Electronic supplementary materials *Mendeleev Commun.*, 2026, **36**, 18–20

Synthesis of the linear octaarabinofuranoside related to the terminal fragment of mycobacterial polysaccharides

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Experimental

General methods

All reactions sensitive to air and/or moisture were carried out under argon atmosphere. The reactions were performed with the use of commercial reagents (Aldrich, Fluka, Acros Organics). Anhydrous solvents were purified and dried (where appropriate) according to standard procedures. Dichloromethane was distilled over P_2O_5 and then over CaH_2 and stored over 4 Å molecular sieves (MS 4 Å). Powdered MS 4 Å and 3 Å molecular sieves (MS 4 Å and MS 3 Å, respectively) (Fluka) were activated before glycosylation reactions by heating at 220 °C in high vacuum (0.2 mbar) for 6 h. Column chromatography was performed on silica gel 60 (40–63 μm, Merck) using a Büchi C-815 Flash chromatograph. Gel permeation chromatography was performed on a 400×20 mm column packed with Bio-Beads S-X3 (200–400 mesh) or on a 450×30 mm column packed with Bio-Beads S-X1 (200–400 mesh). Thin-layer chromatography was carried out on plates with silica gel 60 on aluminum foil (Merck). Spots of compounds were visualized under UV light (254 nm) and by heating the plates (at *ca.* 150 °C) after immersion in a 1:10 (v/v) mixture of 85% aqueous H_3PO_4 and 95% EtOH. A procedure for "co-evaporation" with water (or toluene) involved (multiple) addition of water (or toluene) and evaporation of volatiles on a rotary evaporator. Amberlite MB-3 mixed-bed ion-exchange resin (Fluka) (1 mL) was washed with H_2O (10 mL), 50% EtOH (5 mL), EtOH (5 mL), 50% EtOH (5 mL) and H_2O (10 mL) before use. ^{29}Si NMR spectra were recorded on Bruker AVANCE NEO 300 spectrometer (59.6 MHz). ^{1}H and ^{13}C spectra were recorded on a Bruker AVANCE 600 spectrometer (600.13 and 150.9 MHz for ^{1}H and ^{13}C, respectively). The ^{1}H NMR chemical shifts are referred to the residual signal of $CHCl_3$ (δ_H 7.27 ppm) for solutions in $CDCl_3$, CHD_2OD (δ_H 3.31 ppm) for solutions in CD_3OD, the ^{13}C NMR shifts – to the central line of $CDCl_3$ signal (δ_C 77.00 ppm), CD_3OD signal (δ_C 49.00 ppm). The ^{29}Si chemical shifts are given relative to the signal of external Me_4Si (δ_{Si} 0.00 ppm). Assignments of the signals in the NMR spectra were performed using ^{1}H–^{13}C 2D-spectroscopy (COSY, HSQC, HMBC, ROESY) and DEPT-135 experiments. Position of silyl groups was determined from ^{1}H–^{29}Si HMBC experiments. High resolution mass spectra (HRMS, electrospray ionization (ESI)) were recorded in a positive ion mode on Bruker micrOTOF II or maXis mass spectrometers for $2 \cdot 10^{-5}$ M solutions in MeCN. Optical rotations were measured using a JASCO P-2000 automatic digital polarimeter (Japan).

4-(2-Chloroethoxy)phenyl 2,3-di-*O*-benzoyl-5-*O*-chloroacetyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (3) and 4-(2-chloroethoxy)phenyl 2,3-di-*O*-benzoyl-5-*O*-chloroacetyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside (3′)

A mixture of known trisaccharide glycosyl acceptor **1**[S1] (125 mg, 0.105 mmol) and known trisaccharide thioglycoside[S1] **2** (150 mg, 0.125 mmol) was dried *in vacuo* for 2 h, then anhydrous CH_2Cl_2 (2.5 mL) was added under argon. Freshly activated powdered MS 4 Å (250 g) (100 mg per 1 mL of solvent) were added under argon to the resulting solution. The suspension was stirred under argon at ~22 °C for 1 h, then cooled to −40 °C followed by addition of NIS (33 mg, 0.147 mmol) and (TfOH (2 μL, 0.026 mmol). Then the temperature was allowed to rise to −10 °C during 1 h and this temperature was kept for 20 h. Then the reaction was quenched by addition of Py (10 μL). The reaction mixture was diluted with CH_2Cl_2 (15 mL) and filtered through a Celite pad. The solids were washed with CH_2Cl_2 (5 × 10 mL) and the filtrate was washed with satd aq $Na_2S_2O_3$ (50 mL), H_2O (50 mL) and satd aq $NaHCO_3$ (50 mL). The combined organic layer was filtered through a cotton wool plug, concentrated under reduced pressure, the residue was dried *in vacuo*, then dissolved in toluene (2 mL) and subjected to chromatography on a column (450×30 mm) with Bio-Beads S-X1 (200–400 mesh) in toluene and silica gel chromatography (gradient: 0%→10% EtOAc in toluene) to give the key hexaarabinofuranoside **3** (209 mg, 87%) and the minor nonaarabinofuranoside **3′** (1 mg, 0.3%).

Data for hexaarabinofuranoside 3: R_f = 0.50 (toluene–EtOAc 10:1); $[\alpha]_D^{27}$ +20.6 (c 1.05, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.78 (t, 2 H, *J* 5.9 Hz, CH_2Cl), 3.89–3.98 (m, 5 H, H-5^{I-V}a), 4.02 (s, 2 H, $ClCH_2CO$), 4.16 (t, 2 H, *J* 5.9 Hz, CH_2O), 4.15–4.22 (m, 4 H, H-5^{II-V}b), 4.23 (dd, 1 H, *J* 11.3 Hz, *J* 4.2 Hz, H-5^{I}b), 4.49 (dd, 1 H, *J* 11.8 Hz, *J* 5.4 Hz, H-5^{VI}a), 4.55–4.65 (m, 6 H, H-4^{I-VI}), 4.68 (dd, 1 H, *J* 11.8 Hz, *J* 3.6 Hz, H-5^{VI}b), 5.38 (d, 1 H, *J* 4.7 Hz, H-3^{VI}), 5.40 (s, 1 H, H-1), 5.41 (s, 1 H, H-1), 5.41 (s, 2 H, 2 × H-1), 5.44 (s, 1 H, H-1^{VI}), 5.60 (d, 1 H, *J* 1.3 Hz, H-2^{VI}), 5.62 (dd, 1 H, *J* 4.9 Hz, *J* 1.5 Hz, H-3), 5.63–5.67 (m, 7 H, 4 × H-2, 3 × H-3), 5.75–5.80 (m, 2 H, H-2^{I}, H-3^{I}), 5.83 (s, 1 H, H-1^{I}), 6.81–6.86 (m, 2 H, OC_6H_4O (H-3, H-5)), 7.03–7.09 (m, 2 H, OC_6H_4O (H-2, H-6)), 7.21–7.30 (m, 10 H, 5 × PhCO (H-3, H-5)), 7.36–7.56 (m, 24 H, 7 × PhCO (H-3, H-5), 10 × PhCO (H-4)), 7.56–7.64 (m, 2 H, 2 × PhCO (H-4)), 7.85–7.93 (m, 10 H, 5 × PhCO (H-2, H-6)), 8.00–8.07 (m, 12 H, 6 × PhCO (H-2, H-6)), 8.09 (dd, 2 H, *J* 8.3 Hz, *J* 1.3 Hz, PhCO (H-2, H-6)); ^{13}C NMR (151 MHz, $CDCl_3$): δ 40.63 ($ClCH_2CO$), 41.89 (CH_2Cl), 64.85 (C-5^{VI}), 65.74 (C-5), 65.76 (C-5), 65.81 (2 × C-5), 66.10 (C-5), 68.65 (CH_2O), 77.03 (C-3), 77.13 (2 × C-3), 77.16 (C-3), 77.19 (C-3), 77.51 (C-3^{VI}), 80.92 (C-4^{VI}), 81.36 (C-2^{VI}), 81.51 (2 × C-2), 81.53 (C-2), 81.57 (C-2), 81.85 (C-2^{I}), 81.93 (C-4), 82.04 (C-4), 82.07 (C-4), 82.10 (C-4), 82.77 (C-4^{I}), 104.75 (C-1^{I}), 105.84 (3 × C-1), 105.88 (C-1), 105.92 (C-1), 115.79 (OC_6H_4O (C-3, C-5)), 118.18 (OC_6H_4O (C-2, C-6)), 128.20 (2 × PhCO (C-3, C-5)), 128.22, 128.24, 128.29 (PhCO (C-3, C-5)), 128.44 (2 × PhCO (C-3, C-5)), 128.46 (2 × PhCO (C-3, C-5)), 128.47, 128.51, 128.53 (PhCO (C-3, C-5)), 128.77, 128.86, 128.97, 129.00, 129.02, 129.03 (PhCO (C-1)), 129.05 (2 × PhCO (C-1)), 129.07 (2 × PhCO (C-1)), 129.09, 129.18 (PhCO (C-1)), 129.71 (2 × PhCO (C-2, C-6)), 129.72, 129.74, 129.75, 129.77 (PhCO (C-2, C-6)), 129.78 (3 × PhCO (C-2, C-6)), 129.80, 129.82, 129.88 (PhCO (C-2, C-6)), 133.07 (2 × PhCO (C-4)), 133.12, 133.14 (PhCO (C-4)), 133.30 (3 × PhCO (C-4)), 133.35, 133.38, 133.45,

133.49, 133.60 (PhCO (C-4)), 150.67 (OC_6H_4O (C-1)), 153.63 (OC_6H_4O (C-4)), 164.99 (PhCO), 165.05 (2 × PhCO), 165.07, 165.12, 165.32 (PhCO), 165.54 (2 × PhCO), 165.56 (2 × PhCO), 165.62, 165.69 (PhCO), 167.01 ($ClCH_2CO$); HRMS (ESI): m/z $[M+2NH_4]^{2+}$ Calcd for $C_{124}H_{114}Cl_2N_2O_{39}^{2+}$ 1162.3182; Found: 1162.3188.

Data for nonaarabinofuranoside 3′: R_f = 0.39 (toluene–EtOAc 10:1); $[\alpha]_D^{27}$ +14.6 (c 0.2, $CHCl_3$);^{1}H NMR (600 MHz, $CDCl_3$): δ 3.77 (t, 2 H, *J* 5.9 Hz, CH_2Cl), 3.86–3.97 (m, 8 H, H-5$^{I\text{-}VIII}$a), 4.01 (s, 2 H, $ClCH_2CO$), 4.10–4.19 (m, 9 H, CH_2O, H-5$^{II\text{-}VIII}$b), 4.21 (dd, 1 H, *J* 11.4 Hz, *J* 4.1 Hz, H-5^{I}b), 4.47 (dd, 1 H, *J* 11.7 Hz, *J* 5.3 Hz, H-5^{IX}a), 4.53–4.63 (m, 9 H, H-4$^{I\text{-}IX}$), 4.66 (dd, 1 H, *J* 11.7 Hz, *J* 3.6 Hz, H-5^{IX}b), 5.35–5.40 (m, 8 H, H-3^{IX}, 7 × H-1), 5.42 (s, 1 H, H-1), 5.58 (d, 1 H, *J* 1.2 Hz, H-2^{IX}), 5.60 (d, 1 H, *J* 4.8 Hz, H-3), 5.61–5.66 (m, 13 H, 6 × H-3, 7 × H-2), 5.74–5.77 (m, 2 H, H-3^{I}, H-2^{I}), 5.81 (s, 1 H, H-1^{I}), 6.79–6.85 (m, 2 H, OC_6H_4O (H-3, H-5), 7.01–7.07 (m, 2 H, OC_6H_4O (H-2, H-6)), 7.18–7.27 (m, 16 H, 8 × PhCO (H-3, H-5)), 7.34–7.54 (m, 36 H, 10 × PhCO (H-3, H-5), 16 × PhCO (H-4)), 7.55–7.63 (m, 2 H, 2 × PhCO (H-4)), 7.82–7.91 (m, 16 H, 8 × PhCO (H-2, H-6)), 7.97–8.10 (m, 20 H, 10 × PhCO (H-2, H-6)); ^{13}C NMR (151 MHz, $CDCl_3$): δ 40.65 ($ClCH_2CO$), 41.90 (CH_2Cl), 64.89 (C-5^{XI}), 65.82 (C-5), 65.83 (C-5), 65.85 (C-5), 65.86 (C-5), 65.88 (C-5), 65.90 (C-5), 65.91 (C-5), 66.19 (C-5), 68.75 (CH_2O), 76.83 (2 × C-3), 77.04 (2 × C-3), 77.18 (C-3), 77.25 (3 × C-3), 77.57 (C-3^{IX}), 80.96 (C-4^{IX}), 81.43 (2 × C-2), 81.56 (5 × C-2), 81.63 (C-2), 81.93 (C-2^{I}, C-4), 81.99 (C-4), 82.10 (4 × C-4), 82.15 (C-4), 82.81 (C-4^{I}), 104.85 (C-1^{I}), 105.93 (5 × C-1), 105.96 (C-1), 106.00 (C-1), 106.03 (C-1), 115.87 (OC_6H_4O (C-3, C-5)), 118.26 (OC_6H_4O (C-2, C-6)), 128.23, 128.25, 128.27, 128.32, 128.46, 128.49, 128.55 (PhCO (C-3, C-5)), 129.10, 129.18 (PhCO (C-1)), 129.76, 129.79, 129.82, 129.86, 129.91 (PhCO (C-2, C-6)), 133.06, 133.08, 133.13, 133.15, 133.29, 133.30, 133.32, 133.36, 133.38, 133.45, 133.50, 133.61 (PhCO (C-4)), 165.03, 165.09, 165.56, 165.59 (PhCO); HRMS (ESI): m/z $[M+2NH_4]^{2+}$ Calcd for $C_{181}H_{162}Cl_2N_2O_{57}^{2+}$ 1672.4603; Found: 1672.4597.

4-(2-Chloroethoxy)phenyl 2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside 4

To a solution of the hexaarabinofuranoside **3** (209 mg, 0.09 mmol) in pyridine (3 mL), H_2O (1 mL) was added, and the mixture was stirred at 70 °C for 2.5 h, then cooled and co-evaporated with toluene (5×5 mL). The residue was dried *in vacuo* and purified by silica gel chromatography (gradient: petroleum ether–EtOAc, 65:35 → 55:45) to give alcohol **4** (169 mg, 84%). R_f = 0.33 (petroleum ether – EtOAc 1:1); $[\alpha]_D^{28}$ +22.1 (c 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.30 (br. dd, 1 H, *J* 8.0 Hz, *J* 4.8 Hz, 5^{VI}-OH), 3.78 (t, 2 H, *J* 5.9 Hz, CH_2Cl), 3.88–3.97 (m, 6 H, H-5$^{I\text{-}VI}$a), 3.99 (ddd~dt, 1 H, *J* 12.0 Hz, *J* 3.5 Hz, H-5^{VI}b), 4.16 (t, 4 H, *J* 5.9 Hz, CH_2O), 4.13–4.21 (m, 4 H, H-5$^{II\text{-}V}$b), 4.23 (dd, 2 H, *J* 11.3 Hz, *J* 4.2 Hz, H-5^{I}b), 4.46 (q, 1 H, *J* 4.0 Hz, H-4^{VI}), 4.56–4.61 (m, 4 H, 4 × H-4), 4.62 (td, 1 H, *J* 4.3 Hz, *J* 2.8 Hz, H-4), 5.39 (s, 1 H, H-1), 5.40 (s, 1 H, H-1), 5.40 (s, 3 H, 3 × H-1), 5.42 (dd, 1 H, *J* 4.9 Hz, *J* 1.6 Hz, H-3^{VI}), 5.60–5.67 (m, 9 H, 5 × H-2, 4 × H-3), 5.77 (dd, 1 H, *J* 4.5 Hz, *J* 1.6 Hz, H-3^{I}), 5.78 (d, 1 H, *J* 1.6 Hz, H-2^{I}), 5.82 (s, 1 H, H-1^{I}), 6.80–6.86 (m, 2 H, OC_6H_4O (H-3, H-5)), 7.02–7.08 (m, 2 H, OC_6H_4O (H-2, H-6)), 7.20–7.30 (m, 10 H, 5 × PhCO (H-3, H-5)), 7.36–7.49 (m, 19 H, 7 × PhCO (H-4), 5 × PhCO (H-4)), 7.47–7.56 (m, 5 H, 5 × PhCO (H-4)), 7.55–7.62 (m, 2 H, 2 × PhCO (H-4)), 7.84–7.92 (m, 10 H, 5 × PhCO (H-2, H-6)), 7.99–8.07 (m, 12 H, 6 × PhCO (H-2, H-6)), 8.06–8.11 (m, 2 H, PhCO (H-2, H-6)); ^{13}C NMR (151 MHz, $CDCl_3$): δ 41.89 (CH_2Cl), 62.29 (C-5^{VI}), 65.80 (C-5), 65.82 (C-5), 65.85 (2 × C-5), 66.12 (C-5), 68.71 (CH_2O), 77.07 (C-3), 77.17 (2 × C-3), 77.21 (C-3), 77.28 (C-3), 77.67 (C-3^{VI}), 81.52 (C-2), 81.55 (C-2), 81.57 (2 × C-2), 81.67 (C-2), 81.89 (C-2^{I}), 81.95 (C-4), 82.07 (C-4), 82.10 (C-4), 82.12 (C-4), 82.79 (C-4^{I}), 83.62 (C-4^{VI}), 104.81 (C-1^{I}), 105.84 (C-1), 105.87 (2 × C-1), 105.89 (C-1), 105.93 (C-1), 115.84 (OC_6H_4O (C-3, C-5)), 118.23 (OC_6H_4O (C-2,

C-6)), 128.21 (3 × PhCO (C-3, C-5)), 128.26, 128.27 (PhCO (C-3, C-5)), 128.45 (2 × PhCO (C-3, C-5)), 128.47 (PhCO (C-3, C-5)), 128.48 (3 × PhCO (C-3, C-5)), 128.53 (PhCO (C-3, C-5)), 128.90, 128.97, 129.01 (PhCO (C-1)), 129.06 (4 × PhCO (C-1)), 129.12 (3 × PhCO (C-1)), 129.18, 129.23 (PhCO (C-1)), 129.73 (4 × PhCO (C-2, C-6)), 129.78 (PhCO (C-2, C-6)), 129.80 (3 × PhCO (C-2, C-6)), 129.81 (PhCO (C-2, C-6)), 129.84 (2 × PhCO (C-2, C-6)), 129.89 (PhCO (C-2, C-6)), 133.08 (2 × PhCO (C-4)), 133.11, 133.15, 133.24 (PhCO (C-4)), 133.30 (2 × PhCO (C-4)), 133.36 (2 × PhCO (C-4)), 133.45, 133.46, 133.50 (PhCO (C-4)), 150.72 (OC_6H_4O (C-1)), 153.66 (OC_6H_4O (C-4)), 165.05, 165.07 (PhCO), 165.09 (2 × PhCO), 165.15, 165.34, 165.55 (PhCO), 165.58 (2 × PhCO), 165.60, 165.63, 166.03 (PhCO); HRMS (ESI): m/z $[M+NH_4]^+$ Calcd for $C_{122}H_{109}ClNO_{38}^+$ 2230.6311; Found: 2230.6291.

4-(2-Chloroethoxy)phenyl 2,3,5-tris-*O*-(triisopropylsilyl)-β-D-arabinofuranosyl-(1→2)-3,5-bis-*O*-(triisopropylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside 6

A mixture of known silylated disaccharide thioglycoside **5**[S2] (45 mg, 0.036 mmol) and hexasaccharide alcohol **4** (62 mg, 0.028 mmol) was dried *in vacuo* for 2 h, then anhydrous CH_2Cl_2 (2 mL) was added under argon. Freshly activated powdered MS 4 Å (200 mg) (100 mg per 1 mL of solvent) were added under argon to the resulting solution. The suspension was stirred under argon at ~22 °C for 1 h, then cooled to −60 °C followed by addition of NIS (9.3 mg, 0.04 mmol) and (TfOH (1 μL, 0.06 mmol). Then the temperature was allowed to rise to −30 °C during 15 min and was kept at −30 °C for 85 min. Then the reaction was quenched by addition of Py (5 μL), diluted with CH_2Cl_2 (15 mL) and filtered through a Celite pad. The solids were washed with CH_2Cl_2 (5×10 mL) and the filtrate was washed with satd aq $Na_2S_2O_3$ (50 mL), H_2O (50 mL) and satd aq $NaHCO_3$ (50 mL). The aqueous layer was extracted with CH_2Cl_2 (2×5 mL). Combined organic extracts were filtered through a cotton wool plug, concentrated and dried *in vacuo*. The residue was dissolved in toluene (2 mL) and subjected to chromatography on Bio-Beads S-X1 in toluene. The fractions eluted just after the void volume were collected, concentrated under reduced pressure and additionally purified by silica gel chromatography (gradient: petroleum ether–EtOAc 95:5→75:25) to give the key α-linked octasaccharide **6** (76 mg, 85%). R_f = 0.77 (petroleum ether – EtOAc 3:2); $[\alpha]_D^{22}$ +22.3 (c 0.98, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.93–1.12 (m, 105 H, 5 × $((CH_3)_2CH)_3Si$), 3.68 (dd, 1 H, *J* 9.5 Hz, *J* 4.6 Hz, H-5^{VIII}a), 3.72 (dd, 1 H, *J* 10.7 Hz, *J* 6.1 Hz, H-5^{VII}a), 3.76 (dd, 1 H, *J* 10.9 Hz, *J* 4.6 Hz, H-5^{VI}a), 3.78 (t, 2 H, *J* 5.9 Hz, CH_2Cl), 3.79 (dd, 1 H, *J* 10.7 Hz, *J* 5.1 Hz, H-5^{VII}b), 3.83 (dd, 1 H, *J* 10.4 Hz, *J* 4.7 Hz, H-4^{VIII}), 3.85–3.96 (m, 6 H, H-5^{I}a, H-5^{II}a, H-5^{III}a, H-5^{IV}a, H-5^{V}a, H-5^{VIII}b), 3.99 (d, 1 H, *J* 3.0 Hz, H-2^{VIII}), 4.04 (dd, 1 H, *J* 10.9 Hz, *J* 4.9 Hz, H-5^{VI}b), 4.06–4.12 (m, 1 H, H-4^{VII}), 4.16 (t, 2 H, *J* 5.9 Hz, CH_2O), 4.16–4.20 (m, 5 H, H-2^{VII}, H-5^{II-V}b), 4.22 (dd, 1 H, *J* 11.4 Hz, *J* 4.3 Hz, H-5^{I}b), 4.30 (d, 1 H, *J* 1.1 Hz, H-3^{VIII}), 4.37 (dd, 1 H, *J* 4.4 Hz, *J* 1.7 Hz, H-3^{VII}), 4.54–4.63 (m, 6 H, H-4^{I-VI}), 5.07 (s, 1 H, H-1^{VII}), 5.23 (d, 1 H, *J* 2.7 Hz, H-1^{VIII}), 5.35 (s, 1 H, H-1^{VI}), 5.37 (s, 1 H, H-1), 5.38 (s, 1 H, H-1), 5.40 (s, 2 H, 2 × H-1), 5.50 (dd, 1 H, *J* 4.9 Hz, *J* 1.7 Hz, H-3^{VI}), 5.59 (d, 1 H, *J* 1.6 Hz, H-2^{VI}), 5.61–5.63 (m, 2 H, H-2, H-3), 5.63–5.66 (m, 6 H, 3 × H-3, 3 × H-2), 5.74–5.79 (m, 2 H, H-2^{I}, H-3^{I}), 5.82 (s, 1 H, H-1^{I}), 6.80–6.86 (m, 2 H, OC_6H_4O (H-3, H-5)), 7.02–7.08 (m, 2 H, OC_6H_4O (H-2, H-6)), 7.20–7.27 (m, 10 H, 5 × PhCO (H-3, H-5)), 7.33–7.61 (m, 26 H, 7 × PhCO (H-3, H-5), 12 × PhCO (H-4)), 7.85–7.92 (m, 10 H, 5 × PhCO (H-2, H-6)), 7.96–7.99 (m, 2 H, PhCO (H-2, H-6)), 7.99–8.05 (m, 8 H, 4 × PhCO (H-2, H-6)), 8.05–8.07 (m, 2 H, PhCO (H-2, H-6)), 8.07–8.10 (m, 2 H, PhCO (H-2, H-6)); ^{13}C NMR (151 MHz, $CDCl_3$): δ 11.95, 11.96, 12.23, 12.25, 12.27

(((CH$_3$)$_2$CH)$_3$Si), 17.93 (3 × ((CH$_3$)$_2$CH)$_3$Si), 17.95 (((CH$_3$)$_2$CH)$_3$Si), 18.06 (3 × ((CH$_3$)$_2$CH)$_3$Si), 18.09, 18.13, 18.15 (((CH$_3$)$_2$CH)$_3$Si), 41.90 (CH$_2$Cl), 63.74 (C-5^{VIII}), 64.14 (C-5^{VII}), 65.72, 65.77, 65.79 (C-5), 65.84 (2 × C-5), 66.01 (C-5^{VI}), 68.69 (CH$_2$O), 77.05 (C-3^{I}), 77.14, 77.16 (C-3), 77.21 (2 × C-3), 77.43 (C-3^{VI}), 77.57 (C-3^{VII}), 78.11 (C-2^{VIII}), 78.22 (C-3^{VIII}), 81.46, 81.50, 81.53, 81.55 (C-2), 81.63 (C-2^{VI}), 81.76 (C-4^{VI}), 81.88 (C-2^{I}), 82.07 (2 × C-4), 82.08, 82.11 (C-4), 82.79 (C-4^{I}), 85.70 (C-4^{VIII}), 87.44 (C-4^{VII}), 90.93 (C-2^{VII}), 104.78, 104.82 (C-1^{I}, C-1^{VIII}), 105.87, 105.89 (C-1), 105.91 (2 × C-1), 105.99 (C-1), 106.91 (C-1^{VII}), 115.81 (OC$_6$H$_4$O (C-3, C-5)), 118.21 (OC$_6$H$_4$O (C-2, C-6)), 128.10, 128.18, 128.19, 128.21, 128.26, 128.37, 128.40, 128.44, 128.45 (PhCO (C-3, C-5)), 128.48 (2 × PhCO (C-3, C-5)), 128.53 (PhCO (C-3, C-5)), 128.89, 129.05, 129.07 (PhCO (C-1)), 129.08 (2 × PhCO (C-1)), 129.09 (PhCO (C-1)), 129.11 (2 × PhCO (C-1)), 129.16, 129.22, 129.31, 129.42 (PhCO (C-1)), 129.73 (PhCO (C-2, C-6)), 129.75 (2 × PhCO (C-2, C-6)), 129.77 (2 × PhCO (C-2, C-6)), 129.80 (3 × PhCO (C-2, C-6)), 129.81, 129.84, 129.90, 129.92 (PhCO (C-2, C-6)), 132.84, 132.99, 133.03, 133.06, 133.14, 133.17, 133.23, 133.27, 133.30, 133.36, 133.45, 133.51 (PhCO (C-4)), 150.71 (OC$_6$H$_4$O (C-1)), 153.65 (OC$_6$H$_4$O (C-4)), 165.05 (2 × PhCO), 165.08, 165.10, 165.15, 165.17, 165.35, 165.48, 165.51, 165.53, 165.57, 165.63 (PhCO); ^{29}Si NMR (60 MHz, CDCl$_3$): δ 13.06 (3^{VII}-*O*-TIPS), 13.51, 13.55 (5^{VII}-*O*-TIPS, 5^{VIII}-*O*-TIPS), 13.66 (3^{VIII}-*O*-TIPS), 13.87 (2^{VIII}-*O*-TIPS); HRMS (ESI): m/z [M+2NH$_4$]$^{2+}$ Calcd for C$_{177}$H$_{229}$ClN$_2$O$_{46}$Si$_5^{2+}$ 1646.7083; Found: 1646.7063.

4-(2-Azidoethoxy)phenyl 2,3,5-tris-*O*-(triisopropylsilyl)-β-D-arabinofuranosyl-(1→2)-3,5-bis-*O*-(triisopropylsilyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside 7

A mixture of octasaccharide CEP glycoside **6** (76 mg, 0.023 mmol), NaN$_3$ (7 mg, 0.11 mmol) and 18-crown-6 (5 mg, 0.02 mmol) in DMF (1 mL), was stirred at 70 °C for 17 h and at 80 °C for 18.5 h. Since the reaction was not completed (the probe with Ph$_3$P was used), an additional portion of NaN$_3$ (2 mg, 0.03 mmol) was added and the reaction mixture was stirred at 80 °C for 5 h. The reaction mixture was concentrated, co-evaporated with toluene (5×5 mL) and dried *in vacuo*. The residue was purified by silica gel column chromatography in petroleum ether–EtOAc (gradient: 10% → 22.5% EtOAc in petroleum ether) to give azide **7** (70 mg, 92%). R_f = 0.25 (petroleum ether – EtOAc 2:1); [α]$_D^{28}$ +21.3 (c 1.13; CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$): δ 0.94–1.12 (m, 105 H, 5 × ((CH$_3$)$_2$CH)$_3$Si), 3.56 (dd, 2 H, *J* 5.3 Hz, *J* 4.7 Hz, CH$_2$N$_3$), 3.68 (dd, 1 H, *J* 9.5 Hz, *J* 4.6 Hz, H-5^{VIII}a), 3.72 (dd, 1 H, *J* 10.7 Hz, *J* 6.1 Hz, H-5^{VII}a), 3.76 (dd, 1 H, *J* 11.0 Hz, *J* 4.5 Hz, H-5^{VI}a), 3.79 (dd, 1 H, *J* 10.7 Hz, *J* 5.0 Hz, H-5^{VII}b), 3.83 (dd, 1 H, *J* 10.4 Hz, *J* 4.7 Hz, H-4^{VIII}), 3.86–3.95 (m, 6 H, H-5^{I-V}a, H-5^{VIII}b), 3.99 (d, 1 H, *J* 3.0 Hz, H-2^{VIII}), 4.03 (dd, 1 H, *J* 11.0 Hz, *J* 4.9 Hz, H-5^{VI}b), 4.07–4.09 (m, 2 H, CH$_2$O), 4.07–4.11 (m, 1 H, H-4^{VII}), 4.15–4.20 (m, 5 H, H-2^{VII}, H-5^{II-V}b), 4.22 (dd, 1 H, *J* 11.3 Hz, *J* 4.2 Hz, H-5^{I}b), 4.30 (d, 1 H, *J* 1.1 Hz, H-3^{VIII}), 4.37 (dd, 1 H, *J* 4.4 Hz, *J* 1.8 Hz, H-3^{VII}), 4.53–4.64 (m, 6 H, H-4^{I-VI}), 5.07 (s, 1 H, H-1^{VII}), 5.23 (d, 1 H, *J* 2.7 Hz, H-1^{VIII}), 5.35 (s, 1 H, H-1^{VI}), 5.37 (s, 1 H, H-1), 5.38 (s, 1 H, H-1), 5.40 (s, 2 H, 2 × H-1), 5.49 (dd, 1 H, *J* 4.8 Hz, *J* 1.6 Hz, H-3^{VI}), 5.59 (d, 1 H, *J* 1.6 Hz, H-2^{VI}), 5.61–5.63 (m, 2 H, H-3, H-2), 5.63–5.66 (m, 6 H, 3 × H-3, 3 × H-2), 5.75–5.79 (m, 2 H, H-3^{I}, H-2^{I}), 5.82 (s, 1 H, H-1^{I}), 6.80–6.86 (m, 2 H, OC$_6$H$_4$O (H-3, H-5)), 7.03–7.08 (m, 2 H, OC$_6$H$_4$O (H-2, H-6)), 7.20–7.27 (m, 10 H, 5 × PhCO (H-3, H-5)), 7.33–7.61 (m, 26 H, 7 × PhCO (H-3, H-5), 12 × PhCO (H-4)), 7.85–7.92 (m, 10 H, 5 × PhCO (H-2, H-6)), 7.96–7.98 (m, 2 H, PhCO (H-2, H-6)), 7.98–8.05 (m, 8 H, 4 × PhCO (H-2, H-6)), 8.05–8.07 (m, 2 H, PhCO (H-2, H-6)), 8.07–8.10 (m, 2 H, PhCO (H-2, H-6)); ^{13}C NMR (151 MHz, CDCl$_3$): δ 11.95 (2 × ((CH$_3$)$_2$CH)$_3$Si), 12.22, 12.25, 12.27 (((CH$_3$)$_2$CH)$_3$Si), 17.93 (3 × ((CH$_3$)$_2$CH)$_3$Si), 17.95

(((CH$_3$)$_2$CH)$_3$Si), 18.06 (3 × ((CH$_3$)$_2$CH)$_3$Si), 18.09, 18.13, 18.15 (((CH$_3$)$_2$CH)$_3$Si), 50.18 (CH_2N_3), 63.74 (C-5^{VIII}), 64.14 (C-5^{VII}), 65.71, 65.76, 65.78 (C-5), 65.84 (2 × C-5), 66.01 (C-5^{VI}), 67.52 (CH_2O), 77.05 (C-3^{I}), 77.13, 77.15 (C-3), 77.21 (2 × C-3), 77.43 (C-3^{VI}), 77.57 (C-3^{VII}), 78.10 (C-2^{VIII}), 78.22 (C-3^{VIII}), 81.46, 81.50, 81.53, 81.54 (C-2), 81.63 (C-2^{VI}), 81.76 (C-4^{VI}), 81.87 (C-2^{I}), 82.07 (2 × C-4), 82.08, 82.11 (C-4), 82.79 (C-4^{I}), 85.70 (C-4^{VIII}), 87.44 (C-4^{VII}), 90.93 (C-2^{VII}), 104.79, 104.82 (C-1^{I}, C-1^{VIII}), 105.87, 105.89 (C-1), 105.91 (2 × C-1), 105.99 (C-1), 106.91 (C-1^{VII}), 115.58 (OC_6H_4O (C-3, C-5)), 118.21 (OC_6H_4O (C-2, C-6)), 128.10, 128.18, 128.19, 128.21, 128.25, 128.37, 128.40, 128.44, 128.45 (PhCO (C-3, C-5)), 128.48 (2 ×PhCO (C-3, C-5)), 128.53 (PhCO (C-3, C-5)), 128.89, 129.05, 129.06 (PhCO (C-1)), 129.08 (3 × PhCO (C-1)), 129.11 (2 × PhCO (C-1)), 129.16, 129.21, 129.31, 129.41 (PhCO (C-1)), 129.73 (PhCO (C-2, C-6)), 129.75 (2 × PhCO (C-2, C-6)), 129.77 (2 × PhCO (C-2, C-6)), 129.80 (3 × PhCO (C-2, C-6)), 129.81, 129.84, 129.90, 129.92 (PhCO (C-2, C-6)), 132.84, 132.99, 133.03, 133.06, 133.14, 133.17, 133.23, 133.27, 133.30, 133.36, 133.45, 133.50 (PhCO (C-4)), 150.65 (OC_6H_4O (C-1)), 153.70 (OC_6H_4O (C-4)), 165.06 (2 × PhCO), 165.08, 165.10, 165.15, 165.18, 165.35, 165.49, 165.52, 165.53, 165.57, 165.63 (PhCO); ^{29}Si NMR (60 MHz, $CDCl_3$): δ 13.07 (3^{VII}-*O*-TIPS), 13.51, 13.55 (5^{VII}-*O*-TIPS, 5^{VIII}-*O*-TIPS), 13.66 (3^{VIII}-*O*-TIPS), 13.87 (2^{VIII}-*O*-TIPS); HRMS (ESI): m/z $[M+2NH_4]^{2+}$ Calcd for $C_{177}H_{185}N_5O_{46}Si_5^{2+}$ 1650.2285; Found: 1650.2270.

4-(2-Azidoethoxy)phenyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzoyl-α-D-arabinofuranoside 8

Protected octasaccharide AEP glycoside **7** (69 mg, 0.021 mmol) was dissolved in THF (2 mL), then AcOH (12 μL, 0.21 mmol) and 1 M Bu_4NF in THF (420 μL, 0.42 mmol) were added. The reaction mixture was stirred at 40 °C for 1.5 h, then concentrated under reduced pressure, co-evaporated with toluene (5×5 mL) and dried *in vacuo*. The residue was purified by silica gel chromatography CH_2Cl_2–MeOH (gradient: 0%→5% MeOH in CH_2Cl_2) to give octasaccharide pentaol **8** (40 mg, 76%). R_f = 0.57 (CH_2Cl_2–MeOH 9:1); $[\alpha]_D^{26}$ +19.9 (c 1.0; $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.55 (dd, 2 H, *J* 5.4 Hz, *J* 4.6 Hz, CH_2N_3), 3.57–3.65 (m, 2 H, H-5^{VIII}a, H-5^{VII}a), 3.68–3.75 (m, 2 H, H-4^{VIII}, H-5^{VIII}b), 3.75–3.85 (m, 2 H, H-5^{VII}b, H-5^{VI}a), 3.89–3.96 (m, 6 H, H-5^{I-V}a, H-4^{VII}), 3.96–4.03 (m, 2 H, H-2^{VIII}, H-5^{VI}b), 4.08 (dd, 1 H, *J* 5.7 Hz, *J* 4.8 Hz, CH_2O), 4.14–4.28 (m, 8 H, H-2^{VII}, H-3^{VII}, H-3^{VIII}, H-5^{I-V}b), 4.49 (q, 1 H, *J* 4.3 Hz, H-4^{VI}), 4.55–4.64 (m, 5 H, H-4^{I-V}), 4.93 (d, 1 H, *J* 4.3 Hz, H-1^{VIII}), 5.05 (s, 1 H, H-1^{VII}), 5.388 (s, 1 H, H-1^{VI}), 5.394 (s, 1 H, H-1), 5.397 (s, 1 H, H-1), 5.404 (s, 2 H, 2 × H-1), 5.48 (dd, 1 H, *J* 5.1 Hz, *J* 1.6 Hz, H-3^{VI}), 5.54 (d, 1 H, *J* 1.6 Hz, H-2^{VI}), 5.61–5.67 (m, 8 H, H-2^{II-V}, H-3^{II-V}), 5.75–5.79 (m, 2 H, H-2^{I}, H-3^{I}), 5.82 (s, 1 H, H-1^{I}), 6.80–6.86 (m, 2 H, OC_6H_4O (H-3, H-5)), 7.03–7.08 (m, 2 H, OC_6H_4O (H-2, H-6)), 7.20–7.27 (m, 10 H, 5 × PhCO (H-3, H-5)), 7.31–7.61 (m, 26 H, 7 × PhCO (H-3, H-5), 12 × PhCO (H-4)), 7.84–7.92 (m, 10 H, 5 × PhCO (H-2, H-6)), 7.96–8.06 (m, 12 H, 6 × PhCO (H-2, H-6)), 8.06–8.11 (m, 2 H, PhCO (H-2, H-6)); ^{13}C NMR (151 MHz, $CDCl_3$): δ 50.19 (CH_2N_3), 60.22 (C-5^{VII}), 61.00 (C-5^{VIII}), 65.84 (3 × C-5), 65.90, 66.06 (C-5), 66.81 (C-5^{VI}), 67.55 (CH_2O), 73.09 (C-3^{VIII}), 74.05 (C-3^{VII}), 77.10 (C-3^{I}), 77.19 (2 × C-3), 77.24 (2 × C-3), 77.51 (2 C, C-2^{VIII}, C-3^{VI}), 81.60 (4 C, C-2^{II-V}), 81.67 (C-4^{VI}), 81.89 (2 C), 81.92 (2 C) (C-2^{I}, C-2^{VI}, C-4^{VII}, C-4^{VIII}), 82.12 (2 × C-4), 82.13 (2 × C-4), 82.80 (C-4^{I}), 86.71 (C-2^{VII}), 100.10 (C-1^{VIII}), 104.86 (C-1^{I}), 105.94 (3 × C-1), 105.96 (3 × C-1), 115.63 (OC_6H_4O (C-3, C-5)), 118.26 (OC_6H_4O (C-2, C-6)), 128.22 (2 × PhCO (C-3, C-5)), 128.26 (2 × PhCO (C-3, C-5)), 128.29, 128.43 (PhCO (C-3, C-5)), 128.45 (2 × PhCO (C-3, C-5)), 128.48 (2 × PhCO (C-3, C-5)), 128.49, 128.53 (PhCO (C-3, C-5)), 128.94 (2 × PhCO (C-1)), 129.09 (6 × PhCO (C-1)), 129.15 (2 × PhCO (C-1)), 129.21, 129.25

(PhCO (C-1)), 129.74 (3 × PhCO (C-2, C-6)), 129.76 (2 × PhCO (C-2, C-6)), 129.80 (3 × PhCO (C-2, C-6)), 129.81, 129.84 (PhCO (C-2, C-6)), 129.90 (2 × PhCO (C-2, C-6)), 133.07 (2 × PhCO (C-4)), 133.14 (2 × PhCO (C-4)), 133.23 (PhCO (C-4)), 133.30 (2 × PhCO (C-4)), 133.32, 133.35 (PhCO (C-4)), 133.44 (2 × PhCO (C-4)), 133.49 (PhCO (C-4)), 150.70 (OC_6H_4O (C-1)), 153.75 (OC_6H_4O (C-4)), 165.09, 165.10, 165.12 (PhCO), 165.17 (2 × PhCO), 165.35, 165.56 (PhCO), 165.59 (2 × PhCO), 165.64, 165.71, 165.78 (PhCO); HRMS (ESI): m/z $[M+NH_4]^+$ Calcd for $C_{132}H_{125}N_4O_{46}^+$, 2501.7559; Found: 2501.7537.

4-(2-Azidoethoxy)phenyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside 9

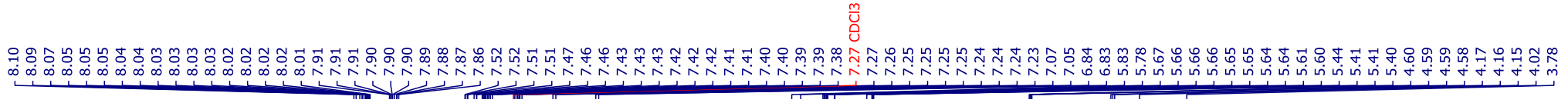
Octaarabinofuranoside **8** (40 mg) was dissolved in a mixture of MeOH (1 mL) and CH_2Cl_2 (0.6 mL) followed by addition of 1 M MeONa in MeOH (50 μL, 0.05 mmol). The reaction mixture was kept at ~25 °C for 19 h. Then the reaction mixture was neutralized with Dowex 50W×8 (H^+) ion-exchange resin (the resin was washed with MeOH before addition) and then filtered. The resin was washed with MeOH (10 mL). The filtrate was concentrated under reduced pressure, dried *in vacuo* and purified by reversed phase chromatography on a Sep-Pak C18 cartridge (particle size: 55–105 μm, pore size: 125 Å, sorbent substrate: silica, sorbent weight: 360 mg), gradient: 0→100% MeOH in H_2O). The eluate was lyophilized to give the residue, which was dissolved in water (0.6 mL) and applied on a small column (ID 5 mm) packed with Amberlite MB-3 mixed-bed ion-exchange resin (1 mL) which was eluted with H_2O (15 mL). The eluate was lyophilized to give deprotected octaarabinofuranoside **9** (14 mg, 71%, 53% over 2 steps). R_f = 0.52 (CH_3CN–H_2O 3:1); $[\alpha]_D^{30}$ +121.0 (c 0.87, MeOH); ^{1}H NMR (600 MHz, CD_3OD): δ 3.54–3.59 (m, 2 H, CH_2N_3), 3.61–3.71 (m, 8 H, H-5^{VII}a, H-5^{VIII}a, H-5$^{I\text{-}VI}$a), 3.73 (dd, 1 H, *J* 12.0 Hz, *J* 3.2 Hz, H-5^{VIII}b), 3.76–3.81 (m, 2 H, H-4^{VIII}, H-5^{VII}b), 3.82–3.88 (m, 6 H, H-5$^{I\text{-}VI}$b), 3.89–3.92 (m, 5 H, H-3$^{II\text{-}VI}$), 3.95 (ddd, 1 H, *J* 7.8 Hz, *J* 5.0 Hz, *J* 2.8 Hz, H-4^{VII}), 3.97–4.10 (m, 14 H, H-2^{VIII}, H-2$^{II\text{-}VI}$, H-3^{VIII}, H-3^{I}, H-3^{VII}, H-4$^{II\text{-}VI}$), 4.12 (dd, 2 H, *J* 5.5 Hz, *J* 4.4 Hz, CH_2O), 4.13–4.18 (m, 2 H, H-2^{VII}, H-4^{I}), 4.22 (dd, 1 H, *J* 4.0 Hz, *J* 1.9 Hz, H-2^{I}), 4.94–4.96 (m, 4 H, 4 × H-1), 4.96 (d, 1 H, *J* 1.6 Hz, H-1), 5.03 (d, 1 H, *J* 4.1 Hz, H-1^{VIII}), 5.07 (d, 1 H, *J* 2.3 Hz, H-1^{VII}), 5.42 (d, 1 H, *J* 1.9 Hz, H-1^{I}), 6.85–6.91 (m, 2 H, OC_6H_4O (H-3, H-5)), 6.97–7.03 (m, 2 H, OC_6H_4O (H-2, H-6)); ^{13}C NMR (151 MHz, CD_3OD): δ 51.43 (CH_2N_3), 62.48 (C-5^{VII}), 64.40 (C-5^{VIII}), 68.02 (C-5^{I}), 68.28 (4 C), 68.34 (C-5$^{II\text{-}VI}$), 68.96 (CH_2O), 75.87 (C-3^{VIII}), 76.42 (C-3^{VII}), 78.78, 78.82 (C-3^{I}, C-2^{VIII}), 78.98, 79.18 (4 C) (C-3$^{II\text{-}VI}$), 83.25 (4 C), 83.30 (C-2$^{II\text{-}VI}$), 83.78 (C-2^{I}), 83.95, 84.05, 84.16 (4 C) (C-4$^{II\text{-}VII}$), 84.35, 84.38 (C-4^{I}, C-4^{VIII}), 89.27 (C-2^{VII}), 102.46 (C-1^{VIII}), 107.58 (C-1^{VII}), 108.68 (C-1^{I}), 109.62, 109.69 (3 C), 109.73 (C-1$^{II\text{-}VI}$), 116.59 (OC_6H_4O (C-3, C-5)), 119.29 (OC_6H_4O (C-2, C-6)), 152.79 (OC_6H_4O (C-1)), 155.14 (OC_6H_4O (C-4); HRMS (ESI): m/z $[M+NH_4]^+$ Calcd for $C_{48}H_{77}N_4O_{34}^+$, 1253.4414; Found: 1253.4393.

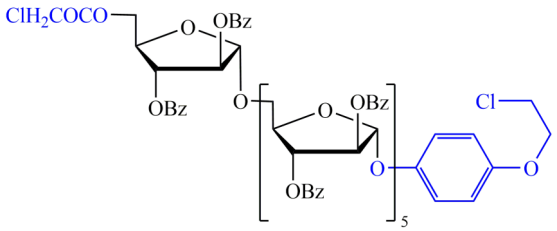
References

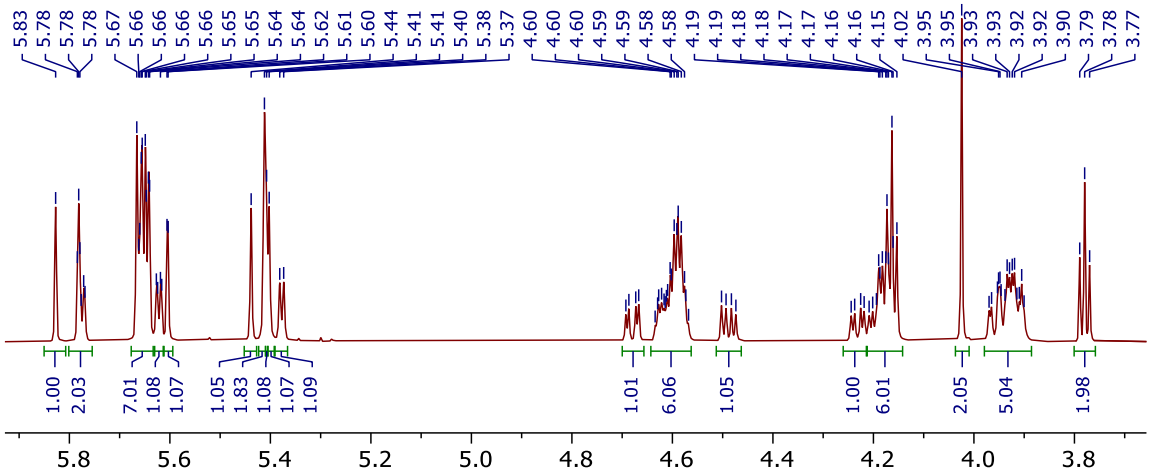
[S1] M. V. Panova, N. M. Podvalnyy, E. L. Okun, P. I. Abronina, A. O. Chizhov and L. O. Kononov, *Carbohydr. Res.*, 2018, **456**, 35; https://doi.org/10.1016/j.carres.2017.11.002.

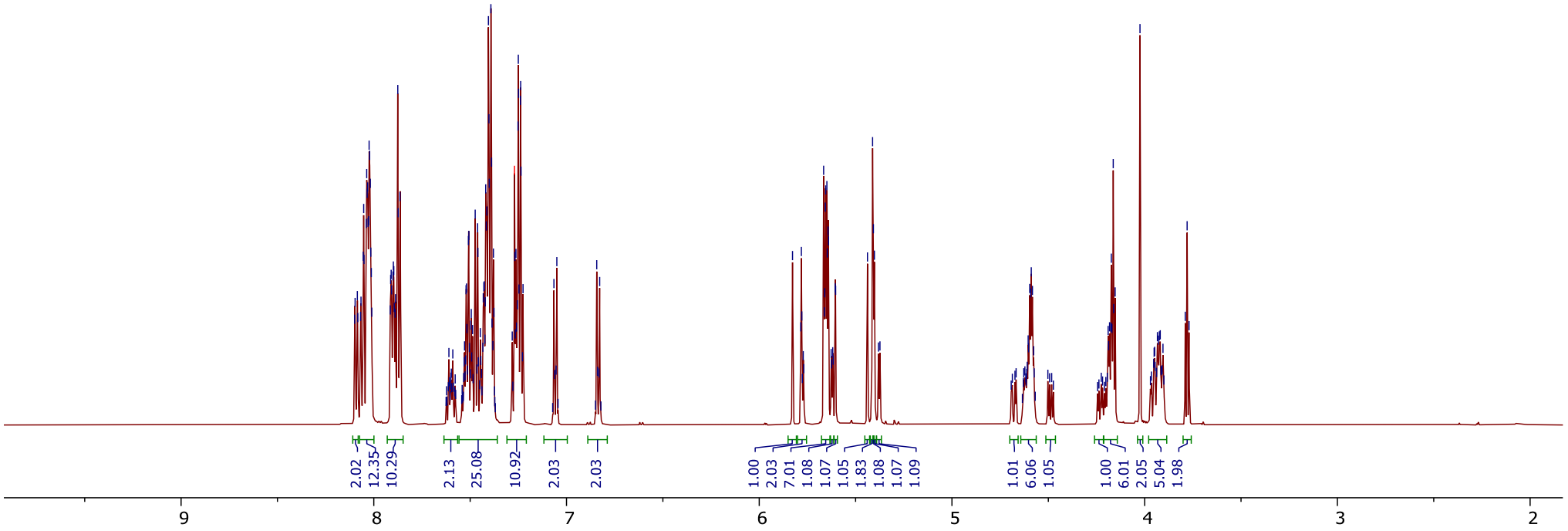
[S2] P. I. Abronina, N. N. Malysheva, E. V. Stepanova, J. S. Shvyrkina, A. I. Zinin and L. O. Kononov, *Eur. J. Org. Chem.*, 2022, e202201110; https://doi.org/10.1002/ejoc.202201110.

^{1}H NMR (600 MHz) spectrum of compound 3 in $CDCl_3$

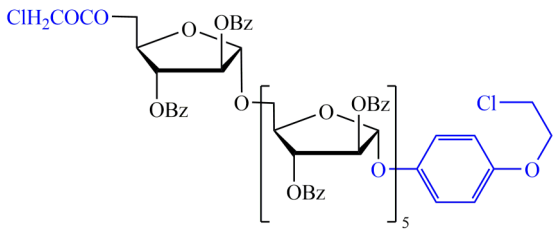




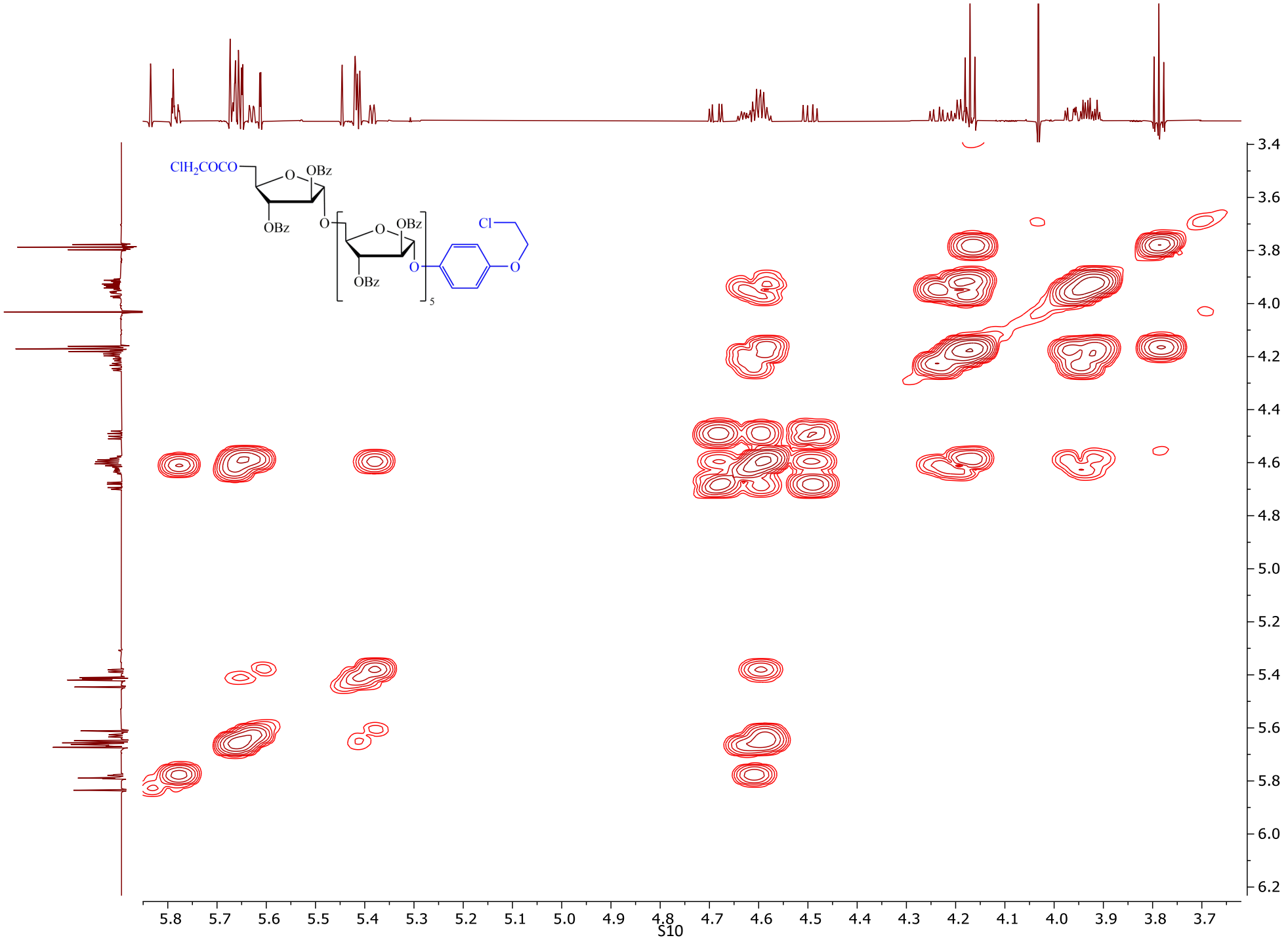




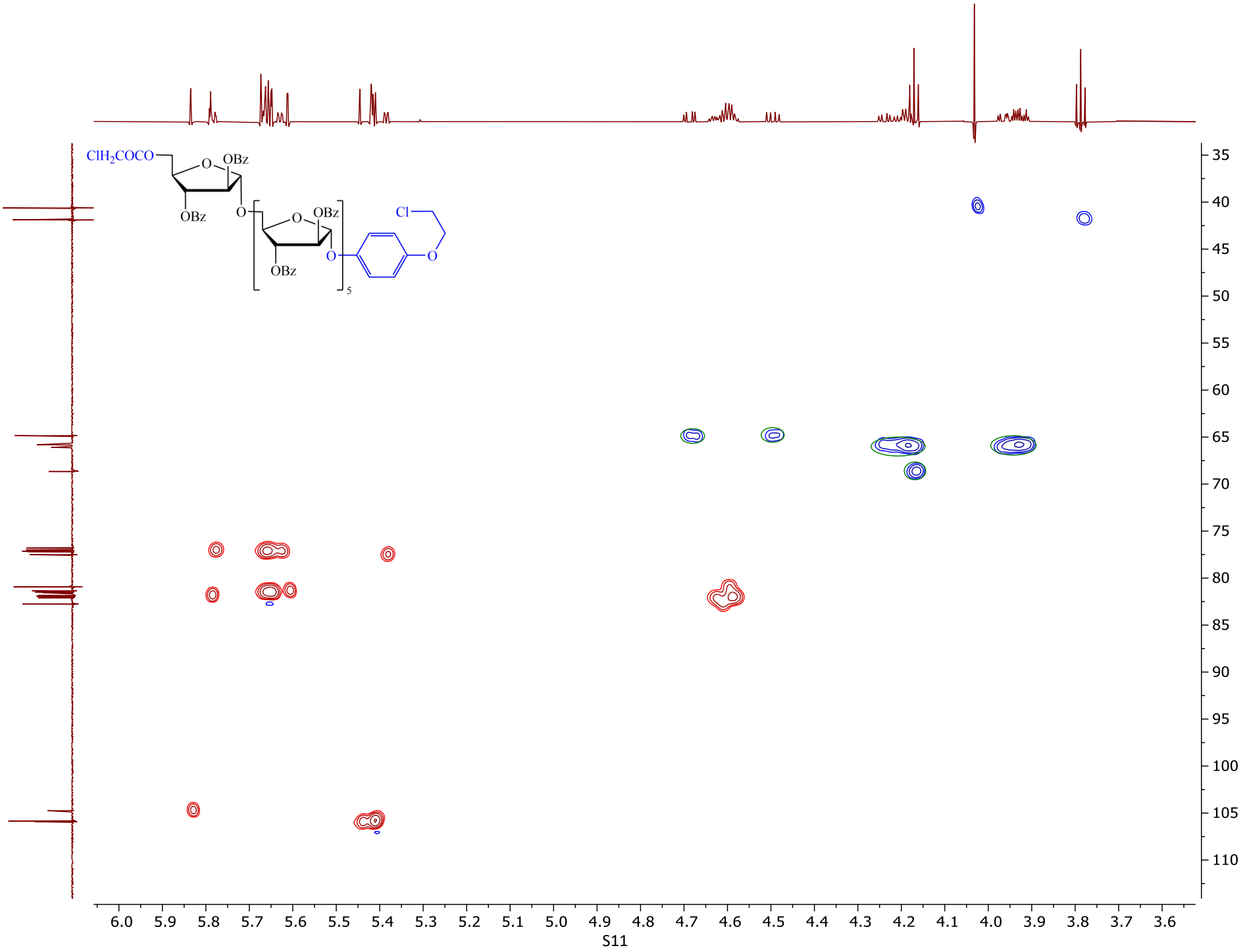
^{13}C NMR (151 MHz) spectrum of compound 3 in $CDCl_3$



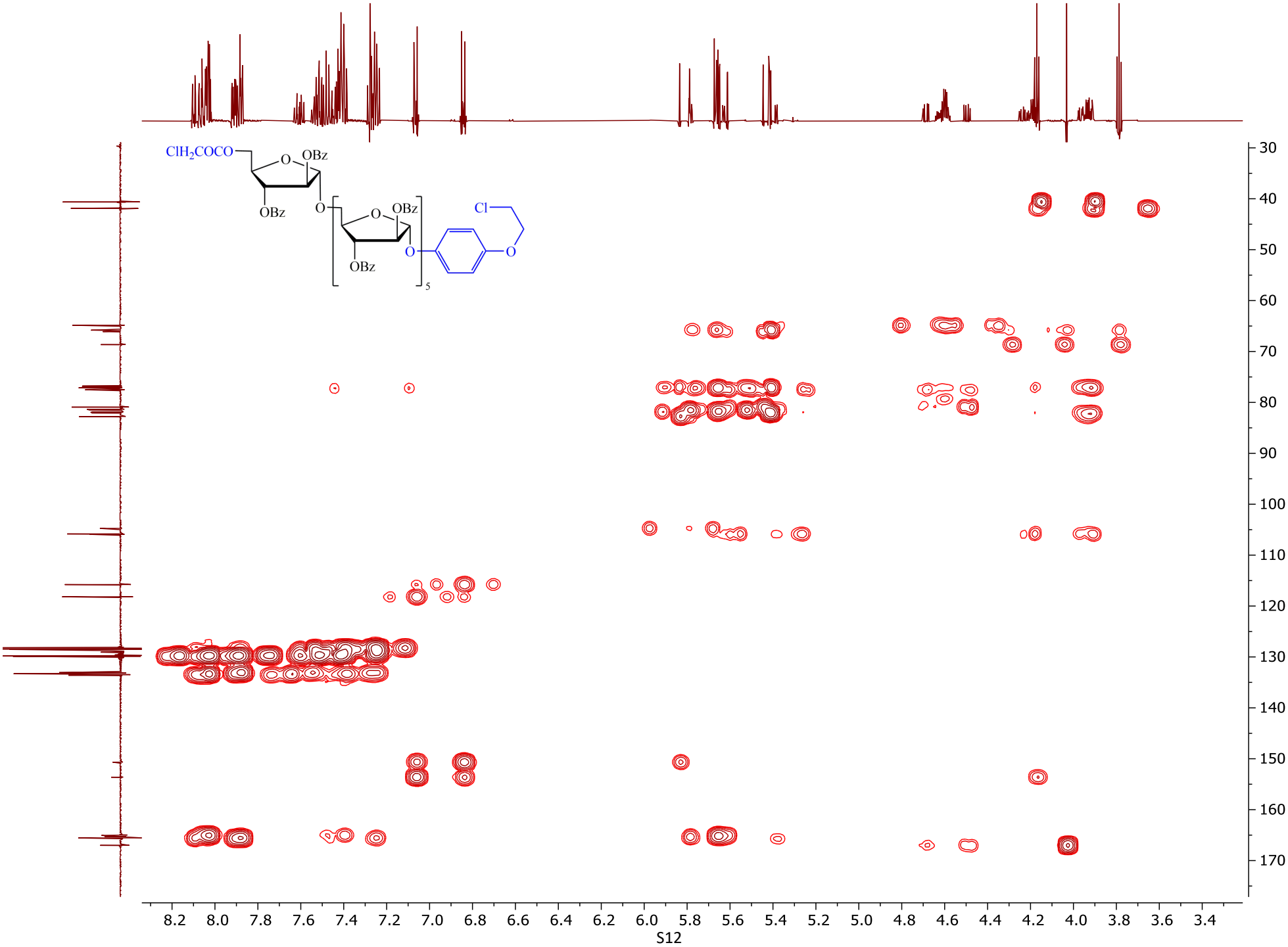
COSY (600 MHz) spectrum of compound 3 in $CDCl_3$



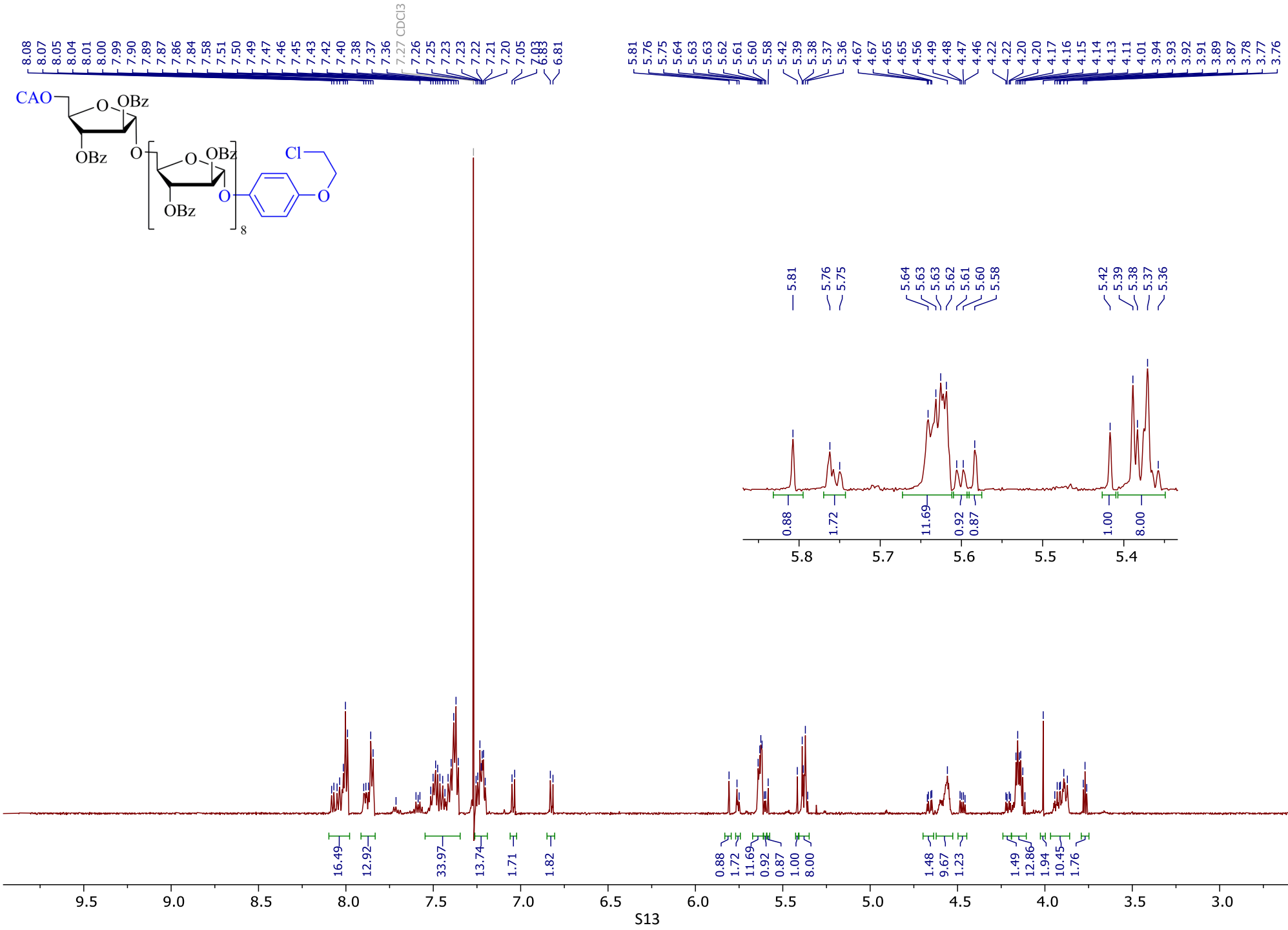
HSQC (600 MHz) spectrum of compound 3 in $CDCl_3$



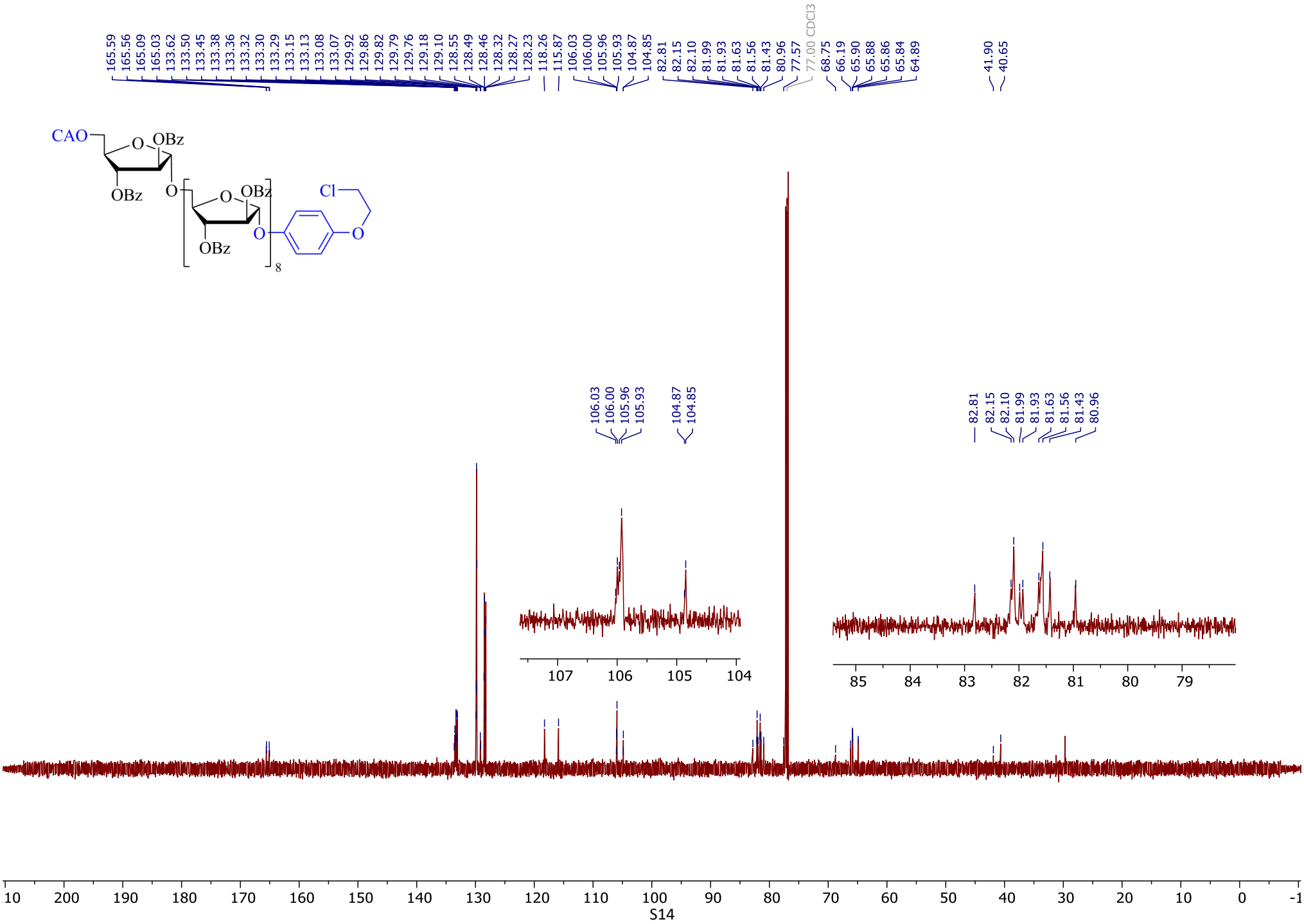
HMBC (600 MHz) spectrum of compound 3 in $CDCl_3$



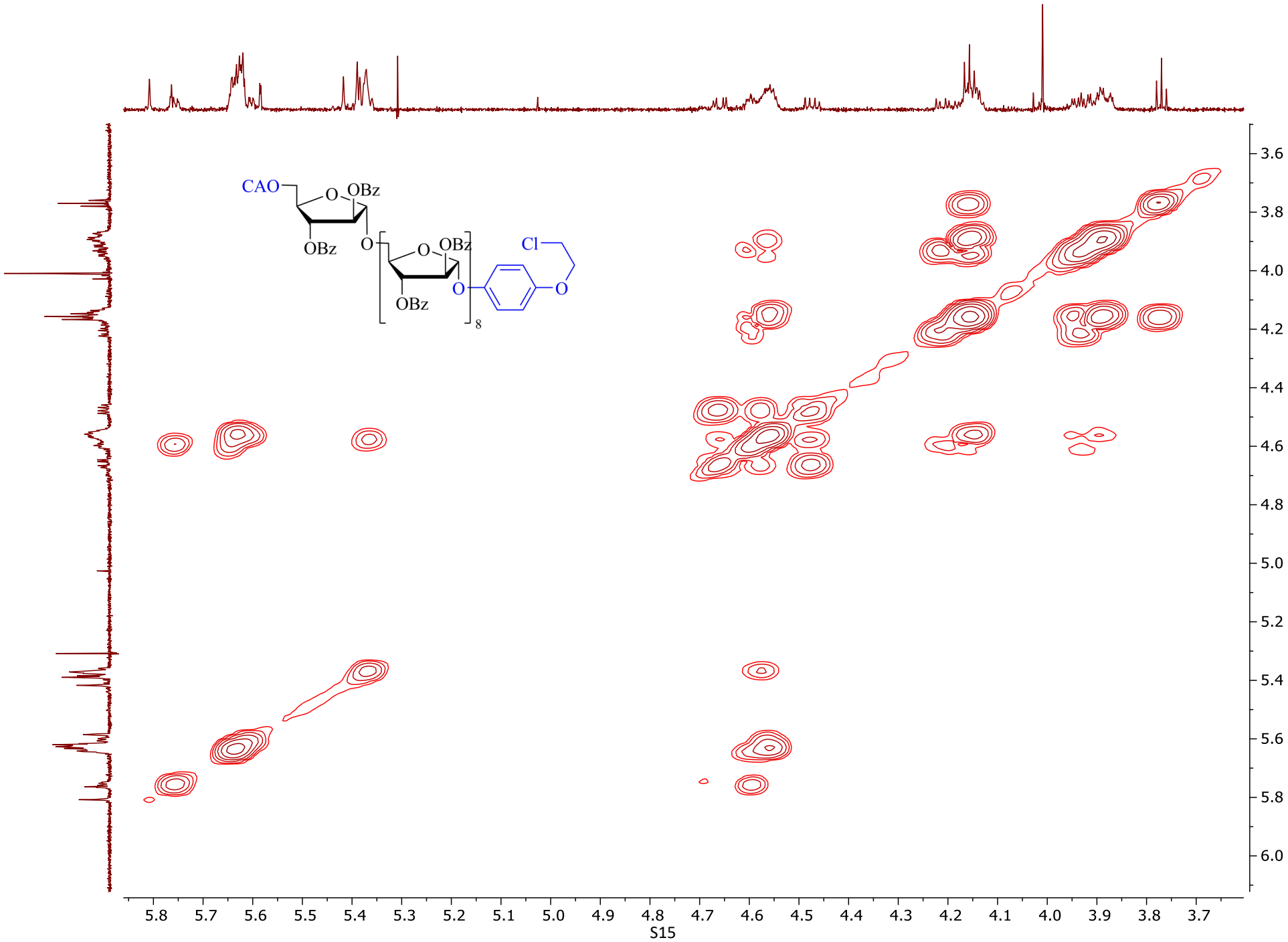
^{1}H NMR (600 MHz) spectrum of compound 3' in $CDCl_3$



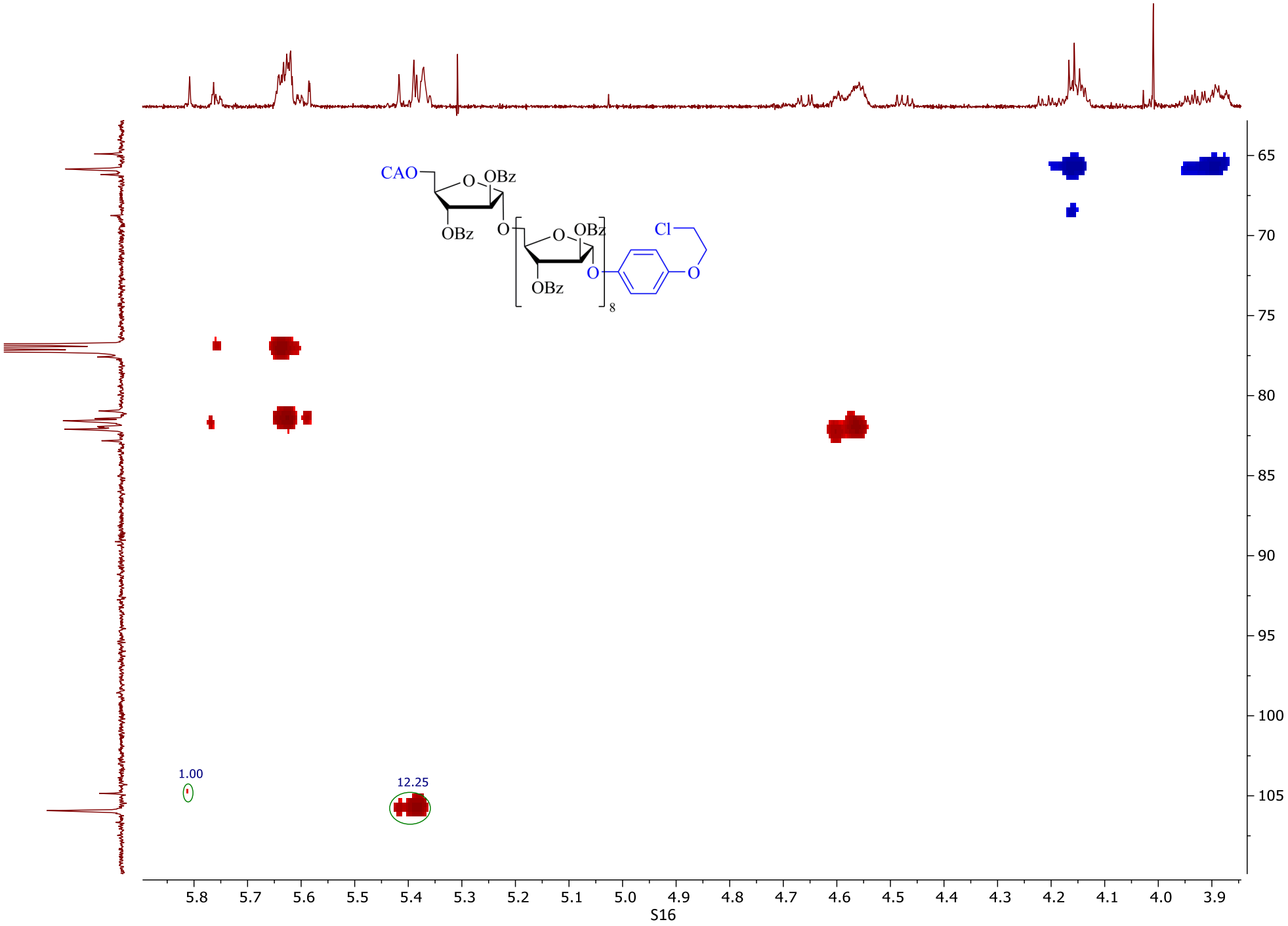
^{13}C NMR (600 MHz) spectrum of compound 3' in $CDCl_3$



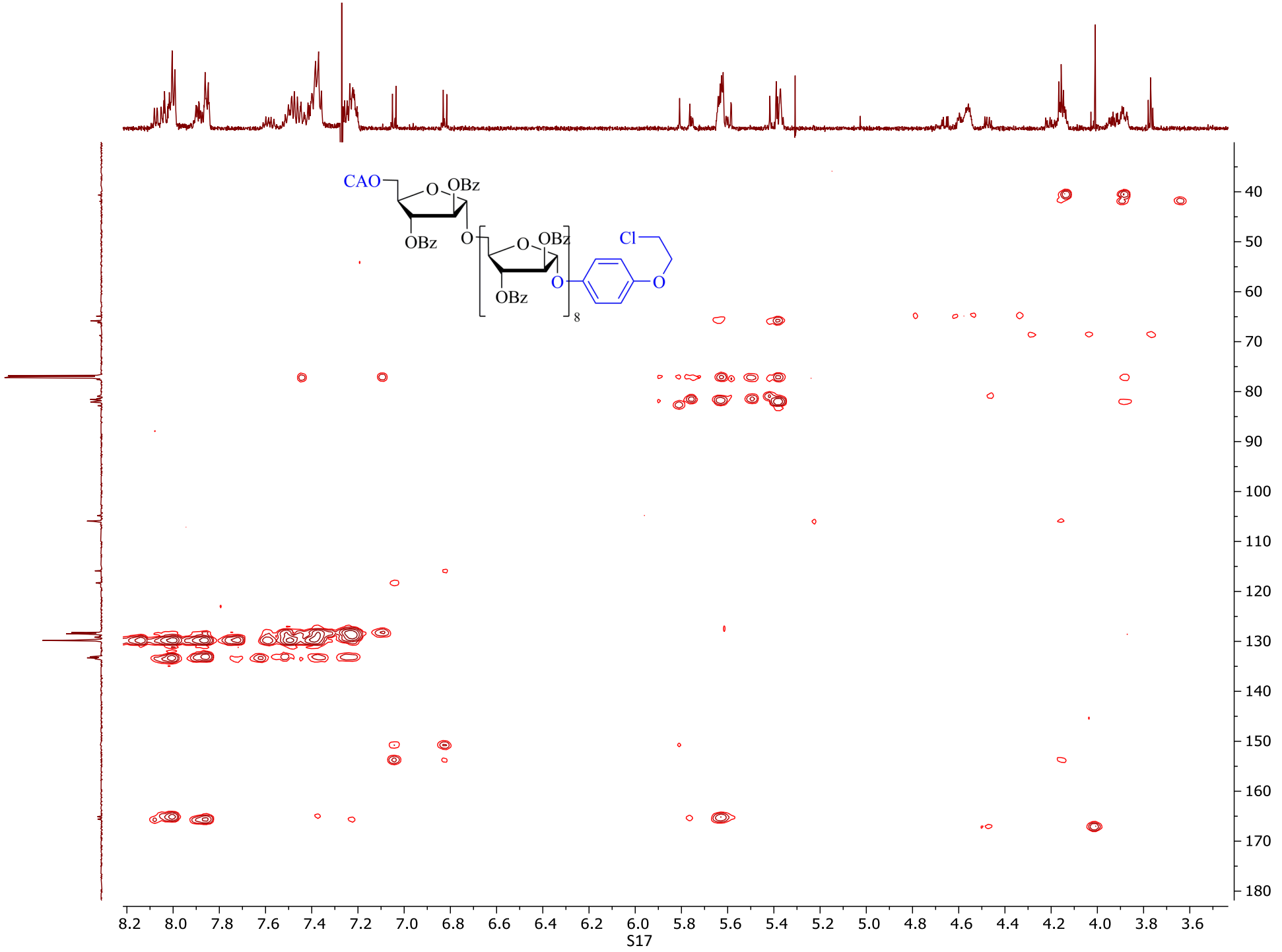
COSY (600 MHz) spectrum of compound 3' in $CDCl_3$



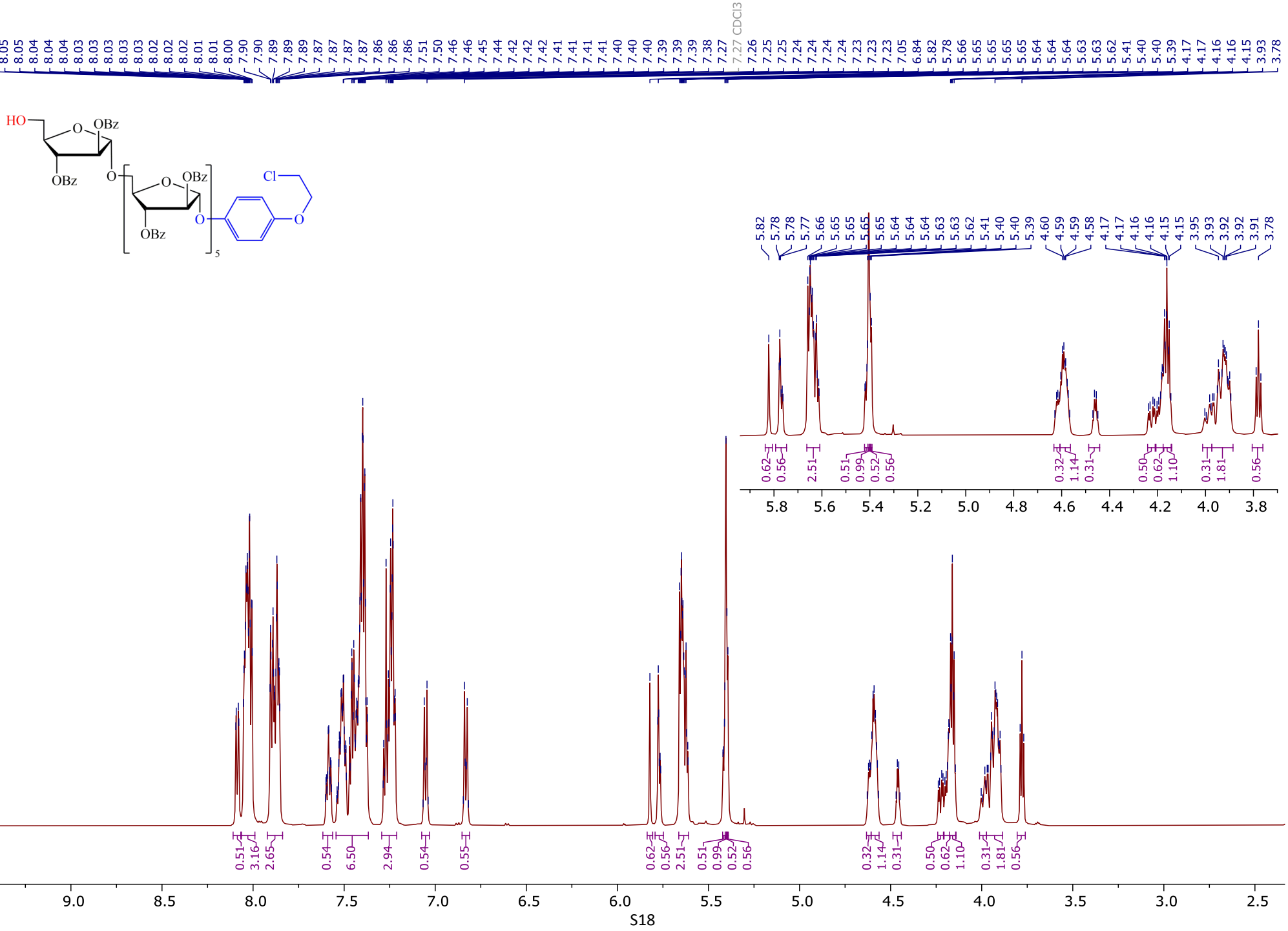
HSQC (600 MHz) spectrum of compound 3' in $CDCl_3$



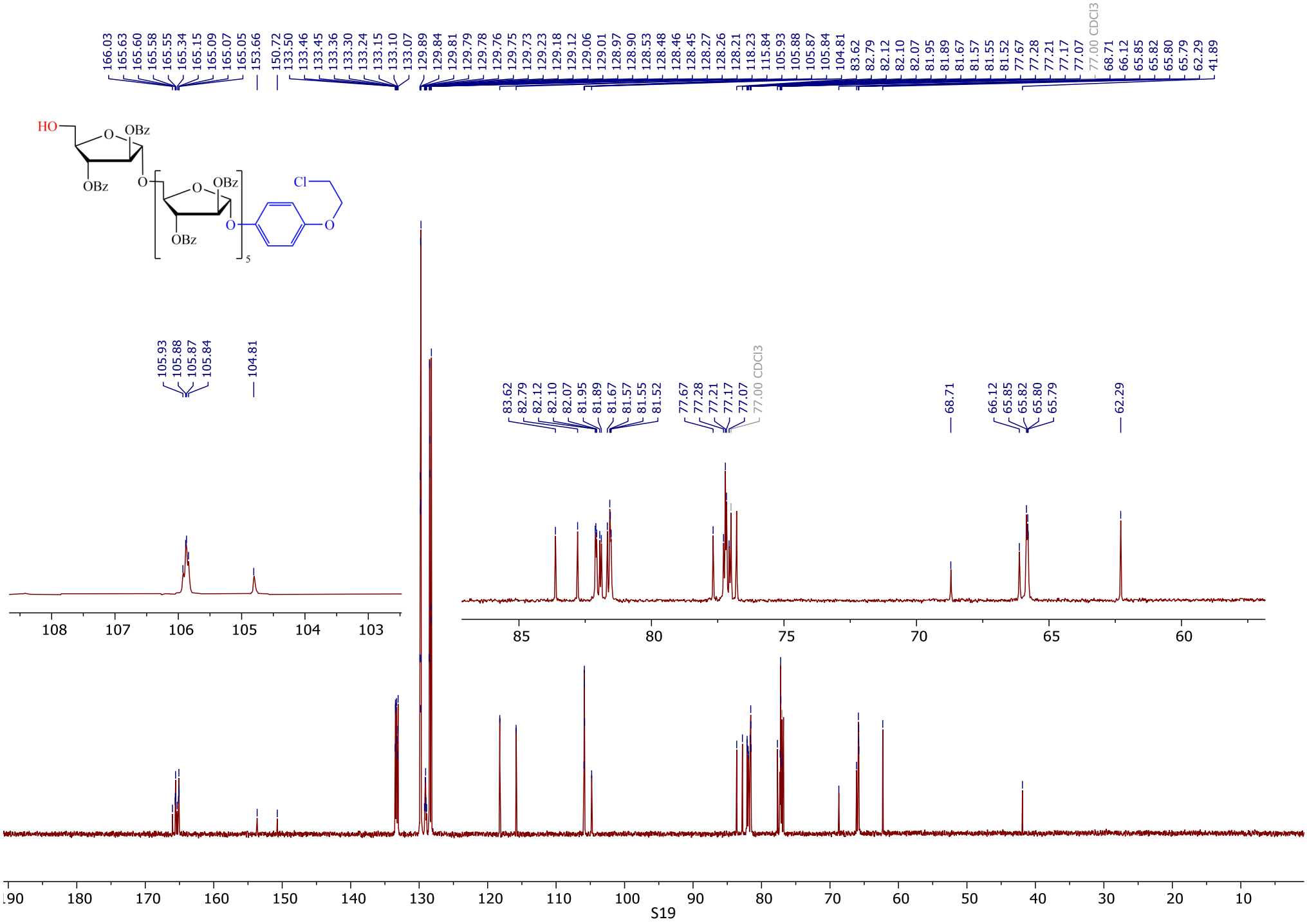
HMBC (600 MHz) spectrum of compound 3' in $CDCl_3$



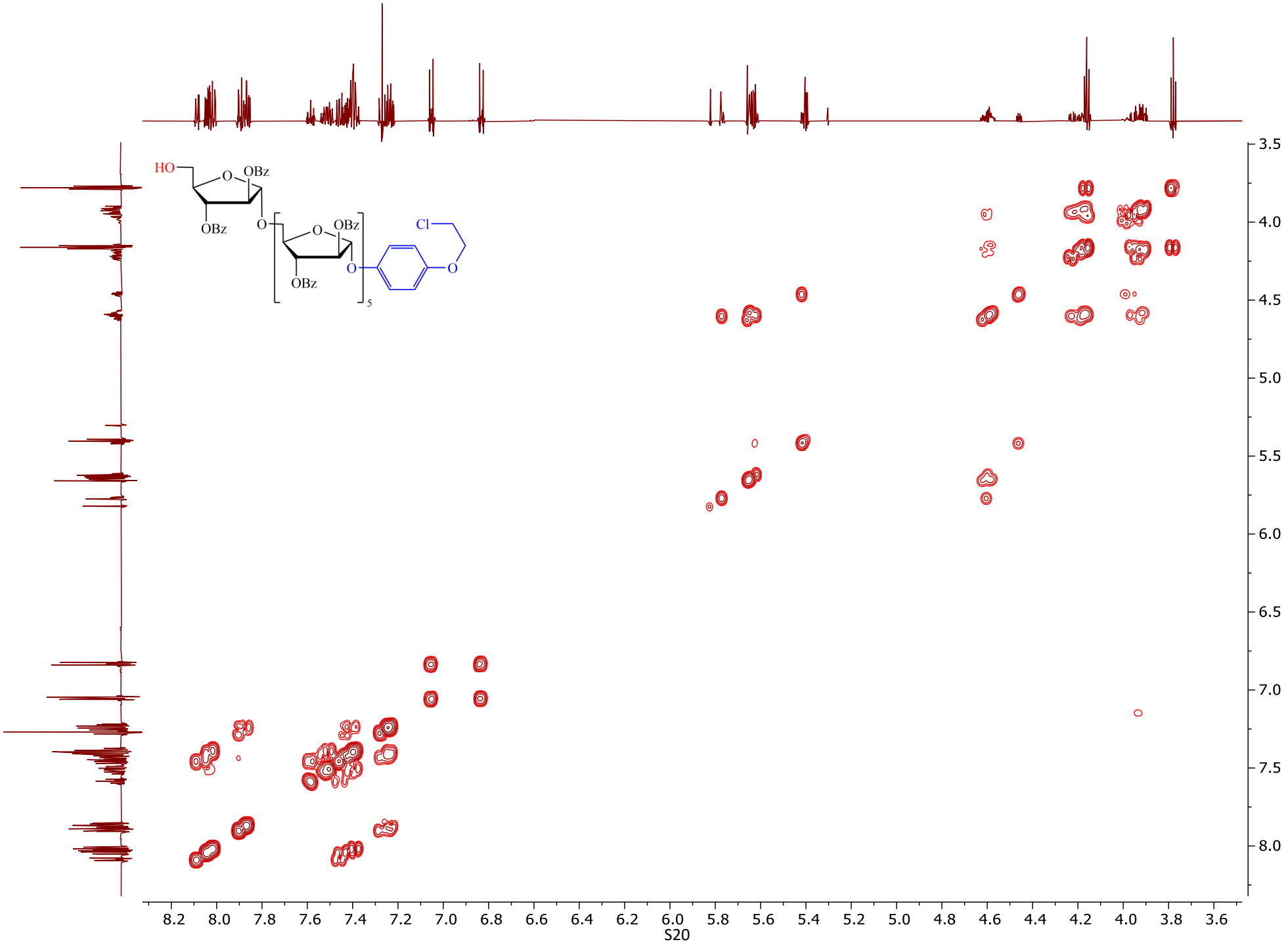
^{1}H NMR (600 MHz) spectrum of compound 4 in $CDCl_3$



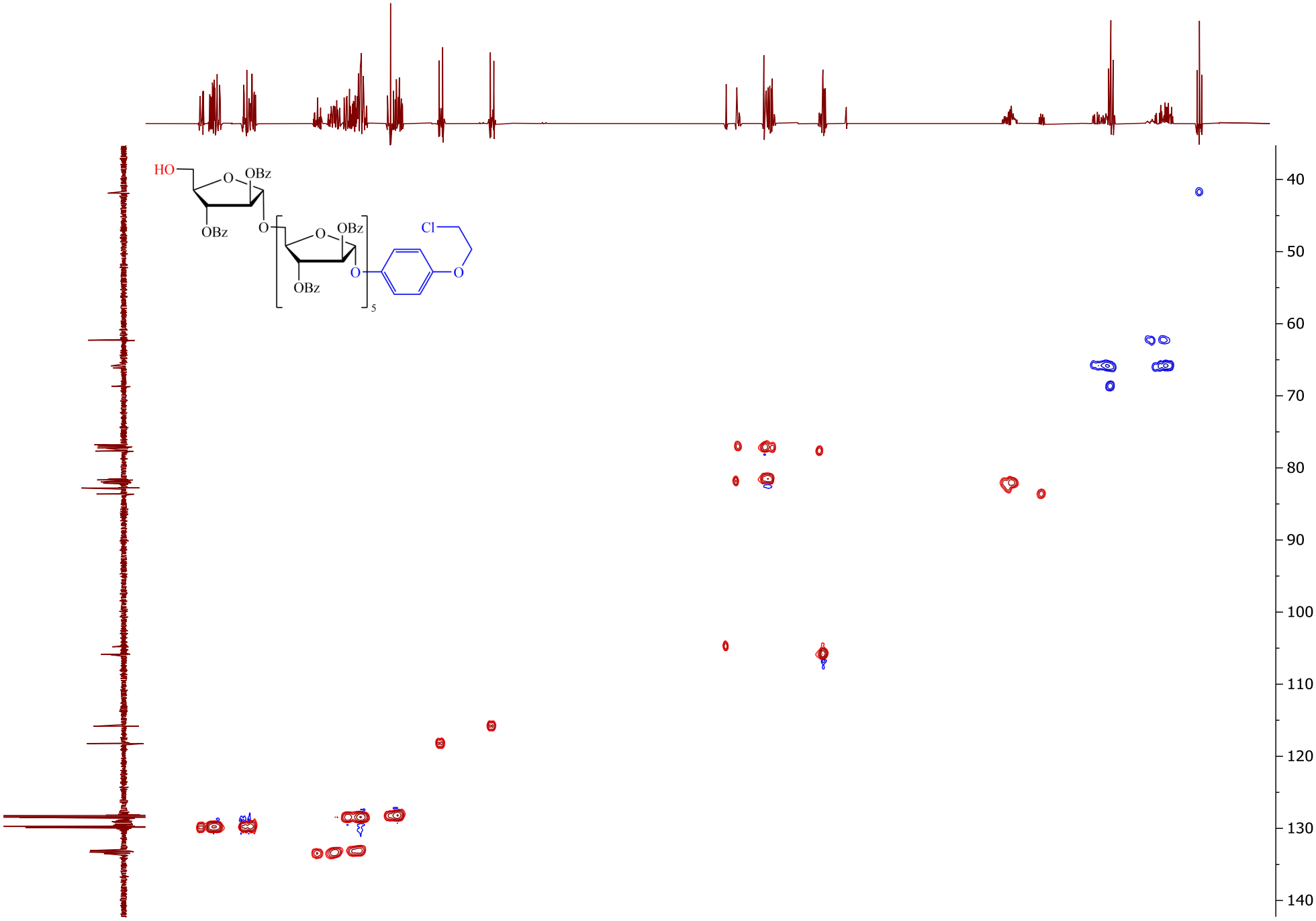
^{13}C NMR (151 MHz) spectrum of compound 4 in $CDCl_3$



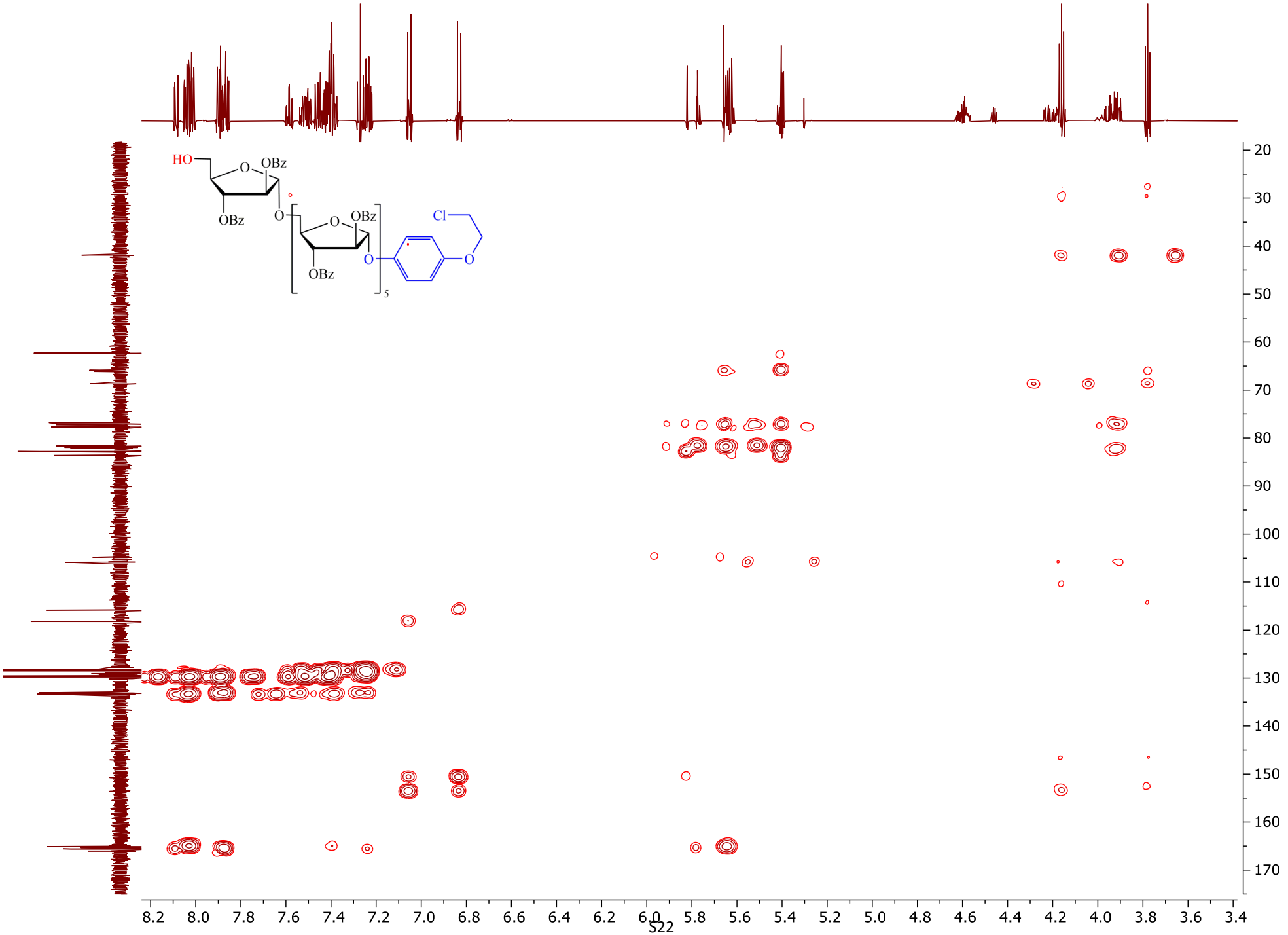
COSY (600 MHz) spectrum of compound 4 in $CDCl_3$



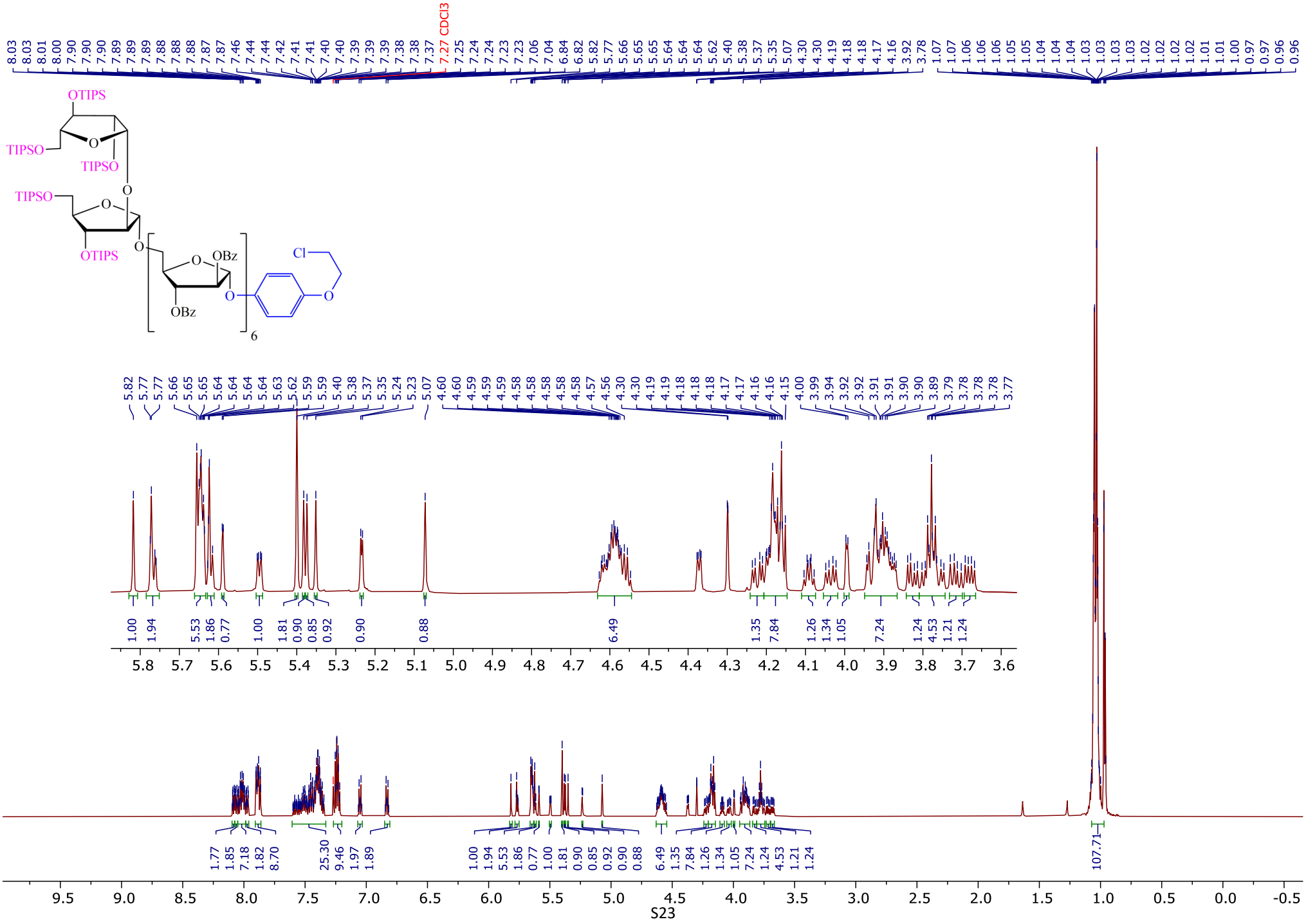
HSQC (600 MHz) spectrum of compound 4 in $CDCl_3$



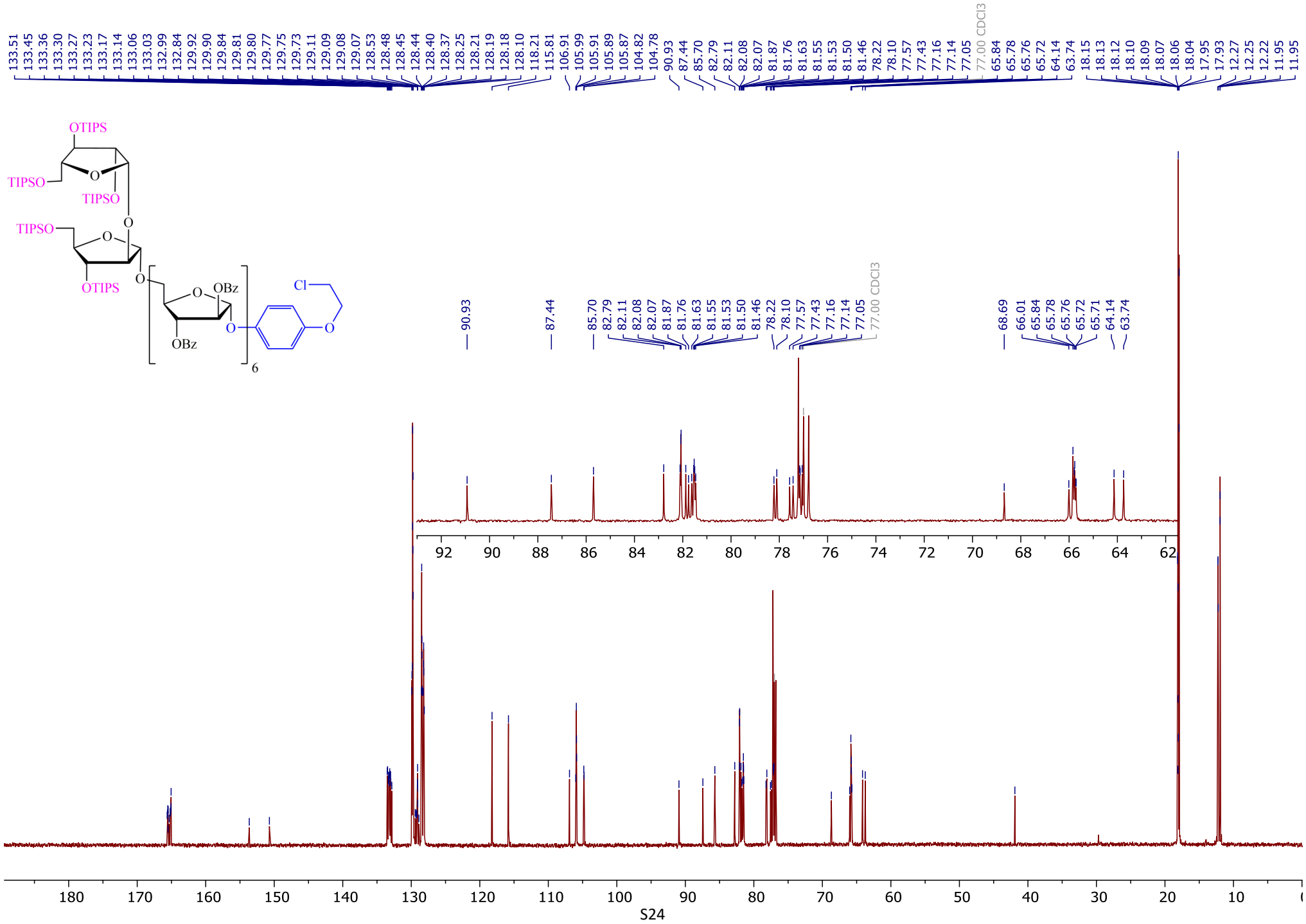
HMBC (600 MHz) spectrum of compound 4 in $CDCl_3$



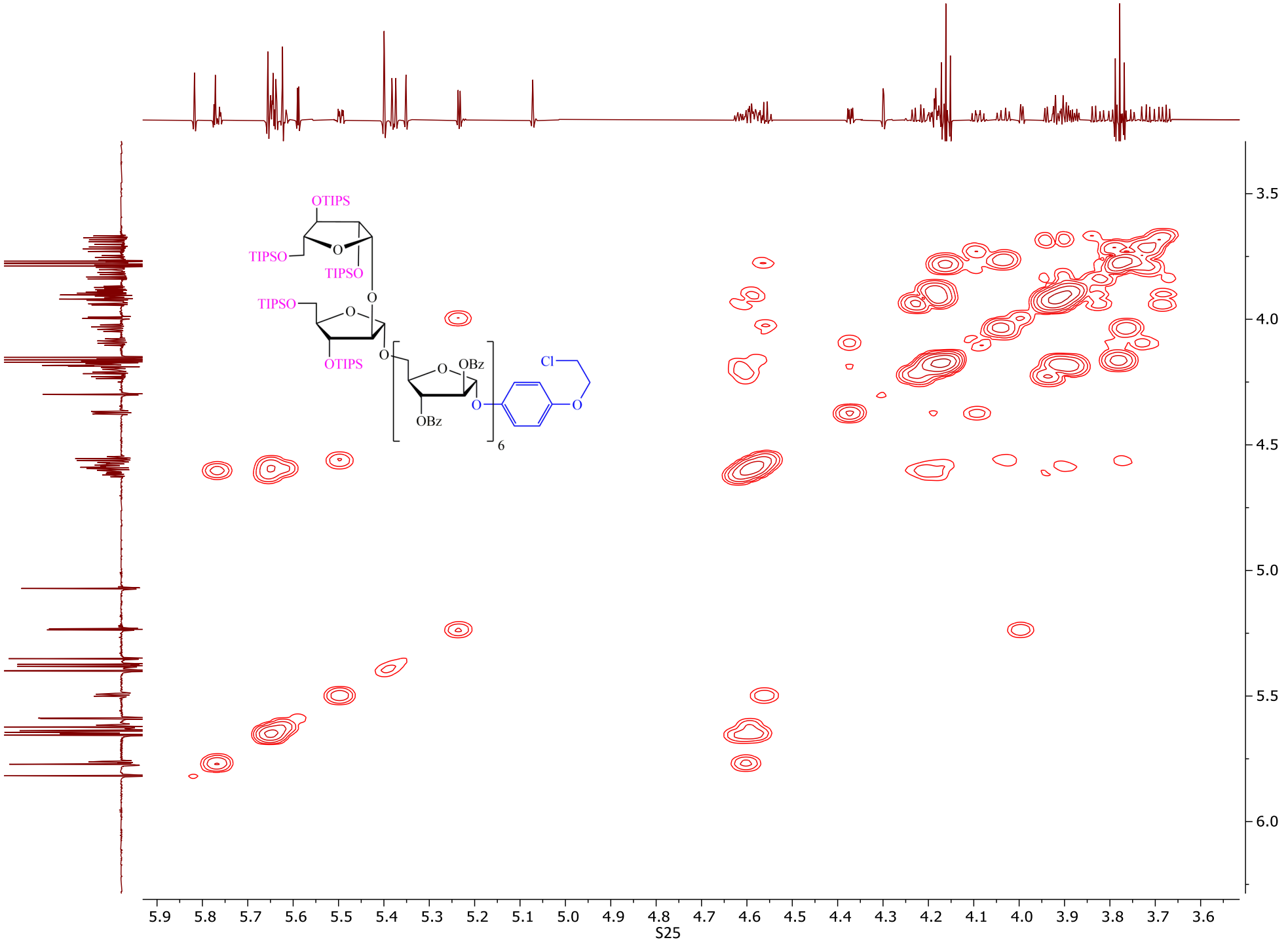
^{1}H NMR (600 MHz) spectrum of compound 6 in $CDCl_3$



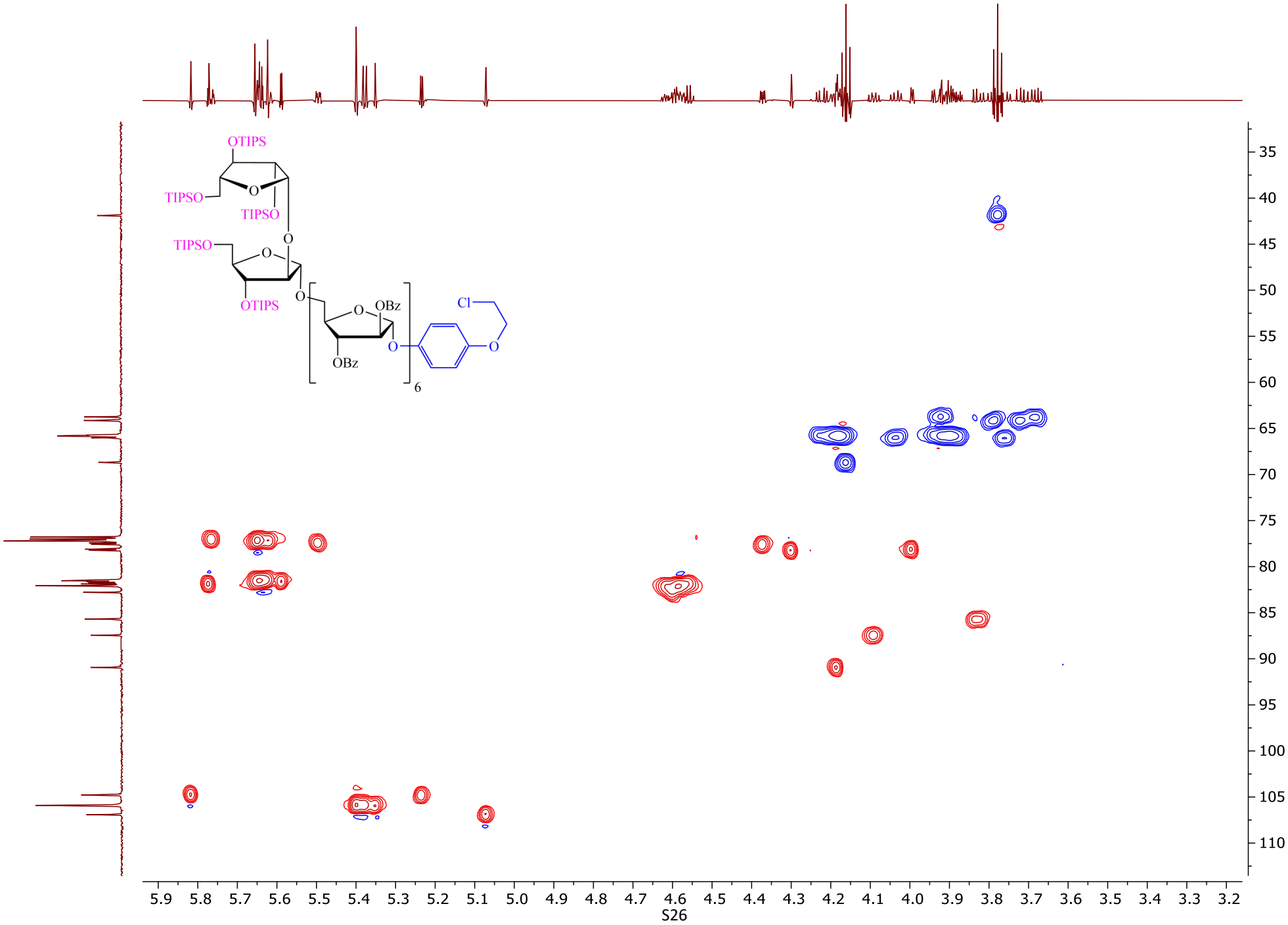
^{13}C NMR (151 MHz) spectrum of compound 6 in $CDCl_3$



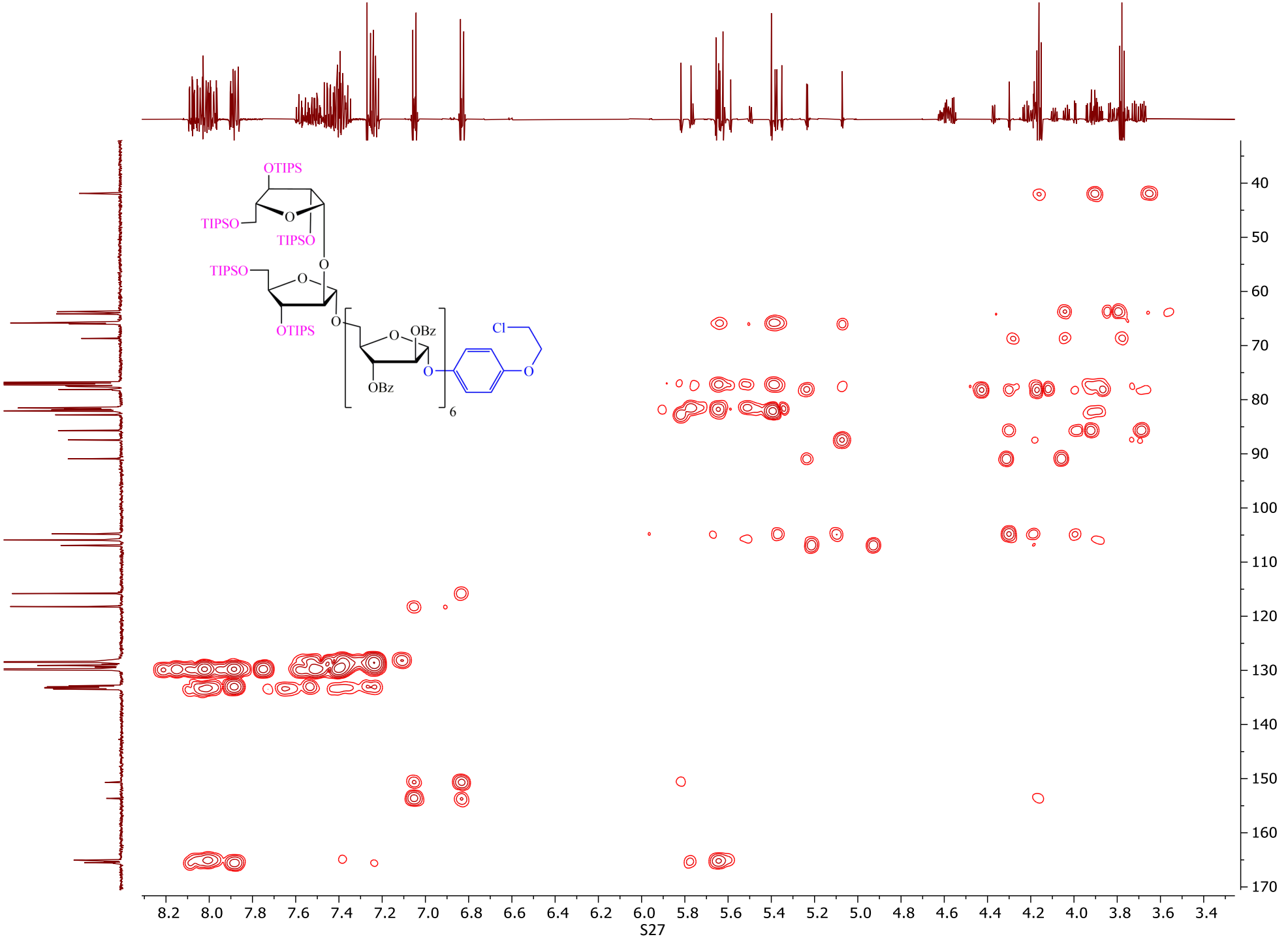
COSY (600 MHz) spectrum of compound 6 in $CDCl_3$



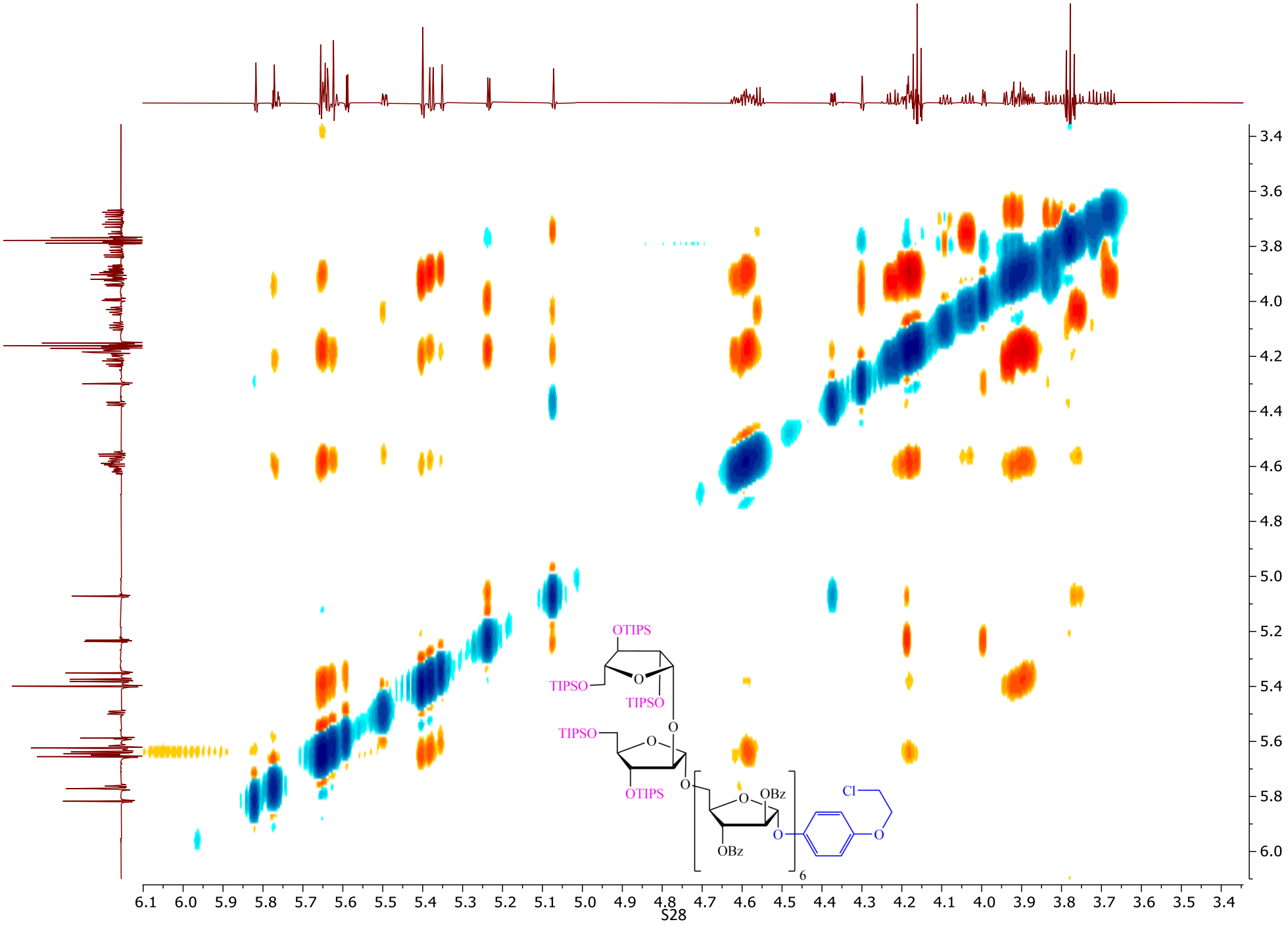
HSQC (600 MHz) spectrum of compound 6 in $CDCl_3$



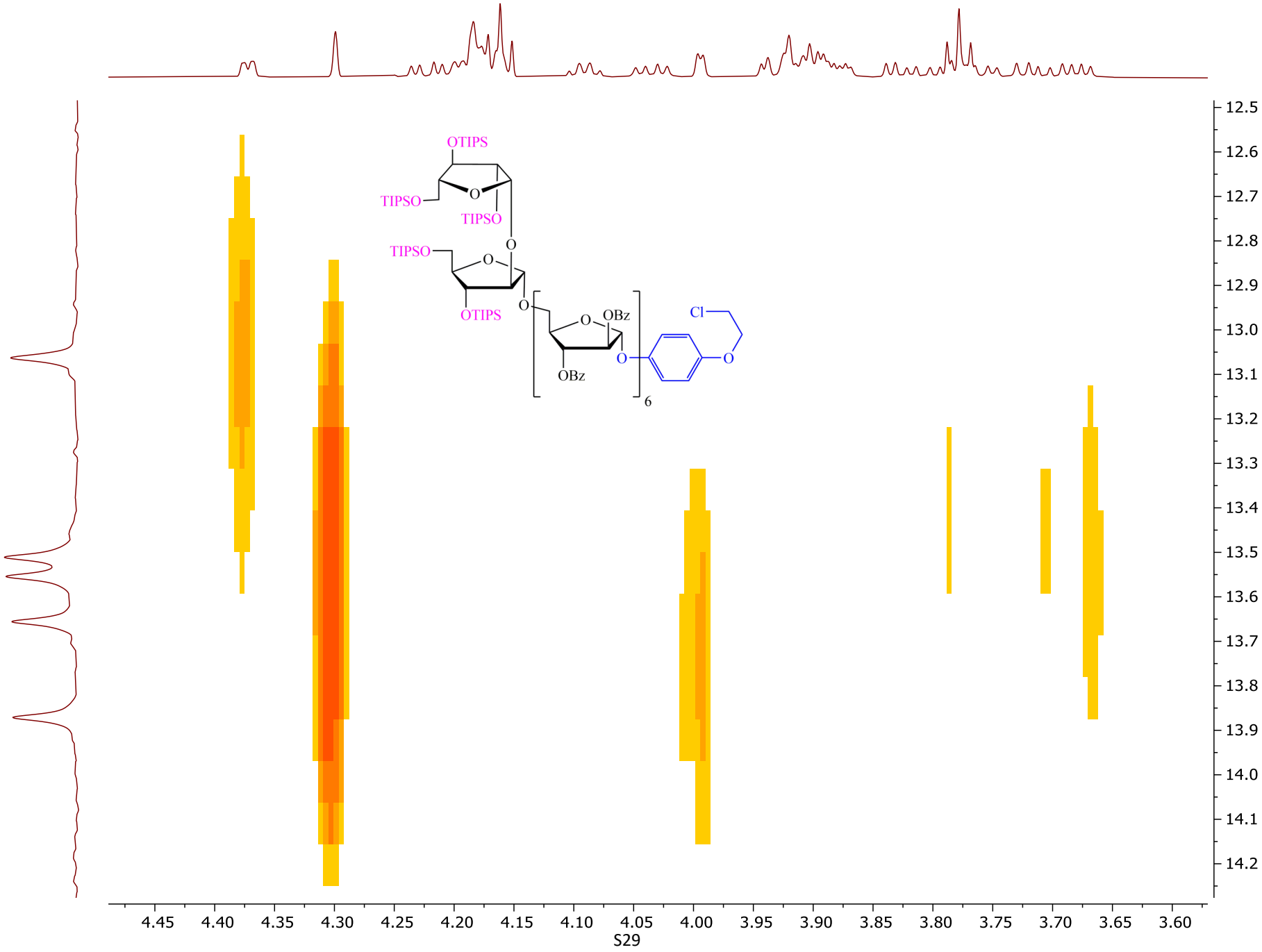
HMBC (600 MHz) spectrum of compound 6 in $CDCl_3$



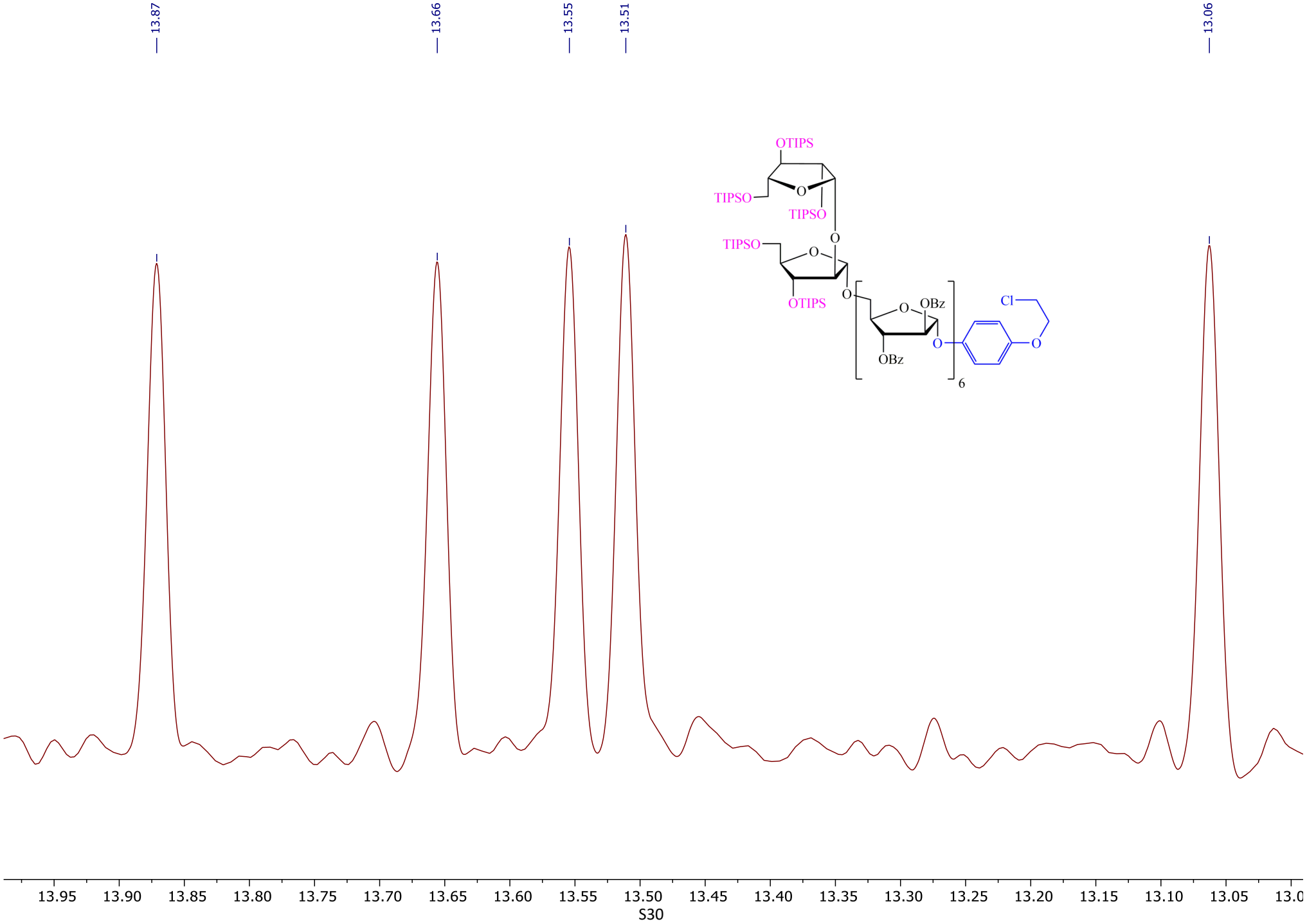
ROESY (600 MHz) spectrum of compound 6 in $CDCl_3$



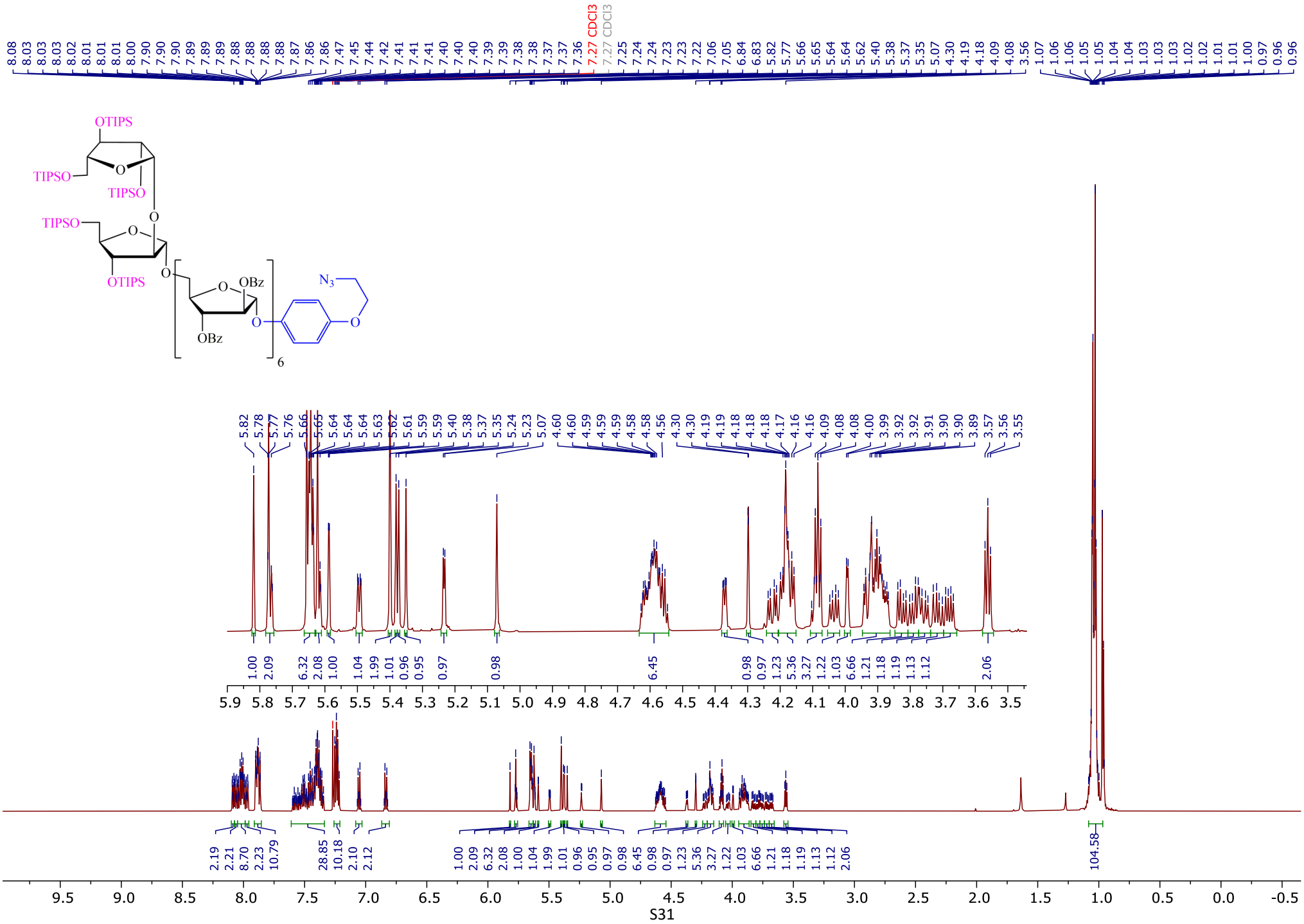
$^{1}H–^{29}Si$ HMBC (300 MHz) spectrum of compound 6 in $CDCl_3$



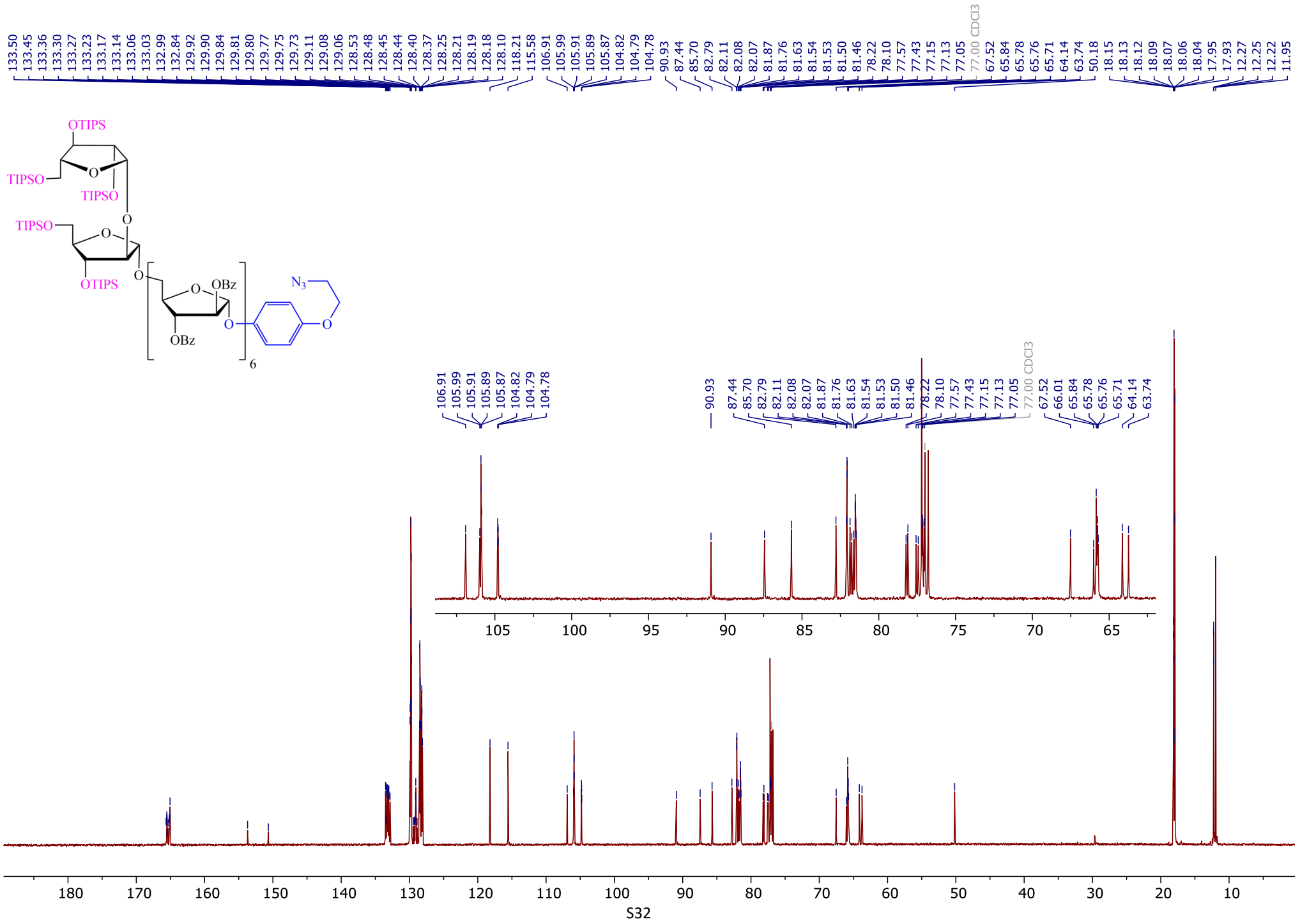
^{29}Si INEPT NMR (59 MHz) spectrum of compound 6 in $CDCl_3$



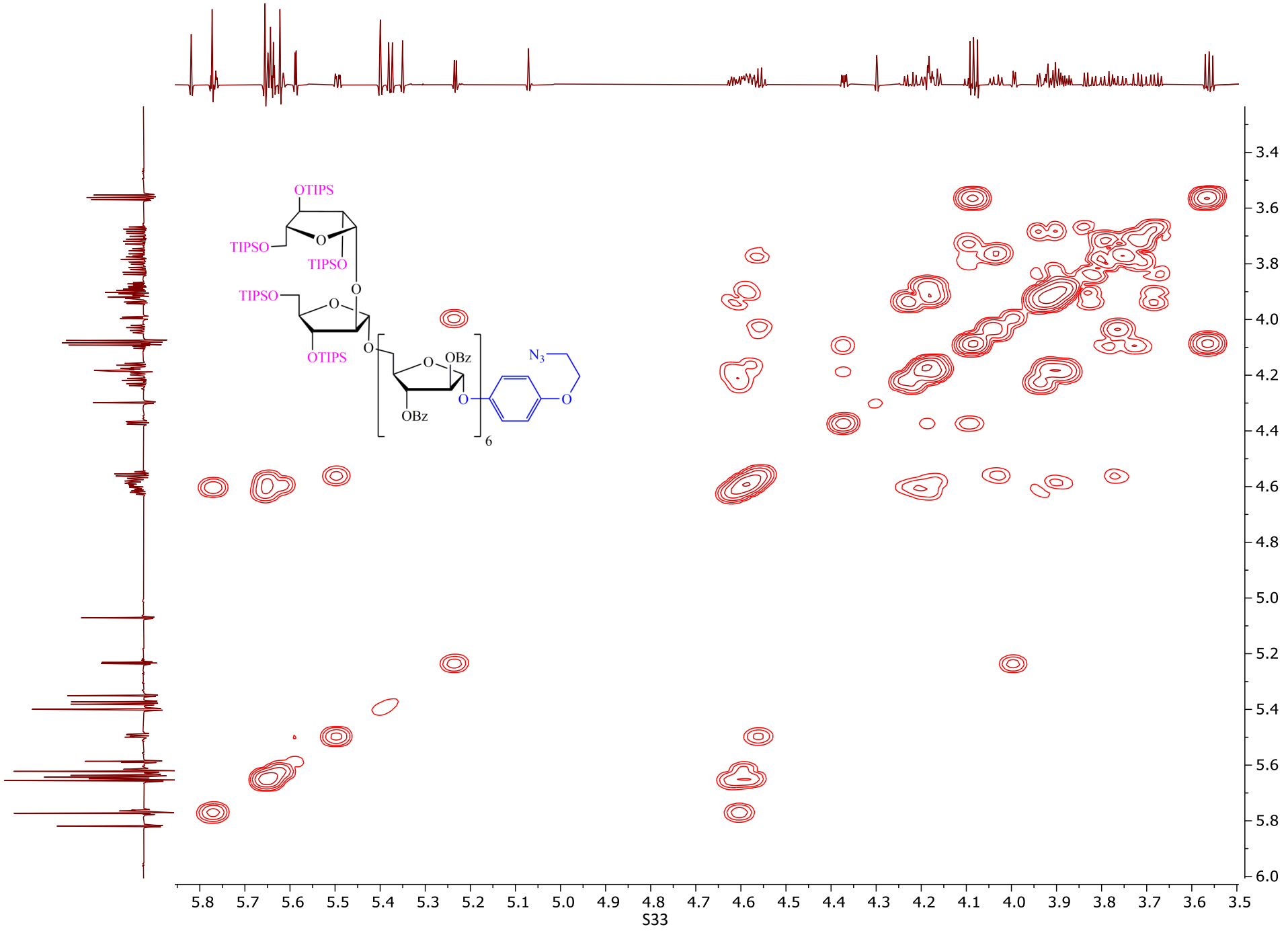
^{1}H NMR (600 MHz) spectrum of compound 7 in $CDCl_3$



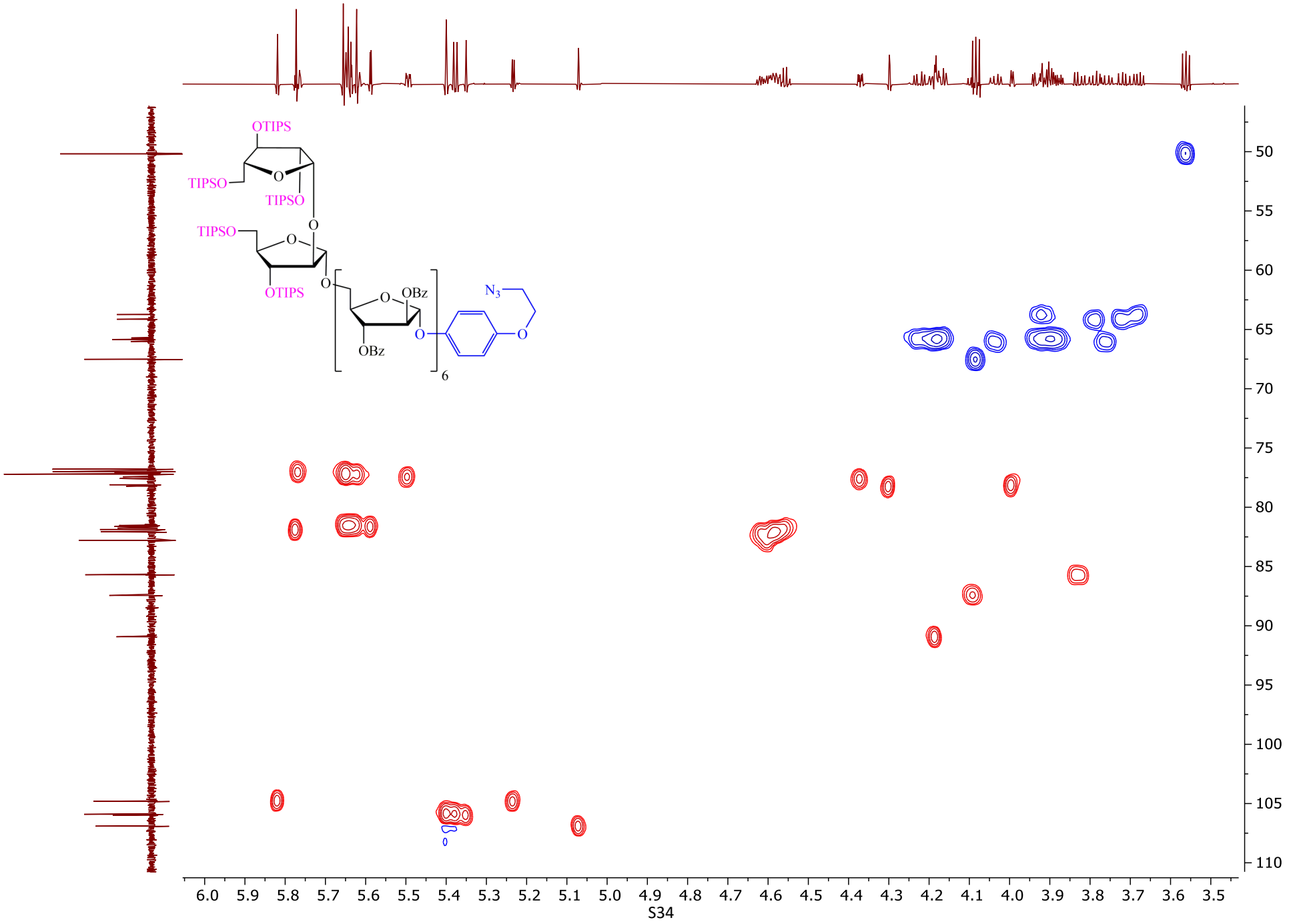
^{13}C NMR (151 MHz) spectrum of compound 7 in $CDCl_3$



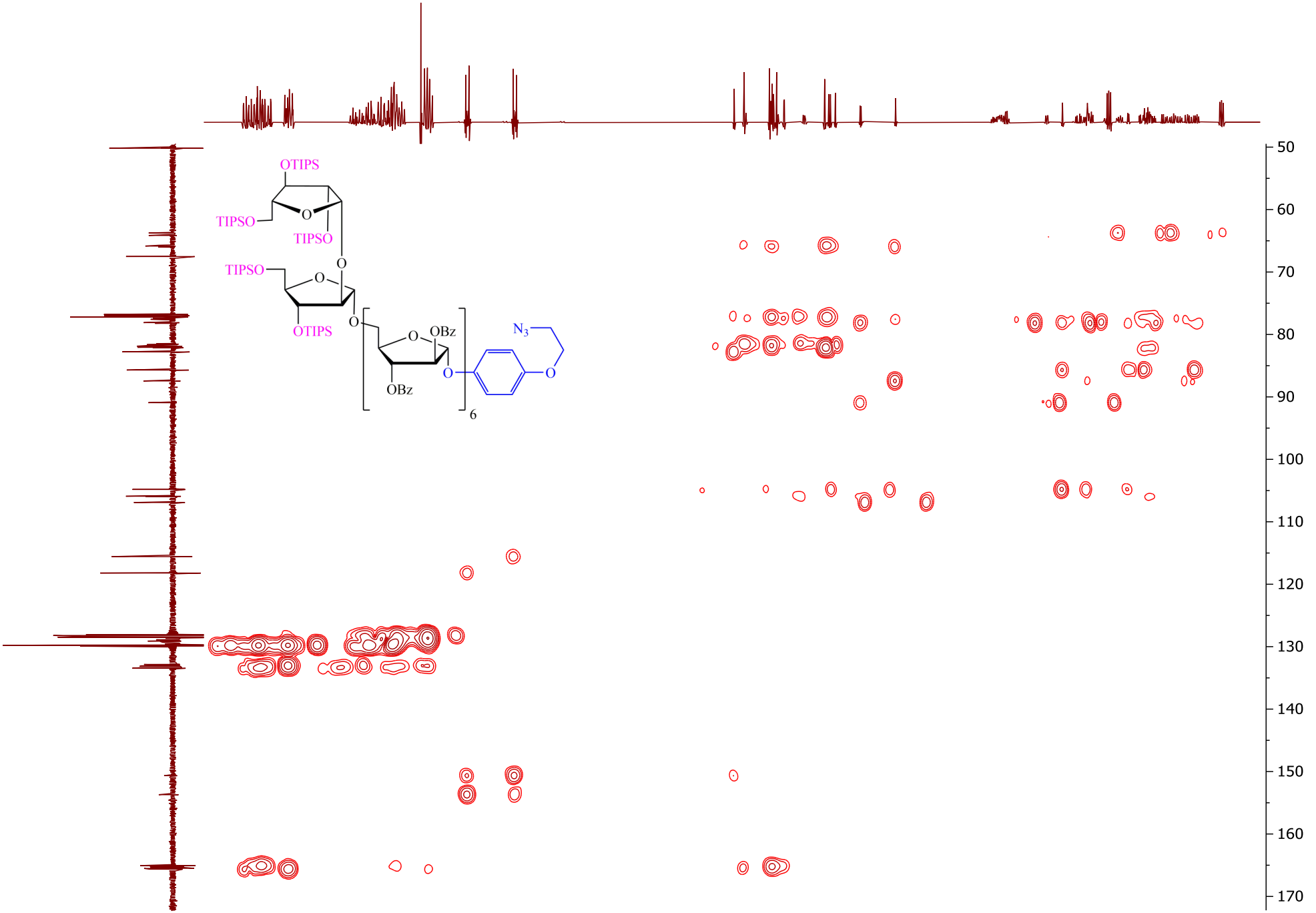
COSY (600 MHz) spectrum of compound 7 in $CDCl_3$



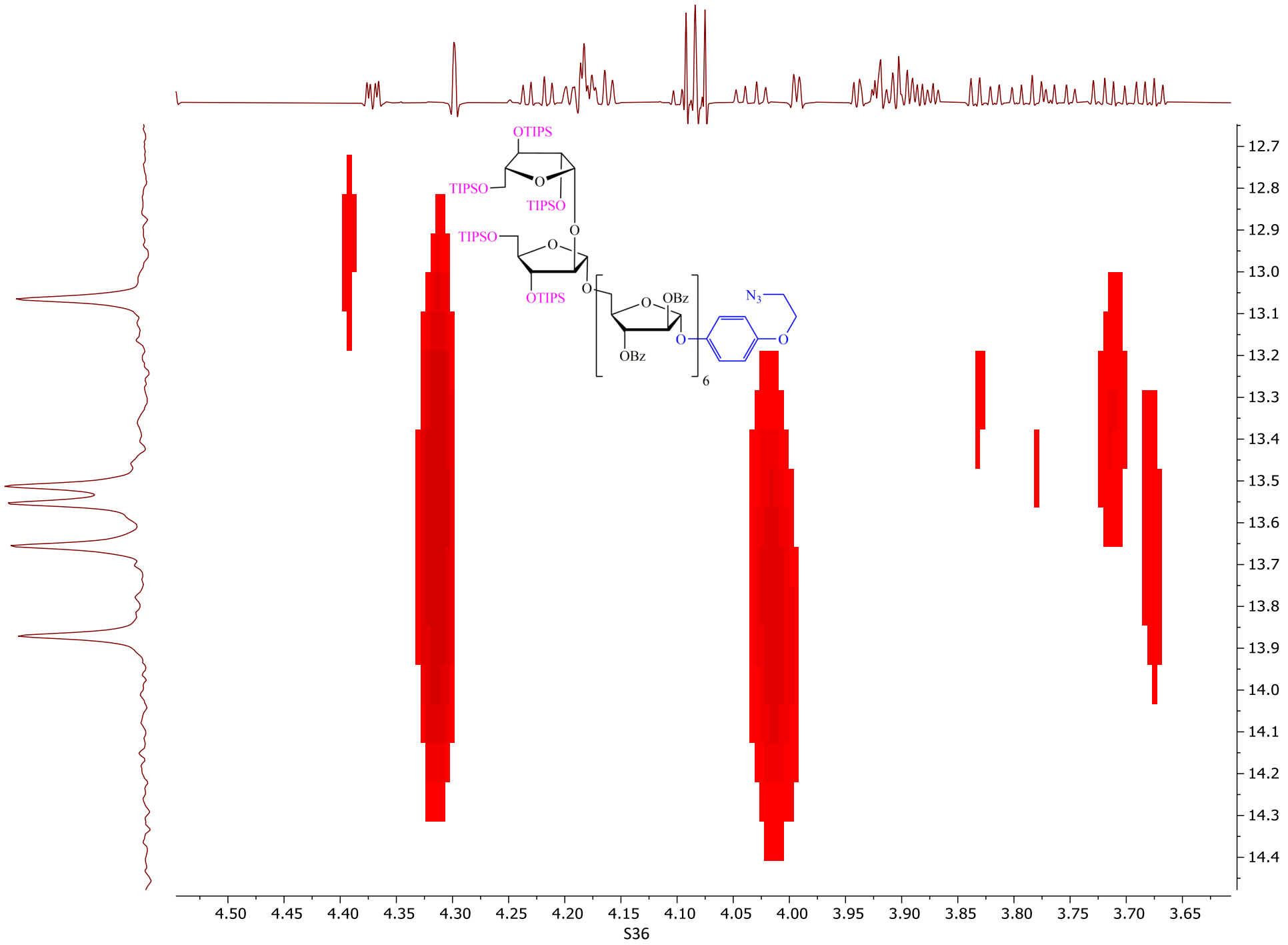
HSQC (600 MHz) spectrum of compound 7 in $CDCl_3$



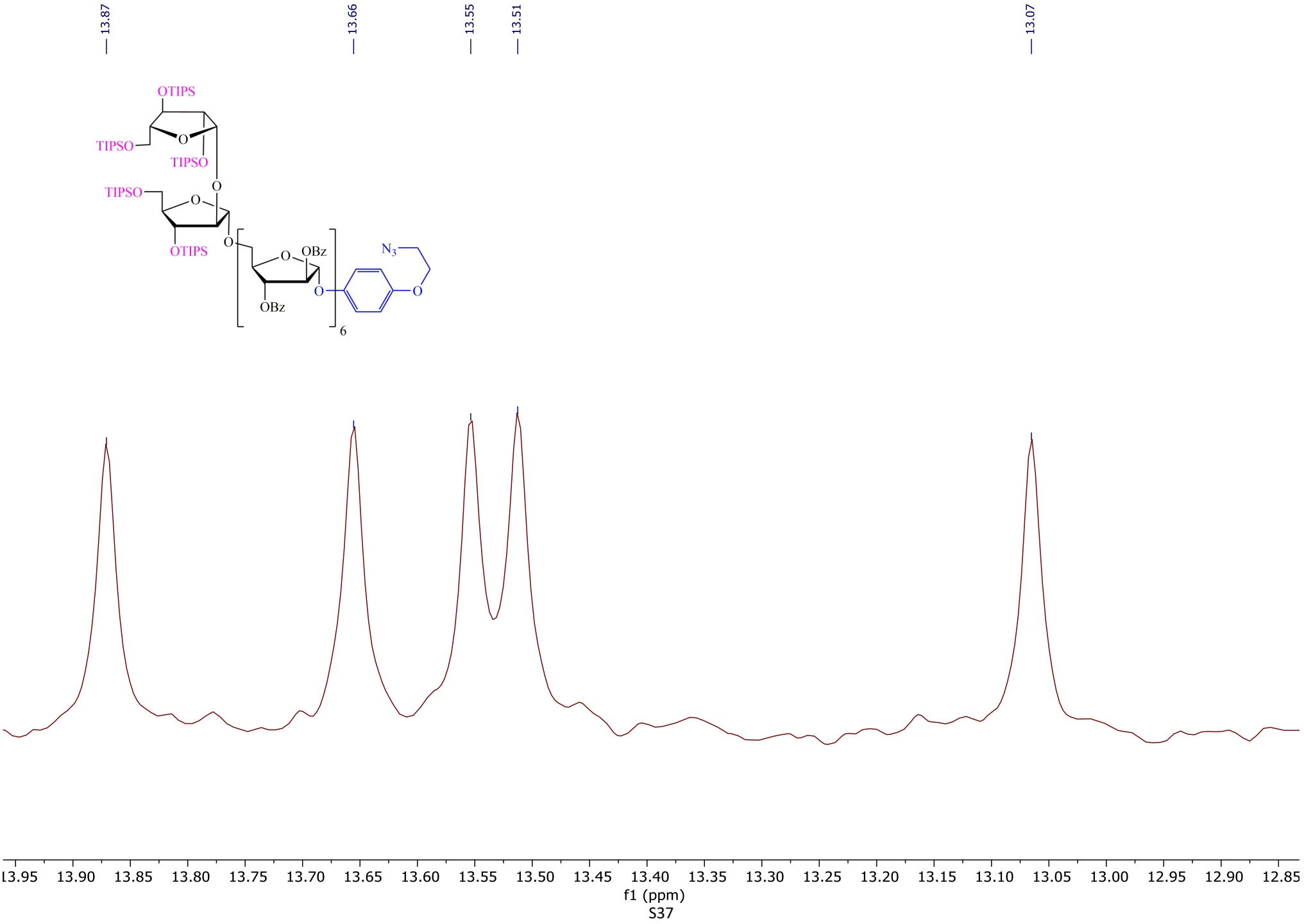
HMBC (600 MHz) spectrum of compound 7 in $CDCl_3$



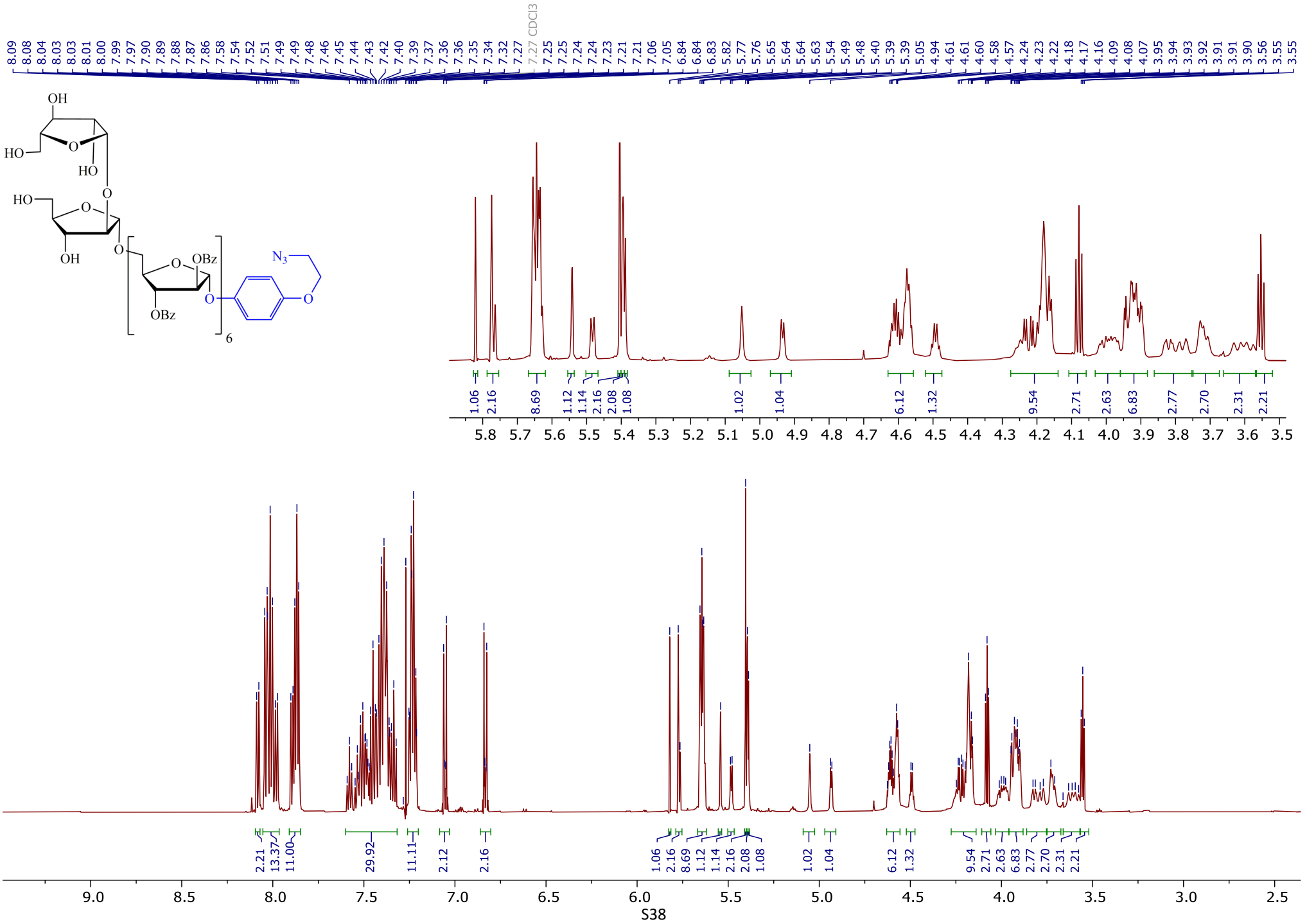
$^{1}H–^{29}Si$ HMBC (300 MHz) spectrum of compound 7 in $CDCl_3$



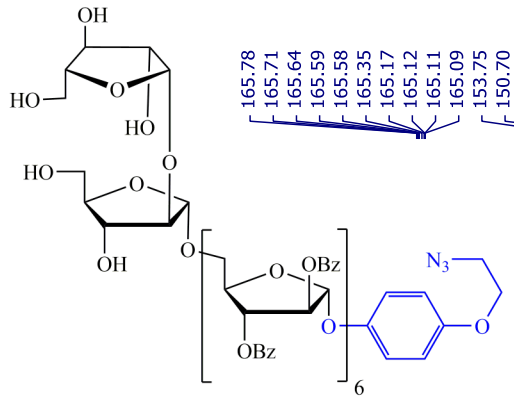
^{29}Si INEPT NMR (59 MHz) spectrum of compound 7 in $CDCl_3$

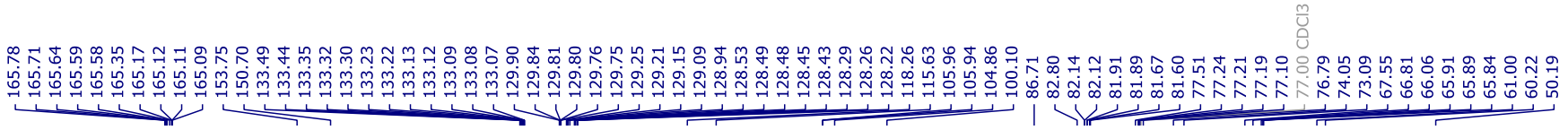


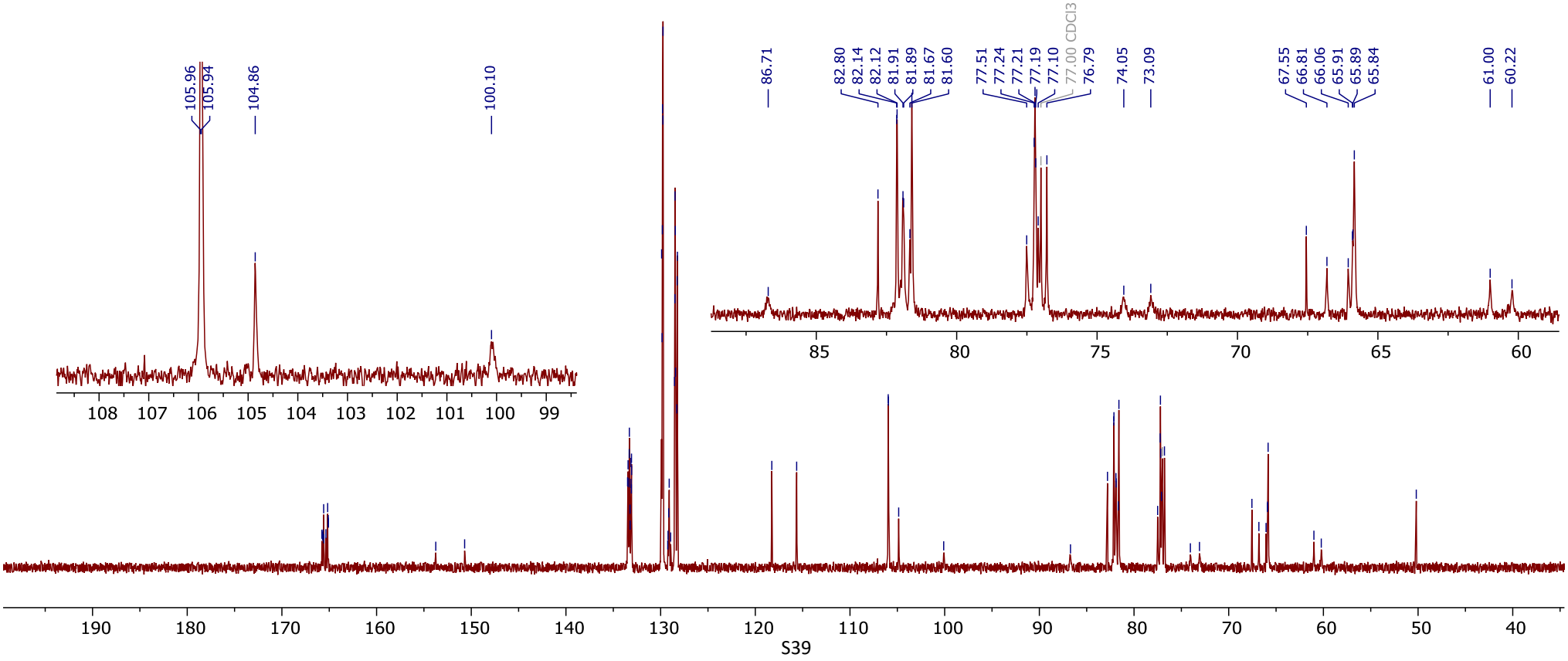
^{1}H NMR (600 MHz) spectrum of compound 8 in $CDCl_3$



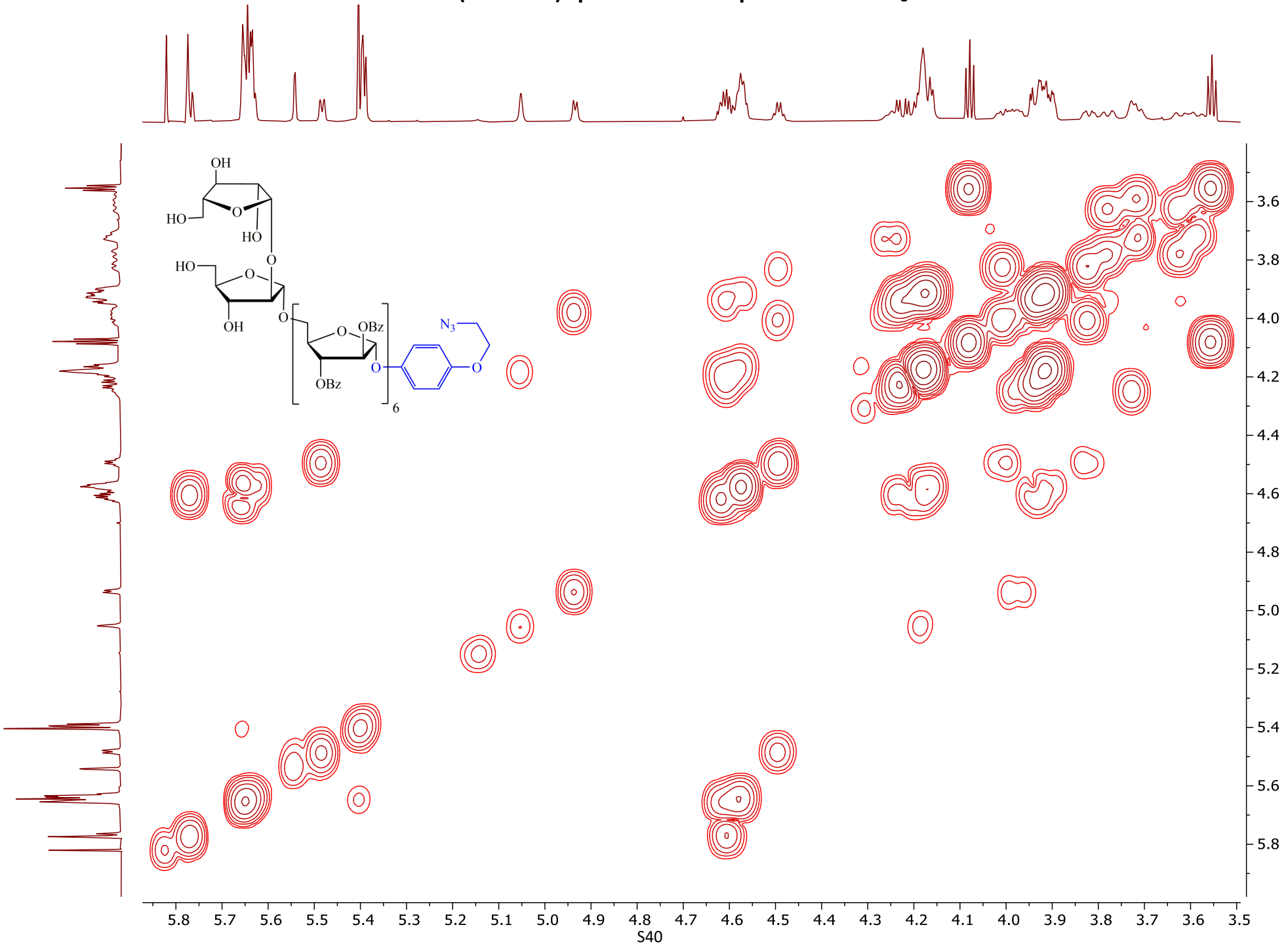
^{13}C NMR (151 MHz) spectrum of compound 8 in $CDCl_3$



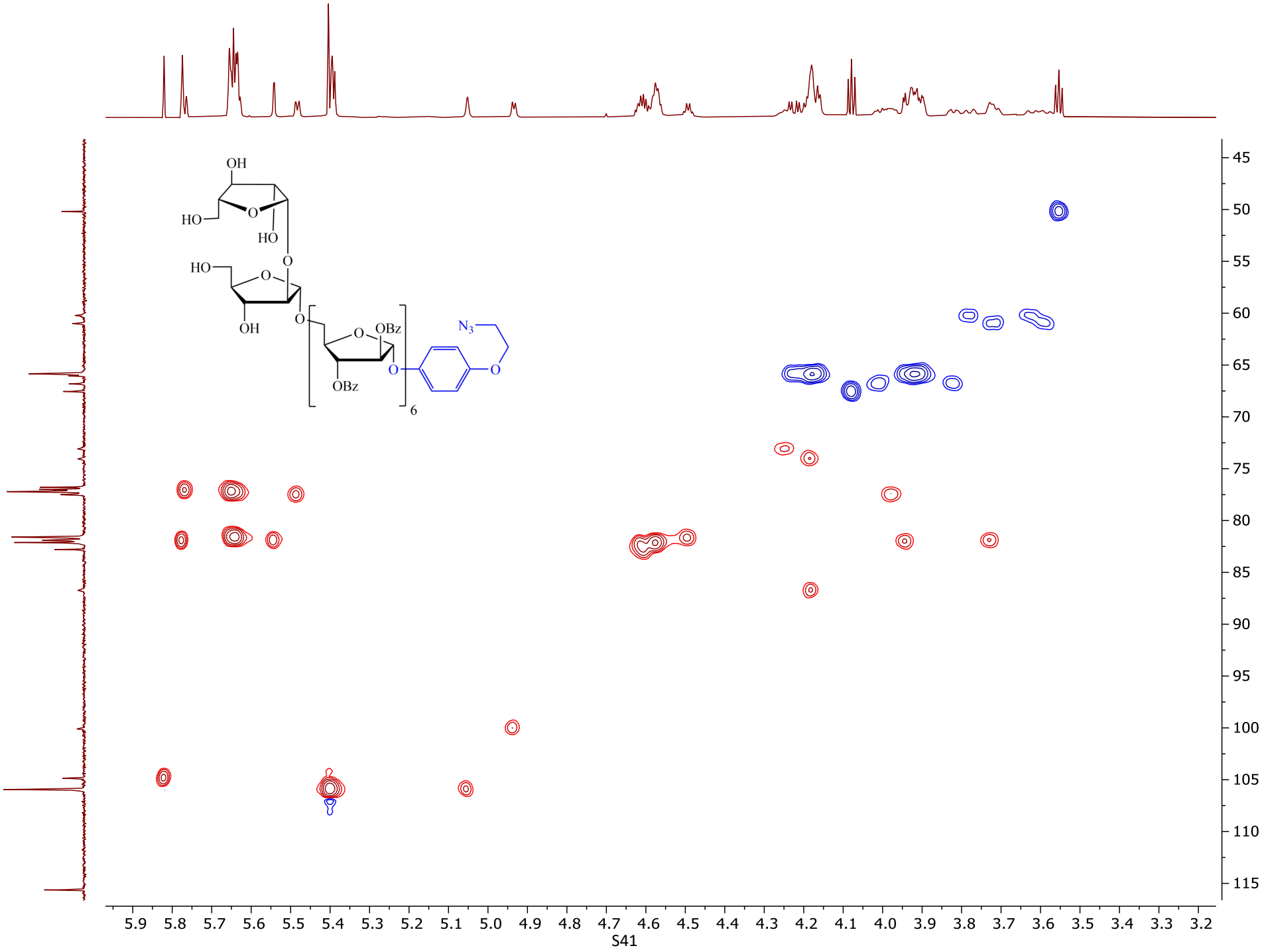




COSY (600 MHz) spectrum of compound 8 in $CDCl_3$



HSQC (600 MHz) spectrum of compound 8 in $CDCl_3$



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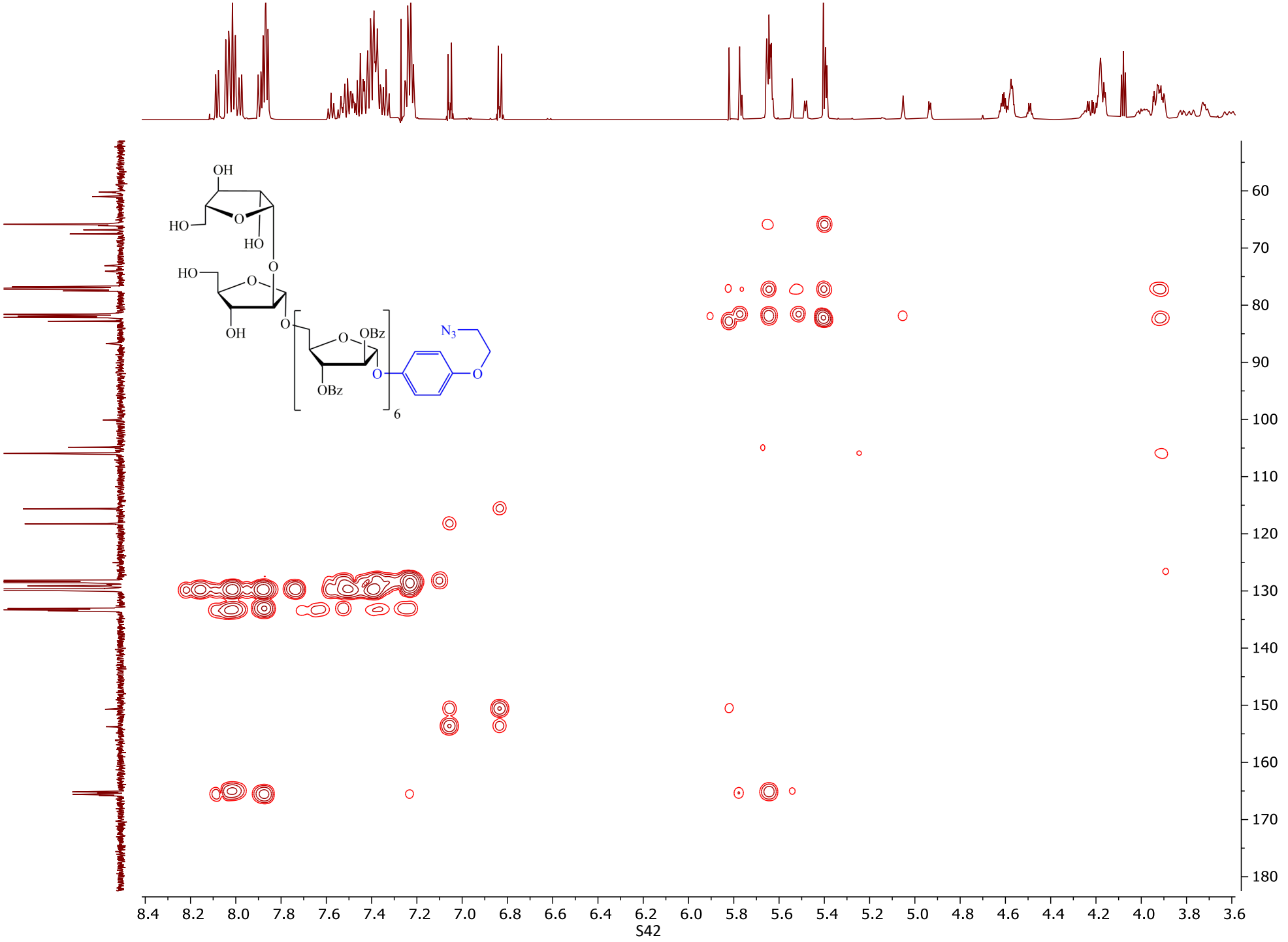
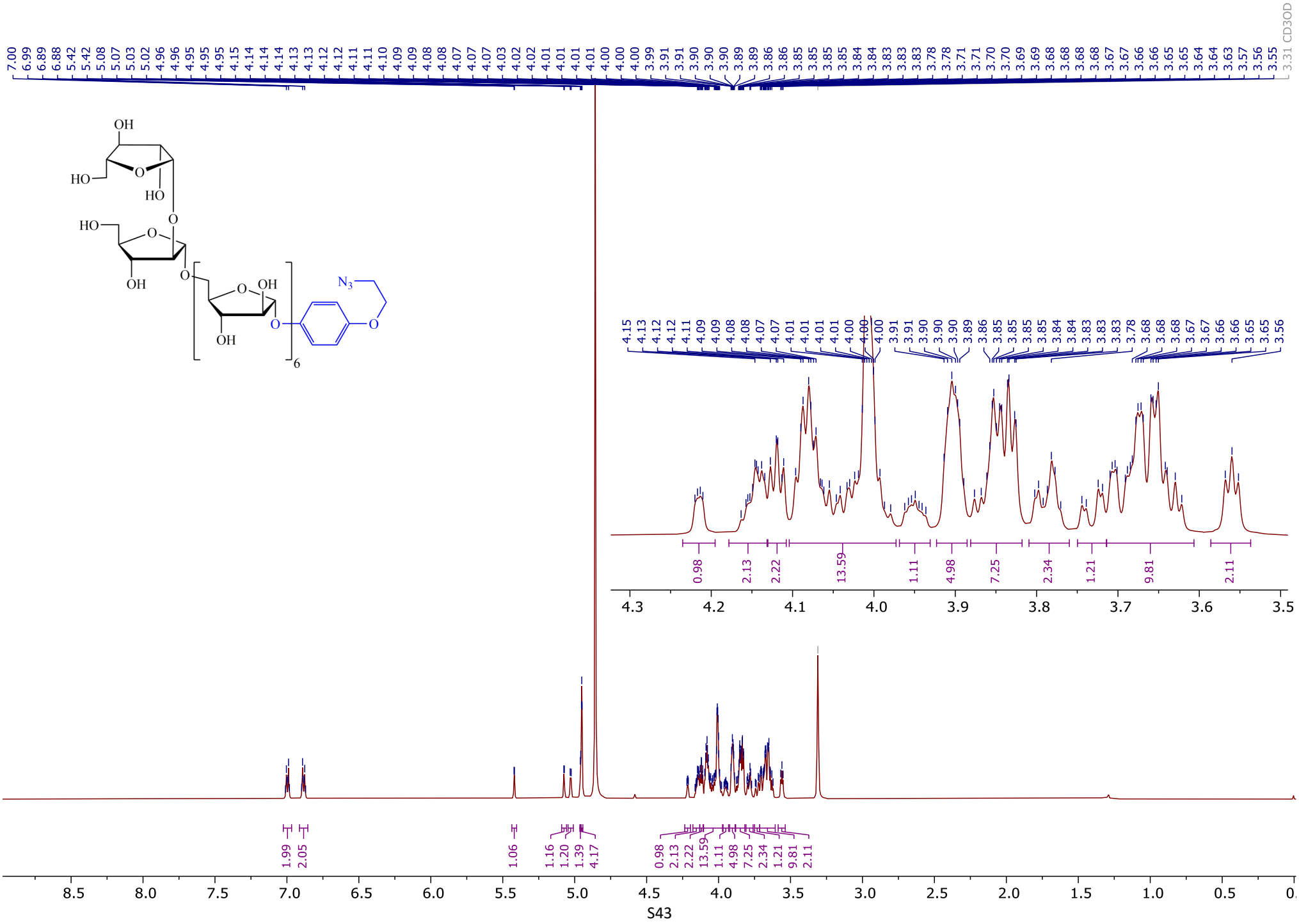
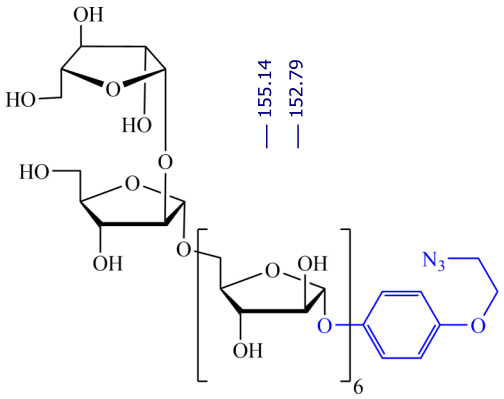


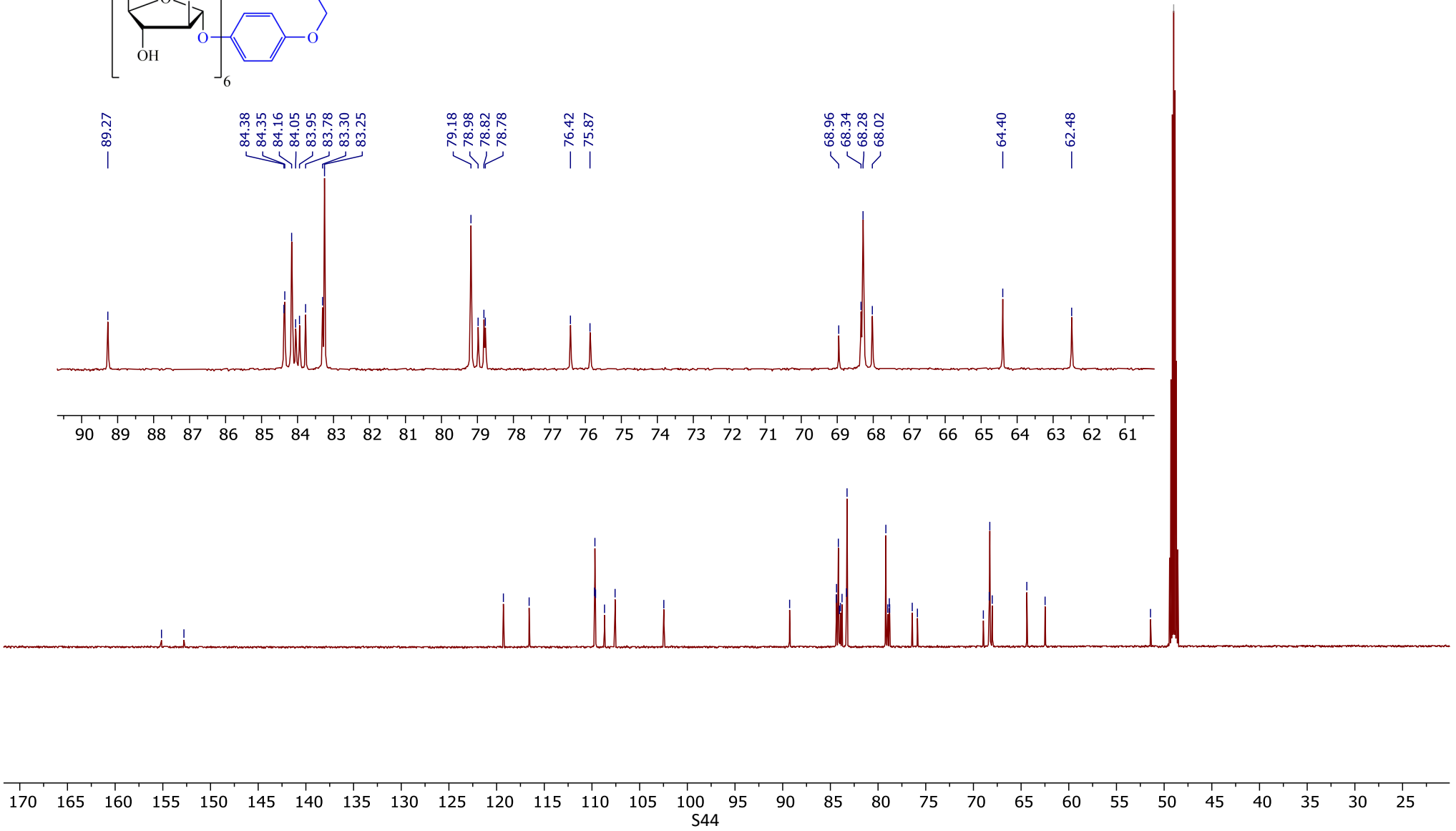
^{1}H NMR (600 MHz) spectrum of compound 9 in CD_3OD



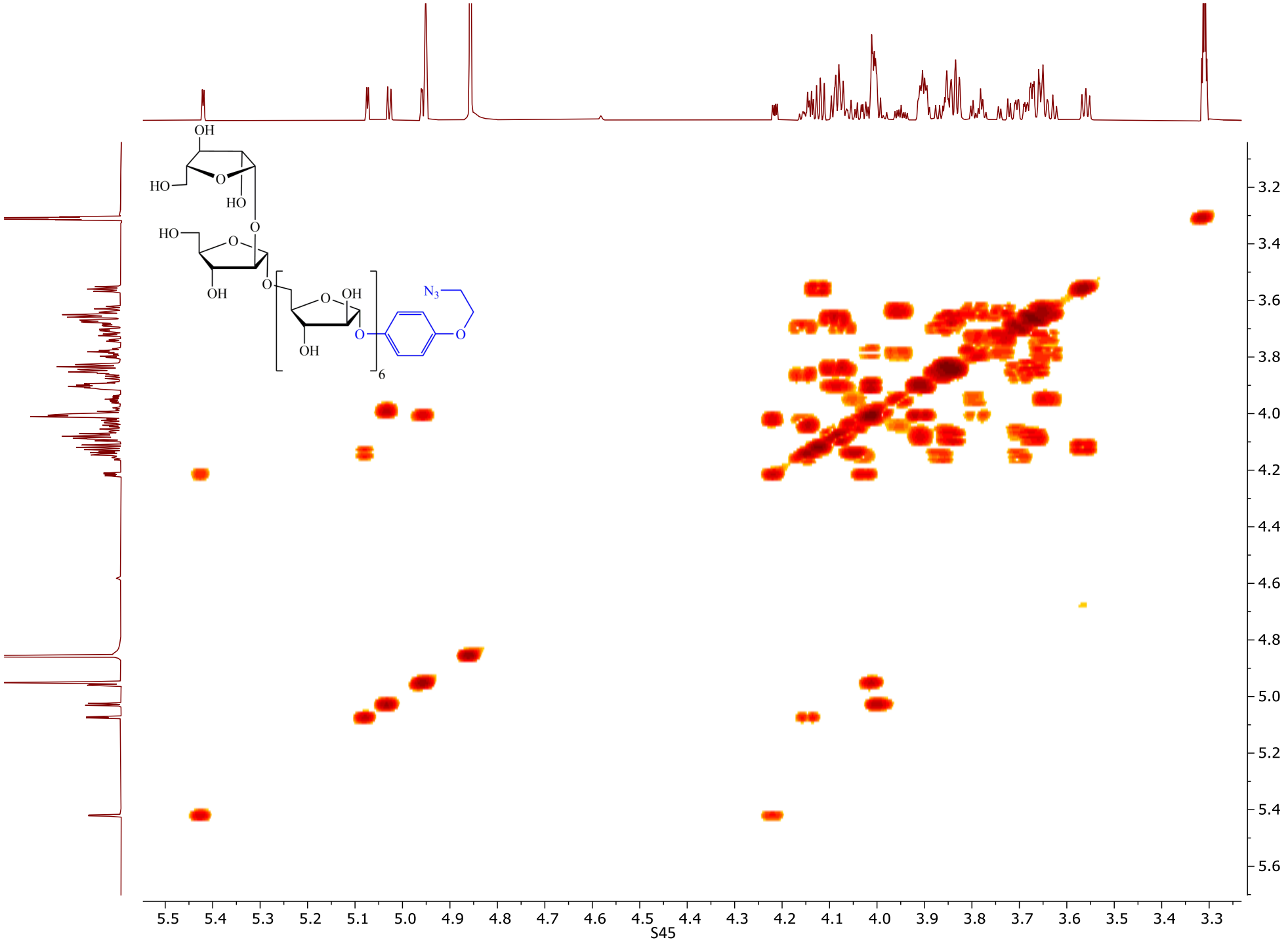
^{13}C NMR (151 MHz) spectrum of compound 9 in CD_3OD



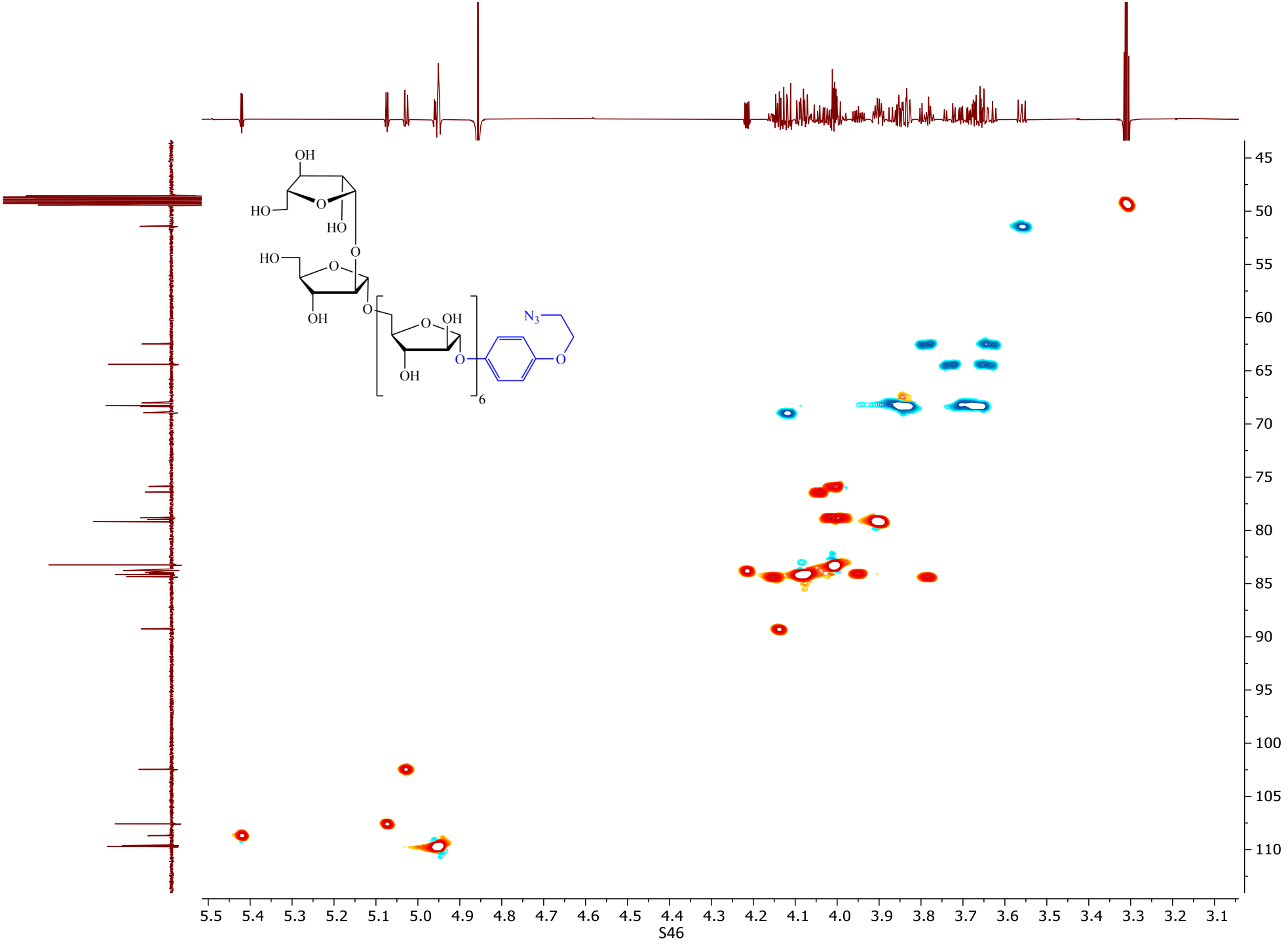
155.14 152.79 119.29 116.59 109.73 109.69 109.62 108.68 107.58 102.46 89.27 84.38 84.35 84.16 84.05 83.95 83.78 83.30 83.25 79.18 78.98 78.82 78.78 76.42 75.87 68.96 68.34 68.28 68.02 64.40 62.48 51.43 49.00 CD3OD



COSY (600 MHz) spectrum of compound 9 in CD_3OD



HSQC (600 MHz) spectrum of compound 9 in CD_3OD



HMBC (600 MHz) spectrum of compound 9 in CD_3OD