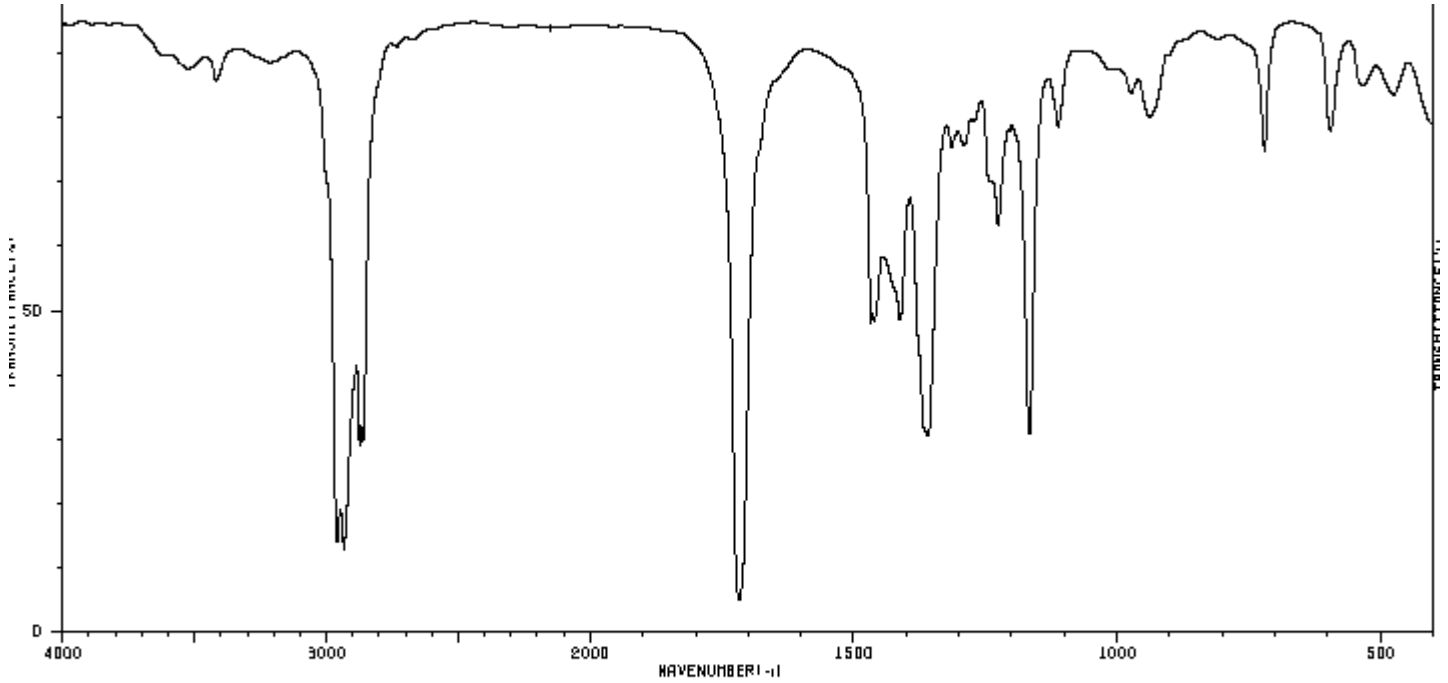
Some problems using C and H 2 D NMR

A compound has a molecular weight of 114 mass units and is know only to contain C, H, and O. What are the possible formulas?

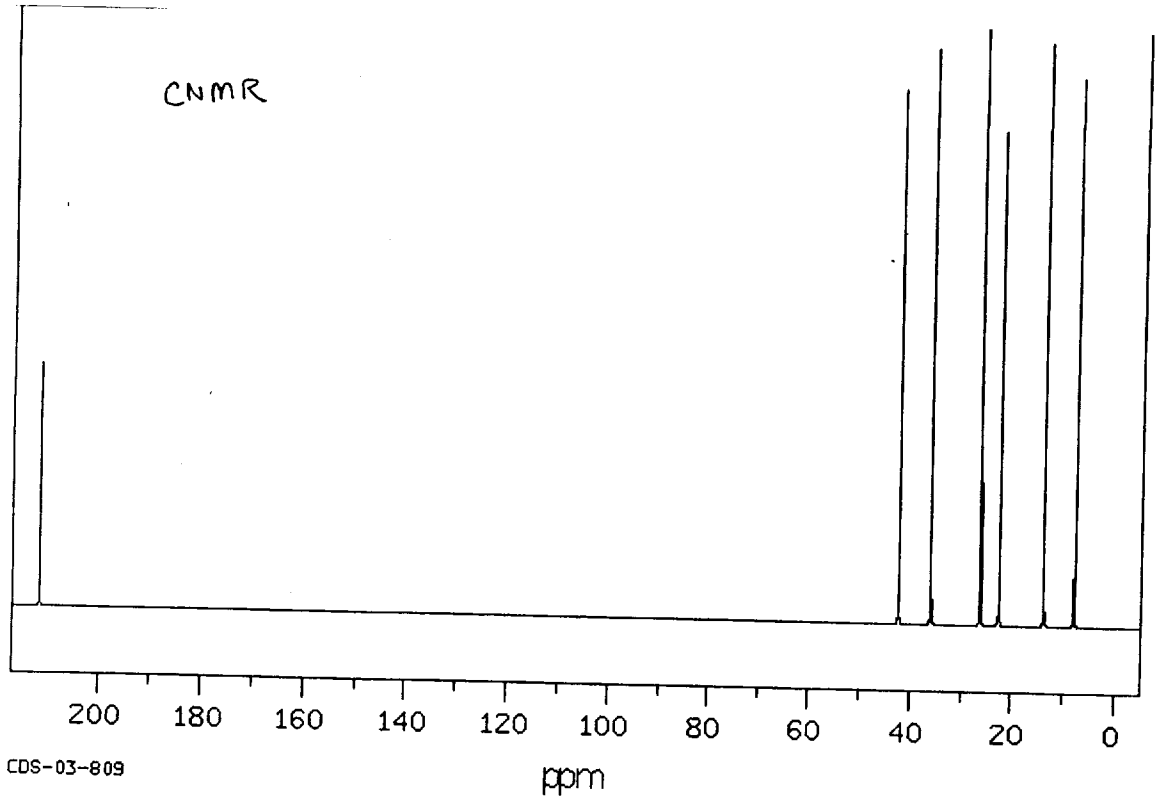


1. A compound has a molecular weight of 114 mass units and is know only to contain C, H, and O. What are the possible formulas?

114/13 = 8.769; 13*0.769 = 10; C_8H_{18};

$C_7H_{14}O$; $C_6H_{10}O_2$ ...

1. carbon count
2. carbonyl group



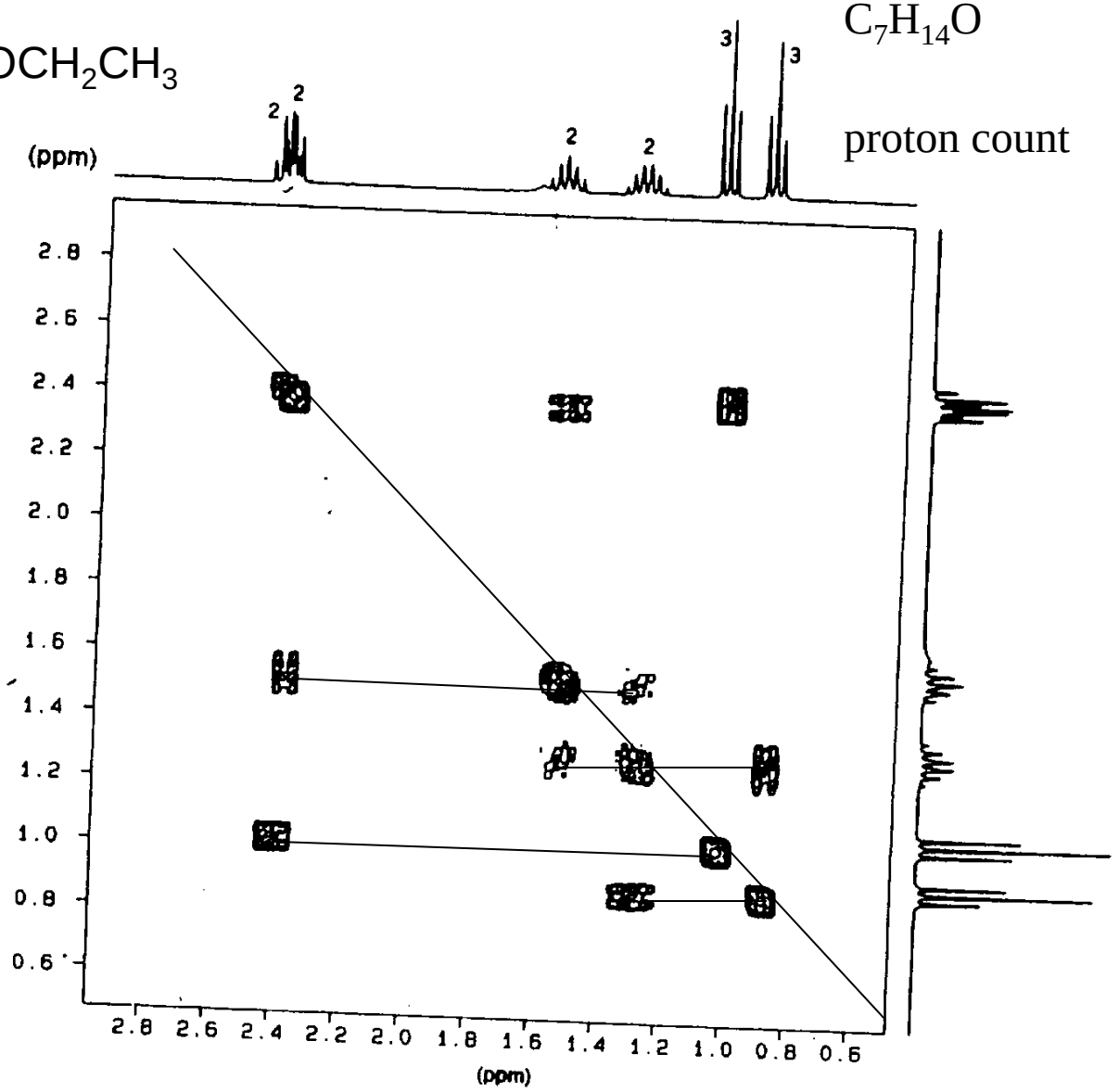
Compound 1 (continued)

COSY

$CH_3CH_2CH_2CH_2COCH_2CH_3$

$C_7H_{14}O$

proton count



Problem 2

A compound has a molecular weight of 102 mass units and is know only to contain C, H, and O. What are the possible formulas?

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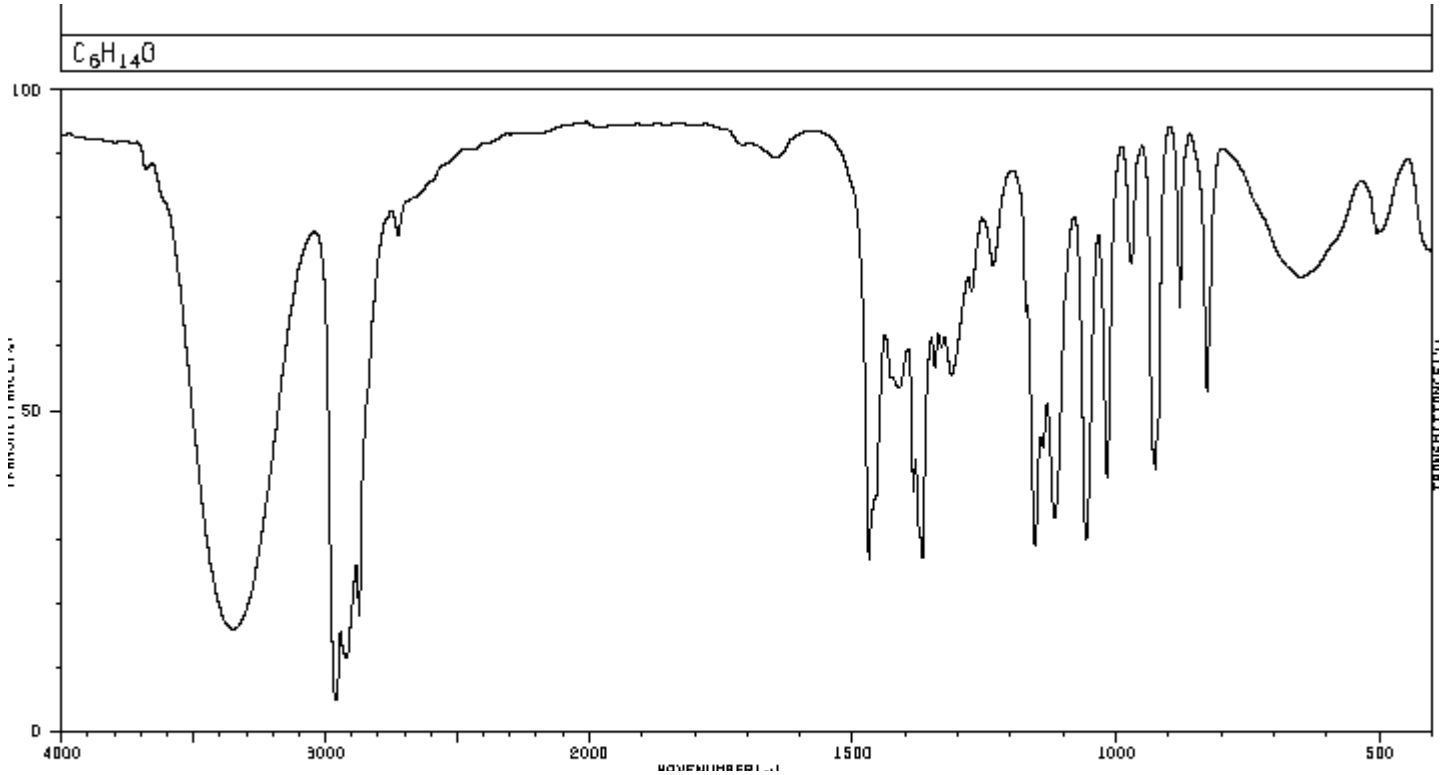
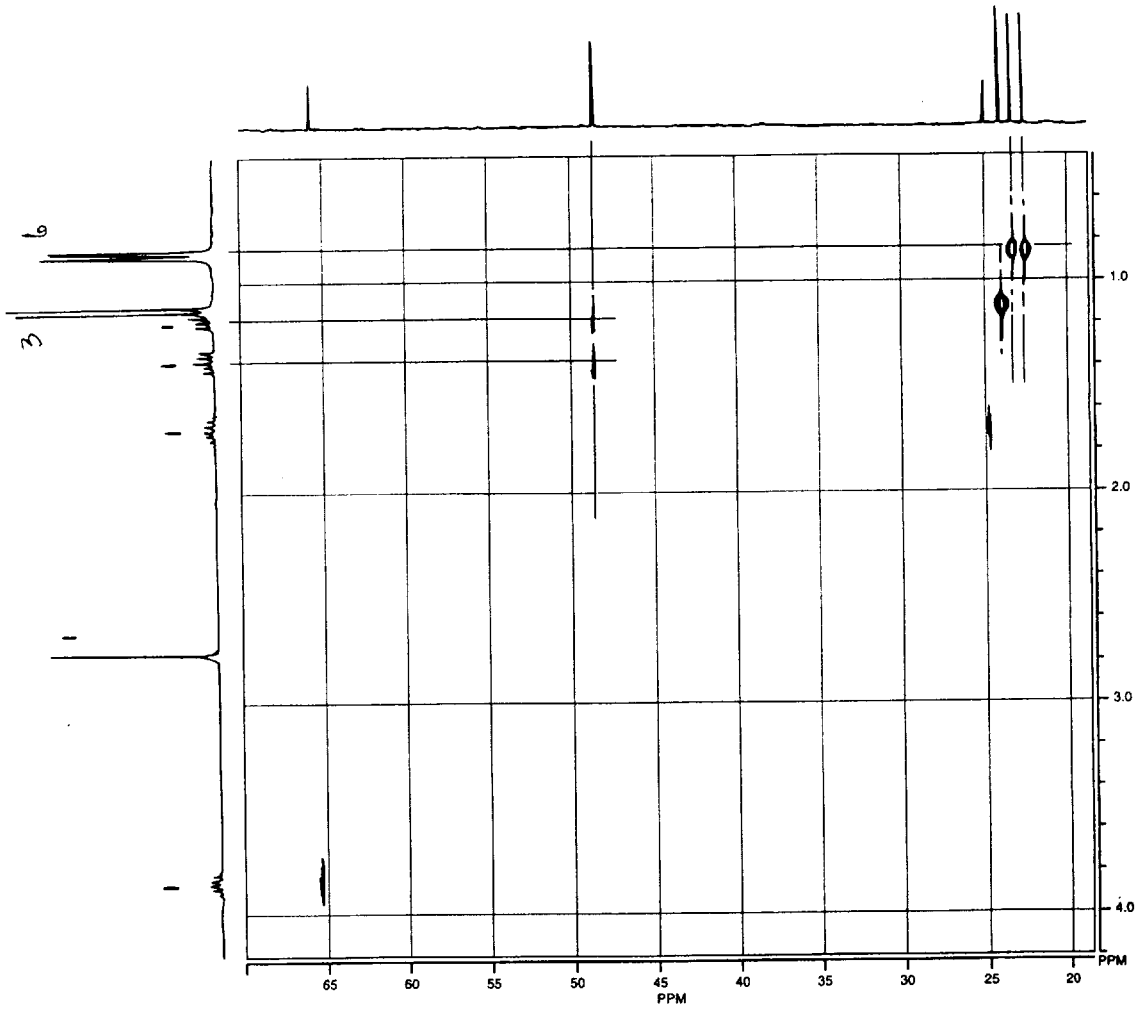
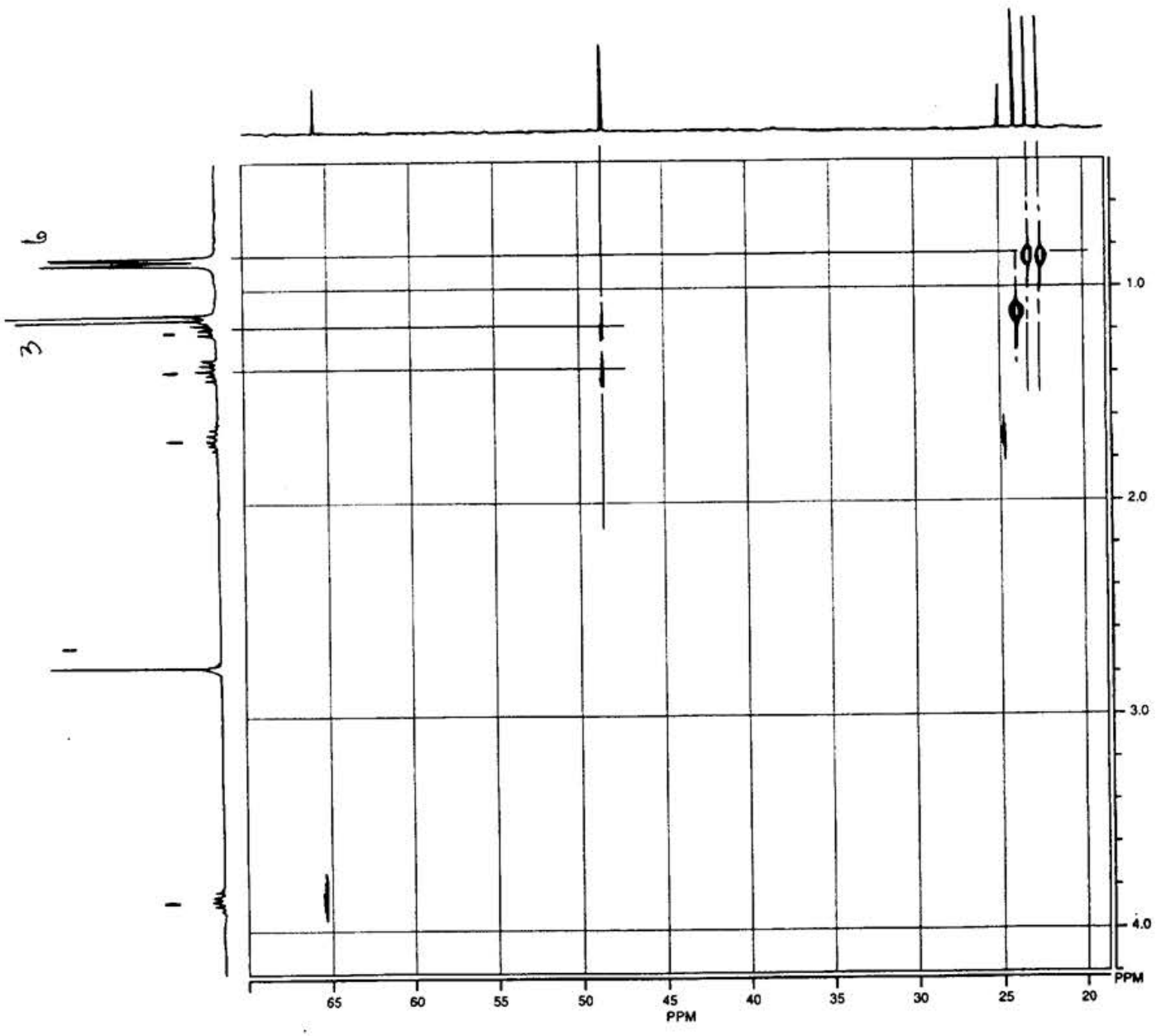


A compound has a molecular weight of 102 mass units and is know only to contain C, H, and O. What are the possible formulas?

102/13 =7.846; 13*0.846 = 11; C_7H_{18};

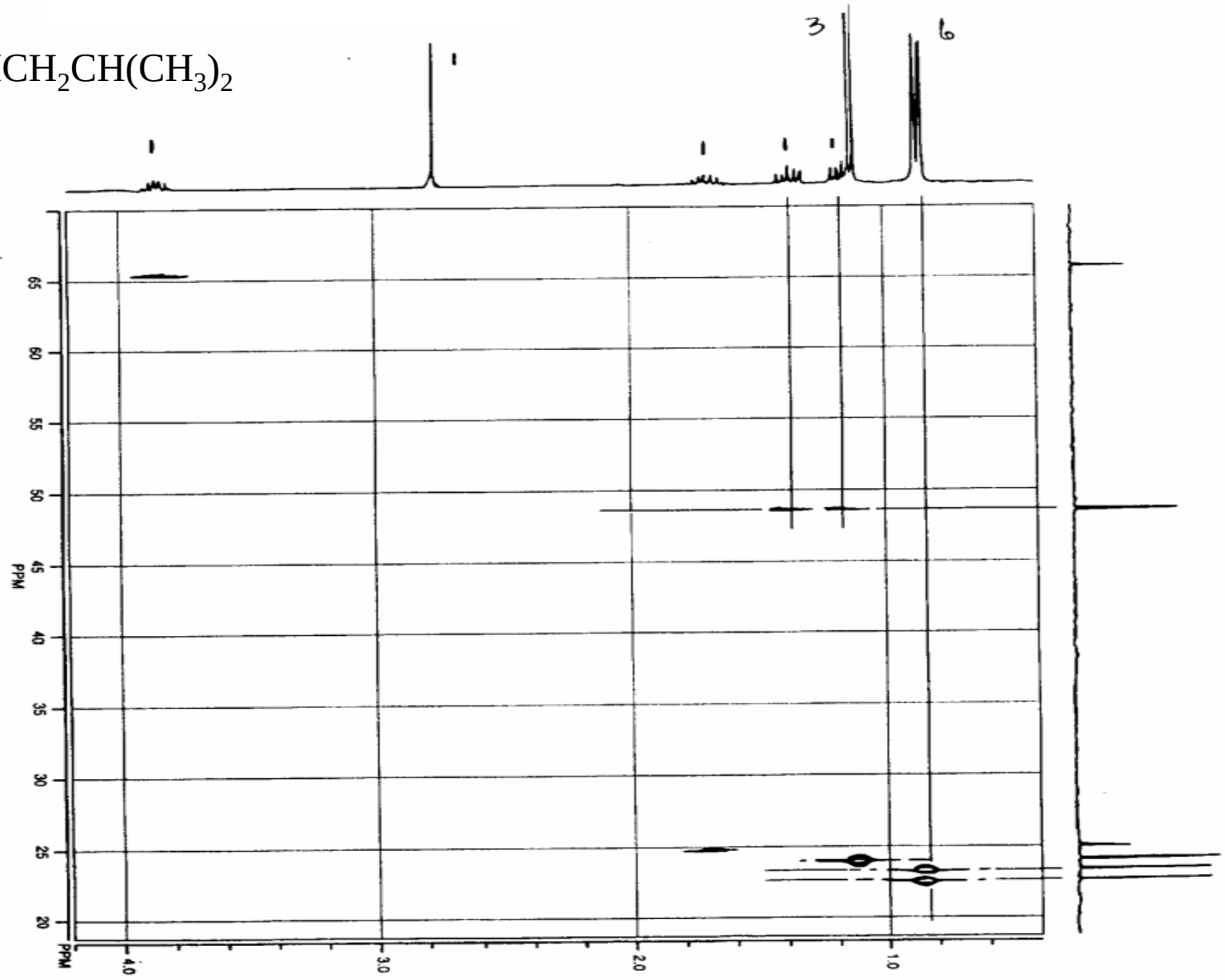
$C_6H_{14}O$; $C_5H_{10}O_2$ ...



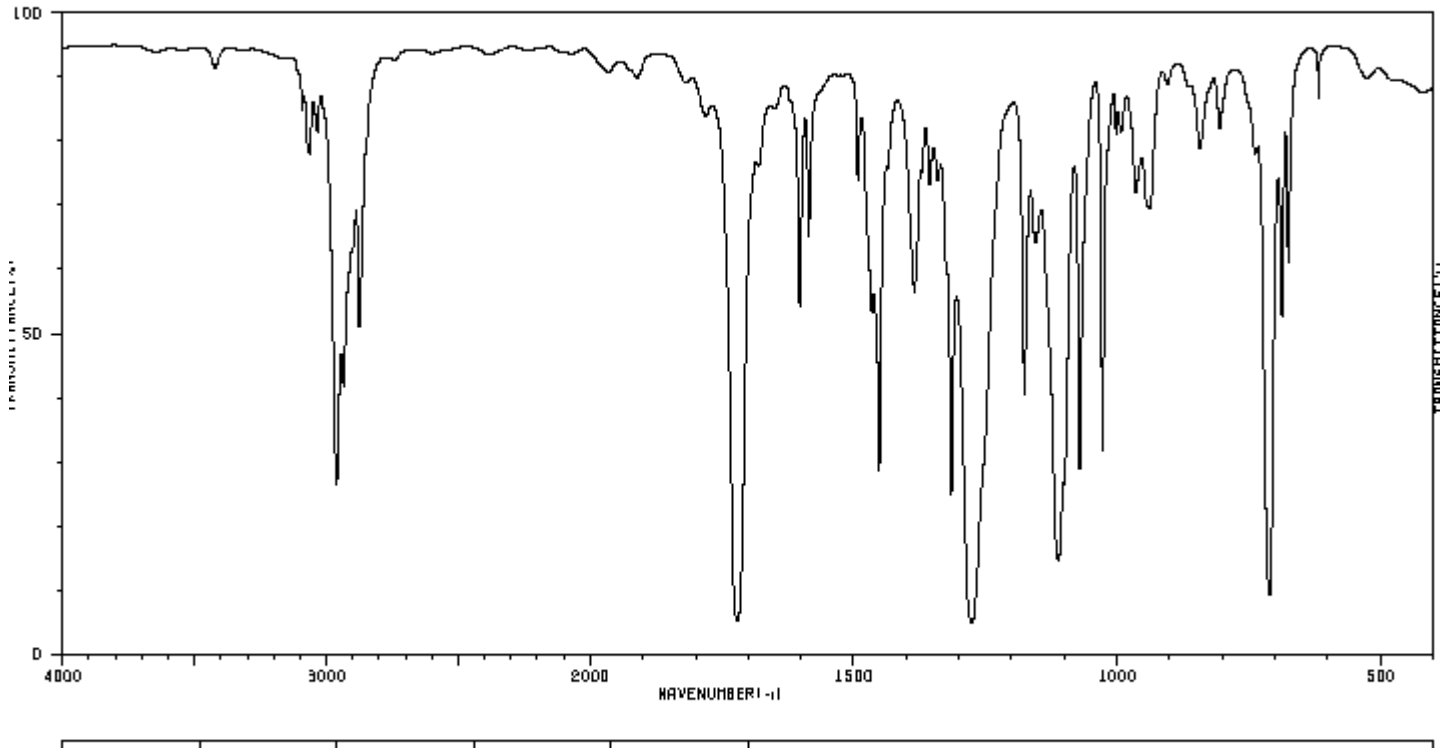

6
3
1.0
2.0
3.0
4.0
PPM
65
60
55
50
45
40
35
30
25
20
PPM

$C_6H_{14}O$

$CH_3CHOHCH_2CH(CH_3)_2$

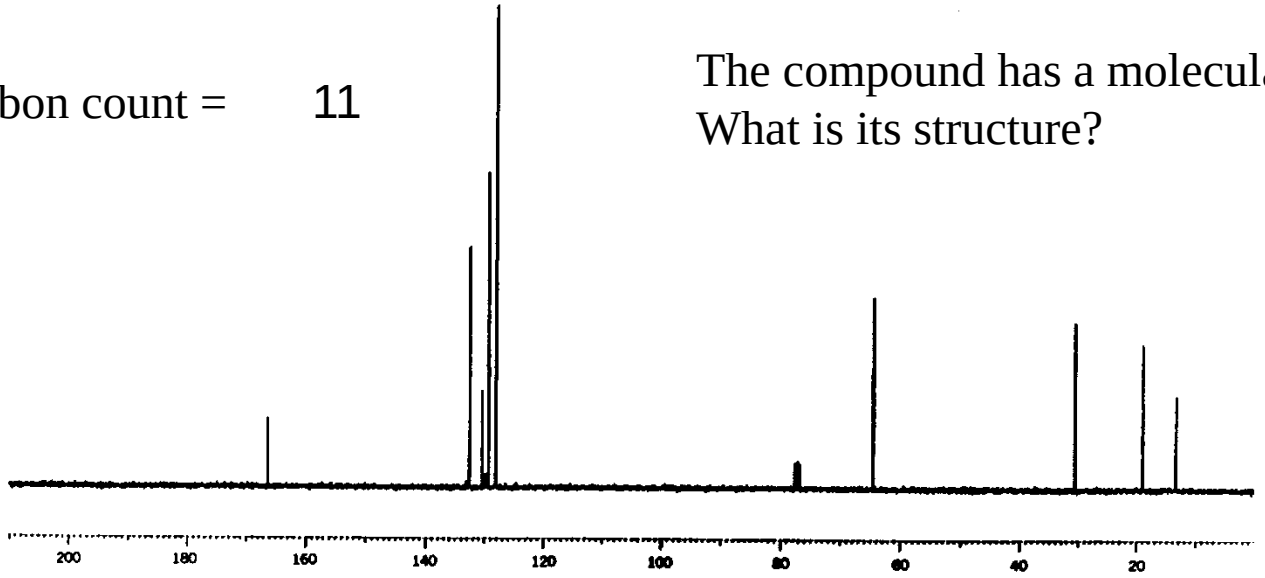


3. The compound has a molecular weight of 178. What is its structure?



C=O 1721 cm^{-1}

PROTON DECOUPLED CARBON SPECTRUM.



Carbon count = 11

The compound has a molecular weight of 178.
What is its structure?

178/13 = 13.692

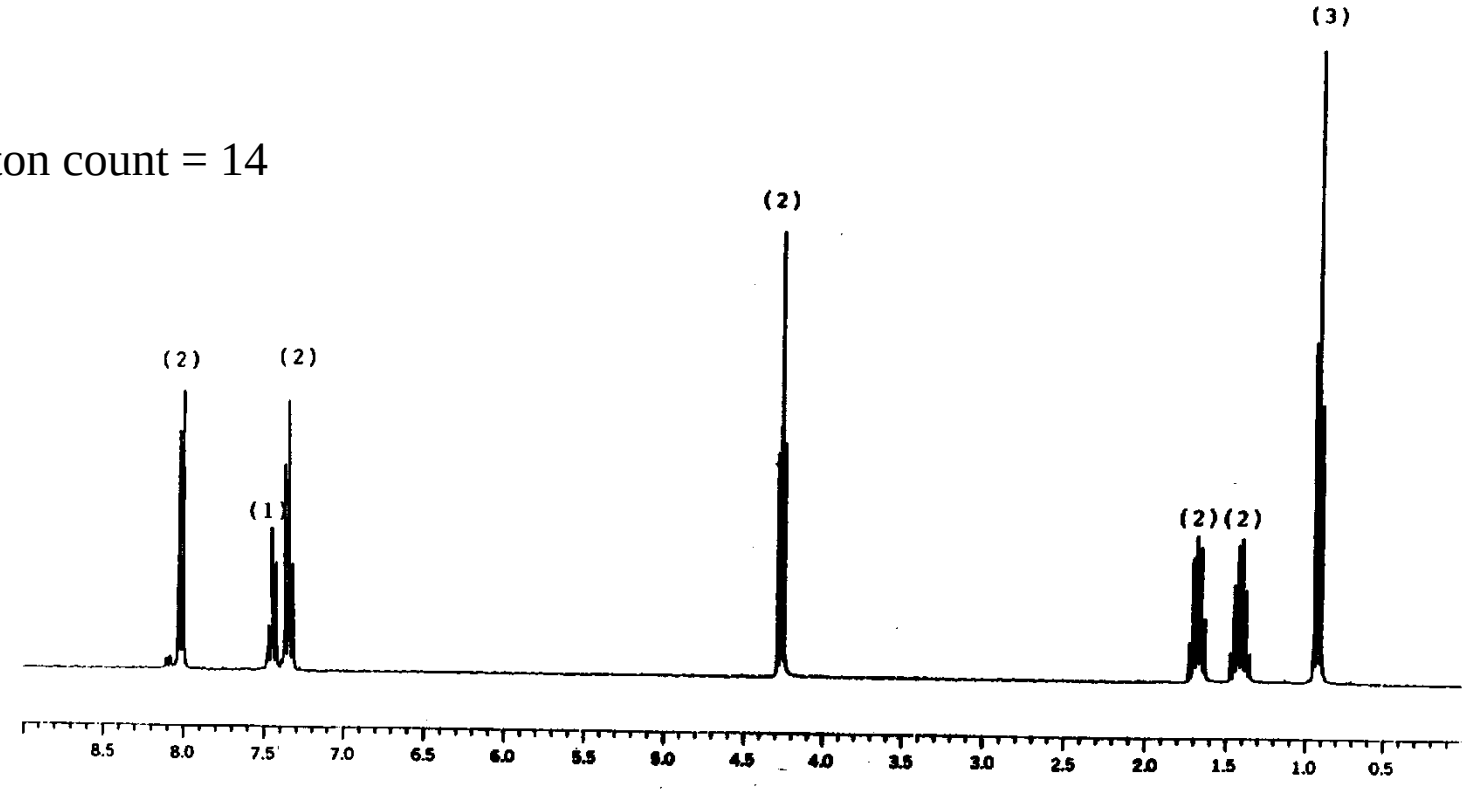
.692*13 = 9

$C_{13}H_{22}$

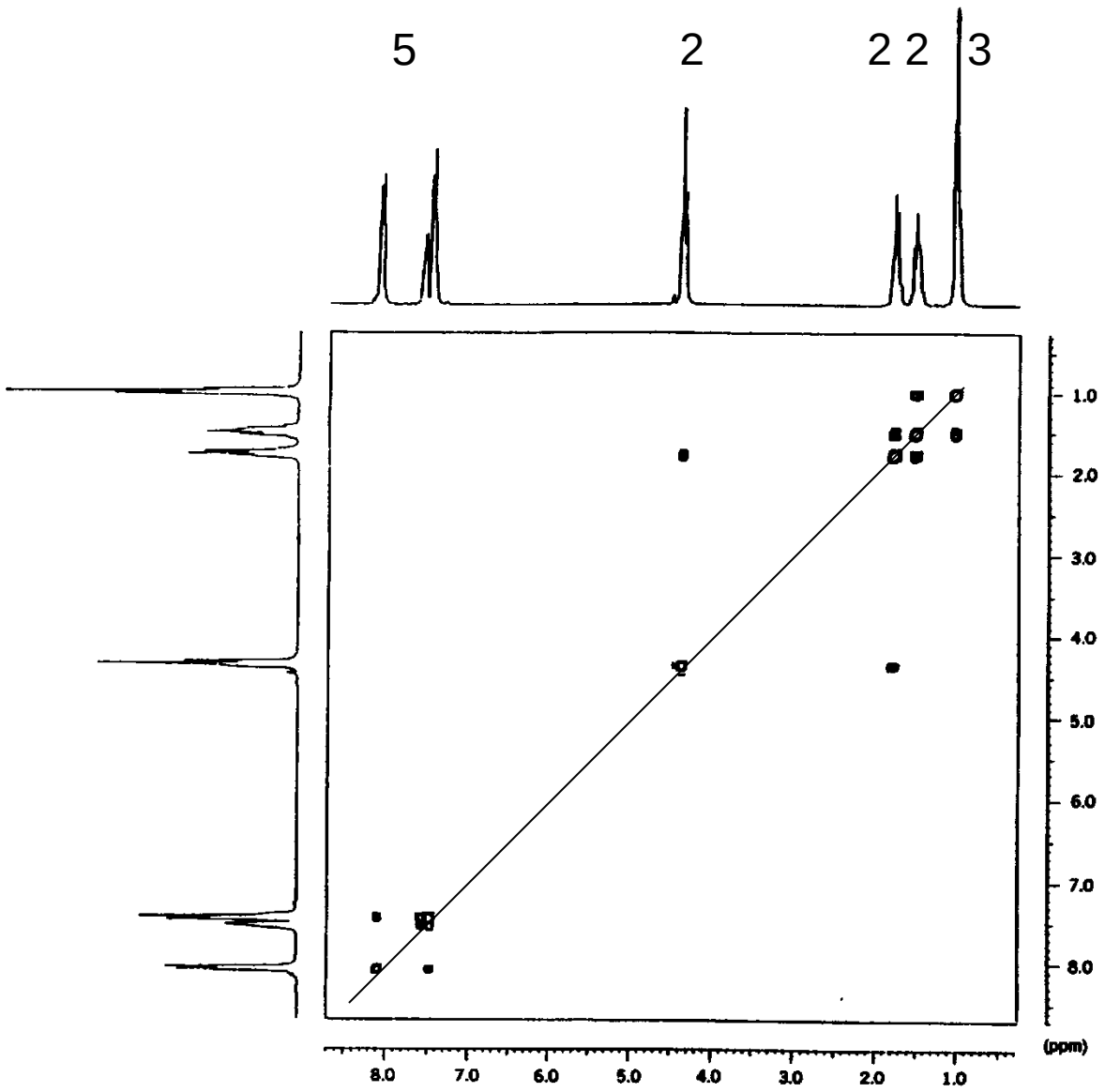
$C_{12}H_{18}O$

$C_{11}H_{14}O_2$

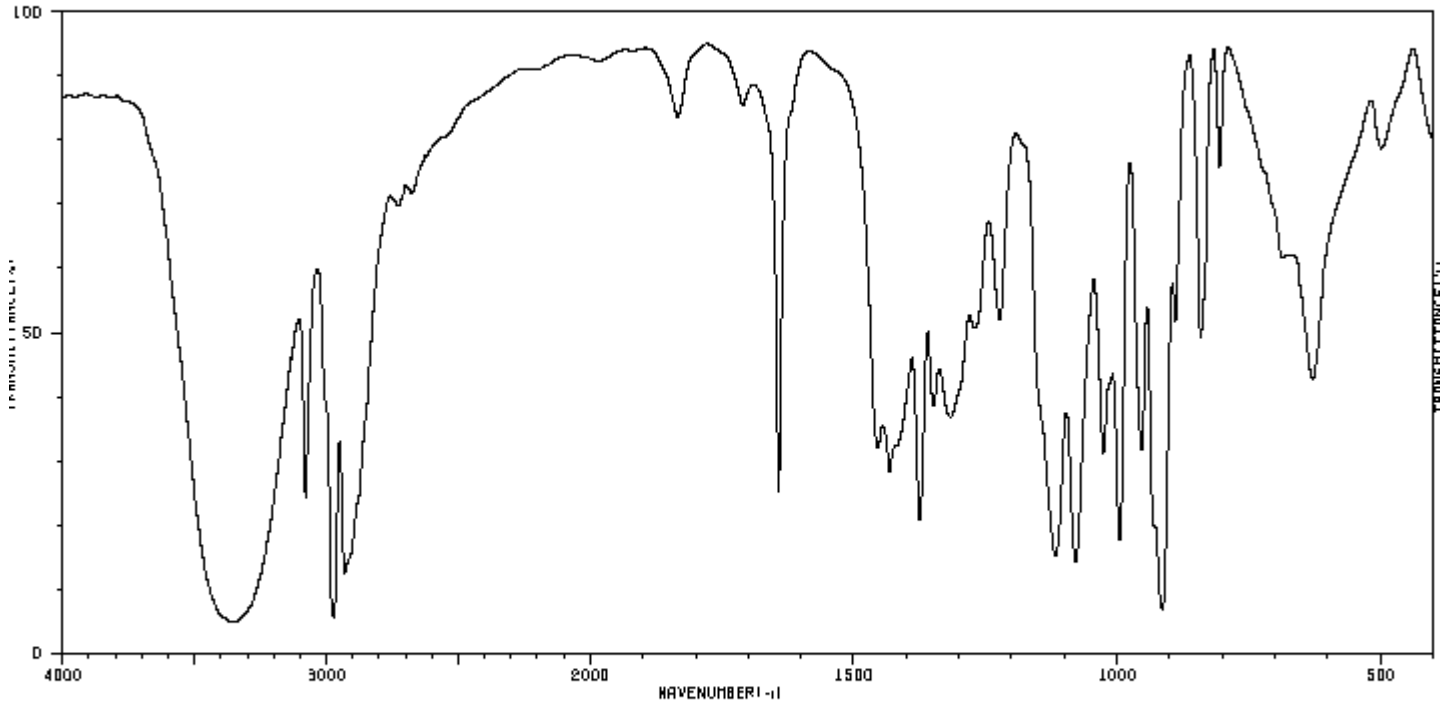
proton count = 14



COSY.



The following spectra refer to a compound with a molecular weight of 86 containing C,H and O.

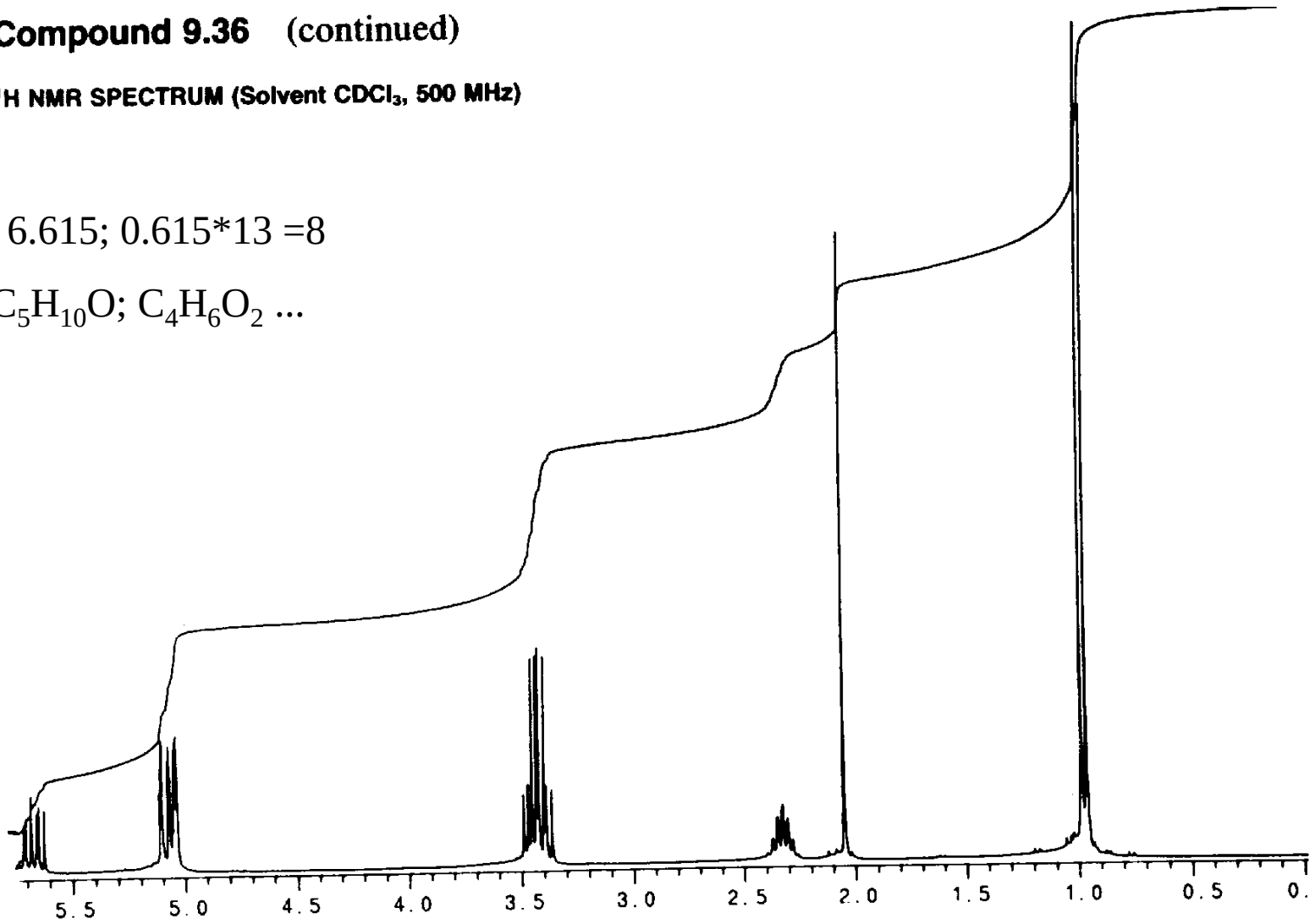


Compound 9.36 (continued)

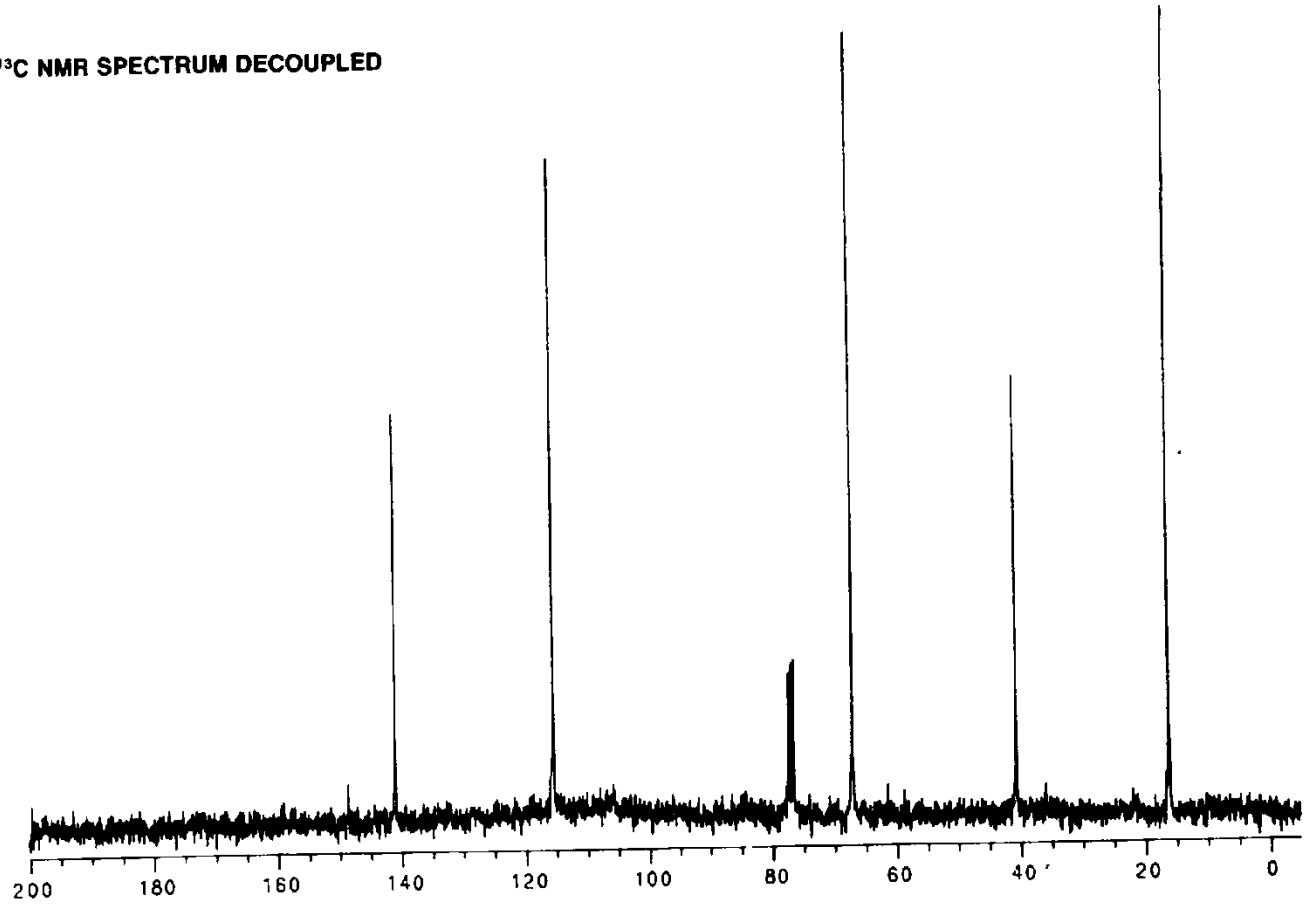
^{1}H NMR SPECTRUM (Solvent $CDCl_3$, 500 MHz)

86/13 = 6.615; 0.615*13 =8

C_6H_{14}; $C_5H_{10}O$; $C_4H_6O_2$ ...



^{13}C NMR SPECTRUM DECOUPLED



Assign the correct structure A or B to the H NMR spectrum given below

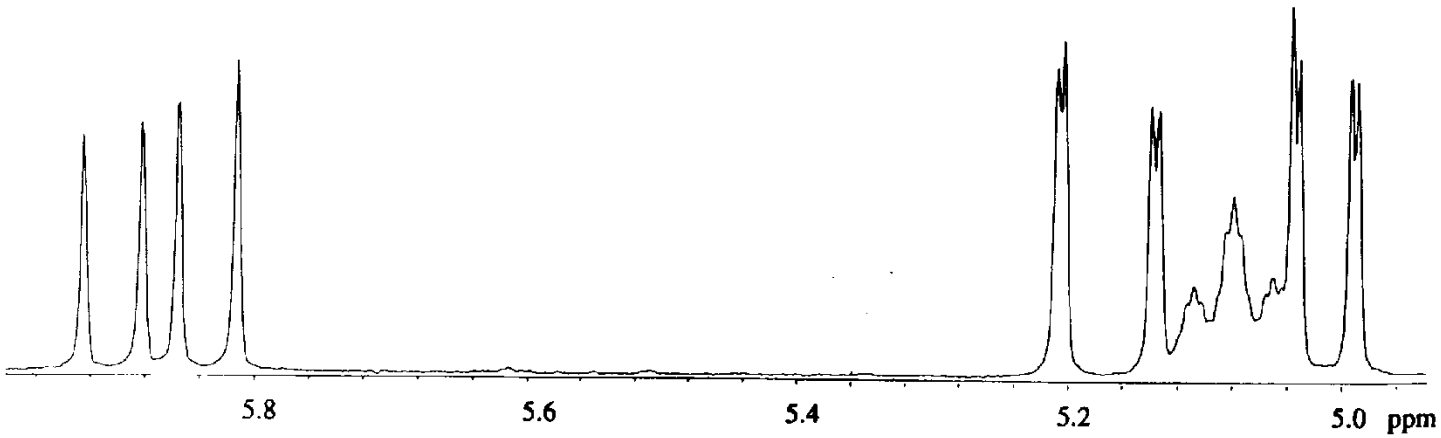
A

B

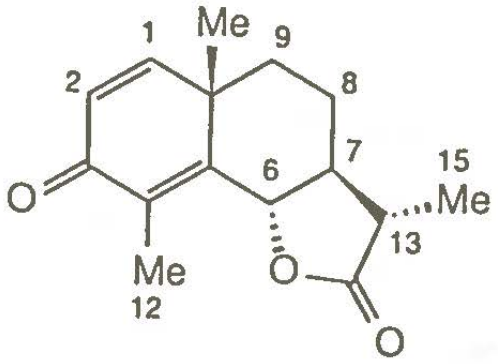
1.8 Hz/mm

1

3

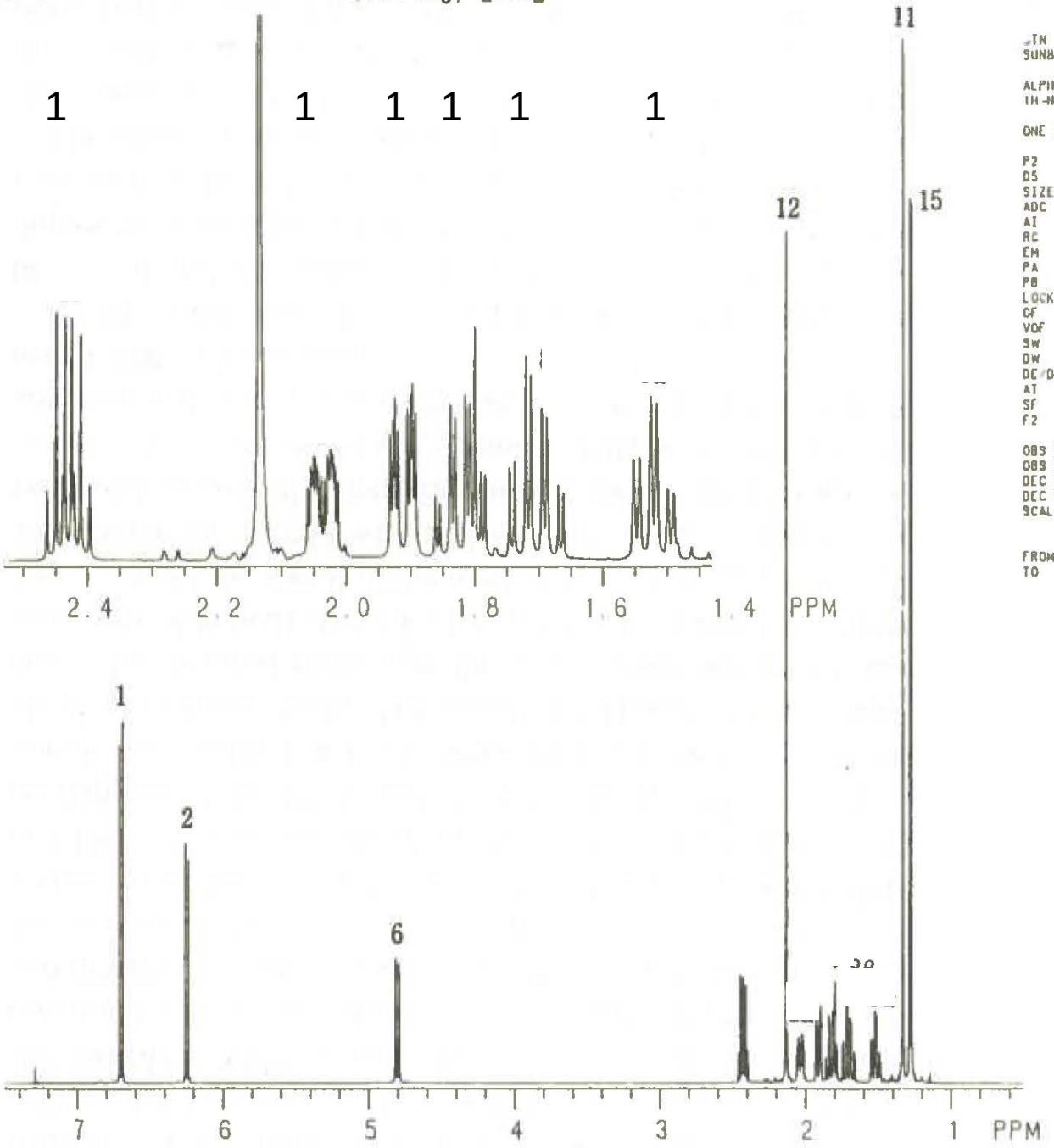


100 Mz NMR

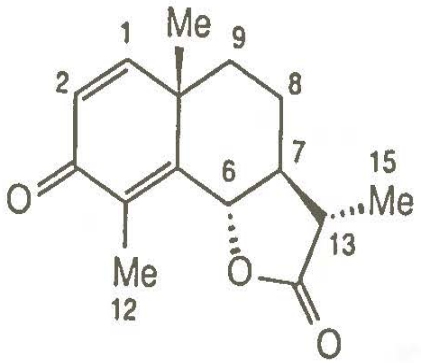


3

(B) 500 MHz ^{1}H-NMR ($CDCl_3$) [TI]

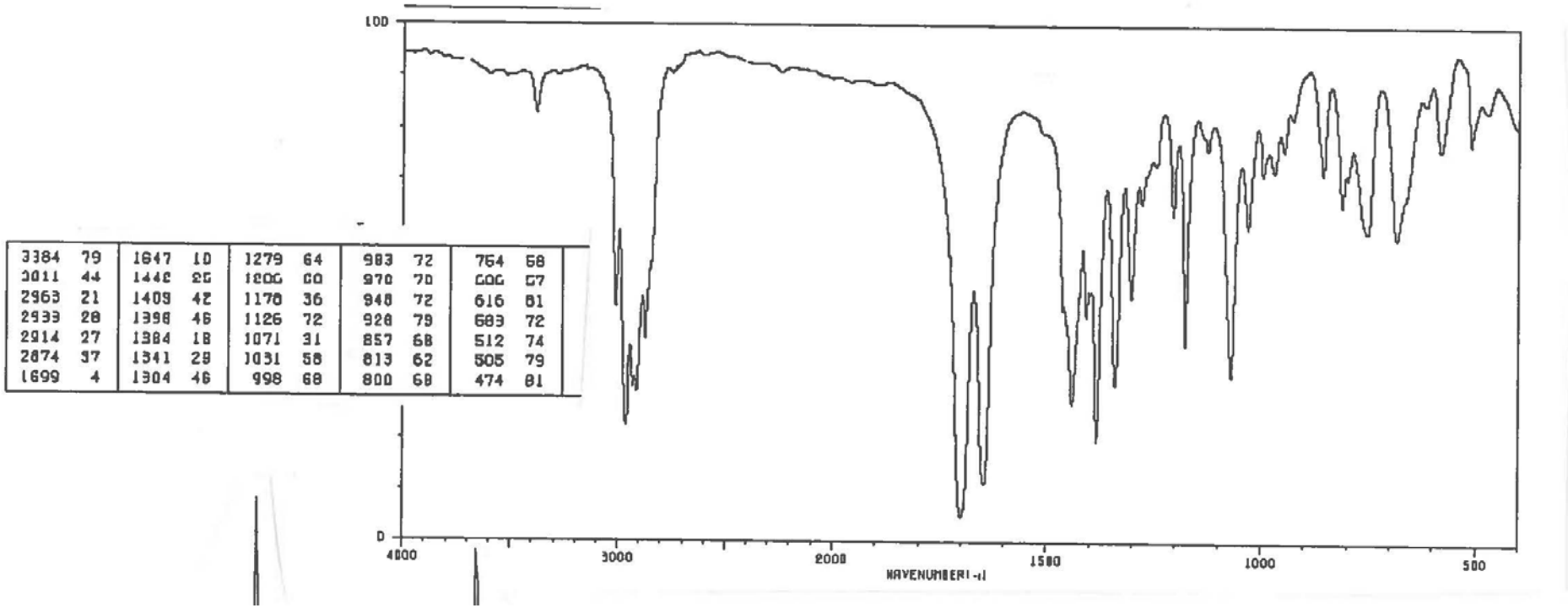



```
ATN      100
SUNBOR   20OCT87

ALPHA-SANTONIN  /CDCL3
1H-NMR

ONE PULSE SEQUENCE

P2       =    3 00 USEC
D5       =    2 00  SEC
SIZE     =   32768
ADC      =      16
AI       =       8
RC       =      10
EM       =          10
PA       =     211 5
PB       =      -5 5
LOCK     =      7 28
OF       =    2006 17
VOF      =    2001 58
SW       =  +/- 2500 00  HZ
DW       =    200 USEC
DE/DW    =      50
AT       =    3 28  SEC
SF     =  500 0994944
F2     =  500 0995168

OBS HI PWR =  63
OBS LO PWR =    0
DEC PWR    =    0
DEC SCHEME =  4
SCALE      142 83 HZ/CM
       =     2858 PPM/CM

FROM     7 50
TO       50 PPM
```



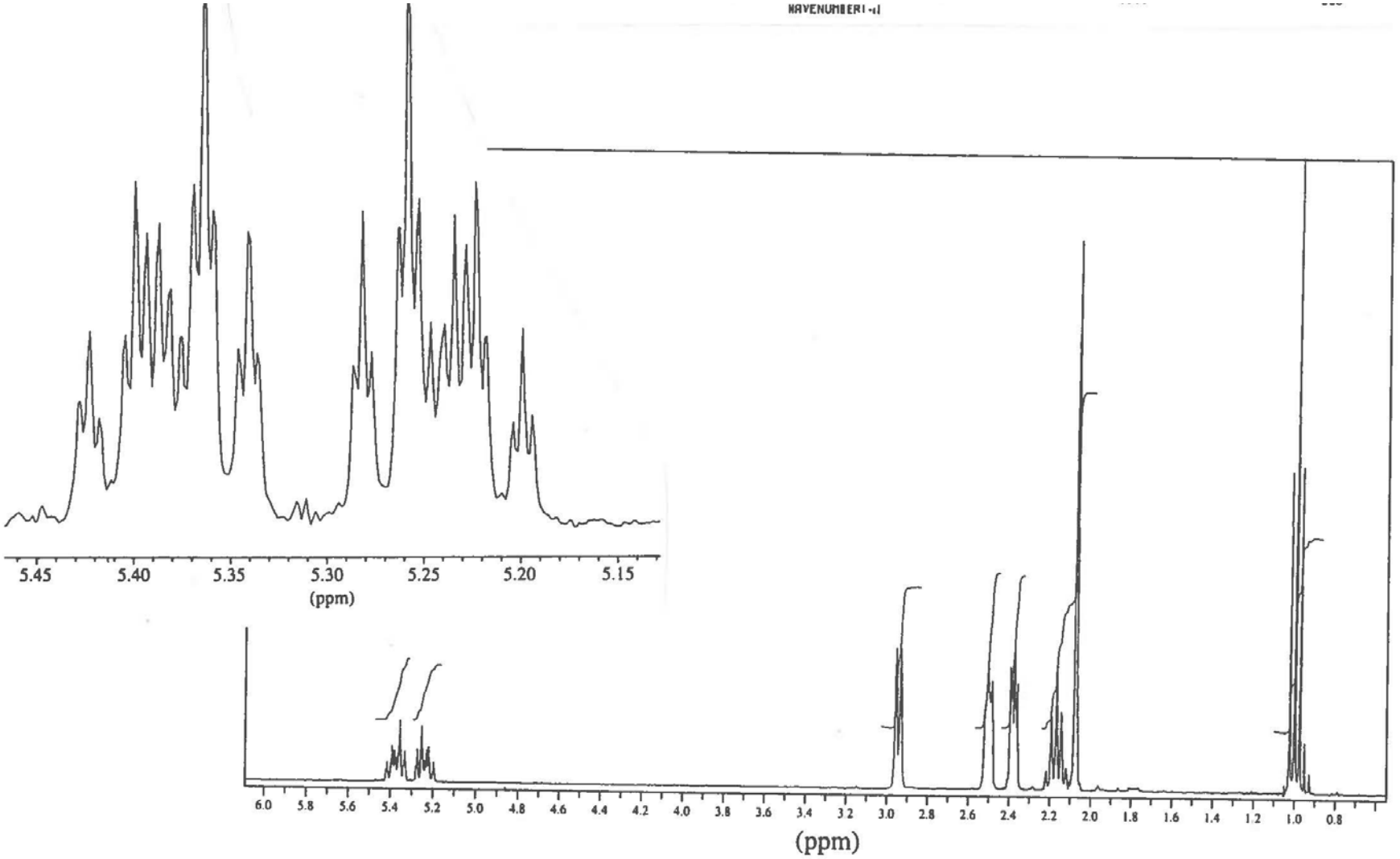
A compound has a molecular weight of 164. The IR of this material is shown below

164/13=12.615; 0.615*13=8; $C_{12}H_{20}$

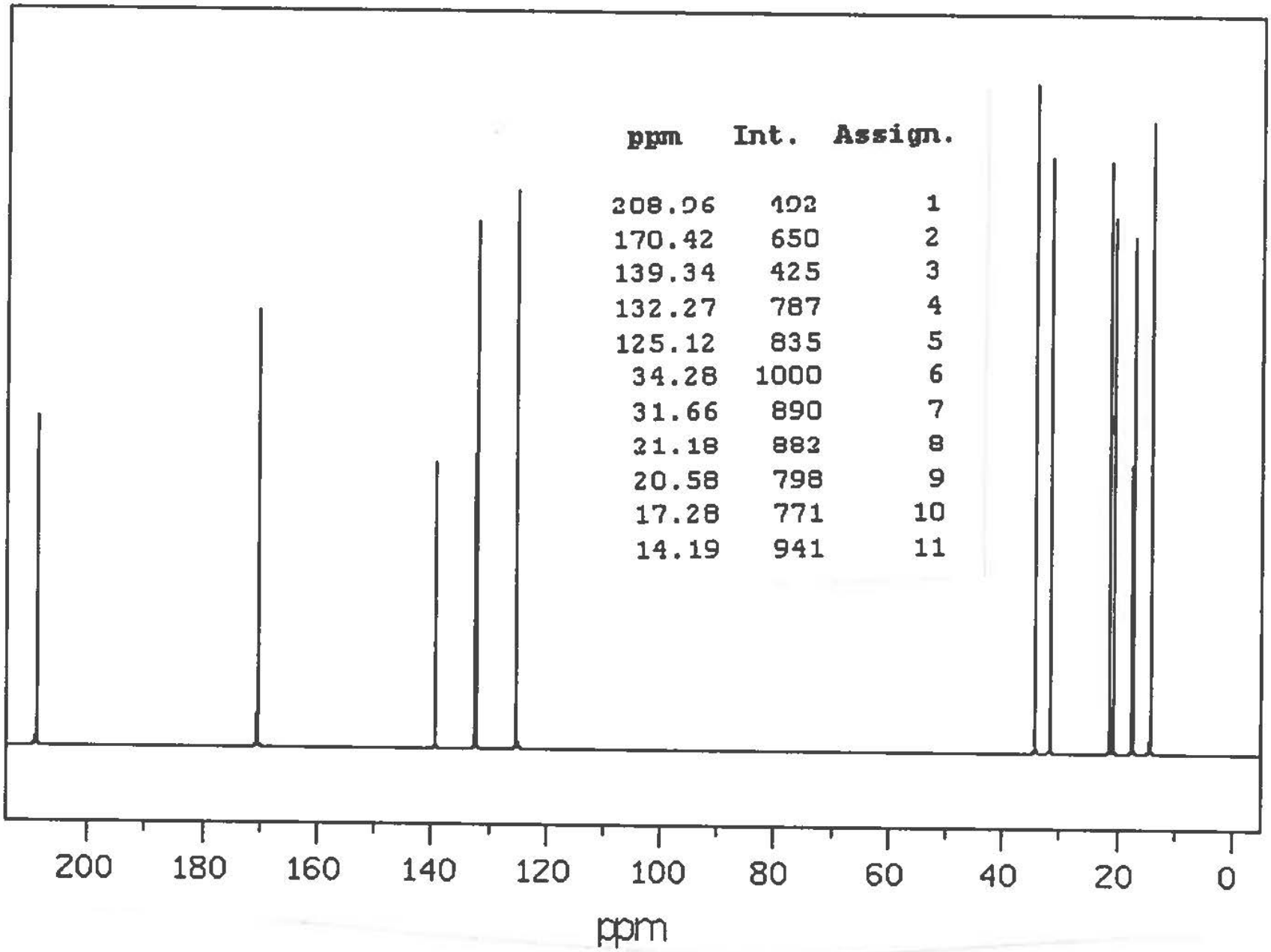


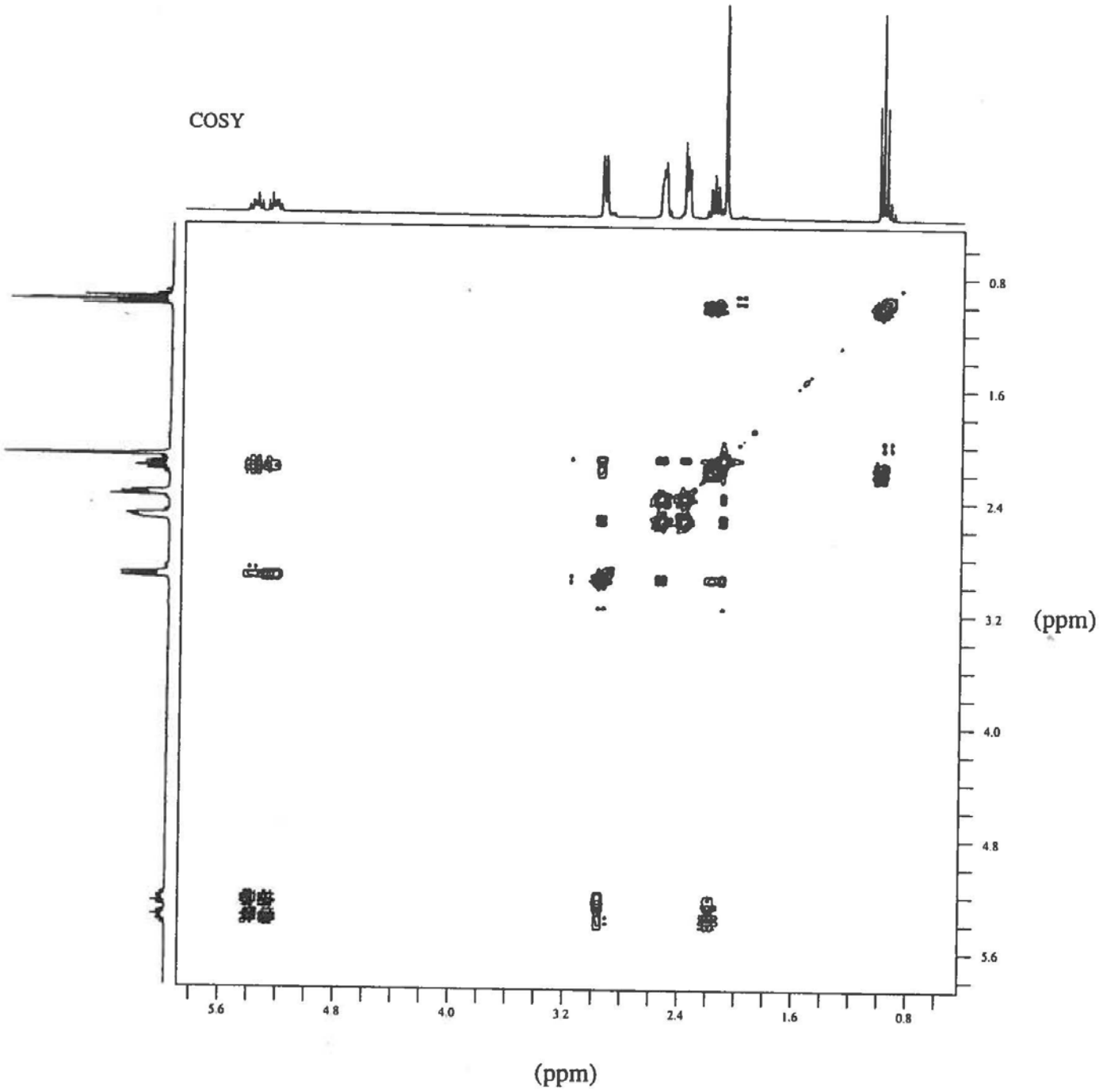
3384	79	1647	10	1279	64	983	72	764	58
3011	44	1442	25	1206	60	970	70	606	67
2963	21	1409	42	1178	36	948	72	616	81
2933	28	1398	46	1126	72	926	79	583	72
2914	27	1384	18	1071	31	857	68	512	74
2874	37	1341	29	1031	58	813	62	505	79
1699	4	1304	46	998	68	800	68	474	81

$C_{11}H_{16}O$; $C_{10}H_{12}O_2$

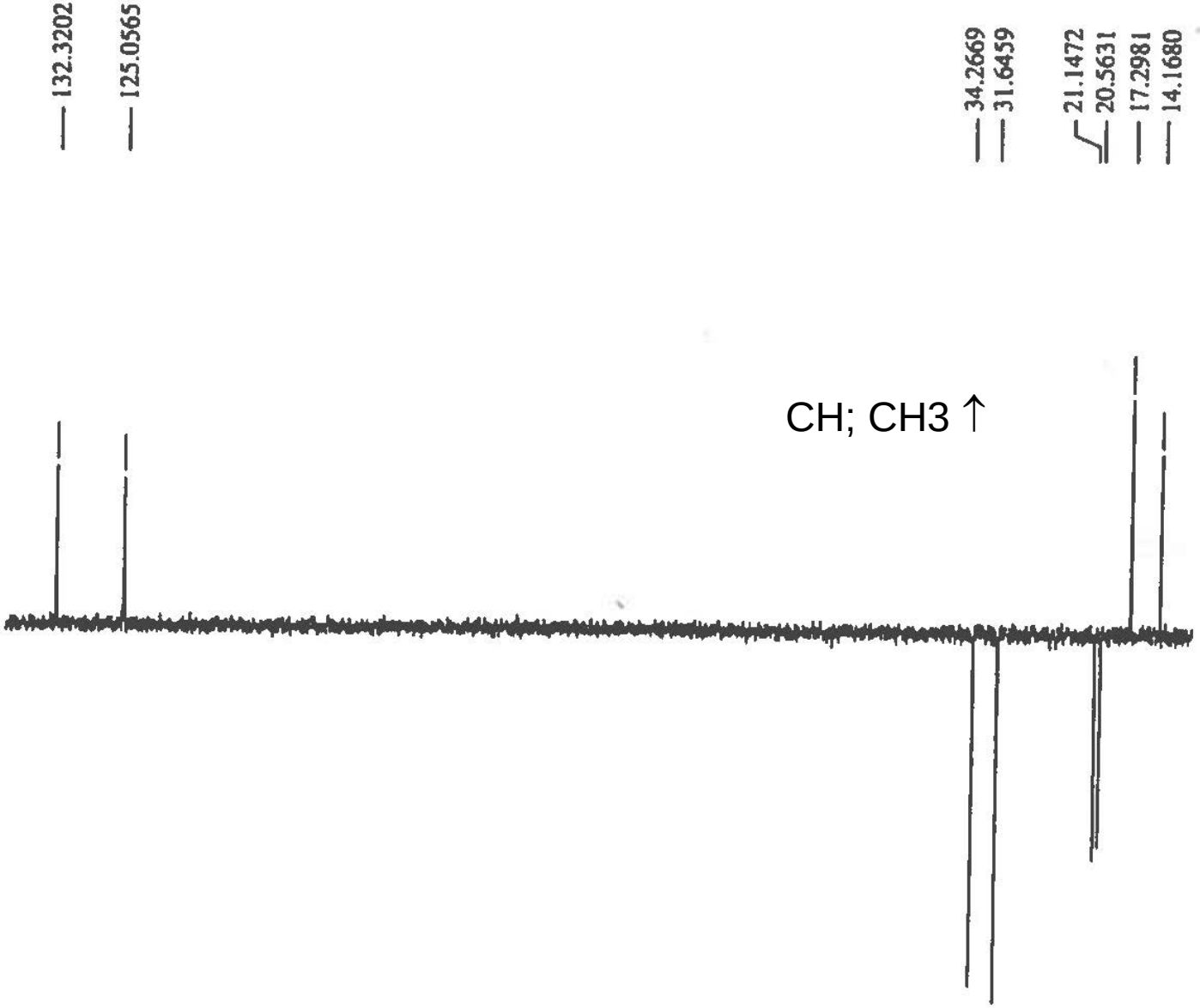


$C_{11}H_{16}O$; $C_{10}H_{12}O_2$

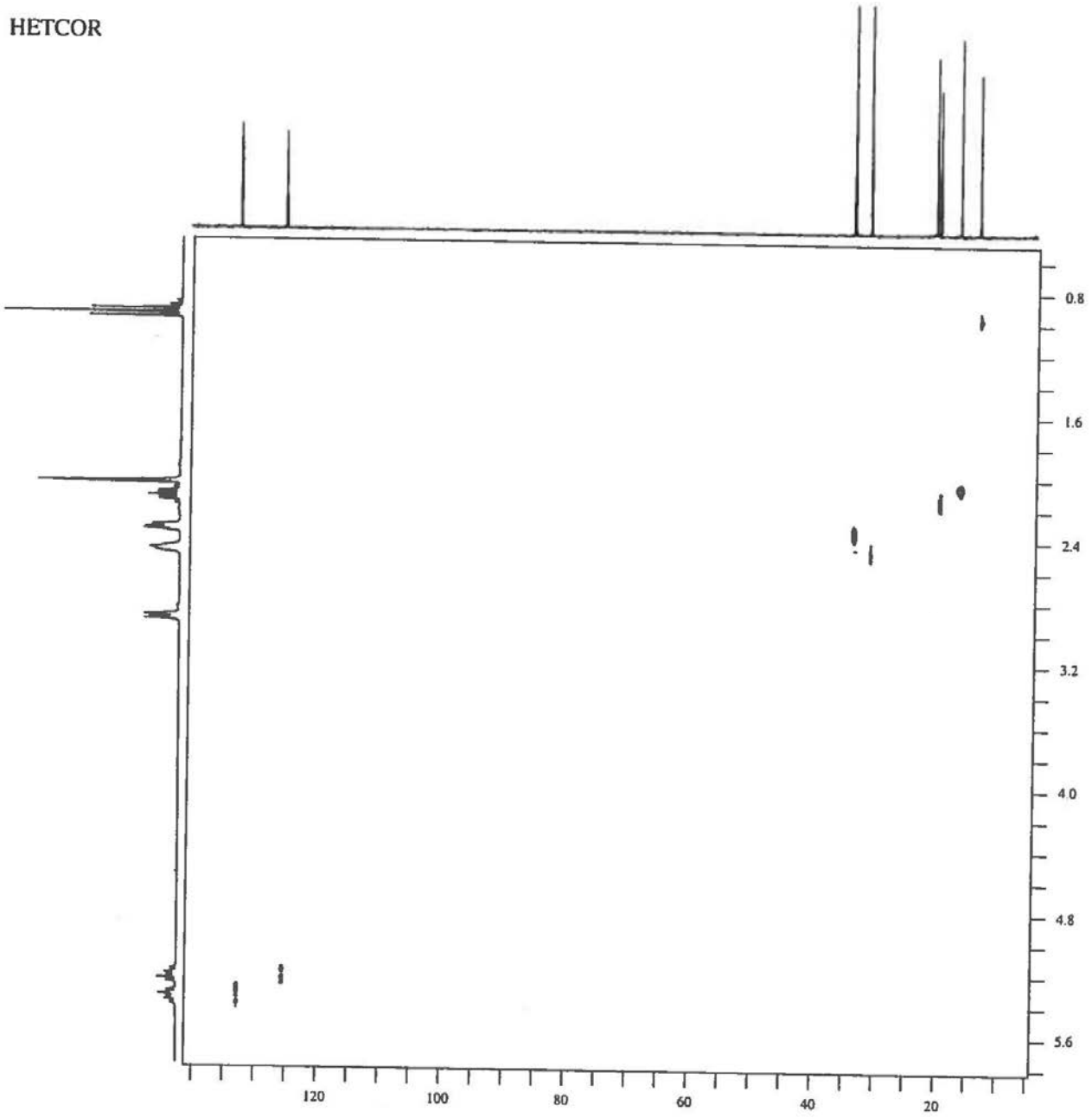

ppm Int. Assign.
208.06 102 1
170.42 650 2
139.34 425 3
132.27 787 4
125.12 835 5
34.28 1000 6
31.66 890 7
21.18 882 8
20.58 798 9
17.28 771 10
14.19 941 11
200
180
160
140
120
100
80
60
40
20
0
ppm


COSY
0.8
1.6
2.4
3.2
4.0
4.8
5.6
(ppm)
5.6
4.8
4.0
3.2
2.4
1.6
0.8
(ppm)

DEPT-135

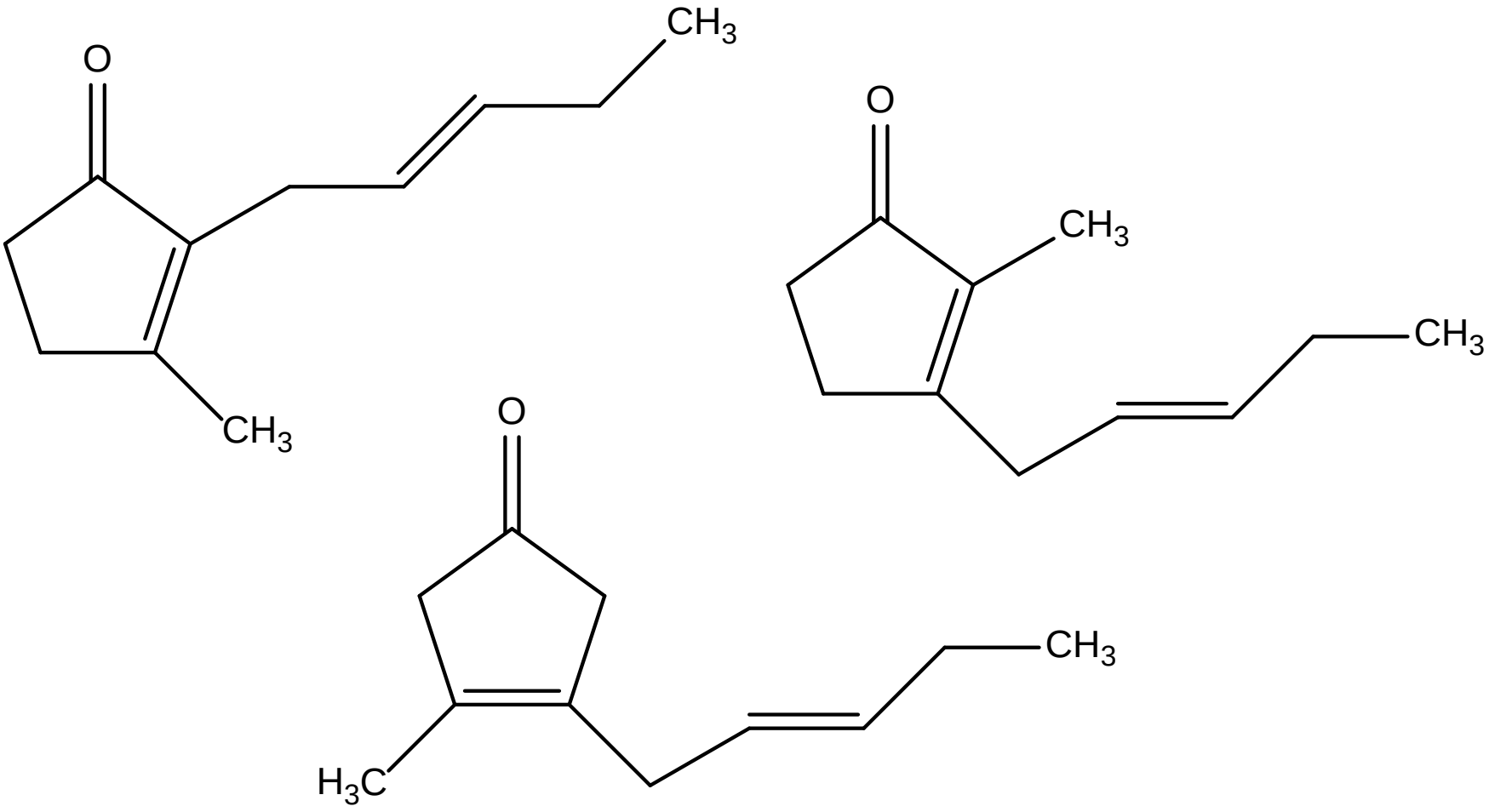

132.3202
125.0565
34.2669
31.6459
21.1472
20.5631
17.2981
14.1680
CH; CH3 ↑

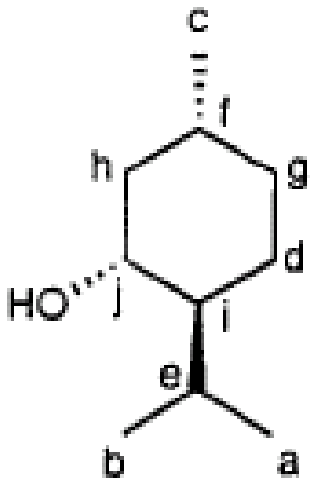
HETCOR



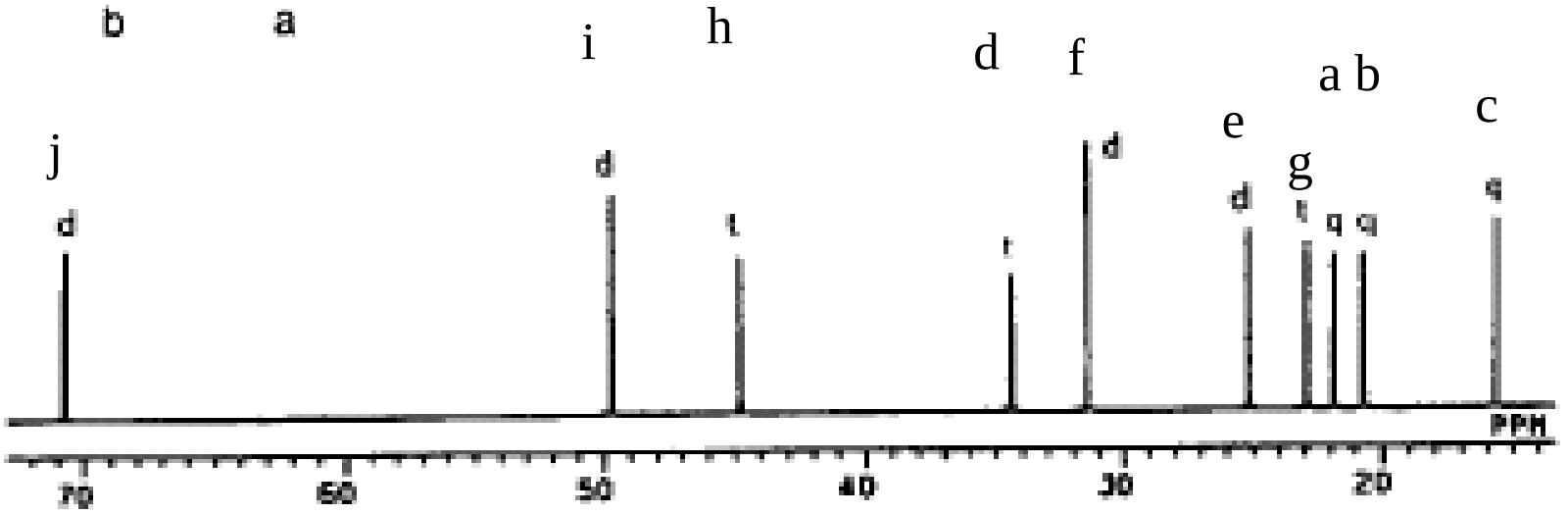
(ppm)

(ppm)


O
CH3
CH3
O
CH3
CH3
O
H3C
CH3

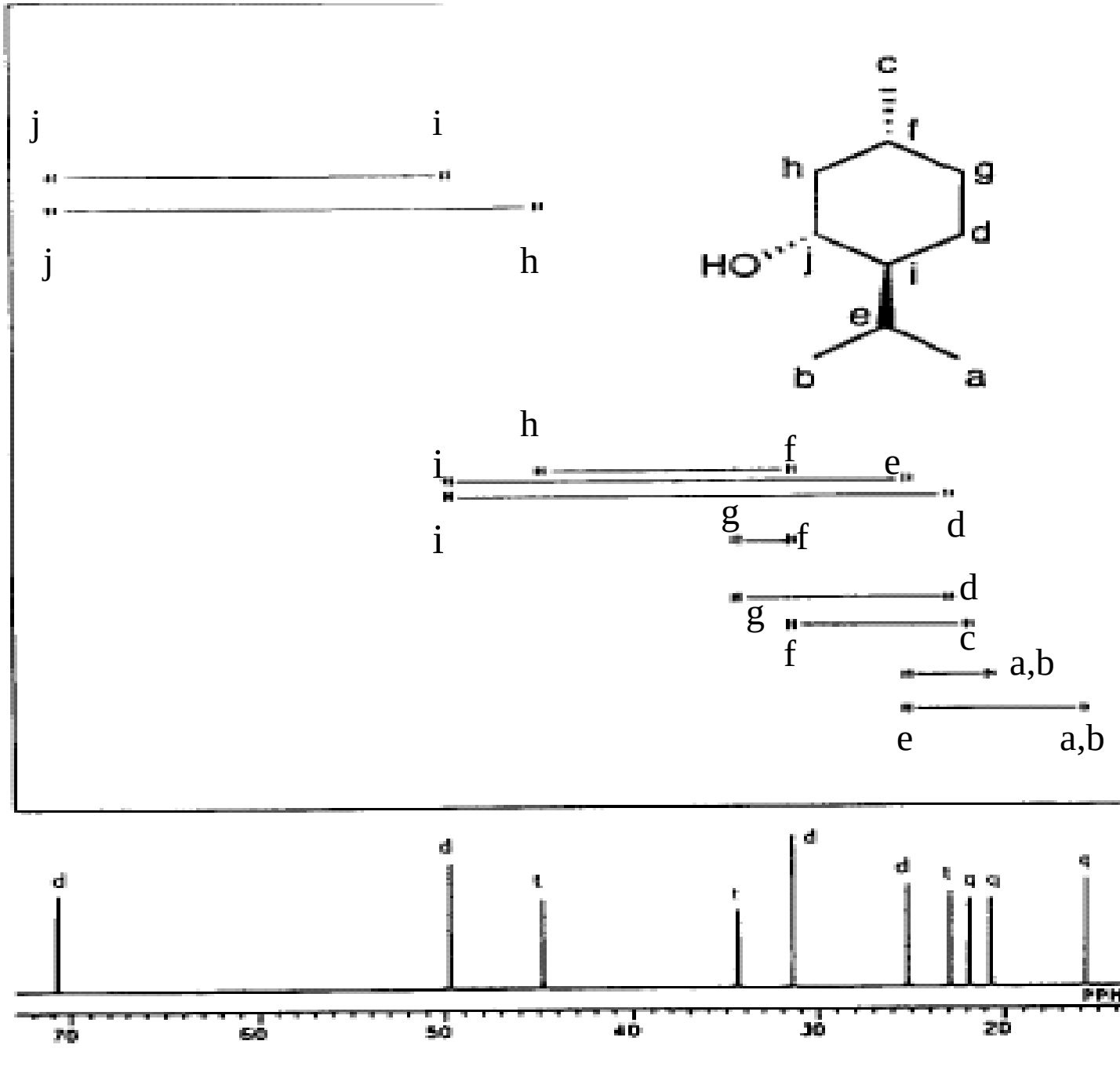


Identify the carbons by chemical shift



100 MHz ^{13}C-NMR (C_6D_6) [JEOL]

An INADEQUATE spectrum (incredible natural abundance double quantum transfer experiment spectroscopy) measures ^{13}C –^{13}C transfer of magnetization between two ^{13}C nuclei using natural abundance C (detection of 1 in 10000 molecules).



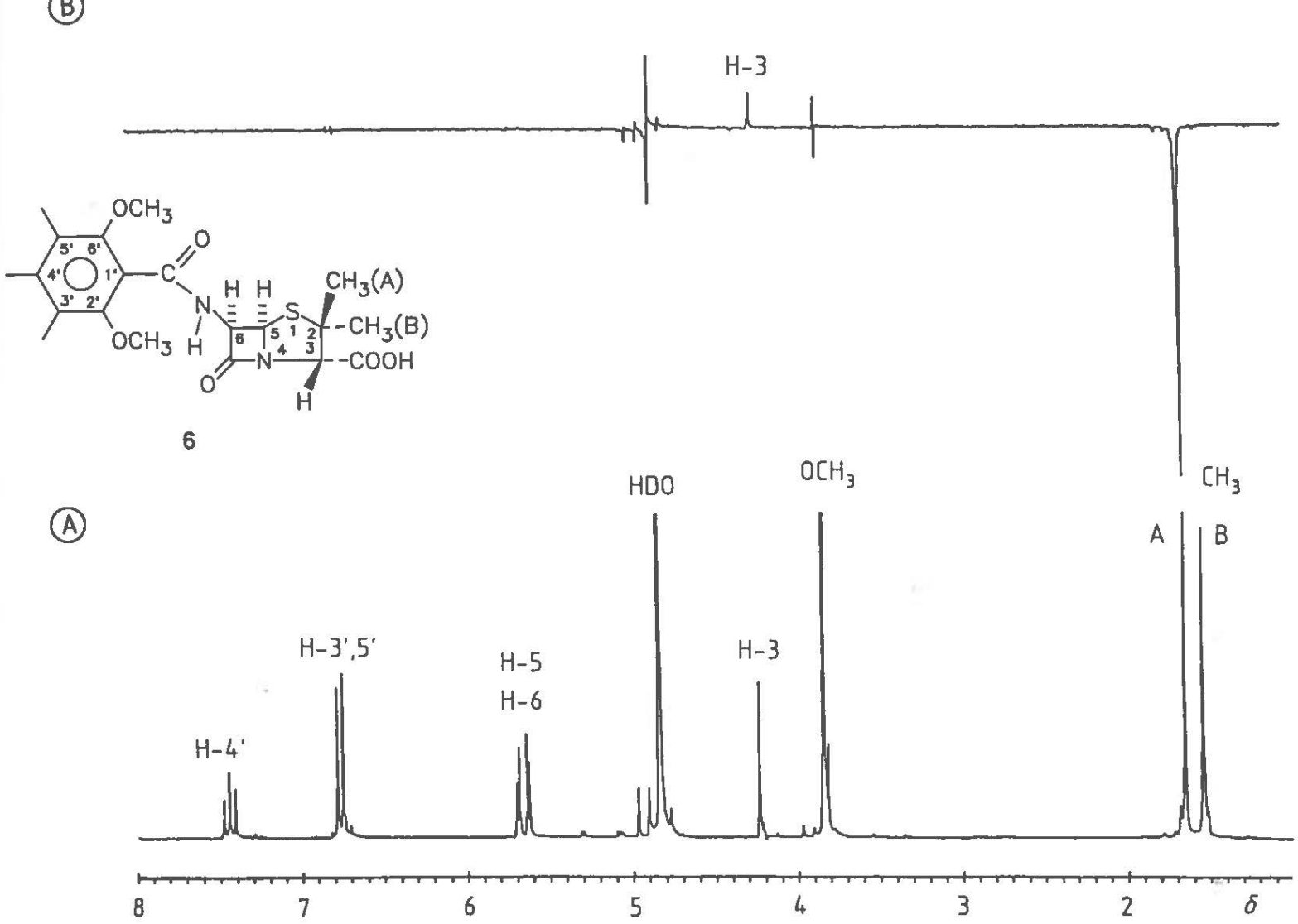


Figure 10-5.
A: 250 MHz ^{1}H NMR spectrum of methicillin (**6**) in 0.2 M sodium acetate buffer (D_2O; pD 7.0), with assignments. On saturating the methyl signal ($\delta \approx 1.7$) the NOE difference spectrum shows an increase in the intensity of the H-3 signal ($\delta \approx 4.25$). The negative signal in the NOE difference spectrum corresponds to the irradiating frequency. Strong signals, such as the residual solvent signals (HDO) or those of the methyl groups, are often found to be not exactly cancelled to zero in the difference spectrum.

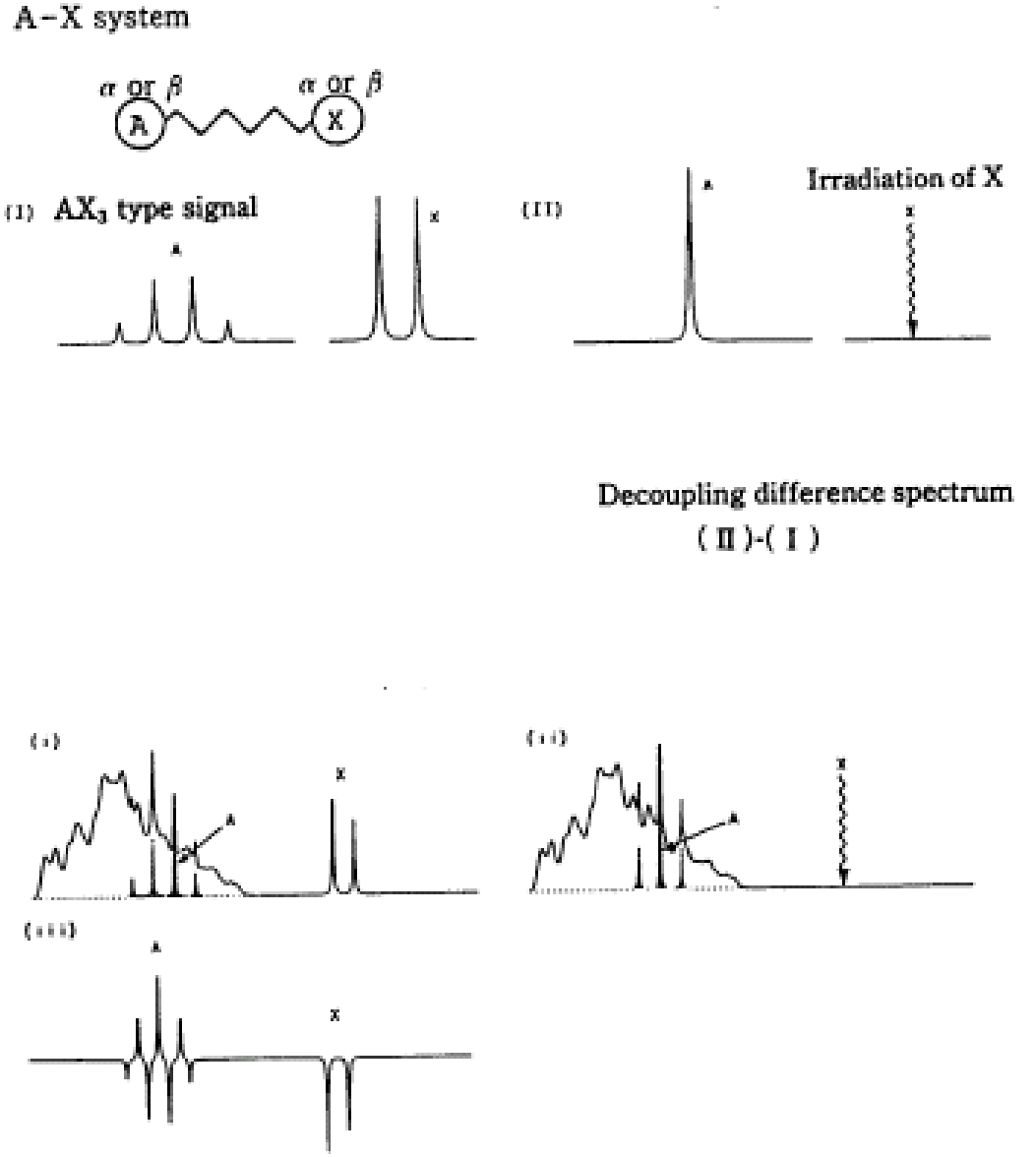
Spin Decoupling Difference Spectrum

AX_3

XAM_2

where $J_{AX} = J_{AM}$

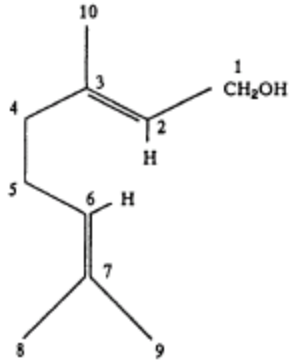
$J_{XM} = 0$



1) H.Günther (translated by R.W.Gleason), *NMR Spectroscopy — An Introduction*, John Wiley & Sons, Ltd., New York (1980), pp.285-292

2) J.K.M.Sanders and J.D.Mersh, *Prog. Nucl. Magn. Reson.*, **15**, 353 (1982), pp.355-361

Can we assign the peaks?



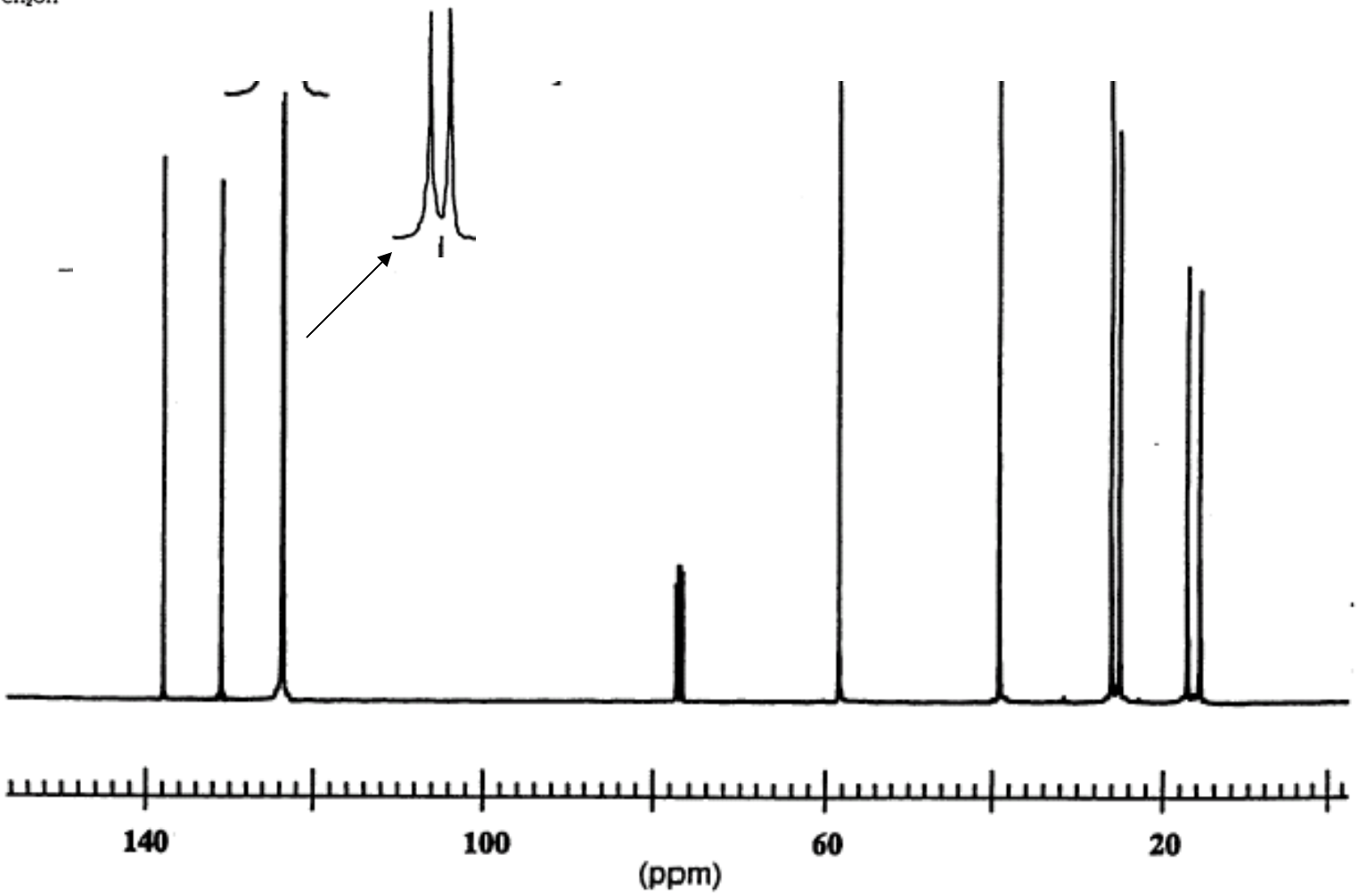


FIGURE 6.6. The ^{13}C broadband-decoupled spectrum of geraniol in $CDCl_3$, using a 500-MHz instrument (125.7 MHz for ^{13}C). The inset is an expansion of two peaks that are almost superimposed in the unexpanded spectrum.

carbon count

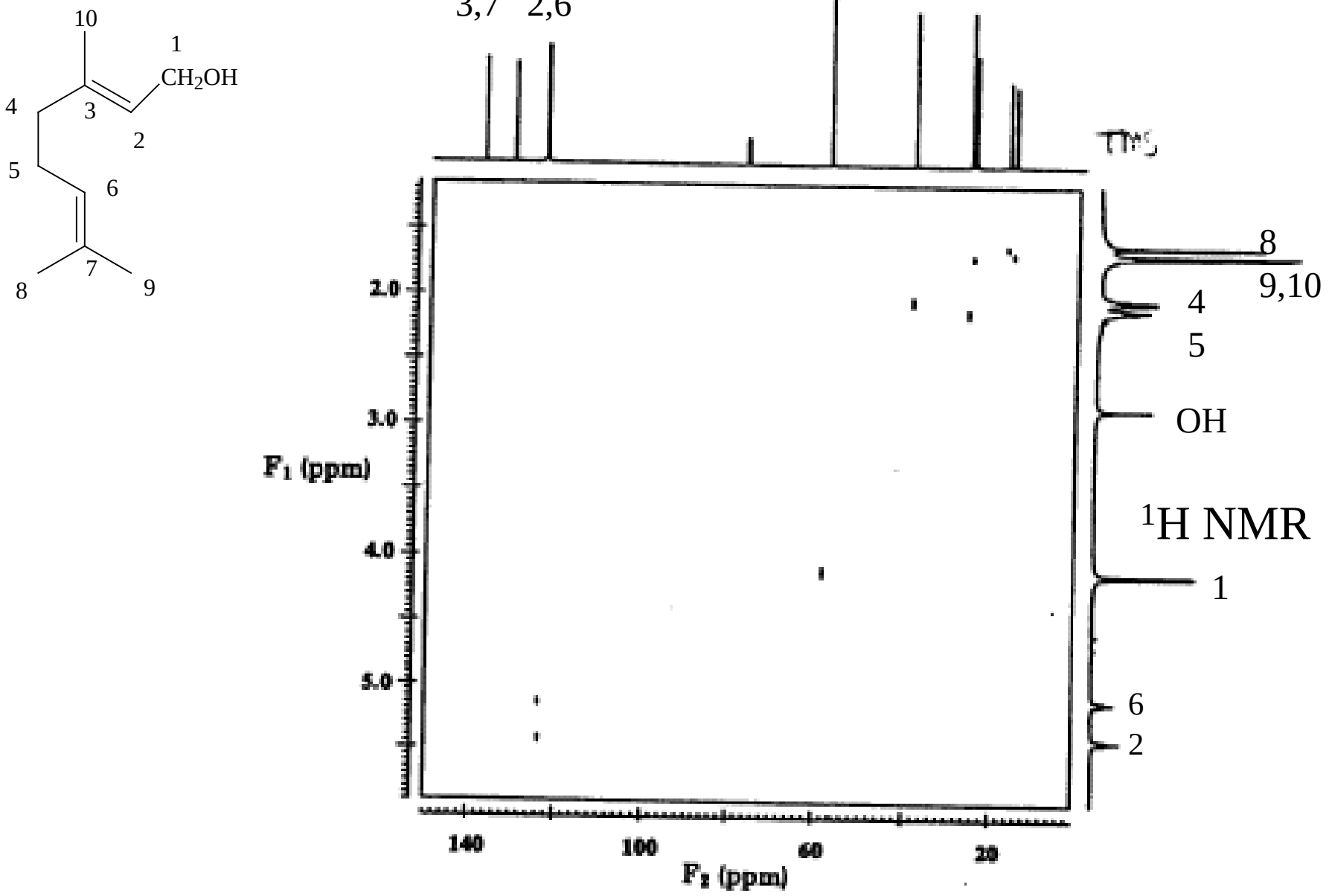


FIGURE 6.13. The HETCOR spectrum of geraniol, in $CDCl_3$ at 500 MHz for ^1H and 125.7 for ^{13}C.

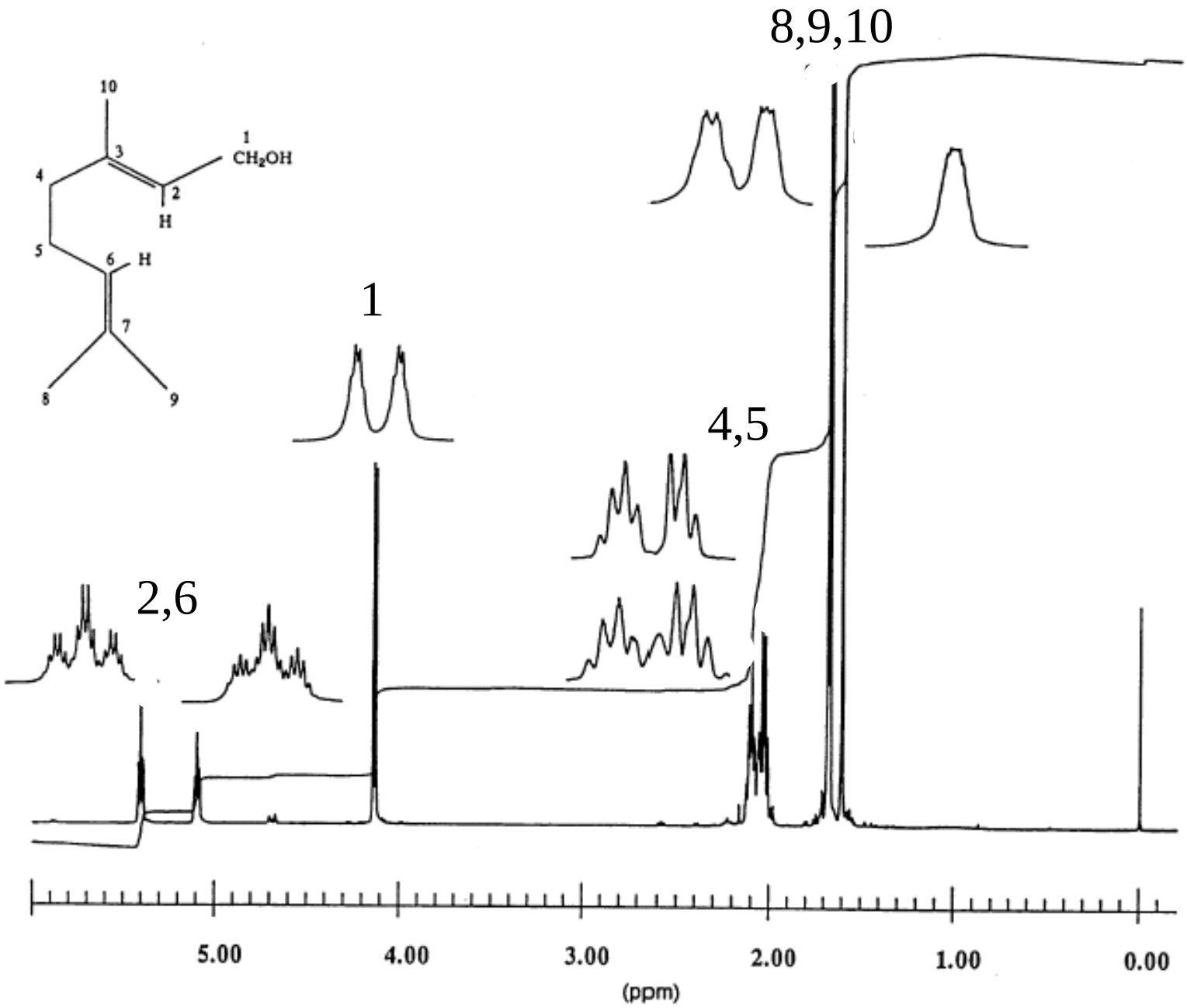
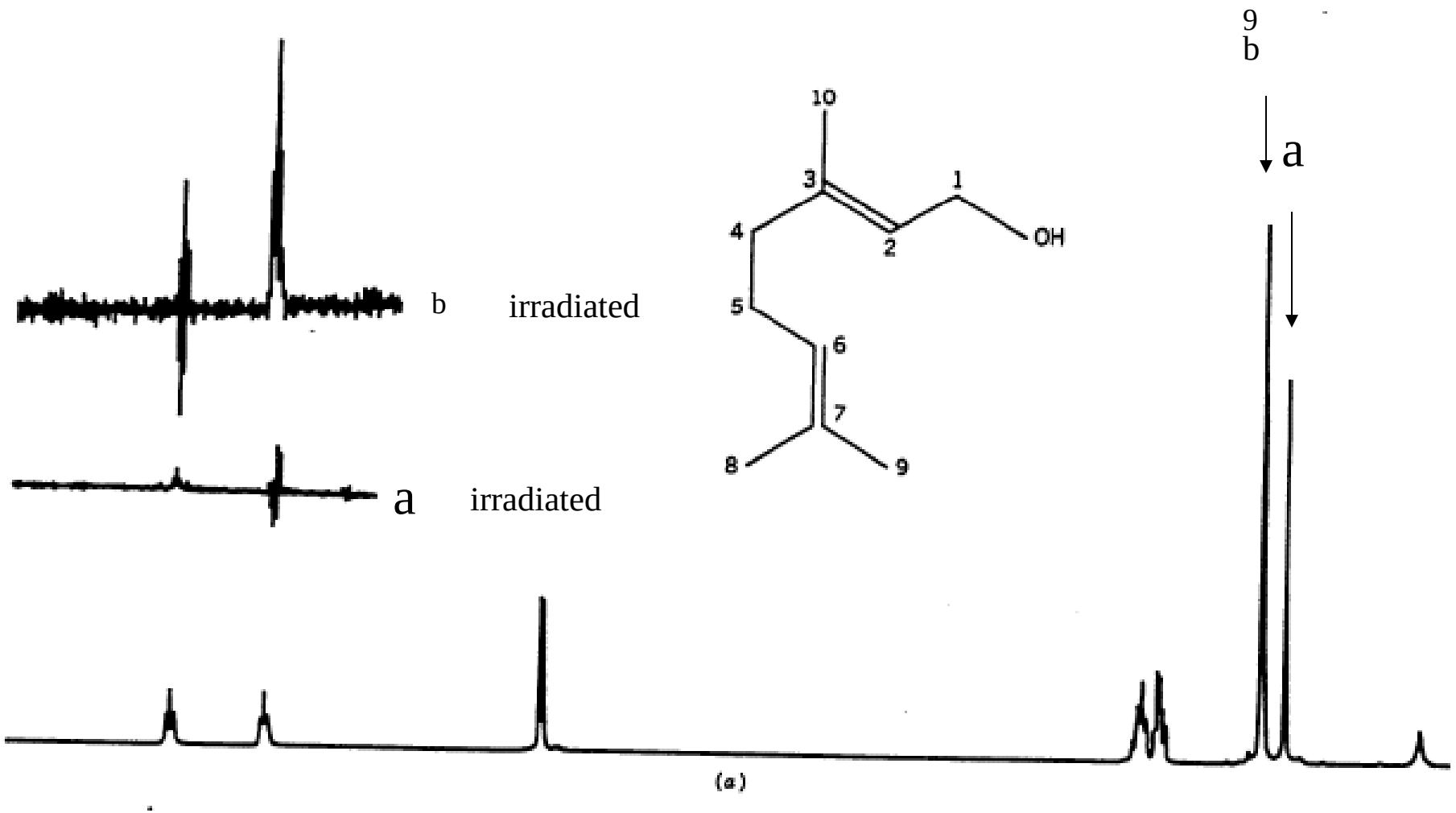


FIGURE 6.5. The ^1H Spectrum of geraniol in $CDCl_3$ at 500 MHz with expanded insets. Lower inset for H-5 and H-4 contains OH peak; upper inset is from a sample in which the OH peak is at higher field.

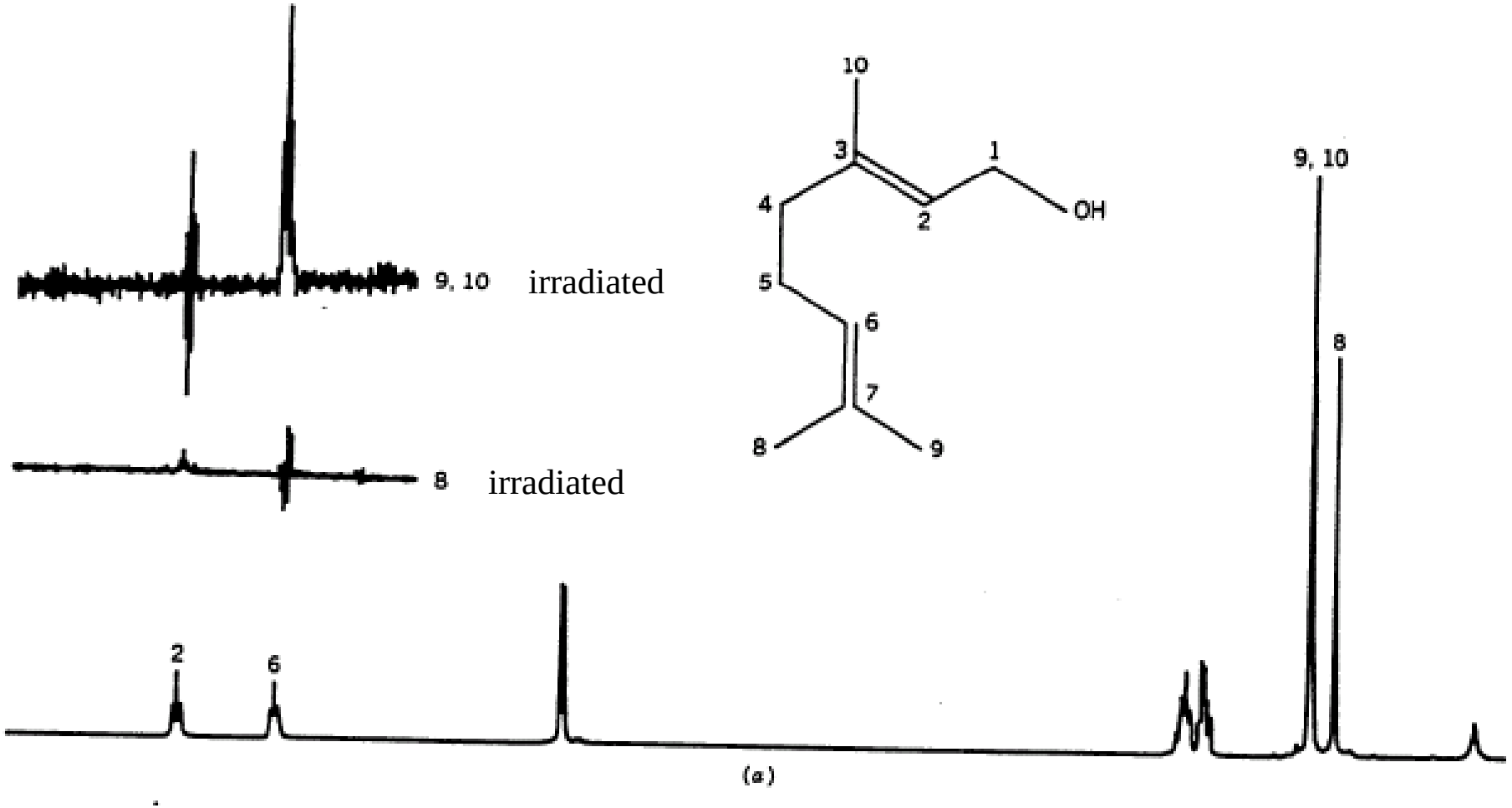
NOE Difference Spectra

Some NOE operates through space as well as through bonding electrons. The through space interaction decreases as the inverse of the sixth power of the through space distance of the nuclei. The through space interaction occurs between nuclei that interact by a dipolar interaction

The NOE difference spectrum is obtained by subtracting a normal spectrum from one in which a specific proton is irradiated. An measurable interaction can be expected up to about 4Å.



Difference NOE spectra of (*a*) geraniol



Difference NOE spectra of (*a*) geraniol ;

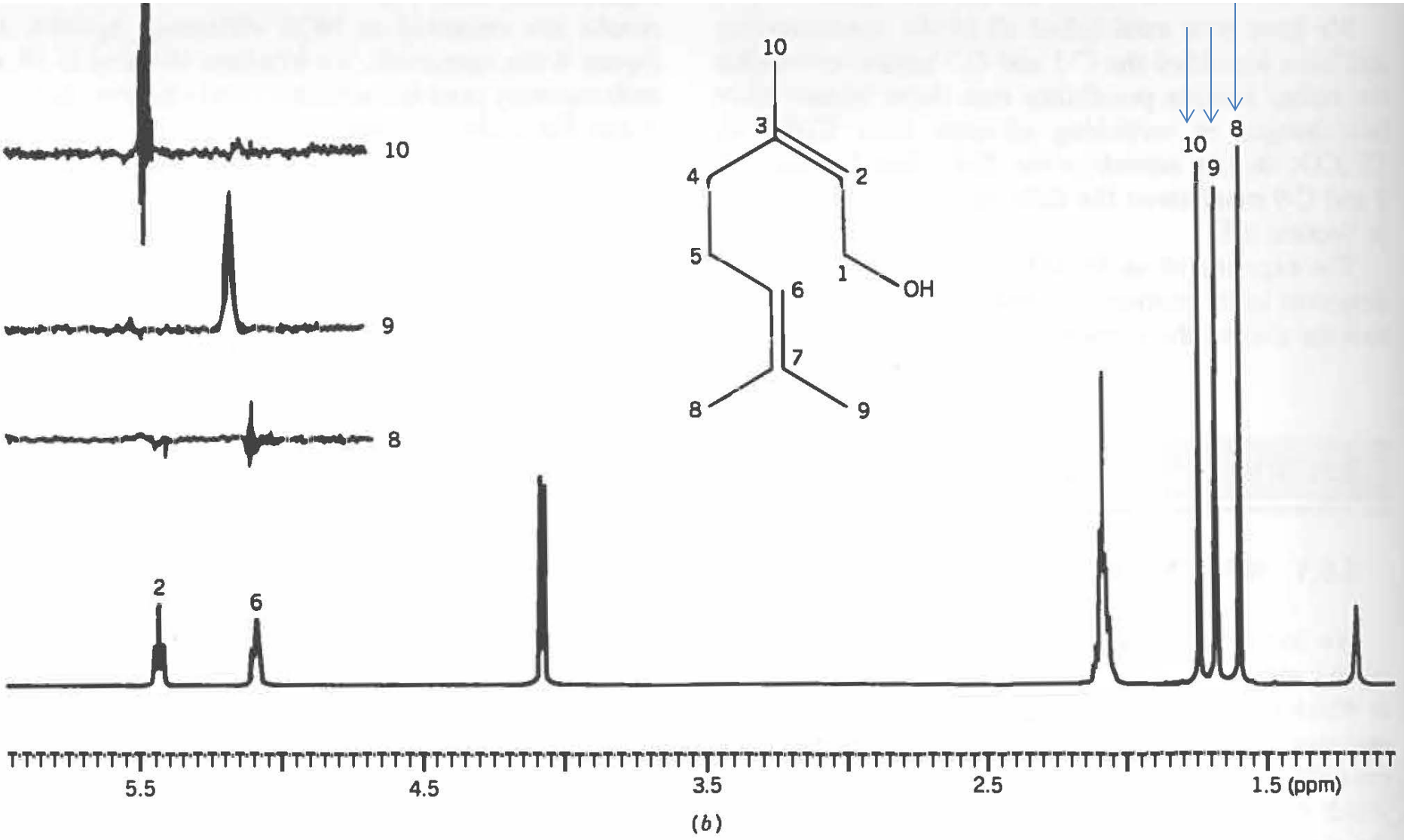


FIGURE 6.15. Difference NOE spectra of (*a*) geraniol and (*b*) nerol in $CDCl_3$ at 500 MHz.

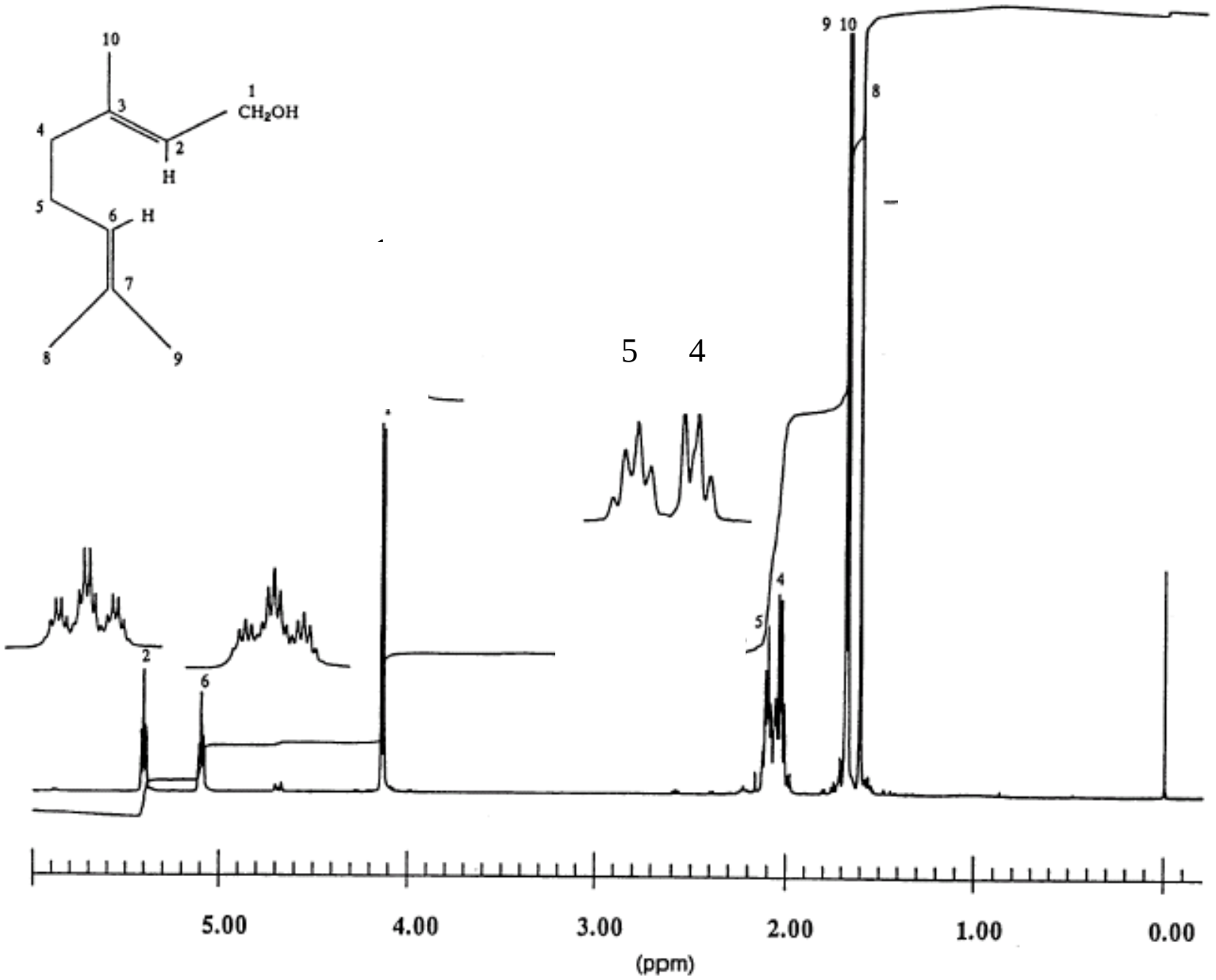
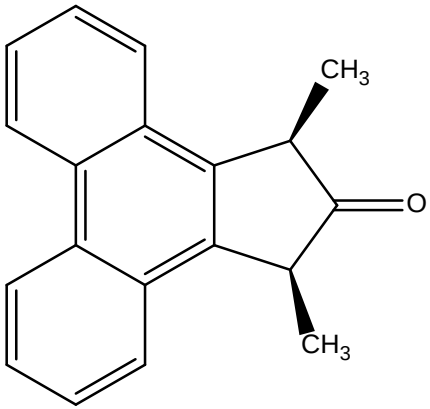
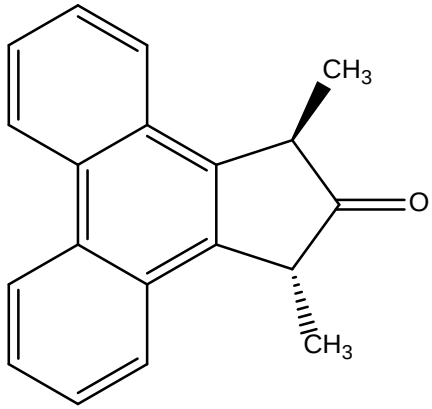


FIGURE 6.5. The ^1H Spectrum of geraniol in $CDCl_3$ at 500 MHz with expanded insets. Lower inset for H-5 and H-4 contains OH peak; upper inset is from a sample in which the OH peak is at higher field.

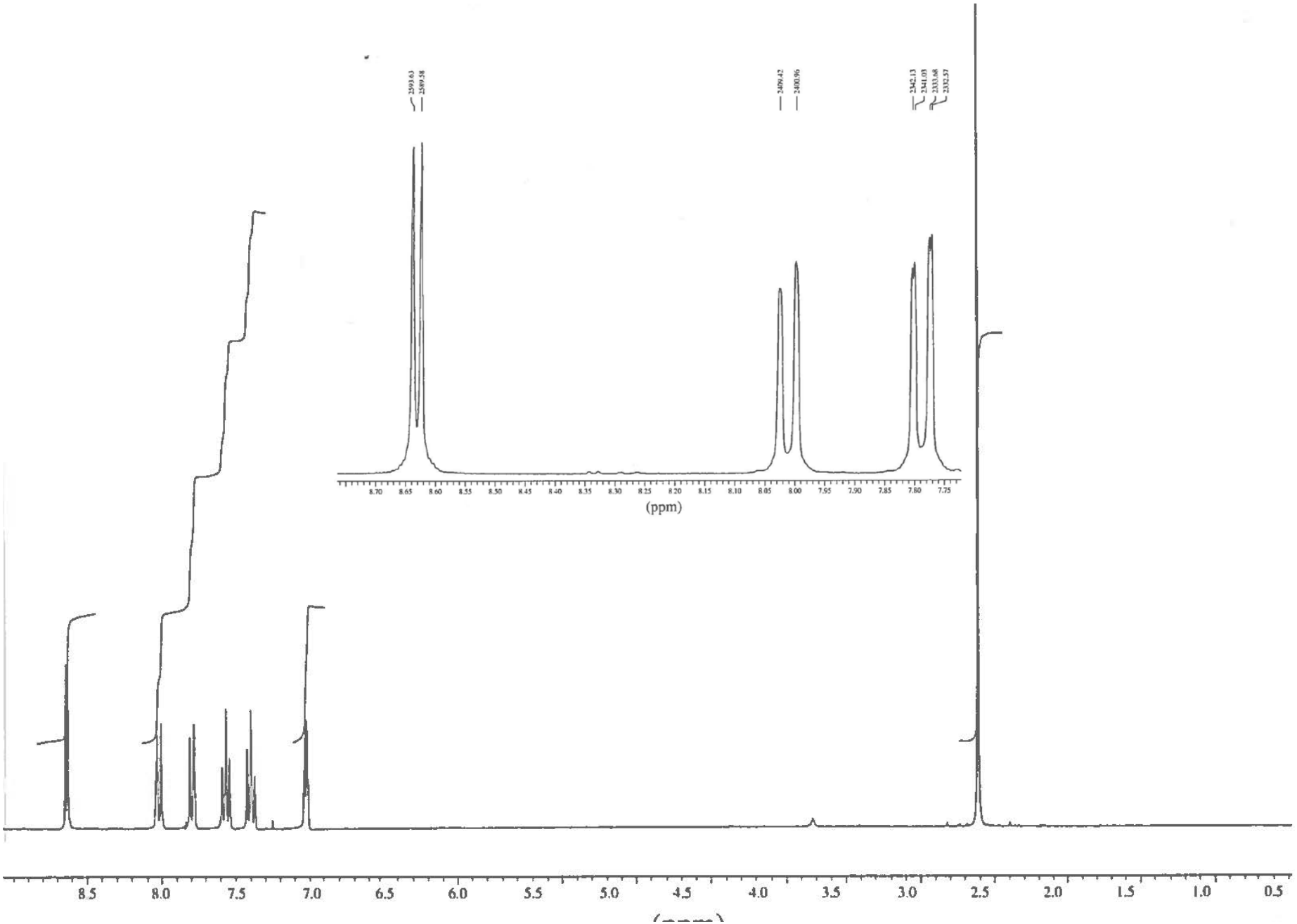
The cis and trans geometry of the isomeric ketones shown below is not easily determined by typical NMR measurements. NMR spectra of the corresponding alcohols obtained by reduction (lithium aluminum hydride) allow an unambiguous assignment of stereochemistry. Why?

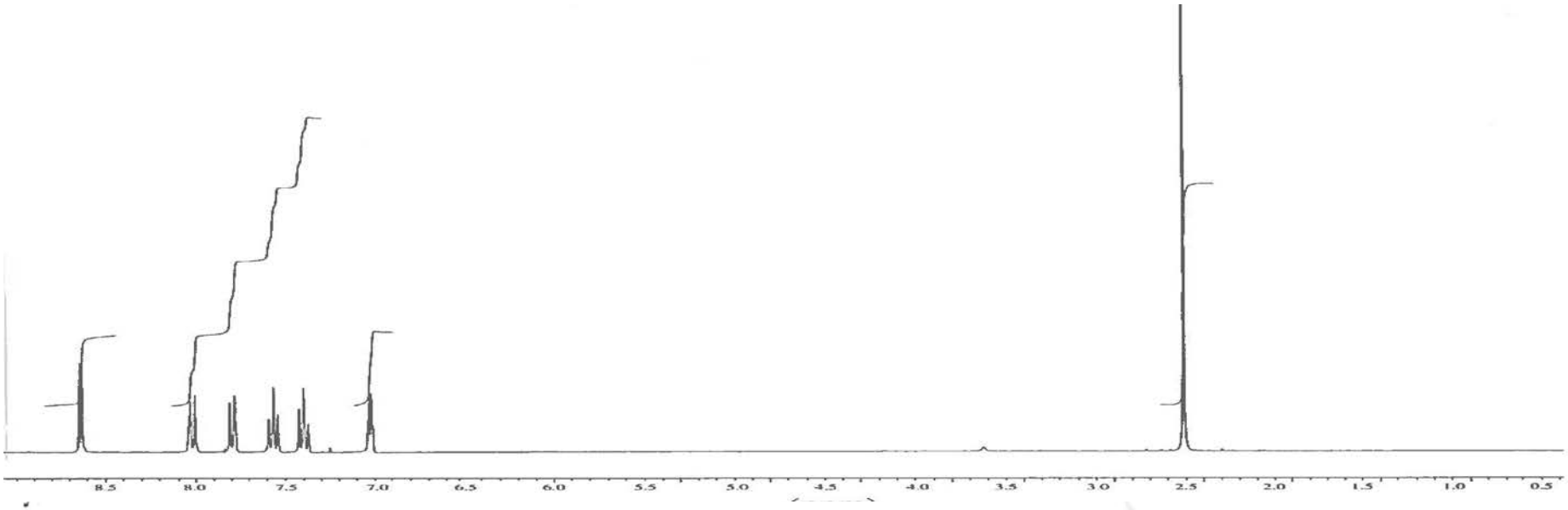


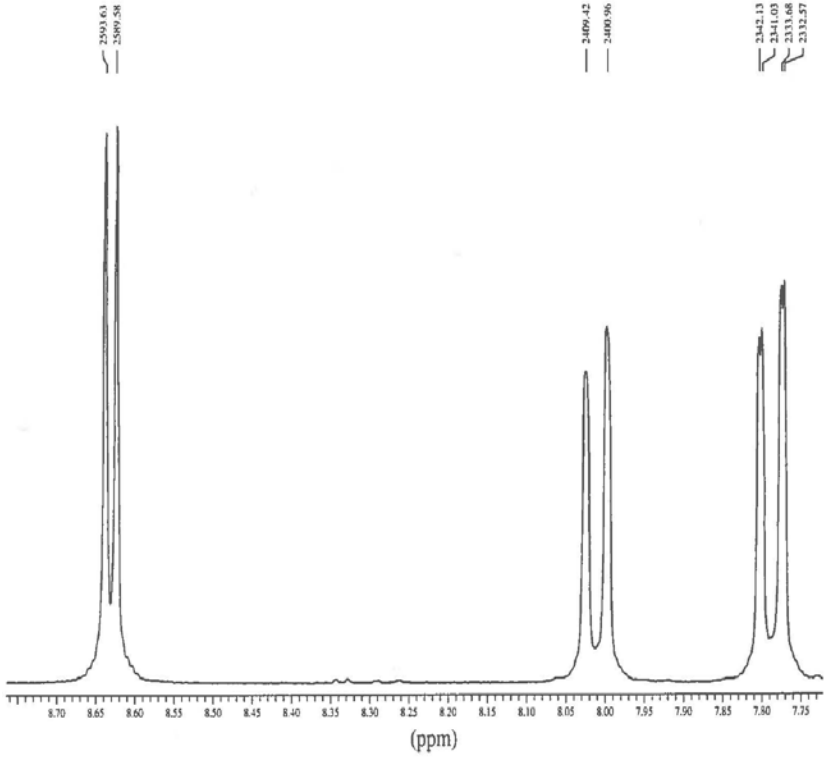


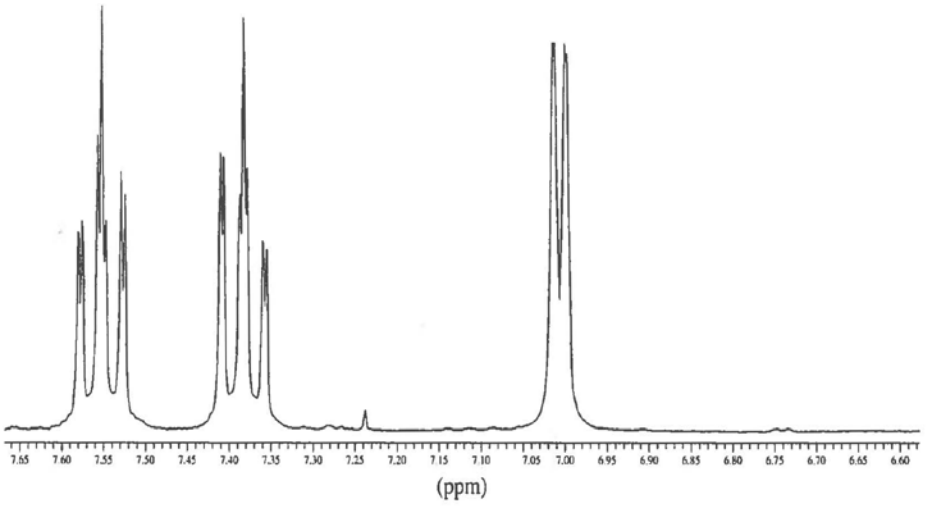
16. The proton NMR spectral information shown in this problem is for a compound with formula $C_{10}H_9N$. Expansions are shown for the region from 8.7 to 7.0 ppm. The normal carbon-13 spectral results, including DEPT-135 and DEPT-90 results, are tabulated:

Normal Carbon	DEPT-135	DEPT-90
19 ppm	Positive	No peak
122	Positive	Positive
124	Positive	Positive
126	Positive	Positive
128	No peak	No peak
129	Positive	Positive
130	Positive	Positive
144	No peak	No peak
148	No peak	No peak
150	Positive	Positive


2599.63
2589.58
2409.42
2400.96
2342.13
2341.03
2333.68
2332.57
(ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

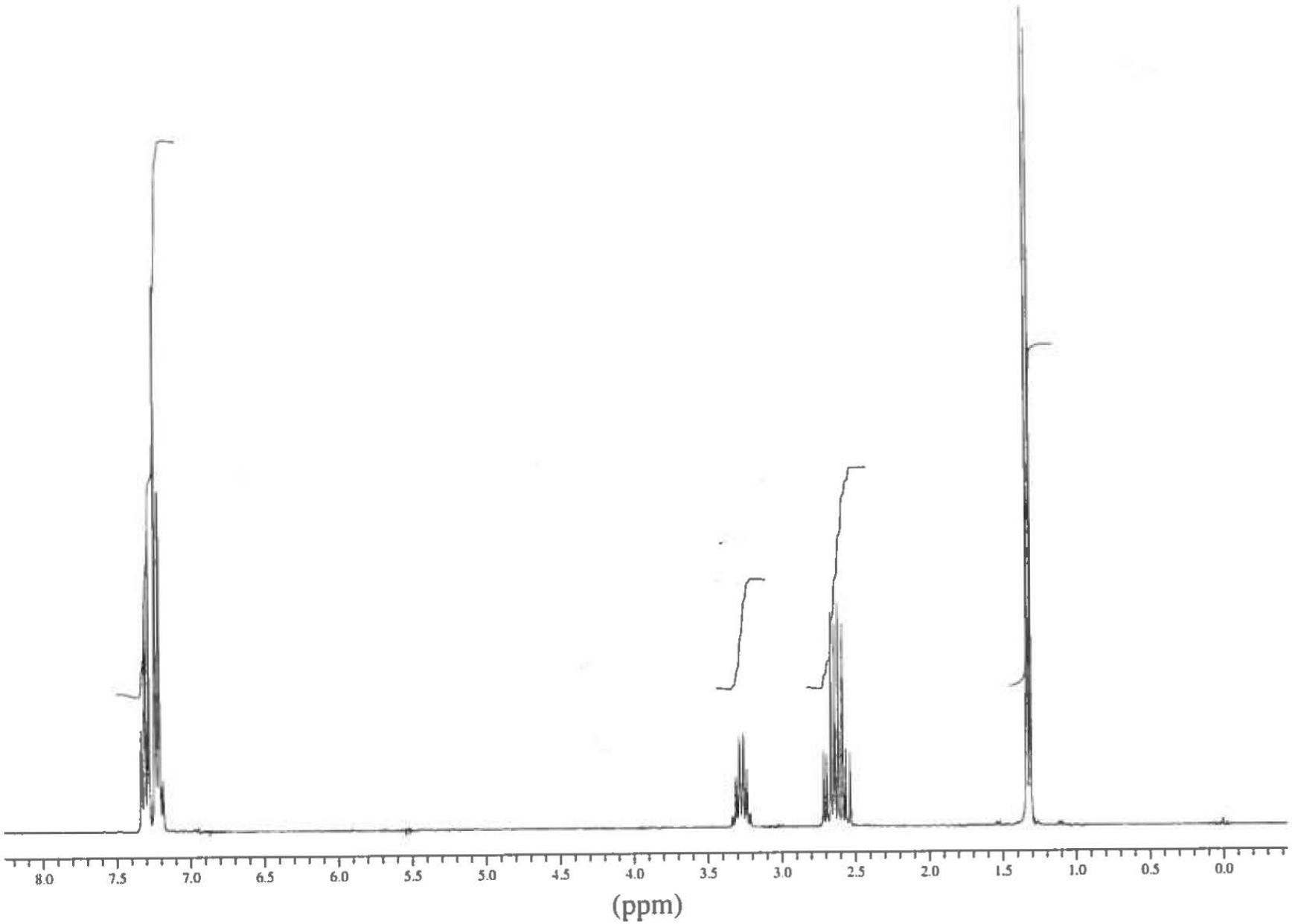

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

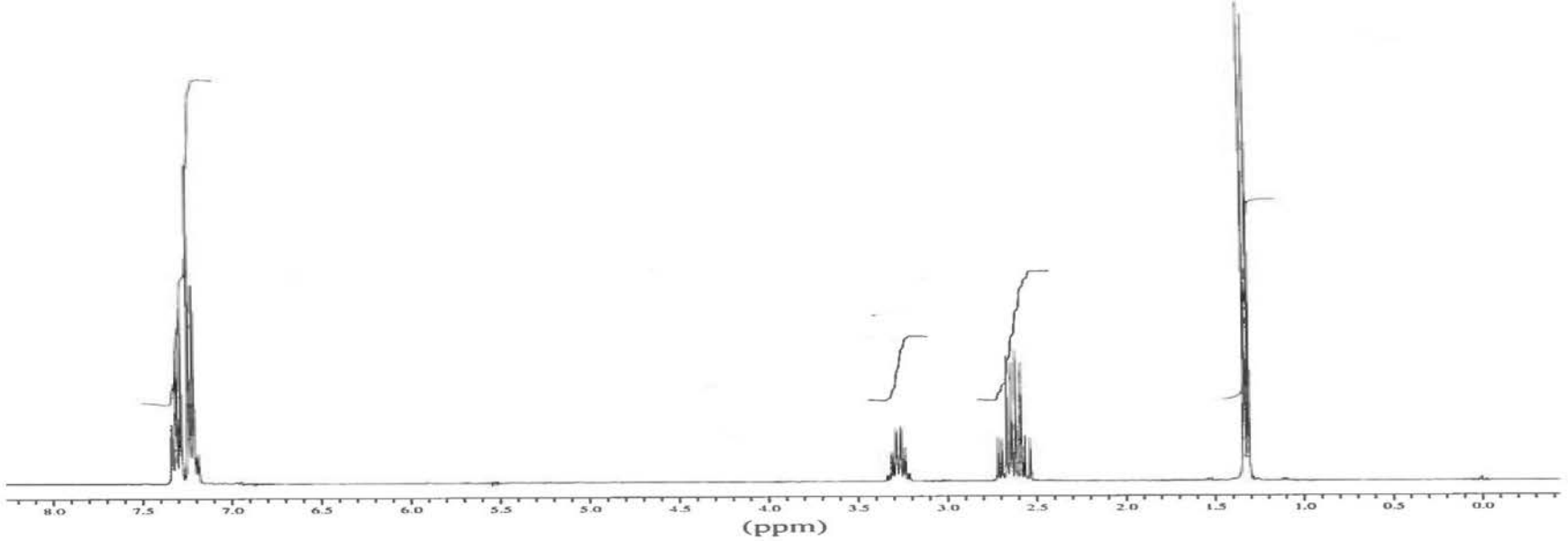

8.70
8.65
8.60
8.55
8.50
8.45
8.40
8.35
8.30
8.25
8.20
8.15
8.10
8.05
8.00
7.95
7.90
7.85
7.80
7.75
(ppm)

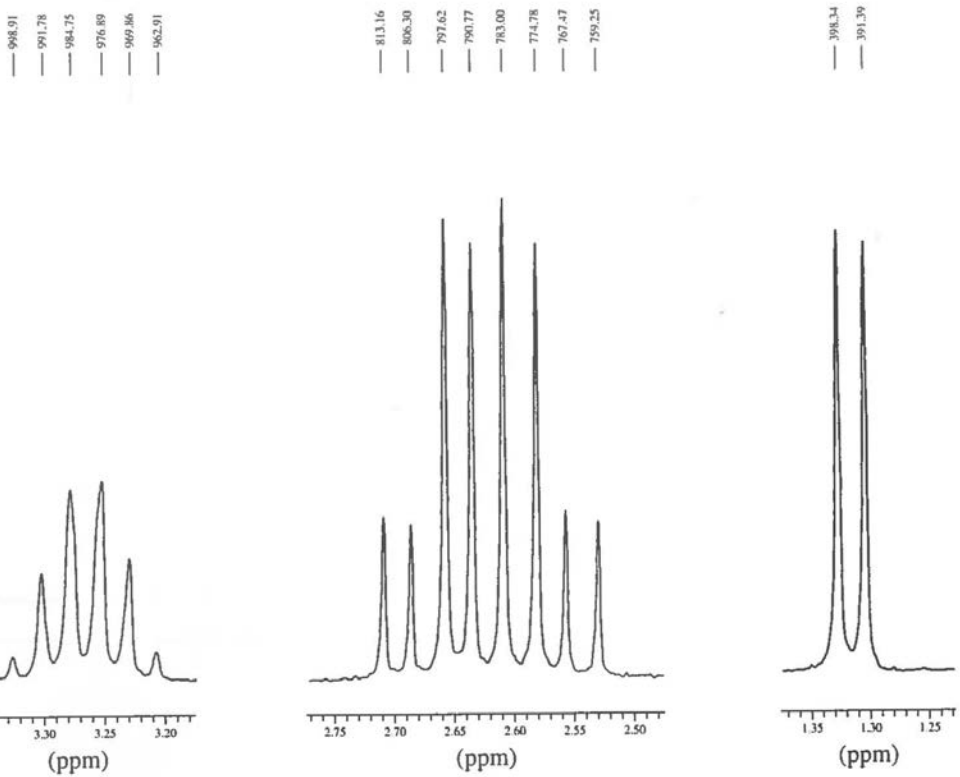

7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
6.80
6.75
6.70
6.65
6.60
(ppm)

18. The proton NMR spectral information shown in this problem is for a compound with formula $C_{10}H_{12}O_2$. One proton, not shown, is a broad peak that appears at about 12.8 ppm. Expansions are shown for the protons absorbing in the region from 3.5 to 1.0 ppm. The monosubstituted benzene ring is shown at about 7.2 ppm but is not expanded because it is uninteresting. The normal carbon-13 spectral results, including DEPT-135 and DEPT-90 results, are tabulated:

Normal Carbon	DEPT-135	DEPT-90
22 ppm	Positive	No peak
36	Positive	Positive
43	Negative	No peak
126.4	Positive	Positive
126.6	Positive	Positive
128	Positive	Positive
145	No peak	No peak
179	No peak	No peak


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


998.91
991.78
984.75
976.89
969.86
962.91
813.16
806.30
797.62
790.77
783.00
774.78
767.47
759.25
398.34
391.39
3.35
3.30
3.25
3.20
(ppm)
2.75
2.70
2.65
2.60
2.55
2.50
(ppm)
1.35
1.30
1.25
(ppm)