

Lecture # 13

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Part Three: Spin–Spin Coupling

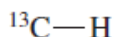
Chapters 5 and 6 covered only the most essential elements of nuclear magnetic resonance (NMR) theory. Now we will consider applications of the basic concepts to more complicated situations. In this chapter, the emphasis is on the origin of coupling constants and what information can be deduced from them. Enantiotopic and diastereotopic systems will be covered as well as more advanced instances of spin–spin coupling, such as second-order spectra.

homonuclear coupling.

heteronuclear coupling

We frequently add a superscript to the symbol J to indicate the number of bonds through which the interaction occurs. If the identity of the two nuclei involved is not obvious, we add this information in parentheses. Thus, the symbol

$${}^1J({}^{13}\text{C}-{}^1\text{H}) = 156 \text{ Hz}$$



Notice that in this arrangement the two nuclei prefer to have opposite spins. When two spin-active nuclei prefer an opposed alignment (have opposite spins), the coupling constant J is usually positive.

If the nuclei are parallel or aligned (have the same spin), J is usually negative. Thus, most one-bond couplings have positive J values. Keep in mind, however, that there are some prominent exceptions, such as ${}^{13}\text{C}-{}^{19}\text{F}$, for which the coupling constants are negative (see Table 7.1).

It is not unusual for coupling constants to depend on the hybridization of the atoms involved. 1J values for ${}^{13}\text{C}-{}^1\text{H}$ coupling constants vary with the amount of s character in the carbon hybrid, according to the following relationship:

$${}^1J_{\text{CH}} = (500 \text{ Hz}) \left(\frac{1}{n+1} \right) \text{ for hybridization type } sp^n \quad \text{Equation 7.1}$$

Notice the specific values given for the ${}^{13}\text{C}-{}^1\text{H}$ couplings of ethane, ethene, and ethyne in Table 7.1.








TABLE 7.1
SOME ONE-BOND COUPLING CONSTANTS (1J)

$^{13}\text{C}-^1\text{H}$	110–270 Hz <i>sp</i> ³ 115–125 Hz (ethane = 125 Hz) <i>sp</i> ² 150–170 Hz (ethene = 156 Hz) <i>sp</i> 240–270 Hz (ethyne = 249 Hz)
$^{13}\text{C}-^{19}\text{F}$	–165 to –370 Hz
$^{13}\text{C}-^{31}\text{P}$	48–56 Hz
$^{13}\text{C}-\text{D}$	20–30 Hz
$^{31}\text{P}-^1\text{H}$	190–700 Hz

Two-Bond Couplings (2J)

Two-bond couplings are quite common in NMR spectra. They are usually called **geminal couplings** because the two nuclei that interact are attached to the same central atom (Latin *gemini* = “twins”). Two-bond coupling constants are abbreviated 2J . They occur in carbon compounds whenever two or more spin-active atoms are attached to the same carbon atom. Table 7.2 lists some two-bond coupling constants that involve carbon as the central atom. Two-bond coupling constants are typically, although not always, smaller in magnitude than one-bond couplings (Table 7.1). Notice that the most common type of two-bond coupling, HCH, is frequently (but not always) negative.

TABLE 7.2
SOME TWO-BOND COUPLING CONSTANTS (2J)

	–9 to –15 Hz		~50 Hz ^a
	0 to 2 Hz		~5 Hz ^a
	~2 Hz ^a		7–14 Hz ^a
	~160 Hz ^a		

^aAbsolute values.

The mechanistic picture for geminal coupling (2J) invokes nuclear–electronic spin coupling as a means of transmitting spin information from one nucleus to the other. It is consistent with the Dirac model that we discussed at the beginning of Section 7.2 and in Section 7.2A. Figure 7.3 shows this mechanism. In this case, another atom (without spin) intervenes between two interacting orbitals. When this happens, theory predicts that the interacting electrons, and hence the nuclei, prefer to have parallel spins, resulting in a negative coupling constant. The preferred alignment is shown on the left side of Figure 7.3.

The amount of geminal coupling depends on the HCH angle α . The graph in Figure 7.4 shows this dependence, where the amount of *electronic* interaction between the two C–H orbitals determines the magnitude of the coupling constant 2J . In general, 2J geminal coupling constants increase as the angle α decreases. As the angle α decreases, the two orbitals shown in Figure 7.3 move closer, and the electron spin correlations become greater. Note, however, that the graph in Figure 7.4 is very approximate, showing only the general trend; actual values vary quite widely.

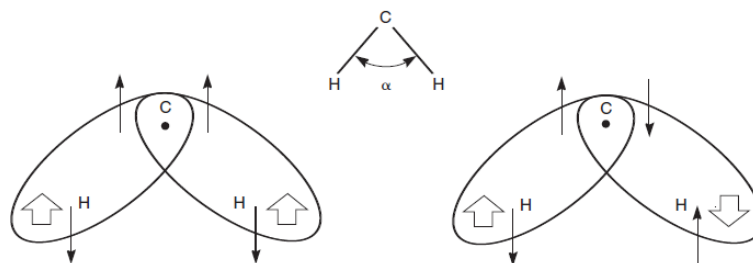


FIGURE 7.3 The mechanism of geminal coupling.

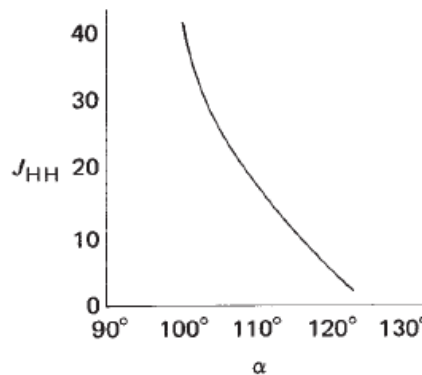


FIGURE 7.4 The dependence of the magnitude of $^2J_{\text{HCH}}$, the geminal coupling constant, on the HCH bond angle α .

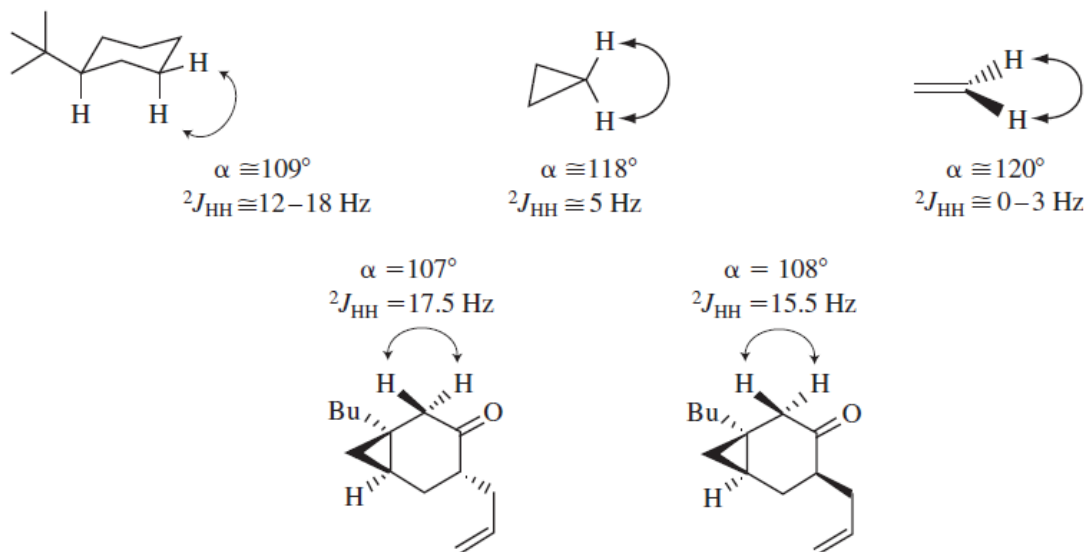


Table 7.3 shows a larger range of variation, with approximate values for a selected series of cyclic compounds and alkenes. Notice that as ring size decreases, the absolute value of the coupling constant 2J also decreases. Compare, for instance, cyclohexane, where 2J is -13 , and cyclopropane, where 2J is -4 .

TABLE 7.3
VARIATIONS IN ${}^2J_{\text{HH}}$ WITH HYBRIDIZATION AND RING SIZE

+2	-2	-4	-9	-11	-13	-9 to -15 Hz

Geminal coupling between nonequivalent protons is readily observed in the ${}^1\text{H}$ NMR spectrum, and the magnitude of the coupling constant 2J is easily measured from the line spacings when the resonances are first order (see Sections 7.6 and 7.7). In second-order spectra, the value of 2J cannot be directly measured from the spectrum but may be determined by computational methods (spectral simulation). In many cases, however, no geminal HCH coupling (no spin-spin splitting) is observed because the geminal protons are magnetically equivalent (see Section 7.3). You have already seen in our discussions of the $n + 1$ Rule that in a hydrocarbon chain the protons attached to the same carbon may be treated as a group and do not split one another. How, then, can it be said that coupling exists in such cases if no spin-spin splitting is observed in the spectrum? The answer comes from deuterium substitution experiments. If one of the hydrogens in a compound that shows

$${}^2J_{\text{HH}} = \gamma\text{H}/\gamma\text{D} ({}^2J_{\text{HD}}) = 6.51({}^2J_{\text{HD}})$$

Equation 7.2

Three-Bond Couplings (3J)

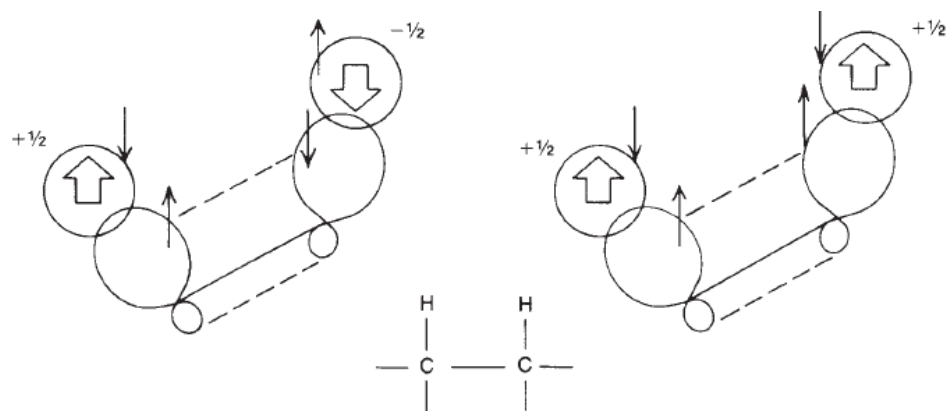


FIGURE 7.5 The method of transferring spin information between two adjacent C-H bonds.

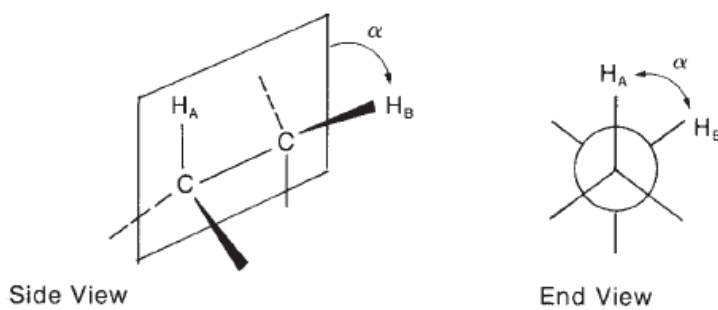
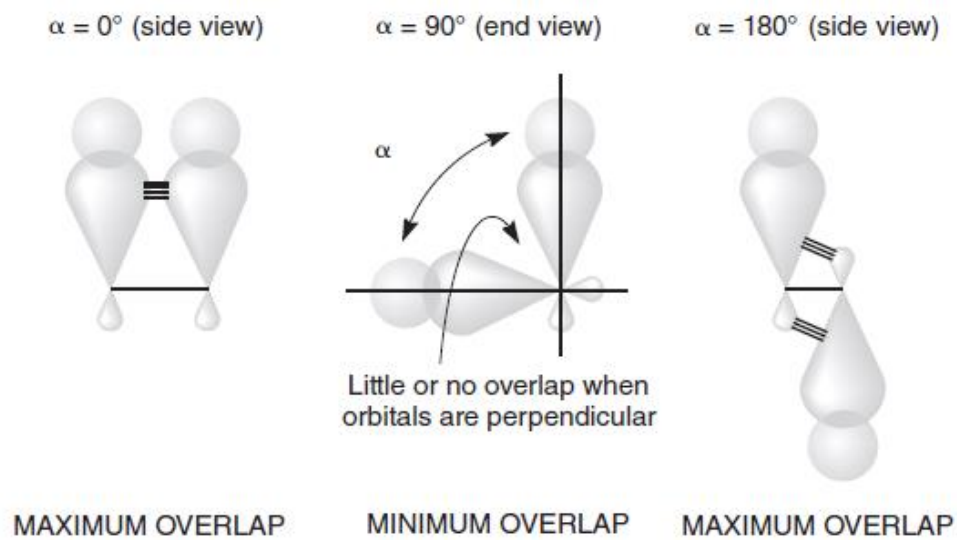


FIGURE 7.6 The definition of a dihedral angle α .



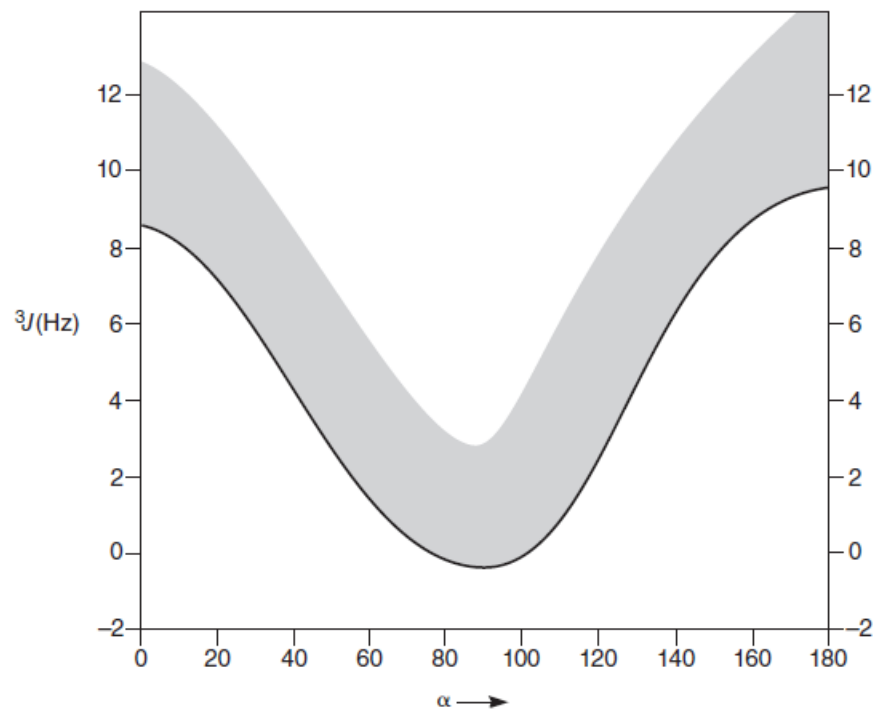


FIGURE 7.7 The Karplus relationship—the approximate variation of the coupling constant 3J with the dihedral angle α .

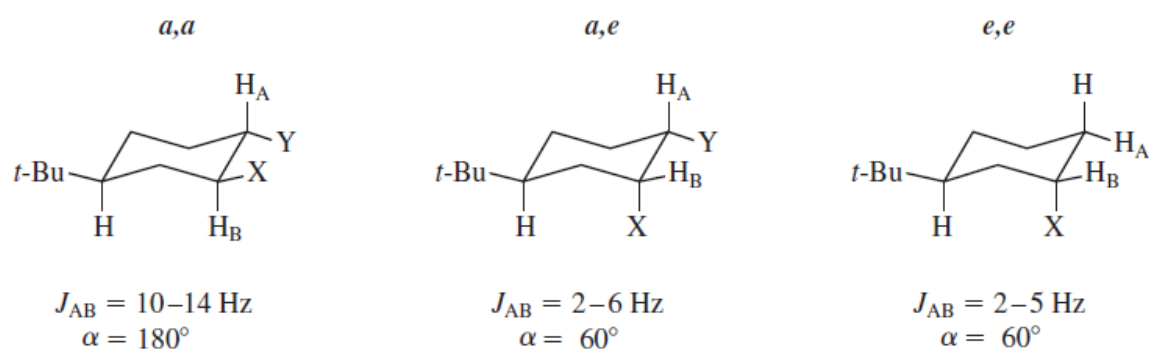
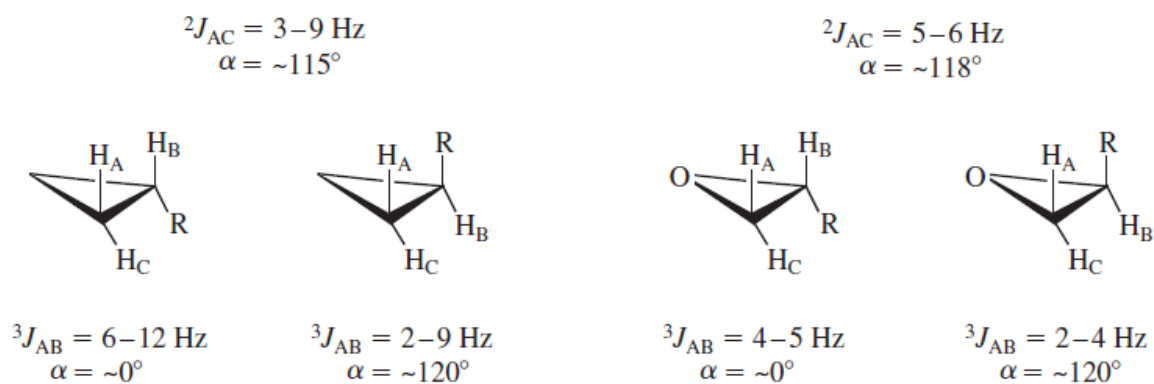


FIGURE 7.9 Vicinal couplings in cyclohexane derivatives.

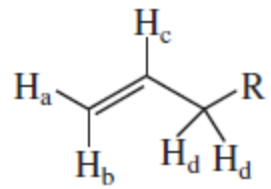


For three-membered rings, $J_{cis} > J_{trans}$

TABLE 7.4
SOME THREE-BOND COUPLING CONSTANTS (${}^3J_{XY}$)

H-C-C-H	6-8 Hz	H-C=C-H	<i>cis</i> 6-15 Hz <i>trans</i> 11-18 Hz
${}^{13}\text{C}-\text{C}-\text{C}-\text{H}$	5 Hz	H-C=C- ${}^{19}\text{F}$	<i>cis</i> 18 Hz <i>trans</i> 40 Hz
${}^{19}\text{F}-\text{C}-\text{C}-\text{H}$	5-20 Hz	${}^{19}\text{F}-\text{C}=\text{C}-{}^{19}\text{F}$	<i>cis</i> 30-40 Hz <i>trans</i> -120 Hz
${}^{19}\text{F}-\text{C}-\text{C}-{}^{19}\text{F}$	-3 to -20		
${}^{31}\text{P}-\text{C}-\text{C}-\text{H}$	13 Hz		
${}^{31}\text{P}-\text{O}-\text{C}-\text{H}$	5-15 Hz		

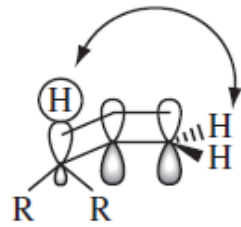
Long-Range Couplings (${}^4J-n$)



$$|{}^4J_{\text{ad}}| = 0 - 3 \text{ Hz}$$

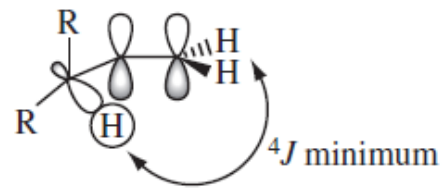
$$|{}^4J_{\text{bd}}| = 0 - 3 \text{ Hz}$$

4J maximum



*C—H σ orbital
parallel to π orbital*

*C—H σ orbital
orthogonal to π orbital*



4J minimum

FIGURE 7.11 Geometric arrangements that maximize and minimize allylic coupling.

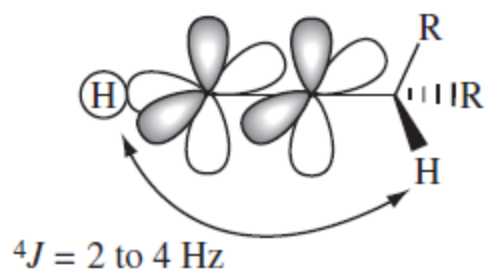


FIGURE 7.12 Propargylic coupling.

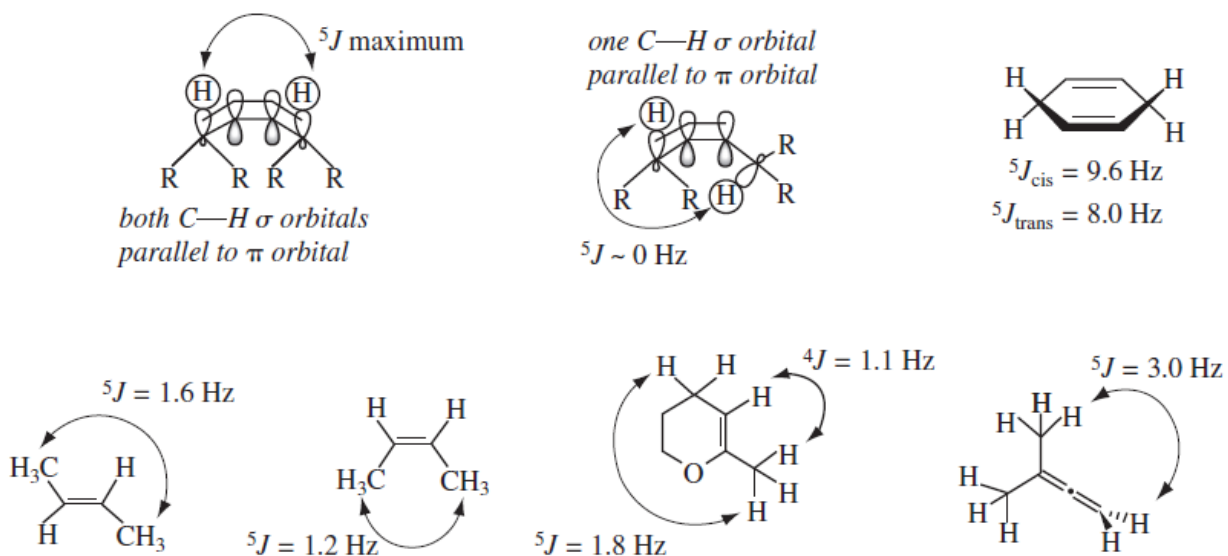


FIGURE 7.13 Homoallylic coupling in alkenes and allenes.

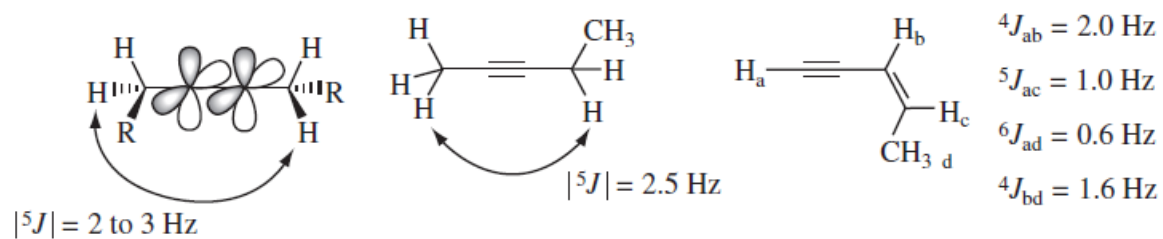


FIGURE 7.14 Homopropargylic coupling in alkynes.

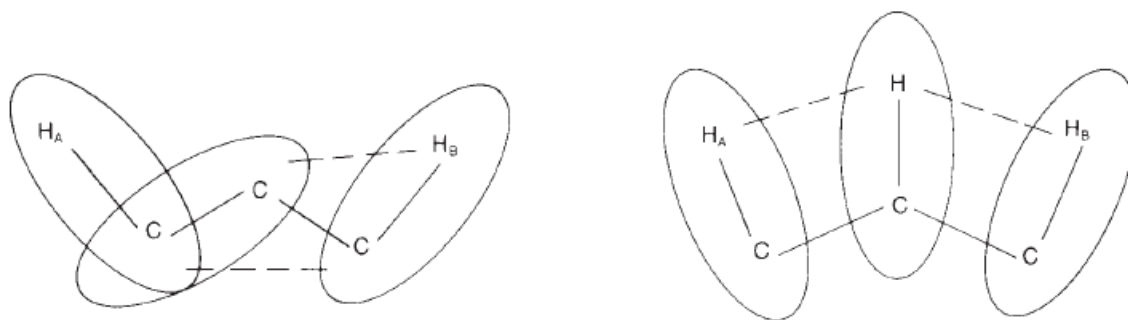


FIGURE 7.15 Possible orbital overlap mechanisms to explain 4J_W coupling.

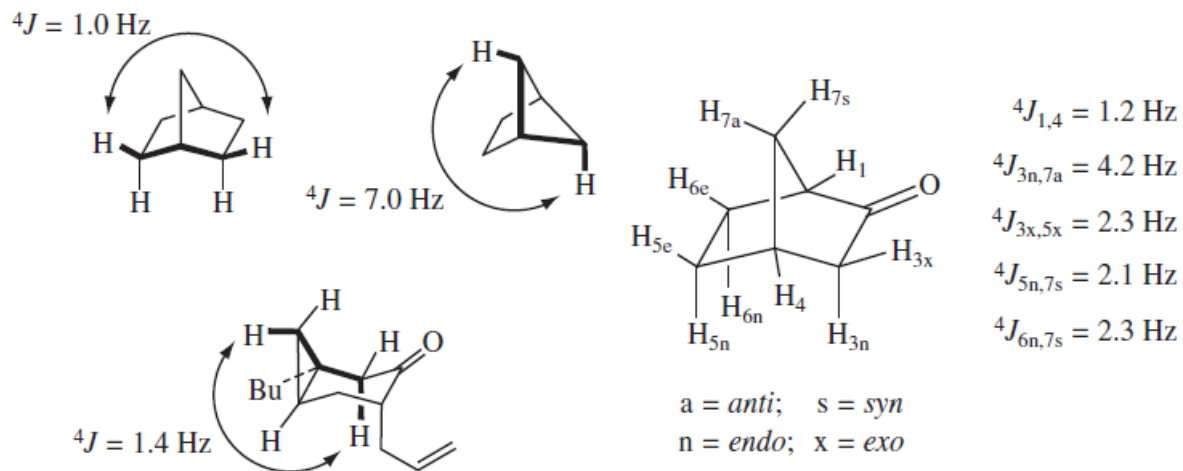


FIGURE 7.16 Examples of 4J W coupling in rigid bicyclic compounds.

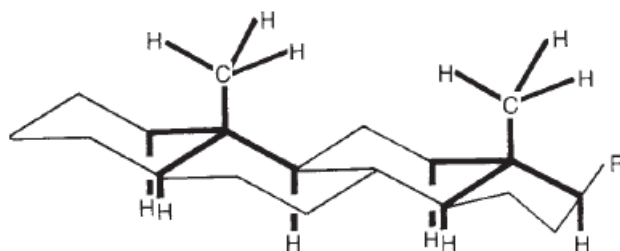
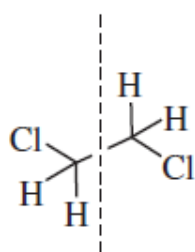
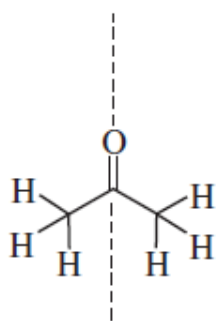


FIGURE 7.17 A steroid ring skeleton showing several possible W couplings (4J).

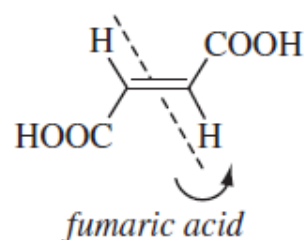
MAGNETIC EQUIVALENCE

plane of symmetry

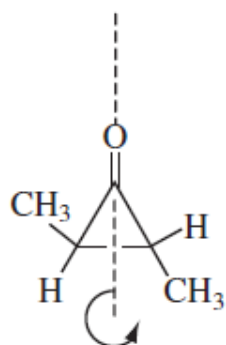


plane of symmetry

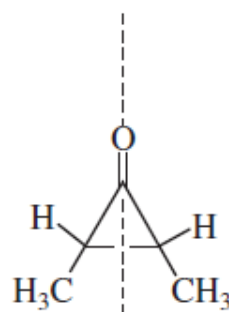
axis of symmetry



fumaric acid



axis of symmetry



plane of symmetry

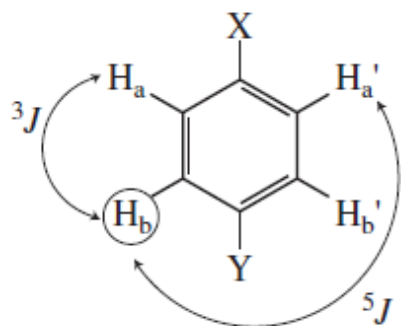
identical types. Magnetic equivalence has two strict requirements:

1. Magnetically equivalent nuclei must be **isochronous**; that is, they must have identical chemical shifts.

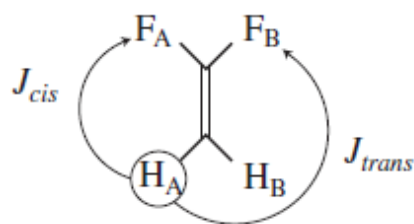
and

2. Magnetically equivalent nuclei must have equal coupling (same J values) to all other nuclei in the molecule.

A corollary that follows from magnetic equivalence is that magnetically equivalent nuclei, even if they are close enough to be coupled, do not split one another, and they give only one signal (for both nuclei) in the NMR spectrum. This corollary does not imply that no coupling occurs between magnetically equivalent nuclei; it means only that no observable spin-spin splitting results from the coupling.

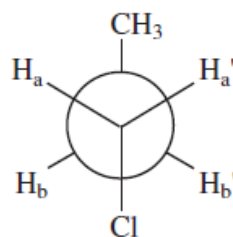
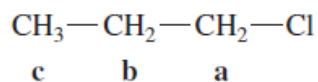


para-Disubstituted benzene



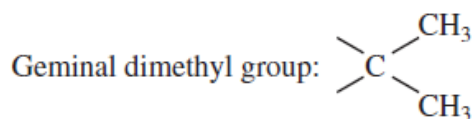
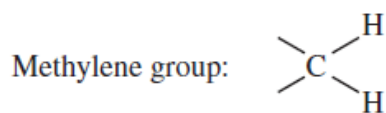
1, 1-Difluoroethene

1-Chloropropane



If conformation is locked (no rotation)

interest. There are three possible relationships for such geminal groups: they can be homotopic, enantiotopic, or diastereotopic.



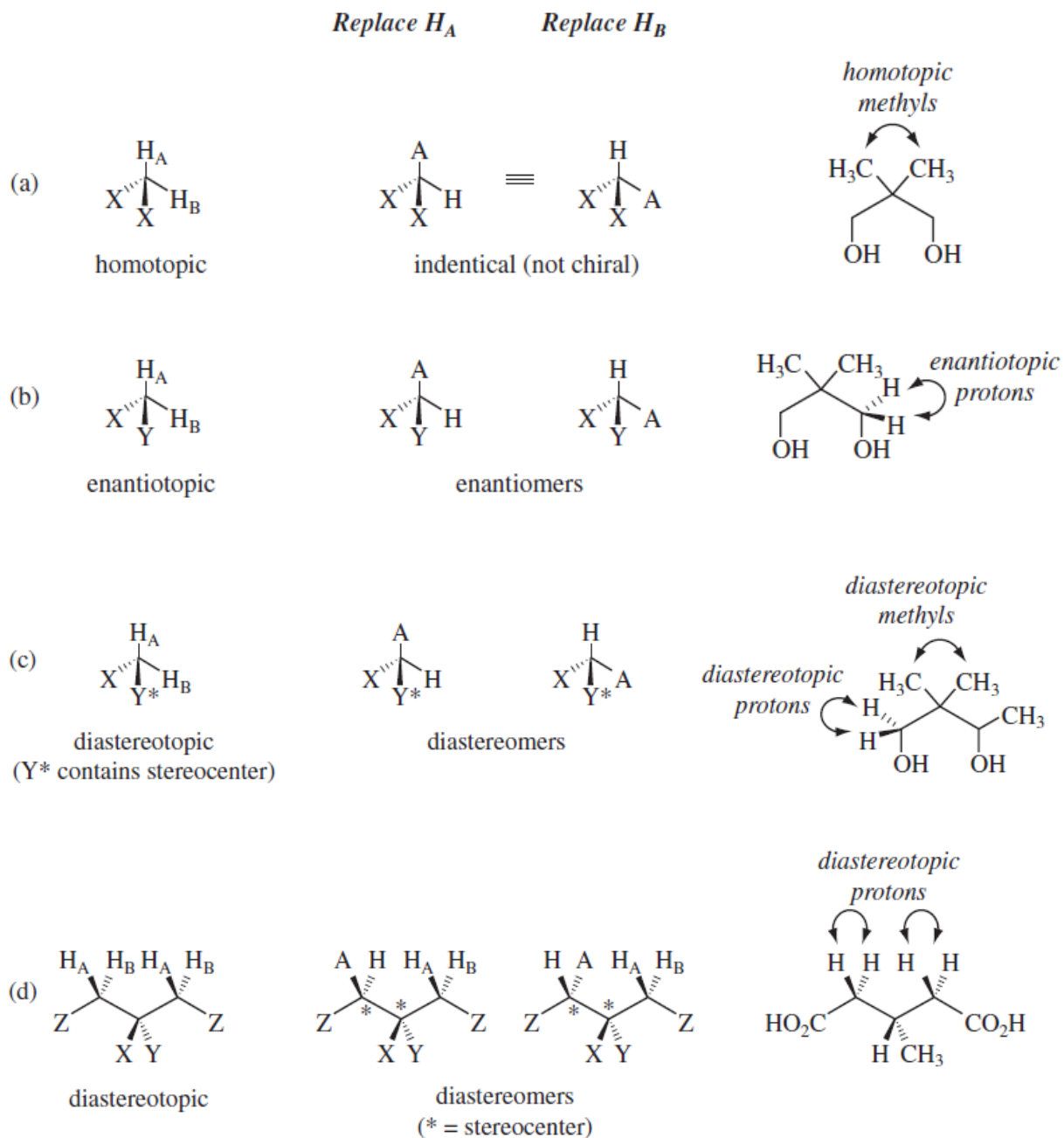
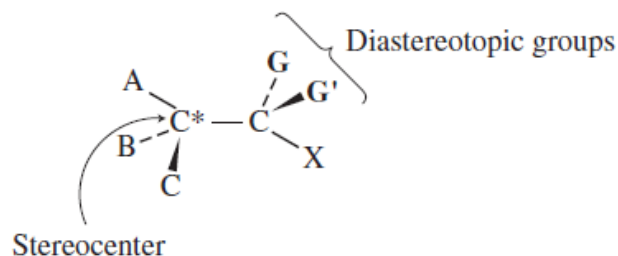


FIGURE 7.18 Replacement tests for homotopic, enantiotopic, and diastereotopic groups.

SPECTRA OF DIASTEREOTOPIC SYSTEMS

In this section, we examine some molecules that have diastereotopic groups (discussed in Section 7.3). Diastereotopic groups are not equivalent, and two different NMR signals are observed. The most common instance of diastereotopic groups is when two similar groups, G and G', are substituents on a carbon *adjacent to a stereocenter*. If first group G and then group G' are replaced by another group, a pair of diastereomers forms (see Fig. 7.18c).²



Diastereotopic Hydrogens: Ethyl 3-Hydroxybutanoate

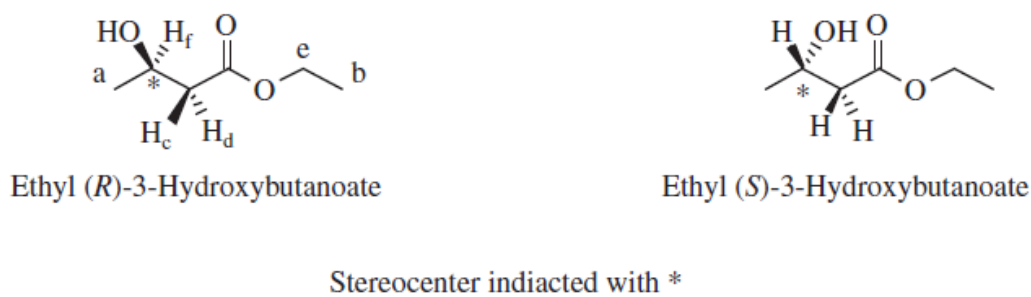


FIGURE 7.19 The structures of the enantiomers in a racemic mixture of ethyl 3-hydroxybutanoate.

A good example of a simple compound with diastereotopic methylene protons is ethyl 3-hydroxybutanoate (Fig. 7.19). The stereocenter at C-3 of the compound makes protons H_c and H_d magnetically inequivalent. When H_c and H_d in a methylene group are in different environments, they will show a ²J (two-bond, or geminal) coupling (Section 7.2B). For an sp³ hybridized carbon atom (~109° for a H–C–H angle), values of ²J are larger (9–18 Hz, typically 15 Hz) than usual ³J coupling constants (6–8 Hz). Values of ²J in methylene groups vary considerably with the degree of hybridization of carbon atoms (Table 7.3).

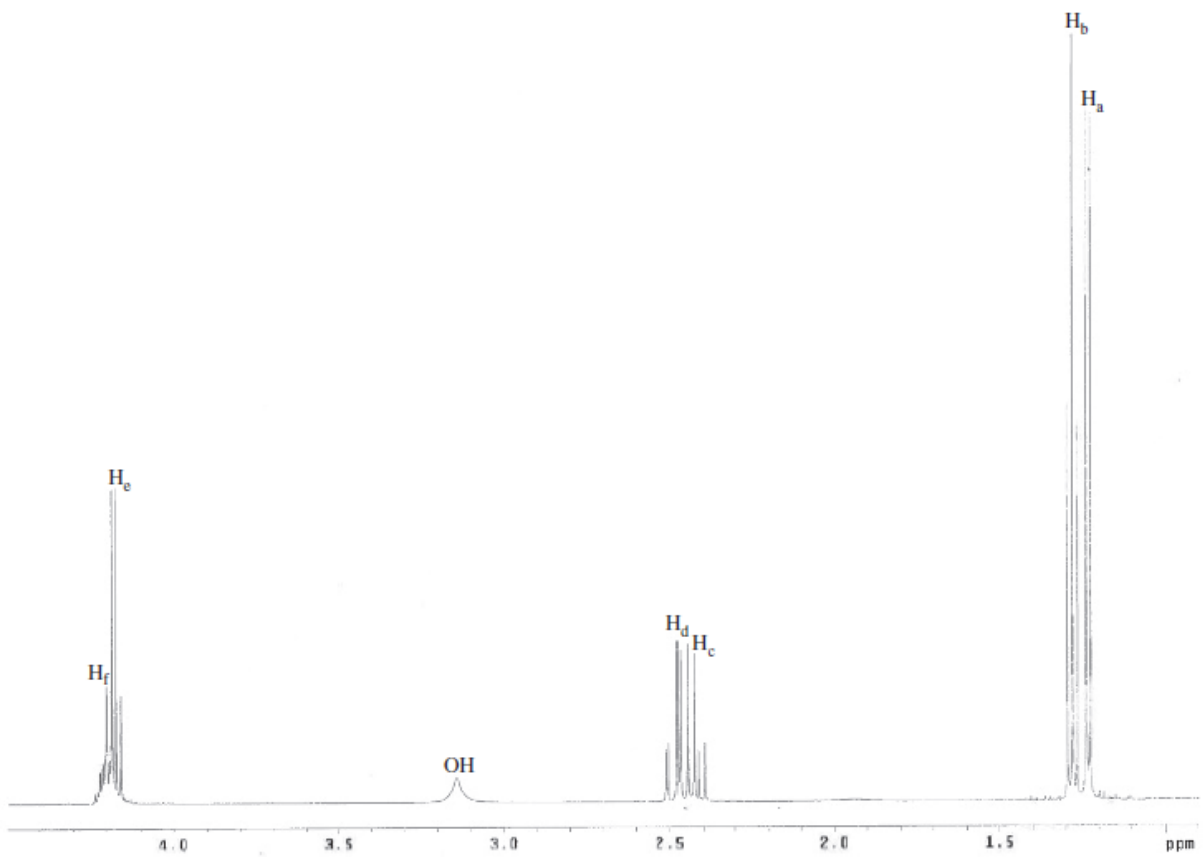


FIGURE 7.20 ^1H NMR spectrum of racemic ethyl 3-hydroxybutanoate (500 MHz, CDCl_3).

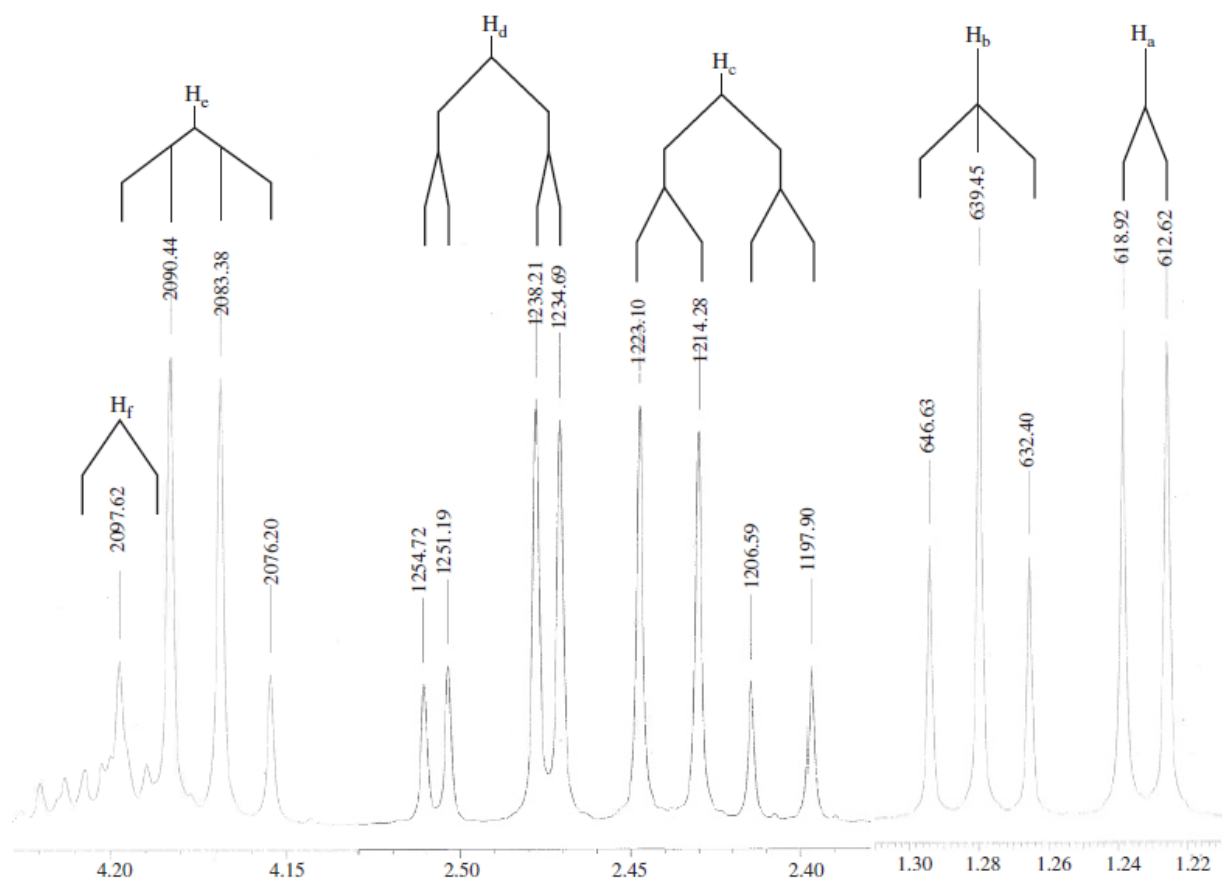
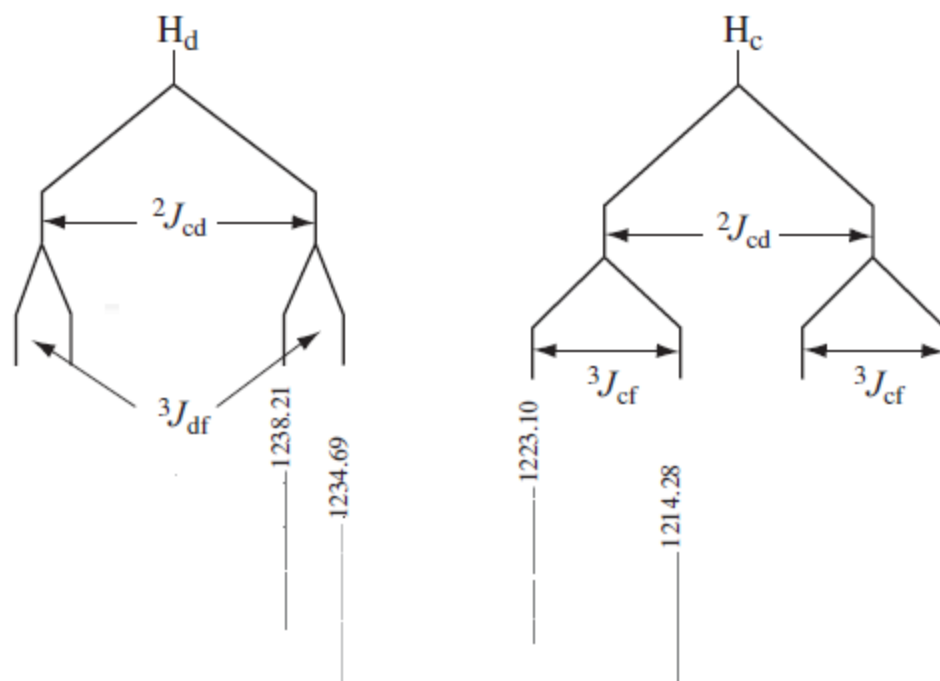


FIGURE 7.21 Expansions of the ¹H NMR spectrum of ethyl 3-hydroxybutanoate (500 MHz, CDCl₃).



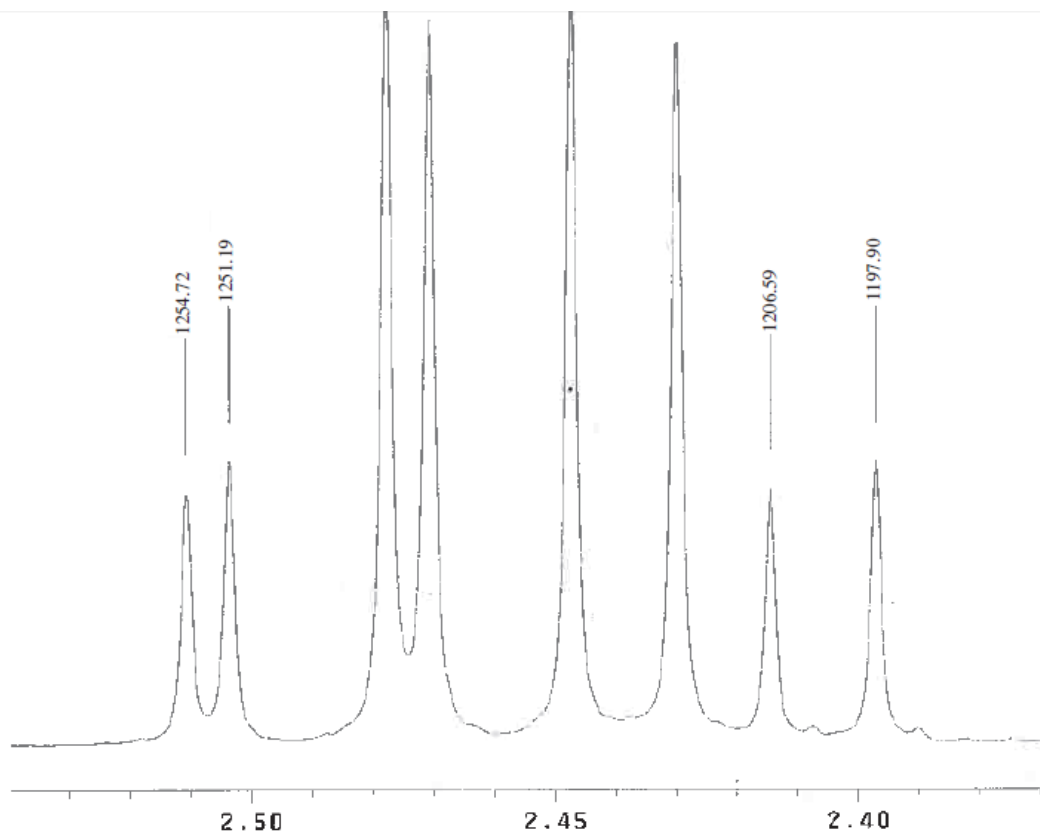
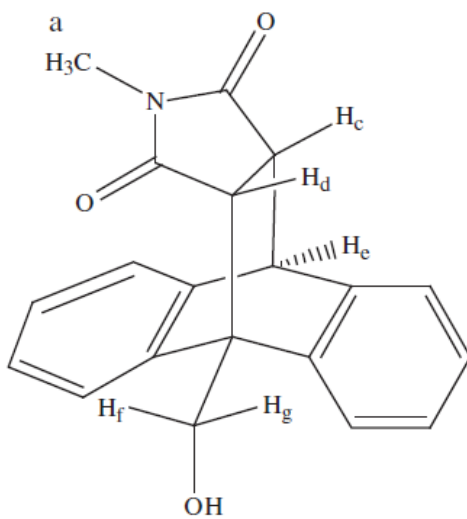


FIGURE 7.22 Expansion of the diastereotopic methylene protons in the ^1H NMR spectrum of ethyl 3-hydroxybutanoate (500 MHz, CDCl_3).

Diastereotopic Hydrogens: The Diels-Alder Adduct of Anthracene-9-methanol and *N*-Methylmaleimide



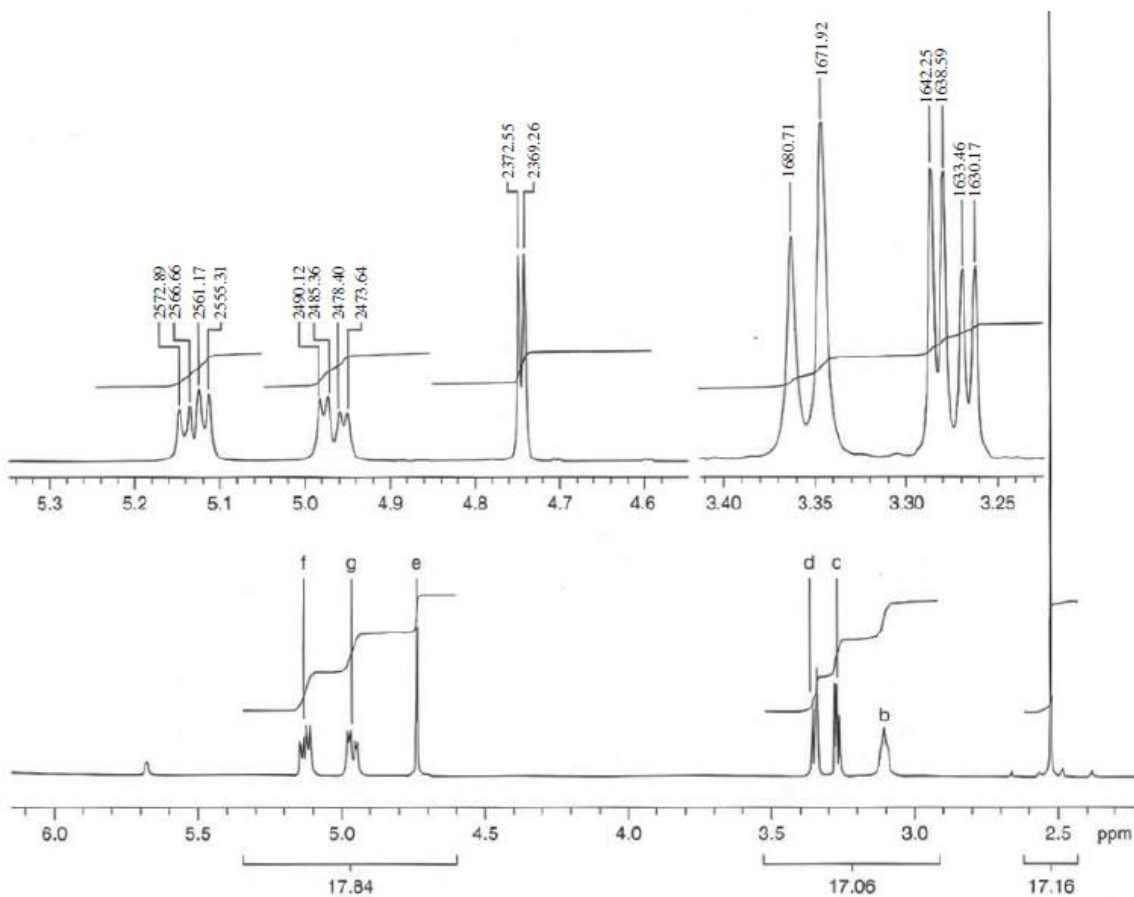
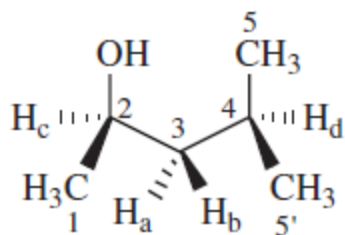


FIGURE 7.24 The 500 MHz NMR spectrum (CDCl_3) of the Diels-Alder product of anthracene-9-methanol and *N*-methylmaleimide. The insets show expansions of the regions from 3.25 to 3.40 ppm and

Diastereotopic Hydrogens: 4-Methyl-2-pentanol



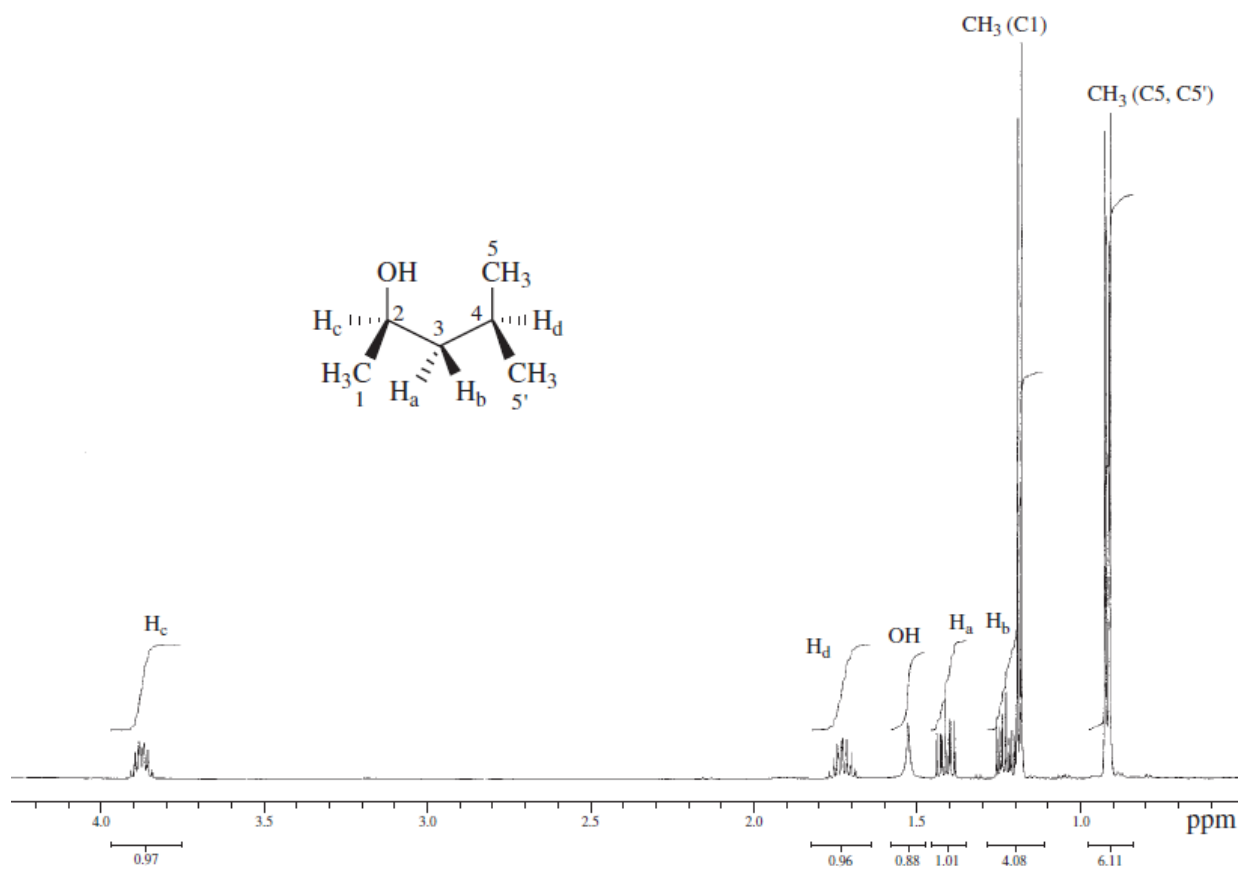


FIGURE 7.25 ¹H spectrum of 4-methyl-2-pentanol showing diastereotopic methyl and methylene groups (500 MHz, CDCl₃).

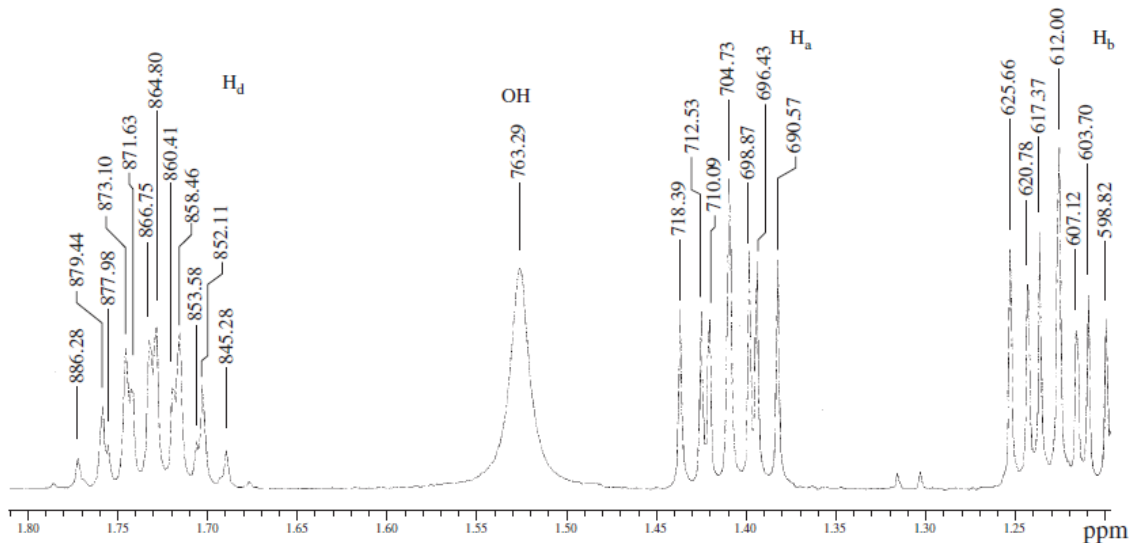
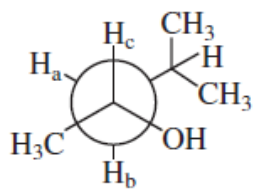
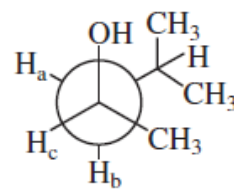
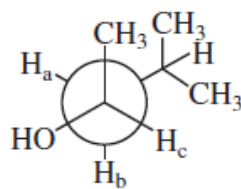


FIGURE 7.26 Expansion of the ¹H spectrum of 4-methyl-2-pentanol showing diastereotopic methylene protons.



lowest energy conformation



highest energy conformation

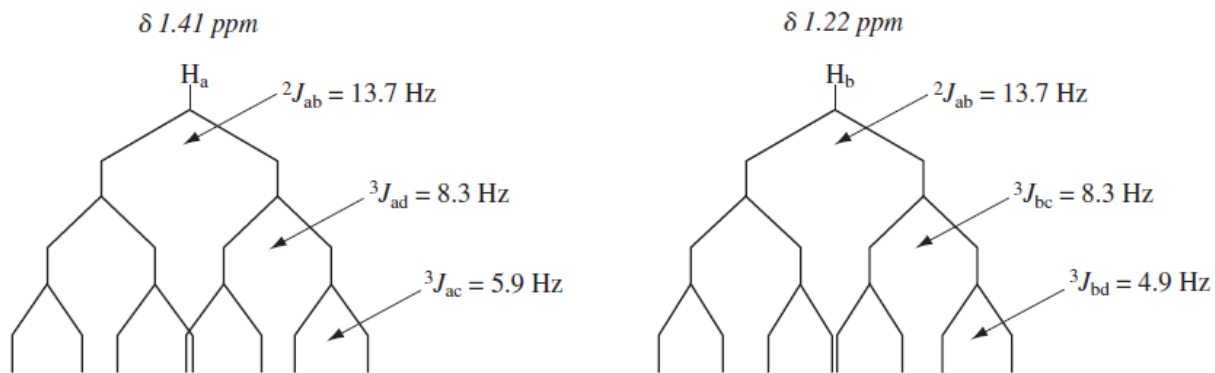


FIGURE 7.27 Splitting diagrams for the diastereotopic methylene protons in 4-methyl-2-pentanol.

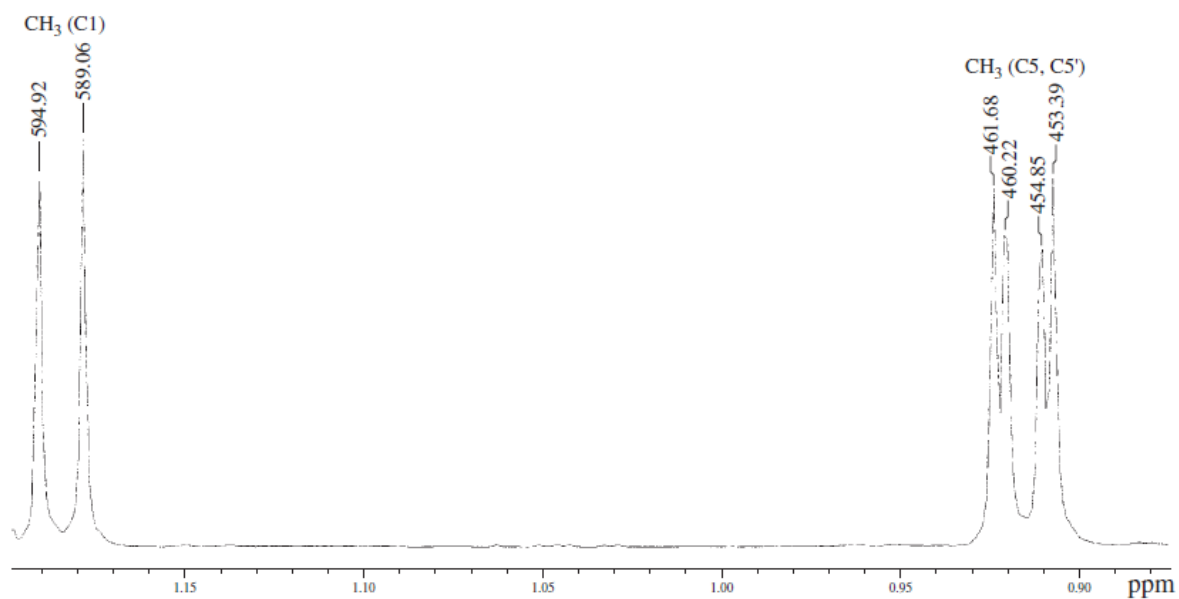


FIGURE 7.29 Upfield region of the ^1H spectrum of 4-methyl-2-pentanol showing diastereotopic methyl groups.

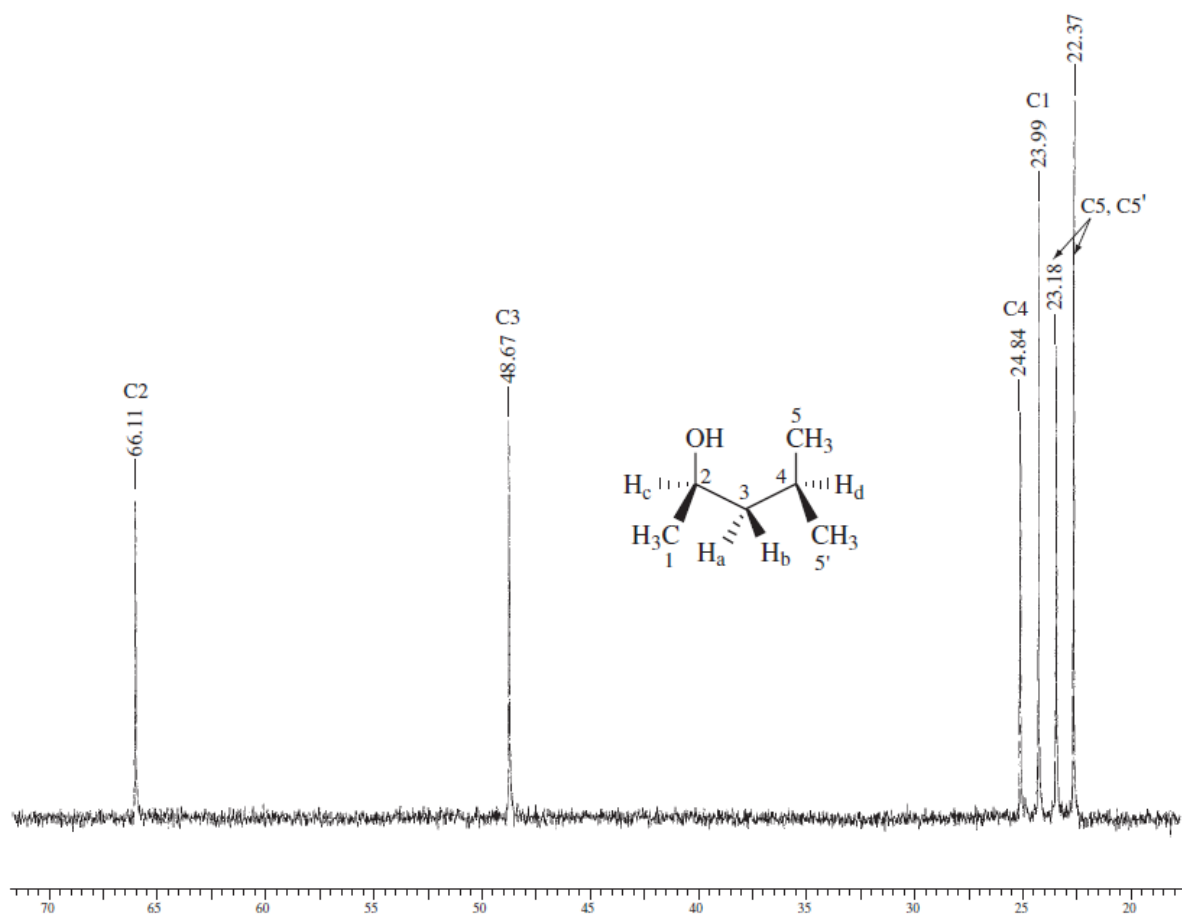
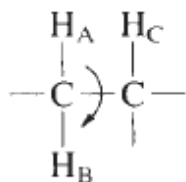


FIGURE 7.28 ^{13}C spectrum of 4-methyl-2-pentanol showing diastereotopic methyl groups.

7.5 NONEQUIVALENCE WITHIN A GROUP—THE USE OF TREE DIAGRAMS WHEN THE $n + 1$ RULE FAILS

(a) Free rotation

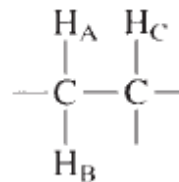
The $n + 1$ rule applies



$$\begin{aligned}
 \delta_A &= \delta_B \\
 J_{AC} &= J_{BC} \\
 J_{AB} &= 0
 \end{aligned}$$

(b) Biased conformation

A tree diagram is required

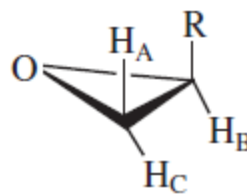
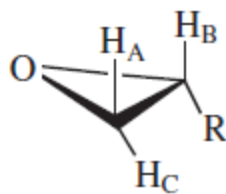


$$\begin{aligned}
 \delta_A &\neq \delta_B \\
 J_{AC} &\neq J_{BC} \\
 J_{AB} &\neq 0
 \end{aligned}$$

FIGURE 7.30 Two cases of splitting.

$${}^2J_{AC} = 5-6 \text{ Hz}$$

$$\alpha = \sim 118^\circ$$



$${}^3J_{AB} = 4-5 \text{ Hz}$$

$$\alpha = \sim 0^\circ$$

$${}^3J_{AB} = 2-4 \text{ Hz}$$

$$\alpha = \sim 120^\circ$$

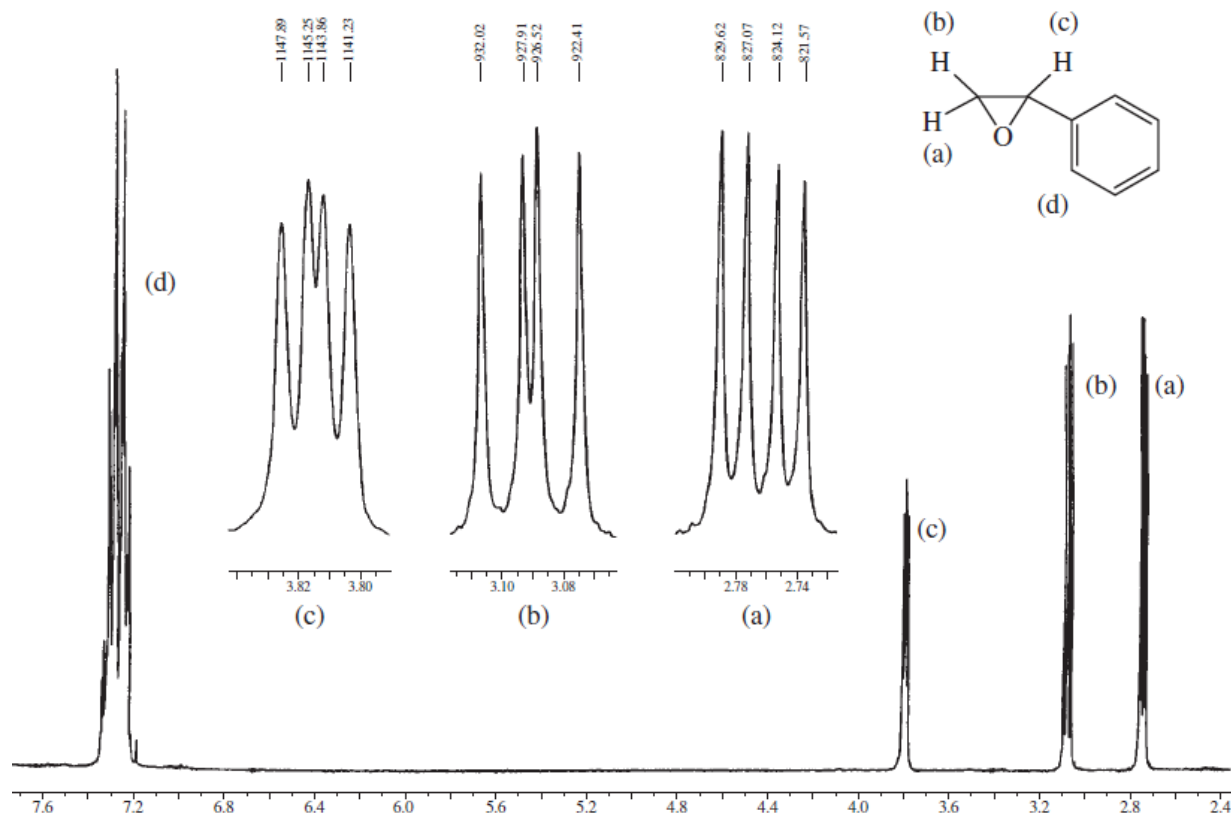


FIGURE 7.31 The ${}^1\text{H}$ NMR spectrum of styrene oxide.

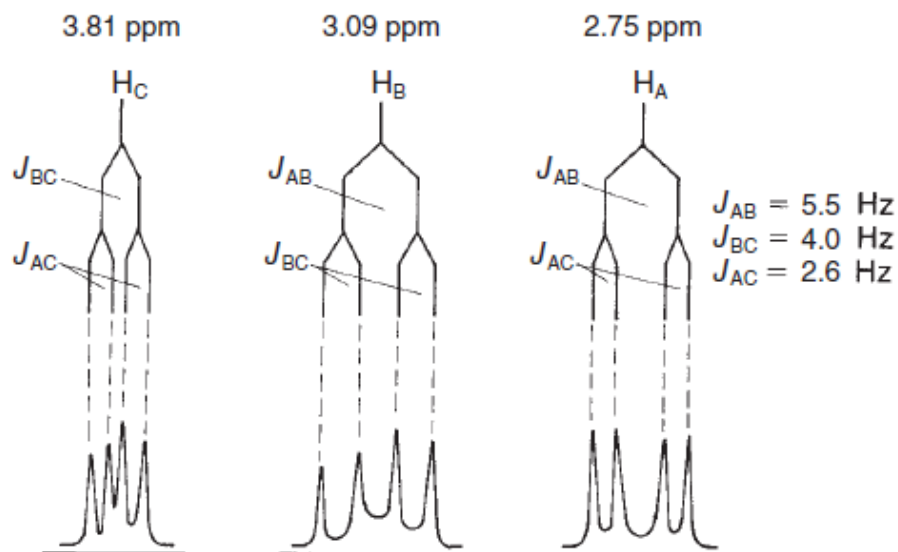


FIGURE 7.32 An analysis of the splitting pattern in styrene oxide.

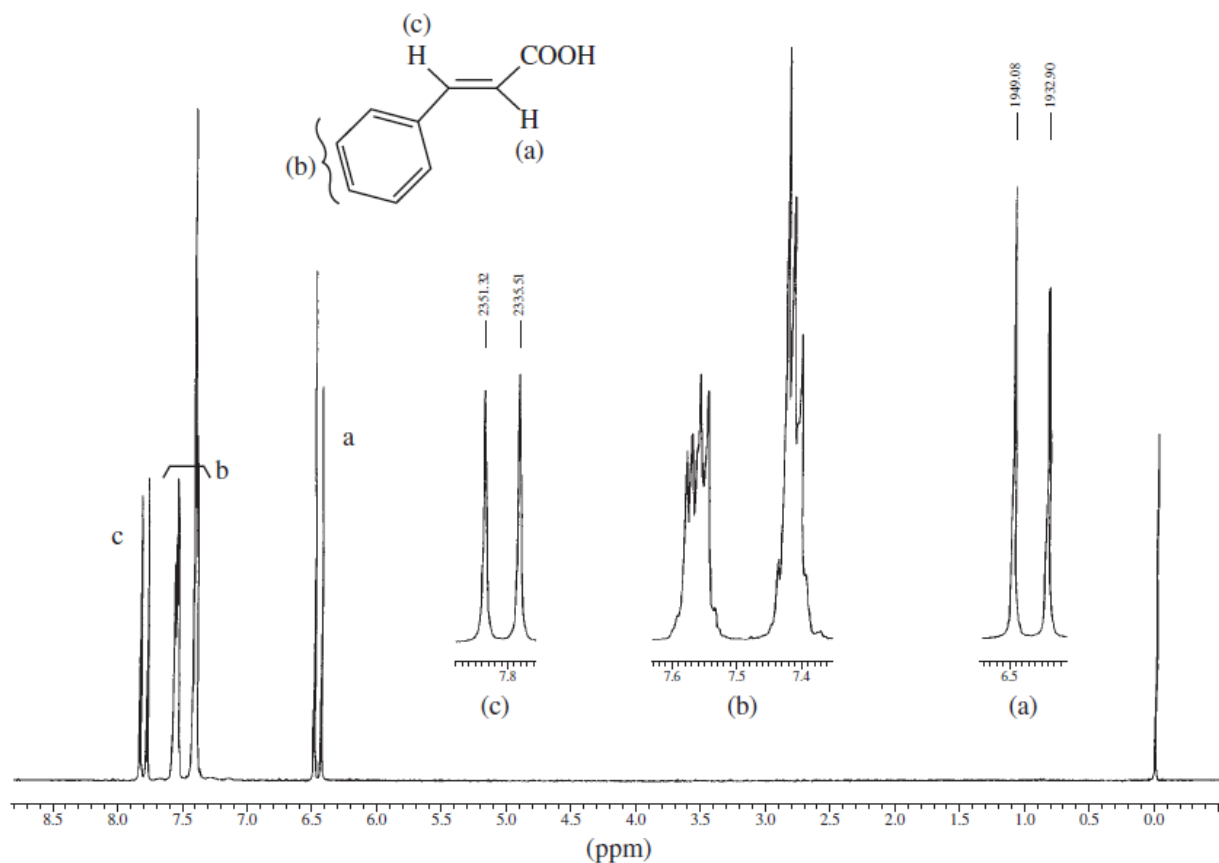


FIGURE 7.49 The 1H NMR spectrum of *trans*-cinnamic acid.

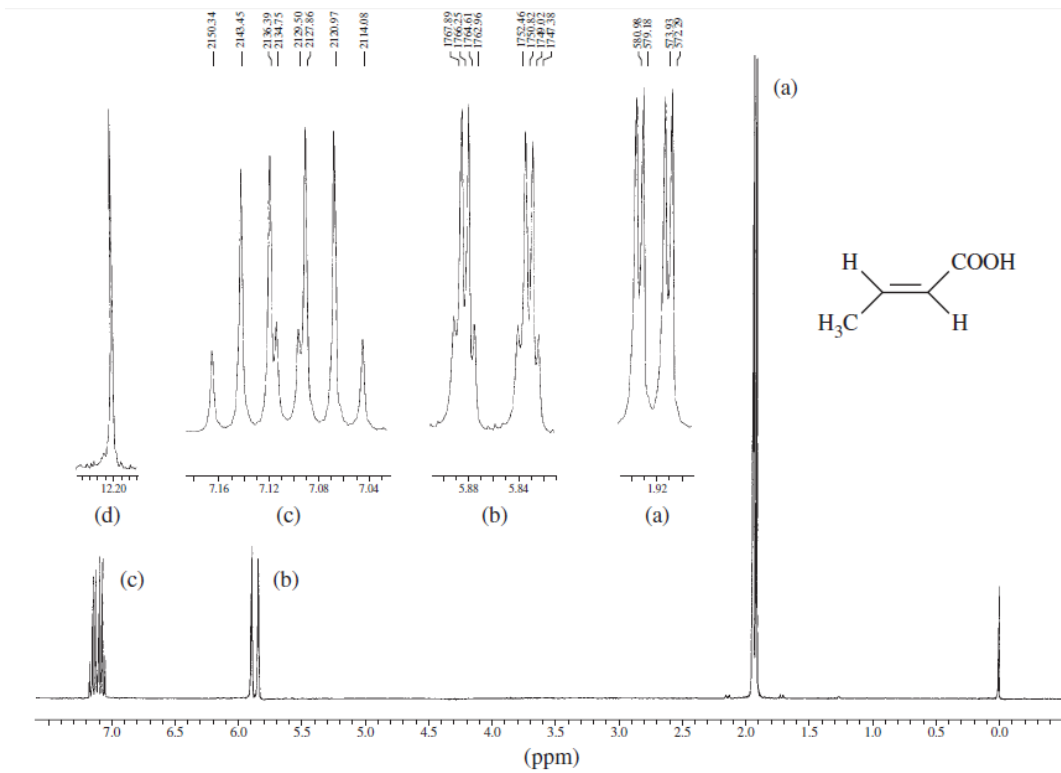
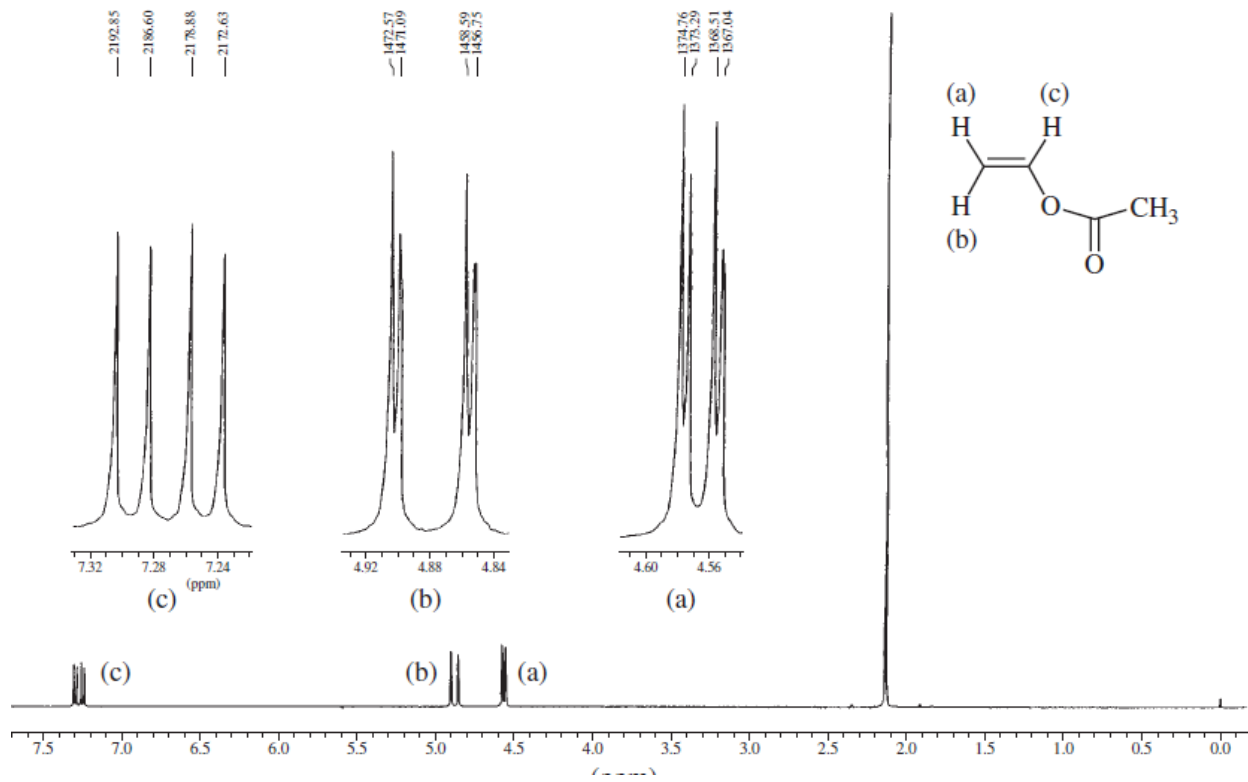


FIGURE 7.53 The 300-MHz ^1H NMR spectrum of crotonic acid (AMX_3).

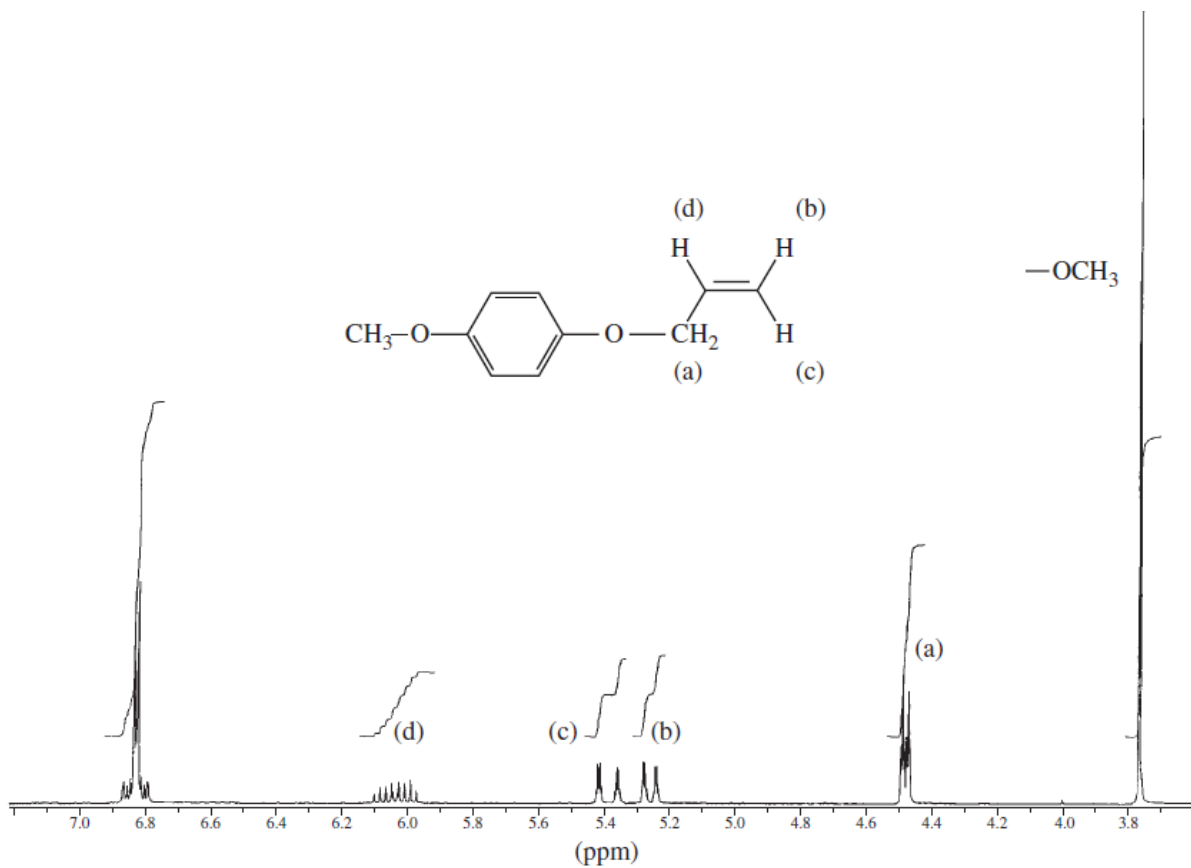


FIGURE 7.54 The 300-MHz ¹H NMR spectrum of 4-allyloxyanisole.

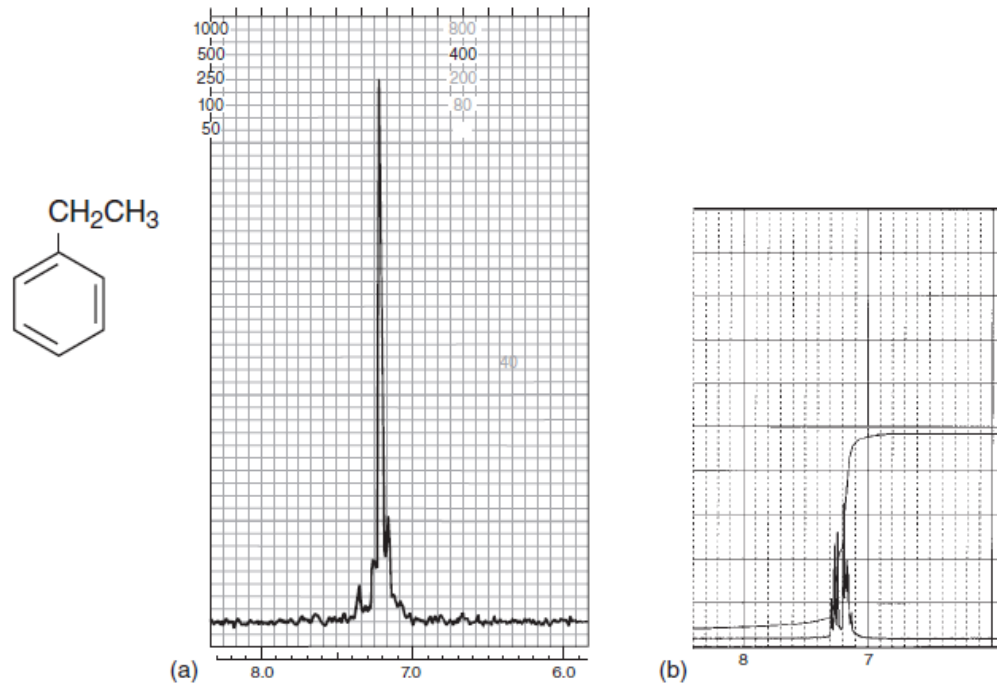


FIGURE 7.59 The aromatic ring portions of the ^1H NMR spectrum of ethylbenzene at (a) 60 MHz and (b) 300 MHz.

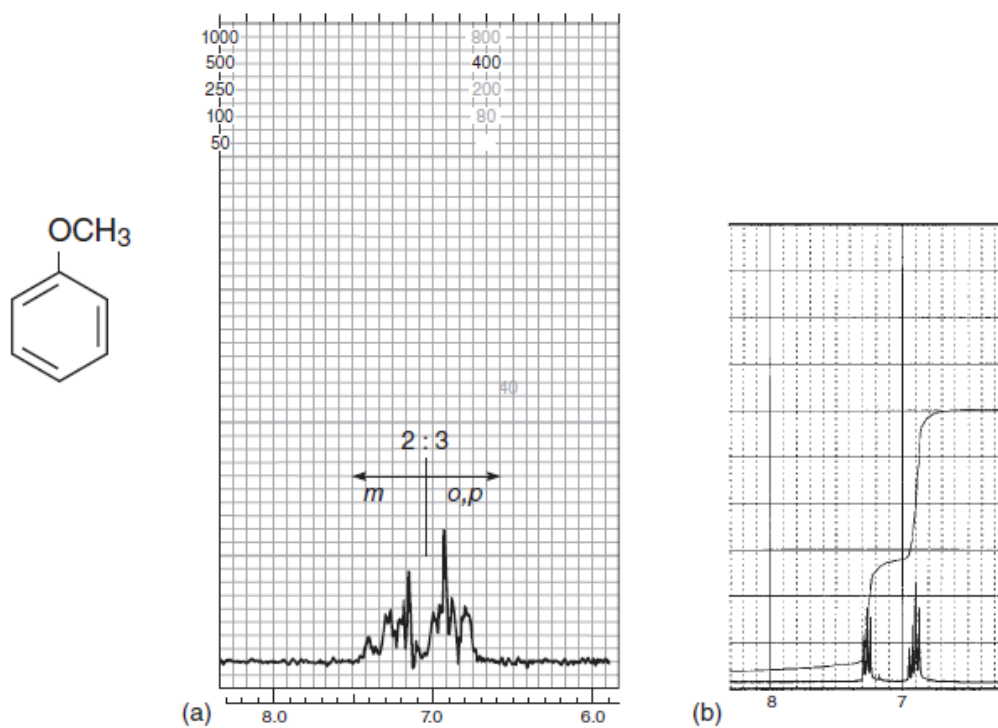


FIGURE 7.60 The aromatic ring portions of the ^1H NMR spectrum of anisole at (a) 60 MHz and (b) 300 MHz.

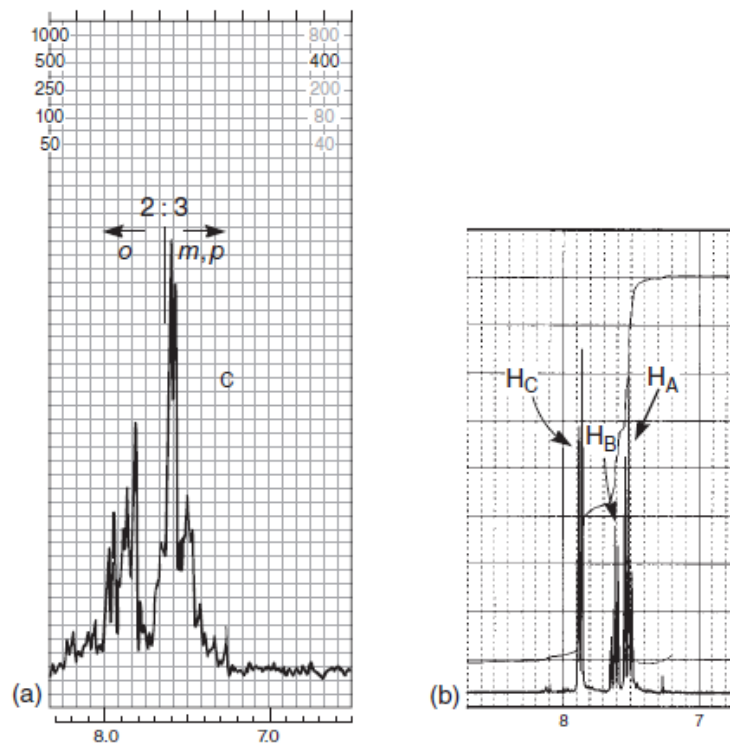
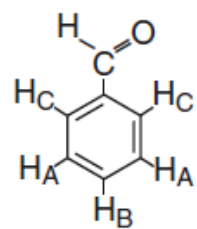
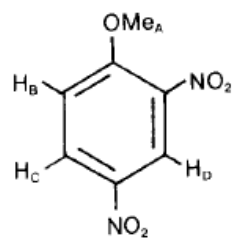
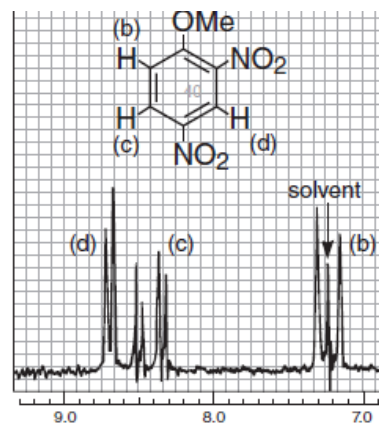
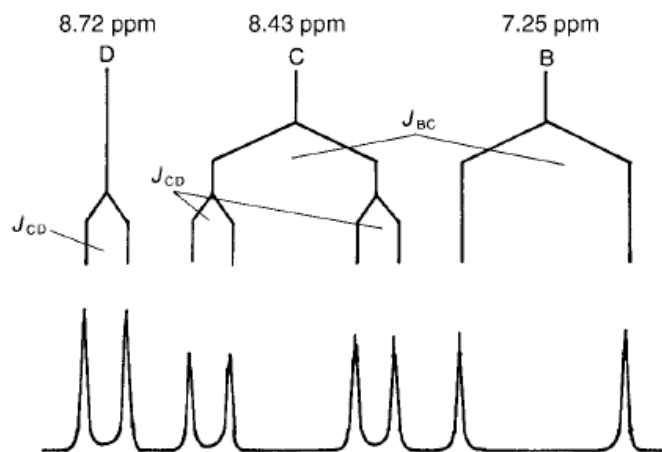


FIGURE 7.62 The aromatic ring portions of the ^1H NMR spectrum of benzaldehyde at (a) 60 MHz and (b) 300 MHz.

FIGURE 7.66 The aromatic ring portion of the 60-MHz ^1H NMR spectrum of 2,4-dinitroanisole.



$^3J_{BC} \sim 8$ ortho
 $^4J_{CD} \sim 2$ meta
 $^5J_{BD} \sim 0$ para



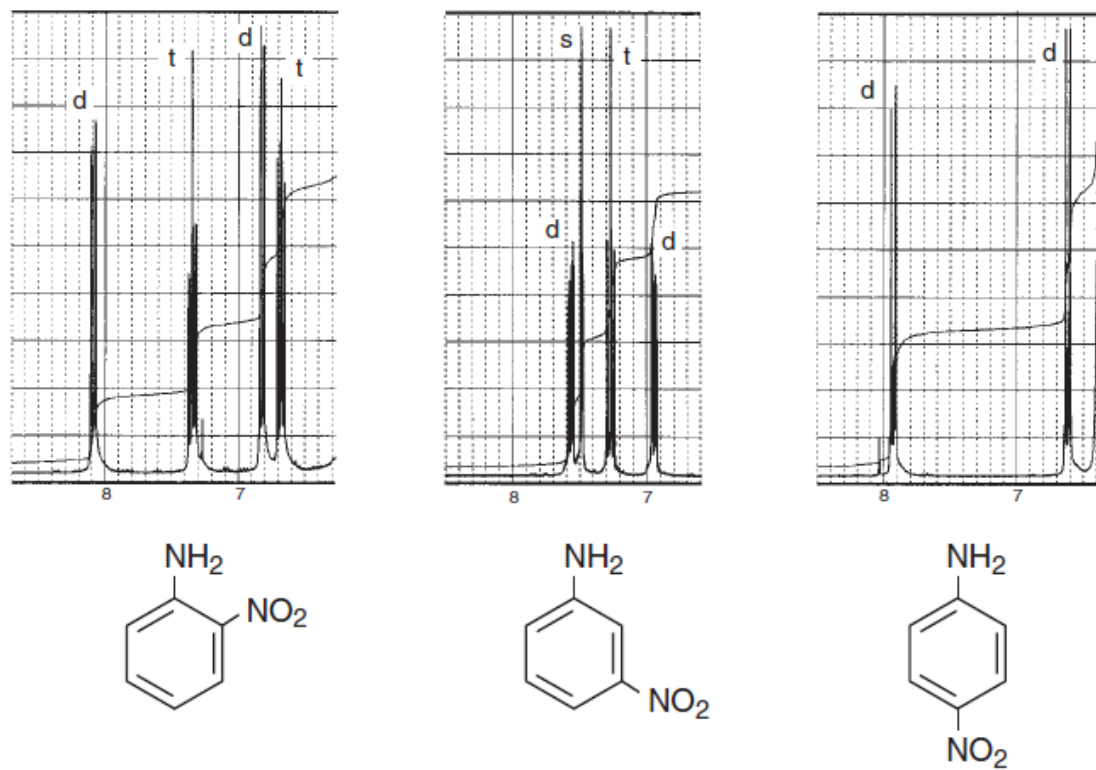


FIGURE 7.68 The 300-MHz ^1H NMR spectra of the aromatic ring portions of 2-, 3-, and 4-nitroaniline.

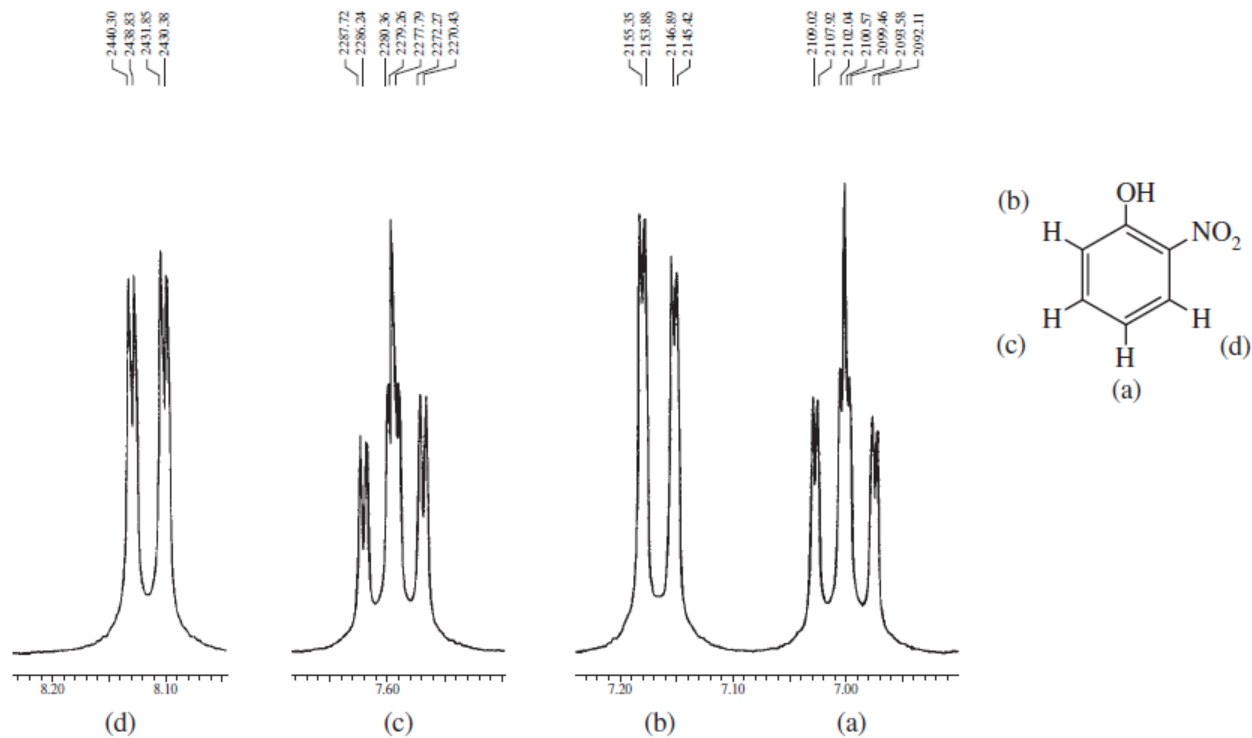


FIGURE 7.69 Expansions of the aromatic ring proton multiplets from the 300-MHz ^1H NMR spectrum of 2-nitrophenol. The hydroxyl resonance is not shown.

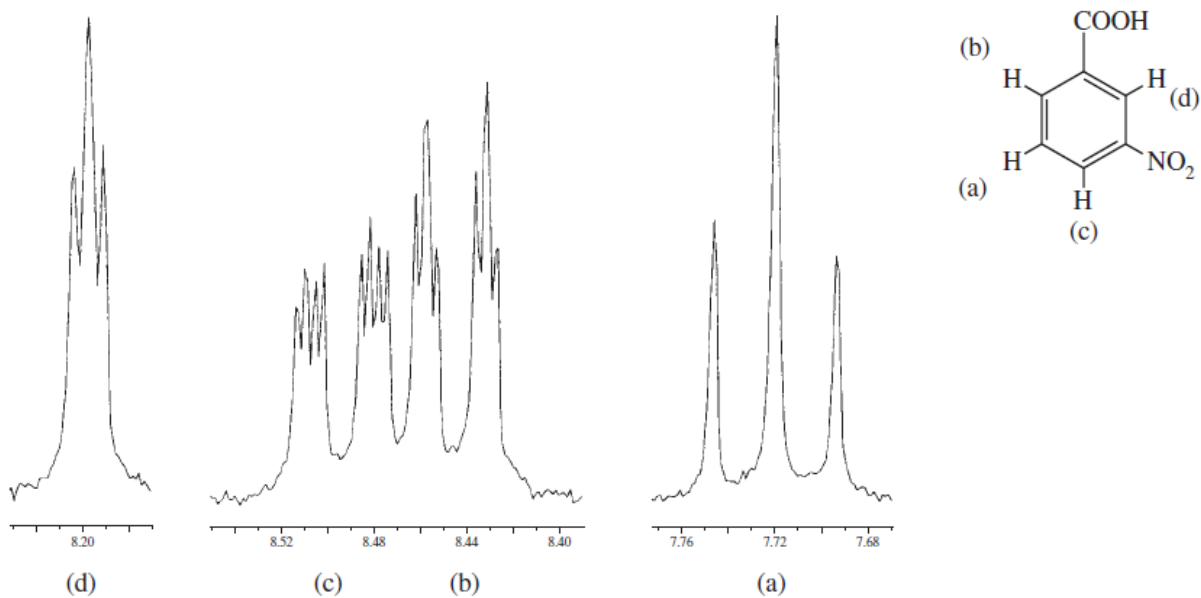
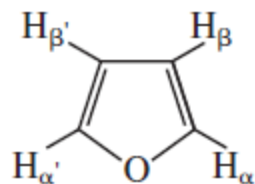


FIGURE 7.70 Expansions of the aromatic ring proton multiplets from the 300-MHz ^1H NMR spectrum of 3-nitrobenzoic acid. The acid resonance is not shown.

COUPLING IN HETEROAROMATIC SYSTEMS



$${}^3J_{\alpha\beta} = 1.6 - 2.0 \text{ Hz}$$

$${}^4J_{\alpha\beta'} = 0.3 - 0.8 \text{ Hz}$$

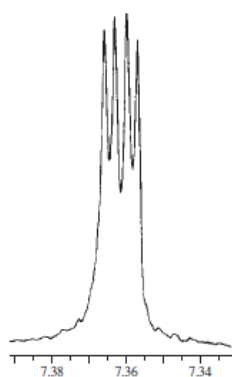
$${}^4J_{\alpha\alpha'} = 1.3 - 1.8 \text{ Hz}$$

$${}^3J_{\beta\beta'} = 3.2 - 3.8 \text{ Hz}$$

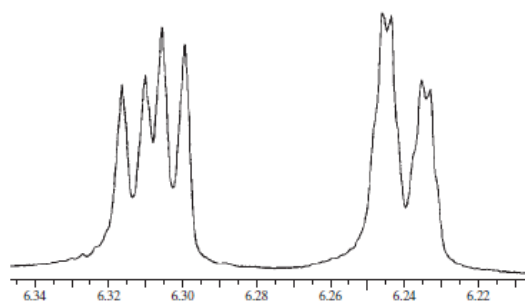
2210.94
2210.08
2209.09
2208.24

1895.93
1894.06
1892.71
1890.86

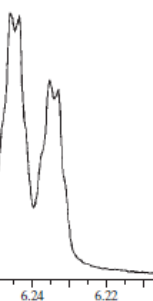
1874.84
1873.98
1871.62
1870.76



(c)



(b)



(a)

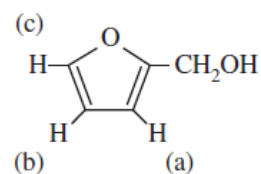
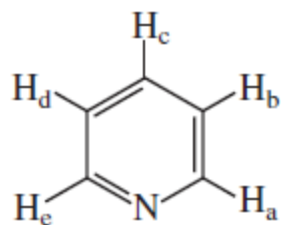


FIGURE 7.71 Expansions of the ring proton resonances from the 300-MHz ${}^1\text{H}$ NMR spectrum of furfuryl alcohol. The resonances from the hydroxymethyl side chain are not shown.



$${}^3J_{ab} = 4 - 6 \text{ Hz}$$

$${}^3J_{bc} = 7 - 9 \text{ Hz}$$

$${}^4J_{ac} = 0 - 2.5 \text{ Hz}$$

$${}^4J_{bd} = 0.5 - 2 \text{ Hz}$$

$${}^5J_{ad} = 0 - 2.5 \text{ Hz}$$

$${}^4J_{ae} < 1 \text{ Hz}$$

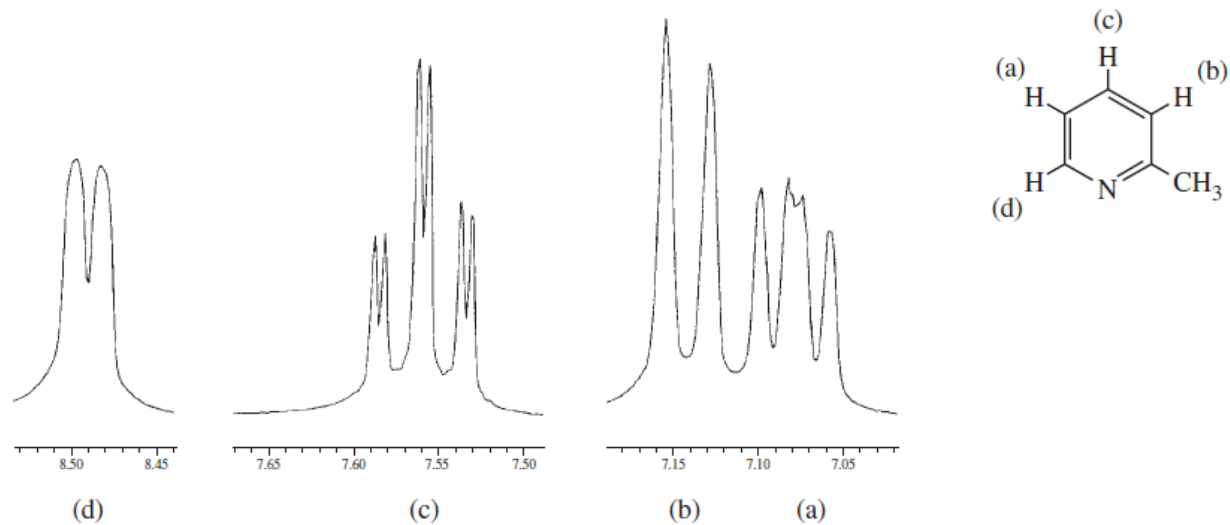


FIGURE 7.72 Expansions of the ring proton resonances from the 300-MHz ^1H NMR spectrum of 2-picoline (2-methylpyridine). The methyl resonance is not shown.

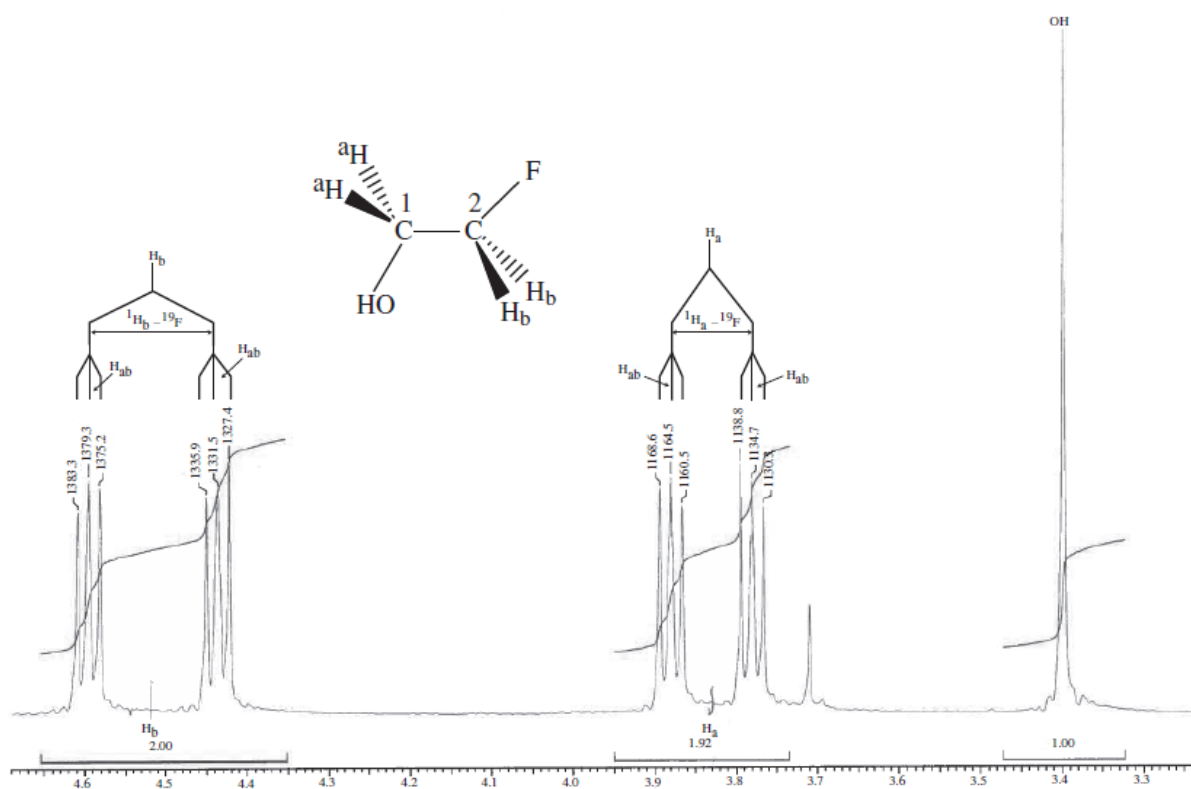


FIGURE 7.73 ^1H NMR Spectrum of 2-fluoroethanol (300 MHz, CDCl_3)

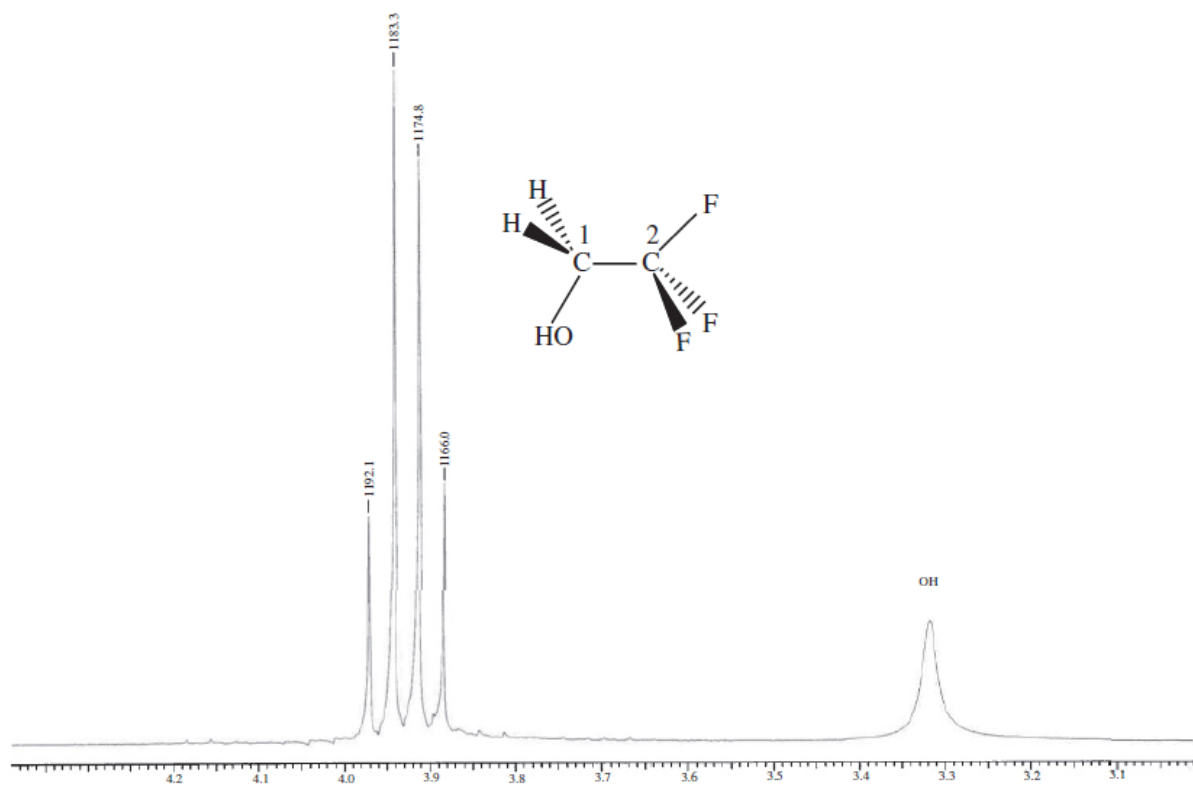


FIGURE 7.74 ^1H NMR Spectrum of 3,3,3-trifluoroethanol (300 MHz, CDCl_3)

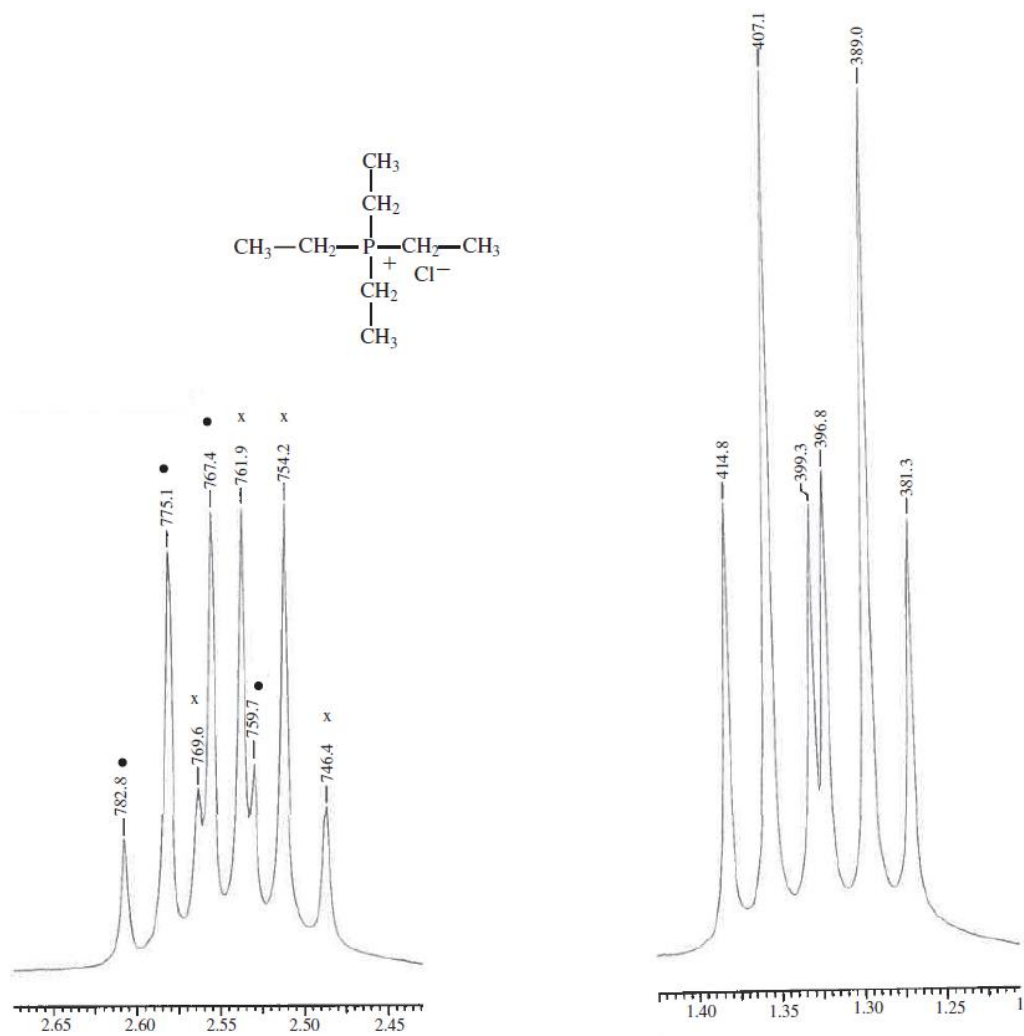
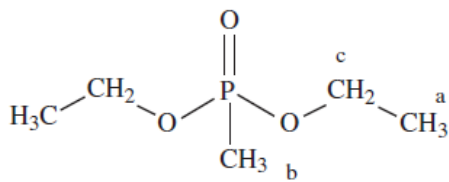
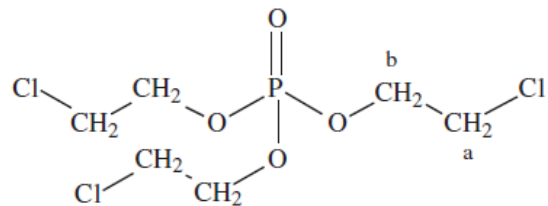


FIGURE 7.75 ^1H NMR Spectrum of tetraethylphosphonium chloride (300 MHz, CDCl_3). The pattern centering on 1.33 ppm is a doublet of triplets. The pattern centering on 2.55 ppm can be described as a doublet of quartets. One of the quartets is indicated with dots. The other quartet is shown with x.



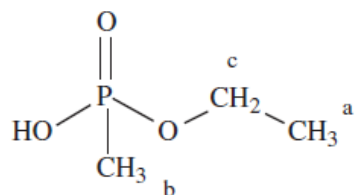
diethyl methylphosphonate

H_a	1.35 ppm	triplet	$^3J_{ac} = 7.1$ Hz
H_b	1.48 ppm	doublet	$^3J_{\text{HP}} = 17.6$ Hz
H_c	4.10 ppm	multiplet	$^3J_{ac} = 7.1$ Hz



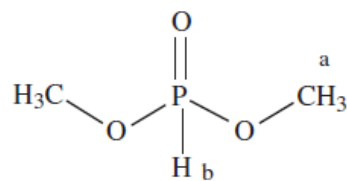
tris(2-chloroethyl) phosphate

H_a	3.74 ppm	triplet	$^3J_{ab} = 5.5$ Hz
H_b	4.34 ppm	doublet of triplets	$^3J_{\text{HP}} = 7.7$ Hz
			$^3J_{ab} = 5.5$ Hz



ethyl methylphosphonate

H _a	1.35 ppm	triplet	$^3J_{ac} = 7 \text{ Hz}$
H _b	1.49 ppm	doublet	$^3J_{HP} = 17.6 \text{ Hz}$
H _c	4.10 ppm	app quintet	$^3J_{ac} = 7 \text{ Hz}$ $^3J_{HP} = 8 \text{ Hz}$



dimethyl phosphonate

H _a	3.77 ppm	doublet	$^3J_{HP} = 11.8 \text{ Hz}$
H _b	6.77 ppm	doublet	$^1J_{HP} = 697.5 \text{ Hz}$