Answers to Problems
Introduction to Spectroscopy, 3rd edition

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CHAPTER 1

1.   (a)   90.50% carbon; 9.50% hydrogen   (b) C_4H_5

2.   32.0% carbon; 5.4% hydrogen; 62.8% chlorine; $C_3H_6Cl_2$

3. $C_2H_5NO_2$

4.   180.2 = molecular mass. Molecular formula is $C_9H_8O_4$.

5.   Equivalent weight = 52.3

6.   (a)   6   (b)   1   (c)   3   (d)   6   (e)   12

7.   The index of hydrogen deficiency = 1. There cannot be a triple bond, since the presence of a triple bond would require an index of hydrogen deficiency of at least 2.

8.   (a)   59.96% carbon; 5.75% hydrogen; 34.29% oxygen   (b) $C_7H_8O_3$
     (c) $C_{21}H_{24}O_9$ (d)   A maximum of two aromatic (benzenoid) rings

9.   (a) $C_8H_8O_2$ (b) $C_8H_{12}N_2$ (c) $C_7H_8N_2O$ (d) $C_5H_{12}O_4$

10.   Molecular formula = $C_8H_{10}N_4O_2$; index of hydrogen deficiency = 6

11.   Molecular formula = $C_{21}H_{30}O_2$; index of hydrogen deficiency = 7

12.   For the hydrolysis product: molecular formula = $C_6H_{12}O_6$; index of hydrogen deficiency = 1

   For the original carbohydrate: molecular formula = $C_{12}H_{22}O_{11}$; index of hydrogen deficiency = 2

CHAPTER 2

1.   (a)   Propargyl chloride (3-chloropropyne)
     (b)   *p*-Cymene (4-isopropyltoluene)

      (c)   *m*-Toluidine (3-methylaniline)
      (d)   *o*-Cresol (2-methylphenol)
      (e)   *N*-Ethylaniline
      (f)   2-Chlorotoluene
      (g)   2-Chloropropanoic acid
      (h)   3-Methyl-1-butanol
      (i)   5-Hexen-2-one
      (j)   1,2,3,4-Tetrahydronaphthalene
      (k)   3-(Dimethylamino)propanenitrile
      (l)   1,2-Epoxybutane

2.   Citronellal

3.   *trans*-Cinnamaldehyde (*trans*-3-phenyl-2-propenal)

4.   Upper spectrum, *trans*-3-hexen-1-ol; Lower spectrum, *cis*-3-hexen-1-ol

5.   (a)   Structure B (ethyl cinnamate)
      (b)   Structure C (cyclobutanone)
      (c)   Structure D (2-ethylaniline)
      (d)   Structure A (propiophenone)
      (e)   Structure D (butanoic anhydride)
      (f)   Structure C (Carvone)
      (g)   Structure B (undecylenic aldehyde)
      (h)   Structure D (2-ethyl-*trans*-2-hexenal)
      (i)   Structure B (*N*-methylcyclohexylamine)
      (j)   Structure B (1-hexanethiol)

6.   Poly(acrylonitrile-styrene); poly(methyl methacrylate); polyamide (nylon)

7.   Propyl acetate, allyl acetate, and ethyl acrylate

8.   2-Ethyl-δ-valerolactone, 3,4-dihydro-6-methyl-2*H*-pyran-2-one, and
      5,6-dihydro-2*H*-pyran-2-one

9.   α-Methylene-γ-butyrolactone, γ–methylene-γ-butyrolactone, and γ-valerolactone

10.   4-Penten-1-ol, 3-methyl-2-buten-1-ol, and 3-methyl-3-buten-1-ol

11.   Resonance effect: the amino group pushes electron density into the ring and into
      the carbonyl group resulting in a lower frequency carbonyl group (more single
      bond character). A nitro group withdraws electrons resulting in higher frequency
      carbonyl absorption (more double bond character).

CHAPTER 3

1. (a) -1, 0, +1 (b) -1/2, +1/2
    (c) -5/2, -3/2, -1/2, +1/2, +3/2, +5/2 (d) -1/2, +1/2

2. 128 Hz/60 MHz = 2.13 ppm

3. (a) 180 Hz (b) 1.50 ppm

4. See Figures 3.22 and 3.23. The methyl protons are in a shielding region.
    Acetonitrile shows similar anisotropic behavior to acetylene.

5. o-Hydroxyacetophenone is intramolecularly hydrogen bonded. The proton is
    deshielded (12.05 ppm). Changing concentration does not alter the extent of
    hydrogen bonding. Phenol is intermolecularly hydrogen bonded. The extent of
    hydrogen bonding depends upon concentration.

6. The methyl groups are in a shielding region of the double bonds. See Figure 3.23.

7. The carbonyl group deshields the *ortho* protons owing to anisotropy.

8. The methyl groups are in the shielding region of the double-bonded system. See
    Figure 3.24.

9. The spectrum will be similar to that in Figure 3.25, with some differences in
    chemical shifts. Spin arrangements: H_A will be identical to the pattern in Figure
    3.32 (triplet); H_B will see one adjacent proton and will appear as a doublet (+1/2
    and -1/2).

10. The isopropyl group will appear as a septet for the α-H (methine). From Pascal's
    triangle, the intensities are 1:6:15:20:15:6:1. The CH_3 groups will be a doublet.

11. Downfield doublet, area = 2, for the protons on carbon 1 and carbon 3; upfield
    triplet, area = 1, for the proton on carbon 2.

12. $X-CH_2-CH_2-Y$, where $X \neq Y$.

13. Upfield triplet for the C-3 protons, area = 3; intermediate sextet for the C-2
    protons, area = 2; and downfield triplet for the C-1 protons, area = 2

14. Ethyl acetate (ethyl ethanoate)

15. Isopropylbenzene

16. 2-Bromobutanoic acid

17. (a) Propyl acetate (b) Isopropyl acetate

18 1,3-Dibromopropane

19. 2,2-Dimethoxypropane

20. (a) Isobutyl propanoate (b) *t*-Butyl propanoate
    (c) Butyl propanoate

21. (a) 3-Chloropropanoic acid (b) 2-Chloropropanoic acid

22. (a) 2-Phenylbutane (b) 1-Phenylbutane (butylbenzene)

23. 2-Phenylethylamine

24. (a) 1-Phenyl-2-butanone (b) 4-Phenyl-2-butanone

25. (a) Ethyl 2-phenylacetate (b) Methyl 3-phenylpropanoate
    (c) 2-Phenylethyl acetate (d) 1-Phenylethyl acetate

26. 3-Hydroxy-3-methyl-2-butanone

27. Ethyl-2-propynoate

28. Diethyl malonate (diethyl propanedioate)

CHAPTER 4

1. Methyl acetate

2. (c) 7 peaks (d) 3 peaks
   (e) 5 peaks (f) 10 peaks
   (g) 10 peaks (h) 4 peaks
   (i) 5 peaks (j) 6 peaks
   (k) 8 peaks

3. (a) 2-Methyl-2-propanol (b) 2-Butanol (c) 2-Methyl-1-propanol

4. Methyl methacrylate (methyl 2-methyl-2-propenoate)

5. (a) 2-Bromo-2-methylpropane (b) 2-Bromobutane
   (c) 1-Bromobutane (d) 1-Bromo-2-methylpropane

6. (a) 4-Heptanone (b) 2,4-Dimethyl-3-pentanone
   (c) 4,4-Dimethyl-2-pentanone

7.   Hexamethylethane (2,2,3,3-tetramethylbutane)

8.   Diethoxymethane

9.   3,3-Dimethyloxetane

10.   Pyruvic aldehyde dimethyl acetal (1,1-dimethoxy-2-propanone)

11.   2-Indanone

12.   4-Methoxyphenylacetone

13.   Prenyl acetate (3-methyl-2-butenyl ethanoate)

14.   Ethyl levulinate (ethyl 4-oxopentanoate)

15.   Methyl 2,2-dichloro-1-methylcyclopropanecarboxylate

16.   Ethyl 2-nitropropanoate

17.   2,3-Dimethyl-2-butene. A primary cation rearranges to a tertiary cation via a hydride shift. E1 elimination forms the tetrasubstituted alkene.

18.   (a) Three equal-sized peaks for ^{13}C coupling to a single D atom; quintet for ^{13}C coupling to two D atoms.

      (b) Fluoromethane: doublet for ^{13}C coupling to a single F atom (^1J >180 Hz). Trifluoromethane: quartet for ^{13}C coupling to three F atoms (^1J >180 Hz). 1,1-Difluoro-2-chloroethane: triplet for carbon-1 coupling to two F atoms (^1J >180 Hz); triplet for carbon-2 coupling to two F atoms ($^2J \approx 40$ Hz). 1,1,1-trifluoro-2-chloroethane: quartet for carbon-1 coupling to three F atoms (^1J >180 Hz); quartet for carbon-2 coupling to three F atoms ($^2J \approx 40$ Hz).

19.   C1 = 128.5 + 9.3 = 137.8 ppm; C2 = 128.5 + 0.7 = 129.2 ppm; C3 = 128.50 - 0.1 = 128.4 ppm; C4 = 128.5 - 2.9 = 125.6 ppm.

20.   The answers are provided in the Textbook, Answers to Selected Problems, page ANS-3 and ANS-4.

CHAPTER 5

1. Refer to Section 5.8 for instructions on measuring coupling constants using the Hertz values that are printed above the expansions of the proton spectra.

(a) Vinyl acetate (Fig. 5.17). All vinyl protons are doublets of doublets.

H_a = 4.57 ppm, $^3J_{ac}$ = 6.25 Hz and $^2J_{ab}$ = 1.47 Hz.

H_b = 4.88 ppm. The coupling constants are not consistent; $^3J_{bc}$ = 13.98 or 14.34 Hz from the spacing of the peaks. $^2J_{ab}$ = 1.48 or 1.84 Hz. It is often the case that the coupling constants are not consistent (see Section 5.8). More consistent coupling constants can be obtained from analysis of proton H_c.

H_c = 7.27 ppm, $^3J_{bc}$ = 13.97 Hz and $^3J_{ac}$ = 6.25 Hz from the spacing of the peaks.

Summary of coupling constants from the analysis of the spectrum: $^3J_{ac}$ = 6.25 Hz, $^3J_{bc}$ = 13.97 Hz and $^2J_{ab}$ = 1.47 Hz. They can be rounded off to: 6.3, 14.0 and 1.5 Hz, respectively.

(b) *trans*-Crotonic acid (Fig. 5.21).
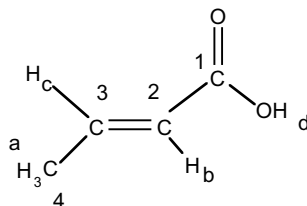
H_a = 1.92 ppm (methyl group at C-4). It appears as a doublet of doublets (dd) because it shows both ^3J and ^4J couplings; $^3J_{ac}$ = 6.9 Hz and $^4J_{ab}$ allylic = 1.6 Hz.

H_b = 5.86 ppm (vinyl proton at C-2). It appears as a doublet of quartets (dq); $^3J_{bc}$ trans = 15.6 Hz and $^4J_{ab}$ allylic = 1.6 Hz.

H_c = 7.10 ppm (vinyl proton at C-3). It appears as a doublet of quartets (dq), with some partial overlap of the quartets; $^3J_{bc}$ trans = 15.6 Hz and $^3J_{ac}$ = 6.9 Hz. Notice that H_c is shifted further downfield than H_b because of the resonance effect of the carboxyl group and also a through-space deshielding by the oxygen atom in the carbonyl group.
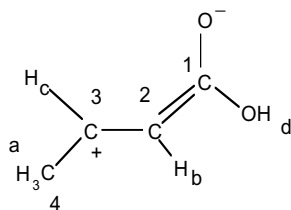
H_d = 12.2 ppm (singlet, acid proton on carboxyl group).

(c) 2-Nitrophenol (Fig. 5.49). H_a and H_b are shielded by the electron releasing effect of the hydroxyl group caused by the non-bonded electrons on the oxygen atom being involved in resonance. They can be differentiated by their appearance: H_a is a triplet

with some fine structure and H_b is a doublet with fine structure. H_d is deshielded by the electron wthdrawing effect and by the anisotropy of the nitro group. Notice that the pattern is a doublet with some fine structure. H_c is assigned by a process of elimination. It lacks any of the above effects that shields or deshields that proton. It appears as a triplet with some fine structure.

H_a = 7.00 ppm (ddd); $^3J_{ac} \cong ^3J_{ad}$ = 8.5 Hz and $^4J_{ab}$ = 1.5 Hz. H_a could also be described as a triplet of doublets (td) since $^3J_{ac}$ and $^3J_{ad}$ are nearly equal.

H_b = 7.16 ppm (dd); $^3J_{bc}$ = 8.5 Hz and $^4J_{ab}$ = 1.5 Hz.

H_c = 7.60 ppm (ddd or td); $^3J_{ac} \cong ^3J_{bc}$ = 8.5 Hz and $^4J_{cd}$ = 1.5 Hz.

H_d = 8.12 ppm (dd); $^3J_{ad}$ = 8.5 Hz and $^4J_{cd}$ = 1.5 Hz; $^5J_{bd}$ = 0.

The OH group is not shown in the spectrum.

(d) 3-Nitrobenzoic acid (Fig. 5.50). H_d if significantly deshielded by the anisotropy of both the nitro and carboxyl groups and appears furthest downfield. It appears as a narrowly space triplet. This proton only shows ^4J couplings. H_b is *ortho* to a carboxyl group while H_c is *ortho* to a nitro group. Both protons are deshielded, but the nitro group shifts a proton further downfield than for a proton next to a carboxyl group (see Appendix 6). Both H_b and H_c are doublets with fine structure consistent with their positions on the aromatic ring. H_a is relatively shielded and appears upfield as a widely spaced triplet. This proton does not experience any anisotropy effect because of its distance away from the attached groups. H_a has only ^3J couplings ($^5J_{ad}$ = 0).

H_a = 7.72 ppm (dd); $^3J_{ac}$ = 8.1 Hz and $^3J_{ab}$ = 7.7 Hz (these values come from analysis of H_b and H_c, below). Since the coupling constants are similar, the pattern appears as an accidental triplet.

H_b = 8.45 ppm (ddd or dt); $^3J_{ab}$ = 7.7 Hz; $^4J_{bd} \cong ^4J_{bc}$ = 1.5 Hz. The pattern is an accidental doublet of triplets.

H_c = 8.50 ppm (ddd); $^3J_{ac}$ = 8.1 Hz and $^4J_{cd} \neq ^4J_{bc}$.

H_d = 8.96 ppm (dd). The pattern appears to be a narrowly spaced triplet, but is actually an accidental triplet since $^4J_{bd} \neq ^4J_{cd}$.

The carboxyl proton is not shown in the spectrum.

(e) Furfuryl alcohol (Fig. 5.51). The chemical shift values and coupling constants for a furanoid ring are given in Appendix 4 and 5.

$H_a = 6.24$ ppm (doublet of quartets); $^3J_{ab} = 3.2$ Hz and $^4J_{ac} = 0.9$ Hz. The quartet pattern results from a nearly equal ^4J coupling of H_a to the two methylene protons in the CH_2OH group and the ^4J coupling of H_a to H_c (n + 1 rule, three protons plus one equals four, a quartet).

$H_b = 6.31$ ppm (dd); $^3J_{ab} = 3.2$ Hz and $^3J_{bc} = 1.9$ Hz.

$H_c = 7.36$ ppm (dd); $^3J_{bc} = 1.9$ Hz and $^4J_{ac} = 0.9$ Hz.

The CH_2 and OH groups are not shown in the spectrum.

(f) 2-Methylpyridine (Fig. 5.52). Typical chemical shift values and coupling constants for a pyridine ring are given in Appendix 4 and 5.

$H_a = 7.08$ ppm (dd); $^3J_{ac} = 7.4$ Hz and $^3J_{ad} = 4.8$ Hz.

$H_b = 7.14$ ppm (d); $^3J_{bc} = 7.7$ Hz and $^4J_{ab} \cong 0$ Hz.

$H_c = 7.56$ ppm (ddd or td). This pattern is a likely accidental triplet of doublets because $^3J_{ac} \cong {}^3J_{bc}$ and $^4J_{cd} = 1.8$ Hz.

$H_d = 8.49$ ppm ("doublet"). Because of the broadened peaks in this pattern, it is impossible to extract the coupling constants. We expect a doublet of doublets, but $^4J_{cd}$ is not resolved from $^3J_{ad}$. The adjacent nitrogen atom may be responsible for the broadened peaks.

2. (a) $J_{ab} = 0$ Hz   (b) $J_{ab} \sim 10$ Hz (c) $J_{ab} = 0$ Hz (d) $J_{ab} \sim 1$ Hz   (e) $J_{ab} = 0$ Hz
    (f) $J_{ab} \sim 10$ Hz   (g) $J_{ab} = 0$ Hz (h) $J_{ab} = 0$ Hz (i) $J_{ab} \sim 10$Hz; $J_{ab} \sim 16$Hz; $J_{ab} \sim 1$ Hz
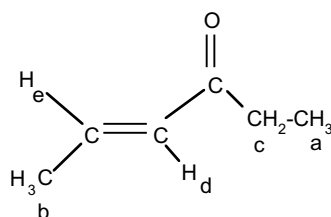
3.
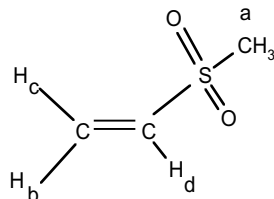
$H_a = 2.80$ ppm (singlet, CH_3).

$H_b = 5.98$ ppm (doublet); $^3J_{bd} = 9.9$ Hz and $^2J_{bc} = 0$ Hz.

$H_c = 6.23$ ppm (doublet); $^3J_{cd} = 16.6$ Hz and $^2J_{bc} = 0$ Hz.

$H_d = 6.61$ ppm (doublet of doublets); $^3J_{cd} = 16.6$ Hz and $^3J_{bd} = 9.9$ Hz.

4.
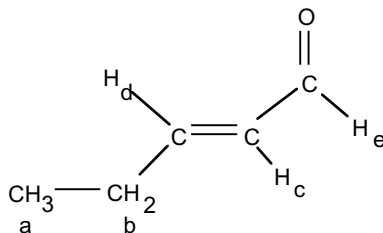

$H_a = 0.88$ ppm (triplet, CH_3); $^3J_{ac} = 7.4$ Hz.

$H_c = 2.36$ ppm (quartet, CH_2); $^3J_{ac} = 7.4$ Hz.

$H_b = 1.70$ ppm (doublet of doublets, CH_3); $^3J_{be} = 6.8$ Hz and $^4J_{bd} = 1.6$ Hz.

$H_d = 5.92$ ppm (doublet of quartets, vinyl proton). The quartets are narrowly spaced, suggesting a four bond coupling, ^4J; $^3J_{de} = 15.7$ Hz and $^4J_{bd} = 1.6$ Hz.

$H_e = 6.66$ ppm (doublet of quartets, vinyl proton). The quartets are widely spaced, suggesting a three bond coupling, ^3J; $^3J_{de} = 15.7$ Hz and $^3J_{be} = 6.8$ Hz. H_e appears further downfield than H_d (see the answer to problem 1b for an explanation).

5.

$H_a = 0.96$ ppm (triplet, CH_3); $^3J_{ab} = 7.4$ Hz.

$H_d = 6.78$ ppm (doublet of triplets, vinyl proton). The triplets are widely spaced suggesting a three bond coupling, ^3J; $^3J_{cd} = 15.4$ Hz and $^3J_{bd} = 6.3$ Hz. H_d appears further downfield than H_c (see the answer to problem 1b for an explanation).

$H_b = 2.21$ ppm (quartet of doublets of doublets, CH_2) resembles a quintet with fine structure. $^3J_{ab} = 7.4$ Hz and $^3J_{bd} = 6.3$ Hz are derived from the H_a and H_d patterns while $^4J_{bc} = 1.5$ Hz is obtained from the H_b pattern (left hand doublet at 2.26 ppm) or from the H_c pattern.

$H_c = 5.95$ ppm (doublet of doublets of triplets, vinyl proton). The triplets are narrowly spaced, suggesting a four bond coupling, ^4J; $^3J_{cd} = 15.4$ Hz, $^3J_{ce} = 7.7$ Hz and $^4J_{bc} = 1.5$ Hz.

H_e = 9.35 ppm (doublet, aldehyde proton); $^3J_{ce}$ = 7.7 Hz.

6. Structure **A** would show allylic coupling. The C-H bond orbital is parallel to the B s system of the double bond leading to more overlap. A stronger coupling of the two protons results.

7. Dimethyl ethylidenemalonate

8. Diethyl diethylmalonate and diethyl ethylmalonate

9. 3-Methoxycinnamic acid

10. *o*-Anisic acid

11. 2,2'-Dinitrobiphenyl

12. 4-(Dimethylamino)benzaldehyde

13. *trans*-Anethole

14. 3-Bromoacetophenone. The aromatic region of the proton spectrum shows one singlet, two doublets and one triplet consistent with a 1,3-disubstituted (*meta*) pattern. Each carbon atom in the aromatic ring is unique leading to the observed six peaks in the carbon spectrum. The downfield peak at near 197 ppm is consistent with a ketone C=O. The integral value (3H) in the proton spectrum and the chemical shift value (2.6 ppm) indicates that a methyl group is present. The most likely possibility is that there is an acetyl group attached to the aromatic ring. A bromine atom is the other substituent on the ring.

15. Valeraldehyde (pentanal). The aldehyde peak on carbon 1 appears at 9.8 ppm. It is split into a triplet by the two methylene protons on carbon 2 (^3J = 1.9 Hz). Aldehyde protons often have smaller three-bond (vicinal) coupling constants than typically found. The pattern at 2.4 ppm (triplet of doublets) is formed from coupling with the two protons on carbon 3 (^3J = 7.4 Hz) and with the single aldehyde proton on carbon 1 (^3J = 1.9 Hz).

16. The DEPT spectral results indicate that the peak at 15 ppm is a CH_3 group; 40 and 63 ppm peaks are CH_2 groups; 115 and 130 ppm peaks are CH groups; 125 and 158 ppm peaks are quaternary (*ipsi* carbons). The 179 ppm peak in the carbon spectrum is a C=O group at a value typical for esters and carboxylic acids. A carboxylic acid is indicated since a broad peak appears at 12.5 ppm in the proton spectrum. The value for the chemical shift of the methylene carbon peak at 63 ppm indicates an attached oxygen atom. Confirmation of this is seen in the proton spectrum (4 ppm, a quartet), leading to the conclusion that the compound has an ethoxy group (triplet at 1.4 ppm for the CH_3 group). A *para* disubstituted aromatic ring is indicated with the

carbon spectrum (two C-H and two C with no protons). This substitution pattern is also indicated in the proton spectrum (two doublets at 6.8 and 7.2 ppm).   The remaining methylene group at 40 ppm in the carbon spectrum is a singlet in the proton spectrum indicating no adjacent protons. The compound is 4-ethoxyphenylacetic acid.

17. Lepidine

18. 2-Pentylfuran

19. 3-Phenylbutyric acid

20. H_a at 3.1 ppm is a doublet of doublets ($^4J_{ac}$ = 3 Hz and $^5J_{ad}$ = 0.5 Hz), H_b at 3.8 ppm is a single for the methoxy group, H_c at 4.6 ppm is a doublet of doublets ($^3J_{cd}$ = 6 Hz and $^4J_{ac}$ = 3 Hz), H_d at 6.4 ppm is a doublet of doublets ($^3J_{cd}$ = 6 Hz and $^5J_{ad}$ ≈ 0.5 Hz)

21. Molecular modeling calculations on the two isomers suggests that the protons on the *trans*-isomer have a dihedral angle of 131°, while the *cis*-isomer has an angle of 4.6°. The H-H coupling constant for spectrum **A** on page 296 is 5.15 Hz, while the coupling of the proton on the carbon bearing the OH is about 1.5 Hz (4.23 ppm, doublet of doublets). The proton on the carbon with the phenyl group appears at about 4.06 ppm (doublet). The H-H coupling constant for spectrum **B** on page 297 is about 15 Hz. Applying the Karplus relationship (Figure 5.7 on page 226) would suggest that spectrum **A** is the *trans* isomer (131°) while spectrum **B** is the *cis* isomer (4.6°).

22. (a) In the proton NMR, one fluorine atom splits the CH_2 ($^2J_{HF}$) into a doublet. This doublet is shifted downfield because of the influence of the electronegative fluorine atom. The CH_3 group is too far away from the fluorine atom and thus appears upfield as a singlet.

    (b) Now the operating frequency of the NMR is changed so that only fuorine atoms are observed. The fluorine NMR would show a triplet for the single fluorine atom because of the two adjacent protons (n + 1 Rule). This would be the only pattern observed in the spectrum. Thus, we do not see protons directly in a fluorine spectrum because the spectrometer is operating at a different frequency. We do see, however, the influence of the protons on the fluorine spectrum. The J values would be the same as those obtained from the proton NMR.

23. The aromatic proton spectral data indicates a 1,3-disubstituted (*meta* substituted) ring. One attached substituent is a methyl group (2.35 ppm, integrating for 3H). Since the ring is disubstituted, the remaining substituent would be an oxygen atom attached to the remaining two carbon atoms with one proton and four fluorine atoms in the "ethoxy" group. This substituent would most likely be a 1,1,2,2-

tetrafluoroethoxy group. The most interesting pattern is the widely spaced triplet of triplets centering on 5.85 ppm; $^2J_{HF} = 53.1$ Hz for the proton on carbon 2 of the ethoxy group coupled to two adjacent fluorine atoms (two bond, ^2J) and $^3J_{HF} = 2.9$ Hz for this same proton on carbon 2 coupled to the remaining two fluorine atoms on carbon 1 (three bond, ^3J) from this proton.   The compound is 1-methyl-3-(1,1,2,2-tetrafluoroethoxy)benzene.

24. The spectrum is of 1-bromo-2-fluoroethane; CH_2 next to the fluorine atom (4.68 ppm) is a doublet of triplets ($^2J_{HF} = 46.7$ Hz and $^3J_{HH} = 5.8$ Hz); CH_2 next to the bromine atom (3.56 ppm) is a doublet of triplets ($^3J_{HF} = 20.9$ Hz and $^3J_{HH} = 5.8$ Hz).

25. In the proton NMR, the attached deuterium, which has a spin = 1, splits the methylene protons into a triplet (equal intensity for each peak, a 1:1:1 pattern). The methyl group is too far removed from deuterium to have any influence, and it will be a singlet. Now change the frequency of the NMR to a value where only deuterium undergoes resonance. Deuterium will see two adjacent protons on the methylene group, splitting it into a triplet (1:2:1 pattern). No other peaks will be observed since, at this NMR frequency, the only atom observed is deuterium. Compare the results to the answers in Problem 22.

26. Two singlets will appear in the proton NMR spectrum: a downfield CH_2 and an upfield CH_3 group. Compare this result to the answer in problem 22a.

27. Phosphorus has a spin of _. The methoxy groups, appearing at about 3.7 ppm in the proton NMR, are split into a doublet by the phosphorus atom ($^3J_{HP} \cong 8$ Hz). Since there are two equivalent methoxy groups, the protons integrate for 6H. The methyl group directly attached to the same phosphorus atom appears at about 1.5 ppm (integrates for 3H). This group is split by the phosphorus into a doublet ($^2J_{HP} \cong 13$ Hz). Phosphorus coupling constants are provided in Appendix 5.

28. The upper spectrum shown on page 301 is the non-carbon 13 labeled compound. One can estimate the ^1H-^{31}P coupling at about 15 Hz (3.28 - 3.23 ppm = 0.05 ppm; multiply this difference by 300 to convert ppm to hertz). The pattern shown in the lower spectrum is a doublet of doublets with the larger coupling resulting from ^1H-^{13}C coupling and the smaller coupling from an ^1H-^{31}P interaction (15 Hz). Estimate the ^1H-^{13}C coupling constant as follows: 3.38 - 2.95 ppm = 0.43 ppm; multiply this difference by 300 to yield 129 Hz. Appendix 9 provides a value for an sp^3 coupling of 115 to 125 Hz for this one bond coupling between carbon-13 and a proton.

29. The upper and lower spectra on page 302 are assigned to compounds c and a, respectively. The spectrum on page 303 is assigned to compound b.

30. The answers are provided in the Textbook, Answers to Selected Problems, page ANS-9.

31. The answers are provided in the Textbook, Answers to Selected Problems, page ANS-9.

32. The answers are provided in the Textbook, Answers to Selected Problems, page ANS-10.

CHAPTER 6

1. The methylene group is a quartet of doublets. Draw a tree diagram where the quartet has spacings of 7 Hz. This represents the ^3J (three bond coupling) to the CH_3 group from the methylene protons. Now split each leg of the quartet into doublets. This represents the ^3J (three bond coupling) of the methylene protons to the O-H group. This pattern can also be interpreted as a doublet of quartets, where the doublet (5Hz) is constructed first, followed by splitting each leg of the doublet into quartets (7 Hz spacings).

2. See page ANS-10.

3. See page ANS-11

4. See page ANS-11

5. See page ANS-11

6. See page ANS-11

7. 1-Methylcyclopropanemethanol

8. 2-(3-Chlorophenoxy)propanoic acid

9. 4-Butylaniline

10. 2,6-Dibromoaniline

11. Top spectrum: 2-methyl-5-nitroaniline; H-3, 7.14 ppm; H-4, 7.51 ppm; H-6, 7.41 ppm. Second spectrum: 2-methyl-4-nitroaniline; H-3, 7.83 ppm; H-5, 7.80 ppm; H-6, 6.72 ppm. Third spectrum: 5-methyl-2-nitroaniline; H-3, 7.91 ppm; H-4, 6.74 ppm, H-6, 6.64 ppm.

12. See page ANS-12

13. Alanine

14. *o*-Toluidine

15. Tyrosine

16. *trans*-2-Methyl-2-pentenoic acid

17. Phenacetin is the amide formed from acylation of 4-ethoxyaniline with acetic anhydride.

18. There is restricted rotation about the carbonyl group (see p. 320) at lower temperatures yielding a pair of broadened quartets for the two methylene groups. Likewise, the two methyl peaks appear as a pair of broadened triplets. At higher temperature, rotation becomes rapid, and the two methylene groups overlap yielding a single quartet. A triplet results for the methyl groups. At even lower temperatures, it should be possible for the broadened peaks to each resolve into a pair of quartets and a pair of triplets.

19. 3-Chloro-1-butene

20. NOE Difference spectroscopy should differential between the two isomers. Irradiation of the methyl group of 2-methyl-5-nitroaniline should show one positive aromatic proton (one *ortho* proton) to the methyl group, while irradiation of the methyl group of 2-nitro-5-methylaniline should show two positive aromatic protons (two *ortho* protons).

21. See page ANS-12

22. See page ANS-12

CHAPTER 7

1. See page ANS-12

2. See page ANS-12

3. See page ANS-12

4. See page ANS-13

5. See page ANS-13

6. See page ANS-13

7. 244 nm, 227 nm, yes

both are 269 nm, no

246 nm, 256 nm, yes

4-ethylphenol in neutral solution (210 nm) and in base solution (235 nm); 4-methylbenzyl alcohol should exhibit nearly the same value under neutral or basic conditions (see Table 7.10 on page 377).

both are 205 nm, they would each show only end absorption

8. a. UV would not be a good method of differentiating between the isomers: 227 nm and 226 nm, respectively.

    b. The carbonyl group in the cyclohexenone ring system will absorb at a lower value than that found in the cyclopentenone ring.

    c. The proton nmr would show one vinyl peak for the reactant and two vinyl peaks for the product. In addition, the two vinyl protons in the reactant would split each other into doublets while the product would show a singlet for the vinyl proton.

    d. A DEPT-135 experiment would show two positive peaks in the vinyl region of the carbon spectrum for the reactant, while the product would show only one positive peak in that region for the carbon with one attached proton while the quaternary carbon in the double bond would not show up at all.

CHAPTER 8

1. See page ANS-13

2. See page ANS-13

3. See page ANS-13

4. See page ANS-13

5. See page ANS-13

6. See page ANS-13

7. See page ANS-13

8. Loss of a methyl group yields a resonance stabilized H-C≡C-CH-OH cation with mass 55 amu.

9. a) loss of a propyl group; loss of a methyl group

   b) splits down the middle to yield an allylic cation, C_5H_9+ ; loss of a methyl group at the branched position to yield an allylic cation, $C_9H_{15}+$

   c) McLafferty rearrangements: fragment m/e = 72 and 58, respectively

   d) loss of propyl group to yield CH_3CHOH+ ; loss of an ethyl group to yield $(CH_3)_2COH+$

   e) a 135 and 137 fragment forms by loss of a methyl group; loss of an ethyl group by α–cleavage yields fragments at 121 and 123.

   f) McLafferty rearrangements: fragment m/e = 74 and 88, respectively

   g) Only one of the compounds, the right one, undergoes a McLafferty rearrangement resulting in a fragment of mass 73.

   h) loss of a propyl group yields a fragment of mass 30; loss of an ethyl group yields a fragment of mass 44

   i) loss of an ethyl group yields a C_6H_5CO+ fragment at 105; loss of a benzyl group yields CH_3CO+ at 43 and loss of an acetyl group yields a benzyl cation at mass 91.

   j) Loss of a methyl group yields a dimethylbenzyl cation; loss of an isopropyl group yields a benzyl cation.

10. a) Methyl 3-bromopropanoate

   b) The formula is incorrect in the problem; should only have one Cl atom: methyl 2-chloropropanoate

   c) Piperonal

   d) Tributylamine

   e) Dibutylamine

CHAPTER 9

1.   2-Butanone
2.   1-Propanol

3. 3-Pentanone
4. Methyl 2,2-dimethylpropanoate
5. Phenylacetic acid
6. 4-Bromophenol
7. Valerophenone (1-phenyl-1-pentanone)
8. Ethyl 3-bromobenzoate; ethyl 4-bromobenzoate
9. *N,N*-dimethylethylamine
10. 2-Pentanone
11. Ethyl formate
12. 2-Bromoacetophenone; 4-bromoacetophenone
13. Butyraldehyde (butanal)
14. 3-Methyl-1-butanol
15. Ethyl 2-bromopropanoate; ethyl 3-bromopropanoate
16. Ethyl 4-cyanobenzoate
17. 3-Chloropropiophenone (3-chloro-1-phenyl-1-propanone)
18. Procaine
19. 1,4-Dibromobutane
20. Ethyl *p*-toluenesulfonate
21. *trans*-Cinnamyl alcohol (3-phenyl-2-propen-1-ol)
22. Propargyl alcohol (2-propyn-1-ol)
23. 2-Methoxy-4-nitroaniline
24. 2-(Diethylamino)acetonitrile
25. Ethyl 2-bromo-2-methylpropanoate
26. 3-Phenyl-1-propanol
27. Mesityl oxide
28. Methyl *trans*-cinnamate
29. Ethyl acrylate
30. 3-methyl-2-pentanone
31. 2-Phenylpropanoic acid
32. 6-Methyl-5-hepten-2-one
33. Methyl 2-furoate
34. 3,4-Methylenedioxyacetophenone

CHAPTER 10

1. See page ANS-14

2. 2-Acetyl-6-methoxynaphthalene.

3. See page ANS-14

4. See page ANS-15

5. See page ANS-15

6. See page ANS-15

7. 3-Methylpentanoic acid

8. *cis*-Jasmone

9. 7-Methoxycoumarin