Chapter 1 – Introduction, Formulas and Spectroscopy Overview

Problem 1 (p 12) -

Helpful equations:

$c = (\nu)(\lambda)$ and $\bar{\nu} = (1/\lambda)$ so $c = (\nu)/(\bar{\nu})$

$c = 3.00 \times 10^{8}$ m/sec $= 3.00 \times 10^{10}$ cm/sec

a. Which photon of electromagnetic radiation below would have the longer wavelength? Convert both values to meters.

$\bar{\nu} = 3500\ \text{cm}^{-1}$

$\bar{\nu} = (1/\lambda)$
$\lambda = (1/\bar{\nu})$
$\lambda = (1/3500\ \text{cm}^{-1})(1\ \text{m}/100\ \text{cm}) = 2.9 \times 10^{-6}\ \text{m}$

$\lambda =$ longer wavelength = lower energy

$\nu = 4 \times 10^{14}$ Hz

$\lambda = (c/\nu)$
$= (3.0 \times 10^{8}\ \text{m/s}) / (4 \times 10^{14}\ \text{s}^{-1})$
$= 7.5 \times 10^{-7}\ \text{m}$

b. Which photon of electromagnetic radiation below would have the higher frequency? Convert both values to Hz.

$\bar{\nu} = 400\ \text{cm}^{-1}$

$\lambda = (1/\bar{\nu}) = 1/[(400\ \text{cm}^{-1})(100\ \text{cm}/1\ \text{m})]$
$\lambda = 2.5 \times 10^{-5}\ \text{m}$

$\nu = (c/\lambda)$
$\nu = (3.0 \times 10^{8}\ \text{m/s}) / (2.5 \times 10^{-5}\ \text{m})$
$\nu = 1.2 \times 10^{13}\ \text{s}^{-1}$

$\lambda = 300$ nm

$\nu = (c/\lambda)$
$\nu = (3.0 \times 10^{8}\ \text{m/s}) / (2.5 \times 10^{-5}\ \text{nm})(1\text{m}/10^{9}\ \text{nm})$
$\nu = (3.0 \times 10^{8}\ \text{m/s}) / (300\ \text{nm})(1\text{m}/10^{9}\ \text{nm})$
$\nu = 1.0 \text{ x } \times 10^{15}\ \text{s}^{-1}$

higher frequency

c. Which photon of electromagnetic radiation below would have the smaller wavenumber? Convert both values to cm^{-1}.

$\lambda = 1$ m

$\bar{\nu} = (1/\lambda)$
$\bar{\nu} = (1/1\text{m}) = 1\ \text{m}^{-1}\left(\frac{100\ \text{cm}^{-1}}{1\ \text{m}^{-1}}\right) = 100\ \text{cm}^{-1}$

smaller wavenumber

$\nu = 6 \times 10^{10}$ Hz

$\bar{\nu} = (\nu/c)$
$\bar{\nu} = (6 \times 10^{10}\ \text{s}^{-1} / 3.0 \times 10^{8}\ \text{m/s}) = 200\ \text{m}^{-1}\left(\frac{100\ \text{cm}^{-1}}{1\ \text{m}^{-1}}\right) = 20{,}000\ \text{cm}^{-1}$

Problem 2 (p 14) - Order the following photons from lowest to highest energy (first convert each value to kjoules/mole). What is the energy of each photon in kcal/mole?

a.

$E = h\nu = hc(1/\lambda) = hc\bar{\nu}$ $\quad E = hc(1/\lambda)$ $\quad E = h\nu$

$E = hc\bar{\nu}$
$E = (6.62 \times 10^{-34}\ \text{j-s})(3.0 \times 10^{8}\ \text{m/s})(10^{5}\ \text{cm}^{-1} \times (100\ \text{m}^{-1}/\text{cm}^{-1}))$
$E = 2 \times 10^{-18}\ \text{j}$

highest

$E = hc(1/\lambda)$

$E = (6.62 \times 10^{-34}\ \text{j-s})(3.0 \times 10^{8}\ \text{m/s})(1 / 10^{3}\ \text{nm} \times (1\ \text{m} / 10^{9}\ \text{nm}))$ — middle

$E = 2 \times 10^{-19}\ \text{j}$

$E = h\nu$

$E = (6.62 \times 10^{-34}\ \text{j-s})(10^{9} / \text{s})$ — lowest

$E = 6.6 \times 10^{-25}\ \text{j}$

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b.

$E = h\nu = hc(1/\lambda) = hc\bar{\nu}$ $\qquad$ $E = hc(1/\lambda)$ $\qquad$ $E = h\nu$

$E = hc\bar{\nu}$

$E = (6.62 \times 10^{-34}\ \text{j-s})(3.0 \times 10^{8}\ \text{m/s})(1\ \text{cm}^{-1} \times (100\ \text{m}^{-1}/\text{cm}^{-1}))$ — middle

$E = 2 \times 10^{-24}\ \text{j}$

$E = hc(1/\lambda)$

$E = (6.62 \times 10^{-34}\ \text{j-s})(3.0 \times 10^{8}\ \text{m/s})(1 / 10^{10}\ \text{nm} \times (1\ \text{m} / 10^{9}\ \text{nm}))$ — lowest

$E = 2 \times 10^{-27}\ \text{j}$

$E = h\nu$

$E = (6.62 \times 10^{-34}\ \text{j-s})(10^{15} / \text{s})$ — highest

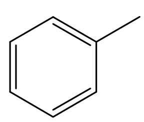
$E = 6.6 \times 10^{-19}\ \text{j}$

Problem 3 (p 22) - Determine the degrees of unsaturation for each of the following formulas. What combinations of pi bonds and rings are possible in each case? Is it possible for any of the following formulas to have an alkene, alkyne, carboxylic acid, ester, amide, nitrile, aromatic ring, ketone, aldehyde, ether, amine or alcohol? Try and draw some examples of such structures.

a. C_7H_8

2(7) + 2 = 16

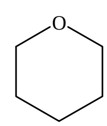
degrees unsaturation = (16 - 8) / 2 = 4°



b. $C_5H_{10}O$

2(5) + 2 = 12

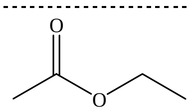
degrees unsaturation = (12 - 10) / 2 = 1°



c. $C_4H_8O_2$

2(4) + 2 = 10

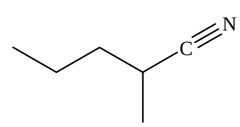
degrees unsaturation = (10 - 8) / 2 = 1°



d. $C_6H_{11}N$

2(6) + 2 + 1 = 15

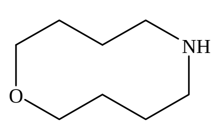
degrees unsaturation = (15 - 11) / 2 = 2°



e. $C_8H_{17}NO$

2(8) + 2 + 1 = 19

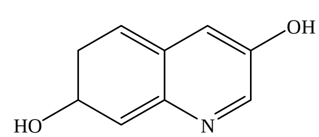
degrees unsaturation = (19 - 17) / 2 = 1°



f. $C_{10}H_9ClN_2O$

2(10) + 2 + 2 = 24

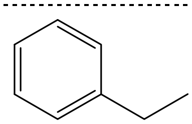
degrees unsaturation = (24 - 10) / 2 = 7°



g. $C_9H_9NO_2$

2(9) + 2 + 1 = 21

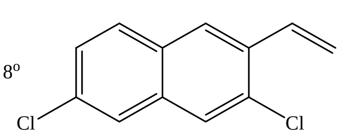
degrees unsaturation = (21 - 9) / 2 = 6°



h. $C_{12}H_8Cl_2$

2(12) + 2 = 26

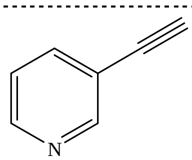
degrees unsaturation = (26 - 10) / 2 = 8°



i. C_7H_5N

2(7) + 2 + 1 = 16

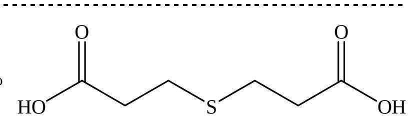
degrees unsaturation = (17 - 5) / 2 = 6°



j. $C_6H_{10}SO_4$

2(6) + 2 = 14

degrees unsaturation = (14 - 10) / 2 = 2°



Problem 4 (p 22) – A low resolution MS on compound X was 150 g/mol. Possible formulas considered were $C_{11}H_{18}$, $C_{10}H_{14}O$, $C_9H_{10}O_2$, $C_8H_6O_3$ and $C_9H_{14}N_2$. What are the possible numbers of pi bonds and rings for each of these formulas?

$C_{11}H_{18}$

2(11) + 2 = 24

degrees unsaturation = (24 - 18) / 2 = 3°

pi	rings
3	0
2	1
1	2
0	3

$C_{10}H_{14}O$

2(10) + 2 = 22

degrees unsaturation = (22 - 14) / 2 = 4°

pi	rings
4	0
3	1
2	2
1	3
0	4

$C_9H_{10}O_2$

2(9) + 2 = 20

degrees unsaturation = (20 - 10) / 2 = 5°

pi	rings
5	0
4	1
3	2
2	3
1	4
0	5

$C_8H_6O_3$

2(8) + 2 = 18

degrees unsaturation = (18 - 6) / 2 = 6°

pi	rings
6	0
5	1
4	2
3	3
2	4
1	5
0	6

$C_9H_{14}N_2$

2(9) + 2 + 2 = 22

degrees unsaturation = (22 - 18) / 2 = 3°

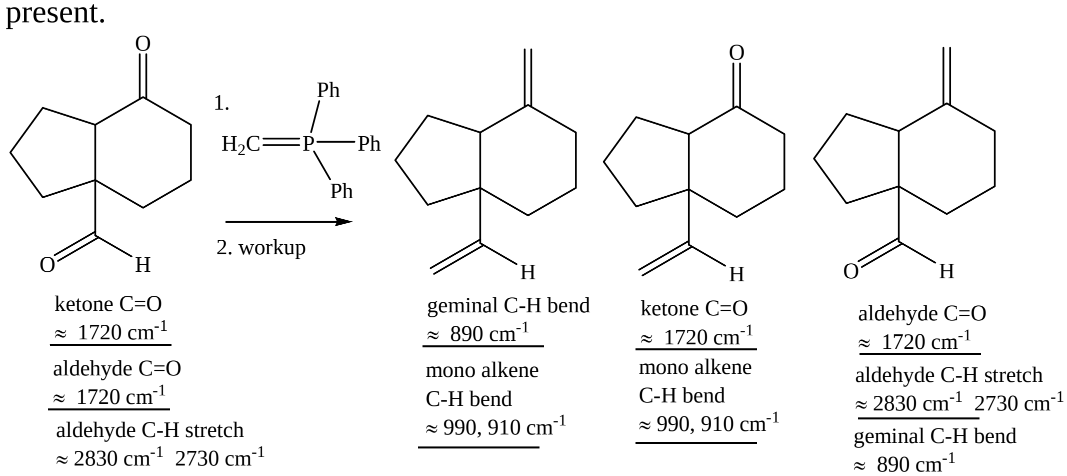
pi	rings
3	0
2	1
1	2
0	3

Chapter 2 - IR

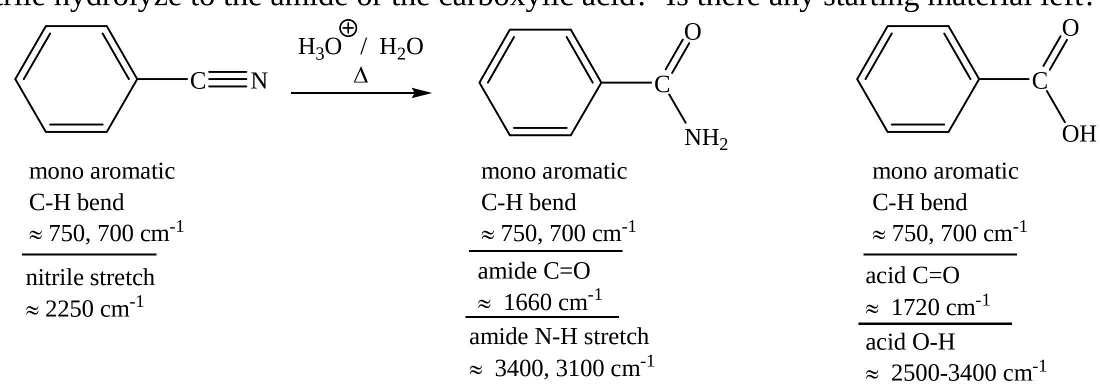
Problem 1 (p 58)

1. Discuss how IR could help answer the following questions. Be specific in your analysis, pointing out the values in wave numbers (cm^{-1}) for absorption peaks that could resolve each question.

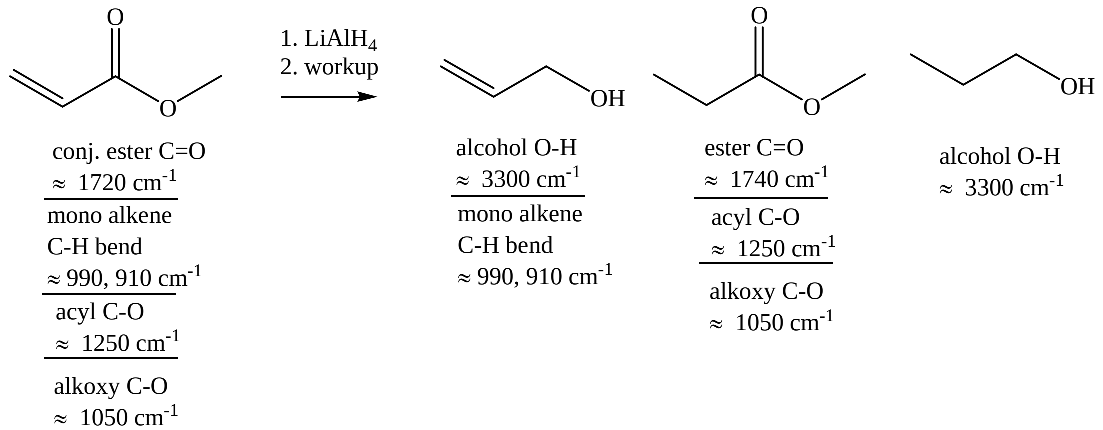
   a. Which product(s) is(are) obtained in the following Wittig reaction. Is starting material is still present.



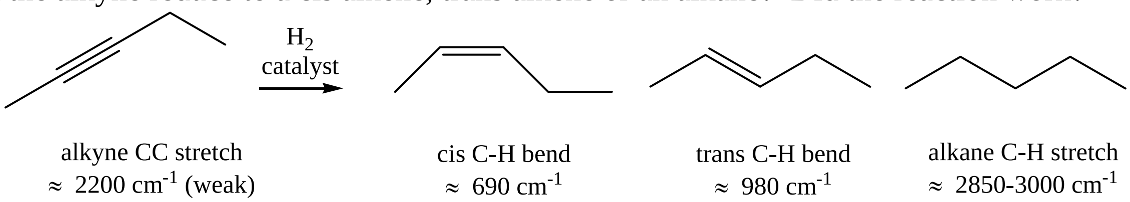
   b. Did the nitrile hydrolyze to the amide or the carboxylic acid? Is there any starting material left?



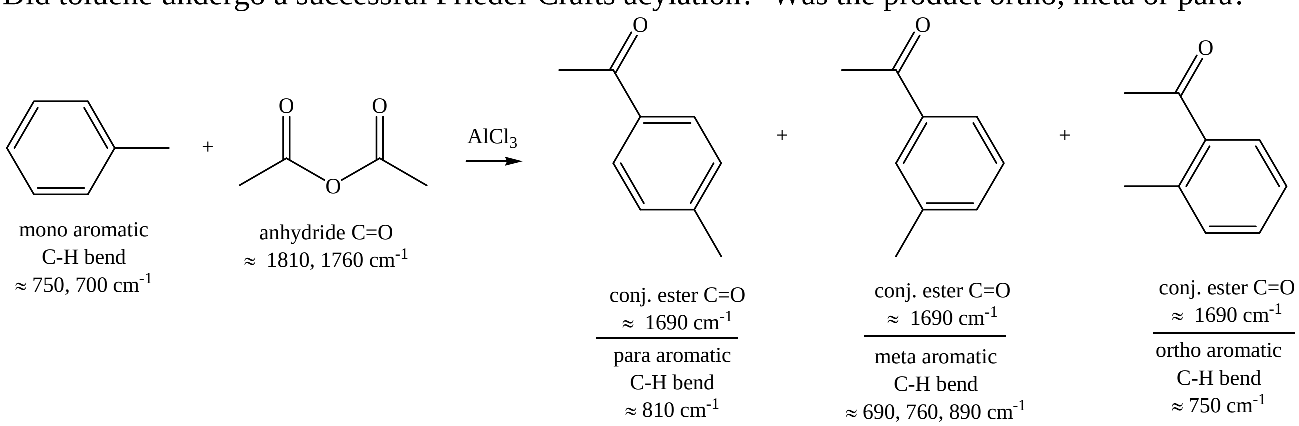
c. Was the unsaturated ester reduced to an allylic alcohol, the saturated ester or the saturated alcohol? Is there any starting material left?



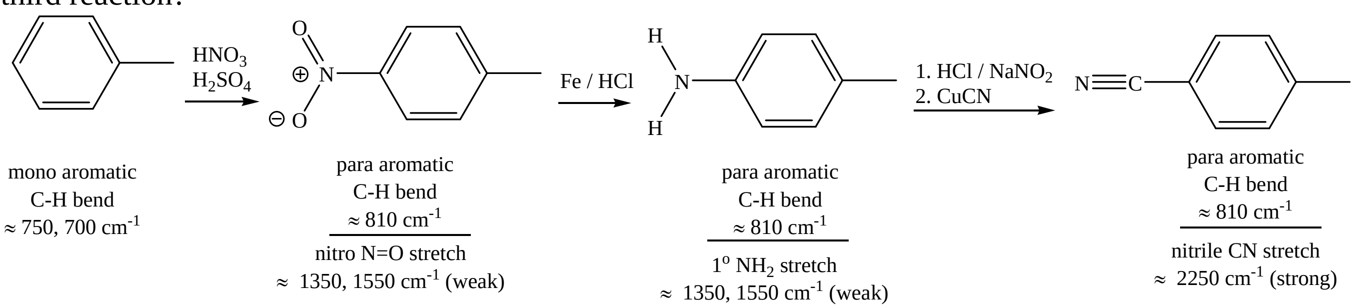
d. Did the alkyne reduce to a cis alkene, trans alkene or an alkane? Did the reaction work?



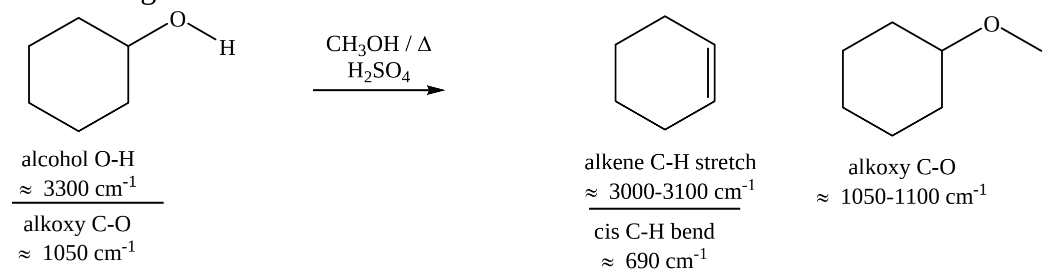
e. Did toluene undergo a successful Friedel-Crafts acylation? Was the product ortho, meta or para?



f. Did nitration work in the first reaction (if so, was it ortho, meta or para)? Did the nitro group reduce to the amine in the second reaction? Was the amino group substituted for a nitrile in the third reaction?

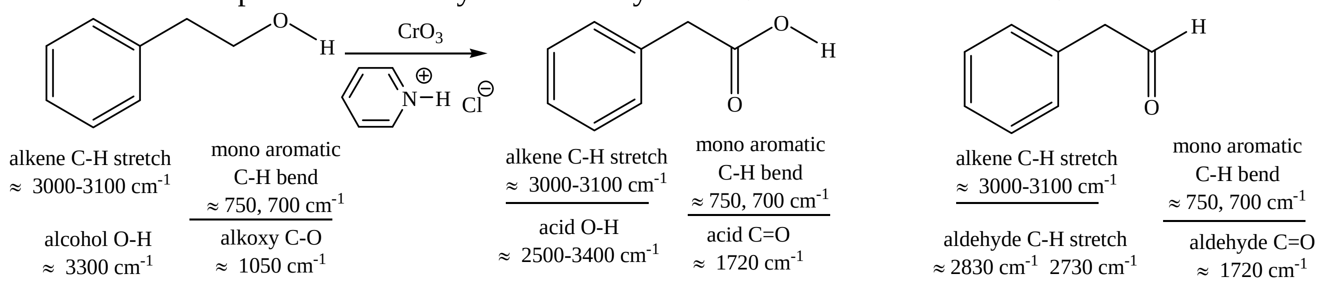


g. Did the alcohol undergo an elimination reaction to an alkene or substitution reaction to an

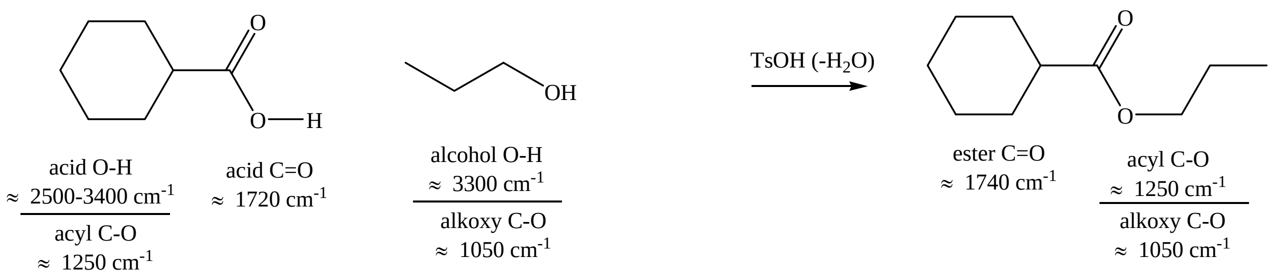


ether?

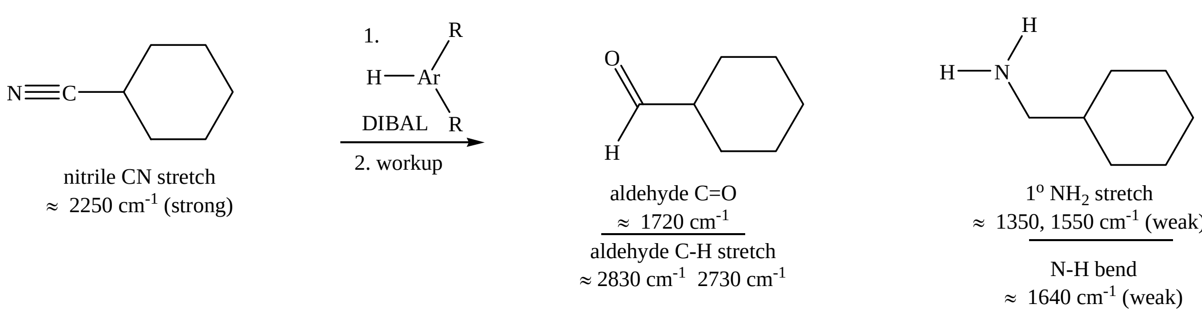
h. Did the oxidation produce an aldehyde or carboxylic acid? Did the reaction work?



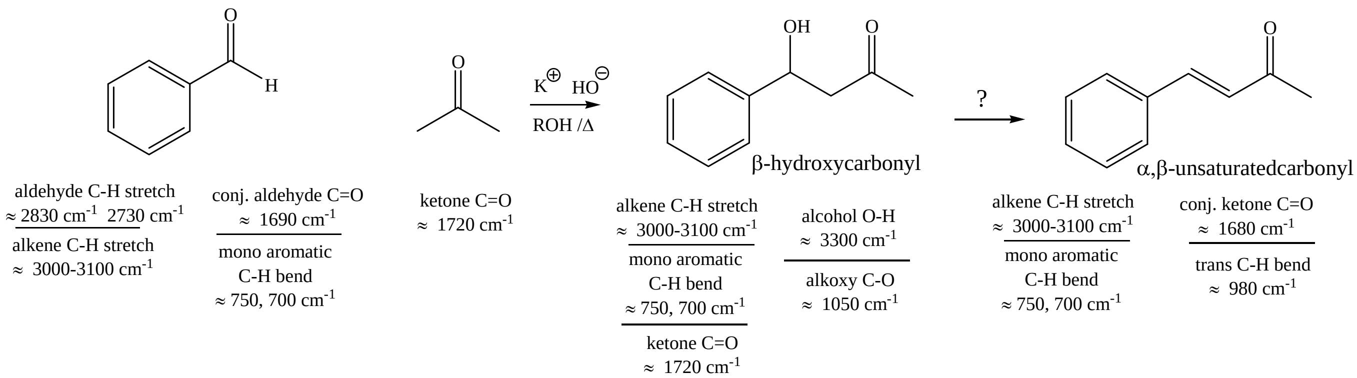
i. Did the esterification reaction work or was the carboxylic acid isolated in the workup?



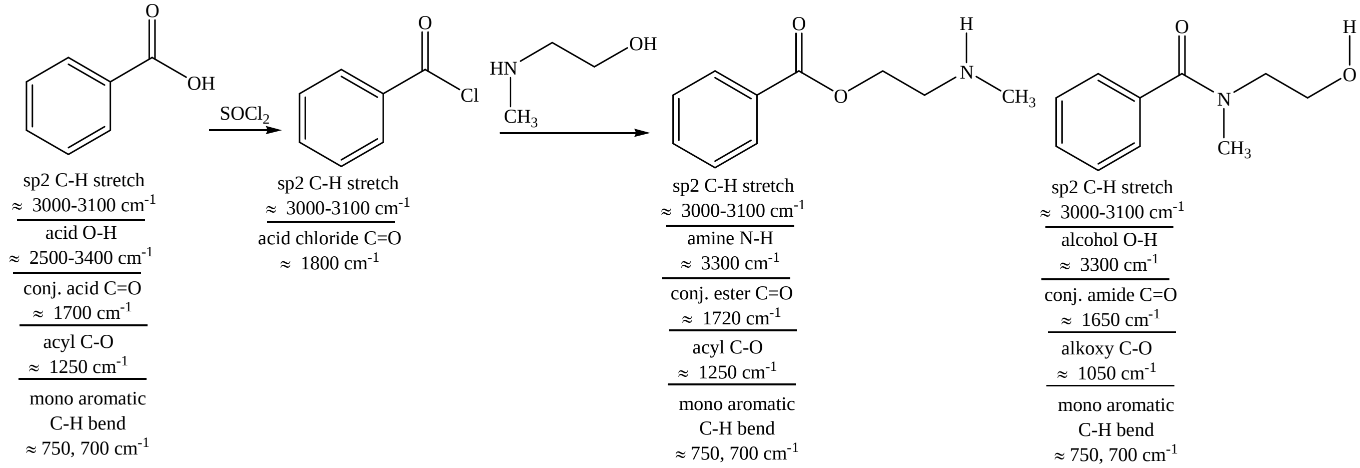
j. Did the DIBAH reduction of the nitrile produce an aldehyde or an amine or did it work?



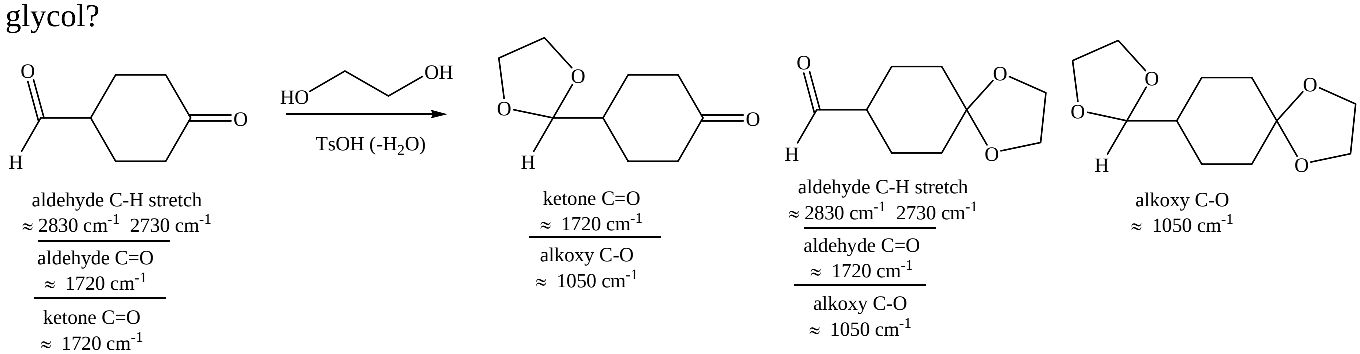
k. Did the aldol reaction produce a β-hydroxycarbonyl or an α,β-unsaturated carbonyl or did it work?



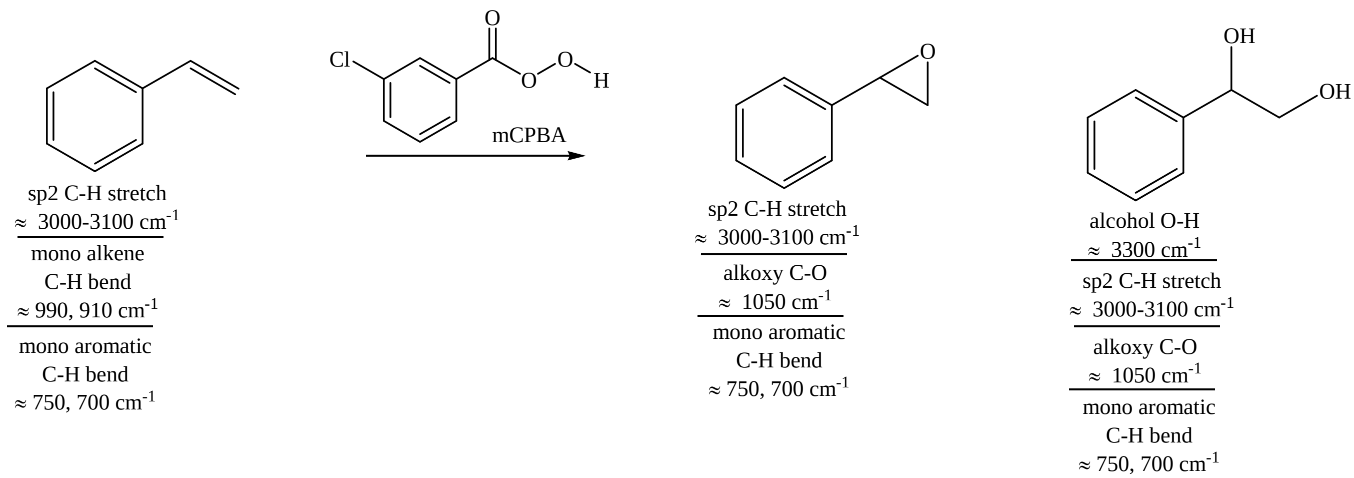
l. Did the reaction of thionyl chloride with benzoic acid produce an acid chloride? Was this converted into an ester or an amide in the second reaction with 2-(N-methylamino)-1-ethanol?



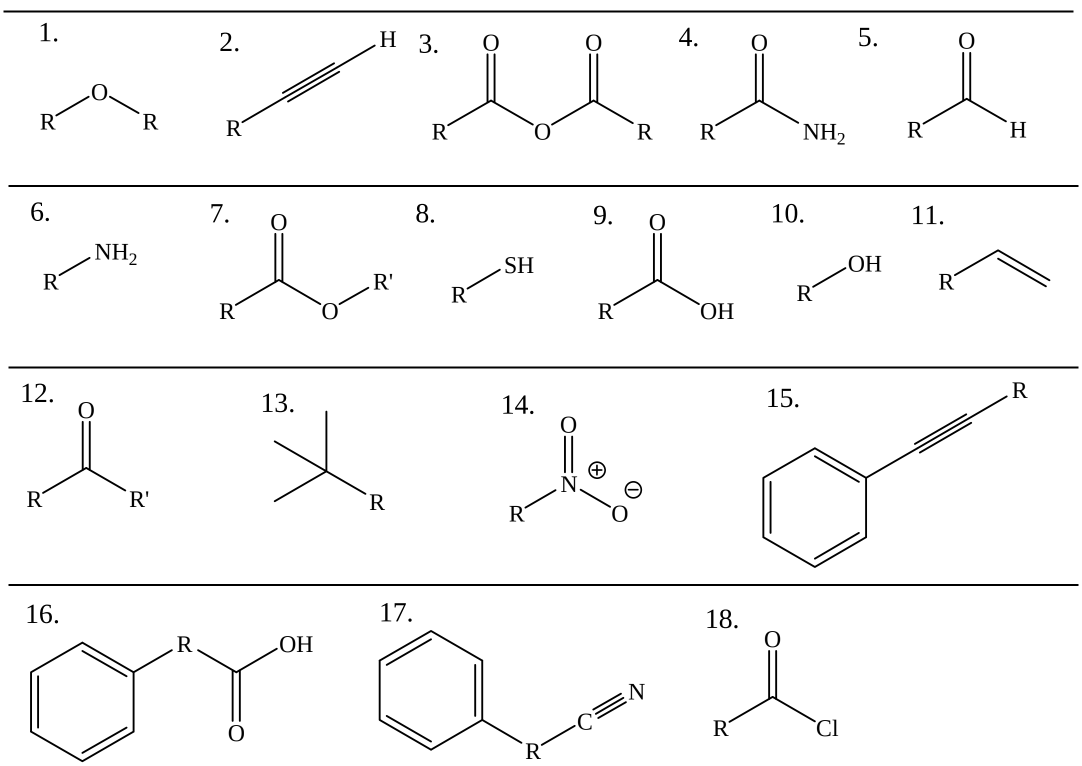
m. Did the ketone, the aldehyde, both or neither get protected as acetals in reaction with ethylene glycol?



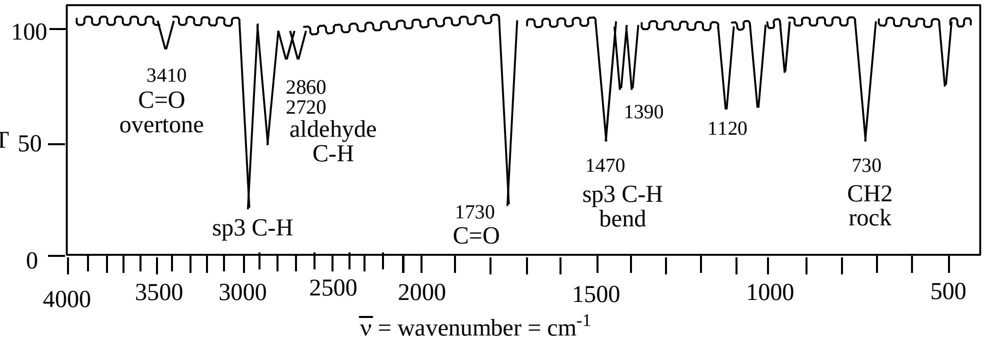
n. Did the alkene get oxidized with mCPBA to an epoxide ether or a 1,2-diol or did the reaction work?



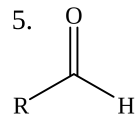
Problem 2 (p 60)
Match each of the following compounds with the IR spectra below. Generic 'alkane' parts are represented with an R symbol. **Identify all distinguishing functional group absorption bands to demonstrate the logic of your choices** (e.g. 2970-2860 sp^3 = CH stretch; 1720 = C=O stretch, etc.)**.**



A.

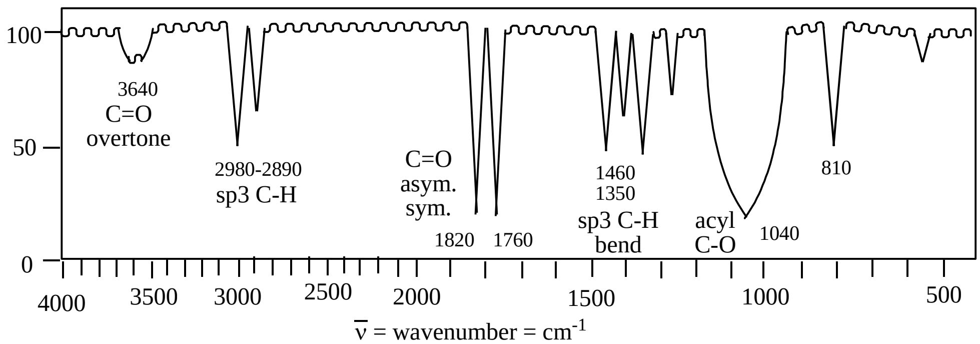


5.

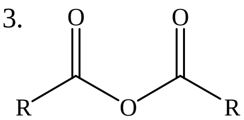


aldehyde

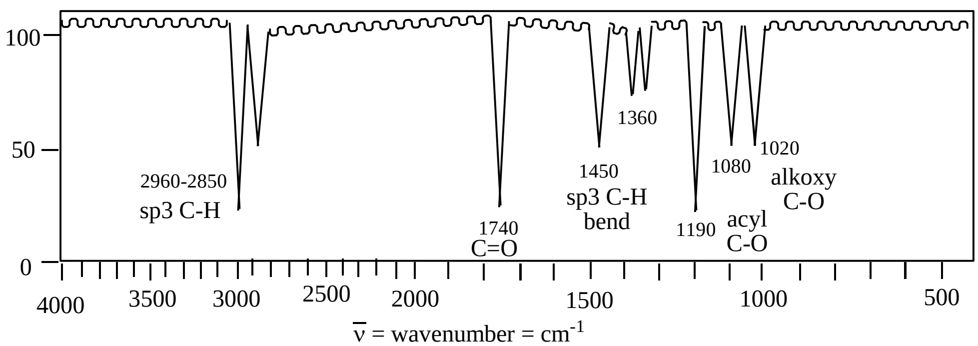
B.



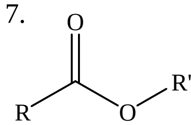
3.



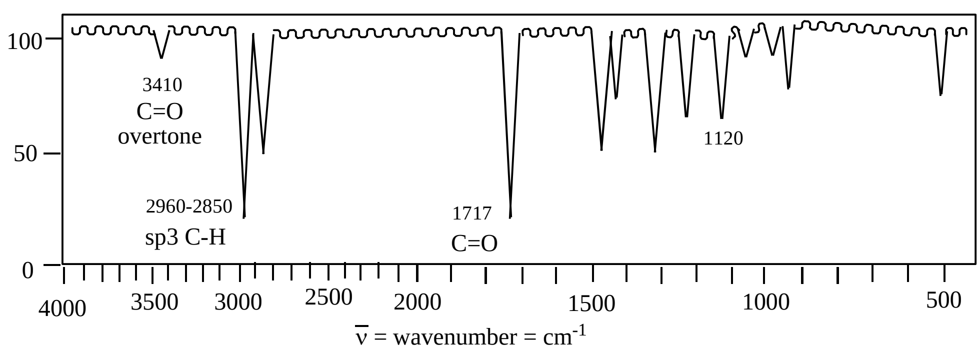
C.



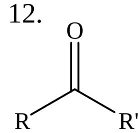
7.



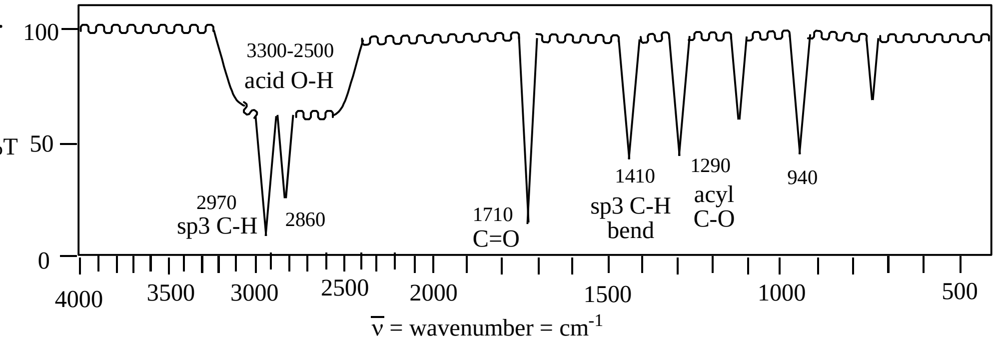
D.



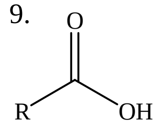
12.



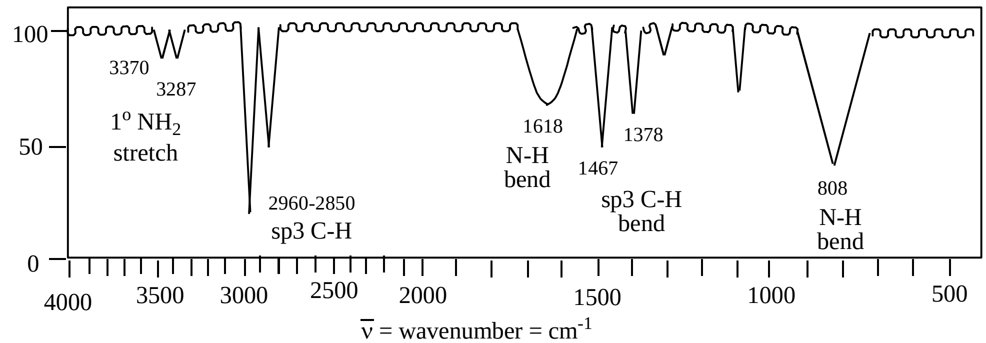
E.


100
%T 50
0
3300-2500
acid O-H
2970
sp3 C-H
2860
1710
C=O
1410
sp3 C-H
bend
1290
acyl
C-O
940
4000 3500 3000 2500 2000 1500 1000 500
$\bar{\nu}$ = wavenumber = cm^{-1}

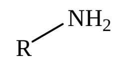
9.


O
R
OH

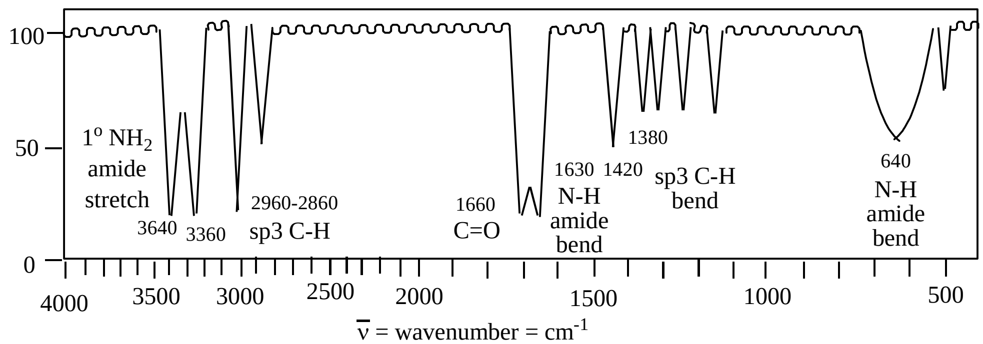
F.


100
%T 50
0
3370
3287
1° NH_2
stretch
2960-2850
sp3 C-H
1618
N-H
bend
1467
1378
sp3 C-H
bend
808
N-H
bend
4000 3500 3000 2500 2000 1500 1000 500
$\bar{\nu}$ = wavenumber = cm^{-1}

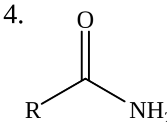
6.


R
NH_2

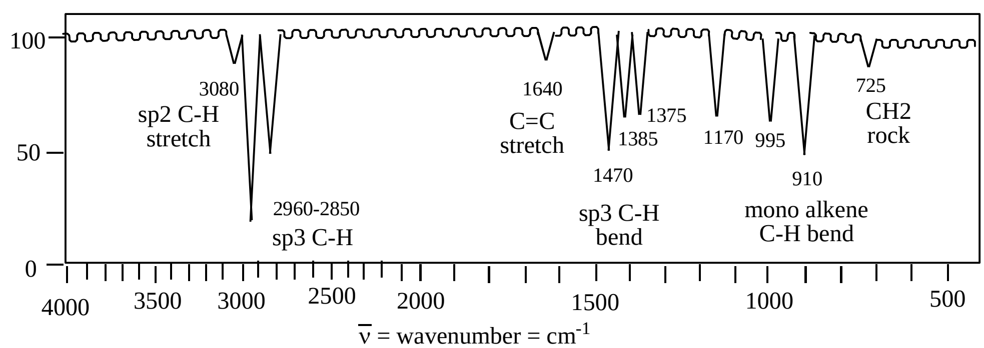
G.


100
%T 50
0
1° NH_2
amide
stretch
3640 3360
2960-2860
sp3 C-H
1660
C=O
1630 1420
N-H
amide
bend
1380
sp3 C-H
bend
640
N-H
amide
bend
4000 3500 3000 2500 2000 1500 1000 500
$\bar{\nu}$ = wavenumber = cm^{-1}

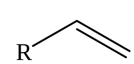
4.


O
R
NH_2

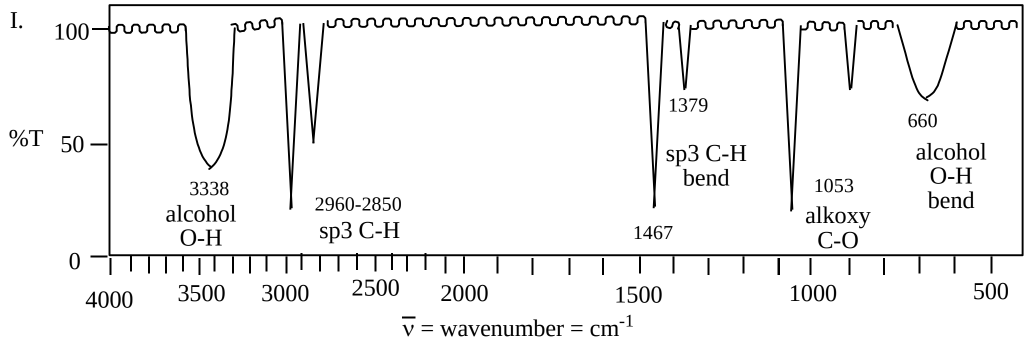
H.


100
%T 50
0
3080
sp2 C-H
stretch
2960-2850
sp3 C-H
1640
C=C
stretch
1470
1385
1375
sp3 C-H
bend
1170
995
910
mono alkene
C-H bend
725
CH2
rock
4000 3500 3000 2500 2000 1500 1000 500
$\bar{\nu}$ = wavenumber = cm^{-1}

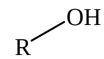
11.


R

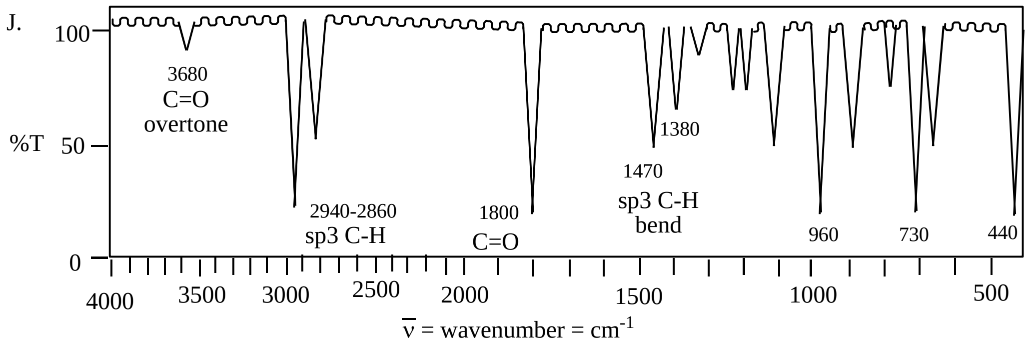
I.



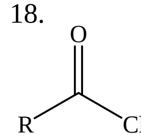
10.



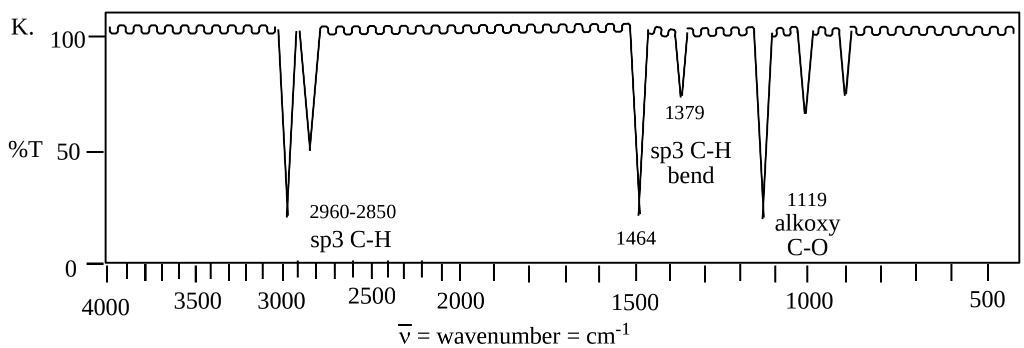
J.



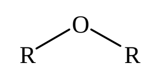
18.



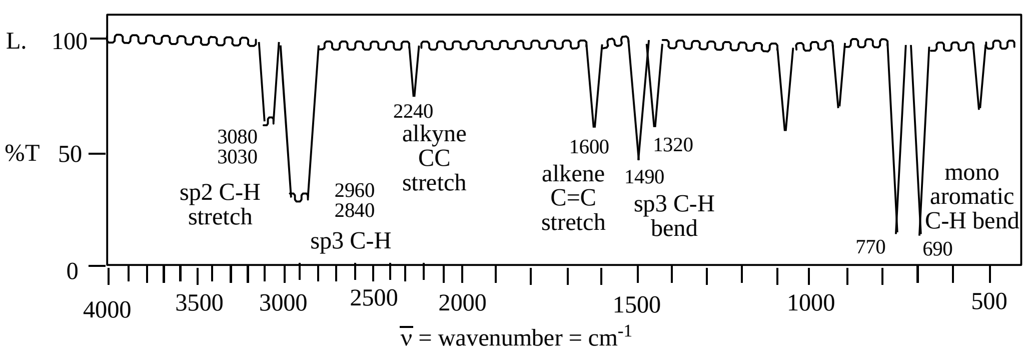
K.



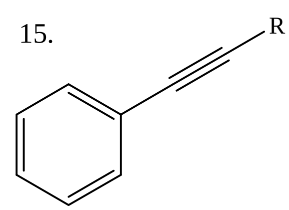
1.



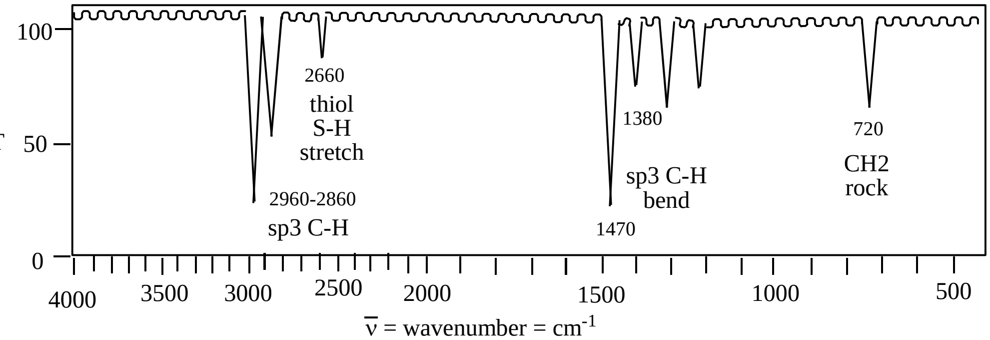
L.



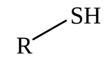
15.



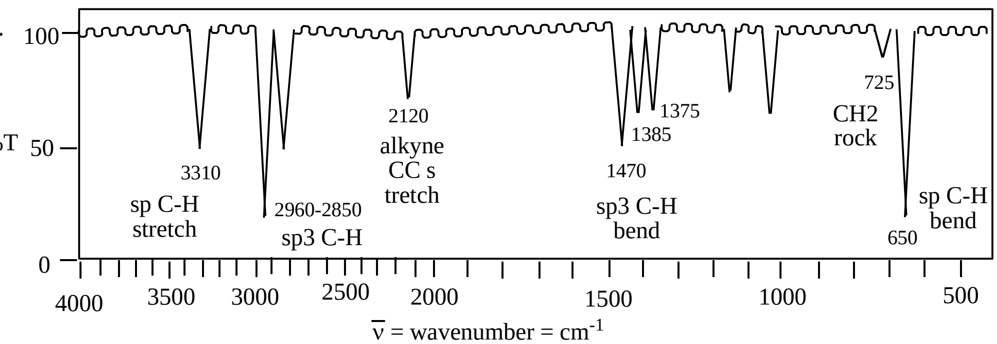
M.


100
%T 50
0
2660
thiol
S-H
stretch
2960-2860
sp3 C-H
1380
sp3 C-H
bend
1470
720
CH2
rock
4000 3500 3000 2500 2000 1500 1000 500
ν̄ = wavenumber = cm-1

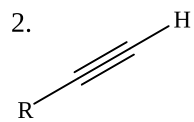
8.


R
SH

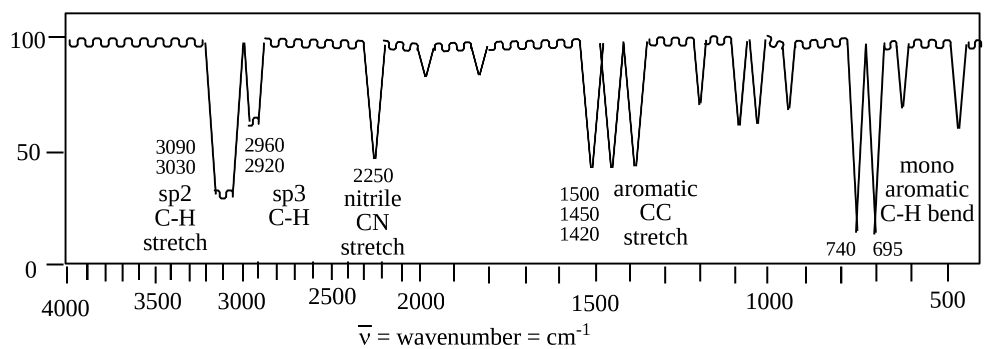
N.


100
%T 50
0
3310
sp C-H
stretch
2960-2850
sp3 C-H
2120
alkyne
CC s
tretch
1375
1385
1470
sp3 C-H
bend
725
CH2
rock
sp C-H
bend
650
4000 3500 3000 2500 2000 1500 1000 500
ν̄ = wavenumber = cm-1

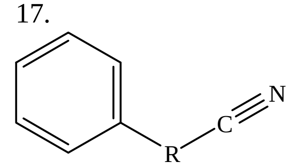
2.


R
H

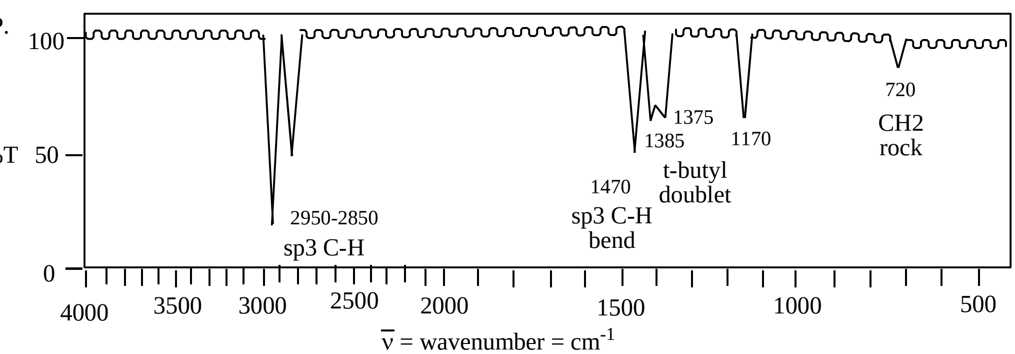
O.


100
%T 50
0
3090
3030
sp2
C-H
stretch
2960
2920
sp3
C-H
2250
nitrile
CN
stretch
1500
1450
1420
aromatic
CC
stretch
mono
aromatic
C-H bend
740
695
4000 3500 3000 2500 2000 1500 1000 500
ν̄ = wavenumber = cm-1

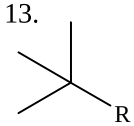
17.


R
C
N

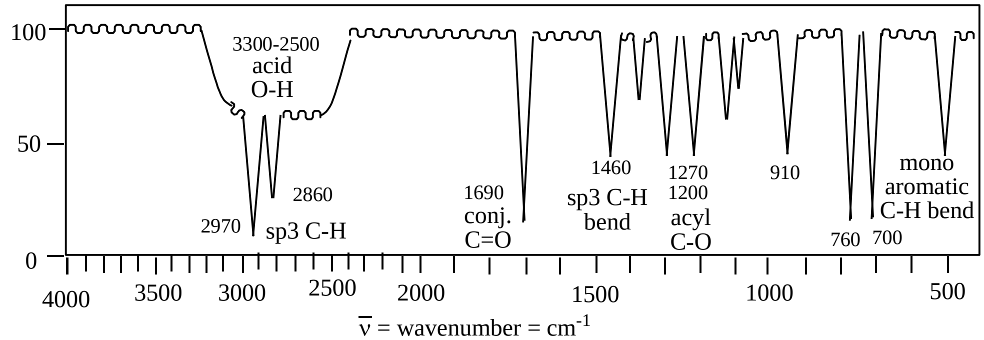
P.


100
%T 50
0
2950-2850
sp3 C-H
1375
1385
1470
sp3 C-H
bend
t-butyl
doublet
1170
720
CH2
rock
4000 3500 3000 2500 2000 1500 1000 500
ν̄ = wavenumber = cm-1

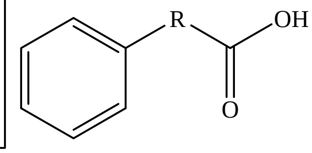
13.


R

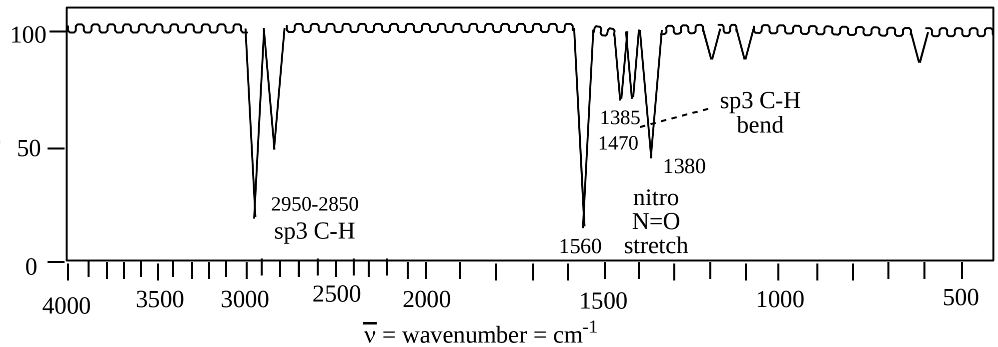
Q.


100
%T 50
0
3300-2500
acid
O-H
2970
2860
sp3 C-H
1690
conj.
C=O
1460
sp3 C-H
bend
1270
1200
acyl
C-O
910
760
700
mono
aromatic
C-H bend
4000
3500
3000
2500
2000
1500
1000
500
ν = wavenumber = cm-1

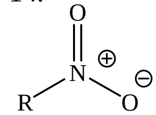
16.


R
OH
O

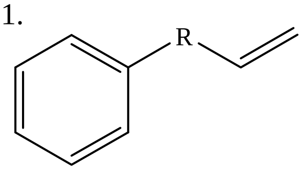
R

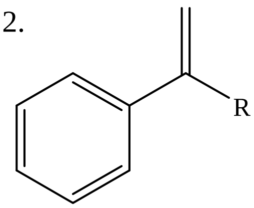

100
%T 50
0
2950-2850
sp3 C-H
1385
1470
1380
sp3 C-H
bend
1560
nitro
N=O
stretch
4000
3500
3000
2500
2000
1500
1000
500
ν = wavenumber = cm-1

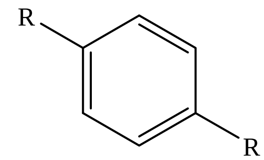
14.

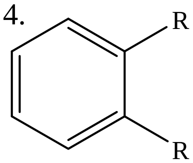

O
N
R
O

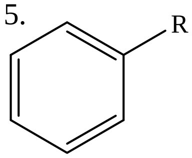
Problem 3 (p 66) – Match each of the following aromatic compounds (and occasional alkene) with its IR spectra below. **Identify all distinguishing absorption bands to demonstrate the logic of your choices.** Write each structure next to the spectra. R = alkane portion.

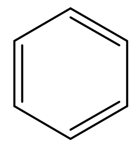
1.


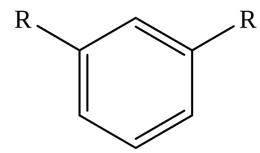
2.


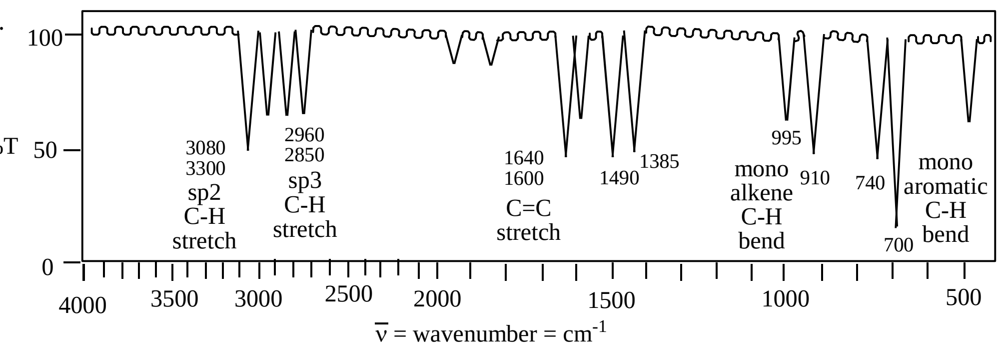
3.


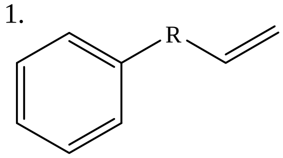
4.


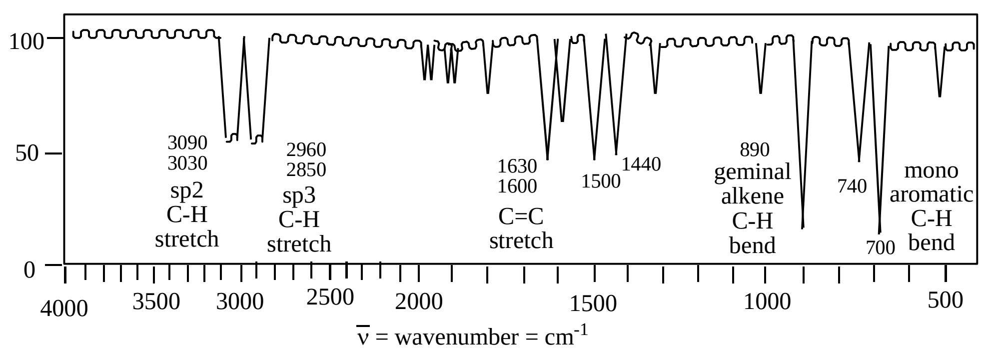
5.


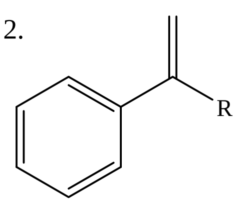
6.


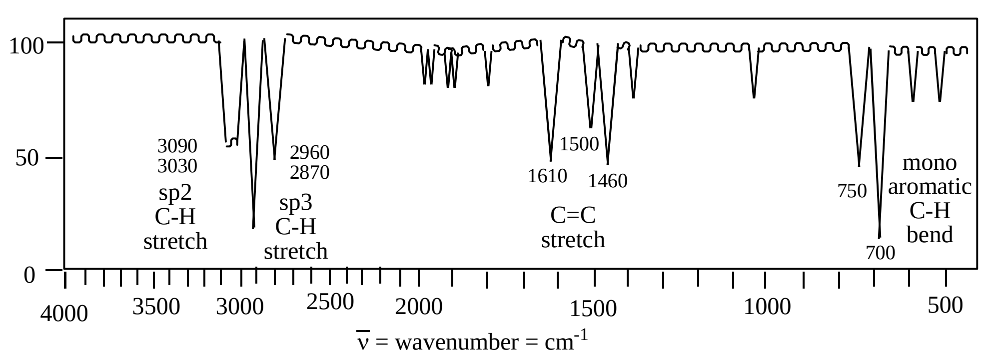
7.


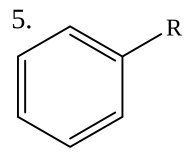
A.


1.


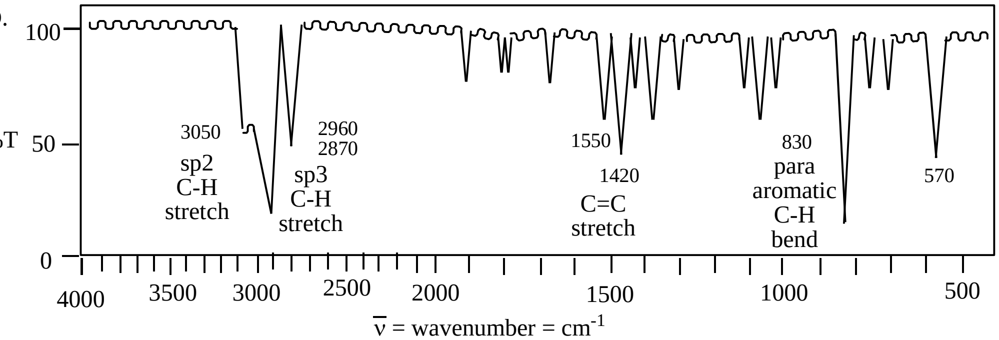
B.


2.


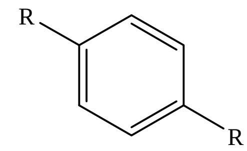
C.


5.


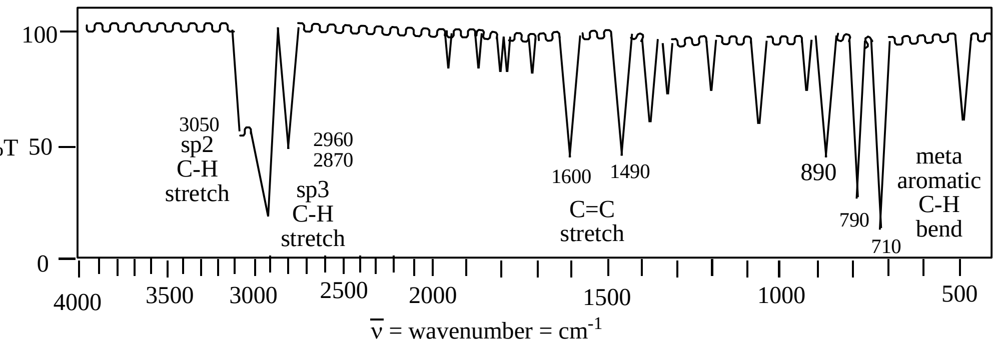
D.


100
%T 50
0
3050
sp2
C-H
stretch
2960
2870
sp3
C-H
stretch
1550
1420
C=C
stretch
830
para
aromatic
C-H
bend
570
4000 3500 3000 2500 2000 1500 1000 500
$\bar{\nu}$ = wavenumber = cm^{-1}

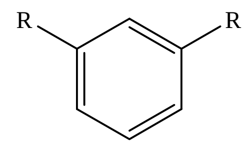
3.


R
R

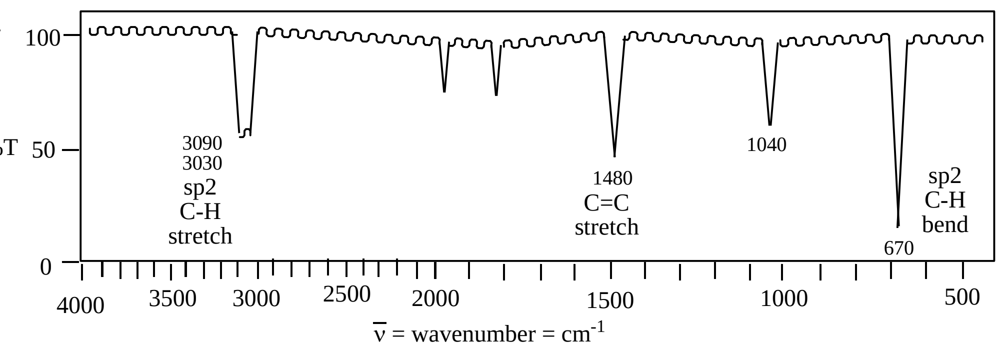
E.


100
%T 50
0
3050
sp2
C-H
stretch
2960
2870
sp3
C-H
stretch
1600
1490
C=C
stretch
890
790
710
meta
aromatic
C-H
bend
4000 3500 3000 2500 2000 1500 1000 500
$\bar{\nu}$ = wavenumber = cm^{-1}

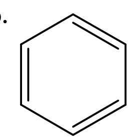
7.


R
R

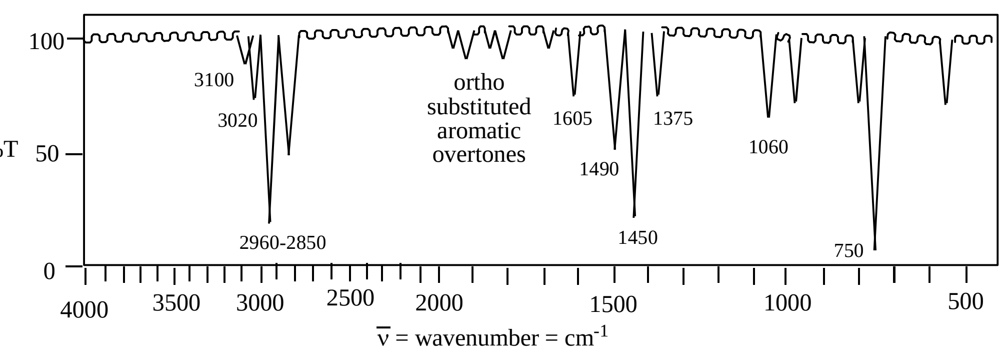
F.


100
%T 50
0
3090
3030
sp2
C-H
stretch
1480
C=C
stretch
1040
670
sp2
C-H
bend
4000 3500 3000 2500 2000 1500 1000 500
$\bar{\nu}$ = wavenumber = cm^{-1}

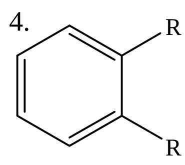
6.



E.

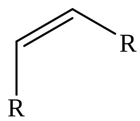

100
%T 50
0
3100
3020
2960-2850
ortho
substituted
aromatic
overtones
1605
1490
1450
1375
1060
750
4000 3500 3000 2500 2000 1500 1000 500
$\bar{\nu}$ = wavenumber = cm^{-1}

4.

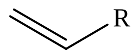

R
R

Problem 4 (p 68) – Match each of the following alkene spectra with the corresponding alkene**. Identify distinguishing absorption bands to demonstrate the logic of your choices.** Write each structure next to the spectra.

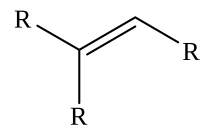
1.



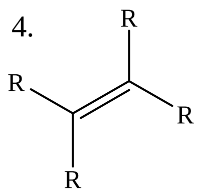
2.



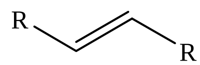
3.



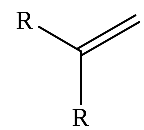
4.



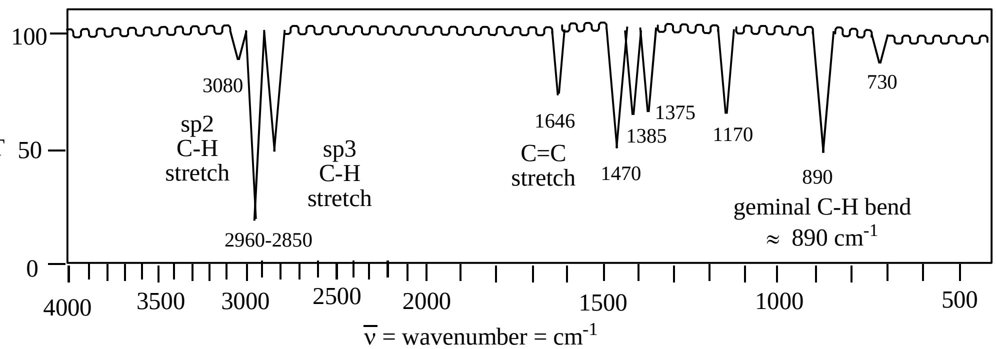
5.



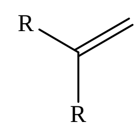
6.



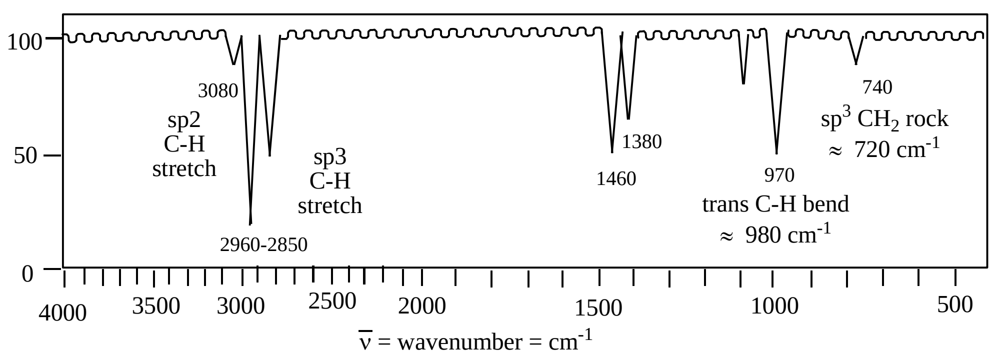
A.



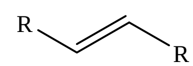
6. geminal alkene



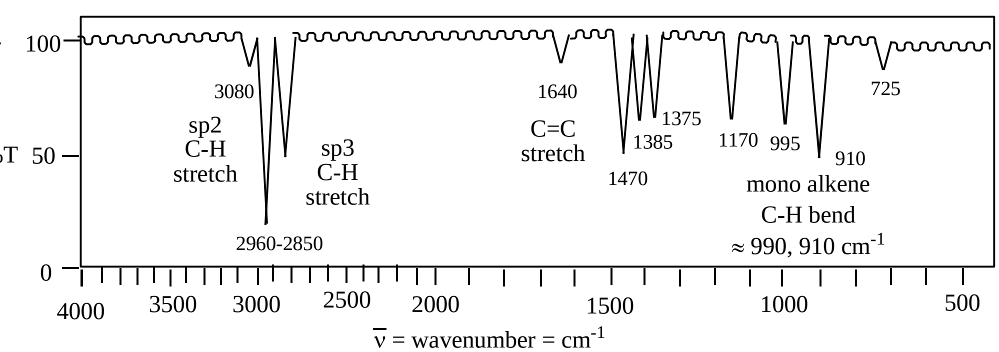
B.



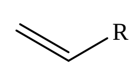
5. trans alkene

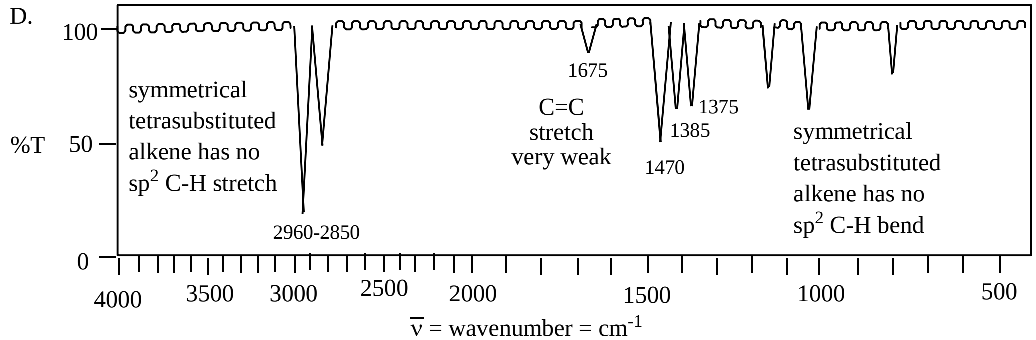


C.

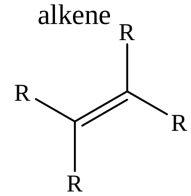


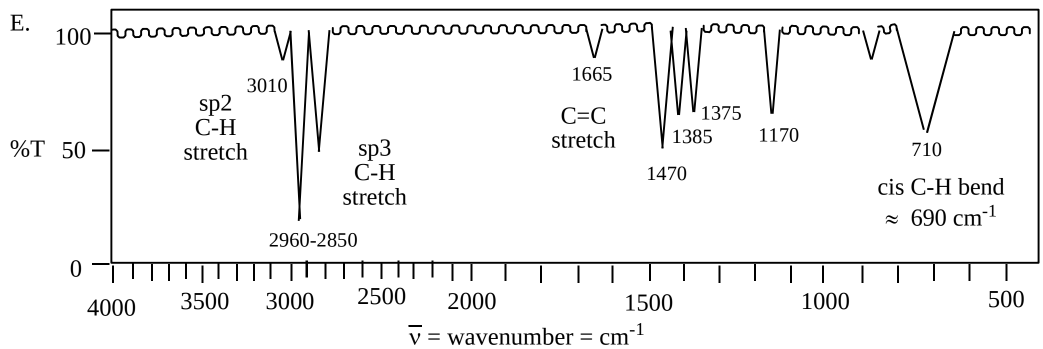
2. monosubstituted alkene



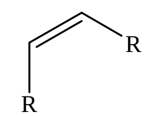


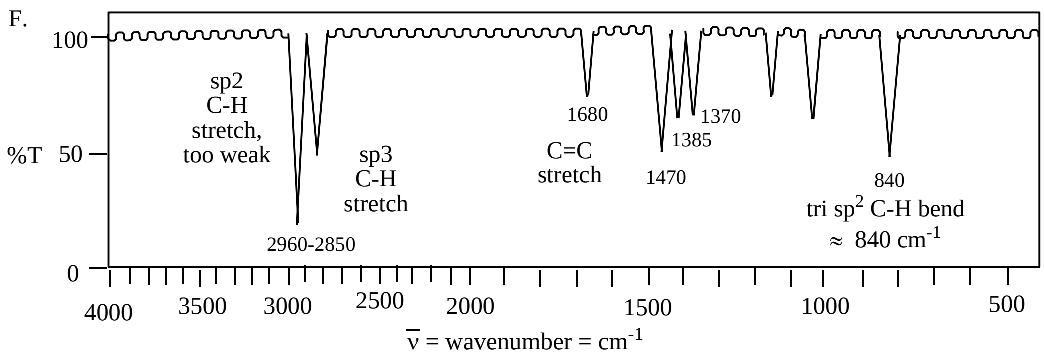
4. tetrasubstituted alkene



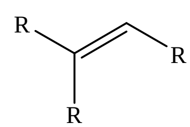


1. cis alkene





3. trisubstituted alkene



Chapter 3 – Mass Spec

Problem 1 (p. 75)- A low-resolution mass spectrum of satosporin C (J. Org. Lett., 2013, *15*, 3864-7) showed the molecular weight to be 364. This molecular weight is correct for the molecular formulas $C_{21}H_{32}O5$, $C_{22}H_{36}O_4$ and $C_{23}H_{40}O_3$. A high-resolution mass spectrum provided a molecular weight of 364.5375. Which of the possible molecular formulas is the correct one? What is the degree of unsaturation in satosporin C?

$C_{21}H_{32}O_5$	$C_{22}H_{36}O_4$	$C_{23}H_{40}O_3$.
(21) x (12.01115) = 252.2234	(22) x (12.01115) = 264.2453	(23) x (12.01115) = 276.2564
(32) x (1.00797) = 32.2550	(36) x (1.00797) = 36.2869	(40) x (1.00797) = 40.3188
(5) x (15.9994) = 79.9970	(4) x (15.9994) = 63.9976	(3) x (15.9994) = 47.9982
total = 364.4862	total = 364.5298	total = 364.5734
Δ = 0.0513	Δ = 0.0077	Δ = 0.0359

experimental molecular mass = 364.5375
appears closest to the second molecular formula

Problem 2 (p. 75)– Penilactone B, (J. Org. Lett., 2013, *15*, 3891-3), a natural product was found by low-resolution mass spectrometry to have a molecular weight of 514. Possible molecular formulas include $C_{28}H_{34}O_9$, $C_{27}H_{30}O_{10}$, and $C_{26}H_{26}O_{11}$. High-resolution mass spectrometry indicated that the precise molecular weight was 514.4996. What is the correct molecular formula of penilactone B? What is the degree of unsaturation?

$C_{28}H_{34}O_9$	$C_{27}H_{30}O_{10}$	$C_{26}H_{26}O_{11}$
(28) x (12.01115) = 336.3122	(27) x (12.01115) = 324.3010	(26) x (12.01115) = 312.2899
(34) x (1.00797) = 34.2710	(30) x (1.00797) = 30.2391	(26) x (1.00797) = 26.2072
(9) x (15.9994) = 143.9946	(10) x (15.9994) = 159.9940	(11) x (15.9994) = 175.9934
total = 514.5778	total = 514.5341	total = 514.4905
Δ = 0.1282	Δ = 0.0845	Δ = 0.0409

experimental molecular mass = 514.4496
appears closest to the third molecular formula

Problem 3 (p. 76)– Calculate the relative intensities (as a percent) of M+, M+1 and M+2 for propene (CH_3-CH=CH_2), ketene (CH_2=C=O) and diazomethane (CH_2=N=N). Can these three formulas (C_3H_6 vs C_2H_2O vs CH_2N_2) be distinguished on the basis of their M+1 and M+2 peaks? Calculate the exact mass (four decimal places) for all of these formulas. Can they be distinguished on the basis of exact mass? Helpful data are on page #.

propene, (CH3-CH=CH2) = C3H6

one ^{13}C = $\frac{1.08}{100.00 + 1.08}$ (3 ways) = 0.0300

one ^{2}H = $\left(\frac{0.012}{100.00 + 0.012}\right)$ (6 ways) = 0.0007

zero ^{17}O =

sum of possibilities = (0.0300) + (0.0007) + (0.0000) = 0.0307

M+1 peak as a percent of M+ peak = (0.0307)x(100%) = 3.07%

two ^{13}C = $\left(\frac{1.08}{101.08}\right)^2 \frac{3 \times 2}{2 \times 1}$ = $(0.0300)^2$(3 ways) = 0.0027

two ^{2}H = $\left(\frac{0.012}{100.012}\right)^2 \left(\frac{6 \times 5}{2 \times 1}\right)$ = (5×10^{-7})(15 ways)

= 7×10^{-6} = too small to consider

zero ^{18}O =

one ^{13}C and one ^{2}H = $\left(\frac{1.08}{101.10}\right)$ (3 ways) x $\left(\frac{0.012}{100.012}\right)$ (6 ways)

= 0.000002 = too small to consider

sum of possibilities = (0.0027) + (0.0000) + (0.0000) = 0.0027

M+2 peak as a percent of M+ peak = (0.0027)x(100%) = 0.27%

diazomethane, (CH2=N=N, CH2N2)

one ^{13}C = $\frac{1.08}{100.00 + 1.08}$ (1 ways) = 0.0107

one ^{2}H = $\left(\frac{0.012}{100.00 + 0.012}\right)$ (2ways) = 0.0002

one ^{15}N = $\left(\frac{0.37}{100.00 + 0.37}\right)$ (1 way) = 0.0037

sum of possibilities = (0.0107) + (0.0002) + (0.0037) = 0.0181

M+1 peak as a percent of M+ peak = (0.0181)x(100%) = 1.81%

two ^{13}C = not possible

two ^{2}H = $\left(\frac{0.012}{100.012}\right)^2$ = 0.0001

two ^{15}N = $\left(\frac{0.37}{100.37}\right)^2$ (1 way) = 0.0000

sum of possibilities = (0.0001) = 0.0001

M+2 peak as a percent of M+ peak = (0.0001)x(100%) = 0.01%

ketene, (CH2=C=O, C2H2O)

one ^{13}C = $\frac{1.08}{100.00 + 1.08}$ (2 ways) = 0.0214

one ^{2}H = $\left(\frac{0.012}{100.00 + 0.012}\right)$ (2 ways) = 0.0002

one ^{17}O = $\left(\frac{0.04}{100.00 + 0.04 + 0.20}\right)$ (1 way) = 0.0220

sum of possibilities = (0.0214) + (0.0002) + (0.0004) = 0.0220

M+1 peak as a percent of M+ peak = (0.0220)x(100%) = 2.20%

two ^{13}C = $\left(\frac{1.08}{101.08}\right)^2$ = $(0.0011)^2$ = 0.0001

two ^{2}H = $\left(\frac{0.012}{100.012}\right)^2$ = too small to consider

one ^{18}O = $\frac{0.20}{100.24}$ (1 way) = 0.0020

one ^{13}C and one ^{2}H = $\left(\frac{1.08}{101.10}\right)$ (2 ways) x $\left(\frac{0.012}{100.012}\right)$ (2 ways)

= too small to consider

sum of possibilities = (0.0001) + (0.0020) + (0.0000) = 0.0021

M+2 peak as a percent of M+ peak = (0.0021)x(100%) = 0.21%

Problem 4 (p. 78)- Calculate the relative intensities (as a percent) of M+, M+2 and M+4 for Cl_2 and Br_2. Use the probabilities from above.

M+ peak relative size

two $^{35}Cl = (0.758)^2$ (1 way) = 0.575

(assigned a referenced value of 100%)

M+2 peak relative size

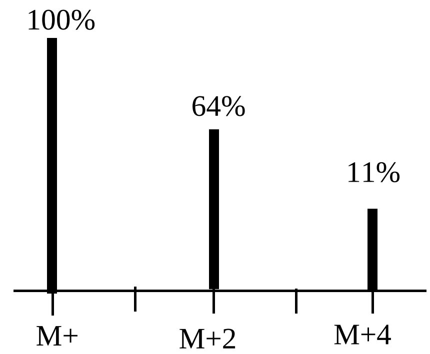
one ^{35}Cl and one ^{37}Cl = (0.758) x (0.242) x (2 ways) = 0.367

percent of M+ peak = [(0.367)/(0.575)] x 100 = 63.8%

M+4 peak relative size

two $^{37}Cl = (0.246)^2$ (1 way) = 0.0605

percent of M+ peak = [(0.0605)/(0.575)] x 100 = 10.5%



M+ peak relative size

two $^{78}Br = (0.507)^2$ (1 way) = 0.257

(assigned a referenced value of 100%)

M+2 peak relative size

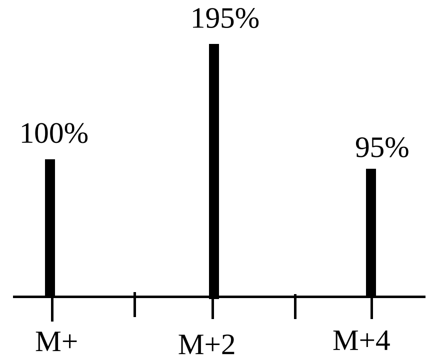
one ^{79}Br and one ^{81}Br = (0.507) x (0.493) x (2 ways) = 0.500

percent of M+ peak = [(0.500)/(0.257)] x 100 = 195%

M+4 peak relative size

two $^{81}Br = (0.493)^2$ (1 way) = 0.243

percent of M+ peak = [(0.243)/(0.257)] x 100 = 95%



Problem 5 (p. 82)– Match the MS data with the correct number of Cl, Br and/or S. For each molecular weight estimate how many carbon atoms are present. The proton count is provided from the proton NMR, as is number of pi bonds from the ^{13}C NMR. Use this information to calculate a chemical formula and degrees of unsaturation and number of rings.

Formula 1 has one Cl = c.
This has to be compound c because the M+2 peak is 32% of the M+ peak (= 330). Subtract 35 from the mass peak gives the residual mass of 295. Subtract 23 proton mass from 295 leaves 260. Divide the M+1 peak (16.6%) by 1.1 suggests there are 15 carbon atoms (= 180 mass units). Subtract 180 from 260 leaves 80 which is divisible by 16, indicating there are 5 oxygen atoms.

Formula 1 = $C_{15}H_{23}ClO_5$

unsaturation = 2(15) + 2 = 32
-24
= 8 ÷ 2 = 4 degrees unsaturation
(3 pi bonds, 1 ring)

Formula 2 has one Br = e.
This has to be compound e because the M+2 peak is 97% of the M+ peak (= 287). Subtract 79 from the mass peak gives the residual mass of 208. Subtract 14 proton mass from 208 leaves 194. Divide the M+1 peak (12.2%) by 1.1 suggests there are 11 carbon atoms (= 132 mass units). Subtract 132 from 194 leaves 62. The M+ peak is odd so there has to be an odd number of nitrogen atoms. Subtract 14 from 62 leaves 48 which is divisible by 16, indicating there are 3 oxygen atoms.

Formula 2 = $C_{11}H_{14}BrNO_3$

unsaturation = 2(11) + 2 + 1 = 25
-15
= 10 ÷ 2 = 5 degrees unsaturation
(3 pi bonds, 2 rings)

Formula 3 has one Cl and one S = d.
This has to be compound e because the M+2 peak is 36.5% (32.0% + 4.5%) of the M+ peak (= 345). Subtract 67 (= 35+32) from the mass peak gives the residual mass of 278. Subtract 24 proton mass from 278 leaves 254. Subtract 0.7 (sulfur) from the M+1 peak (18.5%-0.7% = 17.8% for carbon) divided by 1.1 suggests there are 16 carbon atoms + 1 sulfur atom (= 224 mass units). Subtract 224 from 254 leaves 30. The M+ peak is odd so there has to be an odd number of nitrogen atoms. Subtract 14 from 30 leaves 16 which is divisible by 16, indicating there is 1 oxygen atom.

Formula 3 = $C_{16}H_{24}ClSNO$

unsaturation = 2(16) + 2 +1 = 35
-25
= 10 ÷ 2 = 5 degrees unsaturation
(3 pi bonds, 2 rings)

Formula 4 has one Br and one S = b.
This has to be compound b because the M+2 peak is 101.9% (97.3% + 4.5%) of the M+ peak (= 405). Subtract 111 (= 79+32) from the mass peak gives the residual mass of 294. Subtract 20 proton mass from 294 leaves 274. Subtract 0.7 (sulfur) from the M+1 peak (17.3%-0.7% = 16.6% for carbon) divided by 1.1 suggests there are 15 carbon atoms (= 180 mass units). Subtract 180 from 274 leaves 94. The M+ peak is odd so there has to be an odd number of nitrogen atoms. Subtract 14 from 94 leaves 80 which is divisible by 16, indicating there are 5 oxygen atoms.

Formula 4 = $C_{15}H_{20}BrSNO_5$

unsaturation = 2(15) + 2 +1 = 33
-21
= 12 ÷ 2 = 6 degrees unsaturation
(3 pi bonds, 3 rings)

Formula 5 has two Cl = a.
This has to be compound a because the M+2 peak is 63.9% (32.0% + 32.0%) of the M+ peak (= 361). Subtract 70 from the mass peak gives the residual mass of 291. Subtract 21 proton mass from 291 leaves 270. The M+1 peak (17.7% carbon) divided by 1.1 suggests there are 16 carbon atoms (= 196 mass units). Subtract 196 from 270 leaves 74. The M+ peak is odd so there has to be an odd number of nitrogen atoms. Subtract 14 from 74 leaves 60 which is divisible by 16, indicating there are 5 oxygen atoms.

Formula 4 = $C_{16}H_{21}Cl_2NO_5$

unsaturation = 2(16) + 2 +1 = 35
-23
= 12 ÷ 2 = 6 degrees unsaturation
(3 pi bonds, 3 rings)

Formula 6 has two Br = f.
This has to be compound f because the M+2 peak is 194.6% (97.3% + 97.3%) of the M+ peak (= 445). Subtract 158 (= 2xBr) from the mass peak gives the residual mass of 287. Subtract 21 proton mass from 287 leaves 266. The M+1 peak (17.7% carbon) divided by 1.1 suggests there are 16 carbon atoms (= 192 mass units). Subtract 192 from 266 leaves 74. The M+ peak is odd so there has to be an odd number of nitrogen atoms. Subtract 14 from 74 leaves 60 which is divisible by 16, indicating there are 5 oxygen atoms.

Formula 4 = $C_{16}H_{21}Br_2NO_5$

unsaturation = 2(16) + 2 +1 = 35
-23
= 12 ÷ 2 = 6 degrees unsaturation
(3 pi bonds, 3 rings)

Problem 6 (p. 114)– CHO^+, $CH_3N^+$and $C_2H_5^+$ have fragment masses of approximately 29, yet CHO^+ has a M+1 peak of 1.13% and M+2 peak of 0.20%, CH_3N^+ has a M+1 peak of 1.51% and M+2 peak of 0.01% and $C_2H_5^+$ has a M+1 peak of 2.24% and M+2 peak of 0.01%. High resolution mass spec shows CHO^+, CH_3N^+ and $C_2H_5^+$ all have different masses. Explain these observations and show all of your work. Helpful data follow.

CHO

one $^{13}C = \frac{1.08}{100.00 + 1.08}$ (1 way) = 0.0107	two ^{13}C = not possible
one $^{2}H = \frac{0.012}{100.00 + 0.012}$ (1 way) = 0.0001	two ^{2}H = not possible
one $^{17}O = \frac{0.04}{100.00 + 0.04 + 0.2}$ (1 way) = 0.0004	one $^{18}O = \left(\frac{0.2}{100.24}\right)$ (1 way) = 0.0020
sum of possibilities = (0.0107) + (0.0001) + (0.0004) = 0.0112	sum of possibilities = (0.0020)
M+1 peak as a percent of M+ peak = (0.0112)x(100%) = 1.12%	**M+2 peak as a percent of M+ peak** = (0.0020)x(100%) = 0.20%

CH3N

one $^{13}C = \frac{1.08}{100.00 + 1.08}$ (1 way) = 0.0107	two ^{13}C = not possible
three $^{2}H = \left(\frac{0.012}{100.00 + 0.012}\right)$ (3 ways) = 0.0004	two $^{2}H = \left(\frac{0.012}{100.012}\right)^2$ (3 ways) = 0.0000
one $^{15}N = \left(\frac{0.37}{100.00 + 0.37}\right)$ (1 way) = 0.0037	two $^{15}N = \left(\frac{0.37}{100.37}\right)^2$ (1 way) = 0.000013
sum of possibilities = (0.0107) + (0.0004) + (0.0037) = 0.0181	sum of possibilities = (0.000013) = 0.0001
M+1 peak as a percent of M+ peak = (0.0148)x(100%) = 1.48%	**M+2 peak as a percent of M+ peak** = (0.000013)x(100%) = 0.001%

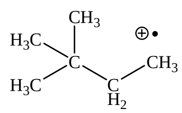
C2H5

one $^{13}C = \frac{1.08}{100.00 + 1.08}$ (2 ways) = 0.0214	two $^{13}C = \left(\frac{1.08}{101.08}\right)^2 = (0.0011)^2 = 0.0001$
one $^{2}H = \left(\frac{0.012}{100.00 + 0.012}\right)$ (5 ways) = 0.0006	two $^{2}H = \left(\frac{0.012}{100.012}\right)^2$ = too small to consider
sum of possibilities = (0.0214) + (0.0006) = 0.0220	one ^{13}C and one $^{2}H = \left(\frac{1.08}{101.10}\right)$ (2 ways) x $\left(\frac{0.012}{100.012}\right)$ (2 ways) = too small to consider
M+1 peak as a percent of M+ peak = (0.0220)x(100%) = 2.20%	sum of possibilities = (0.0001) = 0.0001
	M+2 peak as a percent of M+ peak = (0.0001)x(100%) = 0.01%

Element	Average Atomic Mass	Nuclide (Relative Abundance)	Mass
H	1.00797	^{1}H (100)	1.00783
H		^{2}H (0.012)	2.01410
C	12.01115	^{12}C (100)	12.00000
C		^{13}C (1.08)	13.00336
N	14.0067	^{14}N (100)	14.00307
N		^{15}N (0.37)	15.00011
O	15.9994	^{16}O (100)	15.99492
O		^{17}O (0.04)	16.99913
O		^{18}O (0.20)	17.99916

Problem 7(p. 114) – Radical cations of the following molecules (e- + M → M+ + 2e-) will fragment to yield the indicated masses as major peaks. The molecular ion peak is given under each structure. The base peak is listed as 100%. Other values listed represent some relatively stable possibilities (hence higher relative abundance), or common fragmentations (expected), even if in low amount. Explain 'logical' peaks (alkyl fragments, pi bond, functional group and heteroatom fragments). This may be as easy as drawing a line between two atoms of a bond, or it may require drawing curved arrows to show how electrons move (e.g. McLafferty). This may also involve drawing resonance structures or indicating special substitution patterns ($3^o R^+ > 2^oR^+ > 1^oR^+ > CH_3^+$). If a fragment has an even mass and there is a pi bond, think McLafferty (unless an odd number of nitrogen atoms are present). Even masses can also be formed by elimination of a small molecule such as loss of water from an alcohol or loss of an alcohol from an ether or a retro-Diels-Alder reaction, etc. Make sure you show this. Some fragments may be an extension of a logical fragment by units of 14 amu (CH_2).

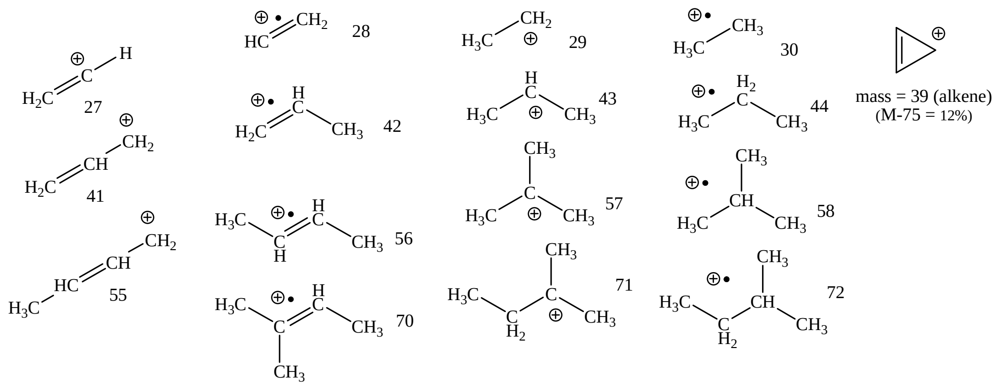
a.



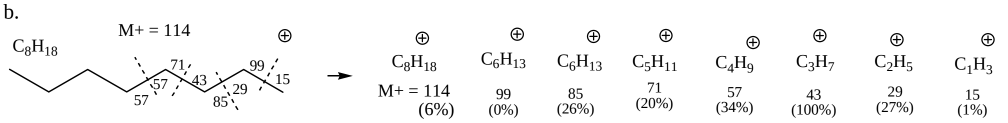
$M^+ = 86$

m/e	% base
27	17
28	3
29	34
30	1
39	14
41	49
42	6
43	**100**
44	3
55	11
56	28
57	98
58	5
70	3
71	77
72	4
86	<1

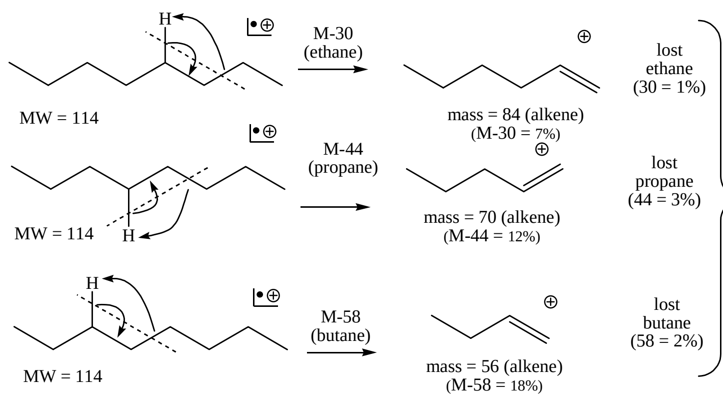
The base peak is not logical from the starting skeleton.



b.



octane - all expected alkane fragments are observed, except 99 (M-15).

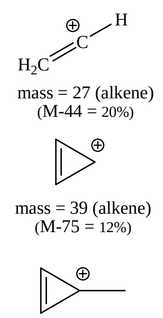


Possible elimination reactions forming alkenes. All are observed in the actual MS of octane.

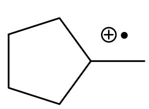
Further alkene fragments (see next functional group)

allylic fragmentation	Alkene & McLafferty fragmentation
41 = 44%	28 = 4%
55 = 11%	42 = 15%
69 = 2 %	56 = 18%
	70 = 12%
	84 = 7%

mass	%
27	20
28	4
29	27
30	1
39	12
41	44
42	15
43	**100** ← base
53	2
55	11
56	18
57	34
69	2
70	12
71	20
84	7
85	26
114	6 ← M+

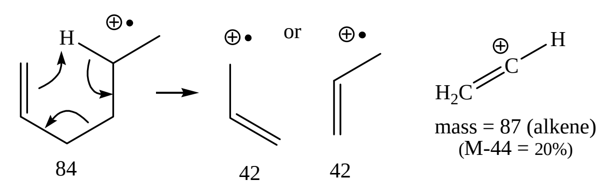


c.

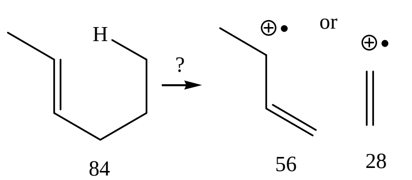


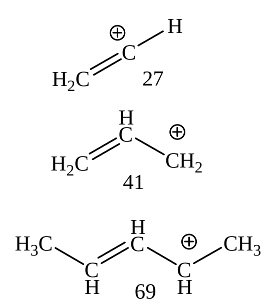
$M^+ = 84$

m/e	% base
27	10
41	50
42	25
43	11
56	**100** ← base
69	35
84	18

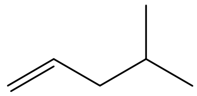


No easy explanation for 56, but if ring opens and forms alkene, McLafferty might work.





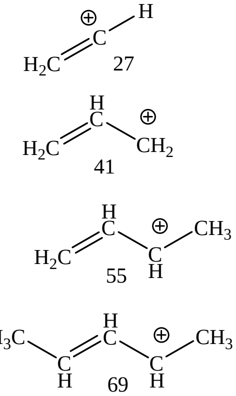
d.

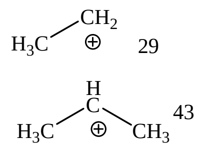


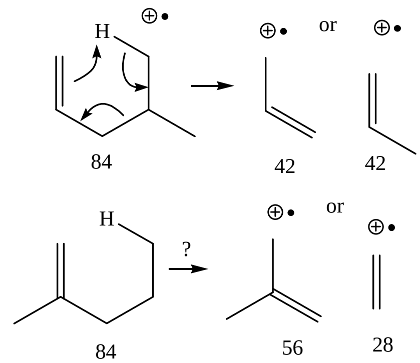
$M^+ = 84$

m/e	% base
27	21
41	68
42	31
43	**100** ← base
55	9
56	50
69	17
70	1
84	12

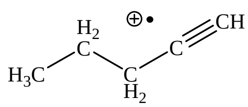
You might have to move the C=C around to get 56.





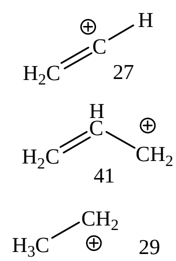


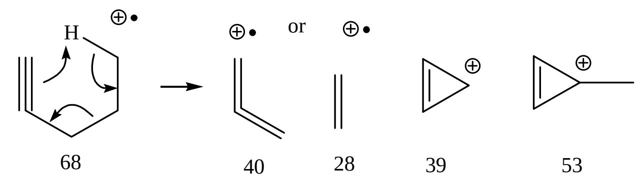
e.

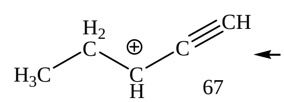


$M^+ = 68$

m/e	% base
27	33
29	24
39	55
40	61
41	23
42	22
53	44
67	**100** ← base
68	15

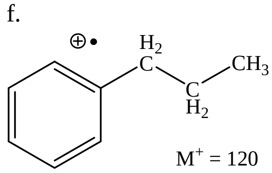




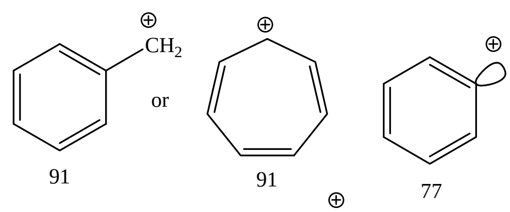


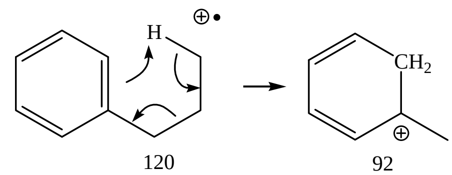
Don't remove the sp C-H, there is a better spot to lose an H atom (resonance).

f.

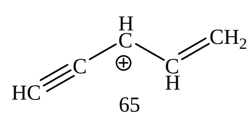


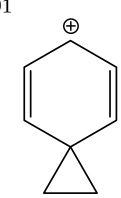
$M^+ = 120$





m/e	% base
65	7
77	3
91	**100** ← base
92	11
105	4
120	26

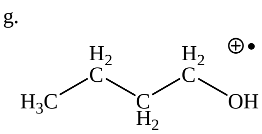




105

Use a bridging ring to make 105 and 91 is easy.

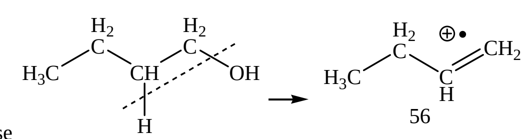
g.

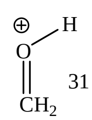


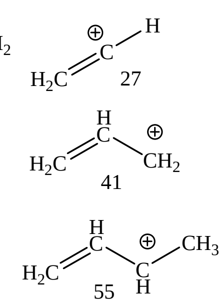
$M^+ = 74$

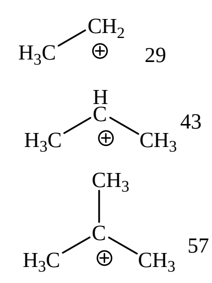
56 is an even mass, but not McLafferty. A small molecule might help explain it.

m/e	% base
27	33
29	16
31	83
41	66
42	32
43	59
55	14
56	**100** ← base
57	6
74	<1

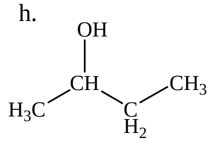








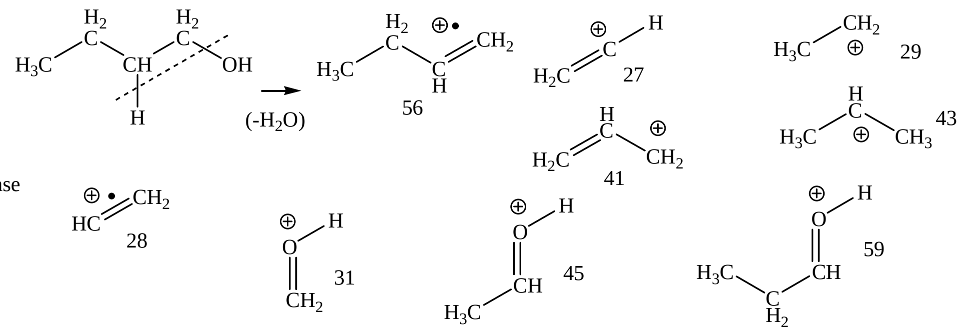
h.



$M^+ = 74$

m/e	% base
27	10
28	52
29	6
31	17
41	12
43	9
45	**100** ← base
56	2
59	20
74	<1

Peak 31 is harder to explain, but common.



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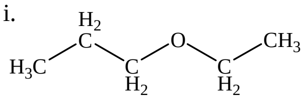
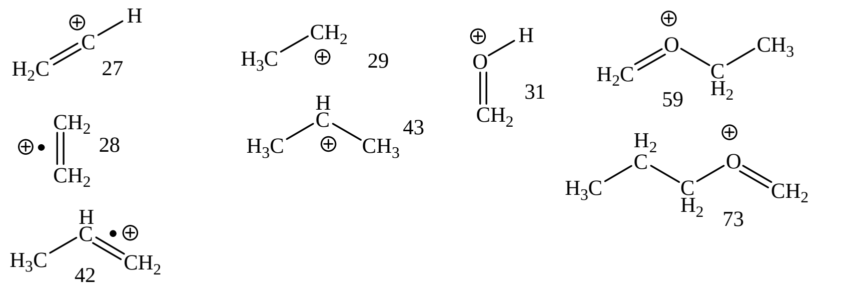
i.



$M^+ = 88$

28 and 42 are even, but not McLafferty. Think like "g", but "organic" water. 31 requires some drastic rearrangements.

m/e	% base
27	23
28	8
29	35
31	**100**
42	4
43	40
59	98
73	3
88	26



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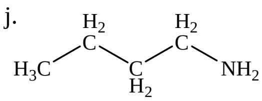
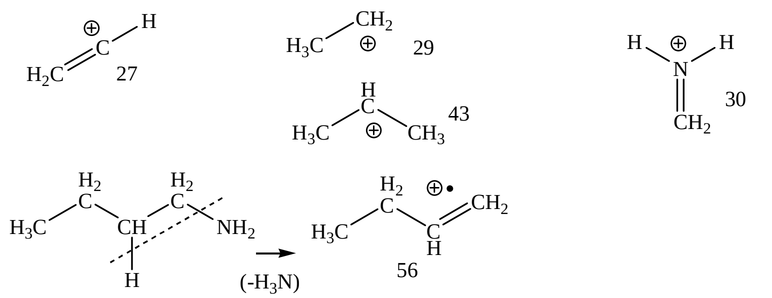
j.



$M^+ = 73$

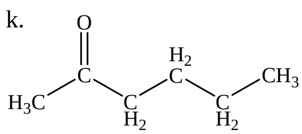
Peak 30 dominates. Think of a small molecule elimination for peak 56.

m/e	% base
27	3
29	2
30	**100** ← base
43	1
56	1
73	7



---

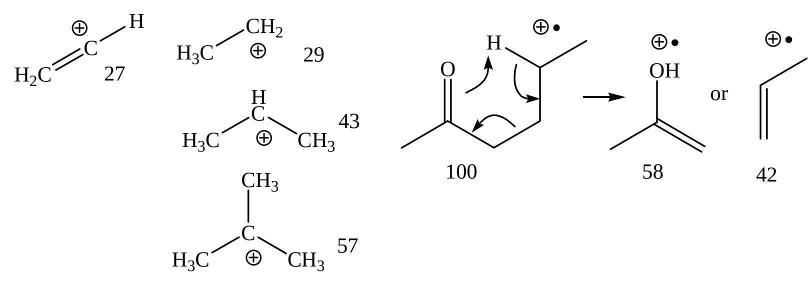
k.

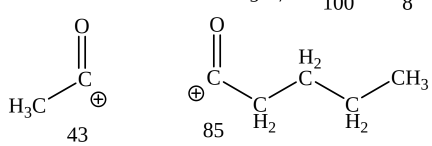


$M^+ = 100$

43 can be different than $C_3H_7^+$

m/e	% base
27	8
29	15
43	100 ← base
57	16
58	50
85	6
100	8





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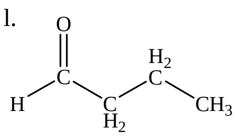
l.

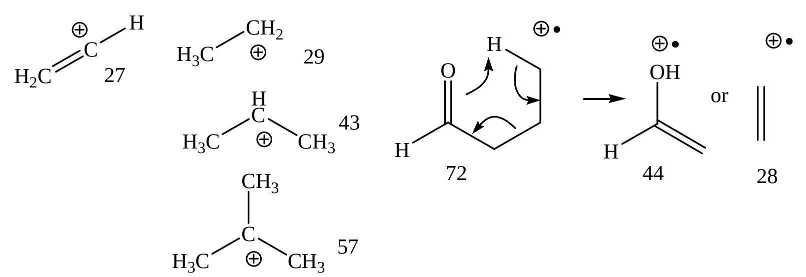


$M^+ = 72$

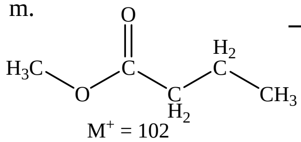
29 can be different than $C_2H_5^+$

44 is an even mass, so...

m/e	% base
27	74
29	55
41	69
43	75
44	**100** ← base
57	23
72	54



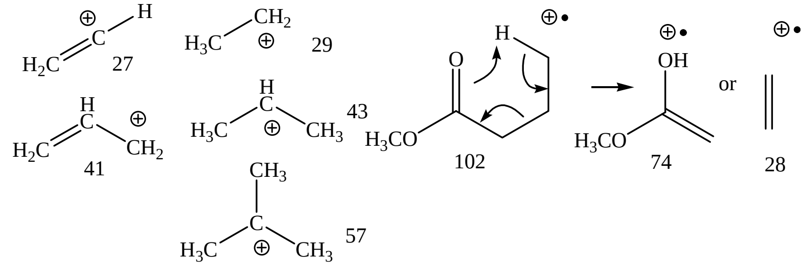
m.

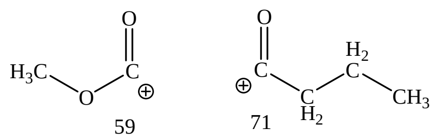


$M^+ = 102$

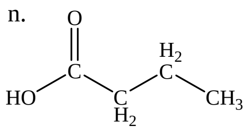
m/e	% base
27	47
29	9
41	45
43	**100** ← **base**
59	22
71	50
74	64
87	16
102	1

74 is an even mass.





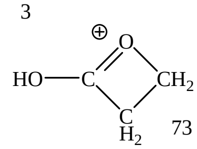
n.

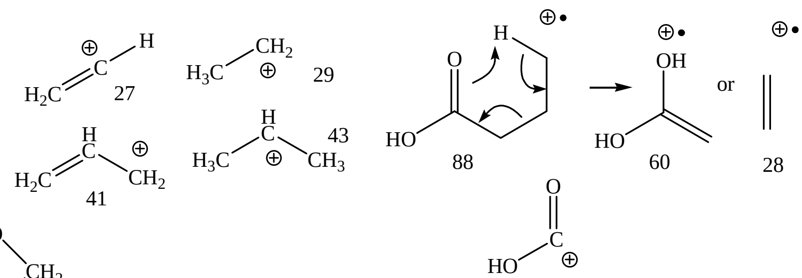


$M^+ = 88$

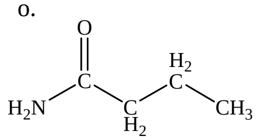
An even mass strikes again at 60. 45 is not common, but expected here.

m/e	% base
27	14
29	8
41	16
43	14
45	10
60	**100** ← **base**
73	32
88	3





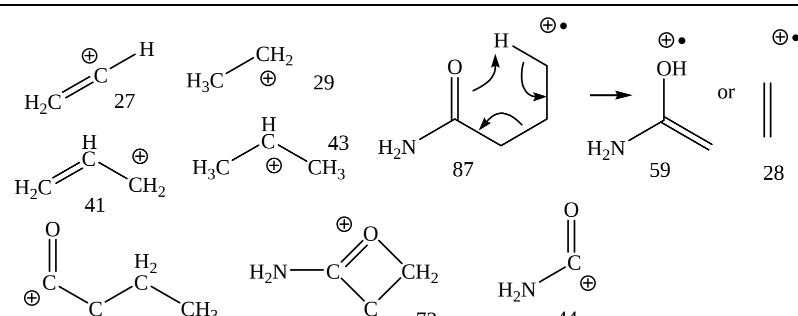
o.



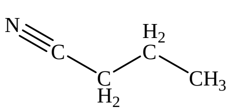
$M^+ = 87$

Normally 59 would be e ven, but there is nitrogen present.

m/e	% base
27	27
29	26
41	53
43	32
44	66
59	**100** ← **base**
71	8
72	19
87	3



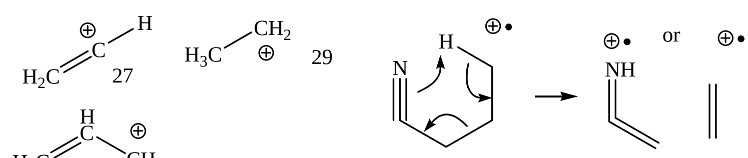
p.



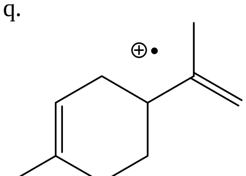
$M^+ = 69$

Normally 41 would be even, but there is nitrogen present (M-28).

m/e	% base
27	29
29	66
40	4
41	**100** ← **base**
42	4
54	1
69	<1



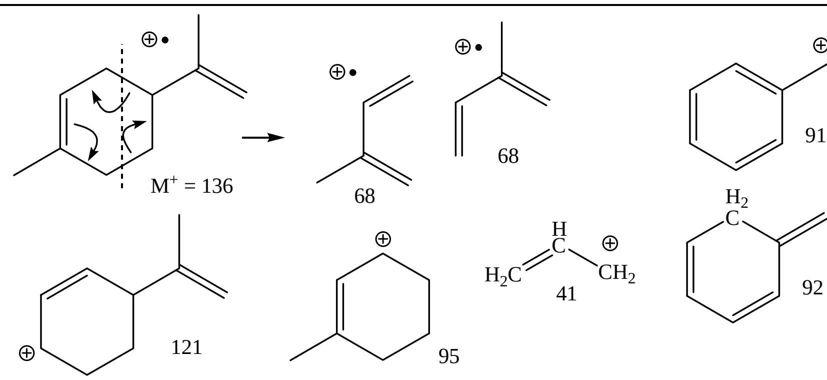
q.



$M^+ = 136$

m/e	% base
2	9
41	19
68	100 ← **base**
91	13
92	19
95	8
121	20
136	23

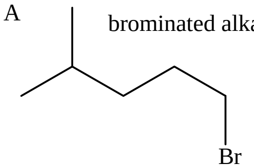
Two famous names goes with 68.



Problem 8 (p. 117)– On the following pages are 11 compounds (these are lettered A-K) from the 11 functional groups numbered below. Try to match each spectrum (A-K) to the class of functional group numbered 1-11, and then try to solve the exact structure of each compound. These are simple monofunctional group compounds. Use the IR data to help identify the functional groups. Explain the major peaks that helped decide on your structure. Why are these peaks formed in preference to others (what is the reason for their special stability)? This problem would be a lot easier if NMRs were available.

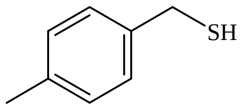
Classes of compounds (IR and MS clues)

A brominated alkane



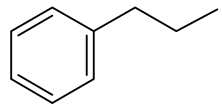
4-methyl-1-bromopentane
MW = 164

B thiol



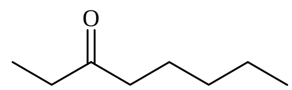
p-thiomethyltoluene
MW = 138

C aromatic



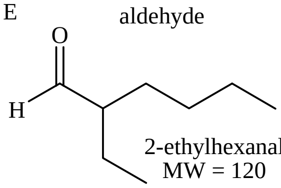
propylbenzene
MW = 120

D ketone



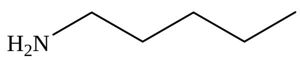
octan-3-one
MW = 120

E aldehyde



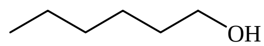
2-ethylhexanal
MW = 120

F amine



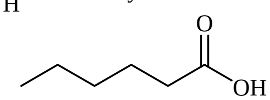
pentylamine
MW = 87

G alcohol



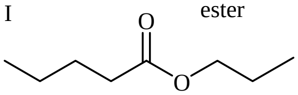
hexan-1-ol
MW = 102

H carboxylic acid



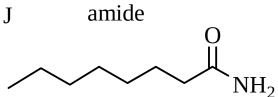
hexanoic acid
MW = 144

I ester



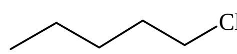
propyl pentanoate
MW = 144

J amide



heptanamide
MW = 143

K chlorinated alkane

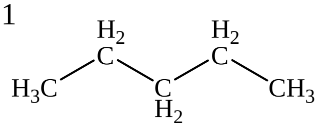


1-chloropentane
MW = 106

Chapter 4 – NMR

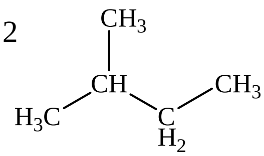
Problem 1 – (p. 146): How many different protons and carbons are in each of the C_5H_{12} isomers and $C_5H_{11}Br$ isomers?

There are three C_5H_{12} isomers

1


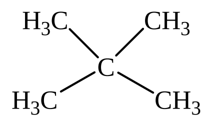
#H = 3

#C = 3

2


#H = 4

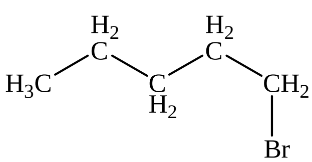
#C = 4

3


#H = 1

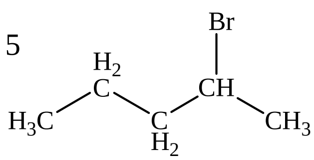
#C = 2

There are eight $C_5H_{11}Br$ isomers

4


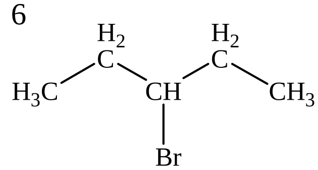
#H = 5

#C = 5

5


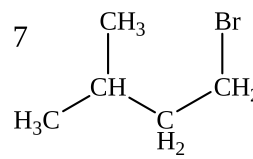
#H = 7

#C = 5

6


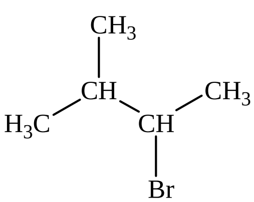
#H = 4

#C = 3

7


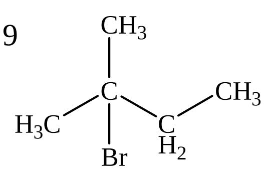
#H = 4

#C = 4

8


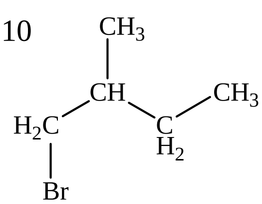
#H = 5

#C = 5

9


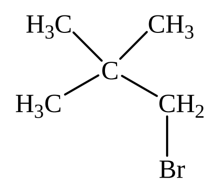
#H = 3

#C = 4

10


#H = 7

#C = 5

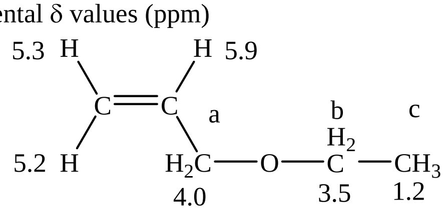
11


#H = 2

#C = 3

Problem 2 (p. 149)– Use the table to estimate the chemical shifts of each type of sp^3 C-H in the structures below.

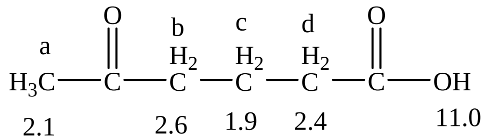
a.experimental δ values (ppm)



Only sp^3 C-H calculations shown here.

	a	b	c	
	1.2	1.2	0.9	
	0.8 (α)	0.1 (γ)	0.0 (–)	alkene
	2.1 (α)	2.1 (α)	0.3 (β)	ether "O"
calculated sp^3 C-H δ values (ppm) =	4.1	3.4	1.2	

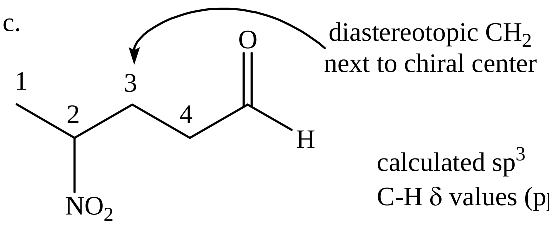
b.



Only sp^3 C-H calculations shown here.

	a	b	c	d	
calculated sp^3	0.9	1.2	1.2	1.2	
	1.2 (α)	1.2 (α)	0.3 (β)	0.0 (γ)	ketone
	0.0 (–)	0.1 (γ)	0.3 (β)	1.1 (α)	acid
C-H δ values (ppm) =	2.1	2.5	1.8	2.3	

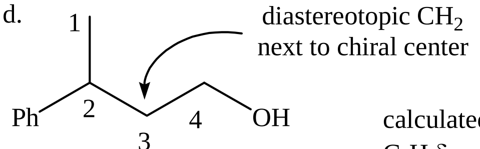
c.



Only sp^3 C-H calculations shown here.

	1	2	3a	3b	4	
calculated sp^3	0.9	1.2	1.2	1.2	1.2	
	0.8 (β)	3.2 (α)	0.8(β)	0.8(β)	0.1 (γ)	nitro
	0.0 (–)	0.1 (γ)	0.4 (β)	0.4 (β)	1.1 (α)	aldehyde
C-H δ values (ppm) =	1.7	4.5	2.4	2.4	2.4	
				-0.3		
				2.1		

d.

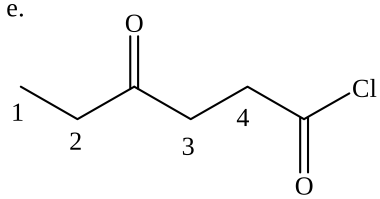


Ph = phenyl = aromatic

Only sp^3 C-H calculations shown here.

	1	2	3a	3b	4	
calculated sp^3	0.9	1.2	1.2	1.2	1.2	
	0.4 (β)	1.4 (α)	0.4 (β)	0.4 (β)	0.1 (γ)	aromatic
	0.0 (–)	0.1 (γ)	0.3 (β)	0.3 (β)	2.3 (α)	alcohol
C-H δ values (ppm) =	1.3	2.7	1.9	1.9	3.6	
				-0.3		
				1.6		

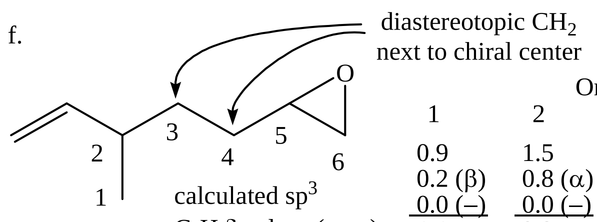
e.



Only sp^3 C-H calculations shown here.

	1	2	3	4	
calculated sp^3	0.9	1.2	1.2	1.2	
	0.4 (β)	1.2 (α)	1.2 (α)	0.4 (β)	ketone
	0.0 (–)	0.0 (–)	0.4 (β)	1.8 (α)	acid chloride
C-H δ values (ppm) =	1.3	2.4	2.8	3.4	

f.

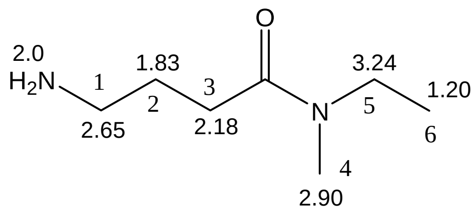


Only sp^3 C-H calculations shown here.

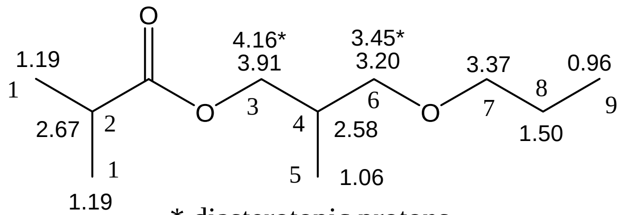
	1	2	3a	3b	4a	4b	5	6	
calculated sp^3	0.9	1.5	1.2	1.2	1.2	1.2	1.5	1.2	
	0.2 (β)	0.8 (α)	0.2 (β)	0.2 (β)	0.1 (γ)	0.1 (γ)	0.0 (–)	0.0 (–)	alkene
	0.0 (–)	0.0 (–)	0.1 (γ)	0.1 (γ)	0.4 (β)	0.4 (β)	1.5 (α)	1.5 (α)	epoxide
C-H δ values (ppm) =	1.1	2.3	1.5	1.5	1.7	1.7	3.0	2.7	
				-0.3		-0.3			
				1.2		1.4			

Additional Problems - Compare your calculated shifts to the chemical shifts values from ChemDraw

g.

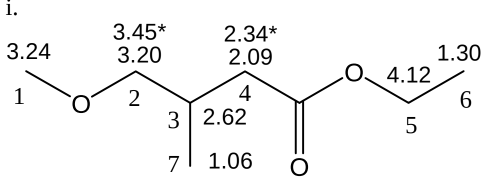


h.



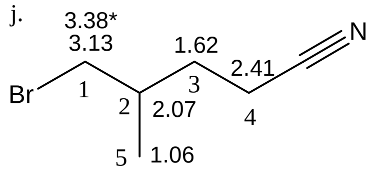
* diasterotopic protons

i.



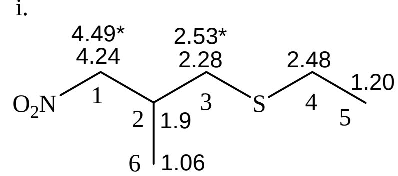
* diasterotopic protons

j.



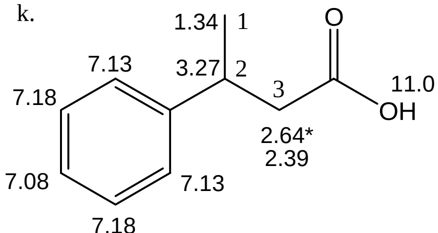
* diasterotopic protons

i.



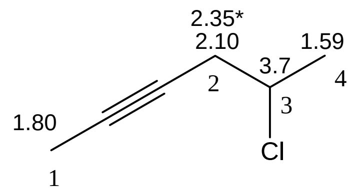
* diasterotopic protons

k.



* diasterotopic protons

l.

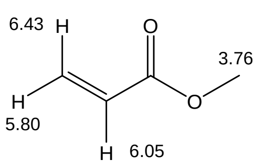


* diasterotopic protons

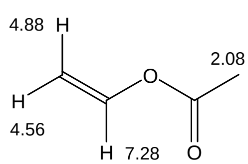
Not all diastereotopic protons next to a chiral center have different chemical shifts. In example 'h' both protons at 1.62 have the same chemical shift, while on the other side of the chiral center there are different chemical shifts.

Problem 3 (p. 153)– Calculate chemical shifts for the following alkene and aromatic sp^2 protons (and compare to the values given).

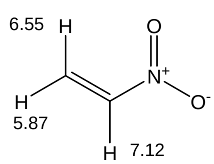
a



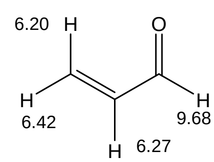
b



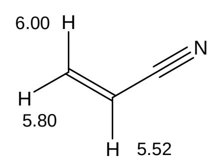
c



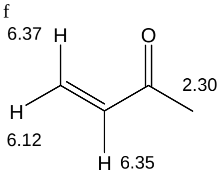
d



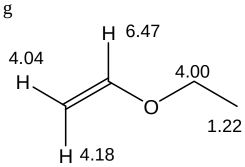
e



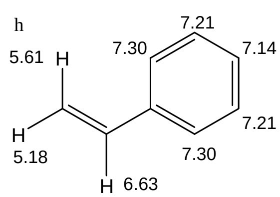
f



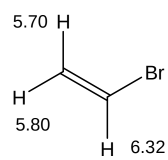
g



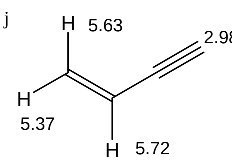
h



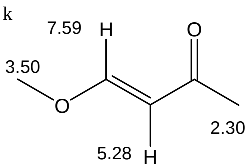
i



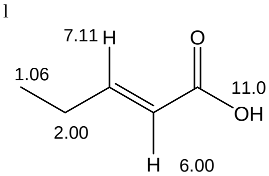
j



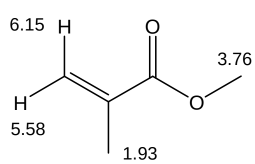
k



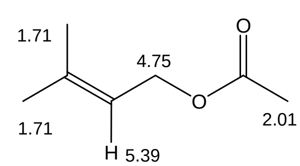
l

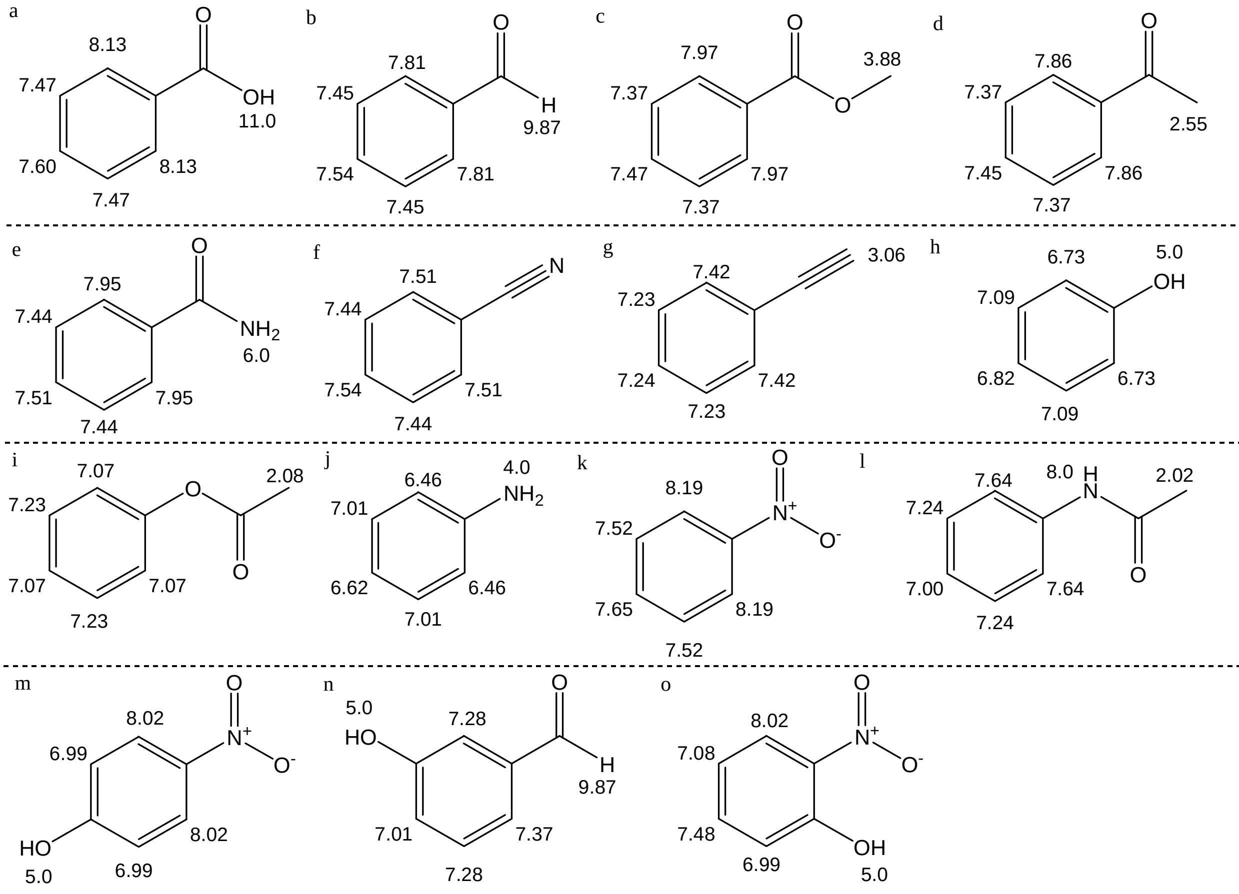


m



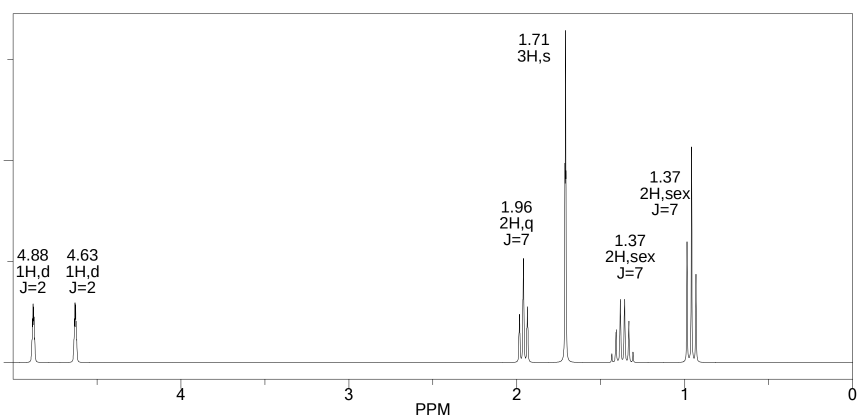
n

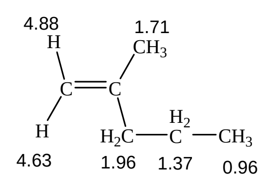




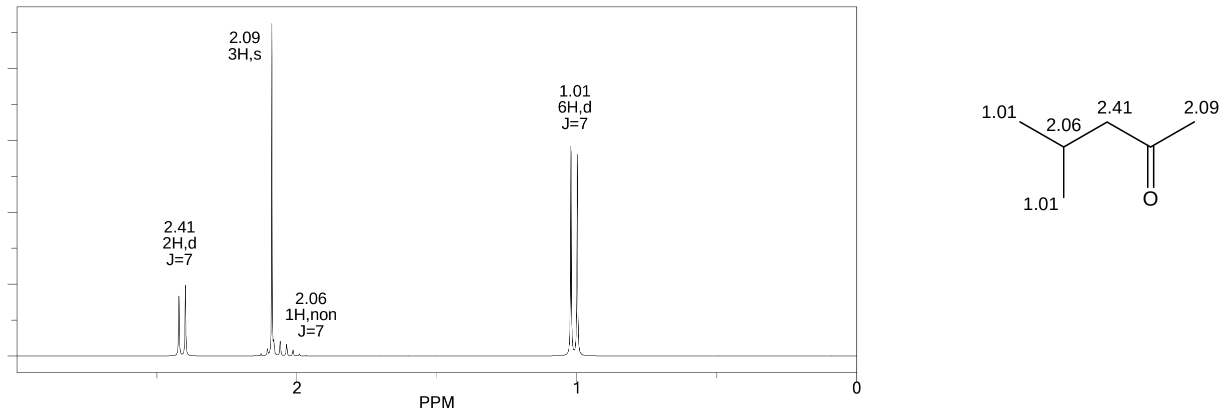
Problem 4 (p. 178)- Predict approximate NMR's for the following compounds. Draw a sketch of your predicted NMR. Include calculations of ^{1}H chemical shifts, estimates of coupling constants and multiplicities as well as the number of hydrogen atoms to be integrated at each chemical shift (by writing the appropriate number of hydrogen atoms above the multiplet). Assume ^{4}J (or higher) = 0 Hz. Actual chemical shifts are written by each type of hydrogen.

a

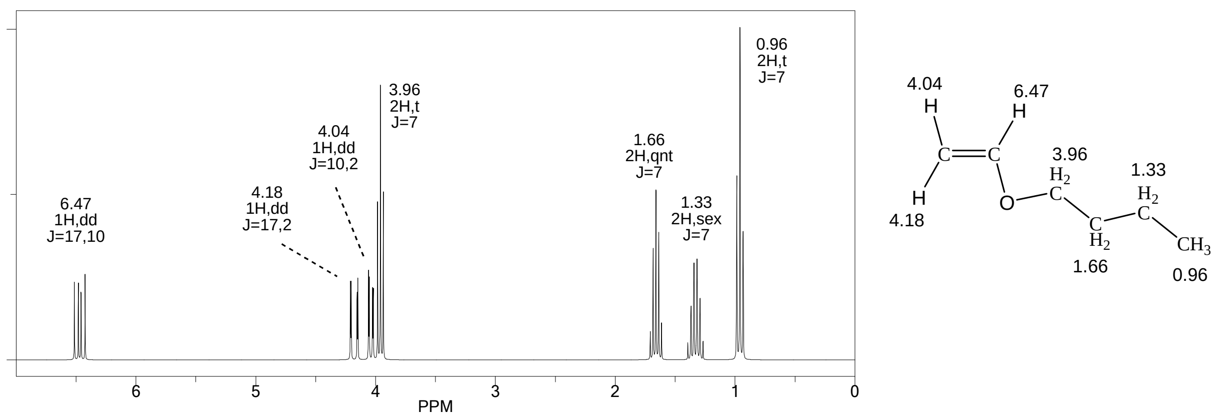




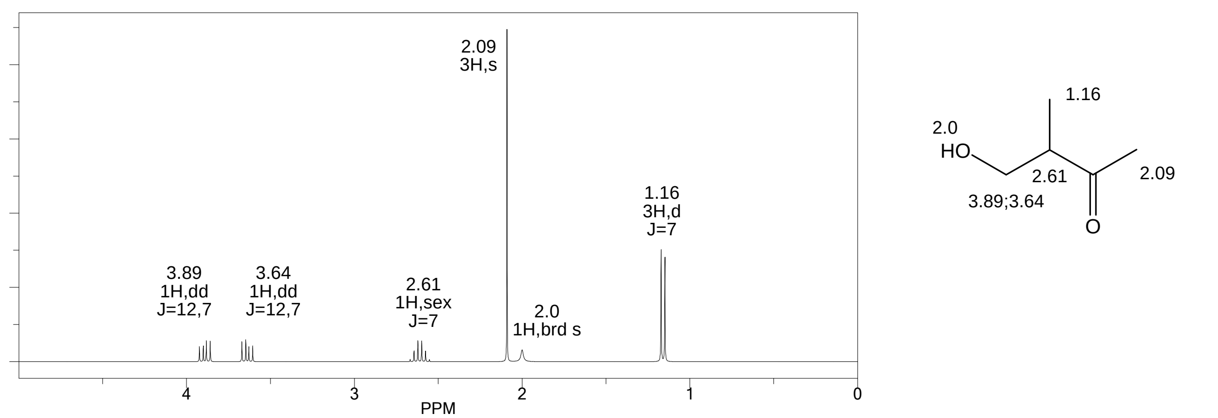
b


2.09
3H,s
1.01
6H,d
J=7
2.41
2H,d
J=7
2.06
1H,non
J=7
2
1
0
PPM
1.01
2.06
2.41
2.09
1.01
O

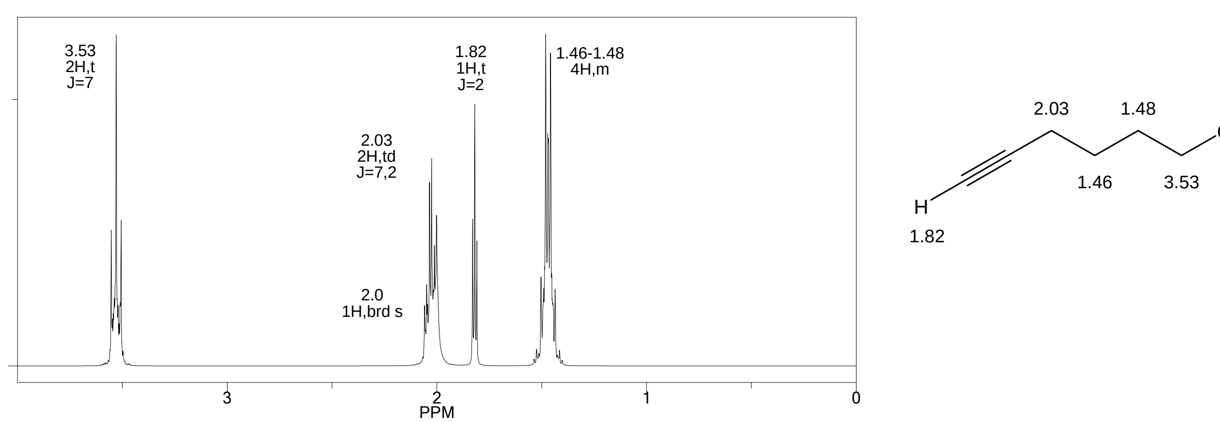
c


0.96
2H,t
J=7
3.96
2H,t
J=7
4.04
1H,dd
J=10,2
1.66
2H,qnt
J=7
4.18
1H,dd
J=17,2
1.33
2H,sex
J=7
6.47
1H,dd
J=17,10
6
5
4
3
2
1
0
PPM
4.04
H
6.47
H
C
C
3.96
H_2
1.33
H_2
H
4.18
O
C
C
C
CH_3
H_2
1.66
0.96

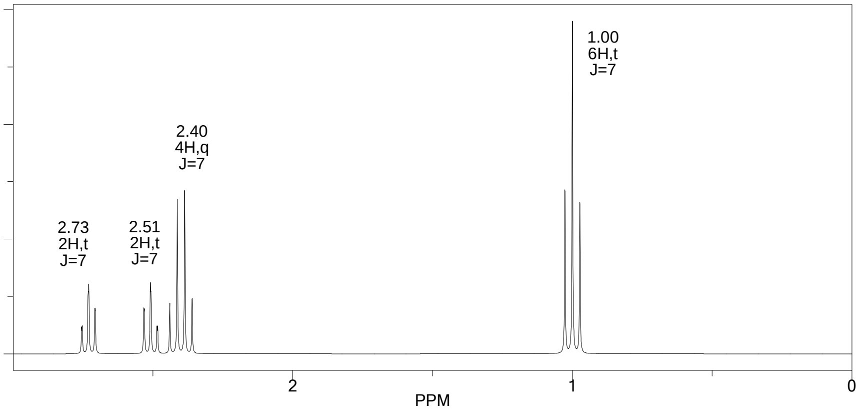
d

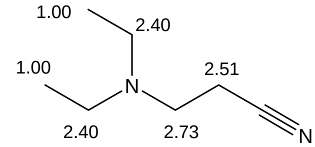

2.09
3H,s
1.16
3H,d
J=7
3.89
1H,dd
J=12,7
3.64
1H,dd
J=12,7
2.61
1H,sex
J=7
2.0
1H,brd s
4
3
2
1
0
PPM
1.16
2.0
HO
2.61
2.09
3.89;3.64
O

e

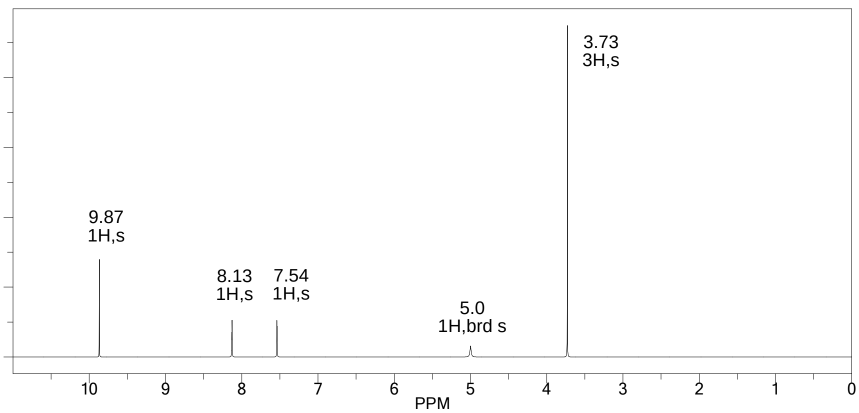

3.53
2H,t
J=7
1.82
1H,t
J=2
1.46-1.48
4H,m
2.03
2H,td
J=7,2
2.0
1H,brd s
3
2
1
0
PPM
2.03
1.48
2.0
OH
1.46
3.53
H
1.82

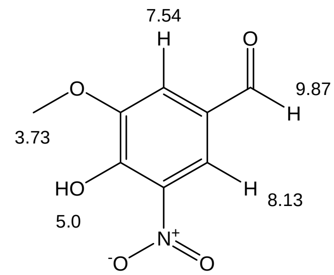
f


1.00
6H,t
J=7
2.40
4H,q
J=7
2.73
2H,t
J=7
2.51
2H,t
J=7
2
1
0
PPM

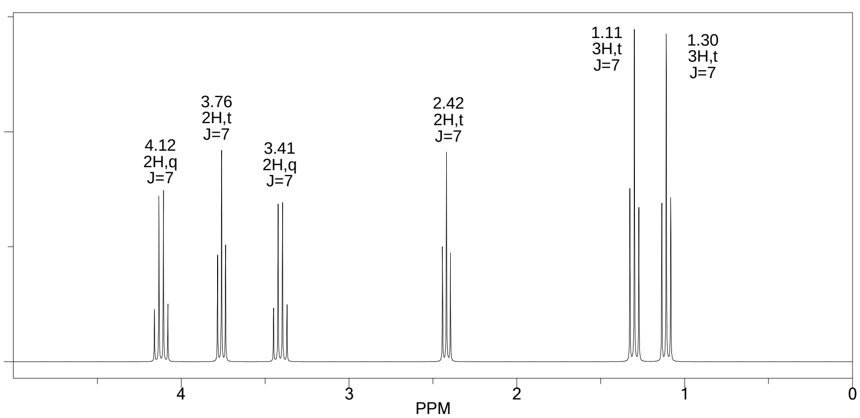

1.00
2.40
1.00
2.51
N
2.40
2.73
N

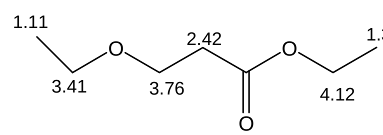
g


3.73
3H,s
9.87
1H,s
8.13
1H,s
7.54
1H,s
5.0
1H,brd s
10
9
8
7
6
5
4
3
2
1
0
PPM

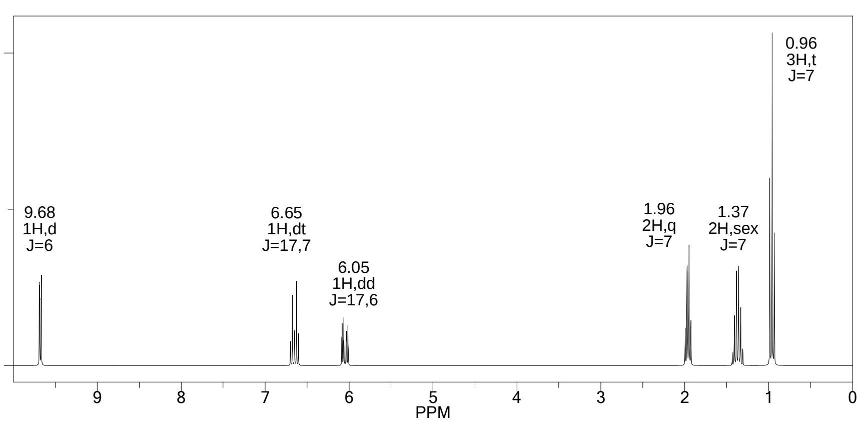

7.54
H
O
O
9.87
H
3.73
HO
H
8.13
5.0
N+
-O
O

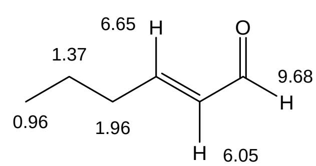
h


1.11
3H,t
J=7
1.30
3H,t
J=7
3.76
2H,t
J=7
2.42
2H,t
J=7
4.12
2H,q
J=7
3.41
2H,q
J=7
4
3
2
1
0
PPM

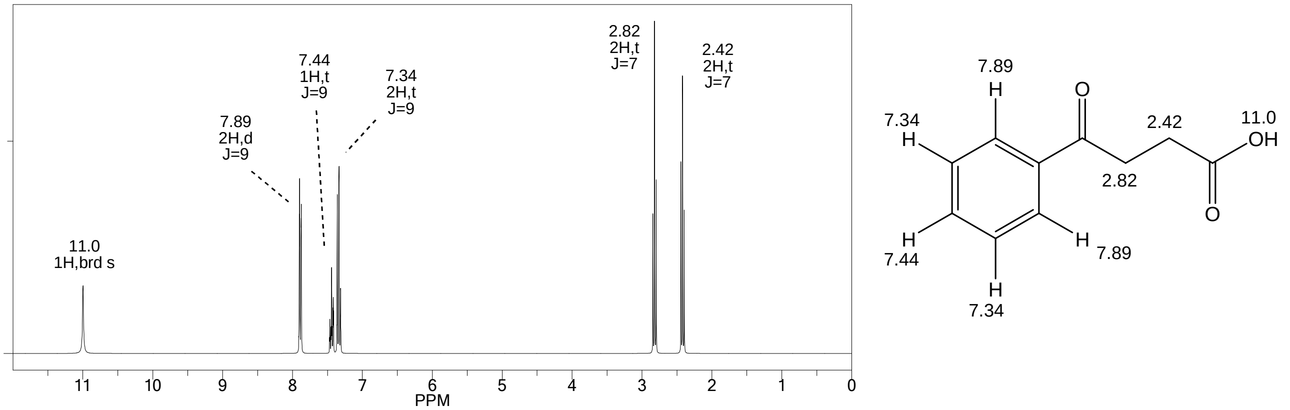

1.11
O
2.42
O
1.30
3.41
3.76
4.12
O

i


0.96
3H,t
J=7
9.68
1H,d
J=6
6.65
1H,dt
J=17,7
6.05
1H,dd
J=17,6
1.96
2H,q
J=7
1.37
2H,sex
J=7
9
8
7
6
5
4
3
2
1
0
PPM

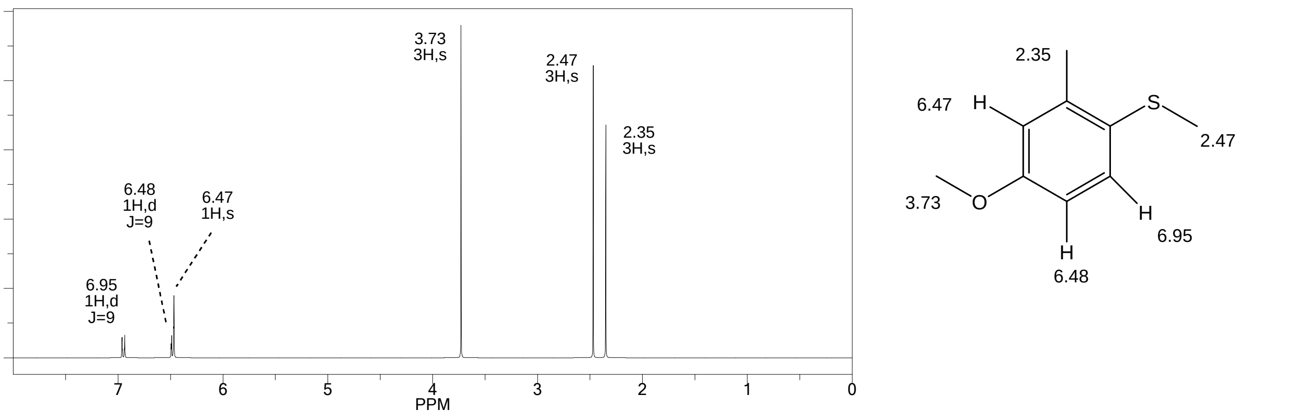

6.65
H
O
1.37
9.68
H
0.96
1.96
H
6.05

j



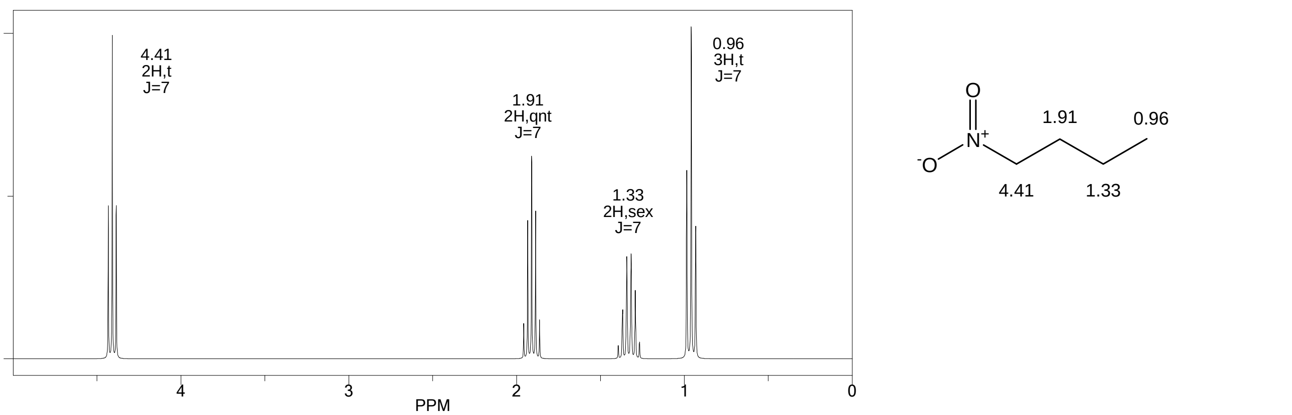
11.0
1H,brd s
7.89
2H,d
J=9
7.44
1H,t
J=9
7.34
2H,t
J=9
2.82
2H,t
J=7
2.42
2H,t
J=7
PPM
7.89
7.34
7.44
7.89
7.34
2.42
2.82
11.0
OH

k



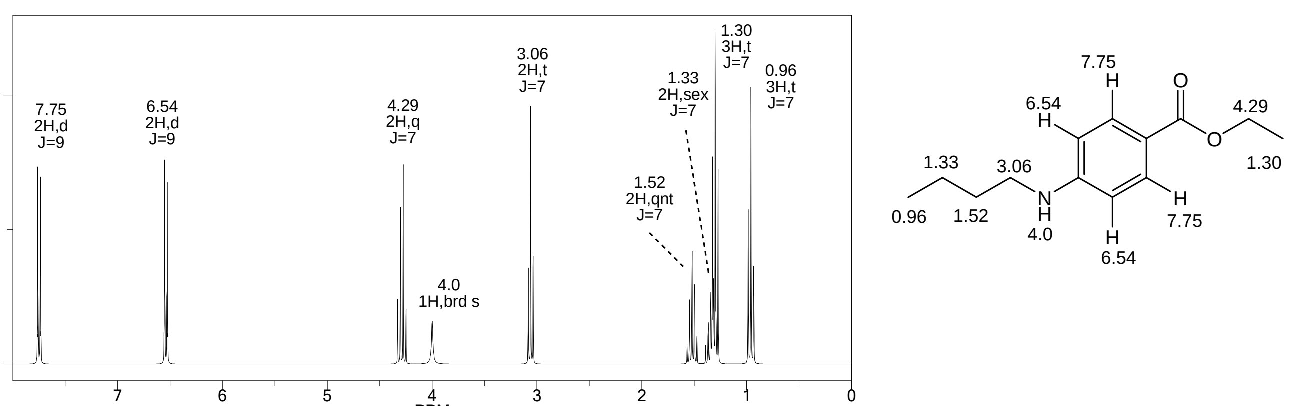
6.95
1H,d
J=9
6.48
1H,d
J=9
6.47
1H,s
3.73
3H,s
2.47
3H,s
2.35
3H,s
PPM
2.35
6.47
2.47
3.73
6.95
6.48

l



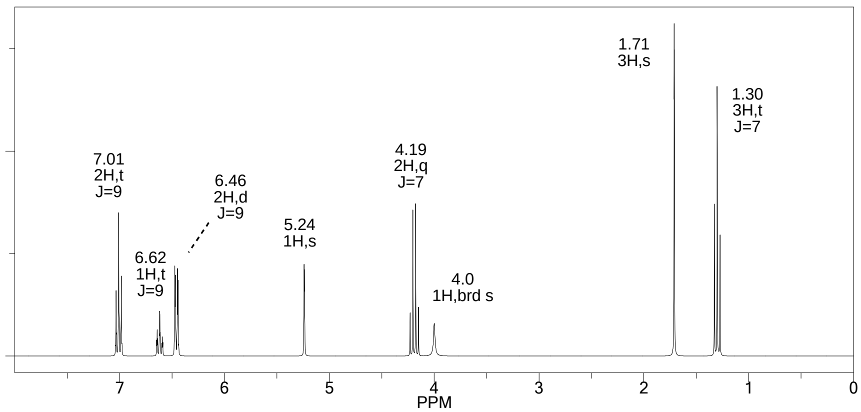
4.41
2H,t
J=7
1.91
2H,qnt
J=7
1.33
2H,sex
J=7
0.96
3H,t
J=7
PPM
1.91
0.96
4.41
1.33

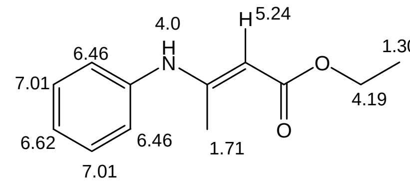
m.



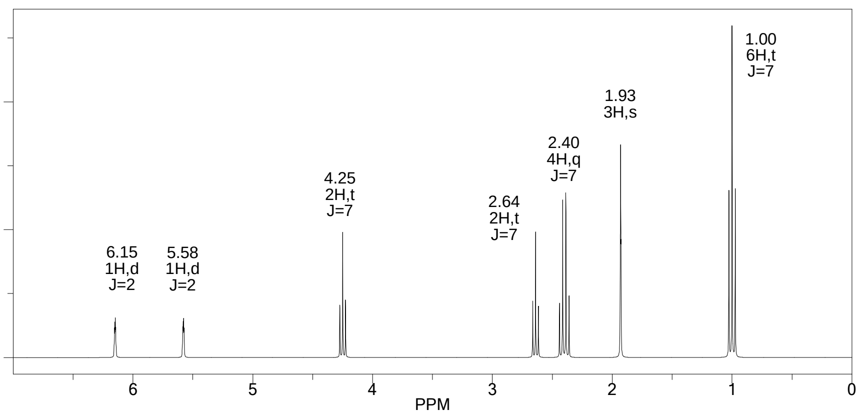
7.75
2H,d
J=9
6.54
2H,d
J=9
4.29
2H,q
J=7
4.0
1H,brd s
3.06
2H,t
J=7
1.52
2H,qnt
J=7
1.33
2H,sex
J=7
1.30
3H,t
J=7
0.96
3H,t
J=7
PPM
7.75
6.54
4.29
1.30
1.33
3.06
0.96
1.52
4.0
7.75
6.54

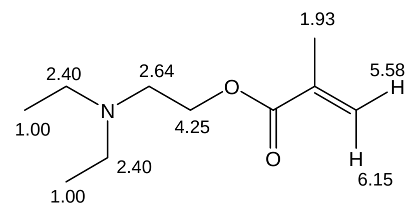
n.





o.



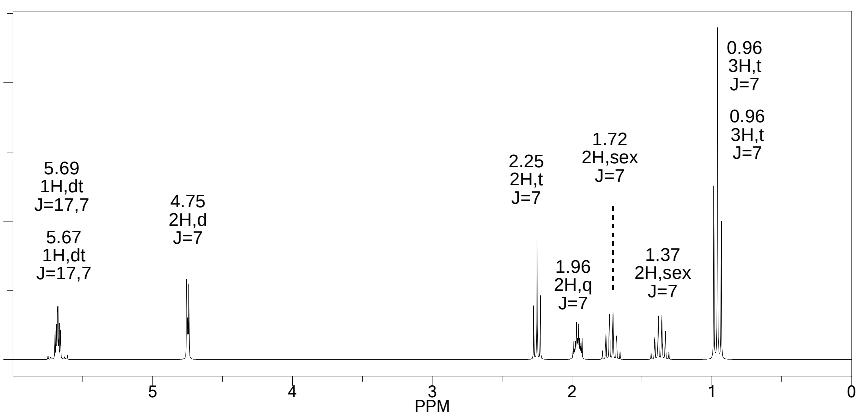


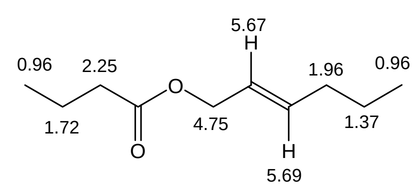
real J values

J_{allyl} = 1.0 Hz (not included)

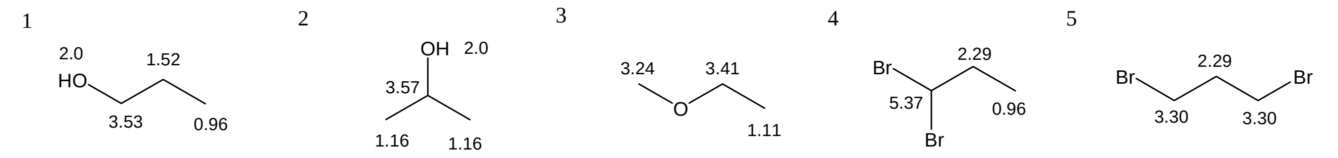
J_{gem} = 1.6 Hz

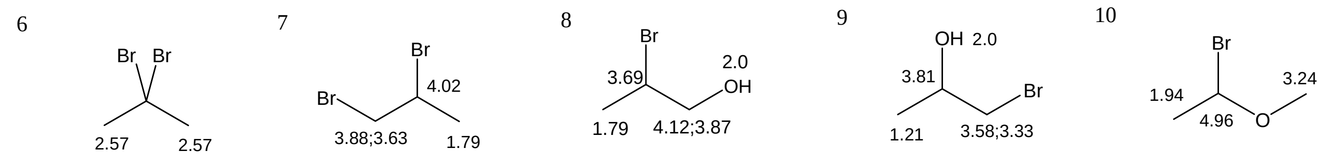
p.



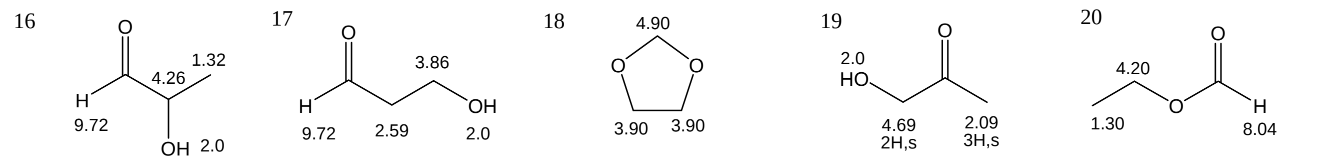


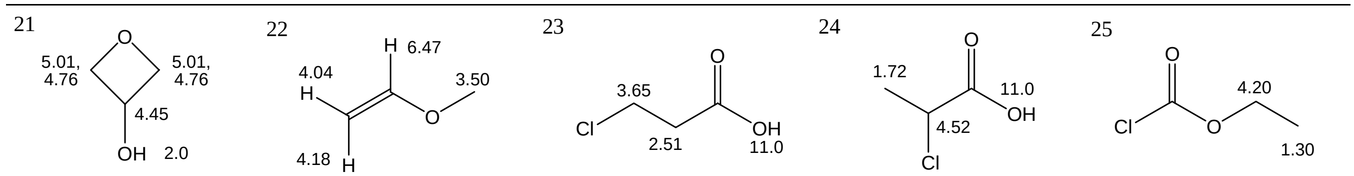
Problem 5 (p. 183)– (^{1}H NMR) – A large number of fairly straight forward 'predict the product' H NMR problems are listed below. Some are really easy and some are a bit more challenging. Use the molecular formulas along with the chemical shifts, multiplicities and integrations to determine a reasonable structure for the following molecules. Approximate coupling constants are indicated. The multiplicities are s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, sex = sextet, se = septet, o = octet, n = nonet, m = multiplet. The degree of unsaturation can help determine the possible number of rings and/or pi bonds. Match each type of hydrogen in the problems with the hydrogen atoms in your structures. Several C NMR problems follow. Propose reasonable structures.

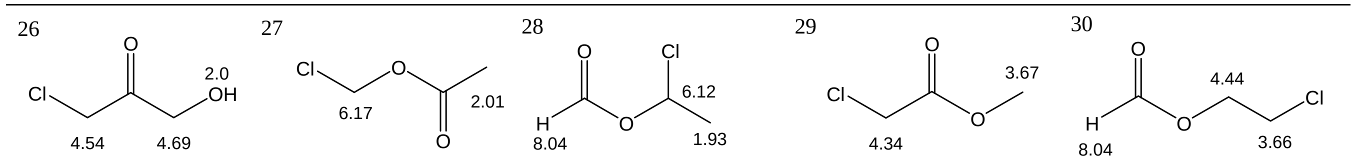

1
2.0
HO
1.52
3.53
0.96
2
OH 2.0
3.57
1.16
1.16
3
3.24
3.41
O
1.11
4
Br
2.29
5.37
0.96
Br
5
Br
2.29
Br
3.30
3.30


6
Br Br
2.57
2.57
7
Br
4.02
Br
3.88;3.63
1.79
8
Br
3.69
2.0
OH
1.79
4.12;3.87
9
OH 2.0
3.81
Br
1.21
3.58;3.33
10
Br
3.24
1.94
4.96
O


11
3.87
3.24
Br
3.47
O
12
Br
O
1.11
5.38
3.41
13
1.98
2.0
Br
OH
3.30
3.53
14
O
3.67
O
2.01
15
O
1.09
11.0
HO
2.27


16
O
1.32
4.26
H
9.72
OH 2.0
17
O
3.86
H
OH
9.72
2.59
2.0
18
4.90
O
O
3.90
3.90
19
O
2.0
HO
4.69
2H,s
2.09
3H,s
20
O
4.20
O
H
1.30
8.04


21
O
5.01,
4.76
5.01,
4.76
4.45
OH 2.0
22
H 6.47
4.04
H
3.50
O
4.18 H
23
O
3.65
Cl
OH
2.51
11.0
24
O
1.72
11.0
OH
4.52
Cl
25
O
4.20
Cl
O
1.30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O
2.0
Cl
OH
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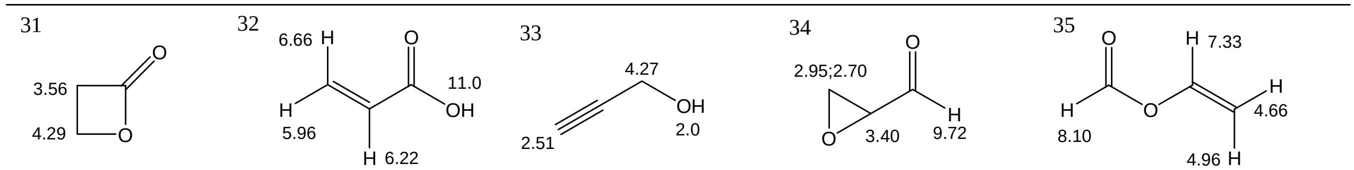
4.69
27
Cl
O
6.17
2.01
O
28
O
Cl
6.12
H
O
8.04
1.93
29
O
3.67
Cl
O
4.34
30
O
4.44
Cl
H
O
8.04
3.66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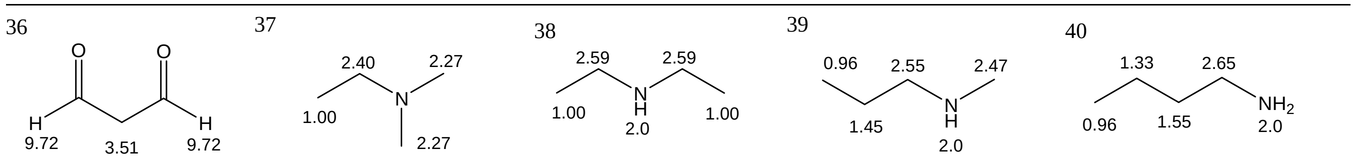
O
3.56
4.29
O
32
6.66 H
O
11.0
H
OH
5.96
H 6.22
33
4.27
OH
2.0
2.51
34
O
2.95;2.70
H
O
3.40
9.72
35
O
H 7.33
H
H
O
4.66
8.10
4.96 H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O
H
H
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9.72
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2.27
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1.00
2.27
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2.59
2.59
N
H
1.00
1.00
2.0
39
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2.65
NH2
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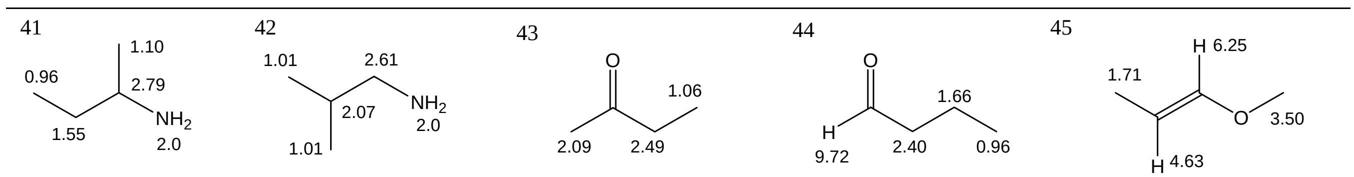
1.55
2.0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NH2
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1.01
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NH2
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2.0
1.01
43
O
1.06
2.09
2.49
44
O
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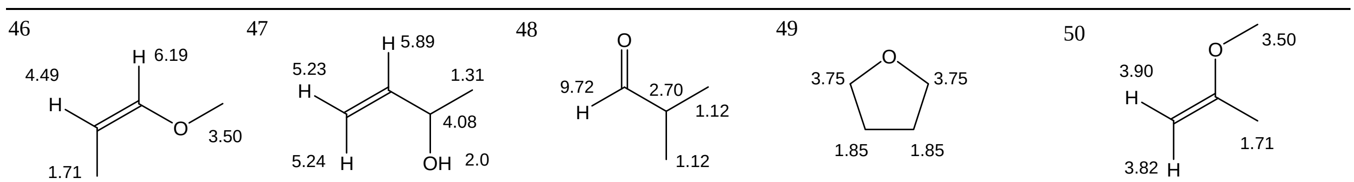
H
9.72
2.40
0.96
45
H 6.25
1.71
O
3.50
H 4.63


46
H 6.19
4.49
H
O
3.50
1.71
47
H 5.89
5.23
H
1.31
4.08
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OH 2.0
48
O
9.72
2.70
H
1.12
1.12
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1.85
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H
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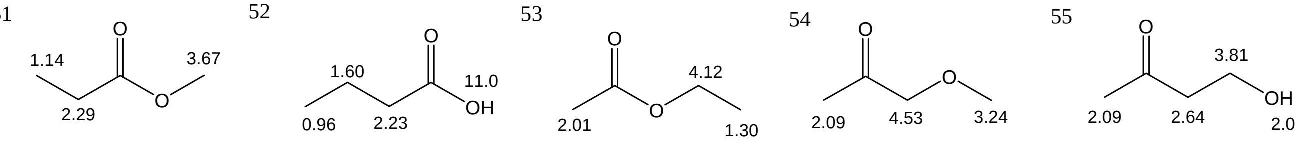

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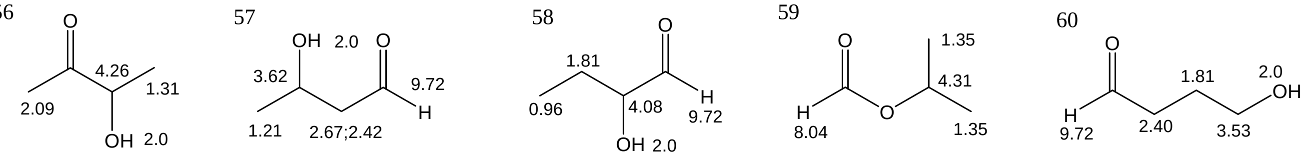

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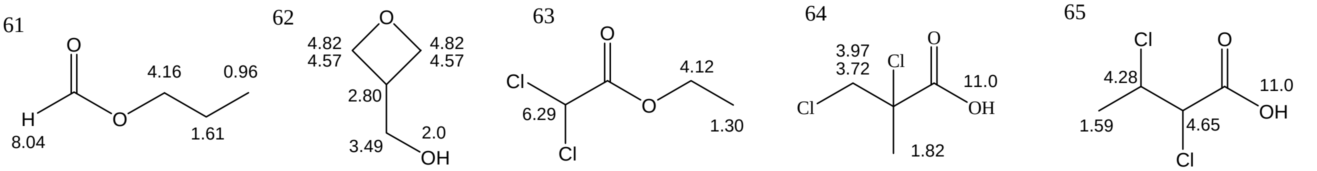

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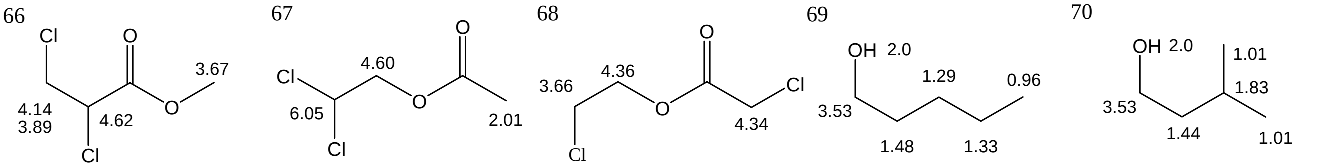

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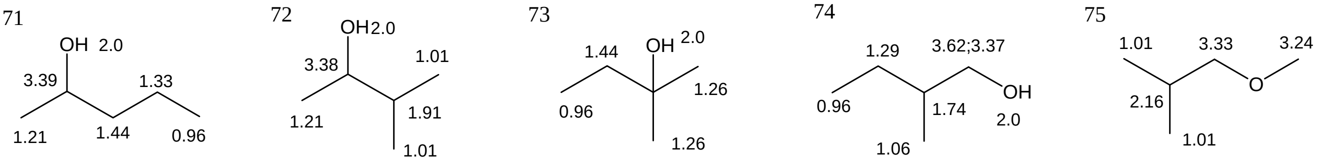

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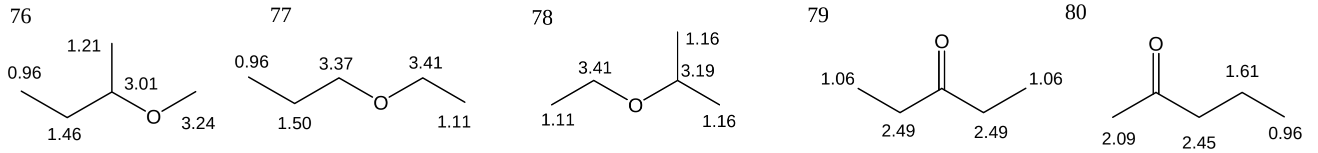

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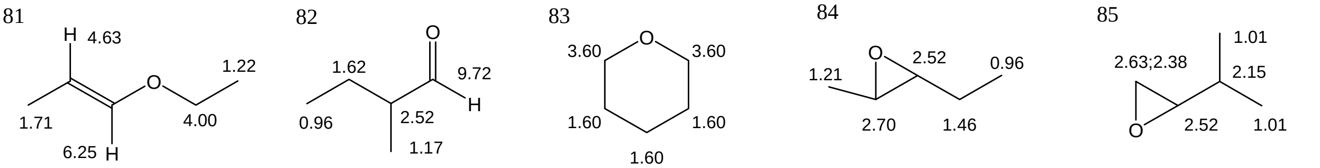

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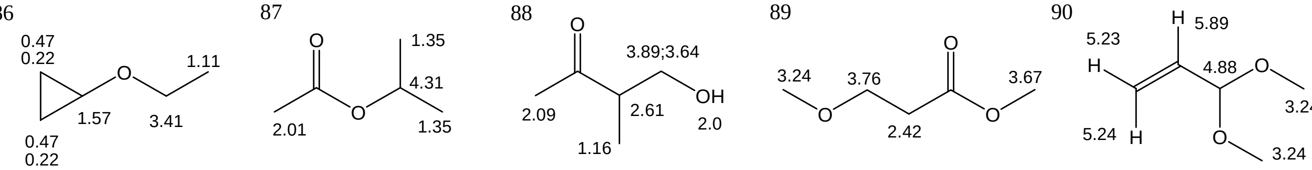

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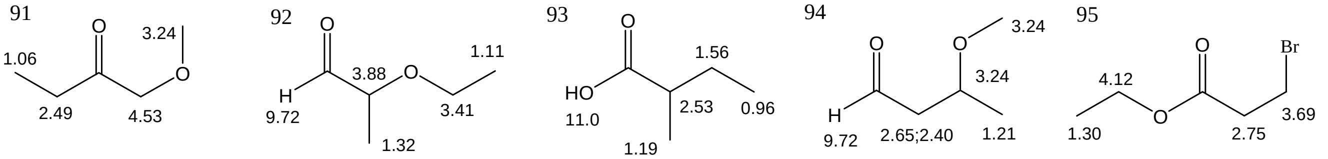

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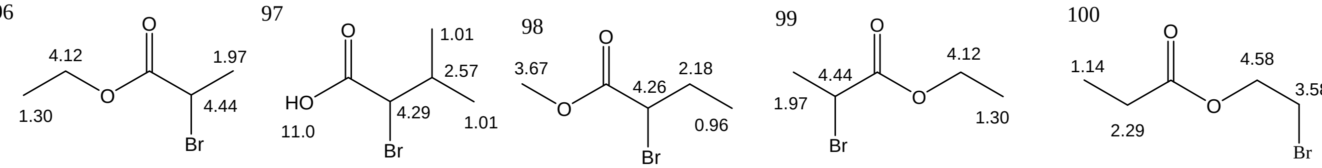

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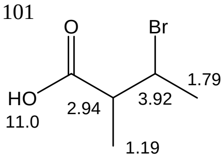

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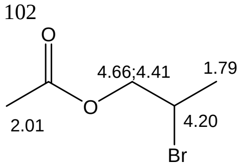

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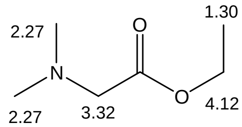

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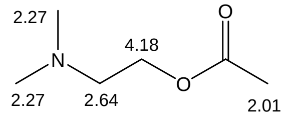

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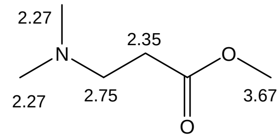

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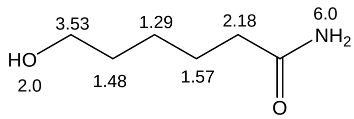

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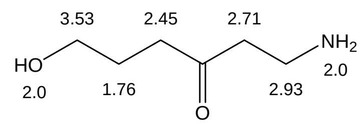

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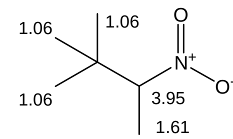

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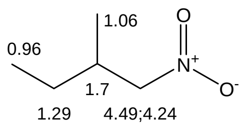

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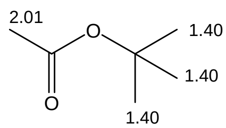

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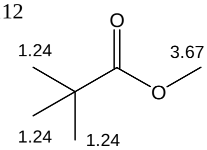

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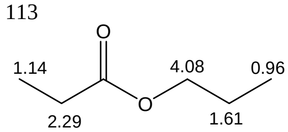

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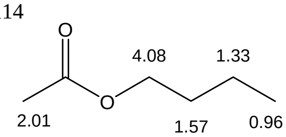

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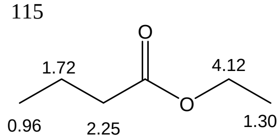

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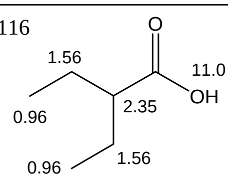

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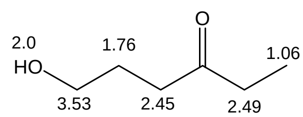

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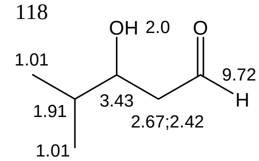

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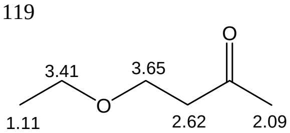

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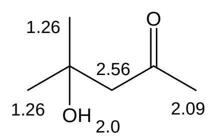

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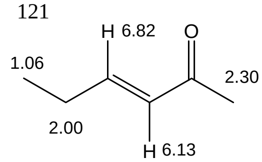

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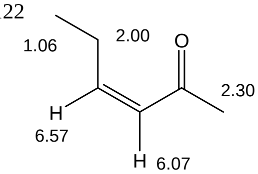

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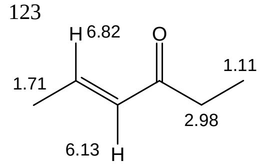

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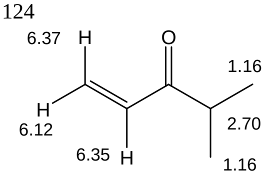

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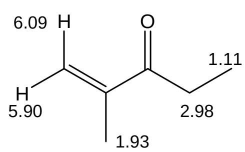

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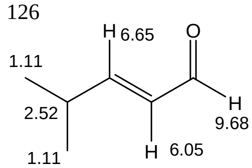

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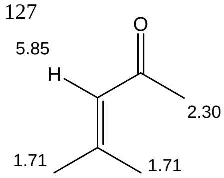

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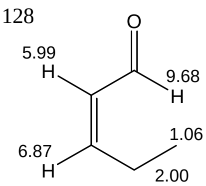

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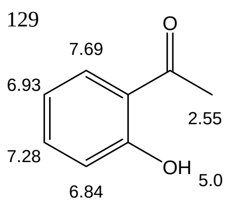

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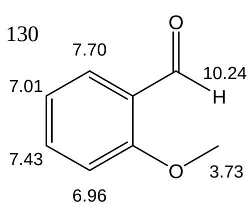

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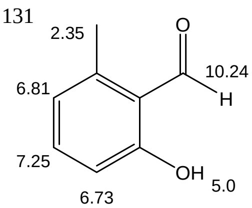

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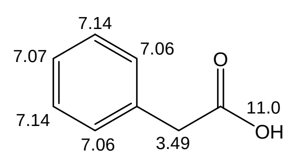

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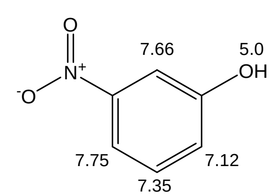

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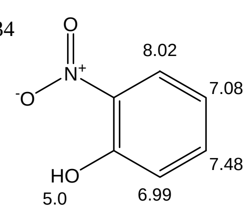

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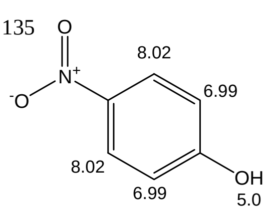

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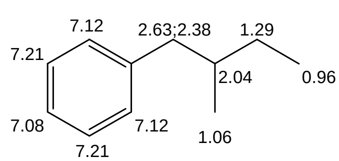

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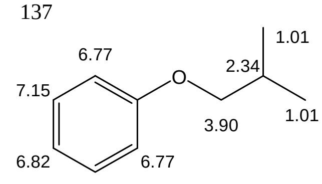

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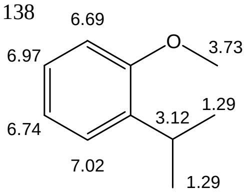

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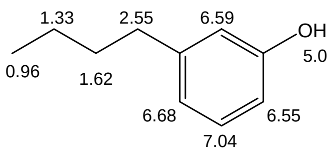

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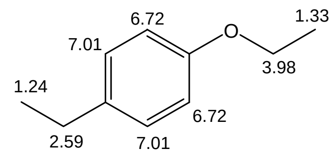

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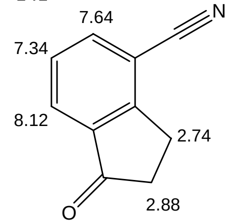

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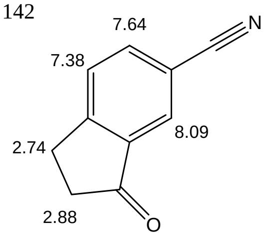

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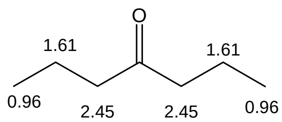

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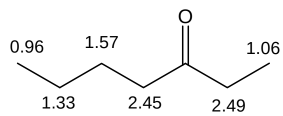

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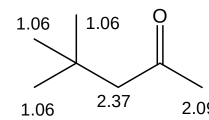

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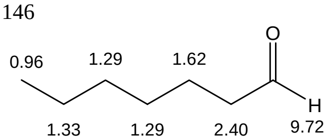

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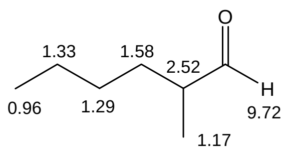

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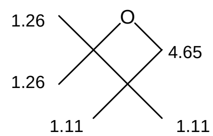

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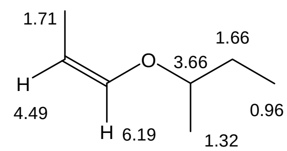

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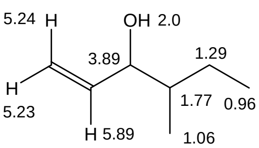

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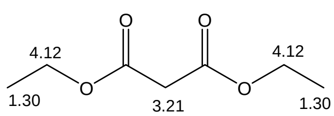

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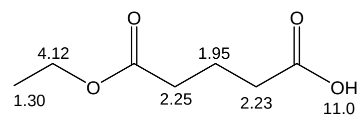

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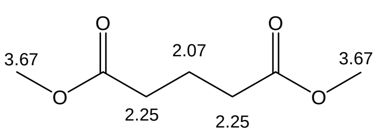

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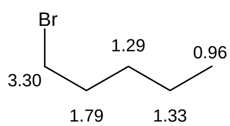

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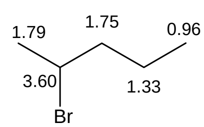

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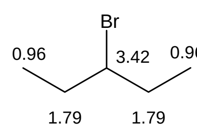

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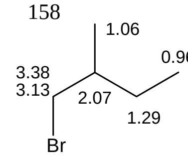

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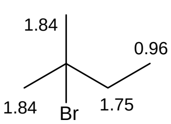

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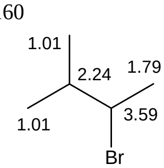

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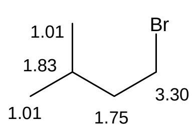

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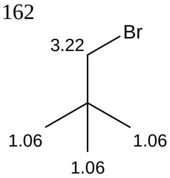

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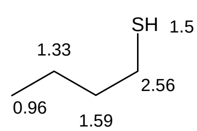

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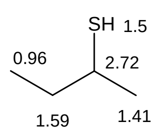

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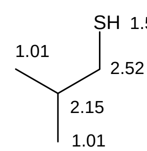

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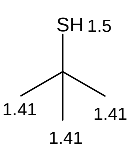

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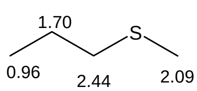

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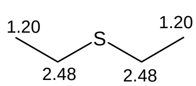

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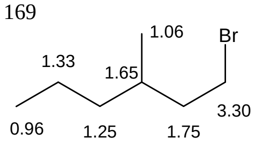

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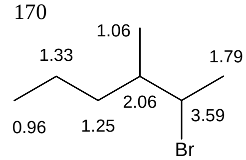

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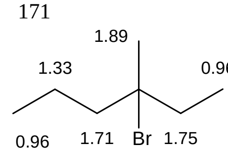

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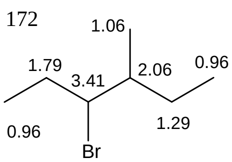

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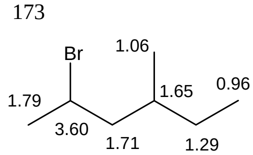

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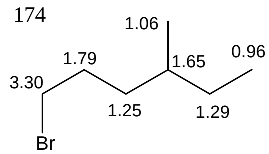

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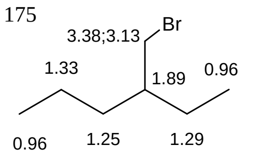

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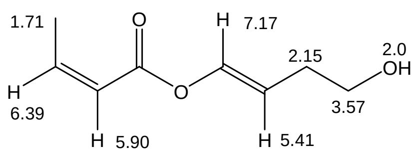

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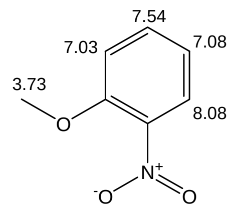

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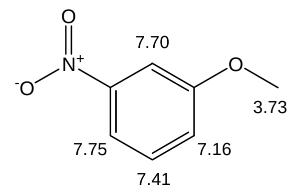

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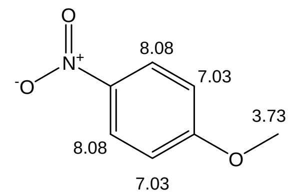

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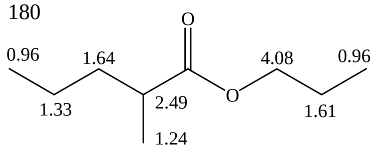

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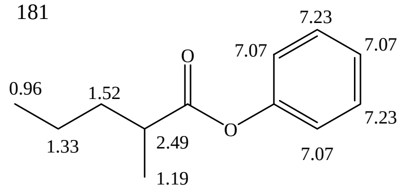

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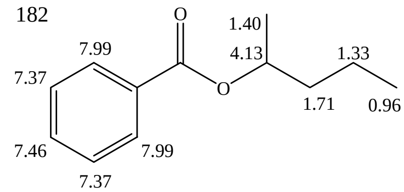

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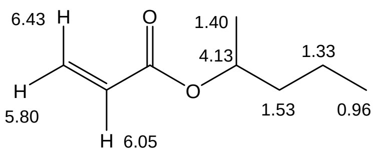

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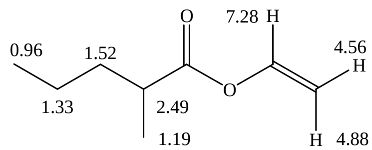

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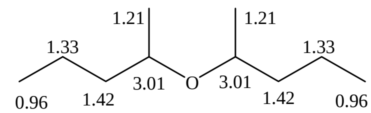

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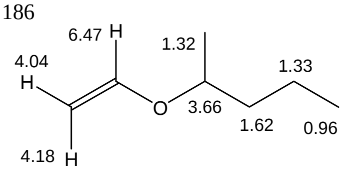

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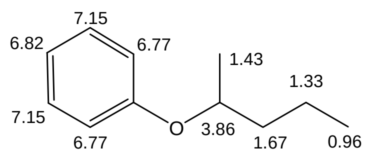

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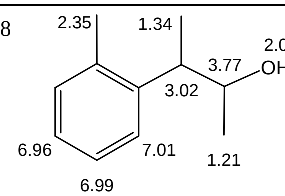
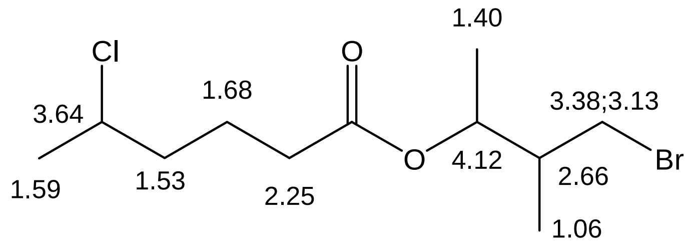


Chapter 5 - Common Proton NMR Problems and Possible Solutions, COSY 2D Interpretation

Problem 1 (p. 222)– Answers to COSY problems.

a. Formula = $C_{11}H_{20}BrClO_2$, Possibly helpful IR bands: 1730, 1230, 1080 cm^{-1}. (assume that sp^3 CH peaks are in all IR spectra)

1

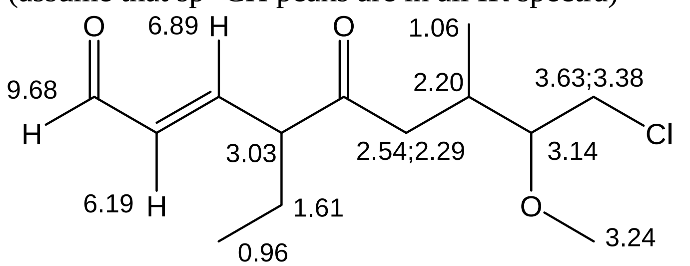


$C_{11}H_{20}BrClO_2$
Exact Mass: 298.03

M+ = 298.03 (77.4%),
M+1 = 299.04 (9.4%),
M+2 = 300.03 (100.0%),
M+3 = 301.03 (11.9%),
M+4 = 302.03 (24.2%),

b. Formula = $C_{13}H_{21}ClO_3$, Possibly helpful IR bands: 3030, 2850, 2780, 1720, 1690, 1660, 980 cm^{-1} (assume that sp^3 CH peaks are in all IR spectra)

2

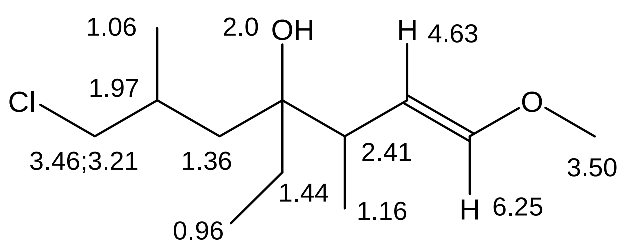


$C_{13}H_{21}ClO_3$
Exact Mass: 260.12

m/e: 260.12 (100.0%),
261.12 (14.4%),
262.11 (32.0%),
263.12 (4.6%),

c. Formula = $C_{12}H_{23}ClO_2$, Possibly helpful IR bands: 3300, 3030, 1640, 1150, 1060 980 cm^{-1} (assume that sp^3 CH peaks are in all IR spectra). Hint: There is one carbon with any protons.

3

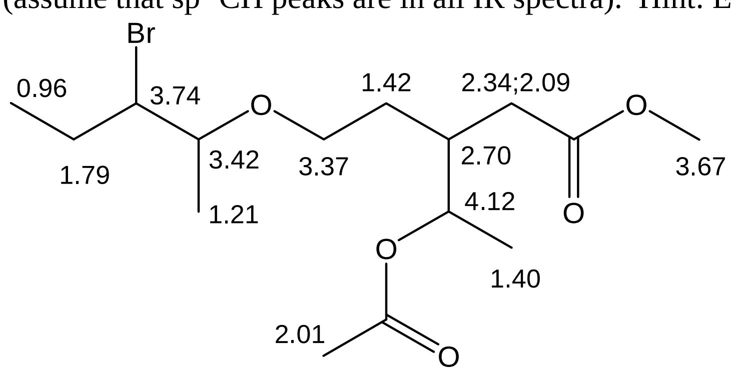


$C_{12}H_{23}ClO_2$
Exact Mass: 234.14

M+ = 234.14 (100.0%),
M+1 = 235.14 (13.3%),
M+2 = 236.14 (32.4%),
M+3 = 237.14 (4.3%)

d. Formula = $C_{15}H_{27}BrO_5$, Possibly helpful IR bands: 1740, 1730, 1250, 1230, 1100, 1070, 1040 cm^{-1} (assume that sp^3 CH peaks are in all IR spectra). Hint: Ether linkage across 3.42 and 3.37.

4

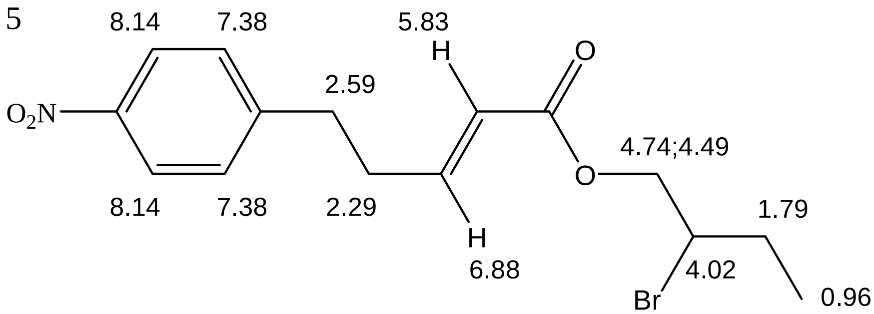


$C_{15}H_{27}BrO_5$
Exact Mass: 366.1

M+ = 366.10 (100.0%),
M+1 = 367.11 (16.7%),
M+2 = 368.10 (97.3%),
M+3 = 369.11 (16.5%),

e. Formula = $C_{16}H_{18}NO_5$, Possibly helpful IR bands: 3030, 2850, 2780, 1720, 1690, 1660, 1550, 1340, 980 cm^{-1} (assume that sp^3 CH peaks are in all IR spectra)

5

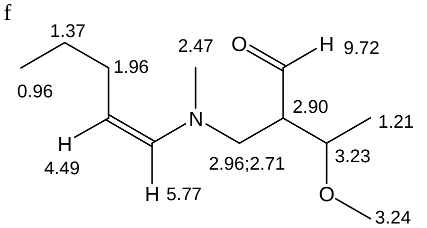


$C_{15}H_{18}BrNO_4$
Exact Mass: 355.04

M+ = 355.04 (100.0%),
M+1 = 356.05 (16.6%),
M+2 = 357.04 (97.3%),
M+3 = 358.04 (16.3%)

Additional possible structures for COSY problems

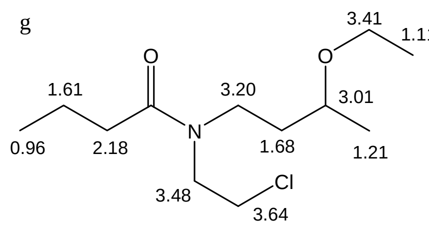
f



$C_{12}H_{23}NO_2$
Exact Mass: 213.17

M+ = 213.17 (100.0%),
M+1 = 214.18 (13.3%),
M+2 = 215.18 (1.2%)

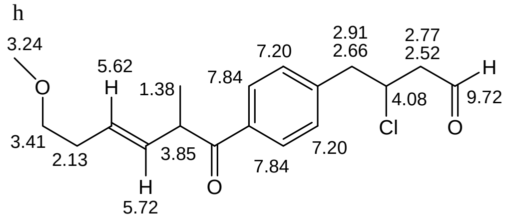
g



$C_{12}H_{24}ClNO_2$
Exact Mass: 249.15

M+ = 249.15 (100.0%),
M+1 = 250.15 (13.4%),
M+2 = 251.15 (32.4%),
M+3 = 252.15 (4.3%)

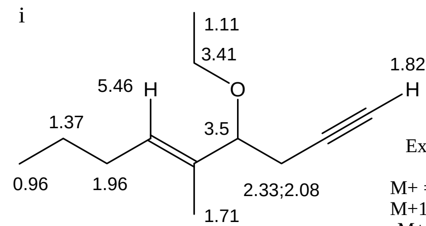
h



$C_{18}H_{23}ClO_3$
Exact Mass: 322.13

M+ = 322.13 (100.0%),
M+1 = 323.14 (19.8%),
M+2 = 324.13 (32.0%),
M+3 = 325.13 (6.3%),

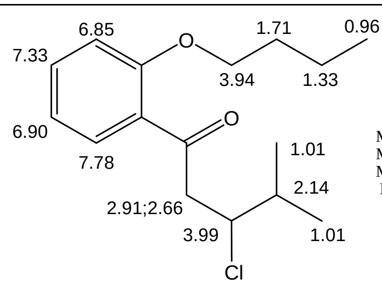
i



$C_{12}H_{20}O$
Exact Mass: 180.15

M+ = 180.15 (100.0%),
M+1 = 181.15 (13.0%),
M+2 = 182.16 (1.0%)

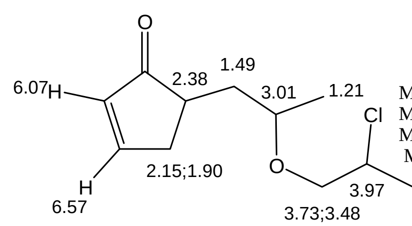
j



$C_{16}H_{23}ClO_2$
Exact Mass: 282.14

M+ = 282.14 (100.0%),
M+1 = 283.14 (17.6%),
M+2 = 284.14 (32.4%),
M+3 = 285.14 (5.6%),

k

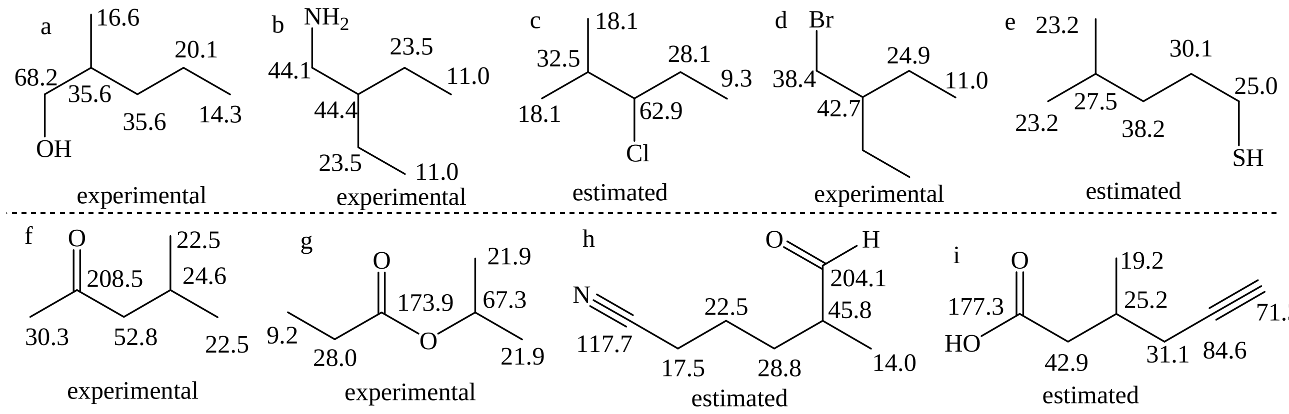


$C_{11}H_{17}ClO_2$
Exact Mass: 216.09

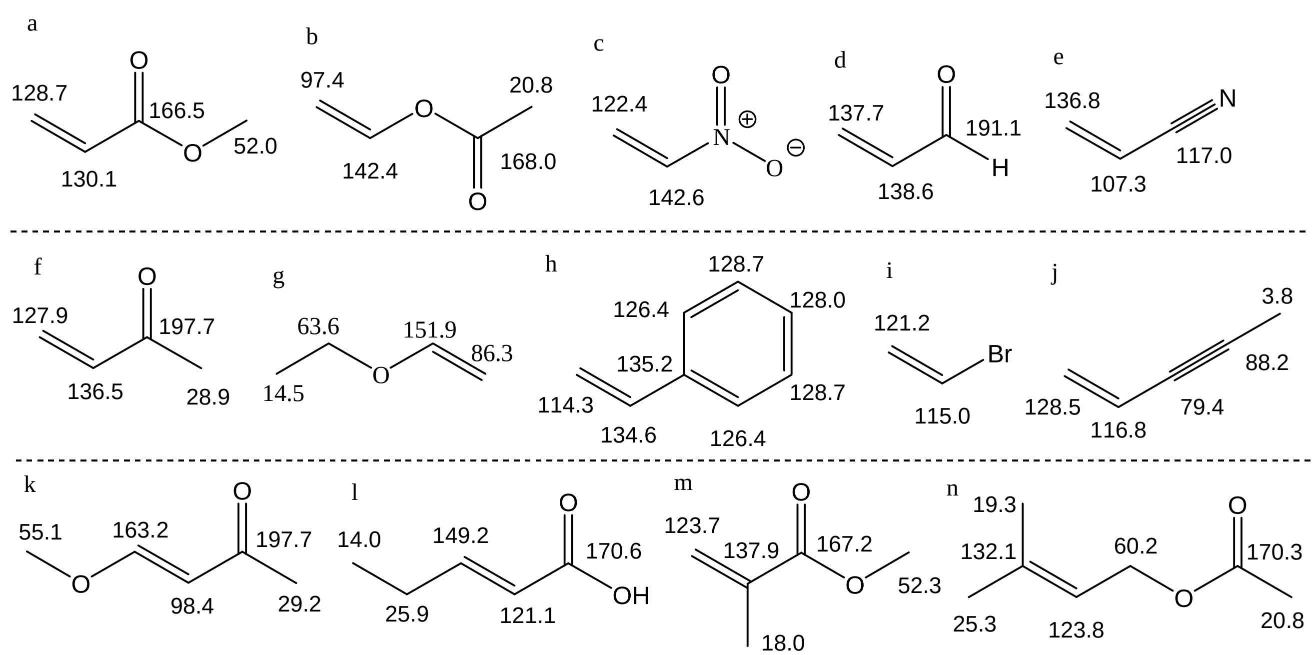
M+ = 216.09 (100.0%),
M+1 = 217.10 (12.2%),
M+2 = 218.09 (32.0%),
M+3 = 219.09 (3.8%),

Chapter 6 - ^{13}C NMR, DEPT Experiments and Other 2D NMR Methods (HETCOR/HSQC and HMBC)

Problem 1 (p. 239)– Estimate the sp^3 carbon chemical shifts of the following molecules. If real values are known, they are listed next to the appropriate carbon atom (experimental), otherwise estimated values are from ChemDraw (estimated). Compare your calculated values to those below.

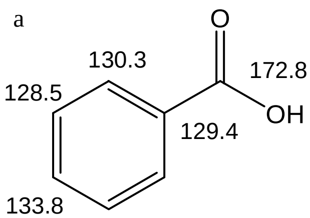


Problem 2 (p. 242)– Calculate the alkene carbon chemical shifts in the following structures. If you don't find an exact match for a particular substituent, look for a close analog to use in place of the actual substituent. The chemical shifts provided are experimental or come from ChemDraw estimates.

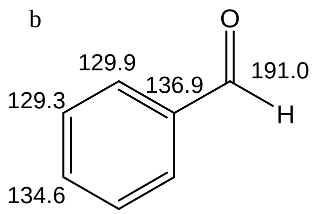


Problem 3 (p. 242)– Calculate the aromatic proton chemical shifts in the following structures. If you don't find and exact match for a particular substituent, look for a close analog to use in place of the actual substituent. The chemical shifts provided are experimental or come from ChemDraw estimates.

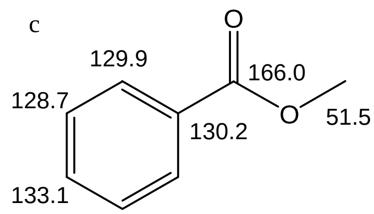
a



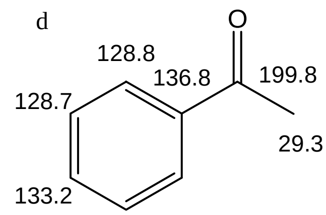
b



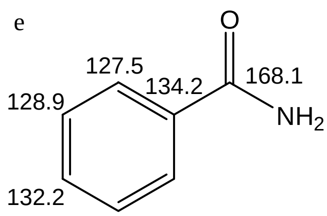
c



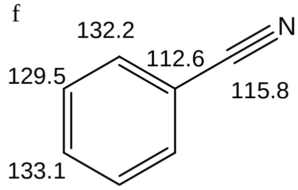
d



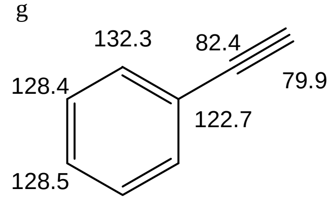
e



f



g



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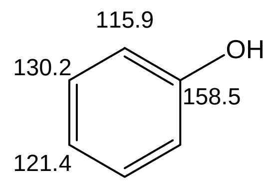

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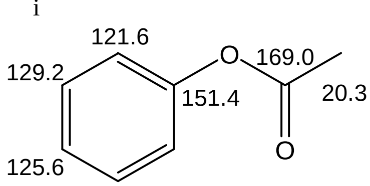

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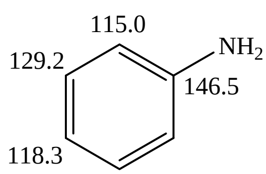
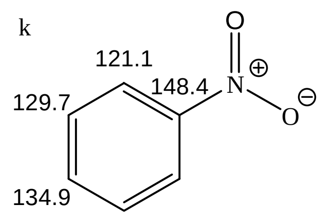
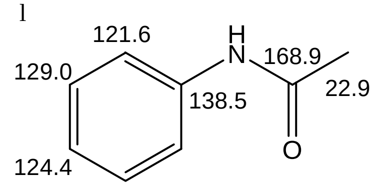


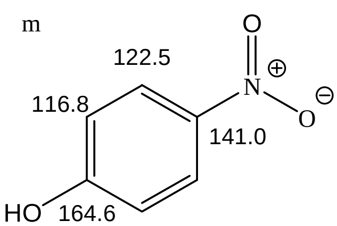
k



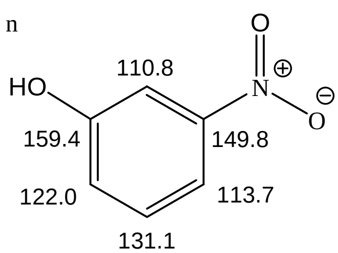
l



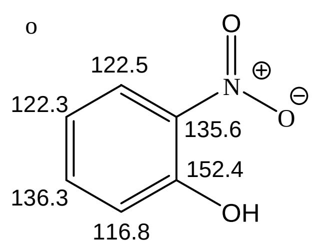
m



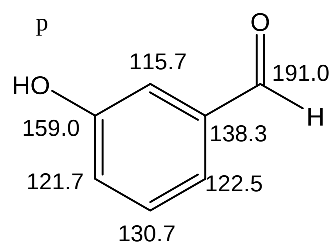
n



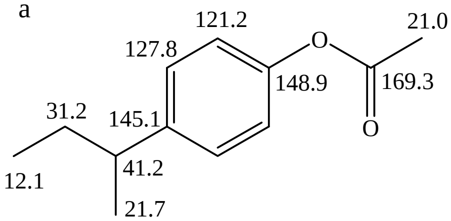
o

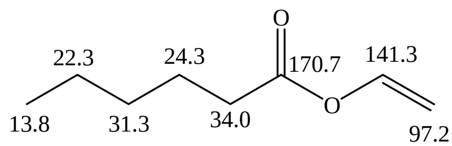


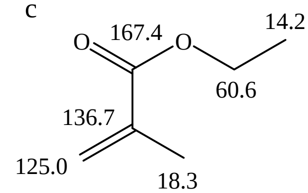
p



Problem 4 (p. 243) – In the following molecules, calculate a chemical shift of any carbon atoms for which a formula is available. If we don't have a formula to calculate a chemical shift, then estimate a range of possibilities from the generic table of shifts. The experimental values are provided for comparison to the estimated values.

a


b


c


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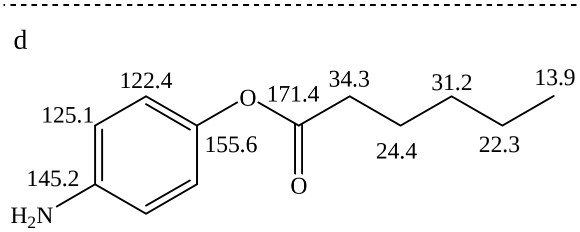
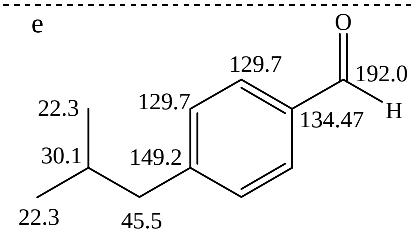
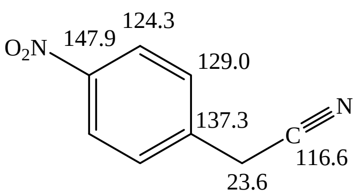
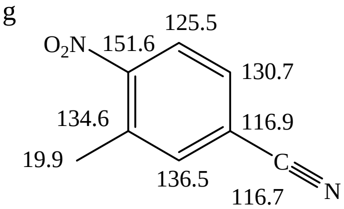
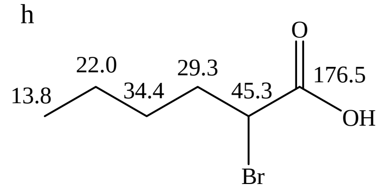
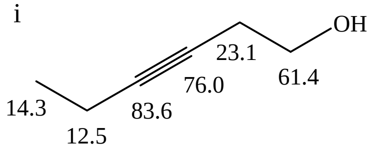


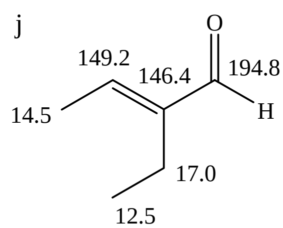
e


f


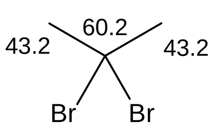
g


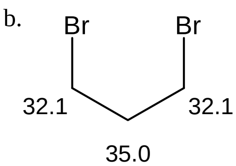
h


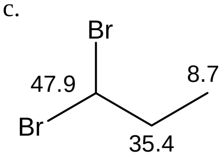
i


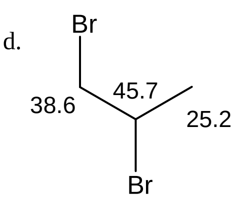
j


Problem 5 (p.254)– $C_3H_6Br_2$

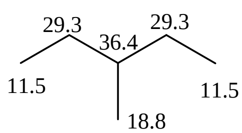
a.


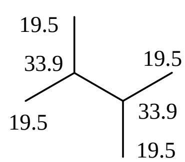
b.


c.


d.


Problem 6 (p. 255) – C_6H_{14}

a.


b.


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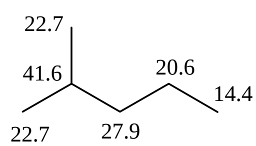
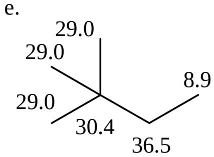
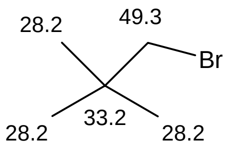
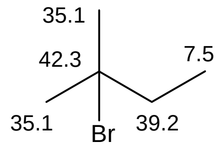


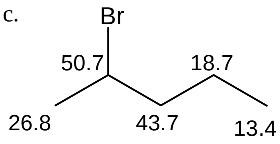
d.

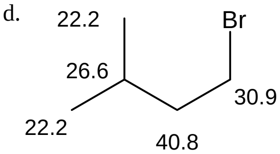

e.


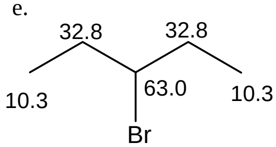
Problem 7 (p. 256) – $C_5H_{11}Br$

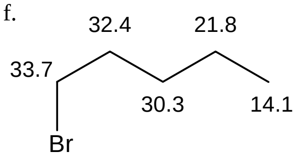
a.


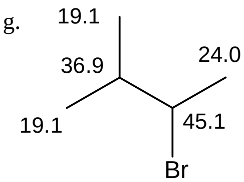
b.


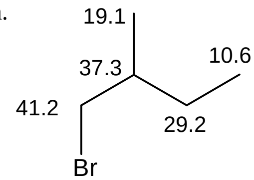
c.


d.


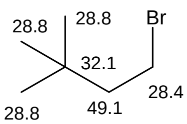
e.


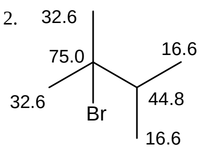
f.


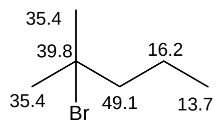
g.


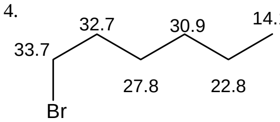
h.


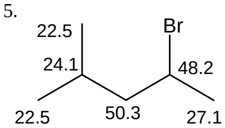
Problem 8 (p. 257) – $C_6H_{13}Br$

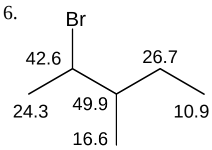
1.


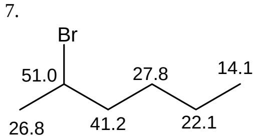
2.


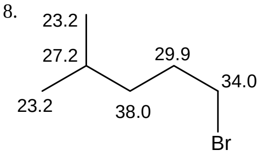
3.


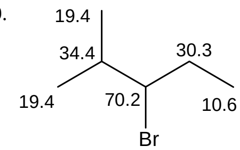
4.


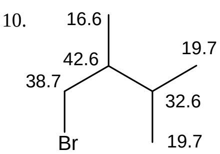
5.


6.


7.


8.


9.


10.


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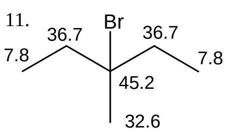
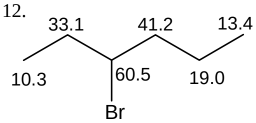
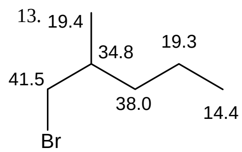
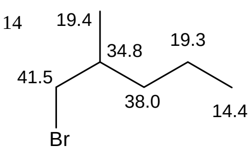
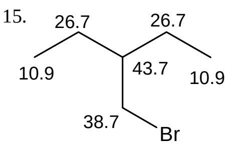
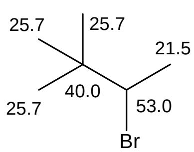


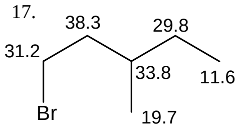
12.


13.


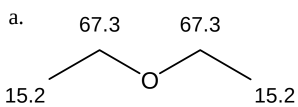
14


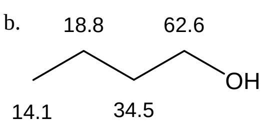
15.


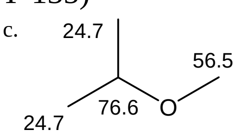
16.


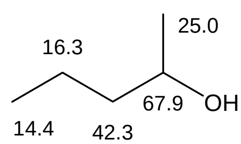
17.


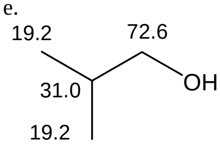
Problem 9 (p. 257)– Provide an acceptable structure for each DEPT spectra below. Formula: $C_4H_{10}O$ (bottom = ^{13}C spectrum, middle = DEPT-90, top = DEPT-135)

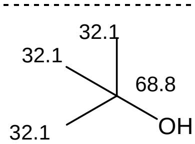
a.


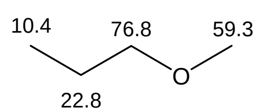
b.


c.


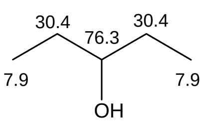
d.


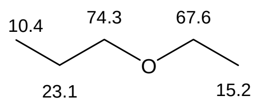
e.


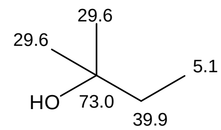
f.


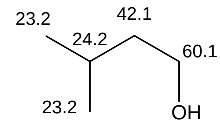
g.


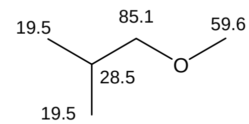
Problem 10 (p. 258) – Provide an acceptable structure for each DEPT spectra below. Formula: $C_5H_{12}O$ (bottom = ^{13}C spectrum, middle = DEPT-90, top = DEPT-135)

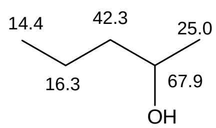
a


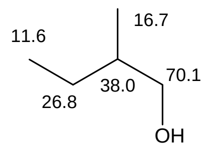
b


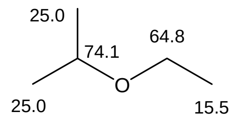
c


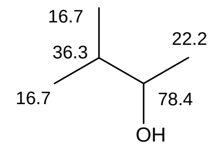
d


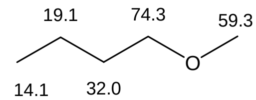
e


f


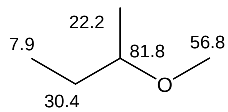
g


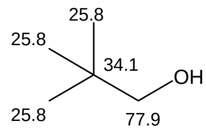
h


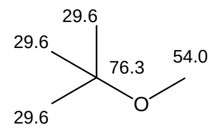
i


j


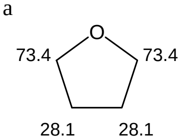
k

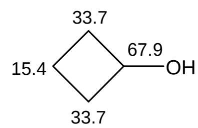

l


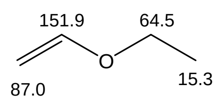
m


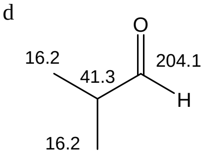
n


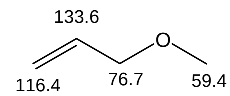
Problem 11 (p. 260) – Provide an acceptable structure for each DEPT spectra below. Formula: C_4H_8O (bottom = ^{13}C spectrum, middle = DEPT-90, top = DEPT-135)

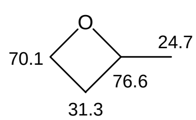
a


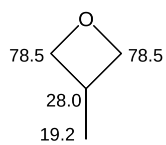
b


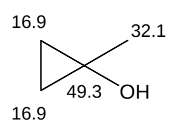
c


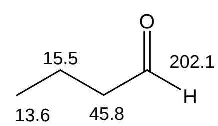
d


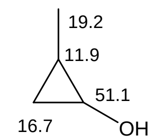
e


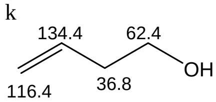
f


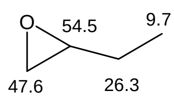
g


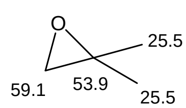
h


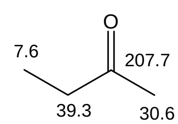
i


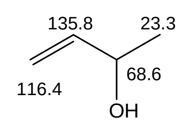
j


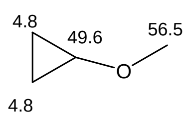
k


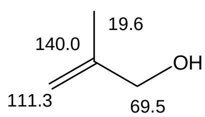
l


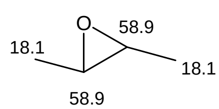
m


n


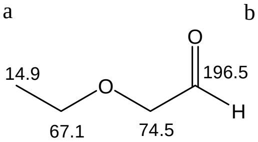
o


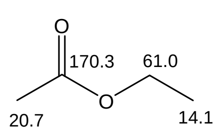
p


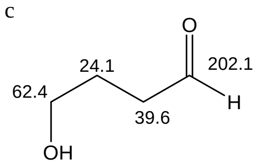
q


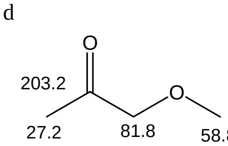
r


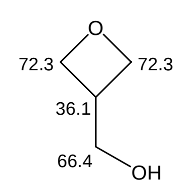
Problem 12 (p. 261) – Provide an acceptable structure for each DEPT spectra below. Formula: $C_4H_8O_2$ (bottom = ^{13}C spectrum, middle = DEPT-90, top = DEPT-135)

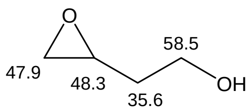
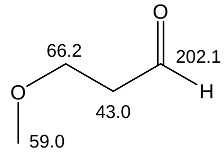
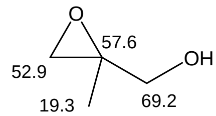
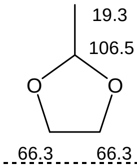
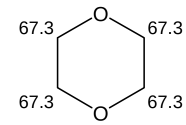
a


b


c


d


e


f

g

h

i

j


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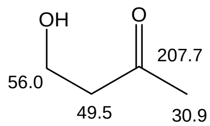
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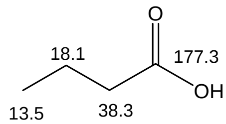
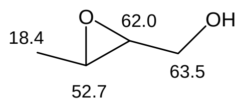
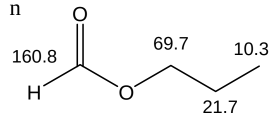
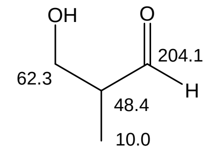
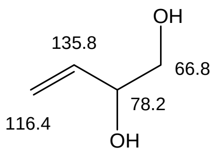
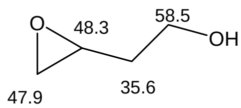
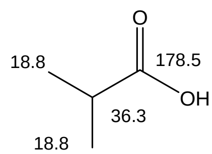
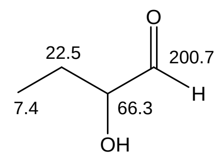
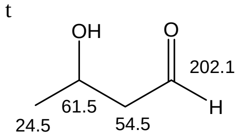
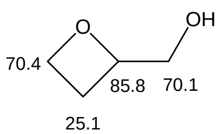
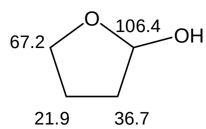

m

n

o


p

q

r

s

t


u

v

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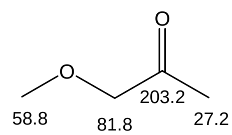
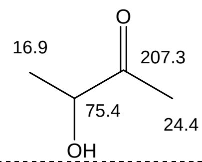
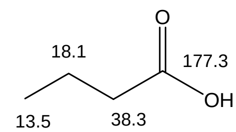
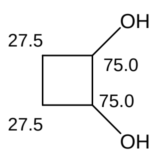
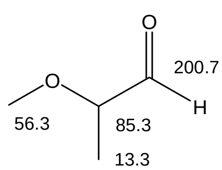
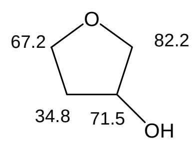
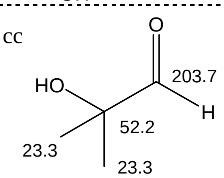
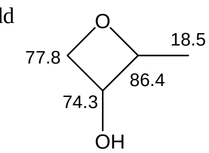
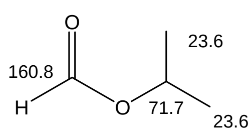
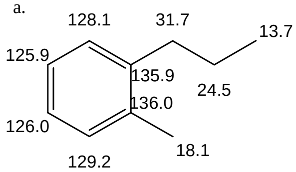
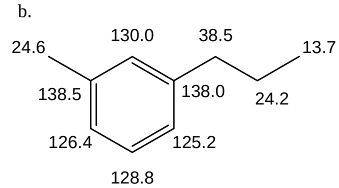
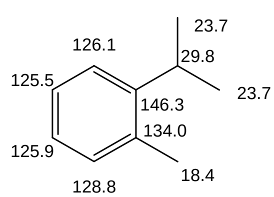
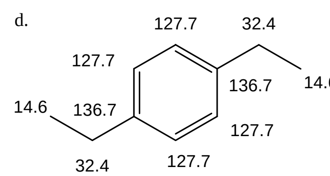
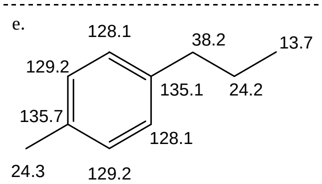
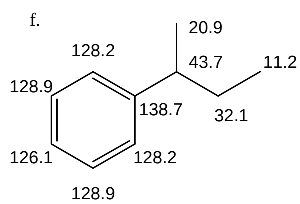
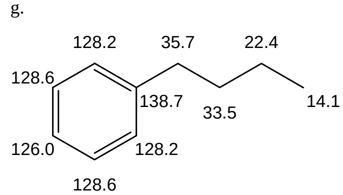
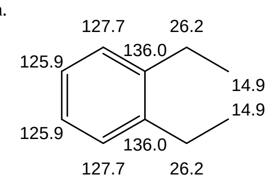

x

y


z

aa

bb

cc

dd


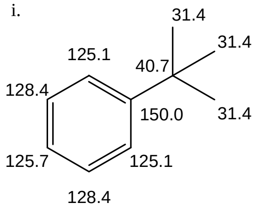
ee


Problem 13 (p. 264) **–** Provide an acceptable structure for each DEPT spectra below. Formula: $C_{10}H_{14}$ (bottom = ^{13}C spectrum, middle = DEPT-90, top = DEPT-135)

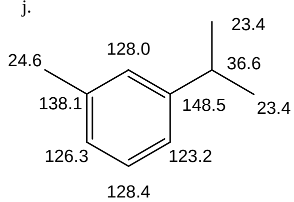
a.

b.

c.

d.


e.

f.

g.

h.


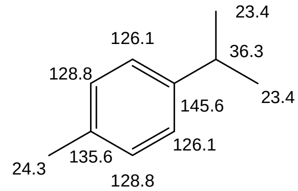
i.


31.4
31.4
125.1
40.7
128.4
150.0
31.4
125.7
125.1
128.4

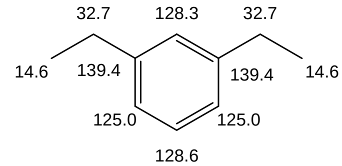
j.


23.4
24.6
128.0
36.6
138.1
148.5
23.4
126.3
123.2
128.4

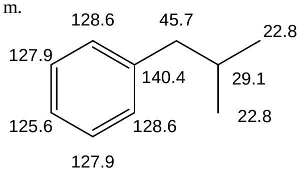
k.


23.4
126.1
36.3
128.8
23.4
145.6
126.1
24.3
135.6
128.8

l.


32.7
128.3
32.7
14.6
139.4
139.4
14.6
125.0
125.0
128.6

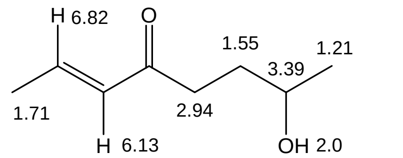
m.


128.6
45.7
22.8
127.9
140.4
29.1
125.6
128.6
22.8
127.9

Chapter 7 - Medium Difficulty Structure Problems

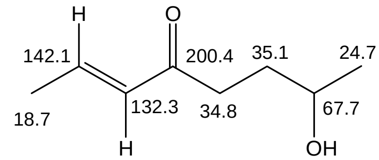
Problem 1 (p. 279)

1.



6.82 6.13 3.39 2.94 2.0 1.71 1.55 1.21

$C_8H_{14}O_2$
Exact Mass: 142.1
M+ = 142.10 (100.0%),
M+1 = 143.10 (8.7%)

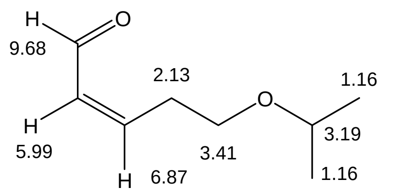


200.4
142.1
132.3
67.7
35.1
34.8
24.7
18.7

IR peaks (cm^{-1}): O-H stretch 3290; alkoxy C-O stretch 1050; sp^2 C-H stretch 3030; C=C stretch 1630; trans alkene C-H bend 980; sp^3 C-H stretch 2960-2850; sp^3 C-H bend 1470, 1380; C=O stretch 1695

Problem 2 (p. 280)

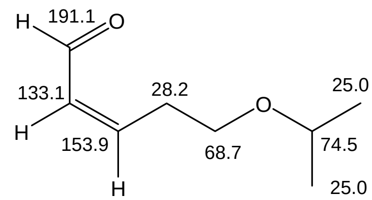
2.



9.68 6.87 5.99 3.41 3.19 2.13 1.16

$C_8H_{14}O_2$
Exact Mass: 142.1

M+ = 142.10 (100.0%),
M+1 = 143.10 (8.7%)

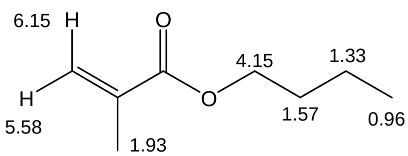


191.1
153.9
133.1
74.5
68.7
28.2
25.0 x 2

IR peaks (cm^{-1}): sp^2 C-H stretch 3030; C=C stretch 1630; trans alkene C-H bend 980; aldehyde C-H stretch 2800 and 2750; C=O stretch 1698; sp^3 C-H stretch 2960-2850; sp^3 C-H bend 1470, 1380; alkoxy C-O stretch 1070, 1030

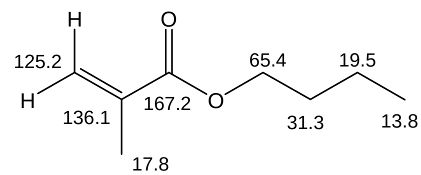
Problem 3 (p. 281)

3.



6.15 5.58 4.15 1.93 1.57 1.33 0.96

$C_8H_{14}O_2$
Exact Mass: 142.1
Mol. Wt.: 142.2
m/e: 142.10 (100.0%), 143.10 (8.7%)
C, 67.57; H, 9.92; O, 22.50

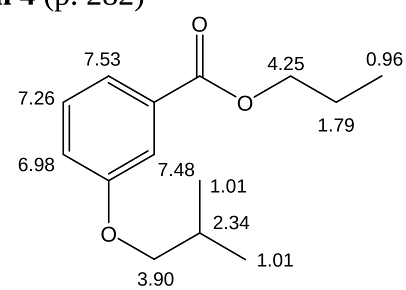


167.2
136.1
125.2
65.4
31.3
19.5
17.8
13.8

IR peaks (cm^{-1}): sp^2 C-H stretch 3030; sp^3 C-H stretch 2960-2850; conj. ester C=O stretch 1720; C=C stretch 1630; sp^3 C-H bend 1470, 1380; acyl C-O stretch 1220; alkoxy C-O stretch 1050; geminal alkene C-H bend 890; sp^3 CH_2 rock 3030

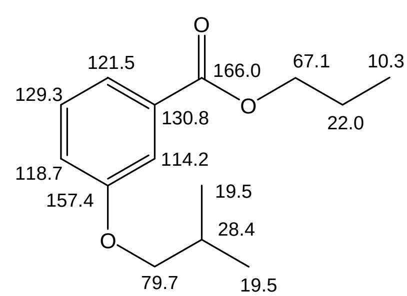
Problem 4 (p. 282)

4.



7.53 7.48 7.26 6.98 4.25 3.90 2.34 1.79 1.01 0.96

$C_{14}H_{20}O_3$
Exact Mass: 236.14
Mol. Wt.: 236.31
C, 71.16; H, 8.53; O, 20.31

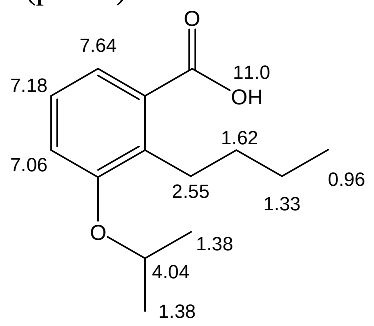


166.0
157.4
130.8
129.3
121.5
118.7
114.2
79.7
67.1
28.4
22.0
19.5x2
10.3

IR peaks (cm^{-1}): sp^2 C-H stretch 3030; sp^3 C-H stretch 2960-2850; conj. ester C=O stretch 1698; C=C stretch 1630; sp^3 C-H bend 1470, 1380; acyl C-O stretch 1220; alkoxy C-O stretch 1050; meta aromatic C-H bend 880, 760, 690

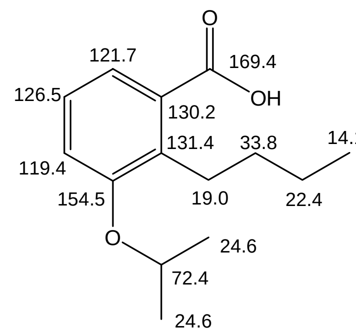
Problem 5 (p. 283)

5.



$C_{14}H_{20}O_3$
Exact Mass: 236.14

M+ = 236.14 (100.0%),
M+1 = 237.14 (15.1%),
M+2 = 238.15 (1.7%)



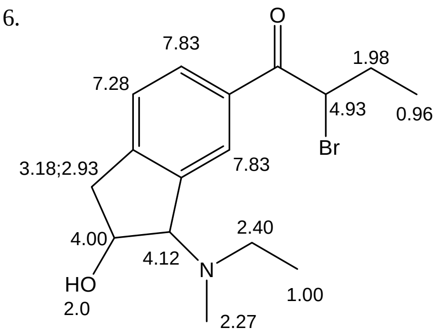
169.4
154.5
131.4
130.2
126.5
121.7
119.4
72.4
33.8
24.6
22.4
19.0
14.1

11.0 7.64 7.18 7.06 4.04 2.55 1.62 1.38 1.33 0.96

IR peaks (cm^{-1}): acid O-H stretch 3400-2500; sp^2 C-H stretch 3030; sp^3 C-H stretch 2960-2850; conj. acid C=O stretch 1690; C=C stretch 1630; sp^3 C-H bend 1470, 1380; acyl C-O stretch 1210; alkoxy C-O stretch 1170, 1050

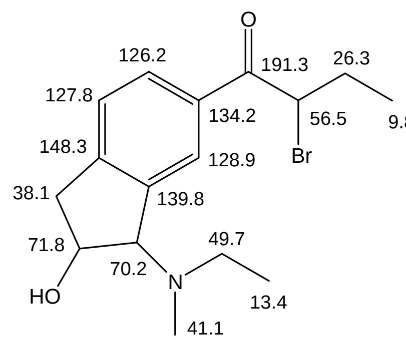
Problem 6 (p. 284)

6.



$C_{16}H_{22}BrNO_2$
Exact Mass: 339.08

M+ = 339.08 (100.0%),
M+1 = 340.09 (17.6%),
M+2 = 341.08 (97.3%),
M+3 = 342.08 (17.2%),
M+4 = 343.09 (1.8%)



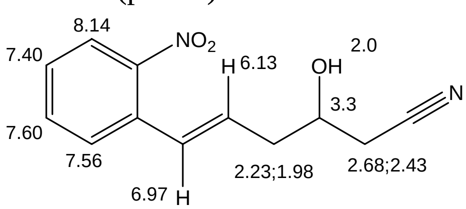
191.3
148.3
139.8
134.2
128.9
126.2
127.8
71.8
70.2
56.5
49.7
41.1
38.1
26.3
13.4
9.8

7.83 7.83 7.28 4.93 4.12 4.00 3.18;2.93 2.40 2.27 2.0 1.98 1.00 0.96

IR peaks (cm^{-1}): alcohol O-H stretch 3300; sp^2 C-H stretch 3030; sp^3 C-H stretch 2960-2850; conj. ketone C=O stretch 1690; C=C stretch 1630; sp^3 C-H bend 1470, 1380; alkoxy C-O stretch 1070, 1030

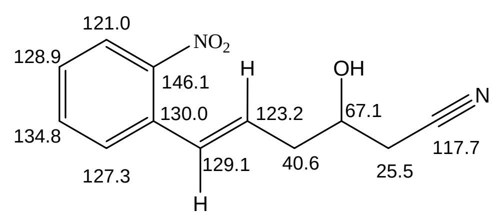
Problem 7 (p. 286)

7.



$C_{12}H_{12}N_2O_3$
Exact Mass: 232.08

M+ = 232.08 (100.0%),
M+1 = 233.09 (13.2%),
M+2 = 234.09 (1.5%)



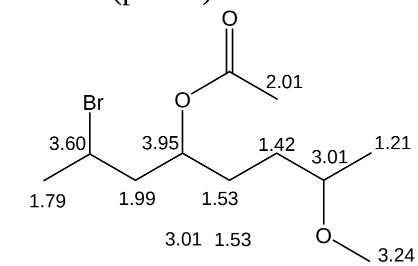
146.1
134.8
130.0
129.1
128.9
127.3
123.2
121.0
117.7
67.1
40.6
25.5

8.14 7.60 7.56 7.40 6.97 6.13 3.3 2.68;2.43 2.23;1.98 2.0

IR peaks (cm^{-1}):

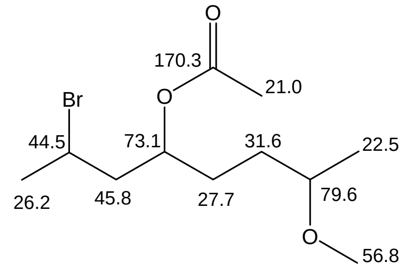
Problem 8 (p. 288)

8.



$C_{11}H_{21}BrO_3$
MW (exact mass): 280.07

M+ = 280.07 (100.0%),
M+1 = 281.07 (12.3%),
M+2 =282.07 (98.6%),
M+3 = 283.07 (11.9%),



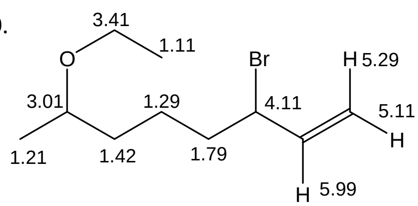
170.3
79.6
73.1
56.8
45.8
44.5
31.6
27.7
26.2
22.5
21.0

3.95 3.60 3.24 3.01 2.01 1.99 1.79 1.53 1.42 1.21

IR peaks (cm^{-1}):

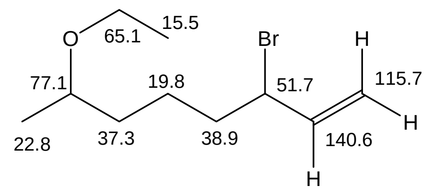
Problem 9 (p. 290)

9.



$C_{10}H_{19}BrO$
Exact Mass: 234.06

M+ = 234.06
M+1 = 235.07 (11.1%),
M+2 = 236.06 (97.3%),
M+3 = 237.06 (10.6%)



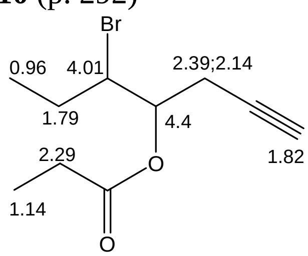
140.6
115.7
77.1
65.1
51.7
38.9
37.3
22.8
19.8
15.5

5.99 5.29 5.11 4.11 3.41 3.01 1.79 1.42 1.29 1.21 1.11

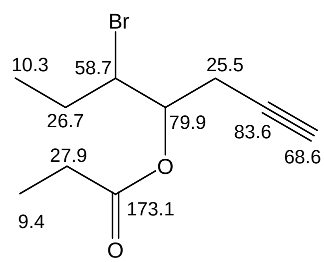
IR peaks (cm^{-1}):

Problem 10 (p. 292)

10.



$C_{10}H_{15}BrO_2$
Exact Mass: 246.03
M+ = 246.03 (100.0%),
M+1 = 247.03 (11.1%),
M+2 = 248.02 (97.3%),
M+3 = 249.03 (10.8%)



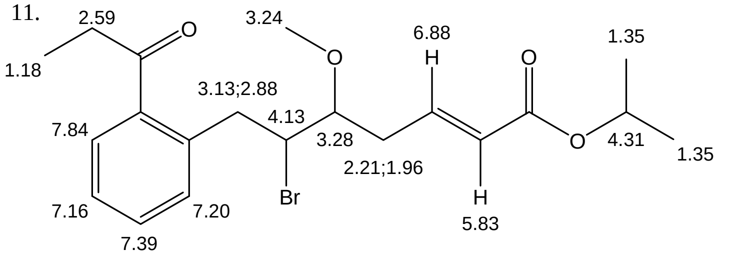
173.1
83.6
79.9
68.6
58.7
27.9
26.7
25.5
10.3
9.4

4.4 4.01 2.39;2.14 2.29 1.82 1.79 1.14 0.96

IR peaks (cm^{-1}):

Problem 11 (p. 294)

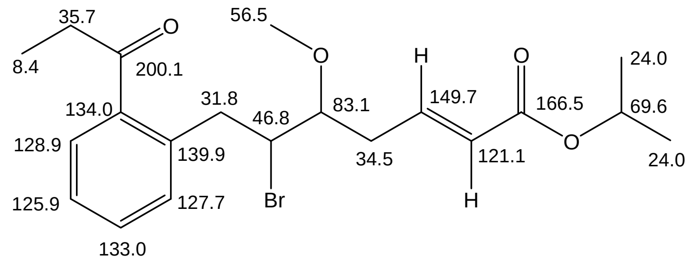
11.



$C_{20}H_{27}BrO_4$
Exact Mass: 410.11

M+ = 410.11 (100.0%),
M+1 = 411.11 (21.8%),
M+2 = 412.11 (98.1%),
M+3 = 413.11 (21.5%),

7.84 7.39 7.20 7.16 6.88 5.83 4.31 4.13 3.28 3.24 3.13;2.88 2.59 2.21;1.96 1.35 1.18

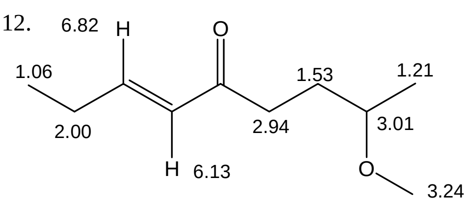


200.1
166.5
149.7
139.9
134.0
133.0
128.9
127.7
125.9
121.1
83.1
69.6
56.5
46.8
35.7
34.5
31.8
24.0 x 2
8.4

IR peaks (cm^{-1}):

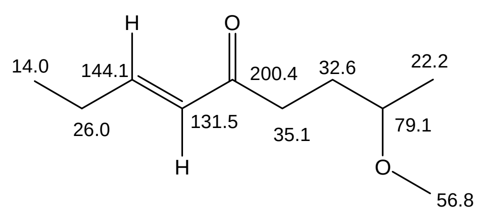
Problem 12 (p. 296)

12.



$C_{10}H_{18}O_2$
Exact Mass: 170.13

M+ = 170.13 (100.0%),
M+1 = 171.13 (10.9%)



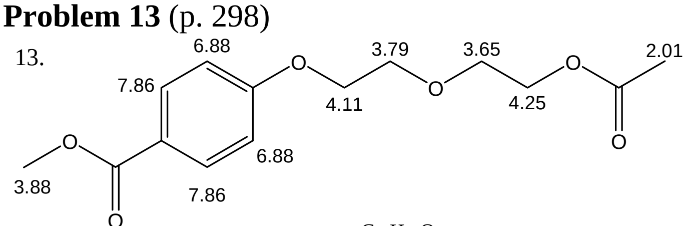
200.4
144.1
131.5
79.1
56.8
35.1
32.6
26.0
22.2
14.0

6.82 6.13 3.24 3.01 2.94 2.00 1.53 1.21 1.06

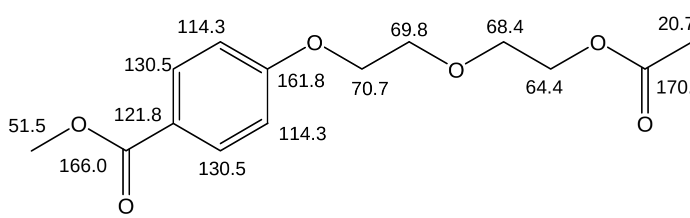
IR peaks (cm^{-1}):

Problem 13 (p. 298)

13.



$C_{14}H_{18}O_6$
Exact Mass: 282.11
M+ = 282.11 (100.0%),
M+1 = 283.11 (15.4%),
M+2 = 284.11 (1.2%), "O"
M+2 = 284.12 (1.1%), "C"



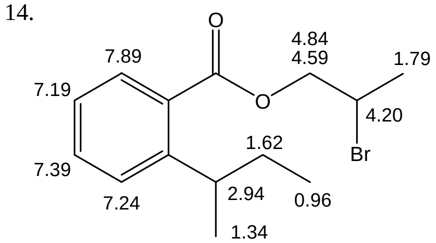
170.3
166.0
161.8
130.5
121.8
114.3
70.7
69.8
68.4
64.4
51.5
20.7

7.86 6.88 4.25 4.11 3.88 3.79 3.65 2.01

IR peaks (cm^{-1}):

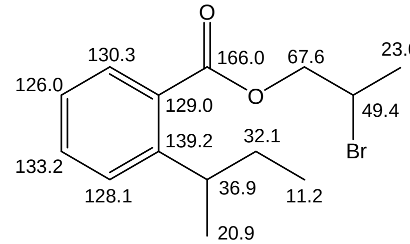
Problem 14 (p. 300)

14.



$C_{14}H_{19}BrO_2$
Exact Mass: 298.06

M+ = 298.06 (100.0%),
M+1 = 299.06 (15.4%),
M+2 = 300.05 (97.3%),
M+3 = 301.06 (15.1%),



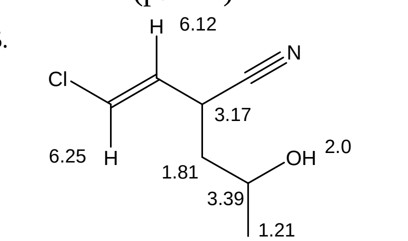
166.0
133.2
139.2
130.3
129.0
128.1
126.0
67.6
49.4
36.9
32.1
23.0
20.9
11.2

7.89 7.39 7.24 7.19 4.84 4.59 4.20 2.94 1.79 1.62 1.34 0.96

IR peaks (cm^{-1}):

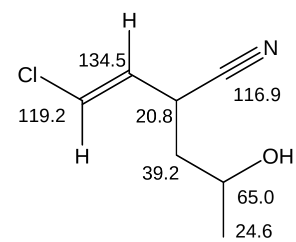
Problem 15 (p. 302)

15.



$C_7H_{10}ClNO$
Exact Mass: 159.05

M+ = 159.05 (100.0%),
M+1 = 160.05 (7.7%),
M+2 = 161.04 (32.0%),
M+3 = 162.05 (2.5%)



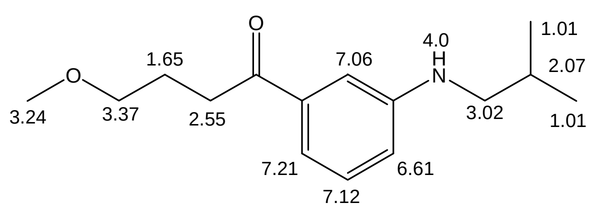
134.5
119.2
116.9
65.0
39.2
24.6
20.8

6.25 6.12 3.39 3.17 2.0 1.81 1.21

IR peaks (cm^{-1}):

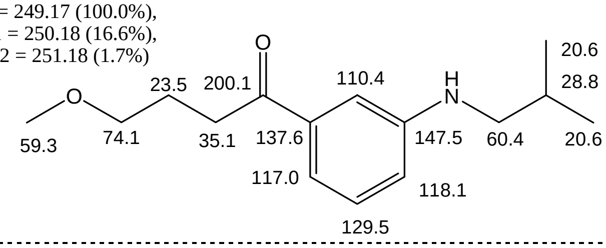
Problem 16 (p. 304)

16.



$C_{15}H_{23}NO_2$
Exact Mass: 249.17

M+ = 249.17 (100.0%),
M+1 = 250.18 (16.6%),
M+2 = 251.18 (1.7%)



200.1
147.5
137.6
129.5
118.1
117.0
110.4
60.4
74.1
59.3
35.1
28.8
23.5
20.6 x2

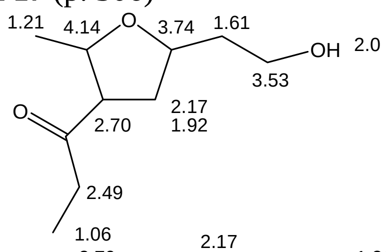
7.21 7.12 7.06 6.61 4.0 3.37 3.24 3.02 2.55 2.07 1.65 1.01

IR peaks (cm^{-1}):

meta aromatic C-H bend 880, 760, 690

Problem 17 (p. 306)

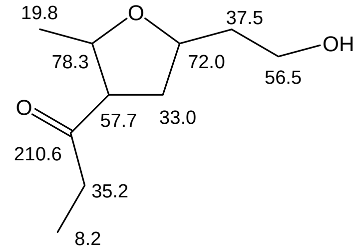
17.



4.14 3.74 3.53 2.70 2.49 2.17 1.92 2.0 1.61 1.21 1.06

$C_{10}H_{18}O_3$

Exact Mass: 186.13
M+ = 186.13 (100.0%),
M+1 = 187.13 (11.1%),
M+2 = 188.13 (1.2%)

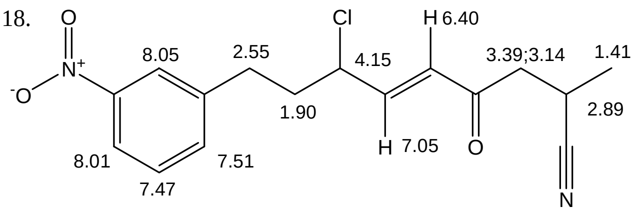


210.6
78.3
72.0
57.7
56.5
37.5
35.2
33.0
19.8
8.2

IR peaks (cm^{-1}):

Problem 18 (p. 308)

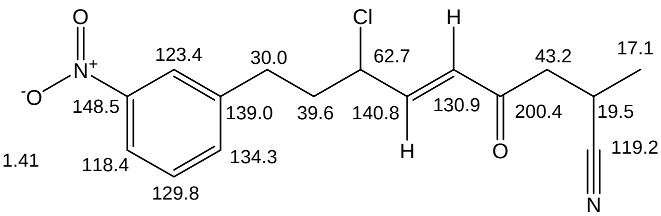
18.



8.05 8.01 7.47 7.51 7.05 6.40 4.15 3.39 3.14 2.89 2.55 1.90 1.41

$C_{16}H_{17}ClN_2O_3$
Exact Mass: 320.09

M+ = 320.09 (100.0%),
M+1 = 321.10 (17.6%),
M+2 = 322.09 (32.1%),
M+3 = 323.09 (5.8%),

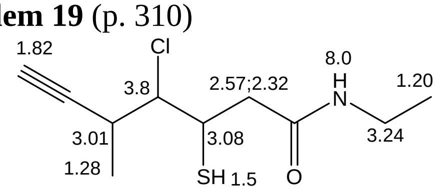


200.4
148.5
140.8
139.0
134.3
130.9
129.8
123.4
119.2
118.4
62.7
43.2
39.6
30.0
19.5
17.1

IR peaks (cm^{-1}):

Problem 19 (p. 310)

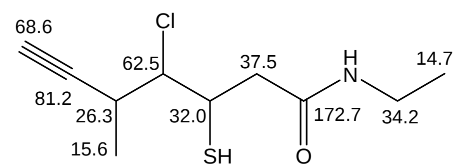
19.



8.0 3.8 3.24 3.08 3.01 2.57;2.32 1.82 1.5 1.28 1.20

$C_{10}H_{16}ClNOS$
Exact Mass: 233.06

M+ = 233.06 (100.0%),
M+1 = 234.07 (11.0%),
M+2 = 235.06 (36.5%),
M+3 = 236.06 (4.3%),

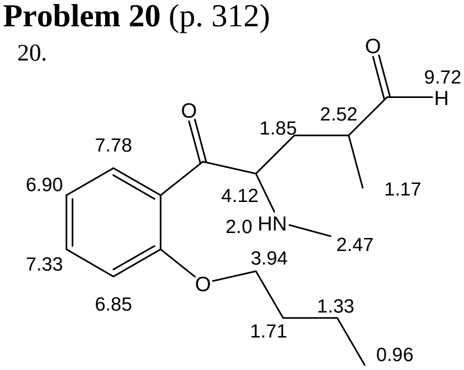


172.7
81.2
68.6
62.5
37.5
34.2
32.0
26.3
15.6
14.7

IR peaks (cm^{-1}):

Problem 20 (p. 312)

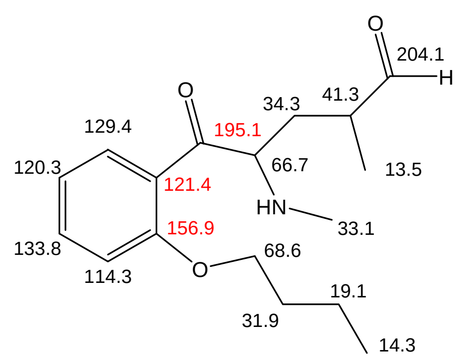
20.



9.72 7.78 7.33 6.90 6.85 4.12 3.94 2.52 2.47 2.0 1.85 1.71 1.33 1.17 0.96

$C_{17}H_{25}NO_3$
Exact Mass: 291.18

M+ = 291.18 (100.0%),
M+1 = 292.19 (18.8%),
M+2 = 293.19 (2.3%)

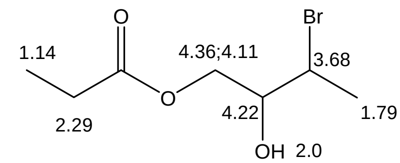


204.1
195.1
156.9
133.8
129.4
121.4
120.3
114.3
68.6
66.7
41.3
34.3
33.1
31.9
19.1
14.3
13.5

IR peaks (cm^{-1}): amine NH stretch 3290 aldehyde C-H stretch 2800 and 2750 C=C stretch 1630 acyl C-O stretch 1250
sp^2 C-H stretch 3030 sp^3 C-H stretch 2960-2850 aldehyde C=O stretch 1720 sp^3 C-H bend 1470, 1380 alkoxy C-O stretch 1070, 1030
conj. ketone C=O stretch 1690 ortho aromatic C-H bend 770-730

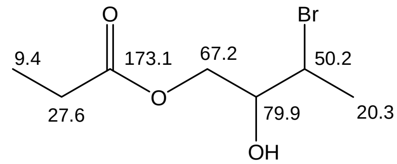
Problem 21 (p. 314)

21.



$C_7H_{13}BrO_3$
Exact Mass: 224

m/e: 224.00 (100.0%),
225.01 (7.8%),
226.00 (97.3%),
227.01 (7.7%)



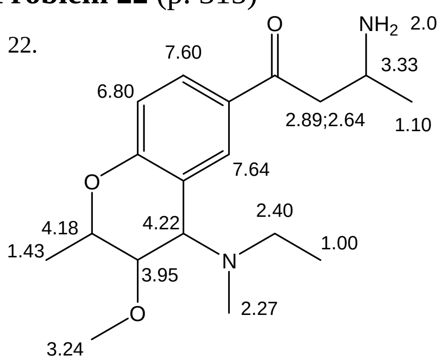
173.1
79.9
67.2
50.2
27.6
20.3
9.4

4.36
4.11 4.22 3.68 2.29 2.0 1.79 1.14

IR peaks (cm^{-1}): ester C=O stretch 1740; sp^3 C-H stretch 2960-2850; sp^3 C-H bend 1470, 1380; acyl C-O stretch 1250; alkoxy C-O stretch 1070, 1030; alcohol O-H stretch 3290

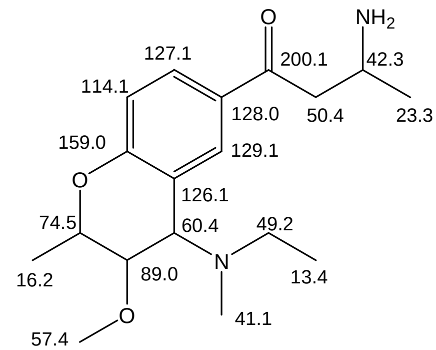
Problem 22 (p. 315)

22.



$C_{18}H_{28}N_2O_3$
Exact Mass: 320.21

M+ = 320.21 (100.0%),
M+1 = 321.21 (20.3%),
M+2 = 322.22 (1.9%)



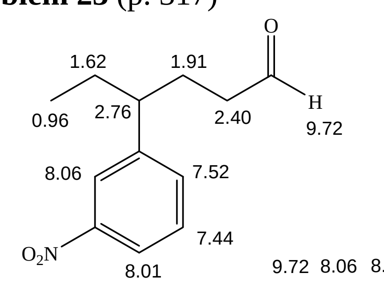
200.1
159.0
129.1
128.0
127.1
126.1
114.1
89.0
74.5
60.4
57.4
50.4
49.2
42.3
41.1
23.3
16.2
13.4

7.64 7.60 6.80 4.22 4.18 3.95 3.33 3.24 2.89;2.64 2.40 2.27 2.0 1.43 1.10 1.00

IR peaks (cm^{-1}): sp^2 C-H stretch 3030; C=C stretch 1630; conj. ketone C=O stretch 1698; alkoxy C-O stretch 1070, 1030; acyl C-O stretch 1250; amine NH_2 stretch 3290; sp^3 C-H stretch 2960-2850; sp^3 C-H bend 1470, 1380

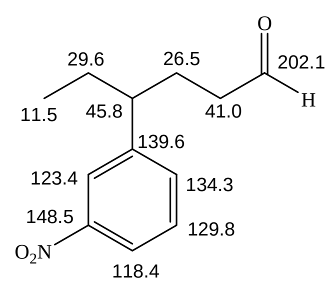
Problem 23 (p. 317)

23.



$C_{12}H_{15}NO_3$
Exact Mass: 221.11

M+ = 221.11 (100.0%),
M+1 = 222.11 (13.3%),
M+2 = 223.11 (1.5%)



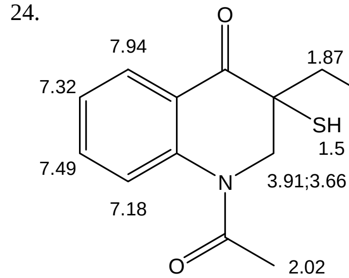
202.1
148.5
139.6
134.3
129.8
123.4
118.4
45.8
41.0
29.6
26.5
11.5

9.72 8.06 8.01 7.52 7.44 2.76 2.40 1.91 1.62 0.96

IR peaks (cm^{-1}): nitro N-O stretch 1550 and 1350; aldehyde C-H stretch 2800 and 2750; aldehyde C=O stretch 1720; sp^3 C-H stretch 2960-2850; sp^3 C-H bend 1470, 1380; sp^2 C-H stretch 3030; C=C stretch 1630; meta aromatic C-H bend 880, 760, 690

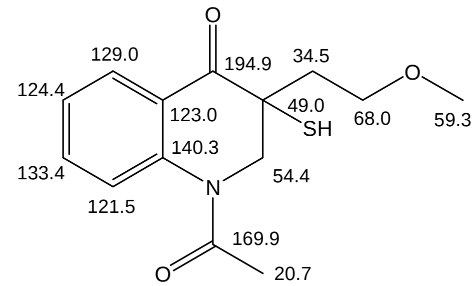
Problem 24 (p. 318)

24.



$C_{14}H_{17}NO_3S$
Exact Mass: 279.09

M+ = 279.09 (100.0%),
M+1 = 280.10 (16.7%),
M+2 = 281.09 (6.5%),



194.9
169.9
140.3
133.4
129.0
124.4
123.0
121.5
68.0
59.3
54.4
49.0
34.5
20.7

7.94 7.49 7.32 7.18 3.91 3.66 3.37 2.02 1.87 1.5

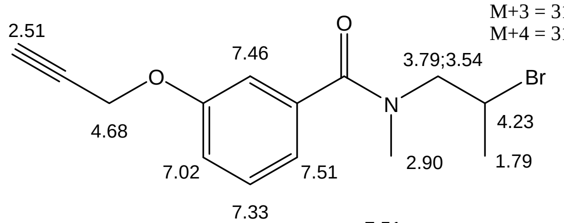
IR peaks (cm^{-1}): sp^2 C-H stretch 3030, C=C stretch 1630, ortho aromatic C-H bend 770-730; conj. ketone C=O stretch 1698, amide C=O stretch 1698, alkoxy C-O stretch 1070, 1030; thiol S-H stretch 2650

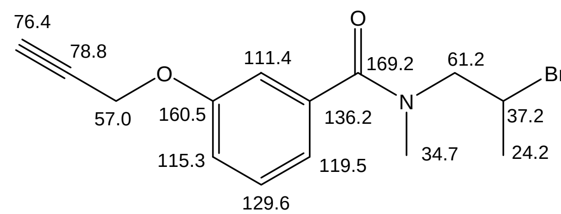
Problem 25 (p. 320)

$C_{14}H_{16}BrNO_2$
Exact Mass: 309.04

25.

M+1 = 309.04 (100.0%),
M+2 = 310.04 (15.4%),
M+3 = 311.03 (98.8%),
M+4 = 312.04 (15.1%),





169.2
160.5
136.2
129.6
119.5
115.3
111.4
78.8
76.4
61.2
57.0
37.2
34.7
24.2

7.46 7.51 7.33 7.02 4.68 4.23 3.79 3.54 2.90 2.51 1.79

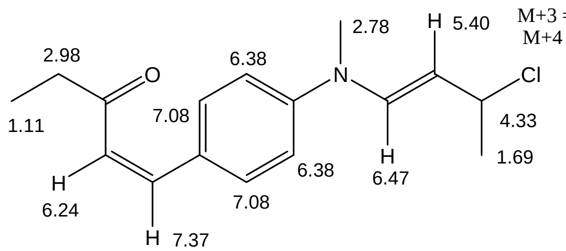
IR peaks (cm^{-1}): sp^2 C-H stretch 3030, C=C stretch 1630, sp C-H stretch 3300; amide C=O stretch 1698, alkoxy C-O stretch 1070, 1030; meta aromatic C-H bend 880, 760, 690, sp^3 C-H stretch 2960-2850, sp^3 C-H bend 1470, 1380

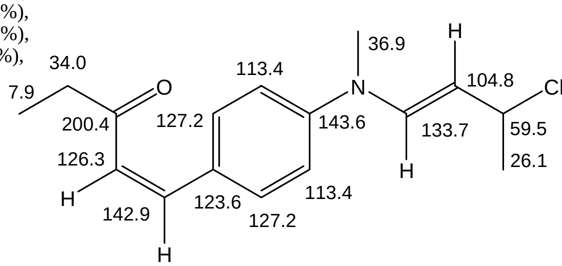
Problem 26 (p. 321)

$C_{16}H_{20}ClNO$
Exact Mass: 277.12

26.

M+1 = 277.12 (100.0%),
M+2 = 278.13 (17.6%),
M+3 = 279.12 (33/7%),
M+4 = 280.12 (5.7%),





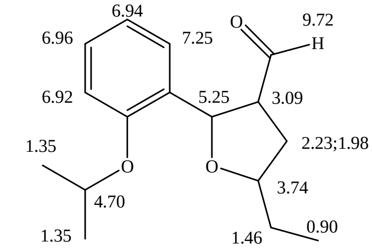
200.4
143.6
142.9
133.7
127.2 x 2
126.3
123.6
113.4 x 2
104.8
59.5
36.9
34.0
26.1
7.9

7.37 7.08 6.47 6.38 6.24 5.40 4.33 2.98 2.78 1.69 1.11

IR peaks (cm^{-1}): sp^2 C-H stretch 3030, C=C stretch 1630; conj. ketone C=O stretch 1698, sp^3 C-H stretch 2960-2850, sp^3 C-H bend 1470, 1380; para aromatic C-H bend 840-790

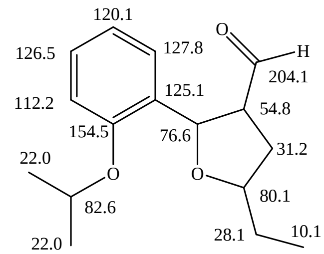
Chapter 8 - Complex Structure Problems

Problem 1. (p. 323)

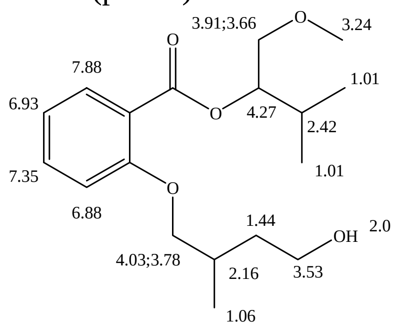


$C_{16}H_{22}O_3$
Exact Mass: 262.16

M+ = 262.16 (100.0%),
M+1 = 263.16 (17.7%),
M+2 = 264.16 (2.0%)

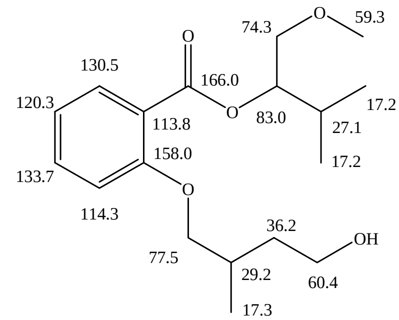


Problem 2. (p. 326)

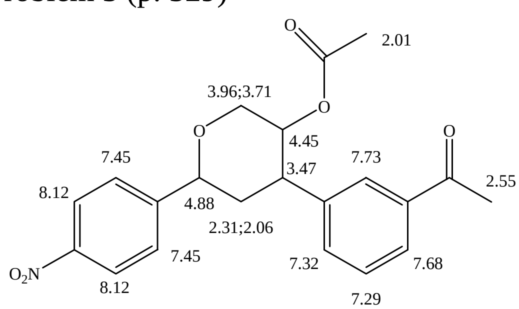


$C_{18}H_{28}O_5$
Exact Mass: 324.19

M+ = 324.19 (100.0%),
M+1 = 325.20 (20.0%),
M+2 = 326.20 (2.9%)

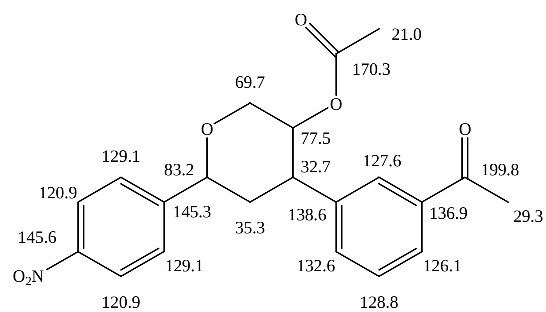


Problem 3 (p. 329)

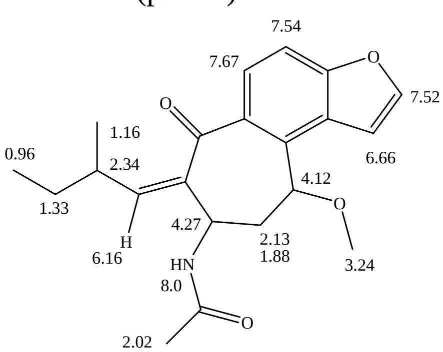


$C_{21}H_{21}NO_6$
Exact Mass: 383.14

M+ = 383.14 (100.0%),
M+1 = 384.14 (23.2%),
M+2 = 385.14 (3.8%)

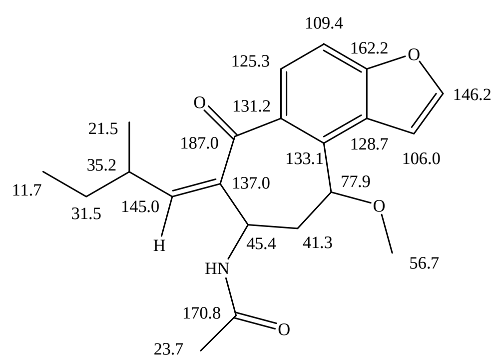


Problem 4 (p. 332)

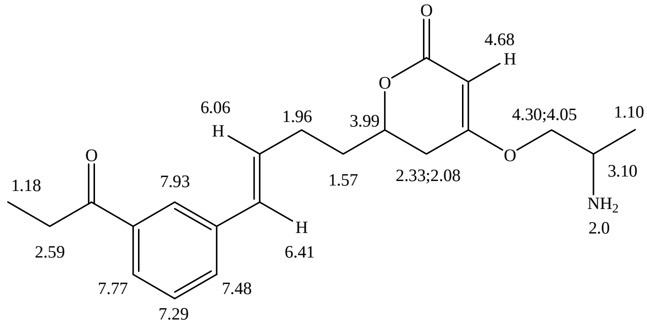


$C_{21}H_{25}NO_4$
Exact Mass: 355.18

M+ = 355.18 (100.0%),
M+1 = 356.18 (23.5%),
M+2 = 357.19 (2.6%)

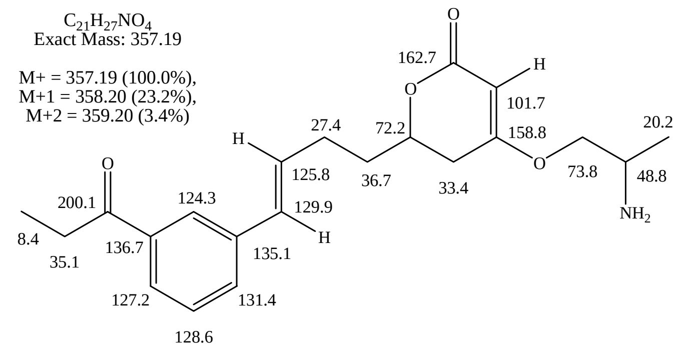


Problem 5 (p. 335)



$C_{21}H_{27}NO_4$
Exact Mass: 357.19

M+ = 357.19 (100.0%),
M+1 = 358.20 (23.2%),
M+2 = 359.20 (3.4%)

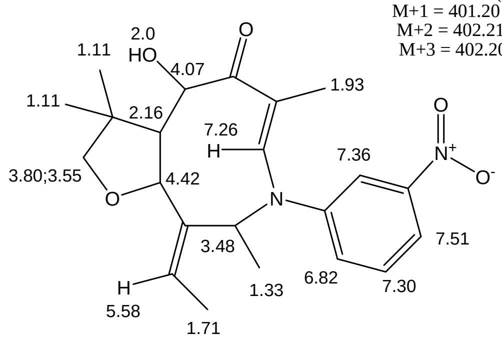


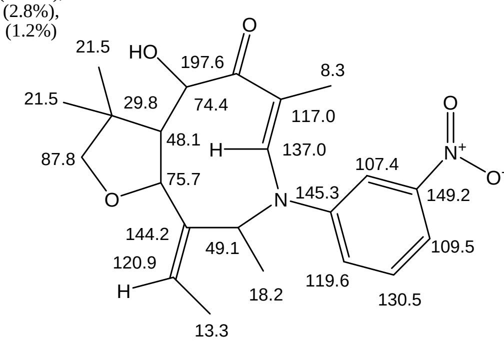
Problem 6 (p. 338)

$C_{22}H_{28}N_2O_5$
Exact Mass: 400.2

M+ = 400.20 (100.0%),
M+1 = 401.20 (24.7%),
M+2 = 402.21 (2.8%),
M+3 = 402.20 (1.2%)

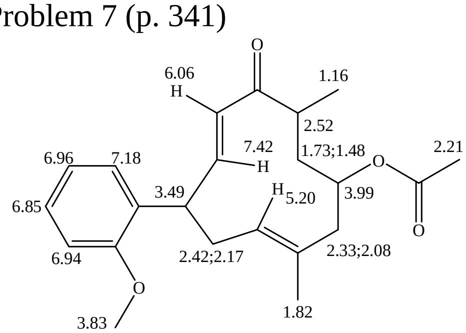
7.51
7.36
7.30
7.26
6.82
5.58
4.42
4.07
3.80;3.55
3.48
2.16
2.0
1.93
1.71
1.33
1.11x2





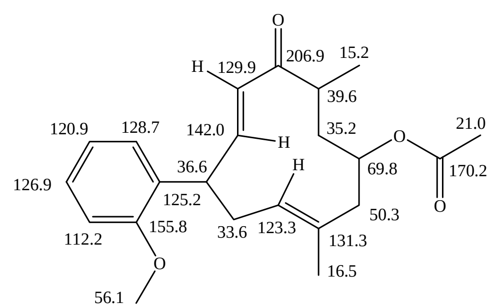
197.6
149.2
145.3
144.2
137.0
130.5
120.9
119.6
117.0
109.5
107.4
87.8
75.7
74.4
49.1
48.1
29.8
21.5 21.5
18.2
13.3
8.3

Problem 7 (p. 341)

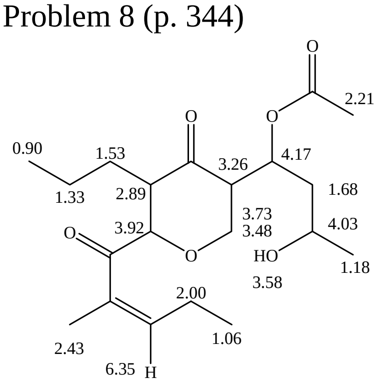


$C_{22}H_{28}O_4$
Exact Mass: 356.2

M+ = 356.20 (100.0%),
M+1 = 357.20 (23.9%),
M+2 = 358.21 (2.8%)

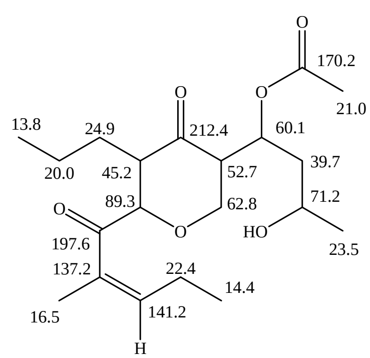


Problem 8 (p. 344)

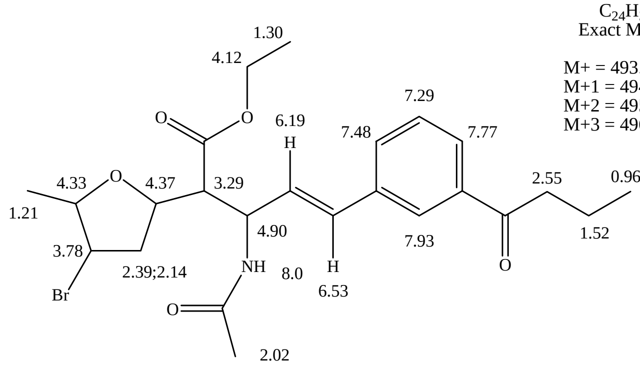


Chemical Formula: $C_{20}H_{32}O_6$
Exact Mass: 368.22

M+ = 368.22 (100.0%),
M+1 = 369.22 (21.9%),
M+2 = 370.23 (2.4%),

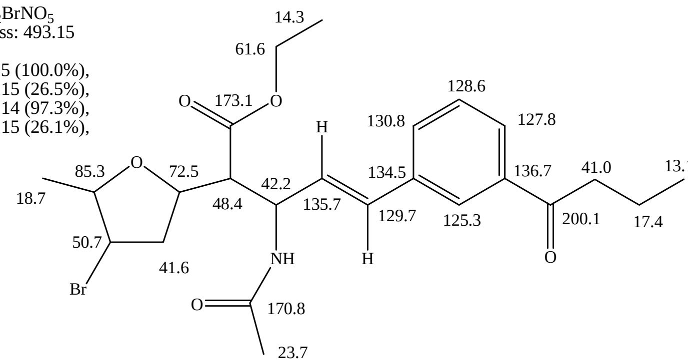


Problem 9 (p. 347)

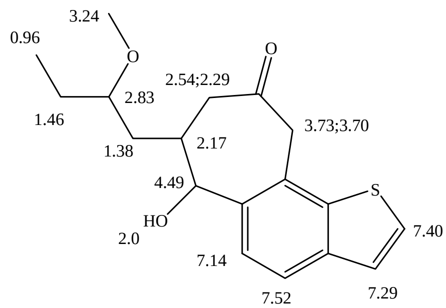


$C_{24}H_{32}BrNO_5$
Exact Mass: 493.15

M+ = 493.15 (100.0%),
M+1 = 494.15 (26.5%),
M+2 = 495.14 (97.3%),
M+3 = 496.15 (26.1%),

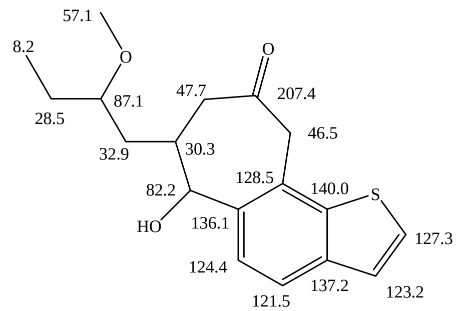


Problem 10 (p. 350)



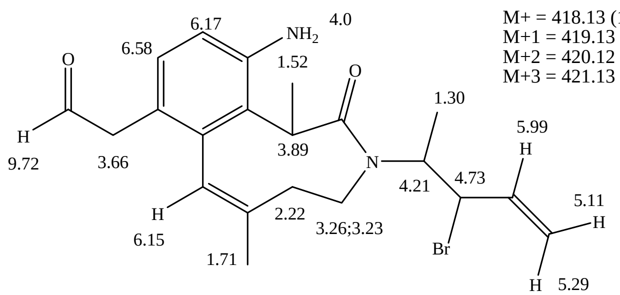
$C_{18}H_{22}O_3S$
Exact Mass: 318.13

M+ = 318.13 (100.0%),
M+1 = 319.13 (20.4%),
M+2 = 320.12 (4.5%),

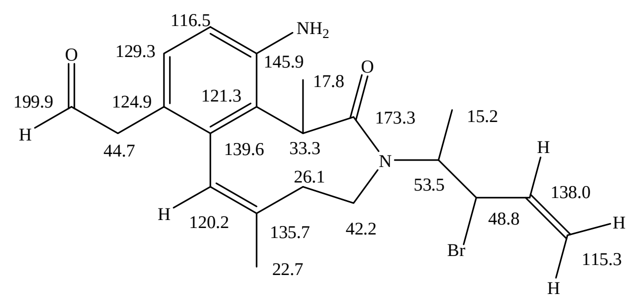


Problem 11 (p. 353)

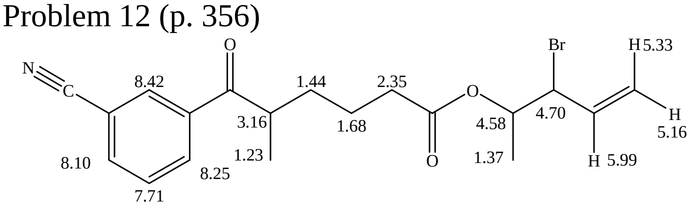
$C_{21}H_{27}BrN_2O_2$
Exact Mass: 418.13



M+ = 418.13 (100.0%),
M+1 = 419.13 (23.1%),
M+2 = 420.12 (97.3%),
M+3 = 421.13 (22.6%),

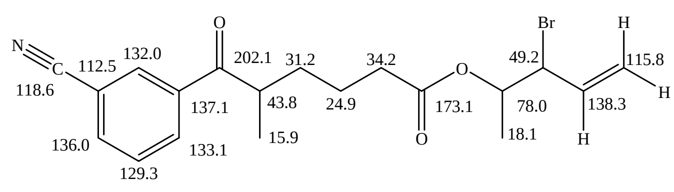


Problem 12 (p. 356)

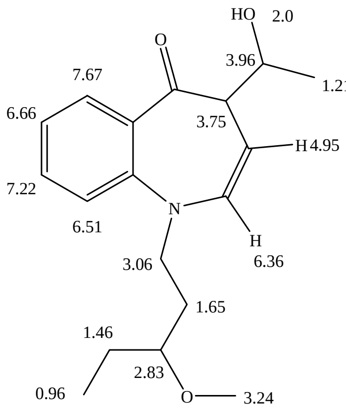


Chemical Formula: $C_{19}H_{22}BrNO_3$
Exact Mass: 391.08

M+ = 391.08 (100.0%),
M+1 = 392.08 (21.3%),
M+2 = 393.08 (98.0%),
M+3 = 394.08 (20.4%),

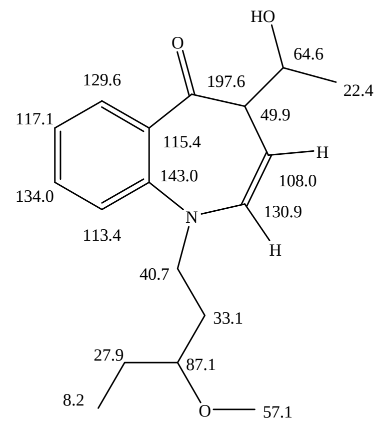


Problem 13 (p. 359)

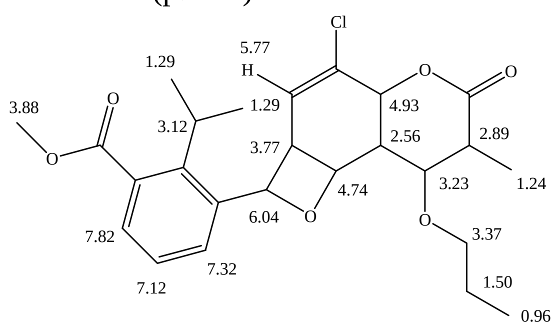


$C_{18}H_{25}NO_3$
Exact Mass: 303.18

M+ = 303.18 (100.0%),
M+1 = 304.19 (19.9%),
M+2 = 305.19 (2.5%)

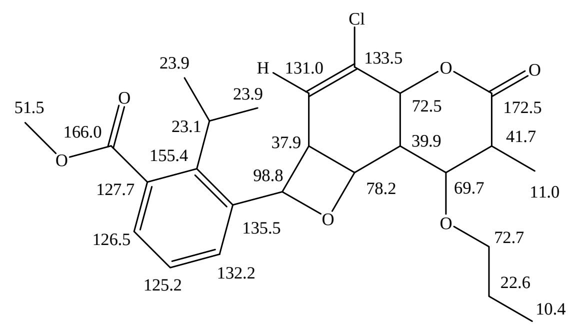


Problem 14 (p. 362)

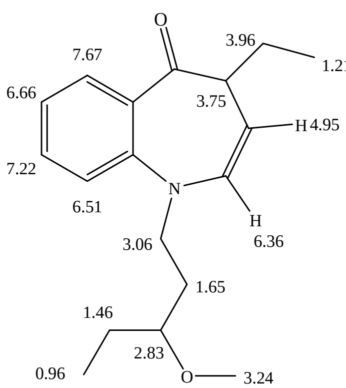


$C_{25}H_{31}ClO_6$
Exact Mass: 462.18

M+ = 462.18 (100.0%),
M+1 = 463.18 (27.0%),
M+2 = 464.18 (32.0%),
M+3 = 465.18 (8.8%),



Problem 15 (p. 365)



$C_{18}H_{25}NO_3$
Exact Mass: 303.18

M+ = 303.18 (100.0%),
M+1 = 304.19 (19.9%),
M+2 = 305.19 (2.5%)