Synthesis of defined mono-de-*N*-acetylated β-(1→6)-*N*-acetyl-D-glucosamine oligosaccharides to characterize PgaB hydrolase activity

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Supplementary Information

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Supplementary figures and tables

Figure S1 TLC plate imaged in Fig. 3A.

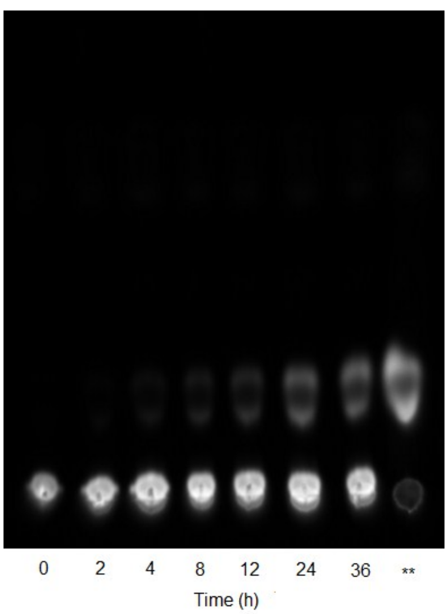


Figure S2 TLC plate from Fig. S1 visualized by fluorescence imaging (exposure time of 80 ms). **Disaccharide **44** labelled by DBCO-Cy5.

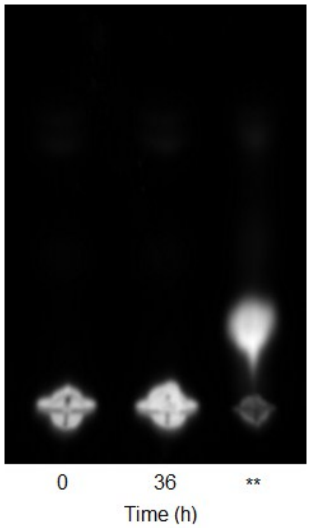


Figure S3 Negative control experiment (no enzyme present) for heptasaccharide **4** (5 mM), incubated in 100 mM HEPES, pH 7.0. Time point aliquots were labelled with DBCO-Cy5 for 1 h by diluting the 1 µL aliquots with 1 µL of 1 mM DBCO-Cy5, then analyzed by TLC (1:1:2 H_2O/AcOH/*n*BuOH) and visualized by fluorescence imaging (exposure time 80 ms). **Disaccharide **44** labelled by DBCO-Cy5.

Figure S4 TLC plate imaged in Fig. 4.

Table S1 Yield of products **35** and **36**.[1,2]

Temp.[a] (°C)	Time[a] (h)	**35** (%)	**36** (%)
40	2	83	-
50	2	7	41
60	20	-	64

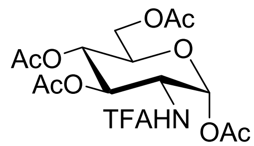
[a] Conditions for the deprotection of **34** using aq. NaOH.

Table S2 Raw fluorescence integration values from Fig. 5, calculated from TLC plates with an exposure time of 80ms (as seen in Fig. S2).

Time (h)	Replicate 1			Replicate 2			Average Turnover (%)
	44	**4**	Turnover (%)	**44**	**4**	Turnover (%)	
0	11	2014	0.5	0	1142	0.0	0.3 ± 0.4
2	102	2109	4.6	47	1676	2.7	3.7 ± 1.3
4	155	2014	7.1	152	1994	7.1	7.1 ± 0.0
8	240	1587	13.1	275	1903	12.6	12.9 ± 0.4
12	467	1918	19.6	423	1951	17.8	18.7 ± 1.2
24	1095	2279	32.5	819	1870	30.5	31.5 ± 1.4
36	1378	2334	37.1	1038	1898	35.4	36.2 ± 1.3

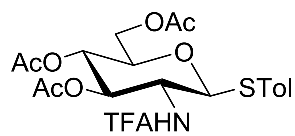
Synthesis

1,3,4,6-Tetra-O-acetyl-2-trifluoroacetamido-2-deoxy-D-glucopyranose (5)



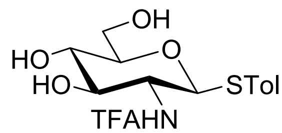
Known[3,4] trifluoroacetamido tetraacetate **5** (2:1 α/β) was synthesized as described previously.[5] ^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.03 (d, *J* = 9.6 Hz, 1H, N-Hβ), 6.57 (d, *J* = 8.7 Hz, 1H, N-Hα), 6.25 (d, *J* = 3.7 Hz, 1H, H-1α), 5.75 (d, *J* = 8.7 Hz, 1H, H-1β), 5.31 (dd, *J* = 10.5, 9.4 Hz, 1H, H-3α), 5.27 (dd, *J* = 10.6, 9.4 Hz, 1H, H-3β), 5.23 (t, *J* = 9.6 Hz, 1H, H-4α), 5.14 (t, *J* = 9.6 Hz, 1H, H-4β), 4.44 (ddd, *J* = 10.7, 8.7, 3.7 Hz, 1H, H-2α), 4.34 (q, *J* = 9.7 Hz, 1H, H-2β), 4.28 (dd, *J* = 12.5, 4.2 Hz, 2H, H-6aα, H-6aβ), 4.14 (dd, *J* = 12.6, 2.3 Hz, 1H, H-6bβ), 4.07 (dd, *J* = 12.3, 2.4 Hz, 1H, H-6bα), 4.03 (ddd, *J* = 10.0, 4.1, 2.4 Hz, 1H, H-5α), 3.86 (ddd, *J* = 9.9, 4.7, 2.3 Hz, 1H, H-5β), 2.20 (s, 3H, 1 × Acα), 2.12 (s, 3H, 1 × Acβ), 2.09 (s, 6H, 1 × Acα, 1 × Acβ), 2.06 (s, 3H, 1 × Acα), 2.06 (s, 6H, 1 × Acα, 1 × Acβ), 2.05 (s, 3H, 1 × Acβ).

***p*-Tolyl 3,4,6-tri-O-acetyl-2-trifluoroacetamido-2-deoxy-β-1-thio-D-glucopyranoside (6)**



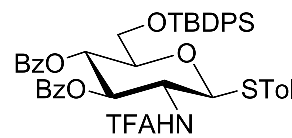
Known[3,4] trifluoroacetamido tetraacetate **5** (9.67 g, 21.8 mmol, 2:1 α/β) and *p*-thiocresol (8.13 g, 65.5 mmol, 3 equiv.) was dissolved in freshly distilled CH_2Cl_2 (97 mL). BF_3**.**Et_2O (13.7 mL, 109.1 mmol, 5 equiv.) was added at room temperature. The reaction was stirred under Ar for 40 h (TLC in 3:7 EtOAc/pentanes, R_f = 0.4). The solution was diluted with CH_2Cl_2 (80 mL) then washed carefully with sat. aq. $NaHCO_3$ (2 × 120 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 30 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 2:8 → 4:6) gave thioglycoside **6** (9.32 g, 84%) as a white/pale yellow flaky solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.32 (d, *J* = 8.1 Hz, 2H, 2 × Ar), 7.24 (d, *J* = 9.4 Hz, 1H, N-H), 7.04 (d, *J* = 8.1 Hz, 2H, 2 × Ar), 5.24 (dd, *J* = 10.2, 9.5 Hz, 1H, H-3), 4.93 (t, *J* = 9.8 Hz, 1H, H-4), 4.63 (d, *J* = 10.4 Hz, 1H, H-1), 4.14 (dd, *J* = 12.3, 5.2 Hz, 1H, H-6a), 4.10 (dd, *J* = 12.3, 4.1 Hz, 1H, H-6b), 4.01 (q, *J* = 10.1 Hz, 1H, H-2), 3.69 (ddd, *J* = 10.0, 4.9, 2.9 Hz, 1H, H-5), 2.27 (s, 3H, ArC*H₃*), 2.00, 1.93, 1.79 (3 s, 9H, 3 Ac). ^{13}C NMR (100 MHz, Chloroform-*d*) δ_C 171.64, 170.66, 169.24 (3 × *C*OCH$_3$), 157.16 (d, *J* = 37.7 Hz, *C*OCF$_3$), 139.18 (1 × 4° Ar), 134.15 (2 × Ar), 129.77 (2 × Ar), 127.24 (1 × 4° Ar), 115.66 (d, *J* = 288.1 Hz, CF$_3$), 86.15 (C-1), 75.83 (C-5), 73.64 (C-3), 68.52 (C-4), 62.34 (C-6), 53.02 (C-2), 21.16 (Ar*C*H$_3$), 20.70, 20.36, 20.30 (3 × CO*C*H$_3$). *m/z* (ESI) calculated for $C_{21}H_{28}N_2O_8F_3S$ $[M+NH_4]^+$ 525.15, found 525.2.

***p*-Tolyl 2-trifluoroacetamido-2-deoxy-β-1-thio-D-glucopyranoside (7)**



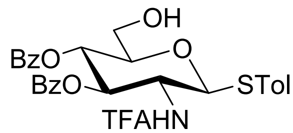
Thioglycoside **6** (5.60 g, 11.0 mmol) was suspended in MeOH (110 mL). Sodium (85 mg, 3.7 mmol, 0.33 equiv.) was added. The reaction was stirred at RT for 2.5 h (TLC in 10:1 CH_2Cl_2/MeOH, R_f = 0.3), then quenched with Dowex 50WX8 cation exchange resin (hydrogen form, 50-100 mesh). The resin was filtered and washed with MeOH (3 × 40 mL). The filtrate was concentrated giving triol **7** (4.30 g, quant.) as a white flaky solid. ^{1}H NMR (400 MHz, Methanol-d_4) δ_H 7.39 (d, J = 8.2 Hz, 2H, 2 × Ar), 7.12 (d, J = 8.0 Hz, 2H, 2 × Ar), 4.75 (d, J = 10.4 Hz, 1H, H-1), 3.87 (dd, J = 12.2, 2.0 Hz, 1H, H-6a), 3.75 (t, J = 10.1 Hz, 1H, H-2), 3.69 (dd, J = 12.1, 5.2 Hz, 1H, H-6b), 3.52 (dd, J = 9.9, 8.0 Hz, 1H, H-3), 3.35 (t, J = 9.7 Hz, 1H, H-4), 3.31 (m, 1H, H-5), 2.30 (s, 3H, CH_3). ^{13}C NMR (100 MHz, Methanol-d_4) δ_C 139.06 (1 × 4° Ar), 133.57 (2 × Ar), 130.97 (1 × 4° Ar), 130.61 (2 × Ar), 87.92 (C-1), 82.25 (C-5), 76.76 (C-3), 71.78 (C-4), 62.83 (C-6), 56.57 (C-2), 21.14 (CH_3). *m/z* (ESI) calculated for $C_{15}H_{18}NO_5F_3NaS$ $[M+Na]^+$ 404.07, found 404.1.

***p*-Tolyl 3,4-di-O-benzoyl-6-*tert*-butyldiphenylsilyl-2-trifluoroacetamido-2-deoxy-β-1-thio-D-glucopyranoside (8)**



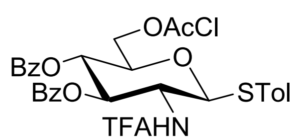
Triol **7** (4.30 g 11.3 mmol) and DMAP (140 mg, 1.15 mmol, 0.1 equiv.) were dissolved in dry pyridine (130 mL). TBDPSCl (5.9 mL, 22.7 mmol, 2 equiv.) was added. The reaction was stirred at RT under Ar for 24 h (TLC in 1:1 CH_2Cl_2/MeOH, R_f = 0.7), then BzCl (7.9 mL, 68.1 mmol, 6 equiv.) was added, and stirring continued under the same conditions for an additional 23 h (TLC in 2:8 EtOAc/pentanes, R_f = 0.6). The solution was co-concentrated with toluene. The residue was dissolved in CH_2Cl_2 (250 mL) then washed with 1 M HCl (2 × 200 mL) then aq. $NaHCO_3$ (200 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 50 mL each). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 1:9 → 3:7) gave **8** (9.30 g, quant.) as a white amorphous solid. ^{1}H NMR (400 MHz, Chloroform-d) δ_H 7.88 (dd, J = 8.4, 1.3 Hz, 2H, 2 × SiPh), 7.80 (dd, J = 8.4, 1.3 Hz, 2H, 2 × Bz), 7.73 (dd, J = 8.0, 1.5 Hz, 2H, 2 × SiPh), 7.57 (dd, J = 8.0, 1.4 Hz, 2H, 2 × Bz), 7.49 – 7.44 (m, 4H, 2 × SAr, 2 × SiPh), 7.40 – 7.27 (m, 8H, 4 × Bz, 4 × SiPh), 7.15 (t, J = 7.9 Hz, 2H, 2 × Bz), 7.05 (d, J = 8.0 Hz, 2H, 2 × SAr), 6.88 (d, J = 9.3 Hz, 1H, N-H), 5.72 (t, J = 9.8 Hz, 1H, H-3), 5.66 (t, J = 9.3 Hz, 1H, H-4), 4.96 (d, J = 10.3 Hz, 1H, H-1), 4.27 (q, J = 9.8 Hz, 1H, H-2), 3.93 – 3.77 (m, 3H, H-5, H-6a, H-6b), 2.32 (s, 3H, ArCH_3), 1.05 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (100 MHz, Chloroform-d) δ_C 167.30, 164.84 (2 × *C*OPh), 157.14 (d, J = 37.8 Hz, *C*OCF_3), 138.73 (1 × 4° SAr), 135.68 (2 × Bz), 135.51 (2 × Bz), 133.78 (2 × SAr), 133.76, 133.35 (2 × 4° Bz), 132.79 (2 × SiPh), 129.95 (2 × SiPh), 129.88 (2 × SAr), 129.71, 129.63 (2 × Bz), 129.57 (2 × SiPh), 129.04 (1 × 4° SiPh), 128.51 (2 × SiPh), 128.42 (2 × SiPh), 128.26 (1 × 4° SiPh), 127.73 (2 × Bz), 127.63 (2 × Bz), 127.55 (1 × 4° SAr), 115.54 (d, J = 288.2 Hz, CF_3), 86.31 (C-1), 79.30 (C-5), 74.48 (C-3), 68.47 (C-4), 62.50 (C-6), 53.84 (C-2), 26.65 ($C(CH_3)_3$, 21.23 (ArCH_3). *m/z* (ESI) calculated for $C_{45}H_{48}N_2O_7F_3SiS$ $[M+NH_4]^+$ 845.29, found 845.3.

***p*-Tolyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-1-thio-D-glucopyranoside (9)**



The di-O-benzoyl ester **8** (6.50 g, 7.9 mmol) was dissolved in dry THF (110 mL). AcOH (4.5 mL, 78.6 mmol, 10 equiv.) was added, followed by TBAF (1.0 M in THF, 39 mL, 39.0 mmol, 5 equiv.). The reaction was stirred at RT under N_2 for 18 h (TLC in 3:7 EtOAc/pentanes, $R_f = 0.5$). The solution was diluted with EtOAc (150 mL) then washed with sat. aq. NH_4Cl (200 mL). The aqueous layer was re-extracted with EtOAc (2 × 50 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (CH_2Cl_2/MeOH, 100:1 → 40:1) gave acceptor **9** (4.5 g, 97%) as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 9.84 (d, *J* = 9.1 Hz, 1H, N-H), 7.84 (dd, *J* = 8.5, 1.5 Hz, 2H, 2 × Bz), 7.75 (dd, *J* = 8.5, 1.4 Hz, 2H, 2 × Bz), 7.65 – 7.57 (m, 2H, 2 × Bz), 7.51 – 7.40 (m, 6H, 4 × Bz, 2 × SAr), 7.20 (d, *J* = 7.9 Hz, 2H, 2 × SAr), 5.64 (t, *J* = 9.7 Hz, 1H, H-3), 5.34 (t, *J* = 9.7 Hz, 1H, H-4), 5.21 (d, *J* = 10.3 Hz, 1H, H-1), 4.98 (t, *J* = 5.6 Hz, 1H, 6-OH), 4.11 (q, *J* = 9.9 Hz, 1H, H-2), 3.92 (ddd, *J* = 10.0, 4.8, 2.3 Hz, 1H, H-5), 3.63 (ddd, *J* = 12.3, 4.9, 2.3 Hz, 1H, H-6a), 3.54 (m, 1H, H-6b), 2.31 (s, 3H, ArC*H*$_3$). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 165.67, 165.01 (2 × *C*OPh), 156.54 (d, *J* = 36.8 Hz, *C*OCF$_3$), 138.04 (1 × 4° SAr), 134.11 (2 × Bz), 132.49 (2 × SAr), 130.20 (2 × SAr), 129.61 (2 × Bz), 129.50 (2 × Bz), 129.27 (1 × 4° Bz), 129.21 (2 × Bz), 129.15 (2 × Bz), 128.98 (1 × 4° Bz), 128.65 (2 × 4° SAr), 116.07 (d, *J* = 288.3 Hz, *C*F$_3$), 84.91 (C-1), 78.71 (C-5), 74.81 (C-3), 69.55 (C-4), 60.60 (C-6), 53.25 (C-2), 21.10 (Ar*C*H$_3$). *m/z* (ESI) calculated for $C_{29}H_{30}N_2O_7F_3S$ $[M+NH_4]^+$ 607.17, found 607.2.

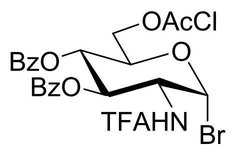
***p*-Tolyl 3,4-di-O-benzoyl-6-chloroacetyl-2-trifluoroacetamido-2-deoxy-β-1-thio-D-glucopyranoside (10)**



Acceptor **9** (3.70 g 6.3 mmol) was dissolved in CH_2Cl_2 (63 mL). Pyridine (2.0 mL, 24.7 mmol, 4 equiv.) was added, followed by chloroacetyl chloride (1.0 mL, 12.6 mmol, 2 equiv.). The reaction was stirred at RT for 15 min (TLC in 3:7 EtOAc/pentanes, $R_f = 0.7$). The solution was diluted with CH_2Cl_2 (30 mL) then washed with 1 M HCl (2 × 75 mL) then aq. $NaHCO_3$ (75 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 15 mL each). The organic layers were dried over Na_2SO_4 and concentrated, giving chloroacetate **10** (4.30 g, quant.) as white crystals/pale yellow flakes. ^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.84 (ddd, *J* = 9.9, 8.3, 1.3 Hz, 4H, 4 × Bz), 7.51 (t, *J* = 7.5 Hz, 1H, 1 × Bz), 7.46 (t, *J* = 7.5 Hz, 1H, 1 × Bz), 7.42 (d, *J* = 8.1 Hz, 2H, 2 × SAr), 7.34 (dd, *J* = 8.3, 7.4 Hz, 2H, 2 × Bz), 7.28 (dd, *J* = 8.5, 7.7 Hz, 2H, 2 × Bz), 7.20 (d, *J* = 9.3 Hz, 1H, N-H), 7.12 (d, *J* = 7.9 Hz, 2H, 2 × SAr), 5.87 (dd, *J* = 10.3, 9.6 Hz, 1H, H-3), 5.50 (t, *J* = 9.8 Hz, 1H, H-4), 5.04 (d, *J* = 10.3 Hz, 1H, H-1), 4.41 (dd, *J* = 12.2, 3.1 Hz, 1H, H-6a), 4.37 (dd, *J* = 12.2, 4.8 Hz, 1H, H-6b), 4.32 (q, *J* = 10.1 Hz, 1H, H-2), 4.08 (ddd, *J* = 10.0, 4.8, 3.0 Hz, 1H, H-5), 3.96 (dd, *J* = 24.5, 15.2 Hz, 2H, CH$_2$Cl), 2.34 (s, 3H, ArC*H*$_3$). ^{13}C NMR (100 MHz, Chloroform-*d*) δ_C 167.14 (*C*OCH$_2$Cl), 166.96, 165.10 (2 × *C*OPh), 157.26 (d, *J* = 37.9 Hz, *C*OCF$_3$), 139.20 (1 × 4° SAr), 134.14 (2 × SAr), 133.97, 133.74 (2 × Bz), 129.88 (2 ×

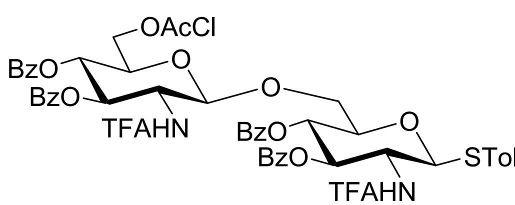
SAr), 129.85 (2 × Bz), 129.60 (2 × Bz), 128.57 (2 × Bz), 128.51 (2 × Bz), 128.36, 127.92 (2 × 4° Bz), 126.83 (1 × 4° SAr), 115.44 (d, J = 288.1 Hz, CF_3), 86.11 (C-1), 75.89 (C-5), 73.71 (C-3), 68.83 (C-4), 63.97 (C-6), 53.60 (C-2), 40.54 (CH_2Cl), 21.21 (ArCH_3). *m/z* (ESI) calculated for $C_{31}H_{31}N_2O_8F_3SCl$ $[M+NH_4]^+$ 683.14, found 683.1.

3,4-Di-O-benzoyl-6-chloroacetyl-2-trifluoroacetamido-2-deoxy-α-D-glucopyranosyl bromide (11)



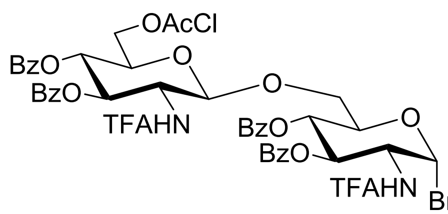
Thioglycoside **10** (3.40 g, 5.10 mmol) was dissolved in dry CH_2Cl_2 (50 mL). Br_2 (300 µL, 5.86 mmol, 1.15 equiv.) was added. The reaction was stirred at RT under Ar in the dark for 1.5 h (TLC in 2:8 EtOAc/pentanes, R_f = 0.6). The solution was diluted with CH_2Cl_2 (30 mL) then washed with 20% aq. $Na_2S_2O_3$ (40 mL), then H_2O (40 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 10 mL). The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure, giving crude bromide donor **11** (3.52 g, quant.) as a yellow amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.95 (dd, J = 8.5, 1.5 Hz, 2H, 2 × Bz), 7.90 (dd, J = 8.4, 1.3 Hz, 2H, 2 × Bz), 7.58 – 7.51 (m, 2H, 2 × Bz), 7.39 (m, 4H, 4 × Bz), 7.12 (d, J = 7.3 Hz, 1H, N-H), 6.69 (d, J = 3.7 Hz, 1H, H-1), 5.80 (t, J = 9.5 Hz, 1H, H-3), 5.76 (t, J = 9.6 Hz, 1H, H-4), 4.58 – 4.50 (m, 2H, H-2, H-5), 4.47 (dd, J = 12.6, 4.1 Hz, 1H, H-6a), 4.40 (dd, J = 12.6, 2.5 Hz, 1H, H-6b), 4.15 (d, J = 2.1 Hz, 2H, CH_2Cl).

3,4-Di-O-benzoyl-6-chloroacetyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-*p*-Tolyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-1-thio-D-glucopyranoside (12)



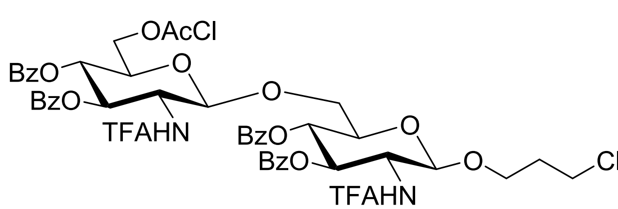
Acceptor **9** (2.00 g, 3.39 mmol) and glycosyl bromide **11** (3.17 g, 5.10 mmol, 1.5 equiv; 3.52 g crude) were dissolved in freshly distilled CH_2Cl_2 (76 mL) containing freshly activated powdered 4Å MS (5.0 g). The mixture was cooled to -45 °C under Ar in the dark for 1 h. AgOTf (1.74 g, 6.77 mmol, 2 equiv.) in dry toluene (10 mL) was added, and the reaction was stirred for 2 h (TLC in 2:8 acetone/pentanes, R_f = 0.2) and then quenched with NEt_3. The mixture was diluted with CH_2Cl_2 (80 mL) and filtered through celite. The solids were washed with CH_2Cl_2 (3 × 80 mL). The filtrate was washed with sat. aq. NaCl (2 × 250 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 100 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (acetone/hexanes, 2:8 → 3:7) gave disaccharide **12** (3.45 g, 90%) as a pale yellow amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.96 – 7.87 (m, 6H, 6 × Bz), 7.82 (dd, J = 8.6, 1.5 Hz, 2H, 2 × Bz), 7.51 (m, 5H, N-H', 4 × Bz), 7.44 (d, J = 8.1 Hz, 2H, 2 × SAr), 7.35 (m, 8H, 8 × Bz), 7.20 (d, J = 8.0 Hz, 2H, 2 × SAr), 6.92 (d, J = 8.7 Hz, 1H, N-H), 5.92 (t, J = 9.9 Hz, 1H, H-3), 5.65 (t, J = 9.7 Hz, 1H, H-3'), 5.58 (t, J = 9.6 Hz, 1H, H-4'), 5.42 (t, J = 9.7 Hz, 1H, H-4), 5.14 (d, J = 10.2 Hz, 1H, H-1), 4.69 (d, J = 8.4 Hz, 1H, H-1'), 4.53 (q, J = 9.2 Hz, 1H, H-2'), 4.34 (d, J = 3.7 Hz, 2H, H-6a, H-6b), 4.25 (dd, J = 12.0, 2.0 Hz, 1H, H-6a'), 3.97 (dd, J = 23.68, 15.14 Hz, 2H, CH_2Cl), 3.95 – 3.88 (m, 3H, H-2, H-5, H-5'), 3.60 (dd, J = 11.9, 4.1 Hz, 1H, H-6b'), 2.37 (s, 3H, Ar*CH₃*). ^{13}C NMR (100 MHz, Chloroform-*d*) δ_C 167.06 (*C*OCH$_2$Cl), 166.45, 166.33, 165.91, 165.12 (4 × *C*OPh), 157.65 (d, J = 37.9 Hz, 1 × *C*OCF$_3$), 157.09 (d, J = 38.0 Hz, 1 × *C*OCF$_3$), 139.40 (1 × 4° SAr), 134.07 (1 × Bz), 133.95 (2 × SAr), 133.68 (2 × Bz), 133.64 (1 × Bz), 130.14 (2 × SAr), 129.91 (2 × Bz), 129.86 (2 × Bz), 129.75 (2 × Bz), 129.72 (2 × Bz), 128.59 (1 × Bz), 128.50 (2 × Bz), 128.49 (2 × Bz), 128.47, 128.45 (2 × Bz), 128.35, 128.20, 128.06 (3 × 4° Bz), 126.35 (1 × 4° SAr), 115.89 (d, J = 287.8 Hz, 1 × CF_3), 115.68 (d, J = 288.0 Hz, 1 × CF_3), 101.44 (C-1'), 84.85 (C-1), 77.19 (C-5), 72.88 (C-3), 72.61 (C-3'), 72.07 (C-5'), 68.94 (C-4), 68.88 (C-4'), 68.13 (C-6'), 63.58 (C-6), 54.58 (C-2'), 53.83 (C-2), 40.55 (CH_2Cl), 21.15 (Ar*C*H$_3$). *m/z* (ESI) calculated for $C_{53}H_{49}N_3O_{15}F_6SCl$ $[M+NH_4]^+$ 1148.25, found 1148.2.

3,4-Di-O-benzoyl-6-chloroacetyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-α-D-glucopyranosyl bromide (13)



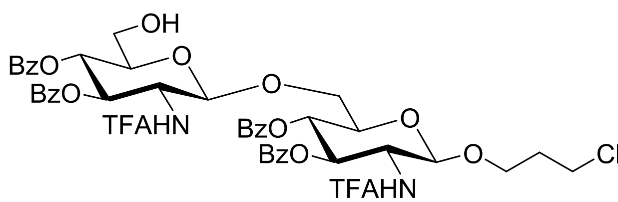
Disaccharide thioglycoside **12** (2.00 g, 1.77 mmol) was dissolved in dry CH_2Cl_2 (18 mL). Br_2 (118 µL, 2.30 mmol, 1.3 equiv.) was added. The reaction was stirred at RT under Ar in the dark for 1.5 h (TLC in 7:13 EtOAc/pentanes, R_f = 0.4). The solution was diluted with CH_2Cl_2 (12 mL) then washed with 20% aq. $Na_2S_2O_3$ (30 mL) then H_2O (30 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 7 mL). The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure, giving crude glycosyl bromide **13** (2.00 g, quant.) as a yellow amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 8.01 (dd, J = 8.5, 1.4 Hz, 2H, 2 × Bz), 7.95 – 7.84 (m, 6H, 6 × Bz), 7.59 (t, J = 7.0 Hz, 1H, 1 × Bz), 7.52 (t, J = 7.5 Hz, 3H, 3 × Bz), 7.44 (t, J = 7.8 Hz, 2H, 2 × Bz), 7.40 – 7.33 (m, 7H, N-H', 6 × Bz), 7.04 (d, J = 7.6 Hz, 1H, N-H), 6.72 (d, J = 3.6 Hz, 1H, H-1), 5.84 (t, J = 9.4 Hz, 1H, H-3), 5.72 (t, J = 9.7 Hz, 1H, H-3'), 5.68 (t, J = 9.4 Hz, 1H, H-4), 5.56 (t, J = 9.6 Hz, 1H, H-4'), 4.67 (d, J = 8.4 Hz, 1H, H-1'), 4.46 (q, J = 8.2 Hz, 1H, H-2'), 4.43 – 4.34 (m, 2H, H-5, H-5', H-6a, H-6b), 4.30 (dd, J = 12.0, 2.1 Hz, 1H, H-6a'), 4.04 (d, J = 1.0 Hz, 2H, CH_2Cl), 3.94 (dt, J = 9.6, 3.7 Hz, 1H, H-2), 3.57 (dd, J = 11.8, 2.8 Hz, 1H, H-6b').

3,4-Di-O-benzoyl-6-chloroacetyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (14)



Crude glycosyl bromide **13** (1.92 g, 1.76 mmol; 2.00 g crude) and 3-chloropropanol (1.5 mL, 17.9 mmol, 10 equiv.) were dissolved in freshly distilled CH_2Cl_2 (25 mL) containing freshly activated powdered 4Å MS (2.5 g). The mixture was cooled to 0 °C under Ar in the dark for 1 h. AgOTf (0.59 g, 2.30 mmol, 1.3 equiv.) in dry toluene (3 mL) was added, and the reaction was stirred under the same conditions for 2 h (TLC in 1:3 acetone/pentanes, R_f = 0.2), then quenched with NEt_3. The mixture was diluted with CH_2Cl_2 (20 mL) and filtered through celite. The solids were washed with CH_2Cl_2 (3 × 20 mL). The filtrate was washed with sat. aq. NaCl (2 × 80 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 20 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 28:72 → 4:6) gave disaccharide **14** (1.72 g, 89%) as a white amorphous solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ_H 8.78 (d, *J* = 9.0 Hz, 1H, N-H'), 8.68 (d, *J* = 9.2 Hz, 1H, N-H), 7.95 (dd, *J* = 8.4, 1.3 Hz, 2H, 2 × Bz), 7.92 – 7.84 (m, 6H, 6 × Bz), 7.66 – 7.53 (m, 4H, 4 × Bz), 7.51 – 7.38 (m, 8H, 8 × Bz), 5.84 (dd, *J* = 10.6, 9.3 Hz, 1H, H-3), 5.81 (dd, *J* = 10.7, 9.3 Hz, 1H, H-3'), 5.49 (t, *J* = 9.6 Hz, 1H, H-4), 5.48 (t, *J* = 9.8 Hz, 1H, H-4'), 5.16 (d, *J* = 8.4 Hz, 1H, H-1), 5.10 (d, *J* = 8.4 Hz, 1H, H-1'), 4.41 (dd, *J* = 12.2, 5.2 Hz, 1H, H-6a'), 4.37 – 4.31 (m, 2H, H-2, H-6b'), 4.31 – 4.14 (m, 6H, H-2, H-5, H-5', H-6a, $COCH_2Cl$), 4.07 (dt, *J* = 10.9, 5.5 Hz, 1H, OC*H*HCH_2), 3.87 (dd, *J* = 11.8, 6.1 Hz, 1H, H-6b), 3.79 (ddd, *J* = 12.7, 7.6, 5.0 Hz, 1H, OCH*H*CH_2), 3.69 (t, *J* = 6.5 Hz, 2H, CH_2CH_2Cl), 2.16 – 1.97 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, Acetone-d_6) δ_C 167.68 (*C*OCH_2Cl), 166.42 (2 × *C*OPh), 166.00, 165.87 (2 × *C*OPh), 134.49, 134.45, 134.37, 134.35 (4 × Bz), 130.52 (2 × Bz), 130.40 (2 × Bz), 130.34 (2 × Bz), 130.32 (2 × Bz), 130.14, 130.06, 130.06, 130.03 (4 × 4° Bz), 129.48 (2 × Bz), 129.44 (2 × Bz), 129.40 (2 × Bz), 129.37 (2 × Bz), 101.16 (C-1), 100.97 (C-1'), 73.87 (C-5), 73.76 (C-3), 73.73 (C-3'), 72.58 (C-5'), 70.83 (C-4), 70.46 (C-4'), 69.08 (C-6), 67.01 (O*C*H_2CH_2), 64.45 (C-6'), 55.78 (C-2'), 55.59 (C-2), 42.21 (CH_2*C*H_2Cl), 41.45 (CO*C*H_2Cl), 33.30 (CH_2*C*H_2CH_2). *m/z* (ESI) calculated for $C_{49}H_{48}N_3O_{16}F_6Cl_2$ $[M+NH_4]^+$ 1128.23, found 1118.24.

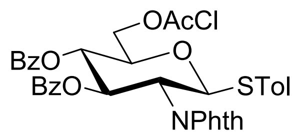
3,4-Di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (15)



Disaccharide **14** (2.08 g, 1.89 mmol) and thiourea (0.72 g, 9.46 mmol, 5 equiv) were dissolved in a 1:1 mixture of pyridine/EtOH (190 mL). The solution was stirred at 70 °C for 18 h (TLC in 4:6 EtOAc/pentanes, R_f = 0.3), then co-concentrated with toluene. The residue was dissolved in CH_2Cl_2 (300 mL) then washed with 1 M HCl (2 × 300 mL) then sat. aq. $NaHCO_3$ (300 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 60 mL each), and the organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 7:13 → 1:1) gave disaccharide acceptor **15** (1.01 g, 52%) as a pale yellow amorphous solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.95 – 7.84 (m, 8H, 8 × Bz), 7.53 – 7.44 (m, 5H, N-H', 4 × Bz), 7.41 – 7.28 (m, 9H, N-H, 8 × Bz), 5.81 (dd, *J* = 10.7, 9.5 Hz, 1H, H-3), 5.69 (dd, *J* = 10.6, 9.6 Hz, 1H, H-3'), 5.52 (t, *J* = 9.5 Hz, 1H, H-4), 5.39 (d, *J* = 9.6 Hz, 1H, H-4'), 4.86 (d, *J* = 8.3 Hz, 1H, H-1), 4.76 (d, *J* = 8.4 Hz, 1H, H-1'), 4.36 (dd, *J* = 9.9, 9.3 Hz, 1H, H-2'), 4.24 (dd, *J* = 11.3, 2.4 Hz, 1H, H-6a), 4.13 (dd, *J* = 10.6, 8.5 Hz, 1H, H-2), 4.04 – 3.99 (m, 1H, OC*H*HCH_2), 3.95 (ddd, *J* =

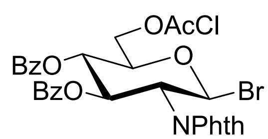
9.7, 4.1, 2.6 Hz, 1H, H-5), 3.84 – 3.74 (m, 1H, H-6a'), 3.71 – 3.57 (m, 6H, H-5', H-6b, H-6b', OCH*H*CH_2, CH_2Cl), 2.11 – 1.92 (m, 2H, $CH_2C\mathit{H_2}CH_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 166.80, 166.70, 166.04, 165.82 (4 × *C*OPh), 157.62 (d, *J* = 37.6 Hz, 1 × *C*OCF_3), 157.51 (d, *J* = 37.7 Hz, 1 × *C*OCF_3), 134.06, 133.84, 133.75, 133.67 (4 × Bz), 129.89 (2 × Bz), 129.85 (2 × Bz), 129.83 (2 × Bz), 129.81 (2 × Bz), 128.66 (2 × Bz), 128.54 (2 × Bz), 128.52 (2 × Bz), 128.49 (2 × Bz), 128.47, 128.34, 128.27, 128.12 (4 × 4° Bz), 115.67 (q, *J* = 289.8 Hz, 1 × CF_3), 115.47 (q, *J* = 287.6 Hz, 1 × CF_3), 100.91 (C-1'), 100.55 (C-1), 74.80 (C-5'), 72.98 (C-5), 72.65 (C-3'), 72.09 (C-3), 69.53 (C-4'), 69.00 (C-4), 67.99 (C-6), 66.25 (O*C*H_2CH_2), 61.05 (C-6'), 55.14 (C-2), 54.65 (C-2'), 41.42 (CH_2Cl), 31.98 ($CH_2\mathit{C}H_2CH_2$). *m/z* (ESI) calculated for $C_{47}H_{47}N_3O_{15}F_6Cl$ $[M+NH_4]^+$ 1042.26, found 1042.26.

_p_-Tolyl 3,4-di-O-benzoyl-6-chloroacetyl-2-phthalimido-2-deoxy-β-1-thio-D-glucopyranoside (16)



Known[6] phthalimido-protected thioglycoside **16** was synthesized as described previously.[7] ^1H NMR (400 MHz, Chloroform-*d*) δ_H 7.92 – 7.85 (m, 3H, 2 × Bz, 1 × Phth), 7.74 – 7.67 (m, 5H, 2 × Bz, 3 × Phth), 7.49 (tt, *J* = 6.8, 1.2 Hz, 1H, 1 × Bz), 7.41 (tt, *J* = 7.0, 1.2 Hz, 1H, 1 × Bz), 7.37 – 7.32 (m, 4H, 2 × SAr, 2 × Bz), 7.24 (t, *J* = 7.9 Hz, 2H, 2 × Bz), 7.12 (d, 2H, 2 × SAr), 6.25 (dd, *J* = 10.3, 9.3 Hz, 1H, H-3), 5.81 (d, *J* = 10.5 Hz, 1H, H-1), 5.54 (dd, *J* = 10.1, 9.3 Hz, 1H, H-4), 4.55 (t, *J* = 10.4 Hz, 1H, H-2), 4.42 (d, *J* = 4.3 Hz, 2H, H-6a, H-6b), 4.14 (ddd, 1H, H-5), 4.08 (d, *J* = 1.8 Hz, 2H, CH_2Cl), 2.35 (s, 3H, ArC*H₃*). ^{13}C NMR (100 MHz, Chloroform-*d*) δ_C 166.92 (*C*OCH_2Cl), 165.60, 165.20 (2 × O*C*OPh), 138.92 (1 × 4° SAr), 134.32, 134.21 (2 × Phth), 134.06 (2 × SAr), 133.56, 133.29 (2 × Bz), 129.80 (2 × Bz), 129.72 (2 × SAr), 129.71 (2 × Bz), 128.56 (1 × 4° Bz), 128.44 (2 × Bz), 128.27 (2 × Bz), 126.84 (1 × 4° SAr), 123.67 (2 × Phth), 83.44 (C-1), 75.81 (C-5), 71.85 (C-3), 69.44 (C-4), 64.00 (C-6), 53.76 (C-2), 40.68 (CH_2Cl), 21.21 (Ar*C*H_3). *m/z* (ESI) calculated for $C_{37}H_{30}NO_9NaSCl$ $[M+Na]^+$ 722.12, found 722.13.

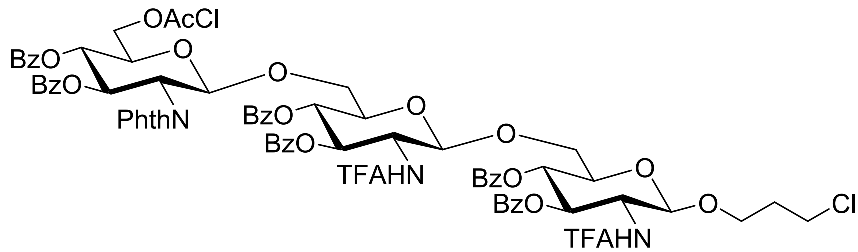
3,4-di-O-benzoyl-6-chloroacetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl bromide (17)



Known[6] thioglycoside **16** (423 mg, 0.604 mmol) was dissolved in dry CH_2Cl_2 (6 mL). Br_2 (36 μL, 0.703 mmol, 1.15 equiv.) was added. The reaction was stirred at RT under Ar in the dark for 1.5 h (TLC in 2:8 EtOAc/pentanes, R_f = 0.3). The solution was diluted with CH_2Cl_2 (4 mL) then washed with 20% aq. $Na_2S_2O_3$ (10 mL) then H_2O (10 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 2 mL). The organic layers were dried and concentrated, giving crude glycosyl bromide **17** (438 mg, quant.) as a white amorphous solid. ^1H NMR (400 MHz, Chloroform-*d*) δ_H 7.89 (dd, *J* = 8.4, 1.3 Hz, 2H, 2 × Bz), 7.83 (bs, 2H, 2 × Phth), 7.77 – 7.69 (m, 4H, 2 × Bz, 2 × Phth), 7.51 (tt, *J* = 7.0, 1.3 Hz, 1H, 1 × Bz), 7.44 (tt, *J* = 7.1, 1.3 Hz, 1H, 1 × Bz), 7.39 – 7.34 (m, 2H, 2 × Bz), 7.30 – 7.24 (m, 2H, 2 × Bz), 6.56 (d, *J* = 9.6 Hz, 1H, H-1), 6.22 (dd, *J* = 10.4, 9.3 Hz, 1H, H-3), 5.69 (dd, *J* = 10.1, 9.4 Hz, 1H, H-4), 4.86 (dd, *J* = 10.4, 9.6 Hz, 1H, H-2), 4.46

(dd, J = 12.5, 4.7 Hz, 1H, H-6a), 4.41 (dd, J = 12.5, 2.7 Hz, 1H, H-6b), 4.22 (ddd, J = 10.2, 4.6, 2.7 Hz, 1H, H-5), 4.16 (d, J = 1.7 Hz, 2H, CH_2Cl).

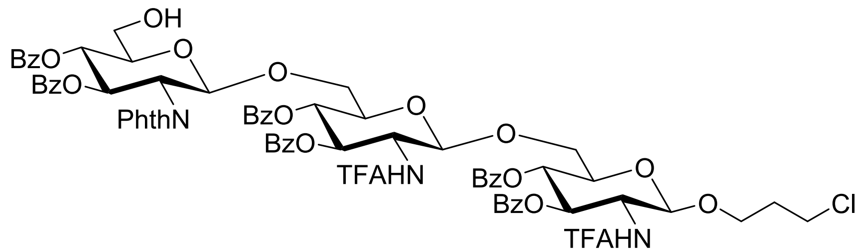
3,4-Di-O-benzoyl-6-chloroacetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (18)



Disaccharide acceptor **15** (310 mg, 0.302 mmol) and glycosyl bromide **17** (397 mg, 0.604 mmol, 2 equiv; 438 mg crude) were dissolved in freshly distilled CH_2Cl_2 (9 mL) containing freshly activated powdered 4Å MS (0.90 g). The mixture was cooled to -45 °C under Ar in the dark for 1 h. AgOTf (210 mg, 0.817 mmol, 2.7 equiv.) in dry toluene (1.8 mL) was added, and the reaction was stirred under the same conditions for 2 h (TLC in 4:6 EtOAc/pentanes, R_f = 0.5), then quenched with NEt_3. The mixture was diluted with CH_2Cl_2 (30 mL) and filtered through celite. The solids were washed with CH_2Cl_2 (3 × 30 mL). The filtrate was washed with sat. aq. NaCl (2 × 90 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 15 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 3:7 → 4:6) gave trisaccharide **18** (435 mg, 90%) as a white/pale yellow amorphous solid. ^{1}H NMR (600 MHz, Chloroform-d) δ_H 8.01 (dd, J = 8.4, 1.2 Hz, 2H, 2 × Bz), 7.92 (dt, J = 8.4, 1.3 Hz, 4H, 4 × Bz), 7.85 – 7.78 (m, 6H, 6 × Bz), 7.74 – 7.67 (m, 2H, 2 × Phth), 7.66 – 7.63 (m, 2H, 2 × Phth), 7.58 (d, J = 9.4 Hz, 1H, N-H), 7.55 – 7.41 (m, 6H, 6 × Bz), 7.38 – 7.29 (m, 8H, 8 × Bz), 7.19 – 7.13 (m, 2H, 2 × Bz), 7.09 (d, J = 8.8 Hz, 1H, N-H'), 6.32 (dd, J = 10.7, 9.1 Hz, 1H, H-3''), 5.97 (dd, J = 10.7, 9.5 Hz, 1H, H-3), 5.65 (dd, J = 10.1, 9.2 Hz, 1H, H-4''), 5.64 (dd, J = 10.5, 9.3 Hz, 1H, H-3'), 5.53 (d, J = 8.4 Hz, 1H, H-1''), 5.40 (t, J = 9.7 Hz, 1H, H-4), 5.19 (t, J = 9.8 Hz, 1H, H-4'), 4.85 (d, J = 8.4 Hz, 1H, H-1), 4.67 (d, J = 8.4 Hz, 1H, H-1'), 4.64 (dd, J = 10.8, 8.4 Hz, 1H, H-2''), 4.37 (dd, J = 12.2, 6.0 Hz, 1H, H-6a''), 4.32 – 4.23 (m, 3H, H-2, H-2', H-6b''), 4.17 – 4.10 (m, 2H, H-5, H-5''), 4.08 (dt, J = 10.0, 5.0 Hz, 1H, OC*H*HCH$_2$), 4.03 – 3.86 (m, 5H, H-5', H-6a, H-6a', $COCH_2Cl$), 3.84 (dd, J = 12.5, 6.4 Hz, 1H, H-6b), 3.79 (dd, J = 12.2, 2.1 Hz, 1H, H-6b'), 3.70 (ddd, J = 13.0, 8.9, 4.2 Hz, 1H, OCH*H*CH$_2$), 3.62 (dd, J = 7.1, 5.4 Hz, 2H, CH$_2$C*H$_2$*Cl), 2.11 (ddq, J = 13.7, 10.1, 5.1 Hz, 1H, CH$_2$C*H*HCH$_2$), 1.96 (dddd, J = 14.6, 11.7, 7.0, 4.9 Hz, 1H, CH$_2$CH*H*CH$_2$). ^{13}C NMR (125 MHz, Chloroform-d) δ_C 167.92 (2 × *C*OPhth), 167.03 (*C*OCH$_2$Cl), 166.39, 166.36, 166.08, 165.60, 165.32, 165.15 (6 × *C*OPh), 157.63 (d, J = 37.6 Hz, 1 × *C*OCF$_3$), 157.41 (d, J = 37.6 Hz, 1 × *C*OCF$_3$), 134.45 (2 × Phth), 133.94, 133.70, 133.63, 133.57, 133.54, 133.36 (6 × Bz), 131.25 (2 × 4° Phth), 130.06 (2 × Bz), 129.89 (2 × Bz), 129.85 (2 × Bz), 129.84 (2 × Bz), 129.81 (2 × Bz), 129.78 (2 × Bz), 128.77 (2 × Bz), 128.61 (1 × 4° Bz), 128.53 (2 × Bz), 128.50 (2 × Bz, 2 × 4° Bz), 128.49 (4 × Bz), 128.47 (2 × Bz), 128.42 (2 × Bz), 128.41, 128.36 (2 × 4° Bz), 128.24 (2 × Bz), 123.69 (2 × Phth), 115.68 (q, J = 288.2 Hz, 1 × CF$_3$), 115.62 (q, J = 288.2 Hz, 1 × CF$_3$), 101.62 (C-1'), 100.54 (C-1), 99.43 (C-1''), 73.81 (C-5'), 73.03 (C-5), 72.42 (C-5''), 72.38 (C-3'), 72.01 (C-3), 70.38 (C-3''), 70.23 (C-4), 70.16 (C-6'), 70.14 (C-6), 69.79 (C-4', C-4''), 66.31 (O*C*H$_2$CH$_2$), 64.01 (C-6''), 55.06 (C-2), 54.96 (C-2'), 54.94

(C-2''), 41.55 ($CH_2\mathit{C}H_2Cl$), 40.64 ($CO\mathit{C}H_2Cl$), 32.04 ($CH_2\mathit{C}H_2CH_2$). *m/z* (ESI) calculated for $C_{77}H_{69}N_4O_{24}F_6Cl_2$ $[M+NH_4]^+$ 1617.36, found 1617.35.

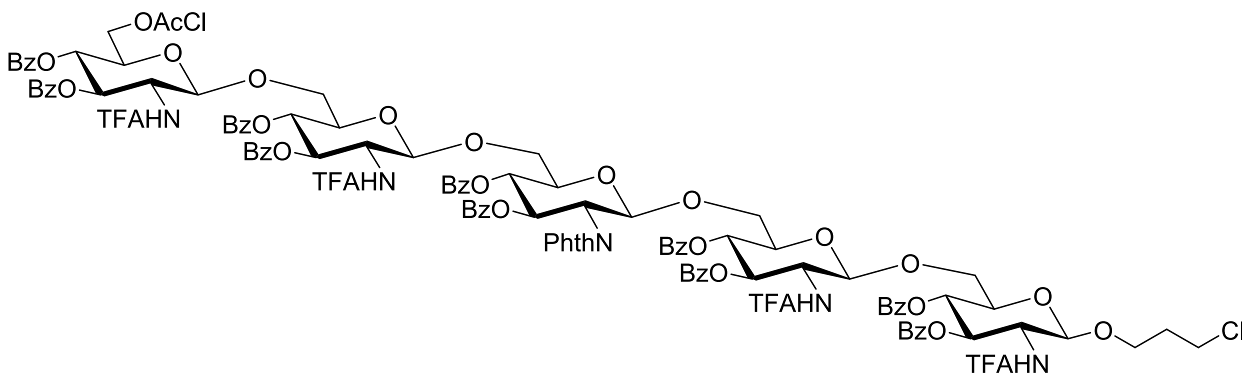
3,4-Di-O-benzoyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (19)



Trisaccharide **18** (424 mg, 0.265 mmol) and thiourea (101 mg, 1.33 mmol, 5 equiv) were dissolved in a 1:1 mixture of pyridine/EtOH (28 mL). The solution was stirred at 70 °C for 18 h (TLC in 4:6 EtOAc/pentanes, R_f = 0.2), then co-concentrated with toluene. The residue was dissolved in CH_2Cl_2 (70 mL) then washed with 1 M HCl (2 × 70 mL) then sat. aq. $NaHCO_3$ (70 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 15 mL), and the organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 4:6) gave trisaccharide acceptor **19** (225 mg, 56%) as a white amorphous solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.96 (dd, *J* = 8.3, 1.1 Hz, 2H, 2 × Bz), 7.92 (dd, *J* = 8.4, 1.2 Hz, 2H, 2 × Bz), 7.87 (dd, *J* = 8.4, 1.2 Hz, 2H, 2 × Bz), 7.82 (dd, *J* = 8.4, 1.2 Hz, 2H, 2 × Bz), 7.76 (dd, *J* = 8.4, 1.2 Hz, 2H, 2 × Bz), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H, 2 × Phth), 7.66 (dd, *J* = 8.3, 1.2 Hz, 2H, 2 × Bz), 7.63 (dd, *J* = 5.5, 3.0 Hz, 2H, 2 × Phth), 7.58 (d, *J* = 9.0 Hz, 1H, N-H), 7.55 – 7.45 (m, 6H, 6 × Bz), 7.42 – 7.38 (m, 3H, 3 × Bz), 7.37 – 7.30 (m, 9H, 9 × Bz), 7.24 – 7.20 (m, 2H, 2 × Bz), 7.03 (d, *J* = 8.7 Hz, 1H, N-H'), 6.32 (dd, *J* = 10.7, 9.2 Hz, 1H, H-3''), 5.80 (dd, *J* = 10.7, 9.5 Hz, 1H, H-3), 5.58 (dd, *J* = 10.7, 9.4 Hz, 1H, H-3'), 5.55 (d, *J* = 8.4 Hz, 1H, H-1''), 5.43 – 5.32 (m, 3H, H-4, H-4', H-4''), 4.87 (d, *J* = 8.4 Hz, 1H, H-1), 4.67 (d, *J* = 8.4 Hz, 1H, H-1'), 4.53 (dd, *J* = 10.8, 8.4 Hz, 1H, H-2''), 4.26 – 4.17 (m, 2H, H-2, H-2'), 4.14 – 4.08 (m, 2H, H-5, H-6a'), 3.97 (dd, *J* = 11.0, 2.3 Hz, 1H, H-6a''), 3.93 – 3.89 (m, 2H, H-6a, $OC\mathit{H}HCH_2$), 3.87 – 3.77 (m, 5H, H-5', H-5'', H-6b, H-6b', H-6b''), 3.69 – 3.64 (m, 3H, $OCH\mathit{H}CH_2$, CH_2Cl), 2.18 – 2.12 (m, 1H, $CH_2C\mathit{H}HCH_2$), 2.07 – 1.98 (m, 1H, $CH_2CH\mathit{H}CH_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 166.46, 166.42, 166.40, 165.90, 165.64, 165.07 (6 × *C*OPh), 157.60 (d, *J* = 37.5 Hz, 1 × $\mathit{C}OCF_3$), 157.39 (d, *J* = 37.7 Hz, 1 × $\mathit{C}OCF_3$), 134.14 (2 × Phth), 133.89, 133.79, 133.58, 133.51, 133.49, 133.34 (6 × Bz), 131.49 (2 × 4° Phth), 129.98 (2 × Bz), 129.96 (2 × Bz), 129.85 (2 × Bz), 129.78 (4 × Bz), 129.71 (2 × Bz), 128.68 (2 × Bz), 128.57 (1 × 4° Bz), 128.50 (2 × Bz), 128.49 (2 × 4° Bz), 128.45 (2 × Bz), 128.42 (2 × Bz, 1 × 4° Bz), 128.42 (1 × 4° Bz), 128.39 (2 × Bz, 1 × 4° Bz), 128.30 (2 × Bz), 123.53 (2 × Phth), 115.66 (q, *J* = 288.2 Hz, 1 × CF_3), 115.58 (q, *J* = 288.3 Hz, 1 × CF_3), 101.67 (C-1'), 100.56 (C-1), 98.28 (C-1''), 74.35 (C-5''), 73.36 (C-5. C-5'), 72.40 (C-3'), 72.20 (C-3), 70.44 (C-3''), 70.13 (C-4''), 70.03 (C-4), 70.01 (C-6), 69.27 (C-4'), 68.36 (C-6''), 66.46 (C-6), 61.06 (O*C*H2CH$_2$), 55.20 (C-2), 54.93 (C-2'), 54.76 (C-2''), 41.58 (CH_2Cl), 32.12 ($CH_2\mathit{C}H_2CH_2$). *m/z* (ESI) calculated for $C_{75}H_{68}N_4O_{23}F_6Cl$ $[M+NH_4]^+$ 1541.39, found 1541.38.

3,4-Di-O-benzoyl-6-chloroacetyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-

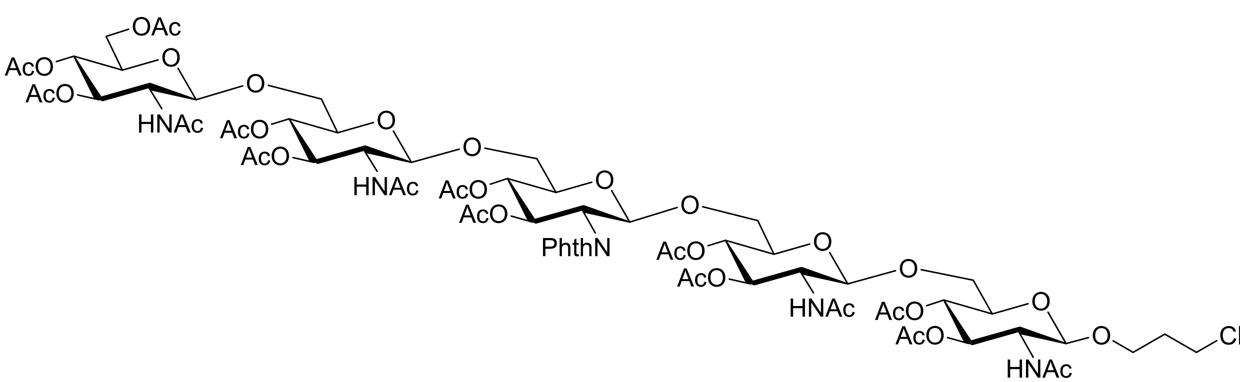
benzoyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (20)



Trisaccharide acceptor **19** (165 mg, 0.108 mmol) and glycosyl bromide **13** (236 mg, 0.217 mmol, 2 equiv; 237 mg crude) were dissolved in freshly distilled CH_2Cl_2 (3 mL) containing freshly activated powdered 4Å MS (300 mg). The mixture was cooled to -45 °C under Ar in the dark for 1 h. AgOTf (75 mg, 0.292 mmol, 2.7 equiv.) in dry toluene (0.6 mL) was added, and the reaction was stirred for 2 h (TLC in 4:6 EtOAc/pentanes, R_f = 0.4), then quenched with NEt_3. The mixture was diluted with CH_2Cl_2 (7 mL) and filtered through celite. The solids were washed with CH_2Cl_2 (3 × 7 mL). The filtrate was washed with sat. aq. NaCl (2 × 25 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 5 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/hexanes, 3:7 → 4:6) gave pentasaccharide **20** (216 mg, 79%) as a white amorphous solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.41 (d, *J* = 6.9 Hz, 1H, 1 × N-H), 8.37 (d, *J* = 9.7 Hz, 1H, 1 × N-H), 8.11 – 7.95 (m, 19H, 1 × N-H, 18 × Bz), 7.94 – 7.91 (m, 2H, 2 × Bz), 7.70 (d, *J* = 7.6 Hz, 1H, 1 × Phth), 7.65 (t, *J* = 7.3 Hz, 1H, 1 × Phth), 7.63 – 7.60 (m, 2H, 2 × Bz), 7.58 – 7.37 (m, 17H, 16 × Bz, 1 × Phth), 7.36 – 7.30 (m, 6H, 6 × Bz), 7.20 (td, *J* = 7.6, 1.7 Hz, 2H, 2 × Bz), 7.17 (td, *J* = 7.6, 1.6 Hz, 2H, 2 × Bz), 7.13 – 7.10 (m, 3H, 2 × Bz, 1 × Phth), 6.90 (d, *J* = 8.1 Hz, 1H, 1 × N-H), 6.55 (dd, *J* = 11.1, 9.0 Hz, 1H, H-3''), 6.32 (dd, *J* = 10.5, 9.1 Hz, 1H, 1 × H-3), 6.04 (dd, *J* = 10.7, 9.7 Hz, 1H, 1 × H-3), 5.90 (dd, *J* = 10.6, 10.1 Hz, 1H, 1 × H-3), 5.77 – 5.67 (m, 3H, 1 × H-3, H-4'', 1 × H-4), 5.55 (dd, *J* = 10.1, 9.1 Hz, 1H, 1 × H-4), 5.39 – 5.34 (m, 2H, 1 × H-1, 1 × H-4), 5.29 (d, *J* = 8.5 Hz, 1H, H-1''), 5.10 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 4.97 (d, *J* = 8.5 Hz, 1H, 1 × H-1), 4.91 (d, *J* = 8.4 Hz, 1H, 1 × H-1), 4.83 (dd, *J* = 11.1, 8.5 Hz, 1H, H-2''), 4.79 – 4.72 (m, 3H, H-5'', 2 × H-5), 4.69 – 4.62 (m, 3H, 1 × H-1, 2 × H-2), 4.57 (q, *J* = 9.0 Hz, 1H, 1 × H-2), 4.31 (dd, *J* = 12.2, 2.3 Hz, 1H, 1 × H-6a), 4.25 (dd, *J* = 12.9, 11.0 Hz, 1H, 1 × H-6a), 4.21 (dd, *J* = 9.7, 2.0 Hz, 1H, 1 × H-5), 4.17 (dd, *J* = 12.3, 5.9 Hz, 1H, 1 × H-6b), 4.13 – 4.09 (m, 3H, H-6a'', 1 × H-6a, OC*H*HCH$_2$), 3.96 (ddd, *J* = 10.1, 5.8, 2.4 Hz, 1H, 1 × H-5), 3.92 (dd, *J* = 7.2, 2.2 Hz, 1H, 1 × H-2), 3.87 (dd, *J* = 12.9, 9.6 Hz, 1H, 1 × H-6a), 3.81 (d, *J* = 15.4 Hz, 1H, COC*H*HCl), 3.69 (td, *J* = 10.1, 3.9 Hz, 1H, OCH*H*CH$_2$), 3.65 – 3.55 (m, 6H, H-6b'', 2 × H-6b, CH$_2$C*H$_2$*Cl, COCH*H*Cl), 3.47 – 3.43 (m, 1H, 1 × H-6b), 2.15 – 2.09 (m, 1H, CH$_2$C*H*HCH$_2$), 1.96 – 1.88 (m, 1H, CH$_2$CH*H*CH$_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 169.18, 167.98 (2 × *C*OPhth), 167.28 (*C*OCH$_2$Cl), 166.84, 166.82, 166.59, 166.54, 166.46, 165.72, 165.57, 165.36, 165.15, 164.94 (10 × *C*OPh), 158.38 (d, *J* = 38.5 Hz, 1 × *C*OCF$_3$), 158.02 (d, *J* = 37.7 Hz, 1 × *C*OCF$_3$), 157.96 (d, *J* = 37.6 Hz, 1 × *C*OCF$_3$), 157.59 (d, *J* = 37.6 Hz, 1 × *C*OCF$_3$), 134.92 (2 × Phth), 133.91, 133.87, 133.83, 133.77, 133.73, 133.53, 133.40 (7 × Bz), 133.35 (2 × Bz), 133.20 (1 × Bz), 130.69, 130.48 (2 × 4° Phth), 130.22

(2 × Bz), 130.21 (2 × Bz), 130.16 (2 × Bz), 130.07 (2 × Bz), 129.90 (6 × Bz), 129.83 (2 × Bz), 129.80 (2 × Bz), 129.70 (2 × Bz), 129.08 (2 × Bz), 129.05 (4° Bz), 128.93 (2 × Bz), 128.87, 128.86, 128.84, 128.84 (4 × 4° Bz), 128.69 (2 × Bz), 128.65 (1 × 4° Bz), 128.64 (2 × Bz), 128.62 (1 × 4° Bz), 128.57 (2 × Bz), 128.43 (1 × 4° Bz), 128.40 (2 × Bz), 128.38 (2 × Bz), 128.35 (2 × Bz), 128.30 (2 × Bz), 128.23 (2 × Bz), 128.22, 128.13 (2 × 4° Bz), 124.36, 123.48 (2 × Phth), 115.96 (q, J = 288.0 Hz, 1 × CF_3), 115.59 (q, J = 287.8 Hz, 1 × CF_3), 115.36 (q, J = 288.4 Hz, 1 × CF_3), 115.04 (q, J = 287.1 Hz, 1 × CF_3), 104.09, 101.65, 100.72 (3 × C-1), 100.50 (C-1''), 100.42 (1 × C-1), 74.65 (1 × C-5), 73.90, 73.55 (C-6'', 1 × C-6), 73.50 (C-5''), 72.59 (1 × C-6), 72.53 (1 × C-3, 1 × C-5), 72.51 (1 × C-5), 72.28 (2 × C-3, 1 × C-5, 1 × C-6), 71.74 (1 × C-4), 71.70 (C-4''), 71.56, 69.91 (2 × C-4), 69.87 (1 × C-3), 69.64 (1 × C-4), 69.43 (C-3''), 66.45 (O*C*$H_2$$CH_2$), 63.67 (1 × C-6), 58.01, 55.44 (2 × C-2), 55.29 (C-2''), 54.70, 54.43 (2 × C-2), 41.61 (CH_2*C*H_2Cl), 40.54 (CO*C*H_2Cl), 32.12 (CH_2*C*$H_2$$CH_2$). *m/z* (MALDI) calculated for $C_{121}H_{101}N_5O_{38}F_{12}Cl_2Na$ $[M+Na]^+$ 2552.52, found 2552.13.

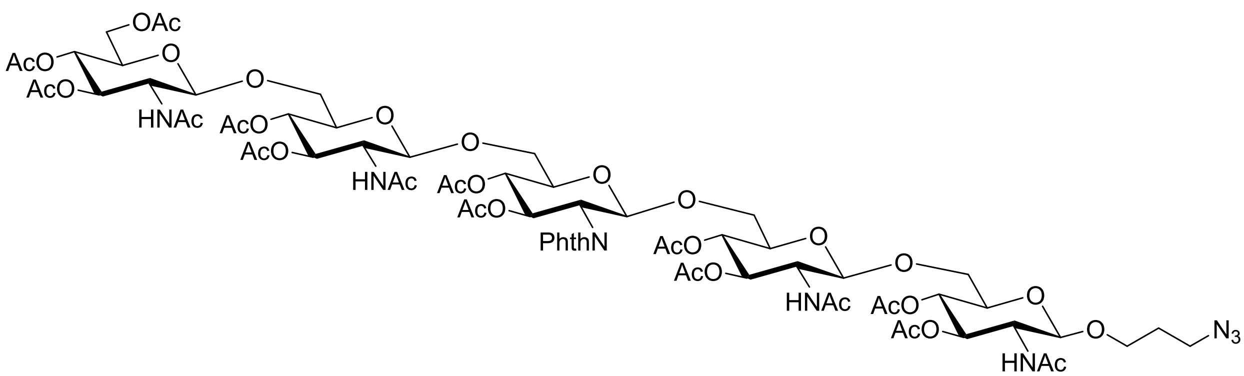
2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-acetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranoside (21)



Pentasaccharide **20** (206 mg, 0.081 mmol) was dissolved in a 2:4:1 mixture of 0.5 M NaOH (16.2 mL, 8.1 mmol, 100 equiv.), THF (32.4 mL), and MeOH (8.1 mL). The reaction was stirred at 40 °C for 3 h. The solution was concentrated and dried under high vacuum. The residue was dissolved in a 1:1 mixture of pyridine (20 mL, 211.6 mmol, 2612 equiv.) and Ac_2O (20 mL, 247.3 mmol, 3052 equiv.). The reaction was stirred at 50 °C for 2 h, then left to attain RT for 16 h (TLC in 17:3 EtOAc/EtOH, R_f = 0.5). The solution co-concentrated with toluene. The residue was dissolved in CH_2Cl_2 (60 mL) then washed with 1 M HCl (60 mL) then aq. $NaHCO_3$ (60 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 15 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/EtOH, 19:1 → 8:2) gave pentasaccharide **21** (101 mg, 75%) as a white amorphous solid. ^{1}H NMR (600 MHz, Acetone-d_6) δ_H 7.94 – 7.90 (m, 4H, 4 × Phth), 7.56 (d, J = 9.5 Hz, 1H, 1 × N-H), 7.31 (d, J = 9.3 Hz, 1H, 1 × N-H), 7.31 (d, J = 9.7 Hz, 1H, 1 × N-H), 7.15 (d, J = 9.5 Hz, 1H, 1 × N-H), 5.85 (dd, J = 10.7, 8.9 Hz, 1H, H-3''), 5.43 (d, J = 8.4 Hz, 1H, H-1''), 5.35 (dd, J = 10.4, 9.4 Hz, 1H, 1 × H-3), 5.26 (dd, J = 10.4, 9.4 Hz, 1H, 1 × H-3), 5.22 – 5.17 (m, 3H, 1 × H-1, 2 × H-3), 5.04 (dd, J = 10.2, 8.9 Hz, 1H, H-4''), 4.98 (t, J = 10.4 Hz, 1H, 1 × H-4), 4.92 (dd, J = 10.0, 9.4 Hz, 1H, 1 × H-4), 4.84 (t, J = 9.8 Hz, 1H, 1 × H-4), 4.76 (d, J = 8.5 Hz, 1H, 1 × H-1), 4.72 – 4.65 (m, 3H, 2 × H-1, 1 × H-4), 4.40 (td, J = 10.5, 9.7, 2.5 Hz, 1H, 1 × H-5), 4.31 (dd, J = 10.8, 8.4 Hz, 1H, H-2''), 4.28 –

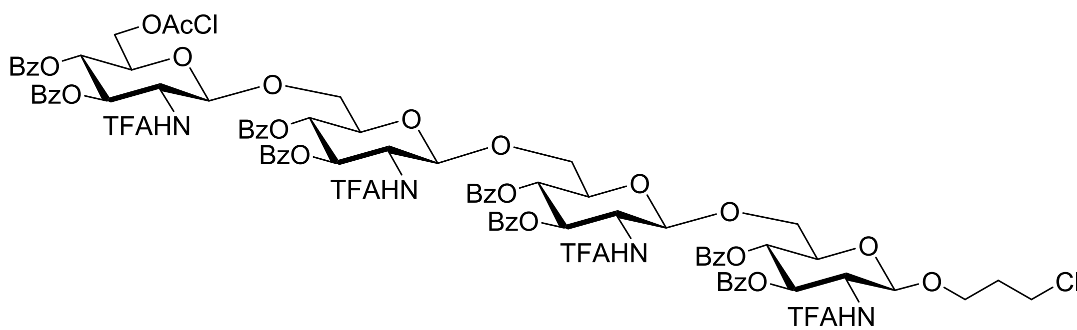
4.20 (m, 2H, 1 × H-2, H-5''), 4.17 (q, *J* = 9.3 Hz, 1H, 1 × H-2), 4.13 – 4.05 (m, 2H, 1 × H-5, 1 × H-6a), 4.03 – 3.97 (m, 4H, 2 × H-2, 1 × H-5, H-6a''), 3.95 – 3.85 (m, 5H, 1 × H-6a, H-6b'', 2 × H-6b, $OC\mathit{H}HCH_2$), 3.84 – 3.80 (m, 2H, 1 × H-5, 1 × H-6a), 3.74 (dd, *J* = 11.7, 2.6 Hz, 1H, 1 × H-6a), 3.68 (ddd, *J* = 12.4, 7.8, 4.6 Hz, 1H, $OCH\mathit{H}CH_2$), 3.67 – 3.62 (m, 3H, 1 × H-6b, CH_2Cl), 3.59 (dd, *J* = 11.7, 8.2 Hz, 1H, 1 × H-6b), 2.11, 2.09, 2.06, 2.05 (4 s, 12H, 4 × Ac), 2.03 – 2.01 (m, 1H, $CH_2C\mathit{H}HCH_2$), 1.99, 1.98, 1.96, 1.96, 1.95 (5 s, 15H, 5 × Ac), 1.96 – 1.93 (m, 4H, $CH_2CH\mathit{H}CH_2$, 1 × Ac), 1.92, 1.89, 1.84, 1.84, 1.83 (5 s, 15H, 5 × Ac). ^{13}C NMR (125 MHz, Acetone-d_6) δ_C 171.18, 170.93, 170.71 (3 × $\mathit{C}OCH_3$), 170.65 (2 × $\mathit{C}OCH_3$), 170.54 (2 × $\mathit{C}OCH_3$), 170.49, 170.45, 170.41, 170.33, 170.23, 170.12, 170.10, 170.06 (8 × $\mathit{C}OCH_3$), 135.88 (2 × Phth), 132.27 (2 × 4° Phth), 124.27 (2 × Phth), 103.99, 102.36, 101.85, 101.14 (4 × C-1), 100.04 (C-1''), 74.66 (1 × C-3), 74.54 (1 × C-5), 74.32, 73.87 (2 × C-3), 73.61 (C-5''), 73.22 (1 × C-5), 73.15 (1 × C-3), 72.69 (1 × C-5), 72.00 (1 × C-5, C-6''), 71.82 (1 × C-6), 71.57 (C-4''), 71.45 (1 × C-4), 71.26 (C-3''), 71.21 (1 × C-4), 70.90 (1 × C-6), 70.50, 69.96 (2 × C-4), 66.90 ($O\mathit{C}H_2CH_2$), 66.58, 63.03 (2 × C-6), 56.21 (C-2''), 54.97, 54.84, 54.70, 52.88 (4 × C-2), 42.63 (CH_2Cl), 33.31 ($CH_2\mathit{C}H_2CH_2$), 23.29, 23.25, 23.16, 23.09 (4 × $NCO\mathit{C}H_3$), 21.05, 20.99, 20.98, 20.90, 20.73 (5 × $OCO\mathit{C}H_3$), 20.71 (2 × $OCO\mathit{C}H_3$), 20.67 (2 × $OCO\mathit{C}H_3$), 20.55, 20.46 (2 × $OCO\mathit{C}H_3$). *m/z* (ESI) calculated for $C_{71}H_{98}N_6O_{38}Cl$ $[M+NH_4]^+$ 1677.56, found 1677.56.

2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-acetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-azidopropyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranoside (22)



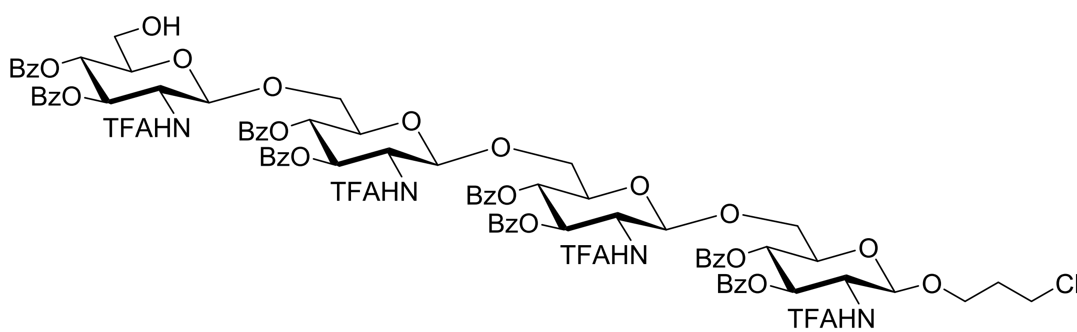
Pentasaccharide **21** (97.0 mg, 0.058 mmol) and NaN_3 (114 mg, 1.75 mmol, 30 equiv.) were dissolved in dry DMF (5.8 mL). The reaction was stirred at 80 °C for 24 h (TLC in 17:3 EtOAc/EtOH, R_f = 0.5). The solution was diluted with EtOAc (90 mL) then washed with H_2O (90 mL). The aqueous layer was re-extracted with EtOAc (2 × 45 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/EtOH, 19:1 → 8:2) gave azidopropyl glycoside **22** (74.4 mg, 76%) as a white amorphous solid. ^1H NMR (600 MHz, Acetone-d_6) δ_H 7.99 – 7.88 (m, 4H, 4 × Phth), 7.54 (d, *J* = 9.4 Hz, 1H, 1 × N-H), 7.31 (d, *J* = 9.4 Hz, 2H, 2 × N-H), 7.14 (d, *J* = 9.5 Hz, 1H, 1 × N-H), 5.85 (dd, *J* = 10.7, 8.9 Hz, 1H, H-3''), 5.43 (d, *J* = 8.5 Hz, 1H, H-1''), 5.34 (dd, *J* = 10.4, 9.4 Hz, 1H, 1 × H-3), 5.26 (dd, *J* = 10.5, 9.4 Hz, 1H, 1 × H-3), 5.22 – 5.18 (m, 3H, 1 × H-1, 2 × H-3), 5.05 (dd, *J* = 10.2, 8.9 Hz, 1H, H-4''), 4.98 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 4.93 (dd, *J* = 10.0, 9.5 Hz, 1H, 1 × H-4), 4.84 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 4.77 (d, *J* = 8.6 Hz, 1H, 1 × H-1), 4.72 – 4.66 (m, 3H, 2 × H-1, 1 × H-4), 4.39 (td, *J* = 9.9, 2.3 Hz, 1H, 1 × H-5), 4.31 (dd, *J* = 10.7, 8.5 Hz, 1H, H-2''), 4.28 – 4.20 (m, 2H, 1 × H-2, H-5''), 4.17 (q, J = 9.4 Hz, 1H, 1 × H-2), 4.11 (dd, J = 12.4, 5.6 Hz, 1H, 1 × H-6a), 4.07 (ddd, J = 10.4, 8.2, 2.7 Hz, 1H, 1 × H-5), 4.03 – 3.97 (m, 4H, 2 × H-2, 1 × H-5, H-6a''), 3.94 (dd, J = 10.4, 1.9 Hz, 1H, 1 × H-6a), 3.91 – 3.85 (m, 4H, H-6b'', 2 × H-6b, OC*H*HCH$_2$), 3.84 – 3.79 (m, 2H, 1 × H-5, 1 × H-6a), 3.75 (dd, J = 11.7, 2.6 Hz, 1H, 1 × H-6a), 3.65 (dd, J = 12.5, 9.7 Hz, 1H, 1 ×H-6b), 3.62 (ddd, J = 12.7, 7.3, 5.6 Hz, 1H, OCH*H*CH$_2$), 3.58 (dd, J = 11.8, 8.2 Hz, 1H, 1 × H-6b), 3.40 (td, J = 6.8, 1.4 Hz, 2H, CH$_2$N$_3$), 2.11, 2.09, 2.07, 2.05, 1.99, 1.98, 1.96 (7 s, 21H, 7 × CH$_3$), 1.95 (s, 6H, 2 × CH$_3$), 1.94, 1.92, 1.89, 1.84, 1.84, 1.83 (6 s, 18H, 6 × CH$_3$), 1.83 – 1.79 (m, 2H, CH$_2$C*H$_2$*CH$_2$). ^{13}C NMR (125 MHz, Acetone-d_6) δ_C 171.18, 170.94, 170.73, 170.67, 170.67 (5 × *C*OCH$_3$), 170.57 (2 × *C*OCH$_3$), 170.51, 170.48, 170.44, 170.33, 170.21, 170.15, 170.12, 170.00 (8 × *C*OCH$_3$), 135.91 (2 × Phth), 132.31 (2 × 4° Phth), 124.59, 124.33 (2 × Phth), 103.98, 102.36, 101.64, 101.18 (4 × C-1), 100.04 (C-1''), 74.67 (1 × C-3), 74.54 (1 × C-5), 74.38, 73.92 (2 × C-3), 73.64 (C-5''), 73.23 (1 × C-5), 73.20 (1 × C-3), 72.75 (1 × C-5), 72.05 (1 × C-5), 71.95 (C-6''), 71.76 (1 × C-6), 71.56 (C-4''), 71.46 (1 × C-4), 71.30 (C-3''), 71.22 (1 × C-4), 70.83 (1 × C-6), 70.52, 69.97 (2 × C-4), 66.90 (O*C*H$_2$CH$_2$), 66.62, 63.05 (2 × C-6), 56.22 (C-2''), 55.00, 54.84, 54.72, 52.91 (4 × C-2), 49.00 (CH$_2$N$_3$), 29.59 (CH$_2$*C*H$_2$CH$_2$), 23.29, 23.26, 23.18, 23.09 (4 × NCO*C*H$_3$), 21.06 (1 × OCO*C*H$_3$), 20.99 (2 × OCO*C*H$_3$), 20.90, 20.74 (2 × OCO*C*H$_3$), 20.72 (2 × OCO*C*H$_3$), 20.67 (2 × OCO*C*H$_3$), 20.53, 20.46 (2 × OCO*C*H$_3$). *m/z* (ESI) calculated for $C_{71}H_{98}N_9O_{38}$ [M+NH$_4$]$^+$ 1684.60, found 1684.60.

3,4-Di-O-benzoyl-6-chloroacetyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (23)



Disaccharide acceptor **15** (1.00 g, 0.98 mmol) and glycosyl bromide **13** (1.59 g, 1.46 mmol, 1.5 equiv; 1.77 g crude) were dissolved in freshly distilled CH$_2$Cl$_2$ (25 mL) containing freshly activated powdered 4Å MS (2.5 g). The mixture was cooled to -45 °C under Ar in the dark for 1 h. AgOTf (0.50 mg, 1.95 mmol, 2 equiv.) in dry toluene (3 mL) was added, and the reaction was stirred under the same conditions for 2 h (TLC in 3:7 acetone/pentanes, R$_f$ = 0.2), then quenched with NEt$_3$. The mixture was diluted with CH$_2$Cl$_2$ (20 mL) and filtered through celite. The solids were washed with CH$_2$Cl$_2$ (3 × 20 mL). The filtrate was washed with sat. aq. NaCl (2 × 80 mL). The aqueous layers were re-extracted with CH$_2$Cl$_2$ (2 × 15 mL). The organic layers were dried over Na$_2$SO$_4$ and concentrated. Column chromatography (acetone/pentanes, 3:7 → 7:13) gave tetrasaccharide **23** (1.52 g, 77%) as a pale yellow amorphous solid, and recovered acceptor **15** (0.11 g, 11%). **Analytical Data for 23:** ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.12 (d, J = 7.7 Hz, 1H, 1 × N-H), 8.05 (ddd, J = 10.4, 8.4, 1.3 Hz, 4H, 4 × Bz), 8.02 – 7.98 (m, 2H, 2 × Bz), 7.99 – 7.93 (m, 9H, 1 × N-H, 8 × Bz), 7.60 – 7.44 (m, 10H, 1 × N-H, 9 × Bz), 7.45 – 7.28 (m, 14H, 1 × N-H, 13 × Bz), 7.25 (s, 2H, 2 × Bz), 7.15 – 7.11 (m, 2H, 2 × Bz), 5.95 (t, *J* = 9.9 Hz, 1H, 1 × H-3), 5.92 (t, *J* = 10.3 Hz, 1H, 1 × H-3), 5.84 (t, *J* = 9.6 Hz, 1H, 1 × H-3), 5.79 (dd, *J* = 10.6, 9.0 Hz, 1H, 1 × H-3), 5.70 (dd, *J* = 12.8, 6.8 Hz, 1H, 1 × H-4), 5.65 (t, *J* = 9.6 Hz, 1H, 1 × H-4), 5.35 (t, *J* = 9.7 Hz, 1H, 1 × H-4), 5.20 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 4.99 (d, *J* = 8.4 Hz, 1H, 1 × H-1), 4.82 (d, *J* = 8.2 Hz, 1H, 1 × H-1), 4.77 (d, *J* = 8.4 Hz, 1H, 1 × H-1), 4.70 – 4.47 (m, 7H, 1 × H-1, 4 × H-2, 1 × H-5), 4.42 (dd, *J* = 12.3, 6.8 Hz, 1H, 1 × H-6a), 4.18 – 4.05 (m, 5H, 1 × H-5, 2 × H-6a, 1 × H-6b, O*C*HHCH$_2$), 3.99 – 3.83 (m, 5H, 1 × H-5, 1 × H-6a, 1 × H-6b, COCH$_2$Cl), 3.82 – 3.77 (m, 1H, OCH*H*CH$_2$), 3.66 – 3.48 (m, 4H, 2 × H-6b, CH$_2$C*H$_2$*Cl), 2.04 (dt, *J* = 20.1, 6.2 Hz, 2H, CH$_2$C*H$_2$*CH$_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 167.02 (*C*OCH$_2$Cl), 166.81, 166.70, 166.52, 166.48, 166.41, 166.29, 165.21, 165.08 (8 × *C*OPh), 158.33 (d, *J* = 38.0 Hz, 1 × *C*OCF$_3$), 158.31 (d, *J* = 38.5 Hz, 1 × *C*OCF$_3$), 158.17 (d, *J* = 37.8 Hz, 1 × *C*OCF$_3$), 157.91 (d, *J* = 37.3 Hz, 1 × *C*OCF$_3$), 133.98 (1 × Bz), 133.84 (2 × Bz), 133.75, 133.69 (2 × Bz), 133.43 (2 × Bz), 133.38 (1 × Bz), 130.14 (2 × Bz), 130.08 (2 × Bz), 130.00 (2 × Bz), 129.92 (2 × Bz), 129.85 (6 × Bz), 129.69 (2 × Bz), 128.89 (2 × Bz), 128.81 (2 × 4° Bz), 128.72 (2 × Bz), 128.68 (4 × 4° Bz), 128.64 (2 × Bz), 128.41 (4 × Bz), 128.38 (4 × Bz), 128.35 (2 × Bz), 128.19, 128.05 (2 × 4° Bz), 115.56 (q, *J* = 287.9 Hz, 2 × CF$_3$), 115.40 (q, *J* = 287.2 Hz, 1 × CF$_3$), 115.16 (q, *J* = 287.2 Hz, 1 × CF$_3$), 103.78, 103.31, 101.77, 99.96 (4 × C-1), 73.93, 73.30 (2 × C-5), 73.24 (1 × C-6), 73.01 (1 × C-5), 72.61, 72.45 (2 × C-3), 72.22 (1 × C-6), 71.77 (1 × C-3), 71.37, 71.33, 71.21, 70.23 (4 × C-4), 68.81 (1 × C-3), 66.53 (O*C*H$_2$CH$_2$), 64.17 (1 × C-6), 55.35, 55.16, 54.52, 53.76 (4 × C-2), 41.47 (CH$_2$*C*H$_2$Cl), 40.69 (CO*C*H$_2$Cl), 31.95 (CH$_2$*C*H$_2$CH$_2$). *m/z* (ESI) calculated for $C_{93}H_{84}N_5O_{30}F_{12}Cl_2$ $[M+NH_4]^+$ 2048.44, found 2048.43.

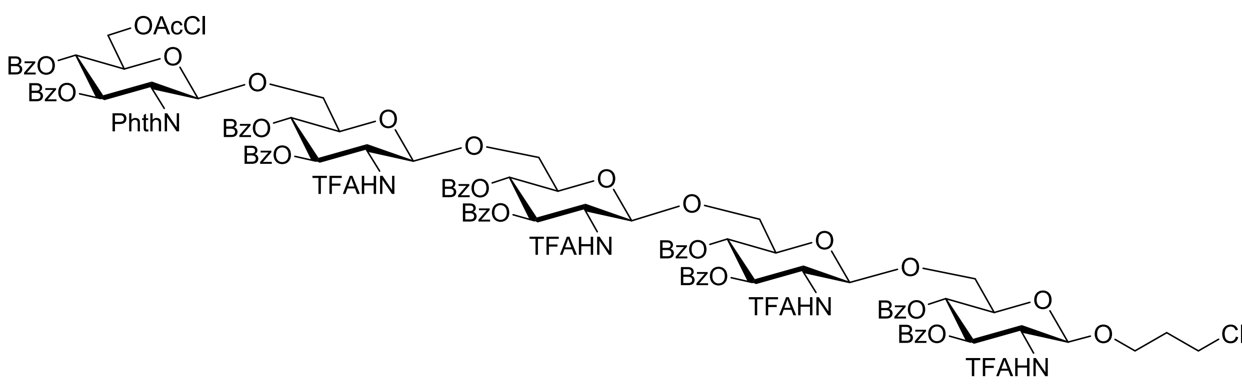
3,4-Di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (24)



Tetrasaccharide **23** (1.22 g, 0.60 mmol) and thiourea (230 mg, 3.02 mmol, 5 equiv) were dissolved in a 1:1 mixture pyridine/EtOH (60 mL). The solution was stirred at 70 °C for 18 h (TLC in 1:1 EtOAc/pentanes, R_f = 0.6), then co-concentrated with toluene. The residue was dissolved in CH_2Cl_2 (150 mL) then washed with 1 M HCl (2 × 150 mL) then sat. aq. $NaHCO_3$ (150 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 30 mL), and the organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 4:6 → 9:11) gave tetrasaccharide acceptor **24** (0.72 g, 62%) as a white/pale yellow amorphous solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.04 (d, *J* = 7.3 Hz, 2H, 2 × Bz), 8.00 – 7.88 (m, 16H, 2 × N-H, 14 × Bz), 7.53 (q, *J* = 7.0 Hz, 3H, 2 × Bz), 7.50 – 7.40 (m, 7H, 7 × Bz), 7.41 – 7.34 (m, 7H, 1 × N-H, 6 × Bz), 7.33 – 7.26 (m, 7H, 1 × N-H, 6 × Bz), 7.20 (t, *J* = 7.9 Hz, 2H, 2 × Bz), 5.94 (t, *J*

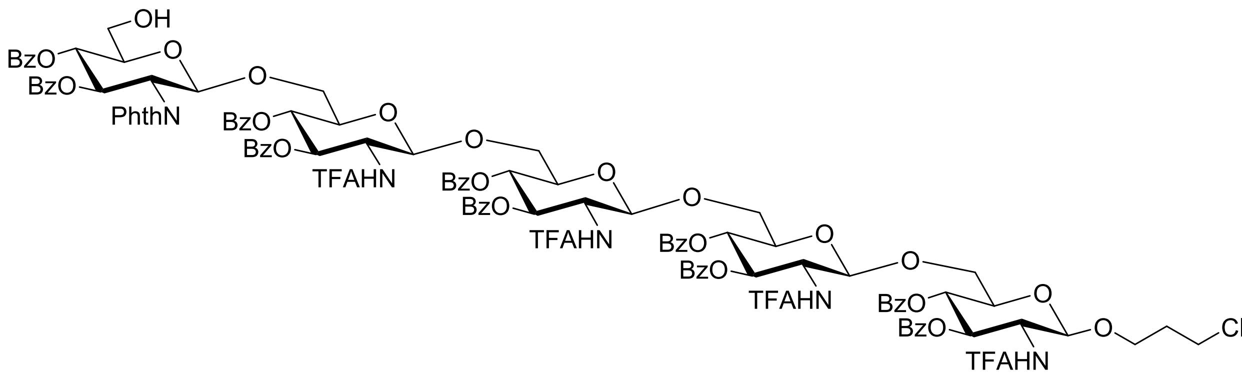
= 10.2 Hz, 1H, 1 × H-3), 5.88 (t, *J* = 10.2 Hz, 1H, 1 × H-3), 5.81 – 5.71 (m, 2H, 2 × H-3), 5.67 (t, *J* = 9.5 Hz, 1H, 1 × H-4), 5.53 (t, *J* = 9.4 Hz, 1H, 1 × H-4), 5.40 (t, *J* = 9.7 Hz, 1H, 1 × H-4), 5.26 (t, *J* = 9.7 Hz, 1H, 1 × H-4), 4.95 (d, *J* = 8.2 Hz, 1H, 1 × H-1), 4.83 (d, *J* = 8.2 Hz, 1H, 1 × H-1), 4.75 (d, *J* = 8.3 Hz, 1H, 1 × H-1), 4.64 – 4.55 (m, 3H, 1 × H-1, 2 × H-2), 4.51 (t, *J* = 9.7 Hz, 1H, 1 × H-5), 4.46 (q, *J* = 9.7 Hz, 1H, 1 × H-2), 4.42 – 4.33 (m, 2H, 1 × H-2, 1 × H-5), 4.24 – 4.19 (m, 1H, 1 × H-5), 4.12 – 3.98 (m, 3H, 2 × H-6a, OC*H*HCH$_2$), 3.89 – 3.82 (m, 2H, , 1 × H-6a, 1 × H-6b), 3.79 – 3.68 (m, 4H, 1 × H-6a, 2 × H-6b, OCH*H*CH$_2$), 3.67 – 3.63 (m, 1H, 1 × H-5), 3.60 (dd, *J* = 12.7, 4.0 Hz, 1H, 1 × H-6b), 3.55 (t, *J* = 7.0 Hz, 2H, CH$_2$Cl), 2.11 – 2.01 (m, 1H, CH$_2$C*H*HCH$_2$), 2.02 – 1.93 (m, 1H, CH$_2$CH*H*CH$_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 166.94, 166.66, 166.53, 166.30 (4 × *C*OPh), 166.20 (2 × *C*OPh), 166.16, 165.33 (2 × *C*OPh), 158.17 (d, *J* = 38.1 Hz, 1 × *C*OCF$_3$), 158.15 (d, *J* = 38.2 Hz, 1 × *C*OCF$_3$), 158.10 (d, *J* = 37.7 Hz, 1 × *C*OCF$_3$), 157.87 (d, *J* = 37.7 Hz, 1 × *C*OCF$_3$), 134.04, 133.86, 133.82, 133.80, 133.71, 133.56, 133.42, 133.41 (8 × Bz), 130.11 (2 × Bz), 130.00 (2 × Bz), 129.97 (2 × Bz), 129.91 (4 × Bz), 129.84 (2 × Bz), 129.80 (4 × Bz), 128.73 (2 × Bz), 128.70, 128.70 (2 × 4° Bz), 128.67 (4 × Bz), 128.65 (2 × 4° Bz), 128.63 (2 × Bz), 128.55 (2 × 4° Bz), 128.43 (2 × Bz), 128.41 (4 × Bz), 128.38 (2 × Bz), 128.24 (2 × 4° Bz), 115.61 (q, *J* = 288.0 Hz, 1 × CF$_3$), 115.54 (q, *J* = 287.8 Hz, 1 × CF$_3$), 115.41 (q, *J* = 287.5 Hz, 1 × CF$_3$), 115.26 (q, *J* = 287.6 Hz, 1 × CF$_3$), 103.15, 102.73, 101.70, 100.17 (4 × C-1), 75.05, 73.97, 73.22, 72.76 (4 × C-5), 72.39 (1 × C-3, 1 × C-6), 72.29, 72.00 (1 × C-3), 71.51 (1 × C-3, 1 × C-6), 71.21 (1 × C-4, 1 × C-6), 70.76, 69.76, 69.32 (3 × C-4), 66.64 (O*C*H$_2$CH$_2$), 61.27 (1 × C-6), 55.37, 55.36, 54.66, 54.64 (4 × C-2), 41.50 (CH$_2$Cl), 32.02 (CH$_2$*C*H$_2$CH$_2$). *m/z* (MALDI) calculated for $C_{91}H_{79}N_4O_{29}F_{12}NaCl$ $[M+Na]^+$ 1977.42, found 1977.65.

3,4-Di-O-benzoyl-6-chloroacetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (25)



Tetrasaccharide acceptor **24** (0.59 g, 0.30 mmol) and glycosyl bromide **17** (0.59 g, 0.90 mmol, 3 equiv.) were dissolved in freshly distilled CH$_2$Cl$_2$ (9 mL) containing freshly activated powdered 4Å MS (0.90 g). The mixture was cooled to -45 °C under Ar in the dark for 1 h. AgOTf (105 mg, 0.409 mmol, 4 equiv.) in dry toluene (0.6 mL) was added, and the reaction was stirred under the same conditions for 2 h (TLC in 4:6 EtOAc/pentanes, $R_f = 0.4$), then quenched with NEt$_3$. The mixture was diluted with CH$_2$Cl$_2$ (25 mL) and filtered through celite. The solids were washed with CH$_2$Cl$_2$ (3 × 25 mL). The filtrate was washed with sat. aq. NaCl (2 × 75 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 15 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 7:13 → 9:11) gave pentasaccharide **25** (0.68 g, 89%) as a pale yellow amorphous solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.49 (d, *J* = 10.1 Hz, 1H, 1 × N-H), 8.44 (d, *J* = 9.5 Hz, 1H, 1 × N-H), 8.20 (d, *J* = 7.2 Hz, 2H, 2 × Bz), 8.16 – 8.11 (m, 2H, 2 × Bz), 8.08 – 8.03 (m, 3H, 1 × N-H, 2 × Bz), 8.03 (d, *J* = 7.3 Hz, 2H, 2 × Bz), 8.00 – 7.92 (m, 12H, 12 × Bz), 7.83 – 7.78 (m, 3H, 3 × Phth), 7.67 – 7.64 (m, 1H, 1 × Phth), 7.60 – 7.53 (m, 5H, 5 × Bz), 7.51 – 7.39 (m, 12H, 12 × Bz), 7.38 – 7.26 (m, 8H, 8 × Bz), 7.18 – 7.13 (m, 5H, 5 × Bz), 6.91 (d, *J* = 8.6 Hz, 1H, 1 × N-H), 6.34 (dd, *J* = 10.7, 8.9 Hz, 1H, H-3^{IV}), 6.25 (dd, *J* = 10.9, 9.4 Hz, 1H, 1 × H-3), 6.01 (t, *J* = 10.3 Hz, 1H, 1 × H-3), 5.86 (t, *J* = 10.3 Hz, 1H, 1 × H-3), 5.76 – 5.63 (m, 4H, 1 × H-3, H-4^{IV}, 2 × H-4), 5.33 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 5.15 (d, *J* = 8.5 Hz, 1H, H-1^{IV}), 5.07 (d, *J* = 8.5 Hz, 1H, 1 × H-1), 5.00 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 4.92 (q, *J* = 10.2 Hz, 1H, 1 × H-2), 4.87 (d, *J* = 8.4 Hz, 1H, 1 × H-1), 4.80 – 4.67 (m, 3H, 1 × H-1, 2 × H-5), 4.66 – 4.55 (m, 6H, 1 × H-1, H-2^{IV}, 3 × H-2, 1 × H-5), 4.37 (dd, *J* = 12.3, 7.3 Hz, 1H, H-6a^{IV}), 4.25 (dd, *J* = 12.9, 10.8 Hz, 1H, 1 × H-6a), 4.21 – 4.09 (m, 3H, 1 × H-5, 1 × H-6a, OC*H*HCH$_2$), 4.06 (dd, *J* = 12.2, 2.0 Hz, 1H, H-6b^{IV}), 4.04 – 4.00 (m, 1H, H-5^{IV}), 3.90 (d, *J* = 15.4 Hz, 1H, COC*H*HCl), 3.84 – 3.79 (m, 2H, OCH*H*CH$_2$, COCH*H*Cl), 3.75 (t, *J* = 13.3, 10.5 Hz, 1H, 1 × H-66), 3.71 – 3.59 (m, 5H, 1 × H-6a, 2 × H-6b, CH$_2$C*H$_2$*Cl), 3.38 (dd, *J* = 13.0, 1.7 Hz, 1H, 1 × H-6a), 3.23 (d, *J* = 11.4 Hz, 1H, 1 × H-6b), 2.21 – 2.12 (m, 1H, CH$_2$C*H*HCH$_2$), 2.11 – 2.01 (m, 1H, CH$_2$CH*H*CH$_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 168.80, 167.37 (2 × *C*OPhth), 167.15 (*C*OCH$_2$Cl), 166.71, 166.60, 166.55, 166.53, 166.44, 166.17, 165.81, 165.65, 164.96, 164.94 (10 × *C*OPh), 158.52 (d, *J* = 38.1 Hz, 1 × *C*OCF$_3$), 158.43 (d, *J* = 38.4 Hz, 1 × *C*OCF$_3$), 158.27 (d, *J* = 37.9 Hz, 1 × *C*OCF$_3$), 158.01 (d, *J* = 37.6 Hz, 1 × *C*OCF$_3$), 135.12, 135.00 (2 × Phth), 133.83 (2 × Bz), 133.78, 133.65 (2 × Bz), 133.54 (2 × Bz), 133.37 (3 × Bz), 133.20 (1 × Bz), 130.69, 130.50 (2 × 4° Phth), 130.22 (2 × Bz), 130.11 (2 × Bz), 129.94 (2 × Bz), 129.92 (4 × Bz), 129.90 (4 × Bz), 129.89 (2 × Bz), 129.69 (2 × Bz), 129.31 (2 × Bz), 129.30 (4° Bz), 128.98 (2 × Bz, 4° Bz), 128.80 (2 × 4° Bz), 128.73 (2 × Bz), 128.71 (2 × Bz), 128.69 (2 × Bz), 128.67 (1 × 4° Bz), 128.59 (2 × Bz), 128.56 (1 × 4° Bz), 128.37 (4 × Bz, 1 × 4° Bz), 128.32 (4 × Bz), 128.26 (1 × 4° Bz), 128.22 (2 × Bz), 128.19, 128.09 (2 × 4° Bz), 124.04, 123.68 (2 × Phth), 115.82 (q, *J* = 287.8 Hz, 1 × CF$_3$), 115.70 (q, *J* = 287.1 Hz, 1 × CF$_3$), 115.58 (q, *J* = 287.8 Hz, 1 × CF$_3$), 115.01 (q, *J* = 287.0 Hz, 1 × CF$_3$), 103.95, 103.34, 101.50 (3 × C-1), 100.94 (C-1^{IV}), 100.14 (1 × C-1), 74.33 (1 × C-6), 74.00 (1 × C-5), 73.68 (1 × C-6), 73.62 (1 × C-5), 73.57 (1 × C-6), 73.09 (C-5^{IV}), 72.75 (1 × C-3), 72.52 (1 × C-5), 72.37 (1 × C-6), 72.36 (1 × C-3), 72.17 (1 × C-5), 72.05 (1 × C-4), 71.98 (1 × C-3), 71.74, 71.54 (2 × C-4), 71.32 (1 × C-3), 70.22 (1 × C-4), 69.97 (C-4^{IV}), 69.78 (C-3^{IV}), 66.81 (O*C*H$_2$CH$_2$), 64.14 (C-6^{IV}), 55.36, 55.28, 55.09 (3 × C-2), 54.65 (C-2^{IV}), 54.42 (1 × C-2), 41.70 (CH$_2$*C*H$_2$Cl), 40.60 (CO*C*H$_2$Cl), 32.34 (CH$_2$*C*H$_2$CH$_2$). *m/z* (MALDI) calculated for $C_{121}H_{101}N_5O_{38}F_{12}NaCl_2$ $[M+Na]^+$ 2552.52, found 2552.41.

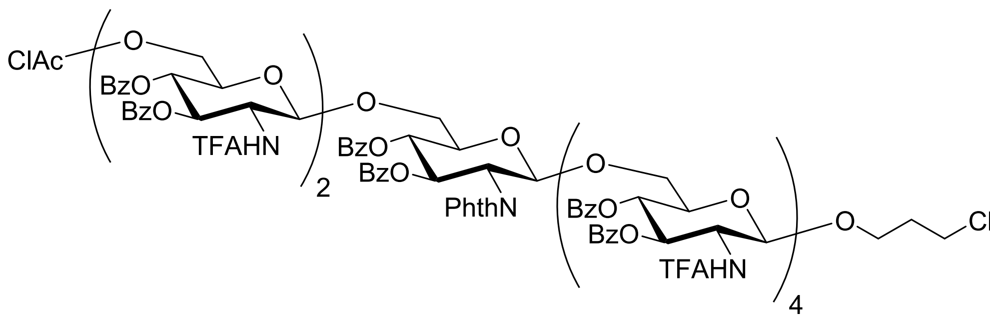
3,4-Di-O-benzoyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-Di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (26)



Pentasaccharide **25** (0.79 g, 0.31 mmol) and thiourea (120 mg, 1.58 mmol, 5 equiv) were dissolved in a 1:1 mixture pyridine/EtOH (30 mL). The solution was stirred at 70 °C for 18 h (TLC in 1:1 EtOAc/pentanes, R_f = 0.6), then co-concentrated with toluene. The residue was dissolved in CH_2Cl_2 (75 mL) then washed with 1 M HCl (2 × 75 mL) then sat. aq. $NaHCO_3$ (75 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 15 mL), and the organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/hexanes, 4:6 → 1:1) gave pentasaccharide acceptor **26** (0.44 g, 57%) as a white/pale yellow amorphous solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.51 (d, *J* = 10.0 Hz, 1H, 1 × N-H), 8.42 (d, *J* = 9.5 Hz, 1H, 1 × N-H), 8.15 (dd, *J* = 8.1, 1.1 Hz, 2H, 2 × Bz), 8.09 (dd, *J* = 8.4, 1.4 Hz, 2H, 2 × Bz), 8.07 (d, *J* = 9.7 Hz, 1H, 1 × N-H), 8.05 – 8.00 (m, 4H, 4 × Bz), 8.01 – 7.92 (m, 8H, 8 × Bz), 7.93 (dd, *J* = 8.1, 1.0 Hz, 2H, 2 × Bz), 7.82 – 7.74 (m, 3H, 3 × Phth), 7.60 – 7.52 (m, 7H, 7 × Bz), 7.49 – 7.37 (m, 14H, 13 × Bz, 1 × Phth), 7.35 – 7.28 (m, 6H, 6 × Bz), 7.25 (t, *J* = 7.9 Hz, 2H, 2 × Bz), 7.21 (t, *J* = 7.9 Hz, 2H, 2 × Bz), 7.16 (t, *J* = 7.9 Hz, 2H, 2 × Bz), 7.08 (d, *J* = 9.1 Hz, 1H, 1 × N-H), 6.37 (dd, *J* = 10.6, 9.1 Hz, 1H, H-3^{IV}), 6.18 (dd, *J* = 10.7, 9.6 Hz, 1H, 1 × H-3), 5.99 (t, *J* = 9.8 Hz, 1H, 1 × H-3), 5.87 (t, *J* = 10.3 Hz, 1H, 1 × H-3), 5.76 – 5.69 (m, 2H, 1 × H-3, 1 × H-4), 5.57 (dd, *J* = 10.7, 9.0 Hz, 1H, 1 × H-4), 5.41 – 5.31 (m, 2H, H-4^{IV}, 1 × H-4), 5.23 (d, *J* = 8.5 Hz, 1H, H-1^{IV}), 5.04 (d, *J* = 8.5 Hz, 1H, 1 × H-1), 5.04 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 4.86 (q, *J* = 10.3 Hz, 1H, 1 × H-2), 4.85 (d, *J* = 8.2 Hz, 1H, 1 × H-1), 4.77 – 4.53 (m, 8H, 2 × H-1, 3× H-2, 3 × H-5), 4.51 (dd, *J* = 10.6, 8.7 Hz, 1H, H-2^{IV}), 4.26 – 4.15 (m, 3H, 1 × H-5, 2 × H-6a), 4.13 – 4.03 (m, 2H, 1 × H-6a, OC*H*HCH$_2$), 3.83 – 3.76 (m, 2H, H-5^{IV}, OCH*H*CH$_2$), 3.77 – 3.70 (m, 2H, H-6a^{IV}, 1 × H-6a), 3.65 – 3.53 (m, 5H, H-6b^{IV}, 2 × H-6b, CH_2Cl), 3.41 (dd, *J* = 12.5, 1.3 Hz, 1H, 1 × H-6b), 3.29 (dd, *J* = 11.9, 0.8 Hz, 1H, 1 × H-6b), 2.14 – 2.09 (m, 1H, CH$_2$C*H*HCH$_2$), 2.06 – 1.99 (m, 1H, CH$_2$CH*H*CH$_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 168.61, 167.53 (2 × *C*OPhth), 167.09, 166.59, 166.53, 166.52, 166.42, 166.25, 166.10, 165.73, 165.46, 164.89 (10 × *C*OPh), 158.72 (d, *J* = 38.1 Hz, 1 × *C*OCF$_3$), 158.41 (d, *J* = 38.7 Hz, 1 × *C*OCF$_3$), 158.29 (d, *J* = 37.8 Hz, 1 × *C*OCF$_3$), 158.01 (d, *J* = 37.6 Hz, 1 × *C*OCF$_3$), 134.93 (2 × Phth), 133.87, 133.81, 133.76 (3 × Bz), 133.68 (2 × Bz), 133.52 (2 × Bz), 133.38, 133.28, 133.20 (3 × Bz), 130.84, 130.52 (2 × 4° Phth), 130.17 (2 × Bz), 130.14 (2 × Bz), 130.09 (2 × Bz), 130.04 (2 × Bz), 129.99 (2 × Bz), 129.93 (2 × Bz), 129.91 (2 × Bz), 129.87 (2 × Bz), 129.81 (2 × Bz), 129.48 (2 × Bz), 129.01, 128.97 (2 × 4° Bz), 128.94 (2 × Bz), 128.86 (2 × Bz), 128.79 (1 × 4° Bz), 128.73 (2 × 4° Bz), 128.72 (1 × 4° Bz), 128.69 (2 × Bz), 128.62 (2 × Bz), 128.59 (2 × Bz, 1 × 4° Bz), 128.42 (1 × 4° Bz), 128.40 (2 × Bz), 128.39 (2 × Bz), 128.33 (2 × Bz, 1 × 4° Bz), 128.32 (2 × Bz), 128.30 (2 × Bz), 128.11 (1 × 4° Bz), 123.94, 123.48 (2 × Phth), 115.76 (q, *J* = 287.7 Hz, 1 × CF$_3$), 115.67 (q, *J* = 287.1 Hz, 1 × CF$_3$), 115.59 (q, *J* = 287.8 Hz, 1 × CF$_3$), 115.02 (q, *J* = 287.0 Hz, 1 × CF$_3$), 104.20, 103.43, 101.61, 100.11 (4 × C-1), 100.09 (C-1^{IV}), 75.12 (C-5^{IV}), 74.64 (1 × C-5), 74.25, 73.71 (2 × C-6), 73.64 (1 × C-5), 72.74 (1 × C-3), 72.67 (1 × C-5), 72.41 (1 × C-6), 72.37 (1 ×

C-3), 72.23 (1 × C-5), 71.89, 71.67 (2 × C-4), 71.62 (1 × C-4, 1 × C-6), 71.52, 71.50 (2 × C-3), 70.36 (C-4^{IV}), 70.03 (C-3^{IV}), 69.83 (1 × C-4), 66.73 (O*C*H$_2$CH$_2$), 61.63 (C-6^{IV}), 55.22, 55.10 (2 × C-2), 55.03 (C-2^{IV}), 54.56, 54.39 (2 × C-2), 41.66 (CH$_2$Cl), 32.24 (CH$_2$*C*H$_2$CH$_2$). *m/z* (MALDI) calculated for $C_{119}H_{100}N_5O_{37}F_{12}ClNa$ [M+Na]$^+$ 2476.55, found 2476.11.

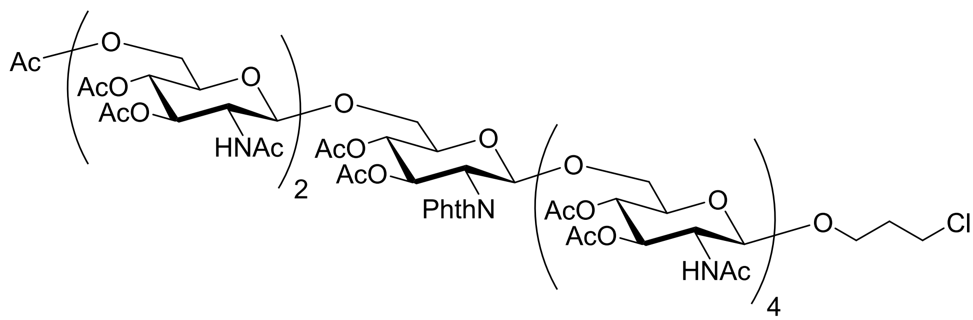
3,4-Di-O-benzoyl-6-chloroacetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-Di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (27)



Pentasaccharide acceptor **26** (430 mg, 0.175 mmol) and glycosyl bromide **13** (381 mg, 0.350 mmol, 2 equiv; 388 mg crude) were dissolved in freshly distilled CH_2Cl_2 (5.2 mL) containing freshly activated powdered 4Å MS (520 mg). The mixture was cooled to -45 °C under Ar in the dark for 1 h. AgOTf (121 mg, 0.471 mmol, 2.7 equiv.) in dry toluene (1.0 mL) was added, and the reaction was stirred under the same conditions for 2 h (TLC in 4:6 EtOAc/pentanes, R_f = 0.3), then quenched with NEt_3. The mixture was diluted with CH_2Cl_2 (15 mL) and filtered through celite. The solids were washed with CH_2Cl_2 (3 × 15 mL). The filtrate was washed with sat. aq. NaCl (2 × 45 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 10 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (acetone/hexanes, 7:13 → 9:11) gave a crude mixture containing heptasaccharide **27** and pentasaccharide acceptor **26**. The crude mixture was dissolved in CH_2Cl_2 (1.8 mL). Pyridine (28.4 µL, 0.351 mmol) was added, followed by chloroacetyl chloride (13.7 µL, 0.176 mmol). The reaction was stirred at RT for 30 min. The solution was diluted with CH_2Cl_2 (5 mL) then washed with 1 M HCl (2 × 5 mL) then sat. aq. $NaHCO_3$ (5 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 1 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (acetone/pentanes, 32:68 → 1:1) gave heptasaccharide **27** (284 mg, 47%) as a pale yellow amorphous solid, and chloroacetylated pentasaccharide **25** (68 mg, 15%) as a pale yellow amorphous solid. **Analytical Data for 27:** ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.47 (d, *J* = 9.9 Hz, 1H, 1 × N-H), 8.32 (d, *J* = 7.0 Hz, 1H, 1 × N-H), 8.26 – 8.23 (m, 2H, 2 × Bz), 8.21 (d, *J* = 9.3 Hz, 1H, 1 × N-H), 8.18 – 8.12 (m, 5H, 1 × N-H, 4 × Bz), 8.10 – 8.08 (m, 2H, 2 × Bz), 8.06 – 8.00 (m, 6H, 6 × Bz), 7.97 (d, *J* = 9.4 Hz, 1H, 1 × N-H), 7.95 – 7.87 (m, 12H, 12 × Bz), 7.74 – 7.70 (m, 4H, 2 × Bz, 2 × Phth), 7.66 – 7.23 (m, 37H, 36 × Bz, 1 × Phth), 7.21 – 7.16 (m, 2H, 2 × Bz), 7.11 (t, *J* = 7.9 Hz, 2H, 2 × Bz), 7.03 (d, *J* = 9.6 Hz, 1H, 1 × N-H), 7.00 (t, *J* = 7.6 Hz, 3H, 2 × Bz, 1 × Phth), 6.51 (dd, *J* = 11.0, 9.1 Hz, 1H, H-3^{IV}), 6.25 – 6.21 (m, 2H, 2 × H-3), 6.07 (t, *J* = 10.1 Hz, 1H, 1 × H-3), 5.99 (t, *J* = 10.1 Hz, 1H, 1 × H-3), 5.94 (t, *J* =

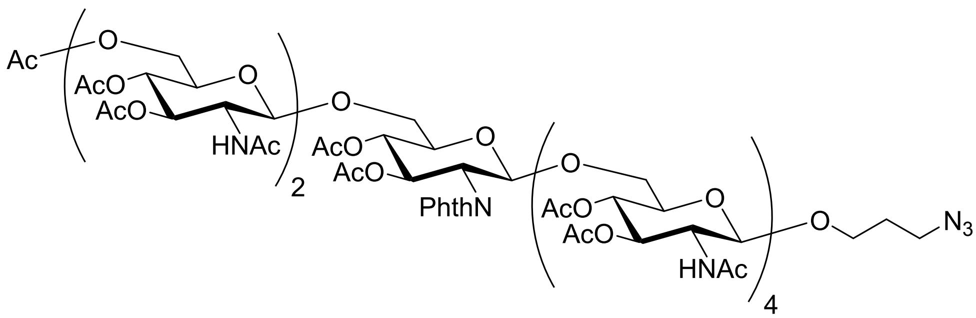
10.3 Hz, 1H, 1 × H-3), 5.68 – 5.64 (m, 1H, 1 × H-3), 5.61 (t, J = 9.7 Hz, 1H, 1 × H-4), 5.53 (t, J = 9.8 Hz, 1H, 1 × H-4), 5.48 – 5.38 (m, 4H, H-4^{IV}, 3 × H-4), 5.33 (d, J = 8.3 Hz, 1H, 1 × H-1), 5.15 (t, J = 9.8 Hz, 1H, 1 × H-4), 5.07 (t, J = 8.7 Hz, 2H, H-1^{IV}, 1 × H-1), 4.93 – 4.80 (m, 4H, 2 × H-1, 1 × H-2, 1 × H-5), 4.79 – 4.67 (m, 5H, 1 × H-1, H-2^{IV}, 1 × H-2, 2 × H-5), 4.64 – 4.52 (m, 5H, 1 × H-1, 3 × H-2, 1 × H-5), 4.30 – 4.24 (m, 2H, 2 × H-6a), 4.21 – 4.10 (m, 5H, H-5^{IV}, H-6a^{IV}, 1 × H-6a, 1 × H-6b, OC*H*HCH_2), 3.98 (dd, J = 13.00, 11.25 Hz, 1H, 1 × H-6a), 3.95 – 3.85 (m, 4H, 1 × H-2, 2 × H-5, 1 × H-6a), 3.83 – 3.73 (m, 3H, H-6b^{IV}, OCH*H*CH_2, COC*H*HCl), 3.69 – 3.60 (m, 3H, 1 × H-6a, $CH_2C\mathit{H_2}Cl$), 3.57 (d, J = 10.4 Hz, 1H, 1 × H-6b), 3.53 (d, J = 15.4 Hz, 1H, COCH*H*Cl), 3.50 – 3.46 (m, 1H, 1 × H-6b), 3.44 – 3.37 (m, 2H, 2 × H-6b), 3.32 – 3.28 (m, 1H, 1 × H-6b), 2.14 – 2.07 (m, 1H, $CH_2C\mathit{H}HCH_2$), 2.05 – 1.98 (m, 1H, $CH_2CH\mathit{H}CH_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 168.64, 168.38 (2 × *C*OPhth), 167.25 (*C*OCH_2Cl), 166.85, 166.84, 166.53, 166.50, 166.38, 166.26, 166.18, 165.95, 165.85, 165.72, 165.60, 165.16, 165.04, 164.88 (14 × *C*OPh), 158.75 (d, J = 38.2 Hz, 1 × *C*OCF_3), 158.52 (d, J = 37.7 H, 1 × *C*OCF_3), 158.48 (d, J = 38.4 Hz, 1 × *C*OCF_3), 158.11 (d, J = 37.7 Hz, 1 × *C*OCF_3), 158.06 (d, J = 37.8 Hz, 1 × *C*OCF_3), 157.60 (d, J = 37.4 Hz, 1 × *C*OCF_3), 135.11, 134.92 (2 × Phth), 133.99, 133.89, 133.87, 133.75, 133.63, 133.62, 133.56, 133.43, 133.28 (9 × Bz), 133.24 (2 × Bz), 133.15 (1 × Bz), 133.12 (2 × Bz), 130.56 (2 × Bz), 130.32 (2 × Bz), 130.31 (2 × Bz), 130.30 (2 × Bz), 130.19 (2 × Bz), 130.05 (2 × Bz), 129.96 (2 × Bz), 129.87 (4 × Bz), 129.84 (2 × Bz), 129.75 (2 × Bz), 129.70 (2 × Bz), 129.67 (2 × Bz), 129.59 (2 × Bz), 129.03 (1 × 4° Bz), 129.00 (2 × 4° Bz), 128.99 (2 × Bz), 128.96 (2 × Bz), 128.95, 128.91, 128.88, 128.78, 128.77 (5 × 4° Bz), 128.72 (2 × Bz), 128.70, 128.66 (2 × 4° Bz), 128.62 (2 × Bz), 128.58 (2 × 4° Bz), 128.57 (2 × Bz), 128.49 (2 × Bz), 128.44 (1 × 4° Bz), 128.40 (2 × Bz), 128.38 (2 × Bz), 128.35 (6 × Bz), 128.26 (4 × Bz), 128.23 (2 × Bz), 128.14 (1 × 4° Bz), 124.33, 123.52 (2 × Phth), 115.78 (q, J = 287.6 Hz, 2 × CF_3), 115.71 (q, J = 287.8 Hz, 1 × CF_3), 115.40 (q, J = 288.5 Hz, 1 × CF_3), 115.20 (q, J = 286.9 Hz, 1 × CF_3), 115.19 (q, J = 287.0 Hz, 1 × CF_3), 103.92, 103.26, 102.65, 101.38 (4 × C-1), 100.80 (C-1^{IV}), 100.43, 100.20 (2 × C-1), 74.32 (C-5^{IV}), 74.00, 73.67, 73.43, 72.97, 72.88, 72.75, 72.67, 72.49, 72.49, 72.47, 72.42, 72.34, 72.15, 72.09, 71.87, 71.48, 71.27, 70.88, 70.28 (C-4^{IV}), 69.97, 69.54, 69.30 (C-3^{IV}), 66.76 (O*C*H$_2$CH$_2$), 63.67 (C-6^{IV}), 57.88, 55.44, 55.30 (3 × C-2), 55.18 (C-2^{IV}), 55.08, 54.95, 54.83 (3 × C-2), 41.67 ($CH_2\mathit{C}H_2Cl$), 40.52 (CO*C*H$_2$Cl), 32.30 ($CH_2\mathit{C}H_2CH_2$). *m/z* (MALDI) calculated for $C_{165}H_{137}N_7O_{52}F_{18}Cl_2Na$ [M+Na]$^+$ 3482.73, found 3482.12.

2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-acetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranoside (28)



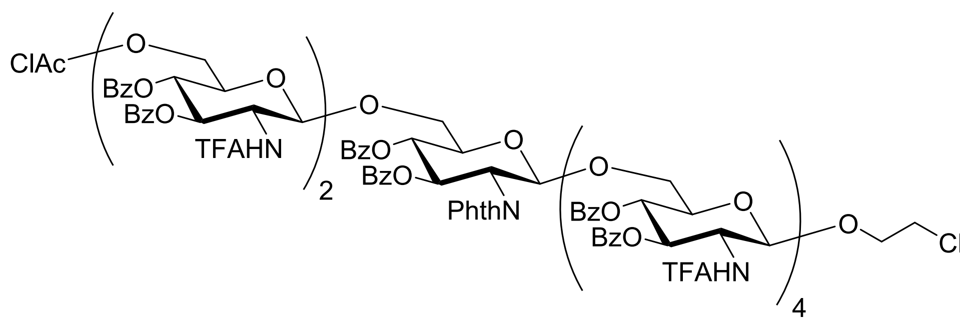
Heptasaccharide **27** (271 mg, 0.078 mmol) was dissolved in a 2:4:1 mixture of 0.5 M NaOH (22 mL, 11.0 mmol, 140 equiv.), THF (44 mL), and MeOH (11 mL). The reaction was stirred at 40 °C for 3 h. The solution was concentrated and dried under high vacuum. The residue was dissolved in a 1:1 mixture of pyridine (25 mL, 309.1 mmol, 3968 equiv.) and Ac_2O (25 mL, 264.5 mmol, 3395 equiv.). The reaction was stirred at 50 °C for 2 h, then left to attain RT for 16 h (TLC in 8:2 EtOAc/EtOH, $R_f = 0.3$). The solution co-concentrated with toluene. The residue was dissolved in $CHCl_3$ (120 mL) then washed with 1 M HCl (60 mL) then aq. $NaHCO_3$ (60 mL). The aqueous layers were re-extracted with $CHCl_3$ (3 × 30 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/EtOH, 19:1 → 9:1) gave heptasaccharide **28** (60 mg, 34%) as a white amorphous solid. ^{1}H NMR (600 MHz, Acetone-d_6) δ_H 8.12 (d, *J* = 10.0 Hz, 1H, 1 × N-H), 8.01 – 7.99 (m, 1H, 1 × Phth), 7.98 – 7.91 (m, 3H, 3 × Phth), 7.87 (d, *J* = 10.0 Hz, 1H, 1 × N-H), 7.85 (d, *J* = 9.8 Hz, 1H, 1 × N-H), 7.51 (d, *J* = 10.1 Hz, 1H, 1 × N-H), 7.47 (d, *J* = 9.8 Hz, 1H, 1 × N-H), 7.46 (d, *J* = 9.5 Hz, 1H, 1 × N-H), 5.92 (dd, *J* = 10.7, 8.8 Hz, 1H, H-3^{IV}), 5.48 – 5.41 (m, 2H, H-1^{IV}, 1 × H-3), 5.41 – 5.33 (m, 3H, 3 × H-3), 5.28 – 5.16 (m, 3H, 1 × H-1, 2 × H-3), 5.13 (dd, *J* = 10.3, 9.0 Hz, 1H, 1 × H-4), 5.05 – 4.91 (m, 5H, H-4^{IV}, 4 × H-4), 4.81 – 4.72 (m, 4H, 3 × H-1, 1 × H-5), 4.70 – 4.61 (m, 4H, 2 × H-1, 1 × H-4, 1 × H-5), 4.55 (td, *J* = 10.4, 3.2 Hz, 1H, 1 × H-5), 4.49 – 4.41 (m, 4H, H-2^{IV}, 2 × H-2, H-5^{IV}), 4.35 (dt, *J* = 10.2, 9.1 Hz, 1H, 1 × H-2), 4.25 (q, *J* = 9.6 Hz, 1H, 1 × H-2), 4.20 (dd, *J* = 12.5, 4.7 Hz, 1H, 1 × H-6a), 4.14 – 4.04 (m, 5H, 2 × H-2, 2 × H-5, H-6a^{IV}), 4.01 – 3.92 (m, 3H, 2 × H-6a, 1 × H-6b), 3.91 – 3.78 (m, 6H, 1 × H-5, 1 × H-6a, H-6b^{IV}, 1 × H-6b, OC*H*HCH$_2$, OCH*H*CH$_2$), 3.75 – 3.66 (m, 6H, 2 × H-6a, 2 × H-6b, CH_2Cl), 3.59 – 3.52 (m, 2H, 2 × H-6b), 3.48 (dd, *J* = 12.5, 2.7 Hz, 1H, 1 × H-6b), 2.20, 2.15, 2.12 (3 s, 9H, 3 × Ac), 2.11 (s, 6H, 2 × Ac), 2.07 (s, 3H, 1 × Ac), 2.05 (m, 1H, CH$_2$C*H*HCH$_2$), 2.03, 2.02 (2 s, 6H, 2 × Ac), 2.00 (m, 1H, CH$_2$CH*H*CH$_2$), 1.98, 1.98, 1.97, 1.96, 1.95, 1.95, 1.92, 1.89, 1.87, 1.86, 1.86, 1.82, 1.77 (13 s, 39H, 13 × Ac). ^{13}C NMR (125 MHz, Acetone-d_6) δ_C 171.62, 171.43, 171.21, 171.08, 170.98, 170.78, 170.72, 170.69, 170.68, 170.64, 170.61, 170.60, 170.54, 170.45, 170.34, 170.33, 170.19, 170.12, 170.08, 169.84, 169.54 (21 × *C*OCH$_3$), 169.31, 169.04 (2 × *C*OPhth), 136.30, 136.05 (2 × Phth), 132.17, 132.06 (2 × 4° Phth), 124.85, 124.22 (2 × Phth), 104.73, 104.32, 104.19, 103.06, 101.25, 100.74 (6 × C-1), 100.69 (C-1^{IV}), 75.31, 75.14 (2 × C-3), 74.70 (1 × C-5), 73.89 (1 × C-3), 73.70 (C-5^{IV}), 73.55 (1 × C-4), 73.43, 73.42 (2 × C-3), 73.39 (2 × C-5), 73.27 (C-6^{IV}), 73.13, 73.01 (2 × C-6), 72.79 (1 × C-3), 72.42 (1 × C-6), 72.27 (1 × C-4), 72.23, 72.20 (2 × C-5), 72.15, 71.97 (2 × C-4), 71.51 (1 × C-5), 71.12 (1 × C-4), 70.93 (C-3^{IV}), 70.59 (C-4^{IV}), 69.80(1 × C-4), 66.73 (O*C*H$_2$CH$_2$), 65.43 (1 × C-6), 62.66 (1 × C-6), 56.61 (C-2^{IV}), 55.75, 55.30, 55.21, 54.91, 54.74, 52.06 (6 × C-2), 42.91 (CH_2Cl), 33.19 (CH$_2$*C*H$_2$CH$_2$), 23.51, 23.32, 23.20, 23.18 (4 × NCO*C*H$_3$), 22.98 (2 × NCO*C*H$_3$), 21.27, 21.07, 21.02 (3 × OCO*C*H$_3$), 20.89 (2 × OCO*C*H$_3$), 20.73 (3 × OCO*C*H$_3$), 20.70 (2 × OCO*C*H$_3$), 20.64 (3 × OCO*C*H$_3$), 20.60, 20.47 (2 × OCO*C*H$_3$). *m/z* (ESI) calculated for $C_{95}H_{129}N_7O_{52}Cl$ [M+H]$^+$ 2234.73, found 2234.72.

2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-acetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-azidopropyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranoside (29)



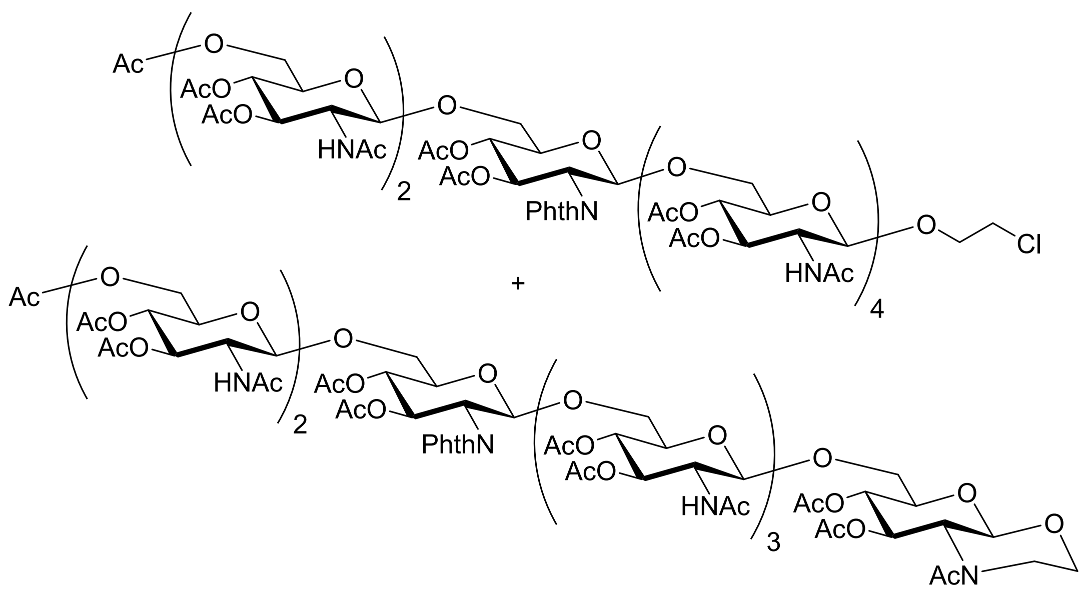
Heptasaccharide **28** (55.0 mg, 0.025 mmol) and NaN_3 (48.0 mg, 0.738 mmol, 30 equiv.) were dissolved in dry DMF (2.5 mL). The reaction was stirred at 80 °C for 45 h (TLC in 8:2 EtOAc/EtOH, R_f = 0.3). The solution was diluted with EtOAc (40 mL) then washed with H_2O (40 mL). The aqueous layer was re-extracted with EtOAc (5 × 20 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/EtOH, 99:1 → 9:1) gave azidopropyl glycoside **29** (35.5 mg, 64%) as a white amorphous solid. ^{1}H NMR (600 MHz, Acetone-d_6) δ_H 8.11 (d, *J* = 10.1 Hz, 1H, 1 × N-H), 8.01 – 7.99 (m, 1H, 1 × Phth), 7.98 – 7.94 (m, 3H, 3 × Phth), 7.87 (d, *J* = 9.7 Hz, 1H, 1 × N-H), 7.83 (d, *J* = 9.8 Hz, 1H, 1 × N-H), 7.51 (d, *J* = 10.2 Hz, 1H, 1 × N-H), 7.46 (d, *J* = 9.5 Hz, 2H, 2 × N-H), 5.92 (dd, *J* = 10.7, 8.7 Hz, 1H, H-3^{IV}), 5.46 – 5.42 (m, 2H, H-1^{IV}, 1 × H-3), 5.41 – 5.33 (m, 3H, 3 × H-3), 5.27 – 5.17 (m, 3H, 1 × H-1, 2 × H-3), 5.13 (dd, *J* = 10.4, 9.0 Hz, 1H, 1 × H-4), 5.05 – 4.91 (m, 5H, H-4^{IV}, 4 × H-4), 4.80 – 4.72 (m, 4H, 3 × H-1, 1 × H-5), 4.70 – 4.62 (m, 4H, 2 × H-1, 1 × H-4, 1 × H-5), 4.55 (td, *J* = 10.4, 3.1 Hz, 1H, 1 × H-5), 4.50 – 4.41 (m, 4H, H-2^{IV}, 2 × H-2, H-5^{IV}), 4.35 (dt, *J* = 10.3, 9.0 Hz, 1H, 1 × H-2), 4.25 (q, *J* = 9.6 Hz, 1H, 1 × H-2), 4.19 (dd, *J* = 12.5, 4.6 Hz, 1H, 1 × H-6a), 4.15 – 4.04 (m, 5H, 2 × H-2, 2 × H-5, H-$6a^{IV}$), 4.02 – 3.93 (m, 3H, 2 × H-6a, 1 × H-6b), 3.89 – 3.81 (m, 5H, 1 × H-5, 1 × H-6a, H-$6b^{IV}$, OC*H*HCH$_2$, OCH*H*CH$_2$), 3.78 – 3.67 (m, 4H, 2 × H-6a, 2 × H-6b), 3.58 – 3.52 (m, 2H, 2 × H-6b), 3.48 (dd, *J* = 12.8, 2.8 Hz, 1H, 1 × H-6b), 3.43 (t, *J* = 7.1 Hz, 2H, CH_2N_3), 2.20, 2.15, 2.11, 2.11, 2.11, 2.07, 2.03, 2.02, 1.98, 1.98, 1.97, 1.96, 1.95, 1.95 (14 s, 39H, 13 × Ac), 1.94 – 1.93 (m, 1H, CH$_2$C*H*HCH$_2$), 1.91, 1.89, 1.87 (3 s, 9H, 3 × Ac), 1.86 (s, 6H, 2 × Ac), 1.81 (s, 3H, 1 × Ac), 1.81 – 1.80 (m, 1H, CH$_2$CH*H*CH$_2$), 1.77 (s, 3H, 1 × Ac). ^{13}C NMR (125 MHz, Acetone-d_6) δ_C 171.61, 171.42, 171.19, 171.08, 170.98, 170.78, 170.71, 170.68, 170.67, 170.64, 170.62, 170.60, 170.54, 170.45 (14 × *C*OCH$_3$), 170.33 (2 × *C*OCH$_3$), 170.17, 170.08, 170.05, 169.84, 169.54 (5 × *C*OCH$_3$), 169.32, 169.04 (2 × *C*OPhth), 136.31, 136.07 (2 × Phth), 132.17, 132.07 (2 × 4° Phth), 124.86, 124.22 (2 × Phth), 104.74, 104.32, 104.20, 103.04, 101.09, 100.73 (6 × C-1), 100.70 (C-1^{IV}), 75.36, 75.14 (2 × C-3), 74.71 (1 × C-5), 73.88 (1 × C-3), 73.70 (C-5^{IV}), 73.57 (1 × C-4), 73.45, 73.42 (2 × C-3), 73.40 (2 × C-5), 73.29 (C-6^{IV}), 73.12, 73.00 (2 × C-6), 72.79 (1 × C-3), 72.42 (1 × C-6), 72.23 (1 × C-4, 1 × C-5), 72.21 (1 × C-5), 72.16, 71.98 (2 × C-4), 71.50 (1 × C-5), 71.11(1 × C-4), 70.93 (C-3^{IV}), 70.59 (C-4^{IV}), 69.82 (1 × C-4), 66.69 (O*C*H$_2$CH$_2$), 65.44, 62.68 (2 × C-6), 56.62 (C-2^{IV}), 55.77, 55.29, 55.23, 54.92, 54.74, 52.06 (6 × C-2), 49.30 (CH_2N_3), 29.26 ($CH_2CH_2CH_2$), 23.43, 23.30, 23.20, 23.17, 23.00, 22.98 (6 × NCOCH_3), 21.25, 21.07, 21.02 (3 × OCOCH_3), 20.89 (2 × OCOCH_3), 20.73 (2 × OCOCH_3), 20.70 (2 × OCOCH_3), 20.68 (1 × OCOCH_3), 20.64 (3 × OCOCH_3), 20.60, 20.47 (2 × OCOCH_3). *m/z* (ESI) calculated for $C_{95}H_{130}N_{10}O_{52}$ $[M+2H]^{2+}$ 1121.89, found 1121.89.

3,4-Di-O-benzoyl-6-chloroacetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-Di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloroethyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (30)



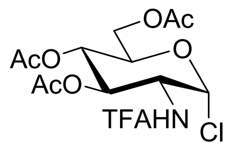
Chloroethyl heptasaccharide **30** was synthesized using the same methods as chloropropyl heptasaccharide **27**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.54 (d, *J* = 9.7 Hz, 1H, 1 × N-H), 8.36 – 8.28 (m, 3H, 3 × N-H), 8.22 – 8.19 (m, 2H, 2 × Bz), 8.18 – 8.16 (m, 2H, 2 × Bz), 8.12 (d, *J* = 7.3 Hz, 2H, 2 × Bz), 8.08 – 8.04 (m, 9H, 1 × N-H, 8 × Bz), 8.03 – 8.01 (m, 2H, 2 × Bz), 7.98 – 7.88 (m, 12H, 12 × Bz), 7.78 – 7.70 (m, 4H, 2 × Bz, 2 × Phth), 7.66 – 7.22 (m, 28H, 27 × Bz, 1 × Phth), 7.18 (t, *J* = 7.1 Hz, 2H, 2 × Bz), 7.15 – 7.11 (m, 3H, 1 × N-H, 2 × Bz), 7.03 – 6.97 (m, 3H, 2 × Bz, 1 × Phth), 6.54 (dd, *J* = 11.0, 9.4 Hz, 1H, H-3^{IV}), 6.28 (t, *J* = 10.6 Hz, 1H, 1 × H-3), 6.26 (t, *J* = 10.2 Hz, 1H, 1 × H-3), 6.12 (t, *J* = 10.0 Hz, 1H, 1 × H-3), 6.07 (t, *J* = 10.2 Hz, 1H, 1 × H-3), 6.01 (t, *J* = 10.2 Hz, 1H, 1 × H-3), 5.71 (dd, *J* = 10.4, 9.3 Hz, 1H, 1 × H-3), 5.59 (t, *J* = 9.7 Hz, 1H, 1 × H-4), 5.54 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 5.53 – 5.43 (m, 2H, 2 × H-4), 5.42 (t, *J* = 9.5 Hz, 1H, 1 × H-4), 5.39 (t, *J* = 9.6 Hz, 1H, H-4^{IV}), 5.35 (d, *J* = 8.2 Hz, 1H, 1 × H-1), 5.21 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 5.17 (d, *J* = 8.5 Hz, 1H, 1 × H-1), 5.08 (d, *J* = 8.4 Hz, 1H, H-1^{IV}), 4.98 – 4.58 (m, 13H, 3 × H-1, H-2^{IV}, 5 × H-2, H-5^{IV}, 3 × H-5), 4.56 (d, *J* = 8.4 Hz, 1H, 1 × H-1), 4.34 – 4.14 (m, 5H, 1 × H-5, 3 × H-6a, 1 × H-6b), 4.10 – 4.05 (m, 1H, OC*H*HCH_2), 4.04 – 3.81 (m, 6H, 2 × H-5, H-6a^{IV}, 1 × H-6a, OCH*H*CH_2, CH_2C*H*HCl), 3.80 – 3.72 (m, 2H, 1 × H-6a, COC*H*HCl), 3.69 – 3.61 (m, 2H, 1 × H-6a, CH_2CH*H*Cl), 3.59 (d, *J* = 11.2 Hz, 1H, 1 × H-6b), 3.55 (d, *J* = 15.4 Hz, 1H, COCH*H*Cl), 3.50 (d, *J* = 11.6 Hz, 1H, 1 × H-6a), 3.47 – 3.39 (m, 3H, H-6b^{IV}, 2 × H-6b), 3.33 (d, *J* = 11.3 Hz, 1H, 1 × H-6b). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 168.62, 168.46 (2 × *C*OPhth), 167.20 (*C*OCH_2Cl), 166.86 (2 × *C*OPh), 166.53, 166.50, 166.30, 166.23, 166.17, 165.94, 165.80, 165.73, 165.62, 165.17, 165.04, 164.91 (12 × *C*OPh), 158.84 (d, *J* = 38.6 Hz, 1 × *C*OCF_3), 158.67 (d, *J* = 38.0 Hz, 1 × *C*OCF_3), 158.52 (d, *J* = 38.6 Hz, 1 × *C*OCF_3), 158.30 (d, *J* = 37.7 Hz, 1 × *C*OCF_3), 158.19 (d, *J* = 37.7 Hz, 1 × *C*OCF_3), 157.60 (d, *J* = 37.6 Hz, 1 × *C*OCF_3), 135.07, 134.95 (2 × Phth), 133.97, 133.92, 133.89, 133.74 (4 × Bz), 133.66 (2 × Bz), 133.45, 133.35 (2 × Bz), 133.25 (2 × Bz), 133.16 (1 × Bz), 133.13 (2 × Bz), 130.56 (4° Phth), 130.35 (2 × Bz), 130.31 (4° Phth), 130.21 (2 × Bz), 130.19 (2 × Bz), 130.09 (2 × Bz), 130.06 (2 × Bz), 129.94 (2 × Bz), 129.88 (2 × Bz), 129.85 (2 × Bz), 129.84 (4 × Bz), 129.74 (4 × Bz), 129.68 (2 × Bz), 129.59 (2 × Bz), 128.99 (6 × Bz), 128.97, 128.93, 128.90, 128.87, 128.79 (5 × 4° Bz), 128.74 (2 × Bz), 128.72, 128.68 (2 × 4° Bz), 128.64 (2 × Bz), 128.62, 128.57 (2 × 4° Bz), 128.56 (2 × Bz), 128.49 (2 × Bz), 128.47 (4° Bz), 128.44 (2 × Bz), 128.37 (4° Bz), 128.34 (6 × Bz), 128.26 (2 × Bz), 128.25 (4 × Bz), 128.18 (4° Bz), 124.29, 123.55 (2 × Phth), 115.79 (q, *J* = 287.2 Hz, 1 × CF_3), 115.72 (q, *J* = 287.7 Hz, 2 × CF_3), 115.41 (q, *J* = 288.5 Hz, 1 × CF_3), 115.22 (q, *J* = 286.7 Hz, 1 × CF_3), 115.20 (q, *J* = 286.8 Hz, 1 × CF_3), 103.98, 103.36, 102.81, 101.51 (4 × C-1), 100.90 (C-1^{IV}), 100.87, 100.41 (2 × C-1), 74.33 (1 × C-5), 74.07 (1 × C-6), 73.75 (C-6^{IV}), 73.70, 73.49 (2 × C-6), 72.99 (C-5^{IV}), 72.89 (1 × C-3, 1 × C-5), 72.78 (1 × C-5), 72.68 (1 × C-3), 72.64 (1 × C-4), 72.42 (C-4^{IV}, 1 × C-4, 2 × C-5), 72.29 (1 × C-5), 72.21 (1 × C-4), 72.05 (1 × C-3), 71.88, 71.53 (2 × C-6), 71.46 (1 × C-4), 71.32, 70.77 (2 × C-3), 70.57 (O*C*$H_2$$CH_2$), 70.34 (1 × C-4), 69.98 (1 × C-3), 69.54 (1 × C-4), 69.31 (C-3^{IV}), 63.69 (1 × C-6), 57.92, 55.53, 55.30 (3 × C-2), 55.18 (C-2^{IV}), 55.05 (1 × C-2), 54.92 (2 × C-), 41.82 (CH_2*C*H_2Cl), 40.52 (CO*C*H_2Cl). *m/z* (MALDI) calculated for $C_{164}H_{135}N_7O_{52}F_{18}Cl_2Na$ $[M+Na]^+$ 3468.71, found 3468.41.

2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-acetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-chloroethyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranoside (31) & Compound (32)



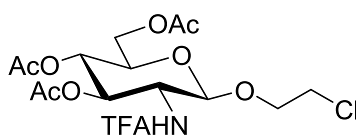
Chloroethyl heptasaccharide **30** (105 mg, 0.030 mmol) was dissolved in a 2:4:1 mixture of 4 M NaOH (1.0 mL, 4.0 mmol, 131 equiv.), THF (2.0 mL), and MeOH (0.5 mL). The reaction was stirred at 50 °C for 5 h. The solution was concentrated and dried under high vacuum. The residue was dissolved in a 1:1 mixture of pyridine (4 mL, 49.5 mmol, 1624 equiv.) and Ac_2O (4 mL, 42.3 mmol, 1390 equiv.). The reaction was stirred at RT for 16 h (TLC in 8:2 EtOAc/EtOH, R_f = 0.2). The solution co-concentrated with toluene. The residue was dissolved in $CHCl_3$ (40 mL) then washed with 1 M HCl (20 mL) then sat. aq. $NaHCO_3$ (20 mL). The aqueous layers were re-extracted with $CHCl_3$ (3 × 10 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/EtOH, 19:1 → 7:3) gave an inseparable mixture (49.6 mg) containing peracetylated heptasaccharide **31** and cyclized compound **32** as a white solid. **Analytical data for 31:** *m/z* (MALDI) calculated for $C_{94}H_{126}N_7O_{52}NaCl$ $[M+Na]^+$ 2242.70, found 2242.73. **Analytical data for 32:** *m/z* (MALDI) calculated for $C_{94}H_{125}N_7O_{52}Na$ $[M+Na]^+$ 2206.72, found 2206.51.

3,4,6-Tri-O-acetyl-2-trifluoroacetamido-2-deoxy-α-D-glucopyranosyl chloride (33)



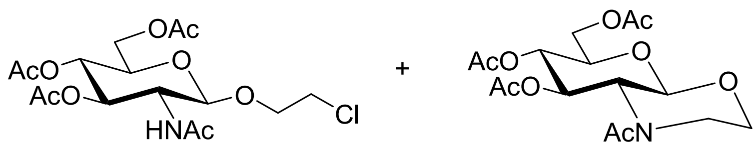
Known[8] compound **33** was synthesized partly based on the methods by Joseph et al.[5] and Horton.[9] ^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 6.71 (d, *J* = 8.2 Hz, 1H, N-H), 6.23 (d, *J* = 3.8 Hz, 1H, H-1), 5.38 (m, 1H, H-3), 5.25 (t, *J* = 9.8 Hz, 1H, H-4), 4.50 (ddd, *J* = 10.7, 8.5, 3.6 Hz, 1H, H-2), 4.35 – 4.27 (m, 2H, H-5, H-6a), 4.15 (m, 1H, H-6b), 2.11, 2.07, 2.06 (3 s, 9H, 3 × Ac). The NMR data are in agreement with those reported in the literature.[8]

Chloroethyl 3,4,6-tri-O-acetyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (34)



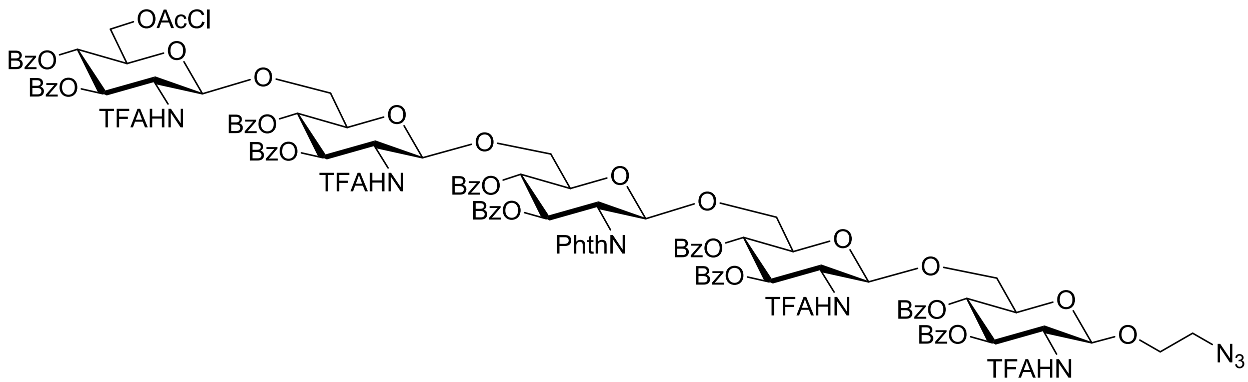
Chloride donor **33** (1.19 g, 2.84 mmol) and 2-chloroethanol (1.9 mL, 28.3 mmol, 10 equiv.) were dissolved in freshly distilled CH_2Cl_2 (40 mL) containing freshly activated powdered 4Å MS (2.4 g). The mixture was stirred at 0 °C under Ar in the dark for 1 h. AgOTf (0.95 g, 3.70 mmol, 1.3 equiv.) in dry toluene (5 mL) was added, and the reaction was stirred under the same conditions for 2 h (TLC in 7:13 EtOAc/pentanes, R_f = 0.3), then quenched with NEt_3. The mixture was diluted with CH_2Cl_2 (30 mL) and filtered through celite. The solids were washed with CH_2Cl_2 (3 × 30 mL). The filtrate was washed with sat. aq. NaCl (2 × 125 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 25 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 3:7 → 6:4) gave chloroethyl glycoside **34** (0.94 g, 72%) as white crystals. ^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 6.77 (d, *J* = 9.1 Hz, 1H, N-H), 5.33 (dd, *J* = 10.7, 9.3 Hz, 1H, H-3), 5.09 (dd, *J* = 10.0, 9.3 Hz, 1H, H-4), 4.77 (d, *J* = 8.3 Hz, 1H, H-1), 4.27 (dd, *J* = 12.3, 4.9 Hz, 1H, H-6a), 4.16 (dd, *J* = 12.4, 2.5 Hz, 1H, H-6b), 4.11 (dt, *J* = 11.2, 4.8 Hz, 1H, OC*H*HCH$_2$), 4.02 (dt, *J* = 10.8, 8.6 Hz, 1H, H-2), 3.81 – 3.72 (m, 2H, H-5, OCH*H*CH$_2$), 3.62 (dd, *J* = 6.5, 4.8 Hz, 2H, CH_2Cl), 2.09, 2.03, 2.03 (3 s, 9H, 3 × Ac). ^{13}C NMR (100 MHz, Chloroform-*d*) δ_C 171.03, 170.67, 169.29 (3 × *C*OCH$_3$), 157.48 (d, *J* = 37.9 Hz, *C*OCF$_3$), 115.53 (d, *J* = 288.2 Hz, CF_3), 100.55 (C-1), 72.07 (C-5), 71.53 (C-3), 69.89 (O*C*H$_2$CH$_2$), 68.34 (C-4), 61.90 (C-6), 54.79 (C-2), 42.70 (CH_2Cl), 20.69, 20.54, 20.37 (3 × CH_3). *m/z* (ESI) calculated for $C_{16}H_{25}N_2O_9F_3Cl$ $[M+NH_4]^+$ 481.12, found 481.12.

Chloroethyl 3,4,6-tri-O-acetyl-2-acetamido-2-deoxy-β-D-glucopyranoside (35) & Compound (36)



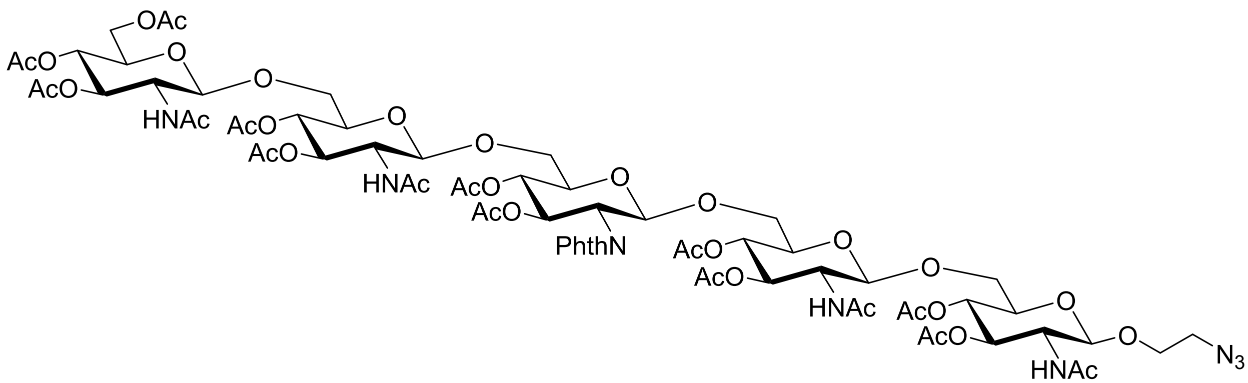
Chloroethyl glycoside **34** (50 mg, 0.108 mmol) was dissolved in a 2:4:1 mixture of 0.5 M NaOH (4.3 mL, 2,15 mmol, 20 equiv.), THF (8.6 mL), and MeOH (2.1 mL). The reaction was stirred at 40-60 °C for 2-20 h (Table 1). The solution was concentrated and dried under high vacuum. The residue was dissolved in a 1:1 mixture of pyridine (5 mL, 61.8 mmol, 572 equiv.) and Ac_2O (5 mL, 52.9 mmol, 490 equiv.). The reaction was stirred at RT for 2h (TLC in 8:2 EtOAc/pentanes, R_f = 0.3, 0.1). The solution co-concentrated with toluene. The residue was dissolved in CH_2Cl_2 (30 mL) then washed with 1 M HCl (2 × 30 mL) then sat. aq. $NaHCO_3$ (30 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 7 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (8:2 → 1:0 EtOAc/pentanes) gave known[1,2] chloroethyl glycoside **35** as a white amorphous solid, and bicyclic compound **36** as a pale yellow amorphous solid (see Table 1 for yields). **Analytical data for 35:** ^1H NMR (400 MHz, Chloroform-*d*) δ_H 5.72 (d, *J* = 8.6 Hz, 1H, N-H), 5.31 (dd, *J* = 10.5, 9.4 Hz, 1H, H-3), 5.05 (t, *J* = 9.6 Hz, 1H, H-4), 4.78 (d, *J* = 8.4 Hz, 1H, H-1), 4.25 (dd, *J* = 12.3, 4.8 Hz, 1H, H-6a), 4.13 (dd, *J* = 12.2, 2.4 Hz, 1H, H-6b), 4.08 (dt, *J* = 11.2, 4.9 Hz, 1H, OC*H*HCH₂), 3.86 (dt, *J* = 10.5, 8.6 Hz, 1H, H-2), 3.78 (dt, *J* = 11.5, 6.3 Hz, 1H, OCH*H*CH₂), 3.72 (ddd, *J* = 9.9, 4.8, 2.4 Hz, 1H, H-5), 3.64 – 3.61 (m, 2H, CH_2Cl), 2.08, 2.02, 2.01 (3 s, 9H, 3 × $OCOCH_3$), 1.95 (s, 3H, $NCOCH_3$). The NMR data are in agreement with those reported in the literature.[2] **Analytical data for 36:** ^1H NMR (400 MHz, Chloroform-*d*) δ_H 6.31 (dd, *J* = 10.9, 9.1 Hz, 1H, H-3), 4.94 (dd, *J* = 10.0, 9.2 Hz, 1H, H-4), 4.65 (d, *J* = 8.2 Hz, 1H, H-1), 4.27 (dd, *J* = 12.4, 4.7 Hz, 1H, H-6a), 4.13 (dd, *J* = 12.3, 2.1 Hz, 1H, H-6b), 4.03 (dt, *J* = 11.5, 3.2 Hz, 1H, $OCHHCH_2$), 3.89 (ddd, *J* = 10.1, 4.7, 2.1 Hz, 1H, H-5), 3.73 (td, *J* = 11.6, 11.0, 3.1 Hz, 1H, $OCHHCH_2$), 3.63 (dt, *J* = 14.6, 3.2 Hz, 1H, C*H*HN), 3.40 (ddd, *J* = 13.8, 10.5, 3.2 Hz, 1H, CH*H*N), 3.22 (dd, *J* = 11.2, 8.2 Hz, 1H, H-2), 2.09 (s, 3H, NAc), 2.05, 2.00, 1.95 (3 s, 9H, 3 × OAc). ^{13}C NMR (100 MHz, Chloroform-*d*) δ_C 170.62, 170.51, 169.93, 169.45 (4 × $COCH_3$), 96.39 (C-1), 72.65 (C-5), 70.86 (C-3), 69.71 (C-4), 65.89 (OCH_2CH_2), 63.73 (C-2), 61.95 (C-6), 47.75 (CH_2N), 23.42 ($NCOCH_3$), 20.88, 20.70, 20.68 (3 × $OCOCH_3$). *m/z* (DART) calculated for $C_{16}H_{24}NO_9$ $[M+H]^+$ 374.14, found 374.1.

3,4-Di-O-benzoyl-6-chloroacetyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-azidoethyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (37)



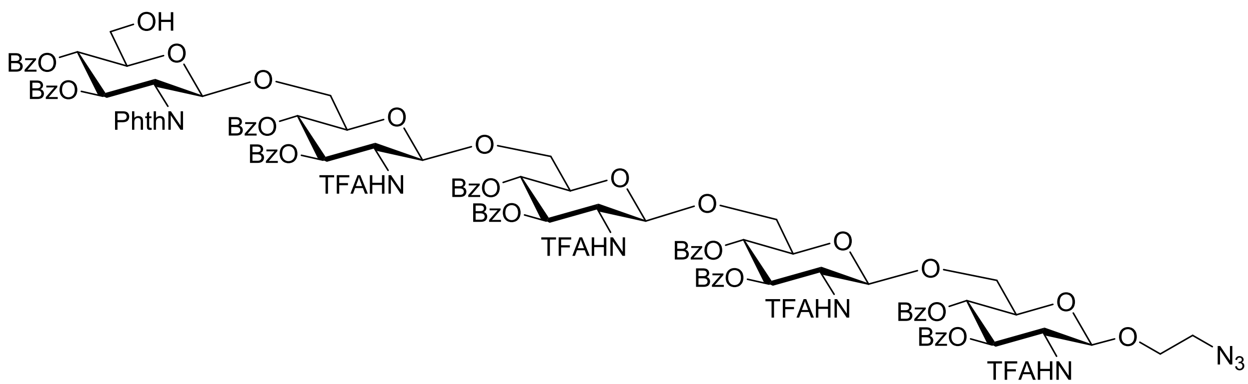
Azidoethyl pentasaccharide **37** was synthesized using similar methods to chloropropyl pentasaccharide **20**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.42 (d, *J* = 6.8 Hz, 1H, 1 × N-H), 8.36 (d, *J* = 10.1 Hz, 1H, 1 × N-H), 8.12 – 8.04 (m, 9H, 1 × N-H, 8 × Bz), 8.02 – 7.96 (m, 10H, 10 × Bz), 7.92 (dd, *J* = 8.4, 1.3 Hz, 2H, 2 × Bz), 7.72 (d, *J* = 7.4 Hz, 1H, 1 × Phth), 7.67 (t, *J* = 7.1 Hz, 1H, 1 × Phth), 7.63 – 7.61 (m, 2H, 2 × Bz), 7.60 – 7.39 (m, 16H, 15 × Bz, 1 × Phth), 7.38 – 7.31 (m, 7H, 7 × Bz), 7.21 (dt, *J* = 7.6, 1.5 Hz, 2H, 2 × Bz), 7.17 (dt, *J* = 7.6, 1.6 Hz, 2H, 2 × Bz), 7.13 (dt, *J* = 7.8, 1.9 Hz, 3H, 2 × Bz, 1 × Phth), 6.99 (d, *J* = 8.4 Hz, 1H, 1 × N-H), 6.56 (dd, *J* = 11.0, 9.0 Hz, 1H, H-3''), 6.31 (dd, *J* = 10.5, 9.1 Hz, 1H, 1 × H-3), 6.06 (dd, *J* = 10.0 Hz, 1H, 1 × H-3), 5.91 (dd, *J* = 10.2 Hz, 1H, 1 × H-3), 5.77 – 5.68 (m, 3H, 1 × H-3, H-4'', 1 × H-4), 5.55 (dd, *J* = 10.1, 9.4 Hz, 1H, 1 × H-4), 5.41 – 5.35 (m, 2H, 1 × H-1, 1 × H-4), 5.30 (d, *J* = 8.5 Hz, 1H, H-1''), 5.10 (t, *J* = 9.9 Hz, 1H, 1 × H-4), 5.04 (d, *J* = 8.4 Hz, 1H, 1 × H-1), 4.91 (d, *J* = 8.4 Hz, 1H, 1 × H-1), 4.84 (dd, *J* = 11.1, 8.6 Hz, 1H, H-2''), 4.79 – 4.62 (m, 6H, 1 × H-1, 2 × H-2, H-5'', 2 × H-5), 4.57 (q, *J* = 9.4 Hz, 1H, 1 × H-2), 4.33 (dd, *J* = 12.3, 2.4 Hz, 1H, 1 × H-6a), 4.26 (dd, *J* = 13.1, 10.9 Hz, 1H, 1 × H-6a), 4.23 – 4.14 (m, 3H, 1 × H-5, 1 × H-6b, OC*H*HCH$_2$), 4.12 (dd, *J* = 13.1, 10.4 Hz, 1H, H-6a''), 4.08 (dd, *J* = 13.0, 1.2 Hz, 1H, 1 × H-6a), 3.98 – 3.90 (m, 2H, 1 × H-2, 1 × H-5), 3.87 (dd, *J* = 12.9, 9.7 Hz, 1H, 1 × H-6b), 3.82 (d, *J* = 15.5 Hz, 1H, C*H*HCl), 3.73 (ddd, *J* = 11.6, 8.7, 3.6 Hz, 1H, OCH*H*CH$_2$), 3.67 – 3.62 (m, 2H, 1 × H-6a, H-6b''), 3.59 (d, *J* = 15.5 Hz, 1H, CH*H*Cl), 3.59 – 3.53 (m, 2H, 1 × H-6b, C*H*HN$_3$), 3.47 (dd, *J* = 12.6, 1.7 Hz, 1H, 1 × H-6b), 3.32 (dt, *J* = 13.3, 4.0 Hz, 1H, CH*H*N$_3$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 169.17, 167.98 (2 × *C*OPhth), 167.30 (*C*OCH$_2$Cl), 166.87, 166.83, 166.51, 166.50, 166.45, 165.72, 165.58, 165.34, 165.14, 164.94 (10 × *C*OPh), 158.13 (d, *J* = 36.0 Hz, 1 × *C*OCF$_3$), 158.10 (d, *J* = 38.0 Hz, 1 × *C*OCF$_3$), 158.00 (d, *J* = 36.3 Hz, 1 × *C*OCF$_3$), 157.57 (d, *J* = 37.3 Hz, 1 × *C*OCF$_3$), 135.03, 134.92 (2 × Phth), 133.93, 133.86, 133.85, 133.77, 133.74, 133.54, 133.39, 133.35, 133.35, 133.21 (10 × Bz), 130.69, 130.52 (2 × 4° Phth), 130.21 (2 × Bz), 130.20 (2 × Bz), 130.16 (2 × Bz), 130.08 (2 × Bz), 129.93 (2 × Bz), 129.90 (4 × Bz), 129.83 (2 × Bz), 129.81 (2 × Bz), 129.70 (2 × Bz), 129.08 (2 × Bz), 129.04 (1 × 4° Bz), 128.93 (2 × Bz), 128.85, 128.81, 128.69, 128.67 (4 × 4° Bz), 128.64 (2 × Bz), 128.62 (1 × 4° Bz), 128.57 (2 × Bz), 128.46 (2 × Bz), 128.40 (1 × 4° Bz), 128.38 (4 × Bz), 128.35 (2 × Bz), 128.31 (2 × Bz), 128.24 (2 × Bz), 128.19, 128.12 (2 × 4° Bz), 124.31, 123.49 (2 × Phth), 115.88 (q, *J* = 288.2 Hz, 1 × CF$_3$), 115.58 (q, *J* = 287.7 Hz, 1 × CF$_3$), 115.36 (q, *J* = 288.5 Hz, 1 × CF$_3$), 115.06 (q, *J* = 286.9 Hz, 1 × CF$_3$), 104.10, 101.70, 100.68 (3 × C-1), 100.53 (C-1''), 100.27 (1 × C-1), 74.65 (1 × C-5), 73.88 (C-6''), 73.56 (1 × C-6), 73.48 (C-5''), 72.65 (1 × C-3), 72.52 (1 × C-6), 72.50 (1 × C-5), 72.40 (1 × C-4), 72.33 (1 × C-5), 72.32 (1 × C-6), 72.31 (1 × C-5), 72.24 (1 × C-3), 71.75 (C-4''), 71.69, 71.52 (2 × C-4), 69.90 (2 × C-3), 69.60 (1 × C-4), 69.40 (C-3''), 68.93 (O*C*H$_2$CH$_2$), 63.64 (1 × C-6), 57.91, 55.38 (2 × C-2), 55.26 (C-2''), 54.54, 54.39 (2 × C-2), 50.31 (CH_2N_3), 40.54 (CH_2Cl). *m/z* (ESI) calculated for $C_{120}H_{103}N_9O_{38}F_{12}Cl$ $[M+NH_4]^+$ 2540.59, found 2540.59.

2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-acetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-azidoethyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranoside (38)



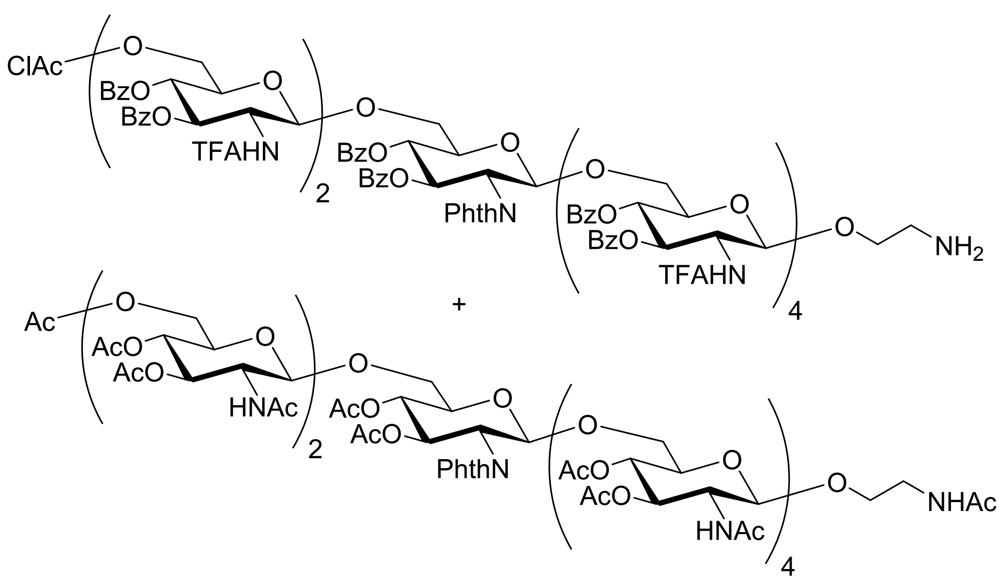
Azidoethyl pentasaccharide **37** (46.5 mg, 0.018 mmol) was dissolved in a 2:4:1 mixture of 0.5 M NaOH (3.6 mL, 1.8 mmol, 100 equiv.), THF (7.2 mL), and MeOH (1.8 mL). The reaction was stirred at 40 °C for 2 h. The solution was concentrated and dried under high vacuum. The residue was dissolved in a 1:1 mixture of pyridine (4.5 mL, 55.6 mmol, 3089 equiv.) and Ac_2O (4.5 mL, 47.6 mmol, 2644 equiv.). The reaction was stirred at 50 °C for 1 h, then left to attain RT for 18 h (TLC in 9:1 EtOAc/EtOH, $R_f = 0.2$). The solution co-concentrated with toluene. The residue was dissolved in CH_2Cl_2 (20 mL) then washed with 1 M HCl (20 mL) then aq. $NaHCO_3$ (20 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 5 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/EtOH, 19:1 → 17:3) gave pentasaccharide **38** (17.1 mg, 56%) as a white amorphous solid. ^1H NMR (600 MHz, Chloroform-*d*) δ_H 7.85 – 7.72 (m, 4H, 4 × Phth), 7.39 (d, *J* = 8.9 Hz, 1H, 1 × N-H), 6.84 (d, *J* = 7.9 Hz, 1H, 1 × N-H), 6.74 (d, *J* = 9.7 Hz, 1H, 1 × N-H), 6.21 (d, *J* = 9.2 Hz, 1H, 1 × N-H), 5.77 (dd, *J* = 10.9, 8.9 Hz, 1H, H-3''), 5.65 (t, *J* = 9.7 Hz, 1H, 1 × H-3), 5.28 – 5.21 (m, 3H, H-1'', 1 × H-1, 1 × H-3), 5.20 (dd, *J* = 10.6, 9.2 Hz, 1H, 1 × H-3), 5.15 (dd, *J* = 10.8, 9.2 Hz, 1H, 1 × H-3), 5.00 (dd, *J* = 10.3, 8.9 Hz, 1H, H-4''), 4.92 – 4.85 (m, 3H, 3 × H-4), 4.73 – 4.68 (dd, *J* = 10.0, 9.2 Hz, 1H, 1 × H-4), 4.58 (d, *J* = 8.5 Hz, 2H, 2 × H-1), 4.48 (d, *J* = 8.5 Hz, 1H, 1 × H-1), 4.41 – 4.31 (m, 4H, H-2'', H-5'', 1 × H-5, 1 × H-6a), 4.29 – 4.19 (m, 3H, 2 × H-2, 1 × H-5), 4.06 (q, *J* = 9.1 Hz, 1H, 1 × H-2), 4.02 – 3.96 (m, 2H, H-6a'', OC*H*HCH$_2$), 3.92 (dd, *J* = 12.1, 2.1 Hz, 1H, 1 × H-6b), 3.89 – 3.84 (m, 2H, 2 × H-5), 3.81 – 3.68 (m, 4H, 1 × H-2, 2 × H-6a, 1 × H-6b), 3.67 – 3.60 (m, 3H, 1 × H-6a, H-6b'', OCH*H*CH$_2$), 3.58 (dd, *J* = 12.3, 2.8 Hz, 1H, 1 × H-6b), 3.54 – 3.51 (m, 1H, 1 × H-6b), 3.49 – 3.42 (m, 1H, C*H*HN$_3$), 3.21 (ddd, *J* = 13.5, 4.7, 3.3 Hz, 1H, CH*H*N$_3$), 2.13, 2.11, 2.08, 2.07, 2.07, 2.06 (6 s, 18H, 6 × OAc), 2.06, 2.05 (2 s, 6H, 2 × NAc), 2.04, 2.01, 2.00 (3 s, 9H, 3 × OAc), 1.97 (s, 3H, 1 × NAc), 1.95 (s, 3H, 1 × OAc), 1.91 (s, 3H, 1 × NAc), 1.90 (s, 3H, 1 × OAc). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 171.72, 171.05, 170.88, 170.78, 170.64, 170.45, 170.36, 170.32, 170.30, 170.18, 169.94, 169.84, 169.78, 169.72, 169.66 (15 × *C*OCH$_3$), 134.90 (2 × Phth), 131.03 (2 × 4° Phth), 124.00, 123.50 (2 × Phth), 103.83, 101.93 (2 × C-1), 100.61 (C-1'', 1 × C-1), 99.65 (1 × C-1), 73.80 (1 × C-5), 73.31, 73.21 (2 × C-3), 72.80 (C-5''), 72.27 (1 × C-5), 72.05 (1 × C-3, 1 × C-6), 71.46 (1 × C-5), 71.33 (1 × C-3), 71.12 (1 × C-6), 71.03 (1 × C-5), 70.82, 70.77 (2 × C-4), 70.67 (C-4''), 70.04 (C-3''), 69.51, 69.17 (2 × C-4), 68.97 (1 × C-6), 68.27 (C-6'', OCH_2CH_2), 62.37 (1 × C-6), 55.44 (1 × C-2), 55.20 (C-2''), 54.36, 54.14, 53.85 (3 × C-2), 50.38 (CH_2N_3), 23.40 (1 × NCOCH_3), 23.26 (2 × NCOCH_3), 22.99 (1 × NCOCH_3), 20.83, 20.78 (2 × OCOCH_3), 20.76 (2 × OCOCH_3), 20.73, 20.67, 20.66, 20.64, 20.57, 20.54, 20.40 (7 × OCOCH_3). *m/z* (ESI) calculated for $C_{70}H_{92}N_8O_{38}Na$ $[M+Na]^+$ 1675.54, found 1675.5.

3,4-Di-O-benzoyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-Di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-azidoethyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (39)



Azidoethyl pentasaccharide **39** was synthesized using similar methods to chloropropyl pentasaccharide **26**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.51 (d, *J* = 9.9 Hz, 1H, 1 × N-H), 8.45 (d, *J* = 9.6 Hz, 1H, 1 × N-H), 8.16 (dd, *J* = 8.6, 1.3 Hz, 2H, 2 × Bz), 8.13 (d, *J* = 9.7 Hz, 1H, 1 × N-H), 8.10 (dd, *J* = 8.5, 1.5 Hz, 2H, 2 × Bz), 8.06 – 7.94 (m, 16H, 16 × Bz), 7.84 – 7.76 (m, 3H, 3 × Phth), 7.61 – 7.52 (m, 6H, 6 × Bz), 7.50 – 7.26 (m, 21H, 20 × Bz, 1 × Phth), 7.23 (t, *J* = 8.2 Hz, 2H, 2 × Bz), 7.18 (t, *J* = 8.1 Hz, 2H, 2 × Bz), 7.16 (d, *J* = 9.4 Hz, 1H, 1 × N-H), 6.37 (dd, *J* = 10.5, 9.1 Hz, 1H, H-3^{IV}), 6.19 (dd, *J* = 10.7, 9.5 Hz, 1H, 1 × H-3), 6.01 (t, *J* = 10.3 Hz, 1H, 1 × H-3), 5.90 (t, *J* = 10.6 Hz, 1H, 1 × H-3), 5.75 (t, *J* = 10.0 Hz, 1H, 1 × H-3), 5.73 (t, *J* = 10.2 Hz, 1H, 1 × H-4), 5.60 (dd, *J* = 10.7, 9.3 Hz, 1H, 1 × H-4), 5.41 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 5.38 (t, *J* = 9.6 Hz, 1H, H-4^{IV}), 5.26 (d, *J* = 8.4 Hz, 1H, H-1^{IV}), 5.12 (d, *J* = 8.5 Hz, 1H, 1 × H-1), 5.04 (t, *J* = 9.8 Hz, 1H, 1 × H-4), 4.91 – 4.83 (m, 2H, 1 × H-1, 1 × H-2), 4.84 – 4.66 (m, 4H, 1 × H-1, 2 × H-2, 1 × H-5), 4.67 – 4.54 (m, 4H, 1 × H-1, 2 × H-2, 1 × H-5), 4.51 (dd, *J* = 10.4, 9.0 Hz, 1H H-2^{IV}), 4.26 – 4.20 (m, 2H, 1 × H-5, 1 × H-6a), 4.14 – 4.06 (m, 3H, H-6a^{IV}, 1 × H-6a, OC*H*HCH$_2$), 3.84 – 3.79 (m, 2H, H-5^{IV}, OCH*H*CH$_2$), 3.76 – 3.72 (m, 2H, 2 × H-6a), 3.63 – 3.55 (m, 3H, 3 × H-6b), 3.49 – 3.41 (m, 2H, H-6b^{IV}, C*H*HN$_3$), 3.36 (dt, *J* = 13.3, 4.8 Hz, 1H, CH*H*N$_3$), 3.31 (d, *J* = 11.7 Hz, 1H, 1 × H-6b), 2.65 (bs, 1H, OH-6^{IV}). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 168.55, 167.50 (2 × *C*OPhth), 166.63, 166.48, 166.46, 166.41, 166.29, 166.04, 166.01, 165.74, 165.42, 164.94 (10 × *C*OPh), 158.49 (d, *J* = 36.5 Hz, 1 × *C*OCF$_3$), 158.47 (d, *J* = 36.4 Hz, 1 × *C*OCF$_3$), 158.16 (d, *J* = 36.6 Hz, 1 × *C*OCF$_3$), 158.14 (d, *J* = 36.6 Hz, 1 × *C*OCF$_3$), 134.90 (2 × Phth), 133.82 (2 × Bz), 133.74 (2 × Bz), 133.62 (1 × Bz), 133.51 (2 × Bz), 133.40, 133.29, 133.19 (3 × Bz), 130.86 (4° Phth), 130.53 (4° Phth), 130.18 (2 × Bz), 130.15 (2 × Bz), 130.08 (2 × Bz), 130.02 (2 × Bz), 129.98 (2 × Bz), 129.92 (2 × Bz), 129.90 (2 × Bz), 129.85 (4 × Bz), 129.49 (2 × Bz), 128.99 (2 × Bz), 128.91 (1 × 4° Bz), 128.79 (2 × Bz), 128.73 (2 × Bz), 128.72, 128.66, 128.61, 128.60 (4 × 4° Bz), 128.58 (2 × 4° Bz), 128.40 (4 × Bz), 128.38 (1 × 4° Bz), 128.35 (2 × Bz), 128.32 (2 × Bz), 128.30 (4 × Bz), 128.28 (2 × Bz), 127.68, 127.03 (2 × 4° Bz), 123.90, 123.51 (2 × Phth), 115.66 (q, J = 287.1 Hz, 1 × CF_3), 115.64 (q, J = 287.8 Hz, 1 × CF_3), 115.61 (q, J = 289.9 Hz, 1 × CF_3), 115.02 (q, J = 286.2 Hz, 1 × CF_3), 104.15, 103.49, 101.62, 100.08 (4 × C-1), 99.97 (C-1^{IV}), 75.18 (C-5^{IV}), 74.62 (1 × C-5), 74.21 (1 × C-6), 73.82 (C-6^{IV}), 73.77 (1 × C-5), 72.78 (1 × C-3), 72.67 (1 × C-5), 72.34 (1 × C-5, 1 × C-6), 72.26 (1 × C-3), 71.86 (1 × C-4), 71.60 (1 × C-3), 71.49 (1 × C-3, 1 × C-4, 1 × C-6), 71.36 (1 × C-4), 70.31 (C-4^{IV}), 70.11 (C-3^{IV}), 69.82 (1 × C-4), 69.13 (O*C*H_2CH_2), 61.65 (1 × C-6), 55.17 (C-2^{IV}), 55.13, 54.99 (2 × C-2), 54.38 (2 × C-2), 50.12 (CH_2N_3). *m/z* (MALDI) calculated for $C_{118}H_{98}N_8O_{37}F_{12}Na$ $[M+Na]^+$ 2469.57, found 2469.84.

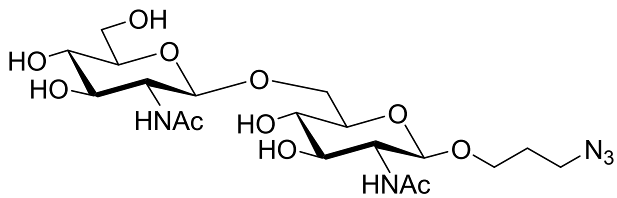
3,4-Di-O-benzoyl-6-chloroacetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-Di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-aminoethyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (40) & 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-O-acetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-acetamidoethyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranoside (41)



Pentasaccharide acceptor **39** (309 mg, 0.126 mmol) and glycosyl bromide **13** (412 mg, 0.379 mmol, 3 equiv.) were dissolved in freshly distilled CH_2Cl_2 (4 mL) containing freshly activated powdered 4Å MS (400 mg). The mixture was stirred at -45 °C under Ar in the dark for 1 h. AgOTf (130 mg, 0.506 mmol, 4 equiv.) in dry toluene (1.0 mL) was added, and the reaction was stirred under the same conditions for 2 h (TLC in 4:6 acetone/pentanes, R_f = 0.2), then quenched with NEt_3. The mixture was diluted with 10 mL CH_2Cl_2 and filtered through celite. The solids were washed with CH_2Cl_2 (3 × 10 mL). The filtrate was washed with sat. aq. NaCl (2 × 30 mL).

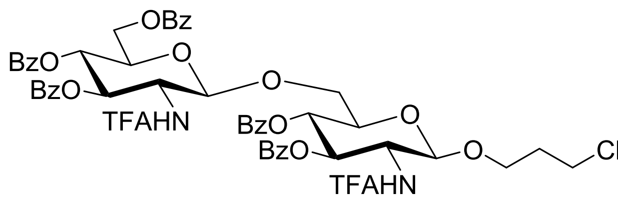
The aqueous layers were re-extracted with CH_2Cl_2 (2 × 5 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (acetone/pentanes, 4:6 → 1:1, then EtOAc/pentanes, 1:1) gave heptasaccharide **40** with small impurities (243 mg) as a yellow solid. A portion of **40** (97 mg, 0.028 mmol) was dissolved in a 2:4:1 mixture of 0.5 M NaOH (8 mL, 4.0 mmol, 140 equiv.), THF (16 mL), and MeOH (4 mL). The reaction was stirred at 40 °C for 3 h. The solution was concentrated and dried under high vacuum. The residue was dissolved in a 1:1 mixture of pyridine (10 mL, 105.8 mmol, 3768 equiv.) and Ac_2O (10 mL, 123.6 mmol, 4414 equiv.). The reaction was stirred at 50 °C for 2 h, then left to attain RT for 16 h (TLC in 7:3 EtOAc/EtOH, $R_f = 0.3$). The solution co-concentrated with toluene. The residue was dissolved in $CHCl_3$ (60 mL) then washed with 1 M HCl (30 mL) then sat. aq. $NaHCO_3$ (30 mL). The aqueous layers were re-extracted with $CHCl_3$ (3 × 15 mL each). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/EtOH, 17:3 → 1:1) gave heptasaccharide **41** (36.2 mg, 32% over three steps) as a yellow solid. **Analytical Data for 40:** *m/z* (MALDI) calculated for $C_{164}H_{137}N_8O_{52}F_{18}NaCl$ $[M+Na]^+$ 3449.76, found 3449.86. **Analytical Data for 41:** ^1H NMR (600 MHz, Acetone-d_6) δ_H 8.13 (d, *J* = 10.0 Hz, 1H, 1 × N-H), 8.02 – 7.99 (m, 1H, 1 × Phth), 7.98 – 7.92 (m, 3H, 3 × Phth), 7.90 (d, *J* = 9.7 Hz, 1H, 1 × N-H), 7.79 (d, *J* = 9.6 Hz, 1H, 1 × N-H), 7.52 (d, *J* = 10.1 Hz, 1H, 1 × N-H), 7.51 (d, *J* = 9.8 Hz, 1H, 1 × N-H), 7.46 (d, *J* = 9.5 Hz, 1H, 1 × N-H), 6.98 (t, *J* = 5.2 Hz, 1H, CH_2NHAc), 5.92 (dd, *J* = 10.7, 8.7 Hz, 1H, H-3^{IV}), 5.45 (d, *J* = 8.5 Hz, 1H, H-1^{IV}), 5.45 (dd, *J* = 10.5, 9.4 Hz, 1H, 1 × H-3), 5.41 – 5.33 (m, 3H, 1 × H-1, 2 × H-3), 5.27 – 5.17 (m, 3H, 3 × H-3), 5.05 – 4.90 (m, 5H, H-4^{IV}, 4 × H-4), 4.81 – 4.76 (m, 4H, 2 × H-1, 1 × H-4, 1 × H-5), 4.74 (d, *J* = 8.6 Hz, 1H, 1 × H-1), 4.70 – 4.61 (m, 4H, 2 × H-1, 1 × H-4, 1 × H-5), 4.58 – 4.51 (m, 1H, 1 × H-5), 4.49 – 4.37 (m, 5H, H-2^{IV}, 2 × H-2, H-5^{IV}, 1 × H-5), 4.35 (dt, *J* = 10.4, 9.2 Hz, 1H, 1 × H-2), 4.26 (q, *J* = 9.4 Hz, 1H, 1 × H-2), 4.18 (dd, *J* = 12.4, 4.6 Hz, 1H, 1 × H-6a), 4.16 – 4.03 (m, 4H, 2 × H-2, 1 × H-5, H-$6a^{IV}$), 4.00 – 3.93 (m, 2H, 1 × H-6a, 1 × H-6b), 3.90 – 3.81 (m, 4H, 1 × H-5, 2 × H-6a, H-$6b^{IV}$), 3.79 (t, *J* = 5.9 Hz, 2H, OCH_2CH_2), 3.76 – 3.71 (m, 2H, 2 × H-6a, 1 × H-6b), 3.69 (dd, *J* = 12.5, 1.9 Hz, 1H, 1 × H-6b), 3.58 (dd, *J* = 7.5, 2.9 Hz, 1H, 1 × H-6b), 3.56 (dd, *J* = 7.7, 2.9 Hz, 1H, 1 × H-6b), 3.47 (dd, *J* = 12.6, 2.7 Hz, 1H, 1 × H-6b), 3.37 – 3.31 (m, 2H, CH_2N), 2.21, 2.15, 2.12, 2.11, 2.11, 2.07, 2.03, 2.02, 1.98, 1.98, 1.97, 1.96, 1.95, 1.95 (14 s, 42H, 14 × CH_3), 1.92 (s, 6H, 2 × CH_3), 1.89, 1.86, 1.86, 1.85, 1.82, 1.77 (6 s, 18H, 6 × CH_3). ^{13}C NMR (125 MHz, Acetone-d_6) δ_C 171.62, 171.48, 171.47, 171.07, 170.94, 170.71, 170.67, 170.66, 170.64, 170.62, 170.59, 170.55, 170.52 (13 × $COCH_3$), 170.46 (2 × $COCH_3$), 170.44, 170.43, 170.38, 170.32, 170.06, 169.88, 169.58 (7 × $COCH_3$), 169.28, 168.97 (2 × *C*OPhth), 136.27, 136.04 (2 × Phth), 132.07, 131.99 (2 × 4° Phth), 124.85, 124.17 (2 × Phth), 104.65, 104.25, 104.10, 102.98, 101.10, 100.67 (6 × C-1), 100.62 (C-1^{IV}), 75.23, 75.00 (2 × C-3), 74.61 (1 × C-5), 73.81 (1 × C-3), 73.63 (1 × C-5), 73.49 (C-6^{IV}), 73.37, 73.32 (2 × C-3), 73.28 (1 × C-5), 72.98, 72.96, 72.92 (3 × C-6), 72.76 (1 × C-3), 72.33 (1 × C-6), 72.16 (1 × C-5), 72.10 (1 × C-4), 72.09 (C-4^{IV}), 72.07 (1 × C-5), 72.05, 71.91 (2 × C-4), 71.56 (C-5^{IV}, 1 × C-5), 71.15 (1 × C-4), 70.88 (C-3^{IV}), 70.53, 69.75 (2 × C-4), 68.82 (OCH_2CH_2), 65.40, 62.66 (2 × C-6), 56.54 (C-2^{IV}), 55.74, 55.21, 55.13, 54.84, 54.69, 52.02 (6 × C-2), 39.83 (CH_2N), 23.50 – 22.79 (7 × $NCOCH_3$), 21.25 – 20.26 (15 × $OCOCH_3$). *m/z* (ESI) calculated for $C_{96}H_{132}N_8O_{53}$ $[M+2H]^{2+}$ 1122.90, found 1122.90.

2-Acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-azidopropyl 2-acetamido-2-deoxy-β-D-glucopyranoside (44)



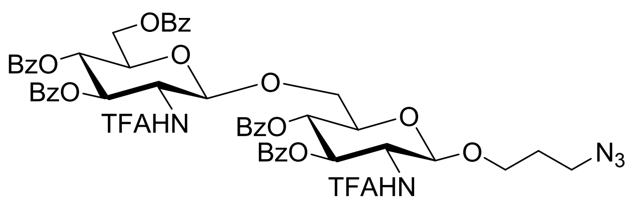
Disaccharide **47** (9.0 mg, 0.0125 mmol) was dissolved in MeOH (1.0 mL). Sodium (0.1 mg, 0.0043 mmol, 0.33 equiv.) was added. The reaction was stirred at RT for 3 h, then quenched with Dowex 50WX8 cation exchange resin (hydrogen form, 50-100 mesh). The resin was filtered and washed with MeOH. The filtrate was concentrated giving deprotected PNAG disaccharide **44** (6.1 mg, 95%) as a white powder. ^{1}H NMR (600 MHz, Deuterium Oxide) δ_H 4.55 (d, *J* = 8.5 Hz, 1H, H-1), 4.50 (d, *J* = 8.5 Hz, 1H, H-1'), 4.22 (dd, *J* = 11.2, 1.8 Hz, 1H, H-6a), 3.96 – 3.92 (m, 2H, H-6a', OC*H*HCH$_2$), 3.79 – 3.72 (m, 3H, H-2, H-6b, H-6b'), 3.69 – 3.63 (m, 2H, H-2', OCH*H*CH$_2$), 3.59 – 3.52 (m, 3H, H-3, H-3', H-5), 3.48 – 3.46 (m, 2H, H-4, H-5'), 3.42 – 3.35 (m, 3H, H-4', CH$_2$N$_3$), 2.06, 2.06 (2 s, 6H, 2 × CH$_3$), 1.85 (p, *J* = 6.5 Hz, 2H, CH$_2$C*H$_2$*CH$_2$). ^{13}C NMR (125 MHz, Deuterium Oxide) δ_C 174.46, 174.40 (2 × *C*OCH$_3$), 101.37 (C-1), 101.02 (C-1'), 75.76 (C-5'), 74.48 (C-5), 73.65 (C-3'), 73.63 (C-3), 69.91 (C-4'), 69.83 (C-4), 68.44 (C-6), 66.88 (O*C*H$_2$CH$_2$), 60.62 (C-6'), 55.46 (C-2'), 55.39 (C-2), 47.70 (CH$_2$N$_3$), 28.01 (CH$_2$*C*H$_2$CH$_2$), 22.14, 22.07 (2 × CH$_3$). *m/z* (ESI) calculated for $C_{19}H_{34}N_5O_{11}$ $[M+H]^+$ 508.22, found 508.23.

3,4,6-Tri-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-chloropropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (45)



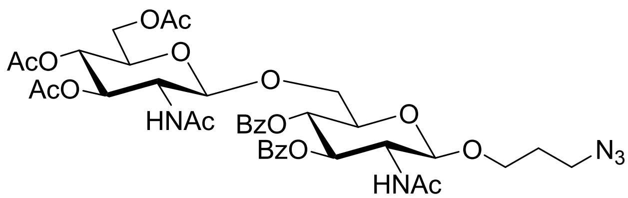
Disaccharide **15** (56.0 mg 0.055 mmol), DMAP (1.3 mg, 0.011 mmol, 0.2 equiv.), and pyr (17.7 µL, 0.219 mmol, 4 equiv.) were dissolved in DCM (1.0 mL). BzCl (12.7 µL, 0.109 mmol, 2 equiv.) was added. The reaction was stirred at RT for 20 h (TLC in 4:6 EtOAc/pentanes, R_f = 0.6). The solution was diluted with CH$_2$Cl$_2$ (4 mL) then washed with 1 M HCl (5 mL) then aq. NaHCO$_3$ (5 mL). The aqueous layers were re-extracted with CH$_2$Cl$_2$ (2 × 1 mL each). The organic layers were dried over Na$_2$SO$_4$ and concentrated. Column chromatography (EtOAc/pentanes, 3:7) gave disaccharide **45** (53.5 mg, 87%) as a white amorphous solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.94 – 7.89 (m, 6H, 6 × Bz), 7.88 – 7.84 (m, 4H, 4 × Bz), 7.52 – 7.46 (m, 5H, N-H', 4 × Bz), 7.42 (t, *J* = 7.3 Hz, 1H, 1 × Bz), 7.38 – 7.29 (m, 8H, 8 × Bz), 7.27 (t, *J* = 7.8 Hz, 2H, 2 × Bz), 6.91 (d, *J* = 8.7 Hz, 1H, H-H), 5.82 (t, *J* = 10.1 Hz, 1H, H-3), 5.72 (t, *J* = 9.5 Hz, 1H, H-4'), 5.70 – 5.64 (m, 1H, H-3'), 5.48 (t, *J* = 9.6 Hz, 1H, H-4), 4.82 (d, *J* = 8.2 Hz, 1H, H-1), 4.75 (d, *J* = 8.4 Hz, 1H, H-1'), 4.60 (q, *J* = 8.8 Hz, 1H, H-2'), 4.57 (dd, *J* = 12.3, 3.0 Hz, 1H, H-6a'), 4.40 (dd, *J* = 12.3, 4.9 Hz, 1H, H-6b'), 4.25 (dd, *J* = 11.6, 1.5 Hz, 1H, H-6a), 4.11 (q, *J* = 8.9 Hz, 1H, H-2), 4.08 – 4.02 (m, 2H, H-5', OC*H*HCH$_2$), 3.90 (ddd, *J* = 9.7, 4.5, 1.4 Hz, 1H, H-5), 3.67 (ddd, *J* = 10.7, 9.0, 4.9 Hz, 1H, OCH*H*CH$_2$), 3.64 – 3.59 (m, 3H, H-6b, C*H$_2$*Cl), 2.13 – 2.03 (m, 1H, CH$_2$C*H*HCH$_2$), 2.01 – 1.92 (m, 1H, CH$_2$CH*H*CH$_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 166.72, 166.56, 166.08, 165.77, 165.01 (5 × *C*OPh), 157.68 (d, *J* = 37.4 Hz, 1 × *C*OCF$_3$), 157.46 (d, *J* = 37.8 Hz, 1 × *C*OCF$_3$), 133.94, 133.76, 133.65, 133.52, 133.16 (5 × Bz), 129.89 (2 × Bz), 129.85 (4 × Bz), 129.76 (2 × Bz), 129.67 (2 × Bz), 129.35 (1 × 4° Bz), 128.65 (1 × 4° Bz), 128.51 (2 × Bz), 128.46 (4 × Bz), 128.42 (2 × Bz), 128.35 (2 × Bz), 128.29 (1 × 4° Bz), 128.16 (1 × 4° Bz), 128.06 (1 × 4° Bz), 115.71 (q, *J* = 288.2 Hz, 1 × CF_3), 115.44 (q, *J* = 288.2 Hz, 1 × CF_3), 101.55 (C-1'), 100.53 (C-1), 73.33 (C-5), 72.82 (C-3'), 72.42 (C-5'), 71.90 (C-3), 69.16 (C-4'), 69.04 (C-4), 68.31 (C-6), 66.23 (O*C*H_2CH_2), 62.79 (C-6'), 55.21 (C-2), 54.79 (C-2'), 41.45 (CH_2Cl), 31.97 (CH_2*C*H_2CH_2). *m/z* (ESI) calculated for $C_{54}H_{51}N_3O_{16}F_6Cl$ $[M+NH_4]^+$ 1146.29, found 1146.29.

3,4,6-Tri-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-azidopropyl 3,4-di-O-benzoyl-2-trifluoroacetamido-2-deoxy-β-D-glucopyranoside (46)

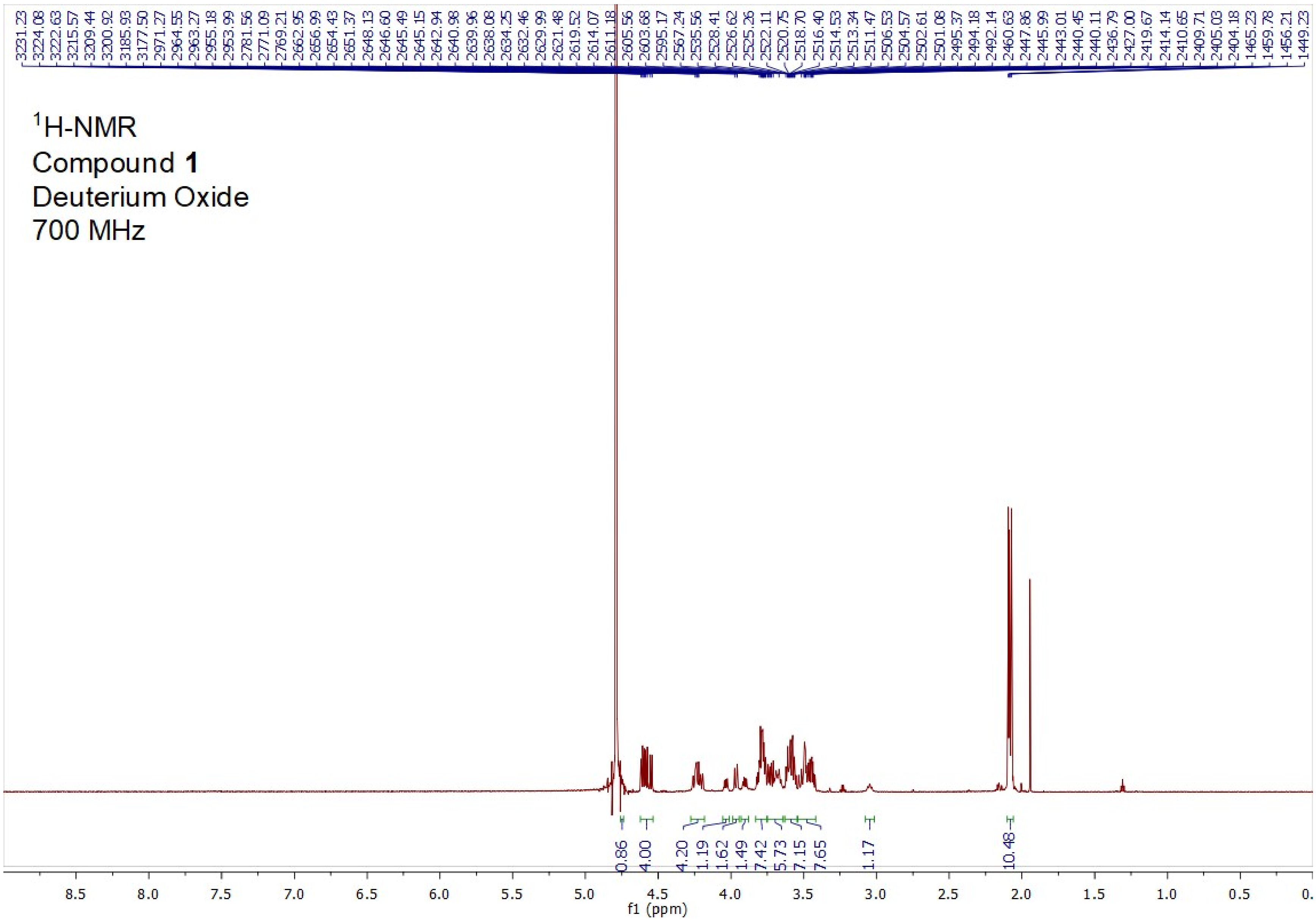


Disaccharide **45** (50.0 mg, 0.044 mmol) and NaN_3 (28.9 mg, 0.445 mmol, 10 equiv.) were dissolved in dry DMF (4.4 mL). The reaction was stirred at 80 °C for 24 h (TLC in 4:6 EtOAc/pentanes, R_f = 0.6). The solution was diluted with EtOAc (40 mL) then washed with H_2O (40 mL). The aqueous layer was re-extracted with EtOAc (2 × 20 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/pentanes, 3:7 → 4:6) gave azidopropyl glycoside **46** (47.0 mg, 93%) as a white amorphous solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.92 – 7.87 (m, 6H, 6 × Bz), 7.86 (dd, *J* = 8.4, 1.2 Hz, 2H, 2 × Bz), 7.83 (d, *J* = 7.8 Hz, 2H, 2 × Bz), 7.56 (d, *J* = 8.8 Hz, 1H, N-H'), 7.50 – 7.45 (m, 4H, 4 × Bz), 7.41 (t, *J* = 7.7 Hz, 1H, 1 × Bz), 7.35 – 7.29 (m, 8H, 8 × Bz), 7.26 (t, *J* = 7.5 Hz, 2H, 2 × Bz), 6.91 (d, *J* = 7.3 Hz, 1H, N-H), 5.81 (t, *J* = 10.1 Hz, 1H, H-3), 5.72 (t, *J* = 9.5 Hz, 1H, H-4'), 5.65 (t, *J* = 10.2 Hz, 1H, H-3'), 5.45 (t, *J* = 9.6 Hz, 1H, H-4), 4.80 (d, *J* = 8.2 Hz, 1H, H-1), 4.73 (d, *J* = 8.4 Hz, 1H, H-1'), 4.61 (q, *J* = 8.7 Hz, 1H, H-2'), 4.56 (dd, *J* = 12.3, 3.0 Hz, 1H, H-6a'), 4.39 (dd, *J* = 12.2, 5.0 Hz, 1H, H-6b'), 4.22 (dd, *J* = 11.8, 1.3 Hz, 1H, H-6a), 4.09 (q, *J* = 10.0, 9.2 Hz, 1H, H-2), 4.03 (ddd, *J* = 9.5, 4.8, 3.3 Hz, 1H, H-5'), 4.00 – 3.95 (m, 1H, OC*H*HCH_2), 3.87 (ddd, *J* = 9.5, 4.7, 1.4 Hz, 1H, H-5), 3.62 (dd, *J* = 11.7, 5.1 Hz, 1H, H-6b), 3.57 (ddd, *J* = 9.5, 7.6, 4.7 Hz, 1H, OCH*H*CH_2), 3.43 – 3.33 (m, 2H, CH_2N_3), 1.91 – 1.77 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 166.68, 166.50, 166.08, 165.75, 165.01 (5 × COPh), 157.70 (d, *J* = 37.9 Hz, 1 × *C*OCF_3), 157.45 (d, *J* = 37.7 Hz, 1 × *C*OCF_3), 133.91, 133.74, 133.63, 133.51, 133.15 (5 × Bz), 129.88 (2 × Bz), 129.84 (4 × Bz), 129.77 (2 × Bz), 129.66 (2 × Bz), 129.35 (1 × 4° Bz), 128.66 (1 × 4° Bz), 128.51 (2 × Bz), 128.49 (2 × Bz), 128.45 (2 × Bz), 128.42 (2 × Bz), 128.34 (2 × Bz), 128.30 (1 × 4° Bz), 128.18 (1 × 4° Bz), 128.03 (1 × 4° Bz), 115.73 (q, *J* = 288.0 Hz, 1 × CF_3), 115.44 (q, *J* = 288.2 Hz, 1 × CF_3), 101.58 (C-1'), 100.34 (C-1), 73.38 (C-5), 72.80 (C-3'), 72.42 (C-5'), 71.84 (C-3), 69.15 (C-4'), 69.03 (C-4), 68.31 (C-6), 66.44 (O*C*H_2CH_2), 62.80 (C-6'), 55.25 (C-2), 54.77 (C-2'), 47.99 (CH_2N_3), 28.82 (CH_2*C*H_2CH_2). *m/z* (ESI) calculated for $C_{54}H_{51}N_6O_{16}F_6$ $[M+NH_4]^+$ 1153.33, found 1153.32.

2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-azidopropyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-β-D-glucopyranoside (47)



46 (44.0 mg, 0.039 mmol) was dissolved in a 2:4:1 mixture of 0.5 M NaOH (3.1 mL, 1.55 mmol, 40 equiv.), THF (6.2 mL), and MeOH (1.5 mL). The reaction was stirred at 40 °C for 2 h. The solution was concentrated and dried under high vacuum. The residue was dissolved in a 1:1 mixture of pyridine (5 mL, 61.8 mmol, 1596 equiv.) and Ac_2O (5 mL, 52.9 mmol, 1366 equiv.). The reaction was stirred at RT for 18 h (TLC in 19:1 EtOAc/EtOH, R_f = 0.3). The solution co-concentrated with toluene. The residue was dissolved in CH_2Cl_2 (20 mL) then washed with 1 M HCl (20 mL) then aq. $NaHCO_3$ (20 mL). The aqueous layers were re-extracted with CH_2Cl_2 (2 × 5 mL). The organic layers were dried over Na_2SO_4 and concentrated. Column chromatography (EtOAc/EtOH, 99:1 → 9:1) gave disaccharide **47** (13.3 mg, 48%) as a white amorphous solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 5.86 (d, *J* = 8.3 Hz, 1H, N-H'), 5.47 (d, *J* = 8.0 Hz, 1H, N-H), 5.22 (dd, *J* = 10.5, 9.4 Hz, 1H, H-3), 5.17 (dd, *J* = 10.4, 9.4 Hz, 1H, H-3'), 5.06 (t, *J* = 9.6 Hz, 1H, H-4'), 5.00 (t, *J* = 9.5 Hz, 1H, H-4), 4.59 (d, *J* = 8.3 Hz, 1H, H-1), 4.50 (d, *J* = 8.4 Hz, 1H, H-1'), 4.25 (dd, *J* = 12.3, 4.7 Hz, 1H, H-6a'), 4.11 (dd, *J* = 12.3, 2.3 Hz, 1H, H-6b'), 4.02 – 3.96 (m, 2H, H-2', H-6a), 3.95 – 3.91 (m, 1H, $OC\mathit{H}HCH_2$), 3.84 (dt, *J* = 10.2, 8.6 Hz, 1H, H-2), 3.64 (m, 2H, H-5, H-5'), 3.58 – 3.54 (m, 1H, $OCH\mathit{H}CH_2$), 3.46 (dd, *J* = 11.3, 5.1 Hz, 1H, H-6b), 3.38 (t, *J* = 6.4 Hz, 2H, CH_2N_3), 2.08, 2.04, 2.02, 2.01, 2.00 (5 s, 15H, 5 × OAc), 1.95, 1.94 (2 s, 6H, 2 × NAc), 1.90 – 1.77 (m, 2H, $CH_2C\mathit{H}_2CH_2$). ^{13}C NMR (125 MHz, Chloroform-*d*) δ_C 170.91, 170.86, 170.69, 170.34, 170.20, 170.00, 169.33 (7 × $\mathit{C}OCH_3$), 101.36 (C-1'), 100.69 (C-1), 72.92 (C-5), 72.79 (C-3'), 72.48 (C-3), 72.04 (C-5'), 68.79 (C-4), 68.38 (C-4'), 67.84 (C-6), 65.90 ($O\mathit{C}H_2CH_2$), 61.97 (C-6'), 54.52 (C-2), 54.25 (C-2'), 48.11 (CH_2N_3), 28.90 ($CH_2\mathit{C}H_2CH_2$), 23.34, 23.15 (2 × $NCO\mathit{C}H_3$), 20.78, 20.75, 20.69, 20.66, 20.61 (5 × $OCO\mathit{C}H_3$). *m/z* (ESI) calculated for $C_{29}H_{47}N_6O_{16}$ $[M+NH_4]^+$ 735.30, found 735.30.



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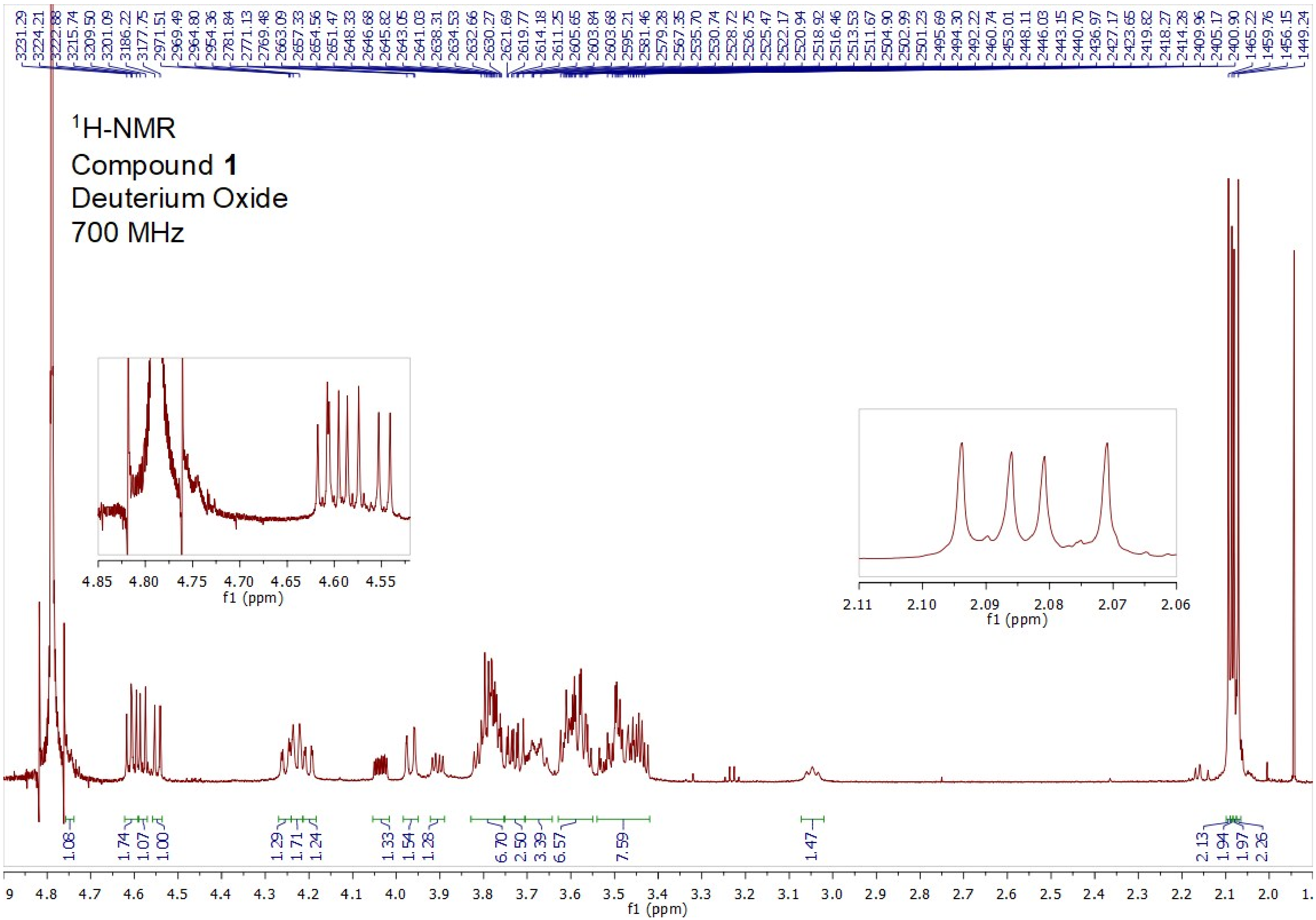
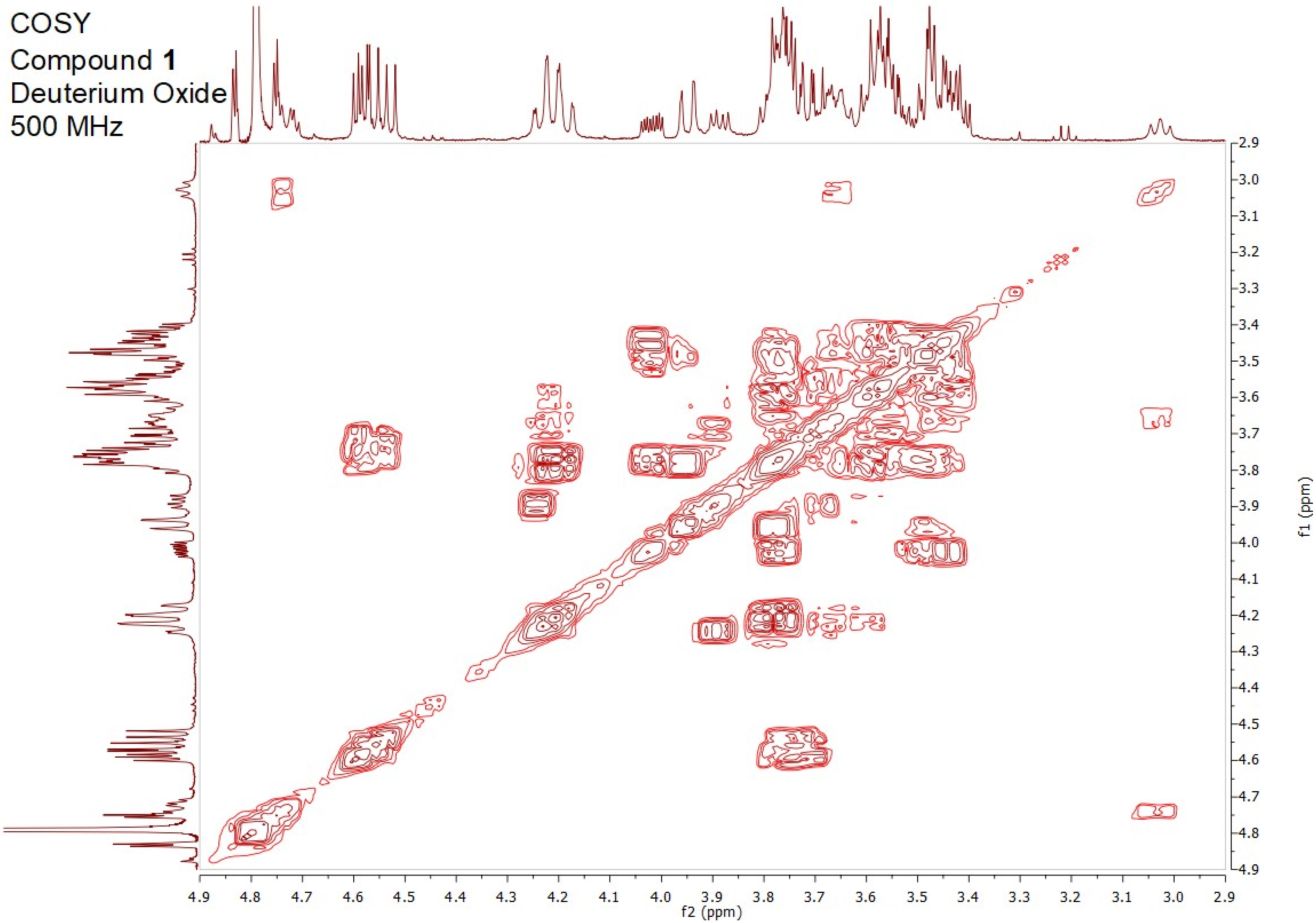
0.
f1 (ppm)

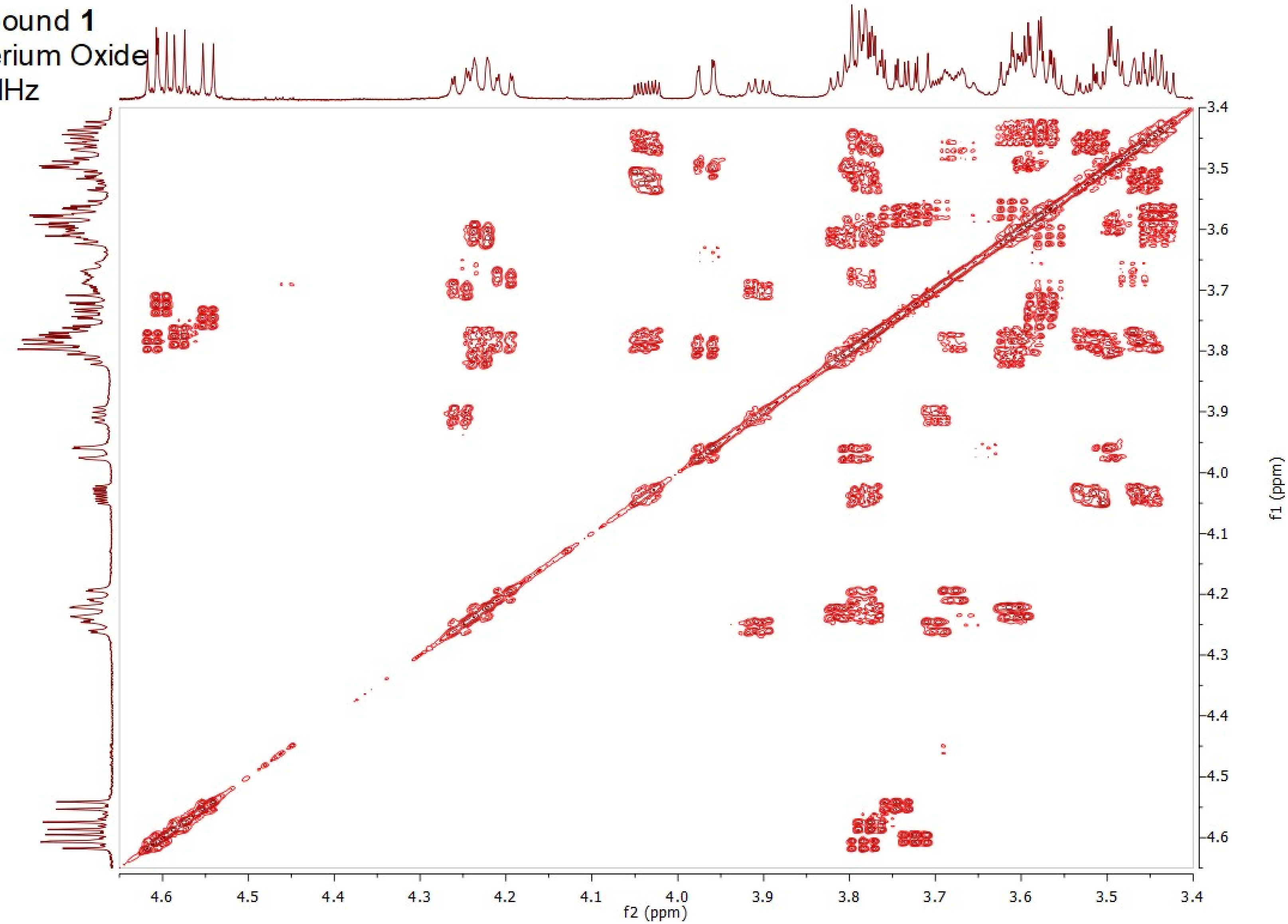


[1]H-NMR
Compound **1**
Deuterium Oxide
700 MHz
f1 (ppm)

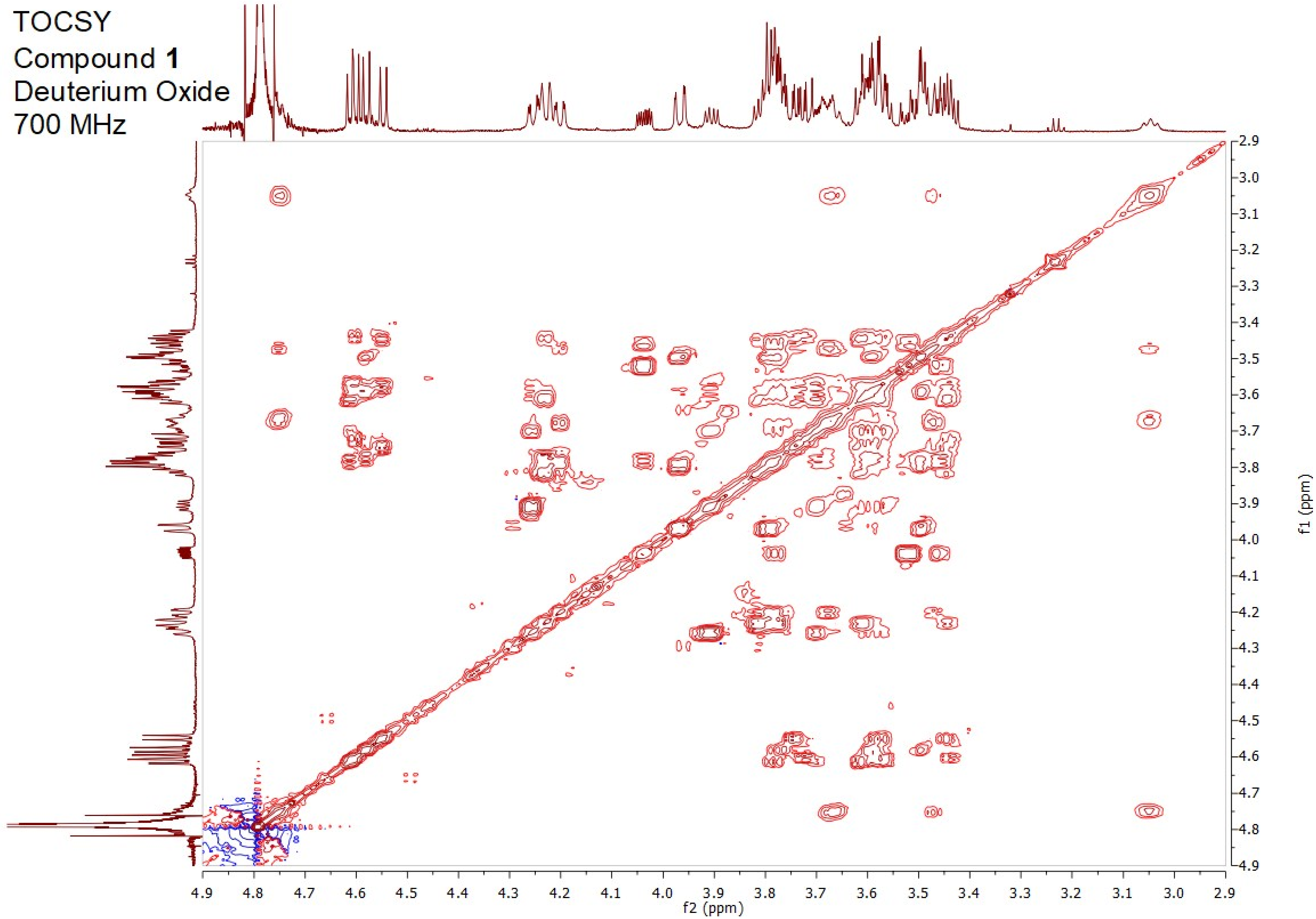
COSY
Compound **1**
Deuterium Oxide
500 MHz

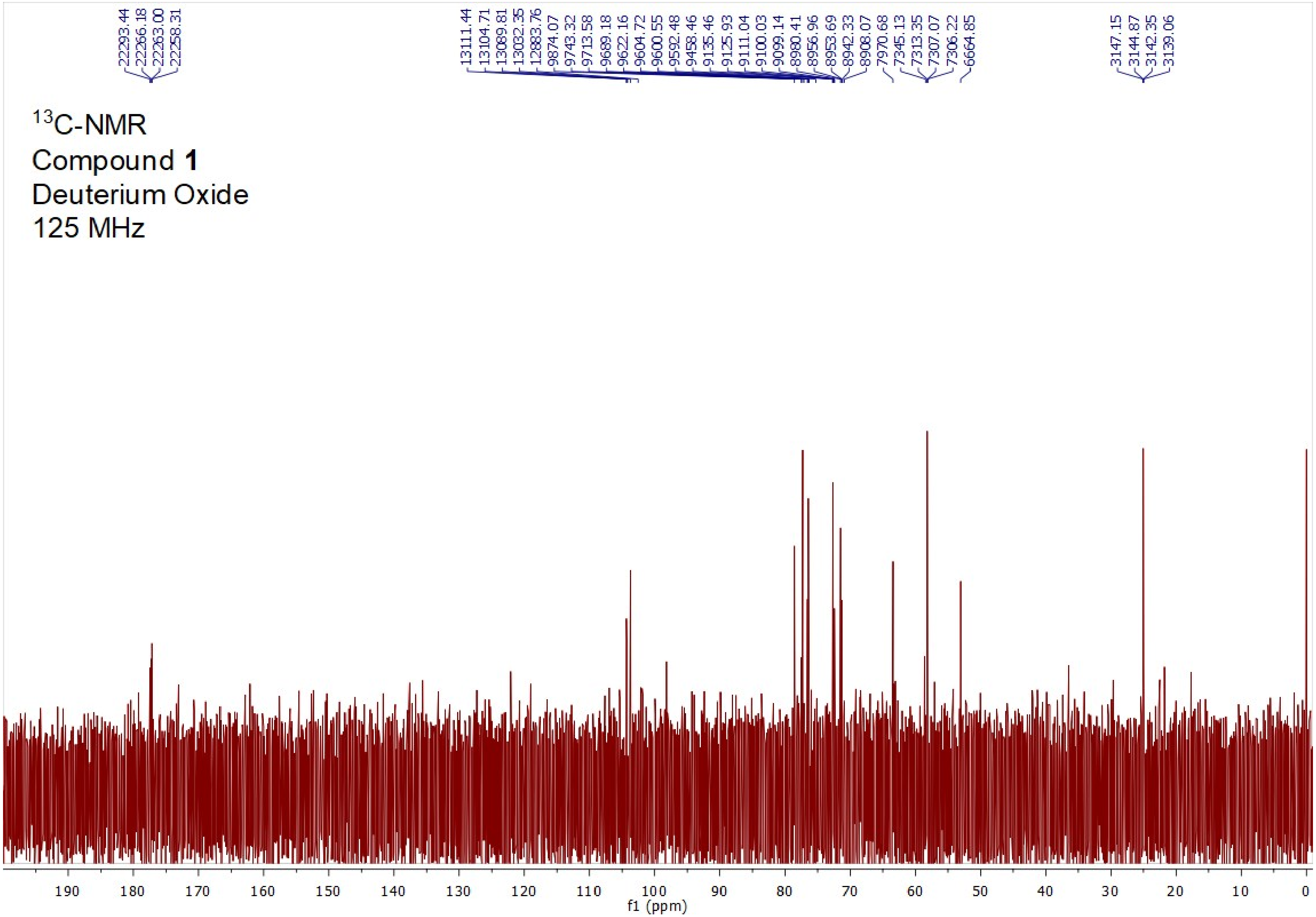


COSY
Compound **1**
Deuterium Oxide
700 MHz

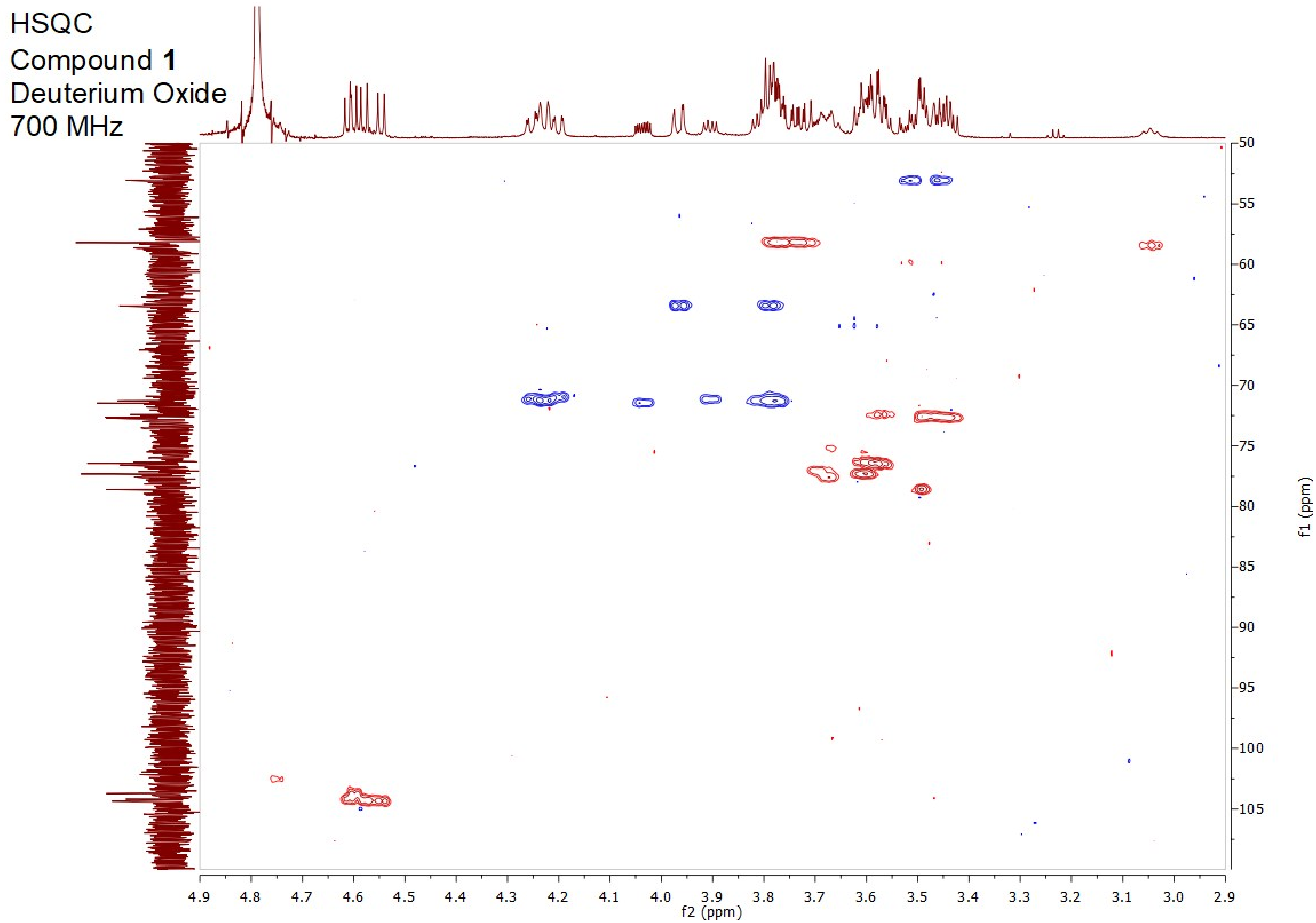


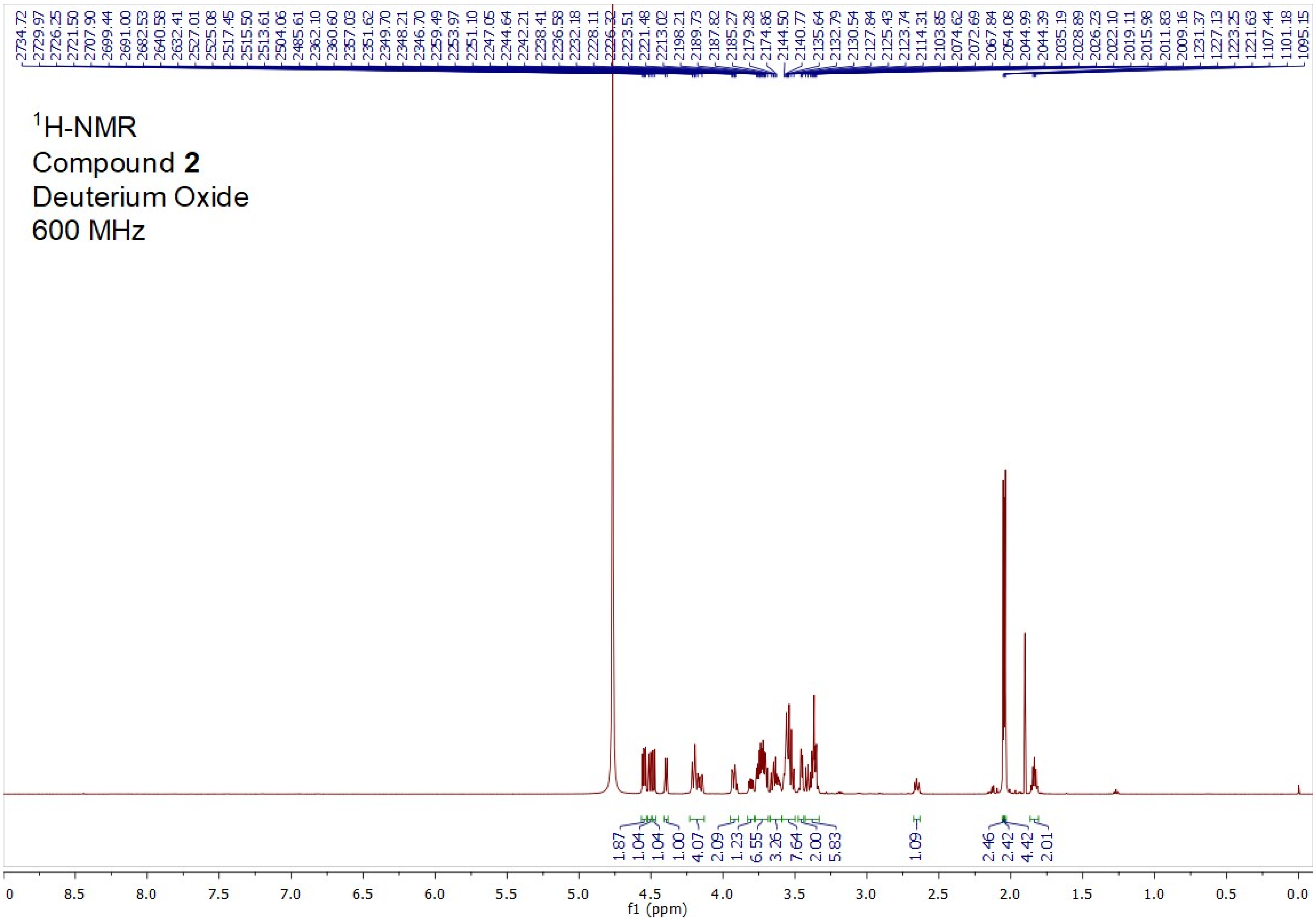
TOCSY
Compound **1**
Deuterium Oxide
700 MHz



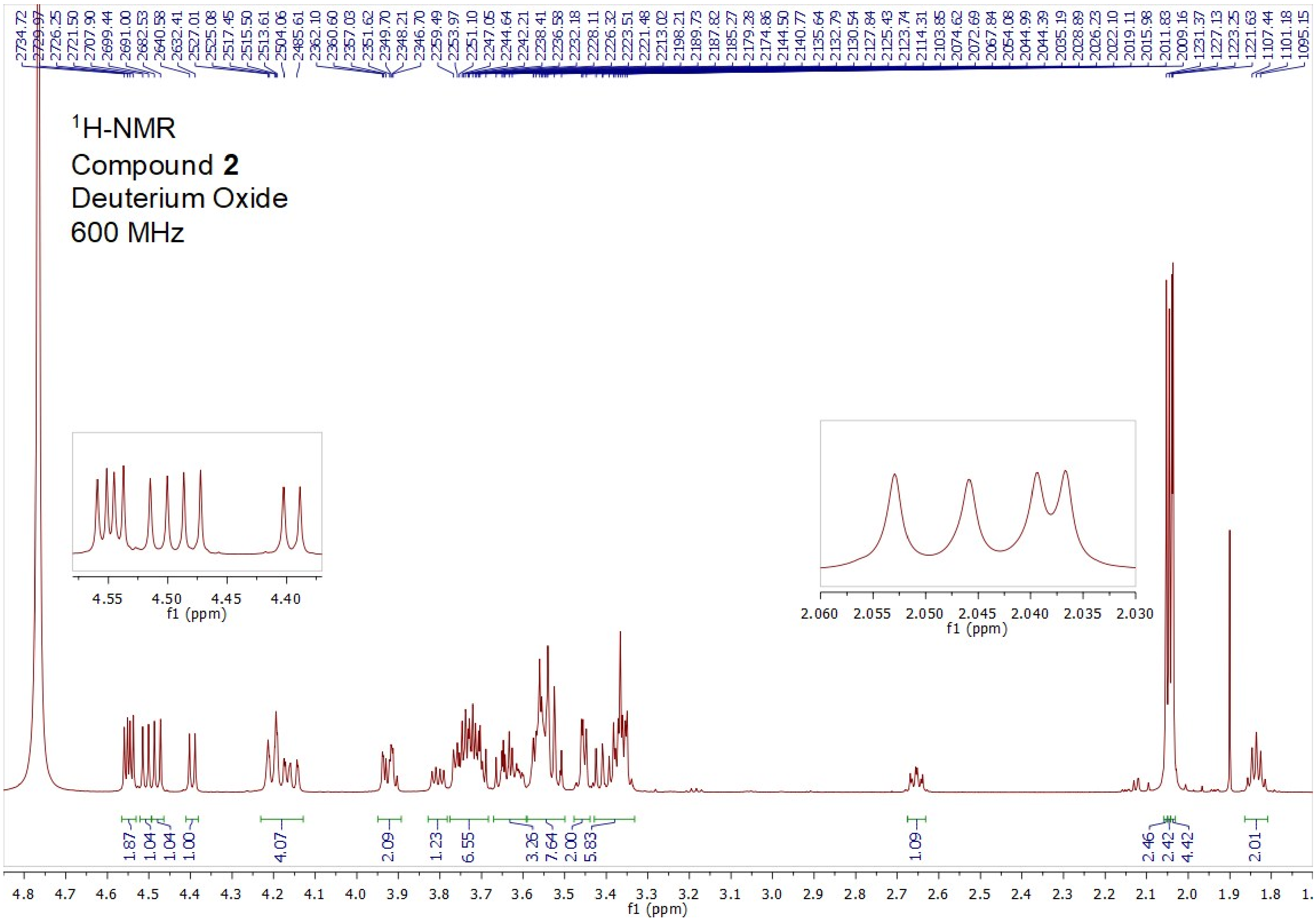


^{13}C-NMR
Compound **1**
Deuterium Oxide
125 MHz
22293.44
22266.18
22263.00
22258.31
13111.44
13104.71
13089.81
13032.35
12883.76
9874.07
9743.32
9713.58
9689.18
9622.16
9604.72
9600.55
9592.48
9458.46
9135.46
9125.93
9111.04
9100.03
9099.14
8980.41
8956.96
8953.69
8942.33
8908.07
7970.68
7345.13
7313.35
7307.07
7306.22
6664.85
3147.15
3144.87
3142.35
3139.06
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

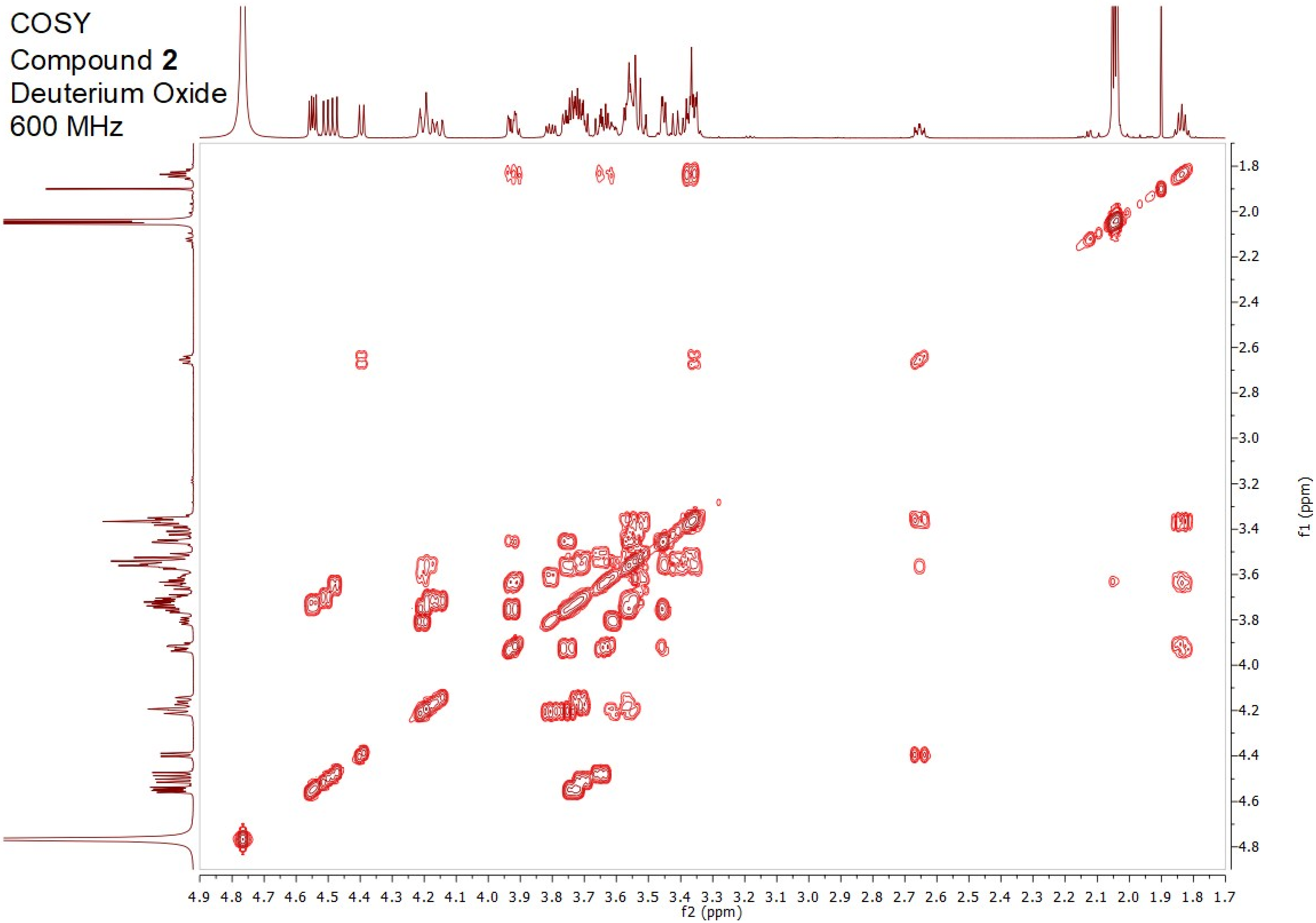

HSQC
Compound **1**
Deuterium Oxide
700 MHz
f2 (ppm)
f1 (ppm)

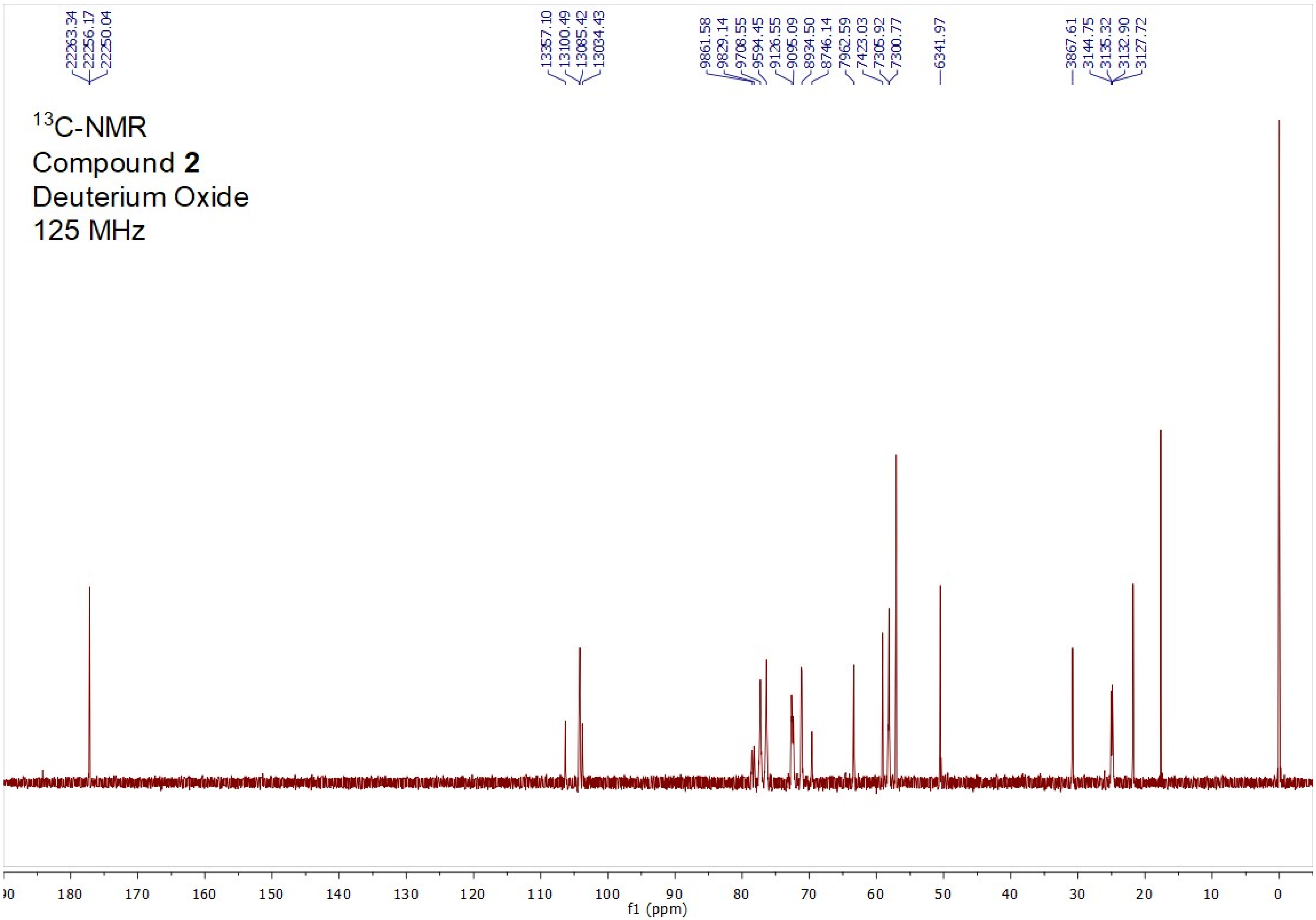


^{1}H-NMR
Compound **2**
Deuterium Oxide
600 MHz
f1 (ppm)



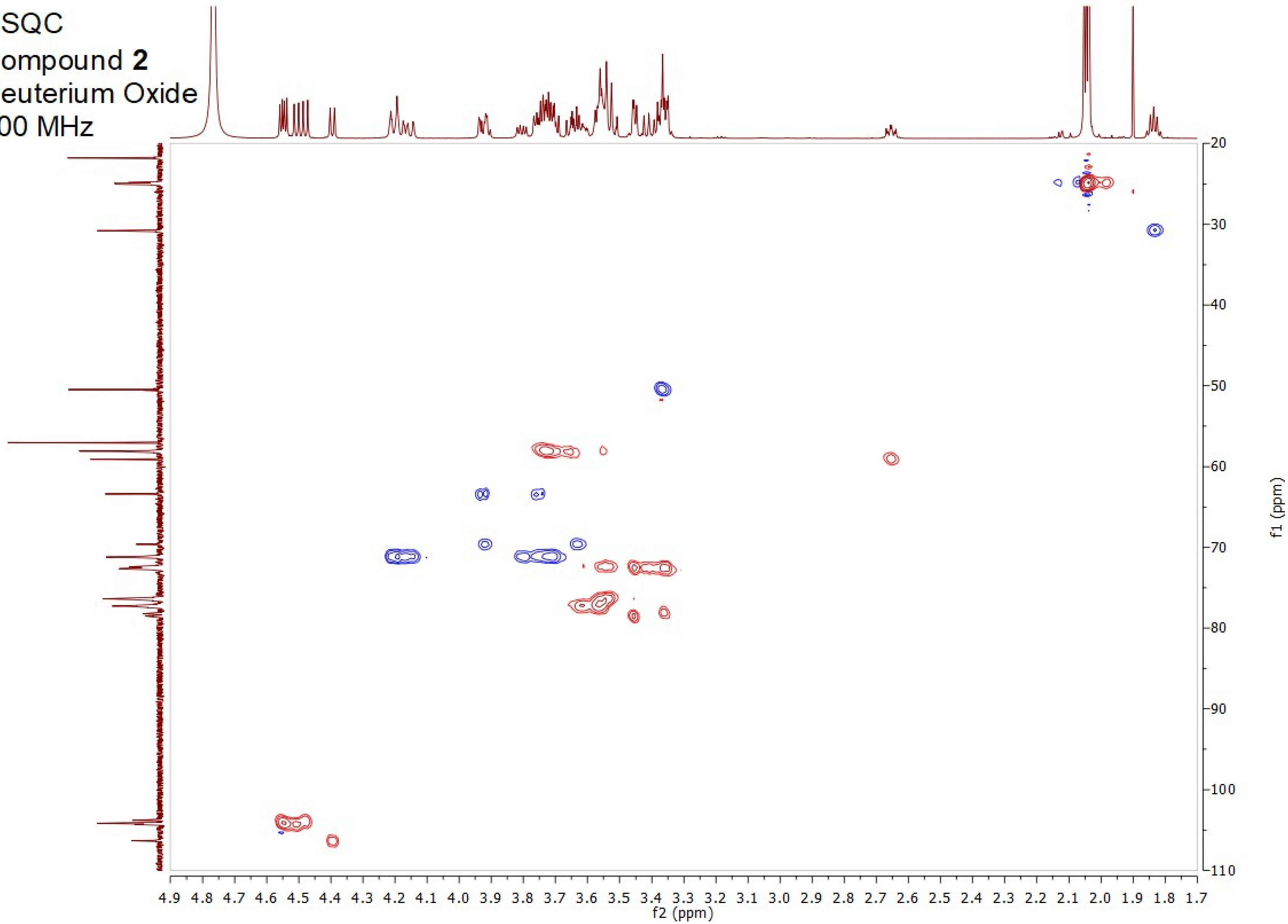
^{1}H-NMR
Compound **2**
Deuterium Oxide
600 MHz
f1 (ppm)

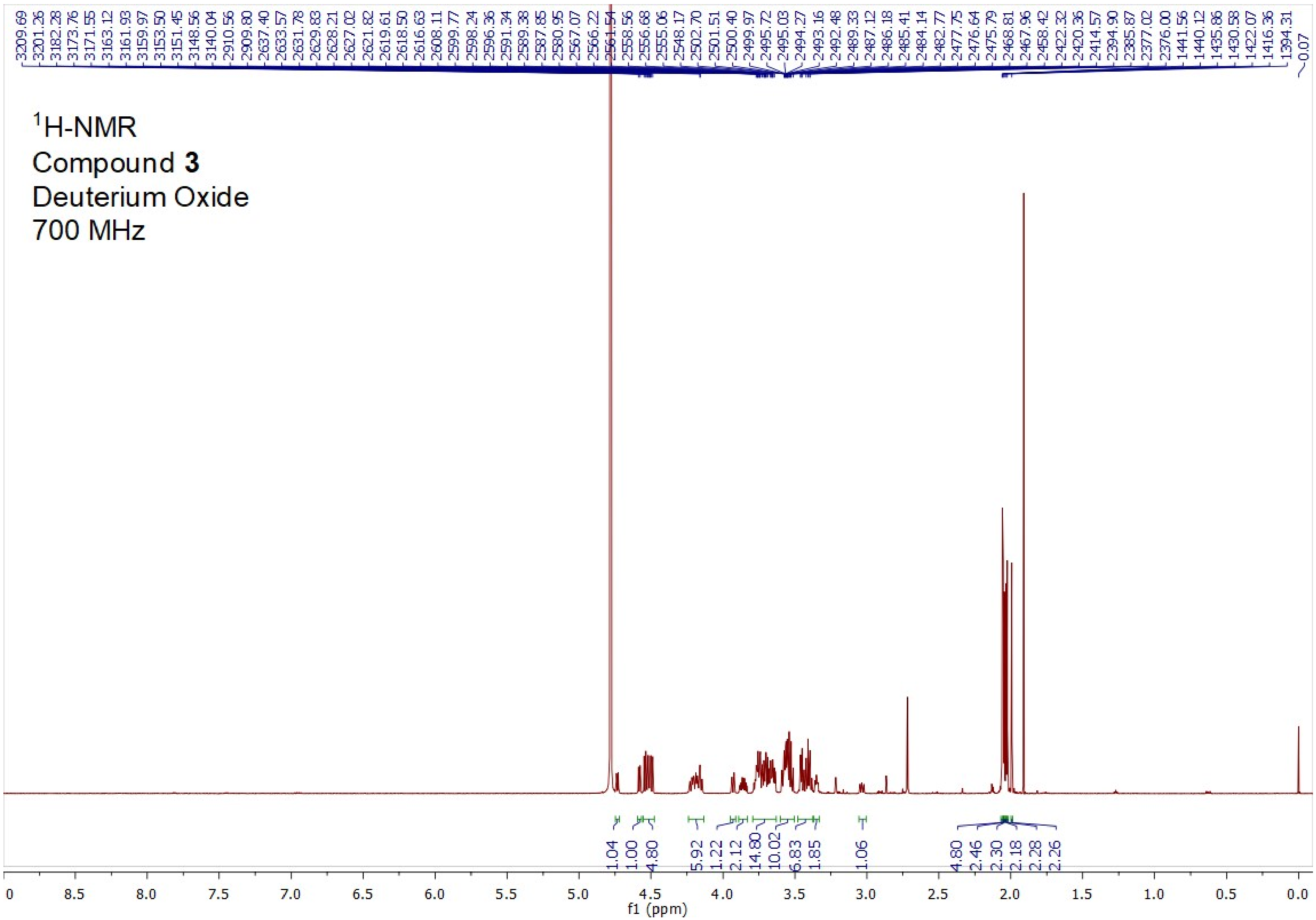

COSY
Compound **2**
Deuterium Oxide
600 MHz
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7
f2 (ppm)
1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8
f1 (ppm)



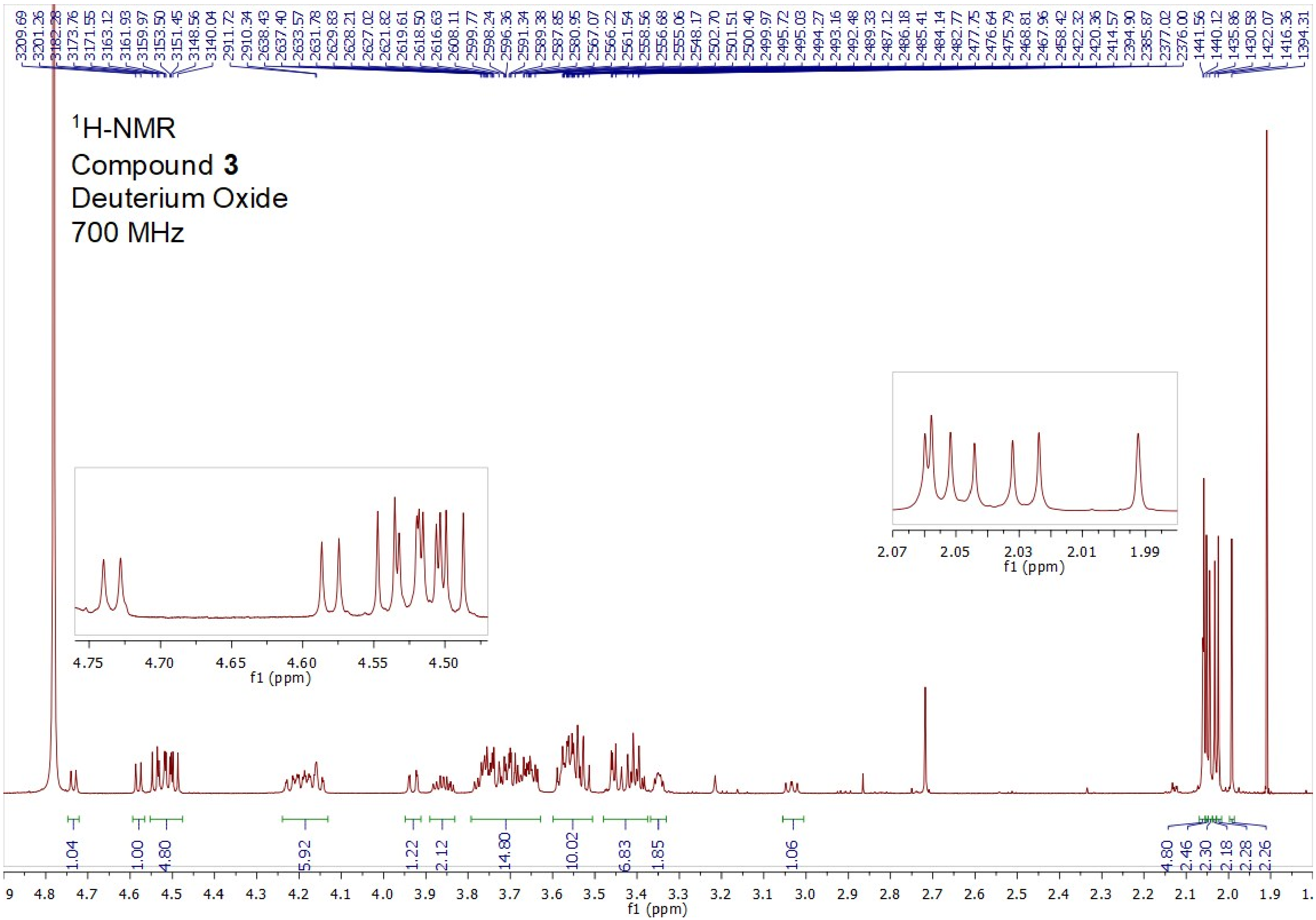
22263.34
22256.17
22250.04
13357.10
13100.49
13085.42
13034.43
9861.58
9829.14
9708.55
9594.45
9126.55
9095.09
8934.50
8746.14
7962.59
7423.03
7305.92
7300.77
6341.97
3867.61
3144.75
3135.32
3132.90
3127.72
^{13}C-NMR
Compound **2**
Deuterium Oxide
125 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

HSQC
Compound **2**
Deuterium Oxide
600 MHz

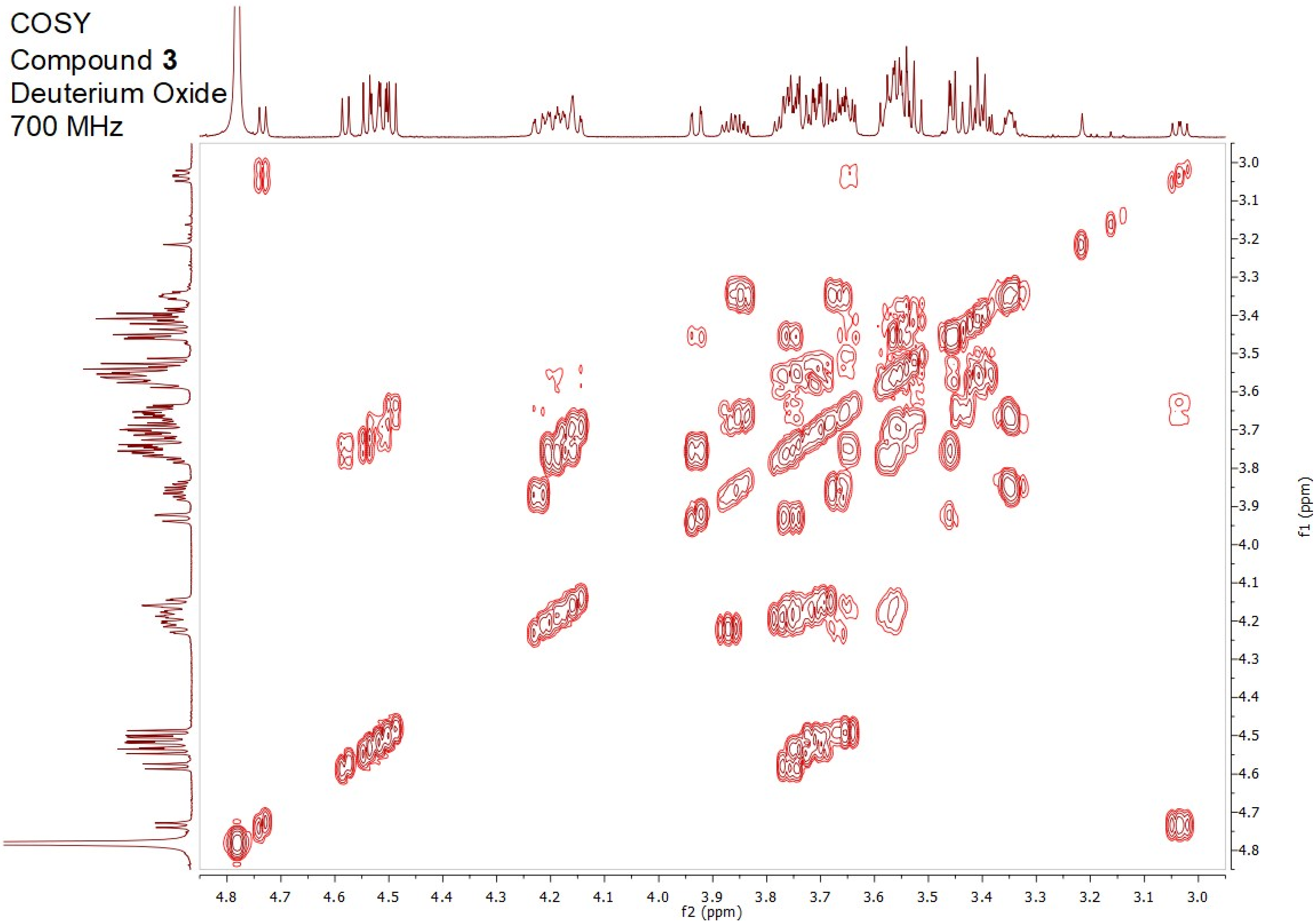




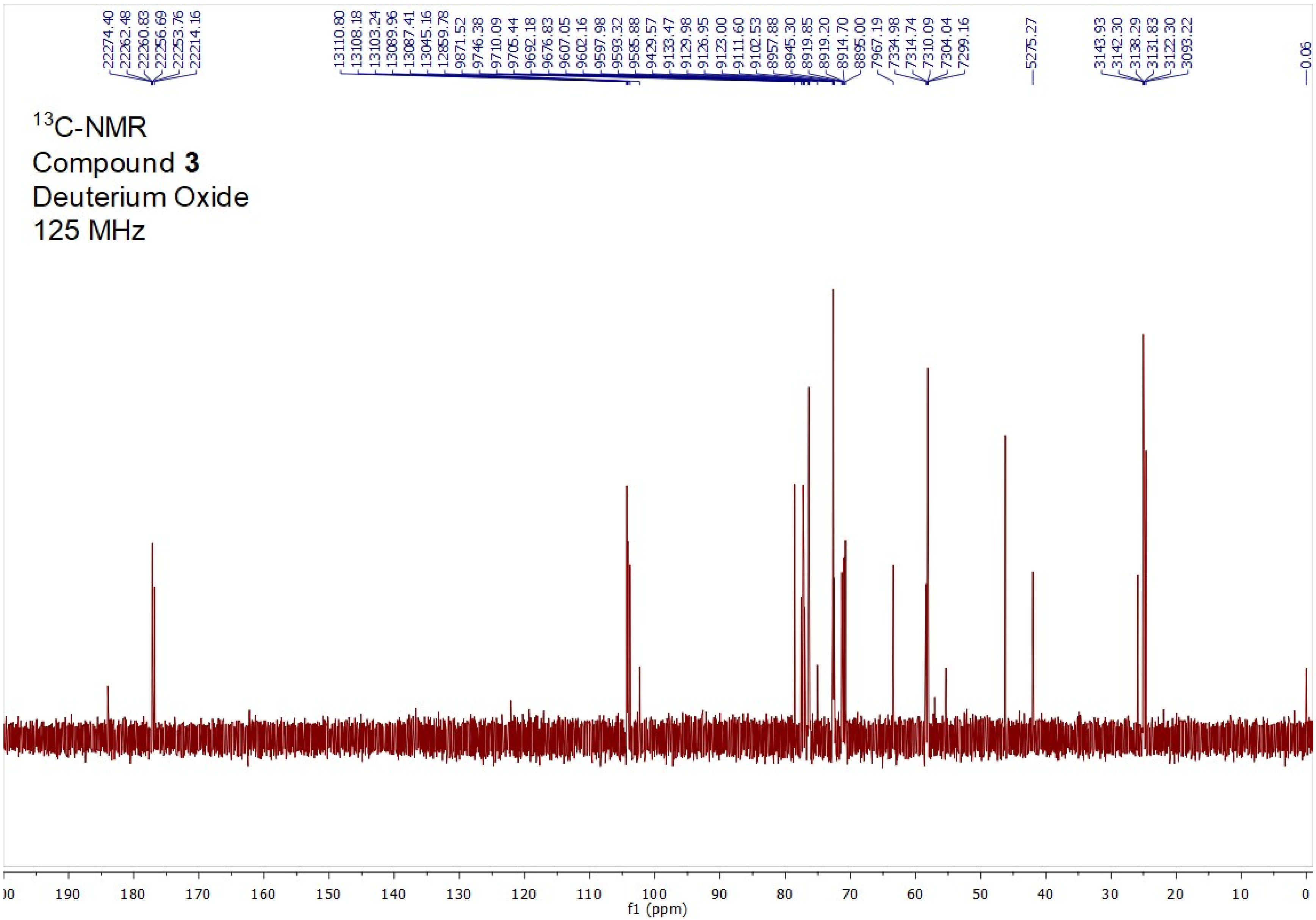
^{1}H-NMR
Compound **3**
Deuterium Oxide
700 MHz
f1 (ppm)



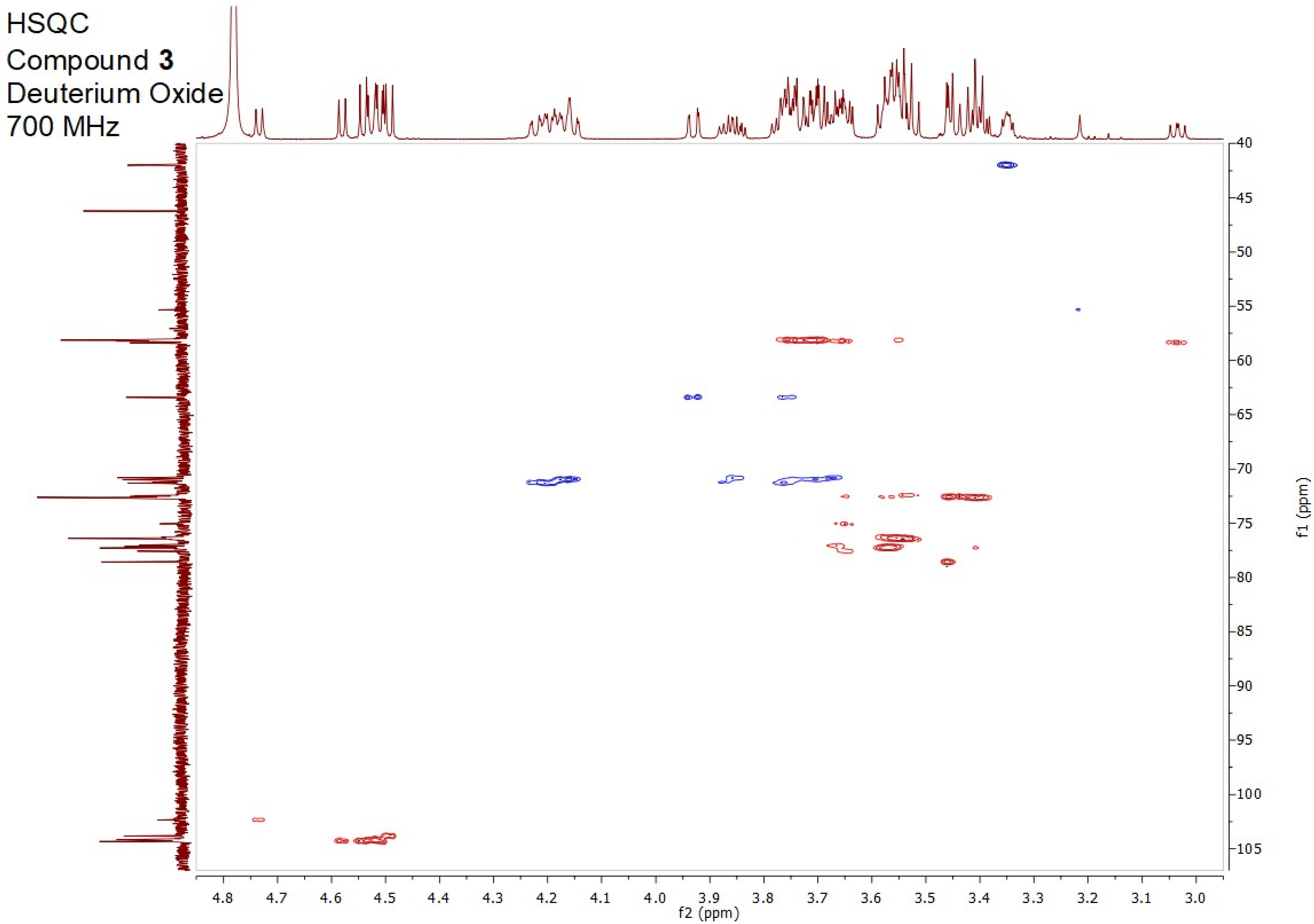
1H-NMR
Compound 3
Deuterium Oxide
700 MHz
f1 (ppm)



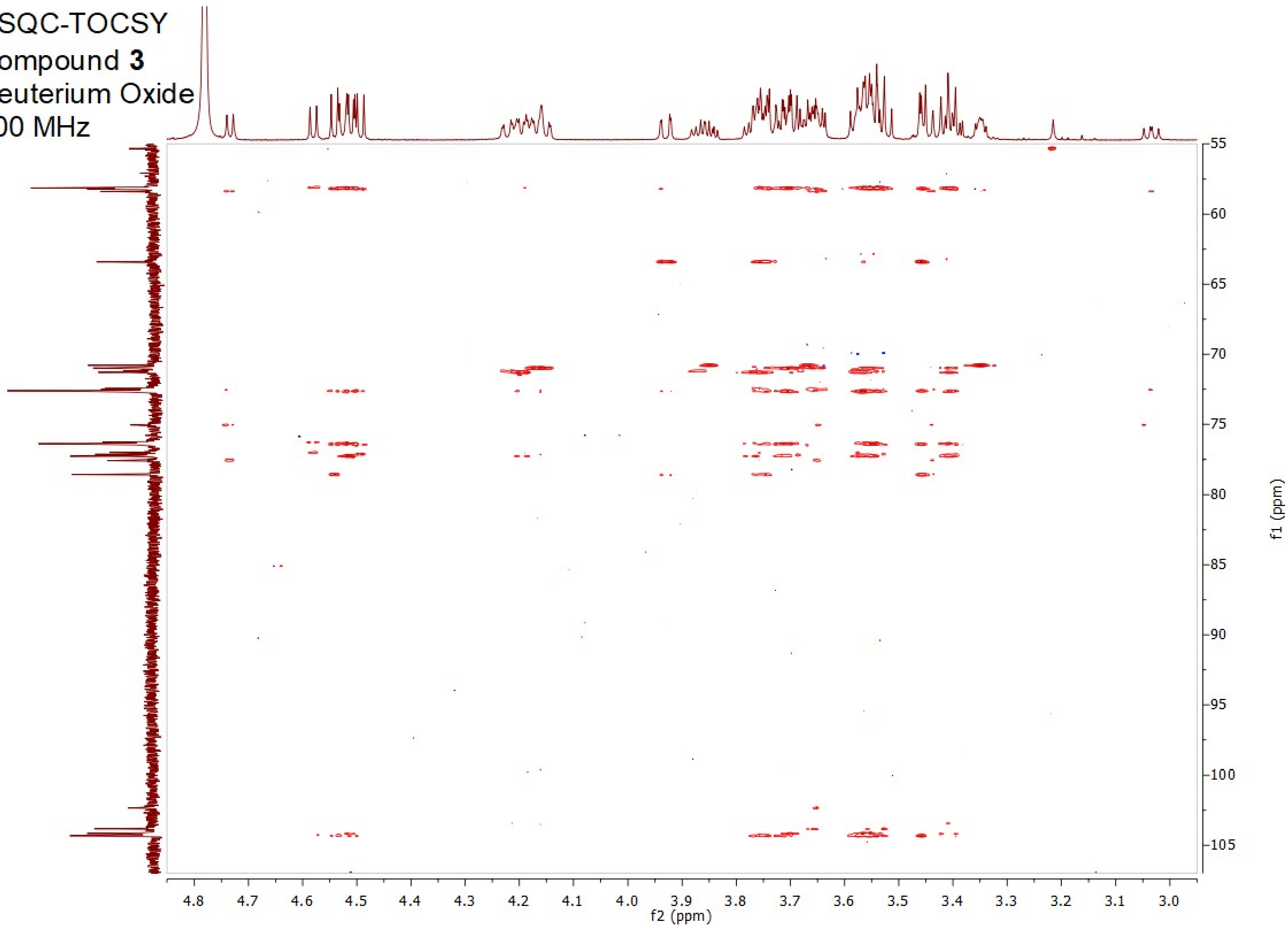
COSY
Compound **3**
Deuterium Oxide
700 MHz
f2 (ppm)
f1 (ppm)



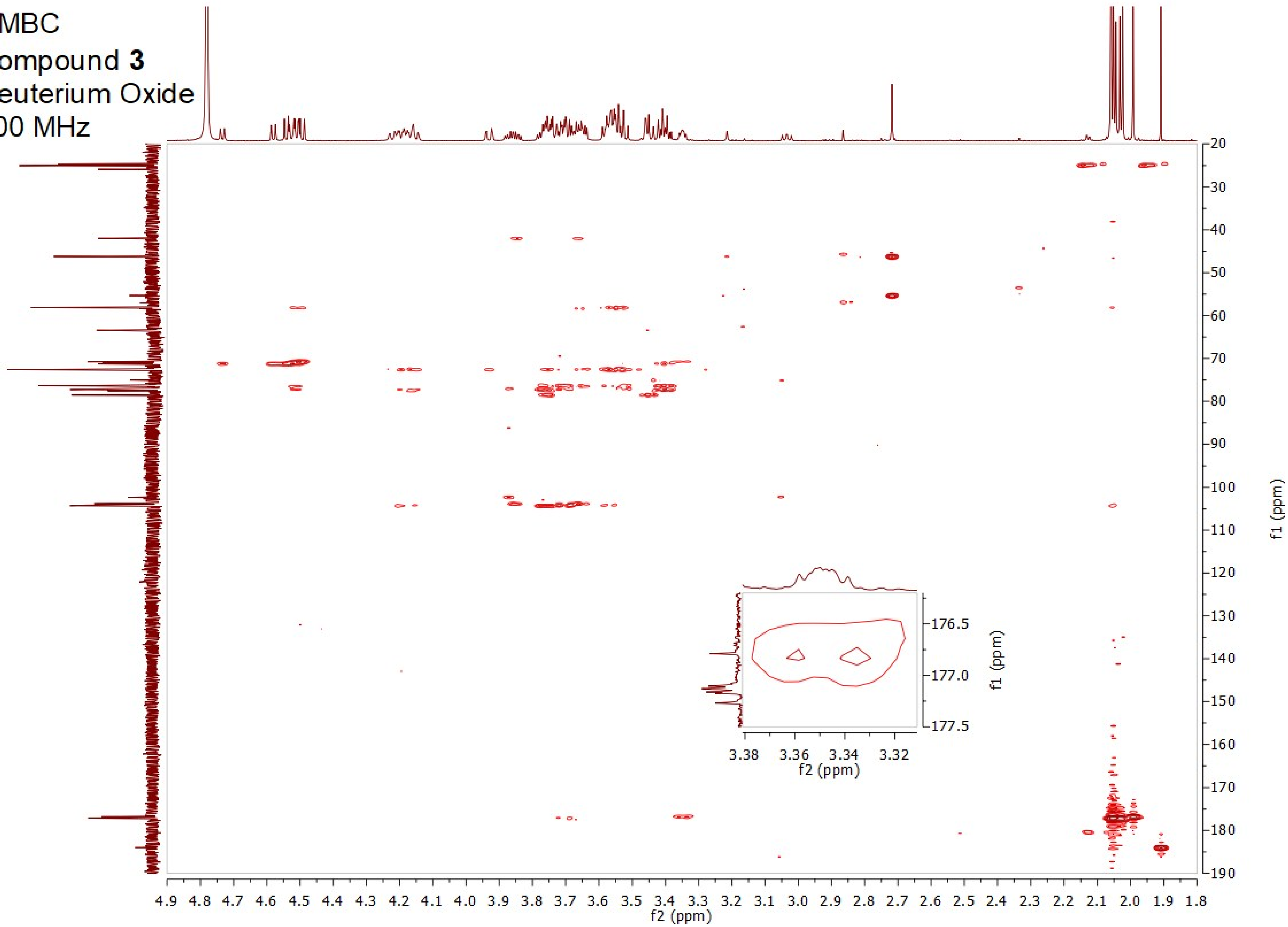
13C-NMR
Compound 3
Deuterium Oxide
125 MHz
f1 (ppm)

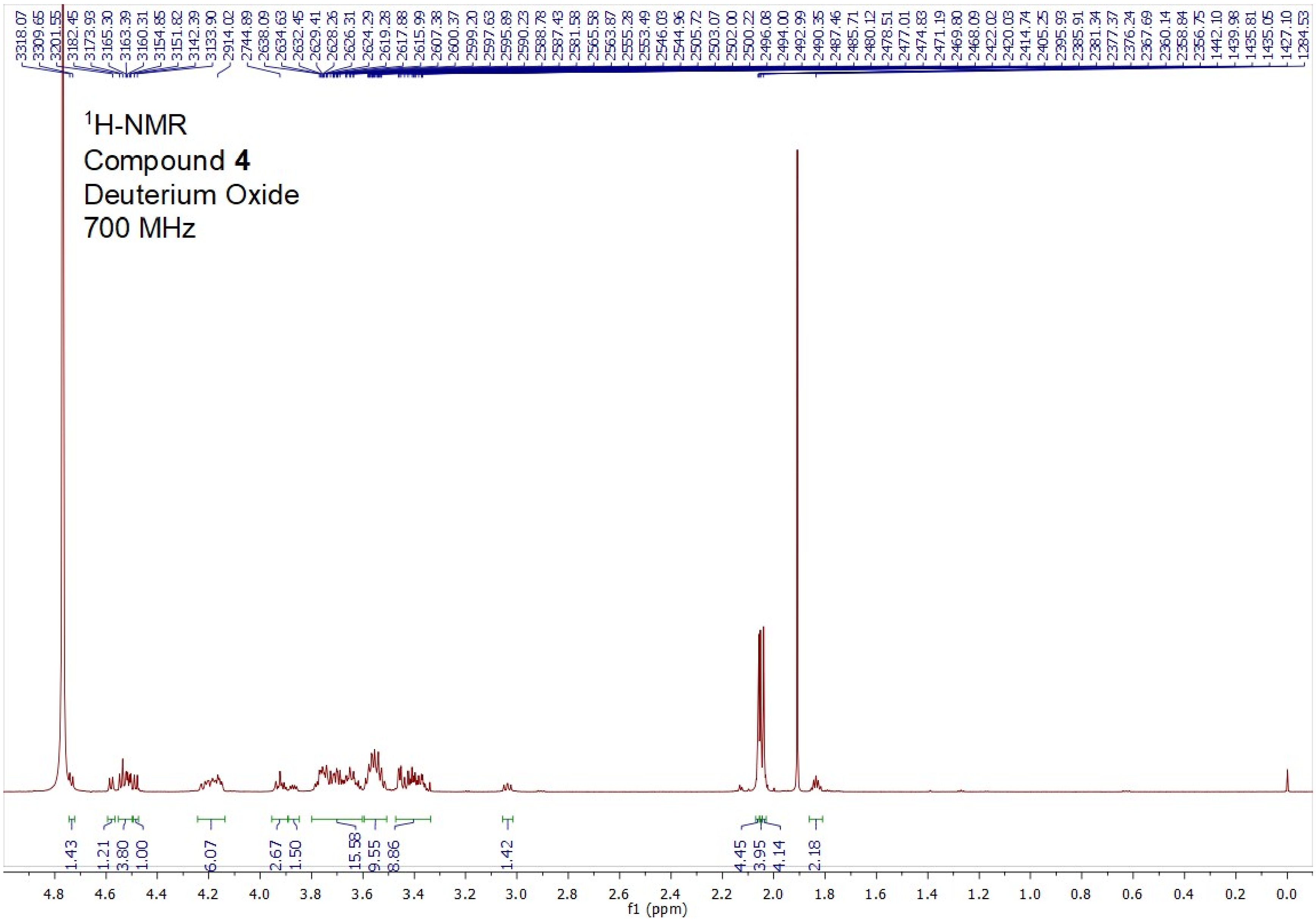

HSQC
Compound 3
Deuterium Oxide
700 MHz
f2 (ppm)
f1 (ppm)

HSQC-TOCSY
Compound **3**
Deuterium Oxide
700 MHz

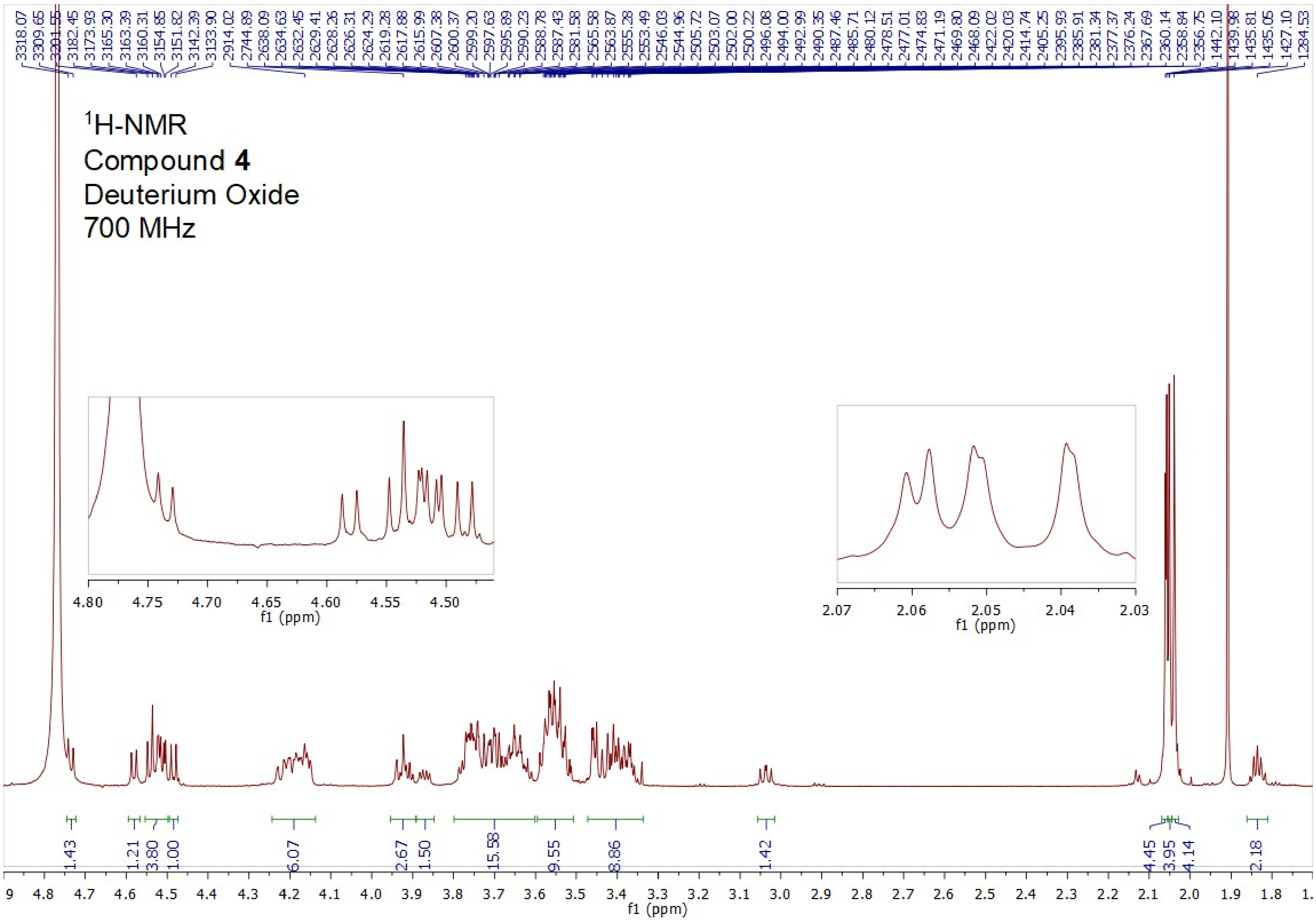


HMBC
Compound **3**
Deuterium Oxide
700 MHz

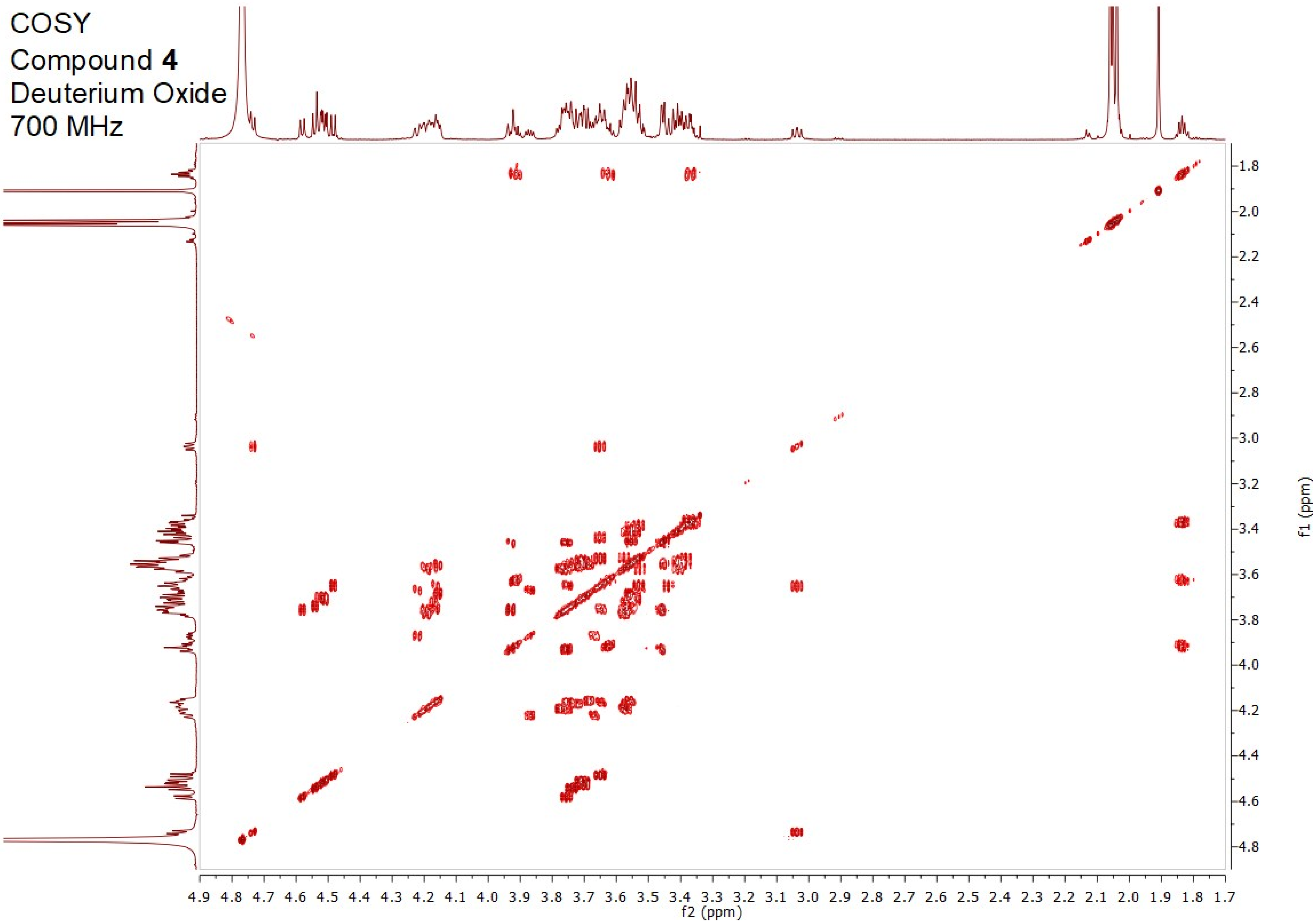


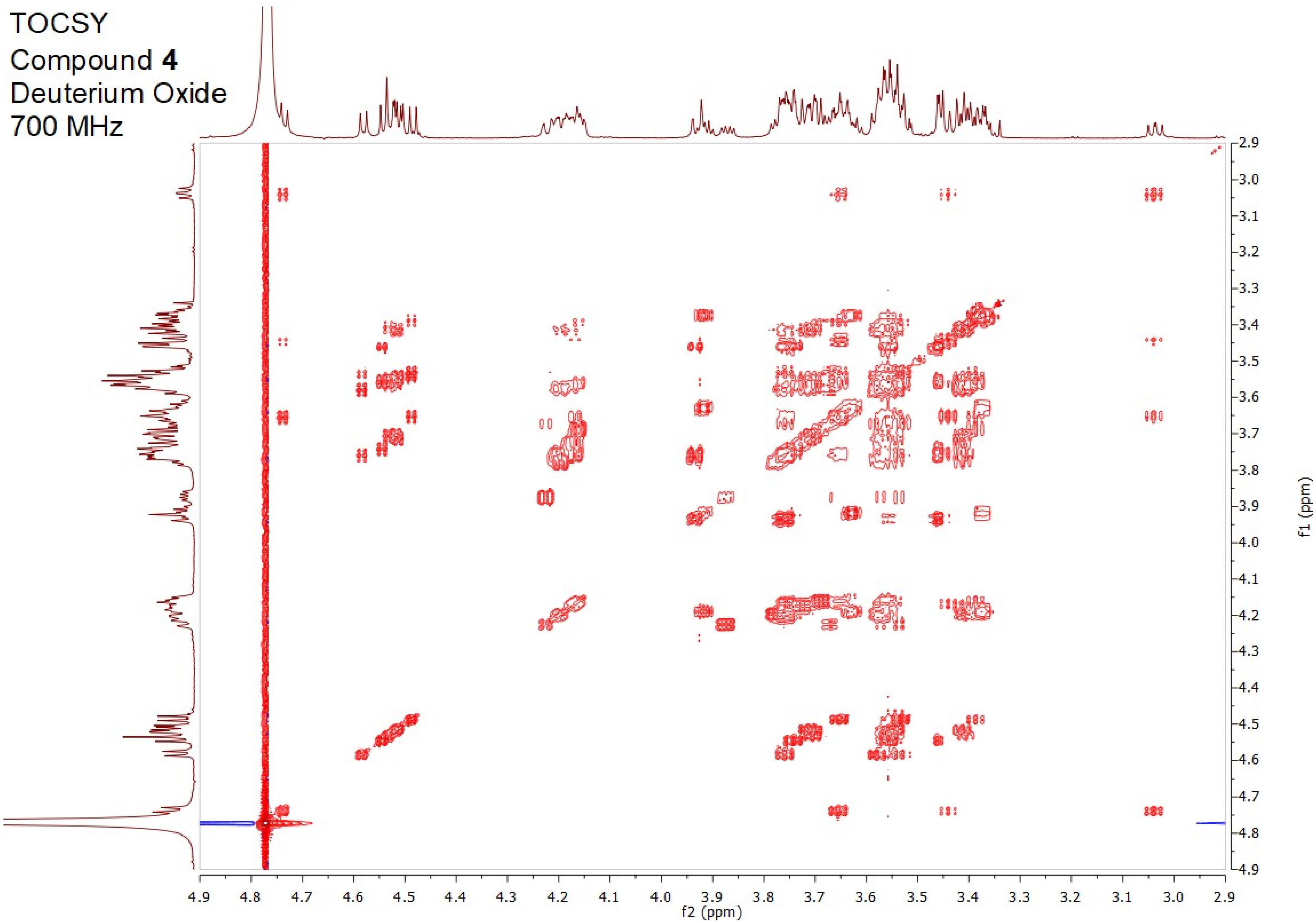


1H-NMR
Compound 4
Deuterium Oxide
700 MHz
f1 (ppm)

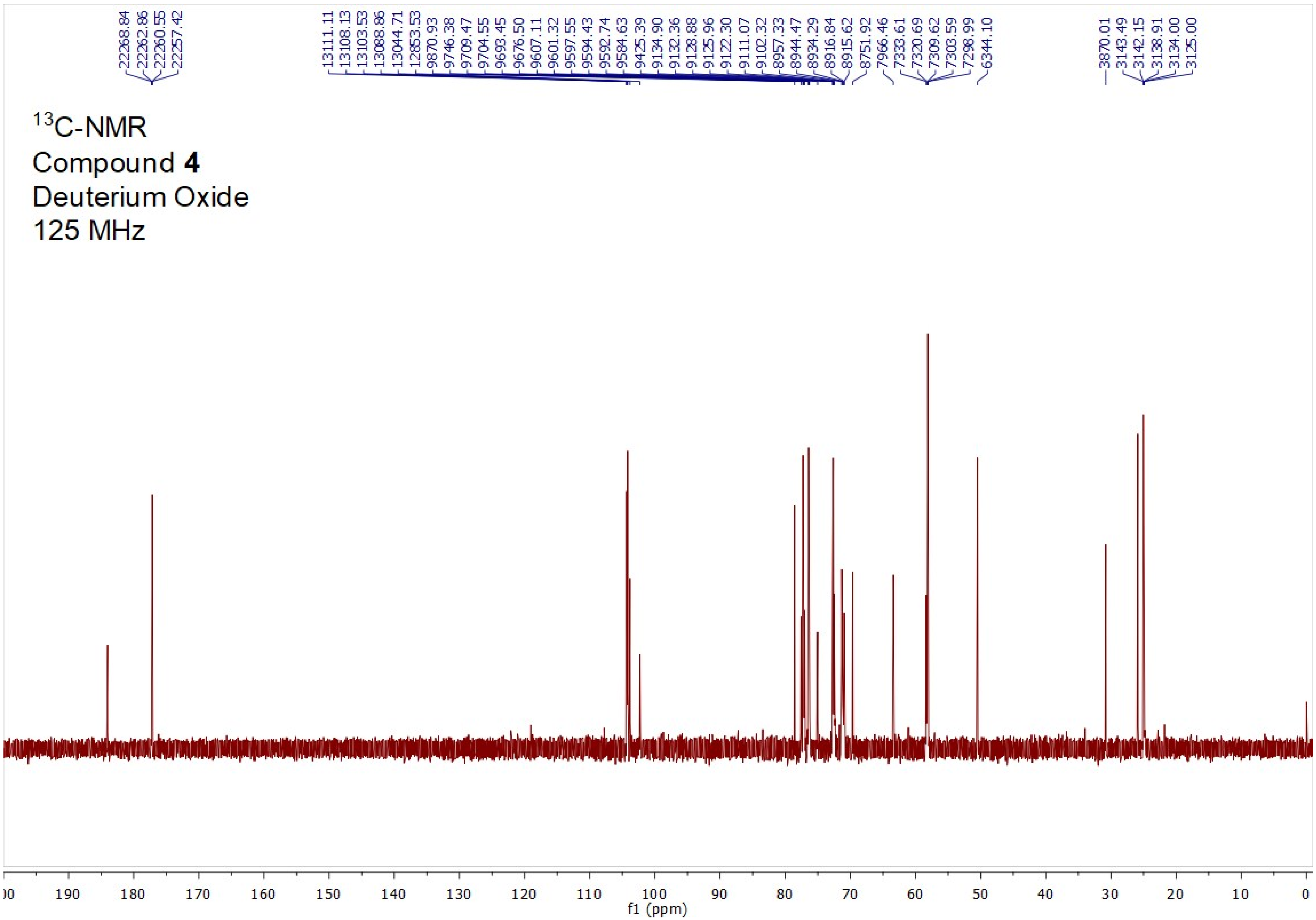


1H-NMR
Compound 4
Deuterium Oxide
700 MHz
f1 (ppm)

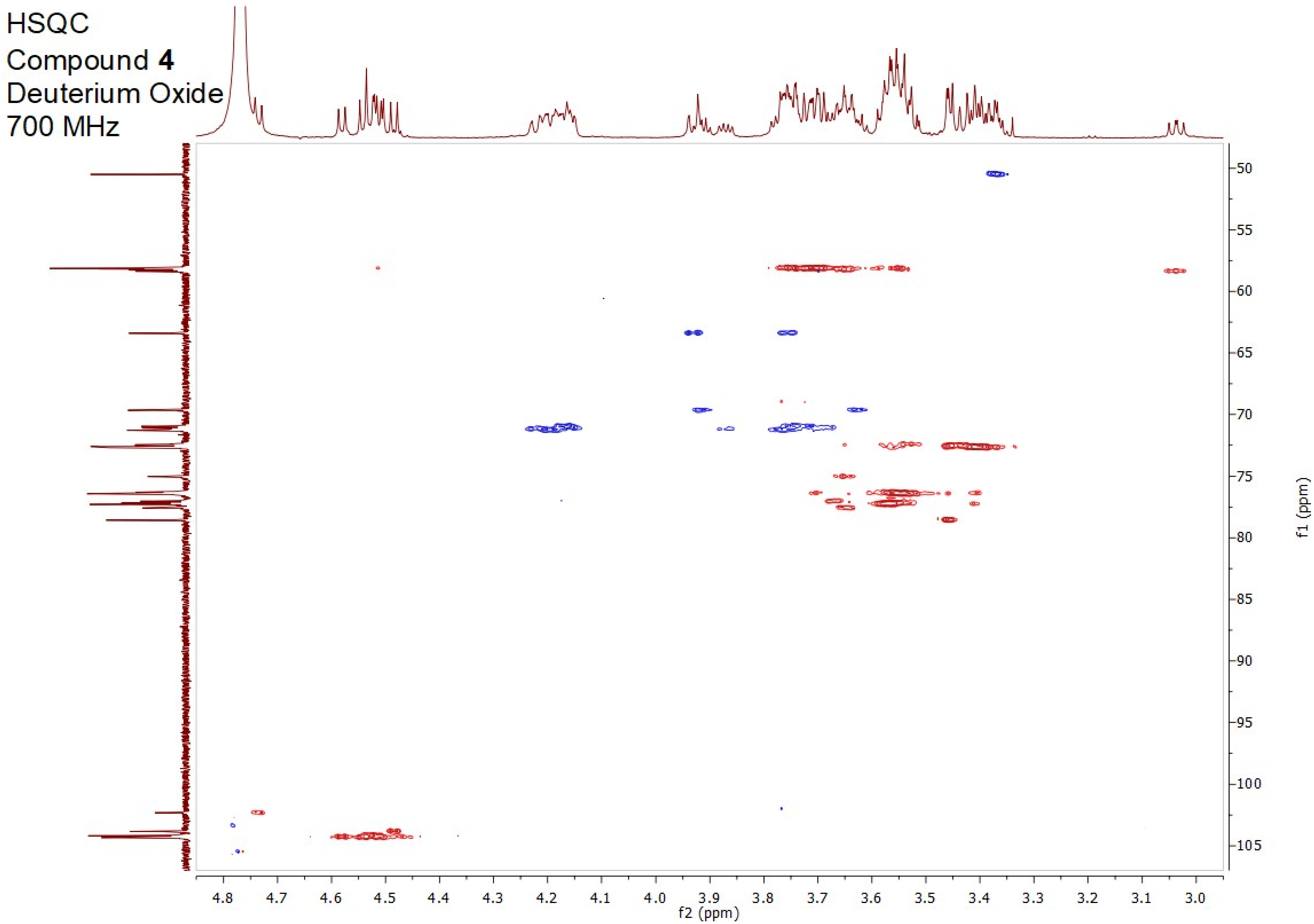

COSY
Compound **4**
Deuterium Oxide
700 MHz
f2 (ppm)
f1 (ppm)



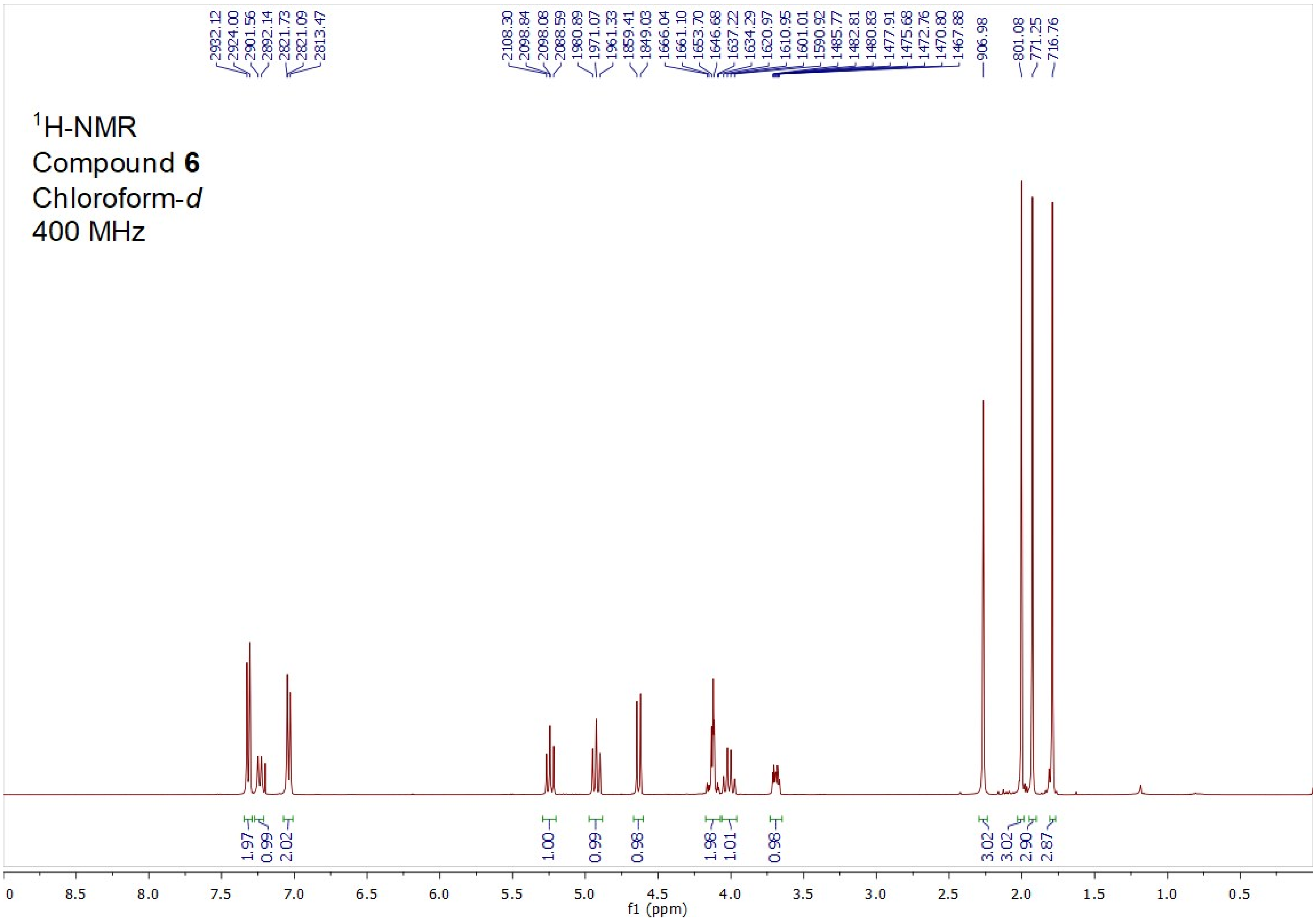
TOCSY
Compound **4**
Deuterium Oxide
700 MHz
f2 (ppm)
f1 (ppm)



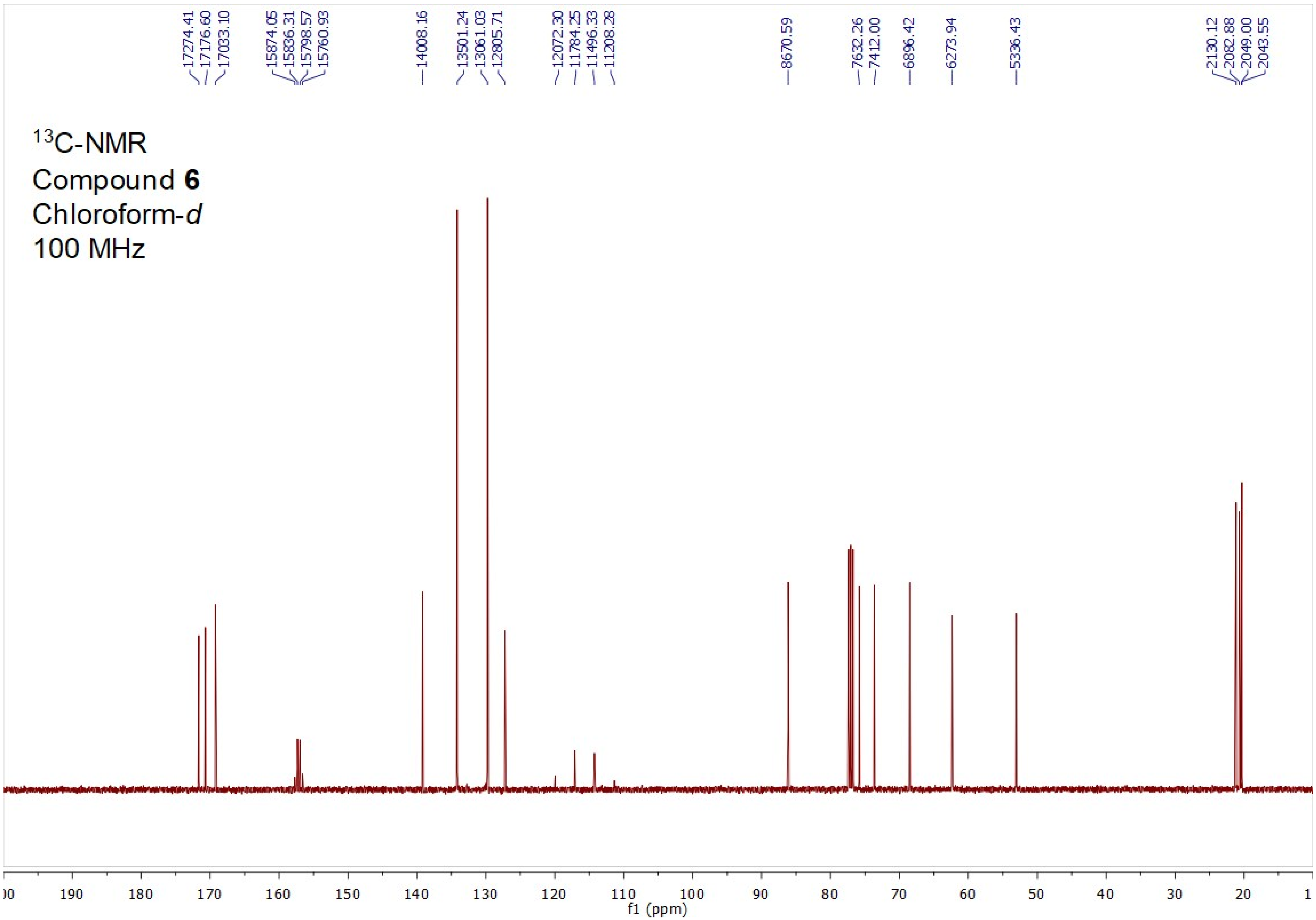
^{13}C-NMR
Compound **4**
Deuterium Oxide
125 MHz
f1 (ppm)

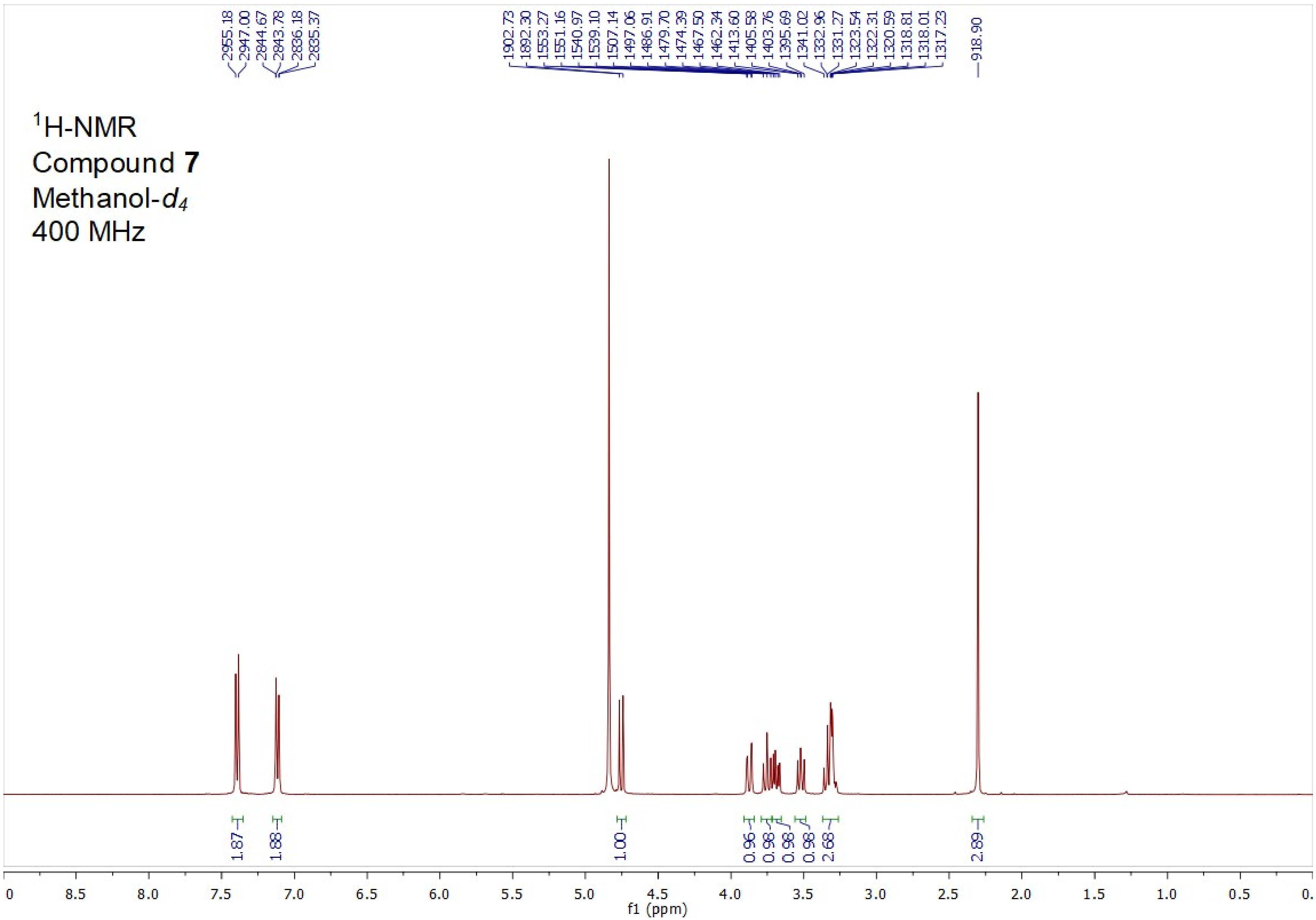


HSQC
Compound **4**
Deuterium Oxide
700 MHz
f2 (ppm)
f1 (ppm)

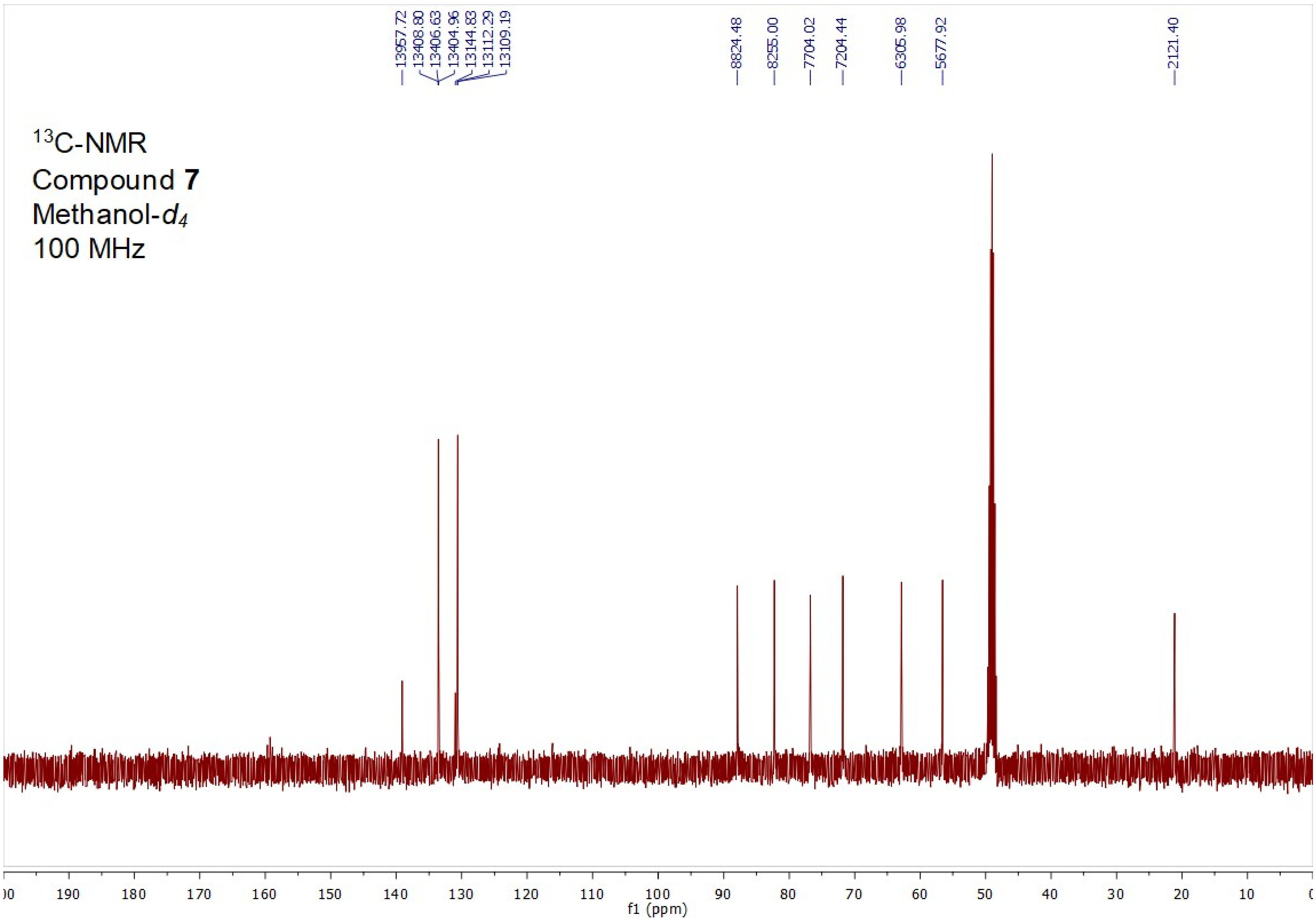


1H-NMR
Compound 6
Chloroform-d
400 MHz
2932.12
2924.00
2901.56
2892.14
2821.73
2821.09
2813.47
2108.30
2098.84
2098.08
2088.59
1980.89
1971.07
1961.33
1859.41
1849.03
1666.04
1661.10
1653.70
1646.68
1637.22
1634.29
1620.97
1610.95
1601.01
1590.92
1485.77
1482.81
1480.83
1477.91
1475.68
1472.76
1470.80
1467.88
906.98
801.08
771.25
716.76
1.97
0.99
2.02
1.00
0.99
0.98
1.98
1.01
0.98
3.02
3.02
2.90
2.87
f1 (ppm)

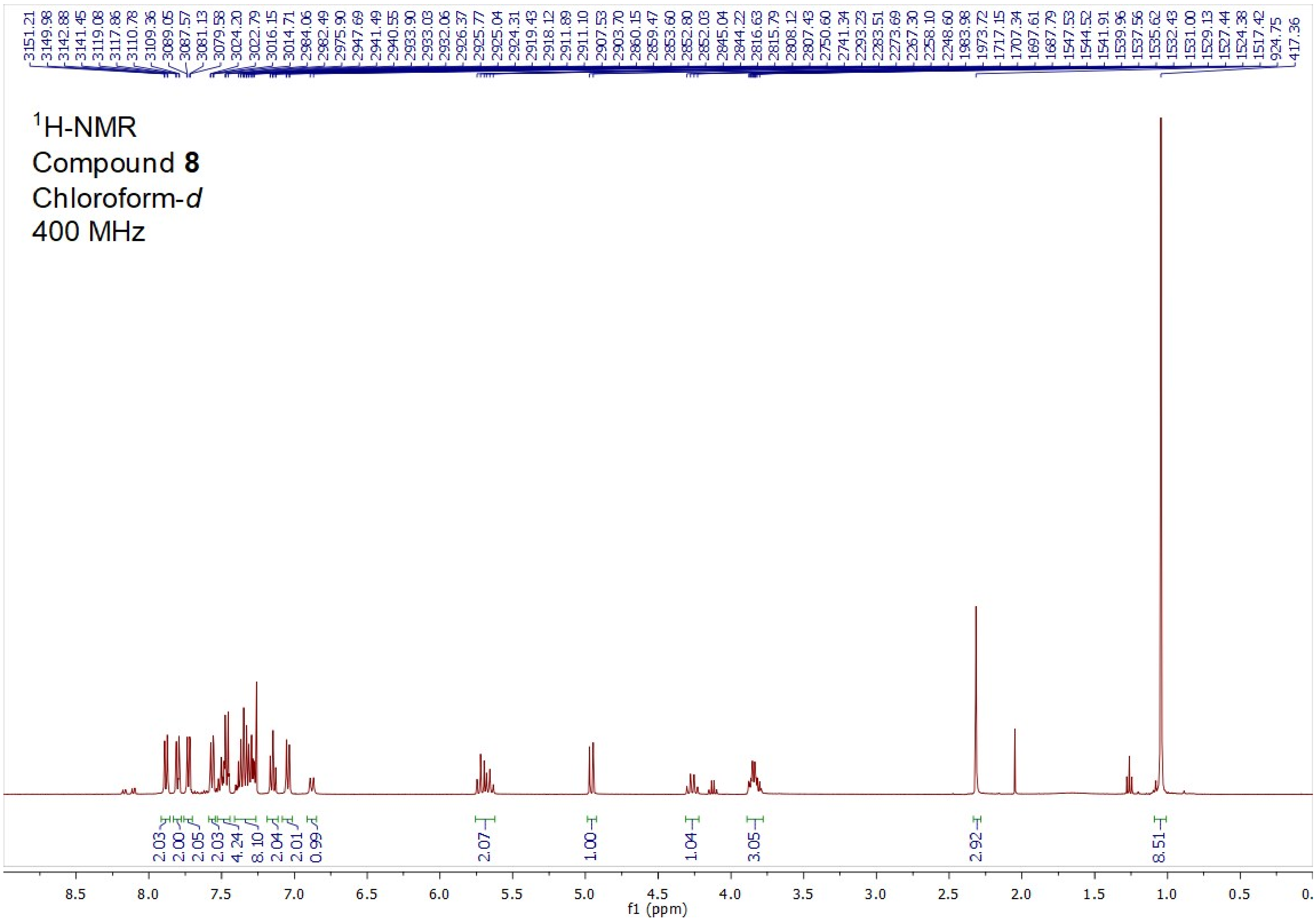

17274.41
17176.60
17033.10
15874.05
15836.31
15798.57
15760.93
14008.16
13501.24
13061.03
12805.71
12072.30
11784.25
11496.33
11208.28
8670.59
7632.26
7412.00
6896.42
6273.94
5336.43
2130.12
2082.88
2049.00
2043.55
^{13}C-NMR
Compound **6**
Chloroform-*d*
100 MHz
f1 (ppm)



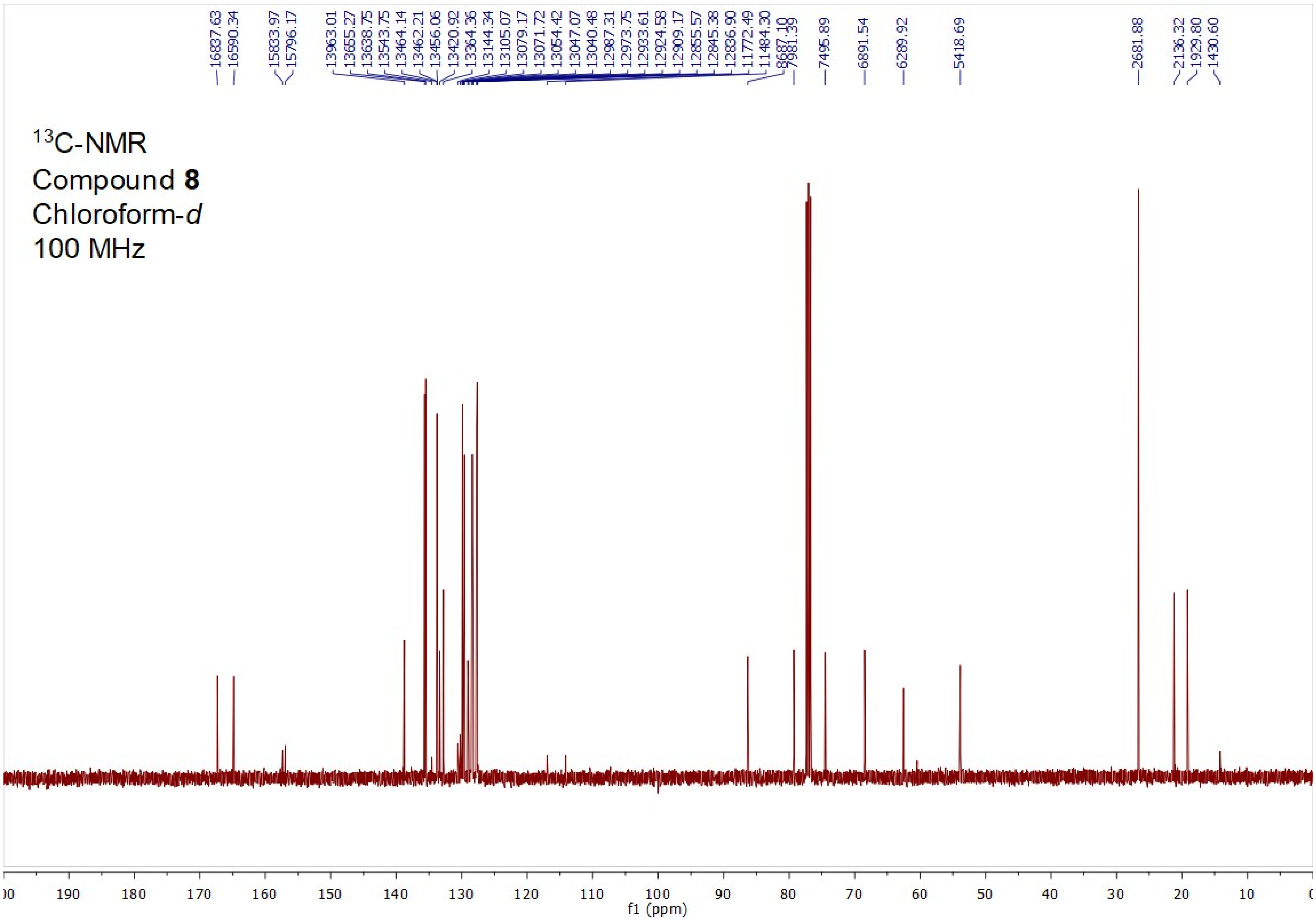
^{1}H-NMR
Compound **7**
Methanol-d_4
400 MHz
f1 (ppm)



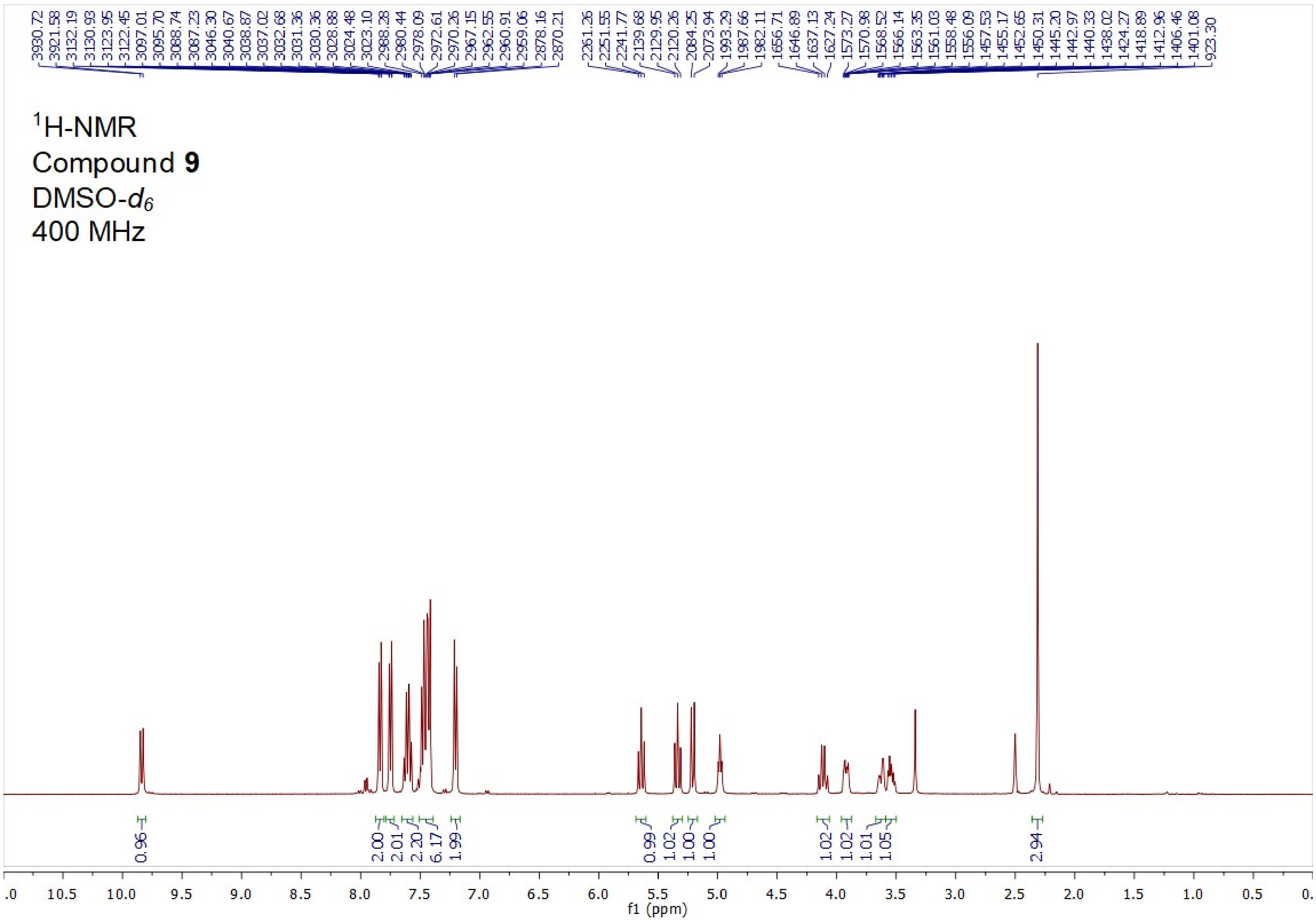
13C-NMR
Compound 7
Methanol-d4
100 MHz
13957.72
13408.80
13406.63
13404.96
13144.83
13112.29
13109.19
8824.48
8255.00
7704.02
7204.44
6305.98
5677.92
2121.40
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



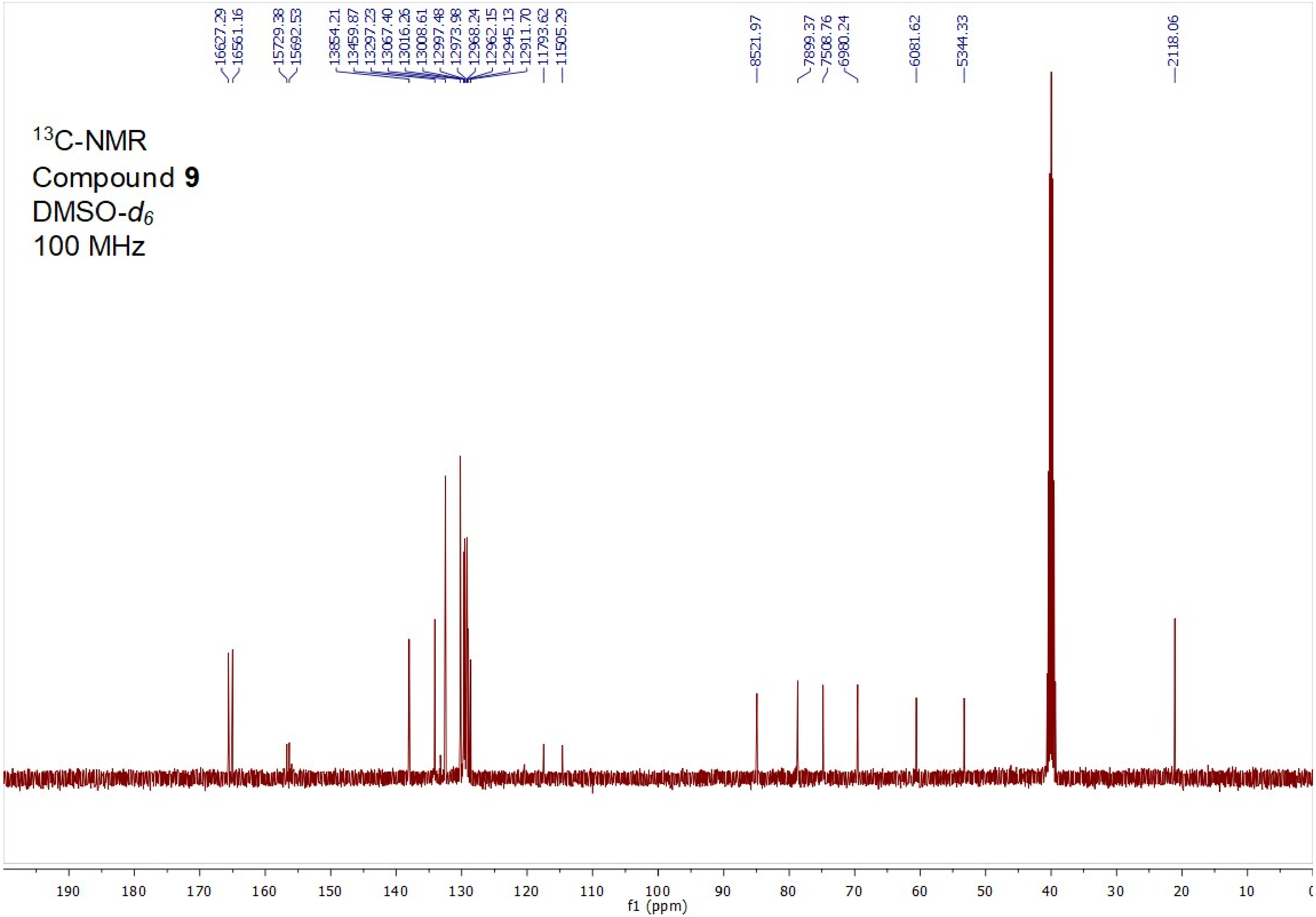
^{1}H-NMR
Compound **8**
Chloroform-*d*
400 MHz
f1 (ppm)



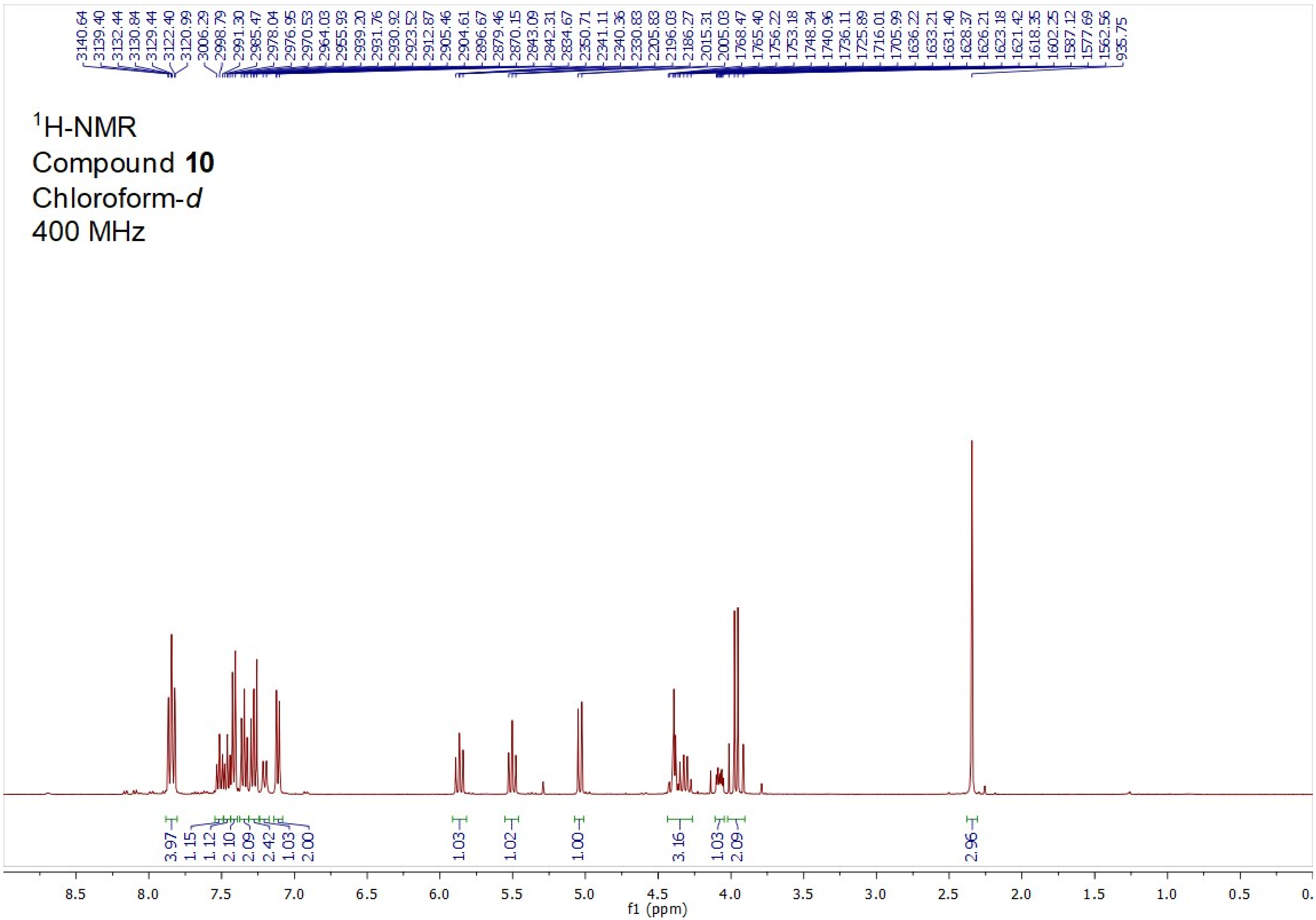
^{13}C-NMR
Compound **8**
Chloroform-*d*
100 MHz
f1 (ppm)



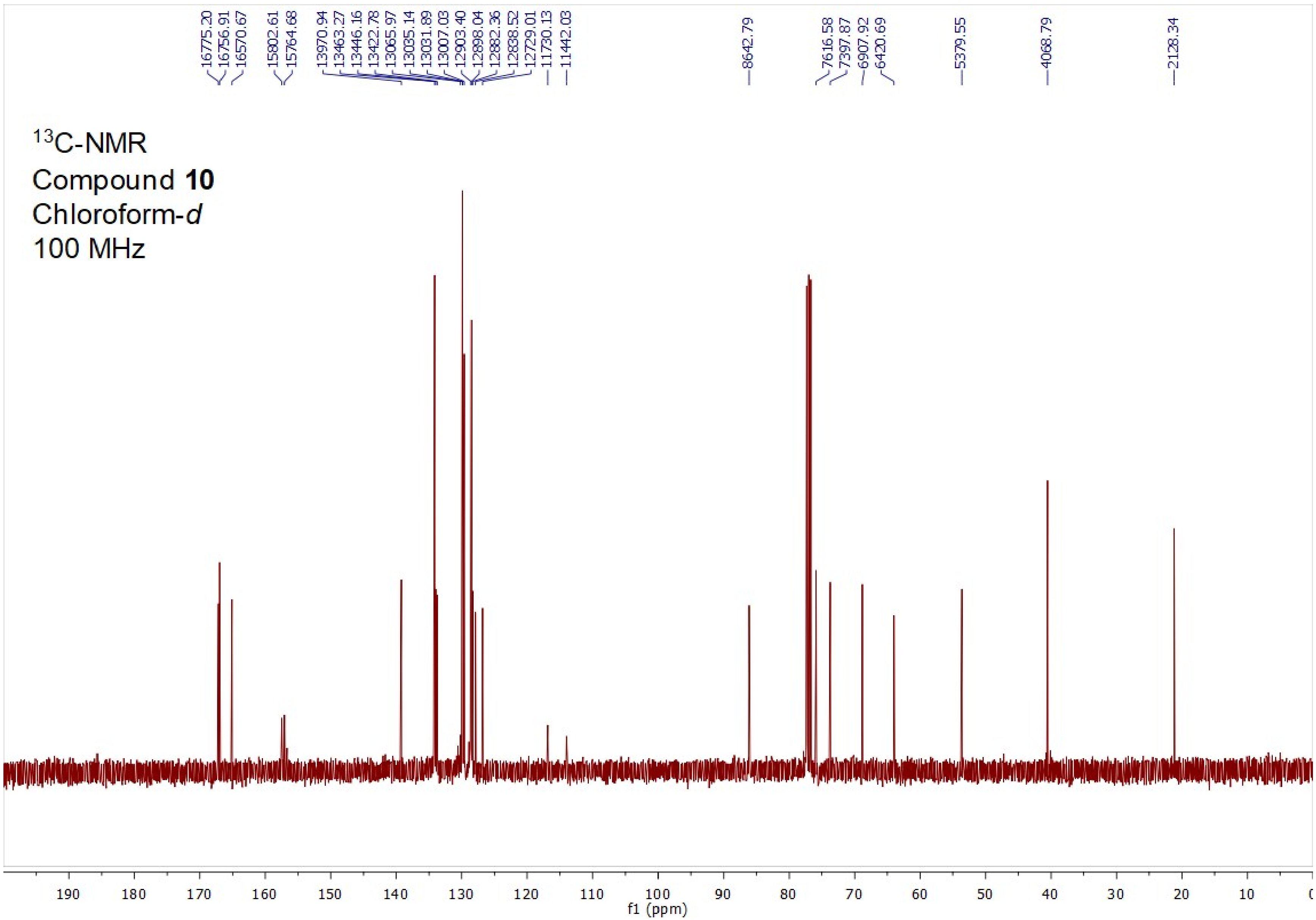
1H-NMR
Compound 9
DMSO-d6
400 MHz
f1 (ppm)



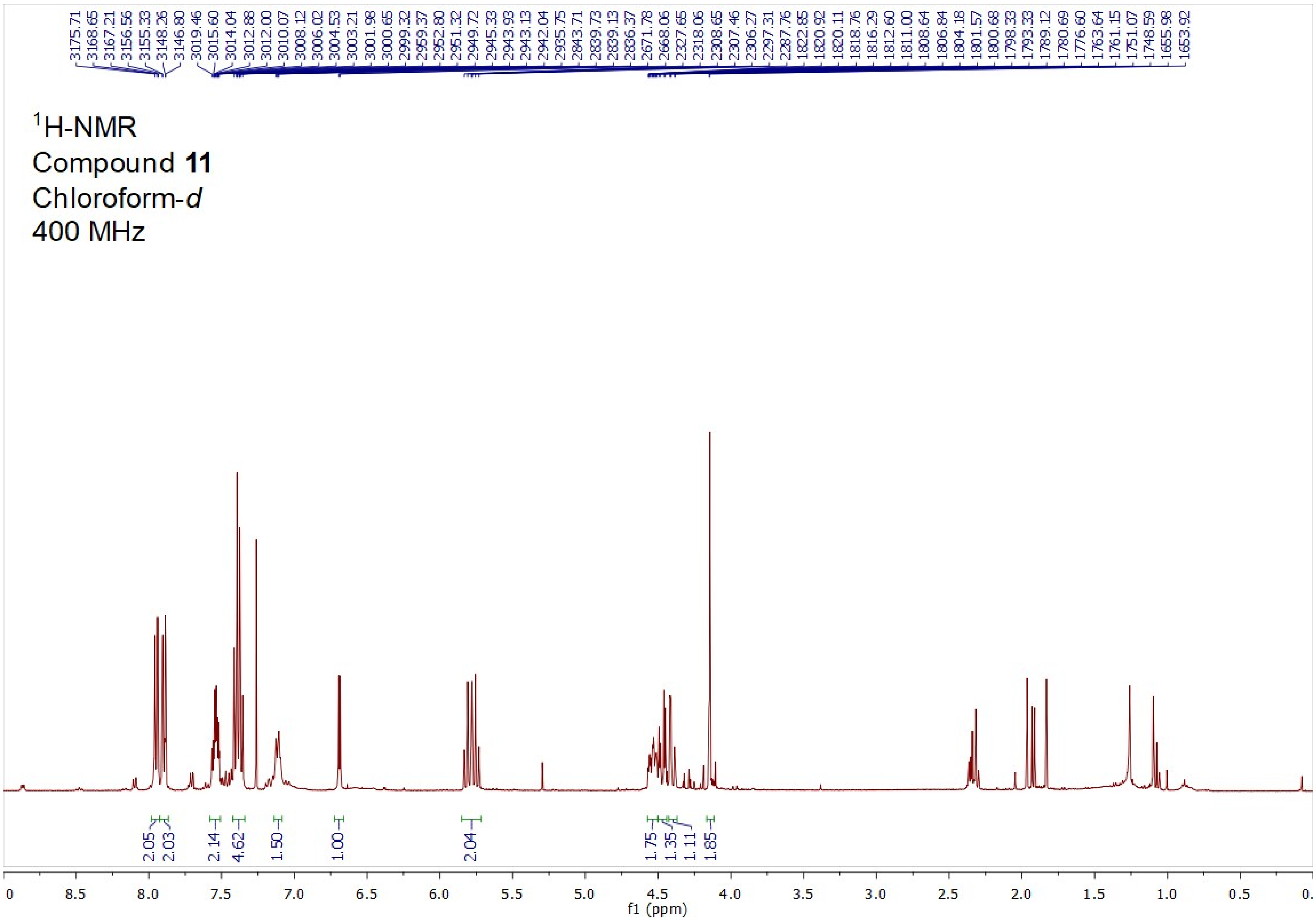
16627.29
16561.16
15729.38
15692.53
13854.21
13459.87
13297.23
13067.40
13016.26
13008.61
12997.48
12973.98
12968.24
12962.15
12945.13
12911.70
11793.62
11505.29
8521.97
7899.37
7508.76
6980.24
6081.62
5344.33
2118.06
^{13}C-NMR
Compound **9**
DMSO-d_6
100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



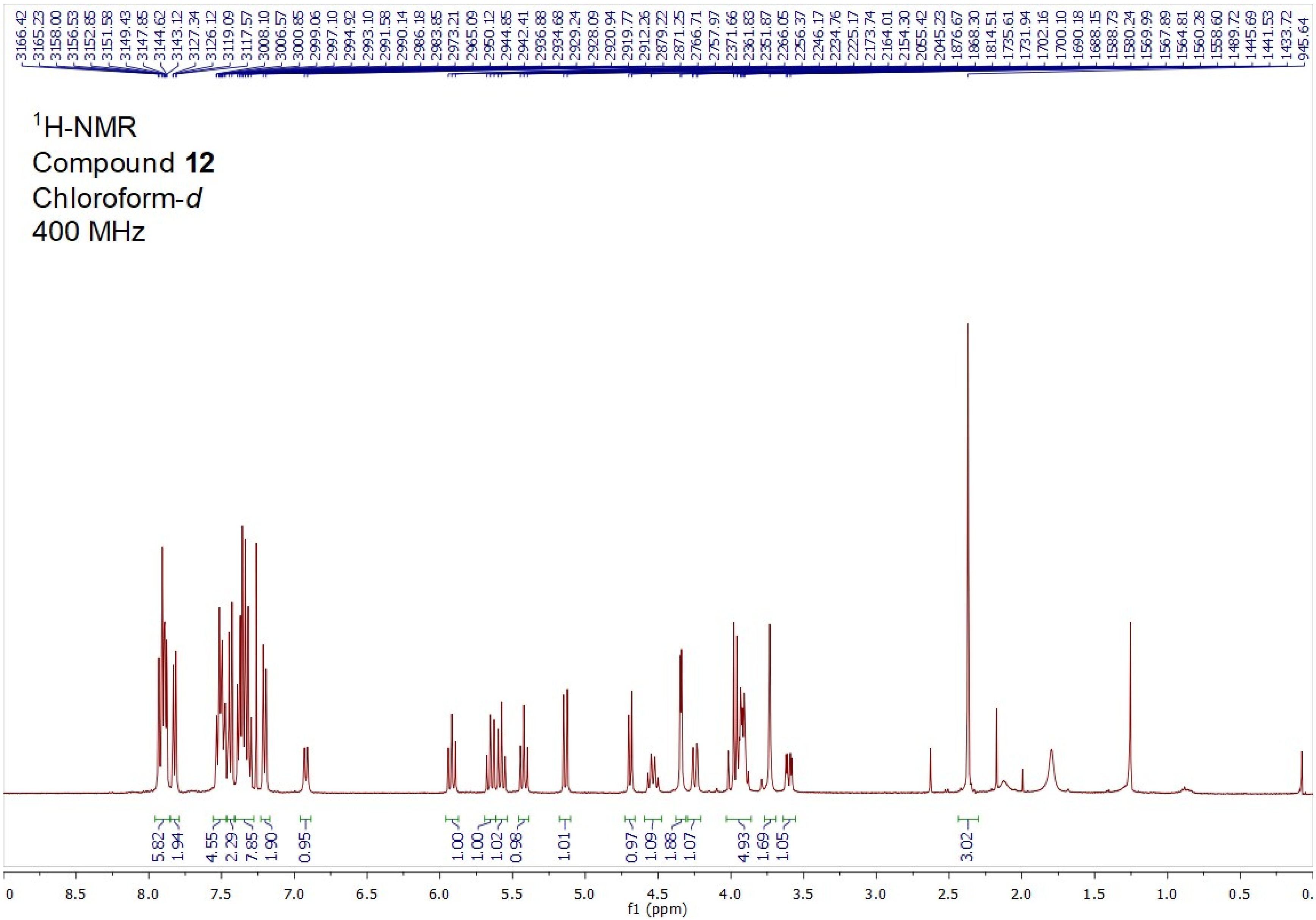
1H-NMR
Compound 10
Chloroform-d
400 MHz
3140.64
3139.40
3132.44
3130.84
3129.44
3122.40
3120.99
3006.29
2998.79
2991.30
2985.47
2978.04
2976.95
2970.53
2964.03
2955.93
2939.20
2931.76
2930.92
2923.52
2912.87
2905.46
2904.61
2896.67
2879.46
2870.15
2843.09
2842.31
2834.67
2350.71
2341.11
2340.36
2330.83
2205.83
2196.03
2186.27
2015.31
2005.03
1768.47
1765.40
1756.22
1753.18
1748.34
1740.96
1736.11
1725.89
1716.01
1705.99
1636.22
1633.21
1631.40
1628.37
1626.21
1623.18
1621.42
1618.35
1602.25
1587.12
1577.69
1562.56
935.75
3.97
1.15
1.12
2.10
2.09
2.42
1.03
2.00
1.03
1.02
1.00
3.16
1.03
2.09
2.96
8.5
8.0
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.
f1 (ppm)



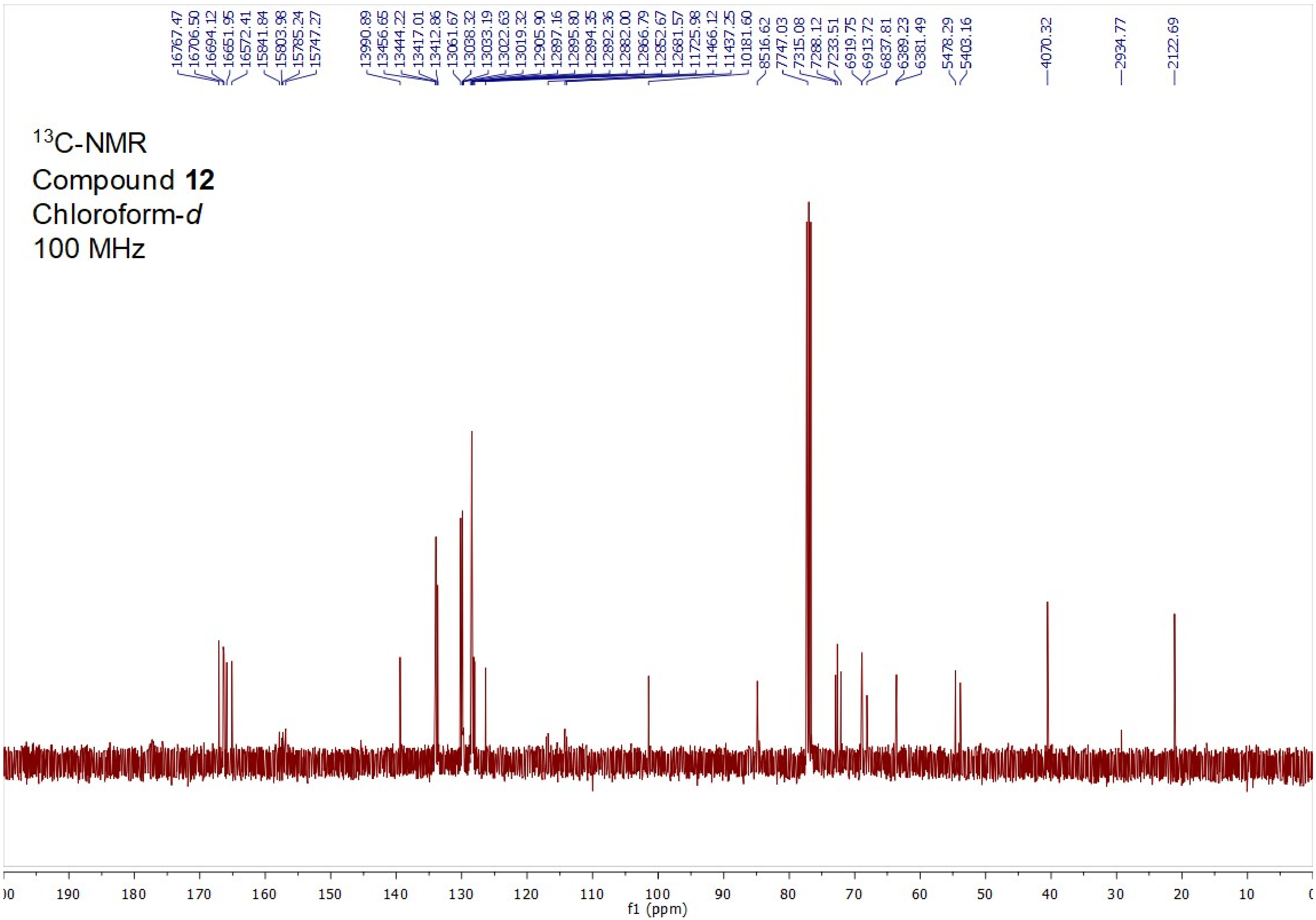
16775.20
16756.91
16570.67
15802.61
15764.68
13970.94
13463.27
13446.16
13422.78
13065.97
13035.14
13031.89
13007.03
12903.40
12898.04
12882.36
12838.52
12729.01
11730.13
11442.03
8642.79
7616.58
7397.87
6907.92
6420.69
5379.55
4068.79
2128.34
^{13}C-NMR
Compound **10**
Chloroform-*d*
100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



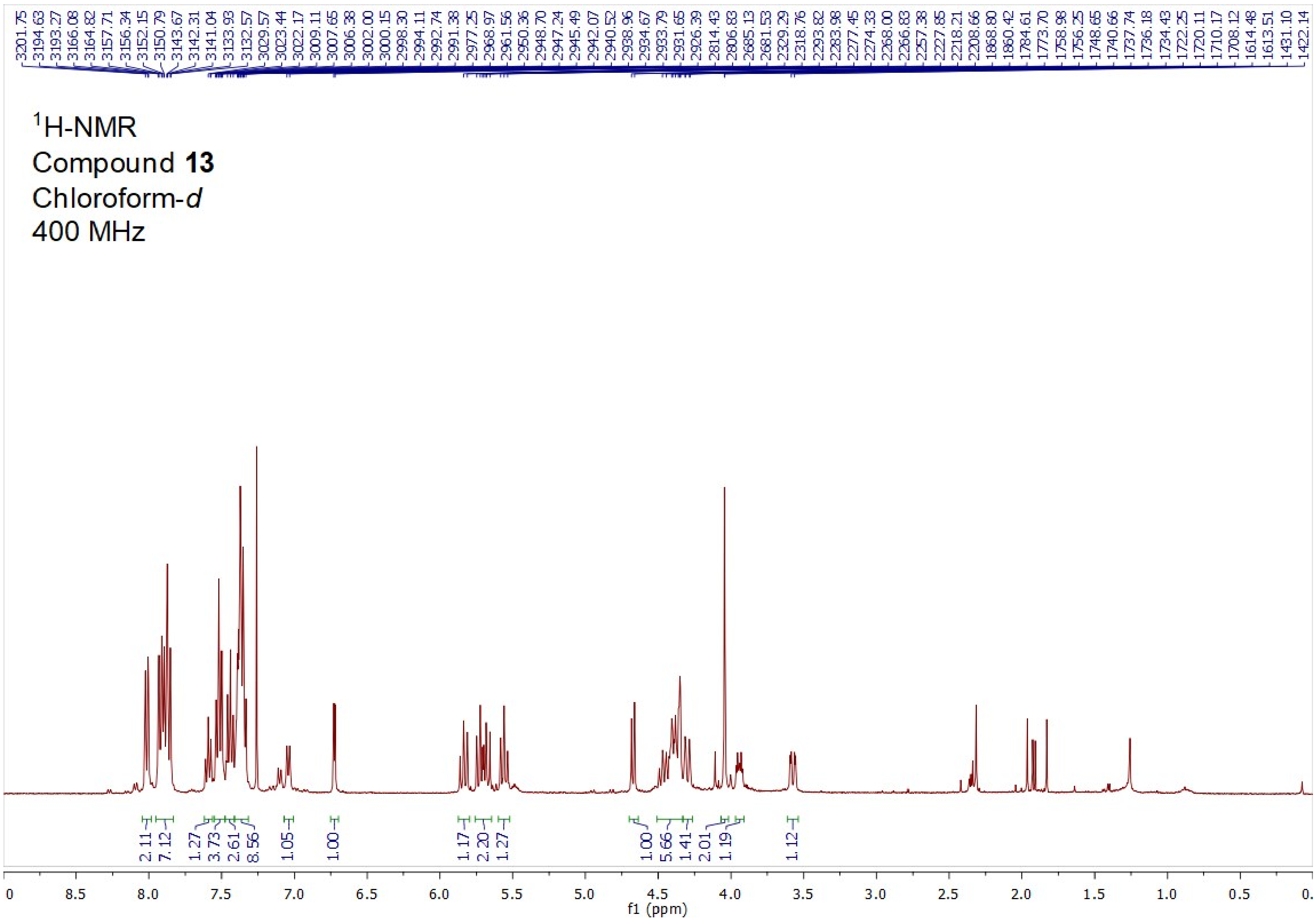
1H-NMR
Compound 11
Chloroform-d
400 MHz
f1 (ppm)



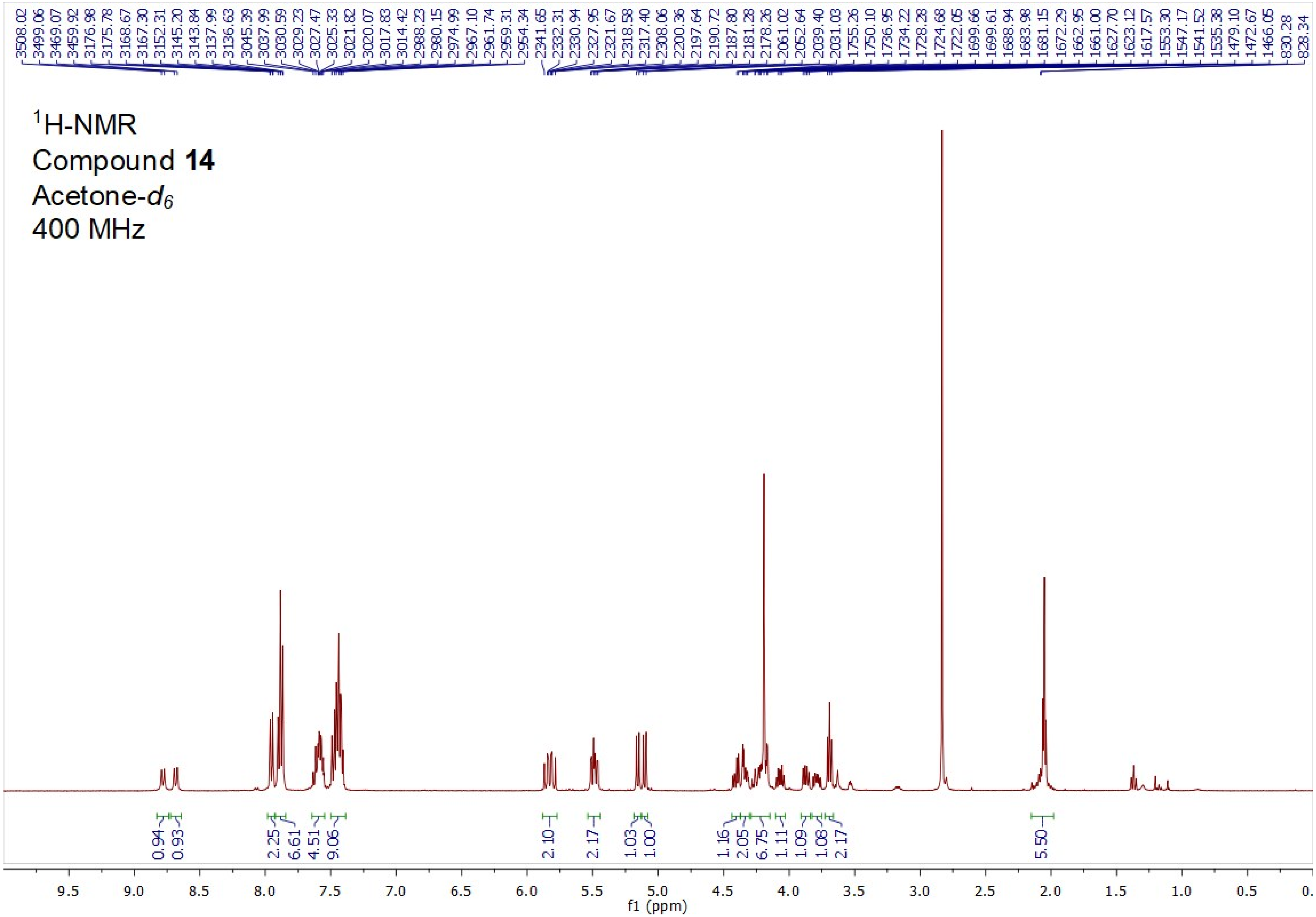
^{1}H-NMR
Compound **12**
Chloroform-*d*
400 MHz
3166.42 3165.23 3158.00 3156.53 3152.85 3151.58 3149.43 3147.85 3144.62 3143.12 3127.34 3126.12 3119.09 3117.57 3008.10 3006.57 3000.85 2999.06 2997.10 2994.92 2993.10 2991.58 2990.14 2986.18 2983.85 2973.21 2965.09 2950.12 2944.85 2942.41 2936.88 2934.68 2929.24 2928.09 2920.94 2919.77 2912.26 2879.22 2871.25 2766.71 2757.97 2371.66 2361.83 2351.87 2266.05 2256.37 2246.17 2234.76 2225.17 2173.74 2164.01 2154.30 2055.42 2045.23 1876.67 1868.30 1814.51 1735.61 1731.94 1702.16 1700.10 1690.18 1688.15 1588.73 1580.24 1569.99 1567.89 1564.81 1560.28 1558.60 1489.72 1445.69 1441.53 1433.72 945.64
5.82 1.94 4.55 2.29 7.85 1.90 0.95 1.00 1.00 1.02 0.98 1.01 0.97 1.09 1.88 1.07 4.93 1.69 1.05 3.02
8.5 8.0 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
f1 (ppm)



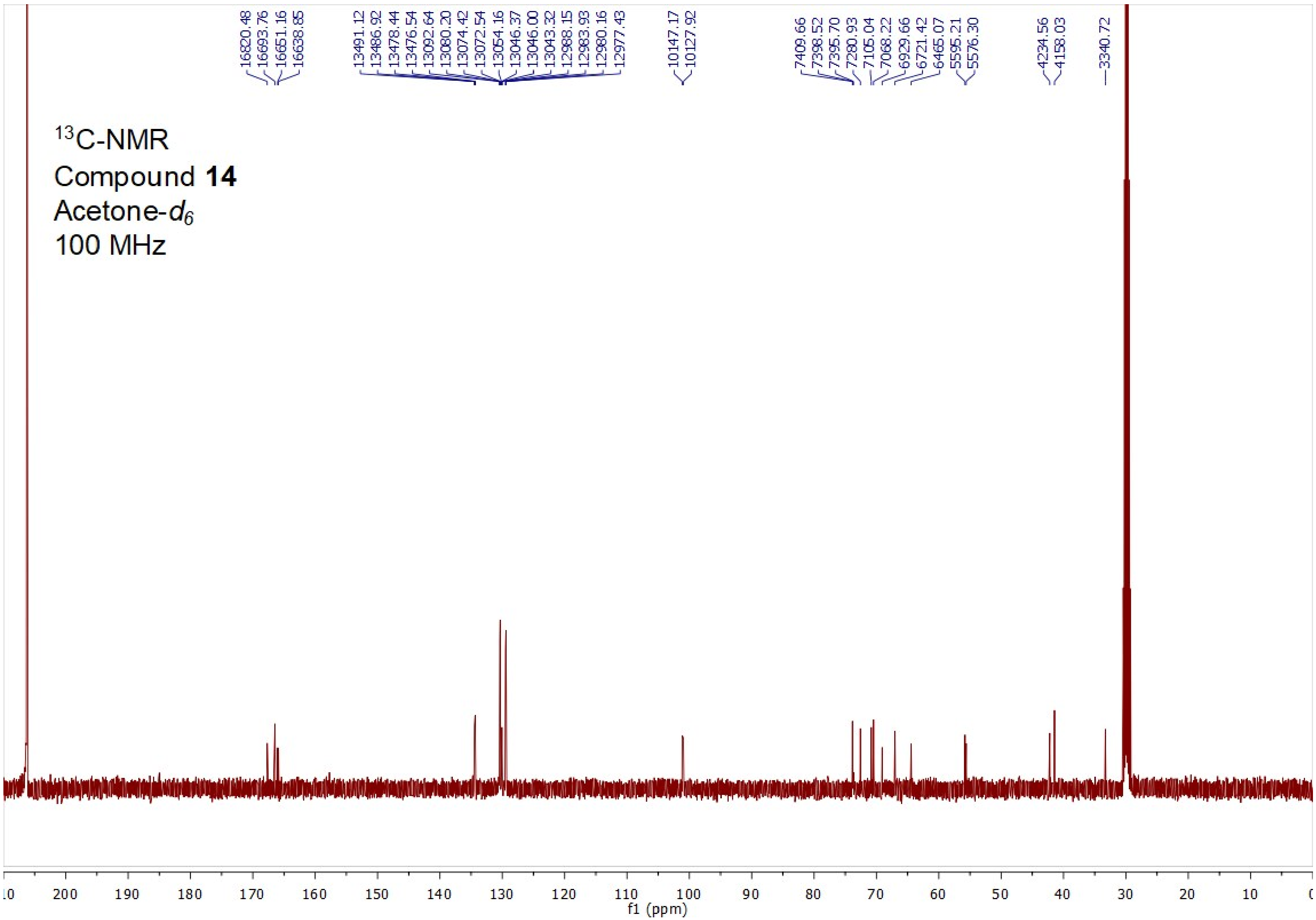
16767.47
16706.50
16694.12
16651.95
16572.41
15841.84
15803.98
15785.24
15747.27
13990.89
13456.65
13444.22
13417.01
13412.86
13061.67
13038.32
13033.19
13022.63
13019.32
12905.90
12897.16
12895.80
12894.35
12892.36
12882.00
12866.79
12852.67
12681.57
11725.98
11466.12
11437.25
10181.60
8516.62
7747.03
7315.08
7288.12
7233.51
6919.75
6913.72
6837.81
6389.23
6381.49
5478.29
5403.16
4070.32
2934.77
2122.69
^{13}C-NMR
Compound **12**
Chloroform-*d*
100 MHz
f1 (ppm)



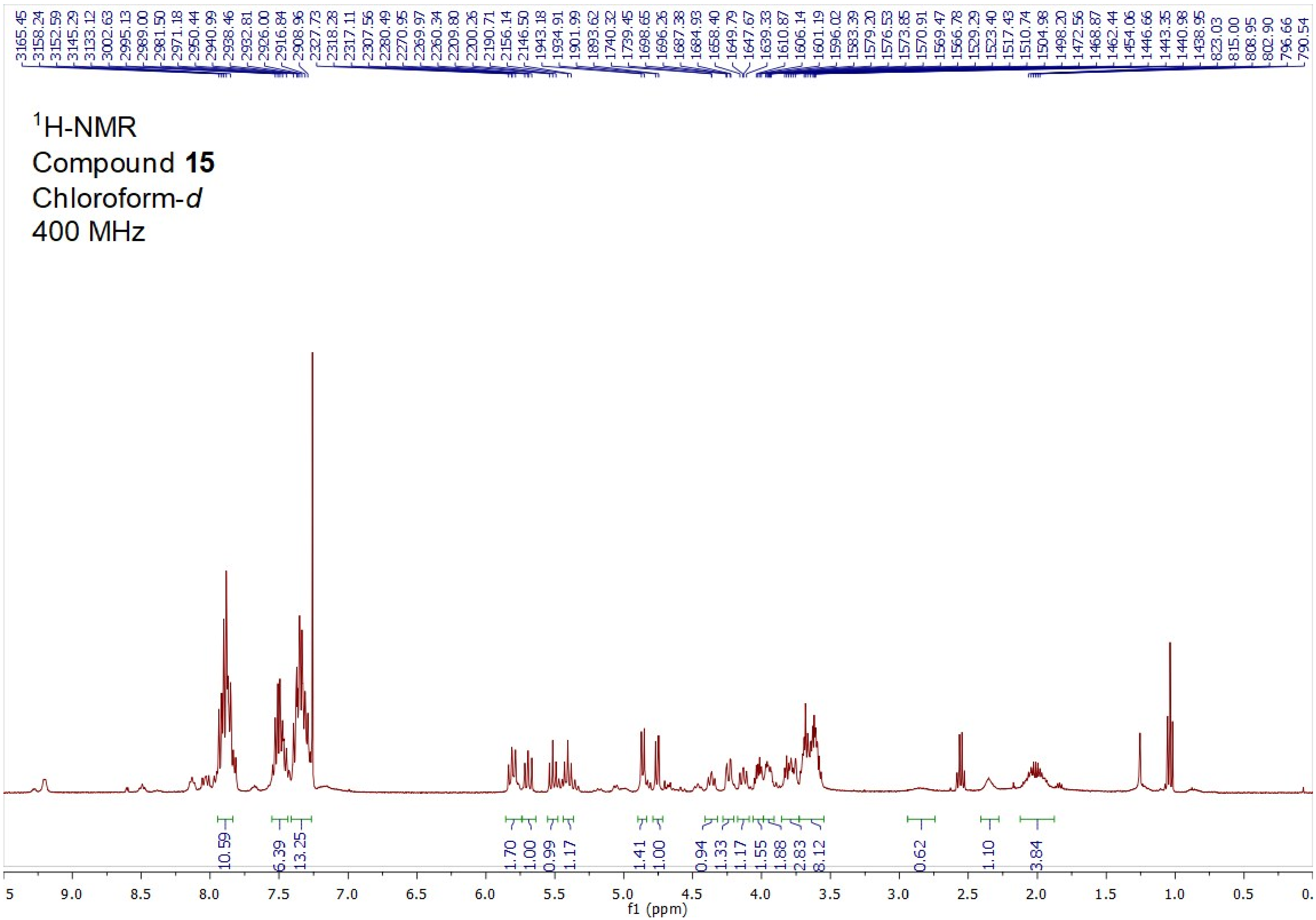
1H-NMR
Compound **13**
Chloroform-*d*
400 MHz
f1 (ppm)



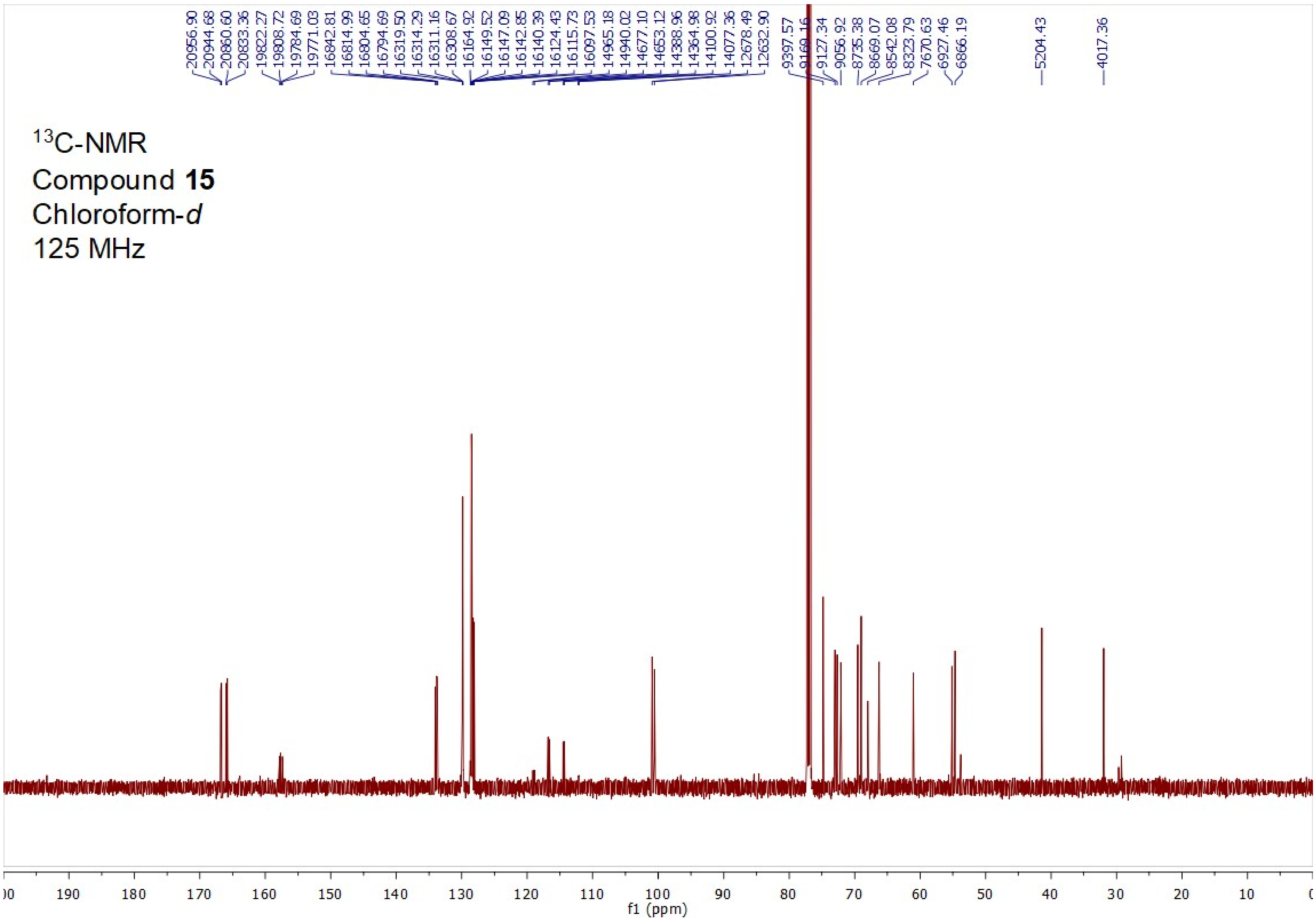
1H-NMR
Compound **14**
Acetone-d_6
400 MHz
3508.02 3499.06 3469.07 3459.92 3176.98 3175.78 3168.67 3167.30 3152.31 3145.20 3143.84 3137.99 3136.63 3045.39 3037.99 3030.59 3029.23 3027.47 3025.33 3021.82 3020.07 3017.83 3014.42 2988.23 2980.15 2974.99 2967.10 2961.74 2959.31 2954.34 2341.65 2332.31 2330.94 2327.95 2321.67 2318.58 2317.40 2308.06 2200.36 2197.64 2190.72 2187.80 2181.28 2178.26 2061.02 2052.64 2039.40 2031.03 1755.26 1750.10 1736.95 1734.22 1728.28 1724.68 1722.05 1699.66 1699.61 1688.94 1683.98 1681.15 1672.29 1662.95 1661.00 1627.70 1623.12 1617.57 1553.30 1547.17 1541.52 1535.38 1479.10 1472.67 1466.05 830.28 828.34
0.94 0.93 2.25 6.61 4.51 9.06 2.10 2.17 1.03 1.00 1.16 2.05 6.75 1.11 1.09 1.08 2.17 5.50
9.5 9.0 8.5 8.0 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.
f1 (ppm)

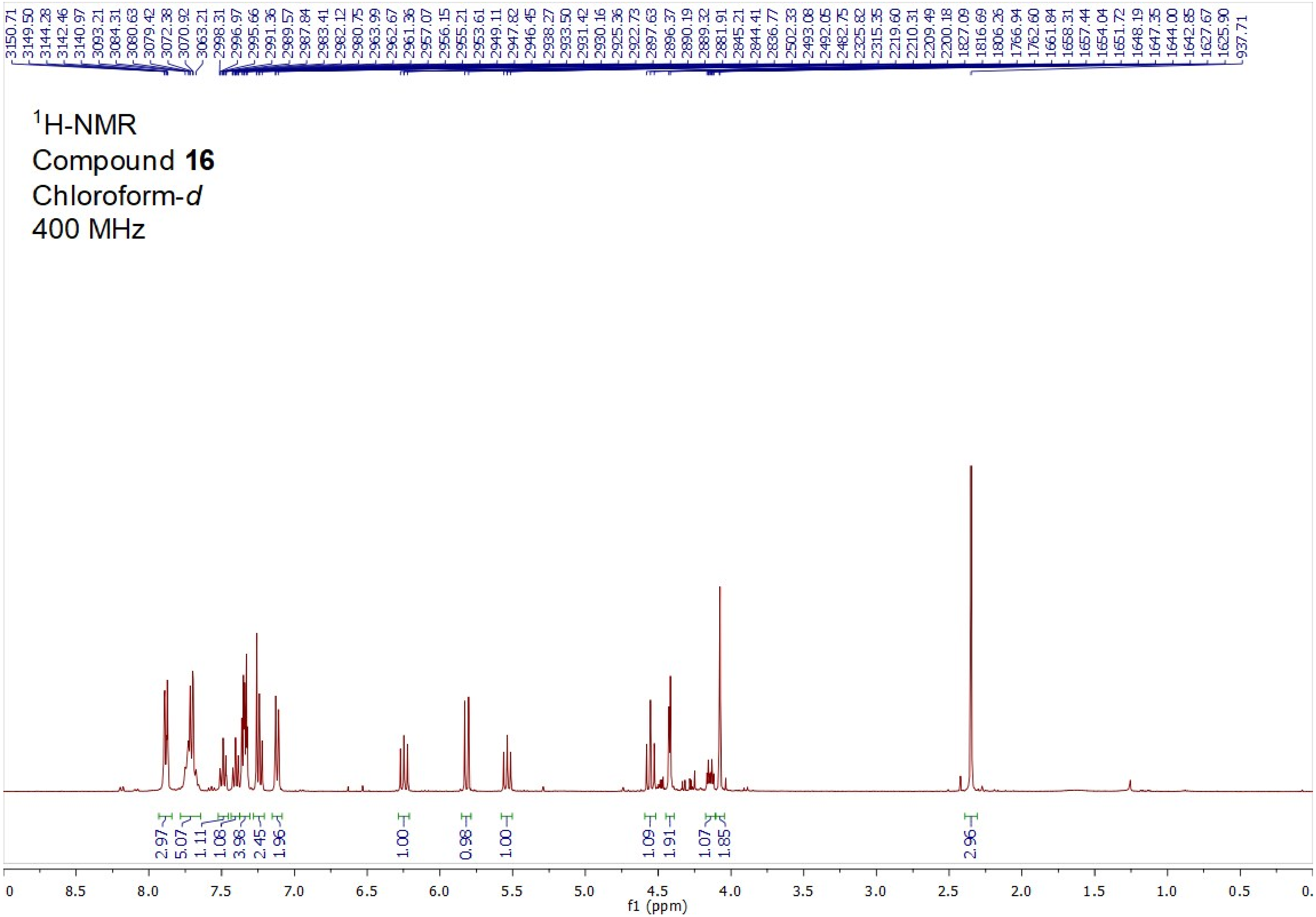


13C-NMR
Compound 14
Acetone-d6
100 MHz
16820.48
16693.76
16651.16
16638.85
13491.12
13486.92
13478.44
13476.54
13092.64
13080.20
13074.42
13072.54
13054.16
13046.37
13046.00
13043.32
12988.15
12983.93
12980.16
12977.43
10147.17
10127.92
7409.66
7398.52
7395.70
7280.93
7105.04
7068.22
6929.66
6721.42
6465.07
5595.21
5576.30
4234.56
4158.03
3340.72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

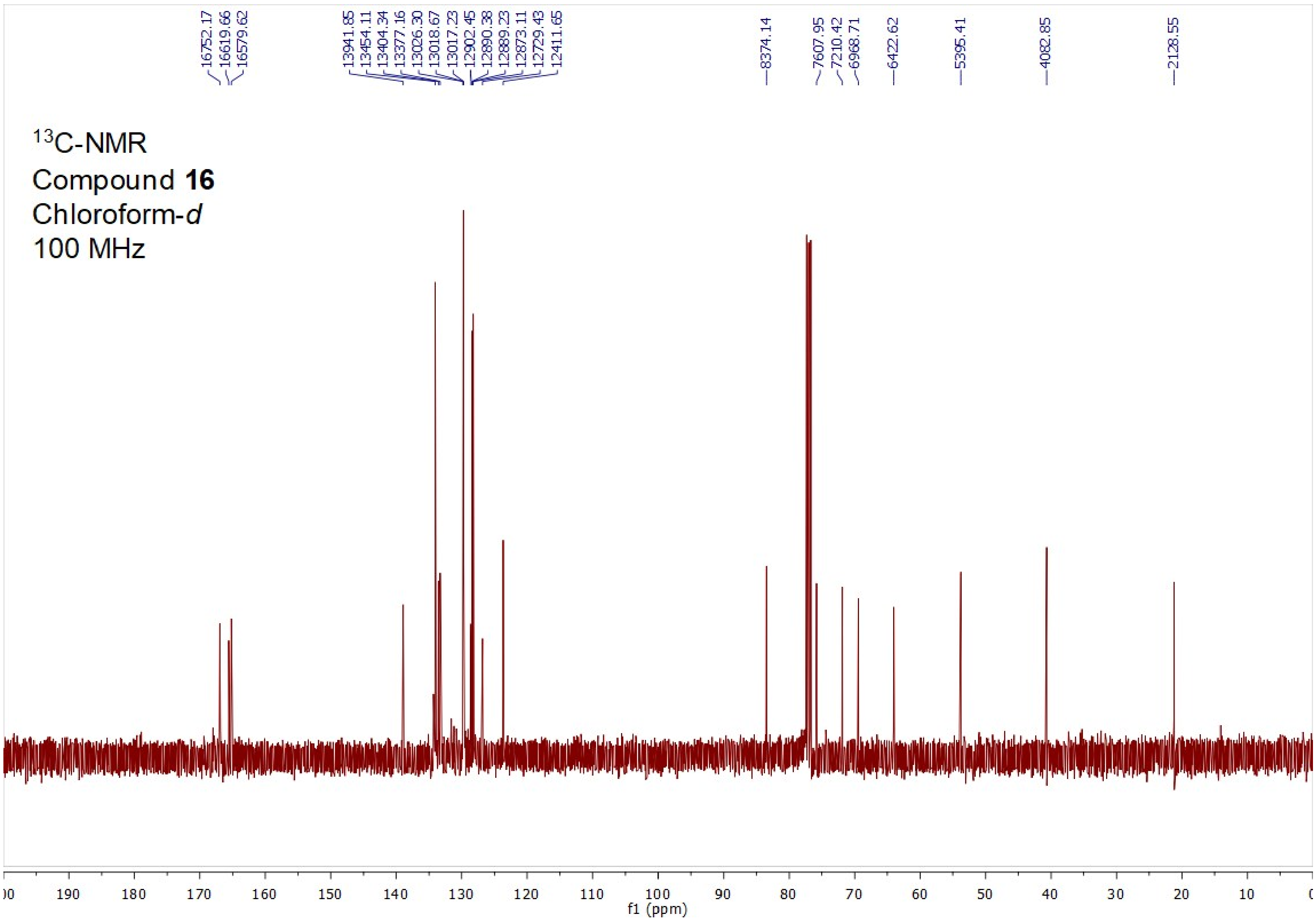


^{1}H-NMR
Compound **15**
Chloroform-*d*
400 MHz
f1 (ppm)

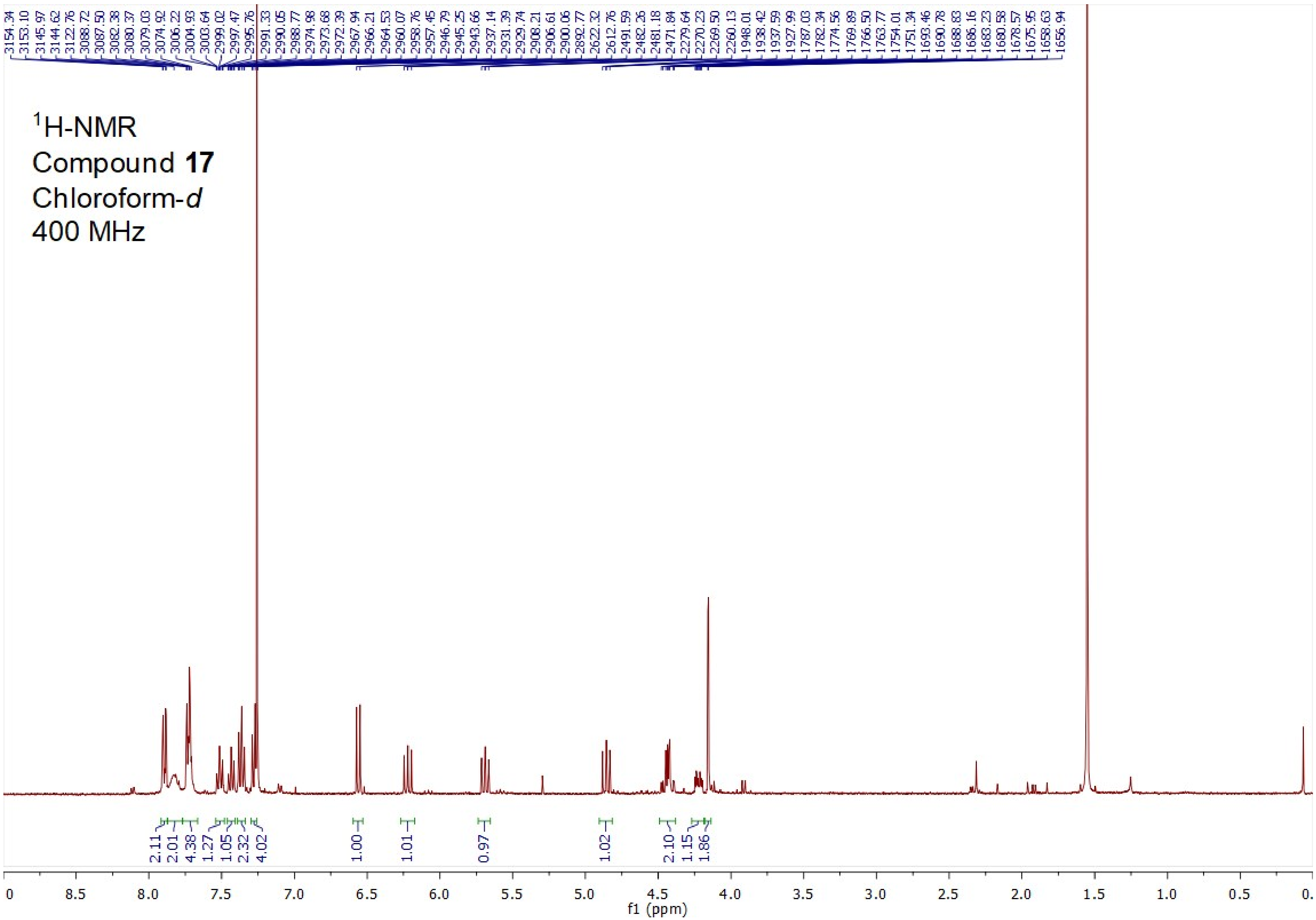

13C-NMR
Compound 15
Chloroform-d
125 MHz
20956.90
20944.68
20860.60
20833.36
19822.27
19808.72
19784.69
19771.03
16842.81
16814.99
16804.65
16794.69
16319.50
16314.29
16311.16
16308.67
16164.92
16149.52
16147.09
16142.85
16140.39
16124.43
16115.73
16097.53
14965.18
14940.02
14677.10
14653.12
14388.96
14364.98
14100.92
14077.36
12678.49
12632.90
9397.57
9169.16
9127.34
9056.92
8735.38
8669.07
8542.08
8323.79
7670.63
6927.46
6866.19
5204.43
4017.36
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



^{1}H-NMR
Compound **16**
Chloroform-*d*
400 MHz
f1 (ppm)

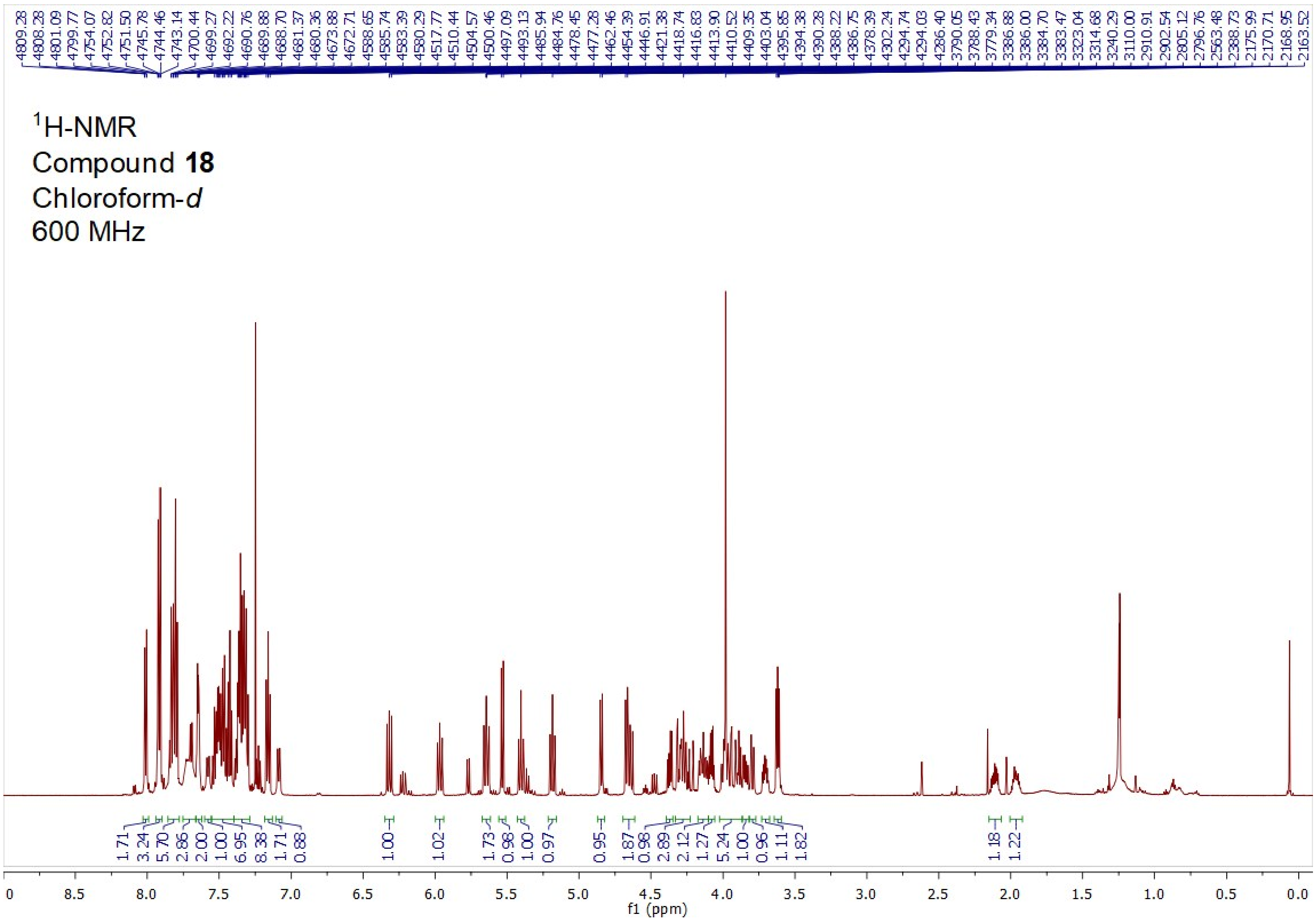


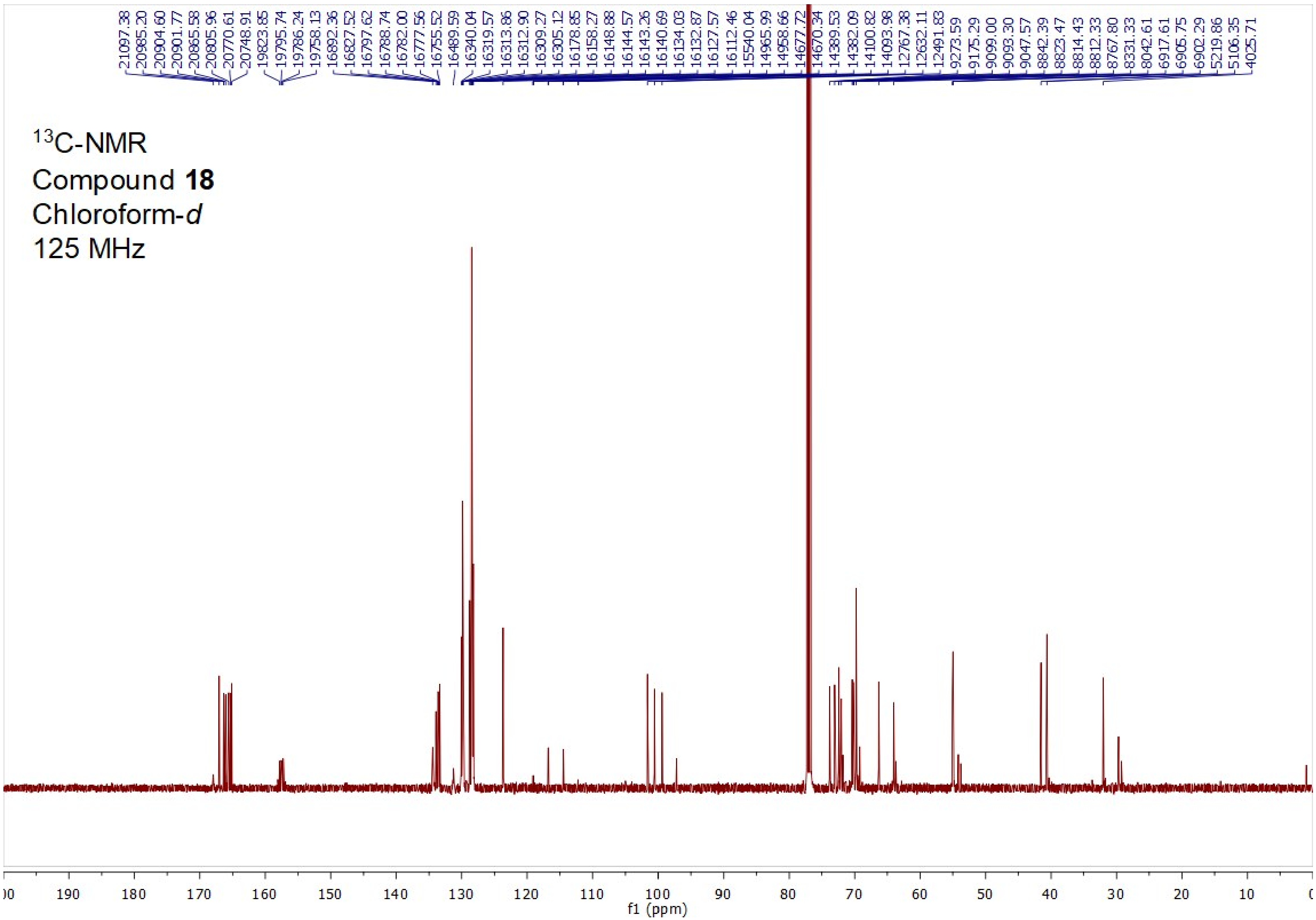
16752.17
16619.66
16579.62
13941.85
13454.11
13404.34
13377.16
13026.30
13018.67
13017.23
12902.45
12890.38
12889.23
12873.11
12729.43
12411.65
8374.14
7607.95
7210.42
6968.71
6422.62
5395.41
4082.85
2128.55
^{13}C-NMR
Compound **16**
Chloroform-*d*
100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



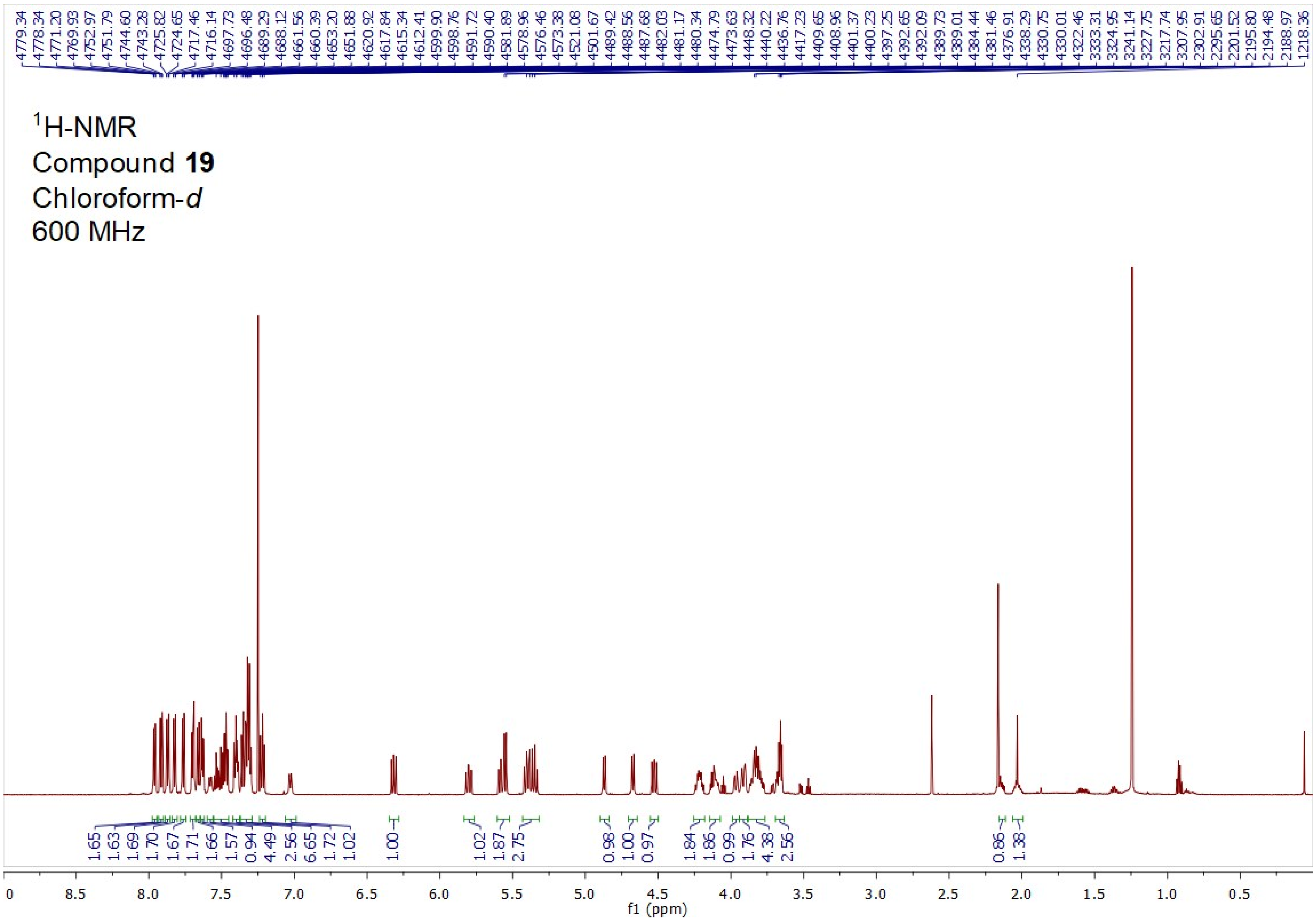
^{1}H-NMR
Compound **17**
Chloroform-*d*
400 MHz
f1 (ppm)

[1]H-NMR
Compound **18**
Chloroform-*d*
600 MHz

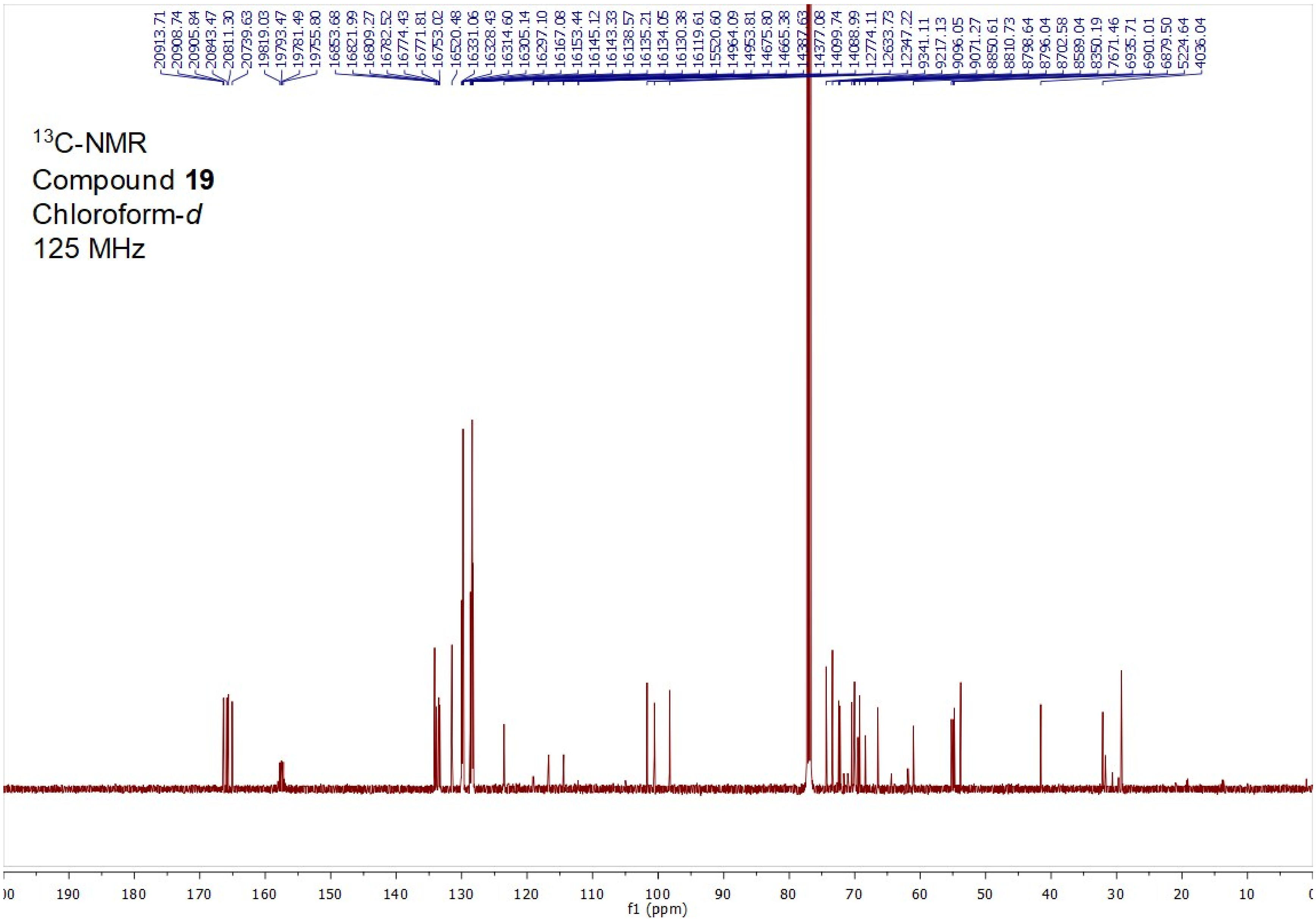




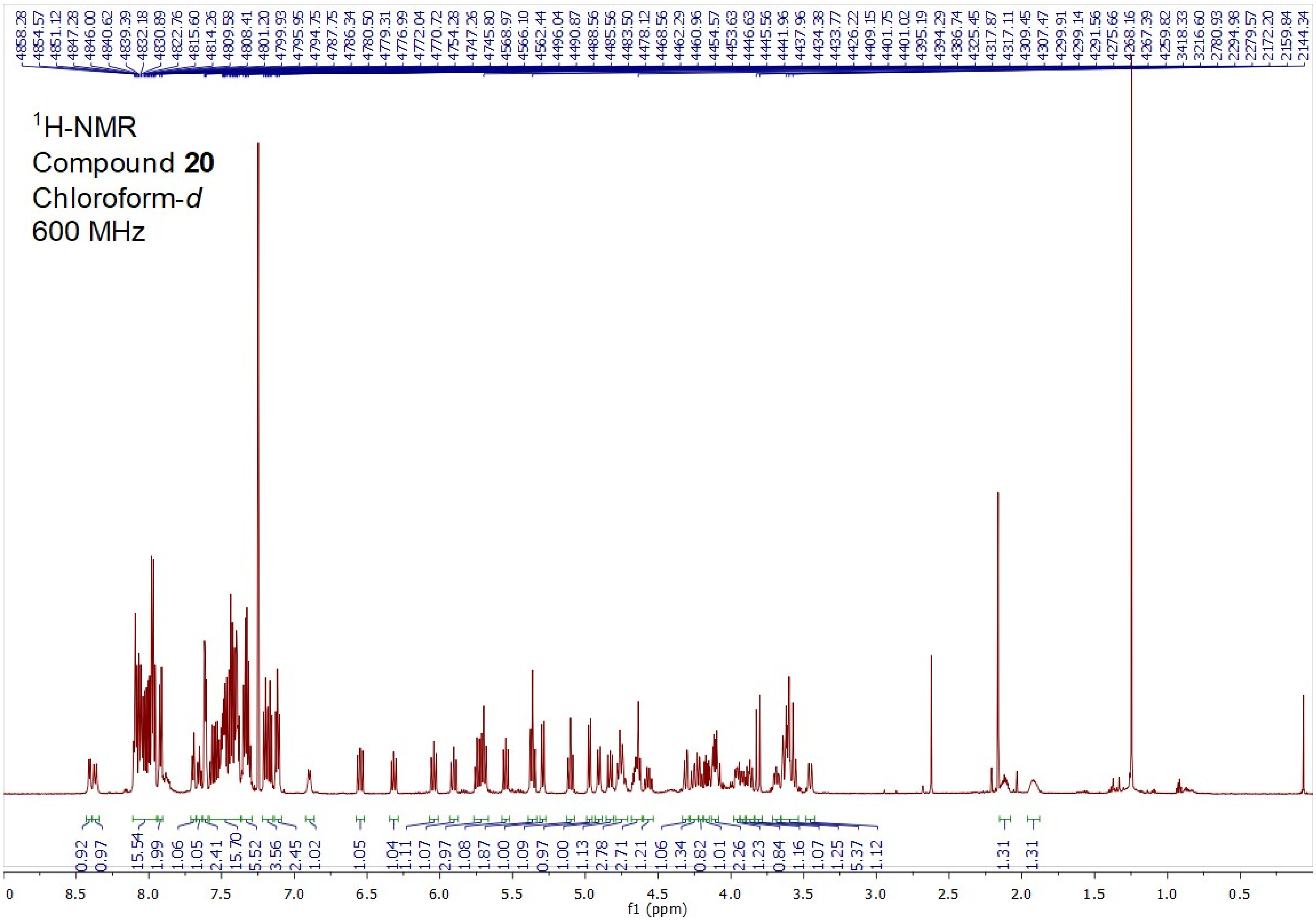
21097.38
20985.20
20904.60
20901.77
20865.58
20805.96
20770.61
20748.91
19823.85
19795.74
19786.24
19758.13
16892.36
16827.52
16797.62
16788.74
16782.00
16777.56
16755.52
16489.59
16340.04
16319.57
16313.86
16312.90
16309.27
16305.12
16178.85
16158.27
16148.88
16144.57
16143.26
16140.69
16134.03
16132.87
16127.57
16112.46
15540.04
14965.99
14958.66
14677.72
14670.34
14389.53
14382.09
14100.82
14093.98
12767.38
12632.11
12491.83
9273.59
9175.29
9099.00
9093.30
9047.57
8842.39
8823.47
8814.43
8812.33
8767.80
8331.33
8042.61
6917.61
6905.75
6902.29
5219.86
5106.35
4025.71
13C-NMR
Compound 18
Chloroform-d
125 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

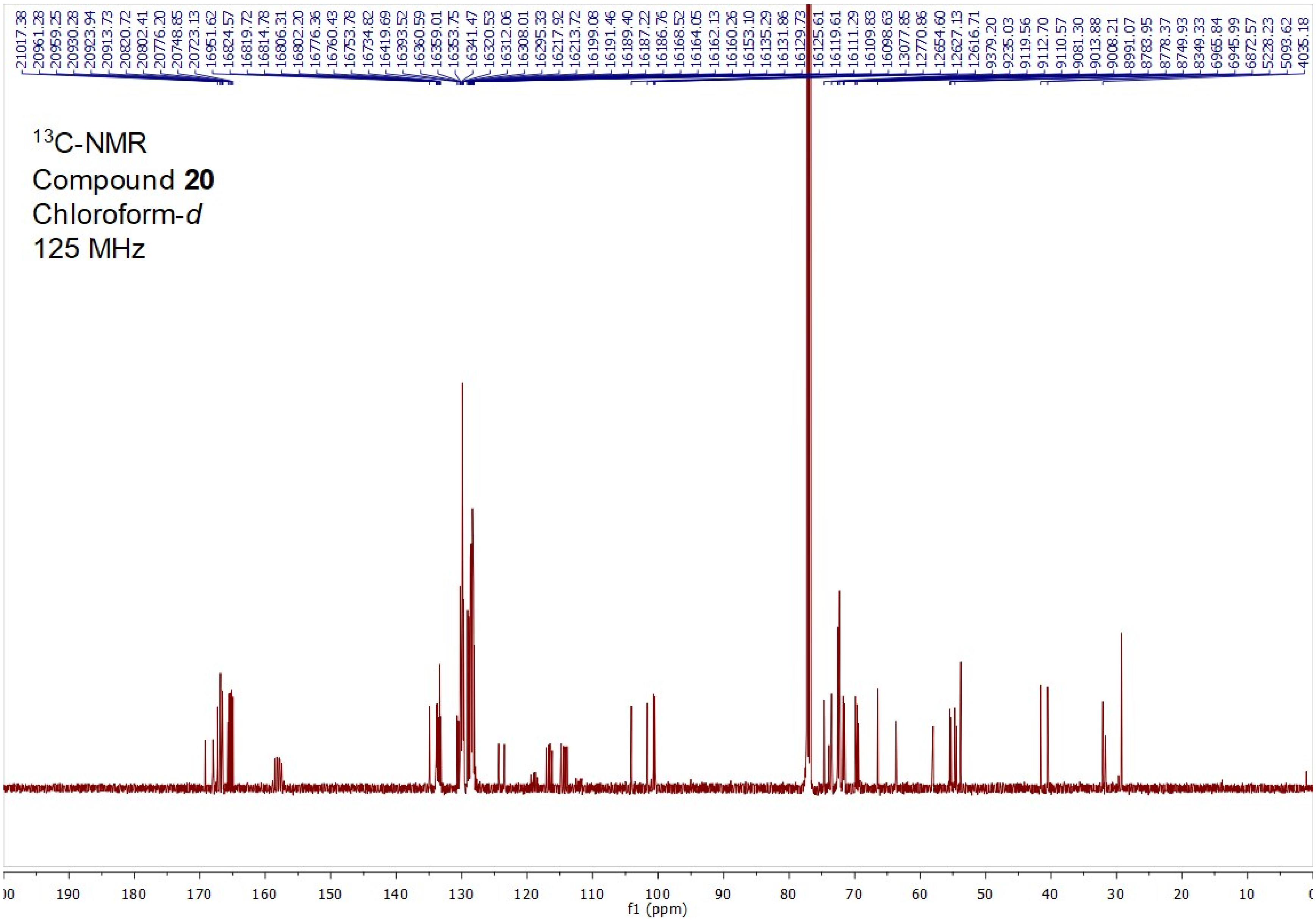


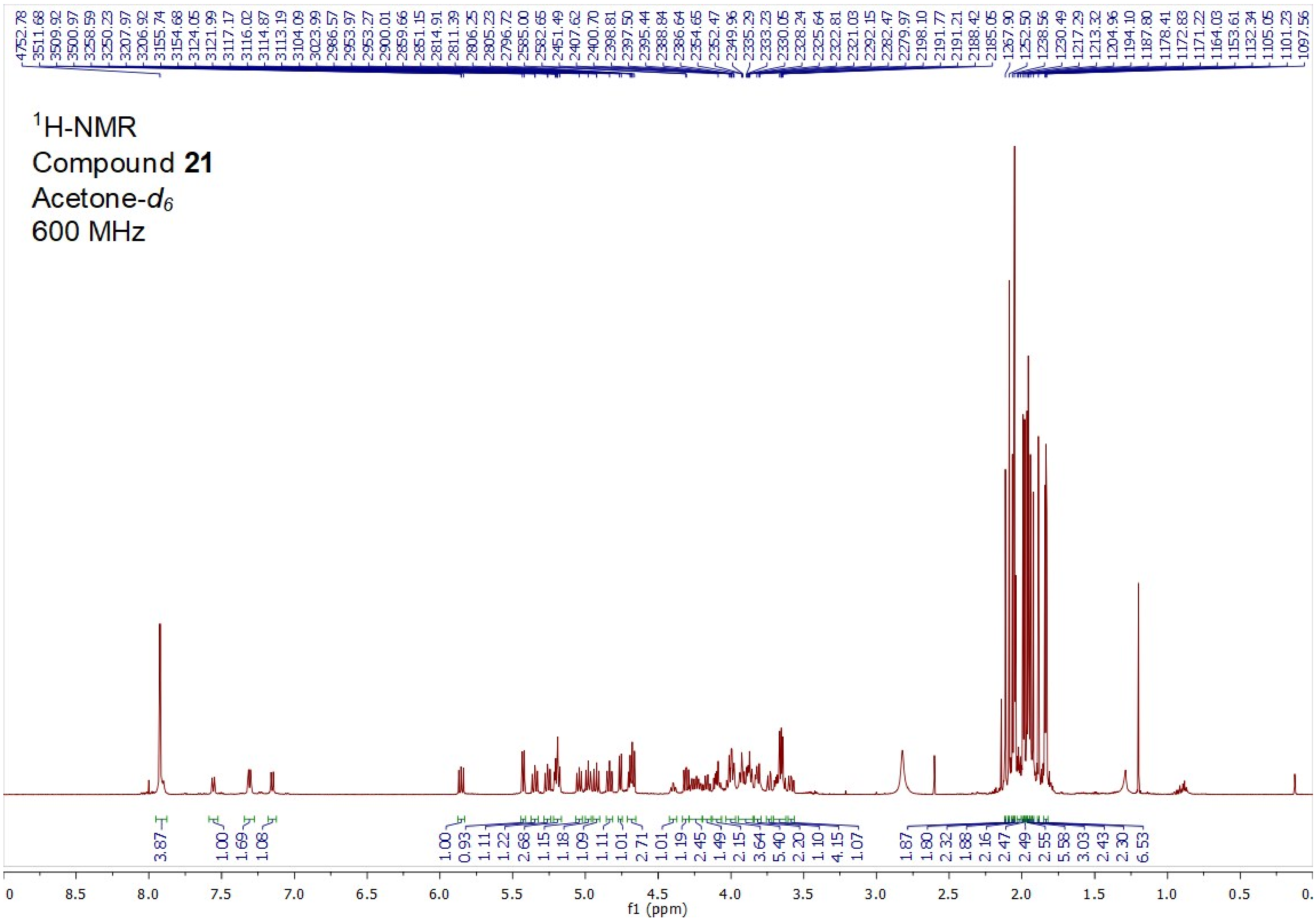
1H-NMR
Compound 19
Chloroform-d
600 MHz
f1 (ppm)



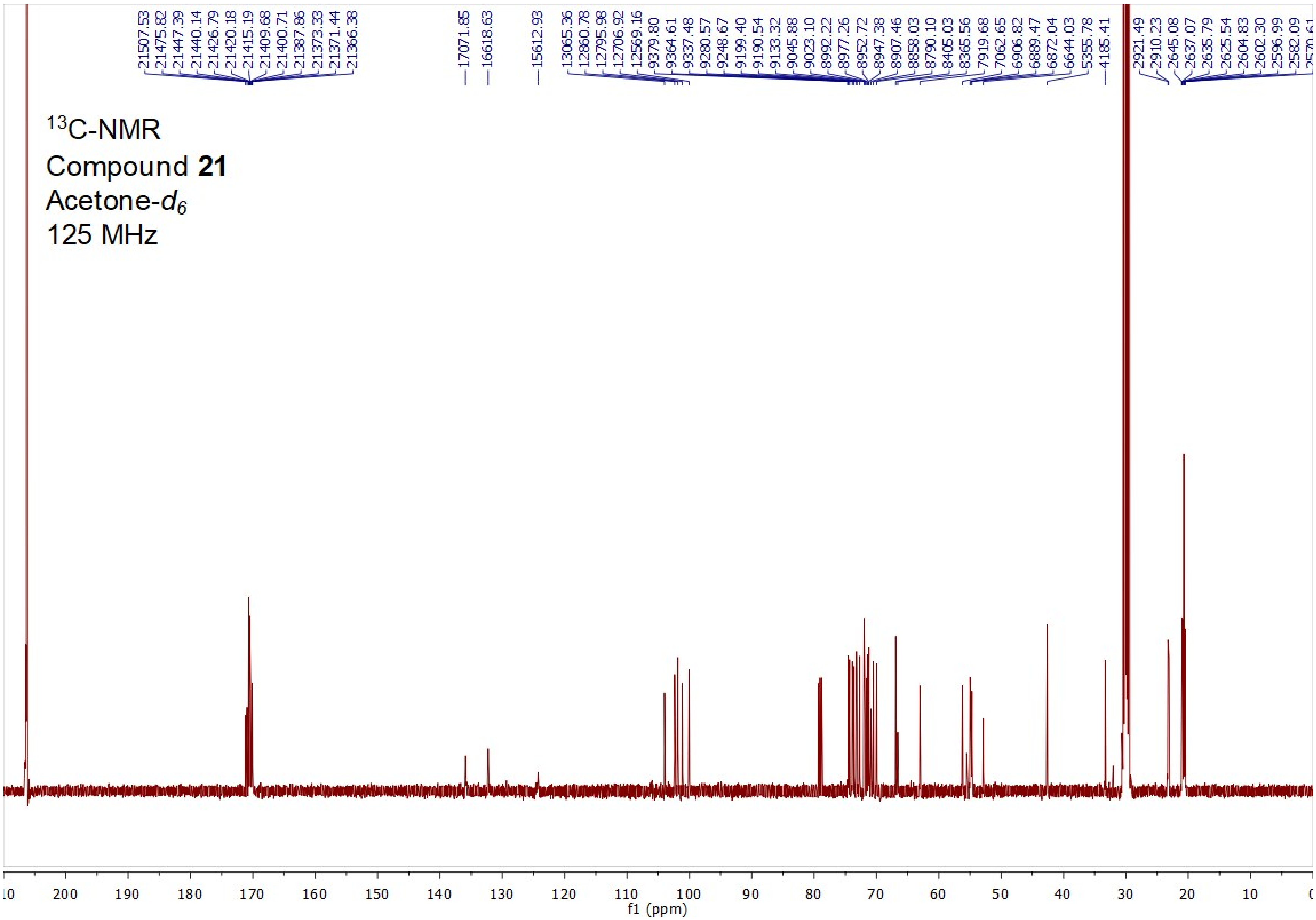
20913.71
20908.74
20905.84
20843.47
20811.30
20739.63
19819.03
19793.47
19781.49
19755.80
16853.68
16821.99
16809.27
16782.52
16774.43
16771.81
16753.02
16520.48
16331.06
16328.43
16314.60
16305.14
16297.10
16167.08
16153.44
16145.12
16143.33
16138.57
16135.21
16134.05
16130.38
16119.61
15520.60
14964.09
14953.81
14675.80
14665.38
14387.63
14377.08
14099.74
14088.99
12774.11
12633.73
12347.22
9341.11
9217.13
9096.05
9071.27
8850.61
8810.73
8798.64
8796.04
8702.58
8589.04
8350.19
7671.46
6935.71
6901.01
6879.50
5224.64
4036.04
^{13}C-NMR
Compound **19**
Chloroform-*d*
125 MHz
f1 (ppm)


4858.28
4854.57
4851.12
4847.28
4846.00
4840.62
4839.39
4832.18
4830.89
4822.76
4815.60
4814.26
4809.58
4808.41
4801.20
4799.93
4795.95
4794.75
4787.75
4786.34
4780.50
4779.31
4776.99
4772.04
4770.72
4754.28
4747.26
4745.80
4568.97
4566.10
4562.44
4496.04
4490.87
4488.56
4485.56
4483.50
4478.12
4468.56
4462.29
4460.96
4454.57
4453.63
4446.63
4445.56
4441.96
4437.96
4434.38
4433.77
4426.22
4409.15
4401.75
4401.02
4395.19
4394.29
4386.74
4325.45
4317.87
4317.11
4309.45
4307.47
4299.91
4299.14
4291.56
4275.66
4268.16
4267.39
4259.82
3418.33
3216.60
2780.93
2294.98
2279.57
2172.20
2159.84
2144.34
^{1}H-NMR
Compound **20**
Chloroform-*d*
600 MHz
0.92
0.97
15.54
1.99
1.06
1.05
2.41
15.70
5.52
3.56
2.45
1.02
1.05
1.04
1.11
1.07
2.97
1.08
1.87
1.00
1.09
0.97
1.00
1.13
2.78
2.71
1.21
1.06
1.34
0.82
1.01
2.26
1.23
0.84
1.16
1.07
1.25
5.37
1.12
1.31
1.31
0
8.5
8.0
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
f1 (ppm)

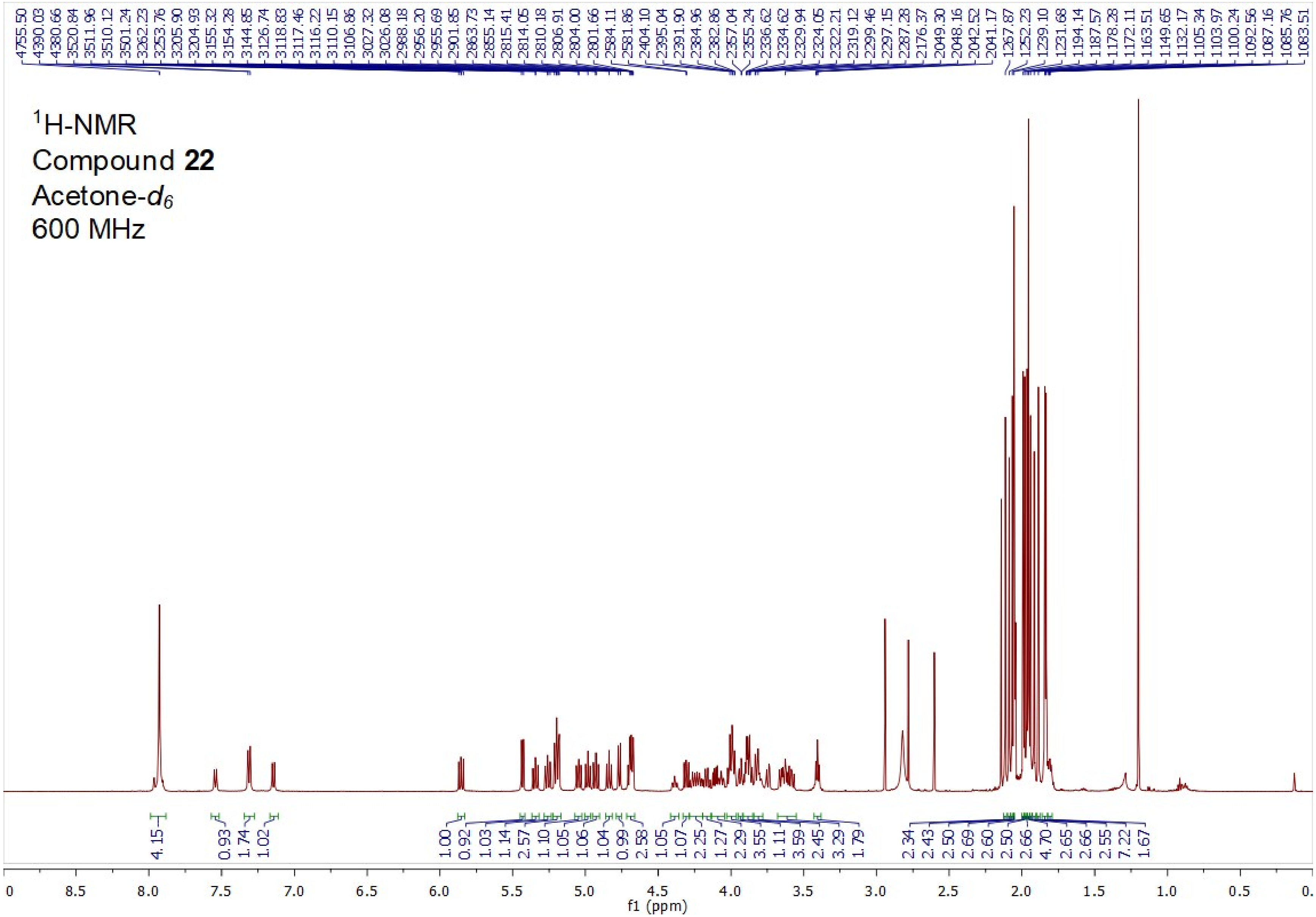

21017.38
20961.28
20959.25
20930.28
20923.94
20913.73
20820.72
20802.41
20776.20
20748.85
20723.13
16951.62
16824.57
16819.72
16814.78
16806.31
16802.20
16776.36
16760.43
16753.78
16734.82
16419.69
16393.52
16360.59
16359.01
16353.75
16341.47
16320.53
16312.06
16308.01
16295.33
16217.92
16213.72
16199.08
16191.46
16189.40
16187.22
16186.76
16168.52
16164.05
16162.13
16160.26
16153.10
16135.29
16131.86
16129.73
16125.61
16119.61
16111.29
16109.83
16098.63
13077.85
12770.86
12654.60
12627.13
12616.71
9379.20
9235.03
9119.56
9112.70
9110.57
9081.30
9013.88
9008.21
8991.07
8783.95
8778.37
8749.93
8349.33
6965.84
6945.99
6872.57
5228.23
5093.62
4035.18
13C-NMR
Compound 20
Chloroform-d
125 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



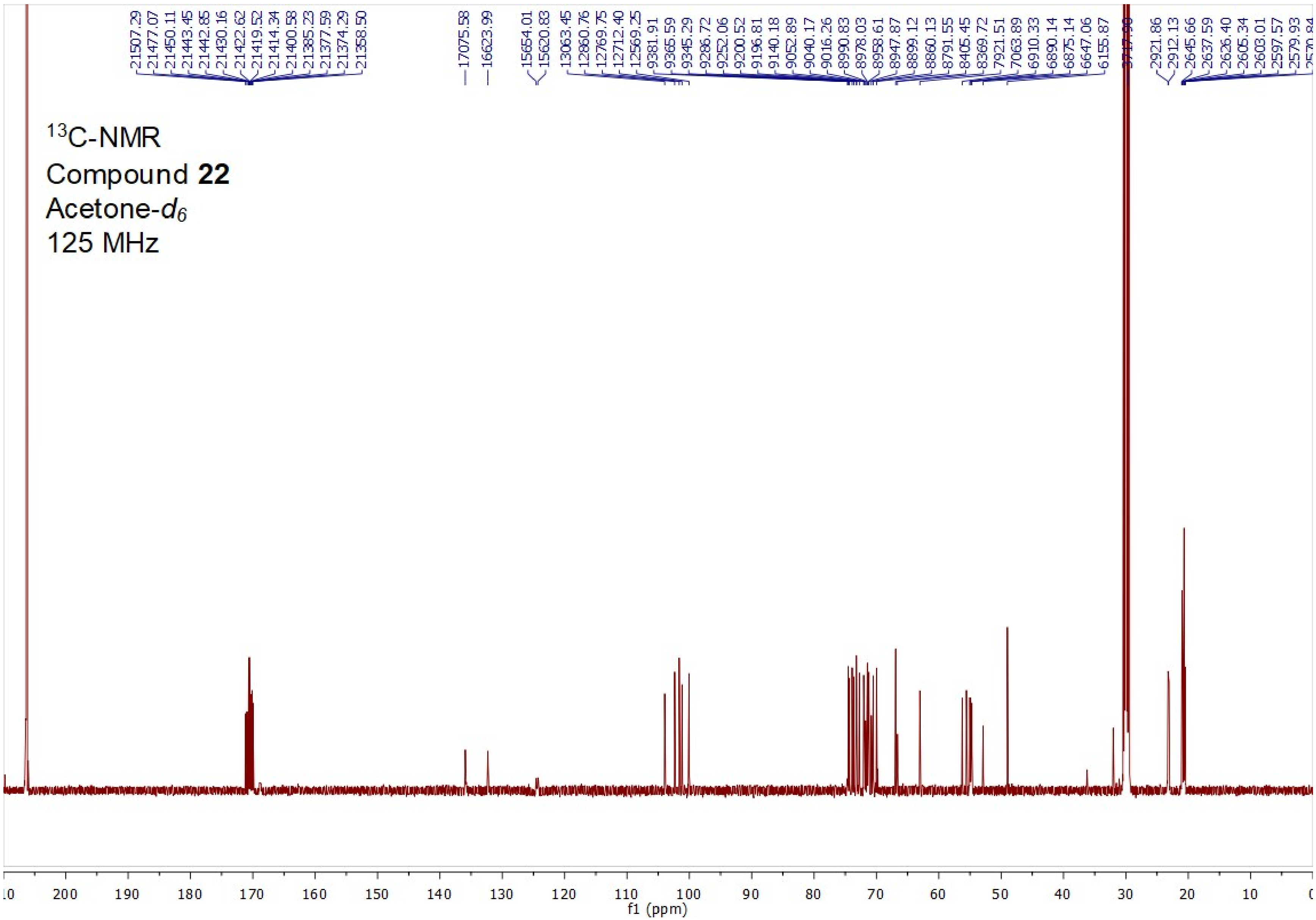
1H-NMR
Compound 21
Acetone-d6
600 MHz
f1 (ppm)



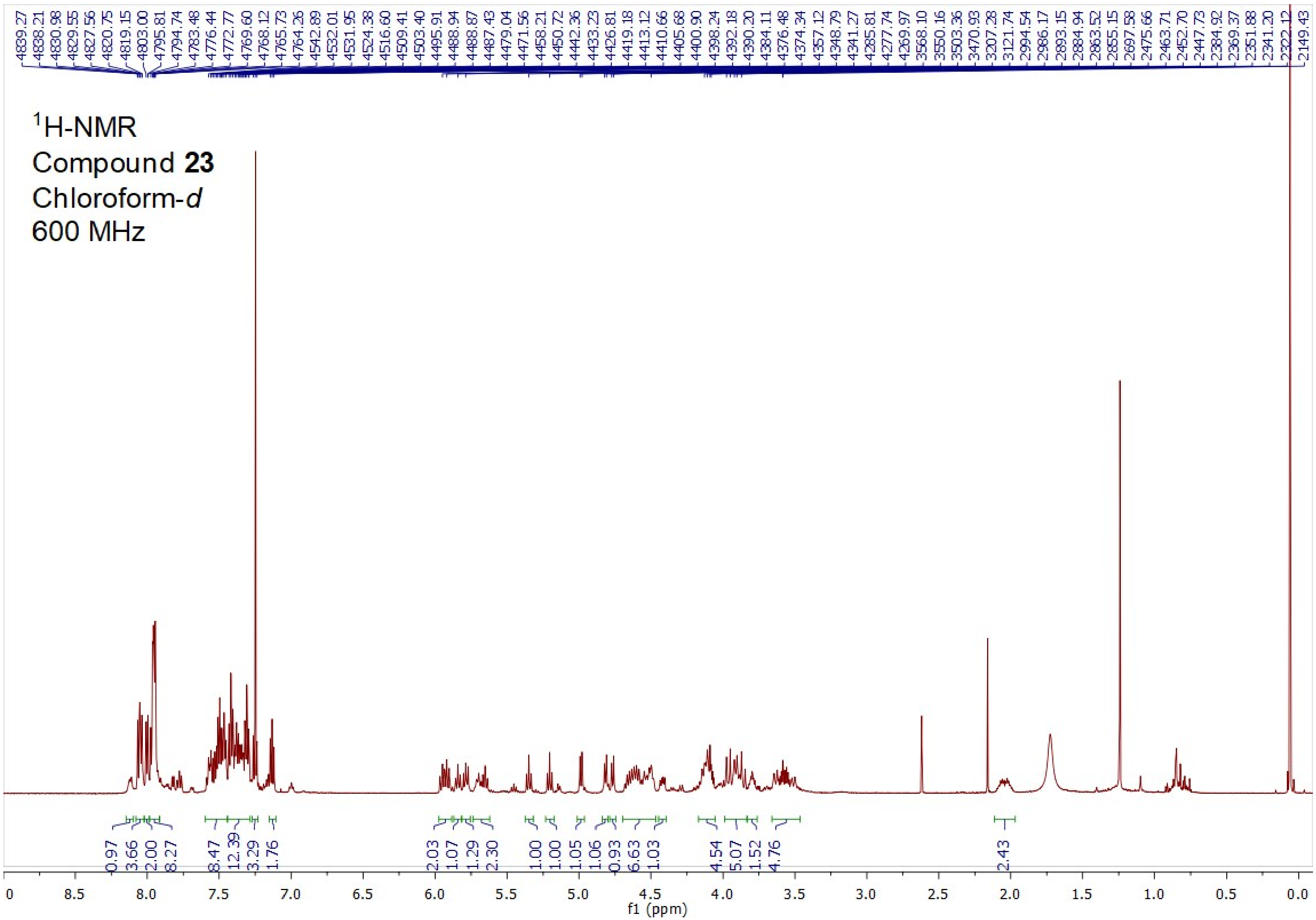
^{13}C-NMR
Compound **21**
Acetone-d_6
125 MHz
f1 (ppm)

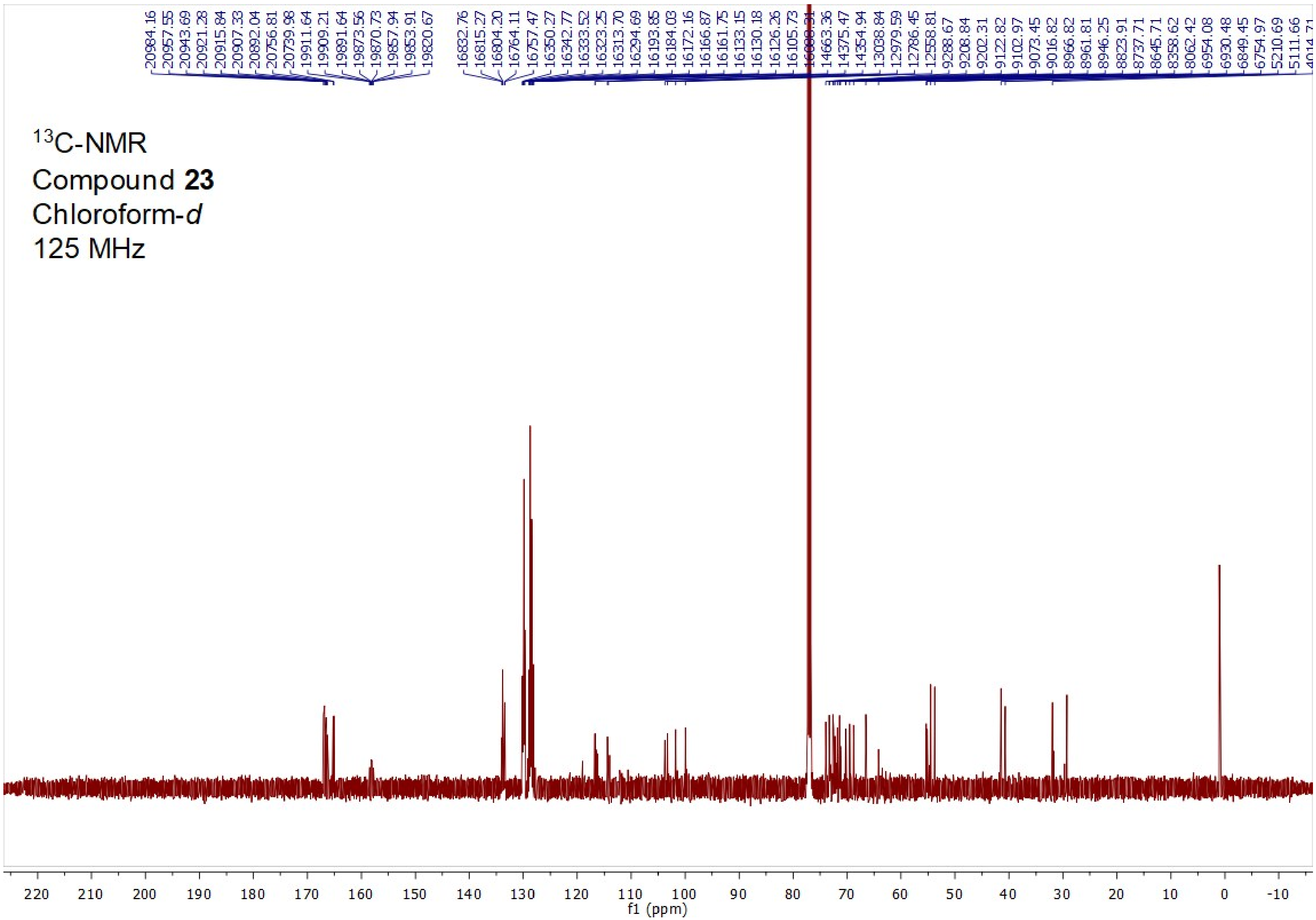


1H-NMR
Compound 22
Acetone-d6
600 MHz
f1 (ppm)

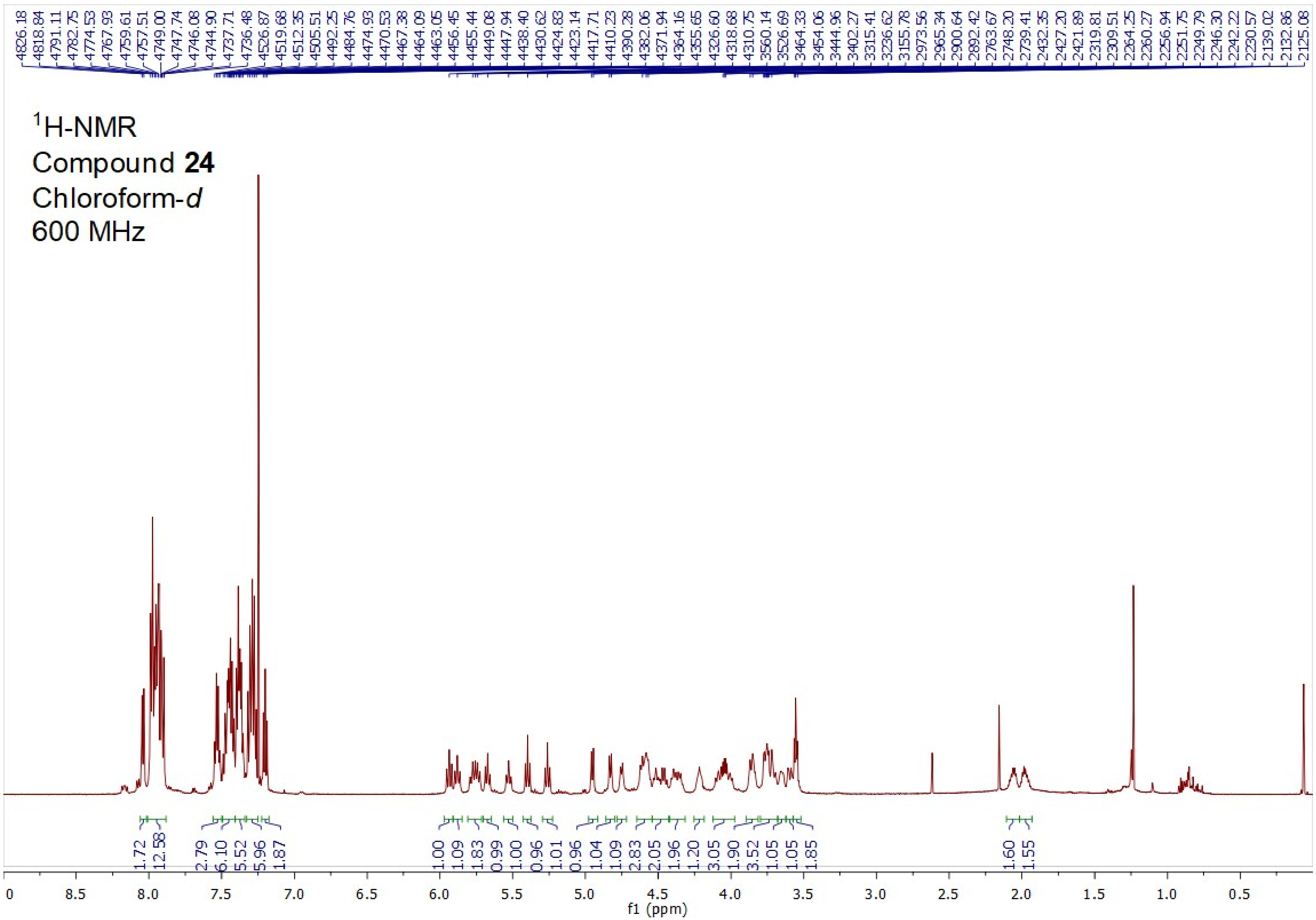


^{13}C-NMR
Compound **22**
Acetone-d_6
125 MHz
f1 (ppm)

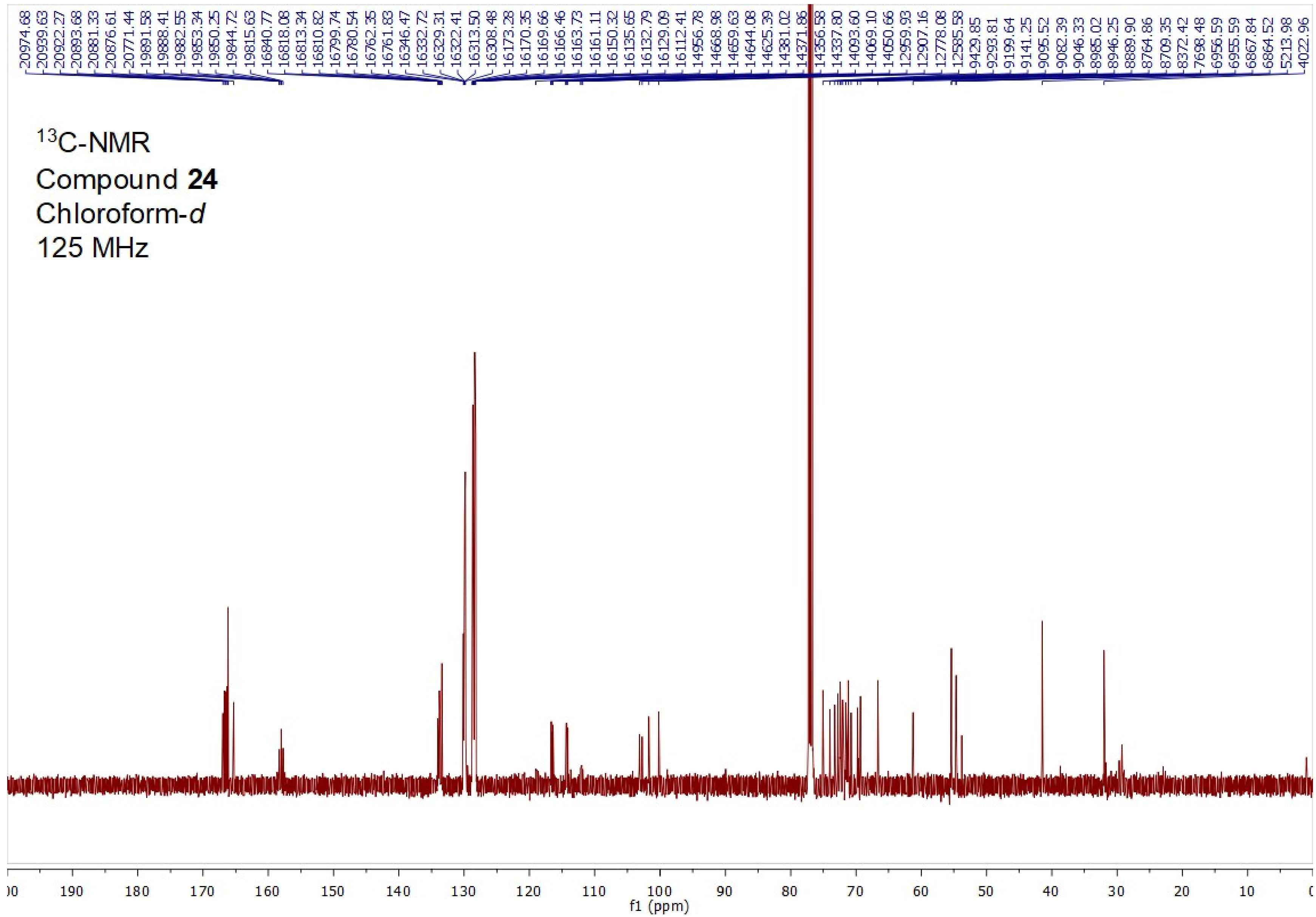

4839.27
4838.21
4830.98
4829.55
4827.56
4820.75
4819.15
4803.00
4795.81
4794.74
4783.48
4776.44
4772.77
4769.60
4768.12
4765.73
4764.26
4542.89
4532.01
4531.95
4524.38
4516.60
4509.41
4503.40
4495.91
4488.94
4488.87
4487.43
4479.04
4471.56
4458.21
4450.72
4442.36
4433.23
4426.81
4419.18
4413.12
4410.66
4405.68
4400.90
4398.24
4392.18
4390.20
4384.11
4376.48
4374.34
4357.12
4348.79
4341.27
4285.81
4277.74
4269.97
3568.10
3550.16
3503.36
3470.93
3207.28
3121.74
2994.54
2986.17
2893.15
2884.94
2863.52
2855.15
2697.58
2475.66
2463.71
2452.70
2447.73
2384.92
2369.37
2351.88
2341.20
2322.12
2149.43
^{1}H-NMR
Compound **23**
Chloroform-*d*
600 MHz
0.97
3.66
2.00
8.27
8.47
12.39
3.29
1.76
2.03
1.07
1.29
2.30
1.00
1.00
1.05
1.06
0.93
6.63
1.03
4.54
5.07
1.52
4.76
2.43
0
8.5
8.0
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)

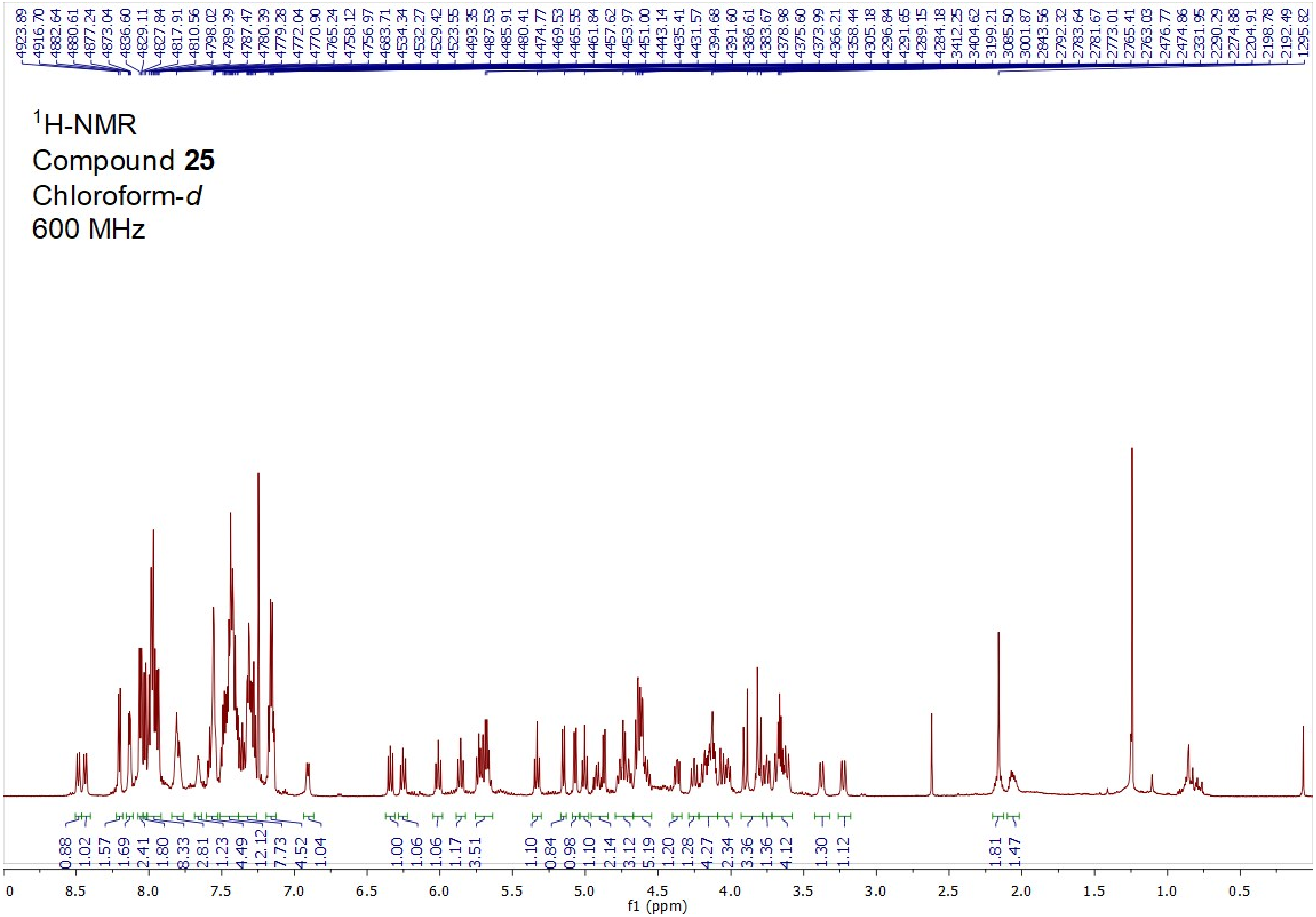


^{13}C-NMR
Compound **23**
Chloroform-*d*
125 MHz
f1 (ppm)

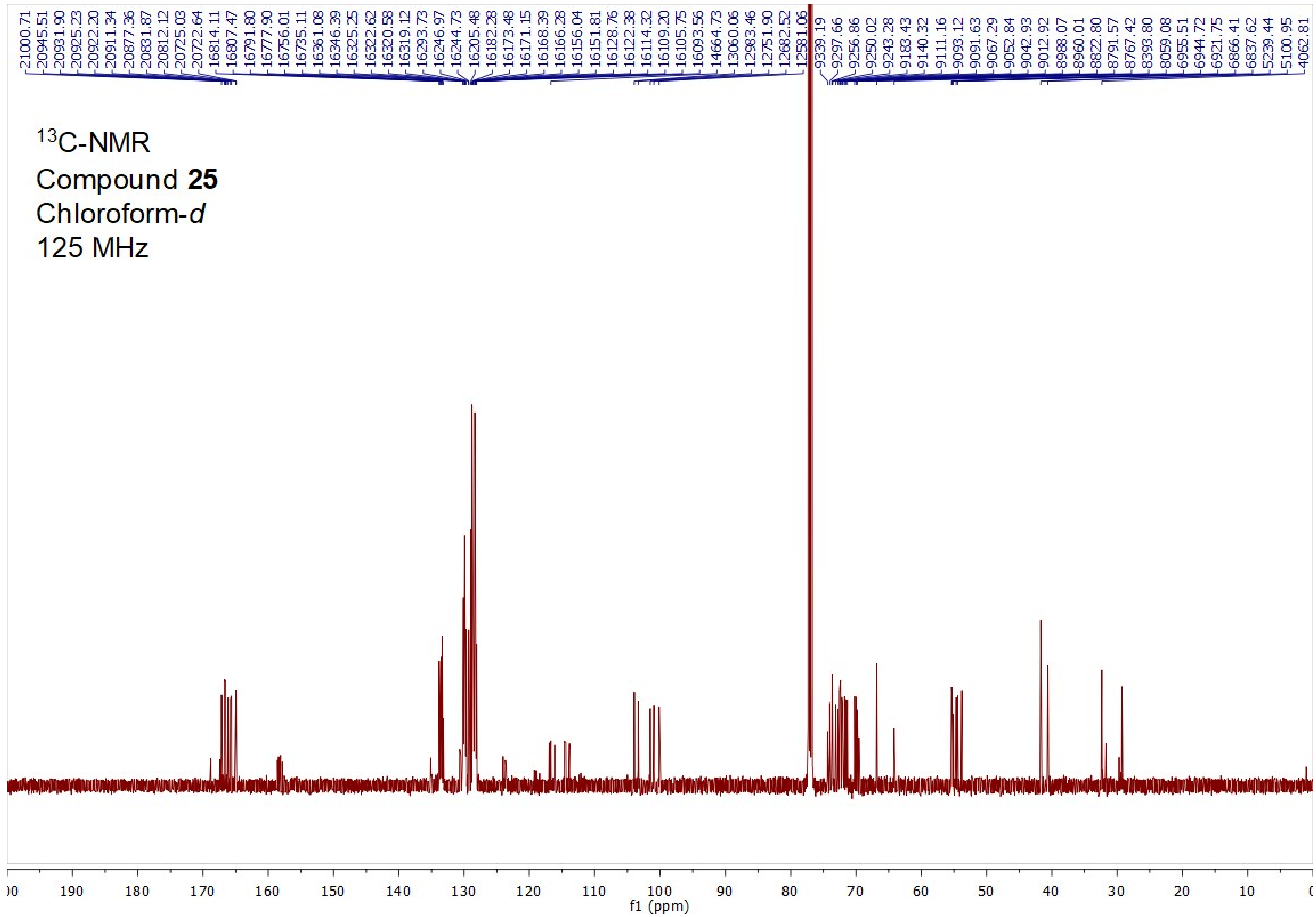


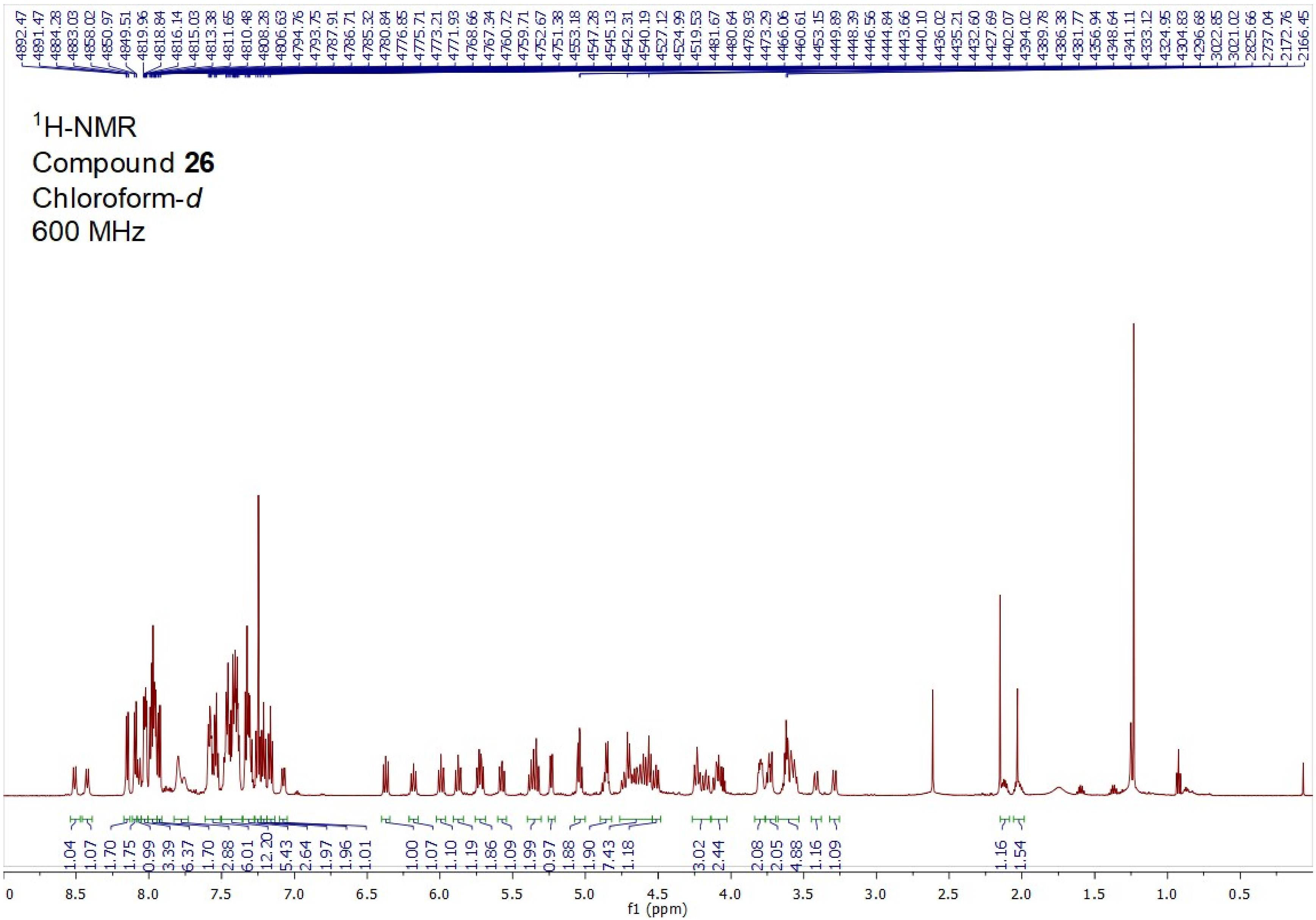
^{1}H-NMR
Compound **24**
Chloroform-*d*
600 MHz
f1 (ppm)


13C-NMR
Compound 24
Chloroform-d
125 MHz
f1 (ppm)

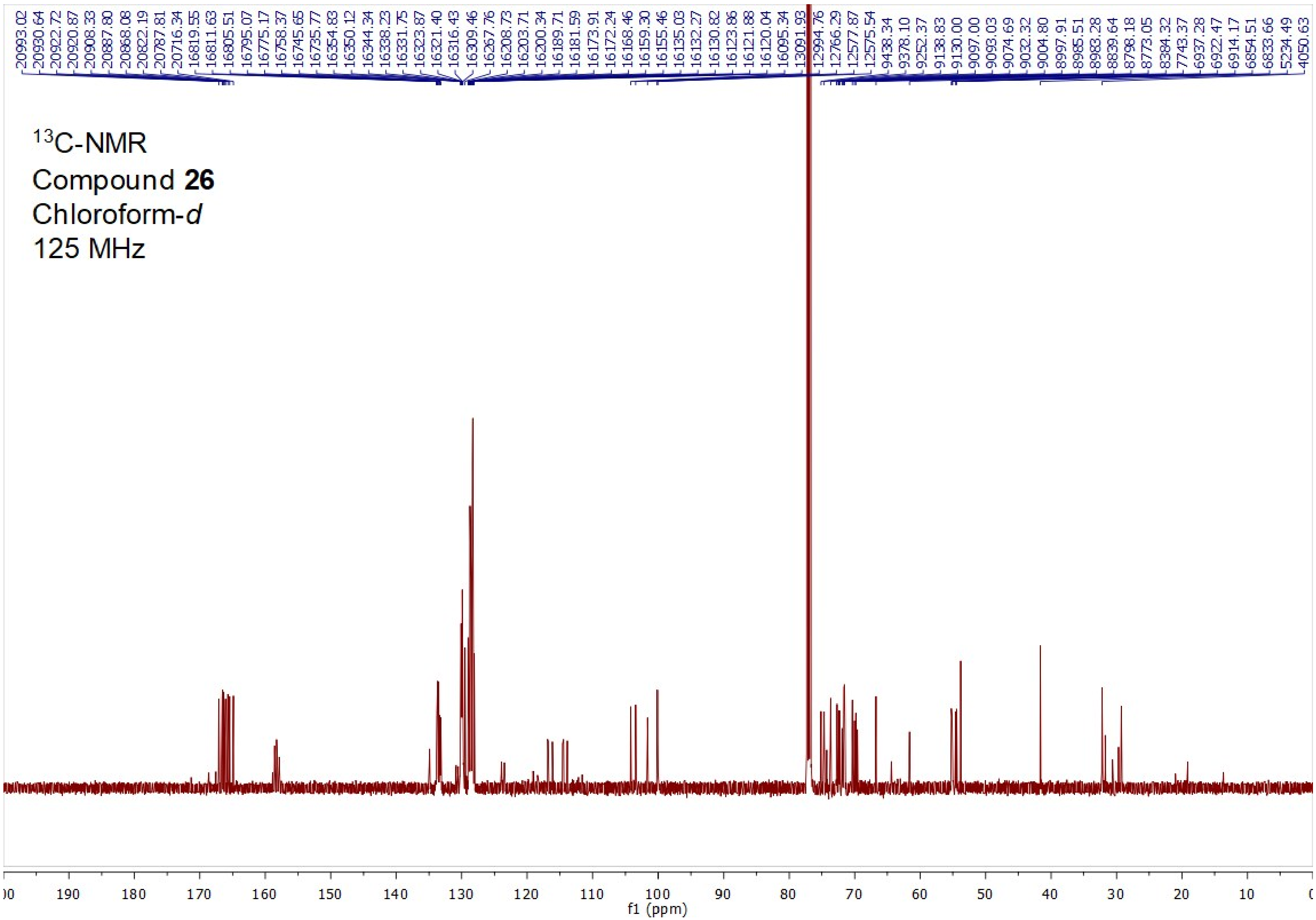


^{1}H-NMR
Compound **25**
Chloroform-*d*
600 MHz
f1 (ppm)

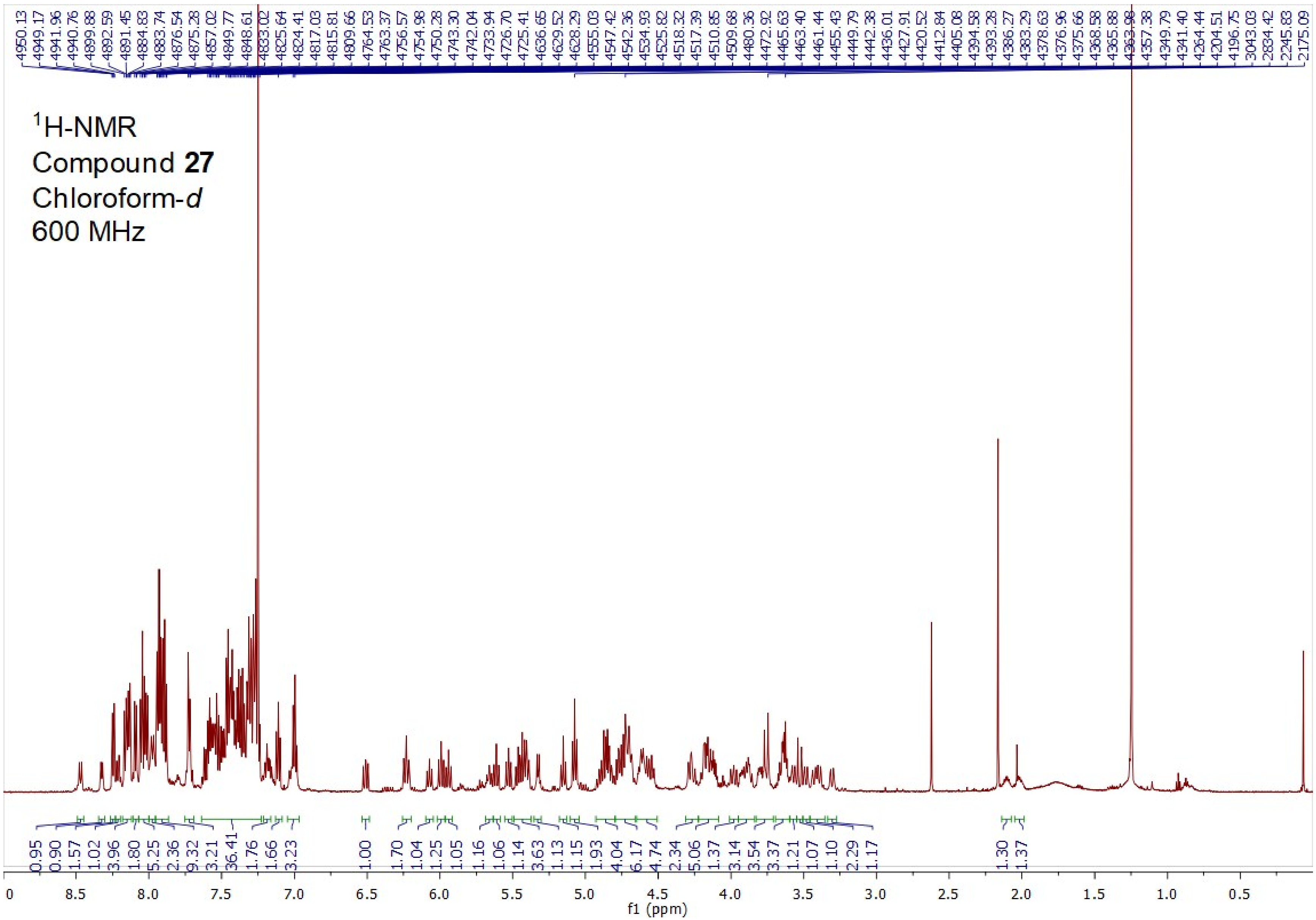

^{13}C-NMR
Compound **25**
Chloroform-*d*
125 MHz
f1 (ppm)



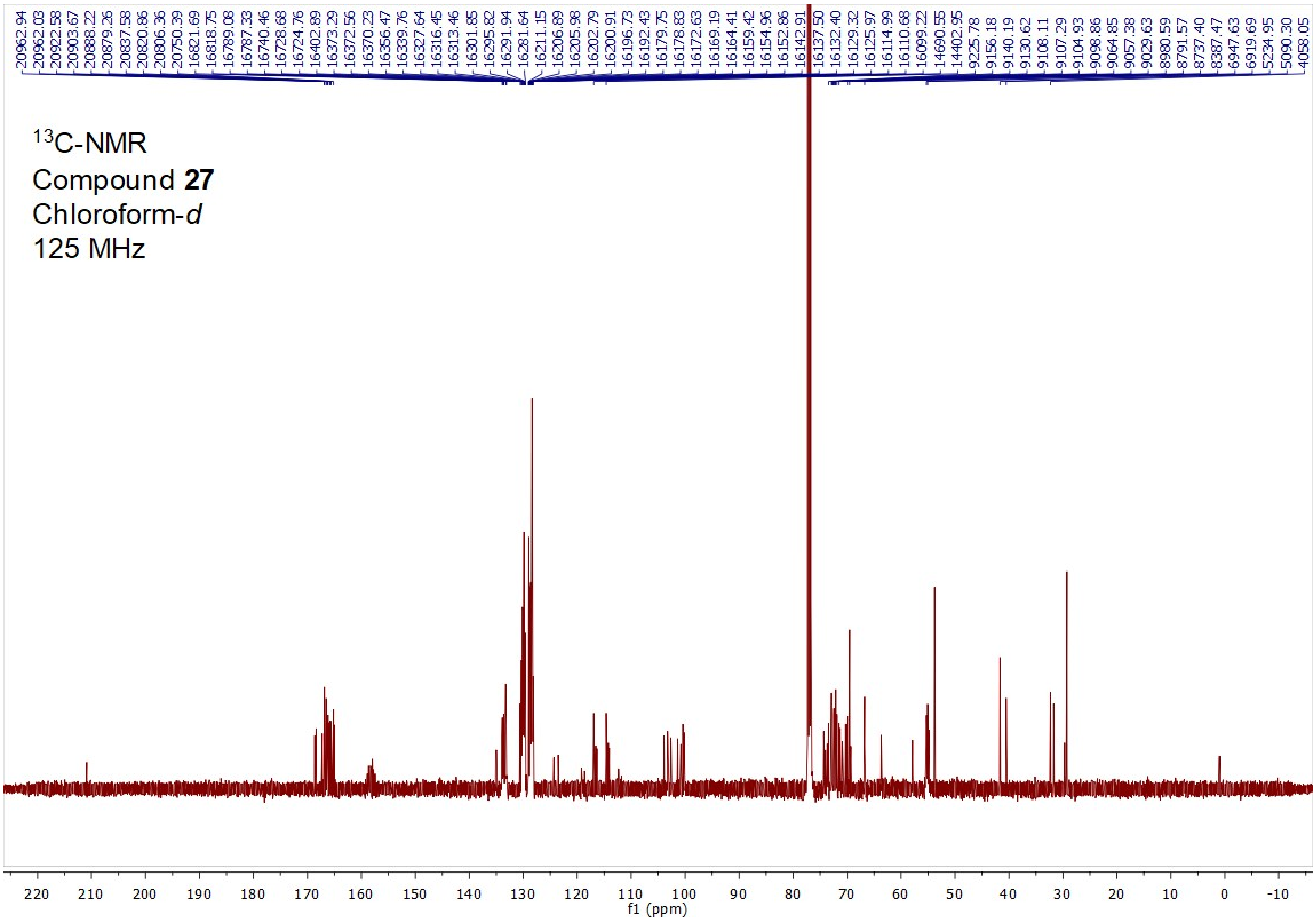
^{1}H-NMR
Compound **26**
Chloroform-*d*
600 MHz
f1 (ppm)



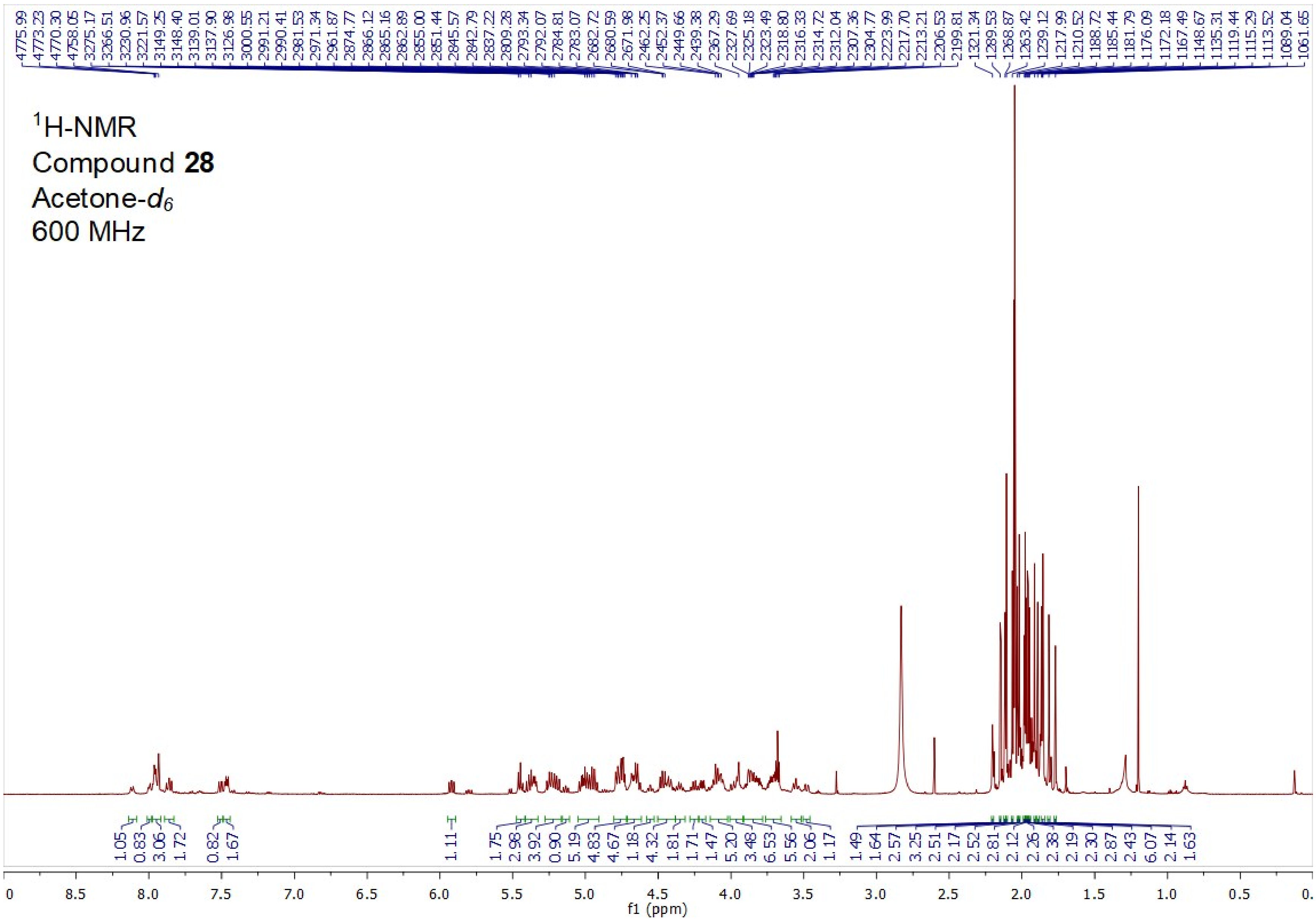
^{13}C-NMR
Compound **26**
Chloroform-*d*
125 MHz
f1 (ppm)



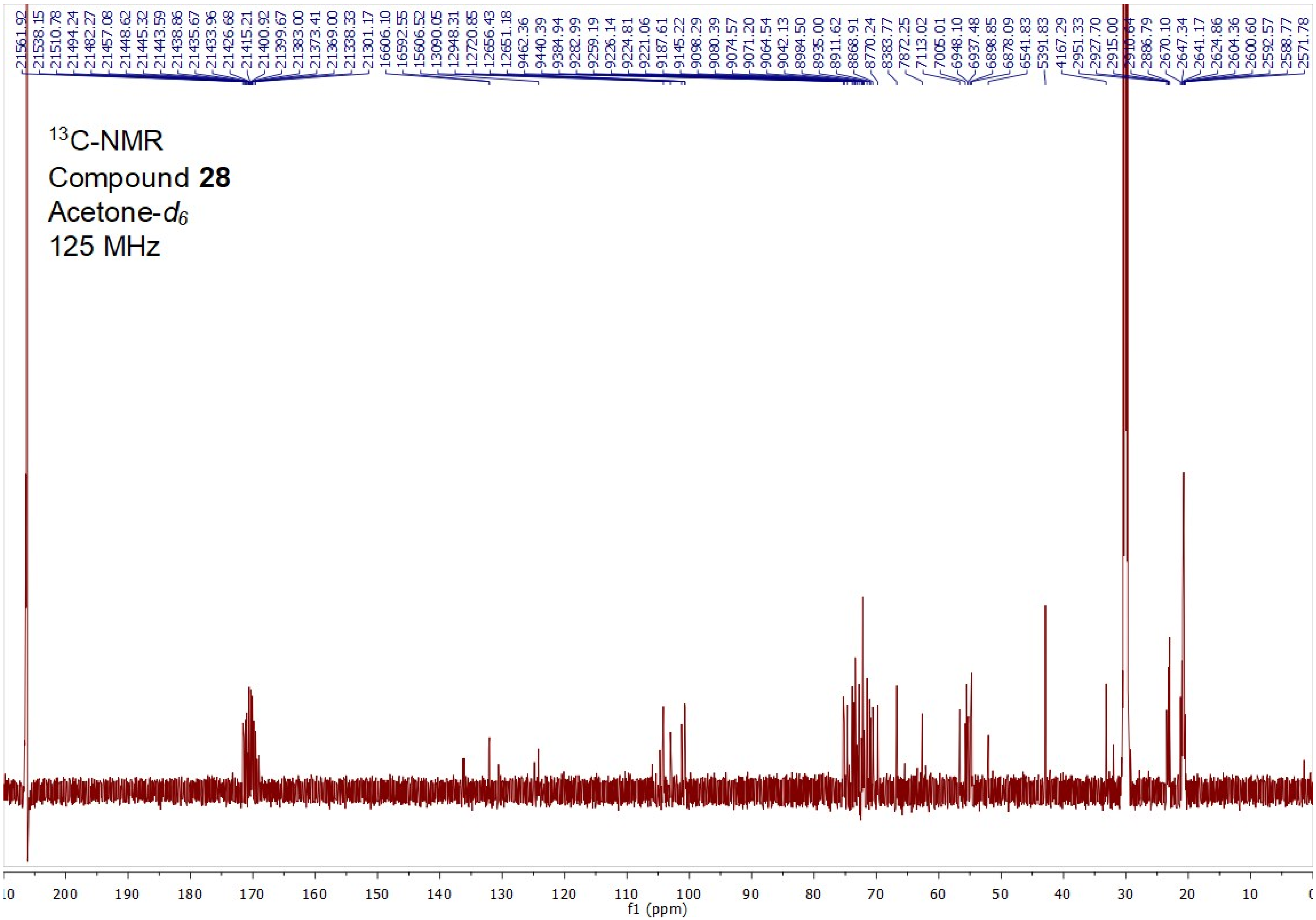
^{1}H-NMR
Compound **27**
Chloroform-*d*
600 MHz
f1 (ppm)



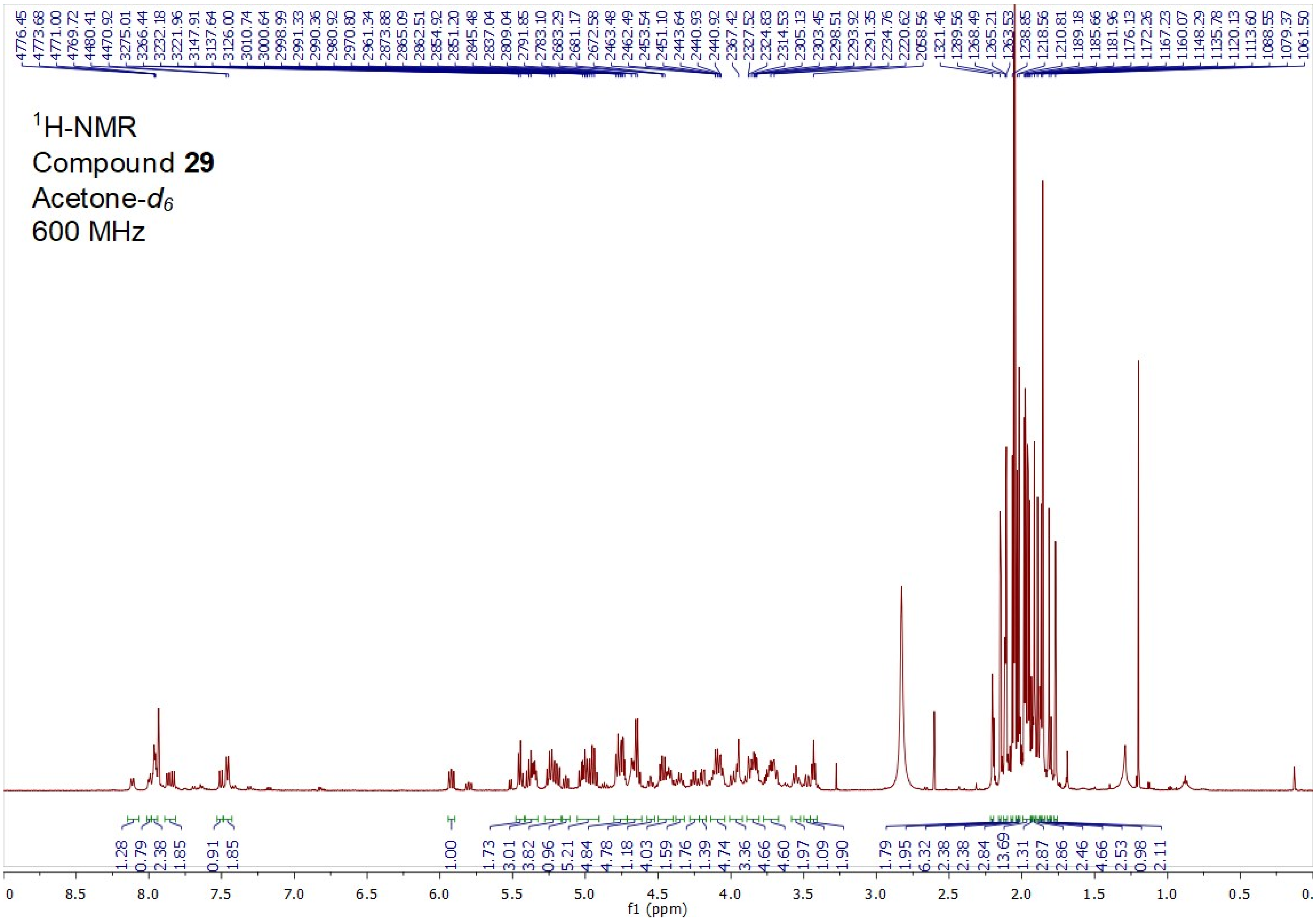
^{13}C-NMR
Compound **27**
Chloroform-*d*
125 MHz
f1 (ppm)



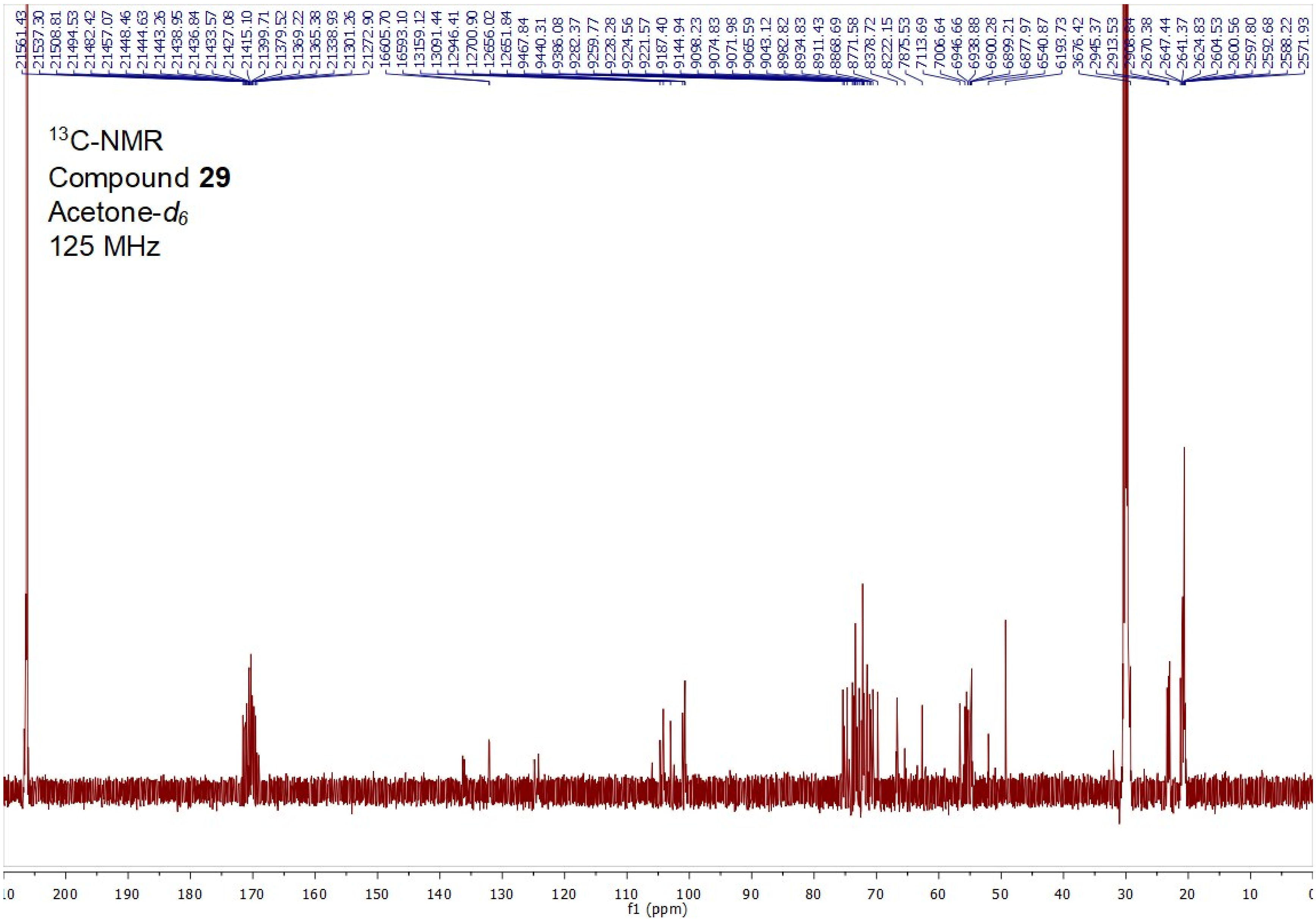
[1]H-NMR
Compound **28**
Acetone-d_6
600 MHz
f1 (ppm)



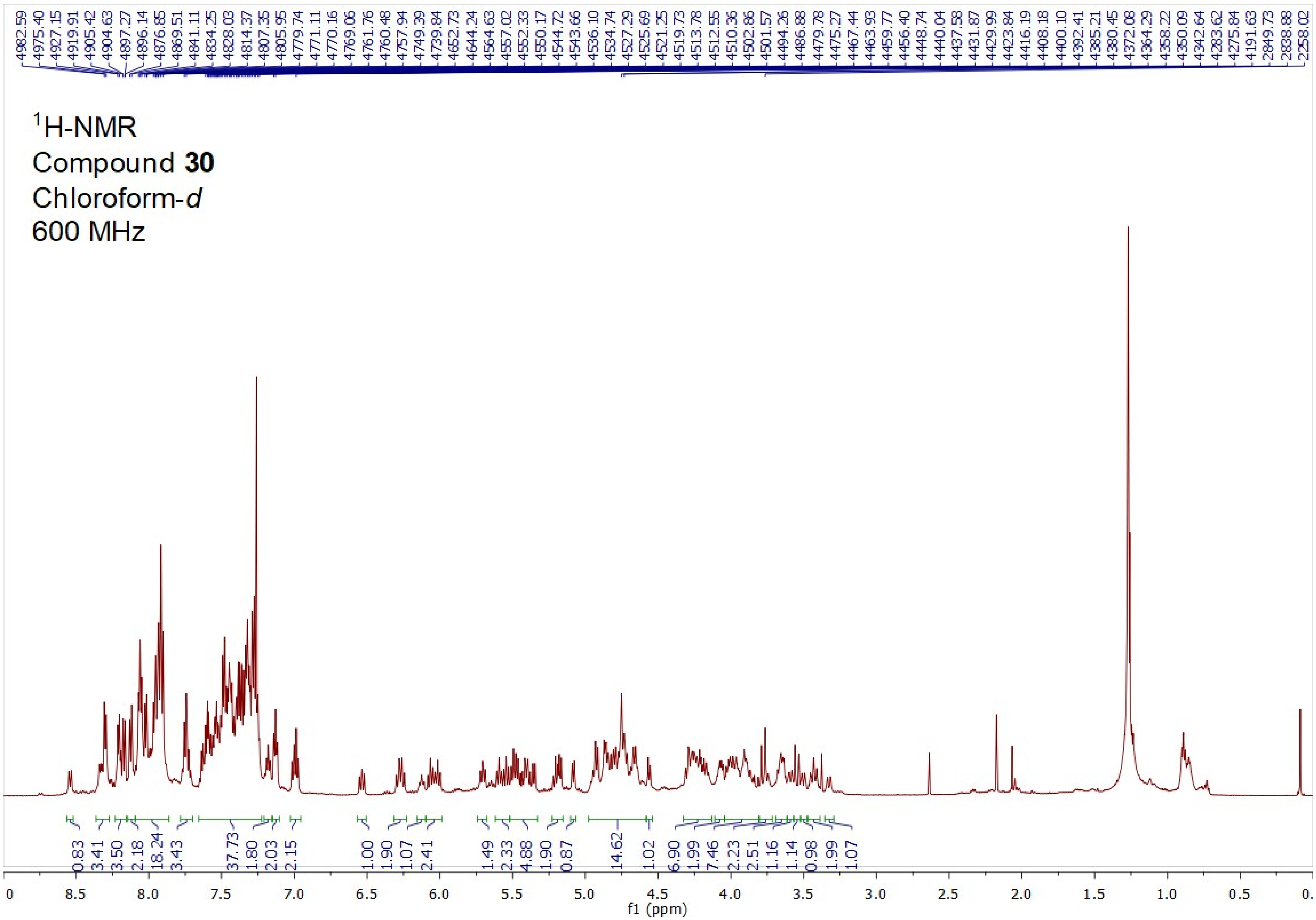
^{13}C-NMR
Compound **28**
Acetone-d_6
125 MHz
21561.92
21538.15
21510.78
21494.24
21482.27
21457.08
21448.62
21445.32
21443.59
21438.86
21435.67
21433.96
21426.68
21415.21
21400.92
21399.67
21383.00
21373.41
21369.00
21338.33
21301.17
16606.10
16592.55
15606.52
13090.05
12948.31
12720.85
12656.43
12651.18
9462.36
9440.39
9384.94
9282.99
9259.19
9226.14
9224.81
9221.06
9187.61
9145.22
9098.29
9080.39
9074.57
9071.20
9064.54
9042.13
8984.50
8935.00
8911.62
8868.91
8770.24
8383.77
7872.25
7113.02
7005.01
6948.10
6937.48
6898.85
6878.09
6541.83
5391.83
4167.29
2951.33
2927.70
2915.00
2886.79
2670.10
2647.34
2641.17
2624.86
2604.36
2600.60
2592.57
2588.77
2571.78
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



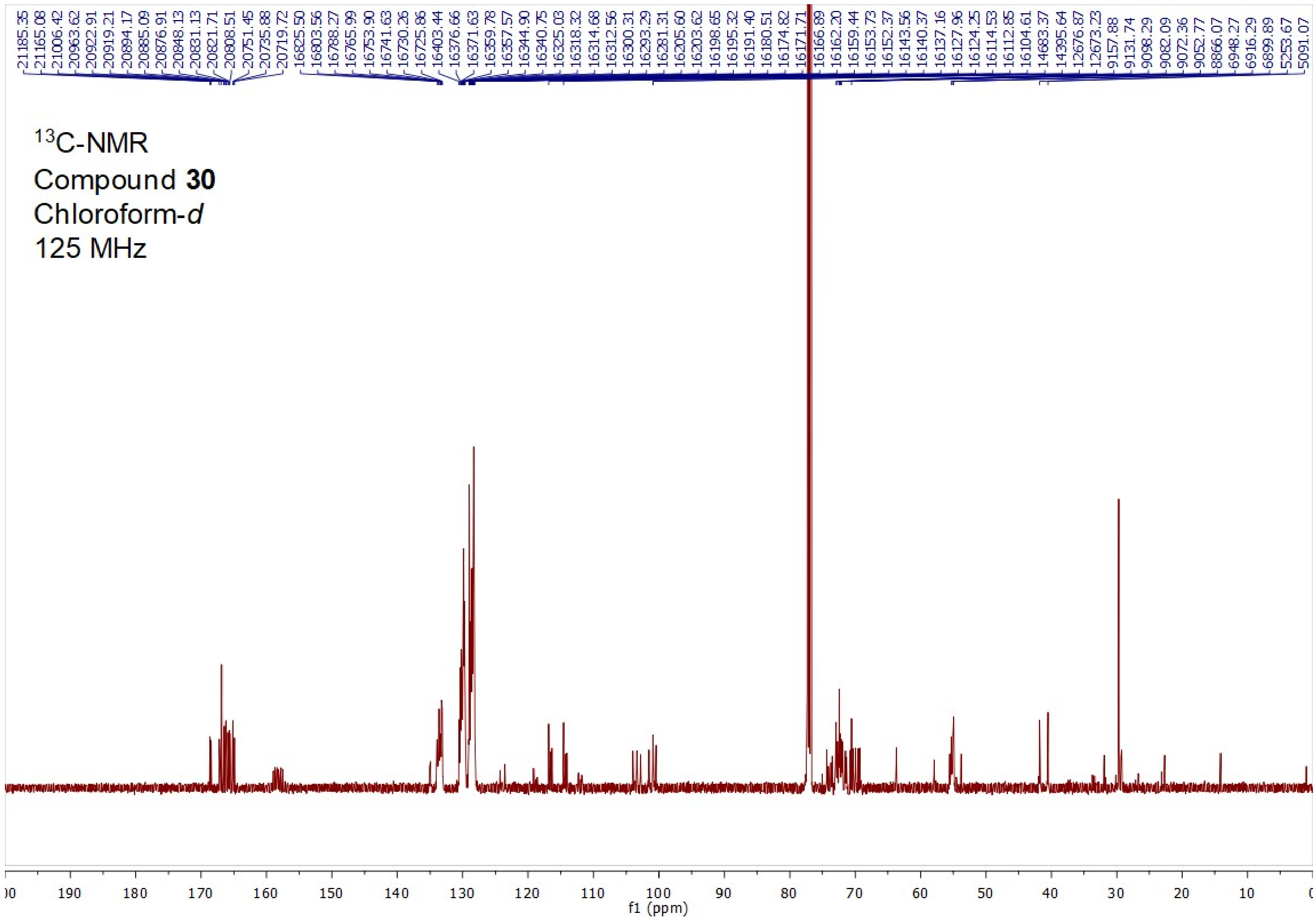
^{1}H-NMR
Compound **29**
Acetone-d_6
600 MHz
f1 (ppm)



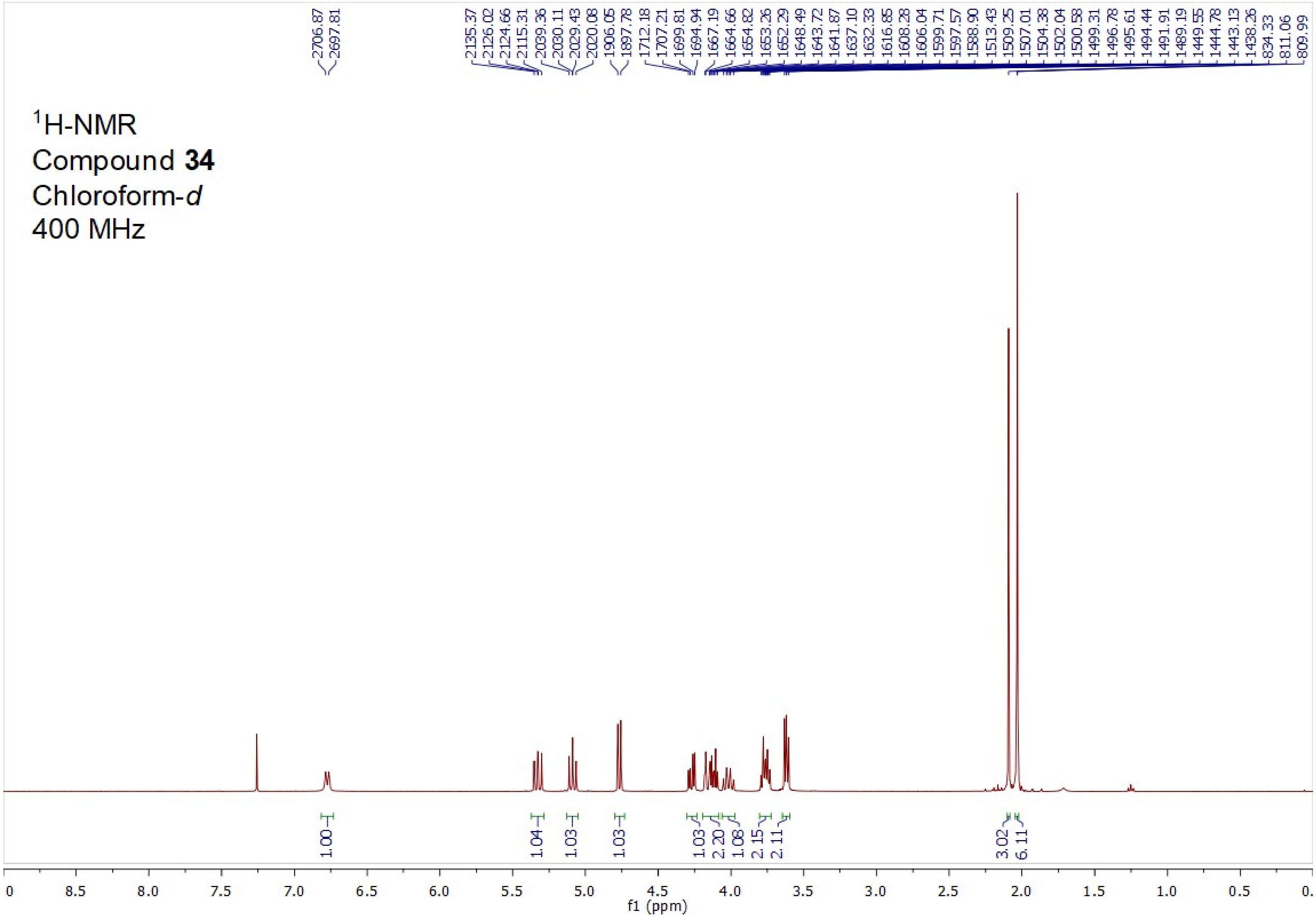
^{13}C-NMR
Compound **29**
Acetone-d_6
125 MHz
f1 (ppm)



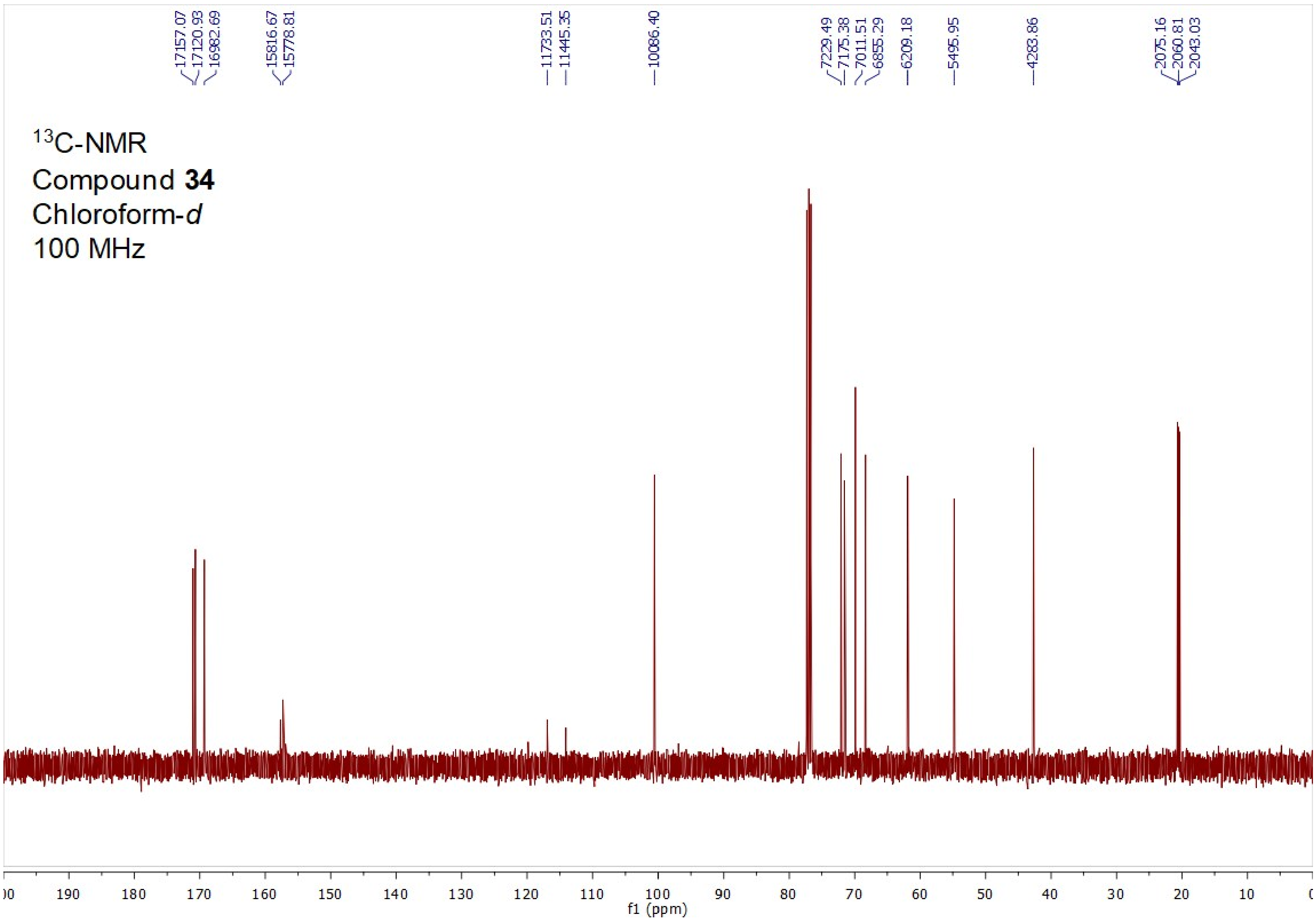
1H-NMR
Compound 30
Chloroform-d
600 MHz
f1 (ppm)



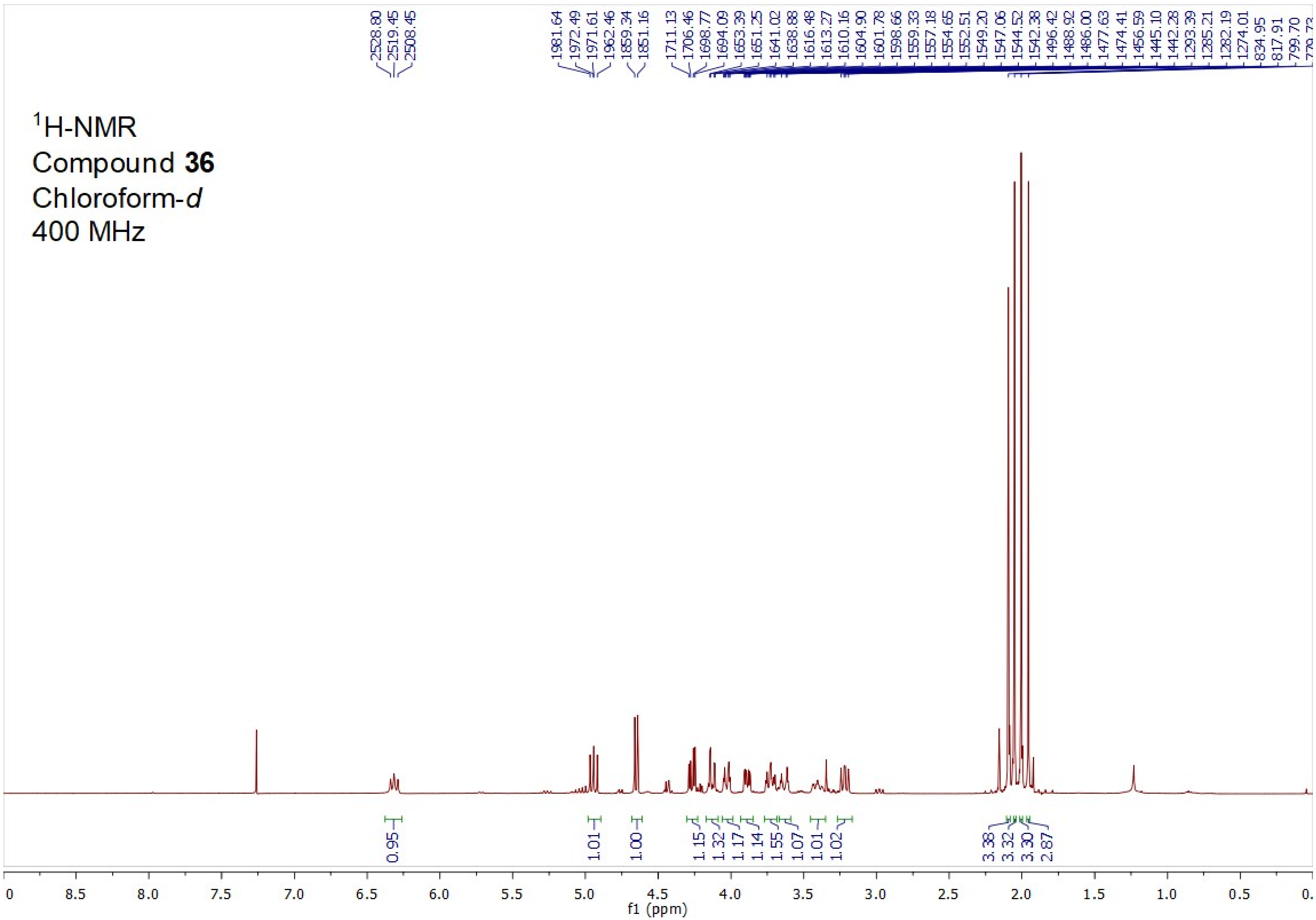
^{13}C-NMR
Compound **30**
Chloroform-*d*
125 MHz
f1 (ppm)



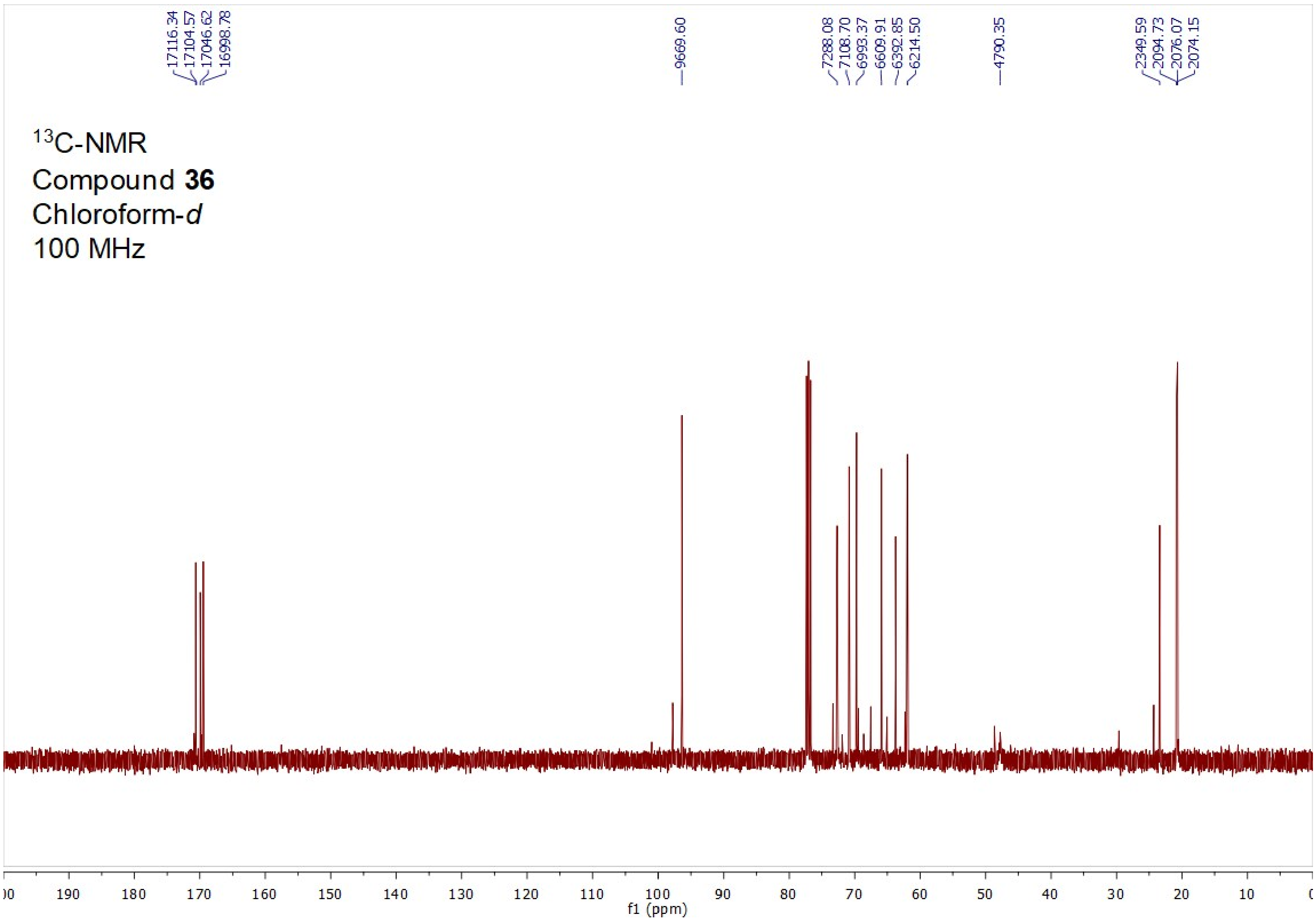
^{1}H-NMR
Compound **34**
Chloroform-*d*
400 MHz
f1 (ppm)



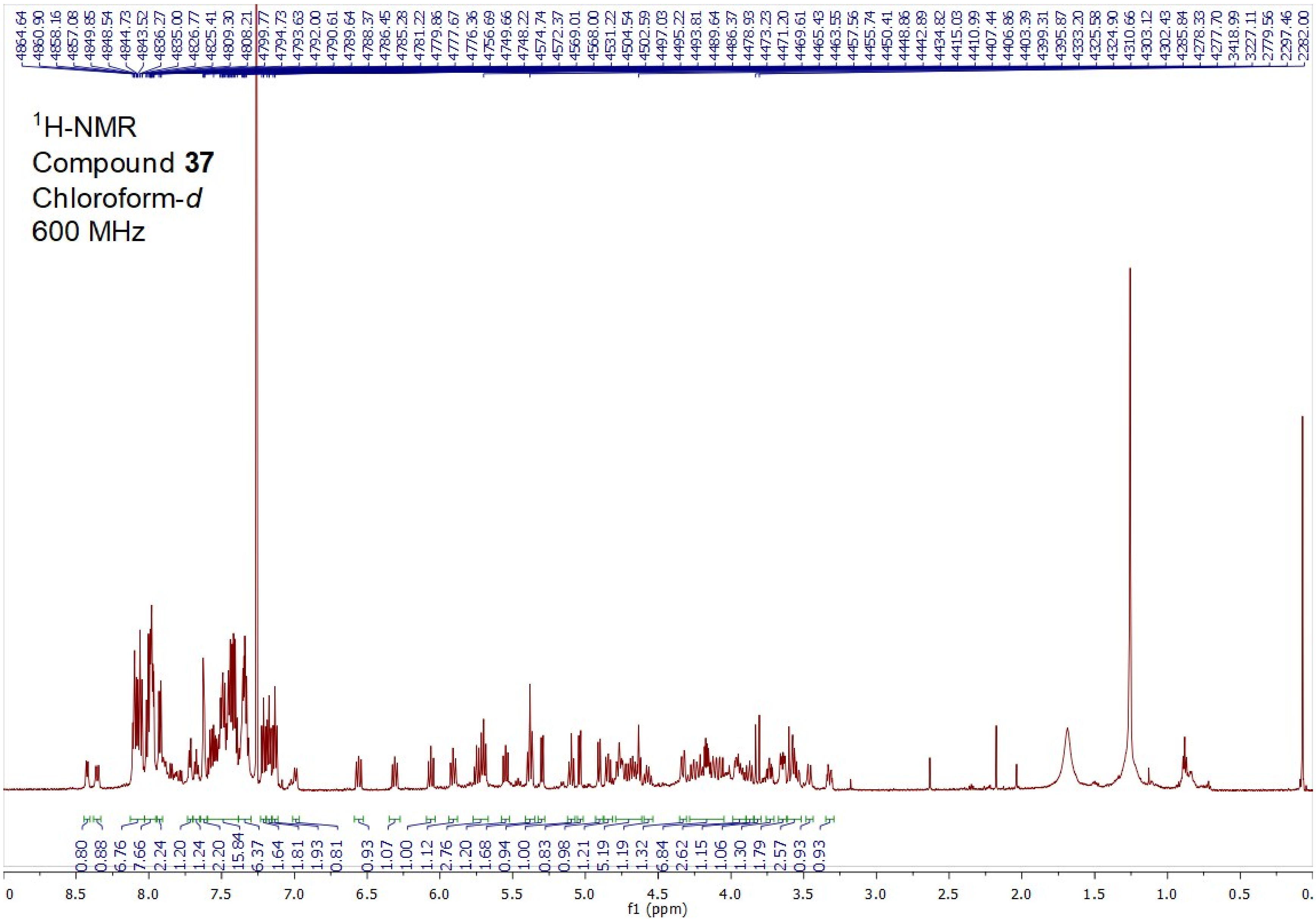
17157.07
17120.93
16982.69
15816.67
15778.81
11733.51
11445.35
10086.40
7229.49
7175.38
7011.51
6855.29
6209.18
5495.95
4283.86
2075.16
2060.81
2043.03
13C-NMR
Compound 34
Chloroform-d
100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



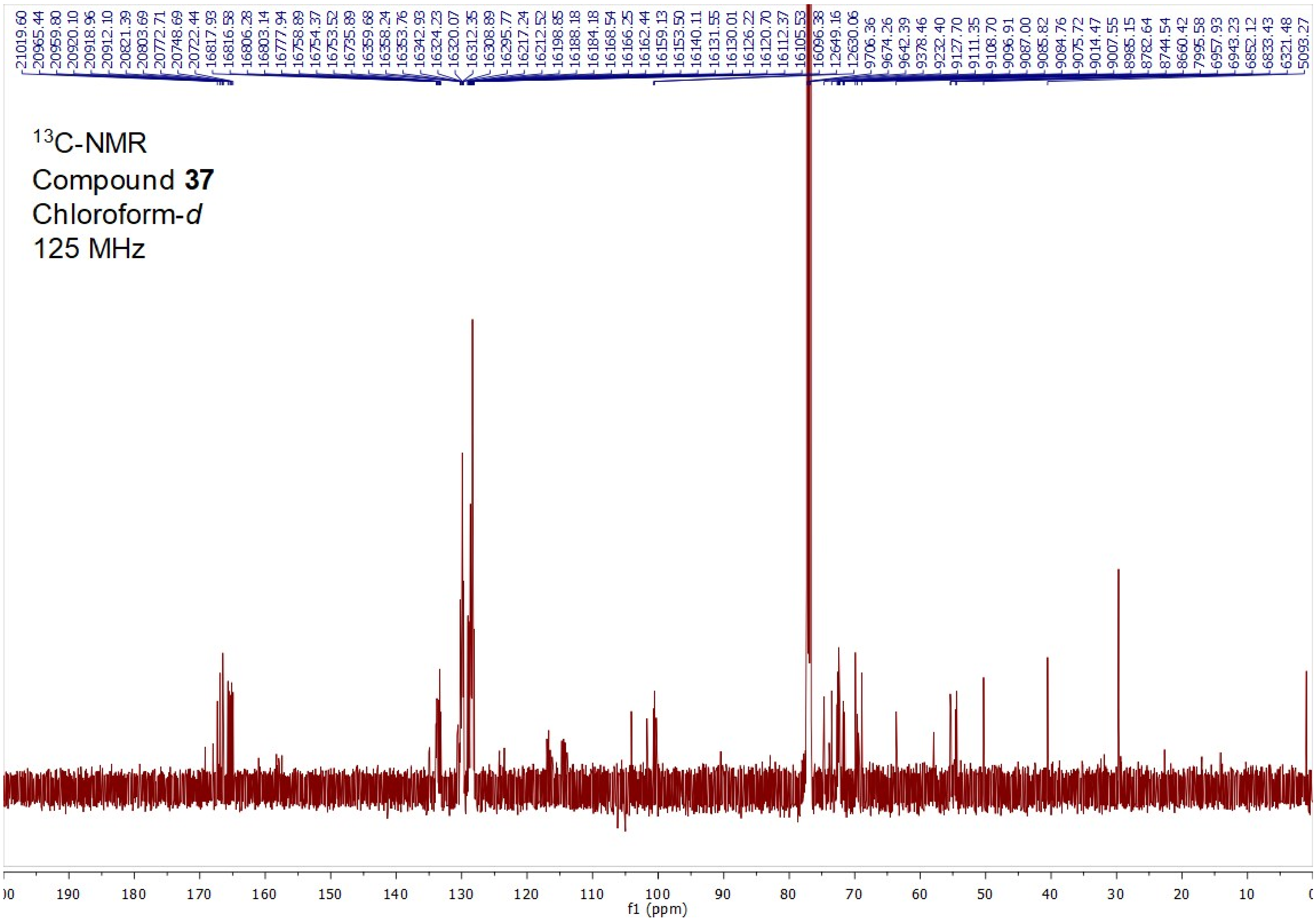
^{1}H-NMR
Compound **36**
Chloroform-*d*
400 MHz
f1 (ppm)

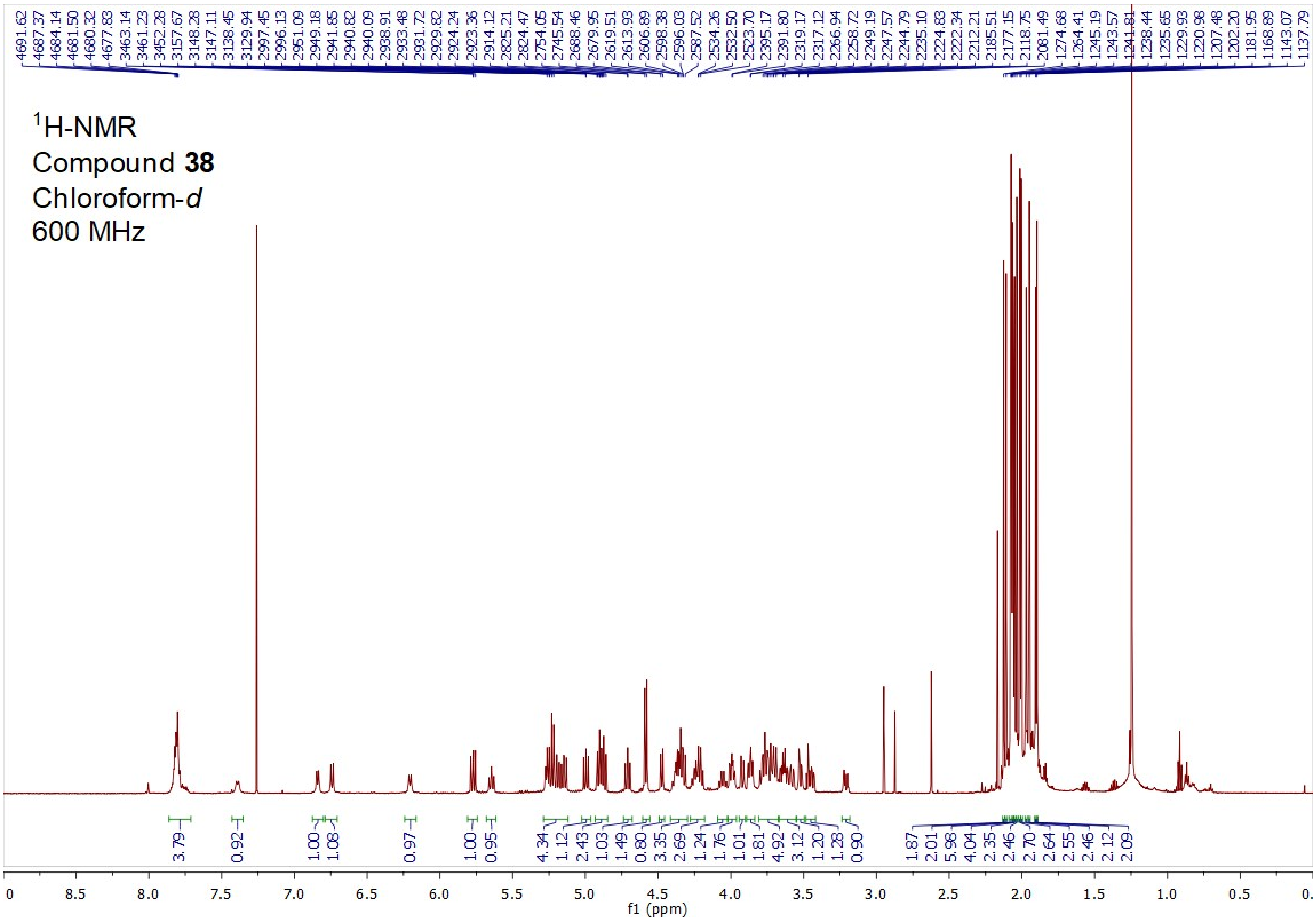


17116.34
17104.57
17046.62
16998.78
9669.60
7288.08
7108.70
6993.37
6609.91
6392.85
6214.50
4790.35
2349.59
2094.73
2076.07
2074.15
^{13}C-NMR
Compound **36**
Chloroform-*d*
100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

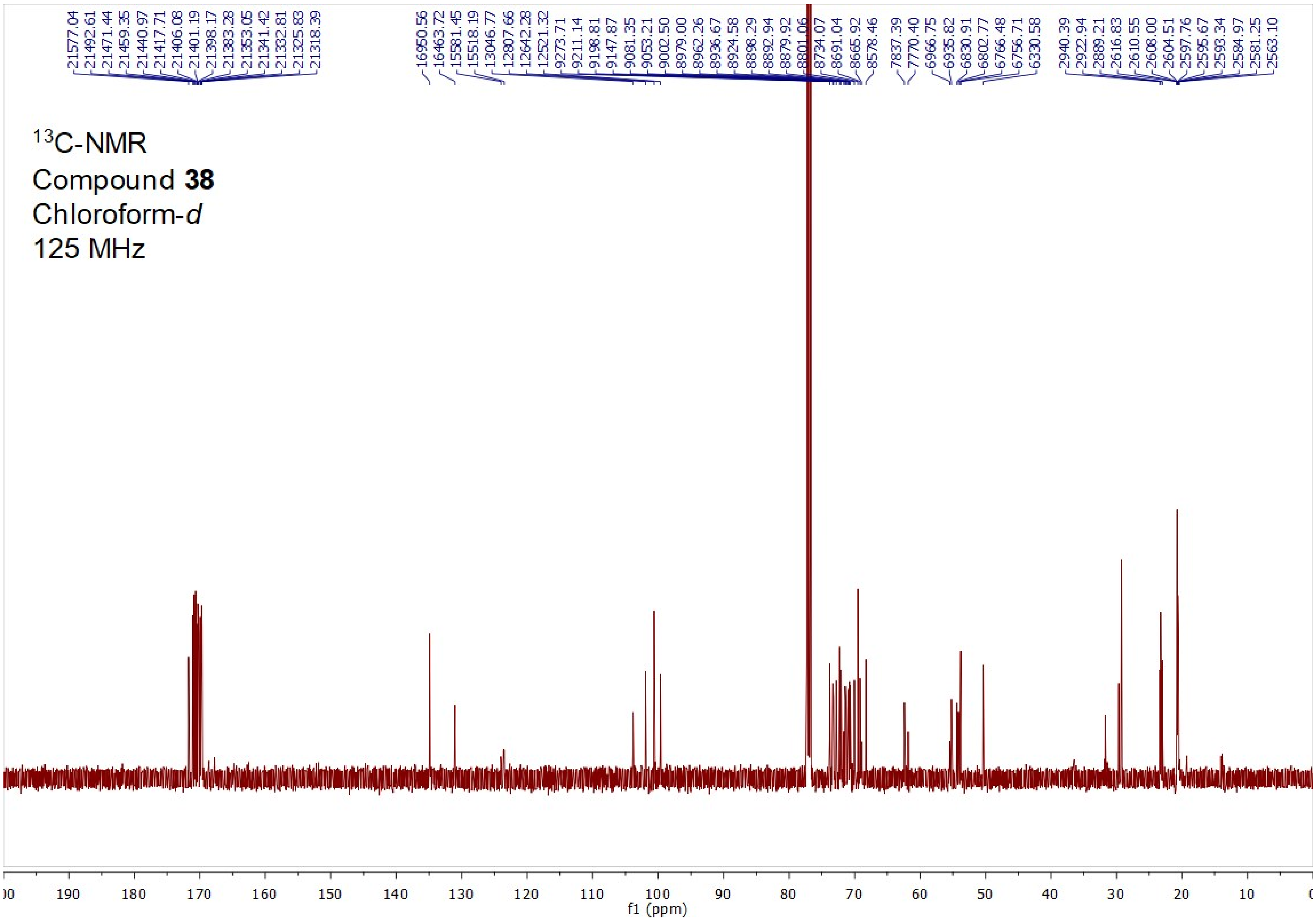


^{1}H-NMR
Compound **37**
Chloroform-*d*
600 MHz
f1 (ppm)

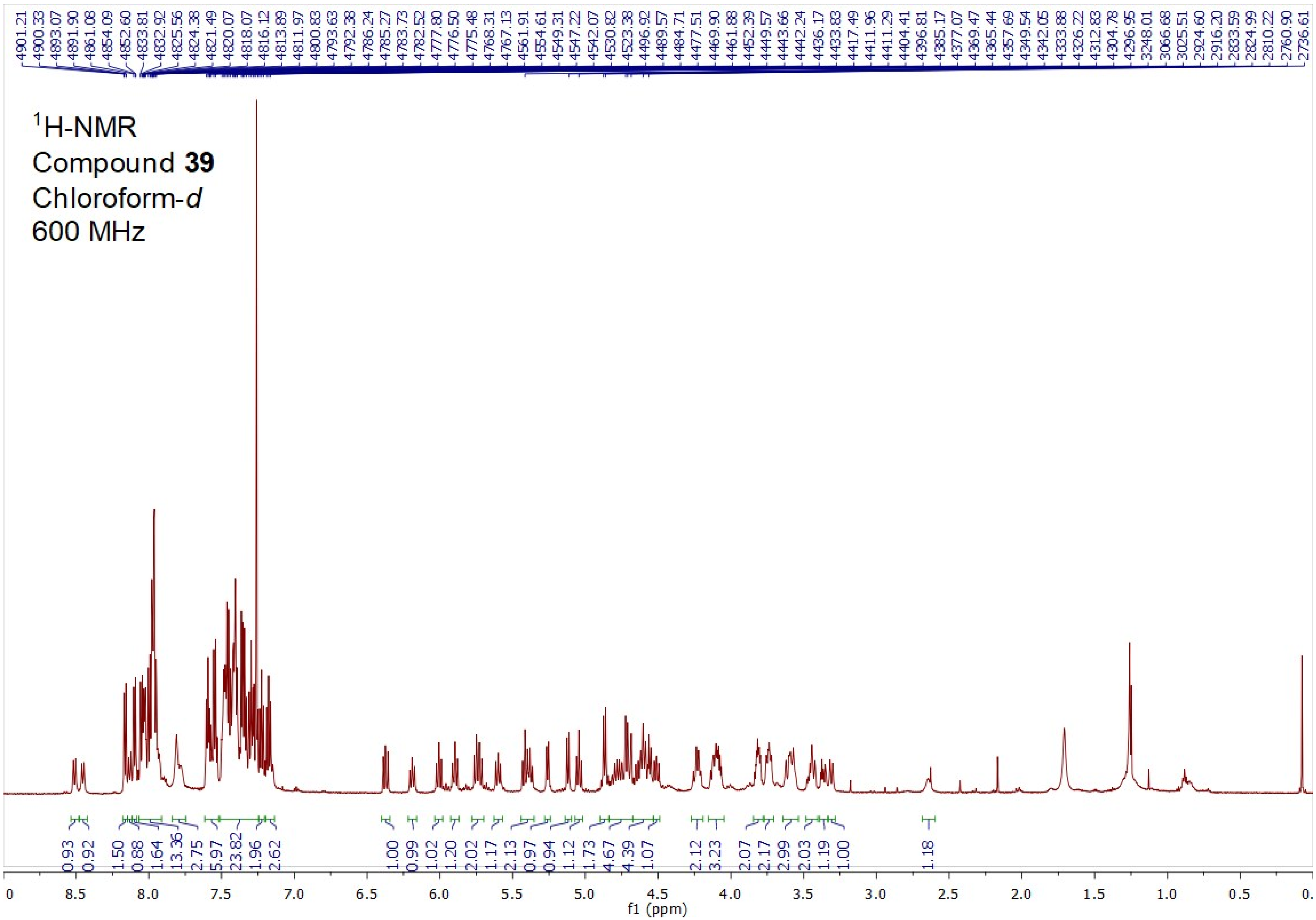

21019.60
20965.44
20959.80
20920.10
20918.96
20912.10
20821.39
20803.69
20772.71
20748.69
20722.44
16817.93
16816.58
16806.28
16803.14
16777.94
16758.89
16754.37
16753.52
16735.89
16359.68
16358.24
16353.76
16342.93
16324.23
16320.07
16312.35
16308.89
16295.77
16217.24
16212.52
16198.85
16188.18
16184.18
16168.54
16166.25
16162.44
16159.13
16153.50
16140.11
16131.55
16130.01
16126.22
16120.70
16112.37
16105.53
16096.38
12649.16
12630.06
9706.36
9674.26
9642.39
9378.46
9232.40
9127.70
9111.35
9108.70
9096.91
9087.00
9085.82
9084.76
9075.72
9014.47
9007.55
8985.15
8782.64
8744.54
8660.42
7995.58
6957.93
6943.23
6852.12
6833.43
6321.48
5093.27
13C-NMR
Compound **37**
Chloroform-*d*
125 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



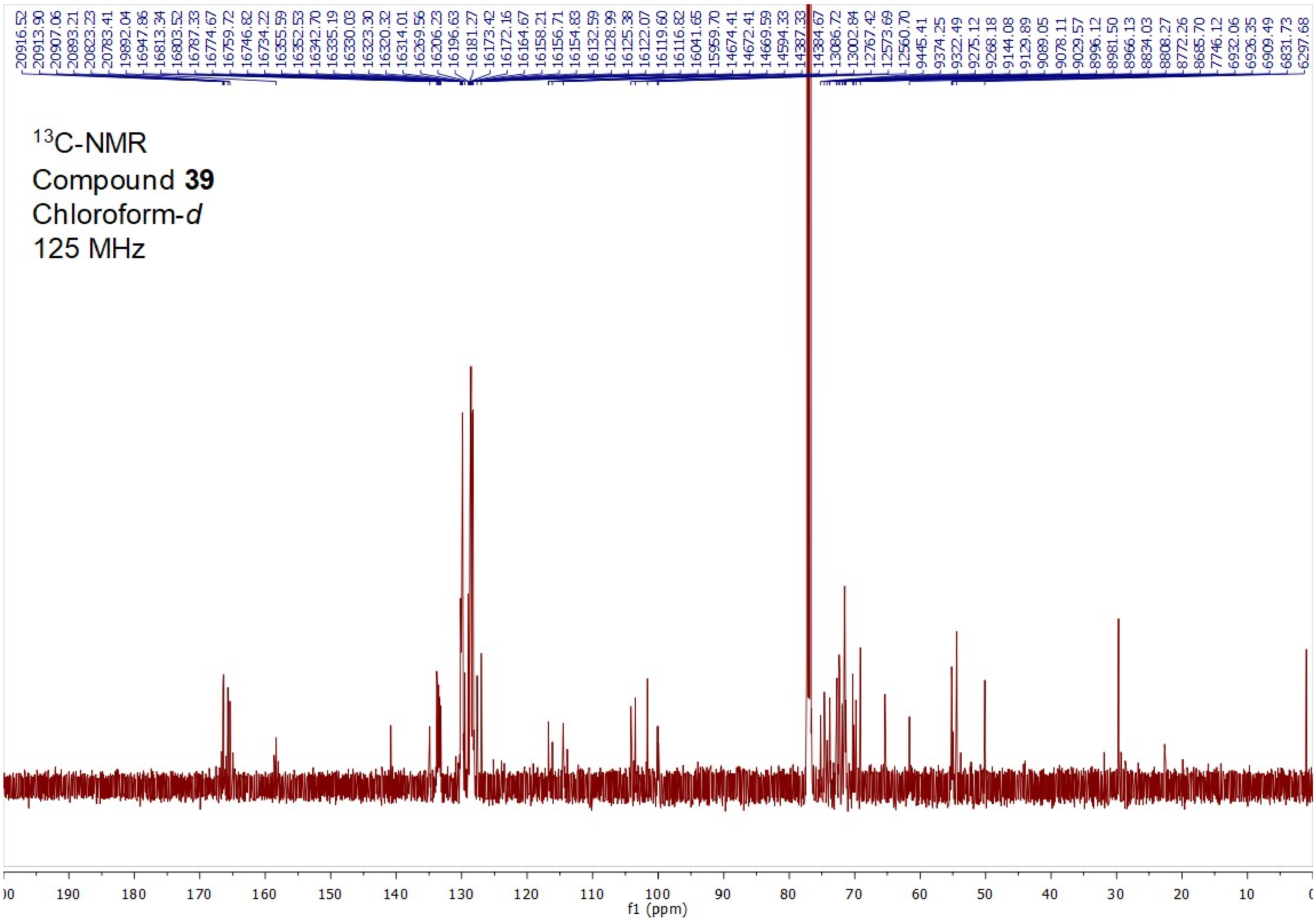
^{1}H-NMR
Compound **38**
Chloroform-*d*
600 MHz
f1 (ppm)



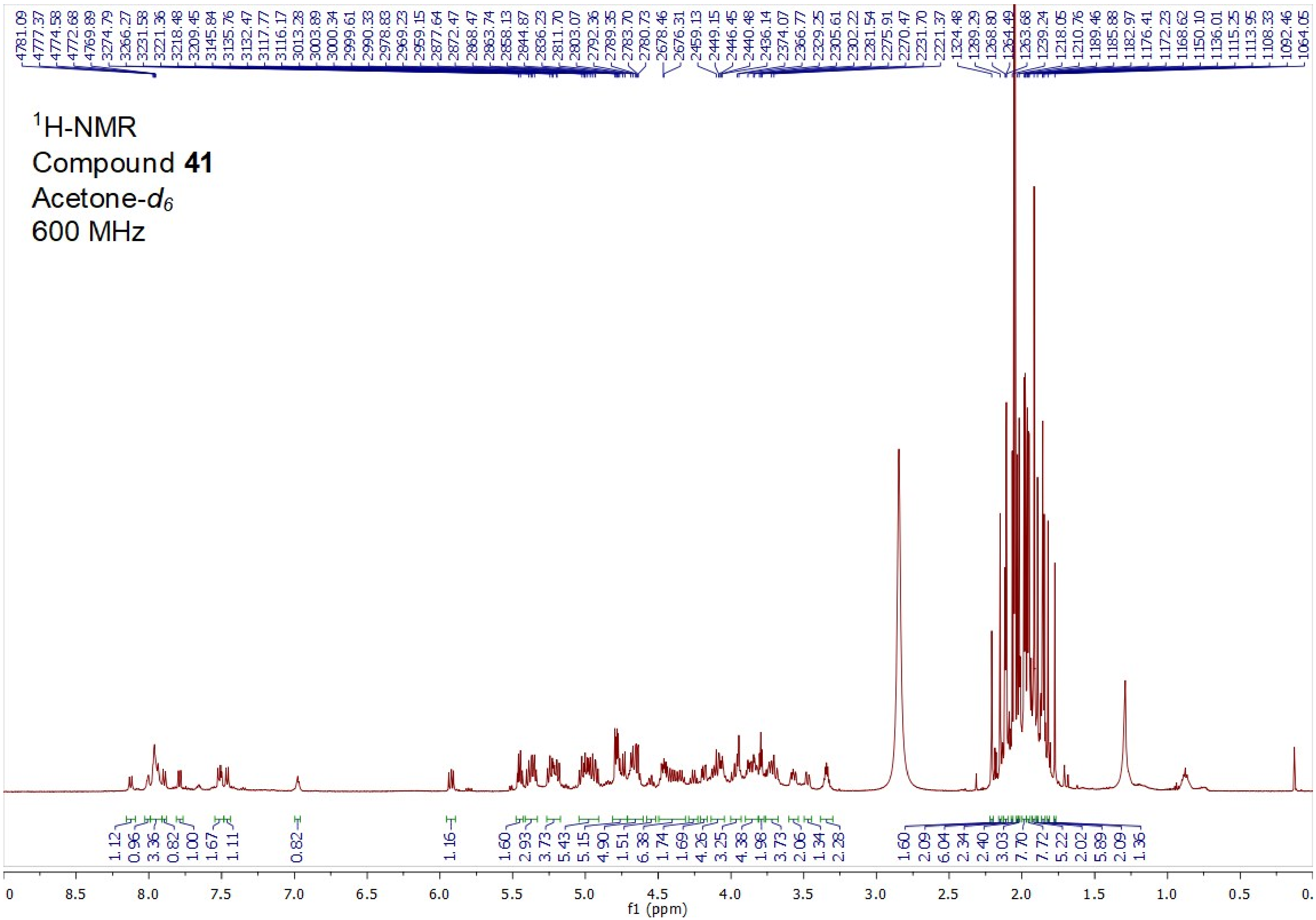
^{13}C-NMR
Compound **38**
Chloroform-*d*
125 MHz
f1 (ppm)



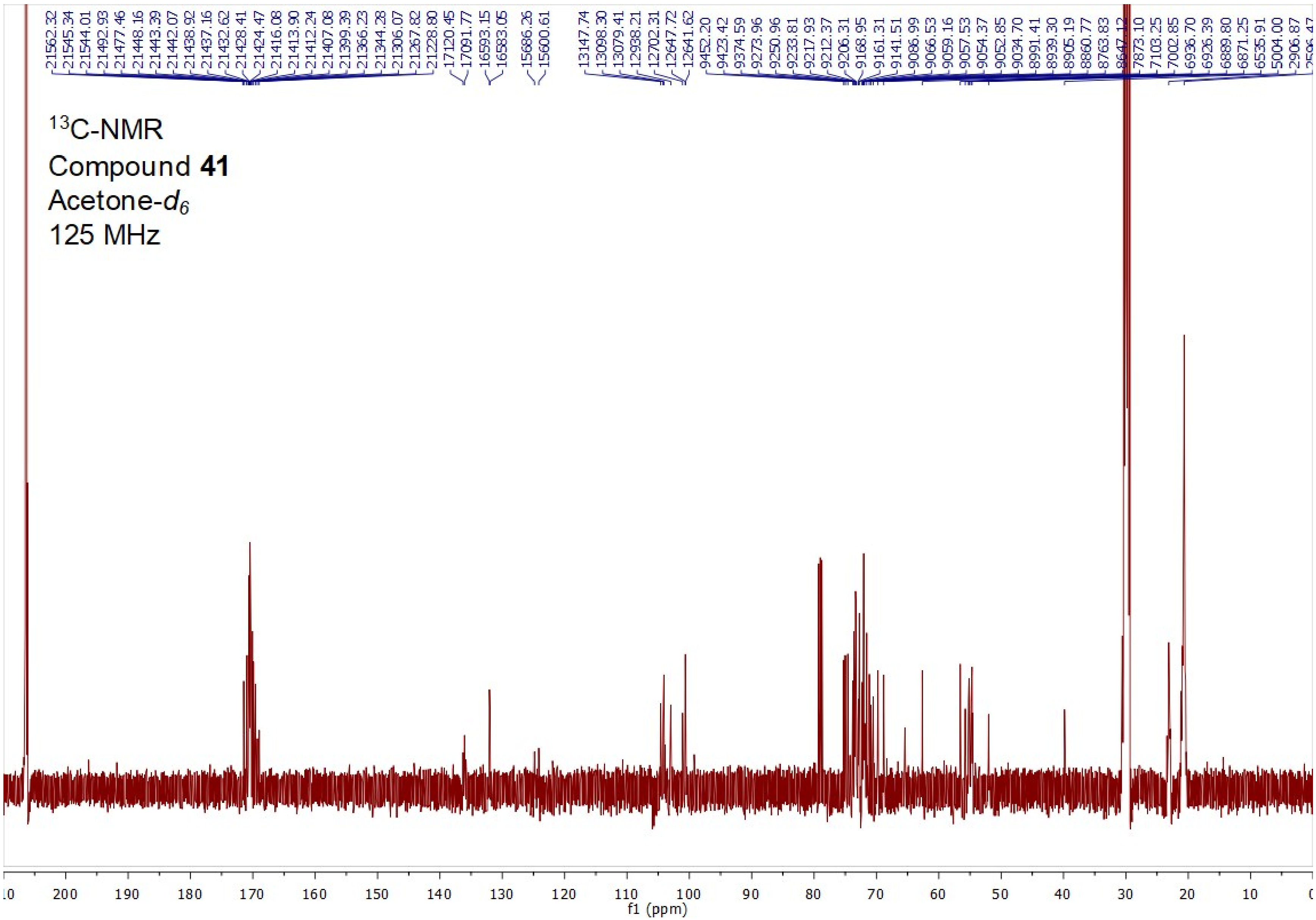
^{1}H-NMR
Compound **39**
Chloroform-*d*
600 MHz
f1 (ppm)



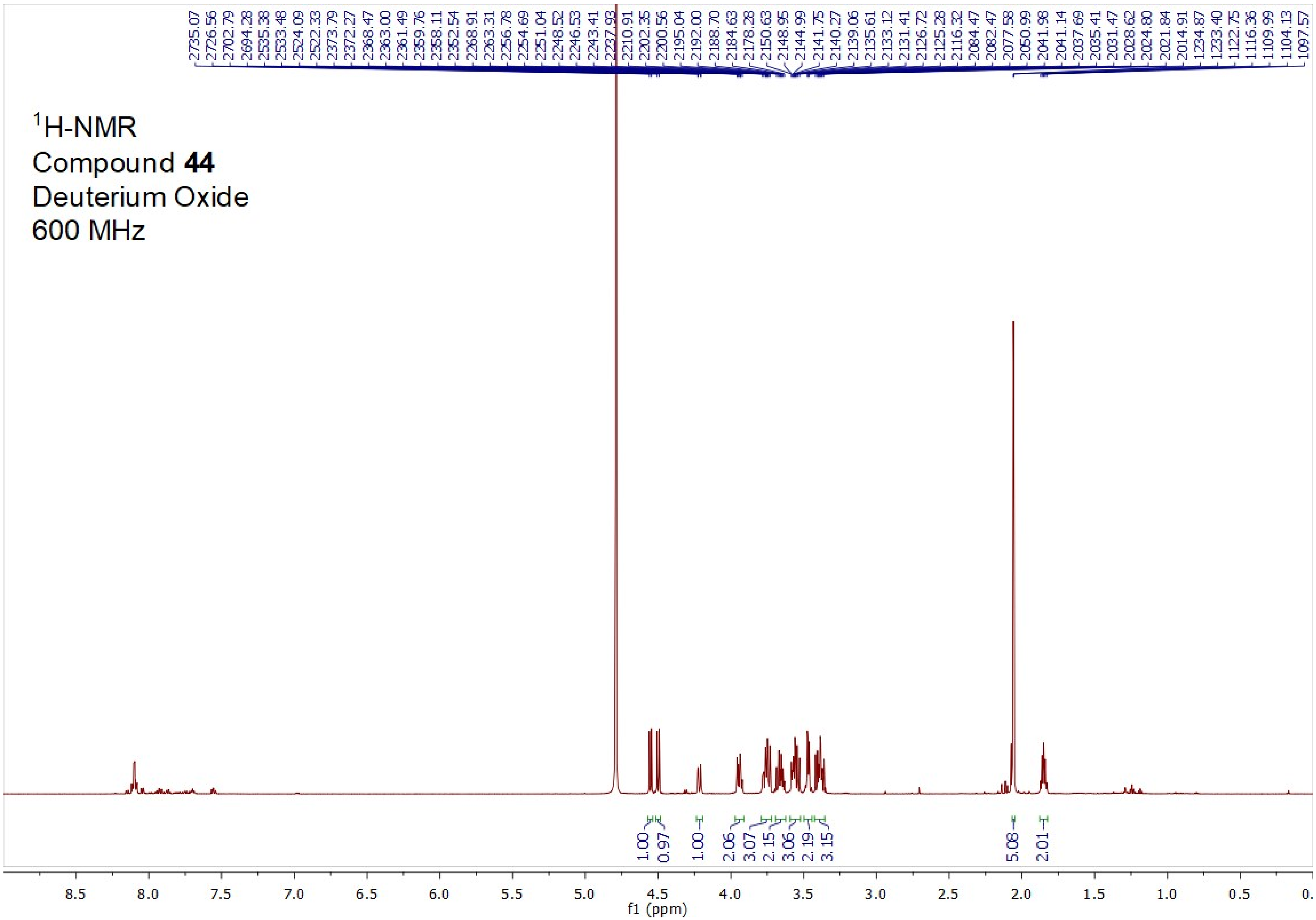
^{13}C-NMR
Compound **39**
Chloroform-*d*
125 MHz
f1 (ppm)



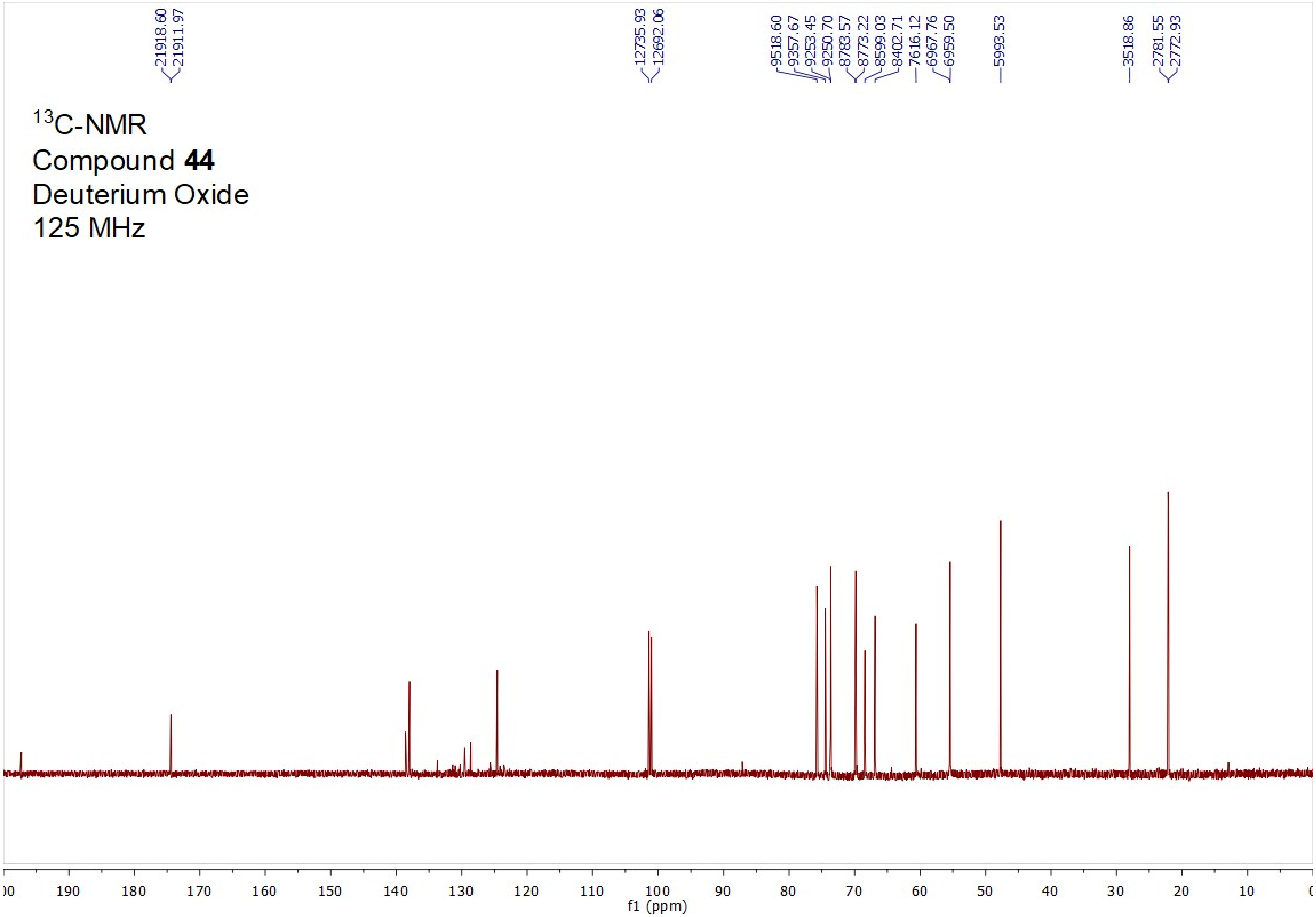
1H-NMR
Compound 41
Acetone-d6
600 MHz
f1 (ppm)



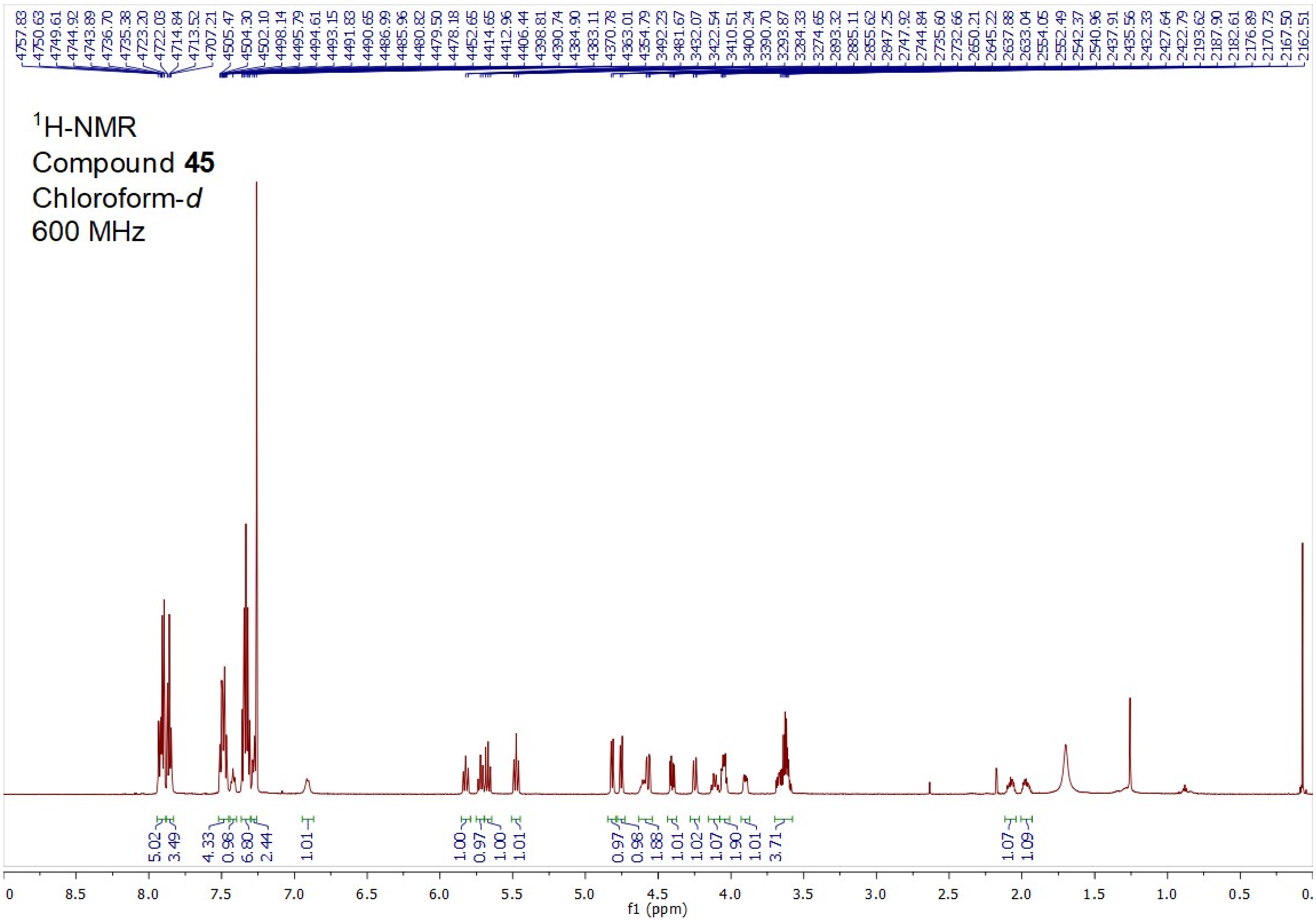
^{13}C-NMR
Compound **41**
Acetone-d_6
125 MHz
f1 (ppm)

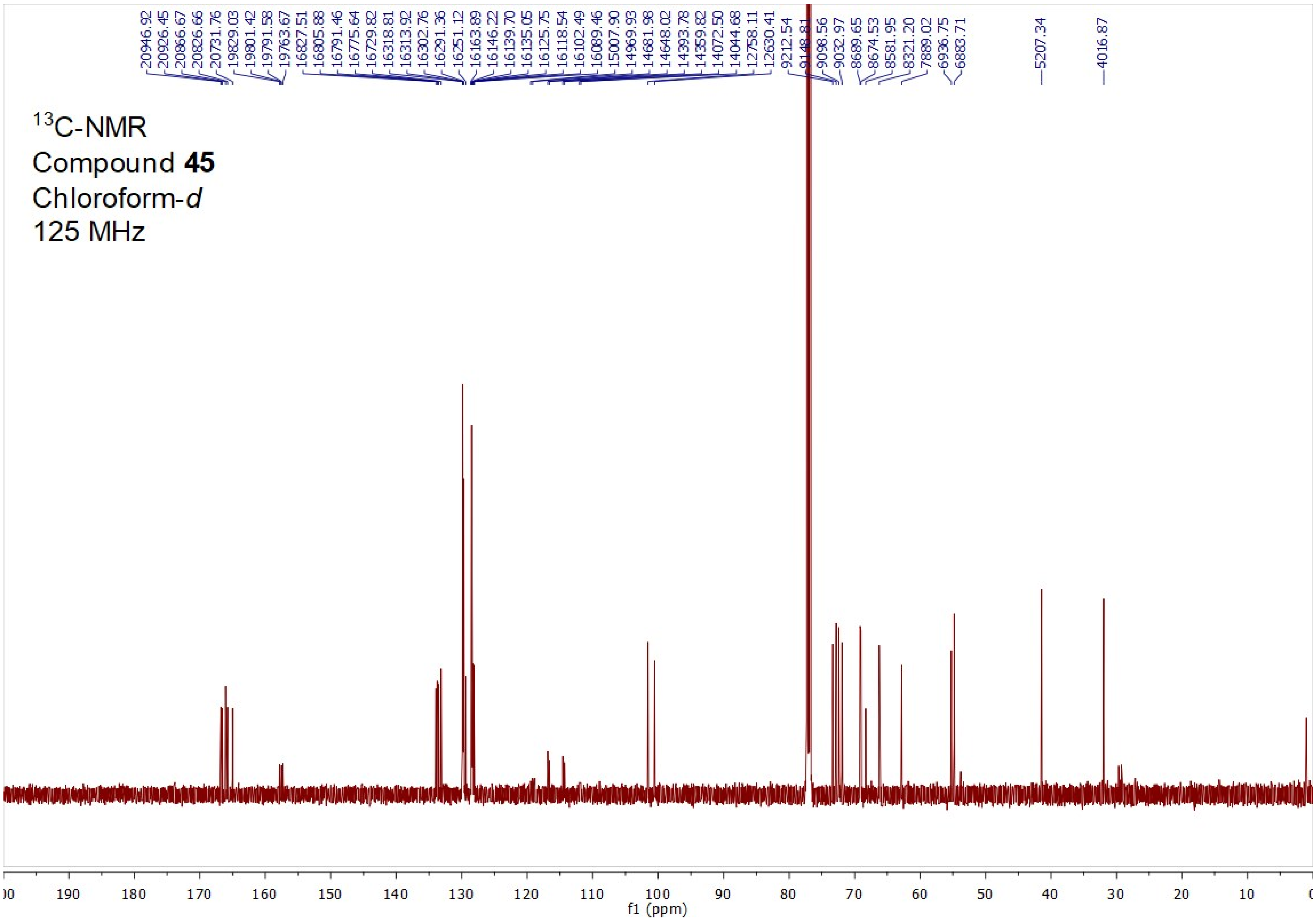


1H-NMR
Compound 44
Deuterium Oxide
600 MHz
f1 (ppm)

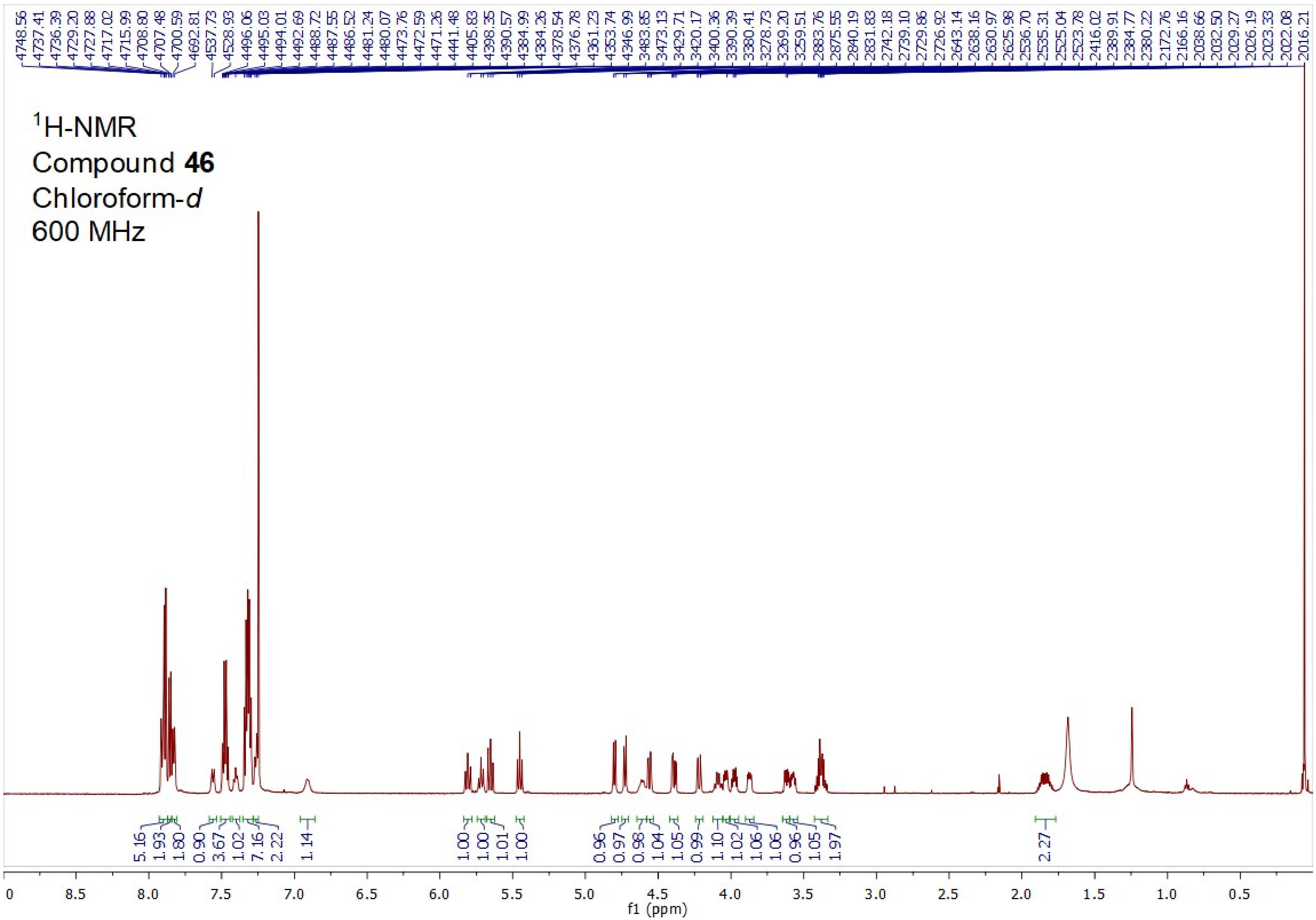


21918.60
21911.97
12735.93
12692.06
9518.60
9357.67
9253.45
9250.70
8783.57
8773.22
8599.03
8402.71
7616.12
6967.76
6959.50
5993.53
3518.86
2781.55
2772.93
^{13}C-NMR
Compound **44**
Deuterium Oxide
125 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

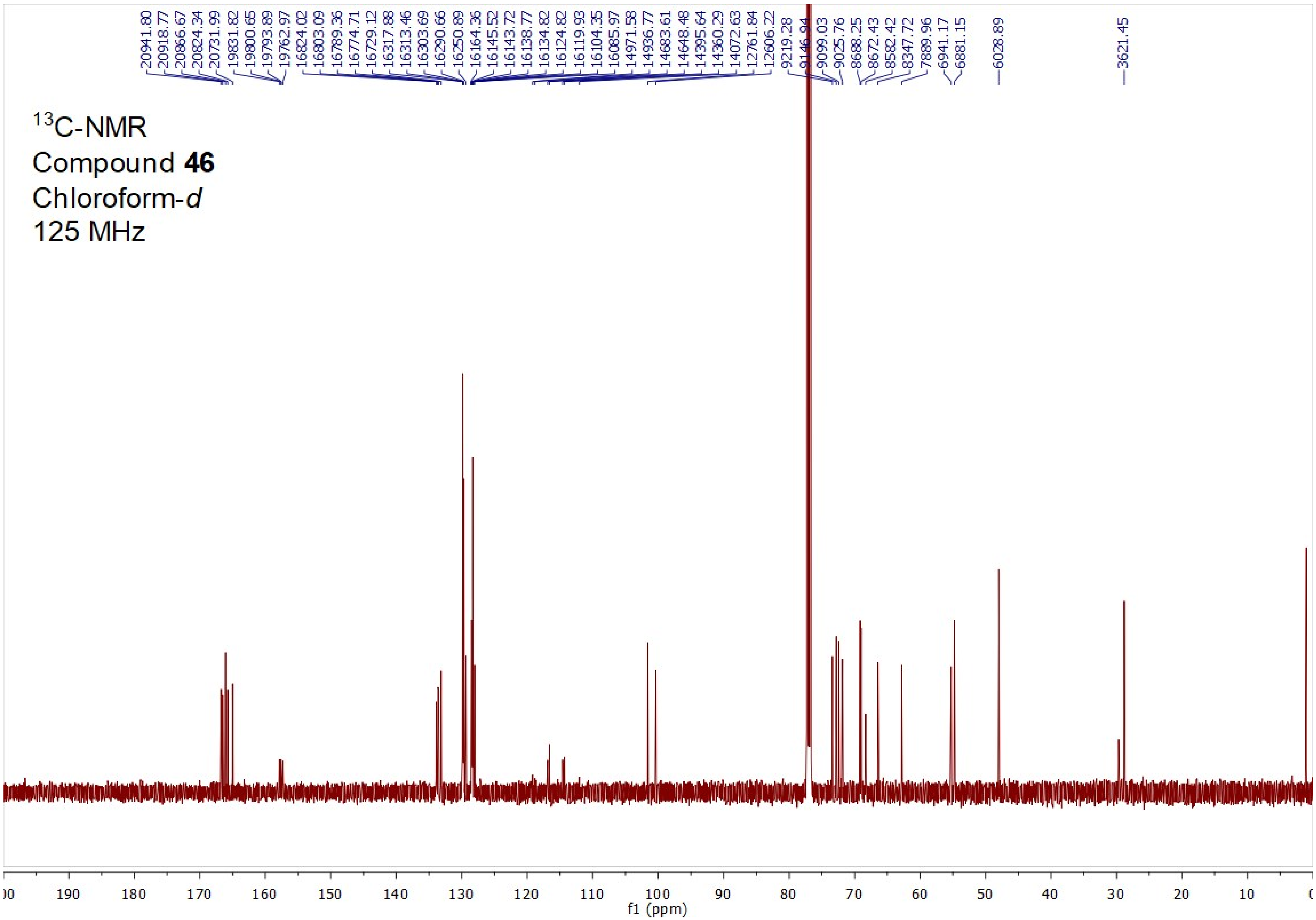

1H-NMR
Compound 45
Chloroform-d
600 MHz
f1 (ppm)



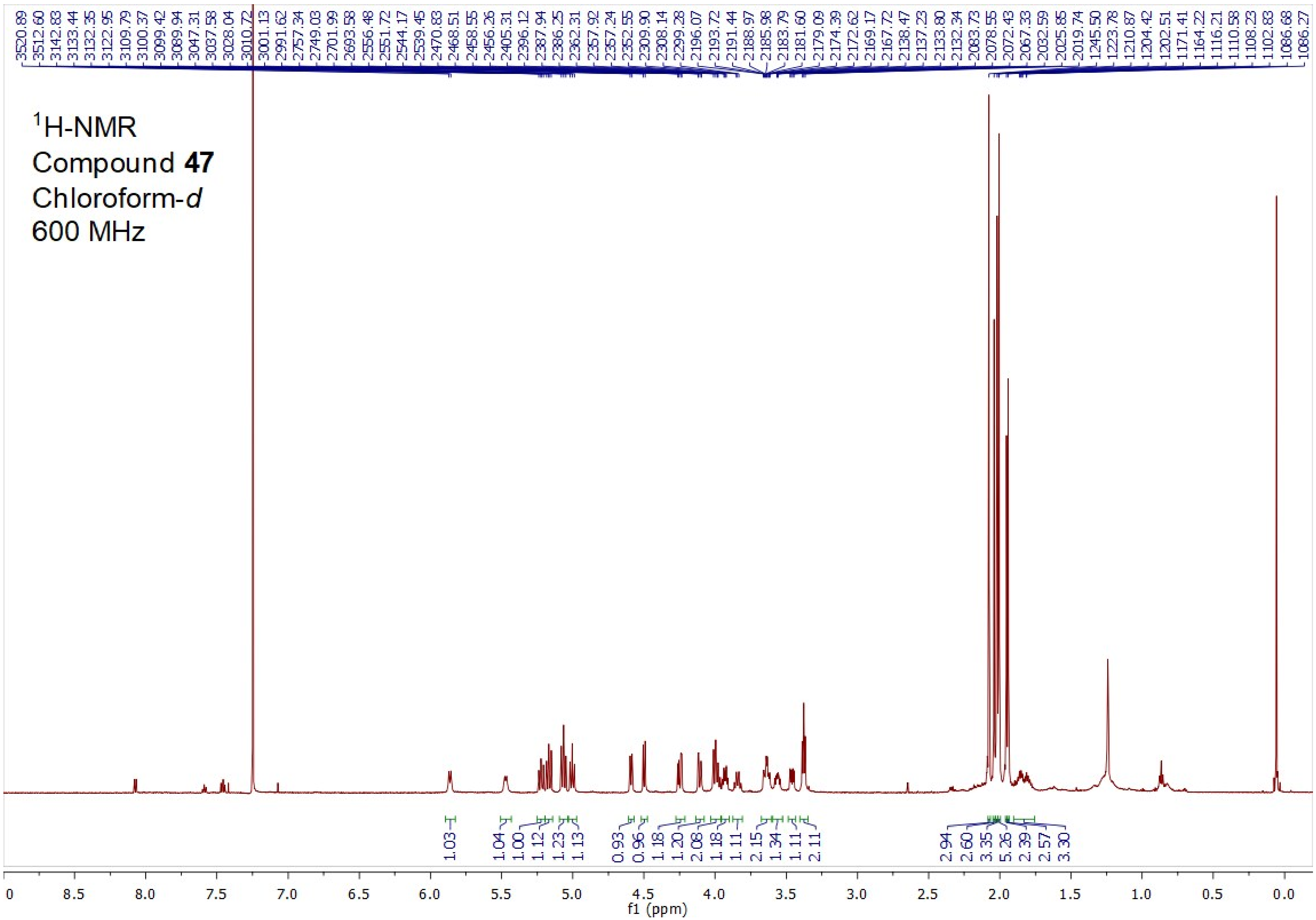
13C-NMR
Compound 45
Chloroform-d
125 MHz
f1 (ppm)



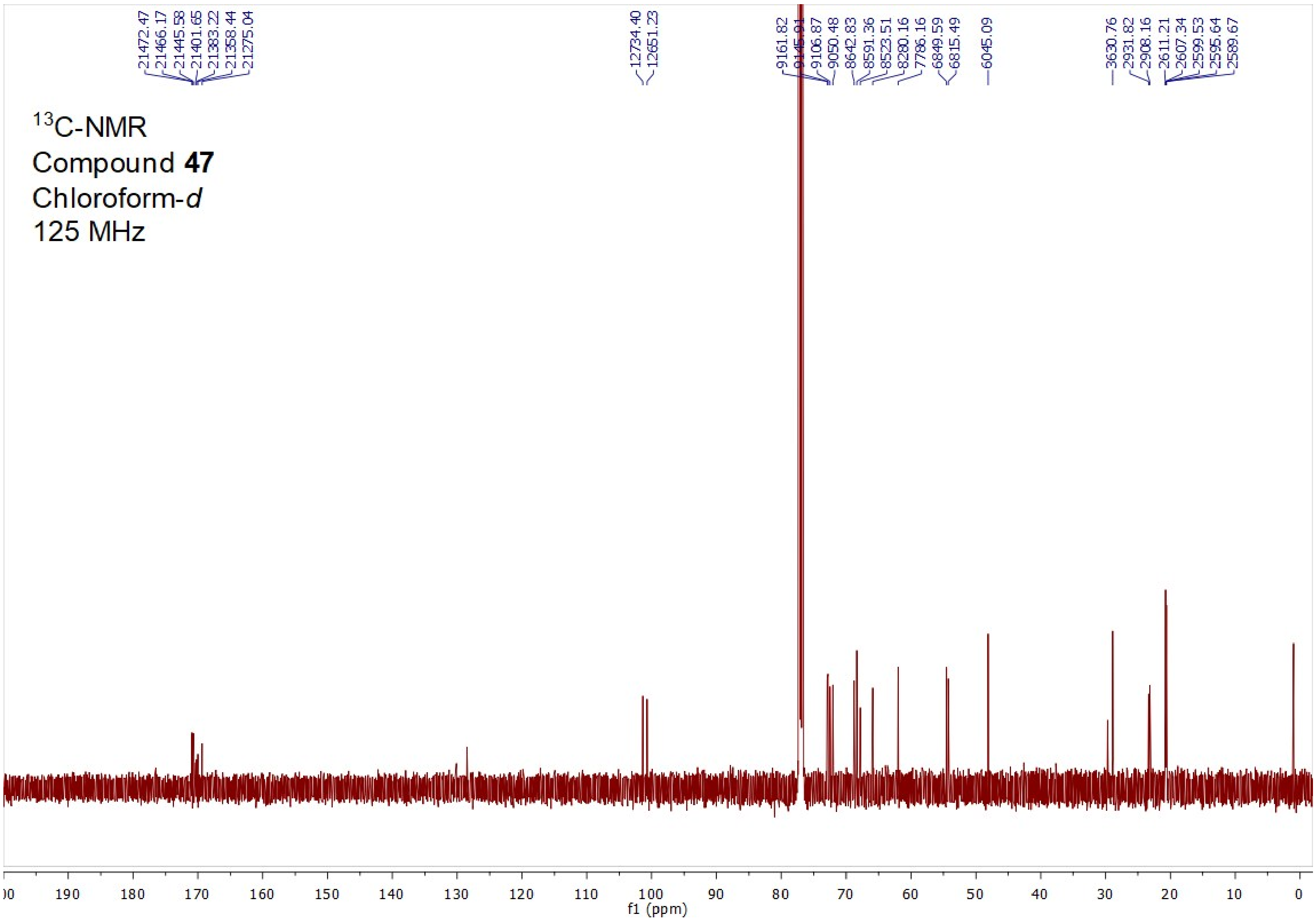
^{1}H-NMR
Compound **46**
Chloroform-*d*
600 MHz
f1 (ppm)



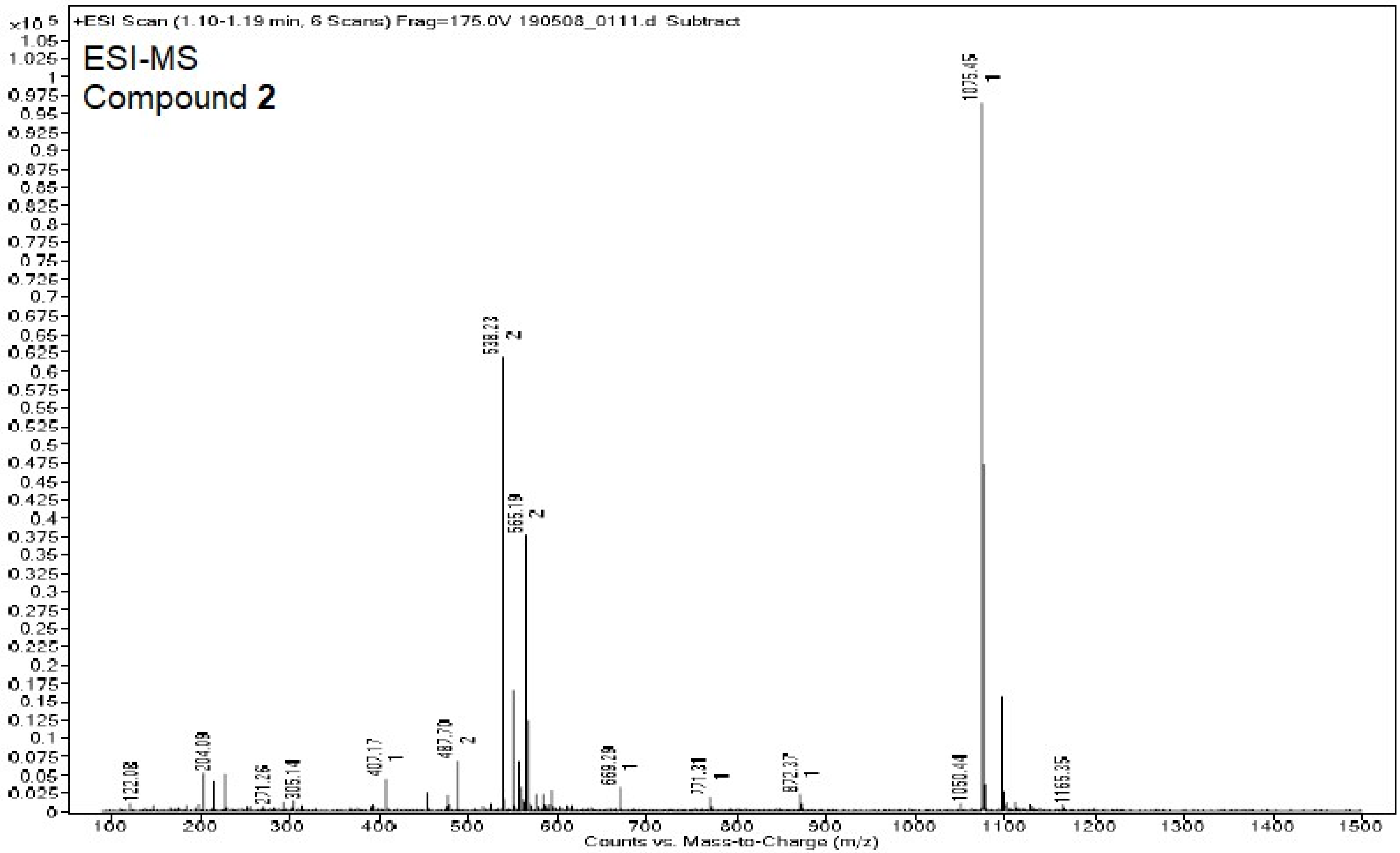
^{13}C-NMR
Compound **46**
Chloroform-*d*
125 MHz
20941.80
20918.77
20866.67
20824.34
20731.99
19831.82
19800.65
19793.89
19762.97
16824.02
16803.09
16789.36
16774.71
16729.12
16317.88
16313.46
16303.69
16290.66
16250.89
16164.36
16145.52
16143.72
16138.77
16134.82
16124.82
16119.93
16104.35
16085.97
14971.58
14936.77
14683.61
14648.48
14395.64
14360.29
14072.63
12761.84
12606.22
9219.28
9146.94
9099.03
9025.76
8688.25
8672.43
8582.42
8347.72
7889.96
6941.17
6881.15
6028.89
3621.45
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

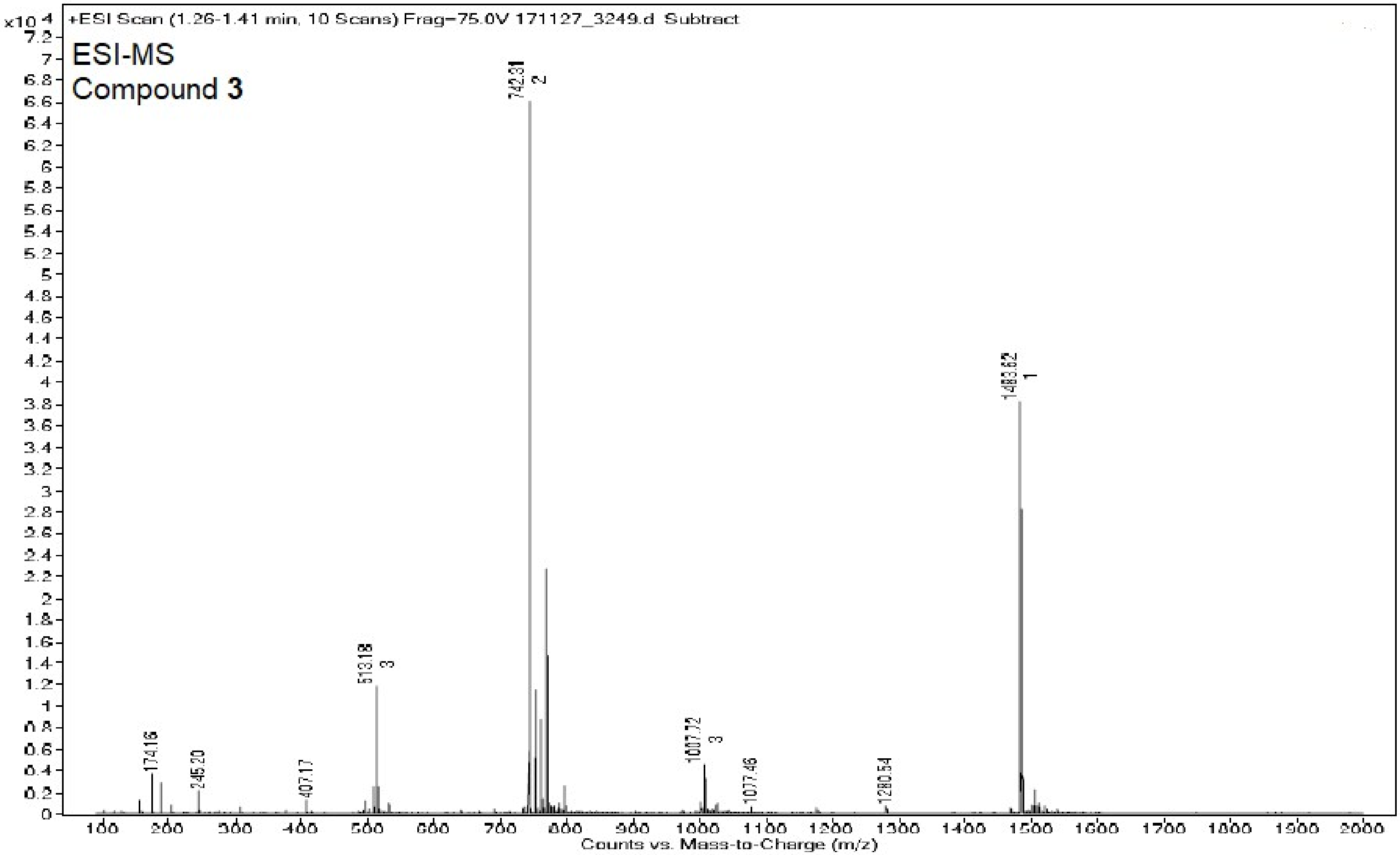


^{1}H-NMR
Compound **47**
Chloroform-*d*
600 MHz
f1 (ppm)

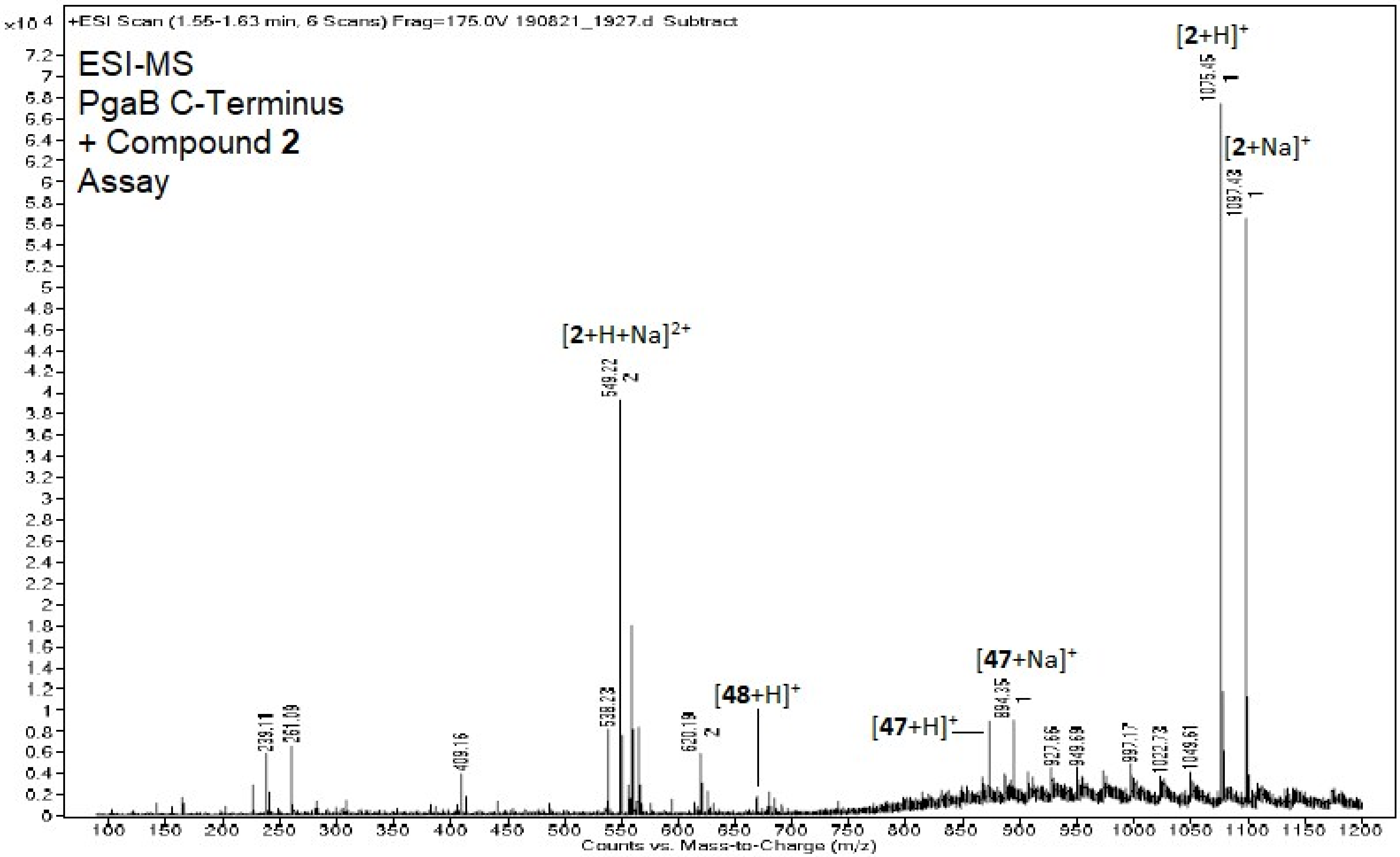


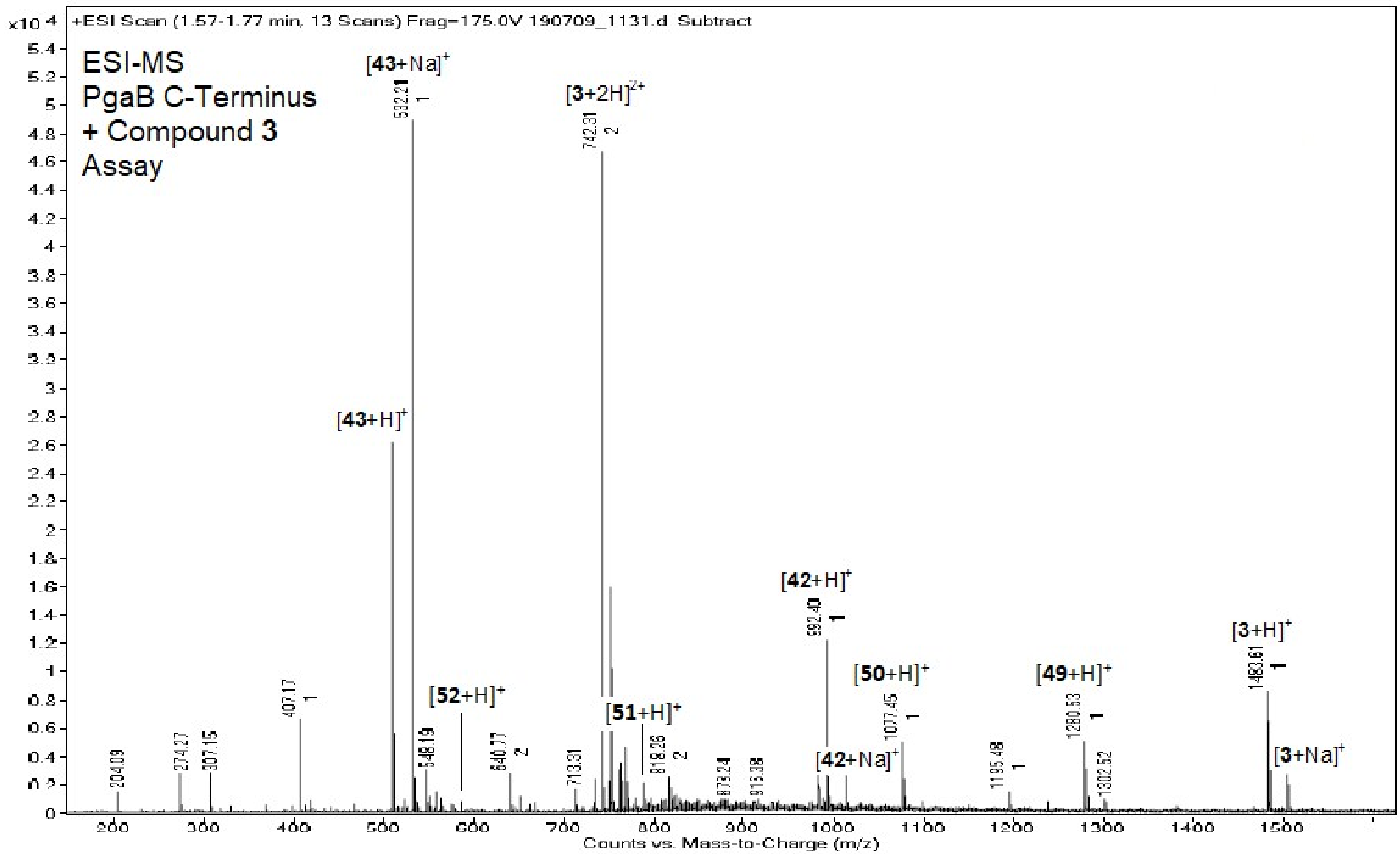
13C-NMR
Compound 47
Chloroform-d
125 MHz
21472.47
21466.17
21445.58
21401.65
21383.22
21358.44
21275.04
12734.40
12651.23
9161.82
9106.87
9050.48
8642.83
8591.36
8523.51
8280.16
7786.16
6849.59
6815.49
6045.09
3630.76
2931.82
2908.16
2611.21
2607.34
2599.53
2595.64
2589.67
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


+ESI Scan (1.10-1.19 min, 6 Scans) Frag=175.0V 190508_0111.d Subtract
ESI-MS
Compound 2
1075.45
538.23
565.19
122.08
204.09
271.26
305.14
407.17
487.70
669.29
771.31
872.37
1050.44
1165.35
Counts vs. Mass-to-Charge (m/z)



+ESI Scan (1.26-1.41 min, 10 Scans) Frag=75.0V 171127_3249.d Subtract
ESI-MS
Compound 3
x10 4
742.31
2
1483.62
1
513.18
3
1007.72
3
174.16
245.20
407.17
1077.46
1280.54
Counts vs. Mass-to-Charge (m/z)


+ESI Scan (1.55-1.63 min, 6 Scans) Frag=175.0V 190821_1927.d Subtract
ESI-MS
PgaB C-Terminus
+ Compound 2
Assay
[2+H]+
1075.45
[2+Na]+
1097.43
[2+H+Na]2+
549.22
239.11
261.09
409.16
538.23
620.19
[48+H]+
[47+H]+
[47+Na]+
894.35
927.66
949.69
997.17
1022.73
1049.61
Counts vs. Mass-to-Charge (m/z)



+ESI Scan (1.57-1.77 min, 13 Scans) Frag=175.0V 190709_1131.d Subtract
ESI-MS
PgaB C-Terminus
+ Compound 3
Assay
[43+Na]+
[3+2H]2+
[43+H]+
[52+H]+
[51+H]+
[42+H]+
[42+Na]+
[50+H]+
[49+H]+
[3+H]+
[3+Na]+
532.21
742.31
992.40
1483.61
1077.45
1280.53
407.17
548.19
640.77
818.26
713.31
204.09
274.27
307.15
873.24
915.38
1195.48
1302.52
Counts vs. Mass-to-Charge (m/z)

References

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