | 1597 | 1595 | 1592 | 1590 |
| 6.3  | 1587                            | 1585 | 1582 | 1580 | 1577 | 1575 | 1572 | 1570 | 1567 | 1565 |
| 6.4  | 1563                            | 1560 | 1558 | 1555 | 1553 | 1550 | 1548 | 1546 | 1543 | 1541 |
| 6.5  | 1538                            | 1536 | 1534 | 1531 | 1529 | 1527 | 1524 | 1522 | 1520 | 1517 |
| 6.6  | 1515                            | 1513 | 1511 | 1508 | 1506 | 1504 | 1502 | 1499 | 1497 | 1495 |
| 6.7  | 1493                            | 1490 | 1488 | 1486 | 1484 | 1481 | 1479 | 1477 | 1475 | 1473 |
| 6.8  | 1471                            | 1468 | 1466 | 1464 | 1462 | 1460 | 1458 | 1456 | 1453 | 1451 |
| 6.9  | 1449                            | 1447 | 1445 | 1443 | 1441 | 1439 | 1437 | 1435 | 1433 | 1431 |
| 7.0  | 1429                            | 1427 | 1425 | 1422 | 1420 | 1418 | 1416 | 1414 | 1412 | 1410 |
| 7.1  | 1408                            | 1406 | 1404 | 1403 | 1401 | 1399 | 1397 | 1395 | 1393 | 1391 |
| 7.2  | 1389                            | 1387 | 1385 | 1383 | 1381 | 1379 | 1377 | 1376 | 1374 | 1372 |
| 7.3  | 1370                            | 1368 | 1366 | 1364 | 1362 | 1361 | 1359 | 1357 | 1355 | 1353 |
| 7.4  | 1351                            | 1350 | 1348 | 1346 | 1344 | 1342 | 1340 | 1339 | 1337 | 1335 |
| 7.5  | 1333                            | 1332 | 1330 | 1328 | 1326 | 1325 | 1323 | 1321 | 1319 | 1318 |
| 7.6  | 1316                            | 1314 | 1312 | 1311 | 1309 | 1307 | 1305 | 1304 | 1302 | 1300 |
| 7.7  | 1299                            | 1297 | 1295 | 1294 | 1292 | 1290 | 1289 | 1287 | 1285 | 1284 |
| 7.8  | 1282                            | 1280 | 1279 | 1277 | 1276 | 1274 | 1272 | 1271 | 1269 | 1267 |
| 7.9  | 1266                            | 1264 | 1263 | 1261 | 1259 | 1258 | 1256 | 1255 | 1253 | 1252 |
| 8.0  | 1250                            | 1248 | 1247 | 1245 | 1244 | 1242 | 1241 | 1239 | 1238 | 1236 |
| 8.1  | 1235                            | 1233 | 1232 | 1230 | 1229 | 1227 | 1225 | 1224 | 1222 | 1221 |
| 8.2  | 1220                            | 1218 | 1217 | 1215 | 1214 | 1212 | 1211 | 1209 | 1208 | 1206 |
| 8.3  | 1205                            | 1203 | 1202 | 1200 | 1199 | 1198 | 1196 | 1195 | 1193 | 1192 |
| 8.4  | 1190                            | 1189 | 1188 | 1186 | 1185 | 1183 | 1182 | 1181 | 1179 | 1178 |
| 8.5  | 1176                            | 1175 | 1174 | 1172 | 1171 | 1170 | 1168 | 1167 | 1166 | 1164 |
| 8.6  | 1163                            | 1161 | 1160 | 1159 | 1157 | 1156 | 1155 | 1153 | 1152 | 1151 |
| 8.7  | 1149                            | 1148 | 1147 | 1145 | 1144 | 1143 | 1142 | 1140 | 1139 | 1138 |
| 8.8  | 1136                            | 1135 | 1134 | 1133 | 1131 | 1130 | 1129 | 1127 | 1126 | 1125 |
| 8.9  | 1124                            | 1122 | 1121 | 1120 | 1119 | 1117 | 1116 | 1115 | 1114 | 1112 |
| 9.0  | 1111                            | 1110 | 1109 | 1107 | 1106 | 1105 | 1104 | 1103 | 1101 | 1100 |
| 9.1  | 1099                            | 1098 | 1096 | 1095 | 1094 | 1093 | 1092 | 1091 | 1089 | 1088 |
| 9.2  | 1087                            | 1086 | 1085 | 1083 | 1082 | 1081 | 1080 | 1079 | 1078 | 1076 |
| 9.3  | 1075                            | 1074 | 1073 | 1072 | 1071 | 1070 | 1068 | 1067 | 1066 | 1065 |
| 9.4  | 1064                            | 1063 | 1062 | 1060 | 1059 | 1058 | 1057 | 1056 | 1055 | 1054 |
| 9.5  | 1053                            | 1052 | 1050 | 1049 | 1048 | 1047 | 1046 | 1045 | 1044 | 1043 |
| 9.6  | 1042                            | 1041 | 1040 | 1038 | 1037 | 1036 | 1035 | 1034 | 1033 | 1032 |
| 9.7  | 1031                            | 1030 | 1029 | 1028 | 1027 | 1026 | 1025 | 1024 | 1022 | 1021 |
| 9.8  | 1020                            | 1019 | 1018 | 1017 | 1016 | 1015 | 1014 | 1013 | 1012 | 1011 |
| 9.9  | 1010                            | 1009 | 1008 | 1007 | 1006 | 1005 | 1004 | 1003 | 1002 | 1001 |
| 10.0 | 1000                            | 999  | 998  | 997  | 996  | 995  | 994  | 993  | 992  | 991  |
|      | 0                               | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |

|                 | Wave number (cm <sup>-1</sup> ) |     |     |     |     |     |     |     |     |     |     |
|-----------------|---------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                 | 0                               | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |     |
| Wavelength (μm) | 10.1                            | 990 | 989 | 988 | 987 | 986 | 985 | 984 | 983 | 982 | 981 |
|                 | 10.2                            | 980 | 979 | 978 | 978 | 977 | 976 | 975 | 974 | 973 | 972 |
|                 | 10.3                            | 971 | 970 | 969 | 968 | 967 | 966 | 965 | 964 | 963 | 962 |
|                 | 10.4                            | 962 | 961 | 960 | 959 | 958 | 957 | 956 | 955 | 954 | 953 |
|                 | 10.5                            | 952 | 951 | 951 | 950 | 949 | 948 | 947 | 946 | 945 | 944 |
|                 | 10.6                            | 943 | 943 | 942 | 941 | 940 | 939 | 938 | 937 | 936 | 935 |
|                 | 10.7                            | 935 | 934 | 933 | 932 | 931 | 930 | 929 | 929 | 928 | 927 |
|                 | 10.8                            | 926 | 925 | 924 | 923 | 923 | 922 | 921 | 920 | 919 | 918 |
|                 | 10.9                            | 917 | 917 | 916 | 915 | 914 | 913 | 912 | 912 | 911 | 910 |
|                 | 11.0                            | 909 | 908 | 907 | 907 | 906 | 905 | 904 | 903 | 903 | 902 |
|                 | 11.1                            | 901 | 900 | 899 | 898 | 898 | 897 | 896 | 895 | 894 | 894 |
|                 | 11.2                            | 893 | 892 | 891 | 890 | 890 | 889 | 888 | 887 | 887 | 886 |
|                 | 11.3                            | 885 | 884 | 883 | 883 | 882 | 881 | 880 | 880 | 879 | 878 |
|                 | 11.4                            | 877 | 876 | 876 | 875 | 874 | 873 | 873 | 872 | 871 | 870 |
|                 | 11.5                            | 870 | 869 | 868 | 867 | 867 | 866 | 865 | 864 | 864 | 863 |
|                 | 11.6                            | 862 | 861 | 861 | 860 | 859 | 858 | 858 | 857 | 856 | 855 |
|                 | 11.7                            | 855 | 854 | 853 | 853 | 852 | 851 | 850 | 850 | 849 | 848 |
|                 | 11.8                            | 847 | 847 | 846 | 845 | 845 | 844 | 843 | 842 | 842 | 841 |
|                 | 11.9                            | 840 | 840 | 839 | 838 | 838 | 837 | 836 | 835 | 835 | 834 |
|                 | 12.0                            | 833 | 833 | 832 | 831 | 831 | 830 | 829 | 829 | 828 | 827 |
|                 | 12.1                            | 826 | 826 | 825 | 824 | 824 | 823 | 822 | 822 | 821 | 820 |
|                 | 12.2                            | 820 | 819 | 818 | 818 | 817 | 816 | 816 | 815 | 814 | 814 |
|                 | 12.3                            | 813 | 812 | 812 | 811 | 810 | 810 | 809 | 808 | 808 | 807 |
|                 | 12.4                            | 806 | 806 | 805 | 805 | 804 | 803 | 803 | 802 | 801 | 801 |
|                 | 12.5                            | 800 | 799 | 799 | 798 | 797 | 797 | 796 | 796 | 795 | 794 |
|                 | 12.6                            | 794 | 793 | 792 | 792 | 791 | 791 | 790 | 789 | 789 | 788 |
|                 | 12.7                            | 787 | 787 | 786 | 786 | 785 | 784 | 784 | 783 | 782 | 782 |
|                 | 12.8                            | 781 | 781 | 780 | 779 | 779 | 778 | 778 | 777 | 776 | 776 |
|                 | 12.9                            | 775 | 775 | 774 | 773 | 773 | 772 | 772 | 771 | 770 | 770 |
|                 | 13.0                            | 769 | 769 | 768 | 767 | 767 | 766 | 766 | 765 | 765 | 764 |
|                 | 13.1                            | 763 | 763 | 762 | 762 | 761 | 760 | 760 | 759 | 759 | 758 |
|                 | 13.2                            | 758 | 757 | 756 | 756 | 755 | 755 | 754 | 754 | 753 | 752 |
|                 | 13.3                            | 752 | 751 | 751 | 750 | 750 | 749 | 749 | 748 | 747 | 747 |
|                 | 13.4                            | 746 | 746 | 745 | 745 | 744 | 743 | 743 | 742 | 742 | 741 |
|                 | 13.5                            | 741 | 740 | 740 | 739 | 739 | 738 | 737 | 737 | 736 | 736 |
|                 | 13.6                            | 735 | 735 | 734 | 734 | 733 | 733 | 732 | 732 | 731 | 730 |
|                 | 13.7                            | 730 | 729 | 729 | 728 | 728 | 727 | 727 | 726 | 726 | 725 |
|                 | 13.8                            | 725 | 724 | 724 | 723 | 723 | 722 | 722 | 721 | 720 | 720 |
|                 | 13.9                            | 719 | 719 | 718 | 718 | 717 | 717 | 716 | 716 | 715 | 715 |
|                 | 14.0                            | 714 | 714 | 713 | 713 | 712 | 712 | 711 | 711 | 710 | 710 |
|                 | 14.1                            | 709 | 709 | 708 | 708 | 707 | 707 | 706 | 706 | 705 | 705 |
|                 | 14.2                            | 704 | 704 | 703 | 703 | 702 | 702 | 701 | 701 | 700 | 700 |
|                 | 14.3                            | 699 | 699 | 698 | 698 | 697 | 697 | 696 | 696 | 695 | 695 |
|                 | 14.4                            | 694 | 694 | 693 | 693 | 693 | 692 | 692 | 691 | 691 | 690 |
|                 | 14.5                            | 690 | 689 | 689 | 688 | 688 | 687 | 687 | 686 | 686 | 685 |
|                 | 14.6                            | 685 | 684 | 684 | 684 | 683 | 683 | 682 | 682 | 681 | 681 |
|                 | 14.7                            | 680 | 680 | 679 | 679 | 678 | 678 | 678 | 677 | 677 | 676 |
|                 | 14.8                            | 676 | 675 | 675 | 674 | 674 | 673 | 673 | 672 | 672 | 672 |
|                 | 14.9                            | 671 | 671 | 670 | 670 | 669 | 669 | 668 | 668 | 668 | 667 |
|                 | 0                               | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |     |

# proton magnetic resonance spectrometry

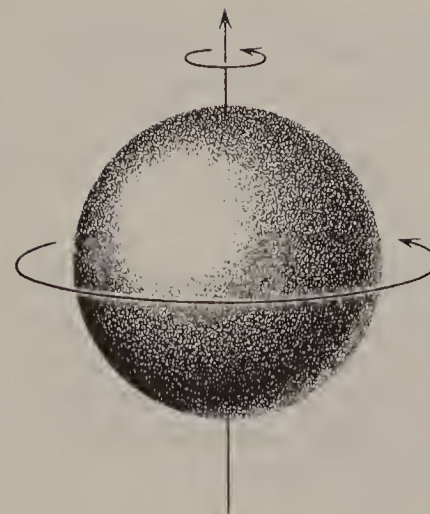


Figure 1. *Spinning charge in proton generates magnetic dipole.*

## I. INTRODUCTION AND THEORY

Nuclear magnetic resonance (NMR) spectrometry is basically another form of absorption spectrometry, akin to infrared or ultraviolet spectrometry. Under appropriate conditions, a sample can absorb electromagnetic radiation in the radio-frequency region at frequencies governed by the characteristics of the sample. Absorption is a function of certain nuclei in the molecule. A plot of the frequencies of the absorption peaks versus peak intensities constitutes an NMR spectrum. This chapter covers proton magnetic resonance ( $^1\text{H}$  NMR or pmr) spectrometry.

With some mastery of basic theory, interpretation of NMR spectra merely by inspection is usually feasible in greater detail than is the case for infrared or ultraviolet spectra. To supplement the material presented here, several nonmathematical introductions to nuclear magnetic resonance are recommended.<sup>1-12</sup> For greater depth several treatises are available.<sup>13-17</sup> Collections of spectra<sup>18-21</sup> and spectra-structure correlations<sup>22-26</sup> are essential for practical use. The present account will suffice for the immediate limited objective: identification of organic compounds in conjunction with other spectrometric information.

We begin by describing some magnetic properties of nuclei. All nuclei carry a charge. In some nuclei this charge "spins" on the nuclear axis, and this circulation of nuclear charge generates a magnetic dipole along the axis (Figure 1). The angular momentum of the spinning charge can be described in terms of spin numbers  $I$ ; these numbers have values of 0,  $1/2$ , 1,  $3/2$ , and so forth ( $I=0$  denotes no spin). The intrinsic magnitude of the generated dipole is expressed in terms of nuclear magnetic moment,  $\mu$ .

Each proton and neutron has its own spin, and  $I$  is a resultant of these spins. If the sum of protons and neutrons is even,  $I$  is zero or integral (0, 1, 2, . . .); if the sum is odd,  $I$  is half-integral ( $1/2$ ,  $3/2$ ,  $5/2$ , . . .); if both protons and neutrons are even-numbered,  $I$  is zero. Both  $^{12}\text{C}$  and  $^{16}\text{O}$

fall in the last category and give no NMR signal

Several nuclei ( $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ) have a spin number  $I$  of  $1/2$  and a uniform spherical charge distribution (Figure 1). Nuclei with a spin number  $I$  of 1 or higher have a nonspherical charge distribution. This asymmetry is described by an electrical quadrupole moment which, as we shall see later, affects the relaxation time and, consequently, the coupling with neighboring nuclei.  $^{14}\text{N}$  and  $^2\text{H}$  have a spin number  $I$  of 1.  $^{11}\text{B}$ ,  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ , and  $^{81}\text{Br}$  are examples of nuclei with  $I = 3/2$ .

In quantum mechanical terms, the spin number  $I$  determines the number of orientations a nucleus may assume in an external uniform magnetic field in accordance with the formulas  $2I + 1$ . We are concerned primarily with the proton whose spin number  $I$  is  $1/2$  (Figure 2); thus, there are 2 energy levels, and a slight excess population in the lower energy state.

Two energy levels for the proton having been established, it should be possible to introduce quanta of energy  $h\nu$  ( $h$  is Planck's constant;  $\nu$  is the frequency of electro-

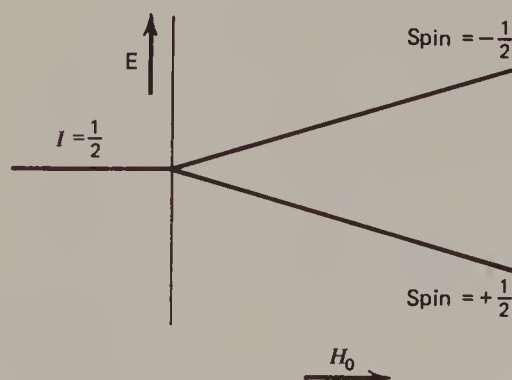


Figure 2. *Two energy levels for a proton in a magnetic field,  $H_0$ .*



magnetic radiation) to effect a transition between these energy levels in a magnetic field of given strength  $H_0$ . The fundamental NMR equation correlating electromagnetic field strength is

$$\nu = \frac{\gamma H_0}{2\pi}$$

A frequency of 60 megahertz (MHz) is needed at a magnetic field  $H_0$  of 14,092 gauss for the proton (or any other desired combination in the same ratio). The constant  $\gamma$  is called the magnetogyric ratio and is a fundamental nuclear constant; it is the proportionality constant between the magnetic moment  $\mu$  and the spin number  $I$ :

$$\gamma = \frac{2\pi\mu}{hI}$$

The problem is how to inject radiofrequency electromagnetic energy into protons aligned in a magnetic field, and how to measure the energy thus absorbed as the proton is raised to the higher spin state. This can best be explained in classical mechanical terms wherein we visualize the proton as spinning in an external magnetic field: the magnetic axis of the proton will precess about the axis of the external magnetic field in the same manner in which a spinning gyroscope precesses under the influence of gravity (Figure 3). The precessional angular velocity (Larmor frequency  $\omega_0$ ) is equal to the product of the magnetogyric ratio and the strength of the applied magnetic field  $H_0$ .

$$\omega_0 = \gamma H_0$$

We recall from the fundamental NMR equation that

$$\gamma H_0 = 2\pi\nu$$

Therefore,

$$\omega_0 = 2\pi\nu$$

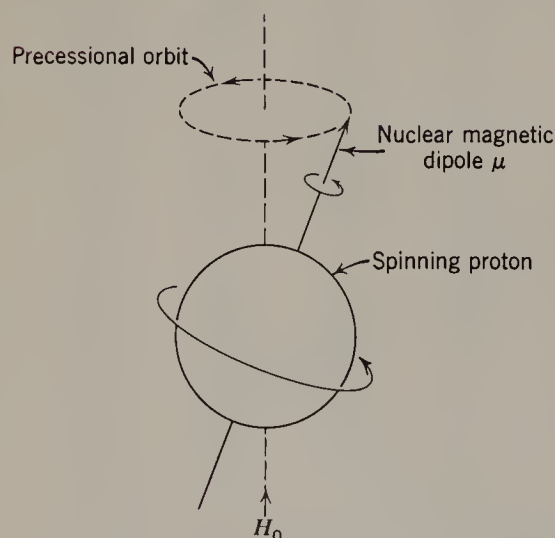


Figure 3. Proton precession in a magnetic field  $H_0$ .

We may now arrange the geometry for an NMR experiment. We subject the protons to a powerful, uniform magnetic field and consider those protons aligned with the field and precessing about the axis of the applied magnetic field  $H_0$ .

Because of thermal disorder, actually only a small fraction of the total population of the protons is properly aligned, but this fraction is sufficient. The radiofrequency electromagnetic energy is applied in such a way that its magnetic component  $H_1$  is at right angles to the main magnetic field  $H_0$  and is rotating with the precessing proton. This is accomplished by a coil with its axis at right angles to the axis of the main magnetic field  $H_0$ . Such a coil will generate an oscillating magnetic field  $H_1$  along the direction of the coil axis as shown in Figure 4. An oscillating magnetic field can be resolved into two components rotating in opposite directions. One of these components is rotating in the same direction as the precessional orbit of the nuclear magnetic dipole (the proton); the oppositely rotating component of  $H_1$  is disregarded. If  $H_0$  is held constant and the oscillator frequency is varied, the angular velocity of the component of rotating magnetic field  $H_1$  will vary until it is equal to (in resonance with) the angular velocity  $\omega_0$  of the precessing proton. At this point, the absorbed energy is at a maximum, and the precessing nuclei are tilted away from alignment with  $H_0$  toward the horizontal plane in Figure 4. The magnetic component thus generated in that plane can be detected. Alternatively, the oscillator frequency is held constant, and  $H_0$  is swept over a narrow range.

Now that we have briefly discussed how a nucleus is excited to a higher energy state by absorption of energy, we need to describe a mechanism for the return of the nucleus to the ground state. In the absence of such a mechanism, all of the small excess population of nuclei in the lower energy state will be raised to the high energy state, and no more energy could be absorbed. Fortunately, there exists a mechanism whereby the nucleus in the higher energy state can lose energy to its environment and thus return to its lower energy state. The mechanism is called a spin-lattice or longitudinal relaxation process and involves transfer of energy from the nucleus in its high-energy state to the molecular lattice. Its efficiency is described as the half-life,  $T_1$ , for the transfer, an efficient relaxation process involving a short time  $T_1$ . The line width is inversely proportional to the lifetime of the excited state. In neat liquids, solutions, and gases, a peak of usable width is obtained. In solids, this mechanism is not effective;  $T_1$  is therefore very long, and, in the absence of any other effects, a crystalline solid would show extremely narrow lines. There is another effect called spin-spin or transverse relaxation, described in terms of time  $T_2$ . This involves transfer of energy from one high-energy nucleus to another. There is no net loss of energy, but the spread of energy among the nuclei concerned results in line broadening. Solids show very broad bands.

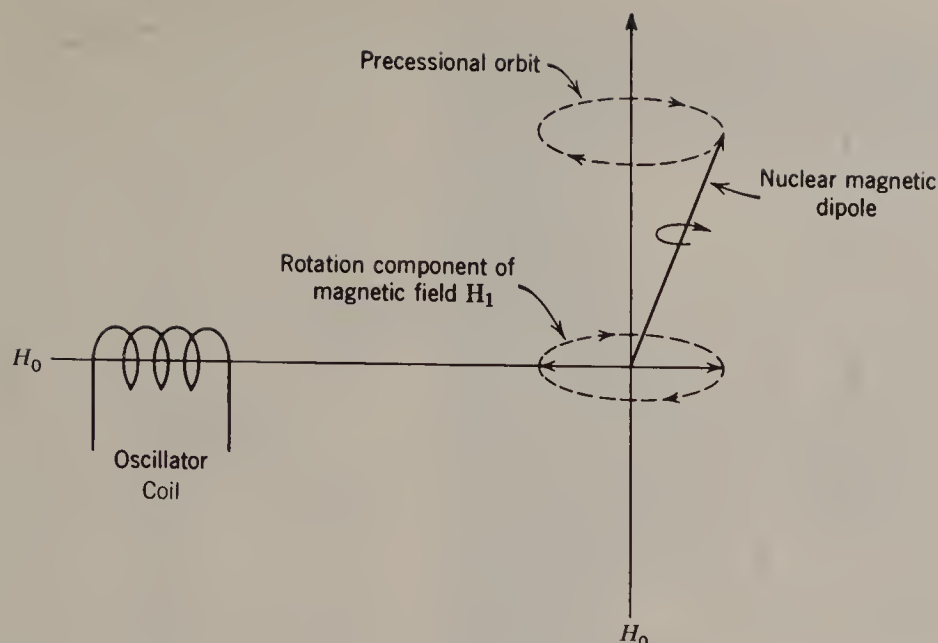


Figure 4. Oscillator generates rotating component of magnetic field  $H_1$ .

We can now consider very briefly the instrumentation necessary to obtain a nuclear magnetic resonance spectrum.

field. A variable-temperature sample holder is also available.

## II. APPARATUS AND SAMPLE HANDLING

Proton NMR spectra are commonly run at 60, 80, 90, or 100 MHz\* corresponding to magnetic fields of 14,092, 18,667, ~21,000 or ~23,500 gauss, respectively. Higher frequencies (up to 400 MHz) are used in conjunction with superconducting, helium-cooled magnets. In addition,  $^{19}\text{F}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^2\text{H}$ ,  $^{15}\text{N}$ , and  $^{31}\text{P}$  and many other nuclei can be examined at appropriate combinations of frequencies and magnetic-field strength.

A schematic diagram of a simple NMR spectrometer is shown in Figure 5. The instrument can be described in terms of the following components:

1. A strong magnet with a homogeneous field that can be varied continuously and precisely over a relatively narrow range. This is accomplished by the sweep generator.
2. A radiofrequency transmitter.
3. A radiofrequency receiver.
4. A recorder, calibrator, and integrator.
5. A sample holder that positions the sample relative to the main magnetic field, the transmitter coil, and the receiver coil. The sample holder also spins the sample to increase the apparent homogeneity of the magnetic

By measuring frequency shifts from a reference marker, an accuracy of  $<1$  Hz can be achieved. The recording is presented as a series of peaks with the peak areas being proportional to the number of protons they represent. Peak areas are measured by an electronic integrator that traces a series of steps with heights proportional to the peak areas. The steps can be superimposed on the peaks. As will be obvious in Chapter 7, proton counting with the integrator is extremely useful. Peaks hidden under other peaks or in the baseline noise can be detected. Proton counting is often useful for determining sample purity and, of course, for quantitative analytical work.

A routine sample on a 60-MHz instrument would consist of about 5-50 mg of the compound in about 0.4 ml of solvent in a 5-ml O.D. glass tube. A microtube consisting of a thick-wall capillary leading to a 25- $\mu\text{l}$  spherical cavity allows usable spectra to be obtained on less than 1 mg of sample. To overcome the lack of inherent sensitivity of NMR spectrometry, repetitive scans can be used. Signals can be accumulated and noise averaged out by a computer attachment to give usable spectra on samples of the order of 150  $\mu\text{g}$ . On more sophisticated instruments, a capillary probe together with Fourier Transform (FT, see Chapter 5) makes it possible to obtain usable spectra on amounts as small as 5  $\mu\text{g}$ .

The ideal solvent should contain no protons in its structure and be inexpensive, low-boiling, nonpolar, and inert. Carbon tetrachloride is ideal when the sample is sufficiently soluble in it. The most widely used solvent is deuterated

\*One hertz, Hz, is 1 cycle per second. MHz is  $1 \times 10^6$  Hz.



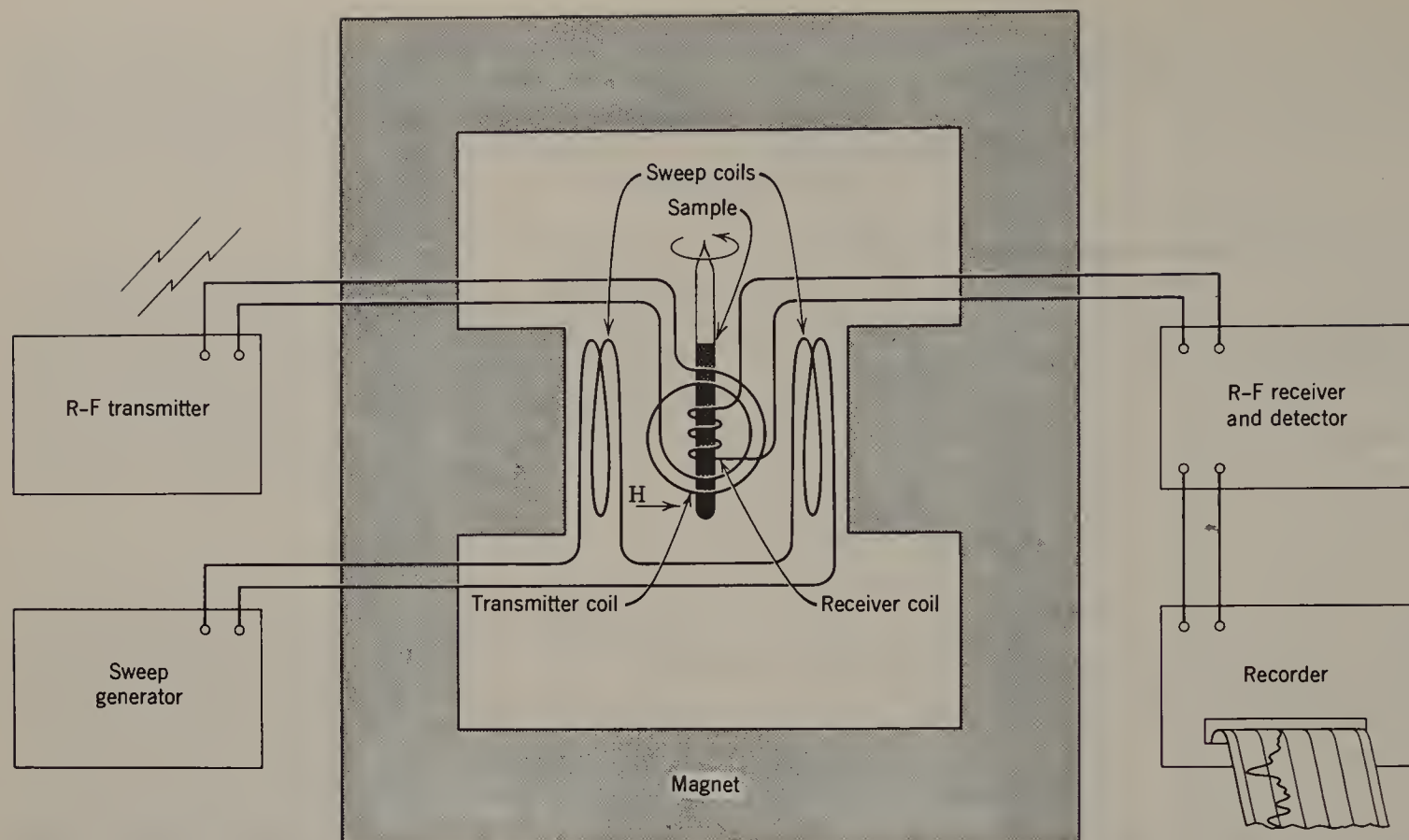


Figure 5. Schematic diagram of an NMR spectrometer.

Courtesy of Varian Associates, Palo Alto, Calif.

chloroform ( $\text{CDCl}_3$ ). The small sharp proton peak from the  $\text{CHCl}_3$  impurity present (see Appendix A) rarely interferes seriously. Carbon disulfide is also a useful solvent. Almost all of the common solvents are available in the deuterated form with an isotopic purity (atom %D) of 98-99.8%. A list of these solvents and the positions of their proton impurity peaks are given in Appendix A.

Small "spinning side bands" (see Figure 6) are often seen, symmetrically disposed on both sides of a strong absorption peak; these result from inhomogeneities in the magnetic field and in the spinning tube. They are readily recognized because of their symmetrical appearance and because their separation from the absorption peak is equal to the rate of spinning. The oscillations often seen at the high-field end of a strong sharp peak are called "ringing" (Figure 7). These are "beat" frequencies resulting from "fast" (normal operation) passage through the absorption peak.

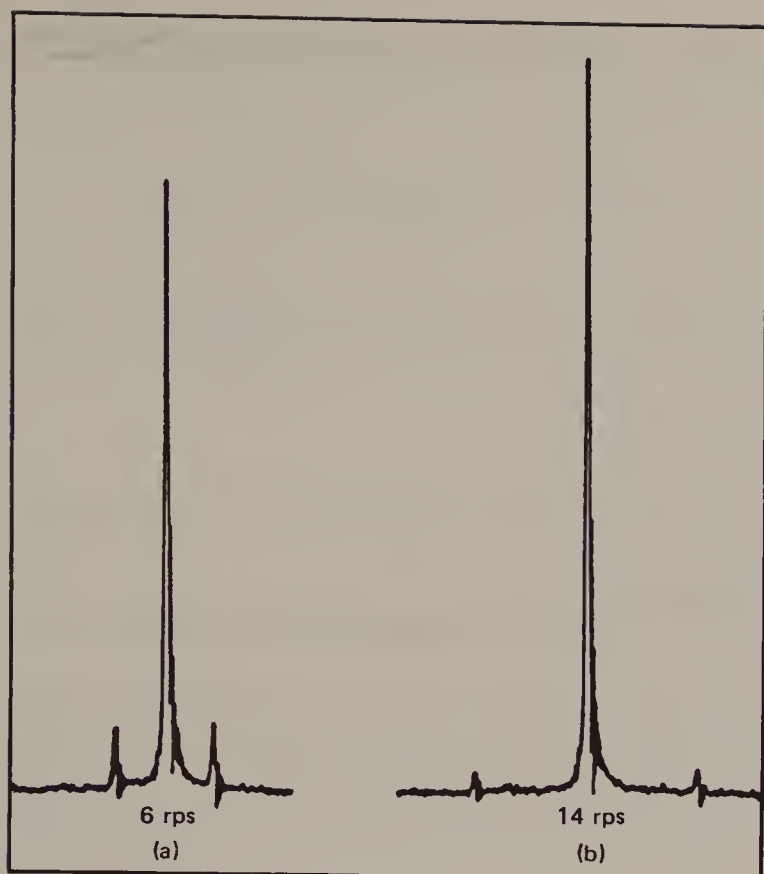
Traces of ferromagnetic impurities cause severe broadening of absorption peaks. Common sources are tap water, steel wool, Raney nickel, and particles from metal spatulas or fittings (Figure 8). These impurities can be removed by dipping a thin bar magnet into the NMR tube, by filtration, or by centrifugation.

### III. CHEMICAL SHIFT

Thus far, we have obtained a single peak from the interaction of radio frequency energy and a strong magnetic field on a proton in accordance with the basic NMR equation in which  $\gamma$ , the magnetogyric ratio, is an intrinsic property of the nucleus. The peak area (measured by the integrator) is proportional to the number of protons it represents. Fortunately, the situation is not quite so simple. The nucleus is shielded to a small extent by its electron cloud whose density varies with the environment. This variation gives rise to different absorption positions usually within the range of about 750 Hz in a magnetic field corresponding to 60 MHz or about 1250 Hz in a field corresponding to 100 MHz. The ability to discriminate among the individual absorptions describes high resolution NMR spectrometry.

Electrons under the influence of a magnetic field will circulate, and, in circulating, will generate their own magnetic field opposing the applied field, hence, the shielding effect (Figure 9). This effect accounts for the diamagnetism exhibited by all organic materials. In the case of materials with an unpaired electron, the paramagnetism associated with the net electron spin far overrides the diamagnetism of the circulating, paired electrons.





**Figure 6.** Signal of neat chloroform with spinning side bands produced by spinning rate of (a) 6 rps and (b) 14 rps.

From Reference 1, with permission.



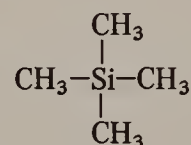
**Figure 7.** Ringing (or "wiggles") seen after passage through resonance. Direction of scan is from left to right.

(From Reference 7, with permission.)

The degree of shielding depends on the density of the circulating electrons, and, as a first, very rough approximation, the degree of shielding of a proton on a carbon atom will depend on the inductive effect of other groups attached to the carbon atom. The difference in the absorption position of a particular proton from the absorption position of a reference proton is called the *chemical shift* of the particular proton.

We now have the concept that protons in "different" chemical environments have different chemical shifts. Conversely, protons in the "same" chemical environment have the same chemical shift. But what do we mean by "different" and "same"? While it is intuitively obvious that the chemically different methylene groups of  $\text{ClCH}_2\text{CH}_2\text{OH}$  have different chemical shifts and that the protons in either one of the methylene groups have the same chemical shift, it may not be so obvious, for example, that the protons of the methylene group of  $\text{C}_6\text{H}_5\text{CH}_2\text{CHBrCl}$  do not have the same chemical shift. For the present, we shall deal with obvious cases and postpone a more rigorous treatment of chemical-shift equivalence to Section VII.

The most generally useful reference compound is tetramethylsilane (TMS).



It has several advantages: it is chemically inert, magnetically isotropic, volatile (b.p.  $27^\circ$ ), and soluble in most organic solvents; it gives a single sharp absorption peak, and absorbs at higher field than almost all organic protons. When water or deuterium oxide is the solvent, TMS can be used as an "external reference," that is, sealed in a capillary immersed in the solution. The methyl protons of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS):



are sometimes used as an internal reference in aqueous solution. Since only enough is used to give a small methyl peak, the diffuse pattern of the  $\text{CH}_2$  peaks barely shows on the base line. Unless hydrogen-bonding effects are involved, a proton peak referenced to TMS in deuterochloroform will be within 0.01 to 0.03 ppm of the same peak referenced to DSS in water or deuterium oxide. Acetonitrile and dioxane are also used as references in aqueous solution.

Let us set up an NMR scale (Figure 10) and set the TMS peak at 0 Hz at the right-hand edge. The magnetic field increases toward the right. When chemical shifts are given in Hz (designated  $\nu$ ), the applied frequency must be specified. Chemical shifts can be expressed in dimensionless units ( $\delta$ ), independent of the applied frequency, by dividing

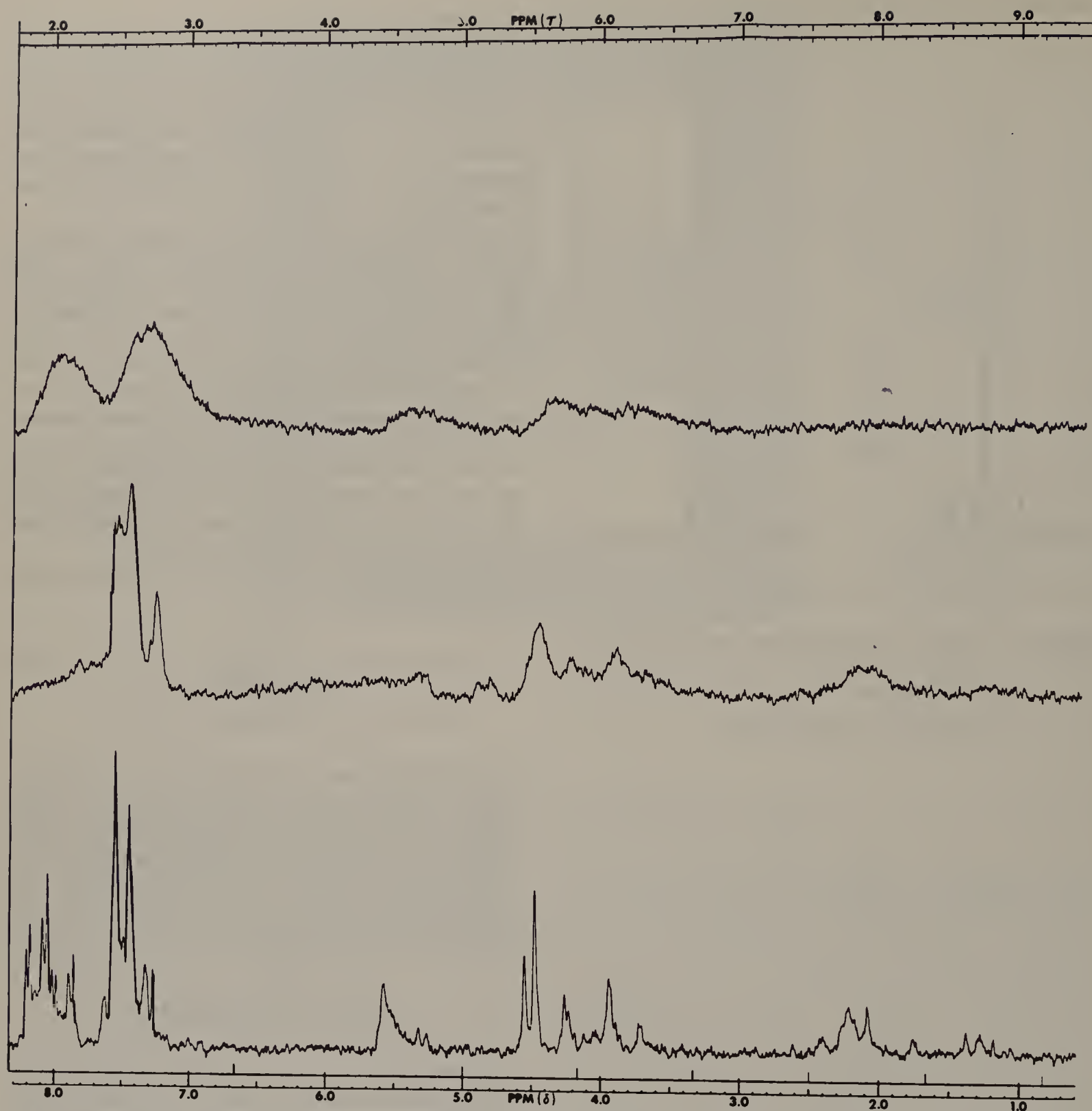


Figure 8. The effect of a tiny ferromagnetic particle on the proton resonance spectrum of a benzoylated sugar. The top and middle curves are repeated runs with the particle present; the bottom curve is the spectrum with the particle removed. (From Reference 7, with permission)

$\nu$  by the applied frequency and multiplying by  $10^6$ . Thus, a peak at 60 Hz ( $\nu$  60) from TMS at an applied frequency of 60 MHz would be at  $\delta$  1.00 or 1.00 ppm.

$$\delta \text{ or ppm} = \frac{60}{60 \times 10^6} \times 10^6 = 1.00$$

sion ppm is often used. The same peak at an applied frequency of 100 MHz would be at  $\nu$  100 but would still be at  $\delta$  1.00.

$$\delta \text{ or ppm} = \frac{100}{100 \times 10^6} \times 10^6 = 1.00$$

Since  $\delta$  units are expressed in parts per million, the expres-

An alternative system assigns a value of 10.00 for tetra-

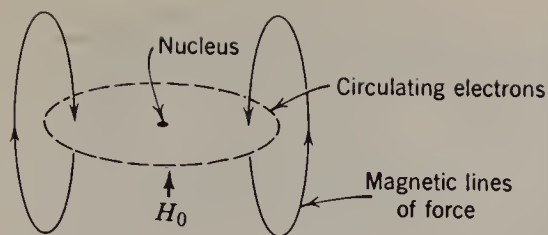


Figure 9. Diamagnetic shielding of nucleus by circulating electrons.

methylosilane, and describes chemical shifts in terms of  $\tau$  values.

$$\tau = 10.00 - \delta$$

Shifts at higher field than TMS ( $\delta$  0.00,  $\tau$  10.00) will be encountered very rarely;  $\delta$  values are then shown with a negative sign, and  $\tau$  values merely increase numerically. The  $\delta$  system is now used almost universally, and will be used here.

It is important to realize that the chemical shift in Hz is directly proportional to the strength of the applied field  $H_0$  and therefore to the applied frequency. This is understandable because the chemical shift is dependent on the diamagnetic shielding induced by  $H_0$ . The strongest magnetic field consistent with field homogeneity should be used to spread out the chemical shifts. This is made clear in Figure 10, and in Figure 11 in which increased applied magnetic field in the NMR spectrum of acrylonitrile means increased separation of signals.

The concept of electronegativity is a dependable guide, up to a point, to chemical shifts. It tells us that the electron density around the protons of TMS is high (silicon is electropositive relative to carbon), and these protons will therefore be highly shielded and their peak will be found at high field. We could make a number of good estimates as to chemical shifts, using concepts of electronegativity and proton acidity. For example, the following values are reasonable on these grounds:

|                           | $\delta$       |
|---------------------------|----------------|
| $(\text{CH}_3)_2\text{O}$ | 3.27           |
| $\text{CH}_3\text{F}$     | 4.30           |
| $\text{RCOOH}$            | 10.8 (approx.) |

But finding the protons of acetylene at  $\delta$  2.35, that is, more shielded than ethylene protons ( $\delta$  4.60), is unsettling. Finding the aldehydic proton of acetaldehyde at  $\delta$  9.97 definitely calls for some augmentation of the electronegativity concept. We shall use diamagnetic anisotropy to explain these and other apparent anomalies, such as the unexpectedly large deshielding effect of the benzene ring (benzene protons  $\delta$  7.27).

Let us begin with acetylene. The molecule is linear, and the triple bond is symmetrical about the axis. If this axis is aligned with the applied magnetic field, the  $\pi$ -electrons of the bond can circulate at right angles to the applied field, thus inducing their own magnetic field opposing the applied field. Since the protons lie along the magnetic axis, the magnetic lines of force induced by the circulating electrons

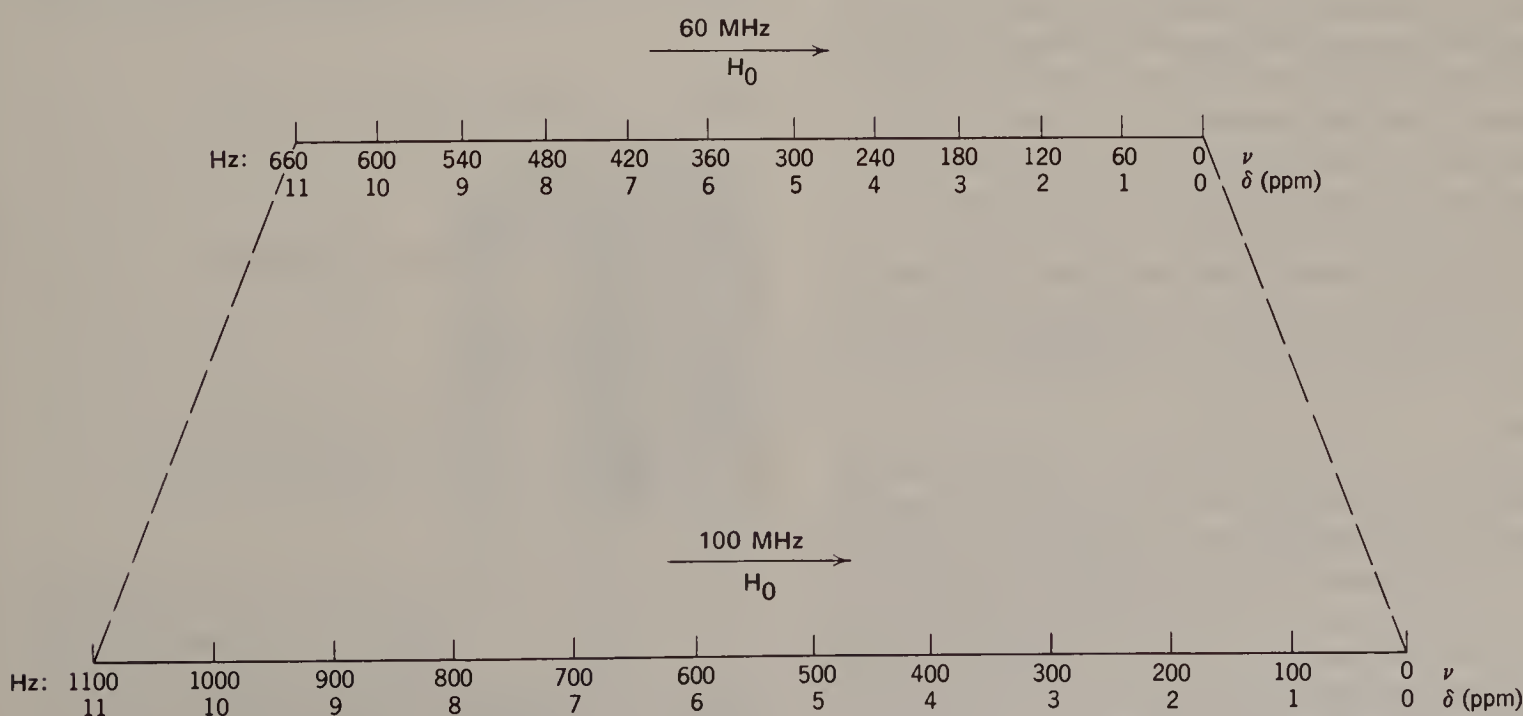


Figure 10. NMR Scale at 60 MHz and 100 MHz.



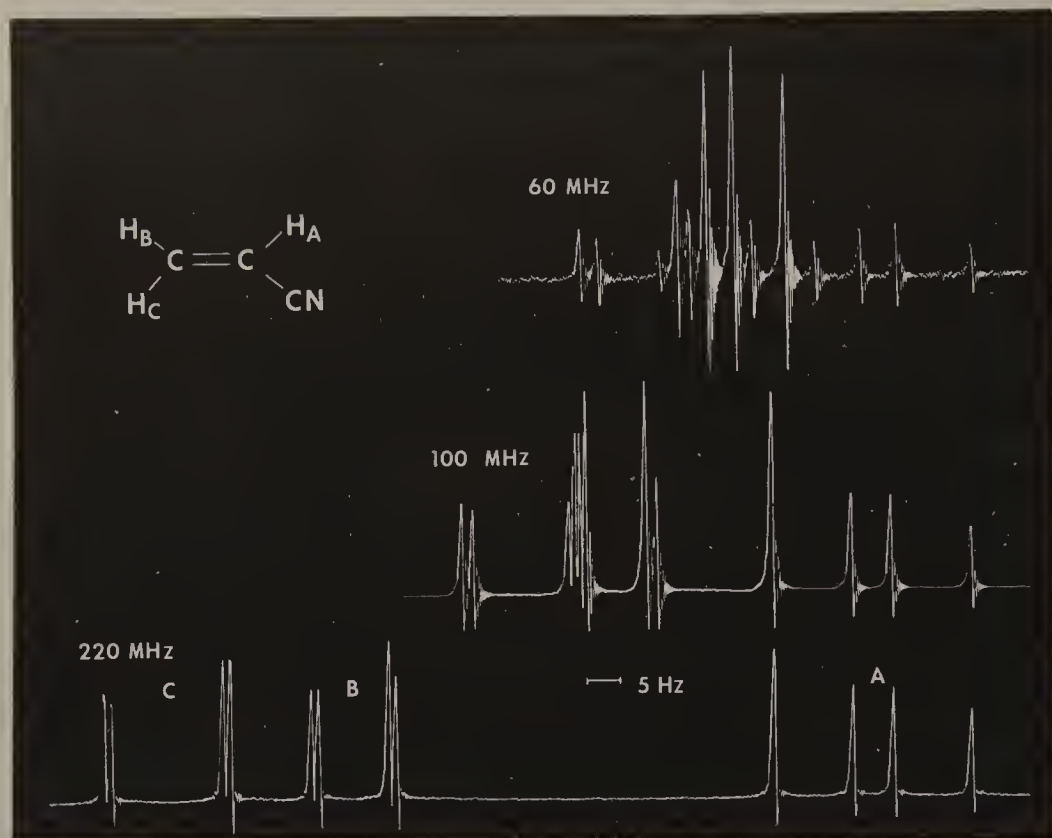


Figure 11. 60-, 100-, and 220-MHz spectra of acrylonitrile. Reprinted from *Anal. Chem.* Copyright 1971 by the American Chemical Society. Reprinted by permission of the copyright owner.

act to shield the protons (Figure 12), and the NMR peak is found further upfield than electronegativity would predict. Of course, only a small number of the rapidly tumbling molecules are aligned with the magnetic field, but the overall average shift is affected by the aligned molecules.

This effect depends on diamagnetic anisotropy, which means that shielding and deshielding depend on the orientation of the molecule with respect to the applied magnetic field. Similar arguments can be adduced to rationalize the unexpected low-field position of the aldehydic proton. In this case, the effect of the applied magnetic field is greatest along the transverse axis of the  $C=O$  bond (i.e., in the plane of the page in Figure 13). The geometry is such that the aldehydic proton, which lies in front of the page, is in the deshielding portion of the induced magnetic field. The same argument can be used to account for at least part of the rather large amount of deshielding of olefinic protons.

The so-called "ring-current effect" is another example of diamagnetic anisotropy and accounts for the large deshielding of benzene ring protons. Figure 14 shows this effect. It also indicates that a proton held directly above or below the ring should be shielded. This has actually been found to be the case for some of the methylene protons in 1,4-polymethylenebenzenes.

All the ring protons of acetophenone are found down-

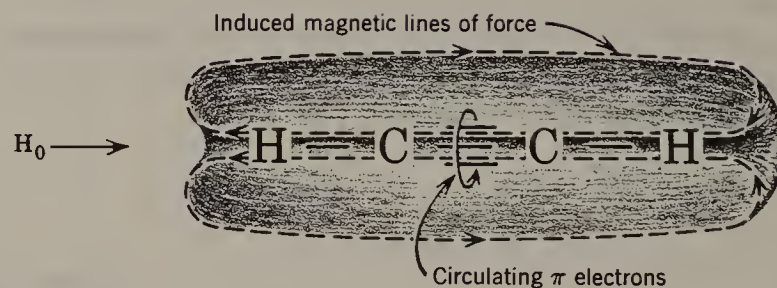


Figure 12. Shielding of acetylenic protons.

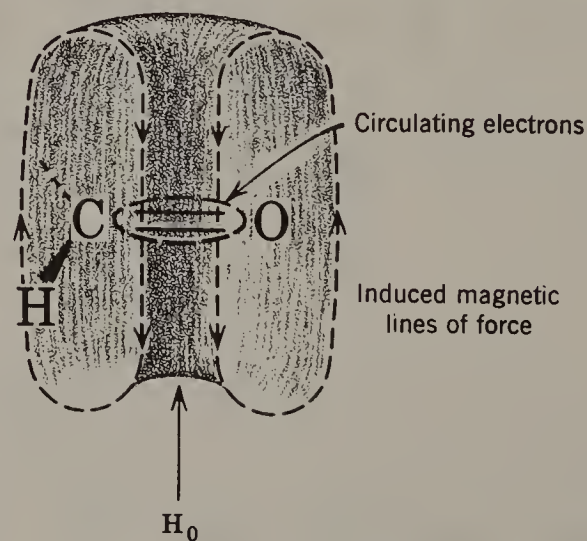


Figure 13. Deshielding of aldehydic protons.

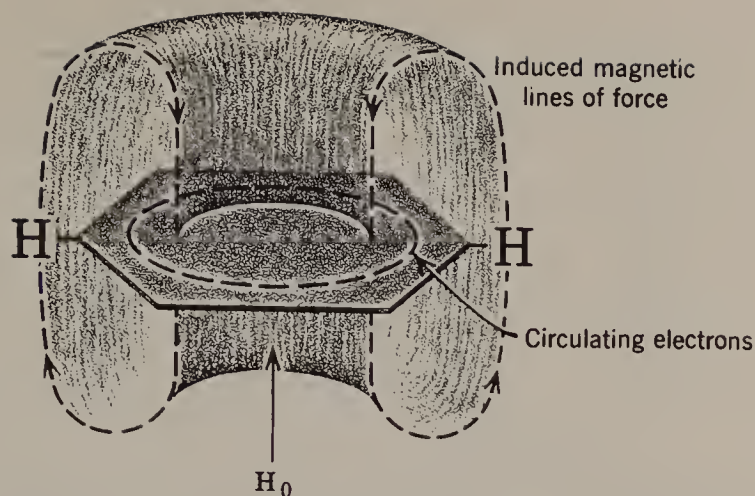


Figure 14. Ring current effects in benzene.

field because of the ring current effect. Moreover, the ortho protons are shifted slightly further downfield (meta, para  $\delta \sim 7.40$ , ortho  $\delta \sim 7.85$ ) because of the additional deshielding effect of the carbonyl group. In Figure 15 the carbonyl bond and the benzene ring are coplanar. If the molecule is oriented so that the applied magnetic field  $H_0$  is perpendicular to the plane of the molecule, the circulating  $\pi$  electrons of the C=O bond shield the conical zones above and below them, and deshield the lateral zones in which the ortho proton is located. Both ortho protons are equally deshielded since another, equally populated, conformation can be written in which the "left hand" ortho proton is deshielded by the anisotropy cone. Nitrobenzene shows a similar effect.

A spectacular example of shielding and deshielding by ring currents is furnished by some of the annulenes.<sup>17</sup> The protons outside the ring of [18]annulene are strongly deshielded ( $\delta$  8.9) and those inside are strongly shielded ( $\delta$  - 1.8).

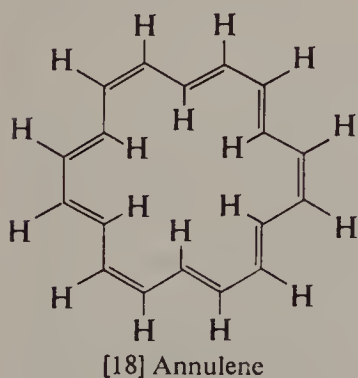


Figure 15. Shielding (+) and deshielding (-) zones of acetophenone.

produce a small effect. The axis of the C—C bond is the axis of the deshielding cone (Figure 16).

This figure accounts for the deshielding effect of successive alkyl substituents on a proton attached to a carbon atom. Thus, the protons are found progressively downfield in the sequence  $RCH_3$ ,  $R_2CH_2$ , and  $R_3CH$ . The observation that an equatorial proton is consistently found further downfield by 0.1-0.7 ppm than the axial proton on the same carbon atom in a rigid six-membered ring can also be rationalized (Figure 17). The axial and equatorial protons on  $C_1$  are oriented similarly with respect to  $C_1-C_2$  and  $C_1-C_6$ , but the equatorial proton is within the deshielding cone of the  $C_2-C_3$  bond (and  $C_5-C_6$ ).

Extensive tables and charts of chemical shifts in the Appendices give the useful impression that chemical shifts of protons in organic compounds fall roughly into eight regions as shown in Figure 18.\*

#### IV. SIMPLE SPIN-SPIN COUPLING

We have obtained a series of absorption peaks representing protons in different chemical environments, each absorp-

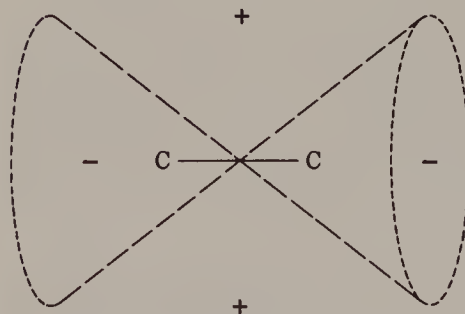


Figure 16. Shielding (+) and deshielding (-) zones of C—C.

\*A rapid method for estimating proton shifts has been published. J.A. D. Jeffreys, *J. Chem. Ed.*, 56, 806 (1979).

Demonstration of such a ring current is probably the best evidence available for aromaticity.

In contrast with the striking anisotropic effects of circulating  $\pi$  electrons, the  $\sigma$  electrons of a C—C bond



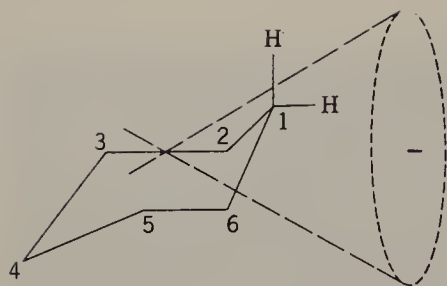


Figure 17. Deshielding of equatorial proton of a rigid six-membered ring.

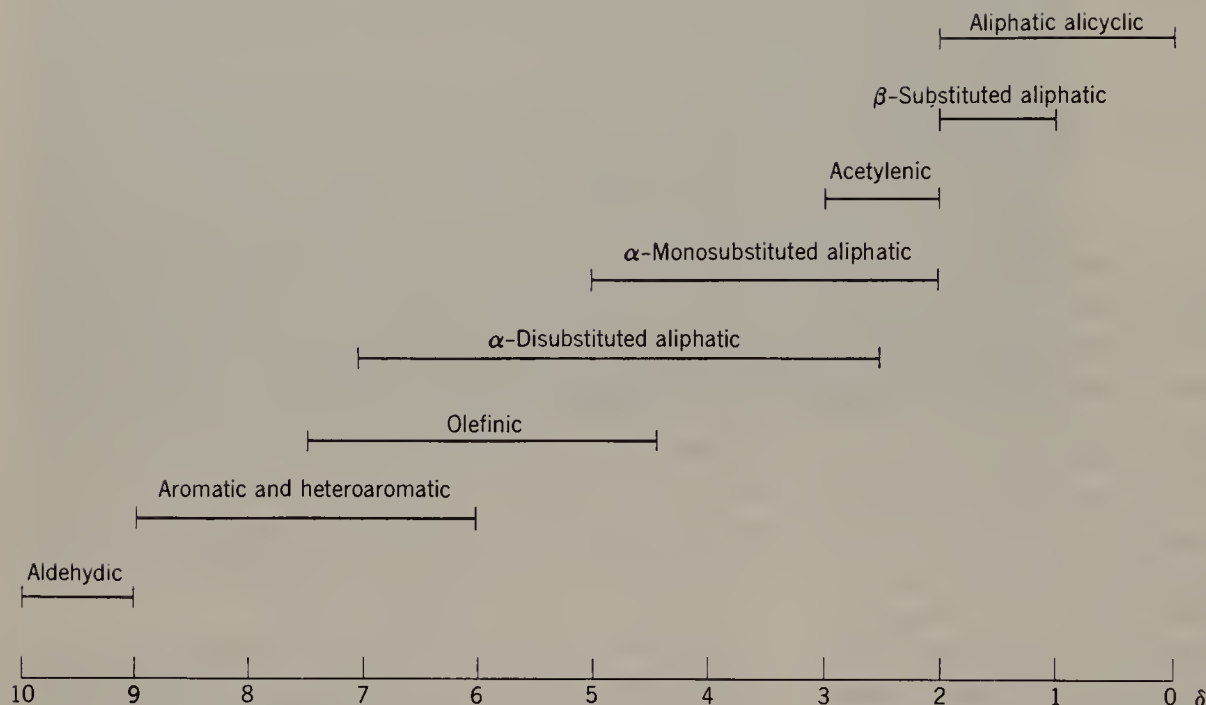


Figure 18. General regions of chemical shifts.

tion area being proportional to the number of protons it represents. We have now to consider one further phenomenon, spin-spin coupling. This can be described as the indirect coupling of proton spins through the intervening bonding electrons. Very briefly, it occurs because there is some tendency for a bonding electron to pair its spin with the spin of the nearest proton; the spin of a bonding electron having been thus influenced, the electron will affect the spin of the other bonding electron and so on through to the next proton. Coupling is ordinarily not important beyond 3 bonds unless there is ring strain as in small rings or bridged systems, or bond delocalization as in aromatic or unsaturated systems.

Suppose that two vicinal protons are in very different chemical environments from one another as in the compound  

$$\begin{array}{c} \text{OR} \quad \text{CR}_3 \\ | \quad | \\ \text{RO}-\text{CH}-\text{CH}-\text{CR}_3 \end{array}$$
 Each proton will give rise to an absorption, and the absorptions will be quite widely separated, but the spin of each proton is affected slightly by the two orientations of the other proton through the intervening electrons so that each absorption appears as a doublet

(Figure 19). The frequency differences between the component peaks of a doublet is proportional to the effectiveness of the coupling and is denoted by a coupling constant,  $J$ , which is independent of the applied magnetic field  $H_0$ . Whereas chemical shifts usually range over about 1250 Hz at 100 MHz, coupling constants between protons rarely exceed 20 Hz (see Appendix F).

So long as the chemical shift difference in Hz ( $\Delta\nu$ ) is much larger than the coupling constant ( $\Delta\nu/J$  is greater than about 10), the simple pattern of 2 doublets appears. As  $\Delta\nu/J$  becomes smaller, the doublets approach one another, the inner 2 peaks increase in intensity, and the outer two peaks decrease (Figure 20). The shift position of each proton is no longer midway between its 2 peaks as in Figure 19 but is at the "center of gravity" (Figure 21); it can be estimated with fair accuracy by inspection or determined precisely by the following formula in which the peak positions (1,2,3, and 4 from left to right) are given in Hz from TMS.

$$(1 - 3) = (2 - 4) = \sqrt{(\Delta\nu)^2 + J^2}$$



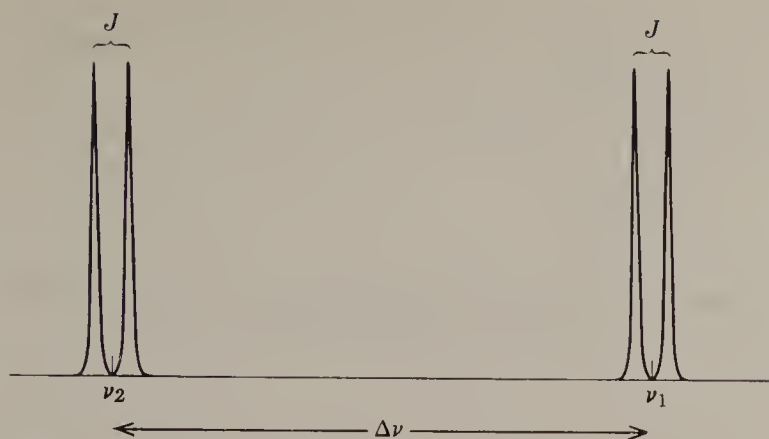


Figure 19. Spin-spin coupling between two protons with very different chemical shifts.

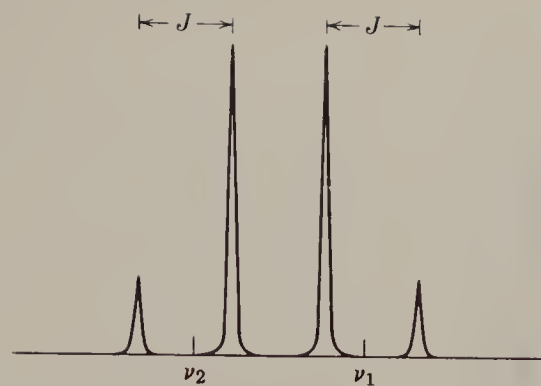


Figure 21. "Center of gravity," instead of linear mid-points, for shift position location (due to "low"  $\Delta\nu/J$  ratio).

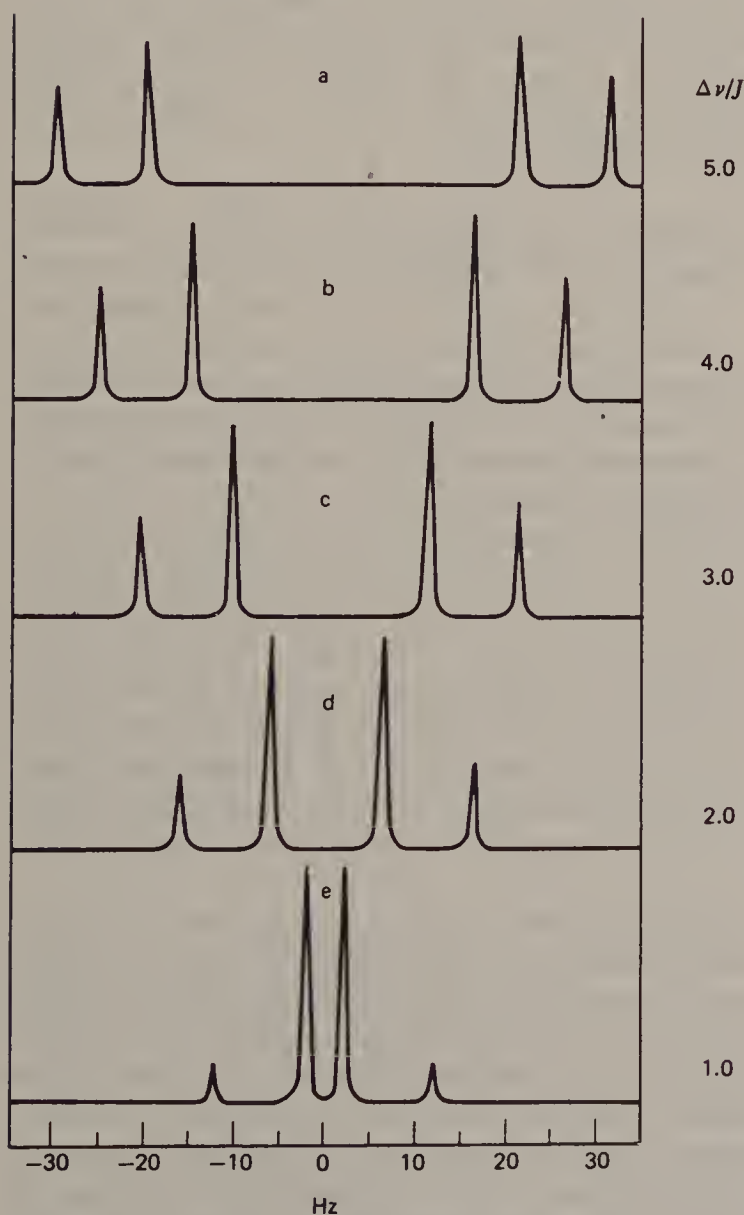


Figure 20. Change in an AX system spin coupling with a decreasing difference in chemical shifts and a large  $J$  value (10 Hz); the AX notation is explained in the text.

The shift position of each proton is  $\Delta\nu/2$  from the midpoint of the pattern. When  $\Delta\nu = J\sqrt{3}$ , the 2 pairs resemble a quartet that we shall see results from splitting by 3 equivalent vicinal protons (Figure 20d is almost at this stage). Failure to note the small outer peaks (i.e., 1 and 4) may lead to mistaking the 2 large inner peaks for a doublet (Figure 20e is almost at this stage). When the chemical shift difference becomes zero, the middle peaks coalesce to give a single peak, and the end peaks vanish; that is, the protons are equivalent. (Equivalent protons do spin-spin couple with one another, but splitting is not observed). A further point to be noted is the obvious one that the spacing between the peaks of 2 coupled multiplets is the same.

The dependence of chemical shift on the applied magnetic field and the independence of the spin-spin coupling afford a method of distinguishing between them. The spectrum is merely run on two different instruments, for example at 60 MHz and 100 MHz. Chemical shifts are also solvent dependent, but  $J$  values are usually only slightly affected by change of solvent, at least to a far lesser degree than are chemical shifts.

The chemical shifts of the methyl and acetylenic protons of methylacetylene are (fortuitously) coincident ( $\delta$  1.80) when the spectrum is obtained in a  $\text{CDCl}_3$  solvent, whereas the spectrum of a neat sample of this alkyne shows the acetylenic proton at  $\delta$  1.80 and the methyl protons at  $\delta$  1.76. Figure 22 illustrates the chemical shift dependence of the protons of biacetyl on solvent. The change from a chlorinated solvent (e.g.,  $\text{CDCl}_3$ ) to an aromatic solvent (e.g.,  $\text{C}_6\text{D}_6$ ) often drastically influences the position and appearance of NMR signals.

Look at the next stage in complexity of spin-spin coupling (Figure 23). Consider the system  $-\text{HC}-\text{CH}_2-$  in the

OR  
 $\text{RO}-\text{CH}-\text{CH}_2-\text{CR}_3$

in which the single methine proton is in a very different chemical environment from the 2 methylene protons. As before, we see 2 sets of absorp-

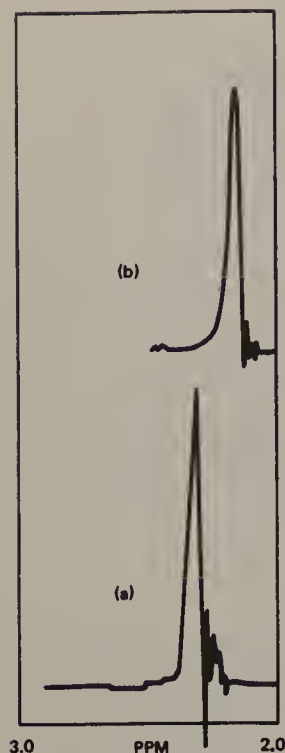


Figure 22. The NMR spectrum of biacetyl (2,3-butanedione): a. in  $\text{CDCl}_3$ ; b. in  $\text{C}_6\text{D}_6$ .

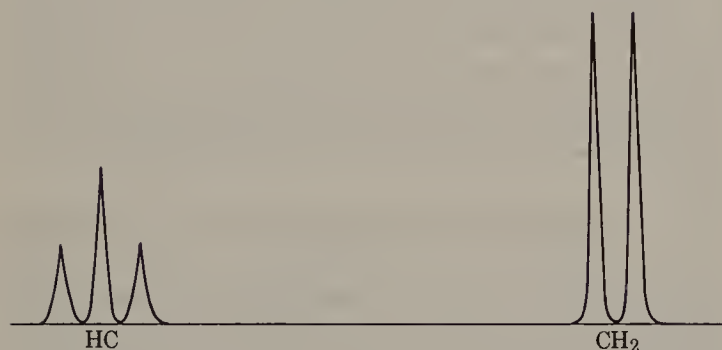


Figure 23. Spin-spin coupling between  $\text{CH}$  and  $\text{CH}_2$  with very different chemical shifts.

tions widely separated, and now the absorption areas are in the ratio of 1:2. The methine proton couples with the methylene protons and splits the methylene proton absorption into a symmetrical doublet, as explained above. The 2 methylene protons split the methine proton absorption into a triplet because 3 combinations of proton spins exist in the two methylene protons ( $a$  and  $b$ ) of Figure 24. Since there are 2 equivalent combinations of spin (pairs 2 and 3) that do not produce any net opposing or concerted field relative to the applied field, there is an absorption of relative intensity 2 at the center of the multiplet. Since there are single pairs (1 and 4) respectively opposed and in concert with the applied field, there are equally spaced ( $J$ ) lines of relative intensity 1 upfield and 1 downfield from the center line. In summary, the intensities of the peaks in the triplet are in the ratio 1:2:1.

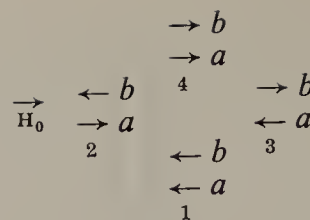


Figure 24. Energy levels for the 3 spin states of a methylene group (protons  $a$  and  $b$ ).

When the methine and methylene protons in the system  $-\text{CH}-\text{CH}_2-$  are in similar environments (i.e.,  $\Delta\nu/J$  is small), the simple doublet-triplet pattern degenerates to a complex pattern of from 7 to 9 lines as a result of second-order splitting; analysis by inspection is no longer possible, since the peak spacings may not correspond to the coupling constants.

Simple splitting patterns that are produced by the coupling of protons that have very different chemical shifts ( $\Delta\nu/J$  is greater than about 10 or so) are called *first-order* splitting patterns. These can usually be interpreted by using two rules:

1. Splitting of a proton absorption is done by neighboring protons, and the multiplicity of the split is determined by the number of these protons. Thus, 1 proton causes a doublet, and 2 equally coupled neighboring protons cause a triplet. The multiplicity then is  $n + 1$ ,  $n$  being the number of neighboring equally coupled protons. The general formula, which covers all nuclei, is  $2nI + 1$ ,  $I$  being the spin number.
2. The relative intensities of the peaks of a multiplet also depend on  $n$ . We have seen that doublet ( $n = 1$ ) peaks are in the ratio 1:1, and triplet peaks are in the ratio 1:2:1. Quartets are in the ratio 1:3:3:1. The general formula is  $(a + b)^n$ ; when this is expanded to the desired value of  $n$ , the coefficients give the relative intensities. The multiplicity and relative intensities may be easily obtained from Pascal's triangle (Figure 25), in which  $n$  is the number of equivalently coupled protons.

Following Pople<sup>14</sup>, we place protons that have the same chemical shift into sets (see Section VII), and we designate sets of protons separated by a small chemical shift with the letters  $A$ ,  $B$ , and  $C$ , and sets separated by a large chemical shift ( $\Delta\nu/J > \sim 10$ ) with the letters  $A$ ,  $M$ , and  $X$ . The number of protons in each set is denoted by a subscript number. Thus, the first case we examined (Figure 19) is an  $AX$  system. The second case (Figure 21) is an  $AB$  system, and the third case (Figure 23) is an  $A_2X$  system. As  $\Delta\nu/J$  decreases, the  $A_2X$  system approaches an  $A_2B$  system, and the simple first-order splitting of the  $A_2X$  system becomes more complex (see Section VII).

Thus far, we have dealt with 2 sets of protons; every proton in each set is equally coupled to every proton in the

| <i>n</i> | Relative intensity     |
|----------|------------------------|
| 0        | 1                      |
| 1        | 1 1                    |
| 2        | 1 2 1                  |
| 3        | 1 3 3 1                |
| 4        | 1 4 6 4 1              |
| 5        | 1 5 10 10 5 1          |
| 6        | 1 6 15 20 15 6 1       |
| 7        | 1 7 21 35 35 21 7 1    |
| 8        | 1 8 28 56 70 56 28 8 1 |

Figure 25. Pascal's triangle. Relative intensities of first-order multiplets; *n* = no. of coupling nuclei of spin 1/2 (e.g., protons).

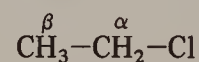
other set, that is, a single coupling constant is involved. Given these conditions and the conditions that  $\Delta\nu/J$  be large (about 10), the two rules above apply, and we obtain a first-order pattern. In general, these are the  $A_aX_x$  systems (a and x are the number of protons in each set); the first-order rules apply only to these systems, but as we have seen, there is a gradual change in the appearances of spectra changing from an  $AX$  to an  $AB$  pattern. In a similar way, it is frequently possible to relate complex patterns back to first-order patterns. With practice, a fair amount of deviation from first-order may be tolerated. Wiberg's collection of calculated spectra<sup>27</sup> can be used to match fairly complex splitting patterns.

A system of 3 sets of protons, each set separated by a large chemical shift, can be designated  $A_aM_mX_x$ . If 2 sets are separated from each other by a small chemical shift, and the third set is widely separated from the other two, we use an  $A_aB_bX_x$  designation. If all shift positions are close, the system is  $A_aB_bC_c$ . Both end sets may be coupled to the middle set with the same or different coupling constants, whereas the end sets may or may not be coupled to one another.  $AMX$  systems are first-order;  $ABX$  systems approximate first-order, but  $ABC$  systems cannot be analyzed by inspection. These more complex patterns are treated in Section VIII.

We can now appreciate the three main features of an NMR spectrum: chemical shifts, peak intensities, and spin-spin couplings that are first-order or that approximate

first-order patterns. We can now analyze first-order NMR spectra.

The 60 MHz NMR spectrum of ethyl chloride is shown in Figure 26. The peak at  $\delta$  0.00 is the internal reference tetramethylsilane (TMS) and that at  $\delta$  7.25 is the  $\text{CHCl}_3$  impurity in the  $\text{CDCl}_3$  solvent. The methylene group ( $\alpha$ )



( $\delta$  3.57) is more deshielded by the chlorine than is the methyl group ( $\delta$  1.48), and thus the methylene group is downfield (higher  $\delta$ ) from the methyl by 2.09 ppm or about 125 Hz. Since the coupling is about 9 Hz,  $\Delta\nu/J$  is about 14, a large enough ratio for first order analysis. The system is  $A_3X_2$ , and the first order rules correctly predict a triplet and a quartet with relative intensities (see integration "steps") of 3 to 2 corresponding to the number of protons causing the absorptions. Note that even at  $\Delta\nu/J = 14$  there is a "leaning" of the two interacting signals toward each other; that is, the intensity of the upfield lines of the methylene signal and the downfield lines of the methyl signal are somewhat larger than they would be if these signals were perfectly symmetrical. This fact, together with the same spacing in both multiplets, is valuable in identifying interacting proton signals in more complex spectra.

We stated earlier that "the peak area (measured by the integrator) is proportional to the number of protons it represents." The "steps" in the integration curve in Figure



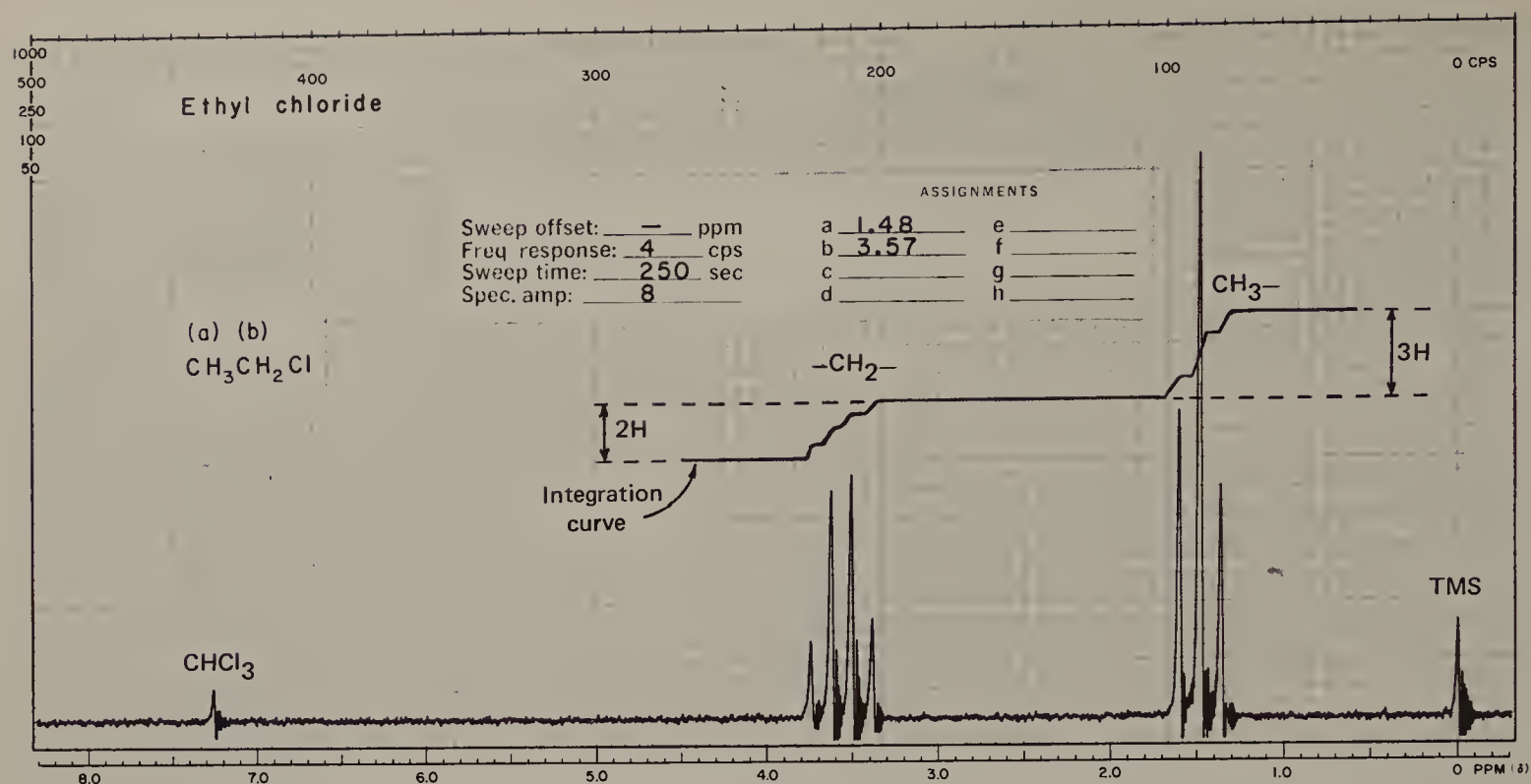


Figure 26. Ethyl chloride in  $\text{CDCl}_3$  at 60 MHz. (Courtesy of Varian Associates, Palo Alto, Calif.)

26 thus provide the ratios of the different kinds of protons in the molecule. This count can be compared with the proton count obtained from the off-resonance decoupled  $^{13}\text{C}$  spectrum (Chapter 5).

Consider the NMR spectrum of cumene in Figure 27. The five aromatic protons,  $\delta$  7.25, although actually not chemical shift equivalent (see Section VII), are fortuitously equivalent and occur as a single absorption downfield from the remaining absorptions (because of the benzene ring current, Figure 14). The side chain is treated as an  $A_6X$  system. The methyl signal occurs as a doublet at  $\delta$  1.25, the methine proton as a 1:6:15:20:15:6:1 septet at  $\delta$  2.90. Note that this signal is completely seen only when the sample is run at high gain (upper lines). Outer lines of complex multiplets may be overlooked, especially when these lines are part of a single proton absorption and when base line noise is substantial.

The vicinal coupling described ( $\text{H}-\text{C}-\text{C}-\text{H}$ ) involves 3 bonds and can be designated by  $J_{\text{HCCH}}$  or  $^3J$ . When geminal protons are not "equivalent" to one another (Section VII), we see coupling designated as  $J_{\text{HCH}}$  or  $^2J$ .

## V. PROTONS ON HETEROATOMS

Protons on a heteroatom differ from protons on a carbon atom in that: (1) they are exchangeable, (2) they are subject to hydrogen bonding, and (3) they are subject to partial or complete decoupling by electrical quadrupole

effects of some heteroatoms. Shift ranges for protons on heteroatoms are given in Appendix E.

## PROTONS ON OXYGEN

### Alcohols

Unless special precautions are taken (see below) the spectrum of neat ethanol usually shows the hydroxylic proton as a slightly broadened peak at  $\delta$  5.35. At the commonly used concentration of about 5 to 20% in a nonpolar solvent, such as carbon tetrachloride or deuteriochloroform, the hydroxylic peak is found between  $\delta$  2 and  $\delta$  4. On extrapolation to infinite dilution or in the vapor phase, the peak is near  $\delta$  0.5. A change in solvent or temperature will also shift the hydroxylic peak.

Hydrogen bonding explains why the shift position of the hydroxylic proton depends on concentration, temperature, and solvent. Hydrogen bonding decreases the electron density around the proton, and thus moves the proton absorption to lower field. The extent of intermolecular hydrogen bonding is decreased by dilution with a nonpolar solvent and with increased temperature. Polar solvents introduce the additional complication of hydrogen bonding between the hydroxylic proton and the solvent. Intramolecular hydrogen bonds are less affected by their environment than are intermolecular hydrogen bonds. In fact the enolic

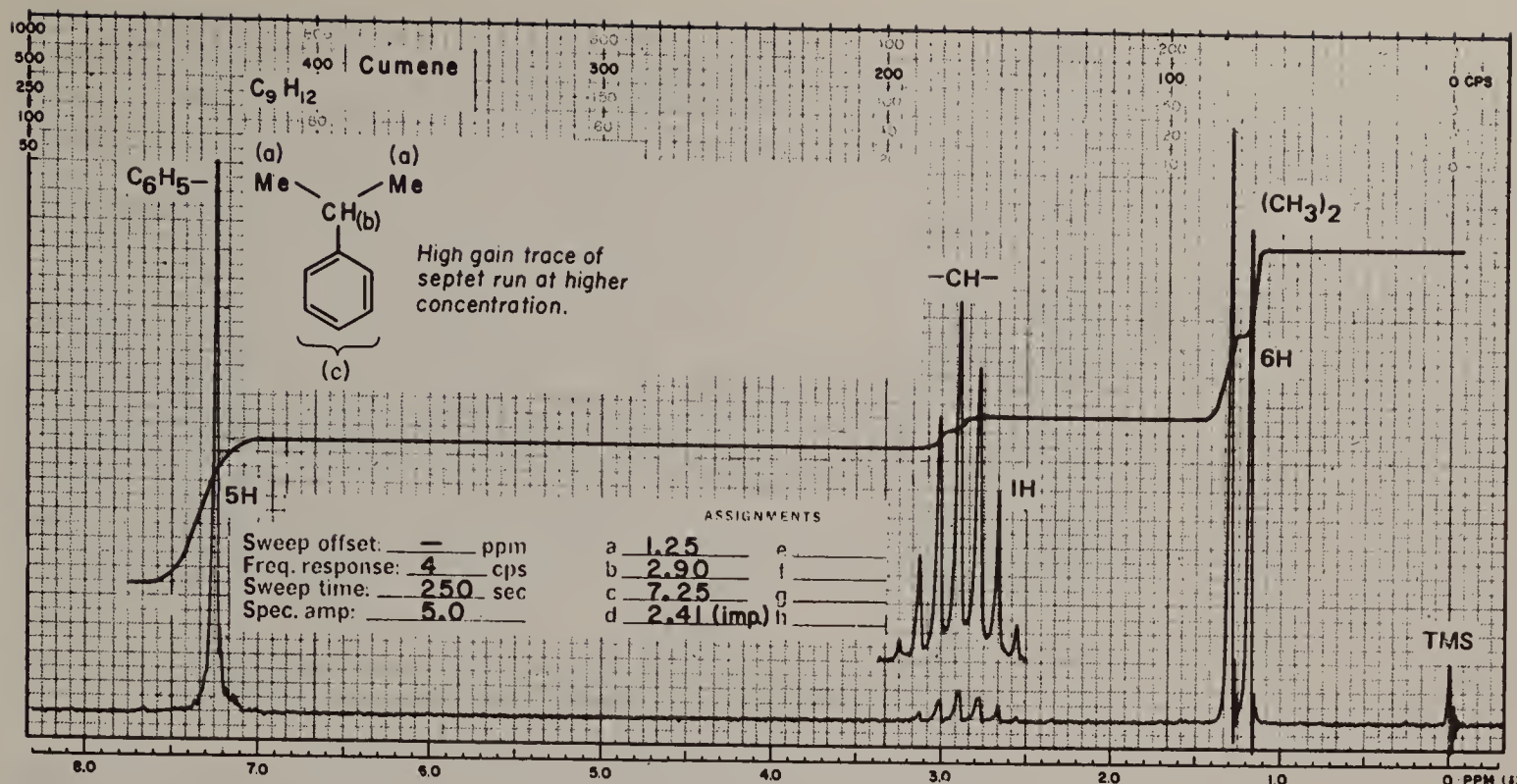
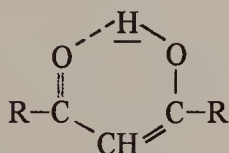


Figure 27. Cumene in  $\text{CDCl}_3$  at 60 MHz. (Courtesy of Varian Associates, Palo Alto, Calif.)

hydroxylic absorption of  $\beta$ -diketones



for example, is hardly affected by change of concentration or solvent, though it can be shifted upfield somewhat by warming. NMR spectrometry is a powerful tool for studying hydrogen bonding.

Exchangeability explains why the hydroxylic peak of ethanol is usually seen as a singlet. Under ordinary conditions, enough acidic impurities are present in solution to catalyze rapid exchange of the hydroxylic proton. The proton is not on the oxygen atom long enough for it to be affected by the three states of the methylene protons, and there is no coupling. The rate of exchange can be decreased by treating the solution or the solvent with anhydrous sodium carbonate, alumina, or molecular sieves immediately before obtaining the spectrum. Purified deuterated dimethyl sulfoxide or acetone, in addition to allowing a lower rate of exchange, shifts the hydroxylic proton to lower field, even in dilute solution, by hydrogen bonding between solute and solvent.\* Since the hydroxylic proton can now couple with the protons on the  $\alpha$ -carbon,

a primary alcohol will show a triplet, a secondary alcohol a doublet, and a tertiary alcohol a singlet. This is illustrated in Figure 28 and a list of successful applications is given in Table I. Exceptions have been reported, but these may be due to the concentration dependence of this phenome-

Table I. Hydroxyl Proton Resonances in Dimethyl Sulfoxide\*

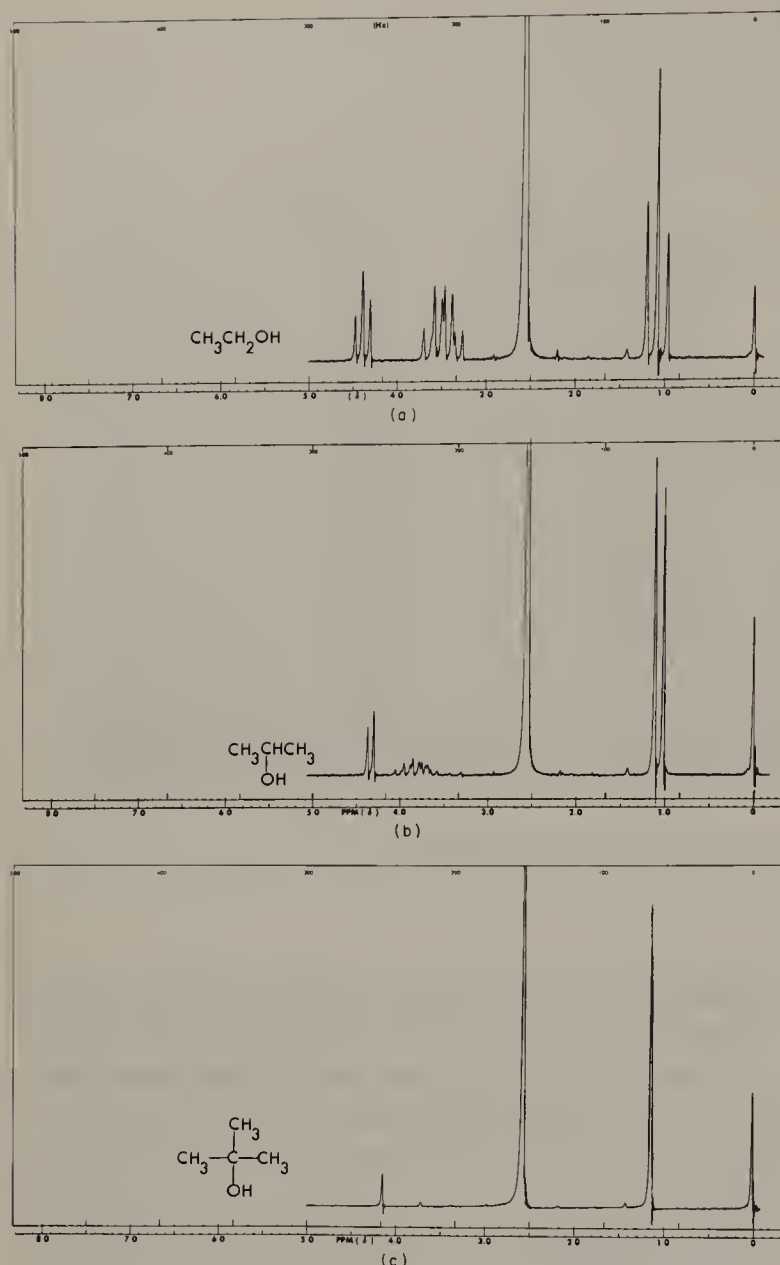
| Compound <sup>a</sup>                              | Chemical Shift, $\delta$ | Multiplicity |
|--|--------------------------|--------------|
| Methanol   | 4.08                     | q            |
| Ethanol  | 4.35                     | t            |
| Isopropyl alcohol                                  | 4.35                     | d            |
| <i>t</i> -Butyl alcohol                            | 4.16                     | s            |
| <i>t</i> -Pentyl alcohol                           | 3.99                     | s            |
| Propylene glycol, 1-OH                             | 4.45                     | t            |
| 2-OH   | 4.38                     | d            |
| Cyclohexanol                                       | 4.38                     | d            |
| <i>cis</i> -4- <i>t</i> -Butylcyclohexyl alcohol   | 4.11                     | d            |
| <i>trans</i> -4- <i>t</i> -Butylcyclohexyl alcohol | 4.45                     | d            |
| Benzyl alcohol                                     | 5.16                     | t            |
| Phenol   | 9.25                     | s            |
| $\beta$ -L-Arabinopyranose, O-C-OH                 | 5.98                     | d            |
| $\alpha$ -D-Glucopyranose, O-C-OH                  | 6.16                     | d            |
| $\alpha$ -D-Fructopyranose, O-C-OH                 | 5.12                     | s            |

\*All spectra were taken of dimethyl sulfoxide solutions with concentrations 10 mole % or less.

\*O. L. Chapman and R. W. King, *J. Am. Chem. Soc.* 86, 1256(1964).  
D. E. McGreer and M. M. Mocek, *J. Chem. Ed.* 40, 358(1963).

\*O. L. Chapman and R.W. King, *J. Am. Chem. Soc.*, 86, 1256 (1964).





**Figure 28.** NMR spectra of typical primary, secondary, and tertiary alcohols run in dimethyl sulfoxide. Absorption at  $\delta$  2.6 is due to dimethyl sulfoxide.

Source: Daniel J. Pasto and Carl R. Johnson, *Organic Structure Determination*, © 1969, pp. 358-359. Reprinted by permission of Prentice-Hall, Inc., Englewood Cliffs, N.J.)

non. At intermediate rates of exchange, the multiplet merges into a broad absorption band; at this point, the exchange rate in Hz is equal to  $\pi J/\sqrt{2}$ .

If water is present in the alcohol solution, rapid interchange results in a single peak at a position intermediate between the actual shift positions of the HOH and ROH peaks. Of course, the presence of water is reflected in the integration for the single peak.

A dihydroxy alcohol may show separate absorption peaks for each hydroxylic proton; in this case, the rate of exchange in Hz is much less than the difference in Hz between the separate absorptions. As the rate increases

(trace of acid catalyst), the two absorption peaks broaden, then merge to form a single broad peak; at this point, the exchange rate in Hz is equal to the original separation in Hz. As the rate increases, the single peak becomes sharper. The relative position of each peak depends on the extent of hydrogen bonding of each hydroxylic proton; steric hindrance to hydrogen bonding frequently accounts for a relative upfield absorption.

The spectrum of a compound containing exchangeable protons can be simplified, and the exchangeable proton absorption removed, simply by shaking the solution with excess deuterium oxide or by obtaining a spectrum in deuterium oxide solution if the compound is soluble. A peak due to HOD will appear, generally between  $\delta$  5 and  $\delta$  4.5 in nonpolar solvents, and near  $\delta$  3.3 in dimethyl sulfoxide (see Appendix E). A  $\text{CDCl}_3$  or  $\text{CCl}_4$  solution in the NMR tube may be shaken vigorously for several minutes with 1 or 2 drops of  $\text{D}_2\text{O}$ , and the mixture allowed to stand (or centrifuged) until the layers are clearly separated. The top aqueous layer does not interfere.

Acetylation or benzylation of a hydroxyl group moves the carbonyl protons of a primary alcohol downfield about 0.5 ppm, and that of a secondary alcohol about 1.0-1.2 ppm. Such shifts provide a confirmation of the presence of a primary or secondary alcohol.

### Phenols

The behavior of a phenolic proton resembles that of an alcoholic proton. The phenolic proton peak is usually a sharp singlet (rapid exchange, no coupling), and its range, depending on concentration, solvent, and temperature, is generally downfield ( $\delta$  ~7.5 -  $\delta$  ~4.0) compared with the alcoholic proton. This is illustrated in Figure 29. Note the concentration dependence of the OH peak. A carbonyl group in the ortho position shifts the phenolic proton absorption downfield to the range of about  $\delta$  12.0 -  $\delta$  10.0 because of intramolecular hydrogen bonding. Thus, *o*-hydroxyacetophenone shows a peak at about  $\delta$  12.05 almost completely invariant with concentration. The much weaker intramolecular hydrogen bonding in *o*-chlorophenol explains its shift range ( $\delta$  ~6.3 at 1 molar concentration to  $\delta$  ~5.6 at infinite dilution), which is broad compared with that of *o*-hydroxyacetophenone but narrow compared with that of phenol.

### Enols

Enols are usually stabilized by intramolecular hydrogen bonding, which varies from very strong in aliphatic  $\beta$ -diketones to weak in cyclic  $\alpha$ -diketones. The enolic proton is downfield relative to alcohol protons and, in the case of the enolic form of some  $\beta$ -diketones, may be found as far downfield as  $\delta$  16.6 (the enolic proton of acetylacetone



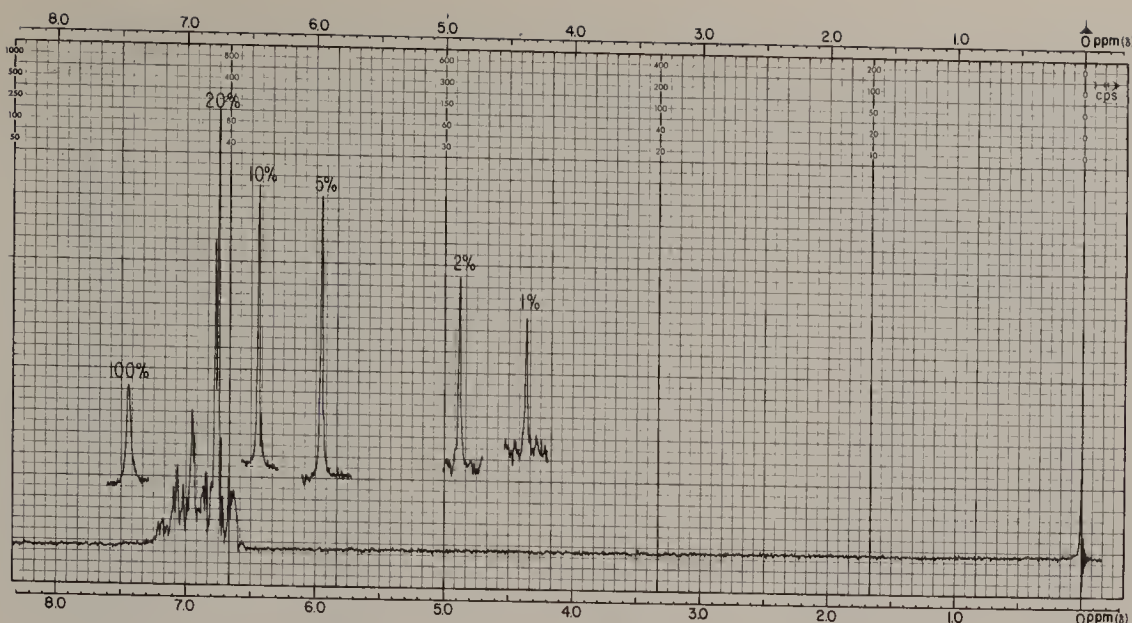


Figure 29. Phenol, in  $\text{CCl}_4$ , at various w/v %, at 60 MHz. Complete sweep is at 20%; single absorptions represent the OH proton at the indicated w/v %.

Source: J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds*, copyright 1965, p. 90. Reprinted by permission of Prentice-Hall, Inc., Englewood Cliffs, N.J.

absorbs at  $\delta$  15.0 and that of dibenzoylmethane at  $\delta$  16.6). The enolic proton peak is frequently broad at room temperature because of slow exchange. Furthermore, the keto-enol conversion is slow enough so that absorption peaks of both forms can be observed, and the equilibrium measured.

When strong intramolecular bonding is not involved, the enolic proton absorbs in about the same range as the phenolic proton.

### Carboxylic Acids

Carboxylic acids exist as stable hydrogen-bonded dimers in nonpolar solvents even at high dilution. The carboxylic proton therefore absorbs in a characteristically narrow range,  $\delta \sim 13.2$  to  $\delta \sim 10.0$ , and is affected only slightly by concentration. Polar solvents partially disrupt the dimer and shift the peak accordingly.

The peak width at room temperature ranges from sharp to broad, depending on the exchange rate of the particular acid. The carboxylic proton exchanges quite rapidly with protons of water and alcohols (or hydroxyl groups of hydroxy acids) to give a single peak whose position depends on concentration. Sulfhydryl or enolic protons do not exchange rapidly with carboxylic protons, and individual peaks are observed.

## PROTONS ON NITROGEN

The  $^{14}\text{N}$  nucleus has a spin number  $I = 1$  and, in accordance with the formula  $2I + 1$ , should cause a proton attached to

it and a proton on an adjacent carbon atom to show three equally intense peaks. There are two factors, however, that complicate the picture: the rate of exchange of the proton on the nitrogen atom, and the electrical quadrupole moment of the  $^{14}\text{N}$  nucleus.

The proton on a nitrogen atom may undergo rapid, intermediate, or slow exchange. If the exchange is rapid, the NH proton(s) is decoupled from the N atom and from protons on adjacent carbon atoms. The NH peak is therefore a sharp singlet, and the adjacent CH protons are not split by NH. Such is the case for most aliphatic amines.\* At an intermediate rate of exchange, the NH proton is partially decoupled, and a broad NH peak results. The adjacent CH protons are not split by the NH proton. Such is the case for *N*-methyl-*p*-nitroaniline. If the NH exchange rate is low, the NH peak is still broad because the electrical quadrupole moment of the nitrogen nucleus induces a moderately efficient spin relaxation and, thus, an intermediate lifetime for the spin states of the nitrogen nucleus. The proton thus sees three spin states of the nitrogen nucleus (spin number = 1) which are changing at a moderate rate, and the proton responds by giving a broad peak. In this case, coupling of the NH proton to the adjacent protons is observed. Such is the case for pyrroles, indoles, secondary and primary amides, and carbamates (Figure 30). Note that H-N-C-H coupling takes place through the C-H, C-N, and N-H bonds, but coupling between nitro-

\*H-C-N-H coupling in several amines has been observed following rigorous removal (with Na-K alloy) of traces of water. This effectively stops proton exchange on the NMR time scale (K. L. Henold, *Chem. Comm.* 1340 (1970)).

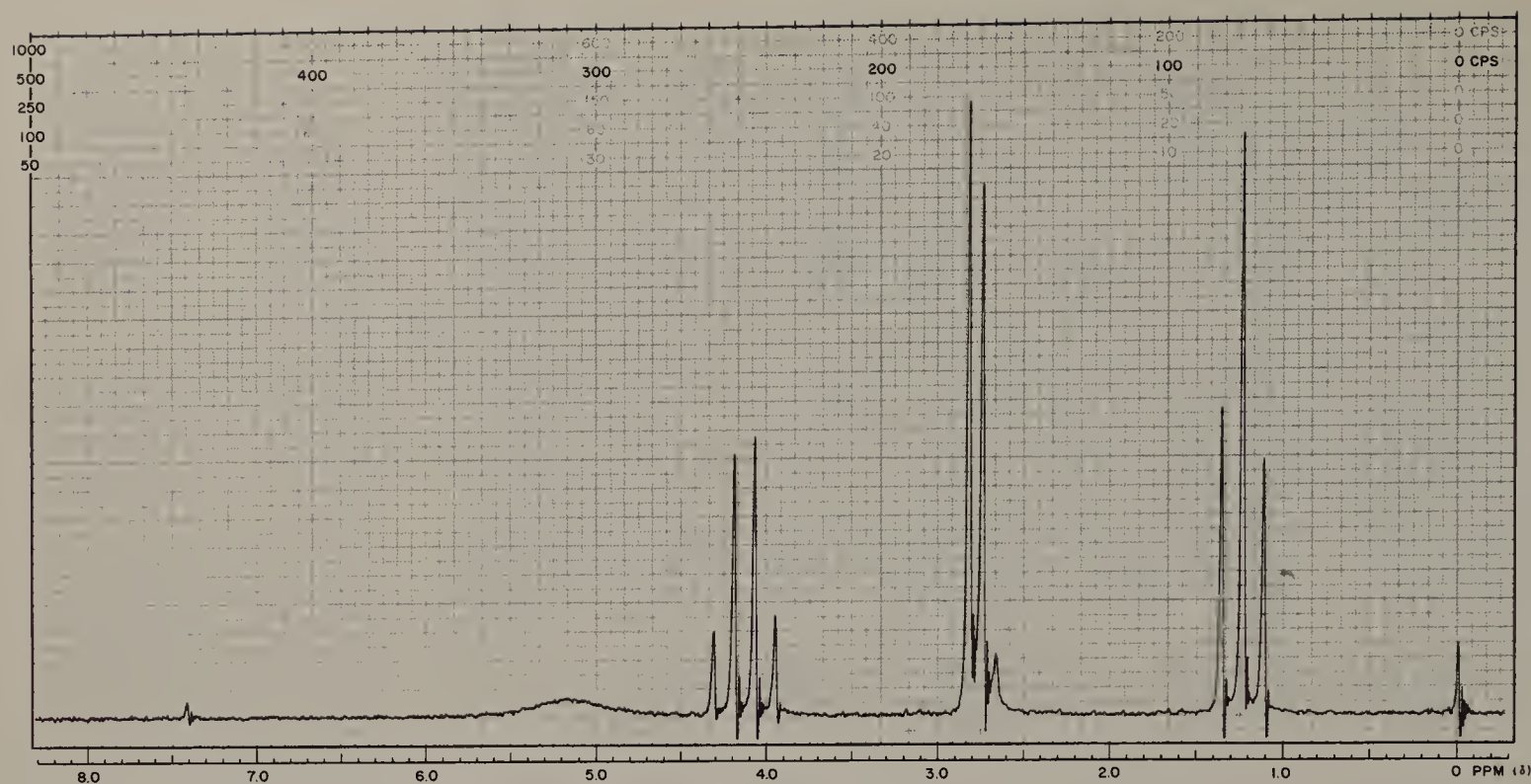


Figure 30. Ethyl *N*-methylcarbamate,  $\text{CH}_3\text{NHCOCH}_2\text{CH}_3$ , 60 MHz.



gen and protons on adjacent carbons is negligible. The coupling is observed in the signal due to hydrogen on carbon; the N-H proton signal is severely broadened by the quadrupolar interaction with nitrogen. In the spectrum of ethyl *N*-methylcarbamate (Figure 30)  $\text{CH}_3\text{NHCOCH}_2\text{CH}_3$ ,



the NH proton shows a broad absorption centered about  $\delta$  5.16, and the N-CH<sub>3</sub> absorption at  $\delta$  2.78 is split into a doublet ( $J \sim 5$  Hz) by the NH proton. The ethoxy protons are represented by the triplet at  $\delta$  1.23 and the quartet at  $\delta$  4.14. The small peak at  $\delta$  2.67 is an impurity.

Aliphatic and cyclic amine NH protons absorb from  $\delta \sim 3.0$ - $\delta \sim 0.5$ ; aromatic amines absorb from  $\delta \sim 5.0$ - $\delta \sim 3.0$ . Because amines are subject to hydrogen bonding, the shift position depends on concentration, solvent, and temperature. Amides, pyrroles, and indoles absorb from  $\delta \sim 8.5$ - $\delta \sim 5.0$ ; the effect on the absorption position of concentration, solvent, and temperature is generally smaller than in the case of amines. The nonequivalence of the protons on the nitrogen atom of a primary amide and of the methyl groups of *N,N*-dimethylamides is caused by hindered rotation around the C-N bond because of the

contribution of the resonance form  $\begin{array}{c} \parallel \\ \text{O} \\ \text{C}=\text{N}^+ \\ | \\ \text{O}^- \end{array}$ .

Protons on the nitrogen atom of an amine salt exchange at a low rate; they are seen as a broad peak downfield ( $\delta \sim 8.5$ - $\delta \sim 6.0$ ), and they are coupled to protons on adjacent carbon atoms ( $J \sim 7$  Hz); the  $\alpha$ -protons are recognized by

their downfield position in the salt compared with that in the free amine. The use of trifluoroacetic acid as both a protonating agent and a solvent frequently allows classification of amines as primary, secondary, or tertiary. This is illustrated in Table II in which the number of protons on nitrogen determines the multiplicity of the methylene unit in the salt (Figure 31). Sometimes the broad  $^+\text{NH}$ ,  $^+\text{NH}_2$ , or  $^+\text{NH}_3$  absorption can be seen to consist of three broad humps. These humps represent splitting by the nitrogen nucleus ( $J \sim 50$  Hz). With good resolution, it is sometimes possible to observe splitting of each of the humps by the protons on adjacent carbon atoms ( $J \sim 7$  Hz).

## PROTONS ON SULFUR

Sulfhydryl protons usually exchange at a low rate so that at room temperature they are coupled to protons on adja-

Table II. Classification of Amines by NMR of Their Ammonium Salts in Trifluoroacetic Acid\*

| Amine Precursor Class | Ammonium Salt Structure                                | Multiplicity of Methylene Unit |
|-----------------------|--|--------------------------------|
| Primary               | $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+$         | Quartet (Figure 31)            |
| Secondary             | $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2\text{R}^+$ | Triplet                        |
| Tertiary              | $\text{C}_6\text{H}_5\text{CH}_2\text{NHR}_2^+$        | Doublet                        |

\*W.R. Anderson, Jr., and R.M. Silverstein, *Anal. Chem.*, **37** 1417 (1965).





**Figure 31.** NMR spectrum of  $\alpha$  methylene unit of a primary amine in  $\text{CF}_3\text{CO}_2\text{H}$ ; corresponds to Table II, first line.

cent carbons ( $J \sim 8$  Hz). Nor do they exchange rapidly with hydroxyl, carboxylic, or enolic protons on the same or on other molecules; thus, separate peaks are seen. However, exchange is rapid enough that shaking for a few minutes with deuterium oxide replaces sulfhydryl protons with deuterium. The absorption range for aliphatic sulfhydryl protons is  $\delta \sim 1.6$ – $\delta \sim 1.2$ . for aromatic sulfhydryl protons,  $\delta \sim 3.6$ – $\delta \sim 2.8$ . Concentration, solvent, and temperature affect the position within these ranges.

## PROTONS ON HALOGENS

Chlorine, bromine, and iodine nuclei are completely decoupled from protons directly attached, or on adjacent carbon atoms, because of strong electrical quadrupole moments.

The  $^{19}\text{F}$  atom has a spin number of  $1/2$  and couples strongly with protons (see Appendix F). The rules for coupling of protons with fluorine are the same as for proton-proton coupling; in general, the proton-fluorine coupling constants are somewhat larger, and long-range effects are frequently found. The  $^{19}\text{F}$  nucleus can be observed at 56.4 MHz at 14,092 gauss. Of course, its spin is split by proton and fluorine spins, and the multiplicity rules are the same as those observed in proton spectra.

## VI. COUPLING OF PROTONS TO OTHER NUCLEI

The organic chemist may encounter proton coupling with such other nuclei (besides  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{14}\text{N}$ ) as  $^{31}\text{P}$ ,  $^{13}\text{C}$ ,

$^2\text{H}$ , and  $^{29}\text{Si}$ . Three factors must be considered: natural abundance, spin number, and electrical quadrupole moment; the nuclear magnetic moment and relative sensitivity are important when a spectrum of the particular nucleus is considered. These properties are listed for a number of nuclei in Appendix I.

The magnetogyric ratio,  $\gamma$ , describes the combined effect of the magnetic moment and spin number of a given type of nucleus. The ratio of the magnetogyric ratios of one type of nucleus to that of another type of nucleus is a measure of the relative coupling constants of those two nuclei to a given reference nucleus. Consider the relative magnitudes of coupling of hydrogen and of deuterium, D, to a particular nucleus, X. Since

$$\frac{J_{\text{HX}}}{J_{\text{DX}}} \sim \frac{\gamma_{\text{H}}}{\gamma_{\text{D}}}$$

we calculate from the magnetogyric ratios in Appendix I that

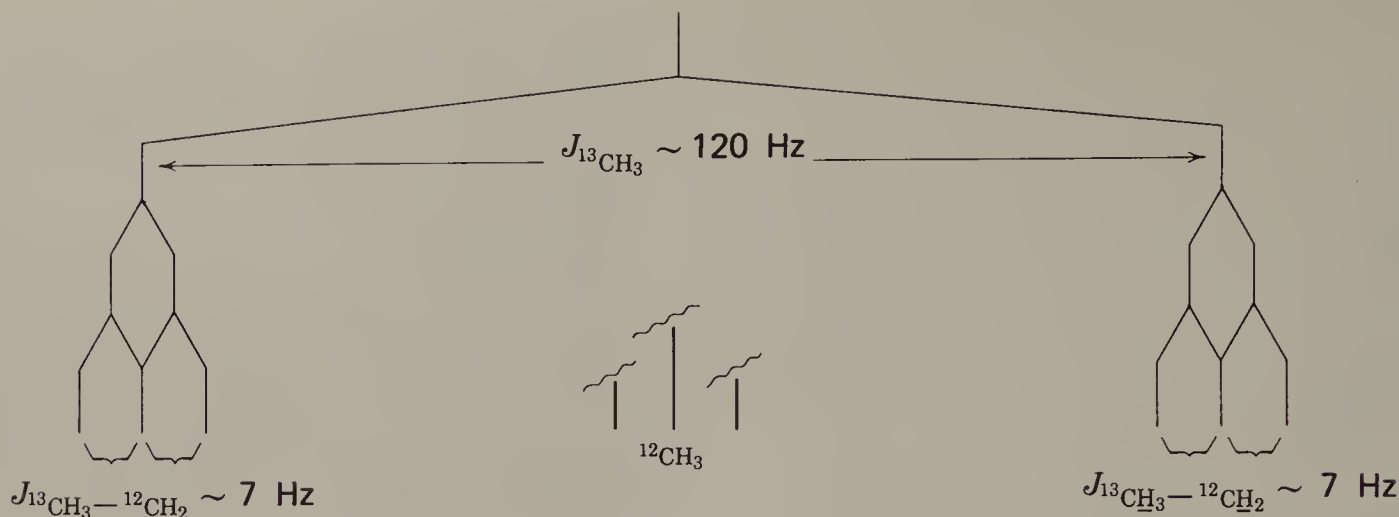
$$\frac{J_{\text{HX}}}{J_{\text{DX}}} = \sim \frac{26.753}{4.107} = 6.51$$

Thus, it is anticipated that deuterium coupling is less than the corresponding hydrogen coupling by a factor of about 6.5.

$^{31}\text{P}$  has a natural abundance of 100% and a spin number of  $1/2$  (therefore no electrical quadrupole moment). The multiplicity rules for proton-phosphorus splitting are the same as those for proton-proton splitting. The coupling constants are large ( $J_{\text{H-P}} \sim 200$ – $700$  Hz, and  $J_{\text{HC-P}}$  is  $0.5$ – $20$  Hz) and are observable through at least four bonds. The  $^{31}\text{P}$  nucleus can be observed at the appropriate frequency and magnetic field.

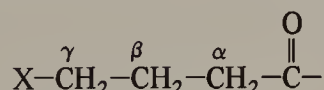
$^{13}\text{C}$  has a natural abundance relative to  $^{12}\text{C}$  of 1.1%, and a spin number of  $1/2$ . Typically, absorption due to coupling of a proton with a  $^{13}\text{C}$  nucleus is seen as weak “ $^{13}\text{C}$  satellite peaks” on both sides of a very strong proton peak. Coupling constants for  $\text{H}-^{13}\text{C}$  have been correlated with hybridization of the  $^{13}\text{C}$  atom:  $J_{\text{sp}^3} \sim 120$  Hz,  $J_{\text{sp}^2} \sim 170$  Hz, and  $J_{\text{sp}} \sim 250$  Hz. The proton attached to the  $^{13}\text{C}$  is also split by protons on adjacent  $^{12}\text{C}$  atoms with the usual  $\text{H}-\text{C}-\text{C}-\text{H}$  coupling constant of about 7 Hz. Thus, the configuration  $^{13}\text{CH}_3-^{12}\text{CH}_2-$  shows a triplet on both sides of an amplified  $^{12}\text{CH}_3$  absorption from the  $^{13}\text{C}-\text{H}$  and the  $^{13}\text{CH}_3-^{12}\text{CH}_2$  couplings. Other molecules in the magnetic field will have the configuration  $^{12}\text{CH}_3-^{13}\text{CH}_2-$ ; these molecules also show a triplet on each side of the very large  $^{12}\text{CH}_3$  absorption, but since  $J_{^{12}\text{CH}_3-^{13}\text{C}}$  is only  $\sim 4.7$  Hz, these peaks are buried on the sides of the  $^{12}\text{CH}_3$  absorption. The  $^{13}\text{C}$  satellite peaks can be distinguished from spinning side bands by their invariance with the rate of spinning of the sample tube. Parenthetically, note that each spinning side band has the same



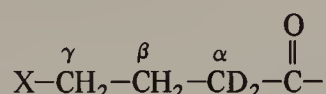


multiplicity as its "parent," but the satellite peaks do not necessarily have the same multiplicity as the parent peak (see page 141 of Jackman and Sternhell<sup>4</sup>).

Deuterium ( $^2\text{H}$  or  $\text{D}$ ) usually is introduced into a molecule to detect a group or to simplify a spectrum.  $^2\text{H}$  has a spin number of 1, a small coupling constant with protons, and a small electrical quadrupole moment. A proton-deuterium coupling constant is approximately 15% of the corresponding proton-proton constant (see the section above on ratio of the magnetogyric ratios). Suppose the protons on the  $\alpha$ -carbon atom of a ketone



were replaced by deuterium:



The original spectrum would consist of a triplet for the  $\alpha$  protons, a quintet (assuming equal coupling) for the  $\beta$ -protons, and a triplet for the  $\gamma$  protons. In the deuterated compound, the  $\alpha$ -proton absorption would be absent, the  $\beta$ -protons would appear as a slightly broadened triplet, and the  $\gamma$  protons would be unaffected. Actually, each peak of the  $\beta$ -proton triplet is a very closely spaced quintet ( $J_{\text{CH}-\text{CD}} \sim 1$  Hz or less), but the effect under ordinary resolution is peak broadening. Even this modest broadening due to the deuterium coupling can be removed by double resonance experiments (see below) involving irradiation at the deuterium resonance; this technique has been used to obtain a more exact measurement of the remaining proton-proton coupling. Most deuterated solvents have residual protonated impurities; the  $\text{CHD}_2$  group in deuterated acetone or dimethyl sulfoxide, for example, is frequently encountered as a closely spaced quintet ( $J \sim 2$  Hz, intensities 1:2:3:2:1).

$^{29}\text{Si}$  has a natural abundance of 5.1% (based on  $^{28}\text{Si} = 100\%$ ), and a spin number of  $1/2$ .  $J_{^{29}\text{Si}-\text{CH}}$  is about 6 Hz. The small doublet caused by the  $^{29}\text{Si}-\text{CH}_3$  coupling can often be seen straddling ( $\pm 3$  Hz) an amplified peak of tetramethylsilane; the  $^{13}\text{C}-\text{H}_3$  doublet can also be seen at  $\pm 59$  Hz.

## VII. CHEMICAL SHIFT EQUIVALENCE AND MAGNETIC EQUIVALENCE

### CHEMICAL SHIFT EQUIVALENCE

The Pople notation (Section IV) is based on the concept of *sets* of nuclei within a *spin system*. A set of nuclei consists of *chemical shift equivalent* (defined below) nuclei. A spin system consists of sets of nuclei that "interact (spin couple) among each other but do not interact with any nuclei outside the spin system. It is not necessary for all nuclei within a spin system to be coupled with all the other nuclei" in the spin system.<sup>4</sup> Spin systems are "insulated" from one another; for example, the ethyl protons in ethyl isopropyl ether constitute one spin system, and the isopropyl protons another.

If nuclei are interchangeable by a symmetry operation or a rapid process, they are chemical shift equivalent (*isochronous*); that is, they have exactly the same chemical shift under all achiral conditions. Nuclei are interchangeable if the structures before and after the operation are indistinguishable. A rapid process means one that occurs faster than once in about  $10^{-3}$  second. Pople proposed that the chemical shift equivalent nuclei be ordered into sets designated  $A_3$ ,  $B$ ,  $X_2$  and so forth.

The symmetry operations are: rotation about a symmetry axis ( $C_n$ ); inversion at a center of symmetry ( $i$ ); reflection at a plane of symmetry ( $\sigma$ ); or higher orders of

rotation about an axis followed by reflection in a plane normal to this axis ( $S_n$ ). The symmetry element (axis, center, or plane) must be a symmetry element for the entire molecule. The term "interchange" will be clarified by the examples below.

Protons a and b in *trans*-1,2-dichlorocyclopropane are chemical shift equivalent, as are the protons c and d (Figure 32). The molecule has an axis of symmetry passing through  $C_3$  and bisecting the  $C_1-C_2$  bond. Rotation of the molecule by  $180^\circ$  around the axis of symmetry interchanges proton  $H_a$  for  $H_b$  and  $H_c$  for  $H_d$ . If the protons were not labeled, it would not be possible to tell if the symmetry operation had been performed merely by inspecting the molecule before and after the operation; the rotated structure is superimposable on the original structure.

Protons that are interchangeable through an axis of symmetry are *homotopic*: that is, they are chemical shift equivalent in any environment (solvent or reagent) whether achiral or chiral. Protons that are interchangeable through any other symmetry operation are called *enantiotopic* (non-superimposable mirror images), and these are chemical shift equivalent only in an achiral environment. Non-interchangeable geminal protons are termed *diastereotopic*, and they are not chemical shift equivalent in any environment. Noninterchangeable protons on different carbon atoms are termed *heterotopic*, and they are not chemical shift equivalent in any environment. However, enantiotopic protons in a chiral environment, or diastereotopic or heterotopic protons, may fortuitously absorb at the same position for a given instrumental resolution.

The concept of interchange through a rapid mechanism can be illustrated by the rapidly interchanging protons on some heteroatoms and by protons in some groups in molecules that are rapidly changing conformations. If the interchange is rapid enough, a single peak will result from, say, the carboxylic acid proton and the hydroxylic proton of a hydroxy carboxylic acid. Chemical shift equivalence of protons on a  $CH_3$  group results from rapid rotation around

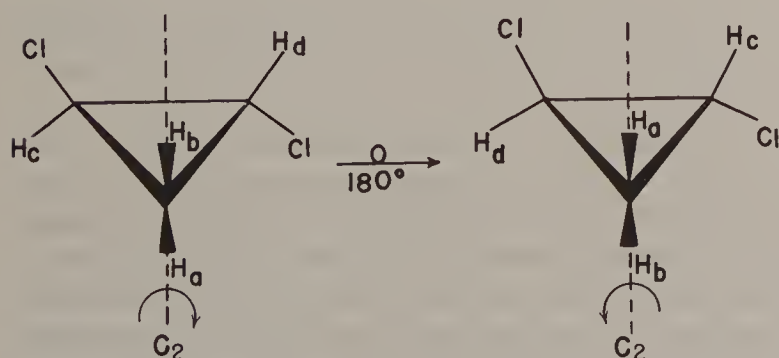
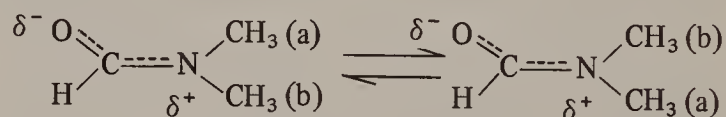


Figure 32. *trans*-1,2-Dichlorocyclopropane showing axis of symmetry and effect of rotation around the axis.

a carbon-carbon single bond even in the absence of a symmetry element. Figure 33 shows Newman projections of the three staggered rotamers of a molecule containing a methyl group attached to another  $sp^3$  carbon atom having four different substituents, that is, a chiral center. In any single rotamer, none of the protons can be interchanged by a symmetry operation. However, the protons are rapidly changing position. The time spent in any one rotamer is short ( $\sim 10^{-6}$  second), because the energy barrier for rotation around a C—C single bond is small. The chemical shift of the methyl group is an average of the shifts of each of the 3 protons. In other words, each proton can be interchanged with the others by a rapid rotational operation. Thus, without the a, b, c labels, the rotamers are indistinguishable.

The chemical shift of cyclohexane protons is an average of the shifts of the axial and the equatorial protons. The chemical shift of equivalence of the cyclohexane protons results from rapid interchange of axial and equatorial protons as the molecule flips between chair forms. The chemical equivalence of its protons is not a consequence of achieving a planar conformation because the planar conformation of cyclohexane is not a reasonable one.

At room temperature, *N,N*-dimethylformamide shows 2  $CH_3$  peaks, which merge at  $\sim 123^\circ$  because of the rate of rotation around the hindered C—N bond.



## MAGNETIC EQUIVALENCE

A further refinement involves the concept of *magnetic equivalent* nuclei. If nuclei in the same set (i.e., chemical shift equivalent nuclei) couple equally to each nucleus (probe nucleus) in every other set of the spin system, they are magnetic equivalent, and the designations  $A_2$ ,  $X_2$ , and so on apply. However, if the nuclei are not magnetic equivalent, the designations  $AA'$ ,  $XX'$  are used.

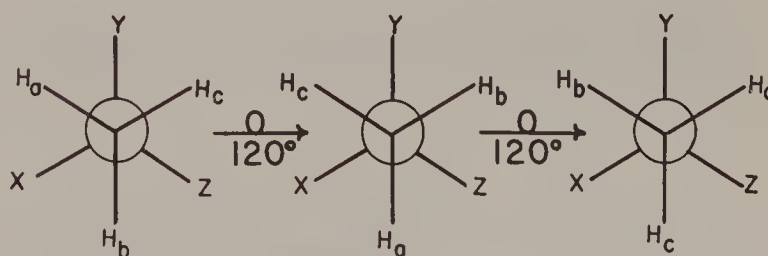


Figure 33. Newman projection of the staggered rotamers of a molecule with a methyl group attached to a chiral  $sp^3$  carbon atom.

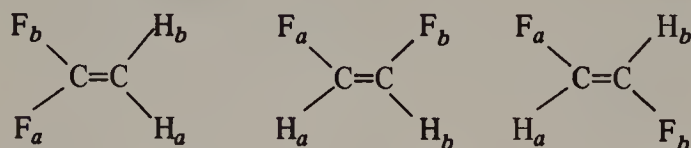


Magnetic equivalence presupposes chemical shift equivalence. To determine whether chemical shift equivalent nuclei are magnetic equivalent, it must be determined whether they are coupled equally to each nucleus (probe nucleus) in every other set in the spin system. This is done by examining geometrical relationships. If the bond distances and angles from each nucleus in relation to the probe nucleus are identical, the nuclei in question are magnetic equivalent. In other words, two chemical shift equivalent nuclei are magnetic equivalent if they are symmetrically disposed with respect to each nucleus (probe) in any other set in the spin system. This means that the two nuclei under consideration can be interchanged through a reflection plane passing through the probe nucleus and perpendicular to a line joining the chemical shift equivalent nuclei. Note that a test for magnetic equivalence is valid only when the *two nuclei are chemical shift equivalent*. The latter point bears repeating: only chemical shift equivalent nuclei are tested for magnetic equivalence.

These rules are applied readily to conformationally rigid structures. Thus, in *p*-chloronitrobenzene (Figure 34) the protons ortho to the nitro group ( $H_A$  and  $H_{A'}$ ) are chemical shift equivalent to each other, and the protons ortho to the chlorine group ( $H_X$  and  $H_{X'}$ ) are chemical shift equivalent to each other. In general for *p*-disubstituted benzene rings,  $J_{AX}$  and  $J_{A'X'}$  are the same, approximately 7 to 10 Hz;  $J_{A'X}$  and  $J_{AX'}$  are also the same but much smaller, approximately 0 to 1 Hz. Since  $H_A$  and  $H_{A'}$  couple differently to another specific proton, they are not magnetic equivalent, and first-order rules do not apply. (Similarly,  $H_X$  is not magnetic equivalent to  $H_{X'}$ ). The system is described as  $AA'XX'$ , and the spectrum is very complex (Figure 34). Fortunately the pattern is readily recognized because of its symmetry and apparent simplicity; under ordinary resolution it resembles an *AB* pattern of two distorted doublets. Closer inspection reveals many additional splittings. As the para substituents become more similar to each other (in their shielding properties), the system tends toward  $AA'BB'$ ; even these absorptions resemble *AB* patterns until they overlap.

The aromatic protons of symmetrically *ortho*-disubstituted benzenes also give  $AA'BB'$  spectra. An example is *o*-dichlorobenzene (Figure 35).

The three isomeric difluoroethylenes furnish additional examples of chemical shift equivalent nuclei that are not magnetic equivalent.



In each case, the protons  $H_a$  and  $H_b$  comprise a set, and fluorines  $F_a$  and  $F_b$  comprise a set (of chemical shift equi-

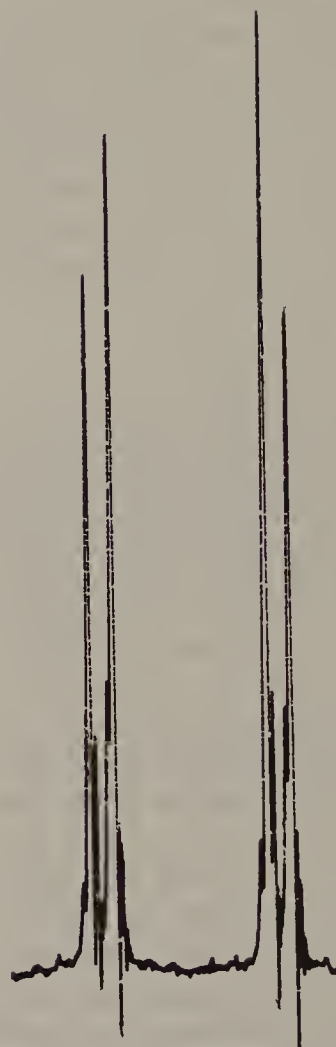
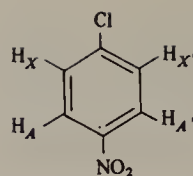


Figure 34. *p*-Chloronitrobenzene, 100 MHz in  $CCl_4$ .

valent nuclei), but the nuclei in each set are not magnetic equivalent and the spectra are complex.

In conformationally mobile systems, the situation becomes involved. We have seen that the  $CH_3$  protons are chemical shift equivalent, even when the molecule has no symmetry element, by rapid rotational interchange. If one of the substituents on the chiral center is a proton ( $Y=H$  in Figure 33), the  $CH_3$  protons are also magnetic equivalent by rapid rotational averaging of the coupling constants among identical rotamers; the system is  $A_3B$  or  $A_3X$ . Consider, in contrast with the methyl group, a methylene group next to a chiral center, as in 1-bromo-1,2-dichloroethane (Figure 36). Protons  $H_a$  and  $H_b$  are not chemical shift equivalent, since they cannot be interchanged by a symmetry operation or by rapid rotation. The molecule has no axis, plane, center, or reflection axis of symmetry.



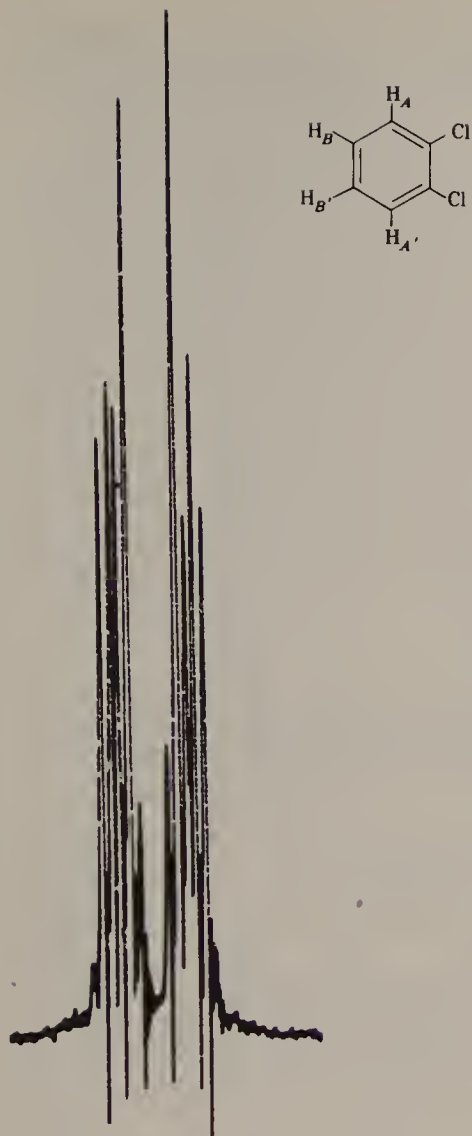


Figure 35. *o*-Dichlorobenzene, 100 MHz, in  $\text{CCl}_4$ .

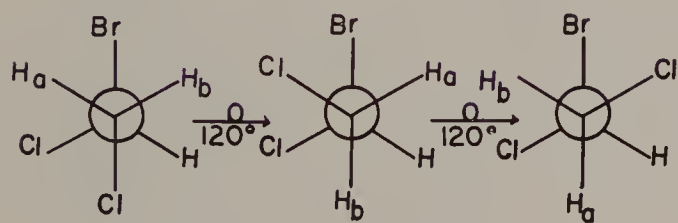


Figure 36. Newman projection of the rotamers of 1-bromo-1,2-dichloroethane.

Although there is a rapid rotation around the carbon-carbon single bond, the protons are not interchangeable by a rotational operation. An observer can detect the difference before and after rotating the methylene group; the rotamers are not superimposable.

The question of magnetic equivalence does not arise since there is no chemical shift equivalence; the system is *ABX*.

In  $\text{ZCH}_2\text{CH}_2\text{Y}$  molecules, we are dealing with an *anti* rotamer and 2 enantiomeric *gauche* rotamers (Figure 37). The analysis is quite complex\*, but in essence, these are  $\text{AA}'\text{XX}'$  systems, which usually give apparent  $\text{A}_2\text{X}_2$  spectra. The spectrum of 2-dimethylaminoethylacetate (Figure 38a) is a case in point. Figure 38 b-d shows the progressive distortions as  $\text{AA}'\text{XX}' \rightarrow \text{AA}'\text{BB}'$  (i.e.,  $\Delta\nu/J$  decreases) in compounds of type  $\text{ZCH}_2\text{CH}_2\text{Y}$ . As the absorptions move closer together, the inner peaks increase in intensity, additional splitting occurs, and some of the outer peaks disappear in the baseline noise. The general appearance of symmetry throughout aids recognition of the type of spin system involved. At the extreme, the two methylene groups become chemical shift equivalent and a single  $\text{A}_4$  peak results. Although 1,3-dichloropropane (Figure 39) is properly described as  $\text{XX}'\text{AA}'\text{XX}'$ , it presents an apparent  $\text{A}_2\text{X}_4$  system (triplet and quintet).

$\text{A}_2\text{B}_2$  or  $\text{A}_2\text{X}_2$  systems are quite rare (examples include difluoromethane, 1,1-difluoroallene and 1,1,3,3-tetrachloropropane); most systems described in the literature as  $\text{A}_2\text{X}_2$  are really  $\text{AA}'\text{XX}'$ .

It turns out that the question of magnetic equivalence in rotamers is readily resolved by examining the individual rotamers in which the protons in question are chemical shift equivalent by a symmetry operation. If the protons are magnetic equivalent in these rotamers, they are so for the molecule.

An interesting situation occurs in a molecule such as 1,3-dibromo-1,3-diphenylpropane, which has a methylene group between two chiral centers (Figure 40). In (1*R*,3*R*)-1,3-dibromo-1,3-diphenylpropane (one of a racemic pair),  $\text{H}_a$  and  $\text{H}_b$  are chemical shift equivalent and so are  $\text{H}_c$  and  $\text{H}_d$ , because of an axis of symmetry ( $\text{C}_2$ ) in the molecule. Rotation around the axis interchanges  $\text{H}_a$  with  $\text{H}_b$ , and  $\text{H}_c$  with  $\text{H}_d$ . On the other hand, in (1*S*,3*R*)-1,3-dibromo-1,3-diphenylpropane (a meso compound),  $\text{H}_c$  and  $\text{H}_d$  are not chemical shift equivalent: they cannot be interchanged by a symmetry operation. (1*S*,3*R*)-1,3-Dibromo-1,3-diphenylpropane does have a plane of symmetry ( $\sigma$ ), but both  $\text{H}_c$  and  $\text{H}_d$  are in that plane and cannot be inter-

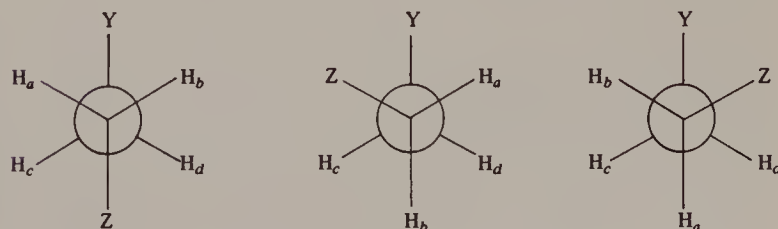


Figure 37. Newman projection of the rotamers of the  $\text{YCH}_2\text{CH}_2\text{Z}$  system.

\*See R. M. Silverstein and R. T. LaLonde, *J. Chem. Ed.*, 57, 343 (1980).

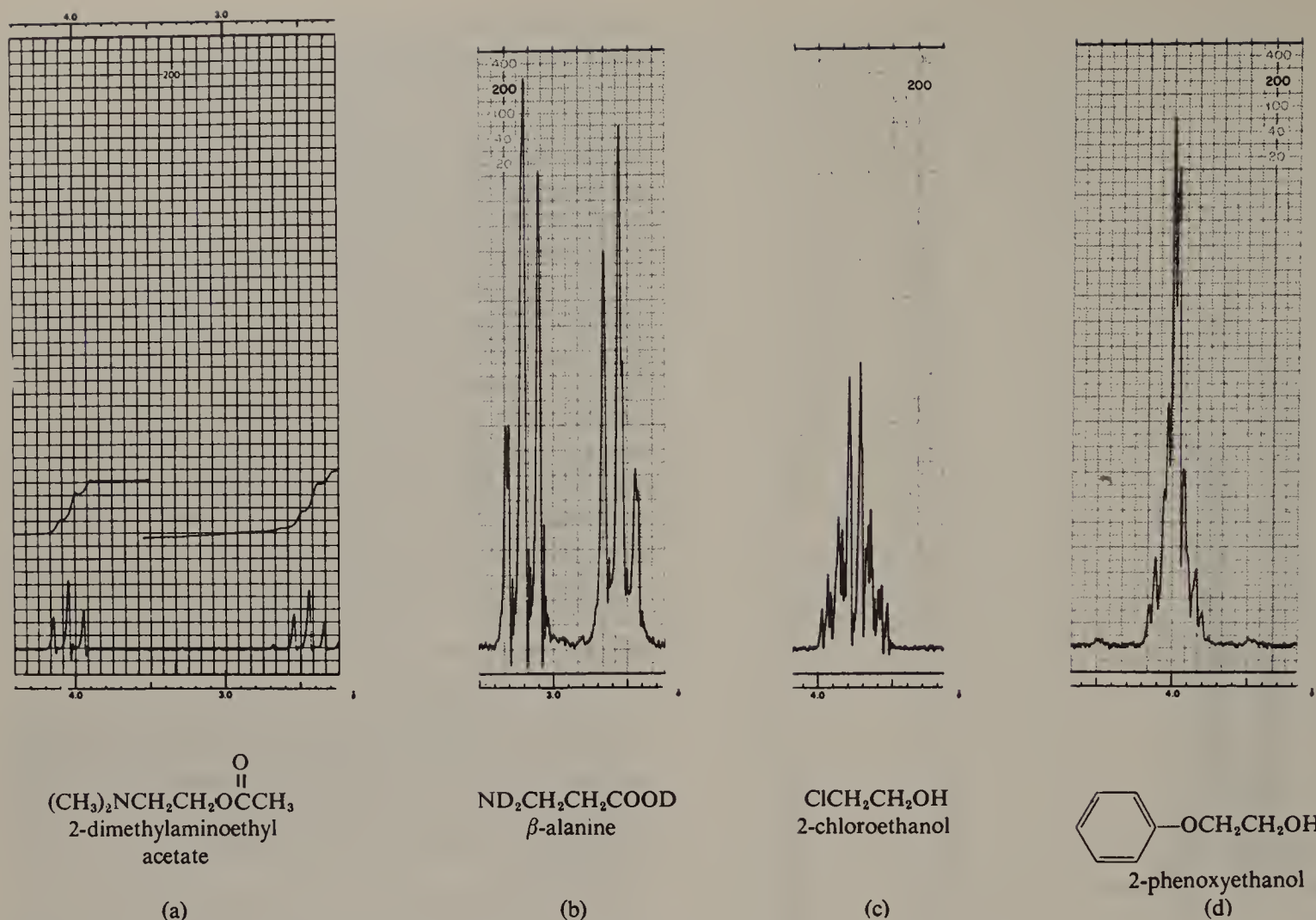


Figure 38. Progressive distortions as  $\text{AA}'\text{XX}' \rightarrow \text{AA}'\text{BB}'$  in  $\text{Z}-\text{CH}_2-\text{CH}_2\text{Y}$ . 60 MHz.

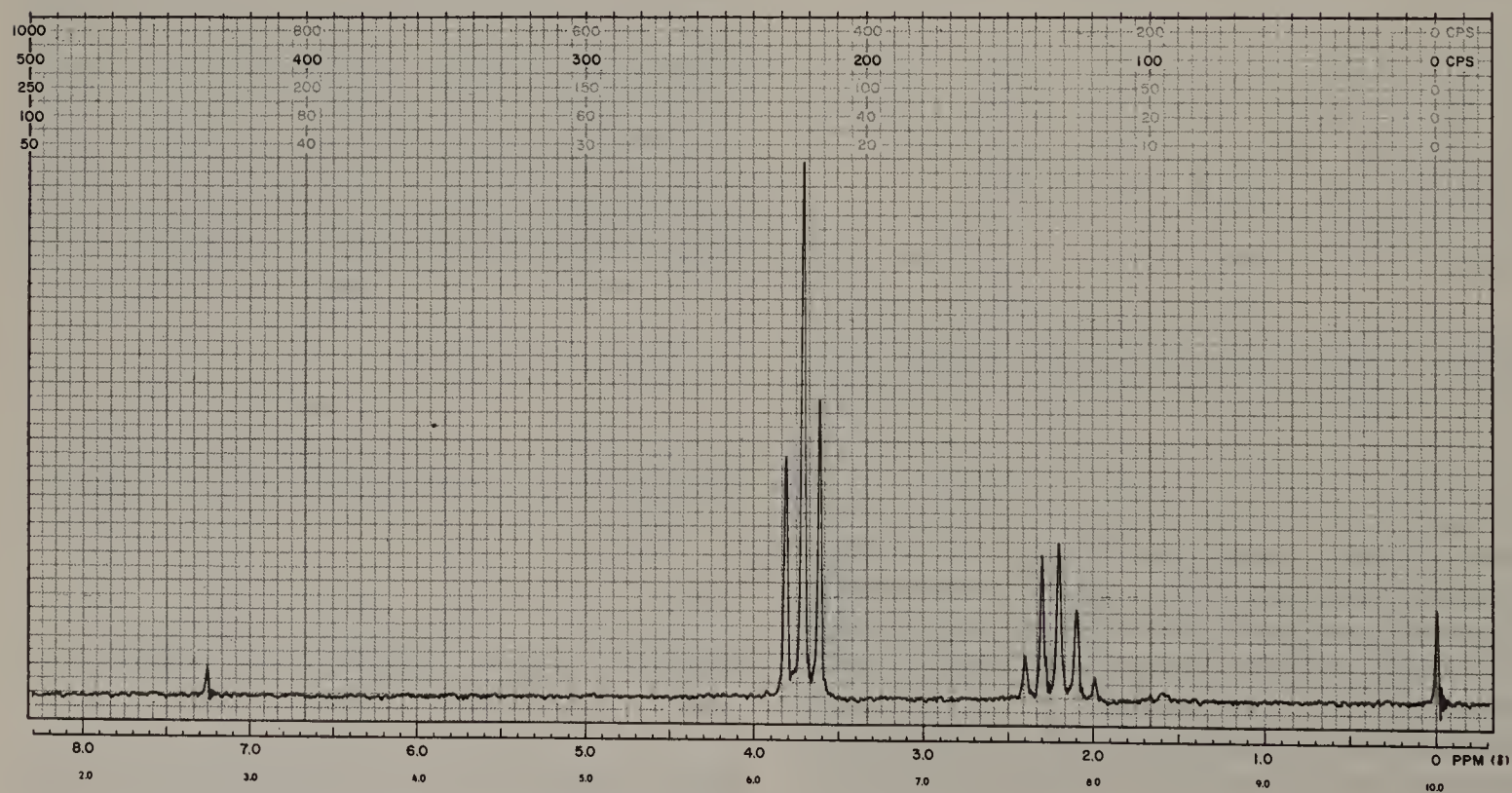


Figure 39. 1,3-Dichloropropane in  $\text{CDCl}_3$ . 60 MHz.  $\text{XX}'\text{AA}'\text{XX}'$  system



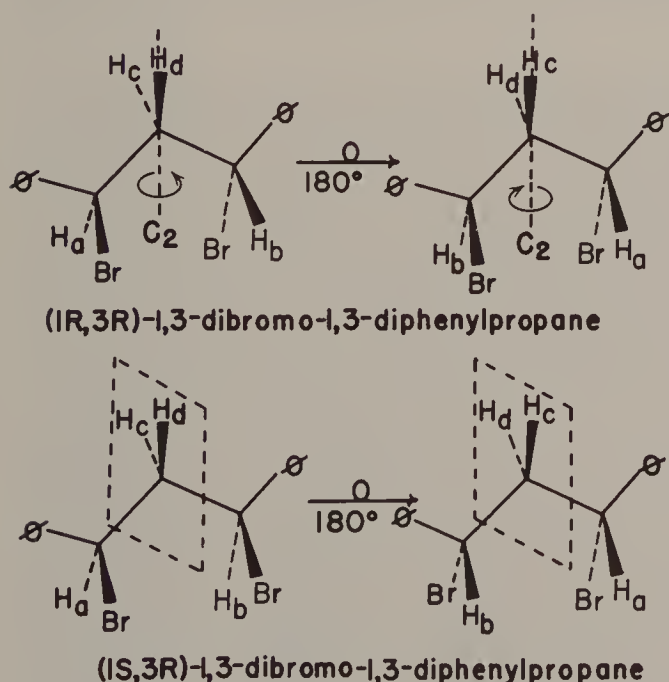
changed.  $H_a$  and  $H_b$  are chemical shift equivalent because they can be interchanged by reflection through the plane of symmetry shown in Figure 40.

In the  $1R,3R$ -compound,  $H_a$  and  $H_b$  are not magnetic equivalent since they do not identically couple to  $H_c$  or to  $H_d$ ;  $H_c$  and  $H_d$  also are not magnetic equivalent since they do not identically couple to  $H_a$  or  $H_b$ . Note that only those rotamers are examined in which the protons in question were chemical shift equivalent. The system is  $AA'XX'$  or more descriptively  $A-XX'-A'$ . In the  $1S,3R$  compound of Figure 40,  $J_{ad} = J_{bd}$  and  $J_{ac} = J_{bc}$ ; thus, in this molecule,  $H_aH_b$  are magnetic equivalent. The question of magnetic equivalence of  $H_c$  and  $H_d$  is not relevant since they are not chemical shift equivalent. The system is  $ABX_2$  or more descriptively,  $X-AB-X$ .

## VIII. AMX, ABX, AND ABC SYSTEMS WITH THREE COUPLING CONSTANTS

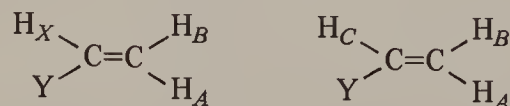
The spectrum of methyl 2-furoate (Chapter 7, compound 7-2) represents a nearly first-order  $AMX$  system with three coupling constants. Each proton is represented by a pair of doublets.

Although  $ABX$  systems with three coupling constants are not first-order, the patterns are frequently recognized if the distortions are not too severe. The degree of distortion

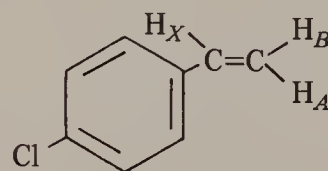


**Figure 40.** Two isomers of 1,3-dibromo-1,3-diphenylpropane. In the  $(1R,3R)$  isomer,  $H_a$  and  $H_b$  are chemical shift equivalent, as are  $H_c$  and  $H_d$ . In the  $(1S,3R)$  isomer,  $H_a$  and  $H_b$  are chemical shift equivalent, but  $H_c$  and  $H_d$  are not.

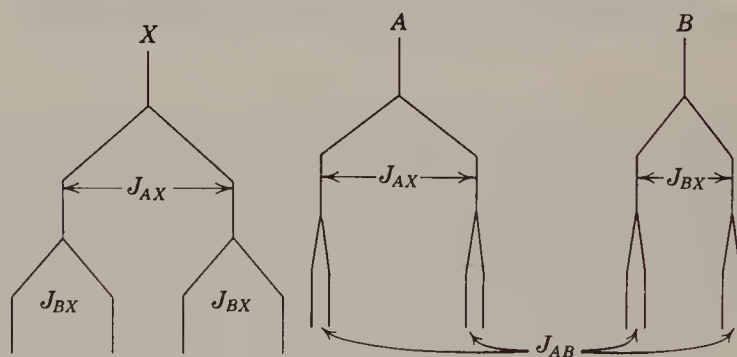
depends on the ratios of the separation of the  $A$  and  $B$  protons to their coupling constants. The vinylic structure gives an  $ABX$  or an  $ABC$  system depending on the nature of the substituent  $Y$ , which determines the shift positions of the protons.



*p*-Chlorostyrene (Figure 41) shows an  $ABX$  spectrum that can readily be related to an  $AMX$  pattern. The following analysis, though not rigorous, is useful.



Protons  $A$  and  $B$  are not chemical shift equivalent. Proton  $A$  ( $\delta \sim 5.70$ ) is deshielded about 25 Hz compared with proton  $B$ , because of its relative proximity to the ring. Proton  $X$  ( $\delta \sim 6.70$ ) is strongly deshielded by the ring and is split by proton  $A$  ( $J \sim 18$  Hz) and by proton  $B$  ( $J \sim 11$  Hz). The  $A$  proton signal is split by the  $X$  proton ( $J \sim 18$  Hz) and by the  $B$  proton ( $J \sim 2$  Hz). The  $B$  proton signal is split by the  $X$  proton ( $J \sim 11$  Hz) and by the  $A$  proton ( $J \sim 2$  Hz).



The coupling constants for a vinylic system are characteristic; the *trans* coupling is larger than the *cis*, and the geminal coupling is very small.

The preceding analysis lacks rigor in several details. The splittings of proton  $X$  do not correspond exactly to  $J_{BX}$  and  $J_{AX}$ , and although this is a good approximation when  $\Delta\nu$  is greater than about 10 for protons  $AB$ , the only exact information obtainable from the  $X$  pattern is that the spread between the outside peaks is equal to  $J_{AX} + J_{BX}$ . The distortions in peak intensities from an  $AMX$  pattern are obvious. The pattern of two closely spaced pairs should not be confused with the quartet resulting from splitting by three equivalent protons.

As the shift positions of protons  $A$  and  $B$  approach each other so that  $\Delta\nu$  becomes much smaller than 10, the



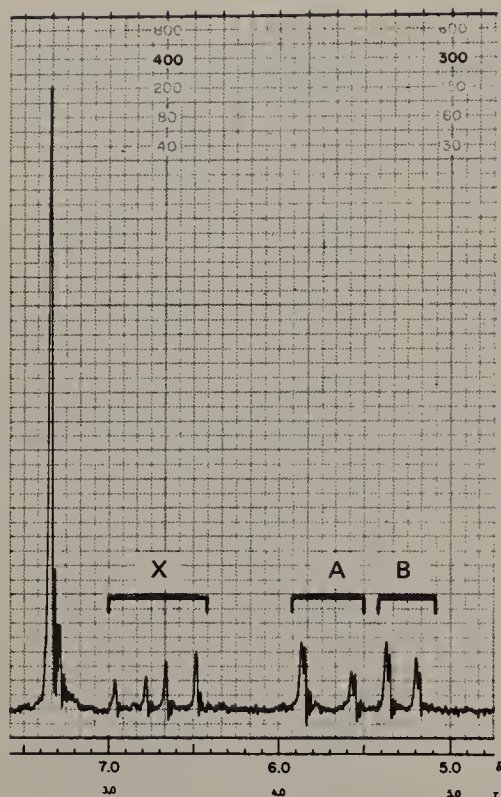
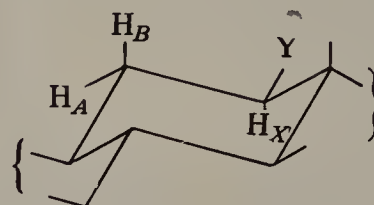


Figure 41. *p*-Chlorostyrene, 60 MHz.

deviations from a first-order spectrum become severe; the *A* and *B* patterns overlap, and the middle peaks of the *X* pattern merge. In the extreme case that  $\nu_A = \nu_B$  and  $J_{AX} = J_{BX}$ , protons *A* and *B* are magnetic equivalent, the spectrum is simply  $A_2X$ , and the *X* proton absorption

is a triplet. Note that a very similar spectrum would arise if the *A* pair were chemical, but not magnetic, equivalent: that is, an  $AA'X$  system. As the shift position of the *X* proton approaches the *A* and *B* absorptions, the spectrum degenerates to a very complex *ABC* pattern.

An equatorial and an axial proton on the same carbon of a conformationally locked 6-membered ring may form the *AB* part of an *ABX* or an *ABC* pattern, depending on the nature of *Y* on an adjacent carbon. Typically,  $H_A$  (equatorial) is deshielded relative to  $H_B$  (axial) by about 0.1 to 0.7 ppm (Section III),  $J_{AB}$  is about 12 to 15 Hz,  $J_{BX}$  (ax.-ax.) is about 5–10 Hz, and  $J_{AX}$  (eq.-ax.) is about 2 to 3 Hz (Section X).



## IX. STRONGLY AND WEAKLY COUPLED SPIN SYSTEMS

The 60 MHz spectrum of 1-nitropropane (Figure 42) is an  $A_3MM'XX'$  system that resembles an  $A_3M_2X_2$  system with  $J_{AM}$  very similar to  $J_{MX}$ . We interpret the upfield triplet as the methyl group split by the adjacent methylene group, the downfield triplet as the methylene group (adjacent to the nitro group) split by the adjacent

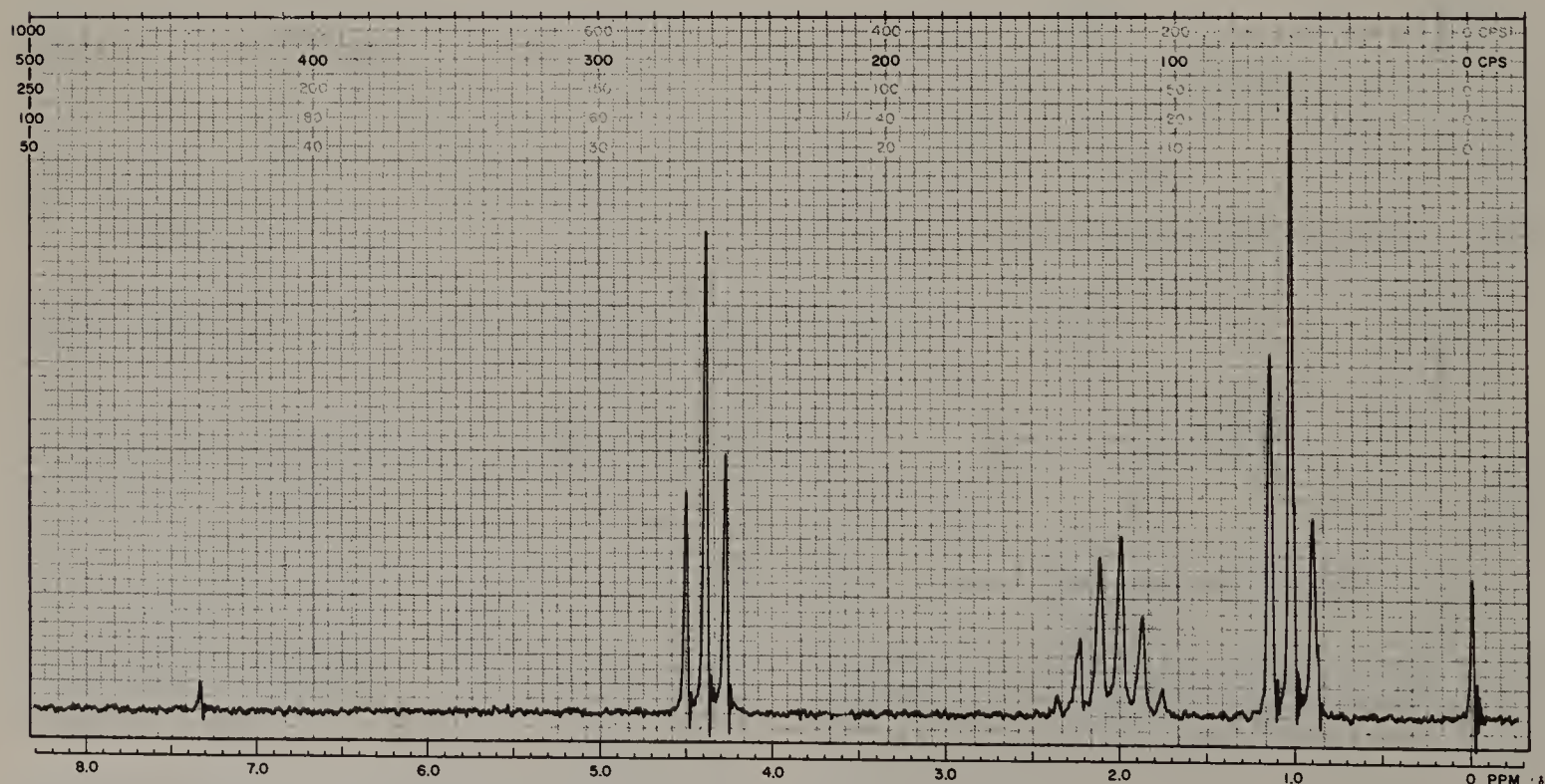


Figure 42. 1-Nitropropane in  $CDCl_3$ , 60 MHz.  $CH_3-CH_2-CH_2-NO_2$ ,  $A_3MM'XX'$

methylene group that in turn is split by 5 neighboring protons to give a sextet. We note some broadening of the sextet peaks since  $J_{AM}$  is not exactly equal to  $J_{MX}$ .

What we have done, in effect, is to mentally cleave the spin system into segments, and are successful in rationalizing the spectrum. Why is it that we can use this kind of oversimplified analysis for 1-nitropropane, but we run into trouble when we predict a triplet for the methyl group (Figure 43a) of heptaldehyde ( $A_3B_2$  portion of the system), or a doublet for the methyl group (Figure 43b) of  $\beta$ -methylglutaric acid,  $\text{HOOC}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{COOH}$  ( $A_2B$  portion of the system)?

The answer is that we have weakly coupled protons in 1-nitropropane, but strongly coupled protons in the latter two compounds. Or, to put it another way, the spins of the methyl protons in 1-nitropropane are affected only (or almost entirely) by the adjacent methylene protons. But in heptaldehyde, the methyl proton spins are affected by all of the adjoining methylene groups that have practically the same chemical shift; that is,  $\Delta\nu/J$  for four of the methylene protons is almost zero, and they are considered to be strongly coupled.

A similar situation exists in  $\beta$ -methylglutaric acid, in which the methylene groups and the methine group are strongly coupled (the system is  $A_3BCC'DD'$ ). To explain

the difficulties arising from attempting to segregate portions of a strongly coupled system, the concept of virtual coupling is invoked. Even though the coupling constant of the methyl group to the methylene group once removed in heptaldehyde or in  $\beta$ -methylglutaric acid is almost zero, the methyl group is considered to be "virtually coupled" to those once removed methylene groups in each compound.

The concept of virtual coupling, then, is convenient but only necessary when one incorrectly considers a portion of a strongly coupled spin system as a separate entity and attempts to apply first-order rules to that proton.

The modus operandi of the organic chemist in interpreting an NMR spectrum is to look initially for first-order absorptions, and then for patterns that can be recognized as distortions of first-order absorptions. There is not usually very much interest in precise solutions of multispin systems. Frequently the emphasis is on portions of spin systems. The above considerations should be of help in setting limits for this convenient, although not rigorous, approach to the interpretation of NMR spectra.

A well-defined multiplet like any one in Figure 42 has a chemical shift that is at the midpoint of the signal (e.g., the triplet at  $\delta$  4.37 in Figure 42). In contrast, an ill-defined multiplet, such as in Figure 43b, should be reported as the range, in Hz, over which the signal extends; the instrument frequency must also be reported.\*

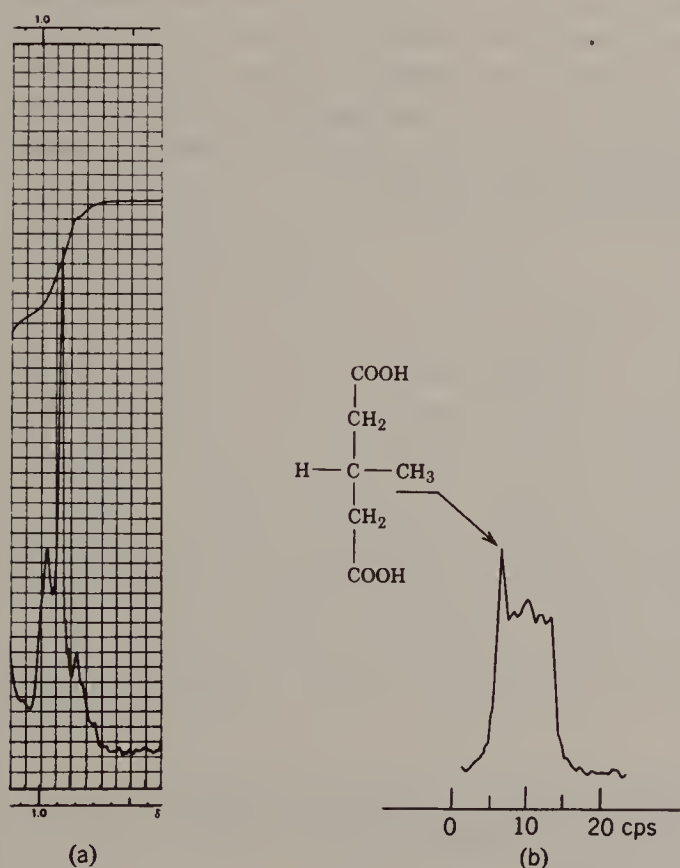


Figure 43. a. Methyl group of heptaldehyde, 60 MHz. b. Methyl group of  $\beta$ -methylglutaric acid, 60 MHz, expanded.

## X. EFFECTS OF A CHIRAL CENTER

The protons of a methylene group near a chiral center are not chemical shift equivalent, as explained in Section VII. They couple with each other, and each may have a different coupling to a vicinal proton. Even assuming fast rotation around the C-C bond, the methylene protons

of a compound  $\begin{array}{c} \text{H}_a \text{ M} \\ | \quad | \\ \text{R}-\text{C}-\text{C}-\text{L} \\ | \quad | \\ \text{H}_b \text{ S} \end{array}$  may show an AB pattern;

that is, they are diastereotopic since they cannot be operationally interchanged (Section VII).

However, a large part of the nonequivalence may result from unequal populations of conformers even at fast rotation. The spectrum may be further complicated by slow rotation caused by low temperature or bulky substituents. Nonequivalence of the methylene protons persists in a

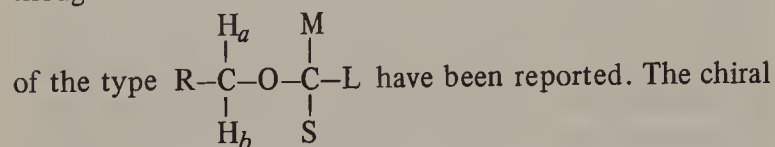
compound such as  $\begin{array}{c} \text{H}_a \text{ M} \text{ H}_a \\ | \quad | \quad | \\ \text{R}-\text{C}-\text{C}-\text{C}-\text{R} \\ | \quad | \quad | \\ \text{H}_b \text{ S} \text{ H}_b \end{array}$  even though the middle

carbon atom is not a chiral center.

\*G. Slomp, *J. Am. Chem. Soc.*, 84, 673 (1962).



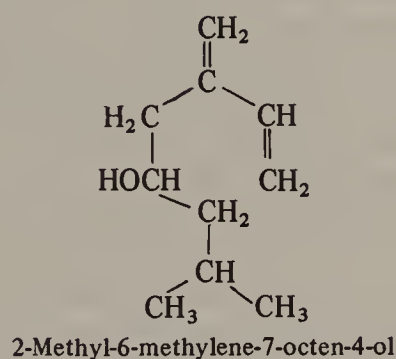
The methylene group may display nonequivalence even though it is once removed from the chiral center. Examples



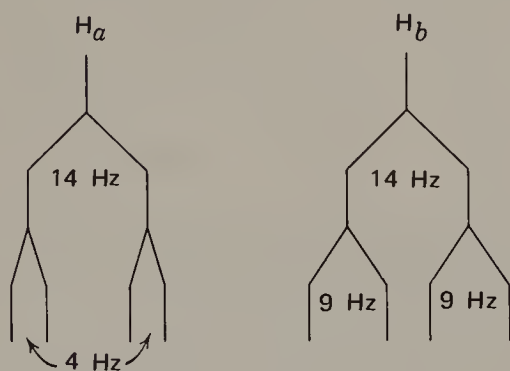
center need not be a carbon atom. The phenomenon has been reported for the methylene protons in quaternary ammonium salts, sulfites, sulfoxides, diethyl sulfide-borane complexes, and thiophosphonates.

Chemical shift nonequivalence of the methyl groups of an isopropyl moiety near a chiral center is frequently observed; the effect has been measured through as many as 7 bonds between the chiral center and the methyl protons.

The protons of the methyl groups in the terpene alcohol 2-methyl-6-methylene-7-octen-4-ol are not chemical shift



equivalent (Figure 44), and even though they are 4 bonds removed from the chiral center, the nonequivalence is detectable at 100 MHz ( $\delta$  0.92 and  $\delta$  0.90); each absorption is split by the vicinal CH, giving rise to two overlapping doublets ( $J = 7$  Hz). The nonequivalent protons of the  $\text{CH}_2$  ( $a$  and  $b$ ) between the  $\text{CH}_2=\text{C}$  and  $\text{CHOH}$  groups



absorb, respectively, at  $\delta$  2.47 and  $\delta$  2.18. Each proton is split by the other ( $J_{\text{gem}} = 14$  Hz) and unequally by the neighboring proton ( $J_{\text{vic}} = 9$  Hz and 4 Hz). The protons of the other  $\text{CH}_2$  groups are also nonequivalent; additional splitting by the adjacent methine proton results in a partially resolved multiplet.

The methylene protons (upfield absorption) in aspartic acid (Figure 45) in  $\text{D}_2\text{O}$  are nonequivalent, and the shift difference between them is small compared with the geminal coupling constant. Thus, the  $AB$  pattern from the geminal

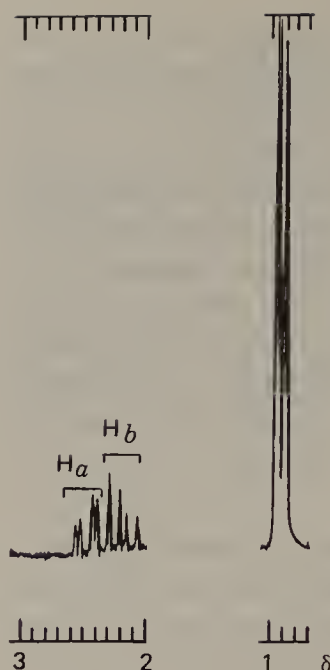
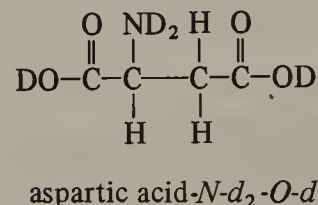
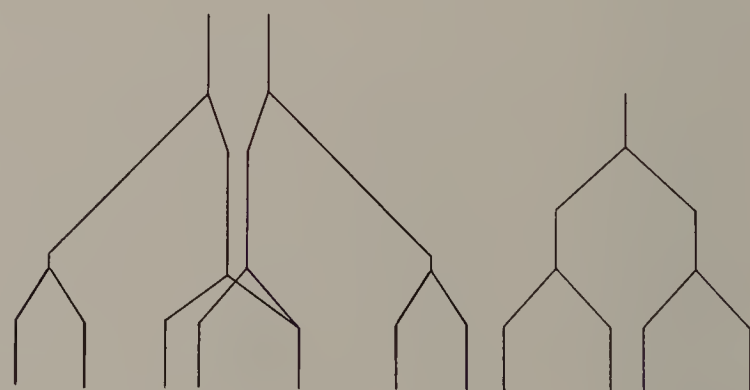


Figure 44. 5-Methylene and methyl protons of 2-methyl-6-methylene-7-octen-4-ol, 100 MHz.



coupling is quite distorted; the inner peaks are strong, the outer peaks weak. Each methylene proton is also split by the vicinal proton with different coupling constants. Two of the peaks coincide, the end peaks are lost in the baseline noise, and the net result is three peaks. The methine proton absorption consists of two pairs.



## XI. VICINAL AND GEMINAL COUPLING IN RIGID SYSTEMS

Coupling between protons on vicinal carbon atoms in rigid systems depends primarily on the dihedral angle  $\phi$  between the  $\text{H}-\text{C}-\text{C}'$  and the  $\text{C}-\text{C}'-\text{H}'$  planes. This angle can be visualized by an end-on view of the bond between the



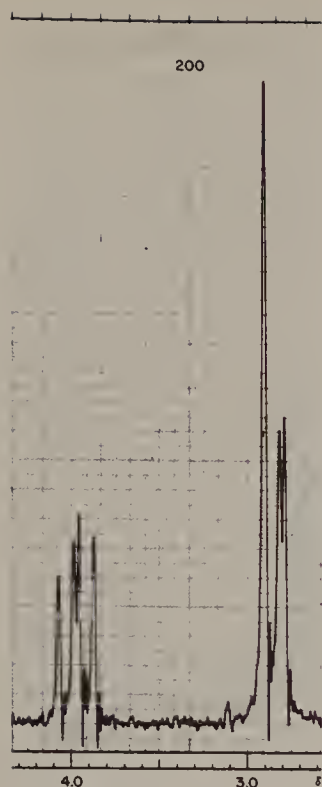
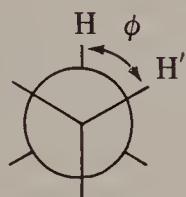


Figure 45. Aspartic acid in  $D_2O$ , 60 MHz.



vicinal carbon atoms and by the perspective in Figure 46 in which the calculated relationship between dihedral angle and vicinal coupling constant is graphed. Karplus emphasized that his calculations are approximations and do not take into account such factors as electronegative substituents, the bond angles  $\theta$  ( $\angle H-C-C'$  and  $\angle C-C'-H'$ ), and bond lengths. Deductions of dihedral angles from measured coupling constants are safely made only by comparison with closely related compounds. The correlation has been very useful in cyclopentanes, cyclohexanes, carbohydrates, and bridged polycyclic systems. In cyclopentanes, the observed values of about 8 Hz for vicinal *cis* protons and about 0 Hz for vicinal *trans* protons are in accord with the corresponding angles of about  $0^\circ$  and about  $90^\circ$ , respectively. In substituted or fused cyclohexane rings, the following relations obtain:

|                       | Calc. $J$ | Observed $J$ (Hz)   |
|-----------------------|-----------|---------------------|
| axial-axial           | 9         | 8-14 (usually 8-10) |
| axial-equatorial      | 1.8       | 1-7 (usually 2-3)   |
| equatorial-equatorial | 1.8       | 1-7 (usually 2-3)   |

A modified Karplus equation can be applied to vicinal coupling in olefins. The prediction of a larger *trans* coupling ( $\varphi = 180^\circ$ ) than *cis* coupling ( $\varphi = 0^\circ$ ) is borne out. The *cis* coupling in unsaturated rings decreases with decreasing ring size (increasing bond angle  $\theta$ ) as follows: cyclohexenes  $J = 8.8$  to  $10.5$ , cyclopentenes  $J = 5.1$  to  $7.0$ , cyclobutenes  $J = 2.5$  to  $4.0$ , and cyclopropenes  $J = 0.5$  to  $2.0$ .

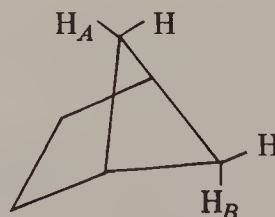
The calculated relationship due to the H-C-H angle of geminal protons is shown in Figure 47. This relationship is quite susceptible to other influences and should be used with due caution. However, it is useful for characterizing methylene groups in a fused cyclohexane ring (approximately tetrahedral,  $J \sim 12$  to  $18$ ), methylene groups of a cyclopropane ring ( $J \sim 5$ ), or a terminal methylene group ( $J \sim 0$  to  $3$ ). Geminal coupling constants are actually negative numbers, but this can be ignored except for calculations.

In view of the many factors other than angle dependence that influence coupling constants, it is not surprising that there have been abuses of the Karplus correlation. Direct "reading off" of the angle from the magnitude of the  $J$  value is risky. The safest application of the relationships is to structure determinations in which molecular geometries have provided the extrema of the high and low expected  $J$  values and for which the  $0^\circ$  and  $90^\circ$  and  $180^\circ$  structures are known for a given system. The limitations of the Karplus correlations are discussed in Jackman and Sternhell.<sup>4</sup>

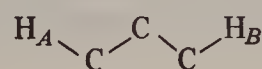
## XII. LONG-RANGE COUPLING

Proton-proton coupling beyond 3 bonds may occur in olefins, acetylenes, aromatics, and heteroaromatics, and in strained ring systems (small or bridged rings). Allylic ( $H-C-C=C-H$ ) coupling constants are about 0 to 3 Hz. Homoallylic ( $H-C-C=C-CH$ ) couplings are usually negligible but may be as much as 1.6 Hz. Coupling through conjugated polyacetylenic chains may occur through as many as 9 bonds. Meta coupling in a benzene ring is 1 to 3 Hz, and para, 0 to 1 Hz. In 5-membered heteroaromatic rings, coupling between the 2,4 protons is 0 to 2 Hz.

$J_{AB}$  in the bicyclo[2.1.1]hexane system is about 7 Hz.



This unusually high long-range coupling constant is attributed to the "W-conformation" of the 4 sigma bonds between  $H_A$  and  $H_B$ :



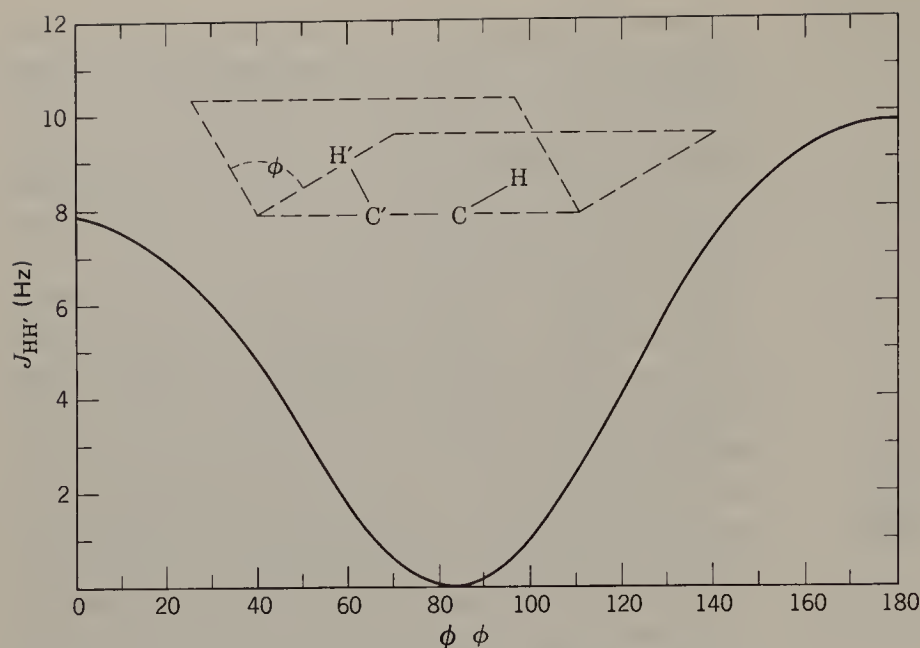


Figure 46. The vicinal Karplus correlation. Relationship between dihedral angle and coupling constant for vicinal protons.

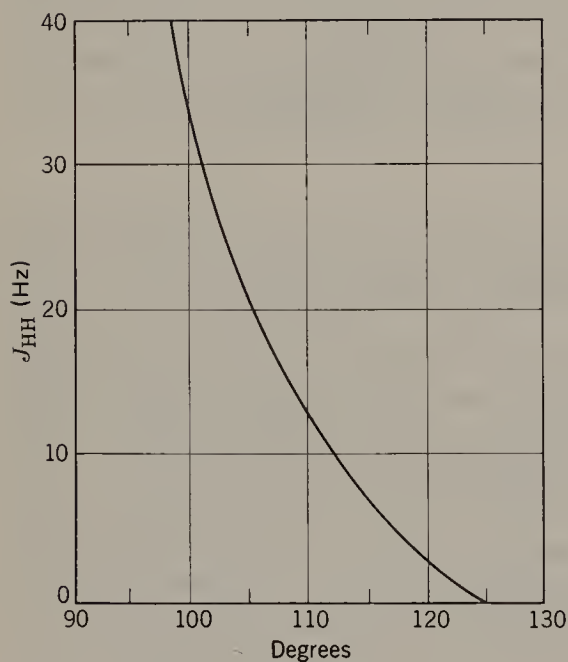


Figure 47. The geminal Karplus correlation.  $J_{HH}$  for  $\text{CH}_2$  groups as function of  $\angle \text{H}-\text{C}-\text{H}$ .

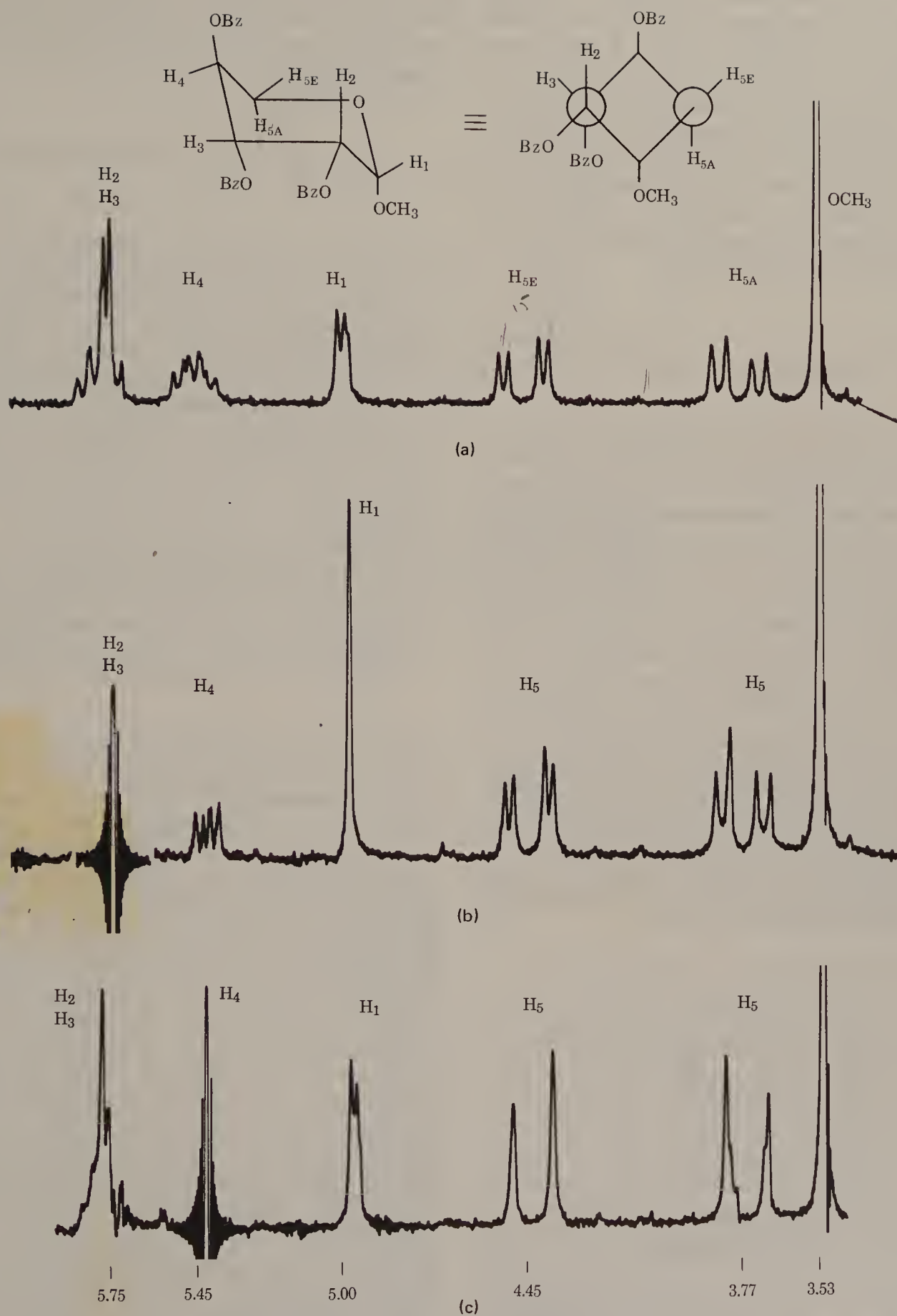
### XIII. SPIN-SPIN DECOUPLING

Spin-spin decoupling (double irradiation or double resonance) is a powerful tool for simplifying a spectrum, for determining the relative positions of protons in a molecule, or for locating a buried absorption.

Spin-spin decoupling is simply a technique for irradiating a nucleus with a strong radiofrequency signal at its resonance frequency, while scanning other nuclei to detect which ones are affected by decoupling from the irradiated

nucleus. The early experiments in spin-spin decoupling were limited to irradiation of other nuclei such as  $^{14}\text{N}$ ,  $^{31}\text{P}$ , or  $^{19}\text{F}$  because of the very large frequency difference from the proton resonance. For example, decoupling of the N atom of a pyrrole or an amide has been used to sharpen the proton absorption, which can be so broad as to be merely a slight bulge on the baseline. As previously pointed out (Section V), this broadening is a result of partial decoupling by the nitrogen electrical quadrupole moment. Irradiation of the nitrogen atom of an amine salt changes the broad  $^+\text{NH}$  absorption to a sharp absorption whose multiplicity depends on the number of  $\alpha$  protons.

Protons can be readily decoupled provided they are more than about 20 Hz apart at 100 MHz. The utility of proton-proton decoupling is shown in the 100 MHz partial spectrum of methyl 2,3,4-tri-*O*-benzoyl- $\beta$ -L-lyxopyranoside (Figure 48). The integration (not shown) gives the following ratios in Figure 48a from high field to low: 3:1:1:1:1:2. The sharp peak at  $\delta$  3.53 is the  $\text{OCH}_3$  group. Decoupling the 2-proton multiplet at  $\delta$  5.75 causes the multiplet at  $\delta$  5.45 to collapse to four peaks, and the doublet at  $\delta$  5.00 to a sharp singlet (Figure 48b). Decoupling the multiplet at  $\delta$  5.45 partially collapses the multiplet at  $\delta$  5.75 and collapses the 2 upfield pairs of doublets (at  $\delta$  4.45 and  $\delta$  3.77) to 2 doublets (Figure 48c). The  $\text{H}_5$  absorption should be upfield since these 2 protons are deshielded by 2 ether oxygens, and  $\text{H}_2$ ,  $\text{H}_3$ , and  $\text{H}_4$  are deshielded by benzoyl groups. The 2  $\text{H}_5$  protons are the *AM* portion of an *AMX* pattern; the  $\text{H}_4$  proton is the *X* portion (with additional splitting). The pair of doublets at  $\delta$  4.45 is 1 ( $\text{H}_5'$ ) proton at  $\text{C}_5$  strongly deshielded by the benzoyl group on  $\text{C}_4$ , and the pair of doublets at  $\delta$  3.77 is



**Figure 48.** (a) Partial spectrum of methyl-2,3,4-tri-O-benzoyl- $\beta$ -L-lyxopyranoside, 100 MHz,  $CDCl_3$ . (b)  $H_2$  and  $H_3$  decoupled. (c)  $H_4$  decoupled. Note that there are two  $H_5$  protons.  $Bz = C_6H_5CO$ .



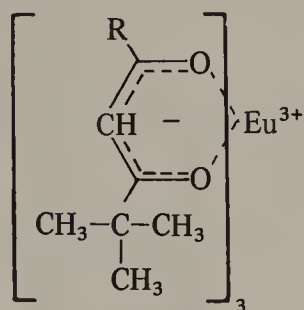
the other ( $H_5$ ) absorption. Further confirmation is provided by the collapse of each pair of doublets to doublets with the characteristic large geminal coupling ( $J = 12.5$  Hz) on irradiation of the multiplet at  $\delta$  5.45, which must therefore be the  $H_4$  absorption (i.e., the  $X$  proton that was further split). The multiplet at  $\delta$  4.75 must therefore represent  $H_2$  and  $H_3$  since irradiation of this multiplet collapsed the multiplet that we identified as  $H_4$  (this now appears as the  $X$  portion of the  $AMX$ ) pattern), and also the doublet at  $\delta$  5.00, which must be the  $H_1$  absorption.

A multiplet caused by coupling to 2 nonequivalent protons can be completely collapsed to a singlet by irradiating both coupling protons simultaneously.

#### XIV. SHIFT REAGENTS

Shift reagents, introduced in 1969, provide a method for spreading out NMR absorption patterns without increasing the strength of the applied magnetic field. Addition of shift reagents to appropriately functionalized samples results in substantial magnification of the chemical shift differences of nonequivalent protons. The shift reagents are ions in the rare earth (lanthanide) series coordinated to organic ligands. Although it had been long known that some metal ions caused shifts, it was not until the application of the more recent shift reagents,  $\text{Eu}(\text{dpm})_3$  and  $\text{Eu}(\text{fod})_3$  that these shifts could be effected without substantial line broadening.

The notation for the more commonly used shift reagents,  $\text{Eu}(\text{dpm})_3$  and  $\text{Eu}(\text{fod})_3$ , come from their names *tris*-(dipivalomethanato)europium and *tris*-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-3,5-octanedionatoeuropium. A more systematic name for the former is *tris*-2,2,6,6-tetramethyl-3,5-heptanedionatoeuropium and thus the (less common) substitute  $\text{Eu}(\text{thd})_3$  for  $\text{Eu}(\text{dpm})_3$ .

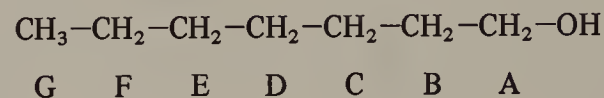


$R = t\text{-butyl}, \text{Eu}(\text{dpm})_3$

$R = \text{CF}_2\text{CF}_2\text{CF}_3, \text{Eu}(\text{fod})_3$

The use of such shift reagents is illustrated in Figure 49 in which the NMR spectrum of 1-heptanol is simplified by the addition of  $\text{Eu}(\text{dpm})_3$ . As is usual for such an alcohol in the absence of shift reagents, the only interpretable sig-

nal (Figure 49a) is that of the methylene adjacent to OH (proton set  $A$ ,  $\delta$  3.8, triplet) and the terminal methyl (distorted set  $G$ , triplet,  $\delta$  0.9). Upon addition of the shift reagent  $\text{Eu}(\text{dpm})_3$ , the signals of the methylene groups closer to the OH group are moved downfield so that a separate signal is available for each of the methylene units (Figure 49c):



The closer the group to the functional group, the greater is the shift per increment of shift reagent (Figure 50). Not all plots analogous to Figure 50 show linearity.

There are two major applications of the shift reagent to structure determination: (1) to simplify the spectrum and (2) to assign the protons from data on the response curves as in Figure 50. The former is straightforward and is subject only to the limit of the dependence of the coupling constant on shift reagent concentration. The latter is less certain because of the many parameters on which these slopes depend.

It is necessary to report the solvent and the concentration of the substrate and shift reagent for a given shift reagent experiment (see Figure 49 legend). Another way to report results is to give the slope of such graphs as Figure 49 as ppm per mole of shift reagent per mole of substrate.

Table III shows the general correlation between basicity

Table III. Variation of the Magnitude of Induced Shift with Functionality<sup>28</sup>

| Functional Group                            | Ppm per Mol of $\text{Eu}(\text{dpm})_3$ per Mol of Substrate in $\text{CCl}_4$ |
|---|---|
| $\text{RCH}_2\text{NH}_2$                   | ~150  |
| $\text{RCH}_2\text{OH}$                     | ~100  |
| $\text{R}_2\text{C}=\text{NOH}$             | ~40   |
| $\text{RCH}_2\text{NH}_2$                   | 30-40   |
| $\text{RCH}_2\text{OH}$                     | 20-25   |
| $\text{RHC}=\text{NOH}$                     | 14-30   |
| $\text{RCH}_2\text{RC}=\text{NOH}$          | 14-10   |
| $\text{RCH}_2\text{COR}$                    | 10-17   |
| $\text{RCH}_2\text{CHO}$                    | 11-19   |
| $\text{RCH}_2\text{SOR}$                    | 9-11  |
| $\text{RCH}_2-\text{O}-\text{CH}_2\text{R}$ | 10 (17-28 in $\text{CDCl}_3$ )  |
| $\text{RCH}_2\text{CO}_2\text{Me}$          | 7   |
| $\text{RCH}_2\text{CO}_2\text{CH}_3$        | 6-5   |
| $\text{RCH}_2\text{CN}$                     | 3-7   |
| $\text{RCH}_2\text{NO}_2$                   | ~0  |
| halides, indoles, alkenes                   | 0   |
| $\text{RCO}_2\text{H}$ and phenols*         | decompose reagent   |

\*Phenols can be studied using  $\text{Eu}(\text{fod})_3$ .

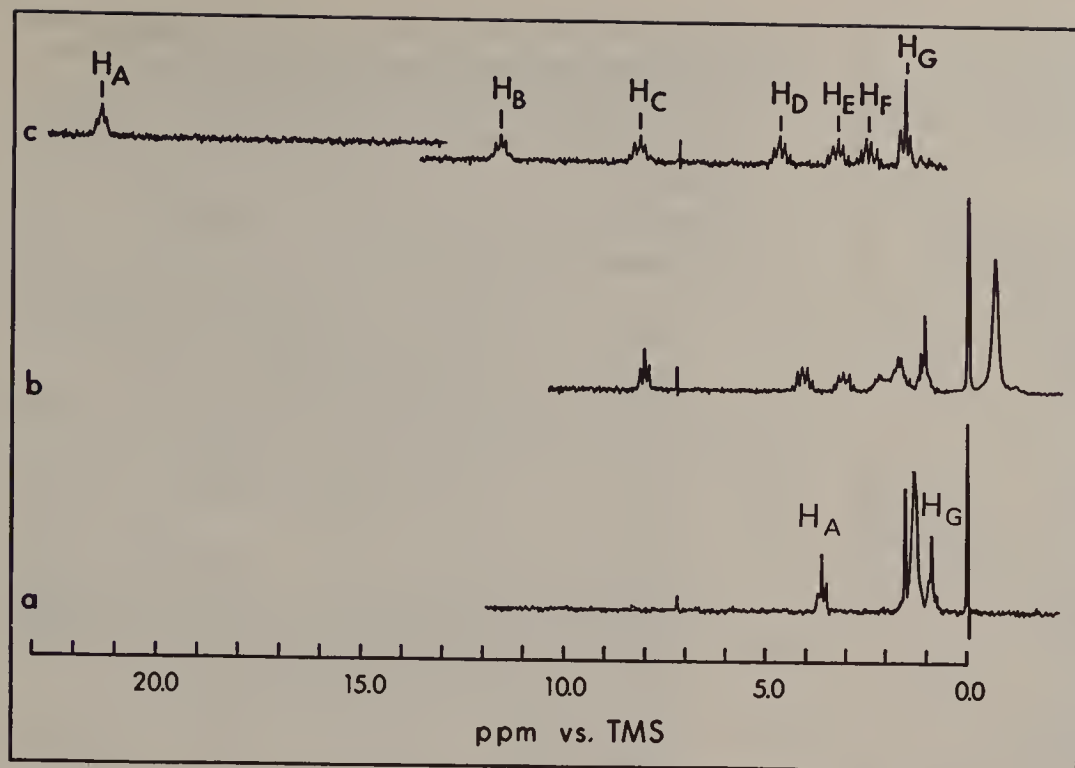


Figure 49. 60 MHz proton NMR spectra of 0.40 ml of  $\text{CDCl}_3$  solution containing 0.300M 1-heptanol at various mole ratios [moles of  $\text{Eu}(\text{dpm})_3$  per mole of 1-heptanol]: (a) 0.00, (b) 0.19, (c) 0.78. Temperature,  $30^\circ\text{C}$ . From *Anal. Chem.*, Vol. 43, p. 1599, Copyright 1971 by the American Chemical Society. Reprinted by permission of the copyright owner.

of the functional group of the substrate and shift magnitude as induced by  $\text{Eu}(\text{dpm})_3$ .  $\text{Eu}(\text{fod})_3$  is normally a "stronger" shift reagent, since it is a stronger Lewis acid; it has the additional advantage of much greater solubility. However quantitative assessments, such as Table II, should be treated with caution, since such data were assembled before it was fully appreciated that shift reagent performance is susceptible to many parameters including the purity of the shift reagent, the method of data handling, and the presence of water. Because of the hygroscopicity of the reagents and the adverse effect of small amounts of water, it is advisable to work in a dry-box for quantitative results.

Experimental limitations are set by the solvents in which the reagents can be used and by the absorption of the protons of the organic ligands on the reagent in the NMR spectrum. Shift reagents are most effective in "non-competitive" solvents, that is, those that do not coordinate strongly to the shift reagent. The most effective solvent is carbon tetrachloride; benzene and deuteriochloroform are also useful, giving shifts that are approximately 90% and 50% as great as in  $\text{CCl}_4$ . One limitation of such solvents is the solubility of the shift reagent alone in the NMR solvent;  $\text{Eu}(\text{dpm})_3$  dissolves to the extent of about 100 mg/ml in benzene and about 200-300 mg/ml in the chlorinated sol-

vents. Effectiveness of the shift reagent analysis may be increased by the use of low temperature NMR. The typical resonances of the ligands in the shift reagents in the presence of substrate are:  $\text{Eu}(\text{fod})_3$ ,  $\delta$  0.4 to 2.0;  $\text{Eu}(\text{dpm})_3$ ,  $\delta$  -1.0 to -2.0;  $\text{Pr}(\text{dpm})_3$ ,  $\delta$  3.0 to 5.0. Deuterated reagents are available to alleviate this interference. The substrates under study may be recovered by the use of tlc or glc.

Most explanations for the effect of shift reagents are based on a pseudocontact mechanism. The dependence of the magnitude of the shift on the distance of the protons of interest from the functional group is only an approximation in the pseudocontact shift equation; this dependence breaks down when the shift reagent coordination with the substrate is not a simple, linear situation, that is, when unique molecular geometry causes an acute proton-functional group-rare earth atom angle. The equilibrium for the shift reagent with the substrate is rapidly established and thus only a single set of time-averaged peaks is observed. Upfield shifts can be effected by the use of diamagnetic shift reagents, for example complexes of Pr. Optical purity (enantiomeric composition) of chiral substrates may be determined by using shift reagents with chiral ligands. Excellent reviews have been published.<sup>28-32</sup>



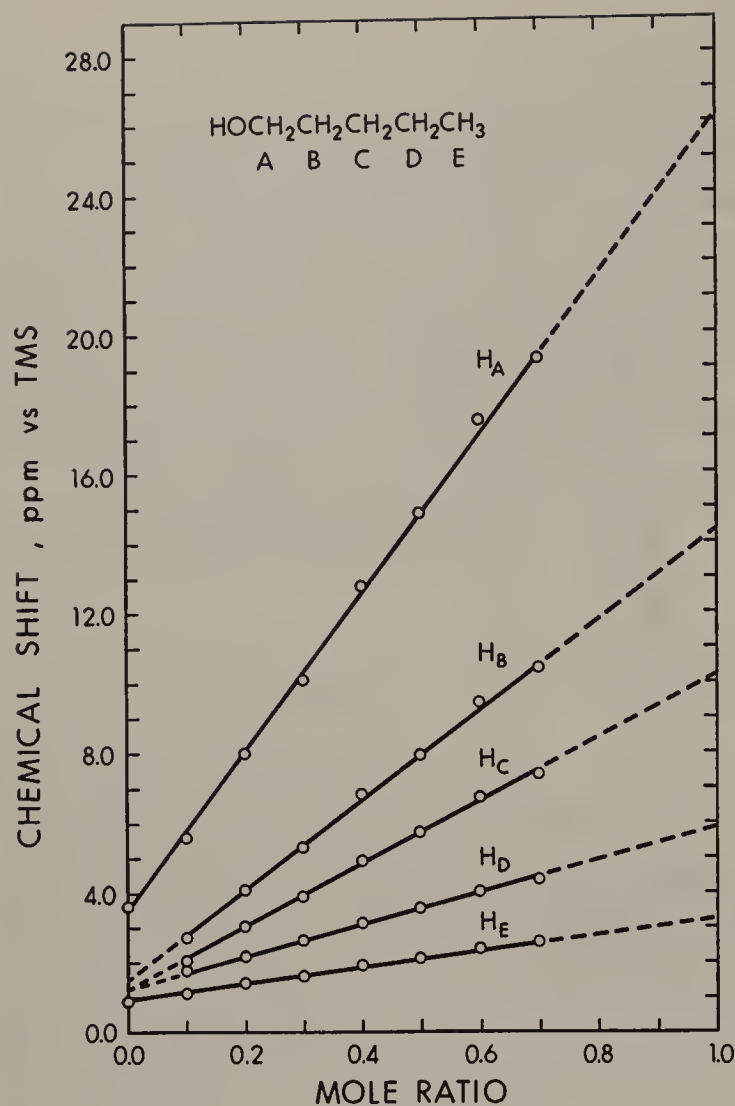


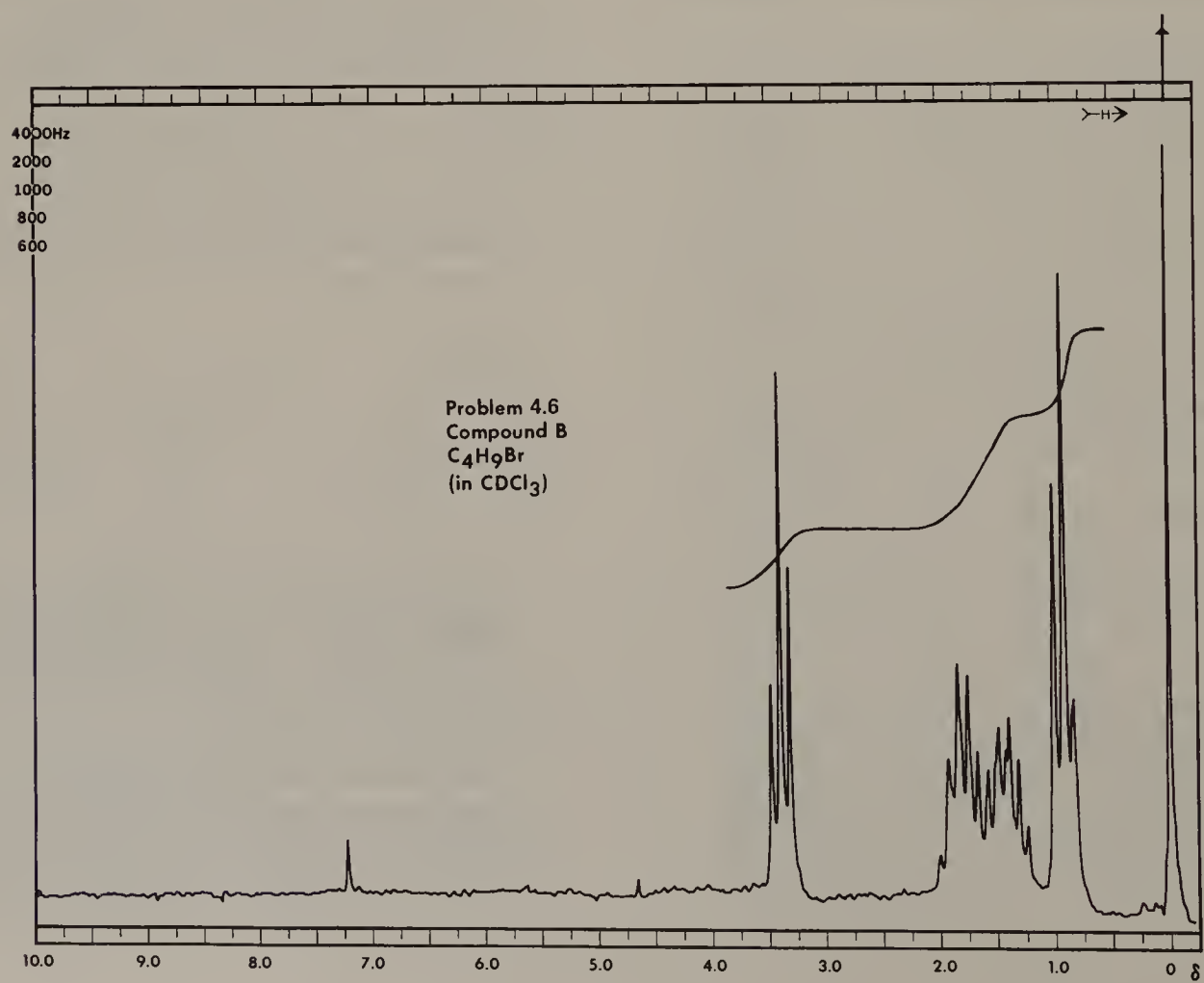
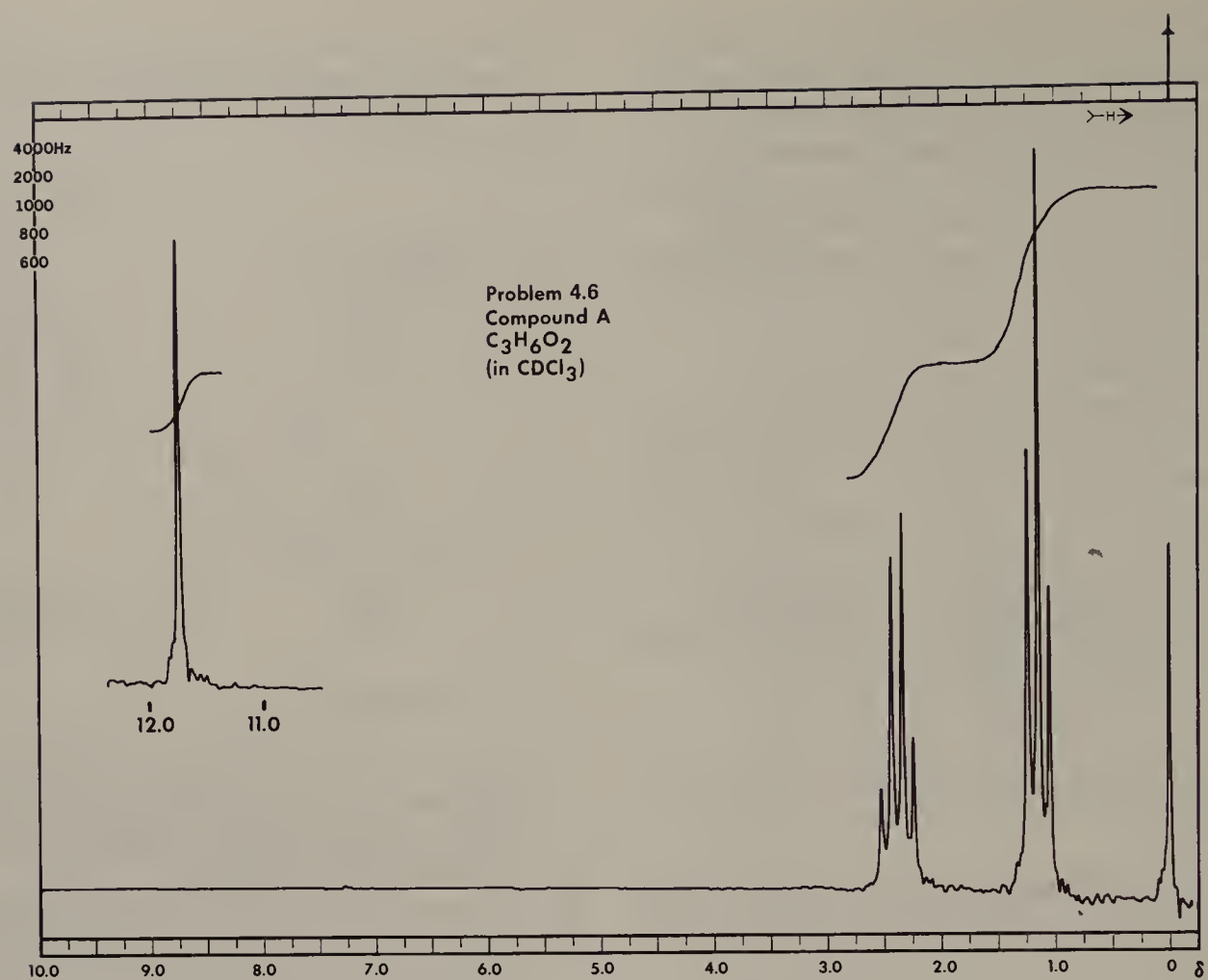
Figure 50. Variation in chemical shift for carbon-bonded protons of 1-pentanol in  $\text{CDCl}_3$  (0.40 ml of 0.300M solution) with increasing concentration of  $\text{Eu(dpm)}_3$ . Temperature,  $30^\circ\text{C}$ . From Anal. Chem., Vol. 43, p. 1599. Copyright by the American Chemical Society (1971) Printed by permission of the copyright owner.

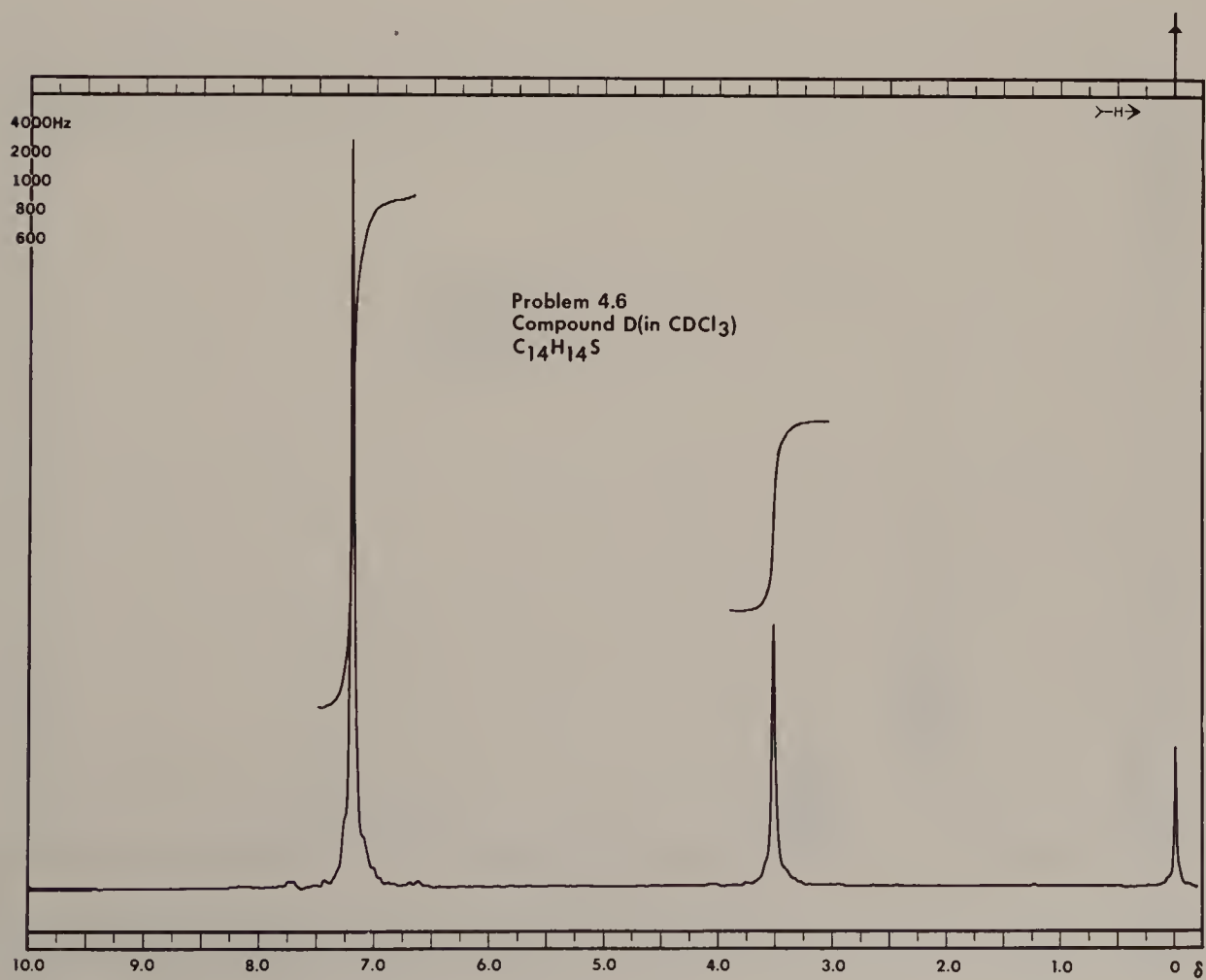
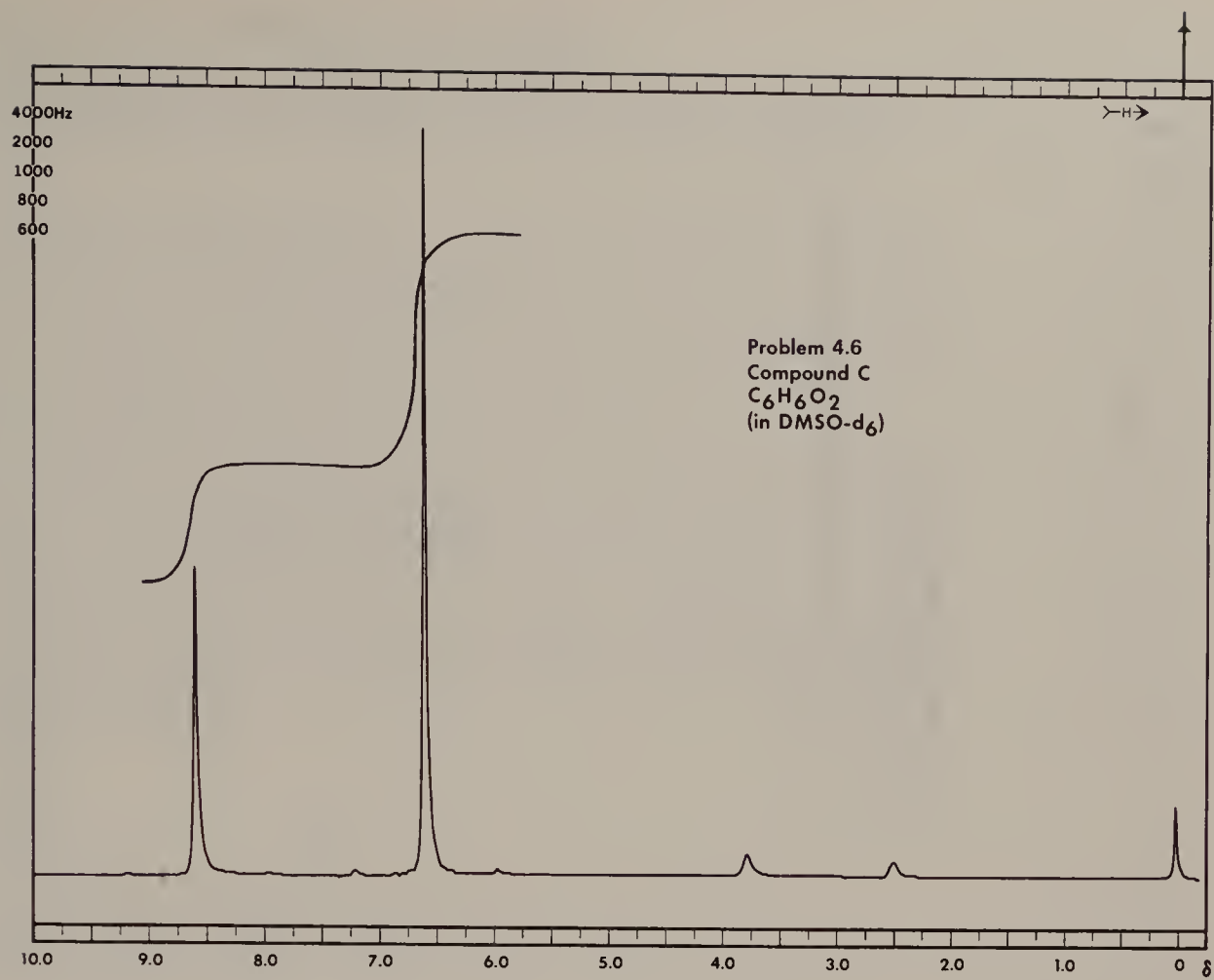
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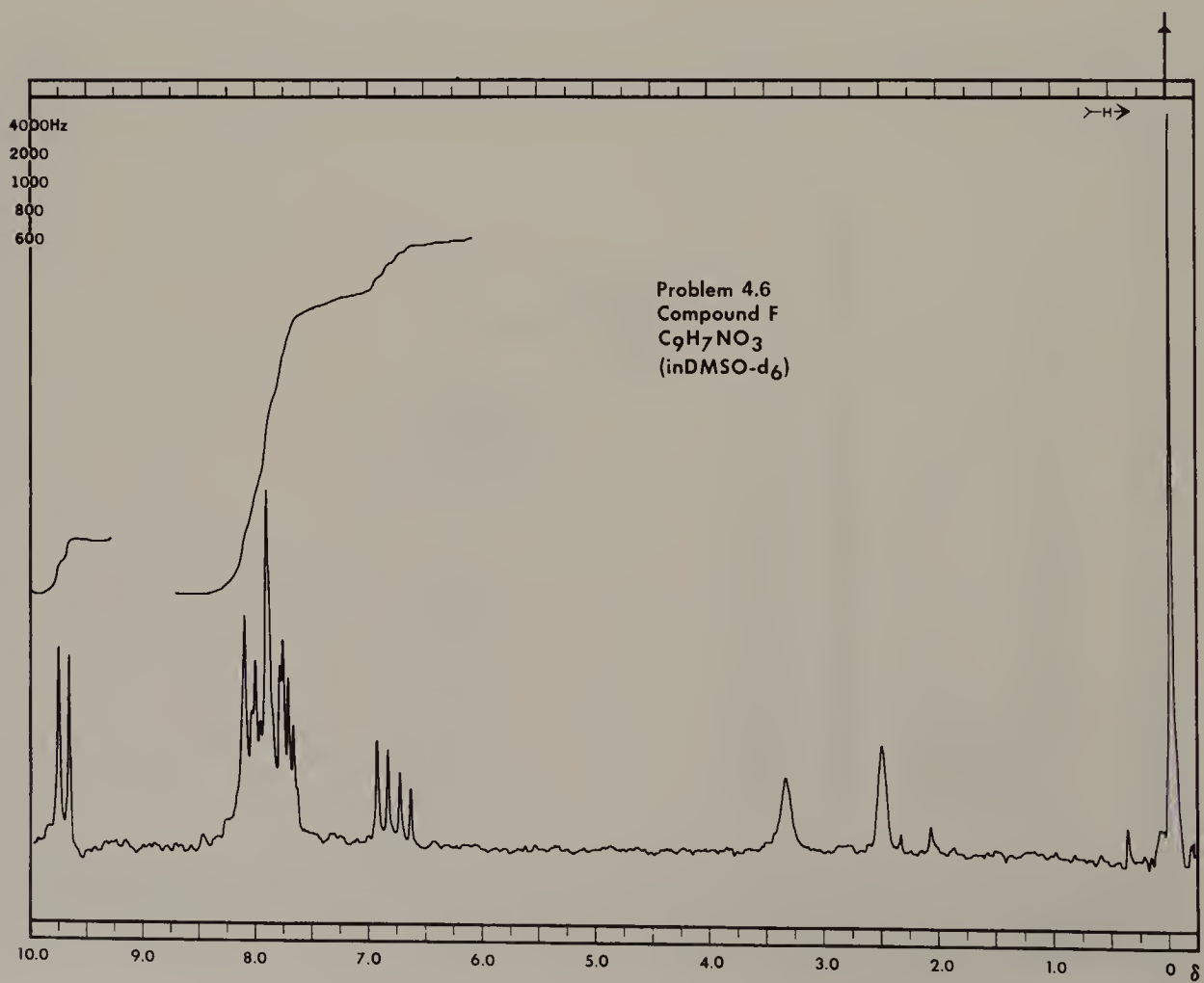
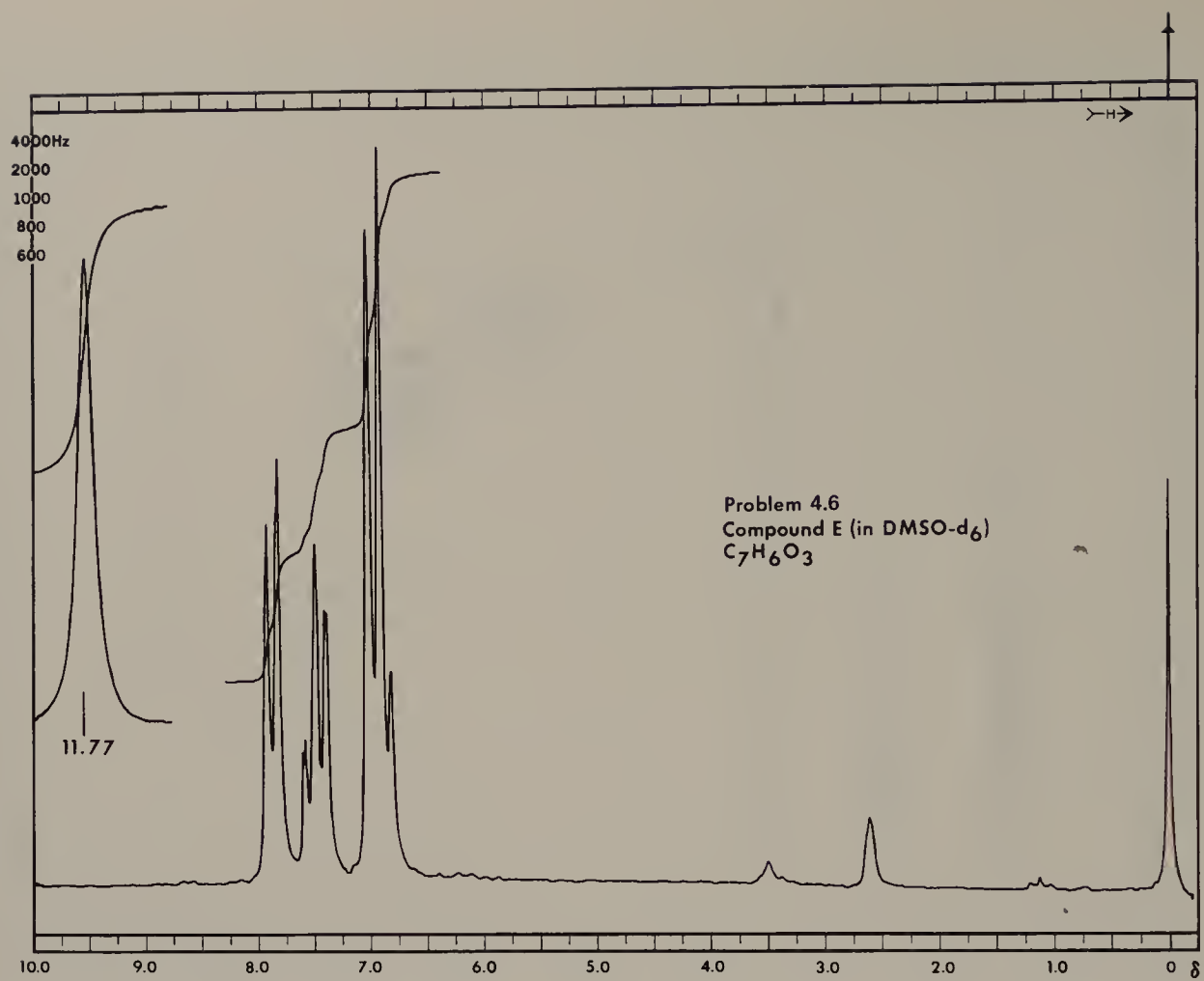












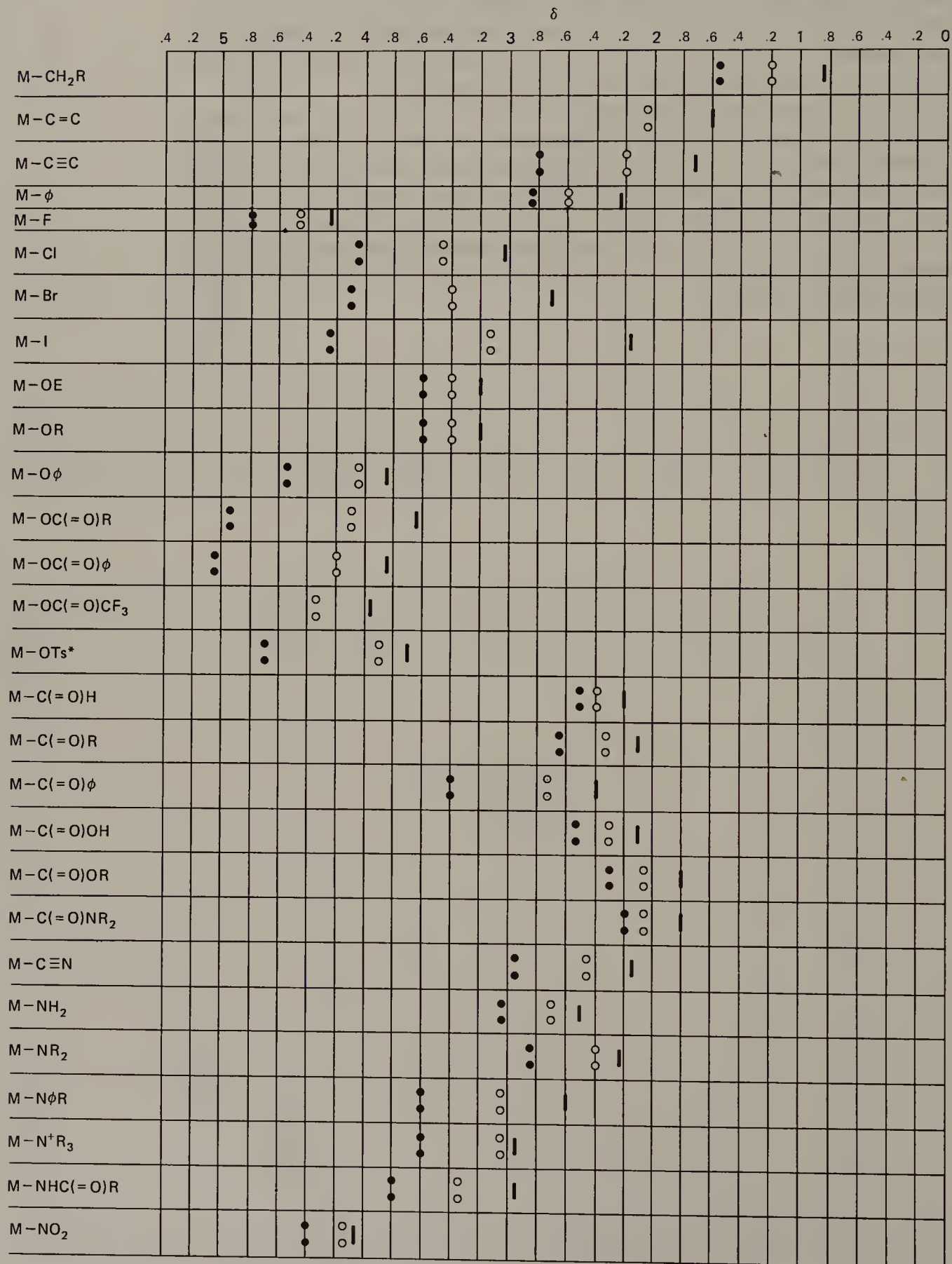
## appendix a. effect on shift positions of a single functional group

Charts 1 and 2 give the chemical shifts of  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  groups that are adjacent to, or once removed from, a functional group in aliphatic compounds. In a hydrocarbon, the methyl protons are at about  $\delta$  0.90, the methylene protons at about  $\delta$  1.25, and the methine protons at about  $\delta$  1.50. The first line of the first chart, for example, shows that the protons of  $\text{CH}_3\text{Br}$  absorb at about  $\delta$  2.70, the methylene protons of  $\text{RCH}_2\text{Br}$  at about  $\delta$  3.40, and the methine protons of  $\text{R}_2\text{CHBr}$  at about  $\delta$  4.10.

The shift positions vary with changes in solvent or concentration, but in general these variations are slight in the absence of a very polar solvent or of hydrogen bonding. The positions shown are average values for ranges that are not greater than 0.5 ppm wide if the common solvents  $\text{CCl}_4$  or  $\text{CDCl}_3$  are used. These values were gathered from several sources: Jackman and Sternhell<sup>4</sup>, Chamberlain<sup>25</sup>, Bovey<sup>26</sup>, K. Nukada, et al. *Anal. Chem.* **35**, 1892 (1963), and G. V. D. Tiers (*NMR Summary*; 3M Company, St. Paul, Minnesota). The functional groups are arranged in the order in which they are covered in organic chemistry textbooks.

# CHART 1. CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ADJACENT ( $\alpha$ - POSITION) TO A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M-Y).

| M = methyl  
 ○ M = methylene  
 • M = methine





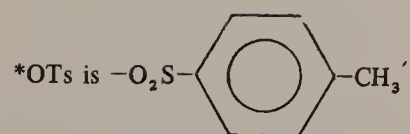
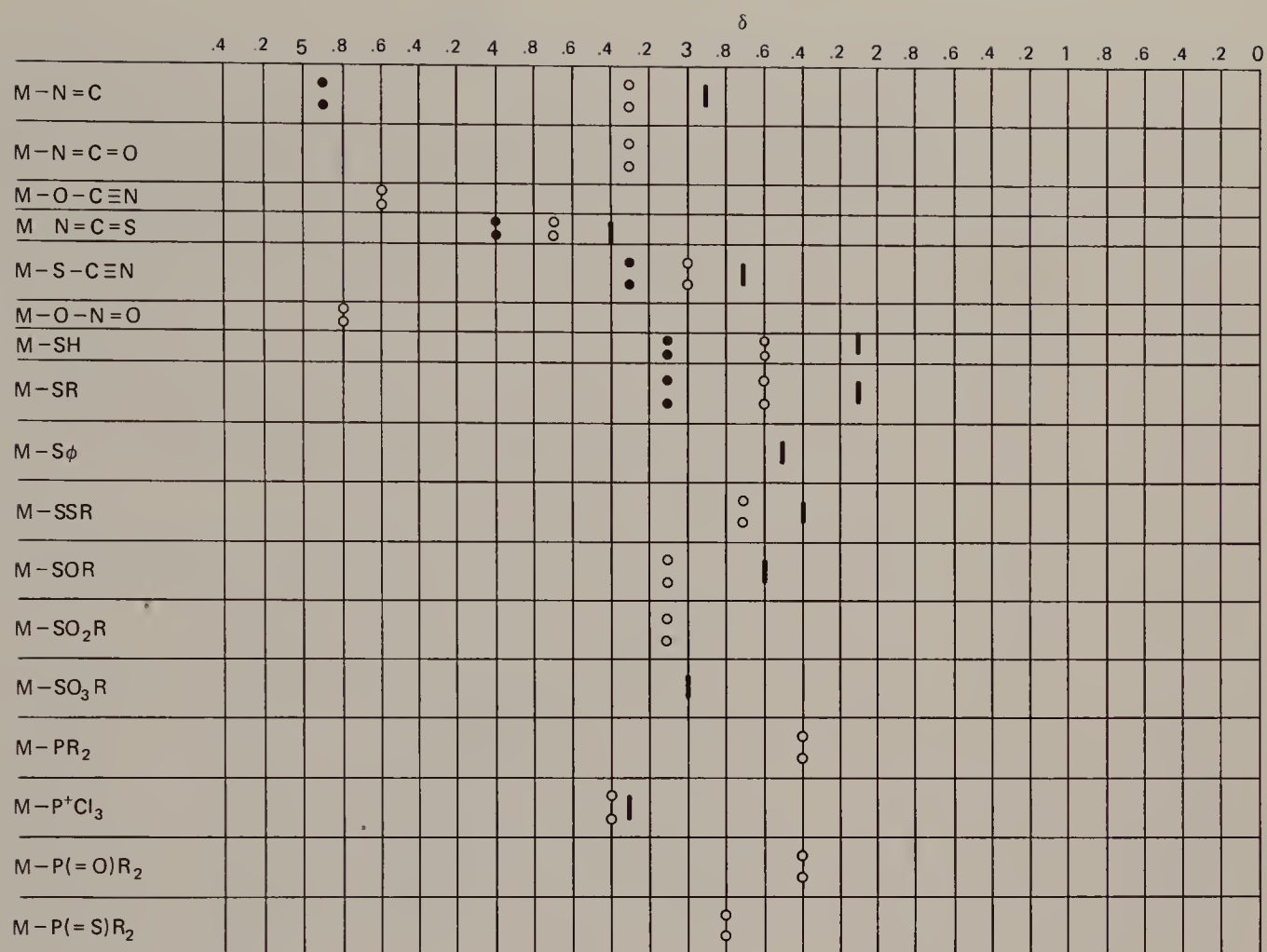
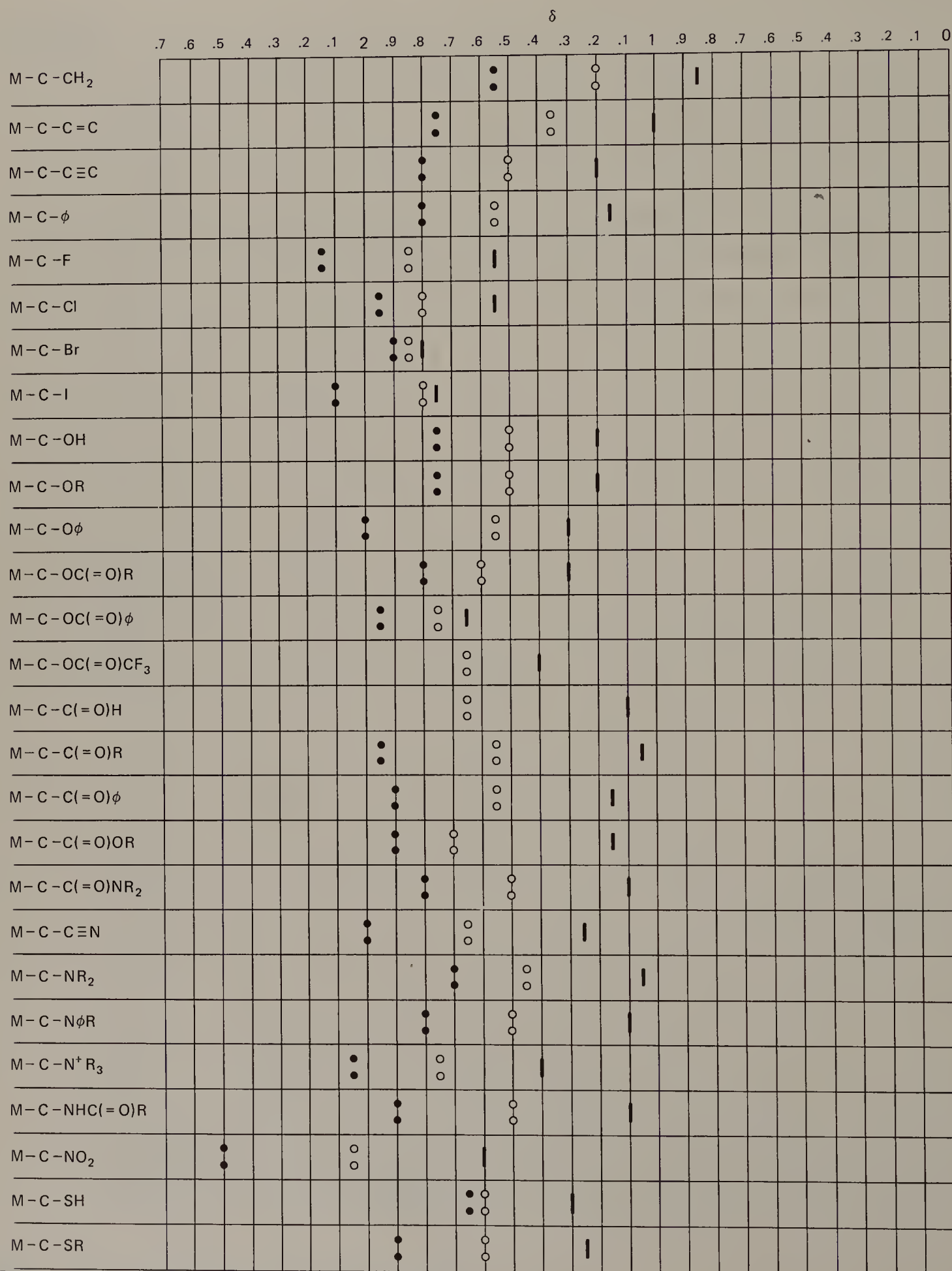


CHART 2. CHEMICAL SHIFTS OF PROTONS ON A CARBON  
 ATOM ONCE REMOVED ( $\beta$  - POSITION) FROM A  
 FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M-C-Y).

M is methyl  
 M is methylene  
 M is methine



## appendix b. effect on chemical shifts of two or three functional groups ( $Y-CH_2-Z$ , and $Y-\underset{\substack{| \\ W}}{CH}-Z$ )

Shoolery's rules (B. P. Dailey and J. W. Shoolery, *J. Am. Chem. Soc.*, 77, 3977 (1955)) permit calculation of a shift position of a methylene group attached to two functional groups by the additive effect of the shielding constants in Table 1, below. The sum of the constants is added to  $\delta$  0.23, the position for  $CH_4$ .

Thus, to calculate the shift for the  $-CH_2-$  protons of  $C_6H_5CH_2Br$ :

$$\begin{array}{rcl} C_6H_5 & = & 1.85 \quad 0.23 \\ Br & = & 2.33 \quad 4.18 \\ \hline & & 4.18 \quad 4.41 = \delta \text{ value for the } -CH_2- \text{ group.} \end{array}$$

Table I. Shielding Constants

| Y or Z       | Shielding<br>Constants | Y or Z       | Shielding<br>Constants |
|--------------|------------------------|--------------|------------------------|
| $-CH_3$      | 0.47                   | $-C(=O)NR_2$ | 1.59                   |
| $-C=C$       | 1.32                   | $-C\equiv N$ | 1.70                   |
| $-C\equiv C$ | 1.44                   | $-NR_2$      | 1.57                   |
| $-\phi$      | 1.85                   | $-NHC(=O)R$  | 2.27                   |
| $-CF_2$      | 1.21                   | $-N_3$       | 1.97                   |
| $-CF_3$      | 1.14                   | $-SR$        | 1.64                   |
| $-Cl$        | 2.53                   | $-OSO_2R$    | 3.13                   |
| $-Br$        | 2.33                   |              |                        |
| $-I$         | 1.82                   |              |                        |
| $-OH$        | 2.56                   |              |                        |
| $-OR$        | 2.36                   |              |                        |
| $-O\phi$     | 3.23                   |              |                        |
| $-OC(=O)R$   | 3.13                   |              |                        |
| $-C(=O)R$    | 1.70                   |              |                        |
| $-C(=O)\phi$ | 1.84                   |              |                        |
| $-C(=O)OR$   | 1.55                   |              |                        |

The shielding constants have been used to prepare the chart on page 224. Several values have been added to the original set of constants.

Alternatively, Chart 1 can be used to find the shift position of a methylene group attached to two functional groups from the  $\delta$  values in the box at the intersection of the horizontal and diagonal groups ("mileage chart"). The upper number in each box is an experimental value; the lower number is calculated from Shoolery's constants.



# CHART 1. CHEMICAL SHIFTS FOR METHYLENE GROUPS ATTACHED TO TWO FUNCTIONAL GROUPS (Y-CH<sub>2</sub>-Z).

| GROUP                 | -CH <sub>3</sub> | -C=C | -C≡C | -φ   | -CF <sub>2</sub> | -CF <sub>3</sub> | -Cl  | -Br  | -I   | -OH  | -OR  | -Oφ  | -O(C=O)R | -(C=O)R | -(C=O)φ | -(C=O)OR | -C(=O)NR <sub>2</sub> | -C≡N | -NR <sub>1</sub> | -NH(C=O)R | -N <sub>3</sub> | -SR  |
|-----------------------|------------------|------|------|------|------------------|------------------|------|------|------|------|------|------|----------|---------|---------|----------|-----------------------|------|------------------|-----------|-----------------|------|
| -CH <sub>3</sub>      | 1.17             | 1.90 | 2.14 | 2.55 | 1.91             | 1.84             | 3.57 | 3.43 | 3.20 | 3.70 | 3.40 |      | 4.25     | 2.47    |         | 2.25     | 2.23                  |      | 2.63             |           |                 | 2.53 |
|                       |                  | 2.02 | 2.60 | 3.39 | 3.30             |                  |      | 3.23 | 3.03 | 2.52 | 3.26 | 3.06 | 3.93     | 3.83    | 2.40    | 2.54     | 2.25                  | 2.29 | 2.40             | 2.27      | 2.97            | 2.67 |
| -C=C                  |                  | 2.87 | 2.99 | 3.40 | 2.76             | 2.69             | 4.08 | 3.88 | 3.37 | 4.13 | 3.91 | 4.78 | 4.68     | 3.25    | 3.39    | 3.10     | 3.14                  | 3.25 | 3.12             | 3.82      | 3.52            | 3.19 |
|                       |                  |      |      |      |                  |                  | 4.09 | 3.90 |      |      |      |      | 4.71     |         |         |          |                       |      |                  |           |                 | 3.08 |
| -C≡C                  |                  | 3.11 |      | 3.52 | 2.88             | 2.81             | 4.20 | 4.00 | 3.49 | 4.28 | 4.03 | 4.90 | 4.80     | 3.37    | 3.51    | 3.22     | 3.26                  | 3.37 | 3.24             | 3.97      | 3.67            | 3.31 |
|                       |                  |      | 3.97 |      | 3.50             | 4.50             | 4.35 |      |      |      | 4.70 | 4.91 | 5.08     | 3.55    |         | 3.40     |                       | 3.65 | 3.48             |           |                 | 3.68 |
| -φ                    |                  | 3.93 | 3.29 | 3.22 | 4.61             | 4.41             | 3.90 | 4.58 | 4.44 | 5.31 | 5.21 | 3.78 | 3.92     | 3.63    | 3.66    | 3.78     | 3.65                  | 3.78 | 3.65             | 4.34      | 4.04            | 3.72 |
|                       |                  |      |      |      |                  |                  |      | 4.01 |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
| -CF <sub>2</sub>      |                  | 2.63 |      |      |                  |                  |      |      |      | 4.01 |      |      |          |         |         |          |                       |      |                  |           |                 |      |
|                       |                  |      |      |      |                  |                  |      | 3.56 |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
| -CF <sub>3</sub>      |                  | 2.51 |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
|                       |                  |      |      |      |                  |                  |      | 3.90 | 3.70 | 3.19 | 3.93 | 4.73 | 4.60     | 4.54    | 3.07    | 3.21     | 2.92                  | 2.96 | 3.07             | 2.94      | 3.64            | 3.34 |
| -Cl                   |                  | 4.99 |      |      |                  |                  |      |      |      |      |      |      |          |         |         | 4.05     | 4.17                  | 4.07 |                  |           |                 |      |
|                       |                  | 5.29 |      |      |                  |                  |      | 5.16 | 5.09 | 4.99 | 5.32 | 5.12 | 5.99     | 5.89    | 4.46    | 4.60     | 4.31                  | 4.35 | 4.46             | 4.37      | 5.13            | 4.73 |
| -Br                   |                  | 4.94 |      |      |                  |                  |      |      |      |      |      | 6.36 |          |         | 4.40    | 3.70     | 3.92                  |      |                  |           |                 |      |
|                       |                  | 4.89 |      |      |                  |                  |      | 4.94 | 4.89 | 4.38 | 5.12 | 4.92 | 5.79     | 5.69    | 4.26    | 3.40     | 4.11                  | 4.15 | 4.26             | 4.13      | 4.83            | 4.53 |
| -I                    |                  | 3.90 |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          | 3.65                  | 3.65 |                  |           |                 |      |
|                       |                  | 3.87 |      |      |                  |                  |      | 3.90 | 3.87 | 4.61 | 4.41 | 5.16 | 5.06     | 3.75    | 3.89    | 3.60     | 3.64                  | 3.75 | 3.62             | 4.32      | 4.02            | 3.69 |
| -OH                   |                  | 4.55 |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
|                       |                  | 4.35 |      |      |                  |                  |      | 4.55 | 4.35 | 5.15 | 6.02 | 5.92 | 4.49     | 4.63    | 4.34    | 4.38     | 4.49                  | 4.35 | 5.06             | 4.76      | 4.43            |      |
| -OR                   |                  | 5.55 |      |      |                  |                  |      |      |      |      |      |      |          |         |         | 4.13     |                       | 4.20 |                  |           |                 |      |
|                       |                  | 4.95 |      |      |                  |                  |      | 5.55 | 4.95 | 5.82 | 5.72 | 4.29 | 4.43     | 4.22    | 4.18    | 4.29     | 4.15                  | 4.94 | 4.64             | 4.23      |                 |      |
| -Oφ                   |                  | 6.69 |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          | 4.45                  |      | 5.03             | 5.86      | 5.56            | 5.10 |
|                       |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
| -OC(=O)R              |                  |      |      |      |                  |                  |      |      |      |      |      |      |          | 4.42    |         |          |                       |      |                  |           |                 |      |
|                       |                  | 6.46 |      |      |                  |                  |      |      |      |      |      |      |          | 5.10    | 5.20    | 4.91     | 4.95                  | 5.10 | 4.92             | 5.63      | 5.37            | 5.00 |
| -C(=O)R               |                  |      |      |      |                  |                  |      |      |      |      |      |      |          | 3.60    |         | 3.37     |                       |      |                  | 4.10      |                 |      |
|                       |                  | 3.63 |      |      |                  |                  |      |      |      |      |      |      |          | 3.77    | 3.48    | 3.52     | 3.63                  | 3.50 | 4.20             | 3.90      | 3.57            |      |
| -C(=O)φ               |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         | 3.91    | 3.62     | 3.66                  | 3.77 | 3.64             | 4.34      | 4.02            | 3.71 |
|                       |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
| -C(=O)OR              |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         | 3.35     |                       |      | 3.17             |           |                 |      |
|                       |                  | 3.33 |      |      |                  |                  |      |      |      |      |      |      |          | 3.37    | 3.48    | 3.35     | 4.05                  | 3.75 | 3.42             |           |                 |      |
| -C(=O)NR <sub>2</sub> |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          | 3.30                  |      |                  |           |                 |      |
|                       |                  | 3.41 |      |      |                  |                  |      |      |      |      |      |      |          | 3.52    | 3.39    | 4.09     | 3.79                  | 3.46 |                  |           |                 |      |
| -C≡N                  |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
|                       |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
| -NR <sub>2</sub>      |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
|                       |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
| -NHC(=O)R             |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
|                       |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
| -N <sub>3</sub>       |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
|                       |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
| -SR                   |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |
|                       |                  |      |      |      |                  |                  |      |      |      |      |      |      |          |         |         |          |                       |      |                  |           |                 |      |

Table II can be used to calculate chemical shifts of  $Y-CH_3$ ,  $Y-CH_2-Z$ , or  $Y-\overset{\overset{2}{\text{CH}_2}}{\underset{\underset{1}{\text{W}}}{\text{CH}}}-Z$  groups. Thus, the  $CH_2$  chemical shifts in  $Br\overset{2}{CH_2}\overset{1}{CH_2}OCH_2CH_2Br$  can be calculated.

| 1-CH <sub>2</sub>                     |             | 2-CH <sub>2</sub>        |             |
|---------------------------------------|-------------|--------------------------|-------------|
| CH <sub>2</sub> standard (footnote b) | 1.20        | CH <sub>2</sub> standard | 1.20        |
| α-OR                                  | 2.35        | α-Br                     | 2.18        |
| β-Br                                  | 0.60        | β-OR                     | 0.15        |
|                                       | <u>4.15</u> |                          | <u>3.53</u> |

Determined: 1-CH<sub>2</sub> at ~δ 3.80; 2-CH<sub>2</sub> at ~δ 3.40.

Table II. Substituent Effects on Chemical Shift<sup>a</sup>

| $\begin{array}{c} \text{C}-\text{C}-\text{H} \\   \quad   \\ \beta \quad \alpha \end{array}$   |                               |                    |            |
|--|-------------------------------|--------------------|------------|
| Substituent  | Type of Hydrogen <sup>b</sup> | Alpha Shift        | Beta Shift |
| -C=C-  | CH <sub>3</sub>               | 0.78               | -          |
|  | CH <sub>2</sub>               | 0.75               | 0.10       |
|  | CH                            | -                  | -          |
| -C=C-C-R<br>  <br>X<br>(X=C or O)  | CH <sub>3</sub>               | 1.08               | -          |
| Aryl   | CH <sub>3</sub>               | 1.40               | 0.35       |
|  | CH <sub>2</sub>               | 1.45               | 0.53       |
|  | CH                            | 1.33               | -          |
| -Cl  | CH <sub>3</sub>               | 2.43               | 0.63       |
|  | CH <sub>2</sub>               | 2.30               | 0.53       |
|  | CH                            | 2.55               | 0.03       |
| -Br  | CH <sub>3</sub>               | 1.80               | 0.83       |
|  | CH <sub>2</sub>               | 2.18               | 0.60       |
|  | CH                            | 2.68               | 0.25       |
| -I   | CH <sub>3</sub>               | 1.28               | 1.23       |
|  | CH <sub>2</sub>               | 1.95               | 0.58       |
|  | CH                            | 2.75               | 0.00       |
| -OH  | CH <sub>3</sub>               | 2.50               | 0.33       |
|  | CH <sub>2</sub>               | 2.30               | 0.13       |
|  | CH                            | 2.20               | -          |
| -OR (R is saturated)   | CH <sub>3</sub>               | 2.43               | 0.33       |
|  | CH <sub>2</sub>               | 2.35               | 0.15       |
|  | CH                            | 2.00               | -          |
| $\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ -\text{OC}-\text{R}, -\text{OC}-\text{OR}, -\text{OAr} \end{array}$              | CH <sub>3</sub>               | 2.88               | 0.38       |
|  | CH <sub>2</sub>               | 2.98               | 0.43       |
|  | CH                            | 3.43 (esters only) | -          |
| $\begin{array}{c} \text{O} \\    \\ -\text{CR}, \text{ where R is alkyl,} \\ \text{aryl, OH, OR}', \text{H, CO,} \\ \text{or N} \end{array}$ | CH <sub>3</sub>               | 1.23               | 0.18       |
|  | CH <sub>2</sub>               | 1.05               | 0.31       |
|  | CH                            | 1.05               | -          |
| -NRR'  | CH <sub>3</sub>               | 1.30               | 0.13       |
|  | CH <sub>2</sub>               | 1.33               | 0.13       |
|  | CH                            | 1.33               | -          |

<sup>a</sup>From the Ph.D. dissertation of T.J. Curphey, Harvard University, by permission.

<sup>b</sup>Standard positions are CH<sub>3</sub>, δ0.87; CH<sub>2</sub>, δ1.20; CH, δ1.55.

# appendix c. chemical shifts in alicyclic and heterocyclic rings

Table I. Chemical Shifts in Alicyclic Rings

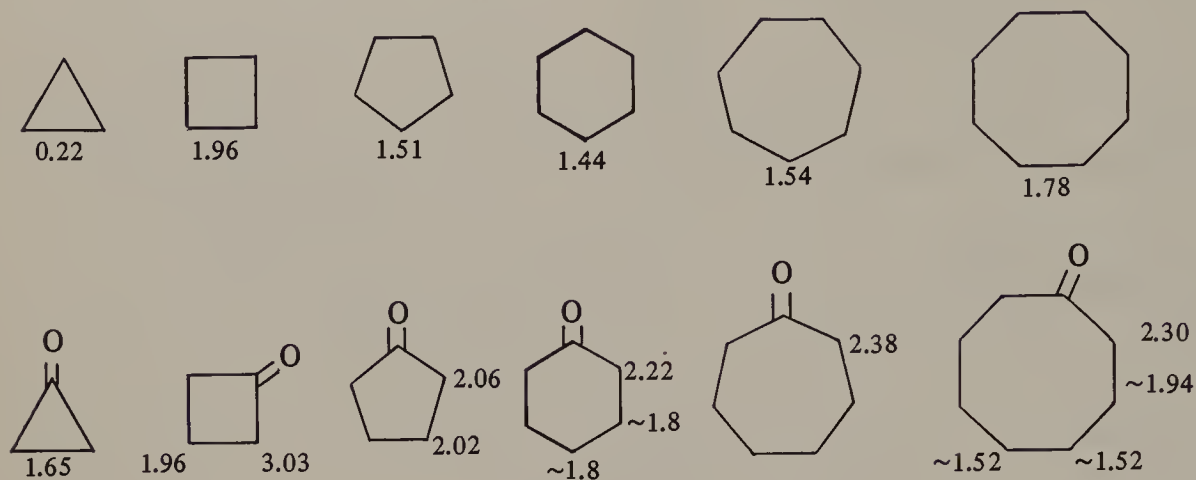
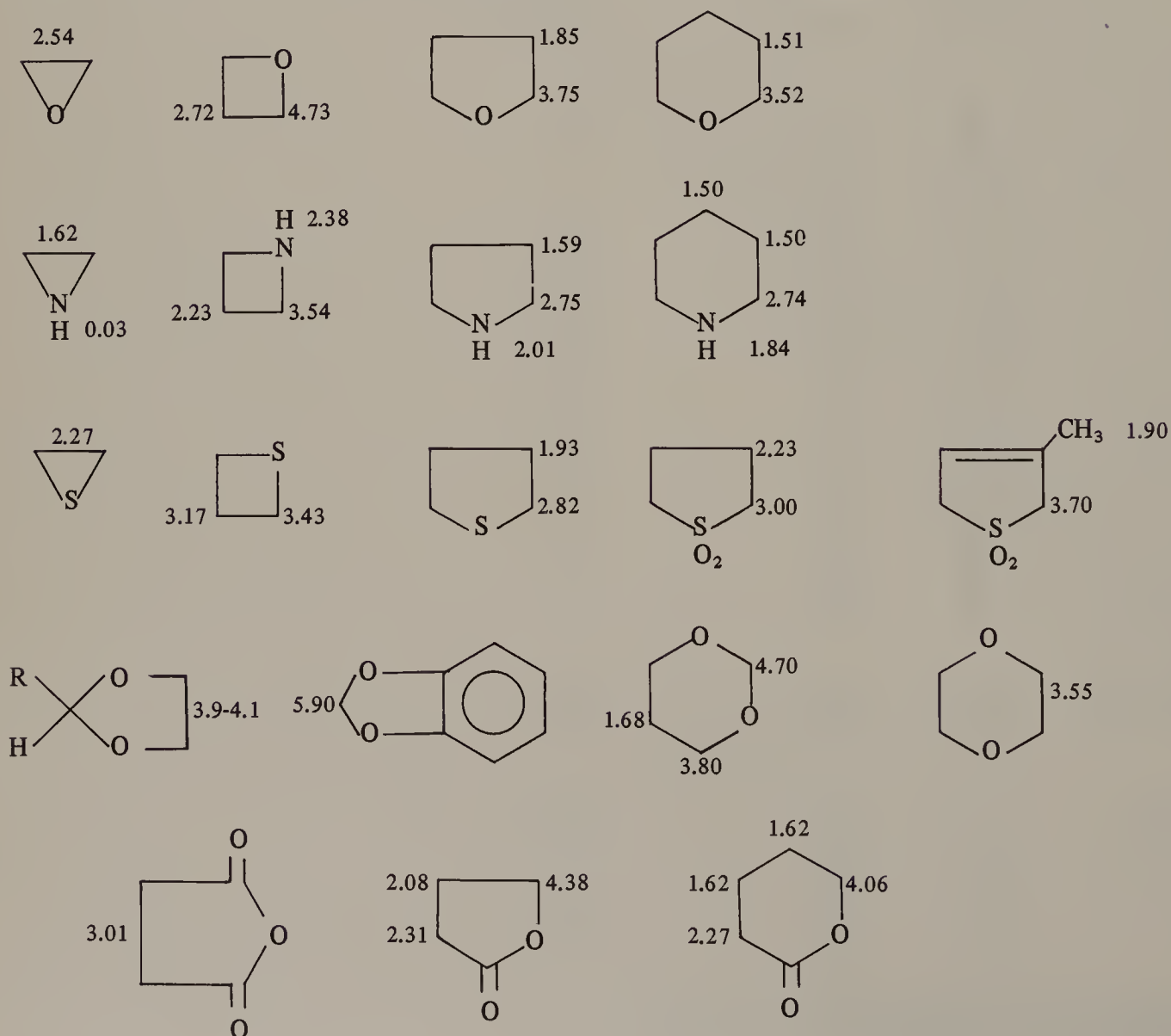
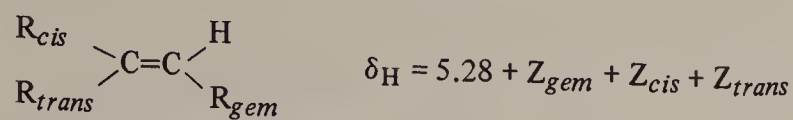


Table II. Chemical Shifts in Heterocyclic Rings

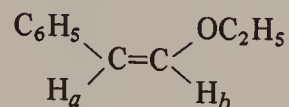




## appendix d. chemical shifts in unsaturated systems



For example, the chemical shifts of the olefinic protons in



are calculated:

|         |                  |             |               |
|---------|------------------|-------------|---------------|
| $H_a$ : | $C_6H_5_{gem}$   | 1.35        | 5.28          |
|         | $OR_{trans}$     | -1.28       | 0.07          |
|         |                  | <u>0.07</u> | $\delta$ 5.35 |
| $H_b$ : | $OR_{gem}$       | 1.18        | 5.28          |
|         | $C_6H_5_{trans}$ | -0.10       | 1.08          |
|         |                  | <u>1.08</u> | $\delta$ 6.36 |

Table I. Substituent Constants (Z) for Chemical Shifts of Substituted Ethylenes (in CCl<sub>4</sub>)

| Substituent R                            | Z          |            |              | Substituent R                             | Z          |            |              |
|--|------------|------------|--------------|---|------------|------------|--------------|
|  | <i>gem</i> | <i>cis</i> | <i>trans</i> |   | <i>gem</i> | <i>cis</i> | <i>trans</i> |
| -H                                       | 0          | 0          | 0            | -C(=O)H                                   | 1.03       | 0.97       | 1.21         |
| -Alkyl                                   | 0.44       | -0.26      | -0.29        | -C(=O)N                                   | 1.37       | 0.93       | 0.35         |
| -Alkyl-Ring <sup>a</sup>                 | 0.71       | -0.33      | -0.30        | -C(=O)Cl                                  | 1.10       | 1.41       | 0.99         |
| -CH <sub>2</sub> O, -CH <sub>2</sub>     | 0.67       | -0.02      | -0.07        | -OR, R:aliph.                             | 1.18       | -1.06      | -1.28        |
| -CH <sub>2</sub> S                       | 0.53       | -0.15      | -0.15        | -OR, R:conj. <sup>b</sup>                 | 1.14       | -0.65      | -1.05        |
| -CH <sub>2</sub> Cl, -CH <sub>2</sub> Br | 0.72       | 0.12       | 0.07         | -OCOR                                     | 2.09       | -0.40      | -0.67        |
| -CH <sub>2</sub> N                       | 0.66       | -0.05      | -0.23        | -Aromatic                                 | 1.35       | 0.37       | -0.10        |
| -C≡C                                     | 0.50       | 0.35       | 0.10         | -Cl                                       | 1.00       | 0.19       | 0.03         |
| -C≡N                                     | 0.23       | 0.78       | 0.58         | -Br                                       | 1.04       | 0.40       | 0.55         |
| -C=C                                     | 0.98       | -0.04      | -0.21        | -N(R) <sub>2</sub> , R:aliph.             | 0.69       | -1.19      | -1.31        |
| -C=C conj. <sup>b</sup>                  | 1.26       | 0.08       | -0.01        | -N(R) <sub>2</sub> , R:conj. <sup>b</sup> | 2.30       | -0.73      | -0.81        |
| -C=O                                     | 1.10       | 1.13       | 0.81         | -SR                                       | 1.00       | -0.24      | -0.04        |
| -C=O conj. <sup>b</sup>                  | 1.06       | 1.01       | 0.95         | -SO <sub>2</sub>                          | 1.58       | 1.15       | 0.95         |
| -COOH                                    | 1.00       | 1.35       | 0.74         |   |            |            |              |
| -COOH conj. <sup>b</sup>                 | 0.69       | 0.97       | 0.39         |   |            |            |              |
| -COOR                                    | 0.84       | 1.15       | 0.56         |   |            |            |              |
| -COOR conj. <sup>b</sup>                 | 0.68       | 1.02       | 0.33         |   |            |            |              |

<sup>a</sup>Alkyl-ring indicates that the double bond is part of the ring:



<sup>b</sup>The Z factor for the conjugated substituent is used when either the substituent or the double bond is further conjugated with other groups.

Source: C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, 49, 164 (1966).

Table II. Chemical Shifts of Miscellaneous Olefins

5.70      6.50   5.02  
 $\text{RCH}=\text{CR}-\text{CH}=\text{CH}_2$

6.01   6.08   7.16   5.62  
 $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}(=\text{O})\text{OC}_2\text{H}_5$

6.73  
 $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H}_3\text{C} \quad \text{C}(=\text{O})\text{OCH}_3 \\ \quad \quad \quad \text{CH}_3 \end{array}$   
 1.73

1.97  
 $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{C}(=\text{O})\text{OCH}_3 \\ \quad \quad \quad \text{CH}_3 \end{array}$   
 5.98

2.12  
 $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{C}(=\text{O})\text{OCH}_3 \\ \quad \quad \quad \text{H} \end{array}$  5.62  
 1.84

2.06  
 $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H}_3\text{C} \quad \text{C}(=\text{O})\text{CH}_3 \\ \quad \quad \quad \text{H} \end{array}$  5.97  
 1.86

1.65  
 $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{OC}(=\text{O})\text{CH}_3 \\ \quad \quad \quad \text{H} \end{array}$  6.79  
 1.65

$\text{CH}_3\text{CH}_2\text{C}(\text{OSiMe}_3)=\text{CH}_2$   
 3.92

$\begin{array}{c} \text{OSiMe}_3 \\ | \\ \text{C}_6\text{H}_5 \end{array}$   
 5.65

$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{OSiMe}_3 \end{array}$  6.19  
 4.90

$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{OSiMe}_3 \end{array}$   
 4.35      5.97

$\begin{array}{c} \text{C}_5\text{H}_9\text{N} \\ | \\ \text{C}_6\text{H}_9 \end{array}$  4.17

$\begin{array}{c} \text{C}_6\text{H}_{11}\text{N} \\ | \\ \text{C}_6\text{H}_9 \end{array}$  4.55



Table II, continued

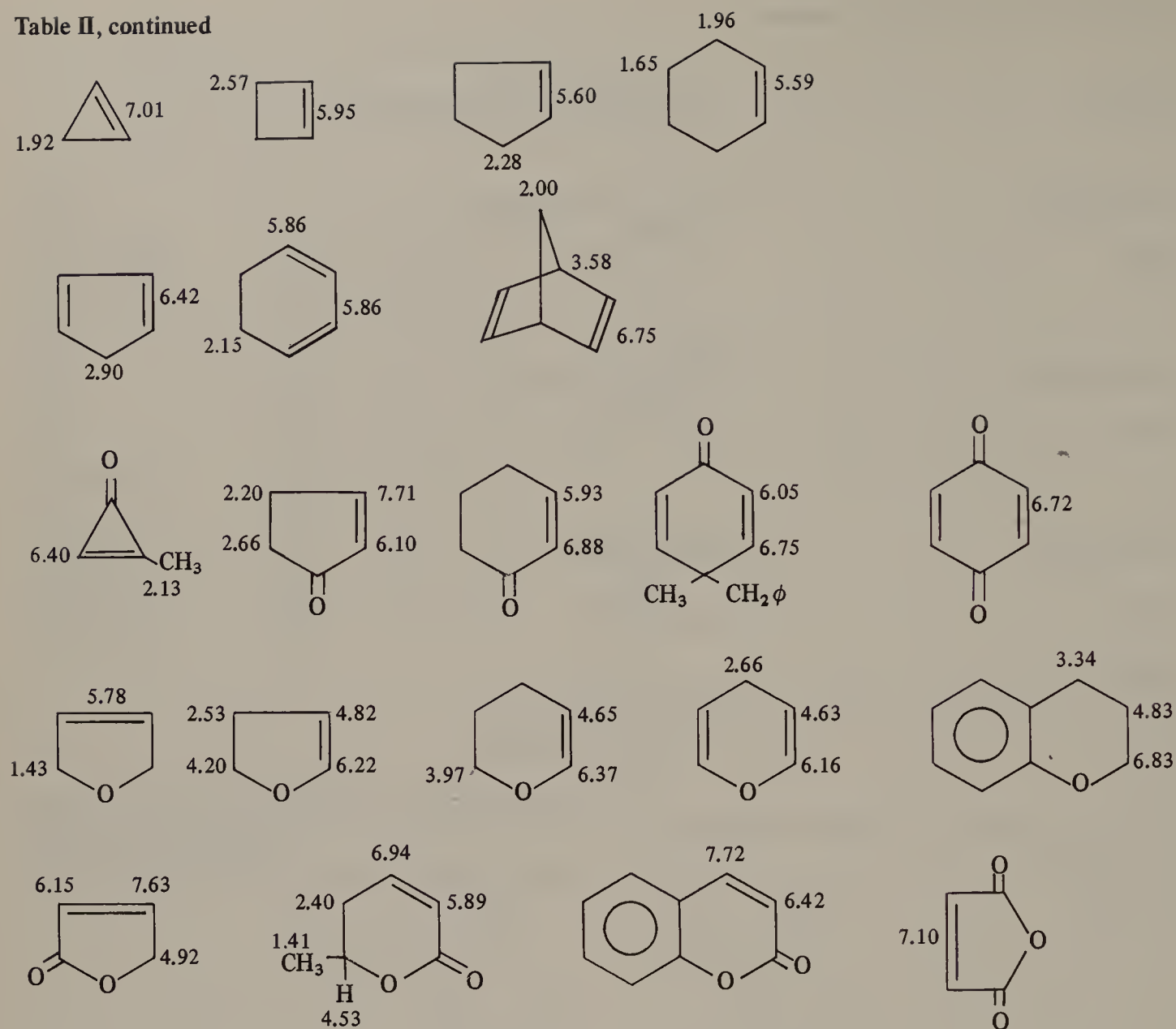


Table III. Chemical Shifts of Alkyne Protons

|   |           |
|---|-----------|
| $\text{HC}\equiv\text{CR}$                        | 1.73-1.88 |
| $\text{HC}\equiv\text{C}-\text{COH}$              | 2.23      |
| $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CR}$ | 1.95      |
| $\text{HC}\equiv\text{CH}$                        | 1.80      |
| $\text{HC}\equiv\text{CAr}$                       | 2.71-3.37 |
| $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CR}$ | 2.60-3.10 |

# CHART 1. CHEMICAL SHIFTS OF PROTONS ON MONOSUBSTITUTED\* BENZENE RINGS

|  | 9 | .8 | .6 | .4 | .2 | 8 | .8 | .6 | .4 | .2 | 7 | .8 | .6 | .4 | .2 | 6 | δ |
|--|---|----|----|----|----|---|----|----|----|----|---|----|----|----|----|---|---|
| Benzene  |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| CH <sub>3</sub> (omp)                              |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| CH <sub>3</sub> CH <sub>2</sub> <sup>1</sup> (omp) |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| (CH <sub>3</sub> ) <sub>2</sub> CH (omp)           |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| (CH <sub>3</sub> ) <sub>3</sub> C o,m,p            |   |    |    |    |    |   |    |    |    | :  | : | :  |    |    |    |   |   |
| C=CH <sub>2</sub> (omp)                            |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| C≡CH o, (mp)                                       |   |    |    |    |    |   |    |    | :  | :  |   |    |    |    |    |   |   |
| Phenyl o, m, p                                     |   |    |    |    |    |   |    |    | :  | :  | : |    |    |    |    |   |   |
| CF <sub>3</sub> (omp)                              |   |    |    |    |    |   |    | :  |    |    |   |    |    |    |    |   |   |
| CH <sub>2</sub> Cl (omp)                           |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| CHCl <sub>2</sub> (omp)                            |   |    |    |    |    |   |    |    | :  |    |   |    |    |    |    |   |   |
| CCl <sub>3</sub> o, (mp)                           |   |    |    |    | :  |   |    | :  |    |    |   |    |    |    |    |   |   |
| CH <sub>2</sub> OH (omp)                           |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| CH <sub>2</sub> OR (omp)                           |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| CH <sub>2</sub> OC(=O)CH <sub>3</sub> (omp)        |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| CH <sub>2</sub> NH <sub>2</sub> (omp)              |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| F m,p,o  |   |    |    |    |    |   |    |    |    | :  | : | :  |    |    |    |   |   |
| Cl (omp)   |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| Br o, (pm)   |   |    |    |    |    |   |    |    | :  | :  |   |    |    |    |    |   |   |
| I o,p,m  |   |    |    |    |    |   | :  |    | :  | :  |   |    |    |    |    |   |   |
| OH m,p,o   |   |    |    |    |    |   |    |    |    | :  | : | :  |    |    |    |   |   |
| OR m, (op)   |   |    |    |    |    |   |    |    |    | :  |   | :  |    |    |    |   |   |
| OC(=O)CH <sub>3</sub> (mp), o                      |   |    |    |    |    |   |    |    |    | :  | : |    |    |    |    |   |   |
| OTs**(mp), o                                       |   |    |    |    |    |   |    |    |    | :  | : |    |    |    |    |   |   |
| CH(=O)o,p,m  |   |    |    |    |    | : |    | :  | :  |    |   |    |    |    |    |   |   |
| C(=O)CH <sub>3</sub> o, (mp)                       |   |    |    |    |    | : |    | :  |    |    |   |    |    |    |    |   |   |
| C(=O)OH o, p, m                                    |   |    |    |    |    | : |    | :  | :  |    |   |    |    |    |    |   |   |
| C(=O)OR o, p, m                                    |   |    |    |    | :  |   |    | :  | :  |    |   |    |    |    |    |   |   |
| C(=O)Cl o, p, m                                    |   |    |    |    | :  |   |    | :  | :  |    |   |    |    |    |    |   |   |
| C≡N  |   |    |    |    |    |   |    | :  |    |    |   |    |    |    |    |   |   |
| NH <sub>2</sub> m,p,o                              |   |    |    |    |    |   |    |    |    | :  | : | :  |    |    |    |   |   |
| N(CH <sub>3</sub> ) <sub>2</sub> m(op)             |   |    |    |    |    |   |    |    |    | :  |   | :  |    |    |    |   |   |
| NHC(=O)R o   |   |    |    |    |    |   |    |    | :  |    |   |    |    |    |    |   |   |
| NH <sub>3</sub> <sup>+</sup> o                     |   |    |    |    |    |   |    | :  |    |    |   |    |    |    |    |   |   |
| NO <sub>2</sub> o,p,m                              |   |    |    |    | :  |   |    | :  | :  |    |   |    |    |    |    |   |   |
| SR (omp)   |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
| N=C=O (omp)  |   |    |    |    |    |   |    |    |    | :  |   |    |    |    |    |   |   |
|  | 9 | .8 | .6 | .4 | .2 | 8 | .8 | .6 | .4 | .2 | 7 | .8 | .6 | .4 | .2 | 6 | δ |

\*The principle of additivity can be used to calculate approximate chemical shifts for polysubstituted rings.

\*\*OTs = *p*-toluenesulfonyloxy group

Table IV. Chemical Shifts of Protons on Fused Aromatic Rings.

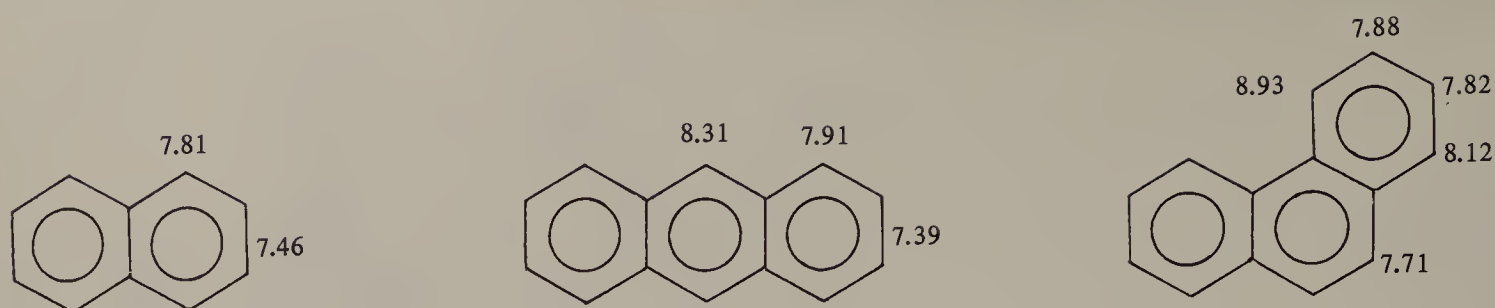


Table V. Chemical Shifts of Protons on Heteroaromatic Rings

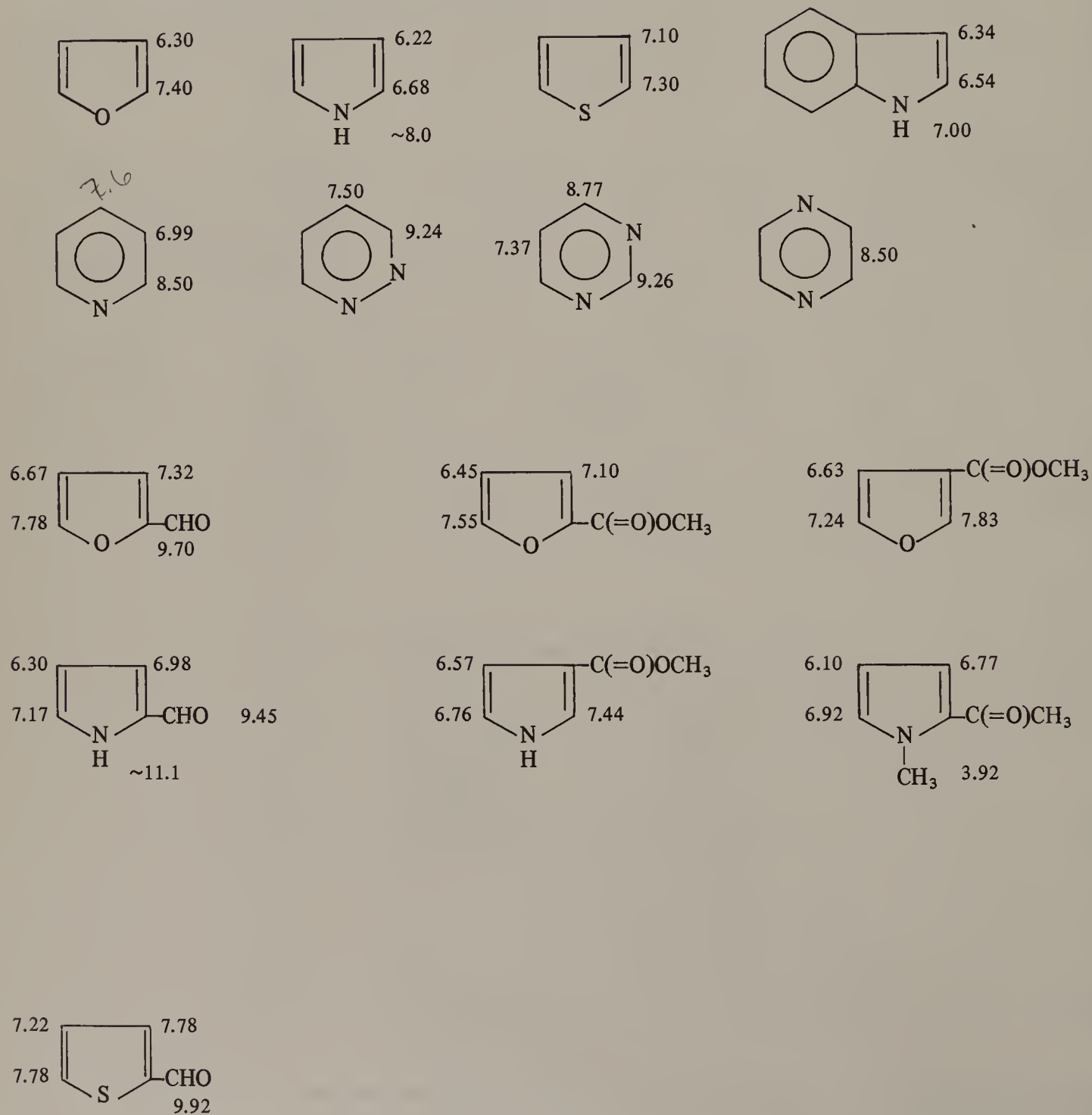

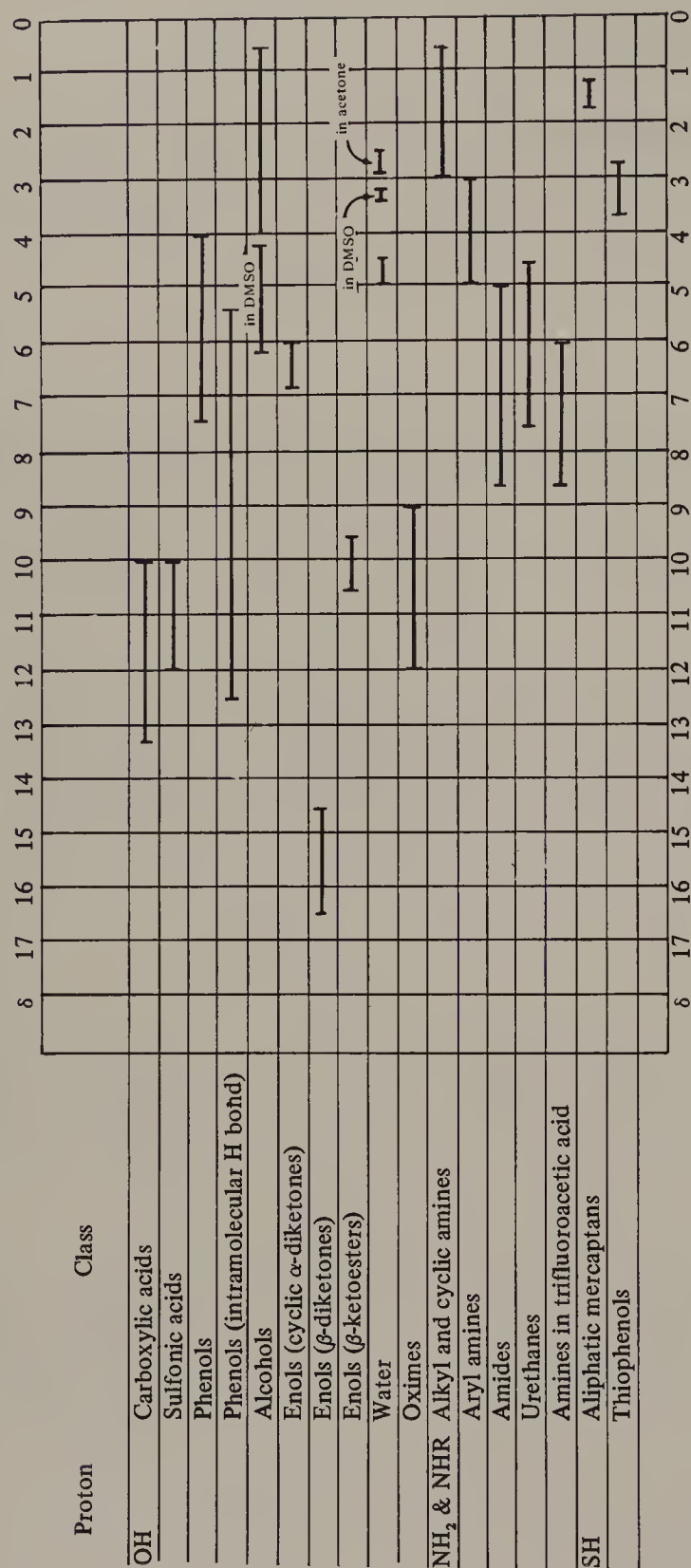




Table VI. Chemical Shifts of HC=O and HC=N Protons  $\left( \text{also HC} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \right)$

|             |      |                       |      |   |      |
|-------------|------|-----------------------|------|---|------|
| RCH=O       | 9.70 | HC(=O)OR              | 8.05 | RCH=NOH <i>cis</i>  | 7.25 |
| $\phi$ CH=O | 9.98 | HC(=O)NR <sub>2</sub> | 8.05 | RCH=NOH <i>trans</i>  | 6.65 |
| RCH=CHCH=O  | 9.78 | HC(OR) <sub>3</sub>   | 5.00 |   |      |
|             |      |                       |      | RCH=N-NH-  | 6.05 |

PROTONS SUBJECT TO HYDROGEN-BONDING EFFECTS (Protons on Heteroatoms)\*



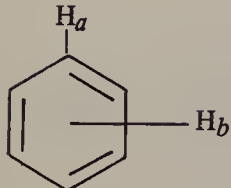
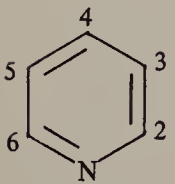


\*Solvent CDCl<sub>3</sub>.

# appendix f

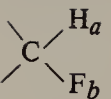
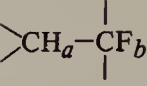
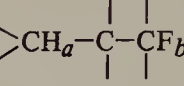
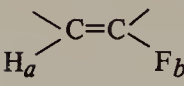
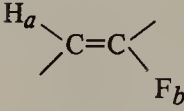
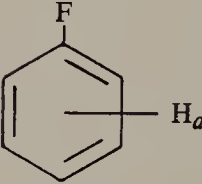
## PROTON SPIN-SPIN-COUPPLING CONSTANTS\* (Absolute Values)<sup>†</sup>

| Type                                      | $J_{ab}$ (Hz)  | $J_{ab}$ Typical   | Type   | $J_{ab}$ (Hz)  | $J_{ab}$ Typical                           |
|---|--|--|--|--|--|
|   | 0 to 30  | 12 to 15   |  | 4-10   | 7  |
| $\text{CH}_a-\text{CH}_b$ (free rotation) | 6-8  | 7  |  | 0-3  | 1.5  |
|   | 0-1  | 0  |  | 0-3  | 2  |
|   | <br>$ax.-ax.$<br>$ax.-eq.$<br>$eq.-eq.$                  | <br>6-14<br>0-5<br>0-5                                     | $\text{C}=\text{CH}_a-\text{CH}_b=\text{C}$        | 9-13   | 10   |
|   | 0-7  | 4-5  | $\text{CH}_a-\text{C}\equiv\text{CH}_b$            | 2-3  |  |
|   | 6-10   | 8  | $-\text{CH}_a-\text{C}\equiv\text{C}-\text{CH}_b-$ | 2-3  |  |
|   |  | 3-5  | $\text{CH}_a-\text{OH}_b$ (no exchange)            | 4-10   | 5  |
|   | 6  |  |  | 1-3  | 2-3  |
|   | 4  |  |  | 5-8  | 6  |
|   | 2.5  |  |  | 12-18  | 17   |
|   | 3 mem.<br>4 mem.<br>5 mem.<br>6 mem.<br>7 mem.<br>8 mem. | 0.5-2.0<br>2.5-4.0<br>5.1-7.0<br>8.8-11.0<br>9-13<br>10-13 |  | 0-3  | 0-2  |
|   |  |  |  | 6-12   | 10   |
|   |  |  |  | 0-3  | 1-2  |
|   |  |  |  | $J(1-2)$<br>$J(1-3)$<br>$J(2-3)$<br>$J(3-4)$<br>$J(2-4)$<br>$J(2-5)$ | 2-3<br>2-3<br>2-3<br>3-4<br>1-2<br>1.5-2.5 |
|   |  |  |  | $J(4-5)$<br>$J(2-5)$<br>$J(2-4)$<br>$J(4-6)$                         | 4-6<br>1-2<br>0-1<br>?                     |
|   |  |  |  | $J(4-5)$<br>$J(2-5)$<br>$J(2-4)$                                     | 3-4<br>1-2<br>~0                           |
|   |  |  | Proton-Fluorine                                    |  |  |



|   |             |         |     |
|---|-------------|---------|-----|
|  | $J$ (ortho) | 6-10    | 9   |
|   | $J$ (meta)  | 1-3     | 3   |
|   | $J$ (para)  | 0-1     | ~0  |
|  | $J$ (2-3)   | 5-6     | 5   |
|   | $J$ (3-4)   | 7-9     | 8   |
|   | $J$ (2-4)   | 1-2     | 1.5 |
|   | $J$ (3-5)   | 1-2     | 1.5 |
|   | $J$ (2-5)   | 0-1     | 1   |
|   | $J$ (2-6)   | 0-1     | ~0  |
|  | $J$ (2-3)   | 1.3-2.0 | 1.8 |
|   | $J$ (3-4)   | 3.1-3.8 | 3.6 |
|   | $J$ (2-4)   | 0-1     | ~0  |
|   | $J$ (2-5)   | 1-2     | 1.5 |
|  | $J$ (2-3)   | 4.9-6.2 | 5.4 |
|   | $J$ (3-4)   | 3.4-5.0 | 4.0 |
|   | $J$ (2-4)   | 1.2-1.7 | 1.5 |
|   | $J$ (2-5)   | 3.2-3.7 | 3.4 |

## Proton-Fluorine

|  |   |
|--|---|
|   | 44-81                                       |
|   | 3-25  |
|   | 0   |
|   | 1-8   |
|   | 12-40                                       |
|  | <i>o</i> 6-10<br><i>m</i> 5-6<br><i>p</i> 2 |

## Proton-Phosphorus

|   |             |            |
|---|-------------|------------|
| $\begin{array}{c} \text{O} \\ \parallel \\ >\text{P}\text{H} \end{array}$                             | 630-707     |            |
| $(\text{CH}_3)_3\text{P}$   | 2.7         |            |
| $(\text{CH}_3)_3\text{P}=\text{O}$  | 13.4        |            |
| $(\text{CH}_3\text{CH}_2)_3\text{P}$  | 13.7 (HCCP) | 0.5 (HCP)  |
| $(\text{CH}_3\text{CH}_2)_3\text{P}=\text{O}$   | 16.3 (HCCP) | 11.9 (HCP) |
| $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{P}(\text{OR})_2 \end{array}$              | 10-13       |            |
| $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}\text{P}(\text{OR})_2 \\   \end{array}$ | 15-20       |            |
| $\text{CH}_3\text{OP}(\text{OR})_2$   | 10.5-12     |            |
| $\text{P}[\text{N}(\text{CH}_3)_2]_3$   | 8.8         |            |
| $\text{O}=\text{P}[\text{N}(\text{CH}_3)_2]_3$  | 9.5         |            |

\*Compiled by Varian Associates.

†Signs of typical coupling constants can be obtained from the Appendixes of Bovey's book.<sup>1</sup>

appendix g. chemical shifts of residual protons in commercially available deuterated solvents. (source: merck sharp and dohme of canada, ltd.)

| Solvent   | Isotopic Purity<br>Atom % D | Positions of Residual Protons |                   |                    |                    |          |                   |
|---|-----------------------------|-------------------------------|-------------------|--------------------|--------------------|----------|-------------------|
|   |                             | Group                         | $\delta$          | Group              | $\delta$           | Group    | $\delta$          |
| Acetic Acid-d <sub>4</sub>                              | 99.5                        | methyl                        | 2.05              | hydroxyl           | 11.53 <sup>a</sup> |          |                   |
| Acetone-d <sub>6</sub>                                  | 99.5                        | methyl                        | 2.05              |                    |                    |          |                   |
| Acetonitrile-d <sub>3</sub>                             | 98                          | methyl                        | 1.95              |                    |                    |          |                   |
| Benzene-d <sub>6</sub>                                  | 99.5                        | methine                       | 7.20              |                    |                    |          |                   |
| Chloroform-d  | 99.8                        | methine                       | 7.25              |                    |                    |          |                   |
| Cyclohexane-d <sub>12</sub>                             | 99                          | methylene                     | 1.40              |                    |                    |          |                   |
| Deuterium Oxide   | 99.8                        | hydroxyl                      | 4.75 <sup>a</sup> |                    |                    |          |                   |
| 1,2-Dichloroethane-d <sub>4</sub>                       | 99                          | methylene                     | 3.69              |                    |                    |          |                   |
| Diethyl-d <sub>10</sub> Ether                           | 98                          | methyl                        | 1.16              | methylene          | 3.36               |          |                   |
| Dimethylformamide-d <sub>7</sub>                        | 98                          | methyl                        | 2.76              | methyl             | 2.94               | formyl   | 8.05              |
| Dimethyl-d <sub>6</sub> Sulfoxide                       | 99.5                        | methyl                        | 2.50              |                    |                    |          |                   |
| p-Dioxane-d <sub>8</sub>                                | 98                          | methylene                     | 3.55              |                    |                    |          |                   |
| Ethyl Alcohol-d <sub>6</sub> (anh.)                     | 98                          | methyl                        | 1.17              | methylene          | 3.59               | hydroxyl | 2.60 <sup>a</sup> |
| Hexafluoroacetone Deuterate                             | 99.5                        | hydroxyl                      | 9.0 <sup>a</sup>  |                    |                    |          |                   |
| Methyl Alcohol-d <sub>4</sub>                           | 99                          | methyl                        | 3.35              | hydroxyl           | 4.84 <sup>a</sup>  |          |                   |
| Methylcyclohexane-d <sub>14</sub>                       | 99                          | methyl                        | 0.92              | methylene          | 1.54               | methine  | 1.65              |
| Methylene-d <sub>2</sub> Chloride                       | 99                          | methylene                     | 5.35              |                    |                    |          |                   |
| Pyridine-d <sub>5</sub>                                 | 99                          | alpha                         | 8.70              | beta               | 7.20               | gamma    | 7.58              |
| Silanar <sup>c</sup> -C<br>(CDCl <sub>3</sub> + 1% TMS) | 99.8                        | methyl                        | 0.00              | methine            | 7.25               |          |                   |
| Tetrahydrofuran-d <sub>8</sub>                          | 98                          | $\alpha$ -methylene           | 3.60              | $\beta$ -methylene | 0.75               |          |                   |
| Tetramethylene-d <sub>8</sub> Sulfone                   | 98                          | $\alpha$ -methylene           | 2.92              | $\beta$ -methylene | 2.16               |          |                   |

<sup>a</sup>This value may vary considerably, depending upon the solute.

<sup>b</sup>By definition.

<sup>c</sup>Trademark.

Note: Several solvents are available in "100%" isotopic purity.

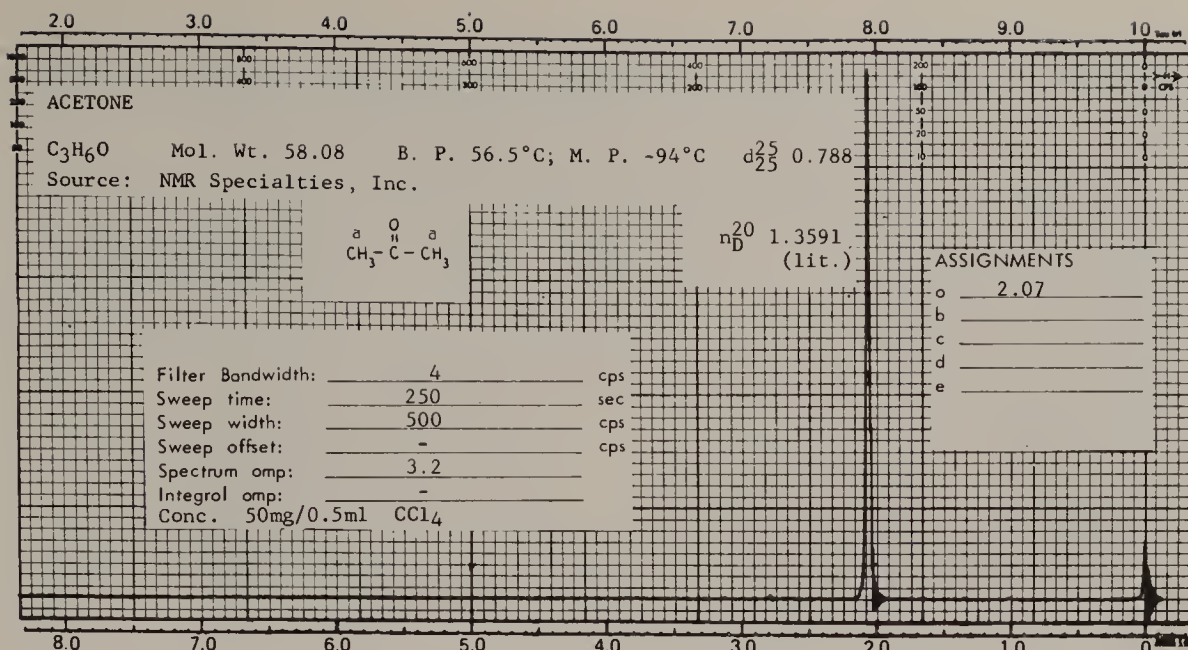
# appendix h

NMR Spectra of Common Solvents and Common Impurities (Source: Sadtler Research Laboratories, Inc.)  
(See Following Pages)

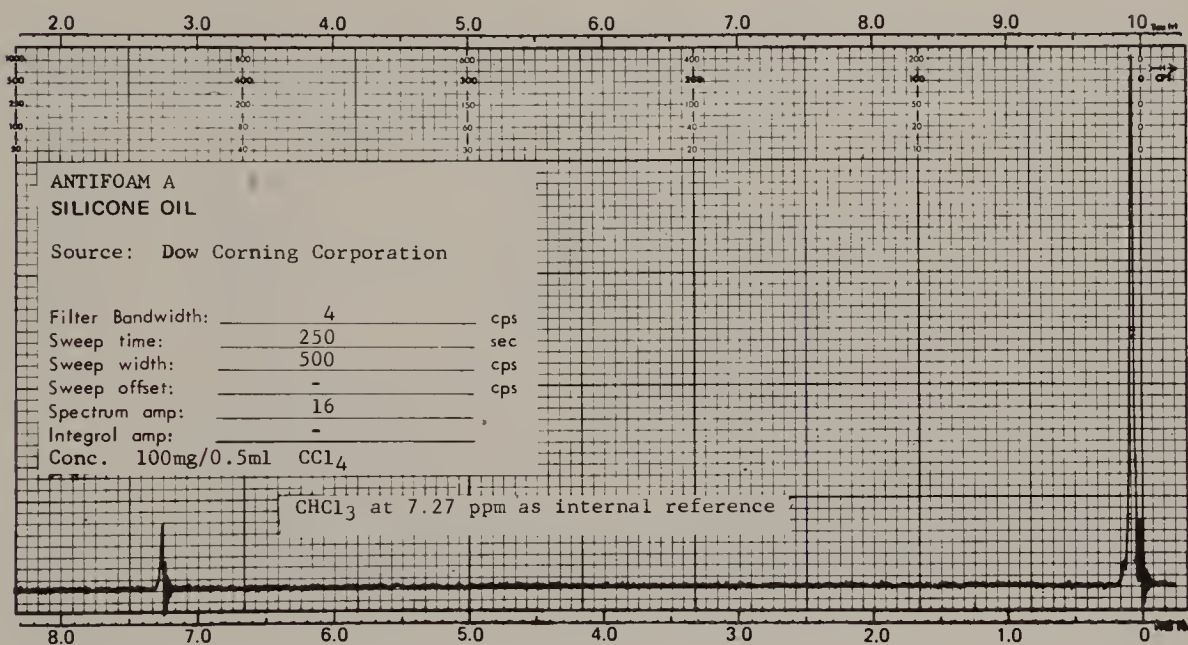
| Spectrum Number                   |    | Spectrum Number                          |    |
|-----------------------------------|----|--|----|
| Acetone                           | 1  | Ethylene glycol                          | 14 |
| Antifoam A <sup>®</sup>           | 2  | Isopropyl Alcohol                        | 15 |
| Apiezon <sup>®</sup> L Grease     | 3  | Lubriseal <sup>®</sup> (Stopcock Grease) | 16 |
| Benzene                           | 4  | Methanol (+ Acid)                        | 17 |
| Chloroform                        | 5  | Methanol                                 | 18 |
| Cyclohexane                       | 6  | Methyl ethyl ketone                      | 19 |
| Difluoroacetic acid               | 7  | Phthalic acid, bis(2-ethylhexyl) ester   | 20 |
| <i>N,N</i> -Dimethylformamide     | 8  | Pyridine-d <sub>5</sub>                  | 21 |
| Dimethyl Sulfoxide-d <sub>6</sub> | 9  | Toluene                                  | 22 |
| <i>p</i> -Dioxane                 | 10 | 3-(Trimethylsilyl) propanesulfonic       |    |
| Dow Corning Stopcock Grease       | 11 | Acid, sodium salt (DSS)                  | 23 |
| Ethanol                           | 12 | Vertex <sup>®</sup> flakes (soap)        | 24 |
| Ethyl Acetate                     | 13 |  |    |



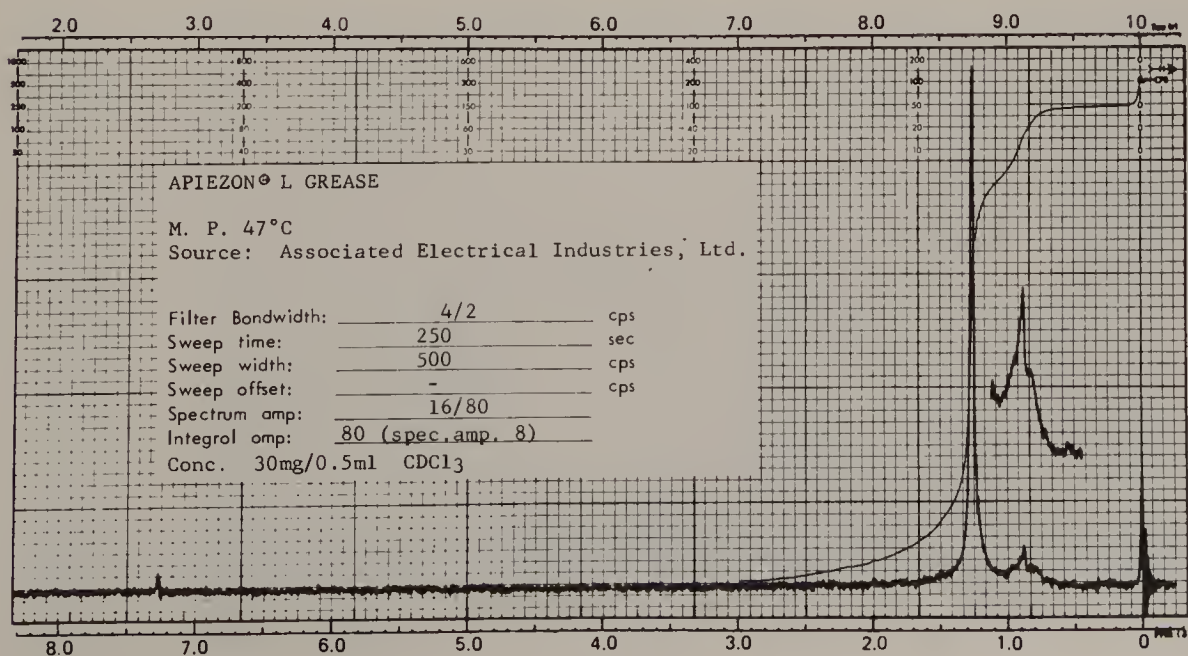
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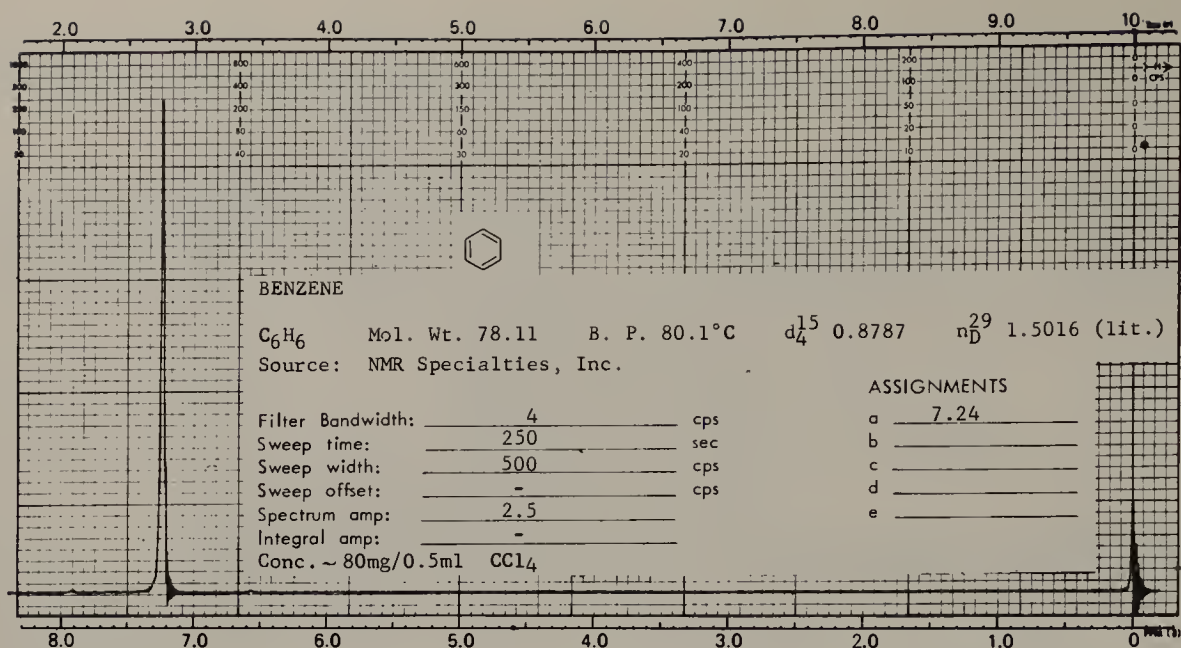
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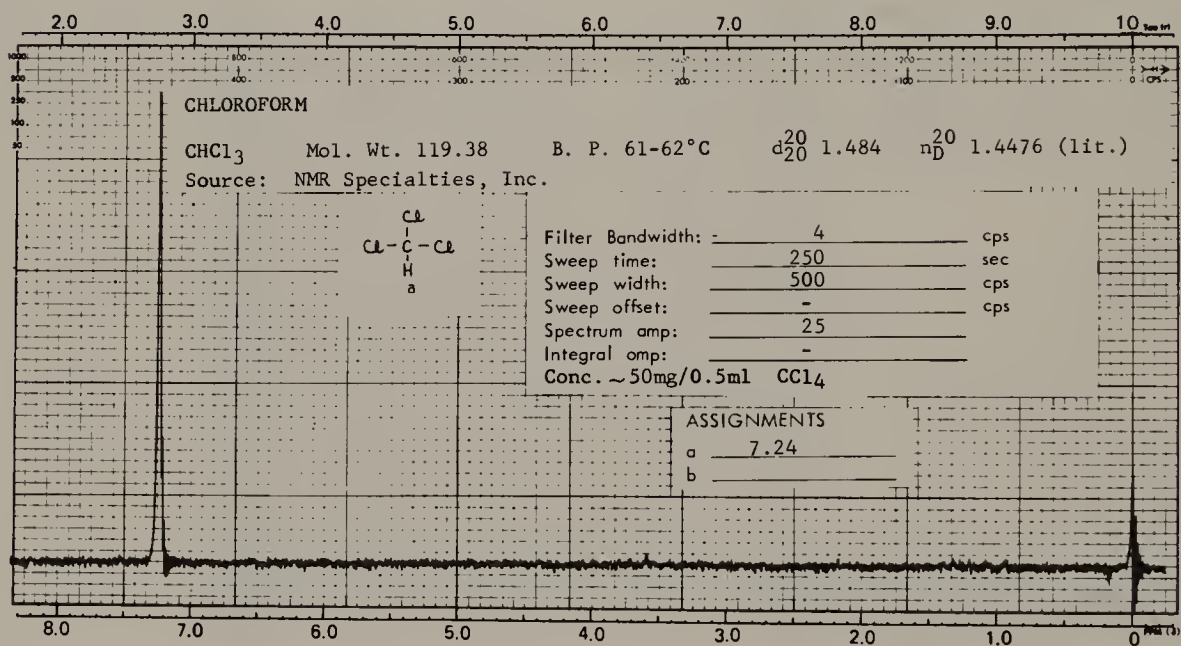
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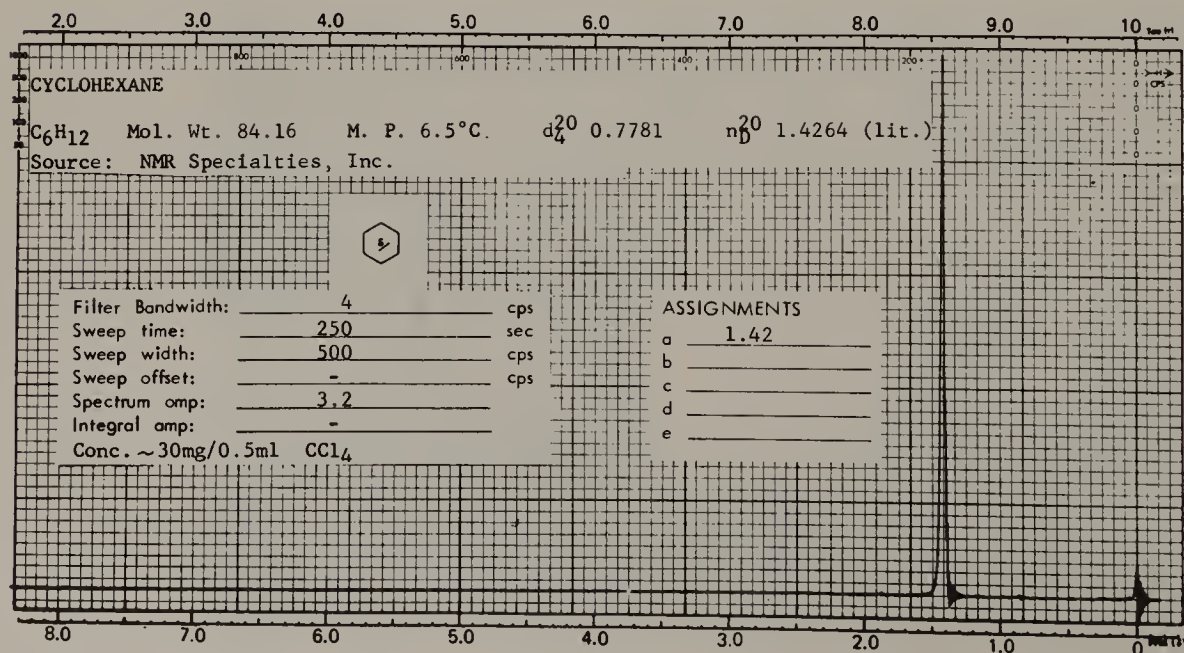
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No. 5

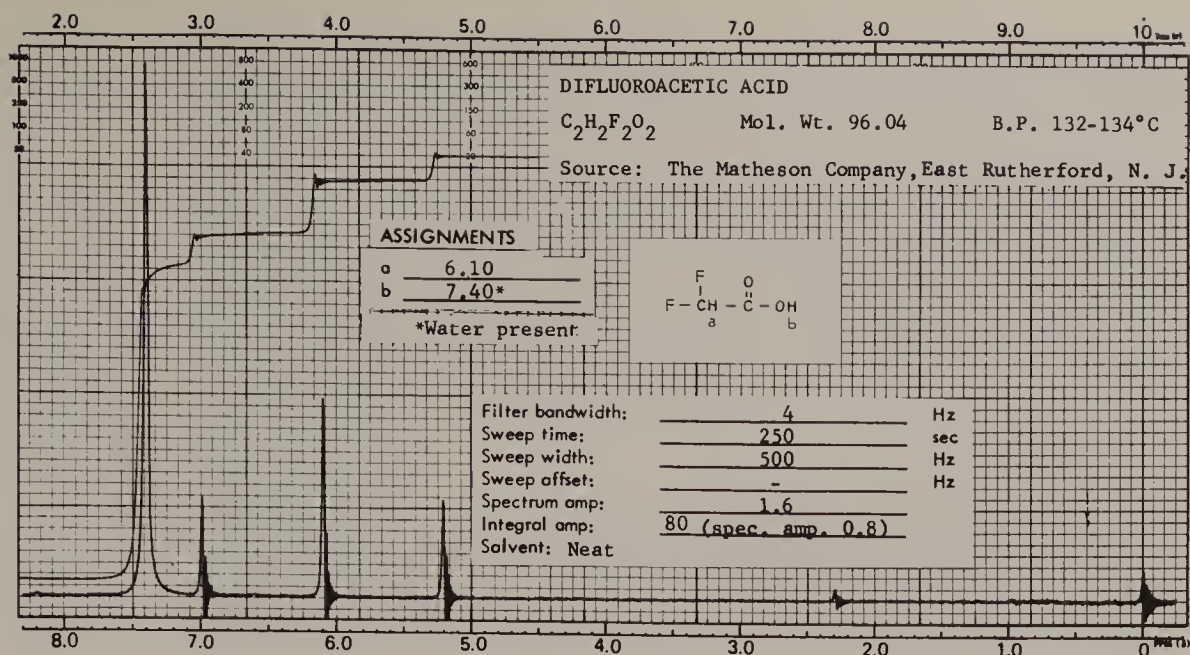


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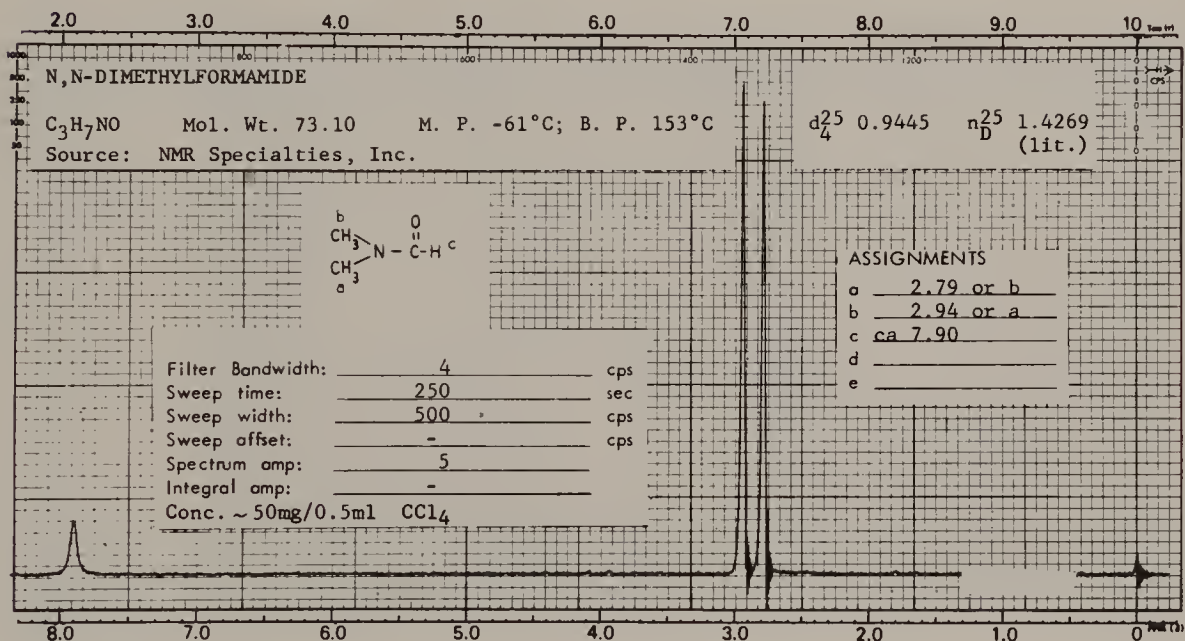




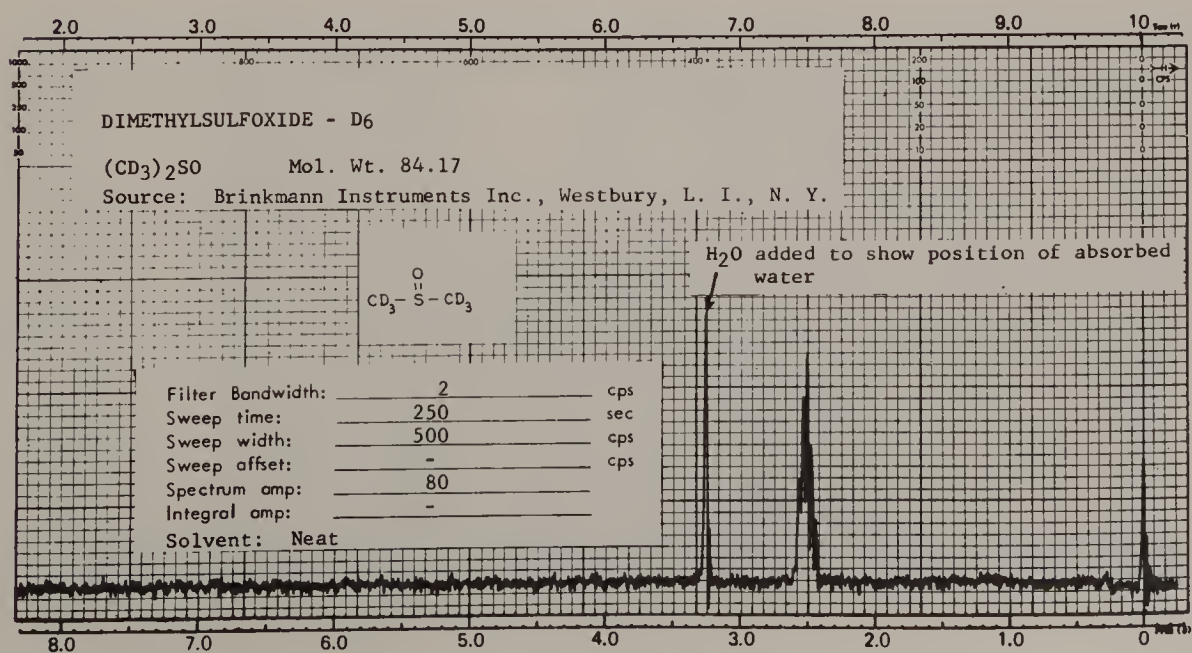
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No. 8

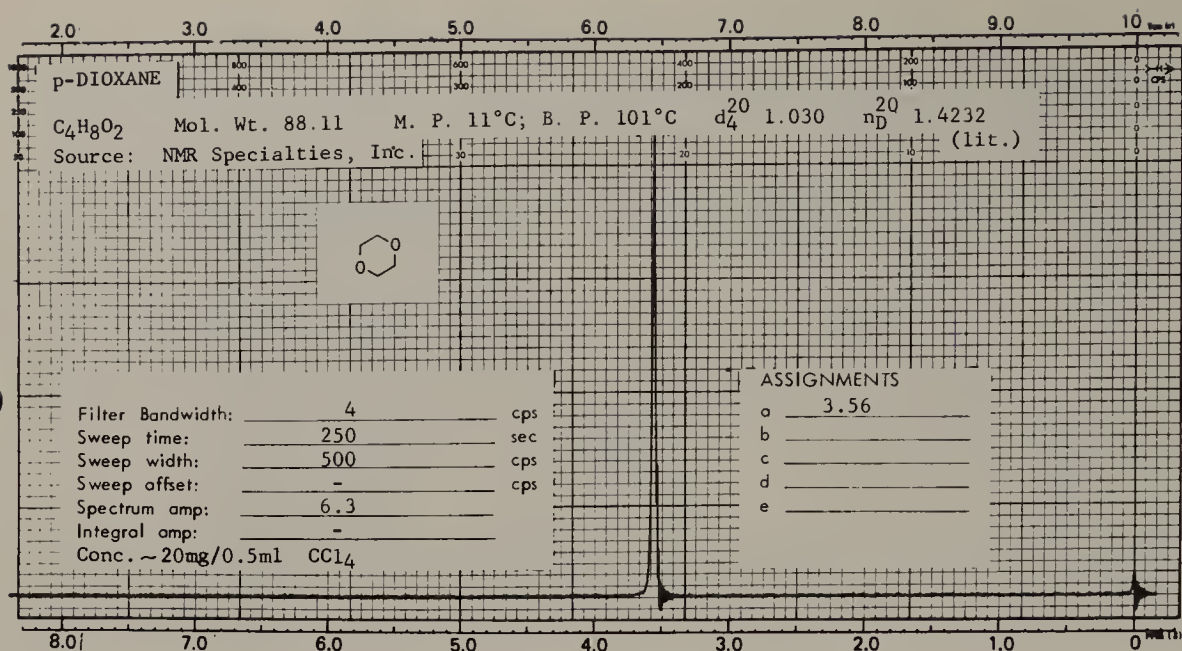


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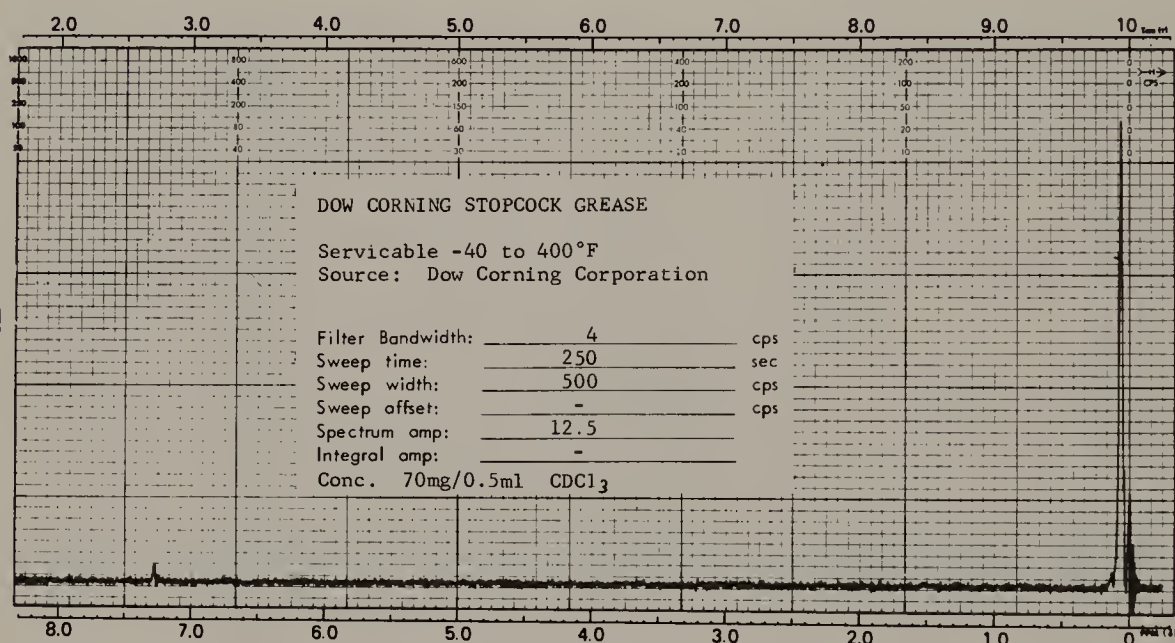




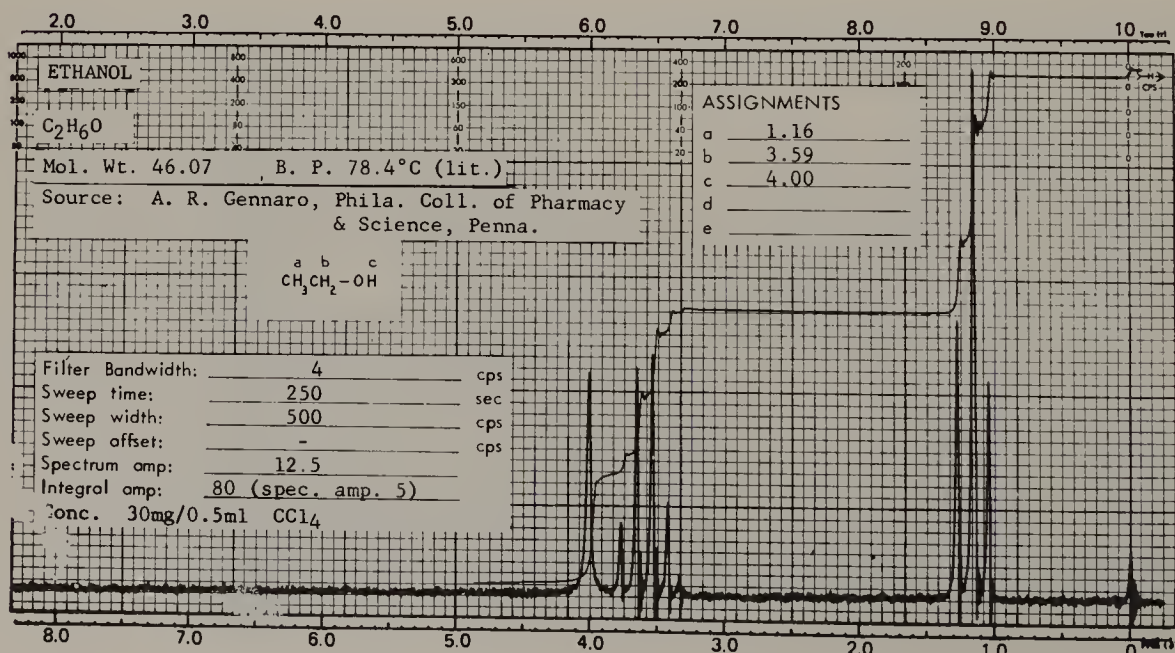
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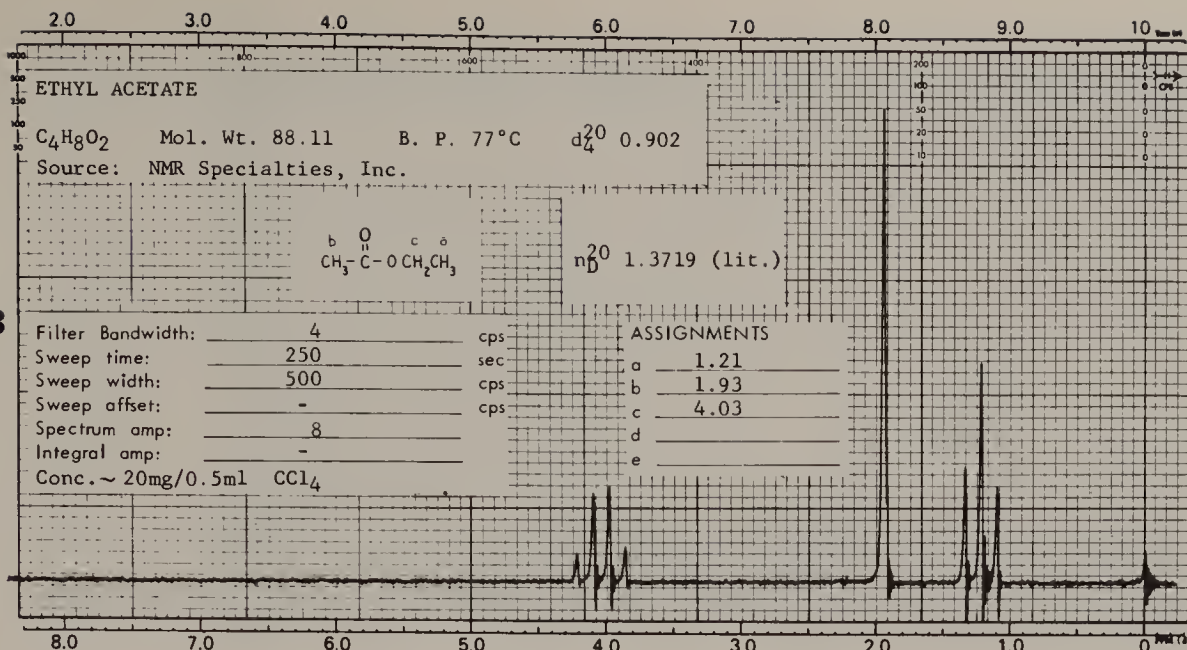
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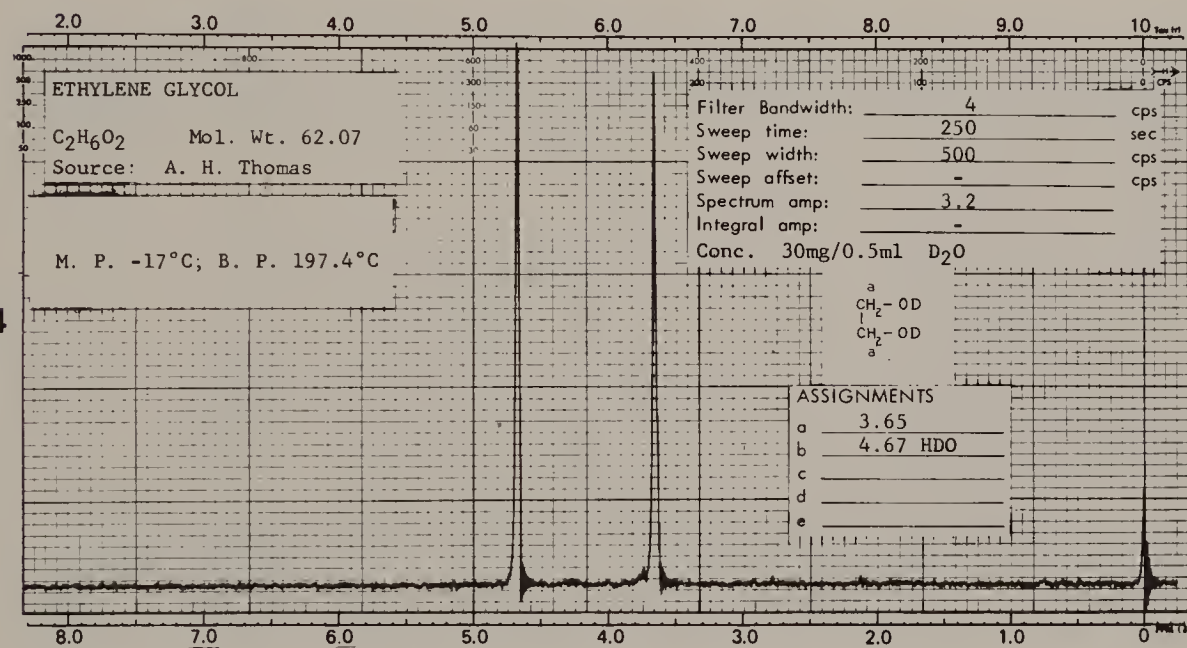
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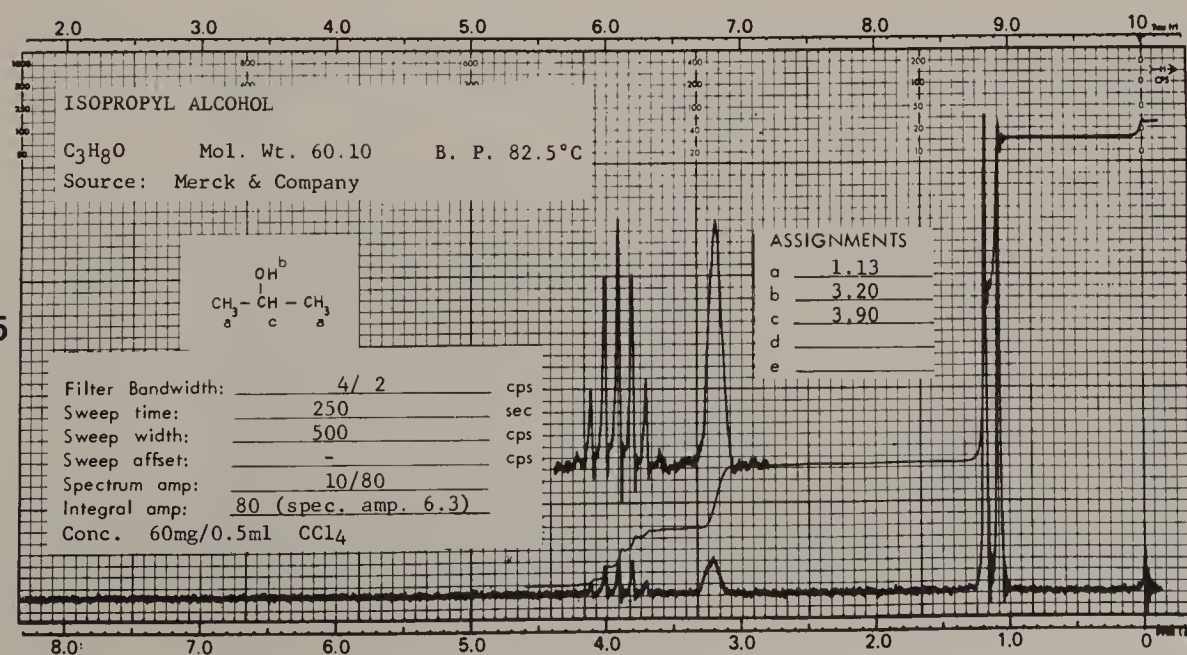
No. 13



No. 14

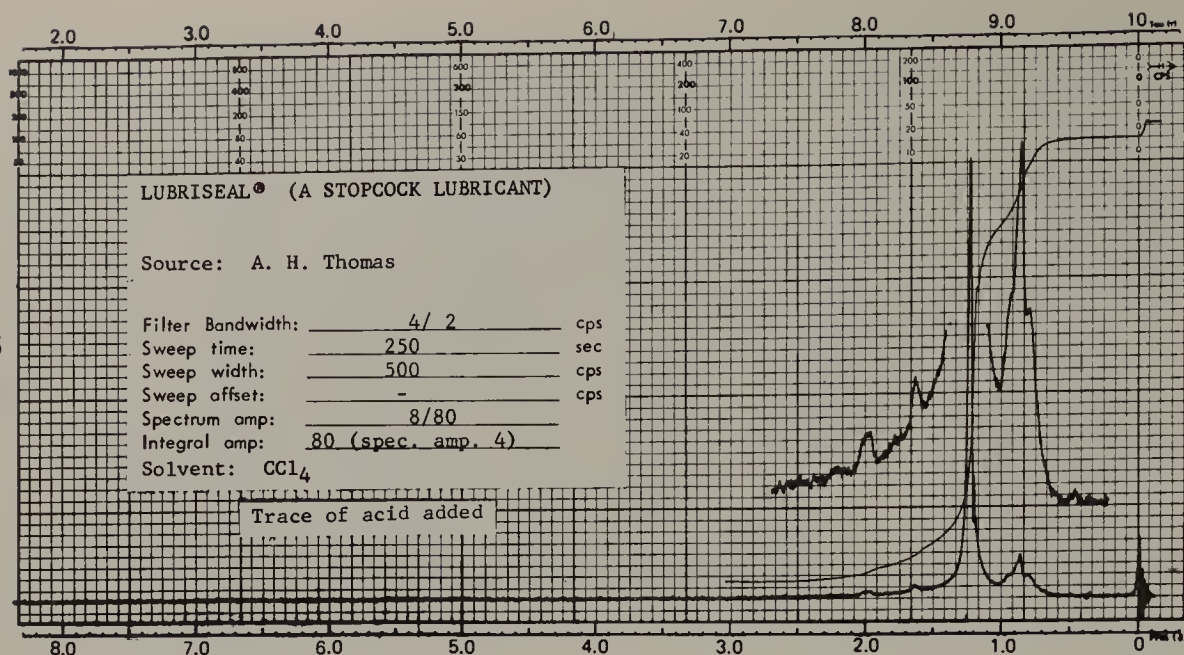


No. 15

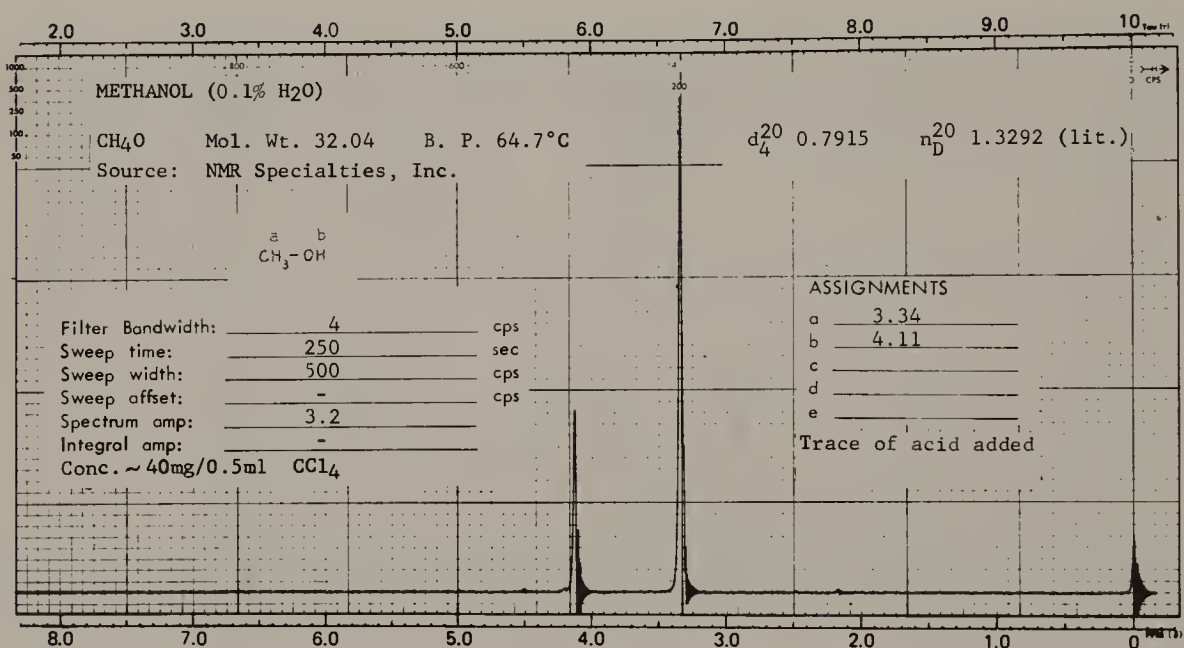




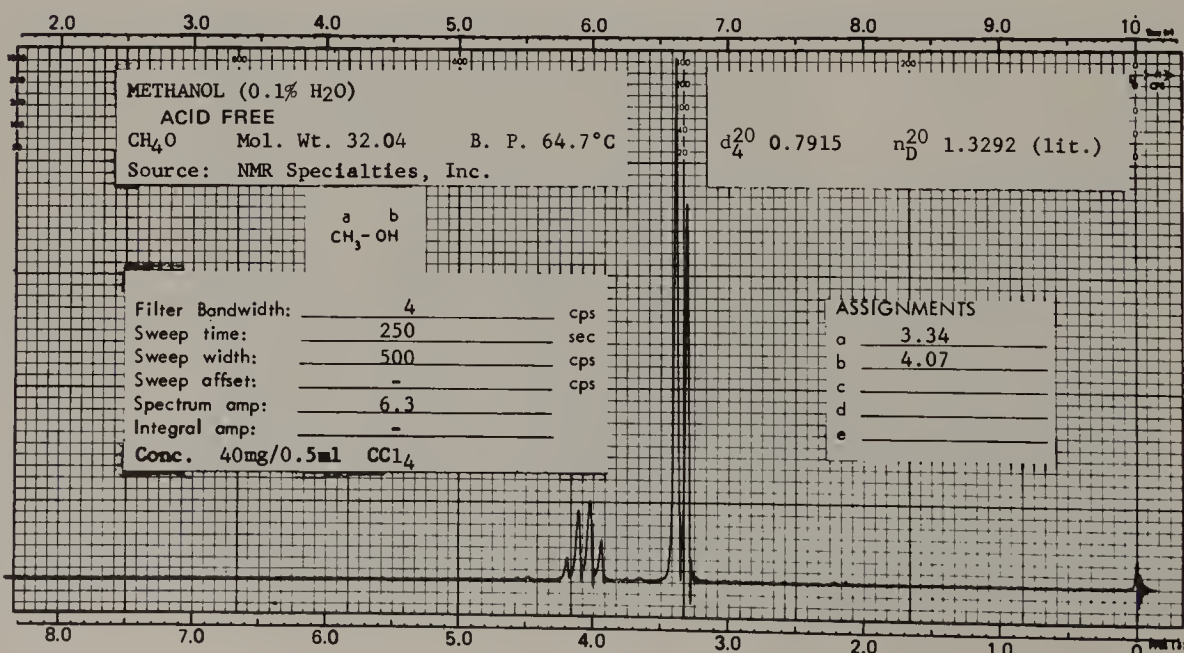
No. 16



No. 17

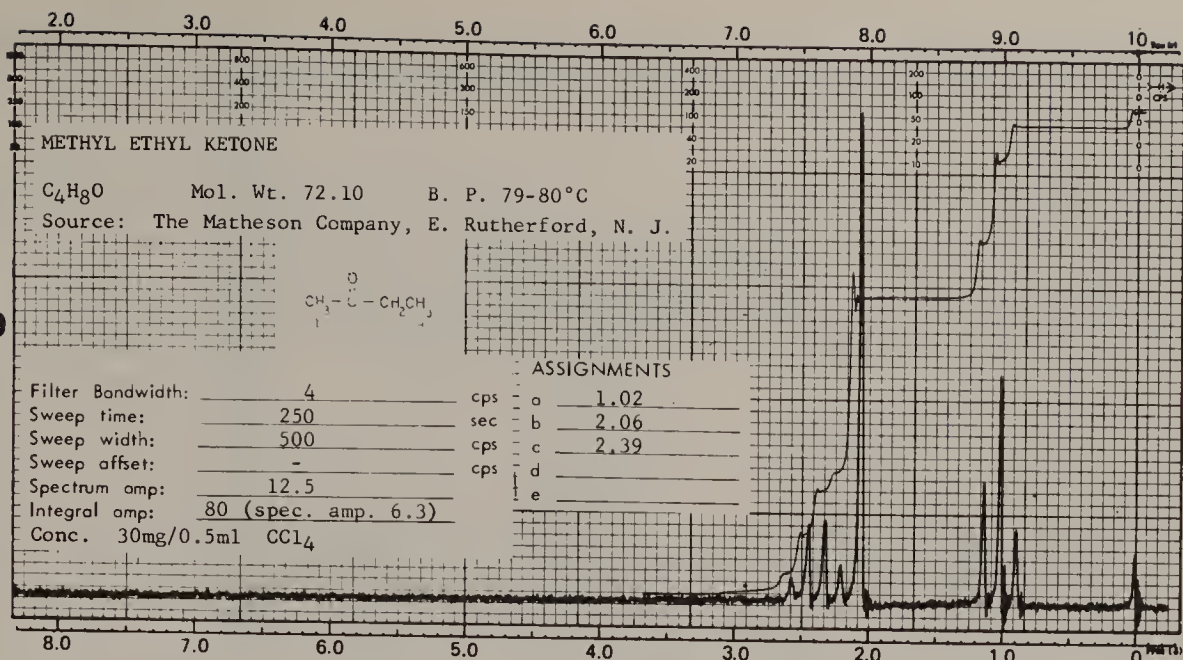


No. 18

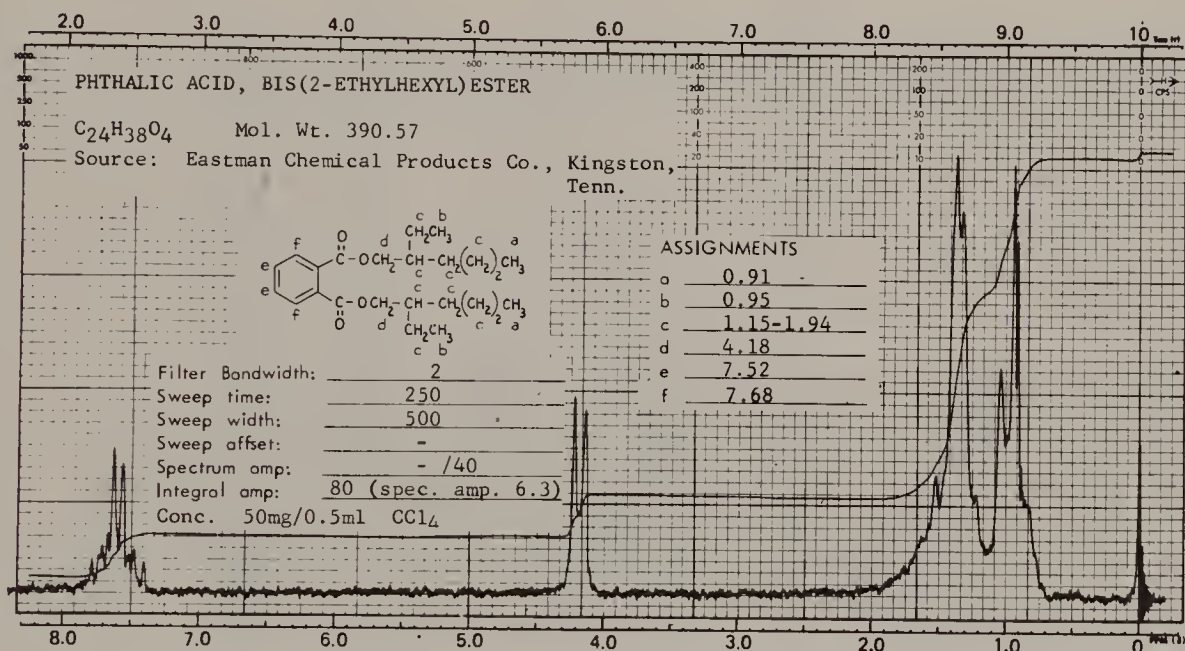




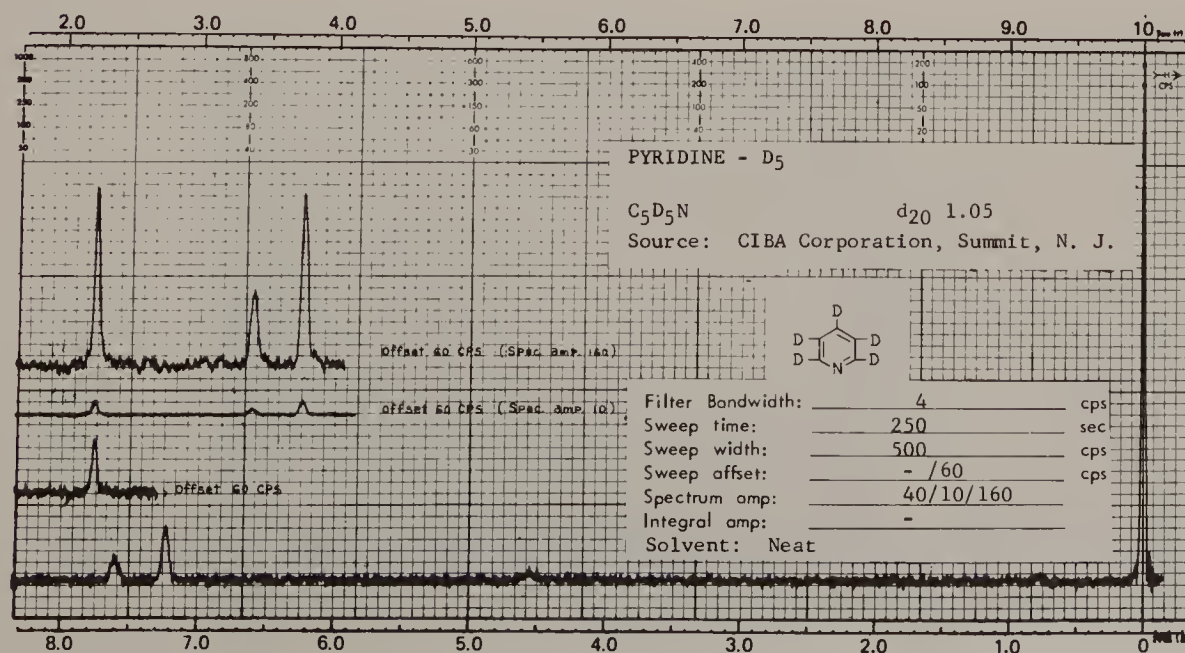
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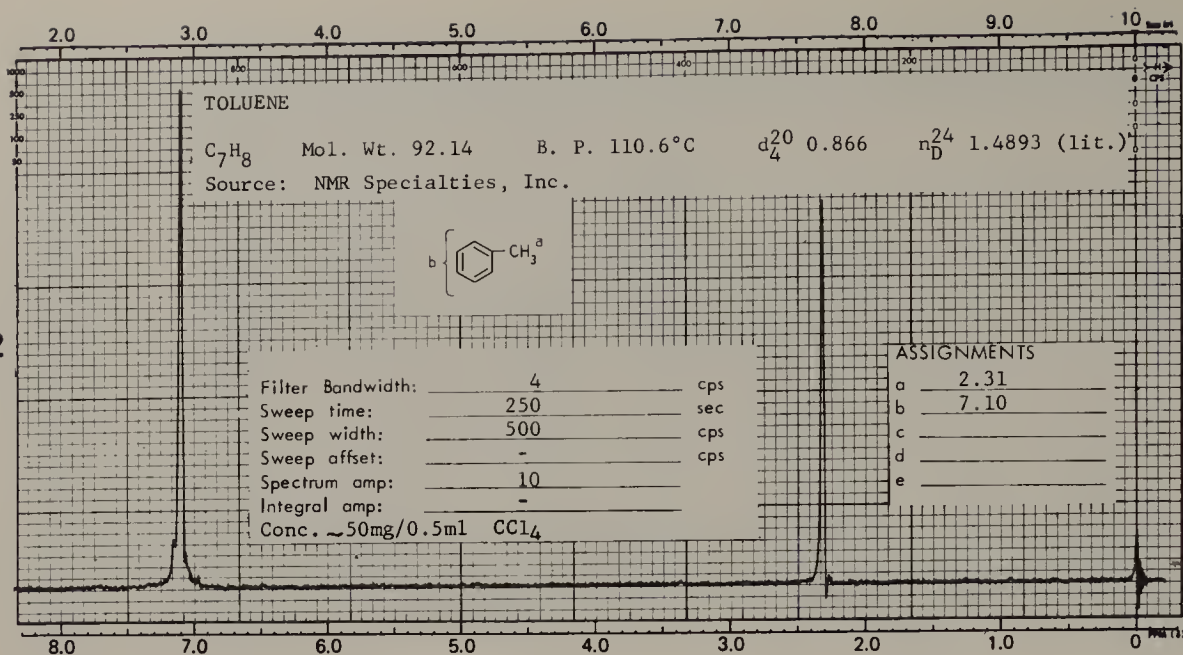
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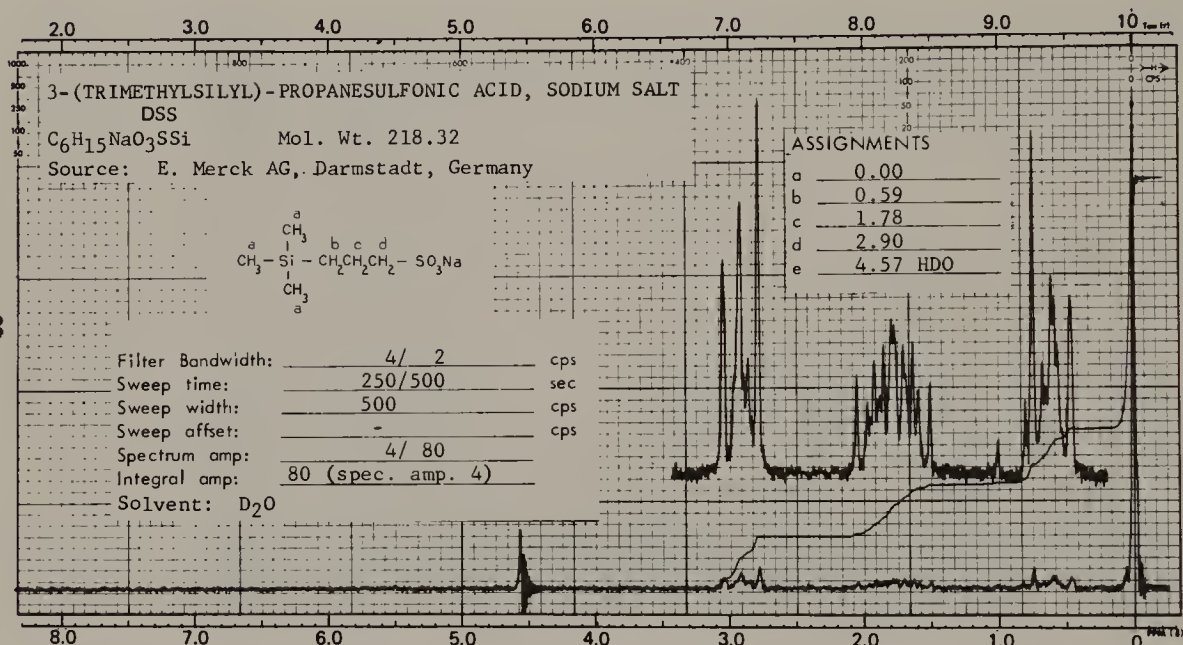
No. 21



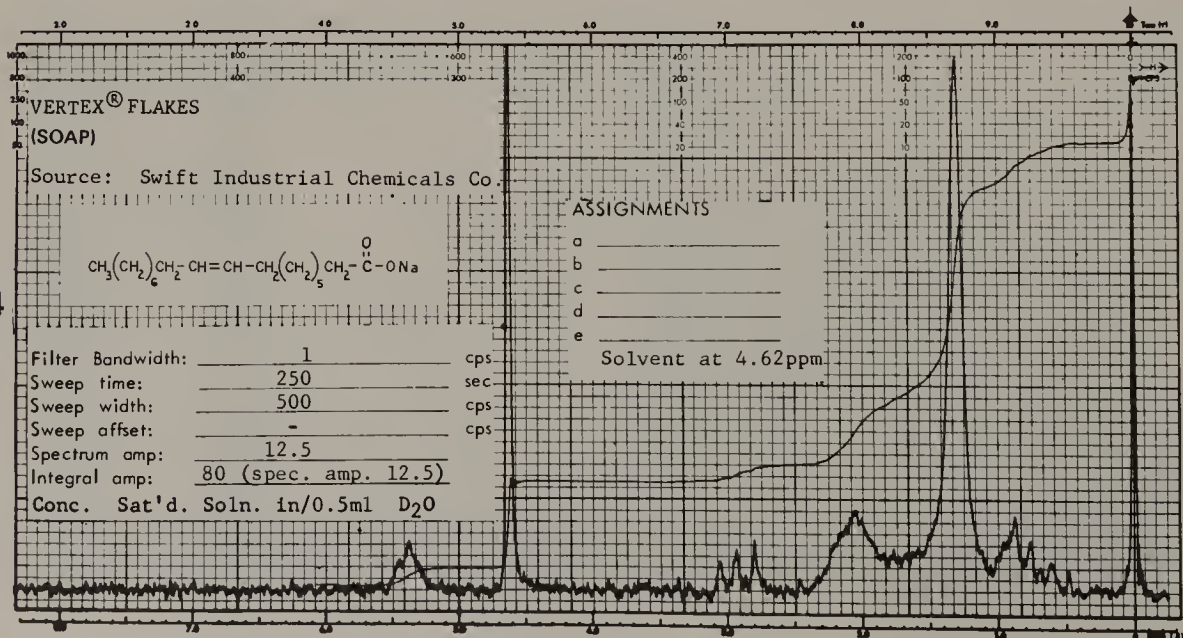
No. 22



No. 23



No. 24





# appendix i

## PROPERTIES OF SEVERAL NUCLEI<sup>a</sup>

| Isotope          | NMR Frequency<br>MHz for a 10-<br>Kilogauss Field | Natural<br>Abundance<br>% | Relative<br>Sensitivity<br>at Constant<br>Field | Magnetic<br>Moment<br>$\mu$ | Spin<br>Number<br>I | Electrical<br>Quadrupole<br>Moment<br>$e \times 10^{-24} \text{ cm}^2$ | Magnetogyric Ratio<br>$\gamma_N$<br>radians <sup>-1</sup> gauss <sup>-1</sup> |
|------------------|---|---------------------------|---|-----------------------------|---------------------|--|---|
| <sup>1</sup> H   | 42.576  | 99.9844                   | 1.000   | 2.79268                     | 1/2                 | —  | 26,753  |
| <sup>2</sup> H   | 6.5357  | $1.56 \times 10^{-2}$     | $9.64 \times 10^{-2}$                           | 0.85739                     | 1                   | $2.77 \times 10^{-3}$  | 4,107   |
| <sup>3</sup> H   | 45.414  | —                         | 1.21  | 2.9788                      | 1/2                 | —  | —   |
| <sup>10</sup> B  | 4.575   | 18.83                     | $1.99 \times 10^{-2}$                           | 1.8005                      | 3                   | $7.4 \times 10^{-2}$   | —   |
| <sup>11</sup> B  | 13.660  | 81.17                     | 0.165   | 2.6880                      | 3/2                 | $3.55 \times 10^{-2}$  | —   |
| <sup>12</sup> C  | —   | 98.9                      | —   | —                           | 0                   | —  | —   |
| <sup>13</sup> C  | 10.705  | 1.108                     | $1.59 \times 10^{-2}$                           | 0.70220                     | 1/2                 | —  | 6,728   |
| <sup>14</sup> N  | 3.076   | 99.635                    | $1.01 \times 10^{-3}$                           | 0.40358                     | 1                   | $7.1 \times 10^{-2}$   | —   |
| <sup>15</sup> N  | 4.315   | 0.365                     | $1.04 \times 10^{-3}$                           | -0.28304                    | 1/2                 | —  | -2,712  |
| <sup>16</sup> O  | —   | 99.76                     | —   | —                           | 0                   | —  | —   |
| <sup>17</sup> O  | 5.772   | $3.7 \times 10^{-2}$      | $2.91 \times 10^{-2}$                           | -1.8930                     | 5/2                 | $-4.0 \times 10^{-3}$  | -3,628  |
| <sup>19</sup> F  | 40.055  | 100                       | 0.834   | 2.6273                      | 1/2                 | —  | 25,179  |
| <sup>28</sup> Si | —   | 92.28                     | —   | —                           | 0                   | —  | —   |
| <sup>29</sup> Si | 8.458   | 4.70                      | $7.85 \times 10^{-2}$                           | -0.55548                    | 1/2                 | —  | -5,319  |
| <sup>30</sup> Si | —   | 3.02                      | —   | —                           | 0                   | —  | —   |
| <sup>31</sup> P  | 17.236  | 100                       | $6.64 \times 10^{-2}$                           | 1.1305                      | 1/2                 | —  | 10,840  |
| <sup>32</sup> S  | —   | 95.06                     | —   | —                           | 0                   | —  | —   |
| <sup>33</sup> S  | 3.266   | 0.74                      | $2.26 \times 10^{-3}$                           | 0.64274                     | 3/2                 | -0.053   | 2,054   |
| <sup>34</sup> S  | —   | 4.2                       | —   | —                           | 0                   | —  | —   |
| <sup>35</sup> Cl | 4.172   | 75.4                      | $4.71 \times 10^{-3}$                           | 0.82091                     | 3/2                 | $-7.9 \times 10^{-2}$  | 2,624   |
| <sup>37</sup> Cl | 3.472   | 24.6                      | $2.72 \times 10^{-3}$                           | 0.68330                     | 3/2                 | $-6.21 \times 10^{-2}$   | 2,184   |
| <sup>79</sup> Br | 10.667  | 50.57                     | $7.86 \times 10^{-2}$                           | 2.0991                      | 3/2                 | 0.34   | —   |
| <sup>81</sup> Br | 11.499  | 49.43                     | $9.84 \times 10^{-2}$                           | 2.2626                      | 3/2                 | 0.28   | —   |
| <sup>127</sup> I | 8.519   | 100                       | $9.35 \times 10^{-2}$                           | 2.7937                      | 5/2                 | -0.75  | —   |

<sup>a</sup>Varian Associates NMR Table, 4th ed., 1964.





## I. INTRODUCTION\*

Direct observation of the carbon skeleton as well as the carbon atoms in carbon-containing functional groups has been available on a practical basis only since the early 1970s. The <sup>12</sup>C nucleus is not magnetically "active" (spin number, *I*, is zero), but the <sup>13</sup>C nucleus, like the <sup>1</sup>H nucleus, has a spin number of ½. However, since the natural abundance of <sup>13</sup>C is only 1.1% that of <sup>12</sup>C, and its sensitivity is only about 1.6% that of <sup>1</sup>H, the overall sensitivity of <sup>13</sup>C compared with <sup>1</sup>H is about 1/5700.

The conventional, continuous-wave, slow-scan procedure requires a large sample and a prohibitively long time to obtain a <sup>13</sup>C spectrum, but the availability of Fourier transform instrumentation, which permits simultaneous irradiation of all <sup>13</sup>C nuclei, has resulted in an explosion of <sup>13</sup>C spectrometry, beginning in the early 1970s, comparable to the burst of activity in <sup>1</sup>H spectrometry that began in the late 1950s.

An important development was the use of wide-band heteronuclear (noise) decoupling. Because of the large *J* values for <sup>13</sup>C–H (~110–320 Hz) and appreciable values for <sup>13</sup>C–C–H and <sup>13</sup>C–C–C–H, nondecoupled (proton coupled) <sup>13</sup>C spectra usually show complex overlapping multiplets that are difficult to interpret, but some nondecoupled spectra such as that of diethyl phthalate (Figure 1a) are quite simple. Noise decoupling (Figure 1b) of the protons by means of a wideband (noise) generator removes these couplings. The result, in the absence of other coupling nuclei, such as <sup>31</sup>P or <sup>19</sup>F, is a *single sharp peak\*\* for each chemically nonequivalent <sup>13</sup>C atom*, except for the infrequent fortuitous coincidence of <sup>13</sup>C chemical shifts. Furthermore, an increase in signal (up to a factor of ~3)

accrues from the nuclear Overhauser effect (NOE). This enhancement results from an increase in population of the lower energy level of the <sup>13</sup>C nuclei concomitant with the increase in population of the high energy level of the <sup>1</sup>H nuclei on irradiation (decoupling) of the <sup>1</sup>H nuclei. The net effect is a very large reduction in the time needed to obtain a noise-decoupled spectrum (Figure 1b) as compared with a nondecoupled spectrum (Figure 1a).

In the Fourier transform mode, a short powerful rf pulse (on the order of a few microseconds) excites all the <sup>13</sup>C nuclei simultaneously. Since the frequencies in the pulse are slightly off-resonance (pulse center at approximately the frequency of <sup>13</sup>C in TMS) for all of the nuclei, each nucleus shows a free induction decay (FID), which is an exponentially decaying sine wave with a frequency equal to the difference between the applied frequency and the resonance frequency for that nucleus (Figure 2a).

The free induction decay display for a compound containing more than one <sup>13</sup>C nucleus consists of superimposed sine waves, each with its characteristic frequency, and an interference ("beat") pattern results (Figure 2b). These data are automatically digitized and stored in a computer, and a series of repetitive pulses, with signal acquisition and accumulation between pulses, builds up the signal. Fourier transformation by the computer converts this information to the conventional presentation of a <sup>13</sup>C NMR spectrum. Figure 2a represents the FID and the conventional <sup>13</sup>C spectra for CH<sub>3</sub>OH. Figure 2b shows the same spectra for C<sub>2</sub>H<sub>5</sub>OH. The free induction decay is a time domain spectrum, whereas the transformed, conventional presentation is a frequency domain spectrum. The sequence (Fig. 2c) is: pulse, acquisition, and pulse delay if required (see below).

The <sup>13</sup>C spectra in this text were run on a Varian XL-100 (25.2 MHz for <sup>13</sup>C) or a Varian CFT 20 (20.0 MHz for <sup>13</sup>C) spectrometer. Since these instruments lock on deuterium, the common deuterated solvents (usually CDCl<sub>3</sub>) are used to furnish the internal lock.\* (A list of common deuterated solvents is given in Appendix A.) As it is with <sup>1</sup>H spectrometry, the common internal reference is tetramethylsilane (TMS), and the scale is given in δ units (ppm) downfield (deshielding) from TMS in positive numbers, and upfield (shielding) from TMS in negative numbers. The shifts encountered in routine <sup>13</sup>C spectra range about 240 ppm downfield from TMS; this is a range of about 20 times that of routine <sup>1</sup>H spectra (~12 ppm). Several cations have been recorded at ~335 ppm downfield, and Cl<sub>4</sub> absorbs at ~-290 ppm (upfield from TMS).

On the Varian XL-100 instrument, the <sup>13</sup>C frequency is 25.2 MHz, and the routine sweep width is 5000 Hz (198.4 ppm). Each of the major divisions on the bottom scale of

\*Familiarity with Chapter 4 is assumed.

\*\*Because of the low natural abundance of <sup>13</sup>C, the occurrence of adjacent <sup>13</sup>C atoms has a low probability; thus, we are free of the complication of <sup>13</sup>C–<sup>13</sup>C coupling.

\*A field-frequency internal lock provides corresponding changes in the irradiating frequency for minor variations in field strength to furnish a constant field/frequency ratio.

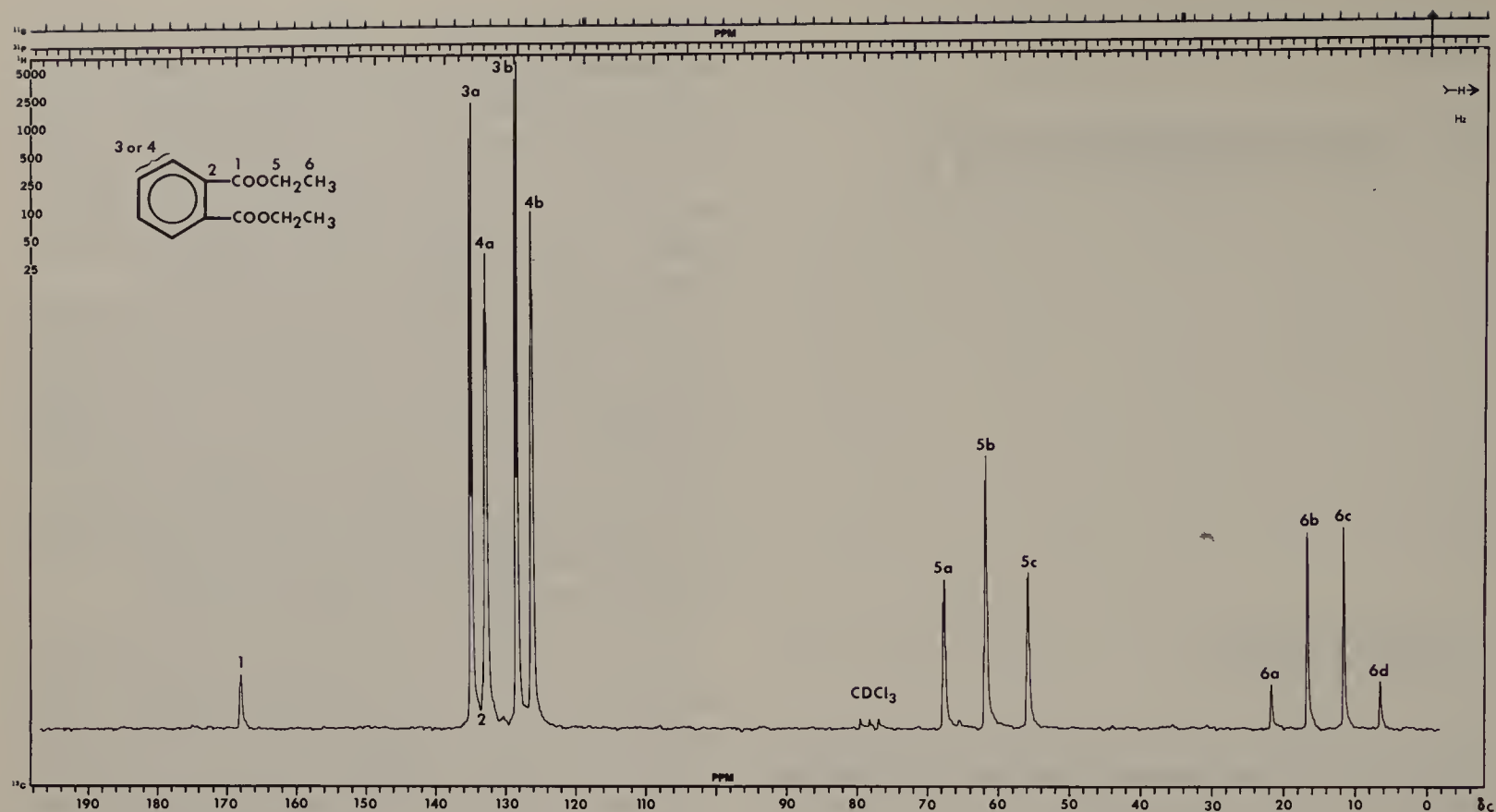


Figure 1a.  $^{13}\text{C}$  NMR spectrum of diethyl phthalate with the protons completely coupled.  $\text{CDCl}_3$  solvent, 25.2 MHz.

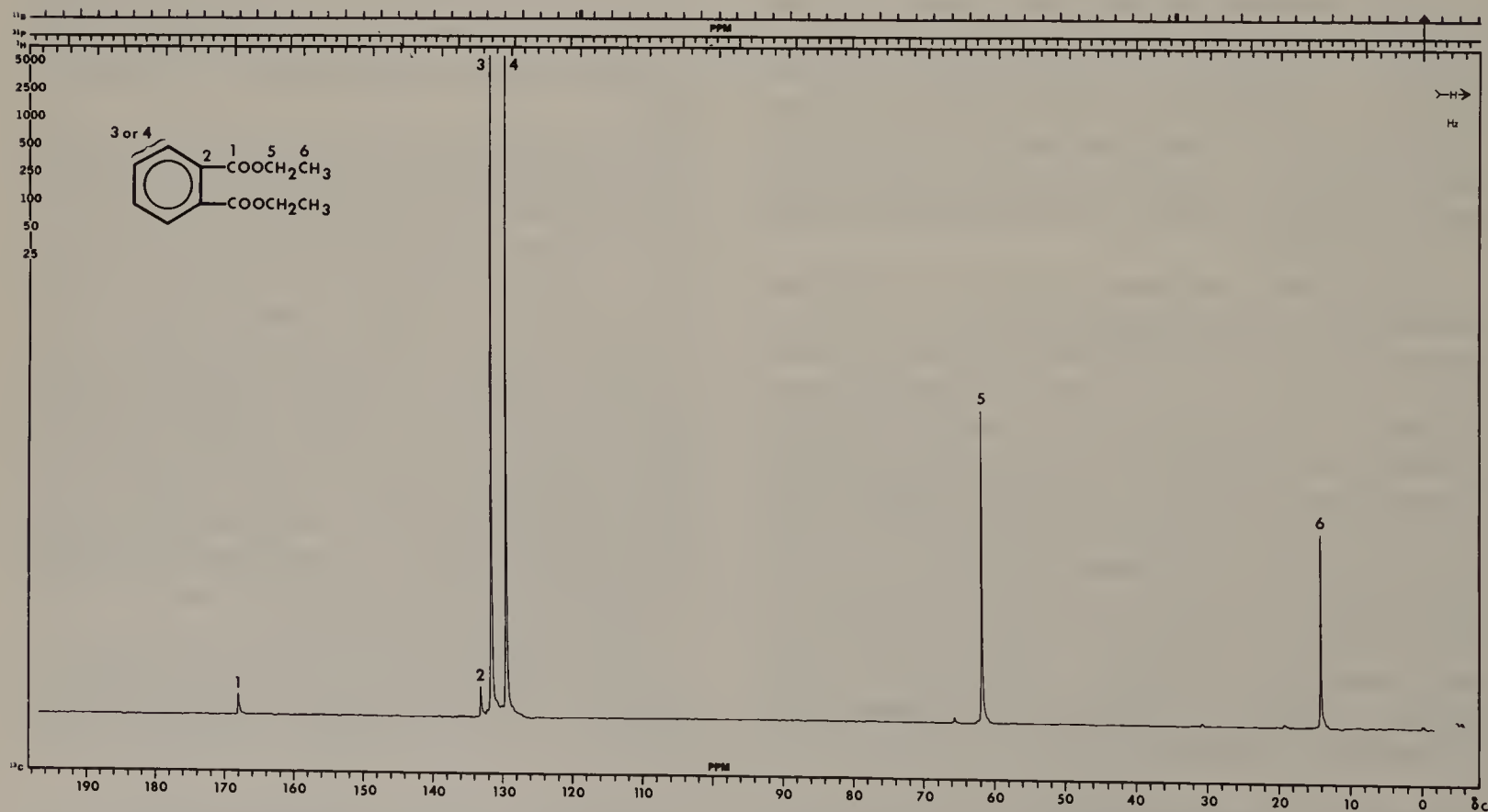


Figure 1b.  $^{13}\text{C}$  NMR spectrum of diethyl phthalate with the protons completely decoupled by broad-band noise.  $\text{CDCl}_3$  solvent, 25.2 MHz.



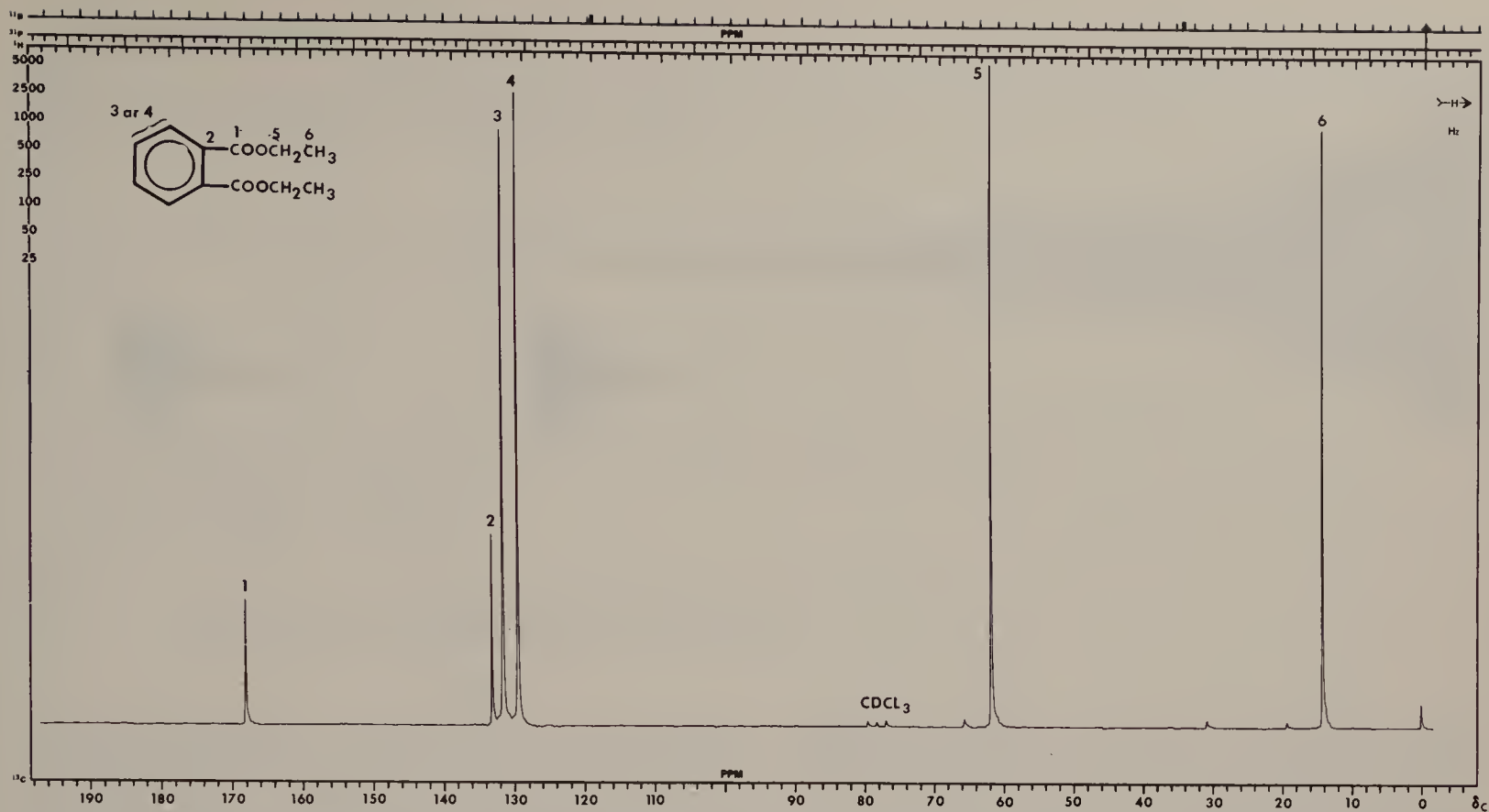


Figure 1c.  $^{13}\text{C}$  NMR spectrum of diethyl phthalate with the protons completely decoupled and a 10 sec. delay between pulses.  $\text{CDCl}_3$  solvent, 25.2 MHz.

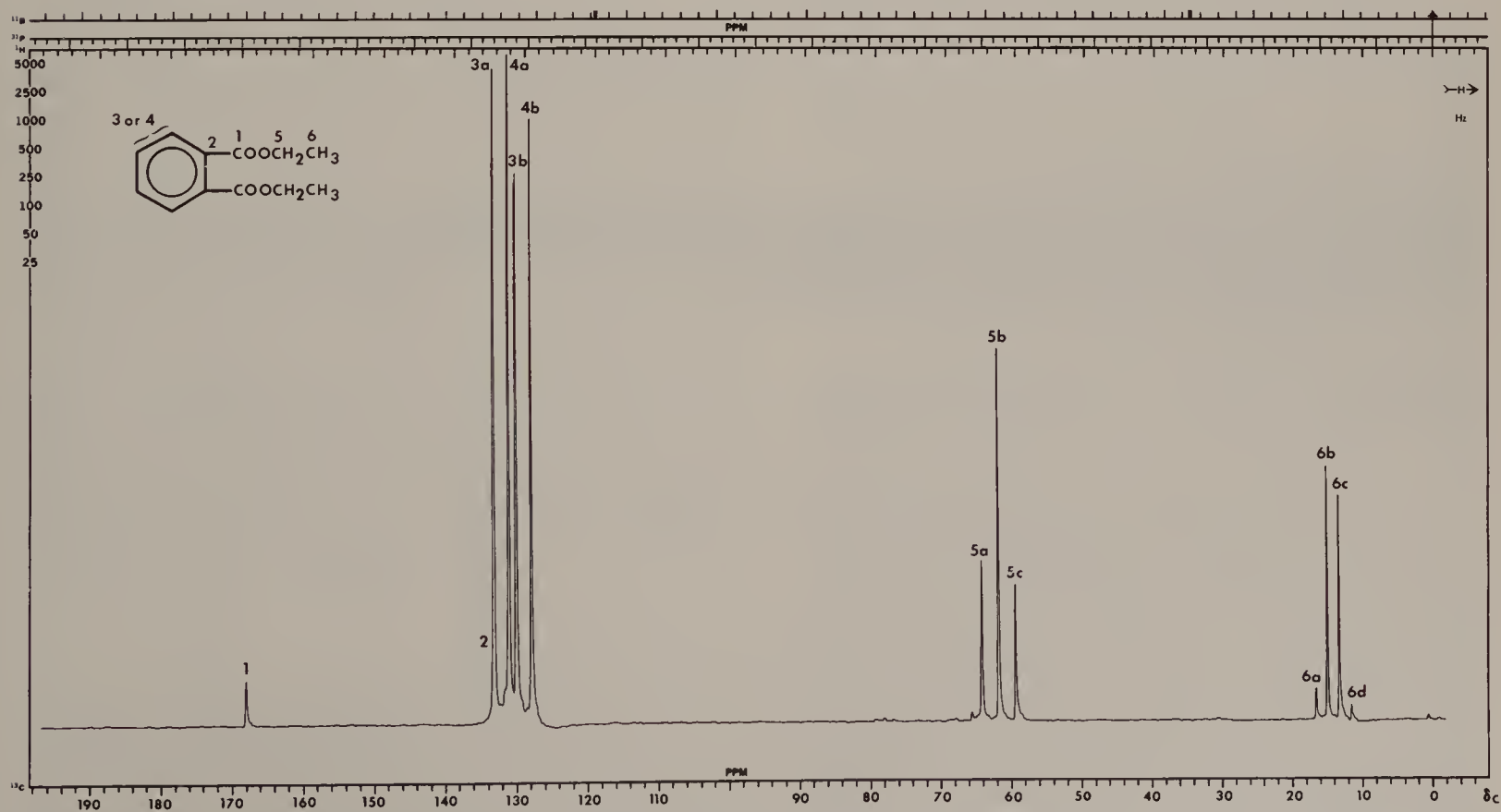


Figure 1d.  $^{13}\text{C}$  NMR spectrum of diethyl phthalate with off-resonance decoupled protons.  $\text{CDCl}_3$  solvent, 25.2 MHz.

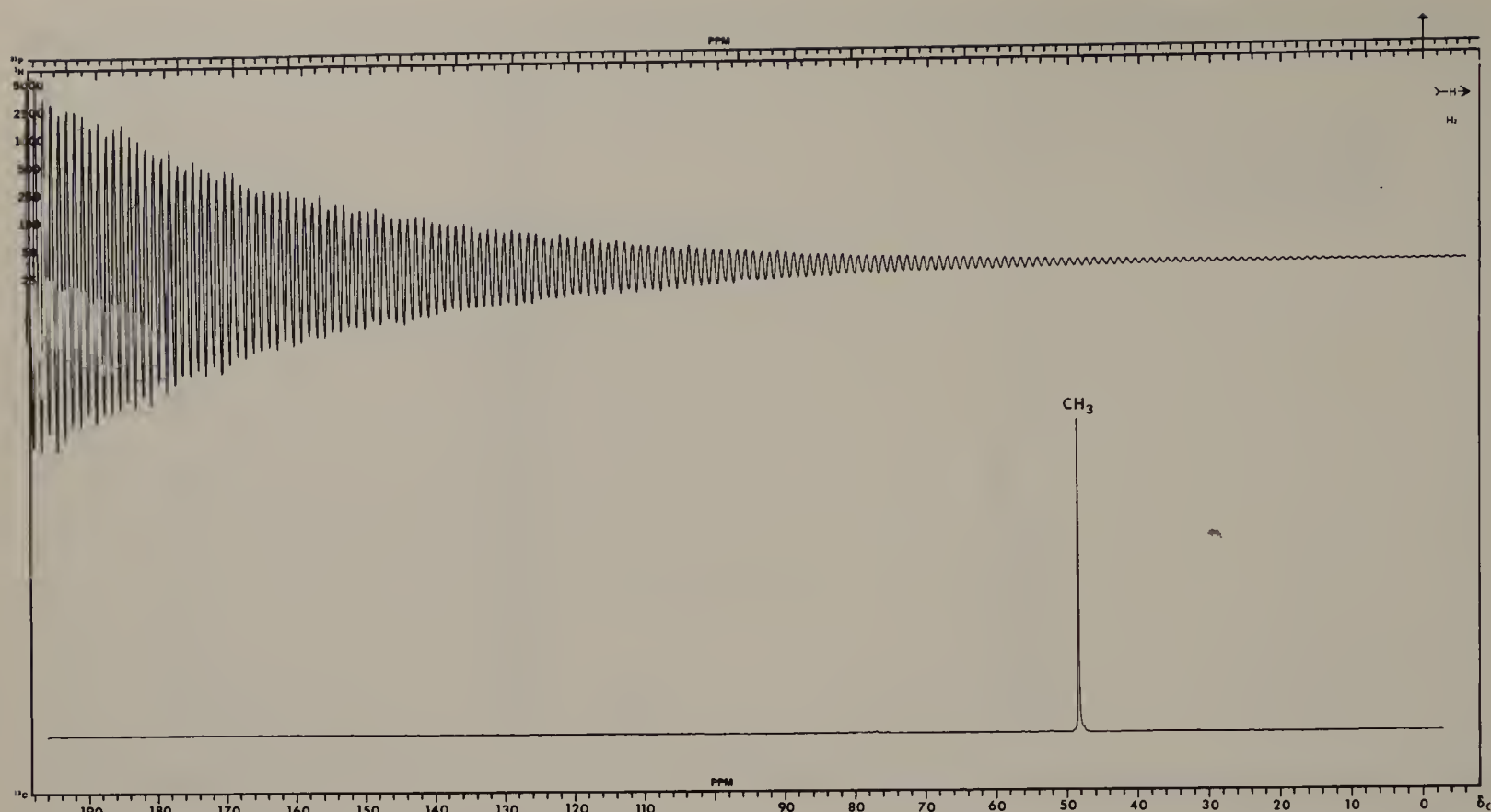


Figure 2a. Free induction decay (above) and transformed  $^{13}\text{C}$  spectrum of methanol (60% in  $\text{CDCl}_3$ , 25.2 MHz).

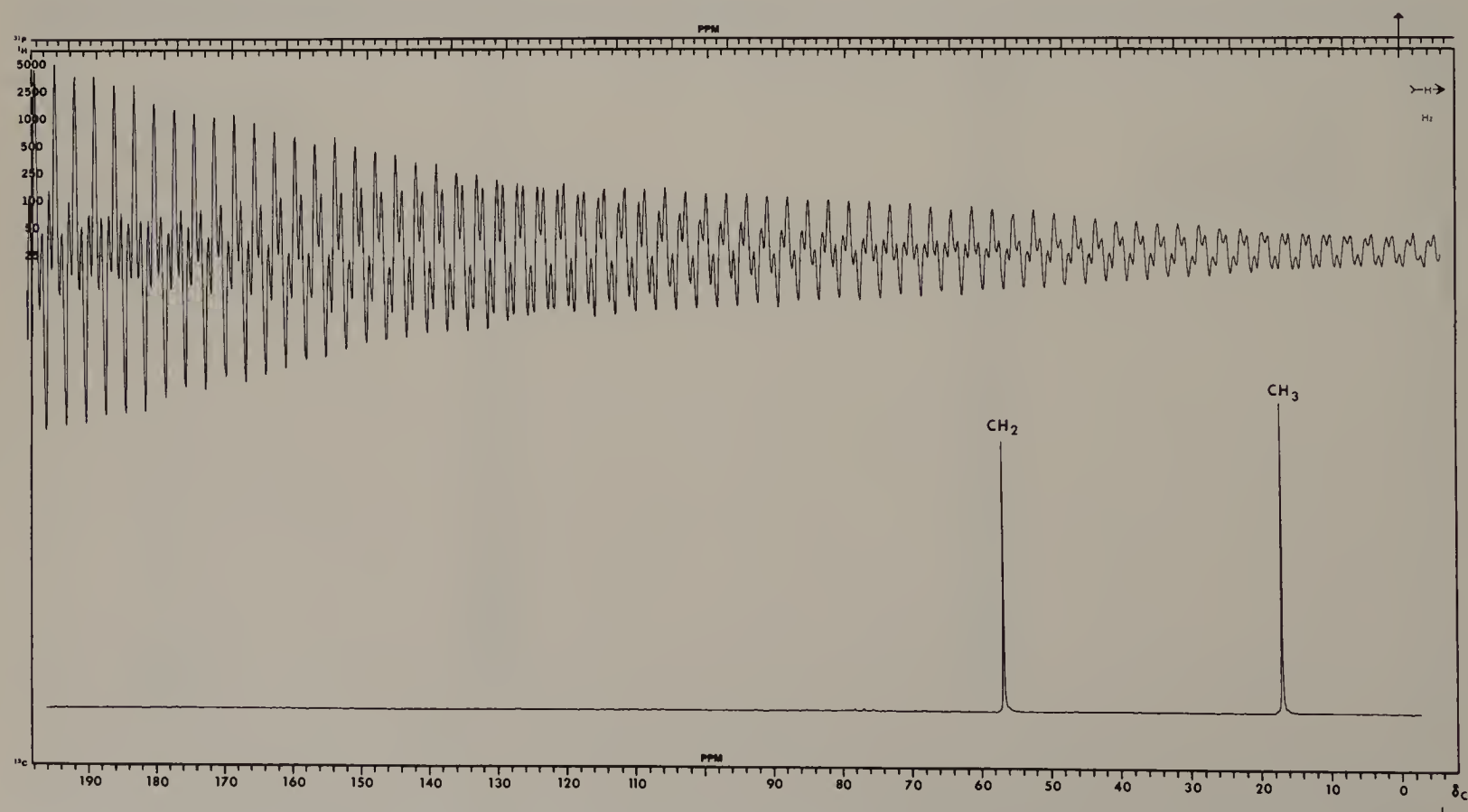


Figure 2b. Free induction decay (above) and transformed  $^{13}\text{C}$  spectrum of methanol (60% in  $\text{CDCl}_3$ , 25.2 MHz).

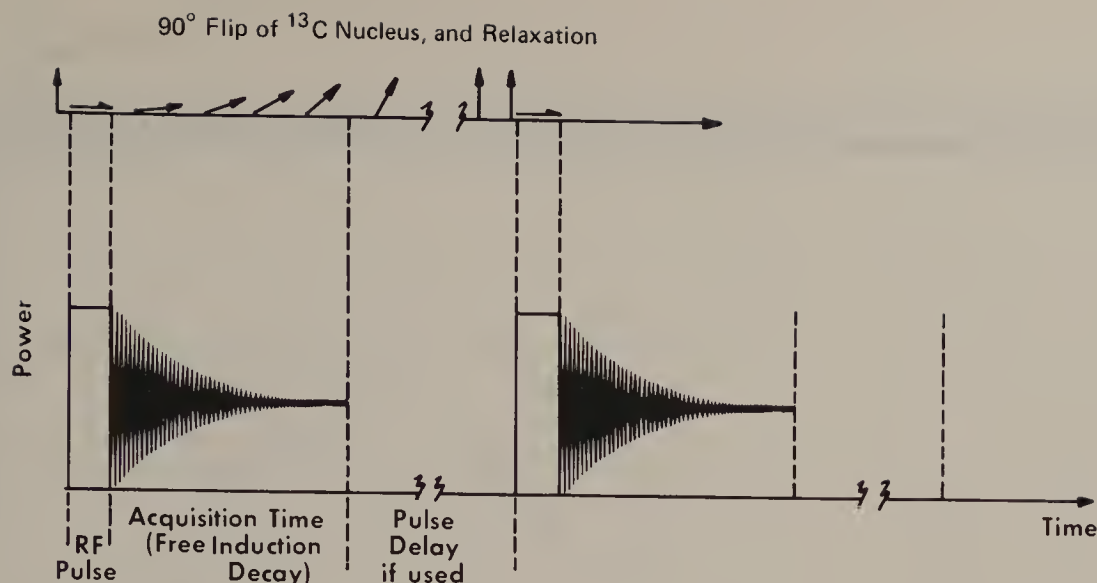


Figure 2c. Schematic representation of the radiofrequency pulse followed by the free induction decay (acquisition time) and pulse delay.

the spectrum represents 10 ppm (Figure 1). If the presence of carbon atoms that absorb further downfield is suspected, the sweep width is increased accordingly. For a sweep width of 5000 Hz (250 ppm) on the Varian CFT 20 instrument, each division of the scale represents 6.25 ppm (see Figure 3).

As a result of the large sweep width and the sharpness of the peaks, impurities (or mixtures) are readily detected. Even stereoisomers that are difficult to separate, or detect by other procedures, show up as discrete peaks.

Routine sample sizes for  $^{13}\text{C}$  NMR are 0.5-2.0 g in 10-, 12-, or 15-mm OD tubes, and these samples require only a few ( $\sim 5$ -10) pulses. Samples of 100-200 mg can be handled in the familiar 5-mm OD tubes if solubility is no problem, but the number of pulses required may take several hours. Samples of 10-100 mg may be handled in the conventional microcells with a volume of about 100  $\mu\text{l}$ . By using a 1.7-mm capillary cell, samples of 1 mg or less can be handled if solubility is no problem.

Several texts on  $^{13}\text{C}$  NMR spectrometry for the organic chemist are available.<sup>1-5</sup> A one-volume collection of  $^{13}\text{C}$  spectra with peak assignments is very useful.<sup>6</sup> The Sadtler collection now includes  $^{13}\text{C}$  spectra.<sup>7</sup> The principles and practice of Fourier Transform NMR are discussed<sup>8-10</sup>, and a set of spectral problems in  $^{13}\text{C}$  spectrometry is available.<sup>11</sup> Breitmaier et al. have recently assembled a three-volume set, *Atlas of Carbon-13 NMR Data*.<sup>12</sup>

## II. INTERPRETATION OF $^{13}\text{C}$ SPECTRA (PEAK ASSIGNMENTS)

How are specific peaks assigned in a noise decoupled  $^{13}\text{C}$  spectrum, such as Figure 1b? First, we do have reference

material and empirical relationships to correlate chemical shift with structure. (See discussion under Chemical Shifts in Section III for the major chemical classes, and Appendices B and C.) However, we lack coupling information because of noise decoupling of protons, and we cannot depend on peak integrations for the following reasons.

Repetitive scan (continuous wave)  $^1\text{H}$  spectrometry usually results in a satisfactory relationship between integrated peak areas and the number of nuclei under those areas because there is sufficient time between irradiations of an individual proton for relaxation to occur. Satisfactory integrations would also result for most  $^{13}\text{C}$  spectra under these conditions, but the time needed for the number of scans required is prohibitive for routine work.

In routine Fourier Transform runs, the repetitive pulses are spaced at intervals of 0.1-1 second (acquisition time) during which the signal is averaged and stored. Under these conditions,  $^{13}\text{C}$  nuclei, whose relaxation times ( $T_1$ ) vary over a wide range, are not equally relaxed between pulses, and the resulting peak areas do not integrate to give the correct number of carbon atoms. Very long pulse delays (following the acquisition period) can be used, but the time required limits this technique to special situations. Furthermore, there is another complication: the Nuclear Overhauser Enhancement (see above) is not the same for all nuclei, and this results in further loss of quantitation.

However, one advantage does result. It is usually possible by "eyeballing" a  $^{13}\text{C}$  spectrum to recognize the nuclei that do not bear protons by their low intensity (peaks 1 and 2 in Figure 1b). The common spin lattice relaxation mechanism for  $^{13}\text{C}$  results from dipole-dipole interaction with directly attached protons. Thus, nonprotonated carbon atoms often have longer relaxation times and give small peaks. It is therefore often possible readily to detect carbonyl groups (except formyl), nitriles, nonprotonated



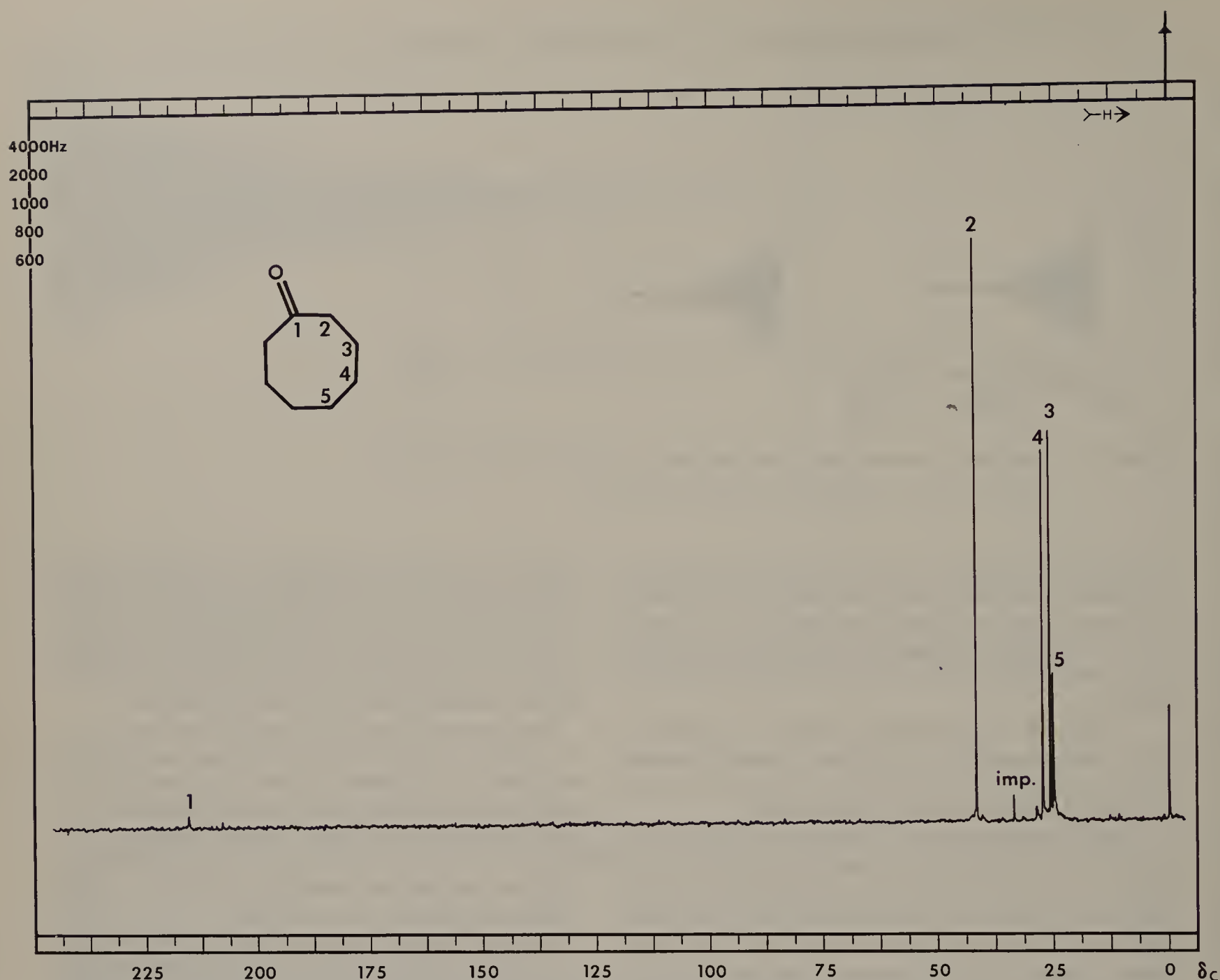
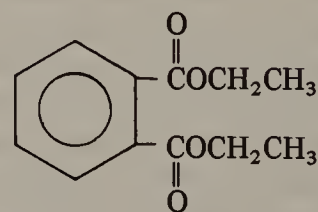


Figure 3a.  $^{13}\text{C}$  NMR spectrum of cyclooctanone with proton coupling completely removed by noise decoupling.  $\text{CDCl}_3$  solvent, 20 MHz, sweepwidth 5000 Hz.

olefinic and acetylenic carbon atoms, and other quaternary carbon atoms. However, care must be taken to allow a sufficient number of pulses or a long enough interval between pulses (to compensate for the long  $T_1$ ) so that these weak signals are not completely lost in the baseline noise. In Figure 1c, a 10-second interval (pulse delay) was used to increase the relative intensities of peaks 1 and 2).

The most useful techniques for assigning peaks, in addition to structure-shift correlations, are off-resonance decoupling, selective proton decoupling, the use of chemical shift reagents, and deuterium substitution. The concept of chemical shift equivalence (Chapter 4) should always be kept in mind. The use of spin relaxation times is beyond the scope of this chapter.

In the noise decoupled spectrum of diethyl phthalate (Figure 1b),



we can assign the very small peak at 167.75 ppm to the 2 equivalent  $\text{C}=\text{O}$  groups, the very small peak at 132.85 ppm to the equivalent substituted aromatic carbons, the large peaks at 131.33 ppm and 129.19 ppm to the remaining aromatic carbons, the medium peaks at 61.63 ppm to the 2 equivalent  $\text{CH}_2$  groups, and the medium peak at 14.15 ppm to the 2 equivalent  $\text{CH}_3$  groups. These assignments can be made on the basis of Appendices B and C and on the assumption that the quaternary carbon atoms are responsible for

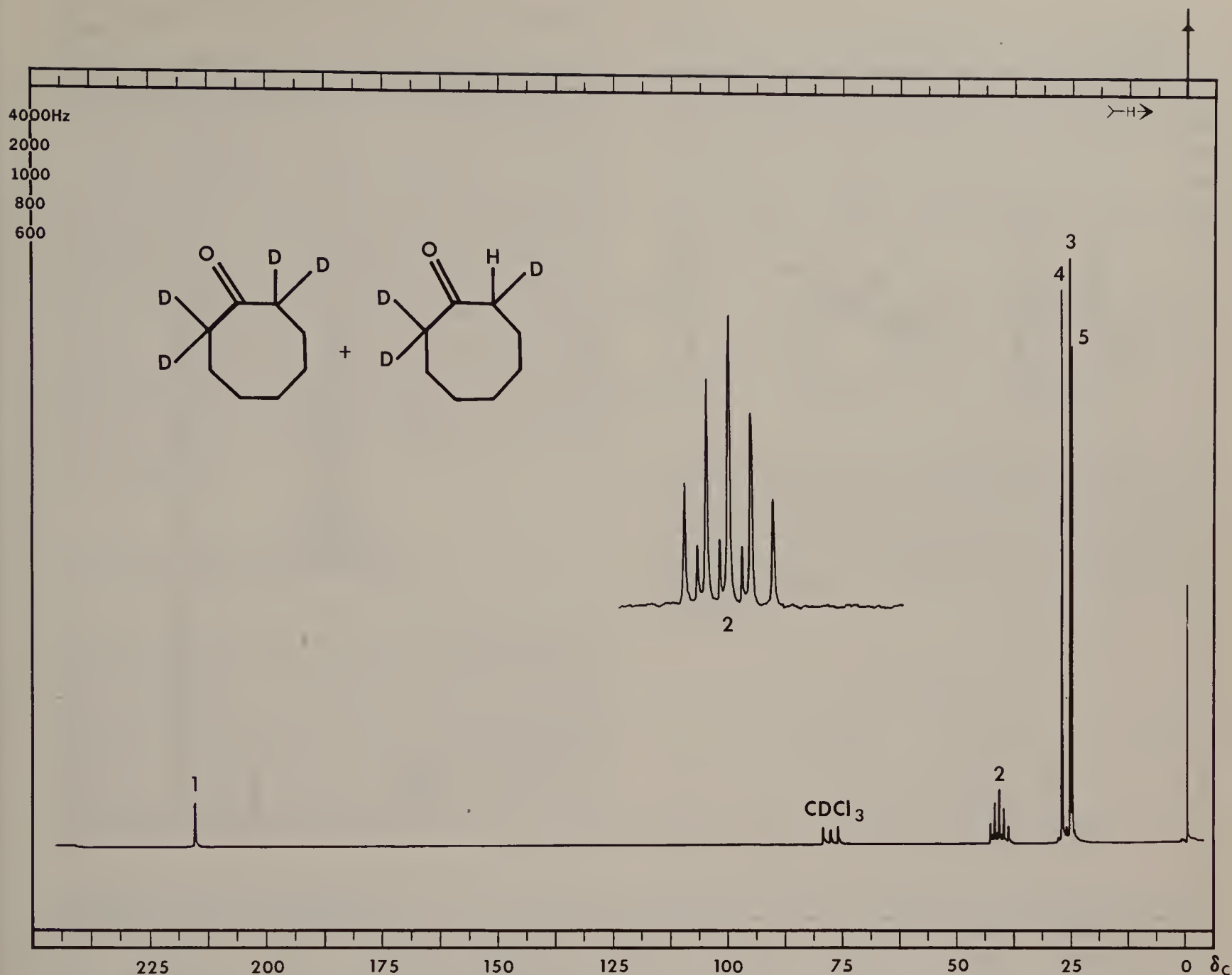


Figure 3b. *N*-Noise decoupled  $^{13}\text{C}$  spectrum of tetradeuterated (major component) and trideuterated (minor component) cyclooctanone.  $\text{CDCl}_3$  solvent, 20 MHz, sweepwidth 5000 Hz. For insert, sweepwidth 1000 Hz.

the weak peaks. Their relative intensity can be increased by inserting a pulse delay (an interval between the acquisition period and the next pulse) as in Figure 1c. Note that the 10-second pulse delay nearly equalizes the intensities of all the peaks except for those representing the quaternary carbons.

## OFF-RESONANCE DECOUPLING

We have seen that proton noise decoupling simplifies the spectrum and increases peak heights, but with the loss of coupling information. Off-resonance decoupling (Figure 1d) gives a simplified spectrum yet retains "residual"  $^{13}\text{C}$ -H coupling ( $J^r$ ) information. Off-resonance decoupling is achieved by offsetting the high-power proton decoupler by

about 1000-2000 Hz upfield or about 2000-3000 Hz downfield from the *proton* frequency of TMS without using the noise generator; that is, we irradiate upfield or downfield of the usual (1000 Hz sweepwidth) *proton* spectrum. This results in residual coupling from protons directly bonded to the  $^{13}\text{C}$  atoms, while long-range coupling is usually lost. The observed residual coupling ( $J^r$ ), which is determined by the amount of offset and the power of the decoupler, is smaller than the true coupling  $J$ .

$$J^r \simeq \frac{2\pi J \Delta\nu}{\gamma H_2}$$

where  $\gamma$  is the magnetogyric ratio for protons,  $\Delta\nu$  is the difference between the resonance frequency of the proton of interest and the decoupler frequency, and  $H_2$  is the

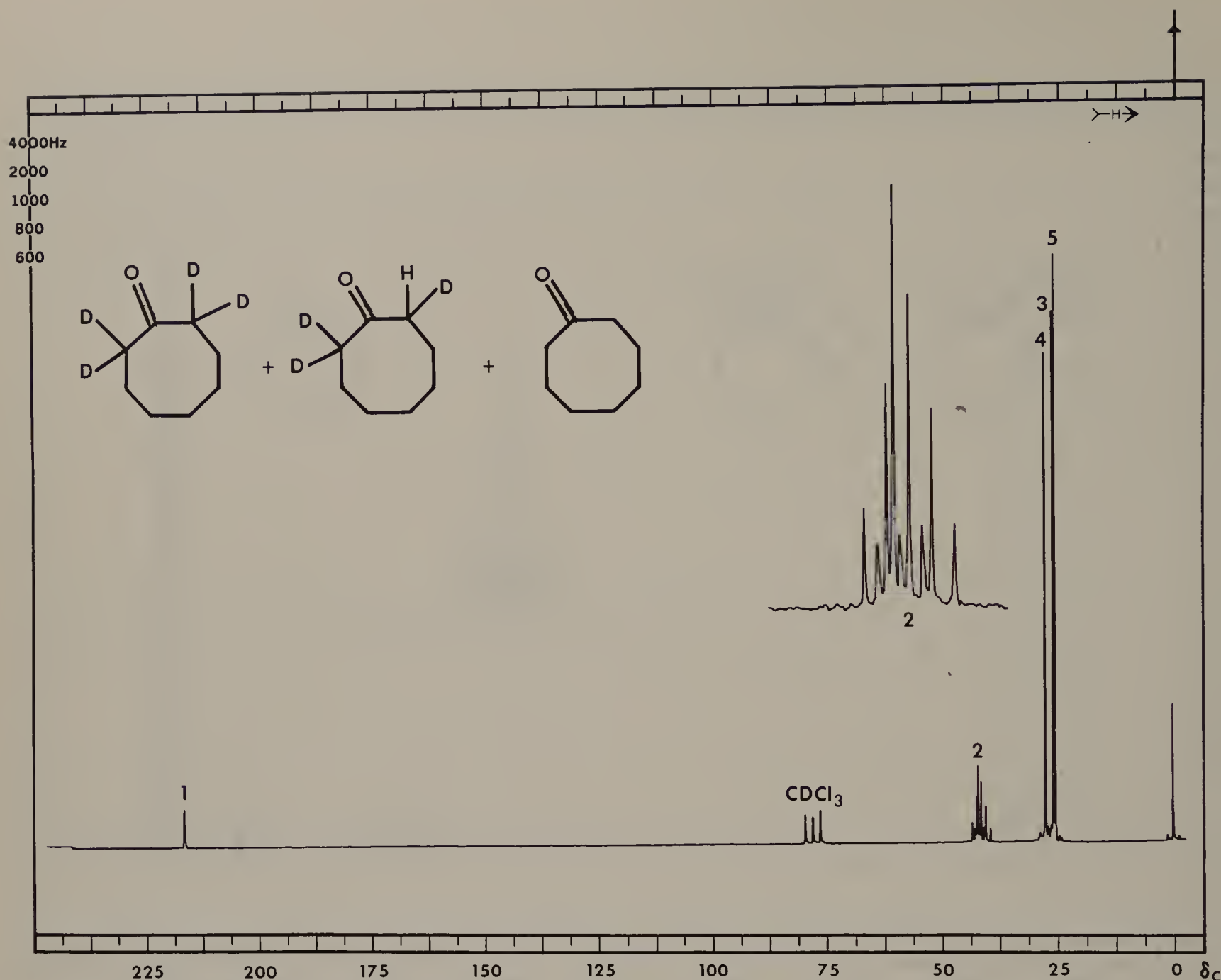


Figure 3c. Noise-decoupled  $^{13}\text{C}$  spectrum of deuterated sample undeuterated cyclooctanone.  $\text{CDCl}_3$  solvent, 20 MHz, sweep width 5000 Hz. For insert, sweepwidth 1000 Hz.

strength of the rotating magnetic field generated by the decoupler frequency. Thus, the multiplicities of the  $^{13}\text{C}$  bands can be readily observed, usually without overlap with other  $^{13}\text{C}$  bands. Methyl carbon atoms appear as quartets, methylenes as triplets (or as pair of doublets if the protons are not equivalent and their coupling constants are sufficiently different), methines as doublets, and quaternary carbon atoms as singlets.\* The procedure, of course, also gives a proton count to corroborate the proton spectrum. A dis-

crepancy between the number of protons obtained from the off-resonance decoupled  $^{13}\text{C}$  spectrum and the molecular formula obtained from the mass spectrum results from elements of symmetry whose presence can be correlated with molecular structure.

In Figure 1d, only the doublets of peaks 3 and 4 overlap. The residual couplings become slightly larger as the frequency increases; in this case, the irradiation is upfield of the proton frequency of TMS. It is convenient to superimpose the off-resonance decoupled spectrum on the noise-decoupled spectrum on a light-table. Thus, we can see that the quaternary carbons (singlets) and the center peak of the  $\text{CH}_2$  triplets are superimposed on the corresponding noise-decoupled singlets, whereas the CH doublet and  $\text{CH}_3$

\*In practice, the outer peaks are usually weaker than expected from the theoretical 1:2:1 or 1:3:3:1 peak height ratios because of decoupler field inhomogeneity. R. Freeman, et al., *J. Am. Chem. Soc.* 100, 5637 (1979).



quartets “straddle” the corresponding noise-decoupled peaks.

A second-order effect is discussed in Section VI and the use of off-resonance decoupling to correlate a particular  $^{13}\text{C}$  peak with the shift position of its attached proton is discussed in Section V.

The off-resonance decoupled spectrum of diethyl phthalate (Figure 1d) allows us to confirm the assignments made on the basis of chemical shifts and peak heights. The multiplicity of peak 1 is unchanged. Peak 2 is buried under peak 3a. Peaks 3 and 4 are overlapping doublets. Peak 5 is a triplet, and peak 6 a quartet. We count 6 carbon atoms and 7 protons, which, given an element of symmetry, corroborates the molecular formula  $\text{C}_{12}\text{H}_{14}\text{O}_4$  and the *ortho* substitution. For this simple molecule, the nondecoupled spectrum (Figure 1a) presents no problem, but in more complex molecules, overlapping multiplets are often difficult to interpret.

## SELECTIVE PROTON DECOUPLING

When a specific proton is irradiated at its exact frequency at a lower power level than is used for off-resonance decoupling, the absorption of the directly bonded  $^{13}\text{C}$  becomes a singlet, while the other  $^{13}\text{C}$  absorptions show residual coupling. This technique has been used for peak assignment, but satisfactory results depend on finding the precise frequency of the proton and the appropriate power level for decoupling it, which can be difficult.

## CHEMICAL SHIFT REAGENTS

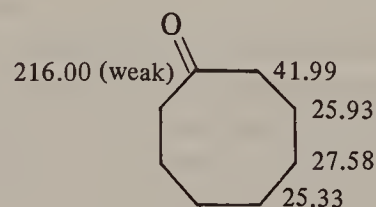
The lanthanide chemical shift reagents (see Chapter 4) can be used to “spread out” a  $^{13}\text{C}$  spectrum in the same way as they are used in  $^1\text{H}$  studies. Two useful results may be obtained: coincident peaks may separate and the proton shifts are also spread out; selective proton decoupling is thus facilitated. However, facile analogies between  $^{13}\text{C}$  and  $^1\text{H}$  effects are risky.

## DEUTERIUM SUBSTITUTION

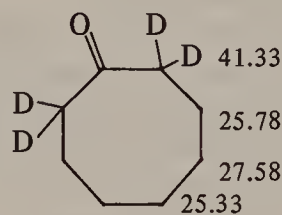
Deuteration of a carbon results in a dramatic diminution of its  $^{13}\text{C}$  signal in a noise-decoupled spectrum for the following reasons. Since deuterium has a spin number of 1 and a magnetic moment 15% that of  $^1\text{H}$ , it will split the  $^{13}\text{C}$  absorption into 3 lines (ratio 1:1:1) with a  $J$  value equal to  $0.15 \times J_{\text{CH}}$ . Furthermore,  $T_1$  for  $^{13}\text{C}-\text{D}$  is longer than that for  $^{13}\text{C}-\text{H}$  because of decreased dipole-dipole relaxation. Finally, the Nuclear Overhauser Effect is lost,

since there is no irradiation of deuterium.\* A separate peak may also be seen for any residual  $^{13}\text{C}-\text{H}$ , since the isotope effect usually results in a slight upfield shift of the  $^{13}\text{C}-\text{D}$  absorption ( $\sim 0.2$  ppm per D atom). The isotope effect may also slightly shift the absorption of the carbon atoms once removed from the deuterated carbon.

The net result depends on the extent of deuteration. A noise-decoupled spectrum of cyclooctanone is shown in Figure 3a, and we note the following assignments.

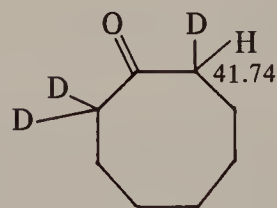


On deuteration of cyclooctanone, the  $\alpha$ - $^{13}\text{C}$  peak at  $\delta$  41.99 in the undeuterated compound is replaced by a very weak cluster of peaks (Figure 3b). In the expanded insert, we can pick out the five larger peaks of a 1:2:3:2:1 quintet (representing the  $\text{CD}_2$  absorption) and a smaller 1:1:1 triplet (representing the  $\text{CHD}$  absorption) of the two compounds.



Major component

and



Minor component

Note the slight upfield shift of the  $\alpha$ - and  $\beta$ -carbon atoms in the deuterated compounds.

\*The same explanation also accounts for the relatively weak signal shown by deuterated solvents. Deuterated chloroform,  $\text{CDCl}_3$ , shows a 1:1:1 *triplet*, deuterated *p*-dioxane a 1:2:3:2:1 *quintet*, and deuterated DMSO  $(\text{CD}_3)_2\text{SO}$ , a 1:3:6:7:6:3:1 *septet* in accordance with the  $nI + 1$  rule (Chapter 4).

Figure 3c is the spectrum of a deuterated cyclooctanone sample that contains approximately 15% of residual non-deuterated cyclooctanone in addition to the *tri*- and *tetra*-deuterated compounds. The CH<sub>2</sub> singlet is clearly seen in the insert in addition to the quintet and the triplet.

### CHEMICAL SHIFT EQUIVALENCE

The definition of chemical shift equivalence given for protons also applies to carbon atoms: interchangeability by a symmetry operation or by a rapid mechanism. The presence of equivalent carbon atoms (or fortuitous coincidence of shift) in a molecule results in a discrepancy between the apparent number of peaks and the actual number of carbon atoms in the molecule.

Thus, <sup>13</sup>C atoms of the methyl groups in *t*-butyl alcohol (Figure 4) are equivalent by rapid rotation in the same sense in which the protons of a methyl group are equivalent. The <sup>13</sup>C spectrum of *t*-butyl alcohol shows 2 peaks, one much larger than the other, but not necessarily exactly 3 times as large; the carbonyl carbon peak (quaternary) is much less than 1/3 the intensity of the peak representing the carbons of the methyl groups.

In the chiral molecule 2,2,4-trimethyl-1,3-pentanediol (Figure 5), we note that CH<sub>3</sub>*a* and CH<sub>3</sub>*b* are not equivalent, and 2 peaks are seen. Even though the 2 methyl groups labelled *c* are not equivalent, they fortuitously show only 1 peak. Two peaks may be seen at higher resolution, or with the help of a shift reagent.

In Chapter 4, Section VII, we noted that the CH<sub>3</sub> protons of (CH<sub>3</sub>)<sub>2</sub>NCH=O gave separate peaks at room temperature, but became chemical shift equivalent at ~123°. Of course, the <sup>13</sup>C peaks show the same behavior.

### III. CHEMICAL SHIFTS

In this section, chemical shifts will be discussed under the headings of the common chemical classes of organic compounds. As noted earlier, the range of shifts generally encountered in routine <sup>13</sup>C studies is about 240 ppm.

As a first reassuring statement, we can say that trends in chemical shifts of <sup>13</sup>C are somewhat parallel to those of <sup>1</sup>H, so that some of the "feeling" for <sup>1</sup>H spectra may carry over to <sup>13</sup>C spectra. Furthermore, the concept of *additivity of substituent effects* is useful for both spectra. Shifts are related mainly to hybridization and diamagnetic anisotropy; solvent effects are important in both spectra. Chemical shifts for <sup>13</sup>C are affected by substitutions as far removed as the δ position; in the benzene ring, pronounced shifts for <sup>13</sup>C are caused by substituents at the ortho, meta, and para positions. <sup>13</sup>C chemical shifts are also moved significantly upfield by steric compression. (See the γ-gauche effect, below.) Upfield shifts, as much as several ppm, may occur on dilution. Hydrogen-bonding effects with polar solvents may cause downfield shifts.

Appendix B gives credence to the statement that <sup>13</sup>C chemical shifts somewhat parallel those of <sup>1</sup>H, but we note some divergences that are not readily explainable and require development of another set of interpretive skills. In general, in comparison with <sup>1</sup>H spectra, it seems more difficult to correlate <sup>13</sup>C shifts with substituent electronegativity.

As in other types of spectrometry, peak assignments are made on the basis of reference compounds. Reference material for many classes of compounds is rapidly accumulating in the literature. The starting point is a general correlation chart for chemical shift regions of <sup>13</sup>C atoms in the major chemical classes (See Appendices B and C);

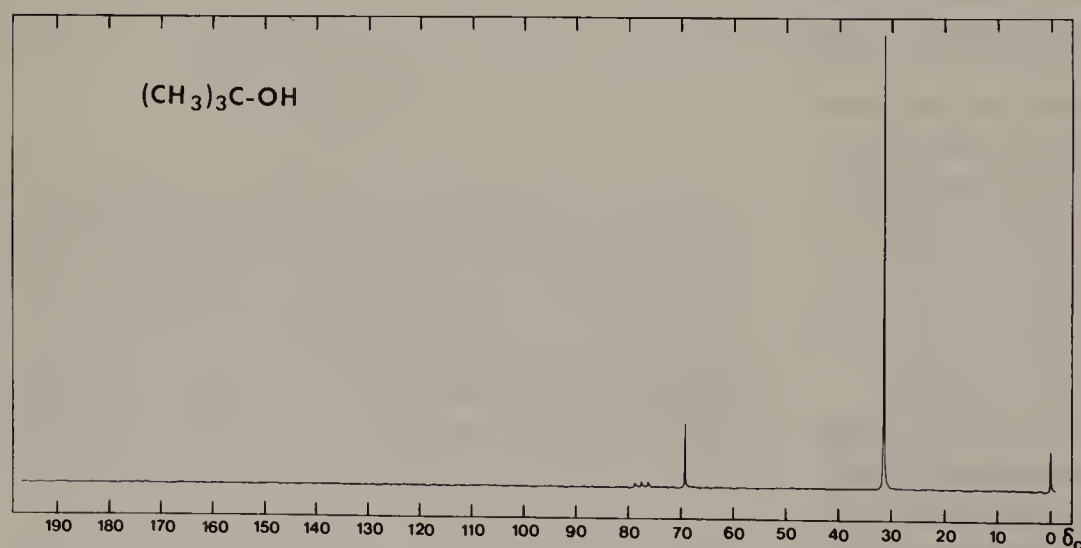


Figure 4. Noise-decoupled <sup>13</sup>C spectrum of *t*-butyl alcohol. Solvent CDCl<sub>3</sub>. 25.2 MHz, 5000 Hz sweep width. From reference 6, spectrum No. 88, with permission.



then, minor changes within these regions are correlated with structure variations in the particular chemical class. The chemical shift values in the following Tables must not be taken too literally because of the use of various solvents and concentration. (Furthermore, much of the early work used various reference compounds, and the values were corrected to give ppm from TMS.) For example, the C=O absorption of acetophenone in  $\text{CDCl}_3$  appears at 2.4 ppm further downfield than in  $\text{CCl}_4$ ; the effect on the other carbon atoms of acetophenone ranges from 0.0-1.1 ppm.

## ALKANES

### Linear and Branched Alkanes

We know from the general correlation chart (Appendix C) that alkane groups unsubstituted by heteroatoms absorb downfield from TMS to about 60 ppm. (Methane absorbs at 2.5 ppm upfield from TMS.) Within this range, we can predict the chemical shifts of individual  $^{13}\text{C}$  atoms in a straight chain or branched chain hydrocarbon from the data in Table I and the formula given below.

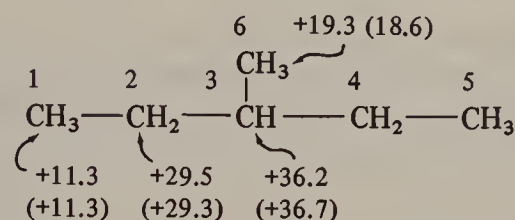
This table shows the additive shift parameters ( $A$ ) in hydrocarbons: the  $\alpha$  effect of +9.1 (downfield), the  $\beta$  effect of +9.4 ppm, the  $\gamma$  effect of -2.5 (upfield), the  $\delta$  effect of +0.3, the  $\epsilon$  effect of +0.1, and the corrections

Table I.  $^{13}\text{C}$  Shift Parameters in Some Linear and Branched Hydrocarbons

| $^{13}\text{C}$ Atoms | Shift (ppm) ( $A$ ) |
|-----------------------|---------------------|
| $\alpha$              | +9.1                |
| $\beta$               | +9.4                |
| $\gamma$              | -2.5                |
| $\delta$              | +0.3                |
| $\epsilon$            | +0.1                |
| $1^\circ (3^\circ)^a$ | -1.1                |
| $1^\circ (4^\circ)^a$ | -3.4                |
| $2^\circ (3^\circ)^a$ | -2.5                |
| $2^\circ (4^\circ)$   | -7.2                |
| $3^\circ (2^\circ)$   | -3.7                |
| $3^\circ (3^\circ)$   | -9.5                |
| $4^\circ (1^\circ)$   | -1.5                |
| $4^\circ (2^\circ)$   | -8.4                |

<sup>a</sup>The notations  $1^\circ (3^\circ)$  and  $1^\circ (4^\circ)$  denote a  $\text{CH}_3$  group bound to a  $\text{R}_2\text{CH}$  group and to a  $\text{R}_3\text{C}$  group, respectively. The notation  $2^\circ (3^\circ)$  denotes a  $\text{RCH}_2$  group bound to a  $\text{R}_2\text{CH}$  group—and so forth.

for branching effects. The calculated (and observed) shifts for the carbon atoms of 3-methylpentane are:



Calculations of shift are made from the formula:  $\delta = -2.5 + \Sigma nA$ , where  $\delta$  is the predicted shift for a carbon atom;  $A$  is the additive shift parameter; and  $n$  is the number of carbon atoms for each shift parameter (-2.5 is the shift of the  $^{13}\text{C}$  of methane). Thus, for carbon atom 1, we have 1  $\alpha$ -carbon, 1  $\beta$ -carbon, 2  $\gamma$ -carbons, and 1  $\delta$  carbon:

$$\begin{aligned}
 \delta_1 &= -2.5 + (9.1 \times 1) + (9.4 \times 1) \\
 &+ (-2.5 \times 2) + (0.3 \times 1) = +11.3
 \end{aligned}$$

Carbon atom 2 has 2  $\alpha$ -carbons, 2  $\beta$ -carbons and 1  $\gamma$ -carbon. Carbon atom 2 is a  $2^\circ$  carbon with a  $3^\circ$  carbon attached [ $2^\circ(3^\circ) = -2.5$ ].

$$\begin{aligned}
 \delta_2 &= -2.5 + (9.1 \times 2) + (9.4 \times 2) \\
 &+ (-2.5 \times 1) + (-2.5 \times 1) = 29.5
 \end{aligned}$$

Carbon atom 3 has 3  $\alpha$ -carbons and 2  $\beta$ -carbons, and it is a  $3^\circ$  atom with two  $2^\circ$  atoms attached [ $3^\circ(2^\circ) = -3.7$ ]. Thus,

$$\begin{aligned}
 \delta_3 &= -2.5 + (9.1 \times 3) + (9.4 \times 2) \\
 &+ (-3.7 \times 2) = +36.2
 \end{aligned}$$

Carbon atom 6 has 1  $\alpha$ -carbon, 2  $\beta$ -carbons, and 2  $\gamma$ -carbons, and it is a  $1^\circ$  atom with a  $3^\circ$  atom attached [ $1^\circ(3^\circ) = -1.1$ ]. Thus,

$$\begin{aligned}
 \delta_6 &= -2.5 + (9.1 \times 1) + (9.4 \times 2) \\
 &+ (-2.5 \times 2) + (-1.1 \times 1) = +19.3
 \end{aligned}$$

The agreement for such calculations is very good. It is essential that the reference compounds used for such additivity calculations be structurally similar to the compound of interest. Another useful calculation has been given.\* The  $^{13}\text{C}$  upfield  $\gamma$ -shift due to the  $\gamma$ -carbon has been attributed to the steric compression of a gauche interaction but has no counterpart in  $^1\text{H}$  spectra. It accounts, for example, for the upfield position of an axial methyl substituent on a conformationally rigid cyclohexane ring, relative to an equatorial methyl, and for the upfield shift of the  $\gamma$  carbon atoms of the ring.

\*L. P. Lindeman and J. Q. Adams, *Anal. Chem.* 43, 1245 (1971).



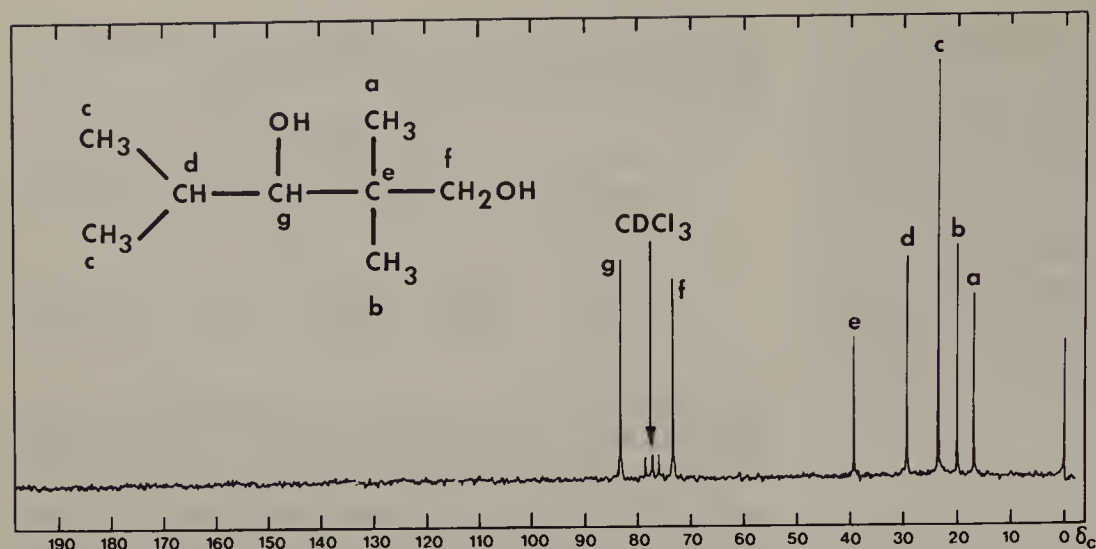


Figure 5. Noise decoupled  $^{13}\text{C}$  spectrum of 2,2,4-trimethyl-1,3-pentanediol. Solvent  $\text{CDCl}_3$ . 25.2 MHz, 5000 Hz sweepwidth. From reference 6, spectrum no. 324, with permission.

Table II lists the shifts in some linear and branched alkanes.

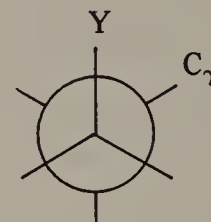
### EFFECT OF SUBSTITUENTS ON ALKANES

Table III shows the effects of a substituent on linear and branched alkanes. The effect on the  $\alpha$ -carbon parallels electronegativity of the substituent except for bromine

and iodine. The effect at the  $\beta$ -carbon seems fairly constant for all the substituents except for the carbonyl, cyano, and nitro groups. The upfield shift at the  $\gamma$ -carbon results (as above) from steric compression of a *gauche* interaction. For Y = N, O, and F, there is also an upfield shift with Y in the *anti* conformation, attributed to hyperconjugation.



*anti*

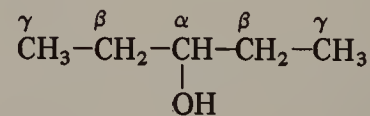


*gauche*

Table II.  $^{13}\text{C}$  Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

| Compound              | C-1  | C-2  | C-3                             | C-4  | C-5  |
|-----------------------|------|------|---------------------------------|------|------|
| Methane               | -2.3 |      |                                 |      |      |
| Ethane                | 5.7  |      |                                 |      |      |
| Propane               | 15.8 | 16.3 | 15.8                            |      |      |
| Butane                | 13.4 | 25.2 | 25.2                            |      |      |
| Pentane               | 13.9 | 22.8 | 34.7                            | 22.8 | 13.9 |
| Hexane                | 14.1 | 23.1 | 32.2                            | 32.2 | 23.1 |
| Heptane               | 14.1 | 23.2 | 32.6                            | 29.7 | 32.6 |
| Octane                | 14.2 | 23.2 | 32.6                            | 29.9 | 29.9 |
| Nonane                | 14.2 | 23.3 | 32.6                            | 30.0 | 30.3 |
| Decane                | 14.2 | 23.2 | 32.6                            | 31.1 | 30.5 |
| Isobutane             | 24.5 | 25.4 |                                 |      |      |
| Isopentane            | 22.2 | 31.1 | 32.0                            | 11.7 |      |
| Isohexane             | 22.7 | 28.0 | 42.0                            | 20.9 | 14.3 |
| Neopentane            | 31.7 | 28.1 |                                 |      |      |
| 2,2-Dimethylbutane    | 29.1 | 30.6 | 36.9                            | 8.9  |      |
| 3-Methylpentane       | 11.5 | 29.5 | 36.9 (18.8, 3-CH <sub>3</sub> ) |      |      |
| 2,3-Dimethylbutane    | 19.5 | 34.3 |                                 |      |      |
| 2,2,3-Trimethylbutane | 27.4 | 33.1 | 38.3                            | 16.1 |      |
| 2,3-Dimethylpentane   | 7.0  | 25.3 | 36.3 (14.6, 3-CH <sub>3</sub> ) |      |      |

From Table III, the approximate shifts for the carbon atoms of, for example, 3-pentanol, may be calculated from the values for *n*-pentane in Table II; that is, the



increment for the functional group in Table III is added to the appropriate value in Table II as follows.

|                   | Calculated         | Found<br>(See Table IX) |
|-------------------|--------------------|-------------------------|
| $\text{C}_\alpha$ | $34.7 + 41 = 75.8$ | 73.8                    |
| $\text{C}_\beta$  | $22.8 + 8 = 30.8$  | 30.0                    |
| $\text{C}_\gamma$ | $13.9 - 5 = 8.9$   | 10.1                    |

Table III. Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal\*

| $\begin{array}{c} \gamma \quad \alpha \\ \backslash \quad / \\ \beta \quad \text{terminal} \end{array} \quad \begin{array}{c} \gamma \quad \alpha \quad \gamma \\ \backslash \quad   \quad / \\ \beta \quad \text{internal} \quad \beta \end{array}$ |          |          |          |          |          |
|--|----------|----------|----------|----------|----------|
| Y  | $\alpha$ |          | $\beta$  |          | $\gamma$ |
|  | terminal | internal | terminal | internal |          |
| CH <sub>3</sub>  | + 9      | + 6      | +10      | + 8      | -2       |
| CH=CH <sub>2</sub>   | +20      |          | + 6      |          | -0.5     |
| C≡CH   | + 4.5    |          | + 5.5    |          | -3.5     |
| COOH   | +21      | +16      | + 3      | + 2      | -2       |
| COO <sup>-</sup>   | +25      | +20      | + 5      | + 3      | -2       |
| COOR   | +20      | +17      | + 3      | + 2      | -2       |
| COC1   | +33      | +28      |          | + 2      |          |
| CONH <sub>2</sub>  | +22      | + 2.5    |          |          | -0.5     |
| COR  | +30      | +24      | + 1      | + 1      | -2       |
| CHO  | +31      |          | 0        |          | -2       |
| Phenyl   | +23      | +17      | + 9      | + 7      | -2       |
| OH   | +48      | +41      | +10      | + 8      | -5       |
| OR   | +58      | +51      | + 8      | + 5      | -4       |
| OCOR   | +51      | +45      | + 6      | + 5      | -3       |
| NH <sub>2</sub>  | +29      | +24      | +11      | +10      | -5       |
| NH <sub>3</sub> <sup>+</sup>   | +26      | +24      | + 8      | + 6      | -5       |
| NHR  | +37      | +31      | + 8      | + 6      | -4       |
| NR <sub>2</sub>  | +42      |          | + 6      |          | -3       |
| NR <sub>3</sub> <sup>+</sup>   | +31      |          | + 5      |          | -7       |
| NO <sub>2</sub>  | +63      | +57      | + 4      | + 4      |          |
| CN   | + 4      | + 1      | + 3      | + 3      | -3       |
| SH   | +11      | +11      | +12      | +11      | -4       |
| SR   | +20      |          | + 7      |          | -3       |
| F  | +68      | +63      | + 9      | + 6      | -4       |
| Cl   | +31      | +32      | +11      | +10      | -4       |
| Br   | +20      | +25      | +11      | +10      | -3       |
| I  | - 6      | + 4      | +11      | +12      | -1       |

From F.W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra*.<sup>3</sup>

\*Add these increments to the shift value of the appropriate carbon atom in Table II or to the shift value calculated from Table I.

Table IV. Chemical Shifts of Cycloalkanes (ppm from TMS)

|                                |      |                                 |      |
|--------------------------------|------|---------------------------------|------|
| C <sub>3</sub> H <sub>6</sub>  | -3.5 | C <sub>7</sub> H <sub>14</sub>  | 28.4 |
| C <sub>4</sub> H <sub>8</sub>  | 22.4 | C <sub>8</sub> H <sub>16</sub>  | 26.9 |
| C <sub>5</sub> H <sub>10</sub> | 25.6 | C <sub>9</sub> H <sub>18</sub>  | 26.1 |
| C <sub>6</sub> H <sub>12</sub> | 26.9 | C <sub>10</sub> H <sub>20</sub> | 25.3 |

## CYCLOALKANES AND SATURATED HETEROCYCLICS

The chemical shifts of the CH<sub>2</sub> groups in monocyclic alkanes are given in Table IV.

The striking feature here is the strong upfield shift of cyclopropane, analogous to the upfield shift of its proton absorptions.

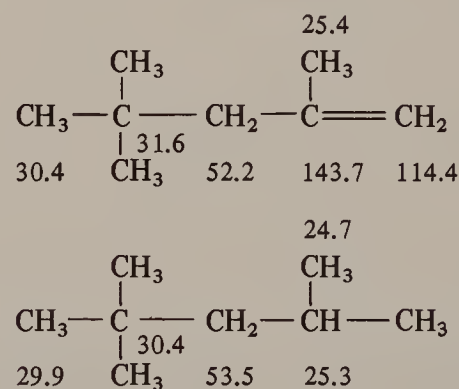
Each ring skeleton has its own set of shift parameters, but a detailed listing of these is beyond the scope of this text. Rough estimates for substituted rings can be made with the substitution increments in Table III.

As mentioned above, one of the striking effects in rigid cyclohexane rings is the upfield shift caused by the  $\gamma$ -gauche steric compression. Thus an axial methyl group at C-1 causes an upfield shift of several ppm at C-3 and C-5.

Table IVa presents chemical shifts for several saturated heterocyclics.

## ALKENES

The sp<sup>2</sup> carbon atoms of alkenes substituted only by alkyl groups absorb in the range of ~110-150 ppm downfield from TMS. The double bond has a rather small effect on the shifts of the sp<sup>3</sup> carbons in the molecule as the following comparisons demonstrate.






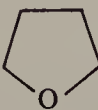
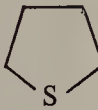
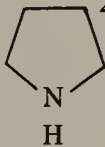
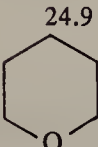
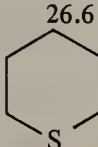
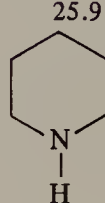


The methyl signal of propene is at 1817 ppm, and of propene at 15.8 ppm. In *cis*-2-butene, the methyl signals are at 12.1 ppm, compared with 17.6 ppm in *trans*-2-butene, because of the  $\gamma$  effect. (For comparison, the methyl signals of butane are at 13.4 ppm.) Note the  $\gamma$ -effect on one of the geminal methyl groups in 2-methyl-2-butene (Table V).

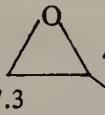
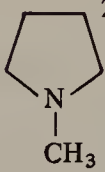
In general, the terminal =CH<sub>2</sub> group (usually a triplet in an off-resonance decoupled spectrum) absorbs upfield from an internal =CH- group, and *cis* -CH=CH- signals are upfield from those of corresponding *trans* groups. Calculations of approximate shifts can be made from the following parameters where  $\alpha$ ,  $\beta$ , and  $\gamma$  represent substituents on the same end of the double bond as the olefinic

Table IVa. Chemical Shifts for Saturated Heterocyclies (ppm from TMS, neat)

Unsubstituted

|  |                |  |                |  |                |
|--|----------------|--|----------------|--|----------------|
|   | 39.5           |   | 18.7           |   | 18.2           |
|   | 22.9 72.6      |   | 29.7 27.5      |  |                |
|   | 26.5 68.4      |   | 31.2 31.7      |   | 25.7 47.1      |
|  | 24.9 27.7 69.5 |  | 26.6 27.8 29.1 |  | 25.9 27.8 47.9 |

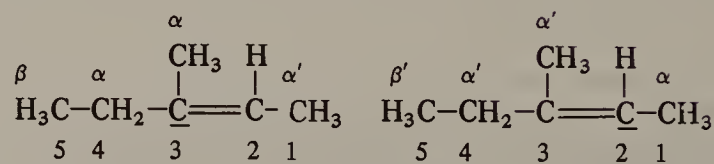
Substituted

|   |                |   |                |
|---|----------------|---|----------------|
|  | 47.6 47.3 18.1 |  | 24.4 56.7 48.0 |
|---|----------------|---|----------------|

carbon of interest, and  $\alpha'$ ,  $\beta'$ , and  $\gamma'$  represent substituents on the far side.

|                       |       |
|-----------------------|-------|
| $\alpha$              | +10.6 |
| $\beta$               | + 7.2 |
| $\gamma$              | - 1.5 |
| $\alpha'$             | - 7.9 |
| $\beta'$              | - 1.8 |
| $\gamma'$             | - 1.5 |
| <i>cis</i> correction | - 1.1 |

These parameters are added to 123.3 ppm, the shift for ethylene. We can calculate the values for *cis*-3-methyl-2-pentene as follows.



$$\begin{aligned}
 \delta_{\text{C-3}} &= 123.3 + (2 \times 10.6) + (1 \times 7.2) \\
 &\quad + (1 \times -7.9) - 1.1 = 142.7 \text{ ppm}
 \end{aligned}$$

$$\begin{aligned}
 \delta_{\text{C-2}} &= 123.3 + (1 \times 10.6) + (2 \times -7.9) \\
 &\quad + (1 \times -1.8) - 1.1 = 115.2 \text{ ppm}
 \end{aligned}$$

The measured values are C-3 = 137.2, C-2 = 116.8. The agreement is fair.

Olefinic carbons in polyenes are treated as though they were alkane carbon substituents on one of the double bonds. Thus, in calculating the shift of C-2 in 1,4-pentadiene, C-4 is treated like a  $\beta$ -sp<sup>3</sup> carbon atom.

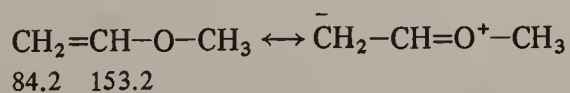
Representative olefins are presented in Table V.



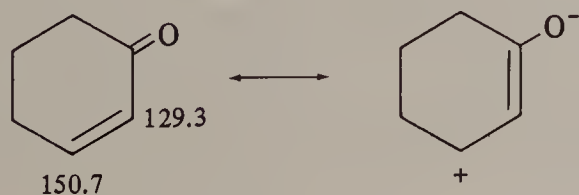
Table V. Alkene Chemical Shifts (ppm from TMS)

|  |                              |  |                                    |                  |
|--|------------------------------|--|------------------------------------|------------------|
| $\text{H}_2\text{C}=\text{CH}_2$<br>123.2        | <br>136.2, 18.7, 115.9       | <br>113.3, 140.2                                       | <br>12.1, 124.6                    | <br>126.0, 17.6  |
| <br>114.3, 14.0, 132.7, 123.2, 138.5, 20.5, 12.3 | <br>133.3, 123.7             | <br>138.7, 114.5, 13.7, 29.4, 22.6, 137.2, 12.6, 124.0 |                                    |                  |
| <br>13.7, 35.3, 125.1, 23.2, 131.7, 17.7         | <br>131.2                    | <br>131.3  |                                    |                  |
| <br>117.5, 137.2                                 | <br>115.9, 137.3             |  |                                    |                  |
| <br>109.3, 149.3                                 | <br>16.9, 131.4, 118.7, 25.3 | <br>109.8, 144.5                                       | <br>112.9, 144.9                   | <br>131.6, 126.6 |
| <br>30.2, 137.2                                  | <br>130.8, 32.6, 22.1        | <br>127.3, 24.5, 22.1                                  | <br>107.1, 149.7, 36.2, 28.9, 26.9 |                  |
| $\text{CH}_2=\text{C}=\text{CH}_2$<br>74.8 213.5 |                              |  |                                    |                  |

There are no simple rules to handle polar substituents on an olefinic carbon. The shifts for vinyl ethers can be rationalized on the basis of electron density of the contributory structures



as can the shifts for  $\alpha, \beta$ -unsaturated ketones.



The same rationalization applies to the proton shifts in these compounds.

Shifts for several substituted alkenes are presented in Table Va.

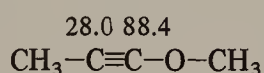
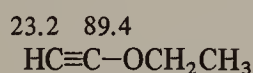
The central carbon atom ( $=\text{C}=\text{C}=\text{C}$ ) of alkyl-substituted allenes absorbs far downfield in the range of  $\sim 200$ -215 ppm, whereas the terminal atoms ( $\text{C}=\text{C}=\text{C}$ ) absorb upfield in the range of  $\sim 75$ -97 ppm.

## ALKYNES

The  $\text{sp}$  carbons of alkynes substituted only by alkyl groups absorb in the range  $\sim 65$ -90 ppm (Table VI). The triple bond shifts the  $\text{sp}^3$  carbons directly attached about 5-15 ppm upfield relative to the corresponding alkane. The terminal  $\equiv\text{CH}$  absorbs upfield from the internal  $\equiv\text{CR}$ . Off-resonance decoupling gives a doublet for the terminal  $\equiv\text{CH}$ . Alkyne carbon atoms with a polar group directly attached absorb from  $\sim 20$ -95 ppm.

Table Va. Chemical Shifts of Substituted Alkenes (ppm from TMS)

|  |  |  |  |  |
|--|--|--|--|--|
|  |  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |  |



Phenanthrene: C-1, 128.3; C-2, 126.3; C-3, 126.3;  
C-4, 122.2; C-4a, 131.9\*; C-9, 126.6; C-10a, 130.1\*.

Polar resonance structures explain these shifts as shown above for vinyl ethers.

## AROMATIC COMPOUNDS

Benzene carbon atoms absorb at 128.5 ppm, neat or as a solution in CDCl<sub>3</sub> or CCl<sub>4</sub>. Substituents shift the attached aromatic carbon atom as much as ±35 ppm. Fused-ring absorptions are as follows:

Naphthalene: C-1, 128.1; C-2, 125.9; C-4a, 133.7.

Anthracene: C-1, 130.1; C-2, 125.4; C-4a, 132.2; C-9, 132.6.

Table VI. Alkyne Chemical Shifts (ppm)

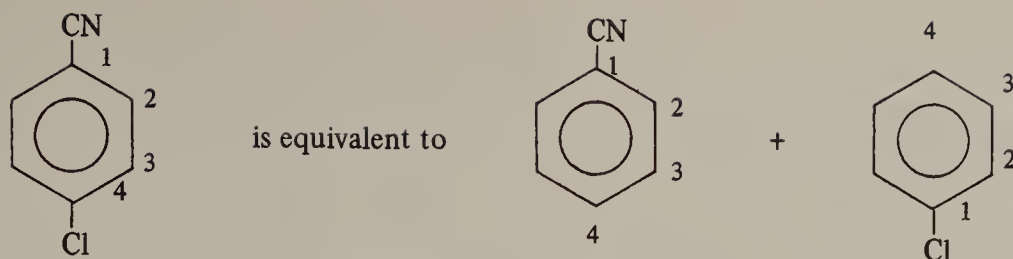
| Compound | C-1  | C-2  | C-3  | C-4  | C-5  | C-6  |
|----------|------|------|------|------|------|------|
| 1-Butyne | 67.0 | 84.7 |      |      |      |      |
| 2-Butyne |      | 73.6 |      |      |      |      |
| 1-Hexyne | 67.4 | 82.8 | 17.4 | 29.9 | 21.2 | 12.9 |
| 2-Hexyne | 1.7  | 73.7 | 76.9 | 19.6 | 21.6 | 12.1 |
| 3-Hexyne | 14.4 | 12.0 | 79.9 |      |      |      |

Shifts of the aromatic carbon atom directly attached to the substituent have been correlated with substituent electronegativity after correcting for magnetic anisotropy effects; shifts at the *para* aromatic carbon have been correlated with the Hammett  $\sigma$  constant. *Ortho* shifts are not readily predictable and range over ~15 ppm. *Meta* shifts are generally small—up to several ppm for a single substituent.

The substituted aromatic carbon atoms can be distinguished from the unsubstituted aromatic carbon atom by its decreased peak height; that is, it lacks a proton and thus suffers from a longer  $T_1$  and a diminished NOE.

Incremental shifts from benzene for the aromatic carbons of representative monosubstituted benzene rings (and shifts from TMS of carbon-containing substituents) are given in Table VII. Shifts from benzene for polysubstituted benzene ring carbons can be approximated by applying the principle of substituent additivity. For example, the shift from benzene for C-2 of the disubstituted compound 4-chlorobenzonitrile is calculated by adding the effect for an *ortho* CN group (+3.6) to that for a *meta* Cl group (+1.3):

\*Not distinguishable.



|    | Calcd. | Observed |    | Observed |    | Observed |
|----|--------|----------|----|----------|----|----------|
| 1. | -17.3  | -16.6    | 1. | -15.4    | 4. | -1.9     |
| 2. | + 4.9  | + 5.1    | 2. | + 3.6    | 3. | +1.3     |
| 3. | + 1.0  | + 1.3    | 3. | + 0.6    | 2. | +0.4     |
| 4. | +10.1  | +10.8    | 4. | + 3.9    | 1. | +6.2     |

Table VII. Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm, + downfield, - upfield). C Atom of Substituents in ppm from TMS

| Substituent                                    | C-1<br>(Attachment) | C-2   | C-3  | C-4  | C of Substituent<br>(ppm from TMS)                               |
|--|---------------------|-------|------|------|--|
| H <sup>b</sup>                                 | 0.0                 | 0.0   | 0.0  | 0.0  |  |
| CH <sub>3</sub> <sup>b</sup>                   | +8.9                | +0.7  | -0.1 | -2.9 | 21.3   |
| CH <sub>2</sub> CH <sub>3</sub> <sup>a</sup>   | +15.6               | -0.5  | 0.0  | -2.6 | 29.2 (CH <sub>2</sub> ), 15.8 (CH <sub>3</sub> )                 |
| CH(CH <sub>3</sub> ) <sub>2</sub> <sup>a</sup> | +20.1               | -2.0  | 0.0  | -2.5 | 34.4 (CH), 24.1 (CH <sub>3</sub> )                               |
| C(CH <sub>3</sub> ) <sub>3</sub> <sup>a</sup>  | +22.2               | -3.4  | -0.4 | -3.1 | 34.5 (C), 31.4 (CH <sub>3</sub> )                                |
| CH=CH <sub>2</sub> <sup>a</sup>                | +9.5                | -2.0  | +0.2 | -0.5 | 135.5 (CH), 112.0 (CH <sub>2</sub> )                             |
| C≡CH <sup>b</sup>                              | -6.1                | +3.8  | +0.4 | -0.2 |  |
| C <sub>6</sub> H <sub>5</sub> <sup>b</sup>     | +13.1               | -1.1  | +0.4 | -1.2 |  |
| CH <sub>2</sub> OH <sup>a</sup>                | +12.3               | -1.4  | -1.4 | -1.4 | 64.5   |
| CH <sub>2</sub> OCCH <sub>3</sub> <sup>c</sup> | +7.7                | ~0.0  | ~0.0 | ~0.0 | 20.7 (CH <sub>3</sub> ), 66.1 (CH <sub>2</sub> ),<br>170.5 (C=O) |
| OH <sup>b</sup>                                | +26.9               | -12.7 | +1.4 | -7.3 |  |
| OCH <sub>3</sub> <sup>b</sup>                  | +31.4               | -14.4 | +1.0 | -7.7 | 54.1   |
| OC <sub>6</sub> H <sub>5</sub> <sup>a</sup>    | +29.2               | -9.4  | +1.6 | -5.1 |  |
| OCCH <sub>3</sub> <sup>a</sup>                 | +23.0               | -6.4  | +1.3 | -2.3 |  |
| CH <sup>a</sup>                                | +8.6                | +1.3  | +0.6 | +5.5 | 192.0  |
| CCH <sub>3</sub> <sup>b</sup>                  | +9.1                | +0.1  | 0.0  | +4.2 | 25.0 (CH <sub>3</sub> ), 195.7 (C=O)                             |
| CC <sub>6</sub> H <sub>5</sub> <sup>b</sup>    | +9.4                | +1.7  | -0.2 | +3.6 |  |
| CCF <sub>3</sub> <sup>b</sup>                  | -5.6                | +1.8  | +0.7 | +6.7 |  |
| COH <sup>b</sup>                               | +2.1                | +1.5  | 0.0  | +5.1 | 172.6  |
| COCH <sub>3</sub> <sup>a</sup>                 | +1.3                | -0.5  | -0.5 | +3.5 | 51.0 (CH <sub>3</sub> )  |
| CCl <sup>b</sup>                               | +4.6                | +2.4  | 0.0  | +6.2 |  |



Table VII (continued)

| Substituent  | C-1<br>(Attachment) | C-2   | C-3  | C-4   | C of Substituent<br>(ppm from TMS) |
|--|---------------------|-------|------|-------|------------------------------------|
| $\begin{array}{c} \text{O} \\ \parallel \\ \text{CCF}_3^b \end{array}$   | -5.6                | +1.8  | -0.7 | +6.7  | 118.7                              |
| $\text{C}\equiv\text{N}^b$   | -15.4               | +3.6  | +0.6 | +3.9  |                                    |
| $\text{NH}_2^b$  | +18.0               | -13.3 | +0.9 | -9.8  |                                    |
| $\text{N}(\text{CH}_3)_2^a$  | +22.4               | -15.7 | +0.8 | -15.7 |                                    |
| $\begin{array}{c} \text{O} \\ \parallel \\ \text{NHCCH}_3^a \end{array}$ | +11.1               | -9.9  | +0.2 | -5.6  |                                    |
| $\text{NO}_2^b$  | +20.0               | -4.8  | +0.9 | +5.8  |                                    |
| $\text{N}=\text{C}=\text{O}^b$   | +5.7                | -3.6  | +1.2 | -2.8  |                                    |
| $\text{F}^b$   | +34.8               | -12.9 | +1.4 | -4.5  |                                    |
| $\text{Cl}^b$  | +6.2                | +0.4  | +1.3 | -1.9  |                                    |
| $\text{Br}^b$  | -5.5                | +3.4  | +1.7 | -1.6  |                                    |
| $\text{I}^a$   | -32.2               | +9.9  | +2.6 | -7.4  |                                    |
| $\text{CF}_3^b$  | -9.0                | -2.2  | +0.3 | +3.2  |                                    |
| $\text{SH}^c$  | +2.3                | +1.1  | +1.1 | -3.1  |                                    |
| $\text{SCH}_3^c$   | +10.2               | -1.8  | +0.4 | -3.6  |                                    |
| $\text{SO}_2\text{NH}_2^c$   | +15.3               | -2.9  | +0.4 | +3.3  |                                    |
| $\text{Si}(\text{CH}_3)_3^a$   | +13.4               | +4.4  | -1.1 | -1.1  |                                    |

<sup>a</sup>Neat<sup>b</sup>In  $\text{CCl}_4$ <sup>c</sup>In  $\text{CDCl}_3$ 

## HETEROAROMATIC COMPOUNDS

Complex rationalizations have been offered for the shifts of carbon atoms in heteroaromatic compounds. As a general rule, C-2 of oxygen- and nitrogen-containing rings is further downfield than C-3. Large solvent and pH effects have been recorded. Table VIII gives values for neat samples of several 5- and 6-membered heterocyclic compounds.

## ALCOHOLS

Substitution of H in an alkane by an OH group causes downfield shifts of 35-52 ppm for C-1, 5-12 ppm for C-2, and upfield shifts of about 0-6 ppm for C-3. Shifts for several acyclic and alicyclic alcohols are given in Table IX. Acetylation provides a useful diagnostic test for an alcohol, the C-1 absorption moving downfield by ~2.5-4.5 ppm, and the C-2 absorption moving upfield by a similar amount; a 1,3-diaxial interaction may cause a slight (~1 ppm) downfield shift of C-3. Table III may be used to calculate shifts for alcohols as described earlier.

## ETHERS

An alkoxy substituent causes a somewhat larger downfield shift at C-1 (~10 ppm larger) than that of a hydroxy

substituent. This is attributed to the C-1' of the alkoxy group having the same effect as a  $\beta$ -C relative to C-1. The O atom is regarded here as an " $\alpha$ -C" to C-1.

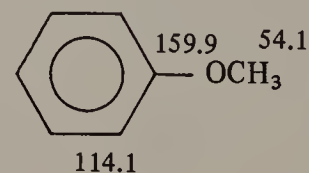
|                                     |   |   |    |
|-------------------------------------|---|---|----|
|                                     | 2                                       | 1 | 1' |
| $\text{CH}_3\text{-CH}_2\text{-OH}$ | $\text{CH}_3\text{-CH}_2\text{-O-CH}_3$ |   |    |
| 17.6 57.0                           | 14.7 67.9 57.6                          |   |    |

Note also that the " $\gamma$ -effect" (upfield shift) on C-2 is explainable by similar reasoning. Conversely, the ethoxy group affects the  $\text{OCH}_3$  group (compare  $\text{CH}_3\text{OH}$ ).

Table X gives shifts of several ethers.

The dioxygenated carbon of acetals and ketals absorbs in the range of ~88-112 ppm.

The alkyl carbons of aralkyl ethers have shifts similar to those of dialkyl ethers. Note the strong upfield shift of the ring *ortho* carbon resulting from electron delocalization as in the vinyl ethers.



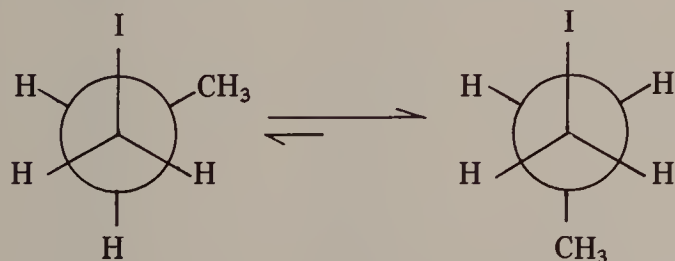
**Table VIII. Shifts for C Atoms of Heteroaromatics (neat, ppm from TMS)**

| Compound                   | C-2   | C-3    | C-4    | C-5    | C-6   | Substituent |
|----------------------------|-------|--------|--------|--------|-------|-------------|
| Furan                      | 142.7 | 109.6  |        |        |       |             |
| 2-Methylfuran              | 152.2 | 106.2  | 110.9  | 141.2  |       | 13.4        |
| Furan-2-carboxaldehyde     | 153.3 | 121.7  | 112.9  | 148.5  |       | 178.2       |
| Pyrrole                    | 118.4 | 108.0  |        |        |       |             |
| 2-Methylpyrrole            | 127.2 | 105.9  | 108.1  | 116.7  |       | 12.4        |
| Pyrrole-2-carboxaldehyde   | 134.0 | 123.0  | 112.0  | 129.0  |       |             |
| Thiophene                  | 124.4 | 126.2  |        |        |       |             |
| 2-Methylthiophene          | 139.0 | 124.7  | 126.4  | 122.6  |       | 14.8        |
| Thiophene-2-carboxaldehyde | 143.3 | 136.4  | 128.1  | 134.6  |       | 182.8       |
| Thiazole                   | 152.2 |        | 142.4  | 118.5  |       |             |
| Imidazole                  | 136.2 |        | 122.3  | 122.3  |       |             |
| Pyridine                   | 150.2 | 123.9  | 135.9  |        |       |             |
| Pyrimidine                 | 159.5 |        | 157.4  | 122.1  | 157.4 |             |
| Pyrazine                   | 145.6 |        |        |        |       |             |
| 2-Methylpyrazine           | 154.0 | 141.8* | 143.8* | 144.7* |       | 21.6        |

\*Assignment not certain.

## HALIDES

The effect of halide substitution is complex. A single fluorine atom (in  $\text{CH}_3\text{F}$ ) causes a large downfield shift from  $\text{CH}_4$  as electronegativity considerations would suggest. Successive geminal substitution by Cl ( $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ) results in increasing downfield effects—again expected on the basis of electronegativity. But with Br and I, the “heavy atom effect” supervenes. The carbon shifts of  $\text{CH}_3\text{Br}$  and  $\text{CH}_2\text{Br}_2$  move progressively downfield, but those of  $\text{CHBr}_3$  and  $\text{CBr}_4$  move progressively upfield. A strong upfield progression for I commences with  $\text{CH}_3\text{I}$ , which is upfield from  $\text{CH}_4$ . There is a progressive downfield effect at C-2 in the order  $\text{I} > \text{Br} > \text{F}$ . Cl and Br show  $\gamma$ -gauche shielding at C-3, but I does not, presumably because of the low population of the hindered gauche rotamer. Table XI shows these trends.



Halides may show large solvent effects; for example, C-1 for iodoethane is at  $-6.6$  in cyclohexane, and at  $-0.4$  in dimethylformamide.

## AMINES

An  $\text{NH}_2$  group attached to an alkyl chain causes a downfield shift of  $\sim 30$  ppm at C-1, a down field shift of

$\sim 11$  ppm at C-2, and an upfield shift of  $\sim 4.0$  ppm at C-3. The  $\text{NH}_3^+$  group shows a somewhat smaller effect. N-alkylation increases the downfield effect of the  $\text{NH}_2$  group at C-1. Shift positions for selected acyclic and alicyclic amines are given in Table XII (See Table IVa for heterocyclic amines).

## FUNCTIONAL GROUPS CONTAINING CARBON

$^{13}\text{C}$  NMR spectrometry permits direct observation of carbon-containing functional groups; the shift ranges for these are given in the Appendix. With the exception of  $\text{CH}=\text{O}$ , the presence of these groups could not be directly ascertained by  $^1\text{H}$  NMR.

### Ketones and Aldehydes

The  $\text{R}_2\text{C}=\text{O}$  and the  $\text{RCH}=\text{O}$  carbons absorb in a characteristic region, downfield. Acetone absorbs at 203.8 ppm and acetaldehyde at 199.3 ppm. Alkyl substitution on the  $\alpha$ -C causes a downfield shift of the  $\text{C}=\text{O}$  absorption of 2-3 ppm until steric effects supervene. Replacement of the  $\text{CH}_3$  of acetone or acetaldehyde by a phenyl group causes an upfield shift of the  $\text{C}=\text{O}$  absorption (acetophenone 195.7 ppm, benzaldehyde 190.7 ppm); similarly  $\alpha,\beta$ -unsaturation causes upfield shifts (acrolein 192.1 ppm, compared with propionaldehyde 201.5 ppm). Presumably, charge delocalization by the benzene ring or the double bond makes the carbonyl carbon less electron deficient. Of the cycloalkanones, cyclopentanone has an anomalously low shift position. Table XIII presents chemical shifts of the  $\text{C}=\text{O}$  group of some ketones and aldehydes. Because of

Table IX. Chemical Shifts of Alcohols (neat, ppm from TMS)

|                                |  |  |  |  |
|--------------------------------|--|--|--|--|
| $\text{CH}_3\text{OH}$<br>49.0 |  |  |  |  |
|                                |  |  |  |  |
|                                |  |  |  |  |
|                                |  |  |  |  |
|                                |  |  |  |  |
|                                |  |  |  |  |
|                                |  |  |  |  |



Table X. Chemical Shifts of Ethers (neat, ppm from TMS)

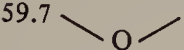
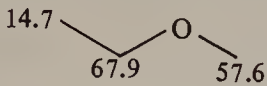
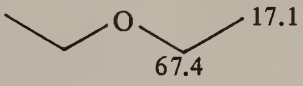
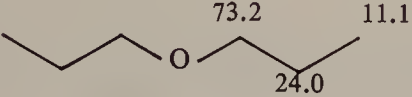
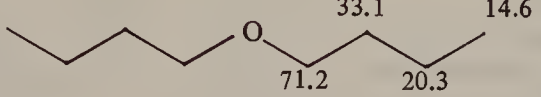
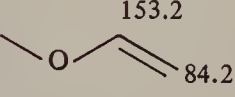

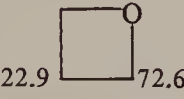
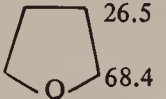
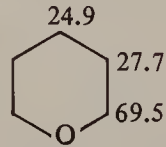
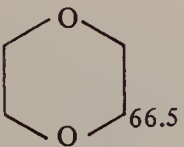
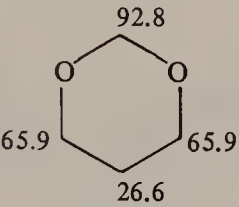
|   |  |   |   |
|---|--|---|---|
|    |     |  |   |
| 59.7  | 14.7<br>67.9<br>57.6   | 67.4<br>17.1  |   |
|    |    |  |   |
| 73.2<br>11.1<br>24.0  | 33.1<br>71.2<br>20.3<br>14.6   | 153.2<br>84.2   |   |
|    |     |   |  |
| 39.5  | 22.9<br>72.6   | 26.5<br>68.4  | 24.9<br>27.7<br>69.5  |
|  |  |   |   |
| 66.5  | 92.8<br>65.9<br>26.6<br>65.9   |   |   |

Table XI. Shift Positions for Alkyl Halides (neat, ppm from TMS)

| Compound   | C-1    | C-2  | C-3  |
|--|--------|------|------|
| CH <sub>4</sub>                                    | -2.3   |      |      |
| CH <sub>3</sub> F                                  | 75.4   |      |      |
| CH <sub>3</sub> Cl                                 | 24.9   |      |      |
| CH <sub>2</sub> Cl <sub>2</sub>                    | 54.0   |      |      |
| CHCl <sub>3</sub>                                  | 77.5   |      |      |
| CCl <sub>4</sub>                                   | 96.5   |      |      |
| CH <sub>3</sub> Br                                 | 10.0   |      |      |
| CH <sub>2</sub> Br <sub>2</sub>                    | 21.4   |      |      |
| CHBr <sub>3</sub>                                  | 12.1   |      |      |
| CBr <sub>4</sub>                                   | -28.5  |      |      |
| CH <sub>3</sub> I                                  | -20.7  |      |      |
| CH <sub>2</sub> I <sub>2</sub>                     | -54.0  |      |      |
| CHI <sub>3</sub>                                   | -139.9 |      |      |
| CI <sub>4</sub>                                    | -292.5 |      |      |
| CH <sub>3</sub> CH <sub>2</sub> F                  | 79.3   | 14.6 |      |
| CH <sub>3</sub> CH <sub>2</sub> Cl                 | 39.9   | 18.7 |      |
| CH <sub>3</sub> CH <sub>2</sub> Br                 | 28.3   | 20.3 |      |
| CH <sub>3</sub> CH <sub>2</sub> I                  | -0.2   | 21.6 |      |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl | 46.7   | 26.5 | 11.5 |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br | 35.7   | 26.8 | 13.2 |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> I  | 10.0   | 27.6 | 16.2 |

rather large solvent effects, there are differences of several ppm from different literature sources. Replacement of CH<sub>2</sub> of alkanes by C=O causes a downfield shift at the α-C (~10-14 ppm) and an upfield shift at the β-C (several ppm in acyclic compounds).

#### Carboxylic Acids, Esters, Chlorides, Anhydrides, Amides, and Nitriles

The C=O groups of carboxylic acids and derivatives are in the range of 150-185 ppm. Dilution and solvent effects are marked for carboxylic acids; anions appear at lower field. The effects of substituents and electron delocalization are generally similar to those for ketones. Nitriles absorb in the range of 115-125 ppm. Alkyl substituents on the nitrogen of amides cause a small (up to several ppm) upfield shift of the C=O group. (See Table XIV.)

#### Oximes

The simple oximes absorb in the range of 145-165 ppm. It is possible to distinguish between *syn* and *anti* isomers since the C=N shift is upfield in the sterically more com-

Table XII. Shift Positions of Acyclic and Alicyclic Amines (neat, ppm from TMS)

| Compound  | C-1  | C-2  | C-3  | C-4                           |
|---|------|------|------|-------------------------------|
| CH <sub>3</sub> NH <sub>2</sub>   | 26.9 |      |      |                               |
| CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>                                 | 35.9 | 17.7 |      |                               |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>                 | 44.9 | 27.3 | 11.2 |                               |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> | 42.3 | 36.7 | 20.4 | 14.0                          |
| (CH <sub>3</sub> ) <sub>3</sub> N   | 47.5 |      |      |                               |
| CH <sub>3</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>                | 58.2 | 13.8 |      |                               |
| Cyclohexylamine   | 50.4 | 36.7 | 25.7 | 25.1                          |
| N-Methylcyclohexylamine   | 58.6 | 33.3 | 25.1 | 26.3 (N-CH <sub>3</sub> 33.5) |

Table XIII. Shift Positions of the C=O Group and Other Carbon Atoms of Ketones and Aldehydes (ppm from TMS).

|          |          |          |          |          |
|----------|----------|----------|----------|----------|
| <p>a</p> | <p>a</p> | <p>b</p> | <p>c</p> | <p>a</p> |
| <p>b</p> | <p>b</p> | <p>a</p> | <p>a</p> | <p>a</p> |
| <p>c</p> | <p>a</p> | <p>a</p> | <p>a</p> |          |
| <p>b</p> | <p>b</p> |          |          |          |

a~50% in CDCl<sub>3</sub>.

bContains ~10% dioxane or methylene chloride.

c~50% in dioxane.

Table XIV. Shift Positions for the C=O group and other Carbon Atoms of Carboxylic Acids, Esters, Lactones, Chlorides, Anhydrides, Amides, Carbamates, and Nitriles (ppm from TMS)

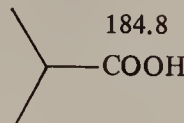
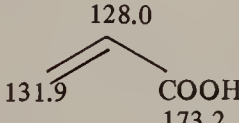
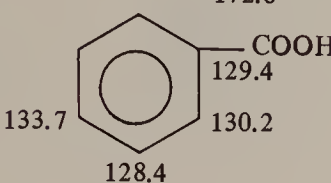
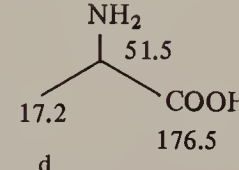
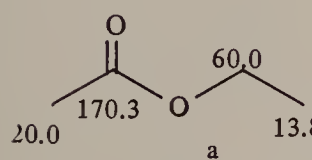
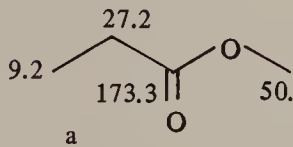
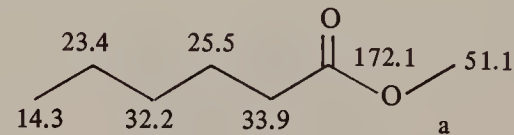
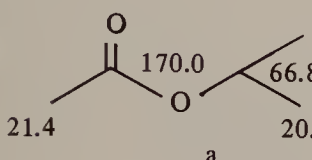
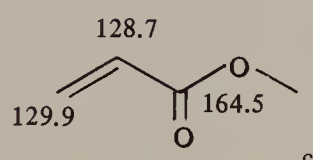
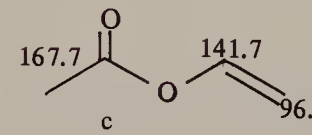
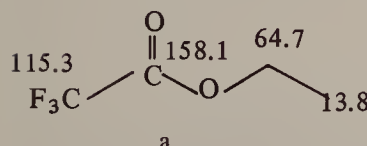
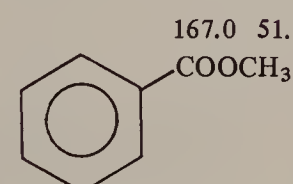
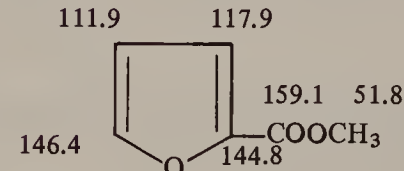
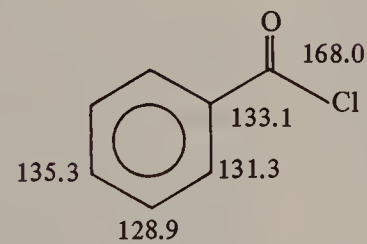
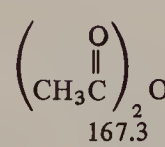
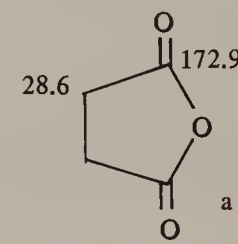
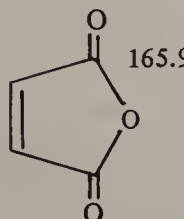
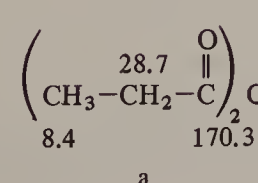
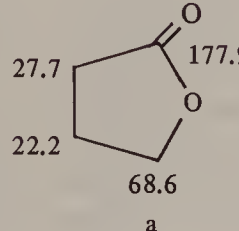
|  |  |  |  |
|--|--|--|--|
| $\text{CH}_3\text{-COOH}$<br>20.6 178.1<br>a   | <br>184.8<br>COOH                                       | <br>128.0<br>131.9 COOH<br>173.2                                   | $\text{CCl}_3\text{-COOH}$<br>89.1 168.0   |
| $\text{F}_3\text{C-COOH}$<br>115.0 163.0<br>a  | <br>172.6<br>129.4 COOH<br>130.2<br>133.7<br>128.4<br>a | $\text{CH}_3\text{-COO}^-\text{Na}^+$<br>181.5<br>b  | <br>51.5<br>17.2 COOH<br>176.5<br>d |
| <br>20.0 170.3 60.0 13.8<br>a   | <br>27.2 9.2 173.3 50.8<br>a                            | <br>23.4 25.5 172.1 51.1<br>14.3 32.2 33.9<br>a                   |  |
| <br>21.4 170.0 66.8 20.4<br>a | <br>128.7 129.9 164.5<br>c                            | <br>167.7 141.7 96.4<br>c  |  |
| <br>115.3 158.1 64.7 13.8<br>a | <br>167.0 51.0<br>COOCH <sub>3</sub>                  | <br>111.9 117.9 159.1 51.8<br>146.4 144.8<br>COOCH <sub>3</sub> |  |
| $\text{CH}_3\text{CCl}_2$<br>169.5<br>c  | <br>168.0 133.1 131.3 128.9<br>a                     | <br>167.3<br>c  | <br>172.9 28.6<br>a               |
| <br>165.9                     | <br>28.7 8.4 170.3<br>a                               | <br>177.9 27.7 22.2 68.6<br>a                                    | $\text{HCNH}_2$<br>165.5<br>c  |
|  |  |  | $\text{CH}_3\text{CNH}_2$<br>172.7<br>c  |



Table XIV (continued)

|   |  |   |   |
|---|--|---|---|
| $  \begin{array}{c}  31.1 \quad 162.4 \\  \text{CH}_3 \quad \text{O} \\  \diagdown \quad \diagup \\  \text{N}-\text{C} \\  \diagup \quad \diagdown \\  \text{CH}_3 \quad \text{H} \\  36.2 \\  \text{a}  \end{array}  $ | $  \begin{array}{c}  \text{NH}_2 \\    \\  \text{O} \\     \\  \text{C} \\    \\  \text{CH}_2 \\    \\  \text{CH} \\    \\  \text{CH}_3 \\  \text{c}  \end{array}  $ | $  \begin{array}{c}  \text{O} \\     \\  \text{C} \\    \\  \text{N} \\    \\  \text{C}_6\text{H}_5 \\  \text{c}  \end{array}  $                                | $  \begin{array}{c}  \text{O} \\     \\  \text{C} \\    \quad   \\  \text{H}_2\text{N} \quad \text{O} \\  \text{a}  \end{array}  $  |
| $  \begin{array}{c}  1.3 \\  \text{CH}_3\text{CN} \\  117.7 \\  \text{a}  \end{array}  $  | $  \begin{array}{c}  10.8 \\  \diagup \quad \diagdown \\  10.6 \quad \text{CN} \\  \text{a}  \end{array}  $  | $  \begin{array}{c}  18.8 \\  \text{H}_3\text{C} \\    \\  \text{C} \\    \quad   \\  \text{H} \quad \text{CN} \\  101.2 \\  117.6 \\  \text{e}  \end{array}  $ | $  \begin{array}{c}  \text{H} \quad \text{H} \\  \diagdown \quad \diagup \\  \text{C}=\text{C} \\  \diagup \quad \diagdown \\  \text{H}_3\text{C} \quad \text{CN} \\  150.2 \quad 100.9 \\  17.3 \quad 116.0 \\  \text{e}  \end{array}  $ |
| $  \begin{array}{c}  118.7 \\  \text{CN} \\    \\  \text{C}_6\text{H}_5 \\  112.3 \quad 132.0 \\  132.7 \\  129.1 \\  \text{a}  \end{array}  $  |  |   |   |

a in  $\text{CHCl}_3$  (~50%).b saturated aqueous solution of  $\text{CH}_3\text{COONa}$ 

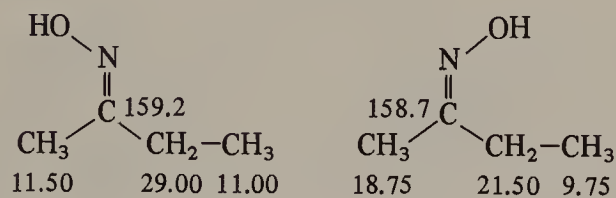
c neat or saturated solution

d in  $\text{H}_2\text{O}$ 

e in DMSO

f in dioxane (~50%).

pressed form, and the more hindered substituent (*syn* to the OH) is upfield of the less hindered:



#### IV. SPIN-SPIN COUPLING

Coupling—at least as an initial consideration—is less important in  $^{13}\text{C}$  NMR than in  $^1\text{H}$  NMR, since routine  $^{13}\text{C}$  spectra are usually noise-decoupled. Thus coupling information is discarded in the interest of obtaining a spectrum in a shorter time or on a smaller sample—a spectrum, furthermore, free of complex overlapping absorptions. However, as mentioned earlier, information from residual

coupling can be regained through off-resonance decoupling.

$^{13}\text{C}$ - $^{13}\text{C}$  coupling is usually not observed, except in compounds that have been deliberately enriched with  $^{13}\text{C}$ , because of the low probability of two adjacent  $^{13}\text{C}$  atoms in a molecule. One-bond  $^{13}\text{C}$ -H coupling ( $^1J_{\text{CH}}$ ) ranges from about 110 to 320 Hz, increasing with increased *s* character of the  $^{13}\text{C}$ -H bond, with substitution on the carbon atom of electron-withdrawing groups, and with angular distortion. Appreciable  $^{13}\text{C}$ -H coupling also extends over two or more (*n*) bonds ( $^nJ_{\text{CH}}$ ). Table XV gives some representative  $^1J_{\text{CH}}$  values. Table XVI gives some representative  $^2J_{\text{CH}}$  values, which range from about -5 to 60 Hz.

$^3J_{\text{CH}}$  values are roughly comparable to  $^2J_{\text{CH}}$  values for  $\text{sp}^3$  carbons. In aromatic rings, however, the  $^3J_{\text{CH}}$  values are characteristically larger than  $^2J_{\text{CH}}$  values. In benzene itself,  $^3J_{\text{CH}} = 7.4$  Hz, and  $^2J_{\text{CH}} = 1.0$  Hz.

Coupling of  $^{13}\text{C}$  to several other nuclei, the most important of which are  $^{31}\text{P}$ ,  $^{19}\text{F}$ , and D, may be observed in proton-decoupled spectra. Representative coupling constants are given in Table XVII.

Table XV. Some  $^1J_{CH}$  Values



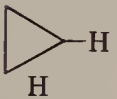

| Compound   | $J$ (Hz) |
|--|----------|
| $sp^3$   |          |
| $CH_3CH_3$   | 124.9    |
| $CH_3CH_2CH_3$   | 119.2    |
| $(CH_3)_3CH$   | 114.2    |
| $CH_3NH_2$   | 133.0    |
| $CH_3OH$   | 141.0    |
| $CH_3Cl$   | 150.0    |
| $CH_2Cl_2$   | 178.0    |
| $CHCl_3$   | 209.0    |
|   | 123.0    |
|   | 134.0    |
|   | 161.0    |
|  | 205.0    |
| $sp^2$   |          |
| $CH_2=CH_2$  | 156.2    |
| $CH_3CH=C(CH_3)_2$   | 148.4    |
| $C_2H_5OCH=O$  | 225.6    |
| $CH_3CH=O$   | 172.4    |
| $NH_2CH=O$   | 188.3    |
| $C_6H_6$   | 159.0    |
| $sp$   |          |
| $CH\equiv CH$  | 249.0    |
| $C_6H_5C\equiv CH$   | 251.0    |
| $HC\equiv N$   | 269.0    |

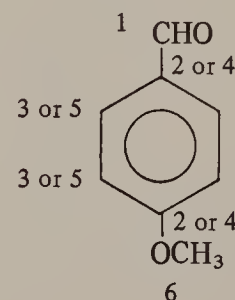
Table XVI. Some  $^2J_{CH}$  Values

| Compound            | $J$ (Hz) |
|---------------------|----------|
| $sp^3$              |          |
| $CH_3CH_3$          | -4.5     |
| $CH_3CCl_3$         | 5.9      |
| $CH_3CH=O$          | 26.7     |
| $sp^2$              |          |
| $CH_2=CH_2$         | -2.4     |
| $(CH_3)_2C=O$       | 5.5      |
| $CH_2=CHCH=O$       | 26.9     |
| $C_6H_6$            | 1.0      |
| $sp$                |          |
| $CH\equiv CH$       | 49.3     |
| $C_6H_5OC\equiv CH$ | 61.0     |

## V. PEAK ASSIGNMENT PROBLEM

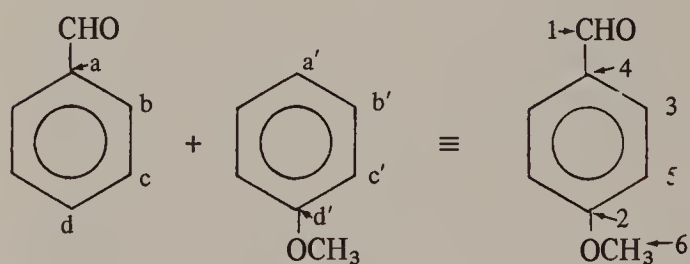
We may review some of the above material by assigning the peaks of *p*-methoxybenzaldehyde from Figure 6a and 6b by using the chemical shift correlation tables, peak heights, off-resonance decoupling, and the concept of symmetry.

We immediately assign the downfield absorption in Figure 6a at  $\delta$  191.0 (peak 1) to the CHO group (Table XIII gives  $\delta$  190.7 for benzaldehyde), and the upfield absorption at  $\delta$  55.6 (peak 6) to the OCH<sub>3</sub> group (Table VII gives  $\delta$  54.1 for anisole). The small peaks 2 and 4 must represent the quaternary ring carbon atoms, and the 2 large peaks 3 and 5 must each represent the 2 pairs of equivalent ring carbons. At this point the following assignments are evident.



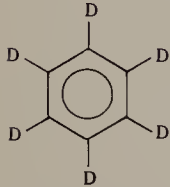
These assignments are confirmed by the off-resonance decoupled spectrum (Figure 6b): doublet for CHO, quartet for OCH<sub>3</sub>, singlets for the quaternary carbons. Peak 4 is buried under the doublet of peak 3.

The ambiguous assignments can be resolved by applying the principle of substituent additivity and the data of Table VII as follows:



| ppm from benzene<br>(128.5 ppm)<br>(see Table VII) |                      | ppm from TMS ( $\delta$ ) |          |
|--|----------------------|---------------------------|----------|
| for CHO  | for OCH <sub>3</sub> | Calcd.                    | Observed |
| a. +8.6  | a. -7.7              | 4. 129.4                  | 4. 130.2 |
| b. +1.3  | b. +1.0              | 3. 130.8                  | 3. 132.1 |
| c. +0.6  | c. -14.4             | 5. 114.7                  | 5. 114.5 |
| d. +5.5  | d. +31.4             | 2. 165.4                  | 2. 164.9 |

Table XVII. Coupling constants for  $^{31}\text{P}$ ,  $^{19}\text{F}$ , and D coupled to  $^{13}\text{C}$

| Compound   | $^1J$ (Hz)             | $^2J$ (Hz)                  | $^3J$ (Hz)            |
|--|------------------------|-----------------------------|-----------------------|
| $\text{CH}_3\text{CF}_3$   | 271                    |                             |                       |
| $\text{CF}_2\text{H}_2$  | 235                    |                             |                       |
| $\text{CF}_3\text{COOH}$   | 284                    | 43.7                        |                       |
| $\text{C}_6\text{H}_5\text{F}$   | 245                    | 21.0                        |                       |
| $(\text{CH}_3\text{CH}_2)_3\text{P}$   | 5.4                    | 10.0                        |                       |
| $(\text{CH}_3\text{CH}_2)_4\text{P}^+ \text{Br}^-$                                 | 49                     | 4.3                         |                       |
| $(\text{C}_6\text{H}_5)_3\text{P}^+ \text{CH}_3 \text{I}^-$                        | 88 ( $\text{CH}_3$ 52) | 10.9                        |                       |
| $\text{CH}_3\text{CH}_2\text{P}(\text{OCH}_2\text{CH}_3)_2$                        | 143                    | 7.1 ( $J_{\text{COP}}$ 6.9) | $J_{\text{CCOP}}$ 6.2 |
| $\text{CDCl}_3$  | 31.5                   |                             |                       |
| $\text{CD}_3\text{CCD}_3$  | 19.5                   |                             |                       |
| $(\text{CD}_3)_2\text{SO}$   | 22.0                   |                             |                       |
|  | 25.5                   |                             |                       |

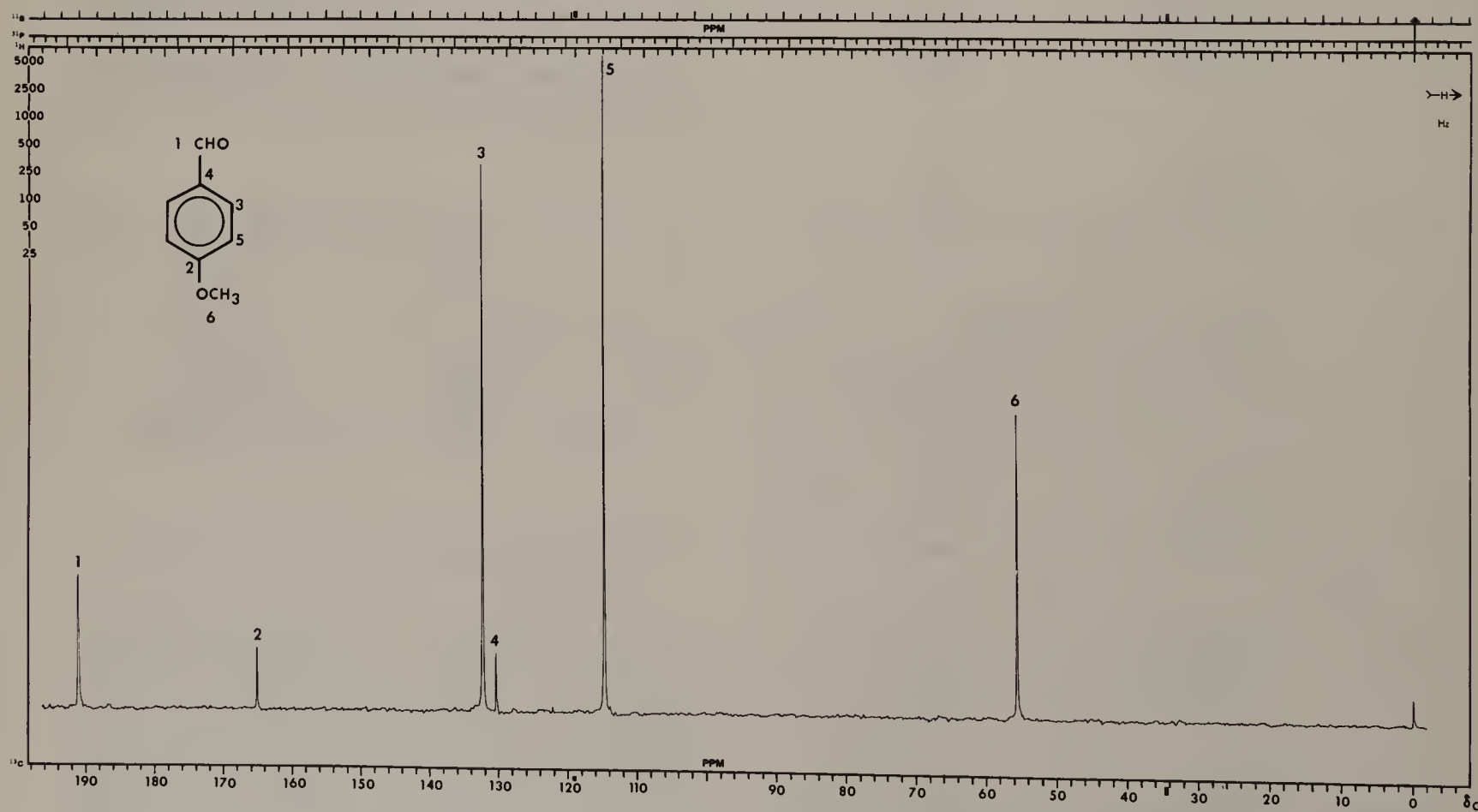


Figure 6a. (a). Noise-decoupled  $^{13}\text{C}$  spectrum of p-methoxybenzaldehyde. Solvent  $\text{CDCl}_3$ , 25.2 MHz, 5000 Hz sweep-width.



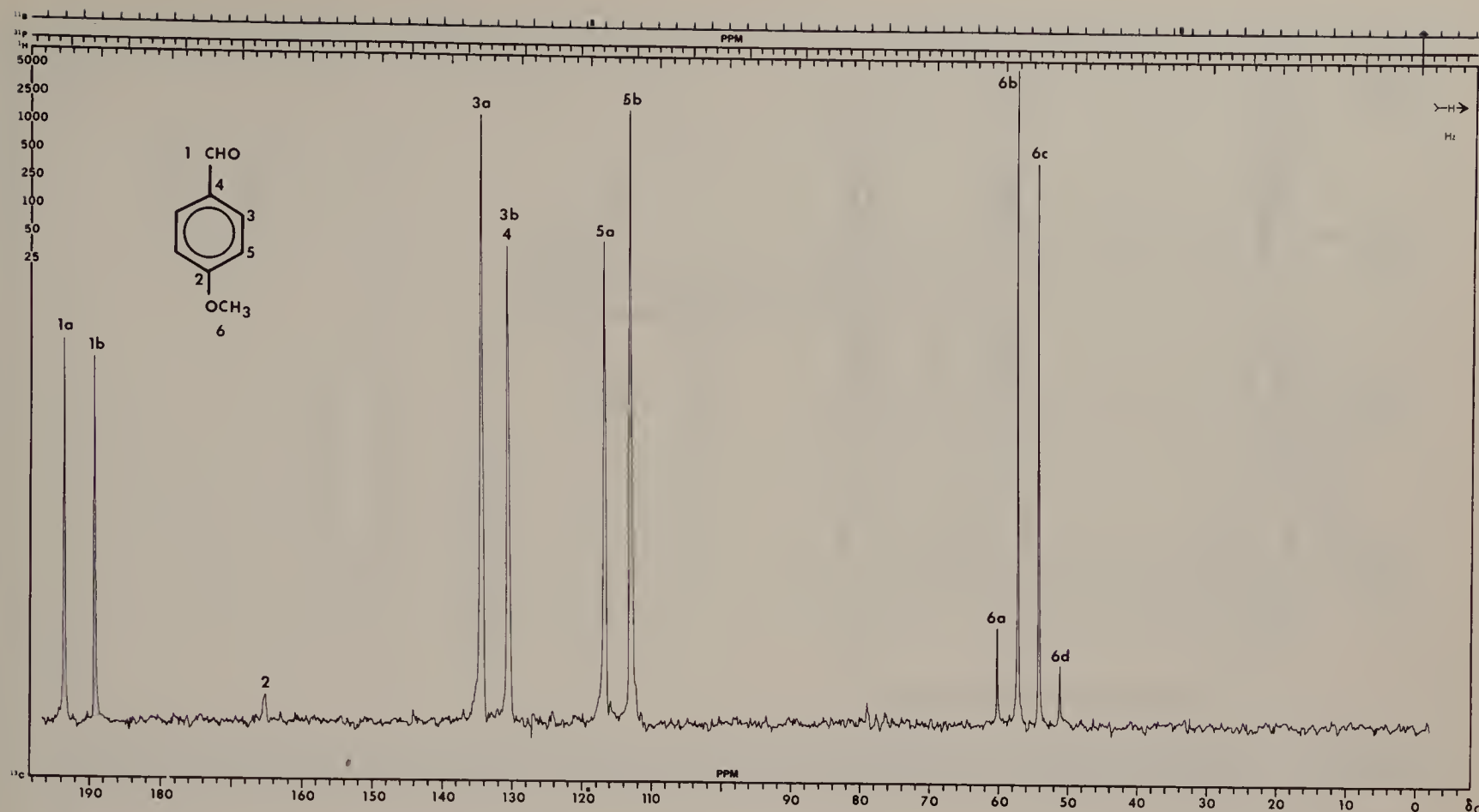


Figure 6b. Off-resonance decoupled  $^{13}\text{C}$  spectrum of p-methoxybenzaldehyde. Solvent  $\text{CDCl}_3$ , MHz, 5000 Hz sweepwidth.

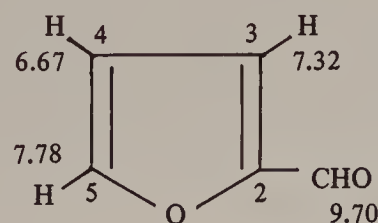
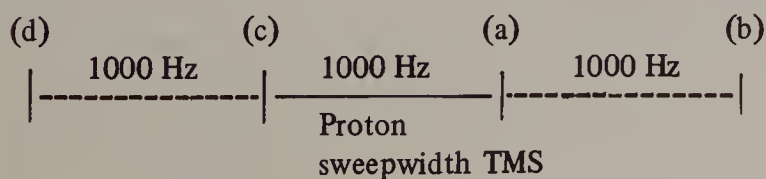
Note also that we count 6 carbon atoms in the noise-decoupled spectrum and 6 protons in the off-resonance decoupled spectrum. The discrepancy between this count and the molecular formula  $\text{C}_8\text{H}_8\text{O}_2$  confirms the *para* substitution in the benzene ring.

## VI. THE "CROSSOVER" EXPERIMENT

It is possible to correlate a particular  $^{13}\text{C}$  peak with the shift position of its attached proton(s) by carrying out a "crossover" experiment (Figure 7a). This is done by obtaining  $^{13}\text{C}$  off-resonance decoupled spectra at 4 different frequencies, 2 upfield of the proton range of frequencies and 2 downfield. Thus, for example, the decoupler might be set (a) at the proton frequency of TMS, (b) at 1000 Hz upfield from TMS, (c) at 1000 Hz downfield from TMS, and at 2000 Hz downfield.

The residual couplings ( $J^I$ ) in the spectrum obtained with the decoupler set at (a) are less than those obtained with the decoupler set at (b). Similarly,  $J^I$  with the decoupler at (c) is less than  $J^I$  with the decoupler at (d). The  $J^I$  values can be obtained accurately from the computer read-out. The ratio  $J_b^I/J_c^I$  for a particular  $^{13}\text{C}$  is a measure of how far upfield (in the proton spectrum) the attached proton(s) is—the larger the ratio, the further upfield. Likewise, the larger the ratio  $J_d^I/J_c^I$ , the further downfield is the attached proton. Either ratio gives the relative shift positions for the attached protons, but the additional assurance provided is worth the effort of obtaining 2 downfield as well as 2 upfield decouplings.

This procedure is shown applied to the problem of assigning the peaks in the  $^{13}\text{C}$  spectrum of furfural (Figure 7b), given the proton assignments; the  $^1\text{H}$  spectrum of the same solution is shown in Figure 7c. The proton assignments for furfural are as follows (see Chapter 4, Appendix D, Table 5).



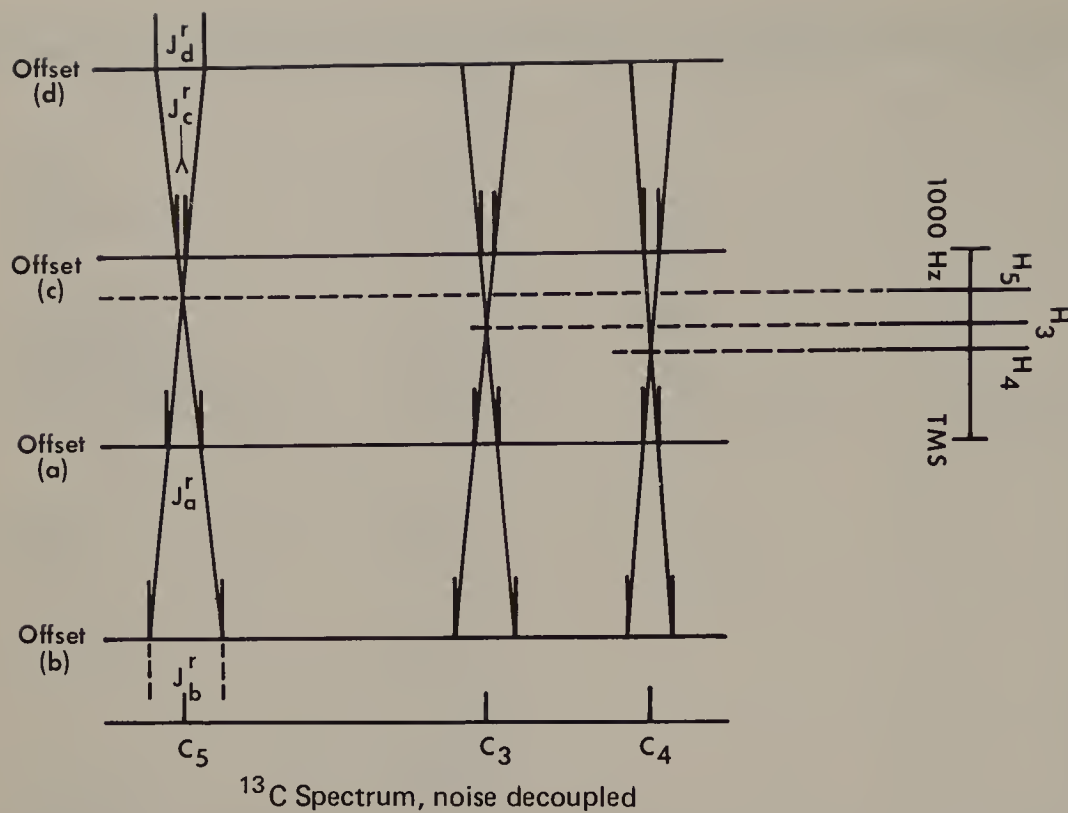


Figure 7a. "Crossover" schematic for furfural. Scale on bottom locates the three carbons bearing protons, and the scale on the right locates these protons.

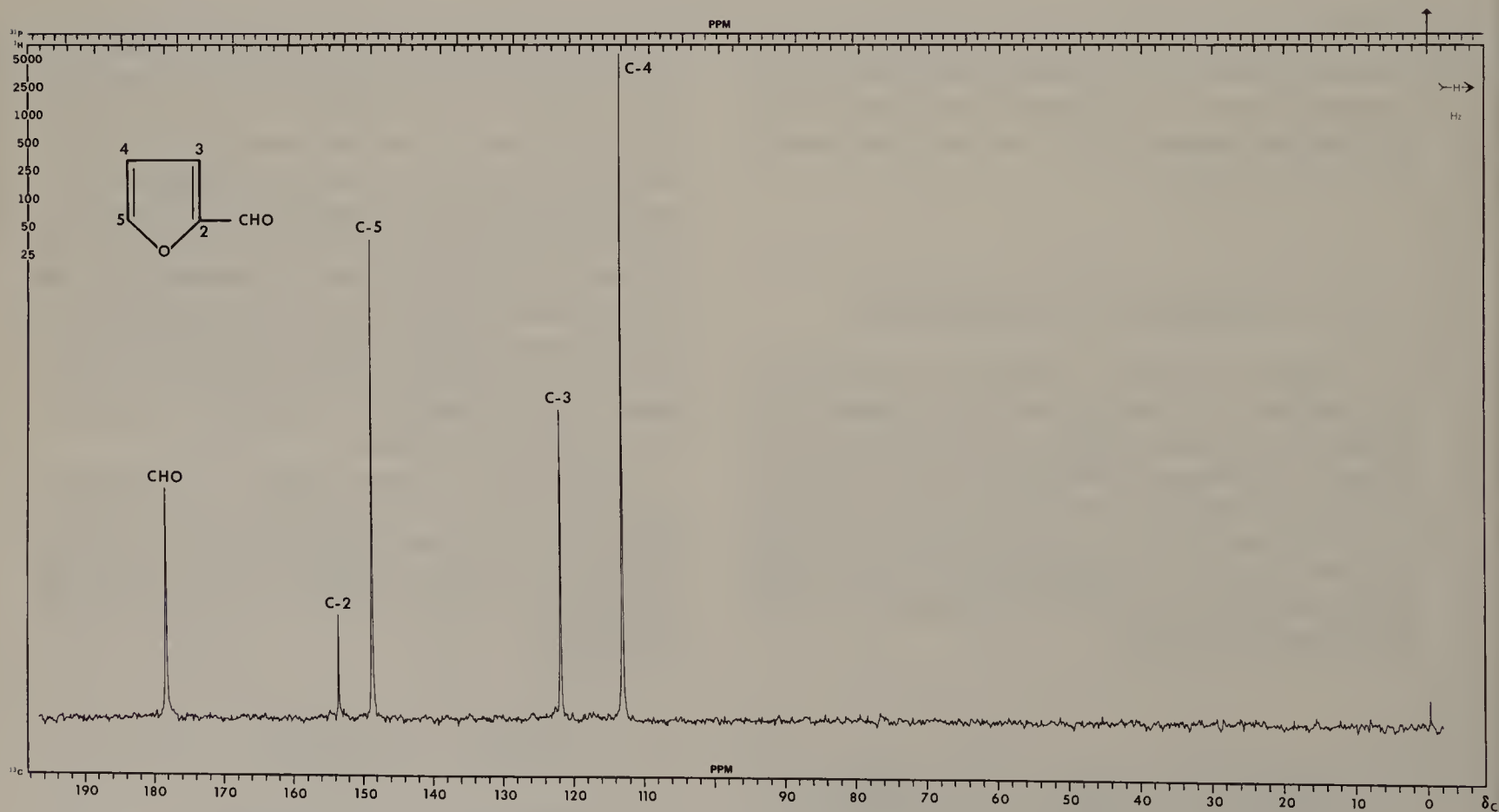


Figure 7b. Noise-decoupled <sup>13</sup>C spectrum for furfural (50% solution in CDCl<sub>3</sub>). 25.2 MHz, 5000 Hz sweepwidth.

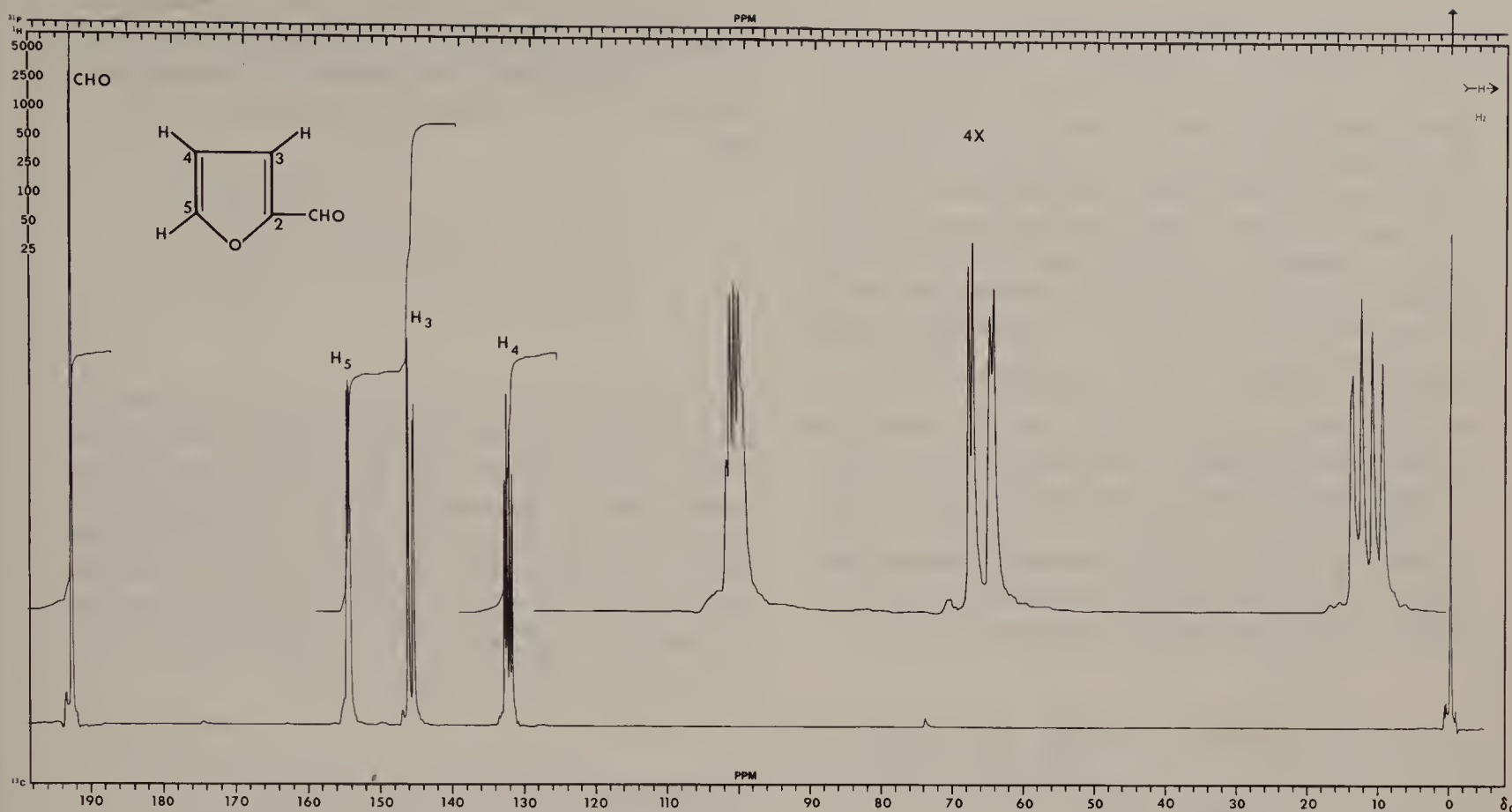


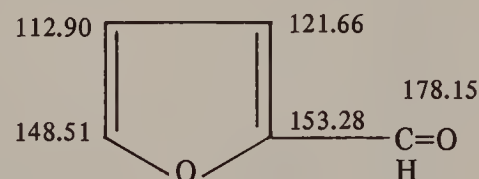
Figure 7c.  $^1\text{H}$  NMR spectrum of the same furfural solution used for Fig. 7b.  $\text{CDCl}_3$  solvent, 25.2 MHz, 5000 Hz sweep-width.

The ring  $^{13}\text{C}$  assignments of  $\text{C}_3$ ,  $\text{C}_4$ , and  $\text{C}_5$  can be made from the following  $J^r$  values and ratios as described above; the downfield position of the  $^{13}\text{CHO}$  (178.15 ppm) is obvious, as is the assignment of  $\text{C}_2$  (153.28 ppm) by virtue of low intensity and its singlet in the off-resonance decoupled spectra.

$\text{C}_3$  and  $\text{C}_4$  is not obvious. The “crossover” experiment gives an unambiguous result despite the fact that the proton shifts are quite close. Here the progression of shift positions for the  $^{13}\text{C}$  atoms and for their attached protons is the same, but this is not always true (see Appendix B). The  $^{13}\text{C}$  assignments in furfural are as follows:

| $^{13}\text{C}(\text{ppm})$ | $J_b^r$ | $J_a^r$ | $J_b^r/J_a^r$ | $J_d^r$ | $J_c^r$ | $J_d^r/J_c^r$ |
|-----------------------------|---------|---------|---------------|---------|---------|---------------|
| 148.51                      | 99.31   | 47.55   | 2.092         | 76.78   | 15.93   | 4.831         |
| 121.66                      | 85.00   | 39.54   | 2.151         | 67.86   | 17.11   | 3.968         |
| 112.90                      | 83.01   | 36.99   | 2.310         | 71.08   | 21.02   | 3.356         |

We see that the ratios  $J_b^r/J_a^r$  and  $J_d^r/J_c^r$  both indicate that the downfield proton (on  $\text{C}_5$ ) is connected to the 148.51 ppm  $^{13}\text{C}$  peak; the next upfield proton (on  $\text{C}_3$ ) is connected to the 121.66 ppm  $^{13}\text{C}$  peak; and the furthest upfield proton (on  $\text{C}_4$ ) is connected to the furthest upfield (112.90 ppm)  $^{13}\text{C}$  peak. Although the  $^{13}\text{C}$  peak at 148.51 ppm might reasonably be assigned to  $\text{C}_5$  because of its proximity to the oxygen atom, the distinction between



The term “crossover” derives from the appearance of a graphical presentation in which lines connect the peaks of  $^{13}\text{C}$  absorptions at offset (b) with the corresponding peaks at offset (a), and similarly connect the peaks at offset (d) and offset (c). The intersection point is a function of  $J_b^r/J_a^r$  and  $J_d^r/J_c^r$  as shown in the schematic diagram in Figure 7a, and is related to the chemical shift of the attached proton. In practice, the graphical method is not satisfactory (because of the very small slopes of the converging lines) unless the protons are widely separated. The slopes in Figure 7a are greatly exaggerated.



## VII. SECOND ORDER EFFECTS

Second-order effects may complicate off-resonance spectra. (Several examples are given on pages 72-75 of Reference 3.) The problem may occur in a  $Y-CH_2CH_2-X$  system in which first order character requires that  $^1J_{CH} \gg {}^2J_{CCH}$  and  $^3J_{HH}$ . Under the influence of the high power decoupler,  $^1J_{CH}$  is reduced to  $^1J_{CH}^r$ . Furthermore, the decoupler reduces the effective shift difference between the 2 sets of protons ( $\Delta\nu$ ), which results in more strongly coupled protons ( $\frac{\Delta\nu}{J}$  is small). These effects result in a distorted "triplet" (with additional peaks) for each  $CH_2$  rather than a clean first-order triplet. If the situation is understood, the deviation from first order is usually no problem. (Similar situations in proton spectra are described as "virtual coupling" in Chapter 4.) An off-resonance decoupled spectrum of thiamine hydrochloride that shows both first order triplets and distorted "triplets" is presented in Figure 8.

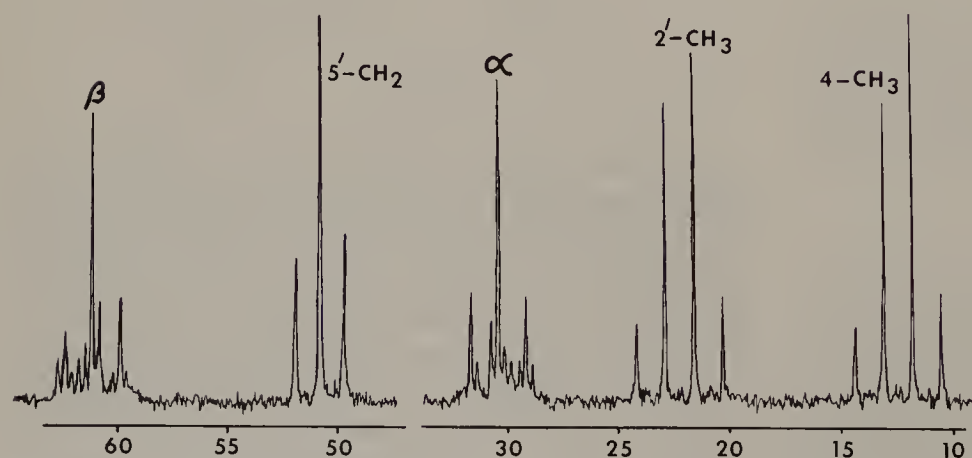
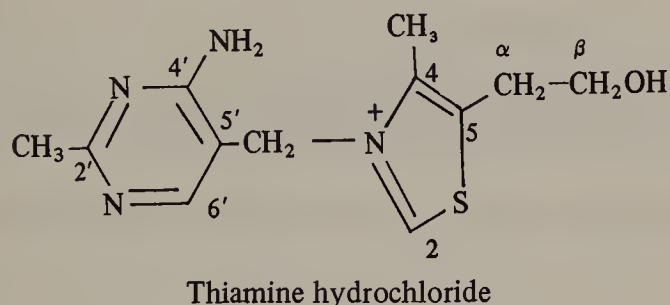
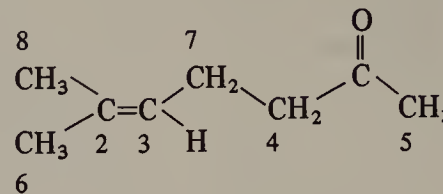


Figure 8. High-field region of the 20 MHz  $^{13}C$  spectrum of thiamine hydrochloride in  $D_2O$ ; off-resonance decoupled. From ref. 3, page 73, with permission.

Figure 9a is a noise-decoupled spectrum of 6-methyl-5-hepten-2-one, and the peak assignments are made on the basis of chemical shifts, peak intensity of the quaternary carbons, and the off-resonance decoupled spectrum (Figure 9b).



In an attempt to reduce the amount of overlapping in the off-resonance decoupled spectrum, the decoupler was moved to a smaller offset. The spectrum in Figure 9b was obtained with the decoupler at 1500 Hz upfield from TMS and in Figure 9c, the decoupler was at 750 Hz upfield from TMS. The smaller residual coupling in Figure 9c had the intended effect of reducing the overlap, but the triplets of peaks 4 and 7 in Figure 9b are distorted in Figure 9c by the second-order effects described above.

## VIII. QUANTITATIVE ANALYSIS

Quantitative  $^{13}C$ -NMR is desirable in two situations. First, in structural determinations, it is clearly useful to know if a signal is due to more than one shift-equivalent carbon.

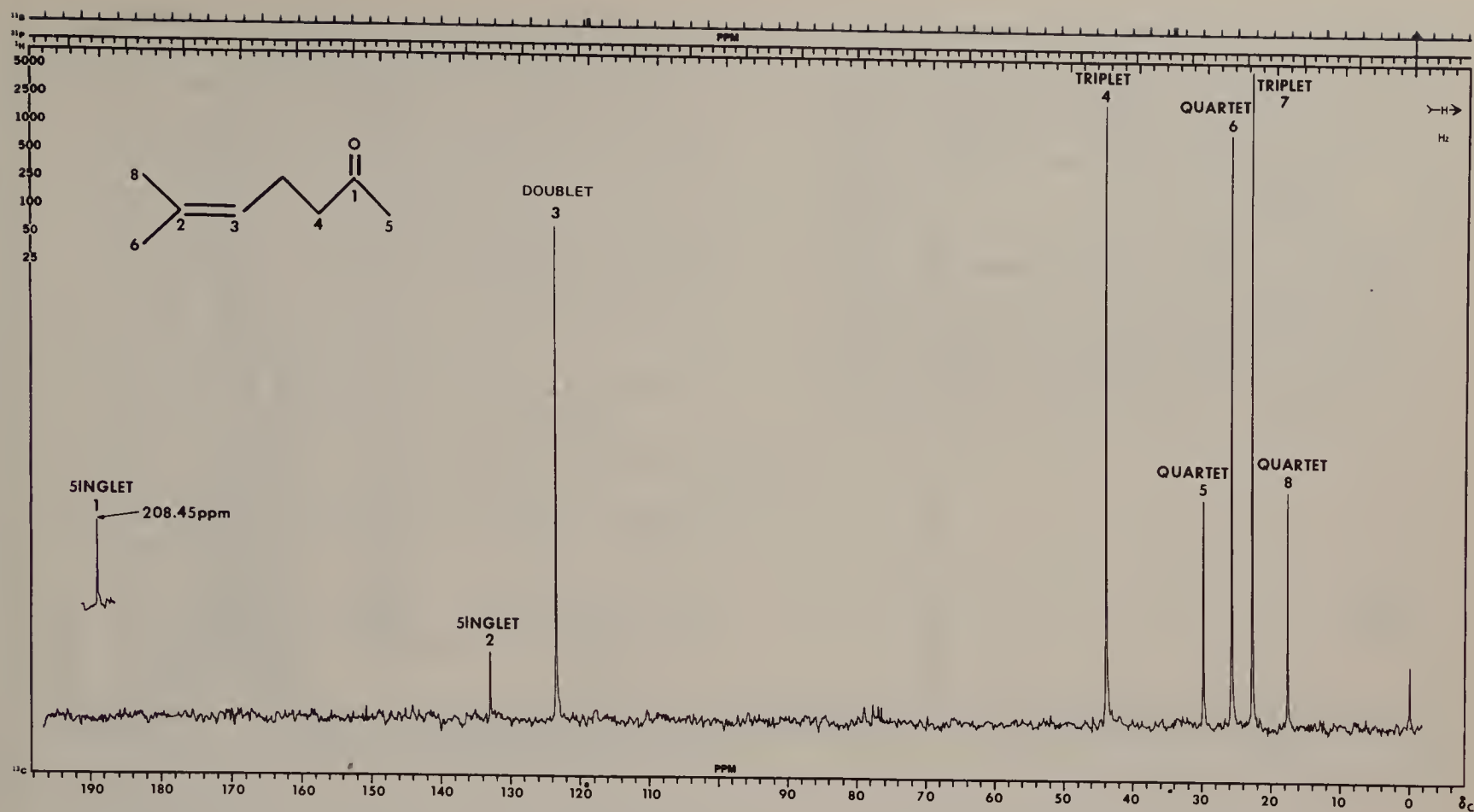


Figure 9a. Noise-decoupled  $^{13}\text{C}$  spectrum of 6-methyl-5-hepten-2-one;  $\text{CDCl}_3$  solvent, 25.2 MHz, 5000 Hz sweepwidth.

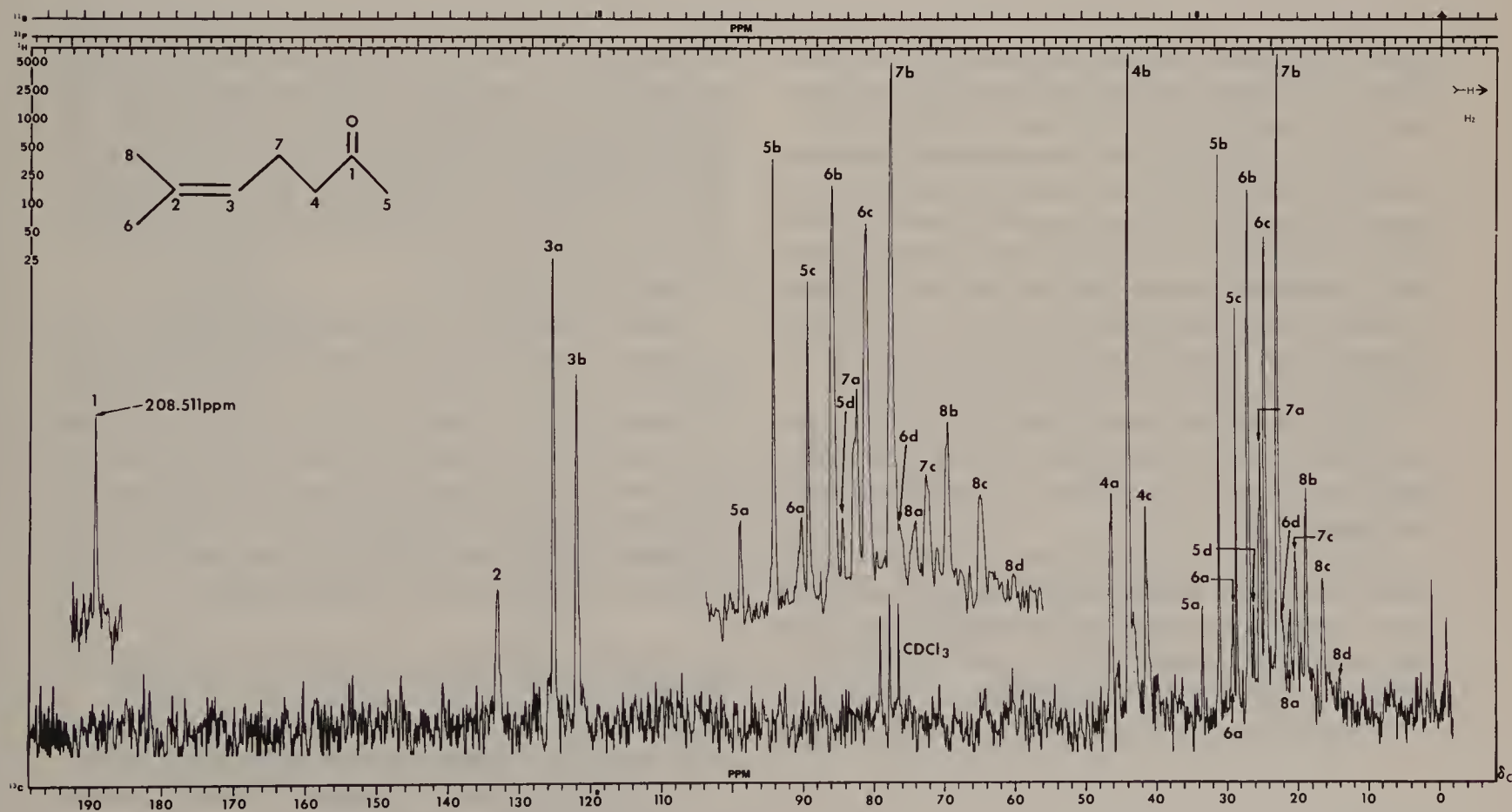


Figure 9b.  $^{13}\text{C}$ -spectrum of 6-methyl-5-hepten-2-one with off-resonance decoupling 1500 Hz upfield of the TMS proton frequency. Solvent  $\text{CDCl}_3$ , 25.2 MHz, 5000 Hz sweepwidth.

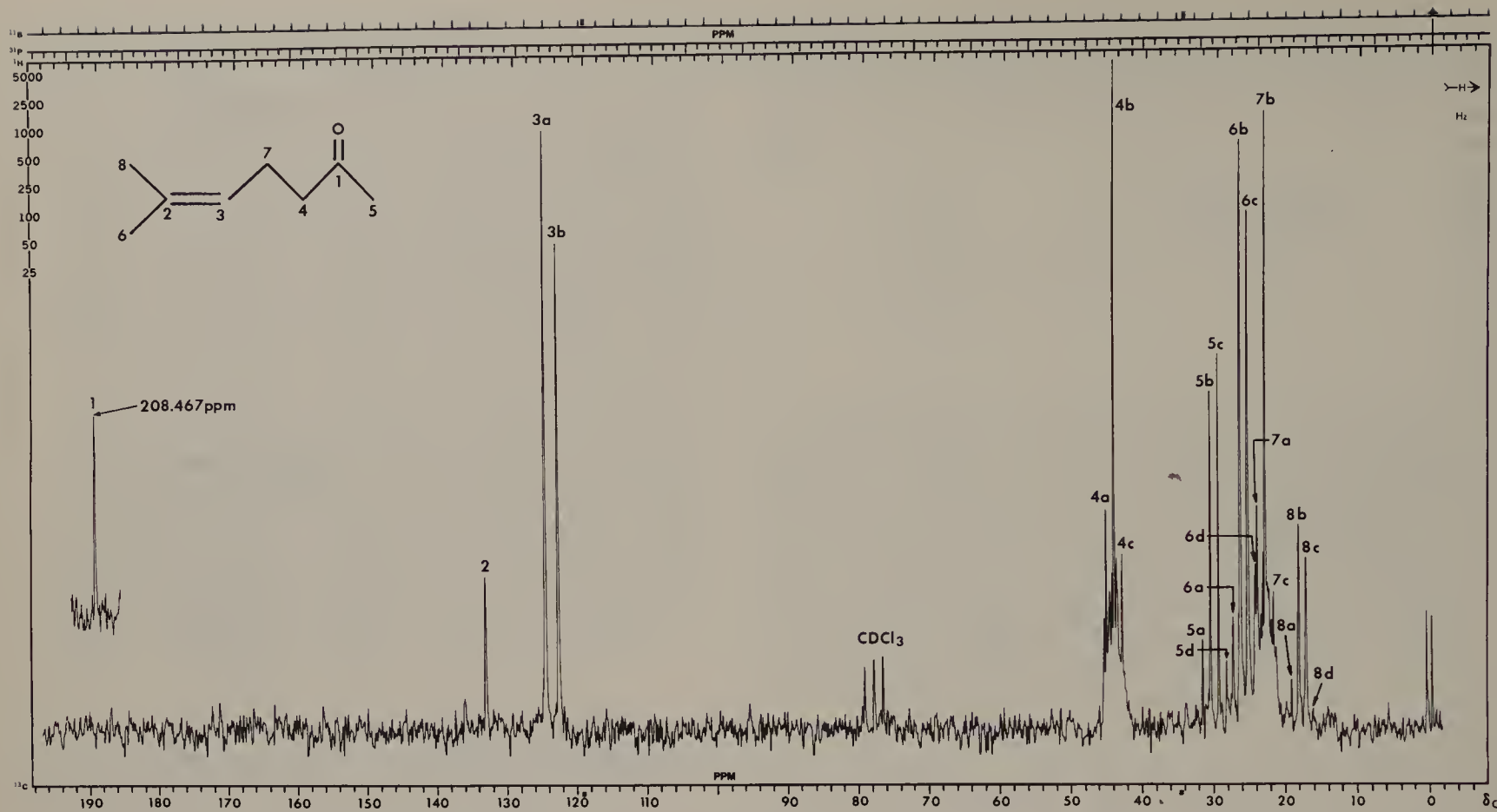


Figure 9c.  $^{13}\text{C}$  spectrum of 6-methyl-5-hepten-2-one with off-resonance decoupling 750 Hz upfield of the TMS proton frequency.

Second, quantitative analysis of a mixture of two or more components requires that the area of a signal be proportional to the number of carbon atoms causing that signal.

There are two reasons why noise-decoupled spectra are usually not quantitative. First, carbons with long spin-lattice relaxation times ( $T_1$ ) may not completely return to a Boltzmann's distribution between pulses, and the resulting signals will be considerably weaker than expected from the number of carbons causing those signals (see Figure 4 and the corresponding text). Second, some carbons give rise to exceptionally small signals due to weak NOE enhancement.\*

Three methods may be employed in an effort to obtain quantitative noise-decoupled spectra: long pulse delays, gated decoupling, and the addition of paramagnetic relaxation reagents.

Delays of tens to hundreds of seconds (to allow return of the nuclei to a Boltzmann's distribution) will remove signal area discrepancies caused by long relaxation times; such delays, unfortunately, will frequently require prohibitively long times to obtain the spectrum.

If the noise decoupler is gated on during the pulse and

the early part of the free induction decay and then is gated off during the pulse delay, NOE enhancement will be minimized for all carbons. This is true because the free induction signal decays quickly in an exponential fashion, while the NOE factor slowly builds up in an exponential fashion. A weakness of the gated decoupling method is the removal of the NOE factor, whose loss requires extended signal acquisition.

Added paramagnetic relaxation reagents lead to more quantitative spectra by reducing all of the spin-lattice relaxation times (by means of an electronic relaxation mechanism) and by levelling all of the NOE factors. These reagents suffer from the fact that the effects are not complete and from the requirement that the sample must be separated (e.g., by chromatography) if it is to be recovered. Successful quantitative analysis has been carried out by combining two or all three of these procedures.<sup>13</sup>

## REFERENCES

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\*See p. 253.



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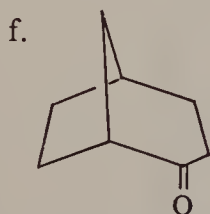
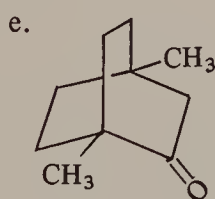
$-\text{CD}_3$ . In each case, assume that only 1-bond C-D coupling is important, and check your results against the footnote on page 257. Recall the  $\text{CDCl}_3$  signal that appears in many  $^{13}\text{C}$  spectra and adapt Pascal's triangle (Figure 25, Chapter 4), to  $^{13}\text{C}$ -D coupling.

- 5.4 Deduce the structure of compounds A-I from their spectra and assign as many  $^{13}\text{C}$  signals as possible. The multiplicities of off-resonance decoupled multiplets are abbreviated: s = singlet, d = doublet, t = triplet, q = quartet. The solvent is  $\text{CDCl}_3$  in all cases except E which is dissolved in  $\text{D}_2\text{O}$ .

## PROBLEMS

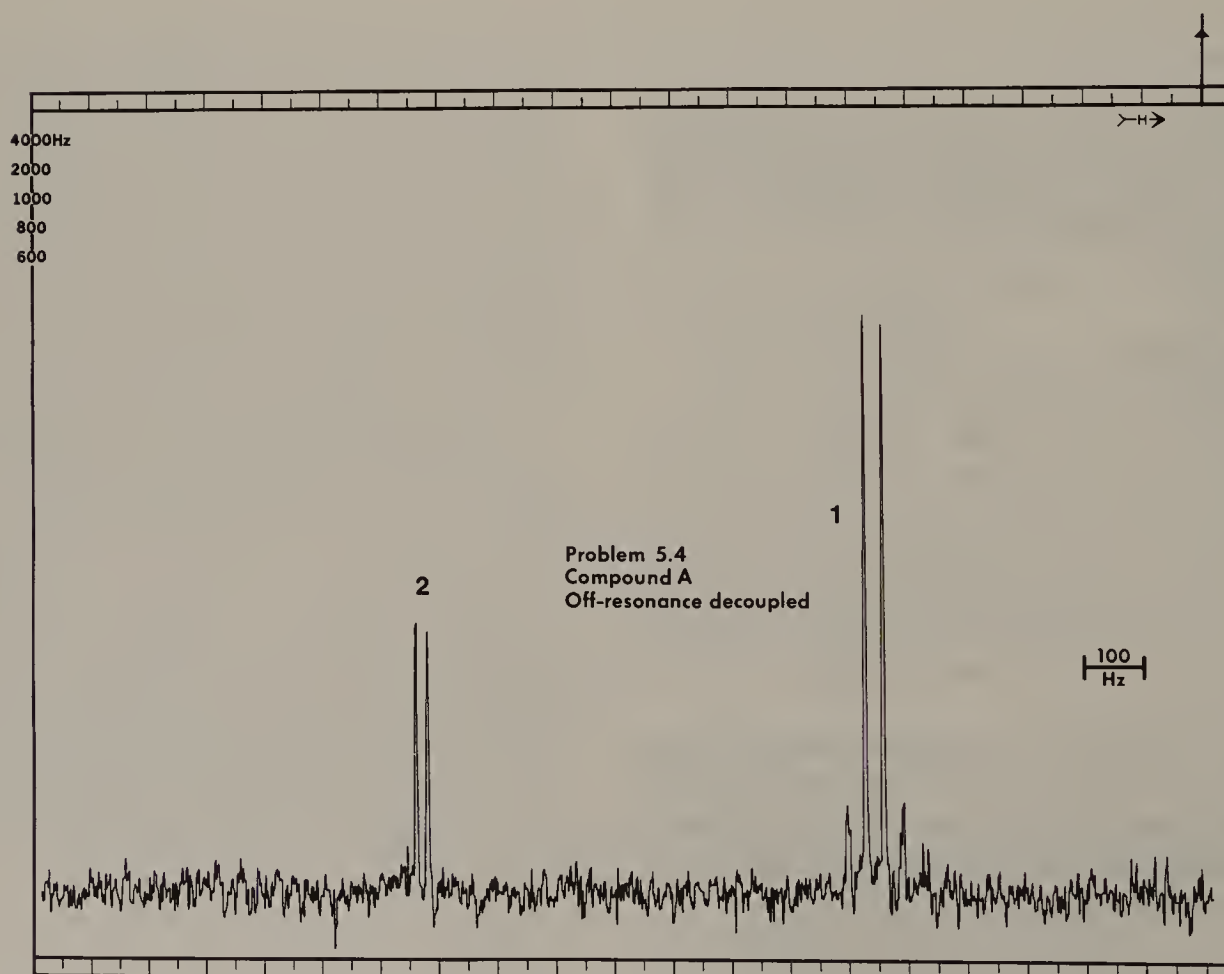
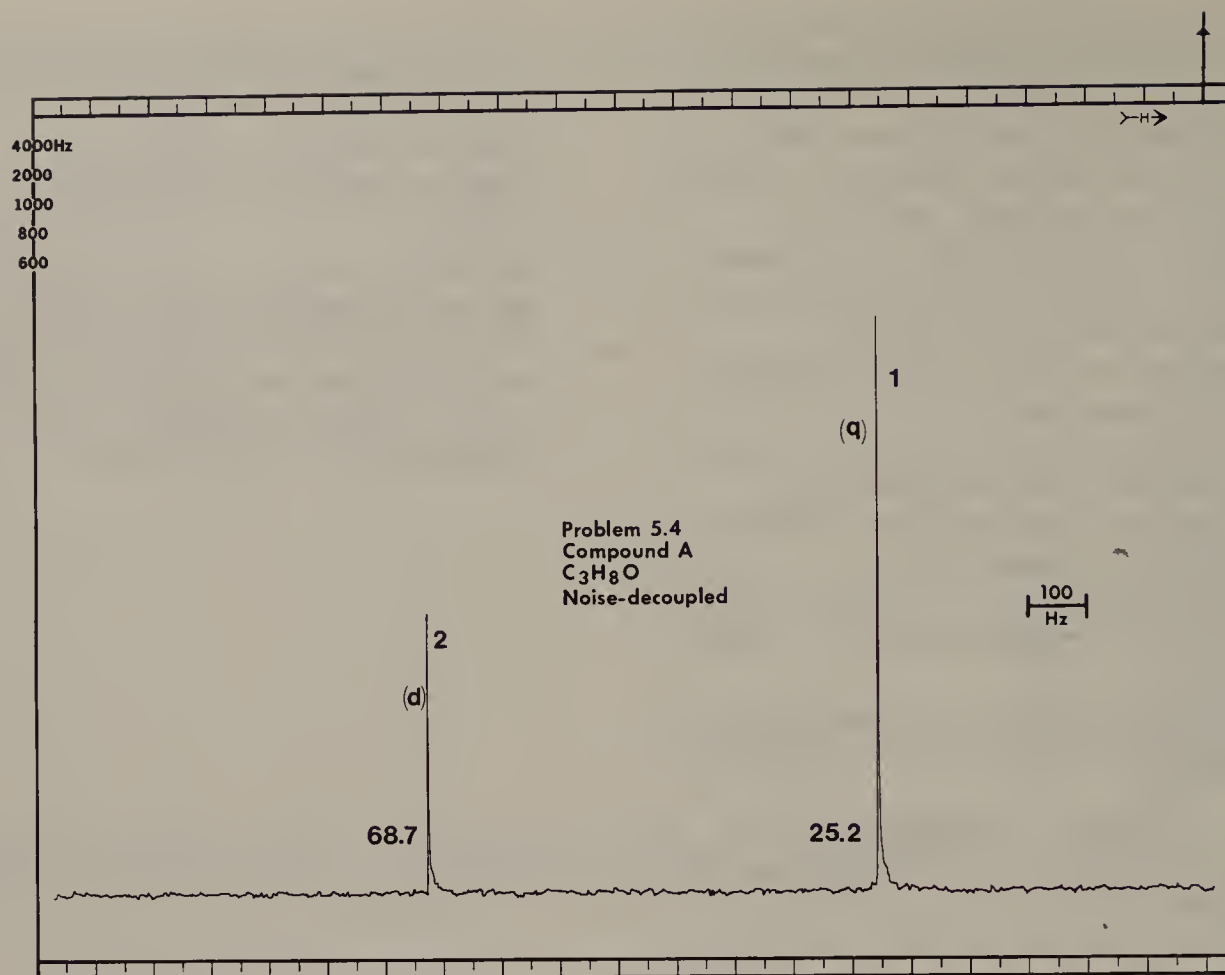
- 5.1 How many  $^{13}\text{C}$  peaks should be seen in the noise-decoupled spectrum of each of the following compounds? Assign the multiplicity expected for each signal in the off-resonance decoupled spectrum.

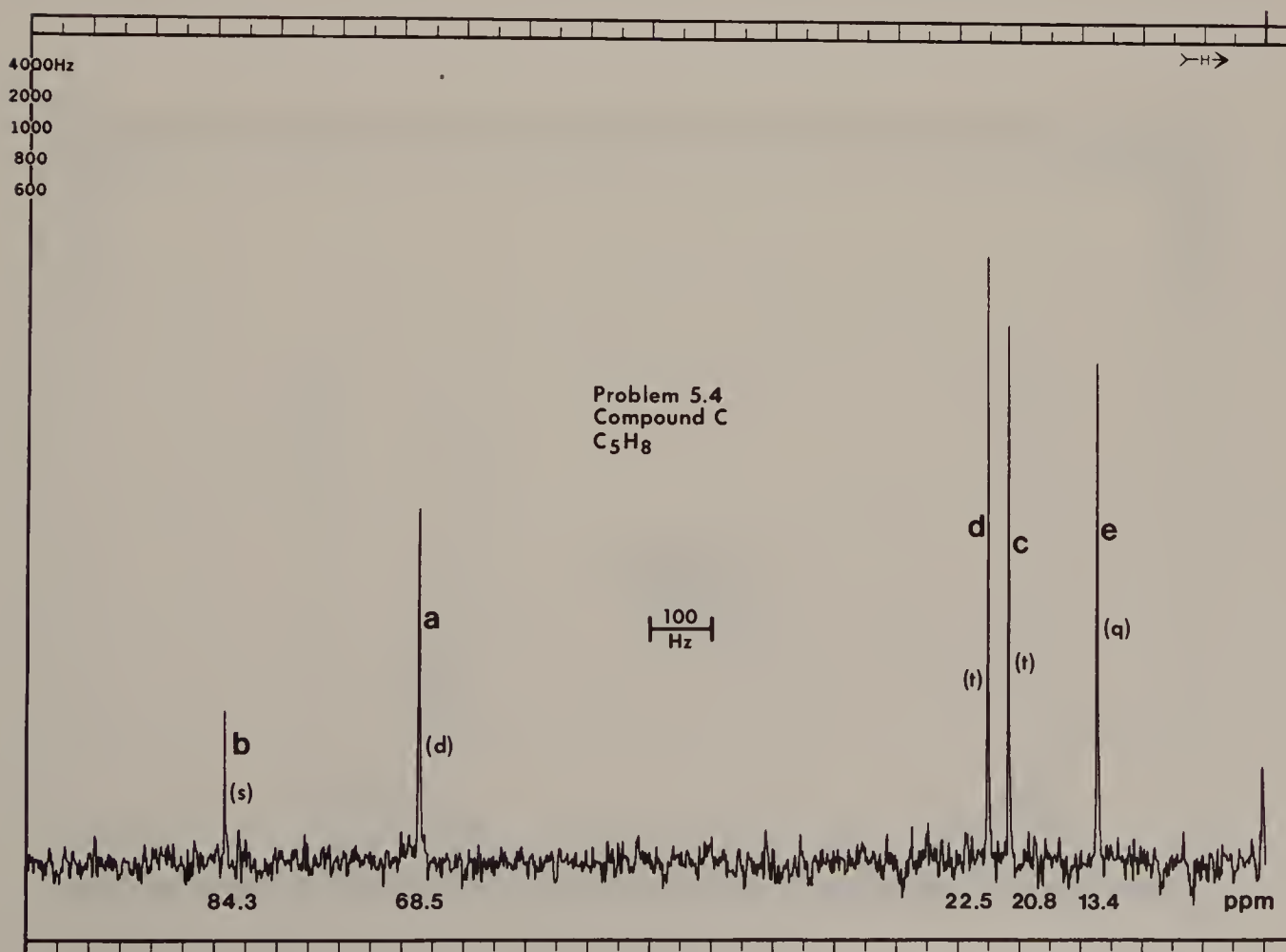
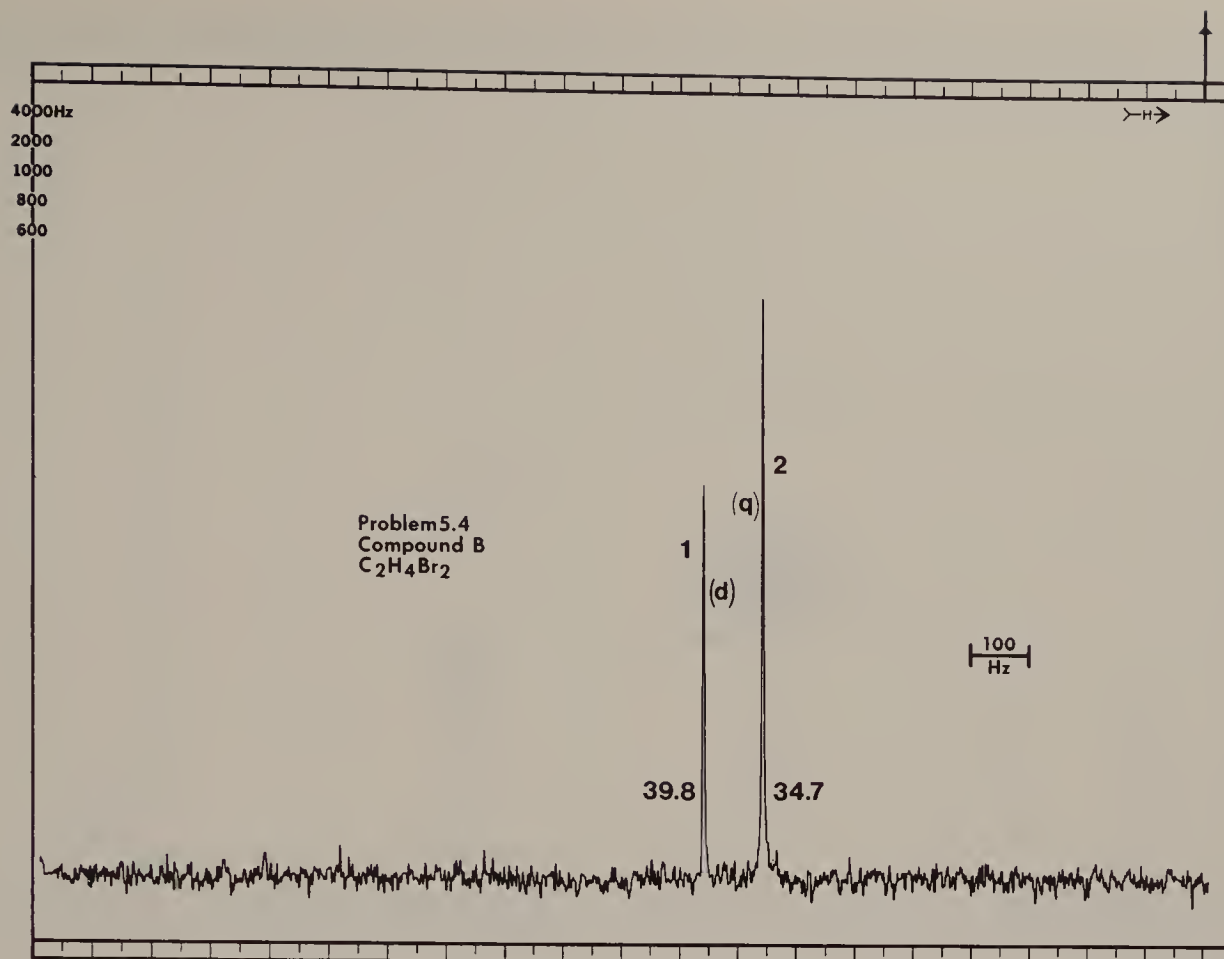
- a. benzene
- b. toluene
- c. naphthalene
- d. dodecane



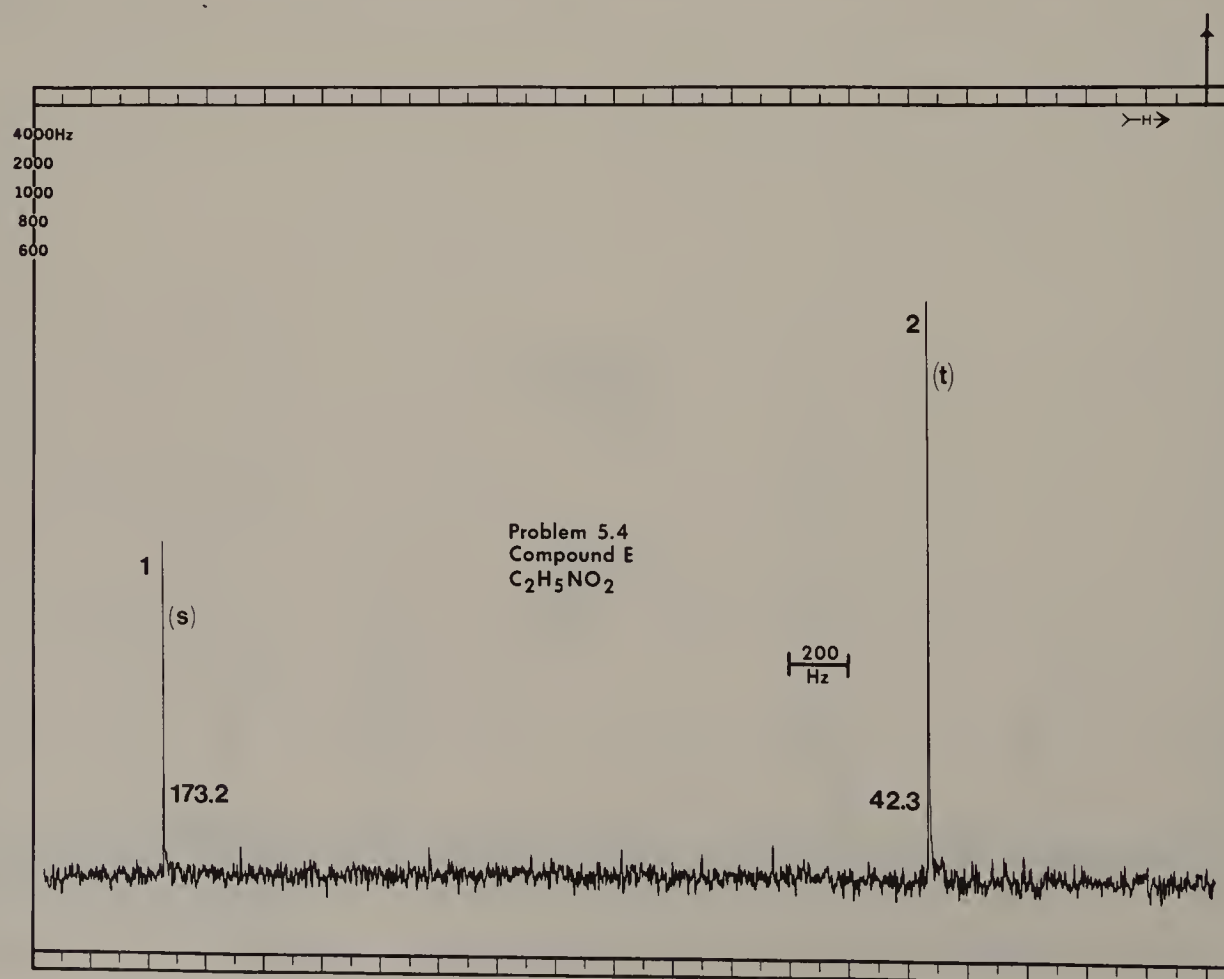
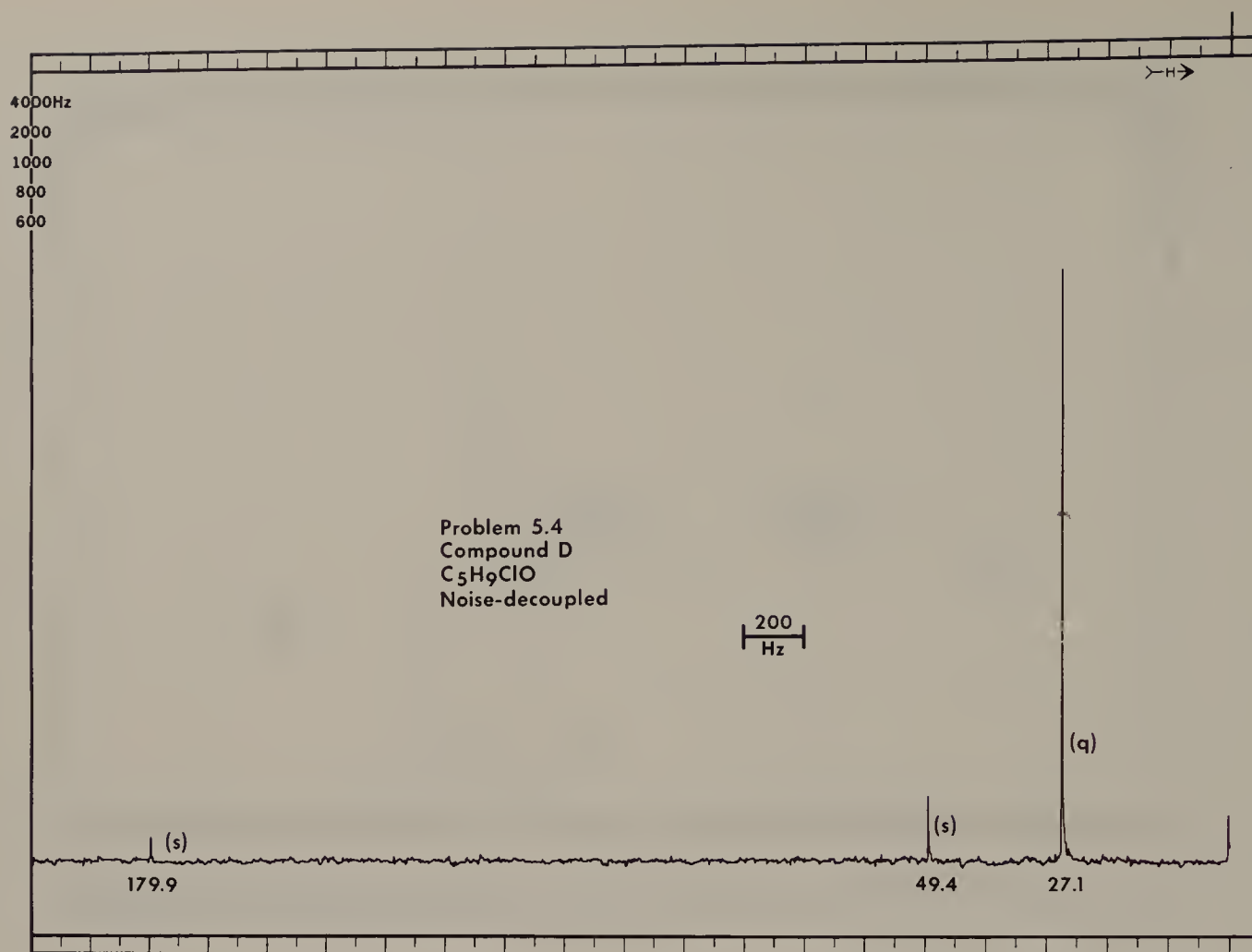
- 5.2 Because a compound of molecular formula  $\text{C}_6\text{H}_8$  is highly symmetrical, it shows just two singlets in the noise-decoupled spectrum. The off-resonance decoupled spectrum shows only a triplet and a doublet. Draw the structure.

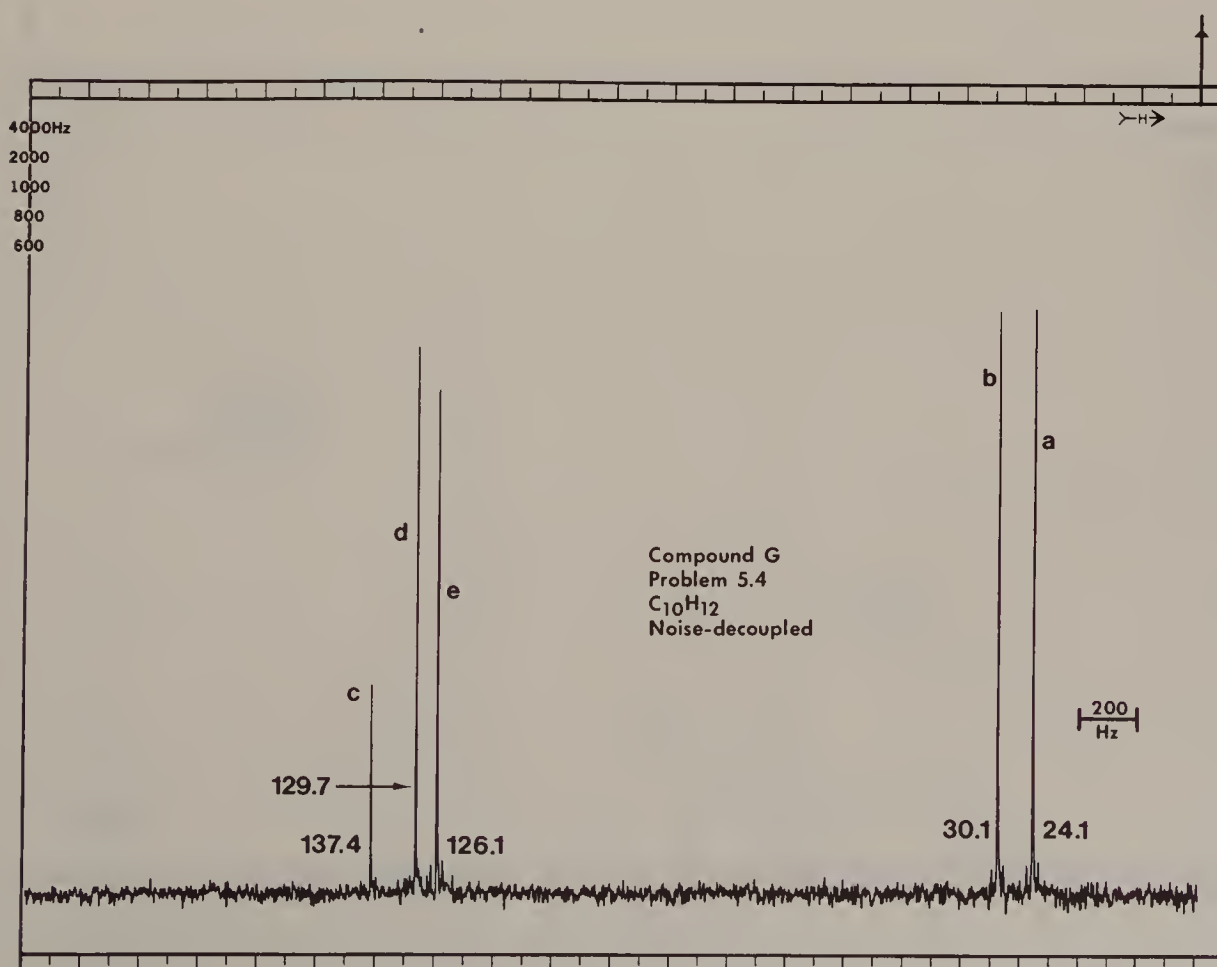
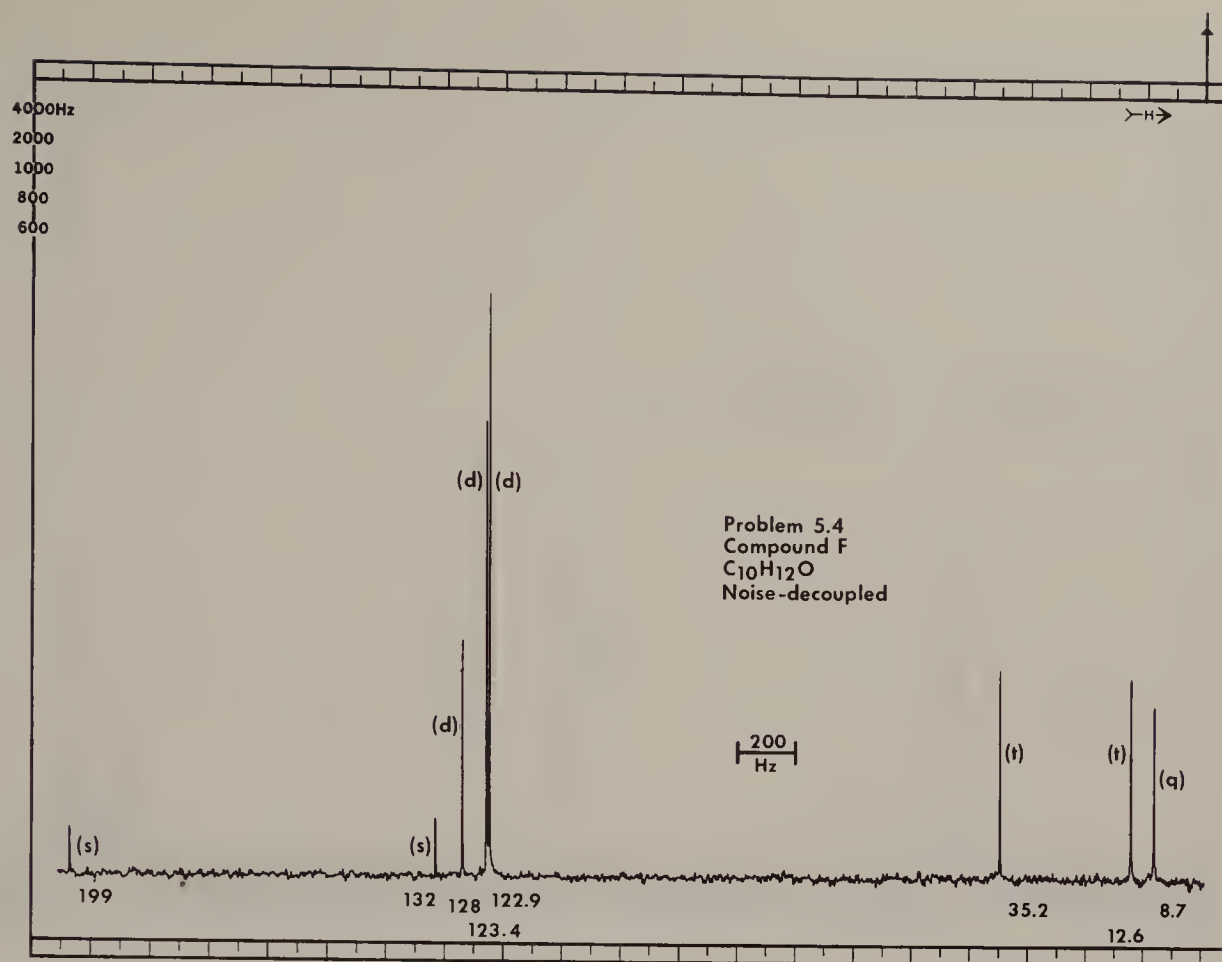
- 5.3 Predict the number of lines for  $-\text{CD}$ ,  $-\text{CD}_2$ , and  $-\text{CD}_3$ .

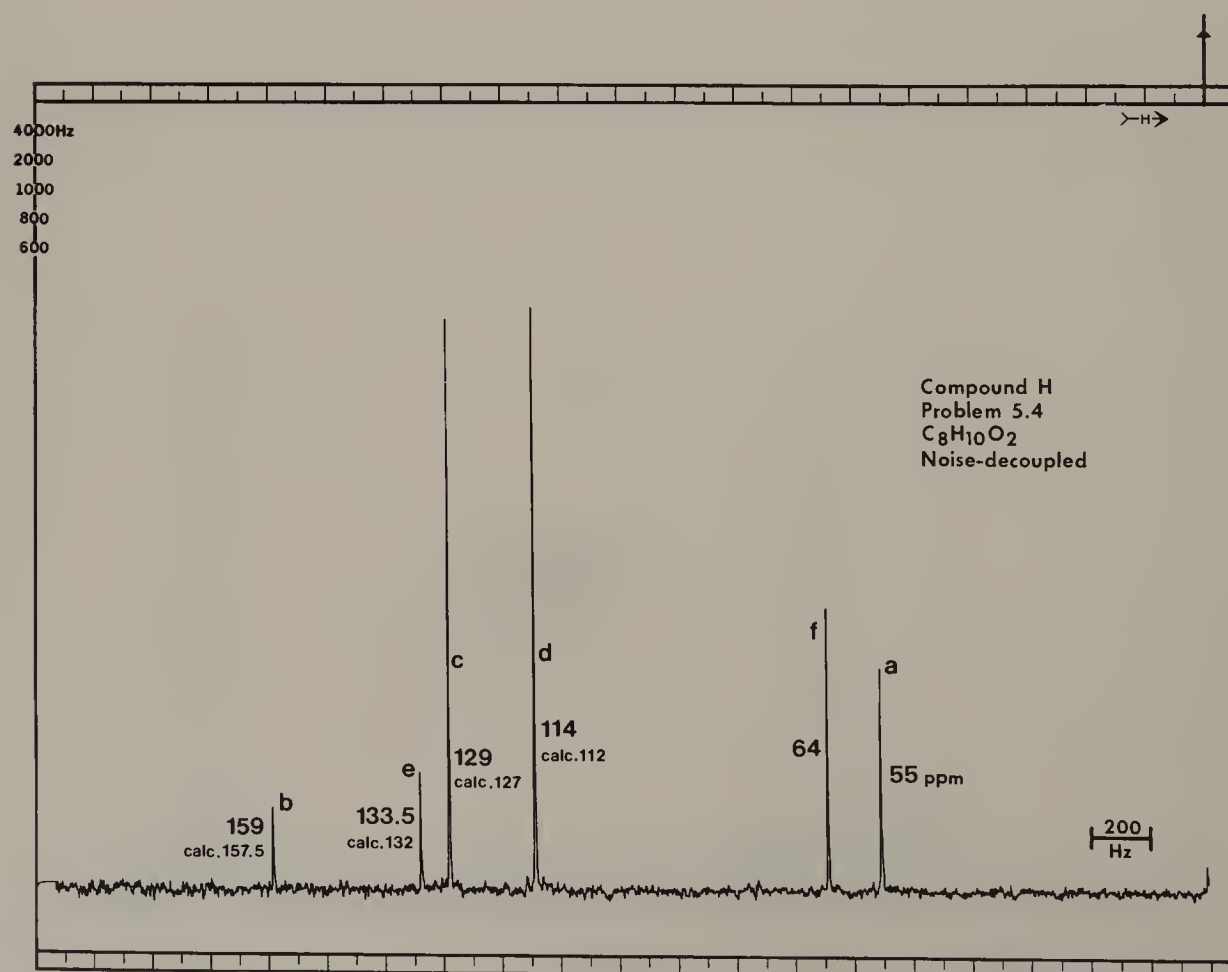
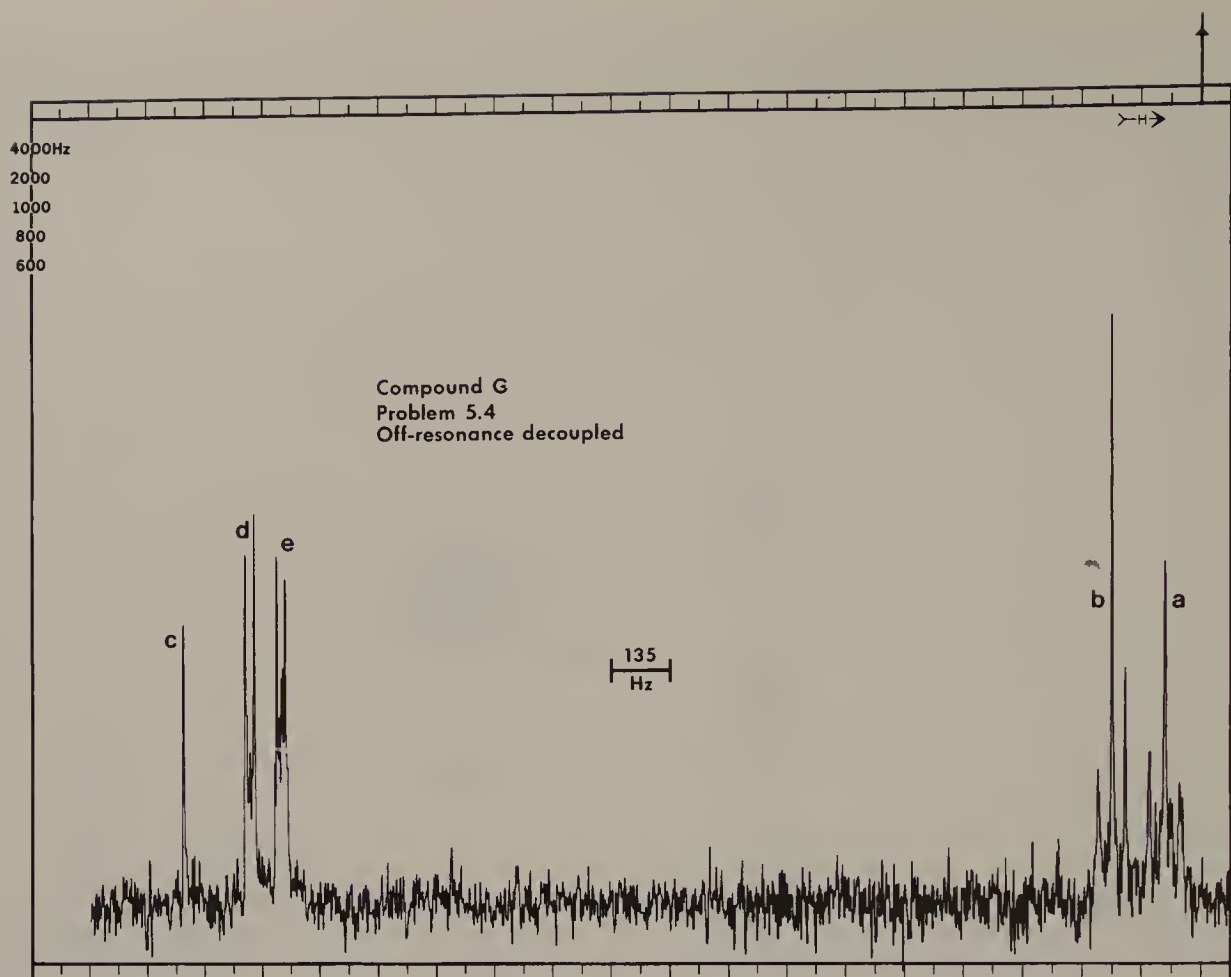




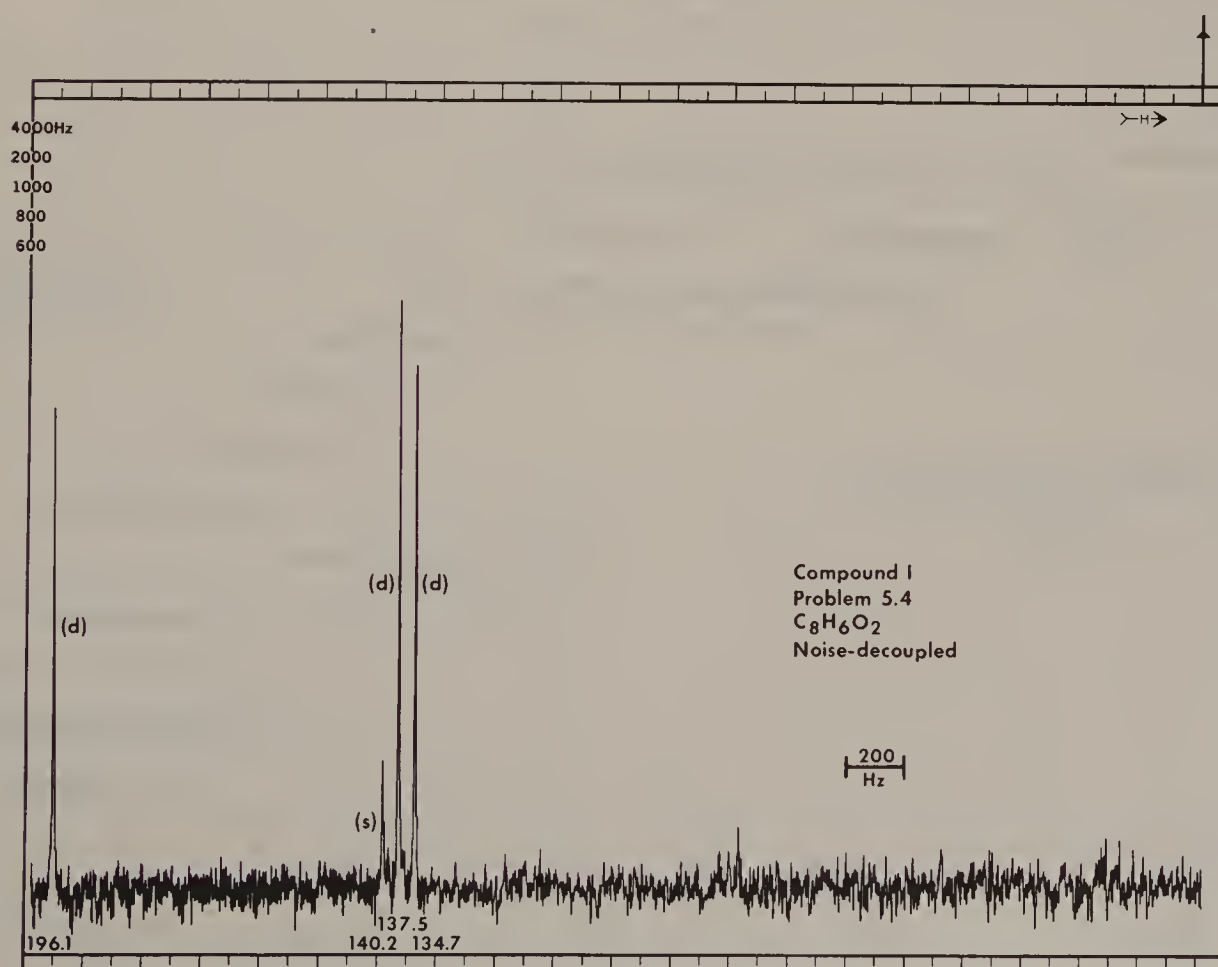
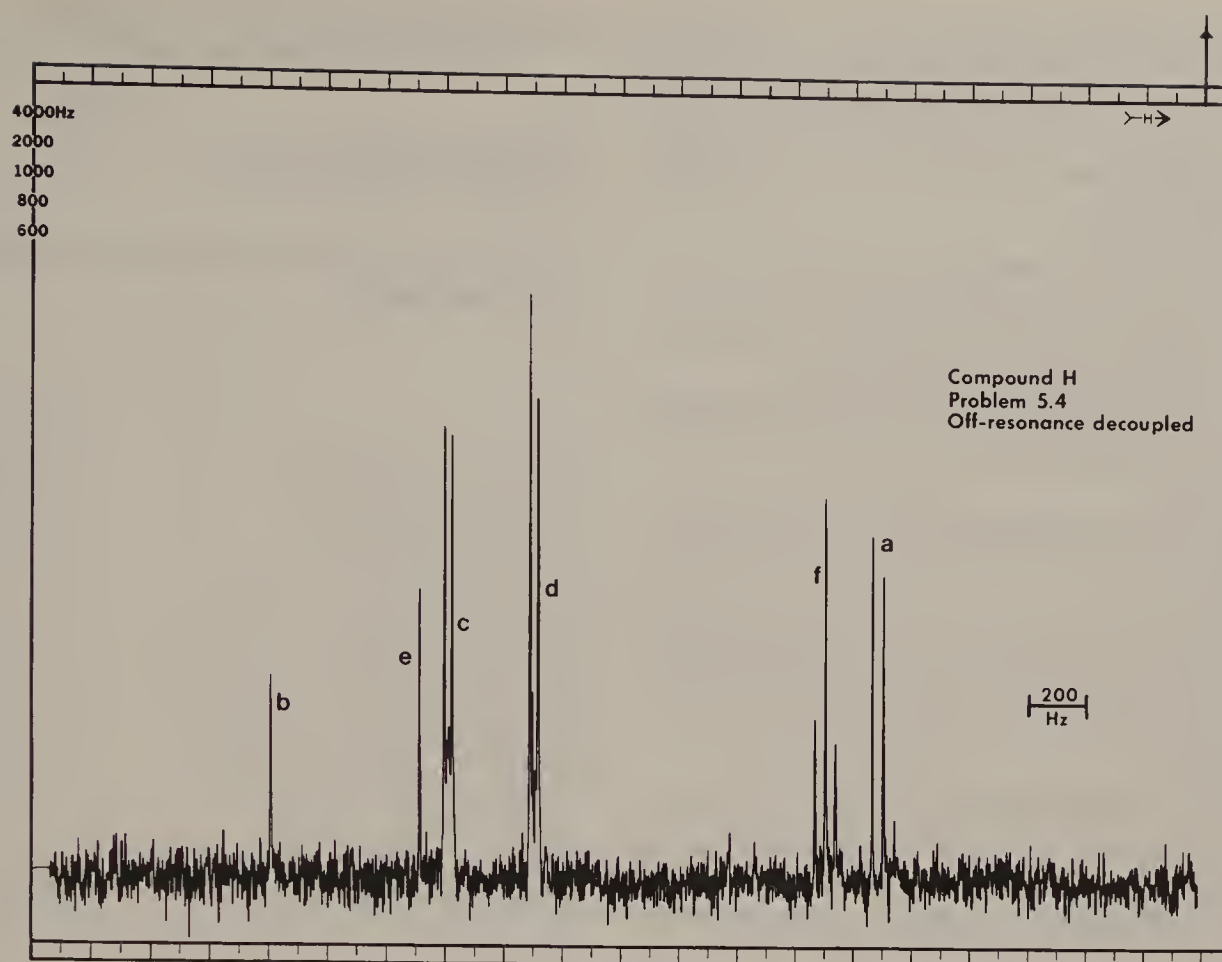












5.5 For each structure represented by the molecular formula, the  $^{13}\text{C}$  peak shifts in ppm and the relative intensities in the noise-decoupled spectrum are given. The multiplicity of each peak in the off-resonance decoupled spectrum is shown as s, a, t, or q. Determine the structure.

- $\text{C}_8\text{H}_{14}\text{O}_3$ . 13.5 ppm (98, q), 18.1 ppm (95, t), 37.3 ppm (91, t), 169.6 ppm (34, s).
- $\text{C}_7\text{H}_{12}\text{O}_4$ . 14.2 ppm (80, q), 41.7 ppm (50, t), 61.4 ppm (100, s), 166.8 ppm (52, s).
- $\text{C}_{13}\text{H}_{12}\text{O}$ . 76.9 ppm (24, d), 128.3 ppm (99, d), 127.4 ppm (57, d), 129.3 ppm (87, d), 144.7 (12, s).
- $\text{C}_5\text{H}_6\text{O}_4$ . 38.2 ppm (100, t), 128.3 ppm (84, t), 136.1 ppm (99, s), 168.2 ppm (77, s), 172.7 (78, s).
- $\text{C}_9\text{H}_{10}\text{O}$ . 63.1 ppm (49, t), 126.4 ppm (98, ?), 127.5 ppm (44, ?), 128.5 ppm (87, ?), 128.7 ppm (60, ?), 130.7 ppm (42, d), 136.8 ppm (11, s).

5.6 Compare diethyl phthalate to the *meta* and *para* isomers with respect to the "carbon count" from the noise-decoupled spectrum, and the "proton count" from the off-resonance decoupled spectrum; that is,

show how molecular symmetry leads to unique spectral results for each compound.

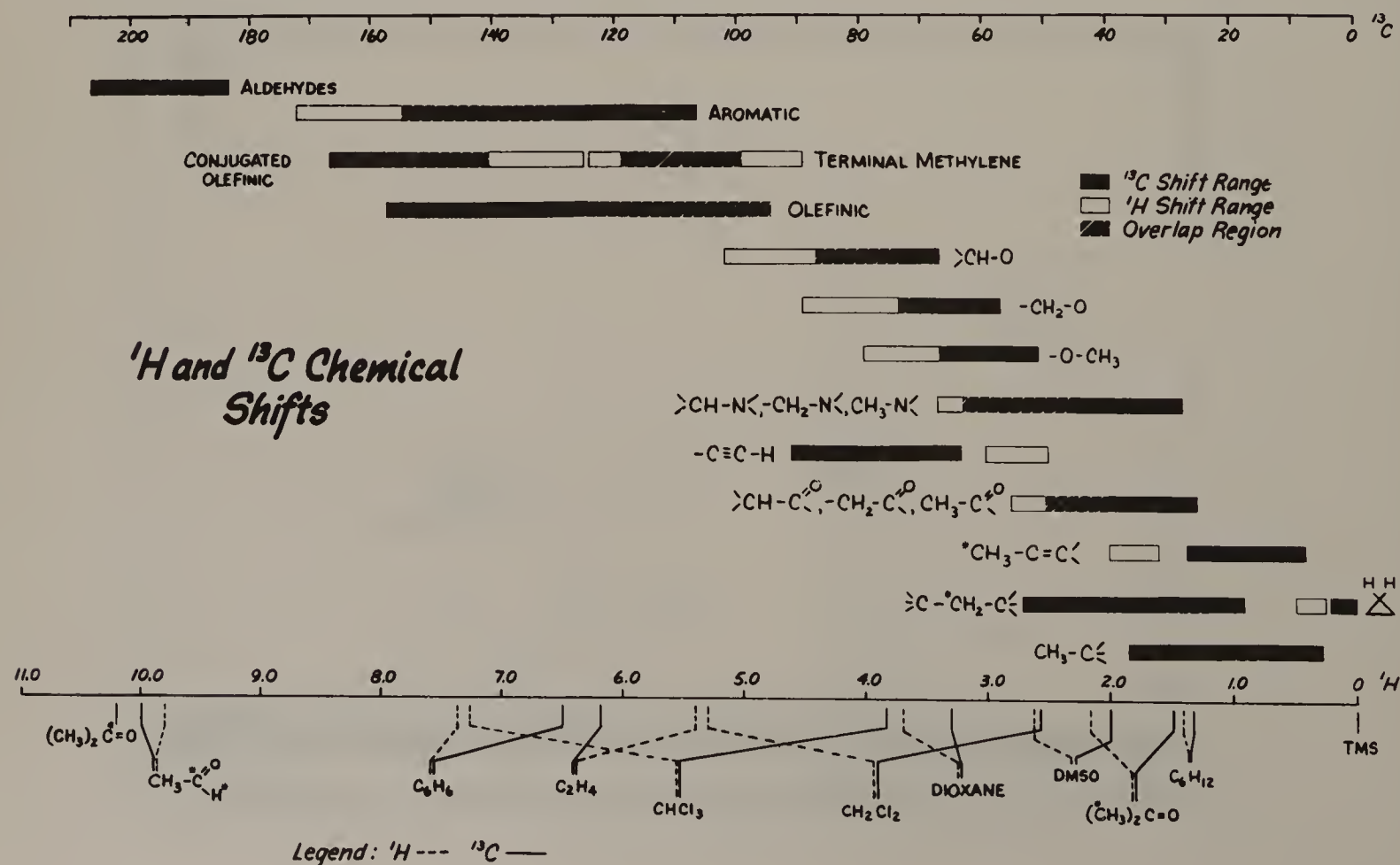
## appendix a

$^{13}\text{C}$  Chemical Shifts for Common Deuterated Solvents (neat, ppm from TMS)

|   | Shift               | Multiplicity |
|---|---------------------|--------------|
| Acetic Acid $\text{CD}_3\text{COOD}$          | 178.4, 20.0         | 1, 7         |
| Acetone $(\text{CD}_3)_2\text{CO}$            | 206.0, 29.8         | 1, 7         |
| Acetonitrile $\text{CD}_3\text{CN}$           | 117.7, 1.3          | 1, 7         |
| Benzene $\text{C}_6\text{D}_6$                | 128.5               | 1            |
| (Carbon tetrachloride $\text{CCl}_4$ )        | 96.0                | 1            |
| Chloroform $\text{CDCl}_3$                    | 77.0                | 3            |
| Dimethyl sulfoxide $(\text{CD}_3)_2\text{SO}$ | 39.5                | 7            |
| Dioxane $\text{C}_4\text{D}_8\text{O}_2$      | 67.4                | 1            |
| Methanol $\text{CD}_3\text{OD}$               | 49.0                | 7            |
| Methylene chloride $\text{CD}_2\text{Cl}_2$   | 53.8                | 5            |
| Nitromethane $\text{CD}_3\text{NO}_2$         | 57.3                | 7            |
| Pyridine $\text{C}_5\text{D}_5\text{N}$       | 149.9, 135.5, 123.5 | 3, 3, 3      |
| (Carbon disulfide $\text{CS}_2$ )             | 192.8               | 1            |

## appendix b. comparison of $^1\text{H}$ and $^{13}\text{C}$ chemical shifts.

From *Application of Fourier Transform NMR to Carbon-13*,  
Varian Associates Lecture Booklet, 1974. Reprinted with permission.

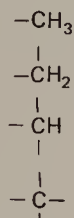


# appendix c. $^{13}\text{C}$ correlation chart for chemical classes.

R = H or alkyl substituents  
Y = polar substituents

$^{13}\text{C}$  Correlation Chart for Chemical Classes

Acyclic hydrocarbons

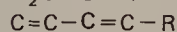
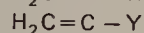
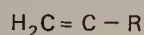


Alicyclic hydrocarbons



$\text{C}_4\text{H}_8$  to  $\text{C}_{10}\text{H}_{20}$

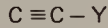
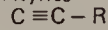
Alkenes



Allenes



Alkynes



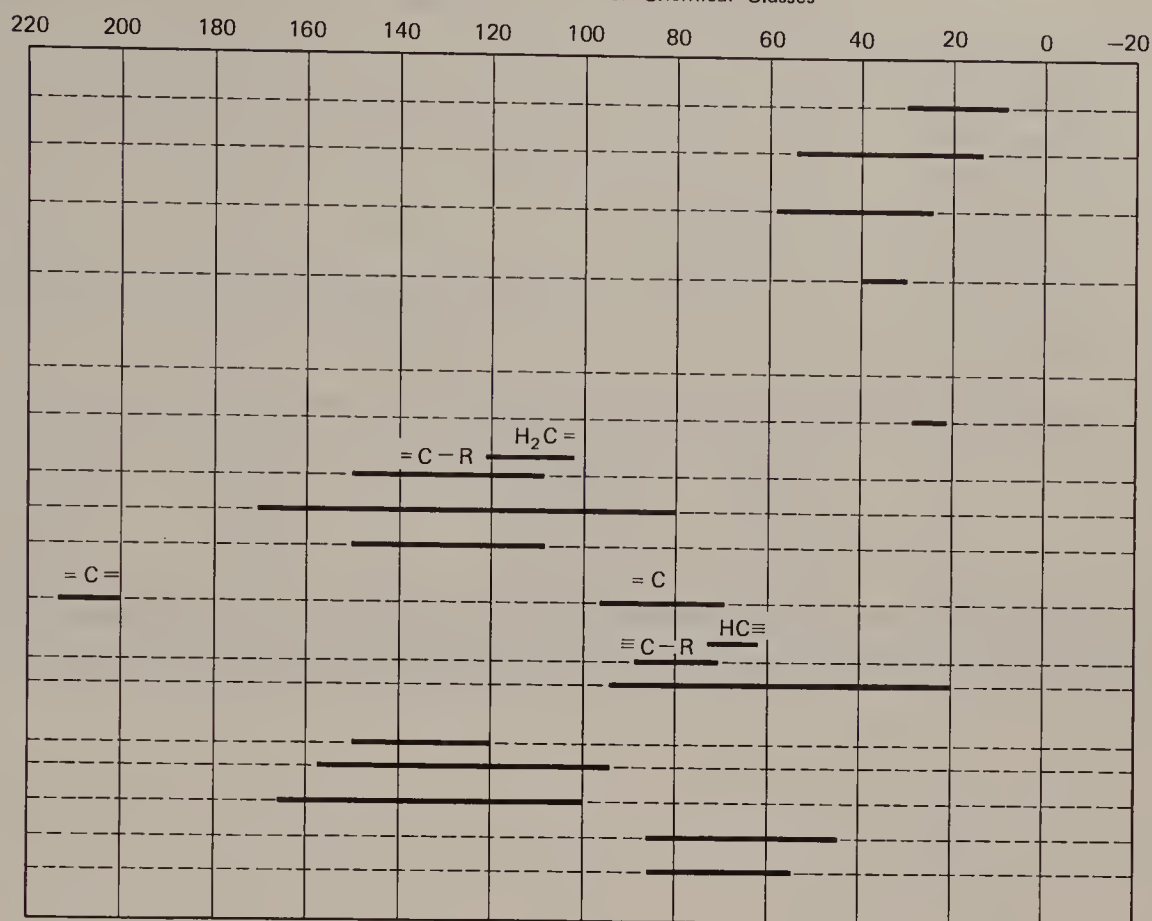
Aromatics



Heteroaromatics

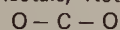
Alcohols  $\text{C}-\text{OH}$

Ethers  $\text{C}-\text{O}-\text{C}$

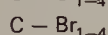
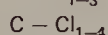
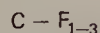


220 200 180 160 140 120 100 80 60 40 20 0 -20

Acetals, Ketals



Halides



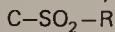
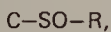
Amines  $\text{C}-\text{NR}_2$

Nitro  $\text{C}-\text{NO}_2$

Mercaptans, Sulfides



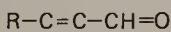
Sulfoxides, Sulfones



Aldehydes, sat.



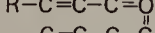
Aldehydes,  $\alpha$ ,  $\beta$ -unsat.



Ketones, sat.



Ketones,  $\alpha$ ,  $\beta$ -unsat.

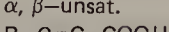


Carboxylic acids, sat.

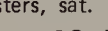


Salts  $\text{RCOO}^-$

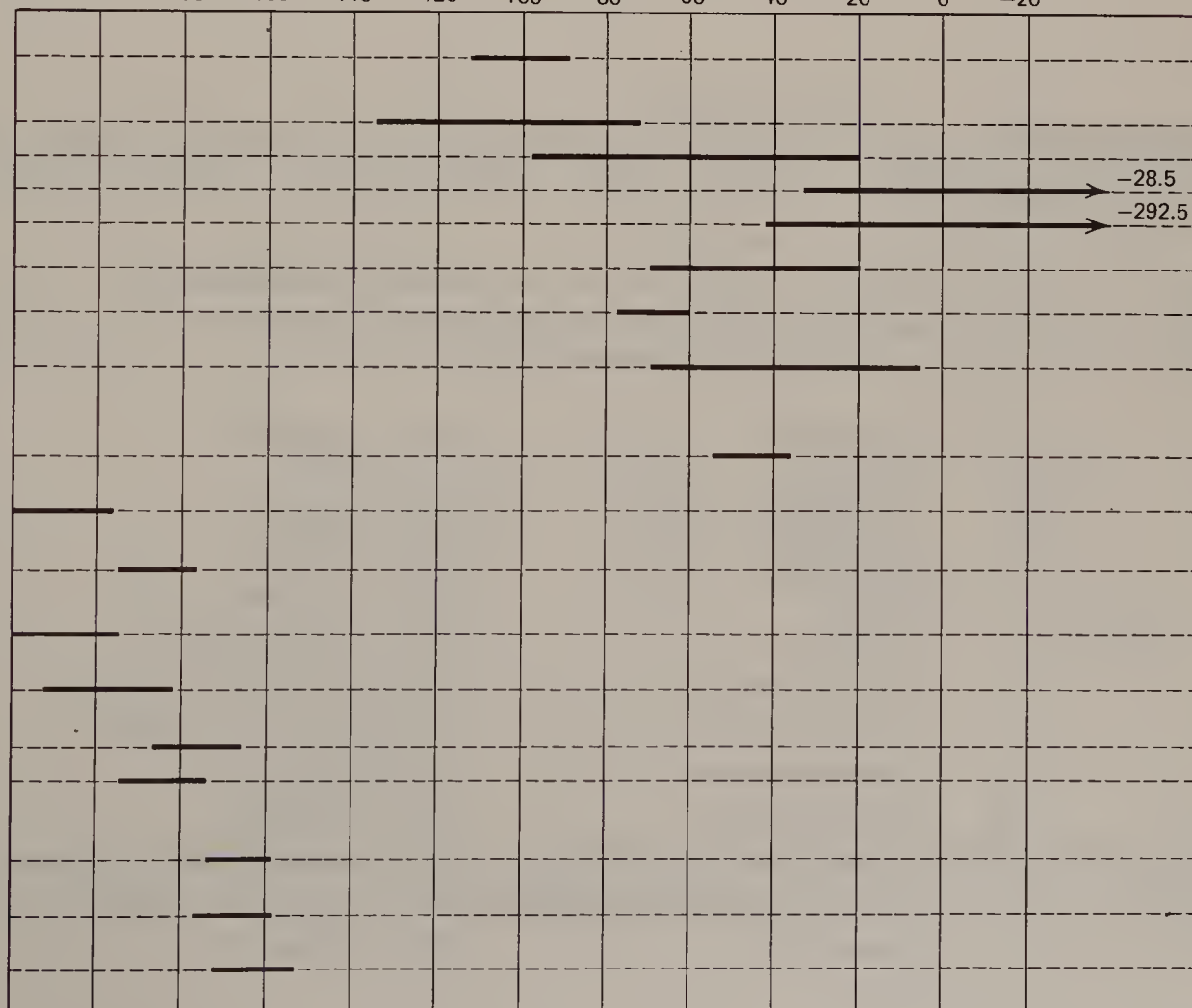
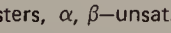
Carboxylic acids,  $\alpha$ ,  $\beta$ -unsat.



Esters, sat.

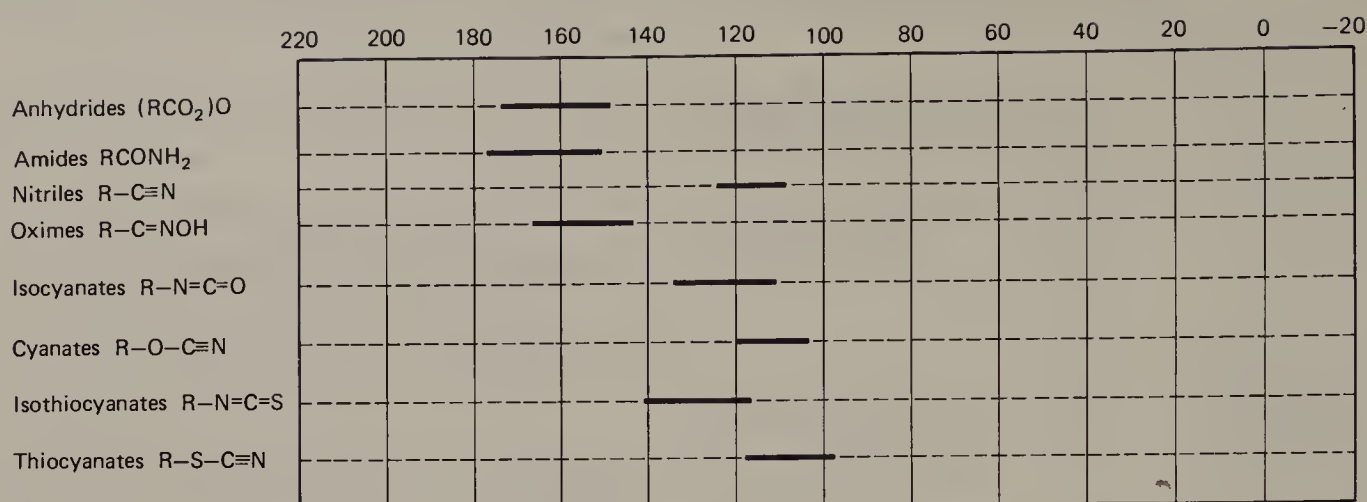


Esters,  $\alpha$ ,  $\beta$ -unsat.





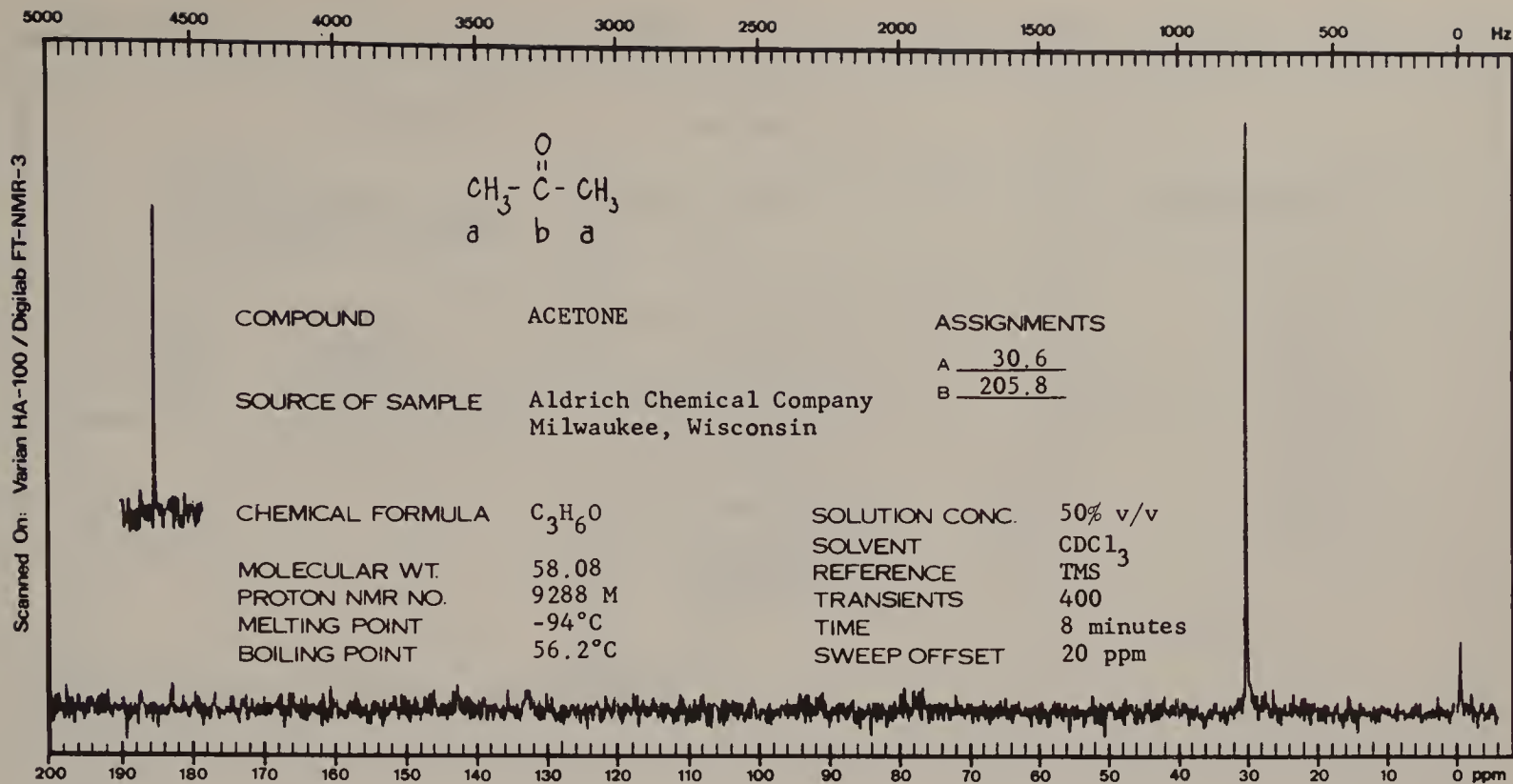
appendix c (continued)



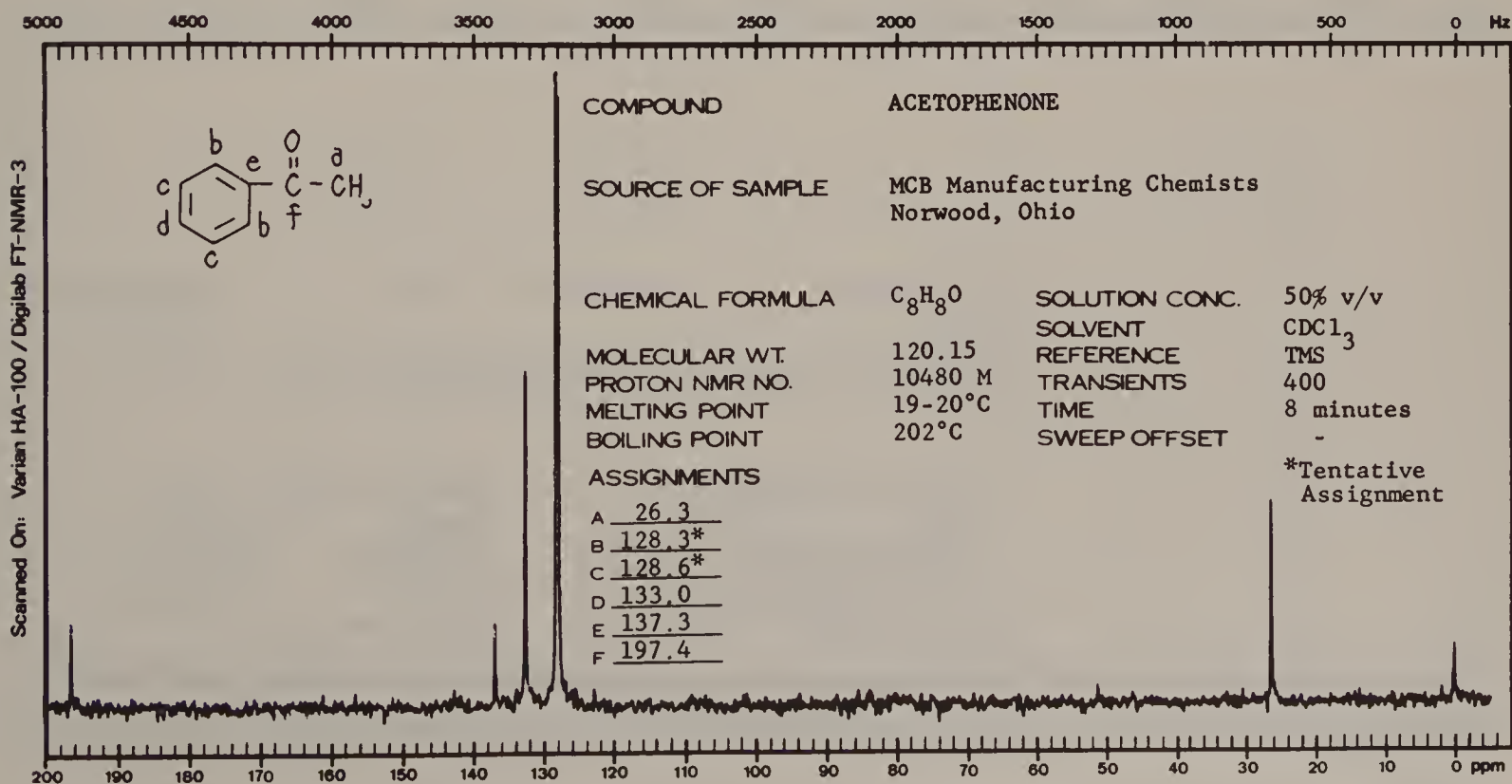
## appendix d. $^{13}\text{C}$ -NMR spectra of common organic compounds.

On the next several pages are  $^{13}\text{C}$ -NMR spectra of common organic compounds. All signals are assigned. Permission for the publication herein of Sadtler Spectra® has been granted, and all rights are reserved by Sadtler Laboratories, Inc.

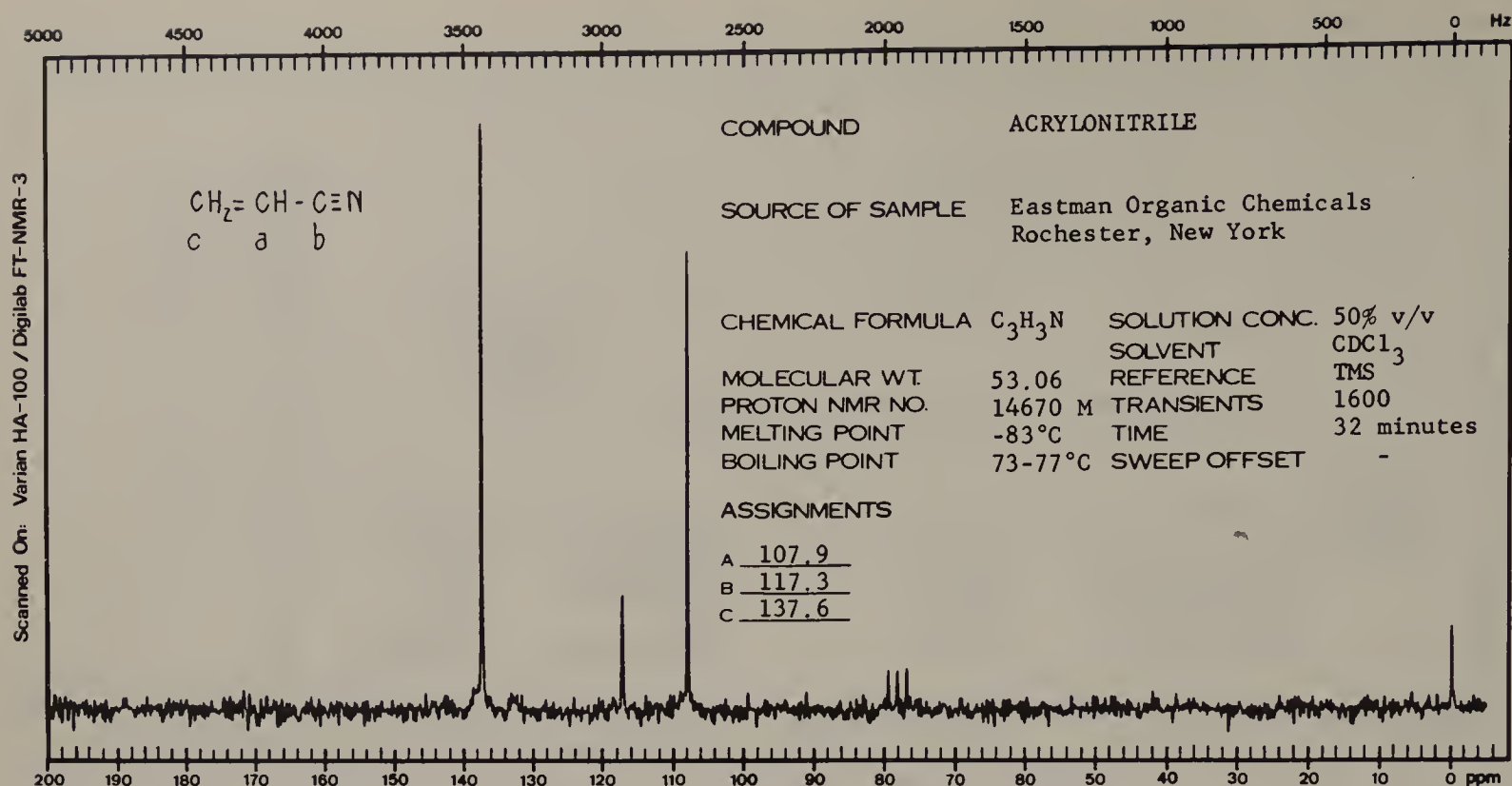
| No. | Compound                            | No. | Compound  |
|-----|-------------------------------------|-----|---|
| 1   | Acetone                             | 14  | Hexane  |
| 2   | Acetophenone                        | 15  | 1-Hexanol   |
| 3   | Acrylonitrile                       | 16  | Iodoethane  |
| 4   | Benzene                             | 17  | Methyl phenyl sulfide                               |
| 5   | Benzofuran                          | 18  | $\alpha$ -Methylstyrene                             |
| 6   | Bromocyclohexane                    | 19  | Myristic Acid, methyl ester                         |
| 7   | Cyclohexanone                       | 20  | Oxalic acid, diallyl ester                          |
| 8   | <i>p</i> -Dichlorobenzene           | 21  | Phenol  |
| 9   | Diethylene glycol                   | 22  | 3-Picoline  |
| 10  | Diphenylamine                       | 23  | Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) |
| 11  | <i>N,N</i> -Dimethylformamide (DMF) | 24  | Tetrahydrofuran (THF)                               |
| 12  | Dipropylamine                       | 25  | Toluene   |
| 13  | Furan                               |     |   |



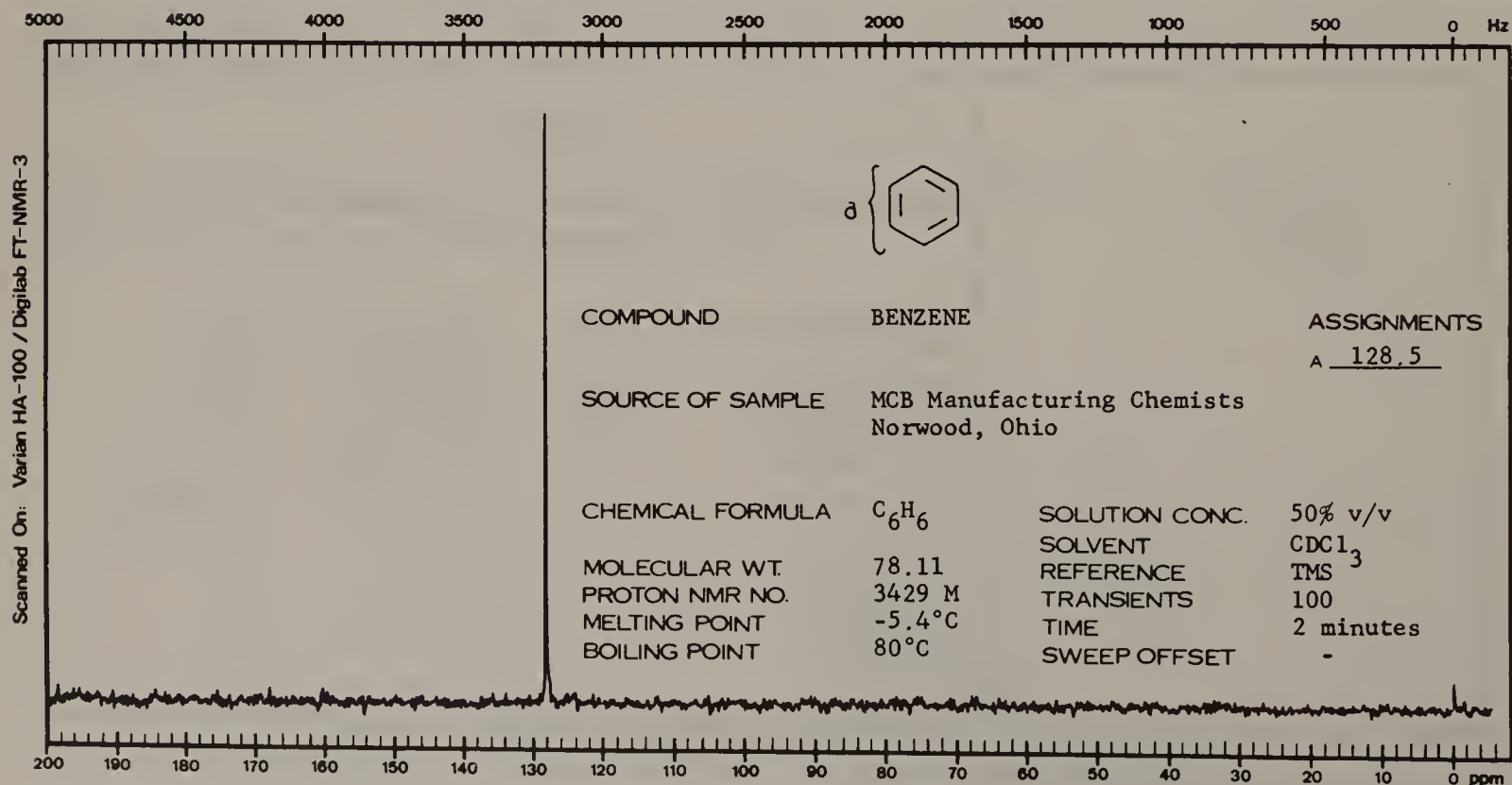
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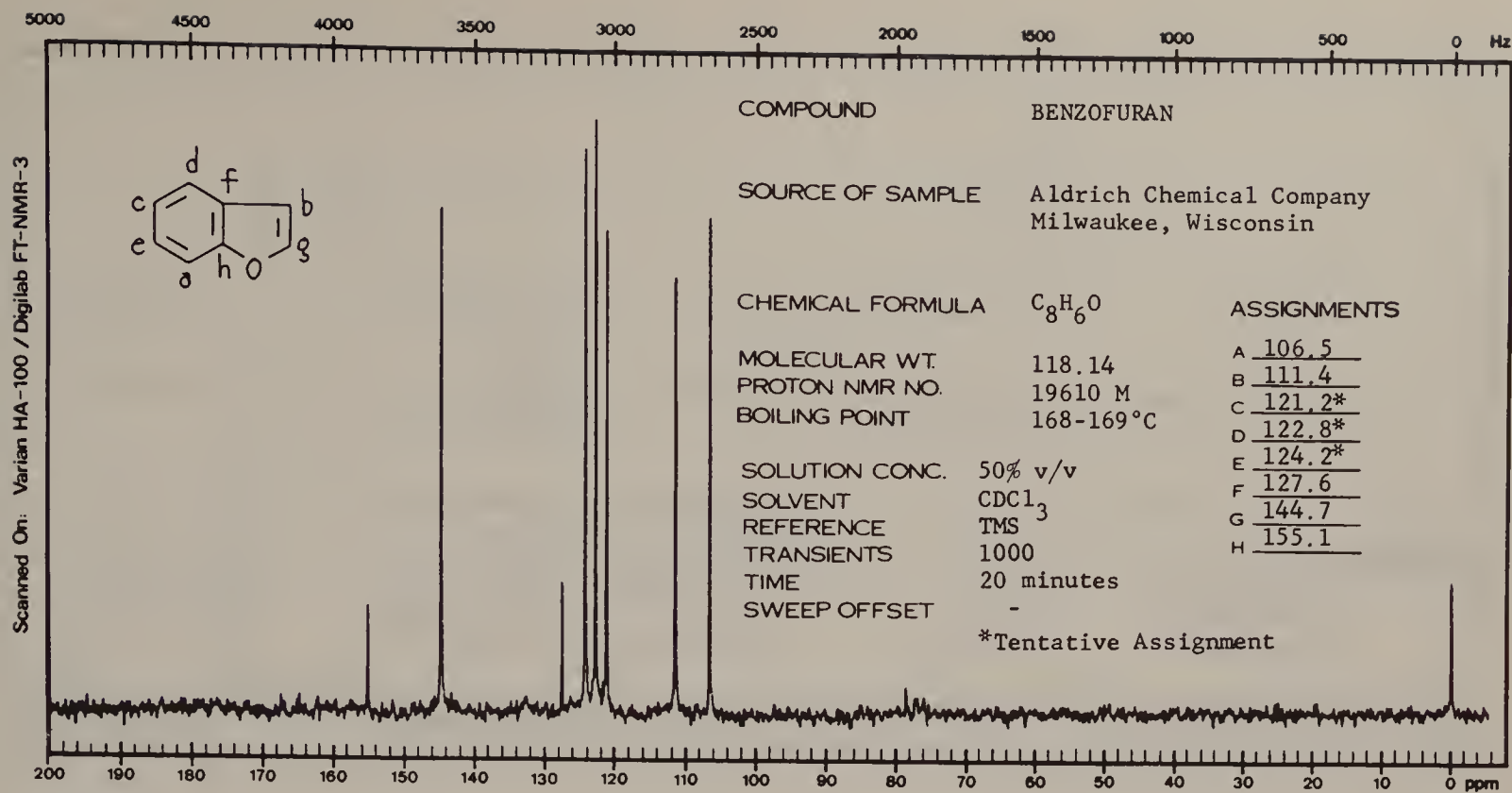


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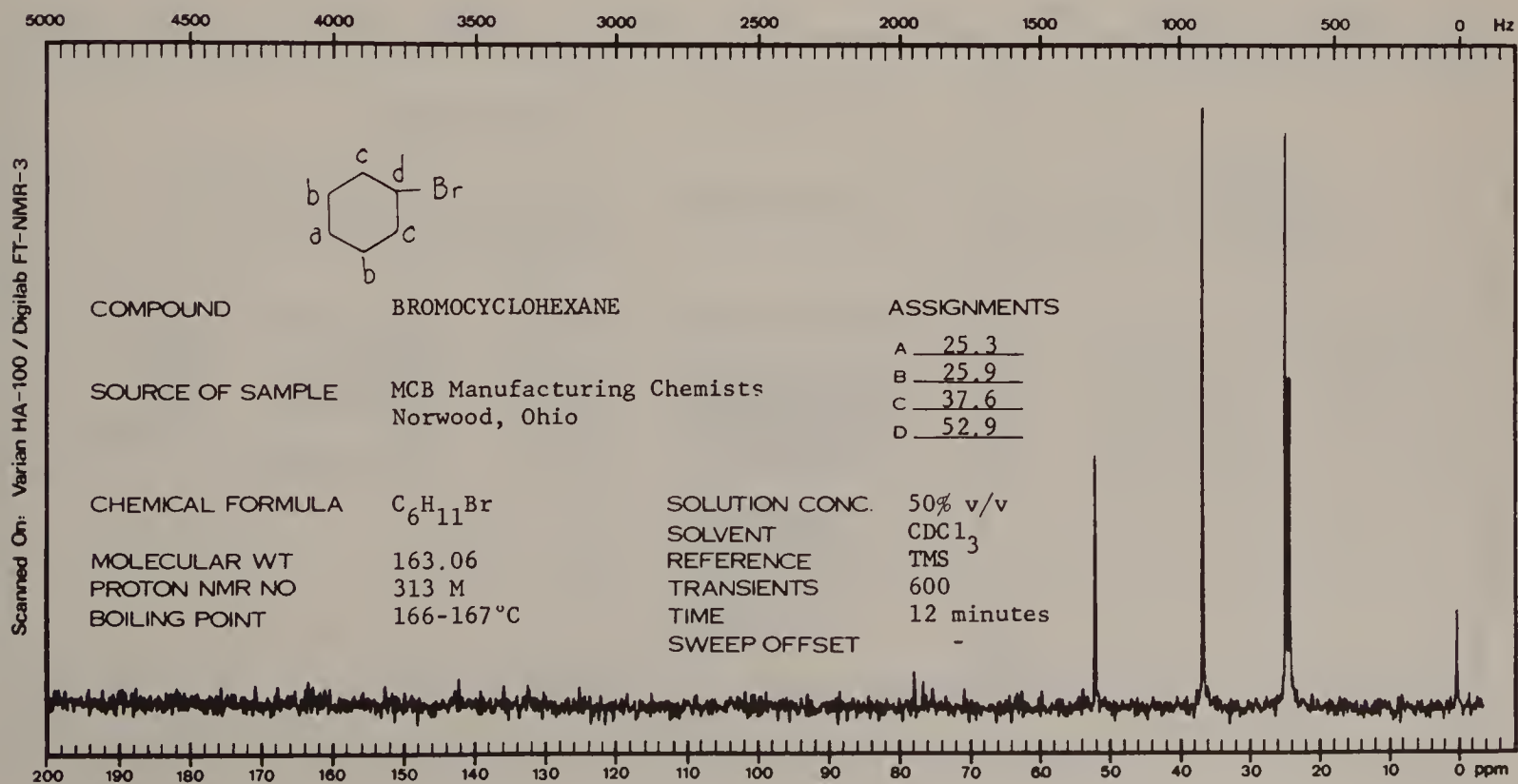


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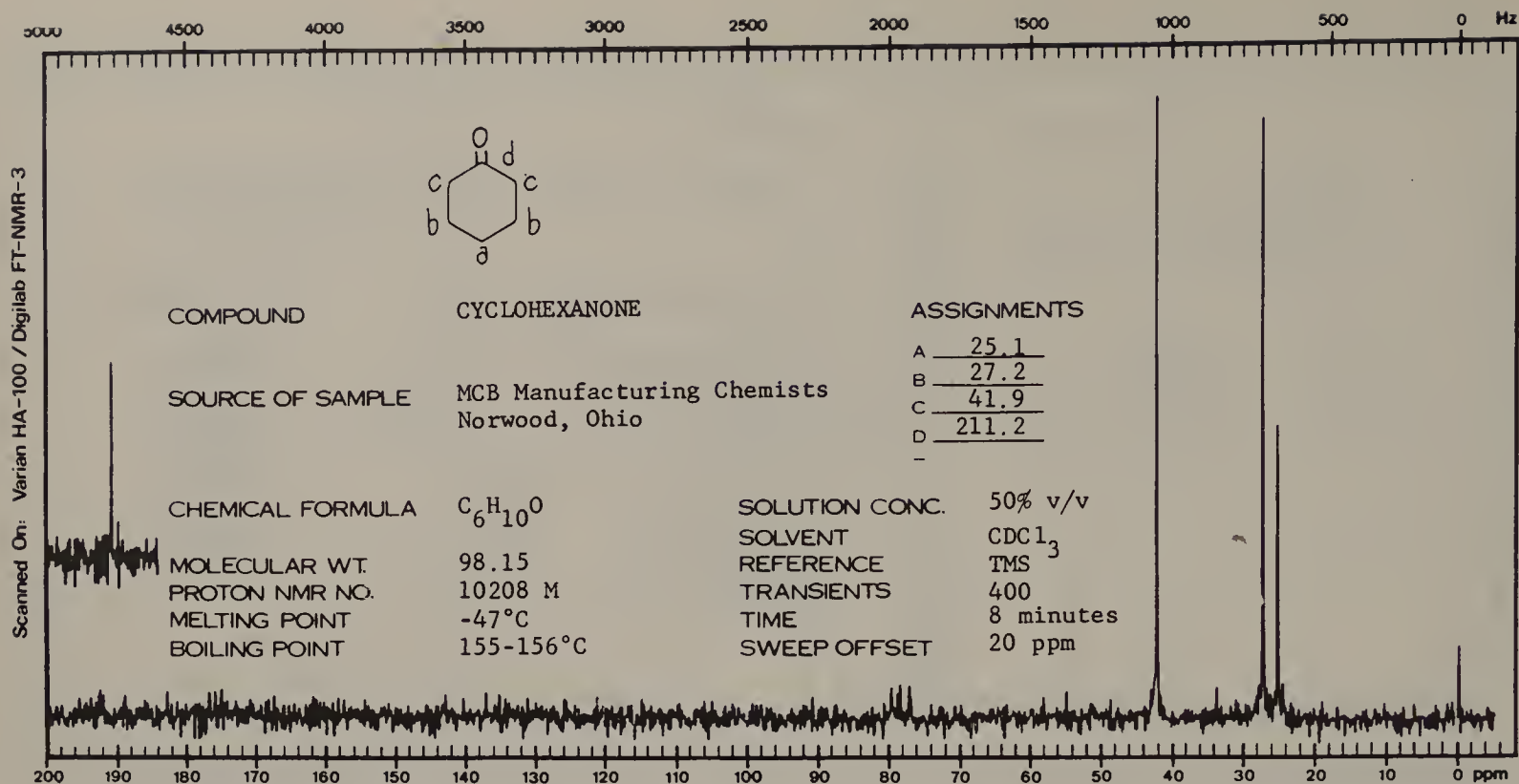




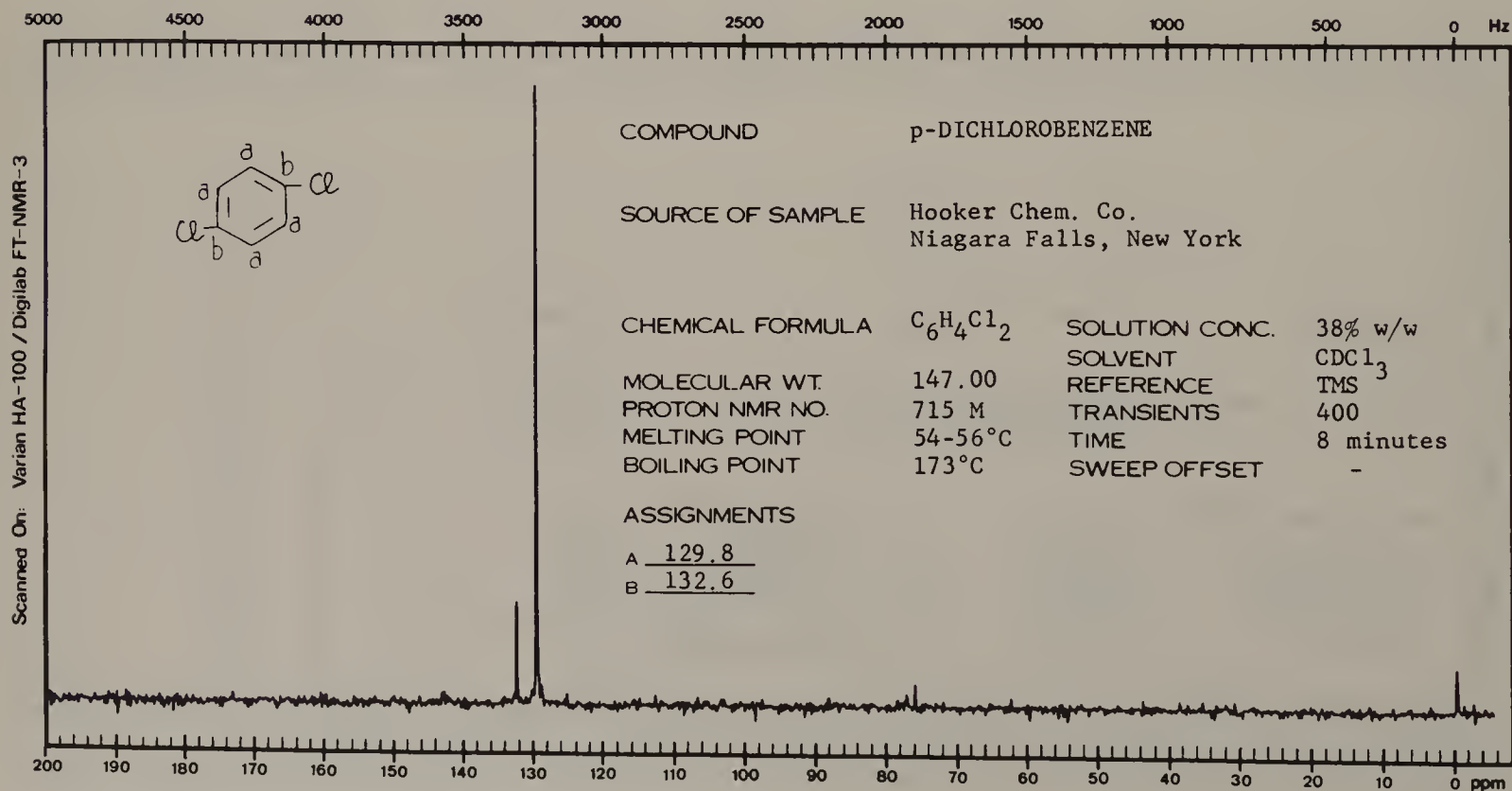
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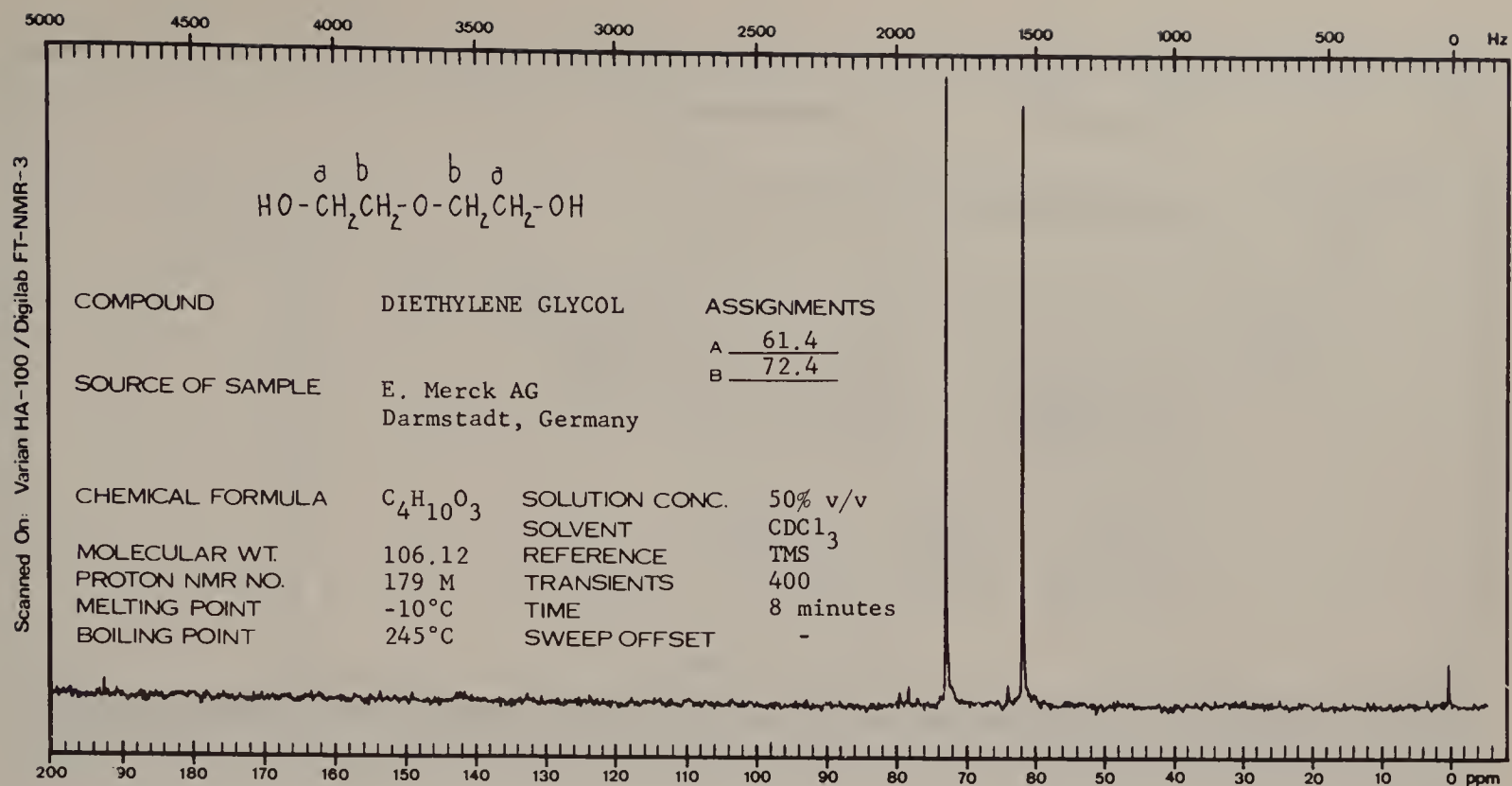
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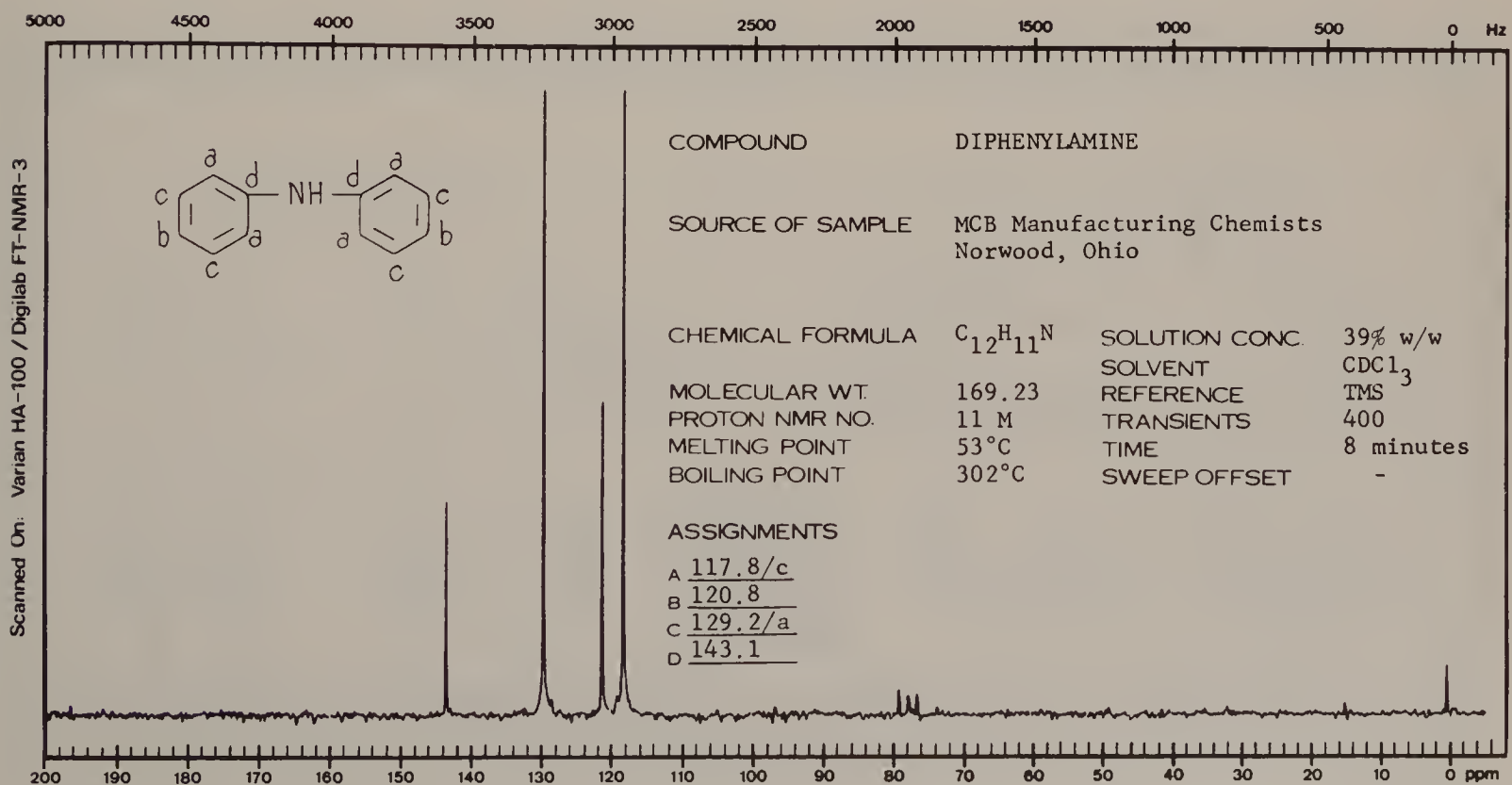
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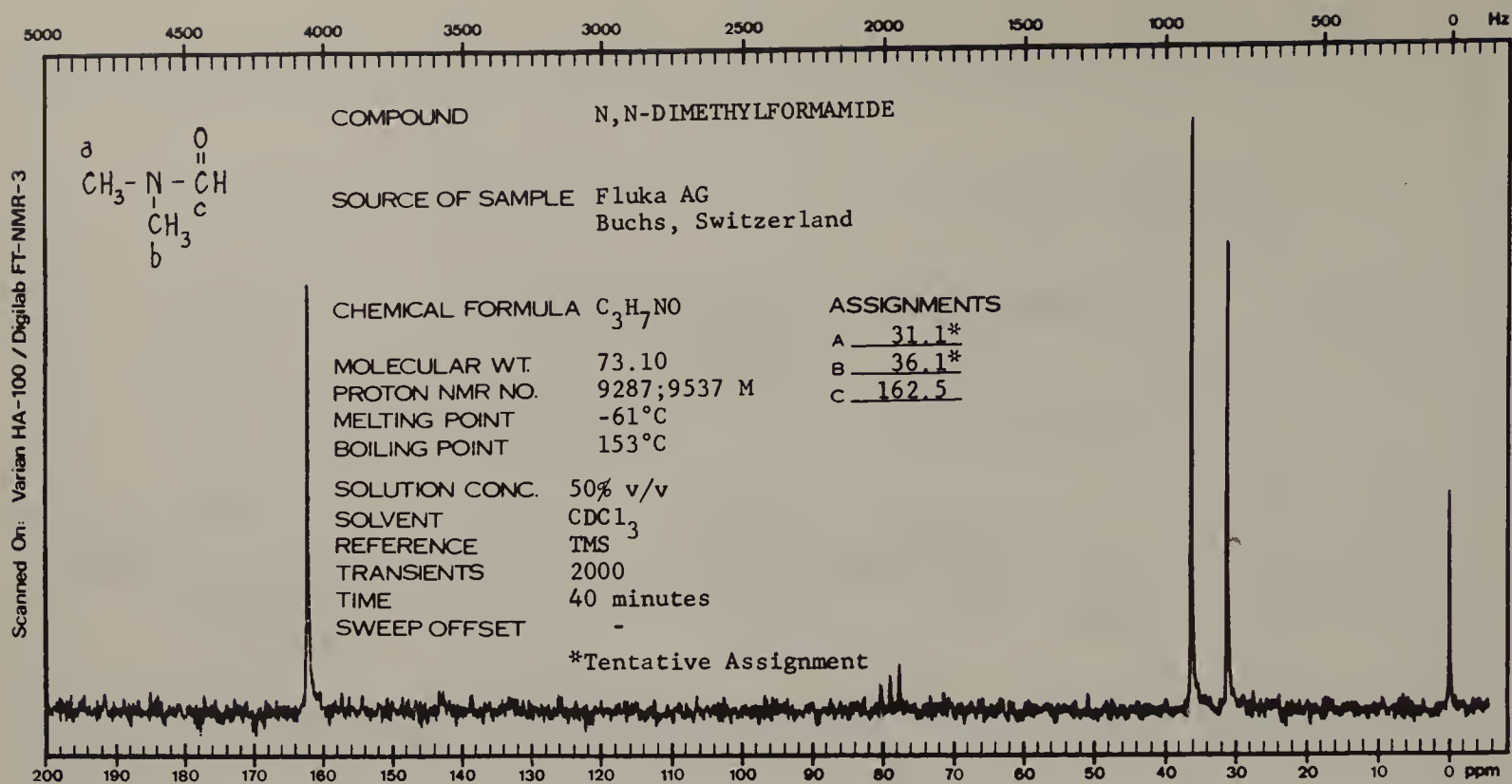


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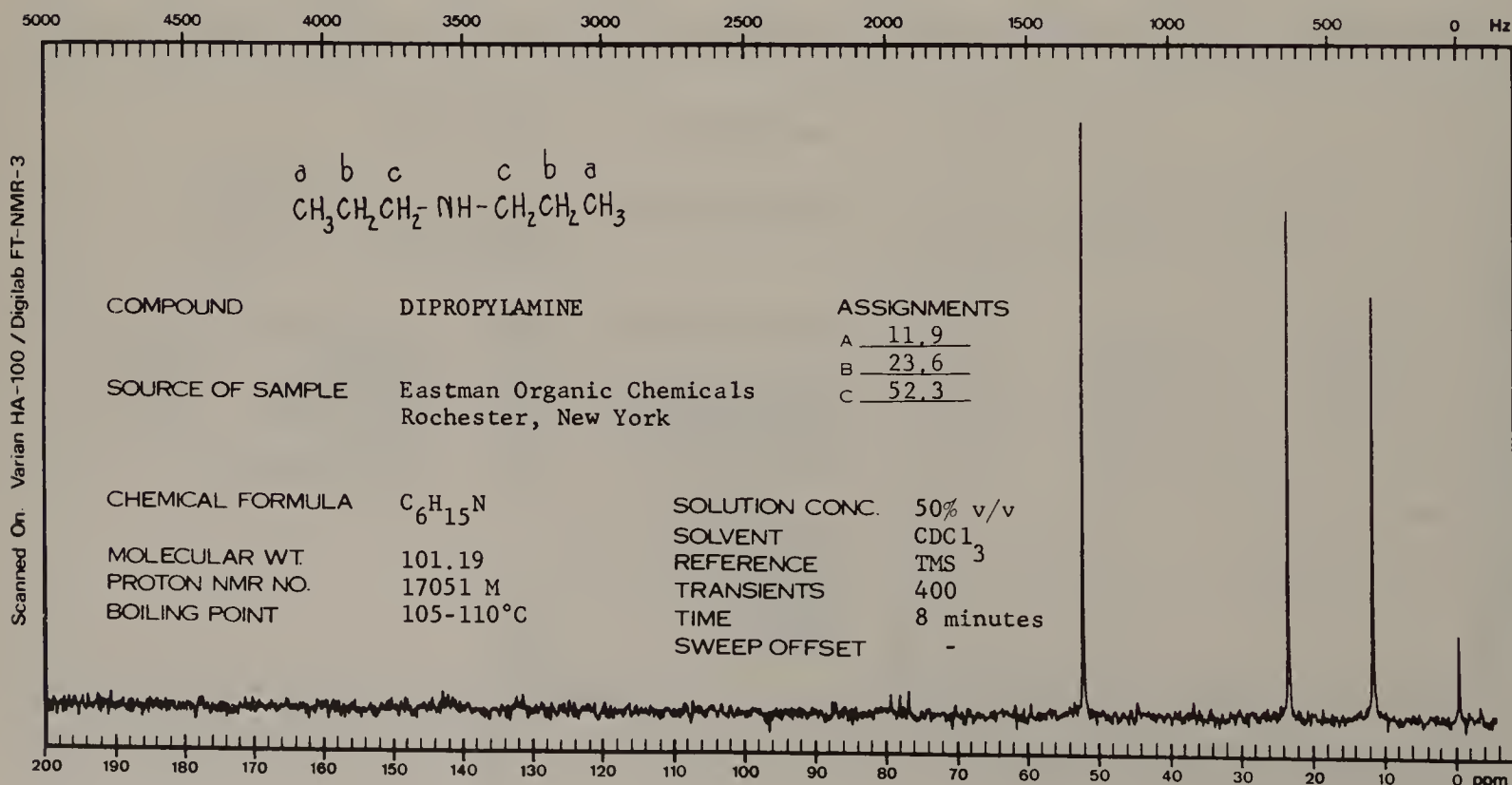


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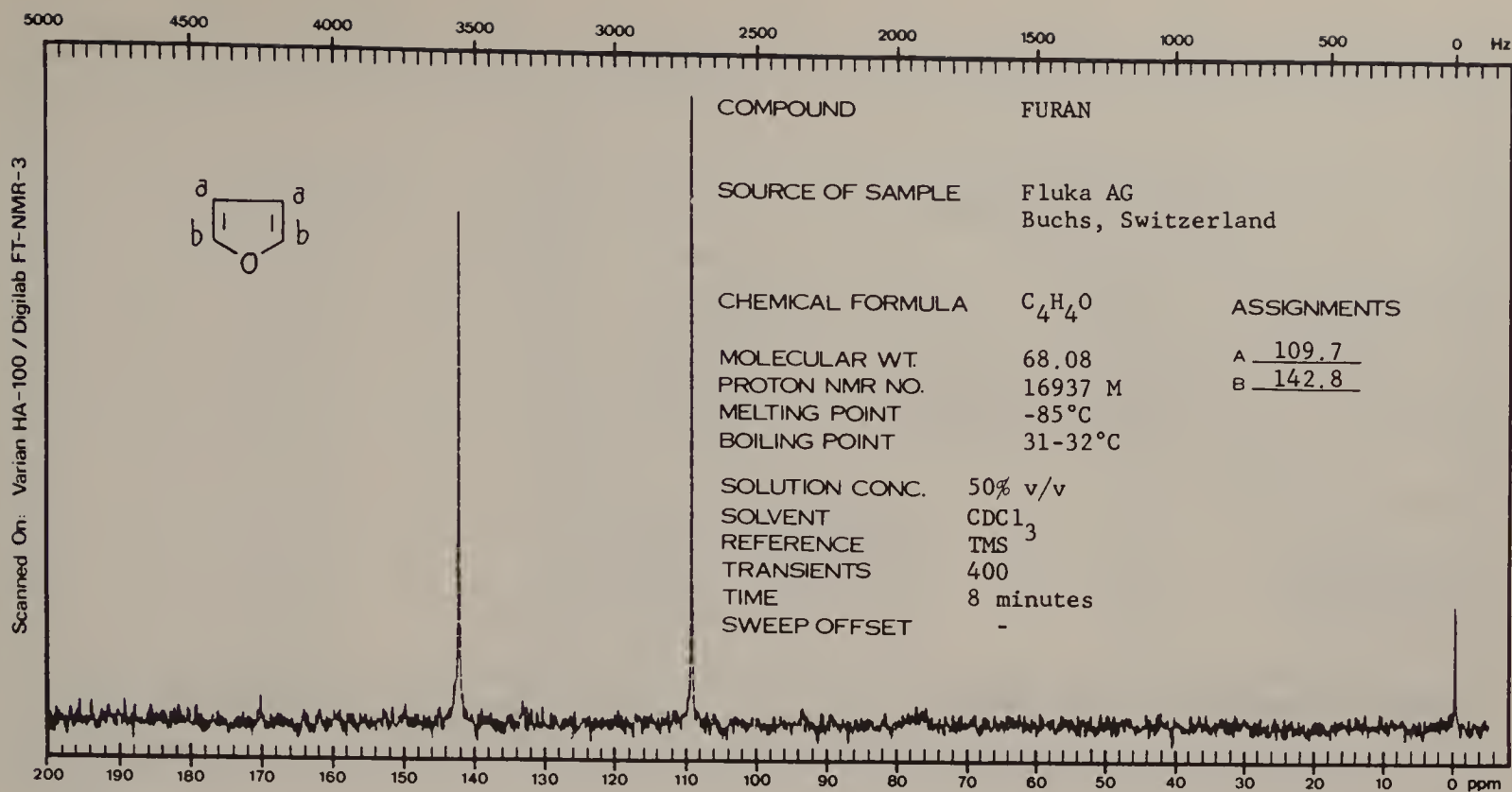




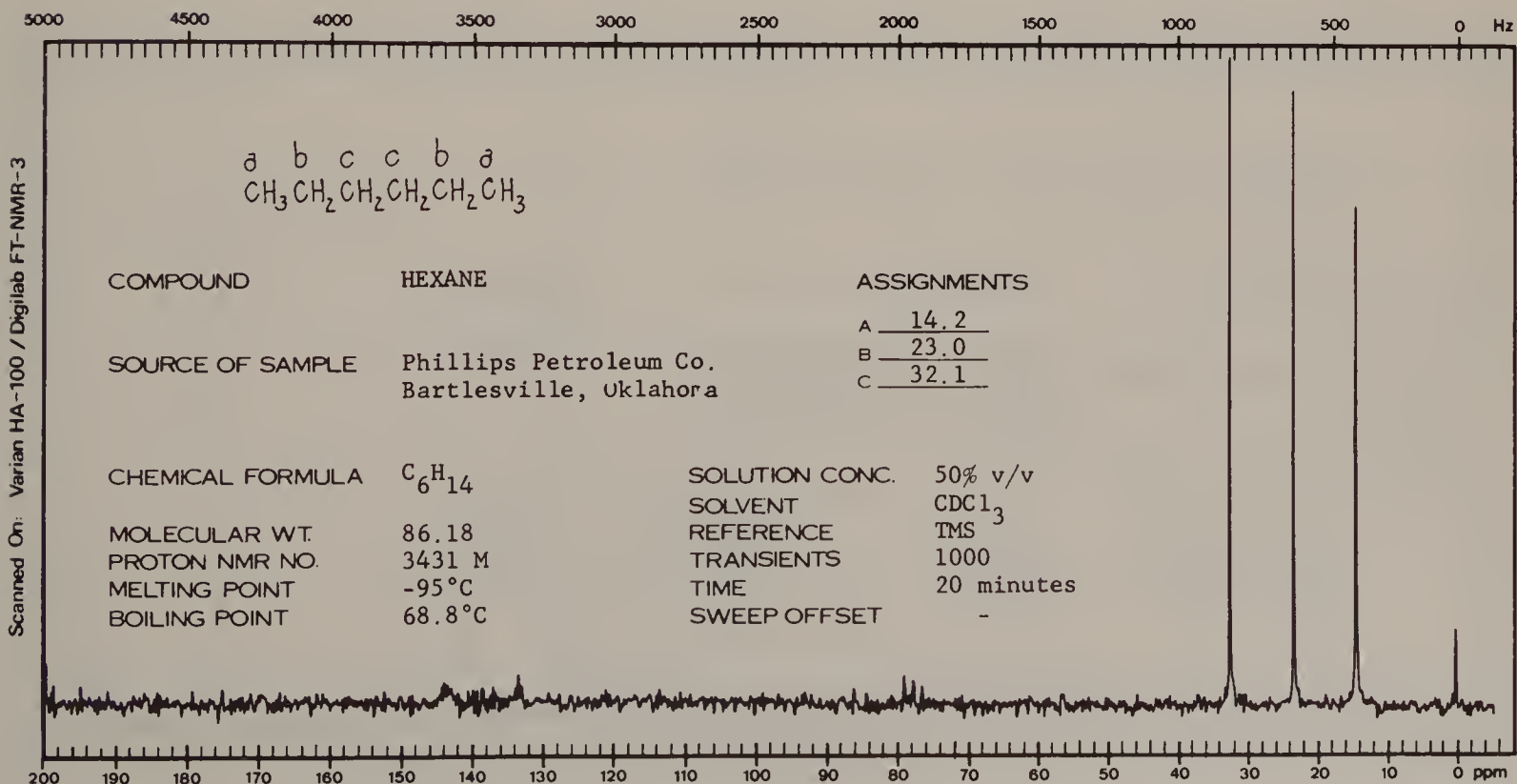
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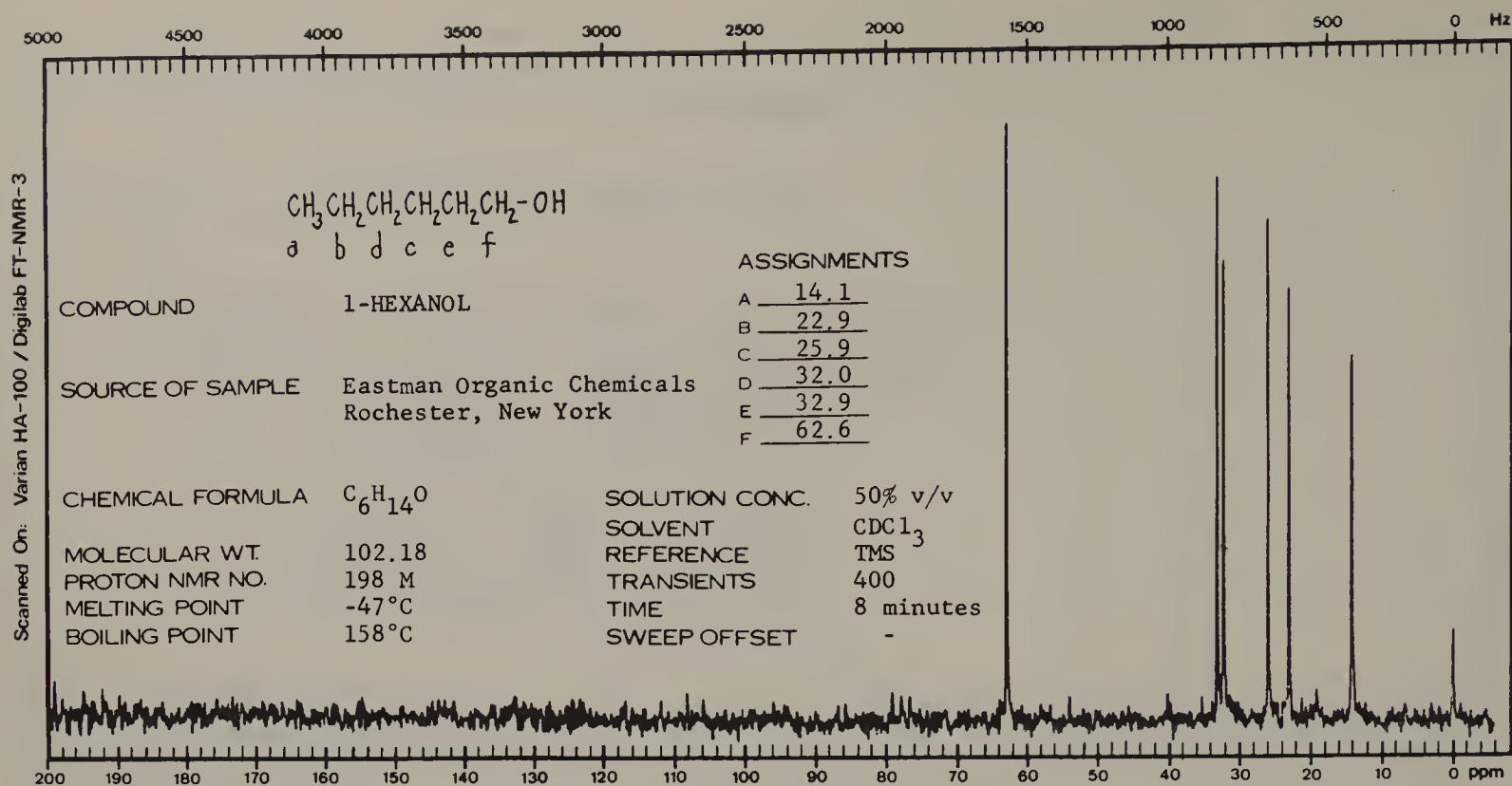
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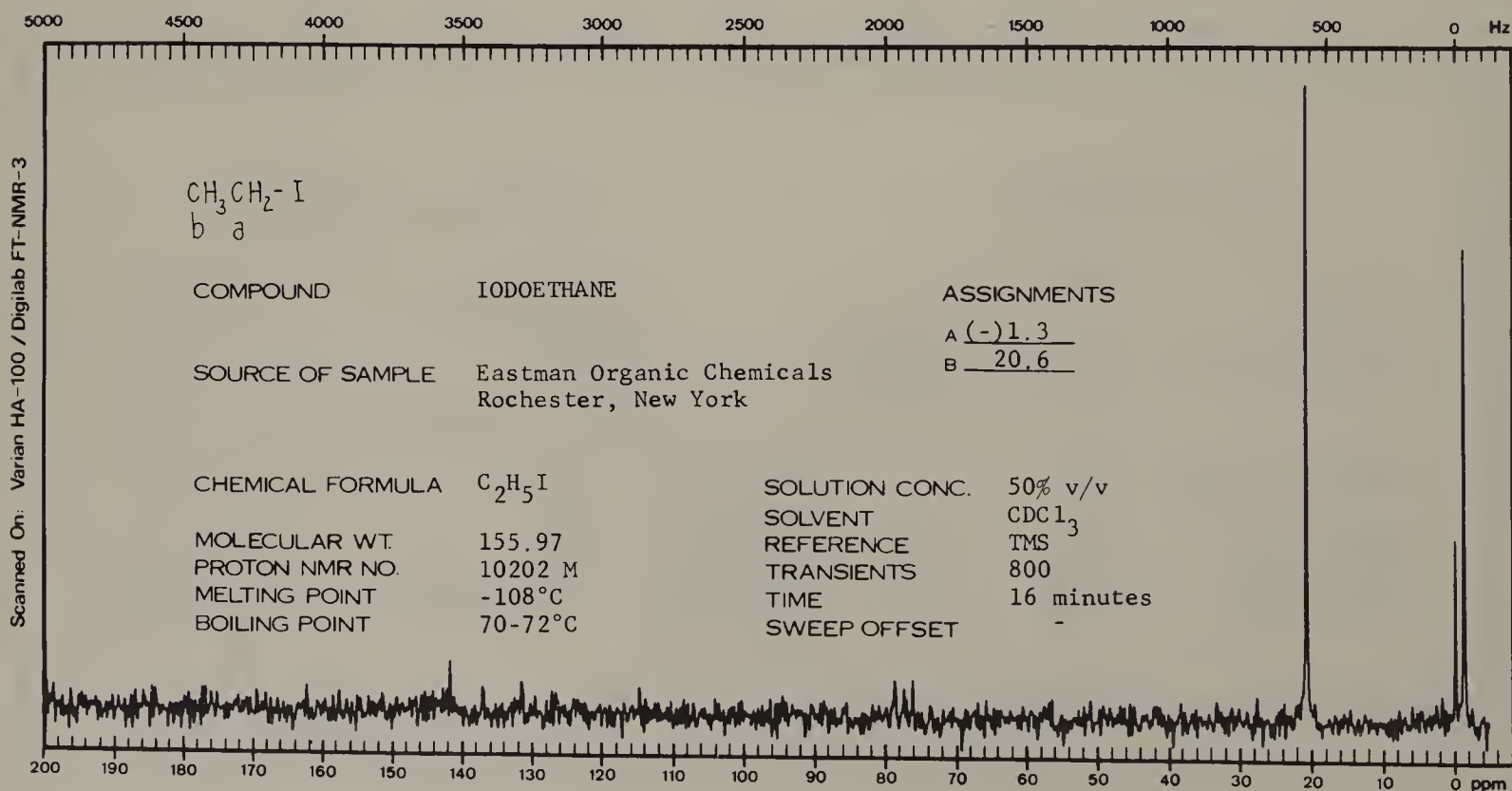
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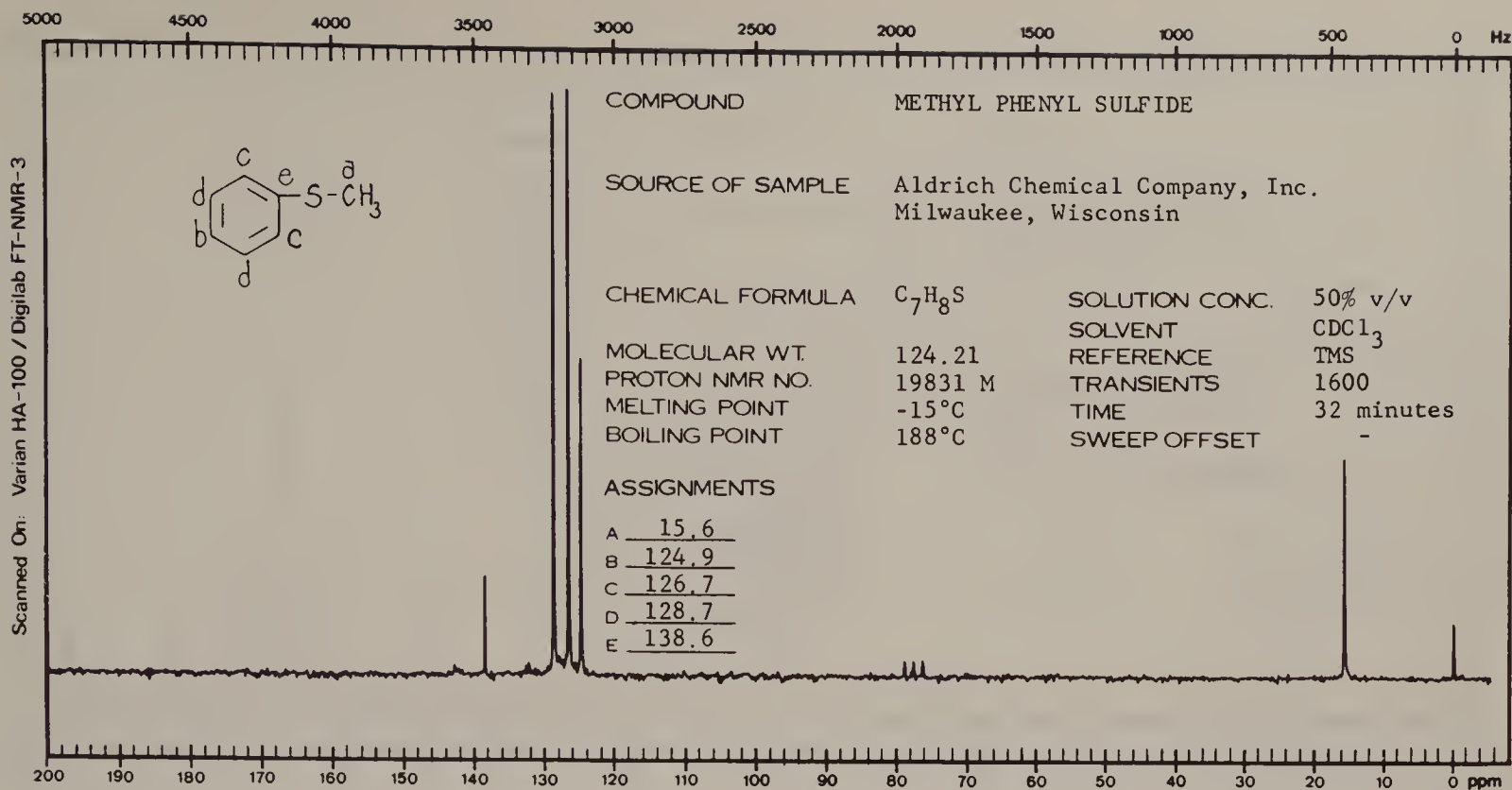


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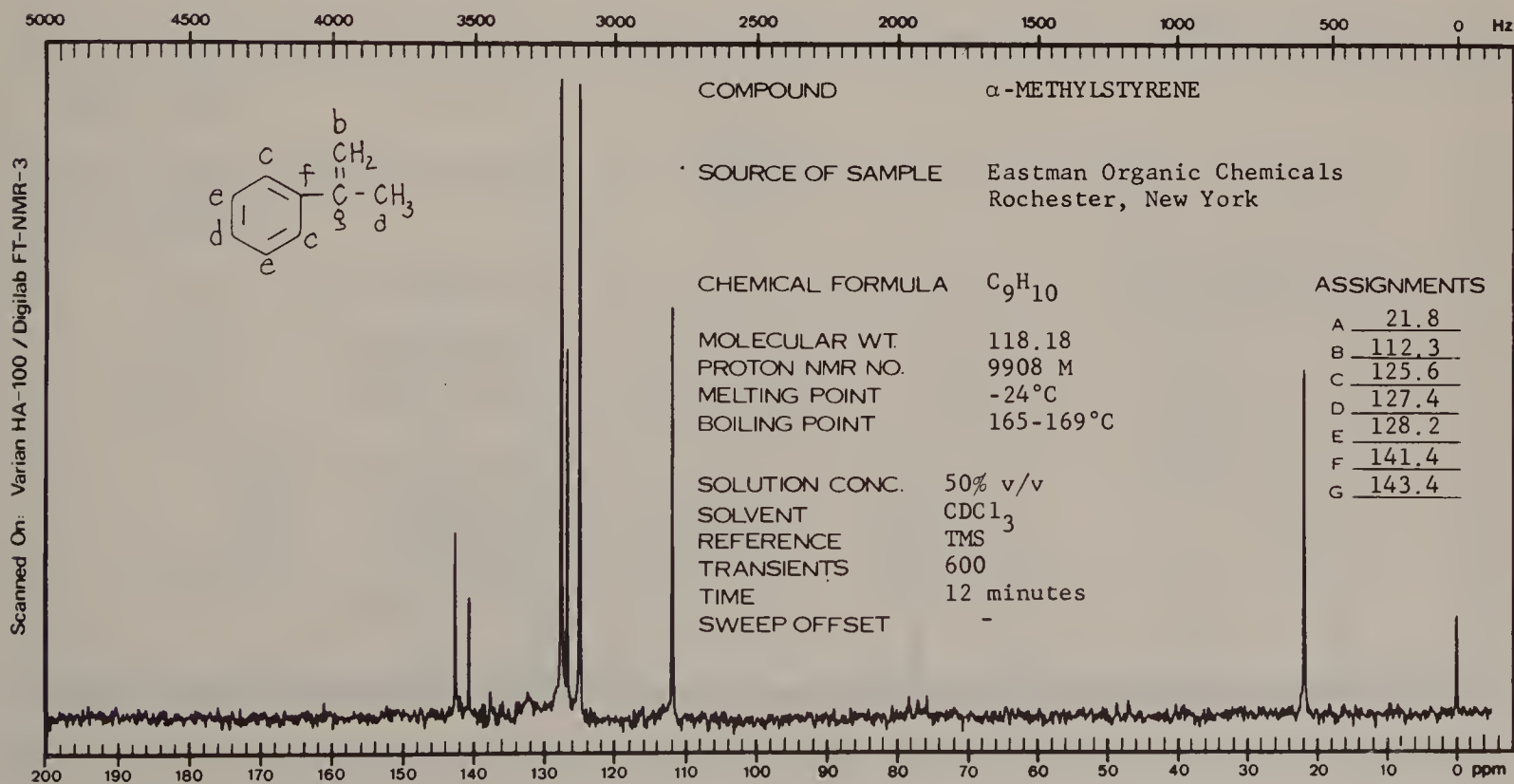


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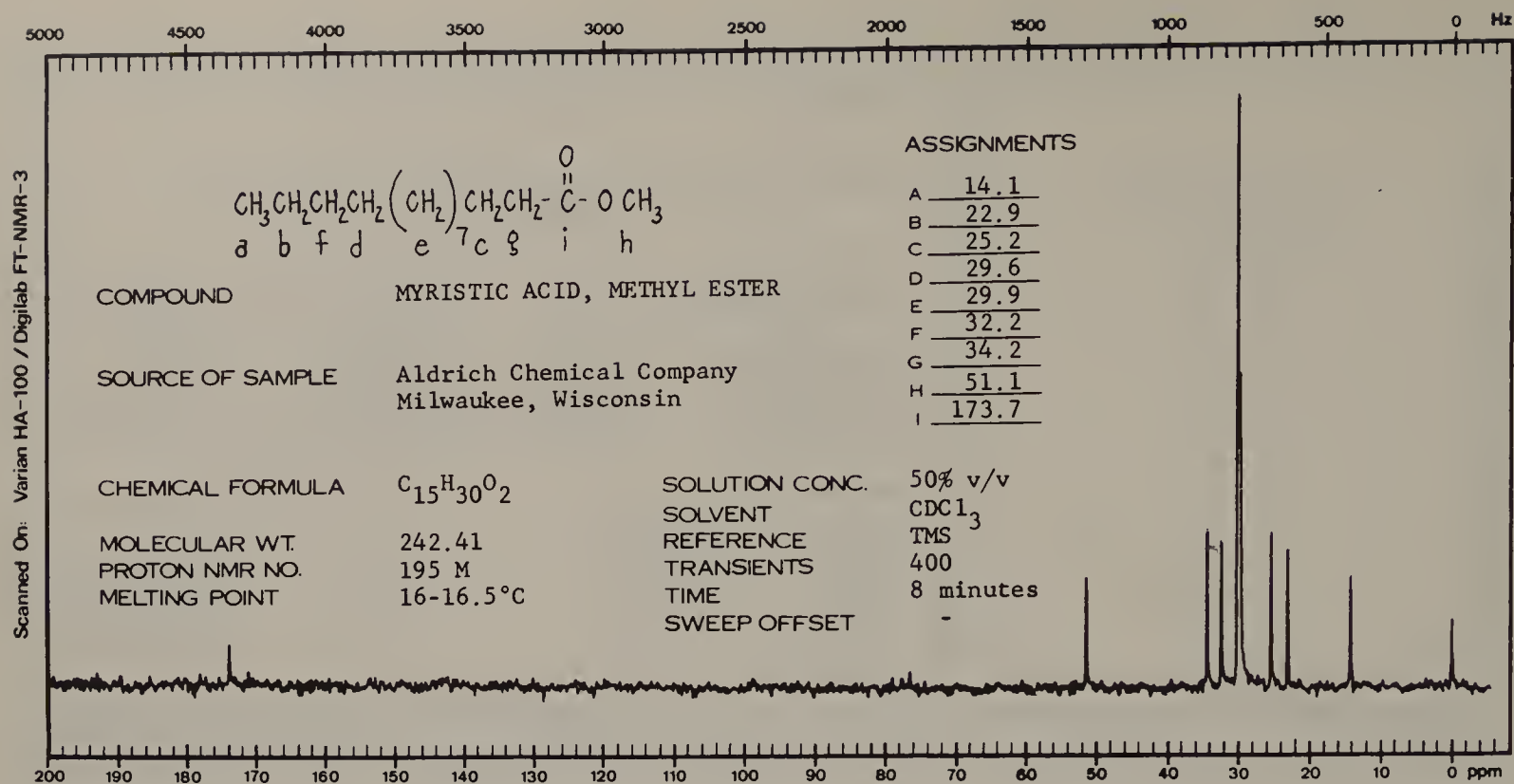




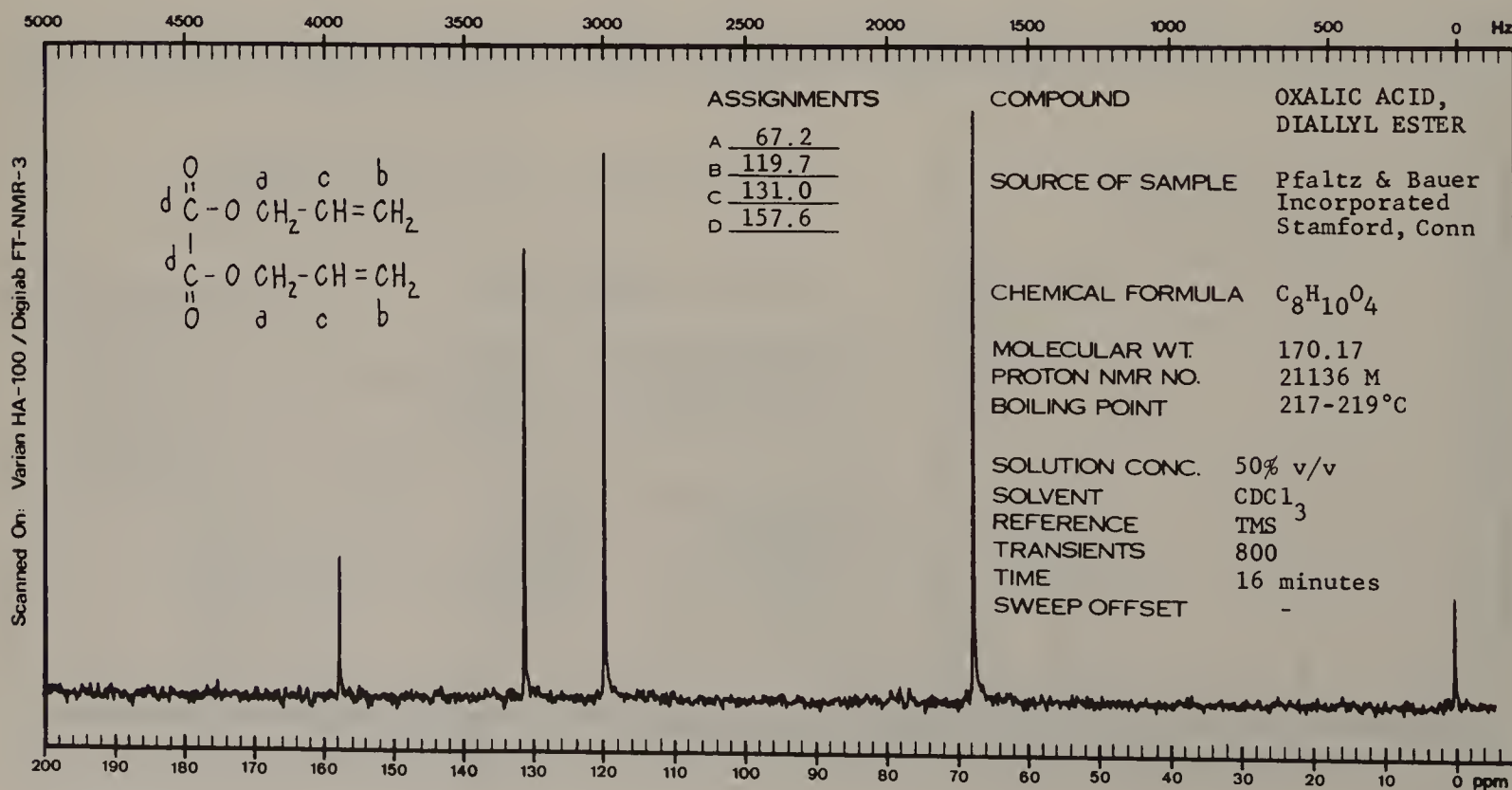
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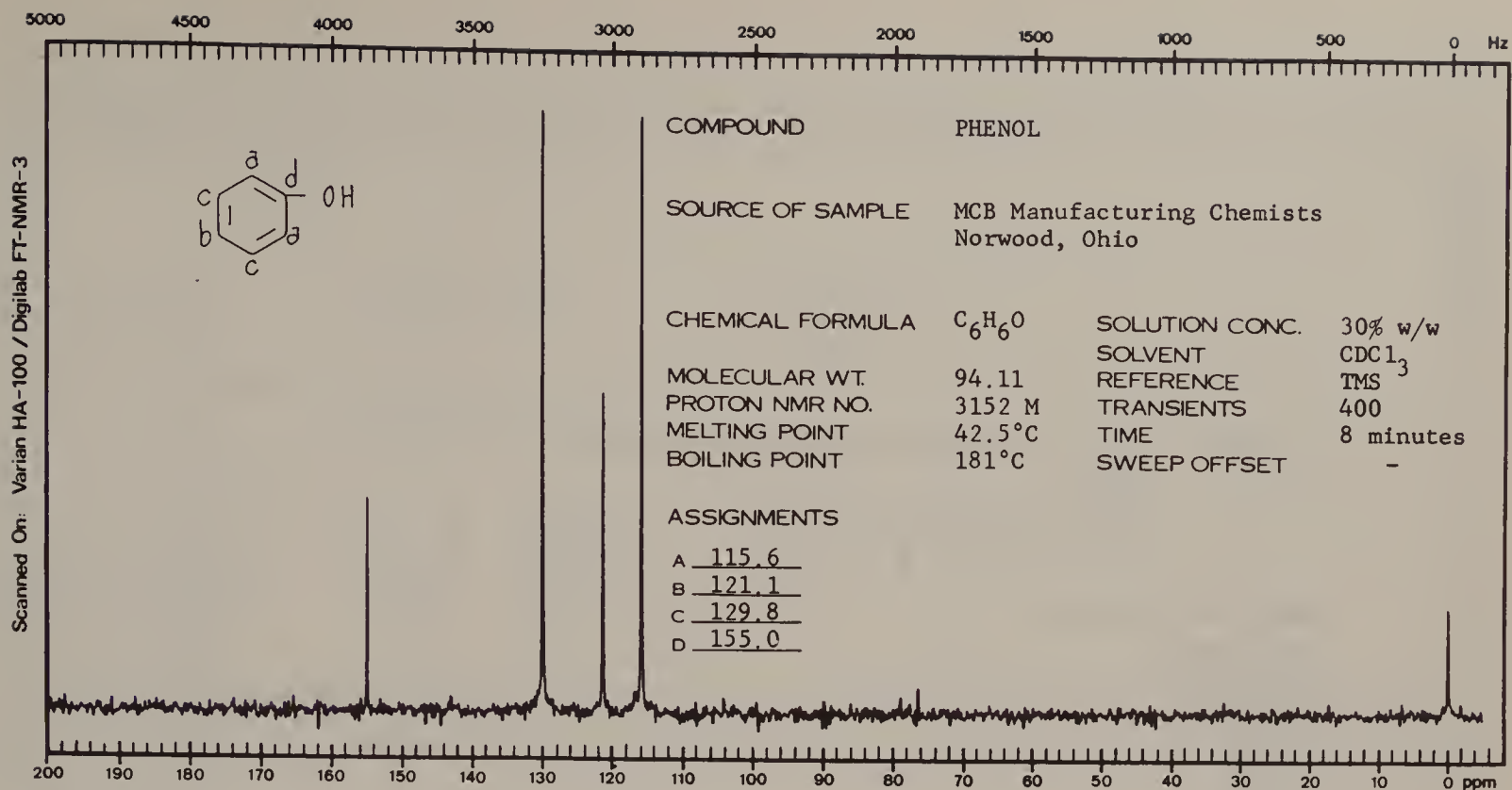
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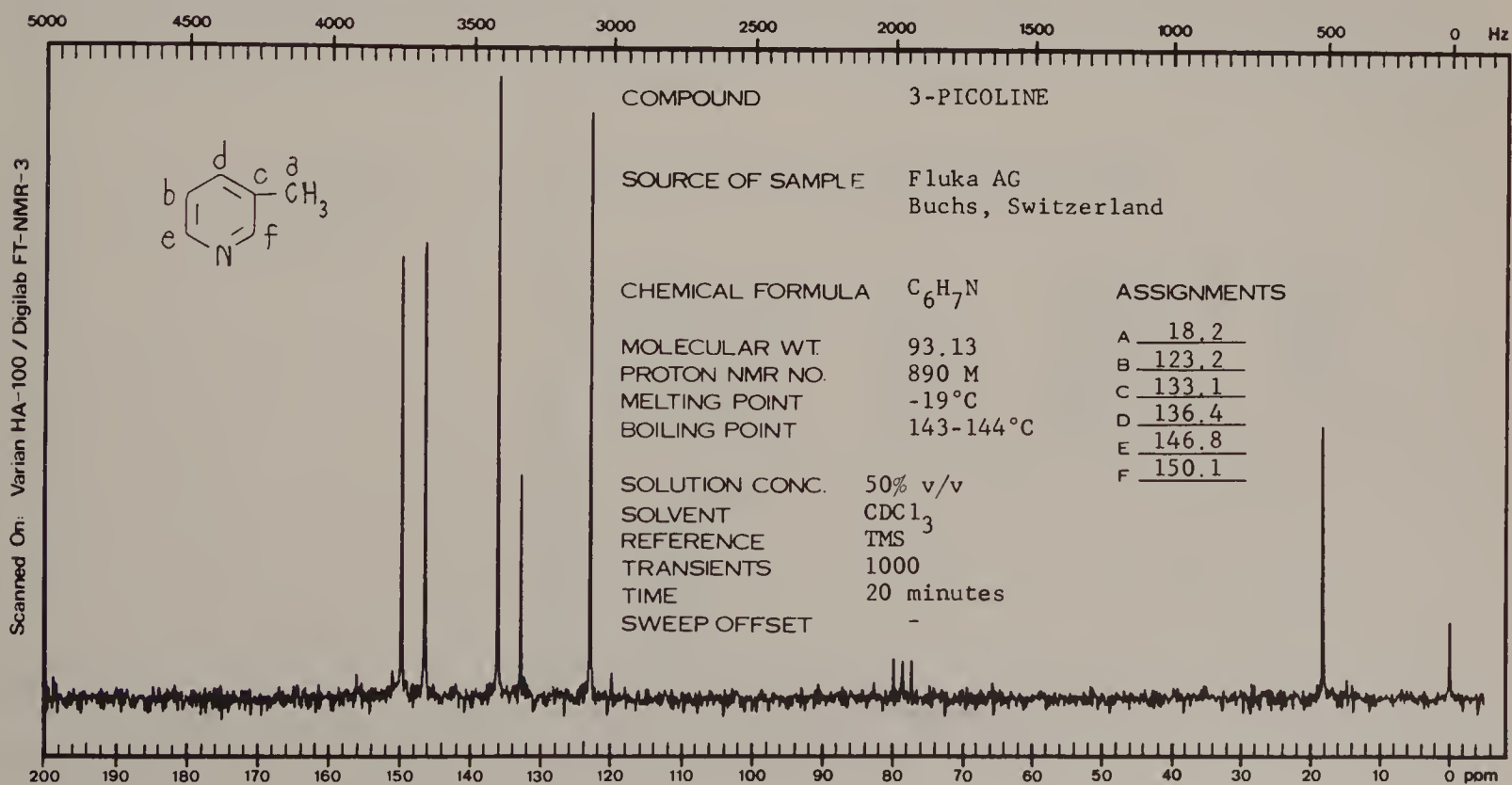
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No. 20

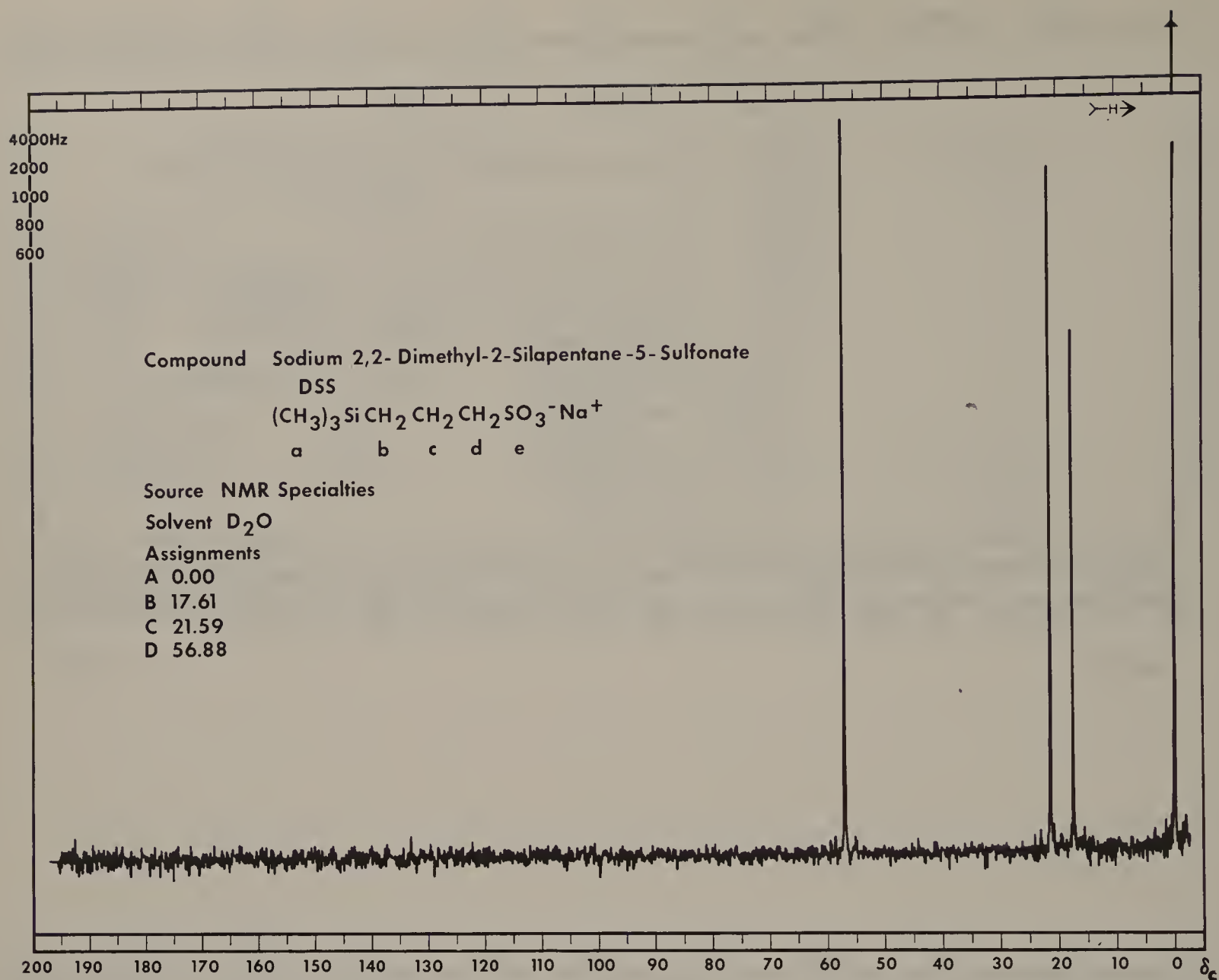


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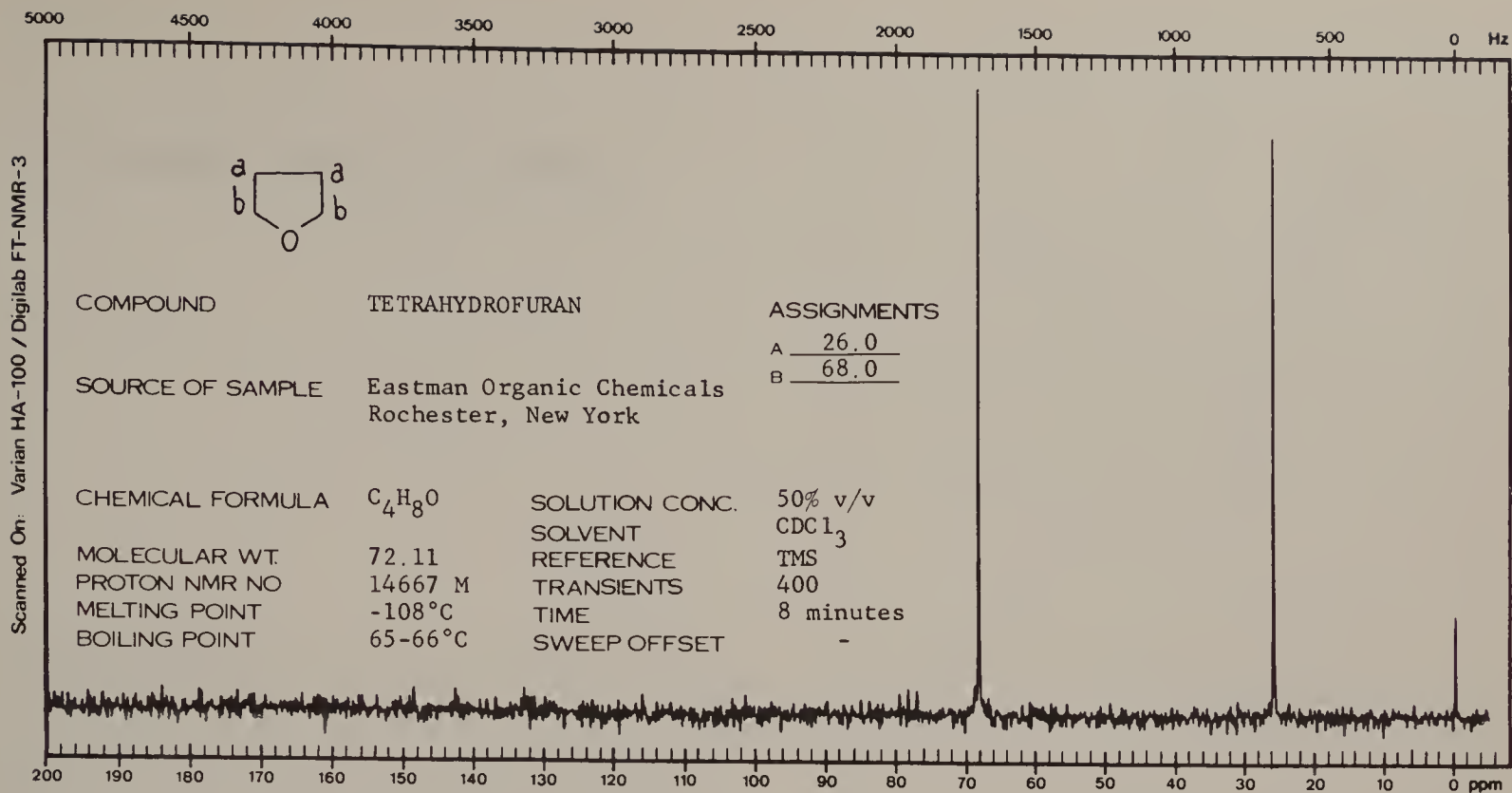


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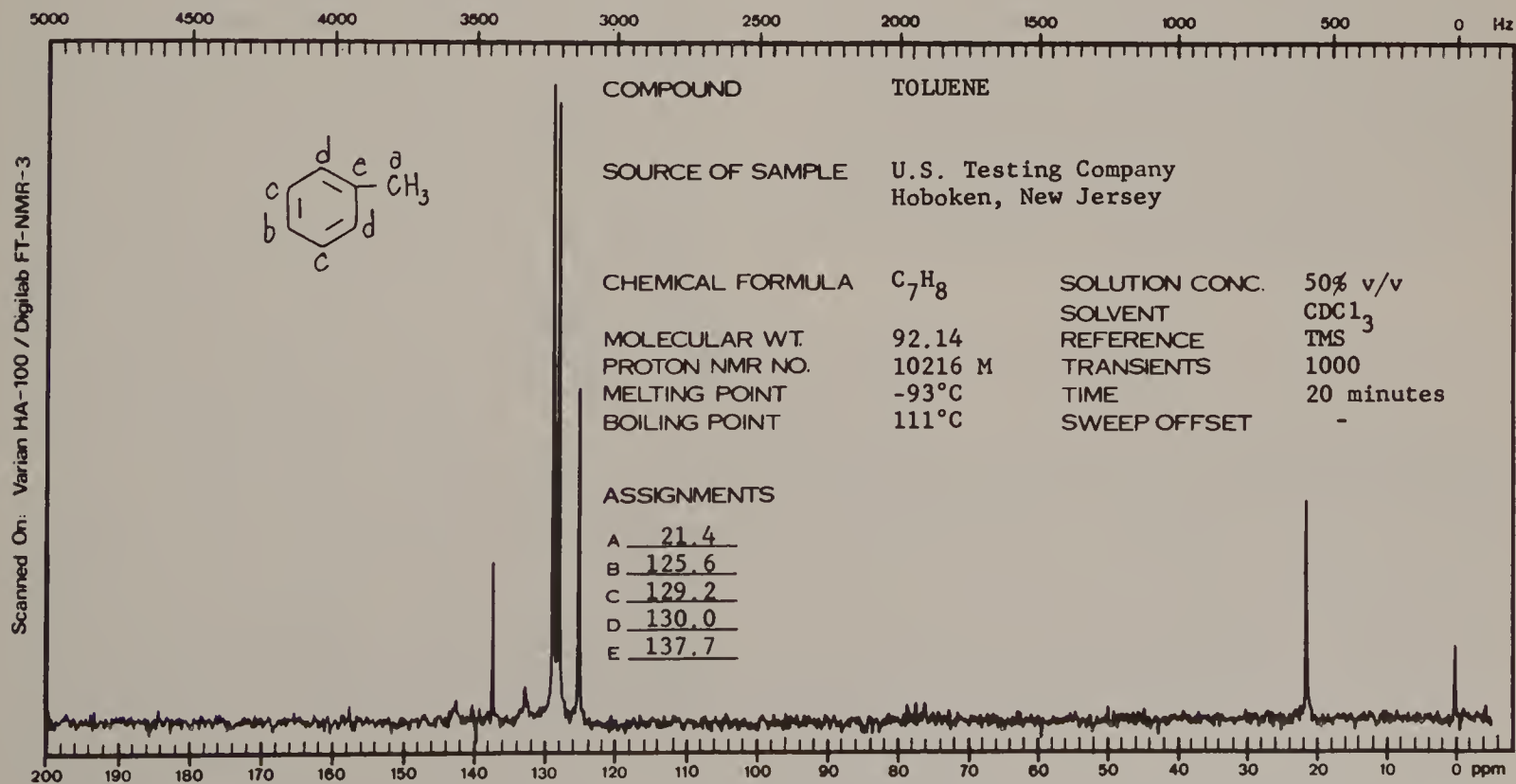




No. 23



No. 24



No. 25





## I. INTRODUCTION

Molecular absorption in the ultraviolet and visible region of the spectrum is dependent on the electronic structure of the molecule. Absorption of energy is quantized, resulting in the elevation of electrons from orbitals in the ground state to higher-energy orbitals in an excited state. For many electronic structures, the absorption does not occur in the readily accessible portion of the ultraviolet region. In practice, ultraviolet spectrometry is limited to conjugated systems for the most part.

There is, however, an advantage to the selectivity of ultraviolet absorption: characteristic groups may be recognized in molecules of widely varying complexities. A large portion of a relatively complex molecule may be transparent in the ultraviolet so that we may obtain a spectrum similar to that of a much simpler molecule. Thus, the spectrum of cholest-4-en-3-one closely resembles the spectrum of mesityl oxide. The absorption results from the conjugated enone portion of the 2 compounds (Figure 1).

A detailed mathematical treatment of the theoretical basis for ultraviolet or electronic spectra is beyond the scope of this chapter. Rather, it is our objective to point out correlations between spectra and structure to be used by the organic chemist. However, enough theory to rationalize these correlations will be presented.

An ultraviolet spectrum obtained directly from an instrument is simply a plot of wavelength (or frequency) of absorption vs. the absorption intensity (absorbance or transmittance). The data are frequently converted to a graphical plot of wavelength vs. the molar absorptivity ( $\epsilon_{\max}$  or  $\log \epsilon_{\max}$  as in Figure 1). The use of molar absorptivity as the unit of absorption intensity has the advantage that all intensity values refer to the same number of absorbing species. A tabular presentation is used in Chapters 7 and 8 of this text.

An abundance of reference material relating to the

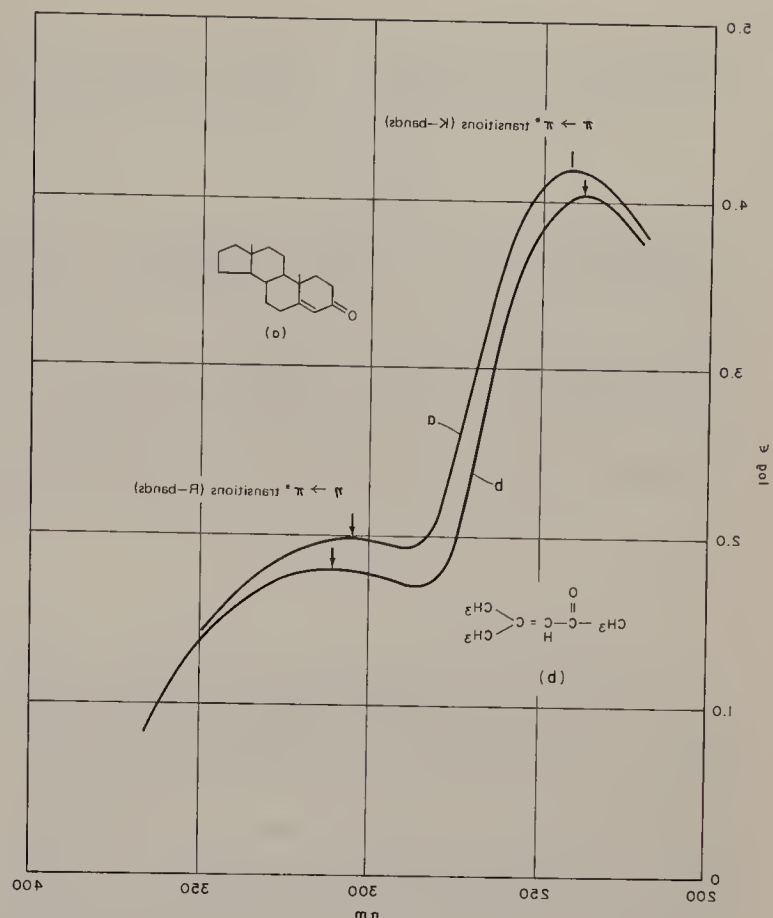
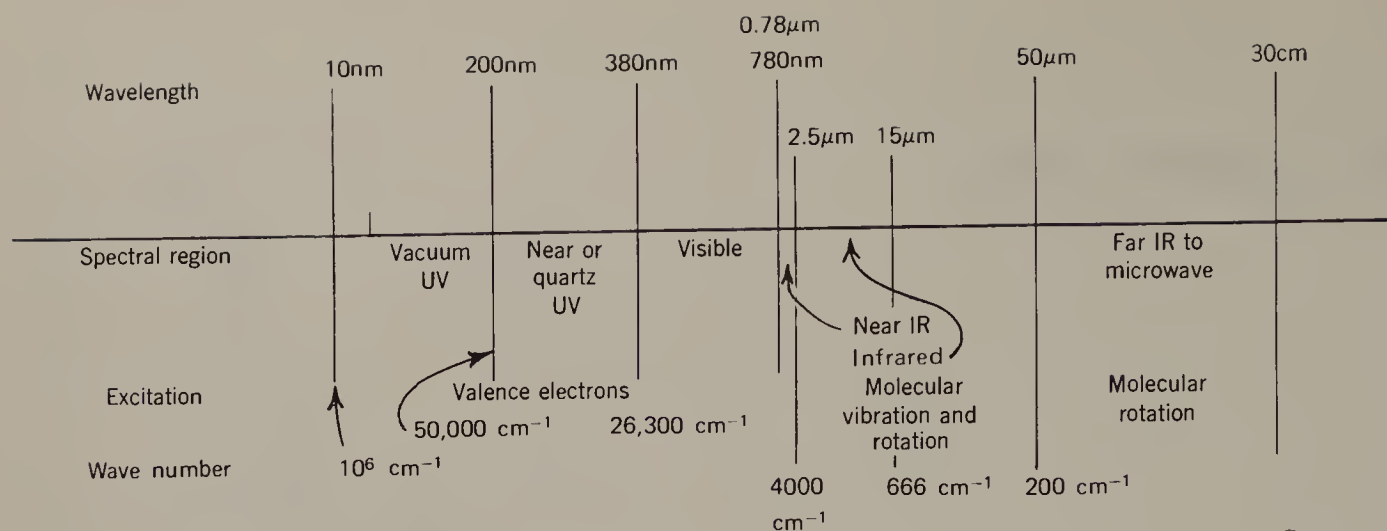


Figure 1. Ultraviolet spectra of (a) cholest-4-en-3-one and (b) mesityl oxide.

theory and interpretation of ultraviolet spectra is available.<sup>1-27</sup> Two of the most useful references for the organic chemist are the texts by Stern and Timmons<sup>3</sup> and by A. I. Scott.<sup>2</sup> The latter is particularly recommended to the natural-products chemist. The text by Jaffé and Orchin is an excellent source of theory for both the spectroscopist and the organic chemist.<sup>1</sup> Several compilations of ultraviolet spectra and absorption data are available.<sup>16-27</sup> The Sadtler spectra<sup>27</sup> and the volumes of "Electronic Spectral Data"<sup>19</sup> are particularly useful to the organic chemist.

## II. THEORY

The ultraviolet portion of the electromagnetic spectrum is indicated in Figure 2. Wavelengths in the ultraviolet region are usually expressed in nanometers ( $1 \text{ nm} = 10^{-9} \text{ m}$ ) or angstroms,  $\text{\AA}$  ( $1 \text{\AA} = 10^{-8} \text{ m}$ ). Occasionally, absorption is reported in wavenumbers ( $\bar{\nu}$ , units =  $\text{cm}^{-1}$ ). We are primarily interested in the near ultraviolet (quartz) region extending from 200-380 nm. The atmosphere is transparent in this region and quartz optics may be used to scan from 200 to 380 nm. Atmospheric absorption starts near 200 nm and extends into the shorter-wavelength region, which is accessible through vacuum ultraviolet spectrometry.



The total energy of a molecule is the sum of its electronic energy, its vibrational energy, and its rotational energy. The magnitude of these energies decreases in the following order:  $E_{\text{elec}}$ ,  $E_{\text{vib}}$ , and  $E_{\text{rot}}$ . Energy absorbed in the ultraviolet region produces changes in the electronic energy of the molecule resulting from transitions of valence electrons in the molecule. These transitions consist of the excitation of an electron from an occupied molecular orbital (usually a nonbonding  $p$  or bonding  $\pi$ -orbital) to the next higher energy orbital (an antibonding,  $\pi^*$  or  $\sigma^*$ , orbital). The antibonding orbital is designated by an asterisk. Thus, the promotion of an electron from a  $\pi$ -bonding orbital to an antibonding ( $\pi^*$ ) orbital is indicated  $\pi \rightarrow \pi^*$ .

The concept of an antibonding orbital can be explained simply by considering the ultraviolet absorption of ethylene. The ethylenic double bond, in the ground state, consists of a pair of bonding  $\sigma$ -electrons and a pair of bonding  $\pi$ -electrons. On absorption of ultraviolet radiation near 165 nm, one of the bonding  $\pi$ -electrons is raised to the next higher energy orbital, an antibonding  $\pi$ -orbital.

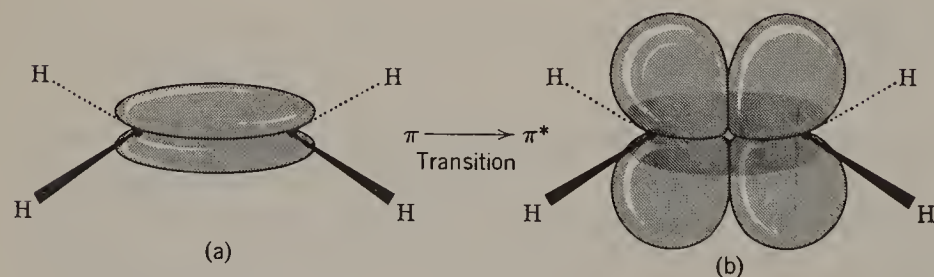
The orbitals occupied by the  $\pi$ -electron in the ground state and in the excited state are diagrammed in Figure 3.

The shaded volumes indicate regions of maximum electron density. It can be seen that the antibonding  $\pi$ -electron no longer contributes appreciably to the overlap of the C-to-C bond. In fact, it negates the bonding power of the remaining unexcited  $\pi$ -electron; the olefinic bond has considerable single-bond character in the excited state.

The relationship between the energy absorbed in an electronic transition and the frequency ( $\nu$ ), wavelength ( $\lambda$ ), and wavenumber ( $\bar{\nu}$ ) of radiation producing the transition is

$$\Delta E = h\nu = \frac{hc}{\lambda} = h\bar{\nu}c$$

where  $h$  is Planck's constant and  $c$  is the velocity of light.  $\Delta E$  is the energy absorbed in an electronic transition in a molecule from a low-energy state (ground state) to a high-energy state (excited state). The energy absorbed is dependent on the energy difference between the ground state and the excited state; the smaller the difference in energy, the longer the wavelength of absorption. The excess energy in the excited state may result in dissociation or ionization of the molecule, or it may be reemitted as heat



**Figure 3.**  $\pi$  and  $\pi^*$  orbitals of ethylene. (a.) Bonding orbital,  $\pi$ . Both  $\pi$  electrons occupying bonding orbital. A bonding  $\pi$  orbital has only 1 nodal plane in the plane of the molecular skeleton. (b.) Antibonding orbital,  $\pi^*$ . One  $\pi$  electron in bonding orbital, one in antibonding orbital. An (antibonding)  $\pi^*$  orbital has an additional nodal plane perpendicular to the plane of the molecule and bisecting the carbon-carbon bond.



or light. The release of energy as light results in fluorescence or phosphorescence.

Since ultraviolet energy is quantized, the absorption spectrum arising from a single electronic transition should consist of a single, discrete line. A discrete line is not obtained since electronic absorption is superimposed on rotational and vibrational sublevels. The spectra of simple molecules in the gaseous state consist of narrow absorption peaks, each representing a transition from a particular combination of vibrational and rotational levels in the electronic ground state to a corresponding combination in the excited state. This is shown schematically in Figure 4, in which the vibrational levels are designated  $\nu_0, \nu_1, \nu_2$ , and so forth. At ordinary temperatures, most of the molecules in the electronic ground state will be in the zero vibrational level ( $G\nu_0$ ); consequently, there are many electronic transitions from that level. In molecules containing more atoms, the multiplicity of vibrational sublevels and the closeness of their spacing cause the discrete bands to coalesce, and broad absorption bands or "band envelopes" are obtained.

The principal characteristics of an absorption band are its position and intensity. The position of absorption corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition. The intensity of absorption is largely dependent on two factors: the probability of interaction between the radiation energy and the electronic system and the difference between the ground and the excited state. The probability of transition is proportional to the square of the transition moment. The transition moment, or dipole moment of transition, is proportional to the change in the electronic charge distribution occurring during excitation. Intense absorption occurs when a transition is accompanied by a large change in the transition moment. Absorption with  $\epsilon_{\max}$  values  $> 10^4$  is high-intensity absorption; low-intensity absorption corre-

sponds to  $\epsilon_{\max}$  values  $< 10^3$ . Transitions of low probability are "forbidden" transitions. The intensity of absorption may be expressed as transmittance ( $T$ ), defined by

$$T = I/I_0$$

where  $I_0$  is the intensity of the radiant energy striking the sample, and  $I$  is the intensity of the radiation emerging from the sample. A more convenient expression of absorption intensity is that derived from the Lambert-Beer law which establishes a relationship between the transmittance, the sample thickness, and the concentration of the absorbing species. This relationship is expressed as

$$\log_{10}(I_0/I) = kcb = A$$

where  $k$  = a constant characteristic of the solute,  
 $c$  = concentration of solute,  
 $b$  = path length through the sample,  
 $A$  = absorbance (optical density in the older literature).

When  $c$  is expressed in moles per liter, and the path length ( $b$ ) through the sample is expressed in centimeters, the preceding expression becomes:

$$A = \epsilon cb$$

The term  $\epsilon$  is known as the molar absorptivity, formerly called the molar extinction coefficient.

If the concentration ( $c$ ) of the solute is now defined as g/liter, the equation becomes:

$$A = abc$$

where  $a$  is the absorptivity and is thus related to the molar absorptivity by

$$\epsilon = aM$$

where  $M$  is the molecular weight of the solute.

The intensity of an absorption band in the ultraviolet spectrum is usually expressed as the molar absorptivity at maximum absorption,  $\epsilon_{\max}$  or  $\log \epsilon_{\max}$ . When the molecular weight of an absorbing material is unknown, the intensity of absorption may be expressed as

$$E_{1\text{cm}}^{1\%} = \frac{A}{cb}$$

where  $c$  = concentration in grams per 100 ml,  
 $b$  = path length through the sample in centimeters.

At this point it is desirable to define certain terms that are frequently used in the discussion of electronic spectra.

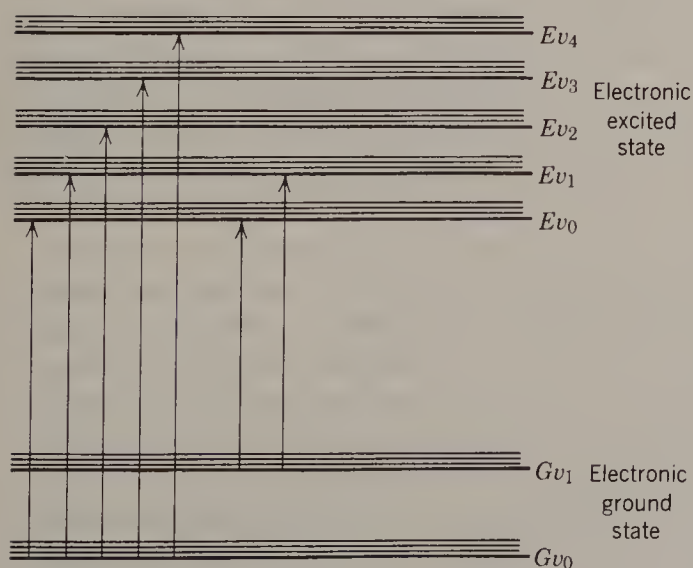




Table I. Summary of Electronic Transitions

| Example                | Electronic Transition            | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ | Band <sup>a</sup> |
|------------------------|----------------------------------|-----------------------|-------------------|-------------------|
| Ethane                 | $\sigma \rightarrow \sigma^*$    | 135                   | —                 | —                 |
| Water                  | $n \rightarrow \sigma^*$         | 167                   | 7,000             | —                 |
| Methanol               | $n \rightarrow \sigma^*$         | 183                   | 500               | —                 |
| 1-Hexanethiol          | $n \rightarrow \sigma^*$         | 224                   | 126               | —                 |
| <i>n</i> -Butyl iodide | $n \rightarrow \sigma^*$         | 257                   | 486               | —                 |
| Ethylene               | $\pi \rightarrow \pi^*$          | 165                   | 10,000            | —                 |
| Acetylene              | $\pi \rightarrow \pi^*$          | 173                   | 6,000             | —                 |
| Acetone                | $\pi \rightarrow \pi^*$          | about 150             | —                 | —                 |
|                        | $n \rightarrow \sigma^*$         | 188                   | 1,860             | —                 |
|                        | $n \rightarrow \pi^*$            | 279                   | 15                | R                 |
| 1,3-Butadiene          | $\pi \rightarrow \pi^*$          | 217                   | 21,000            | K                 |
| 1,3,5-Hexatriene       | $\pi \rightarrow \pi^*$          | 258                   | 35,000            | K                 |
| Acrolein               | $\pi \rightarrow \pi^*$          | 210                   | 11,500            | K                 |
|                        | $n \rightarrow \pi^*$            | 315                   | 14                | R                 |
| Benzene                | Aromatic $\pi \rightarrow \pi^*$ | about 180             | 60,000            | E <sub>1</sub>    |
|                        | Aromatic $\pi \rightarrow \pi^*$ | about 200             | 8,000             | E <sub>2</sub>    |
|                        | Aromatic $\pi \rightarrow \pi^*$ | 255                   | 215               | B                 |
| Styrene                | Aromatic $\pi \rightarrow \pi^*$ | 244                   | 12,000            | K                 |
|                        | Aromatic $\pi \rightarrow \pi^*$ | 282                   | 450               | B                 |
| Toluene                | Aromatic $\pi \rightarrow \pi^*$ | 208                   | 2,460             | E <sub>2</sub>    |
|                        | Aromatic $\pi \rightarrow \pi^*$ | 262                   | 174               | B                 |
| Acetophenone           | Aromatic $\pi \rightarrow \pi^*$ | 240                   | 13,000            | K                 |
|                        | Aromatic $\pi \rightarrow \pi^*$ | 278                   | 1,110             | B                 |
|                        | $n \rightarrow \pi^*$            | 319                   | 50                | R                 |
| Phenol                 | Aromatic $\pi \rightarrow \pi^*$ | 210                   | 6,200             | E <sub>2</sub>    |
|                        | Aromatic $\pi \rightarrow \pi^*$ | 270                   | 1,450             | B                 |

<sup>a</sup>R Band, German *radikalartig*; K-Band, German, *konjugierte*; B-Band, benzenoid; E-Band ethylenic; see: A. Burawoy, *Ber.*, 63, 3155 (1930); *J. Chem. Soc.*, 1177 (1939); also see E.A. Braude.<sup>5</sup>

**CHROMOPHORE.** A covalently unsaturated group responsible for electronic absorption (for example, C=C, C=O, and NO<sub>2</sub>).

**AUXOCHROME.** A saturated group with nonbonded electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption (e.g.,  $\ddot{\text{O}}\text{H}$ ,  $\ddot{\text{N}}\text{H}_2$ , and  $:\ddot{\text{Cl}}:$ ).

**BATHOCHROMIC SHIFT.** The shift of absorption to a longer wavelength due to substitution or solvent effect (a red shift).

**HYPISOCHROMIC SHIFT.** The shift of absorption to a shorter wavelength due to substitution or solvent effect (a blue shift).

**HYPERCHROMIC EFFECT.** An increase in absorption intensity.

**HYPOCHROMIC EFFECT.** A decrease in absorption intensity.

The absorption characteristics of organic molecules in the ultraviolet region depend on the electronic transitions that can occur and the effect of the atomic environment on

the transitions. A summary of electronic structures and transitions that are involved in ultraviolet absorption is presented in Table I.

Representative UV spectra (plots of  $\log \epsilon$  vs.  $\lambda$ ) are shown in Figure 1. Note that the spectrum of the relatively simple model compound mesityl oxide very closely approximates the spectrum of the more complex steroid. Increased molecular structure complexity normally results in increased spectral complexity in NMR, infrared, and mass spectra; Figure 1 shows that this is not necessarily true for UV spectra.

The relative ease with which the various transitions can occur is summarized in Figure 5. Although the energy changes are not shown in scale, it is readily seen, for example, that an  $n \rightarrow \pi^*$  transition requires less energy than a  $\pi \rightarrow \pi^*$  or a  $\sigma \rightarrow \sigma^*$  transition. Several notation systems are used to designate UV absorption bands (Appendix 1 of Jaffe and Orchin<sup>1</sup>). It seems simplest to use electronic transitions or the letter designation assigned by Burawoy as shown in Table I and described below.

The  $n \rightarrow \pi^*$  transitions (also called R-bands) of single

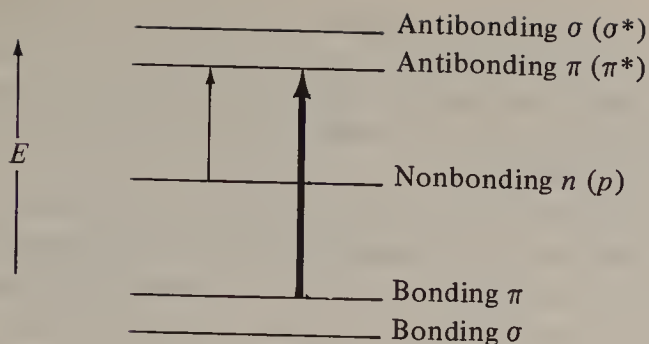


Figure 5. Summary of electronic energy levels. Both  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  (heavy arrow) transitions are represented.

chromophoric groups, such as the carbonyl or nitro group are forbidden and the corresponding bands are characterized by low molar absorptivities,  $\epsilon_{\max}$  generally less than 100. They are further characterized by the hypsochromic or blue shift observed with an increase in solvent polarity. They frequently remain in the spectrum when modifications in molecular structure introduce additional bands at shorter wavelengths. When additional bands make their appearance, the  $n \rightarrow \pi^*$  transition is shifted to a longer wavelength but may be submerged by more intense bands.

Bands attributed to  $\pi \rightarrow \pi^*$  transitions (*K*-Bands) appear in the spectra of molecules that have conjugated  $\pi$ -systems such as butadiene or mesityl oxide. Such absorptions also appear in the spectra of aromatic molecules possessing chromophoric substitution—styrene, benzaldehyde, or acetophenone. These  $\pi \rightarrow \pi^*$  transitions are usually characterized by high molar absorptivity,  $\epsilon_{\max} > 10,000$ .

The  $\pi \rightarrow \pi^*$  transitions (*K*-bands) of conjugated di- or poly-ene systems can be distinguished from those of enone systems by observing the effect of changing solvent polarity. The  $\pi \rightarrow \pi^*$  transitions of diene or polyene systems are essentially unresponsive to solvent polarity; the hydrocarbon double bonds are nonpolar. The corresponding absorptions of enones, however, undergo a bathochromic shift, frequently accompanied by increasing intensity, as the polarity of the solvent is increased. The red shift presumably results from a reduction in the energy level of the excited state accompanying dipole-dipole interaction and hydrogen bonding.

The effect of solvent has been measured for the  $n \rightarrow \pi^*$  transition of acetone. This maximum is at 279 nm in hexane, and decreases to 272 and 264.5 nm for the solvents ethanol and water, respectively.

*B*-Bands (benzenoid bands) are characteristic of the spectra of aromatic or heteroaromatic molecules. Benzene shows a broad absorption band, containing multiple peaks or fine structure, in the near ultraviolet region between 230 and 270 nm ( $\epsilon$  of most intense peak *ca.* 255 nm). The fine structure arises from vibrational sublevels affecting the electronic transitions. When a chromophoric group is

attached to an aromatic ring, the *B*-bands are observed at longer wavelengths than the more intense  $\pi \rightarrow \pi^*$  transitions. For example, styrene has a  $\pi \rightarrow \pi^*$  transition at  $\lambda_{\max}$  244 nm ( $\epsilon_{\max}$  12,000), and a *B*-band at  $\lambda_{\max}$  282 nm ( $\epsilon_{\max}$  450). When an  $n \rightarrow \pi^*$  transition appears in the spectrum of an aromatic compound that contains  $\pi \rightarrow \pi^*$  transitions (including *B*-bands), the  $n \rightarrow \pi^*$  transition is shifted to longer wavelengths. The characteristic fine structure of the *B*-bands may be absent in spectra of substituted aromatics. The fine structure is often destroyed by the use of polar solvents.

*E*-Bands (ethylenic bands), like the *B*-bands, are characteristic of aromatic structures. The  $E_1$ - and  $E_2$ -bands of benzene are observed near 180 nm and 200 nm, respectively. Auxochromic substitution brings the  $E_2$  band into the near ultraviolet region, although in many cases it may not appear at wavelengths much over 210 nm. In auxochromic substitution, the heteroatom with the lone pair of electrons shares these electrons with the  $\pi$ -electron system of the ring, facilitating the  $\pi \rightarrow \pi^*$  transition and thus causing a red shift of the *E*-bands. The molar absorptivity of *E*-bands generally varies between 2000 and 14,000.

A bathochromically displaced  $E_2$ -band is probably responsible for the intense, fine-structured bands of polynuclear aromatics. With the appearance of the *E*-bands as a results of auxochromic substitution, the *B*-band shifts to longer wavelengths and frequently increases in intensity. Molecules such as benzylideneacetone in which more complex conjugated chromophoric substitution occurs, produce spectra with both *E*- and *K*-bands; the *B*-bands are obscured by the displaced *K*-bands.

### III. SAMPLE HANDLING

Ultraviolet spectra of compounds are usually determined either in the vapor phase or in solution.

A variety of quartz cells is available for the determination of spectra in the gas phase. These cells are equipped with gas inlets and outlets and have path lengths from 1.0 mm to 100 mm. Path lengths of 0.5-120 meters can be reached by using cells containing mirrors. Cell jackets are available through which liquids may be circulated for temperature control.

Cells used for the determination of spectra in solution vary in path length from 1 cm to 10 cm. Quartz cells, 1-cm square, are commonly used. These require about 3 ml of solution. Filler plugs are available to reduce the volume and the path length of the 1-cm square cell. Small-volume cells with 1-cm path lengths are also available. Microcells may be used when only a small amount of solution is available: the use of a beam condenser to minimize the loss of energy is advisable when the microcells are used. Microcells with an



internal width of 2 mm and a path length as short as 5 mm are available.

In preparing a solution, a sample is accurately weighed and made up to volume in a volumetric flask. Aliquots are then removed, and additional dilutions made until the desired concentration has been acquired. Clean cells are of utmost importance. The cells should be rinsed several times with solvent and checked for absorption between successive determinations. It may be necessary to clean the cells with a detergent or hot nitric acid to remove traces of previous samples.

Many solvents are available for use in the ultraviolet region. Three common solvents are cyclohexane, 95% ethanol, and 1,4-dioxane. Cyclohexane may be freed of aromatic and olefinic impurities by percolation through activated silica gel and is transparent down to about 210 nm. Aromatic compounds, particularly the polynuclear aromatics, are usually soluble and their spectra generally retain their fine-line structure when determined in cyclohexane. The fine structure is often lost in more polar solvents.

Ninety-five percent ethanol is generally a good choice when a more polar solvent is required. This solvent generally can be used as purchased, but absolute ethanol must be freed of benzene used in its preparation. The last traces of benzene are removed by careful fractional distillation, or by preparative gas chromatography. The lower limit of transparency for ethanol is near 210 nm.

1,4-Dioxane can be purified by distillation from sodium. Benzene contamination can be removed by the addition of methanol followed by distillation to remove the benzene-methanol azeotrope. 1,4-Dioxane is transparent down to about 220 nm.

Many types of "spectral grade" solvents for ultraviolet analysis are now commercially available. These are usually highly purified and are free of interfering absorptions in the shaded regions indicated in Figure 6. Care should be exercised to choose a solvent that will be inert to the solute. For example, the spectra of aldehydes should not be determined in alcohols. Photochemical reactions may be detected by checking for changes in absorbance with time after exposure to the ultraviolet beam in the instrument.

#### IV. CHARACTERISTIC ABSORPTION OF ORGANIC COMPOUNDS

In our discussion of the theory of electronic or ultraviolet spectra, it was shown that the ability of an organic compound to absorb ultraviolet radiation is dependent on its electronic structure. In the following sections we shall discuss the characteristic absorption of basic electronic structures and the effects of molecular geometry and substitution on the absorption.

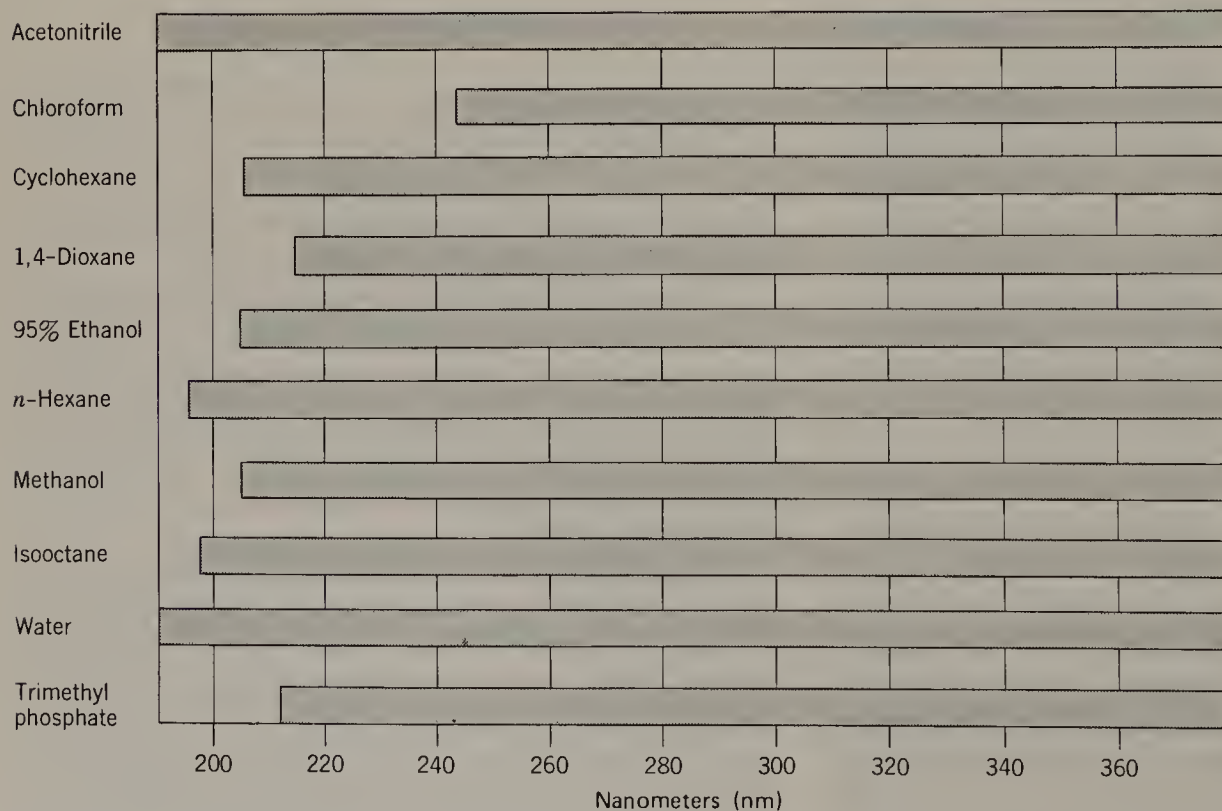


Figure 6. Useful transparency ranges of solvents in near ultraviolet region.



## COMPOUNDS CONTAINING ONLY $\sigma$ -ELECTRONS

Saturated hydrocarbons contain  $\sigma$ -electrons exclusively. Since the energy required to bring about a  $\sigma \rightarrow \sigma^*$  transition is of the order of 185 kcal per mole and is available only in the far (vacuum) ultraviolet region, saturated hydrocarbons are transparent in the near ultraviolet region and thus can be used as solvents.

## SATURATED COMPOUNDS CONTAINING $n$ -ELECTRONS

Saturated compounds containing heteroatoms, such as oxygen, nitrogen, sulfur, or the halogens, possess nonbonding electrons ( $n$ - or  $p$ -electrons) in addition to  $\sigma$ -electrons. The  $n \rightarrow \sigma^*$  transition requires less energy than the  $\sigma \rightarrow \sigma^*$  transition (see Figure 4a), but the majority of compounds in this class still show no absorption in the near ultraviolet.

Alcohols and ethers absorb at wavelengths shorter than 185 nm (Table II) and therefore are commonly used for work in the near ultraviolet region. When these compounds are used as solvents, the intense absorption extends into the near ultraviolet, producing end-absorption or cut-off in the 200-220 nm region (Figure 6).

Sulfides, disulfides, thiols, amines, bromides, and iodides may show weak absorption in the near ultraviolet. Frequently, the absorption appears only as a shoulder or an inflection so that its diagnostic value is questionable.

Absorption data for several saturated compounds bearing heteroatoms are presented in Table II.

Table II. Absorption Characteristics of Saturated Compounds Containing Heteroatoms ( $n \rightarrow \sigma^*$ )

| Compound                      | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ | Solvent     |
|-------------------------------|-----------------------|-------------------|-------------|
| Methanol                      | 177                   | 200               | Hexane      |
| Di- <i>n</i> -butyl sulfide   | 210                   | 1200              | Ethanol     |
|                               | 229 (s)               |                   |             |
| Di- <i>n</i> -butyl disulfide | 204                   | 2089              | Ethanol     |
|                               | 251                   | 398               |             |
| 1-Hexanethiol                 | 224 (s)               | 126               | Cyclohexane |
| Trimethylamine                | 199                   | 3950              | Hexane      |
| <i>N</i> -Methylpiperidine    | 213                   | 1600              | Ether       |
| Methyl chloride               | 173                   | 200               | Hexane      |
| <i>n</i> -Propyl bromide      | 208                   | 300               | Hexane      |
| Methyl iodide                 | 259                   | 400               | Hexane      |
| Diethyl ether                 | 188                   | 1995              | Gas Phase   |
|                               | 171                   | 3981              |             |

(s) Shoulder inflection

## COMPOUNDS CONTAINING $\pi$ -ELECTRONS (CHROMOPHORES)

The absorption characteristics of a list of compounds containing single, isolated chromophoric groups are presented in Table III. All the compounds contain  $\pi$ -electrons, and many also contain nonbonding electron pairs. An examination of the absorption data shows that many of these single chromophoric groups absorb strongly in the far ultraviolet region with no absorption in the near ultraviolet. Those groups containing both  $\pi$ - and  $n$ -electrons can undergo 3 transitions:  $n \rightarrow \sigma^*$ ,  $\pi \rightarrow \pi^*$ , and  $n \rightarrow \pi^*$ . Weak absorption of single chromophores in the near ultraviolet region results from the low-energy, forbidden  $n \rightarrow \pi^*$  transition.

### Ethylenic Chromophore

The isolated ethylenic chromophore is responsible for intense absorption that almost always occurs in the far ultraviolet region. Absorption is due to a  $\pi \rightarrow \pi^*$  transition. Ethylene in the vapor phase absorbs at 165 nm ( $\epsilon_{\max}$  10,000). A second band near 200 nm has been attributed to the elevation of two  $\pi$  electrons to  $\pi^*$  orbitals. The intensity of olefinic absorption is essentially independent of solvent because of the nonpolar nature of the olefinic bond.

Alkyl substitution of the parent compound moves the absorption to longer wavelengths. The bathochromic effect is progressive as the number of alkyl groups increases. A double bond exocyclic to 2 rings absorbs near 204 nm. The bathochromic shift accompanying alkyl substitution results from hyperconjugation in which the  $\sigma$ -electrons of the alkyl group are mobile enough to interact with the chromophoric group.



Attachment of a heteroatom bearing a nonbonded electron pair to the ethylenic linkage brings about a bathochromic shift. Nitrogen and sulfur atoms are most effective, bringing the absorption well into the near ultraviolet region. Methyl vinyl sulfide, for example, absorbs at 228 nm ( $\epsilon_{\max}$  8000).

The absorption characteristics of cyclic monoolefins resemble those of the acyclic compounds, the absorption bearing no apparent relationship to ring size.

When two or more ethylenic linkages appear in a single molecule, isolated from one another by at least 1 methylene group, the molecule absorbs at the same position as the single ethylenic chromophore. The intensity of absorption is proportional to the number of isolated chromophoric groups in the molecule.

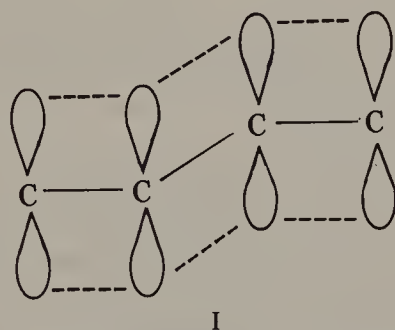
Allenes, which possess the  $C=C=C$  unit, show a strong absorption band in the far ultraviolet region near 170 nm, with a shoulder on the long wavelength side sometimes extending into the near ultraviolet region.

Table III. Absorption Data for Isolated Chromophores

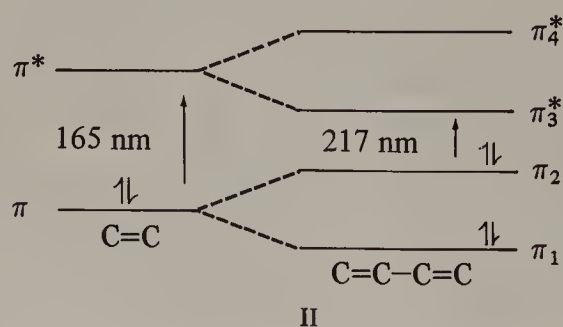
| Chromophoric Group | System  | Example                     | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ | Transition              | Solvent          |
|--------------------|---|-----------------------------|-----------------------|-------------------|-------------------------|------------------|
| Ethylenic          | RCH=CHR   | Ethylene                    | 165                   | 15,000            | $\pi \rightarrow \pi^*$ | Vapor            |
|                    |   |                             | 193                   | 10,000            | $\pi \rightarrow \pi^*$ |                  |
| Acetylenic         | R-C $\equiv$ C-R  | Acetylene                   | 173                   | 6,000             | $\pi \rightarrow \pi^*$ | Vapor            |
| Carbonyl           | RR <sub>1</sub> C=O   | Acetone                     | 188                   | 900               | $\pi \rightarrow \pi^*$ | <i>n</i> -Hexane |
|                    |   |                             | 279                   | 15                | $n \rightarrow \pi^*$   |                  |
| Carbonyl           | RHC=O   | Acetaldehyde                | 290                   | 16                | $n \rightarrow \pi^*$   | Heptane          |
| Carboxyl           | RCOOH   | Acetic acid                 | 204                   | 60                | $n \rightarrow \pi^*$   | Water            |
| Amido              | RCONH <sub>2</sub>  | Acetamide                   | <208                  | —                 | $n \rightarrow \pi^*$   | —                |
| Azomethine         | >C=N-   | Acetoxime                   | 190                   | 5,000             | $\pi \rightarrow \pi^*$ | Water            |
| Nitrile            | -C $\equiv$ N   | Acetonitrile                | <160                  | —                 | $\pi \rightarrow \pi^*$ | —                |
| Azo                | -N=N-   | Azomethane                  | 347                   | 4.5               | $n \rightarrow \pi^*$   | Dioxane          |
| Nitroso            | -N=O  | Nitrosobutane               | 300                   | 100               | $n \rightarrow \pi^*$   | Ether            |
|                    |   |                             | 665                   | 20                |                         |                  |
| Nitrate            | -ONO <sub>2</sub>   | Ethyl nitrate               | 270                   | 12                | $n \rightarrow \pi^*$   | Dioxane          |
| Nitro              |    | Nitromethane                | 271                   | 18.6              | $n \rightarrow \pi^*$   | Alcohol          |
| Nitrite            | -ONO  | Amyl nitrite                | 218.5                 | 1,120             | $\pi \rightarrow \pi^*$ | Petroleum ether  |
|                    |   |                             | 346.5 <sup>a</sup>    |                   | $n \rightarrow \pi^*$   |                  |
| Sulfoxide          | S=O   | Cyclohexyl methyl sulfoxide | 210                   | 1,500             |                         | Alcohol          |
| Sulfone            |  | Dimethyl sulfone            | <180                  | —                 |                         | —                |

<sup>a</sup>Most intense peak of fine structure group.

Source: A.E. Gillam and E.S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, 2nd ed., London: Edward Arnold, 1957.



The olefinic bond is described by two  $\pi$  orbitals of different energy, bonding and antibonding. In conjugated diene molecules such as 1,3-butadiene, when coplanarity permits, there is an effective overlap of  $\pi$  orbitals resulting in a  $\pi$ - $\pi$  conjugated system (I).



This overlap or interaction results in the creation of two new energy levels in butadiene (II). Thus, the  $\pi_2 \rightarrow \pi_3^*$  transition of butadiene is bathochromically shifted relative to the  $\pi \rightarrow \pi^*$  transition of ethylene. There are other  $\pi \rightarrow \pi^*$  transitions possible in the conjugated system. Their intensities depend on the "allowedness" of the transitions.

Acyclic conjugated dienes show intense  $\pi \rightarrow \pi^*$  transition bands (*K*-bands) in the 215-230 nm region. 1,3-Butadiene absorbs at 217 nm ( $\epsilon_{\max}$  21,000). Further conjugation, in open-chain trienes and polyenes, results in additional bathochromic shifts accompanied by increases in absorption intensity. The spectra of polyenes are characterized by fine structure, particularly when the spectra are determined in the vapor phase or in nonpolar solvents. Absorption data for several conjugated olefins are presented in Table IV.

The bathochromic effect of alkyl substitution in 1,3-butadiene is apparent from the data for 2,3-dimethyl-1,3-butadiene.

In cases where *cis* and *trans* isomers are possible, the *trans* isomer absorbs at the longer wavelength with the greater intensity (see Table XXII). This difference becomes more pronounced as the length of the conjugated system



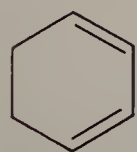
Table IV. Absorption Data for Conjugated Olefins

| Compound                   | $\pi \rightarrow \pi^*$ Transition (K-band) |                   | Solvent     |
|----------------------------|---|-------------------|-------------|
|                            | $\lambda_{\max}$ (nm)                       | $\epsilon_{\max}$ |             |
| 1,3-Butadiene              | 217   | 21,000            | Hexane      |
| 2,3-Dimethyl-1,3-butadiene | 226   | 21,400            | Cyclohexane |
| 1,3,5-Hexatriene           | 253   | ~50,000           | Isooctane   |
|                            | 263   | 52,500            |             |
|                            | 274   | ~50,000           |             |
| 1,3-Cyclohexadiene         | 256   | 8,000             | Hexane      |
| 1,3-Cyclopentadiene        | 239   | 3,400             | Hexane      |

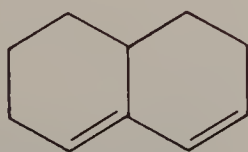
increases. Coplanarity is required for the most effective overlap of the  $\pi$ -orbitals and lower energy of the  $\pi \rightarrow \pi^*$  transition. Of the two isomers, the *cis* isomer is more likely to be forced into a nonplanar conformation by steric effects (see discussion of stilbene below). The greater absorption intensity of the *trans* isomer results from the greater overall magnitude of the transition moment of the excited molecule.

An empirical method for predicting the bathochromic effect of alkyl substitution in 1,3-butadiene has been formulated by Woodward. These rules can be summarized as follows: (1) Each alkyl group, or ring residue, attached to the parent diene (1,3-butadiene) shifts the absorption 5 nm toward the long wavelength region; and (2) the creation of an exocyclic double bond causes an additional bathochromic shift of 5 nm, the shift being 10 nm if the double bond is exocyclic to two rings. For example,  $217 + (2 \times 5)$  is the predicted  $\lambda_{\max}$  value for 2,3-dimethyl-1,3-butadiene; the observed  $\lambda_{\max}$  is 226.

Examination of the data in Table IV shows a marked bathochromic shift and a decrease in absorption intensity for the conjugated, monocyclic diene system compared with 1,3-butadiene. Butadiene exists in the preferred *s-trans* (transoid) conformation, whereas the cyclic dienes are forced into an *s-cis* (cisoid) conformation. The reason for the bathochromic shift in the *s-cis* structure brought about by cyclization is not clear. The decrease in intensity is more easily explained, since the transition moment of the cyclic or homoannular system is less than that of the acyclic or the heteroannular systems.



Homoannular



Heteroannular

Table V. Rules of Diene Absorption

|  |     |
|--|-----|
| Base value for heteroannular diene     | 214 |
| Base value for homoannular diene       | 253 |
| Increments for                         |     |
| Double bond extending conjugation      | +30 |
| Alkyl substituent or ring residue      | +5  |
| Exocyclic double bond                  | +5  |
| Polar groupings: OAc                   | +0  |
| OAlk                                   | +6  |
| SAlk                                   | +30 |
| Cl, Br                                 | +5  |
| N(Alk) <sub>2</sub>                    | +60 |
| Solvent correction*                    | +0  |
| $\lambda_{\text{calc}} = \text{Total}$ |     |

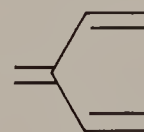
See L.M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15-24; R.B. Woodward, *J. Am. Chem. Soc.*, 63, 1123 (1941); 64, 72, 76 (1942); A.I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon Press (MacMillan), 1964.

\*Solvents have negligible effects upon the  $\lambda_{\max}$  of these  $\pi \rightarrow \pi^*$  transitions.

annular dienes usually display molar absorptivities in the 5000-8000 range.

Rules for predicting the position of absorption of homo- and heteroannular systems are due largely to the work of Fieser. These rules are summarized in Table V.

Poor correlations are obtained when the data of Table V are applied to cross-conjugated polyene systems such as



The value of these rules in structural studies of natural products will be obvious from two examples:

1. Cholesta-3,5-diene

Calc.  $\lambda_{\max}$

|                                 |
|---------------------------------|
| 214 (base)                      |
| + 15 (3 ring residues, 1, 2, 3) |
| + 5 (1 exocyclic C=C)           |
| <hr/> 234                       |

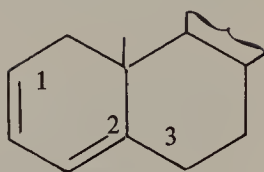
Obs.  $\lambda_{\max} = 235$  ( $\epsilon_{\max}$  19,000)

Heteroannular and acyclic dienes usually display molar absorptivities in the 8000-20,000 range, whereas homo-



2.

Cholesta-2,4-diene

Calc.  $\lambda_{\max}$ 

$$\begin{array}{r}
 253 \text{ (base)} \\
 + 15 \text{ (3 ring residues, 1, 2, 3)} \\
 + 5 \text{ (1 exocyclic C=C)} \\
 \hline
 273
 \end{array}$$

Obs.  $\lambda_{\max} = 275$  ( $\epsilon_{\max} 10,000$ )

The examples above illustrate the typically much higher molar absorptivity of the heteroannular (*transoid*) diene compared to the homoannular (*cisoid*) diene.

The rules outlined in Table V work reasonably well for conjugated systems of 4 double bonds or less. If a

conjugated polyene contains more than 4 double bonds, the Fieser-Kuhn rules are used. In this approach both the  $\lambda_{\max}$  and  $\epsilon_{\max}$  are related to the number of conjugated double bonds, as well as other structural units, by the following equations:

$$\lambda_{\max} = 114 + 5M + n(48.0 - 117n) - 16.5 R_{\text{endo}} - 10R_{\text{exo}}$$

$$\epsilon_{\max} = (1.74 \times 10^4)n$$

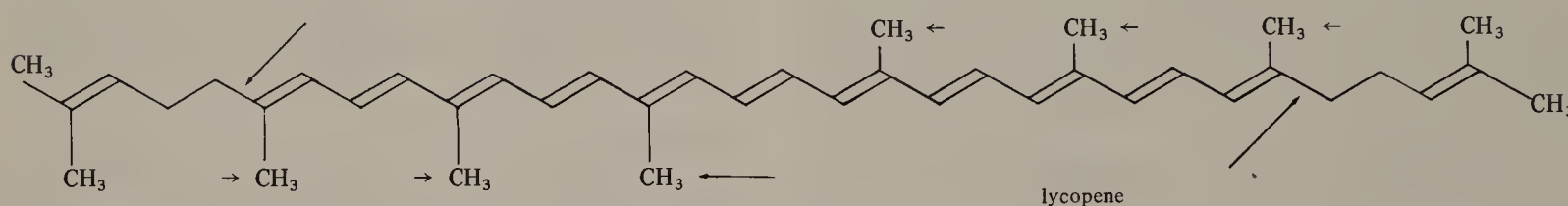
where  $n$  = no. of conjugated double bonds

$M$  = no. of alkyl or alkyl-like substituents on the conjugated system

$R_{\text{endo}}$  = no. of rings with endocyclic double bonds in the conjugated system

$R_{\text{exo}}$  = no. of rings with exocyclic double bonds

The equations may be applied to lycopene as follows:



Since only the 11 internal double bonds of the 13 double bonds of lycopene are conjugated,  $n = 11$ . In addition, since there are 8 substituents (arrows, methyl groups and chain residues) on the polyene system, then  $M = 8$ . Finally, since there are no ring systems, there are neither exocyclic nor endocyclic double bonds in this conjugated system and  $R_{\text{exo}} = R_{\text{endo}} = 0$ . Thus,

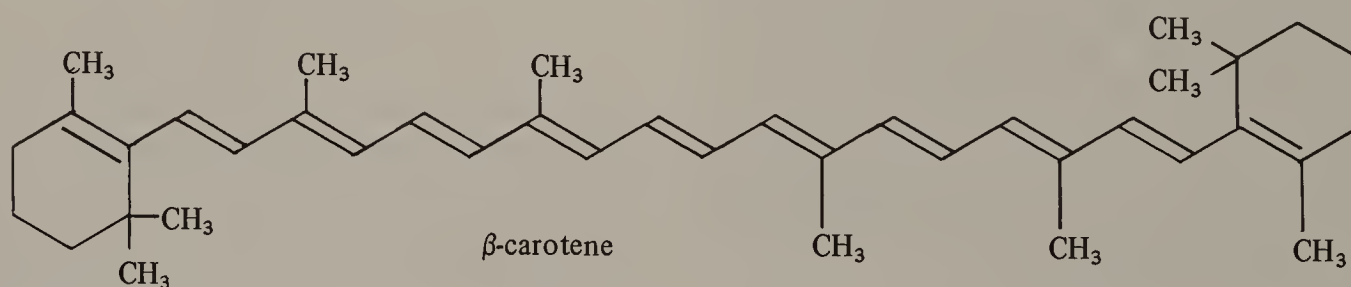
$$\begin{aligned}
 \lambda_{\max}^{\text{calc}} &= 114 + 5(8) + 11[48.0 - 1.7(11)] - 0 - 0 \\
 &= 476 \text{ nm}
 \end{aligned}$$

$$\lambda_{\max}^{\text{obs}} = 474 \text{ nm (hexane)}$$

$$\epsilon_{\max}^{\text{calc}} = 1.74 \times 10^4(11) = 19.1 \times 10^4$$

$$\epsilon_{\max}^{\text{obs}} = 18.6 \times 10^4 \text{ (hexane)}$$

A similar calculation can be carried out for  $\beta$ -carotene:



$$\lambda_{\max}^{\text{calc}} = 453.3 \text{ nm}$$

$$\epsilon_{\max}^{\text{calc}} = 19.1 \times 10^4$$

$$\lambda_{\max}^{\text{obs}} = 452 \text{ nm (hexane)}$$

$$\epsilon_{\max}^{\text{obs}} = 15.2 \times 10^4$$

#### Acetylenic Chromophore

The absorption characteristics of the acetylenic chromophore are more complex than those of the ethylenic

chromophore. Acetylene shows a relatively weak band at 173 nm resulting from a  $\pi \rightarrow \pi^*$  transition. Conjugated polyynes show 2 principal bands in the near ultraviolet which are characterized by fine structure. The short-wavelength band is extremely intense, and all of these bands arise from  $\pi \rightarrow \pi^*$  transitions. Typical absorption data for conjugated polyynes are shown in Table VI.

Table VI. Absorption Data for Conjugated Polyynes

|                      | $\lambda_{\max}(nm)$ | $\epsilon_{\max}$ | $\lambda_{\max}(nm)$ | $\epsilon_{\max}$ |
|----------------------|----------------------|-------------------|----------------------|-------------------|
| 2,4-Hexadiyne        | —                    | —                 | 227                  | 360               |
| 2,4,6-Octatriyne     | 207                  | 135,000           | 268                  | 200               |
| 2,4,6,8-Decatetrayne | 234                  | 281,000           | 306                  | 180               |

### Carbonyl Chromophore

The carbonyl group contains, in addition to a pair of  $\sigma$ -electrons, a pair of  $\pi$ -electrons and 2 pairs of nonbonding ( $n$  or  $p$ ) electrons. Saturated ketones and aldehydes display 3 absorption bands, 2 of which are observed in the far ultraviolet region. A  $\pi \rightarrow \pi^*$  transition absorbs strongly near 150 nm; an  $n \rightarrow \sigma^*$  transition absorbs near 190 nm. The third band ( $R$ -band) appears in the near ultraviolet in the 270-300 nm region. The  $R$ -band is weak ( $\epsilon_{\max} < 30$ ) and results from the forbidden transition of a loosely held  $n$ -electron to the  $\pi^*$  orbital, the lowest unoccupied orbital of the carbonyl group.  $R$ -bands undergo a blue shift as the polarity of the solvent is increased. Acetone absorbs at 279 nm in  $n$ -hexane; in water the  $\lambda_{\max}$  is 264.5. The blue shift results from hydrogen bonding which lowers the energy of the  $n$  orbital. The blue shift can be used as a measure of the strength of the hydrogen bond.

**SATURATED KETONES AND ALDEHYDES.** Absorption data for several saturated ketones and aldehydes are presented in Table VII.

The bathochromic effect accompanying the introduction of larger and more highly branched alkyl groups in the aliphatic ketones can be seen from the data in Table VII.

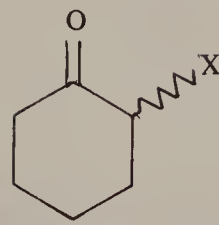
The  $n \rightarrow \pi^*$  absorption of ketones and aldehydes is weak. Spectra of derivatives, such as the semicarbazones or 2,4-dinitrophenylhydrazones, are often used for identification work.

Table VII. Absorption Data for Saturated Aldehydes and Ketones

| Compound            | $n \rightarrow \pi^*$ Transition ( $R$ -band) |                   | Solvent   |
|---------------------|---|-------------------|-----------|
|                     | $\lambda_{\max}(nm)$                          | $\epsilon_{\max}$ |           |
| Acetone             | 279   | 13                | Isooctane |
| Methyl ethyl ketone | 279   | 16                | Isooctane |
| Diisobutyl ketone   | 288   | 24                | Isooctane |
| Hexamethylacetone   | 295   | 20                | Alcohol   |
| Cyclopentanone      | 299   | 20                | Hexane    |
| Cyclohexanone       | 285   | 14                | Hexane    |
| Acetaldehyde        | 290   | 17                | Isooctane |
| Propionaldehyde     | 292   | 21                | Isooctane |
| Isobutyraldehyde    | 290   | 16                | Hexane    |

Table VIII. Shifts in Absorption Maxima for Substituted Cyclohexanones

| X                                |     |     |
|----------------------------------|-----|-----|
|                                  | eq. | ax. |
| —Cl                              | —7  | +22 |
| —Br                              | —5  | +28 |
| —OH                              | —12 | +17 |
| —O <sub>2</sub> CCH <sub>3</sub> | —5  | +10 |



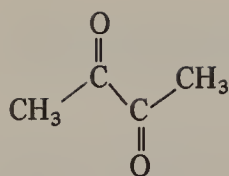
The introduction of an  $\alpha$ -halogen atom in an aliphatic ketone has little effect on the  $n \rightarrow \pi^*$  transition. However,  $\alpha$ -substitution of halogen atoms in saturated cyclic ketones has a marked effect on the absorption characteristics (Table VIII). The  $\lambda_{\max}$  of the parent compound is reduced by 5-10 nm when the substituent is equatorial and a bathochromic shift of 10-30 nm occurs when the substituent is axial. The bathochromic shift is usually accompanied by a strong hyperchromic effect. These effects are valuable in the structure determination of halogenated steroids and terpenes. Some sort of conformational rigidity must be present in the cyclohexanone system so that the substituent, X, is clearly either in an equatorial or an axial position.

The attachment of groups containing lone electron pairs to carbonyl groups has a marked effect upon the  $n \rightarrow \pi^*$  transition. The  $R$ -band is shifted to shorter wavelengths with little effect upon intensity. The shift in absorption results from a combination of inductive and resonance effects. Substitution may change the energy levels of both the ground state and the excited state, but the important factor is the relative energies of the two levels. Absorption values for the  $n \rightarrow \pi^*$  transitions of several simple carbonyl compounds are presented in Table IX.

**$\alpha$ -DIKETONES AND  $\alpha$ -KETO ALDEHYDES.** Acyclic  $\alpha$ -diketones, such as biacetyl, exist in the  $s$ -*trans* conformation (with a dihedral angle,  $\phi$ , of  $180^\circ$ ). The spectrum of biacetyl shows the normal weak  $R$ -band at 275 nm and a

Table IX.  $n \rightarrow \pi^*$  Transitions ( $R$ -Bands) of Simple Carbonyl-Containing Compounds

| Compound         | $\lambda_{\max}(nm)$ | $\epsilon_{\max}$ | Solvent    |
|------------------|----------------------|-------------------|------------|
| Acetaldehyde     | 293                  | 11.8              | Hexane     |
| Acetic acid      | 204                  | 41                | Ethanol    |
| Ethyl acetate    | 207                  | 69                | Pet. ether |
| Acetamide        | 220 ( <i>s</i> )     |                   | Water      |
| Acetyl chloride  | 235                  | 53                | Hexane     |
| Acetic anhydride | 225                  | 47                | Isooctane  |
| Acetone          | 279                  | 15                | Hexane     |

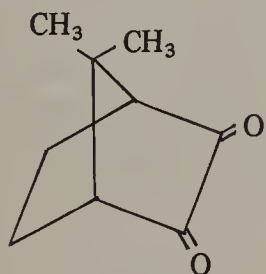


$$\phi = \sim 180^\circ$$

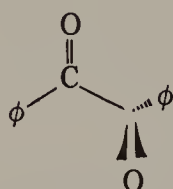
$$\lambda_{\max} = 450 \text{ nm}$$

$$\epsilon = 10$$

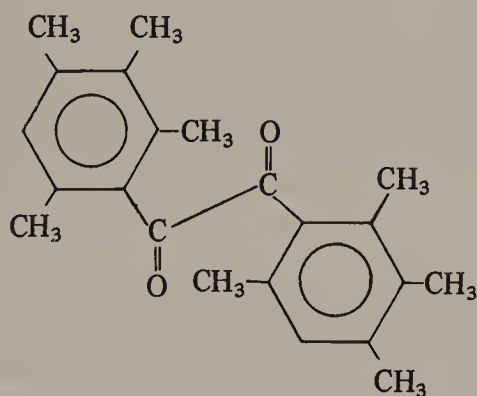
weak band near 450 nm resulting from interaction between the carbonyl groups. The position of the long-wavelength band of  $\alpha$ -diketones incapable of enolization reflects the effect of coplanarity upon resonance, and hence depends on the dihedral angle  $\phi$  between the carbonyl groups (I, II, III):



I Camphorquinone  
 $\phi = 0\text{--}10^\circ$   $\lambda_{\max} 488 \text{ nm}$   
 $\epsilon = 17$

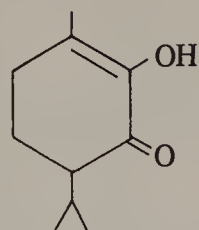


II Benzil  
 $\phi = 90^\circ$   $\lambda_{\max} 370 \text{ nm}$   
 $\epsilon = 40$



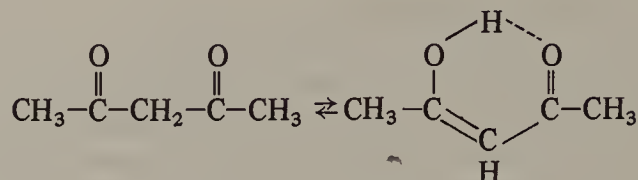
III Isoduril  
 $\phi = 180^\circ$   $\lambda_{\max} 490 \text{ nm}$

Cyclic  $\alpha$ -diketones with  $\alpha$ -hydrogen atoms exist in the enolic form, for example, diosphenol. The absorption characteristics of diosphenol appear later in this chapter.



Diosphenol

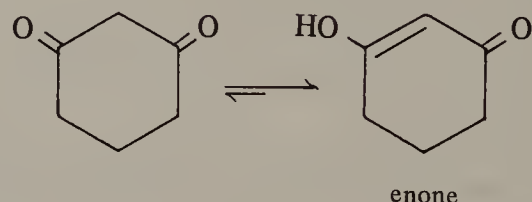
**$\beta$ -DIKETONES.** The ultraviolet spectra of  $\beta$ -diketones depend on the degree of enolization. The enolic form is stabilized when steric considerations permit intramolecular hydrogen bonding. Acetylacetone is a classic example. The enolic species exists to the extent of about 15% in aqueous solution and 91-92% in the vapor phase or in solution in nonpolar solvents. The absorption is directly dependent on the concentration of the enol tautomer.



$$\lambda_{\max}^{\text{H}_2\text{O}} 274, \epsilon_{\max} 2050$$

$$\lambda_{\max}^{\text{Isooctane}} 272, \epsilon_{\max} 12,000$$

Cyclic  $\beta$ -diketones, such as 1,3-cyclohexanedione, exist almost exclusively in the enolic form even in polar solvents. The enolic structures show strong absorption in the 230-260 nm region due to the  $\pi \rightarrow \pi^*$  transition in the *s-trans*



enone system. 1,3-Cyclohexanedione, in ethanol, absorbs at 253 nm ( $\epsilon_{\max} 22,000$ ). The formation of the enolate ion, in alkaline solution, shifts the strong absorption band into the 270 to 300 nm region.

**$\alpha,\beta$ -UNSATURATED KETONES AND ALDEHYDES.** Compounds containing a carbonyl group in conjugation with an ethylenic group are called *enones*. Spectra of enones are characterized by an intense absorption band (*K*-band) in the 215-250 nm region ( $\epsilon_{\max}$  usually 10,000-20,000), and a weak  $n \rightarrow \pi^*$  band (*R*-band) at 310-330 nm. The weak *R*-band is frequently poorly defined. Absorption data for several conjugated ketones and aldehydes are presented in Table X.

Since carbonyl compounds are polar, the positions of the *K*- and *R*-bands of enones are both dependent on the solvent. The hypsochromic effect on the *R*-band with increasing solvent polarity has already been discussed above.

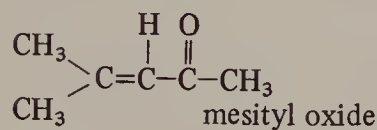
The *K*-bands of enones undergo a bathochromic shift with increasing solvent polarity. The solvent effect on the spectrum of mesityl oxide is summarized in Table XI.



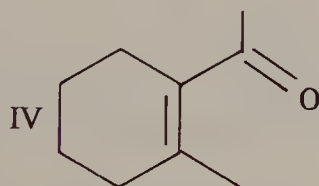
Table X. Absorption Data for Conjugated Ketones and Aldehydes

| Compound                  | K-band                |                        | R-band                |                        | Solvent   |
|---------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------|
|                           | $\lambda_{\max}$ (nm) | $\log \epsilon_{\max}$ | $\lambda_{\max}$ (nm) | $\log \epsilon_{\max}$ |           |
| Methyl vinyl ketone       | 212.5                 | 3.85                   | 320                   | 1.32                   | Ethanol   |
| Methyl isopropenyl ketone | 218                   | 3.90                   | 315                   | 1.4                    | Ethanol   |
| Acrolein                  | 210                   | 4.06                   | 315                   | 1.41                   | Water     |
| Crotonaldehyde            | 220                   | 4.17                   | 322                   | 1.45                   | Ethanol   |
| Crotonaldehyde            | 214                   | 4.20                   | 329                   | 1.39                   | Isooctane |
|                           |                       |                        | 341                   | 1.38                   |           |
|                           |                       |                        | 352 (s)               | 1.25                   |           |

(s) shoulder.

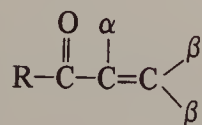


The intensity of the *K*-band may be reduced to less than  $10^4$  where steric hindrance prevents coplanarity. This frequently occurs in cyclic systems, such as IV.



$\lambda_{\max}$  243 nm,  $\epsilon_{\max}$  1400

Woodward has derived empirical generalizations for the effect of substitution on the position of the  $\pi \rightarrow \pi^*$  transition (*K*-band) in the spectra of  $\alpha,\beta$ -unsaturated ketones. The positions of the *K*-bands that result from substitution in the basic formula



are summarized in Table XII.

The spectra of  $\alpha,\beta$ -unsaturated aldehydes (Table XIII) are similar to those of the  $\alpha,\beta$ -unsaturated ketones. The *R*-bands occur in the 350-370 nm region and exhibit some fine structure when the spectra are determined in nonpolar solvents.

Table XI. Effect of Solvent Polarity on the Spectrum of Mesityl Oxide

| Solvent    | Transition                                     |  |
|------------|--|--|
|            | $\pi \rightarrow \pi^*$ ( $\lambda_{\max}$ nm) | $n \rightarrow \pi^*$ ( $\lambda_{\max}$ nm) |
| Isooctane  | 230.6  | 321  |
| Chloroform | 237.6  | 314  |
| Water      | 242.6  | Submerged under <i>K</i> -band               |

Table XII. Maxima of  $\alpha,\beta$ -Unsaturated Ketones

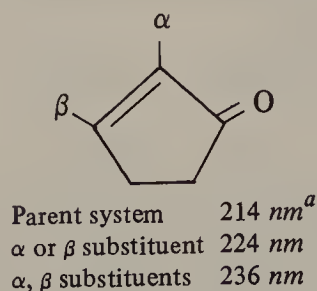
| Substitution                  |                   | Probable $\lambda_{\max}$ (nm) |
|-------------------------------|-------------------|--------------------------------|
| Unsubstituted                 |                   | 215                            |
| $\alpha$ or $\beta$           | No exocyclic C=C  | 225                            |
| $\alpha\beta$ or $\beta\beta$ | No exocyclic C=C  | 235                            |
| $\alpha\beta$ or $\beta\beta$ | One exocyclic C=C | 240                            |
| $\alpha\beta\beta$            | No exocyclic C=C  | 247                            |
| $\alpha\beta\beta$            | One exocyclic C=C | 252                            |

Table XIII. Maxima of Unsaturated Aldehydes

| Substitution                  | Probable $\lambda_{\max}$ (nm) <sup>a</sup> |
|-------------------------------|---|
| Unsubstituted                 | 208   |
| $\alpha$ or $\beta$           | 220   |
| $\alpha\beta$ or $\beta\beta$ | 230   |
| $\alpha\beta\beta$            | 242   |

<sup>a</sup>exocyclic double bond +5

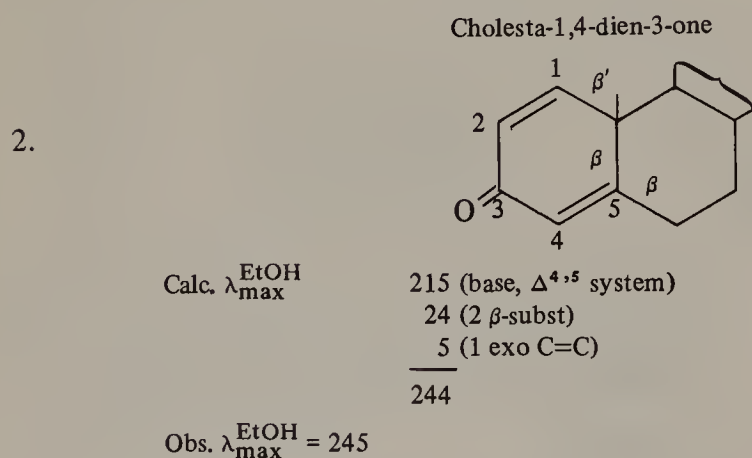
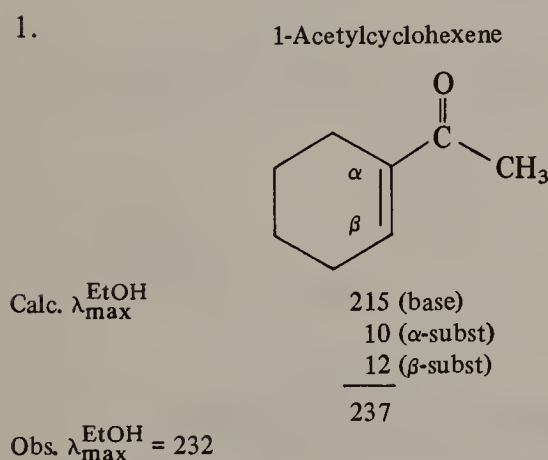
Similar rules apply to the cyclopentenone system:



<sup>a</sup>This value can be calculated from data in Table XIV  
 202 (Base value to form 5-membered cyclic enone)  
 12 (β-substituent, bond to form ring)  
 214

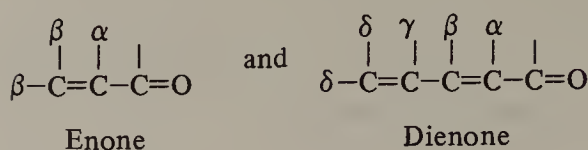
More extensive rules of enone absorption have been summarized by Fieser. These rules appear as Table XIV.

A few examples will serve to illustrate the usefulness of these correlations.



Cross conjugation has little effect on the  $\lambda_{\text{max}}$  of cholesta-1,4-diene-3-one. The calculations used were for an enone (β,β-disubstituted) with no correction required for the 1,2 double bond or for the β' group. The corresponding calculation using the Δ<sup>1,2</sup> system yields 227 nm as the predicted  $\lambda_{\text{max}}$ ; this is an indication that, when such

Table XIV. Rules of Enone and Dienone Absorption (α,β-Unsaturated Carbonyls of Ketones)



Base values:

|  |     |
|--|-----|
| Acyclic α,β-unsaturated ketones              | 215 |
| Six-membered cyclic α,β-unsaturated ketones  | 215 |
| Five-membered cyclic α,β-unsaturated ketones | 202 |
| α,β-Unsaturated aldehydes                    | 210 |
| α,β-Unsaturated carboxylic acids and esters  | 195 |

Increments for

|                                      |                  |
|--------------------------------------|------------------|
| Double bond extending conjugation    | +30              |
| Alkyl group, ring residue            | α +10            |
|                                      | β +12            |
|                                      | γ and higher +18 |
| Polar groupings: -OH                 | α +35            |
|                                      | β +30            |
|                                      | δ +50            |
| -OAc                                 | α,β,δ +6         |
| -OMe                                 | α +35            |
|                                      | β +30            |
|                                      | γ +17            |
|                                      | δ +31            |
| -Salk                                | β +85            |
| -Cl                                  | α +15            |
|                                      | β +12            |
| -Br                                  | α +25            |
|                                      | β +30            |
| -NR <sub>2</sub>                     | β +95            |
| Exocyclic double bond                | +5               |
| Homodiene component <sup>a</sup>     | +39              |
| Solvent correction (see table below) | variable         |

$\lambda_{\text{calc}} = \text{Total}^b$

<sup>a</sup>Two conjugated double bonds, both in the same ring.

<sup>b</sup>The calculated values usually fall within ±3 nm of the observed values. The molar absorptivities of *cisoid* enones are usually less than 10,000, whereas the molar absorptivities of *transoid* enones are greater than 10,000.

#### Solvent Corrections\*

| Solvent     | Correction (nm) |
|-------------|-----------------|
| Ethanol     | 0               |
| Methanol    | 0               |
| Dioxane     | +5              |
| Chloroform  | +1              |
| Ether       | +7              |
| Water       | -8              |
| Hexane      | +11             |
| Cyclohexane | +11             |

\*E.g., if the absorption was determined in cyclohexane, 11 nm would be added to the observed  $\lambda_{\text{max}}^{\text{cyclohexane}}$  to compare it to a calculated  $\lambda_{\text{max}}^{\text{ethanol}}$ .

and the  $p(n-)$  orbitals of a heteroatom. For example,

O=C1C=CC(O)C1
$$\begin{array}{r} 202 \text{ (base)} \\ 12 \text{ (}\beta\text{-subst)} \\ 35 \text{ (}\alpha\text{-OH)} \\ \hline 249 \end{array}$$

The interaction in these apparently nonconjugated systems is known as transannular conjugation.

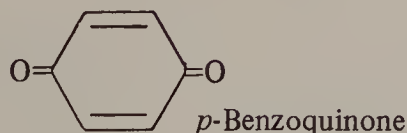
**CARBOXYLIC ACIDS.** Saturated carboxylic acids show a weak absorption band near 200 nm resulting from the forbidden  $n \rightarrow \pi^*$  transition. The position of the band undergoes a small bathochromic shift with an increase in chain length. This band is of little diagnostic value.

$\alpha,\beta$ -Unsaturated acids display a strong *K*-band characteristic of the conjugated system. In the first member of the series, acrylic acid, the absorption occurs near 200 nm,  $\epsilon_{\text{max}}$  10,000. Alkyl substitution in this basic structure results in a bathochromic shift of the *K*-band in much the same manner as observed for  $\alpha,\beta$ -unsaturated ketones. The extension of conjugation produces further bathochromic shifts accompanied by an increase in the band intensity and the appearance of fine structure. The attachment of an electronegative group on the  $\alpha$ -carbon also produces a bathochromic shift. We can calculate expected maxima for the compounds described in Table XV, utilizing the data of Table XIV.

The absorption characteristics of several  $\alpha,\beta$ -unsaturated acids are summarized in Table XVI.

**ESTERS AND LACTONES.** Esters and sodium salts of carboxylic acids show absorption at wavelengths and intensities comparable to the parent acid. Conjugated, unsaturated lactones display spectra similar to unsaturated esters. The spectra of simple unsaturated lactones show end absorption in the 200-240 nm region. Extended conjugation produces a bathochromic shift of the  $\pi \rightarrow \pi^*$  transi-

The spectrum of *p*-benzoquinone is similar to



that of a typical  $\alpha,\beta$ -unsaturated ketone, the strong *K*-band appearing at 245 nm with a weak *R*-band near 435 nm.

There are cases where the C=O and the C=C are non-conjugated in the formal sense but where interaction does occur to produce an absorption band. In structures where this occurs, the C=O and C=C groups must be oriented so that there can be effective overlap of the  $\pi$

orbitals. For example, the structure  $\text{CH}_2=\text{C}=\text{O}$  shows a

moderately strong band near 214 nm with a normal weak *R*-band at 284 nm. Similar effects are observed when there can be effective overlap of the  $\pi$  orbital for the C=O group

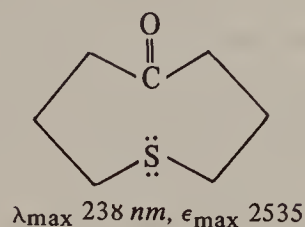


Table XV. Absorption Maxima of Unsaturated Carboxylic Acids and Esters

|  | $\lambda_{\text{max}}^{\text{EtOH}} (\pm 5 \text{ nm})$ |
|--|---|
| $\alpha$ or $\beta$ -monosubstituted             | 208   |
| $\alpha,\beta$ - or $\beta,\beta$ -disubstituted | 217   |
| $\alpha,\beta,\beta$ -trisubstituted             | 225   |
| exocyclic $\alpha,\beta$ double bond             | +5  |
| endocyclic $\alpha,\beta$ double bond in         |   |
| 5 or 7 membered ring                             | +5  |

(Data of Table XIV may be applied here.)

A.T. Nielson, *J. Org. Chem.*, **22**, 1539 (1957).



tion (*K*-band). Table XIV may be used to predict the maxima of such compounds.

**AMIDES AND LACTAMS.**  $\alpha,\beta$ -Unsaturated amides and lactams show absorption in the near ultraviolet at  $\lambda_{\max}$  200-220,  $\epsilon_{\max} < 10,000$ .  $\alpha,\beta$ -Unsaturated lactams show a second band near 250 nm ( $\epsilon_{\max} \sim 1000$ ).

#### Azomethines (Imines) and Oximes

These structures show only weak absorption in the near ultraviolet unless the  $>C=N-$  group is involved in conjugation. In

the spectra of conjugated azomethines and oximes the  $\pi \rightarrow \pi^*$  transition (*K*-band) appears in the 220-230 nm region,  $\epsilon_{\max} > 10,000$ . Acidification of the azomethines, producing a positive charge on the nitrogen, shifts the absorption to the 270-290 nm region. Simple imines show a weak  $n \rightarrow \pi^*$  transition. For example, for  $CH_3CH_2CH_2N=C(CH_3)_2$

$\lambda_{\max} = 246$  nm ( $\epsilon = 140$ , cyclohexane)

$\lambda_{\max} = 232$  nm ( $\epsilon = 200$ , ethanol)

#### Nitriles and Azo Compounds

$\alpha,\beta$ -Unsaturated nitriles absorb just inside the near ultraviolet region, near 213 nm,  $\epsilon_{\max} \sim 10,000$ .

The azo group is analogous to the ethylenic linkage with two  $\sigma$  bonds being replaced by two lone pairs of electrons ( $-\ddot{N}=\ddot{N}-$ ). The  $\pi \rightarrow \pi^*$  transition occurs in the far

(vacuum) ultraviolet. The  $n \rightarrow \pi^*$  band in aliphatic azo compounds appears near 350 nm with the expected low intensity,  $\epsilon_{\max} < 30$ . *trans*-Azobenzene absorbs at 320 nm ( $\epsilon_{\max} 21,000$ ). Comparable absorption for *trans*-stilbene occurs at 295 nm ( $\epsilon_{\max} 28,000$ ).

#### Compounds with N to O Bonds

Four groups contain multiple nitrogen-to-oxygen linkages: nitro, nitroso, nitrates, and nitrites. All of these structures show weak absorption in the near ultraviolet region resulting from an  $n \rightarrow \pi^*$  transition.

The absorption of several typical compounds containing nitrogen-to-oxygen linkages are presented in Table XVII.

The effect of conjugation upon the absorption characteristics of the nitro group is apparent from the data for 1-nitro-1-propene. The strong  $\pi \rightarrow \pi^*$  transition (*K*-band) submerges the weak  $n \rightarrow \pi^*$  transition (*R*-band).

#### Multiply Bonded Sulfur Groups

Aliphatic sulfones are transparent in the near ultraviolet region. The sulfur atom in sulfones has no lone-pair electrons, and the lone pairs of electrons associated with the oxygen atoms appear to be tightly bound. In an  $\alpha,\beta$ -unsaturated sulfone, such as ethyl vinyl sulfone, a band appears in the 210 nm region resulting from resonance between the S to O linkage and the ethylenic linkage.

Saturated sulfoxides absorb near 220 nm with intensities of the order of 1500. This absorption involves an  $n \rightarrow \pi^*$

Table XVI. Absorption of  $\alpha,\beta$ -Unsaturated Acids

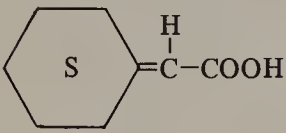
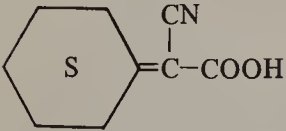
| Compound  | $\lambda_{\max}^{EtOH}$ | $\epsilon_{\max}$ |
|---|-------------------------|-------------------|
| $CH_2=CH-COOH$  | 200 nm                  | 10,000            |
| $CH_3CH=CH-COOH$ ( <i>trans</i> )   | 205                     | 14,000            |
| $CH_3CH=CH-COOH$ ( <i>cis</i> )   | 205.5                   | 13,500            |
| $\begin{array}{c} CH_3 \\   \\ CH_2=C-COOH \end{array}$                             | 210                     | —                 |
|  | 220                     | 14,000            |
|  | 235                     | 12,500            |
| $CH_3-(CH=CH)_2-COOH$   | 254                     | 25,000            |
| $CH_3-(CH=CH)_3-COOH$   | 294                     | 37,000            |
| $CH_3-(CH=CH)_4-COOH$   | 332                     | 49,000            |

Table XVII. Absorption of Compounds Containing Nitrogen-Oxygen Linkages

| Compound                | $n \rightarrow \pi^*$ Transition ( <i>R</i> -band) |                   | Solvent |
|-------------------------|--|-------------------|---------|
|                         | $\lambda_{\max}$                                   | $\epsilon_{\max}$ |         |
| Nitromethane            | 275 nm   | 15                | Heptane |
| 2-Methyl-2-nitropropane | 280.5  | 23                | Heptane |
| 1-Nitro-1-propene       | 229 <sup>a</sup>                                   | 9400              | Ethanol |
|                         | 235 <sup>a</sup>                                   | 9800              |         |
| Nitrosobutane           | 300  | 100               | Ether   |
|                         | 665  | 20                |         |
| Octyl nitrate           | 270 <sup>b</sup>                                   | 15                | Pentane |
| Cyclohexyl nitrate      | 270 <sup>b</sup>                                   | 22                | —       |
| <i>n</i> -Butyl nitrite | 218  | 1050              | Ethanol |
|                         | 313-384 <sup>c</sup>                               | 17-45             |         |

<sup>a</sup>These are  $\pi \rightarrow \pi^*$  transitions.

<sup>b</sup>This is typically a point of inflection in the spectra of nitrates.

<sup>c</sup>This region is one of fine structure with bands roughly 10 nm apart. The band with maximum absorption occurs at 357 nm.

transition in the S=O group and thus undergoes a hypsochromic shift as solvent polarity is increased. Aromatic sulfoxides show an intense *K*-band in addition to the displaced *B*-band.

In compounds containing the  $\begin{array}{c} \text{O} \\ || \\ -\text{S}-\text{X} \end{array}$  grouping, the position of the  $n \rightarrow \pi^*$  band depends on the electronegativity of X; the greater the electronegativity, the shorter will be the wavelength of absorption.

Simple thioketones of the dialkyl or alkylaryl types are unstable and generally exist as trimers. Thiobenzophenone is monomeric as are compounds in which the C=S group is attached to an electron-donating group, such as  $-\text{NR}_2$ . The  $n \rightarrow \pi^*$  transition of the C=S group in thioketones occurs at a longer wavelength than the analogous C=O transition because the energy of the nonbonding electron pair of the sulfur atom lies at a higher level than the corresponding electrons of the oxygen atom. Compounds containing the C=S group also display intense bands in the 250-320 nm region which presumably arise from  $\pi \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$  transitions in the C=S group.

The  $n \rightarrow \pi^*$  bands of some thiocarbonyl compounds are summarized in Table XVIII.

### Benzene Chromophore

Benzene displays 3 absorption bands: 184 nm ( $\epsilon_{\text{max}}$  60,000), 204 nm ( $\epsilon_{\text{max}}$  7900), and 256 nm ( $\epsilon_{\text{max}}$  200). These bands originate from  $\pi \rightarrow \pi^*$  transitions. The intense band near 180 nm results from an allowed transition, whereas the weaker bands near 200 and 260 nm result from forbidden transitions in the highly symmetrical benzene molecule. Different notations have been used to designate the absorption bands of benzene; these are summarized in Table XIX. We shall discuss these bands using Braude's *E* and *B* notation.

The *B*-band of benzene and many of its homologs is characterized by considerable fine structure. This is particularly true of spectra determined in the vapor phase or in nonpolar solvents. The fine structure originates from sub-levels of vibrational absorption upon which the electronic absorption is superimposed (Figure 7, p. 327). In polar

Table XIX. Benzene Bands

| 184 nm                | 204 nm                | 256 nm   | Ref. |
|-----------------------|-----------------------|----------|------|
| <i>E</i> <sub>1</sub> | <i>E</i> <sub>2</sub> | <i>B</i> | a    |
| —                     | <i>K</i>              | <i>B</i> | b    |

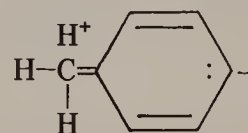
<sup>a</sup>See Reference 5 at the end of the Chapter.

<sup>b</sup>A. Burawoy, *Ber.*, 63, 3155 (1930); *J. Chem. Soc.*, 1177 (1939).

solvents, interactions between solute and solvent tend to reduce the fine structure.

Substitution of alkyl groups on the benzene ring produces a bathochromic shift of the *B*-band, but the effect of alkyl substitution upon the *E*-bands is not clearly defined. The absorption characteristics of the *B*-bands of several alkylbenzenes are presented in Table XX.

The bathochromic shift is attributed to hyperconjugation in which the  $\sigma$ -electrons of an alkyl C—H bond participate in resonance with the ring. The methyl group is more effective in hyperconjugation than other alkyl groups.



The addition of a second alkyl group to the molecule is most effective in producing a red shift if it is in the *para* position. The *para* isomer absorbs at the longest wavelength with the largest  $\epsilon_{\text{max}}$ . The *ortho* isomer generally absorbs at the shortest wavelength with reduced  $\epsilon_{\text{max}}$ . This effect is attributed to steric interactions between the *ortho* substituents, which effectively reduce hyperconjugation.

Substitution on the benzene ring of auxochromic groups (OH, NH<sub>2</sub>, etc.) shifts the *E*- and *B*-bands to longer wavelengths, frequently with intensification of the *B*-band and loss of its fine structure, because of  $n-\pi$  conjugation (Table XXI).

Table XVIII.  $n \rightarrow \pi^*$  Transitions in Thiocarbonyl Compounds

| Compound         | $n \rightarrow \pi^*$ Transition ( <i>R</i> -band) |                             |
|------------------|--|-----------------------------|
|                  | $\lambda_{\text{max}}$ (nm)                        | log $\epsilon_{\text{max}}$ |
| Thiobenzophenone | 599  | 2.81                        |
| Thioacetamide    | 358  | 1.25                        |
| Thiourea         | 291 ( <i>s</i> )                                   | 1.85                        |

(*s*) shoulder.

Table XX. Absorption Data for Alkylbenzenes (*B*-Bands)

| Compound               | $\lambda_{\text{max}}$ (nm)* | $\epsilon_{\text{max}}$ |
|------------------------|------------------------------|-------------------------|
| Benzene                | 256                          | 200                     |
| Toluene                | 261                          | 300                     |
| <i>m</i> -Xylene       | 262.5                        | 300                     |
| 1,3,5-Trimethylbenzene | 266                          | 305                     |
| Hexamethylbenzene      | 272                          | 300                     |

\* $\lambda_{\text{max}}$  of most intense peak in band with fine structure.



Table XXI. Effect of Auxochromic Substitution on the Spectrum of Benzene

| Compound                    | $E_2$ -band           |                   | $B$ -band             |                   | Solvent       |
|-----------------------------|-----------------------|-------------------|-----------------------|-------------------|---------------|
|                             | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ |               |
| Benzene                     | 204                   | 7,900             | 256                   | 200               | Hexane        |
| Chlorobenzene               | 210                   | 7,600             | 265                   | 240               | Ethanol       |
| Thiophenol                  | 236                   | 10,000            | 269                   | 700               | Hexane        |
| Anisole                     | 217                   | 6,400             | 269                   | 1,480             | 2% Methanol   |
| Phenol                      | 210.5                 | 6,200             | 270                   | 1,450             | Water         |
| Phenolate anion             | 235                   | 9,400             | 287                   | 2,600             | Aq. alkali    |
| <i>o</i> -Catechol          | 214                   | 6,300             | 276                   | 2,300             | Water (pH 3)  |
| <i>o</i> -Catecholate anion | 236.5                 | 6,800             | 292                   | 3,500             | Water (pH 11) |
| Aniline                     | 230                   | 8,600             | 280                   | 1,430             | Water         |
| Anilinium cation            | 203                   | 7,500             | 254                   | 160               | Aq. acid      |
| Diphenyl ether              | 255                   | 11,000            | 272                   | 2,000             | Cyclohexane   |
|                             |                       |                   | 278                   | 1,800             |               |

Conversion of a phenol to the corresponding anion results in a bathochromic shift of the  $E_2$ - and  $B$ -bands and an increase in  $\epsilon_{\max}$  because the nonbonding electrons in the anion are available for interaction with the  $\pi$ -electron system of the ring. When aniline is converted to the anilinium cation, the pair of nonbonding electrons of aniline is no longer available for interaction with the  $\pi$ -electrons of the ring, and a spectrum almost identical to that of benzene results.

Confirmation of a suspected phenolic structure may be obtained by comparison of the ultraviolet spectra obtained for the compound in neutral and in alkaline solution (pH 13). Similar confirmatory information for a suspected aniline derivative may be obtained by a comparison of spectra determined in neutral and in acid solution (pH 1).

When the spectra of pure acid and of pure conjugate base cross at some point, the spectra of all solutions containing various ratios of these two species (and no other

Table XXII. Absorption Characteristics of Benzenes Substituted with Chromophores

| Compound                  | $\pi \rightarrow \pi^*$ Transition<br>$K$ -band |                   | $B$ -band             |                   | $n \rightarrow \pi^*$ Transition<br>$R$ -band |                   | Solvent   |
|---------------------------|---|-------------------|-----------------------|-------------------|---|-------------------|-----------|
|                           | $\lambda_{\max}$ (nm)                           | $\epsilon_{\max}$ | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ | $\lambda_{\max}$ (nm)                         | $\epsilon_{\max}$ |           |
| Benzene                   | —   | —                 | 255                   | 215               | —   | —                 | Alcohol   |
| Styrene                   | 244   | 12,000            | 282                   | 450               | —   | —                 | Alcohol   |
| Phenylacetylene           | 236   | 12,500            | 278                   | 650               | —   | —                 | Hexane    |
| Benzaldehyde              | 244   | 15,000            | 280                   | 1,500             | 328   | 20                | Alcohol   |
| Acetophenone              | 240   | 13,000            | 278                   | 1,100             | 319   | 50                | Alcohol   |
| Nitrobenzene              | 252   | 10,000            | 280                   | 1,000             | 330   | 125               | Hexane    |
| Benzoic acid              | 230   | 10,000            | 270                   | 800               | —   | —                 | Water     |
| Benzonitrile              | 224   | 13,000            | 271                   | 1,000             | —   | —                 | Water     |
| Diphenyl sulfoxide        | 232   | 14,000            | 262                   | 2,400             | —   | —                 | Alcohol   |
| Phenyl methyl sulfone     | 217   | 6,700             | 264                   | 977               | —   | —                 | —         |
| Benzophenone              | 252   | 20,000            | —                     | —                 | 325   | 180               | Alcohol   |
| Biphenyl                  | 246   | 20,000            | submerged             | —                 | —   | —                 | Alcohol   |
| Stilbene ( <i>cis</i> )   | 283   | 12,300*           | submerged             | —                 | —   | —                 | Alcohol   |
| Stilbene ( <i>trans</i> ) | 295†  | 25,000*           | submerged             | —                 | —   | —                 | Alcohol   |
| 1-Phenyl-1,3-butadiene    |   |                   |                       |                   |   |                   |           |
| <i>cis</i> -              | 268   | 18,500            | —                     | —                 | —   | —                 | Isooctane |
| <i>trans</i> -            | 280   | 27,000            | —                     | —                 | —   | —                 | Isooctane |
| 1,3-Pentadiene            |   |                   |                       |                   |   |                   |           |
| <i>cis</i> -              | 223   | 22,600            | —                     | —                 | —   | —                 | Alcohol   |
| <i>trans</i> -            | 223.5   | 23,000            | —                     | —                 | —   | —                 | Alcohol   |

\*Intense bands also occur in the 200-230 nm region.

†Most intense band of fine structure.



absorbing species) must also go through this point, the isosbestic point, provided that the sum of the concentrations of both species is constant, and that the spectral characteristics (i.e., the absorption coefficients) of both species are insensitive to the effect of *pH* and of the buffer used. An isosbestic point's presence can be used to verify that one is dealing with a simple acid-base reaction that is not complicated by further equilibria or other phenomena.

Interaction between the nonbonding electron pair(s) of a heteroatom attached to the ring and the  $\pi$ -electrons of the ring is most effective when the *p* orbital of the nonbonding electrons is parallel to the  $\pi$  orbitals of the ring. Thus, bulky substitution in the ortho position of molecules such as *N,N*-dimethylaniline causes a hypsochromic shift in the  $E_2$ -band, accompanied by a marked reduction in  $\epsilon_{\max}$ .

|                                       |                      |                          |
|---------------------------------------|----------------------|--------------------------|
| <i>N,N</i> -Dimethylaniline           | $\lambda_{\max}$ 251 | $\epsilon_{\max}$ 15,500 |
| 2-Methyl- <i>N,N</i> -dimethylaniline | $\lambda_{\max}$ 248 | $\epsilon_{\max}$ 6360   |

Direct attachment of an unsaturated group (chromophore) to the benzene ring produces a strong bathochromic

**Table XXIII.** Calculation of the Principal Band ( $\pi \rightarrow \pi^*$  Transition) of Substituted Benzene Derivatives,  $\text{Ar}-\text{COG}$  (in  $\text{EtOH}$ )<sup>2,\*</sup>

| $\text{ArCOR}/\text{ArCHO}/\text{ArCO}_2\text{H}/\text{ArCO}_2\text{R}$                        |                        | $\lambda_{\max}^{\text{EtOH}}$ (nm) |
|--|------------------------|-------------------------------------|
| Parent chromophore: $\text{Ar} = \text{C}_6\text{H}_5$   |                        |                                     |
| $\text{G} = \text{Alkyl}$ or ring residue, (e.g., $\text{ArCOR}$ )                             |                        | 246                                 |
| $\text{G} = \text{H}$ , ( $\text{ArCHO}$ )   |                        | 250                                 |
| $\text{G} = \text{OH}$ , $\text{OAlk}$ , ( $\text{ArCO}_2\text{H}$ , $\text{ArCO}_2\text{R}$ ) |                        | 230                                 |
| Increment for each substituent on $\text{Ar}$ :  |                        |                                     |
| -Alkyl or ring residue   | <i>o</i> -, <i>m</i> - | +3                                  |
|  | <i>p</i> -             | +10                                 |
| -OH, -OCH <sub>3</sub> , -OAlk   | <i>o</i> -, <i>m</i> - | +7                                  |
|  | <i>p</i> -             | +25                                 |
| -O <sup>-</sup> (oxyanion)   | <i>o</i> -             | +11                                 |
|  | <i>m</i> -             | +20                                 |
|  | <i>p</i> -             | +78 <sup>a</sup>                    |
| -Cl  | <i>o</i> -, <i>m</i> - | +0                                  |
|  | <i>p</i> -             | +10                                 |
| -Br  | <i>o</i> -, <i>m</i> - | +2                                  |
|  | <i>p</i> -             | +15                                 |
| -NH <sub>2</sub>   | <i>o</i> -, <i>m</i> - | +13                                 |
|  | <i>p</i> -             | +58                                 |
| -NHCOCH <sub>3</sub>   | <i>o</i> -, <i>m</i> - | +20                                 |
|  | <i>p</i> -             | +45                                 |
| -NHCH <sub>3</sub>   | <i>p</i> -             | +73                                 |
| -N(CH <sub>3</sub> ) <sub>2</sub>  | <i>o</i> -, <i>m</i> - | +20                                 |
|  | <i>p</i> -             | +85                                 |

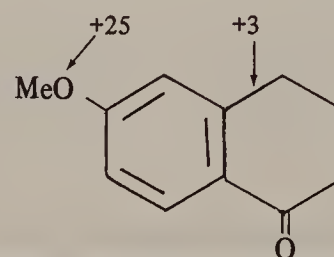
<sup>a</sup>This value may be decreased markedly by steric hindrance to coplanarity.

\*Use of the table is illustrated by the examples on pp. 323-324 and in A.I. Scott's book.<sup>2</sup>

shift of the *B*-band, and the appearance of a *K*-band ( $\epsilon_{\max} > 10,000$ ) in the 200-250 nm region (Table XXII). The overlap of absorption positions of the *K*-band, and the displaced *E*-bands of auxochromically substituted benzenes, may lead to confusion in the interpretation of ultraviolet spectra. Generally *E*-bands are less intense. The *B*-bands are sometimes buried under the *K*-bands.

The data in Table XXII show that in certain structures, such as acetophenone and benzaldehyde, displaced *B*- and *R*-bands can still be recognized.

The data of Table XXIII allow calculation of an expected maximum for aromatic aldehydes, ketones, carboxylic acids and esters. Application of Table XXIII to structure confirmation is illustrated with the following examples:

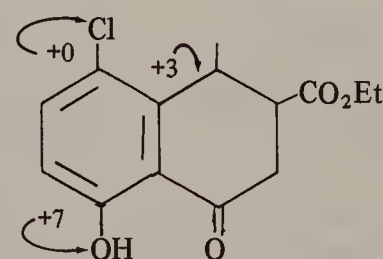


**Example 1.** 6-Methoxytetralone

Calc.:  $\lambda_{\max}^{\text{EtOH}} = 246$  (parent chromophore) + 3(*o*-ring residue) + 25 (*p*-OMe)  
= 274 nm

Obs.:  $\lambda_{\max}^{\text{EtOH}} = 276$  nm

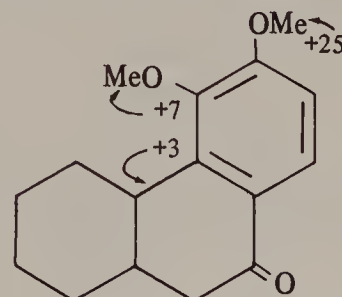
**Example 2.** 3-Carboethoxy-4-methyl-5-chloro-8-hydroxytetralone



Calc.:  $\lambda_{\max}^{\text{EtOH}} = 246 + 3$  (*o*-ring residue) + 7 (*o*-OH)  
= 256 nm

Obs.:  $\lambda_{\max}^{\text{EtOH}} = 257$  nm

**Example 3.** 3,4-Dimethoxy-4b,5,6,7,8,8a,9,10-octahydrophenanthren-10-one



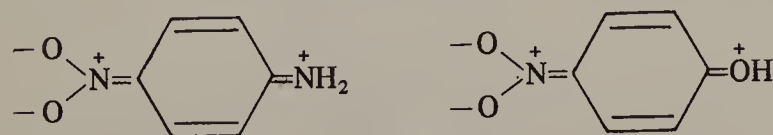
Calc.:  $\lambda_{\max}^{\text{EtOH}} = 246 + 25 + 7 + 3 = 281$  nm

Obs.:  $\lambda_{\max}^{\text{EtOH}} = 278$  nm

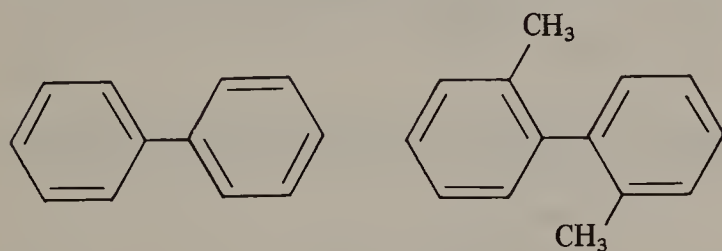
Application of Table XXIII does not give accurate predicted maxima in the 2,6-disubstituted phenyl carbonyl compounds; that this is due to disruption of the planarity necessary for conjugation of the carbonyl and phenyl groups is supported by the large decrease in molar absorptivity accompanying such substitution.

When auxochromic groups appear on the same ring as the chromophore, both groups influence the absorption. The influence is most pronounced when an electron donating group and electron attracting group are para to one another (complementary substitution, Table XXIV).

The red shift and increase in intensity of the *K*-band are related to contributions of the following polar resonance forms:



Biphenyl is the parent molecule of a series of compounds in which two aromatic rings are in conjugation. Resonance energy is at a maximum when the rings are coplanar and essentially zero when the rings are at 90° to one another.



*K*-Band,  $\lambda_{\max}$  252,  $\epsilon_{\max}$  19,000  
Biphenyl

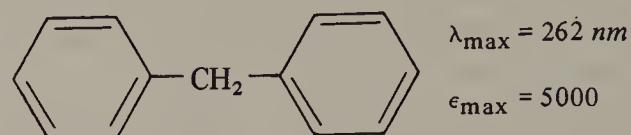
*B*-Band,  $\lambda_{\max}$  270,  $\epsilon_{\max}$  800  
2, 2'-Dimethylbiphenyl

The effect of forcing the rings out of coplanarity is readily seen from a comparison of the absorption characteristics of biphenyl and its 2,2'-dimethyl homolog whose absorption characteristics are similar to those of *o*-xylene.

Table XXIV. Absorption Characteristics of Disubstituted Benzenes

| Compound                          | $\pi \rightarrow \pi^*$ Transition<br><i>K</i> -band |                   | <i>B</i> -band   |                   |
|-----------------------------------|--|-------------------|------------------|-------------------|
|                                   | $\lambda_{\max}$                                     | $\epsilon_{\max}$ | $\lambda_{\max}$ | $\epsilon_{\max}$ |
| <i>o</i> -NO <sub>2</sub> Phenol  | 279  | 6,600             | 351              | 3,200             |
| <i>m</i> -NO <sub>2</sub> Phenol  | 274  | 6,000             | 333              | 1,960             |
| <i>p</i> -NO <sub>2</sub> Phenol  | 318  | 10,000            | submerged        |                   |
| <i>o</i> -NO <sub>2</sub> Aniline | 283  | 5,400             | 412              | 4,500             |
| <i>m</i> -NO <sub>2</sub> Aniline | 280  | 4,800             | 358              | 1,450             |
| <i>p</i> -NO <sub>2</sub> Aniline | 381  | 13,500            | submerged        |                   |

Introduction of a methylene group between two chromophores is generally considered capable of destroying conjugation. Compare the data of diphenylmethane

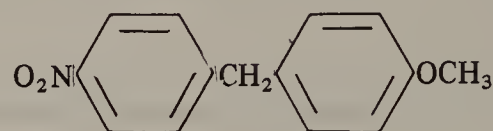


with the  $\epsilon_{\max}$  for biphenyl above and the substituted diphenylmethanes below. In some substituted diphenylmethanes, there is an effective overlap of  $\pi$  orbitals of the two rings resulting in homoconjugation. The  $\epsilon_{\max}$  of 4-nitro-4'-methoxydiphenylmethane is not merely the sum of the  $\epsilon_{\max}$  of *p*-nitrotoluene and *p*-methoxytoluene:



| $\lambda_{\max}$ | $\epsilon_{\max}$ |
|------------------|-------------------|
| 274              | 9,490             |

| $\lambda_{\max}$ | $\epsilon_{\max}$ |
|------------------|-------------------|
| 277              | 2,190             |
| 285.5            | 1,786             |



| $\lambda_{\max}$ | $\epsilon_{\max}$ |
|------------------|-------------------|
| 280              | 24,400            |
| 287              | 16,800            |

Another approach to predicting the  $\lambda_{\max}$  of the primary band of substituted benzenes involves the use of Table XXV. This table has been successfully used with disubstituted compounds when the following rules are used:

1. Para substitution. a. Both groups are either electron donating or electron withdrawing: Only the effect of the group causing the larger shift is used. For example, the  $\lambda_{\max}$  of *p*-nitrobenzoic acid would be expected to be the same as that of nitrobenzene,  $\sim(203.5 + 65.0) = \sim 268.5$  (in alcohol solvent). b. One group is electron donating and the other, electron withdrawing: The calculated  $\lambda_{\max}$  here would usually be much lower than the observed  $\lambda_{\max}$  for the reasons that were discussed above for *p*-nitrophenol and Table XXIV. Table XXIII may be used for some of the above compounds for which Table XXV cannot be used.
2. Ortho, meta substitution. The shift effects are additive.

Benzenoid compounds containing three or more substituents have not been thoroughly tested by the method of Table XXV.

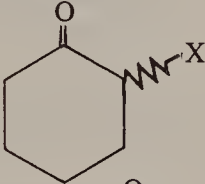
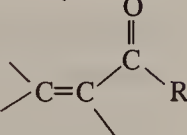
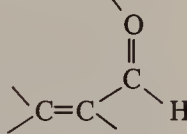
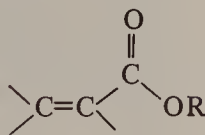
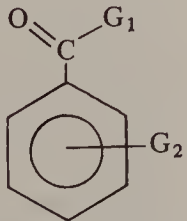
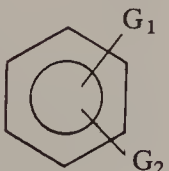
The types of compounds for which there are empirical methods for calculating the  $\lambda_{\max}$  of important bands are listed in Table XXVI.

**Table XXV. Calculation of the Primary Band ( $\pi \rightarrow \pi^*$  transition) of Substituted Benzenes ( $\text{CH}_3\text{OH}$  Solvent). Base value: 203.5 nm**

| Substituent            | Shift | Substituent        | Shift | Substituent     | Shift |
|------------------------|-------|--------------------|-------|-----------------|-------|
| $-\text{CH}_3$         | 3.0   | $-\text{Br}$       | 6.5   | $-\text{OH}$    | 7.0   |
| $-\text{CN}$           | 20.5  | $-\text{Cl}$       | 6.0   | $-\text{O}^-$   | 31.5  |
| $-\text{CHO}$          | 46.0  | $-\text{NH}_2$     | 26.5  | $-\text{OCH}_3$ | 13.5  |
| $-\text{COCH}_3$       | 42.0  | $-\text{NHCOCH}_3$ | 38.5  |                 |       |
| $-\text{CO}_2\text{H}$ | 25.5  | $-\text{NO}_2$     | 65.0  |                 |       |

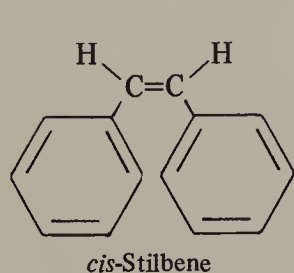
C.N.R. Rao, *J. Sci. Res. (India)*, 17B, 56 (1958); *Current Sci. (India)*, 26, 276 (1957).

**Table XXVI. Empirical Correlations Useful for Predicting the  $\lambda_{\text{max}}$  of Organic Compounds**

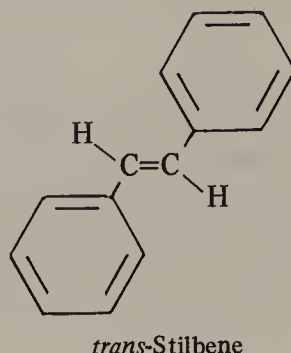
| Molecular Class                           | General Structure  | Table No. | Comment                                   |
|---|--|-----------|---|
| Small Polyenes                            | $(\text{>C}=\text{C}<)_x$<br>$x = 1 - 4$   | V         | Woodward-Fieser Rules                     |
| Larger Polyenes                           | as above, $x > 4$  | VI        | Fieser-Kuhn Rules                         |
| Substituted Cyclohexanones                |                                 | VIII      | includes halo ketone effect               |
| $\alpha,\beta$ -Unsaturated Ketones, etc. |                                 | XII, XIV  | Woodward-Fieser Rules                     |
| $\alpha,\beta$ -Unsaturated Aldehydes     |                                 | XIII, XIV |   |
| $\alpha,\beta$ -Unsaturated Esters        |                                 | XV        |   |
| Aryl Carbonyl Compounds                   | <br>$G_1 = \text{H, R, OH, OR}$ | XXIII     |   |
| Disubstituted Benzenes                    |                                 | XXV       | limited for certain <i>para</i> compounds |



The first homolog in the diphenylpolyene series ( $\phi-(C=C)_n-\phi$ ) is stilbene. Stilbene offers an interesting example of steric effects in electronic spectra.



| $\lambda_{\max}^{\text{EtOH}}$ | $\epsilon_{\max}$ |
|--------------------------------|-------------------|
| 222                            | 25,000            |
| 283                            | 12,300            |



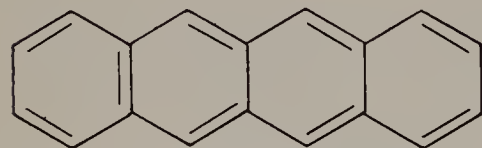
| $\lambda_{\max}^{\text{EtOH}}$ | $\epsilon_{\max}$ |
|--------------------------------|-------------------|
| 229                            | 15,800            |
| 295                            | 25,000            |
| 308                            | 25,000            |
| 320 (shoulder)                 | 15,800            |

The destruction of coplanarity by steric interference, in the *cis*-structure, is reflected by the lower intensity of the 283 nm band compared with the corresponding band (295 nm) in the *trans* isomer. The *B*-band appears to be swamped by this intense absorption.

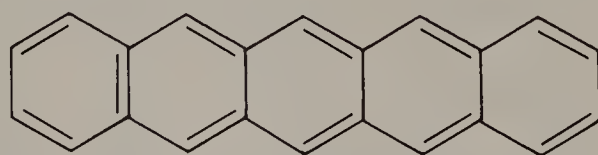
The absorption bands of the parent stilbene molecule move to longer wavelengths and increase in intensity as  $n$ , in  $\phi-(CH=CH)_n-\phi$ , increases. When  $n$  equals 7, the molecule absorbs in the 400-465 nm region with  $\epsilon_{\max}$  135,000.

Two common series of aromatic compounds are the linear series, such as anthracene, and the angular series such as phenanthrene. Although the polynuclear aromatics might well be treated as individual chromophores, a correlation between the bands of benzene and the acenes, as well as naphthalene, can be made. These correlations appear in Table XXVII.

As the number of condensed rings increases in the acene series, the absorption moves to progressively longer wavelengths until it occurs in the visible region.



Naphthalene  
(Yellow)



Pentacene  
(Blue)

Table XXVII. Correlation of Aromatic Absorption

| Compound    | <i>E</i> <sub>1</sub> band                | <i>E</i> <sub>2</sub> -band               | <i>B</i> -band                            | $\lambda_{\max}$<br>( $\epsilon_{\max}$ ) |
|-------------|---|---|---|---|
|             | $\lambda_{\max}$<br>( $\epsilon_{\max}$ ) | $\lambda_{\max}$<br>( $\epsilon_{\max}$ ) | $\lambda_{\max}$<br>( $\epsilon_{\max}$ ) |   |
| Benzene     | 184<br>(60,000)                           | 204<br>(7900)                             | 256<br>(200)                              |   |
| Naphthalene | 221<br>(133,000)                          | 286<br>(9300)                             | 312<br>(289)                              |   |
| Anthracene  | 256<br>(180,000)                          | 375<br>(9000)                             | Submerged                                 | 221<br>(14,500)                           |

The angular polycyclic compounds, the aphenes, also show a bathochromic shift of the 3-band system with an increase in the number of rings. However, the increase in  $\lambda_{\max}$ , per ring added, is less than for the acenes. The 3-band system is still distinct for phenanthrene but in the spectrum of anthracene the *E*<sub>2</sub>-band has already swamped the *B*-band.

The spectra of polynuclear aromatics are characterized by vibrational fine-structure as observed in the spectrum of benzene. Spectra of some polynuclear aromatics are shown in Figure 7.

### Heteroaromatic Compounds

Saturated 5- and 6-membered heterocyclic compounds are transparent at wavelengths longer than 200 nm. Only the unsaturated heterocyclic compounds (heteroaromatics) show absorption in the near ultraviolet region.

**FIVE-MEMBERED RINGS.** The theoretical interpretation of the spectra of 5-membered-ring heteroaromatic compounds is not simple. The absorption of these compounds has been compared to that of cyclopentadiene, the *cis*-diene analog, which shows strong diene absorption near 200 nm, and moderately intense absorption near 238 nm. The aromatic properties increase in the order cyclopentadiene, furan, pyrrole, and thiophene. The absorption of some 5-membered heteroaromatics is compared with cyclopentadiene in Table XXVIII. No attempt has been made to classify the bands, although the band near 200 nm has been likened to the *E*<sub>2</sub>-band of benzene, and the long-wavelength band frequently has fine structure analogous to that of the *B*-band of benzene.

Auxochromic or chromophoric substitution of the five-membered unsaturated heterocyclics causes a bathochromic shift and an increase in the intensity of the bands of the parent molecule (Table XXIX).

**SIX-MEMBERED RINGS.** The spectrum of pyridine is similar to that of benzene. The *B*-band of pyridine, however, is somewhat more intense and has less distinct fine structure than that of benzene (Figure 8). This transition is allowed

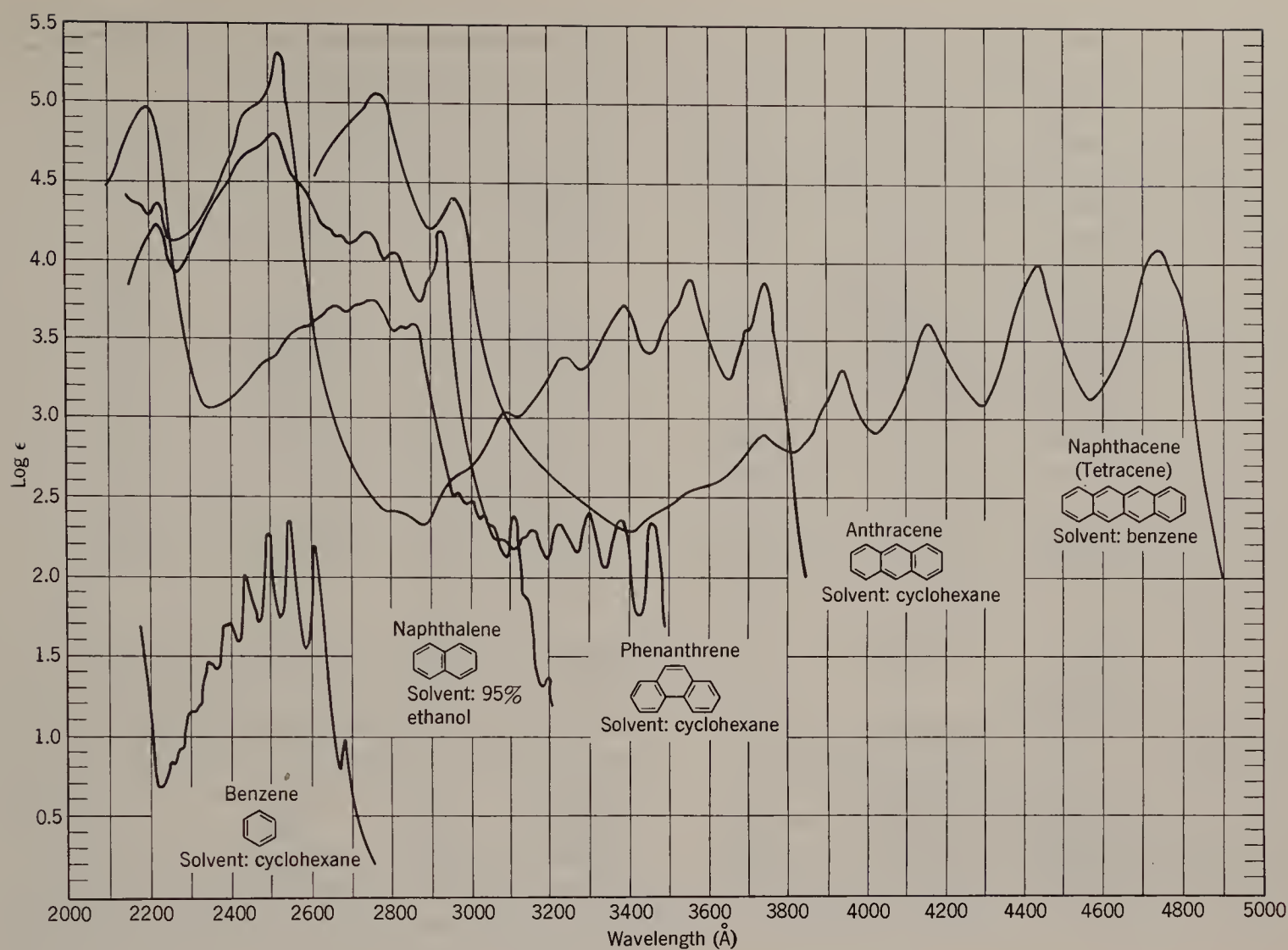


Figure 7. Electronic absorption spectra of benzene, naphthalene, phenanthrene, anthracene, and naphthacene.

for pyridine, but forbidden for the more symmetrical benzene molecule. The weak *R*-band expected for an  $n \rightarrow \pi^*$  transition in pyridine has been observed in vapor phase spectra. This band is generally swamped by the more intense *B*-band when the spectrum is determined in solution.

An increase in solvent polarity has little or no effect on

the position or intensity of the *B*-band of benzene, but produces a marked hyperchromic effect on the *B*-band of pyridine and its homologs. The hyperchromic effect undoubtedly results from hydrogen bonding through the lone pair of electrons of the nitrogen atom. The extreme case is the absorption of a pyridinium salt. The absorption character-

Table XXVIII. Absorption Data for Some 5-Membered Heteroaromatics

| Compound             | Band I           |                   | Band II          |                   | Solvent     |
|----------------------|------------------|-------------------|------------------|-------------------|-------------|
|                      | $\lambda_{\max}$ | $\epsilon_{\max}$ | $\lambda_{\max}$ | $\epsilon_{\max}$ |             |
| [Cyclopentadiene]    | 200              | 10,000            | 238.5            | 3,400             | Hexane      |
| Furan                | 200              | 10,000            | 252              | 1 <sup>a</sup>    | Cyclohexane |
| Pyrrole <sup>b</sup> | 209              | 6,730             | 240              | 300 <sup>a</sup>  | Hexane      |
| Thiophene            | 231              | 7,100             | 269.5            | 1.5 <sup>a</sup>  | Hexane      |
| Pyrazole             | 214              | 3,160             | —                | —                 | Ethanol     |

<sup>a</sup>These weak bands may be due to impurities rather than a forbidden transition ( $n \rightarrow \pi^*$ ) of a heteroaromatic molecule.

<sup>b</sup>See Table XXIX for different assignment of bands in the spectrum of pyrrole.

Table XXIX. Absorption Characteristics of 5-Membered Heteroaromatics

| Parent    | Substituent                     | Band I                |                   | Band II               |                   |
|-----------|---------------------------------|-----------------------|-------------------|-----------------------|-------------------|
|           |                                 | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ |
| Furan     |                                 | 200                   | 10,000            | 252                   | 1                 |
| Furan     | 2-CHO                           | 227                   | 2,200             | 272                   | 13,000            |
| Furan     | $\text{O}=\text{C}-\text{CH}_3$ | 225                   | 2,300             | 270                   | 12,900            |
| Furan     | 2-COOH                          | 214                   | 3,800             | 243                   | 10,700            |
| Furan     | 2-NO <sub>2</sub>               | 225                   | 3,400             | 315                   | 8,100             |
| Furan     | 2-Br, 5-NO <sub>2</sub>         | —                     | —                 | 315                   | 9,600             |
| Pyrrole   |                                 | 183                   | —                 | 209                   | 6,730             |
| Pyrrole   | 2-CHO                           | 252                   | 5,000             | 290                   | 16,600            |
| Pyrrole   | $\text{O}=\text{C}-\text{CH}_3$ | 250                   | 4,400             | 287                   | 16,000            |
| Pyrrole   | 2-COOH                          | 228                   | 4,500             | 258                   | 12,600            |
| Pyrrole   | $\text{O}=\text{C}-\text{CH}_3$ | 234                   | 10,800            | 288                   | 760               |
| Thiophene |                                 | 231                   | 7,100             | —                     | —                 |
| Thiophene | 2-CHO                           | 265                   | 10,500            | 279                   | 6,500             |
| Thiophene | $\text{O}=\text{C}-\text{CH}_3$ | 252                   | 10,500            | 273                   | 7,200             |
| Thiophene | 2-COOH                          | 249                   | 11,500            | 269                   | 8,200             |
| Thiophene | 2-NO <sub>2</sub>               | 268-272               | 6,300             | 294-298               | 6,000             |
| Thiophene | 2-Br                            | 236                   | 9,100             | —                     | —                 |

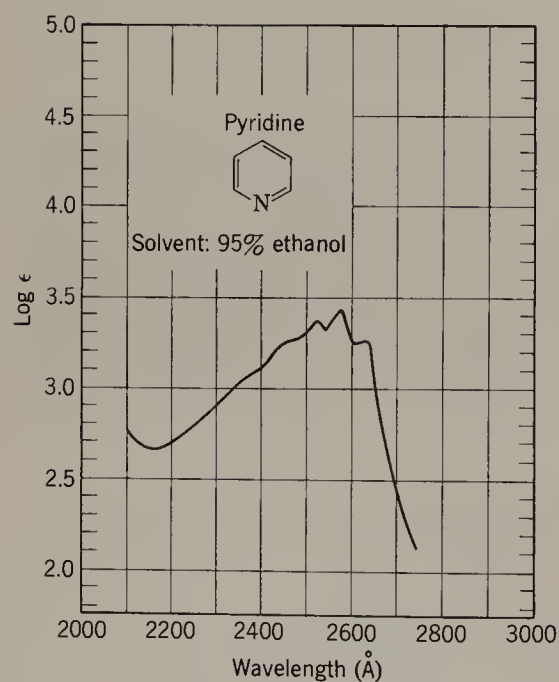


Figure 8. Ultraviolet spectrum of pyridine.

istics of 2-methylpyridine ( $\alpha$ -picoline), in several solvents, are shown in Table XXX.

The effect of substitution on the 257 nm band (*B*-band) of pyridine is illustrated in the data presented in Table XXXI.

The absorption of the 2-OH and 4-OH pyridines is attributed to the pyridone structures. Tautomerism in hydroxy- and aminopyridines is discussed thoroughly in the book by A. I. Scott.<sup>2</sup>

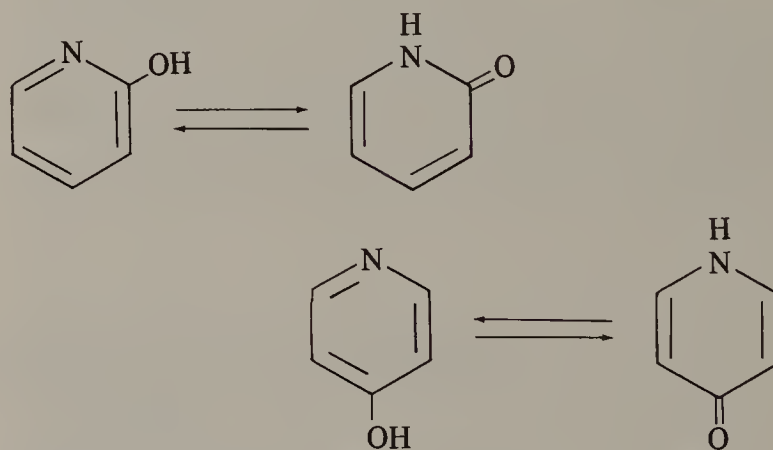


Table XXX. Absorption Characteristics of 2-Methylpyridine

| Solvent          | $\lambda_{\max}$ (nm) | $\epsilon_{\max}$ |
|------------------|-----------------------|-------------------|
| Hexane           | 260                   | 2000              |
| Chloroform       | 263                   | 4500              |
| Ethanol          | 260                   | 4000              |
| Water            | 260                   | 4000              |
| Ethanol-HCl(1:1) | 262                   | 5200              |



**Table XXXI. Absorption Characteristics of Pyridine Derivatives**

| Derivative        | $\lambda_{\max}^{(\text{pH} > 7)}$ | $\epsilon_{\max}$ |
|-------------------|------------------------------------|-------------------|
| Pyridine          | 257                                | 2,750             |
|                   | 270                                | 450               |
| 2-CH <sub>3</sub> | 262                                | 3,560             |
| 3-CH <sub>3</sub> | 263                                | 3,110             |
| 4-CH <sub>3</sub> | 255                                | 2,100             |
| 2-F               | 257                                | 3,350             |
| 2-Cl              | 263                                | 3,650             |
| 2-Br              | 265                                | 3,750             |
| 2-I               | 272                                | 400               |
| 2-OH              | 230                                | 10,000            |
|                   | 295                                | 6,300             |
| 4-OH              | 239                                | 14,100            |
| 3-OH              | 260                                | 2,200             |

The spectra of heteroaromatics appear to be related to their isocyclic analogs (Table XXXII).

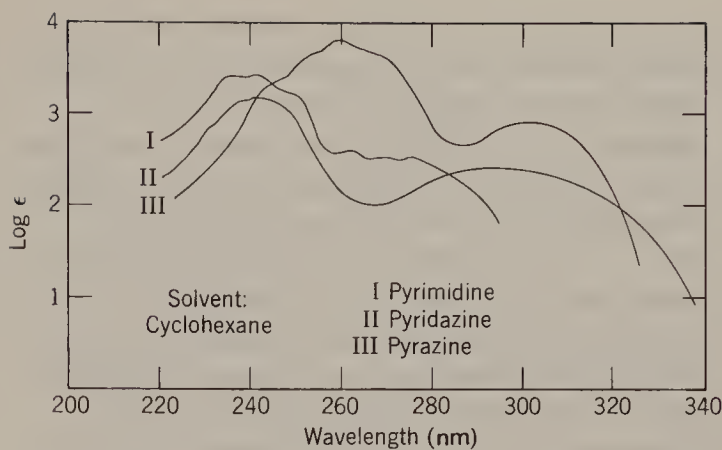
The spectra of the diazines are similar to those of pyridine (Figure 9). In addition to the enhanced *B*-band, still retaining some fine structure, the enhanced  $n \rightarrow \pi^*$  bands are quite prominent.

The absorption of the diazines, for example the pyrazines, respond to solvent polarity in a manner similar to the pyridines. The *B*-band undergoes a hyperchromic shift with an increase in solvent polarity with little or no effect upon  $\lambda_{\max}$ . The *R*-band, of course, disappears in acid solution, since the nonbonding electrons of the free base are now involved in salt formation.

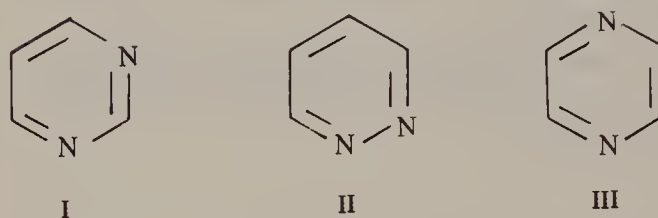
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**Figure 9.**



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**Table XXXII. Absorption Characteristics of Some Heteroaromatics Containing Nitrogen and Their Isocyclic Analogs**

| Compound     | <i>E</i> <sub>1</sub> -band <sup>a</sup> |                   | <i>E</i> <sub>2</sub> -band <sup>a</sup> |                   | <i>B</i> -band <sup>a</sup> |                   | Solvent     |
|--------------|--|-------------------|--|-------------------|-----------------------------|-------------------|-------------|
|              | $\lambda_{\max}$ (nm)                    | $\epsilon_{\max}$ | $\lambda_{\max}$ (nm)                    | $\epsilon_{\max}$ | $\lambda_{\max}$ (nm)       | $\epsilon_{\max}$ |             |
| Benzene      | 184                                      | 60,000            | 204                                      | 7,900             | 256                         | 200               | —           |
| Naphthalene  | 221                                      | 100,000           | 286                                      | 9,300             | 312                         | 280               | —           |
| Quinoline    | 228                                      | 40,000            | 270                                      | 3,162             | 315                         | 2,500             | Cyclohexane |
| Isoquinoline | 218                                      | 63,000            | 265                                      | 4,170             | 313                         | 1,800             | Cyclohexane |
| Anthracene   | 256                                      | 180,000           | 375                                      | 9,000             | —                           | —                 | —           |
| Acridine     | 250                                      | 200,000           | 358                                      | 10,000            | —                           | —                 | Ethanol     |

<sup>a</sup>All of the bands contain fine structure.

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#### Monographs—Narrow Topics

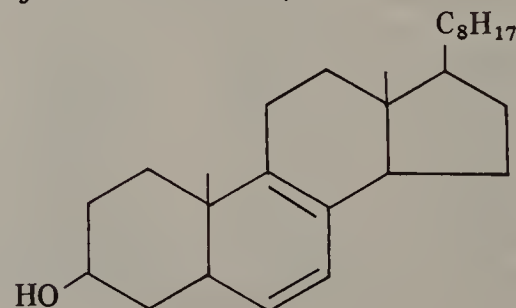
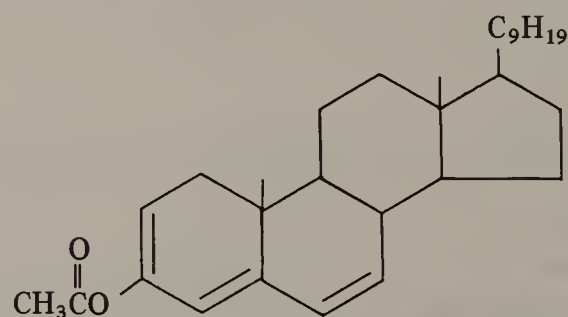
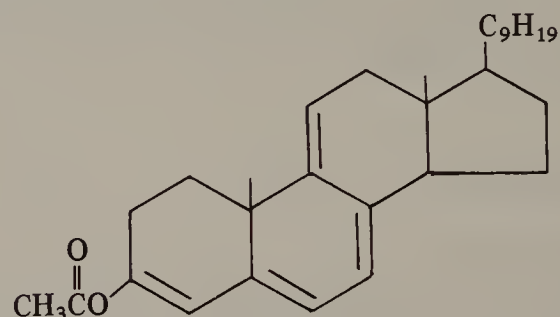
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#### Compilations—Data, Spectra, Indices

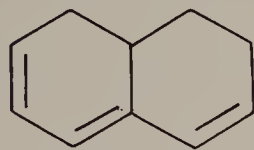
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#### PROBLEMS

- 6.1 Match the 3 steroid structures shown below to the following values for  $\lambda_{\max}^{\text{hexane}}$ : compound A, 257 nm; B, 304 nm, and C, 356 nm.



- 6.2 Partial hydrogenation of the triene shown below results in 2 compounds, D and E, both of molecular formula  $C_{10}H_{14}$ . Compound D shows a  $\lambda_{\max}^{\text{hexane}} = 235 \text{ nm}$  and E, 275 nm. Assign the structures.



- 6.3 Compound F ( $C_7H_{10}O$ ) gives a positive test with 2,4-dinitrophenylhydrazine, with sodium hydroxide/iodine and with bromine in carbon tetrachloride. The UV spectrum of F shows a  $\lambda_{\max}^{C_2H_5OH}$  at 257 nm. Deduce the structure for this compound. Is only one structure possible?
- 6.4 An acetone solution of compound G ( $C_7H_7N_2O_2$ )

shows  $^1H$  NMR signals at  $\delta$  6.63-7.90, 4H, and at  $\delta$  6.55, 3H. The intensity of the  $\delta$  6.55 signal is greatly reduced on treatment with heavy water. The UV spectrum of G shows a  $\lambda_{\max}^{C_2H_5OH}$  at 288 nm. Deduce the structure of compound G. Compound G can be prepared by reducing a nitrobenzoic acid with a mineral acid-metal mixture.

- 6.5 A Nujol mull of compound H ( $C_7H_5BrO_2$ ) shows, among others, the following IR bands: a broad band, with a number of maxima, from 3100 to 2500  $cm^{-1}$ , and a strong band at 1686  $cm^{-1}$ . The  $^1H$  NMR spectrum ( $DMSO-d_6/CDCl_3$ ) shows signals at  $\delta$  7.5 to 8.0 (4H) and at  $\delta$  12.15 (1H). The latter signal is greatly diminished upon heavy water treatment. The UV spectrum shows a  $\lambda_{\max}^{C_2H_5OH}$  at 245 nm. Deduce the structure of compound H.





# introduction to seven and eight

In practice, identification of an organic compound begins with a history, and large areas are quickly excluded from further consideration. Since, with a few exceptions, we dispense with a history, the limits will be set as follows: The compounds are quite pure; they may contain carbon, hydrogen, oxygen, nitrogen, sulfur, and the halogens in any combination; since the table of isotope contributions runs only to a molecular weight of 250, the examples will be limited to this range. Within these restrictions, we can still cover a vast expanse of organic chemistry.

Additional information, usually a history, would probably be necessary to identify a compound that contained boron, silicon, or phosphorus in addition to the above elements, but it is hardly likely that a chemist would encounter such compounds without prior knowledge that these elements are present.

The interpreter and correlator of data has always lived on the edge of uncertainty. How pure is his compound, how reliable his data, how relevant his reference material? There are few unequivocal data, either spectrometric or chemical; thus, there is no substitute for experience and a broad knowledge of chemistry. Nor is there a prescribed procedure. In general, we attempt as a first step to establish a tentative molecular formula from the molecular ion peak and the isotope contributions. In a number of cases, the molecular ion peak is so small that the isotope contributions cannot be accurately measured, and we settle for the molecular weight. In some cases, the molecular ion peak may be missing. We then try to establish the molecular weight from other evidence. Often, this can be done from the fragmentation pattern and from the other spectra at hand. The minimum number of carbon atoms can be obtained from the  $^{13}\text{C}$  NMR spectrum. A difference between the number of peaks in the  $^{13}\text{C}$  spectrum and the number of C atoms in the molecular formula indicates the presence of symmetry elements. (Coincidence of  $^{13}\text{C}$  peaks, though rare, must nonetheless be considered.) The off-resonance-decoupled  $^{13}\text{C}$  spectrum gives the minimum number of protons, which can be compared with the inte-

grated  $^1\text{H}$  spectrum and with the molecular formula. In other cases, we may resort to preparation of appropriate derivatives, to other methods of obtaining molecular weights, or to other methods of determining elemental composition. Recent improvements in combustion analysis permit C, H, and N determinations on less than a milligram of sample. If a high-resolution mass spectrometer is available, we may obtain the molecular formula and the formula of each of the fragments directly.

*We use the obvious features of one spectrum to bring out the more subtle aspects of another. The power of this methodology lies in the complementary features of the spectra.* For example, we can calculate the index of hydrogen deficiency from the molecular formula and determine the presence or absence of certain unsaturated functional groups from the IR spectrum; this information can be confirmed by the  $^1\text{H}$  and  $^{13}\text{C}$  spectra. The UV spectrum quickly establishes the presence or absence of conjugated or aromatic structures. The  $^1\text{H}$  spectrum (with decoupling if necessary) is a powerful tool for distinguishing between isomeric possibilities. When enough information is accumulated, a structure is postulated and spectral features predicted on the basis of the postulated structure are compared with the spectra actually observed. Appropriate structural modifications are made to accommodate the discrepancies. Confirmation is obtained by comparison with the spectra of an authentic sample. Let us work through the samples comprising Chapter 7 as preparation for solving the problems in Chapter 8.

We may not always be able to select an unequivocal structure; nor can we in any system of organic analysis. However, we should at least be able to narrow down the possibilities to several structures (often isomers) and to indicate the steps required to complete the identification.

Mass spectra were obtained on a Consolidated Electrodynamics Corporation Model 21-103C and a Perkin Elmer Model RMU-6E. The lower limit of the fragmentation patterns is mass 20. Peaks of less than 3% relative intensity are not reported except for the molecular ion and isotope peaks. Infrared spectra were run on the Perkin-Elmer Corporation Models 221 and 137. Proton NMR spectra were run on Varian Associates Models A-60, HR-60, HA-100 and a Perkin Elmer Model R-20; samples were dissolved in carbon tetrachloride or deuterated chloroform, and 1% tetramethylsilane in the solution was used as a reference.  $^{13}\text{C}$  NMR spectra were run on Varian XL-100 and CFT-20 instruments with tetramethylsilane as an internal reference. Unless stated otherwise, the samples were dissolved in deuterated chloroform solvent, and the instrument was locked on the deuterium in the solvent. Ultraviolet spectra were obtained from the literature, or were run on an Applied Physics Corporation's Cary Model 14M at pH 7, pH 1, and pH 13. Only the pH 7 spectrum is recorded unless a change occurred at pH 1 or pH 13. In all  $^{13}\text{C}$  data tables in Chapter 8, the intensities are for the completely decoupled spectra.

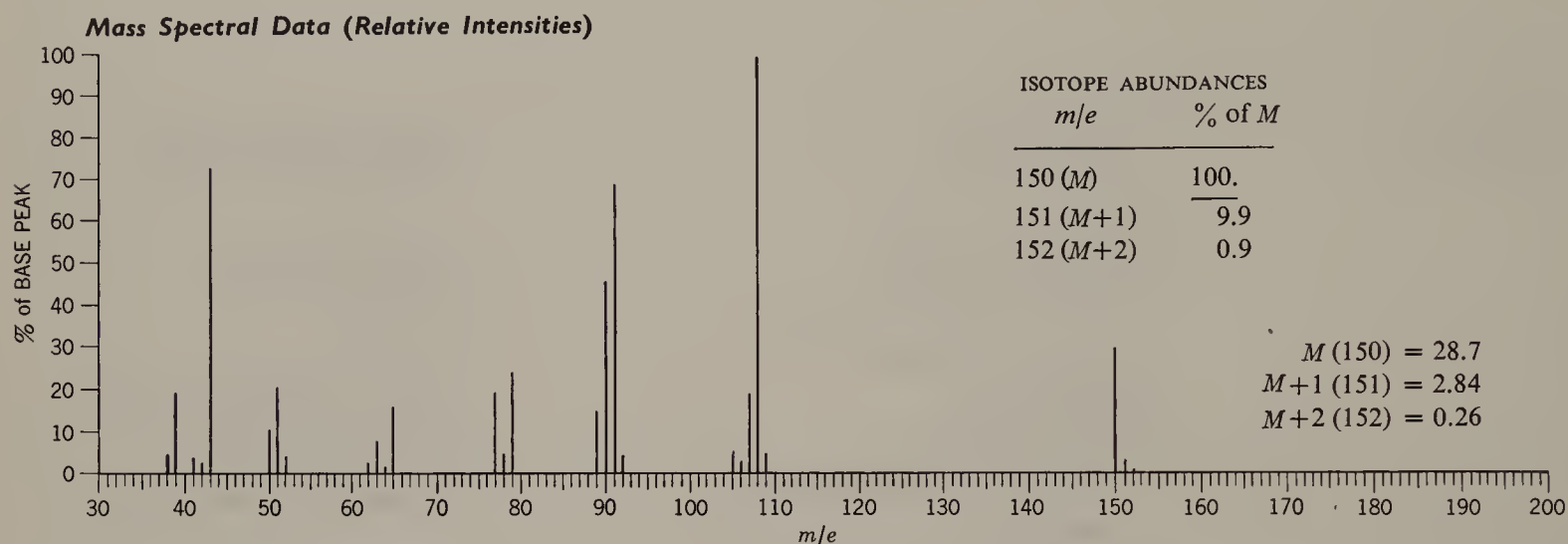
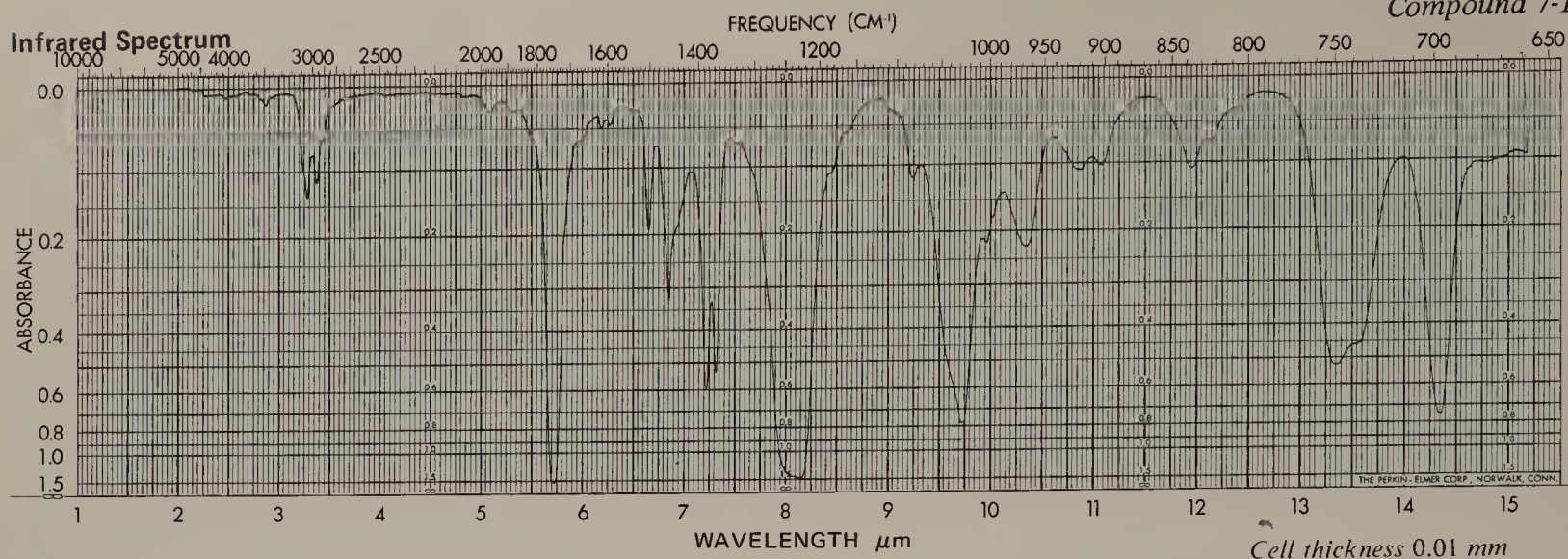




seven

sets of spectra  
translated into  
compounds

| NUMBERS | NAME, PAGE                                     | COMPOUND CLASS                   |
|---------|--|----------------------------------|
| 7-1     | Benzyl Acetate, 337                            | aromatic ester                   |
| 7-2     | Methyl 2-furoate, 341                          | heteroaromatic ester             |
| 7-3     | $\beta, \beta'$ -Dibromodiethyl ether, 343     | halo ether                       |
| 7-4     | 2-Mercaptoethanol, 346                         | hydroxy mercaptan                |
| 7-5     | Isoeugenol, 350                                | aromatic, olefinic, phenol ether |
| 7-6     | Levulinic Acid, 355                            | keto carboxylic acid             |
| 7-7     | Dibutyl(difluoromethyl)phosphine<br>oxide, 357 | halo-aliphatic, organophosphorus |
| 7-8     | Ethyl sorbate, 359                             | olefinic ester                   |

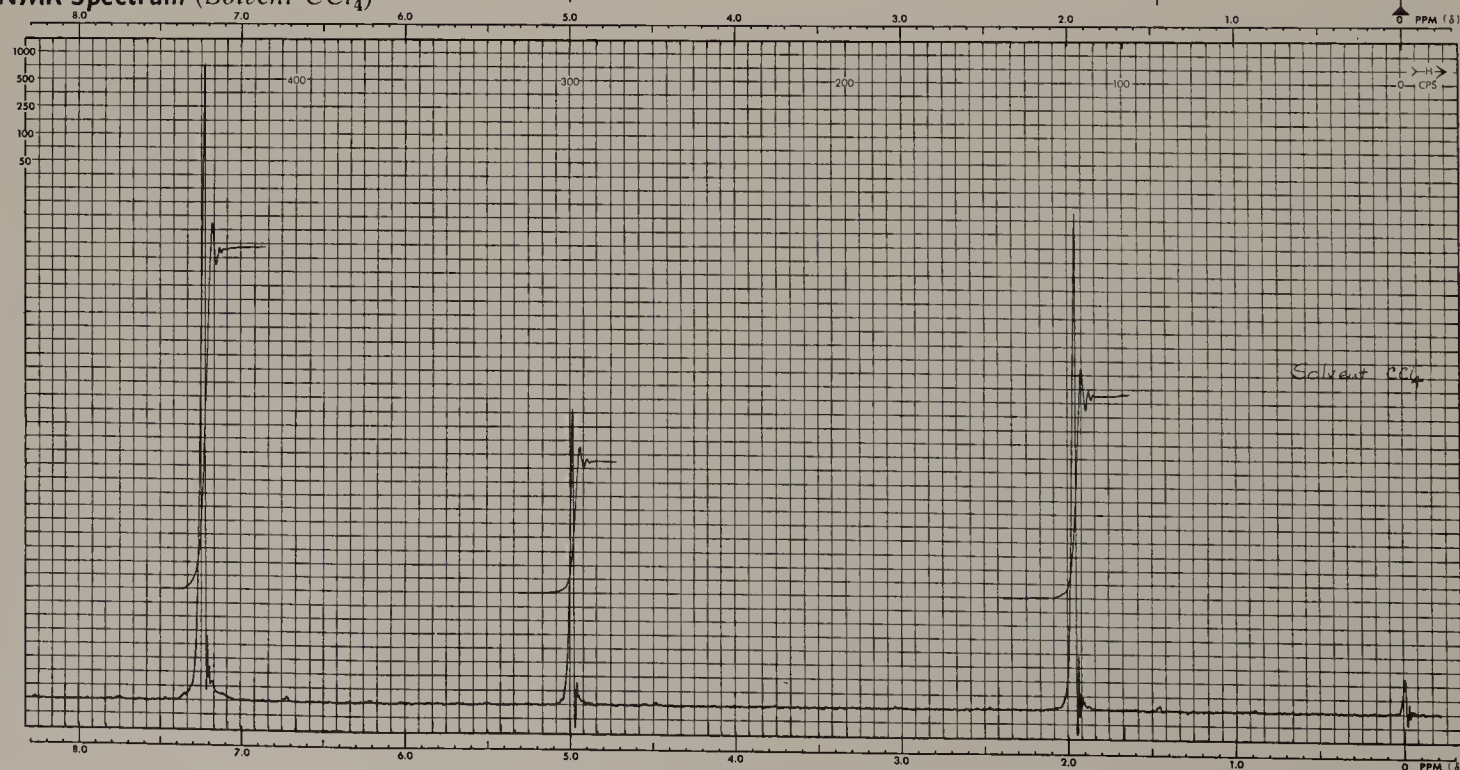


**Ultraviolet Data**

| $\lambda_{\text{max}}^{\text{EtOH}}$ | $\epsilon_{\text{max}}$ |         |     |
|--------------------------------------|-------------------------|---------|-----|
| 268                                  | 101                     | 252     | 153 |
| 264                                  | 158                     | 248 (s) | 109 |
| 262                                  | 147                     | 243 (s) | 78  |
| 257                                  | 194                     |         |     |

(s) = shoulder

**NMR Spectrum (Solvent  $\text{CCl}_4$ )**



# compound number 7-1

The first step in translating these four spectra into a molecular structure is to establish a molecular formula. The molecular ion peak is 150; this is the molecular weight. The molecular ion peak is an even number. We are, therefore, permitted either no nitrogen atoms, or an even number of them. The  $M + 2$  peak obviously does not allow for the presence of sulfur or halogen atoms.

We now look in Appendix A of Chapter 2 under molecular weight 150, and find 29 formulas of molecular weight 150 containing only CHN and O. Our  $M + 1$  peak is 9.9% of the parent peak. We list the formulas with calculated isotopic contributions to the  $M + 1$  peak falling—to be arbitrary—between 9.0 and 11.0; we also list their  $M + 2$  values:

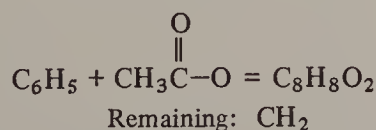
| Formula         | $M + 1$ | $M + 2$ |
|-----------------|---------|---------|
| $C_7H_{10}N_4$  | 9.25    | 0.38    |
| $C_8H_8NO_2$    | 9.23    | 0.78    |
| $C_8H_{10}N_2O$ | 9.61    | 0.61    |
| $C_8H_{12}N_3$  | 9.98    | 0.45    |
| $C_9H_{10}O_2$  | 9.96    | 0.84    |
| $C_9H_{12}NO$   | 10.34   | 0.68    |
| $C_9H_{14}N_2$  | 10.71   | 0.52    |

Three of these formulas can be eliminated because they contain an odd number of nitrogen atoms. The  $M + 2$  peak is 0.9% of the parent; this best fits  $C_9H_{10}O_2$ , which we shall tentatively designate as our molecular formula. We make a mental note that both the intensity of the molecular ion peak and the C to H ratio of the formula indicate aromaticity.

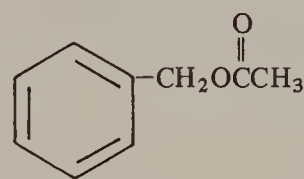
The infrared spectrum shows a  $C=O$  band at about  $1745\text{ cm}^{-1}$  ( $5.73\text{ }\mu\text{m}$ ). This, together with the presence of 2 O atoms in the formula, suggests an ester. We look for confirmation in the  $C-O-C$  stretching region and note the large broad band at about  $1225\text{ cm}^{-1}$  ( $8.15\text{ }\mu\text{m}$ ) characteristic of an acetate. Two large bands at about  $749\text{ cm}^{-1}$  ( $13.35\text{ }\mu\text{m}$ ) and  $697\text{ cm}^{-1}$  ( $14.35\text{ }\mu\text{m}$ ) suggest a singly substituted benzene ring.

The presence of a benzene ring and an acetate group is established. Furthermore, we note from the position of the carbonyl band that the  $C=O$  moiety is not conjugated with the ring. This is confirmed by the wavelengths and intensities of the ultraviolet absorption peaks which also eliminate a ketone from consideration. Subtraction of a singly substituted benzene ring and an acetate group from the molecular formula gives the following:

Molecular formula  $C_9H_{10}O_2$



It takes no great imagination to insert the  $CH_2$  between the ring and the acetate group, and write



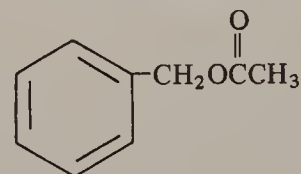
The  $^1H$  NMR spectrum provides almost conclusive confirmation for the above structure. We see 3 sharp unsplit peaks in the following positions and with the following integrated intensities

| $\delta$ | Intensity |
|----------|-----------|
| 7.22     | 5         |
| 5.00     | 2         |
| 1.96     | 3         |

The 5 protons at  $\delta$  7.22 of course are the 5 benzene-ring protons. The singlet of 2 protons at  $\delta$  5.00 represents the methylene group substituted by a phenyl and an ester group. And, of course, the singlet of 3 protons at  $\delta$  1.96 represents the methyl group.

We can obtain additional confirmation by returning to the mass spectrum and considering the fragmentation pattern (see Appendix B, Chapter 2) in view of the information at hand. The base peak at 108 is a rearrangement peak representing cleavage of an acetyl group (43) and rearrangement of a single hydrogen atom (Chapter 2, page 29). The large peak at mass 91 is the benzyl (or tropylium) ion formed by cleavage beta to the ring. And the large peak at mass 43, of course, represents the acetyl fragment. The peaks at 77, 78, and 79 are additional evidence for the benzene ring.

We can state with a high degree of confidence that the compound represented by these spectra is:



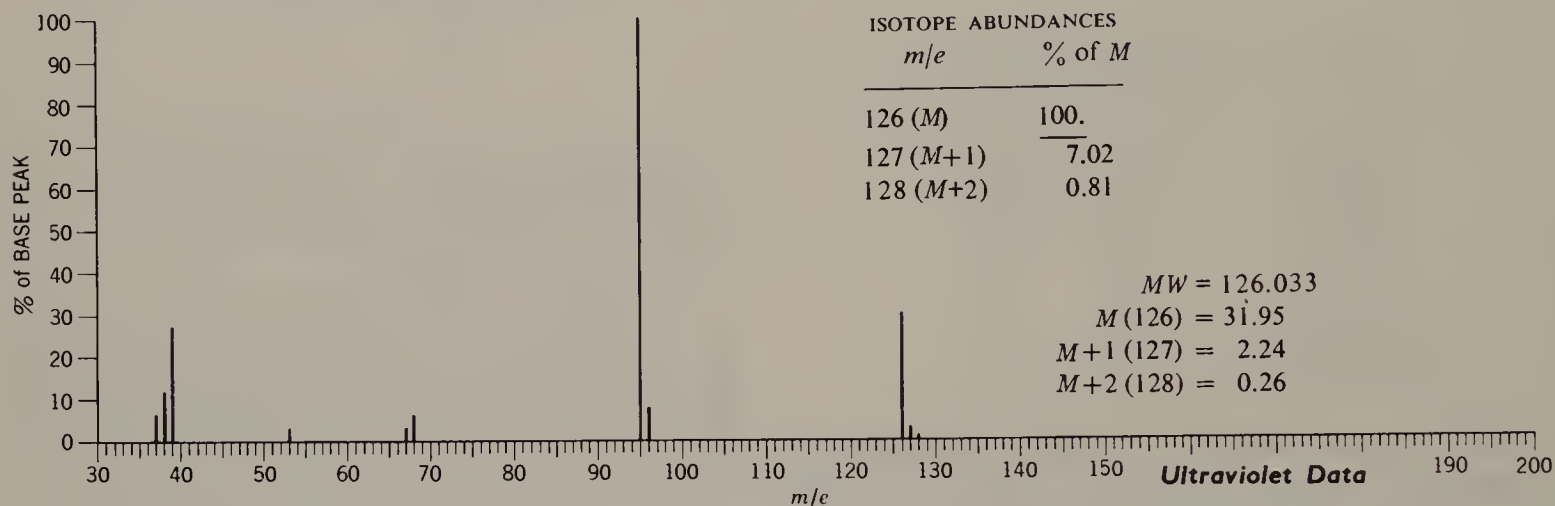
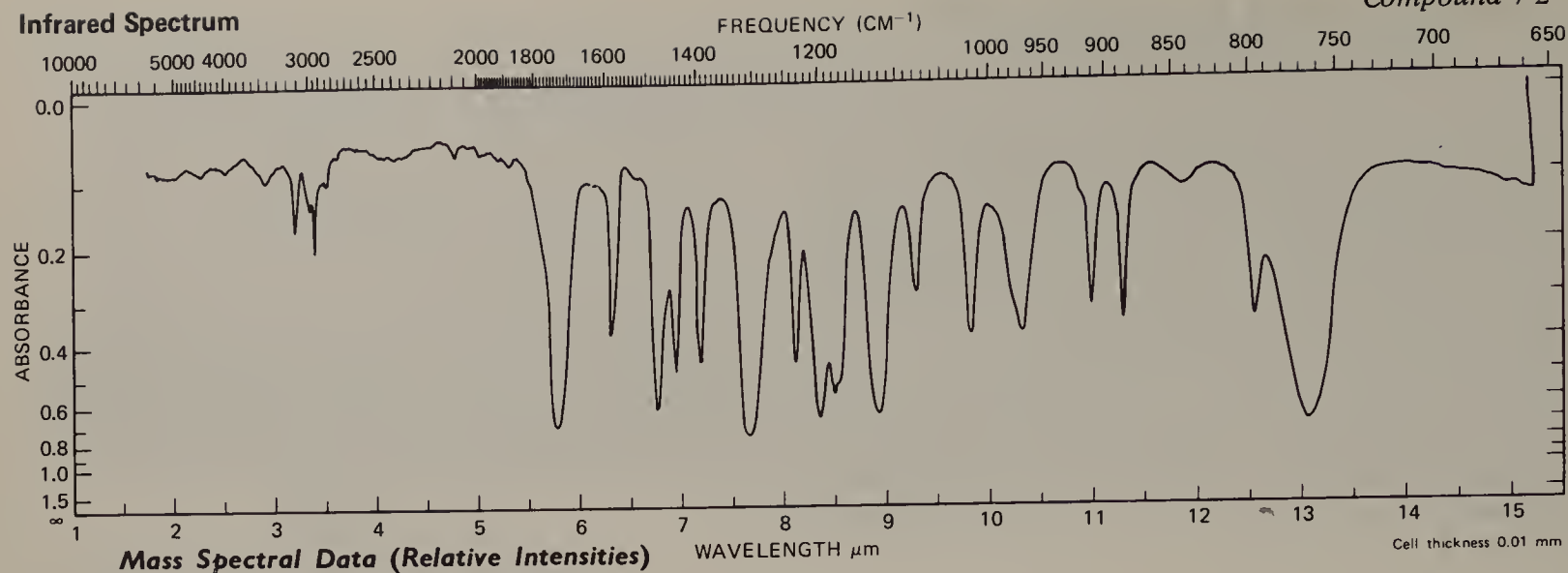
Benzyl acetate

There are, of course a number of other sequences to the identity of this compound. Having established the molecular formula, we could note at once the characteristic benzene ring peak at  $\delta$  7.22 in the NMR spectrum. We could confirm this by the typical "benzenoid" fine structure absorption in the ultraviolet spectrum. The base peak in the mass spectrum is a common rearrangement peak, and the mass 91 peak immediately calls to mind the benzyl (or tropylium) structure. The large mass 43 peak strongly suggests the  $CH_3CO$  group in view of the  $C=O$  peak in the infrared. Subtraction of a benzyl and an acetyl group from the formula leaves a mass of 16; consideration of the infrared spectrum leaves very little question as to how to handle this oxygen atom.

The student will find it instructive to write the possible isomeric structures and to eliminate them on spectrometric grounds.



## Infrared Spectrum



## Ultraviolet Data

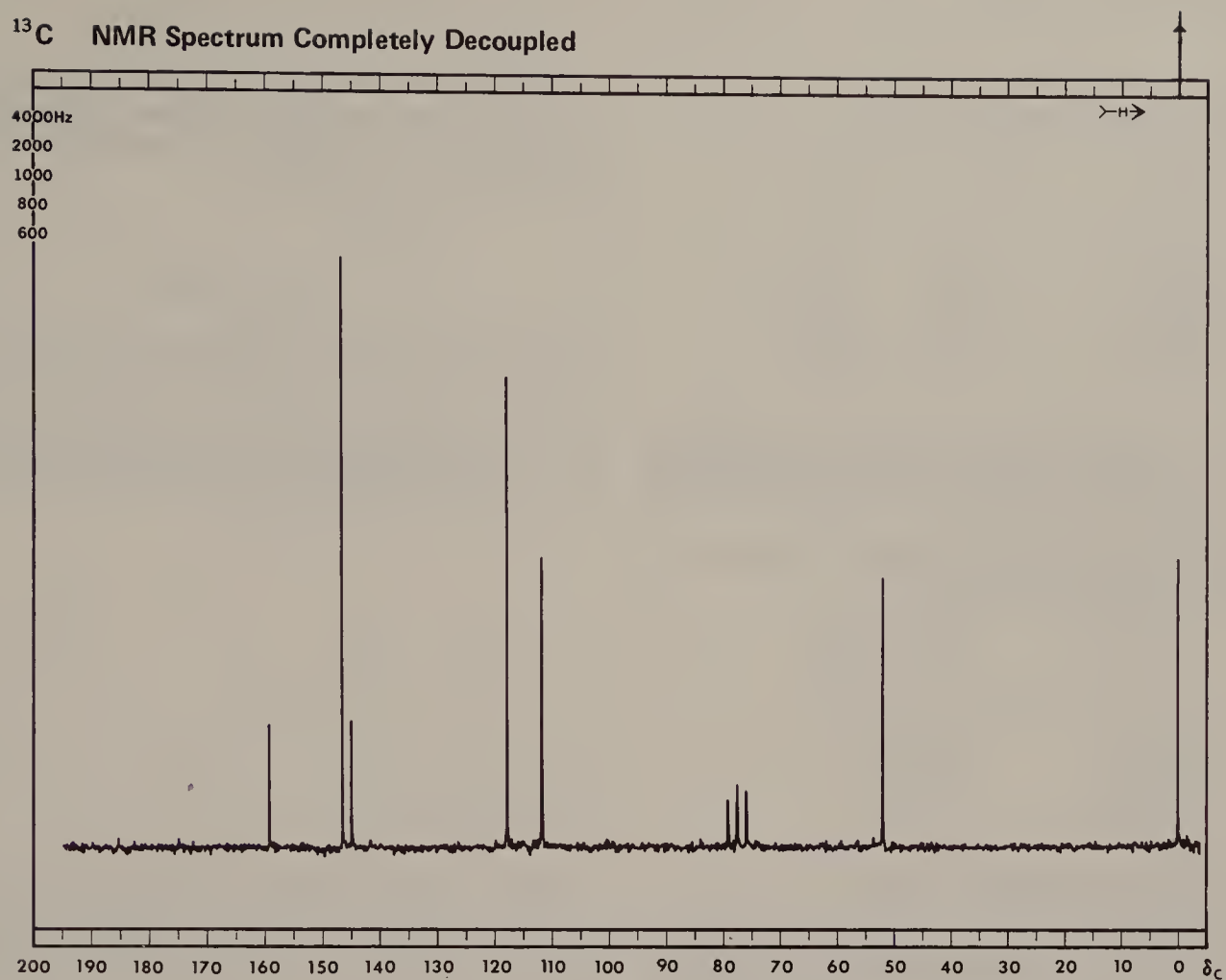
| $\lambda_{\max}^{EtOH}$ | $\log \epsilon_{\max}$ |
|-------------------------|------------------------|
| 220.0 (s)               | 3.47                   |
| 250.5                   | 4.13                   |

(s) = shoulder

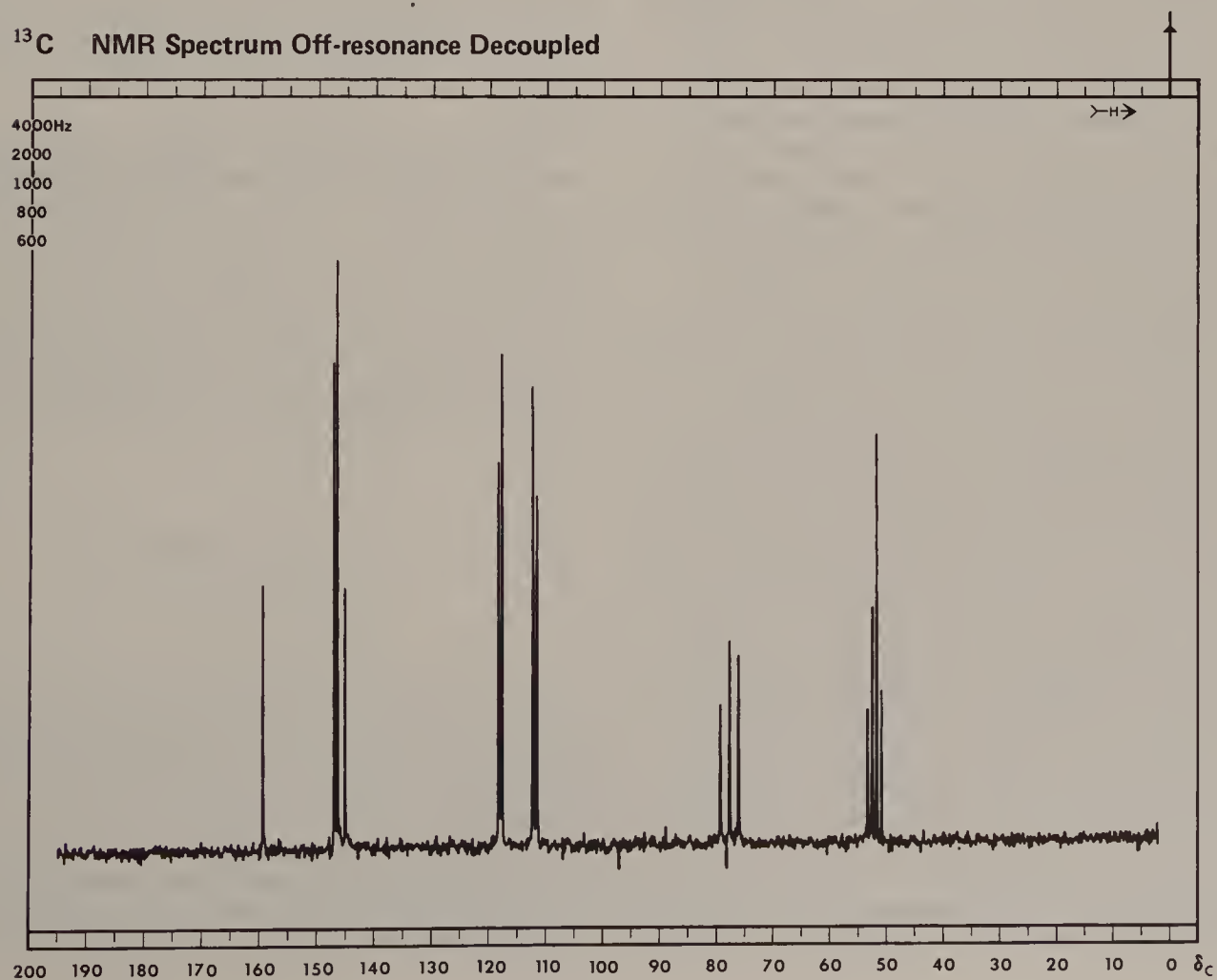
 $^1H$  NMR Spectrum (Solvent  $CCl_4$ )

Compound 7-2 (Continued)

<sup>13</sup>C NMR Spectrum Completely Decoupled



<sup>13</sup>C NMR Spectrum Off-resonance Decoupled



# compound number 7-2

The following molecular formulas fit our data for the molecular ion peak and the  $M + 1$  peak:

| Formula         | $M + 1$ | $M + 2$ |
|-----------------|---------|---------|
| $C_5H_6N_2O_2$  | 6.34    | 0.57    |
| $C_5H_{10}N_4$  | 7.09    | 0.22    |
| $C_6H_6O_3$     | 6.70    | 0.79    |
| $C_6H_{10}N_2O$ | 7.45    | 0.44    |

The formula that best fits our  $M + 2$  peak is  $C_6H_6O_3$ . We should bear in mind, however, that the  $M + 2$  peak may be higher than the calculated figure, and we accept  $C_6H_6O_3$  only as a tentative formula.

The high-resolution molecular weights for each of the four formulas are significantly different:

| Formula         | Molecular Wt. |
|-----------------|---------------|
| $C_5H_6N_2O_2$  | 126.0430      |
| $C_5H_{10}N_4$  | 126.0907      |
| $C_6H_6O_3$     | 126.0317      |
| $C_6H_{10}N_2O$ | 126.0794      |

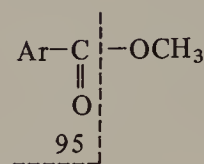
The observed molecular weight fits  $C_6H_6O_3$ .

A quick check of the  $^1H$  and  $^{13}C$  NMR spectra provides support for the tentative molecular formula. The integration of  $^1H$  signals, from low to high field, is 1:1:1:3 which supports the total (6) of hydrogens from the mass spectrum above. The proton-decoupled  $^{13}C$  spectrum shows 6 singlets (aside from the  $CDCl_3$  signals at 75-80 ppm) downfield from TMS. Thus, there are 6 nonequivalent carbons in our compound, again consistent with the formula deduced from the mass spectrum. Finally, the  $^{13}C$  off-resonance decoupled NMR spectrum supports the total of 6 protons since, from low to high field, the signals include a singlet, doublet, singlet, doublet, doublet and quartet, indicating that the corresponding carbons bear 0, 1, 0, 1, 1, and 3 protons.

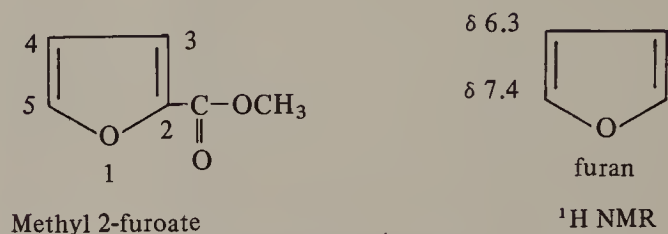
The formula and the general appearance of the infrared spectrum suggest aromaticity. We note strong peaks beyond  $800\text{ cm}^{-1}$  ( $12.5\text{ }\mu\text{m}$ ), 2 strong peaks at  $1587\text{ cm}^{-1}$  ( $6.30\text{ }\mu\text{m}$ ) and  $1479\text{ cm}^{-1}$  ( $6.76\text{ }\mu\text{m}$ ), and a medium peak at  $3106\text{ cm}^{-1}$  ( $3.22\text{ }\mu\text{m}$ ). The intense band in the ultraviolet spectrum at 250 nm is suggestive of a chromophore conjugated with an aromatic ring. The striking pattern at the low-field end of the  $^1H$  NMR spectrum demands an aromatic ring of some sort, as do the  $^{13}C$  NMR signals at  $\delta$  144.82 to 159.10.

A conspicuous feature of the infrared spectrum is the  $C=O$  peak at  $1730\text{ cm}^{-1}$  ( $5.78\text{ }\mu\text{m}$ ). Bearing in mind that we are probably dealing with a conjugated chromophore, we can make a choice between a ketone and an ester. We lean toward an ester because the conjugated ketone  $C=O$  bands are usually at lower frequency. We also look in vain for the long-wavelength  $R$ -band of conjugated ketones in the ultraviolet spectrum. (We should recall, however, that heteroaromatic ketones do not show a detectable  $R$  band.) There are a number of strong bands between 1420 and  $1110\text{ cm}^{-1}$  ( $7.05$  and  $9.0\text{ }\mu\text{m}$ ) some of which may be associated with an ester  $C-O$  absorption. And, of course, the empirical formula permits an ester group plus another oxygen.

Now we can profitably consider the base peak, mass 95, in the mass spectrum. The base peak arises from a loss of mass 31, and this loss is practically diagnostic for a methyl ester. We can write,

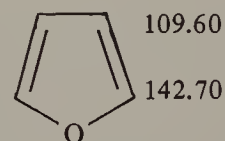


The mass 95 component then must be  $C_4H_3O-C=O$ , and we write the structural formula



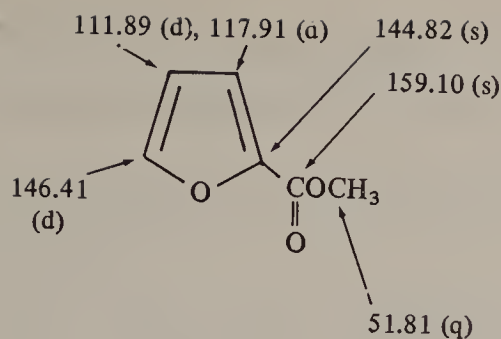
The  $^1H$  NMR spectrum is nicely in accord with this structure. We see 3 separate ring-protons at low field, and the 3 protons of the methyl group as a sharp singlet at  $\delta$  3.81. From low to high field the 3 low-field peaks (multiplets) represent the 5-proton, the 3-proton, and the 4-proton, respectively. Each is shifted downfield, by the carboxylate substituent, from its position in an unsubstituted furan ring, the 3-proton being most strongly affected.

The  $^{13}C$  NMR spectrum supports the furoate structure. The signal at  $\delta$  51.81 (a quartet in the off-resonance decoupled spectrum) corresponds to the methyl carbon of a  $COOCH_3$  group (Table XIV, Chapter 5). Since the  $^{13}C$  spectrum also shows a singlet at  $\delta$  159.10 which is still a singlet in the off-resonance decoupled spectrum, we have more support for a carbonyl group (see Chapter 5, Table XIV). Since the remaining  $^{13}C$  NMR signals total only 4, we have support for the furan aromatic ring with all ring positions being nonequivalent. (Tables VII and XIV, Chapter 5.)



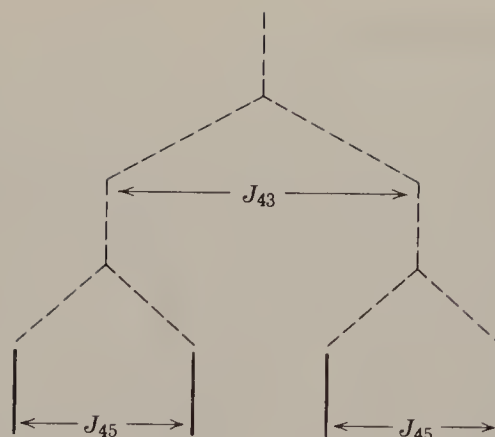
Thus, the lower field signals ( $\delta$  146.41 and 144.82 ppm) are assigned to the ring carbons attached to oxygen, and the signal at  $\delta$  144.82, since it is a singlet in the off-resonance decoupled spectrum, is assigned to C-2. Finally the 2 singlets between  $\delta$  110-120 ppm are assigned to C-3 and C-4, with C-3 being more deshielded. All of the  $^{13}C$  signals due to ring carbons (except the  $\delta$  144.82 signal) are doublets in the off-resonance decoupled spectrum since these carbons each bear 1 proton.



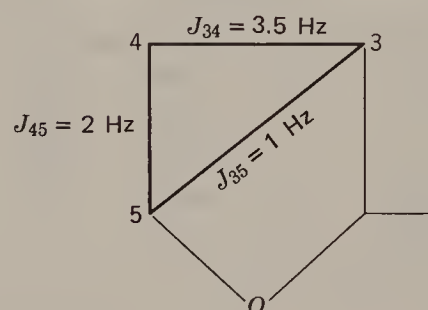
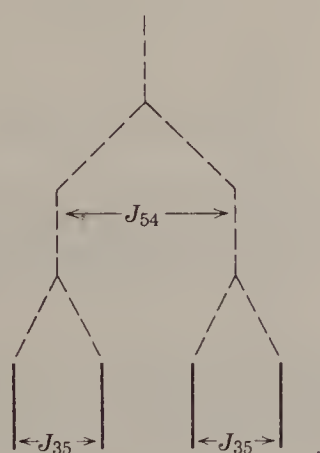


The  $^1\text{H}$  NMR multiplets afford a tidy demonstration of spin-spin coupling. The system is *AMX* with 3 coupling constants. The 5-proton is coupled with the four-proton ( $J_{54} = 1$  Hz) and with the 3-proton ( $J_{53} = 1$  Hz).

The 5-proton, therefore, shows 2 pairs of peaks.

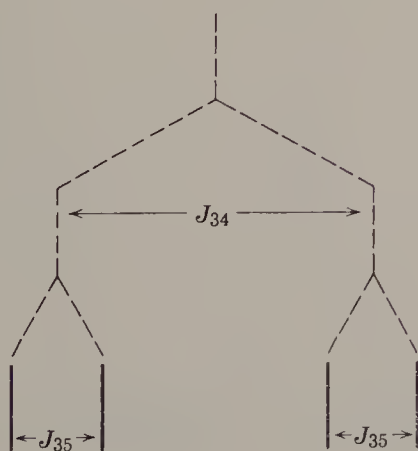


The couplings can be summed up as follows:



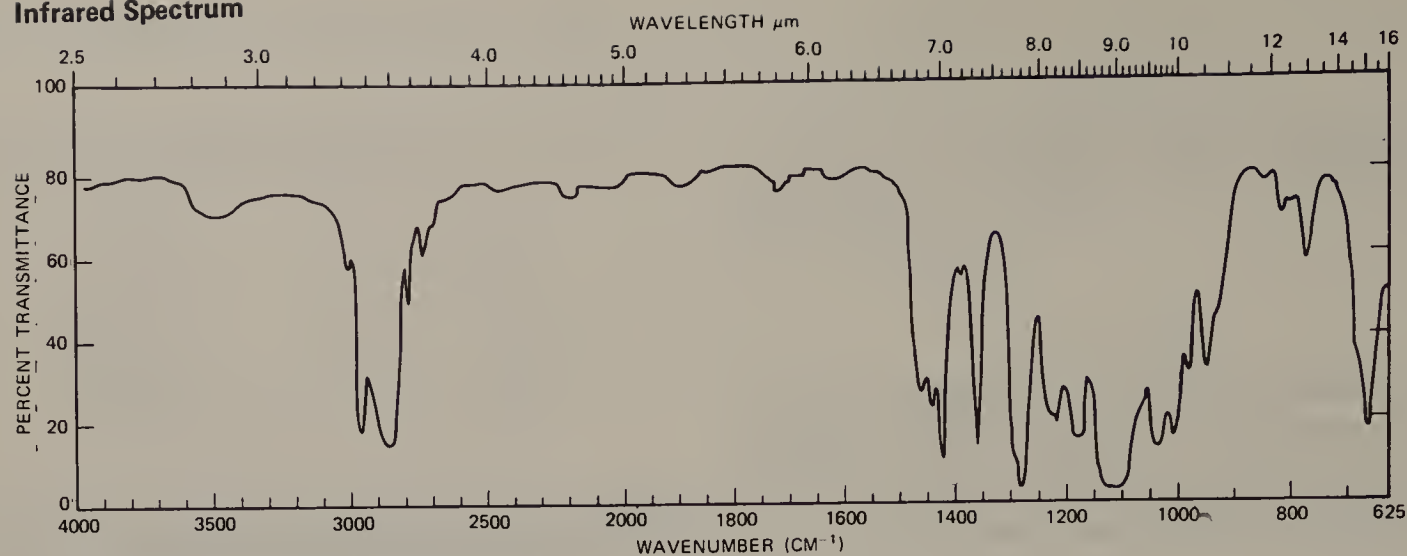
Note that methyl 3-furoate would give an entirely different  $^1\text{H}$  NMR pattern.

The 3-proton is coupled with the 4-proton ( $J_{34} = 3.5$  Hz) and with the 5-proton ( $J_{35} = 1$  Hz). Thus, the 3-proton shows a doublet of doublets.

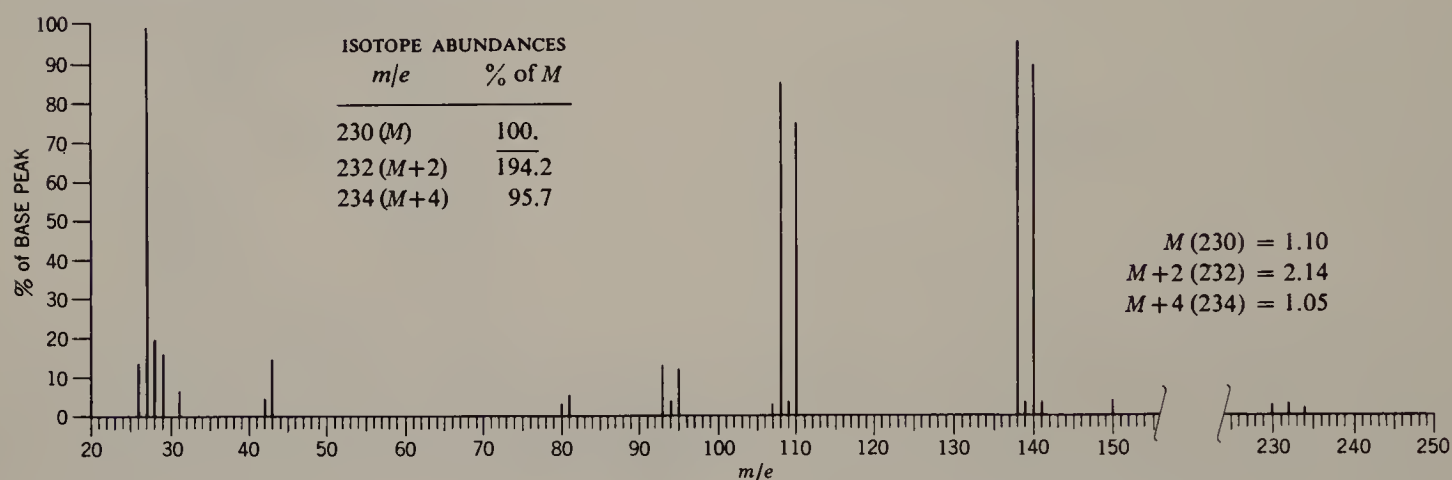


The 4-proton is coupled with the 3-proton ( $J_{43} = 3.5$  Hz) and with the 5-proton ( $J_{45} = 2$  Hz). Again we see a doublet of doublets.

## Infrared Spectrum

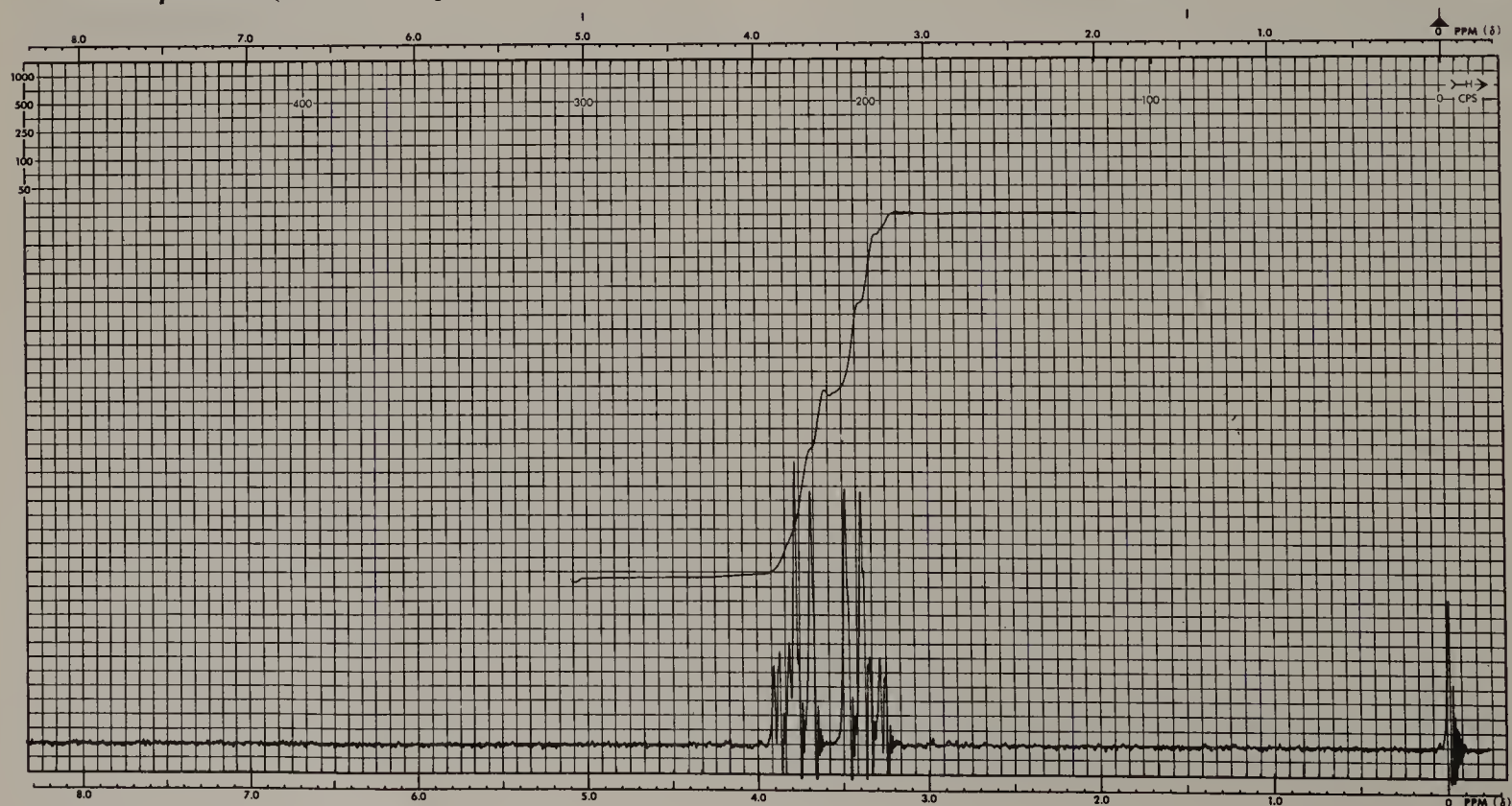


## Mass Spectral Data (Relative Intensities)



## Ultraviolet Data

| $\lambda_{\text{max}}^{\text{EtOH}}$ | $\epsilon_{\text{max}}$ |
|--------------------------------------|-------------------------|
| 305 (inflection)                     | 1.5                     |

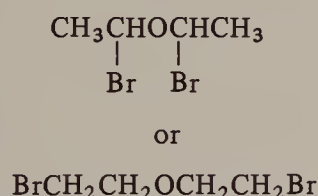
 $^1\text{H}$  NMR Spectrum (Solvent  $\text{CCl}_4$ )

# compound number 7-3

The characteristic  $M + 2$  and  $M + 4$  pattern indicates the presence of two bromine atoms. Subtracting  $2 \times 79$  from the molecular weight leaves a mass of 72 for the rest of the molecule.

The strongest peak in the infrared spectrum at  $1117\text{ cm}^{-1}$  ( $8.95\text{ }\mu\text{m}$ ) strongly suggests an aliphatic ether. Since no nitrogen- or other oxygen-containing group appears to be present, we can assume, tentatively, that the remaining fragment is  $\text{C}_4\text{H}_8\text{O}$ . The weak inflection in the ultraviolet spectrum may simply result from the accumulation of atoms with nonbonding electrons.

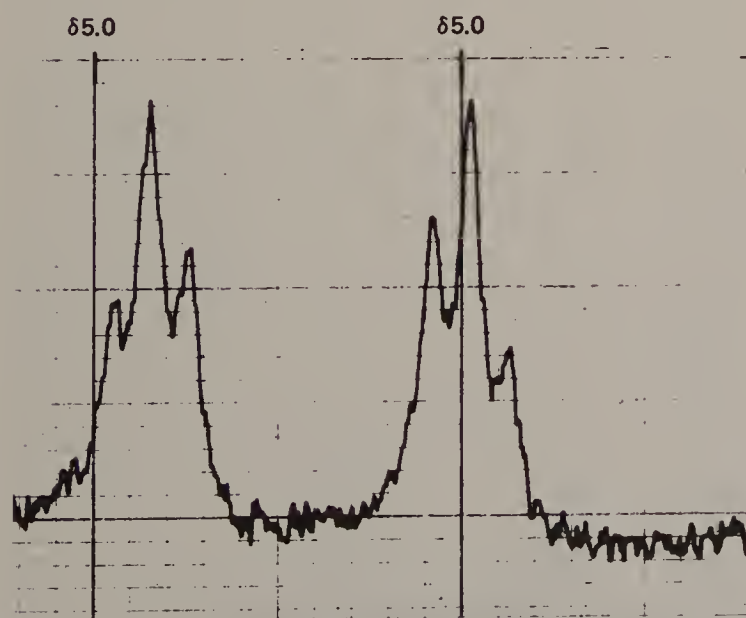
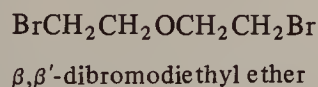
The striking symmetry of the NMR spectrum suggests a symmetrical molecule. If we dispose our fragments,  $\text{Br}_2$ ,  $-\text{O}-$ , and  $\text{C}_4\text{H}_8$ , in a symmetrical pattern, there are two possibilities



The first compound would give an  $\text{A}_3\text{X}$  NMR spectrum consisting of a 1-proton quartet quite far downfield ( $\delta \sim 5.0$ ) and a doublet rather upfield ( $\delta \sim 2.0$ ). The second compound would give an  $\text{AA}'\text{BB}'$  pattern in accord with that observed.

The fragmentation pattern, though complex, affords ample confirmation. Characteristic bromine-containing pairs are discernible at  $m/e$  138 and 140 (loss of  $\text{CH}_2\text{Br}$  with H transfer), 108 and 110 (loss of  $\text{OCH}_2\text{CH}_2\text{Br}$  with H transfer), and 93 and 95 ( $\text{CH}_2\text{Br}^+$ ).

The compound is



Sample 4 (see table, this page) of Shift Reagent study; 600 Hz Sweep Width,  $\text{CCl}_4$  Solvent.

The strong peak in the infrared spectrum at  $1279\text{ cm}^{-1}$  ( $7.82\text{ }\mu\text{m}$ ) is attributed to a  $\text{CH}_2\text{Br}$  wag.

The  $\text{CH}_2$  adjacent to O is deshielded by O by about 2.15 units (the alkane  $\text{CH}_2$  absorption is  $\delta$  1.25 and the position for  $\text{CH}_2\text{O}$  is  $\delta$  3.40). This methylene group is also deshielded by the Br atom by about 0.48 ppm. Its calculated position, then, is about  $\delta$  3.88, in fair agreement with the downfield absorption. Similarly, the position of the methylene adjacent to Br can be calculated to be about  $\delta$  3.40, again in fair agreement with the upfield absorption.

| Sample         | Mole Ratio<br>$\text{Eu(fod)}_3$<br>ether | Chemical Shifts ( $\delta$ ) |                  | Change in Chemical Shifts |                  |
|----------------|---|------------------------------|------------------|---------------------------|------------------|
|                |   | Upfield Signal               | Downfield Signal | Upfield Signal            | Downfield Signal |
| 1              | 0.00                                      | 3.35                         | 3.75             | —                         | —                |
| 2              | 0.12                                      | 3.60                         | 4.16             | +0.25                     | +0.41            |
| 3              | 0.25                                      | 3.80                         | 4.53             | +0.45                     | +0.78            |
| 4 <sup>b</sup> | 0.38                                      | 3.98                         | 4.87             | +0.63                     | +1.12            |

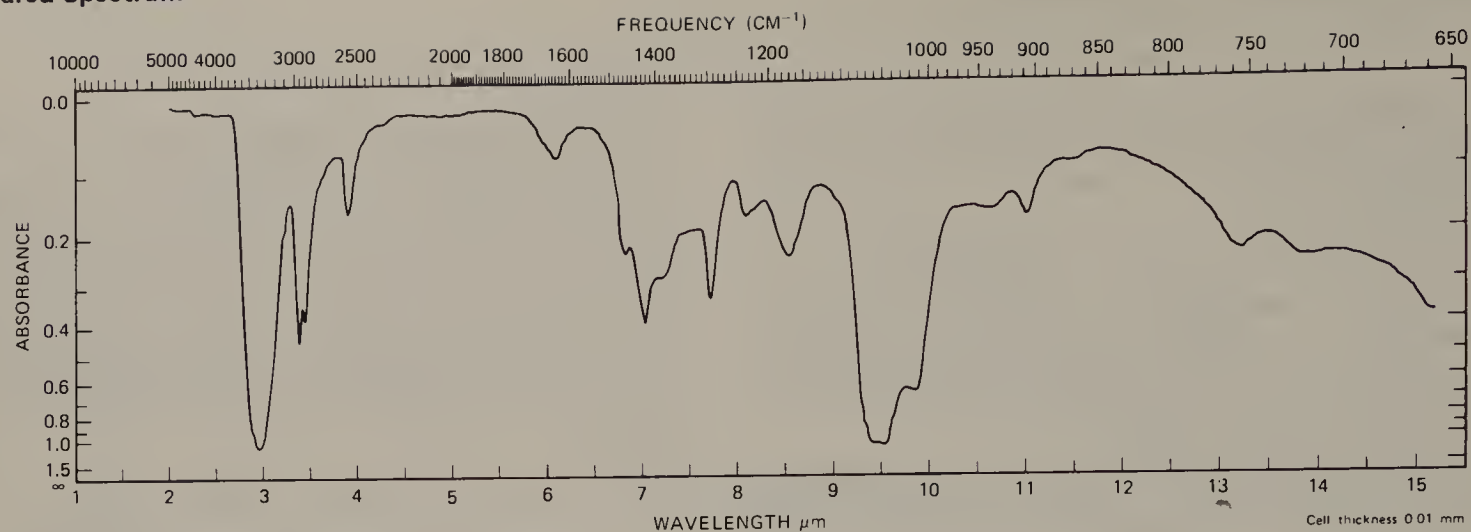
<sup>a</sup>In all experiments, there was 30 mmoles of the bromo ether in about 0.5 ml of  $\text{CCl}_4$ .

<sup>b</sup>This spectrum is displayed at the lower left.

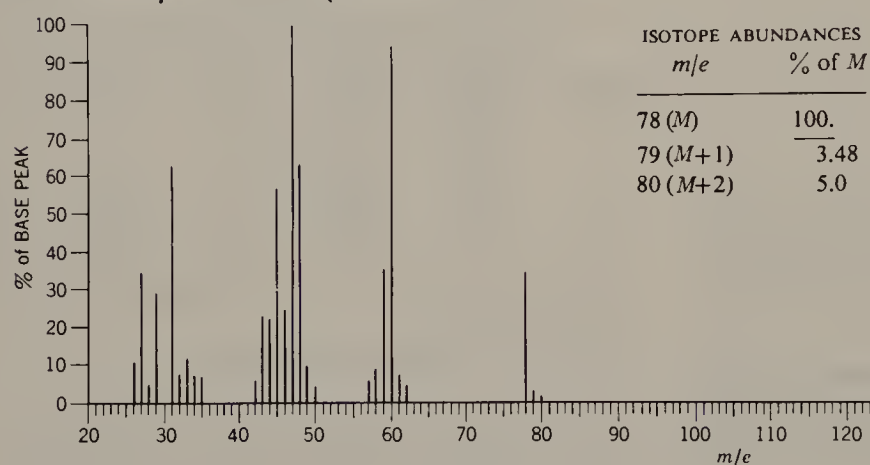
These NMR assignments are in accord with a shift reagent  $[\text{Eu(fod)}_3]$  study. The above table describes a downfield progression of both NMR signals as a function of increased amounts of shift reagent. Such results are consistent with the chemical shift changes being inversely dependent on the distance from the oxygen atom. The table shows that the separation has resulted from the greater downfield shift of the lower field signal per increment of shift reagent and was not the result of a cross-over. Since the shift reagent is expected to coordinate more strongly to the nucleophilic oxygen atom, the signal at lower field ( $\delta$  3.75) in the original spectrum is due to the methylene protons alpha to oxygen. The spectrum of Sample 4 shows that the shift reagent has begun to convert a higher-order system (sample 1,  $\Delta\nu/J = \text{ca. } 24/6 = \text{ca. } 4$ ) to a first-order system (sample 4,  $\Delta\nu/J = \text{ca. } 53/6 = \text{ca. } 9$ ). The benefits clearly outweigh the slight line broadening effect of the shift reagent.



## Infrared Spectrum



## Mass Spectral Data (Relative Intensities)

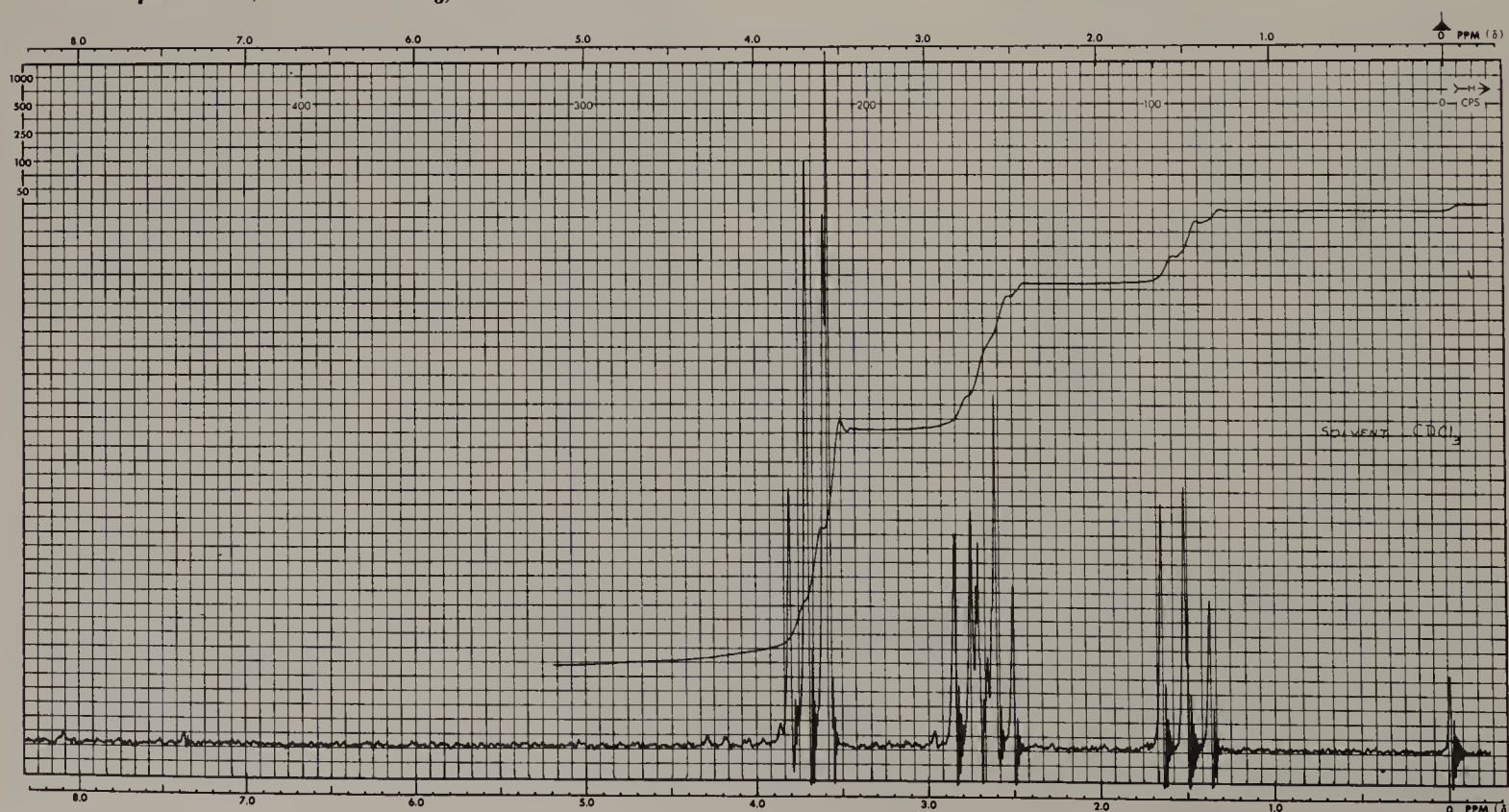


$M$  (78) = 34.0  
 $M+1$  (79) = 1.18  
 $M+2$  (80) = 1.7

## Ultraviolet Data

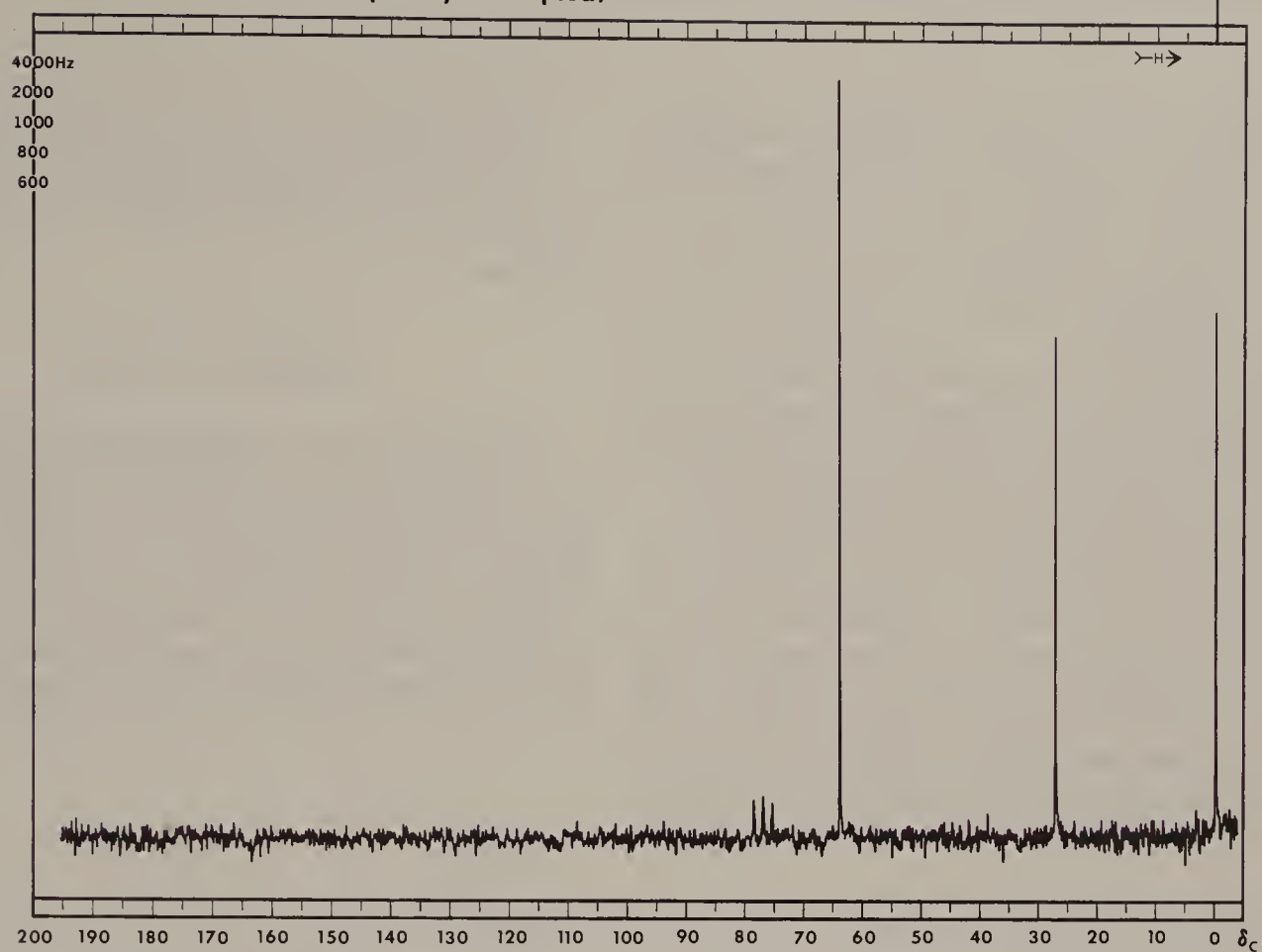
| $\lambda_{infl}^{EtOH}$ | $\epsilon_{infl}$ |
|-------------------------|-------------------|
| 232                     | 136               |

$infl$  = inflection

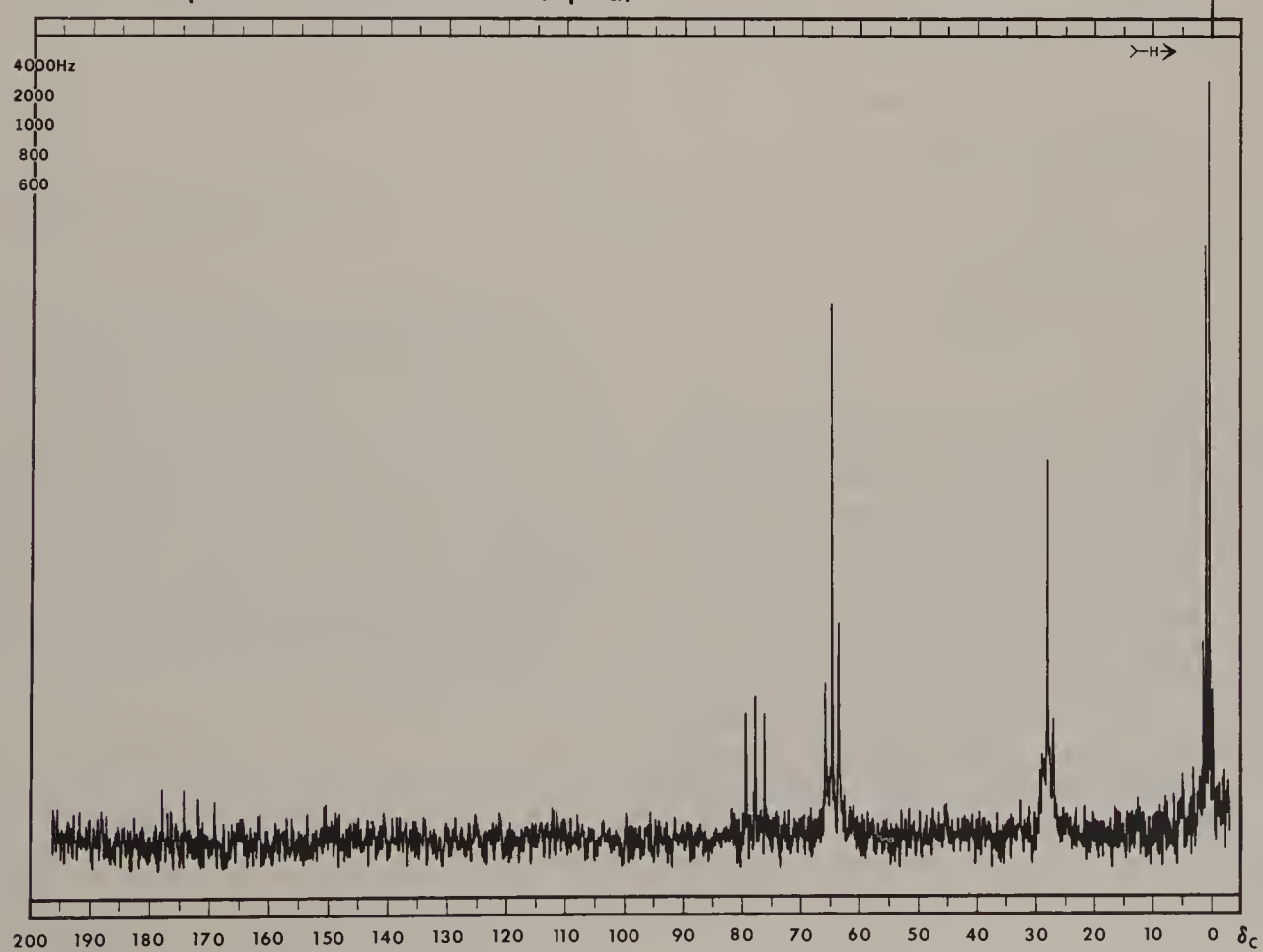
 $^1H$  NMR Spectrum (Solvent  $CDCl_3$ )

<sup>13</sup>C NMR Spectrum (completely decoupled)

Compound 7-4 (Continued)



<sup>13</sup>C NMR Spectrum (off-resonance decoupled)



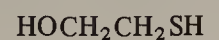
## compound number 7-4

We immediately note the large  $M+2$  peak which suggests that 1 sulfur atom is present. We then list the possible formulas under mass 46 (78 less 32). We should list all except the trivial formulas and those containing an odd number of N atoms; we also subtract 0.78 from the  $M+1$  peak, which leaves 2.70. But this turns out to leave us with only a single choice,  $C_2H_6O$ . The molecular formula, therefore, is  $C_2H_6OS$ .

$^{13}C$  NMR supports a molecular formula with 2 carbon atoms since the noise-decoupled spectrum shows just 2 singlets (at  $\delta$  27.50 and  $\delta$  64.06). Since both  $^{13}C$  signals are triplets in the off-resonance decoupled spectrum, we have shown that 4 of the 6 protons are in methylene groups.

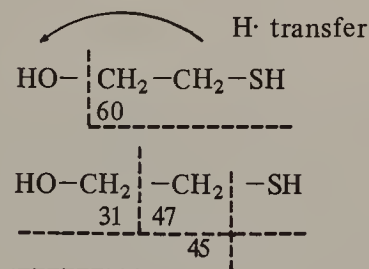
The infrared spectrum shows a strong, rather broad band at  $3367\text{ cm}^{-1}$  ( $2.97\text{ }\mu\text{m}$ ). Our impression is that we are dealing with an alcohol. The very broad band at about  $1050\text{ cm}^{-1}$  ( $3.91\text{ }\mu\text{m}$ ) suggests a primary alcohol. Our attention is then caught by a rather weak band at  $2558\text{ cm}^{-1}$  ( $3.91\text{ }\mu\text{m}$ ), which practically spells out a mercaptan group. In this case, the infrared spectrometer is at some disadvantage with respect to the nose. Had this been a thin film spectrum, we might have missed the S-H stretching band.

We now have the fragments:  $CH_2OH$  and  $SH$ . This only leaves a  $CH_2$  group to fit in, and we write



2-Mercaptoethanol

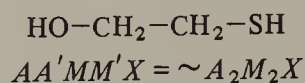
Some of the major fragmentation peaks can be assigned as follows:



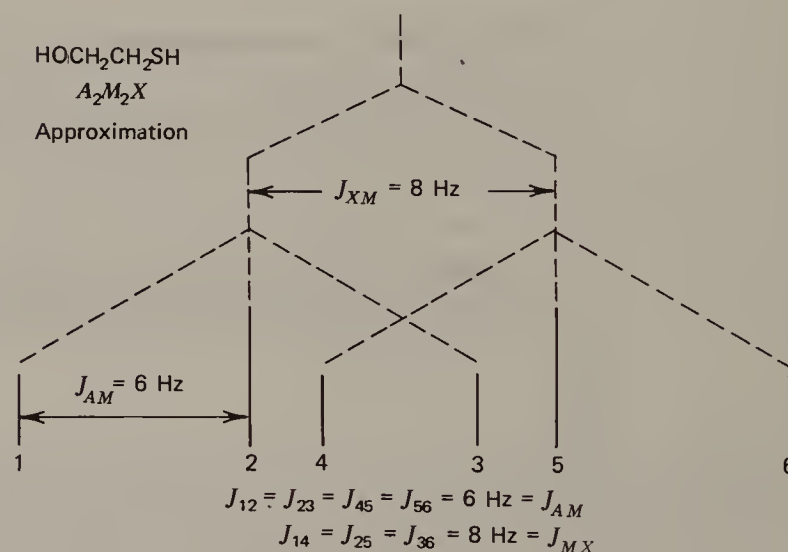
The  $^1H$  NMR spectrum provides exhaustive confirmation for the structure written. It also shows a number of interesting features. The starting point is the distribution of protons as shown by the integration curve. If we assume that the triplet at the high-field position contains 1 proton, then the next cluster of peaks contains 2 protons, and the low-field peaks account for 3 protons. At first glance, this does not seem reasonable. But we must bear several things in mind. First, the positions of the OH peak and the SH peak depend on concentration. Since the OH-group forms stronger hydrogen bonds than the SH group, it is likely to be further downfield at a given concentration. Second, the OH proton will undergo rapid exchange under normal condition and will usually appear as a single peak; the SH proton, under the same conditions will not ex-

change rapidly (at least in a nonaqueous solvent), and the peak will be split by the adjacent methylene group.

The  $^1H$  NMR spectrum represents an  $AA'MM'X$  system (if we neglect the rapidly exchanging OH proton), but we can treat it as  $A_2M_2X$  and examine the  $A_2M_2$  and  $M_2X$  couplings:



We see then that the upfield triplet (with slight second-order splitting of the middle peak) represents the SH proton coupled with (split by) the adjacent methylene group; the coupling constant is 8 Hz. The adjacent methylene signal is split into a doublet by the SH proton (coupling constant, of course is 8 Hz), and again into a triplet by the other methylene group with a coupling constant of 6 Hz. This is a somewhat distorted  $A_2M_2X$  system with 2 coupling constants. An idealized diagram is as follows:



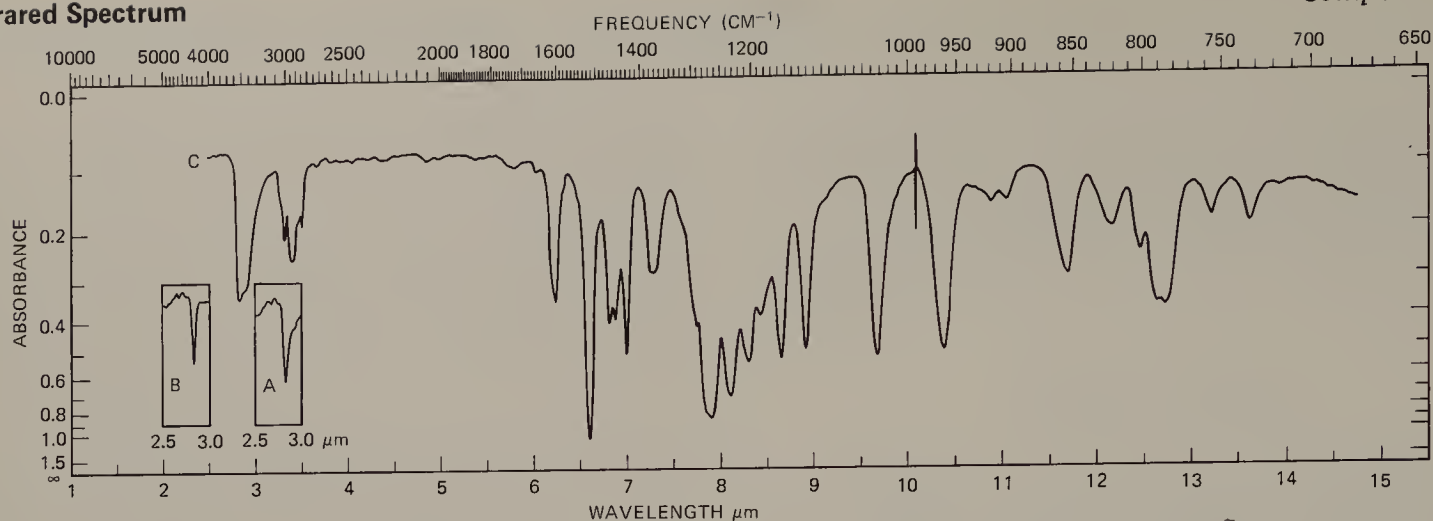
The low-field peaks must then consist of a triplet with a coupling constant of 6 Hz, and it must also contain the OH proton. We do indeed see a triplet with the upfield peak distorted by the peak of the OH proton with which it almost coincides. The hydroxyl proton peak can be shifted by change of concentration, solvent, or temperature. Both the OH and SH peaks can be removed by shaking with deuterium oxide; this, of course, would collapse the  $CH_2S$  multiplet to a symmetrical "apparent triplet" signal.

There are distortions in the spectrum because of marginal  $\Delta\nu/J$  values.

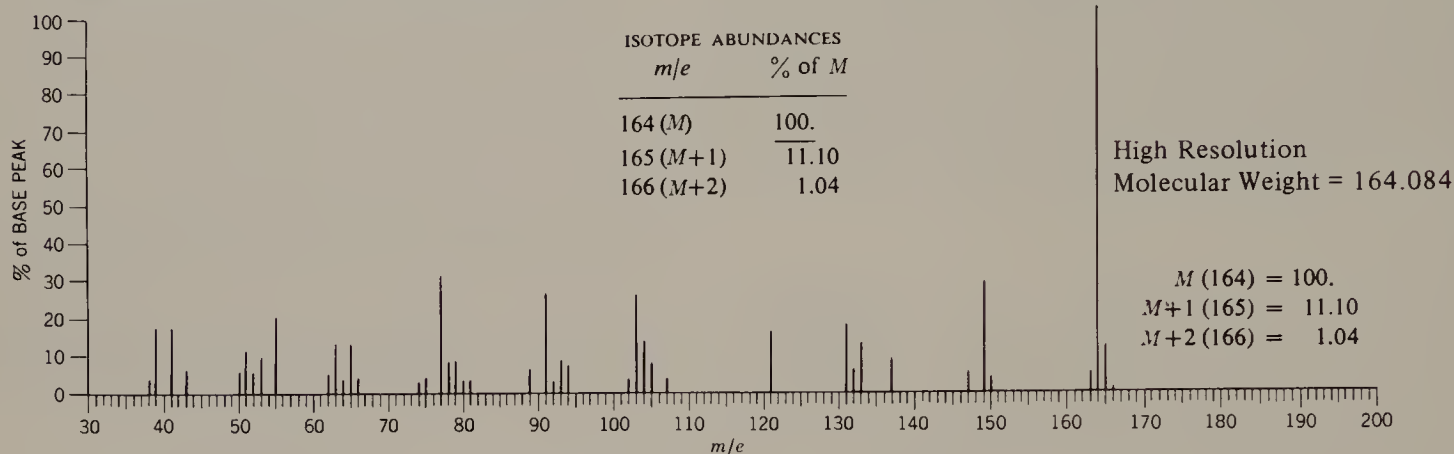


# notes

## Infrared Spectrum



## Mass Spectral Data (Relative Intensities)



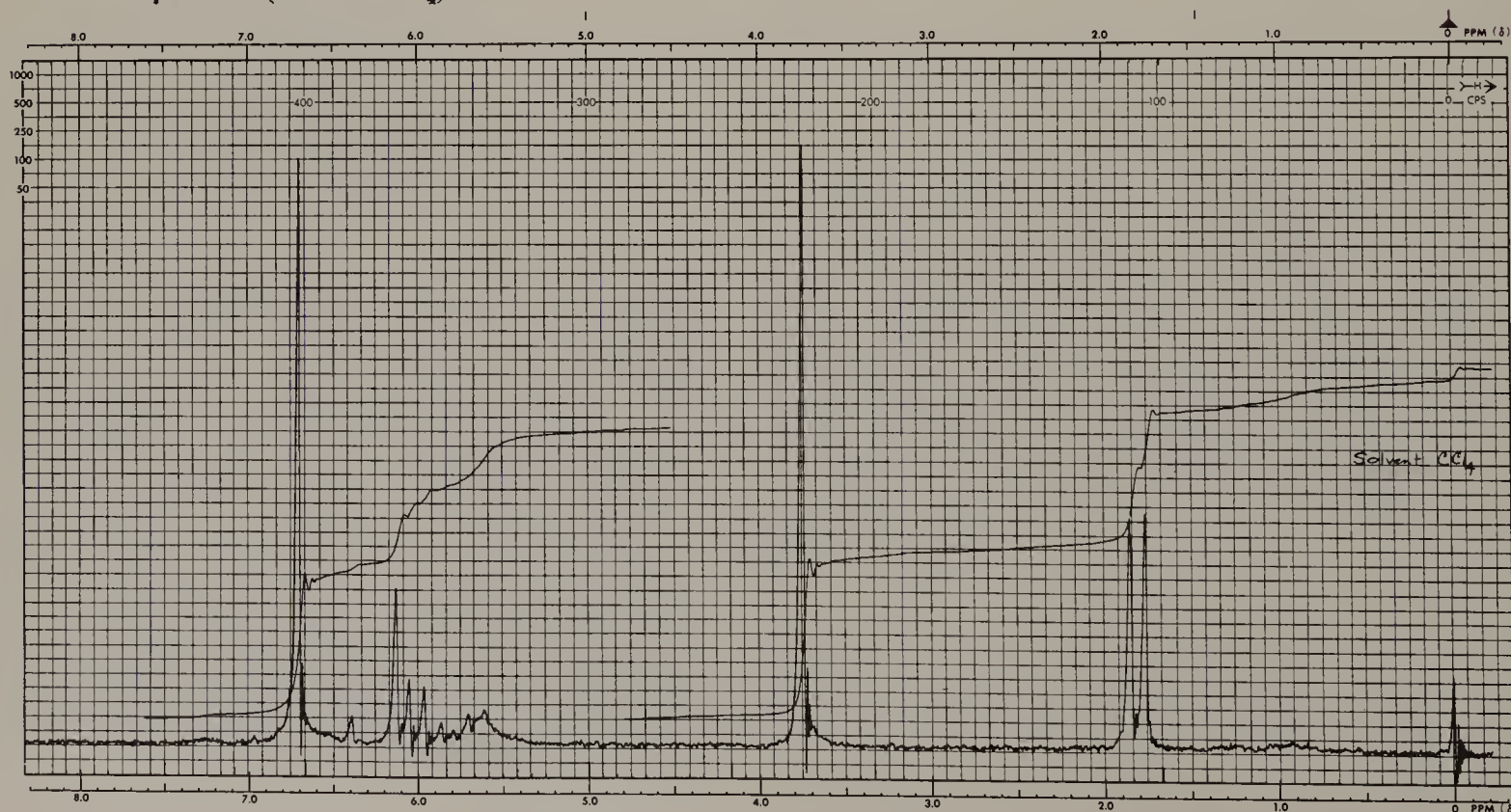
## Ultraviolet Data

$\lambda_{\text{max}}^{\text{EtOH}}$        $\log \epsilon_{\text{max}}$

pH 7  $\left\{ \begin{array}{l} 263 \\ 300(s) \end{array} \right.$        $\left\{ \begin{array}{l} 4.2 \\ 3.6 \end{array} \right.$

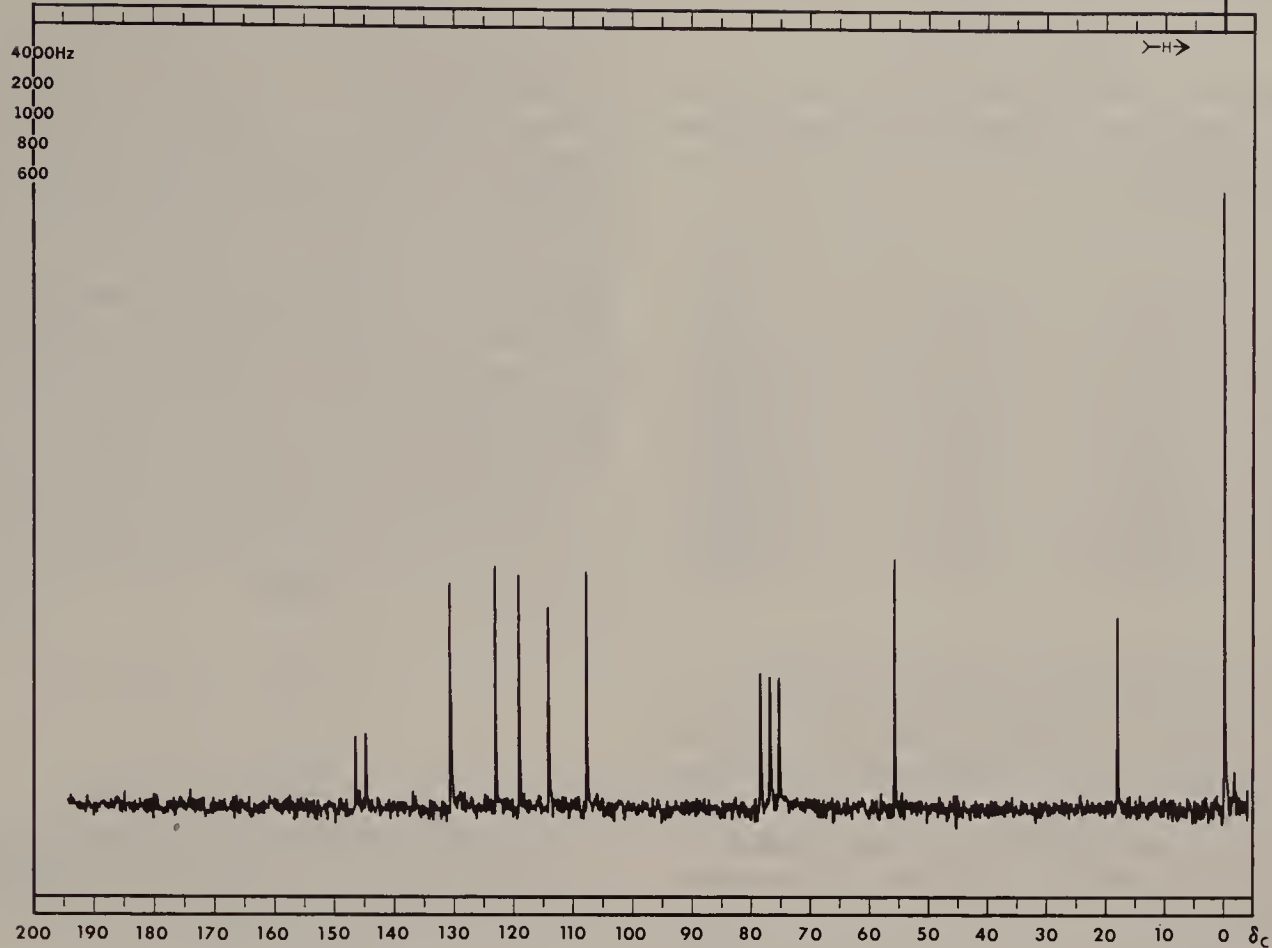
pH 13  $\left\{ \begin{array}{l} 288 \\ 315(s) \end{array} \right.$        $\left\{ \begin{array}{l} 4.0 \\ 3.8 \end{array} \right.$

$s$  = shoulder

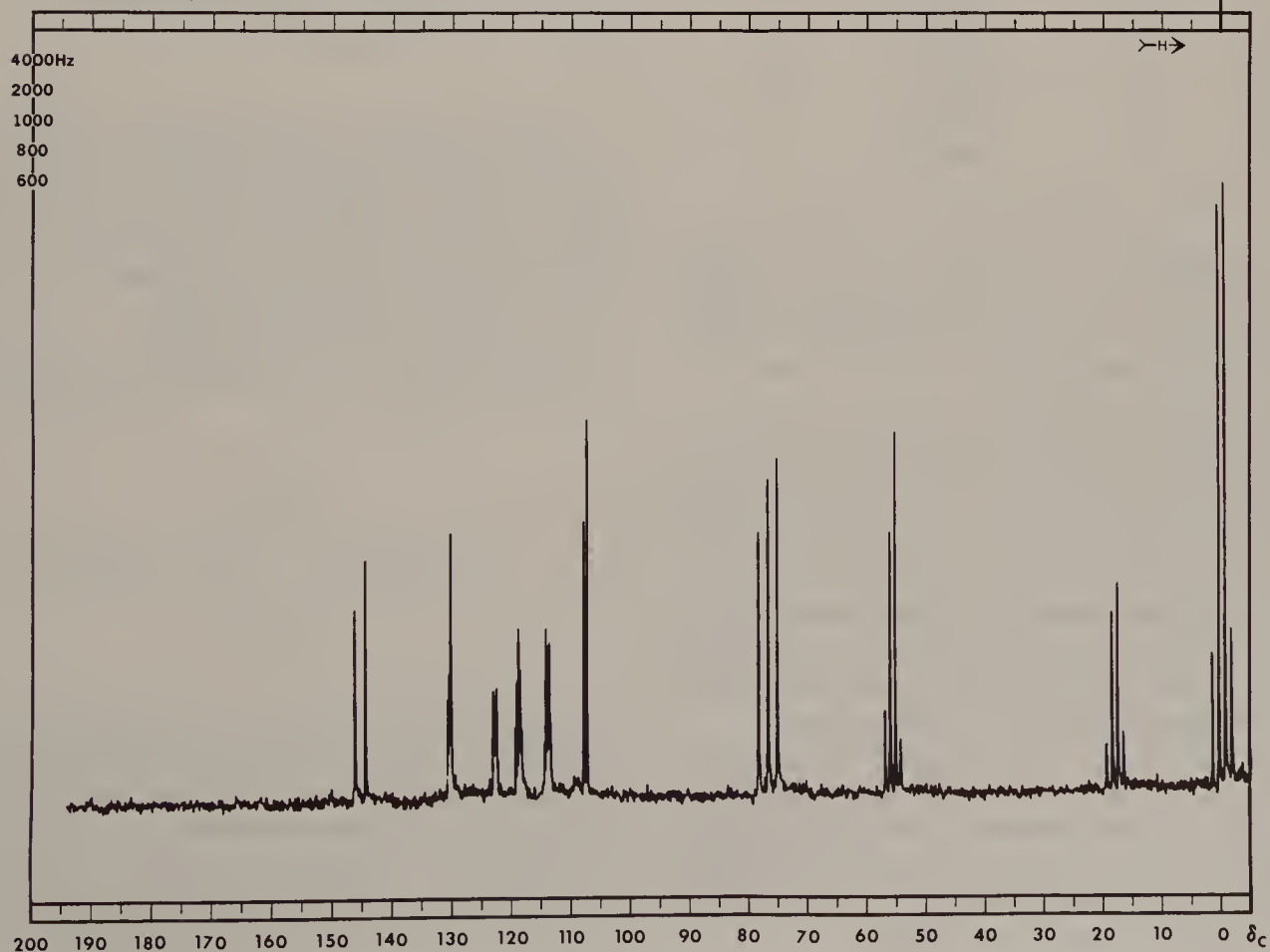
<sup>1</sup>H NMR Spectrum (Solvent CCl<sub>4</sub>)

<sup>13</sup>C NMR Spectrum Completely Decoupled

Compound 7-5 (Continued)



<sup>13</sup>C NMR Spectrum (Off-resonance Decoupled)





## compound number 7-5

The following molecular formulas fit the data for the molecular ion peak and for the  $M+1$  peak. We have eliminated trivial formulas and those containing an odd number of nitrogen atoms.

| Formula           | $M+1$ | $M+2$ | $MW$     |
|-------------------|-------|-------|----------|
| $C_8H_8N_2O_2$    | 9.61  | 0.81  | 164.0584 |
| $C_8H_{12}N_4$    | 10.36 | 0.49  | 164.1064 |
| $C_9H_8O_3$       | 9.97  | 1.05  | 164.0473 |
| $C_9H_{12}N_2O$   | 10.72 | 0.72  | 164.0951 |
| $C_{10}H_{12}O_2$ | 11.08 | 0.96  | 164.0838 |
| $C_{10}H_{16}N_2$ | 11.83 | 0.64  | 164.1315 |

The high-resolution molecular weight, determined to be 164.084, pinpoints  $C_{10}H_{12}O_2$  as the formulas of choice.

The  $^{13}C$  NMR spectrum clearly shows 9 lines and thus we have at least 9 carbons. The computer line printer indicates 10 signals. The presence of more than 1 oxygen functional group is supported below. We have tabulated the  $^{13}C$  multiplets (observed upon application of off-resonance decoupling) here:

| $\delta$ | Mult. | $\delta$ | Mult. |
|----------|-------|----------|-------|
| 18.26    | q     | 123.35   | d     |
| 55.86    | q     | 130.78   | s?    |
| 108.10   | d     | 130.92   | m?    |
| 114.50   | m     | 144.94   | s     |
| 119.44   | m     | 146.67   | s     |

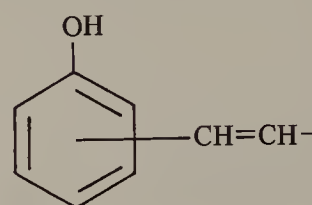
The two signals near  $\delta$  130 overlap in both  $^{13}C$  spectra making their interpretation difficult. Assuming the multiplets are due to carbons each bearing at least 1 proton, we can state that the compound must have at least  $3 + 3 + 1 + 1 + 1 + 1 + 1 = 11$  hydrogens.

The presence of an aromatic ring is indicated by the  $^1H$  NMR peak at  $\delta$  6.70 (distinctly upfield from the position of an unsubstituted benzene ring) and the general appearance of the infrared spectrum. We note a small peak at  $3030\text{ cm}^{-1}$  ( $3.30\text{ }\mu\text{m}$ ), strong peaks between  $1600$  and  $1430\text{ cm}^{-1}$  ( $6.2$  and  $7.0\text{ }\mu\text{m}$ ), and several moderately strong peaks in the low-frequency (long wavelength) region. As additional confirmation of aromaticity, we note that the molecular ion peak in the mass spectrum is also the base peak.

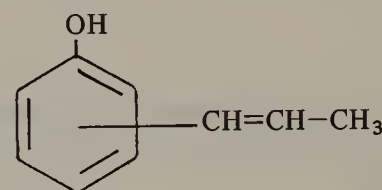
A conspicuous feature of the infrared spectrum is the rather strong absorption at  $3510\text{ cm}^{-1}$  ( $2.85\text{ }\mu\text{m}$ ). This is either an OH or an NH stretching band. We look to the region between  $1230$  and  $1010\text{ cm}^{-1}$  ( $8.13$  and  $9.90\text{ }\mu\text{m}$ ) for confirmation of OH absorption, but we are frustrated by the large number of bands in this region.

The ultraviolet spectrum gives us a good deal of information. The shift in wavelength at pH 13 is diagnostic for a phenol. Furthermore, the intense  $K$ -band at  $263\text{ nm}$  is indicative of a chromophore conjugated with the ring. In the absence of a carbonyl band in the infrared spectrum, we would suspect a  $C=C$  group. We quickly confirm this possibility by the olefinic proton absorption in the  $^1H$  NMR spectrum at about  $\delta$  6.0. A strong peak in the infrared spectrum at  $965\text{ cm}^{-1}$  ( $10.36\text{ }\mu\text{m}$ ) is evidence for *trans* olefinic hydrogens. The peak at  $1605\text{ cm}^{-1}$  ( $6.25\text{ }\mu\text{m}$ ) can partially be ascribed to the conjugated  $C=C$  stretching vibration.

At this point we have the following information:

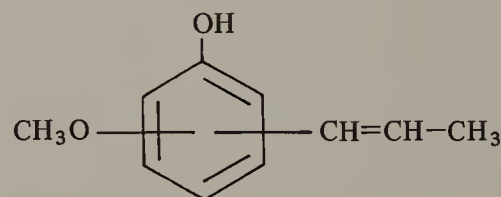


We now turn our attention to the doublet centered at  $\delta$  1.81. The shift position is right for an allylic methyl group, and its existence as a doublet can be justified. We write



The  $^{13}C$  NMR data fit in very nicely at this point. There are 2 quartets in the off-resonance decoupled spectrum. The one at the higher field ( $\delta$  18.26) corresponds to the allylic methyl, and that at a lower field ( $\delta$  55.86) is consistent with a methoxyl methyl. The methoxyl protons occur at  $\delta$  3.75 in the  $^1H$  NMR spectrum.

Thus, the tri-substituted benzene shown below accounts for all of the atoms in the molecular formula  $C_{10}H_{12}O_2$ .

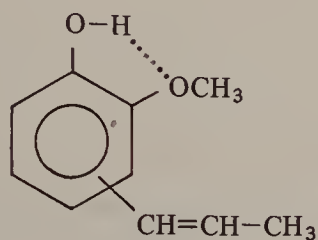


In the  $^1H$  NMR spectrum, the benzene peak at  $\delta$  6.70 contains 3 protons; the complex olefinic multiplet also accounts for 3 protons. Obviously, the phenolic proton is hidden under the olefinic multiplet; it could either be moved by change of temperature, solvent, or concentration, or eliminated by shaking with  $D_2O$ . It is probably the broadened peak at  $\sim \delta$  5.60. The olefinic proton near the ring is

shown by the badly distorted doublet ( $J \sim 16$ ) whose "center of gravity" is  $\sim \delta 6.2$ .

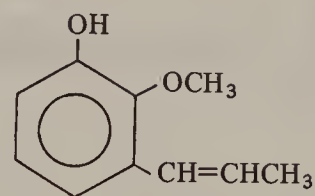
Assignment of the positions of the substituents is not easy. We cannot rely upon the C-H out-of-plane deformations in the long-wavelength region of the infrared spectrum because of the polar nature of the substituents. The  $^1\text{H}$  NMR spectrum, which is usually very helpful for distinguishing among isomers, is of little use because the ring protons are all at the same shift value. We might note that the phenolic OH band in the infrared spectrum is at an unusually high frequency (short wavelength) for a neat sample, and is not shifted on dilution; this suggests intramolecular hydrogen bonding to the ether oxygen. The methoxy group being ortho to the hydroxy group satisfies the geometric requirements for such intramolecular hydrogen bonding. The fragmentation in the mass spectrum is complex.

The  $^{13}\text{C}$  NMR spectrum allows us to narrow down the choices. Since the oxygen-containing groups must be *ortho*, we are concerned with the 4 possible structures implied by this formula:



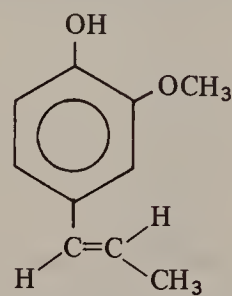
Any structure containing a vicinal (1,2,3) arrangement of the 3 groups will require an unacceptably high  $\delta$  value for

1 of the ring carbons. For example, for the structure



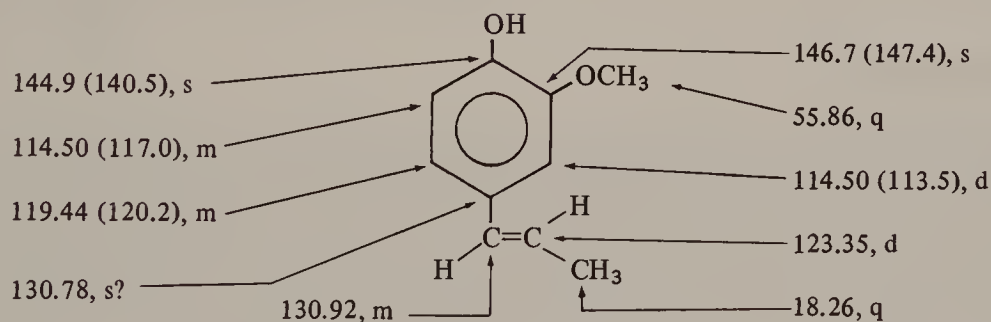
we calculate (Table VII, Chapter 5) that the ring carbon bearing the methoxyl group should be at  $\delta = 128.5 + 31.4 - 12.7 + 9.5 = 156.7$ , and our spectrum provides no signals of shift greater than  $\delta 150$ . We are thus limited to structures in which the  $\text{C}_3$  unit is *para* either to the hydroxyl or to the methoxyl group. The  $^{13}\text{C}$  spectrum, however, does not differentiate between these 2 isomers.

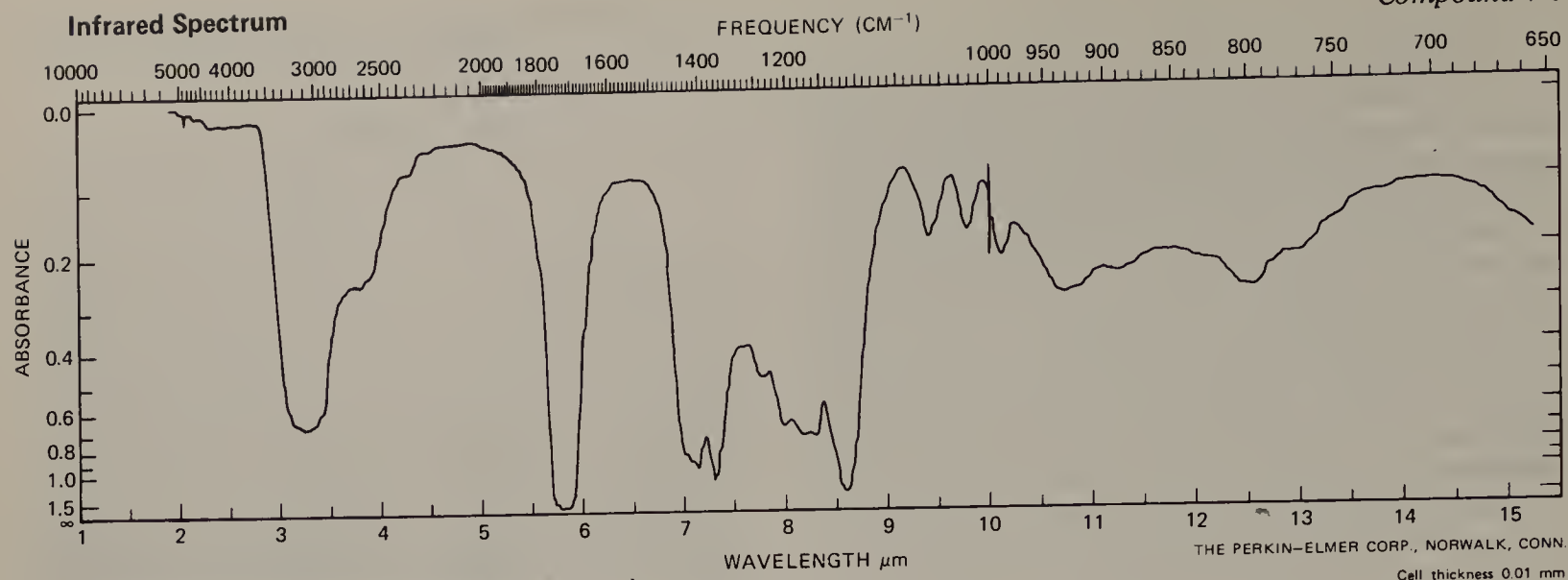
Familiarity with the structures of natural products might suggest isoeugenol, and comparison of our spectra with those of an authentic sample would provide confirmation.



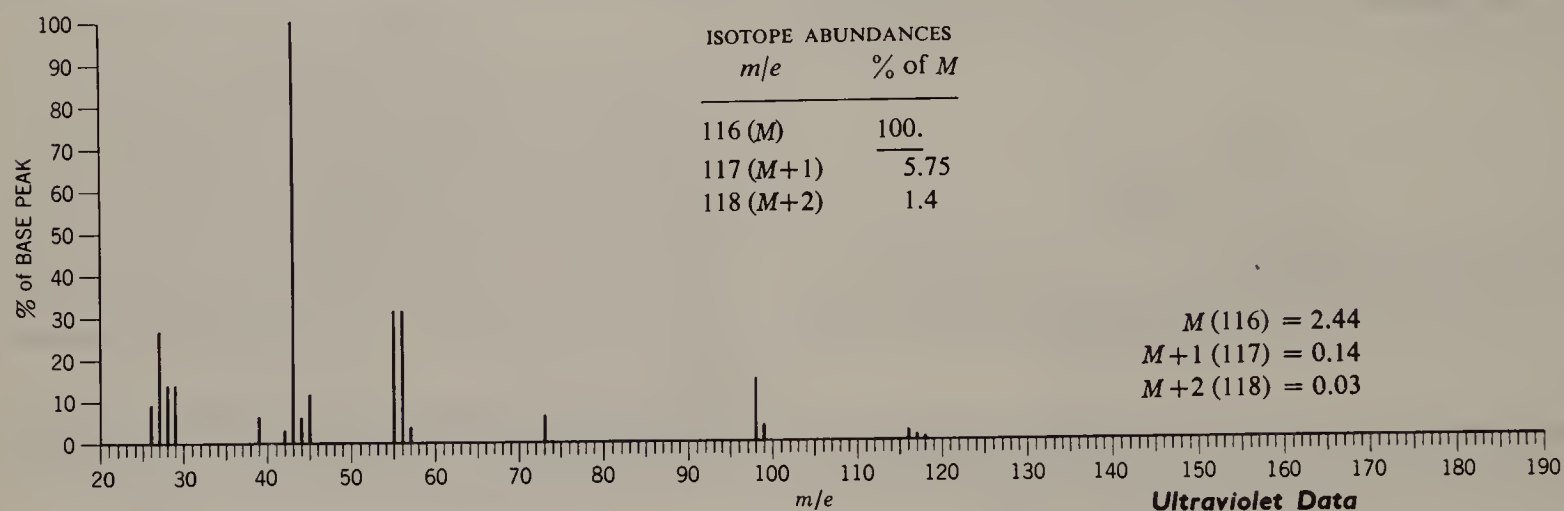
The  $^{13}\text{C}$  NMR spectrum is consistent with the *trans*-isomer.

In the structure below, calculated values are in parentheses (Table VII, Chapter 5). The allyl methyl of the *cis*-isomer is at considerably higher field ( $\delta 14.5$ ).





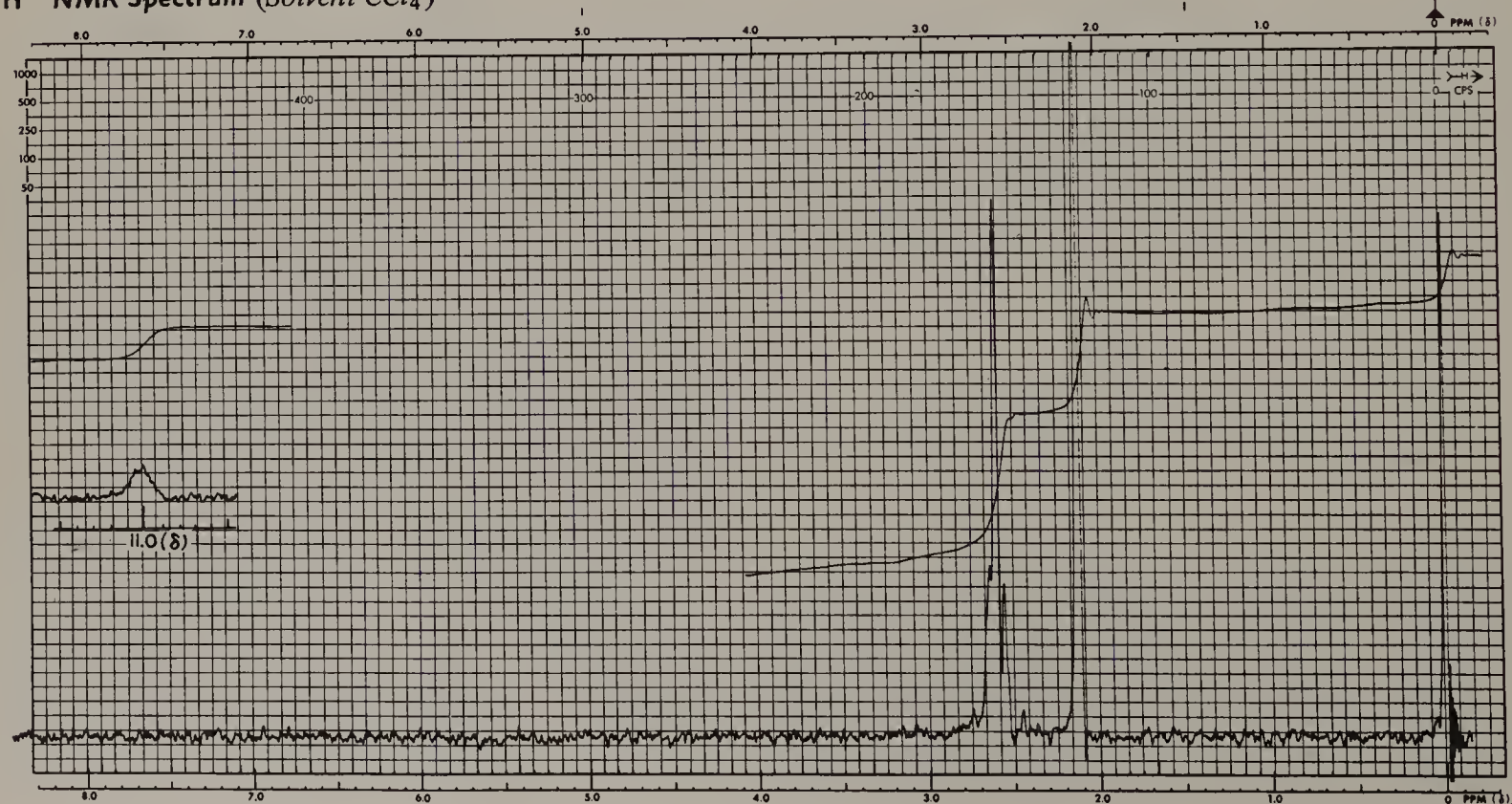
**Mass Spectral Data (Relative Intensities)**



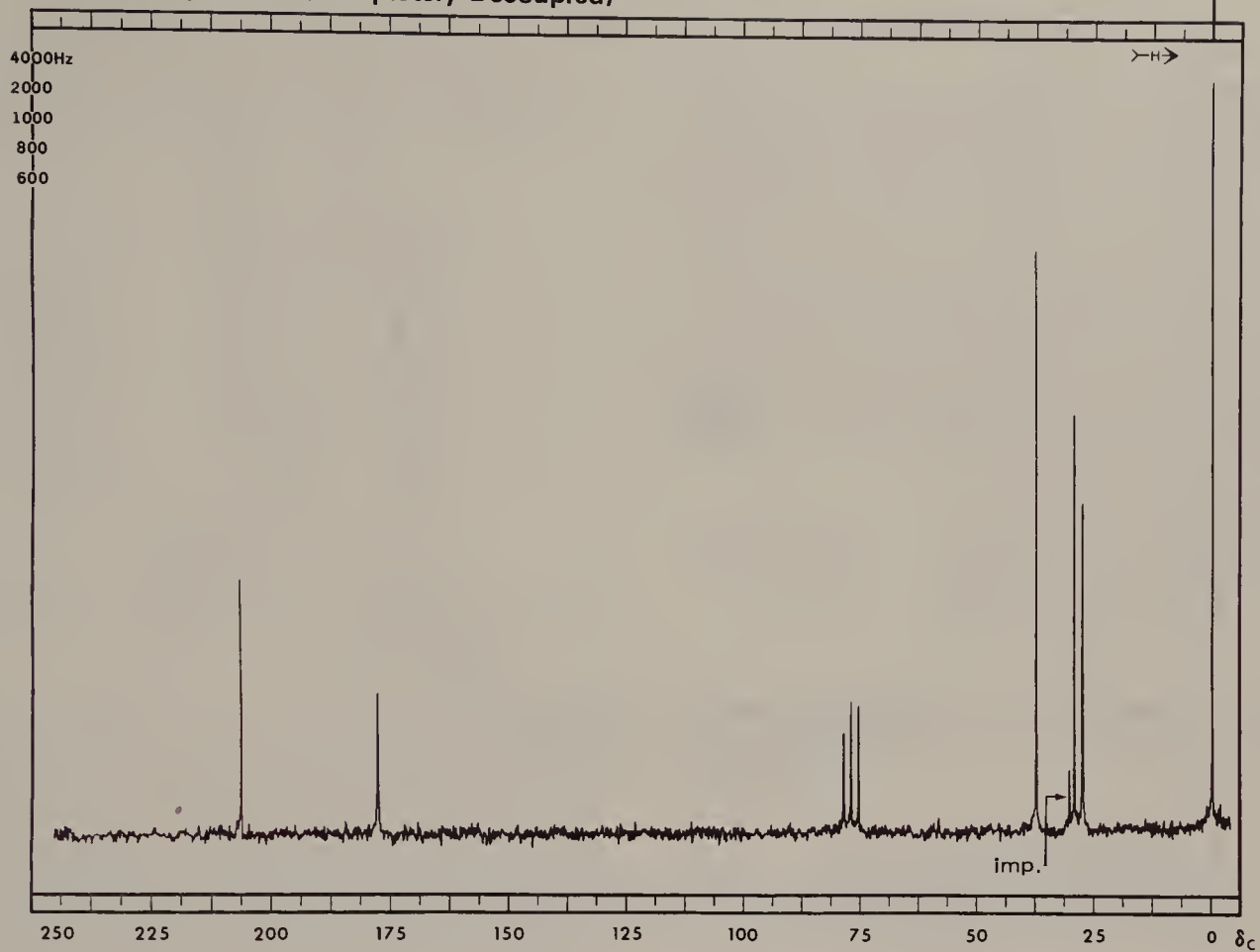
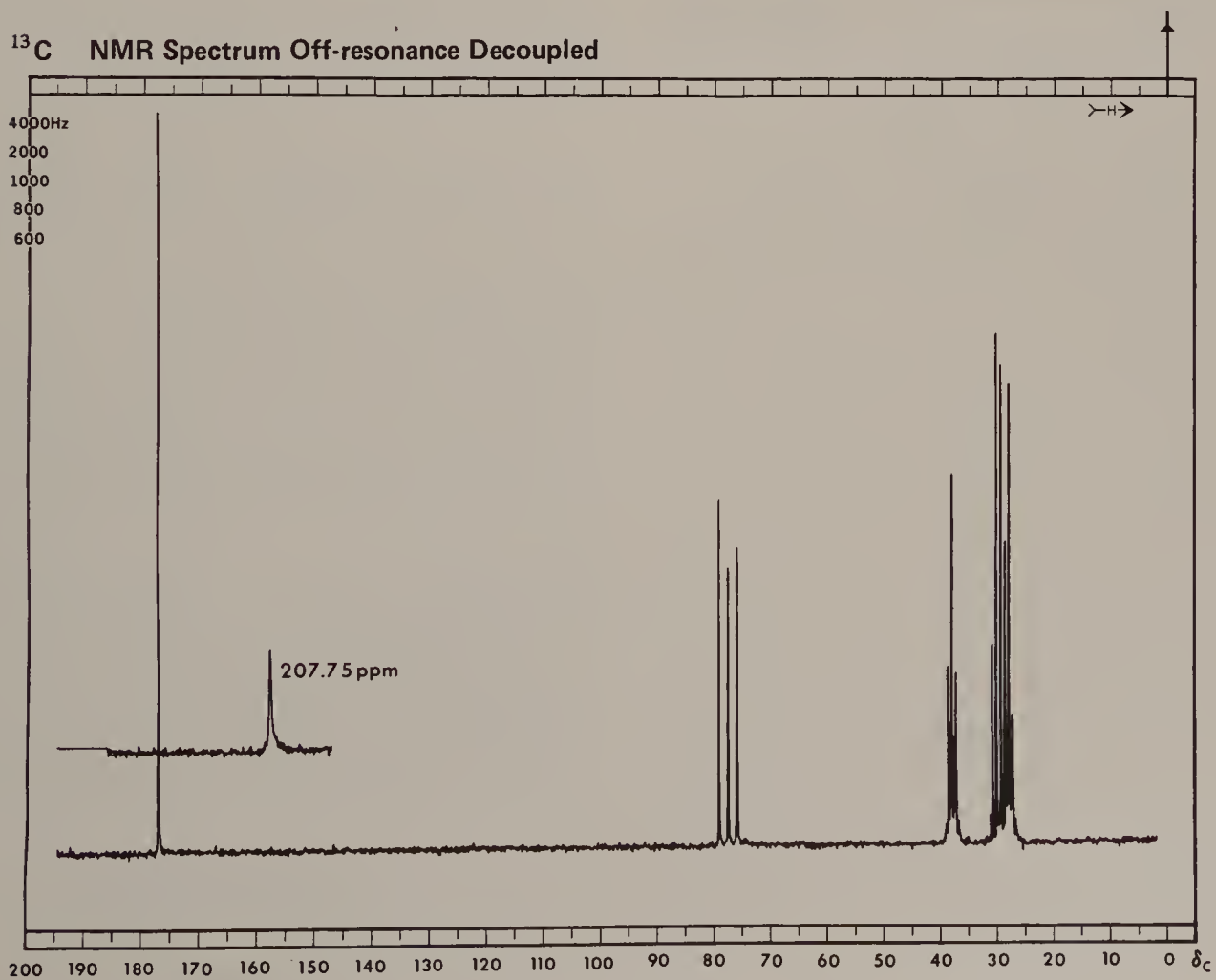
**Ultraviolet Data**

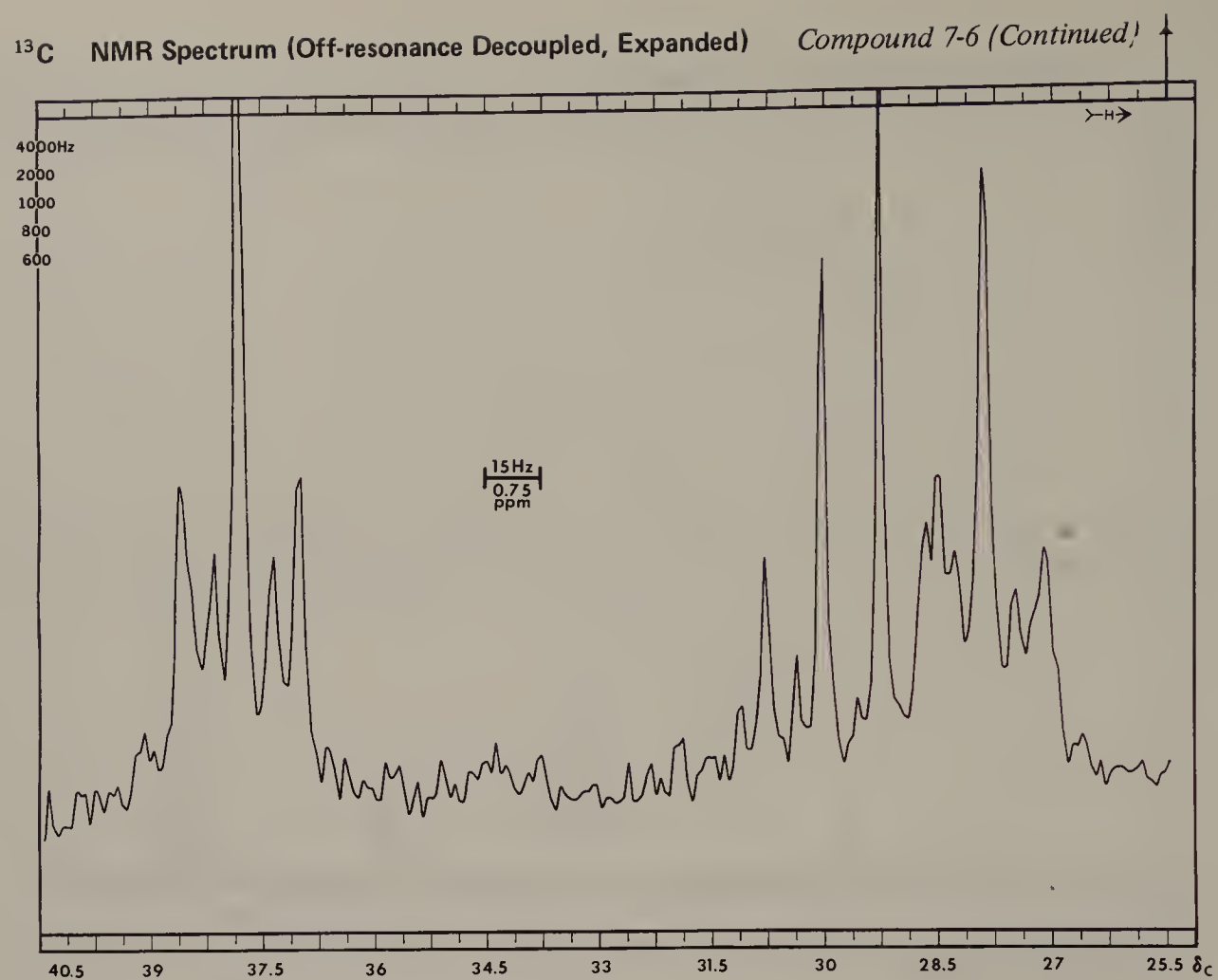
| $\lambda_{\max}^{\text{EtOH}}$ | $\log \epsilon_{\max}$ |
|--------------------------------|------------------------|
| 262                            | 1.5                    |

**$^1\text{H}$  NMR Spectrum (Solvent  $\text{CCl}_4$ )**





<sup>13</sup>C NMR Spectrum (Completely Decoupled)<sup>13</sup>C NMR Spectrum Off-resonance Decoupled



# compound number 7-6

We list the molecular formulas under mass 116 (molecular ion) that give a reasonable fit for the  $M + 1$  value of 5.75%.

| Formula         | $M + 1$ | $M + 2$ |
|-----------------|---------|---------|
| $C_3H_8N_4O$    | 4.94    | 0.30    |
| $C_4H_4O_4$     | 4.54    | 0.88    |
| $C_4H_8N_2O_2$  | 5.29    | 0.52    |
| $C_4H_{12}N_4$  | 6.04    | 0.16    |
| $C_5H_8O_3$     | 5.65    | 0.73    |
| $C_5H_{12}N_2O$ | 6.40    | 0.37    |
| $C_6H_{12}O_2$  | 6.75    | 0.59    |

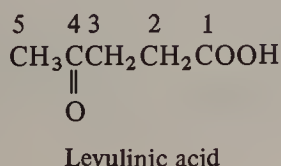
The formulas that best fit our  $M + 1$  value and our  $M + 2$  value (1.4%) are  $C_4H_4O_4$ ,  $C_4H_8N_2O_2$ ,  $C_5H_8O_3$ , and  $C_6H_{12}O_2$ .

The infrared spectrum points to an aliphatic carboxylic acid. We note the very broad, bonded OH-stretching absorption extending between about  $3333$  and  $2300\text{ cm}^{-1}$  ( $3.0$  and  $4.3\text{ }\mu\text{m}$ ) with its characteristic pattern on its low-frequency (long-wavelength) side. The strong  $C=O$  band at  $1715\text{ cm}^{-1}$  ( $5.83\text{ }\mu\text{m}$ ) satisfies the requirement for an aliphatic carboxylic acid. We find ready confirmation by noting the carboxylic acid proton at  $\delta\ 11.0$  in the  $^1\text{H}$  NMR spectrum.

The 2 downfield  $^{13}\text{C}$ -peaks are singlets in the off-resonance decoupled spectrum. They are clearly due to carbonyls, and we may tentatively assign the  $\delta\ 178.23$  peak to a carboxyl group and the  $\delta\ 207.02$  peak to a keto group (see Tables XIII and XIV, Chapter 5).

The UV spectrum provides a low-intensity absorption at  $262\text{ nm}$ , suggesting an aliphatic unconjugated ketone. There is only one  $C=O$  band in the infrared spectrum, but it is rather broad; it must accommodate both the ketone and the acid  $C=O$  band. The fragmentation pattern does not resemble that of an ordinary aliphatic carboxylic acid; for example, there is no pronounced peak at mass 60. Since we are dealing with a keto group in the molecule, we assume that the base peak of 43 in the mass spectrum arises from  $\text{CH}_3\text{C}=\text{O}$ . We now have the fragments  $\text{CH}_3\text{C}=\text{O}$  and  $\text{COOH}$  which add up to mass 88. These leave us with an unknown mass of 28 for which we can write either  $\text{C}=\text{O}$  or  $\text{CH}_2-\text{CH}_2$  or  $\text{N}_2$ .

The NMR spectra allow us to make an unequivocal choice. In the  $^1\text{H}$  NMR spectrum the large singlet at  $\delta\ 2.12$  (3H) must be the methyl protons of the  $\text{CH}_3\text{CO}$  group. If this peak contains 3 protons, then the absorption at  $\delta\ 2.60$  contains 4 protons. These must result from adjacent methylene groups which have almost the same chemical shift ( $AA'BB'$  system). We now write the structure



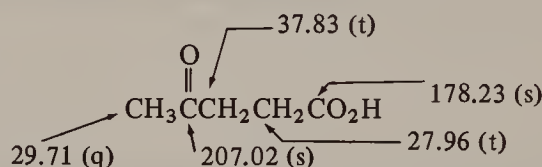
The multiplicity of the  $^{13}\text{C}$  signals in the off-resonance decoupled spectrum would not be an easy starting point for determining the levulinic acid structure. However, now that the structure has been proposed, the  $^{13}\text{C}$  spectra can be used for corroboration. The expanded off-resonance decoupled spectrum shows the  $\delta\ 27.96$  and  $\delta\ 37.83$  signals to be triplets, with additional complexity. The  $\delta\ 29.71$  signal is a quartet and it is thus assigned to the methyl carbon. Table III in Chapter 5 allows us to predict the chemical shifts of levulinic acid by calculating the shift due to the attachment of a carboxyl group to C-4 of 2-butanone.

| $^{13}\text{C}$ Shifts for 2-butanone                  |
|--|
| $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ |
| 2-Butanone   |
| C-1 = 28.8 ppm   |
| C-2 = 206.3  |
| C-3 = 36.4   |
| C-4 = 7.6  |

A carboxyl group is expected to shift the  $\alpha$  carbon +21 ppm, the  $\beta$ , +3 ppm and  $\gamma$ , -2 ppm. Thus, for levulinic acid we calculate:

$$\begin{aligned} \delta_2 &= 7.6 + 21 = 28.6\text{ ppm} \\ \delta_3 &= 36.4 + 3 = 39.4\text{ ppm} \\ \delta_4 &= 206.3 - 2 = 204.3\text{ ppm} \\ \delta_5 &= 28.8\text{ ppm} \end{aligned}$$

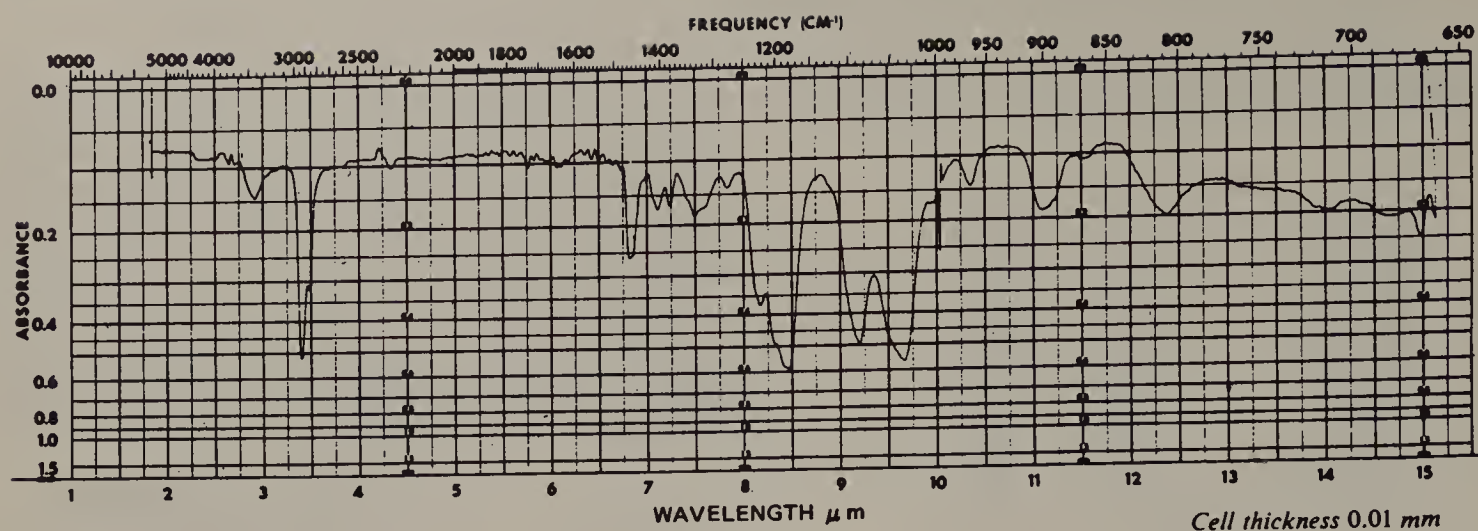
These agree well with following assignments for the observed  $^{13}\text{C}$  shifts:



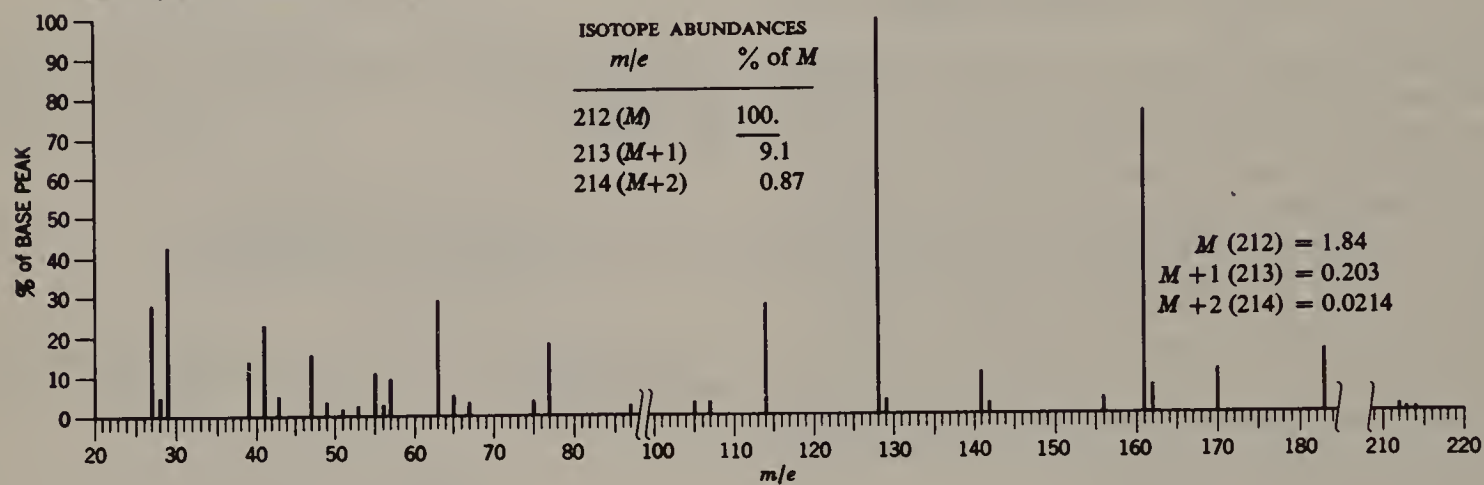
The signal at  $\delta\ 30.82$  is that of an impurity.



## Infrared Spectrum

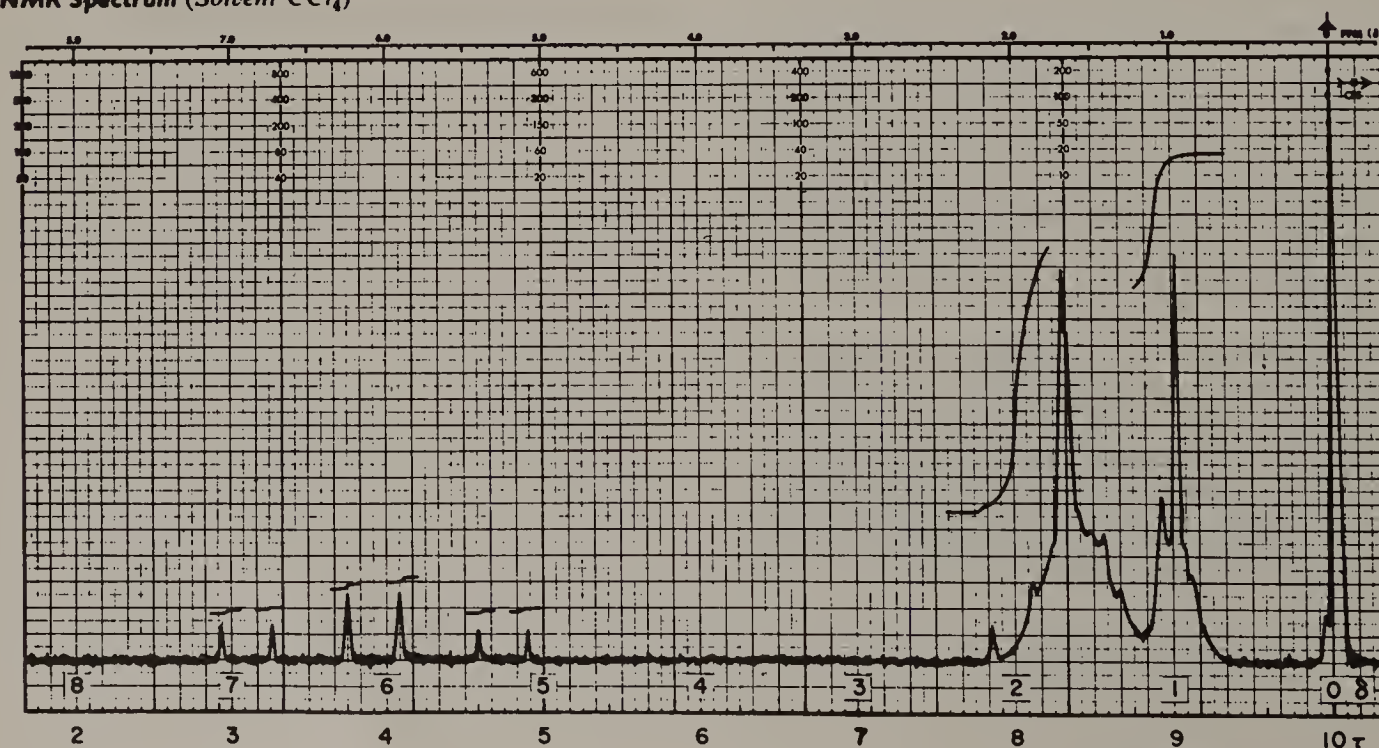


## Mass Spectral Data (Relative Intensities)



## Ultraviolet Data

Featureless beyond 210 nm

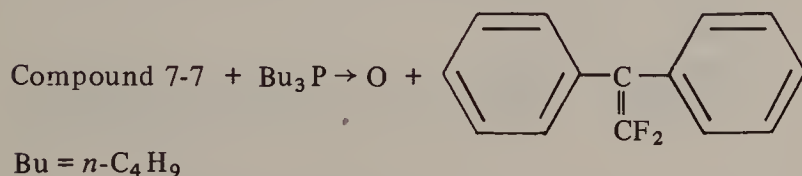
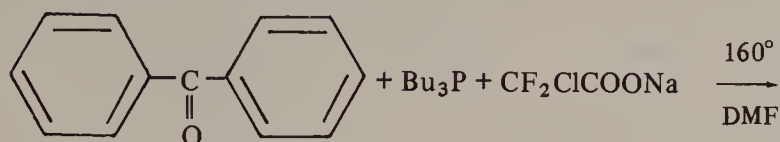
 $^1\text{H}$  NMR Spectrum (Solvent  $\text{CCl}_4$ )

compound number 7-7

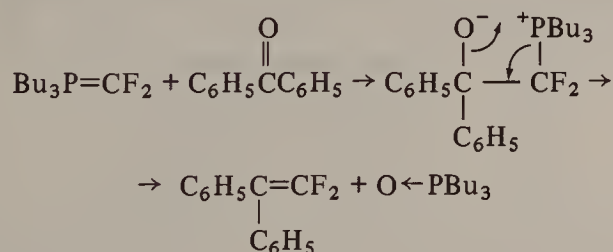
This example is presented to show some of the limitations of the methodology.

It is not likely that the four spectra presented would furnish sufficient evidence to identify this compound. However, given its history, we make the identification quite readily.

The compound was isolated as an unexpected, but rational, by-product from the following synthesis (S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 2543 (1965)):



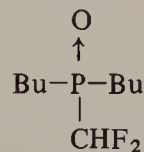
The reaction should proceed by formation of a Wittig reagent from the phosphine and the  $\text{CF}_2$  carbene formed by pyrolysis of sodium chlorodifluoroacetate. The Wittig reagent should react with the ketone.



The molecular weight of the by-product is 212. It is obvious from the spectra (e.g., lack of aromatic character) that the material is not a benzophenone derivative. Rather, aliphatic absorption predominates in the spectra. The compound may contain phosphorus or fluorine or both. Obviously no chlorine is present. The strong absorption at  $1182\text{ cm}^{-1}$  ( $8.46\text{ }\mu\text{m}$ ) may be aliphatic P $\rightarrow$ O absorption, and that at  $1087\text{ cm}^{-1}$  ( $9.20\text{ }\mu\text{m}$ ) and  $1033\text{ cm}^{-1}$  ( $9.68\text{ }\mu\text{m}$ ) may result from C-F stretching. The puzzling thing is that if we have the P $\rightarrow$ O group present, we cannot possibly have sufficient remaining mass for 3 butyl groups; the compound is not the usual product  $\text{Bu}_3\text{P}\rightarrow\text{O}$ .

Suppose we assume displacement of one of the butyl group; this leaves mass 51 short of the molecular weight. It does not take long to propose  $\text{CHF}_2$  as a possible fragment, and to confirm it with the striking NMR pattern. If the upfield protons represent the 18 protons of the butyl groups, the entire downfield pattern represents a single proton, centered at  $\delta$  6.07. The proton is split into a

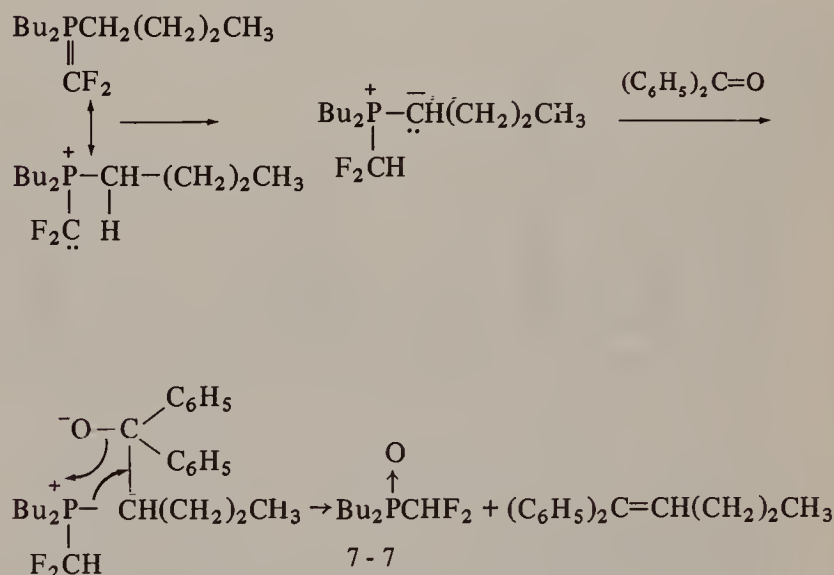
triplet by the geminal F atoms ( $J_{HF}$  49.4 Hz), and each peak is again split into a doublet by the P atom ( $J_{HP}$  19.4 Hz). The compound is therefore



Dibutyl(difluoromethyl)phosphine oxide

Some of the major fragmentation peaks can be accounted for:  $m/e$  183 ( $M$  minus  $\text{CH}_3\text{CH}_2$ ),  $m/e$  161 ( $M$  minus  $\text{CHF}_2$ ),  $m/e$  47 ( $\text{P} \rightarrow \text{O}$ ). The base peak,  $m/e$  128 must result from complex rearrangements. The  $M + 1$  and  $M + 2$  peaks are in agreement with the calculated values for the proposed structure.

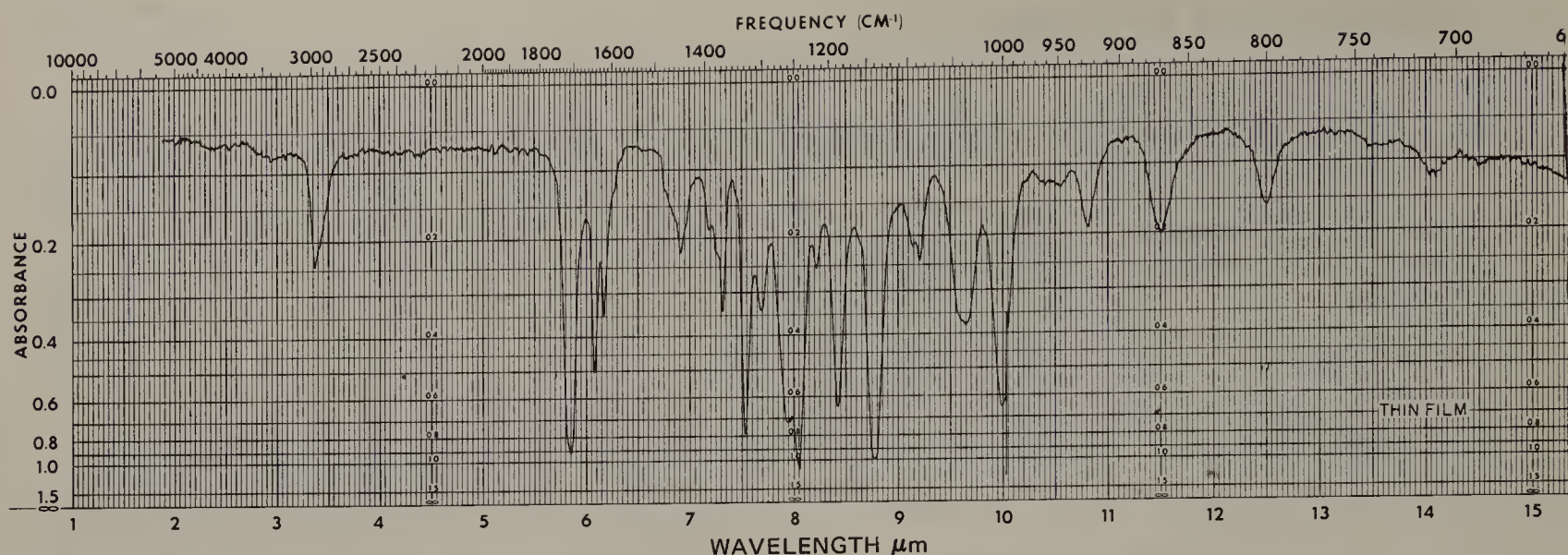
The rationale for this unexpected product depends on rearrangement of the initial Wittig reagent.



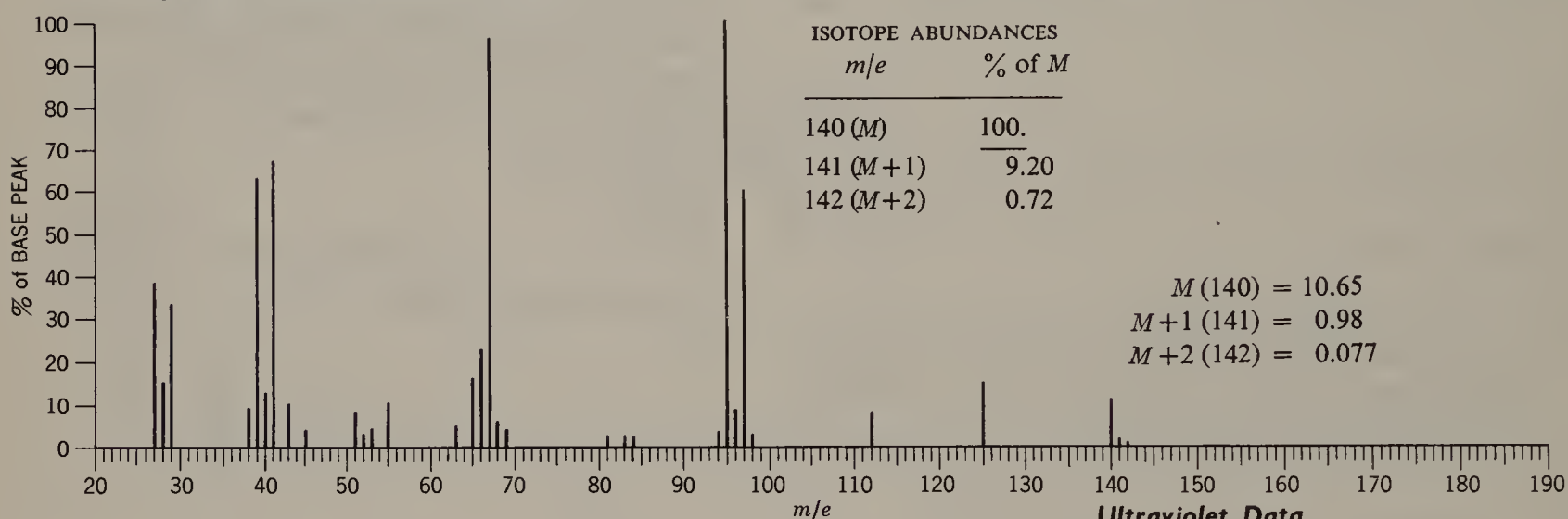
Note: The P → O bond has also been described as a P=O bond.



## Infrared Spectrum



## Mass Spectral Data (Relative Intensities)

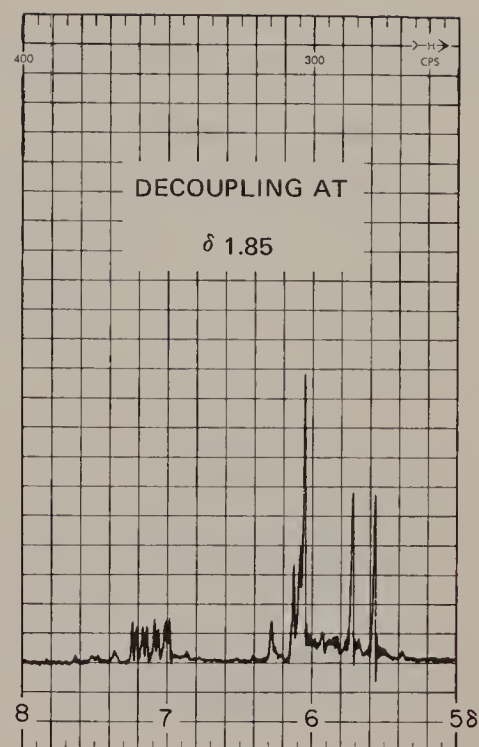
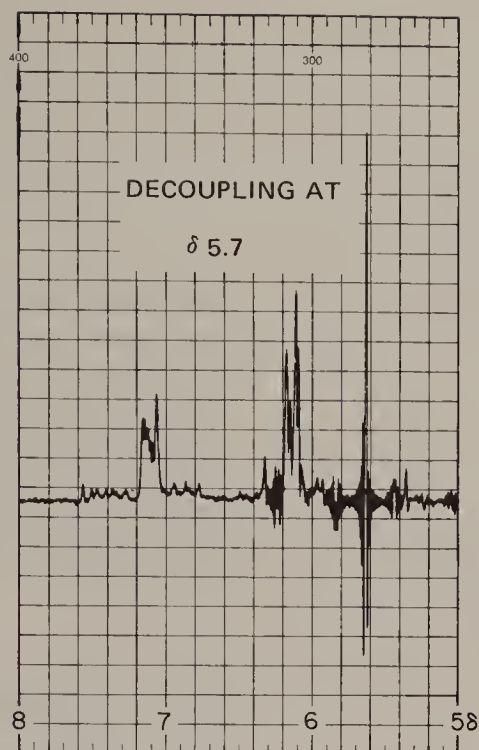
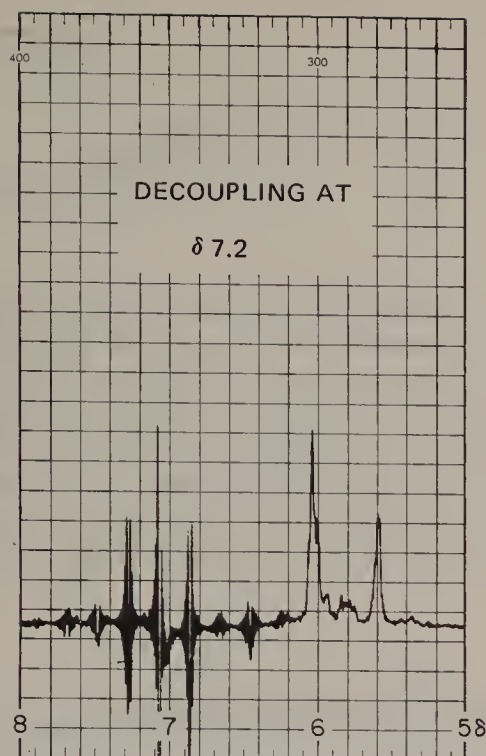


## Ultraviolet Data

| $\lambda_{\max}^{\text{EtOH}}$ | $\log \epsilon_{\max}$ |
|--------------------------------|------------------------|
| 259                            | 4.4                    |

<sup>1</sup>H NMR Spectrum





## compound number 7-8

The molecular ion ( $m/e$  140) and  $M+1$  and  $M+2$  data dictate, after elimination of formulas containing an odd number of  $N$  atoms, consideration of the following formulas:

| Formula         | $M+1$ | $M+2$ |
|-----------------|-------|-------|
| $C_7H_{12}N_2O$ | 8.56  | 0.52  |
| $C_8H_{12}O_2$  | 8.92  | 0.75  |
| $C_8H_{16}N_2$  | 9.66  | 0.42  |

The formula containing 2 oxygen atoms is chosen on the basis of the infrared spectrum: the strong absorption at  $1709\text{ cm}^{-1}$  ( $5.85\text{ }\mu\text{m}$ ) and the multiple bands in the  $1300\text{--}1160\text{ cm}^{-1}$  ( $7.69\text{--}8.62\text{ }\mu\text{m}$ ) region are indicative of

$\text{C}=\text{O}$  and  $\text{C}-\text{C}-\text{O}$  stretching, respectively. We therefore anticipate an ester of molecular formula  $C_8H_{12}O_2$ . An ethyl ester is suggested by the  $^1\text{H}$  NMR triplet at  $\delta$  1.25 (3 protons) and the quartet at  $\delta$  4.10 (2 protons); the chemical shift of the latter signal is consistent with a methylene

group of  $\text{RCOCH}_2\text{CH}_3$ . The  $R$  group, by difference from the molecular formula, is  $C_5H_7-$  and contains two sites of unsaturation, at least one of which must be due to a double bond in view of the olefinic protons,  $\delta$  5.0–6.5, in the NMR spectrum. It is also clear that a double bond is in conjugation with the carbonyl group since the  $\text{C}=\text{O}$  stretch cited above is at a lower wavenumber (higher wavelength) than

for normal, unconjugated, aliphatic esters ( $1730\text{--}1715\text{ cm}^{-1}$ ,  $5.71\text{--}5.76\text{ }\mu\text{m}$ ). The UV spectrum also supports a highly conjugated structure. A  $\text{C}=\text{C}-\text{C}=\text{C}$  system is delineated by the coupled (respectively, symmetric and asymmetric)  $\text{C}=\text{C}$  stretching vibrations at  $1645$  and  $1634\text{ cm}^{-1}$  ( $6.08$  and  $6.22\text{ }\mu\text{m}$ ). Since there is no other reason for low-field protons in our structure (e.g., no indication of aromaticity), the signal at  $\delta$  7.10 is also an olefinic proton of unusually low field position. Integration shows a total of four olefinic protons. The remaining NMR absorption ( $\delta$  1.85) is quite consistent with a methyl group (integration intensity) attached to a double bond (see chemical shift tables) bearing a single proton (hence, the doublet). These data can be satisfied only by placing the methyl group at the end of the conjugated sequence (remote to the ester grouping), thus:



Ethyl sorbate

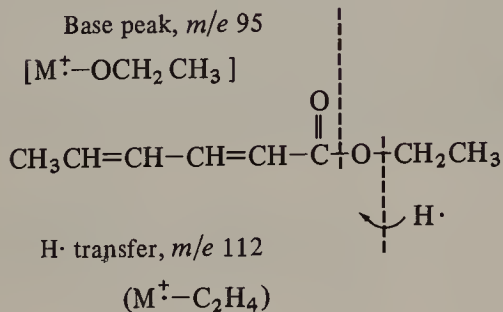
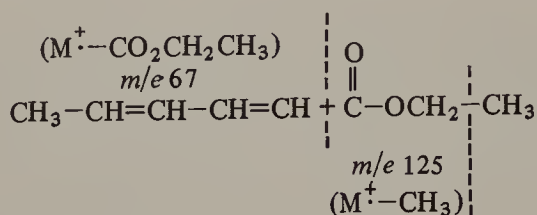
This structure is supported by data from Tables XIV–XVI in Chapter 6:

|   | $\text{nm}$ |
|---|-------------|
| $\text{R}-\text{C}=\text{CCO}_2\text{R}$ basic unit | 208         |
| One $\text{C}=\text{C}$ extending conjugation       | +30         |
| One $\delta$ substituent                            | +18         |

$$(\lambda_{\text{max}}^{\text{EtOH}}) \text{ calc} = 256 \pm 5$$

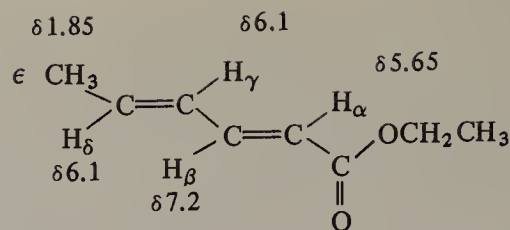
The calculated value agrees very well with the observed 259 nm maximum.

The mass spectral fragmentation pattern is easily rationalized by the following cleavage patterns:

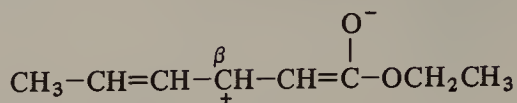


The infrared absorption at  $1000\text{ cm}^{-1}$  ( $10.00\text{ }\mu\text{m}$ ), (C–H bend) is evidence that the configuration about the C=C double bonds is *trans-trans* (see footnote on Table III, Appendix D, Chapter 3).

The NMR spectrum possesses some unusual features that can be interpreted only after spin decoupling experiments:



Irradiation at  $\delta$  7.2 ( $H_\beta$ ) removes  $J_{\beta\delta}$  and  $J_{\beta\alpha}$ , simplifying the signal for  $H_\alpha$  at about  $\delta$  5.65. Note that the *trans* assignment for the  $\alpha,\beta$  double bond is reinforced by the vicinal  $J$  value of about 18 Hz observed for the  $H_\alpha$  absorption. The absorptions for  $H_\delta$  and  $H_\gamma$  at about  $\delta$  6.1 are also partially collapsed. The unusually low field of  $H_\beta$ , compared to usual olefinic protons, can be rationalized by the resonance form that shows a decreased electron density at the  $\beta$ -carbon:



Decoupling at  $\delta$  5.65 ( $H_\alpha$ ) results in partial collapse of the signal at  $\delta$  7.2, as does decoupling at  $\delta$  1.85 ( $H_e$ ).

# eight problems

---

Problems Involving Mass Spectra, IR,  $^1\text{H}$  NMR, and UV Only:  
8-1 to 8-5, 8-21 to 8-30, 8-36, 8-38 to 8-44, 8-47, and 8-49.

Problems Involving the Spectra Listed Above and Chemical  
Information: 8-6 to 8-10.

Problems Involving the Spectra Listed Above and  $^{13}\text{C}$ -NMR:  
8-11 to 8-20, 8-31 to 8-35, 8-37, 8-45, 8-46, 8-48 (Prob.  
8-18, 8-19 and 8-46 have chemical information).

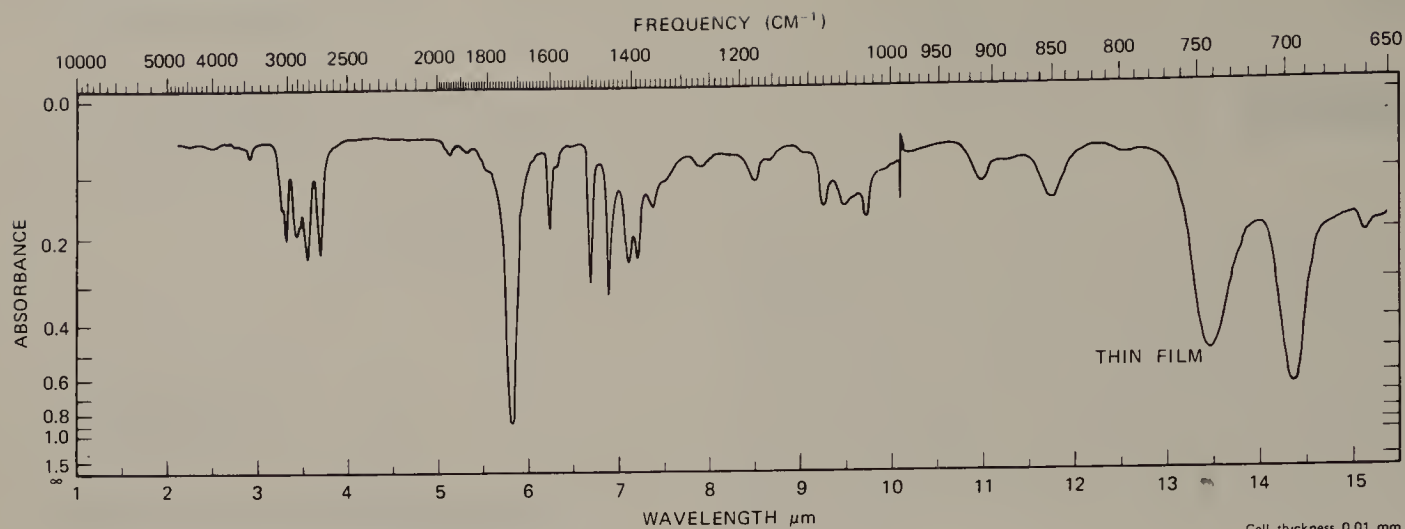
Beilstein references have been provided for the following  
twenty-seven problems: 8-1 to 8-4, 8-9, 8-13 to 8-18,  
8-20 to 8-22, 8-24, 8-25, 8-27, 8-30 to 8-35, 8-39 to 8-41,  
and 8-49.



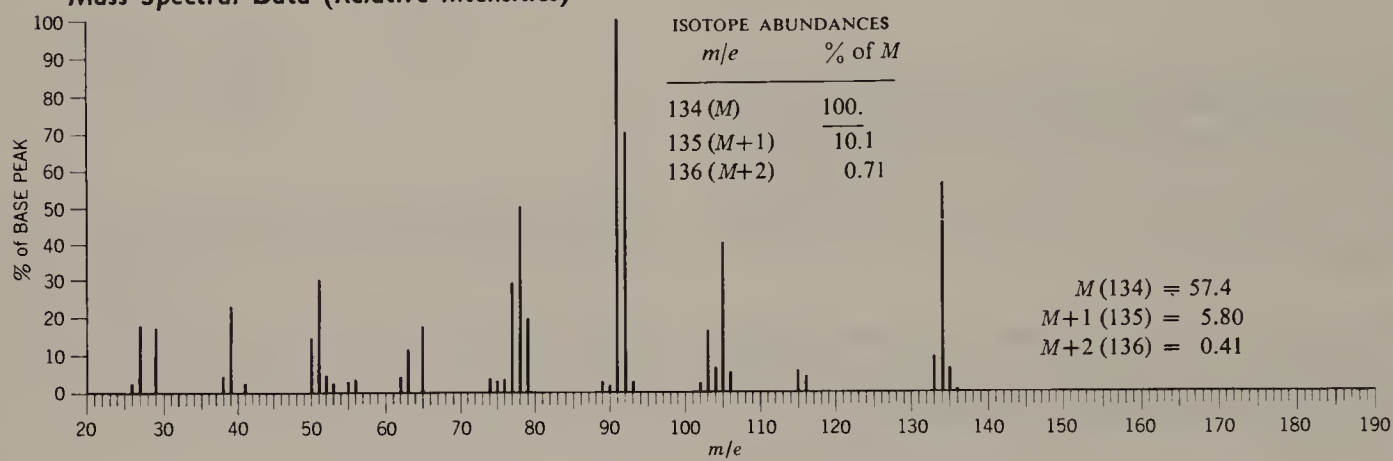
# Infrared Spectrum

Compound 8-1

Beilstein Ref. 5, 436



## Mass Spectral Data (Relative Intensities)

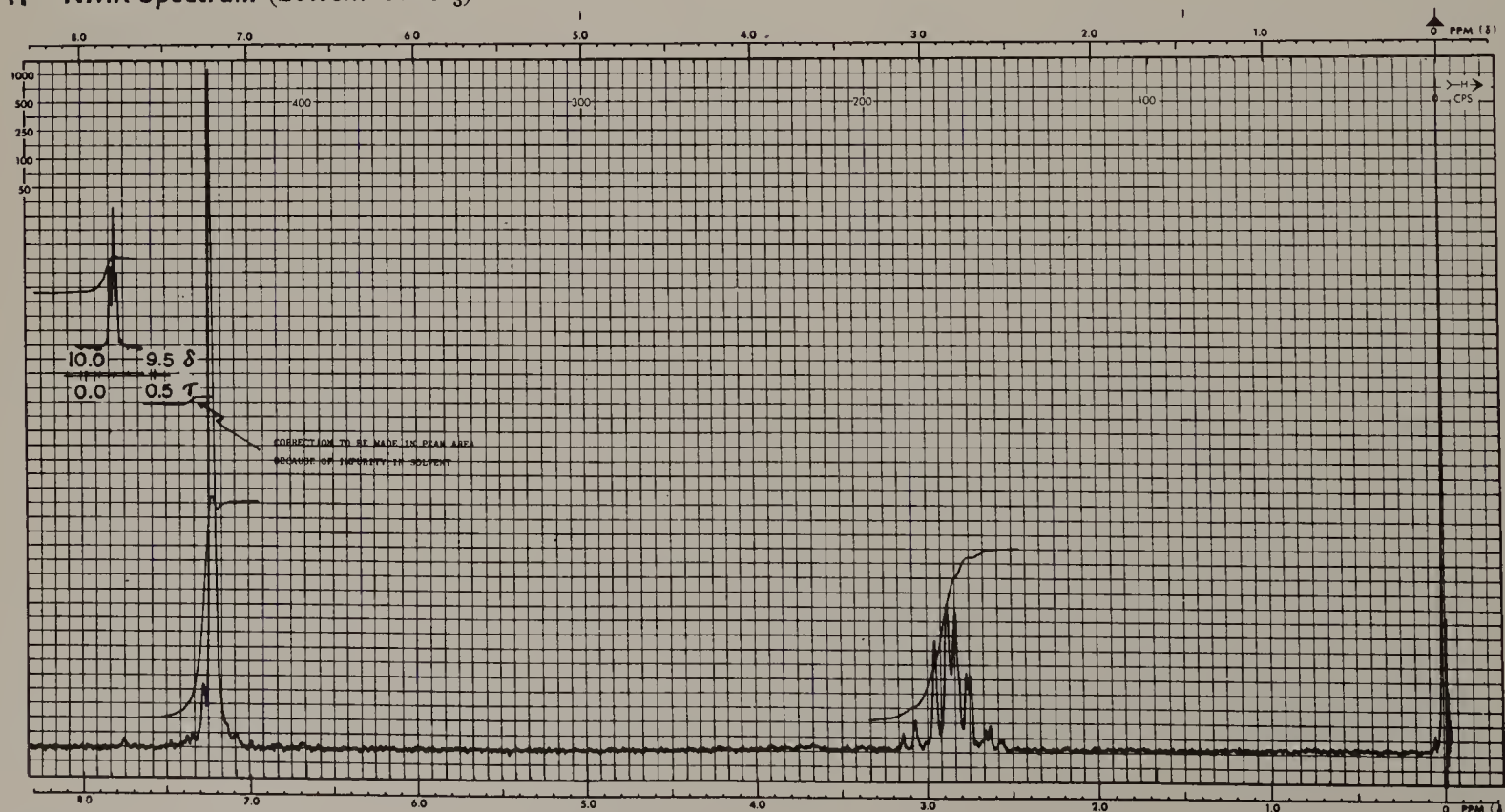


## Ultraviolet Data

|                           |      |      |     |                       |
|---------------------------|------|------|-----|-----------------------|
| <b>Ultraviolet Data</b>   | 255  | 2.50 | 264 | 2.18                  |
| $\lambda_{\max}^{n.s.g.}$ | 259  | 2.47 | 268 | 2.25                  |
| $\log \epsilon_{\max}$    | 262  | 2.43 | 283 | 1.59                  |
| 249                       | 2.31 |      |     |                       |
| 253                       | 2.50 |      |     |                       |
|                           |      |      |     | <i>n.s.g.</i> = no so |

*n.s.g.* = no solvent given

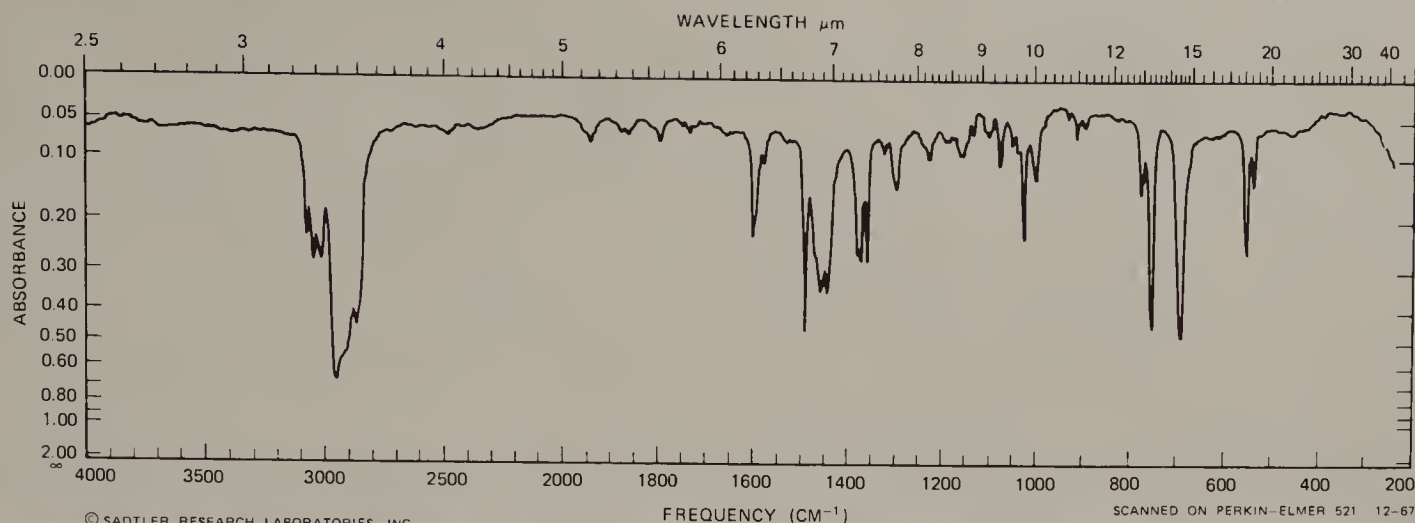
## <sup>1</sup>H NMR Spectrum (Solvent CDCl<sub>3</sub>)



# Infrared Spectrum

Compound 8-2

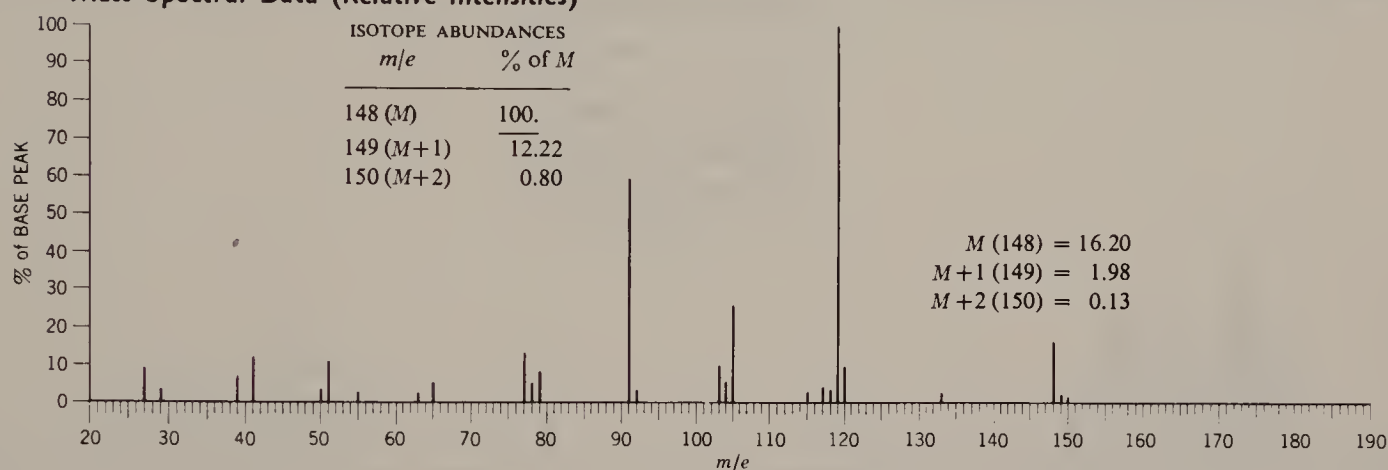
Beilstein Ref. 5, 436  
Capillary Cell: Neat



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Philadelphia, PA 19104 U.S.A.

SCANNED ON PERKIN-ELMER 521 12-67  
EK-1  
Cell thickness 0.01 mm

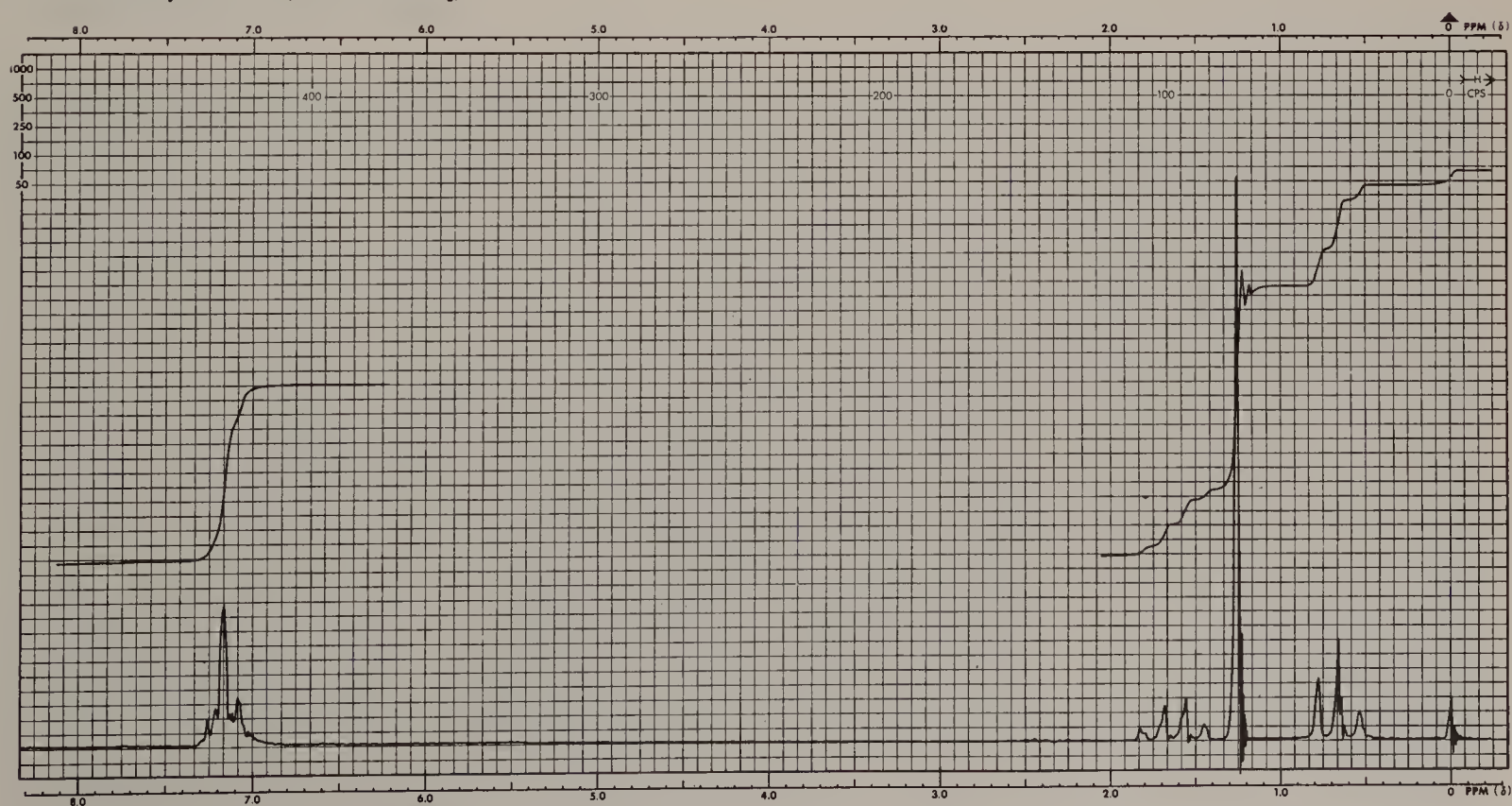
## Mass Spectral Data (Relative Intensities)



| Ultraviolet Data                          |                              | 242 (s)   | 1.85 | 258 | 2.29 |
|---|------------------------------|-----------|------|-----|------|
| $\lambda_{\text{isooctane}}^{\text{max}}$ | $\log \epsilon_{\text{max}}$ | 247.5 (s) | 2.09 | 261 | 2.20 |
|   |                              | 252.5     | 2.19 | 264 | 2.18 |
| 217 (s)                                   | 3.60                         |           |      |     |      |
| 236 (s)                                   | 1.57                         |           |      |     |      |

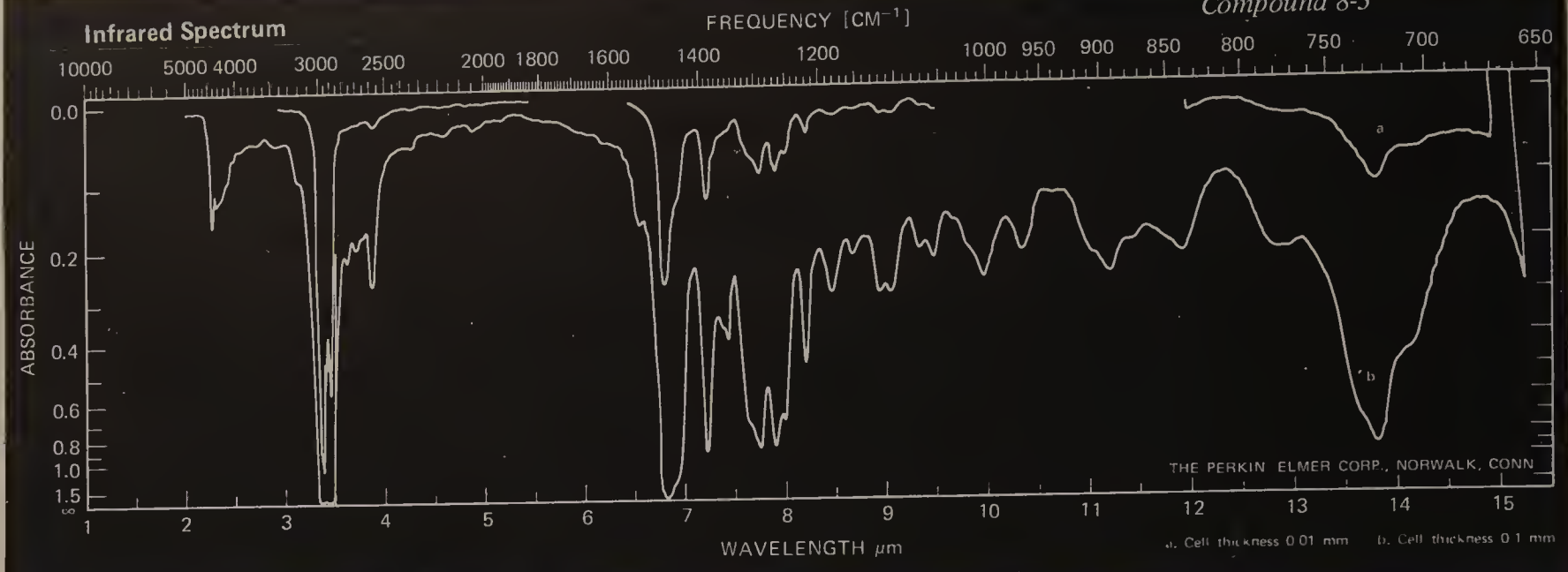
(s) = shoulder

## <sup>1</sup>H NMR Spectrum (Solvent CCl<sub>4</sub>)

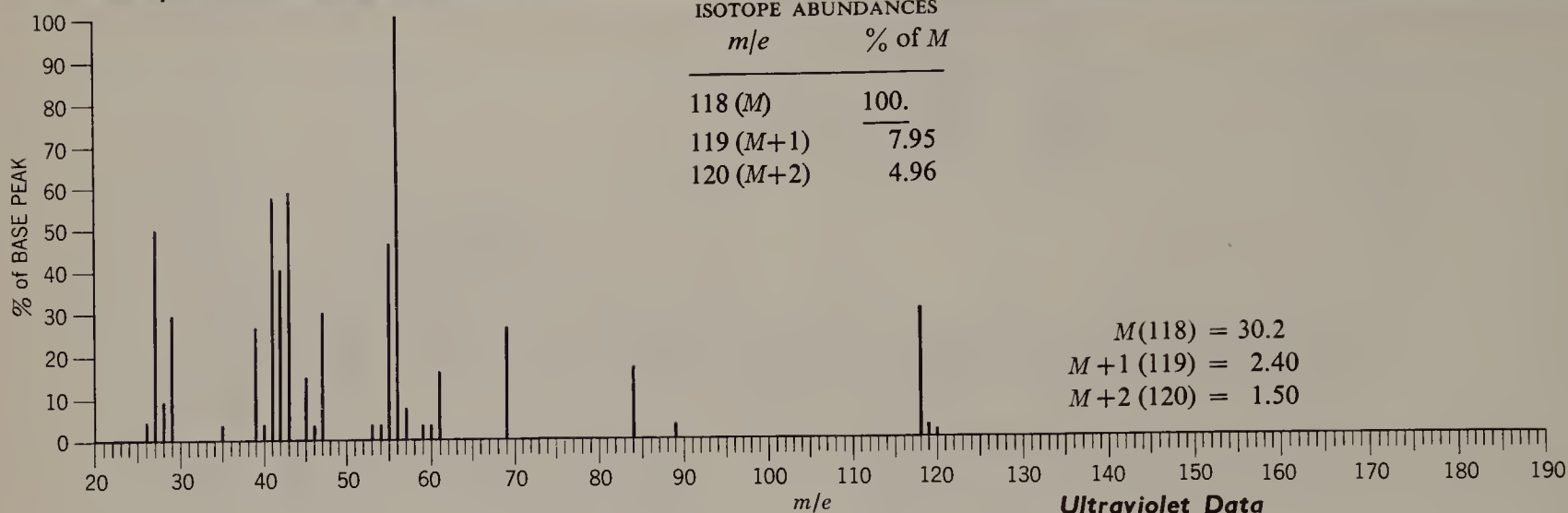




Compound 8-3

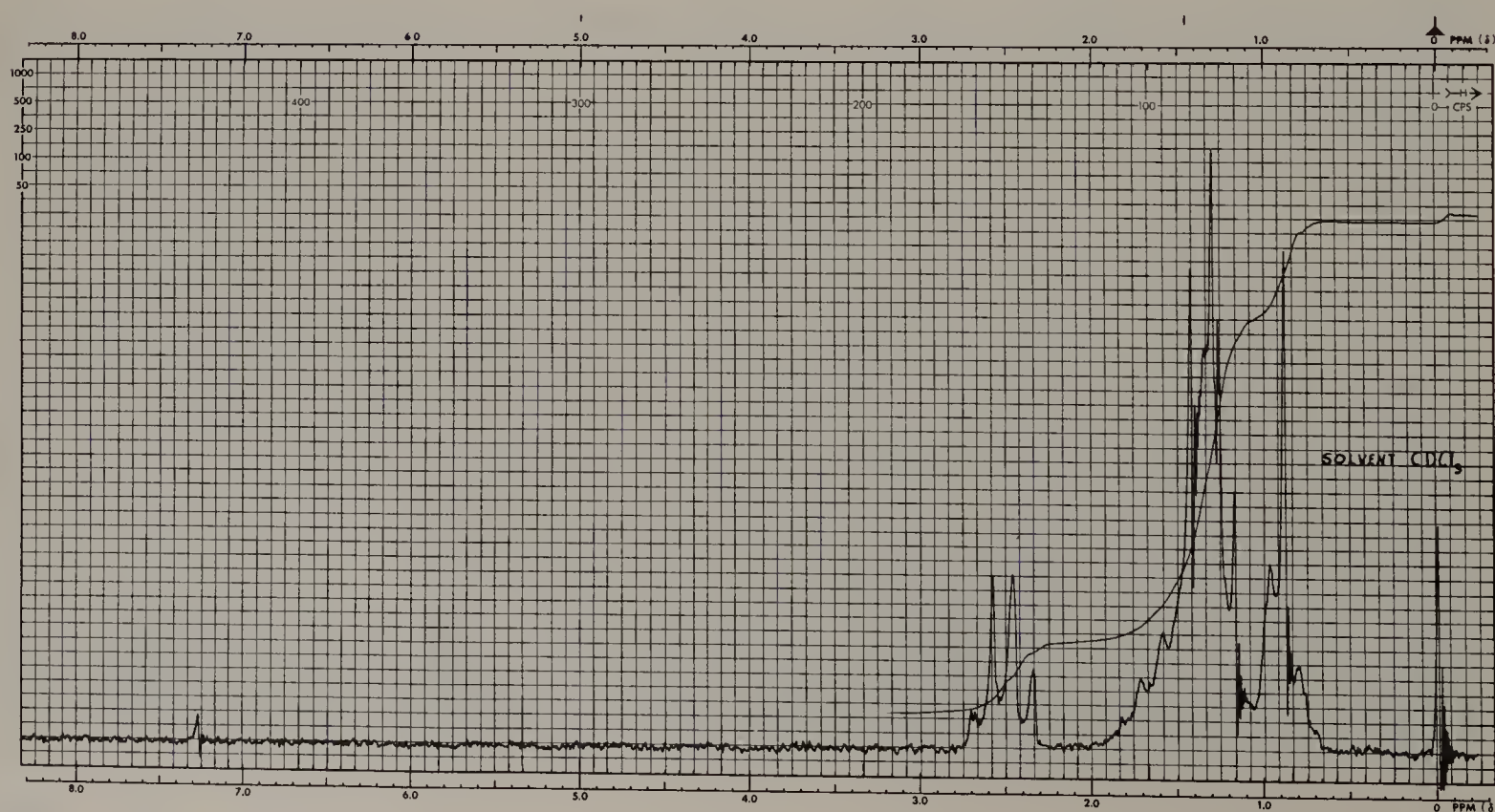


**Mass Spectral Data (Relative Intensities)**



**Ultraviolet Data**

| $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ | $\epsilon_{\text{max}}$ |                |
|--|-------------------------|----------------|
| 225 (s)  | 163                     | (s) = shoulder |



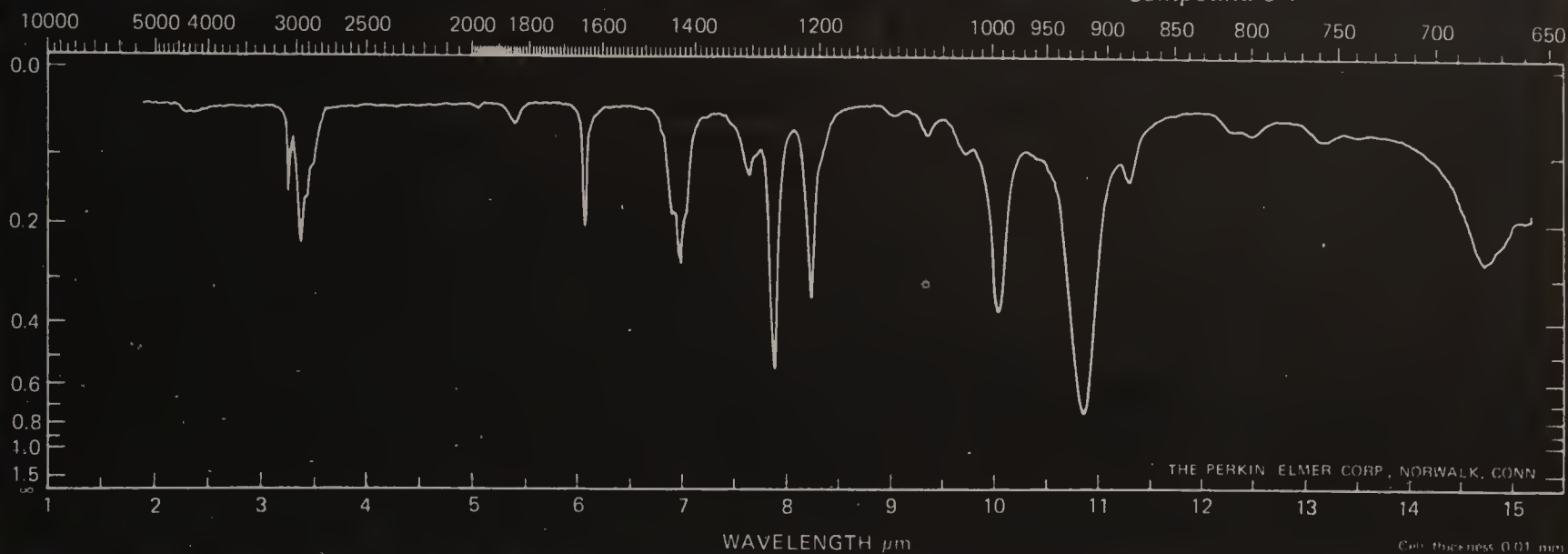


## Infrared Spectrum

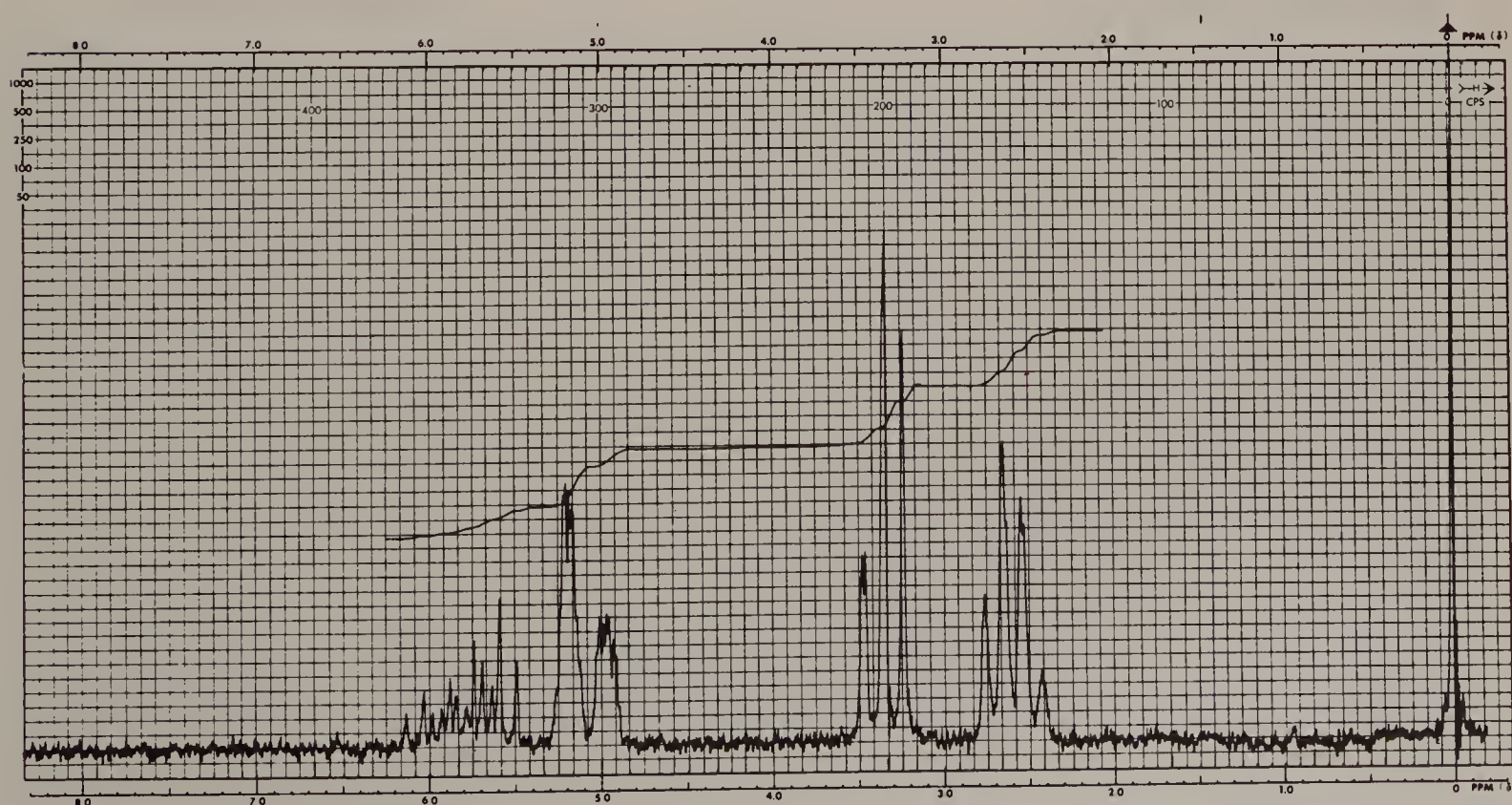
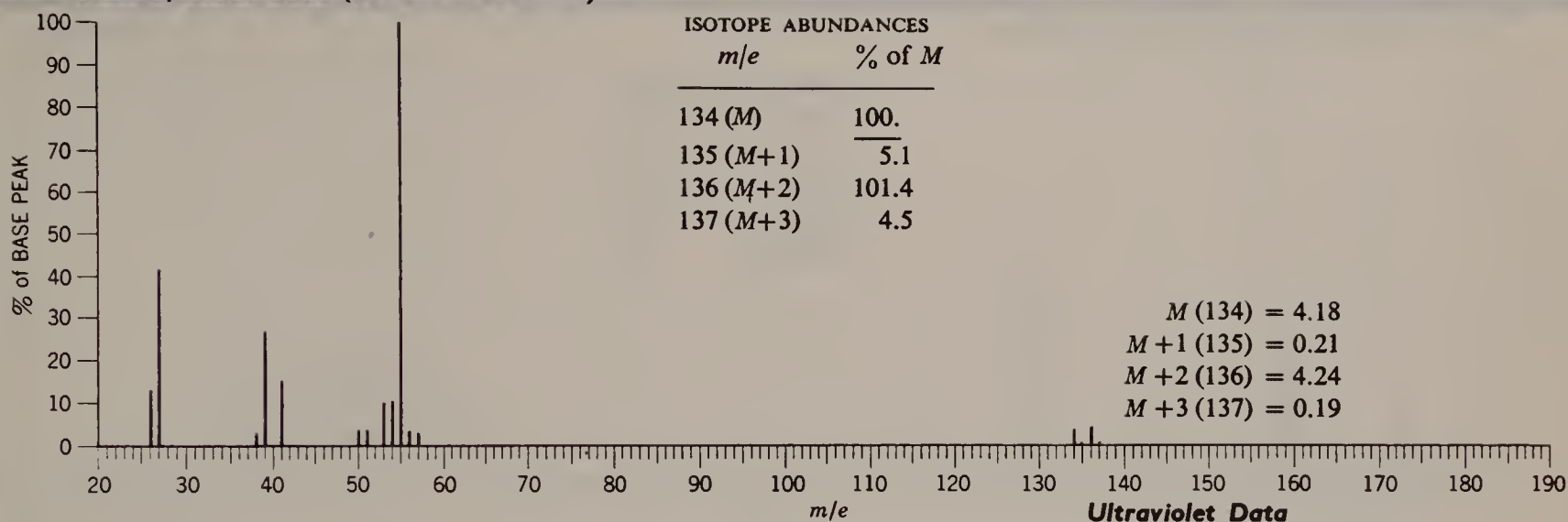
FREQUENCY (CM<sup>-1</sup>)

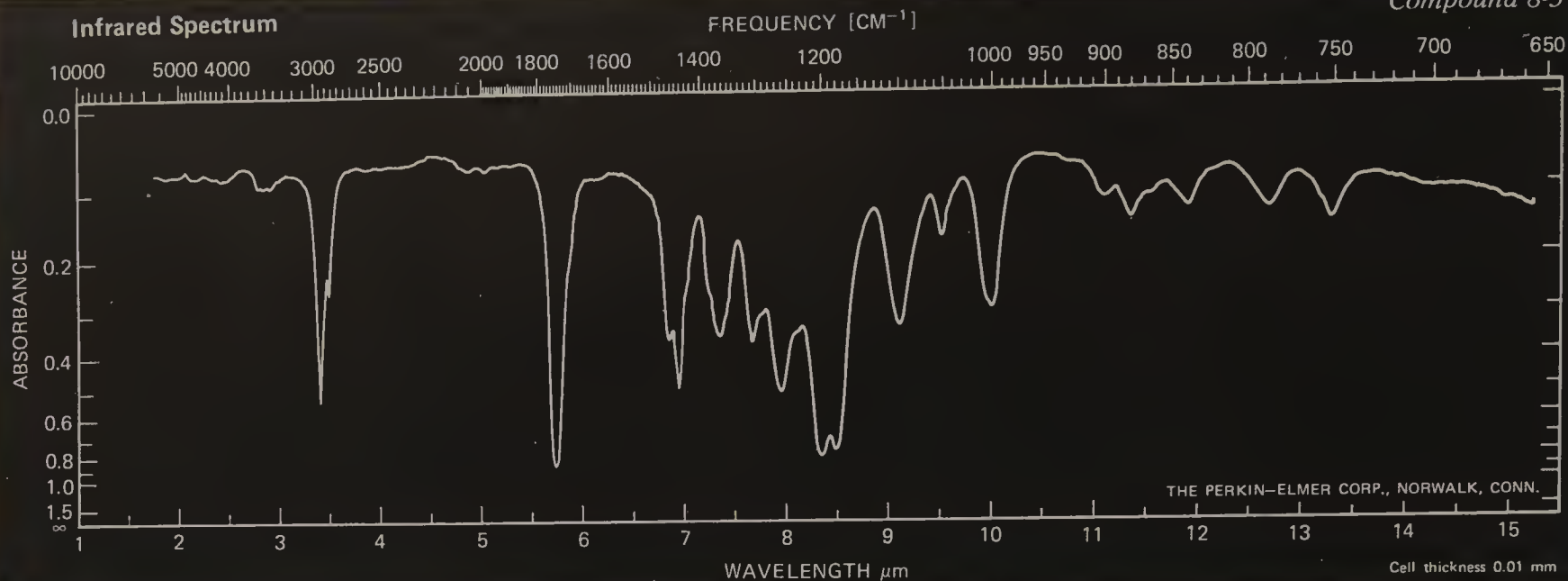
Compound 8-4

Reiten Ref. 1 "Supp. 1" 121

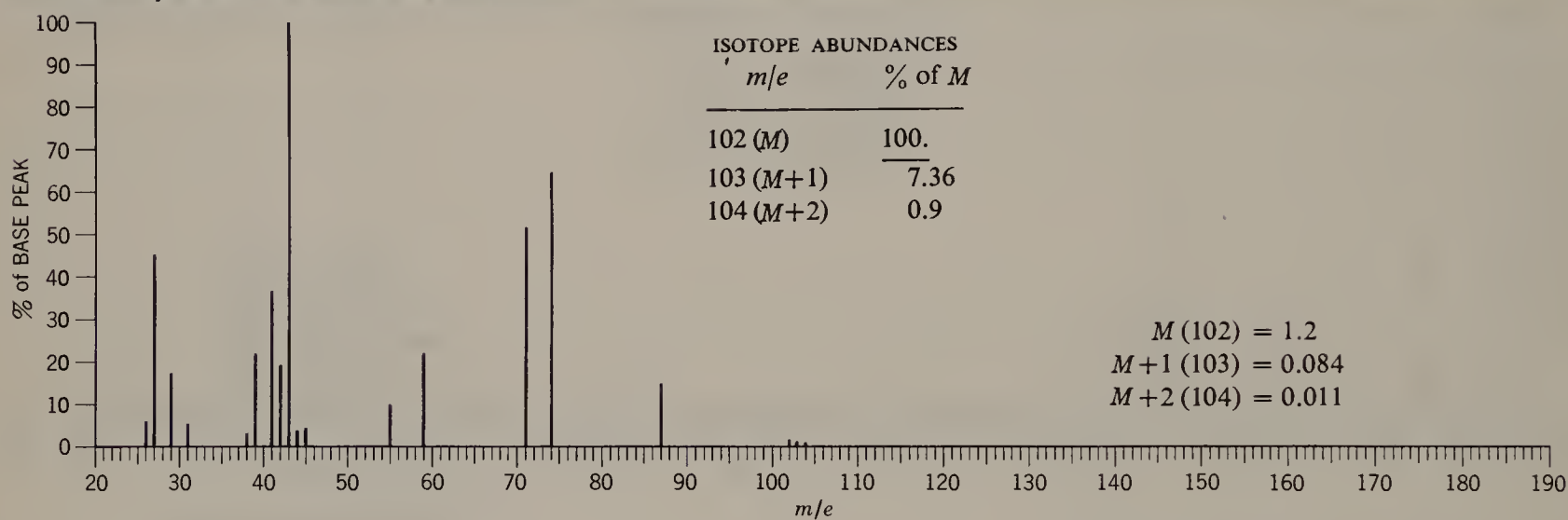


## Mass Spectral Data (Relative Intensities)





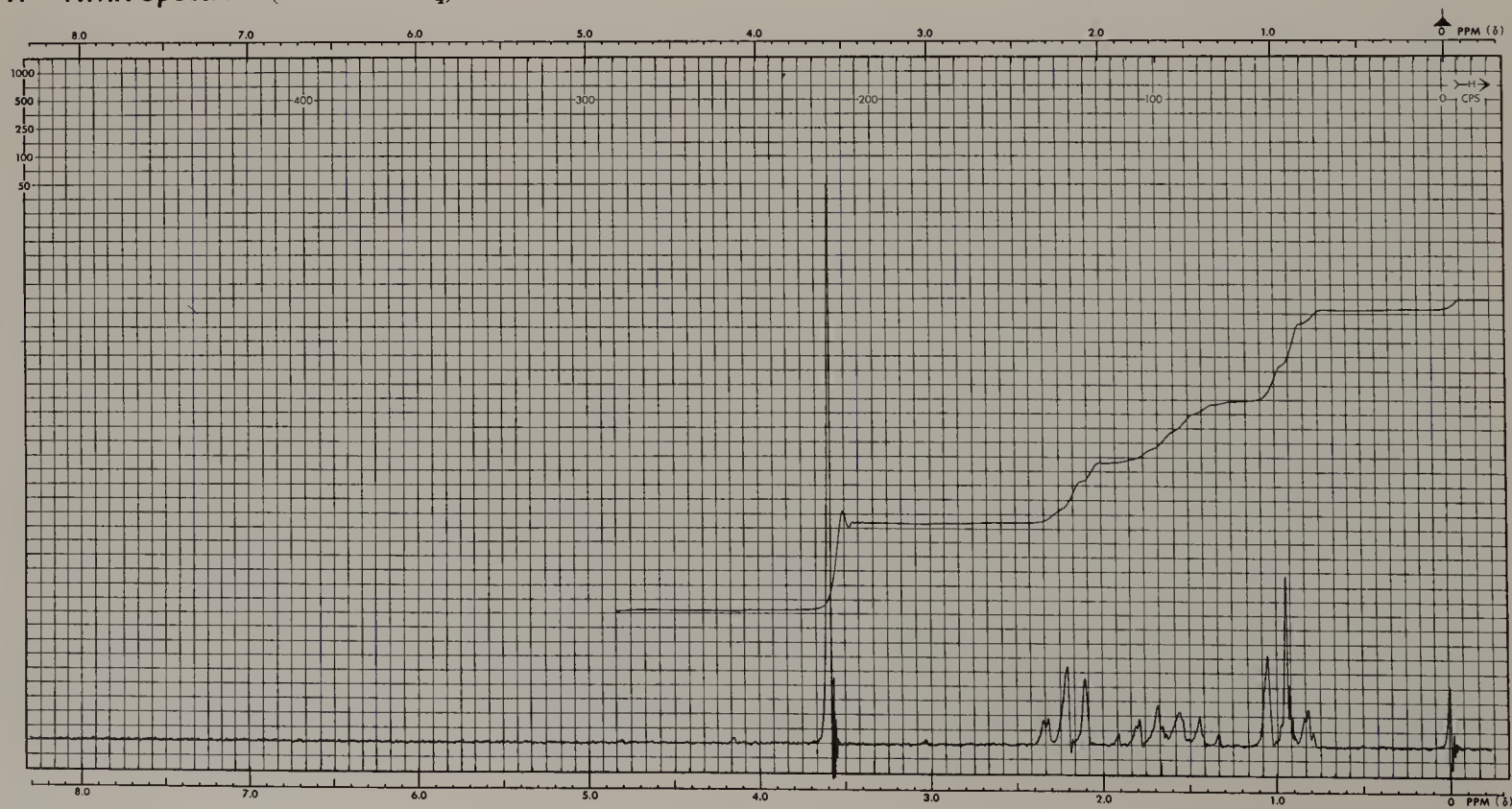
**Mass Spectral Data (Relative Intensities)**



**Ultraviolet Data**

Transparent above 210 nm

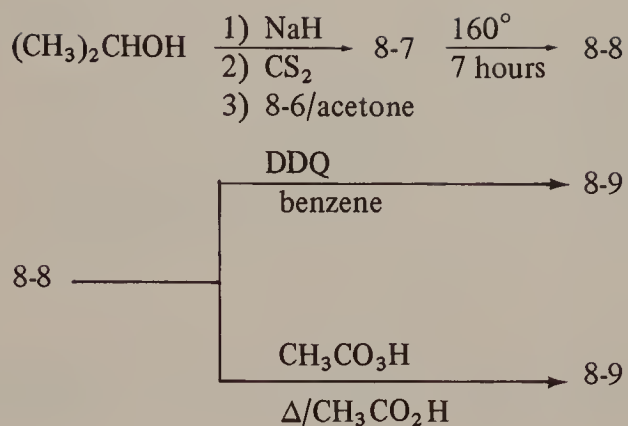
**<sup>1</sup>H NMR Spectrum (Solvent CCl<sub>4</sub>)**



# ROAD MAP PROBLEM (COMPOUNDS 8-6 TO 8-10)

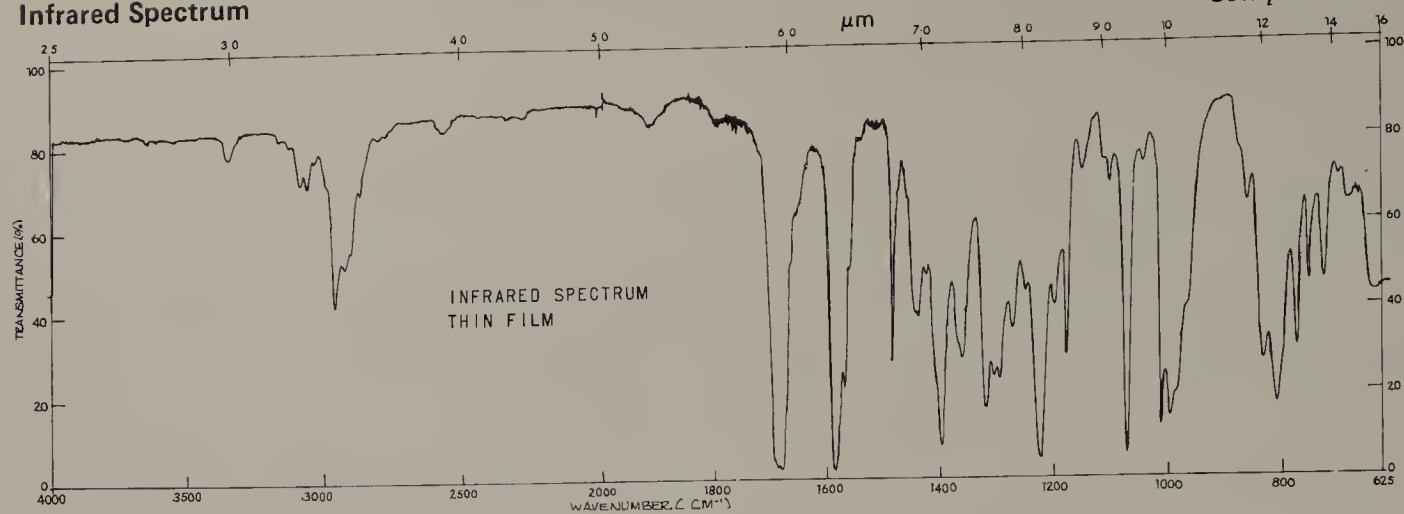
Determine the structure of compound 8-6 from the spectra provided. Treatment of isopropyl alcohol with NaH followed by addition of carbon disulfide results in the formation of an isolable sodium salt; treatment of compound 8-6 with this salt, in acetone solution, results in compound 8-7. Identify 8-7 from the spectra provided. Compound 8-7 was pyrolyzed at  $160^{\circ}$  for 7 hours to give compound 8-8; identify 8-8 from the spectra provided. Treatment of 8-8 with dicyanodichloroquinone (DDQ) in benzene for 20 minutes at room temperature resulted in compound 8-9, and treatment of compound 8-8 with refluxing glacial acetic acid containing hydrogen peroxide resulted in compound 8-10. Identify compounds 8-9 and 8-10 from the spectra.

## Reaction Scheme





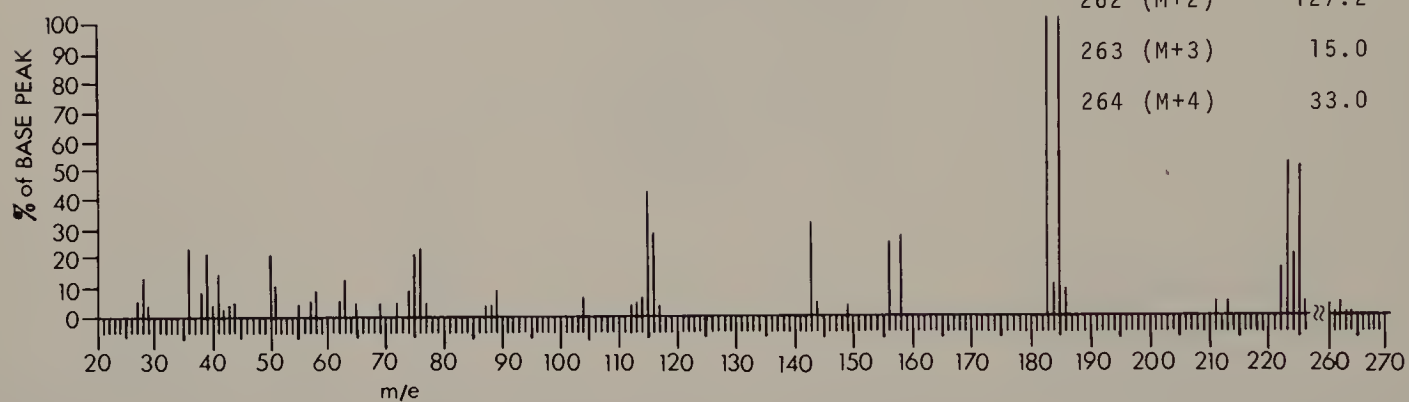
## Infrared Spectrum



## Mass Spectral Data

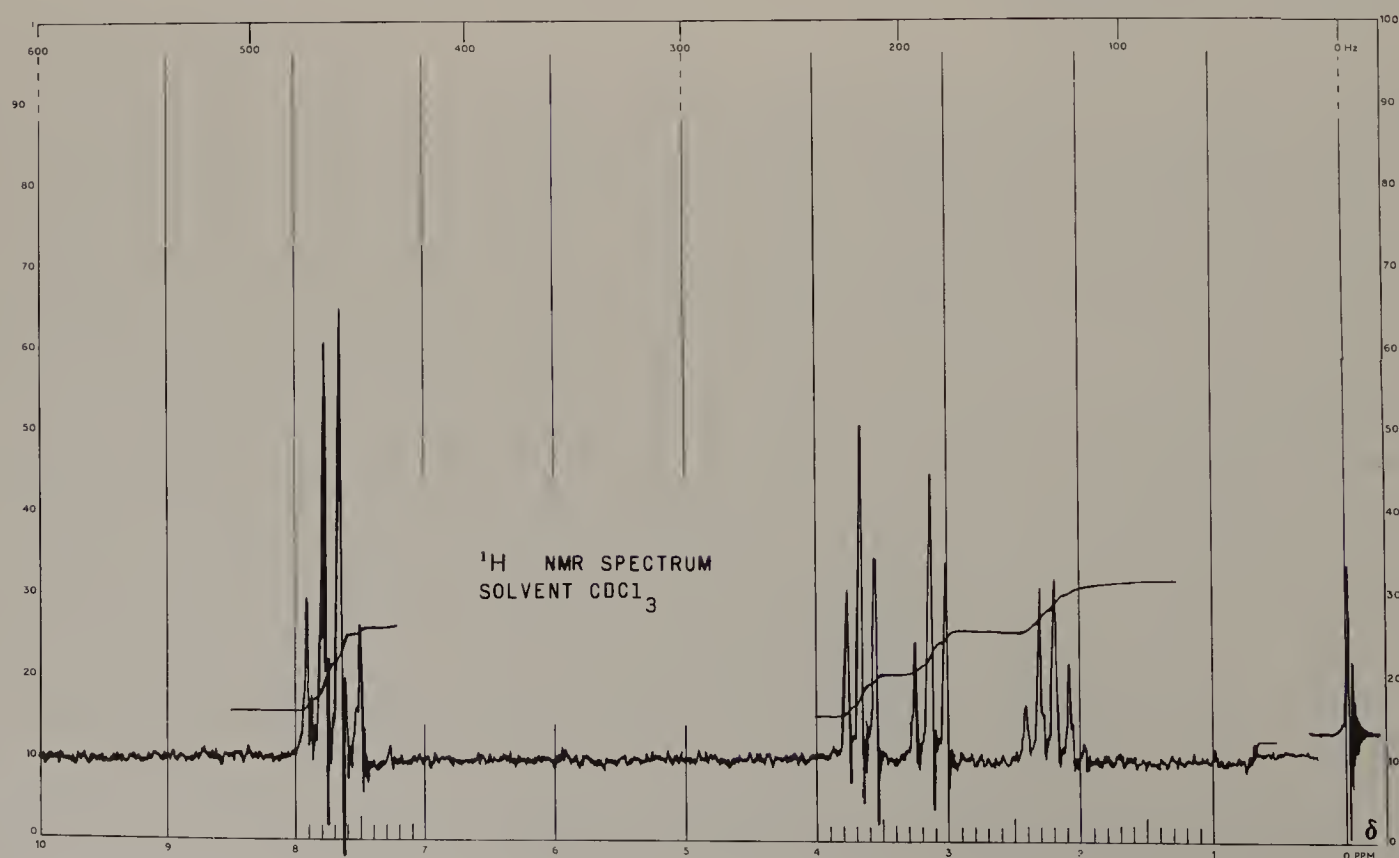
| <u>m/e</u> | <u>% of M</u> |
|------------|---------------|
| 260 (M)    | 100.0         |
| 261 (M+1)  | 13.8          |
| 262 (M+2)  | 127.2         |
| 263 (M+3)  | 15.0          |
| 264 (M+4)  | 33.0          |

## MASS SPECTRAL DATA (Relative Intensity)



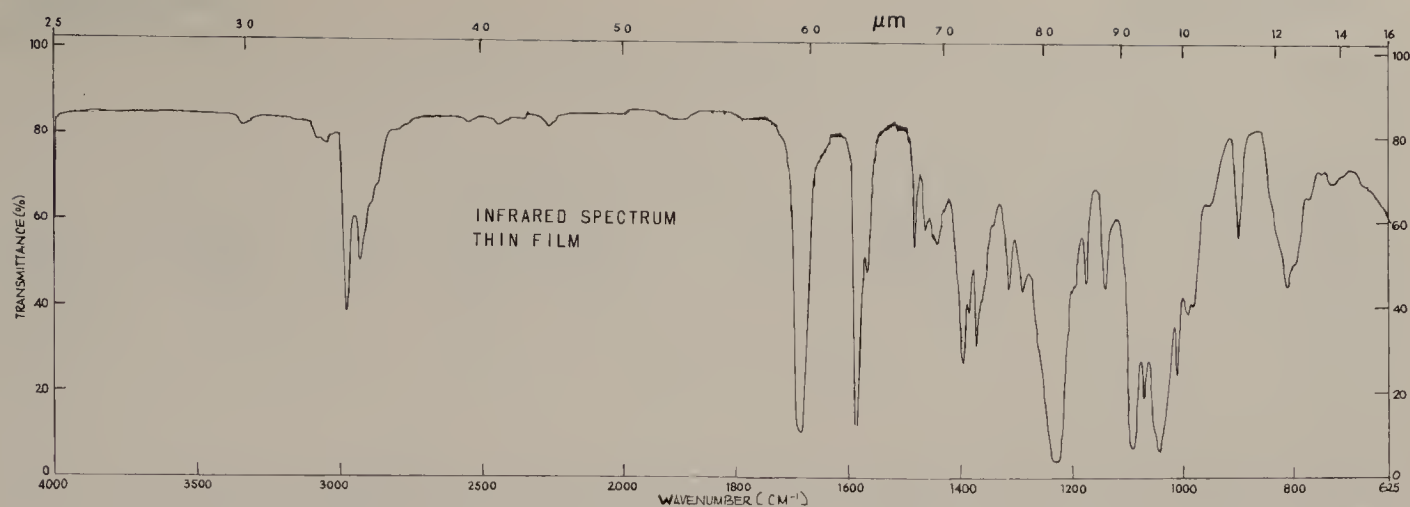
## Ultraviolet Data

| <u><math>\lambda_{\text{max.}}</math></u> | <u><math>\epsilon_{\text{max.}}</math></u> |
|---|--|
| 253                                       | 46,400                                     |

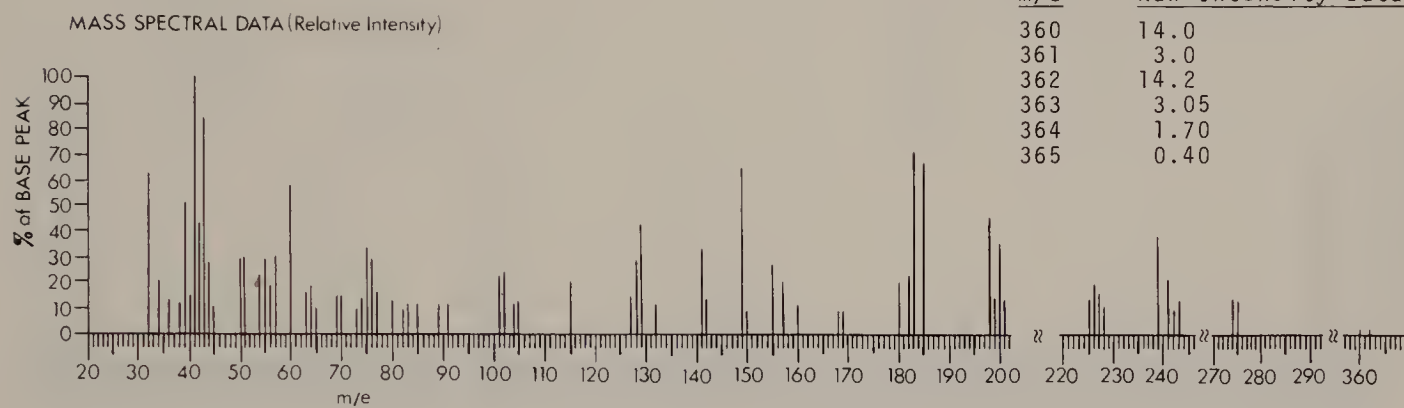


## Infrared Spectrum

Compound 8-7



## Mass Spectral Data

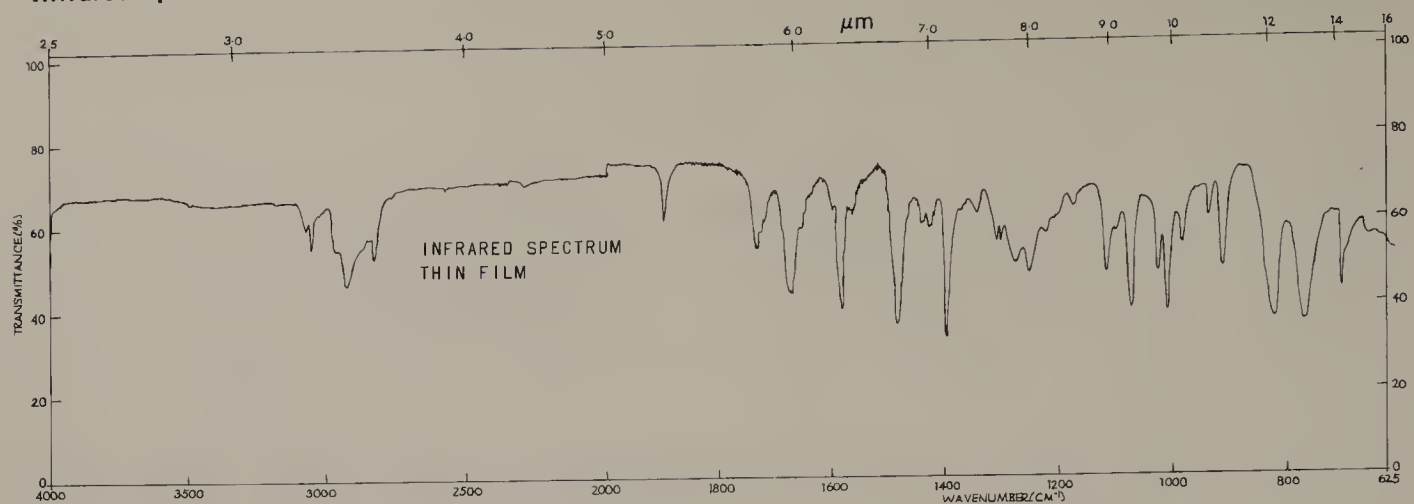


## Ultraviolet Data

| $\lambda_{\max}$<br>(CH <sub>3</sub> OH) | $\epsilon_{\max}$ |
|--|-------------------|
| 253                                      | 46,400            |
| 276                                      | 1,400             |



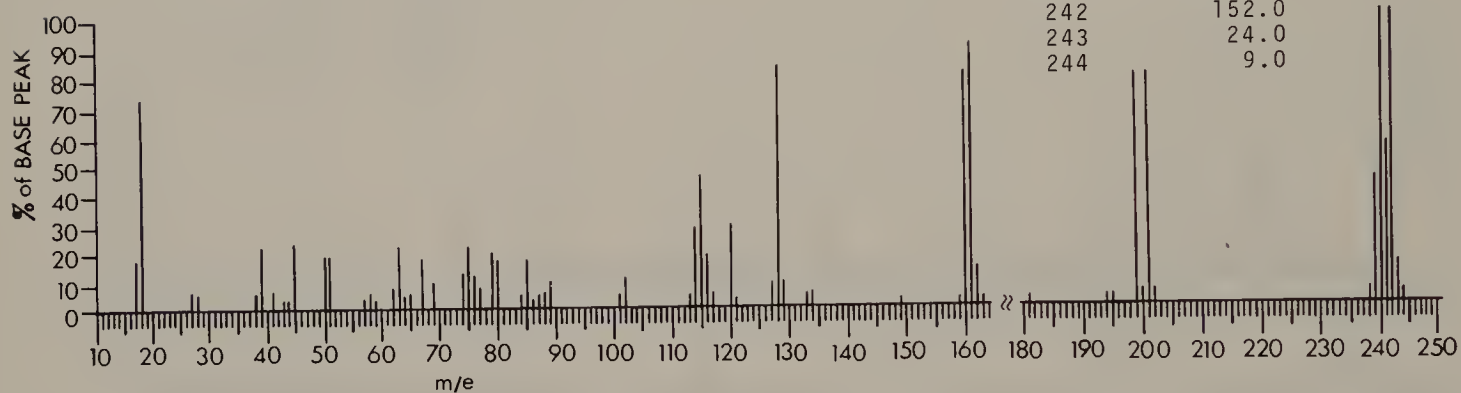
## Infrared Spectrum



## Mass Spectral Data

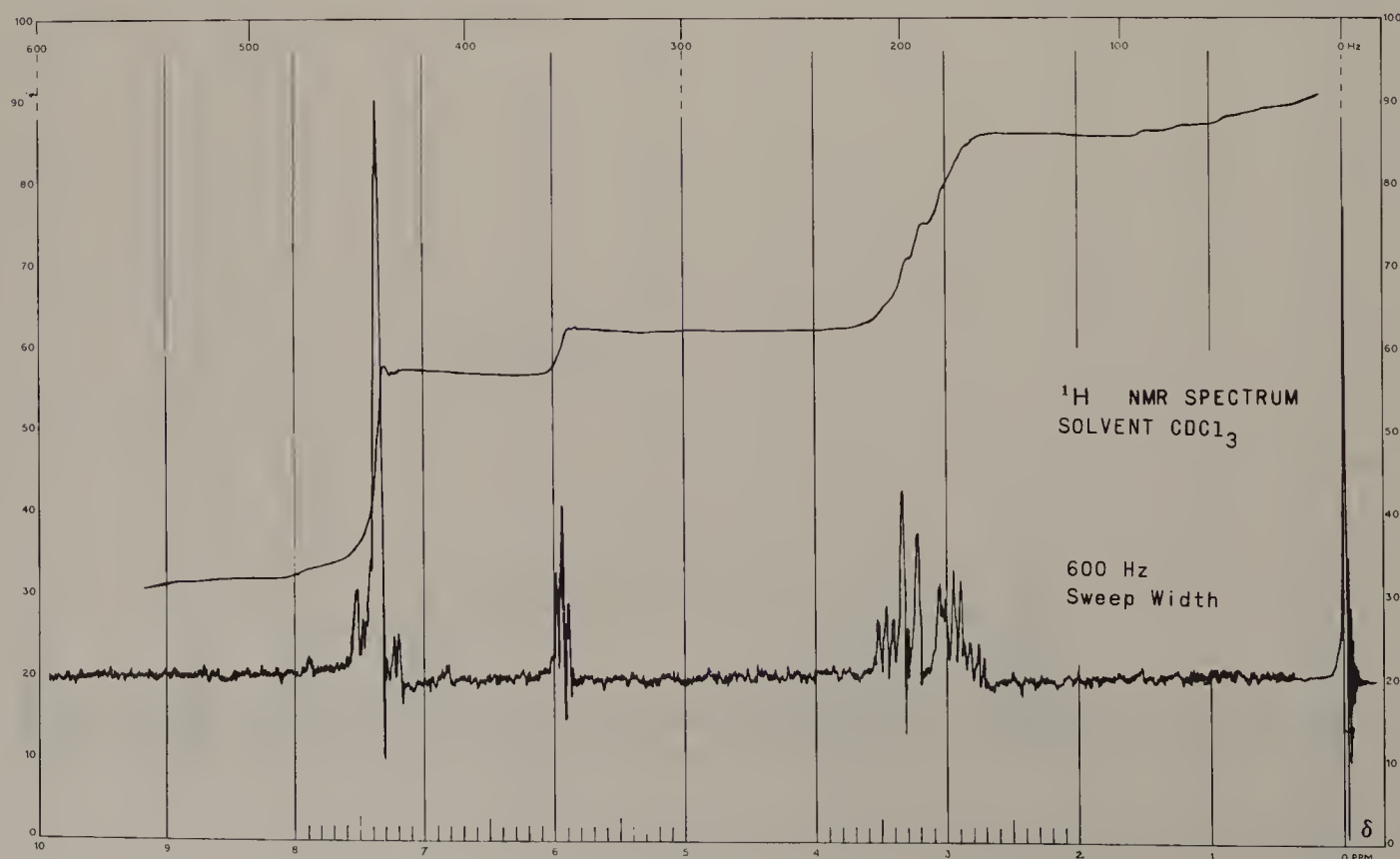
| m/e | Raw Intensity Data |
|-----|--------------------|
| 239 | 68.0               |
| 240 | 153.0              |
| 241 | 88.0               |
| 242 | 152.0              |
| 243 | 24.0               |
| 244 | 9.0                |

## MASS SPECTRAL DATA (Relative Intensity)



## Ultraviolet Data

| $\lambda_{\max}$<br>(CH <sub>3</sub> OH) | $\epsilon_{\max}$ |
|--|-------------------|
| 237                                      | 18,600            |
| 301                                      | 5,540             |

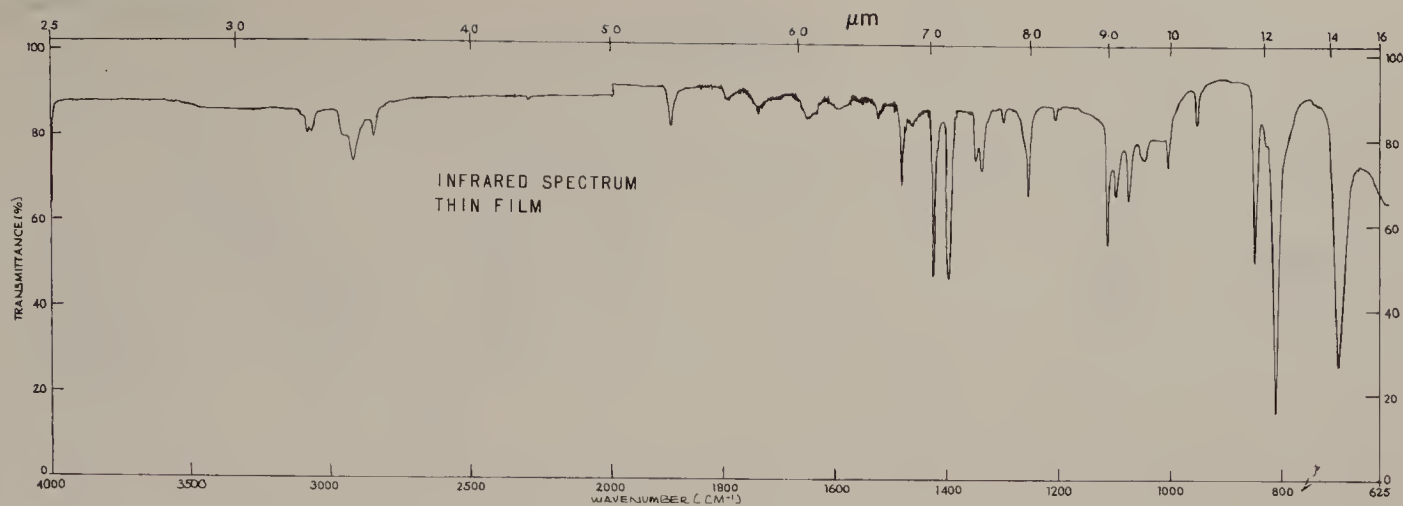




## Infrared Spectrum

Compound 8-9

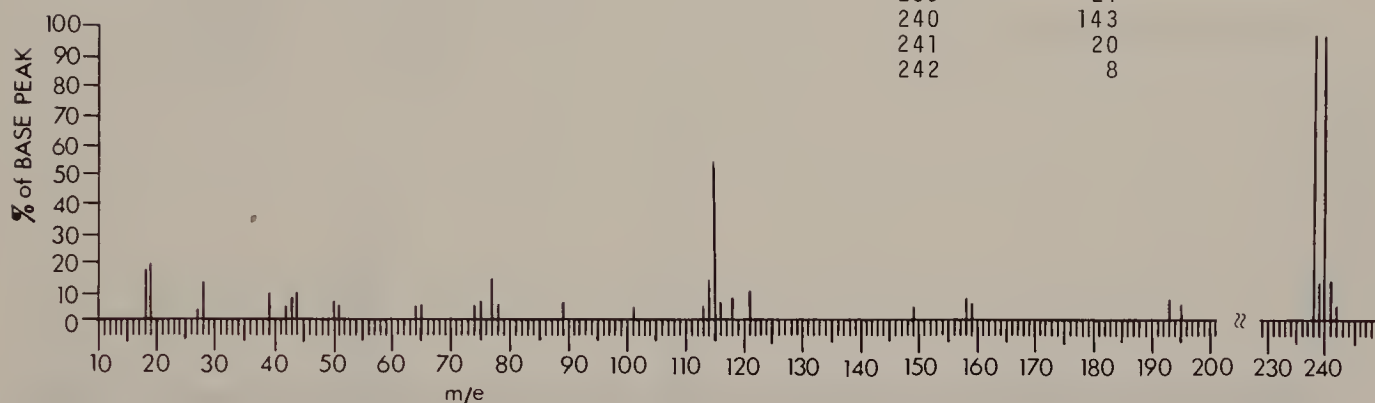
Beilstein Ref. II, (17), 64



## Mass Spectral Data

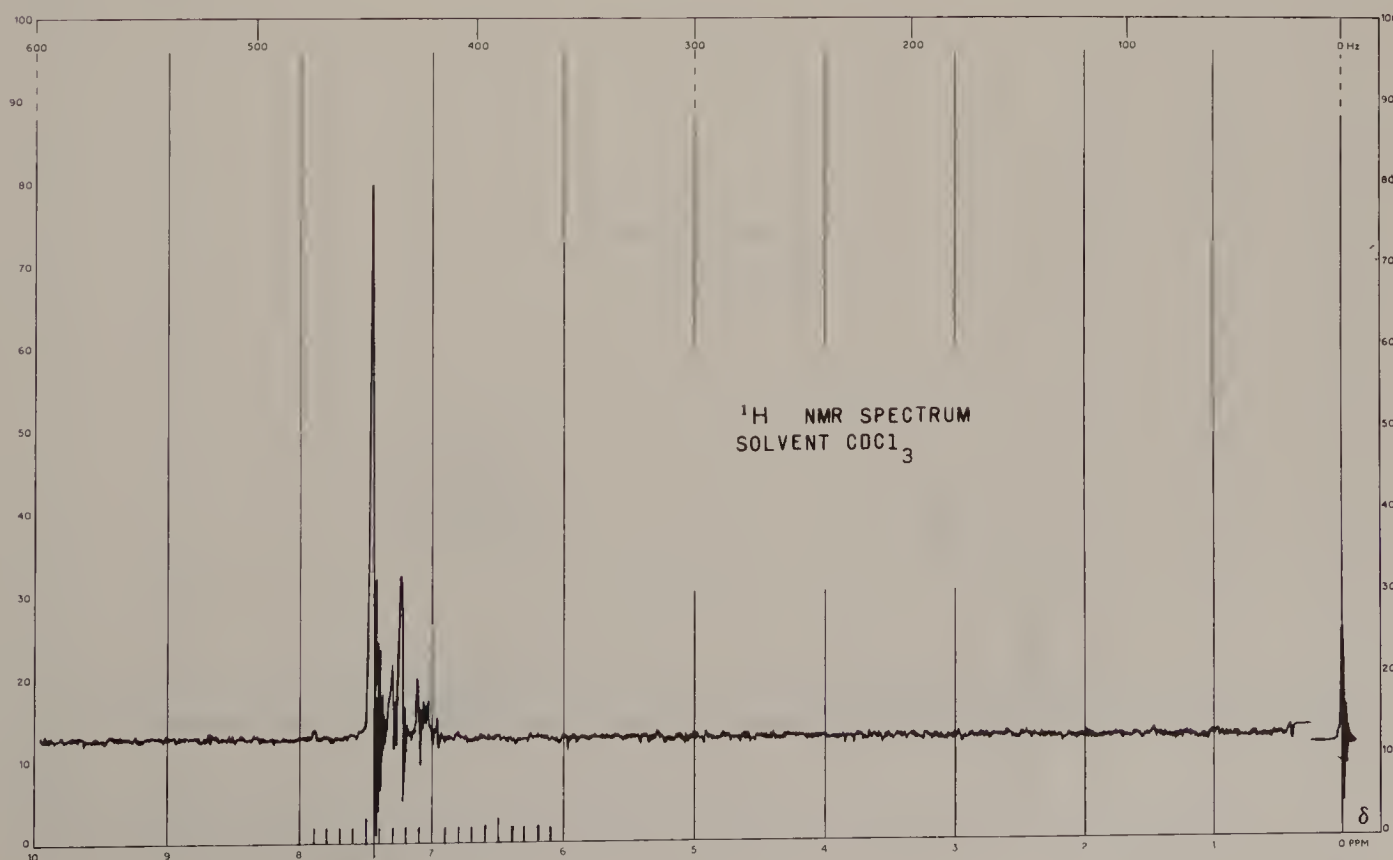
MASS SPECTRAL DATA (Relative Intensity)

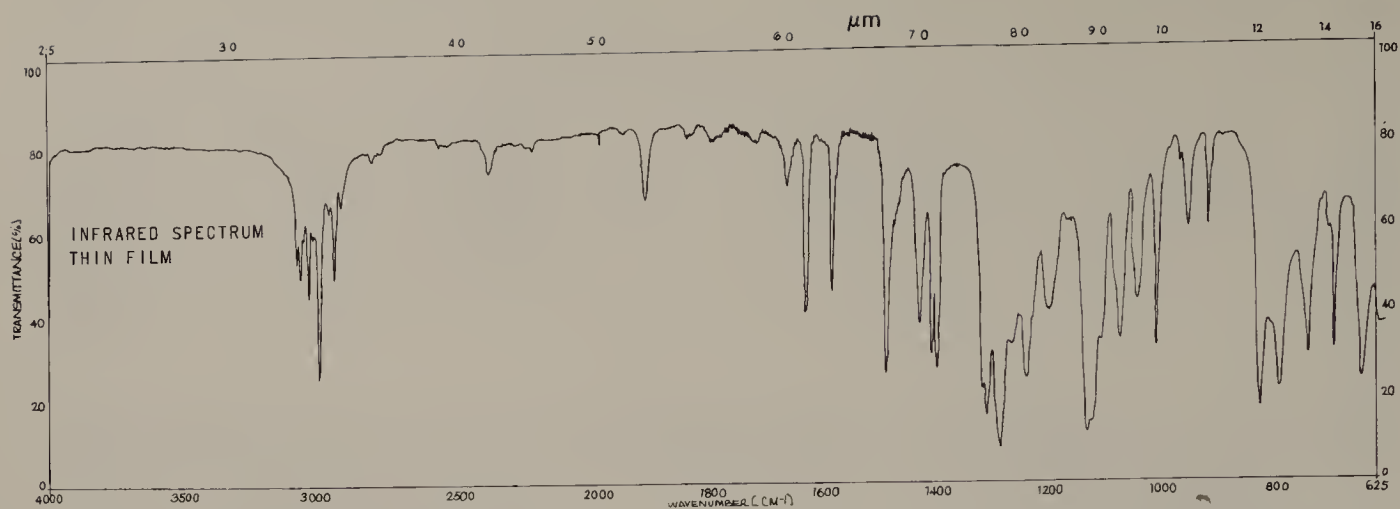
| m/e | Raw Intensity Data |
|-----|--------------------|
| 238 | 144                |
| 239 | 21                 |
| 240 | 143                |
| 241 | 20                 |
| 242 | 8                  |



## Ultraviolet Data

| $\lambda_{\max}$<br>(CH <sub>3</sub> OH) | $\epsilon_{\max}$ |
|--|-------------------|
| 285                                      | 23,400            |

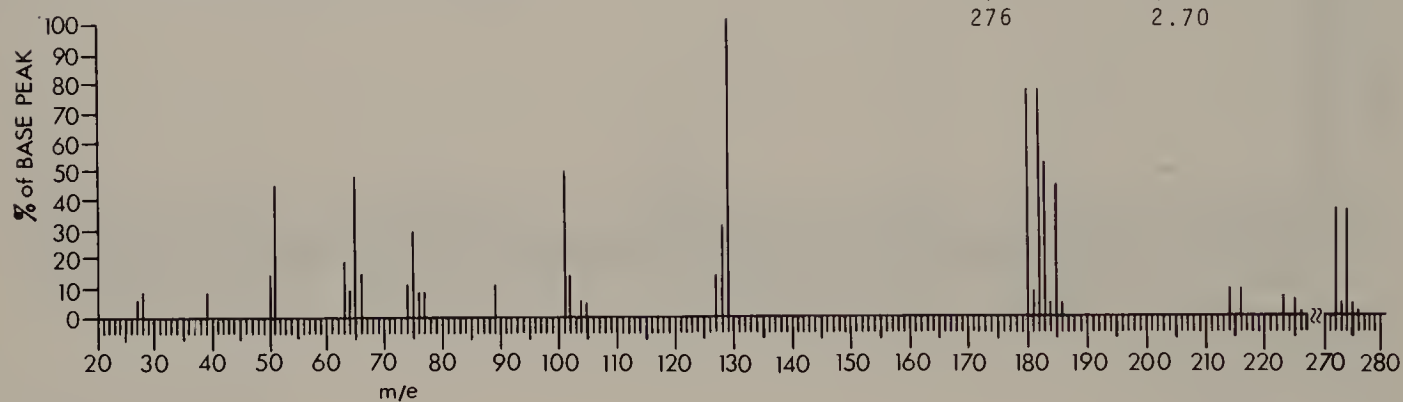




## Mass Spectral Data

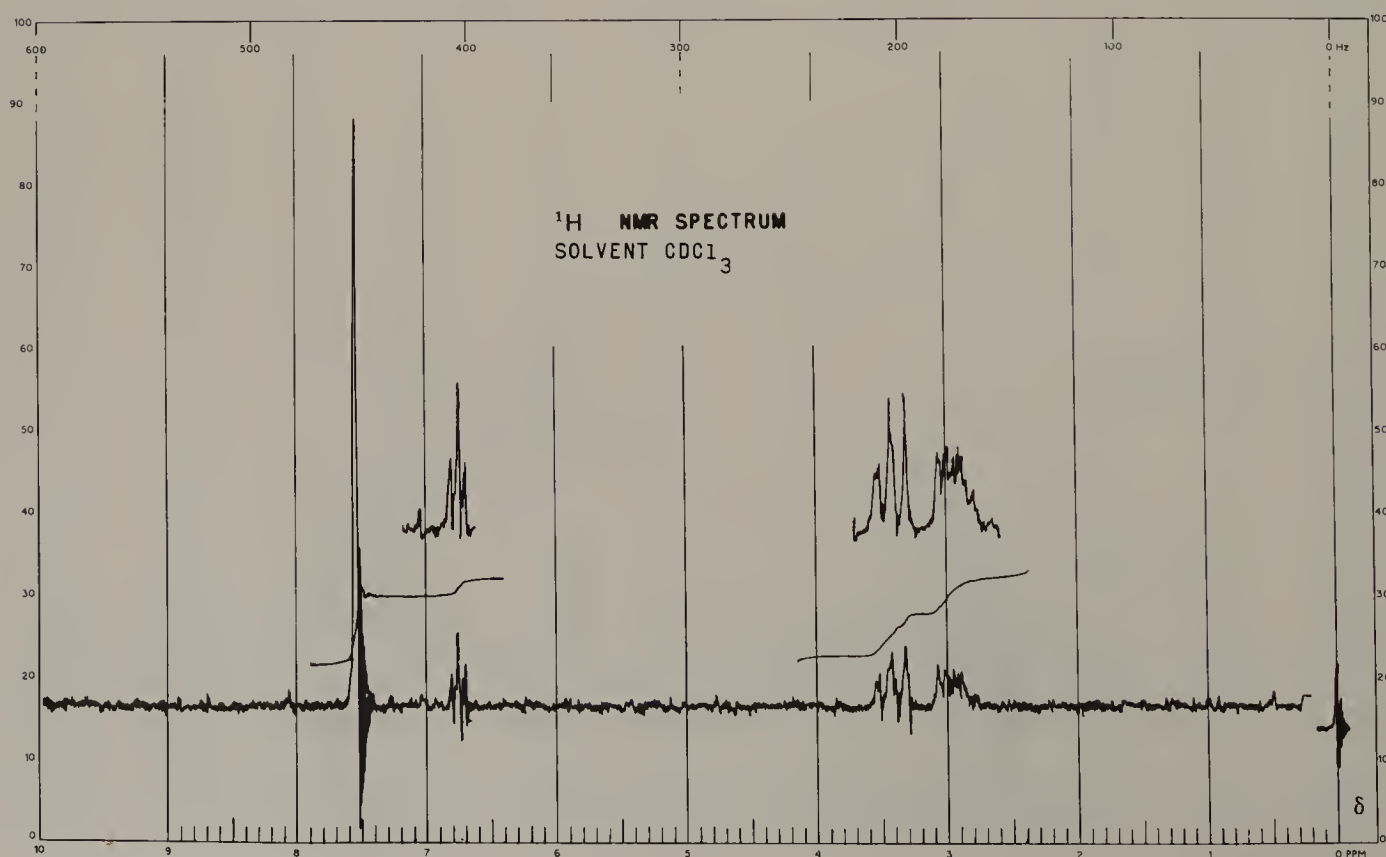
| m/e | Raw Intensity Data |
|-----|--------------------|
| 272 | 36.94              |
| 273 | 5.40               |
| 274 | 36.03              |
| 275 | 4.50               |
| 276 | 2.70               |

## MASS SPECTRAL DATA (Relative Intensity)



## Ultraviolet Data

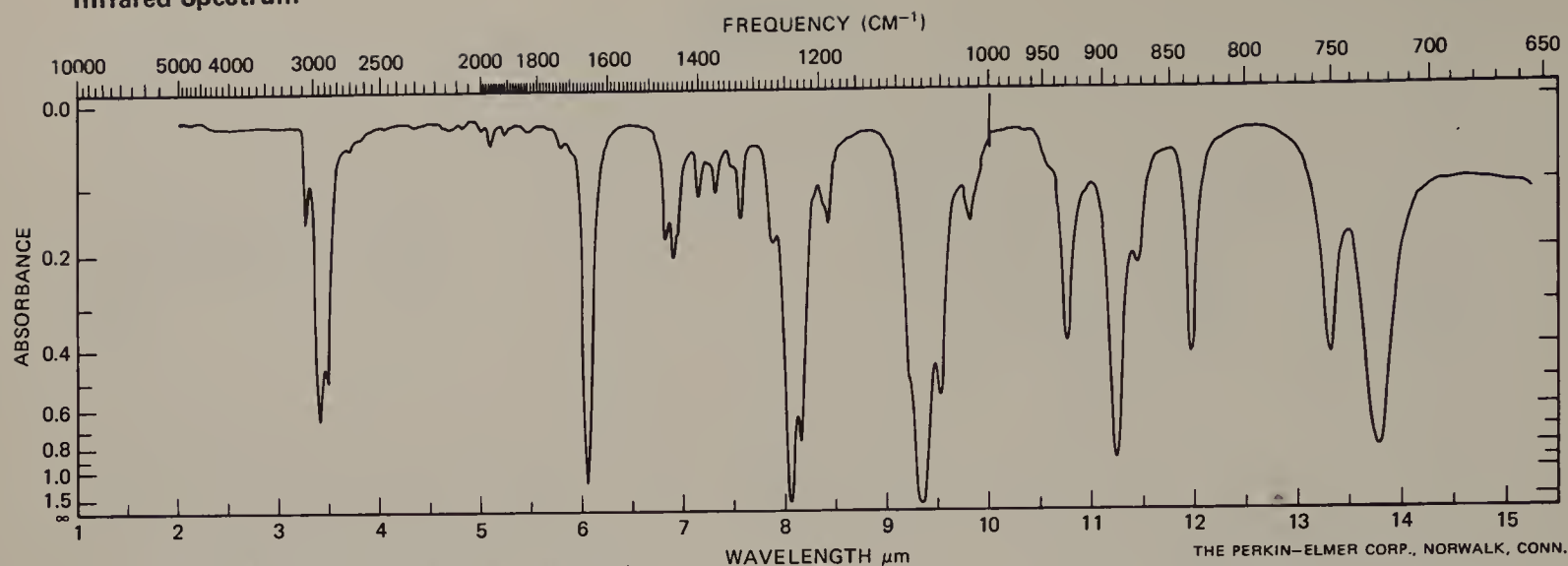
| $\lambda_{\max}$<br>(CH <sub>3</sub> OH) | $\epsilon_{\max}$ |
|--|-------------------|
| 255                                      | 21,800            |



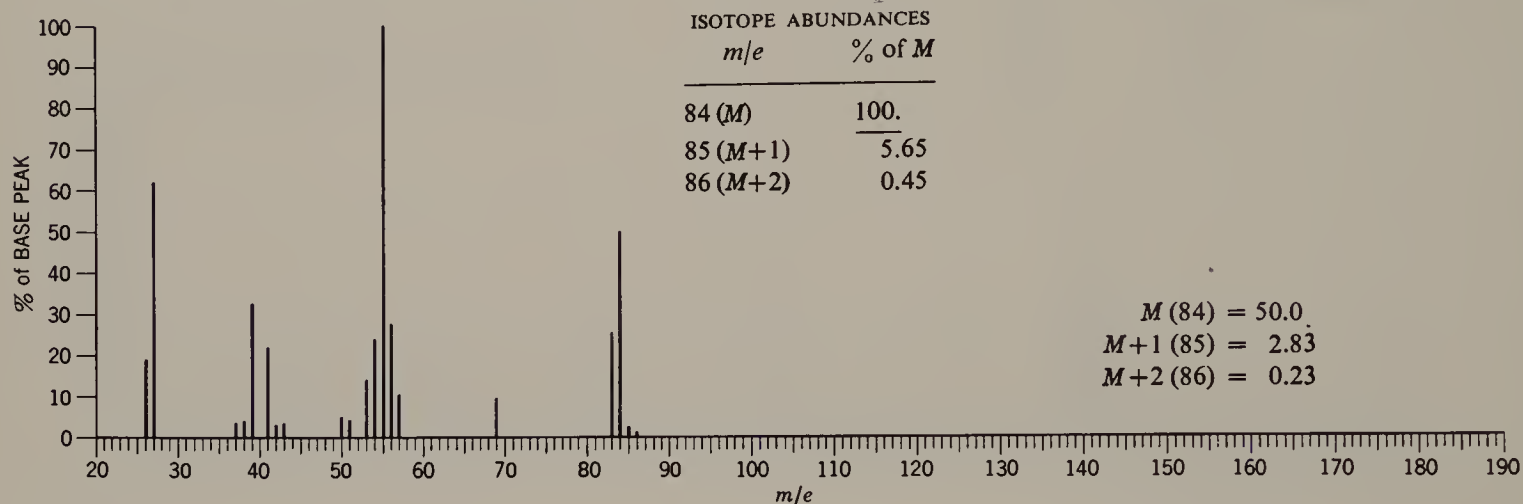
# notes



## Infrared Spectrum

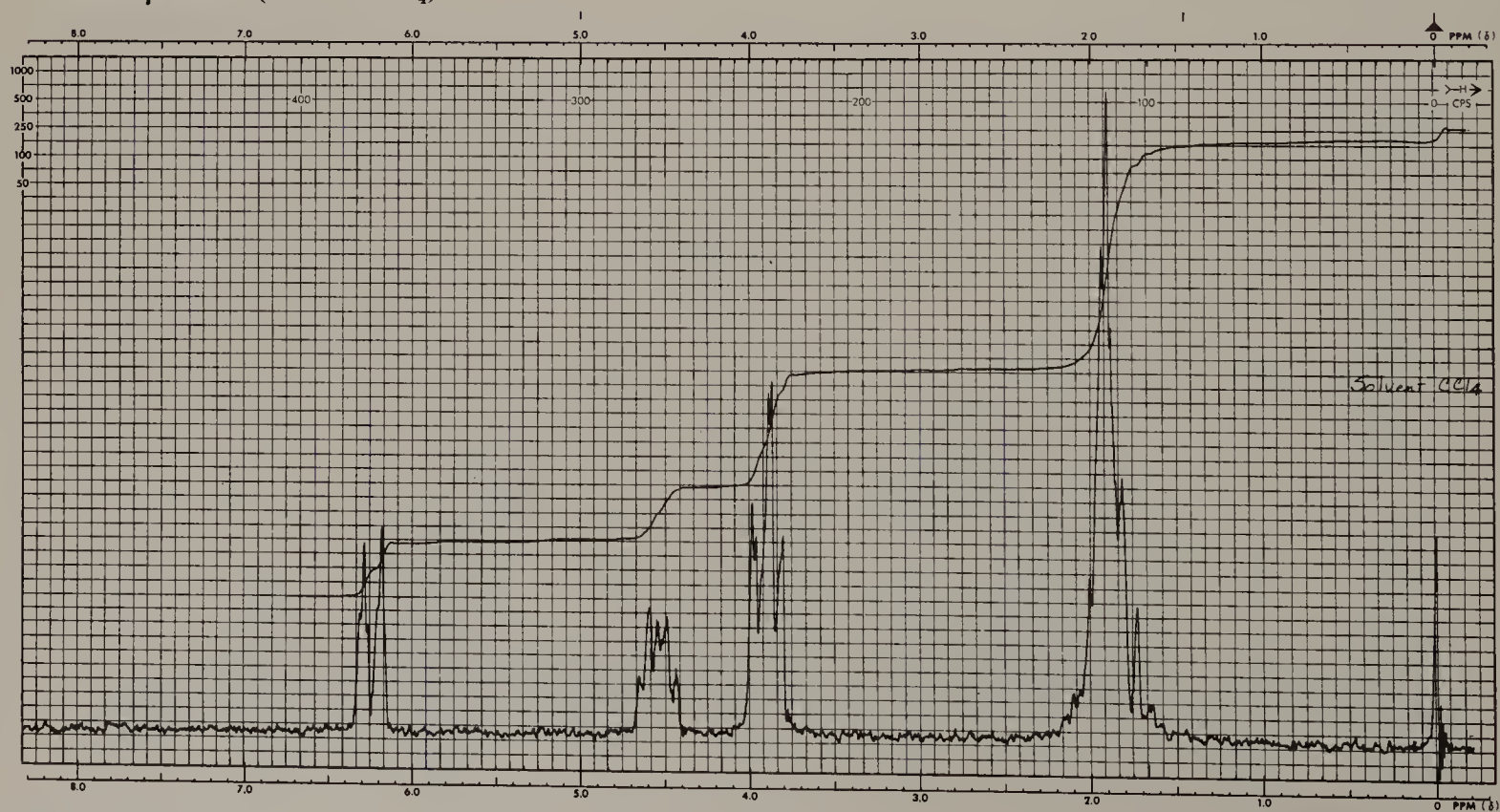


## Mass Spectral Data (Relative Intensities)

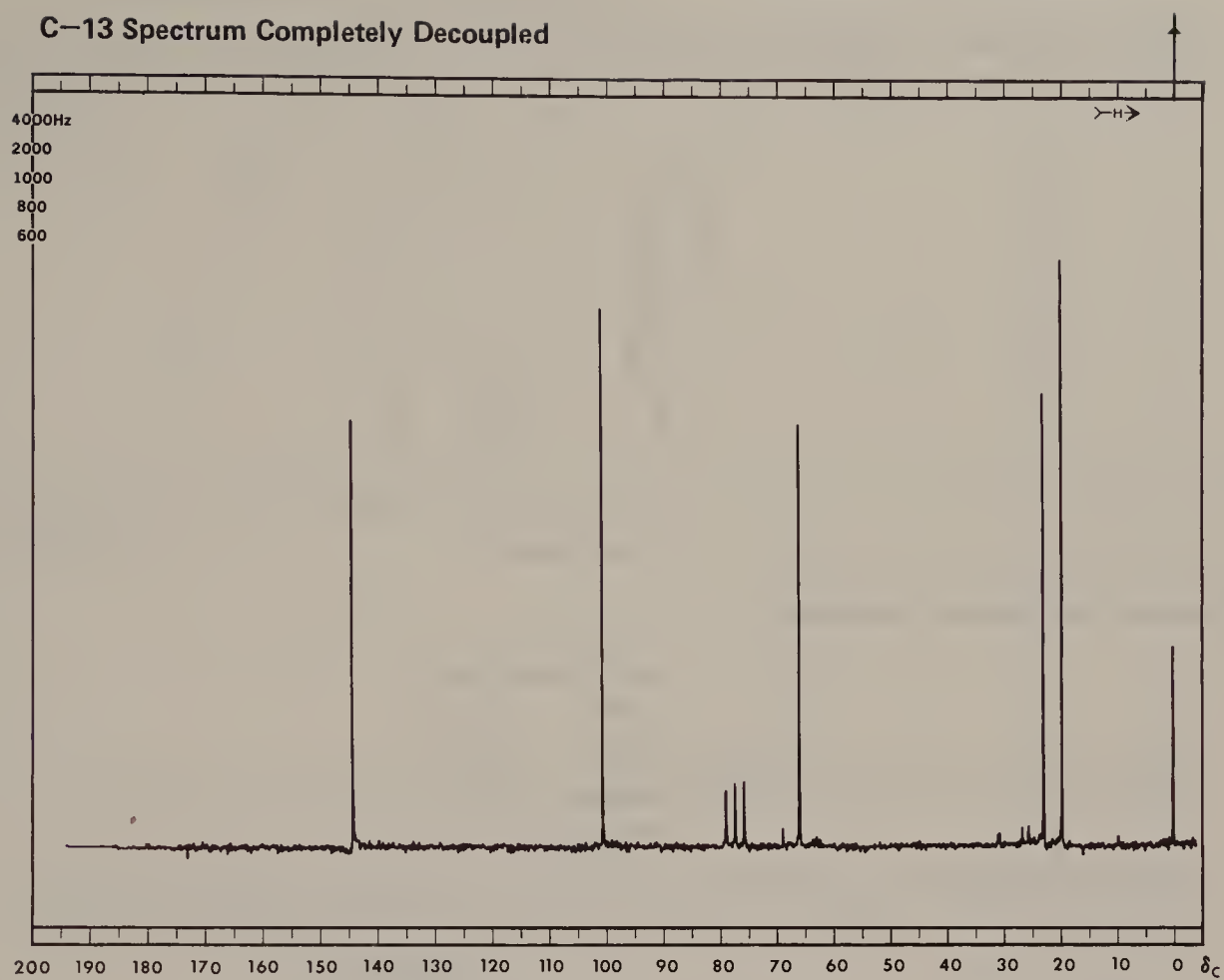


## Ultraviolet Data

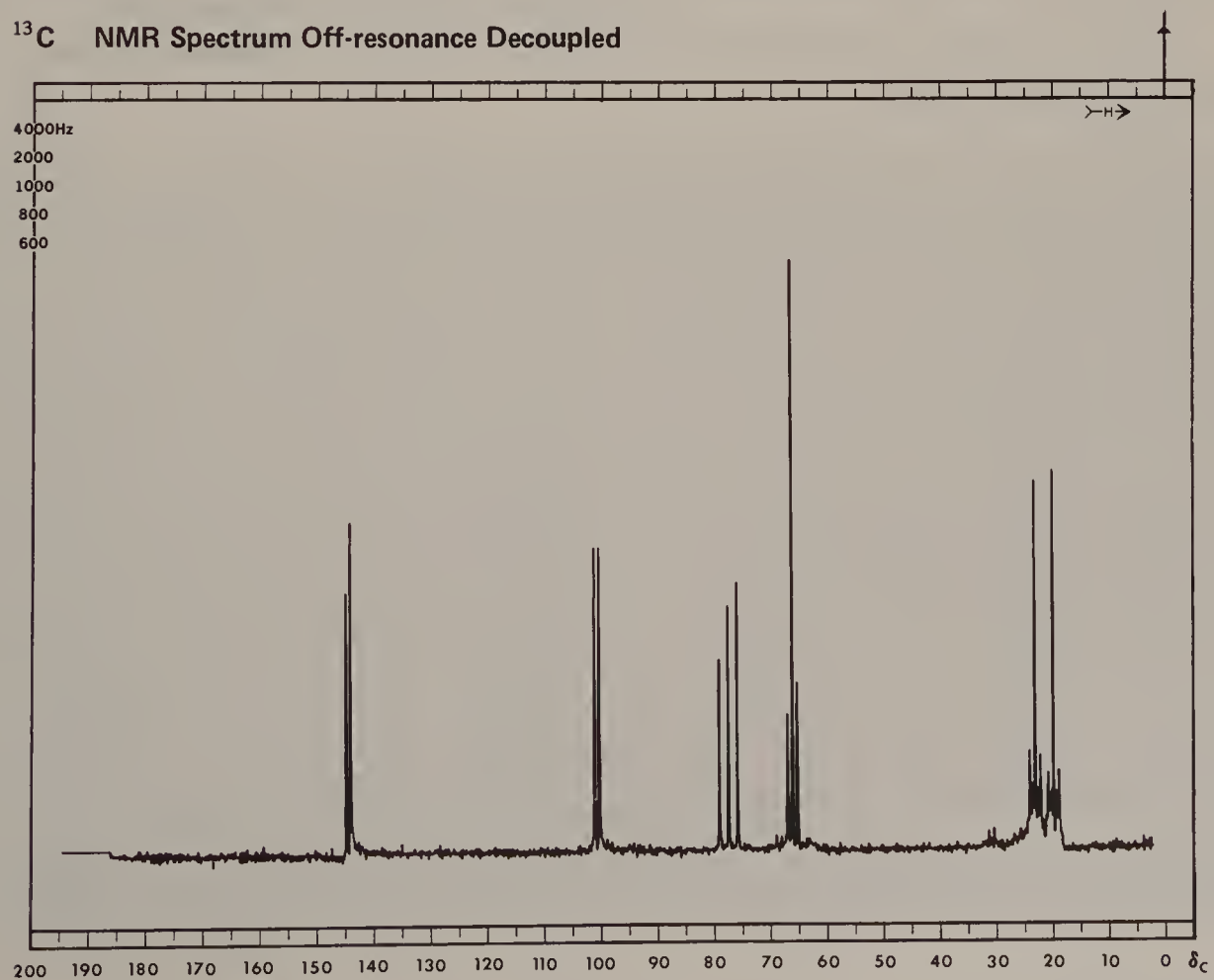
Transparent in  
near ultraviolet.  
(200–380 nm)

 $^1\text{H}$  NMR Spectrum (Solvent  $\text{CCl}_4$ )

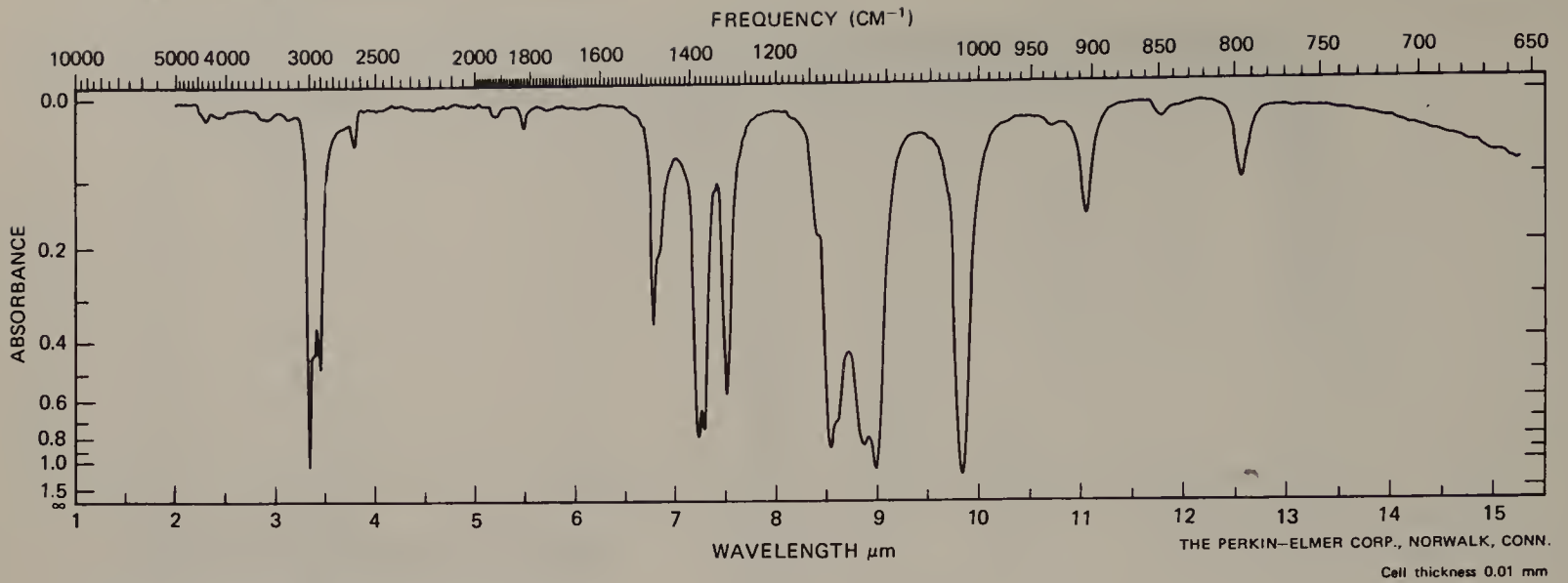
**C-13 Spectrum Completely Decoupled**



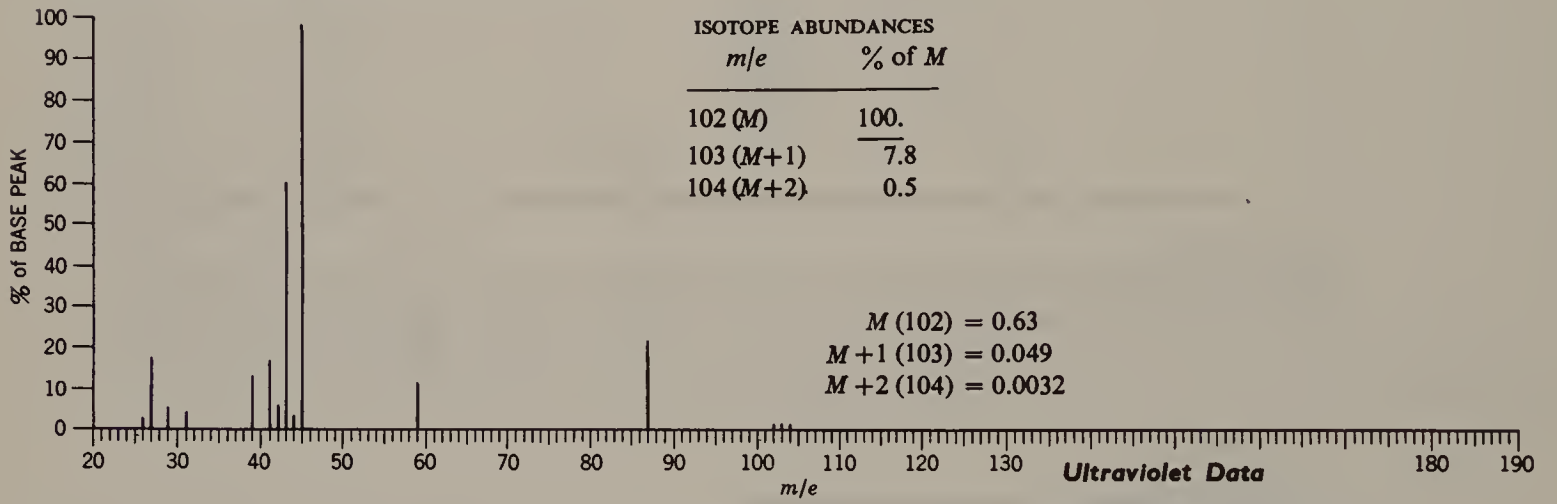
**<sup>13</sup>C NMR Spectrum Off-resonance Decoupled**



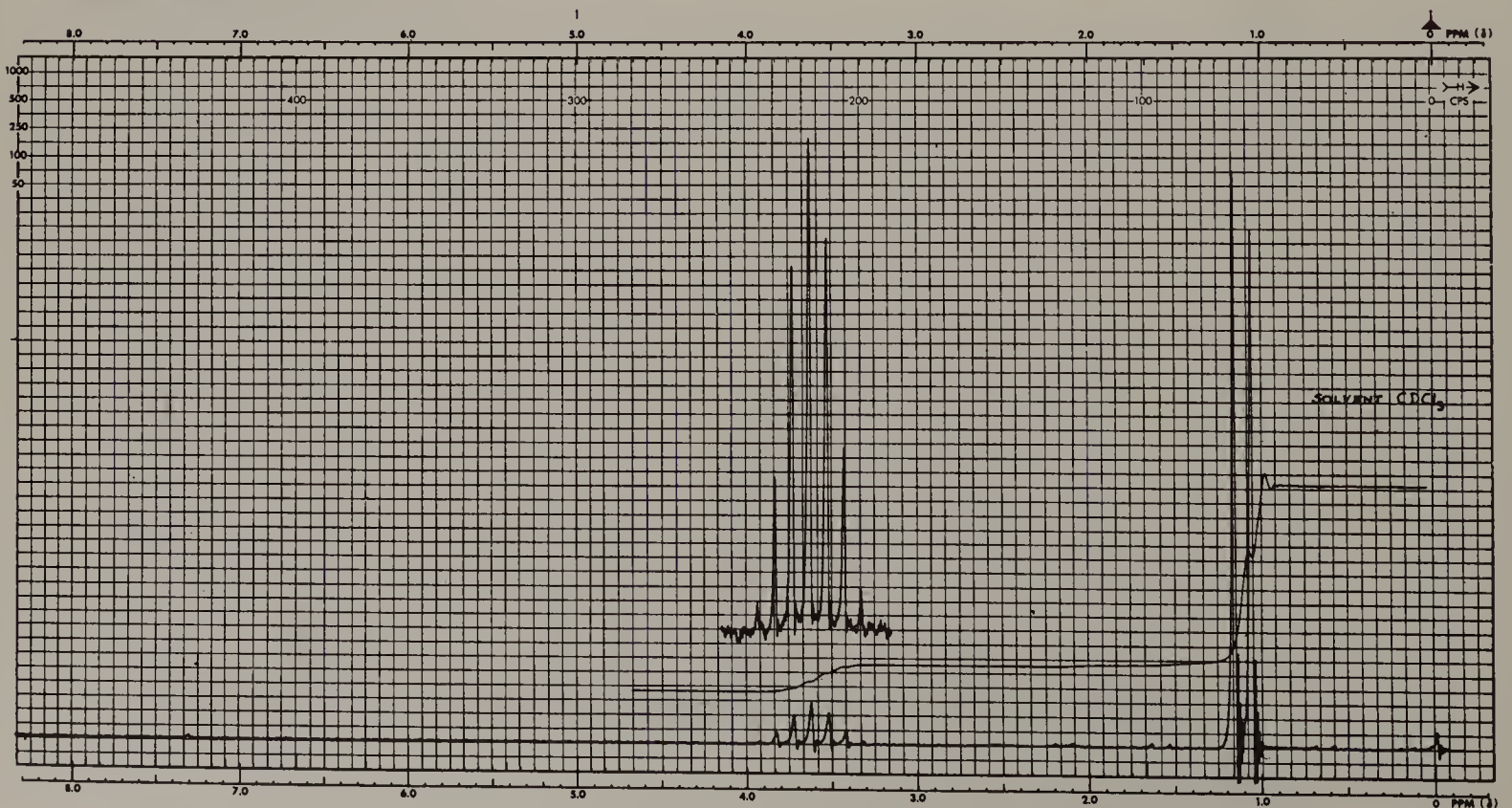
Infrared Spectrum



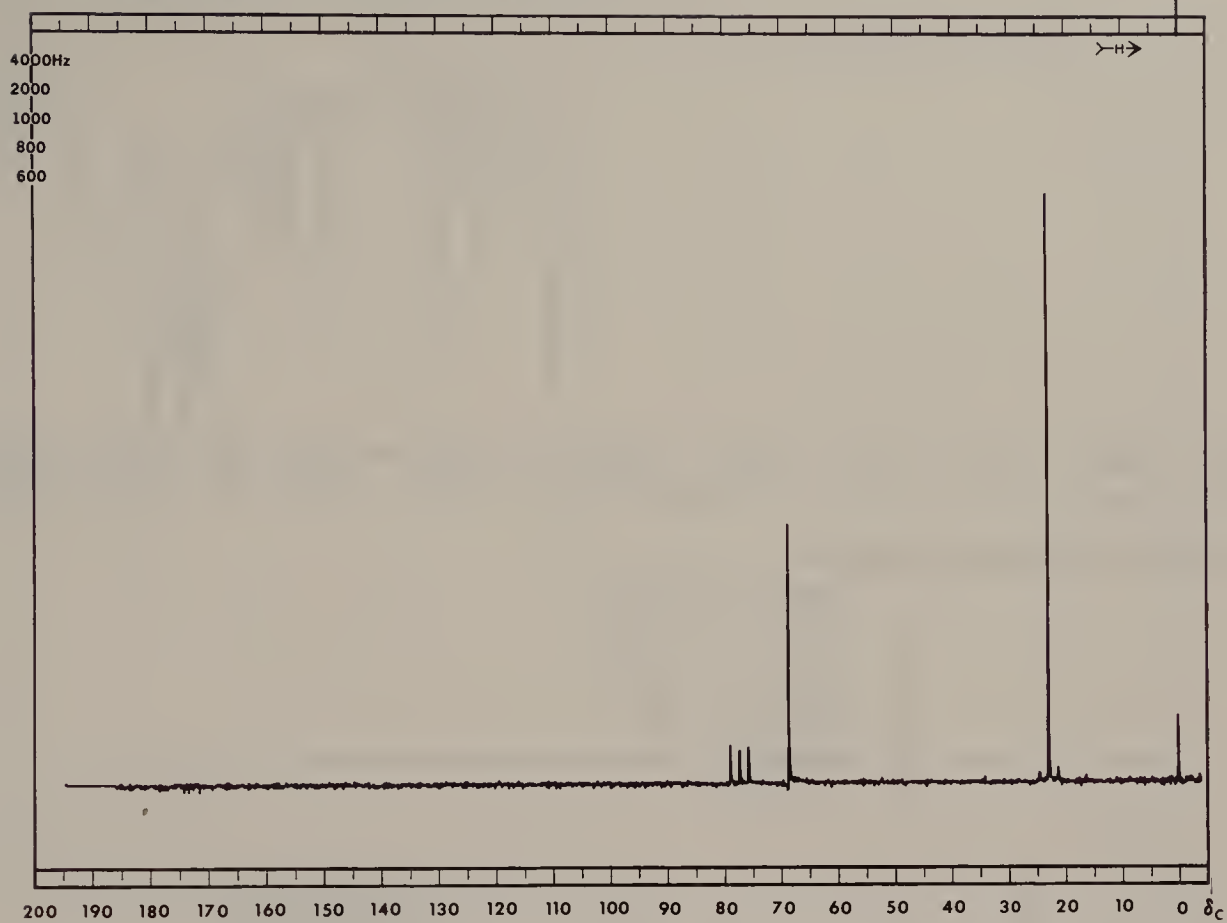
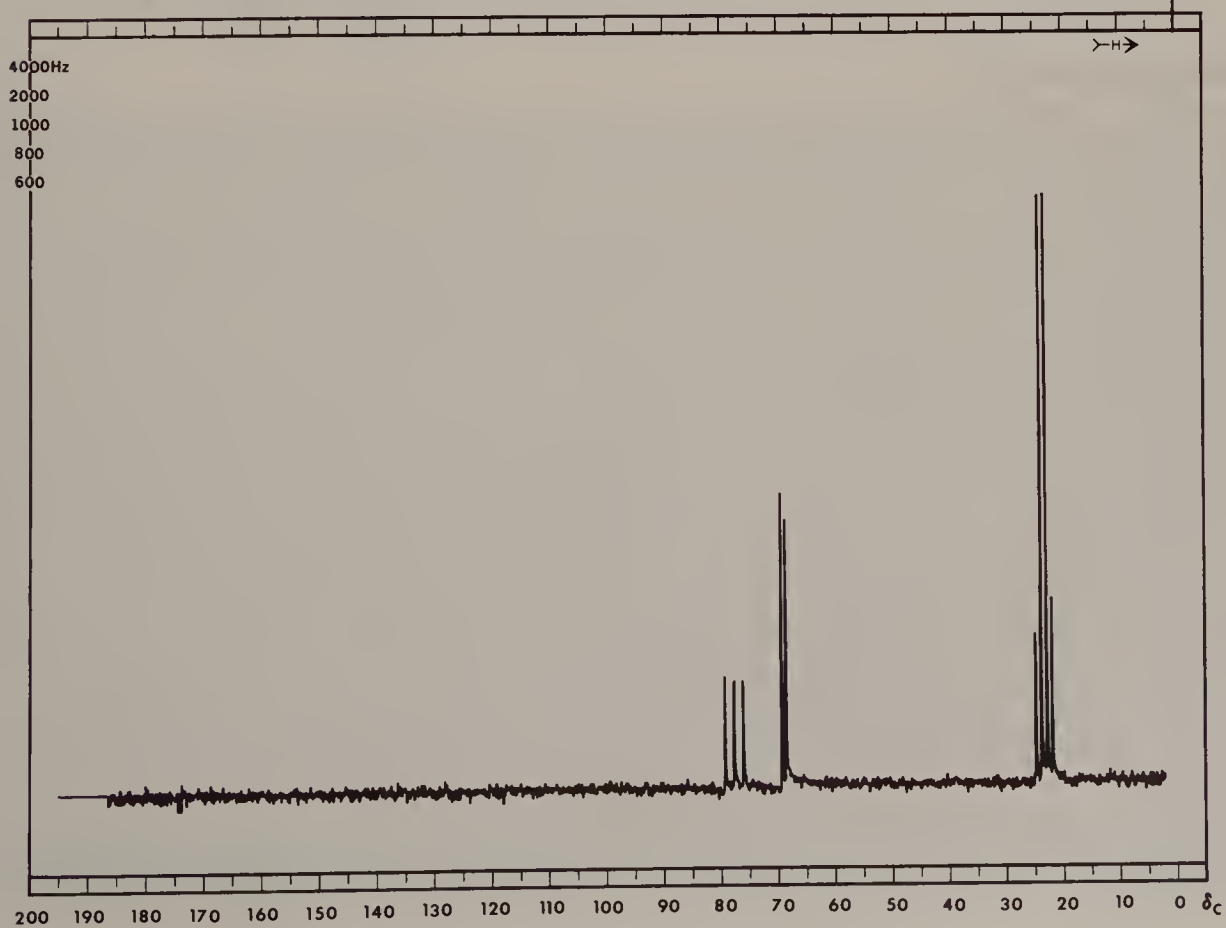
Mass Spectral Data (Relative Intensities)

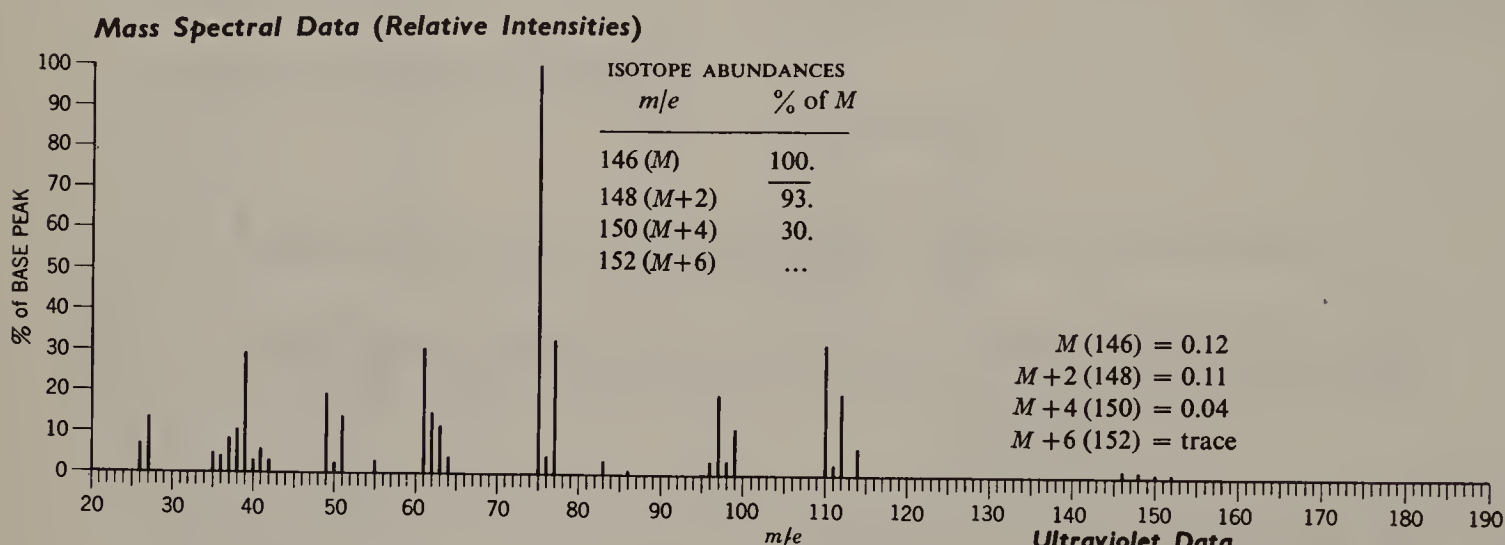
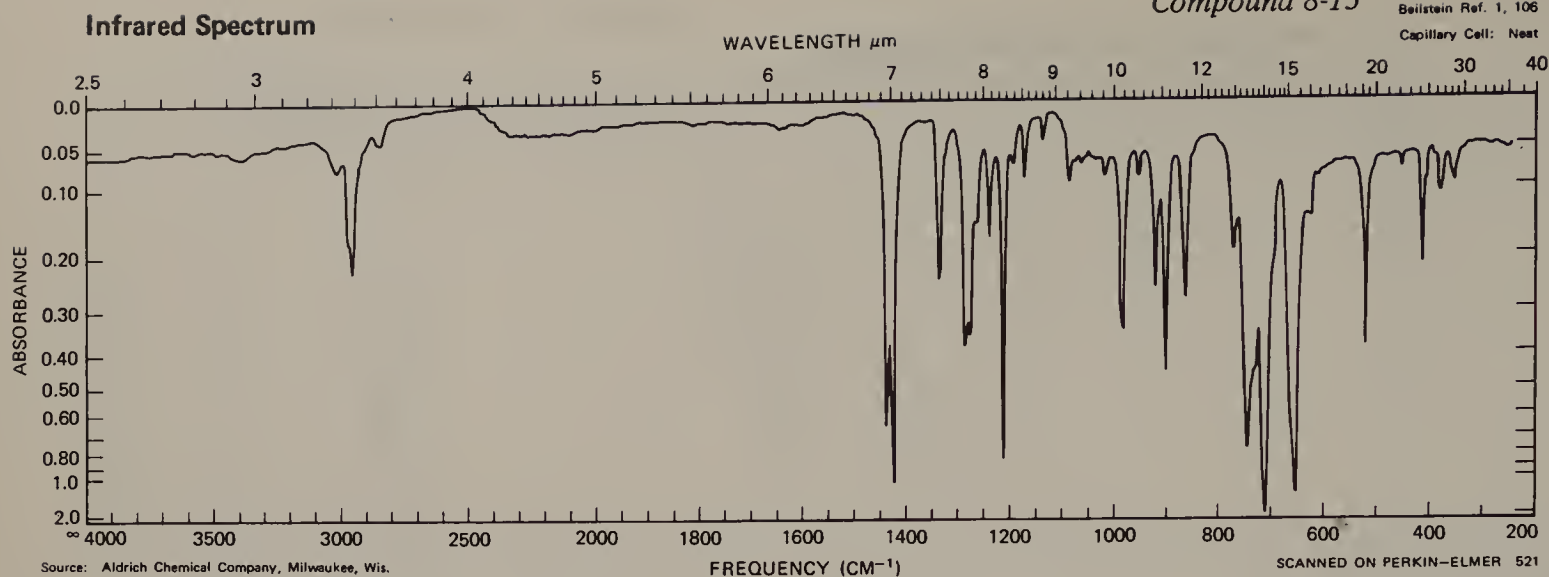


<sup>1</sup>H NMR Spectrum (Solvent CDCl<sub>3</sub>)

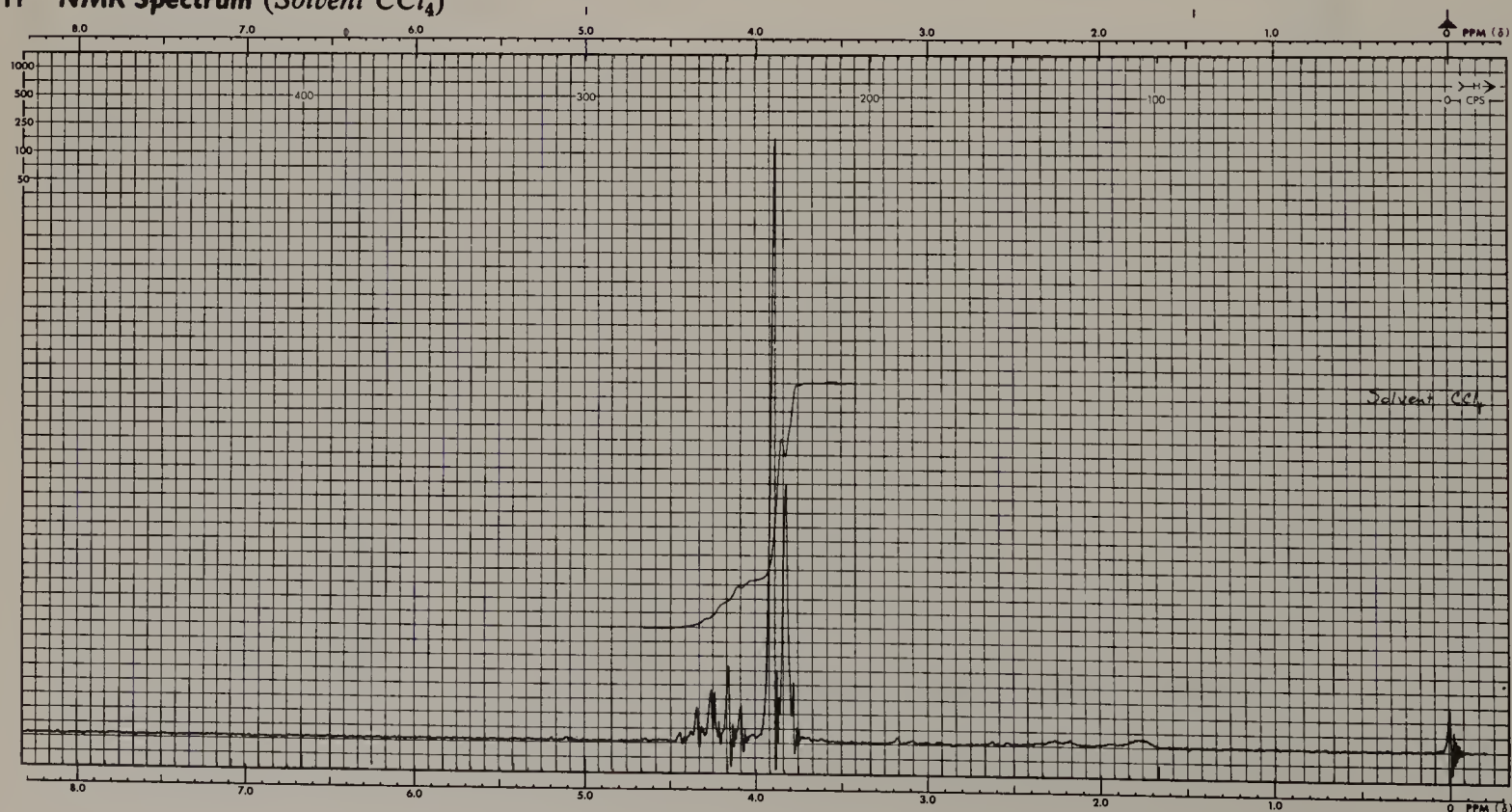




<sup>13</sup>C NMR Spectrum Completely Decoupled<sup>13</sup>C NMR Spectrum Off-resonance Decoupled

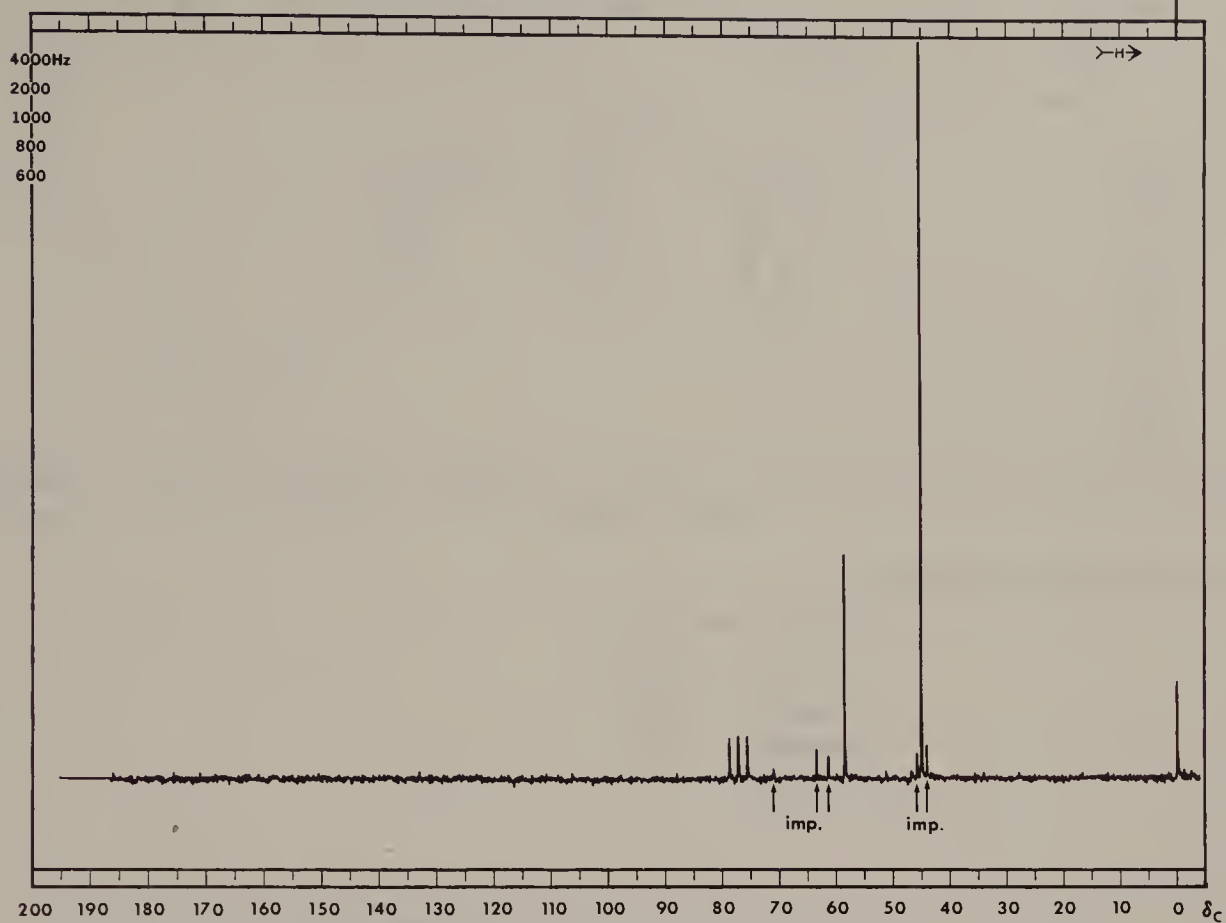
**Ultraviolet Data**

| $\lambda_{\text{max}}^{\text{EtOH}}$ | $\epsilon_{\text{max}}$ |
|--------------------------------------|-------------------------|
| 242                                  | 14.5                    |

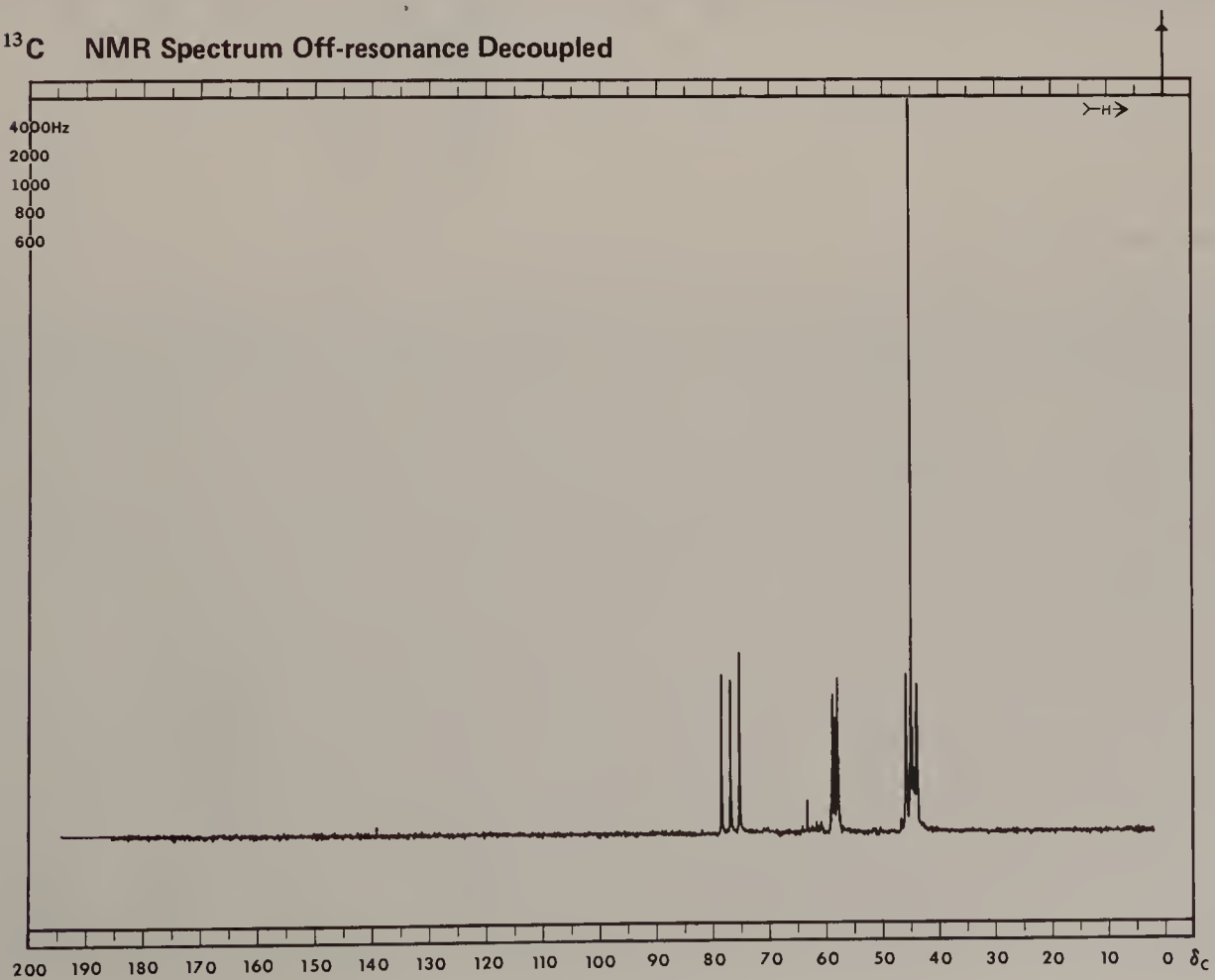
 **$^1\text{H}$  NMR Spectrum (Solvent  $\text{CCl}_4$ )**

<sup>13</sup>C NMR Spectrum Completely Decoupled

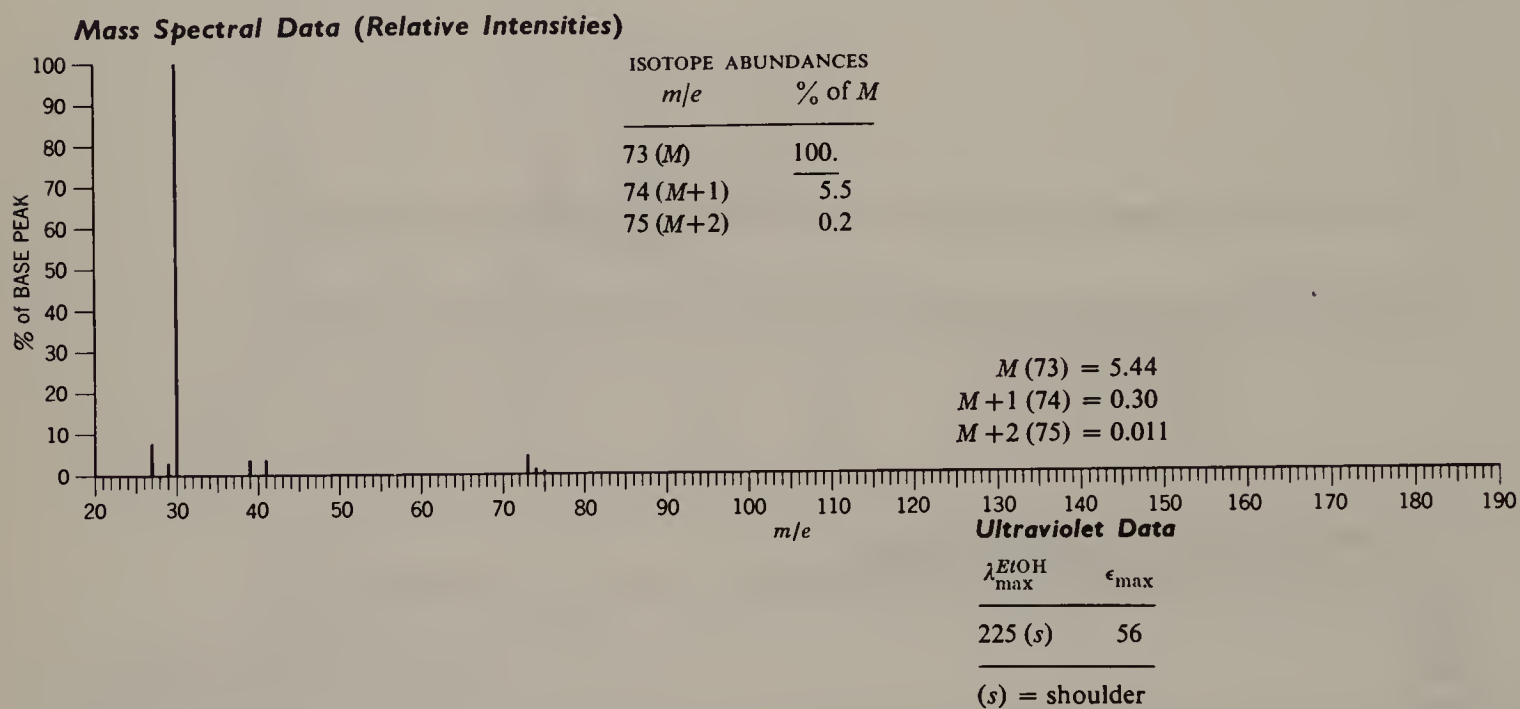
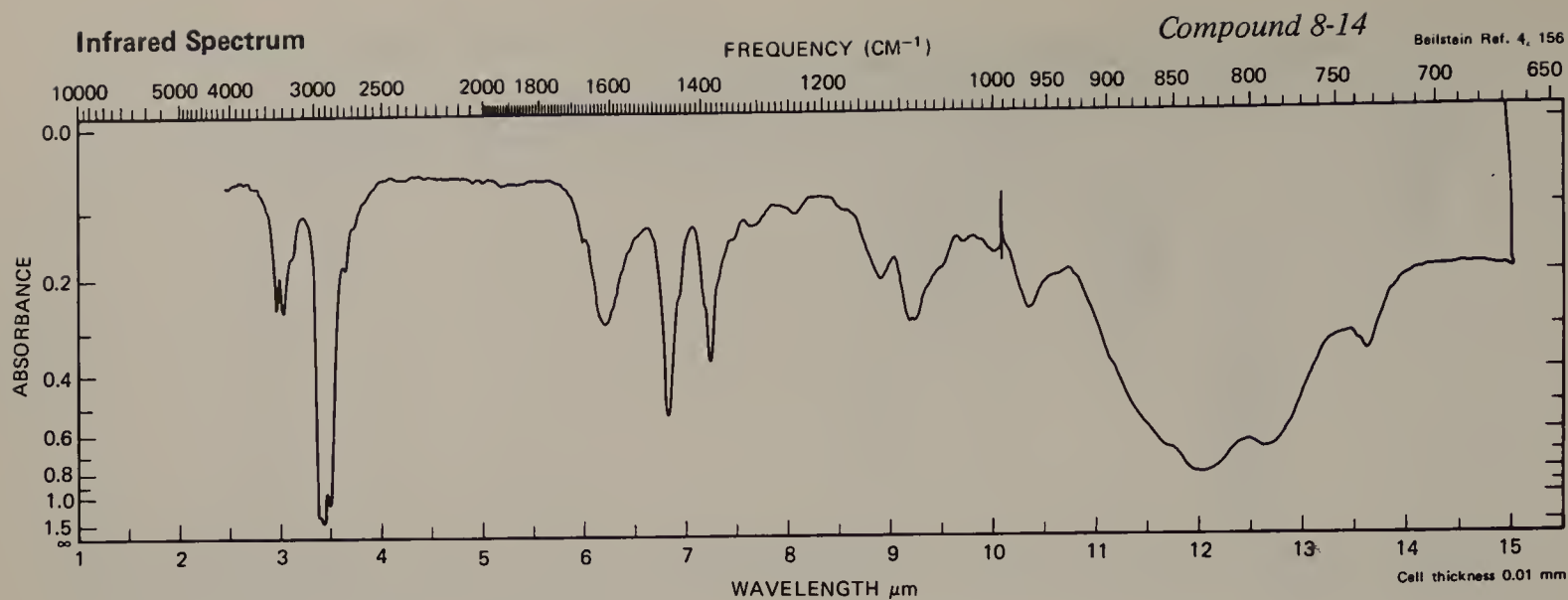
Compound 8-13 (Continued)



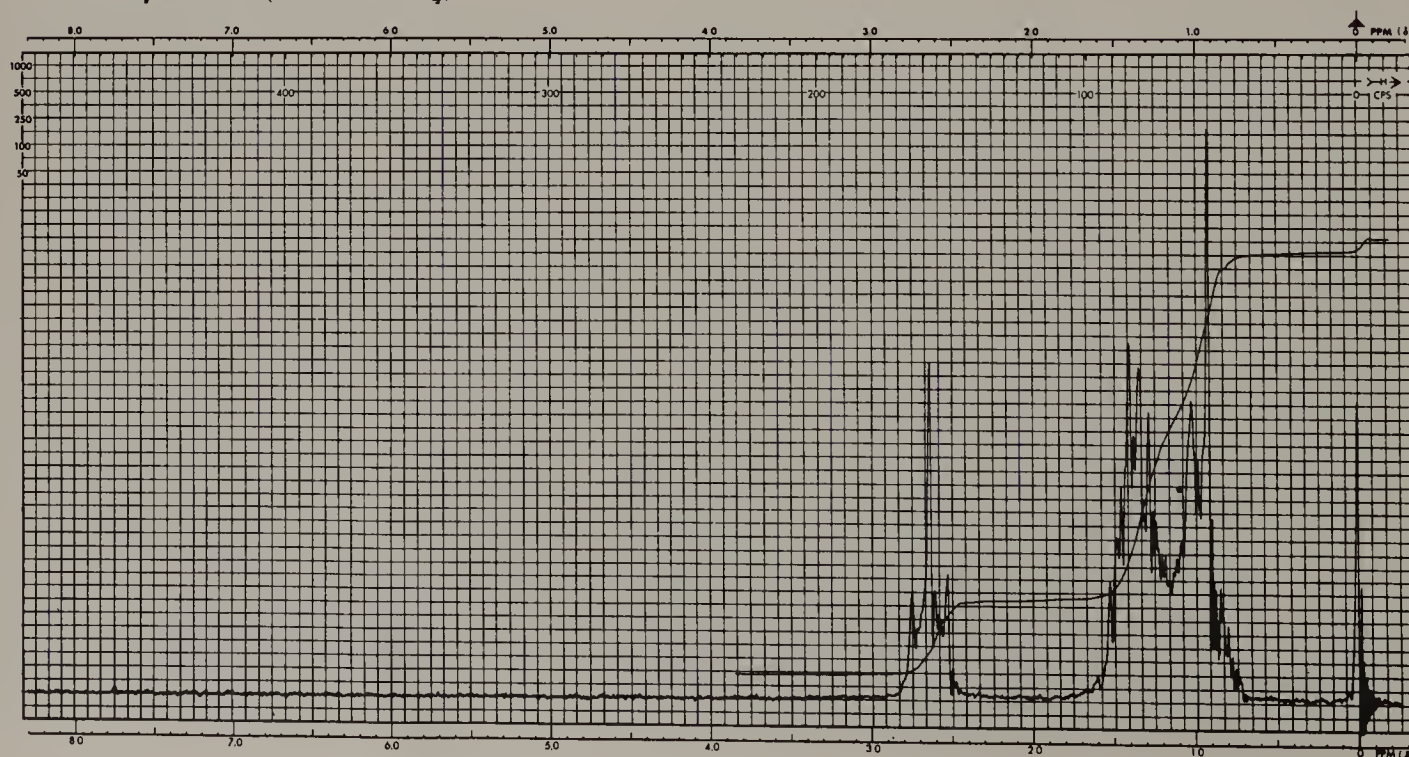
<sup>13</sup>C NMR Spectrum Off-resonance Decoupled





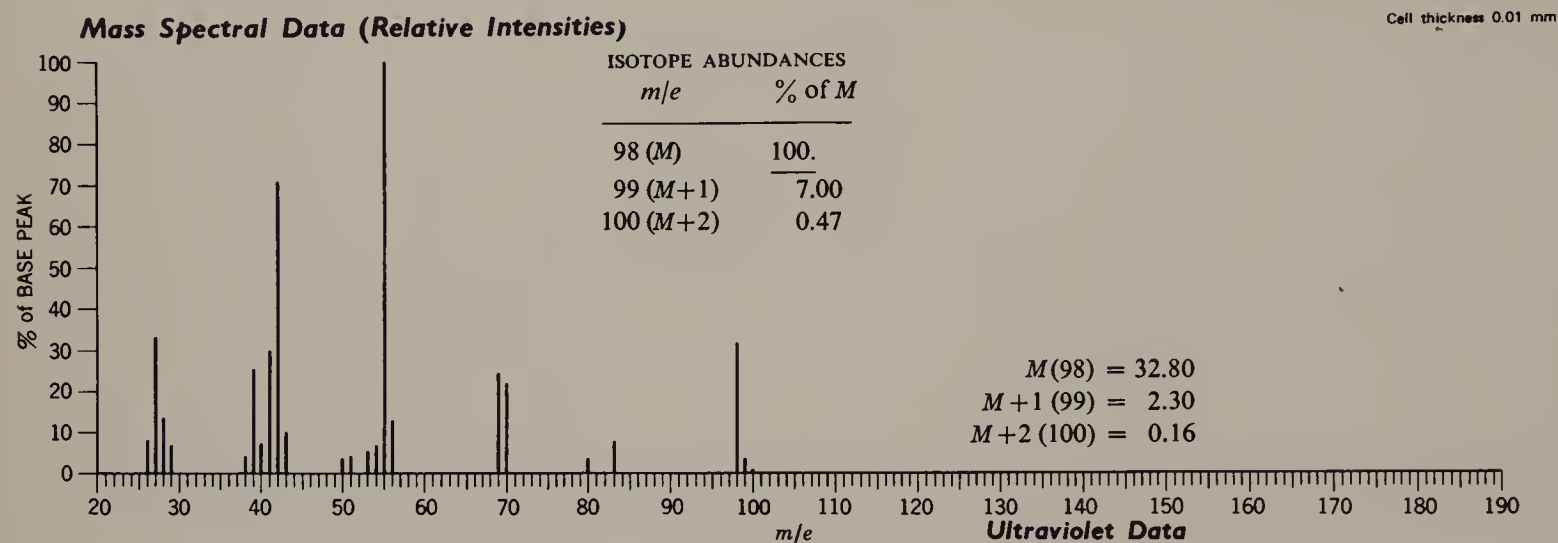
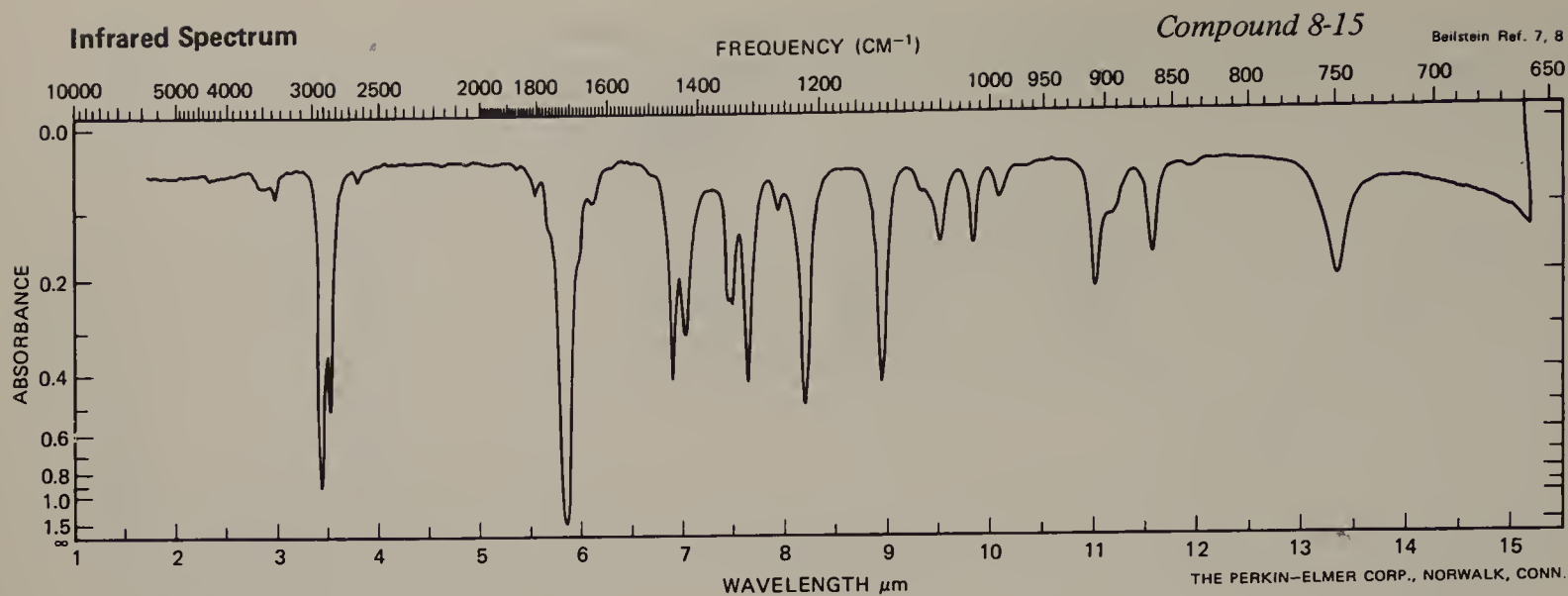


**<sup>1</sup>H NMR Spectrum (Solvent CCl<sub>4</sub>)**



Compound 8-14  $^{13}\text{C}$  NMR Data ( $\text{CDCl}_3$  solvent)

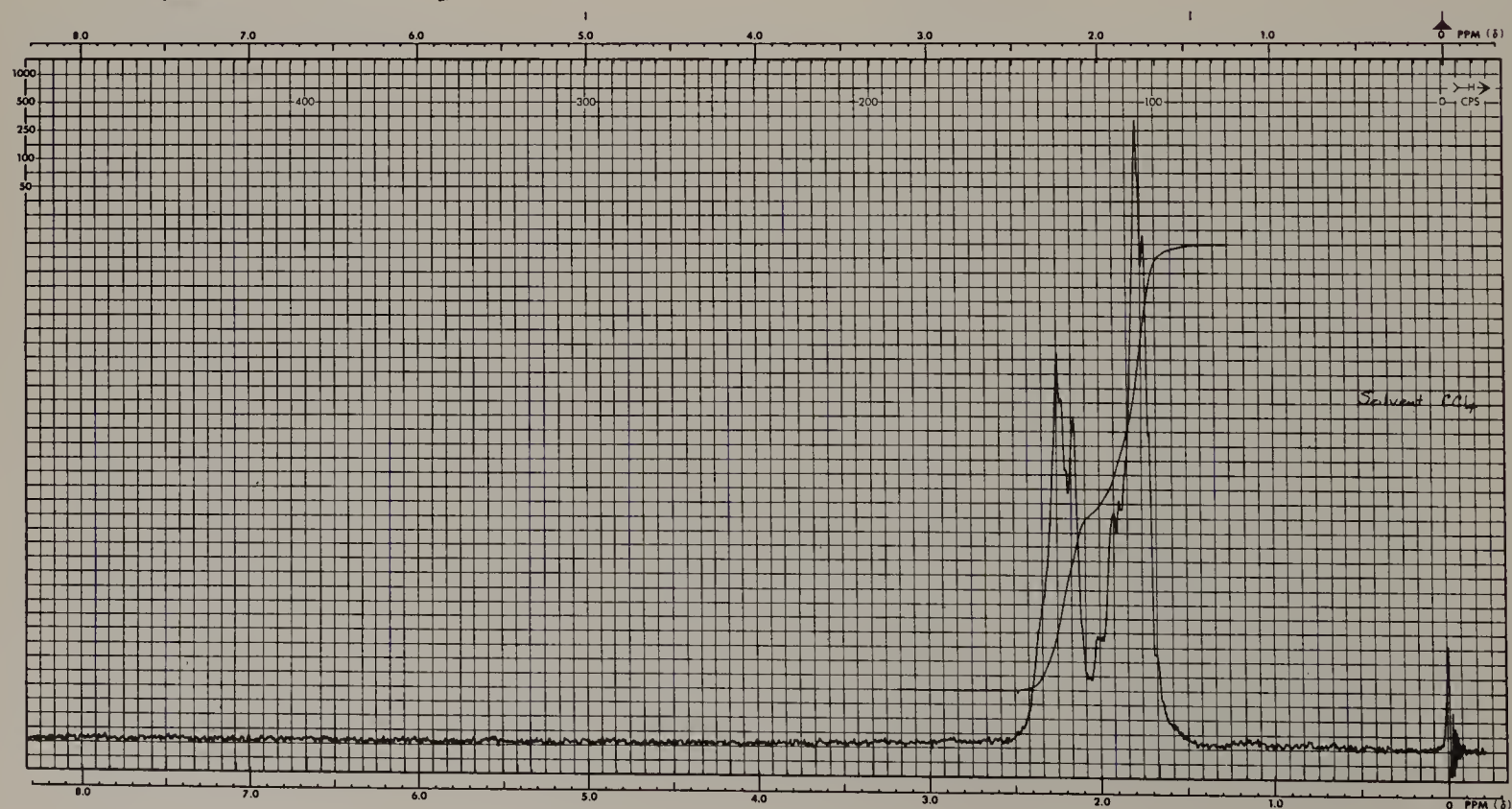
| $\delta$ | Intensity | Off-resonance<br>Decoupled<br>Multiplet |
|----------|-----------|---|
| 13.9     | 95.3      | <i>q</i>                                |
| 20.2     | 100.0     | <i>t</i>                                |
| 36.3     | 85.3      | <i>t</i>                                |
| 42.0     | 93.0      | <i>t</i>                                |



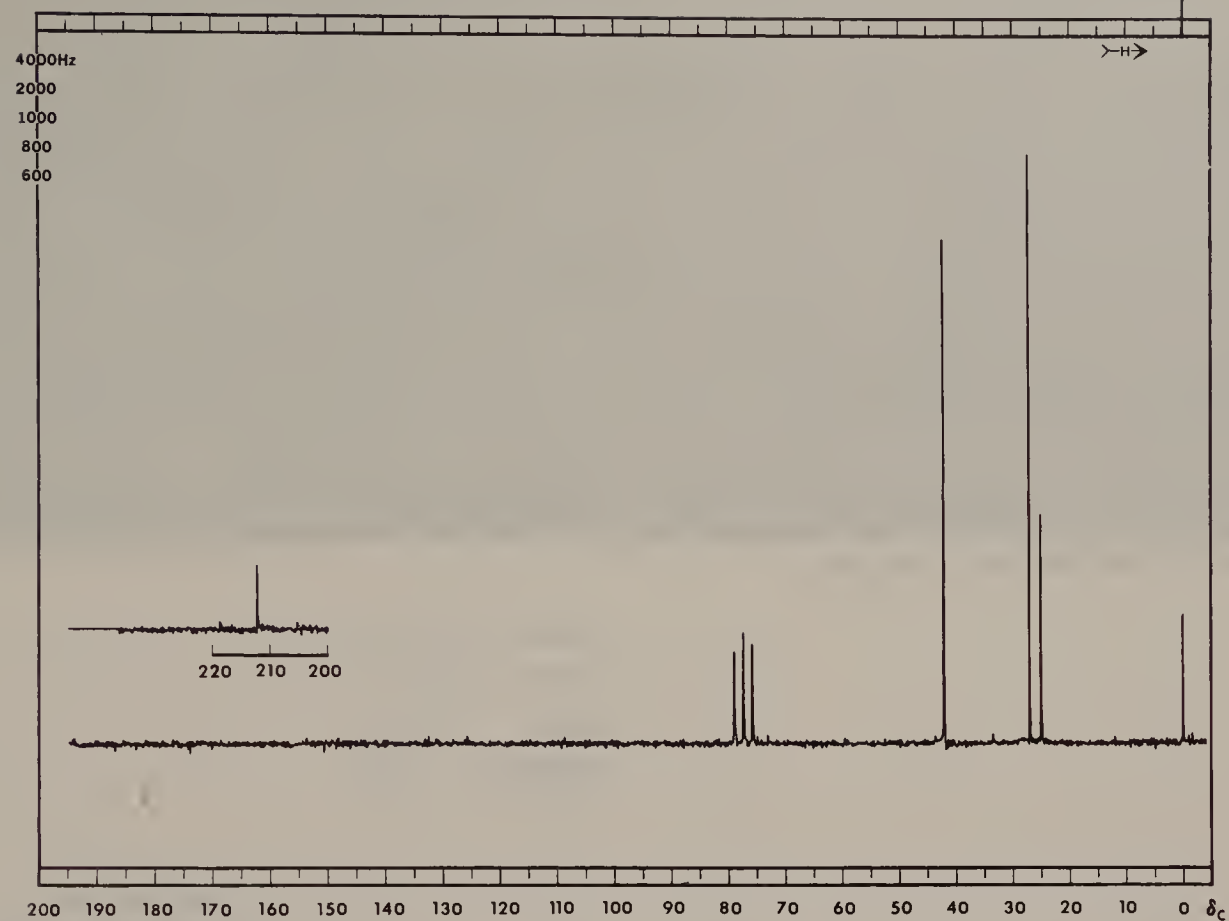
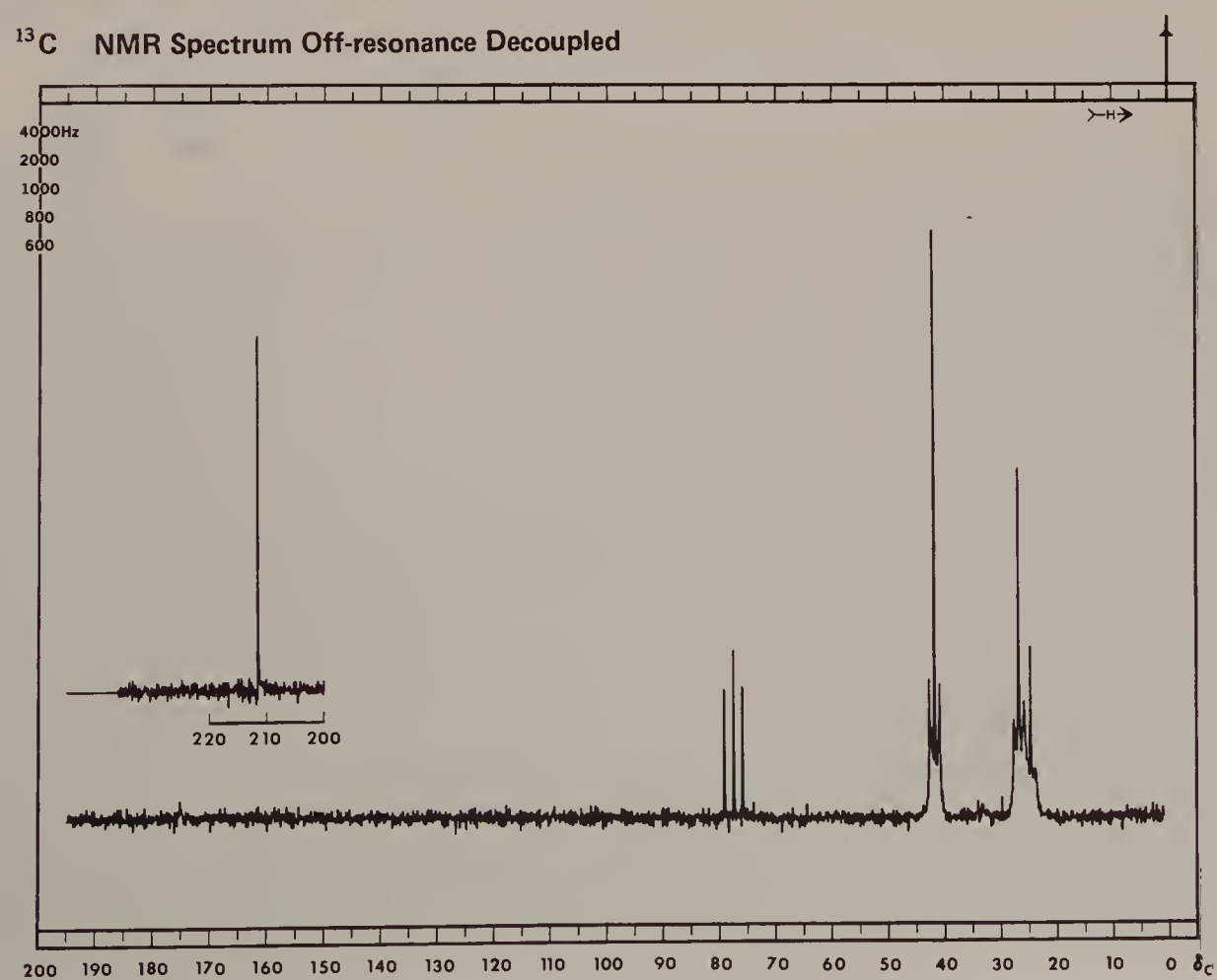
**Ultraviolet Data**

| $\lambda_{\text{max}}^{\text{EtOH}}$ | $\log \epsilon_{\text{max}}$ |
|--------------------------------------|------------------------------|
| 285                                  | 1.2                          |

**<sup>1</sup>H NMR Spectrum (Solvent CCl<sub>4</sub>)**



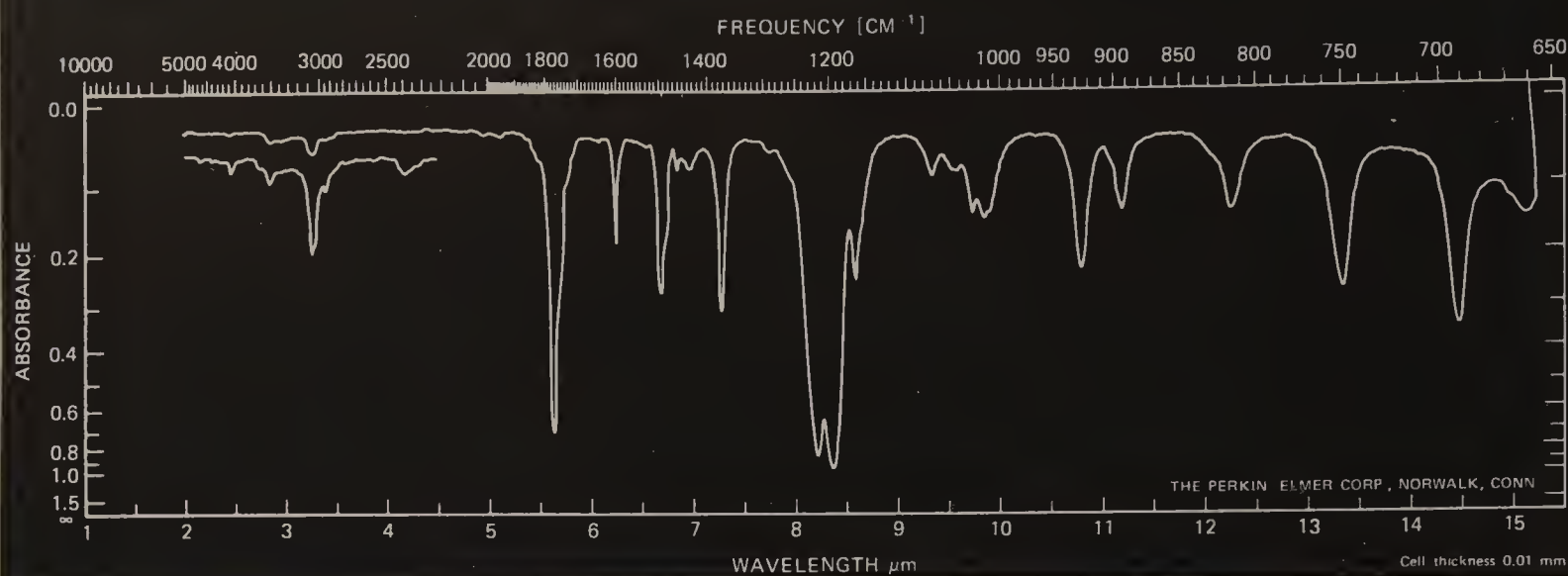


<sup>13</sup>C NMR Spectrum Completely Decoupled<sup>13</sup>C NMR Spectrum Off-resonance Decoupled

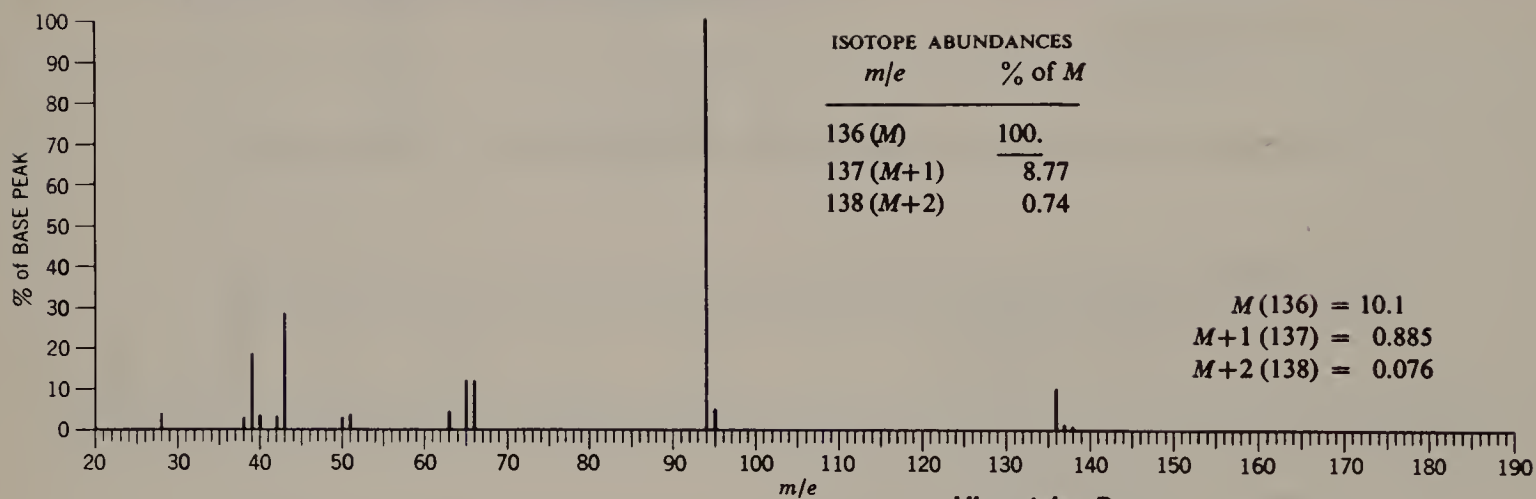
## Infrared Spectrum

Compound 8-16

Beilstein Ref. 6, 152

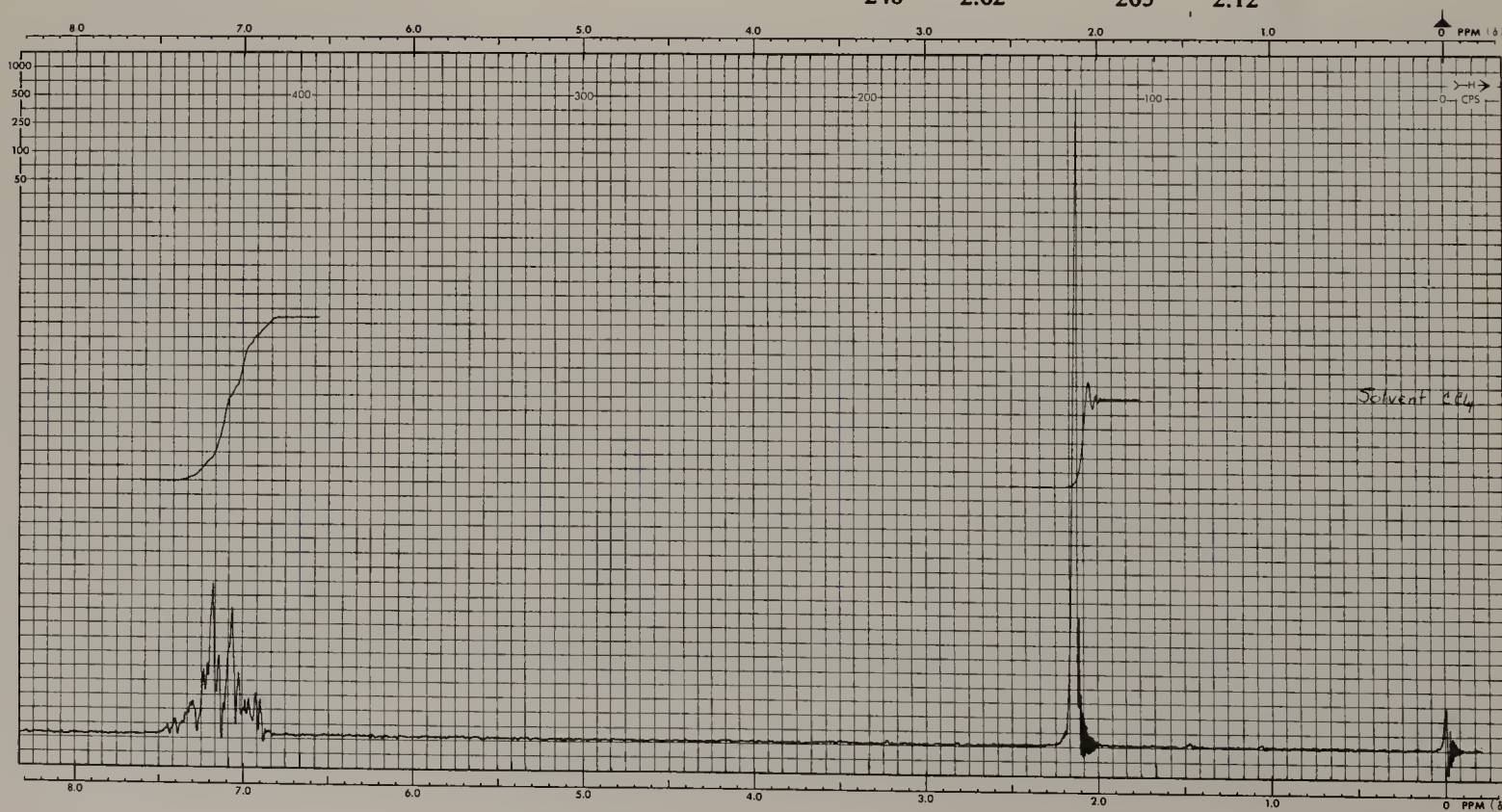


## Mass Spectral Data (Relative Intensities)



## Ultraviolet Data

| $\lambda_{\text{max}}^{\text{EtOH}}$ | $\log \epsilon_{\text{max}}$ |     |      |
|--------------------------------------|------------------------------|-----|------|
| 248                                  | 2.02                         | 253 | 2.15 |
|                                      |                              | 259 | 2.24 |
|                                      |                              | 265 | 2.12 |



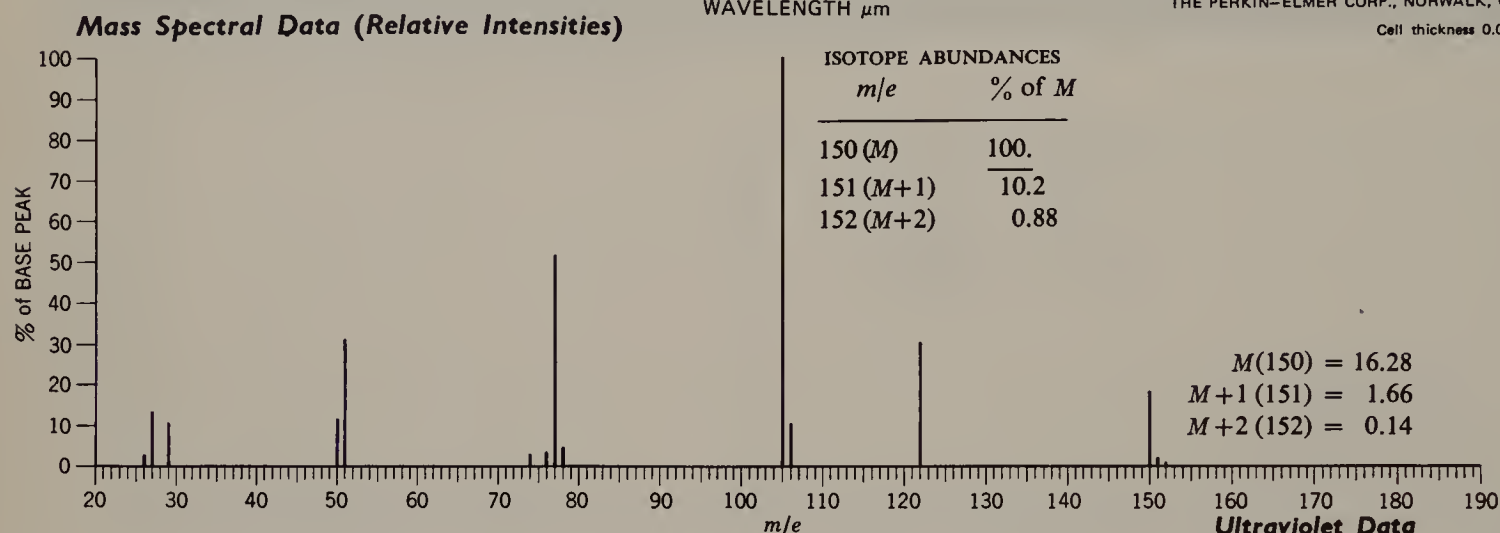
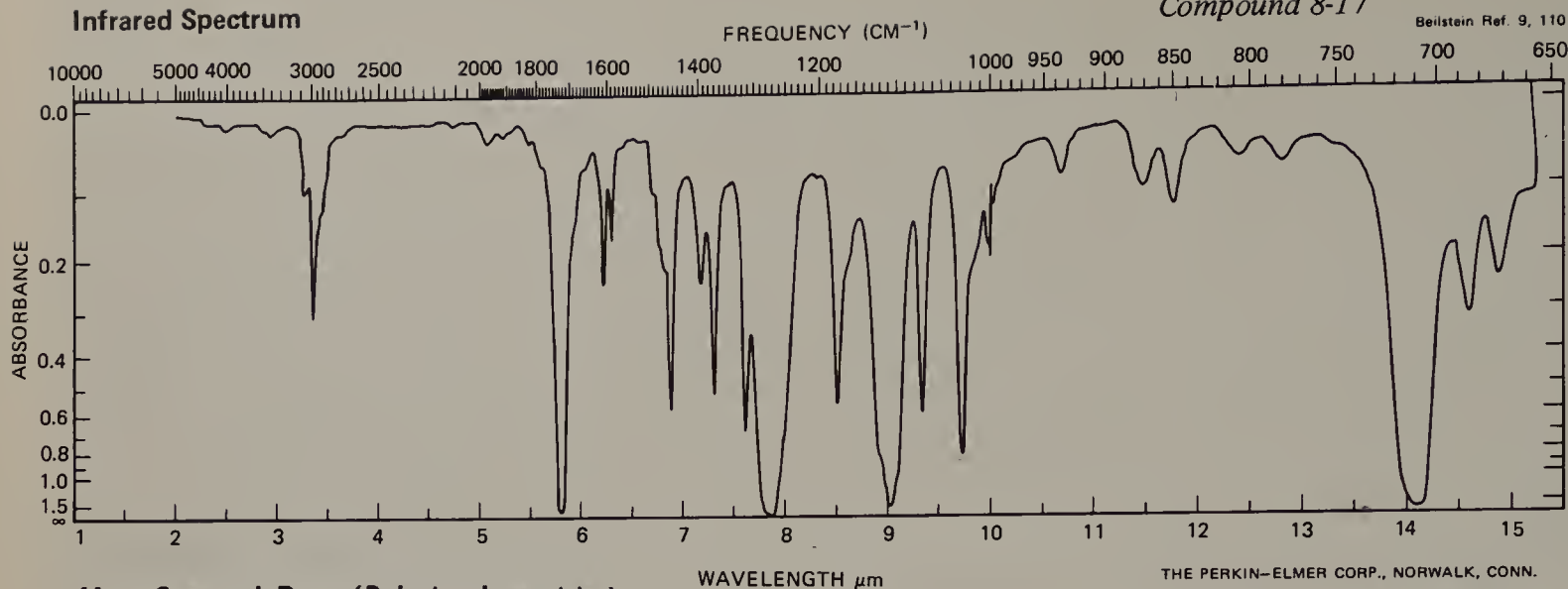
Compound 8-16 <sup>13</sup>C NMR Data (CDCl<sub>3</sub> solvent)

| $\delta$ | Intensity | Off-resonance<br>Decoupled<br>Multiplet |
|----------|-----------|---|
| 41.1     | 48.2      | <i>q</i>                                |
| 127.3    | 43.0      | <i>d</i>                                |
| 128.6    | 89.7      | <i>d</i>                                |
| 129.4    | 100.0     | <i>d</i>                                |
| 133.4    | 13.6      | <i>s</i>                                |
| 178.2    | 16.2      | <i>s</i>                                |



Compound 8-17

Beilstein Ref. 9, 110



**Ultraviolet Data**

| $\lambda_{\text{max}}^{\text{EtOH}}$ | $\log \epsilon_{\text{max}}$ |
|--------------------------------------|------------------------------|
| 229                                  | 4.08                         |
| 272                                  | 2.90                         |
| 280                                  | 2.85                         |

**<sup>1</sup>H NMR Spectrum (Solvent CDCl<sub>3</sub>)**

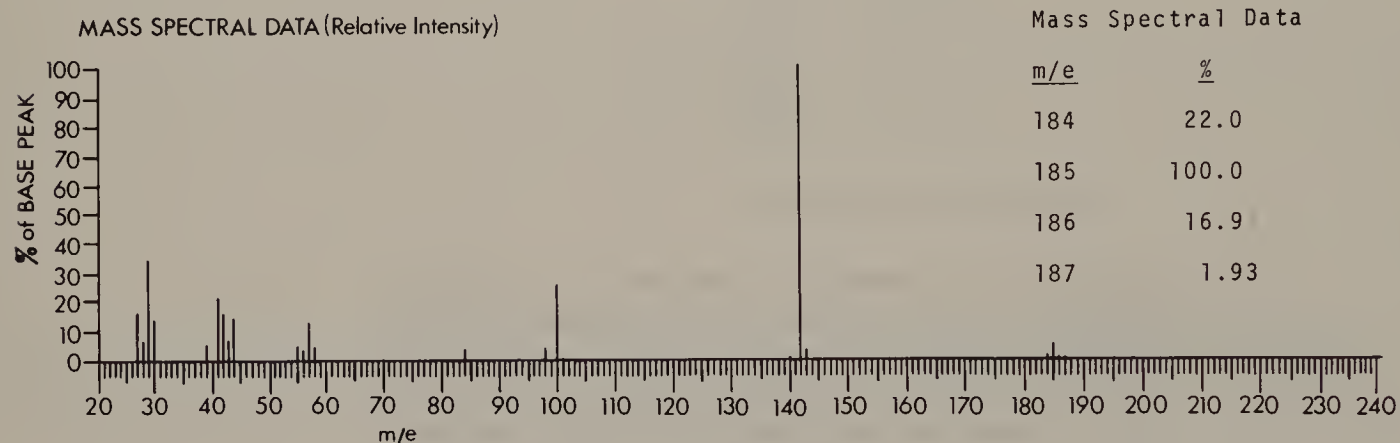
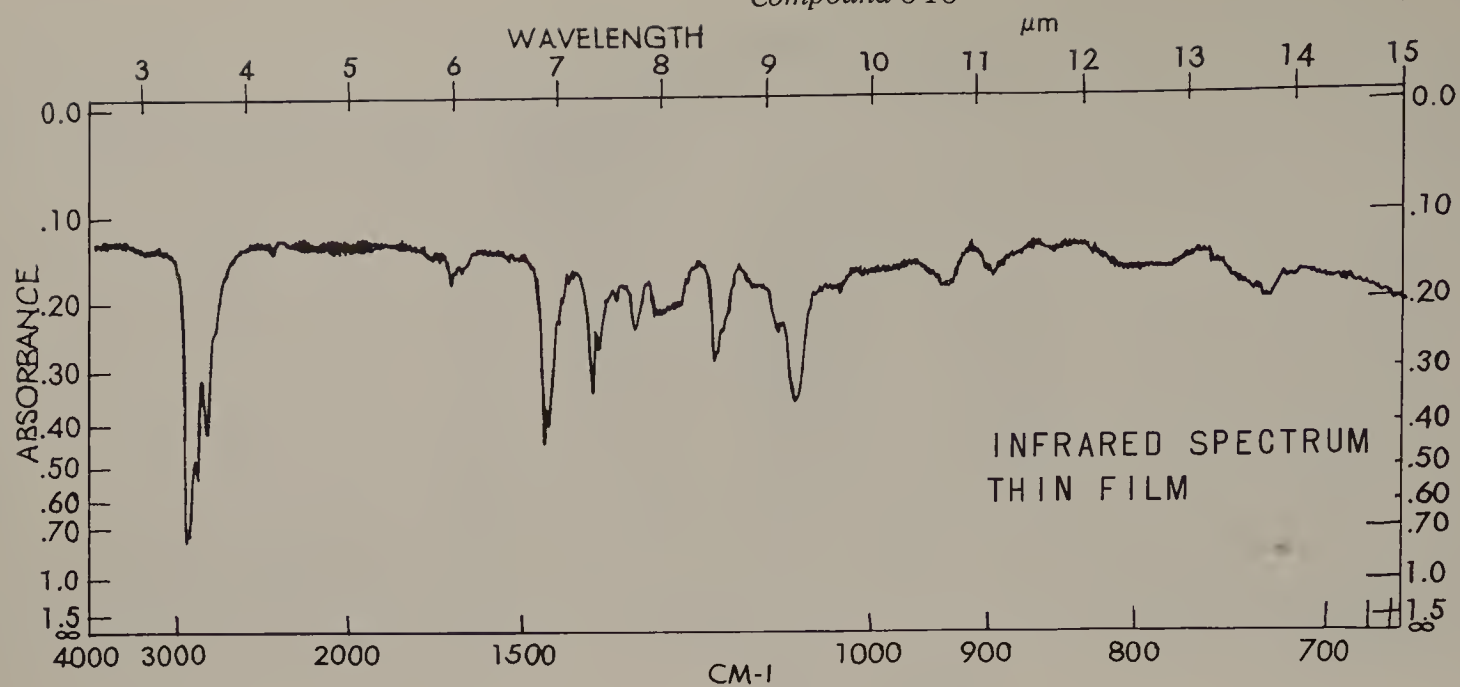


Compound 8-17  $^{13}\text{C}$  NMR Data ( $\text{CDCl}_3$  solvent)

| $\delta$ | Intensity | Off-resonance<br>Decoupled<br>Multiplet |
|----------|-----------|---|
| 14.4     | 47.0      | <i>q</i>                                |
| 60.8     | 39.7      | <i>t</i>                                |
| 128.4    | 87.0      | <i>d</i>                                |
| 129.7    | 100.0     | <i>d</i>                                |
| 130.9    | 8.7       | <i>s</i>                                |
| 132.8    | 50.2      | <i>d</i>                                |
| 166.3    | 9.2       | <i>s</i>                                |

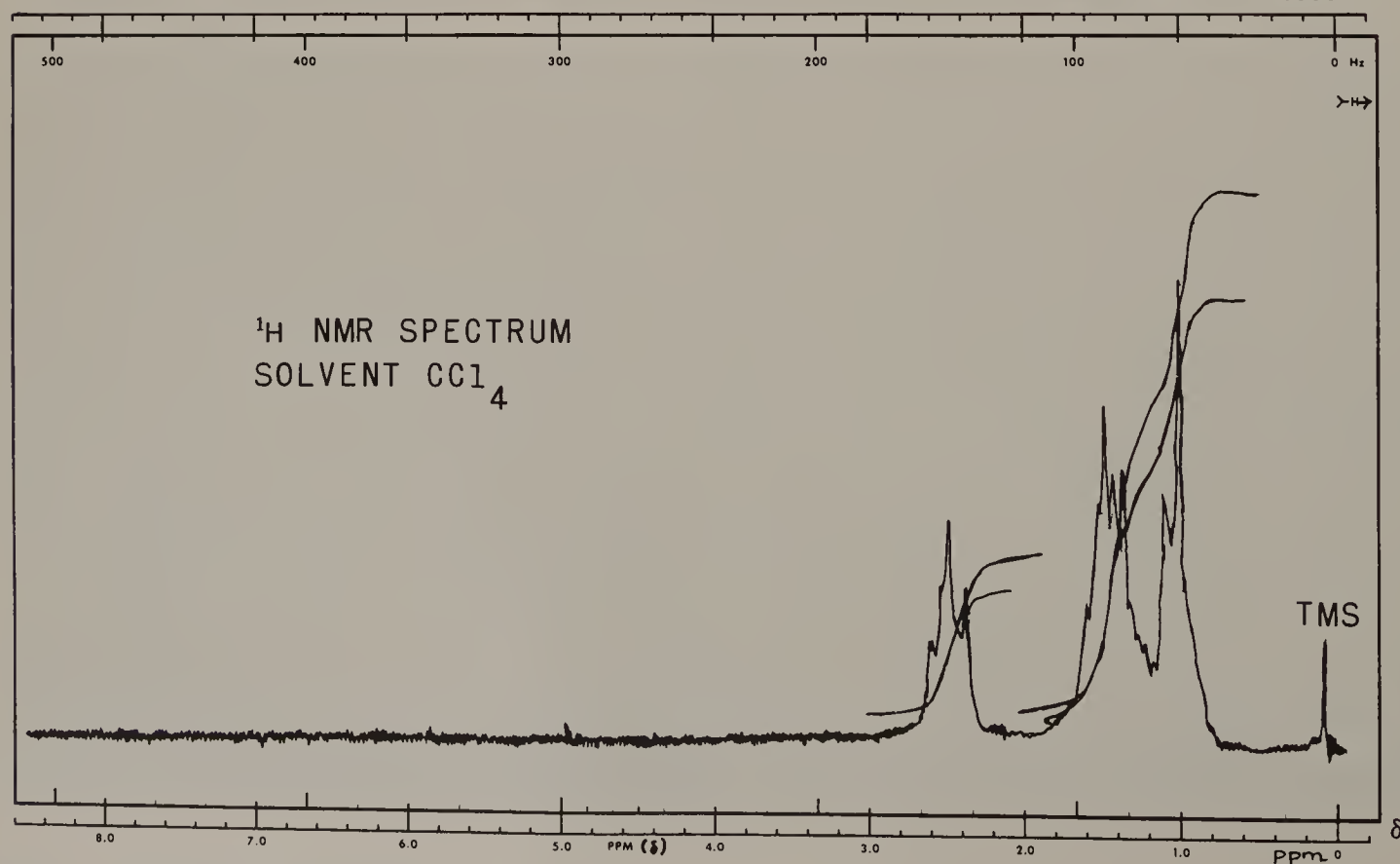
*Compounds 8-18 and 8-19*

Determine the structure of compound 8-18 from the spectra provided. Compound 8-19 is a derivative of 8-18; determine the structure from the spectra provided. Compound 8-19 shows no molecular ion peak in the mass spectrum; however, the mass spectrum shows all the peaks that 8-18 shows (in roughly the same relative intensities). In addition, compound 8-19 shows two peaks, of essentially equal intensities, at  $m/e$  136 and 138. Both compounds are transparent in the UV above 200 nm.

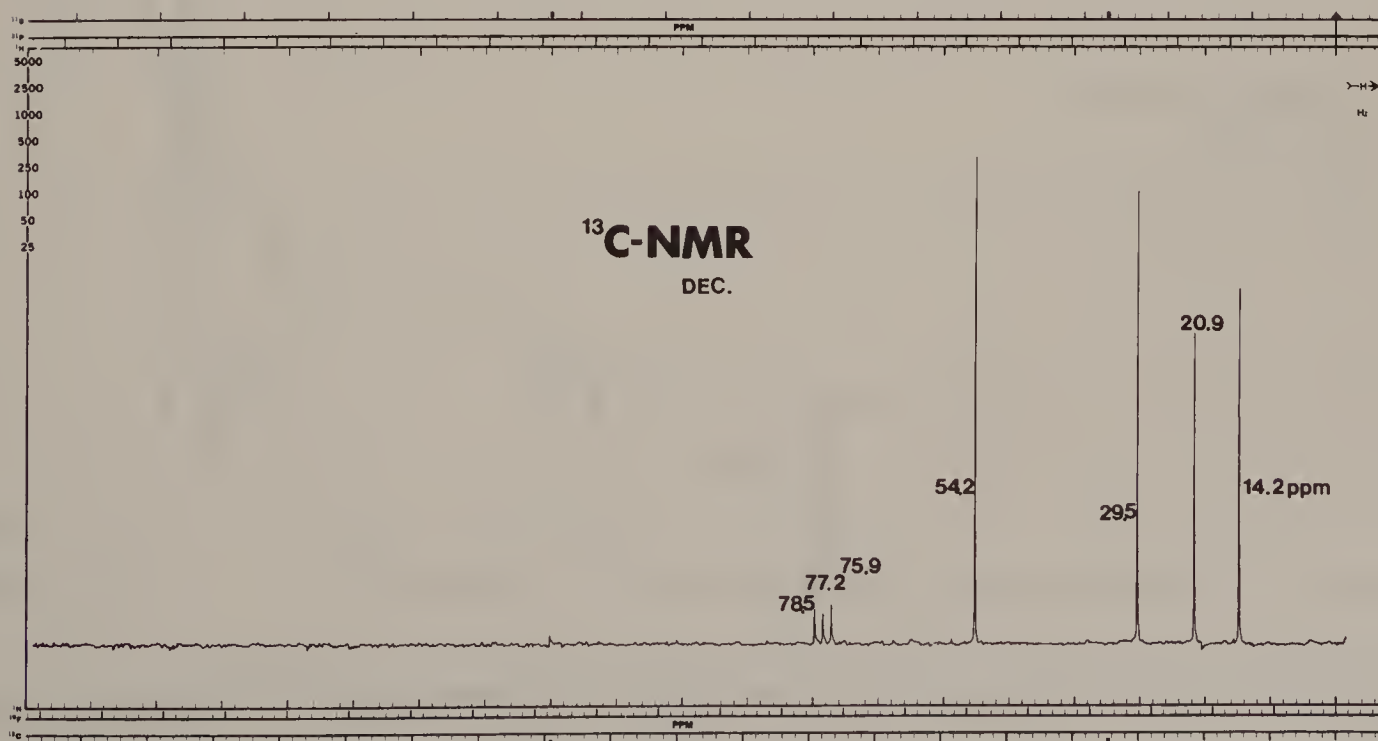
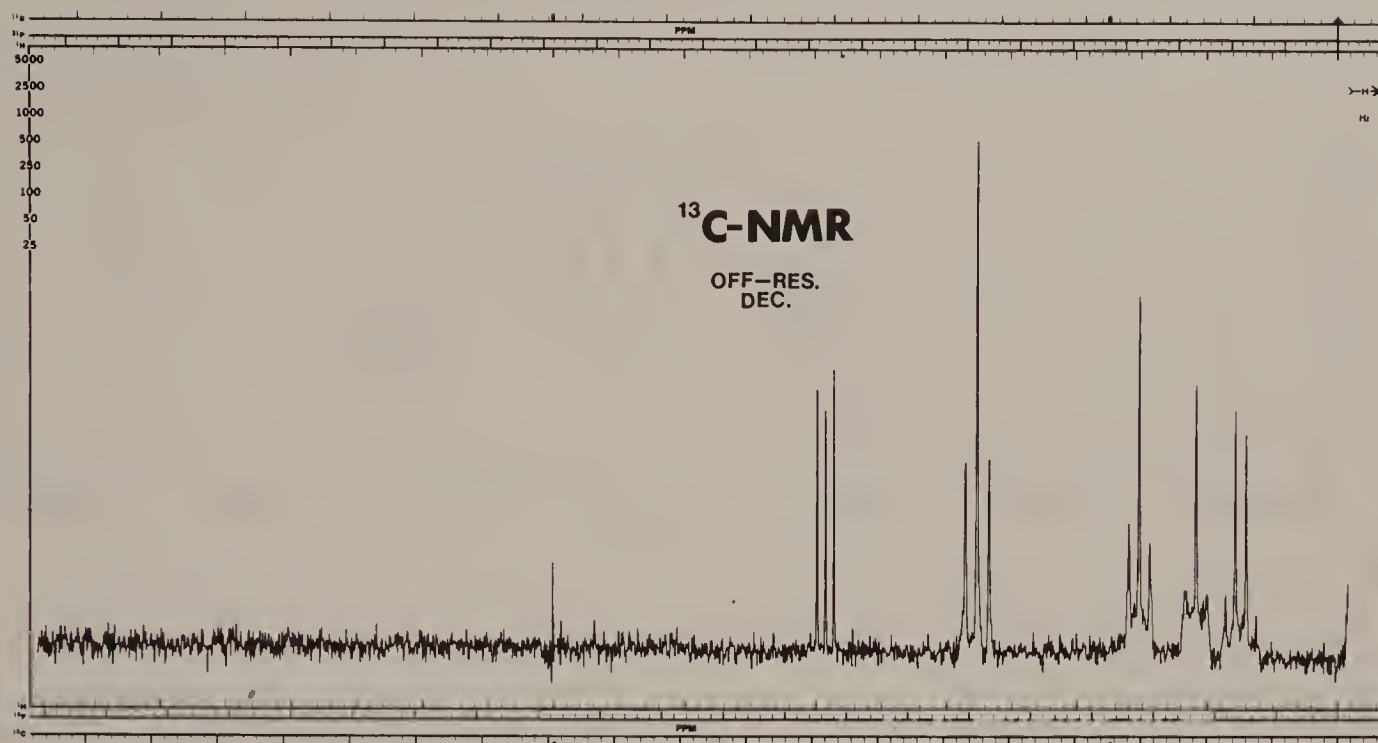


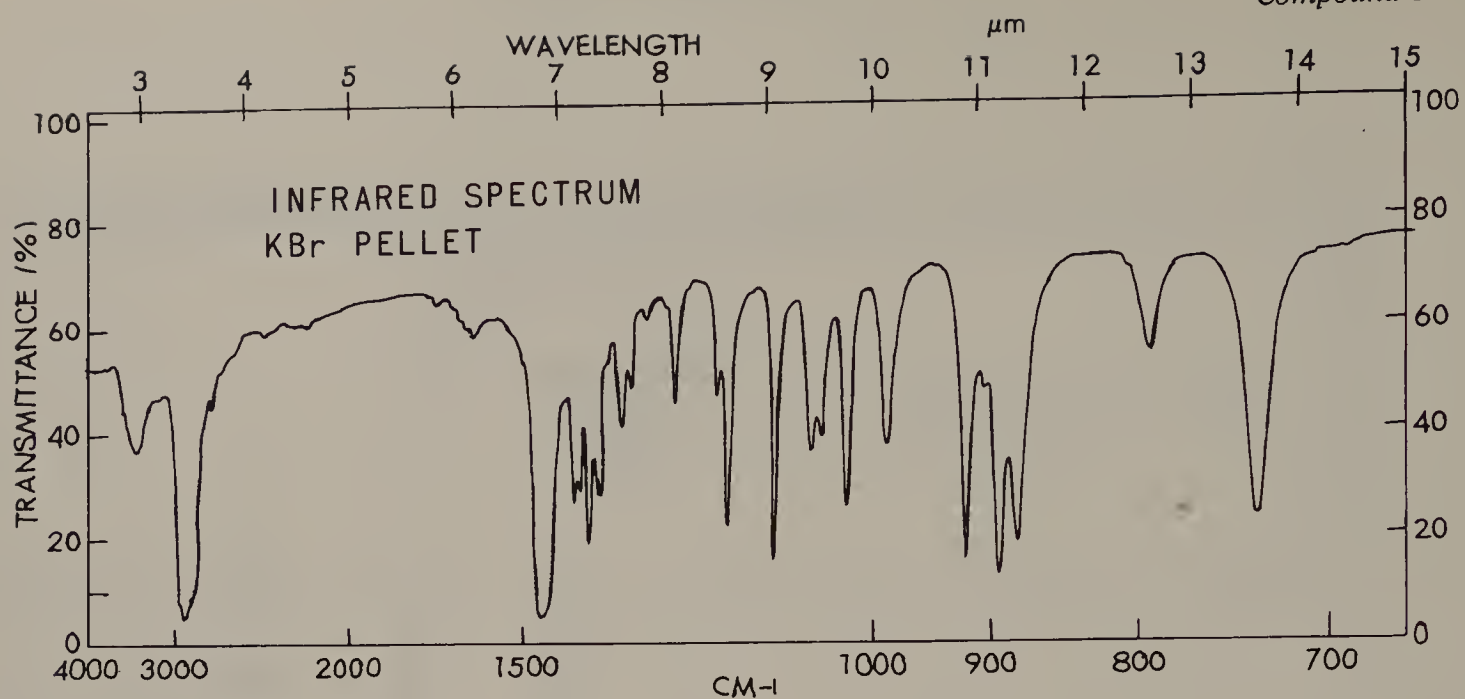
Ultraviolet Data

| $\lambda_{\text{max}}$<br>( $\text{CHCl}_3$ ) | $\epsilon_{\text{max}}$ |
|---|-------------------------|
| 242   | 1000                    |



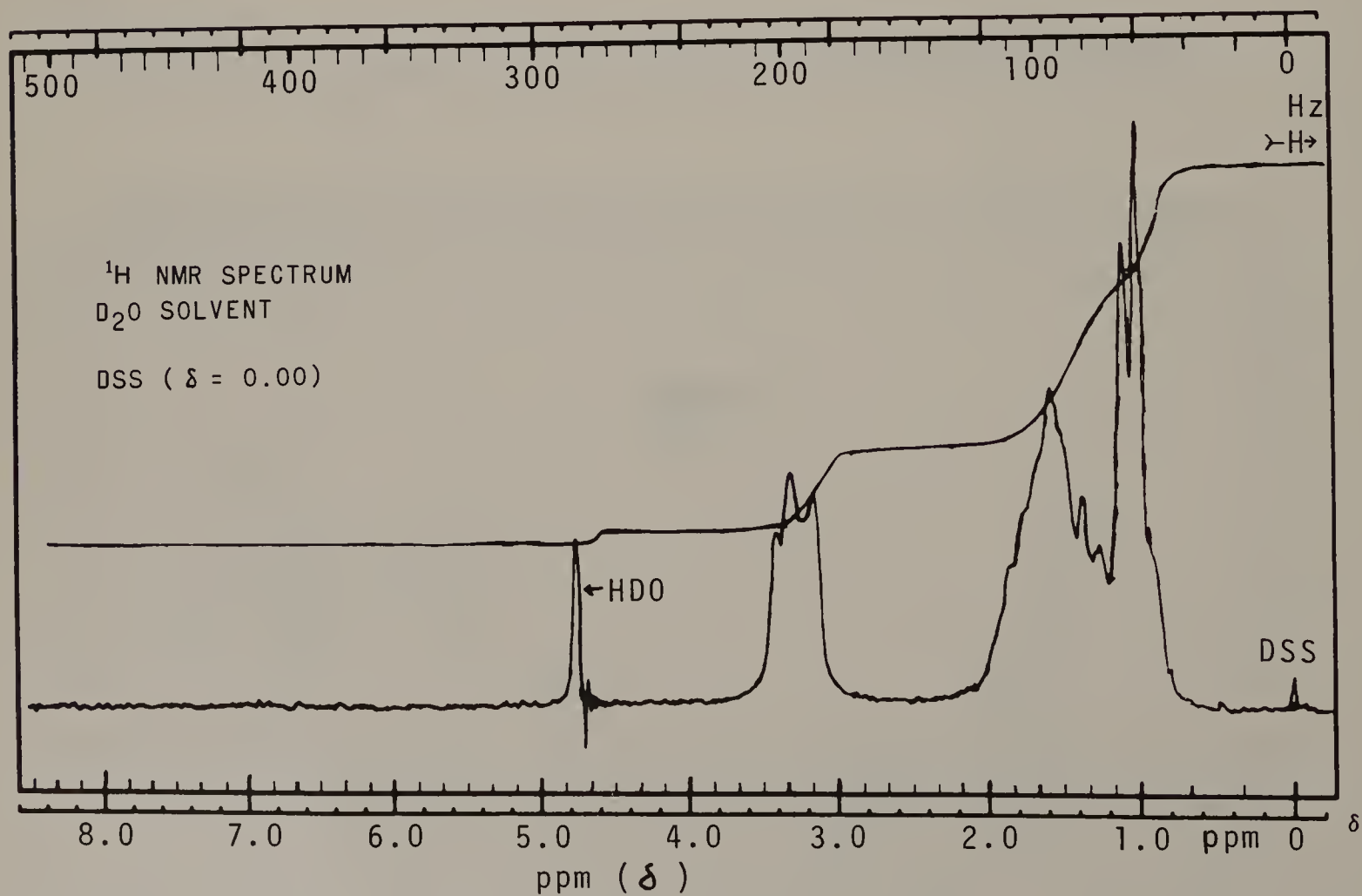




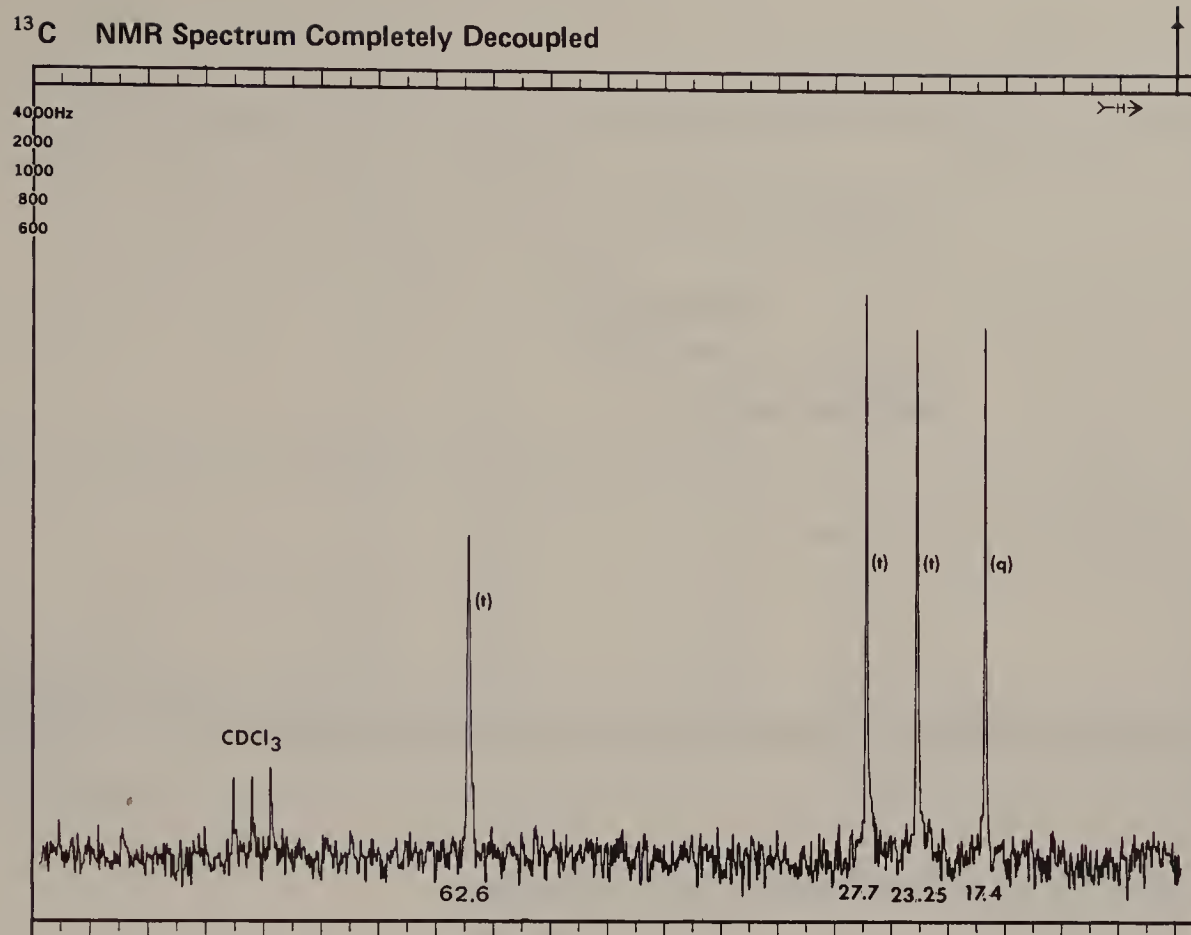


Mass Spectral Data  
see p. 387

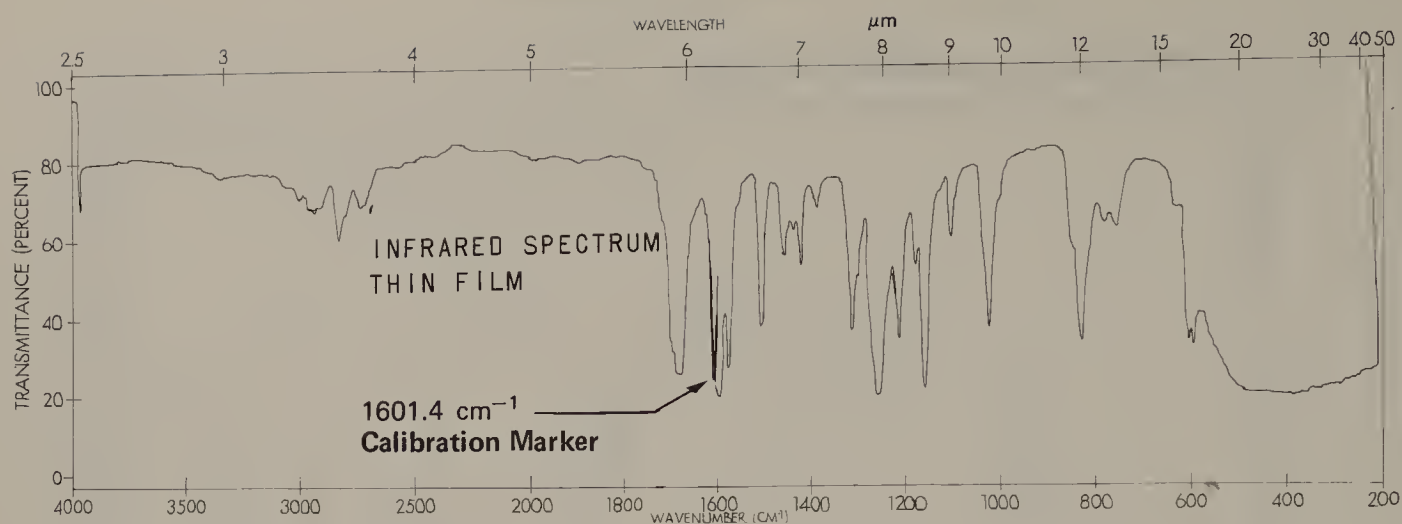
Ultraviolet Data  
No  $\lambda_{\text{max}}$  above 200 nm



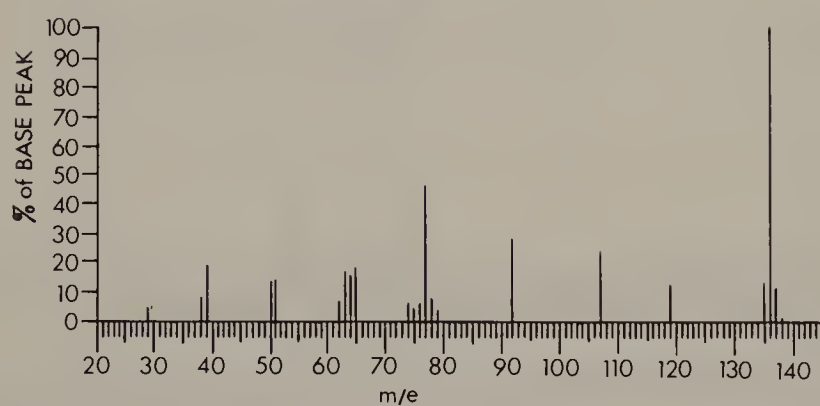
Compound 8-19 (Continued)







## MASS SPECTRAL DATA (Relative Intensity)

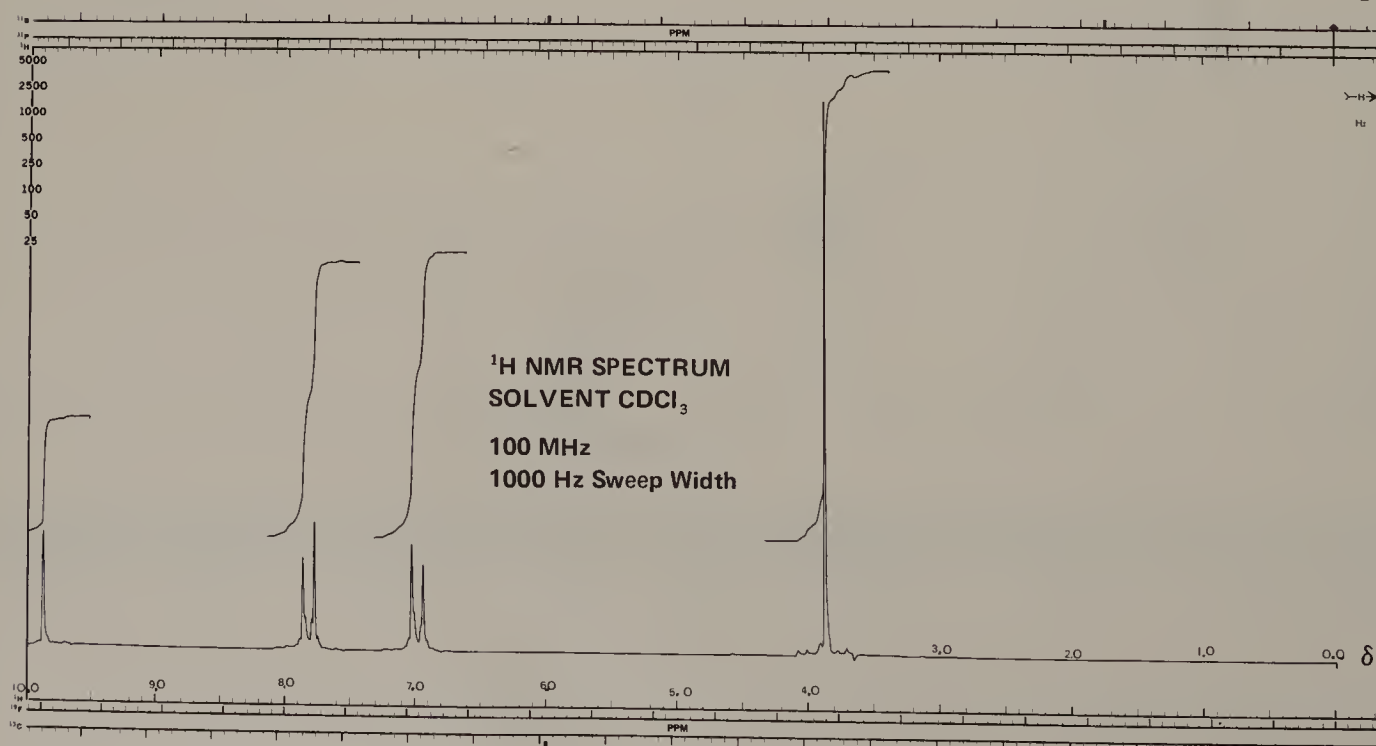


## Mass Spectral Data

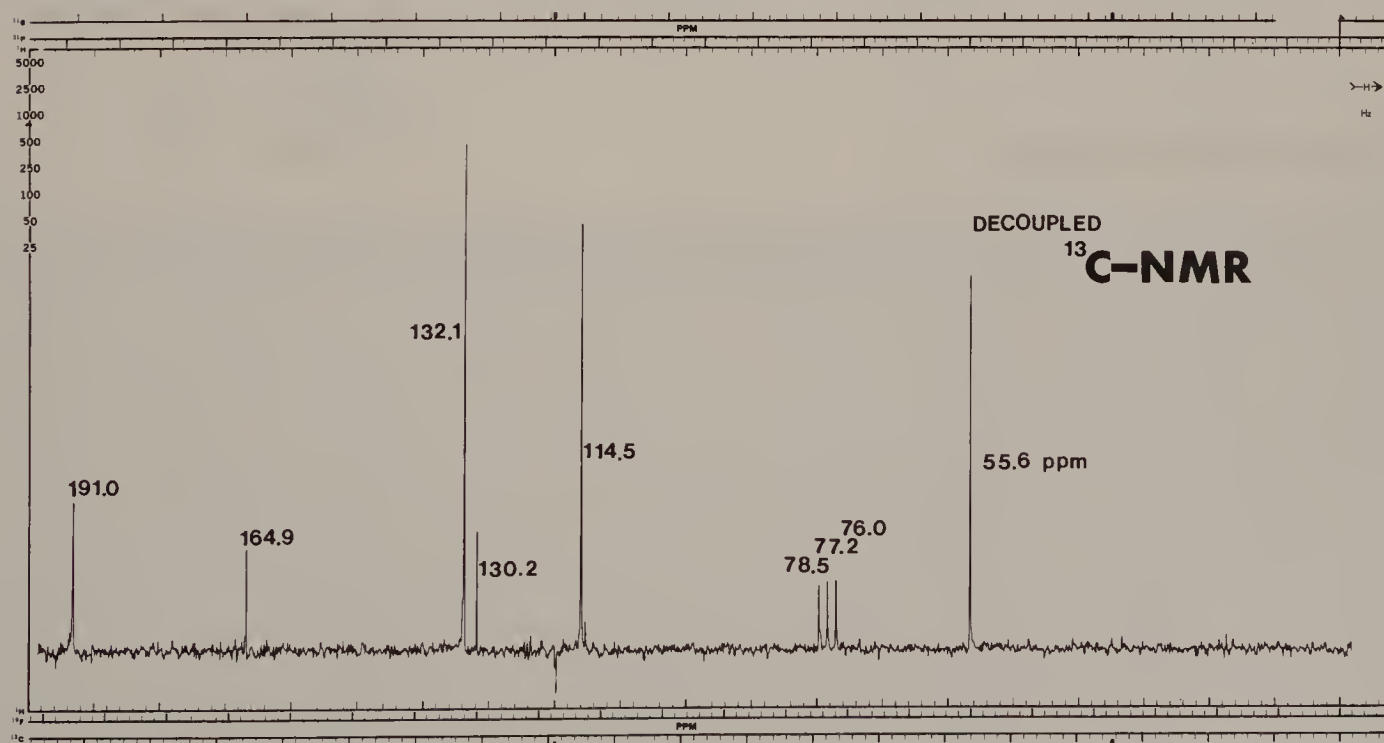
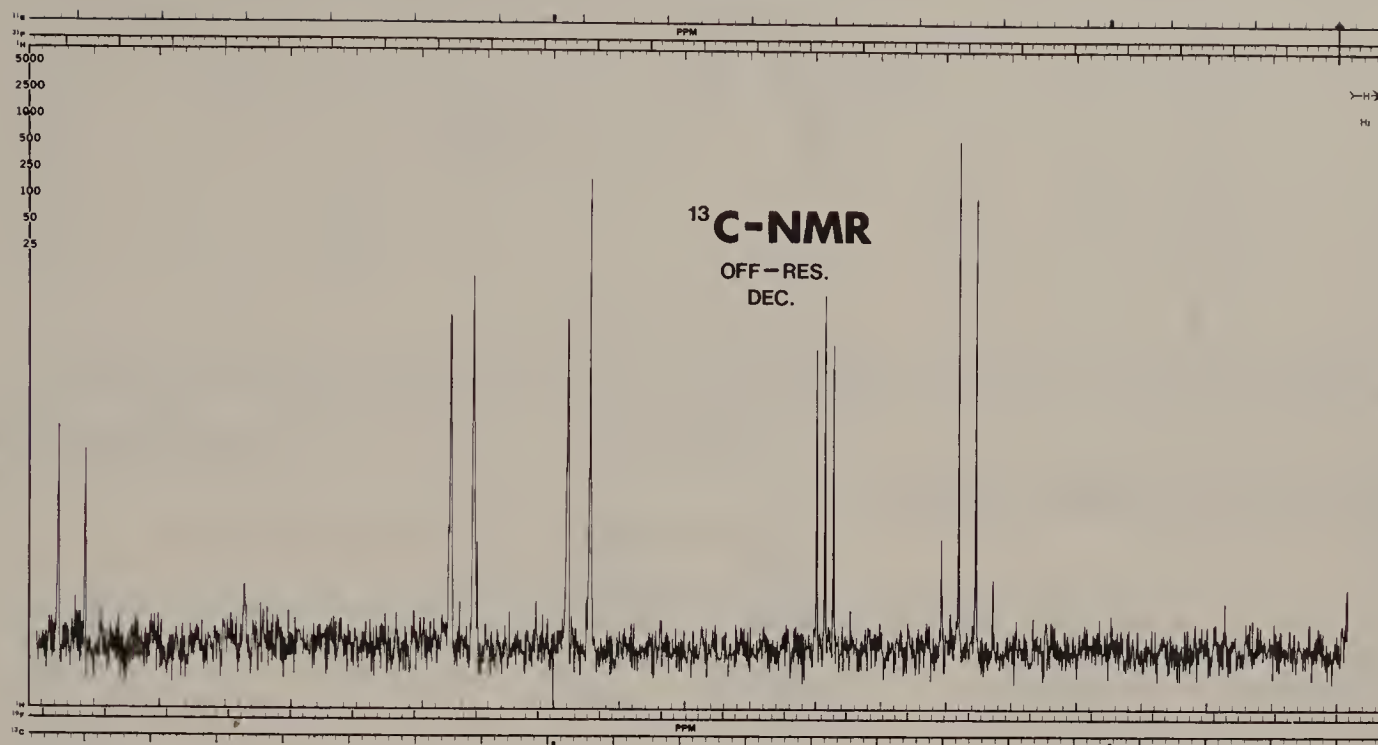
| m/e | Relative Intensity |
|-----|--------------------|
| 135 | 14.0               |
| 136 | 100.0              |
| 137 | 11.1               |
| 138 | 1.1                |

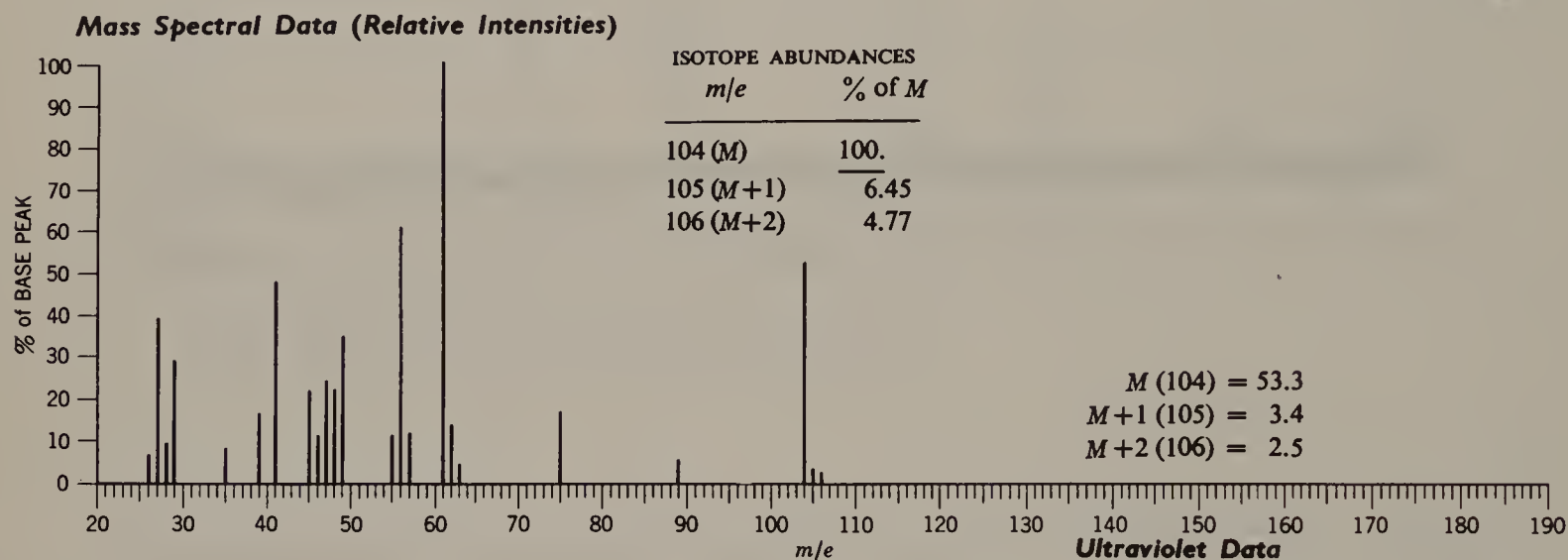
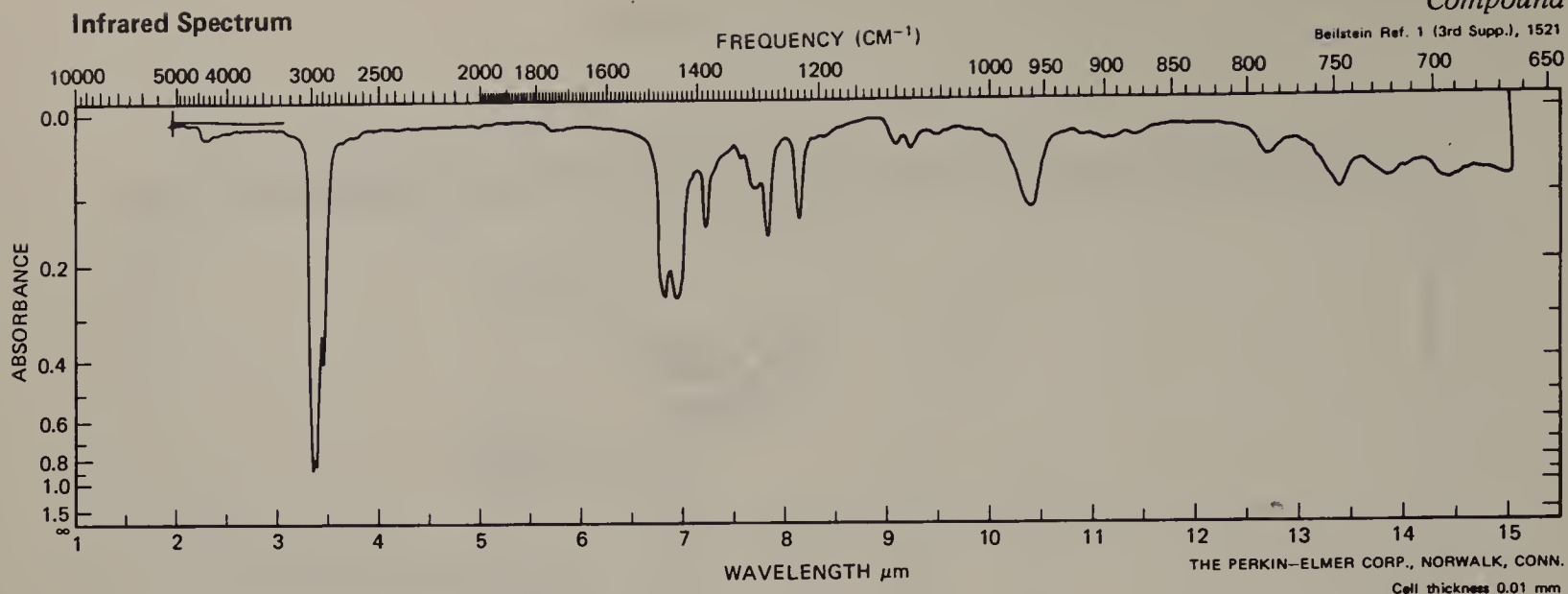
## Ultraviolet Data

| $\lambda_{\text{max}}$<br>(cyclohexane) | $\epsilon_{\text{max}}$ |
|---|-------------------------|
| 215                                     | 21,500                  |
| 221                                     | 20,000                  |
| 266                                     | 25,500                  |
| 288                                     | 8,500                   |
| 312                                     | 90                      |
| 324                                     | 83                      |
| 360                                     | 25                      |



Compound 8-20 (Continued)





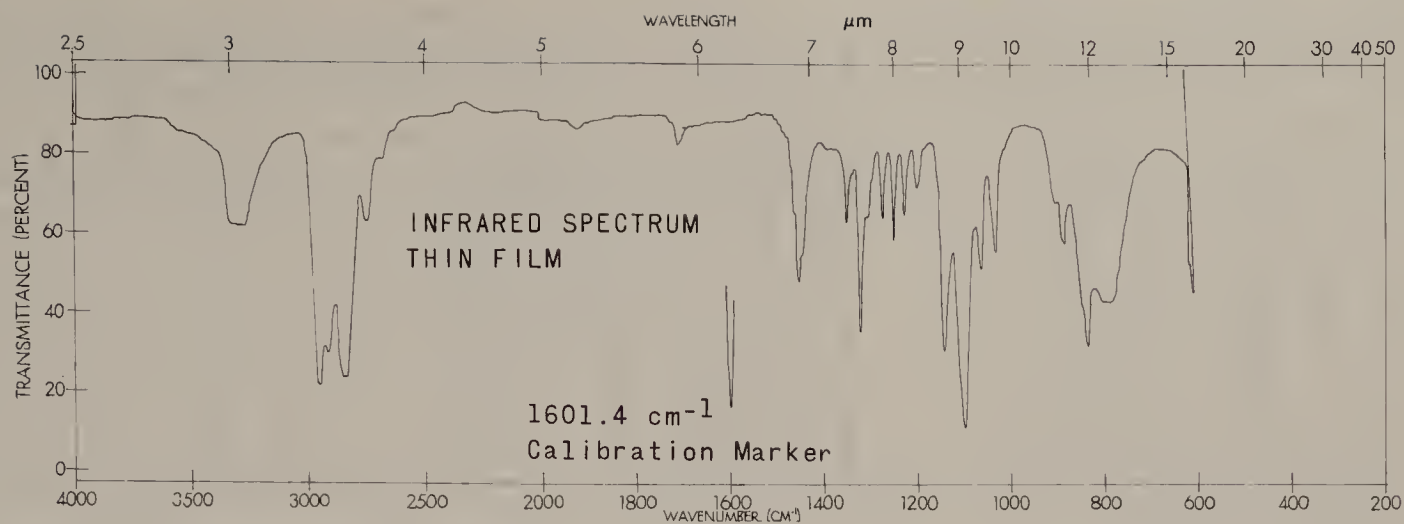
**Ultraviolet Data**

| $\lambda_{\text{max}}^{\text{EtOH}}$ | $\epsilon_{\text{max}}$ |
|--------------------------------------|-------------------------|
| 228 (inflection)                     | 106                     |

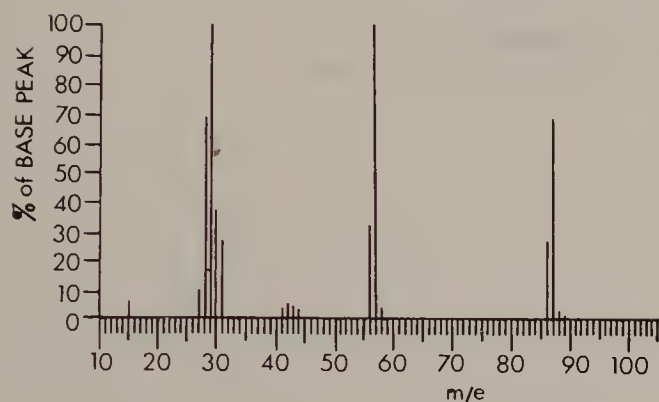
**$^1\text{H}$  NMR Spectrum (Solvent  $\text{CDCl}_3$ )**







## MASS SPECTRAL DATA (Relative Intensity)

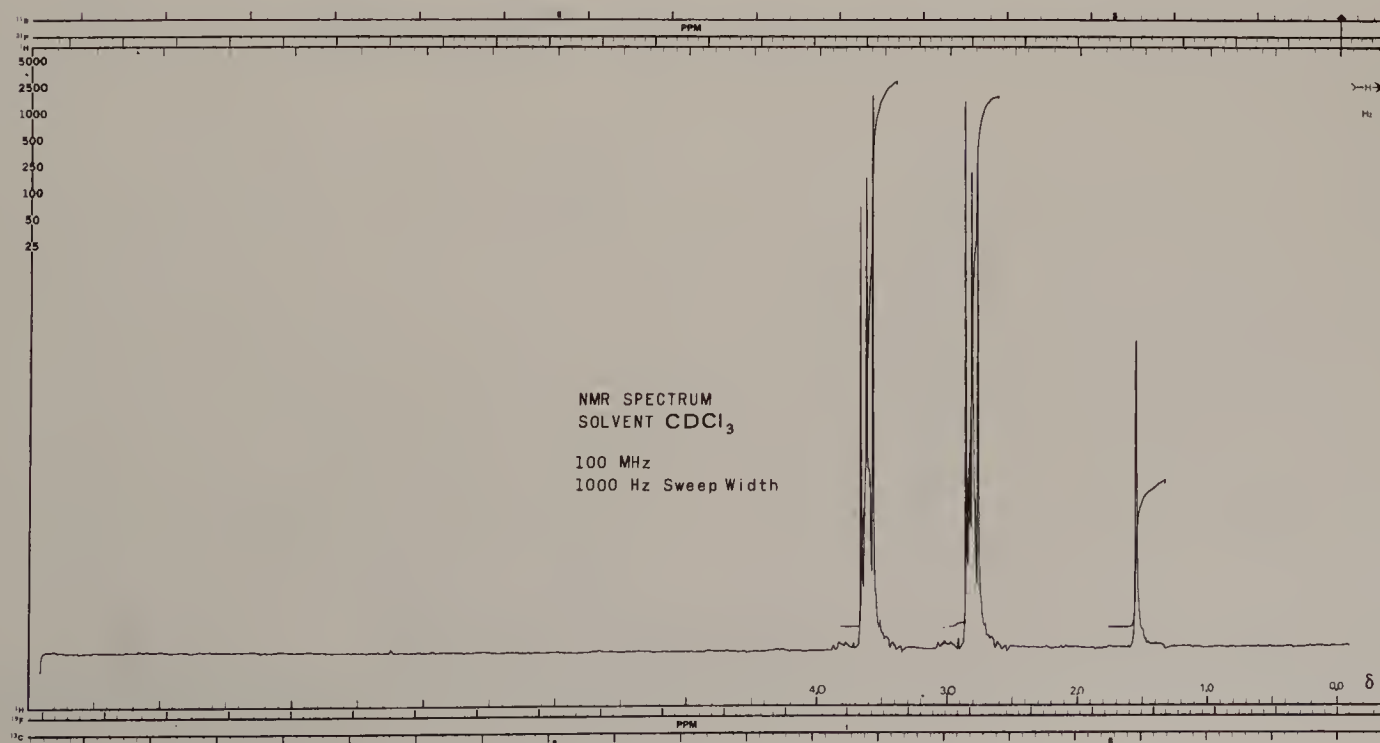


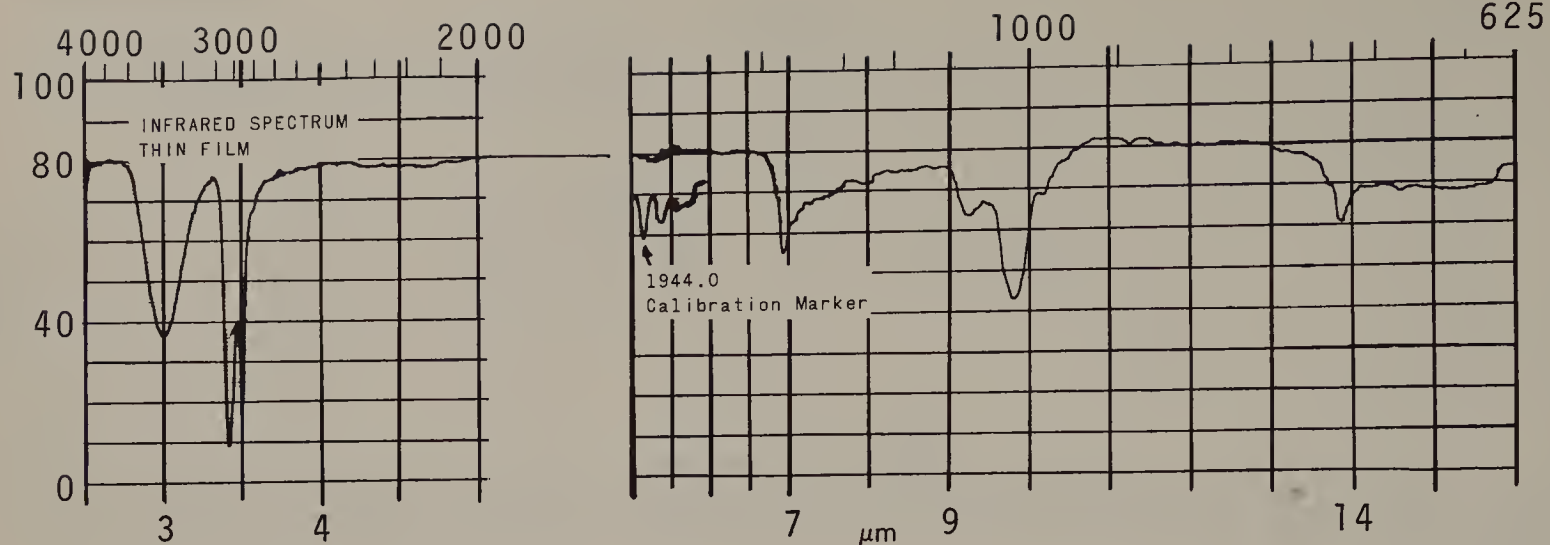
## Mass Spectral Data

| <u>m/e</u> | <u>Relative Intensity</u> |
|------------|---------------------------|
| 86         | 40.70                     |
| 87         | 100.00                    |
| 88         | 4.48                      |
| 89         | 0.29                      |

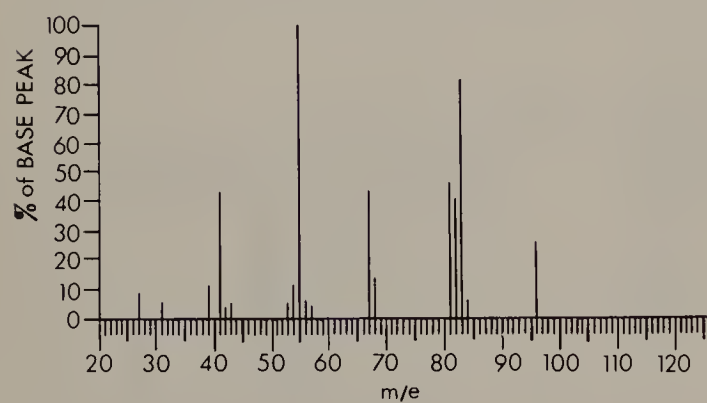
## Ultraviolet Data

Transparent above 200nm





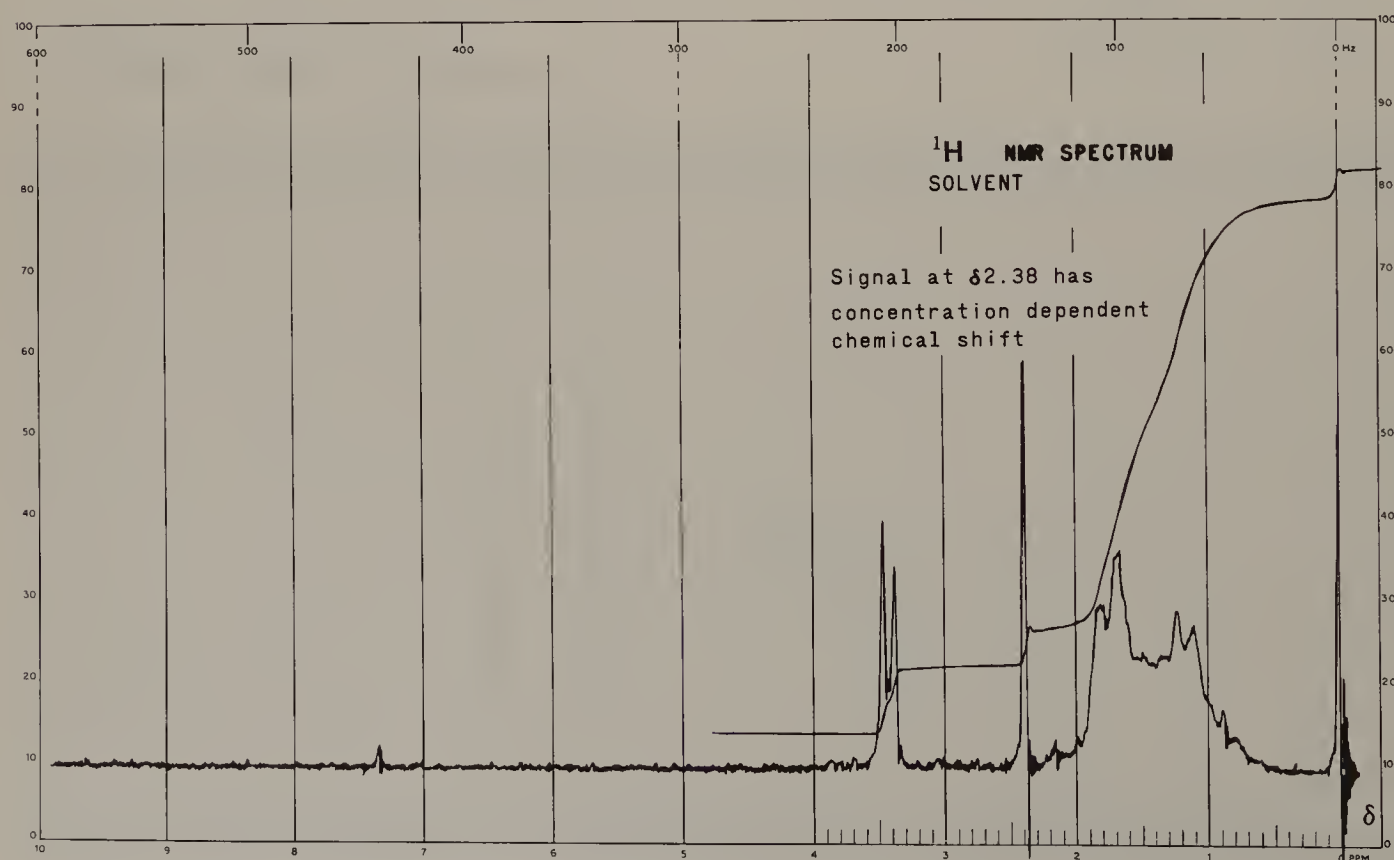
## MASS SPECTRAL DATA (Relative Intensity)



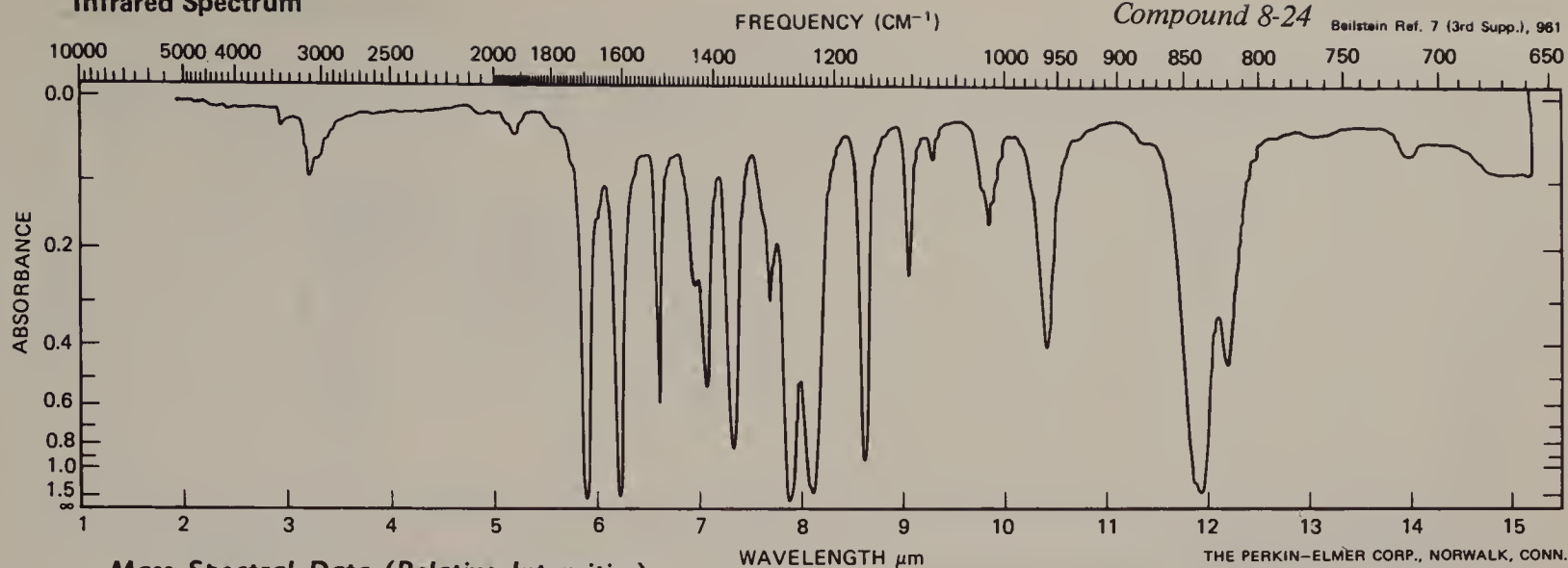
m/e 114, Trace  
m/e 115, 116, too small to measure

## Ultraviolet Data

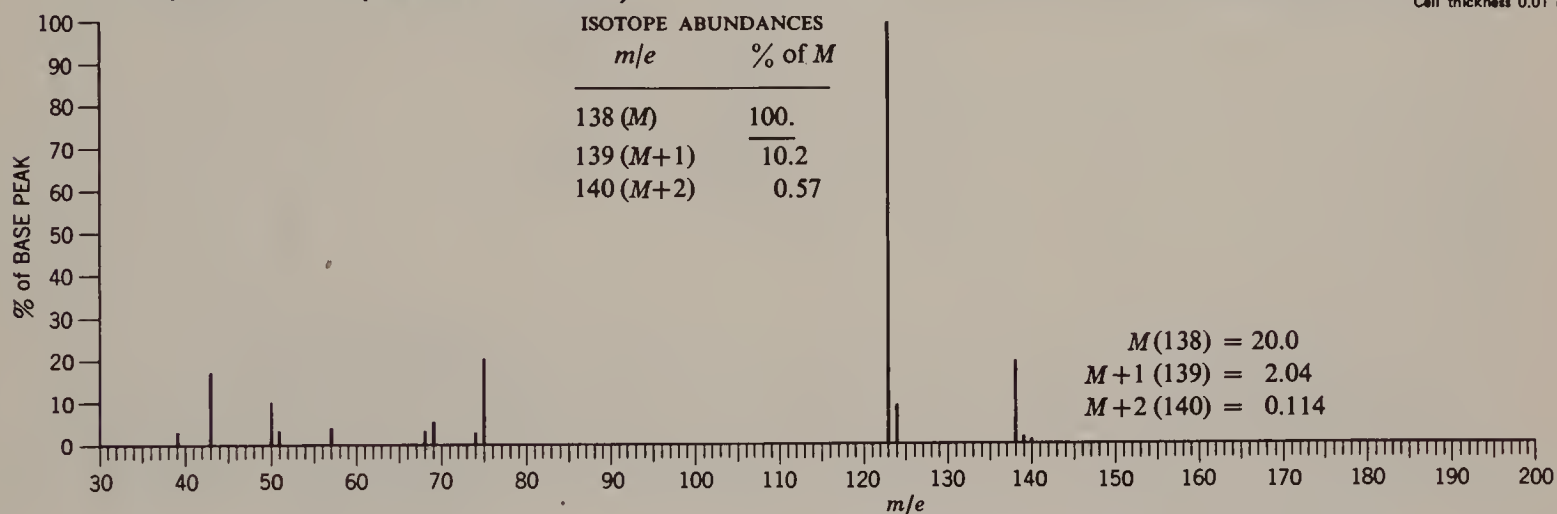
Transparent above 200 nm



# Infrared Spectrum

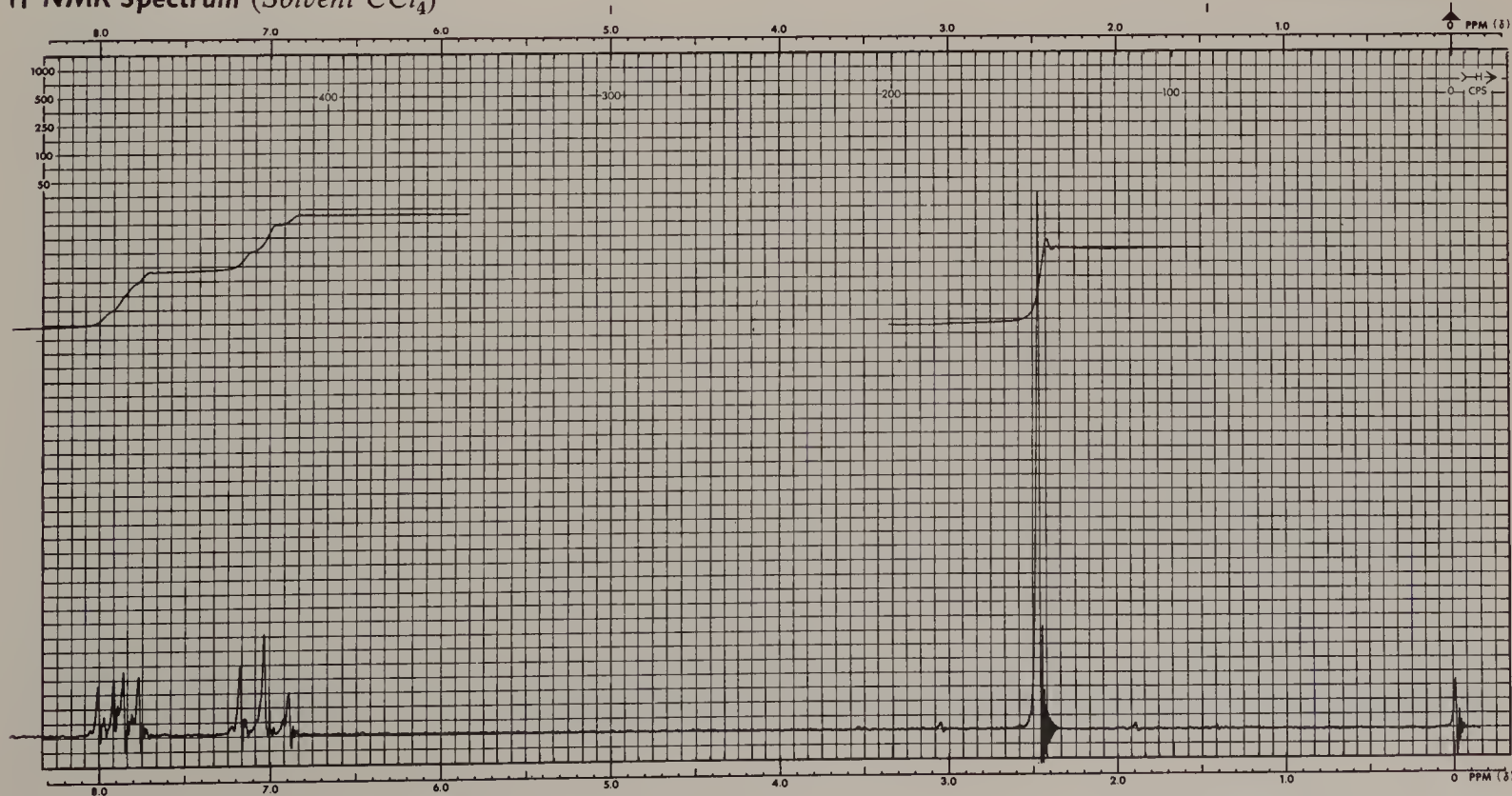


## Mass Spectral Data (Relative Intensities)



| Ultraviolet Data                 |                         | 275              | 466 | 292 ( <i>s</i> ) | 86                      |
|----------------------------------|-------------------------|------------------|-----|------------------|-------------------------|
| $\lambda_{\text{Isooctane max}}$ | $\epsilon_{\text{max}}$ | 278 ( <i>s</i> ) | 258 | 312              | 71                      |
| 240                              | 16,900                  |                  |     |                  | ( <i>s</i> ) = shoulder |
| 268                              | 762                     |                  |     |                  |                         |

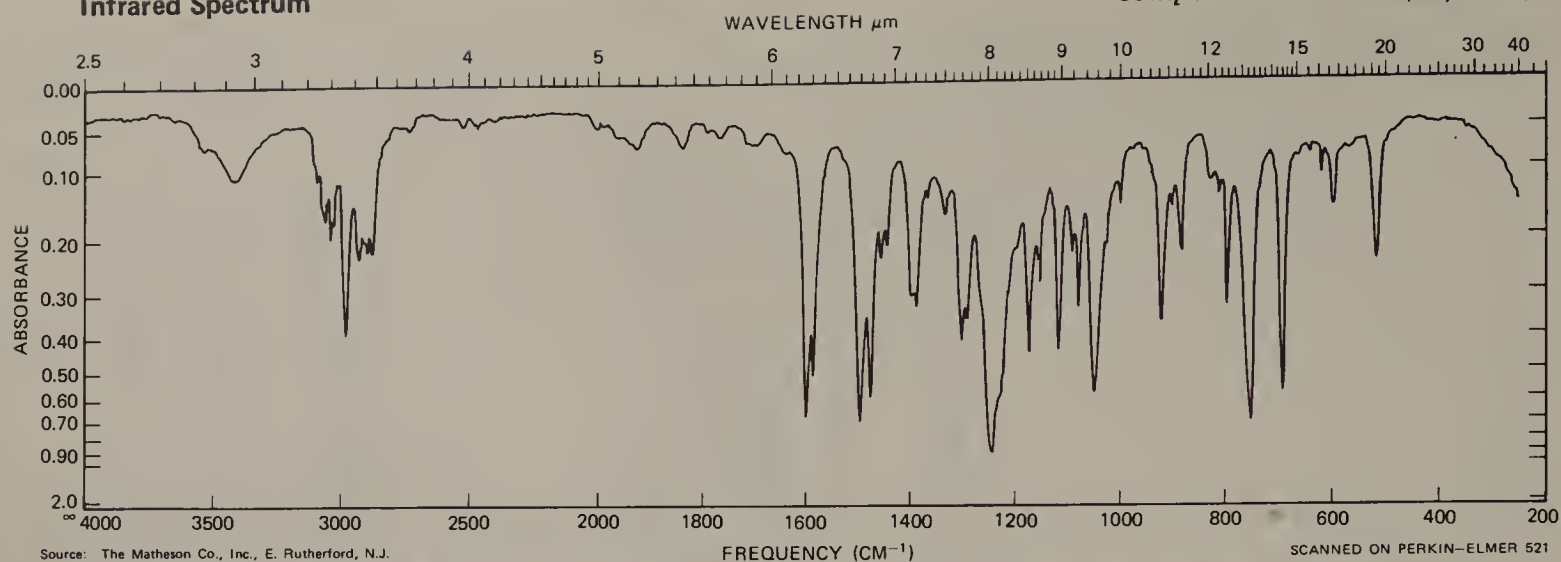
## <sup>1</sup>H NMR Spectrum (Solvent CCl<sub>4</sub>)



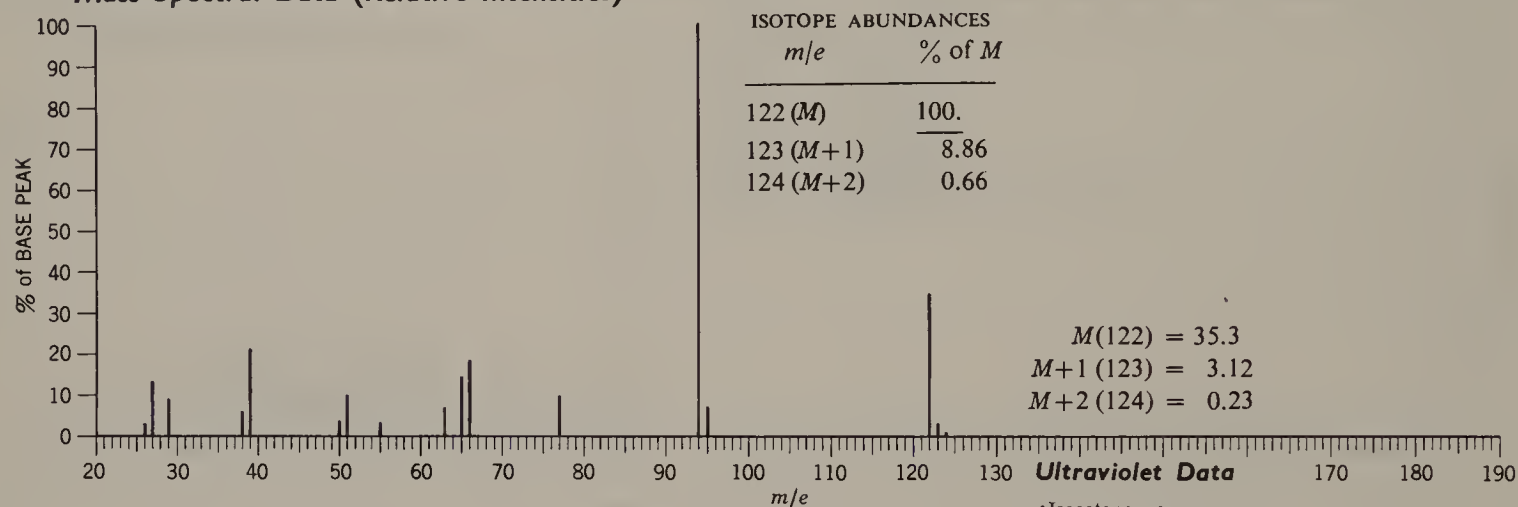


## Compound 8-25

## Infrared Spectrum



## Mass Spectral Data (Relative Intensities)



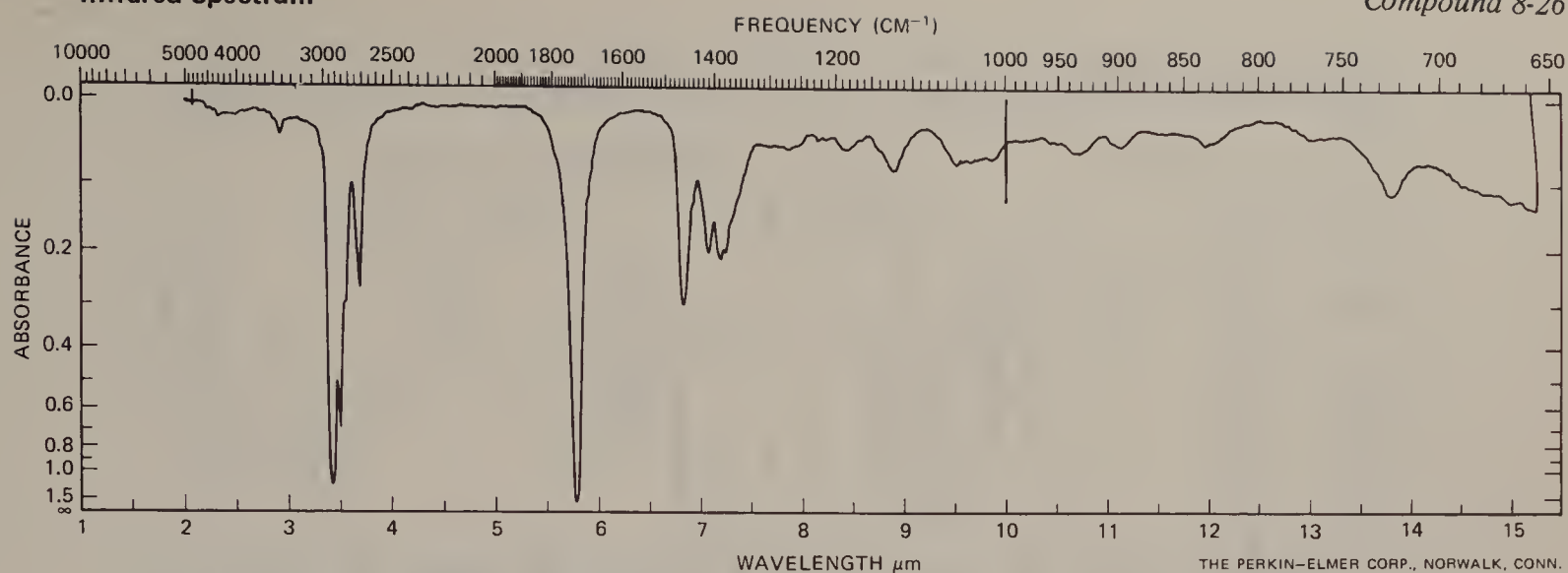
## Ultraviolet Data

| $\lambda_{\text{max}}^{\text{Isooctane}}$ | $\log \epsilon_{\text{max}}$ |
|---|------------------------------|
| 222                                       | 3.88                         |
| 254                                       | 3.12                         |
| 260                                       | 3.28                         |
| 267                                       | 3.25                         |

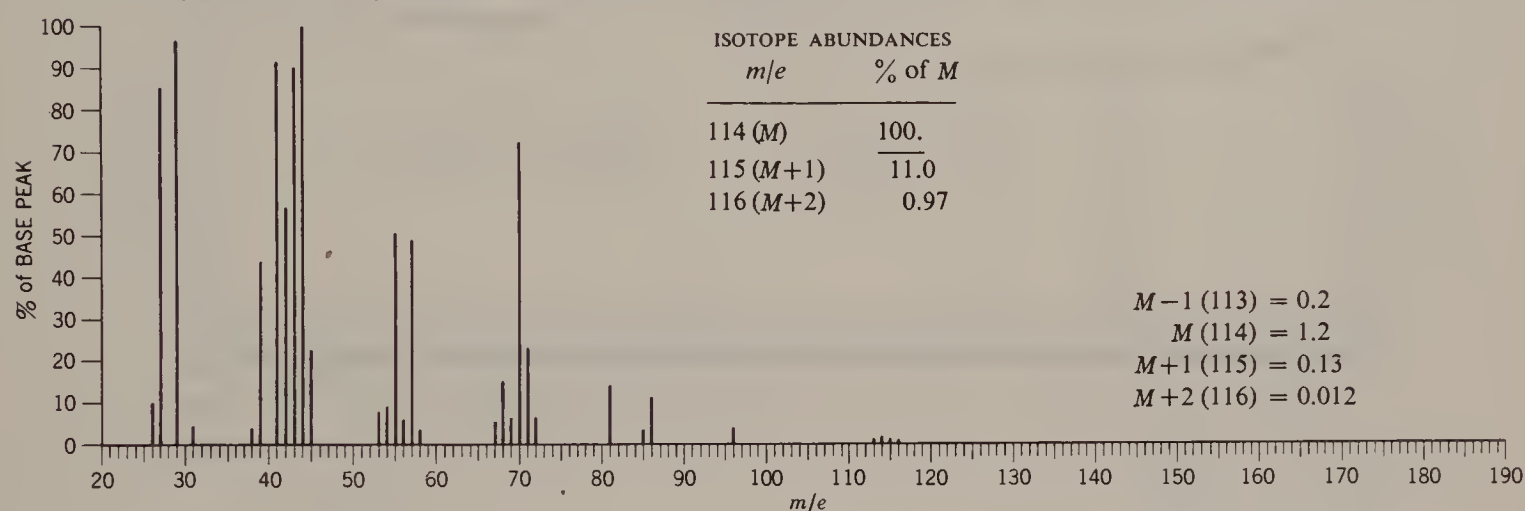
 $^1\text{H}$  NMR Spectrum (Solvent  $\text{CCl}_4$ )

## Infrared Spectrum

Compound 8-26

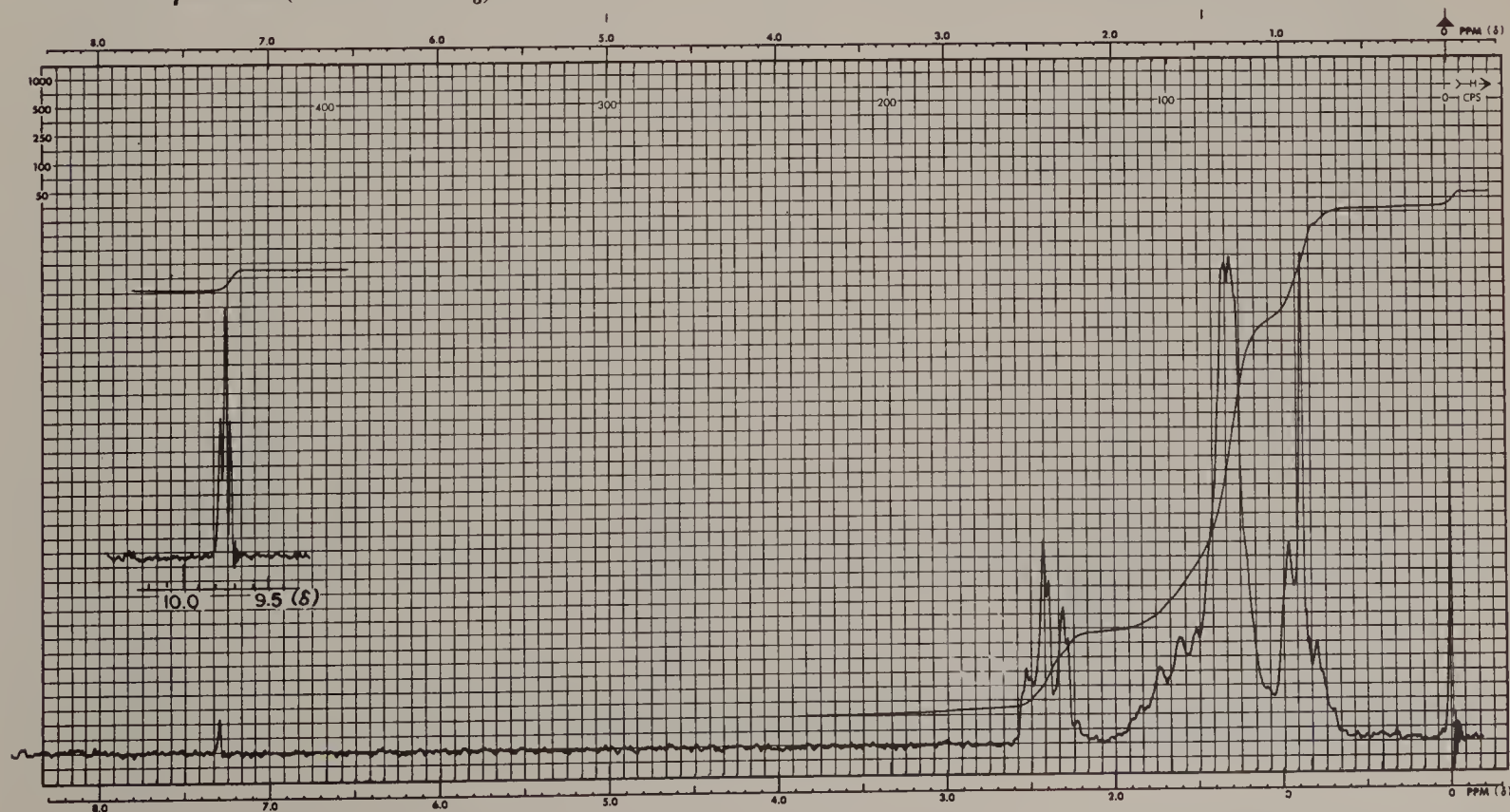


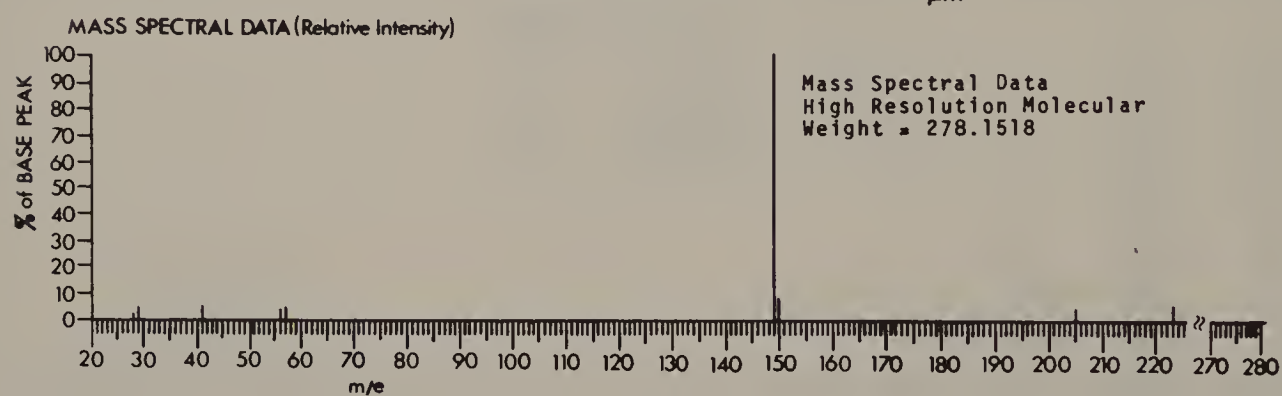
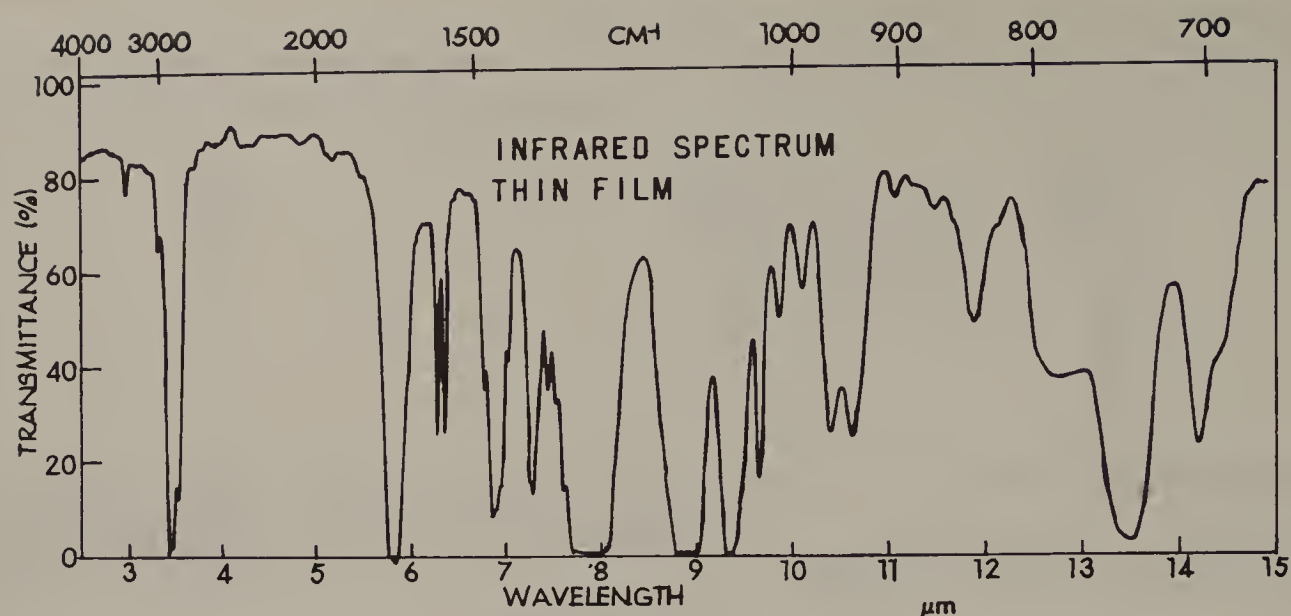
## Mass Spectral Data (Relative Intensities)



## Ultraviolet Data

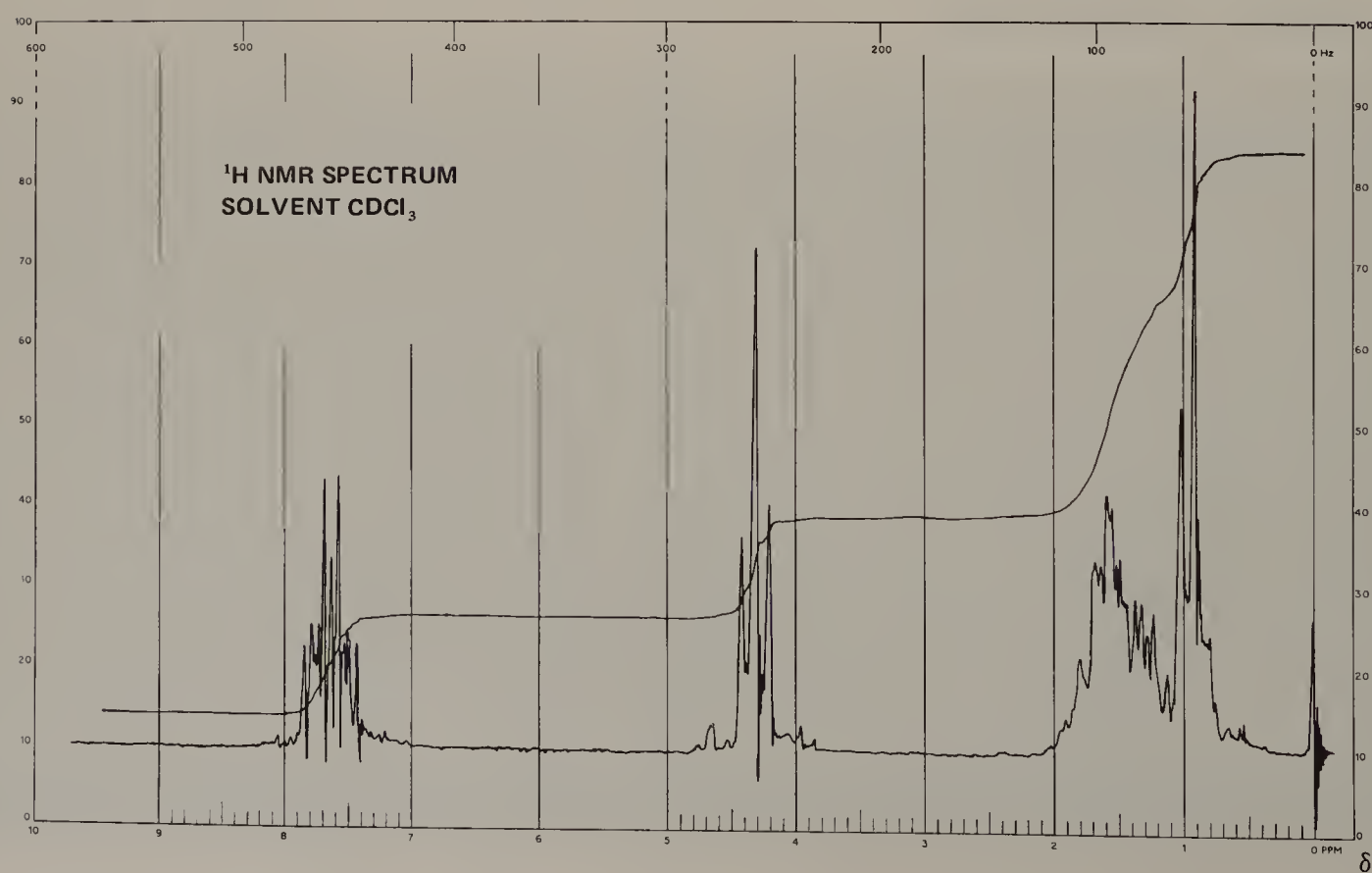
| $\lambda_{\text{Cyclohexane max}}$ | $\epsilon_{\text{max}}$ |
|------------------------------------|-------------------------|
| 292                                | 23.2                    |

<sup>1</sup>H NMR Spectrum (Solvent CDCl<sub>3</sub>)

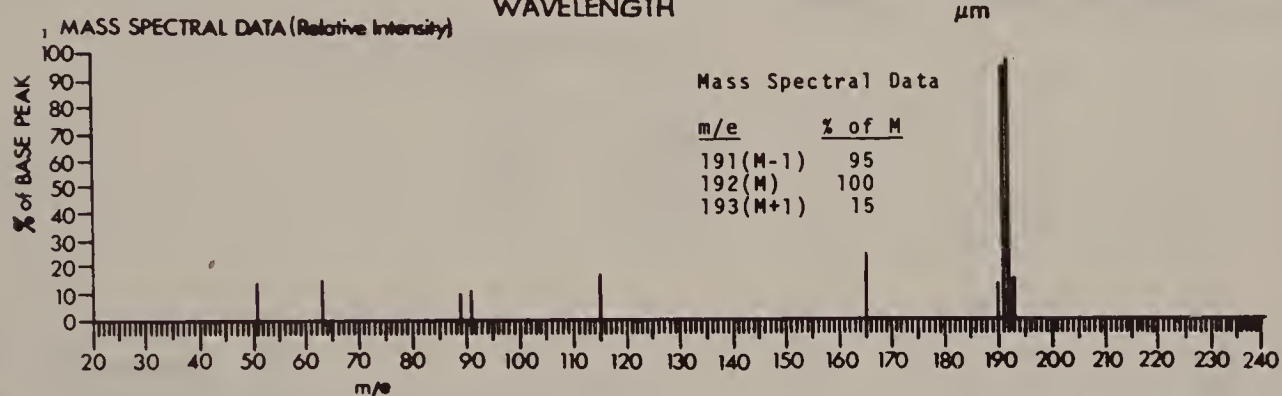
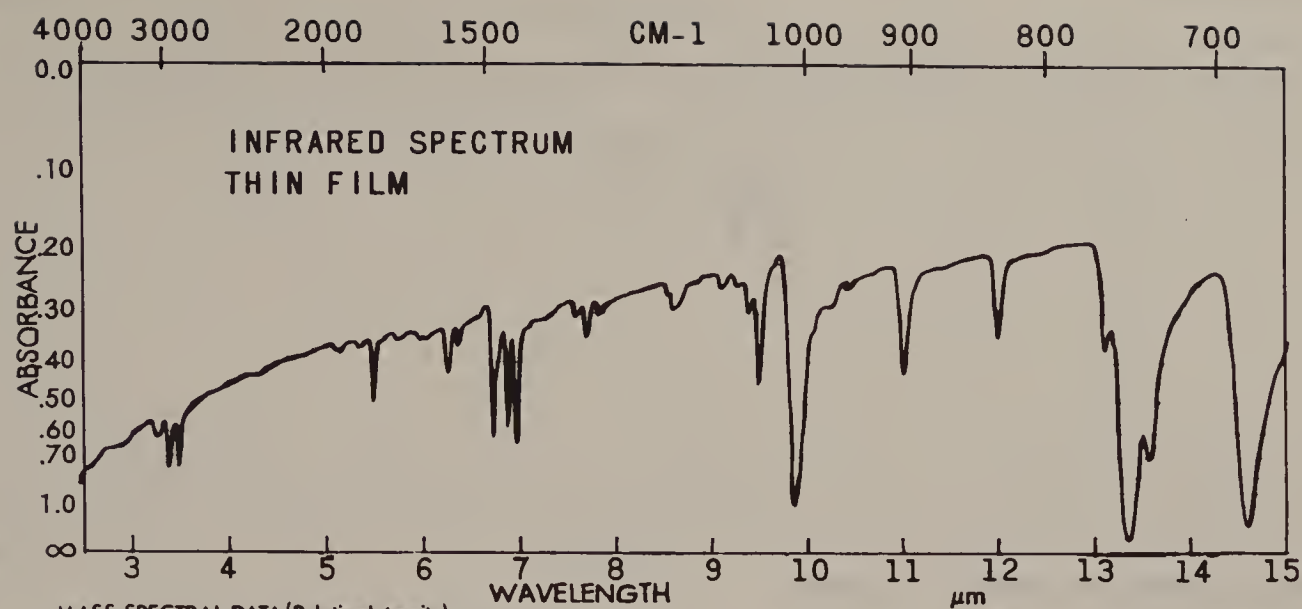


#### Ultraviolet Data

| $\lambda_{\text{max}}$<br>(CH <sub>3</sub> OH) | $\epsilon_{\text{max}}$ |
|--|-------------------------|
| 274  | 1230                    |
| 225  | 7960                    |

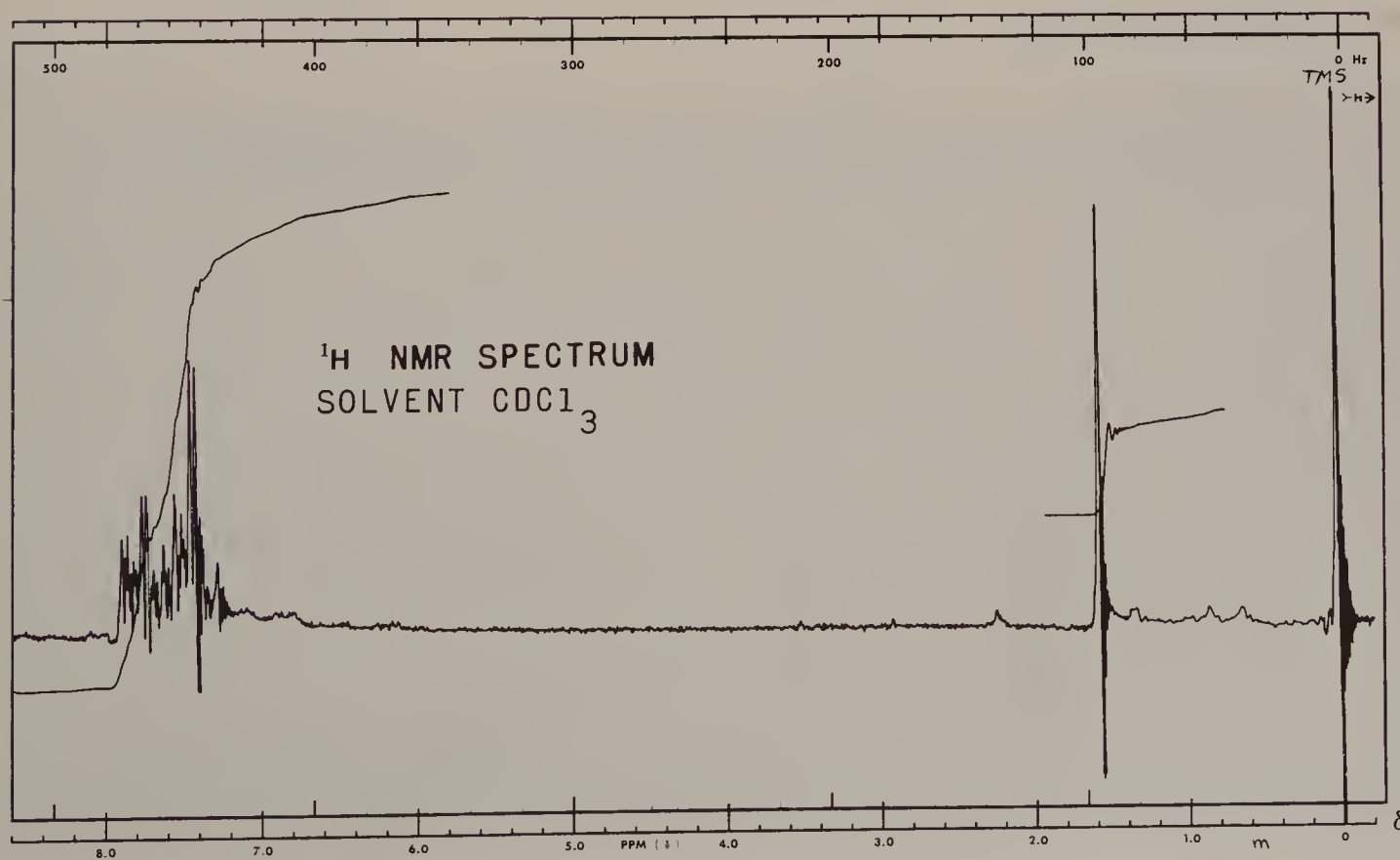




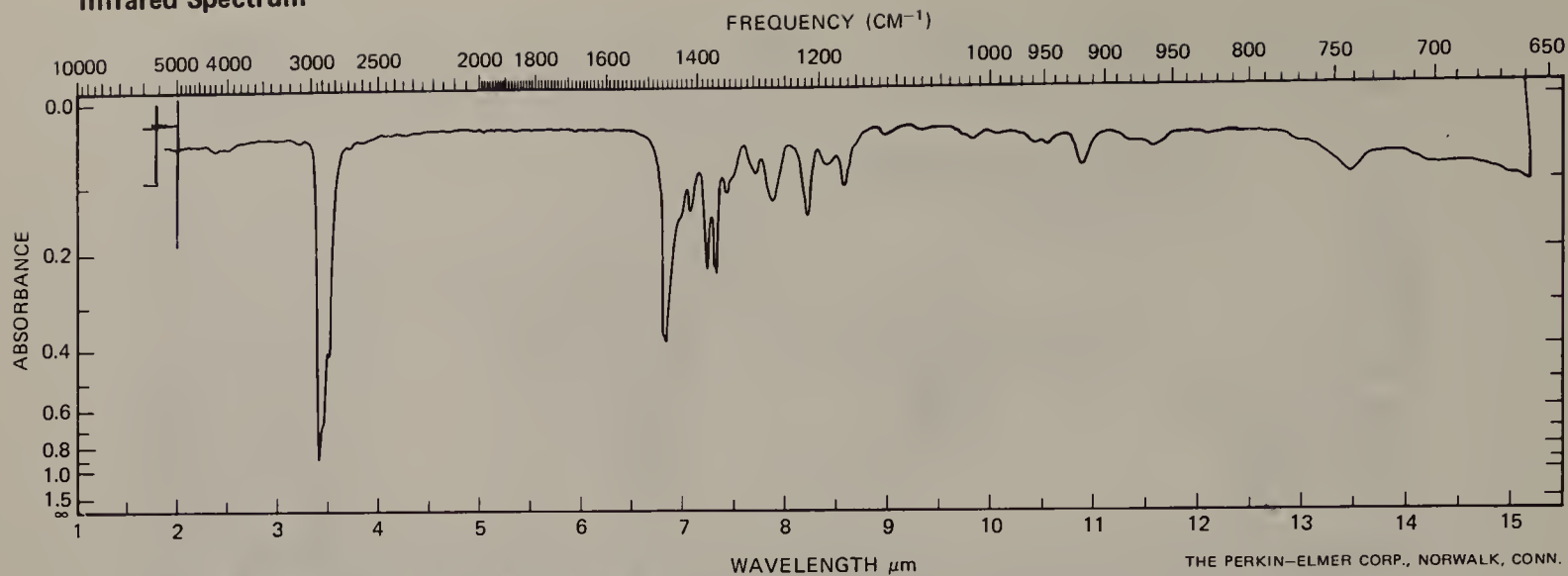


Ultraviolet Data

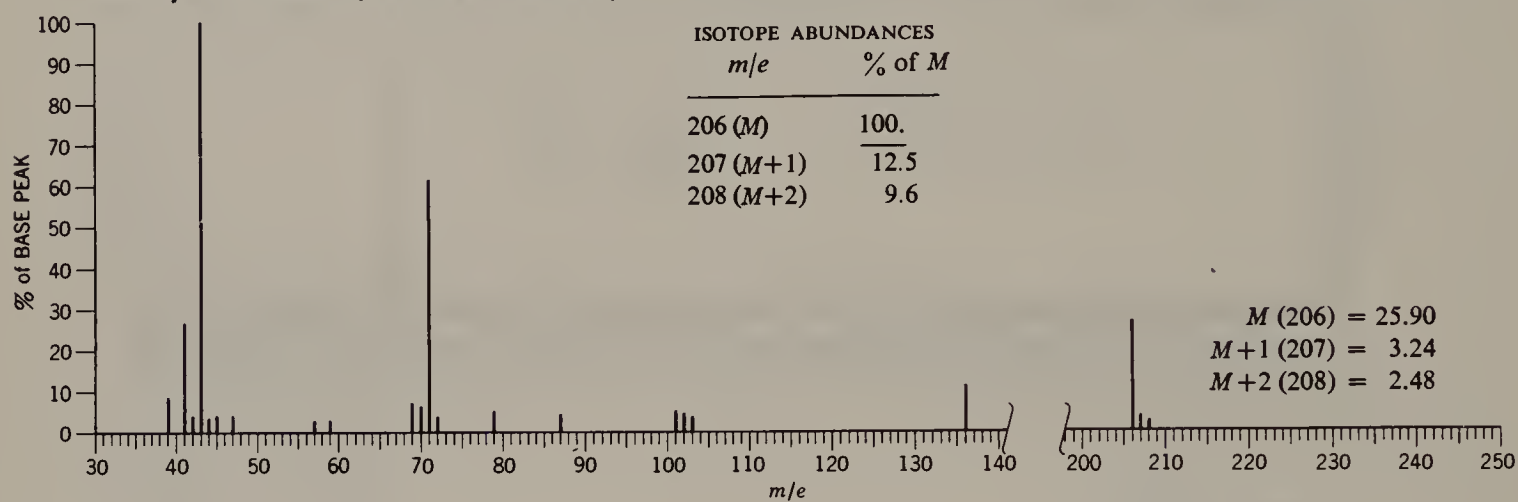
| $\lambda_{\text{max}}$<br>(CH <sub>3</sub> OH) | log $\epsilon_{\text{max}}$ |
|--|-----------------------------|
| 225  | 4.01                        |
| 233  | 3.94                        |
| 307  | 4.16                        |
| 315  | 4.23                        |
| 334  | 4.09                        |



## Infrared Spectrum

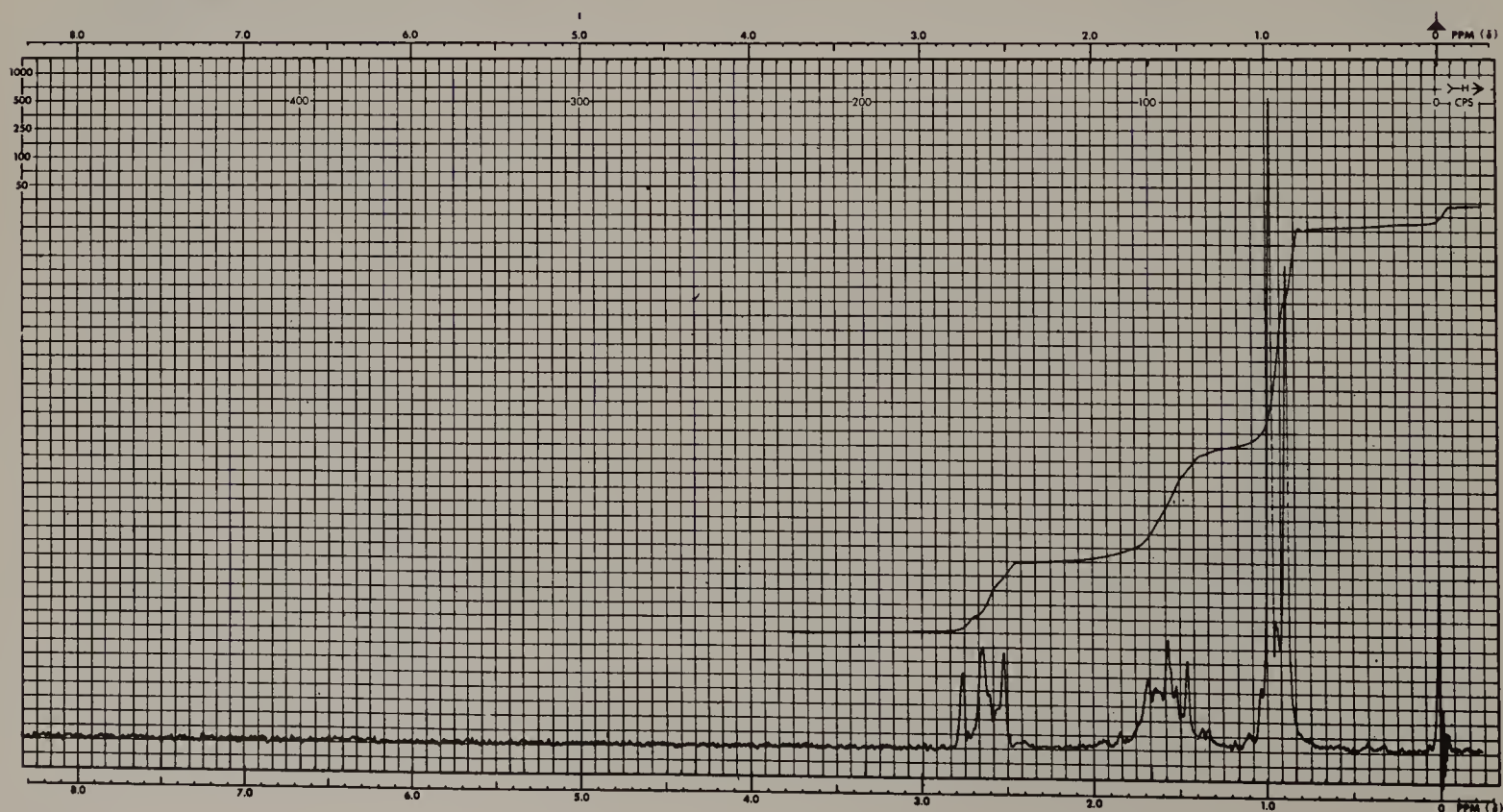


## Mass Spectral Data (Relative Intensities)



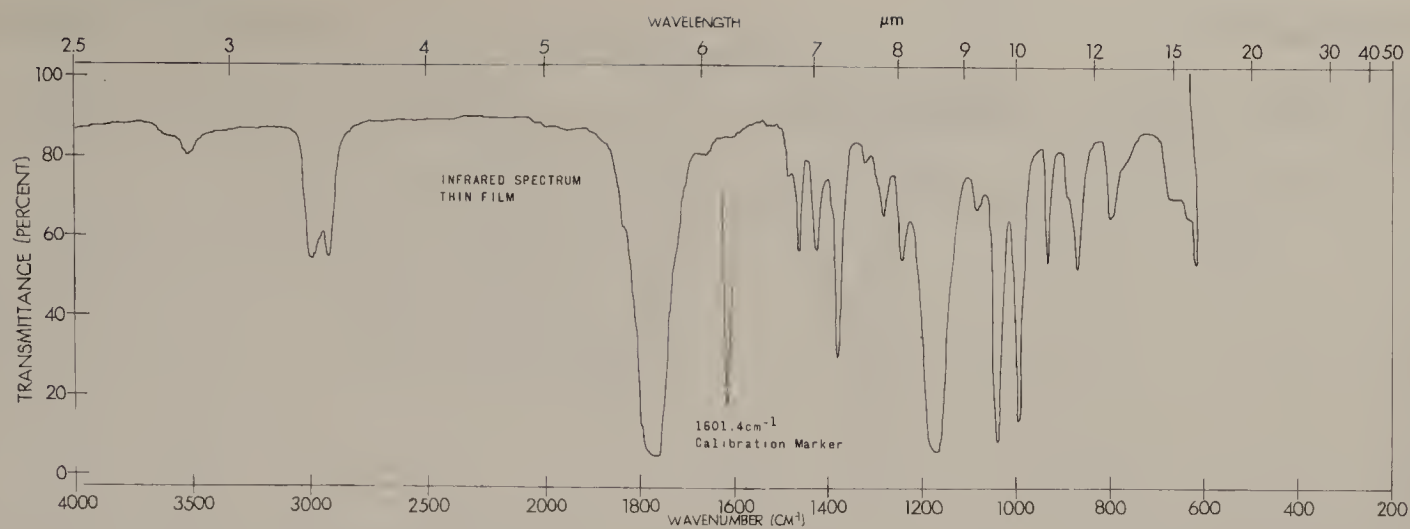
## Ultraviolet Data

| $\lambda_{\max}^{\text{EtOH}}$ | $\log \epsilon_{\max}$ |
|--------------------------------|------------------------|
| 248                            | 2.55                   |

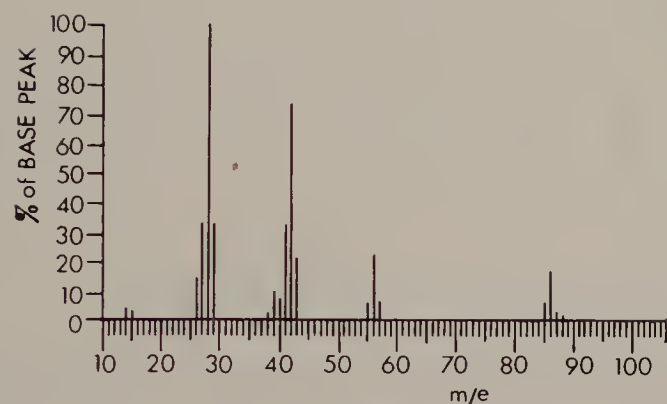
 $^1\text{H}$  NMR Spectrum (Solvent  $\text{CDCl}_3$ )

## Infrared Spectrum

Compound 8-30 Beilstein Ref. 17, 234



## MASS SPECTRAL DATA (Relative Intensity)

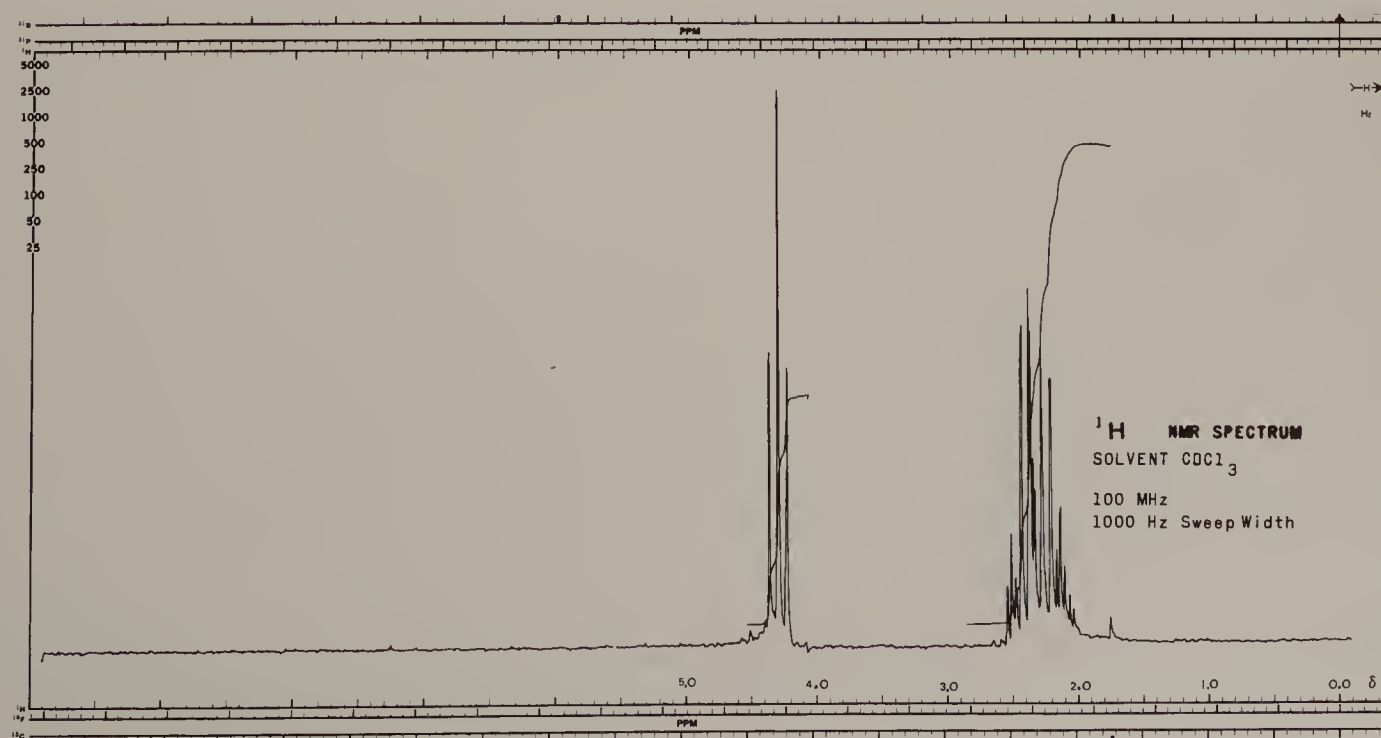


## Mass Spectral Data

| m/e | Relative Intensity |
|-----|--------------------|
| 85  | 34.5               |
| 86  | 100.0              |
| 87  | 10.7               |
| 88  | 0.6                |

## Ultraviolet Data

Transparent above 200nm

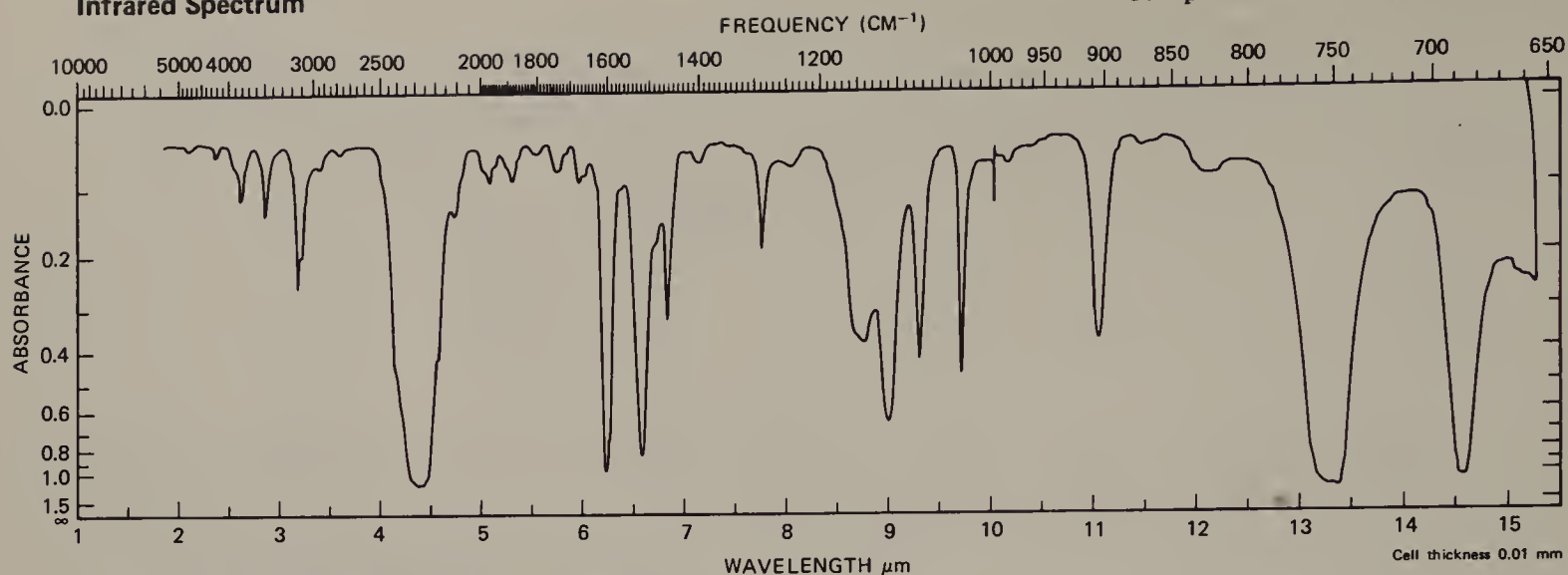




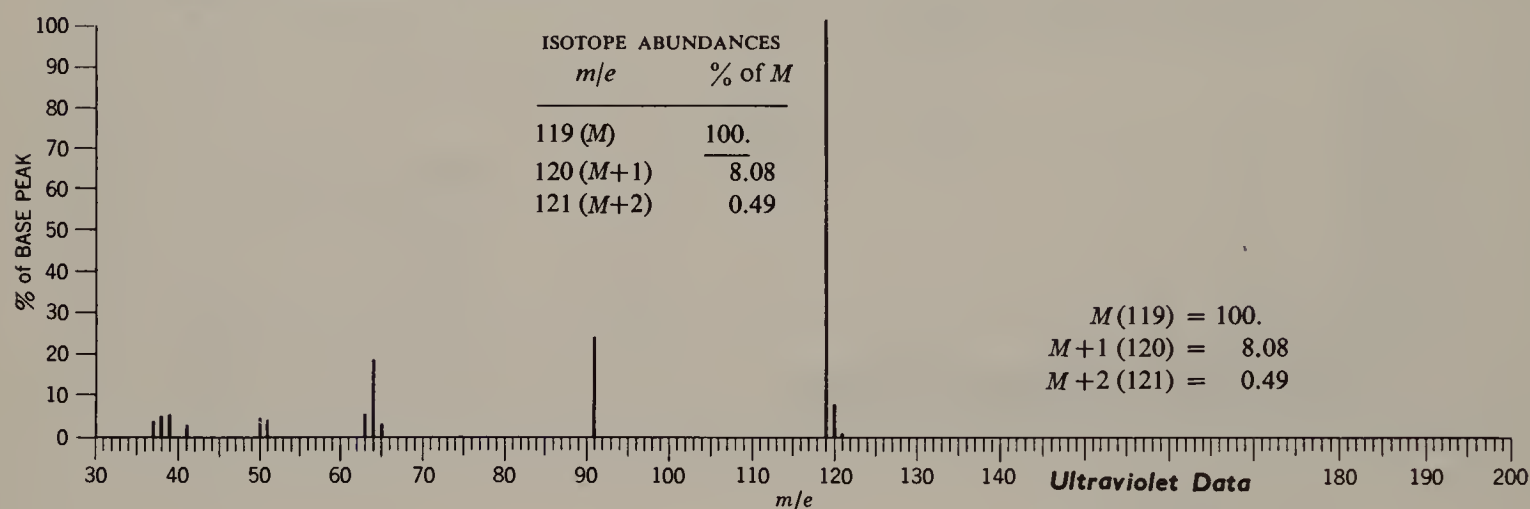
# Infrared Spectrum

Compound 8-31

Beilstein Ref. 12, 437



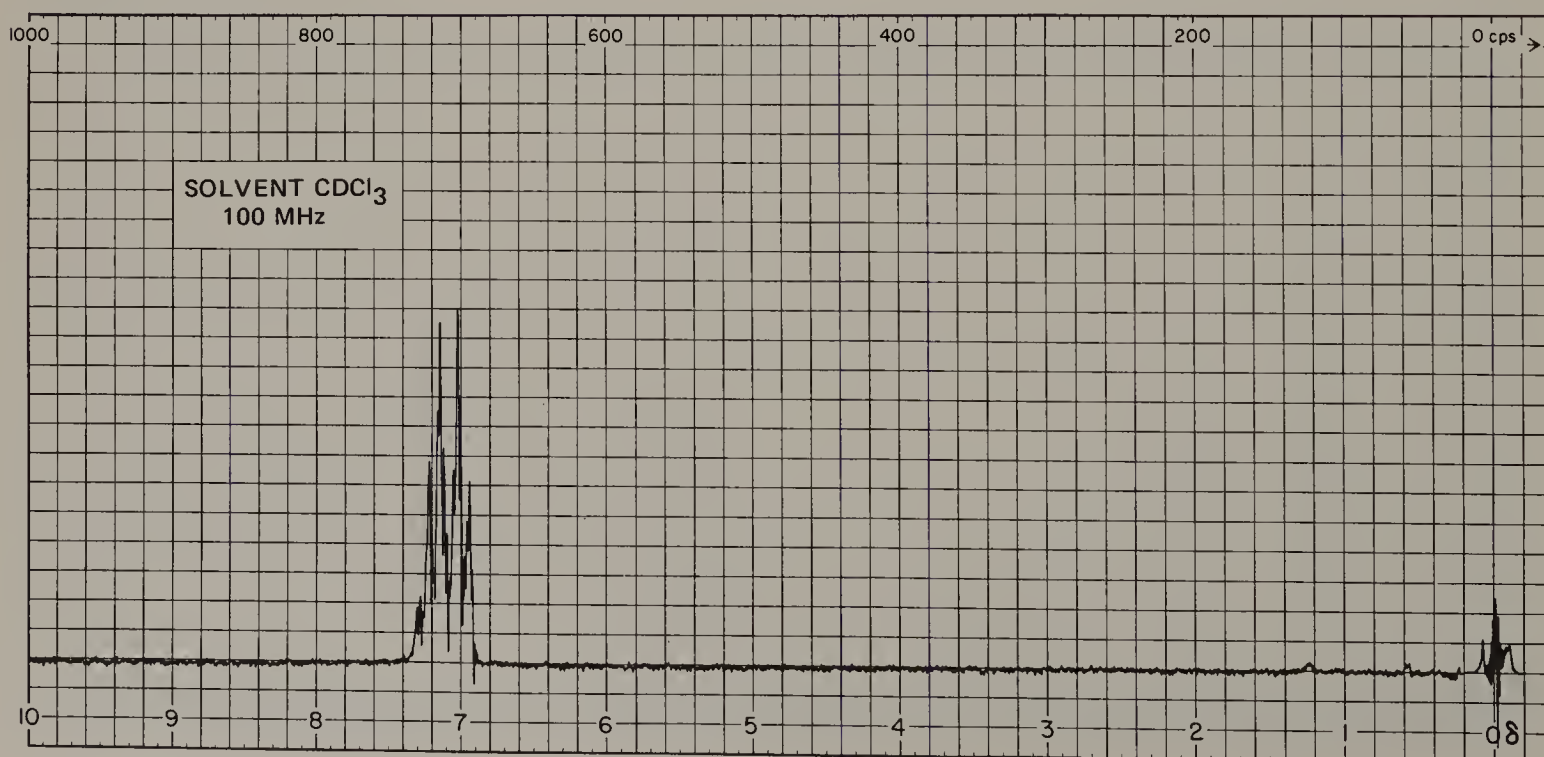
## Mass Spectral Data (Relative Intensities)



## Ultraviolet Data

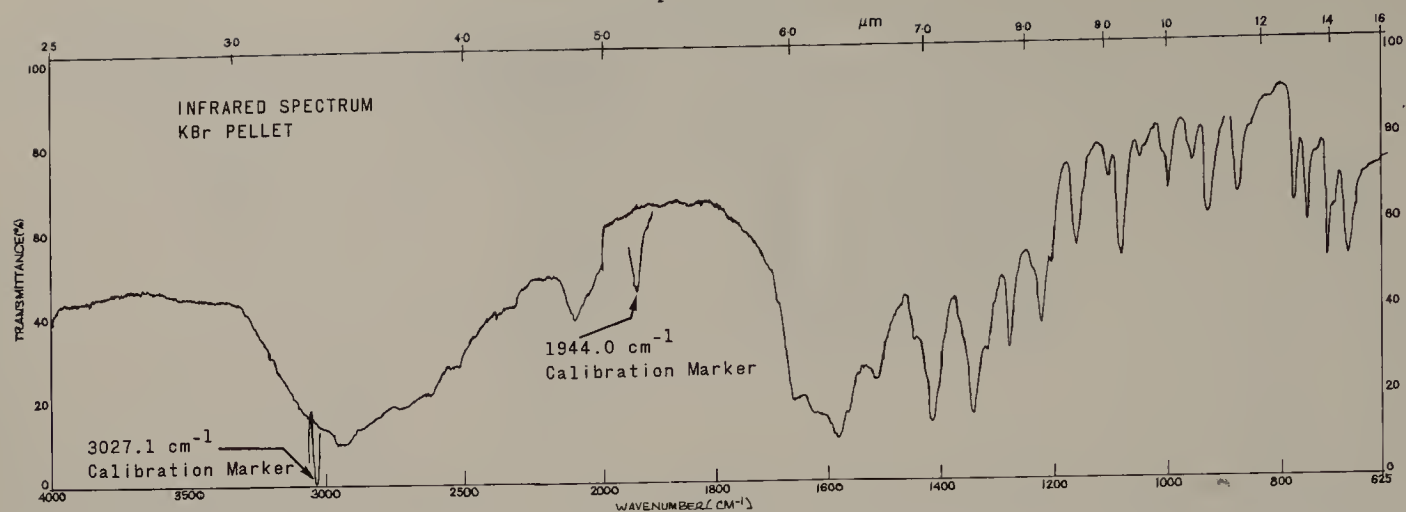
| $\lambda_{\text{max}}^{\text{Hexane}}$ | $\log \epsilon_{\text{max}}$ |     |      |
|--|------------------------------|-----|------|
| 226                                    | 4.04                         |     |      |
| 256                                    | 2.59                         | 270 | 2.76 |
| 263                                    | 2.66                         | 277 | 2.67 |

## <sup>1</sup>H NMR Spectrum

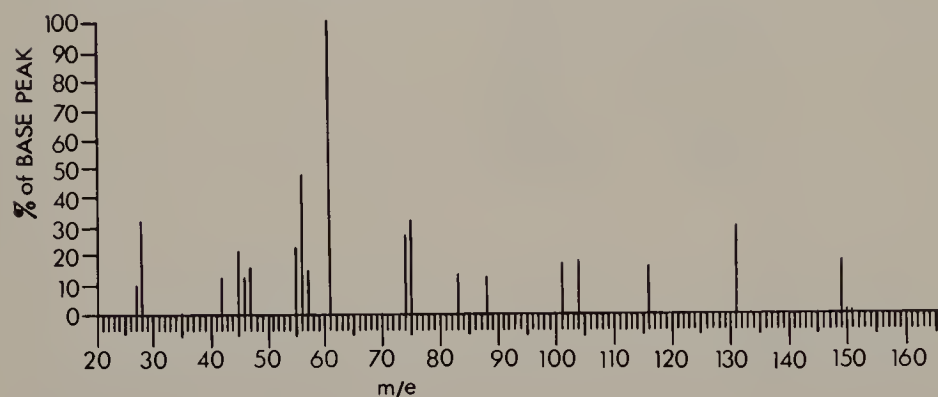


Compound 8-31  $^{13}\text{C}$  NMR Data ( $\text{CDCl}_3$  solvent)

| $\delta$ | Intensity | Off-resonance<br>Decoupled<br>Multiplet |
|----------|-----------|---|
| 124.7    | 90        | <i>s</i>                                |
| 125.7    | 60        | <i>s</i>                                |
| 129.5    | 100       | <i>m</i>                                |
| 133.6    | 10        | <i>s</i>                                |



## MASS SPECTRAL DATA (Relative Intensity)

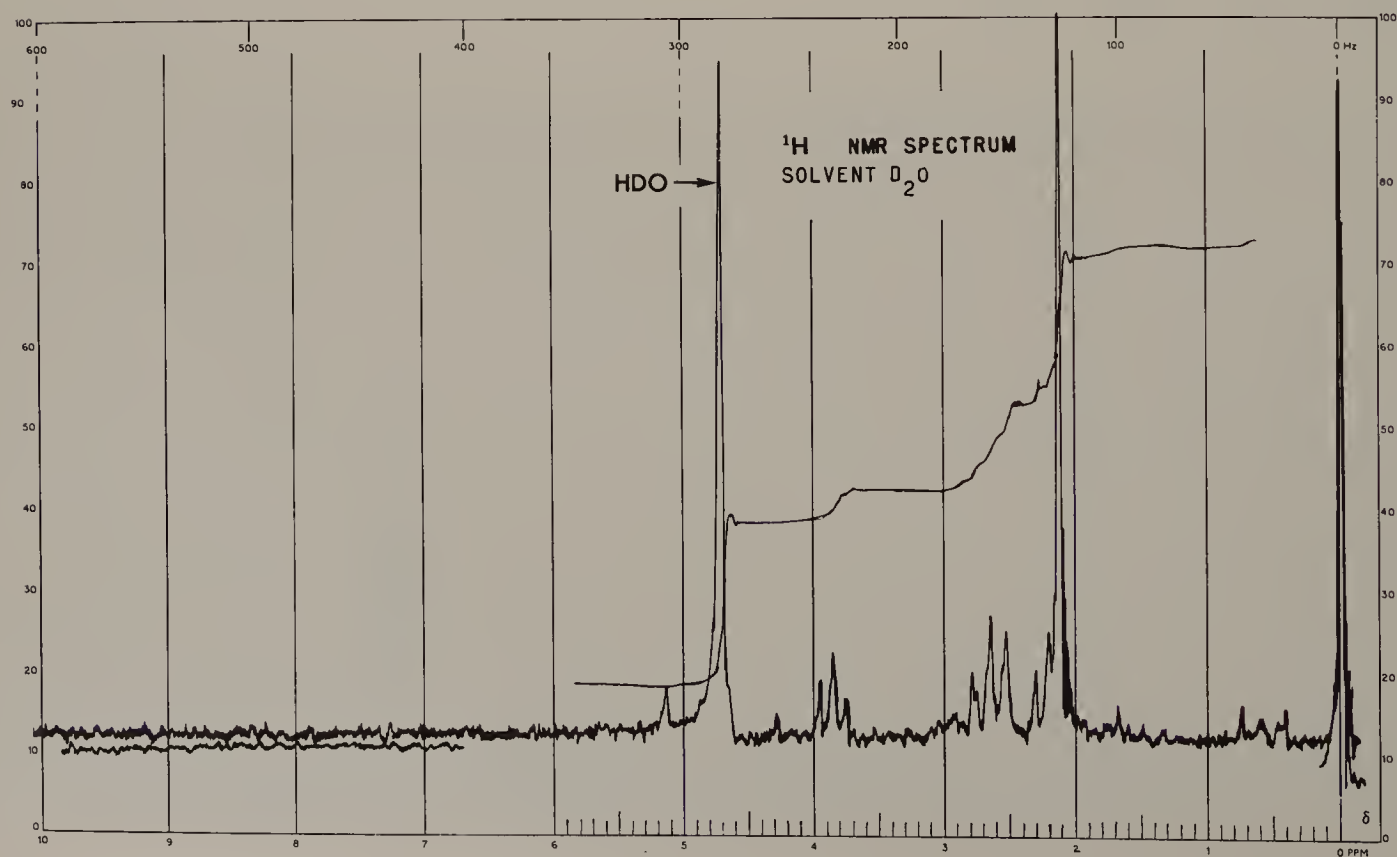


## Mass Spectral Data

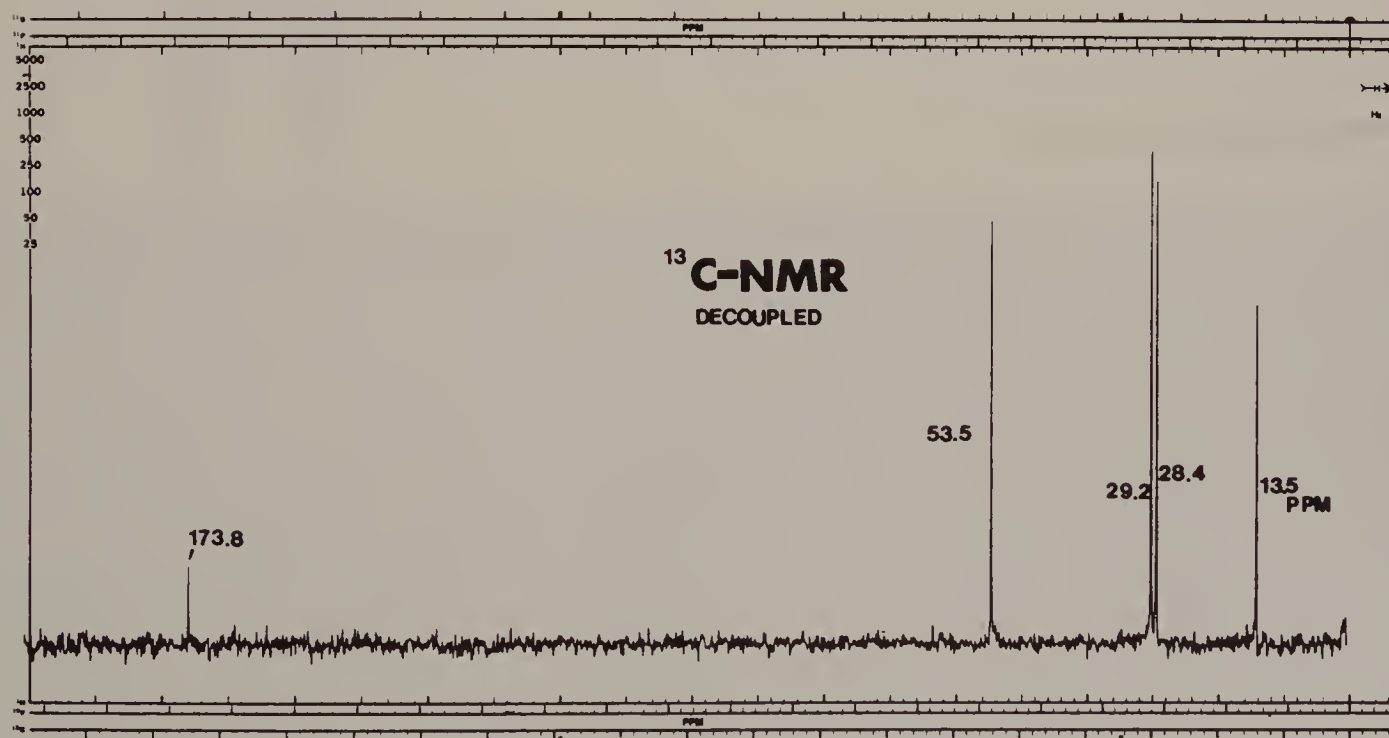
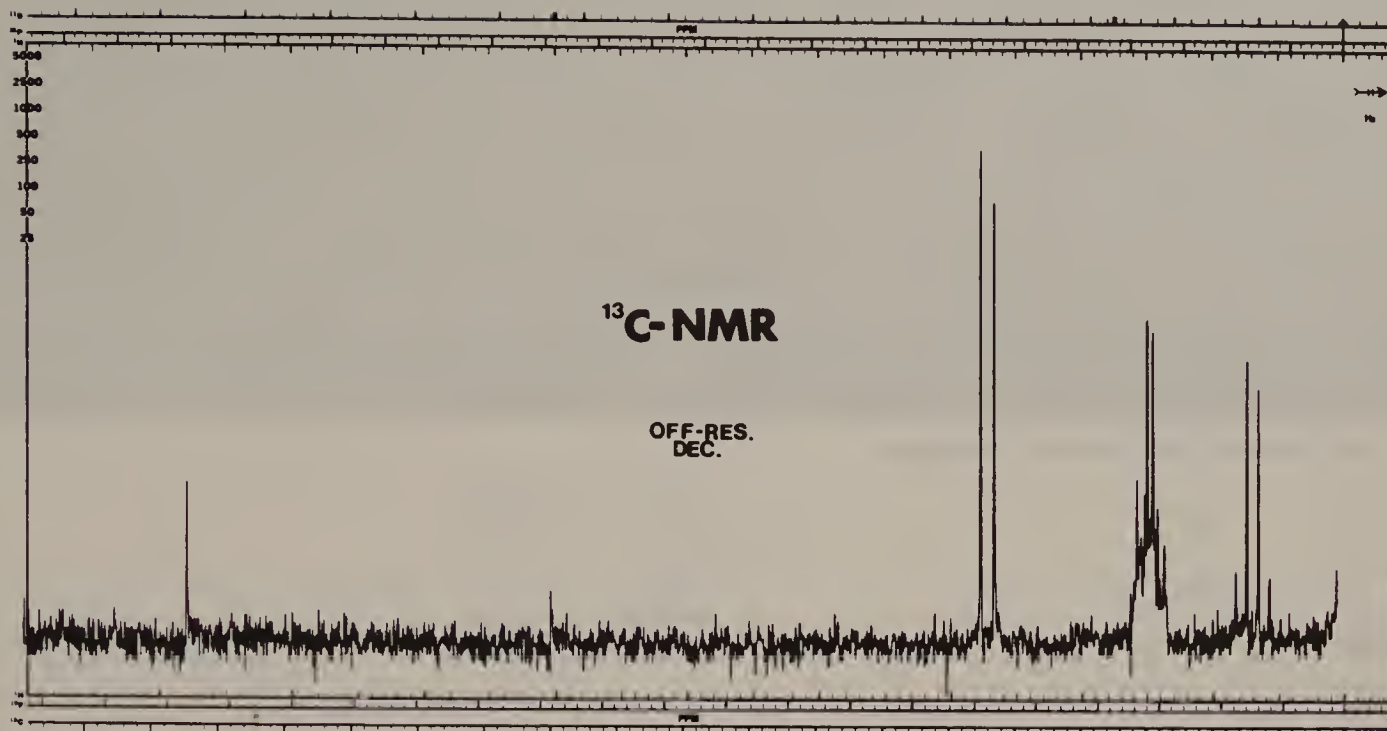
| m/e | Relative Intensity |
|-----|--------------------|
| 149 | 100.0              |
| 150 | 7.8                |
| 151 | 6.1                |

## Ultraviolet Data

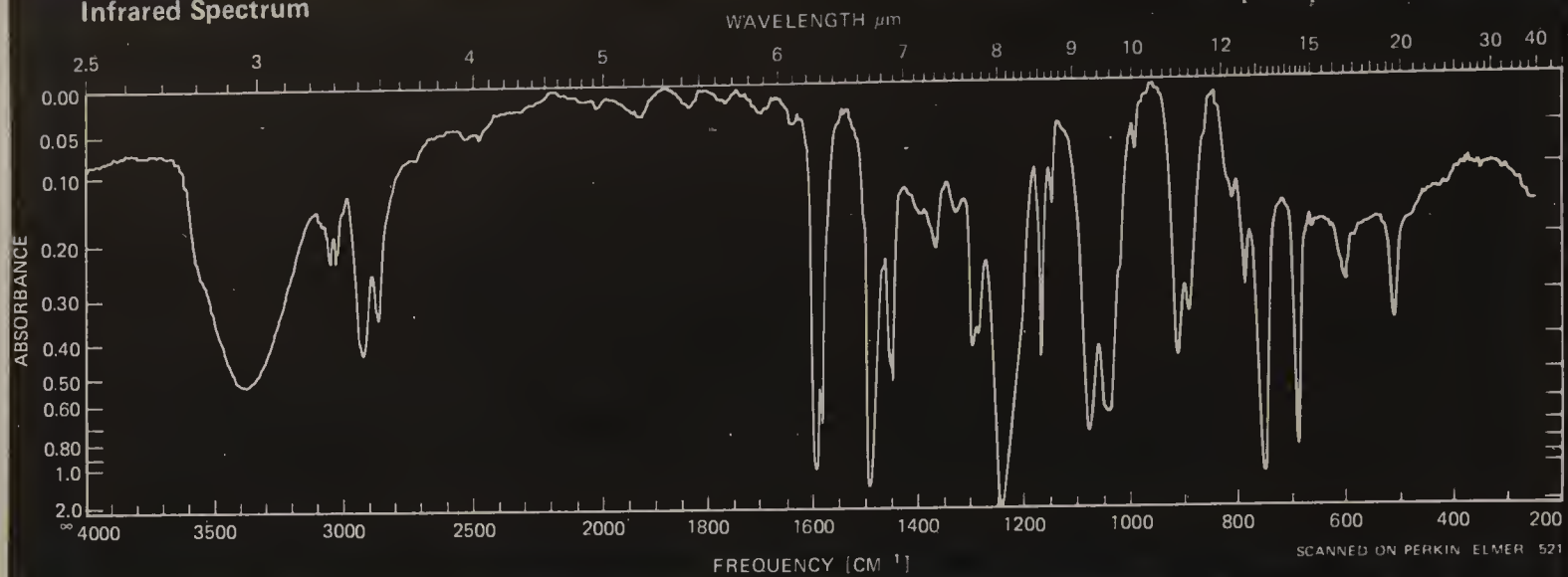
Transparent above 200nm



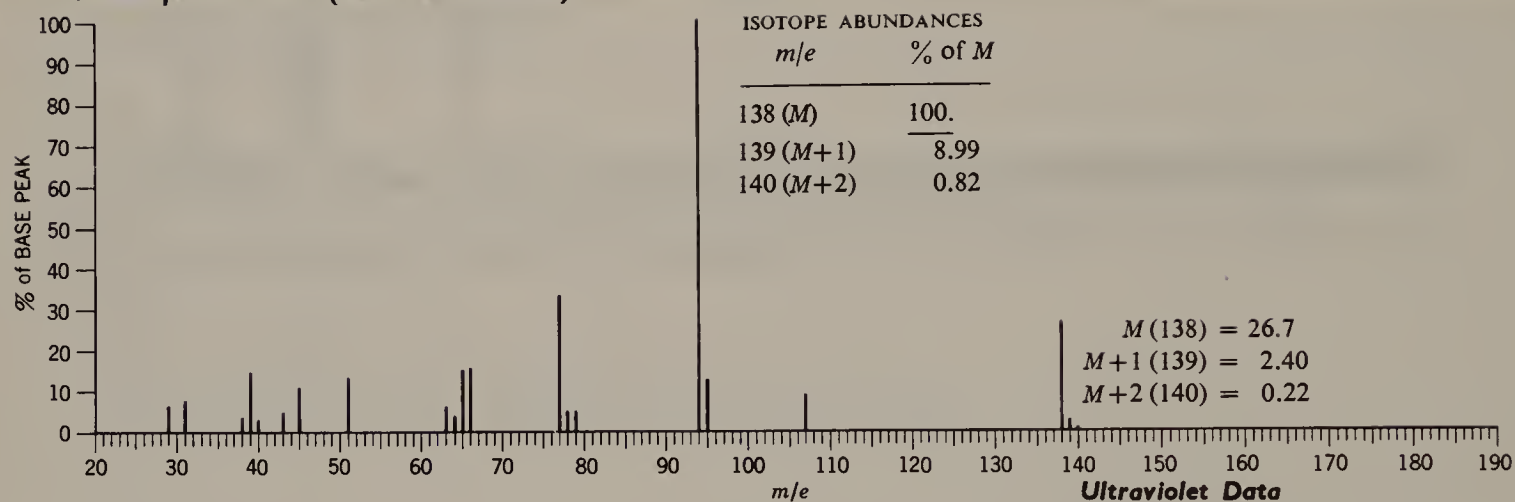




## Infrared Spectrum



## Mass Spectral Data (Relative Intensities)



## Ultraviolet Data

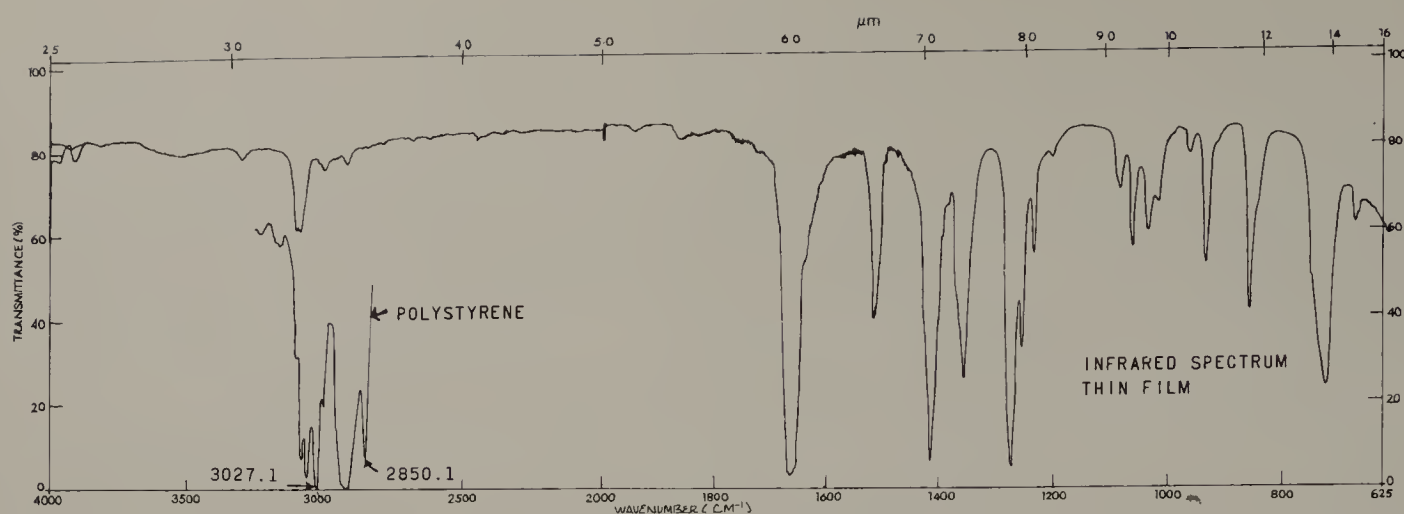
| $\lambda_{\text{Isooctane}}^{\text{max}}$ | $\log \epsilon_{\text{max}}$ |
|---|------------------------------|
| 219                                       | 3.96                         |
| 253                                       | 3.22                         |
| 260                                       | 3.36                         |
| 267                                       | 3.35                         |

 $^1\text{H}$  NMR Spectrum (Solvent  $\text{CCl}_4$ )

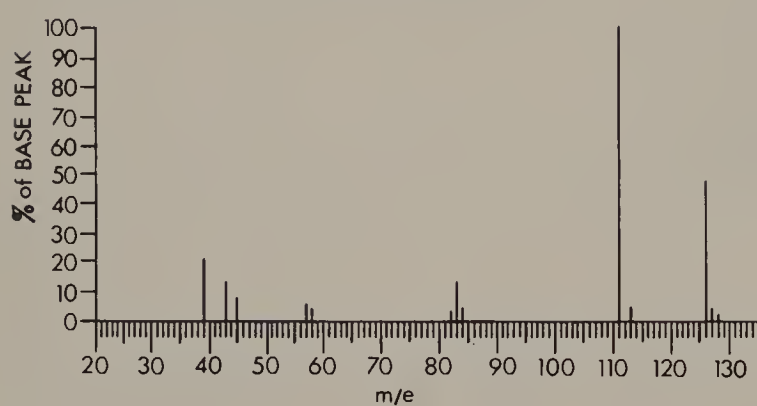
Compound 8-33  $^{13}\text{C}$  NMR Data ( $\text{CDCl}_3$  solvent)

| $\delta$ | Intensity | Off-resonance<br>Decoupled<br>Multiplet |
|----------|-----------|---|
| 60.9     | 40.0      | <i>t</i>                                |
| 69.1     | 47.1      | <i>t</i>                                |
| 114.6    | 88.4      | <i>d</i>                                |
| 120.9    | 38.8      | <i>d</i>                                |
| 129.5    | 100.0     | <i>d</i>                                |
| 158.8    | 18.1      | <i>s</i>                                |





## MASS SPECTRAL DATA (Relative Intensity)



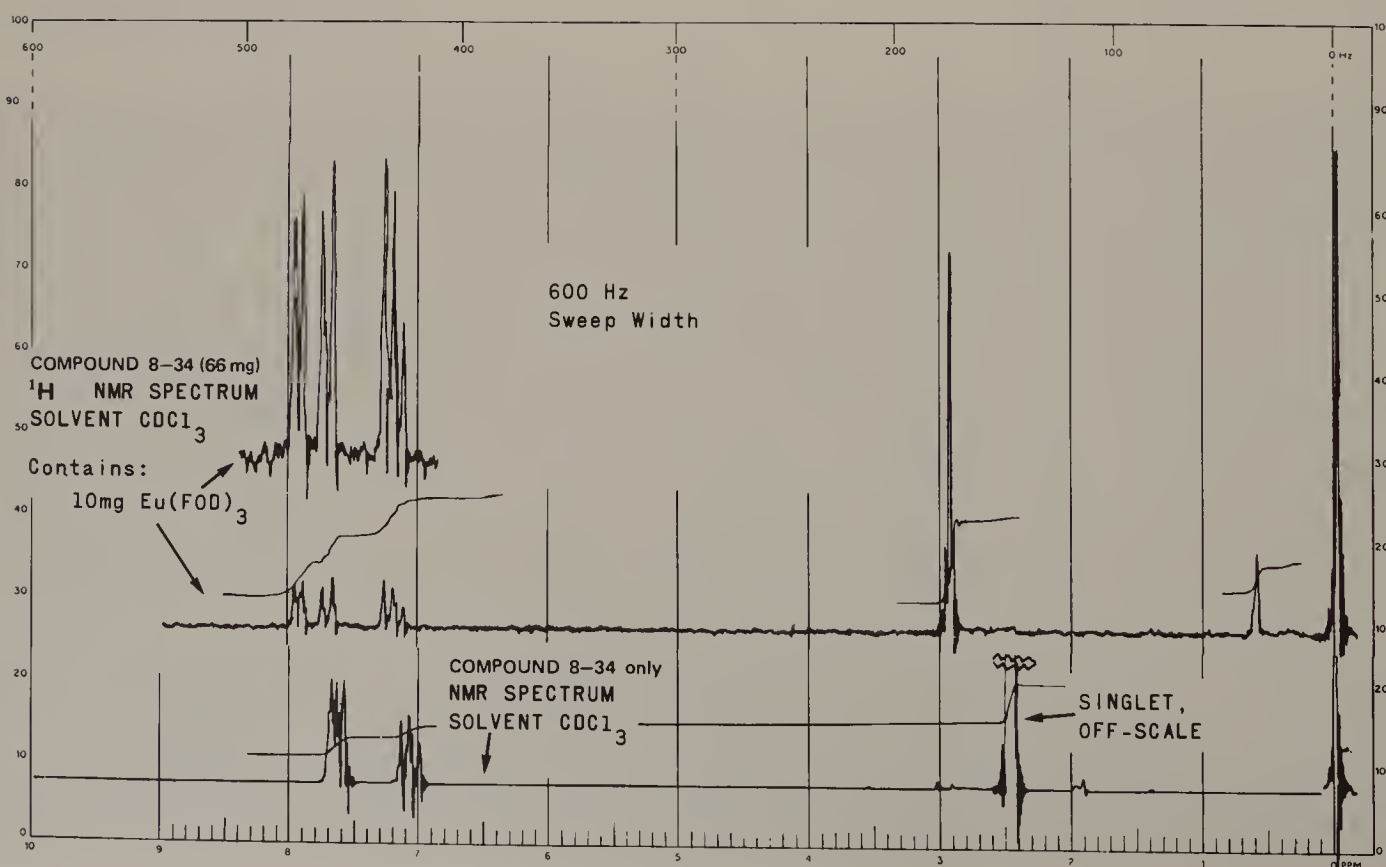
Mass Spectral Data

Molecular Weight 126.0135

(High Resolution Analysis)

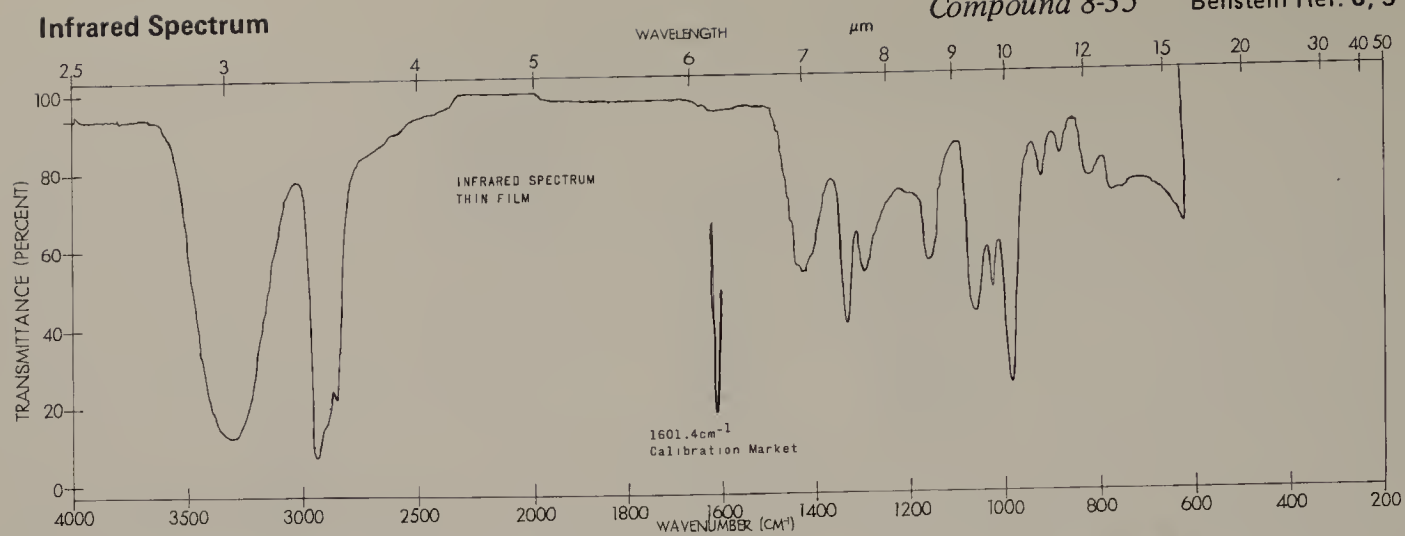
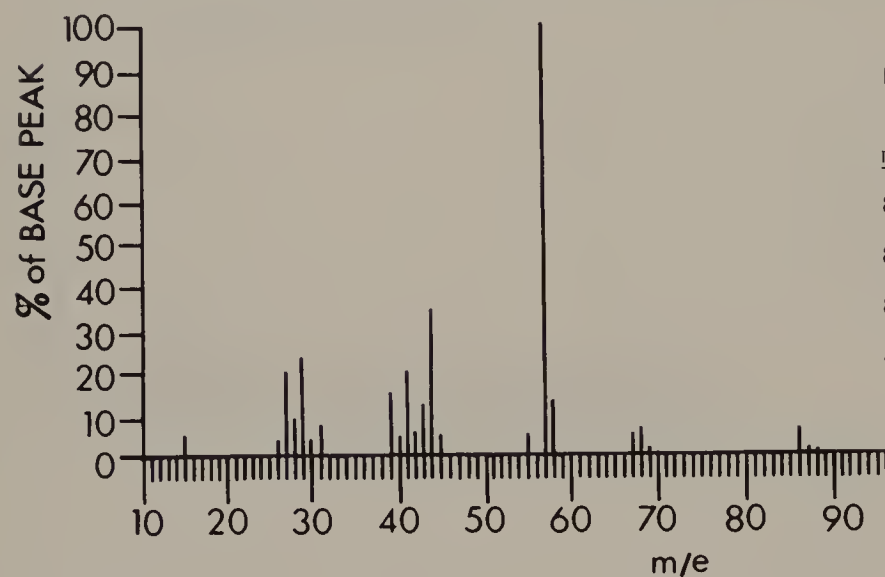
## Ultraviolet Data

| $\lambda_{\max}$<br>(CH <sub>3</sub> OH) | $\epsilon_{\max}$ |
|--|-------------------|
| 257                                      | 10,500            |
| 280                                      | 7,200             |



Compound 8-34  $^{13}\text{C}$  NMR Data ( $\text{CDCl}_3$  solvent)

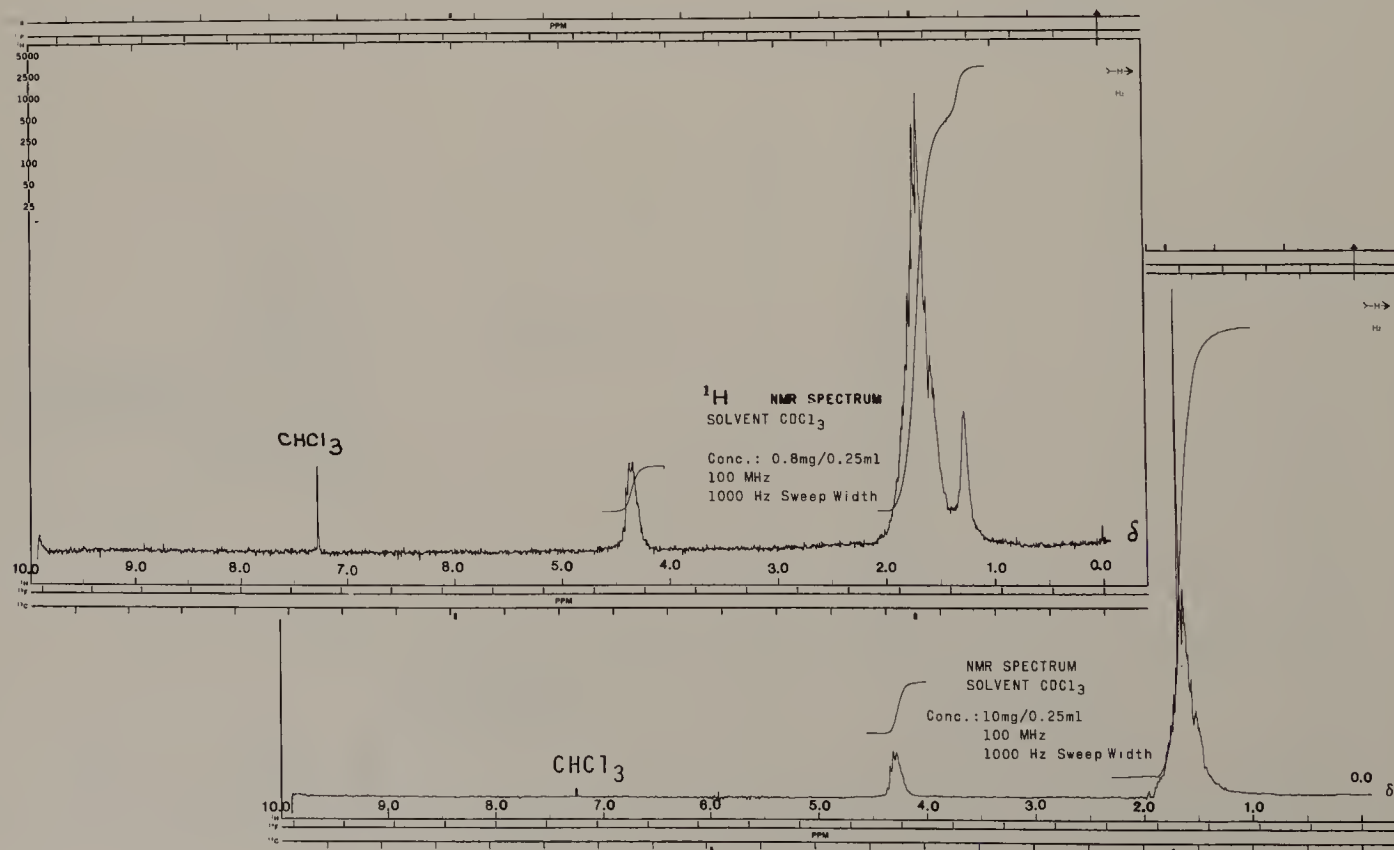
| $\delta$ | Intensity | Off-resonance<br>Decoupled<br>Multiplet |
|----------|-----------|---|
| 26.6     | 76.0      | <i>q</i>                                |
| 128.3    | 89.8      | <i>d</i>                                |
| 132.8    | 100.0     | <i>d</i>                                |
| 133.8    | 98.4      | <i>d</i>                                |
| 144.6    | 25.0      | <i>s</i>                                |
| 190.4    | 34.9      | <i>s</i>                                |

**MASS SPECTRAL DATA (Relative Intensity)****Mass Spectral Data**

| m/e | Relative Intensity |
|-----|--------------------|
| 85  | 10.70              |
| 86  | 100.00             |
| 87  | 6.66               |
| 88  | 1.33               |

**Ultraviolet Data**

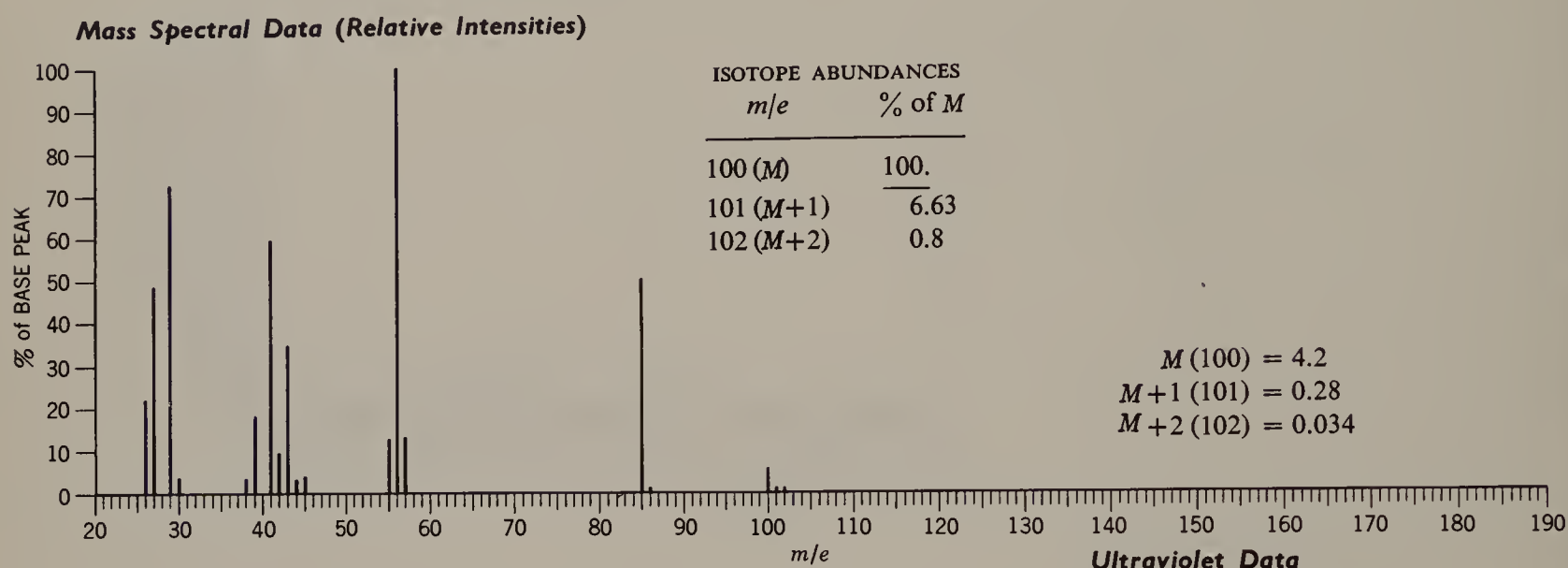
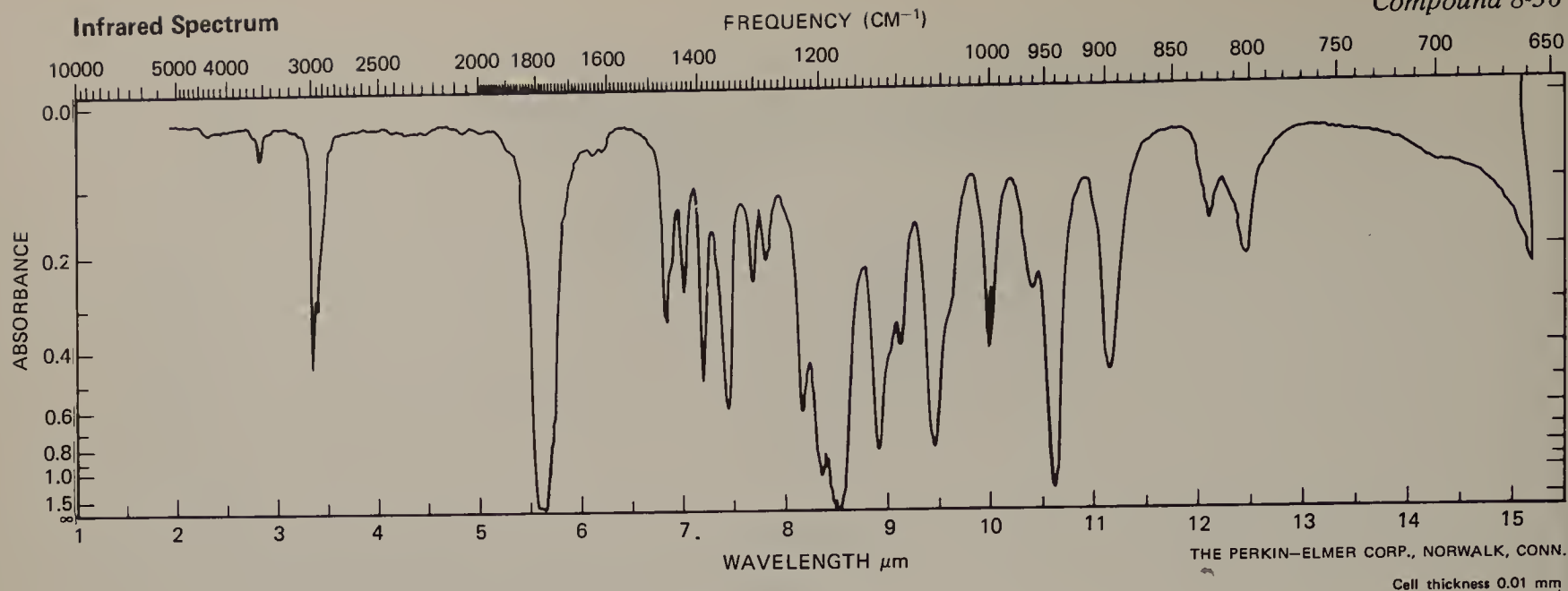
Transparent above 200nm



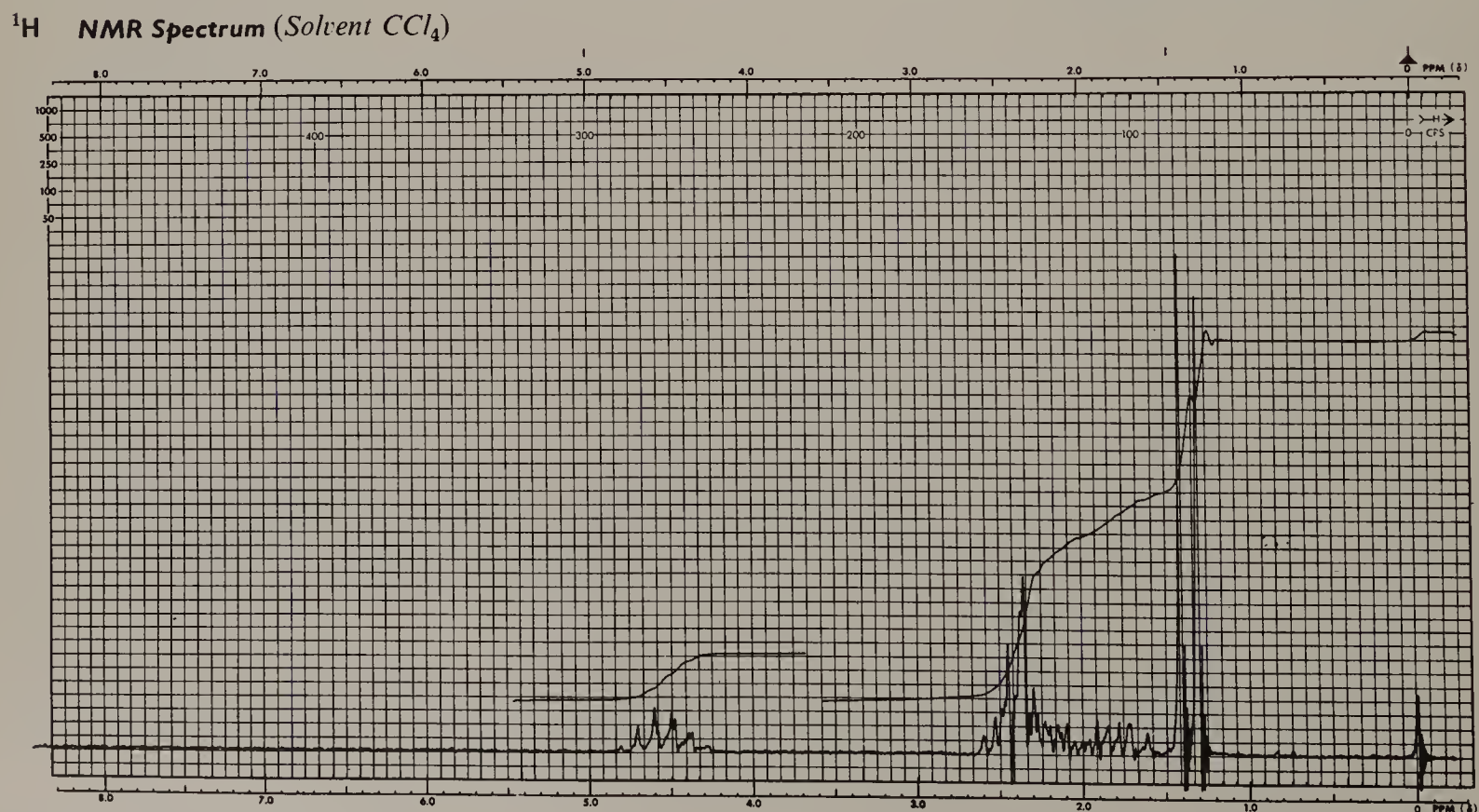


Compound 8-35  $^{13}\text{C}$  NMR Data (Dioxane solvent)

| $\delta$ | Off-resonance<br>Decoupled<br>Multiplet |
|----------|---|
| 23.40    | <i>t</i>                                |
| 35.00    | <i>t</i>                                |
| 73.30    | <i>d</i>                                |

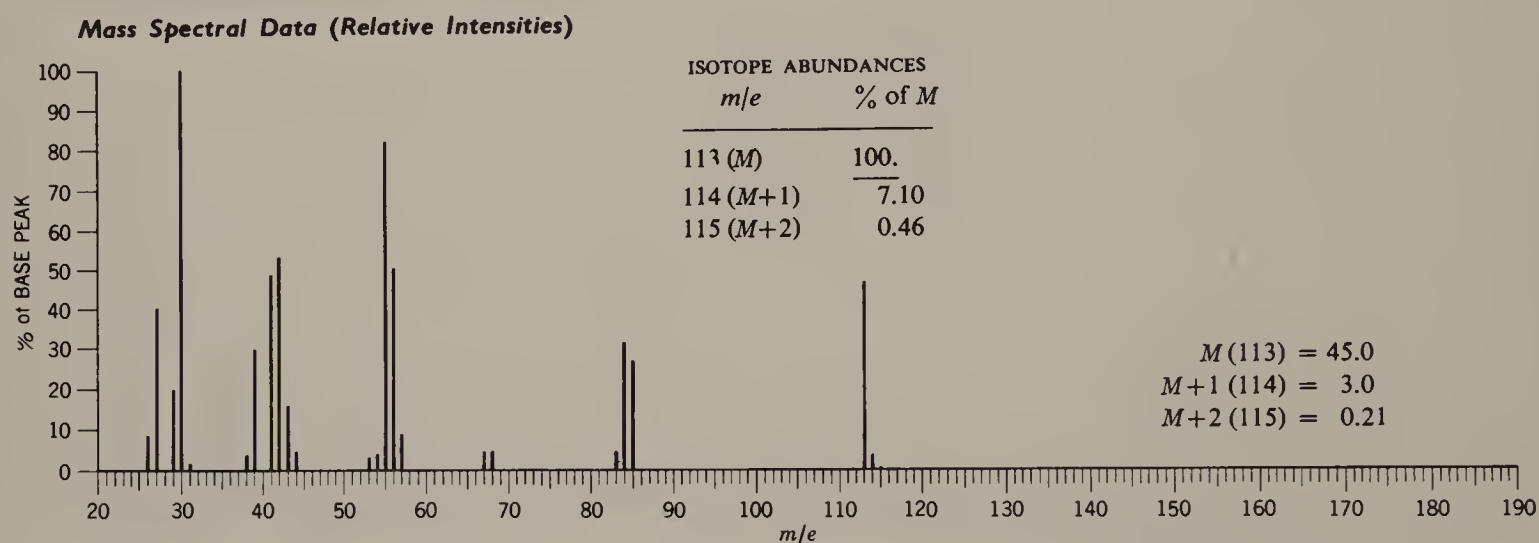
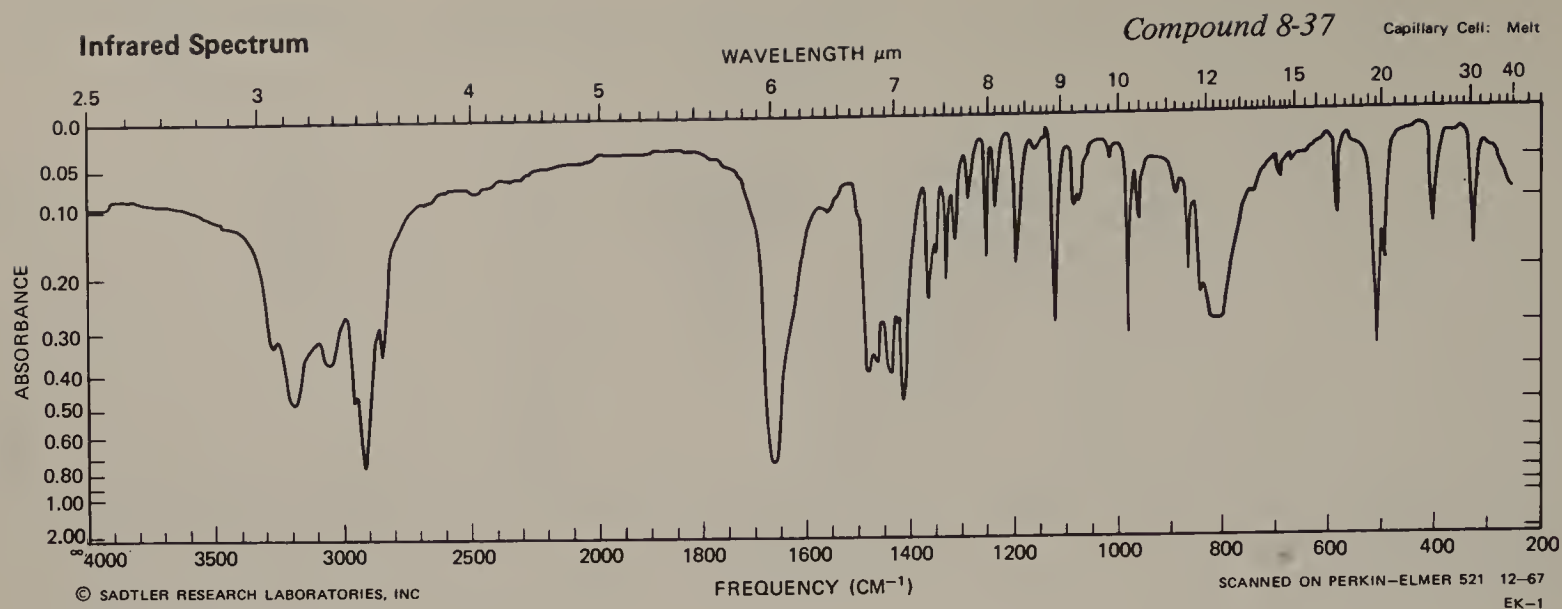
**Ultraviolet Data**

Transparent above 200 nm

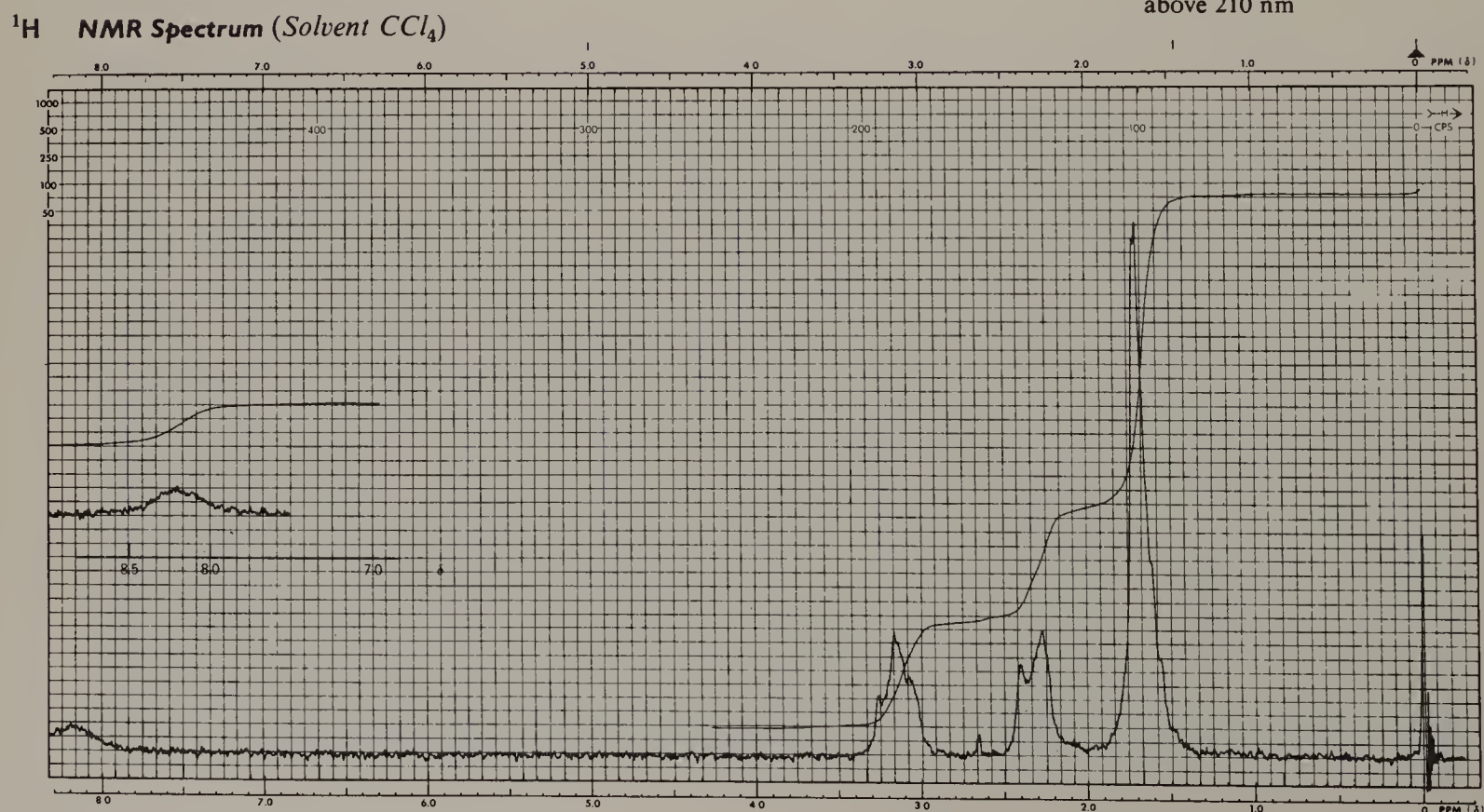


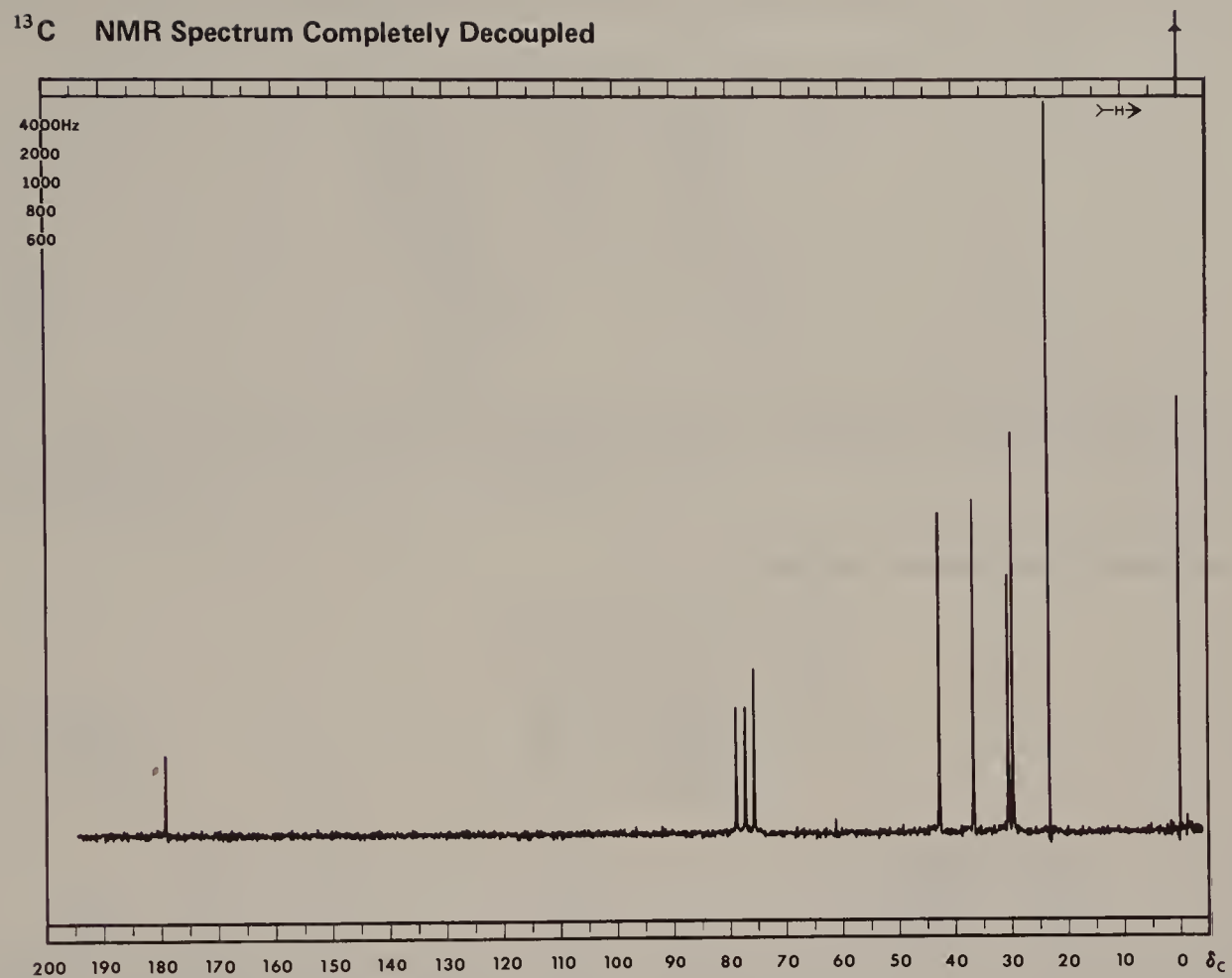
notes

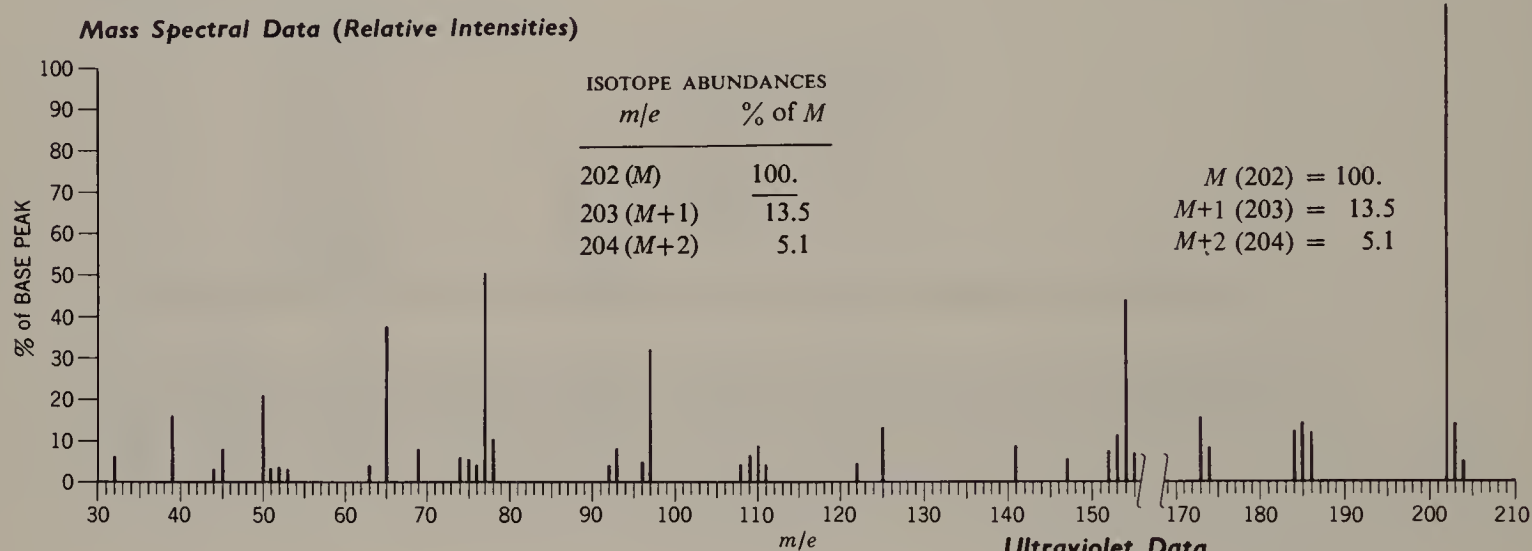
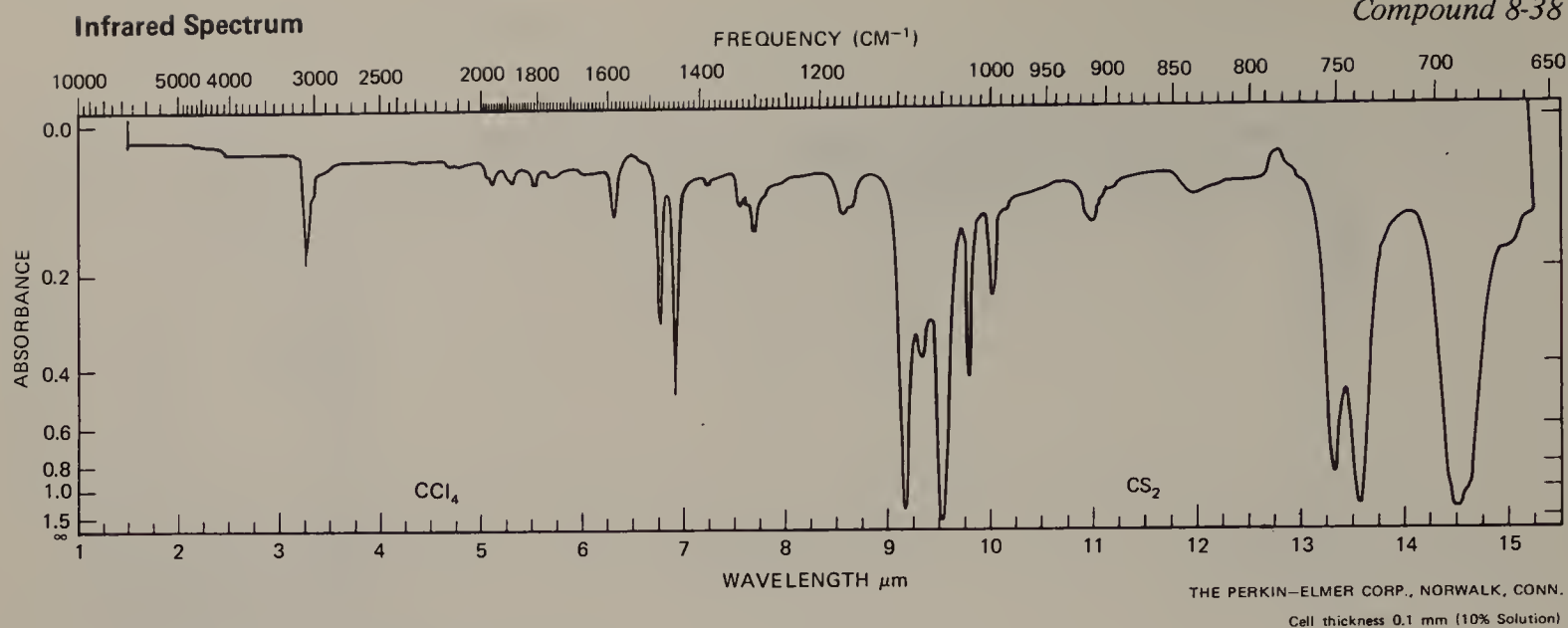




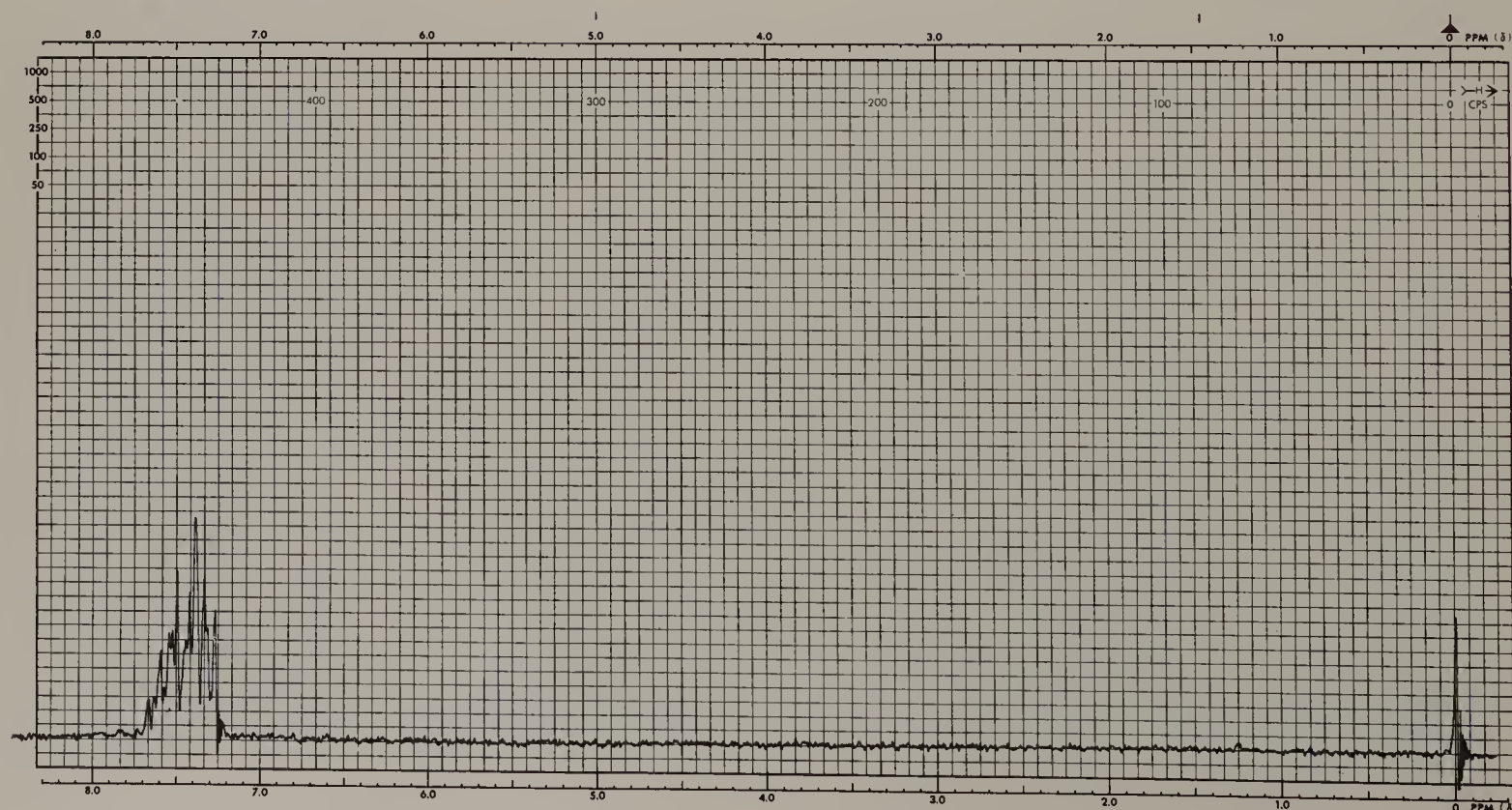
**Ultraviolet Data**  
*EtOH*-Featureless  
 above 210 nm





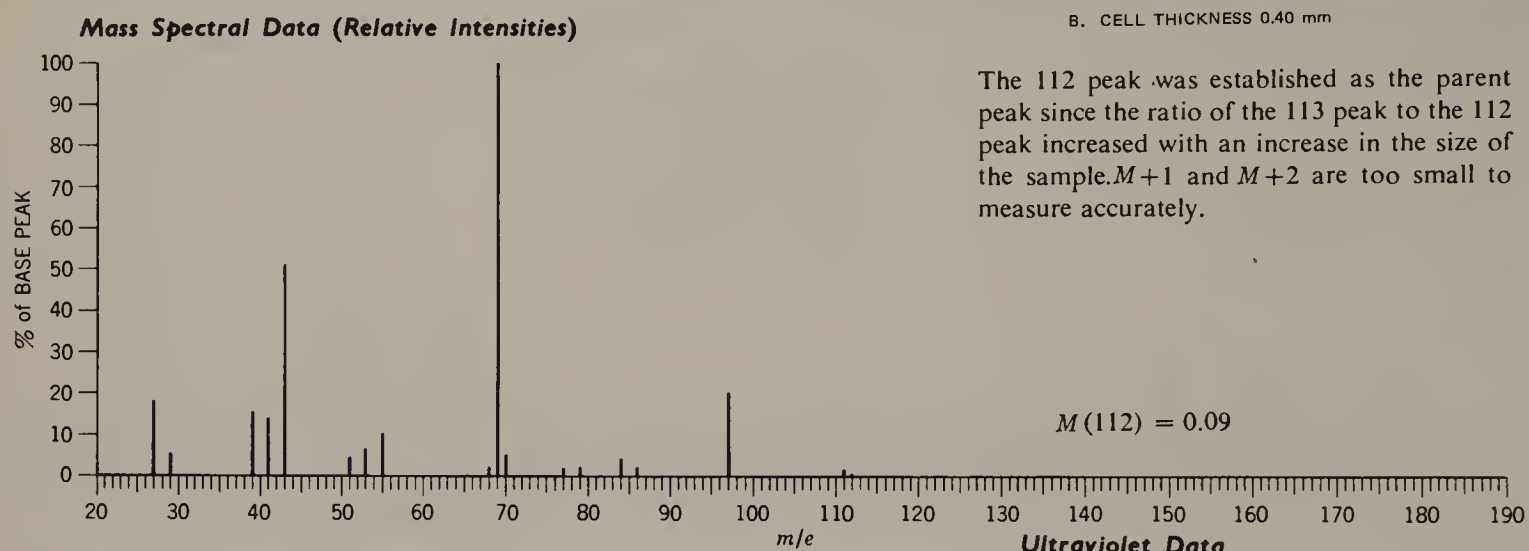
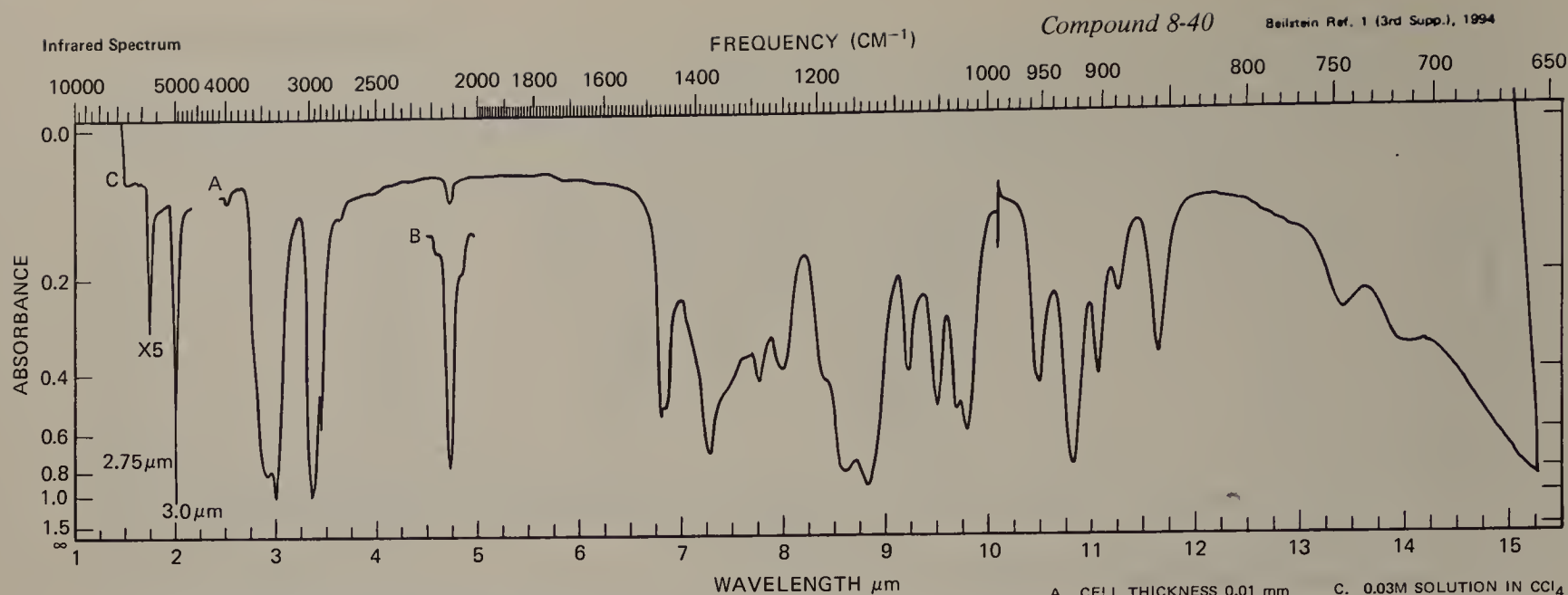
**Ultraviolet Data**

| $\lambda_{\text{max}}^{\text{EtOH}}$ | $\log \epsilon_{\text{max}}$ | 262 (s)        | 3.38 |
|--------------------------------------|------------------------------|----------------|------|
| 232                                  | 4.15                         | (s) = shoulder |      |

**<sup>1</sup>H NMR Spectrum (Solvent CCl<sub>4</sub>)**



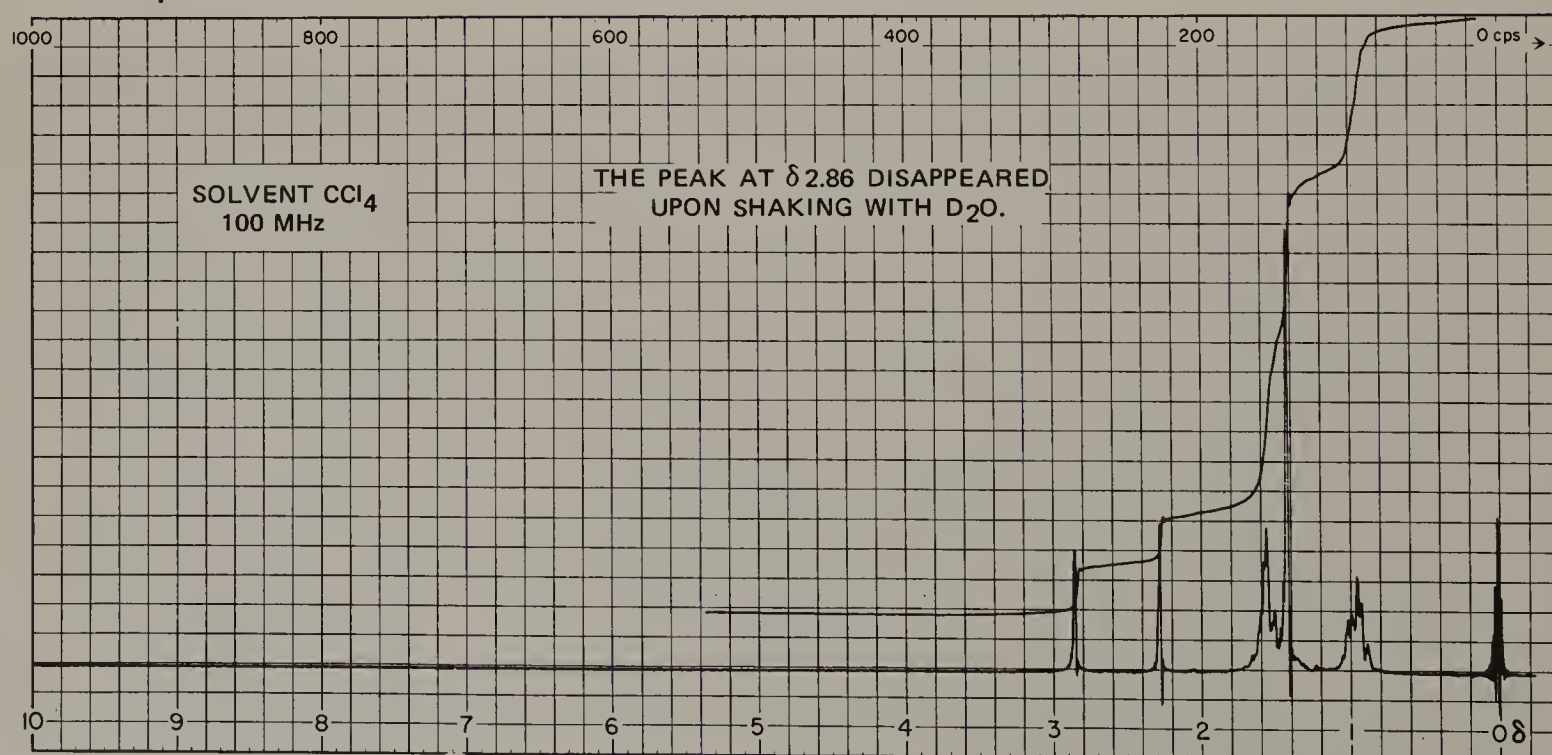




Ultraviolet Data

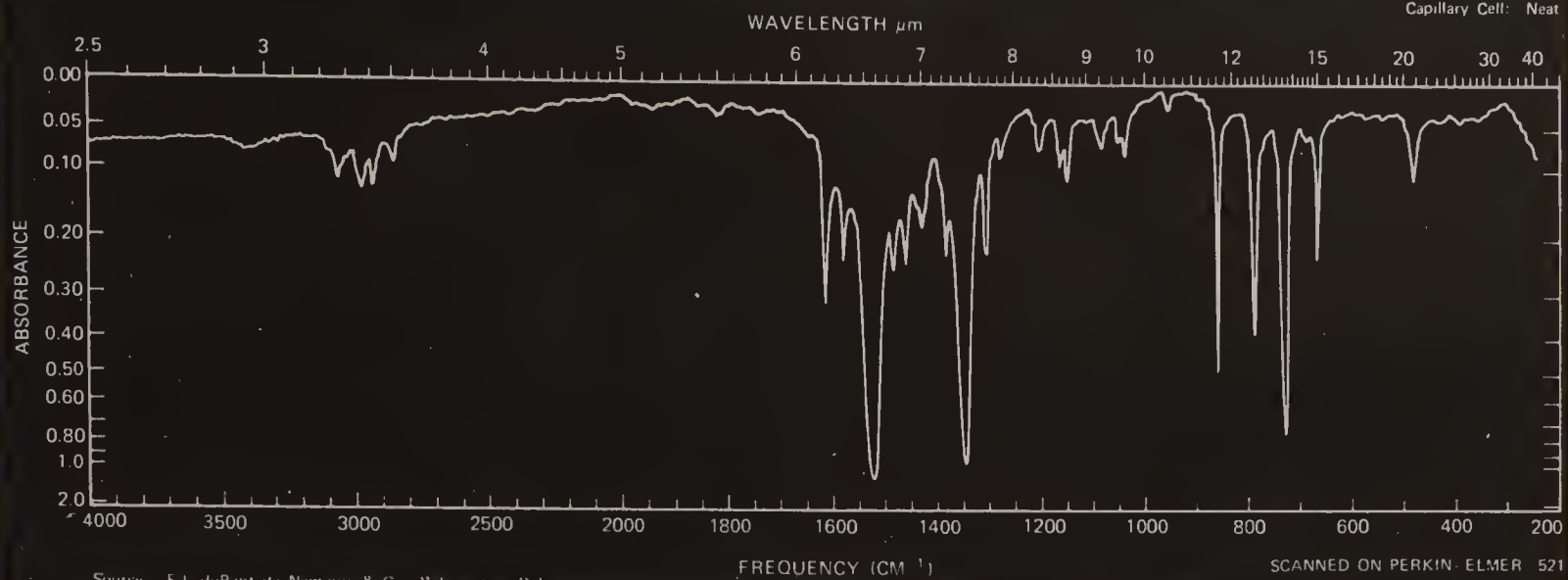
Transparent beyond 200 nm

<sup>1</sup>H NMR Spectrum

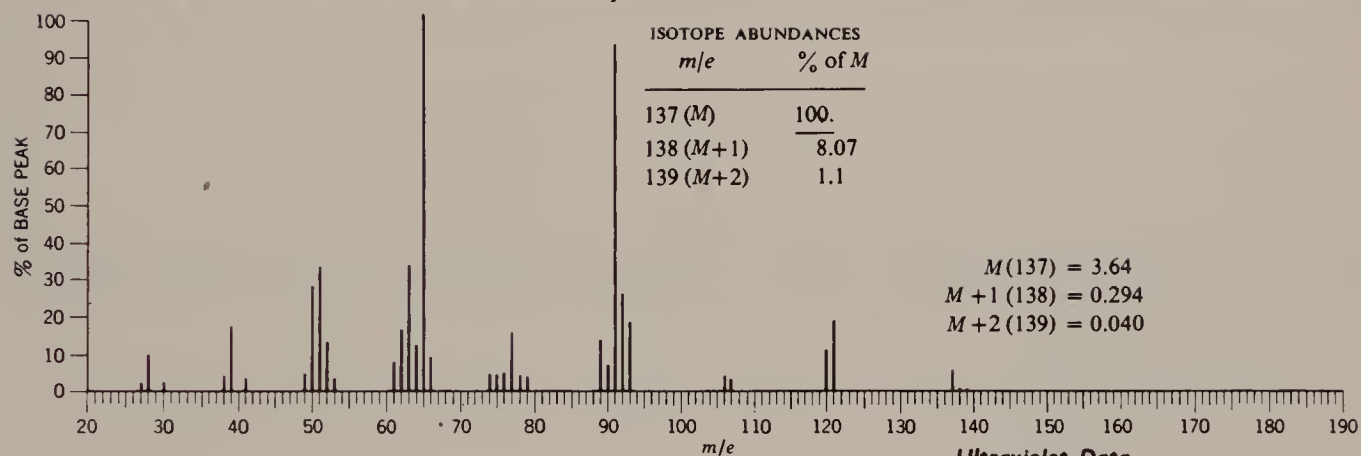


## Infrared Spectrum

Compound 8-41

Beilstein Ref. 5, 318  
Capillary Cell: Neat

## Mass Spectral Data (Relative Intensities)

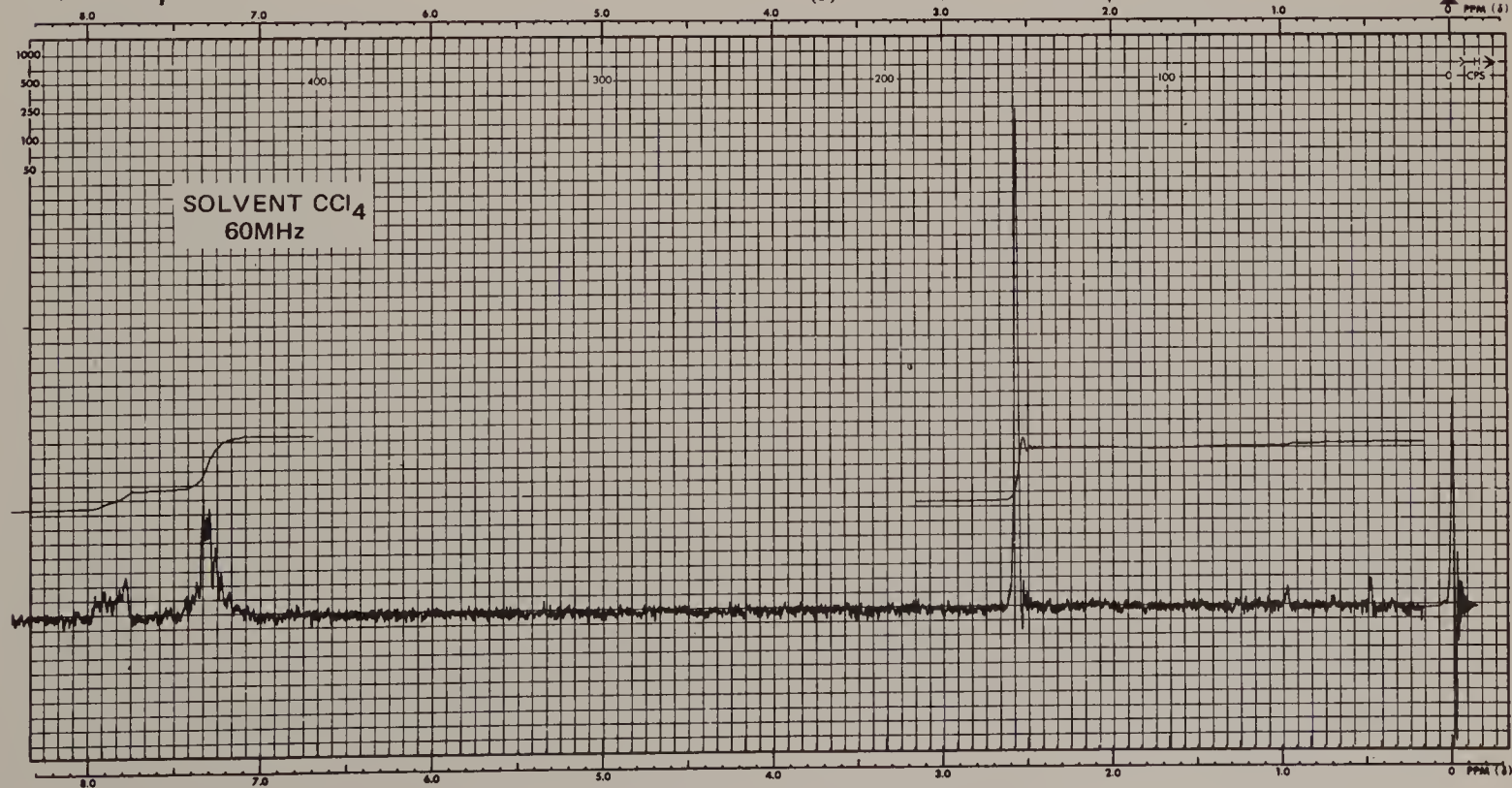


## Ultraviolet Data

| $\lambda_{\text{max}}^{\text{isooctane}}$ | $\log \epsilon_{\text{max}}$ |
|---|------------------------------|
| 251                                       | 3.78                         |
| 285 (s)                                   | 3.21                         |
| 330                                       | 2.44                         |

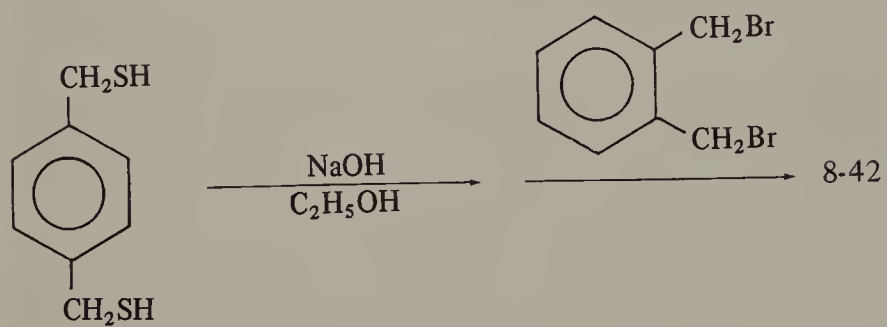
 $^1\text{H}$  NMR Spectrum

(s) = shoulder

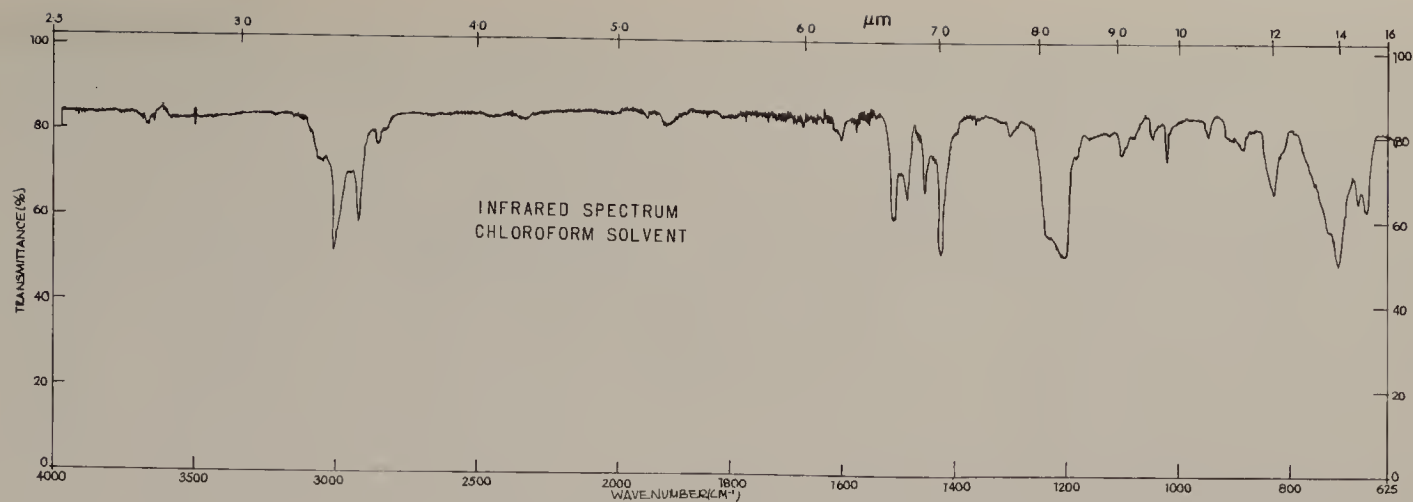




Treatment of an ethyl alcohol solution of  $\alpha,\alpha'$ -dimer-capto-*p*-xylene with sodium hydroxide, followed by  $\alpha,\alpha'$ -dibromo-*o*-xylene treatment resulted in compound 8-42:



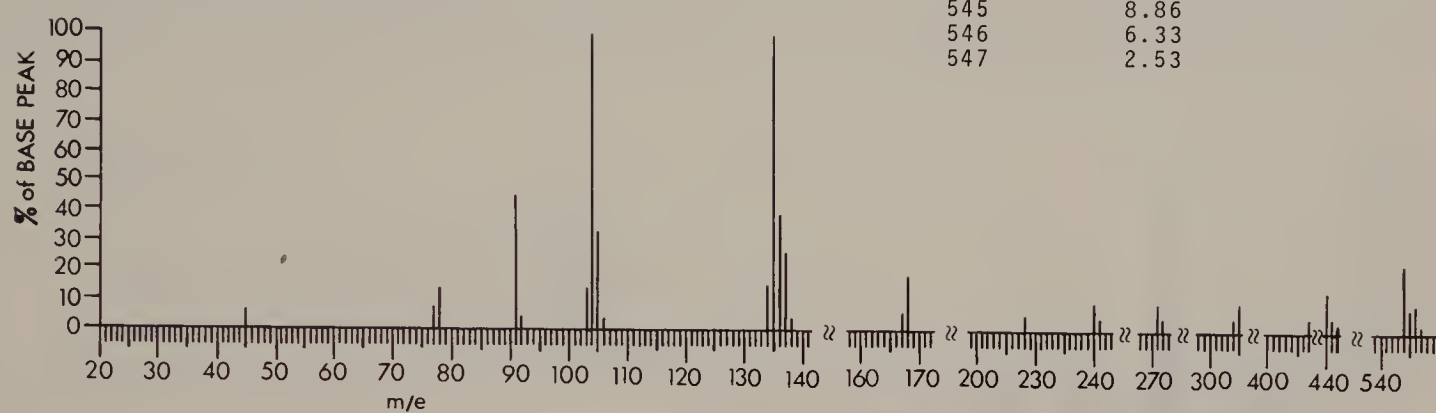
Deduce the structure of 8-42 from the spectra provided.



## Mass Spectral Data

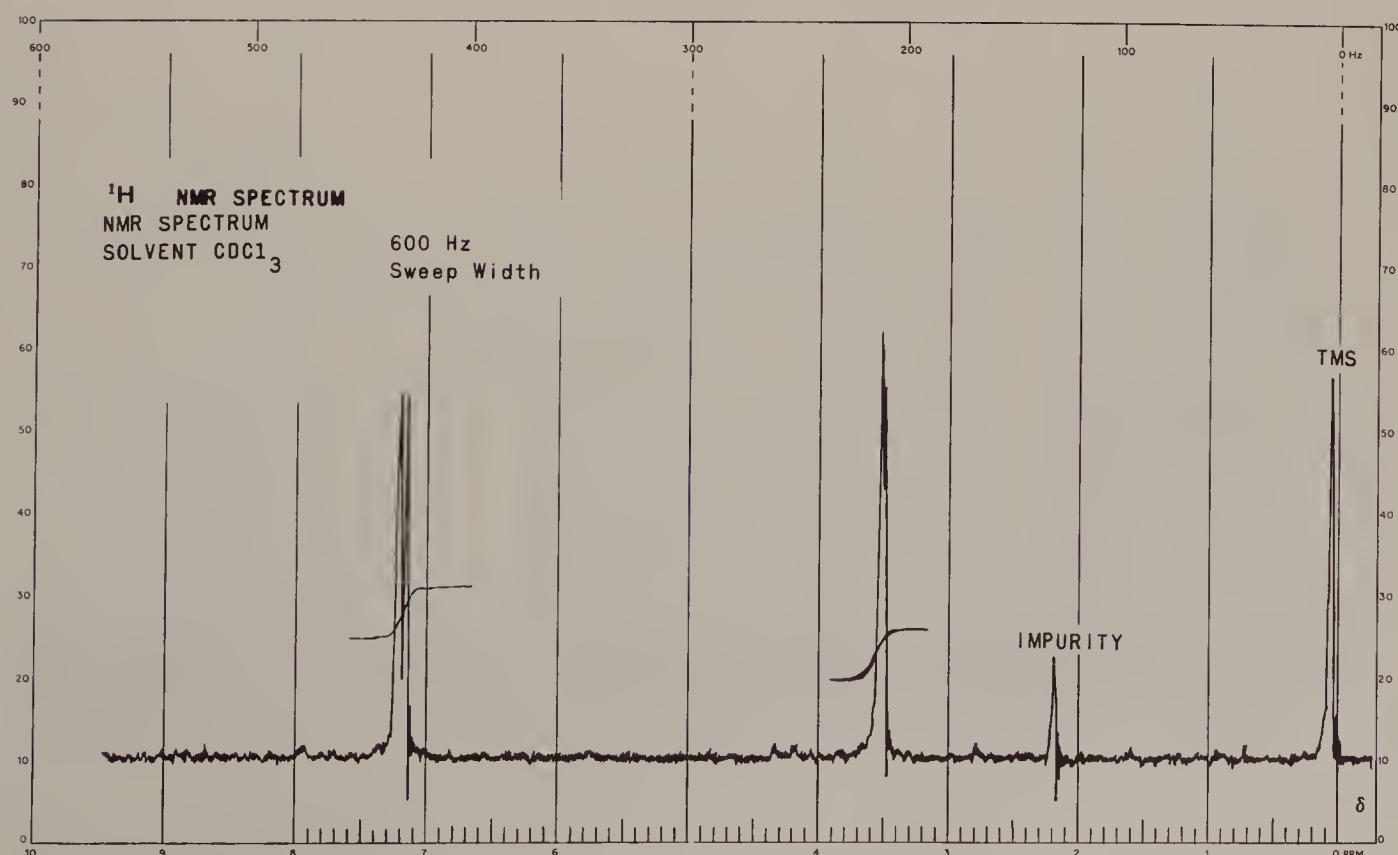
## MASS SPECTRAL DATA (Relative Intensity)

| m/e | Raw Intensity Data |
|-----|--------------------|
| 544 | 22.78              |
| 545 | 8.86               |
| 546 | 6.33               |
| 547 | 2.53               |

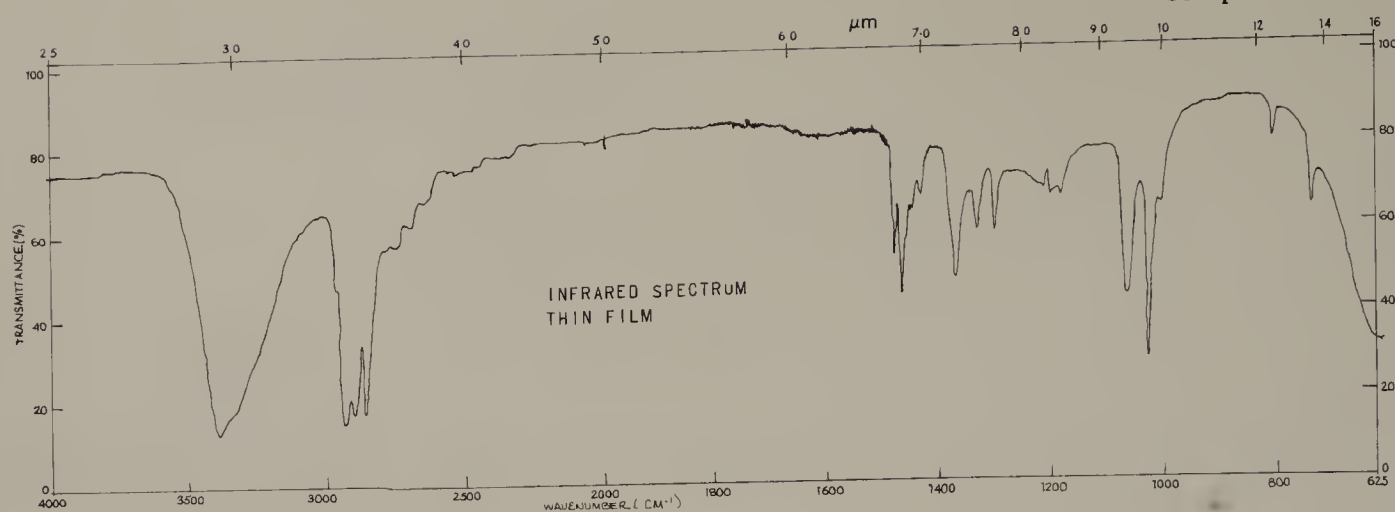


## Ultraviolet Data

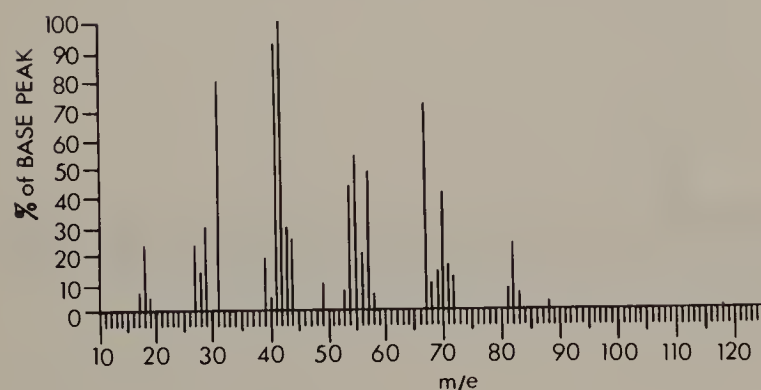
| $\lambda_{\max}$<br>(CH <sub>3</sub> CH <sub>2</sub> OH) | $\epsilon_{\max}$ |
|--|-------------------|
| 267  | 10,600            |
| 215(s)   | 11,780            |



# Compound 8-43



## MASS SPECTRAL DATA (Relative Intensity)



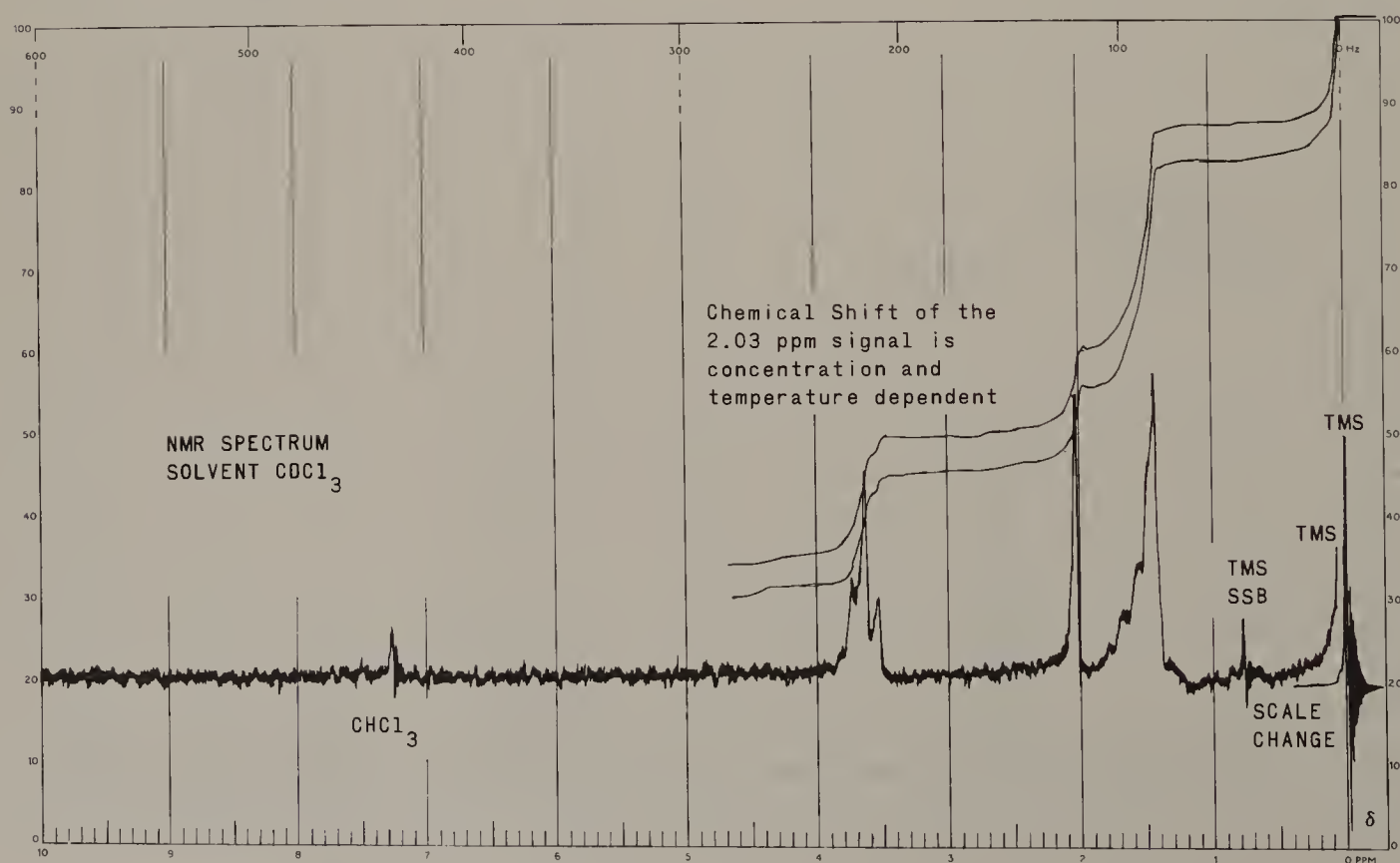
## Mass Spectral Data

Molecular Ion at  $m/e$  118;  
M+1, M+2 too weak to be measured

## Ultraviolet Data

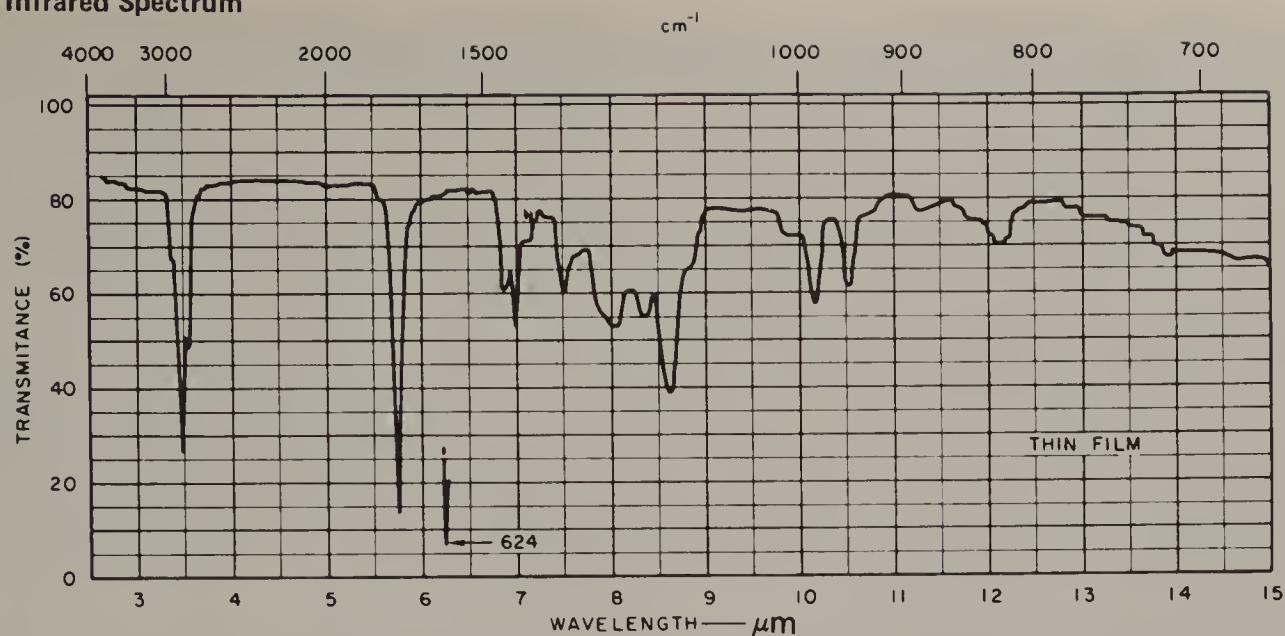
Featureless above 200nm

## <sup>1</sup>H NMR Spectrum

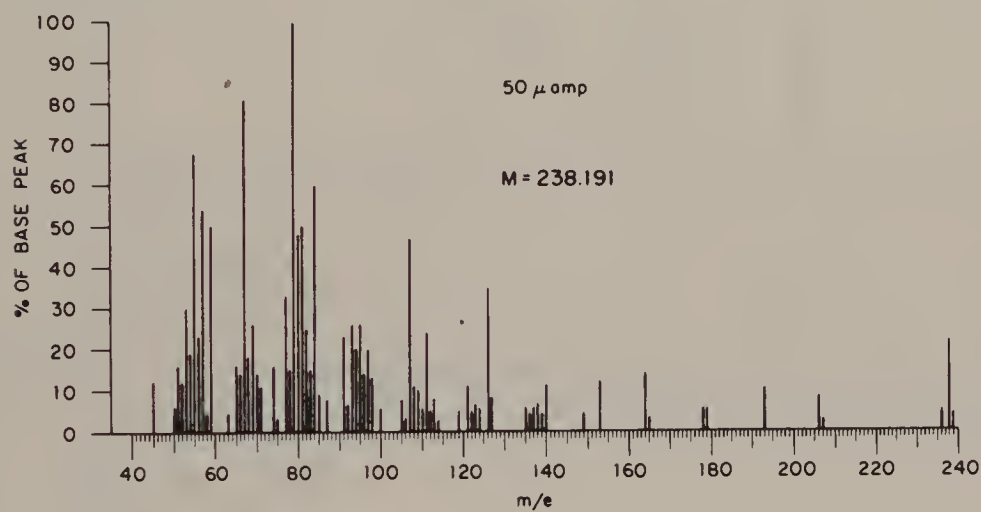




### Infrared Spectrum



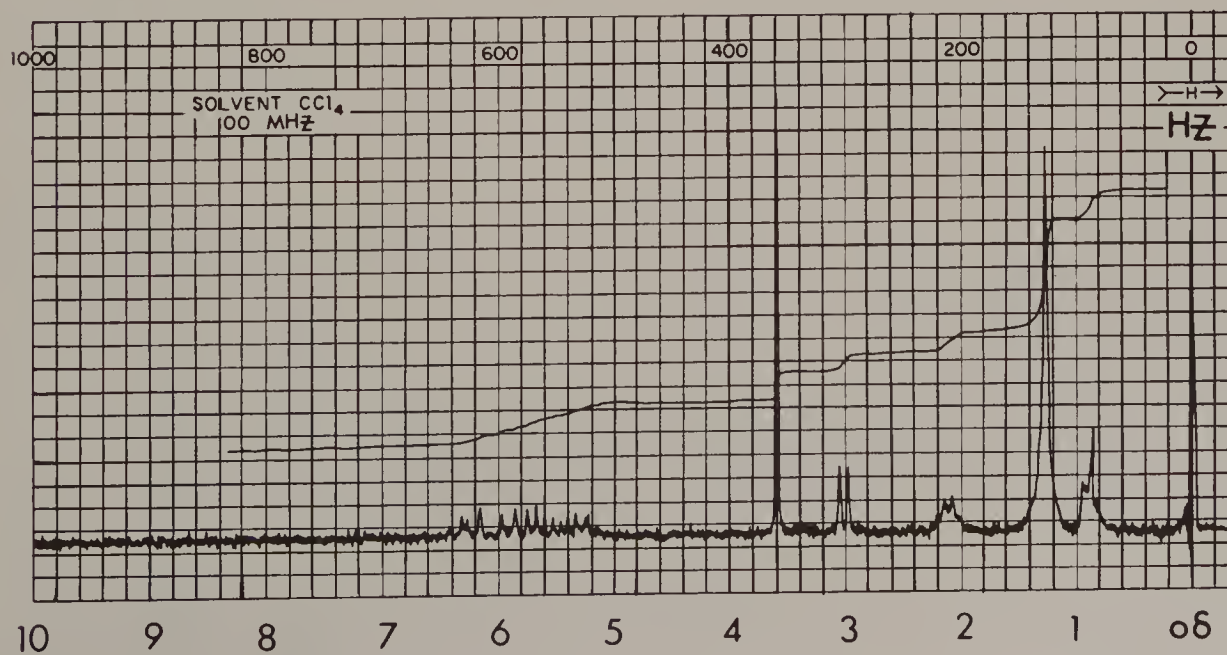
### Mass Spectrum



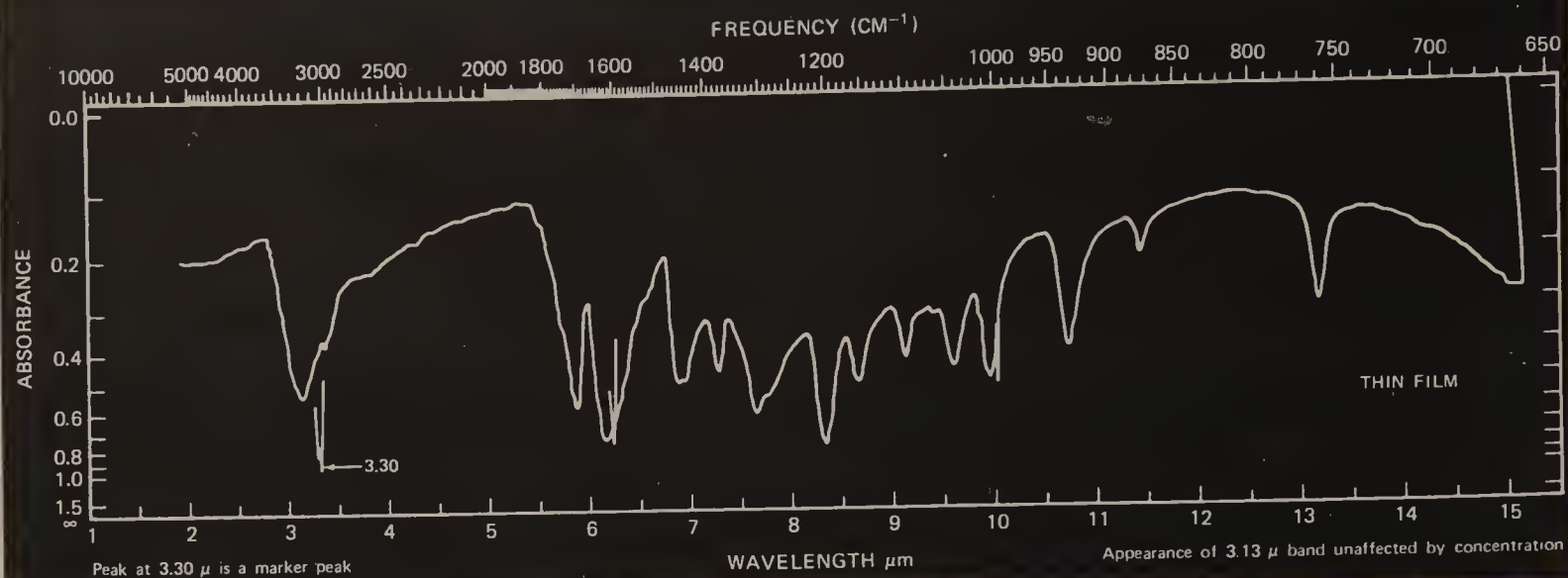
### Ultraviolet Data

| pentane          |                   |
|------------------|-------------------|
| $\lambda_{\max}$ | $\epsilon_{\max}$ |
| 231.5            | ~30,000           |
| nm               |                   |

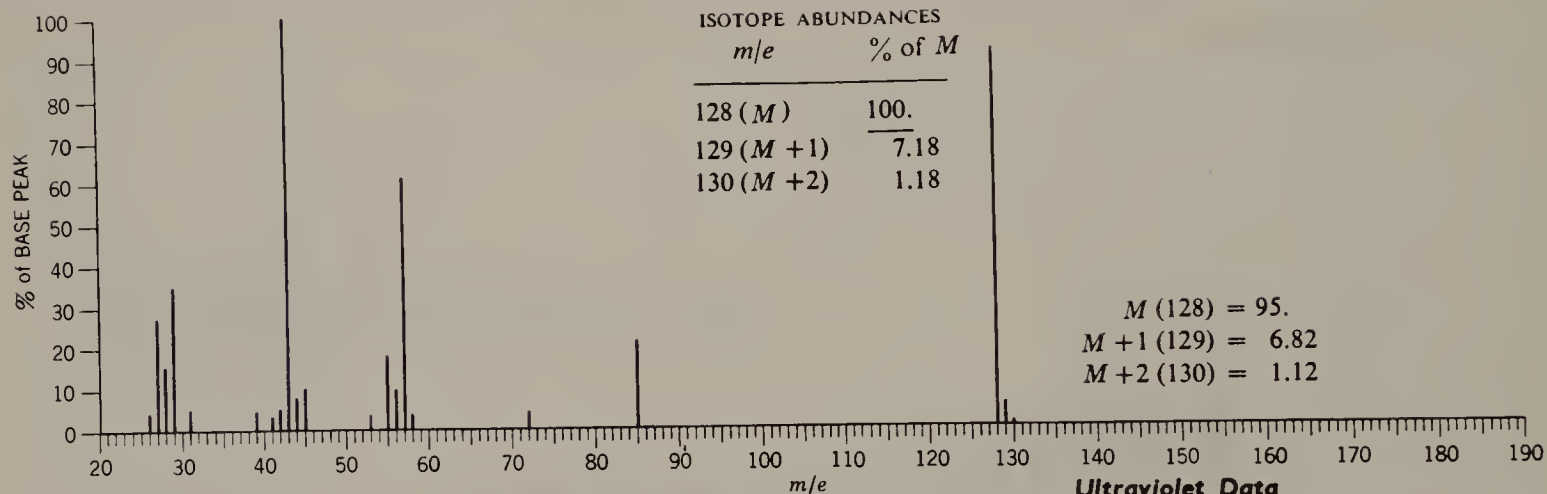
### <sup>1</sup>H NMR Spectrum



## Infrared Spectrum

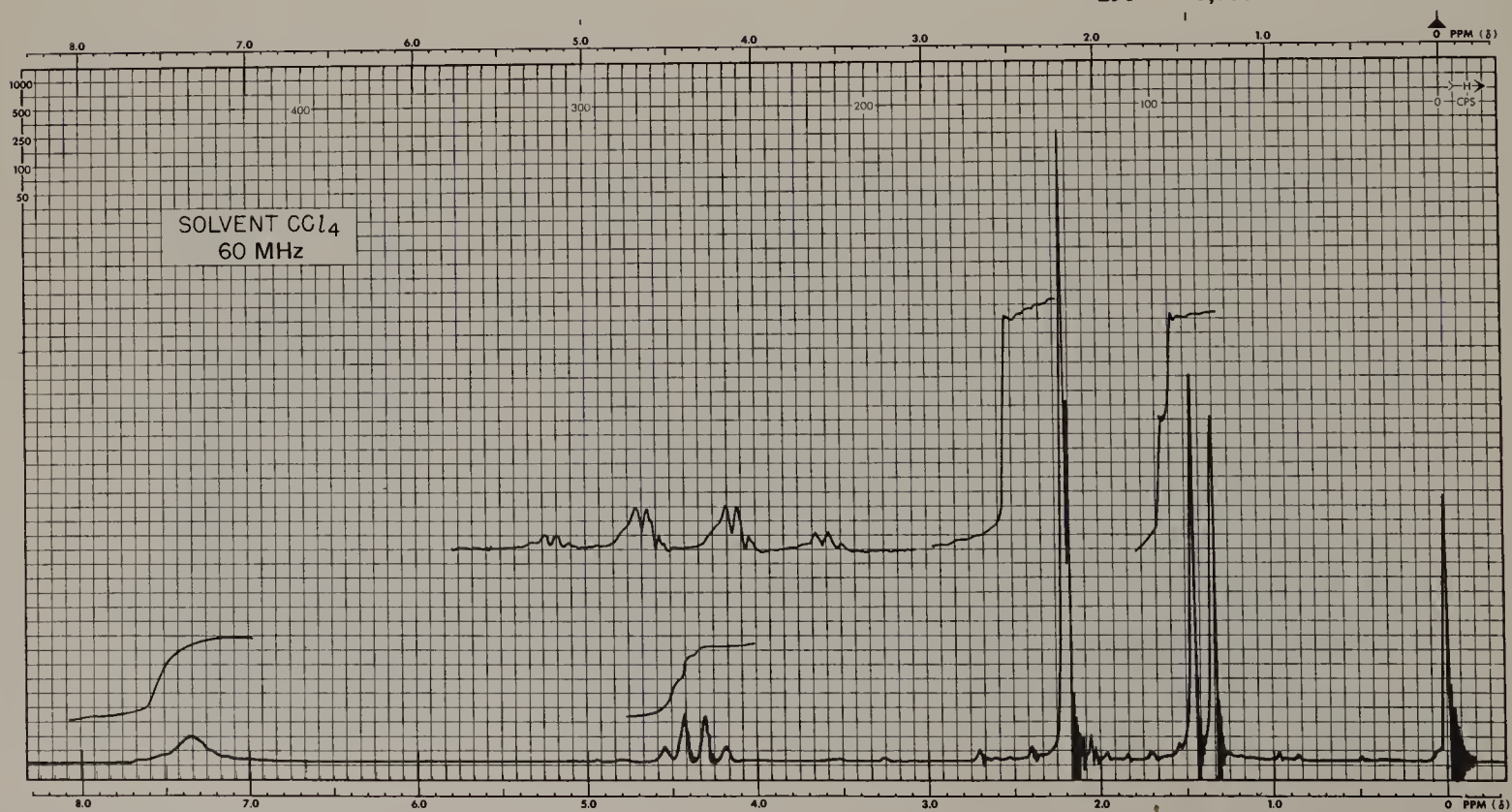


## Mass Spectral Data (Relative Intensities)

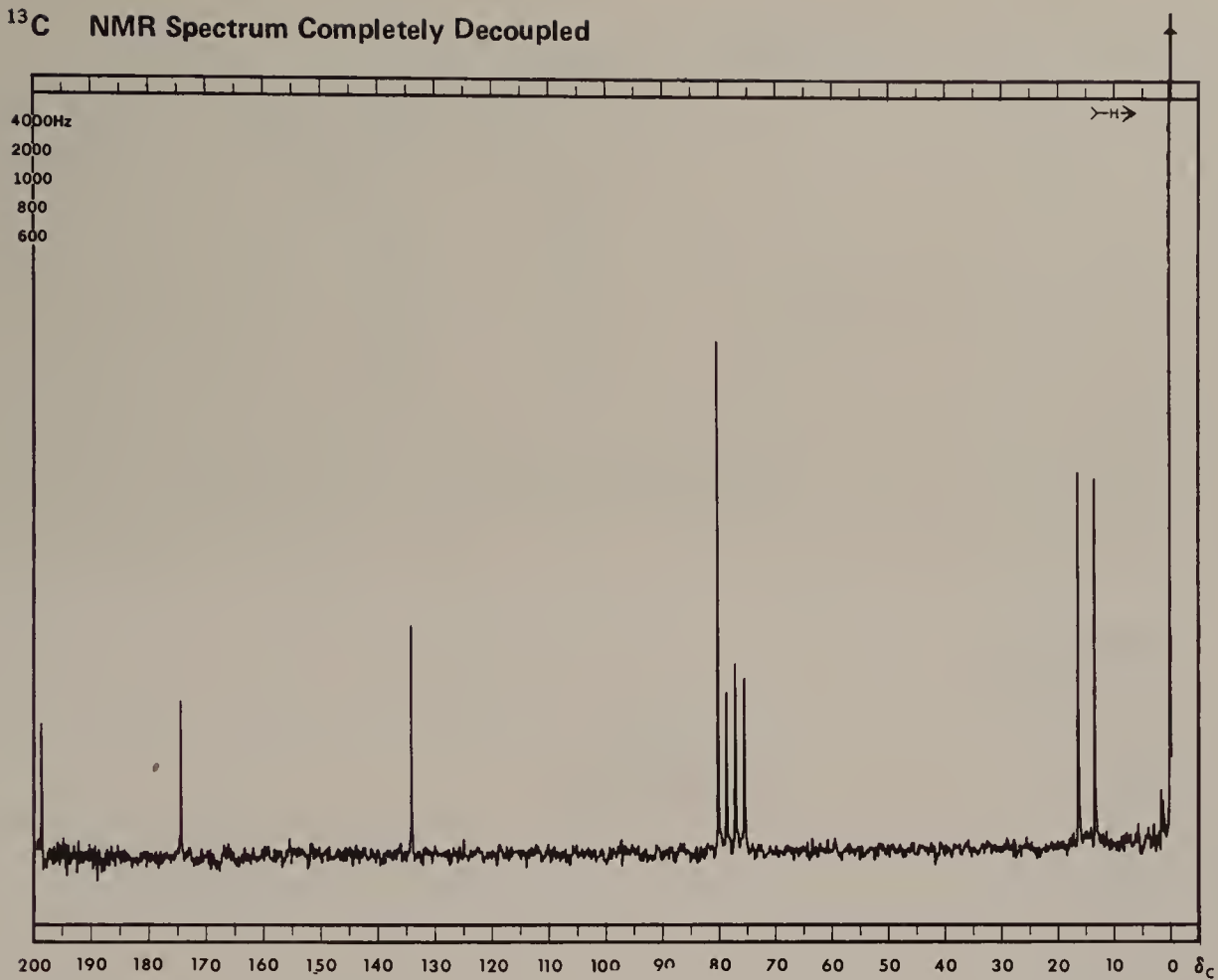


## Ultraviolet Data

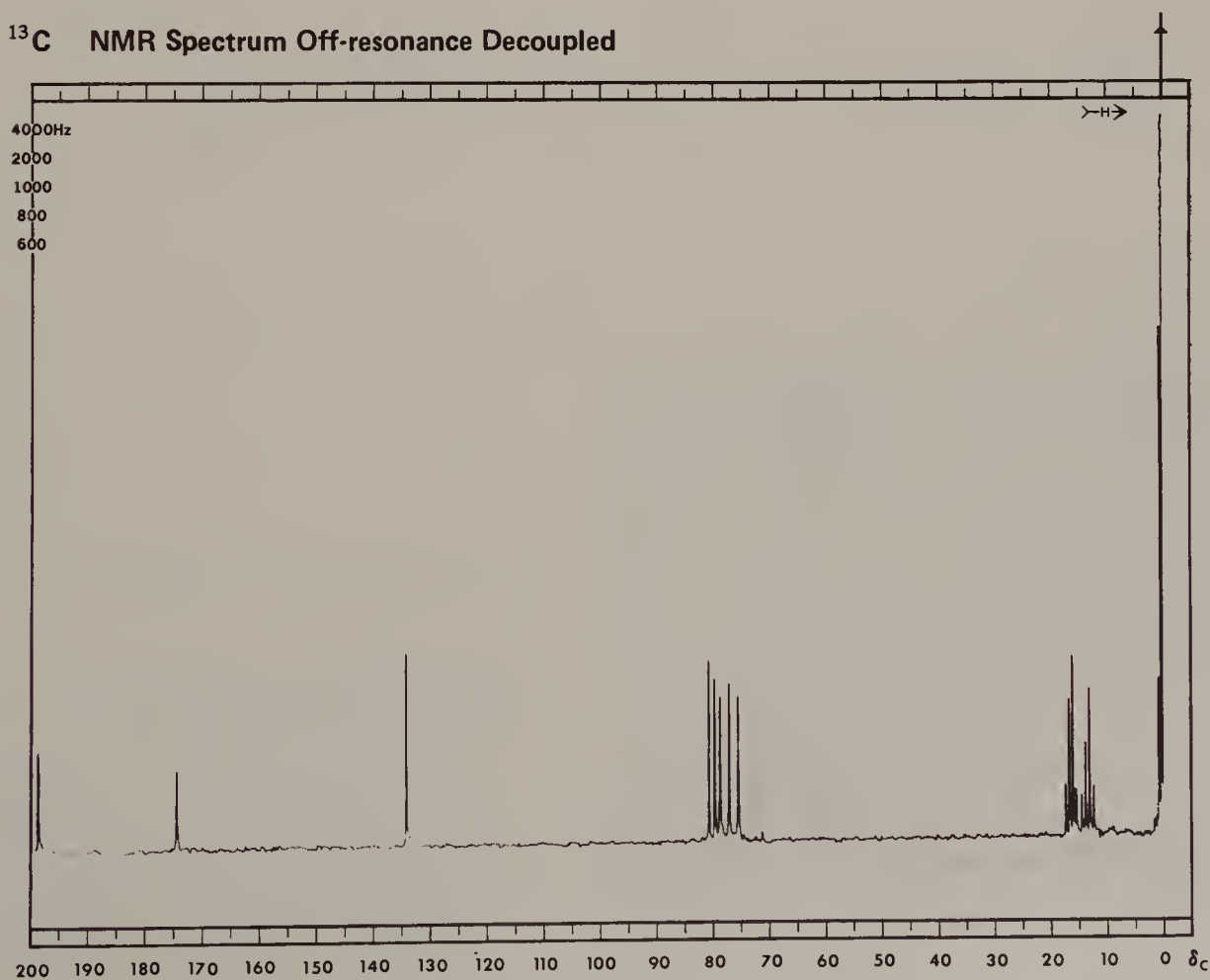
| $\lambda_{\text{max}}^{\text{MeOH}}$ | $\epsilon_{\text{max}}$ |
|--------------------------------------|-------------------------|
| 291                                  | 8,700                   |



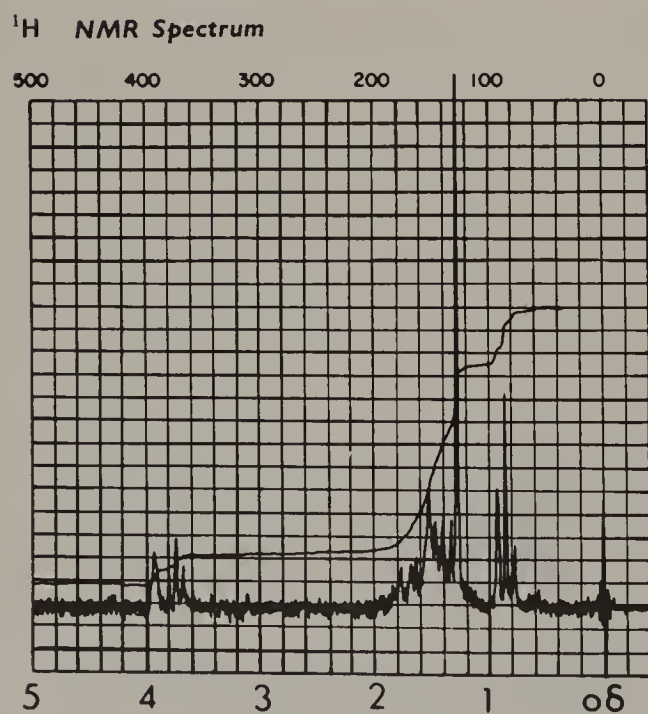
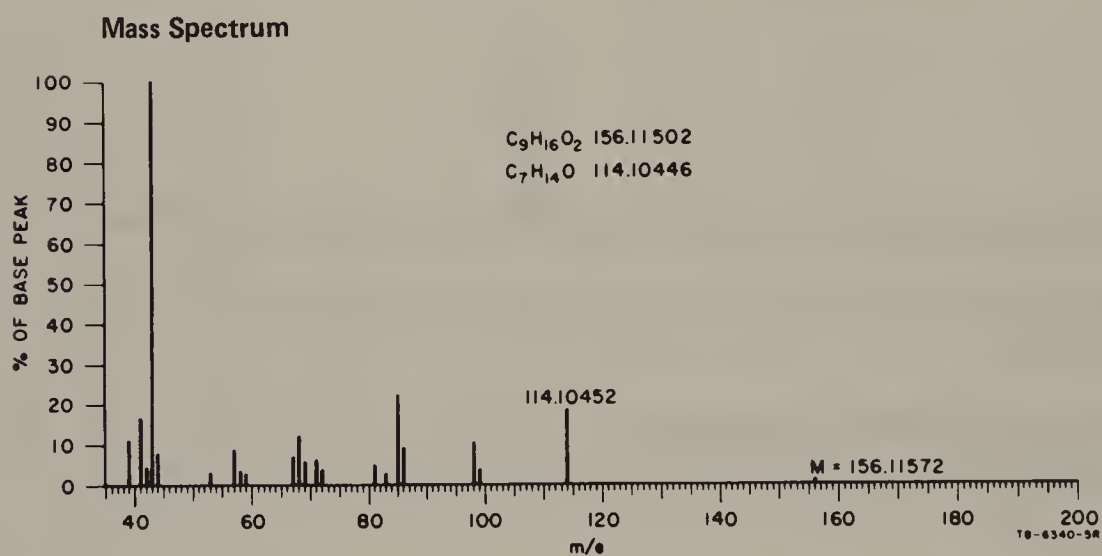
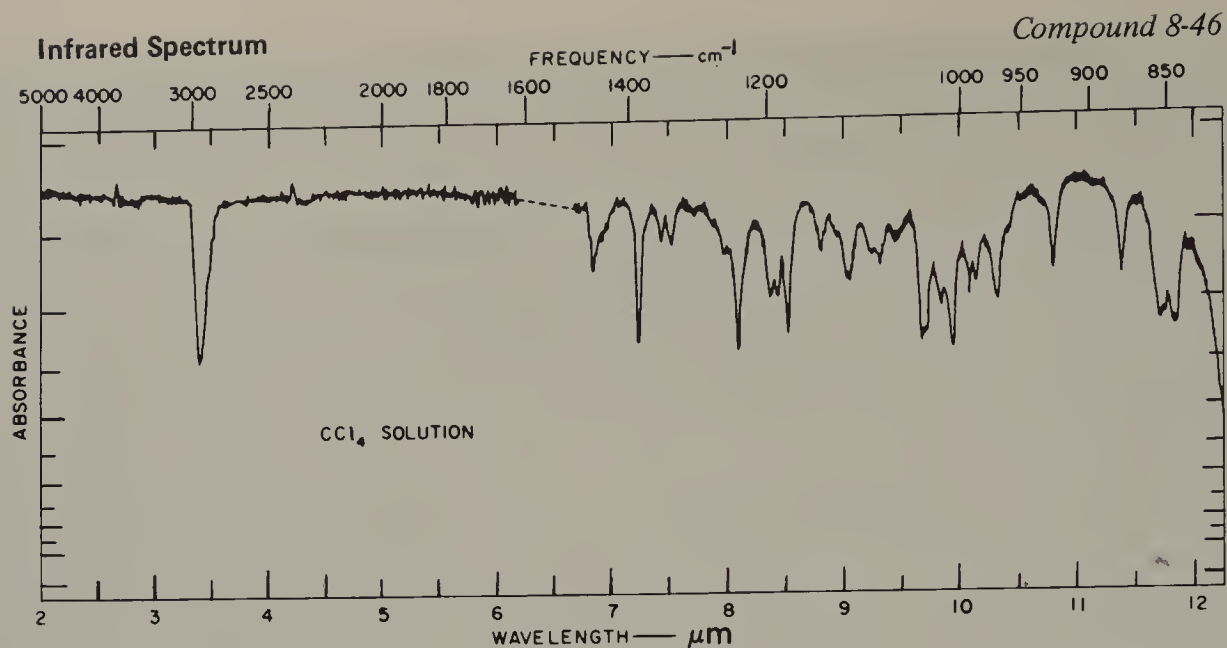
<sup>13</sup>C NMR Spectrum Completely Decoupled



<sup>13</sup>C NMR Spectrum Off-resonance Decoupled







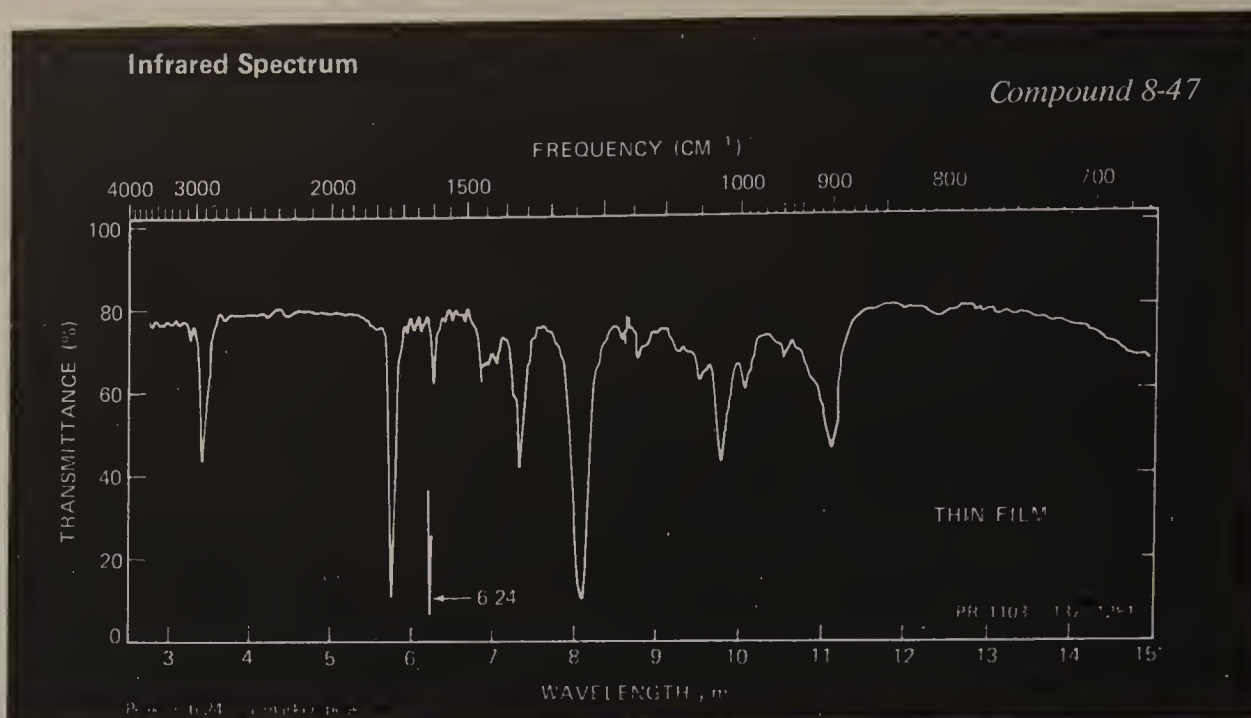
UV: No absorption above 200nm

#### Related Chemical Information

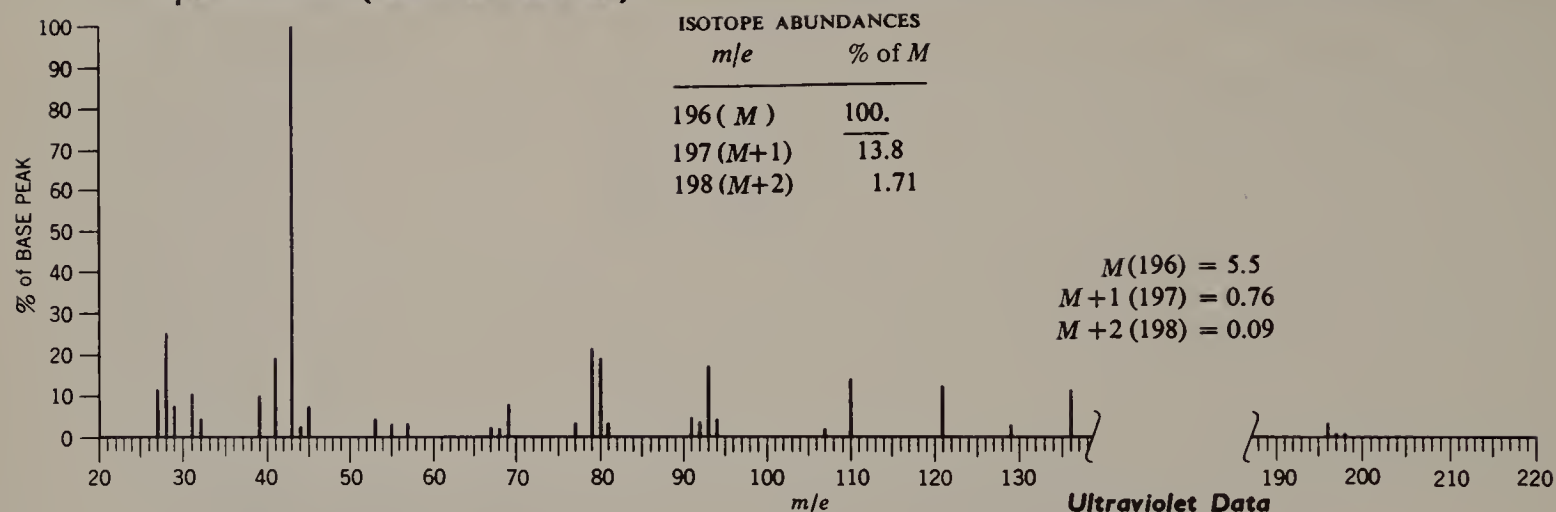
1. Recovered unchanged from treatment with  $\text{LiAlH}_4$ .
2. Catalytic hydrogenolysis ( $250^\circ$ ) gave nonane
3. The compound is part of the aggregation pheromone of the western pine beetle, Dendroctonus brevicomis.

Compound 8-46  $^{13}\text{C}$  NMR Data ( $\text{CDCl}_3$  solvent)

| $\delta$ | Intensity | Off-resonance<br>Decoupled<br>Multiplet |
|----------|-----------|---|
| 9.7      | 82.0      | <i>q</i>                                |
| 17.3     | 97.0      | <i>t</i>                                |
| 25.0     | 80.0      | <i>q</i>                                |
| 28.0     | 95.0      | <i>t</i>                                |
| 28.6     | 100.0     | <i>t</i>                                |
| 35.0     | 97.0      | <i>t</i>                                |
| 78.3     | 80.0      | <i>d</i>                                |
| 81.1     | 85.0      | <i>d</i>                                |
| 107.6    | 35.0      | <i>s</i>                                |

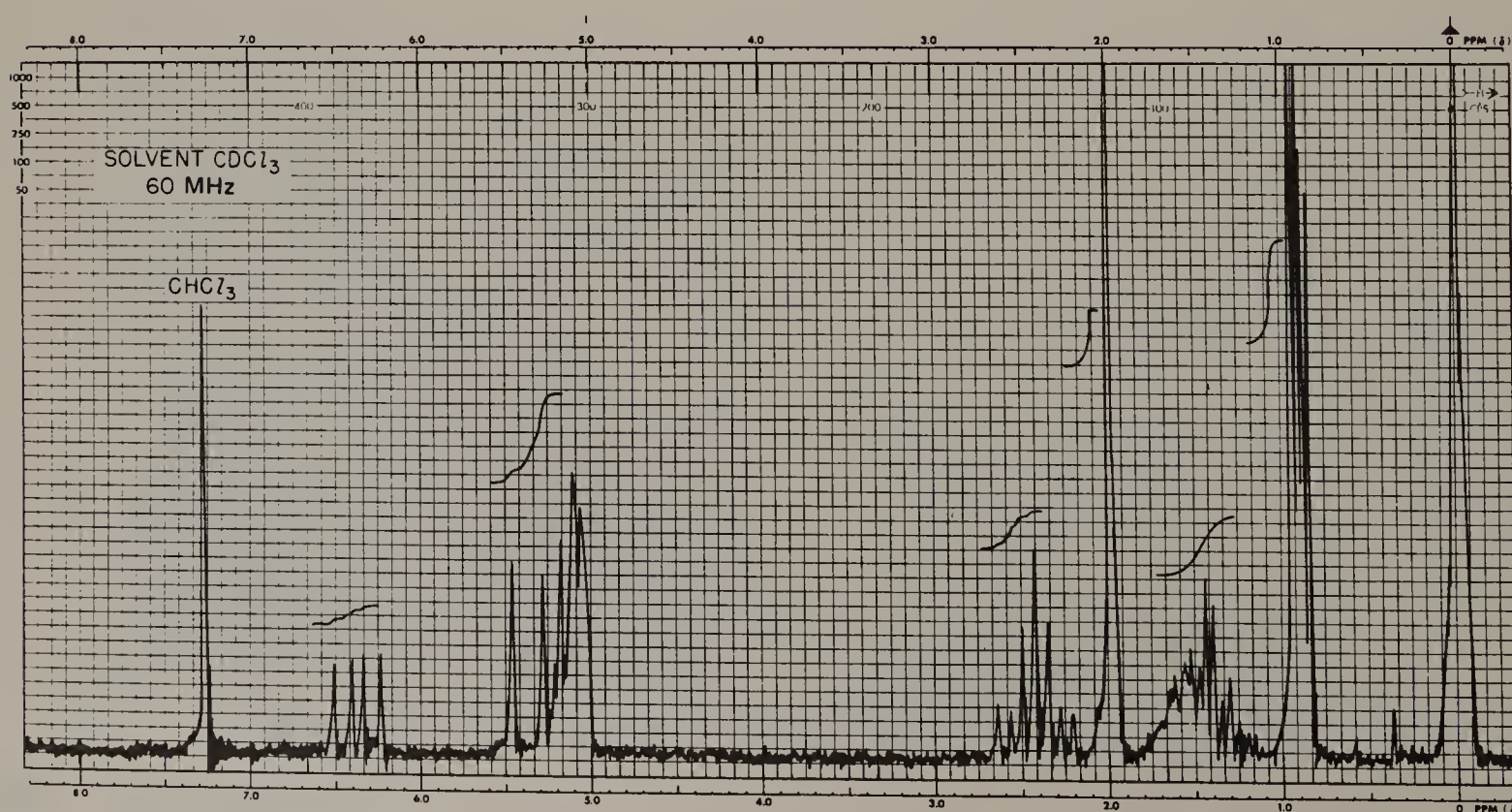


**Mass Spectral Data (Relative Intensities)**

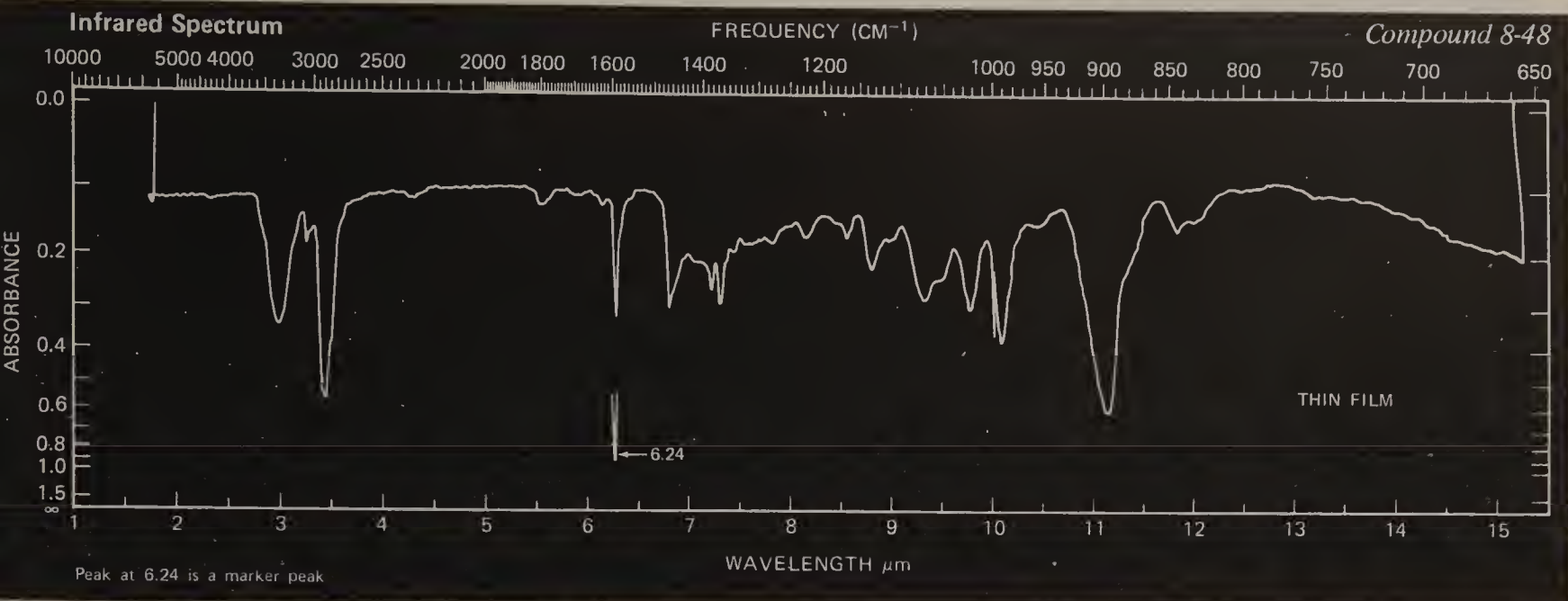


**Ultraviolet Data**

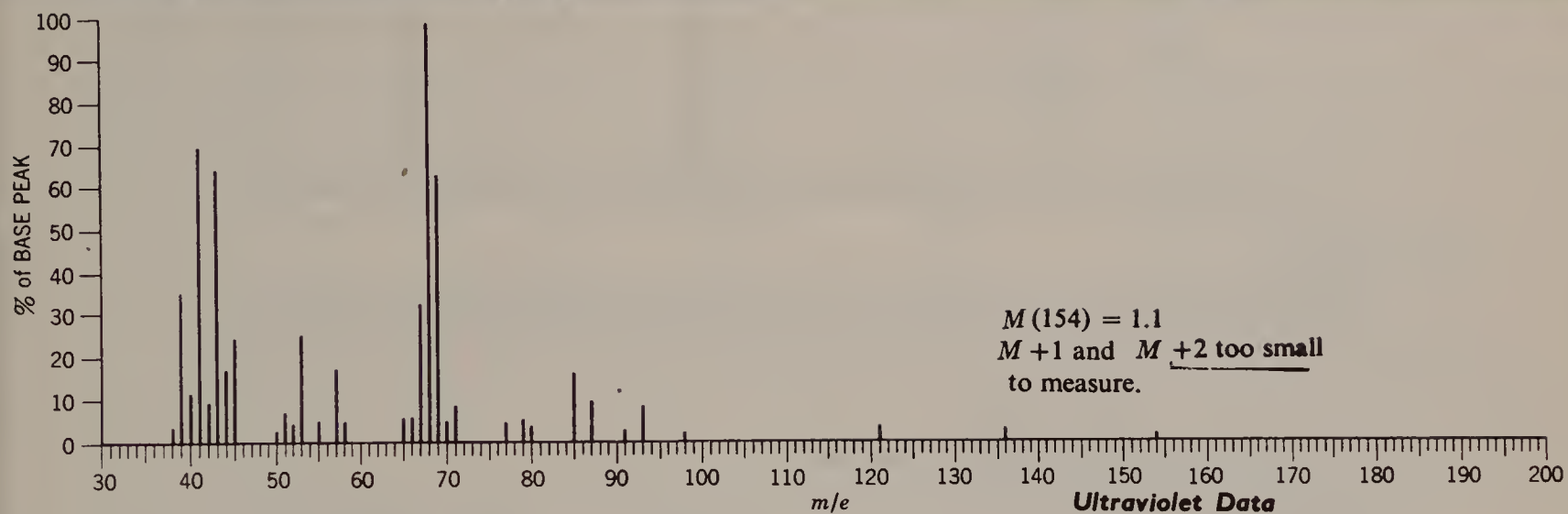
| $\lambda_{\text{Hexane max}}$ | $\epsilon_{\text{max}}$ |
|-------------------------------|-------------------------|
| 225                           | 26,000                  |







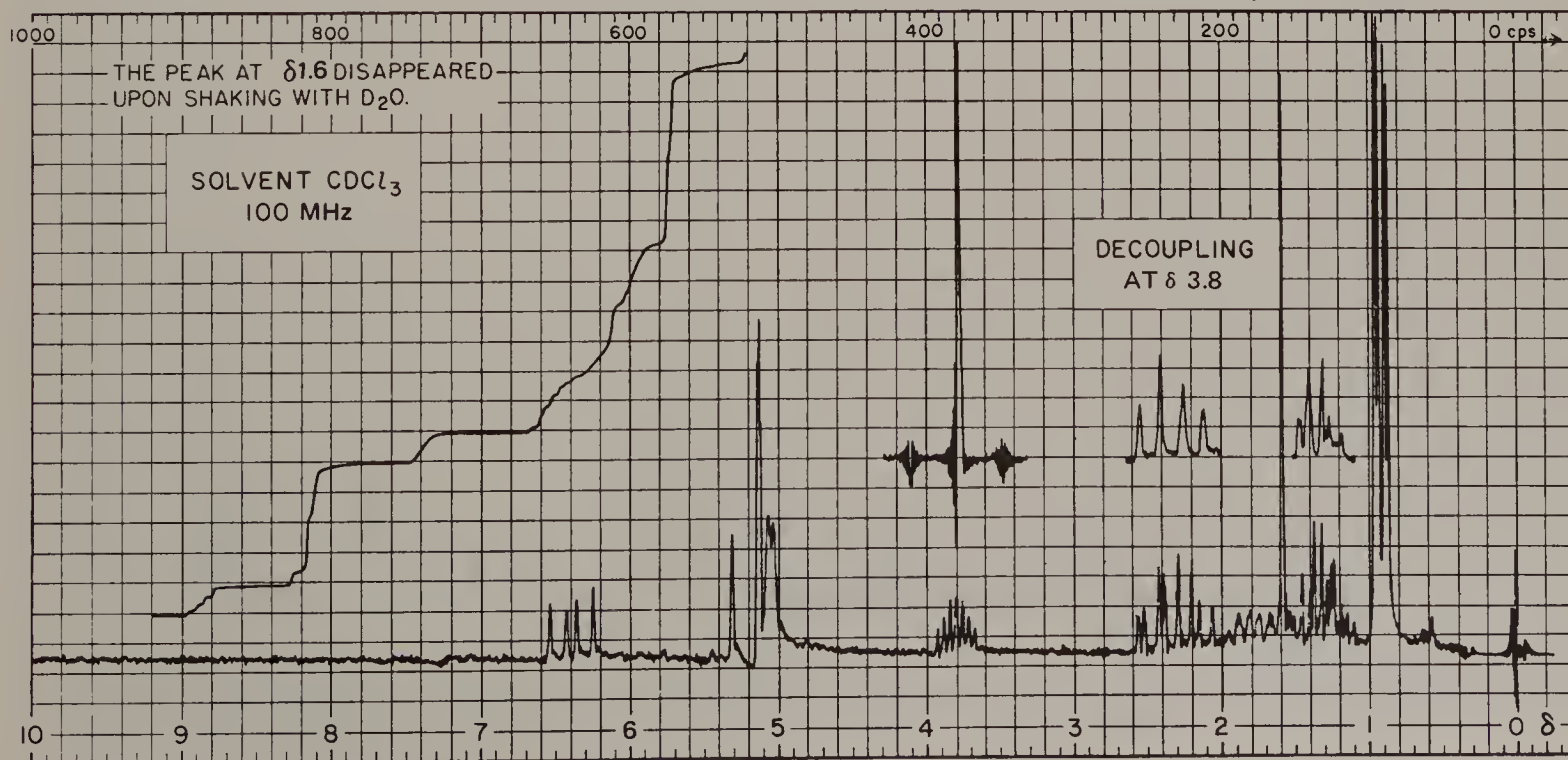
**Mass Spectral Data (Relative Intensities)**



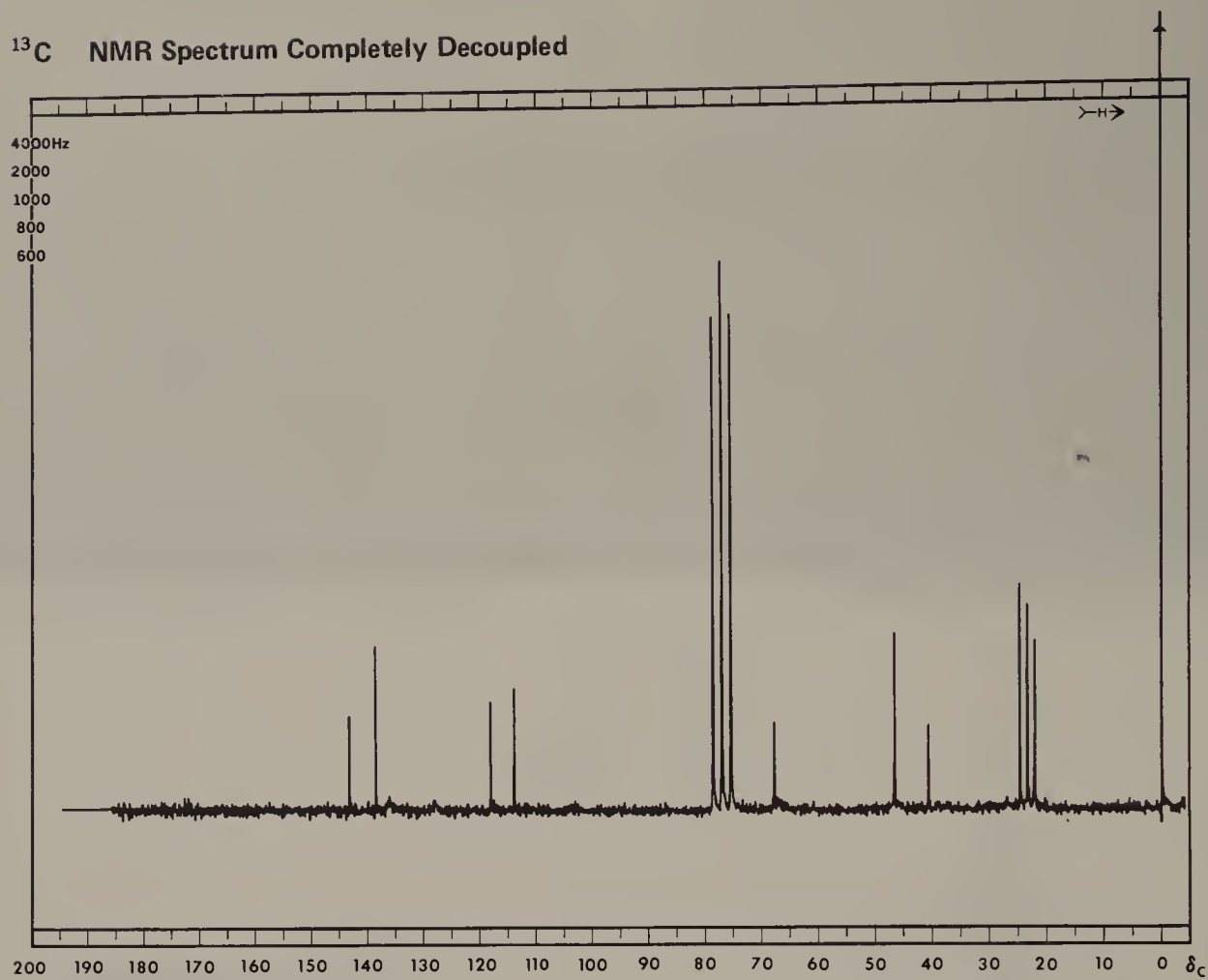
**Ultraviolet Data**

| $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ | $\epsilon_{\text{max}}$ |
|--|-------------------------|
| 226  | 20,000                  |

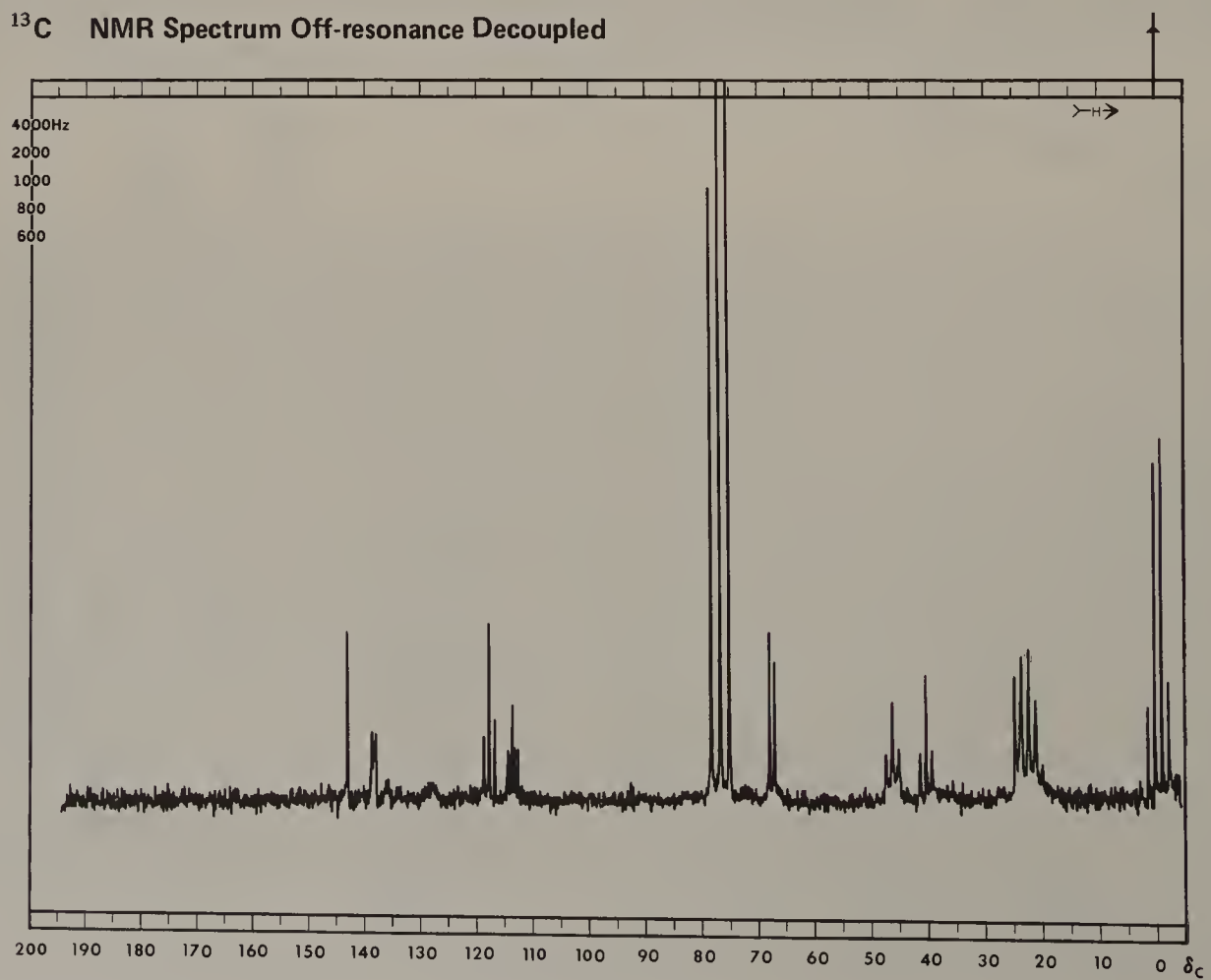
**NMR Spectrum**

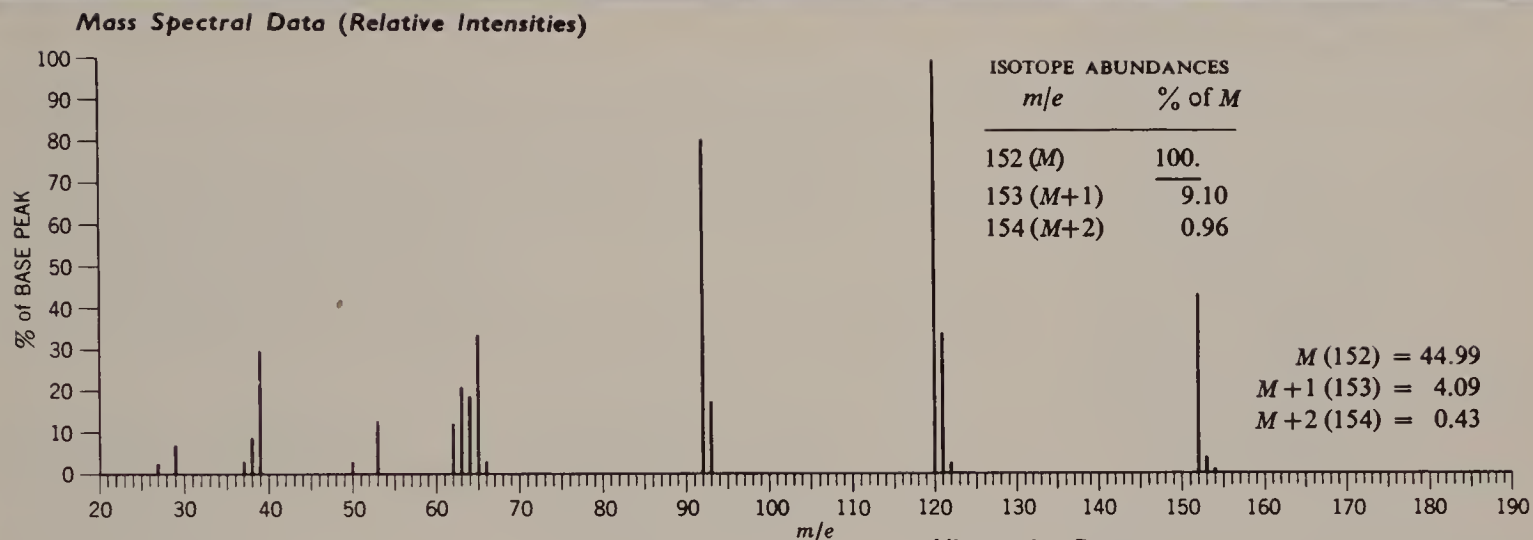
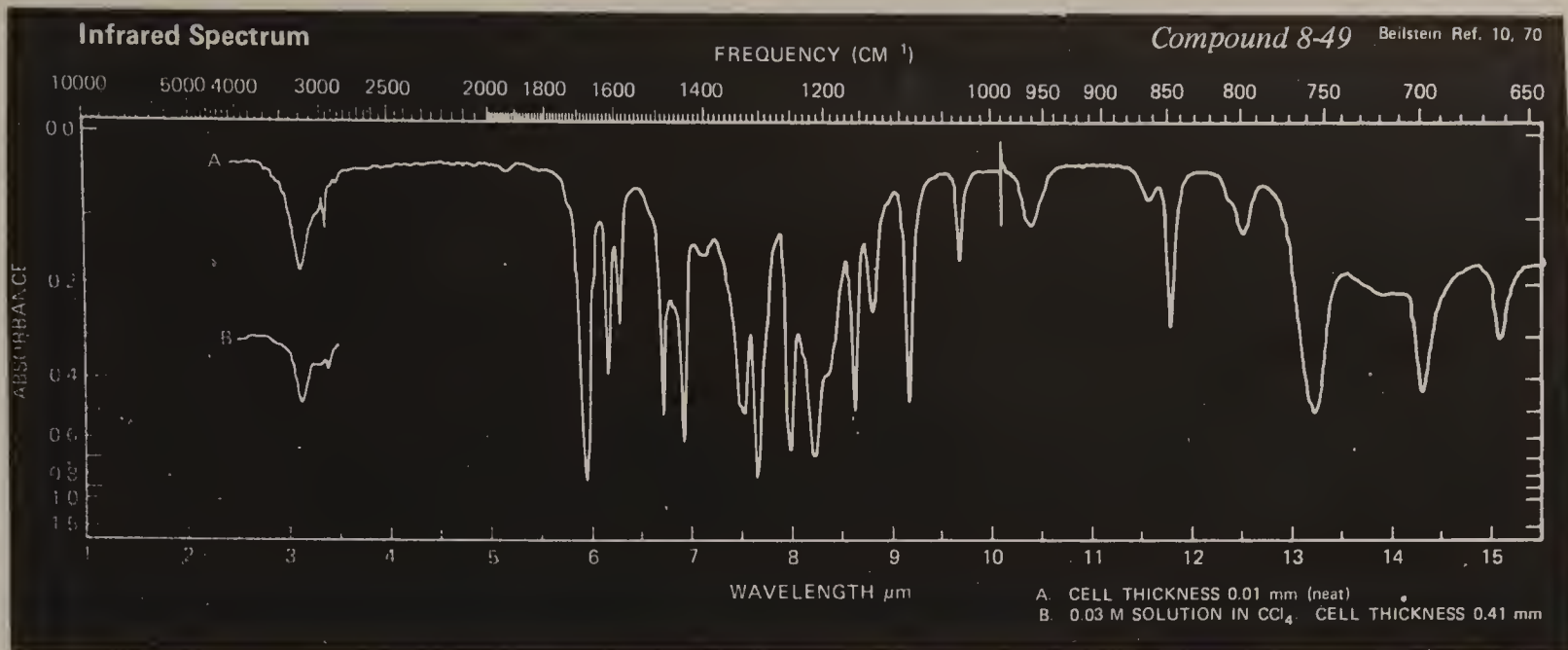


$^{13}\text{C}$  NMR Spectrum Completely Decoupled



$^{13}\text{C}$  NMR Spectrum Off-resonance Decoupled



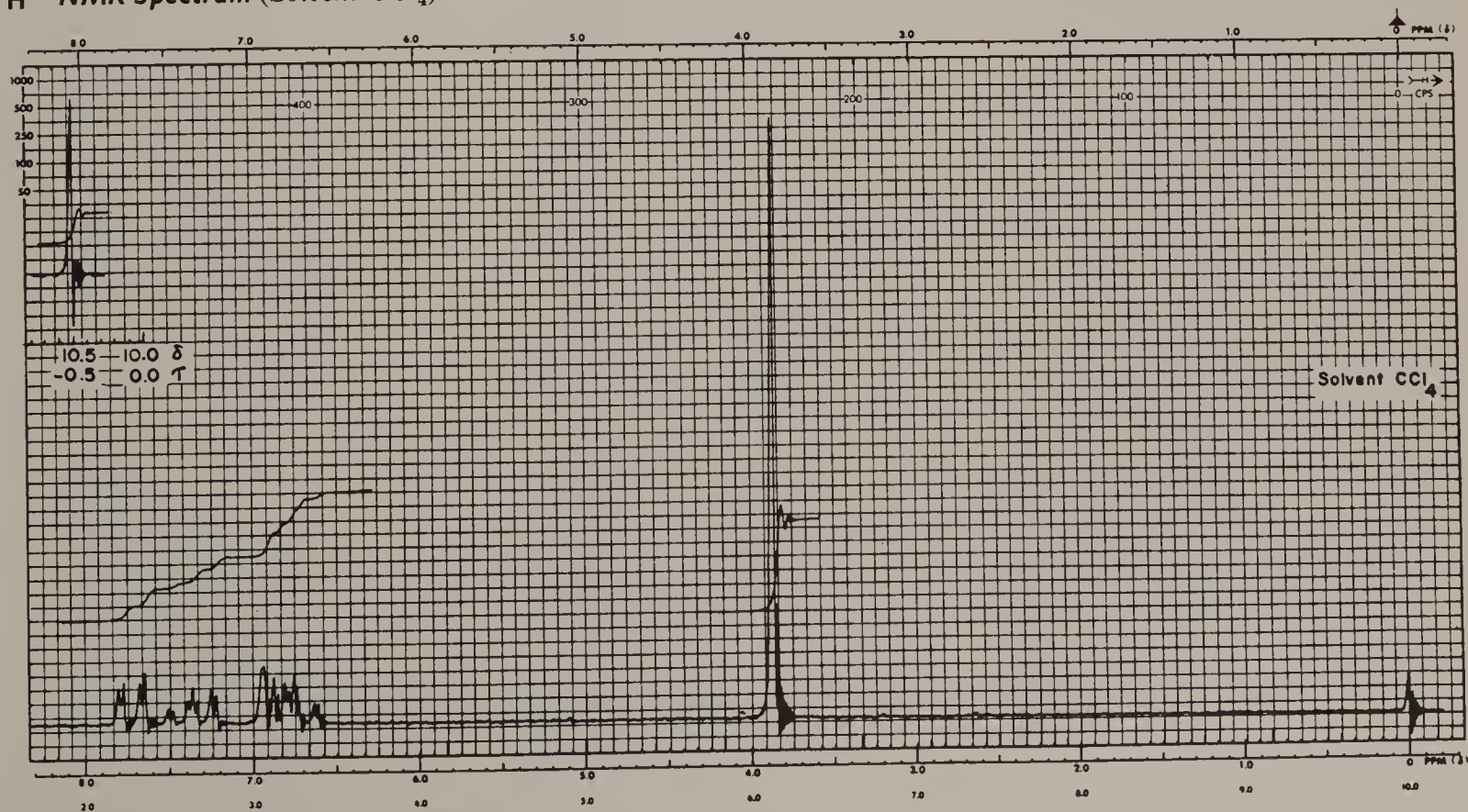


**Ultraviolet Data**

$\lambda_{\text{max}}^{\text{EtOH}}$   $\log \epsilon_{\text{max}}$

pH 7  $\left\{ \begin{array}{ll} 238 & 3.95 \\ 306 & 3.62 \end{array} \right.$       pH 13  $\left\{ \begin{array}{ll} 247 & 3.87 \\ 338 & 3.79 \end{array} \right.$

**<sup>1</sup>H NMR Spectrum (Solvent CCl<sub>4</sub>)**







# SUBJECT INDEX

## Key:

$^{13}\text{C}$  NMR = Carbon-13 nuclear magnetic resonance spectrometry (Chapter 5)  
 $^1\text{H}$  NMR = Proton nuclear magnetic resonance spectrometry (Chapter 4)  
 IR = Infrared spectrometry (Chapter 3)  
 MS = Mass spectrometry (Chapter 2)  
 UV = Ultraviolet spectrometry (Chapter 6)  
 Specific compounds, for which complete spectra or spectral data are referenced, are listed in the Compound Index.

AA' BB' AA', XX':  $^1\text{H}$  NMR, 201  
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   aliphatic: MS, 31  
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   IR, 127, 168, 171, 172  
   MS, 30, 31  
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   UV, 320  
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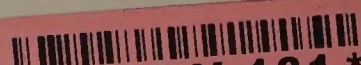
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