Exploiting cross-metathesis reaction in the synthesis of pseudo-oligosaccharides

Paolo Ronchi[a], Stefano Vignando[a], Sara Guglieri[b], Laura Polito[a], Luigi Lay[a*].

[a]*Dipartimento di Chimica Organica e Industriale and Centro Interdisciplinare Studi Bio-molecolari e Applicazioni Industriali (CISI), Università degli Studi di Milano,Milano, Italy. Fax +39 0250314072 ; Tel: +39 0250314062; E-mail: luigi.lay@unimi.it*

[b]*Istituto di Chimica e Biochimica" G. Ronzoni", Milano, Italy. Fax: +39 0270641634 ; Tel +39 0270641627; E-mail: nmrlab@ronzoni.it*

Electronic Supporting Information

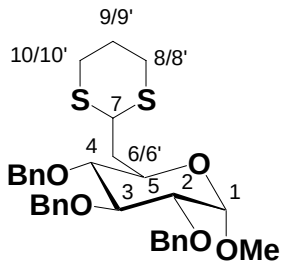
Additional experimental procedures, analytical data and copies of NMR spectra.

General Procedures.

NMR spectra were recorded on Bruker AC 300, Bruker Avance 400 and Bruker Avance 500 spectrometers at 298 K, if not differently reported. In ^{13}C NMR spectra, signals corresponding to aromatic carbons are omitted. Chemical shifts are reported on the δ (ppm) scale and the coupling costants are given in Hz. When possible, peaks assignments were based on the analysis of 2D spectra (H,H-COSY and HSQC or HMQC spectra). In particular, due to the scarce amount of available sample, ^{13}C assignment of compounds **36**/**37** has been based exclusively on HSQC spectrum. HRMS spectra were recorded in positive mode on Bruker Daltonics APEX^{TM} II (FT-ICR). Optical rotations were measured at room temperature with a Perkin-Elmer 241 polarimeter. HPLC analyses were performed with Varian 9050. Column Lichrocart 125-4 RP-18 5μm, flow rate 1 mL min^{-1}, UV monitor λ=210 nm. In all HPLC analyses, acetonitrile-water mixtures were used as eluent.

TLC and HPTLC were carried out on Merck Silica-gel 60 F-254 plates (0.25 mm and 0.2 mm thickness respectively), and spots were visualized by spraying with a solution containing H_2SO_4 (31 mL), ammonium molybdate (21 g) and $Ce(SO_4)_2$ (1 g) in 500 mL water, followed by heating at 110 °C for 5 min. Column chromatography was performed by the flash procedure using Merck Silica-gel 60 (230-400 mesh). Solvents were dried by standard procedures.

Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-[1,3]dithian-2-yl-methyl-α-D-glucopyranoside (3).

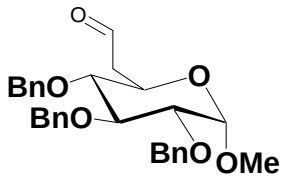


1,3-dithiane[1] (318 g, 2.65 mmol) was dissolved in dry THF (5 mL), under nitrogen atmosphere; the solution was cooled at –30°C and 1.6 M BuLi in hexane (2.62 mmol, 1.63 mL) was slowly added dropwise. After 30 min a solution of known[2] iodomethyl compound (304 mg, 0.53 mmol) in dry THF (5.3 mL) was slowly added at -20°C and successively the reaction was warmed at room temperature. The reaction was monitored by TLC (hexane-AcOEt 8:2).

After 30 min the reaction was diluited with CH_2Cl_2 (20 mL) and washed three times with NH_4Cl satd. sol. in water (3 x 15 mL); the organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. An analytical sample was obtained by flash chromatography (hexane-AcOEt 8:2).

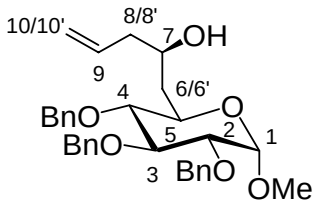
$[\alpha]_D^{22}$= +24.1 (c 1.2 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.40-7.28 (15H, H(Ar)), 5.01(1H, d, *J* 10.8, C*H*HPh), 4.93 (1H, d, *J* 11.0, C*H*HPh), 4.83 (2H, m, 2 x C*H*HPh), 4.68 (1H, d, *J* 11.0, C*H*HPh), 4.64 (1H, d, *J* 11.0, C*H*HPh), 4.55 (1H, d, *J* 3.5, 1-H), 4.19 (1H, dd, *J* 10.6 *J* 3.8, 7-H), 4.01 (1H, t, *J* 9.2, 3-H), 3.97 (1H, m, 5-H), 3.51 (1H, dd, *J* 3.5 *J* 9.6, 2-H), 3.45 (s, 3H, OCH_3), 3.21 (1H, t, *J* 9.3, 4-H), 2.86-2.71 (4H, m, 8-H, 8'-H', 10-H, 10'-H), 2.30 (m, H, 6'-H), 2.09 (m, 1H, 9-H), 1.90 (m, 1H, 9'-H), 1.76 (m, 1H, 6'-H); δ_C (100 MHz, $CDCl_3$) 97.90 (C-1), 82.03 (CH, C-4), 81.94 (CH, C-3), 80.09 (CH, C-2), 75.81-75.23-73.39 (CH_2Ph), 66.74 (CH, C-5), 55.57 (OCH_3), 43.09 (CH, C-7), 37.95 (CH_2, C-6), 29.94 (CH_2, C-8 or C-10), 29.34 (CH_2, C-8 or C-10), 25.98 (C-9); HRESIMS *m/z* 589.2058 (100) ($C_{32}H_{38}O_5S_2Na$ $[M+Na]^+$requires 589.2053).

Methyl 2,3,4-tri-*O*-benzyl-α-D-exodialdo-1,6 pyranoside (4)



Crude compound **3** was dissolved in a CH_3CN/H_2O (10.6 mL and 2.73 mL) mixture, then $NaHCO_3$ (89 mg, 1.06 mmol) and MeI (0.83 mL, 13.25 mmol) were added and the flask covered with an aluminium foil to prevent from light exposure. The reaction was stirred at room temperature for 16 hr and monitored by TLC (hexane-AcOEt 8:2). Then CH_2Cl_2 was added (15 mL) and the organic layer was washed with $NaHCO_3$ satd. sol. in water (3 x 15 mL) and brine (3 x 15 mL). The organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. An analytical sample was obtained by flash chromatography (hexane-AcOEt 8:2 + 1%TEA) afforded aldehyde **4** (184 mg, 73 %) as brown oil. The analytical data for aldehyde[2] **4** were in agreement with those reported in the literature.

(2R)-1-[Methyl 2,3,4-tri-*O*-benzyl-α-D-xilopyranosidyl]-4-penten-2-ol (5a, 5b).



(+)-B-methoxydiisocampheylborane[3] (2.595 g, 8.203 mmol) was dissolved in dry Et_2O (26 mL) under inert atmosphere (N_2). The solution was cooled at -78°C, then 1M AllMgBr solution in Et_2O (8.20 mL, 8.20 mmol) was added dropwise and the resulting mixture was stirred 15 min at -78°C and 1 h at rt. The solution was cooled to -78°C and a solution of the crude aldehyde **4** (5.47 mmol) in dry Et_2O, previously cooled at -78°C, was added dropwise. The solution was stirred for 1.5 h at this temperature then warmed at room temperature and stirred for further 1.5 h, monitoring its progress by TLC (toluene-AcOEt 8:2). $(Ipc)_2B$ group hydrolysis was performed by refluxing overnight the reaction in a 1:1 mixture of 3 N aq. NaOH (25 mL) and 30% v/v H_2O_2 (25 mL).
The reaction was diluted with CH_2Cl_2 (50 mL) and washed with NH_4Cl satd. sol. in water (3 x 30ml). The aqueous phase was re-extracted with CH_2Cl_2 and the collected organic phases were dried and the solvent was evaporated under reduced pressure. The crude was purified by flash chromatography (toluene-AcOEt 85:15 to 8:2 gradient elution) affording **5a** (2.07 g, 73 % yield) as

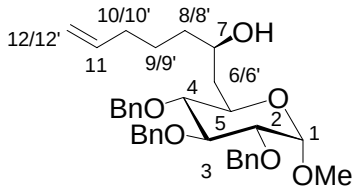
a white foam.

$[\alpha]_D^{22}$= +79.5 (c 0.55 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$, **5a** major isomer (R)):7.41-7.29 (15H, m, , CH(Ar)), 5.88-5.78 (1H, m, 9-H), 5.14-5.11 (2H, m, 10-H 10'-H), 5.03 (1H, d, *J* 11.0, C*H*HPh), 4.93 (1H, d, *J* 11.2, C*H*HPh), 4.86 (1H, d, *J* 10.8, C*H*HPh), 4.84 (1H, d, *J* 12.0, C*H*HPh), 4.70 (1H, d, *J* 12.0, C*H*HPh), 4.63 (1H, d, *J* 11.2, C*H*HPh), 4.59 (1H, d, *J* 3.6, 1-H), 3.99 (1H, t, *J* 9.2, 3-H), 3.89-3.82 (m, 2H, 7-H 5-H), 3.55(1H, dd, *J* 3.6 9.6, 2-H), 3.43 (3H, s, OC*H*$_3$), 3.24 (1H, t, *J* 9.2, 4-H), 3.21 (1H, bs, OH), 2.31-2.17 (m, 2H, 8-H 8'-H), 2.10-2.06 (m, 1H, 6'-H), 1.48-1.40 (m, 1H, 6'-H); δ_H (400 MHz, $CDCl_3$) 134.75 (CH, C-9) 117.49 (CH_2, C-10), 98.11 (CH, C-1), 82.02 (CH, C-4), 81.72 (CH, C-3), 79.87 (CH, C-2), 75.84, 75.43, 73.49 (*C*H_2Ph) 71.44 (CH, C-5 or C-7), 71.17 (CH, C-5 or C-7), 55.44 (O*C*H_3), 39.09 (CH_2, C-8), 34.43 (CH_2, C-6). HRESIMS *m/z* 541.2562 (100) ($C_{32}H_{38}O_6Na$ $[M+Na]^+$ requires 541.2560).

1-[Methyl 2,3,4-tri-*O*-benzyl-α-D-xilopyranosidyl]-6-epten-2-ol (6a, 6b).

Aldehyde **4** (781 mg, 1.65 mmol) was dissolved in dry Et_2O (20 mL) under nitrogen atmosphere. The clear solution was cooled at -78°C and 1M 1-pentenyl magnesium bromide[4] in Et_2O (4.11 mL, 4.11 mmol) was added dropwise under stirring. The resulting solution was stirred 2 h at -78°C and 2 h at rt. The reaction was monitored by TLC (dichloromethane-AcOEt 95:5).

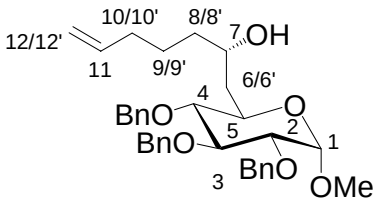
The reaction was diluted with Et_2O (20 mL) was washed with NH_4Cl satd. solution in water (2 x 15), water (2 x 15 mL) and brine (2 x 15 mL). The aqueous phases were re-extracted with CH_2Cl_2 and the collected organic phases were dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The crude was purified by flash chromatography (dichloromethane: AcOEt 97:3 to 95:5 gradient elution) affording **6a** and **6b** (66% overall yield, 600 mg) as two separated diastereoisomers (7R:7S=58:42).



6a

$[\alpha]_D^{25}$ = + 23.7 (c 0.8 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$, **6a**) 7.37-7.28 (m, 15H, H(Ar)), 5.82 (1H, m, 11-H), 5.04-4.91 (4H, m, 12-H 12'-H 2 x C*H*HPh), 4.83 (2H, m, 2 x C*H*HPh), 4.71 (1H, d, *J* 12.8, C*H*HPh), 4.61 (1H, d, *J* 12.8, C*H*HPh), 4.52 (1H, d, *J* 3.3, 1-H), 4.00 (1H, t, *J* 9.2, 3-H), 3.85-3.77 (2H, m, 5-H 7-H), 3.53 (1H, dd, *J* 3.5 *J* 9.7, 2-H), 3.42 (3H, s, OC*H*$_3$), 3.23 (2H, m, 4-H, O*H*),

2.09-2.04 (2H, m, 10'-H 10'-H), 1.98 (1H, bd, *J* 14.4, 6-H), 1.55-1.28 (m, 5H, 8-H, 8'-H, 9-H, 9'-H, 6'-H); δ_C (100 MHz, $CDCl_3$, 3a) 139.41 (CH, C-11), 115.17 (CH_2, C-12), 98.75 (CH, C-1), 82.72 (CH, C-4), 82.36 (CH, C-3), 80.49 (CH, C-2), 76.50, 76.07, 74.14 (*C*H_2Ph), 72.42 (CH, C-5 or C-7), 72.35 (CH, C-5 or C-7), 56.11 (O*C*H_3), 39.00 (CH_2, C-6), 34.37 (CH_2, C-10), 37.65 (CH_2, C-8 or C-9), 25.30 (CH_2, C-8 or C-9); HRESIMS *m/z* 569.2870 (100) ($C_{32}H_{38}O_6Na$ $[M+Na]^+$ requires 569.2873).

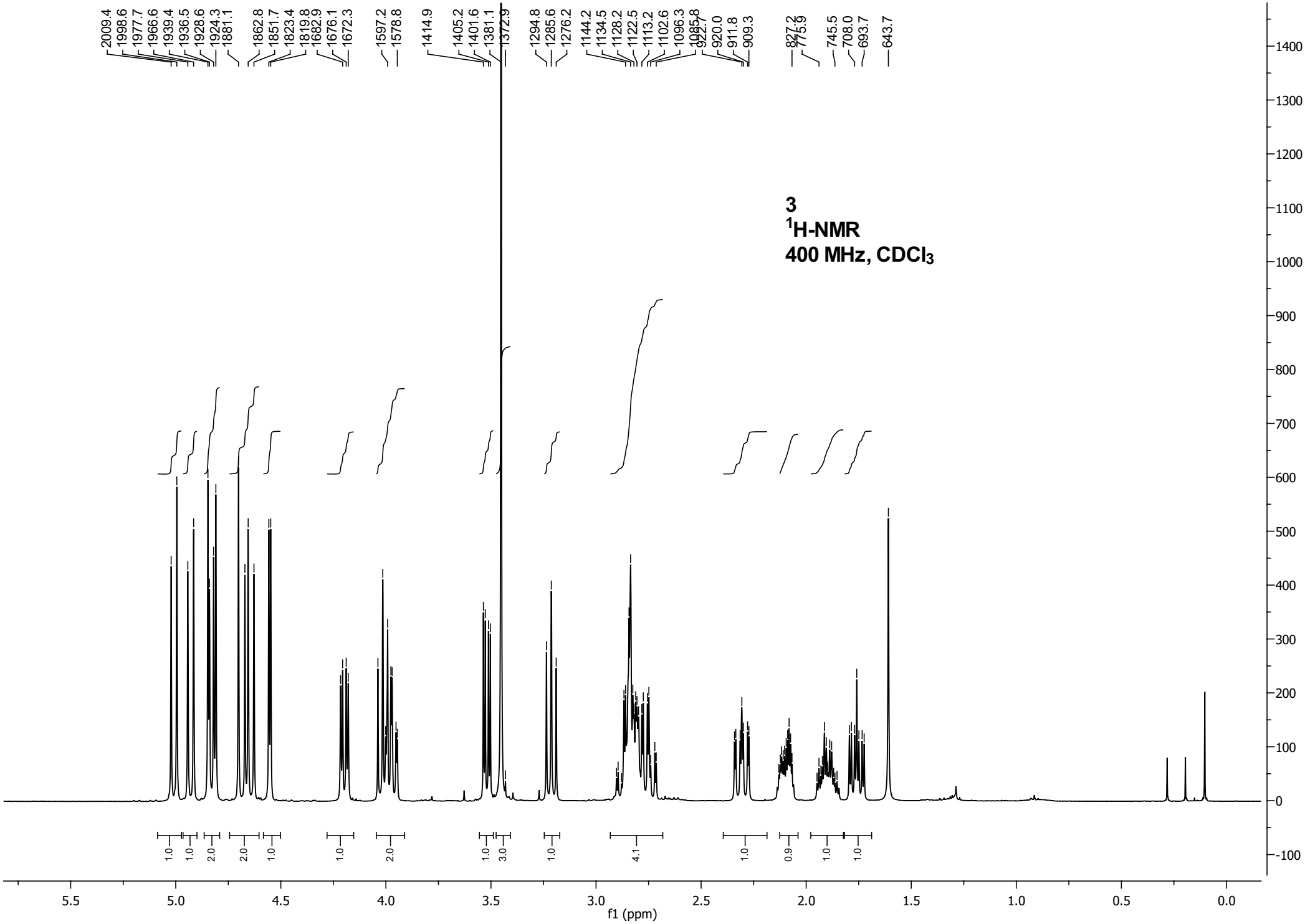


6b

$[\alpha]_D^{25}$ =+ 4.4 (c 0.5 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$, **6b**) 7.39-7.28 (15H, m, H(Ar)), 5.81 (1H, m, 11-H), 5.05-4.96 (4H, m, H-12 H-12' 2 x *CH*HPh), 4.93 (1H, d, *J* 13.4, C*H*HPh), 4.80 (1H, d, C*H*HPh), 4.85-4.81 (2H, m, 2 x C*H*HPh), 4.70 (1H, d, *J* 12.0, C*H*HPh), 4.61 (1H, d, *J* 11.2, C*H*HPh), 4.56 (1H, d, *J* 3.2, 1-H), 4.00 (1H, bt, *J* 9.2, 3-H), 3.99-3.94 (1H, m, 5-H), 3.80 (1H, m, 7-H), 3.53 (1H, dd, *J* 3.2, *J* 9.6, 2-H), 3.41 (3H, s, OC*H*$_3$), 3.28 (1H, bt, *J* 9.2, 4-H) 2.18 (1H, d, O*H*), 2.10-2.07 (2H, m, 10-H 10'-H), 1.82 (1H, m, 6-H), 1.64 (1H, m, 6'-H), 1.53-1.28 (m, 4H, 9-H 9'-H, 8-H 8'-H); δ_C (100 MHz, $CDCl_3$, 3b) 138.66 (CH, C-11), 114.58 (CH_2, C-12), 98.00 (CH, C-1), 82.03 (CH, C-4), 81.15 (CH, C-3), 80.10 (CH, C-2), 75.76, 75.09, 73.41 (*C*H_2Ph) 68.50 (CH, C-7), 67.96 (CH, C-5), 55.45 (O*C*H_3), 38.01 (CH_2, C-10), 33.67 (CH_2, C-6), 37.17 (CH_2, C-8 or C-9), 24.94 (CH_2, C-8 or C-9); HRESIMS *m/z* 569.2874 (100) ($C_{32}H_{38}O_6Na$ $[M+Na]^+$ requires 569.2873).

References

[1] N. Hori, H. Matsukura, G. Matsuo, T. Nakata, *Tetrahedron*, **2002**, 58, 1853-1864.
[2] K.S. Ko, C.J. Zea, N.L. Pohl, *J. Am. Chem. Soc.*, **2004**, *126*, 13188-13189.
[3] J.D. White, R. Hanselmann, R.W. Jackson, W.J. Porter, Y. Ohba, T. Tiller, S. Wang, *J. Org. Chem.,* **2001**, *66*, 5217-5131
[4] S. C. Hung, C. H. Wong, *Tetrahedron Lett.* **1996**, 37, 4903-4906.
[5] Grignard reagent was prepared as follows: Mg (486 mg, 20 mmol) in dry Et_2O (10 mL) was treated with a catalytic amount of 1,2 dibromoethane (100 μL) under N_2 atmosphere until gaseous ethylene appears. The solution was cooled to 0°C and a solution of 5-bromo-pentene (1.2 mL, 10 mmol) was slowly added. When addition was complete the reaction was stirred at rt for 1 hr and the 1M solution immediately used.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1936.5
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1851.7
1823.4
1819.8
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1414.9
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1276.2
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1113.2
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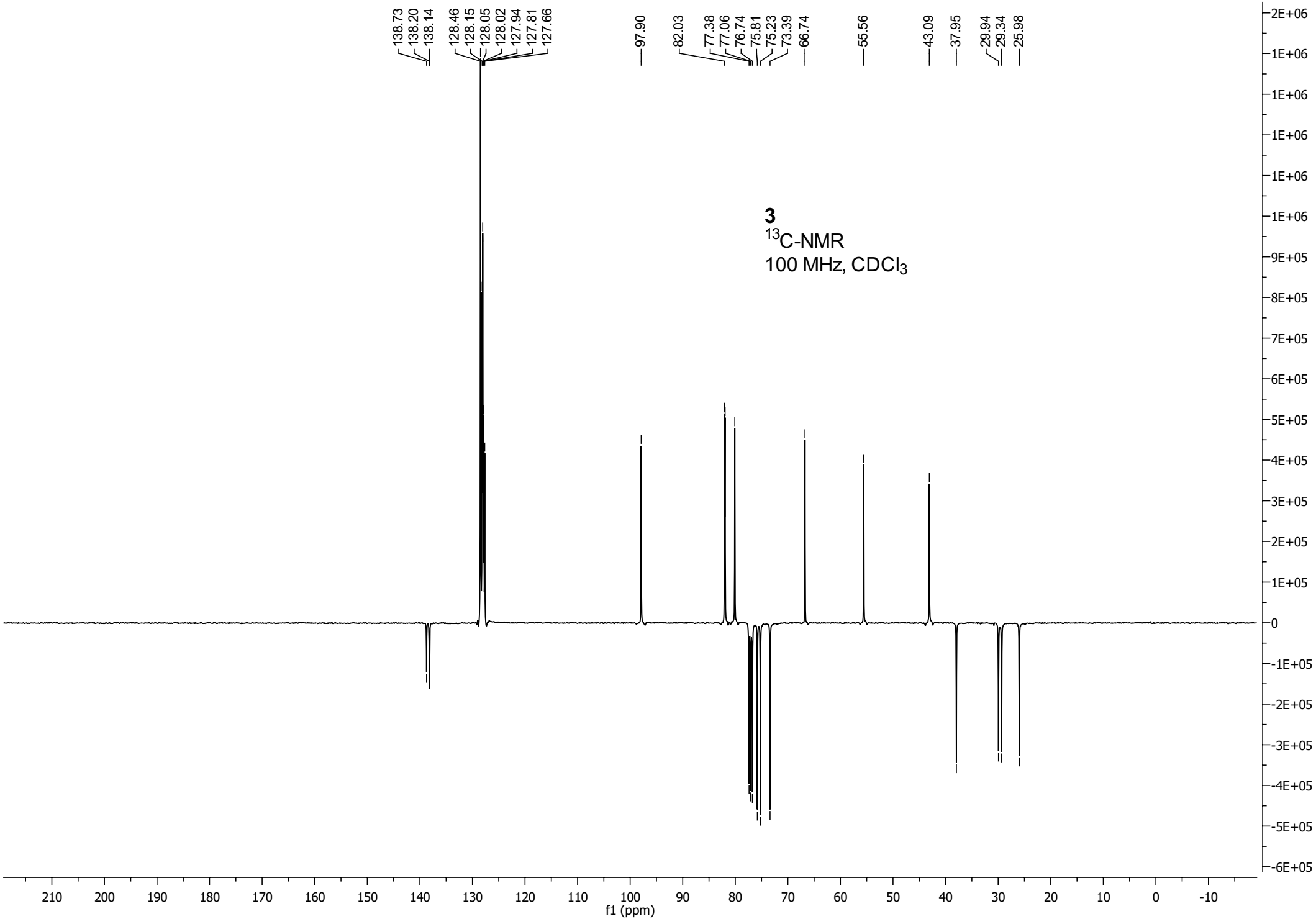
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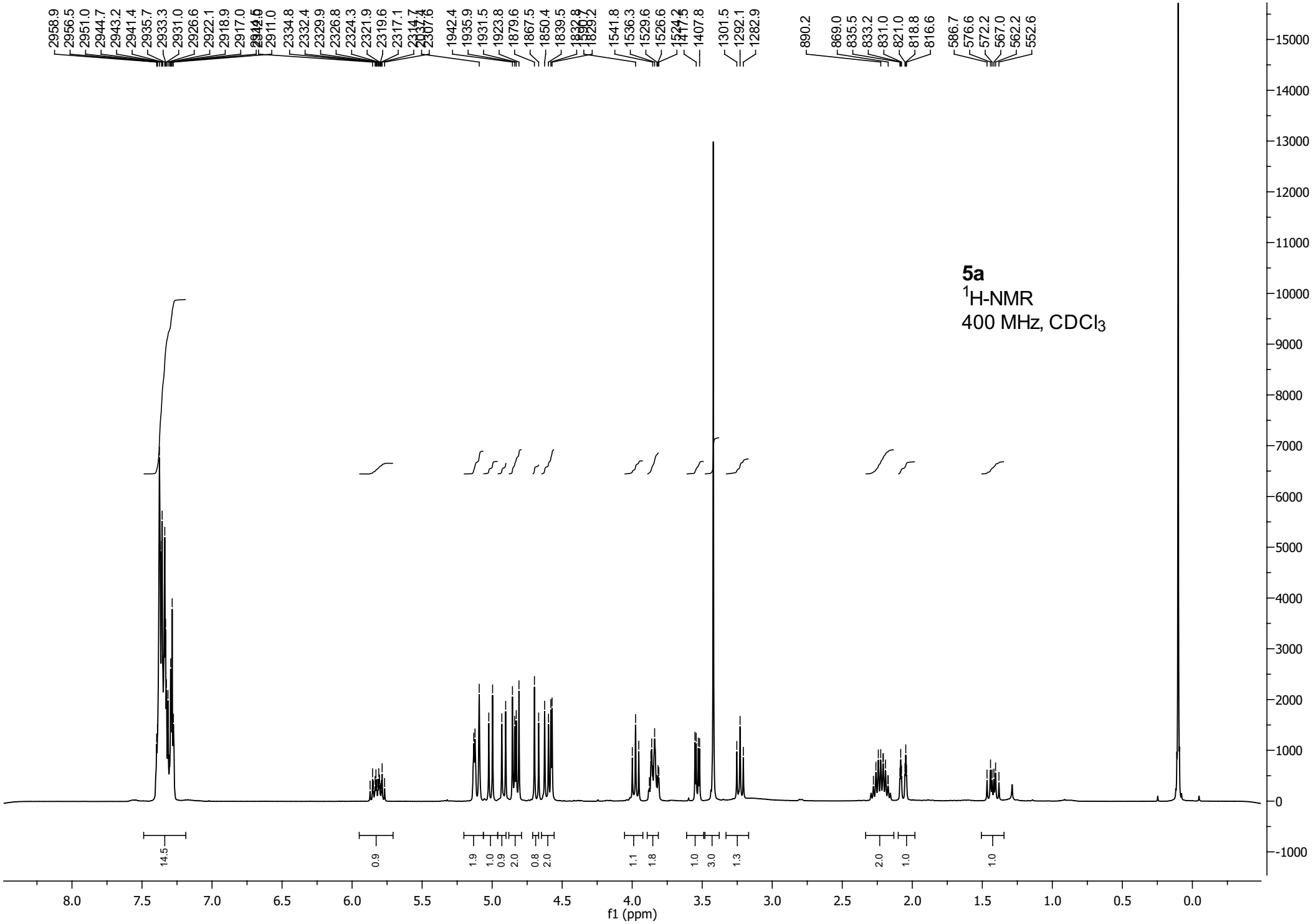
100 MHz, CDCl3
f1 (ppm)


5a
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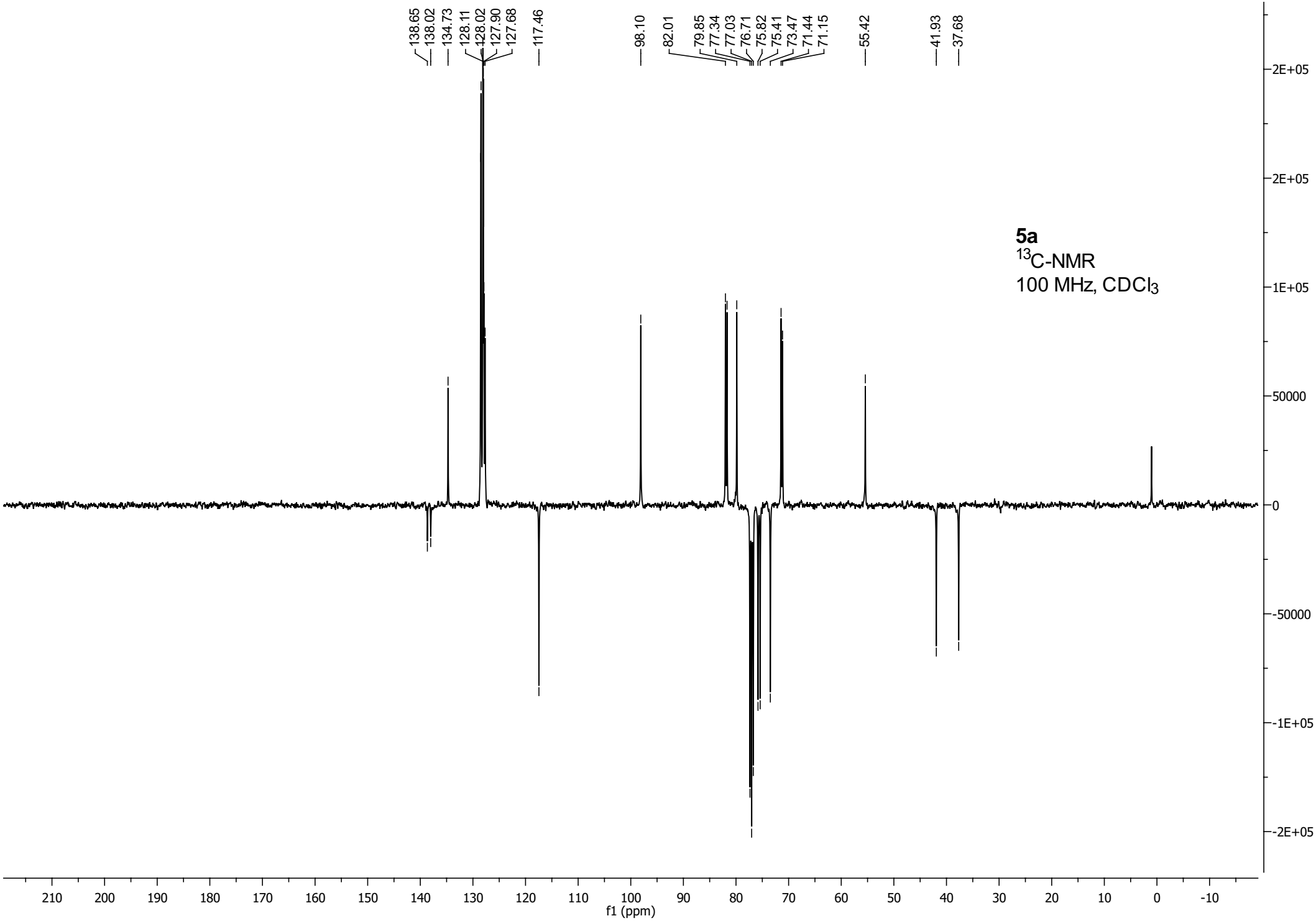
400 MHz, CDCl3
f1 (ppm)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55.42
41.93
37.68
5a
13C-NMR
100 MHz, CDCl3
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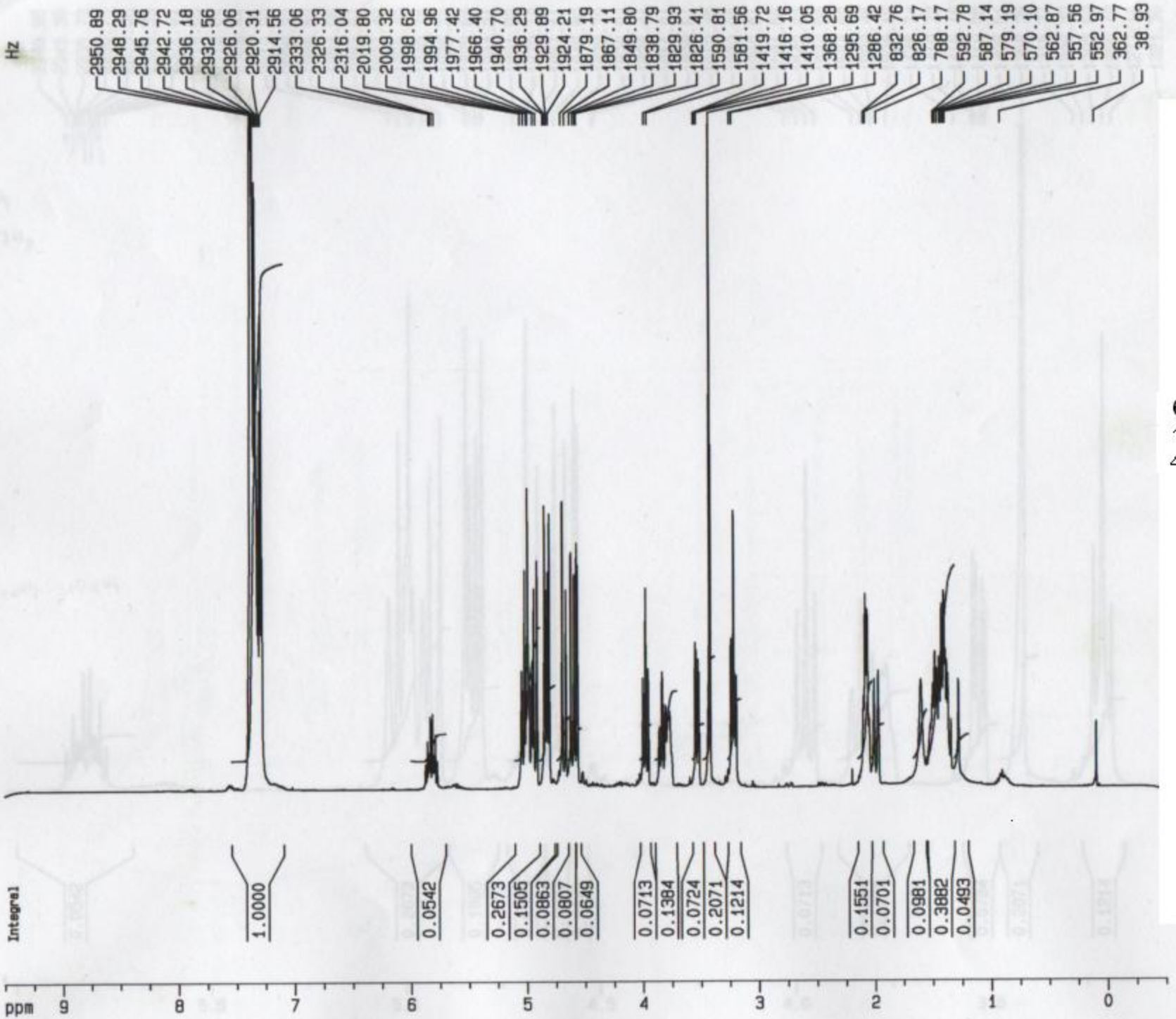
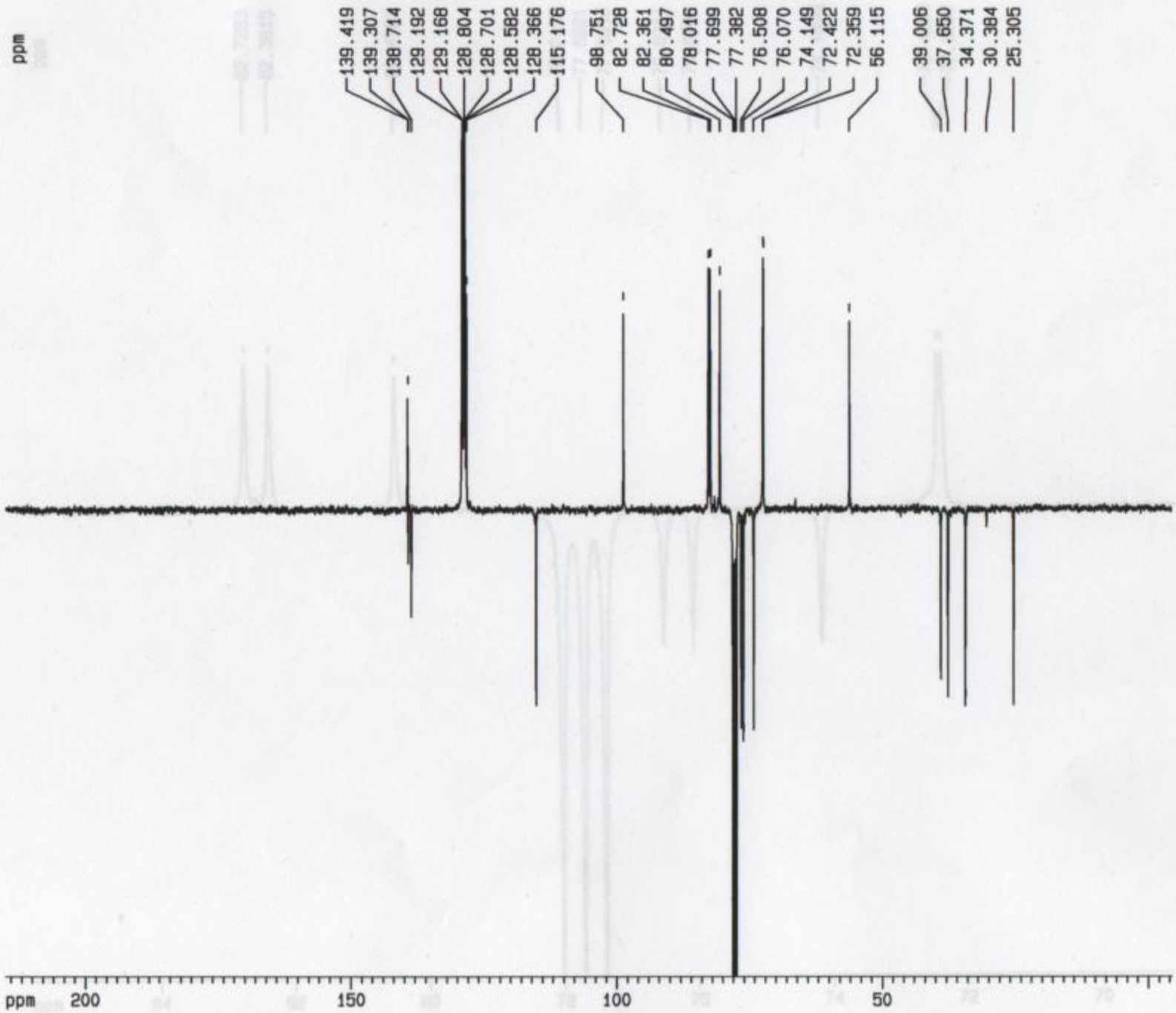


6a
1H-NMR
400 MHz, CDCl3



6a
13C-NMR
100 MHz, CDCl3

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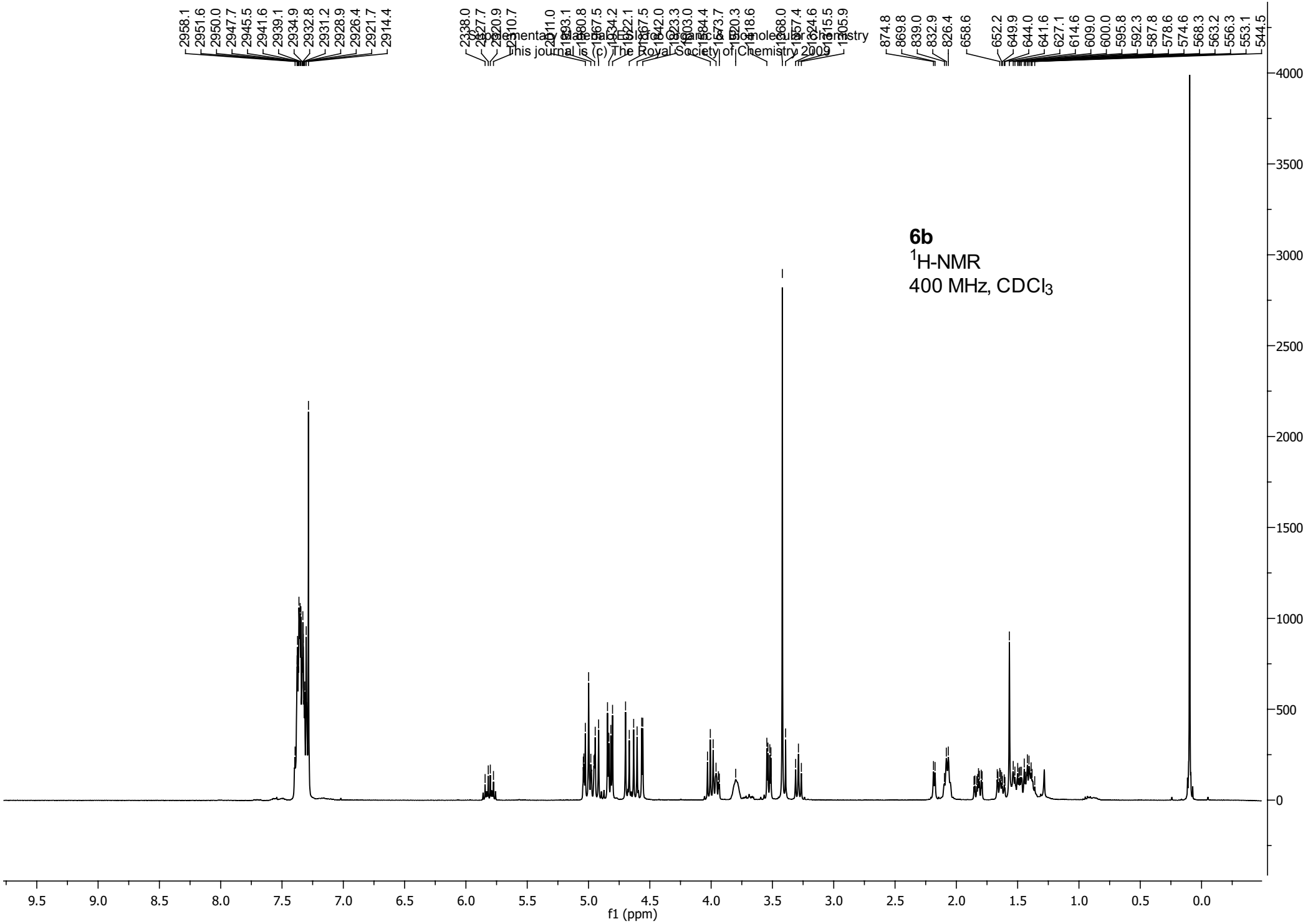

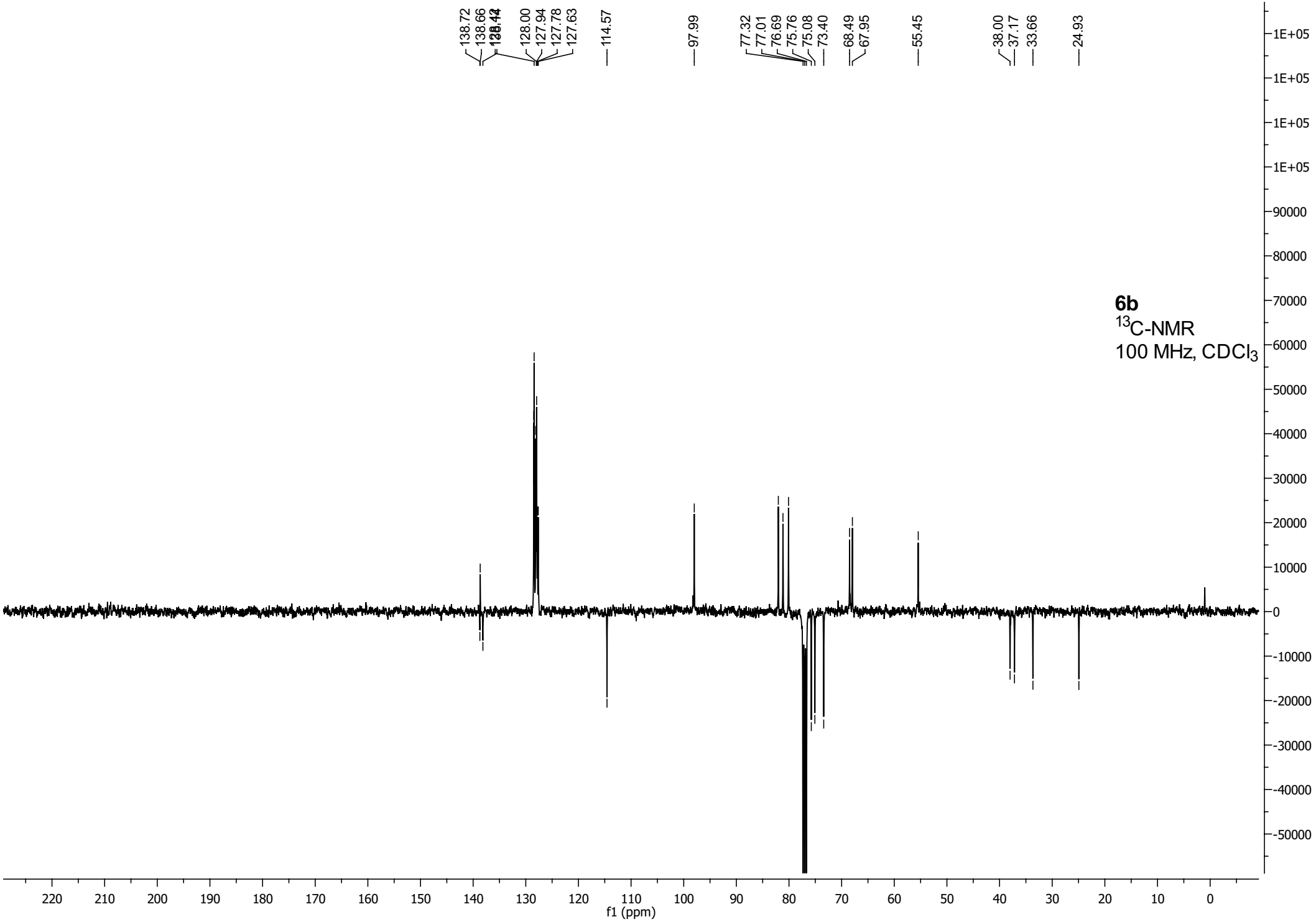
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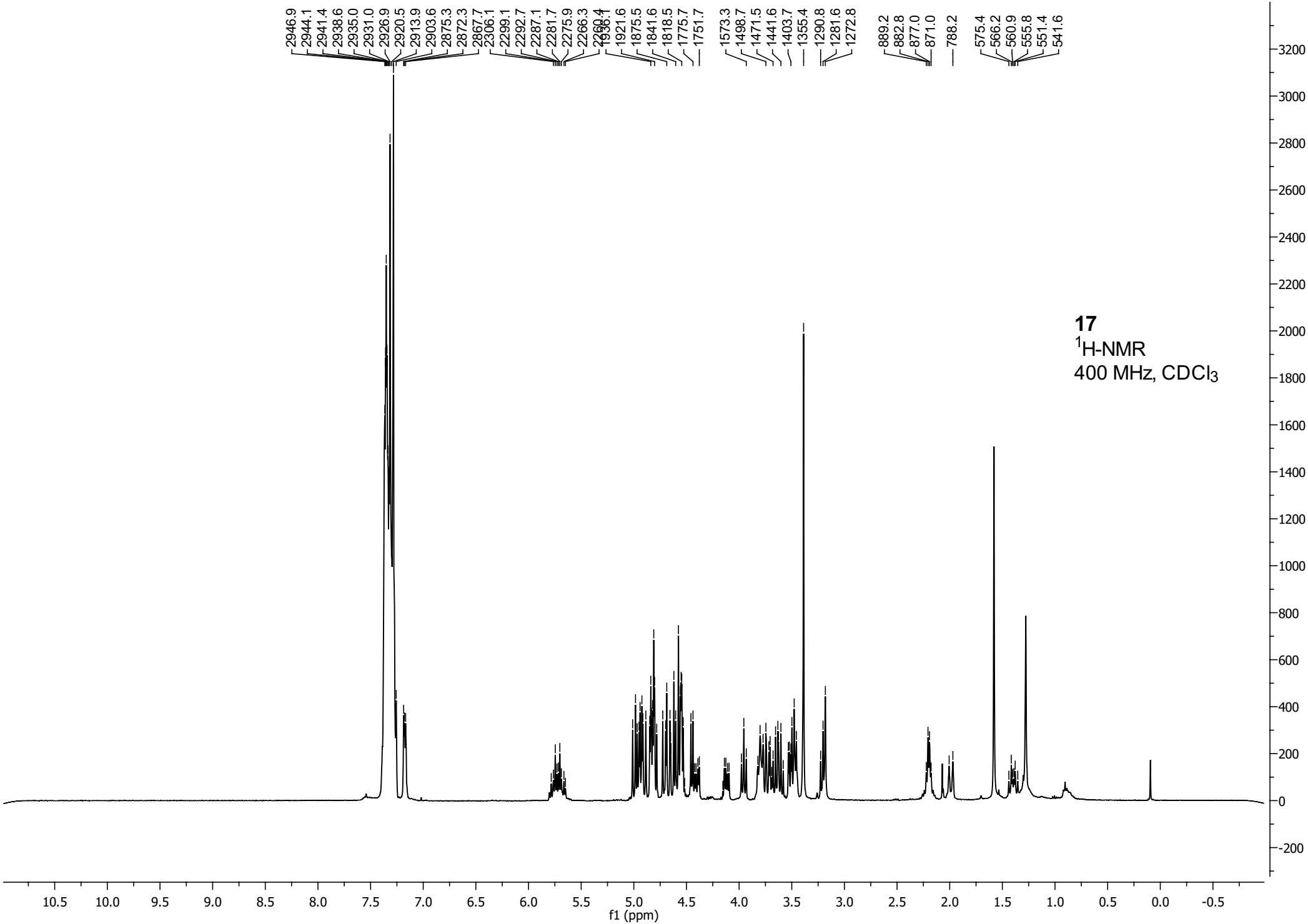
f1 (ppm)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17
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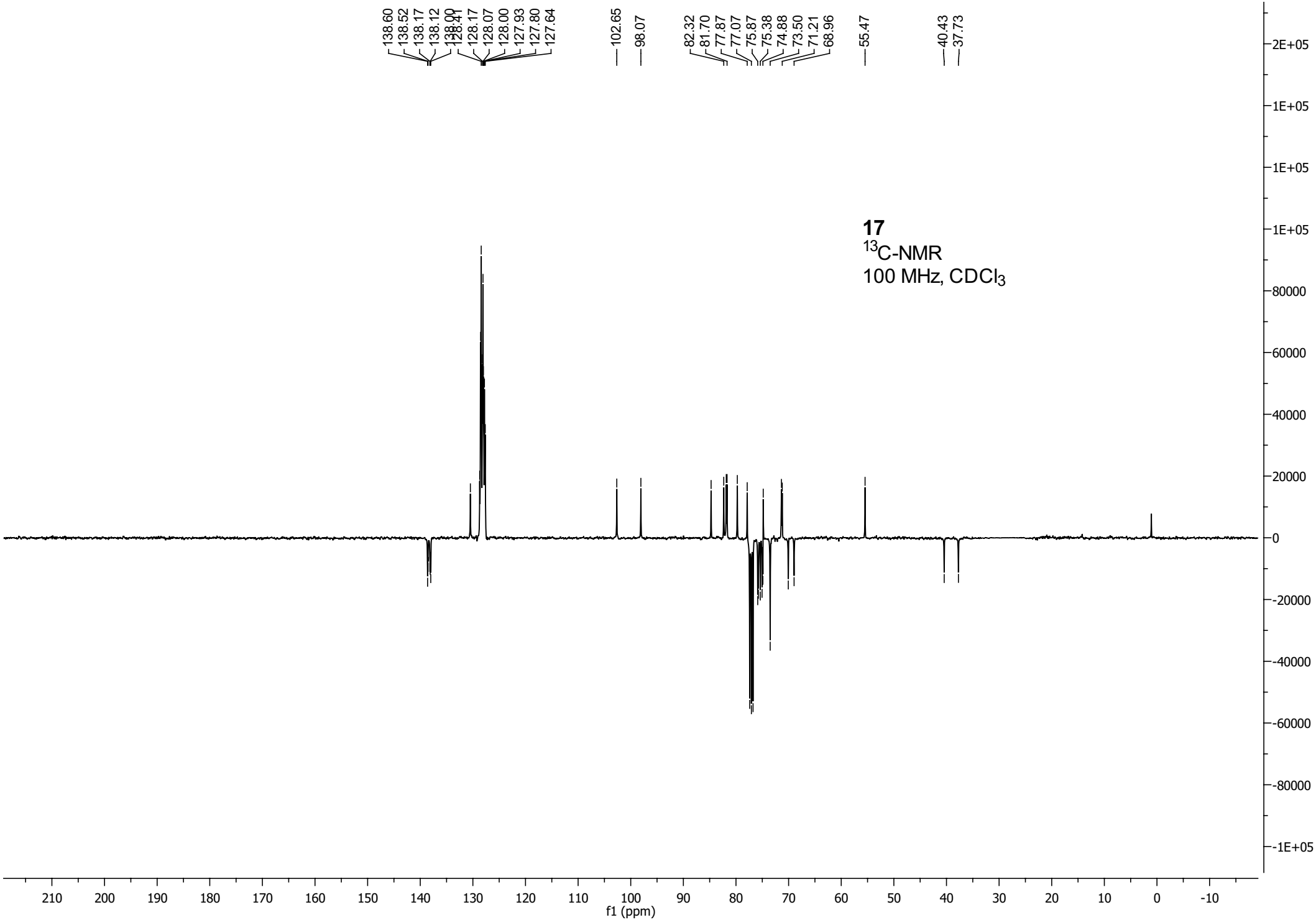
400 MHz, CDCl3
f1 (ppm)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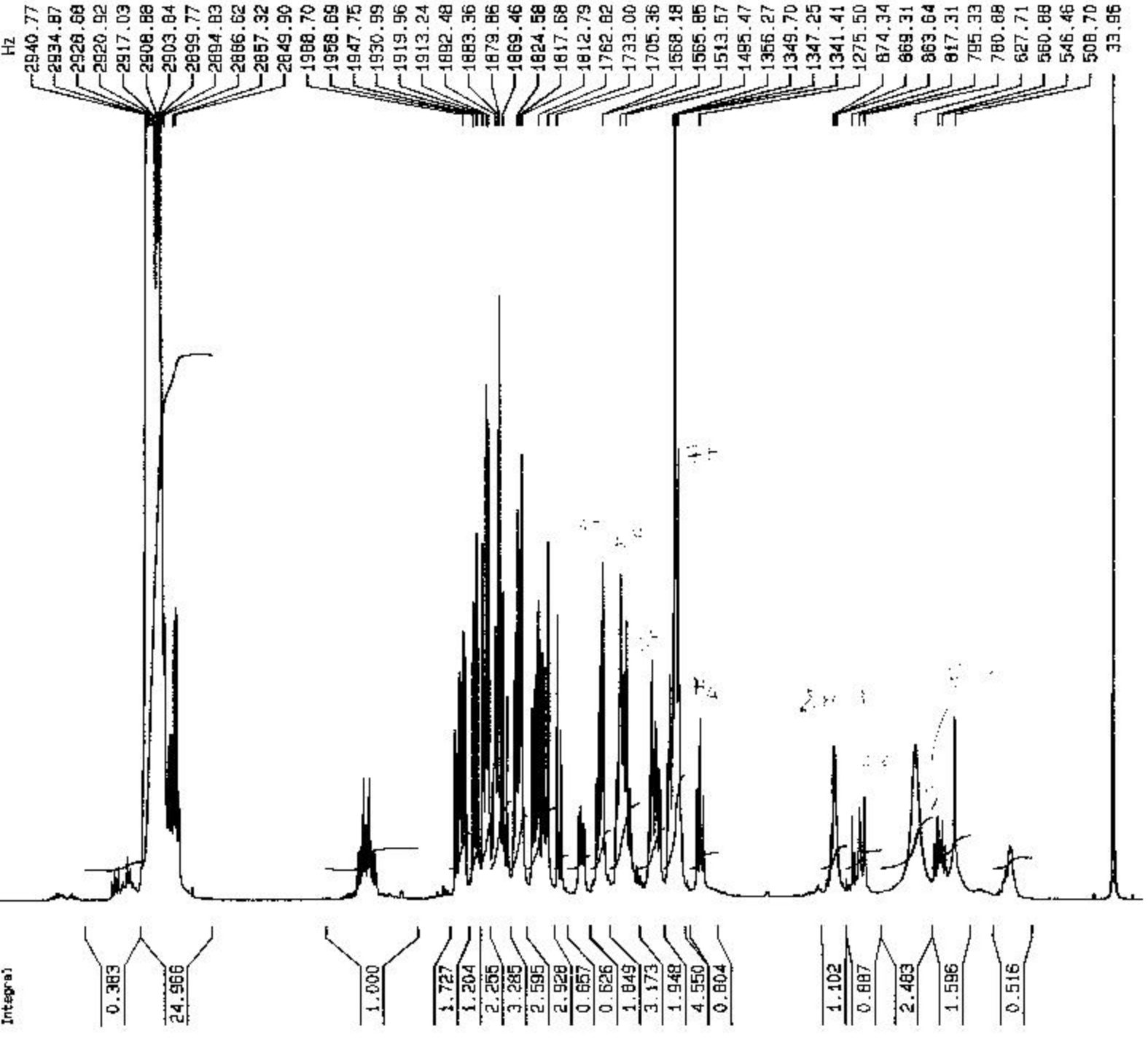
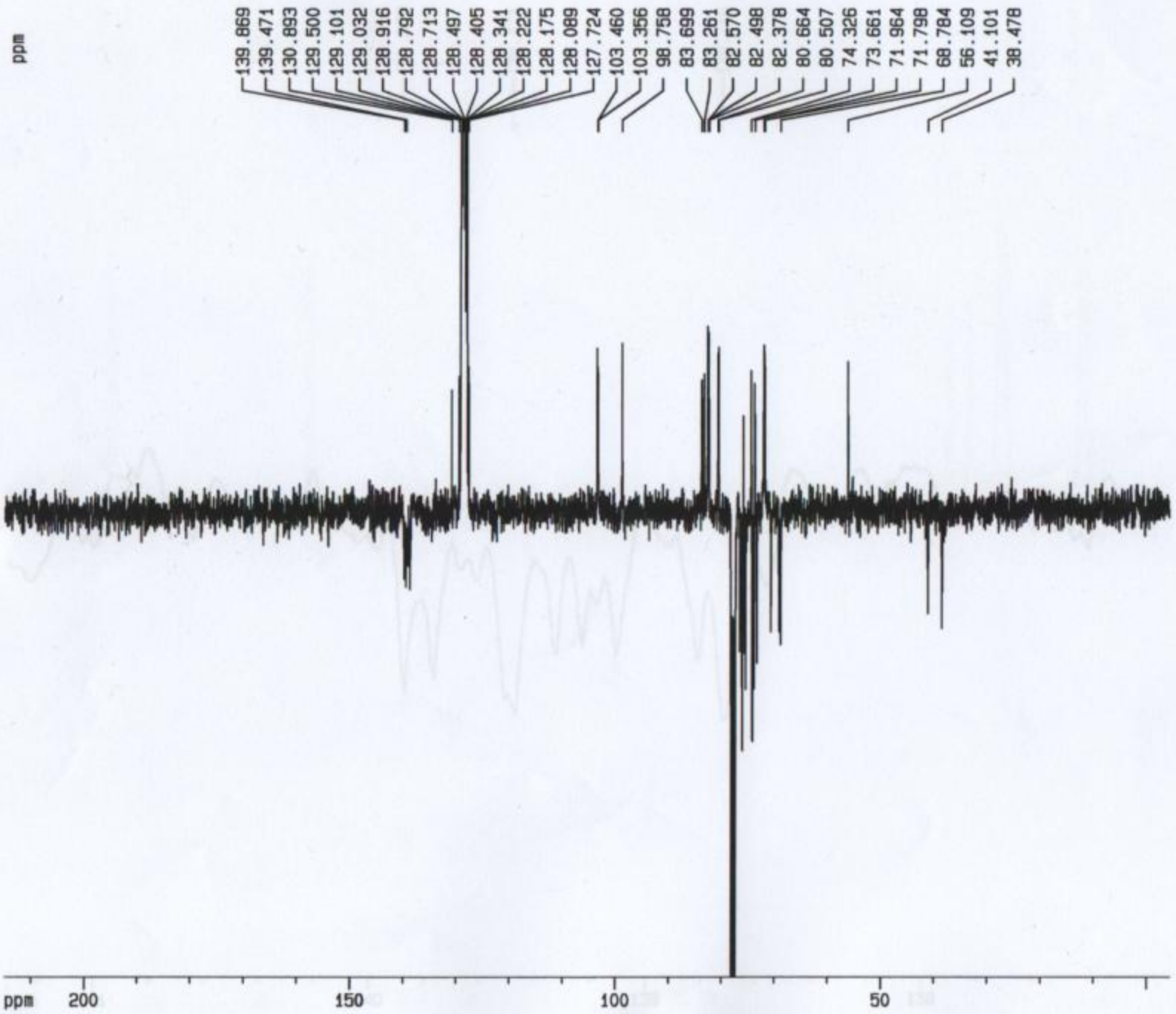
f1 (ppm)



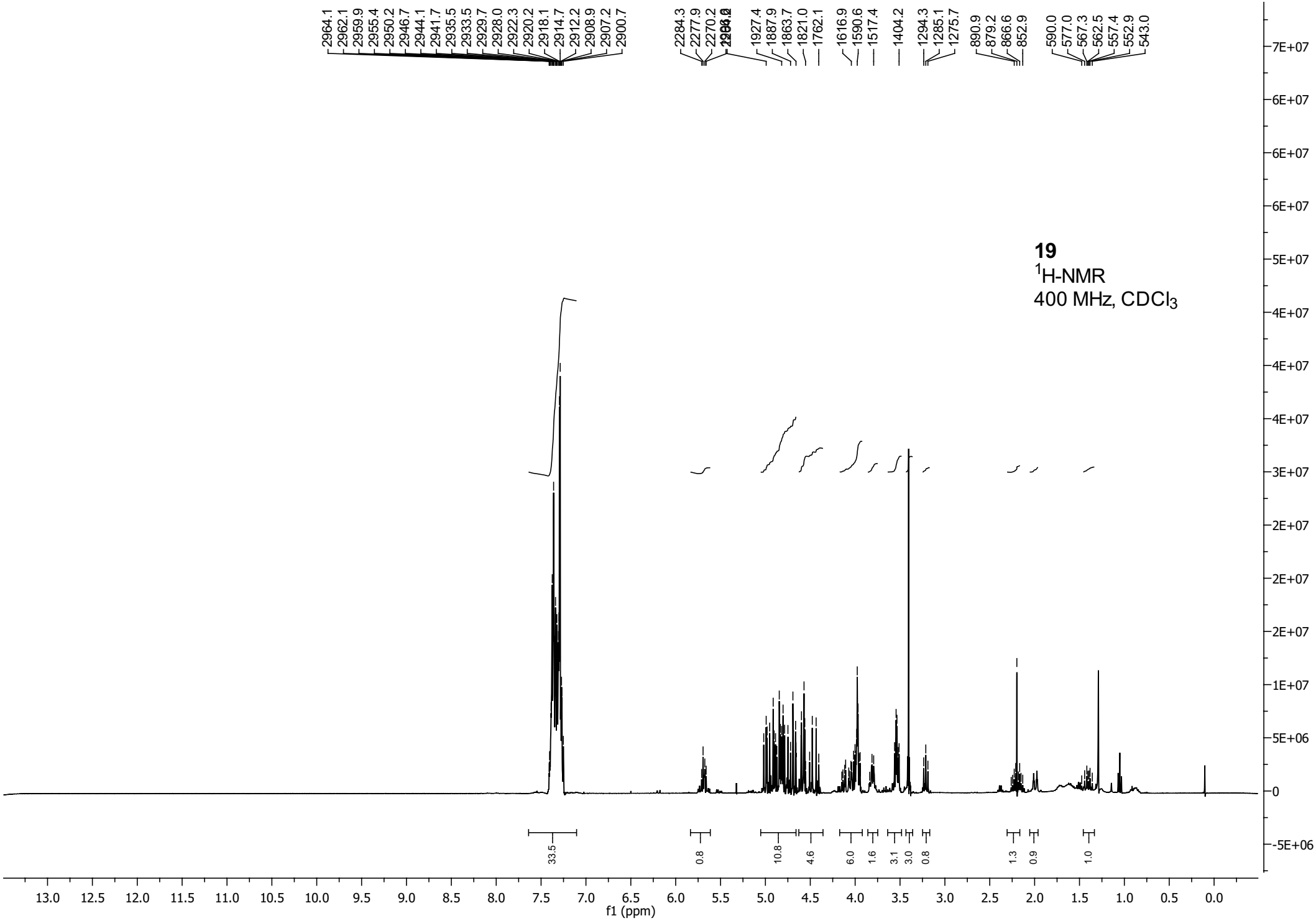
18

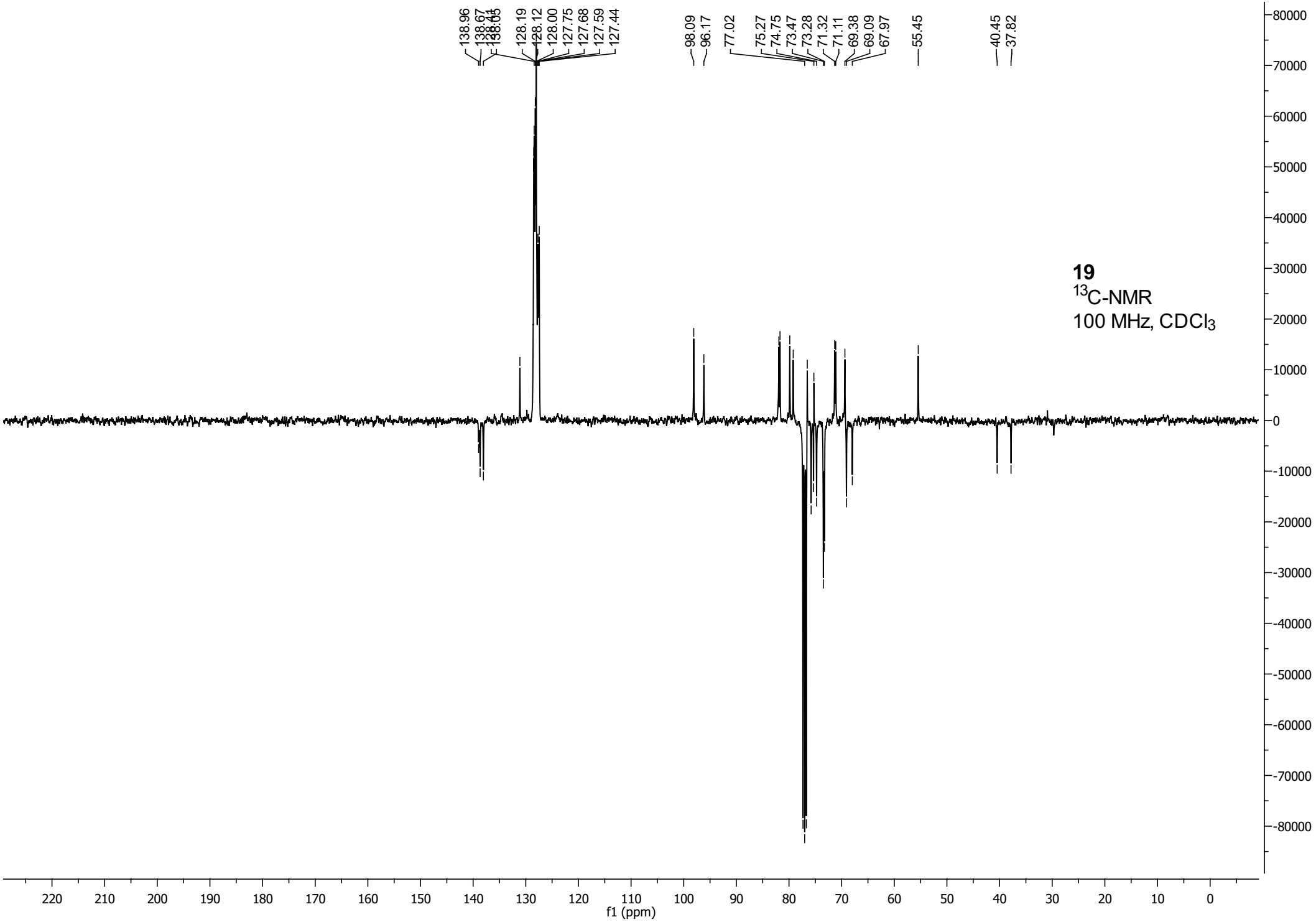
1H-NMR
400 MHz, CDCl3



18

13C-NMR
100 MHz, CDCl3


19
1H-NMR
400 MHz, CDCl3
f1 (ppm)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138.67
128.19
128.12
128.00
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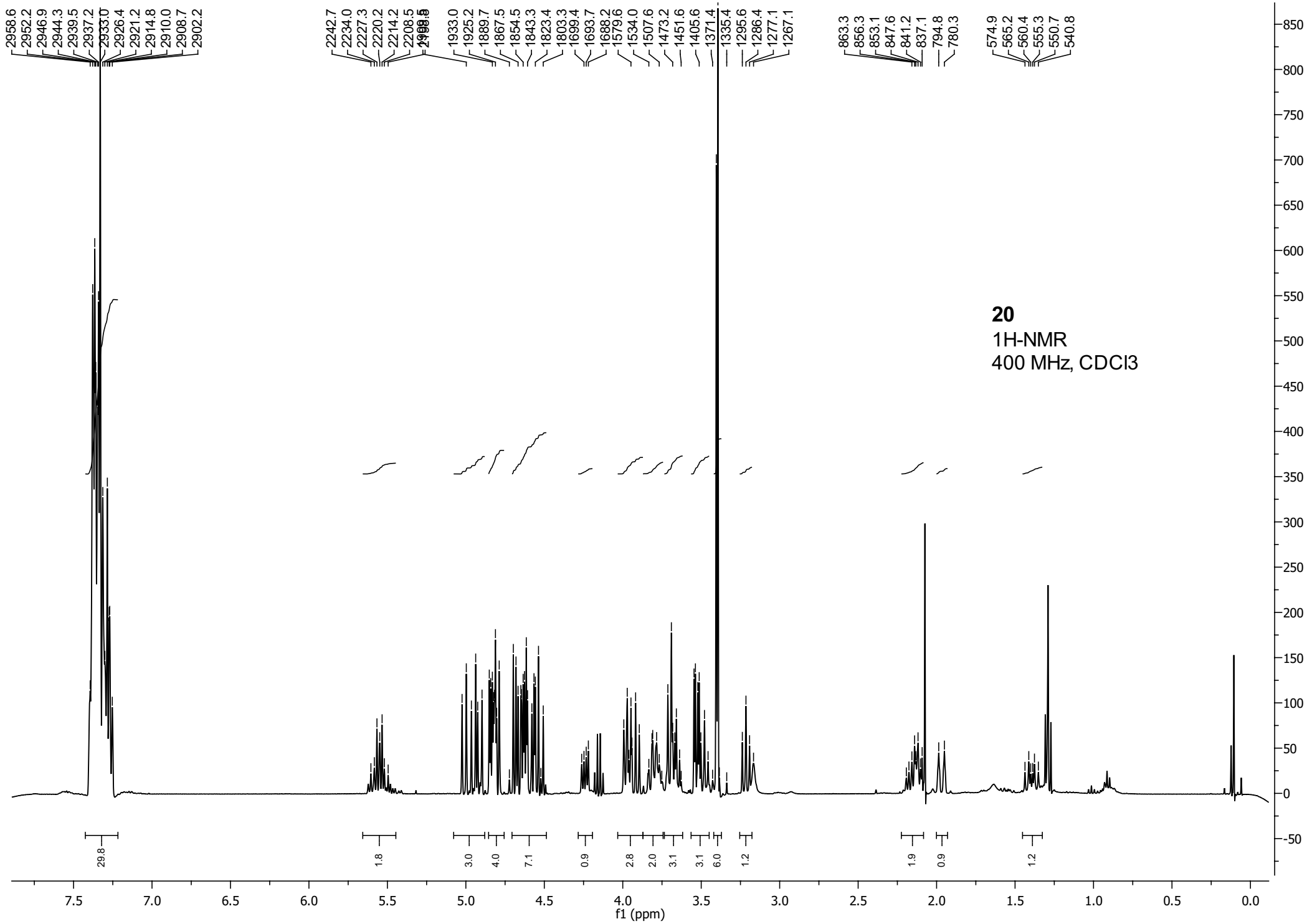
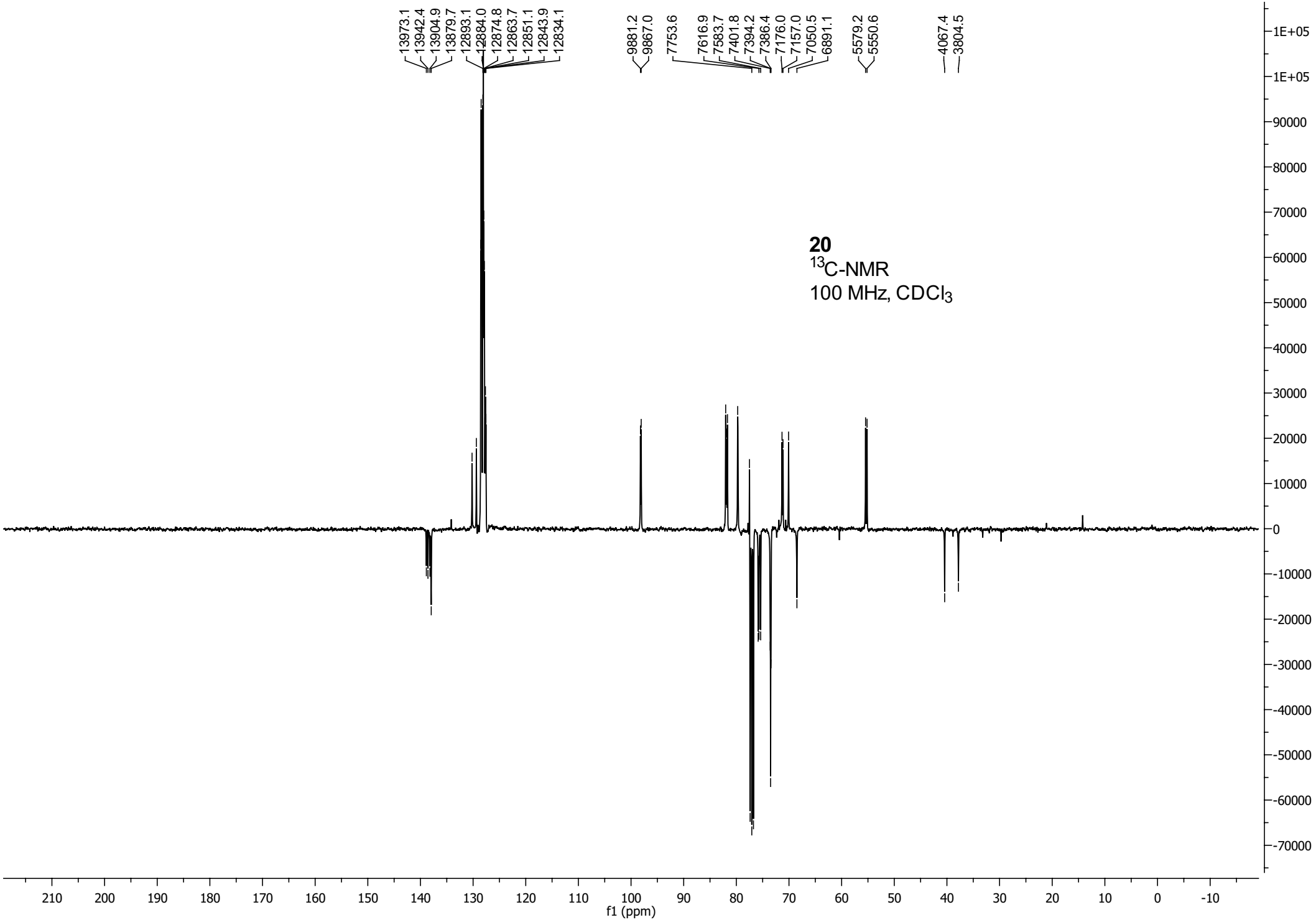
127.59
127.44
98.09
96.17
77.02
75.27
74.75
73.47
73.28
71.32
71.11
69.38
69.09
67.97
55.45
40.45
37.82
19
13C-NMR
100 MHz, CDCl3
f1 (ppm)


20
1H-NMR
400 MHz, CDCl3
f1 (ppm)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13904.9
13879.7
12893.1
12884.0
12874.8
12863.7
12851.1
12843.9
12834.1
9881.2
9867.0
7753.6
7616.9
7583.7
7401.8
7394.2
7386.4
7176.0
7157.0
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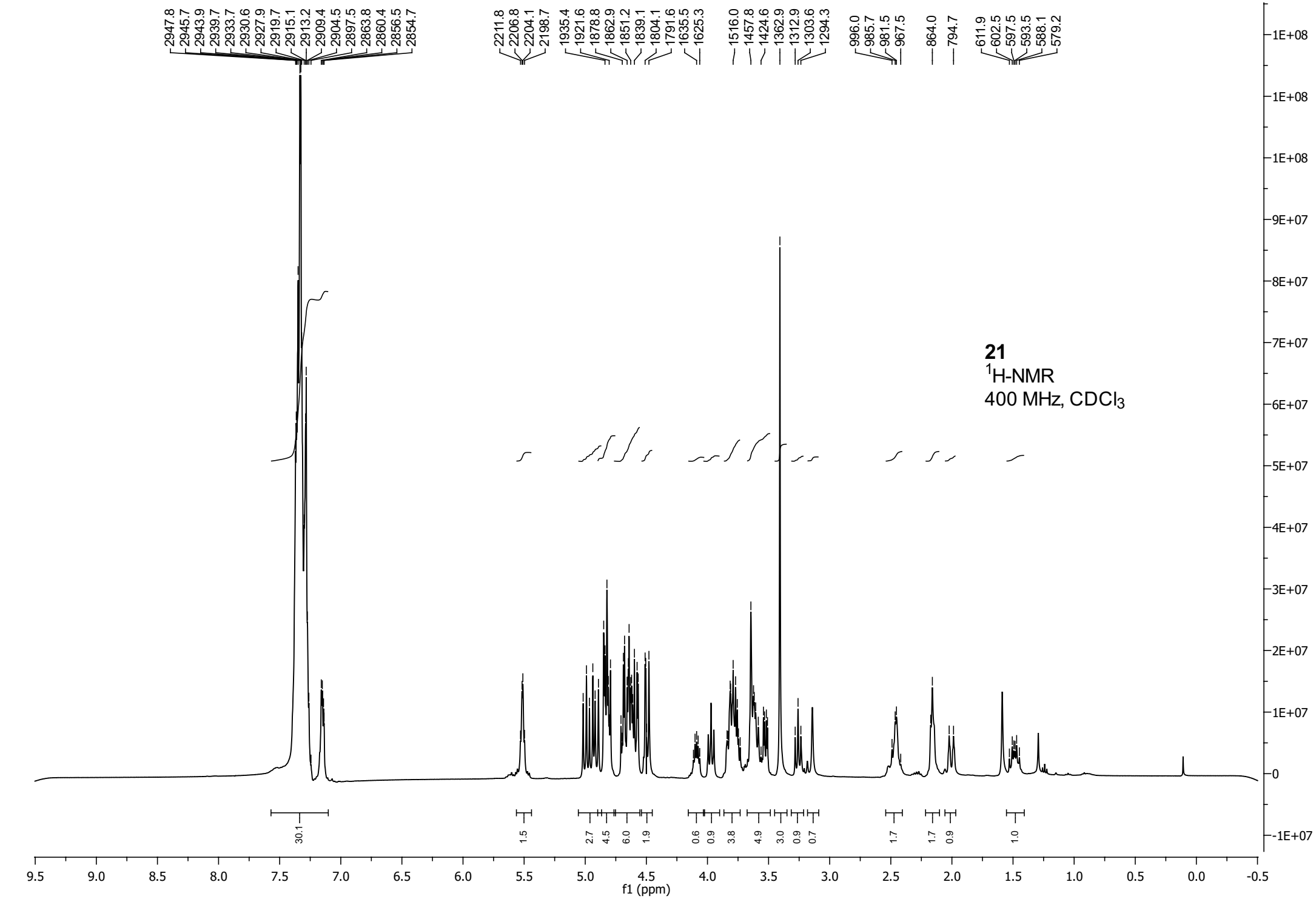
6891.1
5579.2
5550.6
4067.4
3804.5
20
13C-NMR
100 MHz, CDCl3
f1 (ppm)


21
1H-NMR
400 MHz, CDCl3
2947.8
2945.7
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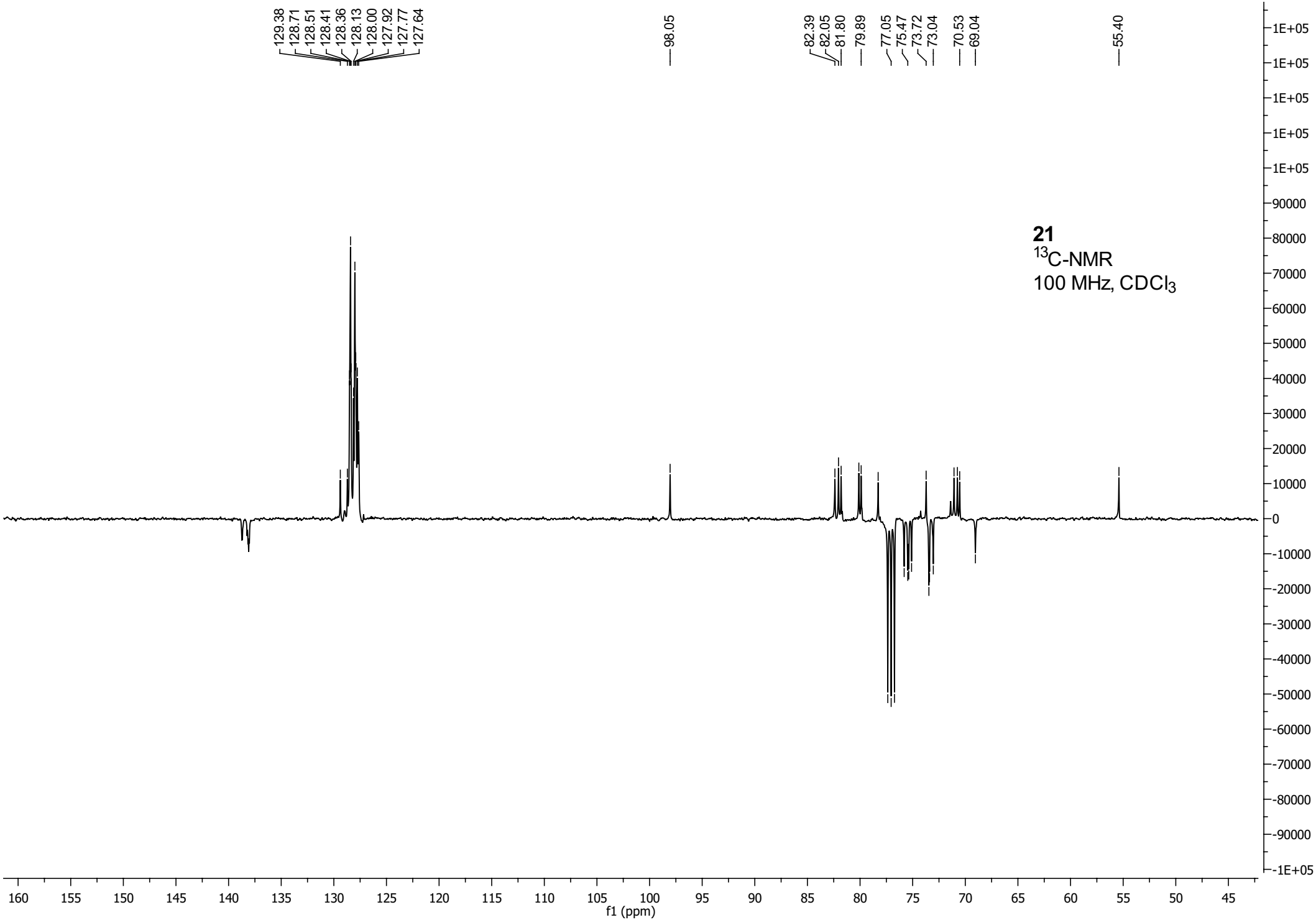
2939.7
2933.7
2930.6
2927.9
2919.7
2915.1
2913.2
2909.4
2904.5
2897.5
2863.8
2860.4
2856.5
2854.7
2211.8
2206.8
2204.1
2198.7
1935.4
1921.6
1878.8
1862.9
1851.2
1839.1
1804.1
1791.6
1635.5
1625.3
1516.0
1457.8
1424.6
1362.9
1312.9
1303.6
1294.3
996.0
985.7
981.5
967.5
864.0
794.7
611.9
602.5
597.5
593.5
588.1
579.2
30.1
1.5
2.7
4.5
6.0
1.9
0.6
0.9
3.8
4.9
3.0
0.9
0.7
1.7
1.7
0.9
1.0
f1 (ppm)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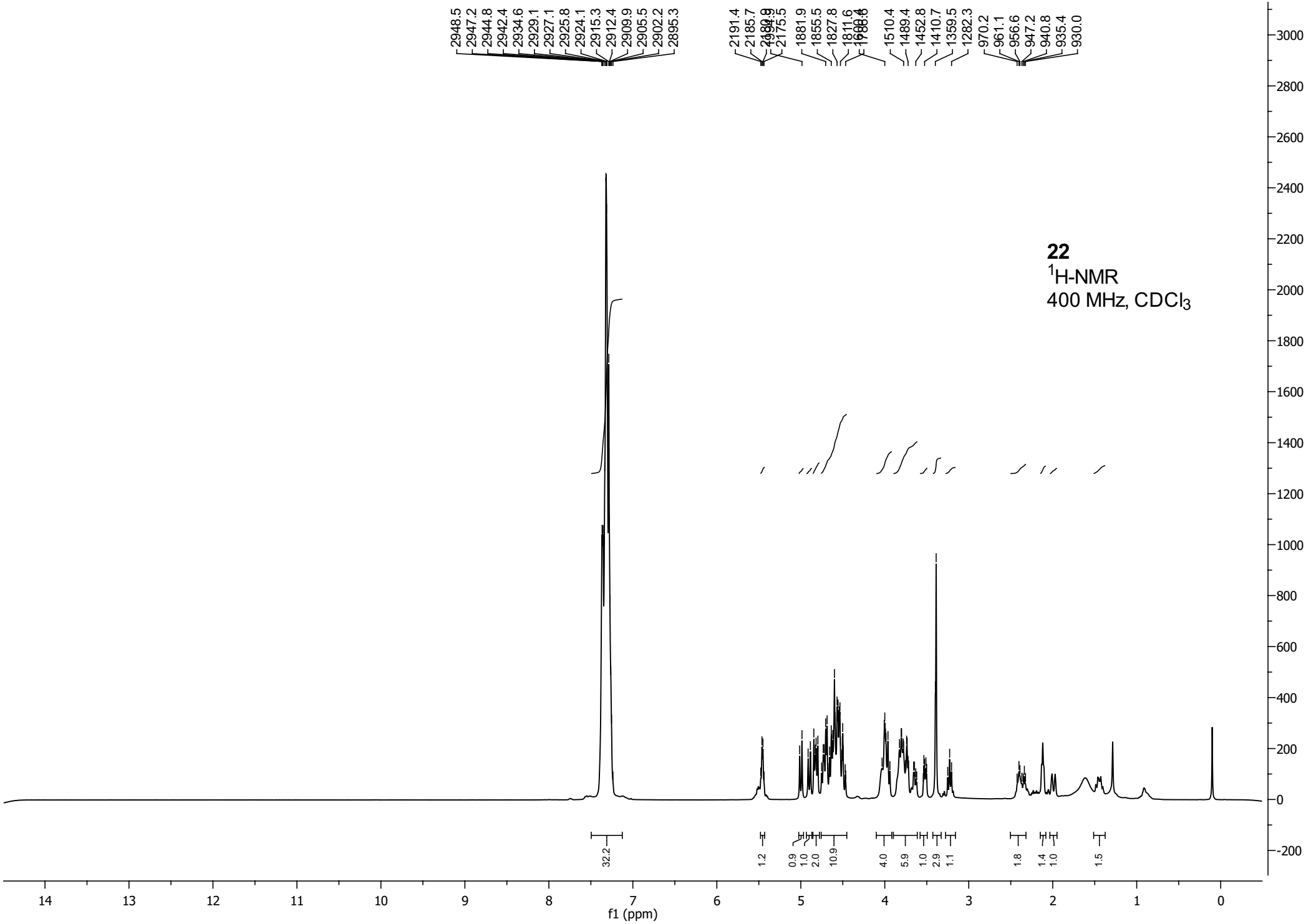
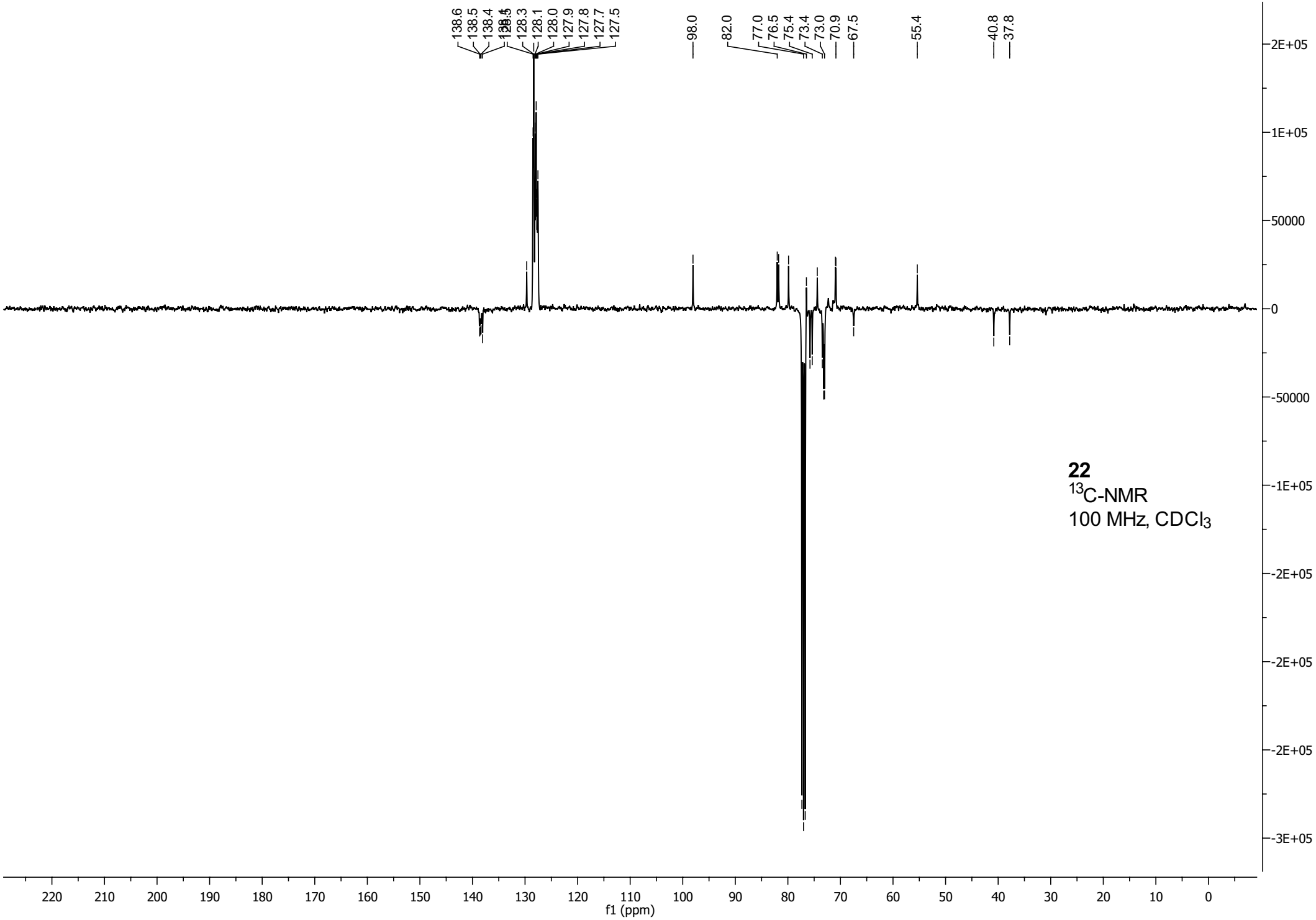
128.71
128.51
128.41
128.36
128.13
128.00
127.92
127.77
127.64
98.05
82.39
82.05
81.80
79.89
77.05
75.47
73.72
73.04
70.53
69.04
55.40
21
13C-NMR
100 MHz, CDCl3
f1 (ppm)


22
1H-NMR
400 MHz, CDCl3
f1 (ppm)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138.5
138.4
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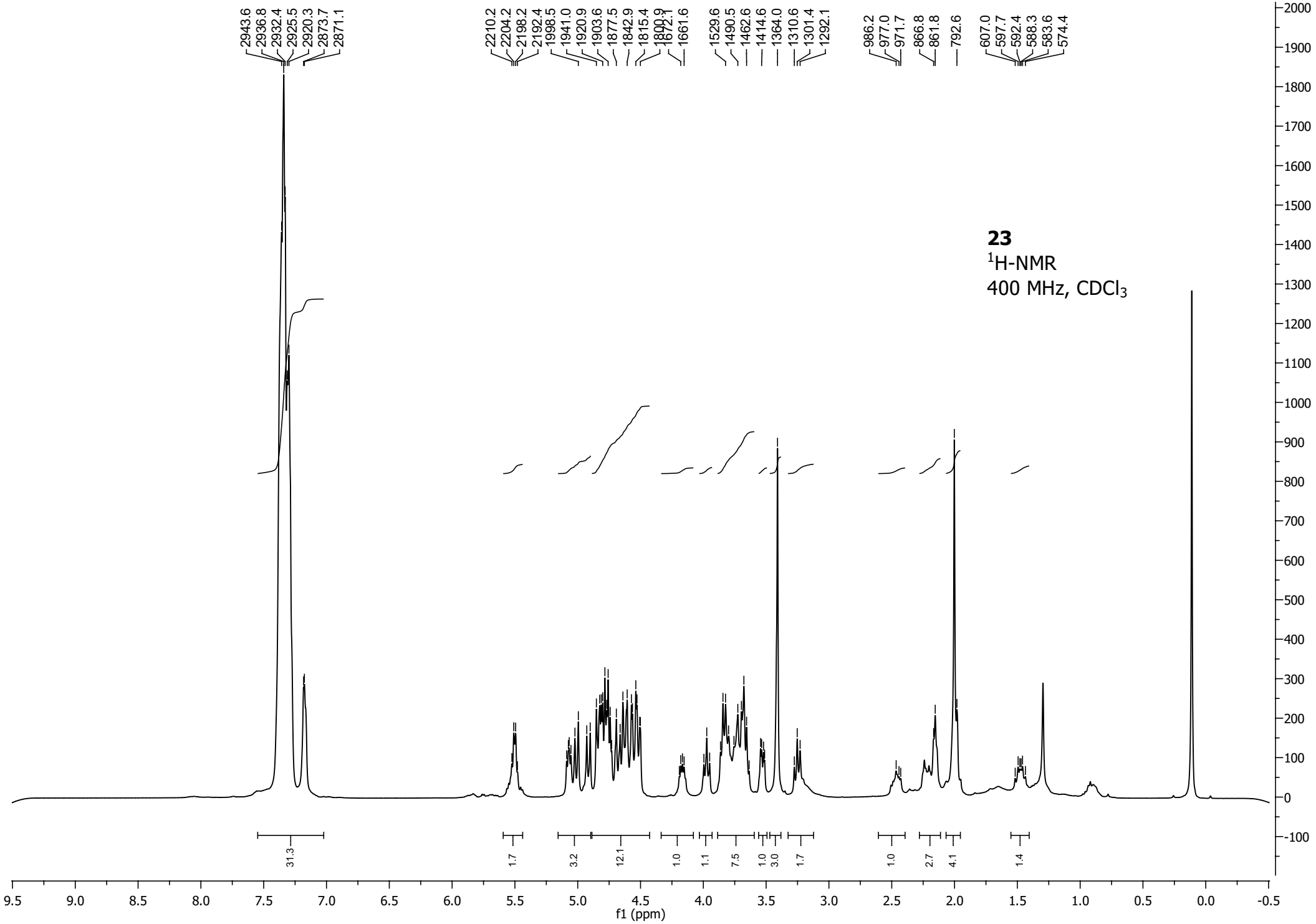
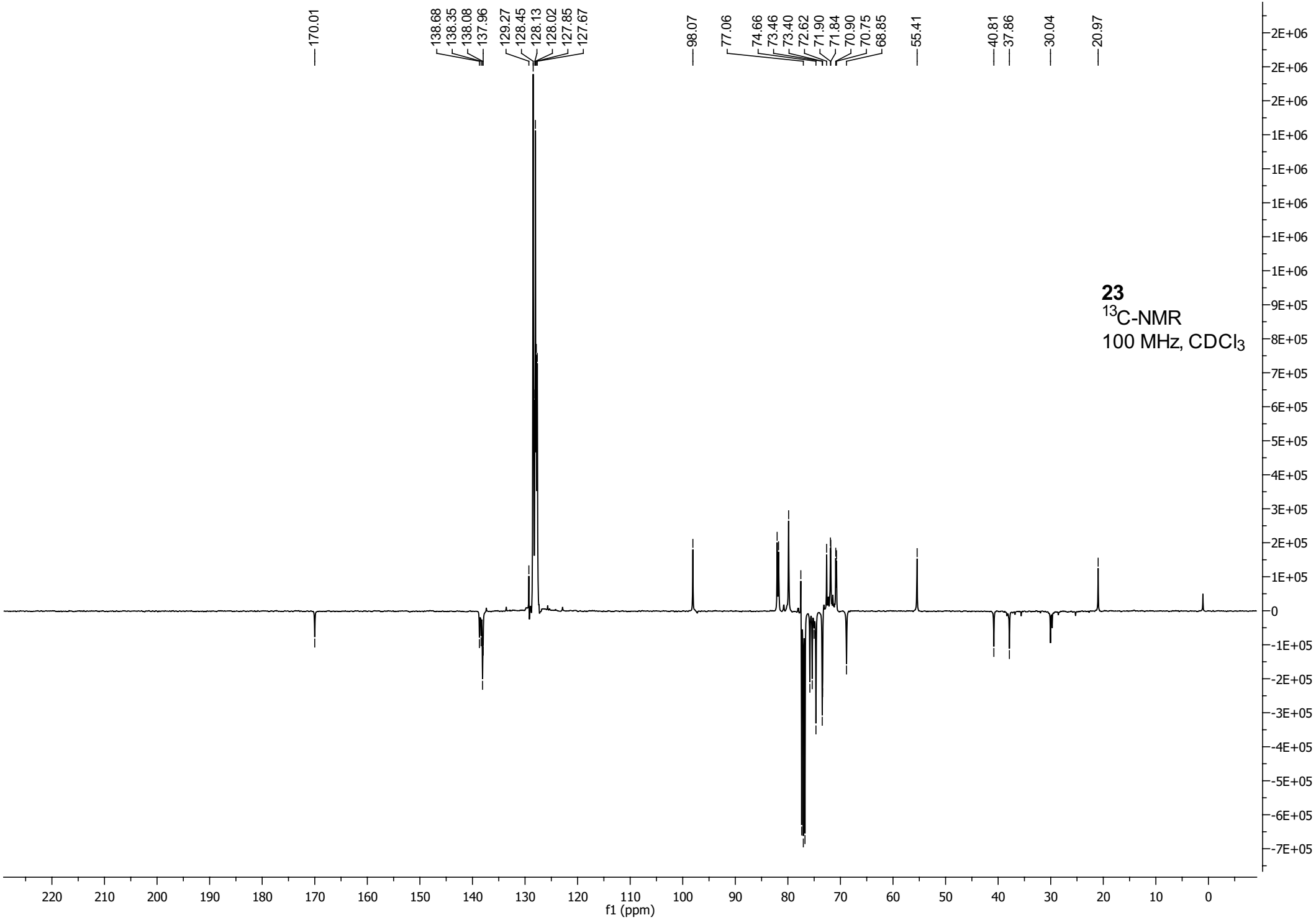
128.1
128.0
127.9
127.8
127.7
127.5
98.0
82.0
77.0
76.5
75.4
73.4
73.0
70.9
67.5
55.4
40.8
37.8
2E+05
1E+05
50000
0
-50000
-1E+05
-2E+05
-2E+05
-2E+05
-3E+05
22
13C-NMR
100 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


23
1H-NMR
400 MHz, CDCl3
2943.6
2936.8
2932.4
2925.5
2920.3
2873.7
2871.1
2210.2
2204.2
2198.2
2192.4
1998.5
1941.0
1920.9
1903.6
1877.5
1842.9
1815.4
1800.9
1672.1
1661.6
1529.6
1490.5
1462.6
1414.6
1364.0
1310.6
1301.4
1292.1
986.2
977.0
971.7
866.8
861.8
792.6
607.0
597.7
592.4
588.3
583.6
574.4
31.3
1.7
3.2
12.1
1.0
1.1
7.5
1.0
3.0
1.7
1.0
2.7
4.1
1.4
f1 (ppm)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138.68
138.35
138.08
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129.27
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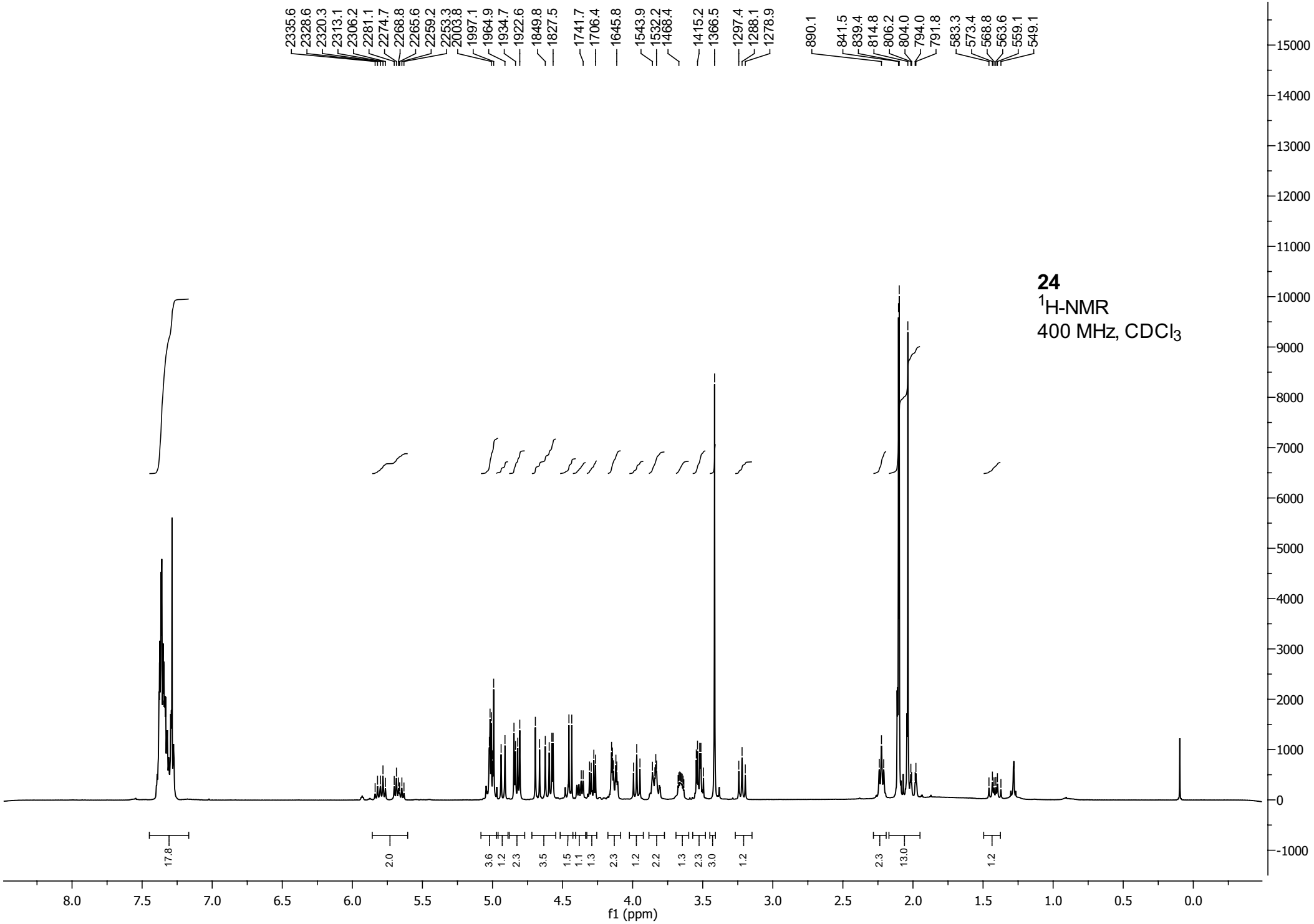
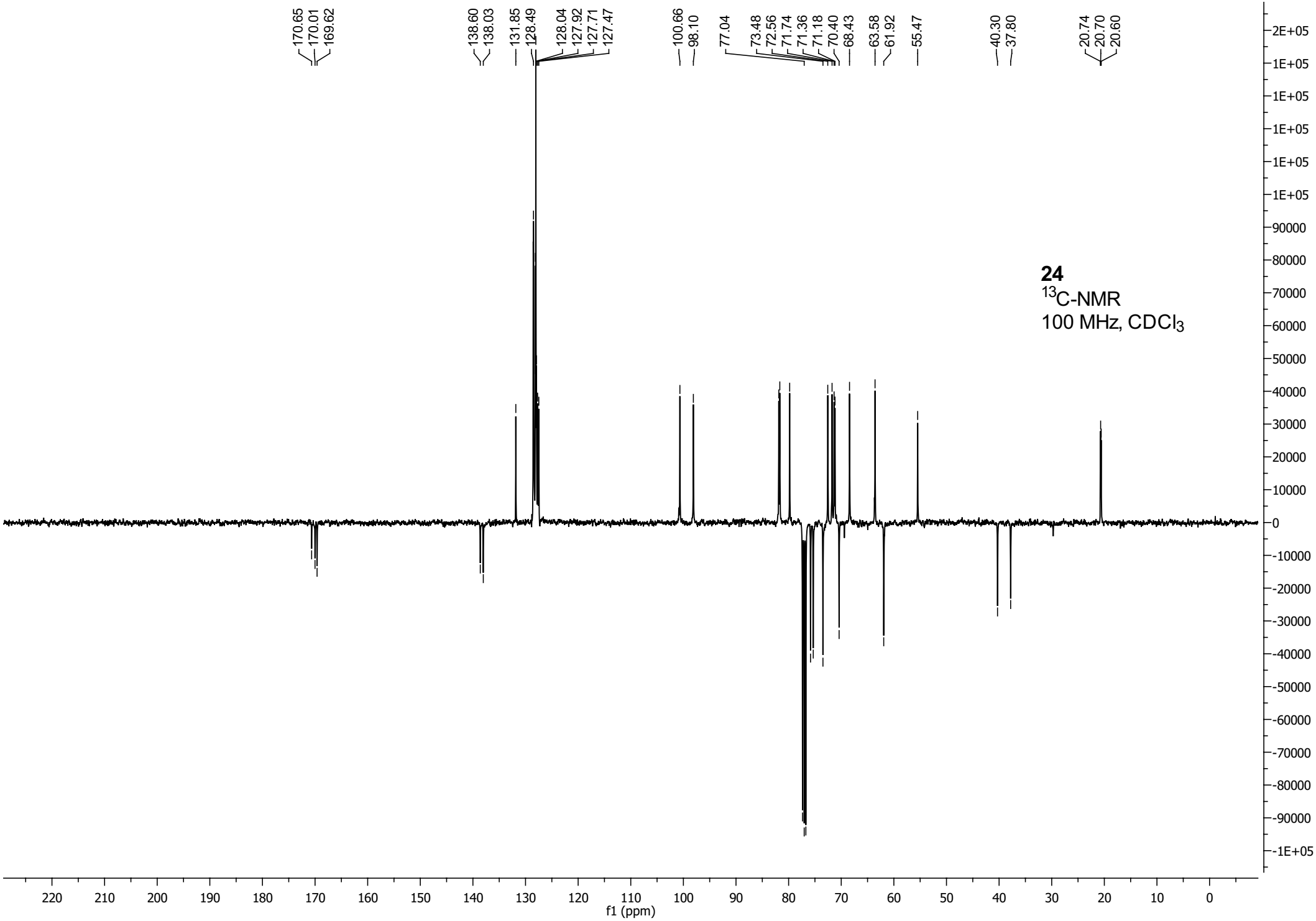
128.13
128.02
127.85
127.67
98.07
77.06
74.66
73.46
73.40
72.62
71.90
71.84
70.90
70.75
68.85
55.41
40.81
37.86
30.04
20.97
23
13C-NMR
100 MHz, CDCl3
f1 (ppm)


24
1H-NMR
400 MHz, CDCl3
2335.6
2328.6
2320.3
2313.1
2306.2
2281.1
2274.7
2268.8
2265.6
2259.2
2253.3
2003.8
1997.1
1964.9
1934.7
1922.6
1849.8
1827.5
1741.7
1706.4
1645.8
1543.9
1532.2
1468.4
1415.2
1366.5
1297.4
1288.1
1278.9
890.1
841.5
839.4
814.8
806.2
804.0
794.0
791.8
583.3
573.4
568.8
563.6
559.1
549.1
17.8
2.0
3.6
1.2
2.3
3.5
1.5
1.1
1.3
2.3
1.2
2.2
1.3
2.3
3.0
1.2
2.3
13.0
1.2
f1 (ppm)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169.62
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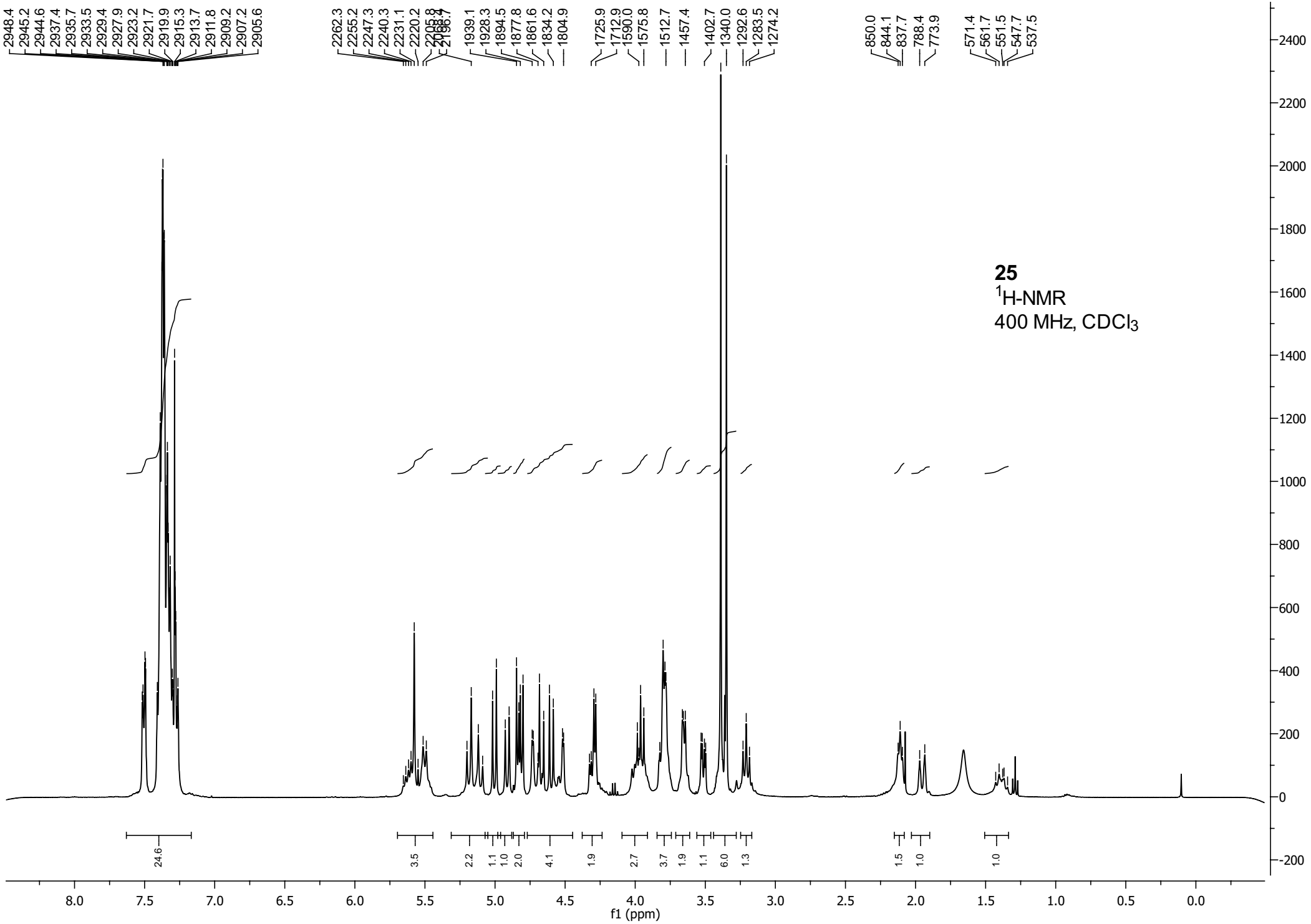
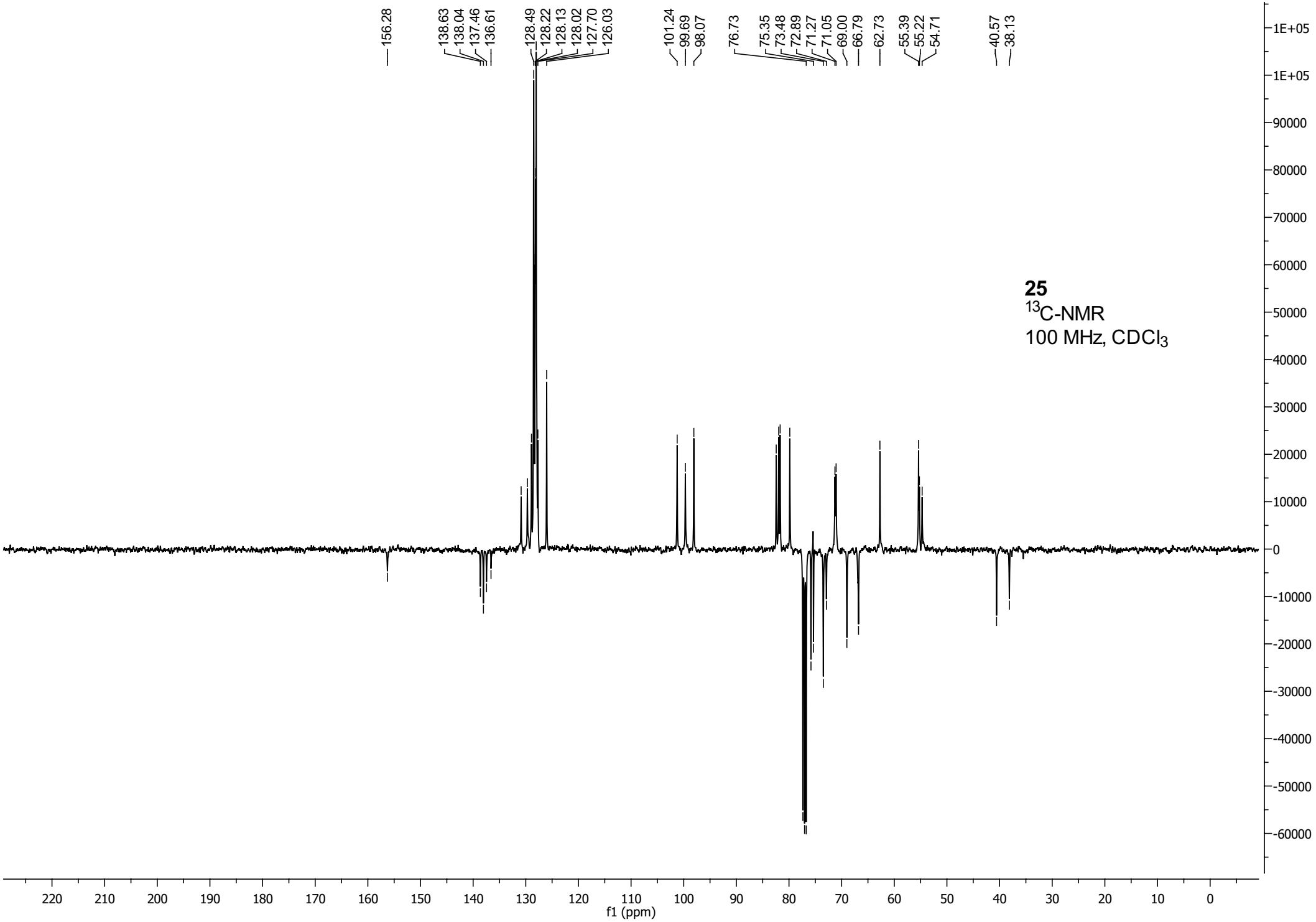
138.03
131.85
128.49
128.04
127.92
127.71
127.47
100.66
98.10
77.04
73.48
72.56
71.74
71.36
71.18
70.40
68.43
63.58
61.92
55.47
40.30
37.80
20.74
20.70
20.60
24
13C-NMR
100 MHz, CDCl3
f1 (ppm)


25
1H-NMR
400 MHz, CDCl3
f1 (ppm)


156.28
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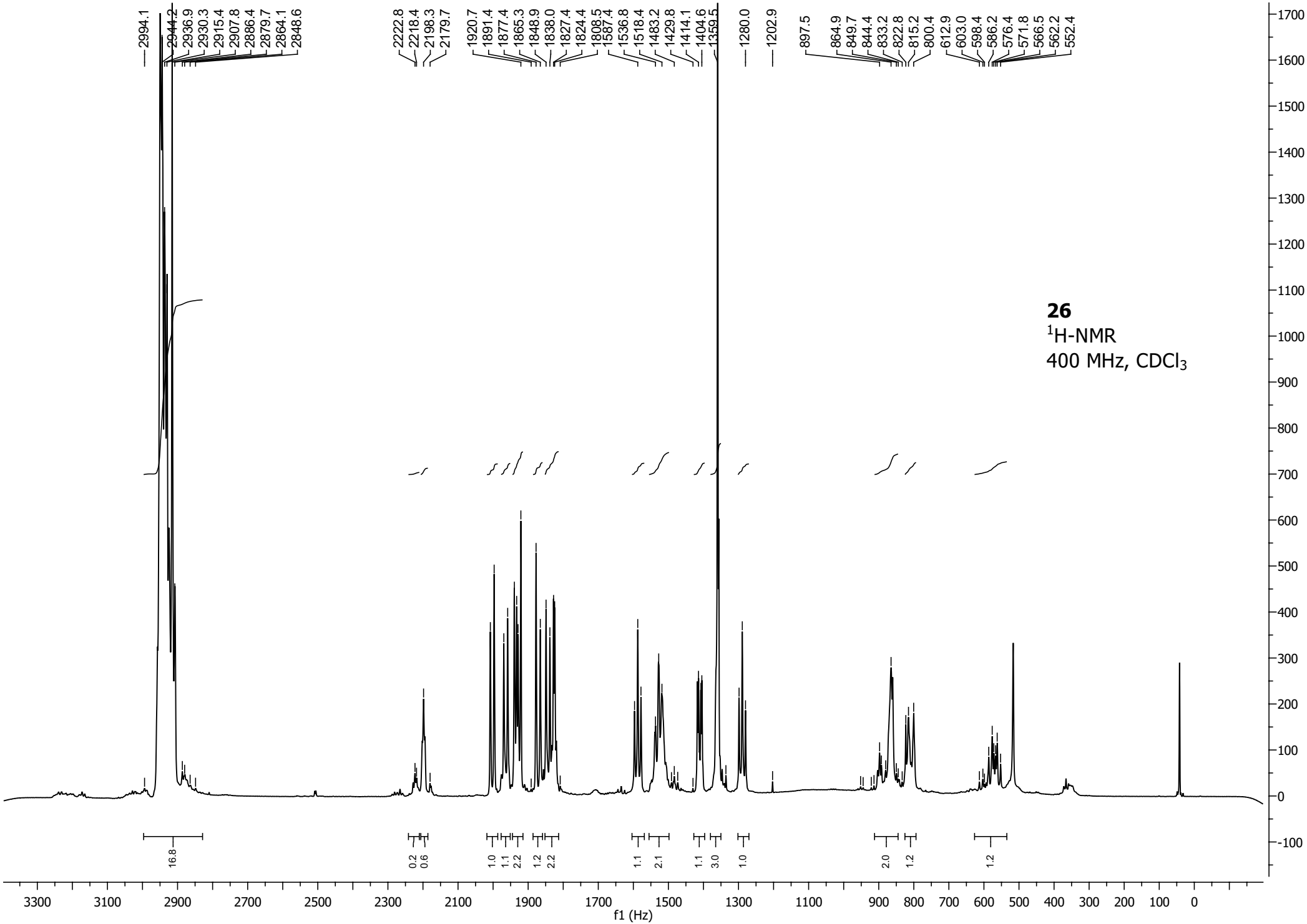
138.04
137.46
136.61
128.49
128.22
128.13
128.02
127.70
126.03
101.24
99.69
98.07
76.73
75.35
73.48
72.89
71.27
71.05
69.00
66.79
62.73
55.39
55.22
54.71
40.57
38.13
25
13C-NMR
100 MHz, CDCl3
f1 (ppm)


26
1H-NMR
400 MHz, CDCl3
2994.1
2944.2
2936.9
2930.3
2915.4
2907.8
2886.4
2879.7
2864.1
2848.6
2222.8
2218.4
2198.3
2179.7
1920.7
1891.4
1877.4
1865.3
1848.9
1838.0
1827.4
1824.4
1808.5
1587.4
1536.8
1518.4
1483.2
1429.8
1414.1
1404.6
1359.5
1280.0
1202.9
897.5
864.9
849.7
844.4
833.2
822.8
815.2
800.4
612.9
603.0
598.4
586.2
576.4
571.8
566.5
562.2
552.4
16.8
0.2
0.6
1.0
1.1
2.2
1.2
2.2
1.1
2.1
1.1
3.0
1.0
2.0
1.2
1.2
f1 (Hz)

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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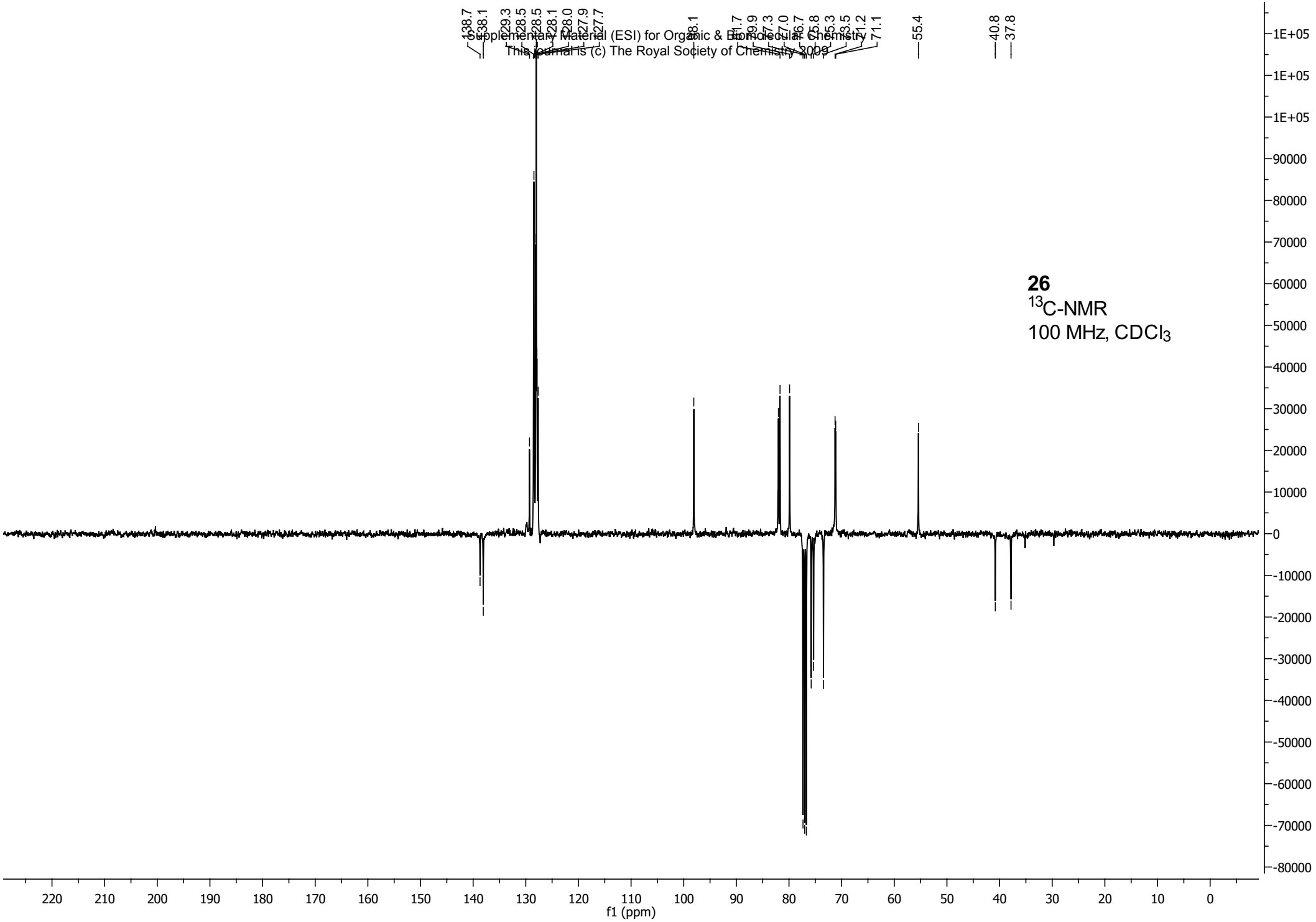
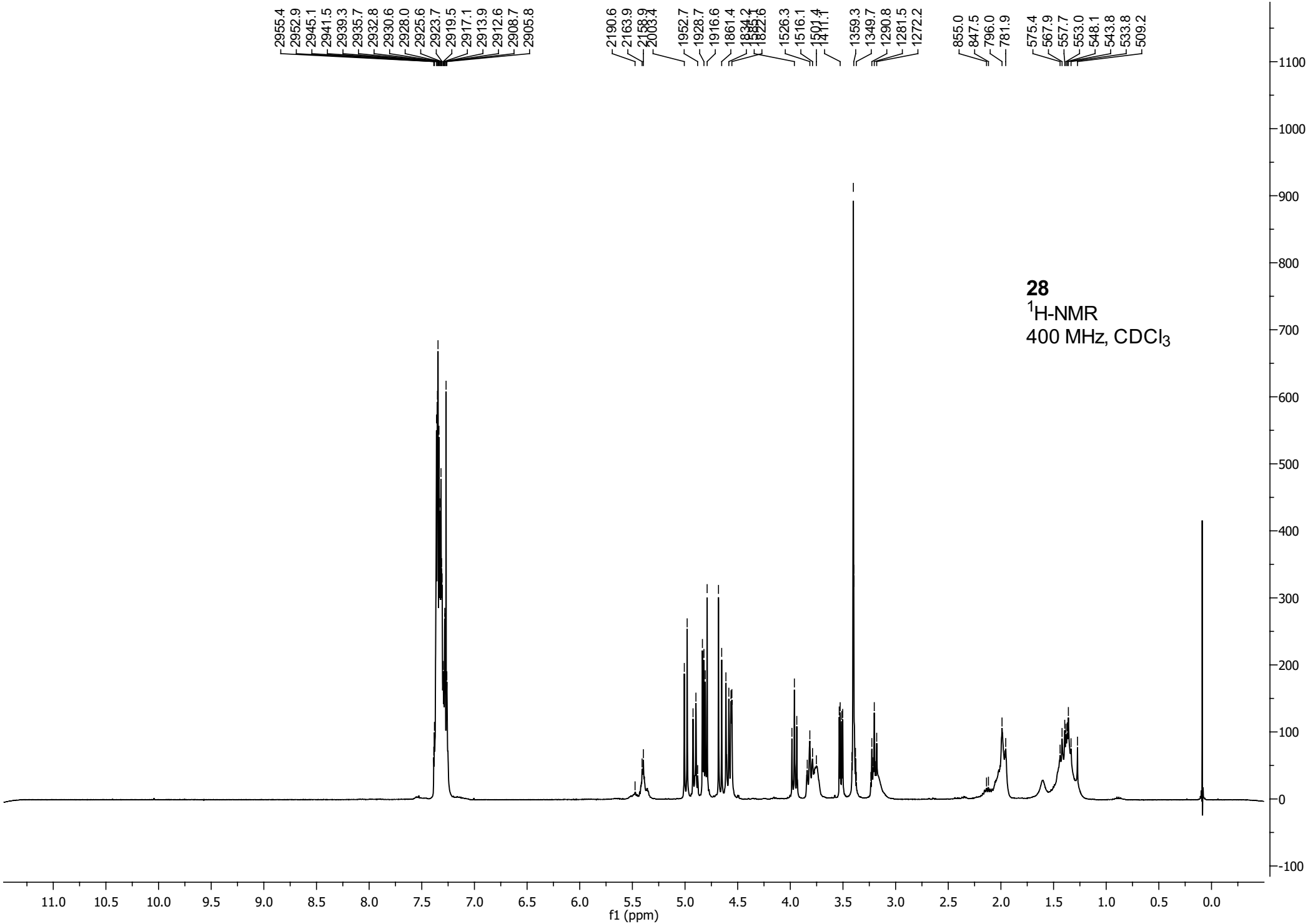
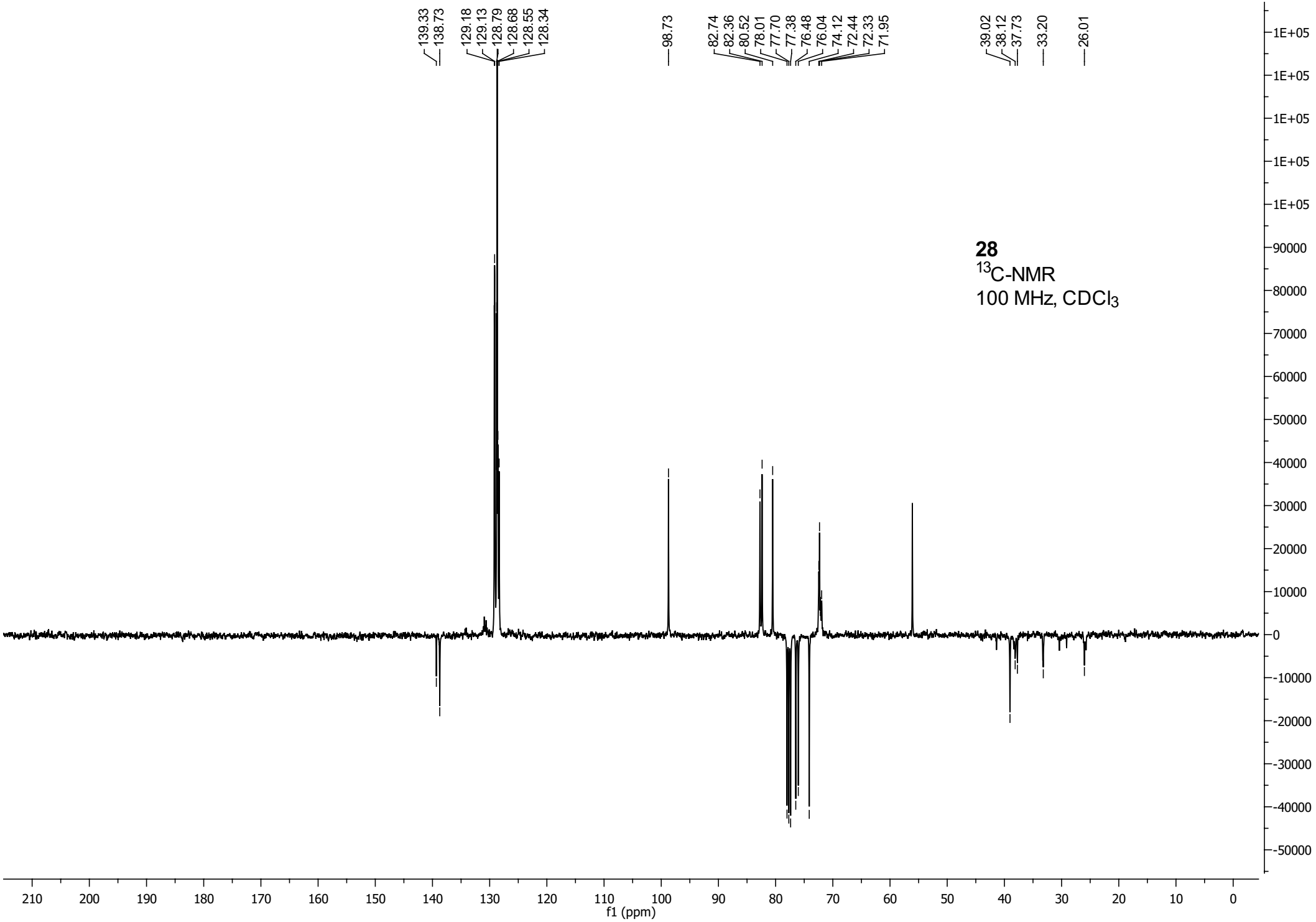



28
1H-NMR
400 MHz, CDCl3
f1 (ppm)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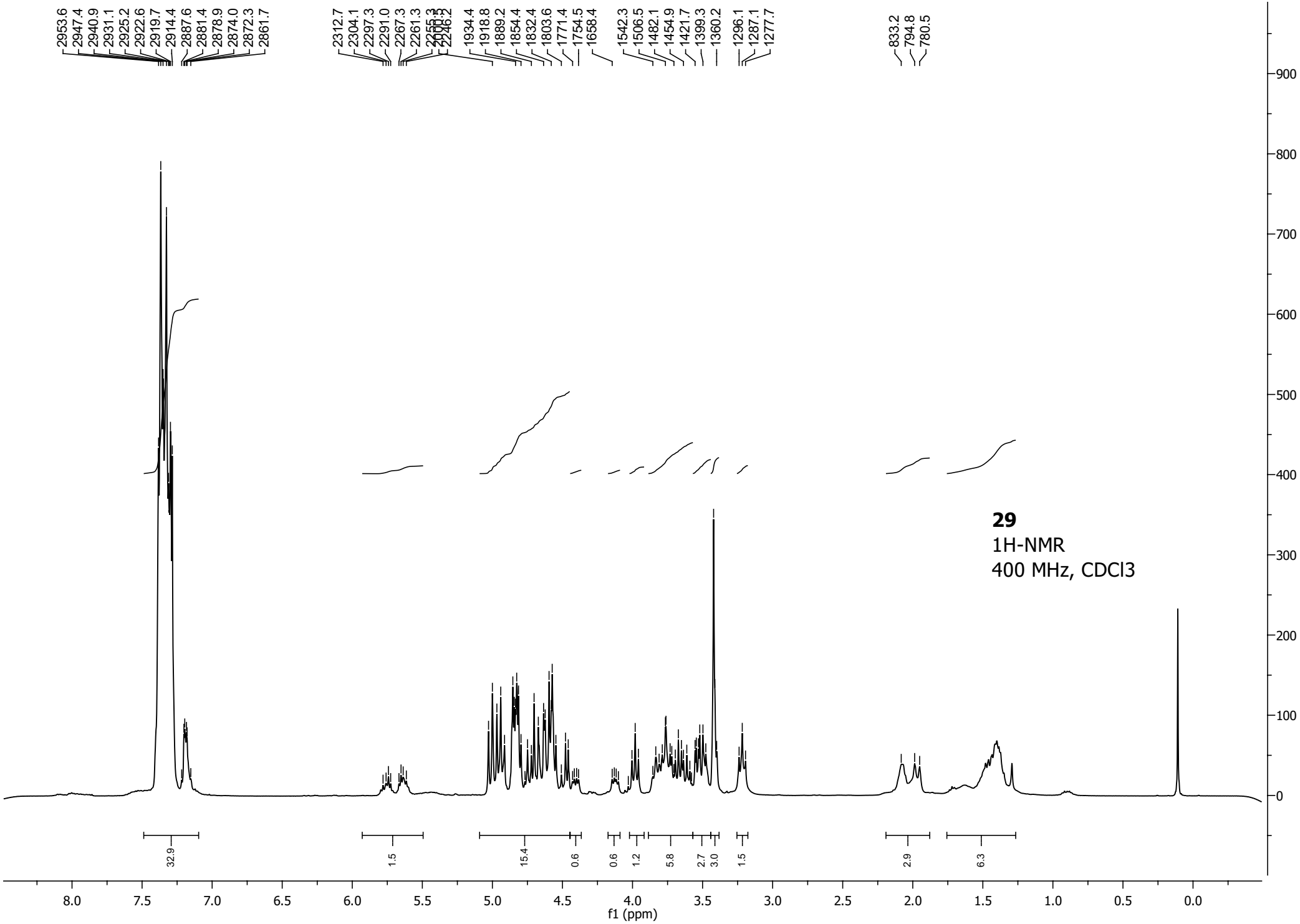
82.36
80.52
78.01
77.70
77.38
76.48
76.04
74.12
72.44
72.33
71.95
39.02
38.12
37.73
33.20
26.01
28
13C-NMR
100 MHz, CDCl3
f1 (ppm)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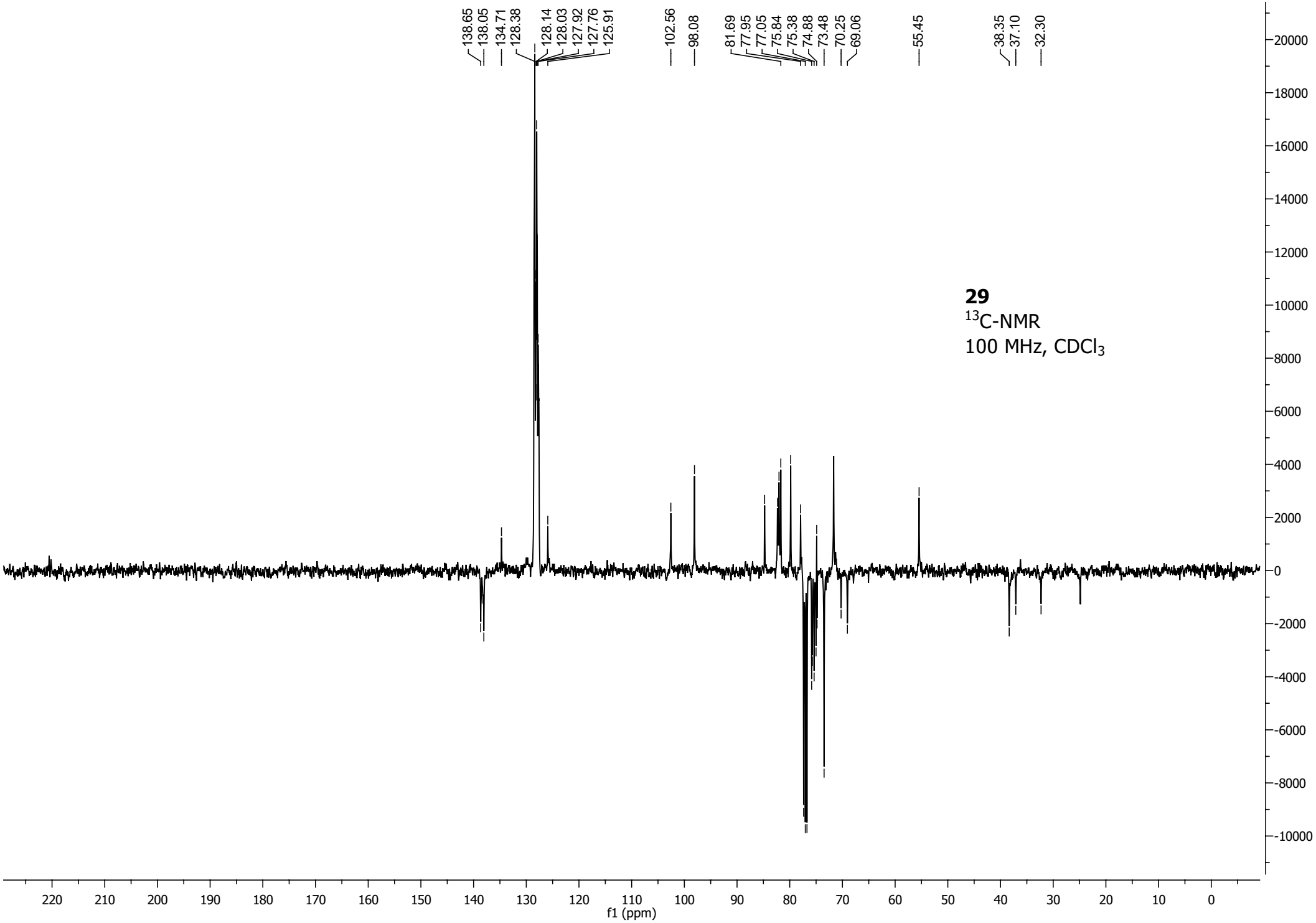
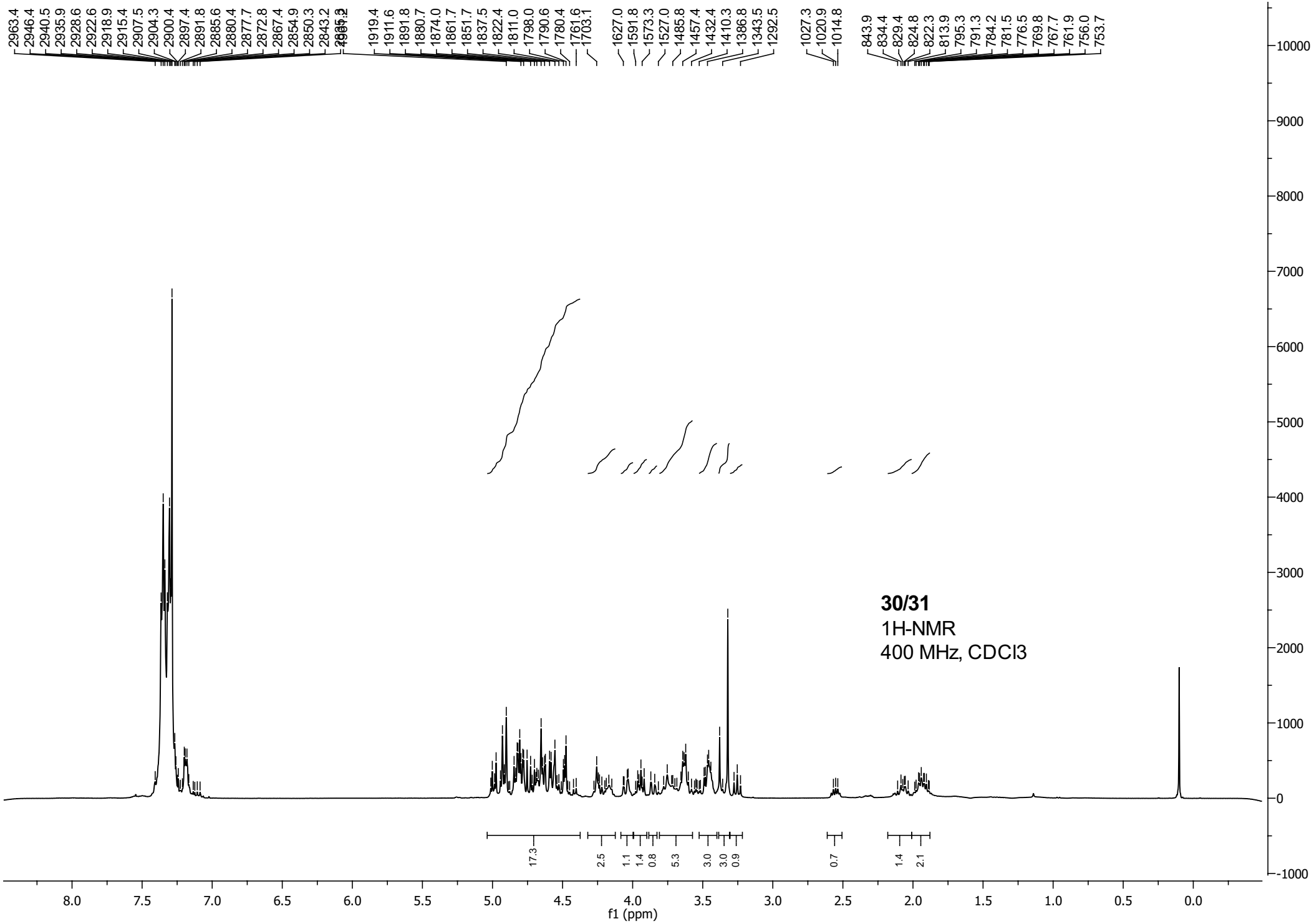
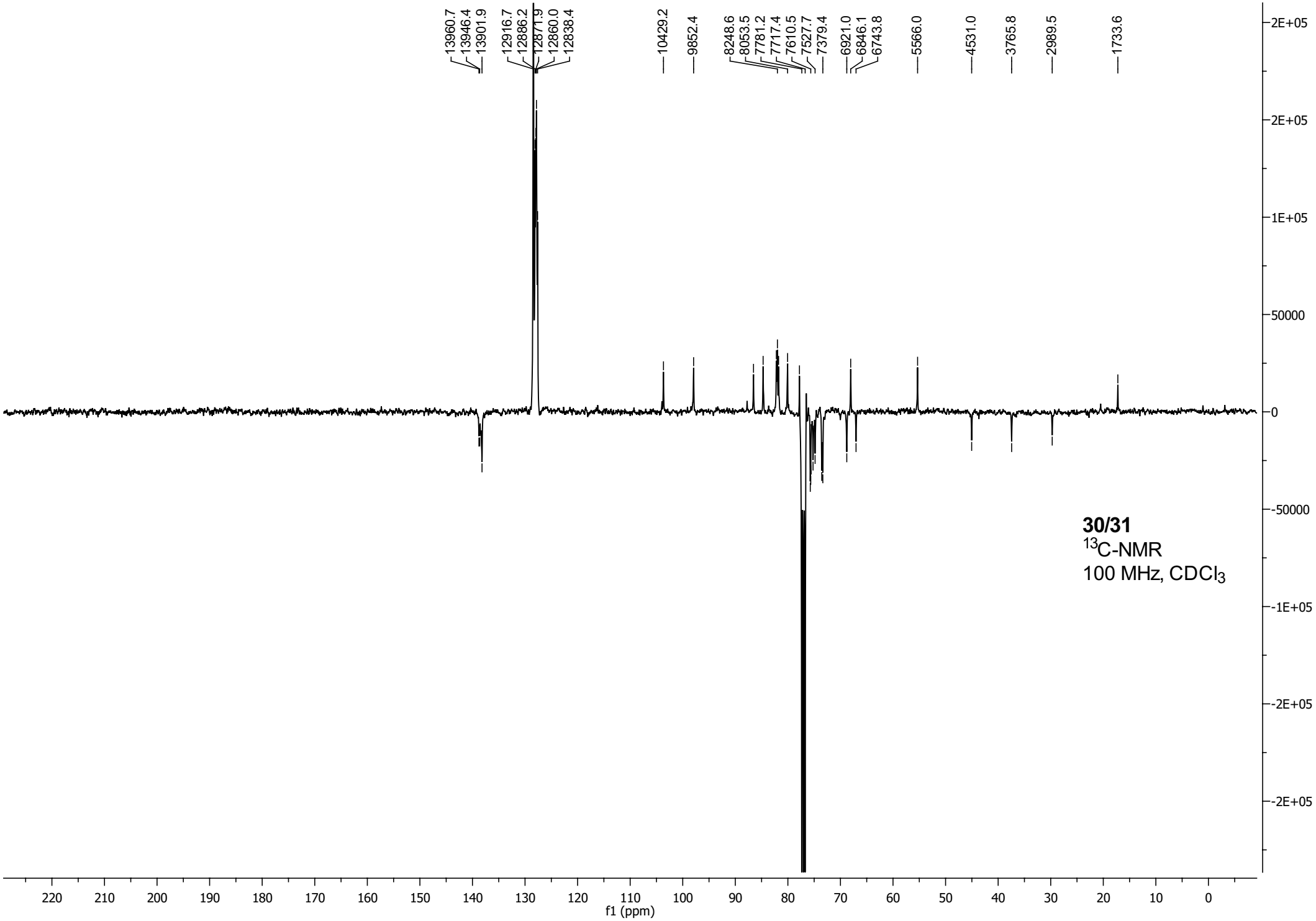
2919.7
2914.4
2887.6
2881.4
2878.9
2874.0
2872.3
2861.7
2312.7
2304.1
2297.3
2291.0
2267.3
2261.3
1934.4
1918.8
1889.2
1854.4
1832.4
1803.6
1771.4
1754.5
1658.4
1542.3
1506.5
1482.1
1454.9
1421.7
1399.3
1360.2
1296.1
1287.1
1277.7
833.2
794.8
780.5
29
1H-NMR
400 MHz, CDCl3
32.9
1.5
15.4
0.6
0.6
1.2
5.8
2.7
3.0
1.5
2.9
6.3
f1 (ppm)


138.65
138.05
134.71
128.38
128.14
128.03
127.92
127.76
125.91
102.56
98.08
81.69
77.95
77.05
75.84
75.38
74.88
73.48
70.25
69.06
55.45
38.35
37.10
32.30
29
13C-NMR
100 MHz, CDCl3
f1 (ppm)


30/31
1H-NMR
400 MHz, CDCl3
f1 (ppm)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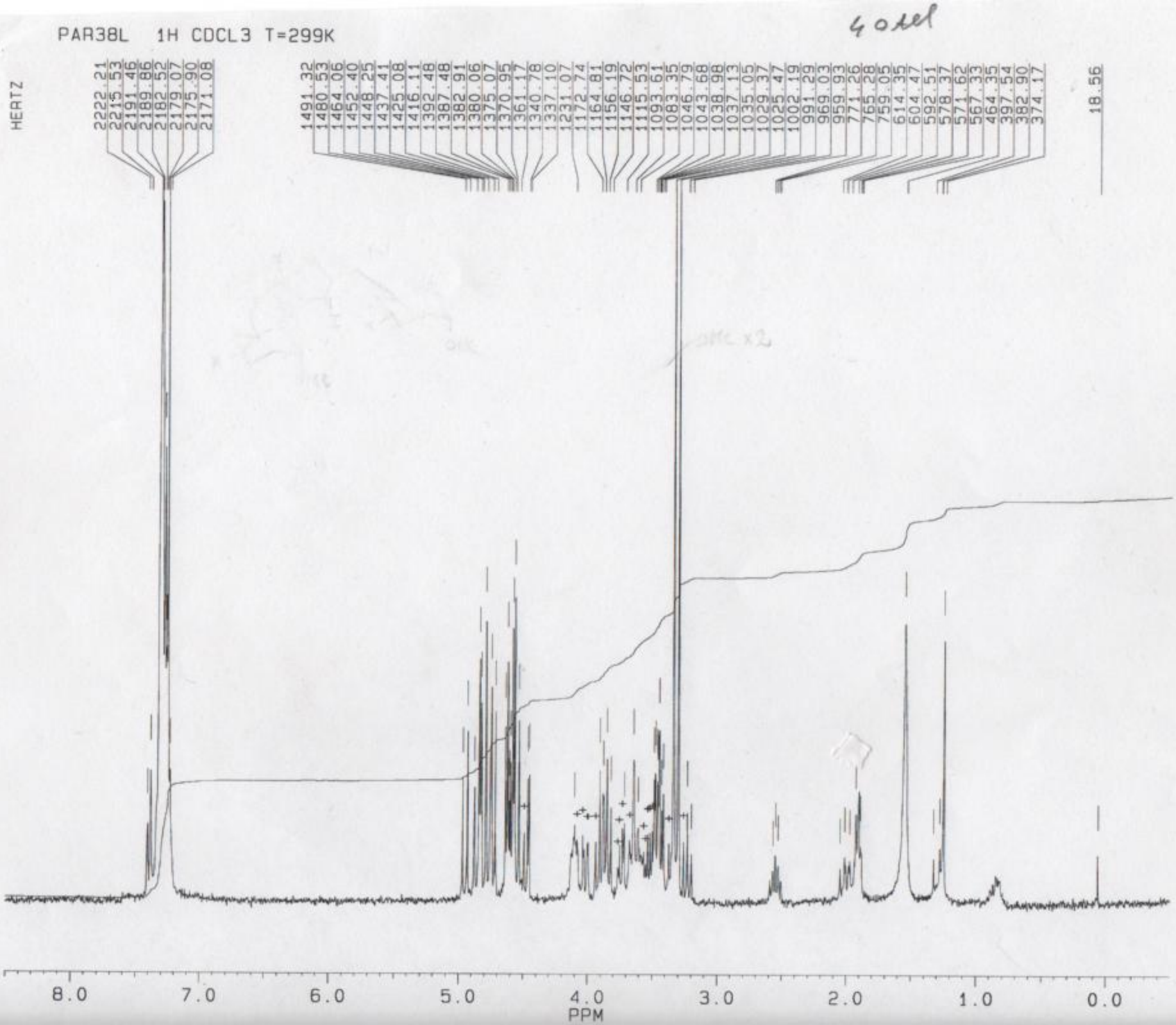
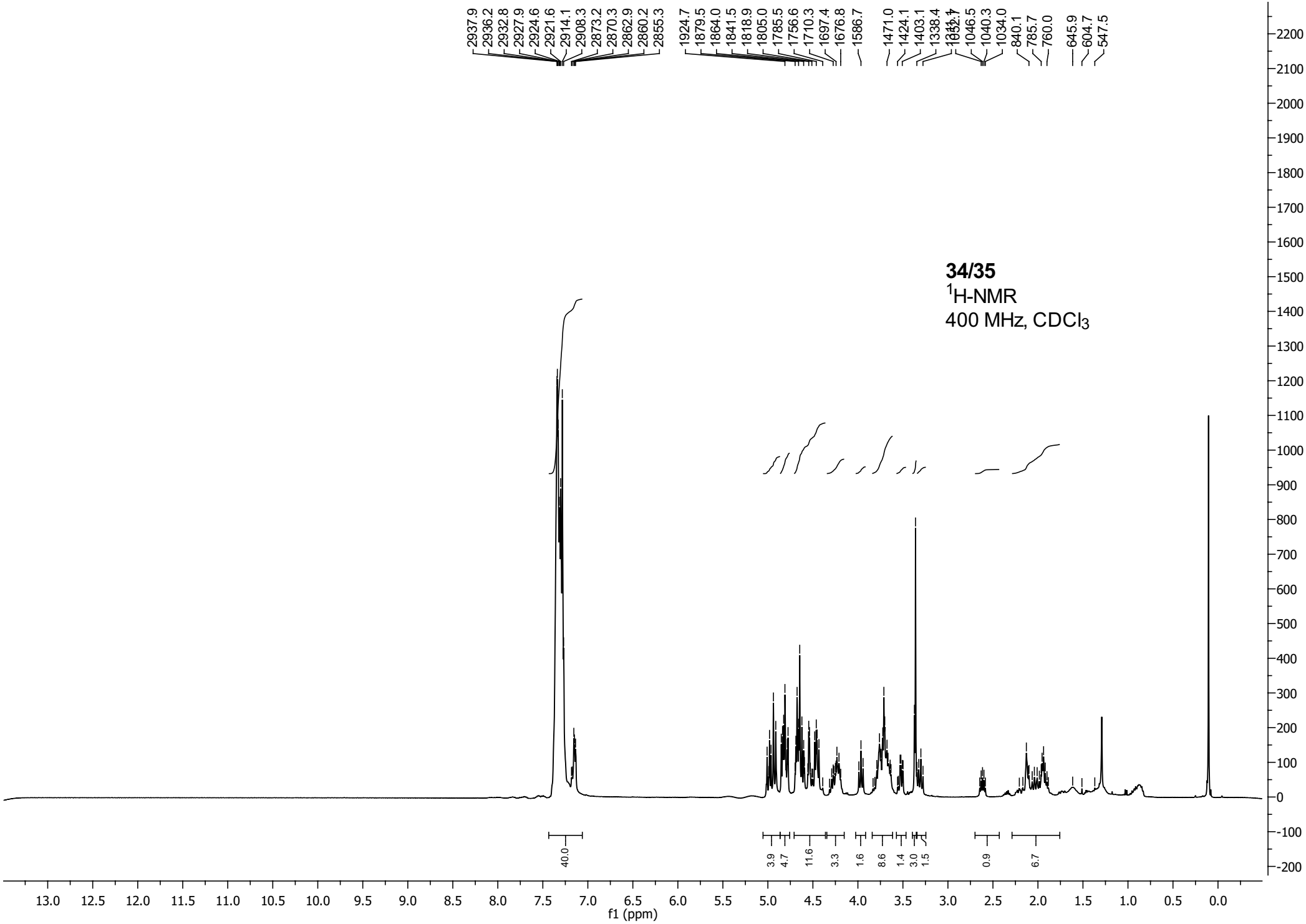
8248.6
8053.5
7781.2
7717.4
7610.5
7527.7
7379.4
6921.0
6846.1
6743.8
5566.0
4531.0
3765.8
2989.5
1733.6
2E+05
2E+05
1E+05
50000
0
-50000
-1E+05
-2E+05
-2E+05
30/31
13C-NMR
100 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



32/33
1H-NMR
300 MHz, CDCl3


34/35
1H-NMR
400 MHz, CDCl3
2937.9
2936.2
2932.8
2927.9
2924.6
2921.6
2914.1
2908.3
2873.2
2870.3
2862.9
2860.2
2855.3
1924.7
1879.5
1864.0
1841.5
1818.9
1805.0
1785.5
1756.6
1710.3
1697.4
1676.8
1586.7
1471.0
1424.1
1403.1
1338.4
1046.5
1040.3
1034.0
840.1
785.7
760.0
645.9
604.7
547.5
40.0
3.9
4.7
11.6
3.3
1.6
8.6
1.4
3.0
1.5
0.9
6.7
f1 (ppm)

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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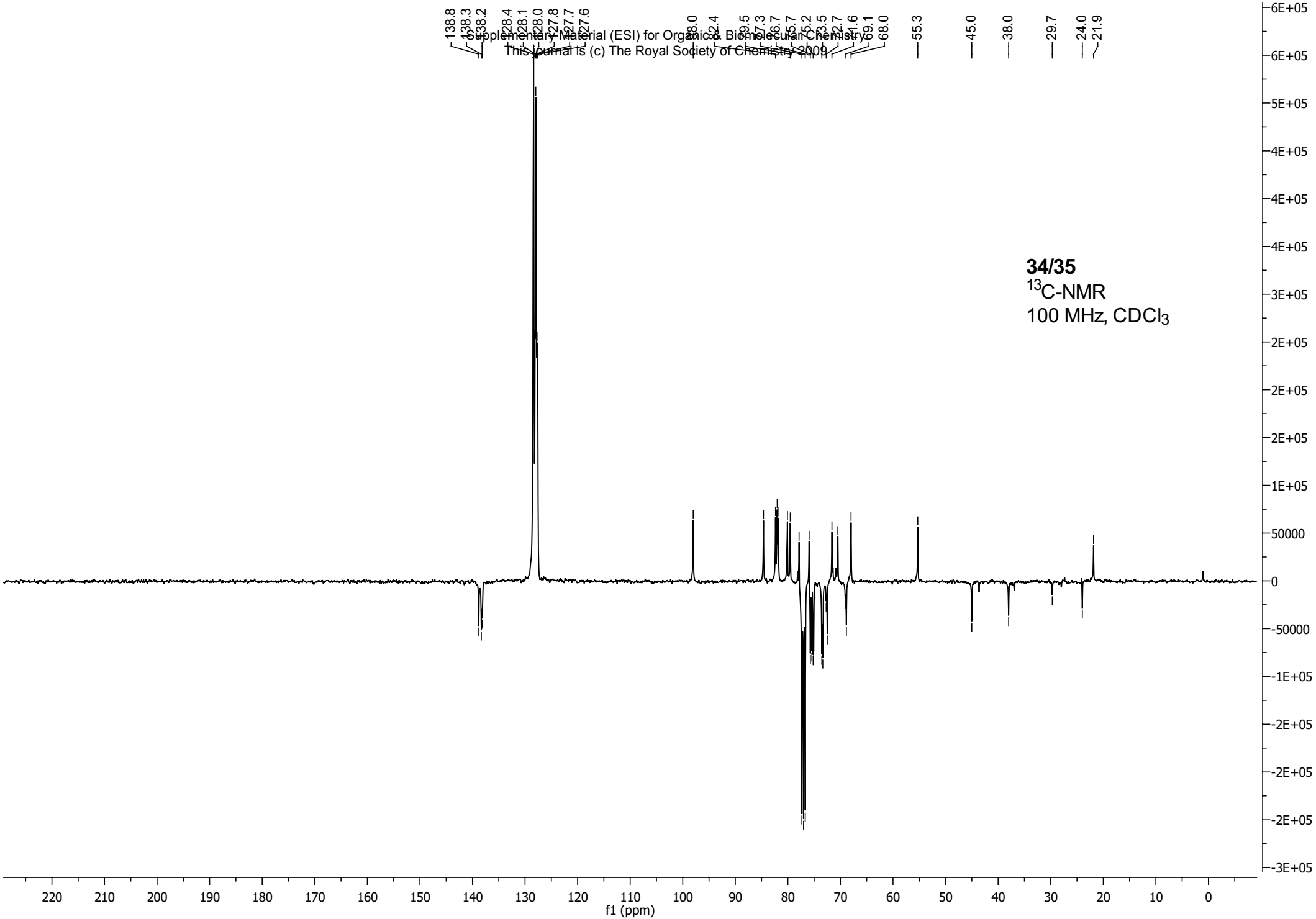

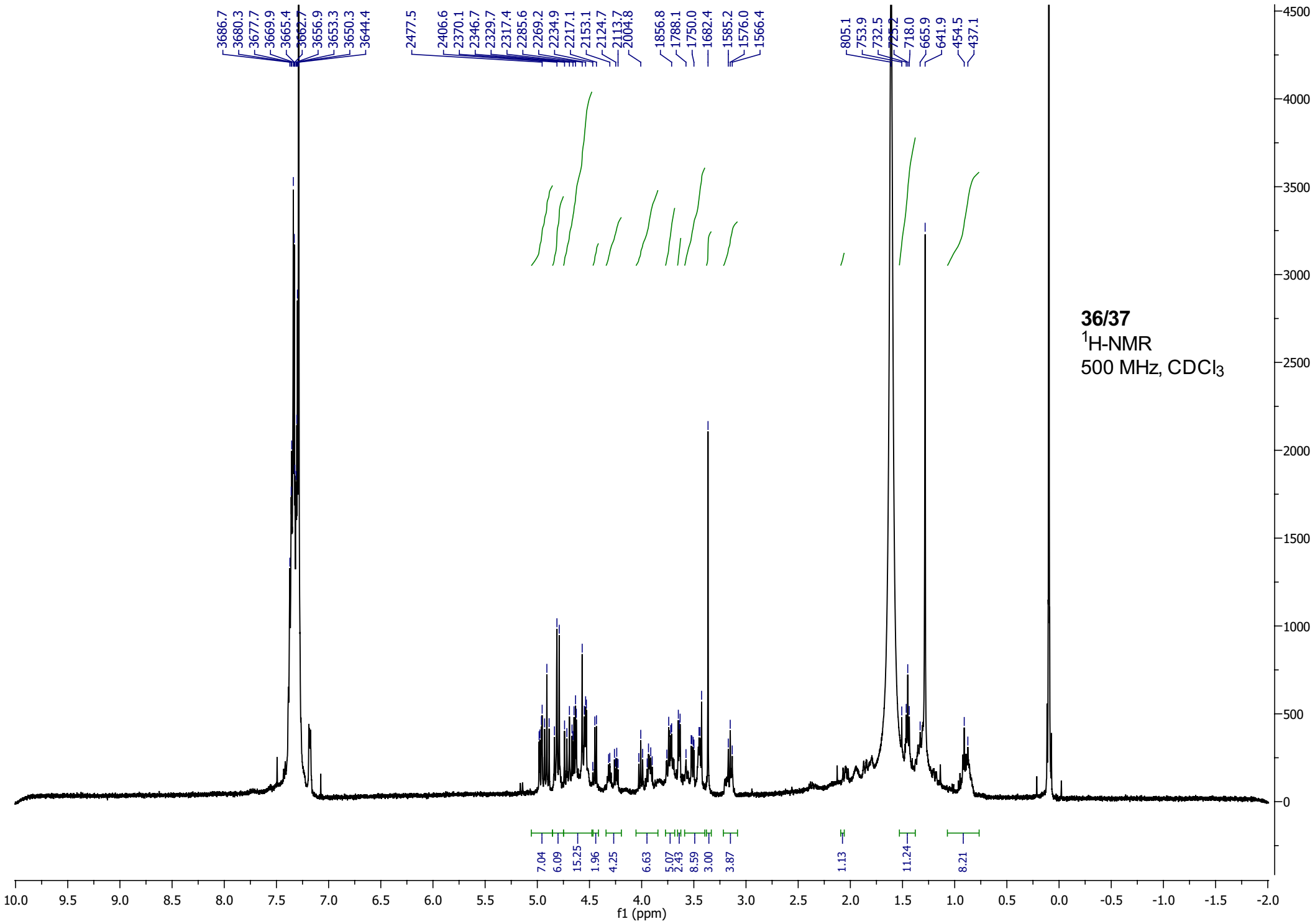
36/37
1H-NMR
500 MHz, CDCl3
f1 (ppm)
3686.7
3680.3
3677.7
3669.9
3665.4
3662.7
3656.9
3653.3
3650.3
3644.4
2477.5
2406.6
2370.1
2346.7
2329.7
2317.4
2285.6
2269.2
2234.9
2217.1
2153.1
2124.7
2113.7
2004.8
1856.8
1788.1
1750.0
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1585.2
1576.0
1566.4
805.1
753.9
732.5
725.2
718.0
665.9
641.9
454.5
437.1
7.04
6.09
15.25
1.96
4.25
6.63
5.07
2.43
8.59
3.00
3.87
1.13
11.24
8.21

36/37HSQC 500 MHz $CDCl_3$