Platinum-Catalysed Intermolecular Addition of Carbonyl Compounds to 1,6-Enynes: Investigation of a new reaction pathway.

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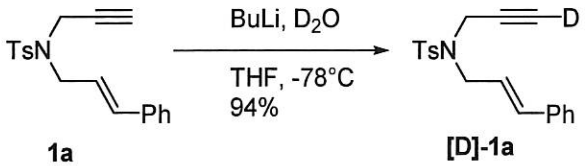
1. General information

All commercially available reagents were used as received. Silver salts were stored under argon in Schlenk tubes. Unless otherwise stated, all reactions were run under Argon using Schlenk techniques. THF was dried under N_2 using a solvent purification system (SPS). DCE was distillated under CaH_2. NMR spectra were recorded at 25 °C on a DPX300 or Fourier 300 Ultrashield spectrometers with TMS as internal reference. The following abbreviations were used throughout: s = singulet, d = doublet, t =triplet, m = multiplet. The assignments of signals of compounds **3** and **5** were confirmed by ^1H, ^{13}C, COSY, HSQC, DEPT135 and NOESY experiments. Mass spectra analyses were performed on a API-365 spectrometer (ESI) and on a TSQ 7000 Thermoquest instrument (DCI). High resolution mass spectra (HMRS) were recorded using a Waters Xevo G2 QTof instrument. X-ray structures were determined on Gemini and Xcalibur diffractometers.

2. Preparation of the Pt-complexes and the substrates

Starting Pt-phospholes complexes were prepared according to literature procedures. [1]
Starting enynes, **1a-1c**[2], **1d**[3], **1e** [4],[5], **1f-g**[2], **1h**[3] and deuterated benzaldehyde **[D]-4b**[6] were prepared according to the literature procedures. Synthesis and spectroscopic data of compound **6** have been previously described.[7] The deuterated enyne **[D]-1a** was prepared via the following procedure.



1a **[D]-1a**

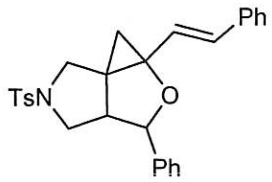
Enyne (300 mg, 0.92 mmol, 1 eq) was dissolved in 10 mL of THF. The mixture was cooled down to -78 °C and n-BuLi (0.633 mL, 1.012 mmol, 1.1 eq) was added dropwise and stirred 20 min at -78 °C. Then the reaction was quenched with few drops of D_2O and allowed to warm up to room temperature. After 1 h of stirring at room temperature, the mixture was concentrated and the crude was purified by column chromatography using AcOEt/Hexane (1/5).

[D]-1a. white solid, m.p.=82 °C, yield: 94%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, 2H, CH_{tosyl}), 7.28-7.17 (m, 7H, CH_{Ph} and CH_{tosyl}), 6.50 (d, 1H, =C*H*-Ph), 6.01 (dt, 1H, -C*H*=CH_2), 4.06 (s, 2H, -C*H*$_2$-N), 3.91 (d, 2H, N-C*H*$_2$-CH=), 2.37 (s, 3H, CH_{3tosyl}). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5 (Cq), 136.1 (Cq), 136.0 (Cq), 135.0 (CH), 129.6 ($2CH_{Ar}$), 128.7 ($2CH_{Ar}$), 128.1

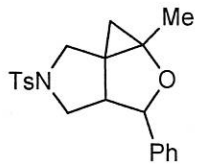
(CH), 127.9 ($2CH_{Ar}$), 126.6 ($2CH_{Ar}$), 123.0 (CH), 48.6 (CH_2), 35.8 (CH_2), 21.6 (CH_3). C-D not seen. MS (ESI): *m/z* (%) : 327.1 (100) [M+H].

3. General procedure for Pt(II)-catalysed reaction of 1,6 enynes with aldehydes.

A solution of platinum catalyst (0.027 mmol, 0.05 eq) and silver salt (0.054 mmol, 0.1 eq) was stirred in DCE (1.3 mL), in a vial for 5 min at room temperature. Then it was added through a PTFE membrane filter on a solution of enyne (0.54 mmol, 1 eq), and aldehyde (1.62 mmol, 3 eq) in DCE. The reaction was monitored by TLC. Then the crude was concentrated and subjected to silica gel chromatography, eluting with AcOEt/pentane.

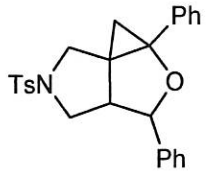


3a. white solid, m.p.=169 °C, yield: 58%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, *J* = 9 Hz, 2H, CH_{tosyl}), 7.23-7.15 (m, 10H, CH_{Ph}), 7.04 (d, *J* = 9 Hz, 2H, CH_{tosyl}), 6.55 (d, *J* = 15 Hz, 1H, Ph-CH=), 5.69 (d, *J* = 15 Hz, 1H, C*H*=CHPh), 4.99 (d, *J* = 6 Hz, 1H, CH-Ph), 3.70 (d, *J* = 9 Hz, 1H, N-CH_2-Cq), 3.15-3.09 (m, *3*H, N-CH_2-Cq + N-CH_2-C*H* + N-CH_2-CH), 2.49 (t, *J* = 9 Hz, 1H, N-CH_2-CH), 2.10 (s, 3H, CH_{3tosyl}) 1.77 (d, *J* = 9 Hz, 1H, $CH_{cylopropyl}$), 1.17 (d, *J* = 9 Hz, 1H, $CH_{cyclopropyl}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7 (Cq), 137.4 (Cq), 136.5 (Cq), 132.8 (Cq), 129.7 (Ph-*C*H=), 129.6 (CH_{Ar}), 128.6 (CH_{Ar}), 128.5 (CH_{Ar}), 127.7 (CH_{Ar}), 127.6 (CH_{Ar}), 127.4 (CH_{Ar}), 126.4 (CH_{Ar}), 125.2 (CH_{Ar}), 124.3 (*C*H=CH-Ph), 78.6 (CH-Ph), 69.7 (C-CH=), 49.2 (N-*C*H_2-CH), 48.9 (N-CH_2-*C*H), 48.7 (N-*C*H_2-Cq), 30.0 (Cq), 21.6 (CH_{3tosyl}), 15.8 ($CH_{2cyclopropyl}$). HRMS (ESI): *m/z*: calc. for $C_{28}H_{28}NO_3S$ [M+H]: 458.1790, found 458.1780.

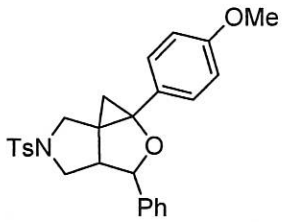


5a. white solid, m.p.=86 °C, yield: 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* = 9 Hz, 2H, CH_{tosyl}), 7.29-7.18 (m, 5H, CH_{Ph}), 7.13 (d, *J* = 9 Hz, 2H, CH_{tosyl}), 4.73 (d, *J* = 6 Hz, 1H, CH-Ph), 3.54 (d, *J* = 9 Hz, 1H, N-CH_2-Cq), 2.99-2.95 (m, 2H, N-CH_2-CH + N-CH_2-Cq), 2.86 (m, 1H, N-CH_2-C*H*), 2.45 (t, *J* = 9 Hz, 1H, N-CH_2-CH), 2.39 (s, 3H, CH_{3tosyl}), 1.36 (d, *J* = 9 Hz, 1H, $CH_{cylopropyl}$), 0.97 (s, 3H, CH_3), 0.54 (d, *J* = 9 Hz, 1H, $CH_{cyclopropyl}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7 (C_q), 137.6 (C_q), 133.3 (C_q), 129.7 (CH_{Ar}), 128.4 (CH_{Ar}), 127.7 (CH_{Ar}), 127.5

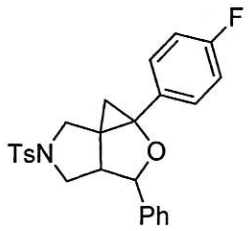
(CH_{Ar}), 125.1 (CH_{Ar}), 78.2 (CH-Ph), 65.9 (*C*-CH_3), 49.1 (N-CH_2-Cq), 49.0 (N-CH_2-*C*H), 48.7 (N-*C*H_2-***C***H), 35.3 (Cq), 21.6 (CH_{3tosyl}), 16.2 (CH_3), 14.3 ($CH_{2cyclopropyl}$). HRMS (ESI): *m/z*: calc. for $C_{21}H_{24}NO_3S$ [M+H]: 370.1477, found 370.1472.



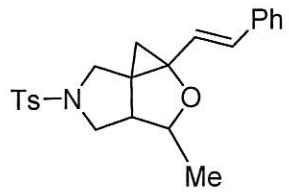
5b. white solid, m.p.=140 °C, yield: 30%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.02 (m, 14H, CH_{tosyl} and CH_{Ph}), 5.03 (d, *J* = 6 Hz, 1H, CH-Ph), 3.60 (d, *J* = 9 Hz, 1H, N-CH_2-Cq), 3.14 (m, 2H, N-C*H*$_2$-CH + N-CH_2-C*H*), 2.18 (d, *J* = 9 Hz, 1H, N-CH_2-Cq), 2.51 (t, *J* = 12 Hz, 1H, N-C*H*$_2$-CH), 2.41 (s, 3H, CH_{3tosyl}) 1.74 (d, *J* =, 1H, $CH_{cylopropyl}$), 1.40 (d, *J* =, 1H, $CH_{cyclopropyl}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.2 (Cq), 137.7 (Cq), 135.4 (Cq), 133.1 (Cq), 129.7 (CH_{Ar}), 128.5 (CH_{Ar}), 128.5 (CH_{Ar}), 128.0 (CH_{Ar}), 127.6 (CH_{Ar}), 127.2 (CH_{Ar}), 126.5 (CH_{Ar}), 125.1 (CH_{Ar}), 78.5 (CH-Ph), 71.2 (Cq), 49.3 (N-*C*H_2-Cq), 49.1 (N-CH_2-*C*H), 47.9 (N-*C*H_2-CH), 39.3 (Cq), 21.7 (CH_{3tosyl}), 12.9 ($CH_{2cyclopropyl}$). MS (DCI/NH_3): *m/z* (%) : 432.1 (100) [M+H$^+$].



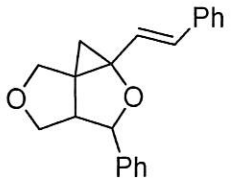
5c. white solid, m.p.=103 °C, yield: 28%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 9 Hz, 2H, CH_{tosyl}), 7.28-7.19 (m, 5H, CH_{Ph}), 7.12 (d, *J* = 9 Hz, 2H, CH_{tosyl}), 6.91 (d, *J* = 9 Hz, 2H, CH_{PhOMe}), 6.63 (d, *J* = 9 Hz, 2H, CH_{PhOMe}), 4.95 (d, *J* = 6 Hz, 1H, CH-Ph), 3.77 (s, 3H, OCH_3), 3.50 (d, *J* = 9 Hz, 1H, N-CH_2-Cq), 3.09 (m, 2H, N-C*H*$_2$-CH + N-CH_2-C*H*), 2.70 (d, *J* = 9 Hz, 1H, N-CH_2-Cq), 2.51 (m, 1H, N-C*H*$_2$-CH), 2.40 (s, 3H, CH_{3tosyl}), 1.72 (d, *J* = 9 Hz, 1H, $CH_{cyclopropyl}$), 1.34 (d, *J* = 9 Hz, 1H, $CH_{cyclopropyl}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1 (Cq), 143.3 (C_q), 137.7 (C_q), 133.4 (C_q), 129.6 (CH_{Ar}), 128.5 (CH_{Ar}), 128.5 (CH_{Ar}), 127.5 (CH_{Ar}), 127.4 (CH_{Ar}), 127.2 (CH_{Ar}), 125.1 (Cq), 114.0 (CH_{Ar}), 78.4 (CH-Ph), 71.2 (Cq), 55.3 (OCH_3), 53.6 (N-*C*H_2-Cq), 49.2 (N-CH_2-*C*H), 48.2 (N-*C*H_2-CH), 38.5 (Cq), 21.6 (CH_{3tosyl}), 13.1 ($CH_{2cyclopropyl}$). HRMS (ESI): *m/z*: calc. for $C_{27}H_{28}NO_4S$ [M+H]: 462.1739, found 462.1747.



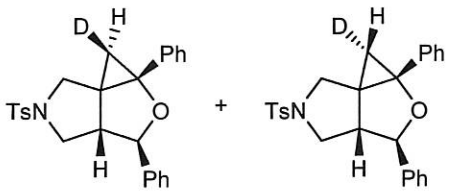
5d. white solid, m.p.=143 °C, yield: 36%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.28 (m, 7H, CH_{tosyl} and CH_{Ph}), 7.17 (m, 2H, CH_{tosyl}), 7.0 (m, 2H, $CH_{Ph\text{-}F}$), 6.86 (m, 2H, $CH_{Ph\text{-}F}$), 5.06 (d, J = 6 Hz, 1H, CH-Ph), 3.62 (d, J = 9 Hz, 1H, N-CH_2-Cq), 3.19 (m, 2H, N-CH_2-CH + N-CH_2-CH), 2.73 (d, J = 9 Hz, 1H, N-CH_2-Cq), 2.52 (t, J = 12 Hz, 1H, N-CH_2-CH), 2.47 (s, 3H, CH_{3tosyl}) 1.84 (d, J = 9 Hz, 1H, $CH_{cylopropyl}$), 1.47 (d, J = 9 Hz, 1H, $CH_{cyclopropyl}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.07 (d, J_{CF}= 247 Hz, Cq_F), 143.4 (C_q), 137.5 (C_q), 133.2 (C_q), 131.3 (d, J_{CF}= 3 Hz, $Cq_)$, 129.6 (CH_{Ar}), 128.6 (CH_{Ar}), 128.1 (CH_{Ar}, $J_{C\text{-}F}$ = 8 Hz), 127.7 (CH_{Ar}), 127.3 (CH_{Ar}), 125.0 (CH_{Ar}), 115.6 (d,$^2J_{C\text{-}F}$= 22 Hz, CH_{Ar}), 78.6 (CH-Ph), 70.7 (Cq), 49.1 (N-CH$_2$-Cq), 49.1 (N-CH$_2$-CH), 47.8 (N-CH$_2$-CH), 39.2 (Cq), 21.6 (CH_{3tosyl}), 13.4 ($CH_{2cyclopropyl}$). HRMS (ESI): *m/z*: calc. for $C_{26}H_{25}NO_3FS$ [M+H]: 450.1539, found 450.1531.



3b. white solid, m.p.=81 °C, yield: 57%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, 2H, CH_{tosyl}), 7.25-7.11 (m, 5H, CH_{Ph}), 6.94 (d, 2H, CH_{tosyl}), 6.28 (d, J = 15 Hz, 1H, Ph-CH=), 5.55 (d, J = 15 Hz, 1H, CH=CH-Ph), 3.89 (m, 1H, CH-CH_3), 3.56 (d, J = 12 Hz, 1H, N-CH_2-Cq), 3.43 (m, 1H, N-CH_2-CH), 3.02 (d, J = 12 Hz, 1H, N-CH_2-Cq), 2.65 (m, 2H, N-CH_2-CH + N-CH_2-CH), 2.04 (s, 3H, CH_{3tosyl}) 1.52 (d, J = 9 Hz, 1H, $CH_{cylopropyl}$), 1.16 (d, J = 6 Hz, 3H, CH_3-CH) 1.02 (d, J = 9 Hz, 1H, $CH_{cyclopropyl}$).^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6 (Cq), 136.6 (Cq), 132.8 (Cq), 129.6 (Ph-CH=), 128.5 (CH_{Ar}), 127.5 (CH_{Ar}), 126.3 (CH_{Ar}), 124.7 (*C*H=CH-Ph), 73.7 (*C*H-CH_3), 69.5 (Cq), 48.5 (N-CH$_2$-Cq), 48.2 (N-CH$_2$-CH), 47.9 (N-CH$_2$-CH), 39.8 (Cq), 21.3 (CH_{3tosyl}), 15.6 (CH_3), 15.6 ($CH_{2cyclopropyl}$). HRMS (ESI): *m/z*: calc. for $C_{23}H_{26}NO_3S$ [M+H]: 396.1633, found 396.1628.



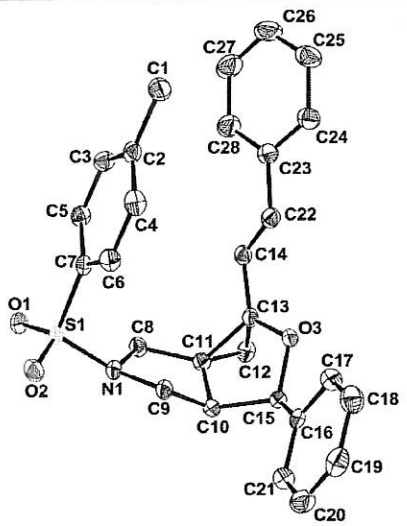
3g. yellow oil, yield: 15%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.18 (m, 10H, CH_{Ph}), 6.79 (d, *J* = 15 Hz, 1H, Ph-CH=), 6.11 (d, *J* = 15 Hz, 1H, C*H*=CH-Ph), 5.07 (d, *J* = 6 Hz, 1H, CH-Ph), 3.96 (d, *J* = 9 Hz, 1H, O-CH_2-Cq), 3.73 (d, *J* = 9 Hz, 1H, O-CH_2-Cq), 3.44 (m, 1H, O-*C*H_2-CH), 3.13 (m, 2H, O-C*H*$_2$-CH + CH-Ph), 1.79 (d, *J* = 9 Hz, 1H, $CH_{cyclopropyl}$), 1.28 (d, *J* = 9 Hz, 1H, $CH_{cyclopropyl}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.3 (Cq), 135.9 (Cq), 128.6 (Ph-CH=), 127.6 (CH_{Ar}), 127.3 (CH_{Ar}), 126.38 (CH_{Ar}), 126.36 (CH_{Ar}), 125.3 (CH_{Ar}), 124.8 (*C*H=CH-Ph), 124.4 (CH_{Ar}), 79.2 (CH-Ph), 69.1 (C-O), 67.9 (O-CH_2), 67.4 (O-CH_2), 50.0 (O-CH_2-*C*H), 41.0 (C-Cq), 15.7 ($CH_{2cyclopropyl}$). HRMS (ESI): *m/z*: calc. for $C_{21}H_{21}NO_2$ [M+H] 305.1542, found 305.1537.



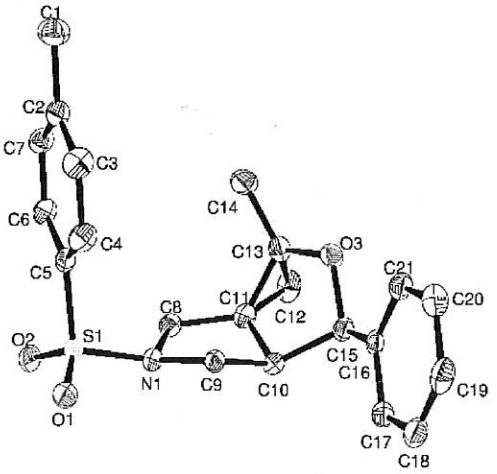
0.8 0.2

[D]-5b and [D]-5b'. white solid, m.p.=145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.02 (m, 14H, CH_{tosyl} and CH_{Ph}), 5.03 (d, *J* = 6 Hz, 1H, CH-Ph), 3.60 (d, *J* = 9 Hz, 1H, N-CH_2-Cq), 3.14 (m, 2H, N-C*H*$_2$-CH + N-CH_2-C*H*), 2.18 (d, *J* = 9 Hz, 1H, N-CH_2-Cq), 2.51 (t, *J* = 12 Hz, 1H, N-C*H*$_2$-CH), 2.41 (s, 3H, CH_{3tosyl}) 1.73 (s, 0.8 H, $CH_{cylopropyl}$), 1.40 (s, 0.2 H, $CH_{cyclopropyl}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.0 (Cq), 136.6 (Cq), 134.3 (Cq), 132.1 (Cq), 128.5 (CH_{Ar}), 127.5 (CH_{Ar}), 127.4 (CH_{Ar}), 126.50 (CH_{Ar}), 126.2 (CH_{Ar}), 126.1 (CH_{Ar}), 125.3 (CH_{Ar}), 124.0 (CH_{Ar}), 76.5 (CH-Ph), 70.1 (Cq), 48.2 (N-*C*H_2-Cq), 48.0 (N-CH_2-*C*H), 48.9 (N-*C*H_2-CH), 38.2 (Cq), 20.5 (CH_{3tosyl}), 12.2 (t, $J_{C\text{-}D}$=23.5 Hz, C*H*D). MS (DCI/NH_3): *m/z* (%) : 432.1 (100) [M+H^+].

4. X-ray structure of 3a and 5a.



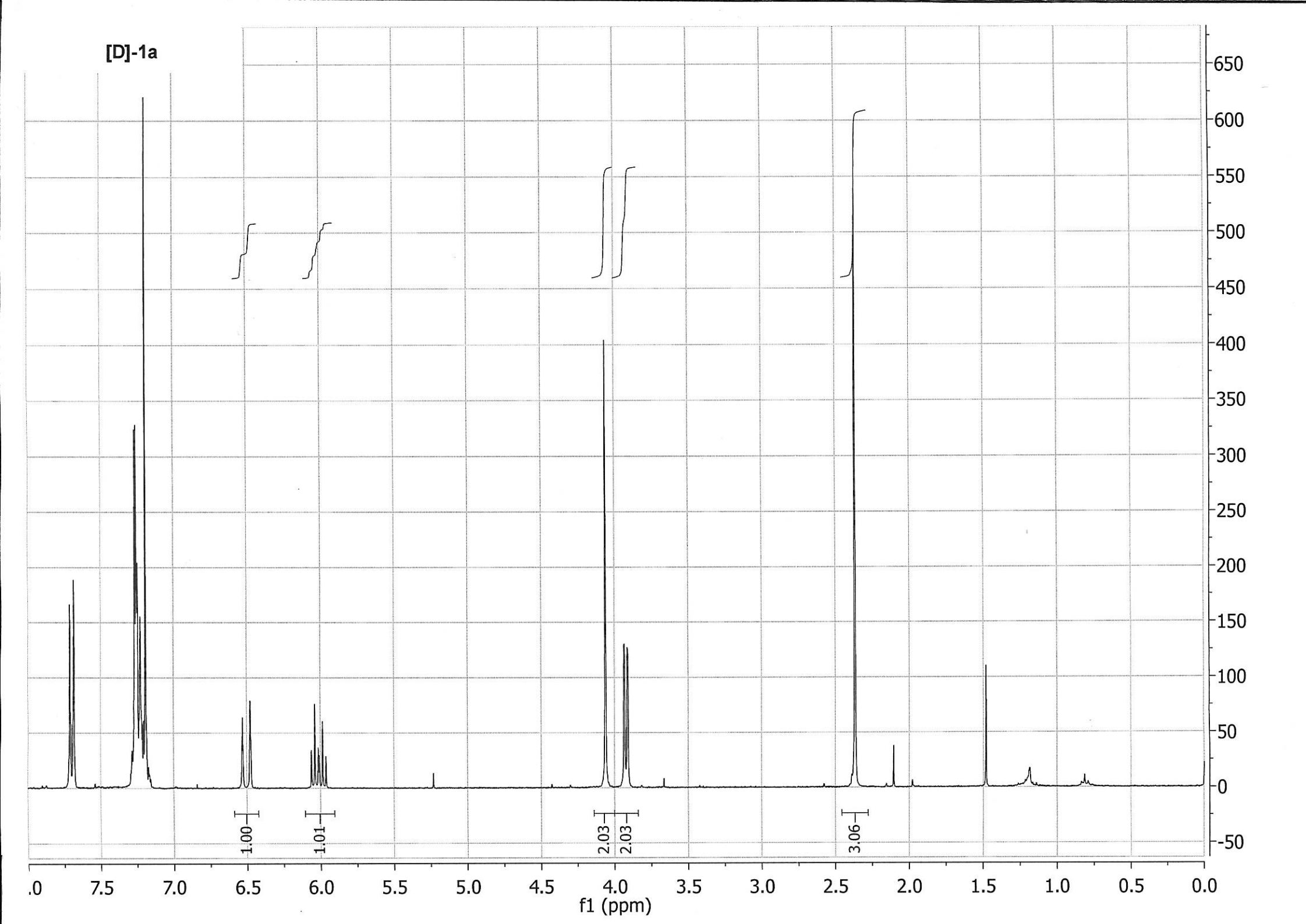
Molecular structure of **3a**. Only one enantiomer is represented. Selected bond lengths (Å) and angles (°): C(11)-C(12) = 1.502(3), C(11)-C(13) = 1.515(3), C(12)-C(13) = 1.524(3), O(3)-C(13) = 1.417(2), O(3)-C(15) = 1.433(2), C(12)-C(11)-C(13) = 60.66(13), C(11)-C(12)-C(13) = 60.10(12), C(11)-C(13)-C(12) = 59.24(12).

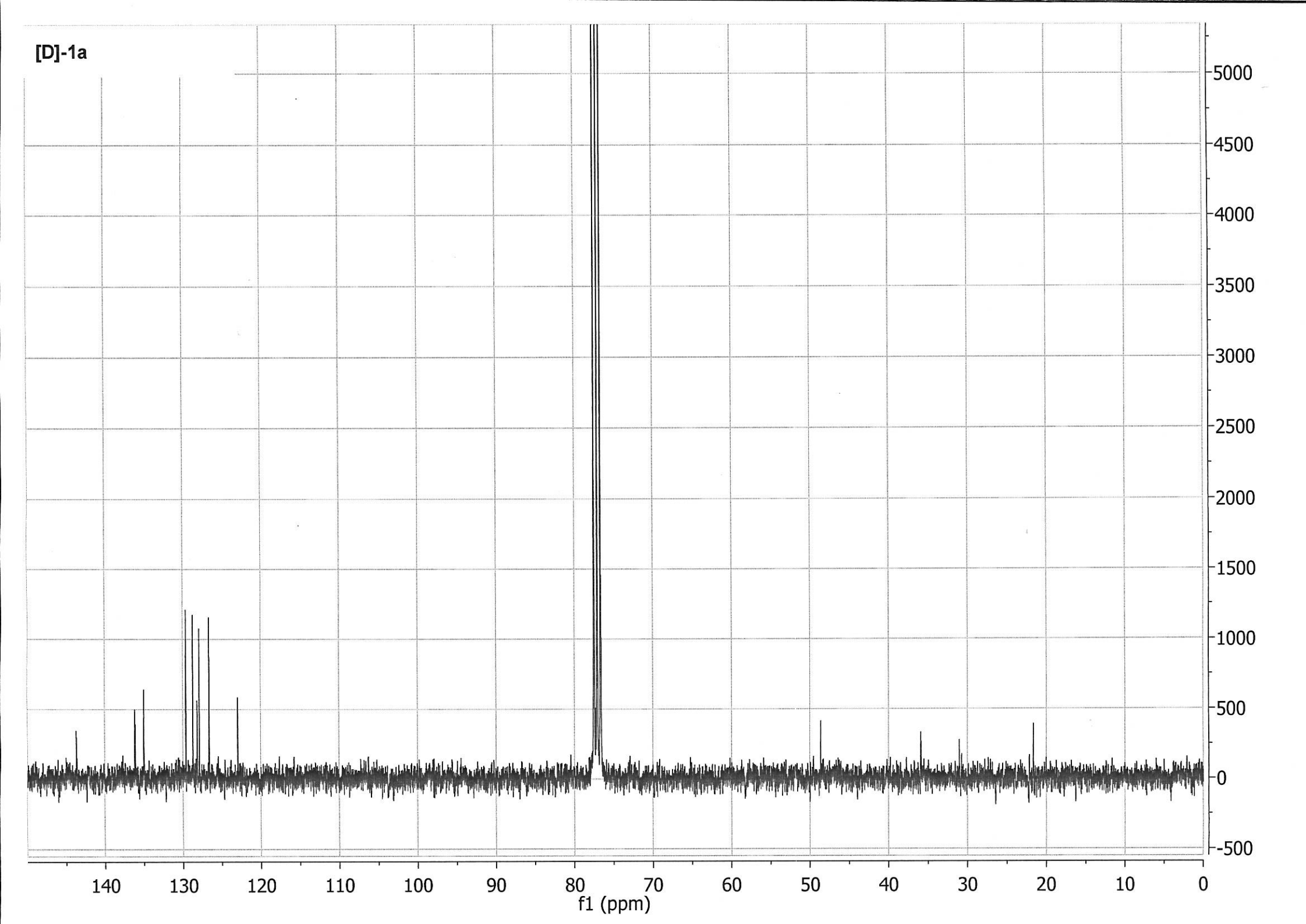


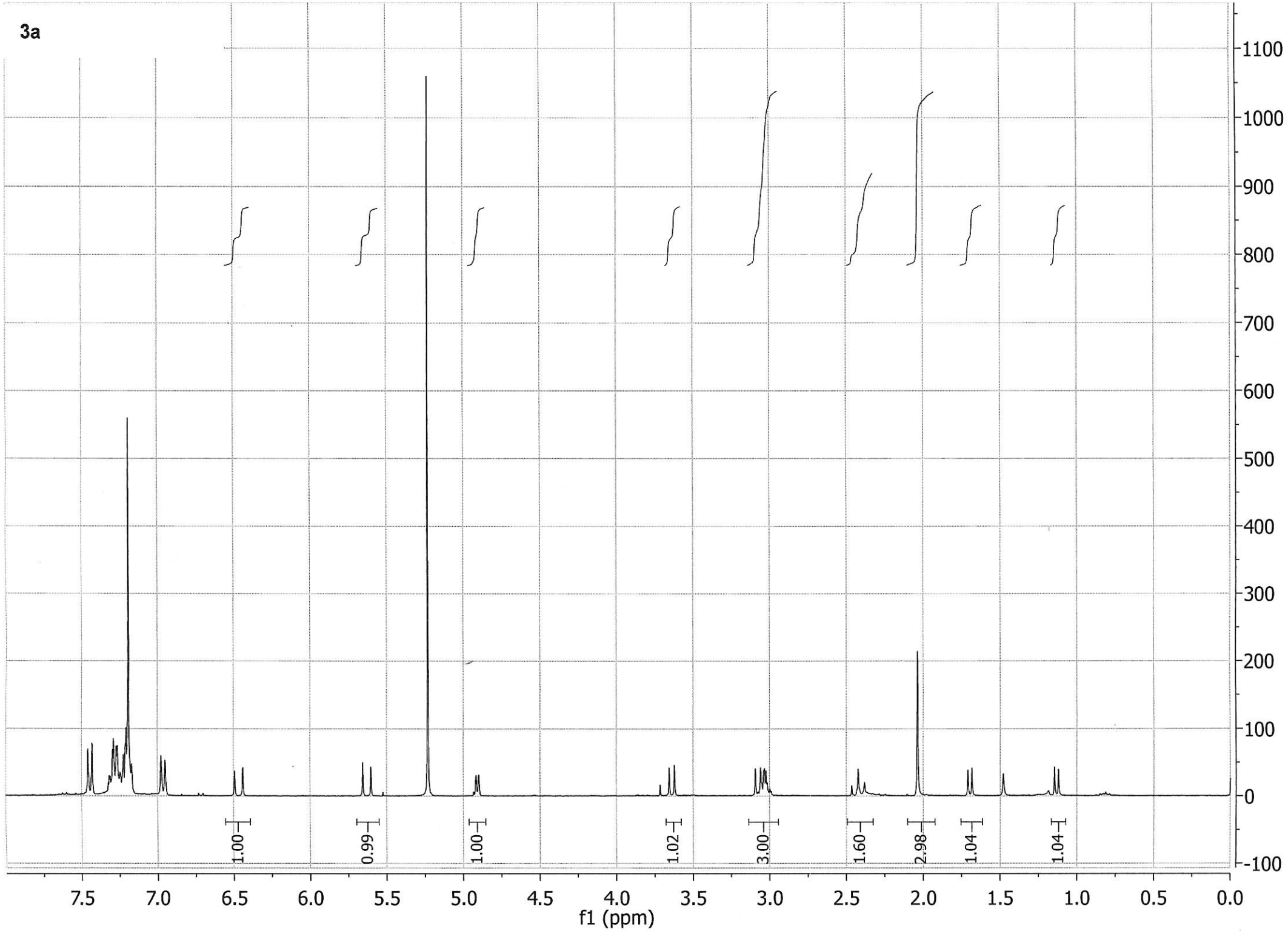
Molecular structure of **5a**. Only one enantiomer is represented. Selected bond lengths (Å) and angles (°): C(11)-C(12) = 1.507(4), C(11)-C(13) = 1.500(4), C(12)-C(13) = 1.493(4), C(13)-O(3) = 1.425(3),C(13)-O(3)= 1.425(3), C(13)-C(12)-C(11) = 60.00(16), C(13)-C(11)-C(12) = 59.51(18), C(12)-C(13)-C(11) = 60.49(17)

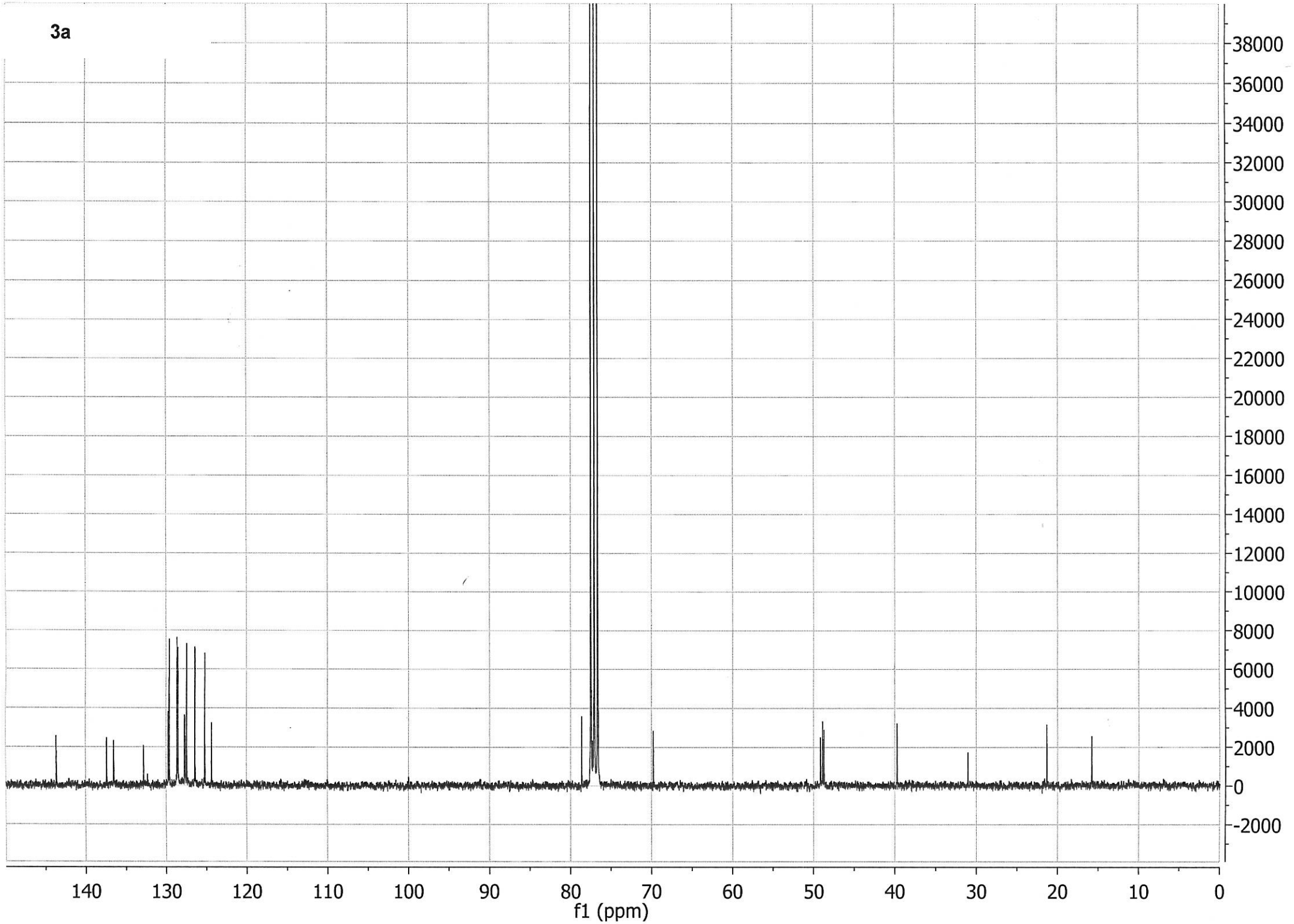
Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre with deposition numbers CCDC 1412293 (**3a**) and CCDC 1411933 (**5a**). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

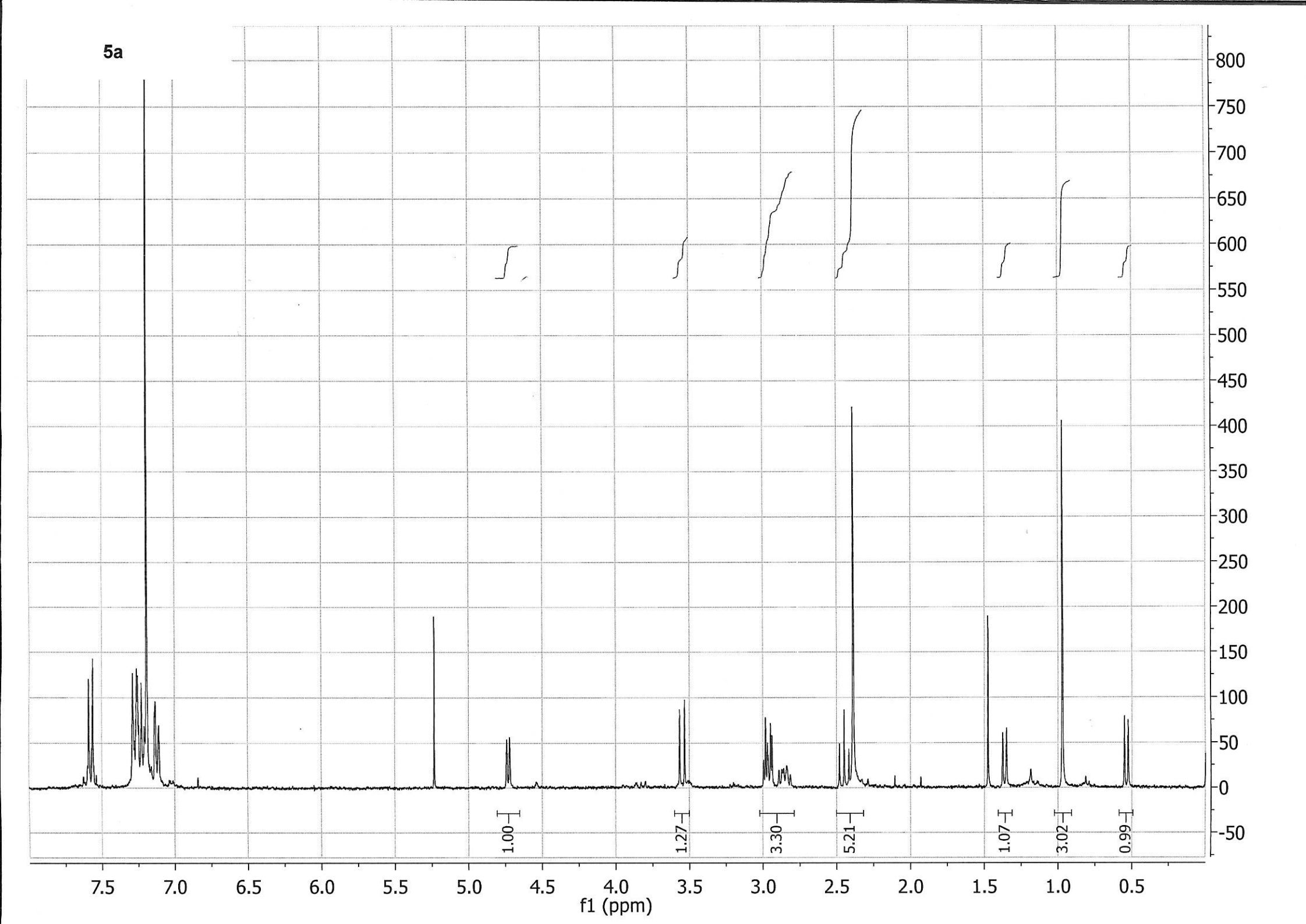
5. NMR spectra

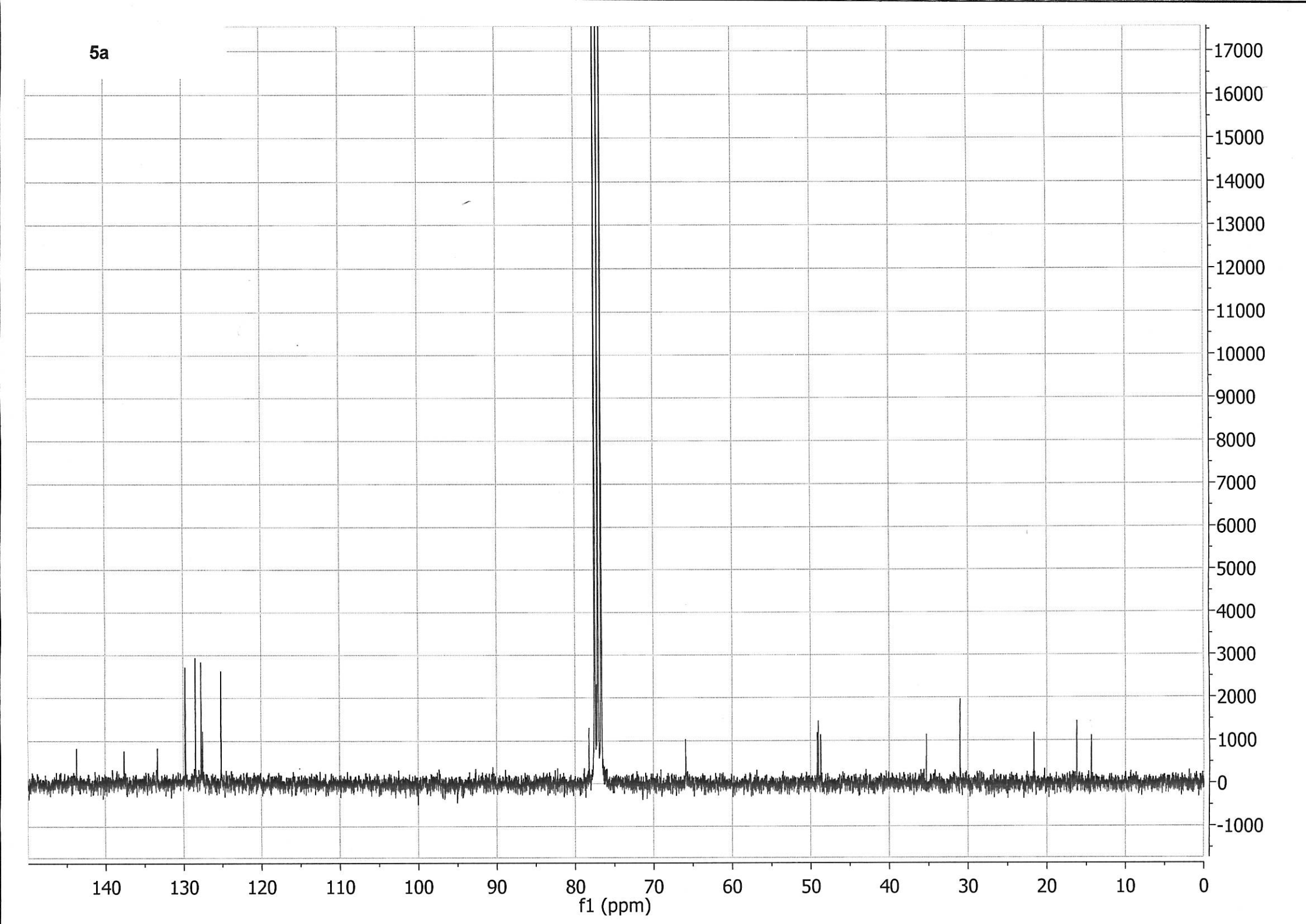

[D]-1a
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
1.00
1.01
2.03
2.03
3.06
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

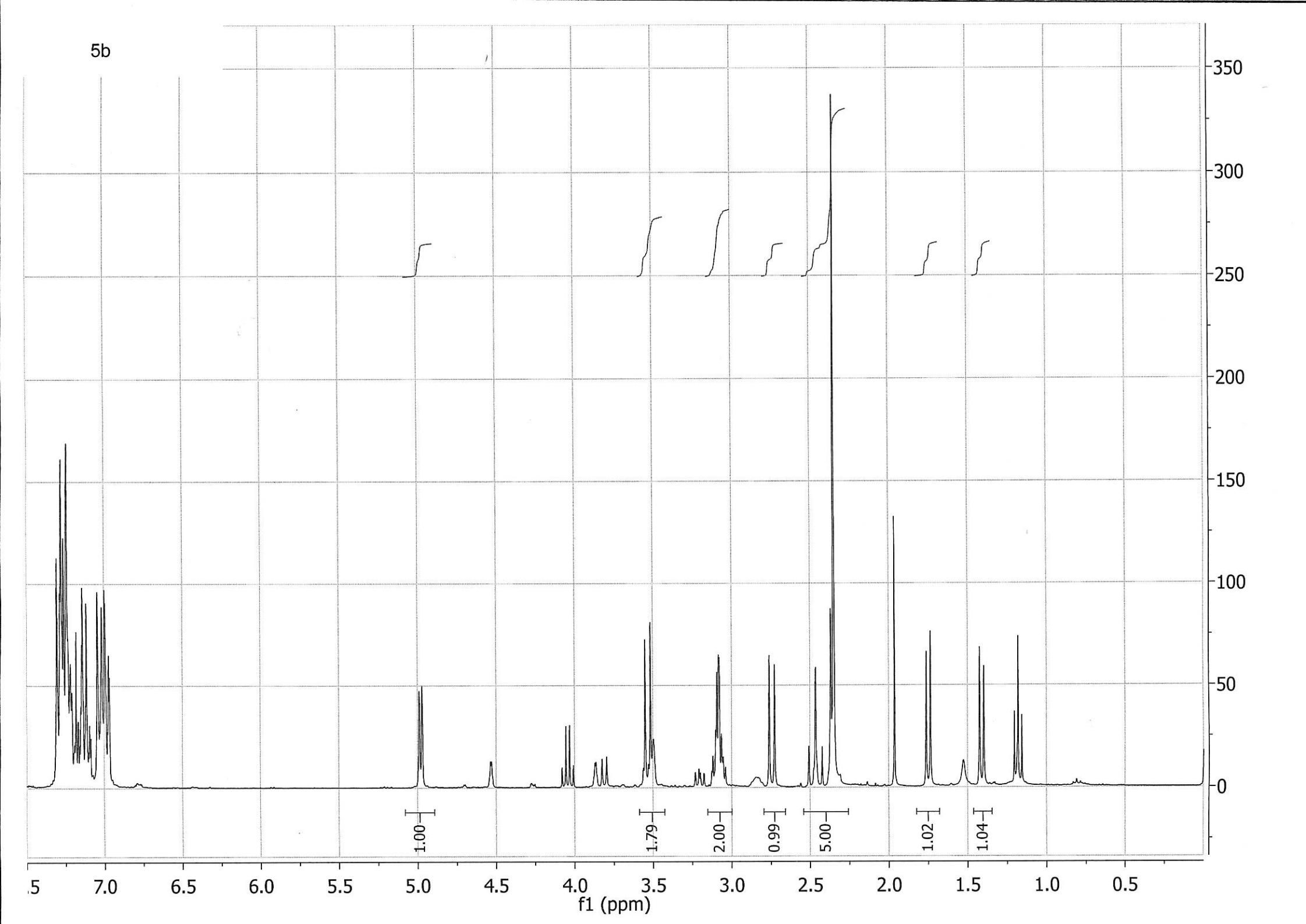

[D]-1a
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

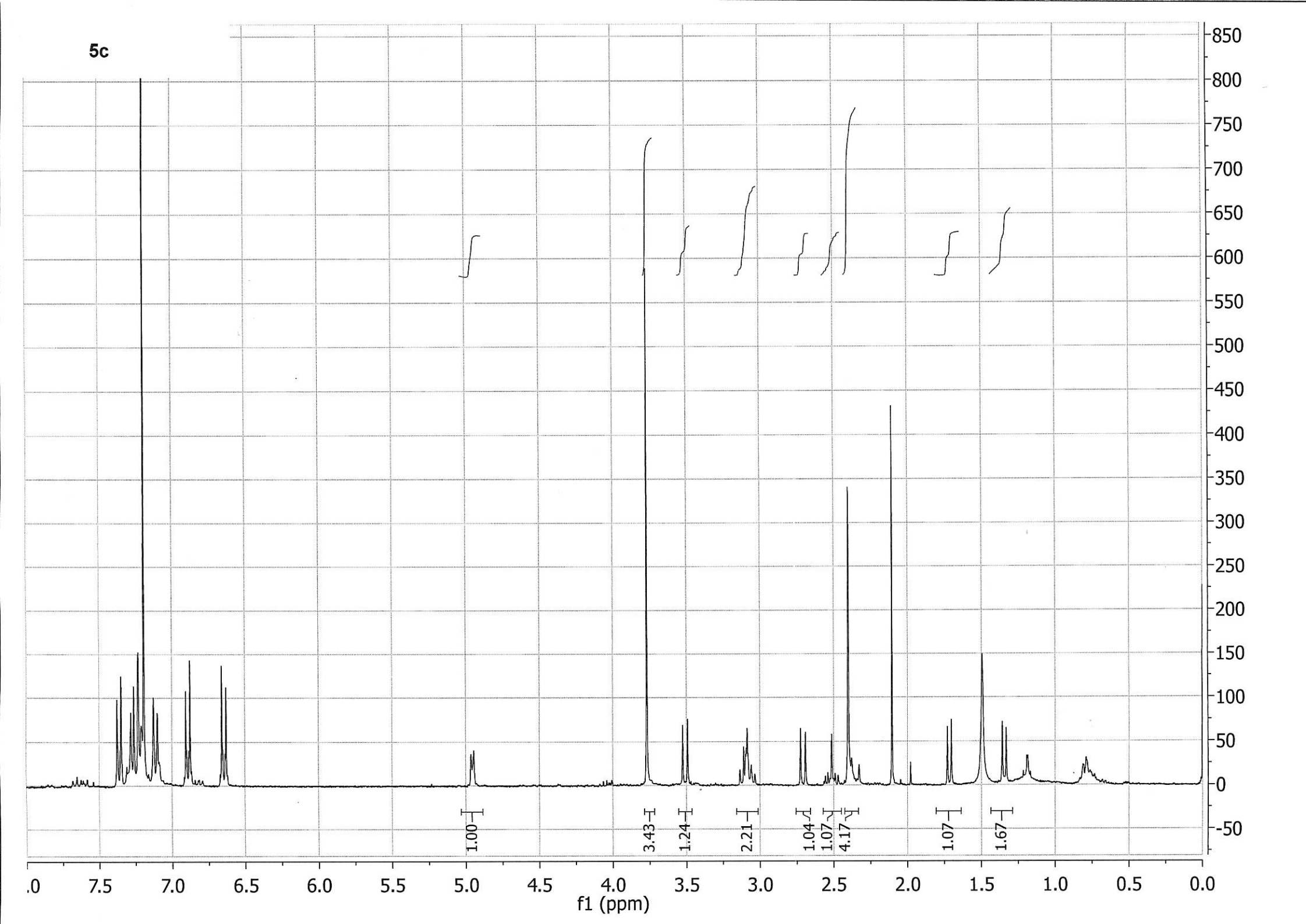

3a
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
1.00
0.99
1.00
1.02
3.00
1.60
2.98
1.04
1.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

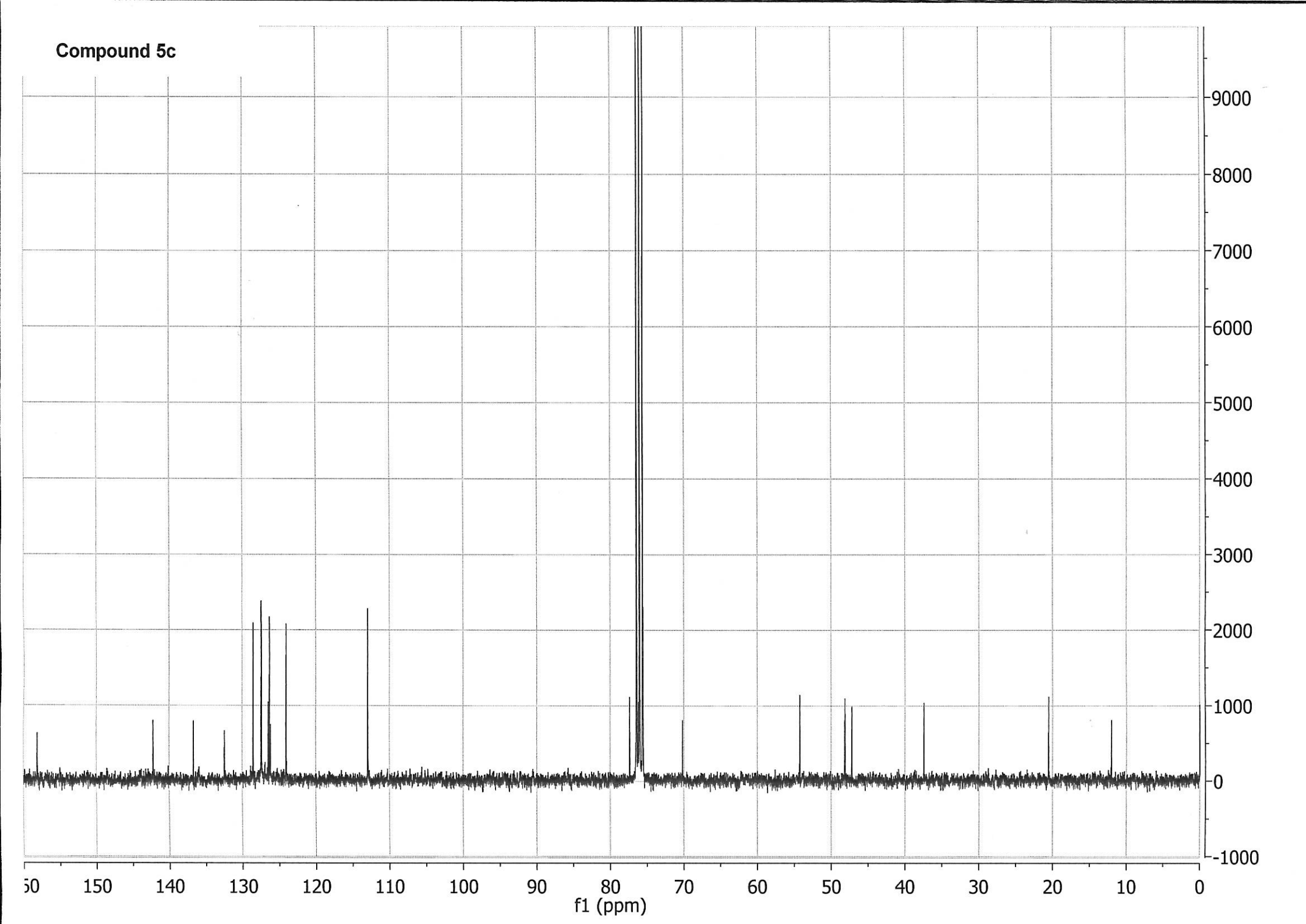

3a
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

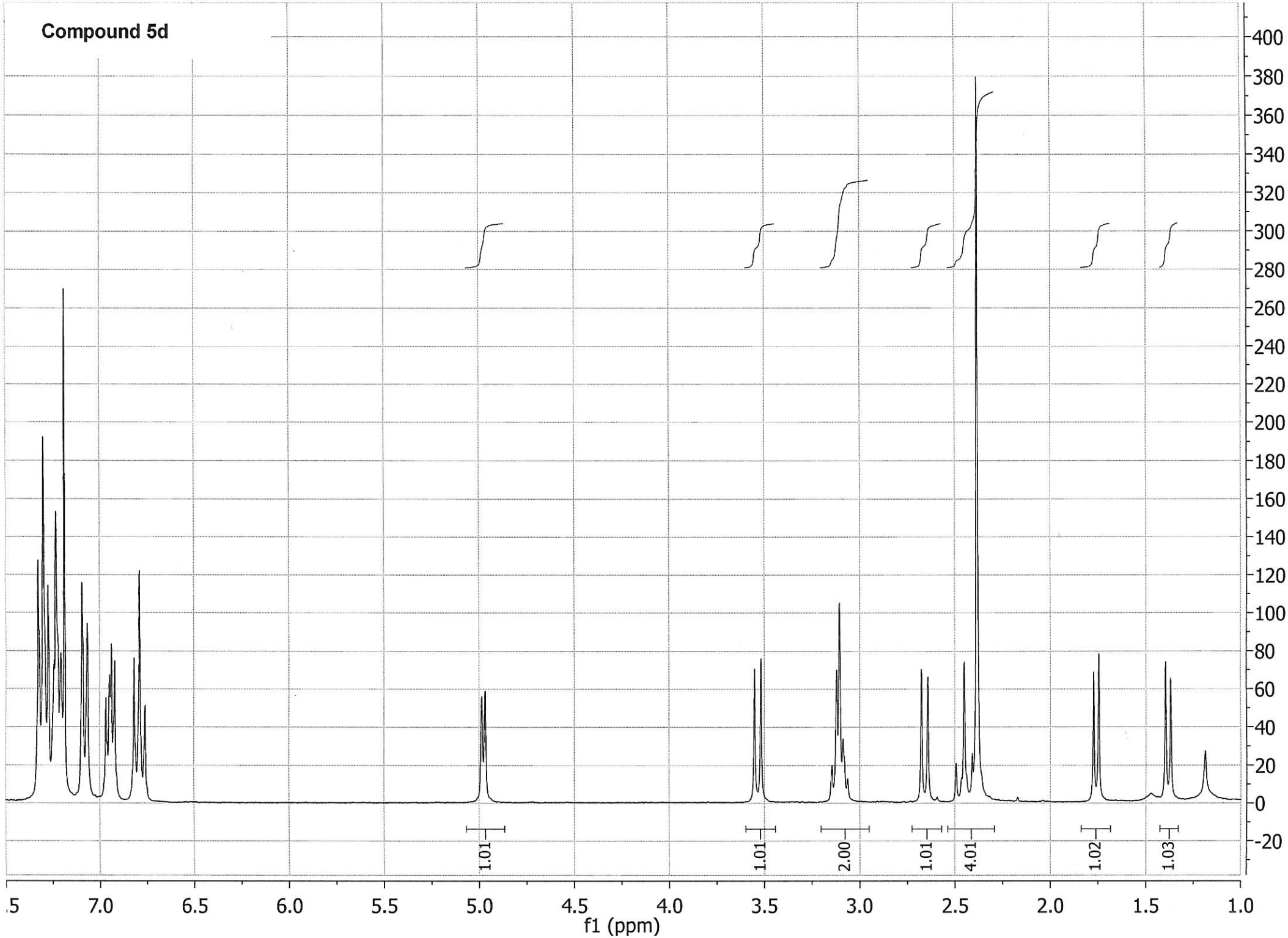

5a
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
1.00
1.27
3.30
5.21
1.07
3.02
0.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

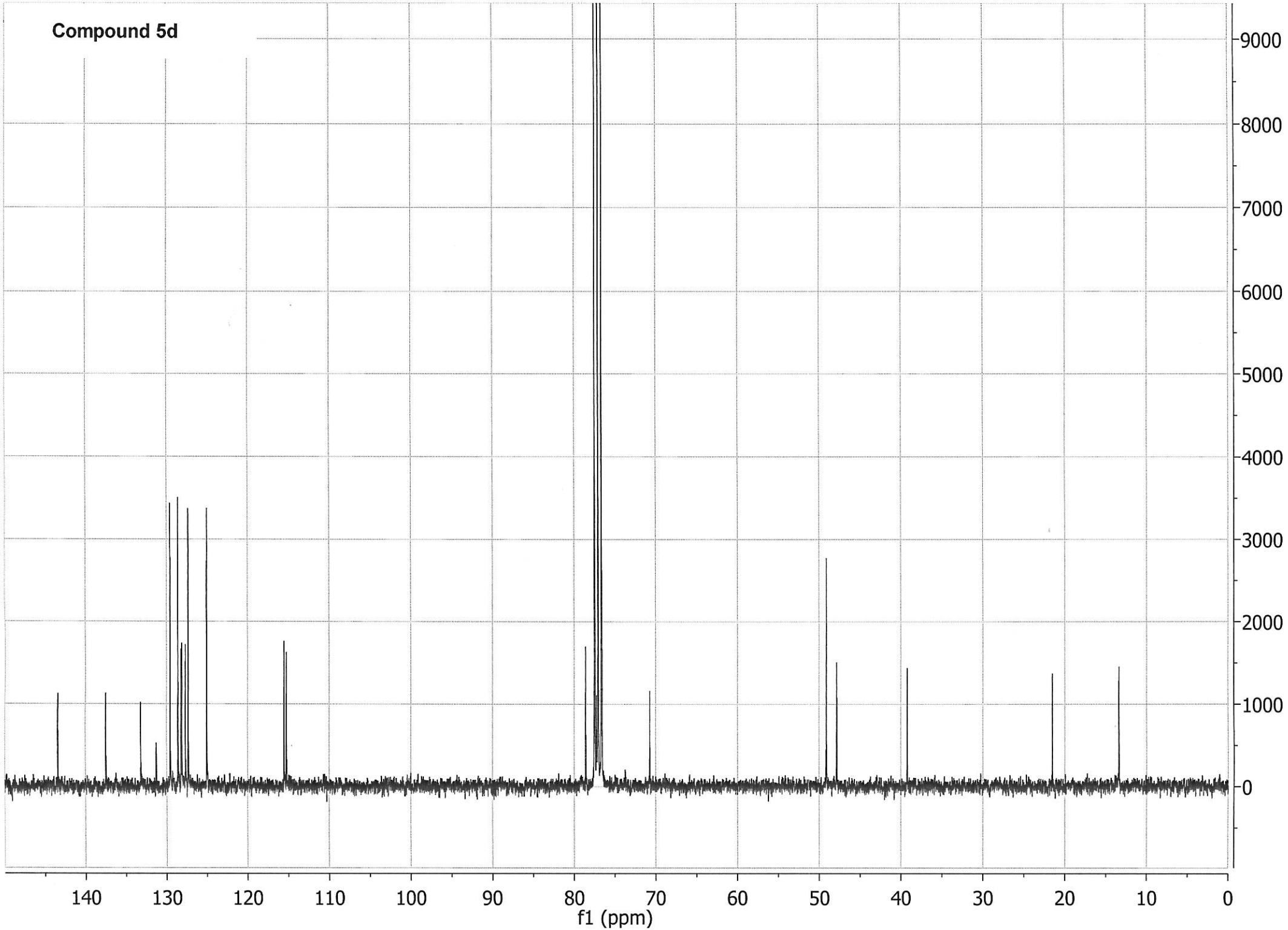

5a
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

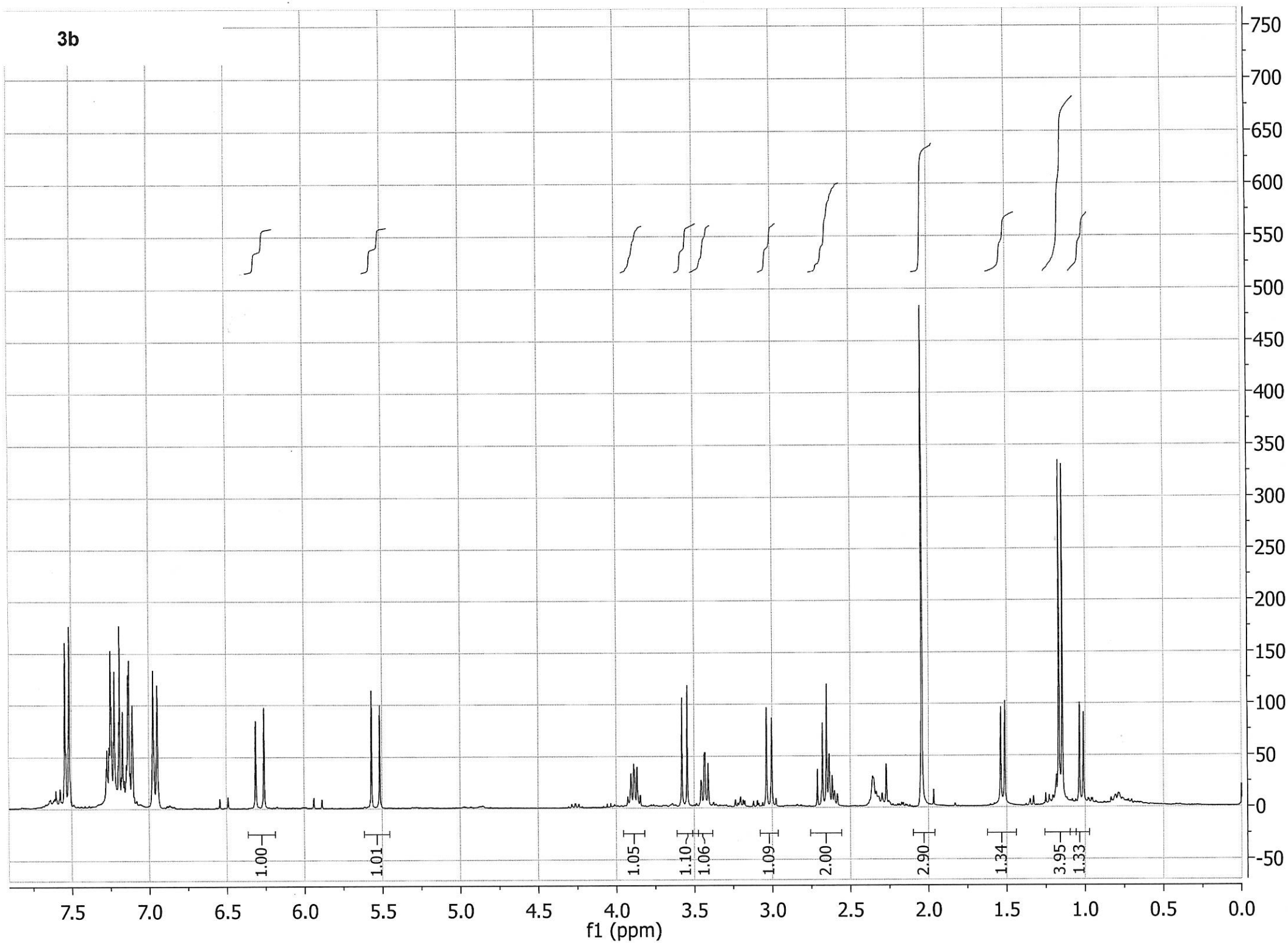

5b
350
300
250
200
150
100
50
0
1.00
1.79
2.00
0.99
5.00
1.02
1.04
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

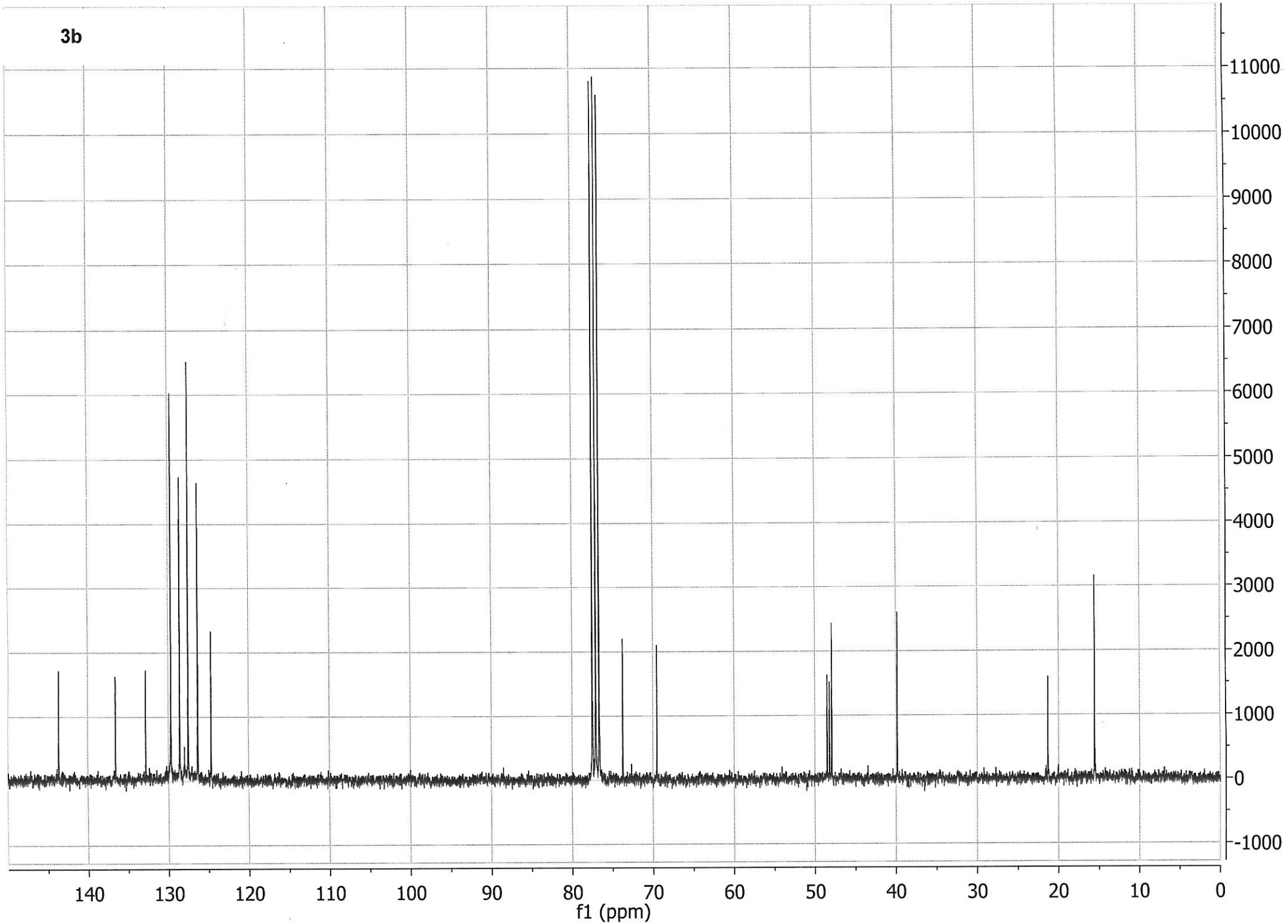

5c
1.00
3.43
1.24
2.21
1.04
1.07
4.17
1.07
1.67
f1 (ppm)

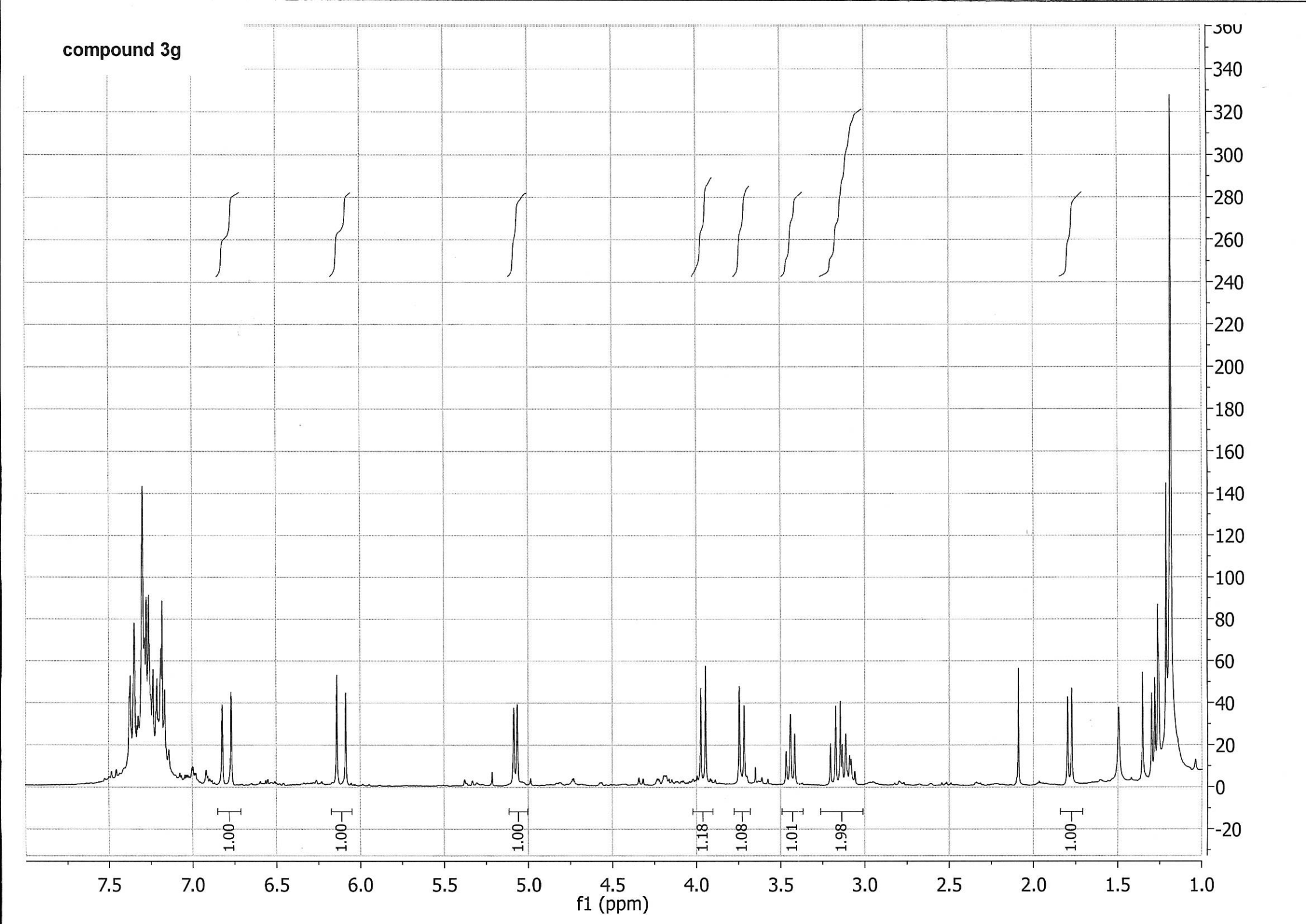

Compound 5c
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

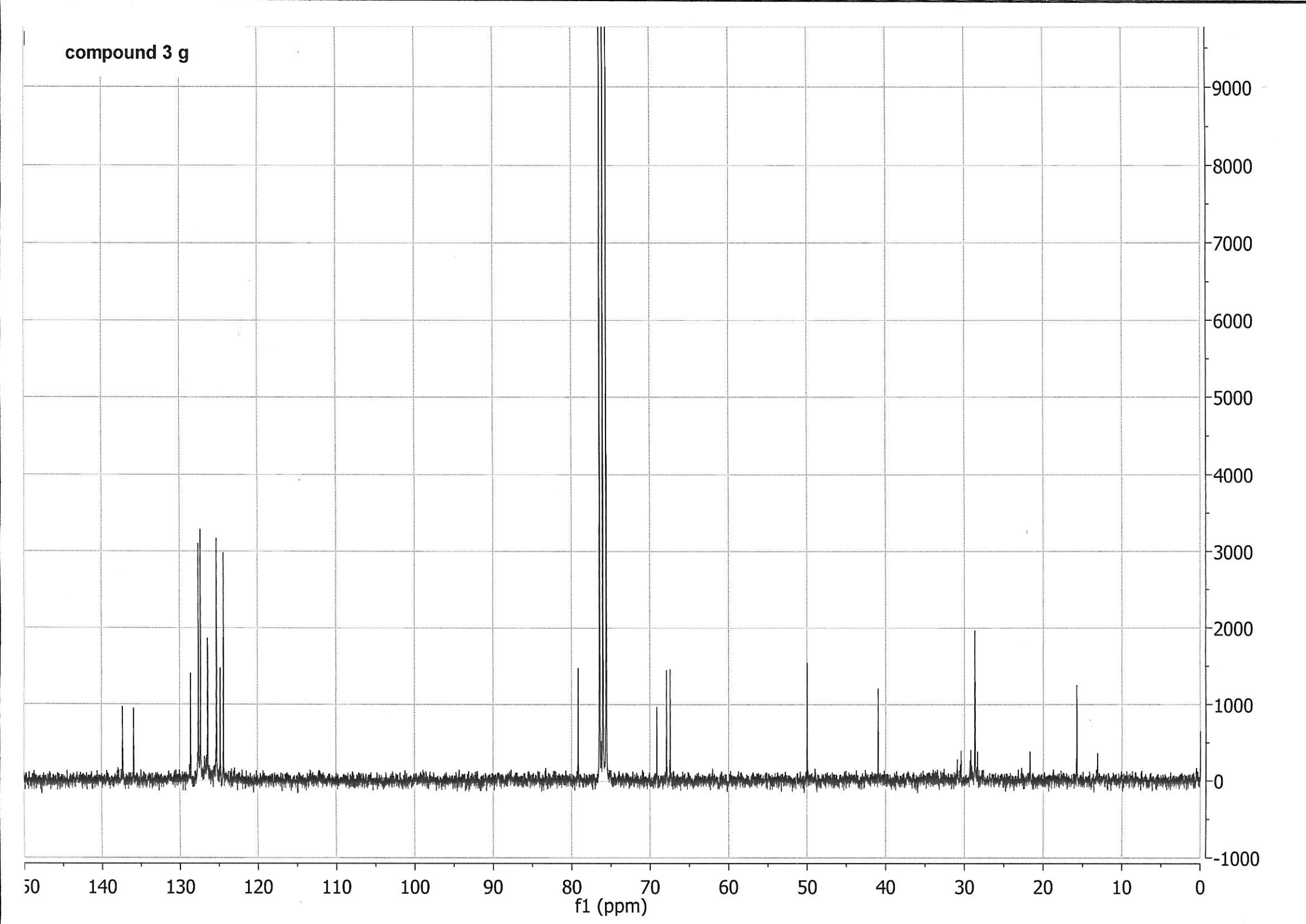

Compound 5d
1.01
1.01
2.00
1.01
4.01
1.02
1.03
f1 (ppm)

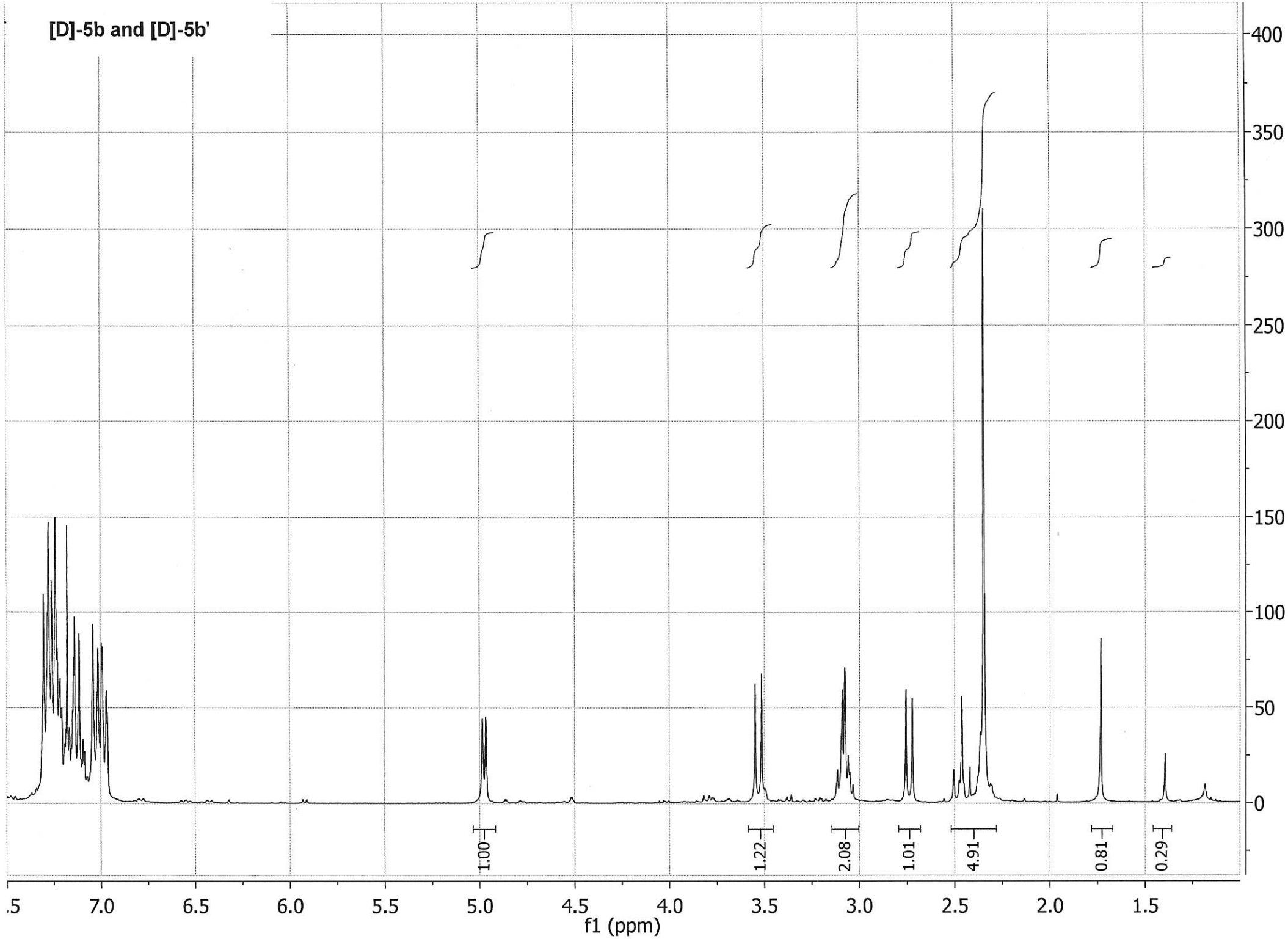

Compound 5d
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

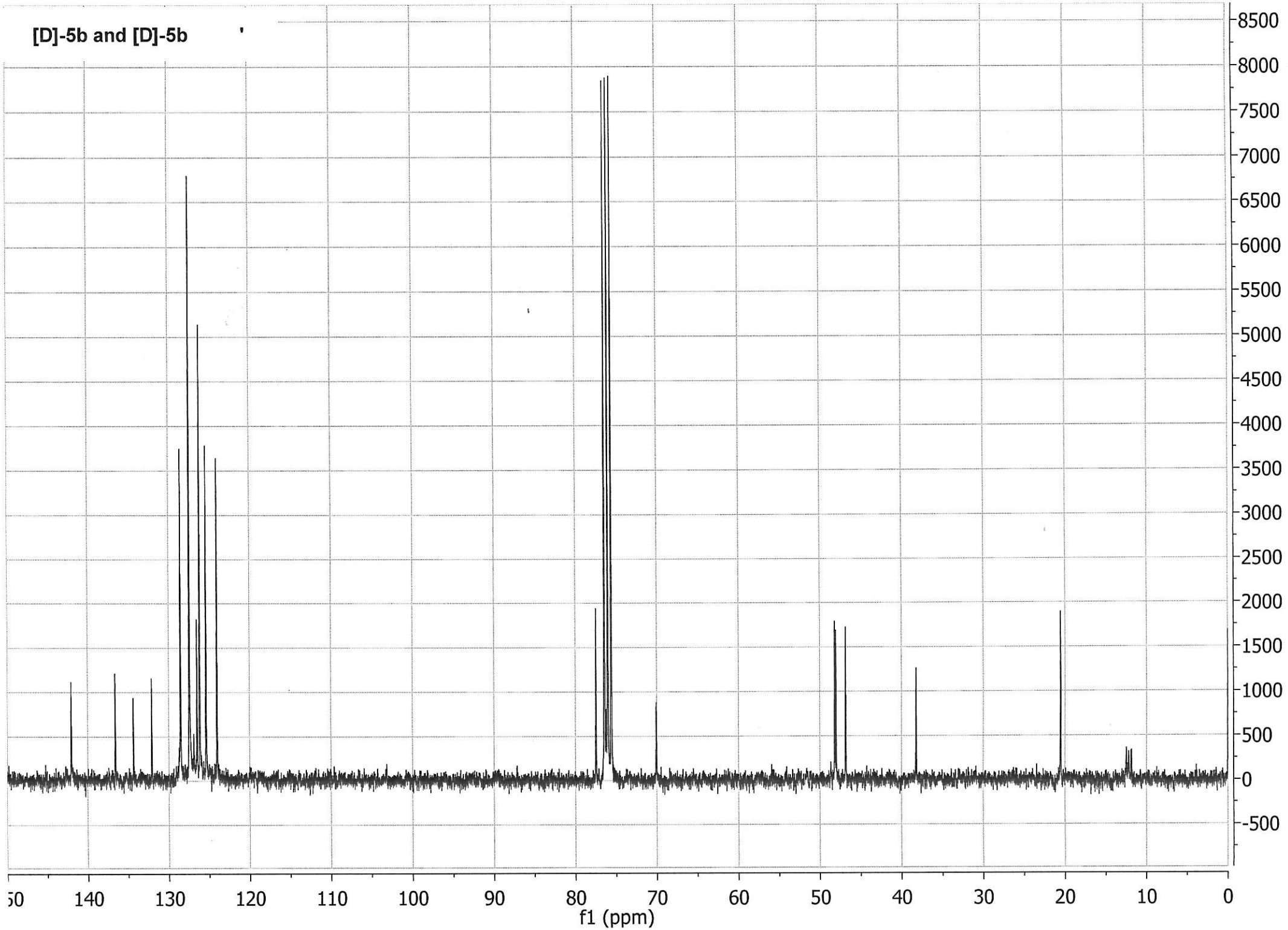

3b
1.00
1.01
1.05
1.10
1.06
1.09
2.00
2.90
1.34
3.95
1.33
f1 (ppm)

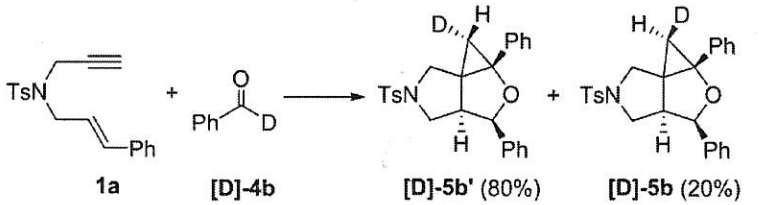

3b
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


compound 3g
1.00
1.00
1.00
1.18
1.08
1.01
1.98
1.00
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
f1 (ppm)

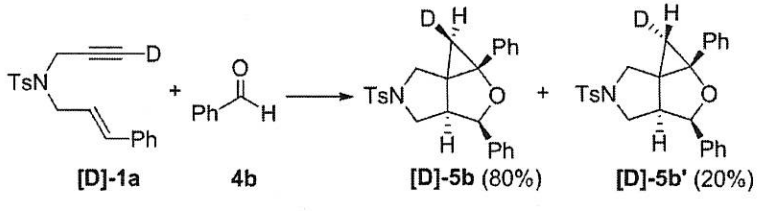

compound 3 g
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


[D]-5b and [D]-5b'
400
350
300
250
200
150
100
50
0
1.00
1.22
2.08
1.01
4.91
0.81
0.29
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

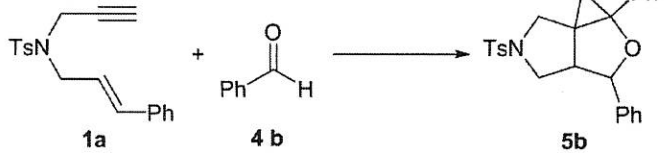

[D]-5b and [D]-5b
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



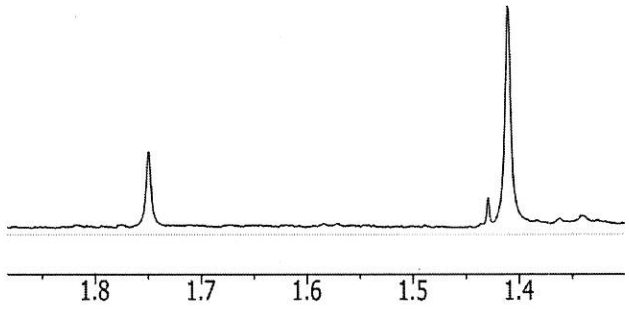
1a **[D]-4b** **[D]-5b'** (80%) **[D]-5b** (20%)

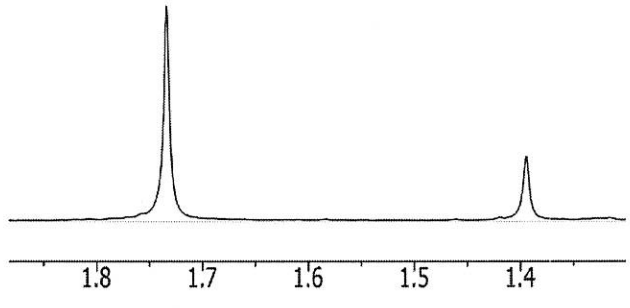


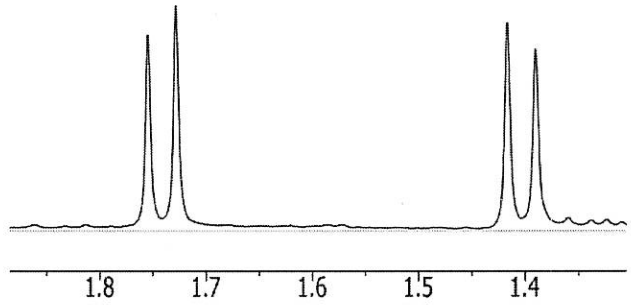
[D]-1a **4b** **[D]-5b** (80%) **[D]-5b'** (20%)



1a **4 b** **5b**







6. References

[1] K. Fourmy, S. Mallet-Ladeira, O. Dechy-Cabaret and M. Gouygou, *Dalton Trans.* **2014**, *43*, 6728-6734.
[2] K. Miura, H. Saito, N. Fujisawa and A. Hosomi, *J. Org. Chem.* **2000**, *65*, 8119-8122.
[3] K. T. Sylvester and P. J. Chirik, *J. Am. Chem. Soc.* **2009**, *131*, 8772-8774.
[4] A. Fürstner, F. Stelzer and H. Szillat, *J. Am. Chem. Soc.* **2001**, *123*, 11863-11869.
[5] T. Morimoto, K. Fuji, K. Tsutsumi and K. Kakiuchi, *J. Am. Chem. Soc.* **2002**, *124*, 3806-3807.
[6] J. T. Spletstoser, J. M. White and G. I. Georg, *Tetrahedron Lett.* **2004**, *45*, 2787-2789.
[7] a) K.-G. Ji, J. Chen, H.-T. Zhu, F. Yang, A. Shaukat and Y.-M. Liang, *Chem. Eur. J.* **2011**, *17*, 305-311; b) K.-G. Ji, X.-Z. Shu, S.-C. Zhao, H.-T. Zhu, Y.-N. Niu, X.-Y. Liu and Y.-M. Liang, *Org. Lett.* **2009**, *11*, 3206-3209.