Supporting Information for:

Synthesis of the Docosanasaccharide Arabinan Domain of Mycobacterial Arabinogalactan and a Proposed Octadecasaccharide Biosynthetic Precursor

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Experimental Details and Characterization Data for Monosaccharide Building Blocks

8-Azidooctyl 2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranoside (10). To a mixture of **9**[1] (5.51 g, 7.82 mmol), 8-azido-1-octanol (1.34 g, 7.82 mmol), and 4 Å molecular sieves (3.0 g) in CH_2Cl_2 (100 mL) was added NIS (2.04 g, 8.62 mmol) followed by AgOTf (0.403 g, 1.57 mmol) at 0 °C. After stirring for 30 min at 0 °C, the solution turned dark red and Et_3N was added. The mixture was then diluted with CH_2Cl_2 (300 mL) and filtered through Celite. The filtrate was washed with a saturated aqueous $Na_2S_2O_3$ solution (300 mL), dried (Na_2SO_4), and concentrated to give a crude residue that was purified by column chromatography (8:1, hexanes–EtOAc) to afford **10** (5.38 g, 92%) as a colorless oil. R_f 0.67 (4:1, hexanes–EtOAc); $[\alpha]_D$ –4.3 (*c* 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.11–8.07 (m, 2 H, Ar), 8.03–7.99 (m, 2 H, Ar), 7.77–7.72 (m, 4 H, Ar), 7.64–7.55 (m, 2 H, Ar), 7.50–7.32 (m, 10 H, Ar), 5.63 (dd, 1 H, *J* = 5.0, 1.6 Hz, H-3), 5.48 (d, 1 H, *J* = 1.6 Hz, H-2), 5.24 (s, 1 H, H-1), 4.40 (ddd, 1 H, *J* = 5.0, 4.9, 4.9 Hz, H-4), 4.08–4.01 (m, 2 H, H-5 × 2), 3.79 (ddd, 1 H, *J* = 9.5, 6.7, 6.7 Hz, octyl OCH_2), 3.55 (ddd, 1 H, *J* = 9.5, 6.3, 6.3 Hz, octyl OCH_2), 3.24 (dd, 2 H, *J* = 7.0, 7.0 Hz, octyl N_3CH_2), 1.72–1.55 (m, 4 H, octyl CH_2), 1.48–1.30 (m, 8 H, octyl CH_2), 1.08 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 165.4 (C=O), 165.3 (C=O), 135.5(9) (Ar), 135.5(7) (Ar), 133.3 (Ar), 133.2 (Ar), 133.1(8) (Ar), 133.1(6) (Ar), 129.8 (Ar), 129.6 (Ar), 129.5 (Ar), 129.2 (Ar), 128.3 (Ar), 127.7 (Ar), 105.6 (C-1), 82.9 (C-2), 82.2 (C-3), 77.5 (C-4), 67.3 (octyl OCH_2), 63.6 (C-5), 51.4 (octyl N_3CH_2), 29.4 (octyl CH_2), 29.2 (octyl CH_2), 29.0 (octyl CH_2), 28.7 (octyl CH_2), 26.7 ($C(CH_3)_3$), 26.6 (octyl CH_2), 25.9 (octyl CH_2), 19.2 ($C(CH_3)_3$). ESIMS *m/z* calcd. for (M + Na) $C_{43}H_{51}N_3O_7SiNa$ 772.3388. Found: 772.3389; FTIR 2094.8 cm^{-1} (N_3).

8-Azidooctyl 2,3-di-*O*-benzoyl-α-D-arabinofuranoside (11). To a solution of **10** (5.32 g, 7.09 mmol) in pyridine (12 mL) and THF (50 mL) was added HF–pyridine (2.7 mL) at 0 °C, and the resulting mixture was slowly warmed up and stirred for 18 h at rt. The reaction mixture was concentrated, diluted with EtOAc (200 mL), and washed with a saturated aqueous $NaHCO_3$ solution (150 mL × 2). The organic layer was then dried ($NaSO_4$), filtered, and concentrated. The residue was purified by column chromatography (4:1, hexanes–EtOAc) to afford **11** (3.02 g, 83%) as a white foam. R_f 0.25 (4:1, hexanes–EtOAc); $[\alpha]_D$ –10.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) 8.10–8.03 (m, 4 H, Ar), 7.62–7.56 (m, 2 H, Ar), 7.48–7.42 (m, 4 H, Ar), 5.53 (d, 1 H, *J* = 1.4 Hz, H-2), 5.43–5.41 (m, 1 H, H-3), 5.24 (s, 1 H, H-1), 4.32 (ddd, 1 H, *J* = 4.2, 4.2, 3.7 Hz, H-4), 4.03 (dd, 1 H, *J* = 12.0, 3.7 Hz, H-5), 3.98 (dd, 1 H, *J* = 12.0, 4.2 Hz, H-5), 3.76 (ddd, 1 H, *J* = 9.4, 6.7, 6.7 Hz, octyl OCH_2), 3.53 (ddd, 1 H, *J* = 9.4, 6.2, 6.2 Hz, octyl OCH_2), 3.22 (dd, 2 H, *J* = 7.0, 7.0 Hz, octyl CH_2N_3), 2.40–2.08 (br, 1 H, OH), 1.70–1.52 (m, 4 H, octyl CH_2), 1.45–1.22 (m, 8 H, octyl CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 165.2 (C=O), 133.4 (Ar × 2), 129.8 (Ar × 2), 129.7 (Ar × 2), 129.1 (Ar), 129.0 (Ar), 128.4 (Ar × 2), 128.3 (Ar × 2), 105.4 (C-1), 83.5 (C-4), 81.6 (C-2), 77.8 (C-3), 67.3 (octyl OCH_2), 62.3 (C-5), 51.3 (octyl CH_2N_3), 29.3 (octyl CH_2), 29.1 (octyl CH_2), 28.9 (octyl CH_2), 28.6 (octyl CH_2), 26.5 (octyl CH_2), 25.9 (octyl CH_2). ESIMS *m/z* calcd. for (M + Na) $C_{27}H_{33}N_3O_7$: 534.2210. Found: 534.2209; FTIR 3502.1 cm^{-1} (OH), 2095.9 cm^{-1} (N_3).

2,3-Di-*O*-benzoyl-5-*O*-*tert*-butyldiphenylsilyl-D-arabinofuranose (12). To a solution of thioglycoside **9** (2.0 g, 2.8 mmol) in THF–water (40:1, 41 mL) was added *N*-iodosuccinimide (1.15 g, 5.1 mmol) and silver triflate (0.29 g, 1.1 mmol) at 0 °C. The reaction mixture was stirred well for 3.5 h and neutralized with Et_3N, followed by the addition of solid $Na_2S_2O_3$ (10 g). The suspension was stirred for 20 min, diluted with CH_2Cl_2 (30 mL) and filtered through Celite.

The filtrate was directly concentrated to give a syrup that was purified by column chromatography (6:1, hexanes–EtOAc) to afford **12** (1.44 g, 1:1 α:β mixture, 85%) as a syrup. R_f 0.26 (4:1, hexanes–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.17–7.96 (m, 4 H, Ar), 7.84–7.20 (m, 16 H, Ar), 6.05 (dd, 0.5 H, *J* = 5.6, 4.2 Hz, H-2), 5.73 (d, 0.5 H, *J* = 4.7 Hz, H-1), 5.67 (dd, 0.5 H, *J* = 4.8, 1.2 Hz, H-2), 5.63 (s, 0.5 H, H-1), 5.59 (dd, 0.5 H, *J* = 4.8 Hz, H-3), 5.51 (d, 0.5 H, *J* = 1.2 Hz, H-3), 4.60 (dd, 0.5 H, *J* = 9.3, 4.6 Hz, H-4), 4.28 (dd, 0.5 H, *J* = 6.6, 2.7 Hz, H-4), 4.10 (dd, 0.5 H, *J* = 11.1, 3.0 Hz, H-5), 4.05–3.98 (m, 1 H, H-5), 3.94 (dd, 0.5 H, *J* = 11.1, 2.0 Hz, H-5), 1.14 (s, 4.5 H, $C(CH_3)_3$), 1.06 (s, 4.5 H, $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.0 (C=O), 165.7 (C=O), 165.6 (C=O), 165.5 (C=O), 135.9 (Ar), 135.6(4) (Ar), 135.6(2) (Ar), 135.5 (Ar), 133.4 (Ar), 133.3(9) (Ar), 133.3(4) (Ar), 133.2 (Ar), 133.1 (Ar), 132.0 (Ar), 131.7 (Ar), 130.1 (Ar), 130.0 (Ar), 129.9(7) (Ar), 129.9(2) (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.3 (Ar), 129.2 (Ar), 129.1(8) (Ar), 129.1(0) (Ar), 128.4(7) (Ar), 128.4(3) (Ar), 128.4(0) (Ar), 128.3 (Ar), 127.9(6) (Ar), 127.9(4) (Ar), 127.7 (Ar), 127.6 (Ar), 101.1 (C-1), 95.4 (C-1), 83.3, 82.9, 82.6, 79.2, 77.5, 76.4, 65.0 (C-5), 63.6 (C-5), 26.8 ($C(\mathit{C}H_3)_3$), 26.7 ($C(\mathit{C}H_3)_3$), 19.2 ($\mathit{C}(CH_3)_3$). ESIMS *m/z* calcd for (M + Na) $C_{35}H_{36}O_7Si$: 619.2123. Found: 619.2122.

***p*-Methoxyphenyl 2,3,5-Tri-*O*-benzoyl-α-D-arabinofuranoside (20).** To a mixture of **19**[2] (2.57 g, 4.52 mmol), *p*-methoxyphenol (0.84 g, 6.78 mmol), and 4 Å molecular sieves (2.0 g) in CH_2Cl_2 (60 mL) was added *N*-iodosuccinimide (1.27 g, 5.42 mmol) followed by silver triflate (0.348 g, 1.36 mmol) at 0 °C. After stirring for 25 min, another portion of *N*-iodosuccinimide (0.7 g, 3 mmol) and *p*-methoxyphenol (0.372 g, 3 mmol) were added, and the reaction was slowly warmed up to 10 °C and kept for another 30 min before Et_3N was added. The mixture was then diluted with CH_2Cl_2 (100 mL) and filtered through Celite. The filtrate was washed with a saturated aqueous $Na_2S_2O_3$ solution (300 mL), dried (Na_2SO_4), and concentrated to give a crude residue that was purified by column chromatography (6:1 hexanes–EtOAc) to afford **20** (2.31 g, 90%) as a yellowish amorphous solid. R_f 0.35 (6:1, hexanes–EtOAc); $[\alpha]_D$ +33.4 (*c* 0.7, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.16–8.13 (m, 2 H, Ar), 8.08–8.04 (m, 4 H, Ar), 7.64–7.58 (m, 2 H, Ar), 7.54–7.47 (m, 3 H, Ar), 7.44–7.40 (m, 2 H, Ar), 7.33–7.29 (m, 2 H, Ar), 7.13–7.09 (m, 2 H, Ar), 6.89–6.86 (m, 2 H, Ar), 5.89 (s, 1 H, H-1), 5.82 (s, 1 H, H-2), 5.72 (d, 1 H, *J* = 4.0 Hz, H-3), 4.85 (dd, 1 H, *J* = 11.3, 3.1 Hz, H-5), 4.80–4.76 (m, 2 H, H-4, H-5), 3.78 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.2 (C=O), 165.7 (C=O), 165.4 (C=O), 155.3 (Ar), 150.0 (Ar), 133.6 (Ar × 2), 133.0 (Ar), 129.9(9) (Ar × 2), 129.9(4) (Ar × 2), 129.8 (Ar × 2), 129.7 (Ar), 129.1 (Ar), 128.9 (Ar), 128.5(8) (Ar × 2), 128.5(6) (Ar × 2), 128.3 (Ar × 2), 118.4 (Ar × 2), 114.7 (Ar × 2), 105.1 (C-1), 82.2 (C-2), 81.8 (C-4), 77.8 (C-3), 63.6 (C-5), 55.6 (OCH_3). ESIMS *m/z* calcd. for (M + Na) $C_{33}H_{28}O_9$: 591.1626. Found: 591.1630.

***p*-Methoxyphenyl α-D-Arabinofuranoside (21).** To a solution of **20** (1.65 g, 2.90 mmol) in CH_3OH (30 mL) and CH_2Cl_2 (30 mL) was added $NaOCH_3$ until the pH of the solution was ~9. The mixture was stirred for 12 h, neutralized by the addition of HOAc and then concentrated to give a crude residue, which was purified by column chromatography (10:1 CH_2Cl_2–CH_3OH) to yield **21** (0.643 g, 87%) as a yellowish amorphous solid. R_f 0.34 (10:1, CH_2Cl_2–CH_3OH); $[\alpha]_D$ +171.5 (*c* 0.6, CH_3OH); ^1H NMR (400 MHz, CD_3OD, δ_H) 7.00–6.96 (m, 2 H, Ar), 6.83–6.79 (m, 2 H, Ar), 5.40 (d, 1 H, *J* = 1.8 Hz, H-1), 4.20 (dd, 1 H, *J* = 4.0, 1.8 Hz, H-2), 4.05 (ddd, 1 H, *J* = 6.5, 5.1, 3.2 Hz, H-4), 3.95 (dd, 1 H, *J* = 6.5, 4.0 Hz, H-3), 3.76 (dd, 1 H, *J* = 12.0, 3.2 Hz, H-5), 3.71 (s, 3 H, OCH_3), 3.65 (dd, 1 H, *J* = 12.0, 5.1 Hz, H-5); ^{13}C NMR (100 MHz, CD_3OD, δ_C) 156.2 (Ar), 152.2 (Ar), 119.0 (Ar × 2), 115.3 (Ar × 2), 108.6 (C-1), 85.8 (C-4), 83.5 (C-2), 78.1 (C-3), 62.6 (C-5), 55.9 (OCH_3). ESIMS *m/z* calcd. for (M + Na) $C_{12}H_{16}O_6$: 279.0839. Found: 279.0838.

***p*-Methoxyphenyl 3,5-*O*-(Di-*tert*-butylsilanediyl)-α-D-arabinofuranoside (22)**. To a solution of **21** (520 mg, 2.03 mmol) in a mixture of CH_2Cl_2 (15 mL) and DMF (5 mL) at 0 °C was added 2,6-lutidine (1.0 mL, 8.12 mmol) and di-*tert*-butylsilyl *bis*(trifluoromethanesulfonate) (0.75 mL, 2.23 mmol). The resulting reaction mixture was stirred for 2 h, diluted with CH_2Cl_2 (25 mL) and washed with a saturated aqueous $NaHCO_3$ solution (20 mL) and then brine (20 mL). The organic layer was then dried (Na_2SO_4) and concentrated to give a crude residue, which was purified by column chromatography (10:1 hexanes–EtOAc) to afford **22** (702 mg, 87%) as a white amorphous solid. R_f 0.54 (6:1 hexanes–EtOAc); $[\alpha]_D$ +109.9 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 6.98–6.94 (m, 2 H, Ar), 6.83–6.80 (m, 2 H, Ar), 5.44 (d, 1 H, *J* = 3.5 Hz, H-1), 4.46–4.42 (m, 1 H, H-2), 4.37 (dd, 1 H, *J* = 9.3, 5.6 Hz, H-5), 4.13–4.04 (m, 2 H, H-4, H-3), 3.96 (dd, 1 H, *J* = 9.7, 9.3 Hz, H-5), 3.78 (s, 3 H, OCH_3), 3.16 (d, 1 H, *J* = 4.7 Hz, OH), 1.09 (s, 9 H, $C(CH_3)_3$), 1.02 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 155.0 (Ar), 150.8 (Ar), 117.8 (Ar × 2), 114.6 (Ar × 2), 106.6 (C-1), 81.6 (C-2), 81.3 (C-3), 74.2 (C-4), 67.4 (C-5), 55.6 (OCH_3), 27.4 ($C(CH_3)_3$), 27.1 ($C(CH_3)_3$), 22.6 ($C(CH_3)_3$), 20.1 ($C(CH_3)_3$). ESIMS *m/z* calcd. for (M + Na) $C_{20}H_{32}O_6Si$: 419.1860. Found: 419.1864.

***p*-Methoxyphenyl 2-*O*-Benzoyl-α-D-arabinofuranoside (24).** To a solution of compound **22** (4.78 g, 12.1 mmol) in pyridine (50 mL) was added BzCl (2.2 mL, 18.6 mmol) at 0 °C, and the mixture was allowed to warm to room temperature and stirred for 6 h. The reaction mixture was diluted with CH_2Cl_2 (150 mL) and poured into ice-cold water (150 mL), stirred for 20 min. The organic layer was separated and washed with a saturated aqueous $NaHCO_3$ solution (150 mL × 2), water (150 mL), and brine (150 mL), dried (Na_2SO_4), filtered, and concentrated. The syrupy residue was dissolved in THF–pyridine (5:1, 150 mL), and HF–pyridine (5.0 mL) was added dropwise at 0 °C. The reaction mixture was worked up after 18 h, as described for **5**, to afford **24** (3.78 g, 87% over two steps from **22**) as a syrup. R_f 0.26 (1:1, hexanes–EtOAc); $[\alpha]_D$ +134.0 (*c* 0.1, CH_3OH); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.06–8.00 (m, 2 H, Ar), 7.62–7.56 (m, 1 H, Ar), 7.48–7.42 (m, 2 H, Ar), 7.06–7.00 (m, 2 H, Ar), 6.86–6.80 (m, 2 H, Ar), 5.80 (s, 1 H, H-1), 5.36 (d, 1 H, *J* = 2.9 Hz, H-2), 4.38–4.31 (m, 2 H, H-3, H-4), 3.95 (dd, 1 H, *J* = 12.2, 2.6 Hz, H-5), 3.82 (dd, 1 H, *J* = 12.2, 3.6 Hz, H-5'), 3.76 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.8 (C=O), 155.2 (Ar), 150.1 (Ar), 133.7 (Ar), 129.8 (Ar × 2), 128.8 (Ar), 128.5 (Ar × 2), 118.3 (Ar × 2), 114.6 (Ar × 2), 104.8 (C-1), 86.9 (C-2), 84.2 (C-4), 76.3 (C-3), 61.5 (C-5), 55.6 (OCH_3). ESIMS *m/z* calcd for (M + Na) $C_{19}H_{20}O_7$: 383.1097. Found: 383.1101.

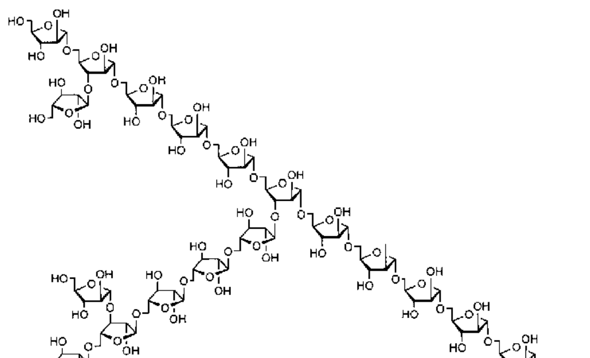
***p*-Tolyl 3,5-*O*-(Di-*tert*-butylsilanediyl)-2-*O*-levulinoyl-1-thio-α-D-arabinofuranoside (30).** A mixture of **29**[3] (109 mg, 0.275 mmol), levulinic acid (42 μL, 0.412 mmol), 1,3-dicyclohexylcarbodiimide (85 mg, 0.412 mmol), and 4-(dimethylamino)pyridine (17 mg, 0.137 mmol) in CH_2Cl_2 (5 mL) was stirred for 1 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL), filtered through Celite, washed with a saturated aqueous $NaHCO_3$ solution (10 mL), and brine (10 mL). The organic layer was then dried (Na_2SO_4), filtered, and concentrated to give a residue, which was purified by column chromatography (6:1, hexanes–EtOAc) to afford **30** (122 mg, 90%) as a white solid. R_f 0.27 (6:1, hexanes–EtOAc); $[\alpha]_D$ +129.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.42 (d, 2 H, *J* = 8.0 Hz, Ar), 7.12 (d, 2 H, *J* = 8.0 Hz, Ar), 5.26–5.20 (m, 2 H, H-1, H-2), 4.34 (dd, 1 H, *J* = 8.1, 7.8 Hz, H-5), 4.12 (dd, 1 H, *J* = 8.7, 7.2 Hz, H-3), 4.02–3.92 (m, 2 H, H-4, H-5), 2.83–2.79 (m, 2 H, levulinoyl CH_2), 2.73–2.62 (m, 2 H, levulinoyl CH_2), 2.32 (s, 3 H, tolyl CH_3), 2.20 (s, 3 H, levulinoyl $COCH_3$), 1.04 (s, 9 H, $C(CH_3)_3$), 0.97 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.1 (C=O), 171.8 (C=O), 138.0 (Ar), 132.7 (Ar × 2), 129.8 (Ar × 2), 129.7 (Ar), 89.5 (C-1), 81.1 (C-2), 79.6 (C-3), 73.4 (C-4), 67.1 (C-5), 37.8 (levulinoyl CH_2), 29.8 (levulinoyl CH_3), 27.8 (levulinoyl CH_2), 27.3 ($C(CH_3)_3$), 27.0 ($C(CH_3)_3$), 22.6 ($C(CH_3)_3$), 21.1 (tolyl CH_3), 20.0 ($C(CH_3)_3$). ESIMS *m/z* calcd. for (M + Na) $C_{25}H_{38}O_6SiSNa$ 517.2051. Found: 517.2053.

References

1. Callam, C. S.; Gadikota, R. R.; Lowary, T. L. *J. Org. Chem.* **2001**, *66*, 4549–4558.
2. Callam, C. S.; Lowary, T. L. *J. Chem. Educ.* **2001**, *78*, 73–74.
3. Crich, D.; Pedersen, C. M.; Bowers, A. A.; Wink, D. J. *J. Org. Chem.* **2007**, *72*, 1553–1565.

compound-3-H
600 MHz 1D in D2O (ref. to 0.1 % ext. acetone @ 2.225 ppm)

Pulse Sequence: s2pul



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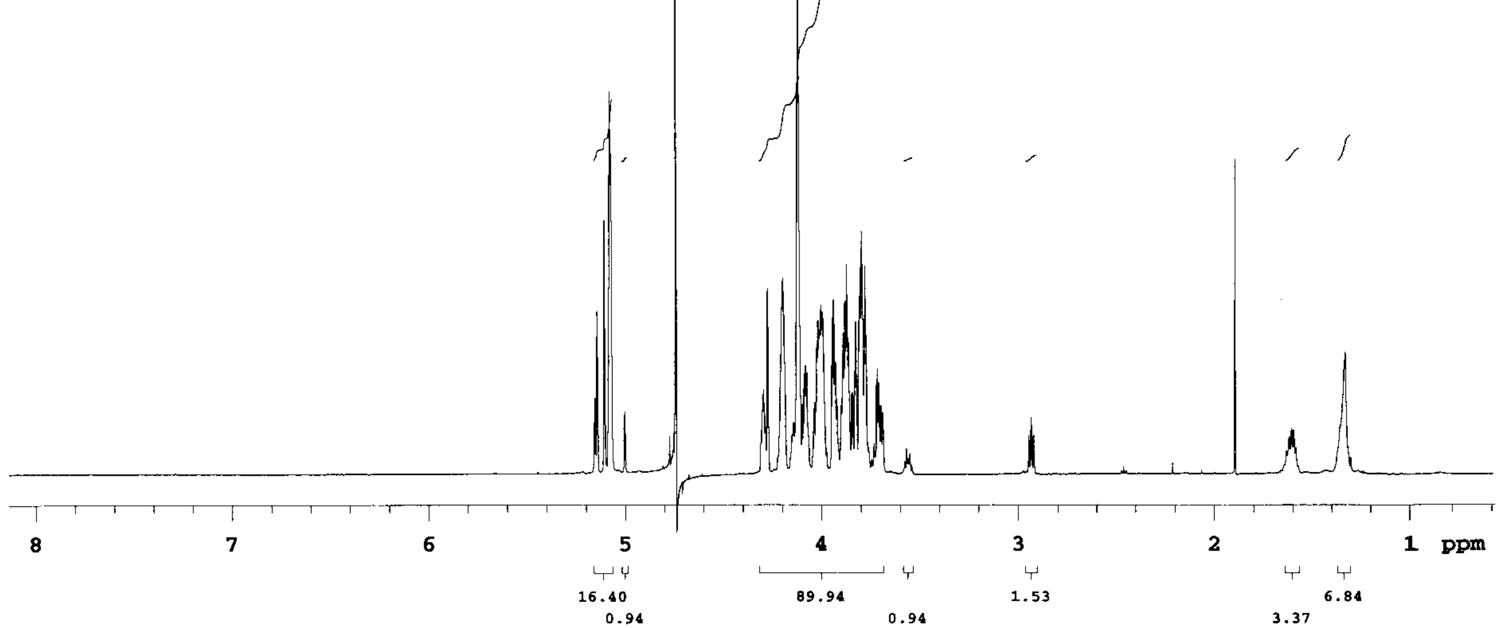

compound-3-C
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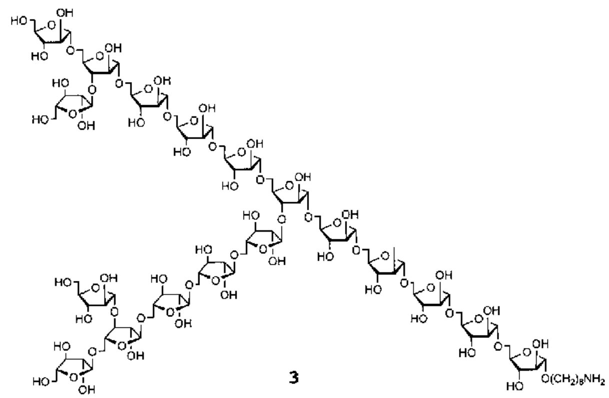

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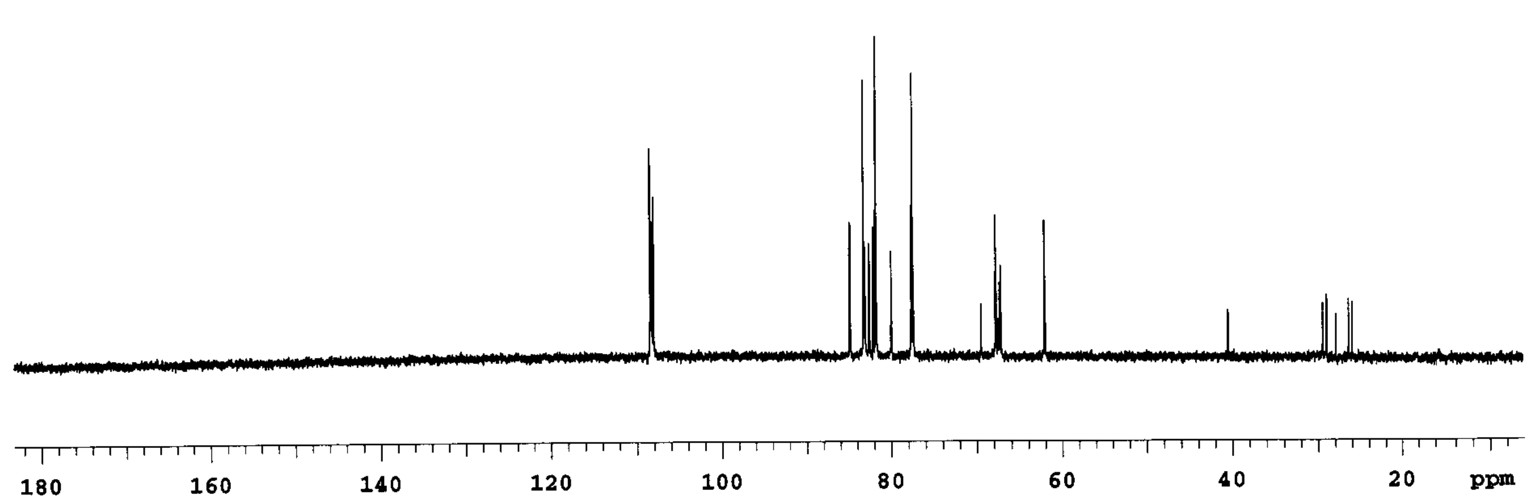

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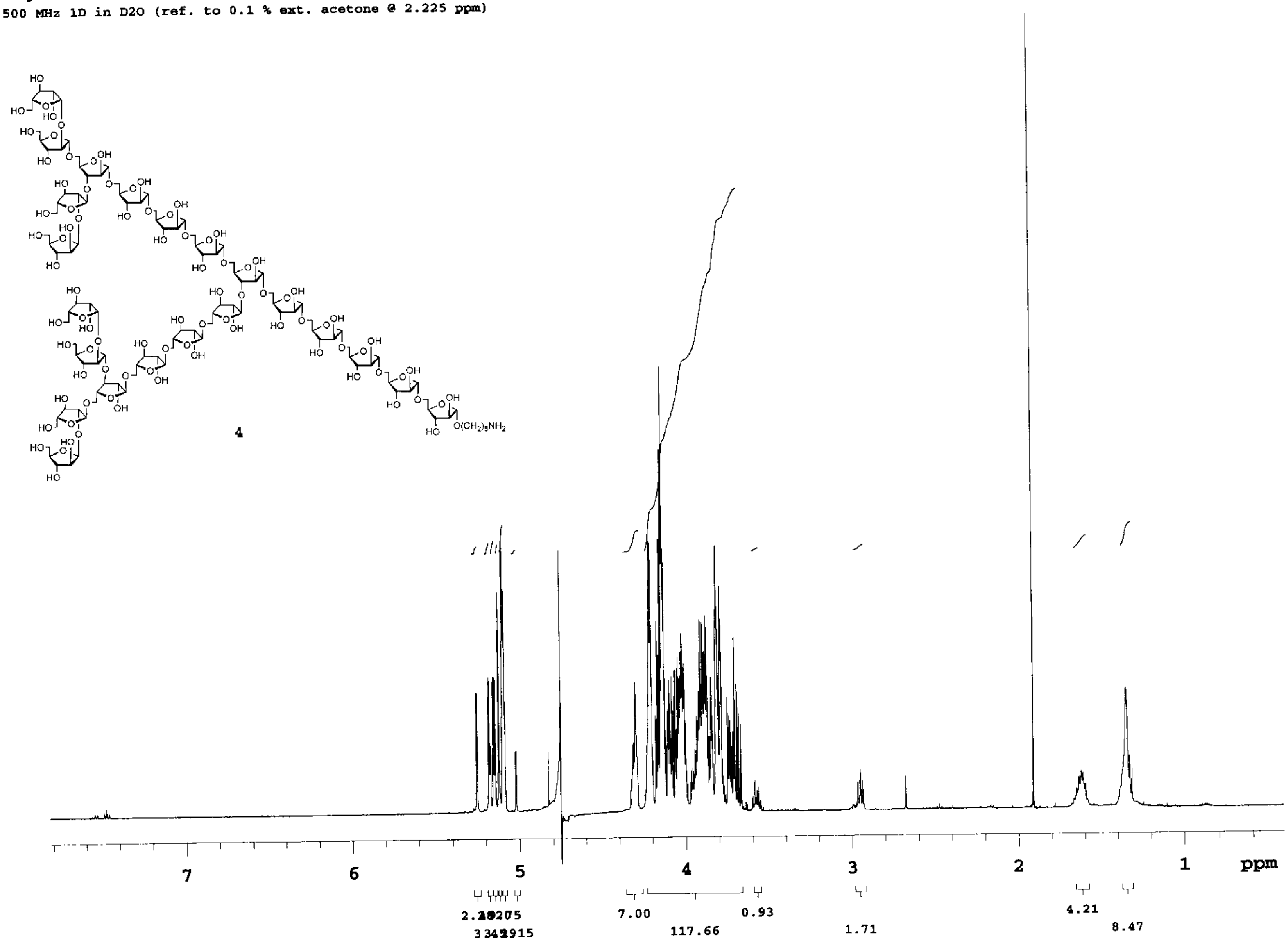

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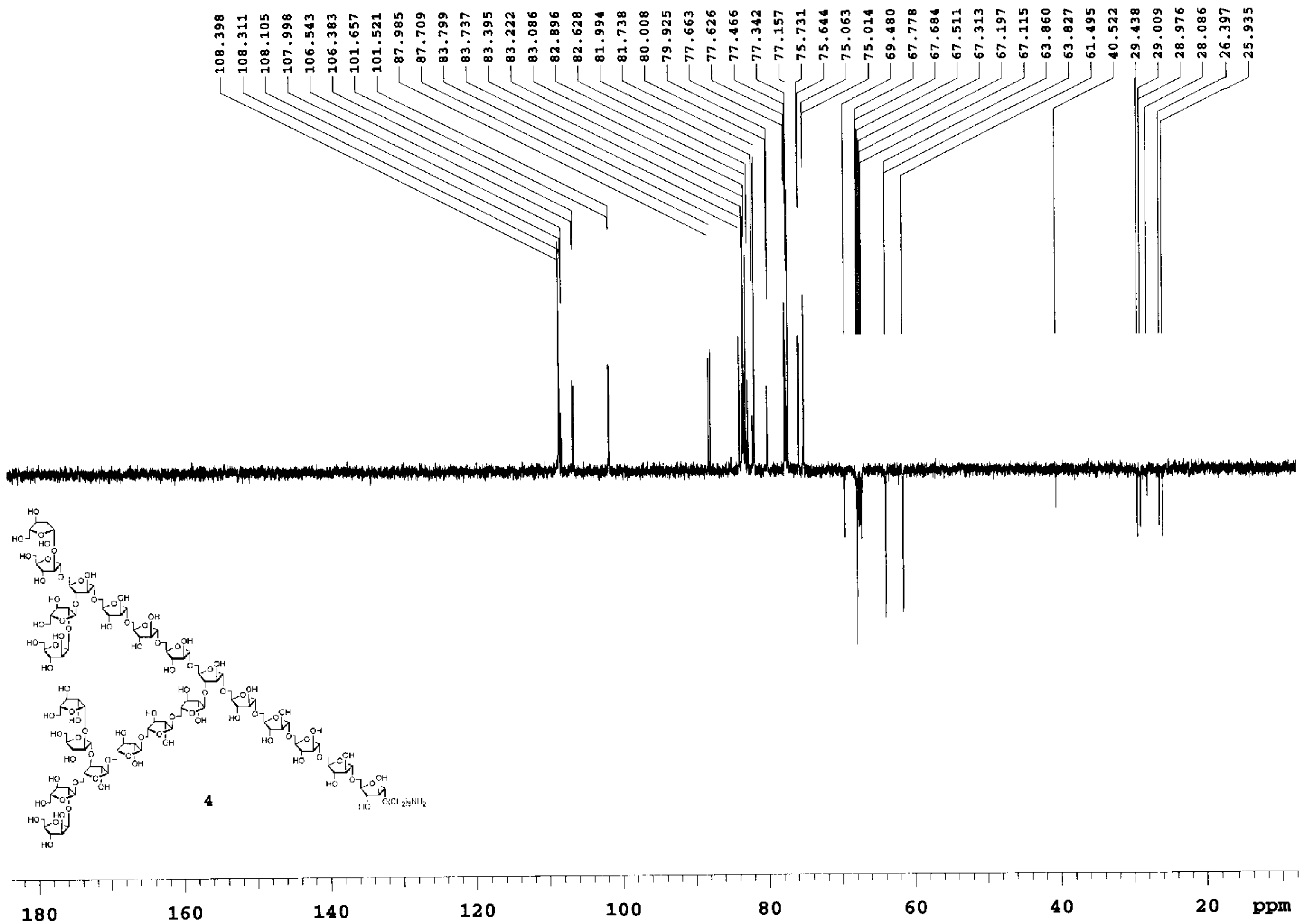
C & CH2 opposite side of CH & CH3

Pulse Sequence: apt



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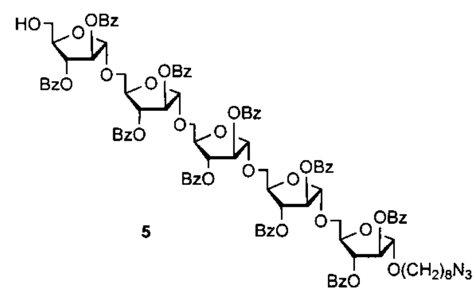

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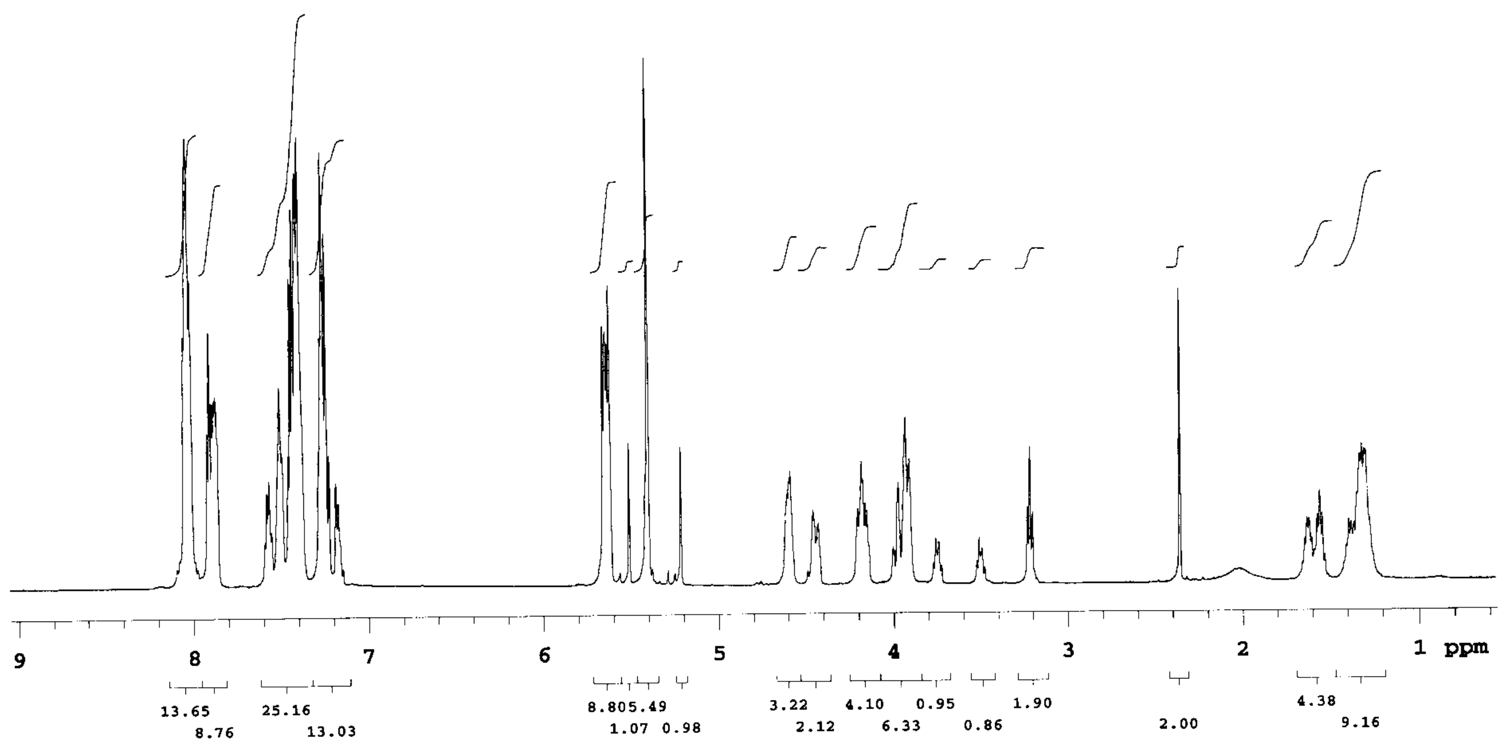

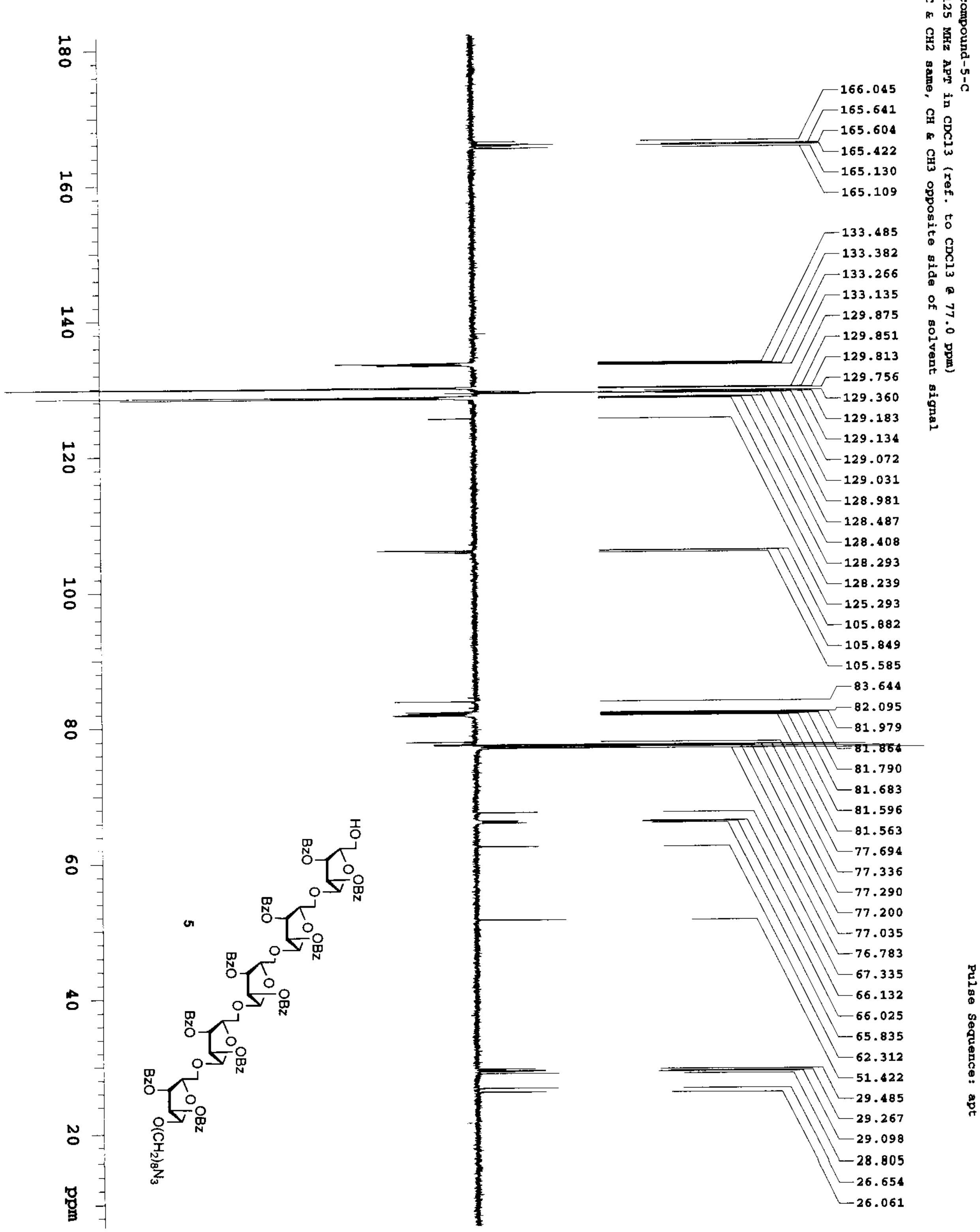
compound-5-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
166.045
165.641
165.604
165.422
165.130
165.109
133.485
133.382
133.266
133.135
129.875
129.851
129.813
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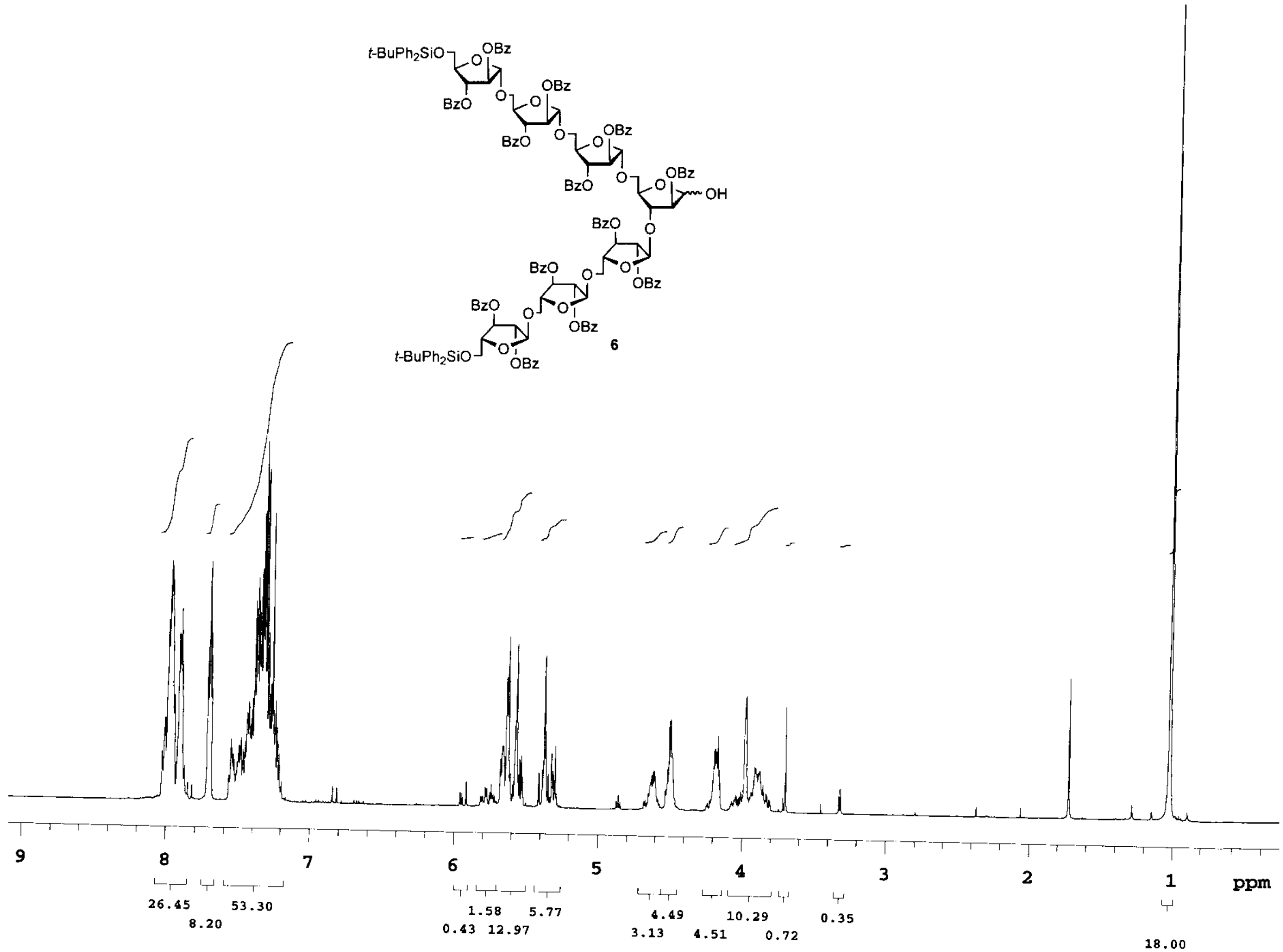
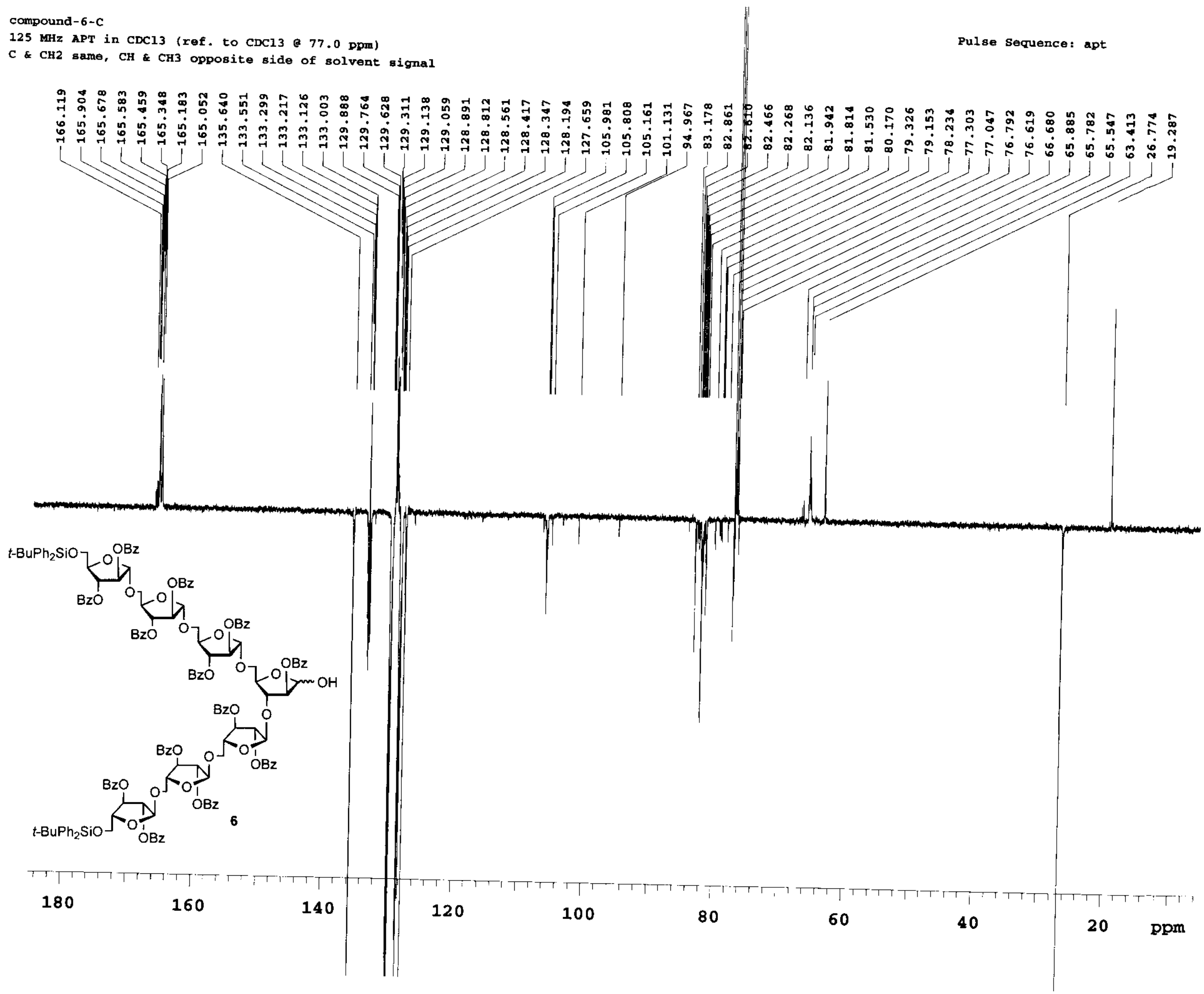
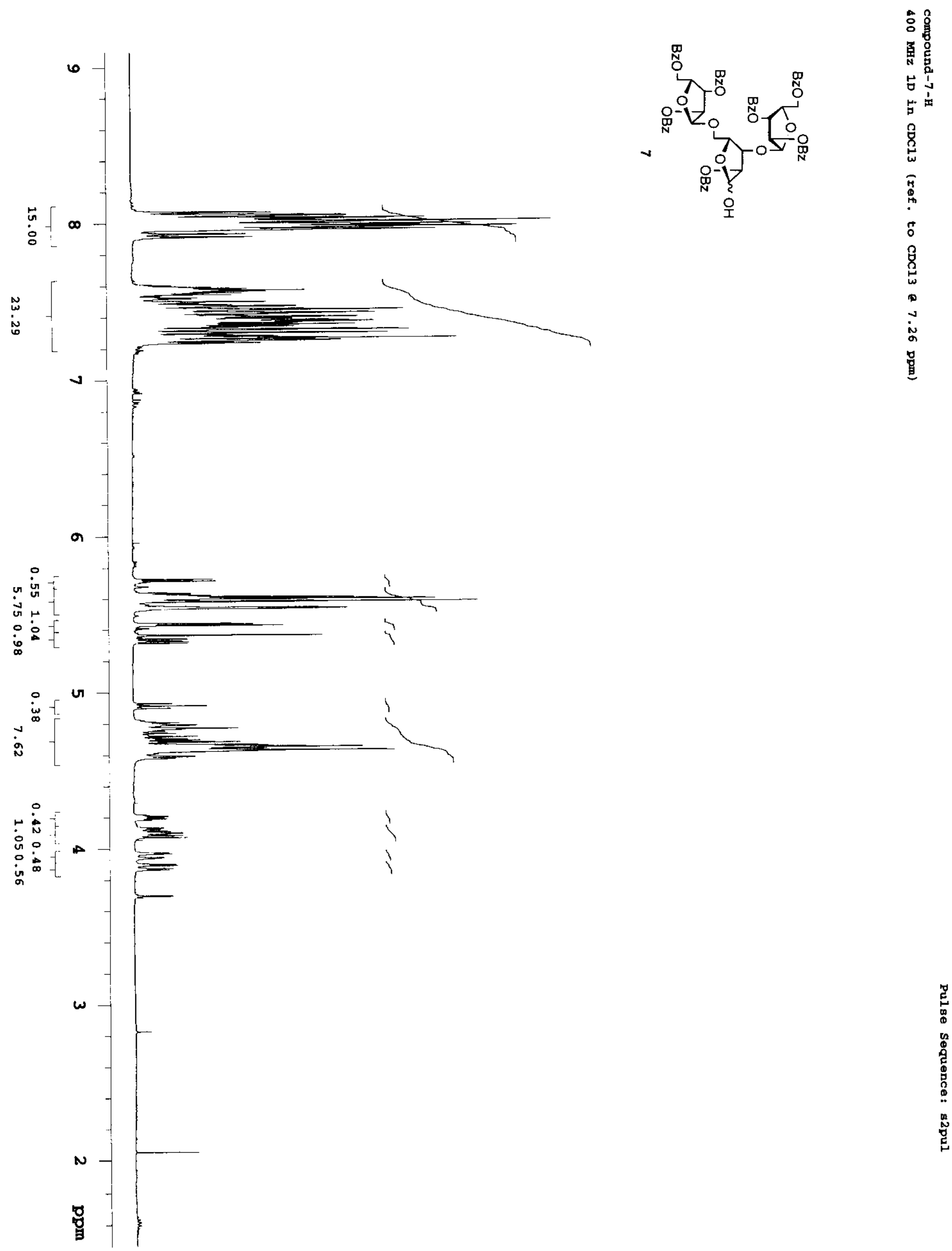
77.200
77.035
76.783
67.335
66.132
66.025
65.835
62.312
51.422
29.485
29.267
29.098
28.805
26.654
26.061
HO
BzO
OBz
O
O(CH2)8N3
5
180
160
140
120
100
80
60
40
20
ppm

compound-6-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

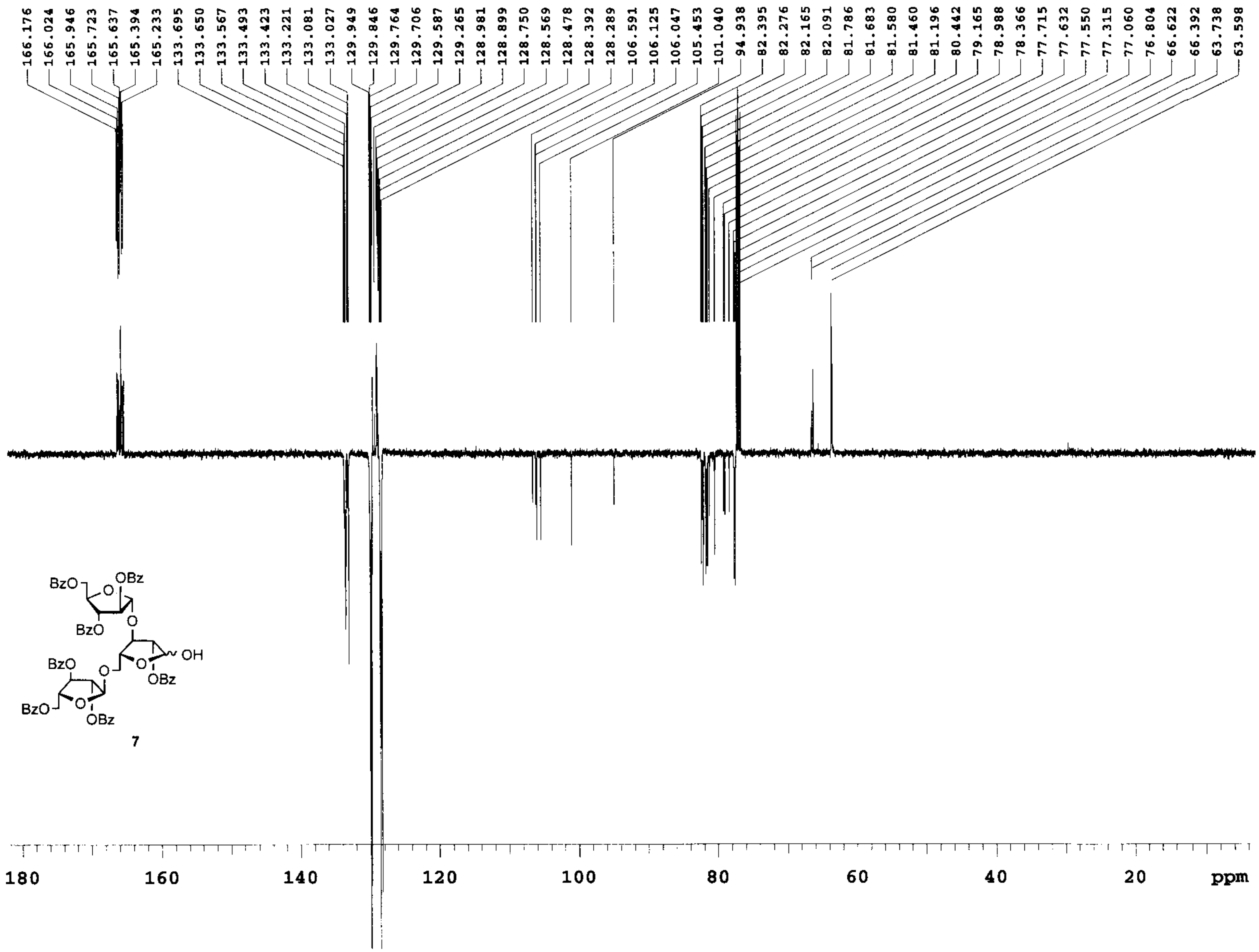



compound-6-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
166.119
165.904
165.678
165.583
165.459
165.348
165.183
165.052
135.640
133.551
133.299
133.217
133.126
133.003
129.888
129.764
129.628
129.311
129.138
129.059
128.891
128.812
128.561
128.417
128.347
128.194
127.659
105.981
105.808
105.161
101.131
94.967
83.178
82.861
82.610
82.466
82.268
82.136
81.942
81.814
81.530
80.170
79.326
79.153
78.234
77.303
77.047
76.792
76.619
66.680
65.885
65.782
65.547
63.413
26.774
19.287
t-BuPh2SiO
OBz
BzO
OH
6
180
160
140
120
100
80
60
40
20
ppm


compound-7-H
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)
Pulse Sequence: s2pul
BzO
OBz
OH
7
15.00
23.29
0.55 1.04
5.75 0.98
0.38
7.62
0.42 0.48
1.05 0.56
9
8
7
6
5
4
3
2
ppm

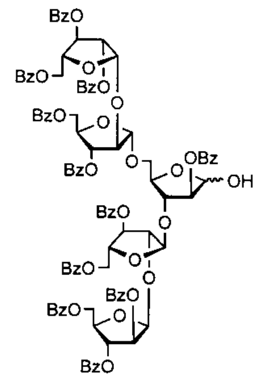
compound-7-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)

Pulse Sequence: apt

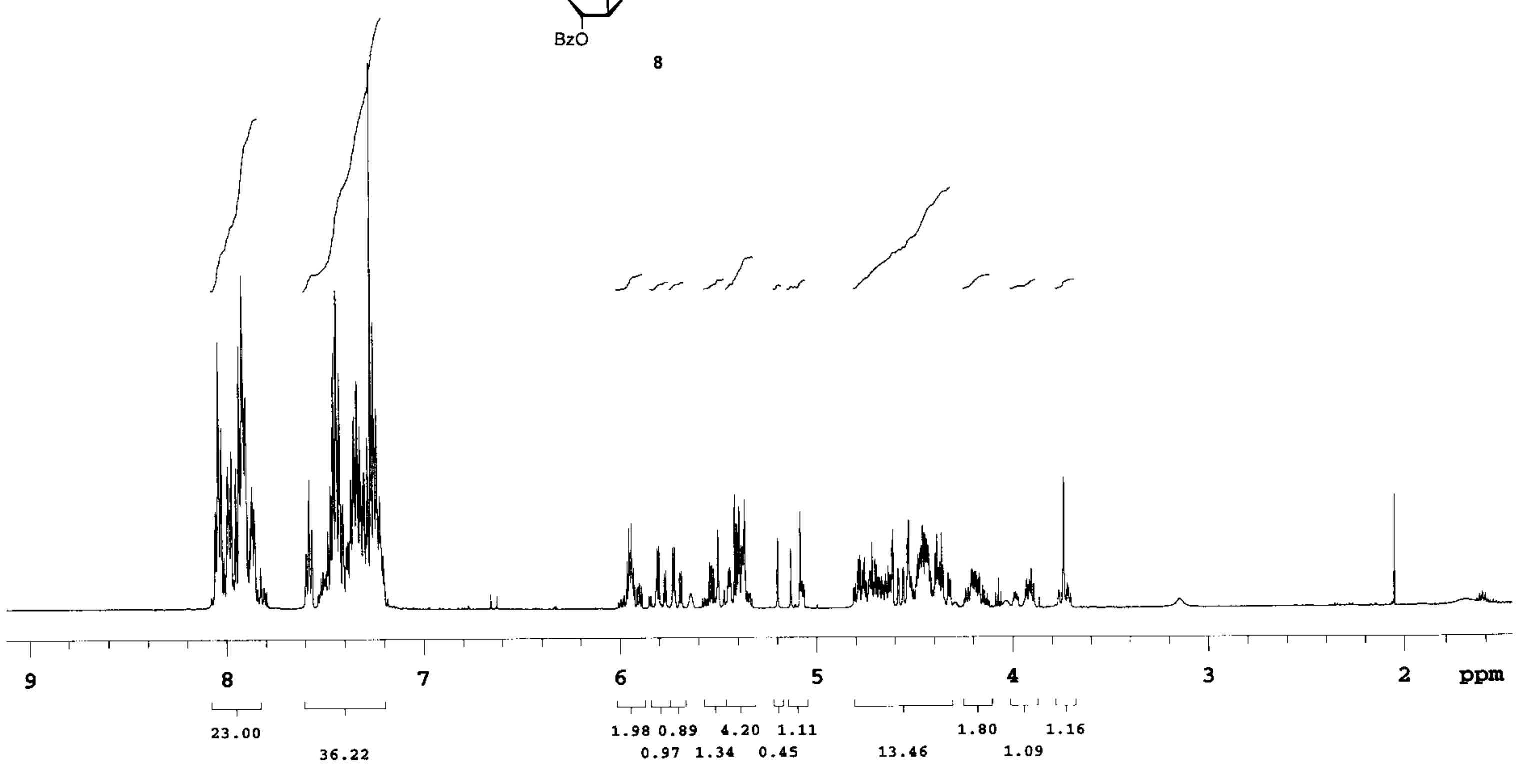


compound-8-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

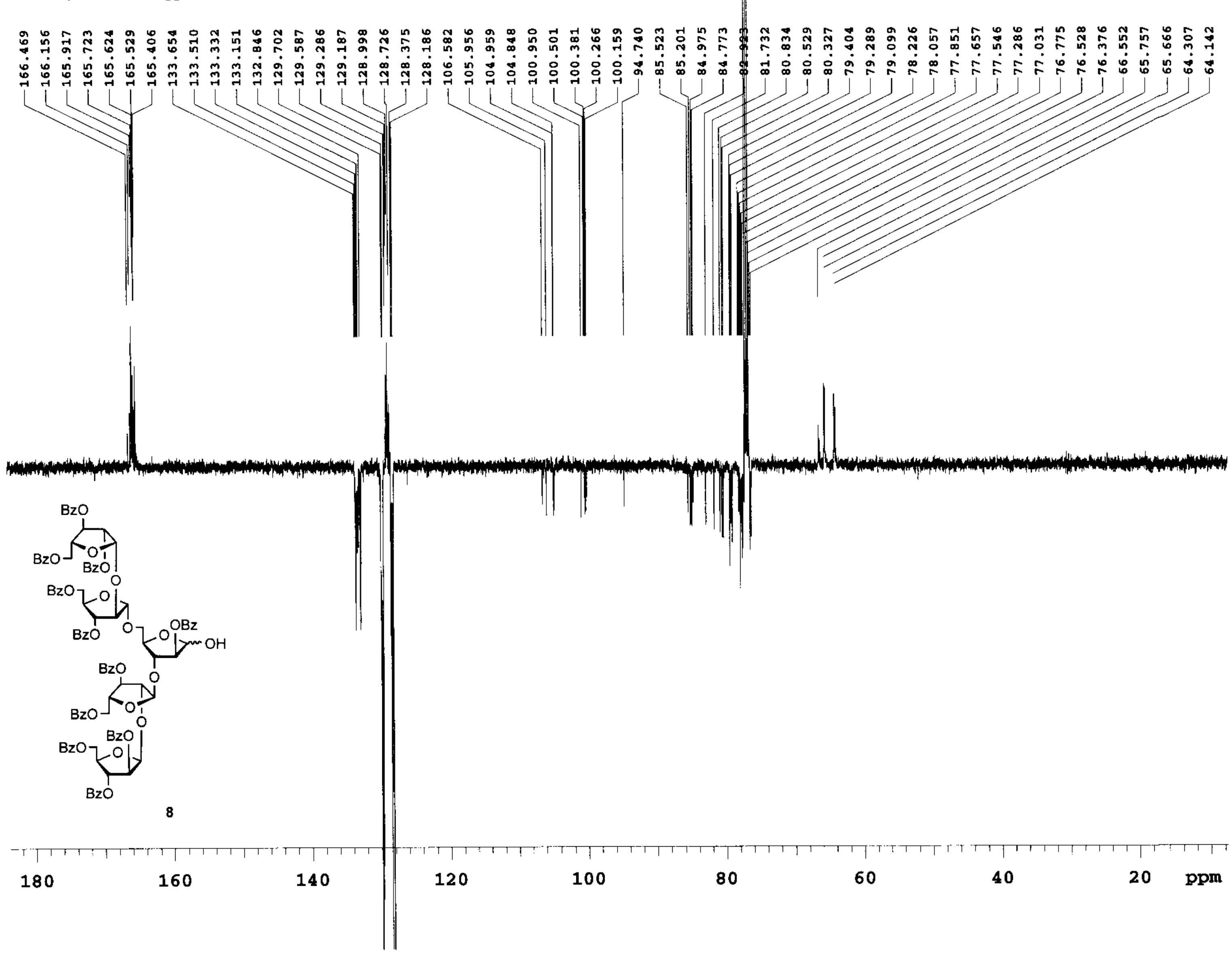


8



compound-8-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

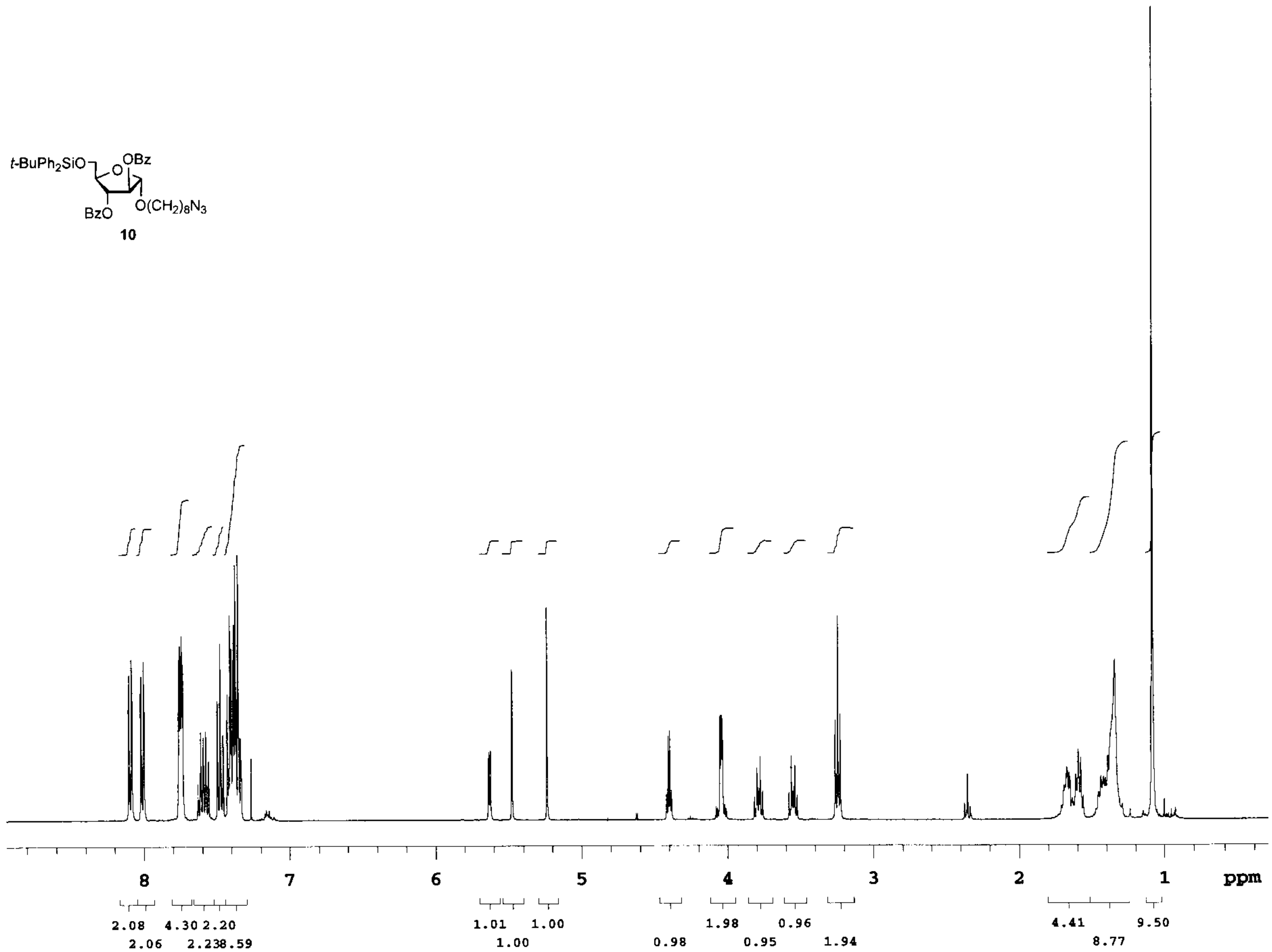
Pulse Sequence: apt

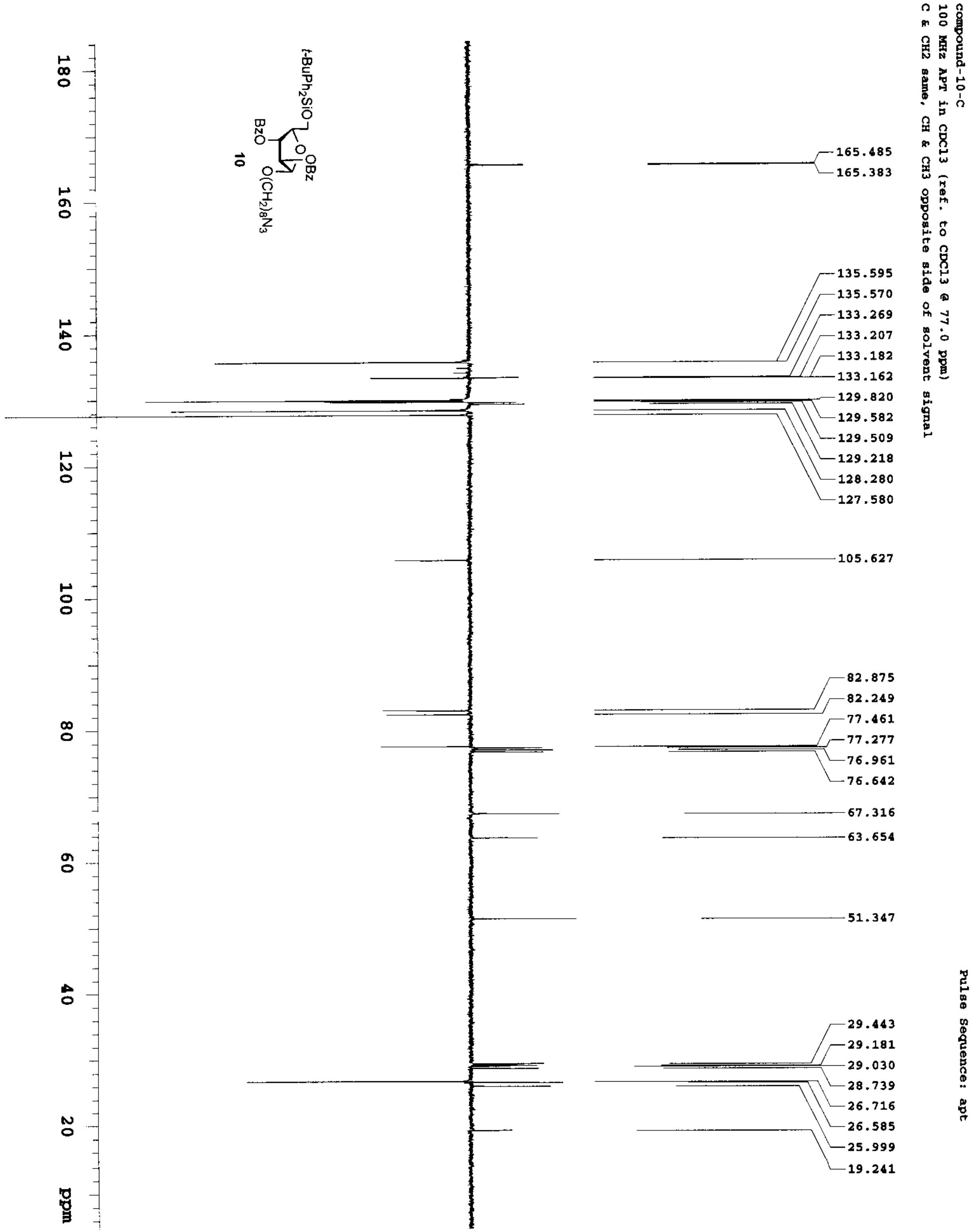


8

compound-10-H
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

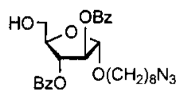
Pulse Sequence: s2pul



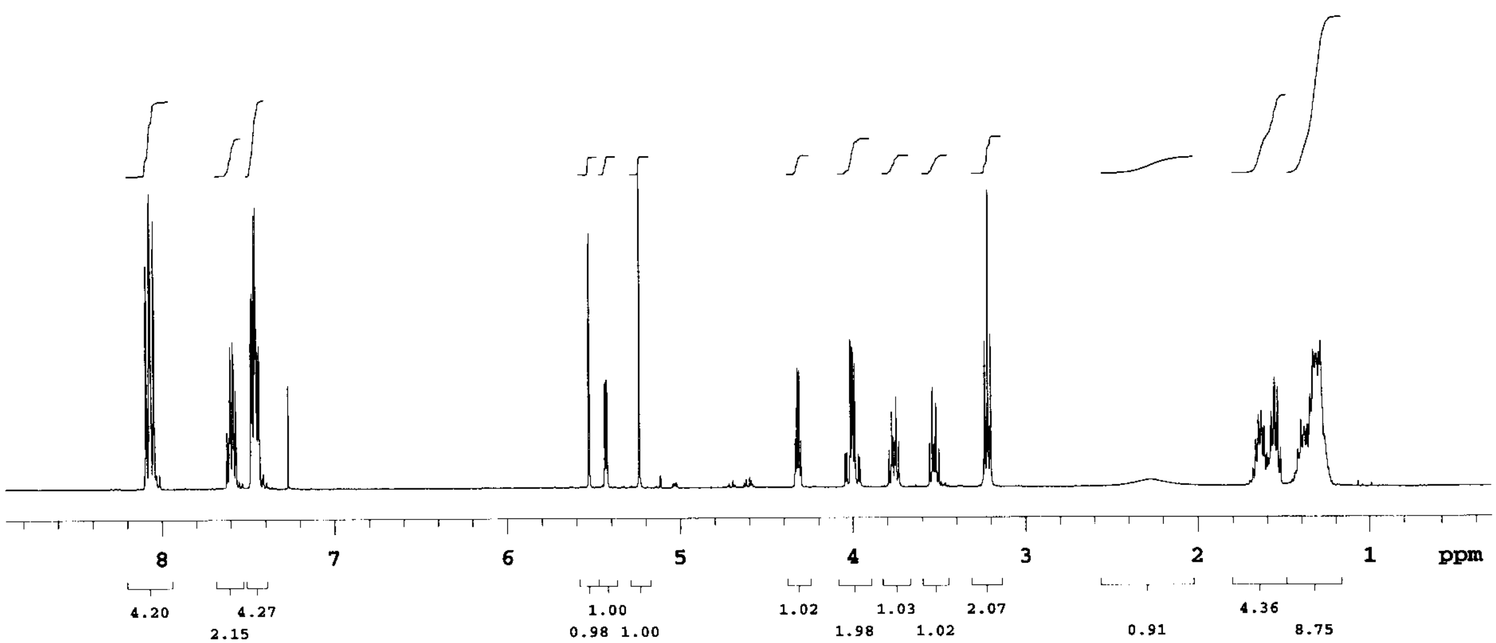

compound-10-C
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
165.485
165.383
135.595
135.570
133.269
133.207
133.182
133.162
129.820
129.582
129.509
129.218
128.280
127.580
105.627
82.875
82.249
77.461
77.277
76.961
76.642
67.316
63.654
51.347
29.443
29.181
29.030
28.739
26.716
26.585
25.999
19.241
t-BuPh2SiO
OBz
BzO
O(CH2)8N3
10
180
160
140
120
100
80
60
40
20
ppm

compound-11-H
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

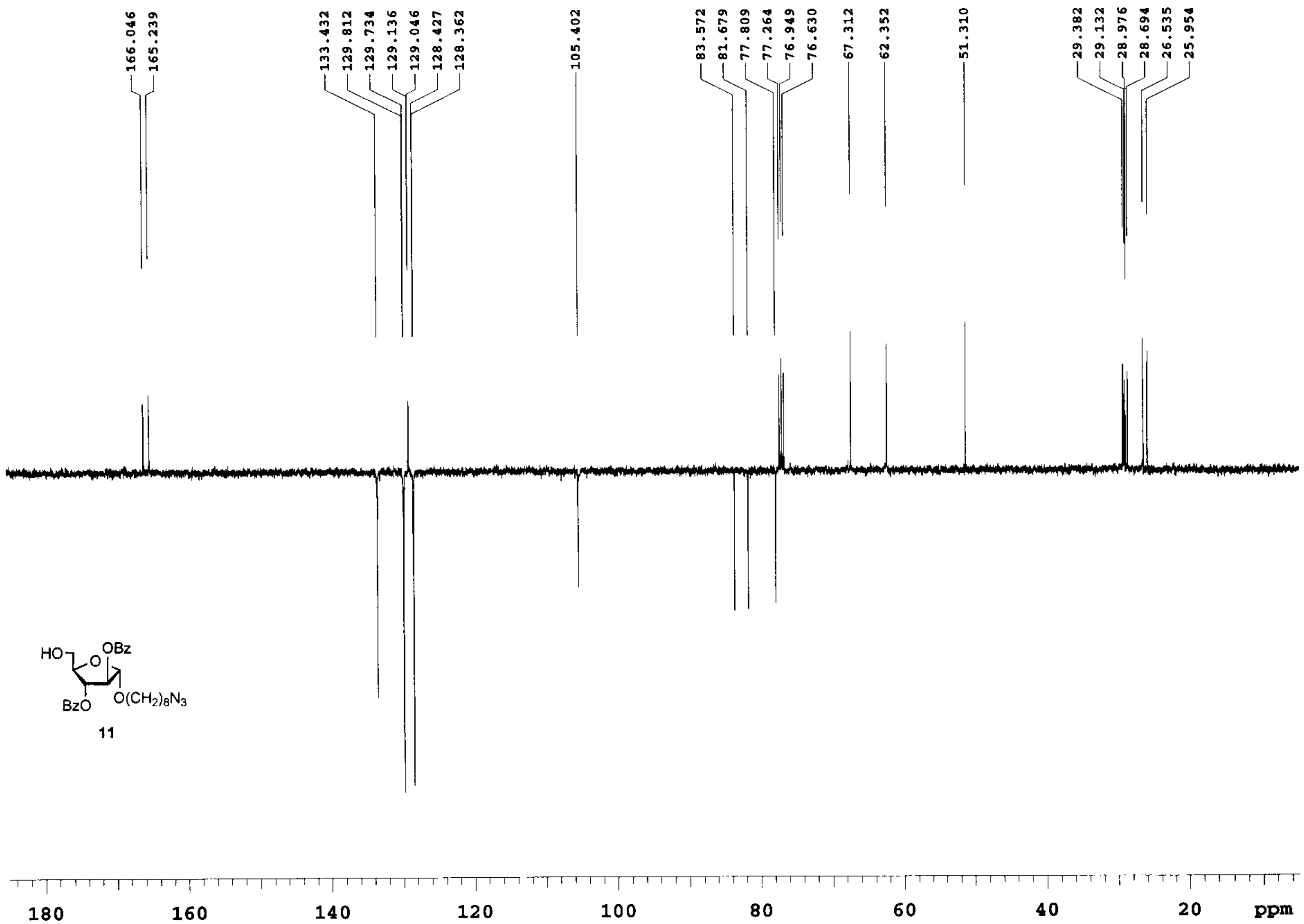


11



compound-11-C
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

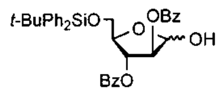
Pulse Sequence: apt



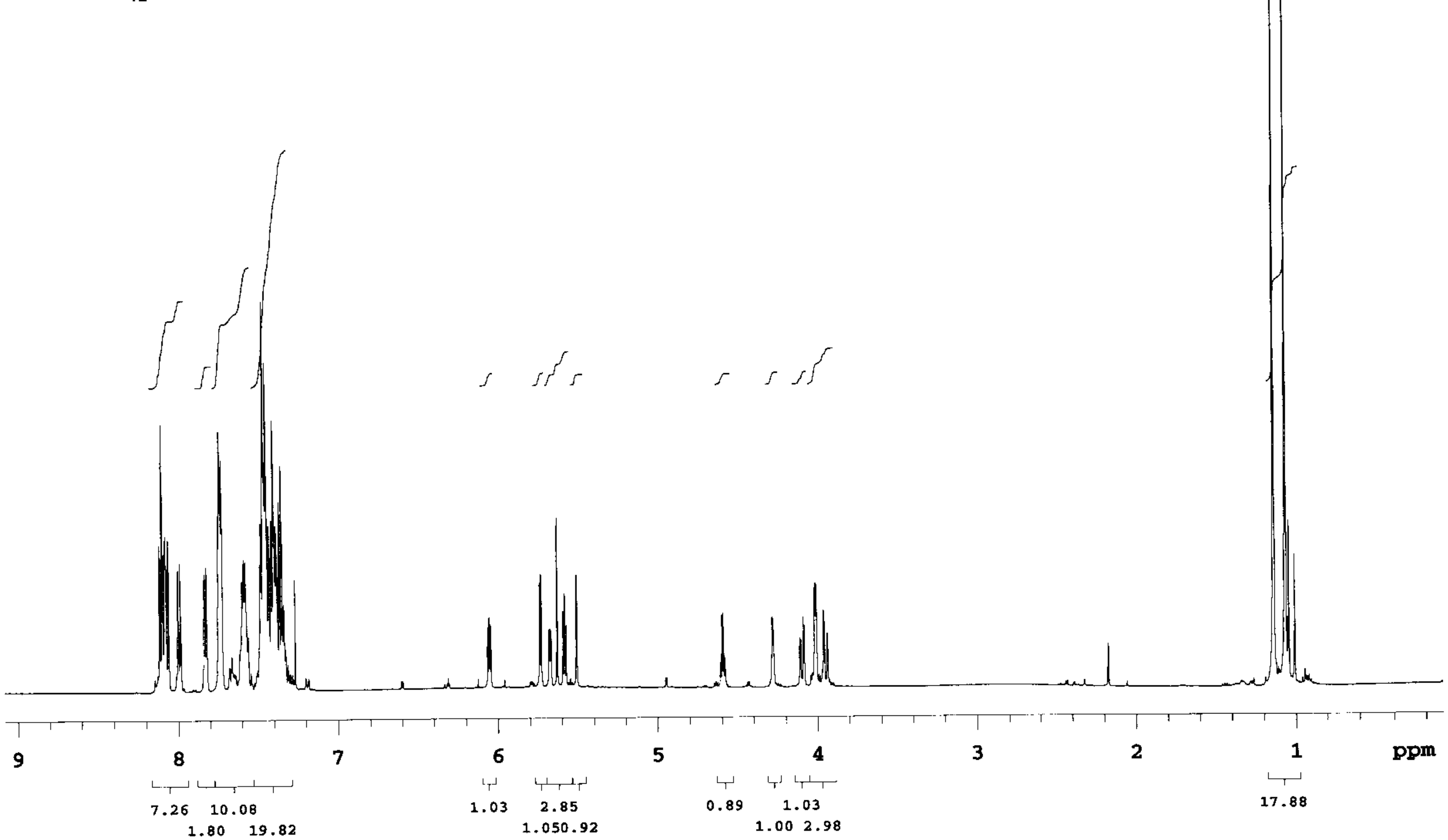
11

compound-12-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

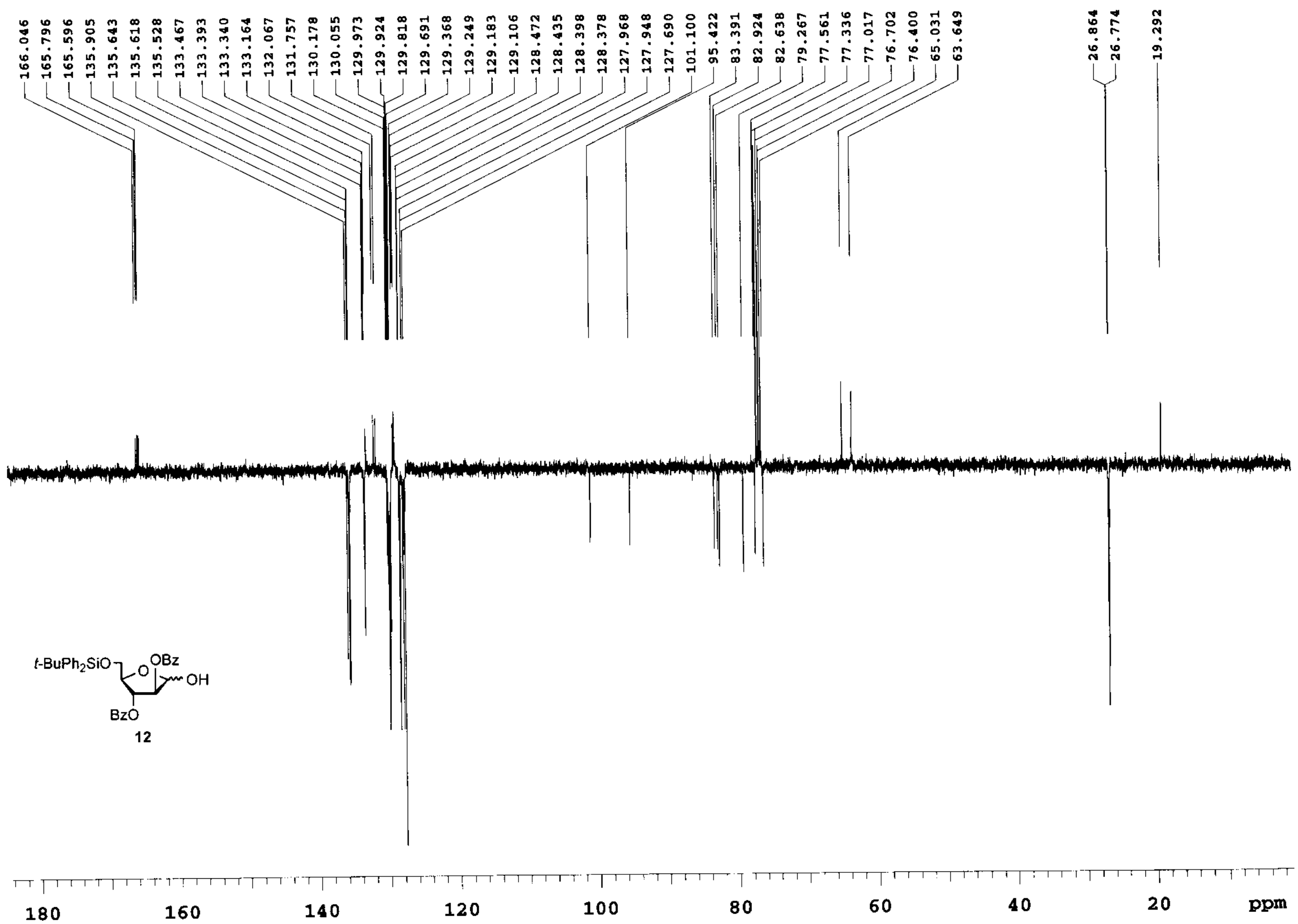


12



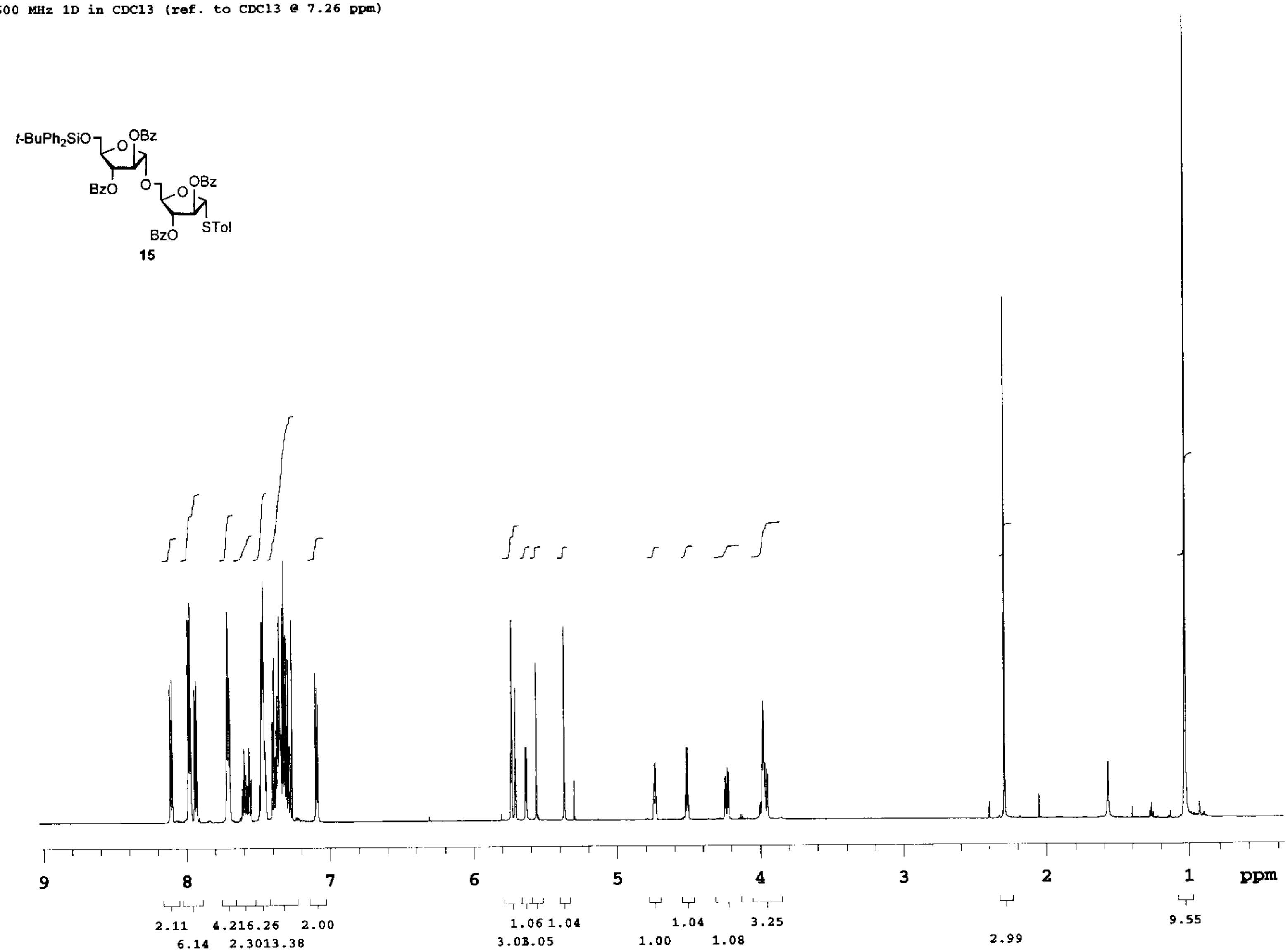
compound-12-C
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

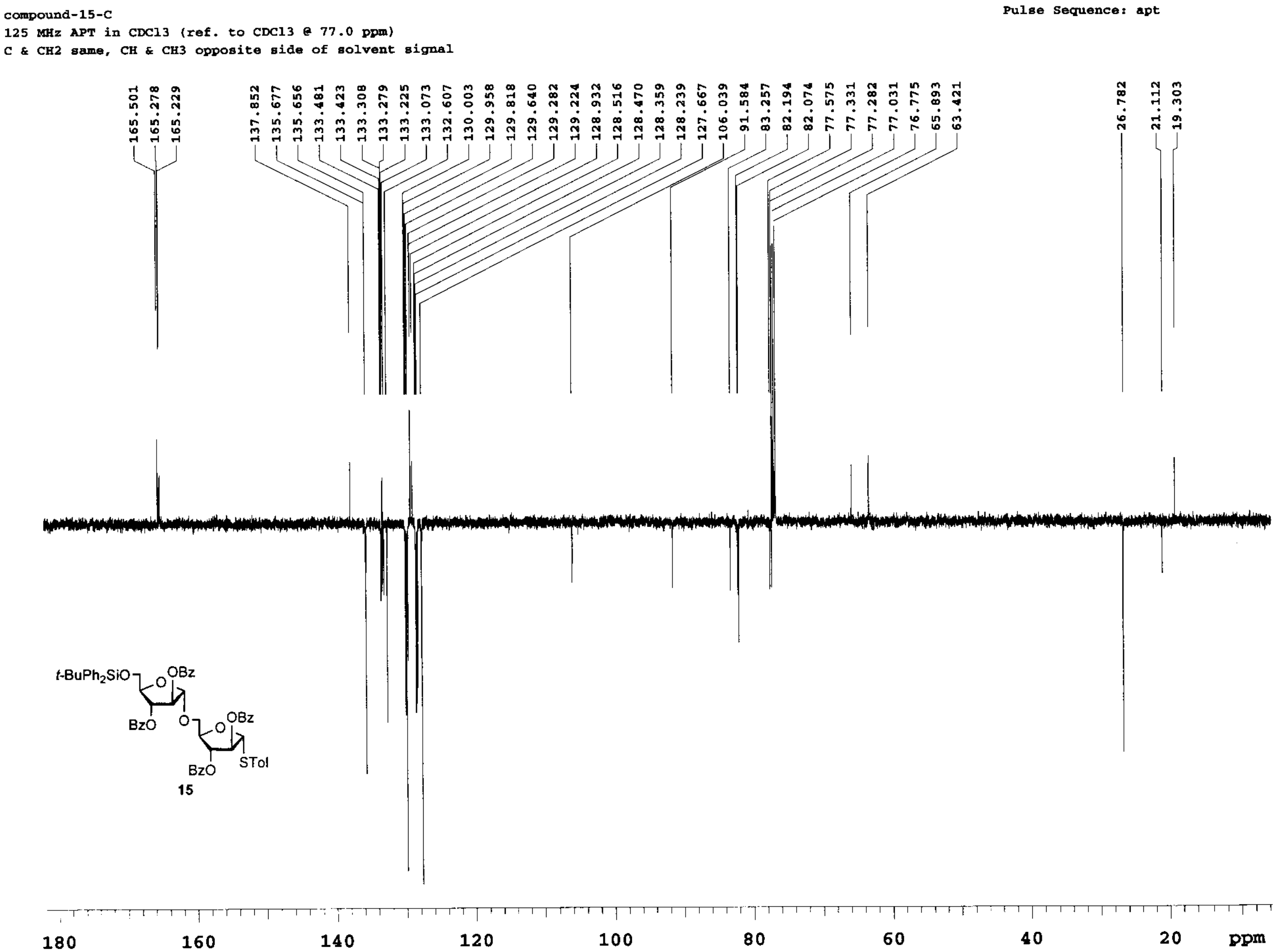
Pulse Sequence: apt



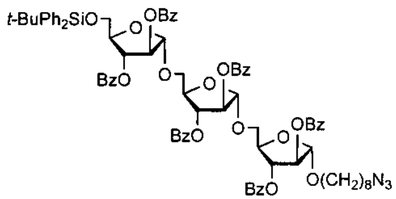
compound-15-H
600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

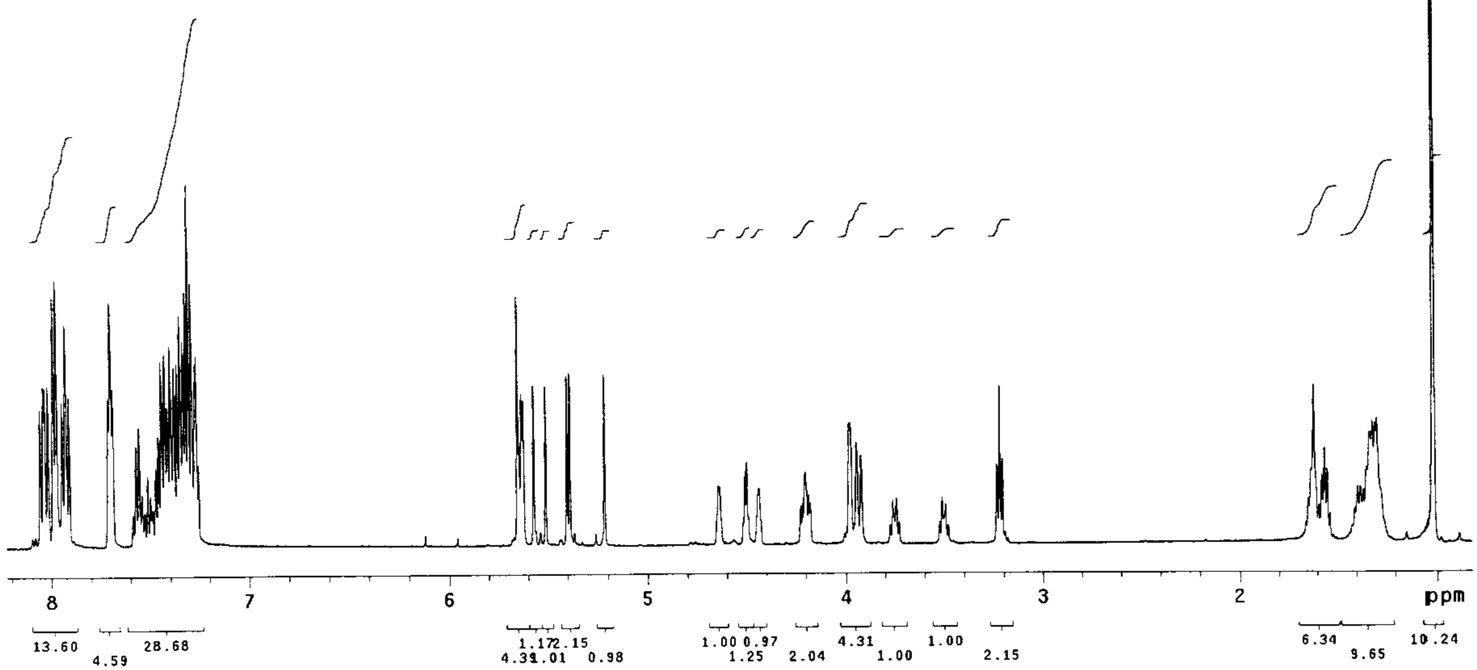



compound-15-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
165.501
165.278
165.229
137.852
135.677
135.656
133.481
133.423
133.308
133.279
133.225
133.073
132.607
130.003
129.958
129.818
129.640
129.282
129.224
128.932
128.516
128.470
128.359
128.239
127.667
106.039
91.584
83.257
82.194
82.074
77.575
77.331
77.282
77.031
76.775
65.893
63.421
26.782
21.112
19.303
t-BuPh2SiO
OBz
O
BzO
O
O
OBz
BzO
STol
15
180
160
140
120
100
80
60
40
20
ppm

compound-16-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

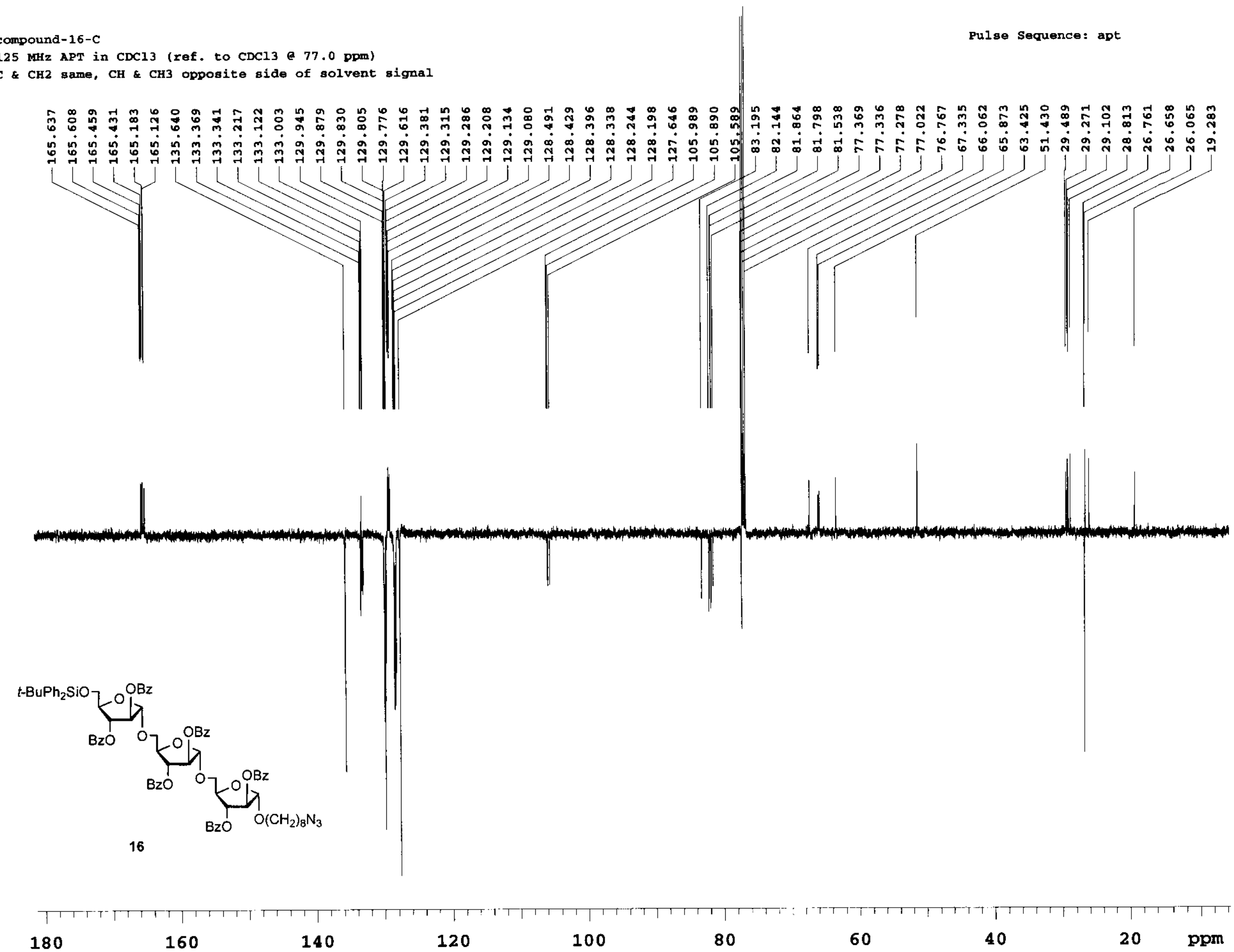


16



compound-16-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

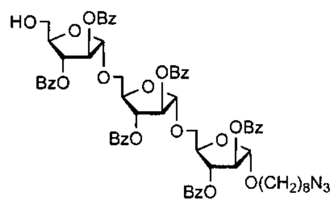
Pulse Sequence: apt



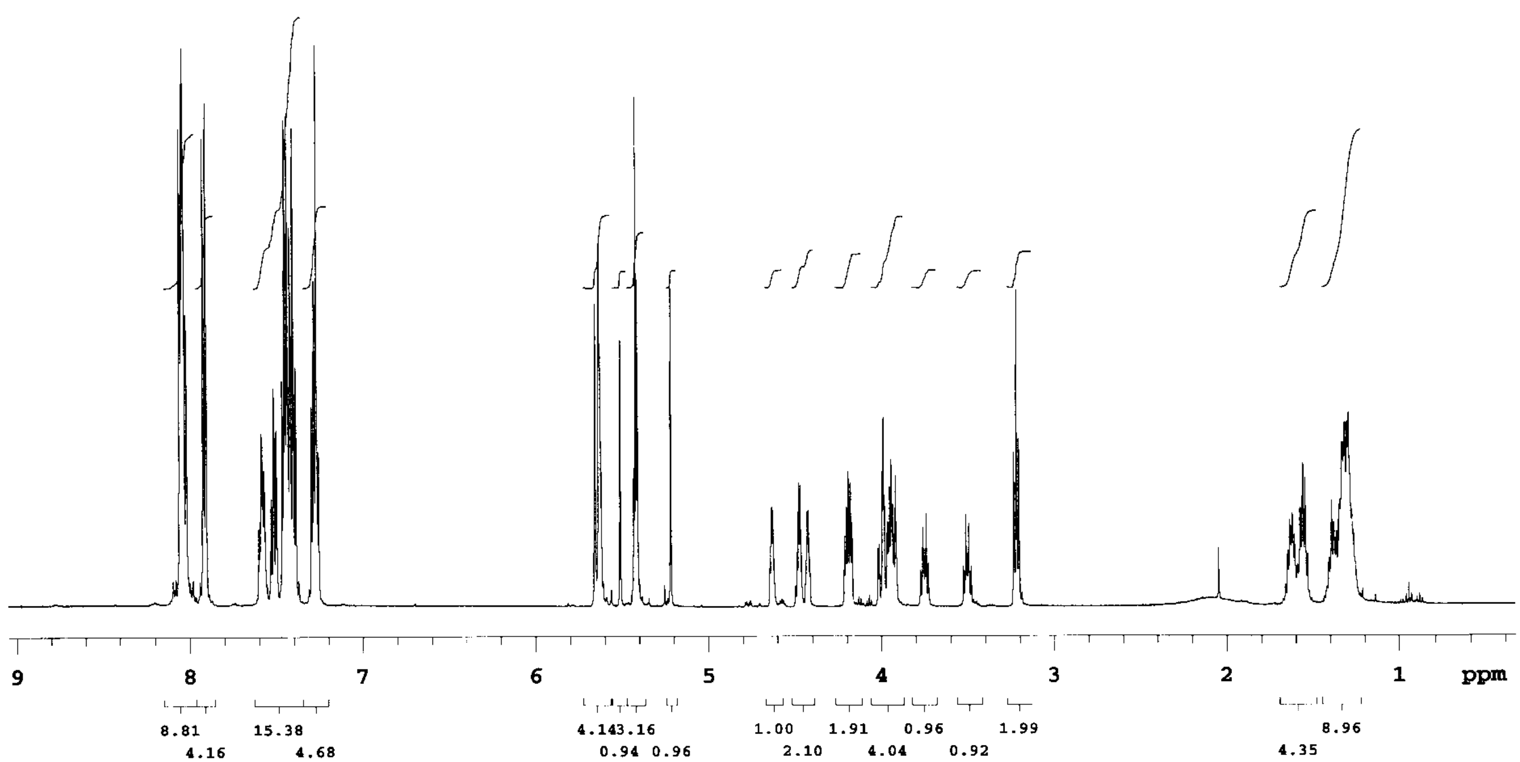
16

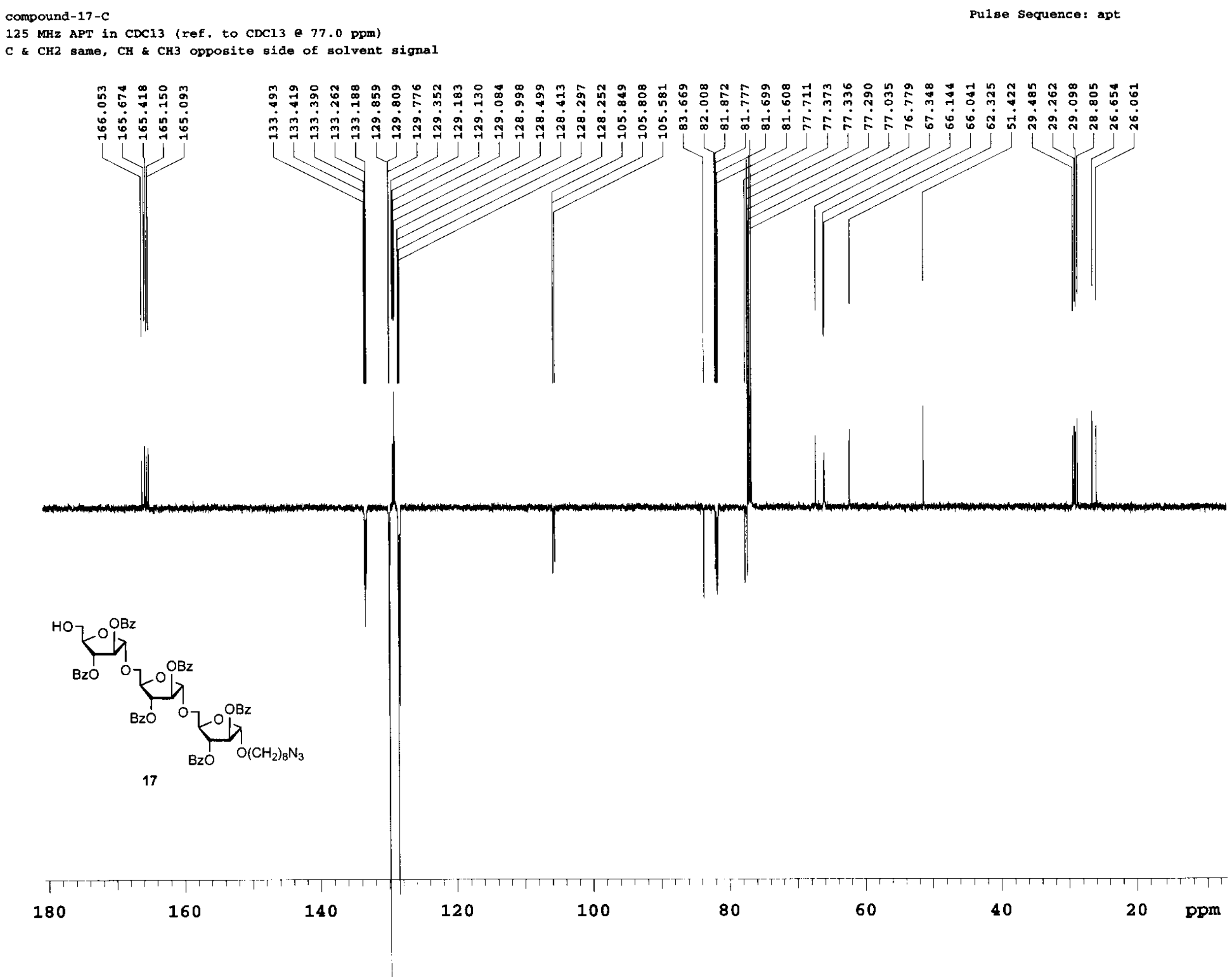
compound-17-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul



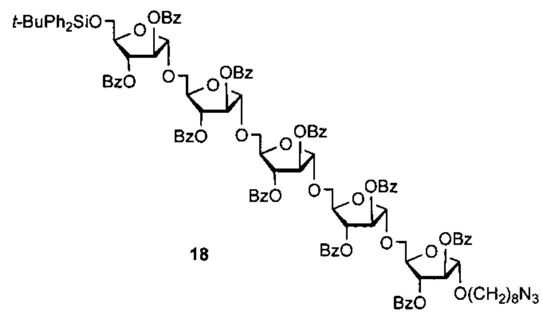
17



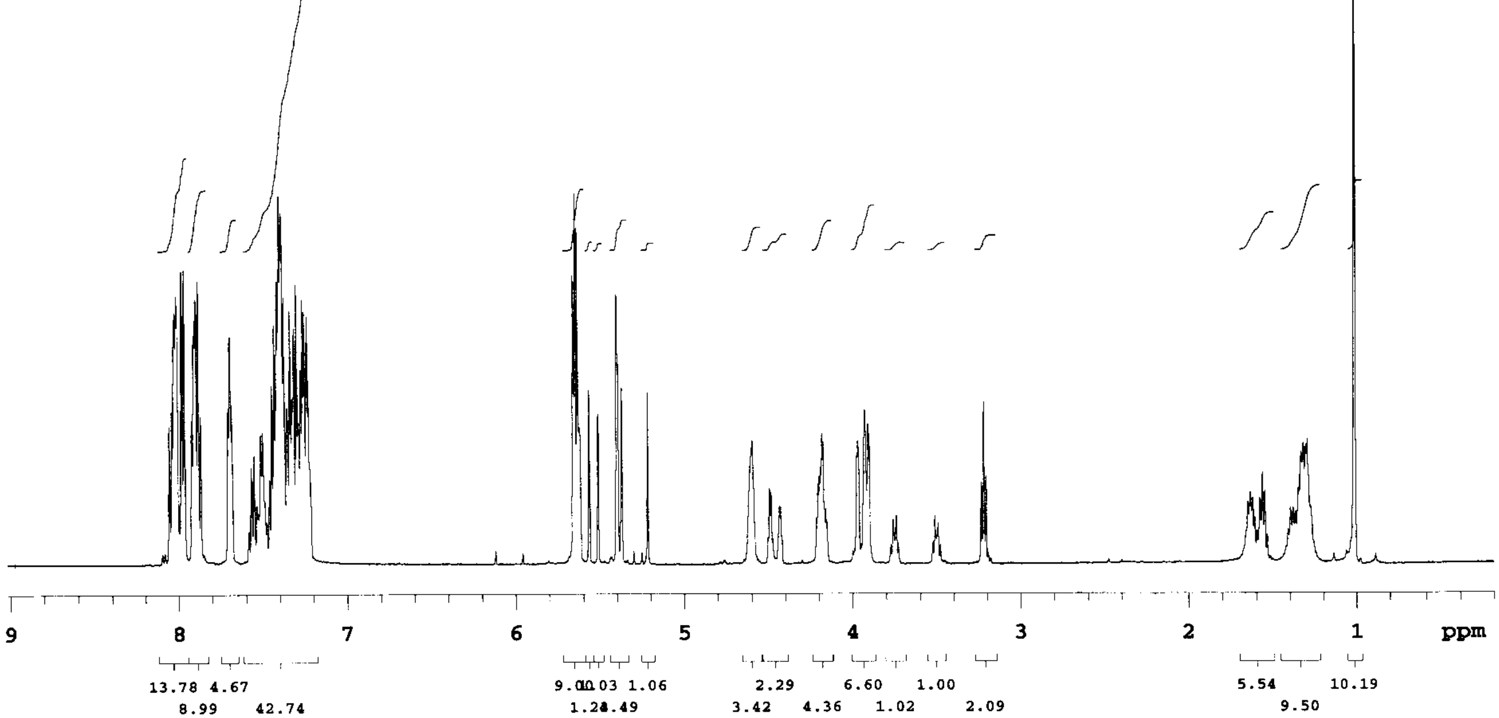

compound-17-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
166.053
165.674
165.418
165.150
165.093
133.493
133.419
133.390
133.262
133.188
129.859
129.809
129.776
129.352
129.183
129.130
129.084
128.998
128.499
128.413
128.297
128.252
105.849
105.808
105.581
83.669
82.008
81.872
81.777
81.699
81.608
77.711
77.373
77.336
77.290
77.035
76.779
67.348
66.144
66.041
62.325
51.422
29.485
29.262
29.098
28.805
26.654
26.061
HO
OBz
BzO
O
OBz
BzO
O
OBz
BzO
O(CH2)8N3
17
180
160
140
120
100
80
60
40
20
ppm

compound-18-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

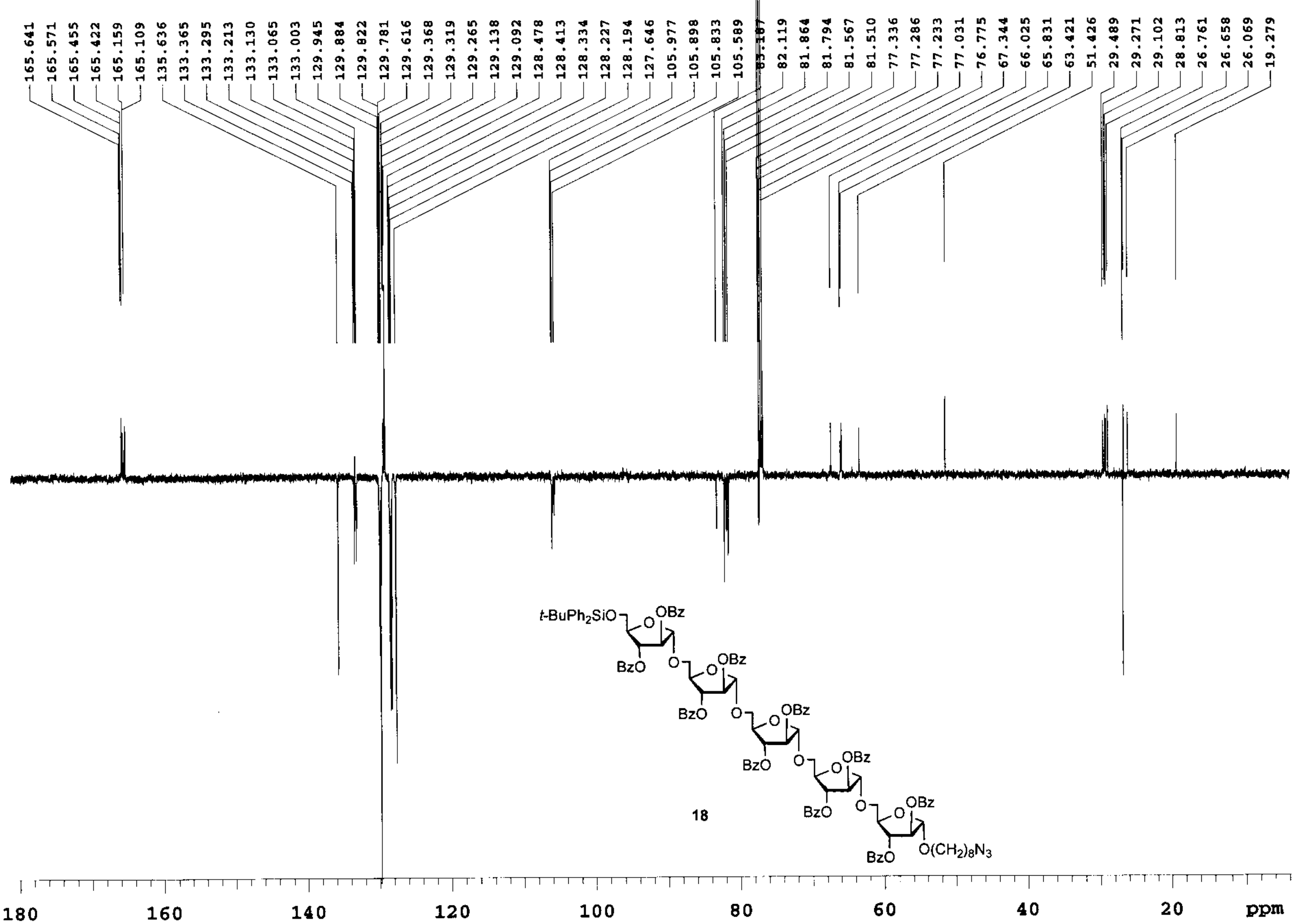


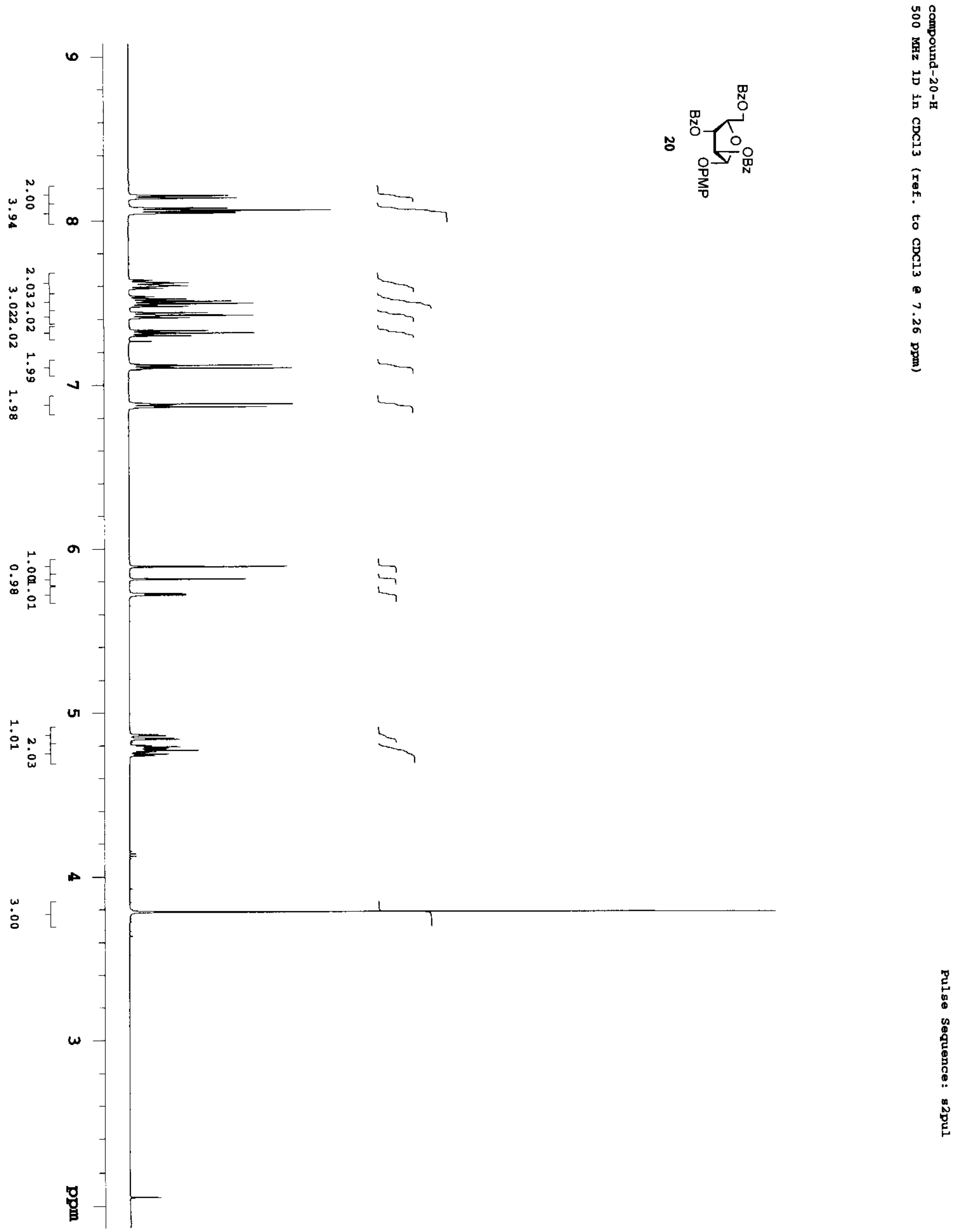
18



compound-18-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

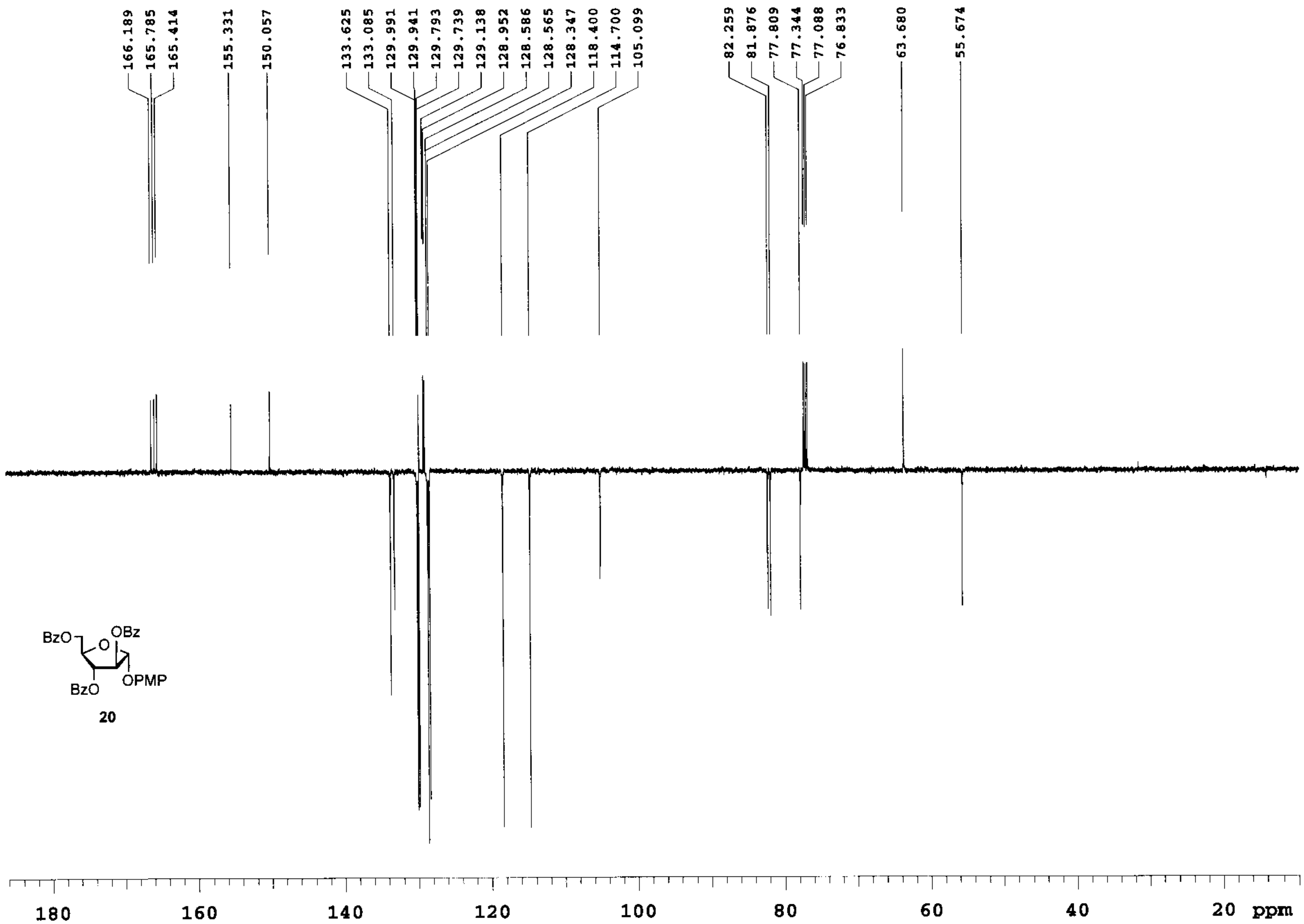
Pulse Sequence: apt

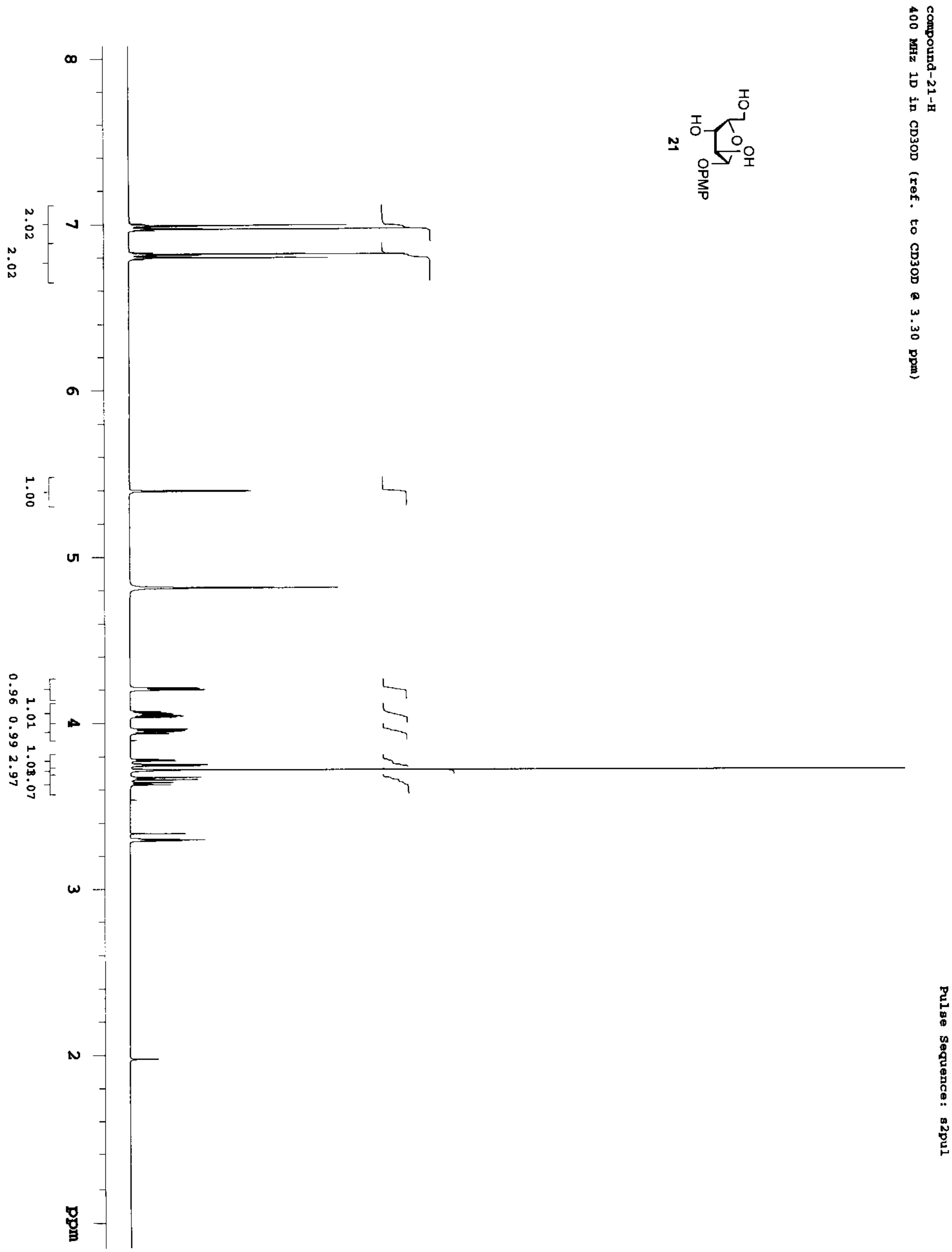


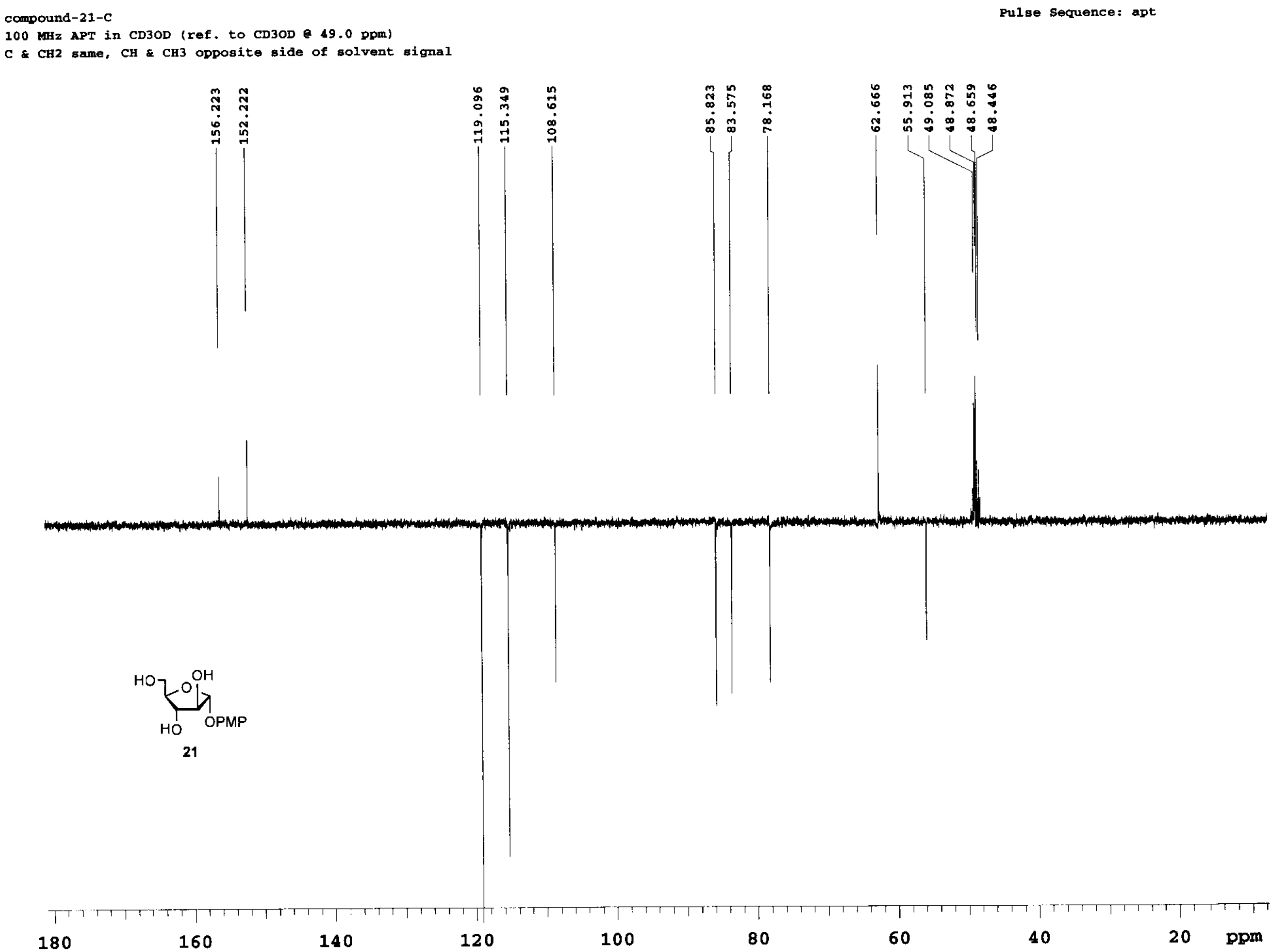

compound-20-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)
BzO
OBz
BzO
OPMP
20
Pulse Sequence: s2pul
2.00
3.94
2.032.02
3.022.02
1.99
1.98
1.001.01
0.98
2.03
1.01
3.00
9
8
7
6
5
4
3
ppm

compound-20-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

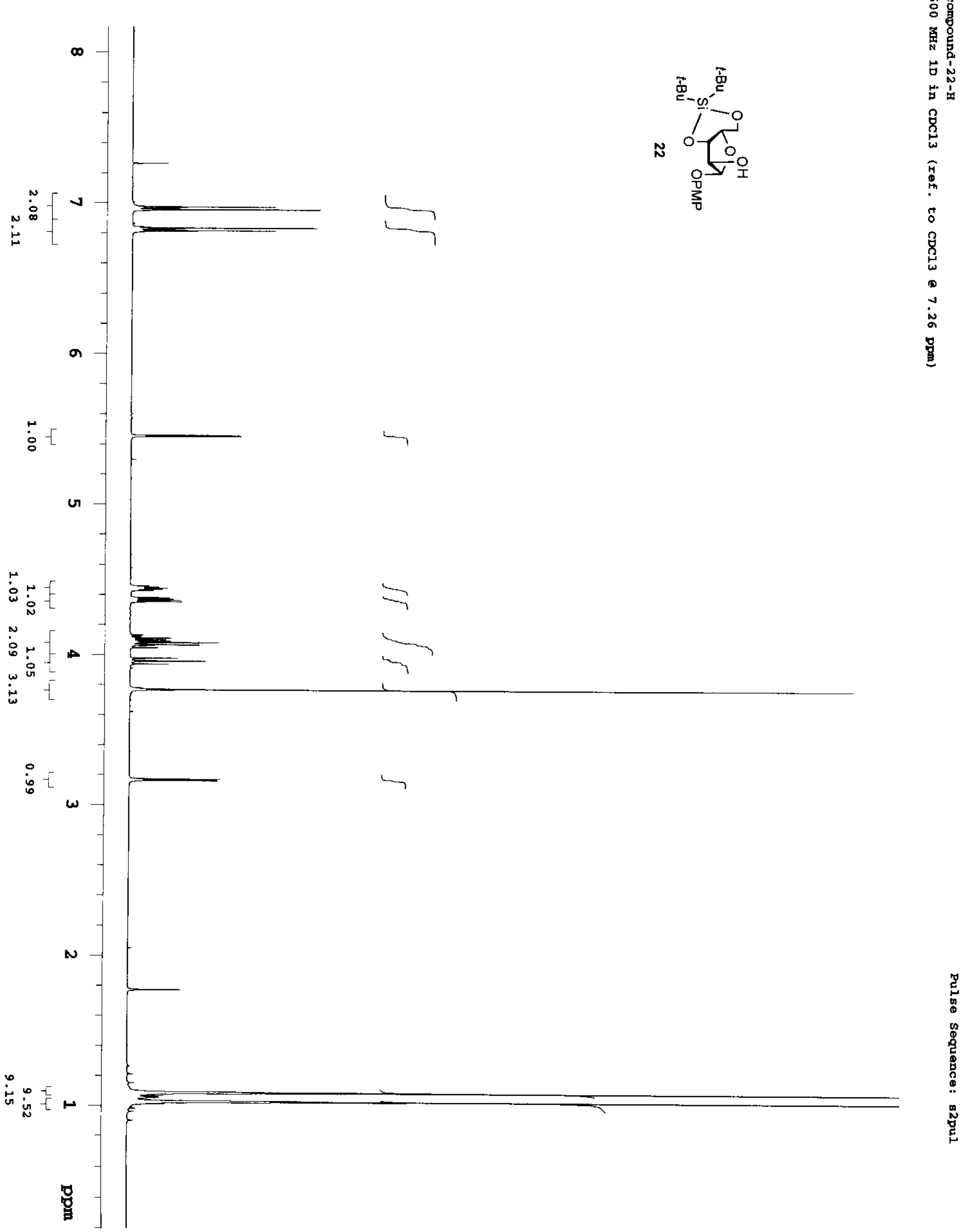
Pulse Sequence: apt

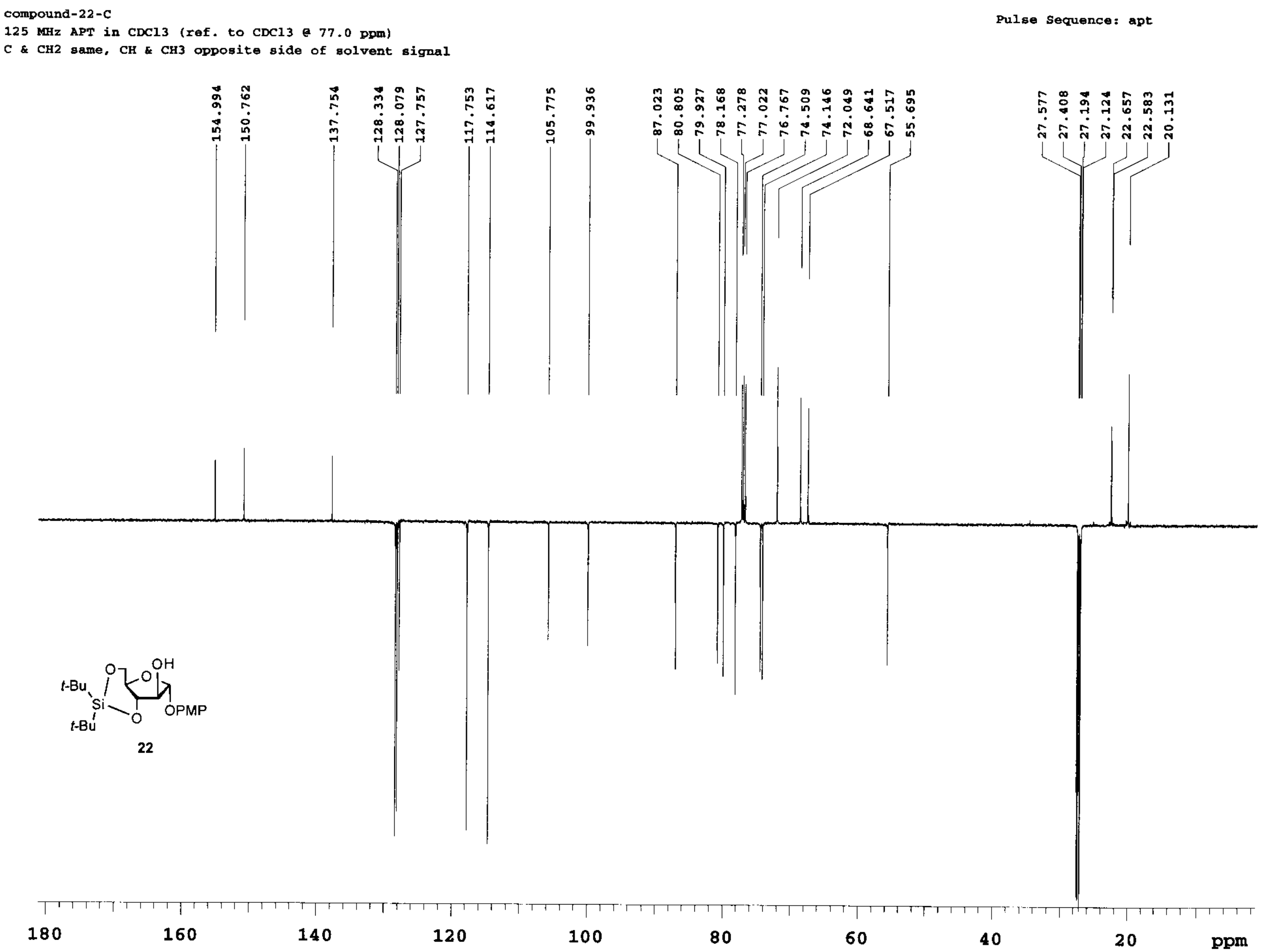



compound-21-H
400 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm)
Pulse Sequence: s2pul
HO
HO
O
OH
OPMP
21
2.02
2.02
1.00
1.01
0.96 0.99 2.97
1.03.07
8
7
6
5
4
3
2
ppm



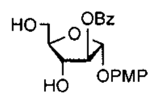
compound-21-C
100 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
156.223
152.222
119.096
115.349
108.615
85.823
83.575
78.168
62.666
55.913
49.085
48.872
48.659
48.446
HO
OH
O
HO
OPMP
21
180
160
140
120
100
80
60
40
20
ppm


compound-22-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)
Pulse Sequence: s2pul
t-Bu
t-Bu
Si
OH
OPMP
22
2.08
2.11
1.00
1.02
1.03
2.09
1.05
3.13
0.99
9.52
9.15
8
7
6
5
4
3
2
1
ppm

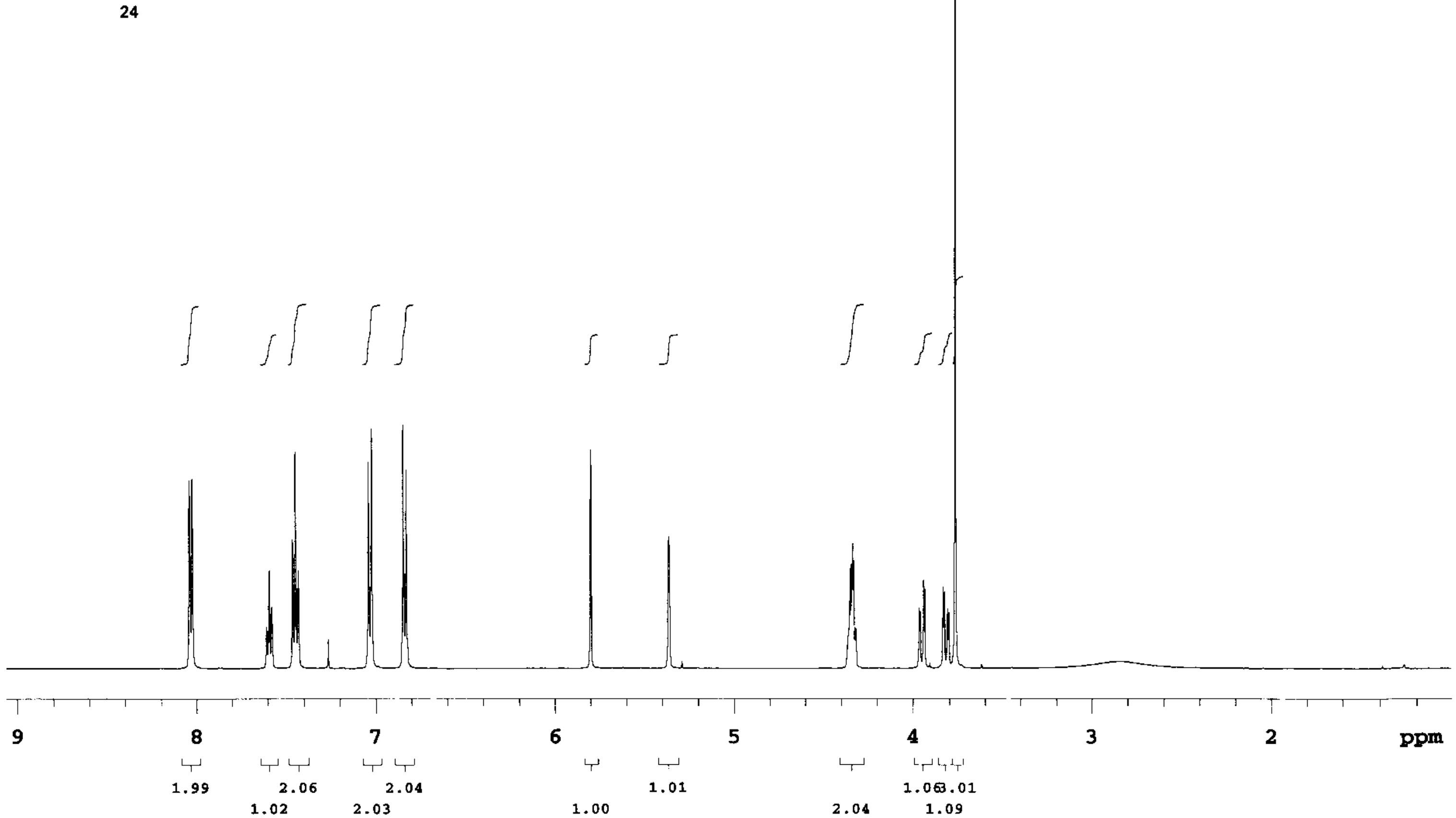

compound-22-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
154.994
150.762
137.754
128.334
128.079
127.757
117.753
114.617
105.775
99.936
87.023
80.805
79.927
78.168
77.278
77.022
76.767
74.509
74.146
72.049
68.641
67.517
55.695
27.577
27.408
27.194
27.124
22.657
22.583
20.131
t-Bu
Si
t-Bu
O
OH
OPMP
22
180
160
140
120
100
80
60
40
20
ppm

compound-24-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

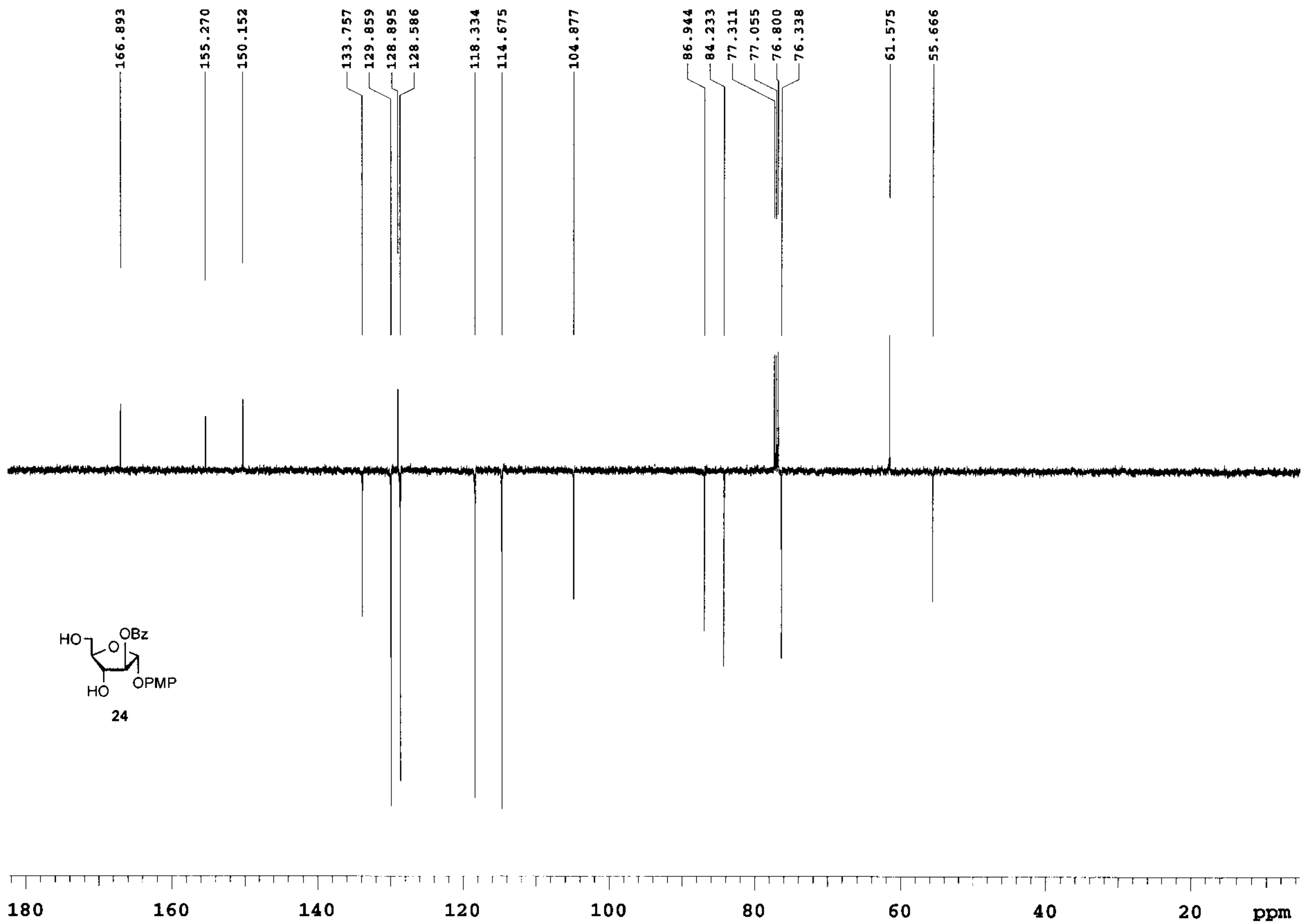


24



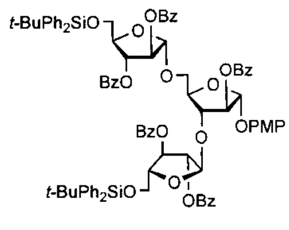
compound-24-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

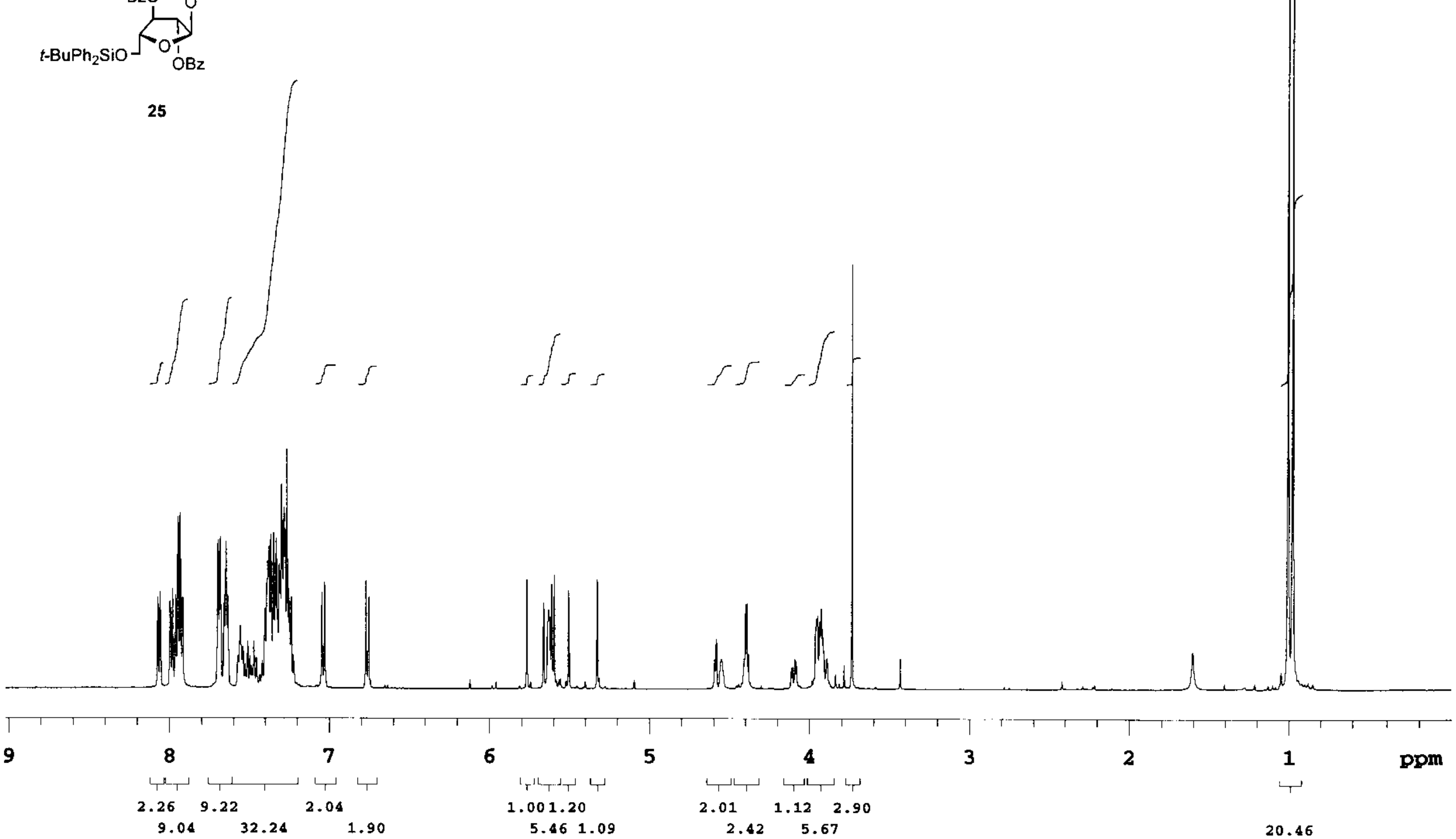


compound-25-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

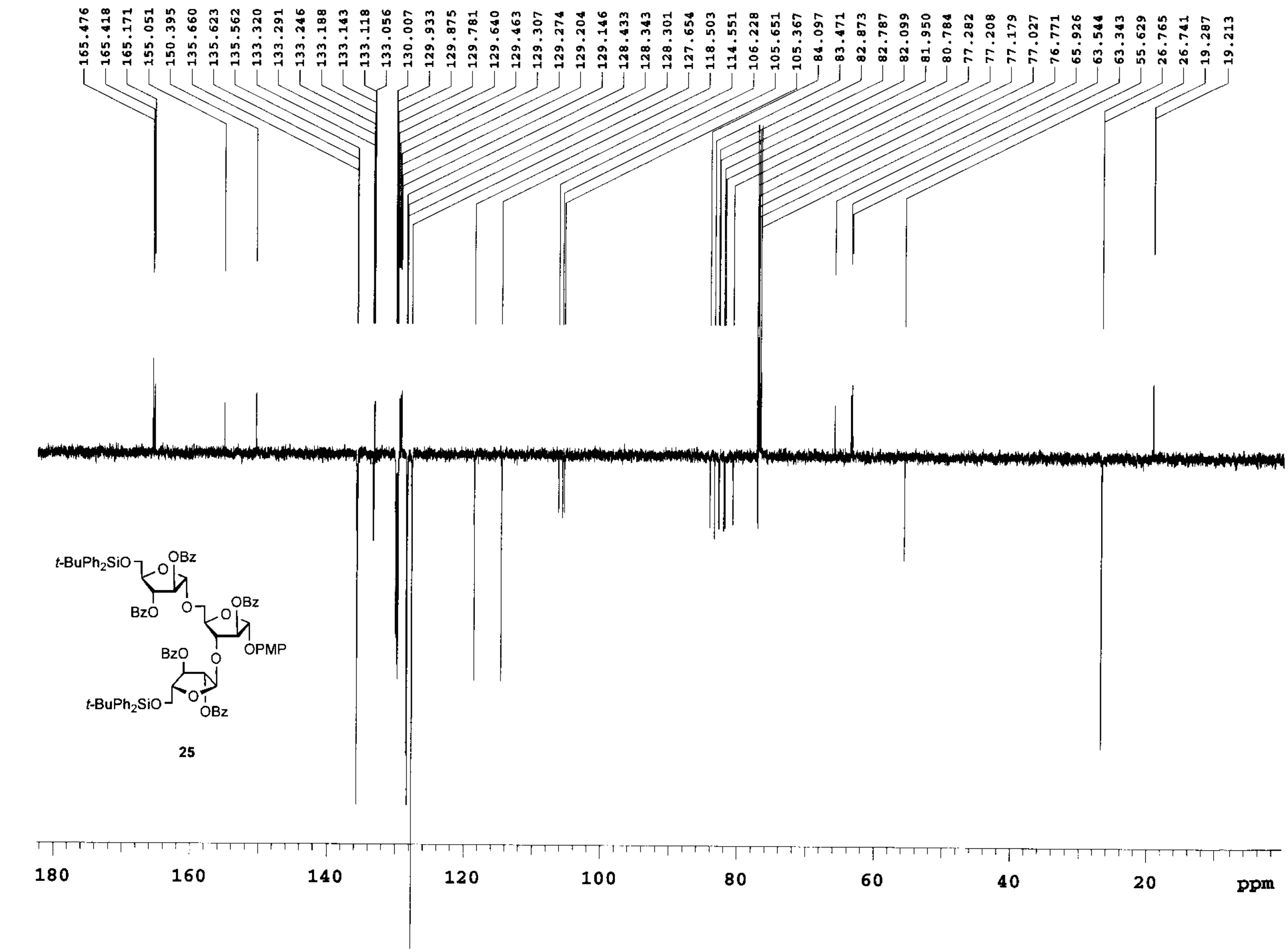


25



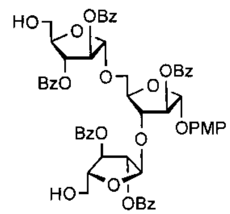
compound-25-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

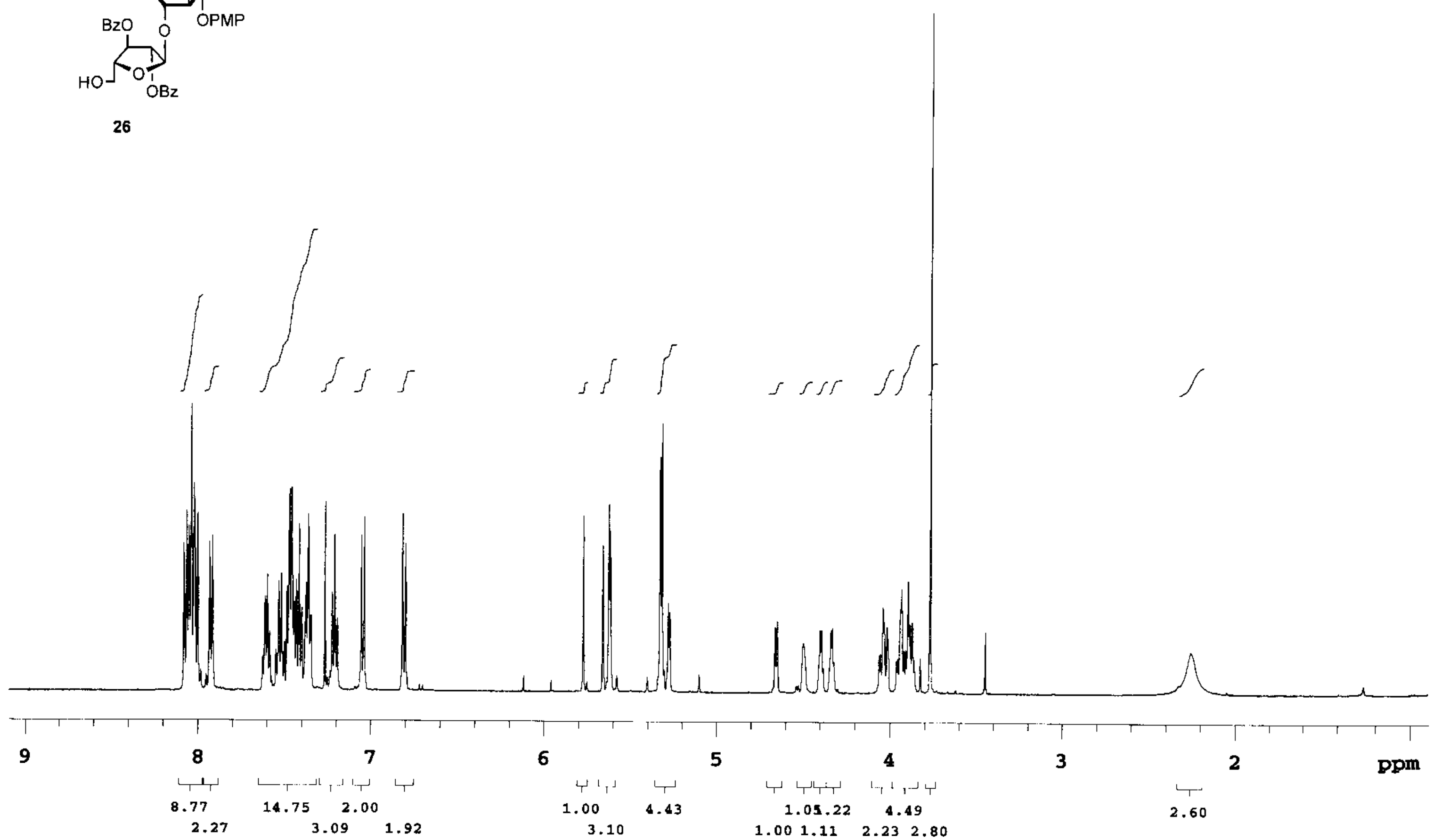


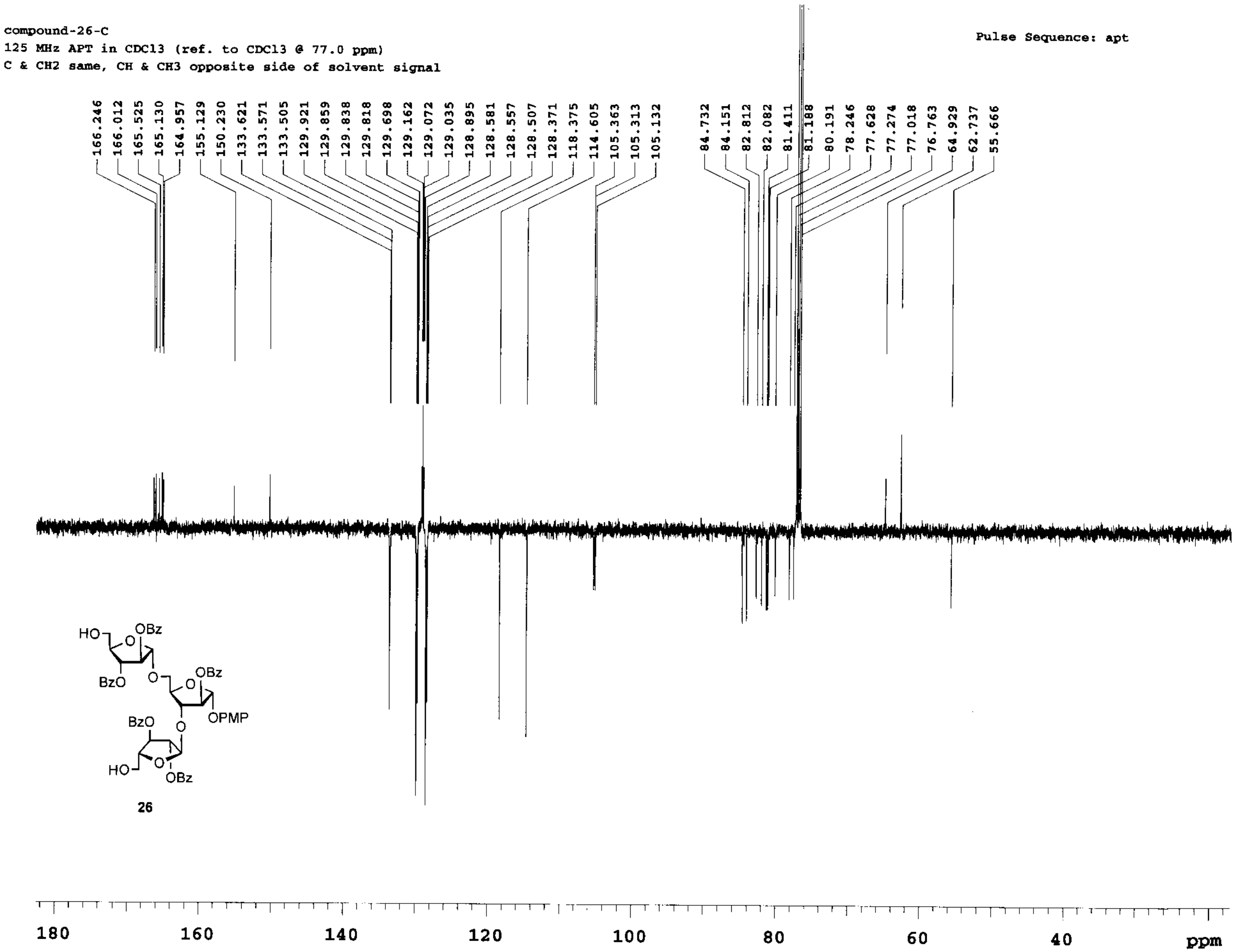
compound-26-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul



26

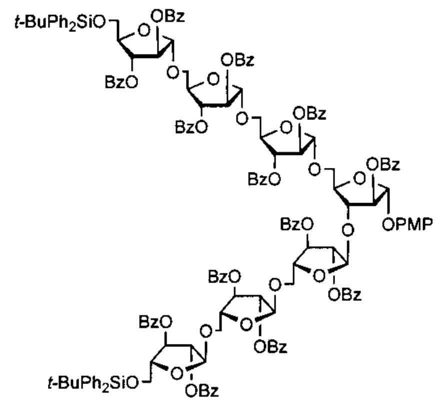




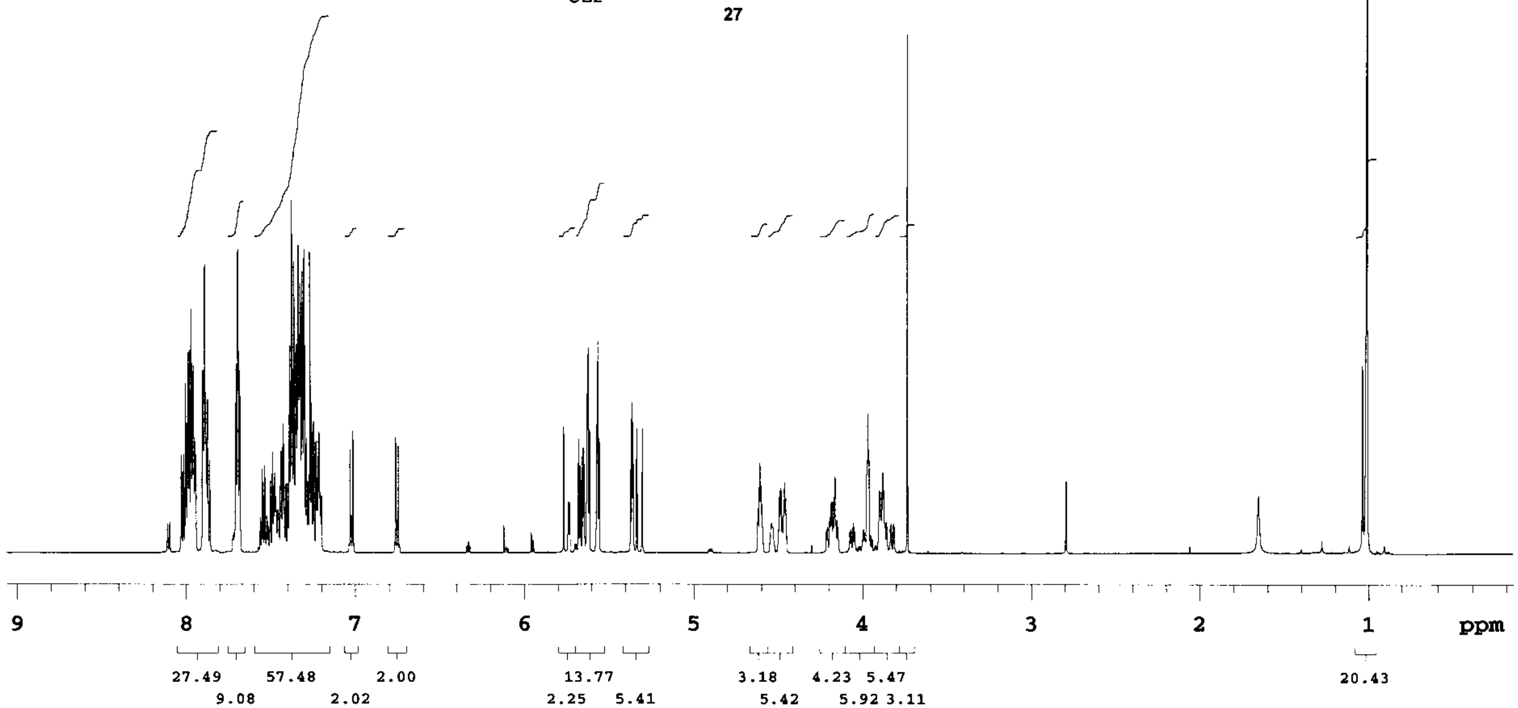
compound-26-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
166.246
166.012
165.525
165.130
164.957
155.129
150.230
133.621
133.571
133.505
129.921
129.859
129.838
129.818
129.698
129.162
129.072
129.035
128.895
128.581
128.557
128.507
128.371
118.375
114.605
105.363
105.313
105.132
84.732
84.151
82.812
82.082
81.411
81.188
80.191
78.246
77.628
77.274
77.018
76.763
64.929
62.737
55.666
HO
OBz
O
BzO
OPMP
26
180
160
140
120
100
80
60
40
ppm

compound-27-H
600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

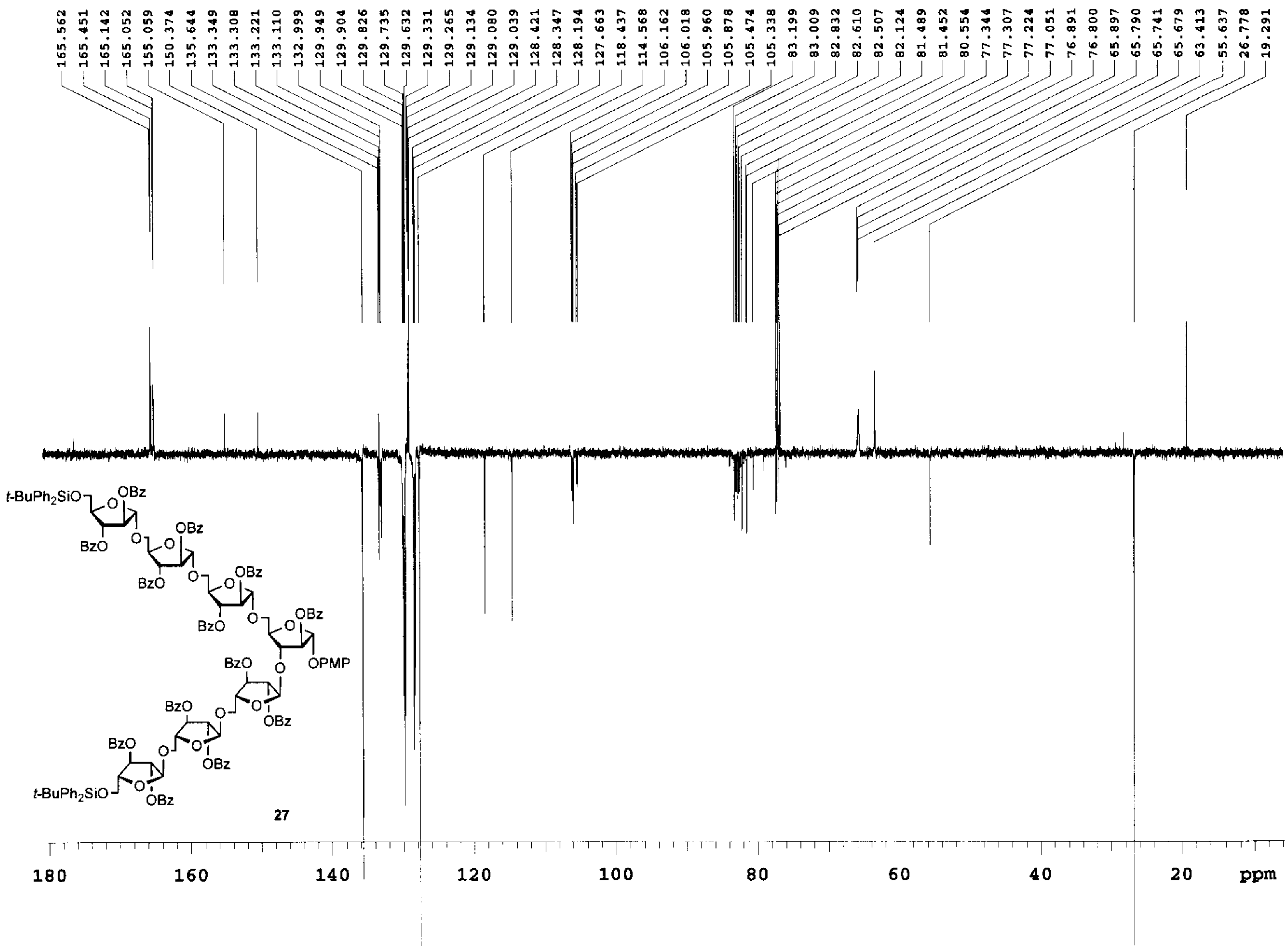


27



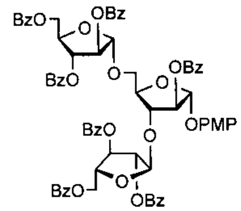
compound-27-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

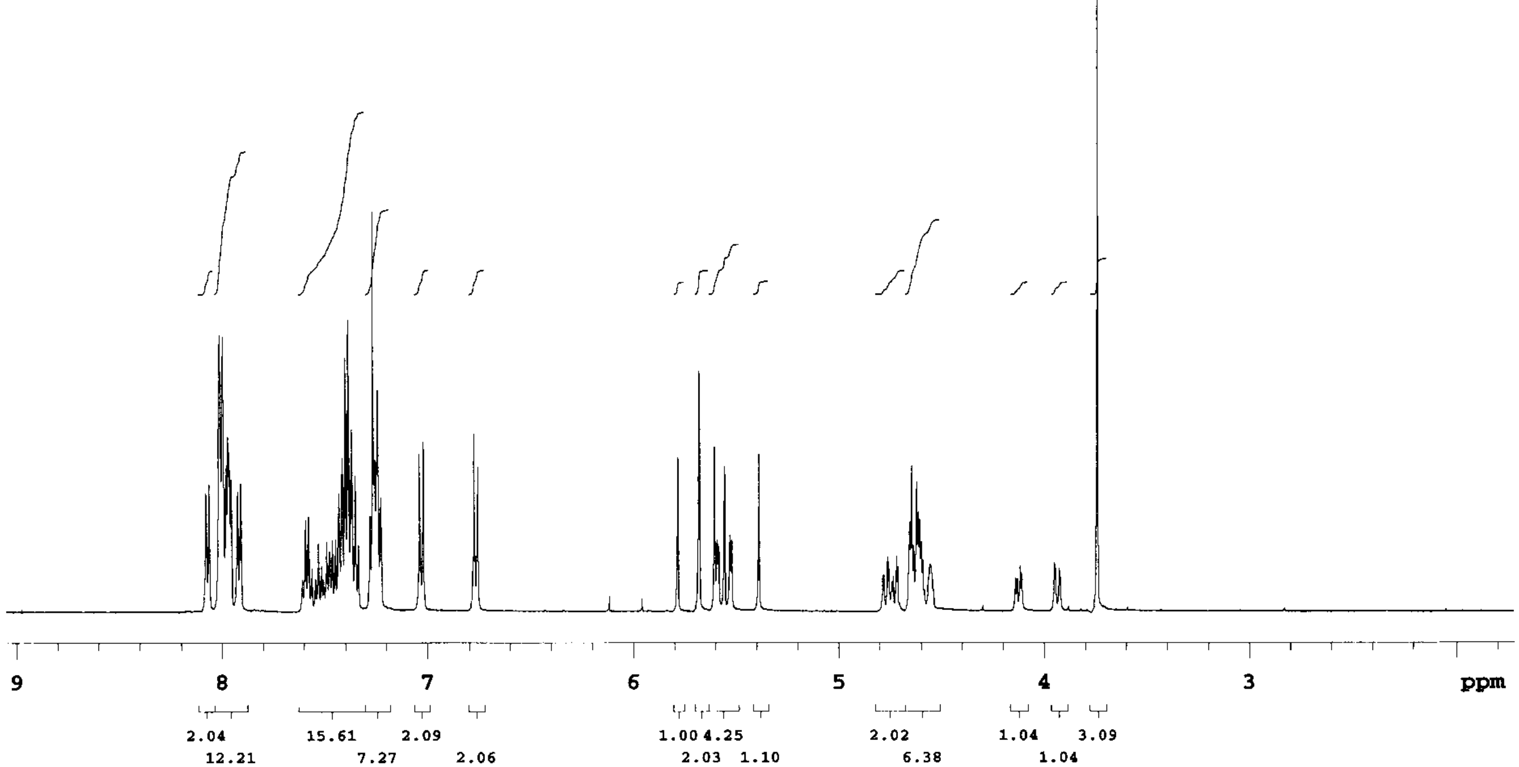


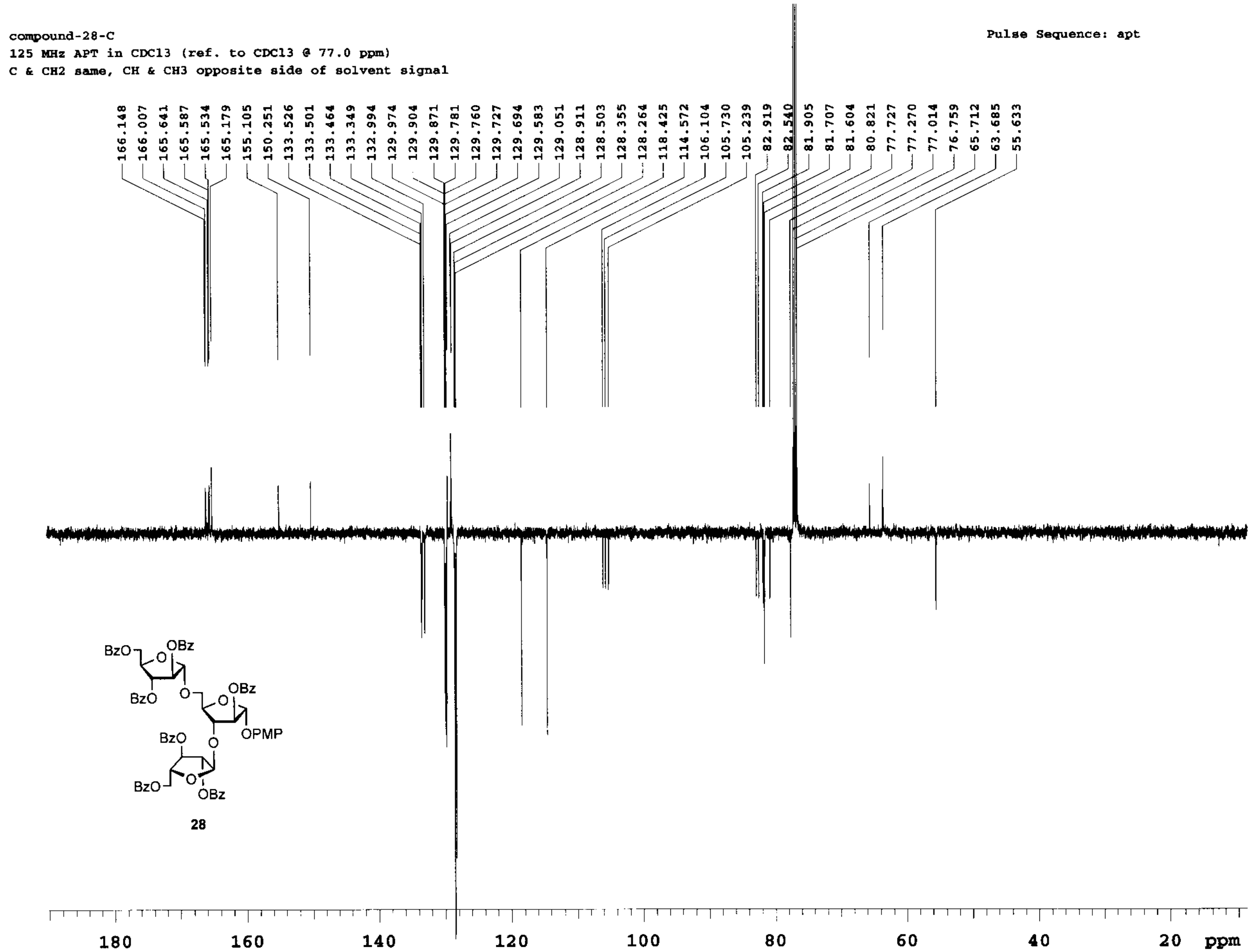
compound-28-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul



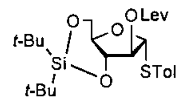
28



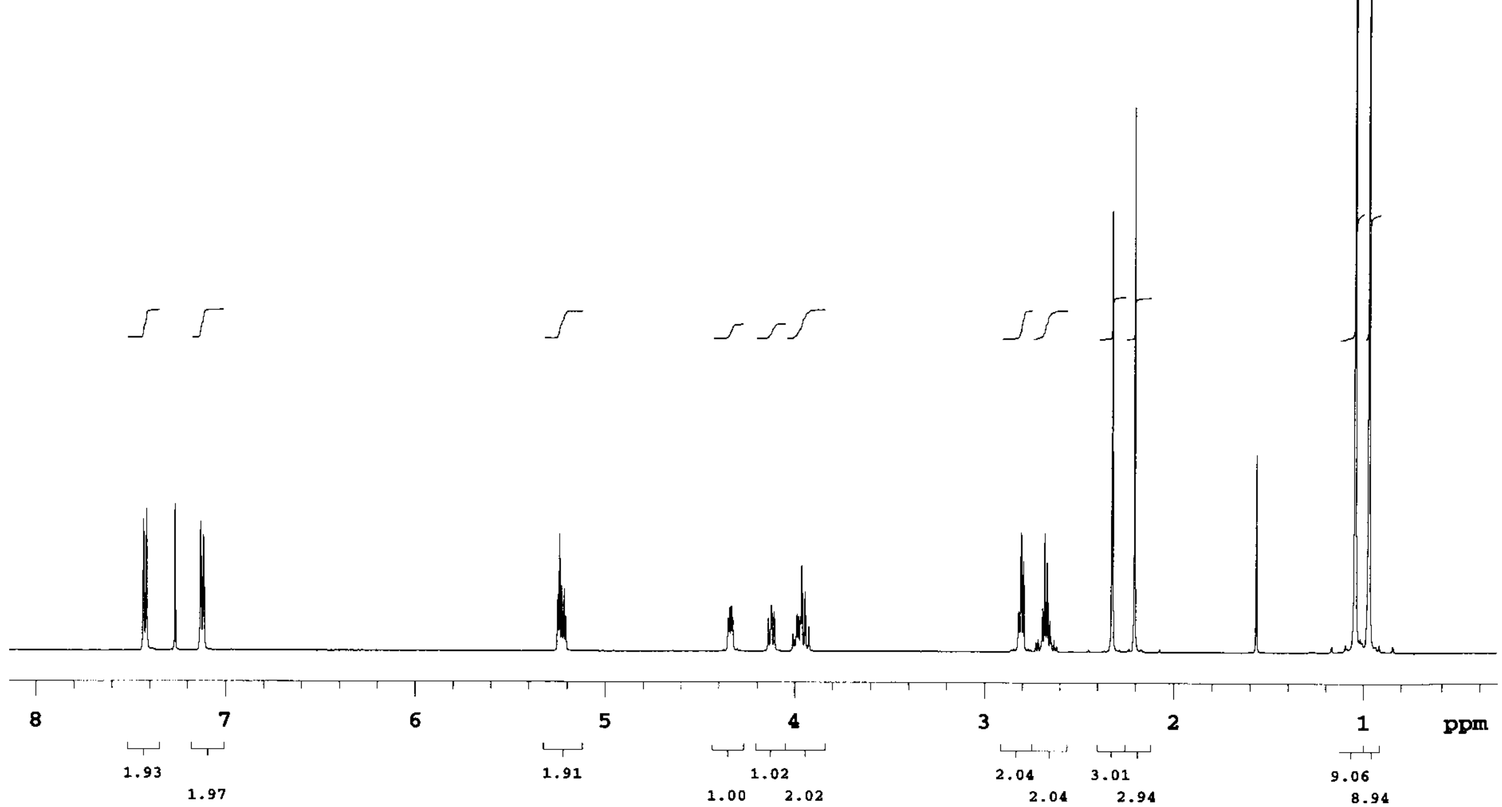

compound-28-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
166.148
166.007
165.641
165.587
165.534
165.179
155.105
150.251
133.526
133.501
133.464
133.349
132.994
129.974
129.904
129.871
129.781
129.760
129.727
129.694
129.583
129.051
128.911
128.503
128.355
128.264
118.425
114.572
106.104
105.730
105.239
82.919
82.540
81.905
81.707
81.604
80.821
77.727
77.270
77.014
76.759
65.712
63.685
55.633
BzO
OBz
O
BzO
OBz
OPMP
28
180
160
140
120
100
80
60
40
20
ppm

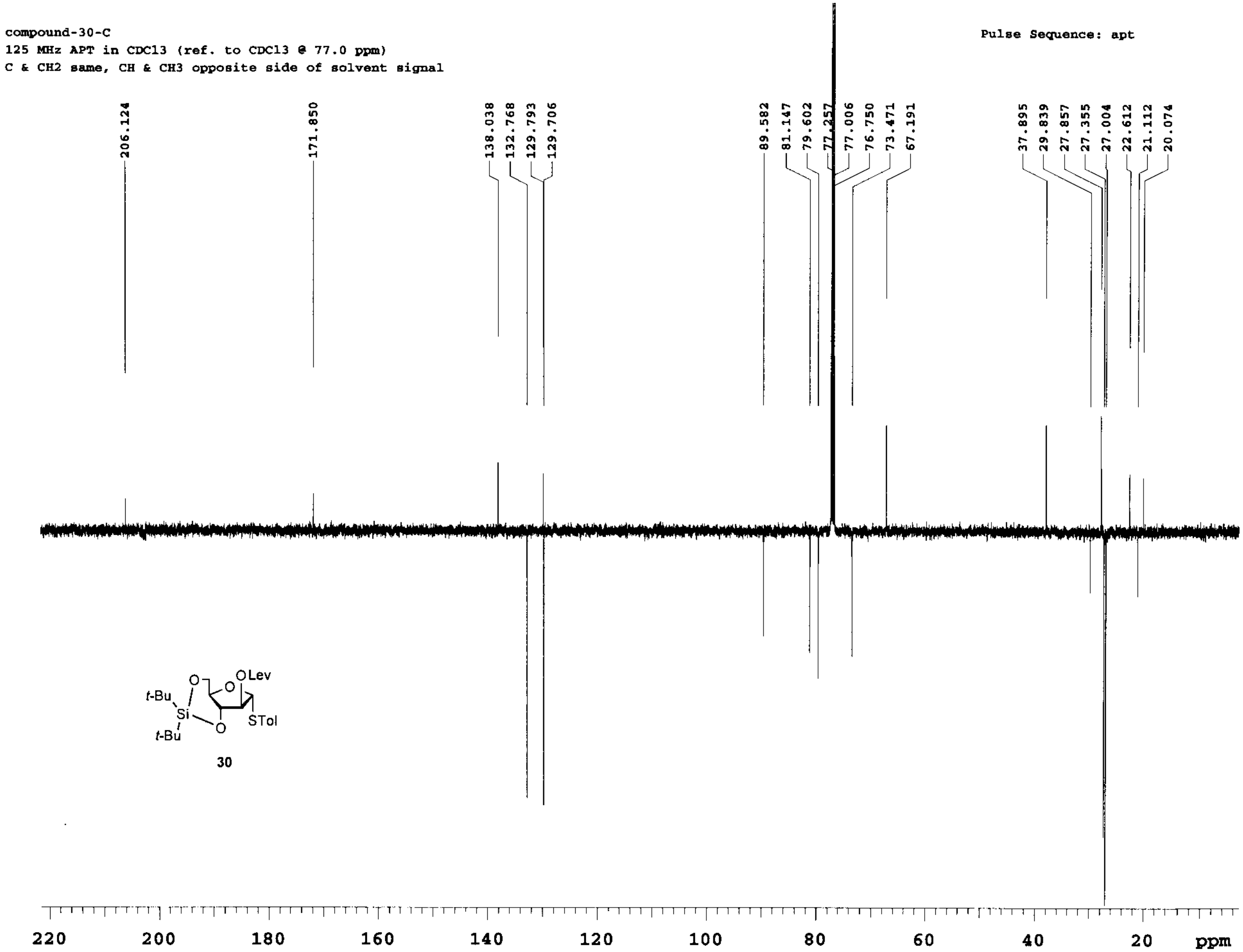
compound-30-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul



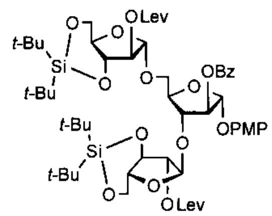
30



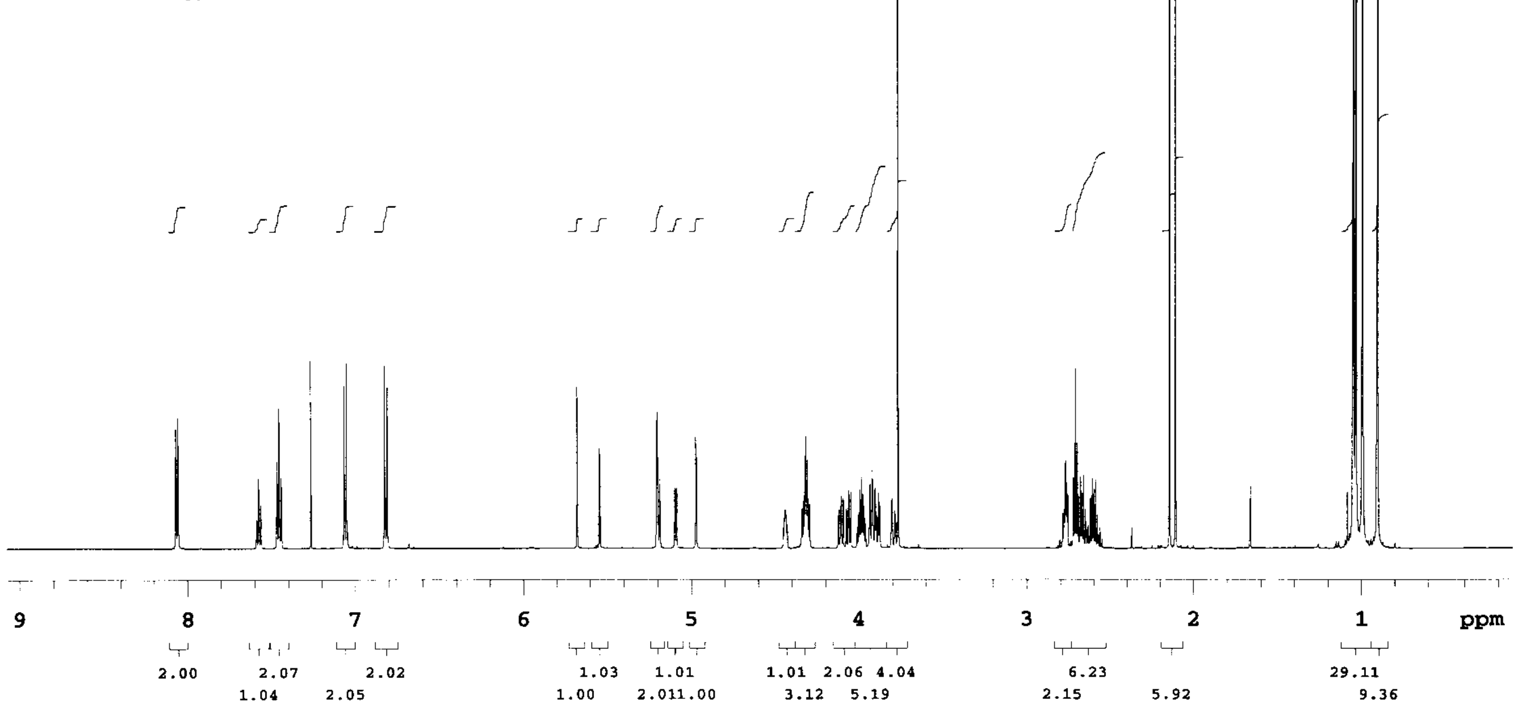

compound-30-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
206.124
171.850
138.038
132.768
129.793
129.706
89.582
81.147
79.602
77.257
77.006
76.750
73.471
67.191
37.895
29.839
27.857
27.355
27.004
22.612
21.112
20.074
t-Bu
Si
t-Bu
O
OLev
STol
30
220
200
180
160
140
120
100
80
60
40
20
ppm

compound-31-H
600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

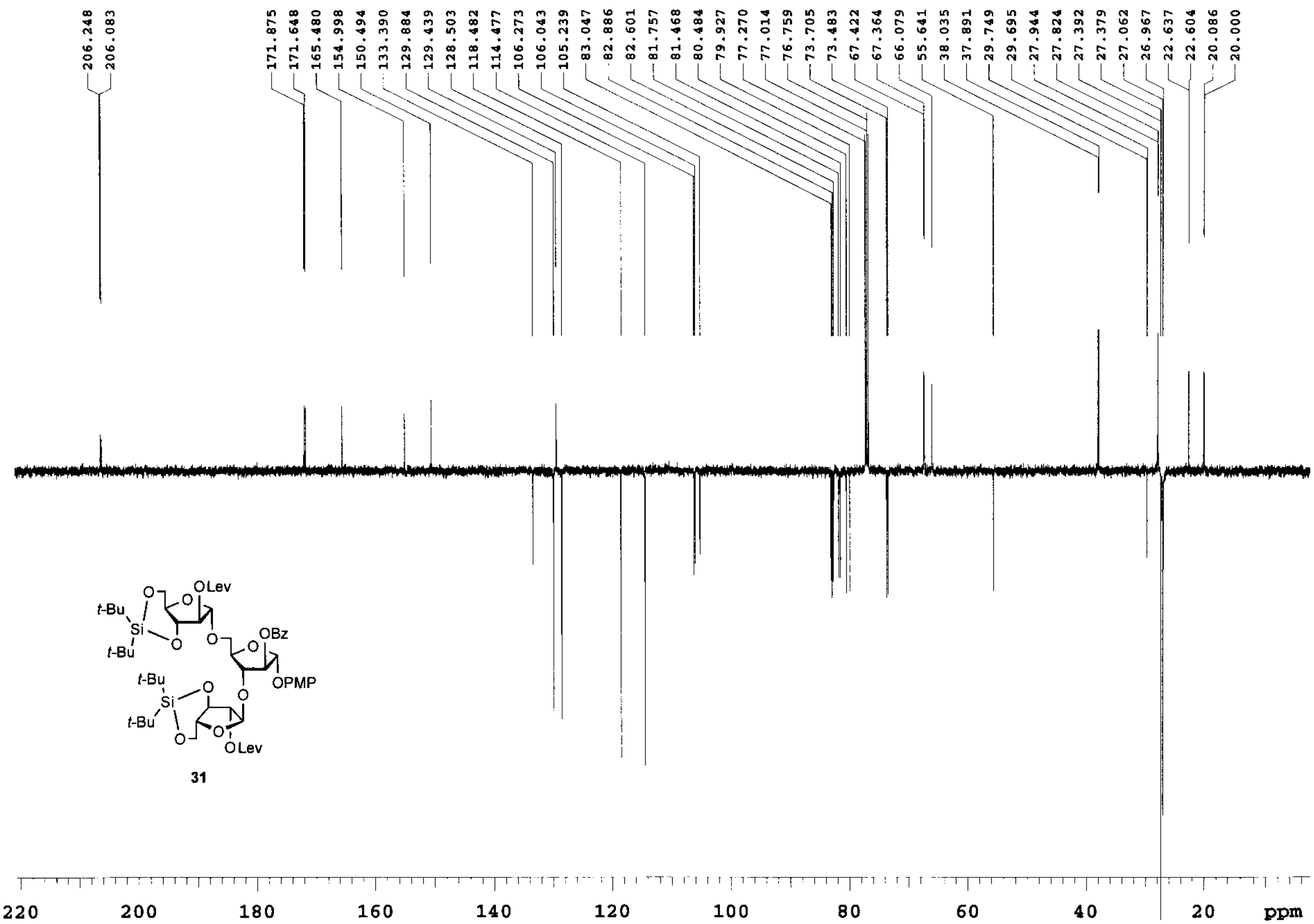


31



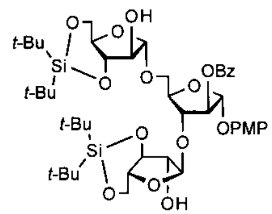
compound-31-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

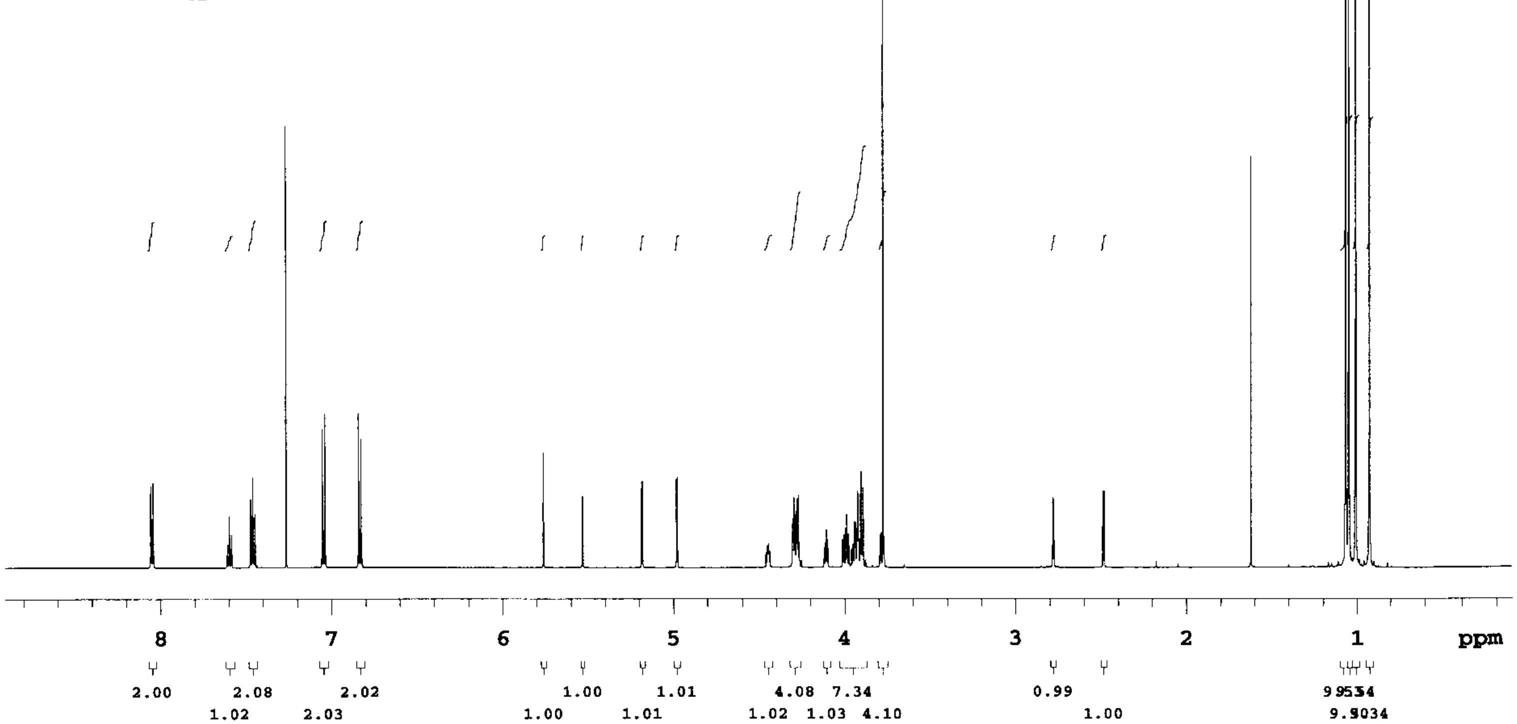


compound-32-H
600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

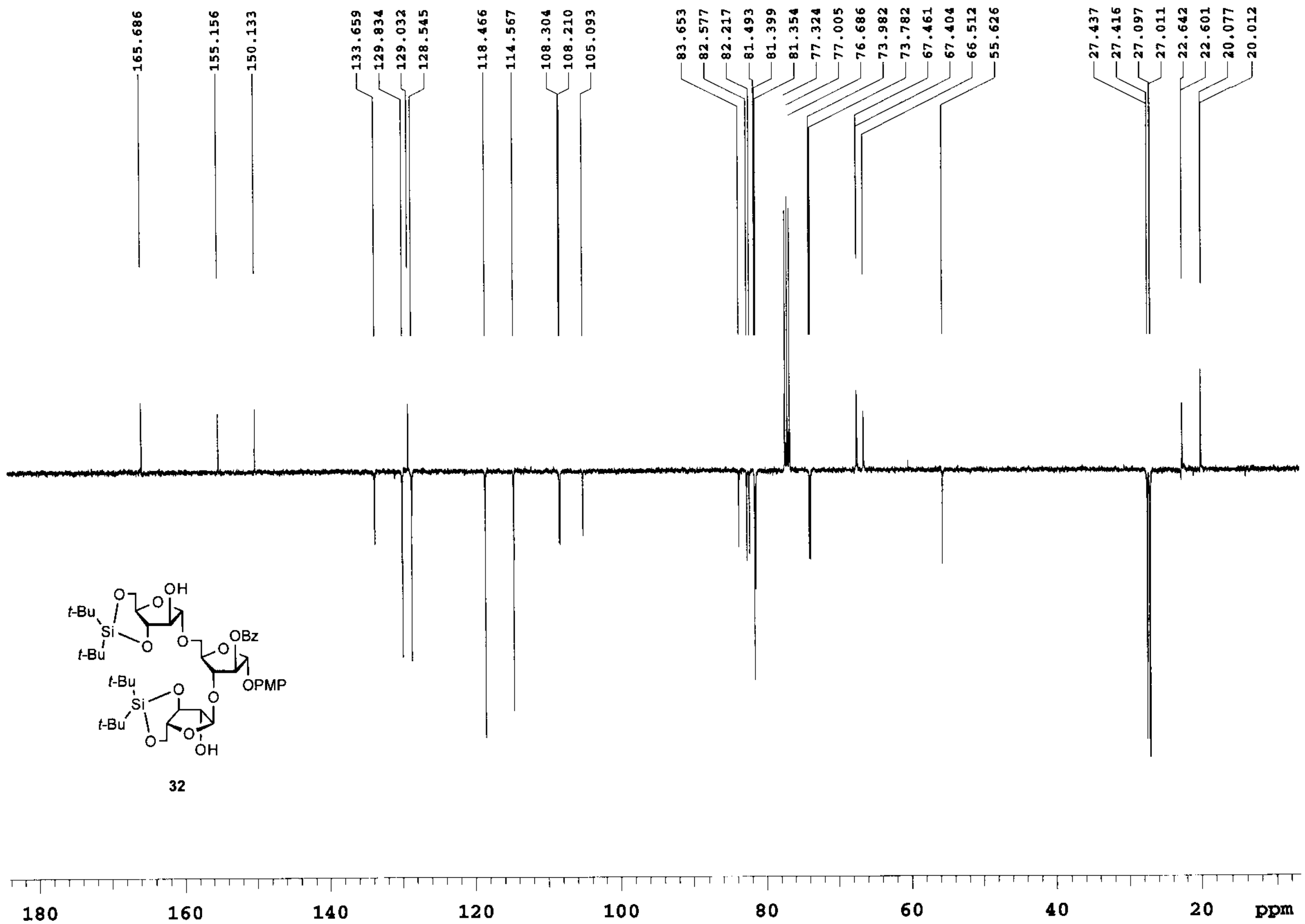


32



compound-32-C
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

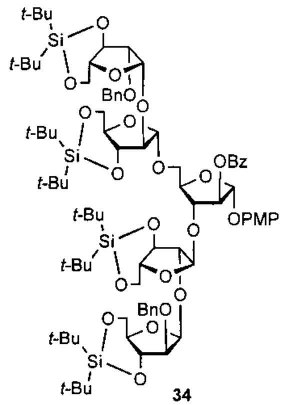
Pulse Sequence: apt



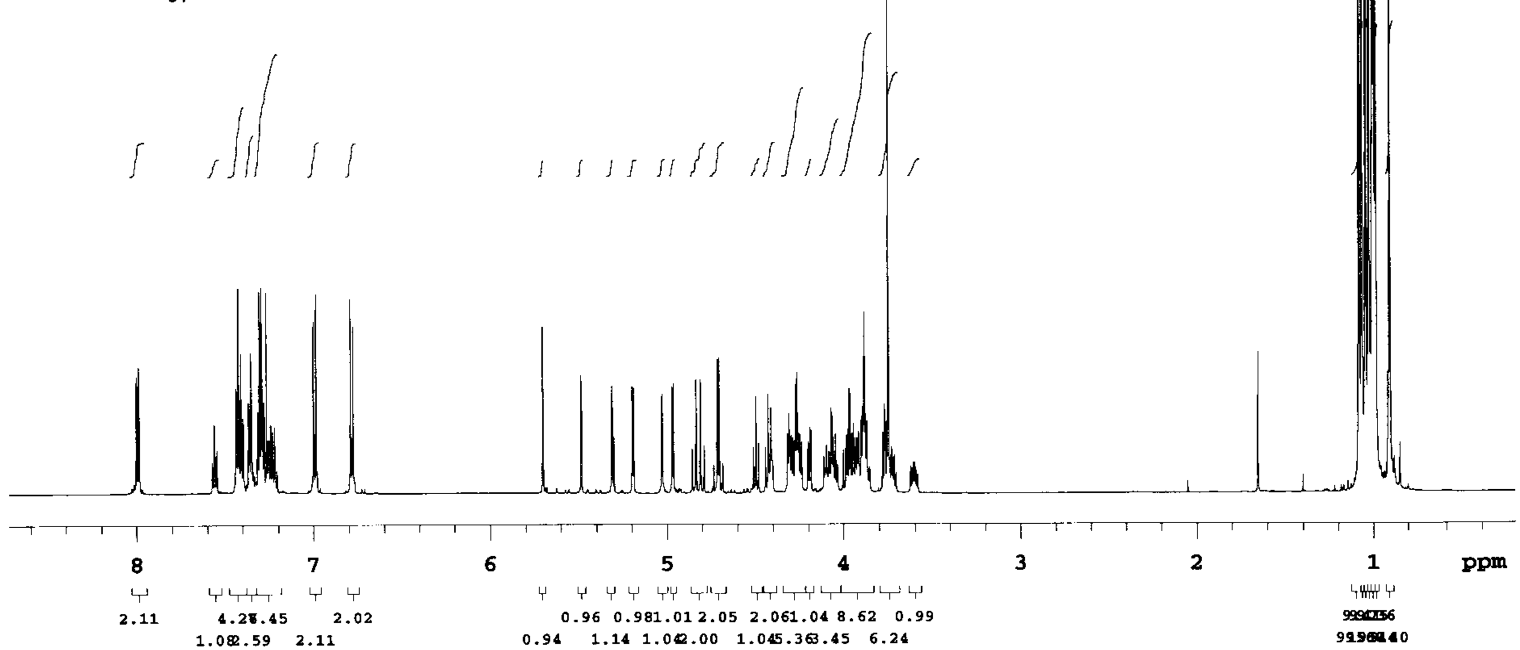
compound-34-H

600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

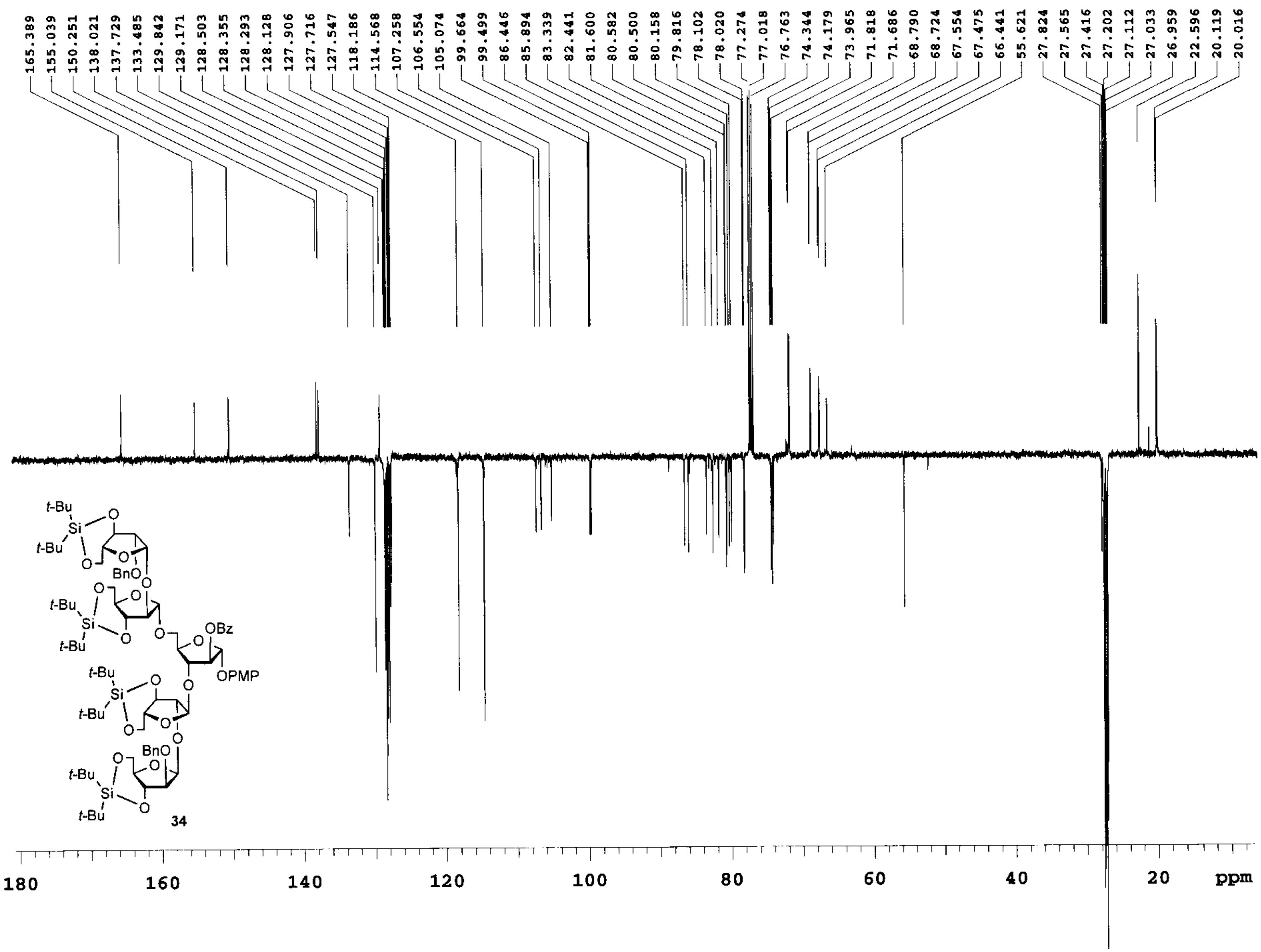


34



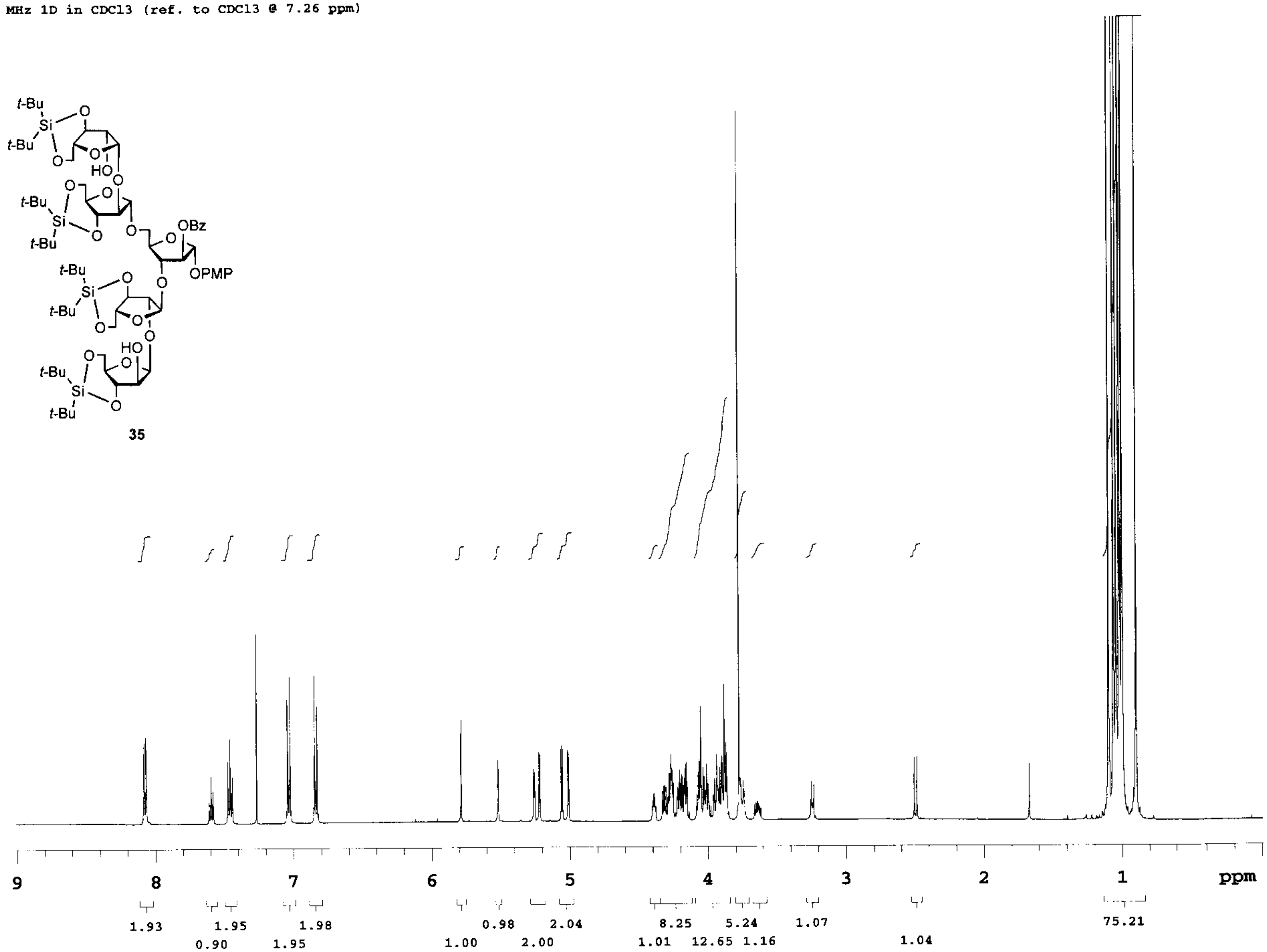
compound-34-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt



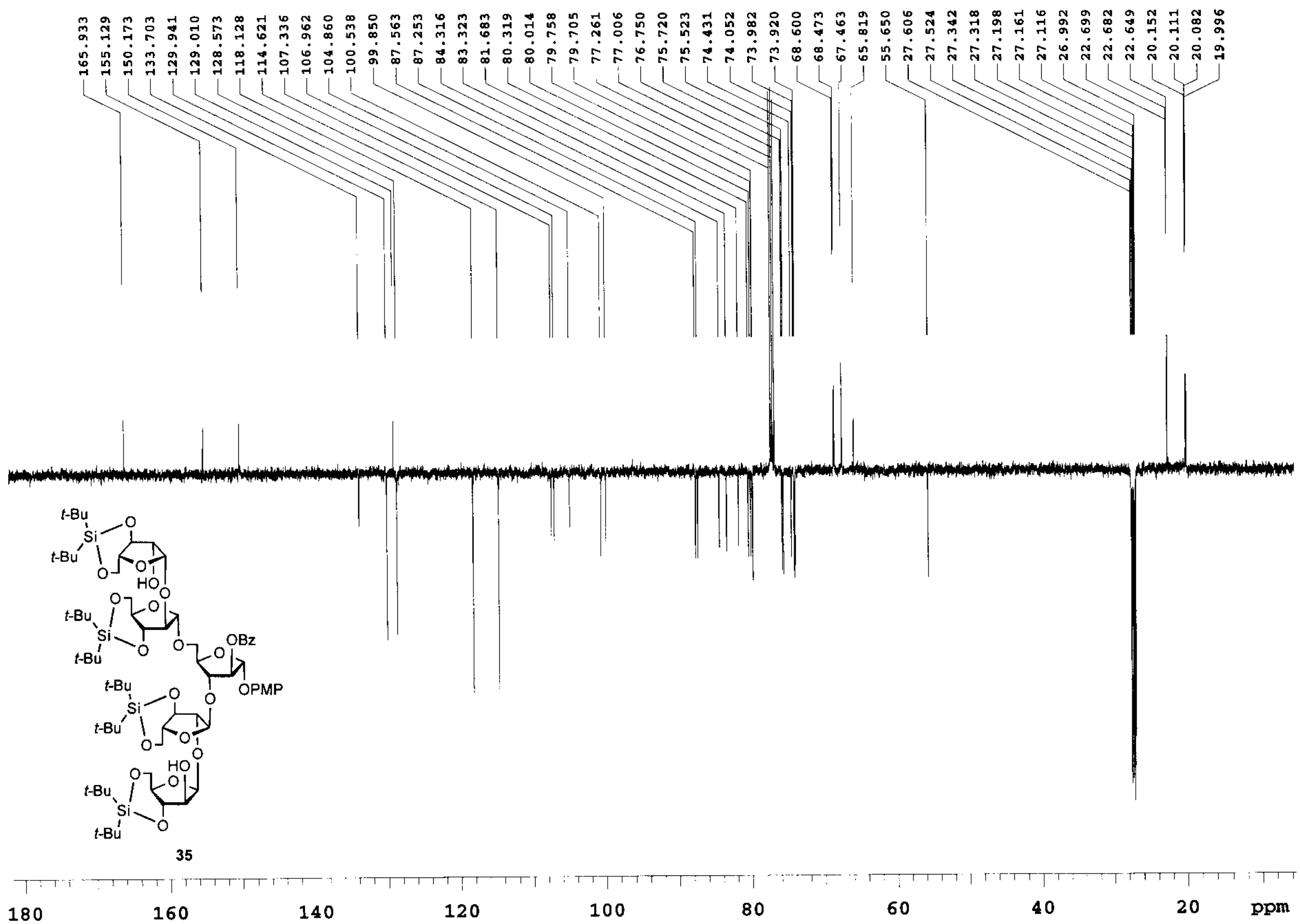
compound-35-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul



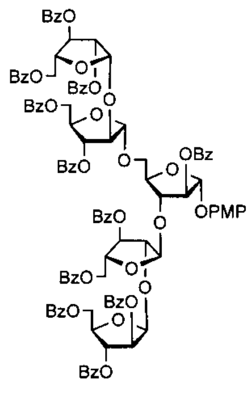
compound-35-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

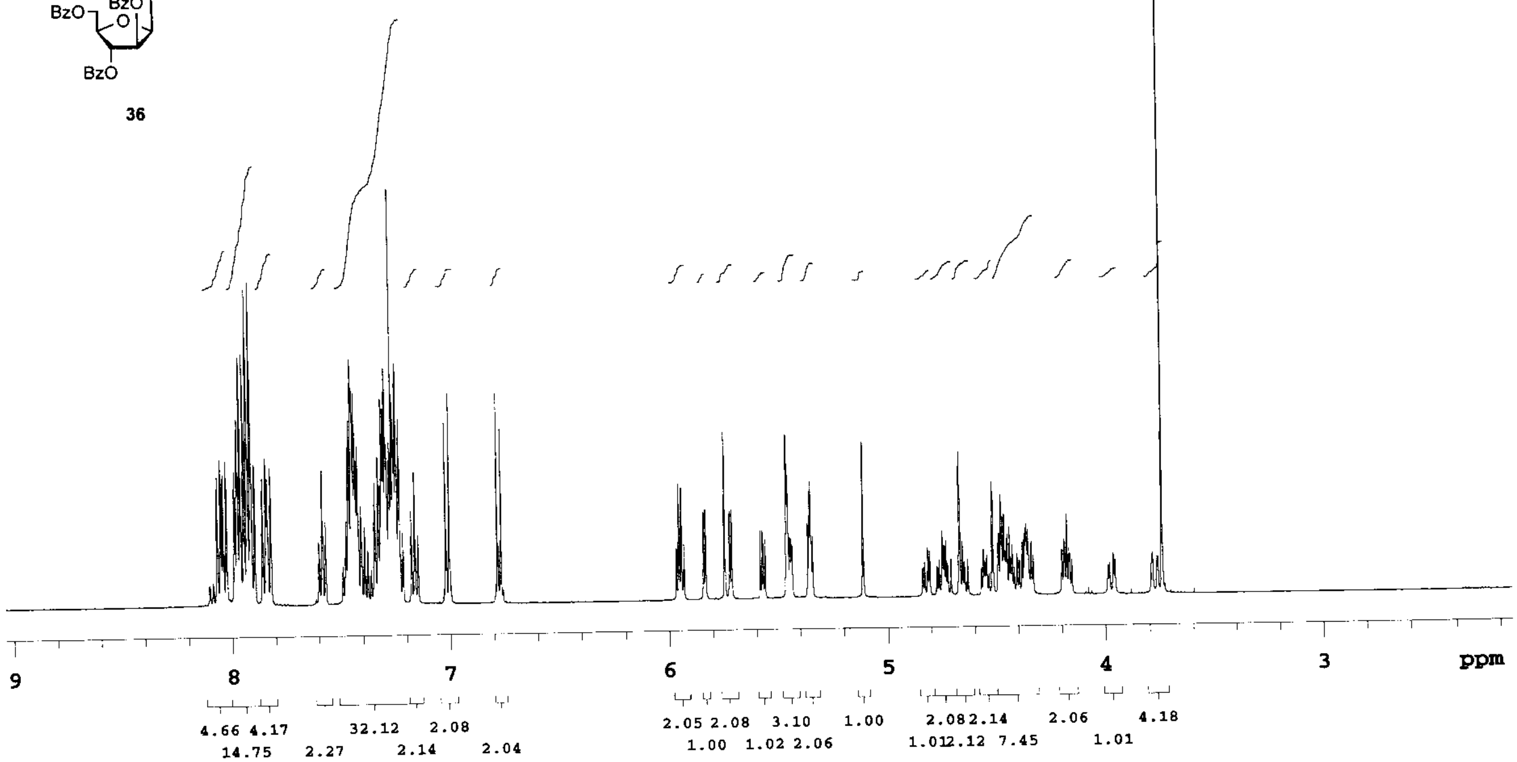


compound-36-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

Pulse Sequence: s2pul

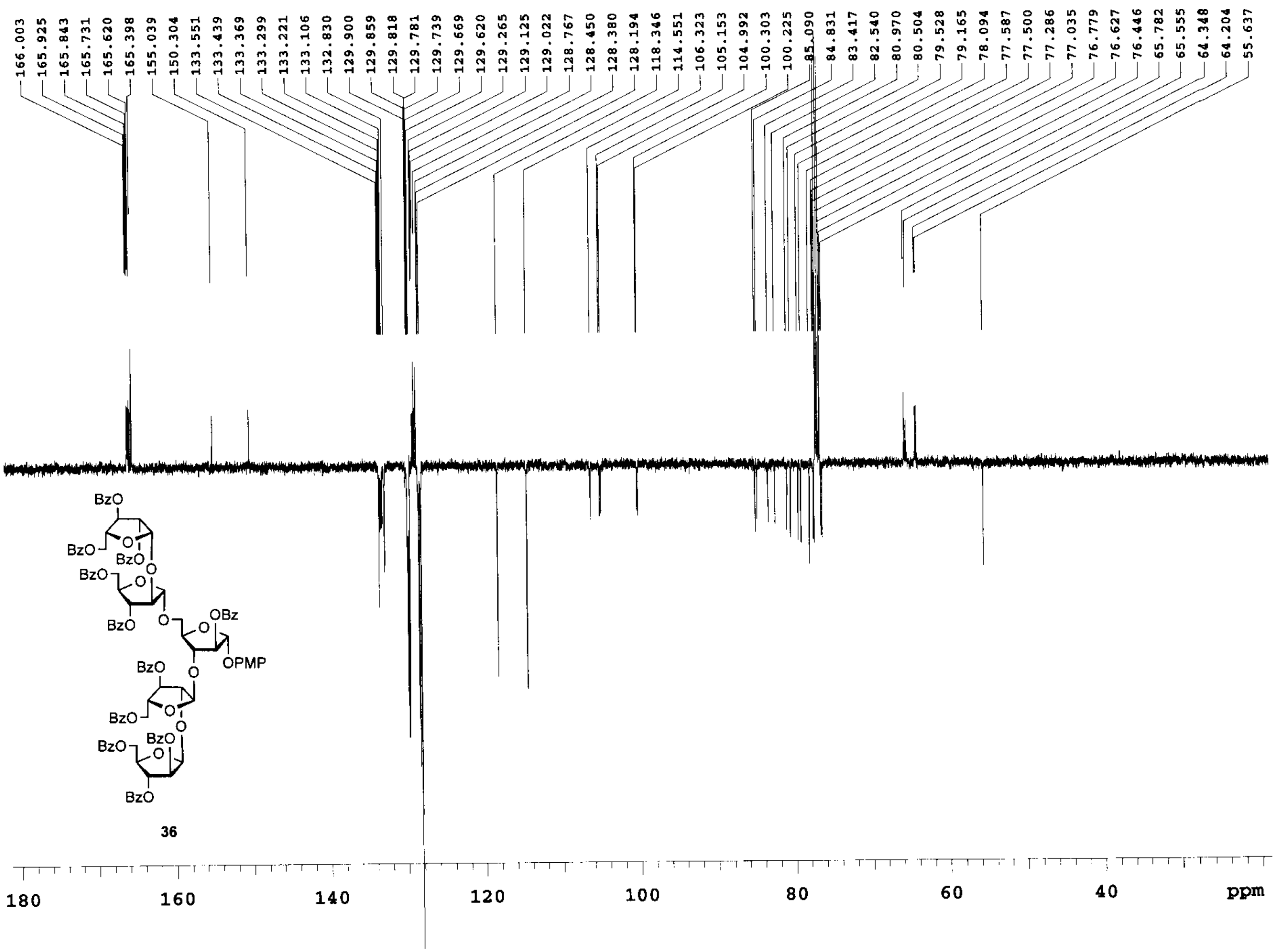


36



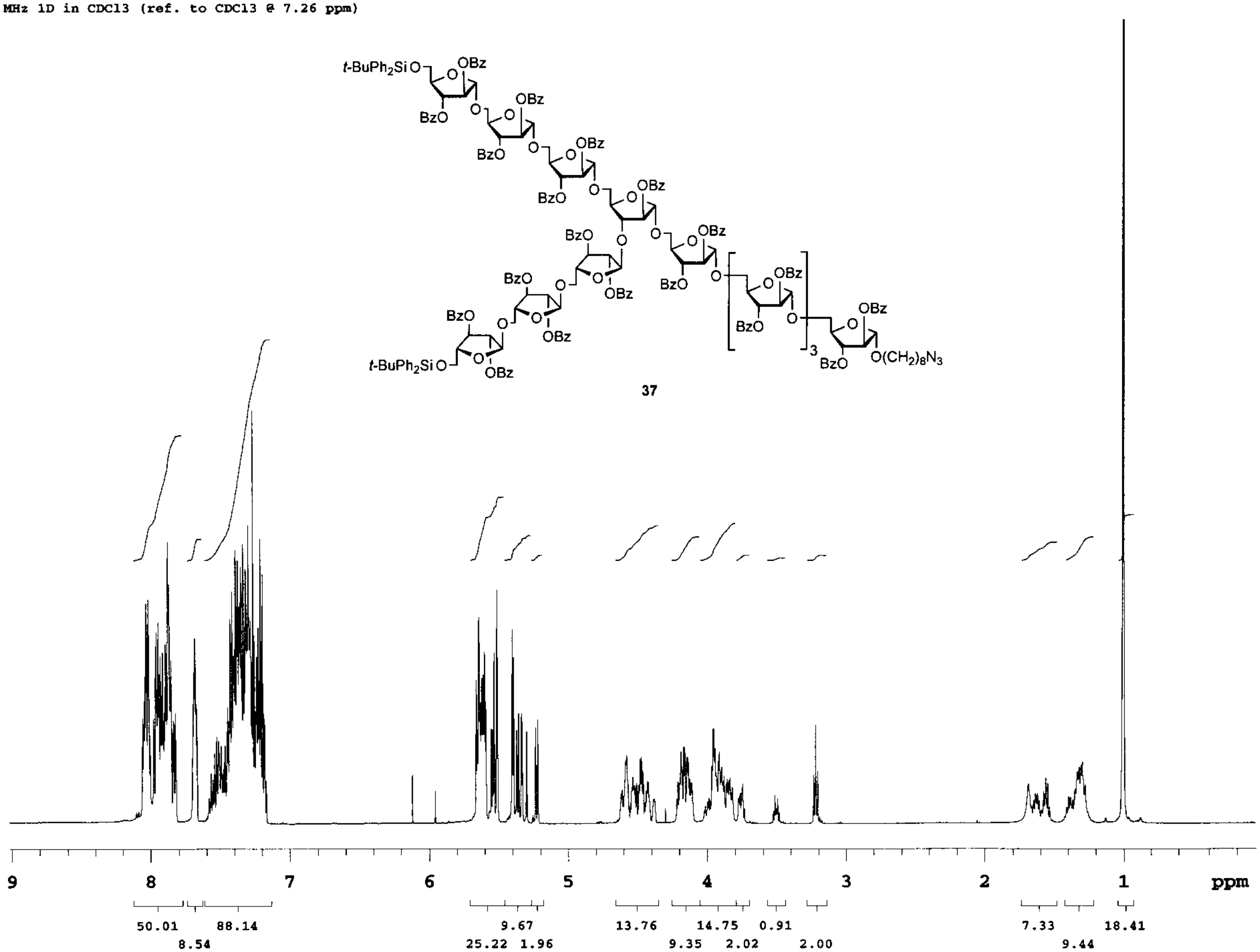
compound-36-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

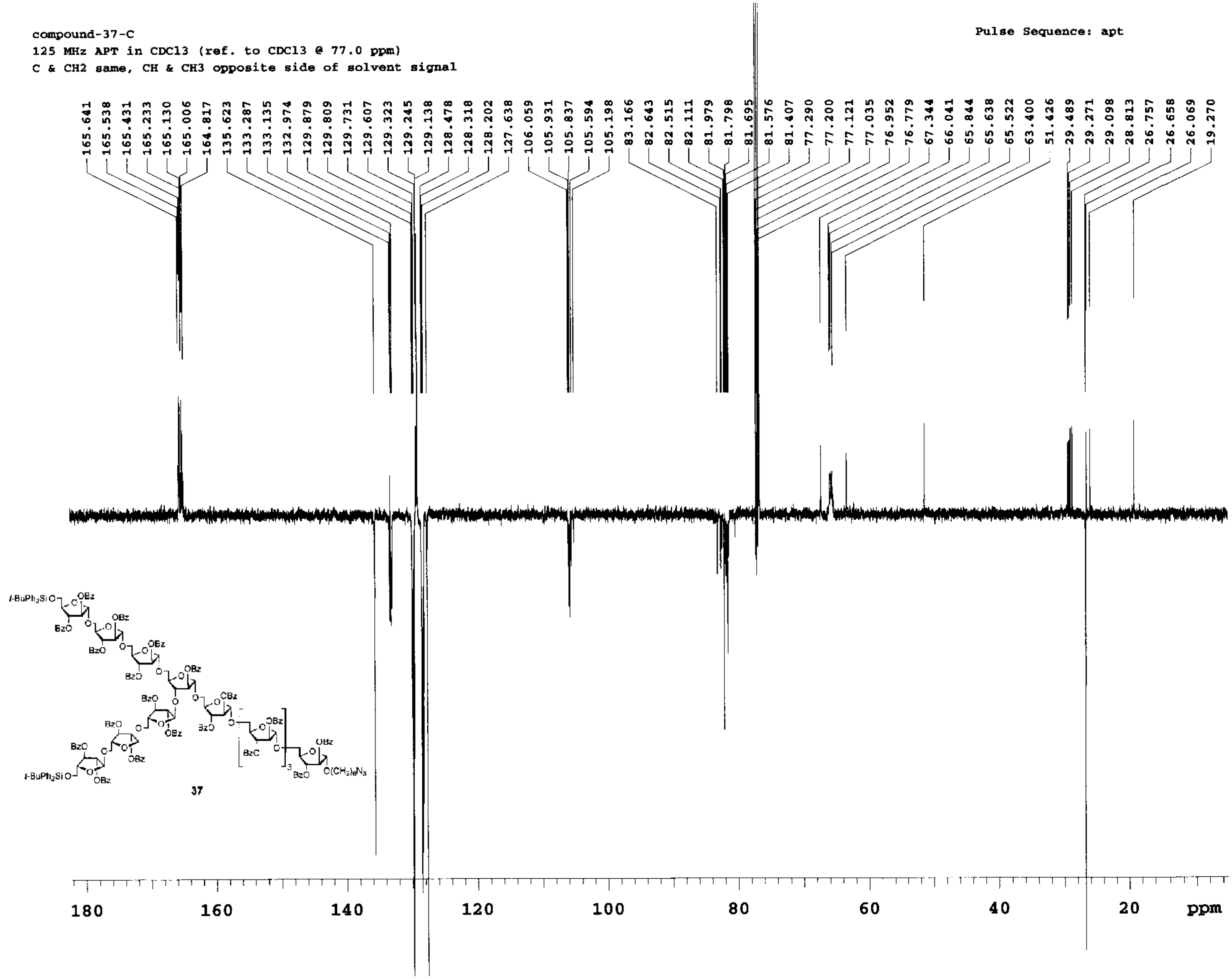
Pulse Sequence: apt



compound-37-H
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

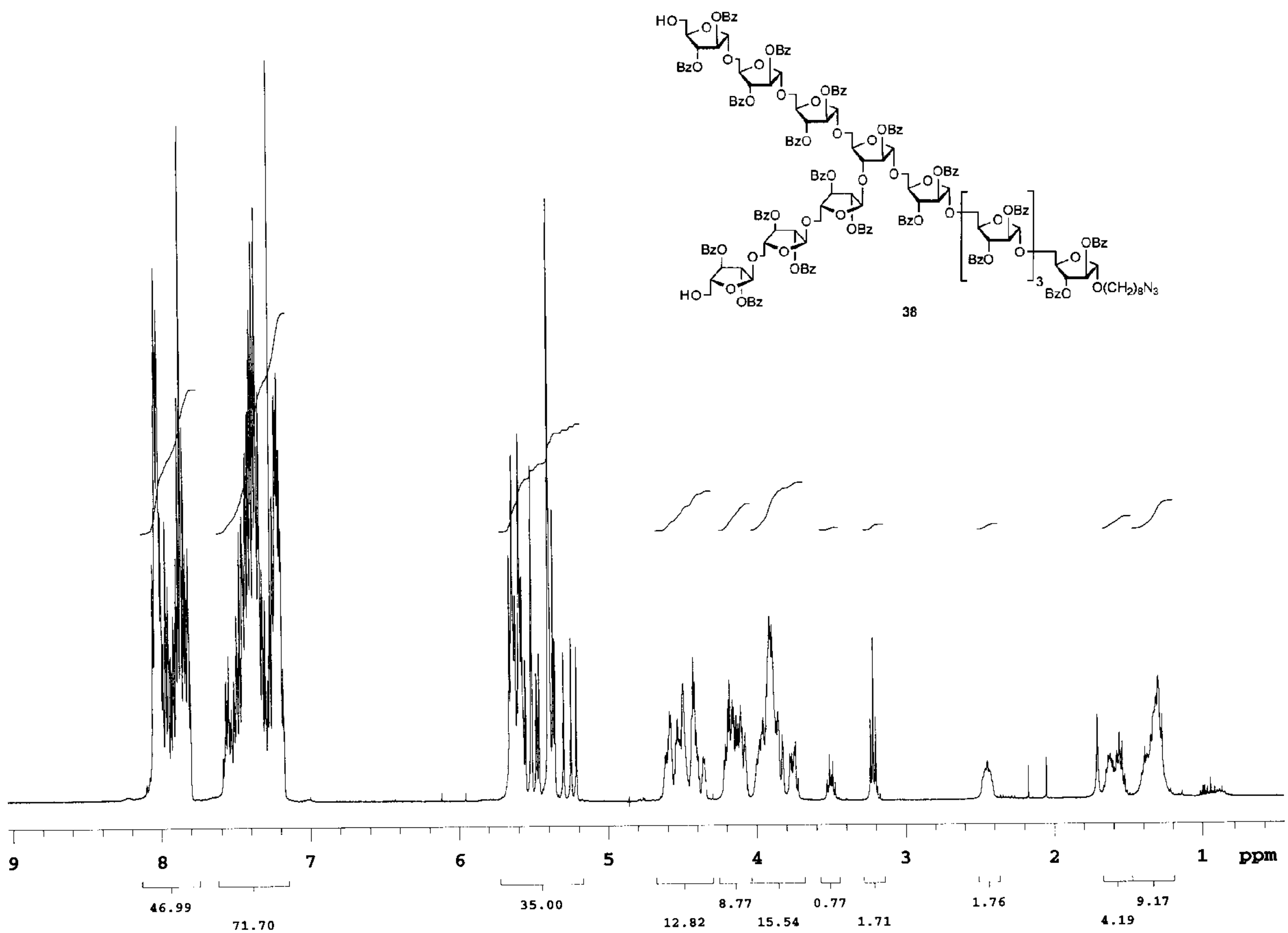
Pulse Sequence: s2pul

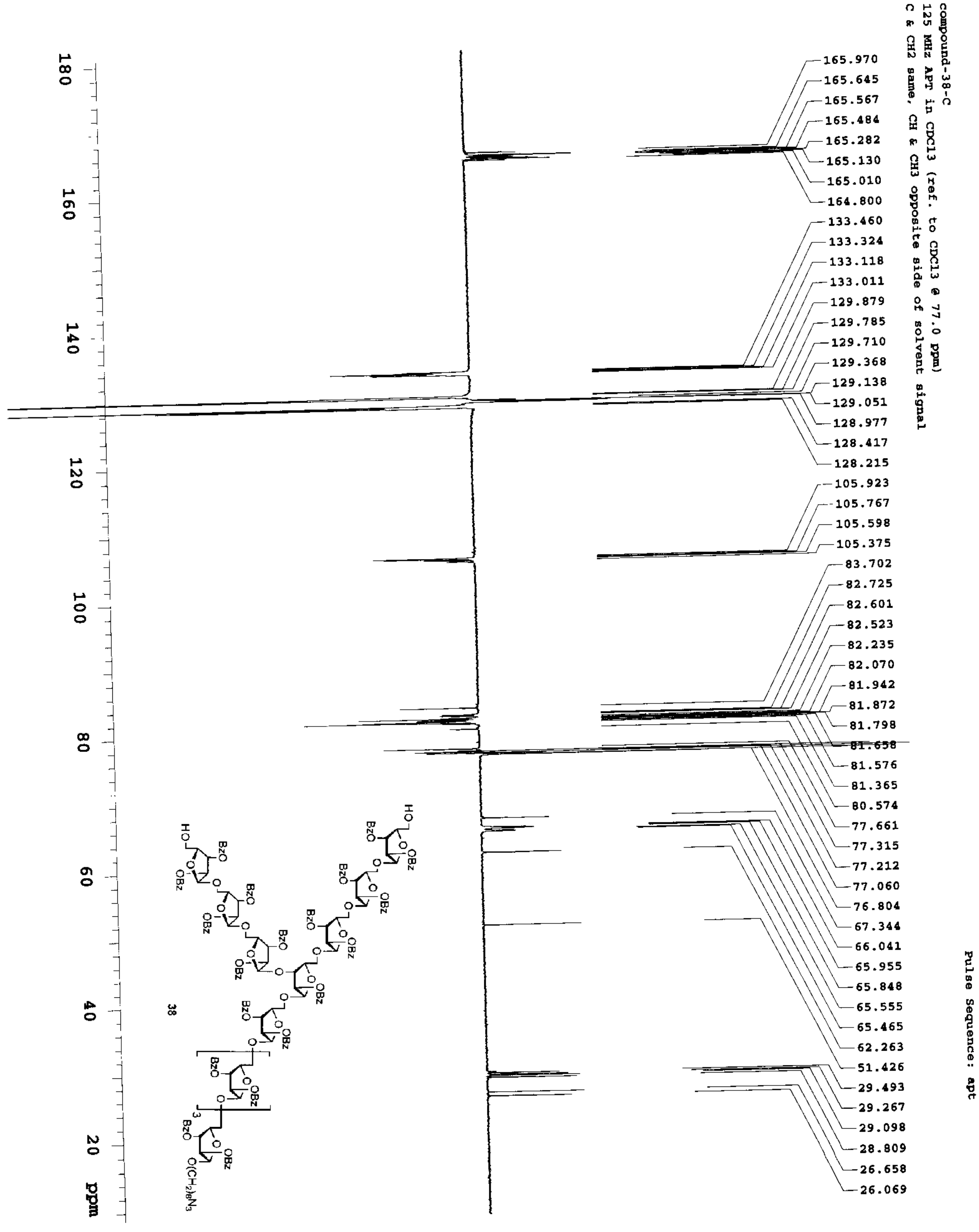



compound-37-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
165.641
165.538
165.431
165.233
165.130
165.006
164.817
135.623
133.287
133.135
132.974
129.879
129.809
129.731
129.607
129.323
129.245
129.138
128.478
128.318
128.202
127.638
106.059
105.931
105.837
105.594
105.198
83.166
82.643
82.515
82.111
81.979
81.798
81.695
81.576
81.407
77.290
77.200
77.121
77.035
76.952
76.779
67.344
66.041
65.844
65.638
65.522
63.400
51.426
29.489
29.271
29.098
28.813
26.757
26.658
26.069
19.270
180
160
140
120
100
80
60
40
20
ppm
37

Pulse Sequence: s2pul

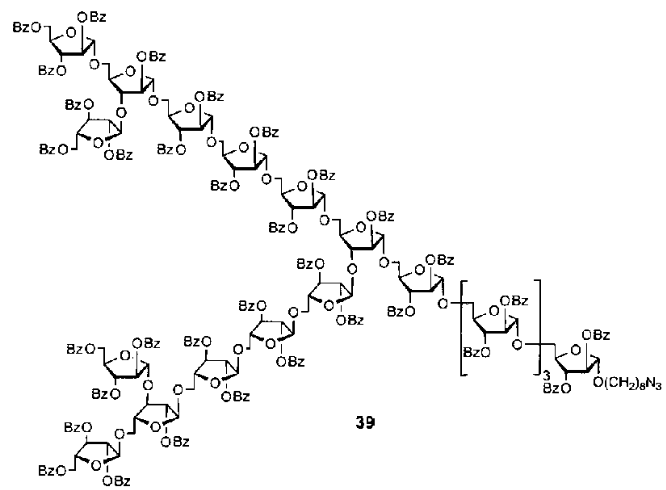
compound-38-H
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)



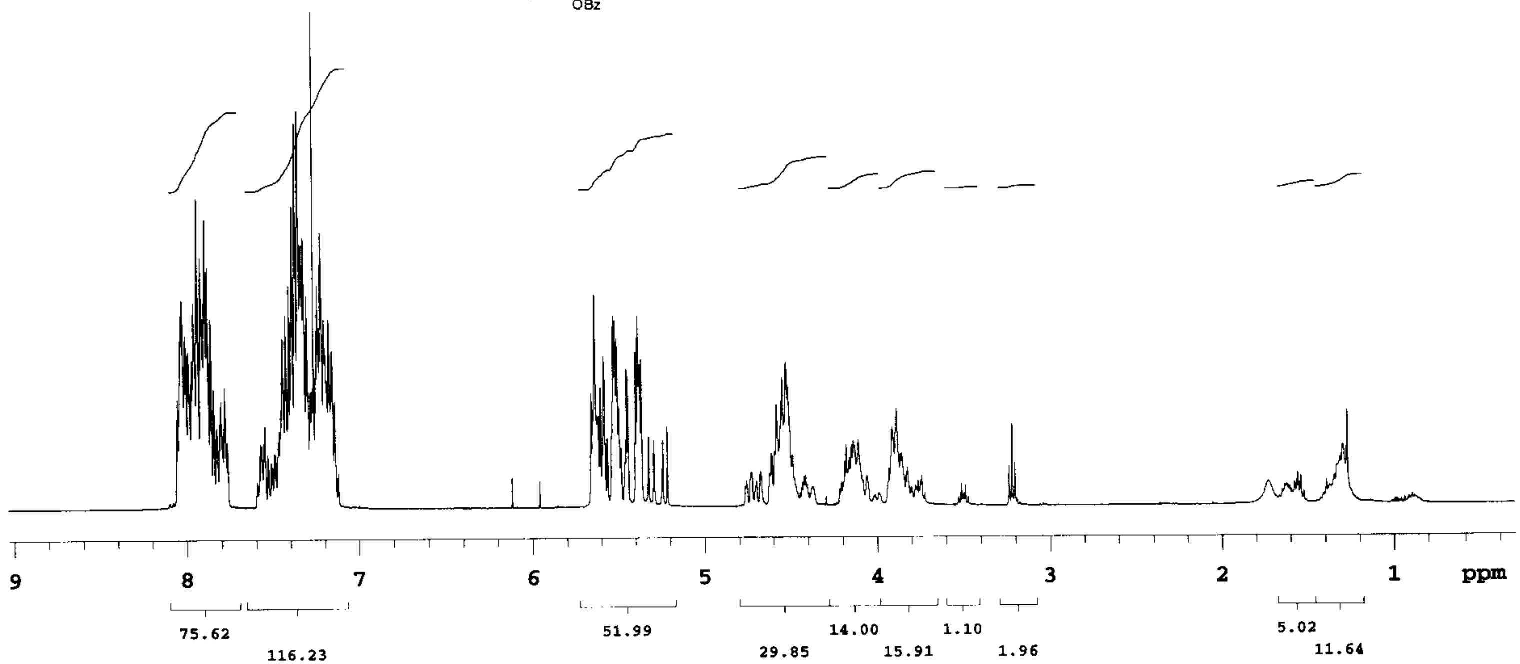

Pulse Sequence: apt
compound-38-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
165.970
165.645
165.567
165.484
165.282
165.130
165.010
164.800
133.460
133.324
133.118
133.011
129.879
129.785
129.710
129.368
129.138
129.051
128.977
128.417
128.215
105.923
105.767
105.598
105.375
83.702
82.725
82.601
82.523
82.235
82.070
81.942
81.872
81.798
81.658
81.576
81.365
80.574
77.661
77.315
77.212
77.060
76.804
67.344
66.041
65.955
65.848
65.555
65.465
62.263
51.426
29.493
29.267
29.098
28.809
26.658
26.069
180
160
140
120
100
80
60
40
20
ppm
HO
OBz
BzO
O(CH2)8N3
3
38

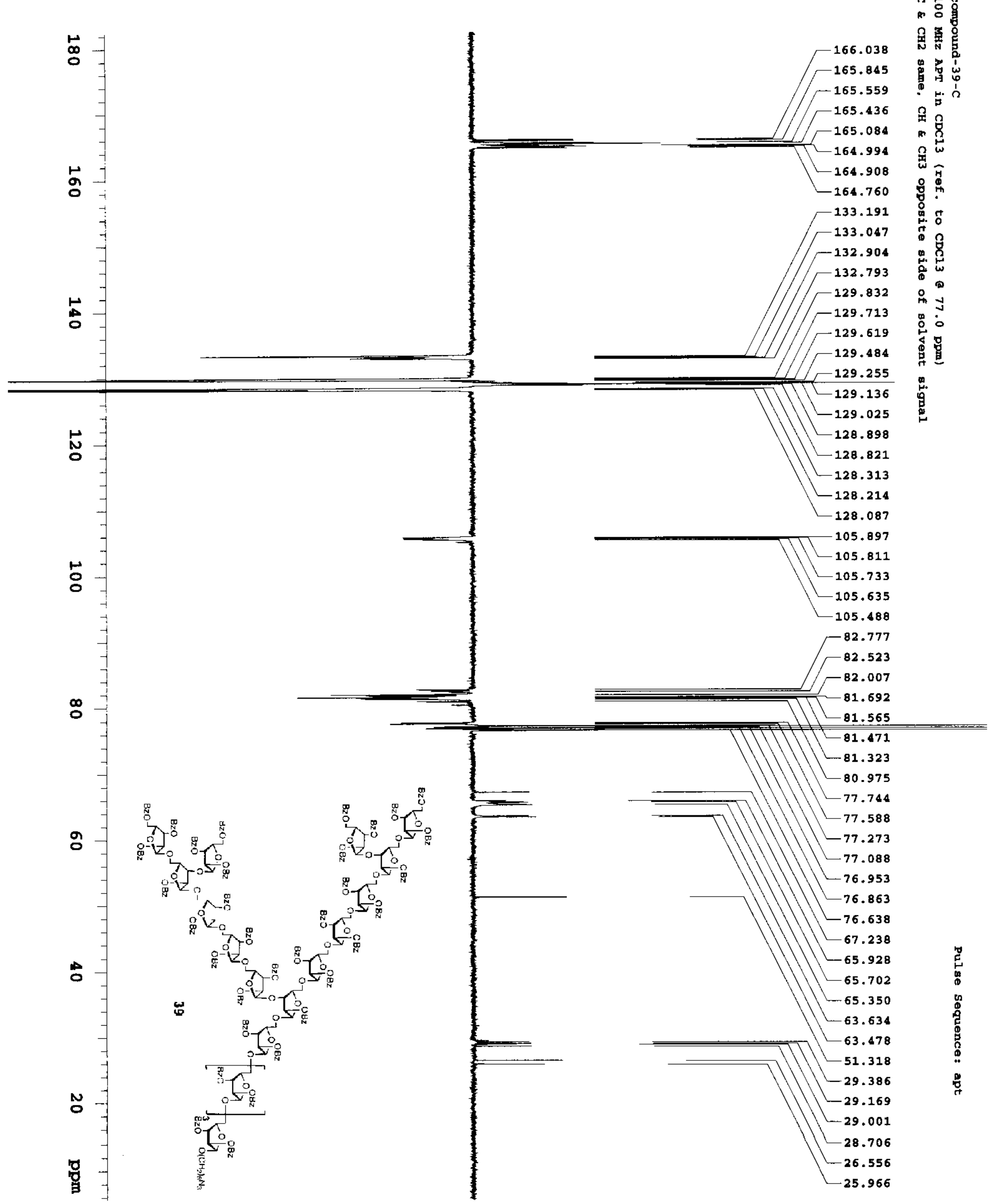
Pulse Sequence: s2pul

compound-39-H
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)



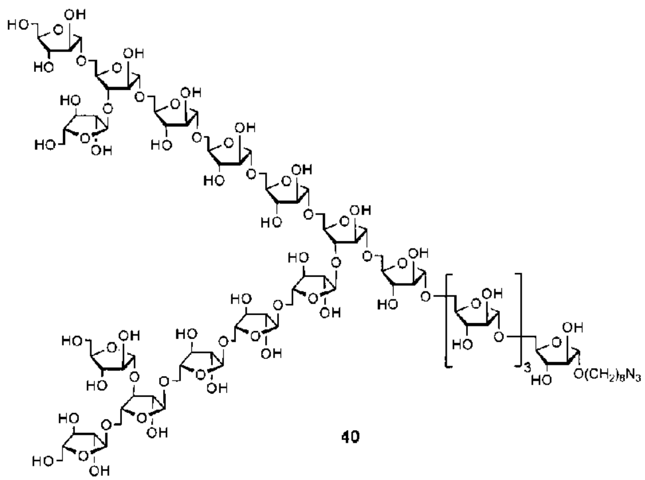
39



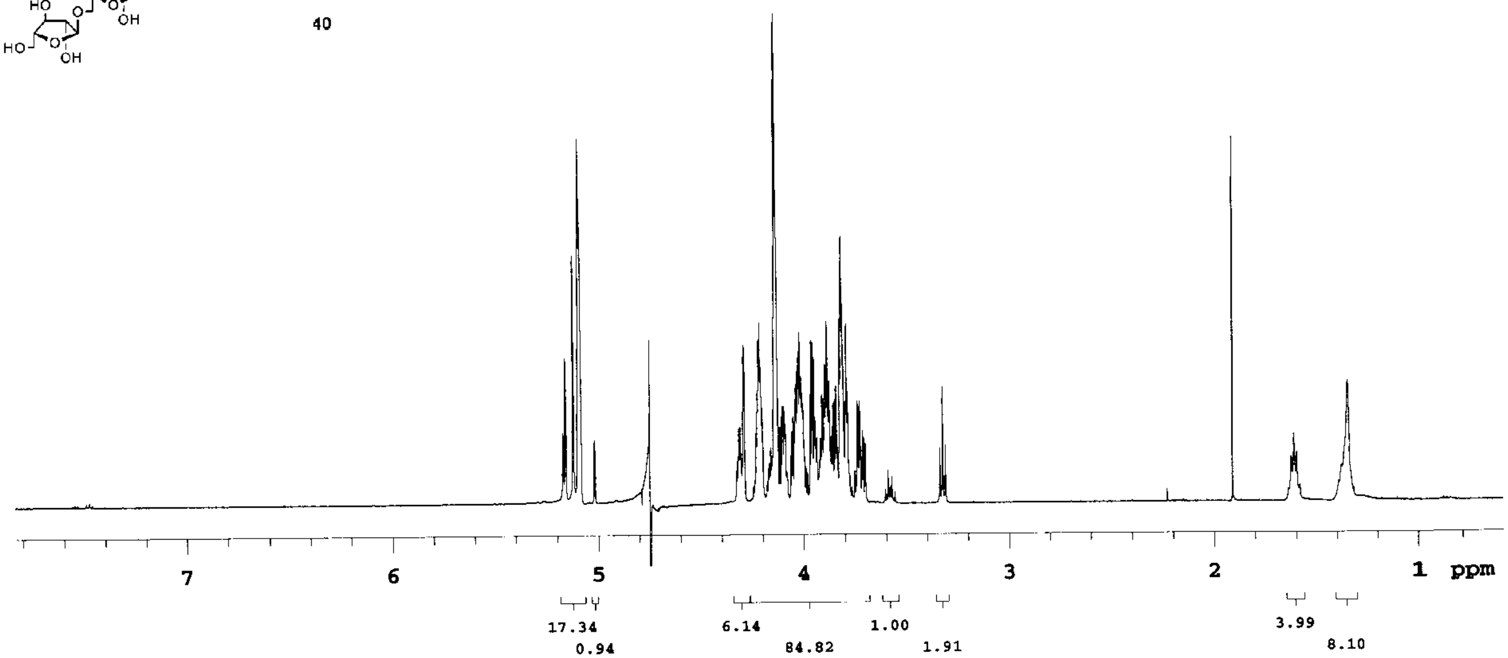

compound-39-C
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
166.038
165.845
165.559
165.436
165.084
164.994
164.908
164.760
133.191
133.047
132.904
132.793
129.832
129.713
129.619
129.484
129.255
129.136
129.025
128.898
128.821
128.313
128.214
128.087
105.897
105.811
105.733
105.635
105.488
82.777
82.523
82.007
81.692
81.565
81.471
81.323
80.975
77.744
77.588
77.273
77.088
76.953
76.863
76.638
67.238
65.928
65.702
65.350
63.634
63.478
51.318
29.386
29.169
29.001
28.706
26.556
25.966
180
160
140
120
100
80
60
40
20
ppm
39

Pulse Sequence: s2pul

compound-40-H
500 MHz 1D in D2O (ref. to 0.1 % ext. acetone @ 2.225 ppm)

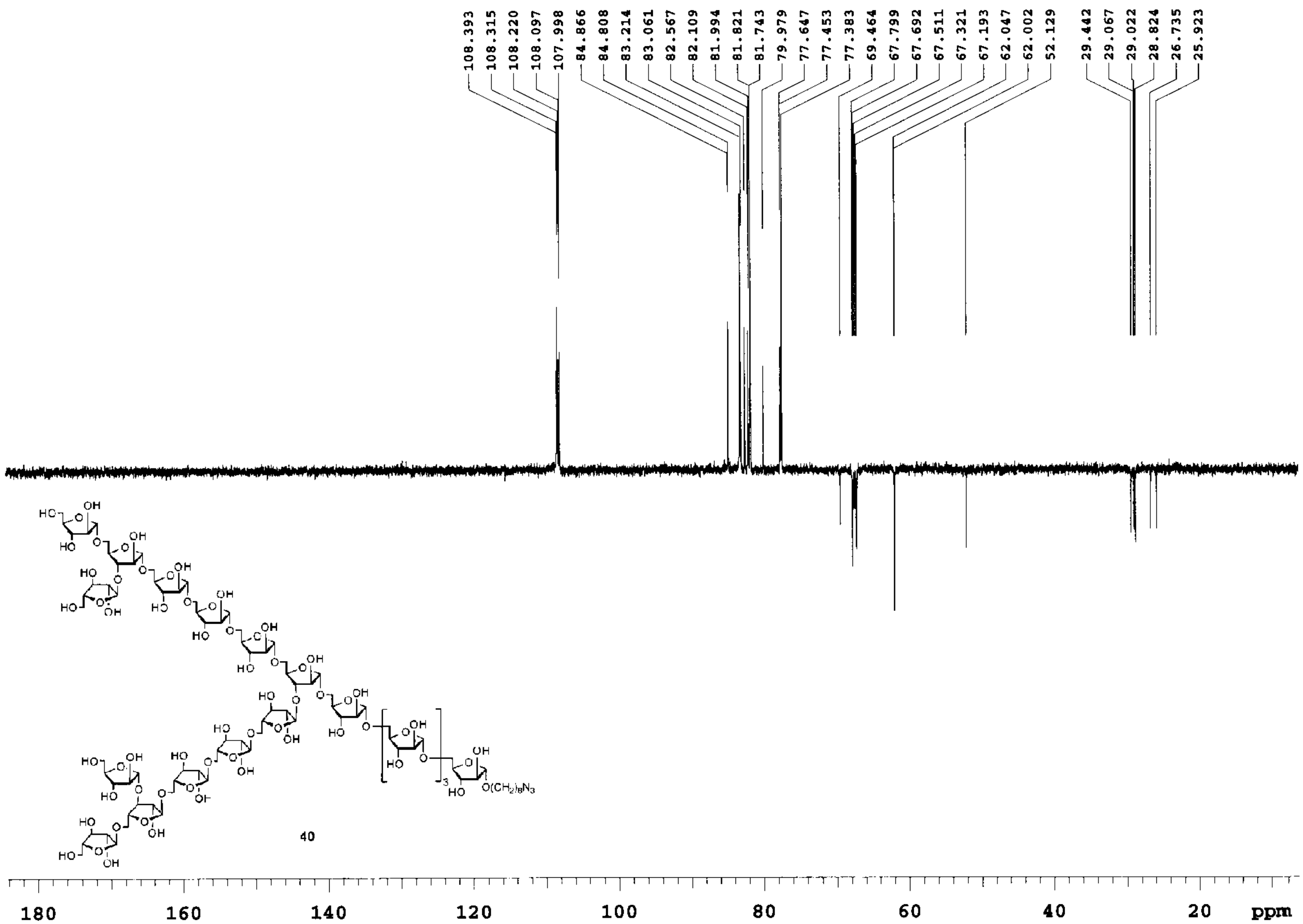


40



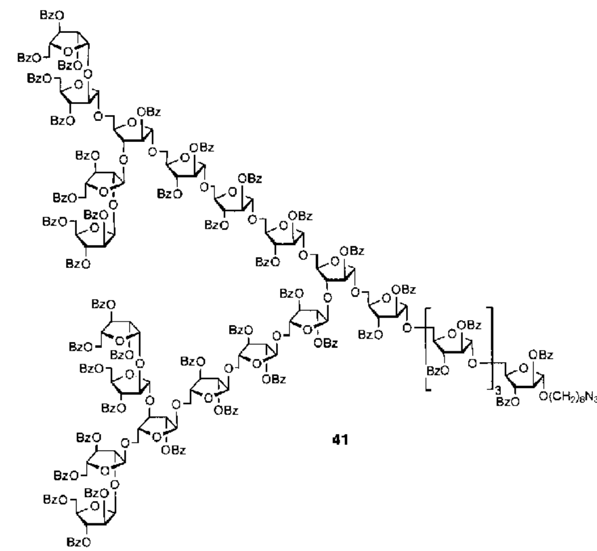
compound-40-C
mj-7-95-18sacch-alloh-13c5 125 MHz APT in D2O (ref. to 1% acetone @ 31.07 ppm)
C & CH2 opposite side of CH & CH3

Pulse Sequence: apt

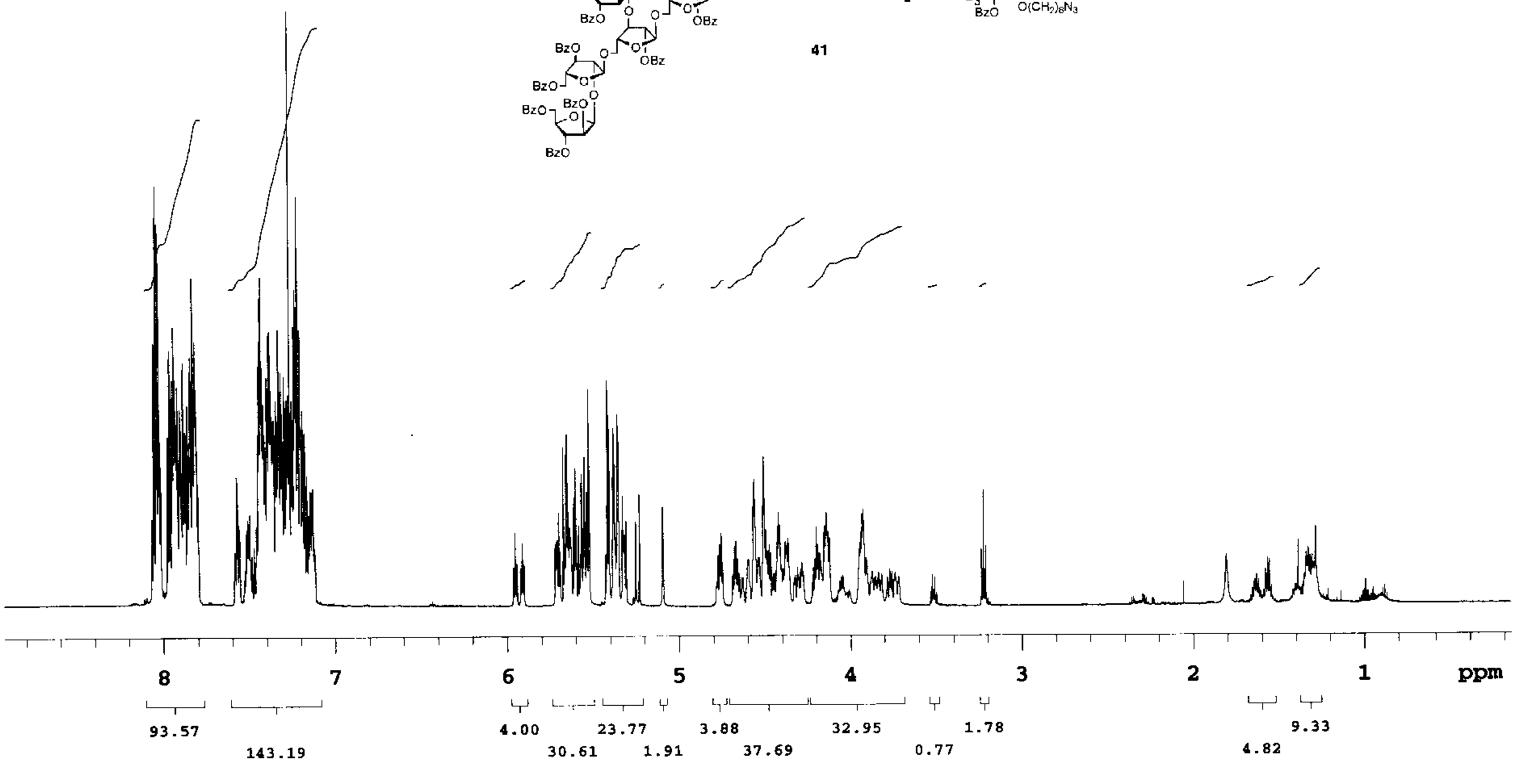


Pulse Sequence: s2pul

compound-41-H
600 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm)

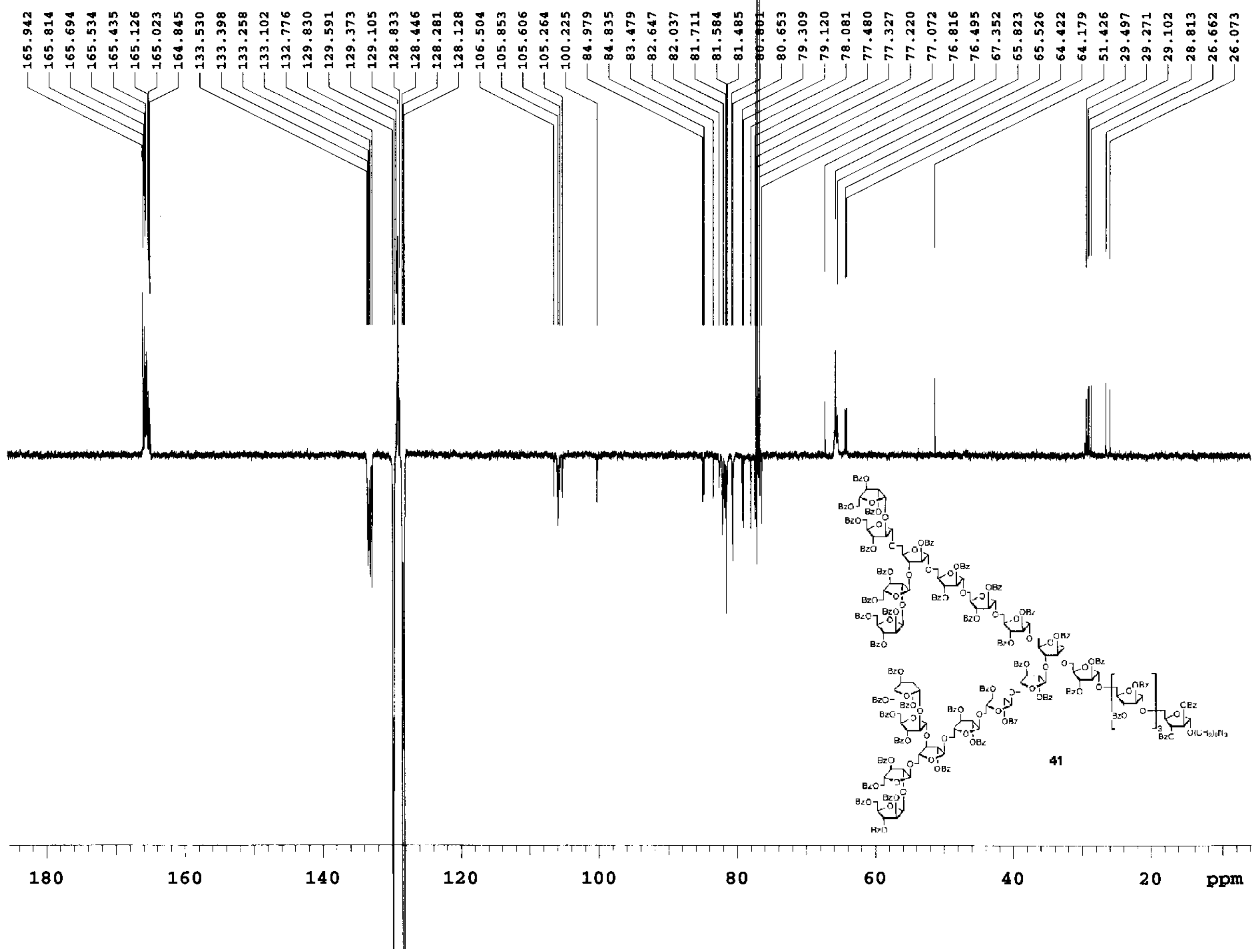


41



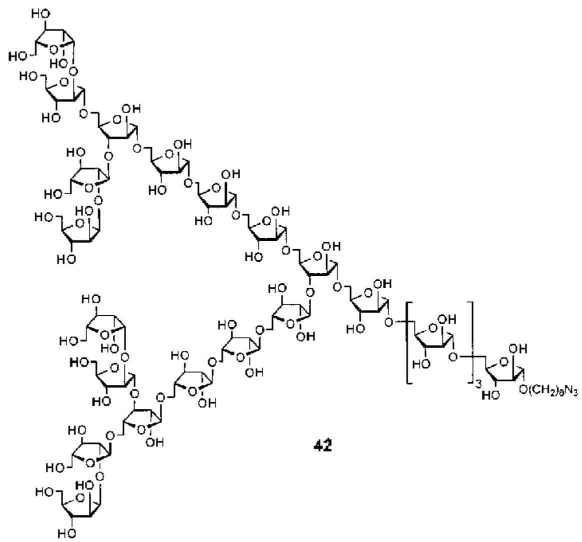
compound-41-C
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm)
C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

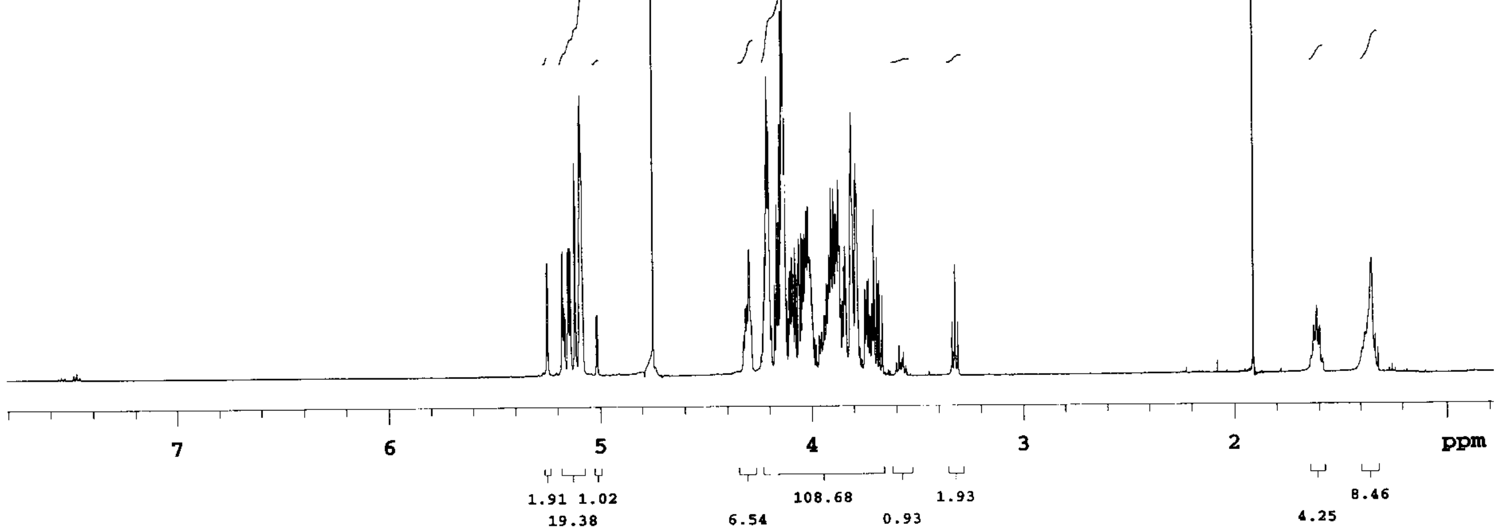


Pulse Sequence: s2pul

compound-42-H
500 MHz 1D in D2O (ref. to 0.1 % ext. acetone @ 2.225 ppm)



42



compound-42-C
125 MHz APT in D2O (ref. to 1% acetone @ 31.07 ppm)
C & CH2 opposite side of CH & CH3

Pulse Sequence: apt