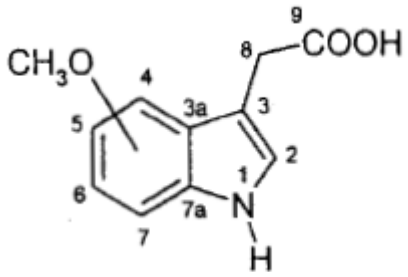
Problem 1

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?

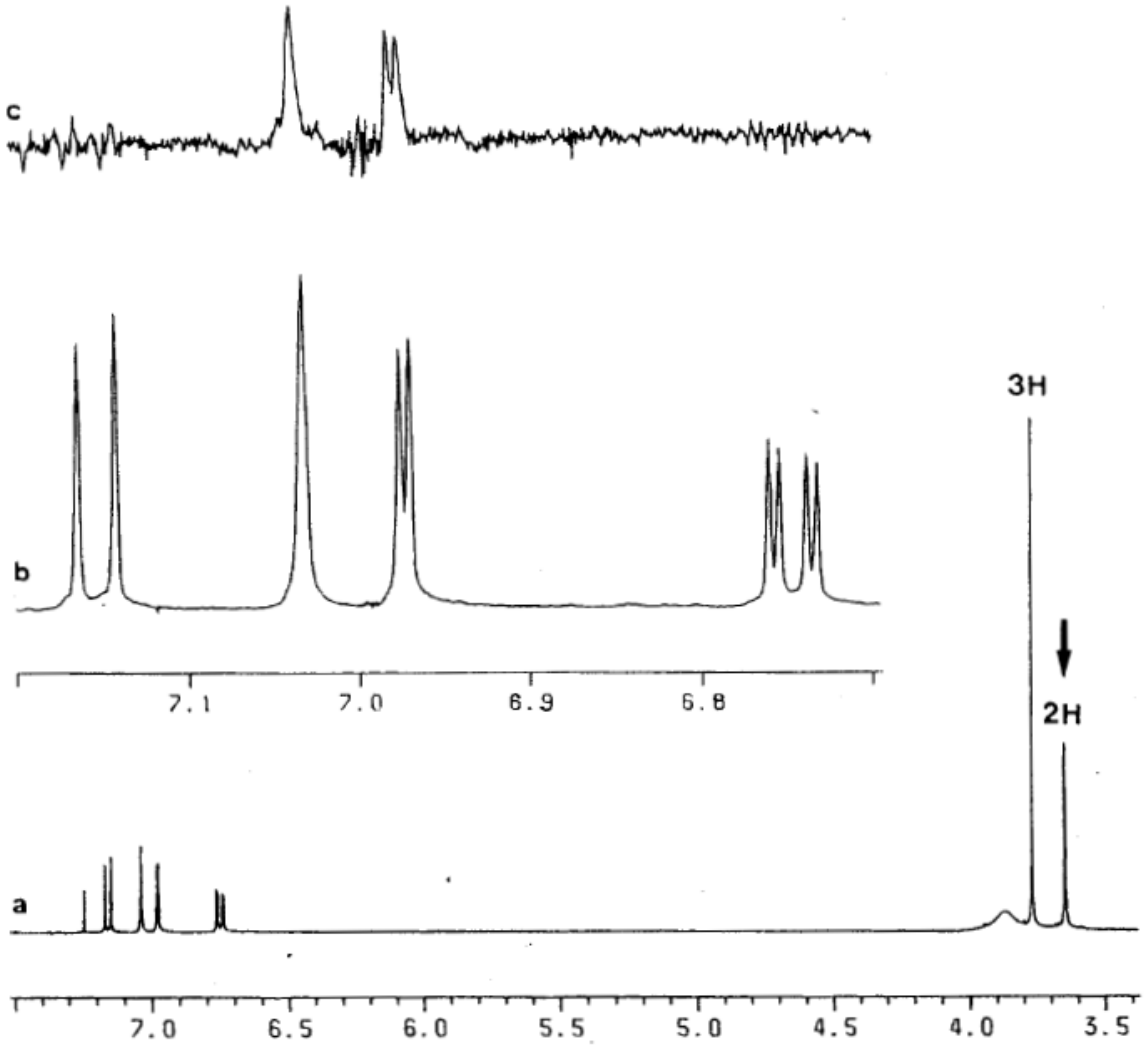
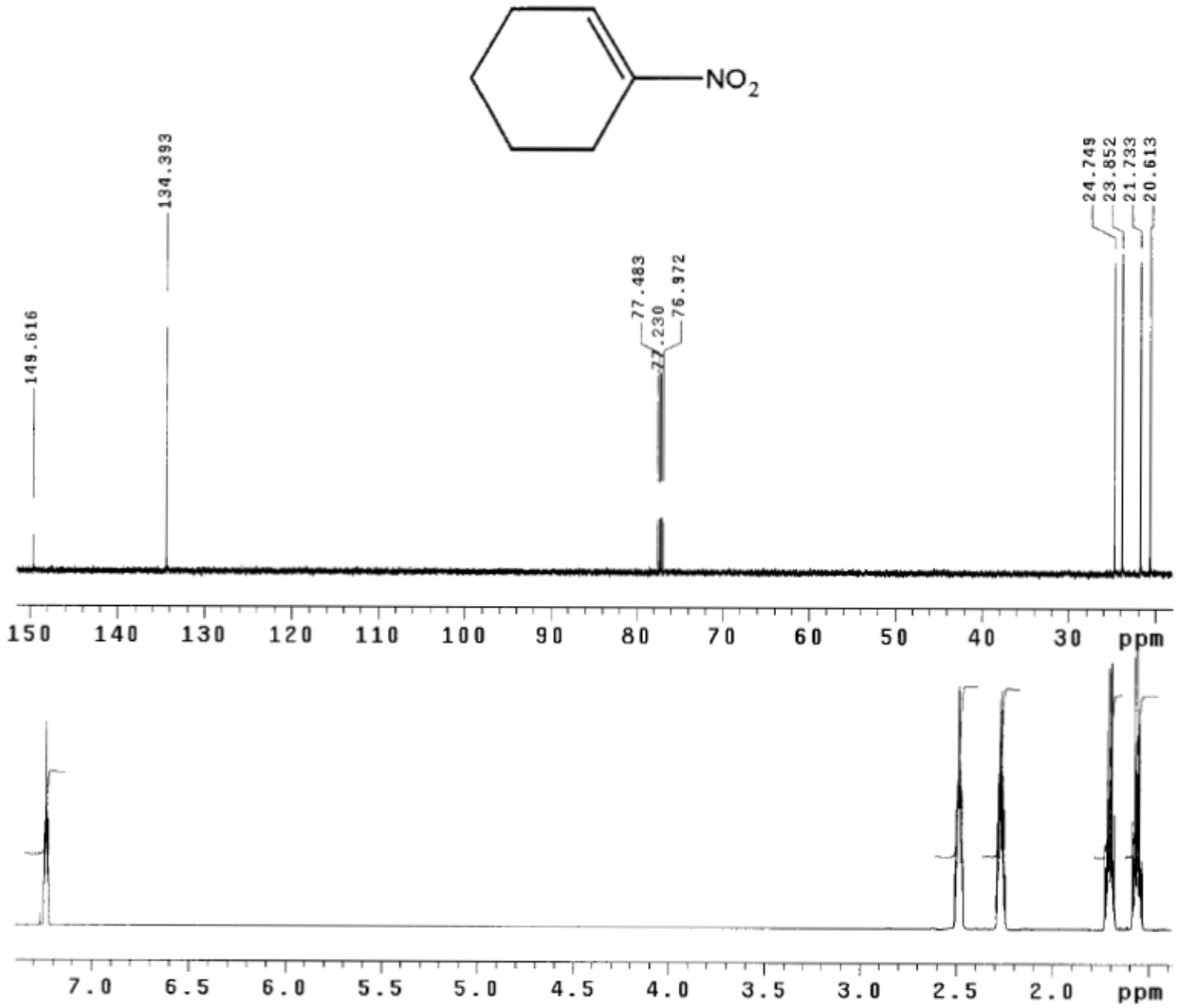


Figure 4.1 400 MHz ^{1}H NMR spectrum of **13** in a mixture of CDC_3 and CD_3OD. **a** Full spectrum; **b** expanded section of the aromatic proton signals; **c** ^{1}H NOE difference spectrum, same section as in **b**, irradiation position at δ=3.64.

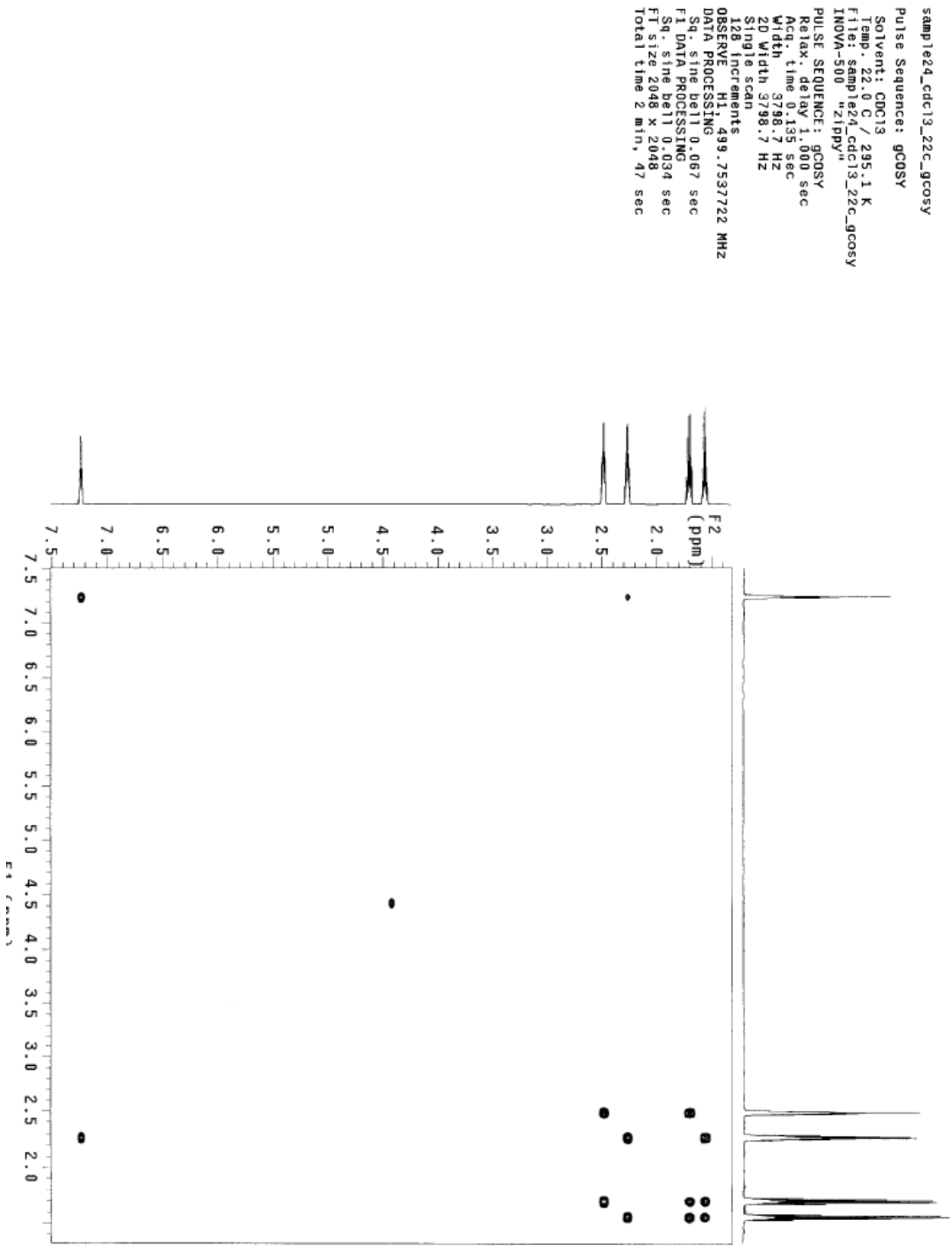
Problem 2

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.

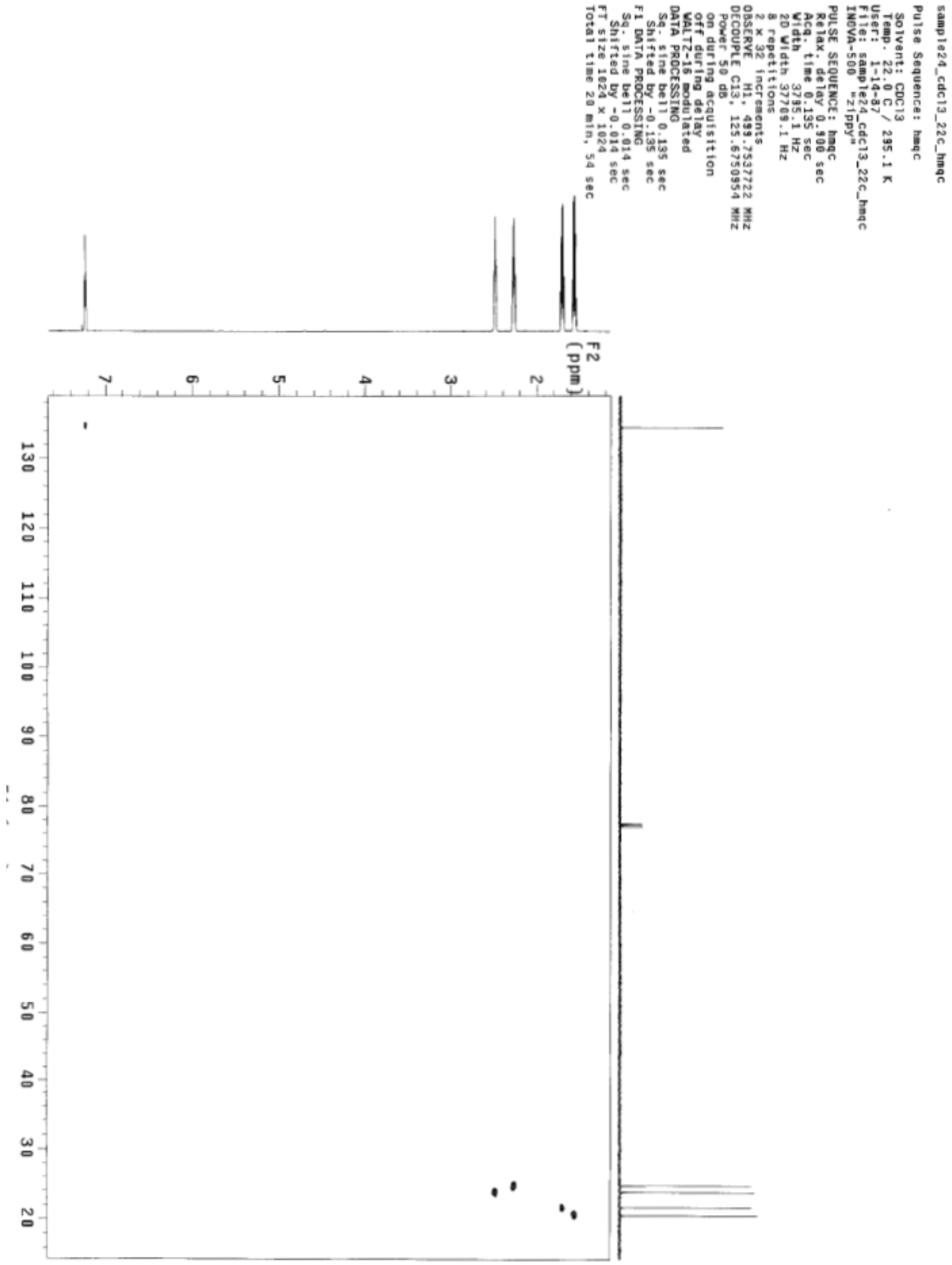
(a) assign the ^1H resonances using the ^1H 1d and the ^1H-^1H gCOSY spectra. Explain your reasoning.
(b) Assign the ^{13}C resonances using your answer from (a) and the ^1H -^{13}C HMQC spectrum. Use the ^{13}C 1D spectrum below to obtain the ^{13}C shifts.
(c) Explain why the ^1H on the sp^2 hybridized carbon is farther downfield compared to where we normally observe a vinyllic proton resonance.



Problem 2 continued



Problem 2 continued

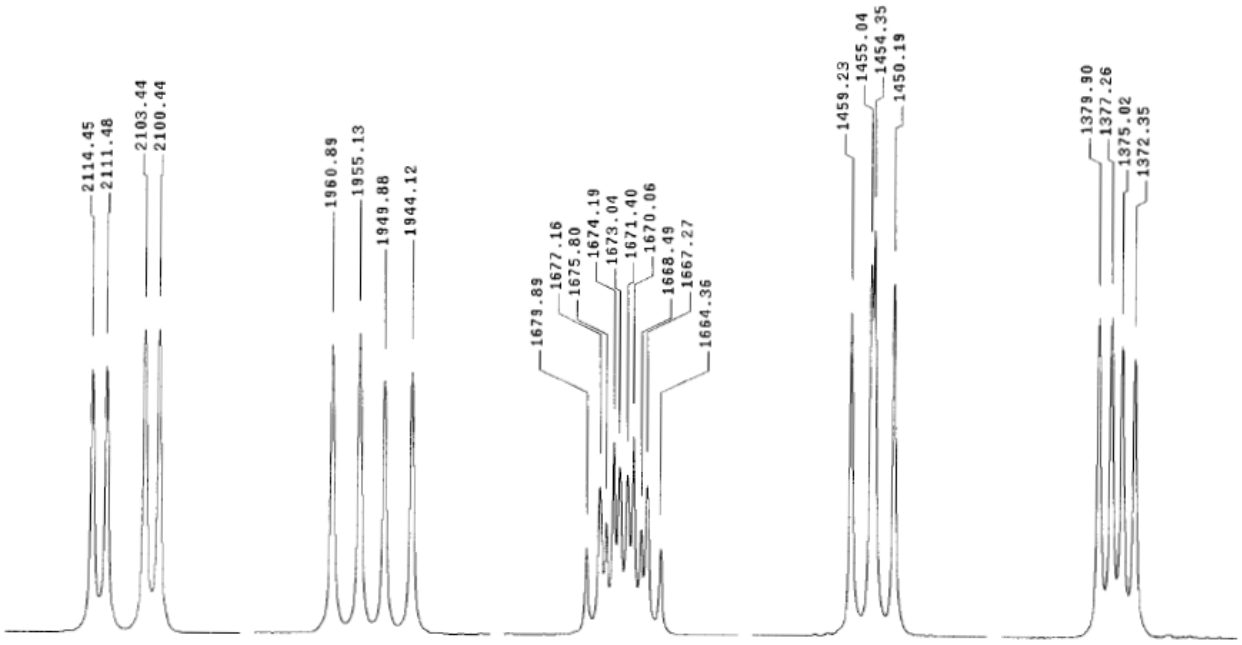


Problem 3

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

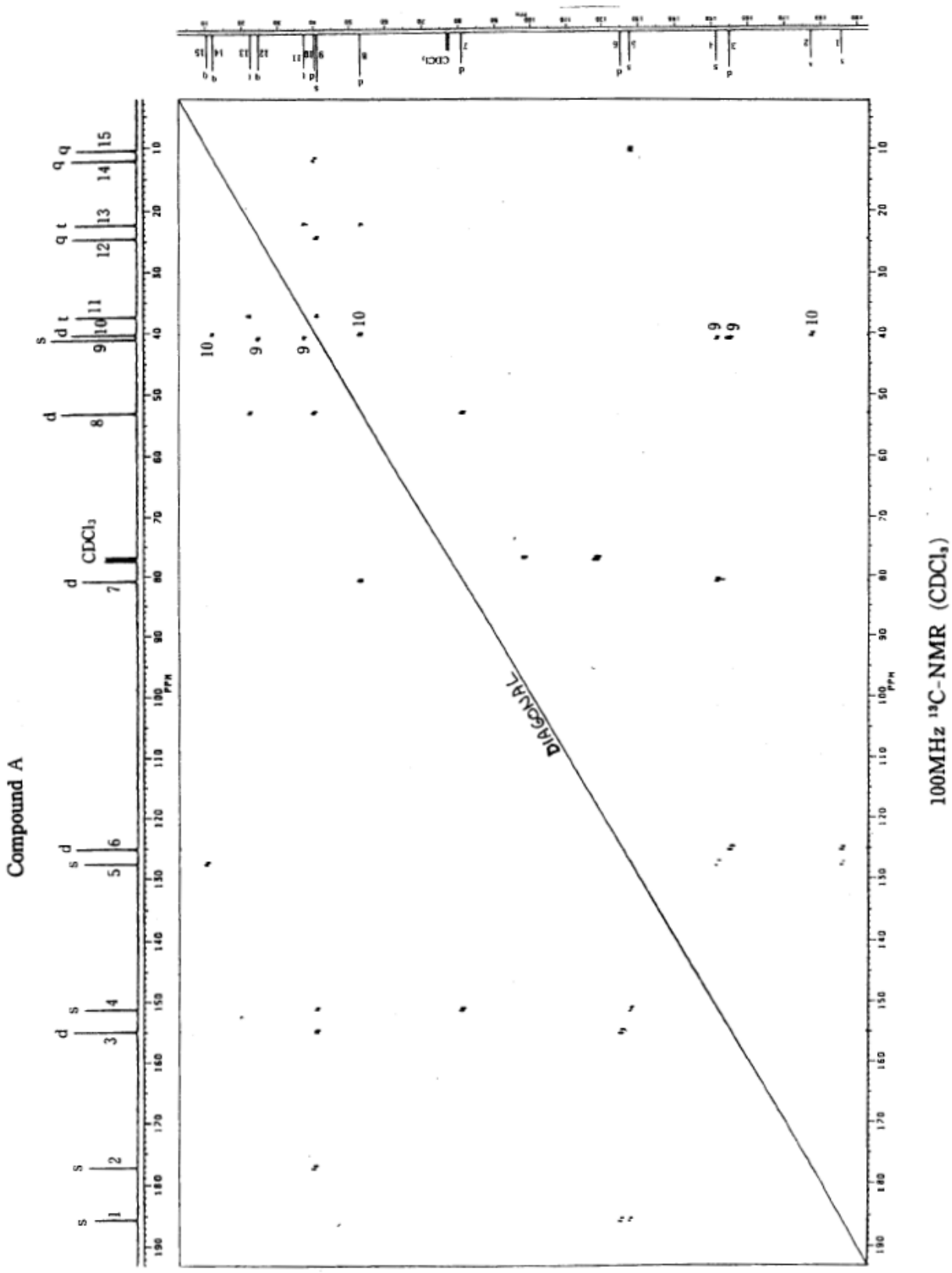
Compound A is readily available from the wormwood plant and was originally sold by Pfizer, Inc. in the 1920s to treat tapeworm parasites. It is known to have one ketone carbonyl group and one ester carbonyl group.

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.


Compound A
100MHz ¹³C-NMR (CDCl₃)
DIAGONAL
CDCl₃
PPM

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 cross peaks between carbons and their directly-attached protons)
- ^{1}H TOCSY w/ 30 ms mixig 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)

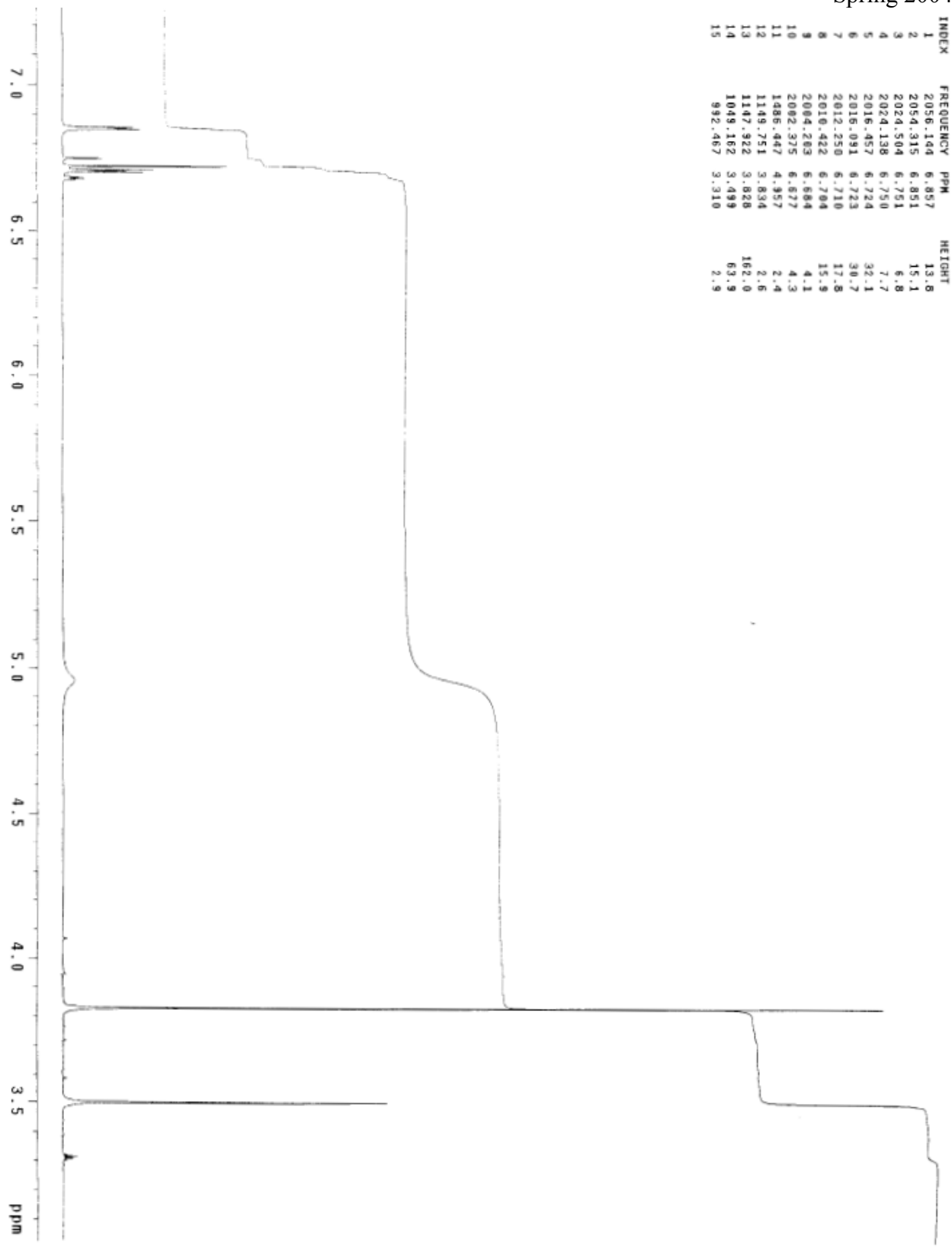
The 2D spectra were obtained at 11.7T (500 MHz ^{1}H frequency) and were collected at 20°C.

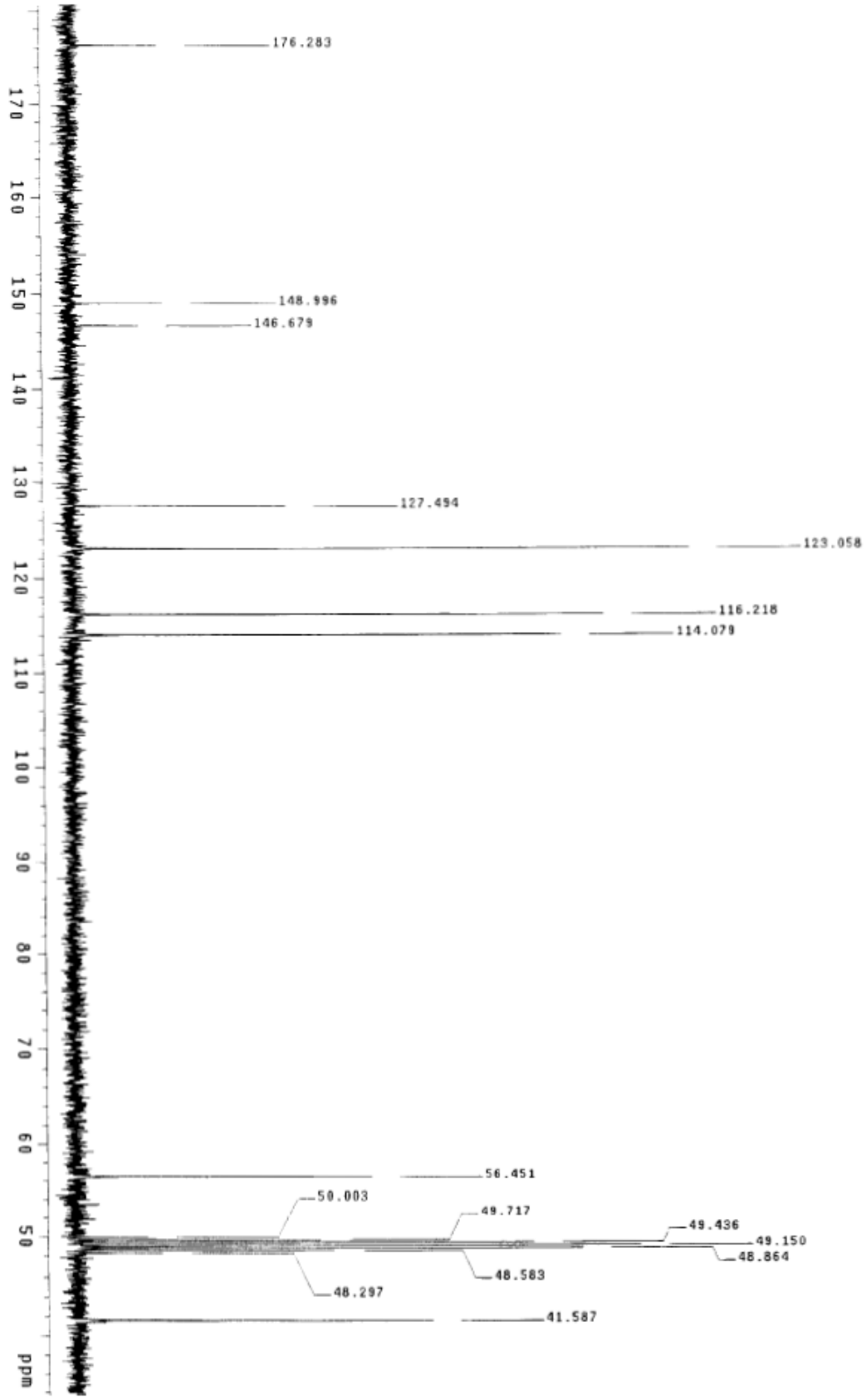
Items to note:

- 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, 15.9999; 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
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm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146.679
127.494
123.058
116.218
114.079
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50.003
49.717
49.436
49.150
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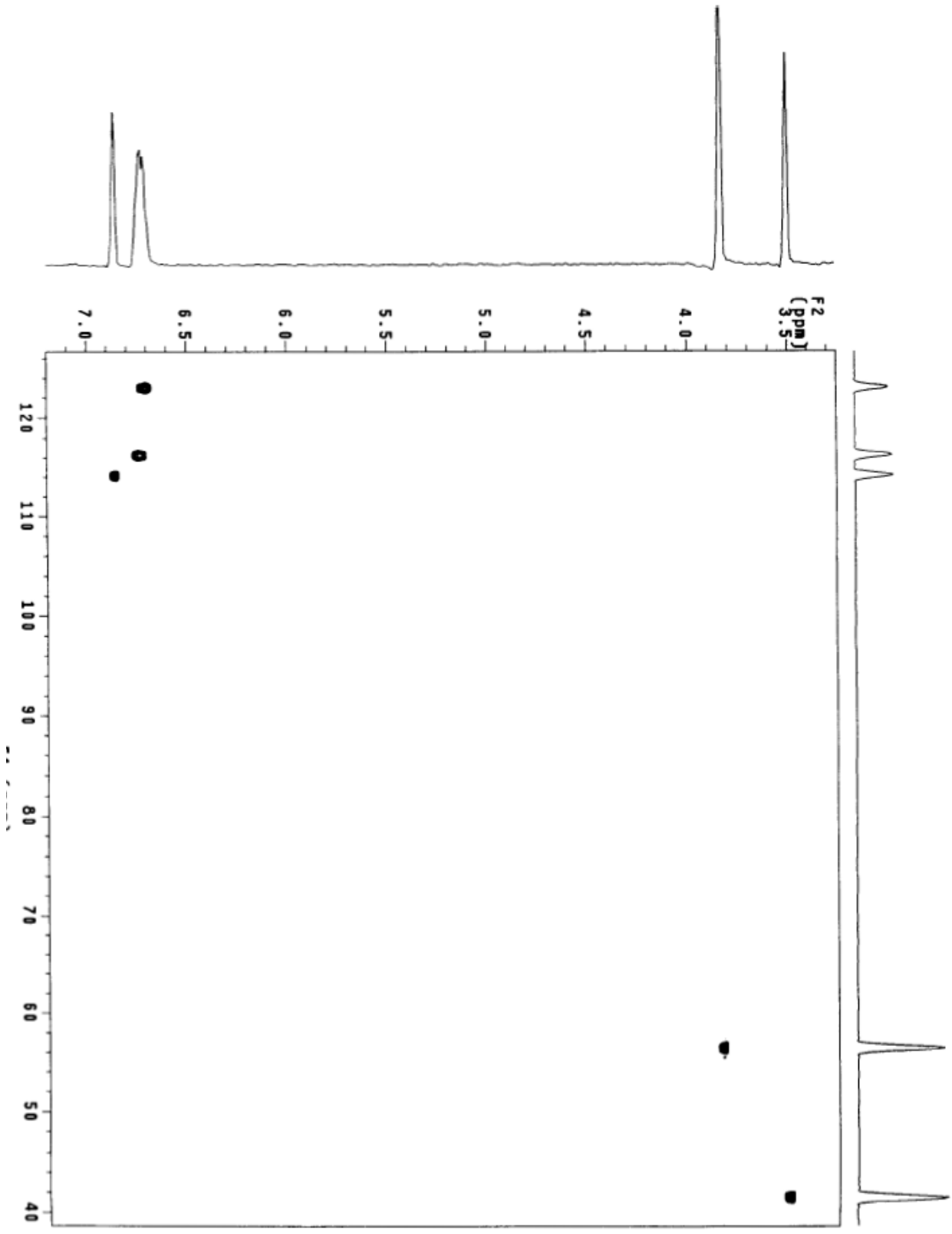
130
120
110
100
90
80
70
60
50
ppm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6.0
5.5
5.0
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4.0
3.5
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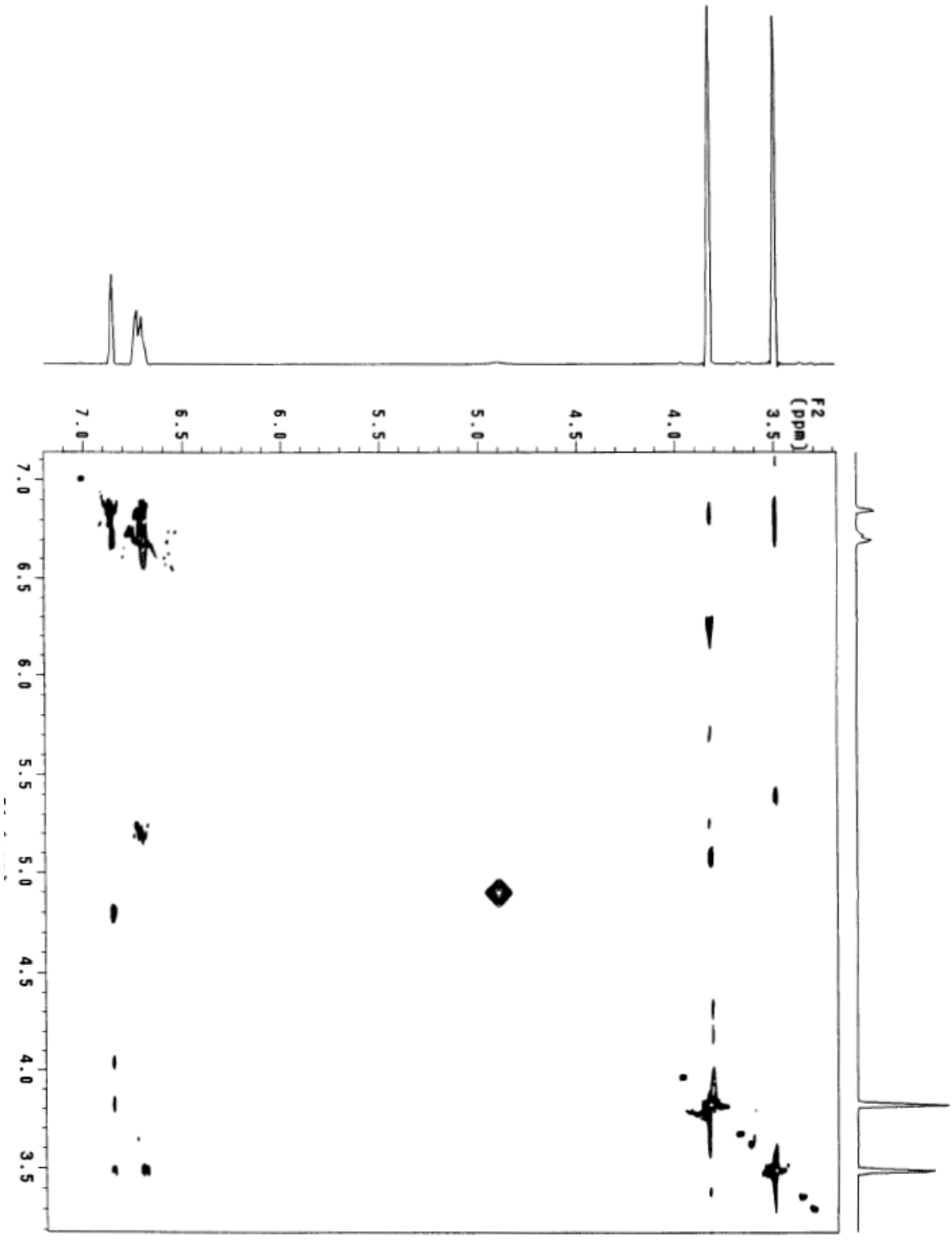
110
100
90
80
70
60
50
40


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

Problem 6

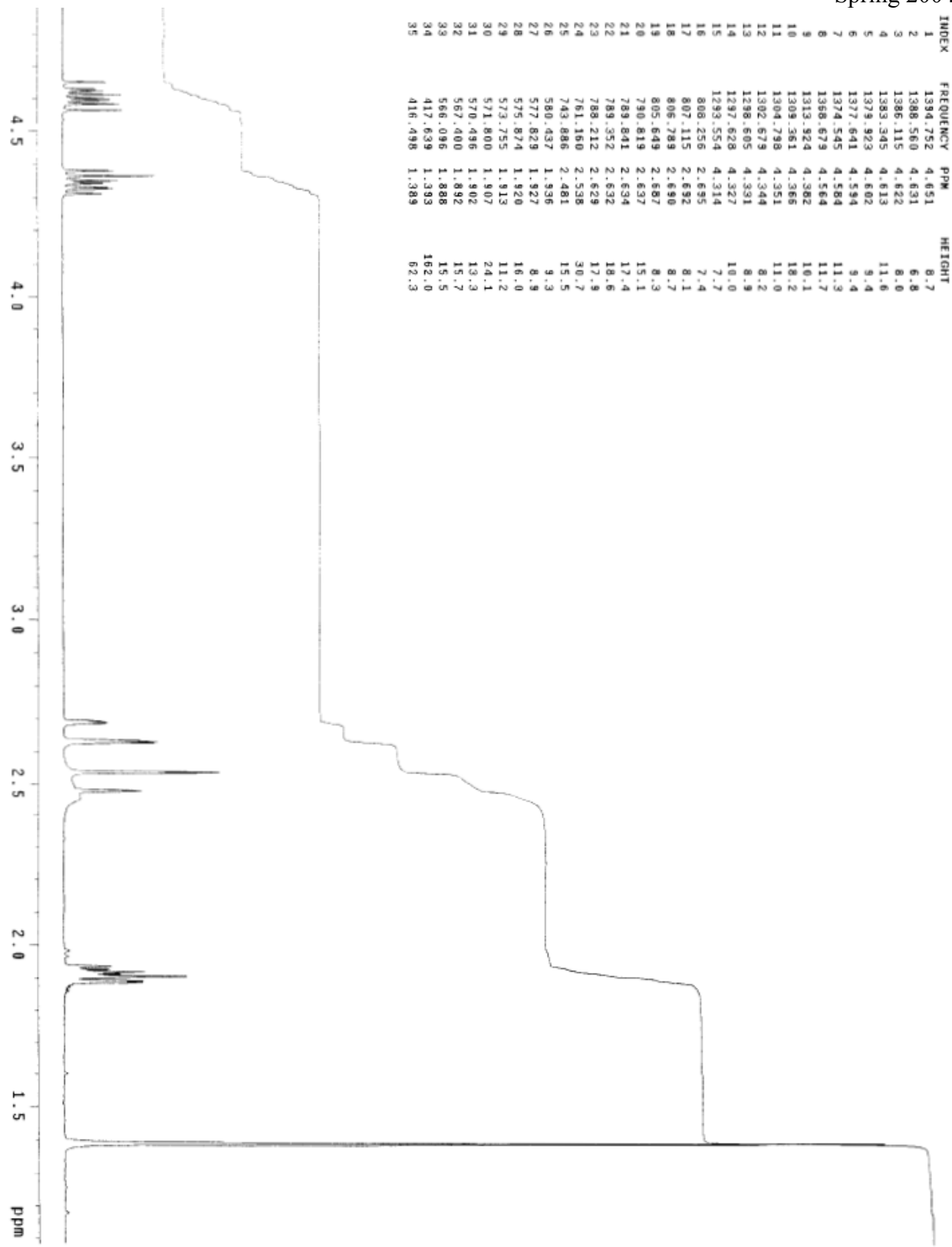
The following spectra were obtained from an organic compound with a molecular weight of 130.1. The sample was dissolved in $CDCl_3$ (proton: 7.27p, carbon 77.23p). Deduce its structure and explain your logic.

In order, the spectra given are:

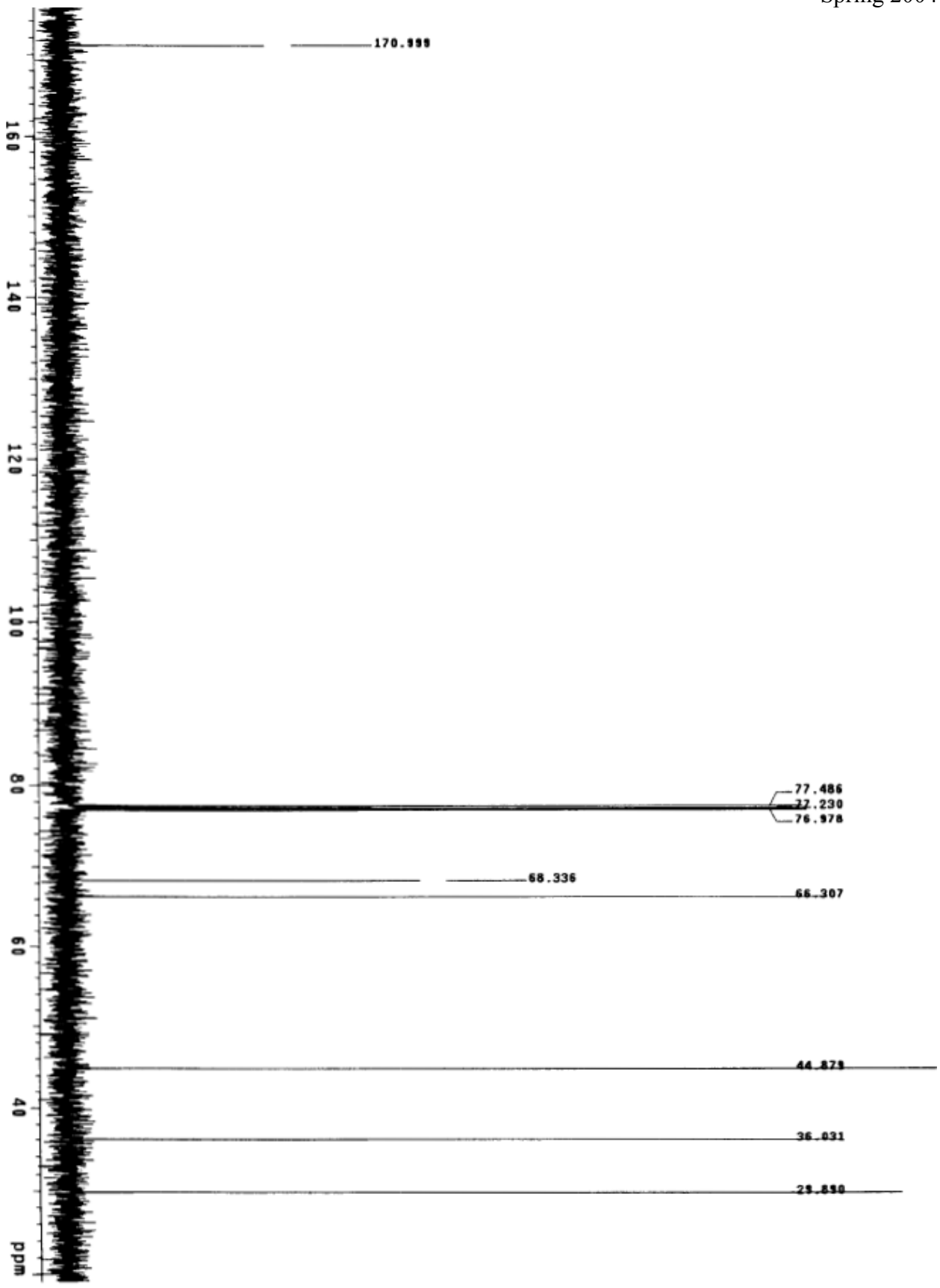
- ^{1}H 1D
- ^{13}C 1D
- ^{1}H-^{13}C HMQC
- ^{1}H TOCSY w/ 30 ms mixing time

Note:

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



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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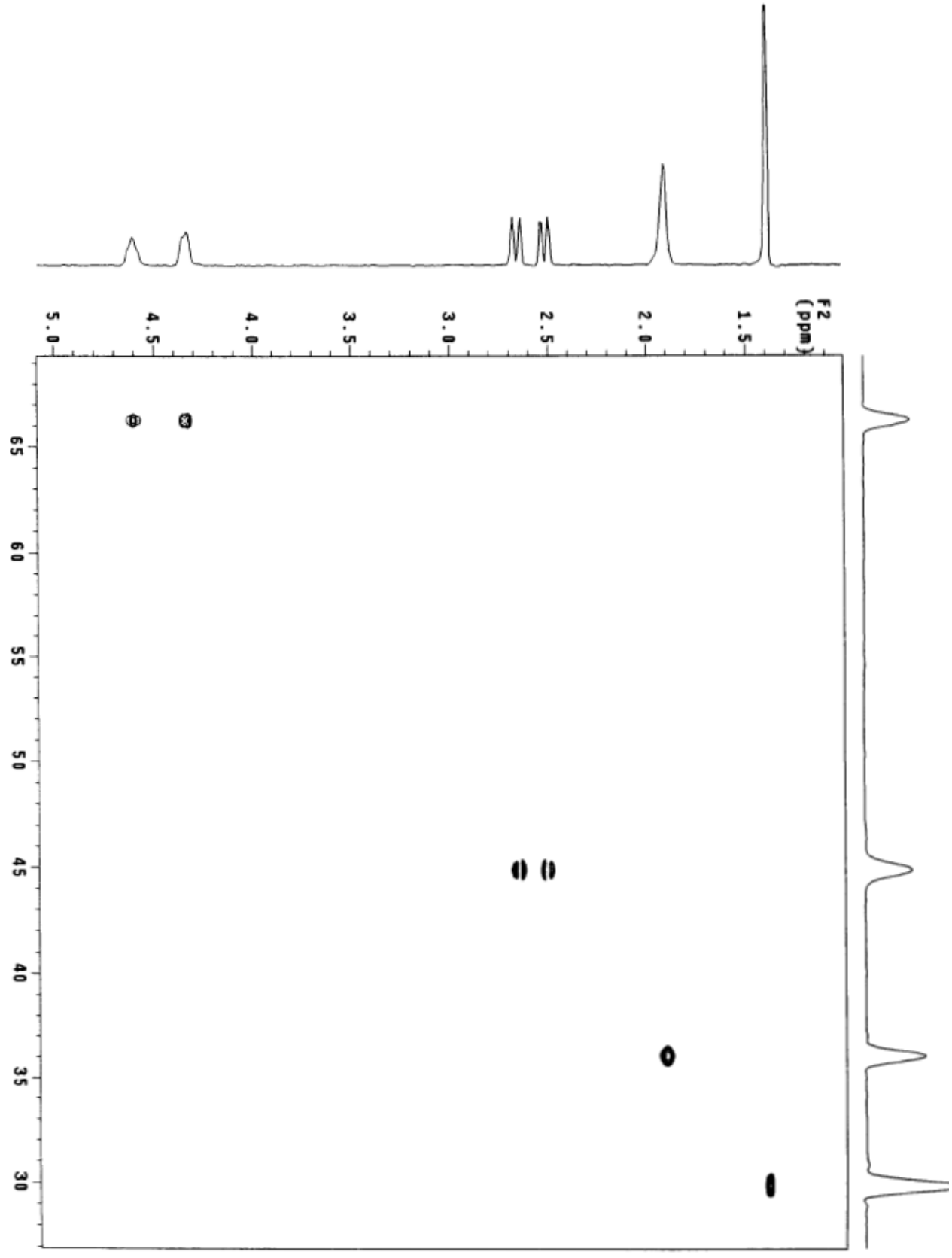
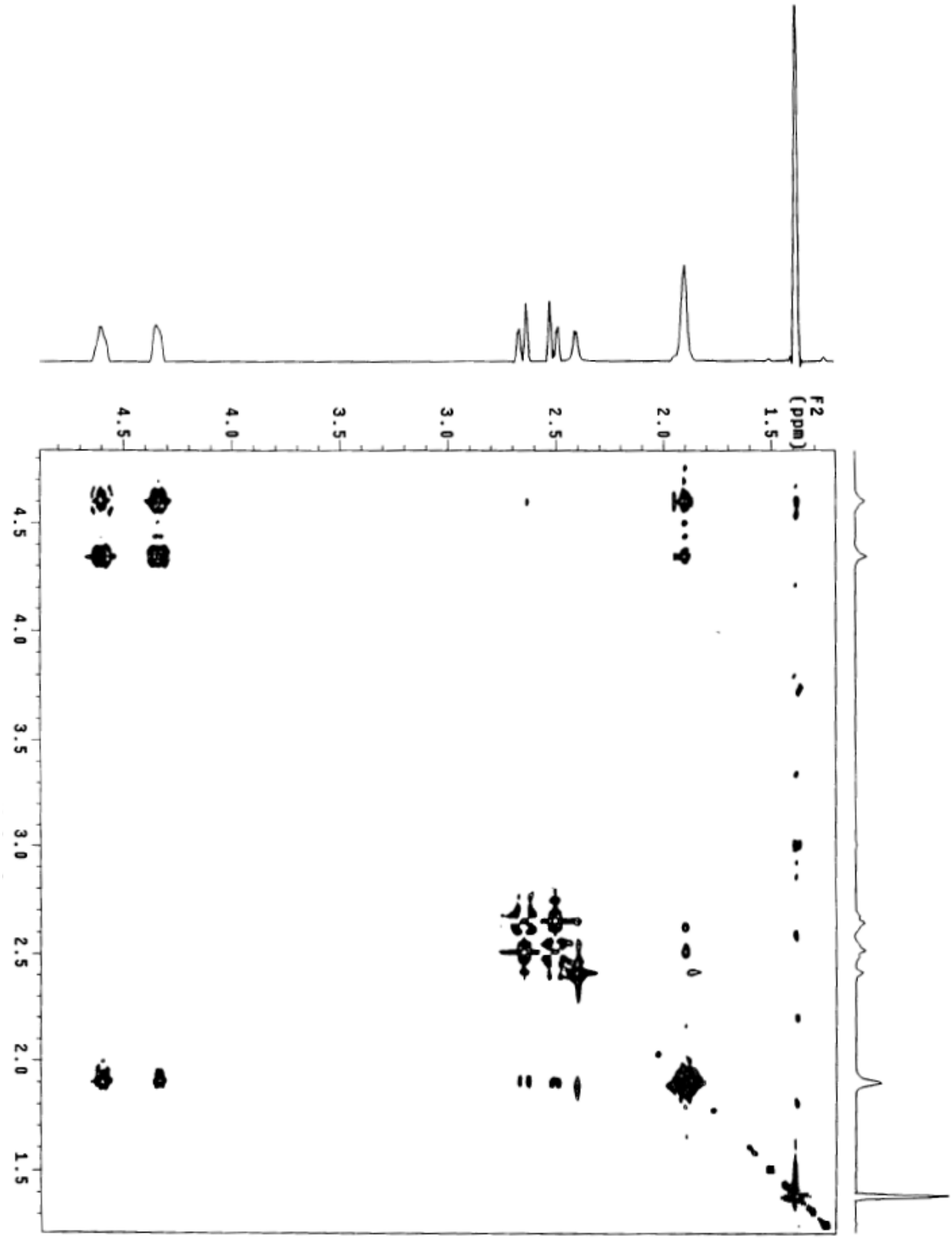
60
40
ppm


F2 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
65
60
55
50
45
40
35
30


F2 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5

Problem 7

$C_{10}H_7Cl$