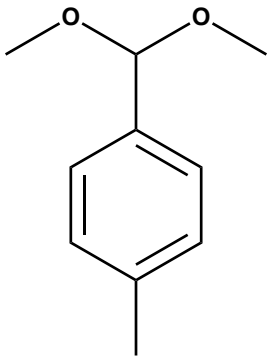
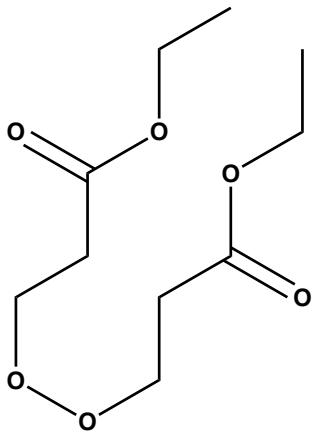
Problem Set 2
CHM 2211 – Spring 21
Prof. Joel M. Smith

On the compounds below, indicate the number of chemically distinct carbons and hydrogens by drawing them on the compound. Also, give the total number of each. Then give the expected multiplicity (s, d, t, q, etc.) for each hydrogen.

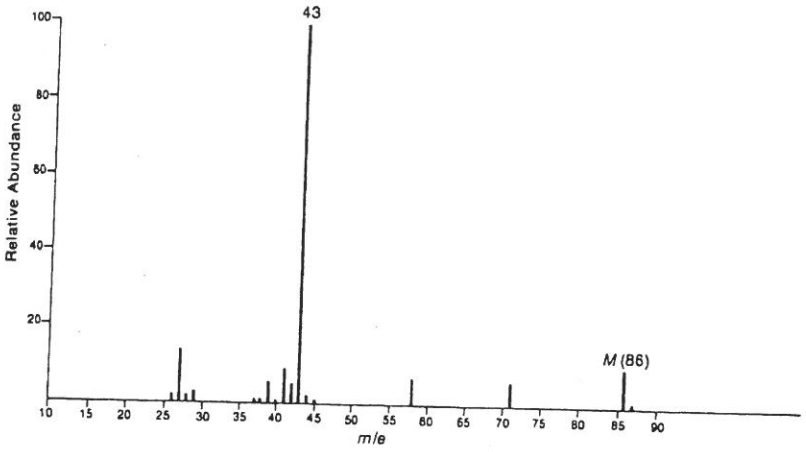




(*10.) The UV spectrum of this compound is determined in 95% ethanol: λ_{max} 280 nm (log ε 1.3). This compound has the formula $C_5H_{10}O$.

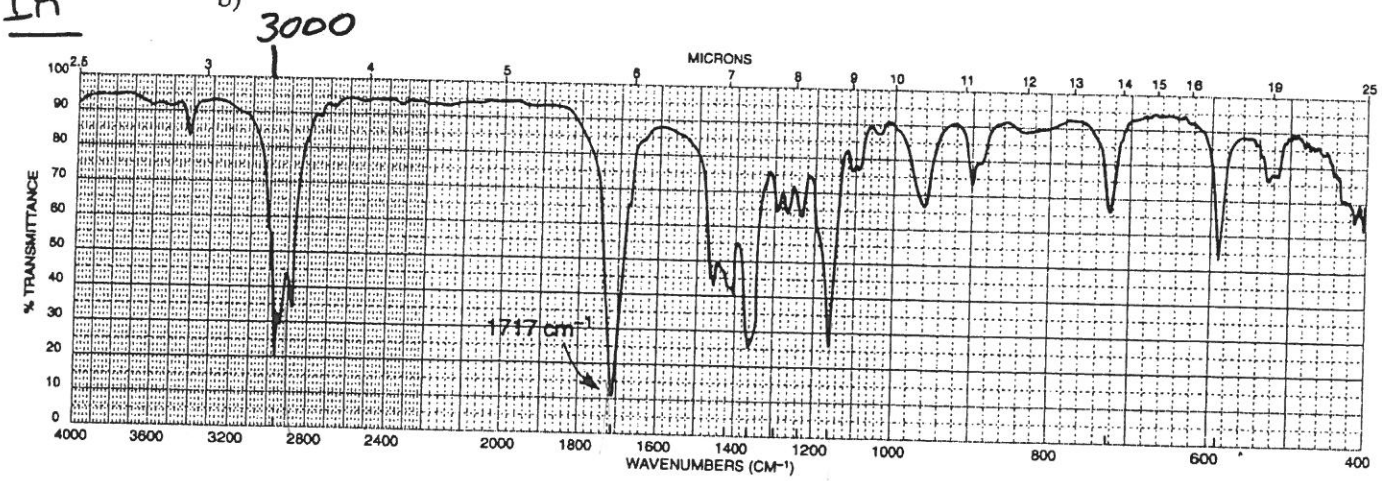
a)

Mass Spectrum



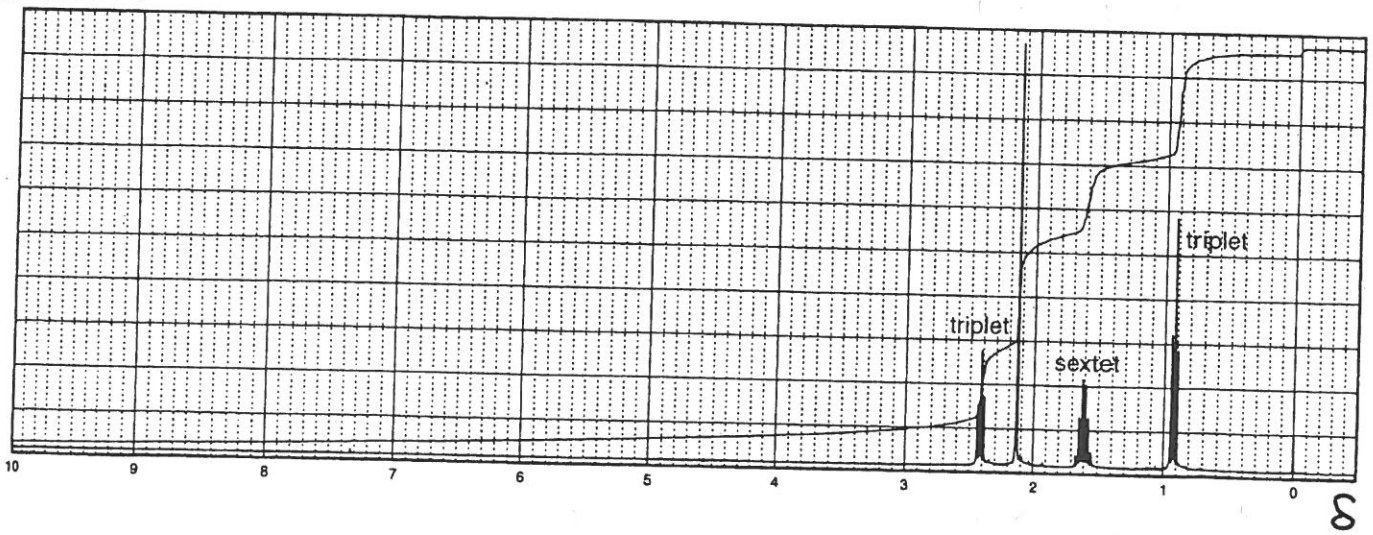
IR

b)



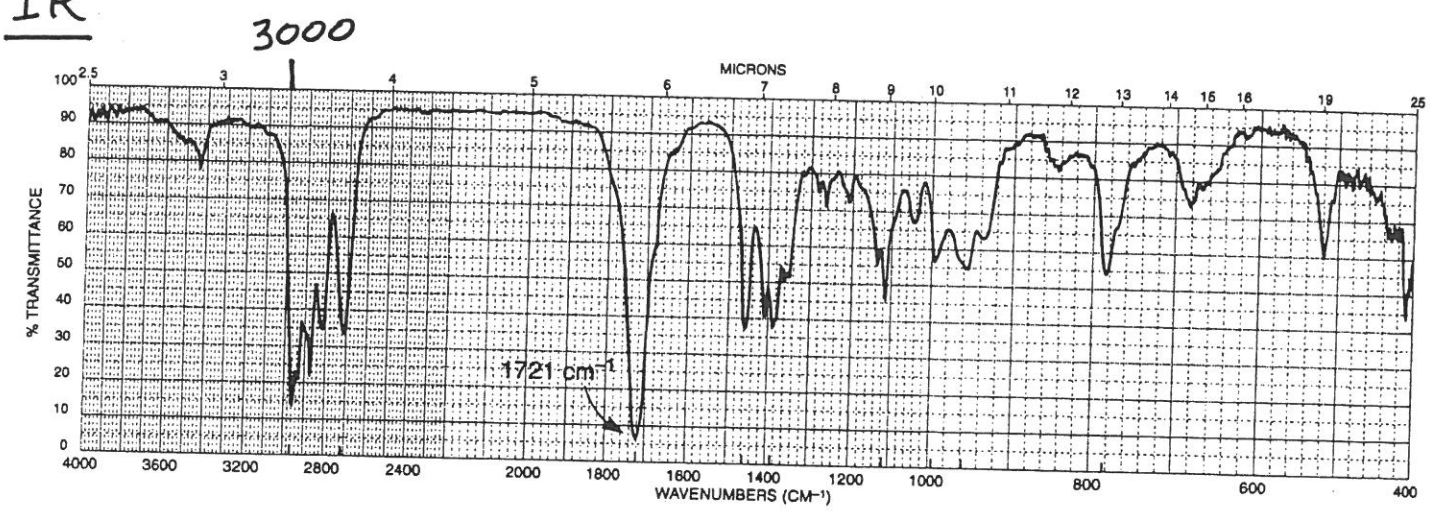
H-1 NMR

c)

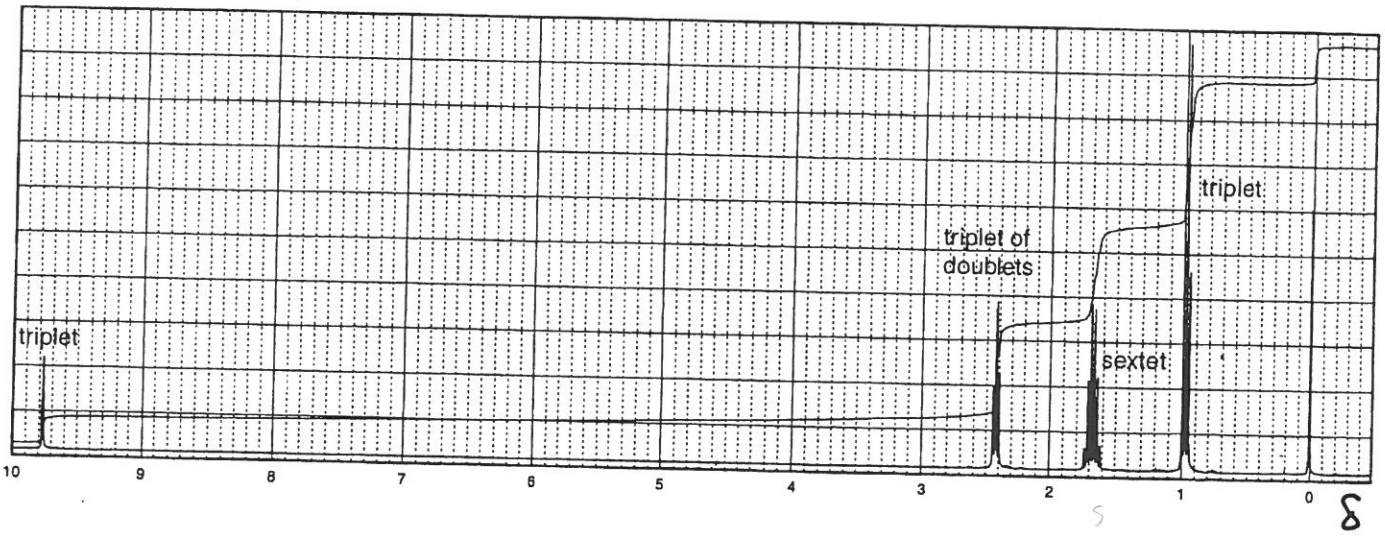


*13. This compound has the formula C_4H_8O. When expanded, the singlet peak at 9.8 ppm in the proton spectrum is actually a triplet. The triplet pattern at 2.4 ppm turns out to be a triplet of doublets when expanded.

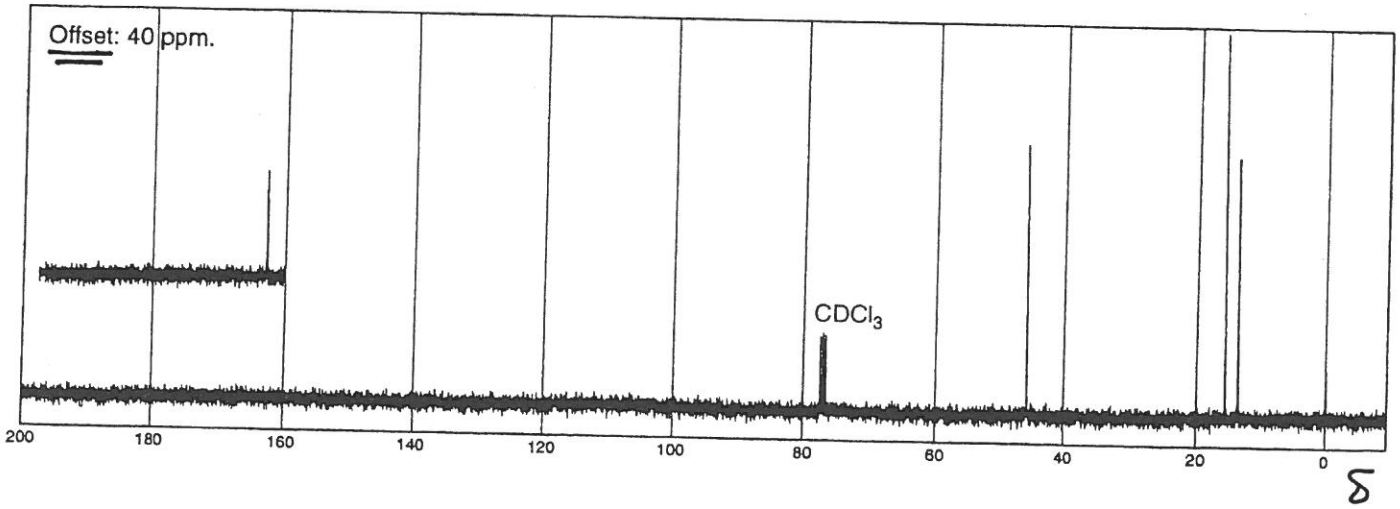
IR



H-1 NMR

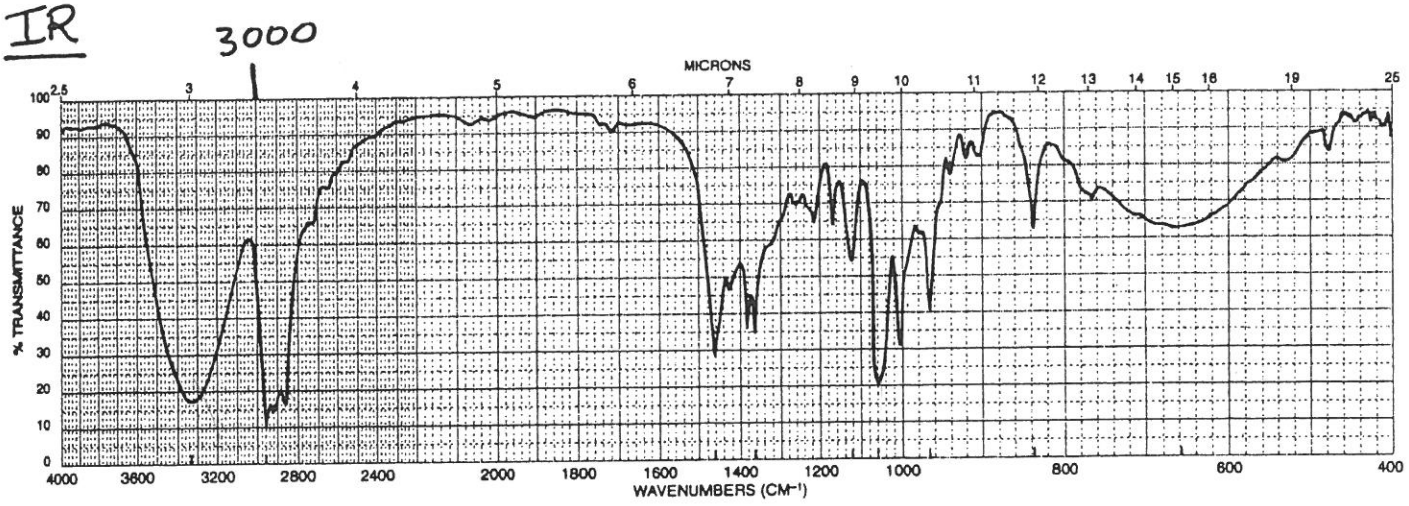


C-13 NMR

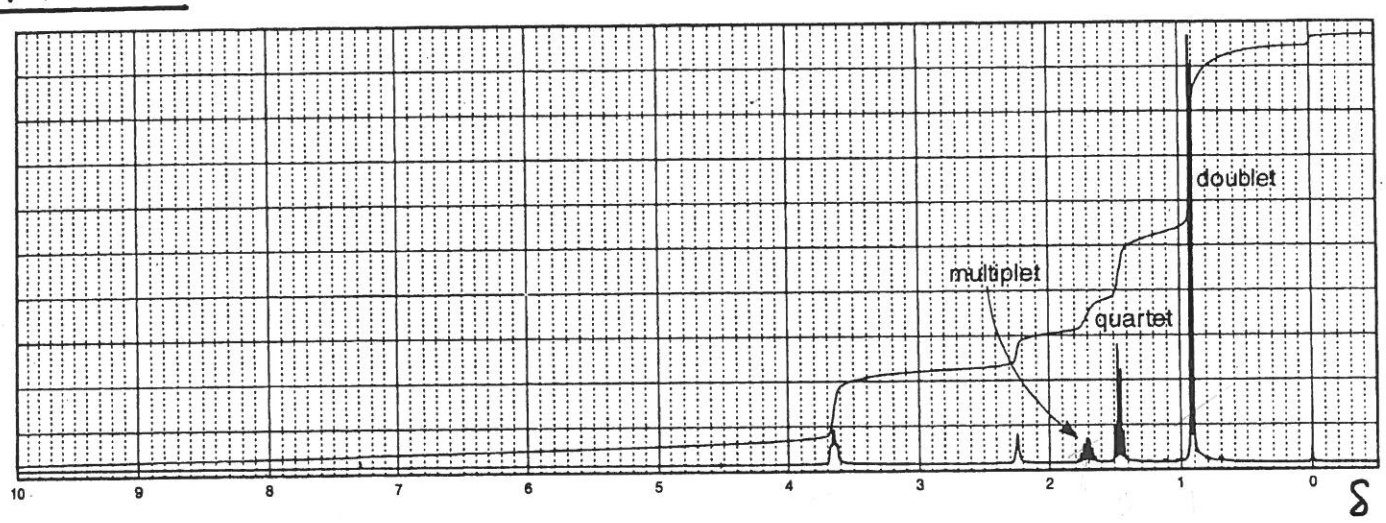


***14.** This compound has the formula $C_5H_{12}O$. When a trace of aqueous acid is added to the sample, the proton NMR spectrum resolves into a clean triplet at 3.6 ppm, and the broad peak at 2.2 ppm moves to 4.5 ppm.

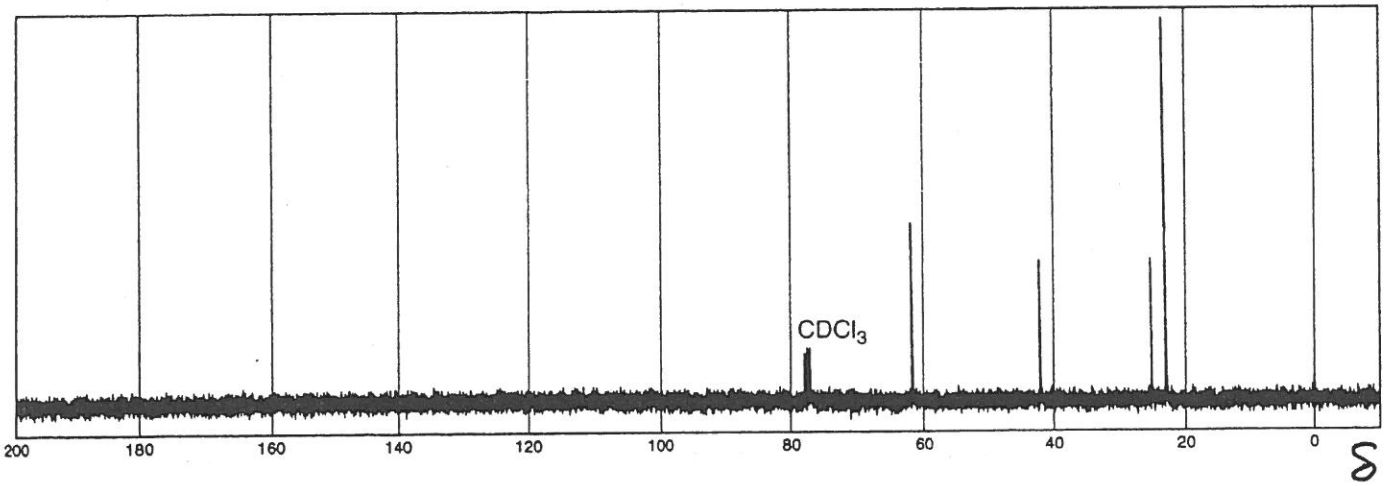
IR



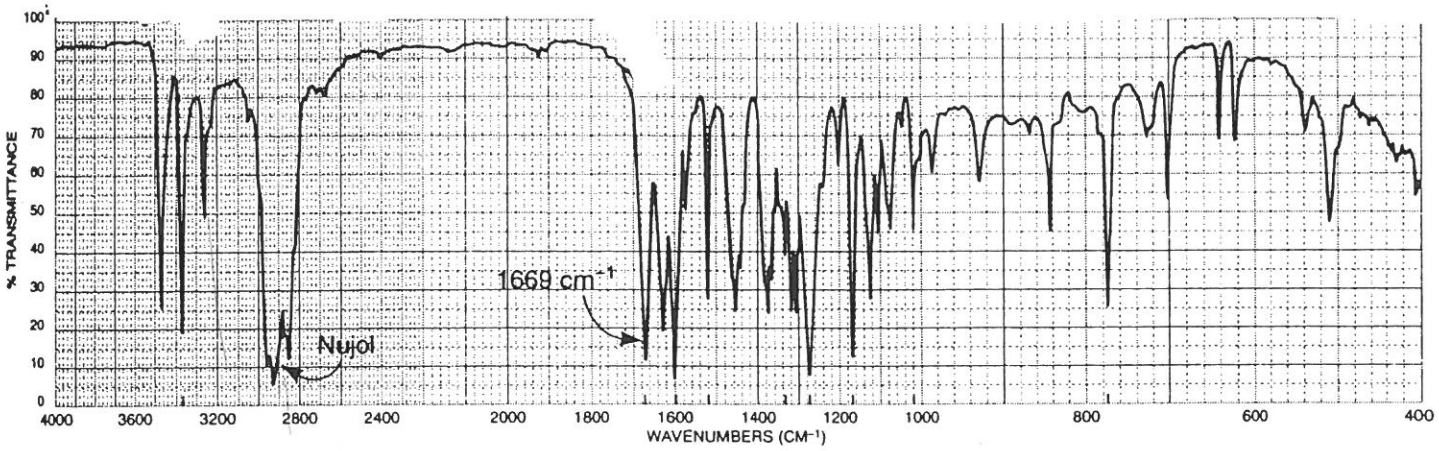
H-1 NMR

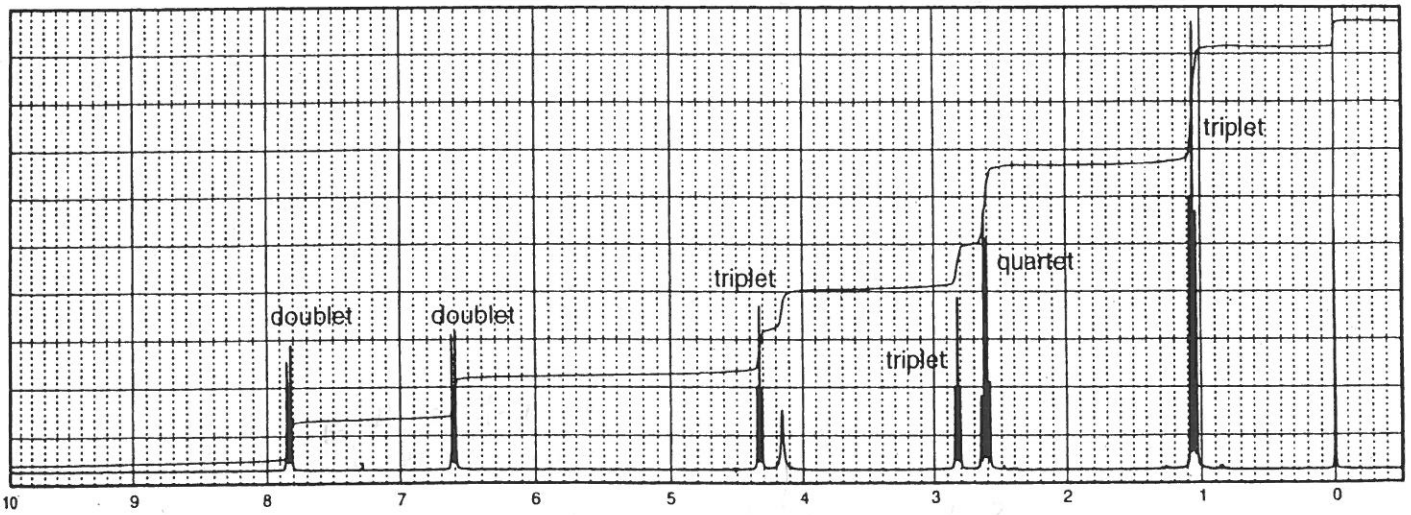


C-13 NMR



18. The anesthetic procaine (Novocaine) has the formula $C_{13}H_{20}N_2O_2$. In the proton NMR spectrum, each pair of triplets at 2.8 and 4.3 ppm has a coupling constant of 6 Hz. The triplet at 1.1 and the quartet at 2.6 ppm have coupling constants of 7 Hz. The IR spectrum was determined in Nujol. The C—H absorption bands of Nujol at about 2920 cm^{-1} in the IR spectrum obscure the entire C—H stretch region. The carbonyl group appearing at 1669 cm^{-1} in the IR spectrum has an unusually low frequency. Why?

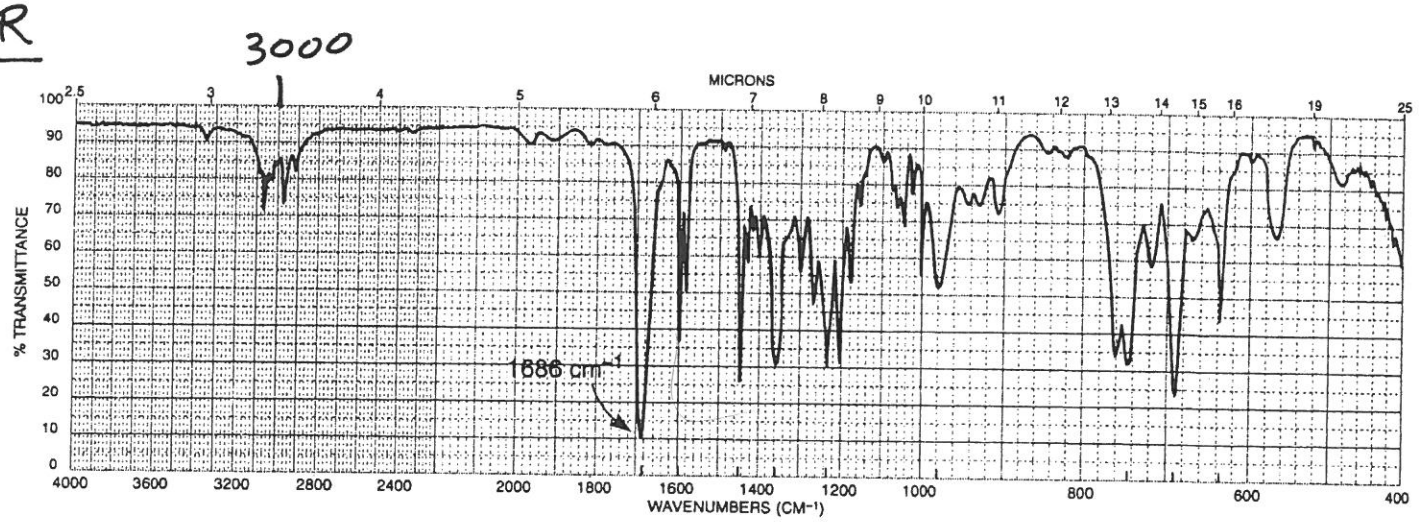




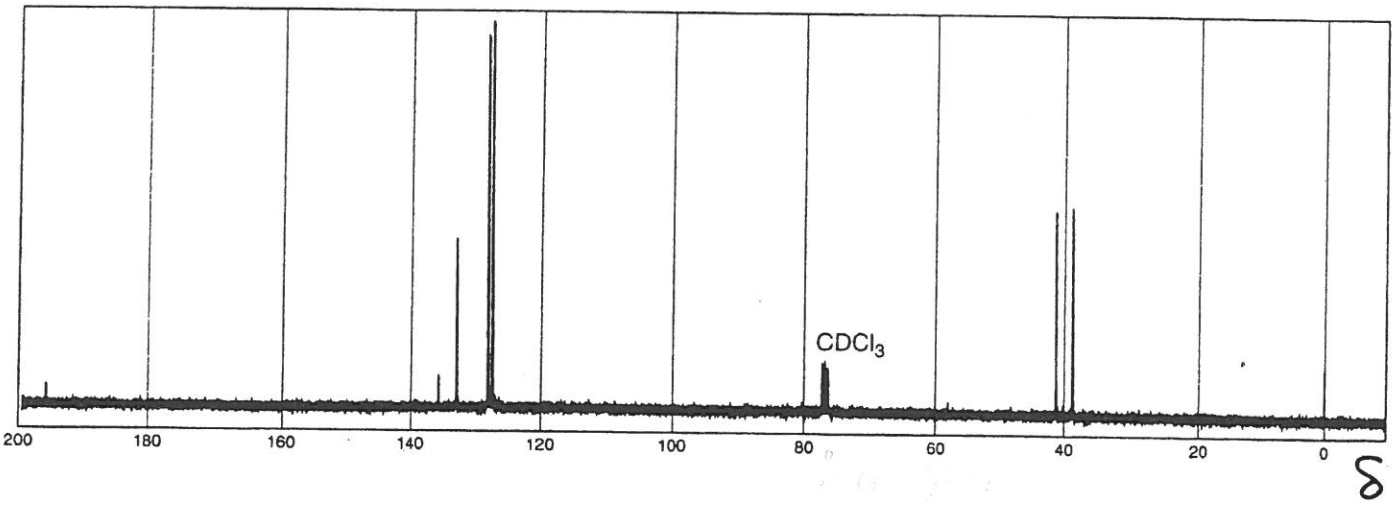
Normal Carbon	DEPT-135	DEPT-90
12 ppm	Positive	No peak
48	Negative	No peak
51	Negative	No peak
63	Negative	No peak
114	Positive	Positive
120	No peak	No peak
132	Positive	Positive
151	No peak	No peak

*17. This compound has the formula C_9H_9ClO. The full proton NMR spectrum is shown along with expansions of individual patterns.

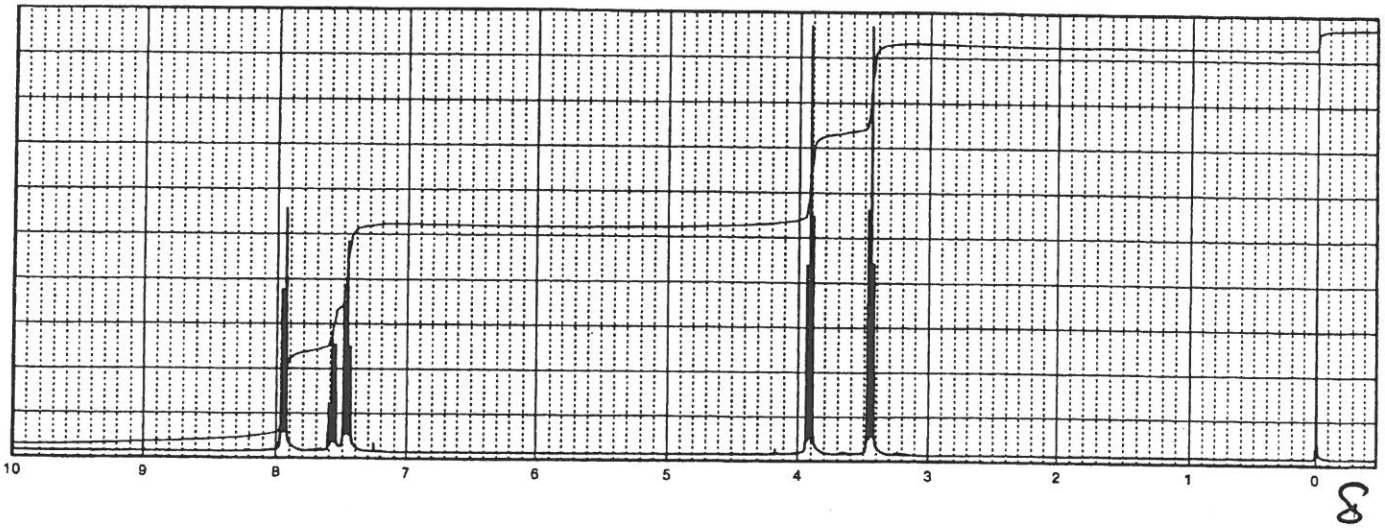
IR



C-13 NMR

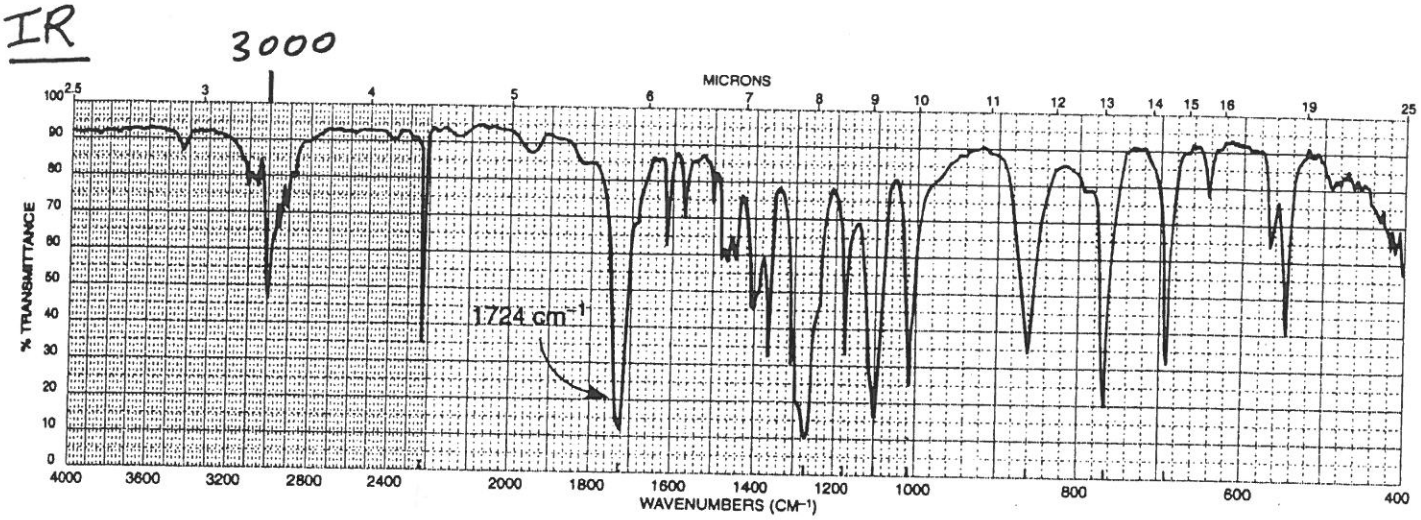


H-1 NMR

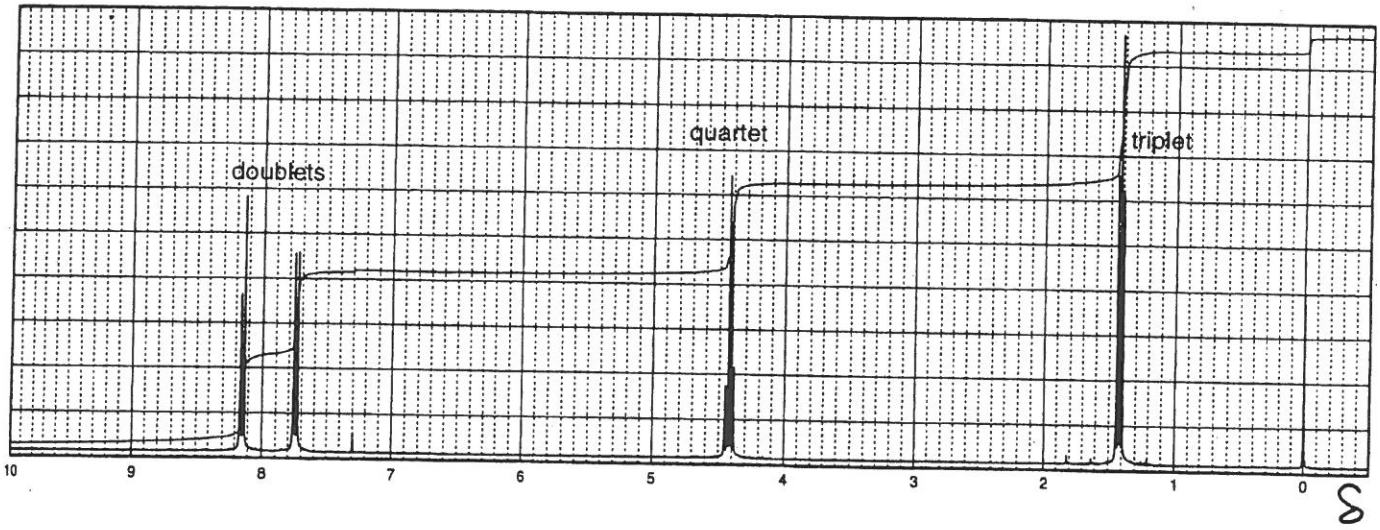


***16.** This compound has the molecular formula $C_{10}H_9NO_2$.

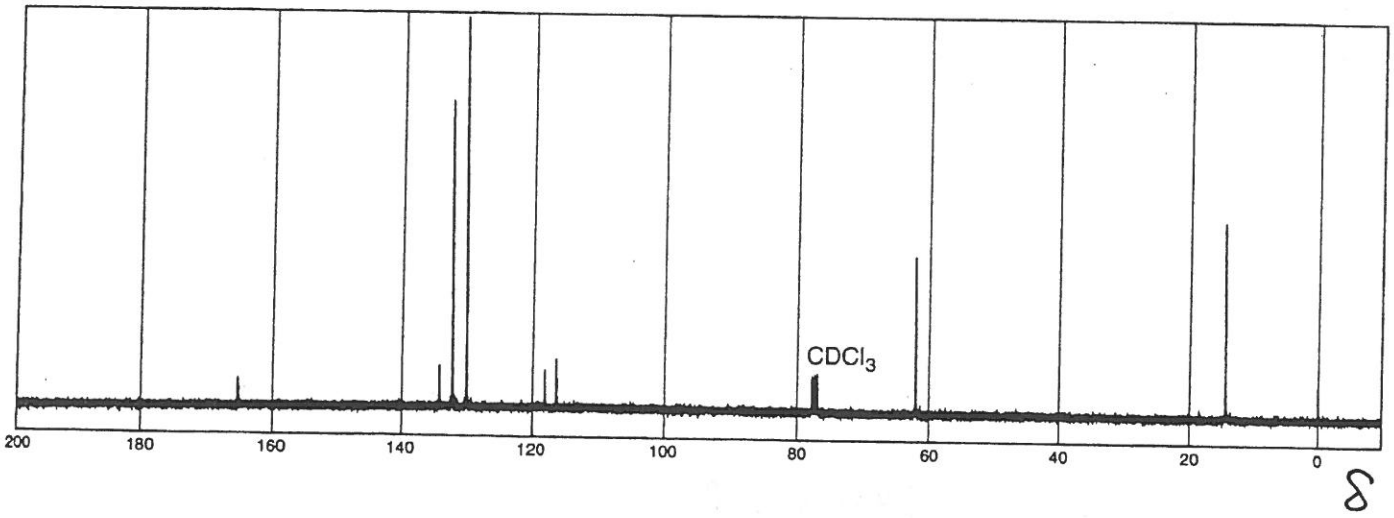
IR



H-1 NMR

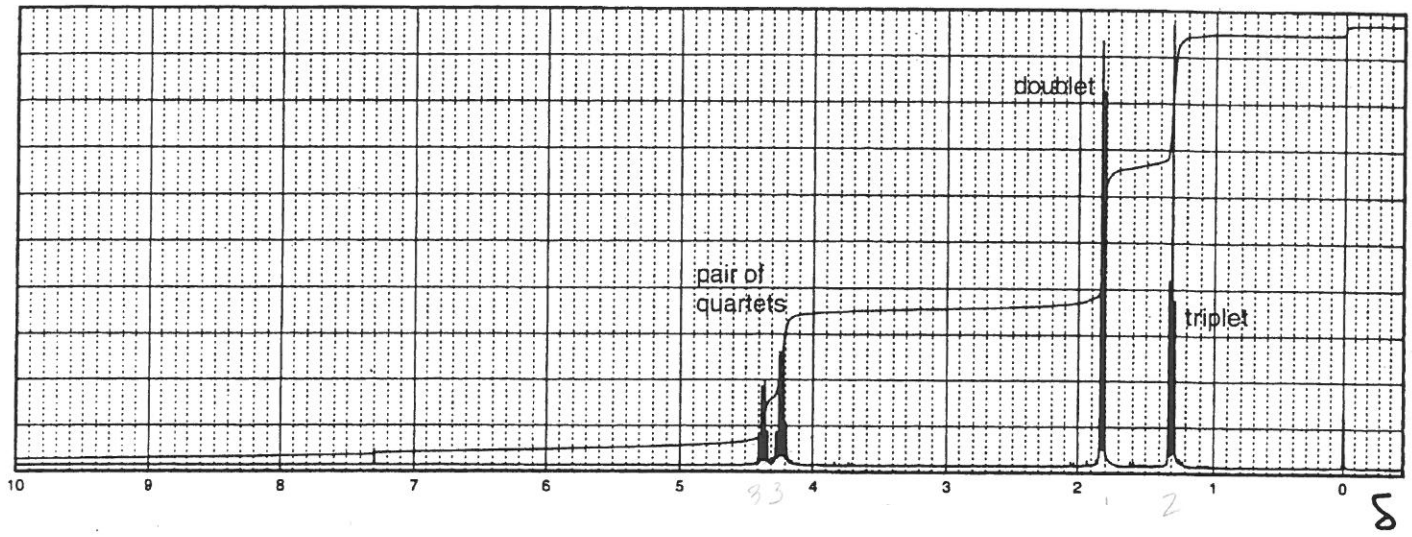


C-13 NMR

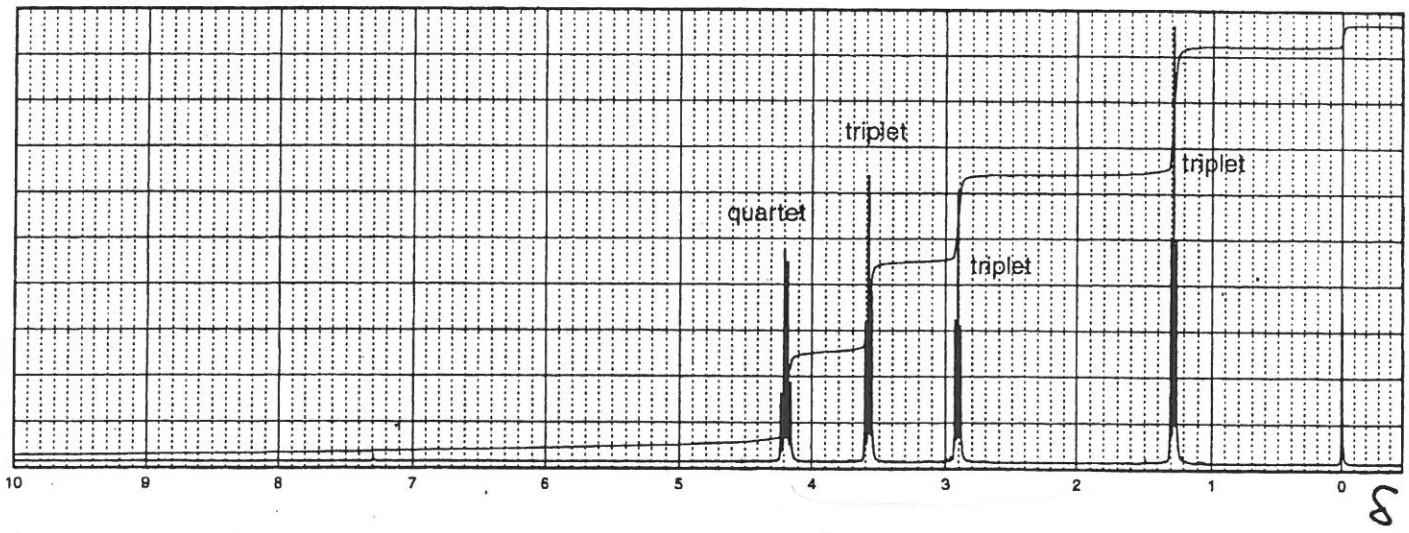


*15. Determine the structures of the isomeric compounds with the formula $C_5H_9BrO_2$. The proton NMR spectra for both compounds follow. The IR spectrum corresponding to the first proton NMR spectrum has strong absorption bands at 1739, 1225, and 1158 cm^{-1}, and that corresponding to the second one has strong bands at 1735, 1237, and 1182 cm^{-1}.

H-1 NMR

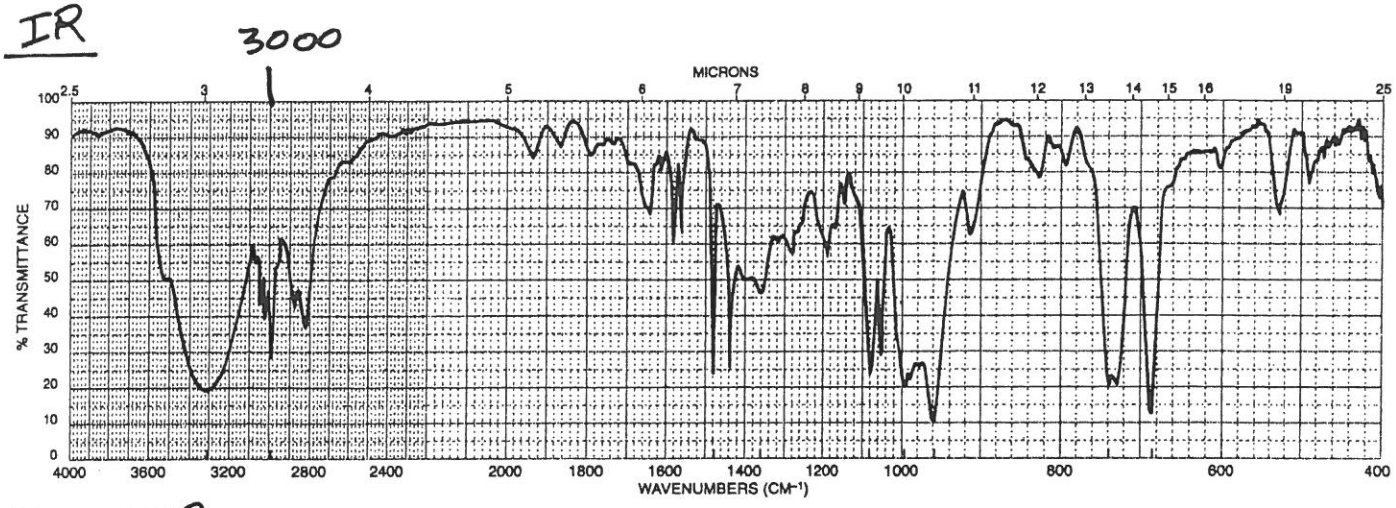


H-1 NMR

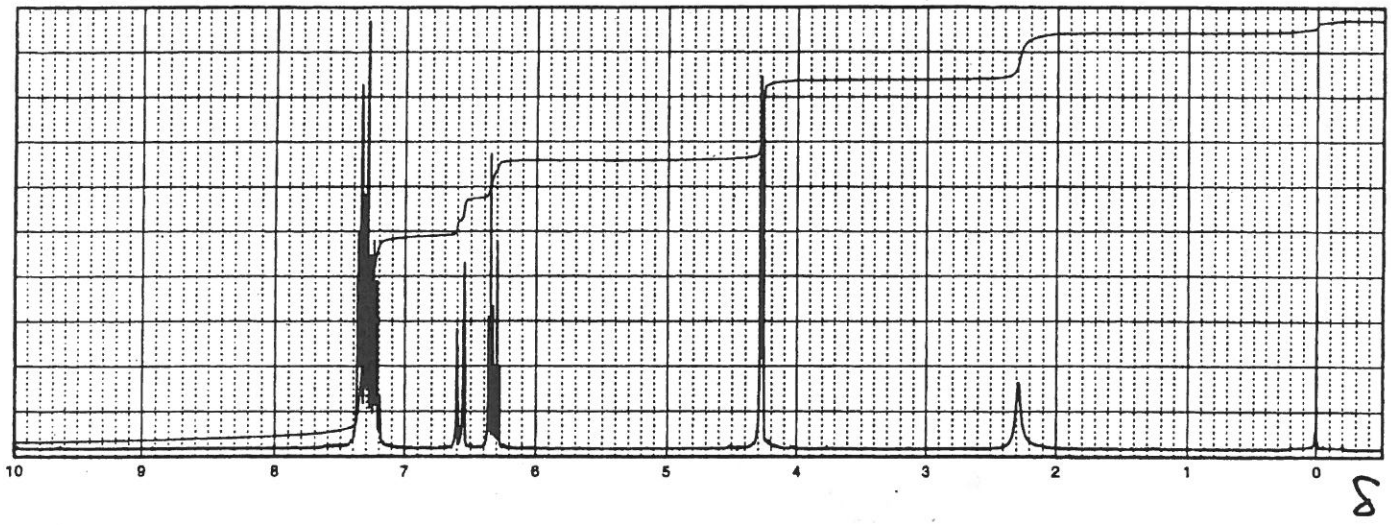


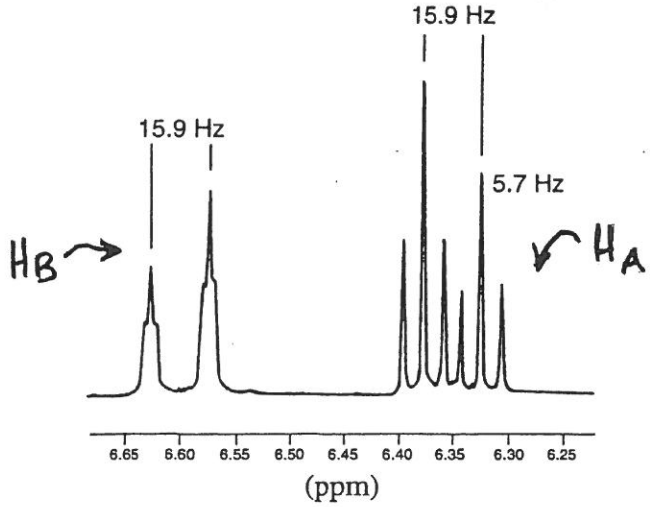
21. This compound has the molecular formula $C_9H_{10}O$. We have supplied you with the IR and proton NMR spectra. The expansions of the interesting sets of peaks centering near 4.3, 6.35, and 6.6 ppm in the proton NMR are provided, as well. Do not attempt to interpret the messy pattern near 7.4 ppm for the aromatic protons. The broad peak at 2.3 ppm (one proton) is solvent and concentration dependent.

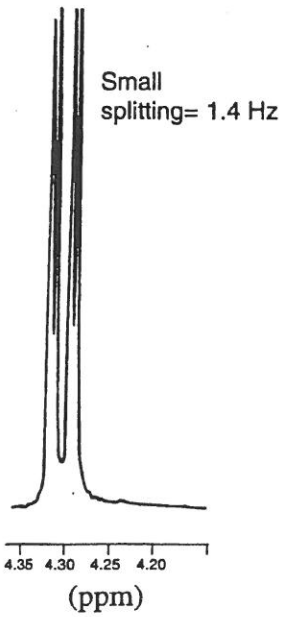
IR



H-1 NMR



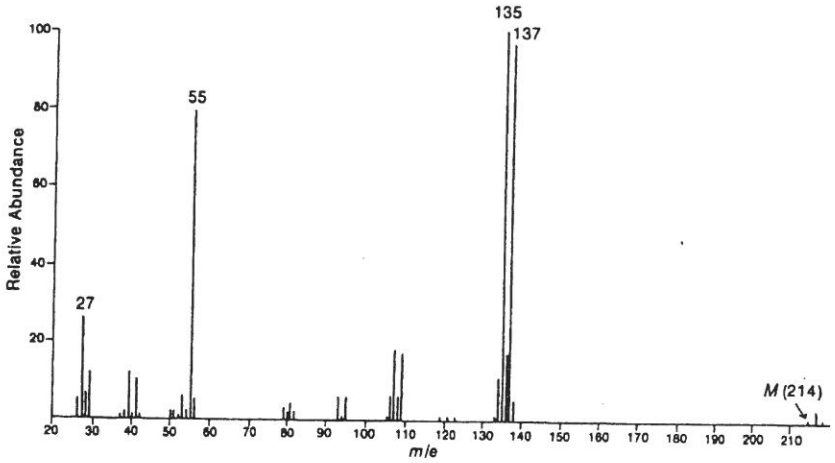




19. The UV spectrum of this compound shows no maximum above 250 nm. In the mass spectrum, notice that the patterns for the M, $M + 2$, and $M + 4$ peaks have a ratio of 1:2:1 (214, 216, and 218 amn). Draw the structure of the compound and comment on the structures of the mass 135 and 137 fragments.

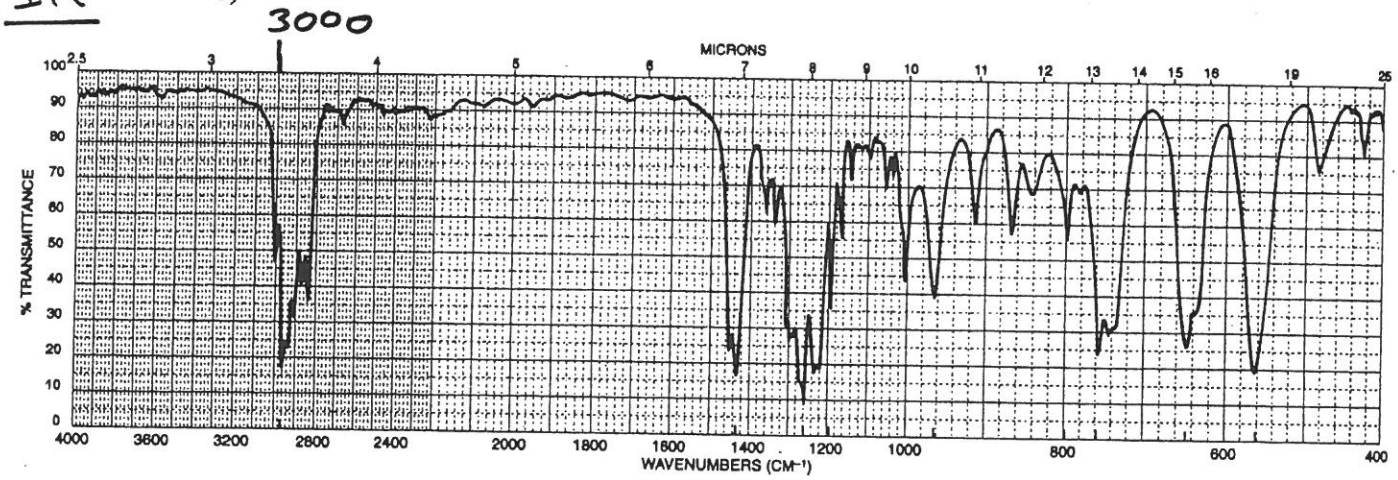
a)

Mass Spectrum



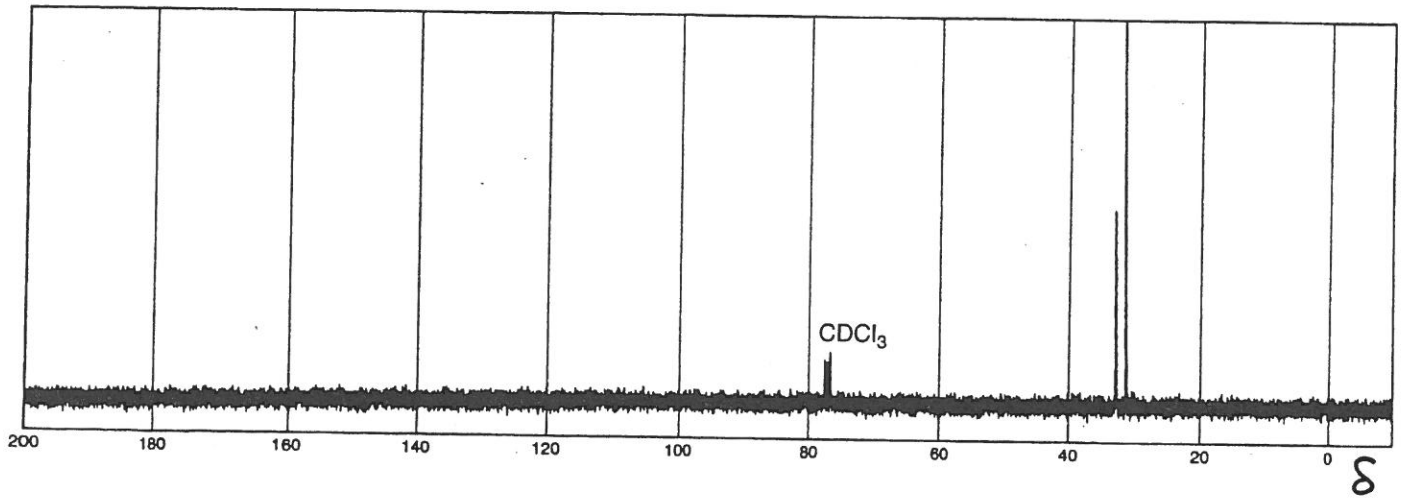
IR

b)



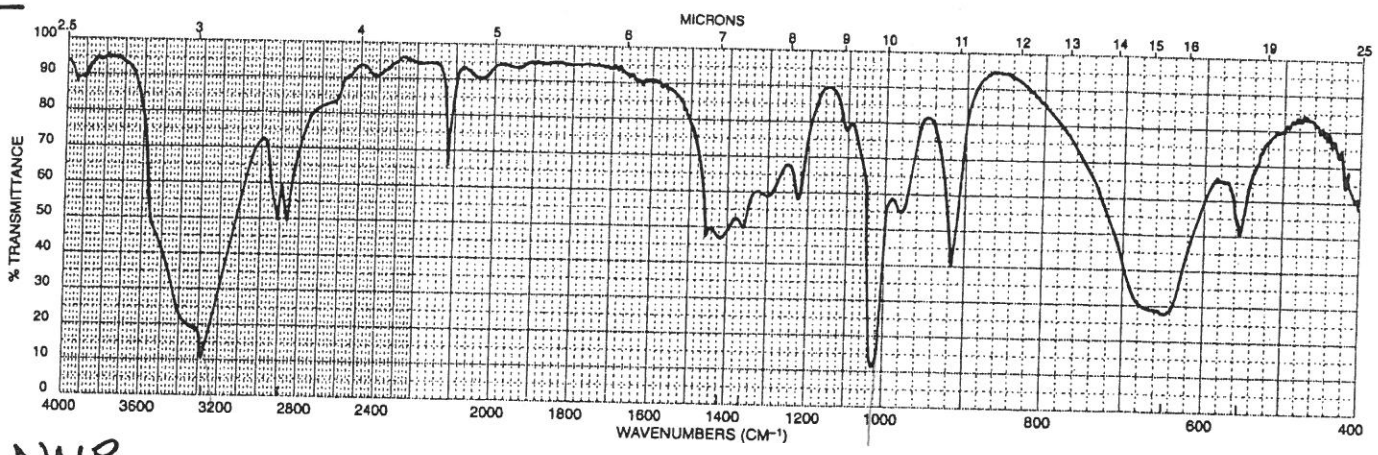
C-13 NMR

c)

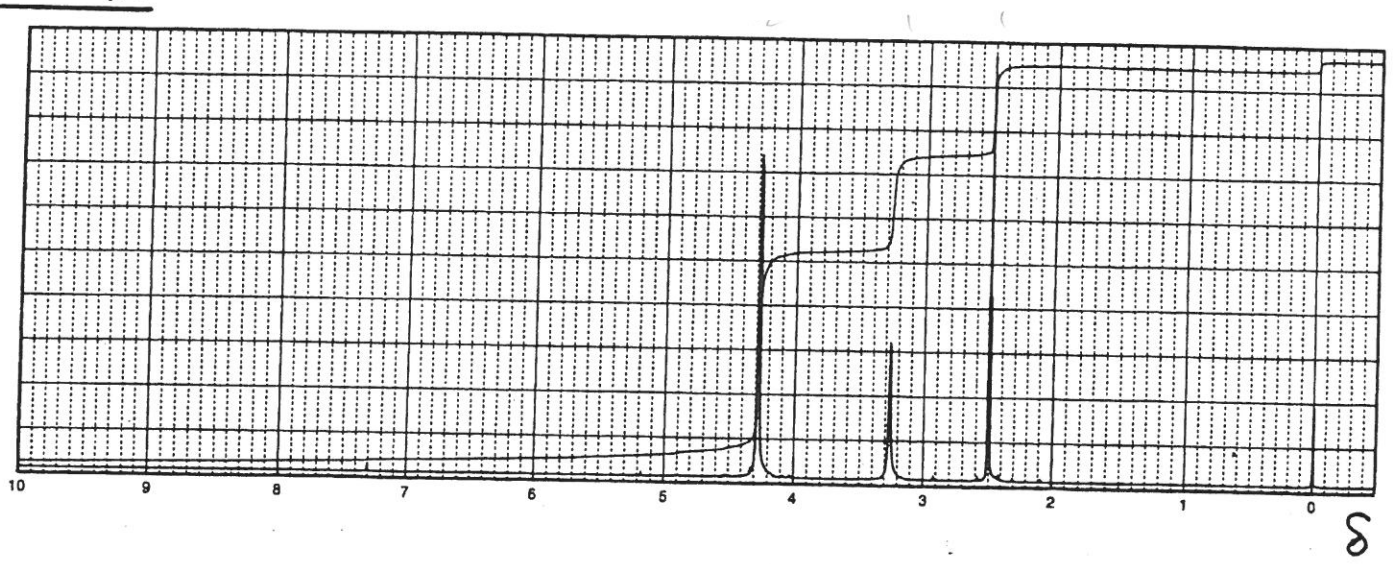


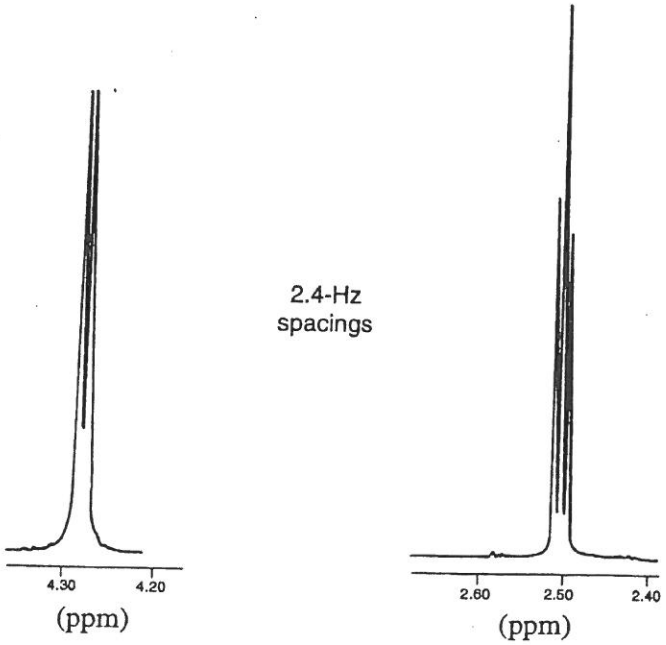
22. This compound has the formula C_3H_4O. We have supplied you with the IR and proton NMR spectra. Notice that a single peak at 3300 cm^{-1} overlaps the broad peak there. The expansions of the interesting sets of peaks centering near 2.5 and 4.3 ppm in the proton NMR are provided, as well. The peak at 3.25 ppm (one proton) is solvent and concentration dependent.

IR



H-1 NMR

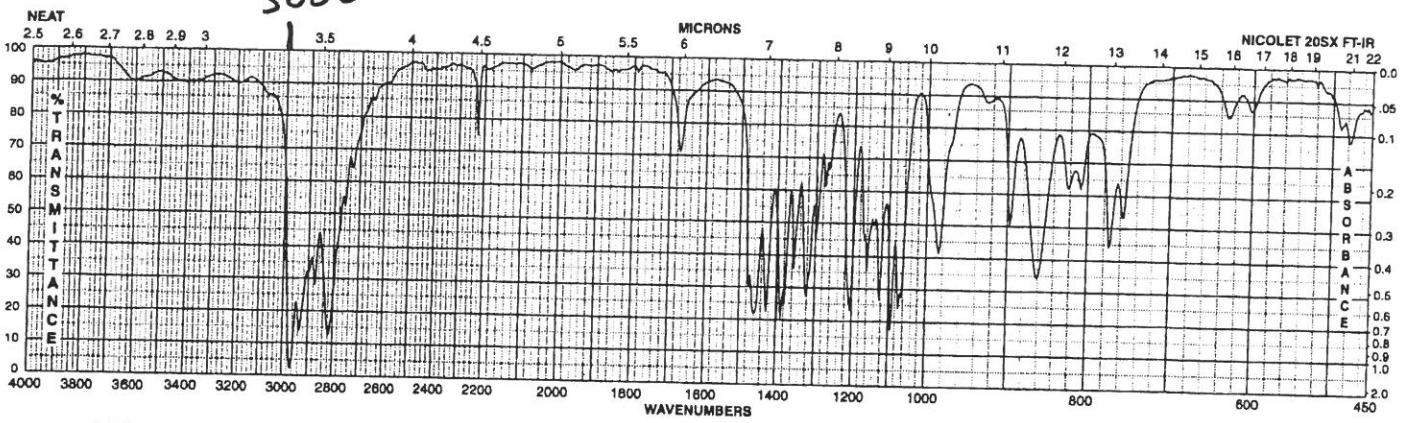




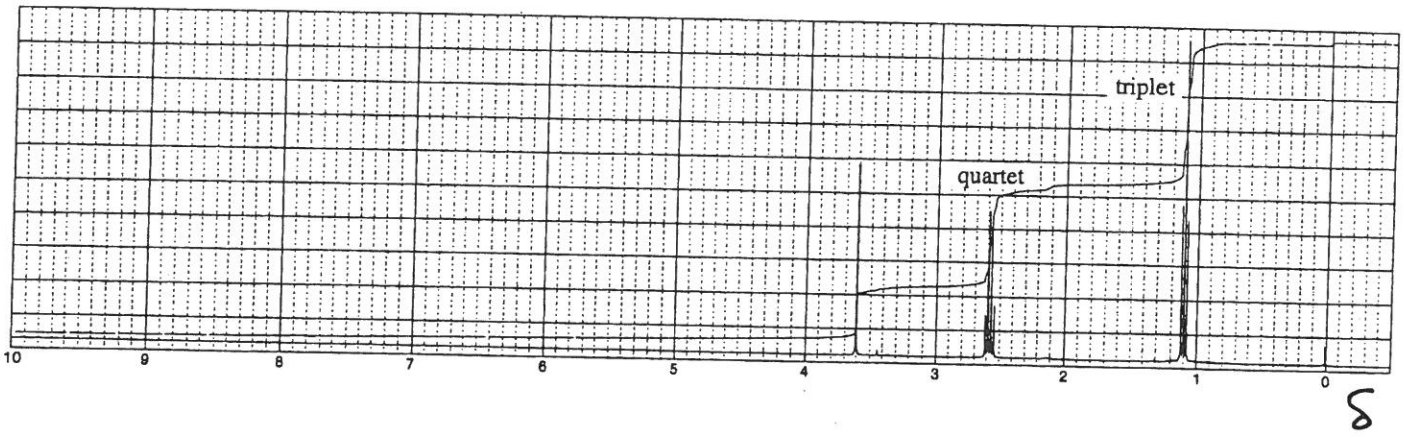
IR

(24.) This compound has the formula $C_6H_{12}N_2$.

3000

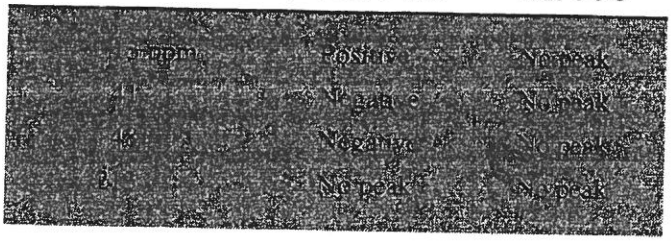


H-1 NMR



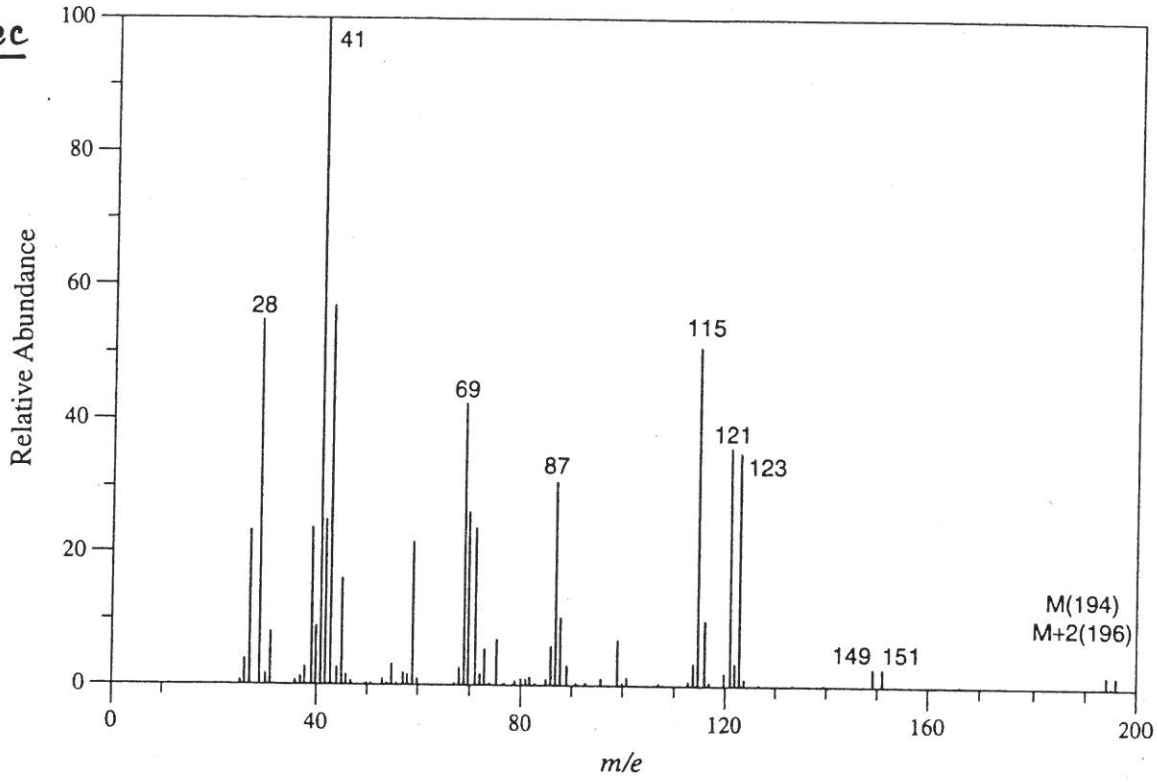
δ

Normal Carbon	DEPT-135
18 ppm	positive
41 ppm	negative
48 ppm	negative
125 ppm	no peak

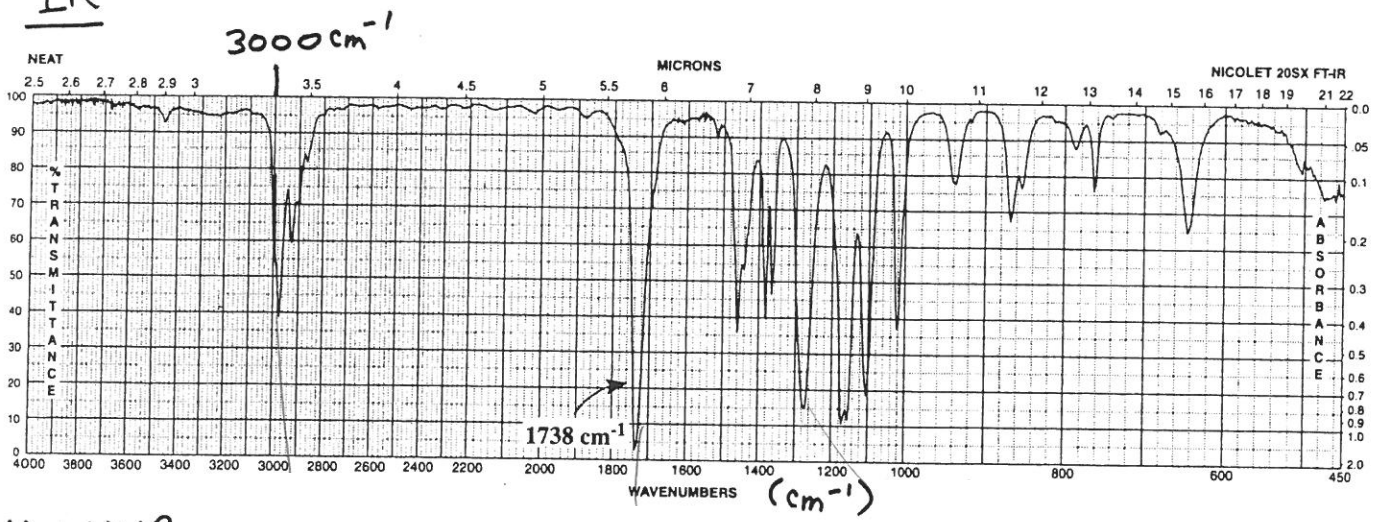


25. This compound has the formula $C_6H_{11}BrO_2$. Determine the structure of this compound. Draw the structures of the fragments observed in the mass spectrum at 121/123 and 149/151. The carbon-13 spectrum shows peaks at 14, 31, 56, 62, and 172 ppm.

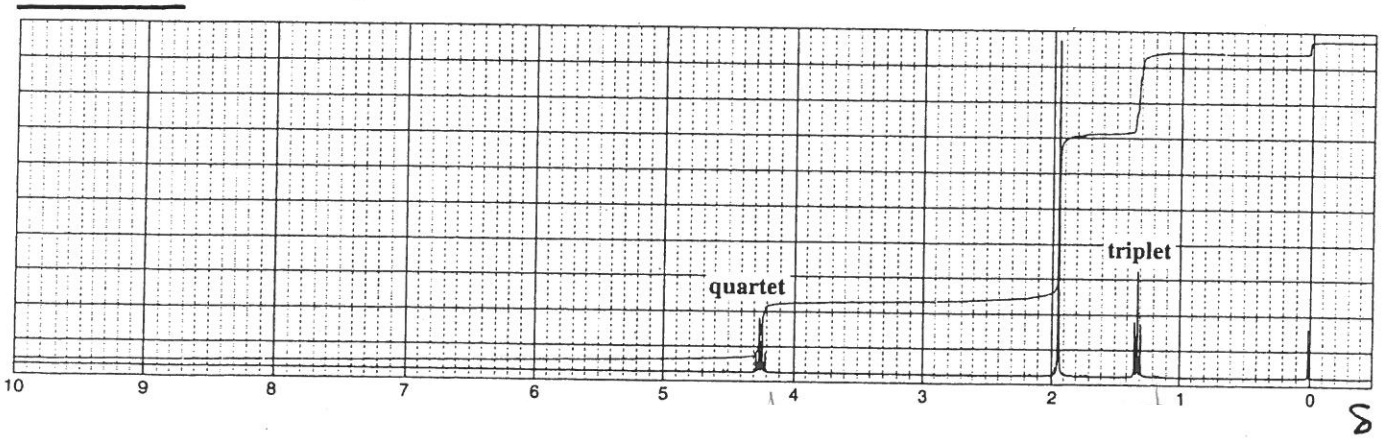
Mass Spec



IR

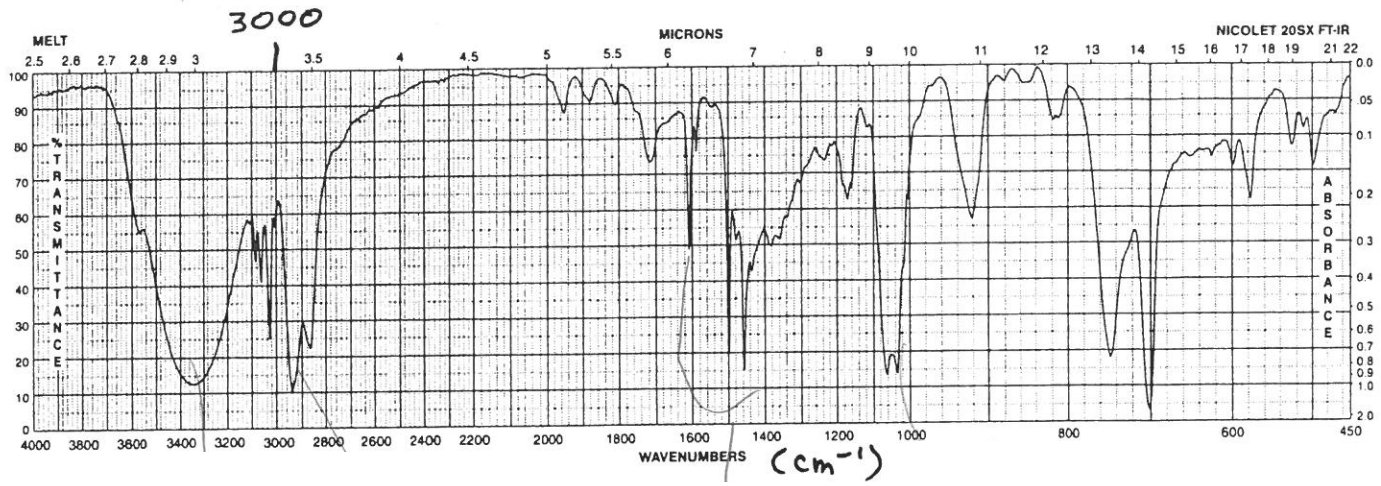


H-1 NMR

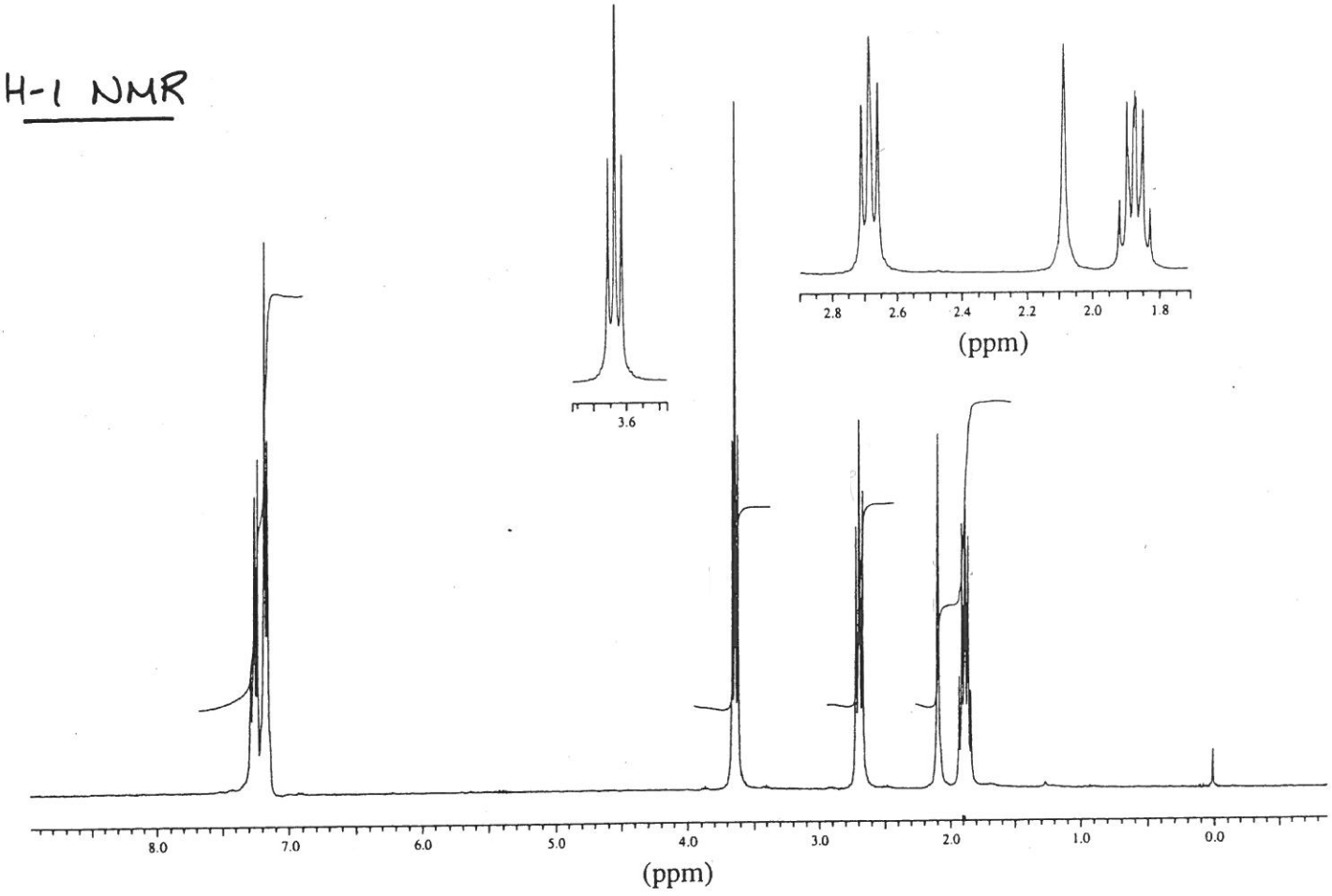


(26.) This compound has the formula $C_9H_{12}O$. The carbon-13 spectrum shows peaks at 28, 31, 57, 122, 124, 125, and 139 ppm.

IR

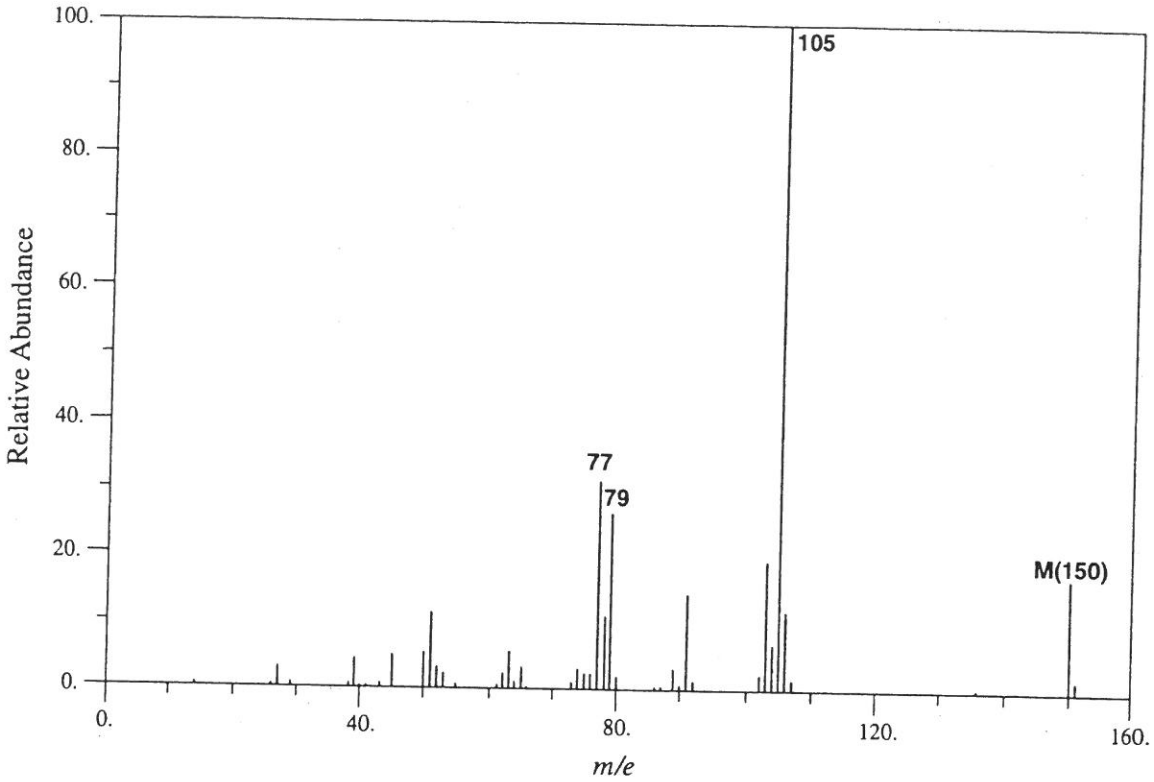


H-1 NMR

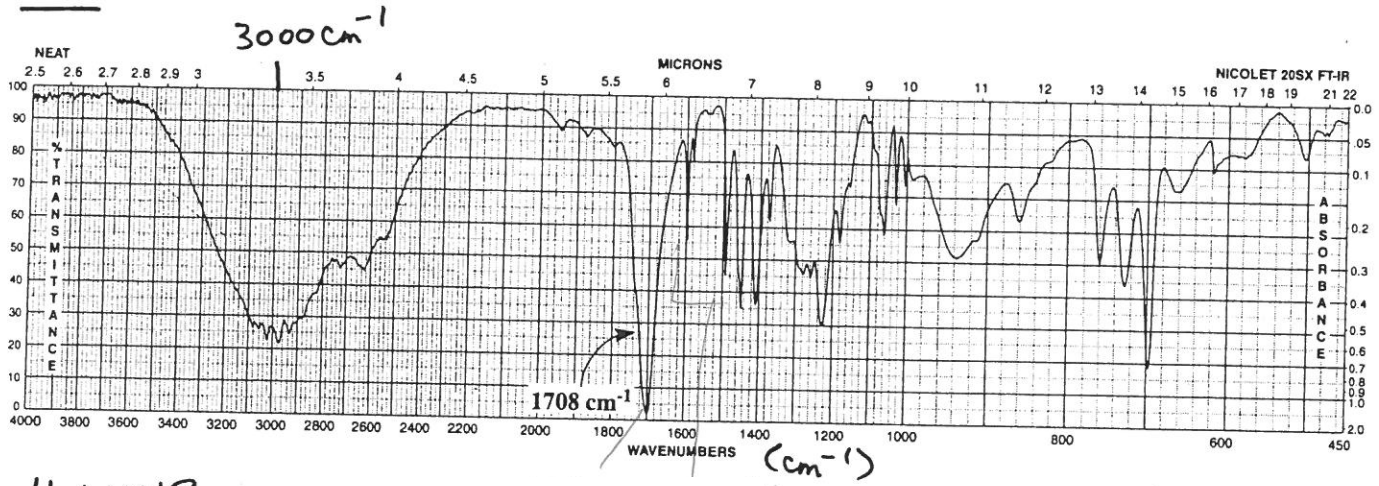


31. This compound has the formula $C_9H_{10}O_2$.

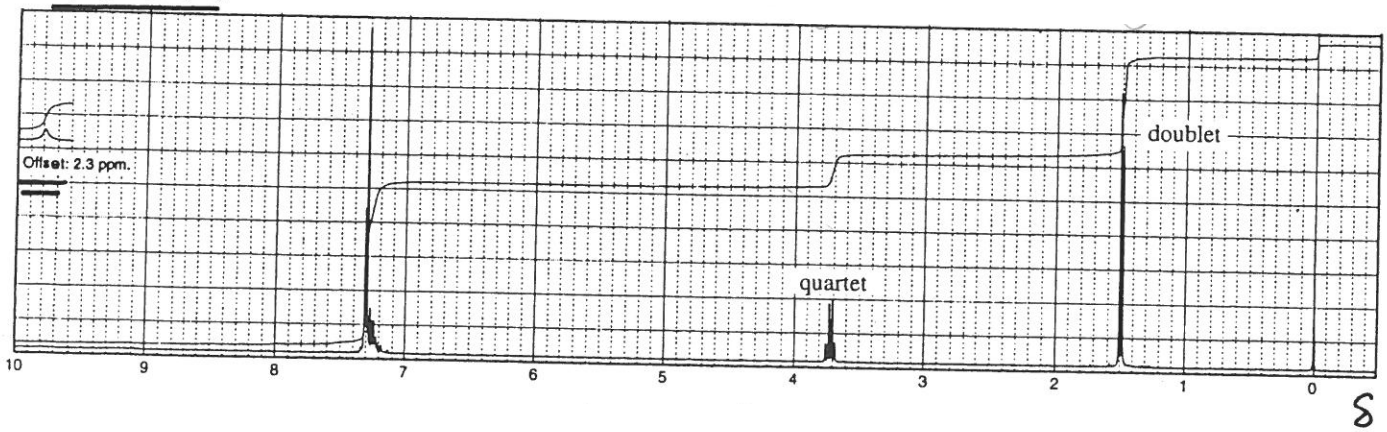
Mass Spectrum



IR



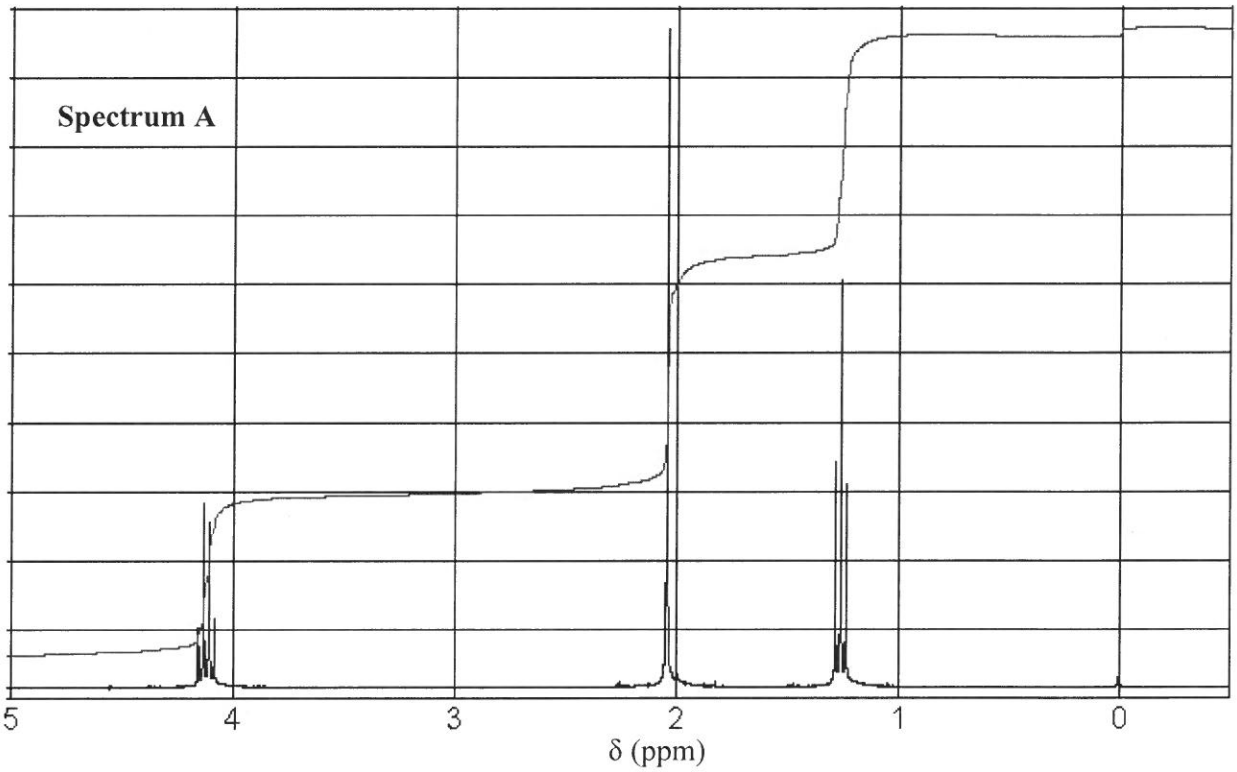
H-1 NMR

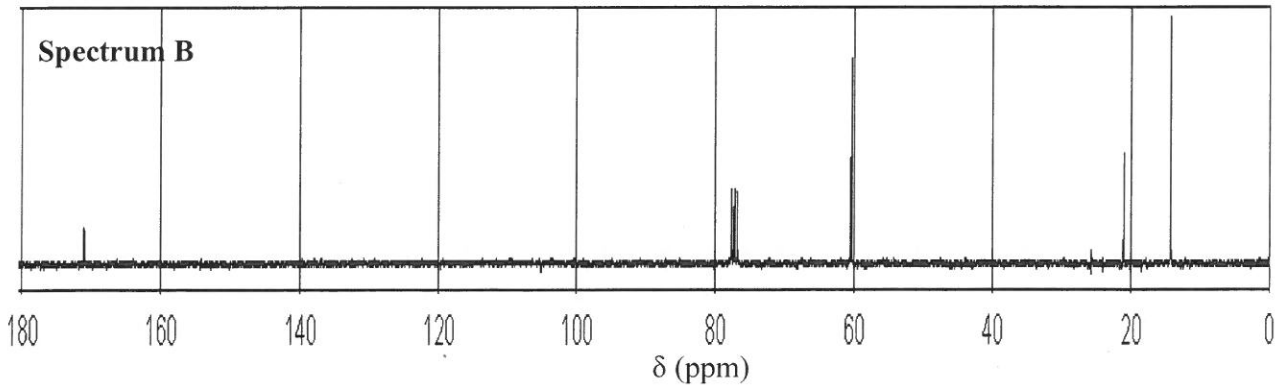


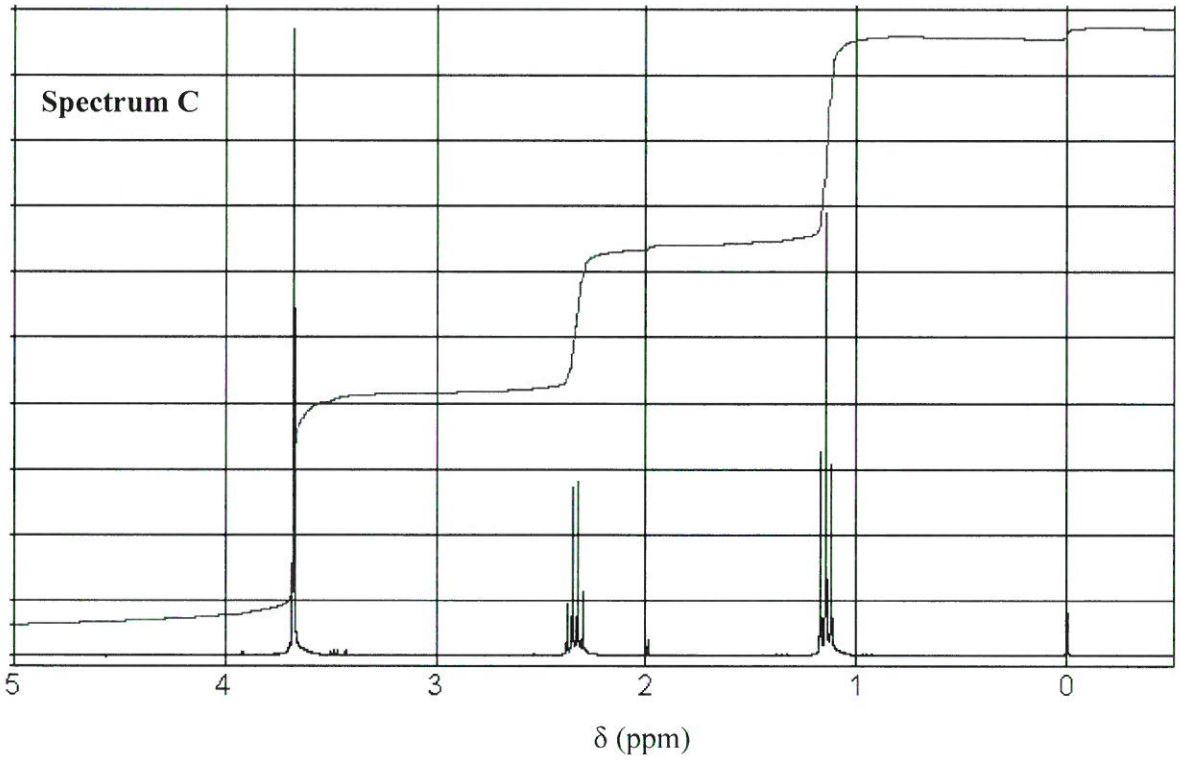
1. **Spectrum A** is the 300 MHz ^{1}H-NMR spectrum of **Compound X** whose molecular formula is $C_4H_8O_2$; the solvent is $CDCl_3$. There are no additional peaks downfield from $\delta = 5.0$ ppm in **Spectrum A**. **Spectrum B** is the proton-decoupled ^{13}C-NMR spectrum of **Compound X** in $CDCl_3$. There are no additional peaks downfield from $\delta = 180.0$ ppm in **Spectrum B**.

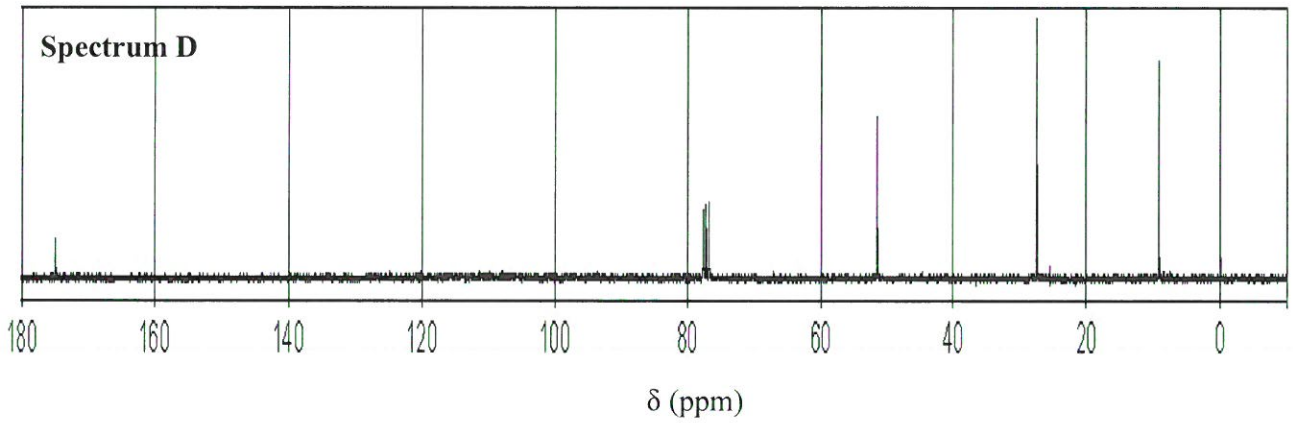
Spectrum C is the 300 MHz ^{1}H-NMR spectrum of **Compound Y** which is an isomer of **Compound X**; the solvent is $CDCl_3$. There are no additional peaks downfield from $\delta = 5.0$ ppm in **Spectrum C**. **Spectrum D** is the proton-decoupled ^{13}C-NMR spectrum of **Compound Y** in $CDCl_3$. There are no additional peaks downfield from $\delta = 180.0$ ppm in **Spectrum D**.

Provide a structural formula for **Compound X**. Provide a structural formula for **Compound Y**. Assign appropriately peaks in each spectrum to structural features in each molecule.



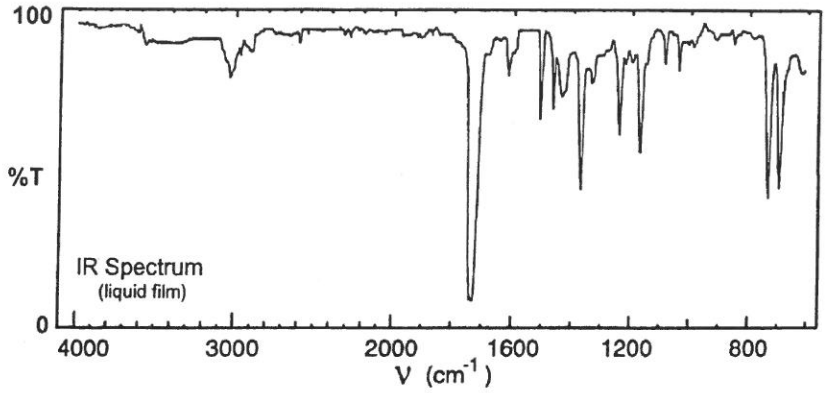


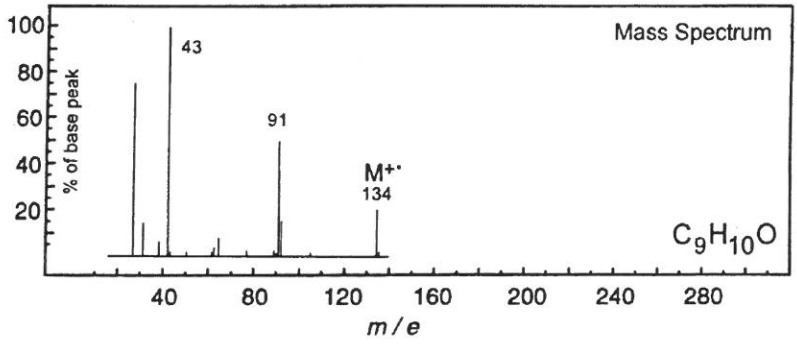


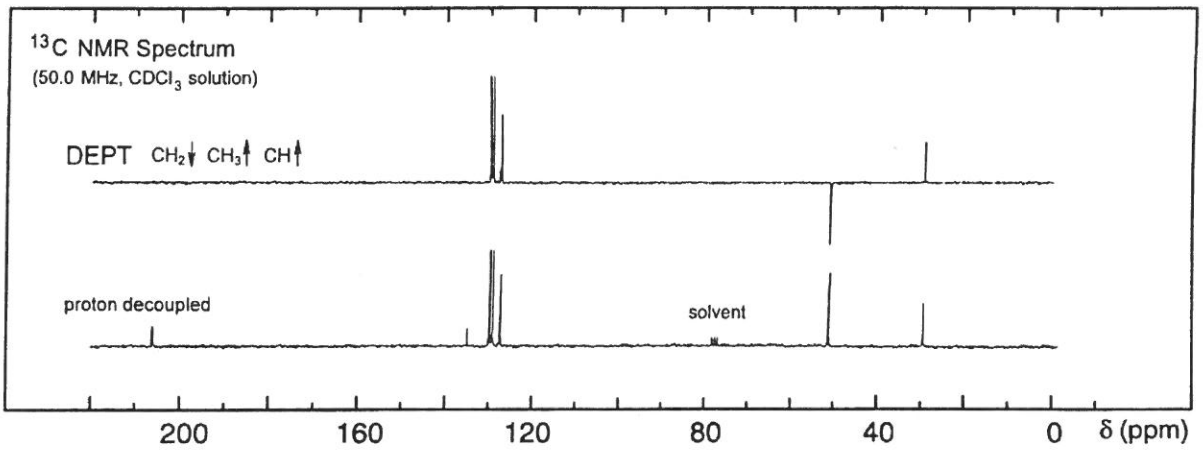


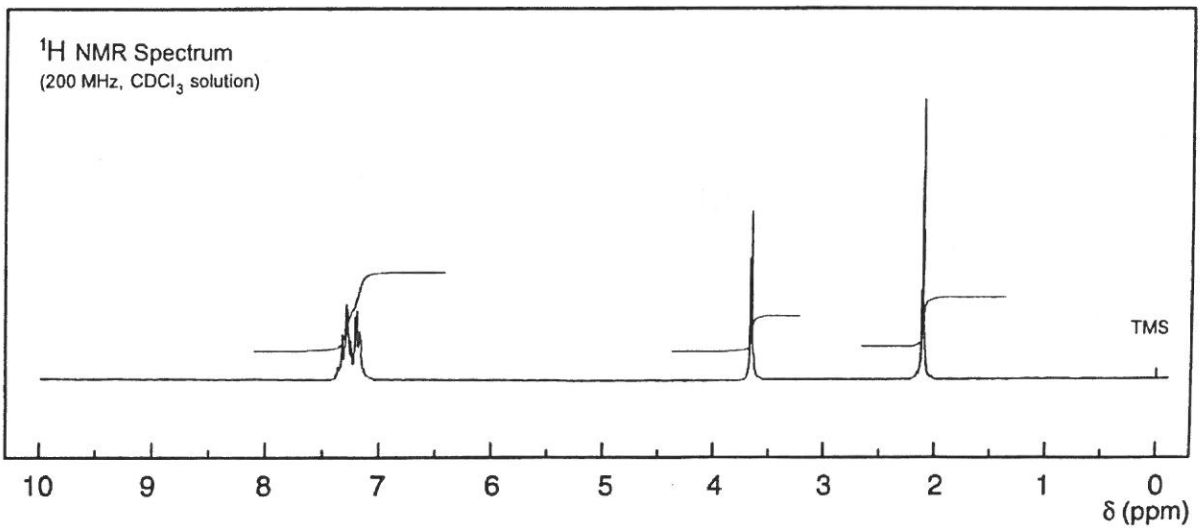
2. For each set of spectra labeled "Problem 2a," "Problem 2b," "Problem 2c," "Problem 2d," and "Problem 2e," give a structural formula for a compound that is consistent with all the spectral information given for each set of spectra. For each set of spectra, assign appropriately peaks in each spectrum to structural features in each molecule.

problem **2a**

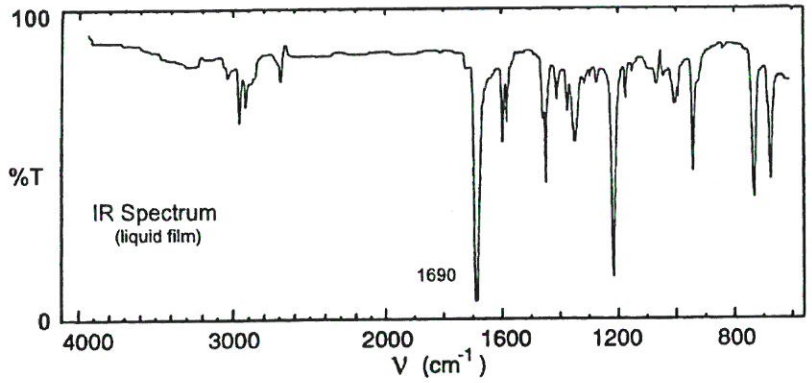

100
%T
0
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

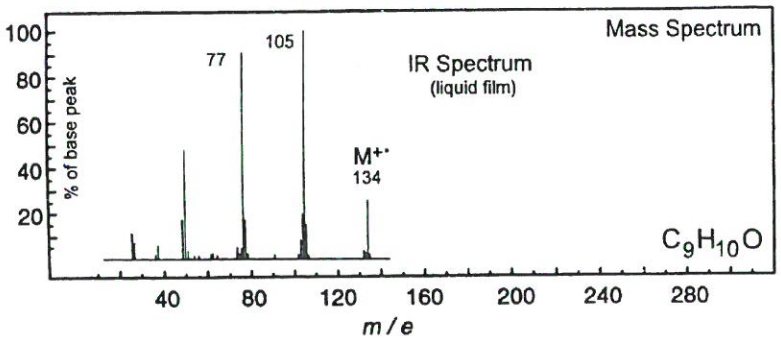

Mass Spectrum
100
80
60
40
20
% of base peak
43
91
M+·
134
C9H10O
40
80
120
160
200
240
280
m/e

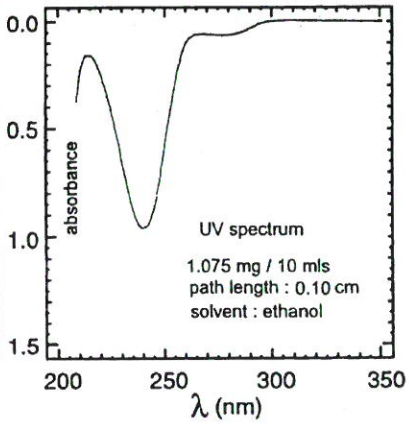

13C NMR Spectrum
(50.0 MHz, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

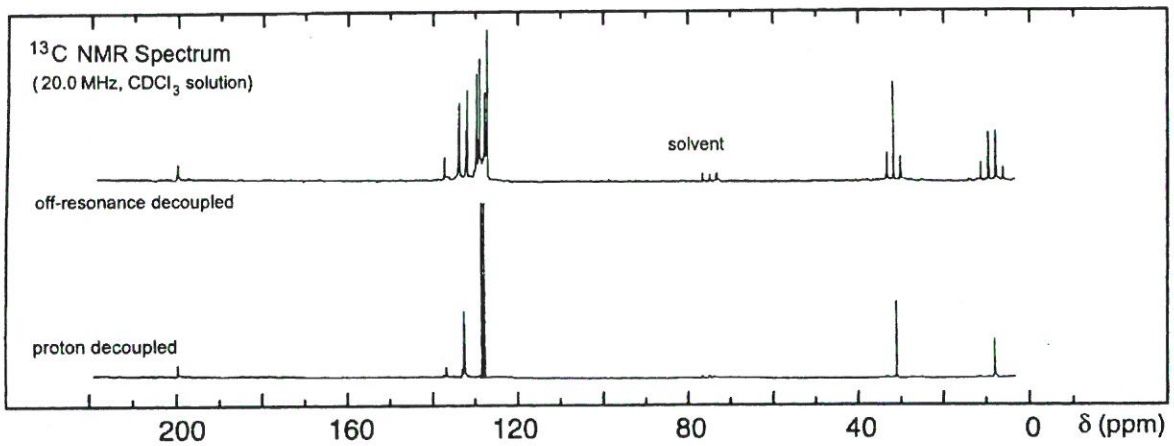

1H NMR Spectrum
(200 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

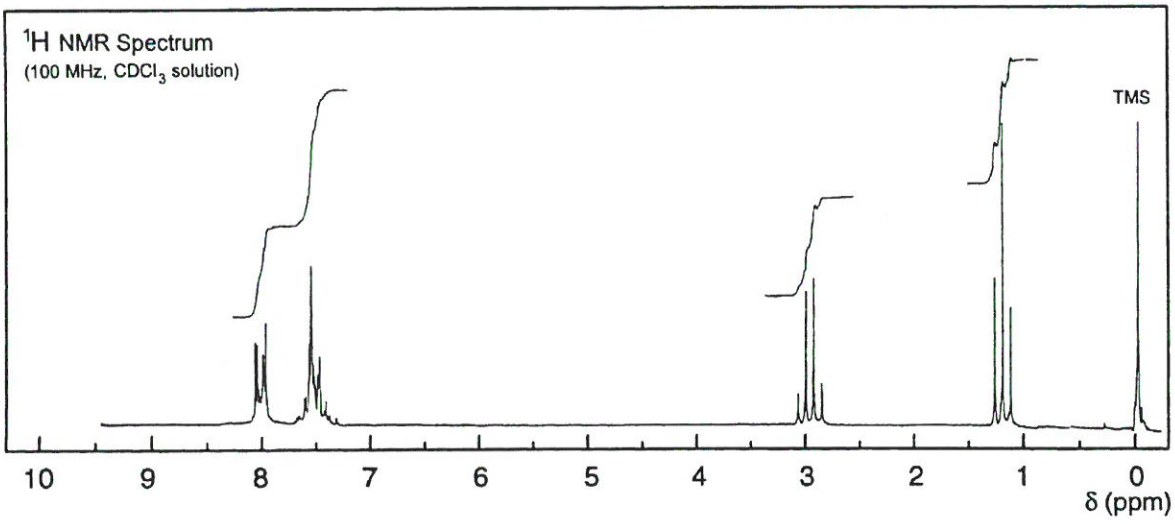
problem **2b**


100
%T
0
IR Spectrum
(liquid film)
1690
4000
3000
2000
1600
1200
800
ν (cm-1)

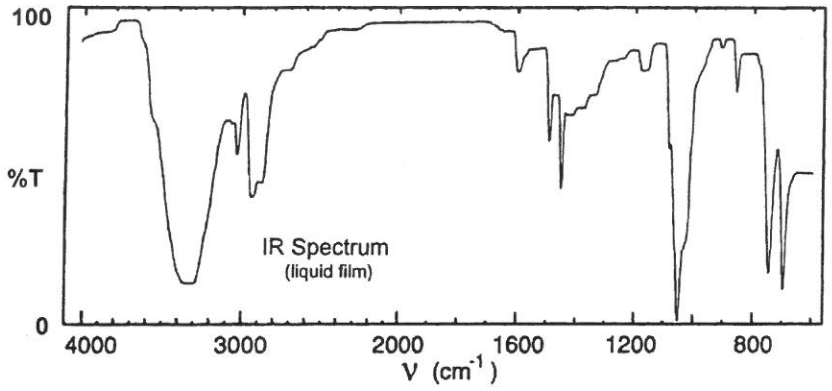

100
80
60
40
20
% of base peak
77
105
M+·
134
Mass Spectrum
IR Spectrum
(liquid film)
C9H10O
40
80
120
160
200
240
280
m/e

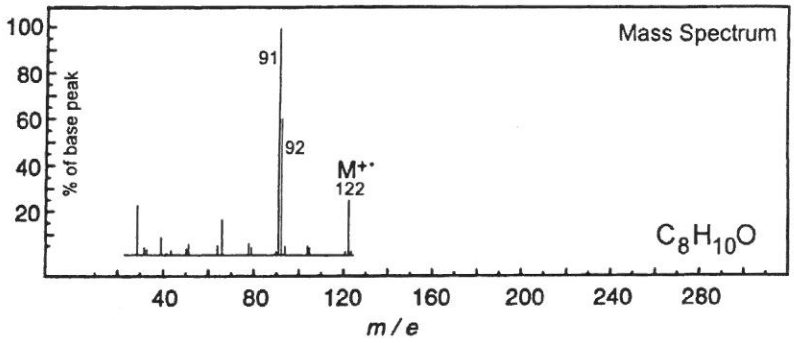

0.0
0.5
1.0
1.5
absorbance
UV spectrum
1.075 mg / 10 mls
path length : 0.10 cm
solvent : ethanol
200
250
300
350
λ (nm)

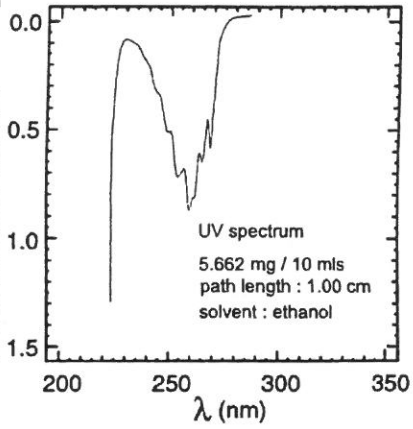

13C NMR Spectrum
(20.0 MHz, CDCl3 solution)
solvent
off-resonance decoupled
proton decoupled
200
160
120
80
40
0
δ (ppm)

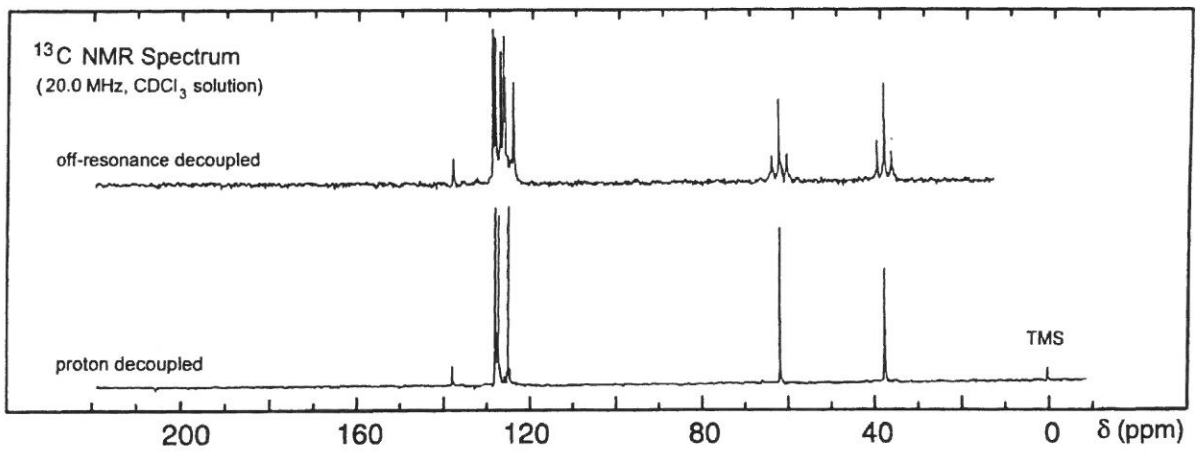

1H NMR Spectrum
(100 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

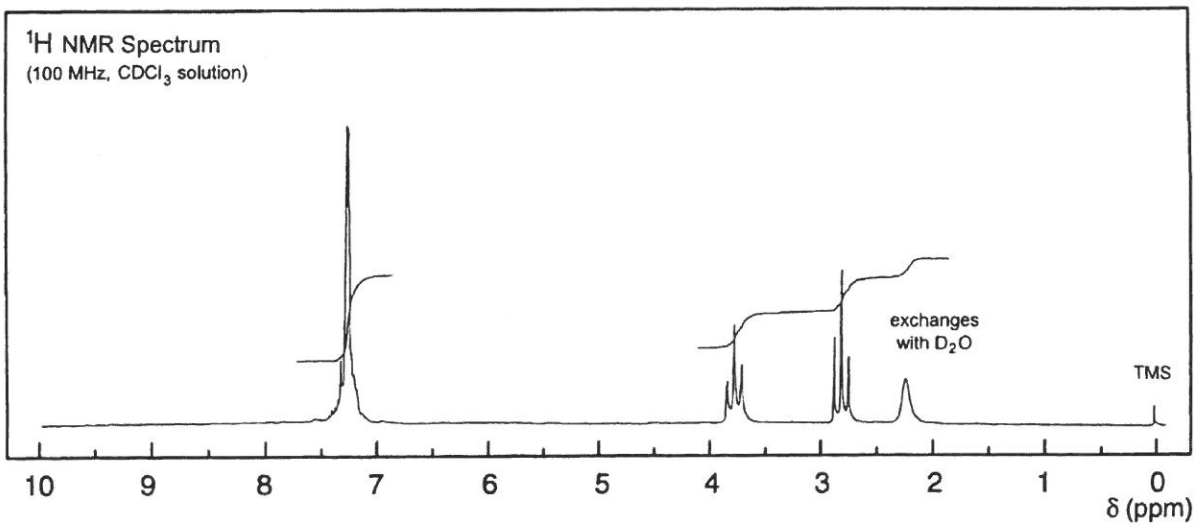
problem **2c**


100
%T
0
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

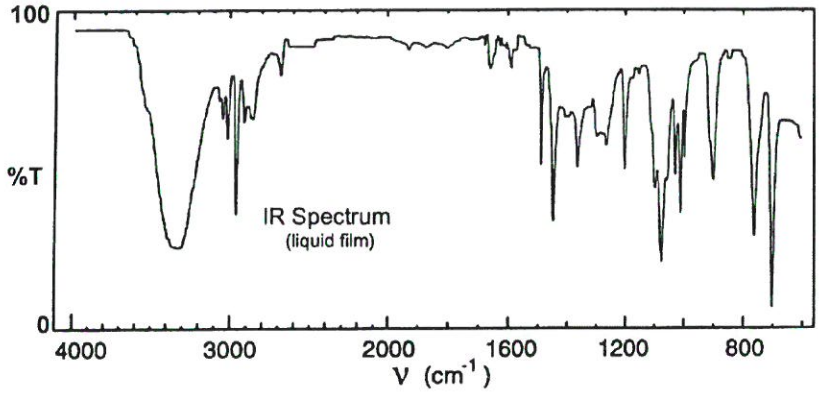

Mass Spectrum
% of base peak
100
80
60
40
20
91
92
M+·
122
C8H10O
40
80
120
160
200
240
280
m/e

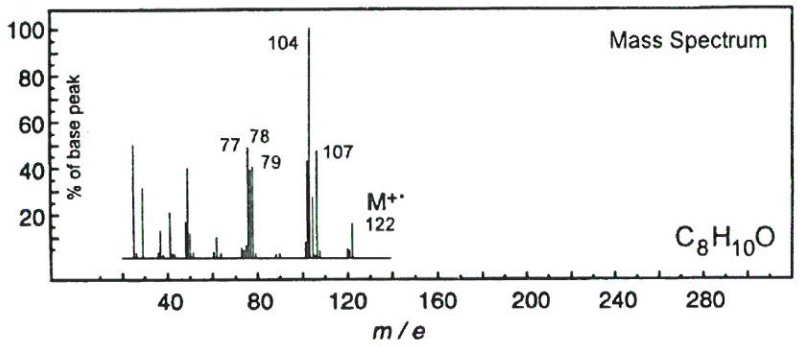

0.0
0.5
1.0
1.5
UV spectrum
5.662 mg / 10 mls
path length : 1.00 cm
solvent : ethanol
200
250
300
350
λ (nm)

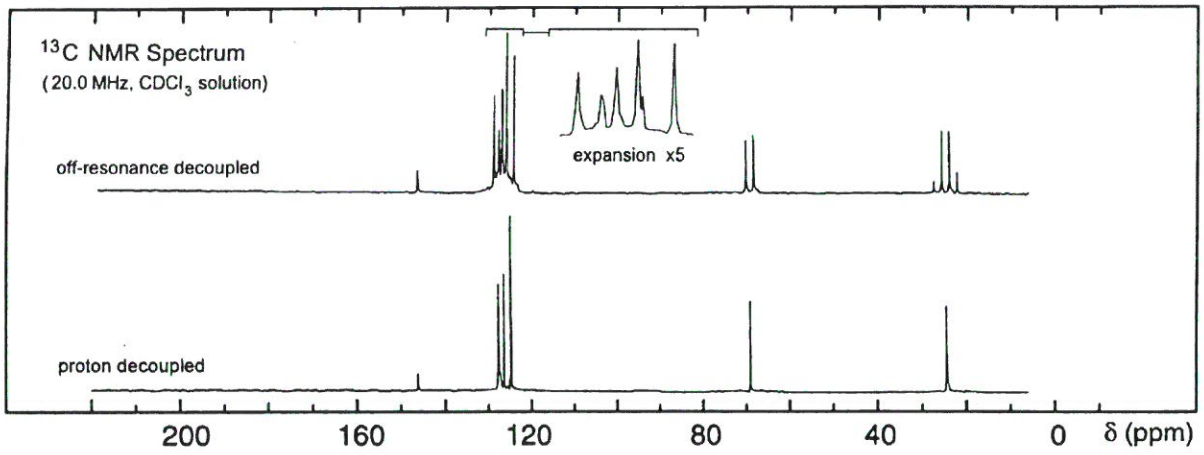

13C NMR Spectrum
(20.0 MHz, CDCl3 solution)
off-resonance decoupled
proton decoupled
TMS
200
160
120
80
40
0
δ (ppm)

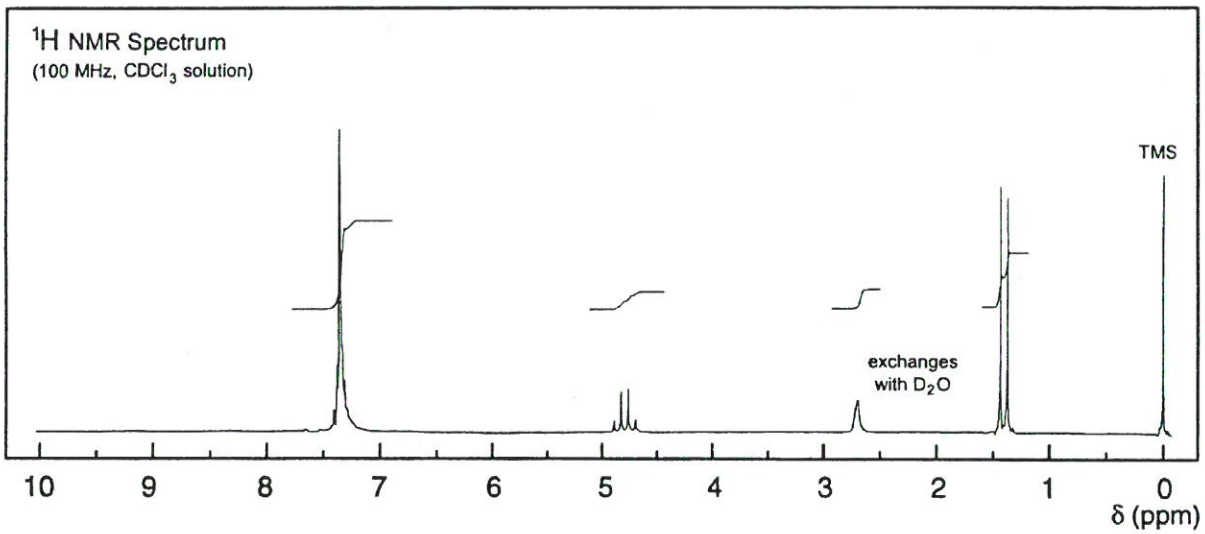

1H NMR Spectrum
(100 MHz, CDCl3 solution)
exchanges
with D2O
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

problem **2d**

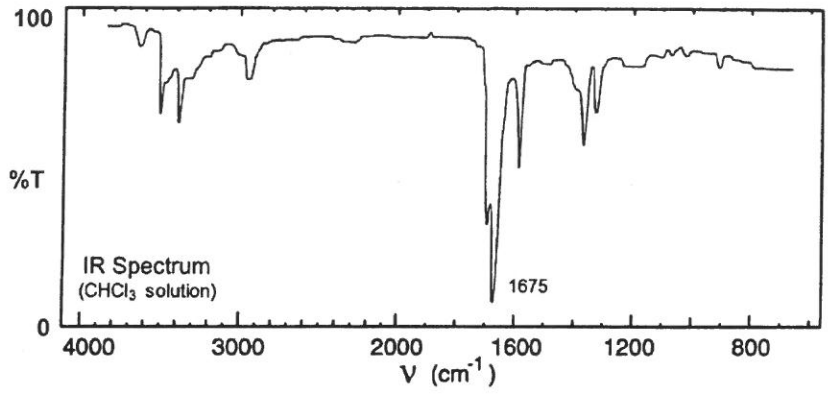

100
%T
0
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm-1)

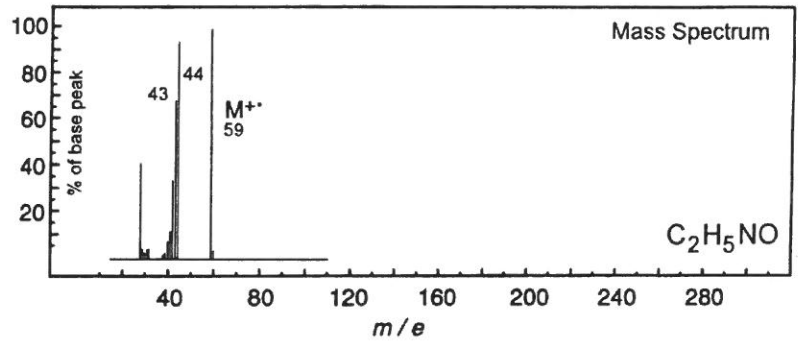

100
80
60
40
20
% of base peak
104
77
78
79
107
M+·
122
Mass Spectrum
C8H10O
40
80
120
160
200
240
280
m/e

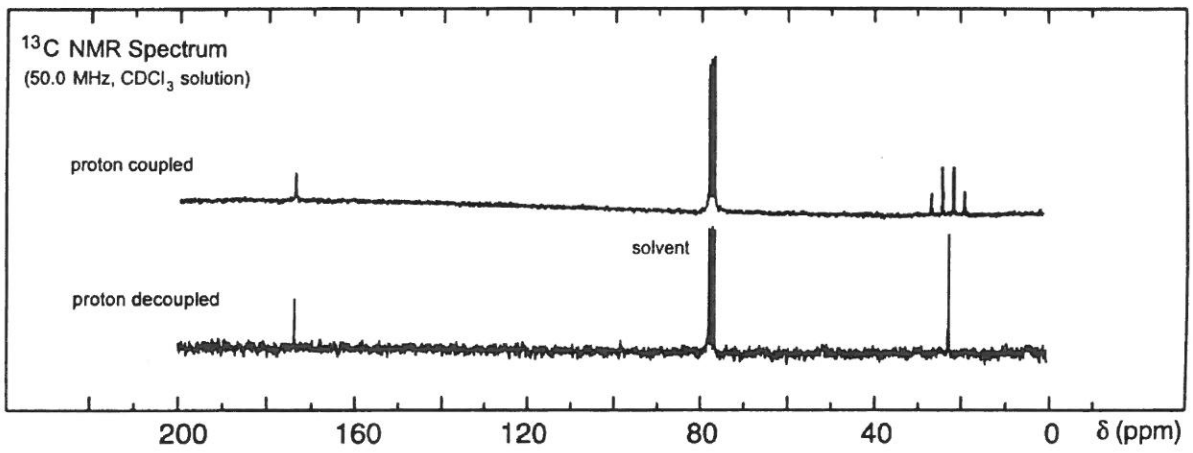

13C NMR Spectrum
(20.0 MHz, CDCl3 solution)
off-resonance decoupled
expansion x5
proton decoupled
200
160
120
80
40
0
δ (ppm)

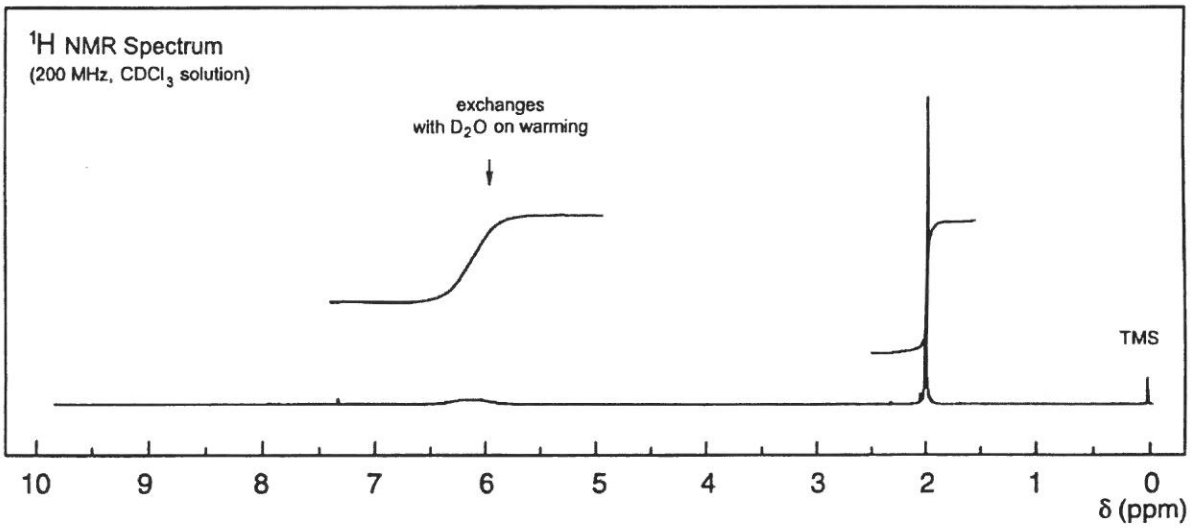

1H NMR Spectrum
(100 MHz, CDCl3 solution)
TMS
exchanges
with D2O
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

problem **2e**


100
%T
0
IR Spectrum
(CHCl3 solution)
1675
4000
3000
2000
1600
1200
800
ν (cm-1)


Mass Spectrum
100
80
60
40
20
% of base peak
43
44
M+·
59
C2H5NO
40
80
120
160
200
240
280
m/e


13C NMR Spectrum
(50.0 MHz, CDCl3 solution)
proton coupled
solvent
proton decoupled
200
160
120
80
40
0
δ (ppm)


1H NMR Spectrum
(200 MHz, CDCl3 solution)
exchanges
with D2O on warming
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)