Chemistry 5361/8361 Friday, December 20, 2002

Final Exam

Please do not open or sign this packet until you are instructed to do so.

Please write all of your answers for this exam this exam packet. Although you may use as many blue books for scratch work as you would like, the blue books will not be collected at the end of the exam or graded. Answer each question in the space provided if you can, but feel free to continue your answer on the back of the page if you need more room. (Please write a note by your answer pointing us to the continuation if you do this.) Feel free to remove the corner staple if this helps you analyze the spectra; you will have the opportunity to re-staple your exam at the end. The exam in this packet is designed to take 1 hour to complete. You will be given 2 hours total to finish the test.

This exam contains one problem, which is split into parts. Many of these parts can be answered independently. *Do not get stuck* on one part and then assume that you will be unable to answer the rest of the question—move on. In addition, partial credit will be given for incorrect but still plausible answers, so *guess* on problems you cannot answer perfectly.

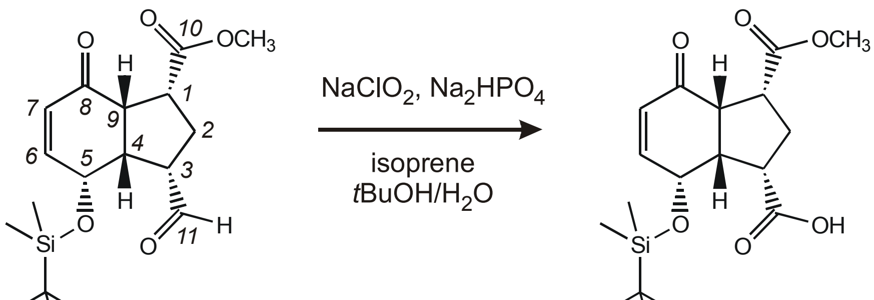
At the end of the 2 hour exam period you will be asked to return your exam to the proctor. (You may, of course, also turn the packet in earlier if you choose.) You are allowed to use any materials you brought with you before the exam. However, we ask that you not bring any materials in or out of the room while you are taking the exam. Please do not take any part of the exam packet with you when you are done; everything will be returned to you after the exams are graded.

This packet should contain 21 pages, including this one. (The last page contains a chart of isotope ratios and exact atomic masses, and is not part of the graded exam.) Please check to make sure that your packet contains 21 pages before beginning your exam.

Name: ______________________________________

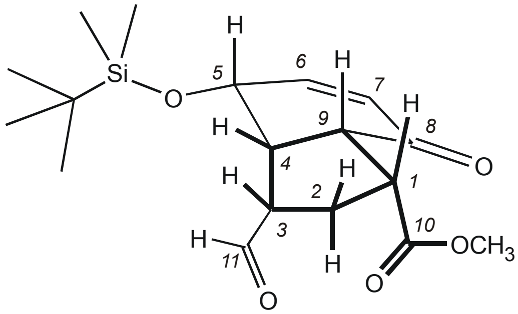
Signature: ______________________________________

Andy Judd (Hoye Group) subjected the aldehyde **1** to a hypochlorite oxidation reaction that he expected would give the carboxylic acid **2**. MS, IR and NMR data suggested, however, that this product was not generated. Instead, Andy postulated that his reaction had yielded a different product **3** that had the same bicyclic carbon skeleton as **1** and **2**. As part of this problem, you will follow Andy's footsteps and suggest a structure for **3**.



1 **2**

(not observed)



1

A three dimensional representation of **1** is shown above; **2** differs only at carbon 11.

Page	Description
9	IR (KBr pellet)
10	CI-MS, NH_3 reagent, direct insertion probe
11	^{1}H NMR, 500 MHz, $CDCl_3$.
12-15	Close-ups of page 9, w/ integrations and peak labels.
16	^{1}H-^{1}H COSY NMR, 500 MHz, $CDCl_3$.
17	^{13}C NMR, 125 MHz, $CDCl_3$.
18	^{1}H-^{13}C HMQC NMR, 500 MHz, $CDCl_3$.
19-20	^{1}H NOE (1-D), 500 MHz, $CDCl_3$.

NMR Hint: The multiplet at $\delta = 4.83$ ppm looks like a triplet, with two coupling partners. One of these couplings is a typical, $^3J_{HH}$ coupling, but the other is an unusually large $^4J_{HH}$ coupling.

a. (15 pts) The IR spectrum alone would have been enough to tell Andy that something unexpected had occurred with his reaction. What about the IR spectrum is inconsistent with the structure for **2**? Give as many good reasons as you can.

b. (10 pts) The CI-MS suggested a product with a higher molecular weight than **2**. (Expected MW(**2**) = 368.) Below is a copy of the output of the Elemental Composition Calculator (http://medlib.med.utah.edu/masspec/elcomp.htm) for all masses within 0.003 amu of *m/z* = 437.0983, the exact value for one of the peaks in the CI-MS:

Elemental Composition Calculator v1.0

Calculations for : 437.0983 +/- 0.003 amu
monoisotopic mass

C	12.0000	15	20
H	1.0078	20	40
N	14.0030	0	2
O	15.9949	0	10
P	30.9737	0	1
Cl(35)	34.9688	0	2
Si	27.9769	0	1
Na	22.9897	0	1

C	H	N	O	P	Cl	Si	Na	mass	diff	ppm
20	22	0	9	1	0	0	0	437.1001	-0.0018	-4.2
16	22	2	10	0	1	0	0	437.0962	0.0020	4.5
17	25	1	8	1	1	0	0	437.1006	-0.0023	-5.3
18	25	1	7	0	2	0	0	437.1008	-0.0025	-5.7
15	27	0	10	0	2	0	0	437.0981	0.0001	0.4
20	25	1	4	1	1	1	0	437.0978	0.0004	0.9
18	27	0	6	0	2	1	0	437.0953	0.0029	6.6
17	28	2	3	1	2	1	0	437.0983	-0.0000	-0.1
18	23	0	9	1	0	0	1	437.0977	0.0005	1.2
19	23	0	8	0	1	0	1	437.0979	0.0003	0.8
18	24	2	5	1	1	0	1	437.1009	-0.0026	-5.9
15	26	1	8	1	1	0	1	437.0982	0.0000	0.1
19	24	2	4	0	2	0	1	437.1010	-0.0027	-6.3
16	26	1	7	0	2	0	1	437.0983	-0.0000	-0.2
16	22	2	9	0	0	1	1	437.0992	-0.0009	-2.1
15	27	0	9	0	1	1	1	437.1010	-0.0027	-6.2
18	26	1	4	1	1	1	1	437.0954	0.0028	6.4
19	26	1	3	0	2	1	1	437.0956	0.0026	6.0
20	29	0	1	1	2	1	1	437.1000	-0.0017	-3.8
15	29	2	3	1	2	1	1	437.0959	0.0023	5.3

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(All of the atoms present in the reaction mixture were included as possible components of the *m/z* = 437 ion in this calculation. This does not mean they all are present in the structure of this ion.)

Based on what you know about the starting material, which is the most likely chemical formula for the *m/z* = 437 ion?

c. (10 pts) What are the molecular formulae for the ions at *m*/*z* = 439, 454 and 456?

d. (10 pts) Based on your answers to the questions above, suggest a molecular formula for **3**.

e. (10 pts) What is the structure of **3**? Draw both a two-dimensional and a three-dimensional representation of your structure. *You will probably want to work on section (f) before answering this question definitively. Feel free to skip this question and come back to it.*

2-D representation

3-D representation

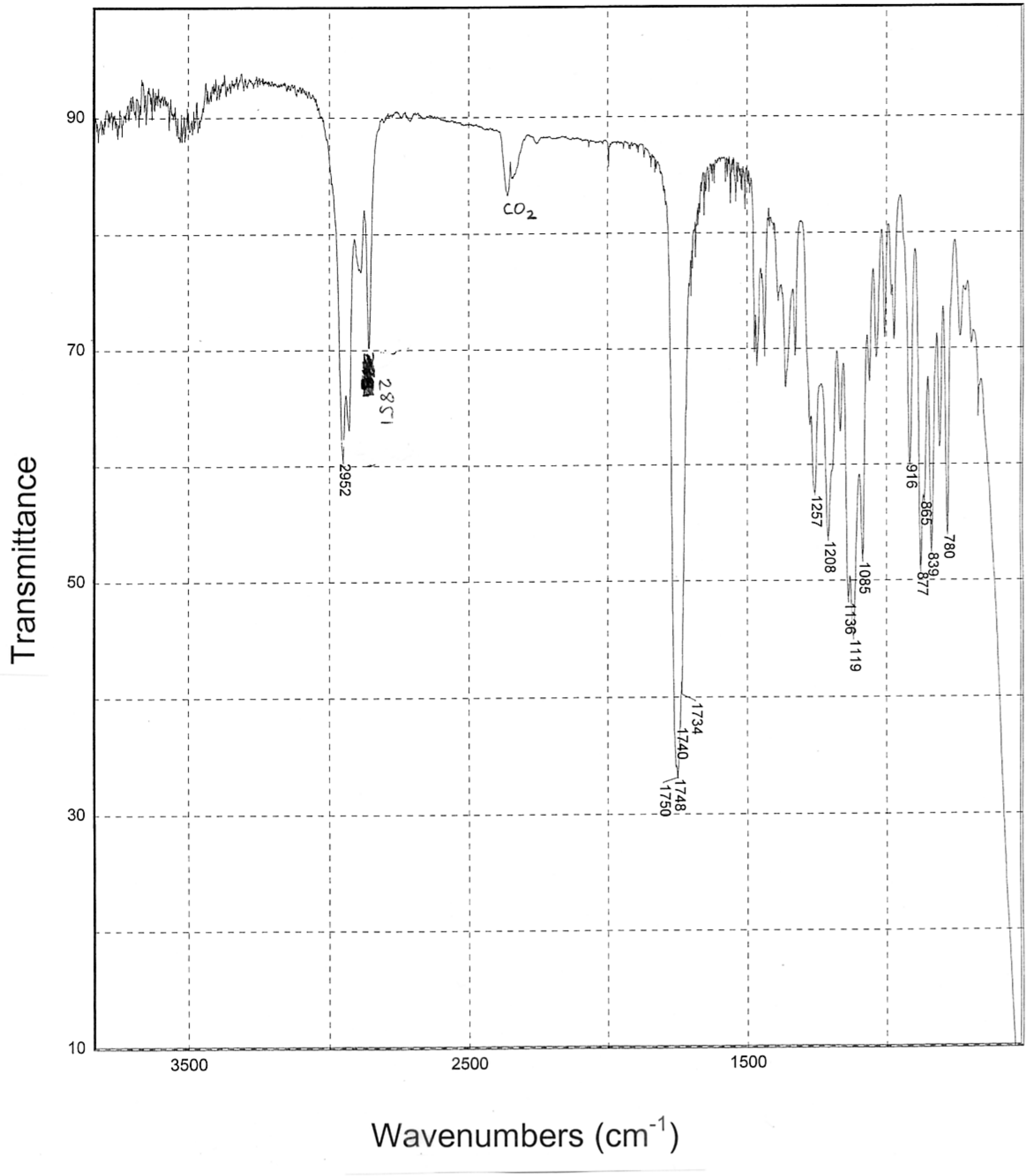
f. (25 pts) Fill out the chart below with ^{1}H chemical shifts (within 0.05 ppm) for protons attached to the carbon skeleton of **3**. If a carbon has multiple protons attached to it, then write multiple ^{1}H chemical shifts in the box. If a carbon has no protons attached to it, leave the box blank. *We will grade this section with respect to your answer to (e); incorrect answers that are consistent with your structure will receive partial credit.*

carbon #	^{1}H δ (ppm)
1	
2	
3	
4	
5	
6	
7	
8	
9	

g. (10 pts) The hint on page 3 indicated that one pair of protons shows a large $^4J_{HH}$ coupling. Re-draw your 3-D representation of **3**, and show this coupling on your structure. In ten words or less, why is $^4J_{HH}$ particularly large for this coupling?

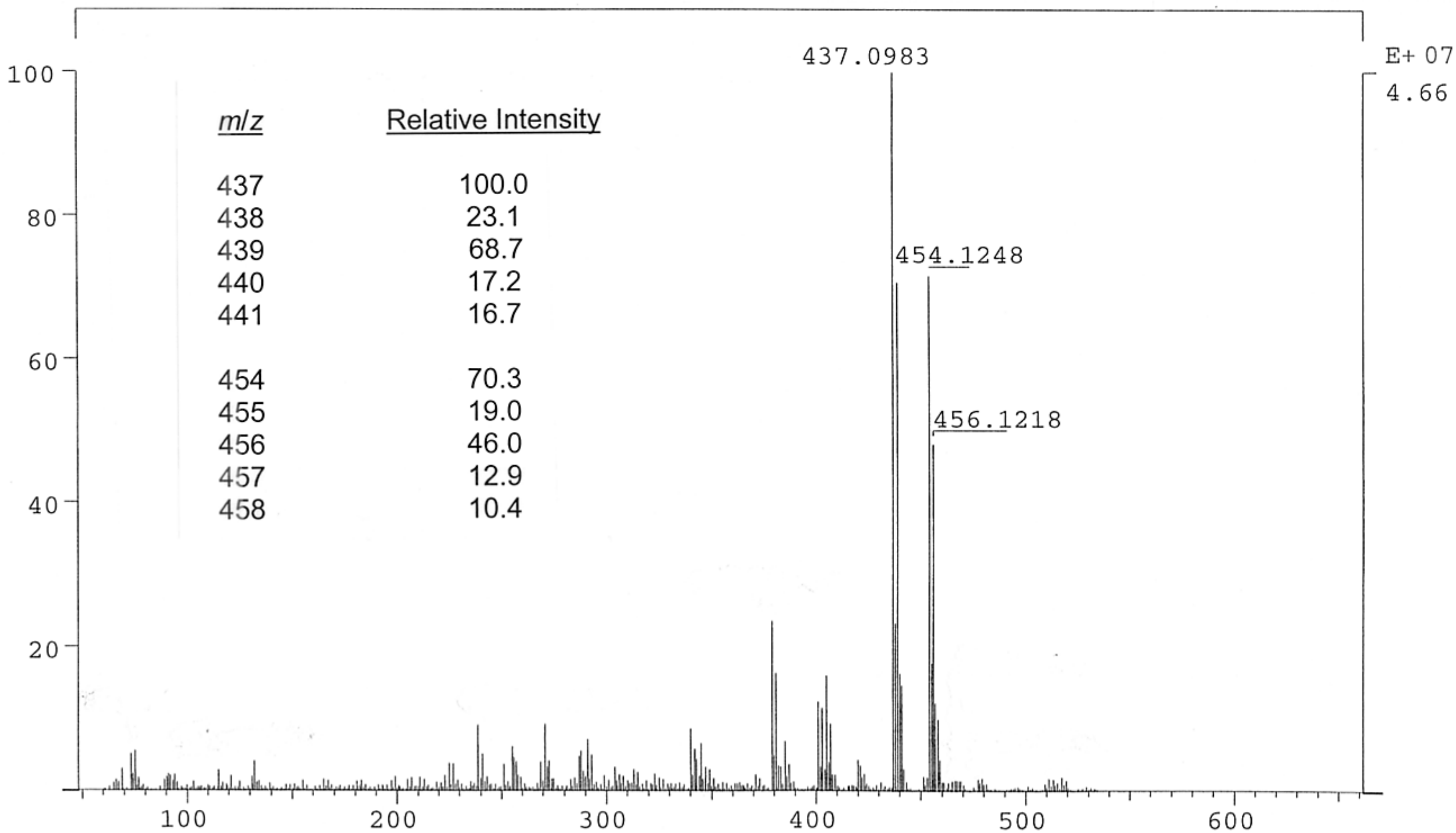
h. (10 pts) To verify some of the stereochemical relationships in **3**, Andy did some NOE experiments. The results of two of these are shown on pages 17 and 18. In the boxes below, redraw your 3-D representations of **3** and draw arrows that show the NOE transfers that occurred.

page 18 NOE	**page 19 NOE**



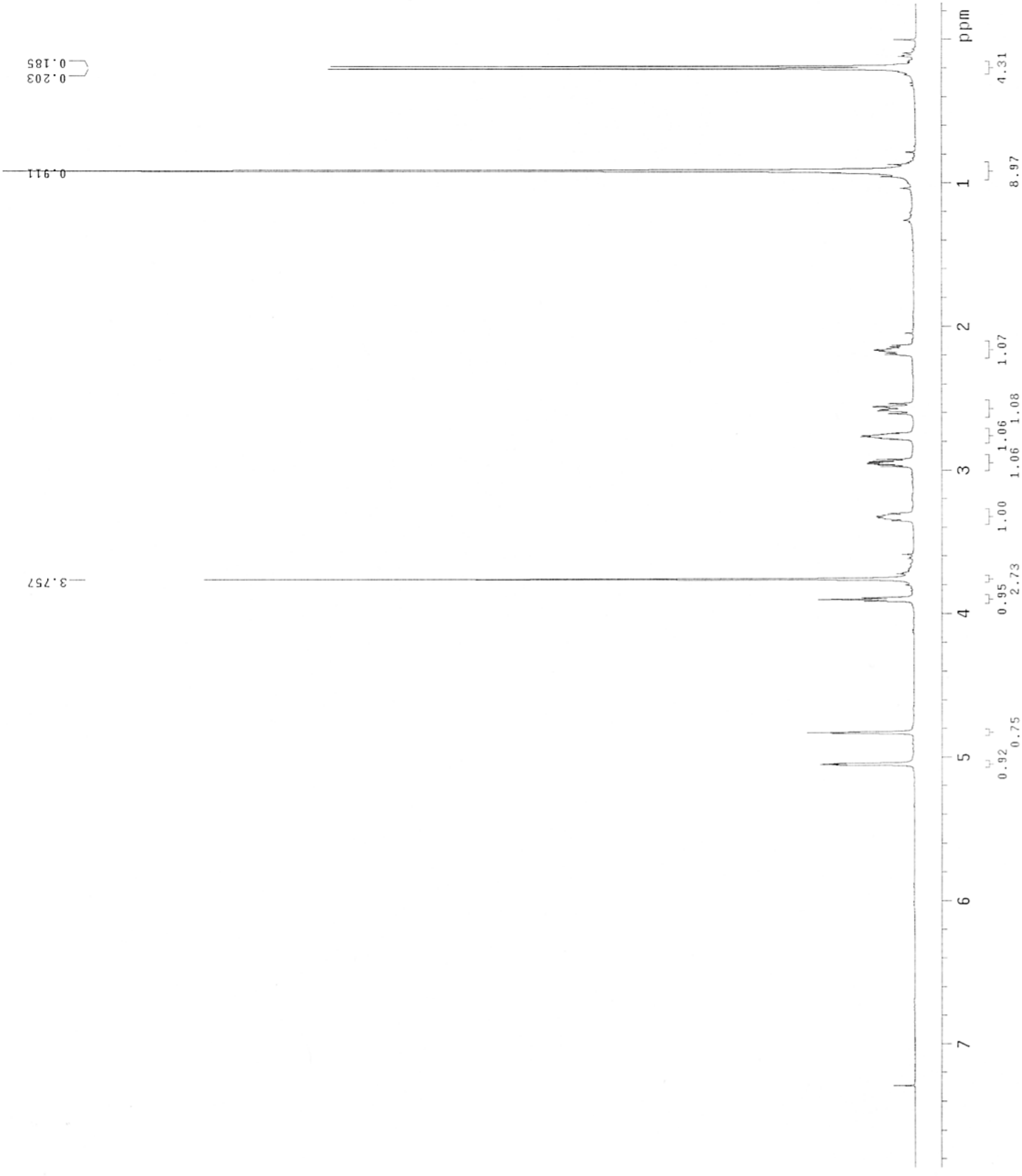
IR (KBr pellet)

CI-MS (positive-ion mode), NH_3 reagent
DIP (direct insertion probe)

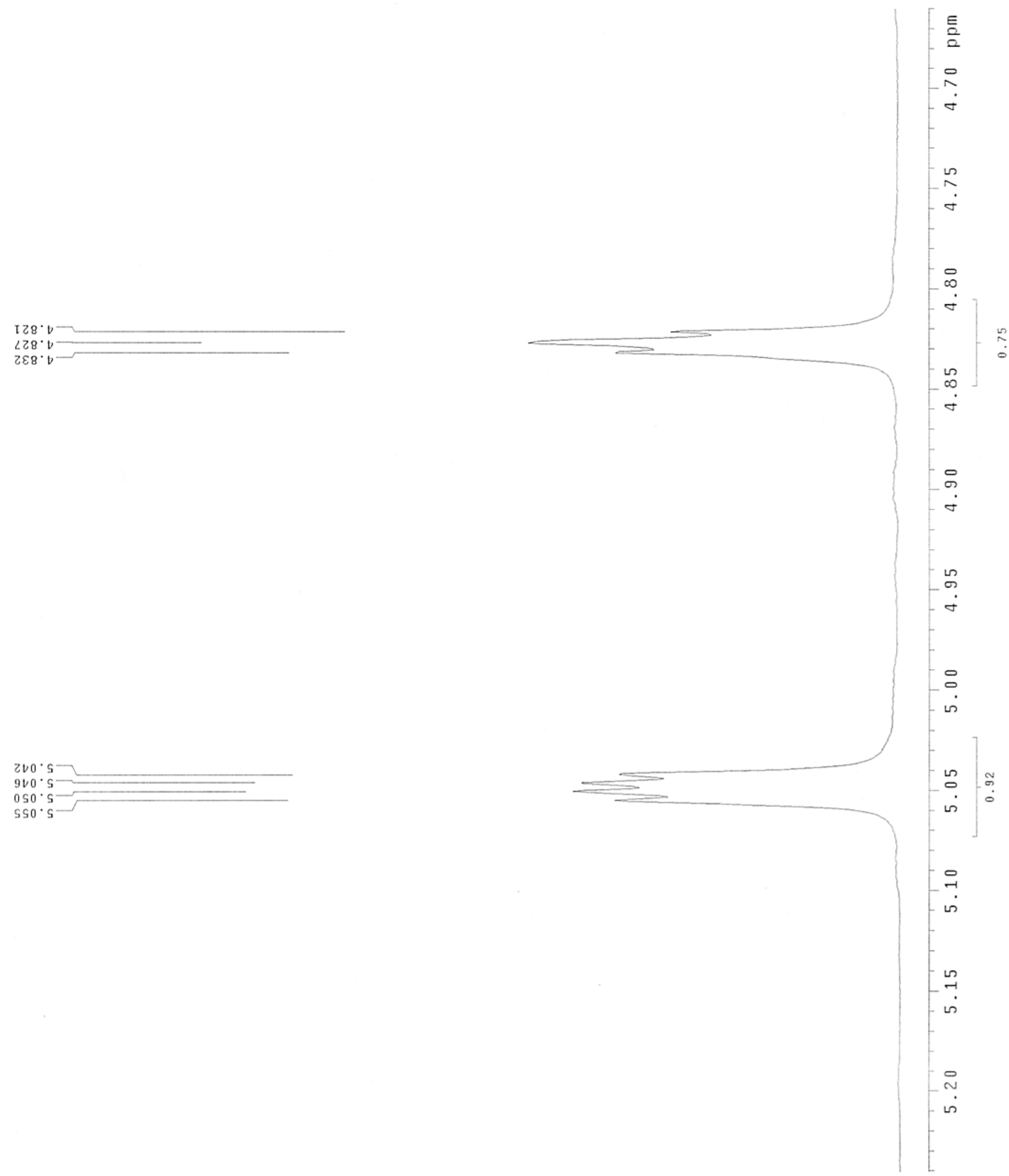


m/z	Relative Intensity
437	100.0
438	23.1
439	68.7
440	17.2
441	16.7
454	70.3
455	19.0
456	46.0
457	12.9
458	10.4

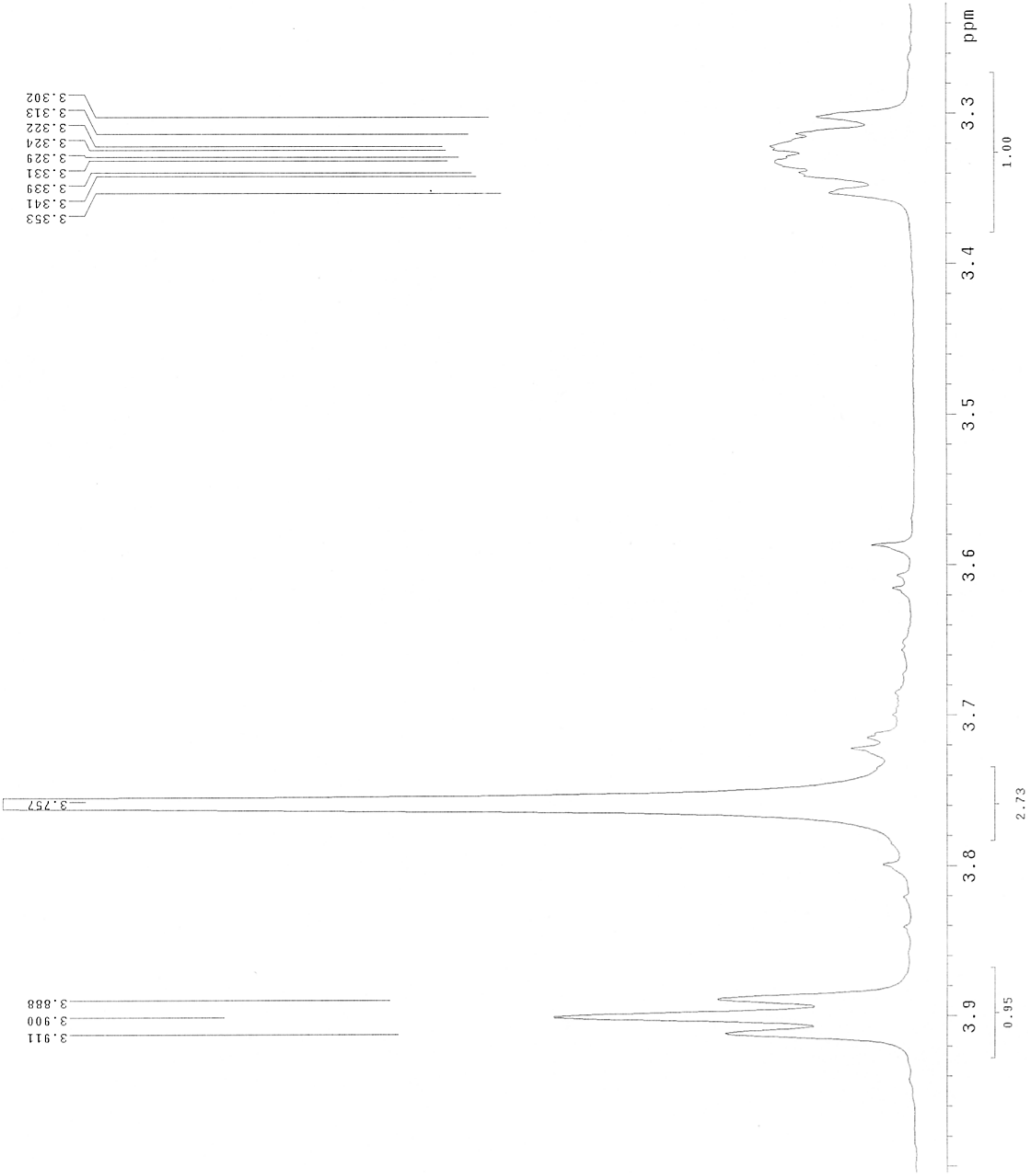
^{1}H NMR, 500 MHz, $CDCl_3$



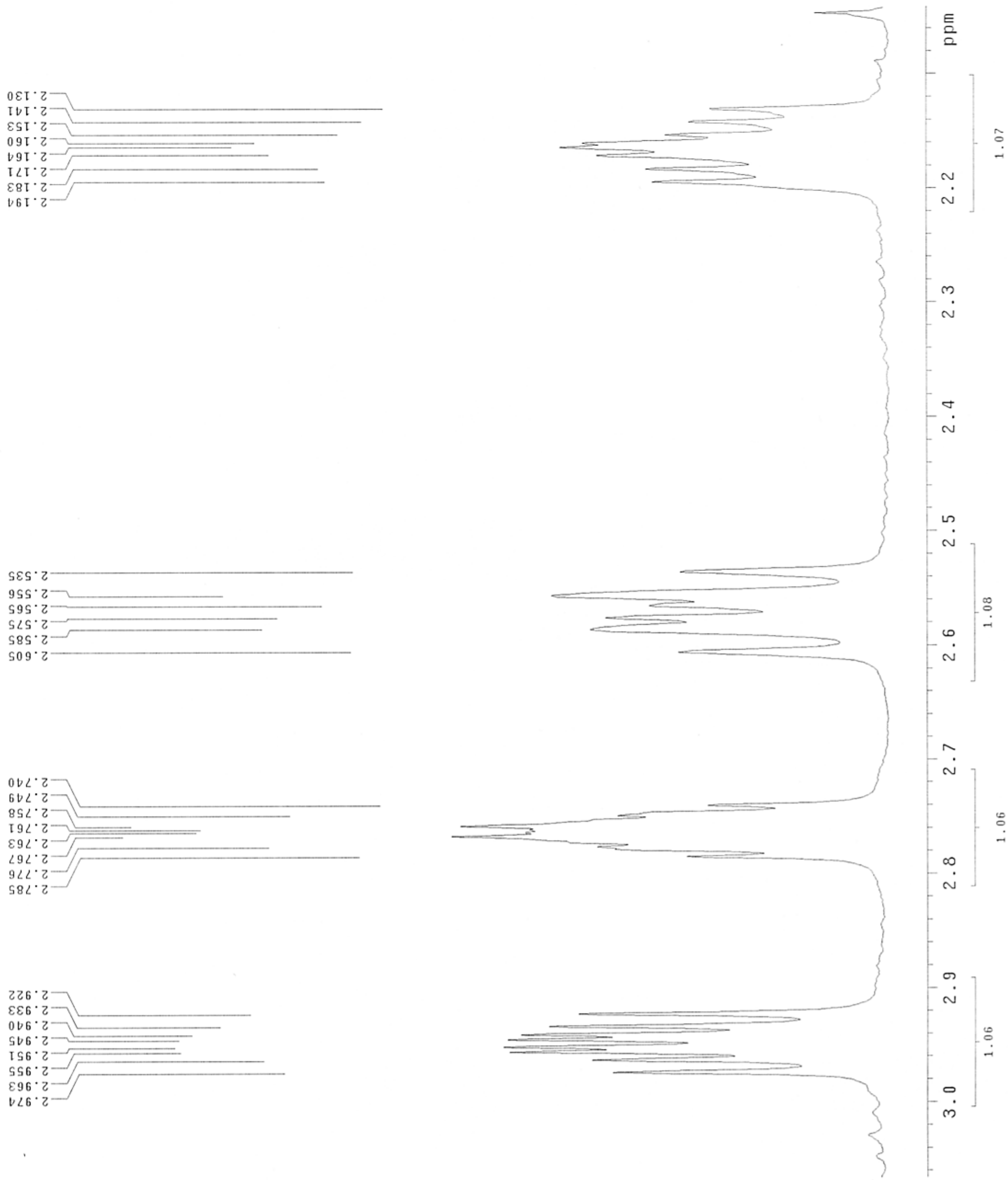
^{1}H NMR, 500 MHz, $CDCl_3$



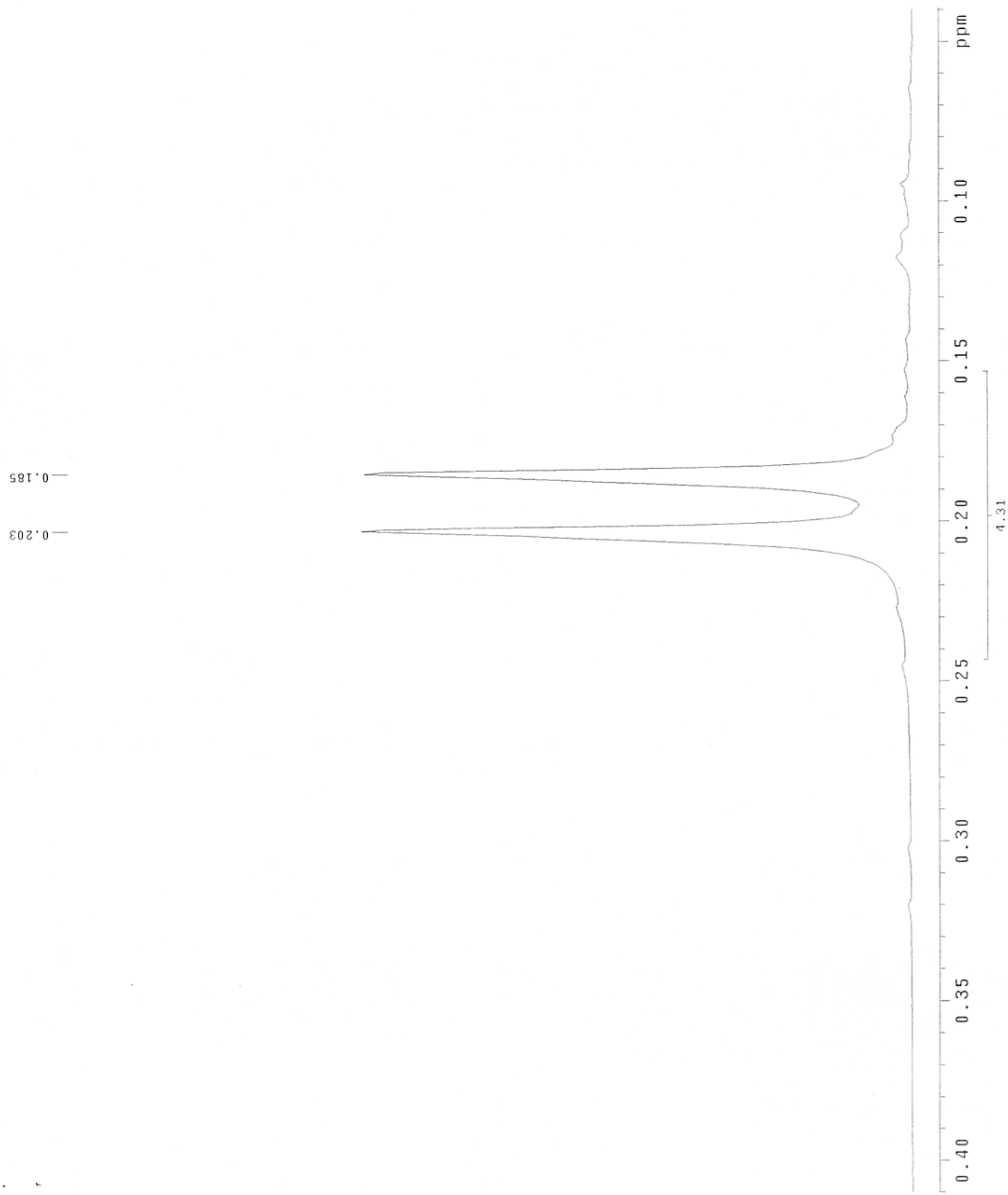
^1H NMR, 500 MHz, $CDCl_3$

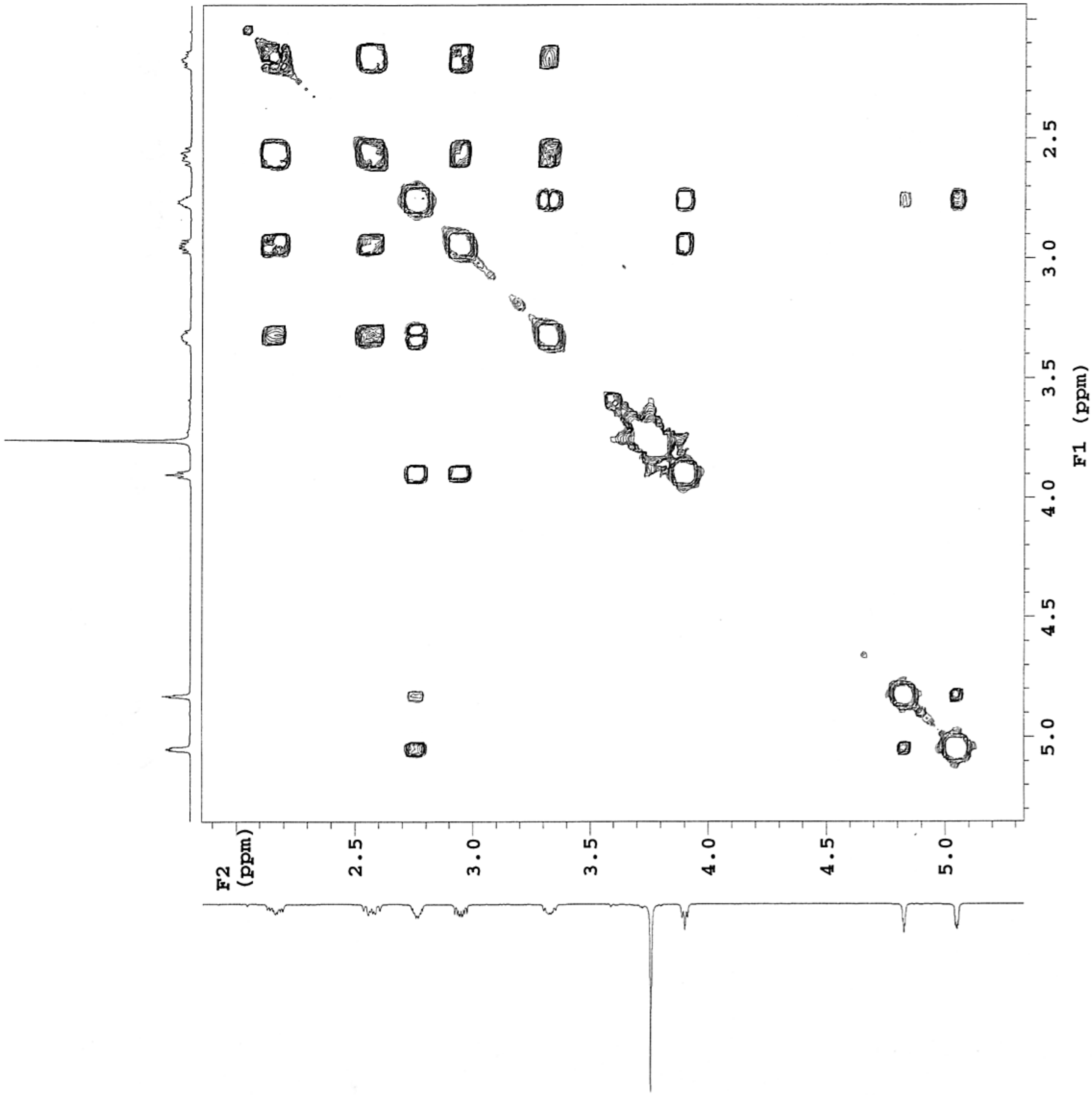


^1H NMR, 500 MHz, $CDCl_3$

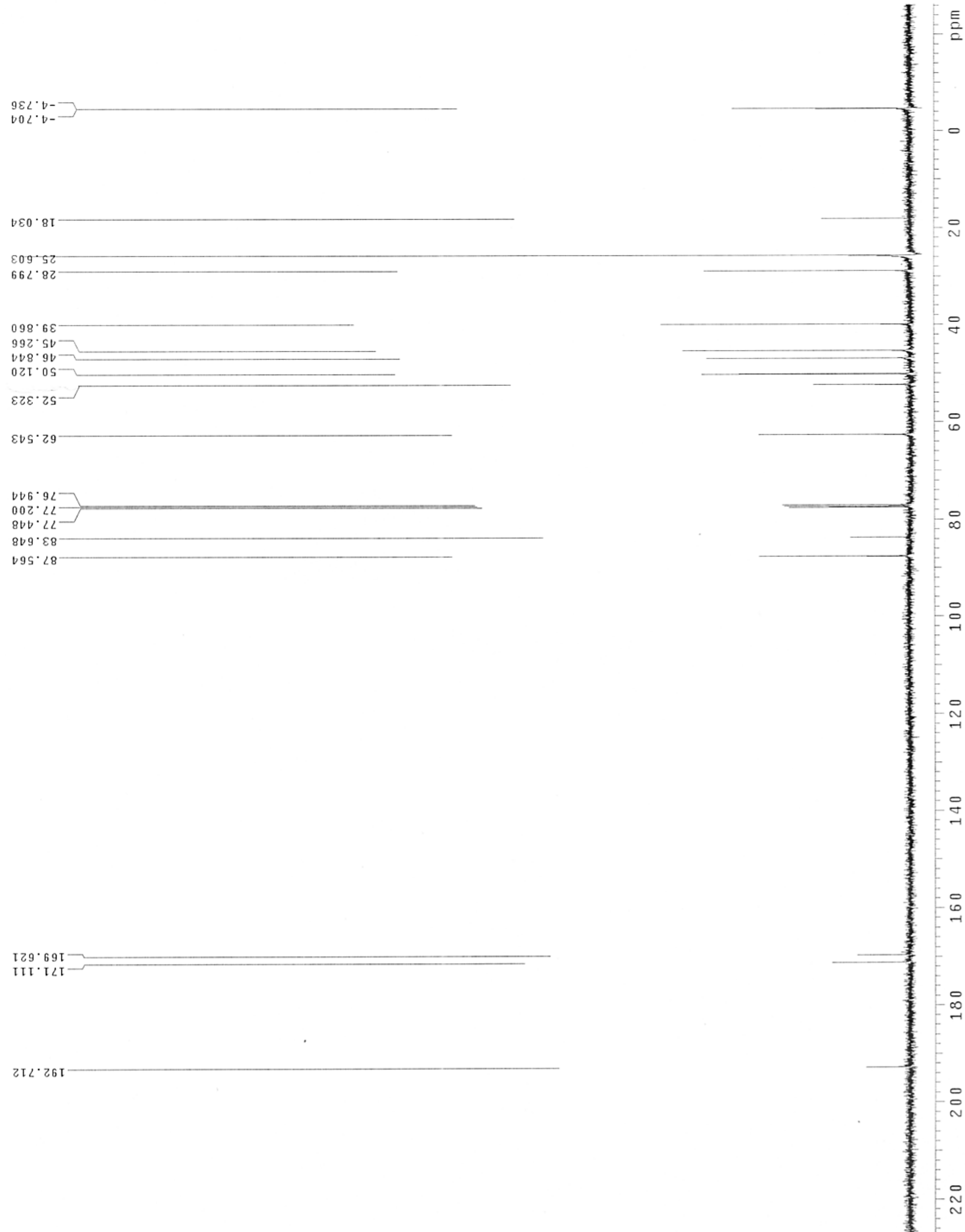


^{1}H NMR, 500 MHz, $CDCl_3$

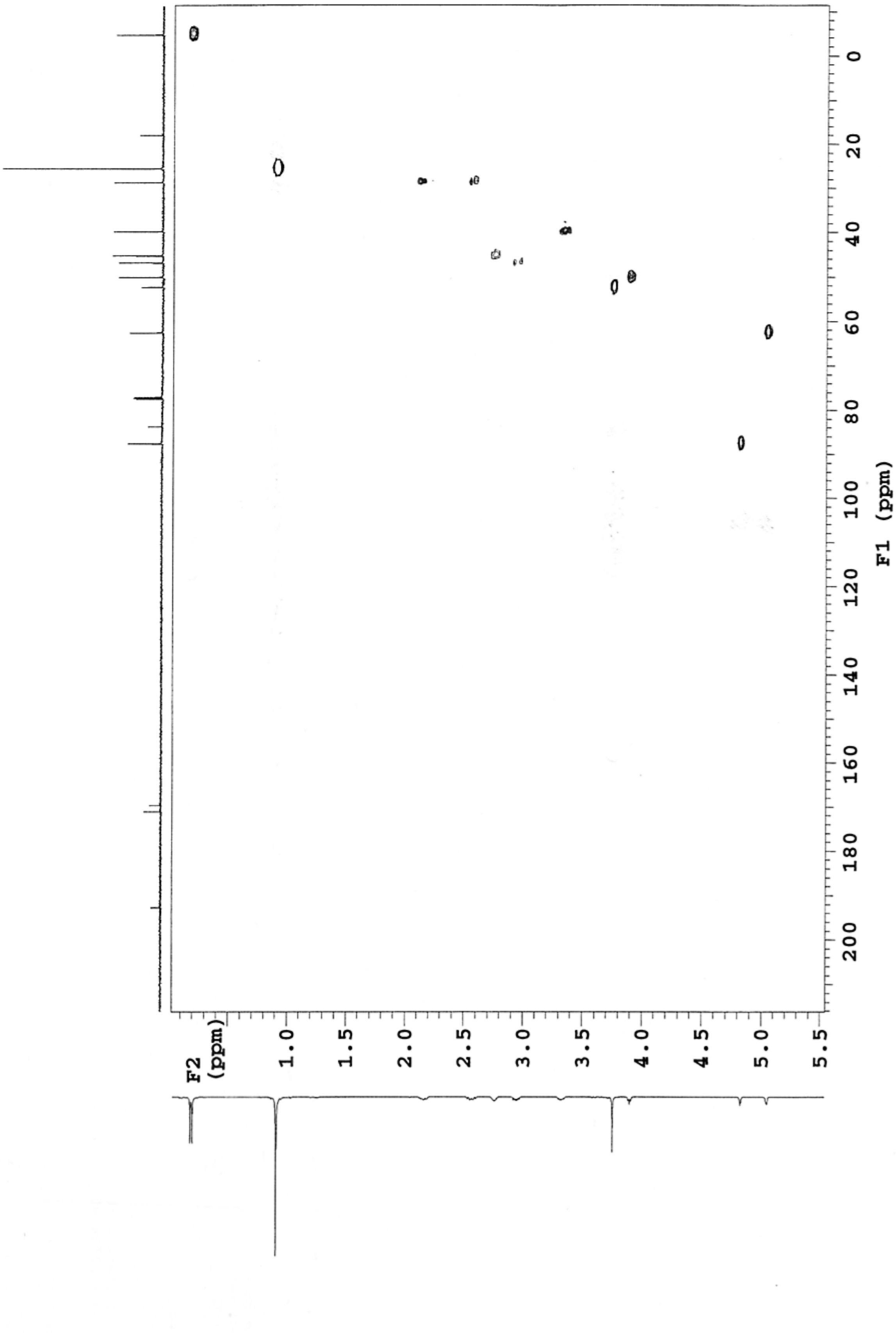




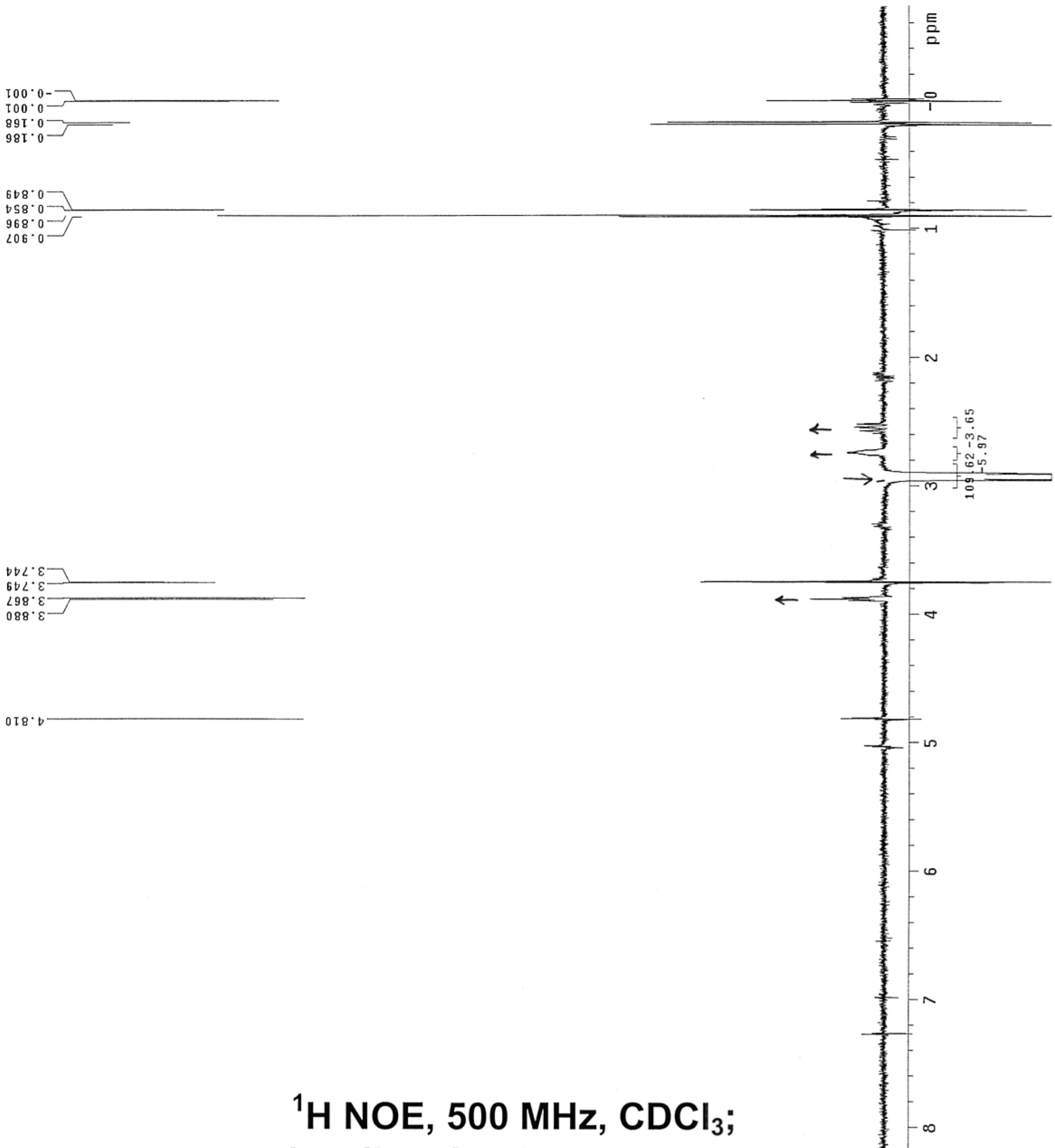
^{1}H-^{1}H COSY NMR, 500 MHz, $CDCl_3$



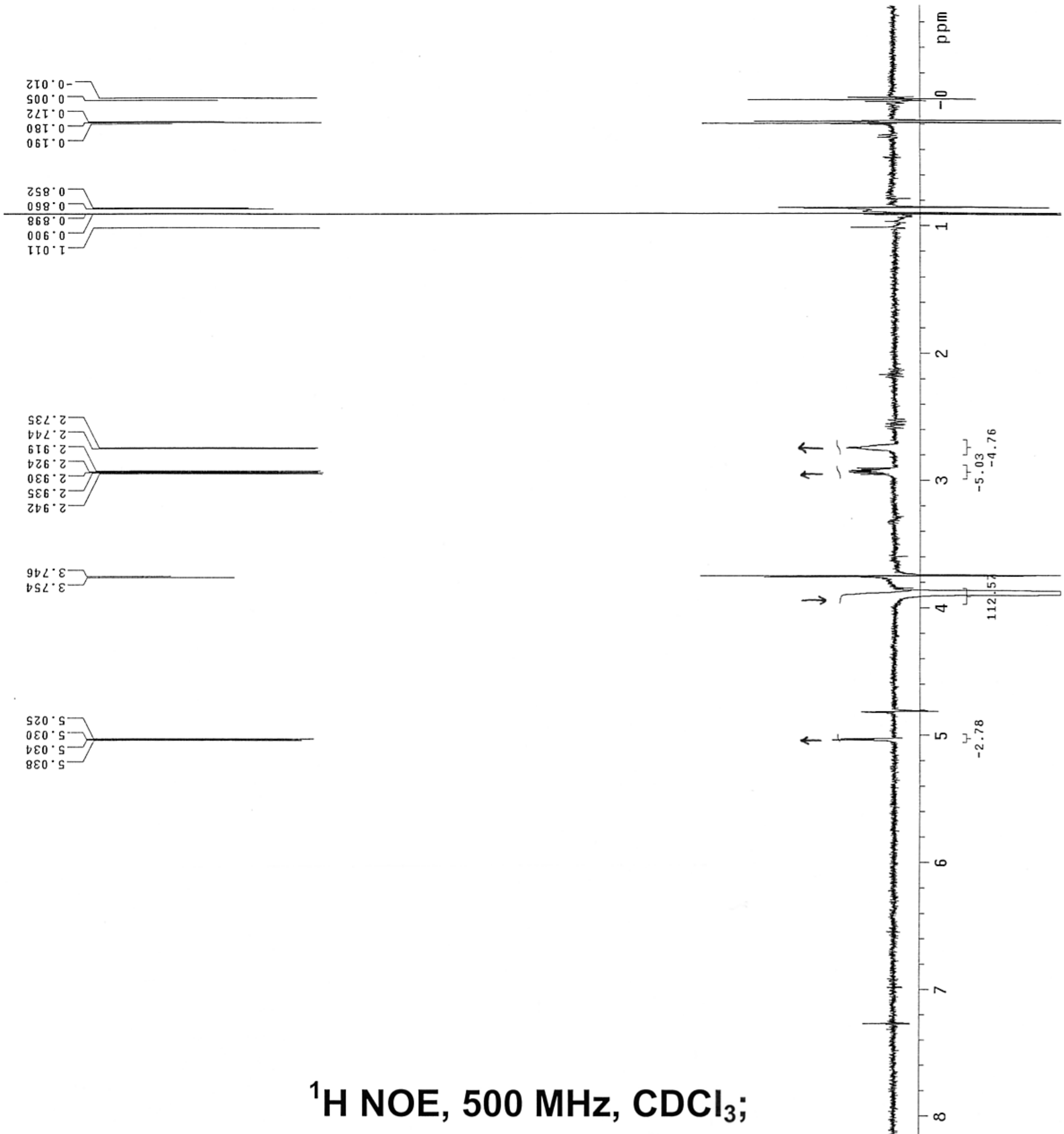
^{13}C NMR, 125 MHz, $CDCl_3$



^{1}H-^{13}C HMQC NMR, 500 MHz, $CDCl_3$



^{1}H NOE, 500 MHz, $CDCl_3$; irradiated at δ = 2.95 ppm



^{1}H NOE, 500 MHz, $CDCl_3$; irradiated at δ = 3.90 ppm

TABLE 6.1 Exact Isotope Masses for Calculating MS Molecular Weights of Important Elements[a]

Element	*Atomic Weight*	*Nuclide*	*Mass*	*Relative Abundance*
Hydrogen	1.00797	^{1}H	1.00783	100.0
		$D(^{2}H)$	2.01410	0.015
Carbon	12.01115	^{12}C	12.00000[b]	100.0
		^{13}C	13.00336	1.11
Nitrogen	14.0067	^{14}N	14.0031	100.0
		^{15}N	15.0001	0.37
Oxygen	15.9994	^{16}O	15.9949	100.0
		^{17}O	16.9991	0.04
		^{18}O	17.9992	0.20
Fluorine	18.9984	^{19}F	18.9984	100.0
Silicon	28.086	^{28}Si	27.9769	100.0
		^{29}Si	28.9765	5.06
		^{30}Si	29.9738	3.36
Phosphorus	30.974	^{31}P	30.9738	100.0
Sulfur	32.064	^{32}S	31.9721	100.0
		^{33}S	32.9715	0.79
		^{34}S	33.9679	4.43
Chlorine	35.453	^{35}Cl	34.9689	100.0
		^{37}Cl	36.9659	31.98
Bromine	79.909	^{79}Br	78.9183	100.0
		^{81}Br	80.9163	97.3
Iodine	126.904	^{127}I	126.9045	100.0

[a] Round-off to the nearest 0.0001 amu when analyzing high resolution data. Round-off to the nearest amu when examining low resolution data.
[b] Standard.

Table 2.2. *Isotopic contributions for carbon and hydrogen. If the abundance of the peak A is 100 (after correction for isotopic contributions to it), then its isotopic contributions will be:*

	(A + 1)	(A + 2)		(A + 1)	(A + 2)	(A + 3)
C_1	1.1	0.00	C_{16}	18	1.5	0.1
C_2	2.2	0.01	C_{17}	19	1.7	0.1
C_3	3.3	0.04	C_{18}	20	1.9	0.1
C_4	4.4	0.07	C_{19}	21	2.1	0.1
C_5	5.5	0.12	C_{20}	22	2.3	0.2
C_6	6.6	0.18	C_{22}	24	2.8	0.2
C_7	7.7	0.25	C_{24}	26	3.3	0.3
C_8	8.8	0.34	C_{26}	29	3.9	0.3
C_9	9.9	0.44	C_{28}	31	4.5	0.4
C_{10}	11.0	0.54	C_{30}	33	5.2	0.5
C_{11}	12.1	0.67	C_{35}	39	7.2	0.9
C_{12}	13.2	0.80	C_{40}	44	9.4	1.3
C_{13}	14.3	0.94	C_{50}	55	15	2.6
C_{14}	15.4	1.1	C_{60}	66	21	4.6
C_{15}	16.5	1.3	C_{100}	110	60	22

For each additional element present, add *per atom*:
(A + 1): N, 0.37; O, 0.04; Si, 5.1; S, 0.79.
(A + 2): O, 0.20; Si, 3.4; S, 4.4; Cl, 32.0; Br, 97.3.
Typical values for (A + 4): C_{25}, 0.02; C_{40}, 0.13; C_{100}, 5.7.