ANSWERS TO SELECTED PROBLEMS

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

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

CHAPTER 3

1. (a) −1, 0, +1 (b) $-\frac{1}{2}, +\frac{1}{2}$ (c) $-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2}$ (d) $-\frac{1}{2}, +\frac{1}{2}$
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 ($+\frac{1}{2}$ and $-\frac{1}{2}$).
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) 2-Chloropropanoic acid (b) 3-Chloropropanoic acid

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

23. 2-Phenylethylamine

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

18. 2,3-Dimethyl-2-butene. A primary cation rearranges to a tertiary cation via a hydride shift. E1 elimination forms the tetrasubstituted alkene.

19. (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).

20. C1 = 128.5 + 9.3 = 137.8 ppm; C2 = 128.5 + 0.7 = 129.2 ppm; C3 = 128.5 – 0.1 = 128.4 ppm; C4 = 128.5 – 2.9 = 125.6 ppm.

21. All carbons are numbered according to IUPAC rules. The following information is given: the name of the compound, the number of the table used (A8.2–A8.7, Appendix 8), and, where needed, the name of the reference compound used (from A8.1, Appendix 8). If actual values are known, they are given in parentheses.

    (a) Methyl vinyl ether, A8.2 (actual: 153.2, 84.2 ppm)
    C1 = 123.3 + 29.4 = 152.7 C2 = 123.3 – 38.9 = 84.4

    (b) Cyclopentanol, A8.3-cyclopentane (actual: 73.3, 35.0, 23.4 ppm)
    C1 = 25.6 + 41 = 66.6 C2 = 25.6 + 8 = 33.6 C3 = 25.6 – 5 = 20.6

    (c) 2-Pentene, A8.5 (actual: 123.2, 132.7 ppm)
    C2 = 123.3 + 10.6 – 7.9 – 1.8 = 124.2 C3 = 123.3 + 10.6 + 7.2 – 7.9 = 133.2
    Using Table A8.4:
    C2 = 123.3 + 12.9 – 9.7 = 126.5 C3 = 123.3 + 17.2 – 7.4 = 133.1

(d) *ortho*-Xylene, A8.7
C1,C2 = 128.5 + 9.3 + 0.7 = 138.5
C3,C6 = 128.5 + 0.7 − 0.1 = 129.1
C4,C5 = 128.5 − 0.1 − 2.9 = 125.5
meta-Xylene, A8.7 (actual: 137.6, 130.0, 126.2, 128.2 ppm)
C1,C3 = 128.5 + 9.3 − 0.1 = 137.7
C2 = 128.5 + 0.7 + 0.7 = 129.9
C4,C6 = 128.5 + 0.7 − 2.9 = 126.3
C5 = 128.5 − 0.1 − 0.1 = 128.3
para-Xylene, T7
C1,C4 = 128.5 + 9.3 − 2.9 = 134.9
C2,C3,C5,C6 = 128.5 + 0.7 − 0.1 = 129.1

(e) 3-Pentanol, A8.3-pentane (actual: 9.8, 29.7, 73.8 ppm)
C1,C5 = 13.9 − 5 = 8.9   C2,C4 = 22.8 + 8 = 30.8   C3 = 34.7 + 41 = 75.7

(f) 2-Methylbutanoic acid, A8.3-butane
C1 = 13.4 + 2 = 15.4   C2 = 25.2 + 16 = 41.2   C3 = 25.2 + 2 = 27.2   C4 = 13.4 − 2 + 11.4

(g) 1-Phenyl-1-propene, A8.4
C1 = 123.3 + 12.5 − 7.4 = 128.4   C2 = 123.3 + 12.9 − 11 = 125.2

(h) 2,2-Dimethylbutane, A8.3 or A8.2 (actual: 29.1, 30.6, 36.9, 8.9 ppm)
Using Table A8.3: C1 = 13.4 + 8 + 8 = 29.4   C2 = 25.2 + 6 + 6 = 37.2
C3 = 25.2 + 8 + 8 = 41.2   C4 = 13.4 − 2 − 2 = 9.4
Using Table A8.2:
C1 = −2.3 + [9.1(1) + 9.4(3) − 2.5(1)] + [(−3.4)] = 29.1
C2 = −2.3 + [9.1(4) + 9.4(1)] + [3(−1.5) + (−8.4)] = 30.6
C3 = −2.3 + [9.1(2) + 9.4(3)] + [(0) + (−7.5)] = 36.6
C4 = −2.3 + [9.1(1) + 9.4(1) − 2.5(3)] + [(0)] = 8.7

(i) 2,3-Dimethyl-2-pentenoic acid, A8.6
C2 = 123.3 + 4 + 10.6 − 7.9 − 7.9 − 1.8 = 120.3
C3 = 123.3 + 10.6 + 10.6 + 7.2 + 9 − 7.9 = 152.8

(j) 4-Octene, A8.5, and assume *trans* geometry
C4,C5 = 123.3 + [10.6 + 7.2 − 1.5] − [7.9 + 1.8 − 1.5] = 131.4
To estimate *cis*, correct as follows: 131.4 − 1.1 = 130.3

(k) 4-Aminobenzoic acid, A8.7
C1 = 128.5 + 2.1 − 10.0 = 120.6   C2 = 128.5 + 1.6 + 0.8 = 130.9
C3 = 128.5 − 13.4 + 0.1 = 115.2   C4 = 128.5 + 18.2 + 5.2 = 151.9

(l) 1-Pentyne, A8.3-propane
C3 = 15.8 + 4.5 = 20.3   C4 = 16.3 + 5.4 = 21.7   C5 = 15.8 − 3.5 = 12.3

(m) Methyl 2-methylpropanoate, A8.3-propane
C2 = 16.3 + 17 = 33.3   C3 = 15.8 + 2 = 17.8

(n) 2-Pentanone, A8.3-propane
C3 = 15.8 + 30 = 45.8   C4 = 16.3 + 1 = 17.3   C5 = 15.8 − 2 = 13.8

(o) Bromocyclohexane, A8.3-cyclohexane
C1 = 26.9 + 25 = 51.9   C2 = 26.9 + 10 = 36.9   C3 = 26.9 − 3 = 23.9
C4 = 26.9 (no correction)

(p) 2-Methylpropanoic acid, A8.3-propane
C1 = 15.8 + 2 = 17.8   C2 = 16.3 + 16 = 32.3

(q) 4-Nitroaniline, A8.7 (actual: 155.1, 112.8, 126.3, 136.9 ppm)
C1 = 128.5 + 18.2 + 6.0 = 152.7   C2 = 128.5 − 13.4 + 0.9 = 116.0
C3 = 128.5 + 0.8 − 4.9 = 124.4   C4 = 128.5 + 19.6 − 10.0 = 138.1
2-Nitroaniline, A8.7
C1 = 128.5 + 18.2 − 4.9 = 141.8   C2 = 128.5 − 13.4 + 19.6 = 134.7
C3 = 128.5 − 4.9 + 0.8 = 124.4   C4 = 128.5 + 0.9 − 10.0 = 119.4
C5 = 128.5 + 0.8 + 6 = 135.3   C6 = 128.5 − 13.4 + 0.9 = 114.2

(r) 1,3-Pentadiene, A8.4
C3 = 123.3 + 13.6 − 13.6 = 129.5   C4 = 123.3 + 12.9 − 7 = 129.2

(s) Cyclohexene, A8.5 (actual: 127.3 ppm)
C1,C2 = 123.3 + [10.6 + 7.2 − 1.5] − [7.9 + 1.8 − 1.5] + [−1.1] = 130.3

(t) 4-Methyl-2-pentene, A8.5, and assume *trans*
C2 = 123.3 + [10.6(1)] − [7.9(1) + 1.8(2)] = 122.4
C3 = 123.3 + [10.6(1) + 7.2(2)] − [7.9(1)] + 2.3 = 142.7

CHAPTER 5

1. Refer to Sections 5.6 and 5.9 for instructions on measuring coupling constants using the Hertz values that are printed above the expansions of the proton spectra.

(a) Vinyl acetate (Fig. 5.45): all vinyl protons are doublets of doublets.

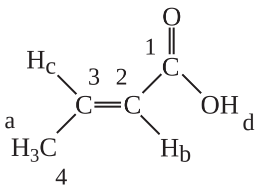
H_a = 4.57 ppm, $^3J_{ac}$ = 6.25 Hz and $^2J_{ab}$ = 1.47 Hz.

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 5.9). 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.

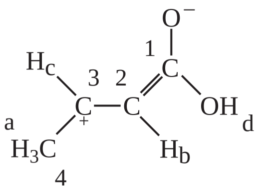
(b) *trans*-Crotonic acid (Fig. 5.48).



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. 5.64). 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 withdrawing 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. 5.65). H_d is significantly deshielded by the anisotropy of both the nitro and carboxyl groups and appears furthest downfield. It appears as a narrowly spaced 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. 5.66). 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. 5.67). 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.

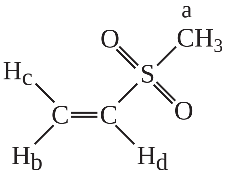
H_b = 7.14 ppm (d); $^3J_{bc}$ = 7.7 Hz and $^4J_{ab} \cong$ 0 Hz.

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; $J_{ac} \sim 16$ Hz; $J_{bc} \sim 1$ Hz

3.



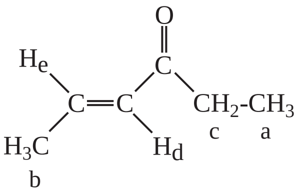
H_a = 2.80 ppm (singlet, CH_3).

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.

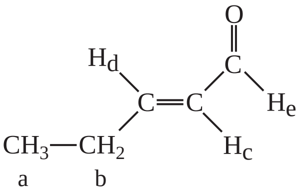
H_c = 2.36 ppm (quartet, CH_2; $^3J_{ac}$ = 7.4 Hz.

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 π system of the double bond leading to more overlap. A stronger coupling of the two protons results.

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.

25. (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 *fluorine* 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.

26. 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.

28. 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 25.

29. 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 25a.

30. Phosphorus has a spin of $\frac{1}{2}$. The two 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 phosphorus into a doublet ($^2J_{HP} \cong 13$ Hz). Phosphorus coupling constants are provided in Appendix 5.

33. (a) δ_H ppm = 0.23 + 1.70 = 1.93 ppm
    (b) δ_H ppm (α to two C=O groups) = 0.23 + 1.70 + 1.55 = 3.48 ppm
        δ_H ppm (α to one C=O group) = 0.23 + 1.70 + 0.47 = 2.40 ppm
    (c) δ_H ppm = 0.23 + 2.53 + 1.55 = 4.31 ppm
    (d) δ_H ppm = 0.23 + 1.44 + 0.47 = 2.14 ppm
    (e) δ_H ppm = 0.23 + 2.53 + 2.53 + 0.47 = 5.76 ppm
    (f) δ_H ppm = 0.23 + 2.56 + 1.32 = 4.11 ppm

34. (a) δ_H ppm (*cis* to $COOCH_3$) = 5.25 + 1.15 – 0.29 = 6.11 ppm
        δ_H ppm (*trans* to $COOCH_3$) = 5.25 + 0.56 – 0.26 = 5.55 ppm
    (b) δ_H ppm (*cis* to CH_3) = 5.25 + 0.84 – 0.26 = 5.83 ppm
        δ_H ppm (*cis* to $COOCH_3$) = 5.25 + 1.15 + 0.44 = 6.84 ppm
    (c) δ_H ppm (*cis* to C_6H_5) = 5.25 + 0.37 = 5.62 ppm
        δ_H ppm (*gem* to C_6H_5) = 5.25 + 1.35 = 6.60 ppm
        δ_H ppm (*trans* to C_6H_5) = 5.25 – 0.10 = 5.15 ppm
    (d) δ_H ppm (*cis* to C_6H_5) = 5.25 + 0.37 + 1.10 = 6.72 ppm
        δ_H ppm (*cis* to $COCH_3$) = 5.25 + 1.13 + 1.35 = 7.73 ppm
    (e) δ_H ppm (*cis* to CH_3) = 5.25 + 0.67 – 0.26 = 5.66 ppm
        δ_H ppm (*cis* to CH_2OH) = 5.25 – 0.02 + 0.44 = 5.67 ppm
    (f) δ_H ppm = 5.25 + 1.10 – 0.26 – 0.29 = 5.80 ppm

35. In the answers provided here, numbering begins with the group attached at the top of the ring.

(a) δ_{H} (proton 2 and 6) = 7.27 – 0.14 + 0.26 = 7.39 ppm
δ_{H} (proton 3 and 5) = 7.27 – 0.06 + 0.95 = 8.16 ppm

(b) δ_{H} (proton 2) = 7.27 – 0.48 + 0.95 = 7.74 ppm
δ_{H} (proton 4) = 7.27 – 0.44 + 0.95 = 7.78 ppm
δ_{H} (proton 5) = 7.27 – 0.09 + 0.26 = 7.44 ppm
δ_{H} (proton 6) = 7.27 – 0.48 + 0.38 = 7.17 ppm

(c) δ_{H} (proton 3) = 7.27 – 0.09 + 0.95 = 8.13 ppm
δ_{H} (proton 4) = 7.27 – 0.44 + 0.26 = 7.09 ppm
δ_{H} (proton 5) = 7.27 – 0.09 + 0.38 = 7.56 ppm
δ_{H} (proton 6) = 7.27 – 0.48 + 0.26 = 7.05 ppm

(d) δ_{H} (proton 2 and 6) = 7.27 + 0.71 – 0.25 = 7.73 ppm
δ_{H} (proton 3 and 5) = 7.27 + 0.10 – 0.80 = 6.57 ppm

(e) δ_{H} (proton 3) = 7.27 + 0.10 – 0.80 = 6.57 ppm
δ_{H} (proton 4) = 7.27 + 0.21 – 0.25 = 7.23 ppm
δ_{H} (proton 5) = 7.27 + 0.10 – 0.65 = 6.72 ppm
δ_{H} (proton 6) = 7.27 + 0.71 – 0.25 = 7.73 ppm

(f) δ_{H} (proton 2 and 6) = 7.27 + 0.71 – 0.02 = 7.96 ppm
δ_{H} (proton 3 and 5) = 7.27 + 0.10 + 0.03 = 7.40 ppm

(g) δ_{H} (proton 3) = 7.27 + 0.18 + 0.03 + 0.38 = 7.86 ppm
δ_{H} (proton 4) = 7.27 + 0.30 – 0.02 + 0.26 = 7.81 ppm
δ_{H} (proton 5) = 7.27 + 0.18 – 0.09 + 0.95 = 8.31 ppm

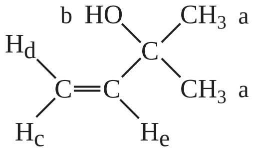
(h) δ_{H} (proton 2) = 7.27 + 0.85 + 0.95 – 0.02 = 9.05 ppm
δ_{H} (proton 5) = 7.27 + 0.18 + 0.26 + 0.03 = 7.74 ppm
δ_{H} (proton 6) = 7.27 + 0.85 + 0.38 – 0.02 = 8.48 ppm

(i) δ_{H} (proton 2 and 6) = 7.27 – 0.53 – 0.02 = 6.72 ppm
δ_{H} (proton 3 and 5) = 7.27 – 0.17 + 0.03 = 7.13 ppm

CHAPTER 6

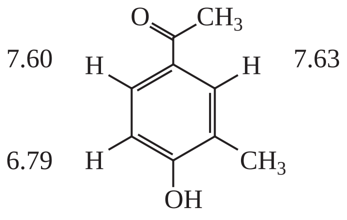
1. The methylene group is a quartet of doublets. Draw a tree diagram where the quartet has spacings of 7 Hz. This represents the ^{3}J (three bond coupling) to the CH_3 group from the methylene protons. Now split each leg of the quartet into doublets (5 Hz). This represents the ^{3}J (three bond coupling)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

2. 2-Methyl-3-buten-2-ol. H_a = 1.3 ppm; H_b = 1.9 ppm; H_c = 5.0 ppm (doublet of doublets, $^3J_{ce}$ = 10.7 Hz (*cis*) and $^2J_{cd}$ = 0.9 Hz (*geminal*)); H_d = 5.2 ppm (doublet of doublets, $^3J_{de}$ = 17.4 Hz (*trans*) and $^2J_{cd}$ = 0.9 Hz (*geminal*)); H_e = 6.0 ppm (doublet of doublets, $^3J_{de}$ = 17.4 Hz and $^3J_{ce}$ = 10.7 Hz.

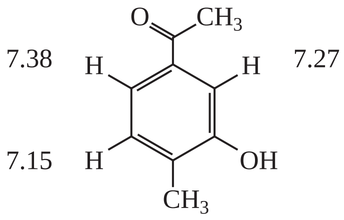


3. 2-Bromophenol. The unexpanded spectrum shows two doublets and two triplets, consistent with a 1,2-disubstituted (*ortho*) pattern. Each shows fine structure in the expansions (^4J). Assignments can be made by assuming that the two upfield protons (shielded) are *ortho* and *para* with respect to the electron-releasing OH group. The other two patterns can be assigned by a process of elimination.

4. The two structures shown here are the ones that can be derived from 2-methylphenol. The infrared spectrum shows a significantly shifted conjugated carbonyl group which suggests that the OH group is releasing electrons and providing single bond character to the C=O group, consistent with 4-hydroxy-3-methylacetophenone (the other compound would not have as significant a shift in the C=O). The 3136 cm^{-1} peak is an OH group, also seen in the NMR spectrum as a solvent-dependent peak. Both structures shown would be expected to show a singlet and two doublets in the aromatic region of the NMR spectrum. The positions of the downfield singlet and doublet in the spectrum fit the calculated values from Appendix 6 for 4-hydroxy-3-methylacetophenone more closely than for 3-hydroxy-4-methylacetophenone (calculated values are shown on each structure). The other doublet appearing at 6.9 ppm is a reasonable fit to the calculated value of 6.79 ppm. It is interesting to note that the two *ortho* protons in 3-hydroxy-4-methylacetophenone are deshielded by the C=O group and shielded by the OH group leading to little shift from the base value of 7.27 (Appendix 6). In conclusion, the NMR spectrum and calculated values best fit 4-hydroxy-3-methylacetophenone.

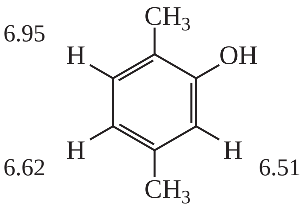


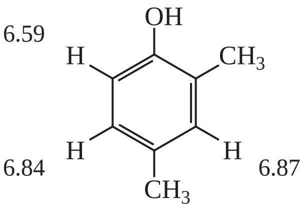
4-hydroxy-3-methylacetophenone

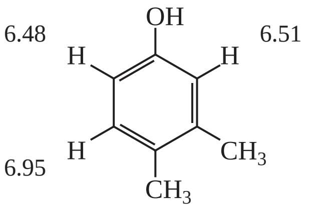


3-hydroxy-4-methylacetophenone

5. All of the compounds would have a singlet and two doublets in the aromatic portion of the NMR spectrum. When comparing the calculated values to the observed chemical shifts, it is important to compare the *relative* positions of each proton (positions of doublet, singlet, and doublet). Don't be concerned with slight differences (about ± 0.10 Hz) in the calculated *vs* observed values. The calculated values for third compound fits the observed spectral data better than the first two.







			observed
6.51 s	6.59 d	6.48 d	6.57 d
6.62 d	6.84 d	6.51 s	6.64 s
6.95 d	6.87 s	6.95 d	6.97 d

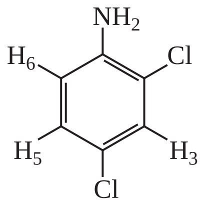
6. 3-Methyl-3-buten-1-ol. The DEPT spectral results show a CH_3 group at 22 ppm, two CH_2 groups at 41 and 60 ppm. The peaks at 112 ppm (CH_2) and 142 ppm (C with no attached H) are part of a vinyl group. The peaks at 4.78 and 4.86 ppm in the proton spectrum are the

protons on the terminal double bond. The 4.78 ppm pattern (fine structure) shows long range coupling (^{4}J) to the methyl and methylene groups. The methylene group at 2.29 ppm is broadened because of non-resolved ^{4}J coupling.

9. 4-Butylaniline

10. 2,6-Dibromoaniline

12. 2,4-Dichloroaniline. The broad peak at about 4 ppm is assigned to the $-NH_2$ group. The doublet at 7.23 ppm is assigned to the proton on carbon 3 (it appears as a near singlet in the upper trace). Proton 3 is coupled, long range, to the proton on carbon 5 ($^4J = 2.3$ Hz). The doublet of doublets centering on 7.02 ppm is assigned to the proton on carbon 5. It is coupled to the proton on carbon 6 ($^3J = 8.6$ Hz) and also to proton 3 ($^4J = 2.3$ Hz). Finally, the doublet at 6.65 ppm is assigned to the proton on carbon 6 ($^3J = 8.6$ Hz), which arises from coupling to the proton on carbon 5. There is no sign of ^5J coupling in this compound.



13. Alanine

21. Rapid equilibration at room temperature between chair conformations leads to one peak. As one lowers the temperature, the interconversion is slowed down until, at temperatures below –66.7°C, peaks due to the axial and equatorial hydrogens are observed. Axial and equatorial hydrogens have different chemical shifts under these conditions.

22. The *t*-butyl-substituted rings are conformationally locked. The hydrogen at C4 has different chemical shifts, depending upon whether it is axial or equatorial. 4-Bromocyclohexanes are conformationally mobile. No difference between axial and equatorial hydrogens is observed until the rate of chair–chair interconversion is decreased by lowering the temperature.

CHAPTER 7

1. (a) $\varepsilon = 13{,}000$ (b) $I_0/I = 1.26$

2. (a) 2,4-Dichlorobenzoic acid or 3,4-dichlorobenzoic acid (b) 4,5-Dimethyl-4-hexen-3-one
(c) 2-Methyl-1-cyclohexenecarboxaldehyde

3. (a) Calculated: 215 nm observed: 213 nm
(b) Calculated: 249 nm observed: 249 nm
(c) Calculated: 214 nm observed: 218 nm
(d) Calculated: 356 nm observed: 348 nm
(e) Calculated: 244 nm observed: 245 nm
(f) Calculated: 303 nm observed: 306 nm
(g) Calculated: 249 nm observed: 245 nm
(h) Calculated: 281 nm observed: 278 nm
(i) Calculated: 275 nm observed: 274 nm
(j) Calculated: 349 nm observed: 348 nm

4. 166 nm: $n \rightarrow \sigma^*$
   189 nm: $\pi \rightarrow \pi^*$
   279 nm: $n \rightarrow \pi^*$

5. Each absorption is due to $n \rightarrow \sigma^*$ transitions. As one goes from the *chloro* to the *bromo* to the *iodo* group, the electronegativity of the halogens decreases. The orbitals interact to different degrees, and the energies of the n and the σ^* states differ.

6. (a) $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $\pi \rightarrow \sigma^*$
   (b) $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, and $n \rightarrow \pi^*$
   (c) $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$
   (d) $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, and $n \rightarrow \pi^*$
   (e) $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$
   (f) $\sigma \rightarrow \sigma^*$

CHAPTER 8

1. $C_{43}H_{50}N_4O_6$
2. $C_{34}H_{44}O_{13}$
3. $C_{12}H_{10}O$
4. C_6H_{12}
5. C_7H_9N
6. C_3H_7Cl
7. (a) Methylcyclohexane
   (b) 2-Methyl-1-pentene
   (c) 2-Methyl-2-hexanol
   (d) Ethyl isobutyl ether
   (e) 2-Methylpropanal
   (f) 3-Methyl-2-heptanone
   (g) Ethyl octanoate
   (h) 2-Methylpropanoic acid
   (i) 4-Methylbenzoic acid
   (j) Butylamine
   (k) 2-Propanethiol
   (l) Nitroethane
   (m) Propanenitrile
   (n) Iodoethane
   (o) Chlorobenzene
   (p) 1-Bromobutane
   (q) Bromobenzene
   (r) 1,1-Dichloroethane
   (s) 1,2,3-Trichloro-1-propene

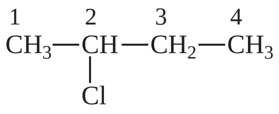
CHAPTER 9

1. 2-Butanone
2. 1-Propanol
3. 3-Pentanone
4. Methyl trimethylacetate (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-bromopropionate (ethyl 2-bromopropanoate); ethyl 3-bromopropionate (ethyl 3-bromopropanoate)
16. Ethyl 4-cyanobenzoate
17. 3-Chloropropiophenone (3-chloro-1-phenyl-1-propanone)

CHAPTER 10

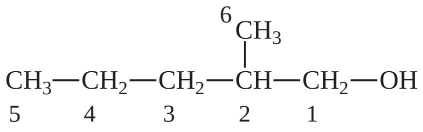
1.



$$\overset{1}{CH_3}-\underset{Cl}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

Proton #1: 1.5 ppm   Carbon #1: 24 ppm
Proton #2: 4.0 ppm   Carbon #2: 60 ppm
Proton #3: 1.7 ppm   Carbon #3: 33 ppm (inverted peak indicates CH_2)
Proton #4: 1.0 ppm   Carbon #4: 11 ppm

3.

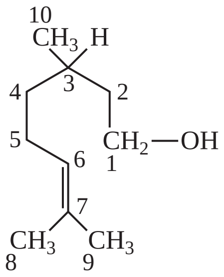


$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{\overset{{}^{6}CH_3}{CH}}-\underset{1}{CH_2}-OH$$

Carbon #1: 68 ppm
Carbon #2: 35.2 ppm
Carbon #3: 35.3 ppm
Carbon #4: 20 ppm
Carbon #5: 14 ppm
Carbon #6: 16 ppm

3-Methyl-1-pentanol and 4-methyl-1-pentanol would be expected to give similar DEPT spectra. They are also acceptable answers based on the information provided.

4.

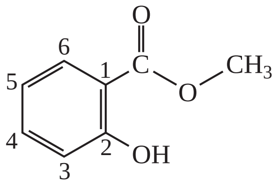


Proton #1: 3.8 ppm	Carbon #1: 61 ppm
Proton #2: 1.4 and 1.6 ppm	Carbon #2: 40 ppm
Proton #3: 1.6 ppm	Carbon #3: 30 ppm
Proton #4: 1.2 and 1.3 ppm	Carbon #4: 37 ppm
Proton #5: 2.0 ppm	Carbon #5: 25 ppm
Proton #6: 5.2 ppm	Carbon #6: 125 ppm
Proton #7: —	Carbon #7: 131 ppm
Proton #8: 1.6 ppm	Carbon #8: 17 ppm
Proton #9: 1.7 ppm	Carbon #9: 25 ppm
Proton #10: 0.9 ppm	Carbon #10: 19 ppm

5.

Proton #1: 4.1 ppm	Carbon #1: 59 ppm
Proton #2: 5.4 ppm	Carbon #2: 124 ppm
Proton #3: —	Carbon #3: —
Proton #4: 2.1 ppm	Carbon #4: 39 ppm
Proton #5: 2.2 ppm	Carbon #5: 26 ppm
Proton #6: 5.1 ppm	Carbon #6: 124.5 ppm
Proton #7: —	Carbon #7: —
Proton #8: 1.6 ppm	Carbon #8: 18 ppm
Proton #9: 1.7 ppm	Carbon #9: 16 or 25 ppm
Proton #10: 1.7 ppm	Carbon #10: 16 or 25 ppm

6.



Proton #3: 6.95 ppm	Carbon #3: 117 ppm
Proton #4: 7.40 ppm	Carbon #4: 136 ppm
Proton #5: 6.82 ppm	Carbon #5: 119 ppm
Proton #6: 7.75 ppm	Carbon #6: 130 ppm

$J_{3,4} = 8$ Hz $J_{3,5} = 1$ Hz $J_{3,6} \sim 0$ Hz

$J_{4,5} = 7$ Hz $J_{4,6} = 2$ Hz $J_{5,6} = 8$ Hz