^{13}CNMR spectroscopy

4th 2020/2021

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^{13}CNMR spectroscopy

- The ^{12}C nucleus is not magnetically "active" (spin number, I, is zero), but the ^{13}C nucleus, like the ^{1}H, has a spin number ½ .
- The natural abundance of ^{13}C is only 1.1% that of ^{12}C and its sensitivity is only about 1.6% that of 1H, the overall sensitivity of ^{13}C compared to ^{1}H is about 1/5700.

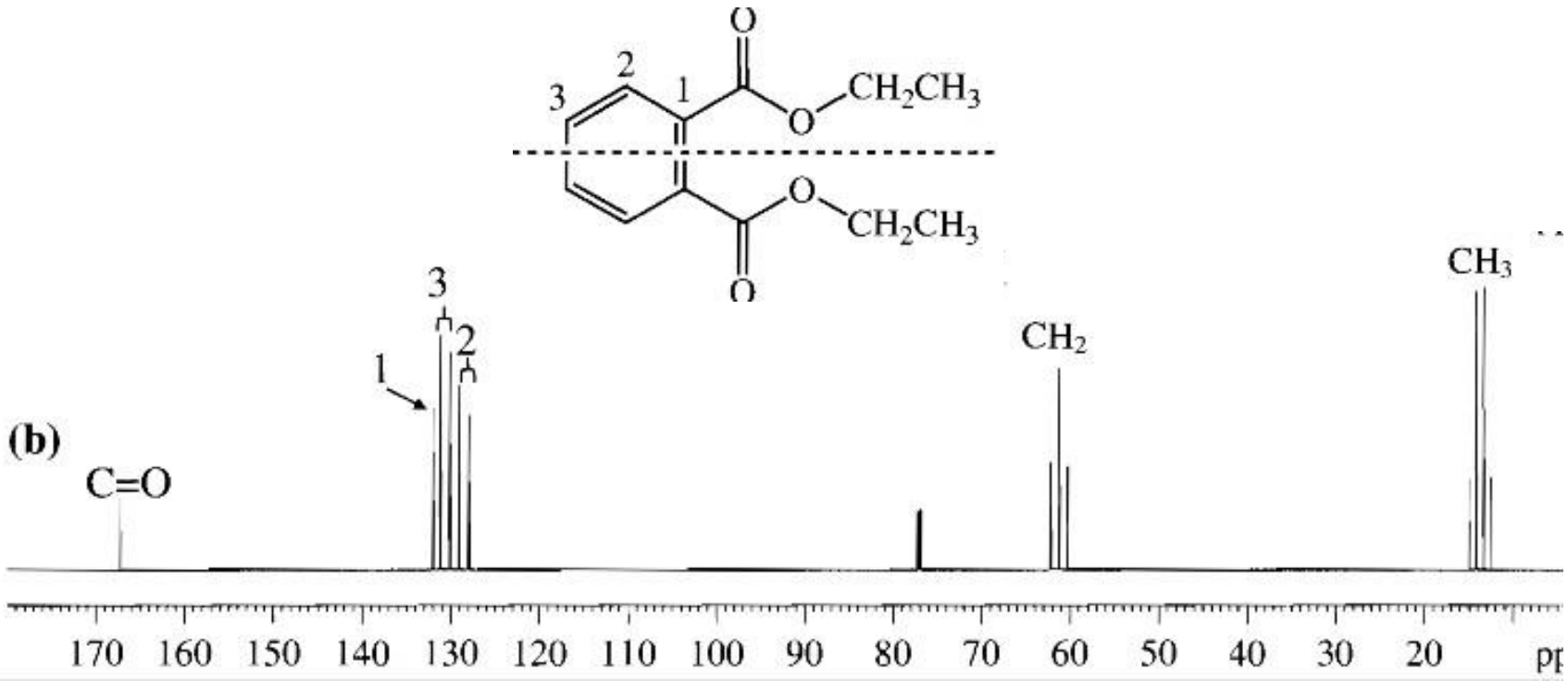
^{13}CNMR spectroscopy

There are some differents between ^{1}H and ^{13}C-:

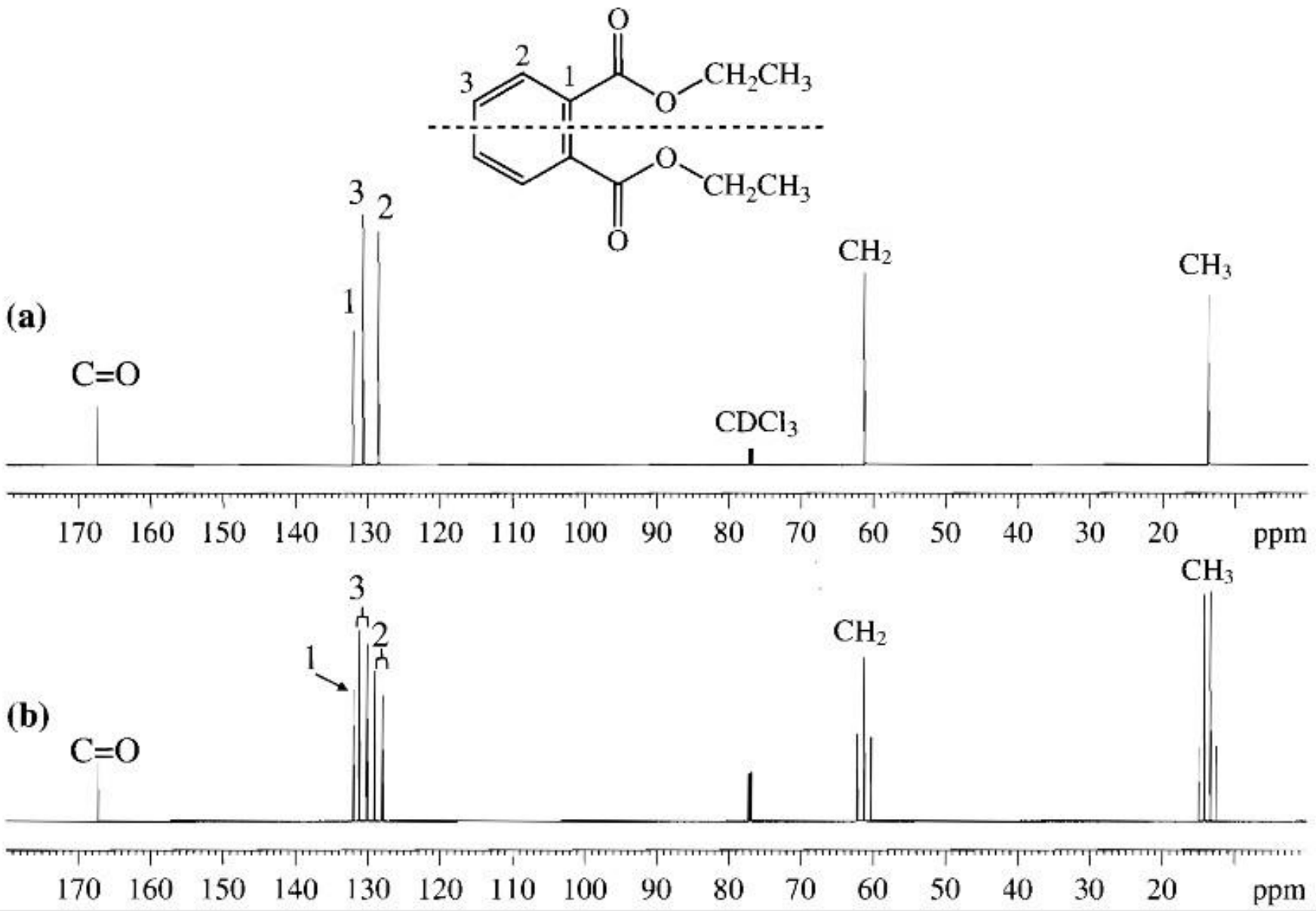
- The broadband proton decoupled technique allow the ^{13}C peak to appear as a singlet unless the molecule has other magenitic active nucleus like ^{2}H, ^{19}F or ^{31}P..
- The ^{13}C peaks are distributed over a larger chemical shift range in comparison with the proton range.
- The ^{13}C nuclei are much less abundant and much less sensitive than proton. Larger samples and longer times are needed.
- For a given deuterated solvent, the ^{13}C and ^{1}H solvent peaks differ in multiplicities.

1H Decoupling Techinques

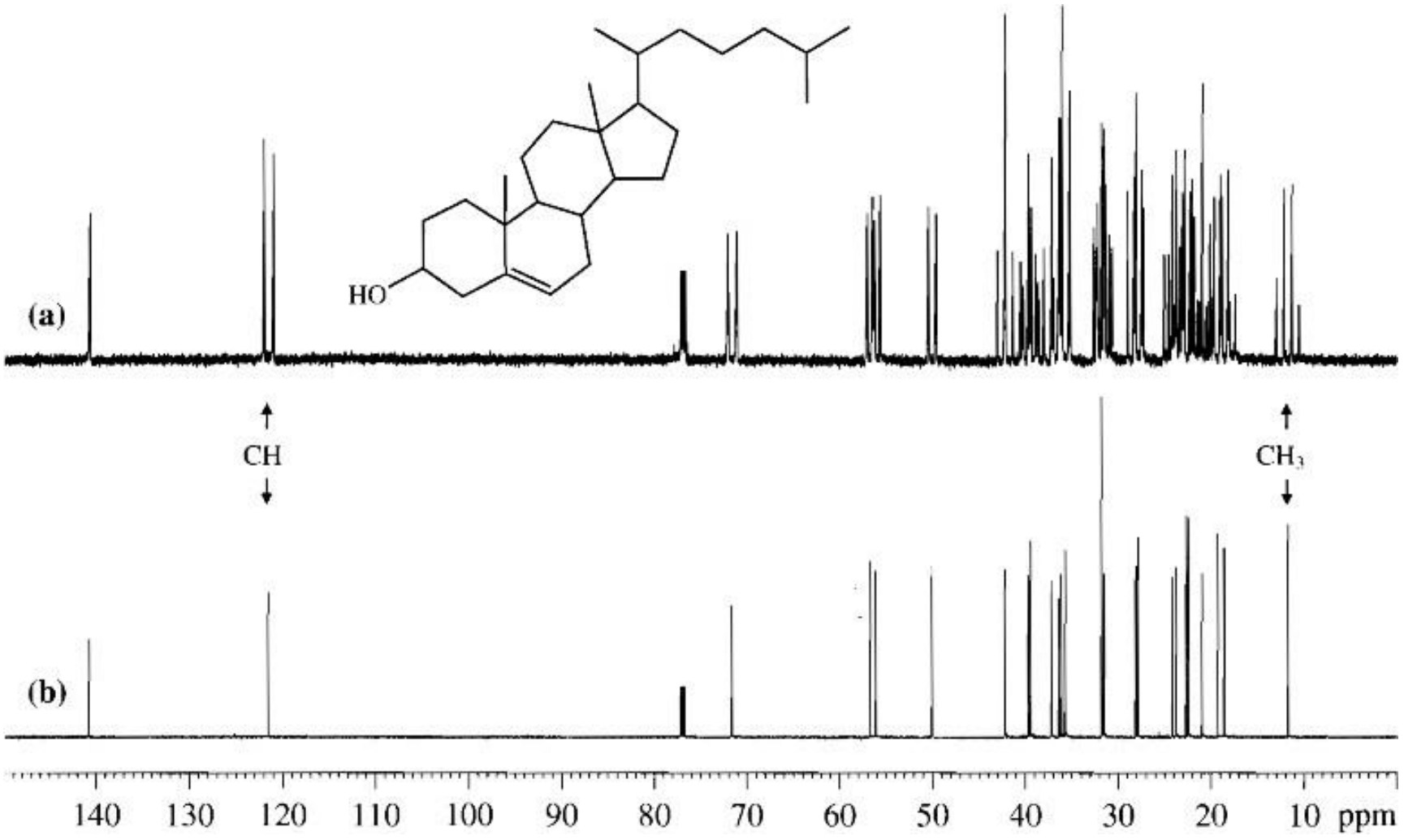
Because the larger $^{1}J_{CH}$ values for ^{13}C-^{1}H (about 110-320 Hz) and appreciable $^{2}J_{CH}$, $^{3}J_{CH}$ values for ^{13}C-C-^{1}H and ^{13}C-C-C-^{1}H (about 0-60 Hz) coupling, proton-coupled ^{13}C spectra usually show complex overlapping multiplets that are diffecult to interpret.



1H Decoupling Techinques



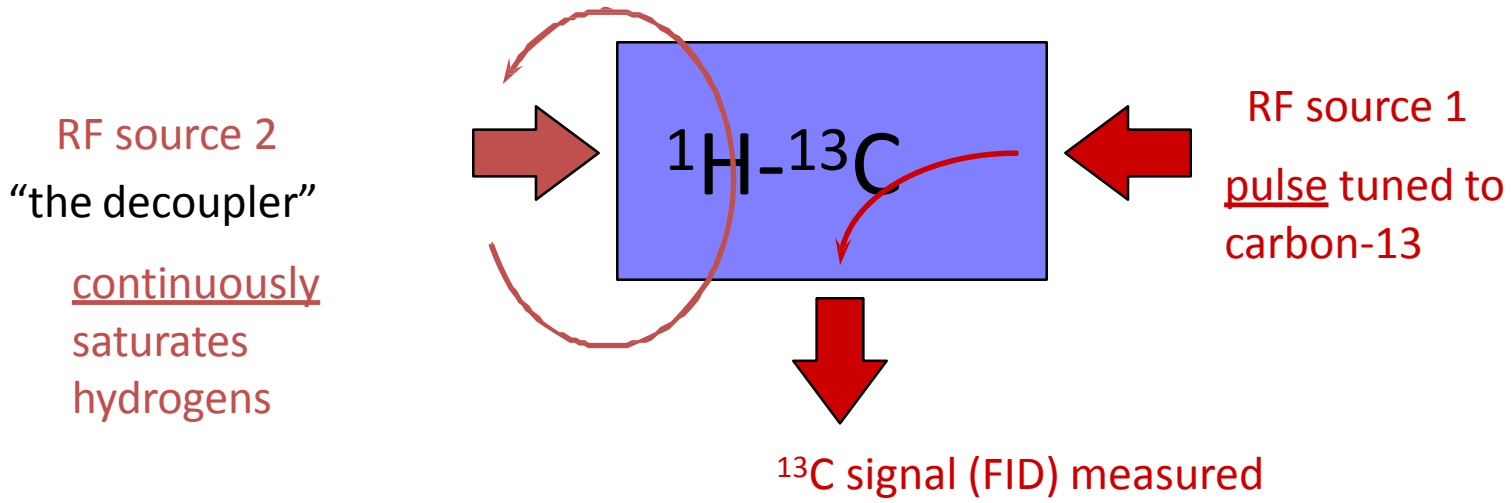
1H Decoupling Techinques



DECOUPLING THE PROTON SPINS

A common method used in determining a carbon-13 NMR spectrum is to irradiate all of the hydrogen nuclei in the molecule at the same time the carbon resonances are being measured.

This requires a second radiofrequency (RF) source (the decoupler) tuned to the frequency of the hydrogen nuclei, while the primary RF source is tuned to the ^{13}C frequency.



In this method the hydrogen nuclei are “saturated”,a situation where there are as many downward as there are upward transitions, all occuring rapidly.

During the time the carbon-13 spectrum is being determined, the hydrogen nuclei cycle rapidly between their two spin states (+1/2 and -1/2) and the carbon nuclei see an average coupling (i.e., zero) to the hydrogens.

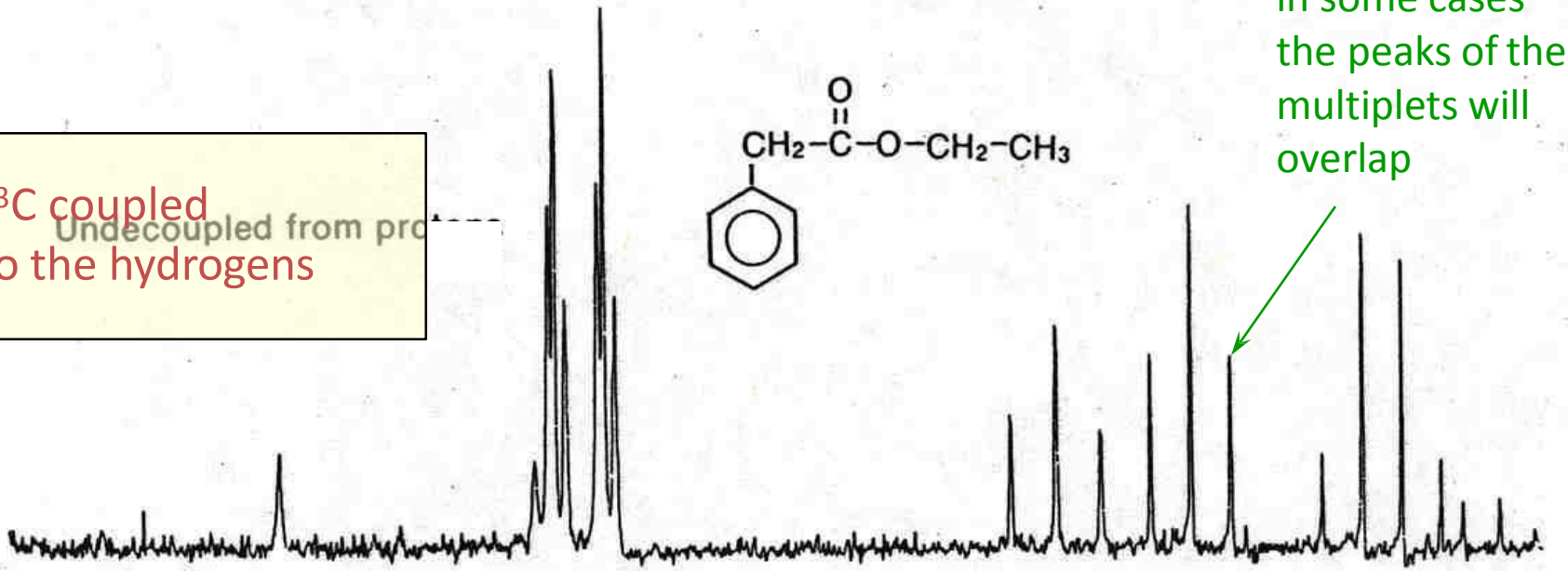
The hydrogens are said to be decoupled from the carbon-13 nuclei.

You no longer see multiplets for the ^{13}C resonances.
Each carbon gives a singlet, and the spectrum is easier to nterpret.

ETHYL PHENYLACETATE

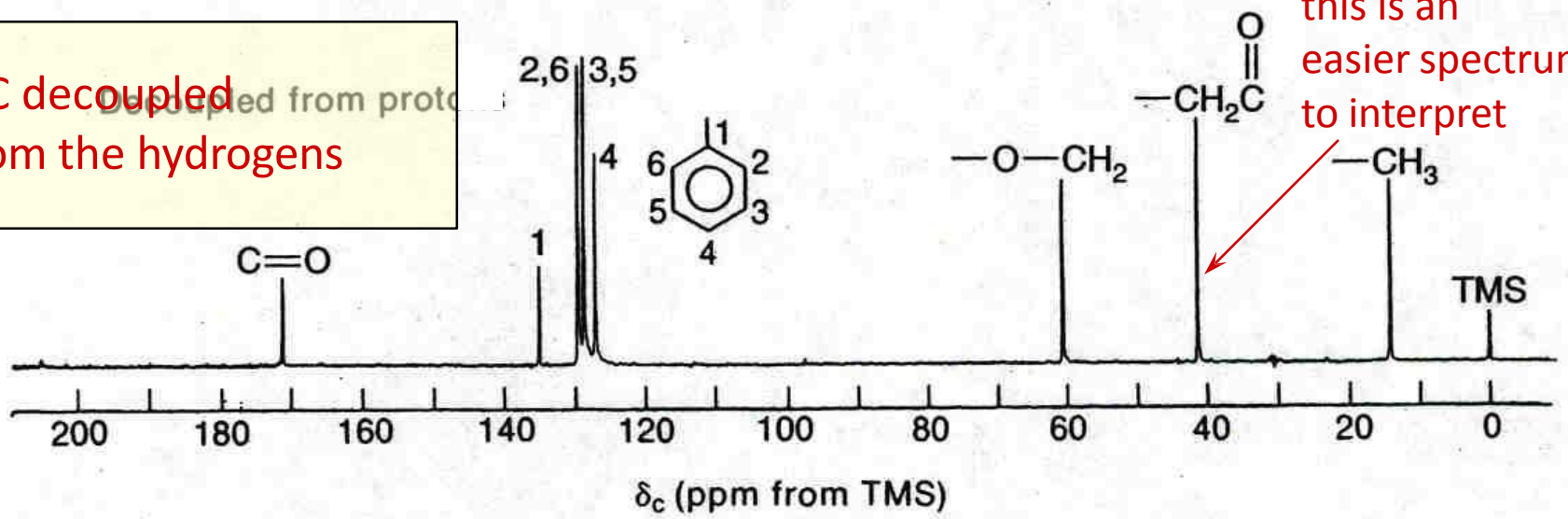
in some cases the peaks of the multiplets will overlap

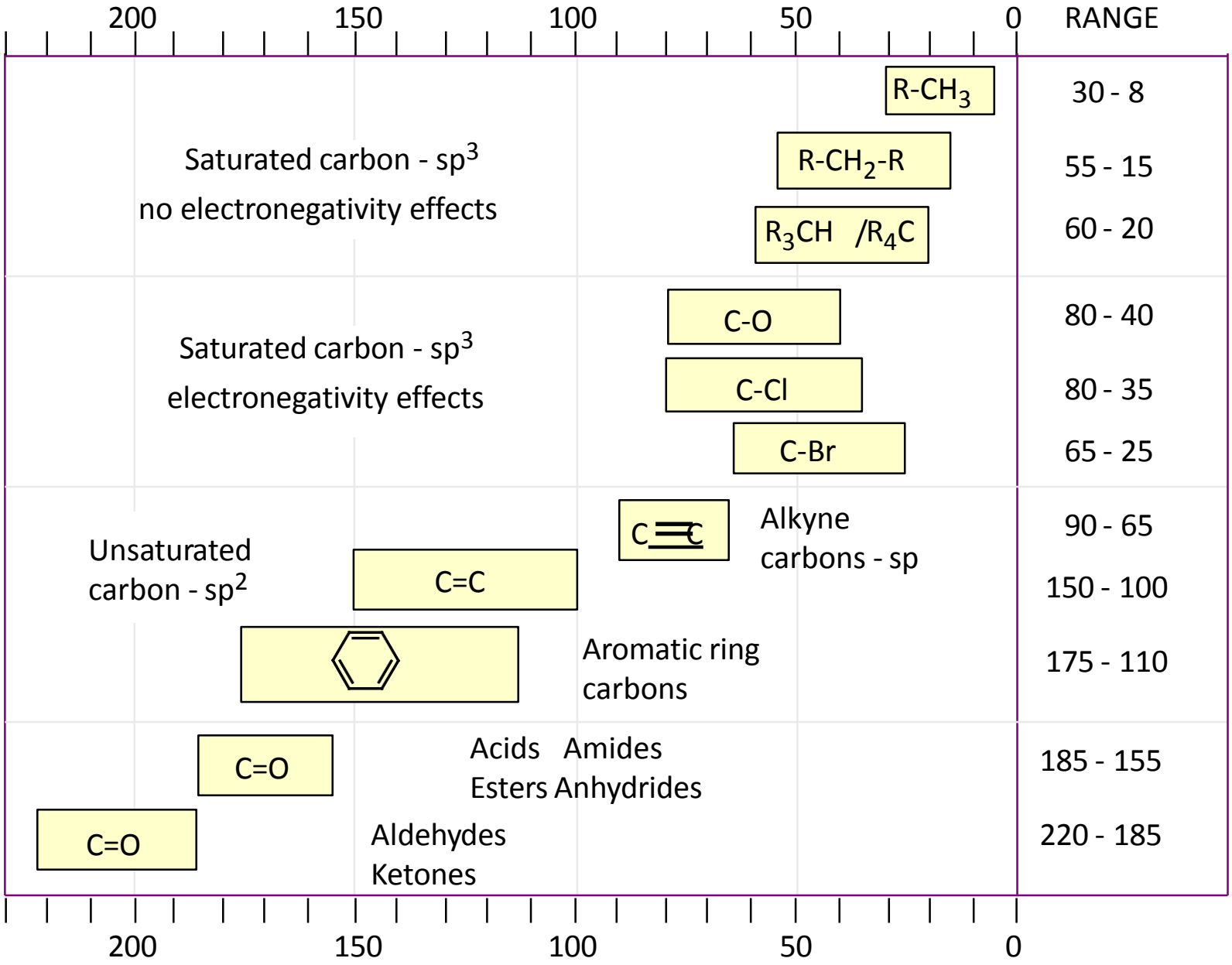
^{13}C coupled to the hydrogens



^{13}C decoupled from the hydrogens

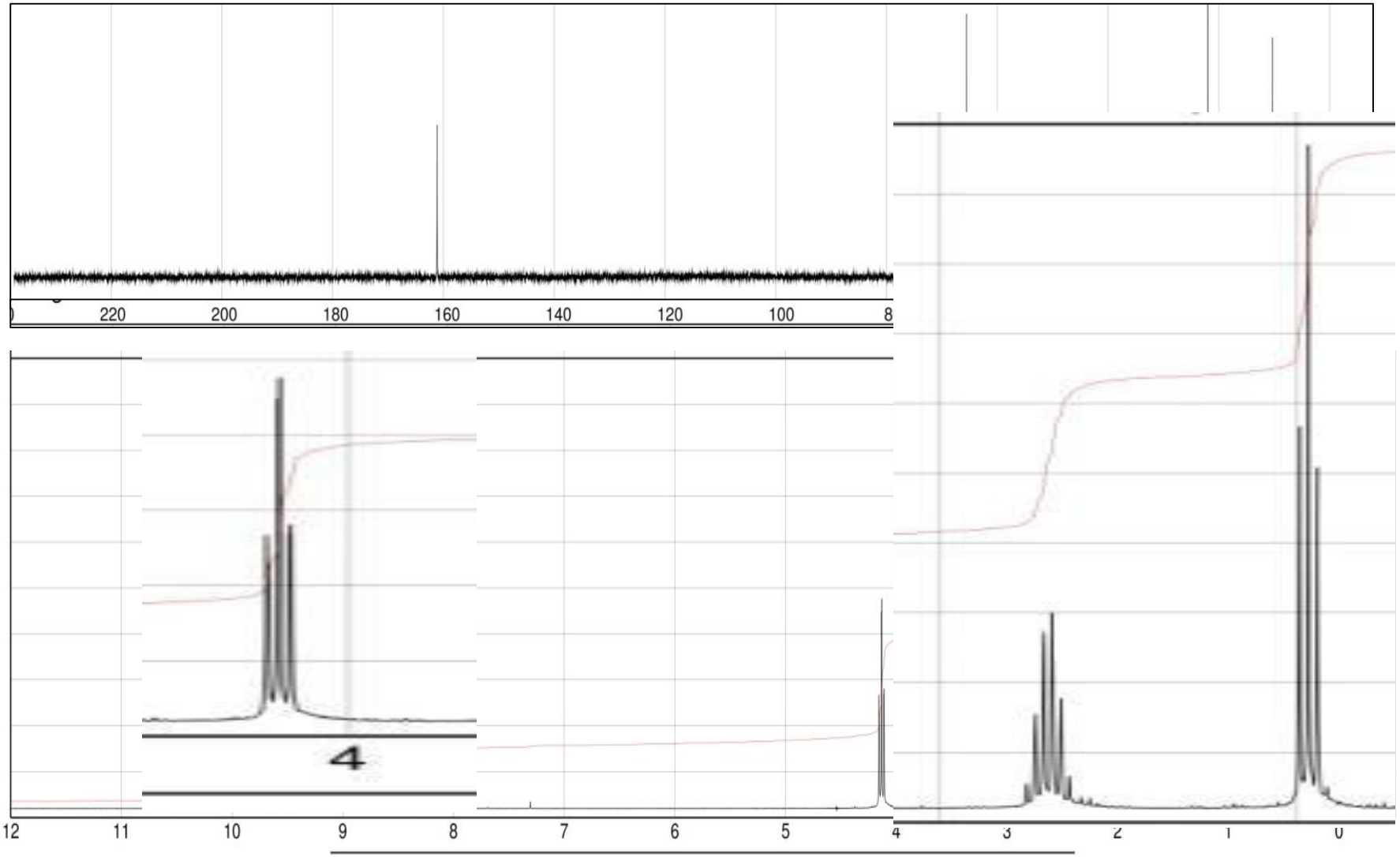
this is an easier spectrum to interpret



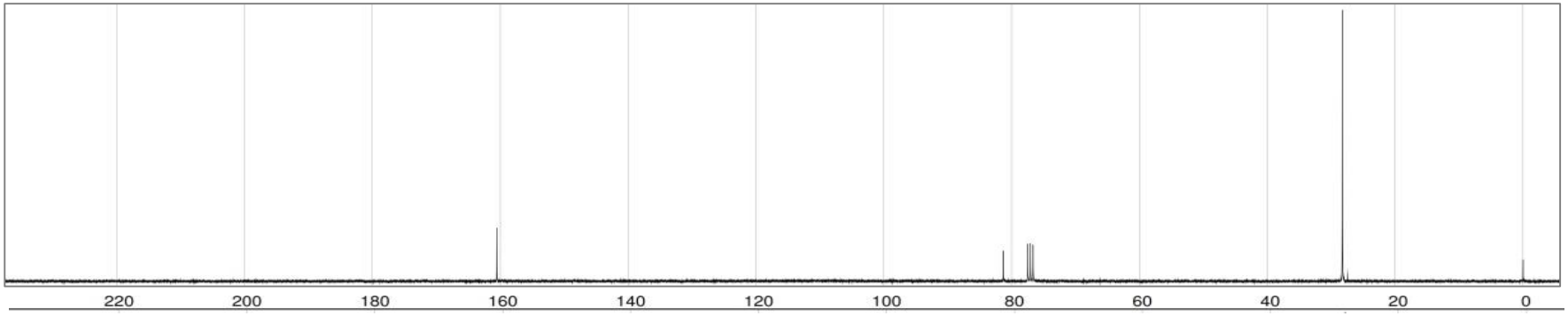


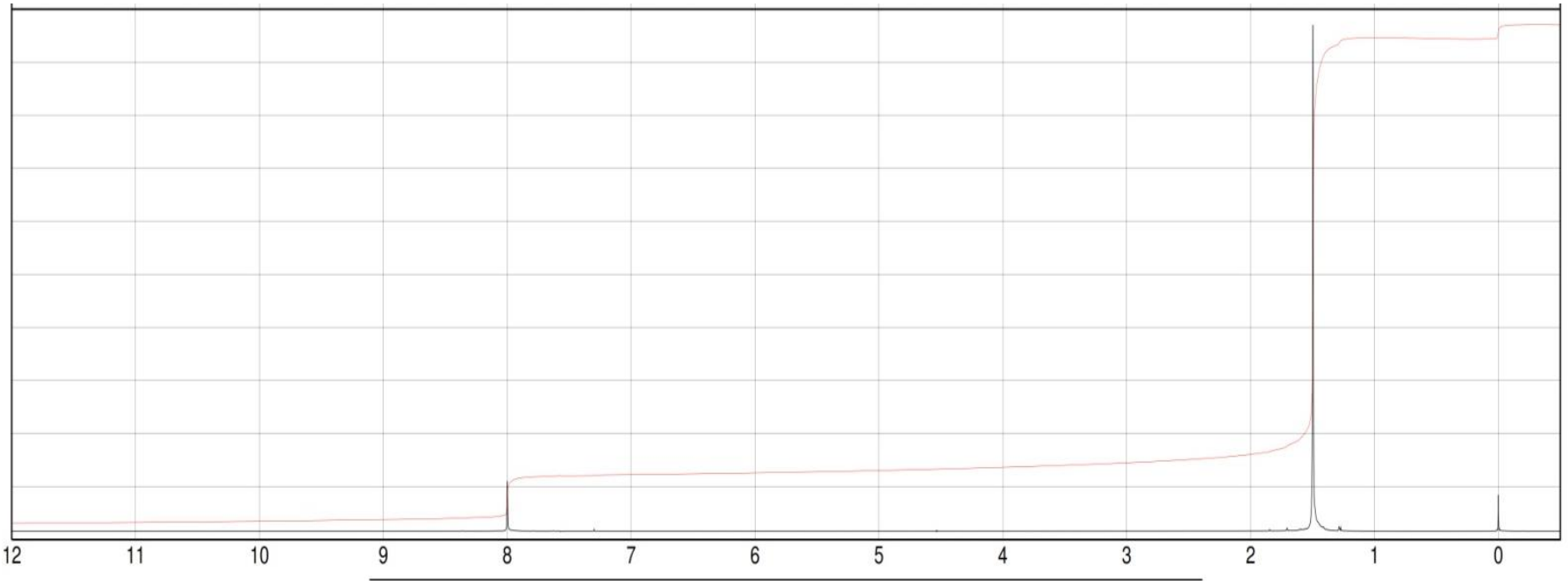
Correlation chart for ^{13}C Chemical Shifts (ppm(

$C_4H_8O_2$

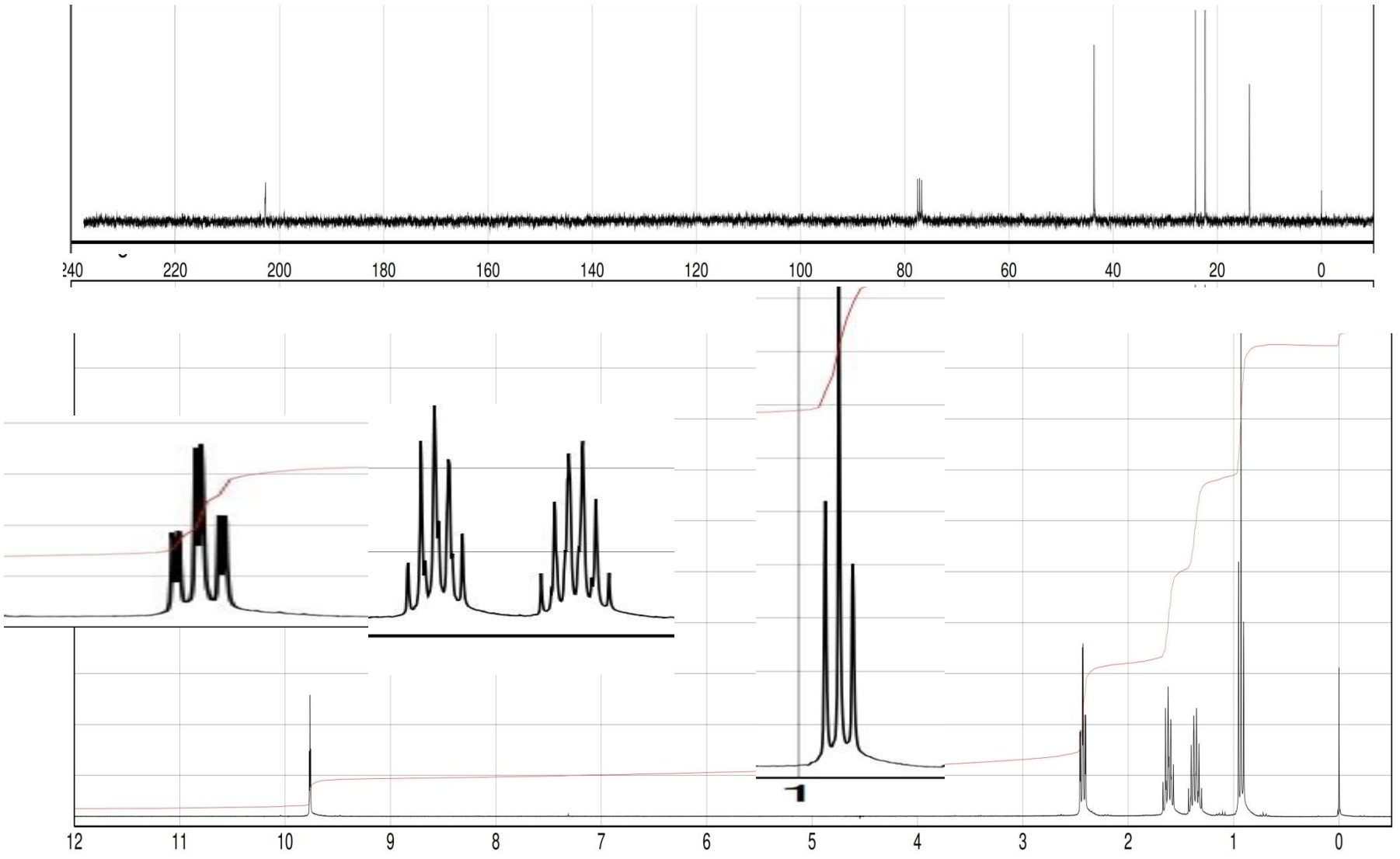


$C_5H_{10}O_2$

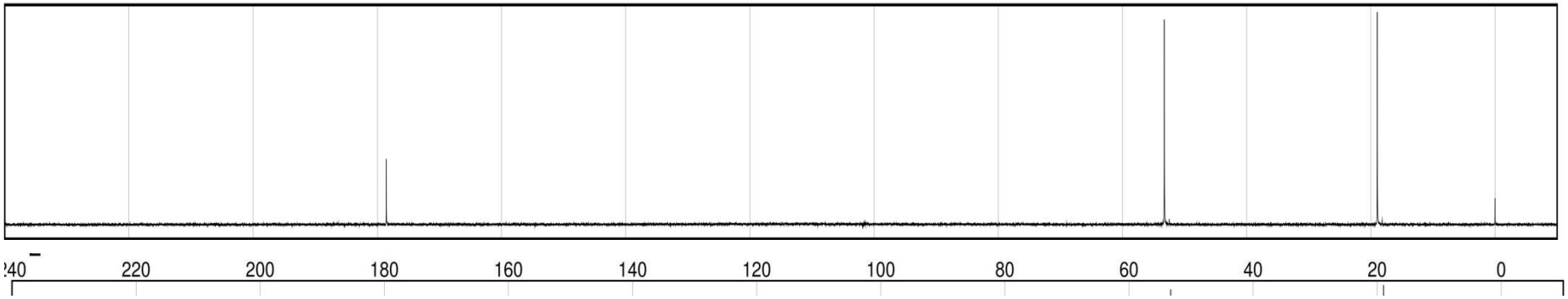


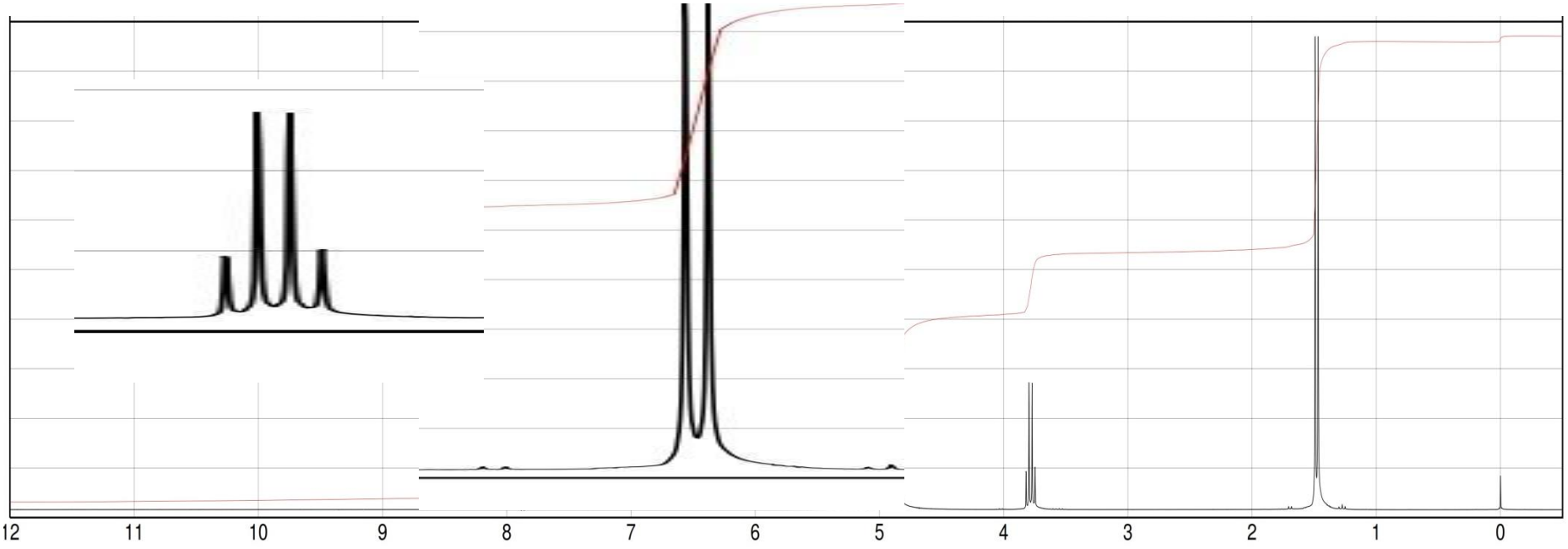


$C_5H_{10}O$

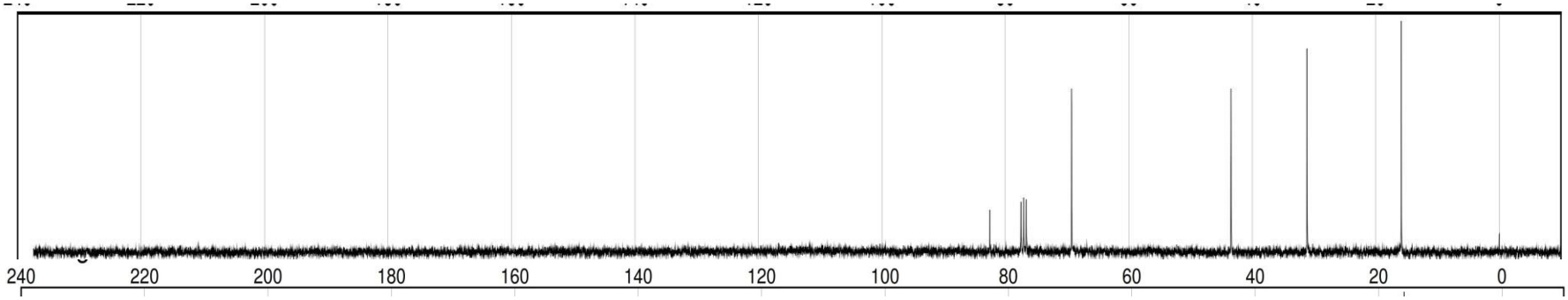


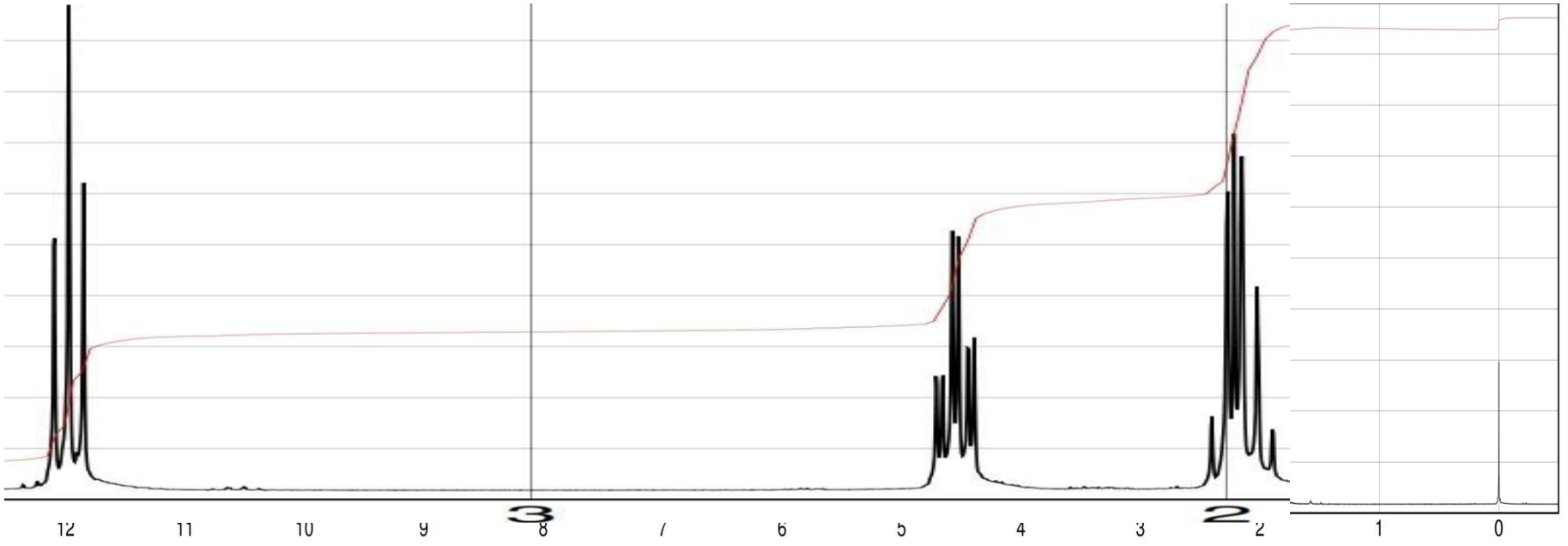
$C_3H_7NO_2$





C_5H_7Cl


240
220
200
180
160
140
120
100
80
60
40
20
0


3
2
12
11
10
9
8
7
6
5
4
3
2
1
0

The DEPT Experiment

Distortions enhancement by polarization transfer (DEPT(

Used to distinguish carbon atoms according to the number of attached hydrogen atoms. A multipulse experiment – uses pulses on both the H-1 and C-13 channels.

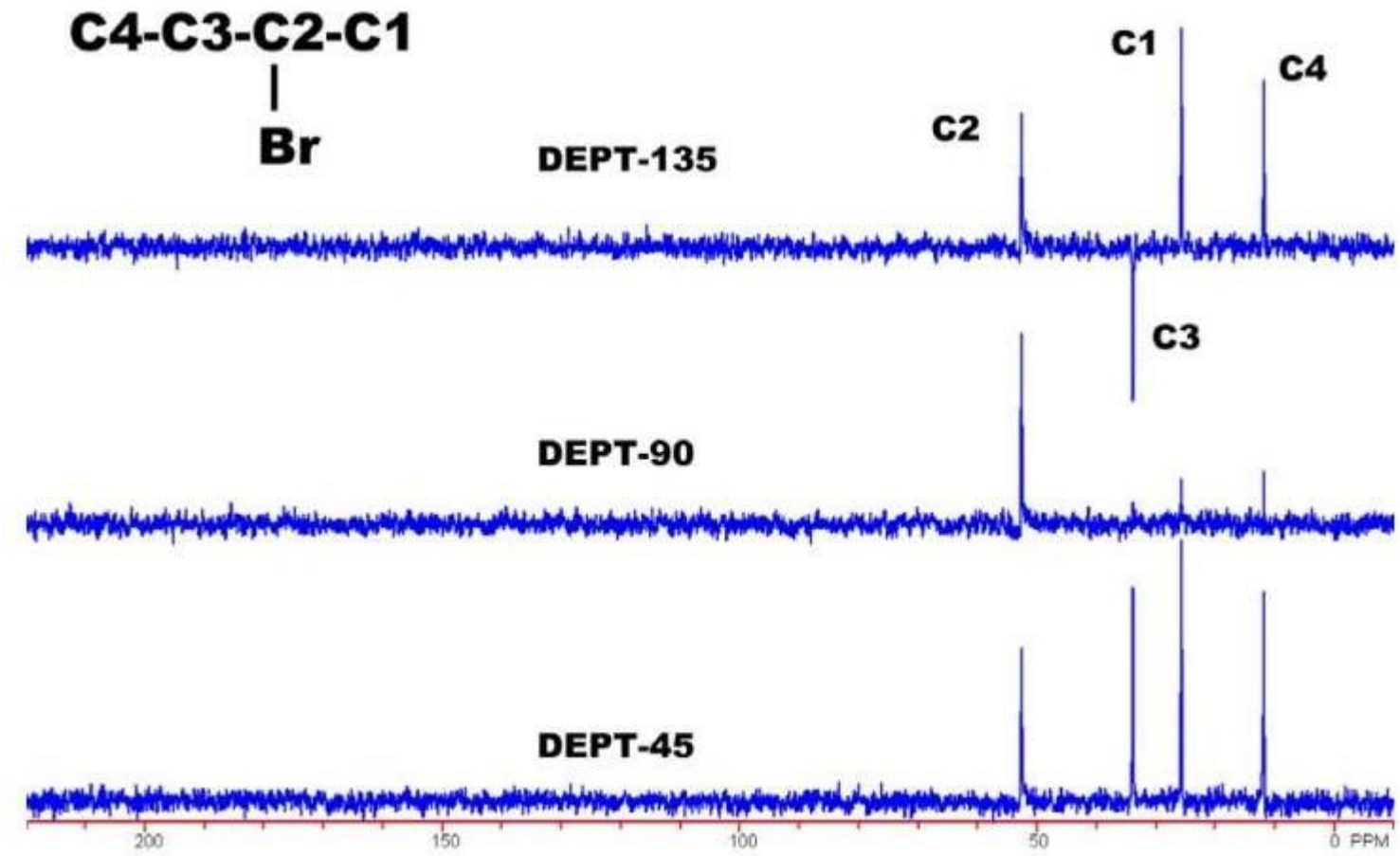
Dept 45 – only shows carbons that have attached hydrogen atoms (quaternary carbon atoms do not appear.(

Dept 90 – only carbon atoms with a single attached hydrogen atom (methine carbon atoms) appear.

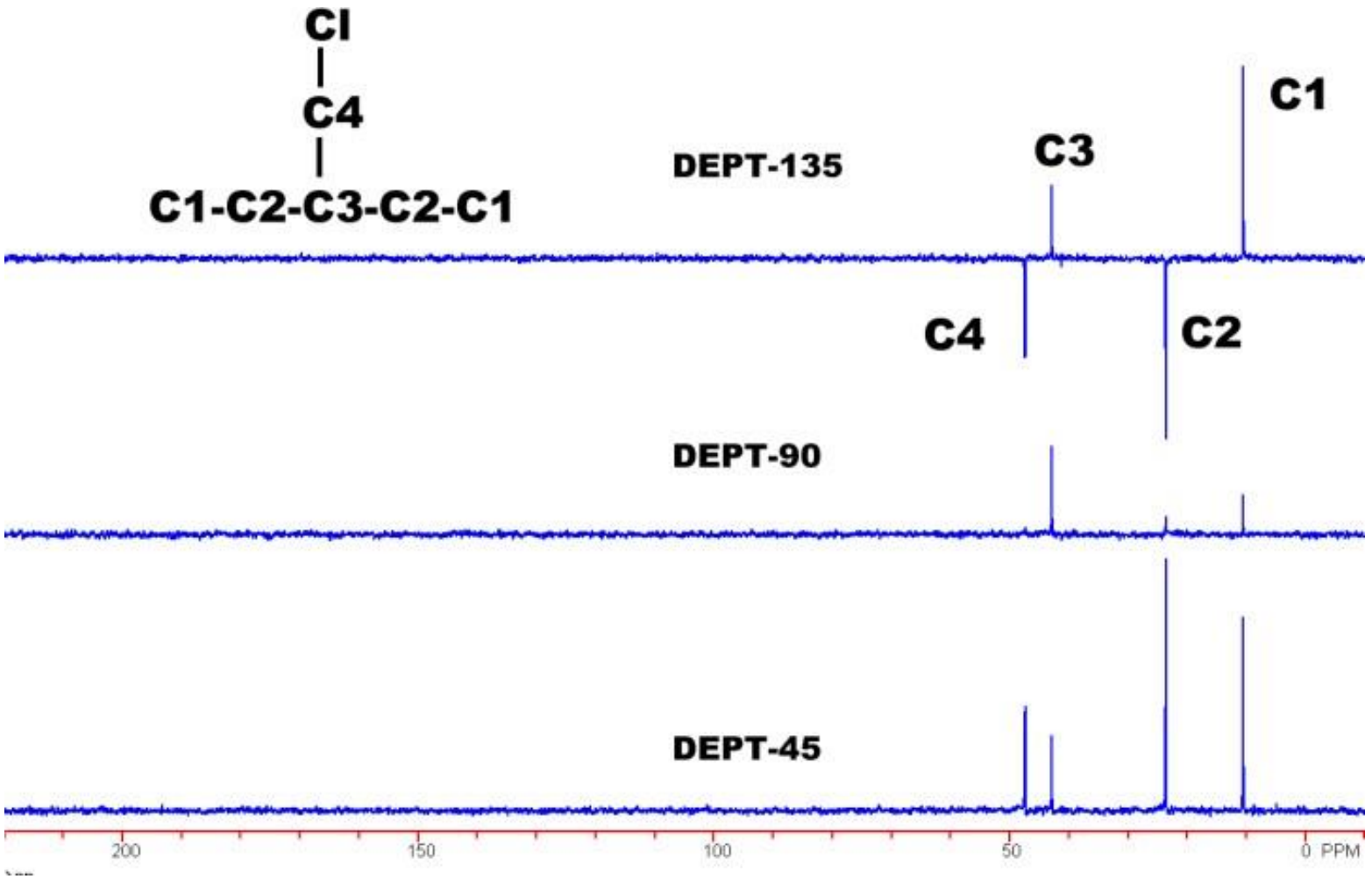
Dept 135 – distinguishes between carbon atoms based on their phasing CH and CH3 carbon atoms are phased the same way (usually positive), CH_2 carbon atoms are phased the opposite way (usually negative.(

DEPT experiments of 2-Bromobutane

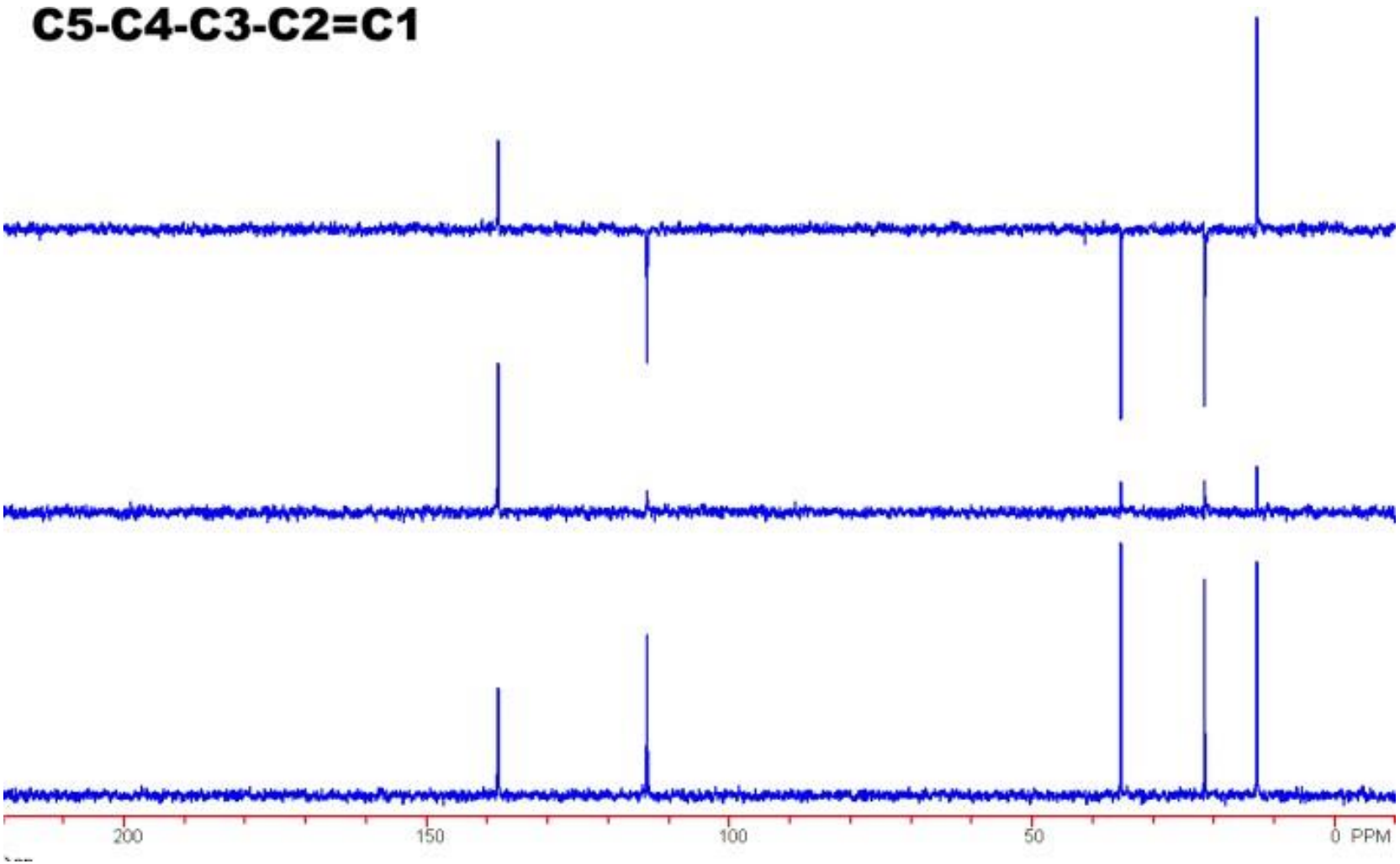
All carbons appear on DEPT-45 (all carbon atoms have attached protons(
On the DEPT-90 only the C2 carbon appears (the only carbon atom with one attached proton) On the DEPT-135 only the C3 carbon exhibits negative phasing (the only methylene carbon(



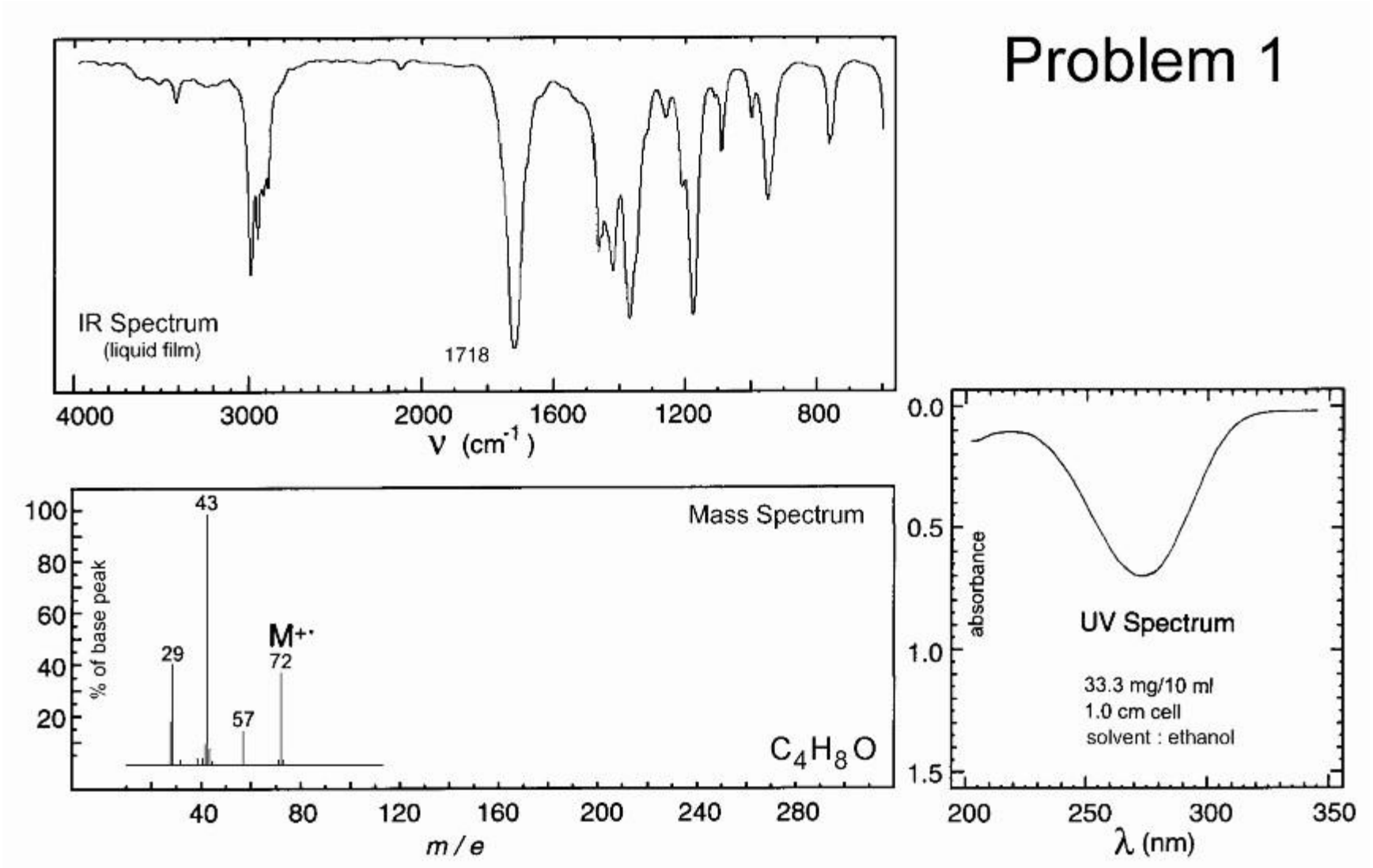
Dept experiments of 3-(1-chloromethyl)pentane



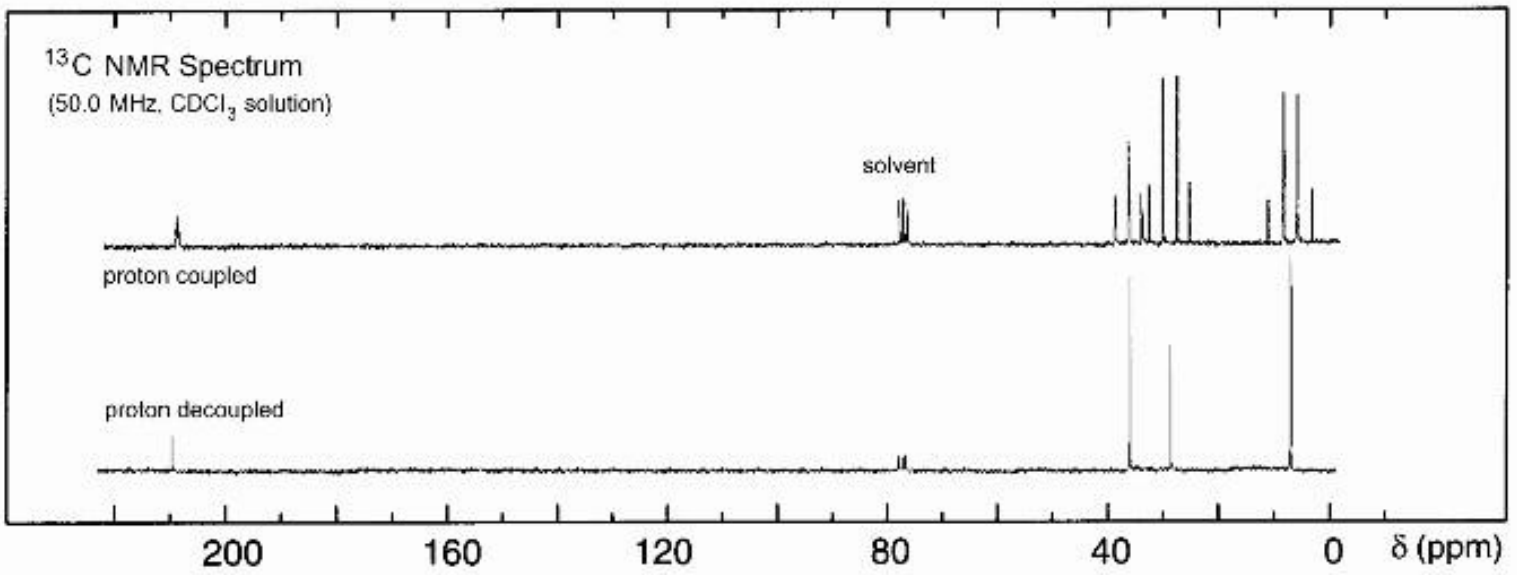
Dept experiments of 1-pentene

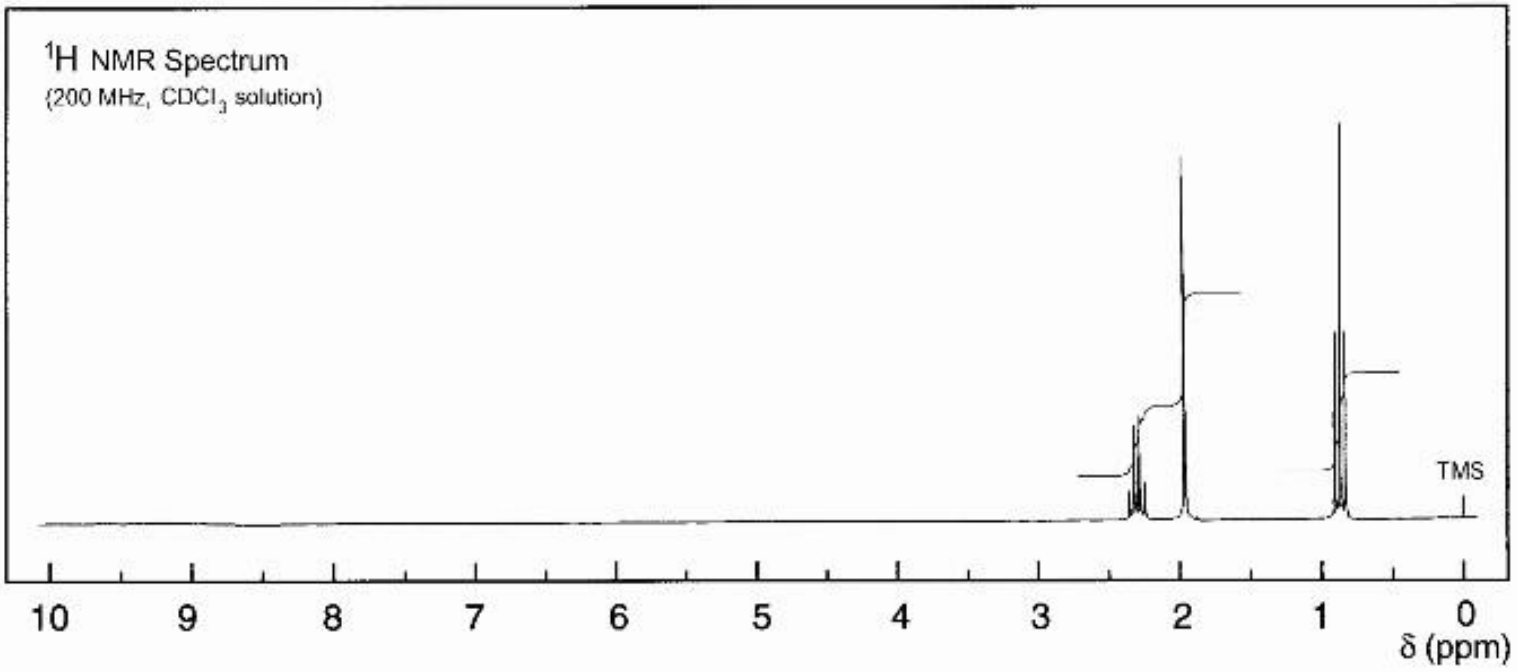


Problem 1

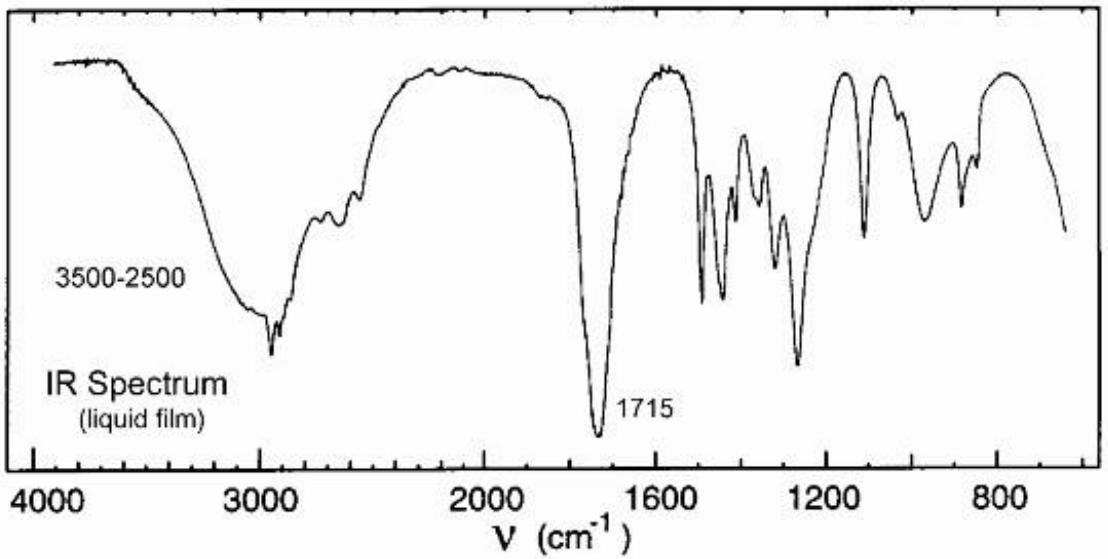

Problem 1
IR Spectrum
(liquid film)
1718
4000
3000
2000
1600
1200
800
ν (cm-1)
Mass Spectrum
% of base peak
100
80
60
40
20
43
29
M+·
72
57
C4H8O
40
80
120
160
200
240
280
m/e
0.0
0.5
1.0
1.5
absorbance
UV Spectrum
33.3 mg/10 ml
1.0 cm cell
solvent : ethanol
200
250
300
350
λ (nm)

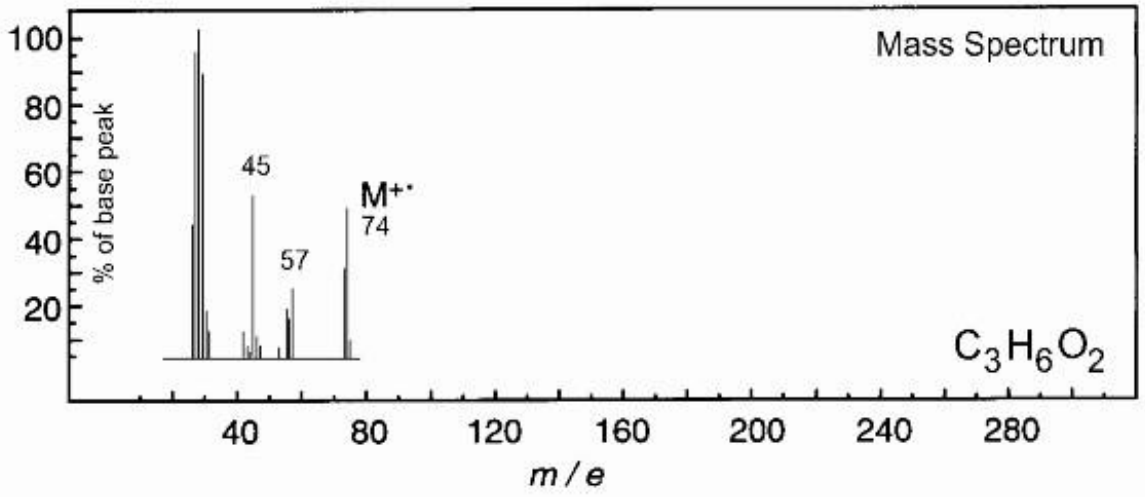
Problem 1


^{13}C NMR Spectrum
(50.0 MHz, $CDCl_3$ solution)
solvent
proton coupled
proton decoupled
200
160
120
80
40
0
δ (ppm)


^{1}H NMR Spectrum
(200 MHz, $CDCl_3$ solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 2

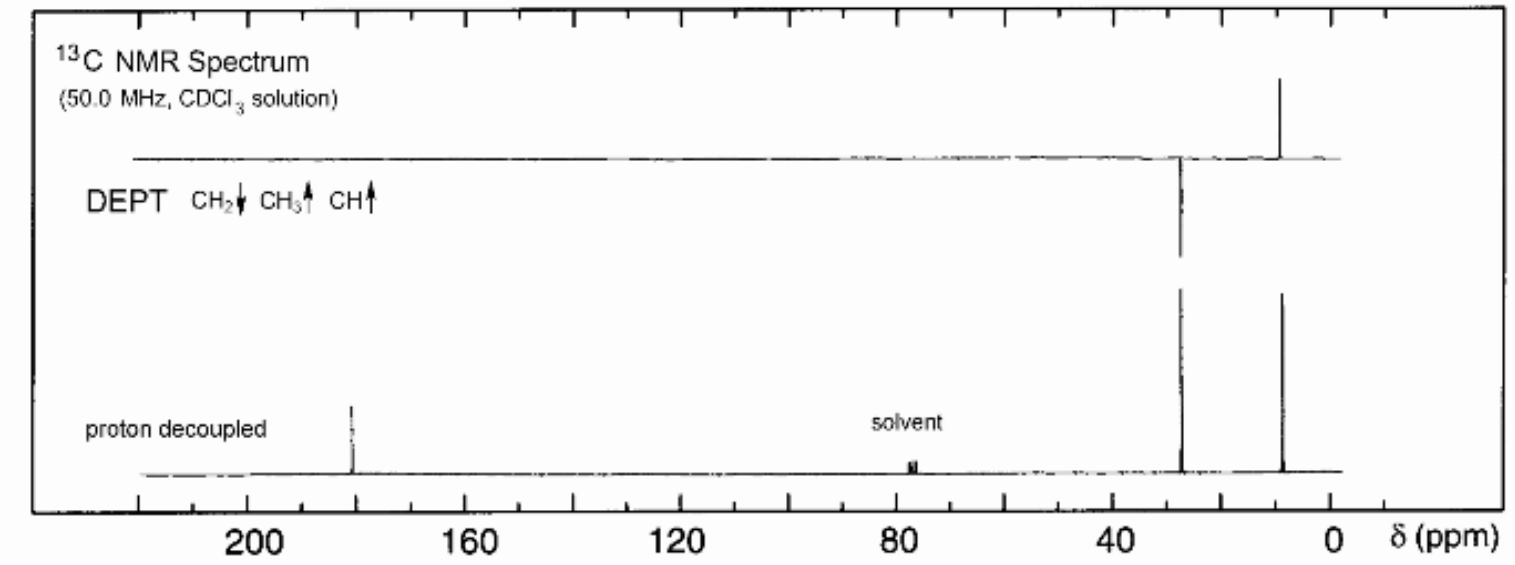


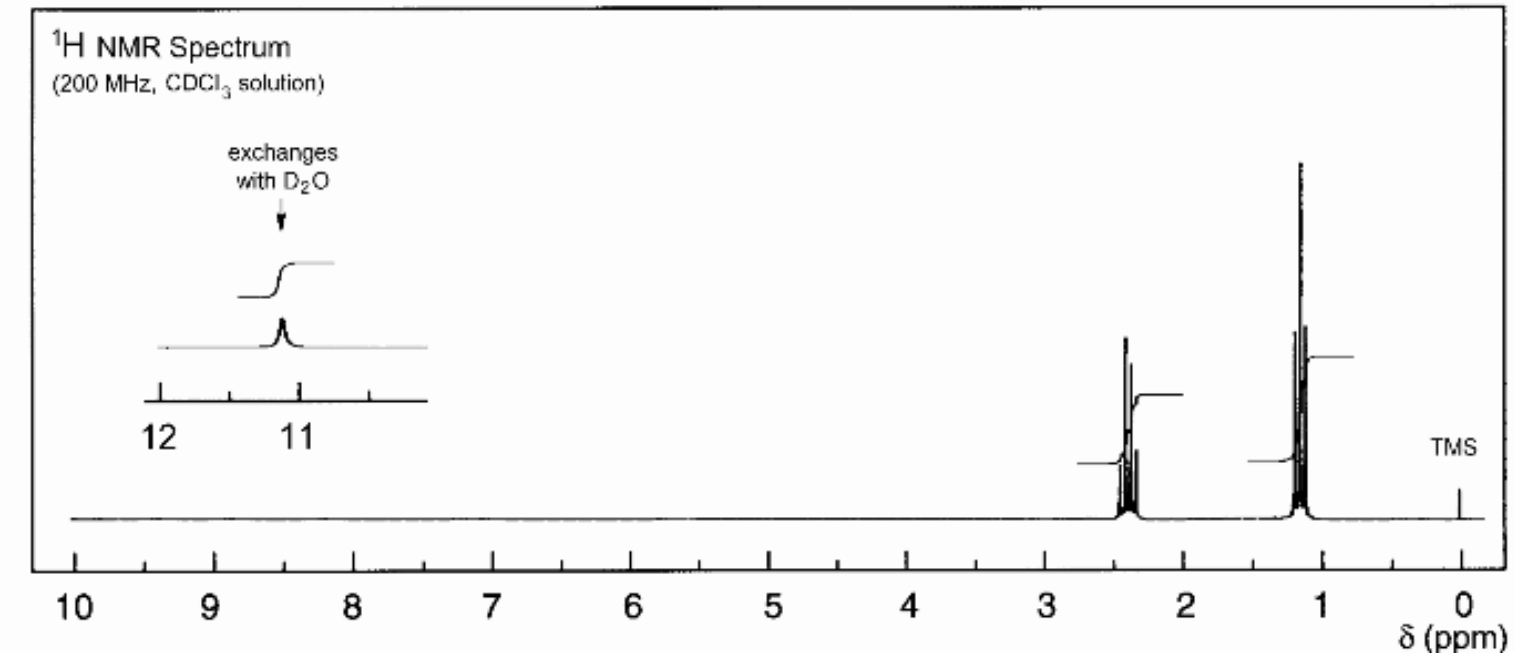


Problem 2

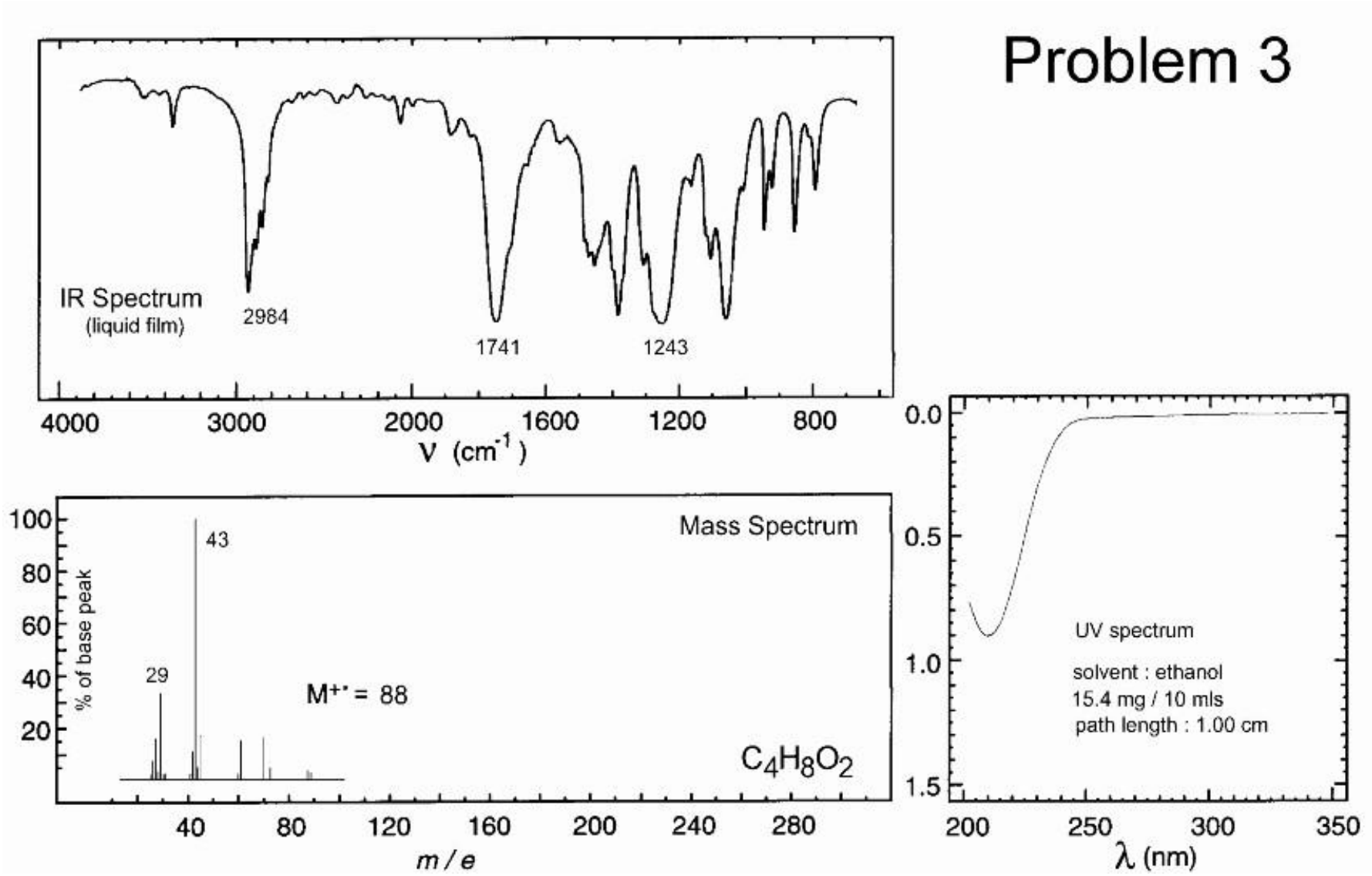
No significant UV absorption above 220 nm

Problem 2

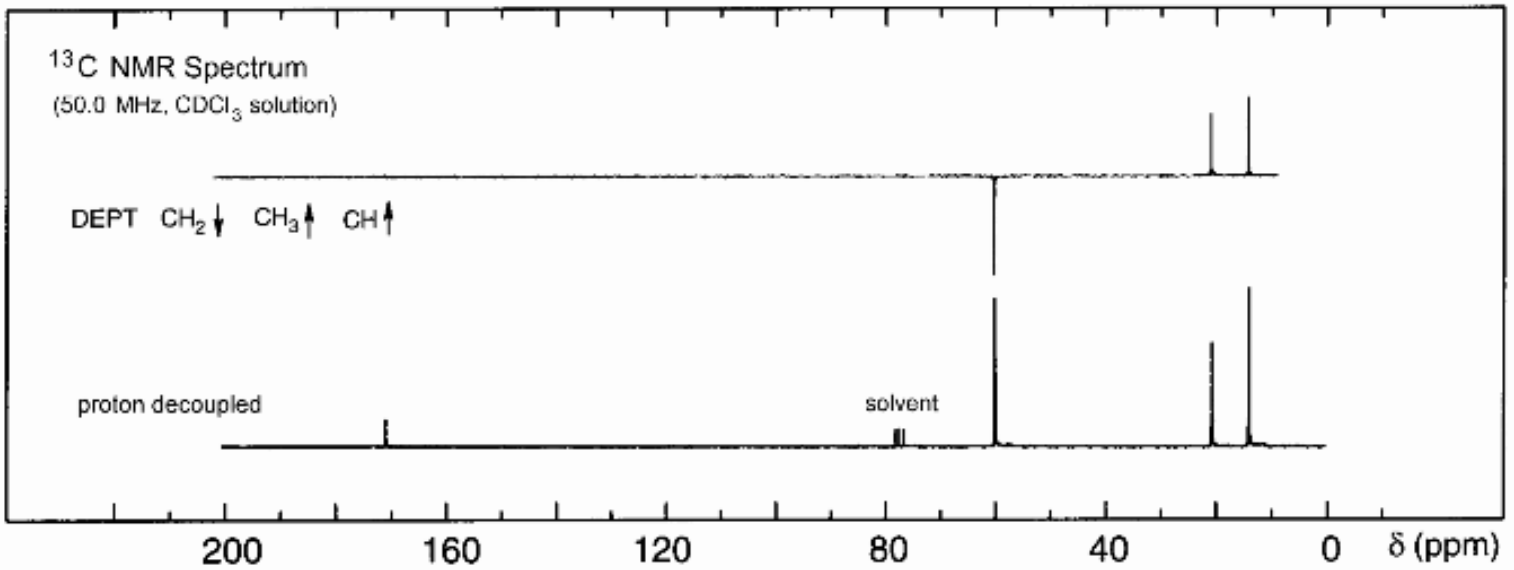

^{13}C NMR Spectrum
(50.0 MHz, $CDCl_3$ solution)
DEPT CH_2 CH_3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

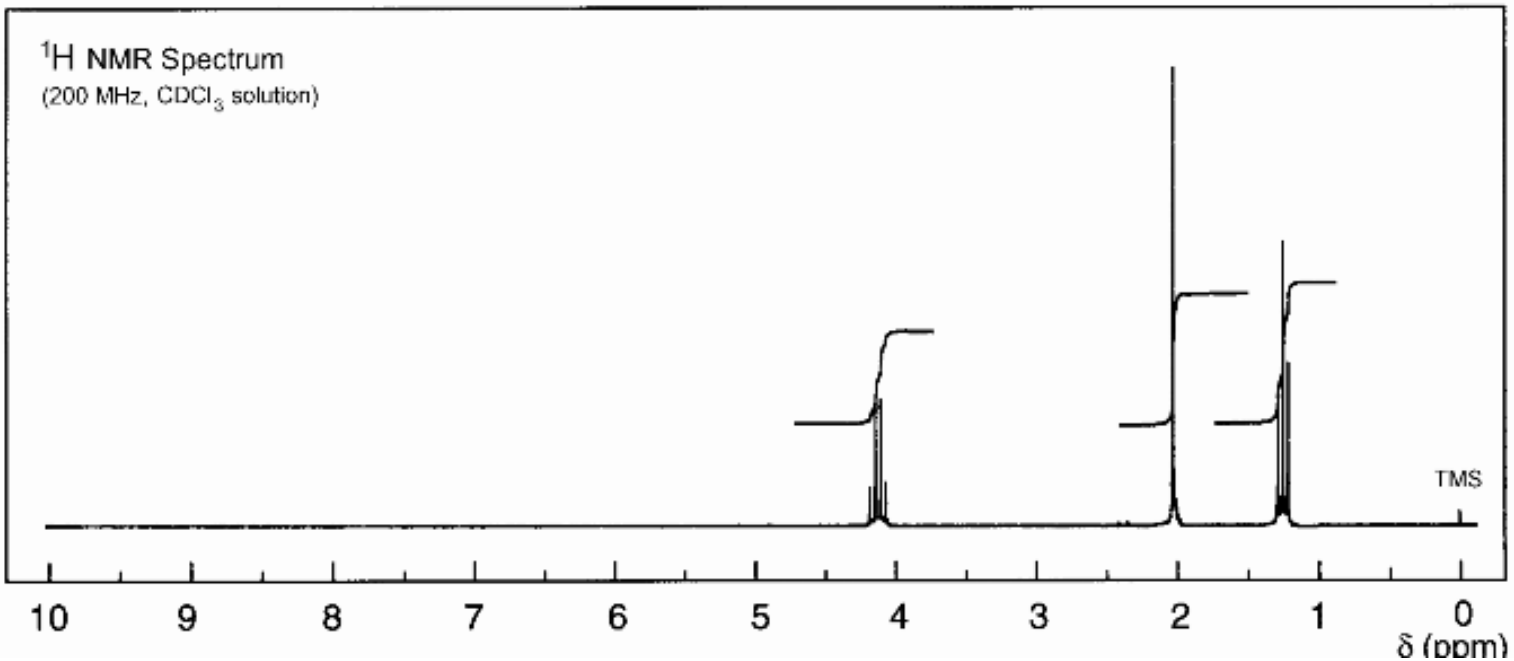

^{1}H NMR Spectrum
(200 MHz, $CDCl_3$ solution)
exchanges with D_2O
12
11
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 3

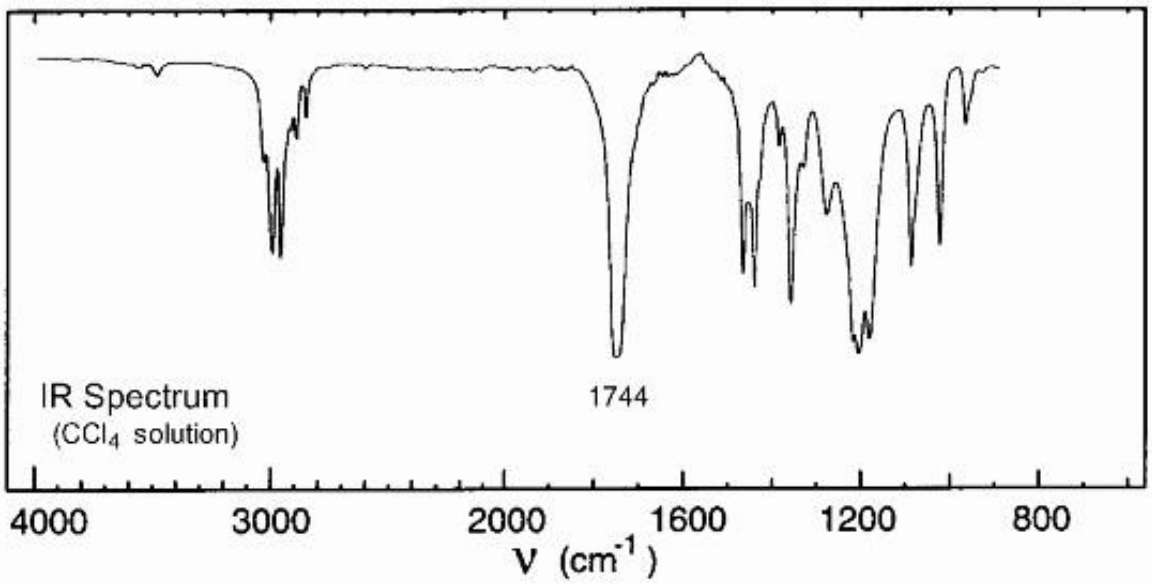

Problem 3
IR Spectrum
(liquid film)
2984
1741
1243
4000
3000
2000
1600
1200
800
ν (cm-1)
Mass Spectrum
43
29
M+• = 88
C4H8O2
% of base peak
100
80
60
40
20
40
80
120
160
200
240
280
m / e
UV spectrum
solvent : ethanol
15.4 mg / 10 mls
path length : 1.00 cm
0.0
0.5
1.0
1.5
200
250
300
350
λ (nm)

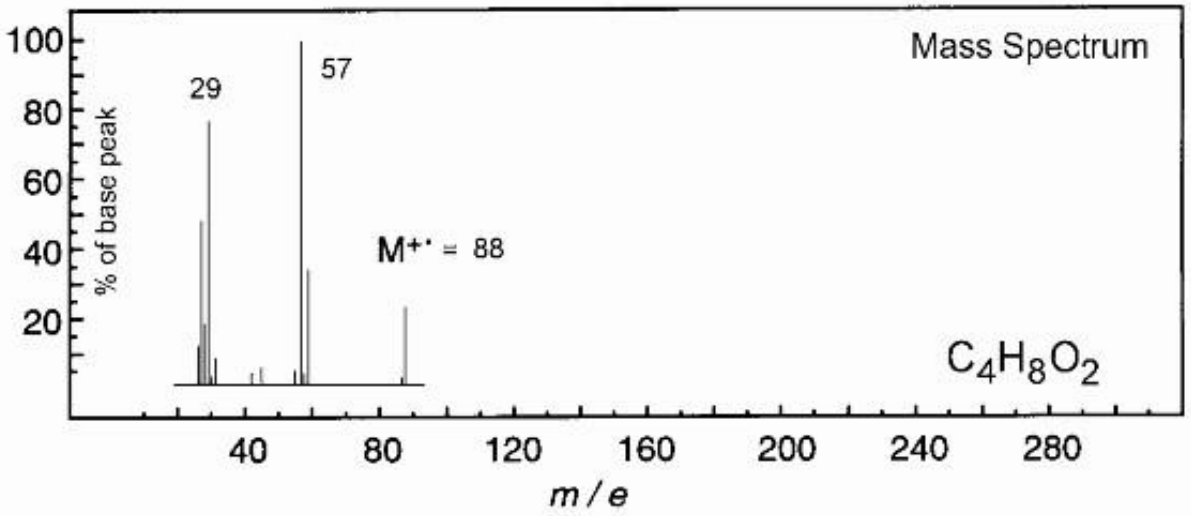
Problem 3


^{13}C NMR Spectrum
(50.0 MHz, $CDCl_3$ solution)
DEPT CH_2 CH_3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


^{1}H NMR Spectrum
(200 MHz, $CDCl_3$ solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 4

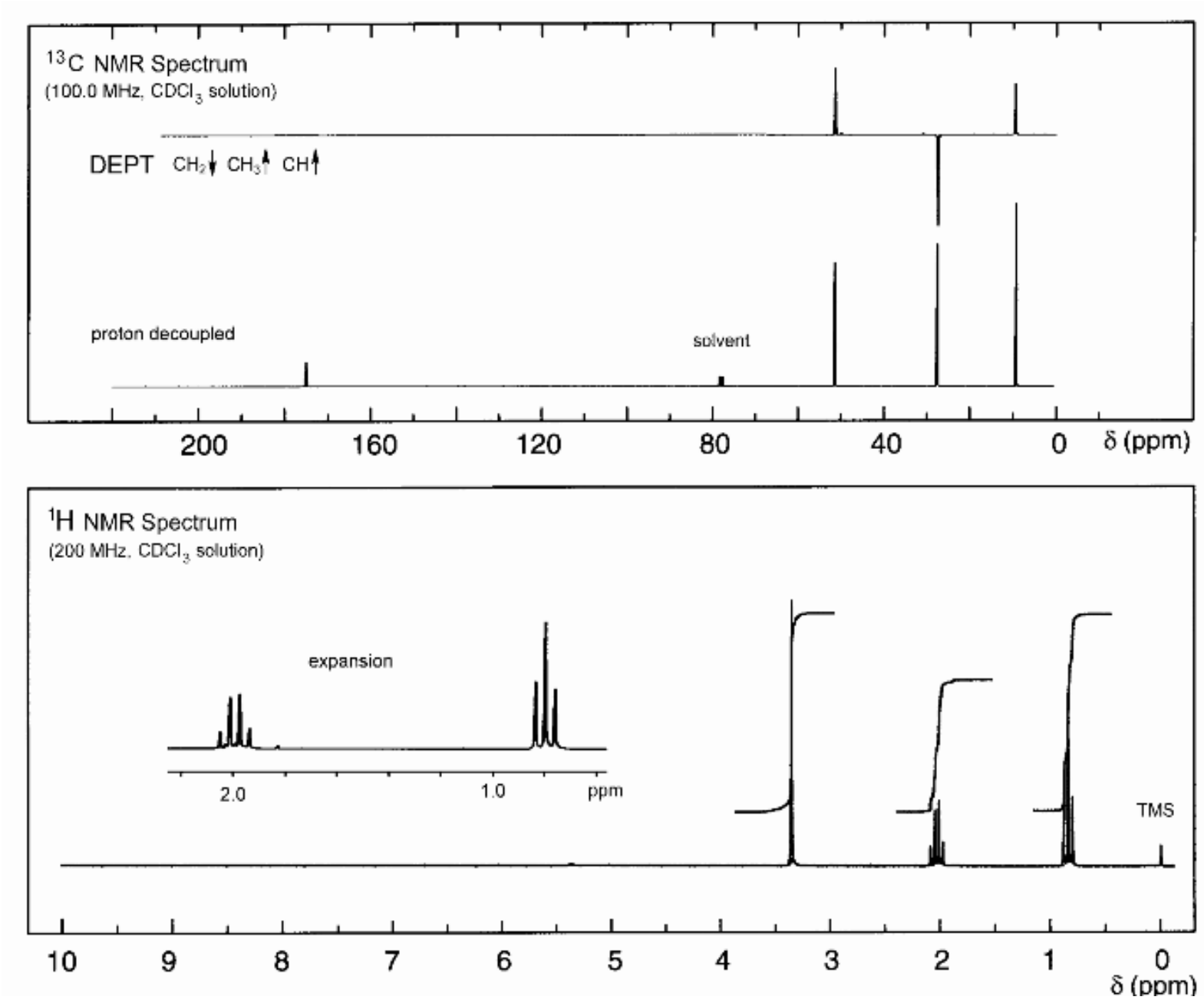




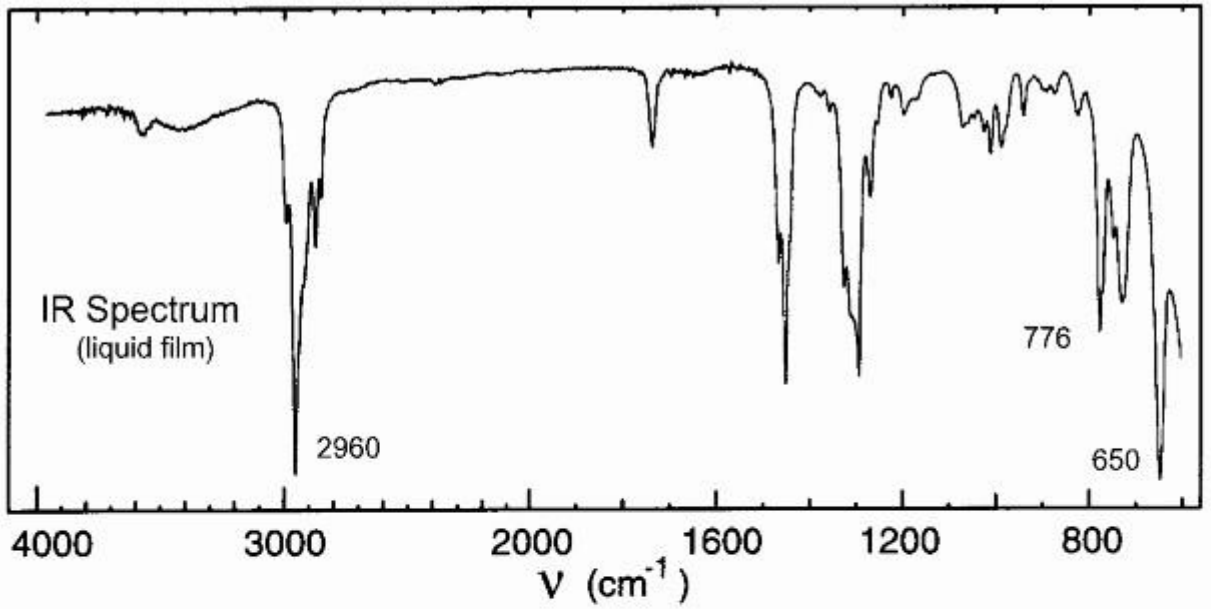
Problem 4

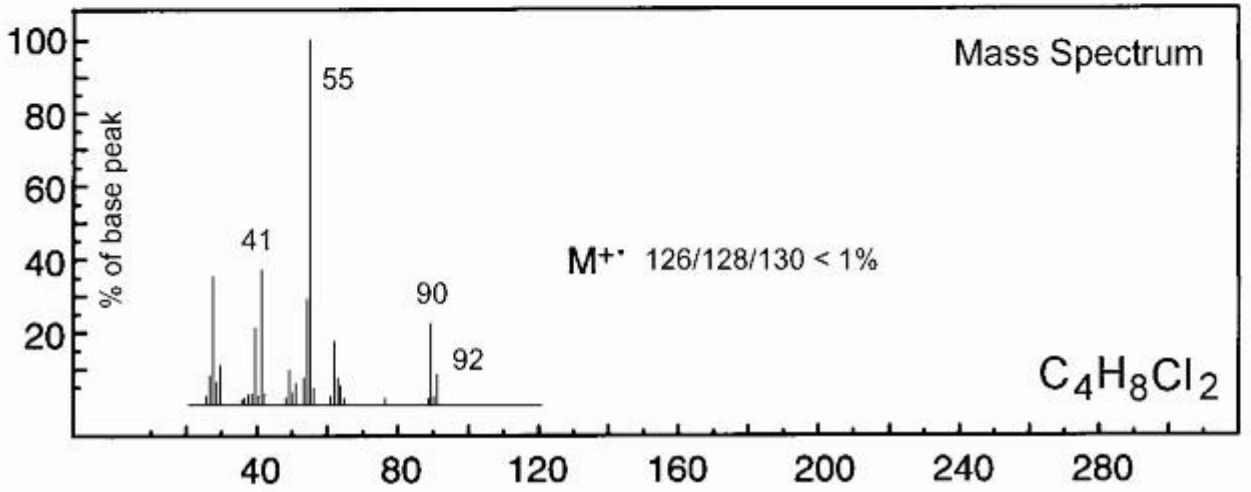
No significant UV absorption above 220 nm

Problem 4


13C NMR Spectrum
(100.0 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)
expansion
2.0
1.0
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Problem 5

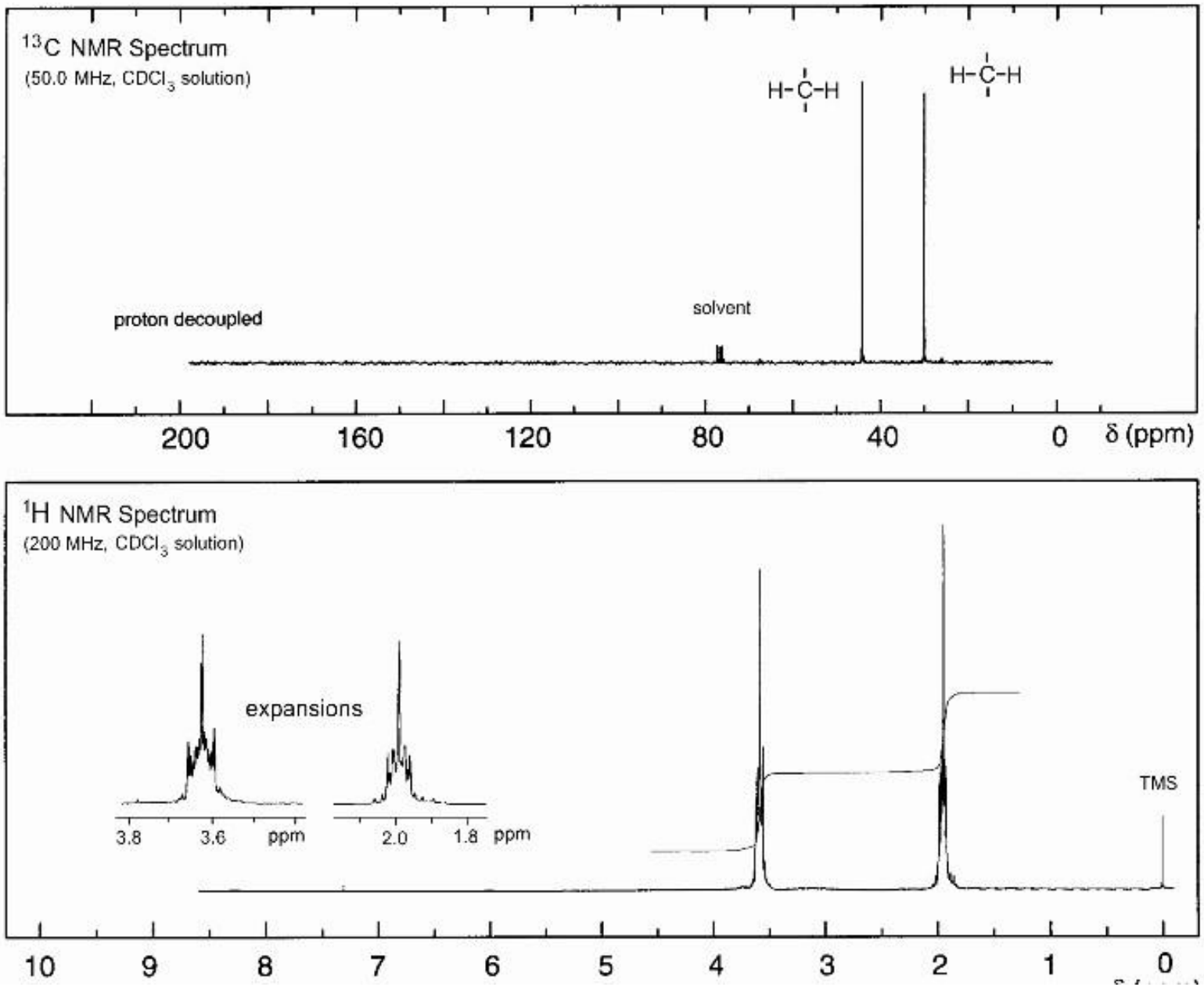




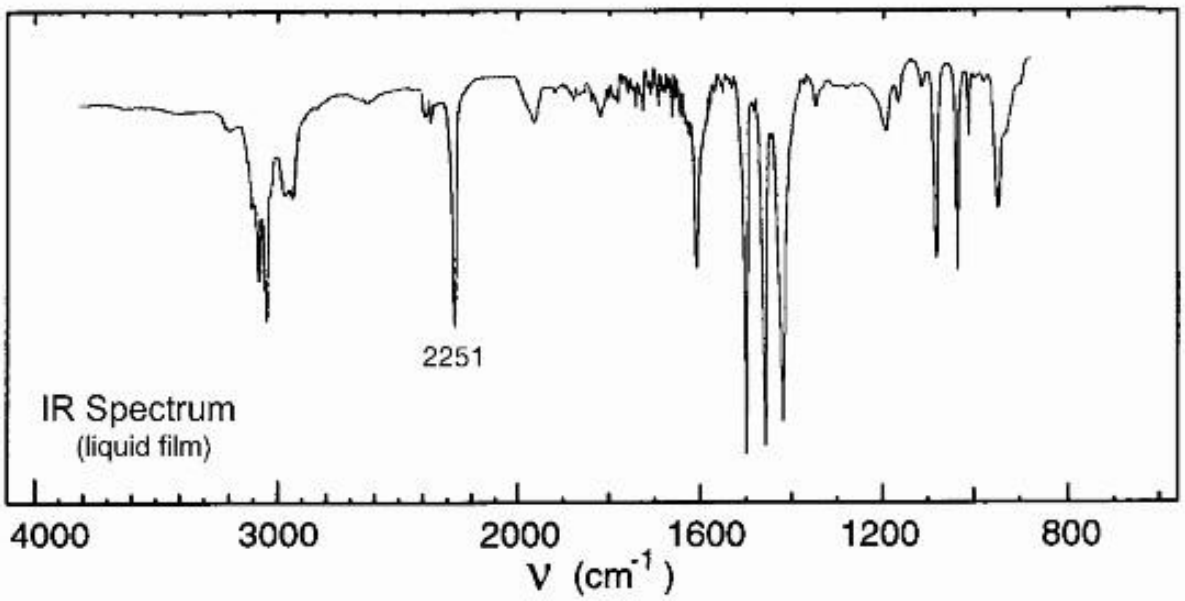
Problem 16

No significant UV absorption above 220 nm

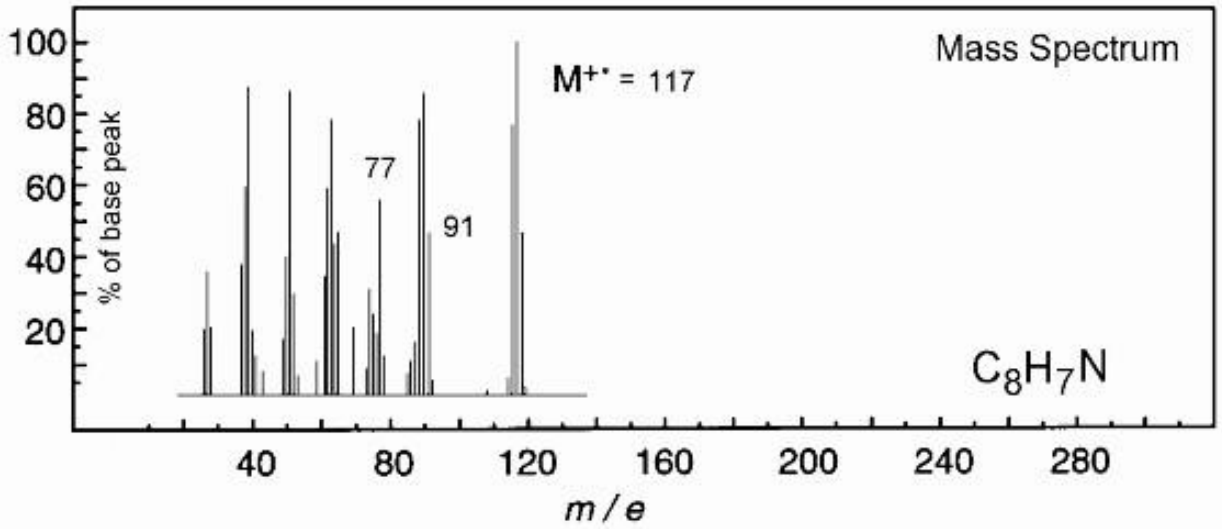
Problem 5


13C NMR Spectrum
(50.0 MHz, CDCl3 solution)
H-C-H
H-C-H
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)
1H NMR Spectrum
(200 MHz, CDCl3 solution)
expansions
3.8
3.6
ppm
2.0
1.8
ppm
TMS
10
9
8
7
6
5
4
3
2
1
0

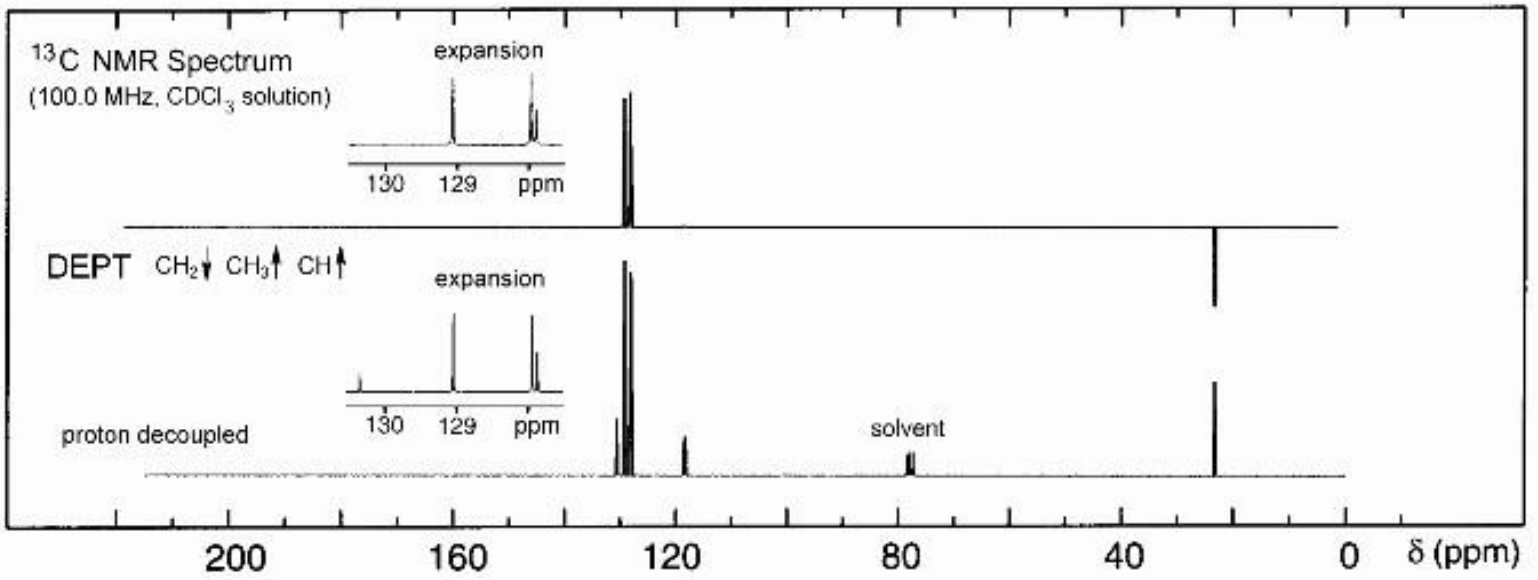
Problem 6

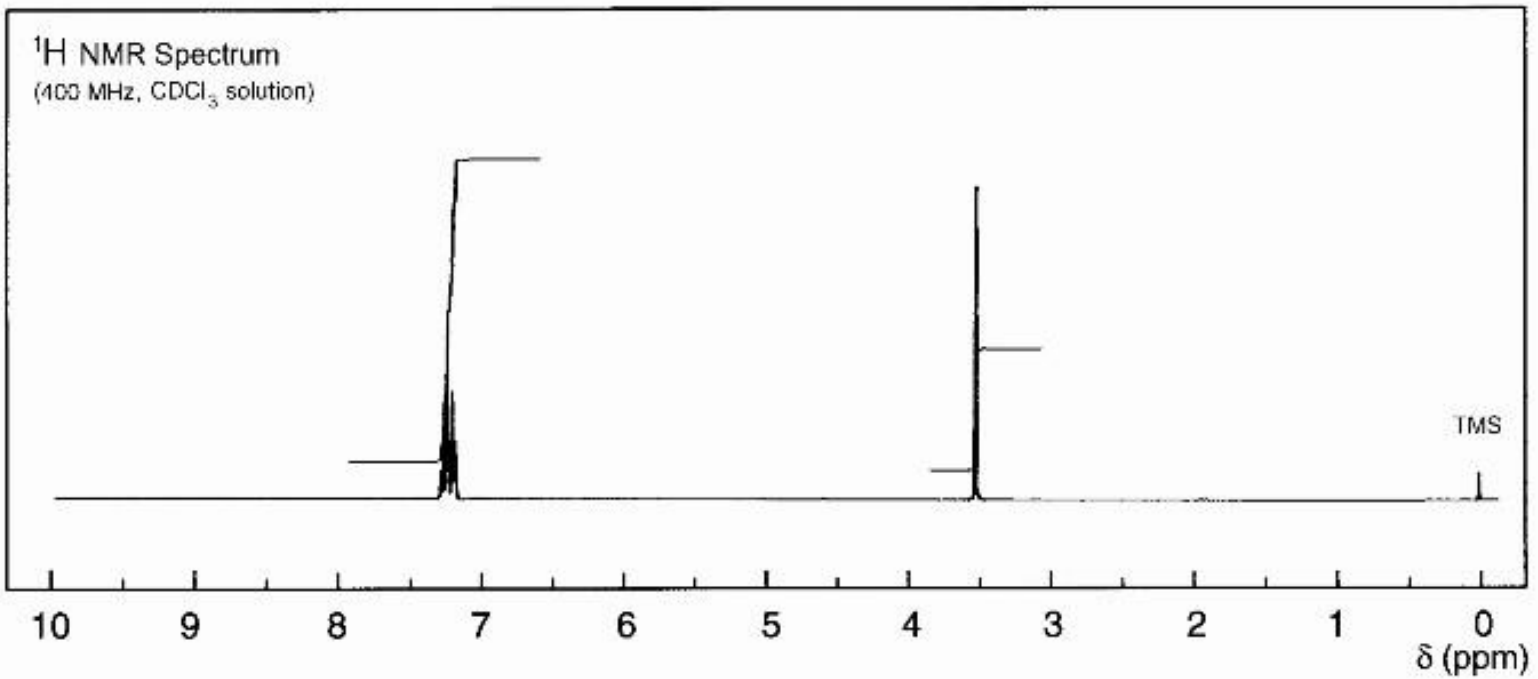


Problem 25



Problem 6


^{13}C NMR Spectrum
(100.0 MHz, $CDCl_3$ solution)
expansion
130
129
ppm
DEPT CH_2 CH_3 CH
expansion
130
129
ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)


^{1}H NMR Spectrum
(400 MHz, $CDCl_3$ solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)