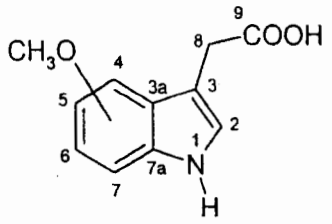
CHEMISTRY 5.46
ORGANIC STRUCTURE DET'N
SPRING 2004

PROBLEM 1

Figure 4.1 shows the ^{1}H NMR and a ^{1}H NOE difference spectrum of a 3-indolylacetic acid derivative **13** bearing a methoxy group at the benzenoic ring.



What is the position of the methoxy group?

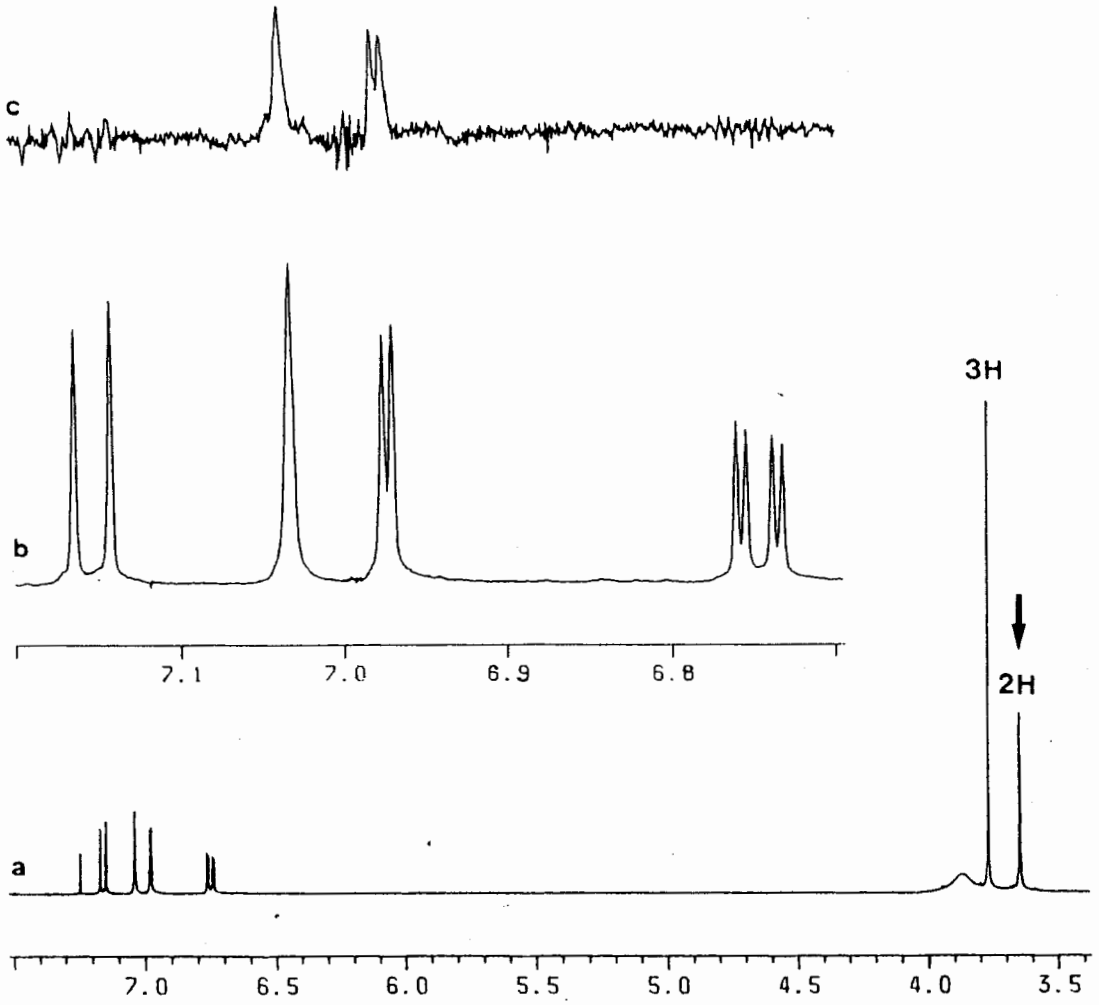


Fig. 4.1. 400 MHz ^{1}H NMR spectrum of **13** in a mixture of $CDCl_3$ and CD_3OD. **a** Full spectrum; **b** expanded section of the aromatic proton signals; **c** ^{1}H NOE difference spectrum, same section as in **b**, irradiation position at $\delta = 3.64$.

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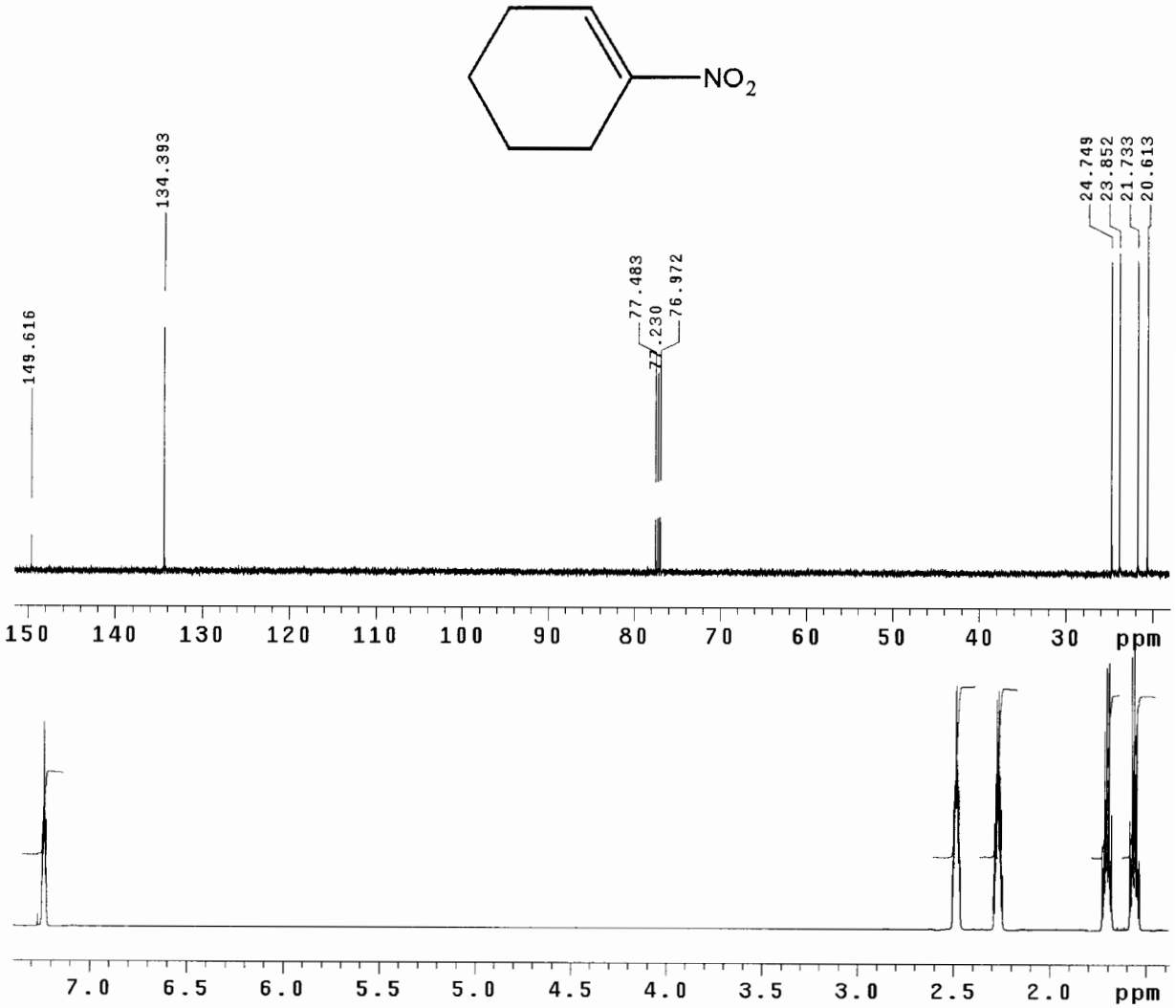
Problem 2

A sample of 1-nitro-1-cyclohexene was dissolved in $CDCl_3$ (^1H: 7.27p, ^{13}C: 77.23p). The ^{13}C 1D (upper) and ^1H 1D (lower) are at the bottom of this page.

(a) Assign the ^1H resonances using the ^1H 1D and ^1H-^1H gCOSY spectra. Explain your reasoning.

(b) Assign the ^{13}C resonances using your answer from (a) and the ^1H-^{13}C HMQC spectrum. Use the ^{13}C 1D spectrum below to obtain the ^{13}C shifts.

(c) Explain why the ^1H on the sp^2 hybridized carbon is farther downfield compared to where we normally observe a vinylic proton resonance.



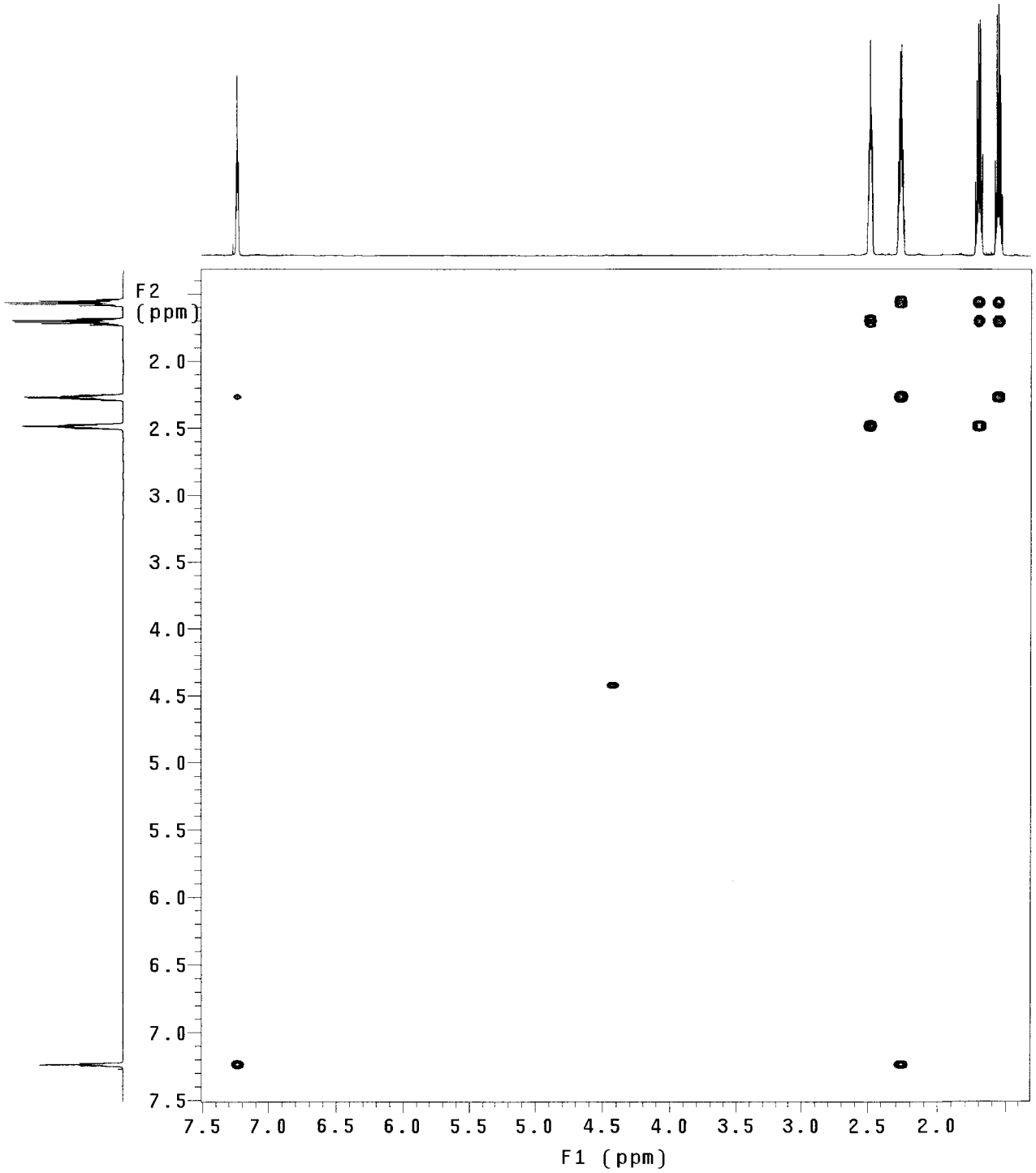
sample24_cdcl3_22c_gcosy

Pulse Sequence: gCOSY

Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: sample24_cdcl3_22c_gcosy
INOVA-500 "zippy"

PULSE SEQUENCE: gCOSY
Relax. delay 1.000 sec
Acq. time 0.135 sec
Width 3798.7 Hz
2D Width 3798.7 Hz
Single scan
128 increments
OBSERVE H1, 499.7537722 MHz
DATA PROCESSING
Sq. sine bell 0.067 sec
F1 DATA PROCESSING
Sq. sine bell 0.034 sec
FT size 2048 x 2048
Total time 2 min, 47 sec

(PROBLEM 2)



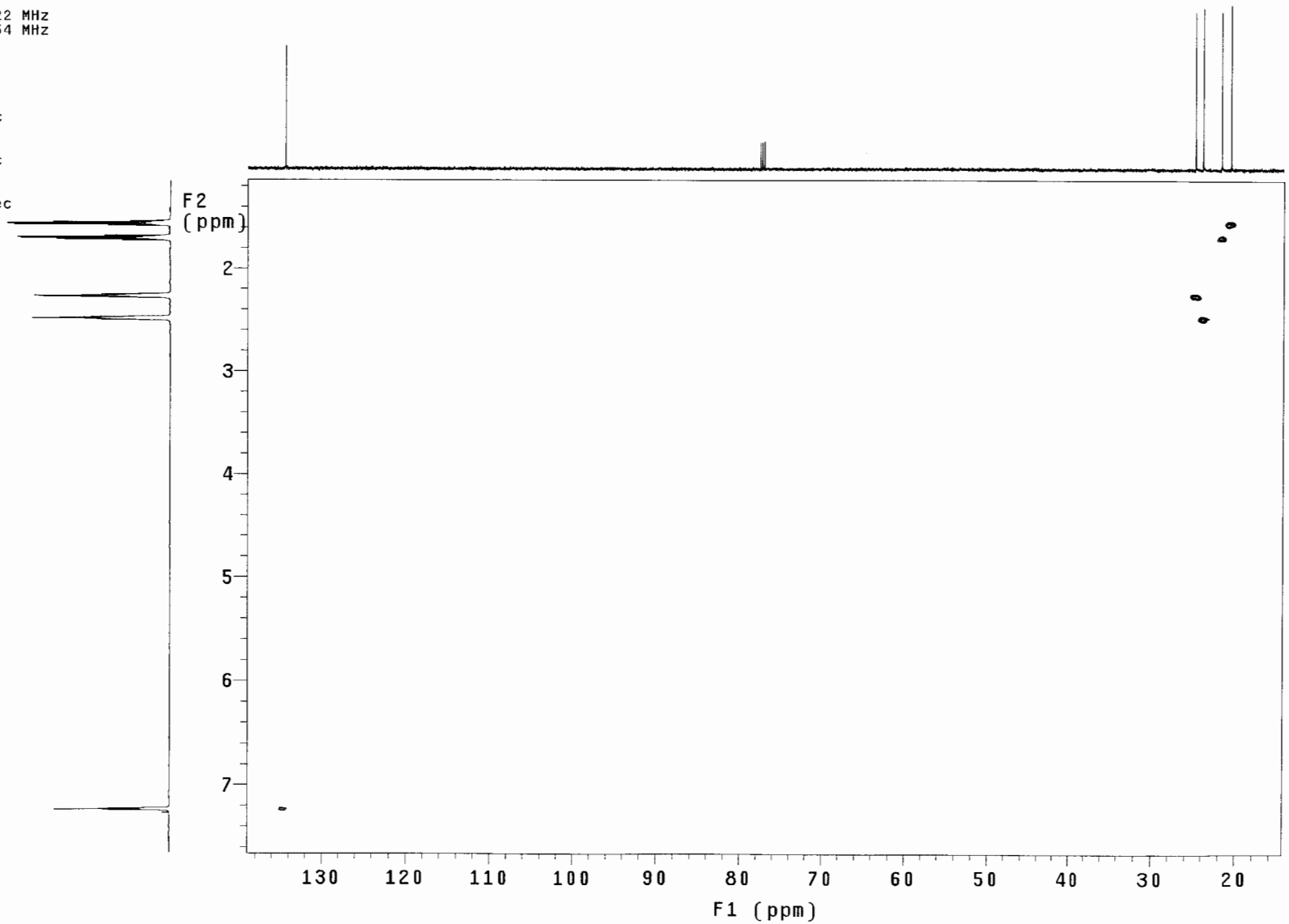
sample24_cdcl3_22c_hmqc

Pulse Sequence: hmqc

Solvent: CDCl3
Temp. 22.0 C / 295.1 K
User: 1-14-87
File: sample24_cdcl3_22c_hmqc
INOVA-500 "zippy"

PULSE SEQUENCE: hmqc
Relax. delay 0.900 sec
Acq. time 0.135 sec
Width 3795.1 Hz
2D Width 37709.1 Hz
8 repetitions
2 x 32 increments
OBSERVE H1, 499.7537722 MHz
DECOUPLE C13, 125.6750954 MHz
Power 50 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Sq. sine bell 0.135 sec
Shifted by -0.135 sec
F1 DATA PROCESSING
Sq. sine bell 0.014 sec
Shifted by -0.014 sec
FT size 1024 x 1024
Total time 20 min, 54 sec

(PROBLEM 2)



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Problem 3

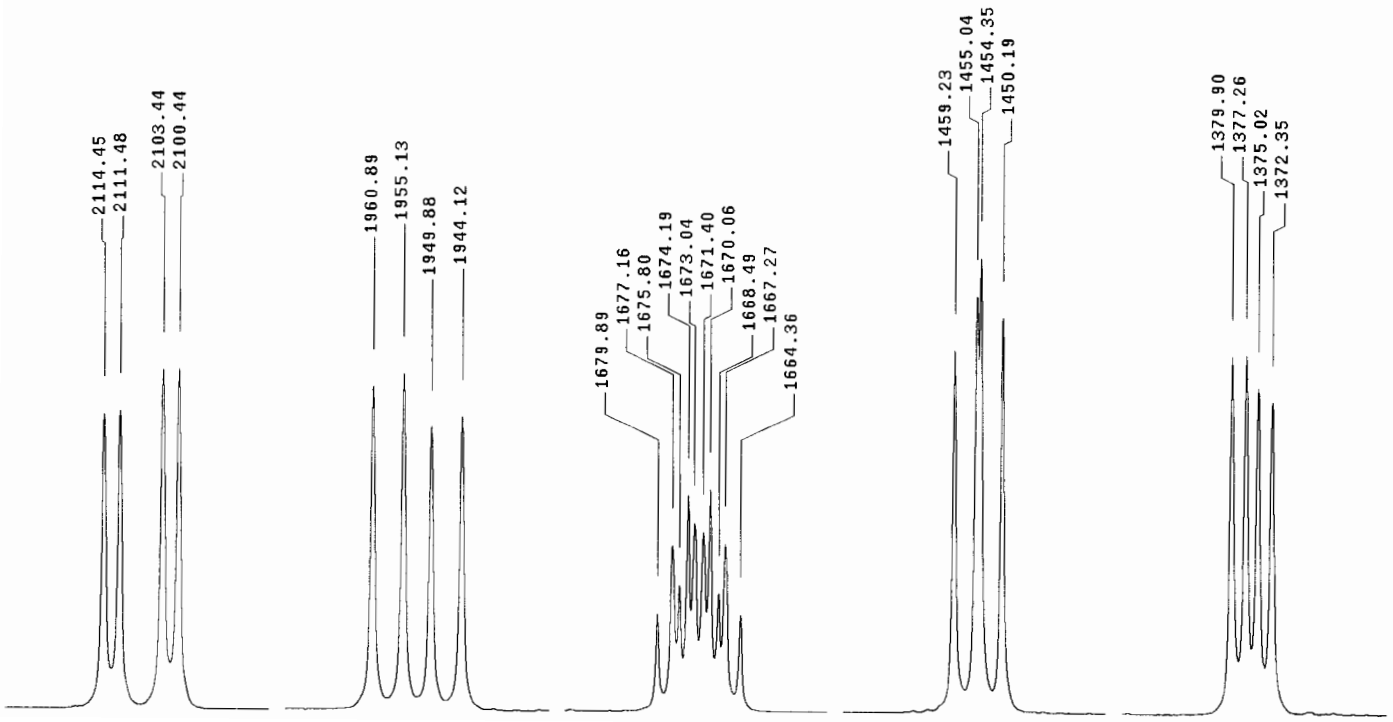
Below are the signals from five protons bound to carbons. The proton resonances are split into multiplets by homonuclear J-couplings.

(a) Calculate all the homonuclear J-couplings for each multiplet.

(b) Determine the number of protons to which each resonance is coupled.

(c) Give the connectivity that must result from the observed splittings. For example, $R_2CH\text{-}CH_2\text{-}CH_2\text{-}R'$.

Explain your reasoning.



PROBLEM 4 Compound A is readily available from the wormwood plant and was originally sold by Pfizer, Inc. in the 1920s to treat tapeworm parasites. It is known to have **one ketone carbonyl group and one ester carbonyl group.**

Attached is the 13C-13C INADEQUATE spectrum with carbon spectra shown on both axes (although the 2D spectrum is symmetrized, it was not plotted as a square).

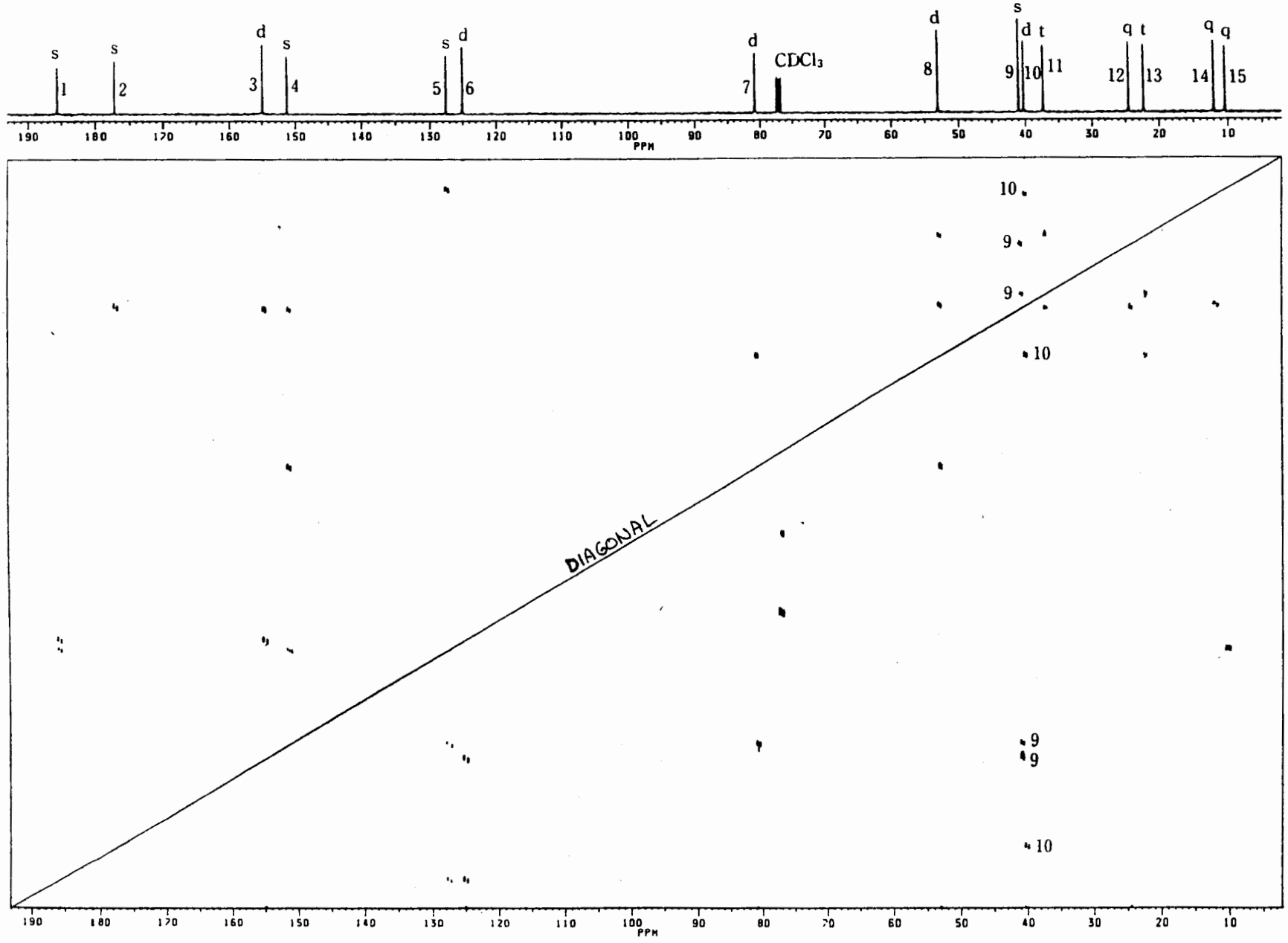
a) Using the multiplicity data provided on the ^{13}C spectrum (**s , d=CH, t=CH_2, q=CH_3** e.g., from a DEPT experiment), deduce the molecular formula of **A** and the unsaturation number.

b) How many double bonds and how many rings are in Compound A? Which carbonyl carbon and which other carbon are attached to the ester oxygen?

c) By tracing out the cross peaks in the 2D spectrum, deduce the molecular structure of Compound A.

(Progam 4)

Compound A



100MHz ^{13}C-NMR ($CDCl_3$)

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PROBLEM 5

The following spectra were obtained from an organic molecule with a MW of 182.2 dissolved in CD_3OD (proton: quintet at 3.31p, singlet at ~4.87p, carbon: heptet at 49.15p). Deduce its structure and explain your reasoning for assignments.

In order, the spectra given are:

- ^{1}H 1D (300 MHz)
- ^{13}C 1D
- ^{1}H-^{13}C HMQC (gives crosspeaks between carbons and their directly-attached protons)
- ^{1}H TOCSY w/ 30 ms mixing time (this TOCSY shows some cross peaks due to small ^{4}J's and ^{5}J's that should allow you to fully assign this molecule)

The 2D spectra were obtained at 11.7T (500 MHz ^{1}H frequency) and were collected at 20°C.

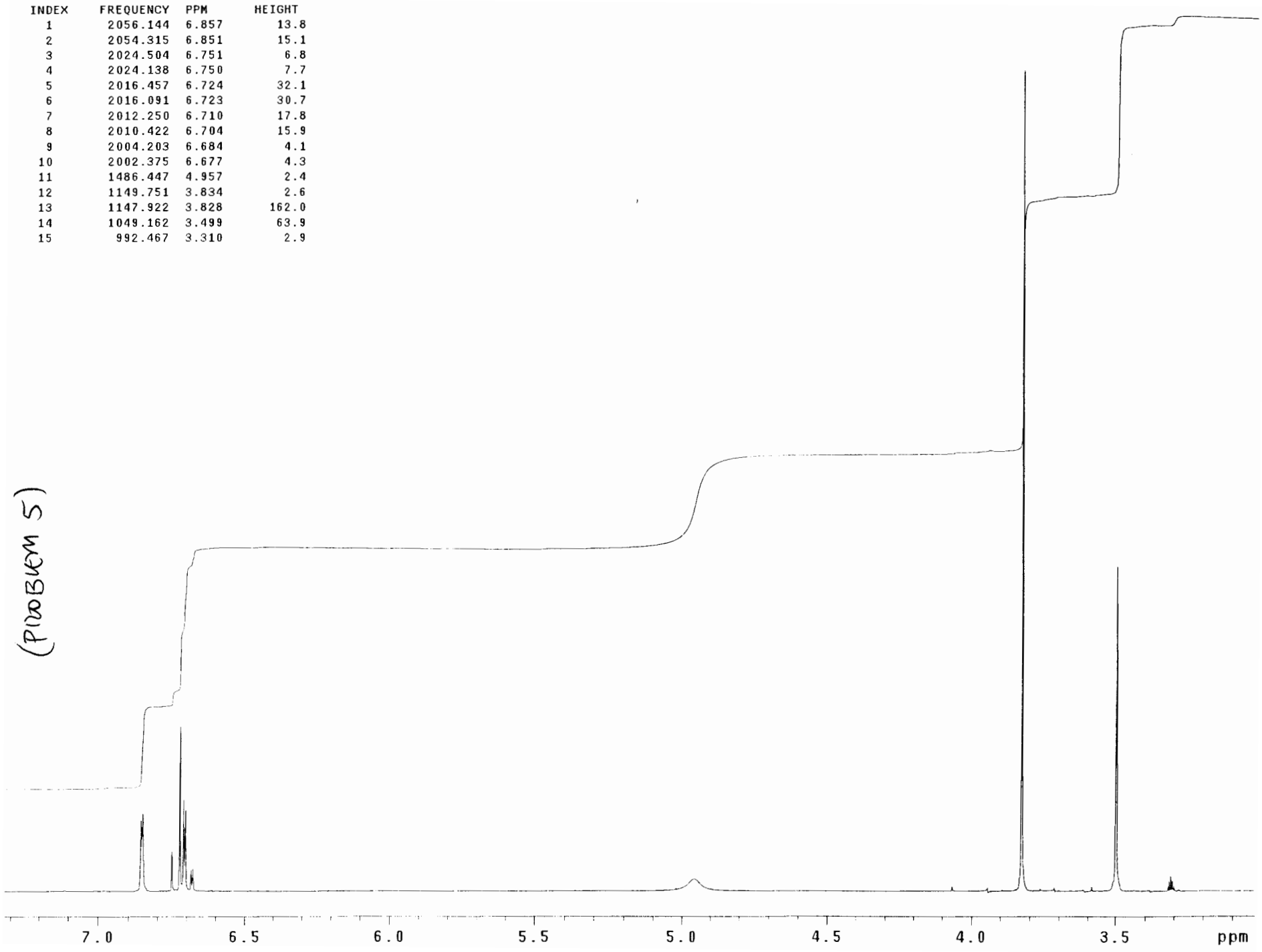
Items to note:

- The solvent will 'exchange away' all ionizable protons (e.g., hydroxyl, carboxyl, or amino protons).
- The HMQC and TOCSY can shift resonances due to rf heating (caused by ^{13}C decoupling and the spin lock during mixing, respectively), so TOCSY and HMQC shifts may differ substantially from the ^{1}H and ^{13}C 1D spectra.

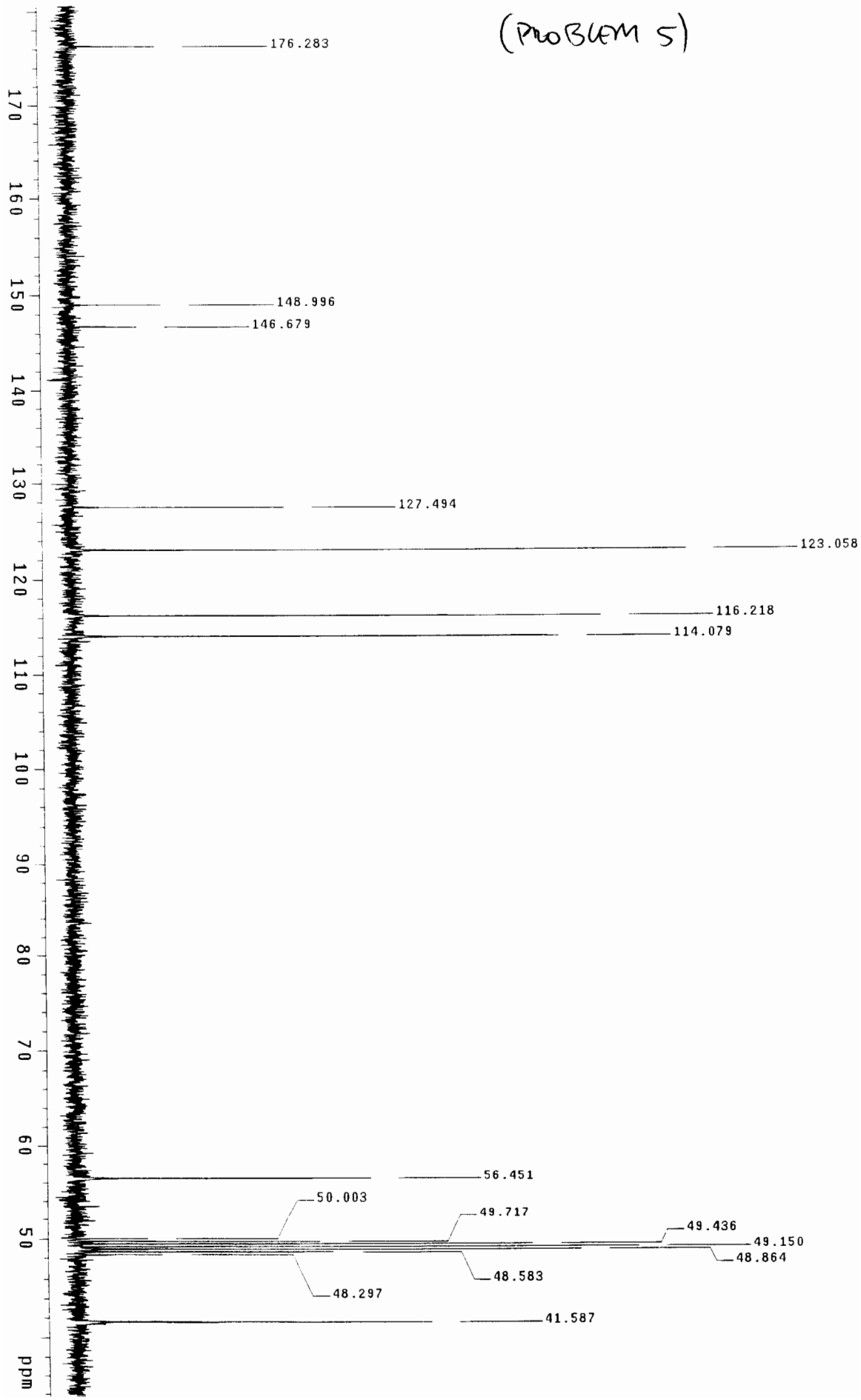
Hints:

- Recall the effects contributions of electronegative versus electron-withdrawing groups.
- Atomic weights you might need: H, 1.008; Li, 6.939; B, 10.811; C, 12.011; N, 14.007; O, 15.999; F, 18.998; Na, 22.990; Mg, 24.312; Si, 28.086; P, 30.974; S, 32.064; Cl, 35.453; Br, 79.909; I, 126.90

INDEX	FREQUENCY	PPM	HEIGHT
1	2056.144	6.857	13.8
2	2054.315	6.851	15.1
3	2024.504	6.751	6.8
4	2024.138	6.750	7.7
5	2016.457	6.724	32.1
6	2016.091	6.723	30.7
7	2012.250	6.710	17.8
8	2010.422	6.704	15.9
9	2004.203	6.684	4.1
10	2002.375	6.677	4.3
11	1486.447	4.957	2.4
12	1149.751	3.834	2.6
13	1147.922	3.828	162.0
14	1049.162	3.499	63.9
15	992.467	3.310	2.9



(PROBLEM 5)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146.679
127.494
123.058
116.218
114.079
56.451
50.003
49.717
49.436
49.150
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41.587
170
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150
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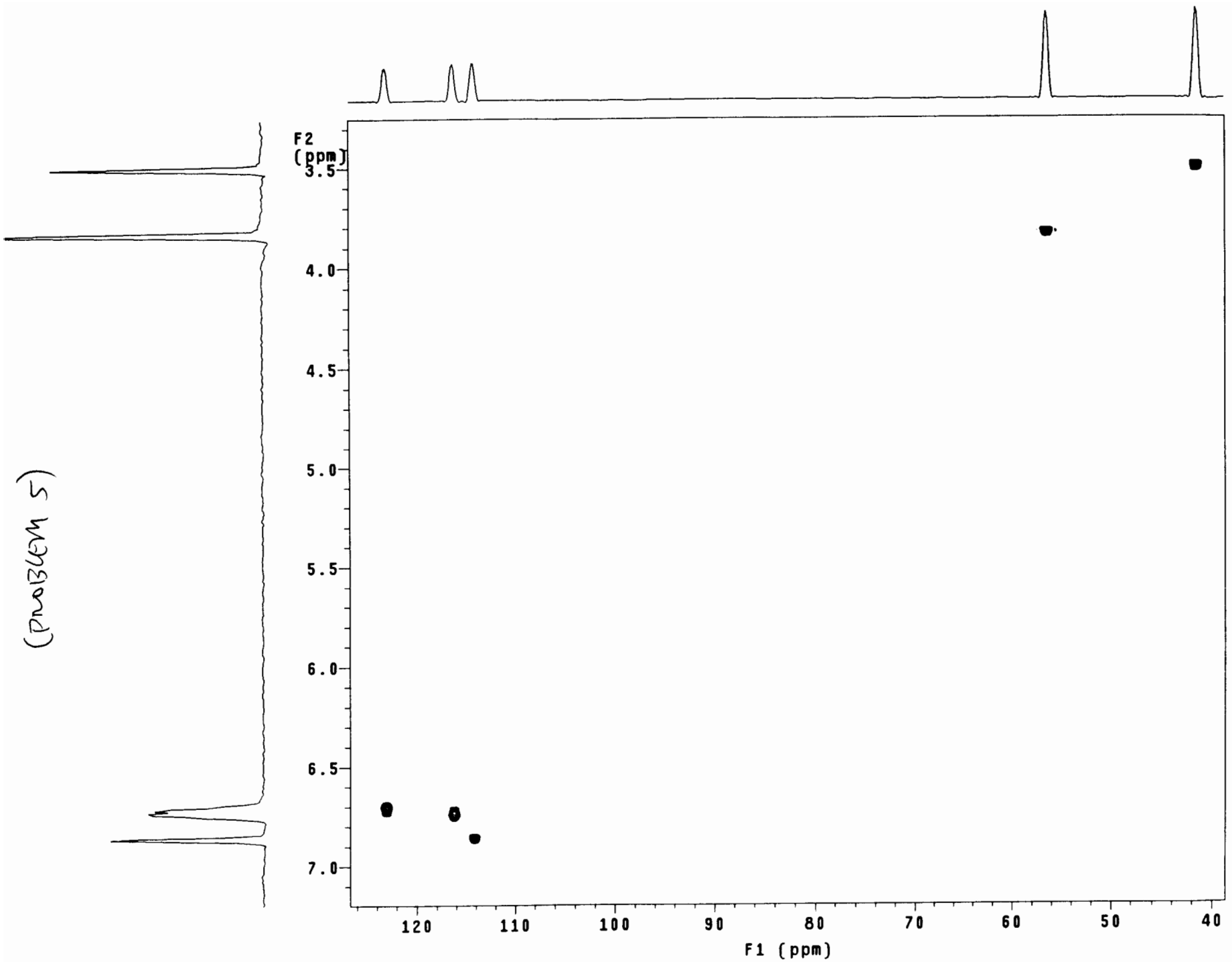
130
120
110
100
90
80
70
60
50
ppm


F2 (ppm)
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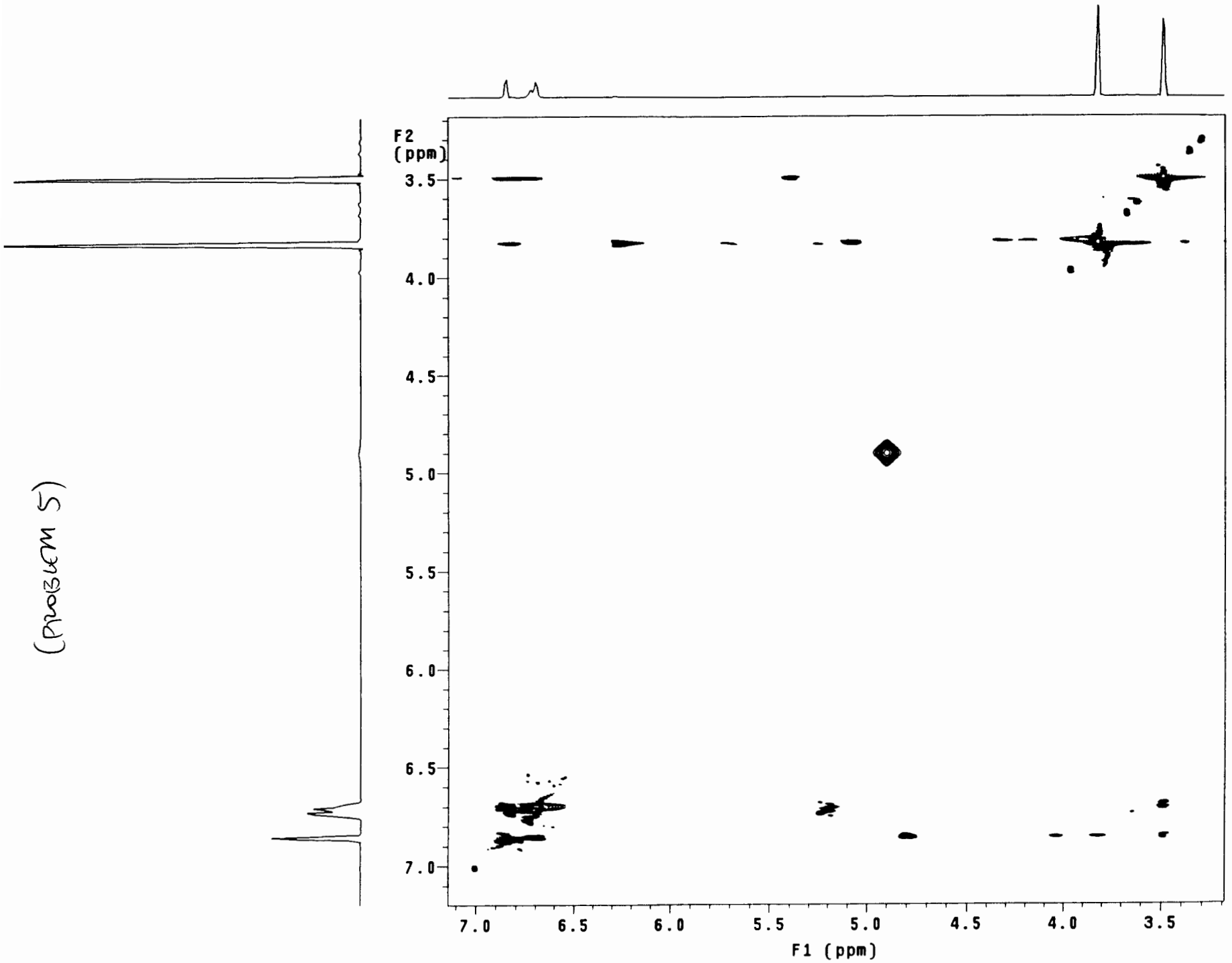
4.0
4.5
5.0
5.5
6.0
6.5
7.0
120
110
100
90
80
70
60
50
40
F1 (ppm)
(problem 5)


F2
(ppm)
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
F1 (ppm)
(PROBLEM 5)

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PROBLEM 6

The following spectra were obtained from an organic compound with a molecular weight of 130.1. The sample was dissolved in $CDCl_3$ (proton: 7.27p, carbon 77.23p). Deduce its structure and explain your logic.

In order, the spectra given are:

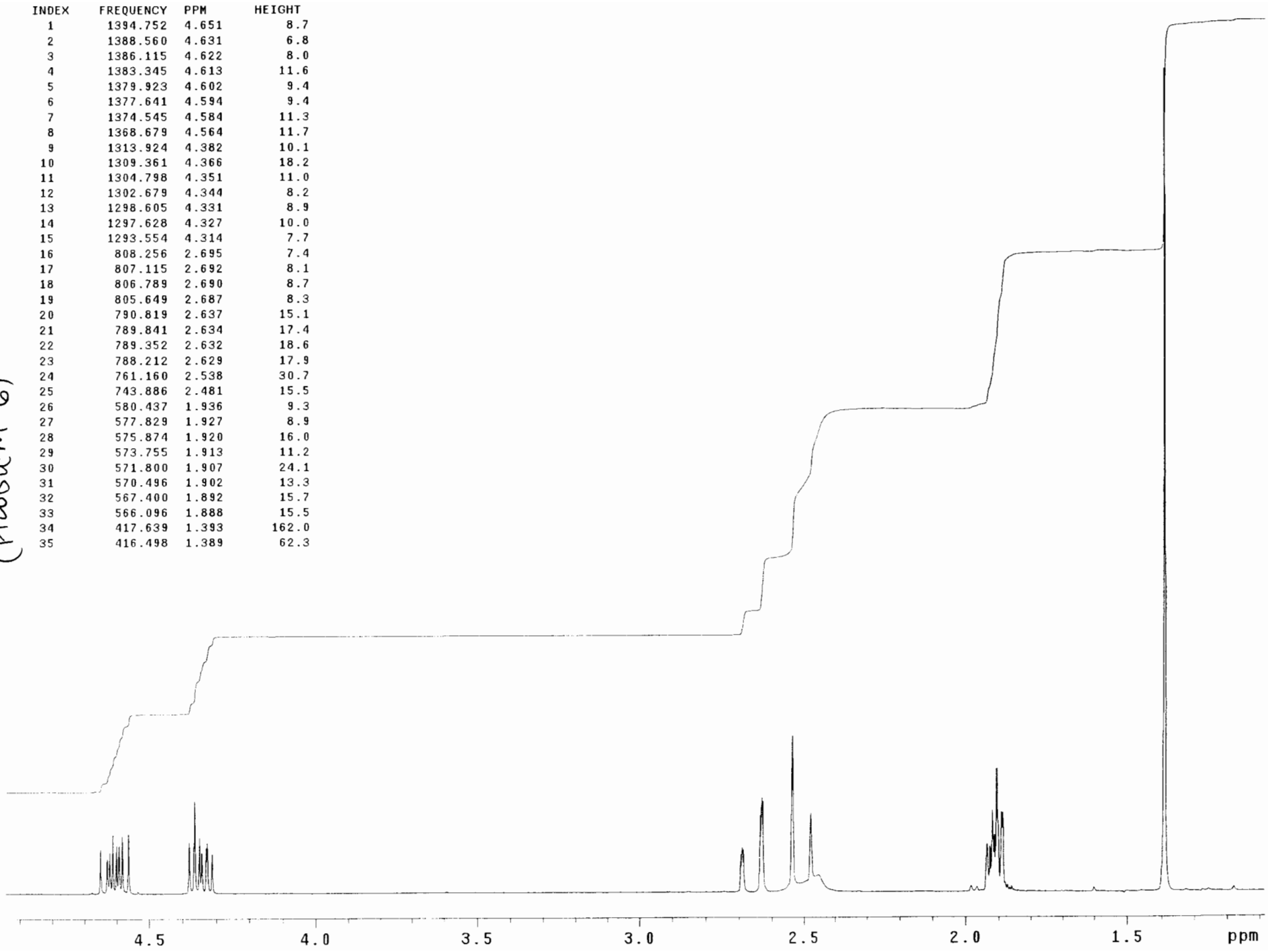
- ^{1}H 1D
- ^{13}C 1D
- ^{1}H-^{13}C HMQC
- ^{1}H TOCSY w/ 30 ms mixing time

Note:

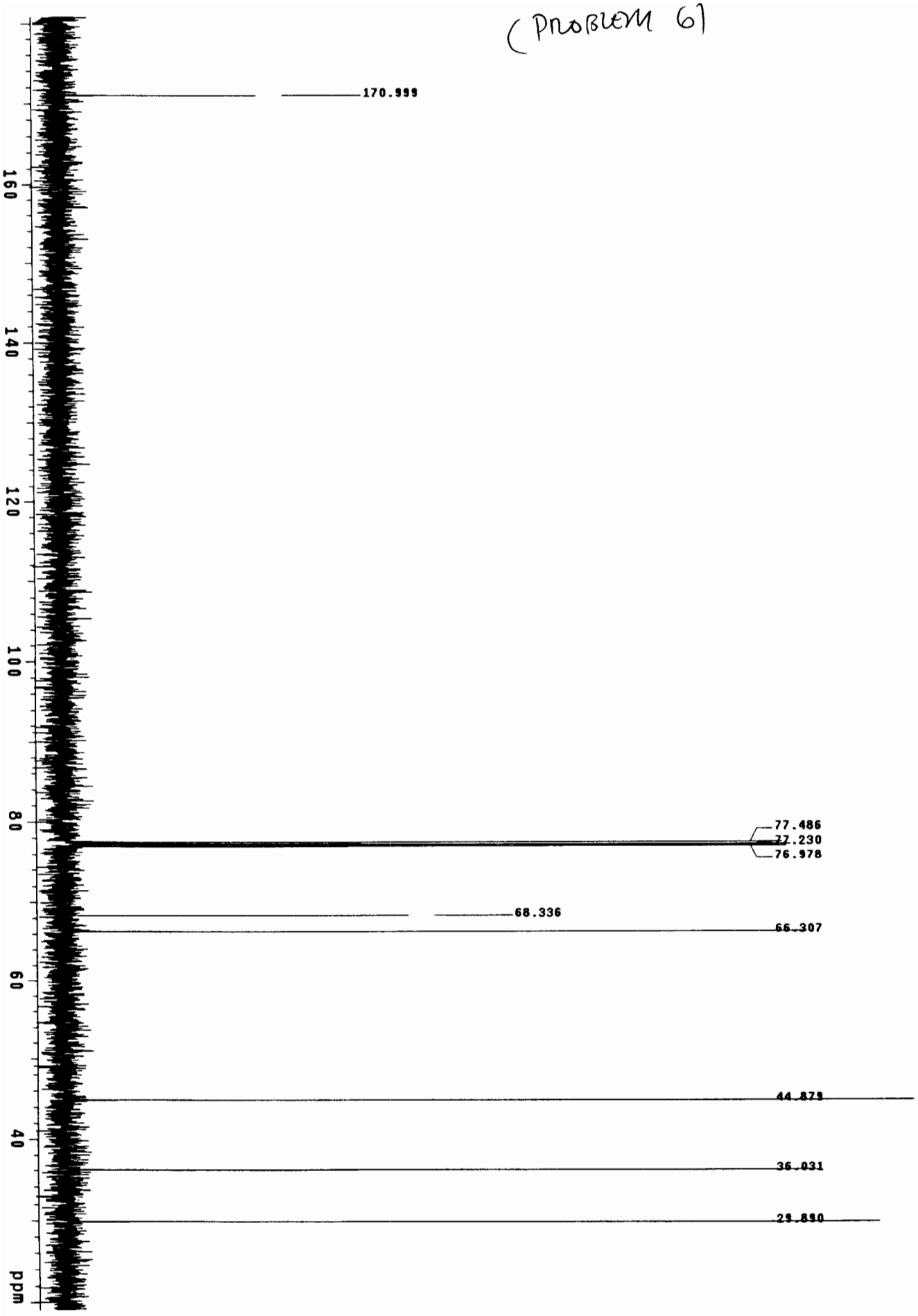
- No crosspeaks lay outside the window for any of the 2D spectra given.

(PROBLEM 6)

INDEX	FREQUENCY	PPM	HEIGHT
1	1394.752	4.651	8.7
2	1388.560	4.631	6.8
3	1386.115	4.622	8.0
4	1383.345	4.613	11.6
5	1379.923	4.602	9.4
6	1377.641	4.594	9.4
7	1374.545	4.584	11.3
8	1368.679	4.564	11.7
9	1313.924	4.382	10.1
10	1309.361	4.366	18.2
11	1304.798	4.351	11.0
12	1302.679	4.344	8.2
13	1298.605	4.331	8.9
14	1297.628	4.327	10.0
15	1293.554	4.314	7.7
16	808.256	2.695	7.4
17	807.115	2.692	8.1
18	806.789	2.690	8.7
19	805.649	2.687	8.3
20	790.819	2.637	15.1
21	789.841	2.634	17.4
22	789.352	2.632	18.6
23	788.212	2.629	17.9
24	761.160	2.538	30.7
25	743.886	2.481	15.5
26	580.437	1.936	9.3
27	577.829	1.927	8.9
28	575.874	1.920	16.0
29	573.755	1.913	11.2
30	571.800	1.907	24.1
31	570.496	1.902	13.3
32	567.400	1.892	15.7
33	566.096	1.888	15.5
34	417.639	1.393	162.0
35	416.498	1.389	62.3



(PROBLEM 6)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76.978
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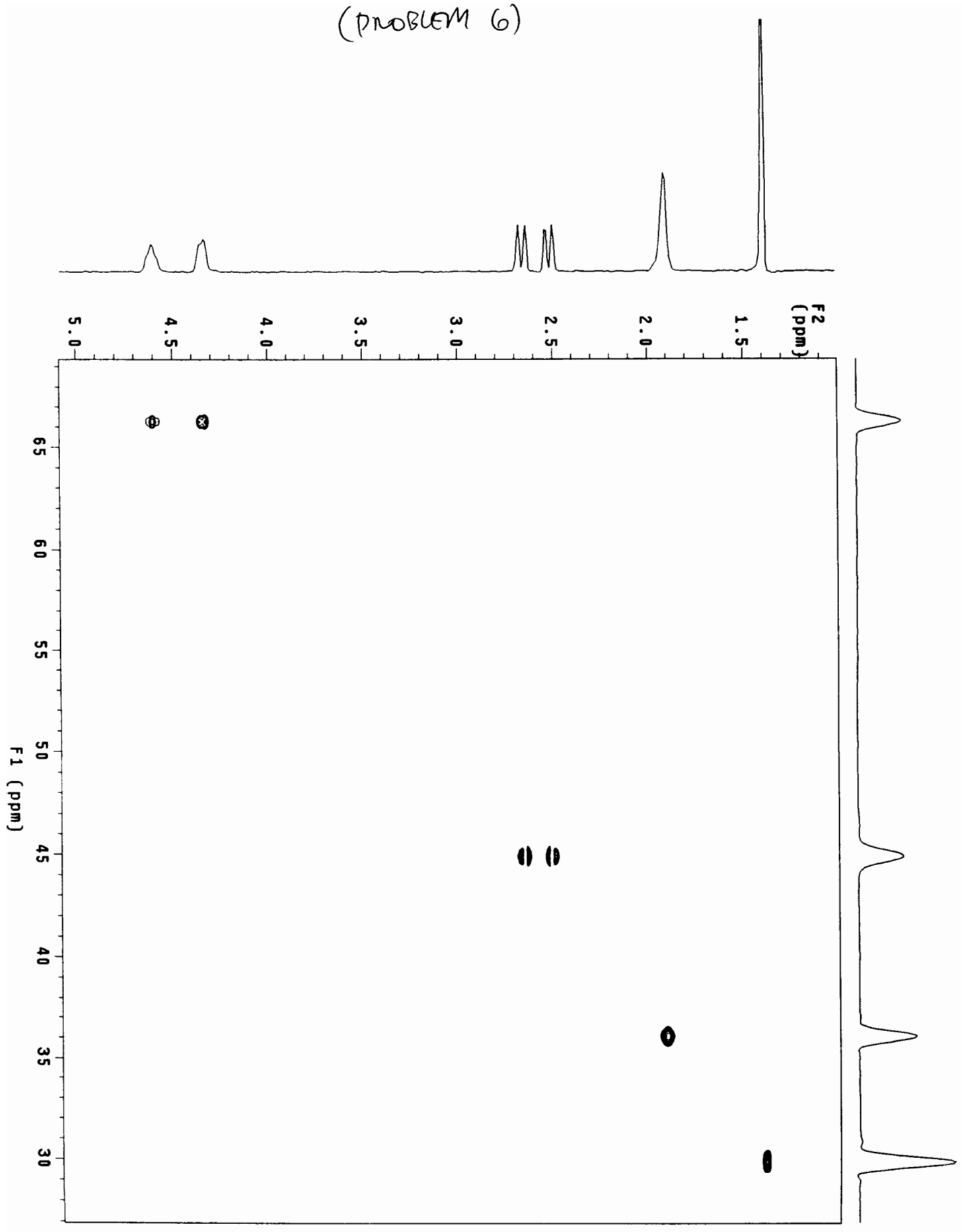
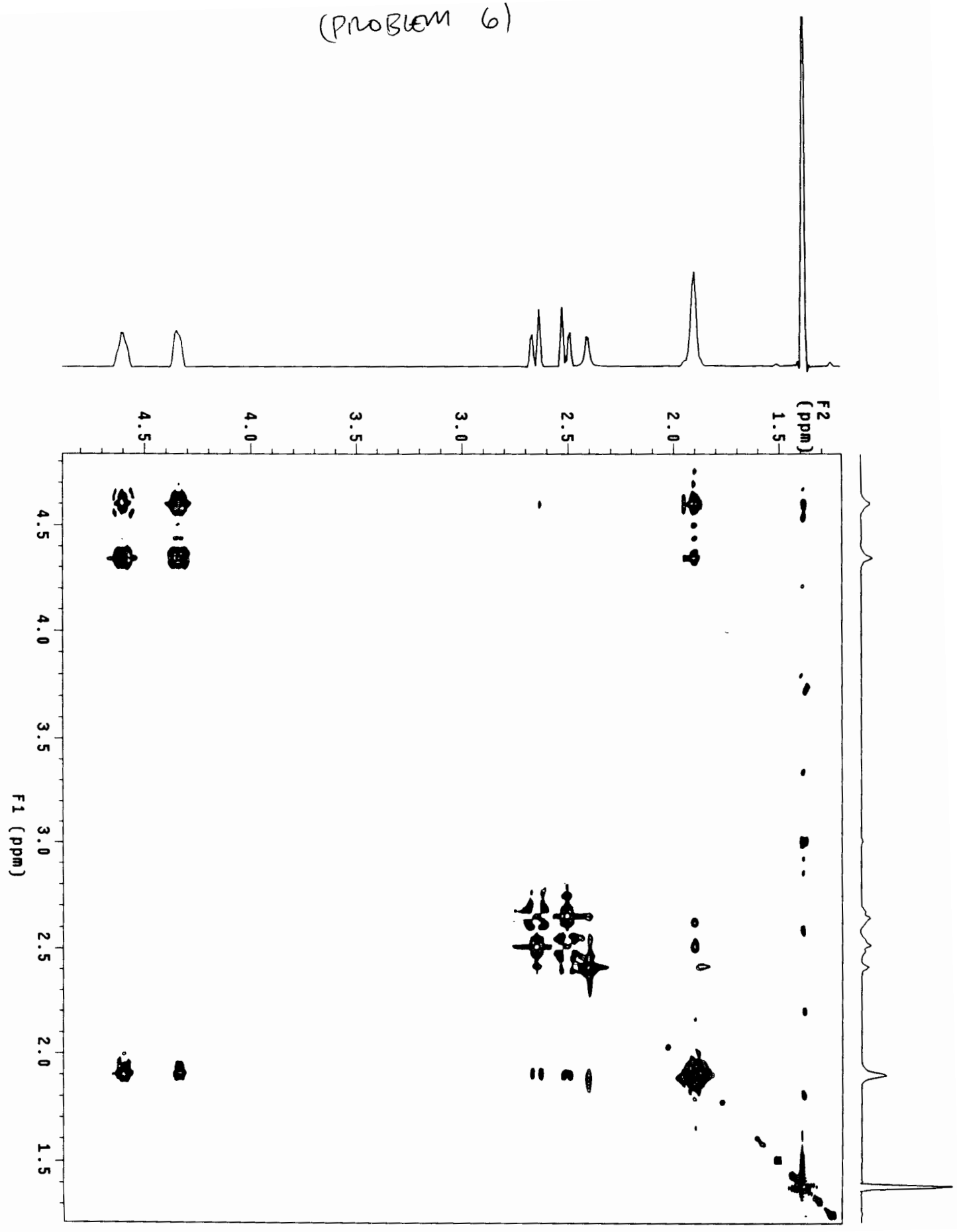
44.879
36.031
29.890
160
140
120
100
80
60
40
ppm

(PROBLEM 6)



(PROBLEM 6)



PROBLEM 7

$C_{10}H_7Cl$