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Supporting information for

Silver-assisted Gold-catalyzed Solid Phase Synthesis of Linear and Branched Oligosaccharides

Yogesh Sutar, Madhuri Vangala,* and Srinivas Hotha*

Department of Chemistry, Indian Institute of Science Education and Research, Pune – 411 008, MH, India

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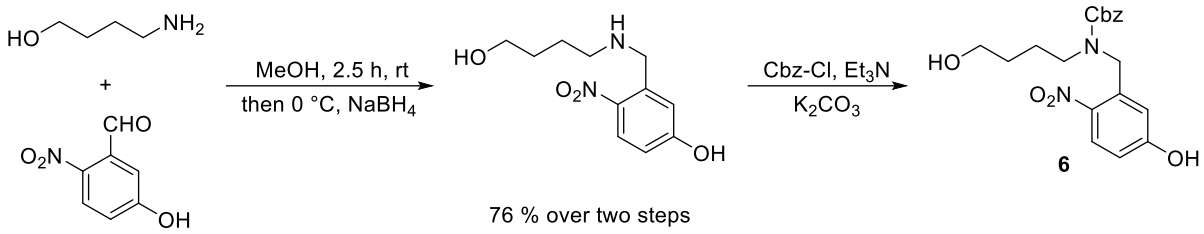
1.0 General methods

All chemicals used were reagent grade and used as supplied, except where noted. Gold-phosphite catalyst was purchased from Proactive Molecular Research, Florida (USA) and AgOTf was purchased from Sigma-Aldrich. All air and/or moisture sensitive reactions were carried out under argon/nitrogen atmosphere with anhydrous solvents. Freshly distilled CH_2Cl_2 was stored over activated 4Å molecular sieves (pre-heated to 200-250 °C). Column chromatography purification for all compounds was performed by using silica gel of 100-200 mesh. Reverse phase HPLC purification was performed using Agilent 1260 infinity II series. Products obtained as solids or syrups were dried under high vacuum. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates (0.25 mm). Compounds were visualized by UV light or by dipping the plate in anisaldehyde solution. Optical rotations were measured at 589 nm (sodium D-line) at 25 °C in $CHCl_3$ solution with the use of a digital polarimeter. IR spectra were recorded in $CHCl_3$ on a FT-IR spectrometer. NMR spectra were recorded either on a 400, 500 and/or 600 MHz in $CDCl_3$ (δ, 7.26), methanol-D_4 (δ, 3.31), or D_2O (δ, 4.80). HRMS was recorded using an ESI-TOF mass analyser and MALDI-ToF mass analyser. Low resolution mass spectroscopy (LRMS) was performed on UPLC-MS with TLC interface. Percentage conversion or yield of the solid phase reaction was deduced based on the UV trace of the LC-MS profile of the photolytically released compounds. Spectroline UV cabinet equipped with a 4W UV light source of wavelength 365 nm was used for the cleavage reaction.

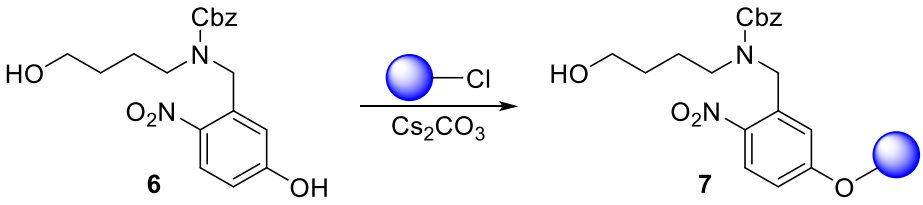
2.0 Preparation of linker and attachment to the Merrifield resin[1]

2.1 Synthesis of Benzyl (5-hydroxy-2-nitrobenzyl)(4-hydroxybutyl)carbamate



A solution of 5-Hydroxy-2-nitrobenzaldehyde (2.44 g, 14.58 mmol) and 4-aminobutanol (1.3 g, 14.58 mmol) in anhydrous methanol (45 mL) at 25 °C was stirred for 2.5 h under argon atmosphere. The reaction mixture was cooled to 0 °C and $NaBH_4$ (0.55 g, 14.58 mmol) was added portion-wise and brought to 25 °C over 30 min. After 1 h, excess $NaBH_4$ was quenched by the addition of acetone (50.16 mL) and stirred for 5 min. The solvents were evaporated to furnish the secondary amine which was then re-dissolved in anhydrous MeOH (300 mL), triethylamine (4.09 mL, 43.70 mmol) and Cbz-Cl (6.21 mL, 36.42 mmol) and stirred for 1 h at 25 °C. K_2CO_3 (9.68 g) was added to the reaction mixture and stirred for an hour. The reaction mixture was then filtered through a bed of Celite® and the filtrate was evaporated to dryness. The crude residue was redissolved in CH_2Cl_2 and washed with 0.1 M HCl and water. Combined organic layers were dried over anhydrous Na_2SO_4, filtered through cotton plug and concentrated *in vacuo* to obtain a residue that was purified by silica gel column chromatography (ethyl acetate:hexane) to obtain photocleavable linker **6** in 76% yield (4.12 g) as tanish green coloured liquid. R_f = 0.28 (ethyl acetate:hexane 60:40); IR (cm^{-1}): 3611, 3212, 2934, 1676, 1584, 1516, 1460, 1310, 1249, 1132, 1067, 982, 838, 745, 695; ^1H NMR (400.31 MHz, $CDCl_3$, mixture of rotamers[2]): δ 8.16-7.98 (m,1H), 7.37 – 7.04 (m, 5H), 6.85 – 6.64 (m, 2H), 5.15-5.05 (m, 2H), 4.90-4.87 (m, 2H), 3.60 (m, 2H), 3.36 – 3.29 (m, 2H), 2.54 – 2.00 (brs, 1H), 1.72 – 1.59 (m, 2H), 1.55 – 1.46 (m, 2H); ^{13}C NMR (100.66 MHz, $CDCl_3$): δ 162.9(2C), 157.3(2C), 140.4, 139.8, 137.5, 137.0, 136.2, 135.9, 129.1, 128.8, 128.7(4C), 128.3(2C), 128.1, 127.6(3C), 115.1, 114.8, 114.3, 113.3, 68.0, 67.9, 62.4, 62.3, 49.7, 49.6, 48.7, 48.1, 29.8, 29.3, 25.0, 24.8. HRMS (ESI-MS): m/z calcd. for $[C_{19}H_{22}O_6N_2Na]^+$: 397.1376; found: 397.1375.

2.2 Coupling Linker 6 to Merrifield Resin



To a suspension of Merrifield resin (2.0 g, 2.2 mmol, loading 1.1 mmol/g) in CH_2Cl_2 (20 mL), the photocleavable linker **6** (4.12 g, 2.0 mmol) in CH_2Cl_2 (5 mL) was added and subsequently anhydrous DMF (20 mL) was injected into the flask. Solid Cs_2CO_3 (1.697 g, 8.8 mmol) and TBAI

(3.25 g, 8.8 mmol) were added and the resulting solution was stirred overnight on the rotavap at ~60 °C and washed successively with DMF/water (1:1), DMF, THF, MeOH, CH_2Cl_2, MeOH, and CH_2Cl_2 (2 times each). The resin was again transferred into a flask containing CsOAc (0.844 g, 1.57 mmol) in DMF (20 mL) and stirred overnight on rotavap at 60 °C for capping of the unreacted resin. The resin was then washed successively with DMF/water (1:1), DMF, THF, MeOH, CH_2Cl_2, MeOH, and CH_2Cl_2 (2 times each) and dried under high vacuum to obtain resin **7**. Loading value (0.94 mmol/g) was determined as described in procedure 2.3.

2.3 Loading value Determination[2]

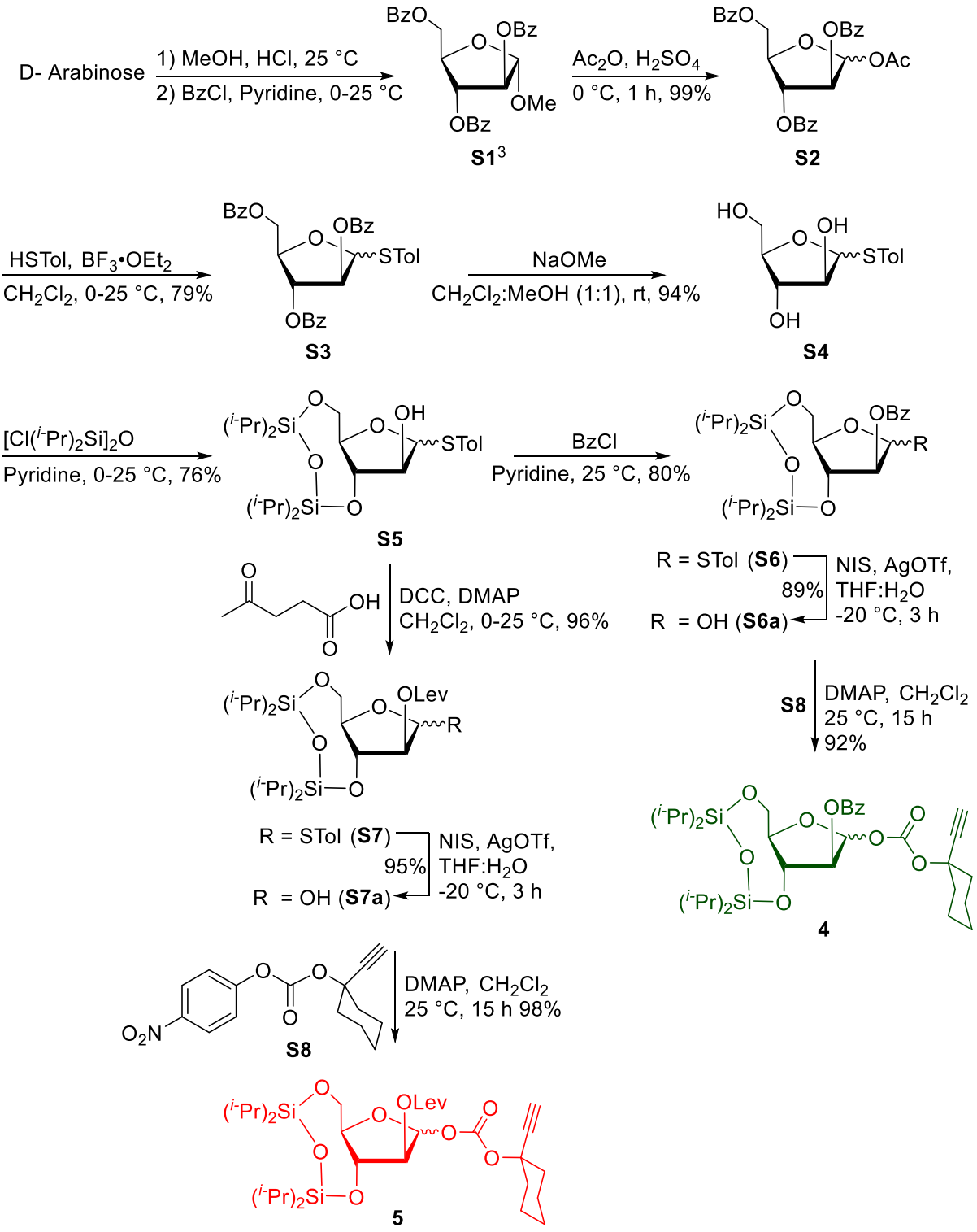
Dry resin **7** (50 mg, theoretical loading: 1.1 mmol/g, 0.055 mmol) was placed in a syringe equipped with a frit. CH_2Cl_2 (3 mL) was added for swelling the resin, CH_2Cl_2 was drained and FmocCl (149.60 mg, 0.60 mmol) in pyridine (0.14 mL, 1.80 mmol) and CH_2Cl_2 (2 mL) was added. Mixing of the reaction mixture was performed by bubbling N_2 gas for 6 h, solvents were drained and the resin was washed with CH_2Cl_2, MeOH and CH_2Cl_2 (2 times each). Subsequently, a freshly prepared DBU solution (2% in DMF, v/v; 2 mL) was added to the resin and stirred for 1 h. The solution was drained into a vial and washed with 1 mL of DBU solution to ensure complete transfer of dibenzofulvene. An aliquot of this solution (45 µL) was diluted with acetonitrile to a total volume of 10 mL and the UV absorption of this solution was measured at 294 and 304 nm. The loading of the resin was calculated as follows:

For $\lambda_{304,}$ [Fmoc] = Absorbance at 304 nm x dilution factor/ Molar extinction coefficient
Similarly, for wavelength 294 nm was calculated. The average of these two loading value was found as 0.94 mmol/g.

3.0 Synthesis of donors 4 and 5

Acetyl 2,3,5-tri-*O*-benzoyl-α/β-D-arabinofuranose [α:β(4.4:1)](S2): To a solution of compound **S1**[3] (30.0 g, 62.96 mmol) in Ac_2O (190 mL), conc. H_2SO_4 (1.7 mL, 31.48 mmol) was added dropwise at 0 °C, stirred for 1 h. After completion of the reaction as adjudged by TLC analysis, solid $NaHCO_3$ was dumped and a few pieces of ice were added carefully while vigorously stirring. The compound **S2** was extracted into ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give crude residue which was subjected to silica gel column chromatography to yield compound **S2** (31.44 g, 99.0%) as a sticky colourless liquid. R_f = 0.46 (ethyl acetate:hexane 20:80); IR (cm^{-1}): 3440, 3066, 2952, 1724, 1451, 1366, 1264, 1177, 1105, 1022, 959, 710; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 8.11 – 8.00 (m, 12H), 7.60 (p, *J* = 7.6 Hz, 4H), 7.54 – 7.36 (m, 10H), 7.30 (t, *J* = 7.8 Hz, 4H), 6.66 (d, *J* = 4.7 Hz, 1H), 6.49 (s, 1H), 6.02 – 5.97 (m, 1H), 5.81 (dd, *J* = 6.8, 4.8 Hz, 1H), 5.66 (s, 1H), 5.64 (d, *J* = 3.9 Hz, 1H), 4.82 – 4.70 (m, 3H), 4.70 – 4.64 (m, 2H), 4.58 (dd, *J* = 10.1, 5.7 Hz, 1H), 2.19 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100.66 MHz, $CDCl_3$): δ 169.2(2C), 166.2, 166.1, 165.9, 165.6, 165.4, 165.2, 133.8(2C), 133.8, 133.7, 133.2, 133.2, 130.0(3C), 129.9, 129.9(4C), 129.8, 129.8(3C), 129.7, 129.6, 129.0, 128.8, 128.7, 128.7, 128.6(3C),

128.6(5C), 128.4, 128.4(3C), 99.5, 93.7, 83.2, 81.3, 80.0, 77.5, 76.1, 75.5, 64.8, 63.6, 21.1, 20.9; HRMS (ESI-MS): m/z calcd. for $[C_{28}H_{24}O_9Na]^+$: 527.1318; found: 527.1317.



***p*-Tolyl 2,3,5-tri-*O*-benzoyl 1-thio-α/β-D-arabinofuranoside [α:β (5.75:1.00)] (S3):** $BF_3.OEt_2$ (17.39 mL, 140.93 mmol) was added slowly to a solution of compound **S2** (35.55 g, 70.47 mmol) in anhydrous CH_2Cl_2 (350 mL) at 0 °C. The reaction mixture was warmed to 25 °C and stirred. After 1 h, the reaction mixture was cooled to 0 °C and $BF_3.OEt_2$ was neutralized by adding Et_3N

(18 mL), diluted with water, extracted with CH_2Cl_2, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to obtain a crude residue which was subjected to silica gel column chromatography (hexane:ethyl acetate) to yield pure desired product **S3** (59.12 g, 79%) as a colourless liquid. R_f = 0.47 (ethyl acetate:hexane 20:80); IR (cm^{-1}): 3440, 3069, 2977, 1723, 1601, 1451, 1104, 1069, 1026, 995, 879, 766, 684; ^1H NMR (400.31 MHz, $CDCl_3$): δ 8.16-8.12 (m, 4H), 8.1-8.0 (m, 8H), 7.65 – 7.56 (m, 4H), 7.55 – 7.38 (m, 14H), 7.35 – 7.29 (m, 4H), 7.15-7.10 (m, 4H), 5.95 (dd, *J* = 4.6, 3.5 Hz, 1H), 5.83 (d, *J* = 4.9 Hz, 1H), 5.80 (d, *J* = 3.6 Hz, 1H), 5.78 (s, 1H), 5.73 (d, *J* = 1.2 Hz, 1H), 5.67 (dd, *J* = 4.8, 0.7 Hz, 1H), 4.88 (dd, *J* = 8.8, 4.7 Hz, 1H), 4.84 (d, *J* = 3.7 Hz, 2H), 4.83 – 4.80 (m, 1H), 4.75 (dd, *J* = 11.9, 5.1 Hz, 1H), 4.51 (dd, *J* = 9.7, 5.6 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 166.3, 166.2, 165.6, 165.4, 165.3, 165.3, 138.2, 138.1, 133.7, 133.6, 133.1, 133.0(2C), 132.7, 130.2, 130.1(4C), 129.9(4C), 129.9(4C), 129.8, 129.8(4C), 129.7(2C), 129.5(2C), 129.0(2C), 128.9(2C), 128.7, 128.6(4C), 128.6(4C), 128.5, 128.3(3C), 128.3, 91.7, 90.2, 82.5, 81.2, 81.1, 78.1 ,77.1, 78.0, 64.4, 63.6, 21.2, 21.2; HRMS (ESI-MS): m/z calcd. for $[C_{33}H_{28}O_7SNa]^+$: 591.1453; found: 591.1450.

***p*-Tolyl 1-thio-α/β-D-arabinofuranoside [α:β (12.61:1)] (S4)[5]:** Solid sodium methoxide (2.53 g, 46.83 mmol) was added to a solution of the tri-*O*-benzoate **S3** (26.63 g, 46.83 mmol) in 300 mL of 1:1 MeOH:CH_2Cl_2 and stirred for 12 h. After ensuring the completion of reaction, it was neutralized with IR-120 (H^+) resin, filtered and the filtrate was evaporated to obtain a crude residue that was purified by silica gel column chromatography using hexane, ethyl acetate as mobile phase to afford compound **S4** (11.25 g, 94%) as a colourless liquid. The major isomer that was isolated and characterized as α-isomer.[4] R_f = 0.33 (ethyl acetate:hexane 80:20); IR (cm^{-1}): 3338, 2923, 1639, 1027, 860, 804, 697; ^1H NMR (400.31 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.30 (d, *J* = 4.0 Hz, 1H), 5.09 (brs, 1H), 4.78 (brs, 1H), 4.15 – 3.96 (m, 3H), 3.77 (dd, *J* = 12.3, 2.7 Hz, 1H), 3.69 (dd, *J* = 12.4, 2.7 Hz, 1H), 3.37 (brs, *1*H), 2.26 (s, 3H); ^{13}C NMR (100.66 MHz, $CDCl_3$): δ 137.9, 132.6(2C), 130.0(2C), 129.9, 92.0, 82.8, 81.9, 76.5, 60.9, 21.2. HRMS (ESI-MS): m/z calcd for $[C_{12}H_{16}O_4SNa]^+$: 279.0667; found: 279.0669.

***p*-Tolyl 3,5-*O*-(tetra-isopropylsiloxane-1,3-diyl)-1-thio-α/β-D-arabinofuranoside [α:β (16.0:1)] (S5)[5]:** To a solution of triol **S4** (16.73 g, 65.27 mmol) in pyridine (180 mL) at 0 °C, 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (22.65 g, 71 80 mmol) was added dropwise over 30 min. The reaction mixture was warmed to 25 °C and stirred for 2 h. After completion of the reaction as adjudged by the TLC, disiloxane was quenched by addition of excess amount of methanol and water, volatiles were evaporated *in vacuo*, extracted with CH_2Cl_2, washed with brine, dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography using hexane, ethyl acetate as mobile phase to give the 3,5-*O*-tetraisopropyldisiloxane **S5** (24.14 g, 76%) as a colourless syrup. R_f = 0.61 (ethyl acetate:hexane 10:90); IR (cm^{-1}): 3445, 2939, 2867, 2356, 1646, 1150, 1093, 1032, 864, 695; Data of major isomer α: ^1H NMR (400.31 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 5.25 (d, *J* = 5.5 Hz, 1H), 4.26 – 4.16 (m, 2H), 3.98 (d, *J* = 3.4 Hz, 2H), 3.94 (dt, *J* = 6.6, 2.3 Hz, 1H), 2.40 (d, *J* = 4.2 Hz, 1H), 2.32 (s, 3H), 1.11 – 1.02 (m, 28H); ^{13}C NMR (100.66 MHz, $CDCl_3$): δ 137.6, 132.0(2C), 130.9, 129.8(2C), 91.2, 81.9, 80.6, 76.4, 61.4, 21.2, 17.6, 17.4(2C), 17.4, 17.2, 17.2(2C),

17.1, 13.6, 13.3, 12.9, 12.7. HRMS (ESI-MS): m/z calcd for $[C_{24}H_{42}O_5SSi_2H]^+$: 499.2370; found: 499.2365.

***p*-Tolyl 2-*O*-benzoyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-1-thio-α/β-D-arabinofurano-side [α:β (4.9:1.0)] (S6)[4]:** Benzoyl chloride (3 .43 g, 24.38 mmol) was added to a vigorously stirred solution of compound **S5** (7.47 g, 16.26 mmol) in pyridine (50 mL) at 0 °C. The reaction mixture was stirred for 3 h at 25 °C, diluted with water, extracted with CH_2Cl_2, washed with 1 M aqueous HCl followed by saturated aqueous $NaHCO_3$ solution and treated with brine solution. Combined organic phases were pooled and dried over anhydrous Na_2SO_4, filtered and the filtrate was evaporated to dryness under diminished pressure to obtain a residue that was purified by silica gel column chromatography using hexane and ethyl acetate to furnish the titled compound **S6** (7.35g, 80 %, α/β:4.9:1.0) as a sticky liquid. R_f = 0.48 (ethyl acetate:hexane 5:95); IR (cm^{-1}): 3611, 2942, 2868, 1730, 1461, 1389, 1102, 1035, 806, 701; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 8.13 (d, *J* = 0.7 Hz, 1H), 8.11 (d, *J* = 1.5 Hz, 1H), 8.05 (d, *J* = 0.8 Hz, 1H), 8.03 (d, *J* = 1.5 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.52 – 7.48 (m, 2H), 7.48 – 7.41 (m, 4H), 7.36 – 7.33 (m, 2H), 7.12 - 7.06 (m, 4H), 5.77 (d, *J* = 6.0 Hz, 1H), 5.59 (dd, *J* = 5.2, 3.8 Hz, 1H), 5.55 (d, *J* = 6.6 Hz, 1H), 5.46 (d, *J* = 3.7 Hz, 1H), 4.71 (t, *J* = 6.6 Hz, 1H), 4.56 (dd, *J* = 7.9, 5.3 Hz, 1H), 4.22 (dt, *J* = 7.7, 3.7 Hz, 1H), 4.15 – 4.10 (m, 2H), 4.10 – 4.00 (m, 2H), 3.95 (ddd, *J* = 8.0, 6.5, 4.2 Hz, 1H), 2.31 (s, 6H), 1.18 – 0.91 (m, 56H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 165.9, 165.6, 137.9, 137.6, 133.5, 133.5, 133.1(2C), 132.3(2C), 130.8(2C), 130.0(2C), 129.9(2C), 129.8, 129.8, 129.7(2C), 129.5, 129.5, 128.6(2C), 128.6(2C), 89.8, 88.3, 83.3, 82.5, 81.0, 80.3, 77.0, 75.6, 65.1, 61.5, 21.2(2C), 17.7, 17.6, 17.6, 17.6, 17.5, 17.5(2C), 17.2, 17.1(2C), 17.0(2C), 17.0(2C), 17.0(2C), 13.6, 13.5, 13.5, 13.3, 13.0, 13.0, 12.6, 12.6. HRMS (ESI-MS): m/z calcd for $[C_{31}H_{46}O_6SSi_2NaK]^+$: 664.2088; found: 664.2096 .

***p*-Tolyl 2-*O*-Levulinoyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-1-thio-α/β-D-arabinofuranoside [α:β (14.1:1)] (S7)[6]:** Compound **S6** (6.76 g, 13.55 mmol) was dissolved in anhydrous CH_2Cl_2 (60 mL), DMAP (3.31 mg, 2.71 mmol), Levulinic acid (2.07 mL, 20.33 mmol) and *N,N'*-Diisopropylcarbodiimide (4.16 mL, 16.26 mmol) were added at 0 °C under N_2 atmosphere. The reaction mixture was stirred at 25 °C for 2 h. After completion of reaction, the compound was extracted into CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ solution, brine and dried over anhydrous Na_2SO_4. Organic solvent was evaporated on rotary evaporator and then desired compound was isolated by silica gel column chromatography using hexane:ethyl acetate system to afford corresponding levulinoate ester **S7** (7.80 g, 96%, α/β:14.1:1) as colourless liquid. R_f = 0.43 (ethyl acetate:hexane 20:80). Data of the major α-isomer: IR (cm^{-1}): 3615, 2941, 2869, 2353, 1736, 1465, 1369, 1145, 1034, 783, 695; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.32 – 5.27 (m, 2H), 4.36 (dd, *J* = 7.9, 5.0 Hz, 1H), 4.14 – 4.09 (m, 1H), 4.03 (dd, *J* = 12.7, 3.1 Hz, 1H), 3.96 (dd, *J* = 12.6, 4.6 Hz, 1H), 2.79 – 2.74 (m, 2H), 2.64 – 2.58 (m, 2H), 2.31 (s, 3H), 2.19 (s, 3H), 1.12 – 0.99 (m, 28H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 206.2, 171.9, 137.6, 132(2C), 130.7, 129.7(2C), 89.5, 83.1, 80.9, 75.6, 61.5, 37.9, 30.0, 27.9, 21.2, 17.6, 17.4(3C), 17.1, 17.0(3C), 13.6, 13.3, 12.9, 12.6; HRMS (ESI-MS): m/z calcd for $[C_{29}H_{48}O_7SSi_2Na]^+$: 619.2557; found: 619.2565.

4.0 General experimental procedures:

Deprotection of –STol:[7] To a solution of thioglycoside (12.93 mmol) in THF–H_2O (40:1, 93 mL), NIS (22.49 mmol) and AgOTf (0.11 mmol) were added at 0 °C. The reaction mixture was stirred at 0 °C for 3 h (the reaction mixture turned to brown) and neutralized by the addition of excess amount of Et_3N. All volatiles were evaporated, the residue was diluted with 50 mL of dichloromethane and 50 mL of water, extracted with CH_2Cl_2 and washed with a saturated aq. solution of $Na_2S_2O_3$ and then washed with aqueous brine solution. Combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to obtain a crude residue that was purified by silica gel column chromatography using hexane and ethyl acetate to accomplish the corresponding hemi acetals **S6a**, **S7a**.

Synthesis of carbonate donors 4 and 5:[8] To a solution of hemiacetal **S6a** or **S7a** (9.80 mmol) in anhydrous CH_2Cl_2 (50 mL), DBU (12.74 mmol) and 1-Ethynylcyclohexyl 4-nitrophenyl carbonate **S8** (14.71 mmol) were added portion wise and stirred for 6 h at room temperature. After consumption of the starting material, the reaction mixture was concentrated *in vacuo* to obtain an oily residue which was partially purified by silica gel column chromatography. The eluents of the column fractions contained trace quantity of *p*-nitrophenol and hence, the crude residue was redissolved in minimum volume of CH_2Cl_2 (30 mL) and washed several times with aqueous saturated $NaHCO_3$ solution until aqueous layer becomes completely colourless. Finally, organic layers were dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to obtain pure alkynyl arabinofuranosyl donors **4** and **5**.

2-*O*-benzoyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-α/β-D-arabinofuranose [α:β(0.85:1)] (S6a): Colourless sticky liquid; Yield = 89% ; R_f = 0.31 (ethyl acetate:hexane 20:80); IR (cm^{-1}): 2939, 1729, 1451, 1362, 1264, 1100, 756, 708; ^1H NMR (400.31 MHz, $CDCl_3$): δ 8.08 (dt, *J* = 8.5, 1.5 Hz, 2H), 8.03 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.49 – 7.42 (m, 4H), 5.63 (t, *J* = 4.5 Hz, 1H), 5.37 (dd, *J* = 4.5, 1.5 Hz, 1H), 5.31 (dd, *J* = 4.8, 1.7 Hz, 1H), 5.14 (dd, *J* = 7.8, 4.5 Hz, 1H), 4.78 (dd, *J* = 7.8, 6.0 Hz, 1H), 4.55 (dd, *J* = 7.0, 4.8 Hz, 1H), 4.24 (ddd, *J* = 7.1, 5.5, 3.4 Hz, 1H), 4.12 – 4.01 (m, 2H), 4.00 – 3.89 (m, 3H), 3.42 (d, *J* = 4.6 Hz, 1H), 3.11 (d, *J* = 4.6 Hz, 1H), 1.16 – 0.99 (m, 56H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 166.4, 166.3, 133.6, 133.5, 130.0(2C), 129.9(2C), 129.5, 129.4, 128.6(2C), 128.6(2C), 100.4, 93.7, 85.3, 82.2, 80.9, 80.1, 75.7, 75.3, 65.5, 62.2, 17.7, 17.6, 17.6(2C), 17.5, 17.5(2C), 17.5, 17.2, 17.1, 17.1, 17.1, 17.1 (3C), 17.0, 13.6, 13.6, 13.4, 13.4, 13.1, 12.9, 12.6(2C); (MALDI-TOF) $[M+Na]^+$ m/z calcd for $[C_{24}H_{40}O_7Si_2Na]^+$: 519.2210 ; found: 519.2216.

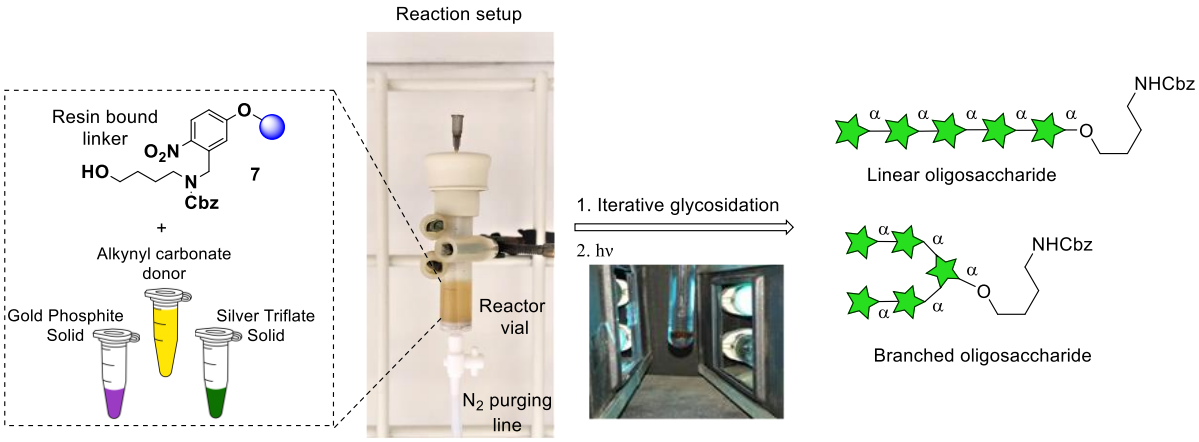
2-*O*-levulinoyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-α/β-D-arabinofuranose [α:β (1:1)] (S7a): Colourless sticky liquid; Yield = 95 % ; R_f = 0.14 (ethyl acetate:hexane 30:70); IR (cm^{-1}): 3613, 3439, 2942, 2869, 1728, 1463, 1369, 1242, 1148, 1029; ^1H NMR (400.31 MHz, $CDCl_3$): δ 5.45 (d, *J* = 4.3 Hz, 1H), 5.21 (s, 1H), 5.05 (d, *J* = 4.8 Hz, 1H), 4.88 (dd, *J* = 7.7, 4.4 Hz, 1H), 4.57 (t, *J* = 7.0 Hz, 1H), 4.34 (dd, *J* = 6.9, 5.1 Hz, 1H), 4.17 – 4.11 (m, 1H), 4.00 (ddd, *J* = 14.8, 11.9, 3.3 Hz, 2H), 3.93 – 3.80 (m, 3H), 2.81 – 2.73 (m, 4H), 2.68 – 2.56 (m, 4H), 2.18 (s, 6H), 1.12 – 0.98 (m, 56H); ^{13}C NMR (100.66 MHz, $CDCl_3$): δ 207.1, 206.5, 172.6, 172.5, 100.1, 93.5, 85.0, 82.0, 80.7, 79.9,

75.7, 75.5, 65.7, 62.2, 38.1, 37.9, 29.9(2C), 27.9, 27.9, 17.6, 17.6, 17.5(2C), 17.5, 17.5, 17.5, 17.4, 17.1(5C), 17.0(3C), 13.5, 13.5, 13.4, 13.4, 13.0, 12.9, 12.6(2C); HRMS (ESI-MS): m/z calcd for $[C_{22}H_{42}O_8Si_2H]^+$: 491.2496; found: 491.2496 .

1-*O*-(((1-ethynylcyclohexyl)oxy)carbonyl)-2-*O*-benzoyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-α/β-D-arabinofuranose [α:β (1.74:1)] (4): Colourless solid; Yield = 92% ; R_f = 0.42 (ethyl acetate:hexane 5:95); IR (cm^{-1}): 3616, 3292, 2941, 2868, 1748, 1460, 1377, 1238, 1104, 1029, 892, 778, 700; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 8.08-8.00 (m, 4H), 7.62-7.54 (m, 2H), 7.48 – 7.41 (m, 4H), 6.30 (d, *J* = 4.3 Hz, 1H), 6.08 (d, *J* = 1.4 Hz, 1H), 5.61 (dd, *J* = 5.0, 1.7 Hz, 1H), 5.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.81 (dd, *J* = 8.2, 6.1 Hz, 1H), 4.57 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.25 – 4.19 (m, 1H), 4.12 – 4.01 (m, 3H), 4.01 – 3.89 (m, 2H), 2.63 (s, 1H), 2.38 (s, 1H), 2.23 - 2.13 (m, 1H), 2.09 – 1.99 (m, 1H), 1.98 – 1.79 (m, 4H), 1.78 – 1.59 (m, 5H), 1.58 – 1.40 (m, 7H), 1.38-1.26 (m, 2H), 1.18 – 0.95 (m, 56H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 165.8, 165.5, 151.3, 151.0, 133.6, 133.4, 130.1(2C), 129.9(2C), 129.3(2C), 128.6(2C), 128.4(2C), 101.9, 96.0, 83.5, 83.2, 82.8, 82.7, 82.3, 78.3, 78.2, 77.9, 76.4, 75.3, 75.0, 74.9, 65.4, 61.9, 36.9, 36.8, 36.7, 36.6, 25.1, 25.0, 22.6, 22.6, 22.4, 22.4, 17.6, 17.6, 17.5, 17.5, 17.5(2C), 17.4(2C), 17.2, 17.1, 17.0(5C), 17.0, 13.5, 13.5, 13.4, 13.3, 13.0, 12.9, 12.6, 12.5. HRMS (ESI-MS): m/z calcd for $[C_{33}H_{50}O_9Si_2K]^+$: 685.2630; found: 685.2639.

1-*O*-(((1-ethynylcyclohexyl)oxy)carbonyl)-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-2-*O*-(4-oxopentanoyl)-α/β-D-arabinofuranose [α:β (1.5:1)] (5): Colourless solid; Yield = 98% ; R_f = 0.51 (ethyl acetate:hexane 30:70); IR (cm^{-1}): 3294, 2940, 2867, 1756, 1720, 1361, 1269, 1240, 1153, 1116, 1070, 1036, 1004; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 6.11 (d, *J* = 4.3 Hz, 1H), 5.92 (s, 1H), 5.32 (dd, *J* = 4.7, 1.3 Hz, 1H), 5.16 (dd, *J* = 8.3, 4.3 Hz, 1H), 4.61 (dd, *J* = 8.2, 6.3 Hz, 1H), 4.37 (dd, *J* = 7.3, 4.8 Hz, 1H), 4.16 – 4.09 (m, 1H), 4.06 – 3.82 (m, 5H), 2.83 – 2.67 (m, 4H), 2.66 – 2.57 (m, 6H), 2.17 (s, 6H), 2.15 – 2.05 (m, 3H), 1.97 – 1.82 (m, 4H), 1.70 – 1.48 (m, 11H), 1.38 – 1.28 (m, 2H), 1.14 – 0.98 (m, 56H); ^{13}C NMR (100.66 MHz, $CDCl_3$): δ 206.2, 206.1, 172.1, 171.8, 151.3, 151.1, 101.7, 95.8, 83.3, 83.3, 83.0, 82.8, 82.2, 78.2, 78.0, 77.9, 76.4, 75.2, 75.1, 74.7, 65.3, 62.0, 38.0, 37.9, 37.1, 36.9, 36.8, 36.5, 30.0, 29.9, 27.8, 27.7, 25.1, 25.1, 22.6(2C), 22.5(2C), 17.6, 17.6, 17.5, 17.5, 17.5, 17.5, 17.4(2C), 17.1, 17.0(6C), 17.0, 13.5, 13.5, 13.4, 13.3, 13.0, 12.9, 12.6, 12.5; HRMS (ESI-MS): m/z calcd for $[C_{31}H_{52}O_{10}Si_2K]^+$: 679.2736; found: 679.2738.

5.0 General procedures and set-up for manual solid phase oligosaccharide synthesis



5.1 Preparation of Solutions and Reagents for SPOS

Preparation of the solution of building blocks: 4 equivalents of building block (e.g. glycosyl alkynyl carbonate donor) into an Eppendorf tube and dissolved in 2 mL of anhydrous CH_2Cl_2.

Activator reagents: Solid gold phosphite (10 mol%) and AgOTf (15 mol%) were weighed into individual Eppendorf tubes and the tubes were sealed with parafilm until their utilization.

HF.py solution for TBDPS and Disiloxane deprotection: HF•Pyridine/Pyridine in (0.4:1 mL proportion) was prepared.

Saponification of Benzoates: Commercially available solution of 0.5 M NaOMe in MeOH was used.

Levulinoate deprotection solution: Hydrazine acetate (550 mg) was dissolved in a mixture of Pyridine:AcOH (40 mL; 4:1) and used as a stock solution (0.15 M solution).

5.2. Protocol 1 – Swelling of resin:

The functionalized resin was loaded into the reaction vessel, dry CH_2Cl_2 was added and kept for 5 min for swelling of the resin. The solvent was drained before starting the reaction.

5.3 Protocol 2 - Glycosylation with carbonate donor:

The building block donor solution (4 equiv, 0.125 mmol) in 2 mL dry CH_2Cl_2 was delivered under nitrogen atmosphere to the reaction vessel containing the resin. The resin was then allowed to mix with donor solution for 10 min by bubbling N_2 gas. After that, with the small interruption of N_2 bubbling, solid gold phosphite (10 mol %); Silver triflate (15 mol%) was added to the reaction vessel. The reaction mixture is then left for 30 min under Nitrogen bubbling. The solution is drained and the resin is washed with CH_2Cl_2, DMF and CH_2Cl_2 (3x with 2 mL for 15 s sequentially).

With the use of CH_2Cl_2 solvent resin was then transferred to another reaction vessel and washed it with 2 mL dry CH_2Cl_2 three times. Resin is then dried using vacuum pump.

5.4 Protocol 3 – TBDPS deprotection using HF/Pyridine:

The resin was washed with dry CH_2Cl_2 two times and then dry Pyridine (1.5 mL) was added. The resin was agitated using N_2 bubbling for 5 min then 0.6 mL of HF.Pyridine solution (70% HF in Pyridine) was added drop wise under inert atmosphere at room temperature for 15 h. The reaction vessel was emptied into the waste, washed with CH_2Cl_2, DMF, and CH_2Cl_2 (3x2mL). Resin was then dried under high vacuum.

5.5 Protocol 4 - Bz deprotection using NaOMe solution:

To the swollen resin in CH_2Cl_2 (2 mL), NaOMe solution (0.5 N NaOMe in MeOH) in 1 mL was added. Resin was agitated using N_2 bubbling for 1 h, the solution was drained. Washed resin with MeOH and CH_2Cl_2, (3x2 mL each). Resin was then dried under high vacuum.

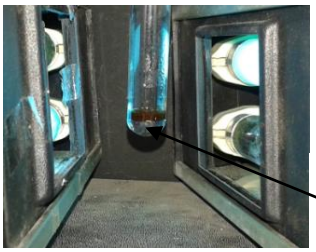
5.6 Protocol 5 - Levulinoate deprotection using Hydrazine Acetate solution:

The resin is washed with CH_2Cl_2 (3x2 mL), swollen in 1.5 mL CH_2Cl_2, at the room temperature. For Lev deprotection, 0.8 mL of 0.15 M solution of hydrazine acetate in pyridine/acetic acid (stock solution) was added. After 30 min, the reaction solution was drained and the resin was washed with 0.2 M acetic acid in CH_2Cl_2 and CH_2Cl_2 (6x2 mL). The entire procedure is repeated twice.

6.0 Post-synthesis Protocols

6.1 Protocol I - Photocleavage: The resin ready for deprotection was transferred to the 15 mL glass test tube fitted with a rubber septum, dry CH_2Cl_2 (1 mL) was added under nitrogen atmosphere and then kept under the UV-visible cabinet fitted with a light of wavelength range 365 nm for 4 h. The resin was then carefully filtered through a column with a frit. The resin was washed with CH_2Cl_2 (5x2 mL), combined filtrates were evaporated under vacuum to obtain a residue which was redissolved in CH_2Cl_2 and UPLC-MS was performed.

Photocleavage reaction setup



6.2 Protocol II - Purification of protected oligosaccharide: Protected oligosaccharides after cleavage from the solid support were purified by silica gel column chromatography using hexane:ethyl acetate system for complete characterization.

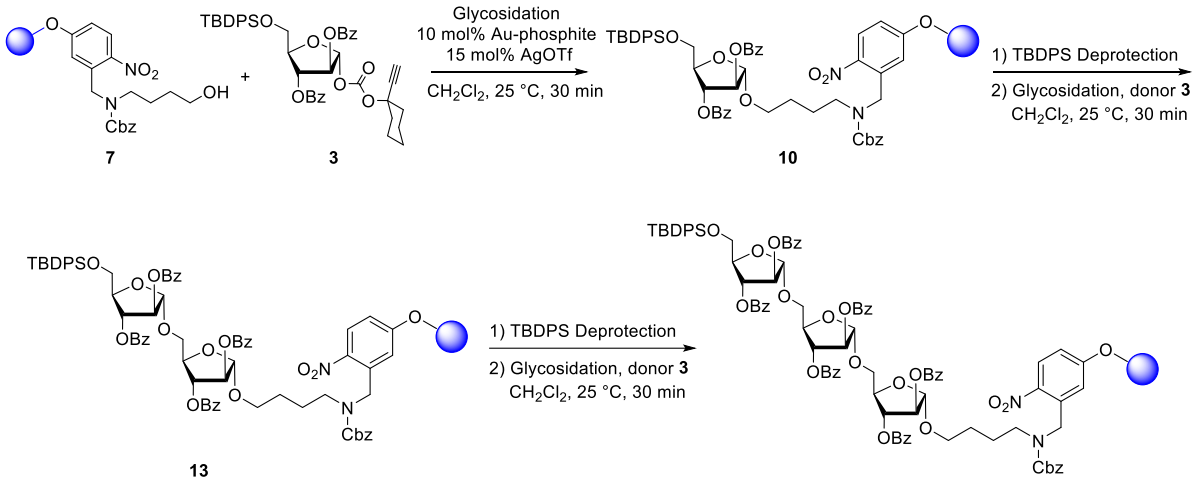
6.3 Protocol III - HPLC purification of partially protected oligosaccharide: The crude oligosaccharide mixtures were purified by semi-preparative HPLC (Agilent 1260 infinity II series) recording on DAD at a wavelength of 214 nm. Column: RP-C_{18} (10µ 250 × 10 mm, 110 Å). Eluent A: 0.1% TFA in water/CH_3CN (95:5) and B: 0.1% TFA in CH_3CN/water (95:5) were used in a linear gradient of 0 to 40% (10 min) to 60% (25 min) to 100% (30 min) at a flow rate of 2 mL/min.

6.4 Protocol IV HPLC purity analysis: Purity of compounds **1** and **2** was ascertained by re-injecting the purified sample into semi preparative HPLC (Agilent 1260 infinity II series) and was recorded by DAD using a flow of 2 mL/min on a RP-C_{18} column (5 µm, 250 mm, 4.6 mm, 110 Å). Eluents A (0.1% TFA in water) and B (0.1% TFA in CH_3CN) were used in a linear gradient of 0 to 40% (10 min) to 60% (25 min) to 100% (30 min) at a flow rate of 2 mL/min.

7.0 Optimization of glycosidation and deprotection:

7.1 Glycosidation reaction on solid support:

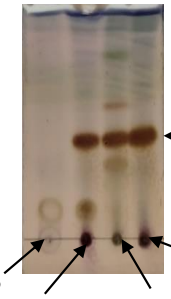
The first glycosidation reaction on the solid support was performed in dry CH_2Cl_2 using 4 equivalents of donor and 10 mol% of solid gold-phosphite, 15 mol% of silver triflate at room temperature for 30 min. Photocleaved products at regular intervals were subjected to TLC analysis. The first glycosidation reaction was completed with one time coupling using 4 equivalents of the donor.



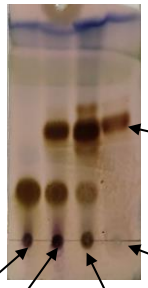
Note: (a) Reduction of the number of the equivalents of donor was found to be detrimental for the complete conversion. (b) Concentration of 0.3 g per 2.0 mL of solvent was found to yield best results. (c) 30 min for the glycosylation reaction was found to be the best.

TLC of the first glycosylation	Optimization of the second glycosylation with number of equivalents of donor

Monosaccharide with TBDPS



Optimization of the third glycosylation with number of equivalents of donor



TBDPS and Bz deprotection standardization: For the cleave of the TBDPS moiety, the resin was treated with 0.4 mL of HF•pyridine in 1 mL anhydrous pyridine for 15 h. For saponification of benzoates, the resin was treated with 0.5 M NaOMe in methanol solution (1 mL) for 1 h.

8.0 Synthesis of linear and branched oligosaccharides:

8.1 Scheme for synthesis of linear oligosaccharide 14:

The reaction vessel (10 mL PTFE vial) was charged with the functionalized resin **7** (150 mg; loading 0.94 mmol/g; 0.141 mmol) and CH_2Cl_2 (2 mL) was added for swelling. To start the synthesis, the resin was washed with dry CH_2Cl_2 (2x) and then coupling/deprotection cycle were performed as depicted in Table S1. This cycle was repeated 5 times to produce pentasaccharide **14**.

Supplementary Table: All Coupling/ deprotection cycle were carried out at room temperature.

Table S1: general protocol for linear pentasaccharide **14** synthesis.

Glycosidation sequence	Protocol	Details	Time	Cycle
1 monosaccharide synthesis	1	2 mL dry CH_2Cl_2	5 min	2
	2	4 eq of donor **3** in 2 mL dry CH_2Cl_2	30 min	1
Resin was transferred to another flask				
2	1	2 mL dry CH_2Cl_2	5 min	2

disaccharide synthesis	3	1 mL dry Py + 70% HF/Py 0.4 mL	15 h	1
	2	4 eq of donor **3** in 2 mL dry CH_2Cl_2	30 min	1
Resin was transferred to another flask				
3 trisaccharide synthesis	1	2 mL dry CH_2Cl_2	5 min	2
	3	1 mL dry Py + 70% HF/Py 0.4 mL	15 h	1
	2	4 eq of donor **3** in 2 mL dry CH_2Cl_2	30 min	1
Resin was transferred to another flask				
4 tetrasaccharide synthesis	1	2 mL dry CH_2Cl_2	5 min	2
	3	1 mL dry Py + 70% HF/Py 0.4 mL	15 h	1
	2	4 eq of donor **3** in 2mL dry CH_2Cl_2	30 min	1
Resin was transferred to another flask				
5 pentasaccharide synthesis	1	2 ml dry CH_2Cl_2	5 min	2
	3	1 mL dry Py + 70% HF/Py 0.4 mL	15 h	1
	2	4 eq of donor **3** in 2 mL dry CH_2Cl_2	30 min	1
Resin was transferred to another flask				

At every stage of the glycosylation and deprotection cycle, 3 mg of the resin was removed and subjected to the photocleavage (Protocol **I**) and the crude filtrate was subjected to UPLC to understand efficiency of the reaction.

After completion of synthesis of linear pentasaccharide, the total weight of substrate attached resin was found to be 320 mg that was divided into two portions (70 mg and 250 mg). Resin (70 mg) was exposed to UV light to identify fully protected linear pentasacchride **14** and another portion of 250 mg resin was subjected to deprotection of silyl- and Bz- moieties as described above. Subsequently, resin bound fully deprotected glycan with NHCbz linker was exposed to the UV light to obtain desired glycan **1**.

Sample preparation: Photocleaved product obtained from the 3 mg of the resin was filtered, concentrated, redissolved in 300 µL of acetonitrile and transferred to septum sealed, screw capped 1 mL Wheaton vial.

Experimental:

UPLC conditions

UPLC system: *Acquity* UPLC H-Class with PDA detector
Sample manager: Flow-through needle
Column: ACQUITY UPLC BEH C18 1.7 µm (2.1x 50 mm column)
Mobile Phase A: Water+ Formic acid (0.1% solution)
Mobile Phase B: Acetonitrile + Formic acid (0.017% solution)
Column temp.: 25 °C
Sample temp.: 25 °C
Flow rate: 0.5 mL/min
Run time: 30 min

Injection volume: 5 µL
UV detection: 190 nm – 500 nm (20 points/sec)

Gradient:

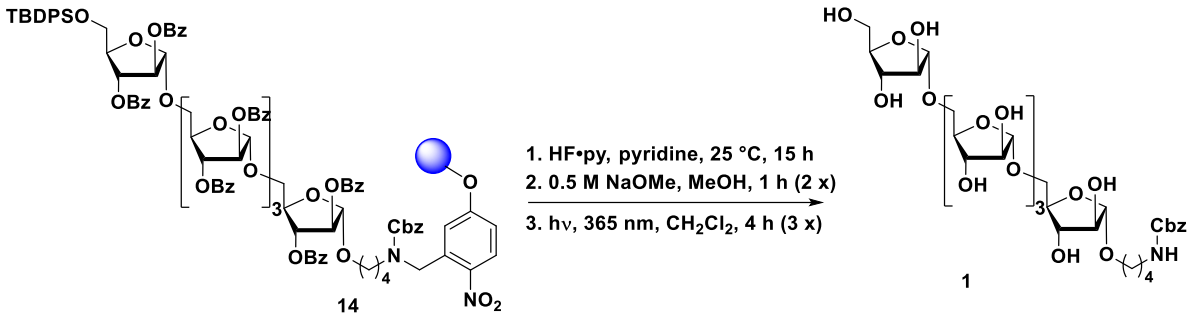
Time (min)	%A	%B
0.0	100	0.0
5.0	50.0	50.0
8.0	20.0	80.0
11.0	10.0	90.0
23.0	0.0	100.0
24.0	40.0	60.0
25.0	70.0	30.0
26.0	100	0.0
30.0	100	0.0

Cleavage, purification and analysis of protected linear pentasaccharide **14**:

Pentasaccharide **14** was cleaved off from the solid support as delineated in protocol **I**, concentrated and the residue was purified by normal phase silica gel column chromatography (hexane:ethyl acetate) to give the linker attached fully protected arabinofuranosyl pentasaccharide **14** (13.4 mg, 20% yield, 0.031 mmol) as a white solid.

***N*-benzyloxycarbonyl 4-aminobutyl 2,3-di-*O*-benzoyl-5-*O*-[2,3-di-*O*-benzoyl-5-*O*-[2,3-di-*O*-benzoyl-5-*O*-[2,3-di-*O*-benzoyl-5-*O*-[2,3-di-*O*-benzoyl-5-*O*-^{t}butyldiphenylsilyl-α-D-arabinofuranosyl]-α-D-arabinofuranosyl]-α-D-arabinofuranosyl]-α-D-arabinofuranosyl]-α-D-arabinofuranoside (14):** $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0): +1.0; IR (cm^{-1}): 3845, 3740, 3671, 3615, 2924, 2860, 2355, 1720, 1523, 1461, 1262, 1107, 969, 706; ^{1}H NMR (600.40 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 10.8, 7.9 Hz, 7H), 7.96 (dd, *J* = 7.0, 5.2 Hz, 4H), 7.88 (dt, *J* = 16.6, 8.4 Hz, 7H), 7.68 (t, *J* = 6.2 Hz, 4H), 7.56 – 7.35 (m, 23H), 7.34 – 7.27 (m, 14H), 7.25 – 7.20 (m, 6H), 5.62 (dd, *J* = 11.3, 4.6 Hz, 7H), 5.54 (s, 1H), 5.47 (s, 1H), 5.37 (dd, *J* = 9.6, 8.0 Hz, 4H), 5.19 (s, 1H), 5.05 (s, 1H), 4.86 (s, 1H), 4.58 (dd, *J* = 8.1, 3.9 Hz, 3H), 4.47 (q, *J* = 4.6 Hz, 1H), 4.42 (d, *J* = 2.7 Hz, 1H), 4.20 – 4.12 (m, 4H), 3.98 – 3.87 (m, 6H), 3.78 – 3.72 (m, 1H), 3.50 (d, *J* = 12.4 Hz, 3H), 3.22 (d, *J* = 5.8 Hz, 2H), 1.60 (s, 4H), 0.99 (s, 9H); ^{13}C NMR (150.99 MHz, $CDCl_3$): δ 165.6, 165.6, 165.6, 165.6, 165.5, 165.5, 165.2, 165.2, 165.1, 165.1, 136.6, 135.7(2C), 135.6(2C), 133.4(2C), 133.4, 133.4, 133.3, 133.3, 133.2, 133.2, 133.2, 133.1(2C), 133.0, 129.9(2C), 129.8(11C), 129.8(9C), 129.6(2C), 129.3, 129.2(2C), 129.1(3C), 129.1, 129.0(2C), 129.0, 128.5(10C), 128.4(2C), 128.3(2C), 128.3(2C), 128.2(4C), 128.2(2C), 128.1, 128.1, 127.6(4C), 105.9(2C), 105.9, 105.8, 105.6, 83.1, 82.1(4C), 81.9, 81.9, 81.5, 81.5, 81.5, 77.2(5C), 67.0, 66.6, 66.0, 65.8, 65.8, 65.7, 63.4, 40.8, 26.8, 26.7(3C), 26.7, 19.3; (MALDI-TOF) $[M+Na]^+$ m/z calcd for $[C_{123}H_{115}NO_{33}SiNa]^+$: 2184.7018; found: 2184.7018.

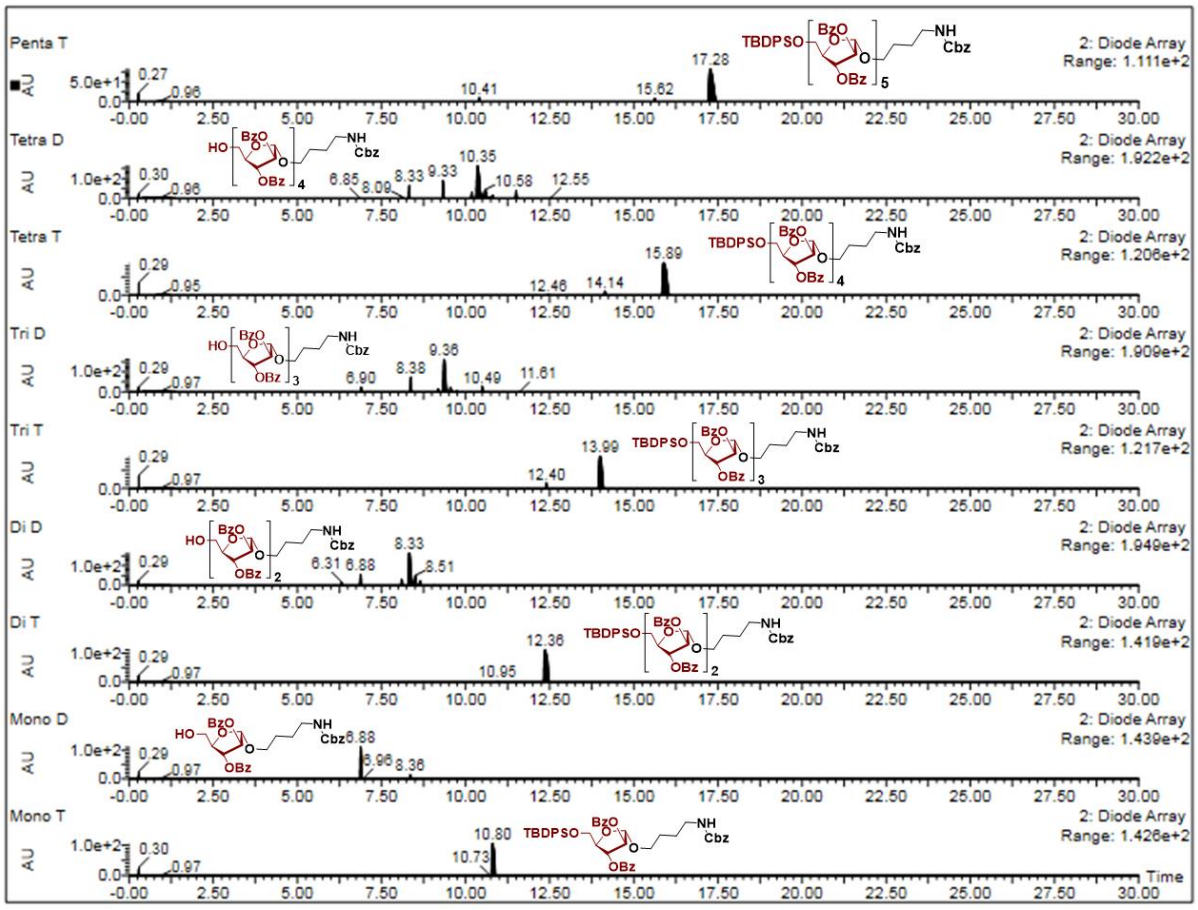
Synthesis of partially deprotected linear pentasaccharide 1:



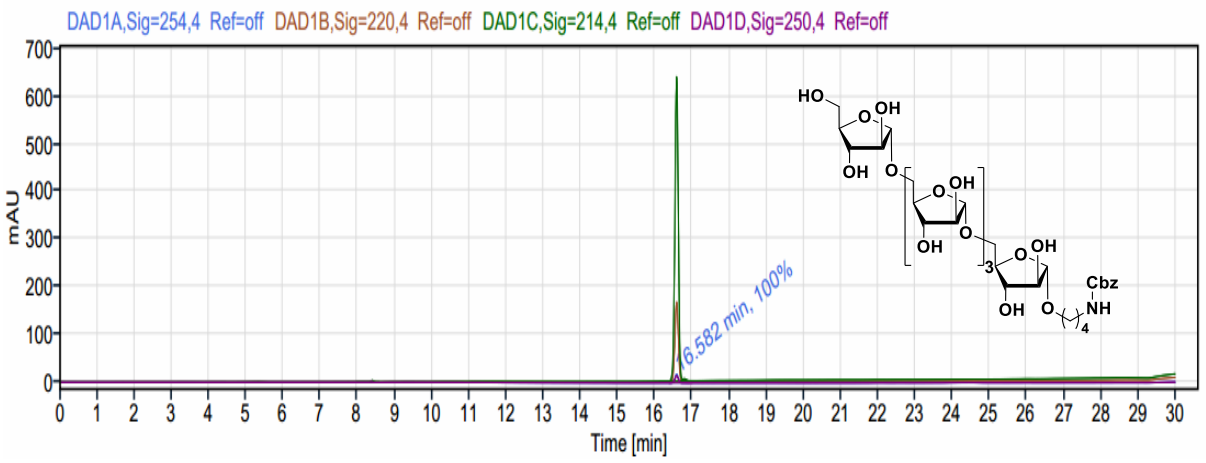
Portion of functionalized resin **14** was treated with HF•py in pyridine followed by 0.5 M NaOMe solution to remove all temporary protecting groups. Pentasaccharide **1** was cleaved from solid support using protocol **I** and the desired pentasaccharide **1** was purified by semi-preparative HPLC (protocol **III**) to afford compound **1** (8.9 mg, 9% yield, 0.110 mmol).

***N*-benzyloxycarbonyl 4-aminobutyl 5-*O*-[5-*O*-[5-*O*-[5-*O*-[α-D-arabinofuranosyl]-α-D-arabinofuranosyl]-α-D-arabinofuranosyl]-α-D-arabinofuranosyl]-α-D-arabinofuranoside (1):** $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0): +92.0; ^{1}H NMR (400.31 MHz, CD_3OD): δ 7.38 – 7.28 (m, 5H), 5.08 (s, 2H), 4.96 (s, 5H), 4.11-4.07 (m, 3H), 4.03 – 4.00 (m, 5H), 3.97 – 3.95 (m, 1H), 3.93 - 3.88 (m, 5H), 3.88 – 3.81 (m, 5H), 3.76 (dd, *J* = 11.9, 3.3 Hz, 1H), 3.70 – 3.62 (m, 6H), 3.48 - 3.42 (m, 1H), 3.16 (t, *J* = 6.5 Hz, 2H), 1.65 – 1.56 (m, 4H); ^{13}C NMR (150.99 MHz, CD_3OD): δ 158.9, 138.5, 129.4(2C), 128.9, 128.8(2C), 109.7(3C), 109.6, 109.5, 85.9, 84.1(3C), 83.6, 83.5, 83.2(3C), 83.1, 79.1(3C), 79.1, 78.7, 68.5, 68.2, 68.2, 68.1(2C), 67.3, 63.1, 41.5, 27.9, 27.7. (MALDI-TOF) $[M+Na]^+$ m/z calcd for $[C_{37}H_{57}NO_{23}Na]^+$: 906.3225; found: 906.3230.

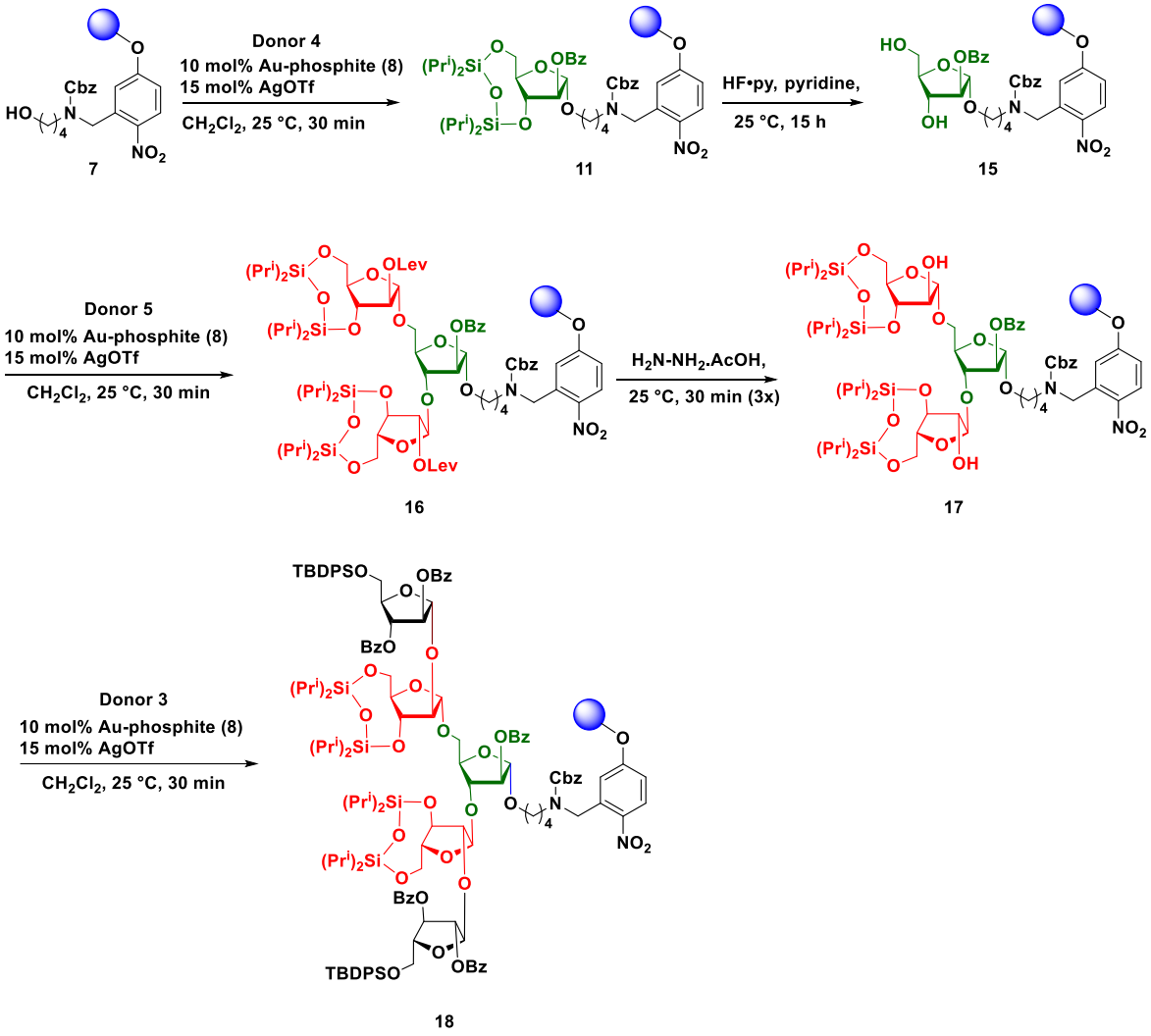
UPLC traces of the Linear Pentasaccharide **1** Synthesis



Analytical purity of pentasaccharide **1** using Semi-preparative HPLC
(DAD trace, Protocol **IV**, tR = 30.0 min)



8.2 Scheme for synthesis of branched pentasaccharide 18



Functionalized resin **7** (100 mg; loading 0.94 mmol/g; 0.094 mmol) was loaded into the reaction vessel (10 mL PTFE vial) and allowed to swell by adding 2 mL of CH_2Cl_2. Coupling/deprotection cycles were performed as depicted in Table S2. Importantly, double glycosidation using donor **5** was also completed in a stereoselective manner within 0.5 h to give compound **16**. This cycle was repeated to furnish branched pentasaccharide **18**.

Supplementary Table: All Coupling/deprotection cycle were carried out at room temperature.

Table S2: General protocol for branched pentasaccharide **18** synthesis.

Glycosidation sequence	Protocol	Details	Time	Cycle
1 monosaccharide synthesis	1	2 mL dry CH_2Cl_2	5 min	2
	2	4 eq of donor **4** in 2 mL dry CH_2Cl_2	30 min	1
Transfer resin to another flask using CH_2Cl_2				

2 trisaccharide synthesis	3	2 mL dry Py + 70% HF/Py 0.8 mL	15 h	1
	1	2 mL dry CH_2Cl_2	5 min	2
	2	8 eq of donor **5** in 2 mL dry CH_2Cl_2	30 min	1
Transfer resin to another flask using CH_2Cl_2				
3 pentasaccharide synthesis	5	1 mL Hydrazine Acetate 0.15 M solution	1 h	3
	1	2 mL dry CH_2Cl_2	5 min	2
	2	8 eq of donor **3** in 2 mL dry CH_2Cl_2	30 min	1

At every stage of the glycosylation and deprotection cycle, 3 mg of the resin was removed and subjected to the photocleavage (Protocol **I**) and the crude filtrate was subjected to UPLC to understand efficiency of the reaction.

After completion of the synthesis of branched trisaccharide, the total weight of substrate attached resin was found to be 150 mg from which 60 mg of the resin was exposed to UV light to identify fully protected trisaccharide **16** in protected form. Remaining resin-bound fully protected trisaccharide was subjected to the glycosidation to afford branched pentasaccharide **18**; resulting resin of 130 mg was divided into two portions (50 mg and 80 mg), 50 mg resin was exposed to UV light to identify fully protected branched pentasaccharide **18** and another portion of 80 mg resin was treated with reagents to carry out on resin deprotection of all silyl- and Bz-groups. Subsequently, we irradiated the resin with UV light to obtain N-Cbz protected aminobutyl pentaarabinofuranoside **2**.

Sample preparation: Photocleaved product obtained from the 3 mg of the resin was filtered, concentrated, redissolved in 300 µL of acetonitrile and transferred to septum sealed, screw capped 1 mL Wheaton vial.

Experimental:

UPLC conditions

UPLC system: *Acquity* UPLC **H-**Class with PDA detector
Sample manager: Flow-through needle
Column: ACQUITY UPLC BEH C18 1.7µm (2.1x 50 mm column)
Mobile Phase A: Water+ Formic acid (0.1% solution)
Mobile Phase B: Acetonitrile + Formic acid (0.017% solution)
Column temp.: 25 °C
Sample temp.: 25 °C
Flow rate: 0.5 mL/min
Run time: 30 min
Injection volume: 5 µL
UV detection: 190 nm – 500 nm (20 points/sec)
Gradient:

Time (min)	%A	%B
0.0	100	0.0
5.0	50.0	50.0

8.0	20.0	80.0
11.0	10.0	90.0
23.0	0.0	100.0
24.0	40.0	60.0
25.0	70.0	30.0
26.0	100	0.0
30.0	100	0.0

Cleavage, purification and analysis of protected branched oligosaccharide **16** and **18**:

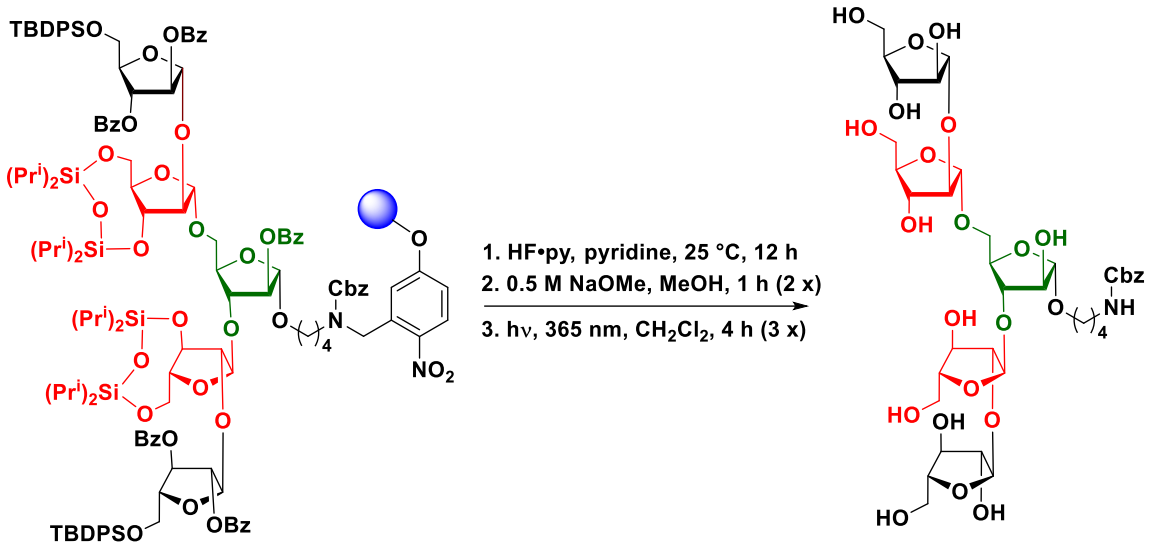
Compound **16** was then cleaved from solid support as described in protocol **I**. The crude product was purified by normal phase chromatography (Silica, hexane: ethyl acetate) to give linker attached fully protected trisaccharide arabinofuranoside **16** (13.8 mg, 26% from 0.038 mmol) as a colourless liquid which was confirmed by NMR.

***N*-benzyloxycarbonyl 4-aminobutyl 2-*O*-benzoyl-3,5-di-*O*-[2-*O*-levulinoyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-α-D-arabinofuranosyl]-α-D-arabinofuranoside (16):** $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0): +0.037**;** ^{1}H NMR (600.40 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.27 (m, 5H), 5.29 – 5.19 (m, 4H), 5.14 – 5.08 (m, 4H), 4.94 (d, *J* = 1.1 Hz, 1H), 4.30 – 4.25 (m, 2H), 4.23 (s, 2H), 4.00 – 3.90 (m, 6H), 3.87 (dd, *J* = 10.3, 3.4 Hz, 1H), 3.75 (s, 1H), 3.72 – 3.69 (m, 1H), 3.52 – 3.46 (m, 1H), 3.26 (d, *J* = 5.4 Hz, 2H), 2.73 – 2.68 (m, 4H), 2.61 – 2.54 (m, 4H), 2.14 (s, 3H), 2.11 (s, 3H), 1.63 – 1.59 (m, 4H), 1.10 – 0.98 (m, 56H); ^{13}C NMR (150.97 MHz, $CDCl_3$): δ 206.4, 206.3, 172.0, 171.7, 165.8, 156.7, 137.0, 133.4, 130.0(2C), 129.6, 128.6(2C), 128.6(3C), 128.2, 128.1, 106.0, 105.3, 104.4, 84.0, 84.0, 82.6, 81.3, 81.2, 81.1, 80.9, 76.1, 75.9, 67.1, 66.5, 66.5, 61.6, 61.6, 41.0, 38.0, 37.9, 29.9, 29.9, 28.0, 27.9, 26.7, 26.7, 17.6(2C), 17.5(3C), 17.5(3C), 17.1, 17.1, 17.1(2C), 17.1(2C), 17.0(2C), 13.6, 13.5, 13.3(2C), 12.9, 12.9, 12.6, 12.6; (MALDI-TOF) $[M+Na]^+$ m/z calcd for $[C_{68}H_{109}NO_{22}Si_4Na]^+$: 1426.6416; found: 1426.6420.

***N*-benzyloxycarbonyl 4-aminobutyl 2-*O*-benzoyl-3,5-di-*O*-[2-*O*-[2,3-di-*O*-benzoyl-5-*O*-^{t}-butyldiphenylsilyl-α-D-arabinofuranosyl]-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-α-D-arabinofuranosyl]-α-D-arabinofuranoside (18):** (14.0 mg, 27% from 0.022 mmol); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0): +0.036; IR (cm^{-1} $CHCl_3$); 3845, 3740, 3671, 3616, 2925, 2861, 2354, 1917, 1726, 1523, 1462, 1261, 1106, 1042, 881, 792, 702. ^{1}H NMR (600.40 MHz, $CDCl_3$) δ 8.08 – 8.06 (m, 2H), 8.05 – 8.02 (m, 2H), 7.96 – 7.92 (m, 4H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.69 – 7.64 (m, 9H), 7.59 – 7.51 (m, 5H), 7.45 – 7.38 (m, 7H), 7.37 – 7.32 (m, 7H), 7.32 – 7.28 (m, 8H), 7.25 – 7.21 (m, 4H), 5.74 (d, *J* = 4.5 Hz, 1H), 5.63 (d, *J* = 4.7 Hz, 1H), 5.49 (s, 1H), 5.47 (d, *J* = 1.1 Hz, 1H), 5.39 (d, *J* = 3.7 Hz, 2H), 5.36 (d, *J* = 2.2 Hz, 1H), 5.21 (s, 1H), 5.06 (d, *J* = 2.0 Hz, 1H), 5.03 (s, 1H), 4.91 (s, 1H), 4.84 (t, *J* = 5.5 Hz, 1H), 4.60 (dd, *J* = 8.9, 4.5 Hz, 1H), 4.41 (q, *J* = 4.5 Hz, 1H), 4.26 – 4.22 (m, 3H), 4.21 – 4.17 (ddd, *J* = 8.0, 6.2, 2.2 Hz, 2H), 4.15 (dd, *J* = 7.3, 4.7 Hz, 1H), 4.06 (dd, *J* = 10.9, 3.7 Hz, 1H), 4.00 – 3.94 (m, 4H),

3.94 - 3.88 (m, 4H), 3.83 – 3.73 (m, 4H), 3.70 (dd, *J* = 11.0, 2.4 Hz, 1H), 3.50-3.46 (m, 1H), 3.22 – 3.17 (m, 1H), 2.99 (d, *J* = 5.8 Hz, 1H), 1.64 – 1.61 (m, 4H), 1.07 – 0.97 (m, 60H), 0.95 – 0.92 (m, 14H). ^{13}C NMR (150.97 MHz, $CDCl_3$) δ 165.7, 165.6, 165.2, 165.2(2C), 156.3, 136.8, 135.6(8C), 133.3(3C), 133.3, 133.2, 133.1(2C), 133.1, 133.1, 129.9(11C), 129.8(3C), 129.8(3C), 129.7, 129.6, 129.6, 129.6(3C), 129.5, 129.4, 129.2, 129.2, 128.4, 128.4, 128.4(2C), 128.3(2C), 128.0, 127.9, 127.7(4C), 127.6(3C), 106.5, 106.2, 105.8, 105.6, 104.3, 88.6, 88.4, 83.4, 83.3, 82.3, 82.3, 82.1, 81.9, 80.5, 79.8, 79.6, 77.6, 77.3, 75.9, 75.6, 66.6, 66.5, 66.4, 63.3, 63.2, 61.0, 60.8, 40.6, 26.7(6C), 26.4, 26.4, 19.3, 19.3, 17.5, 17.5, 17.4, 17.3(3C), 17.3(2C), 17.1(2C), 17.0, 17.0, 16.9, 16.9, 16.9(2C), 13.5, 13.4, 13.1, 13.1, 12.8, 12.7, 12.4, 12.4. (MALDI-TOF) $[M+K]^+$ m/z calcd for $[C_{128}H_{165}NO_{30}Si_6Na]^+$: 2386.9930; found: 2386.9927.

Synthesis of partially deprotected branched pentasaccharide **2**



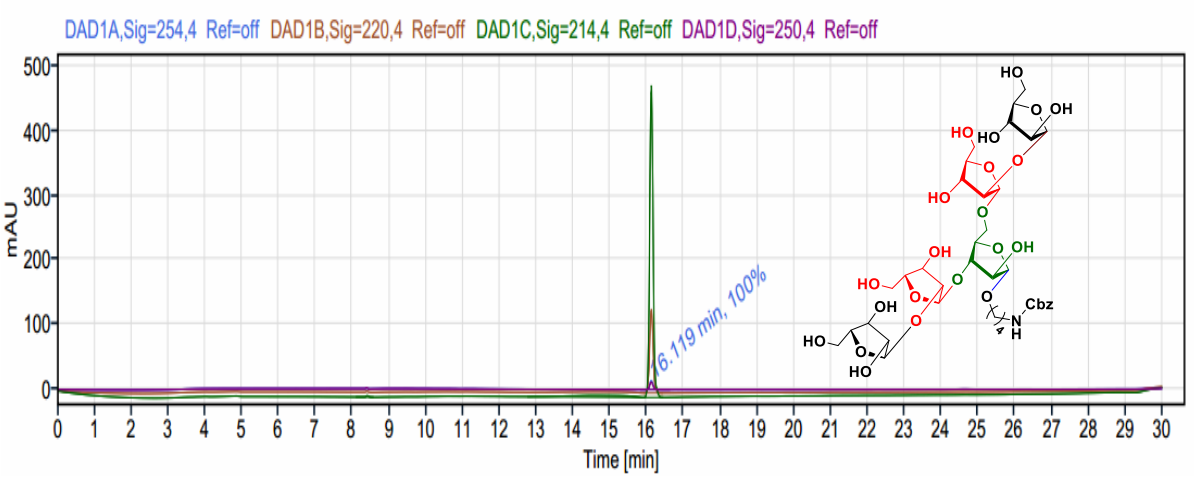
Cleavage, purification and analysis of partially deprotected branched oligosaccharide 2:

Portion of functionalized resin **18** was treated with HF.Py, Pyridine followed by 0.5 M NaOMe solution to remove all temporary protecting group. After that pentasaccharide **2** was released from the solid support by employing above delineated protocol **I**. The desired product **2** was purified by using semi-preparative HPLC (protocol **III**) to afford compound **2** (3.4 mg, 11% from 0.035 mmol).

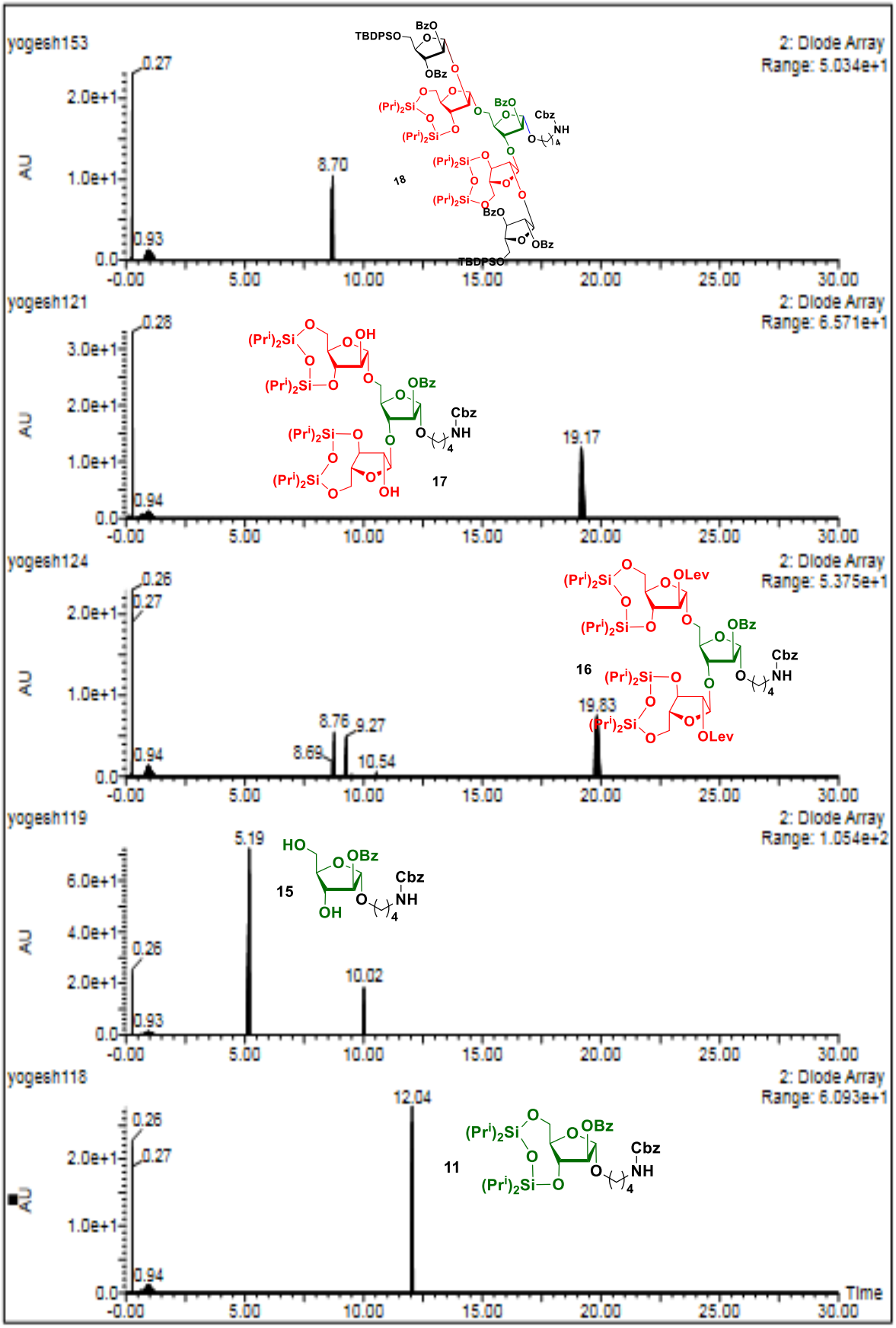
***N*-benzyloxycarbonyl 4-aminobutyl 3,5-di-*O*-[2-*O*-[α-D-arabinofuranosyl]-α-D-arabinofuranosyl]-α-D-arabinofuranoside (2):** $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0): +92.00; ^{1}H NMR (600.40 MHz, CD_3OD): δ 7.38 – 7.26 (m, 5H), 5.23 (d, *J* = 1.6 Hz, 1H), 5.11 (d, *J* = 1.2 Hz, 1H), 5.08 (d, *J* = 1.8 Hz, 1H), 5.07 (s, 1H), 5.05 (d, *J* = 1.9 Hz, 1H), 4.17 (dd, *J* = 3.1, 1.5 Hz, 1H), 4.14 (td, *J* = 5.7, 3.0 Hz, 1H), 4.09 (dd, *J* = 3.4, 1.3 Hz, 1H), 4.04 (dd, *J* = 6.4, 3.1 Hz, 1H), 4.02 (dd, *J* = 4.3, 1.6 Hz, 1H), 4.00 (dd, *J* = 4.0, 1.8 Hz, 1H), 3.99 – 3.98 (m, 2H), 3.97 – 3.93 (m, 5H), 3.92 – 3.87 (m, 3H), 3.86 – 3.81 (m,

3H), 3.80 – 3.74 (m, 5H), 3.73 – 3.69 (m, 2H), 3.66 – 3.61 (m, 5H), 3.44 (dd, *J* = 10.6, 5.7 Hz, 1H), 3.15 (t, *J* = 6.6 Hz, 2H), 1.62 – 1.58 (m, 4H); ^{13}C NMR (150.99 MHz, CD_3OD): δ 158.9, 138.5, 129.5(2C), 128.9(2C), 128.8, 109.9, 109.6, 109.3, 108.0, 107.7, 90.9, 89.6, 85.5(2C), 84.7, 84.5, 83.9, 83.8(2C), 82.5, 82.2, 78.6, 78.6, 77.5, 77.2, 68.3, 67.9, 67.3, 63.1, 62.9, 62.8, 62.5, 41.6, 27.9, 27.7; (MALDI-TOF) $[M+Na]^+$ m/z calcd for $[C_{37}H_{57}NO_{23}Na]^+$: 906.3219; found: 906.3230.

Analytical Purity of **2** using Semi-preparative HPLC (DAD trace, Protocol **IV**, tR= 30.0 min)



UPLC traces of the Branched Pentasaccharide **2** Synthesis



9.0 References:

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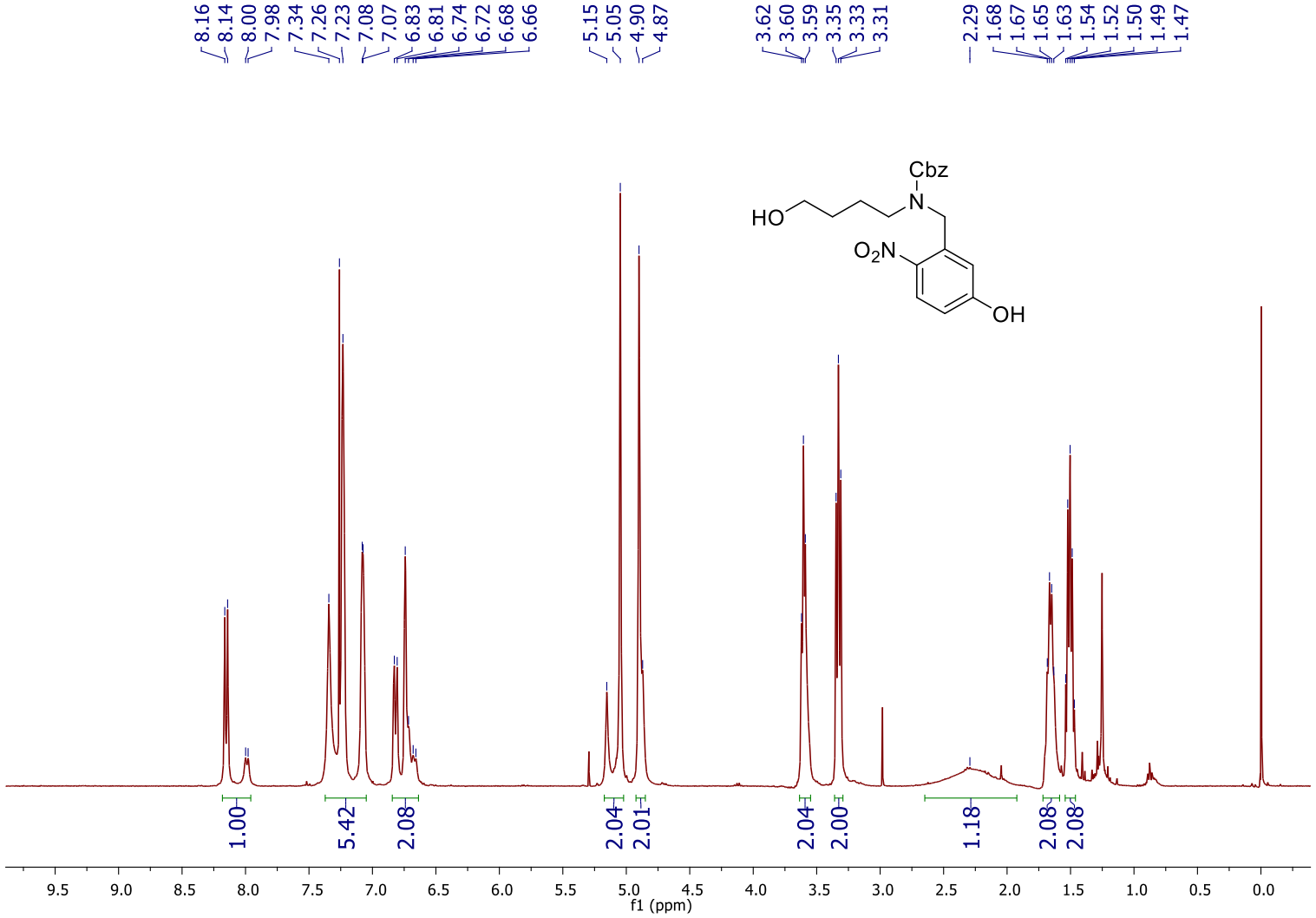
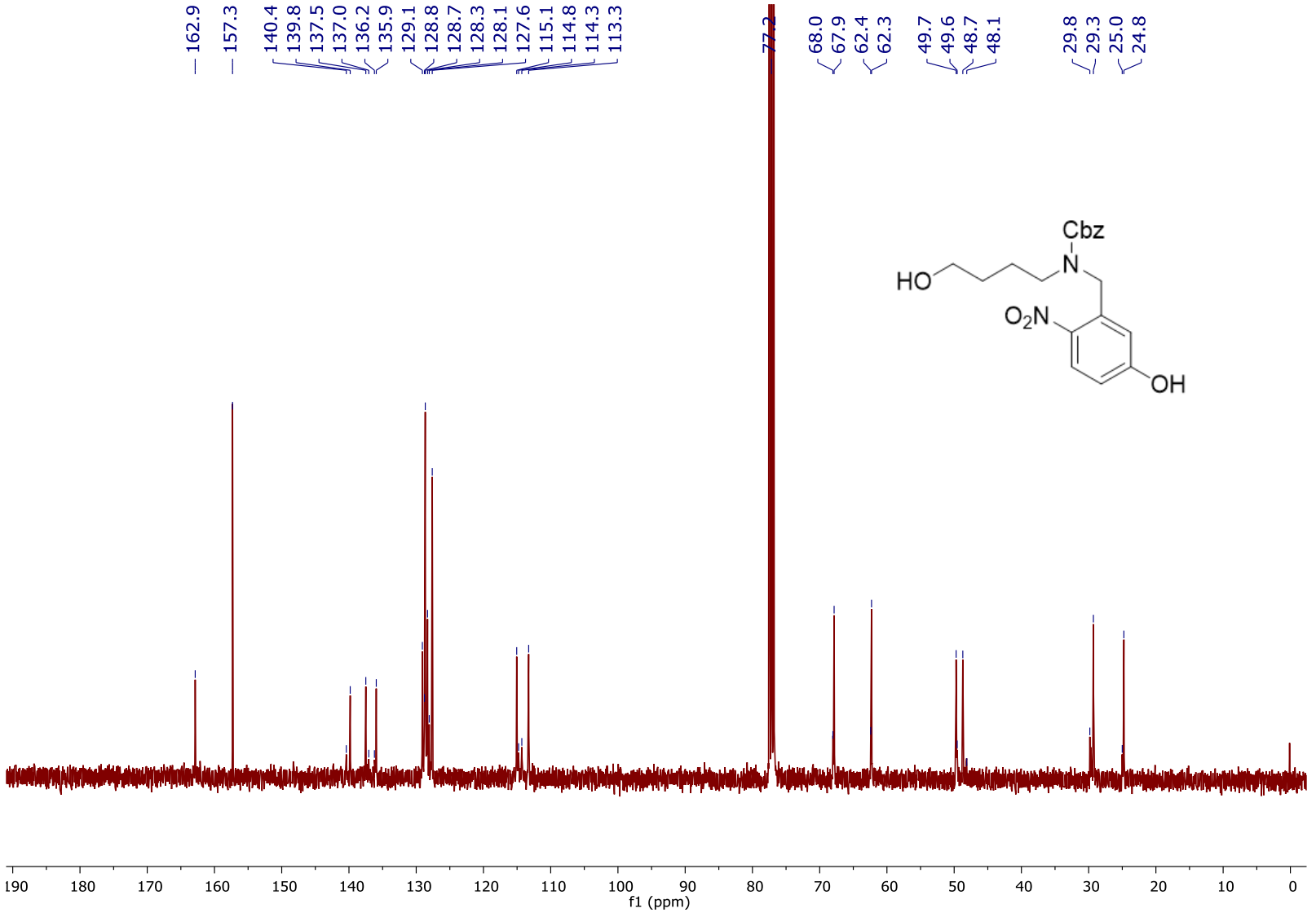
10.0 ^{1}H, ^{13}C and DEPT NMR Spectral charts of compounds

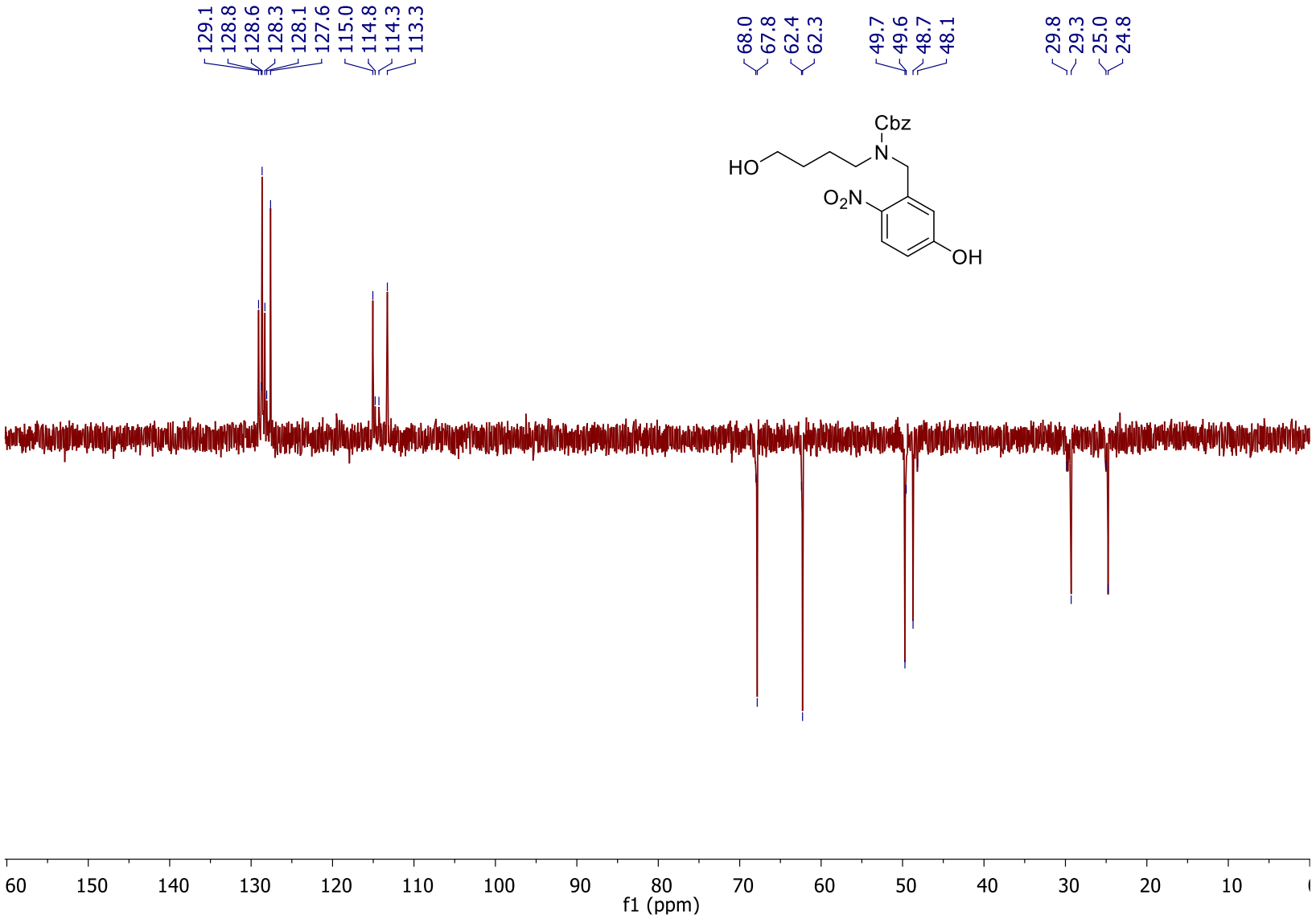
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **6**



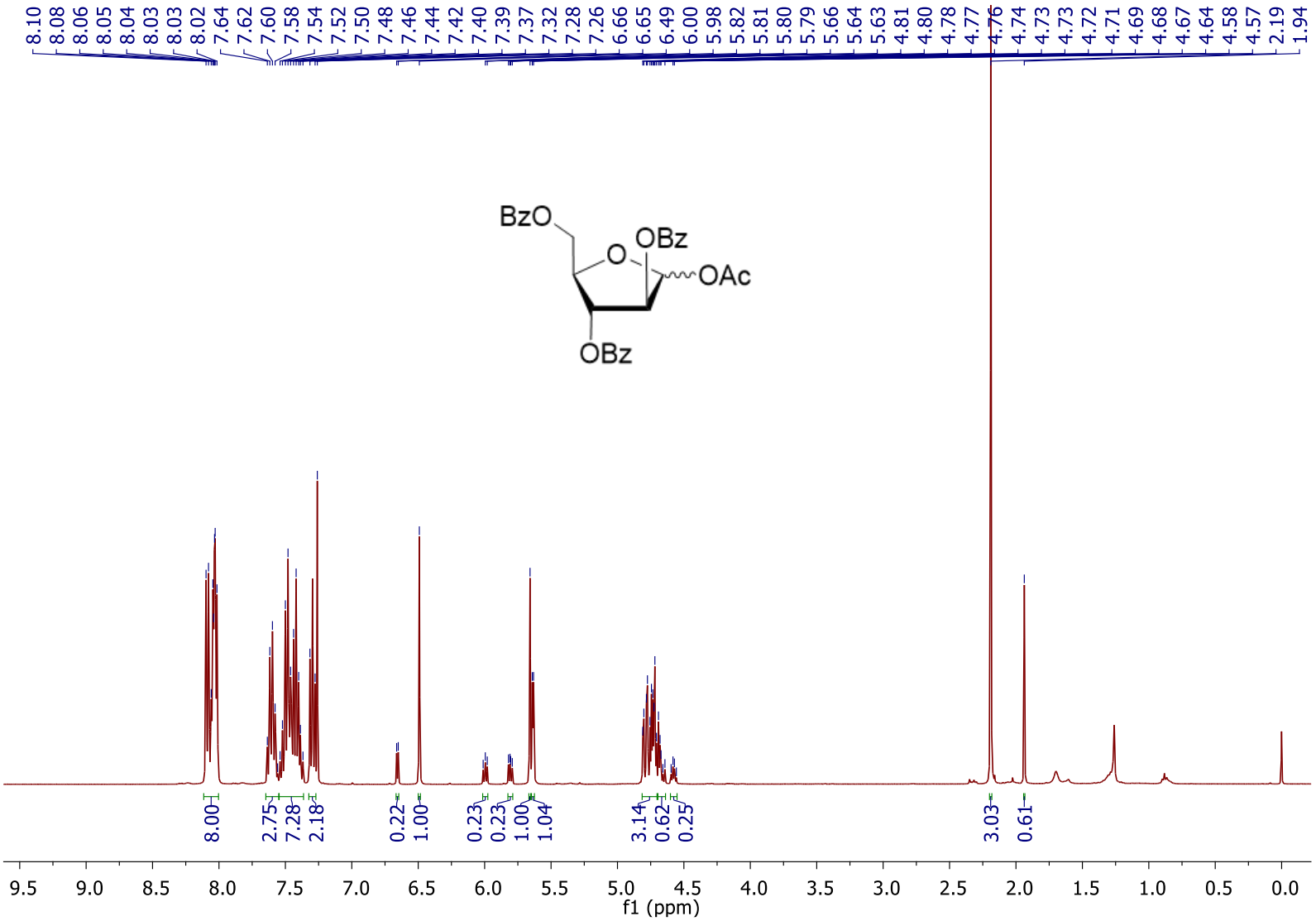
^{13}C NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **6**



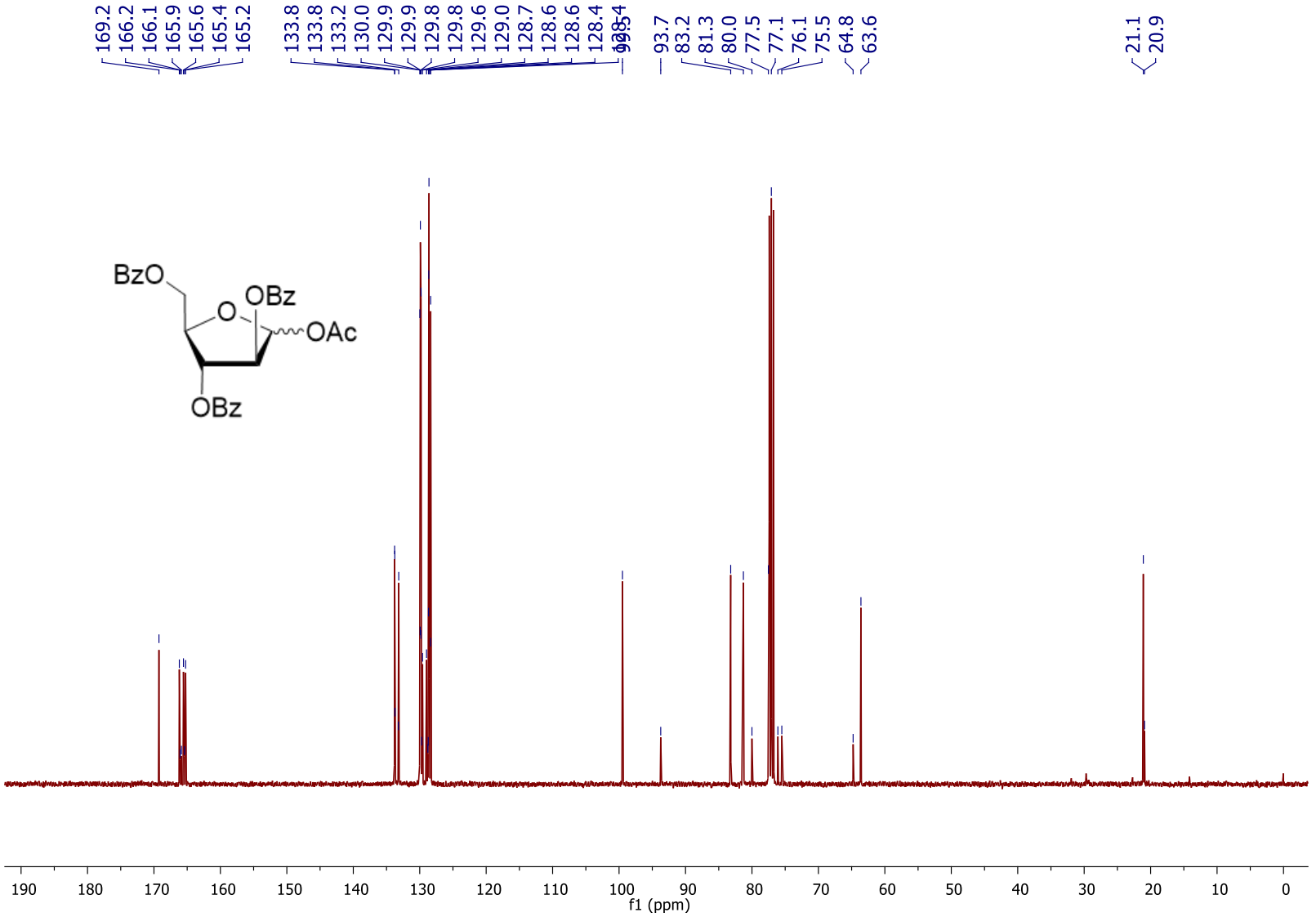
DEPT-135 NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **6**



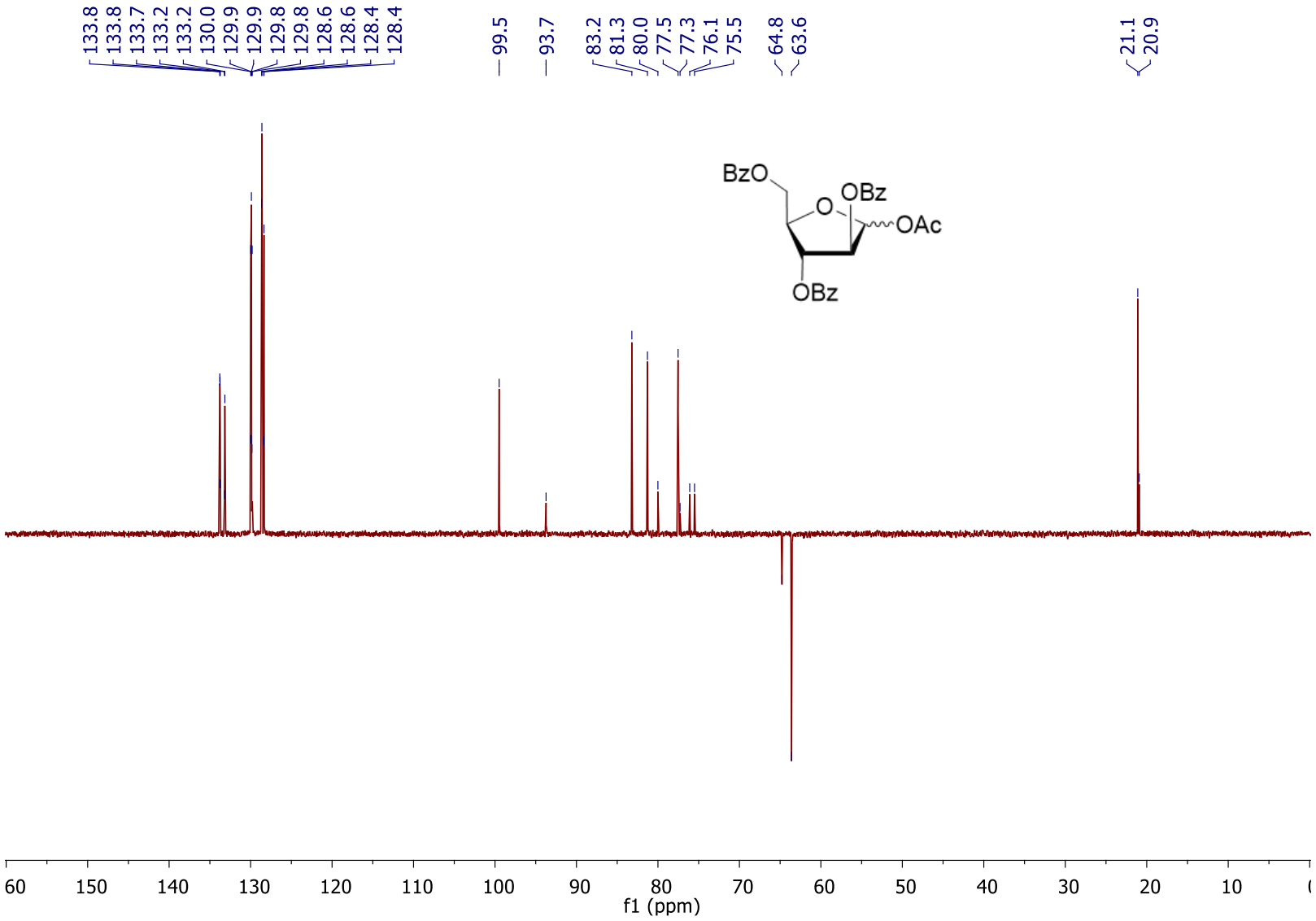
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **S2**



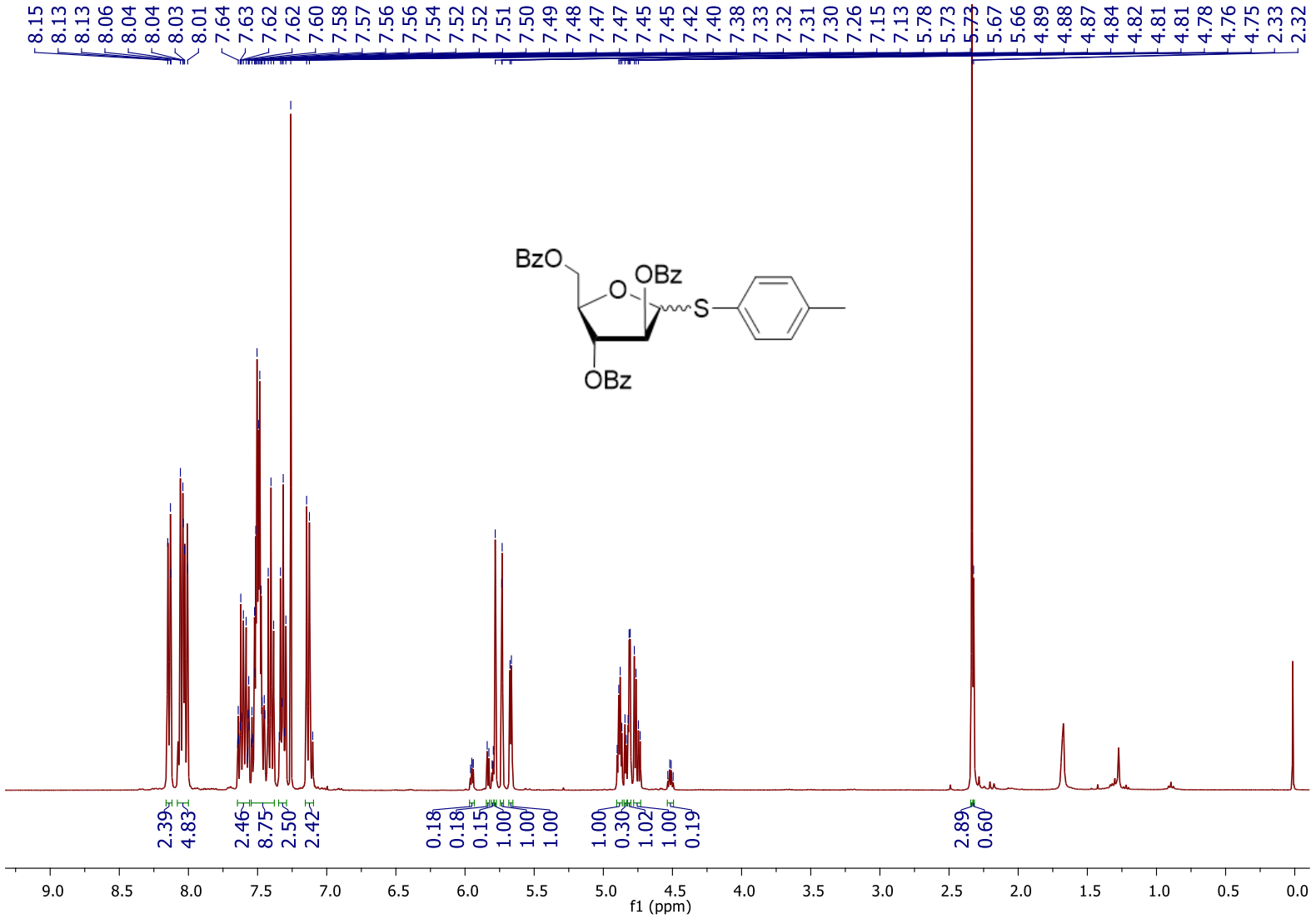
^{13}C NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **S2**



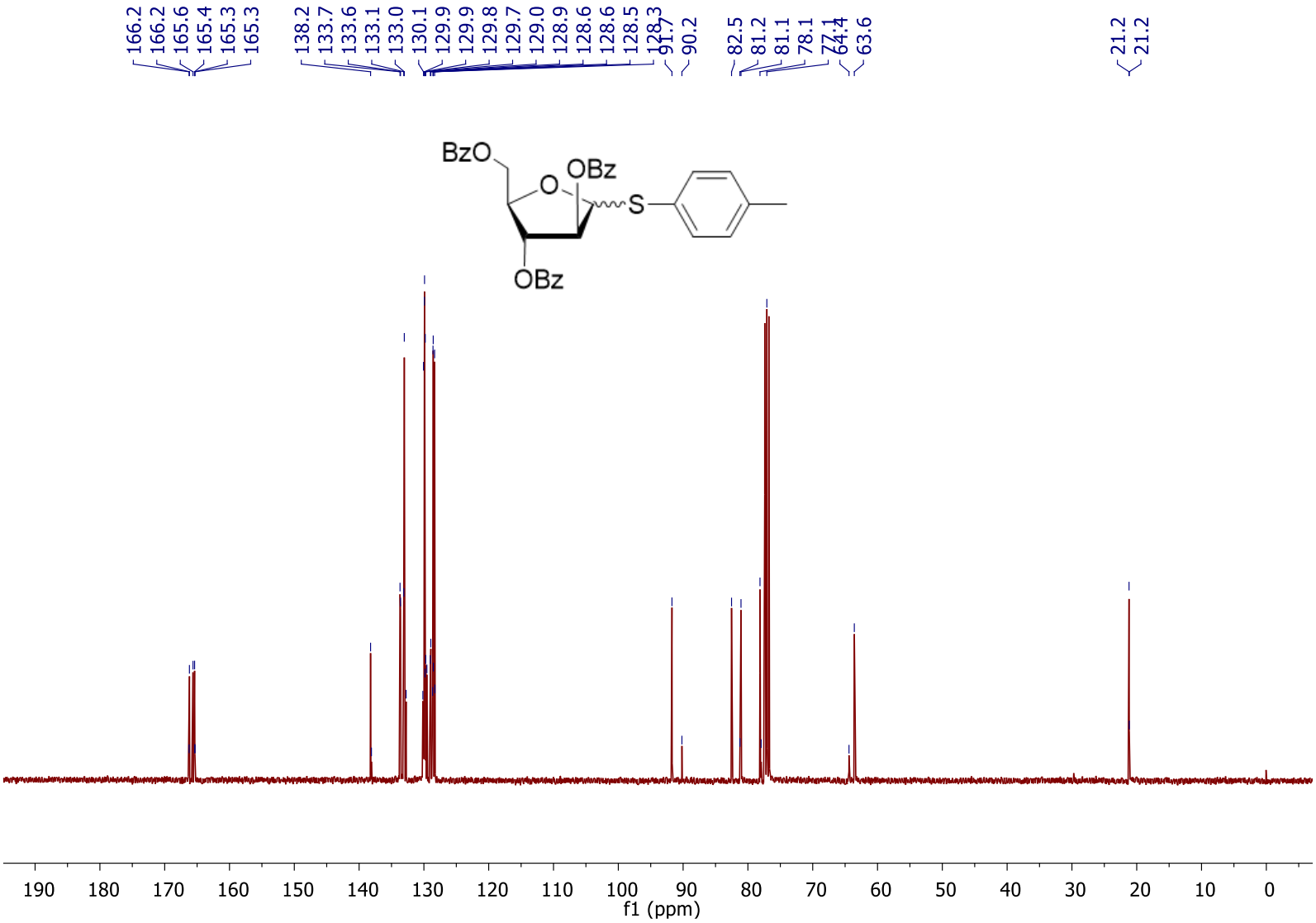
DEPT-135 NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **S2**



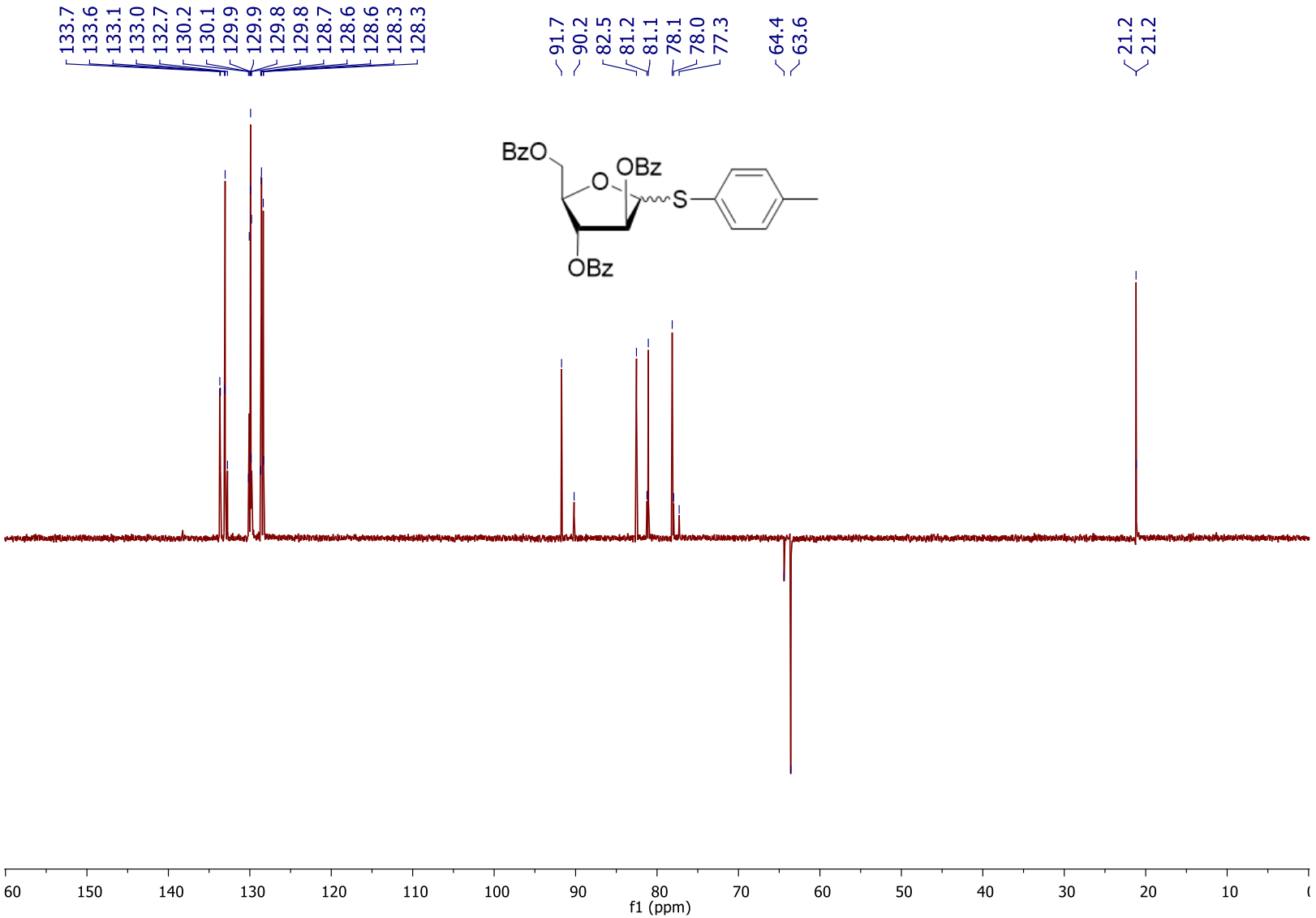
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **S3**



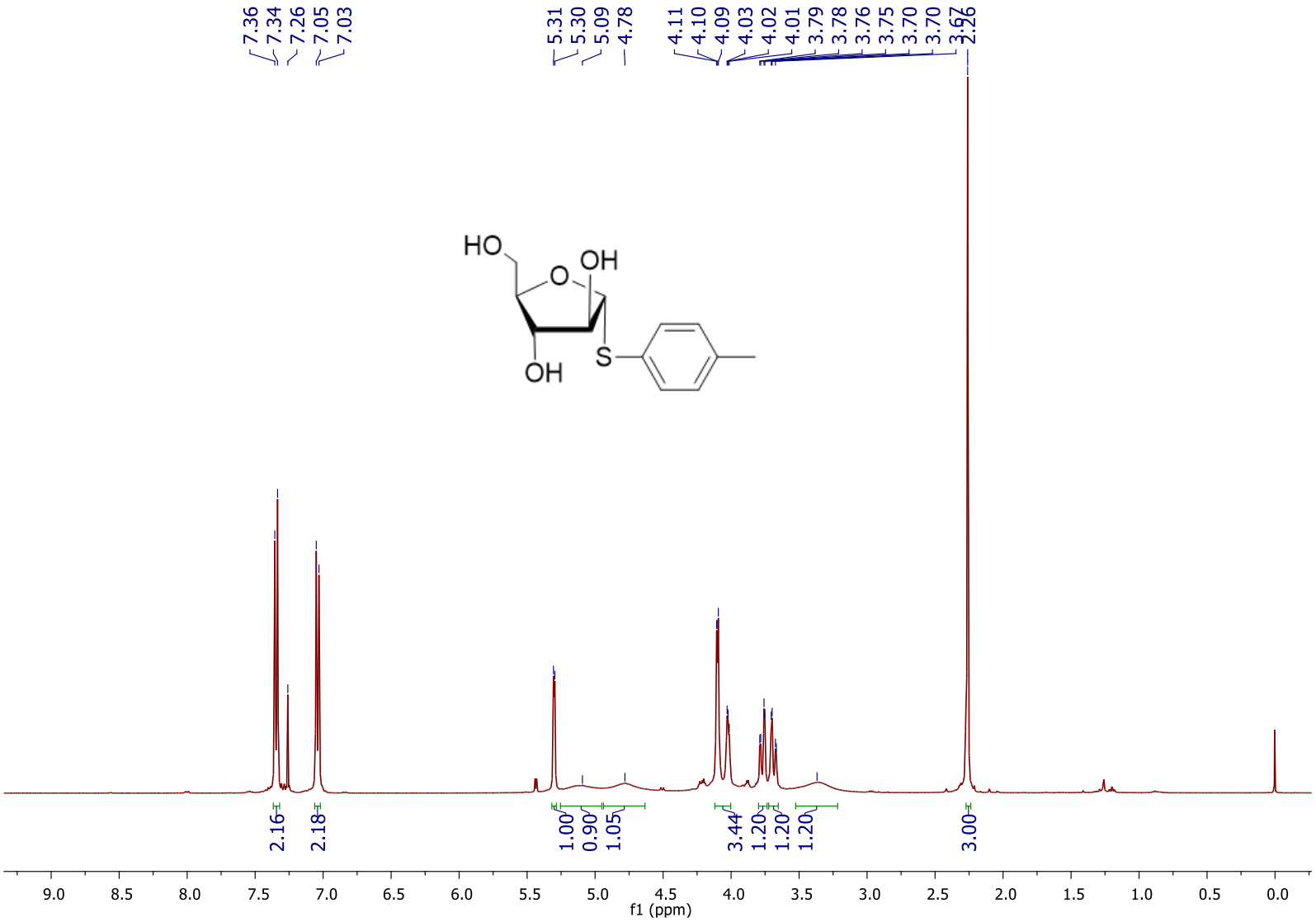
^{13}C NMR Spectrum (100.67 MHz, $CDCl_3$) of Compound **S3**



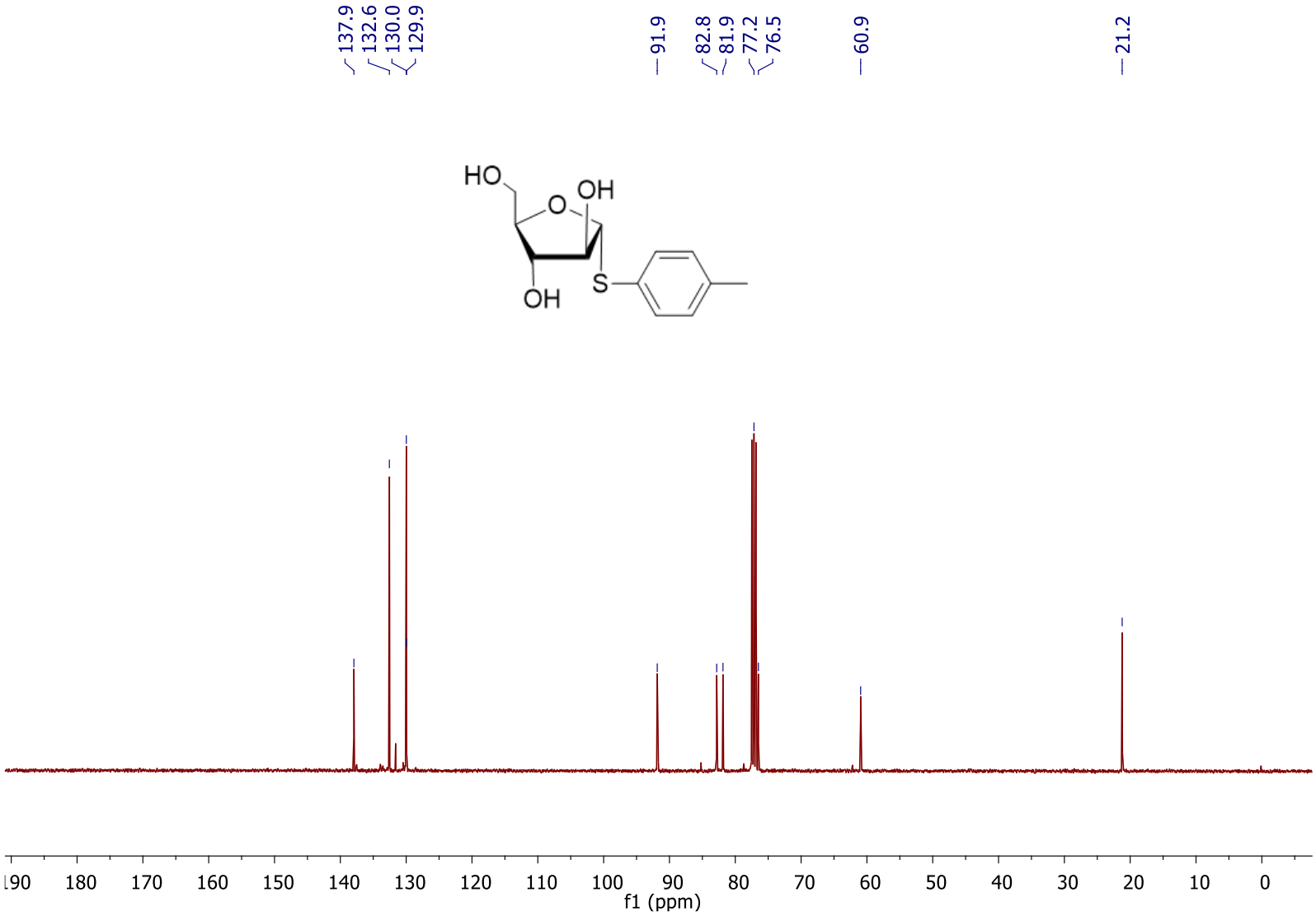
DEPT-135 NMR Spectrum (100.67 MHz, $CDCl_3$) of Compound **S3**



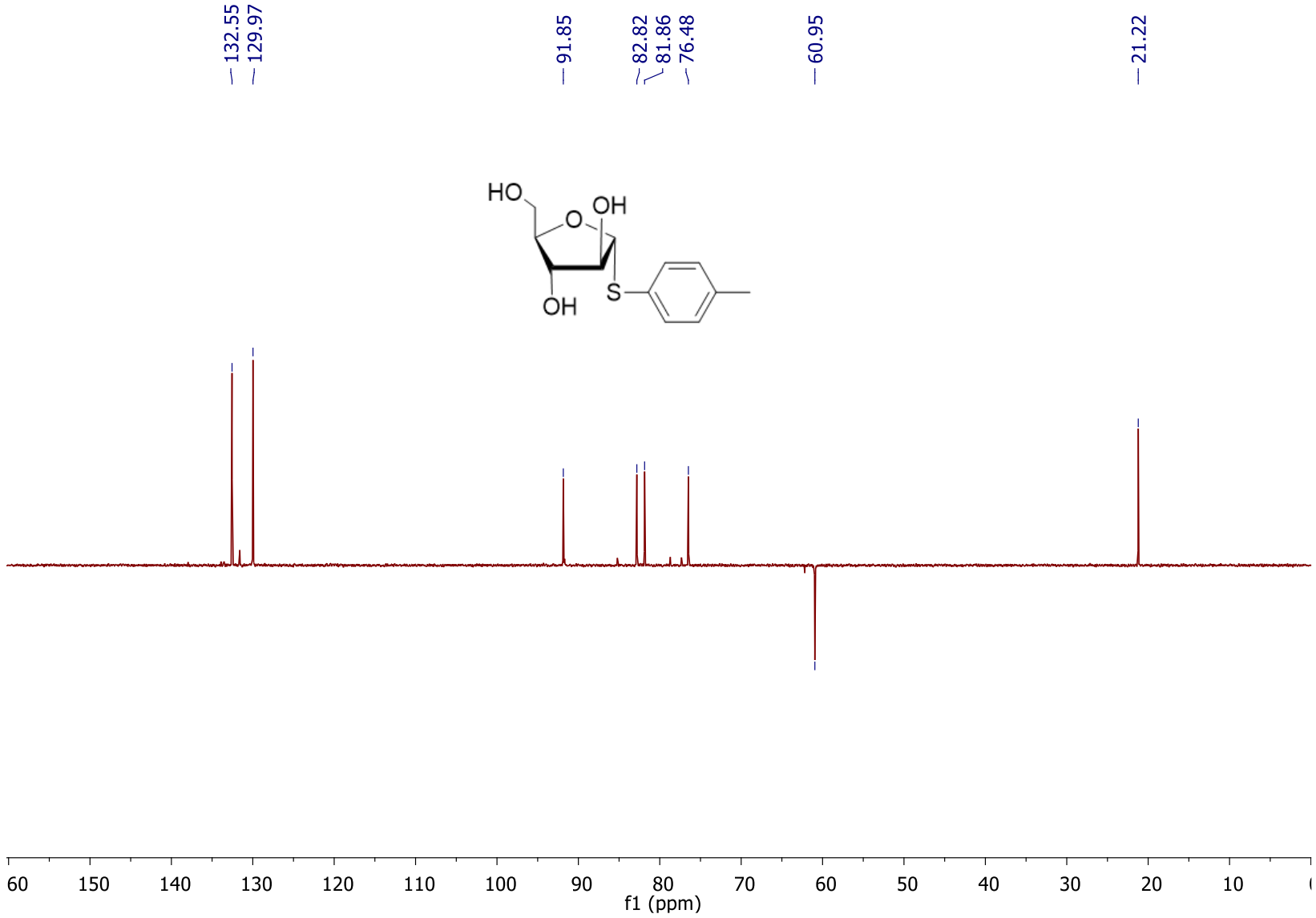
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **S4**



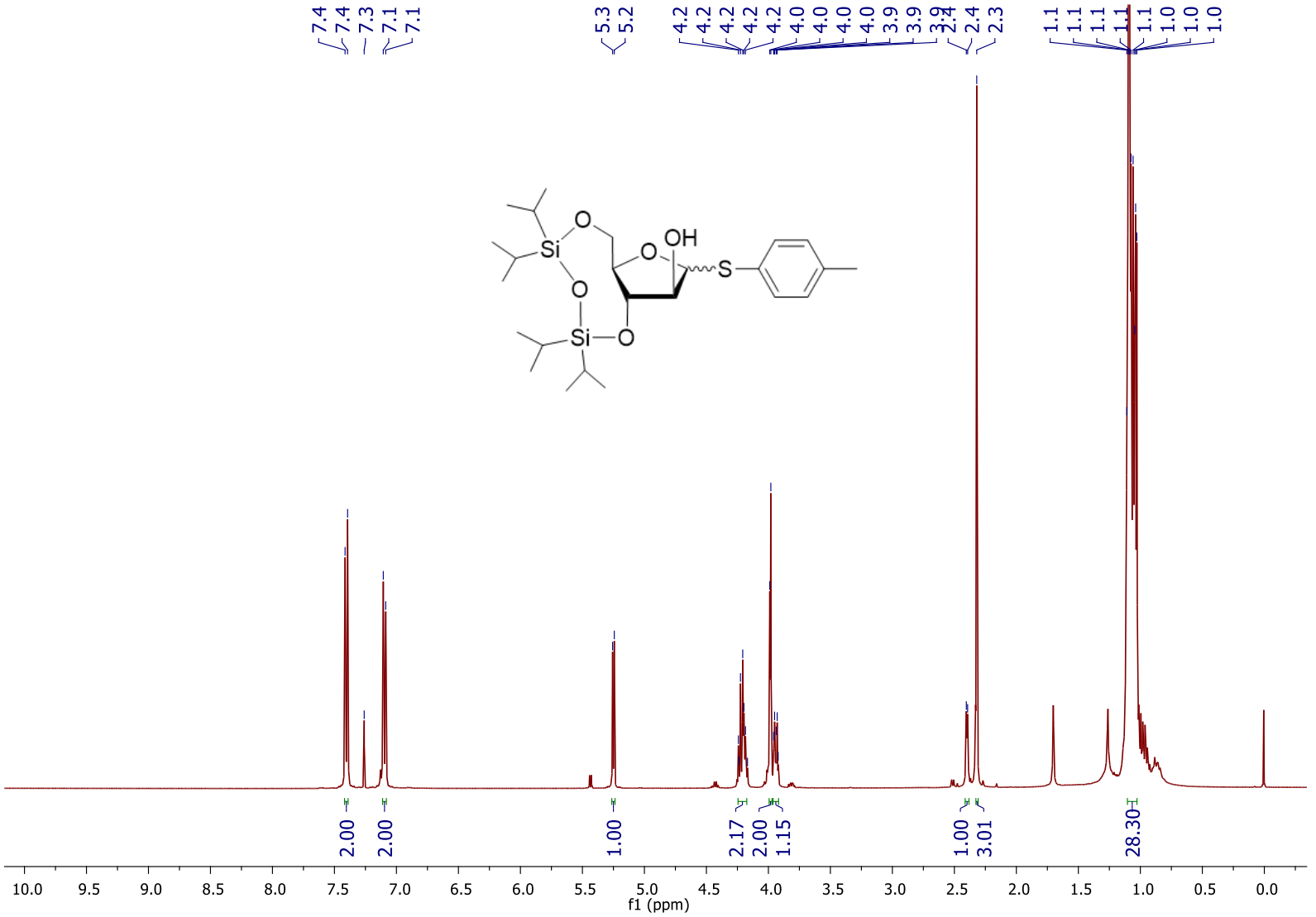
^{13}C NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **S4**



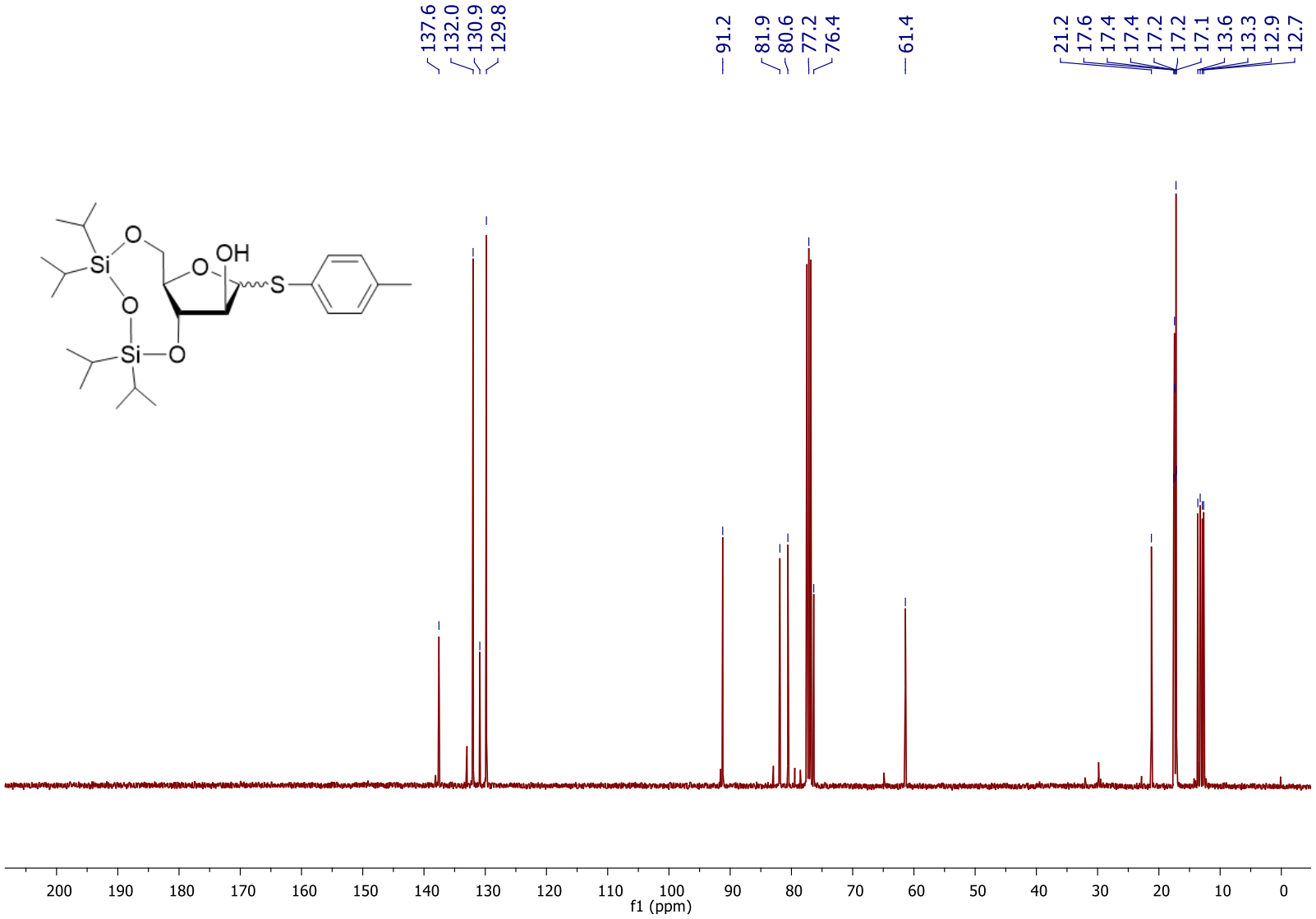
DEPT-135 NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **S4**



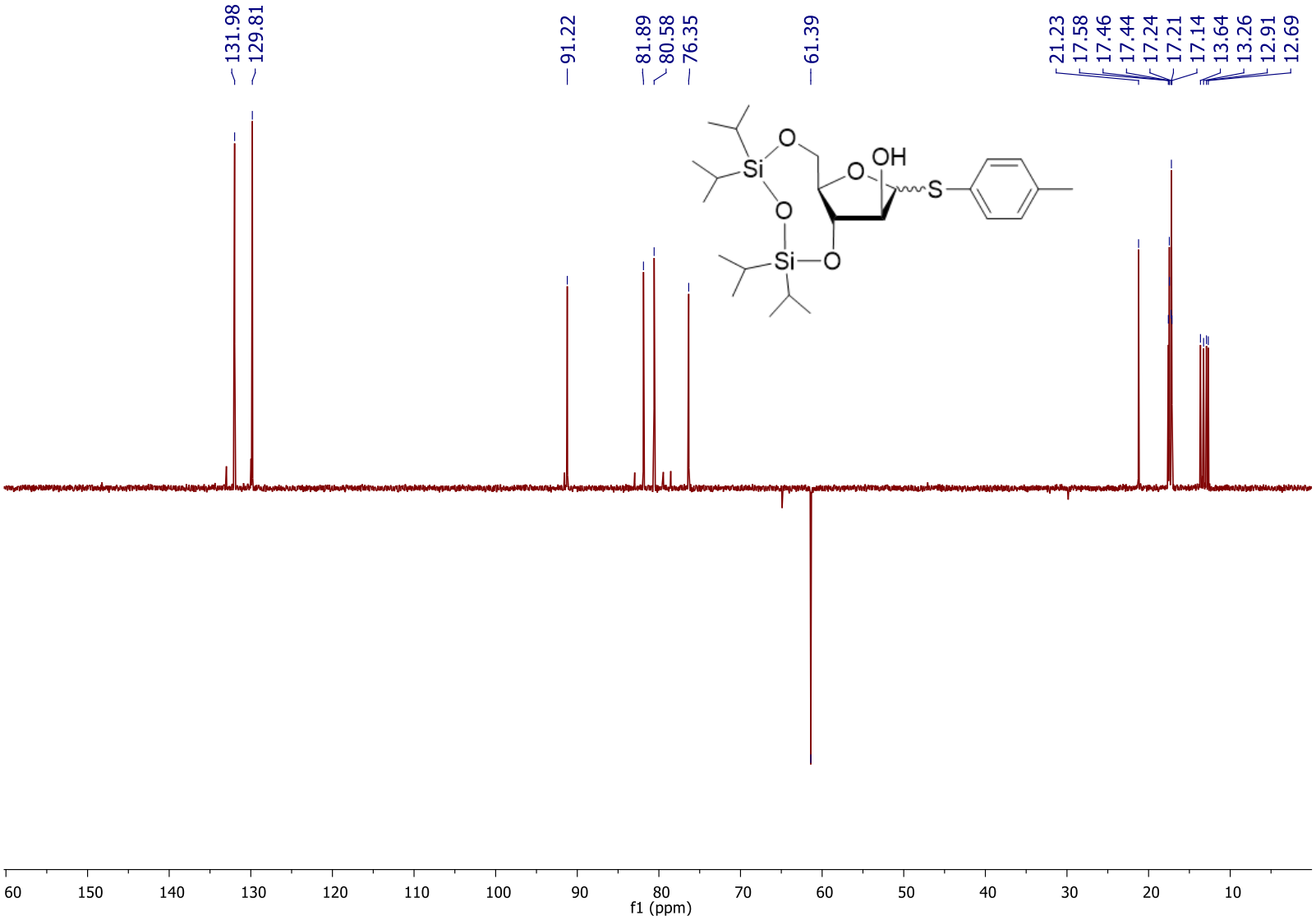
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **S5**



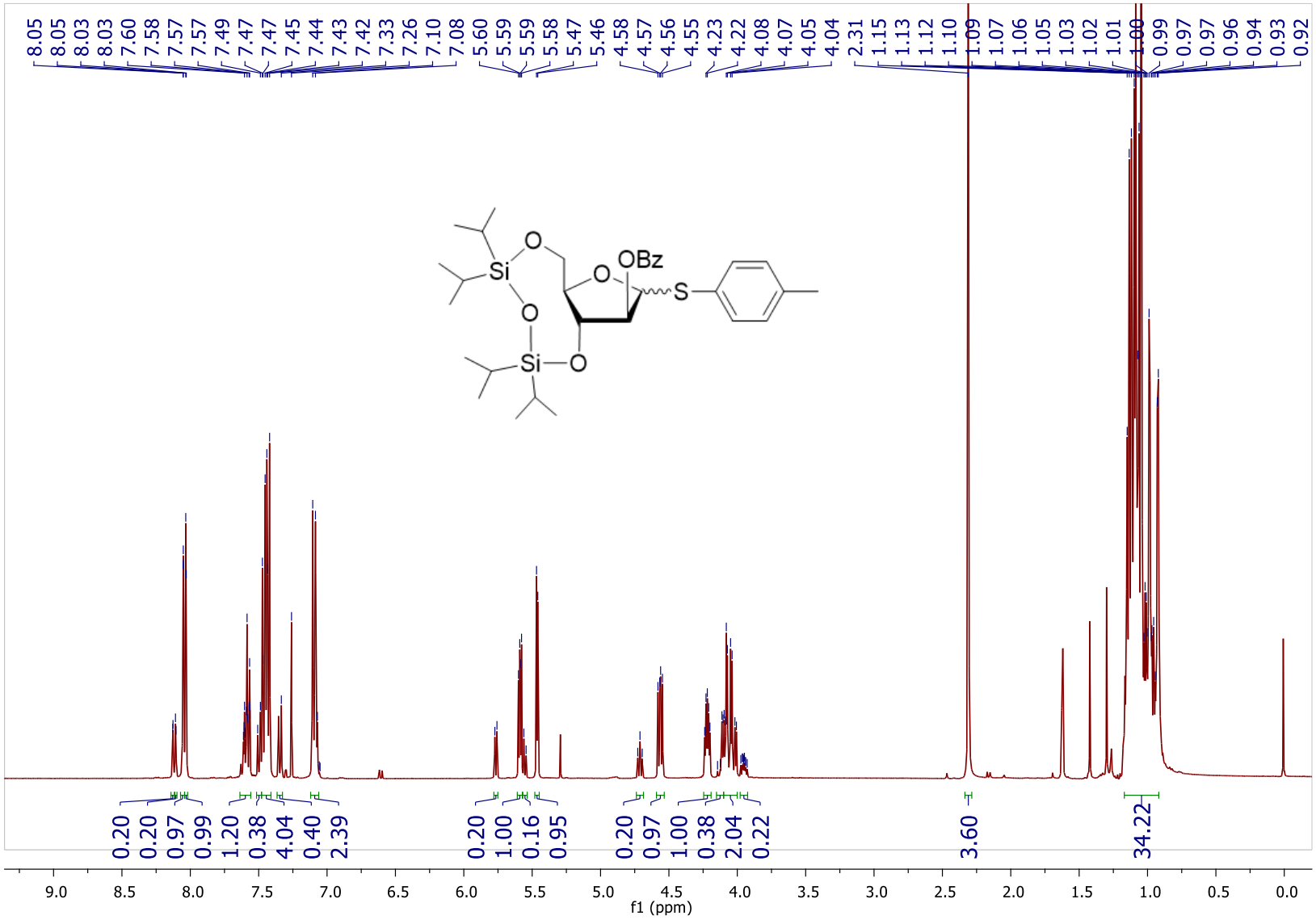
^{13}C NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **S5**



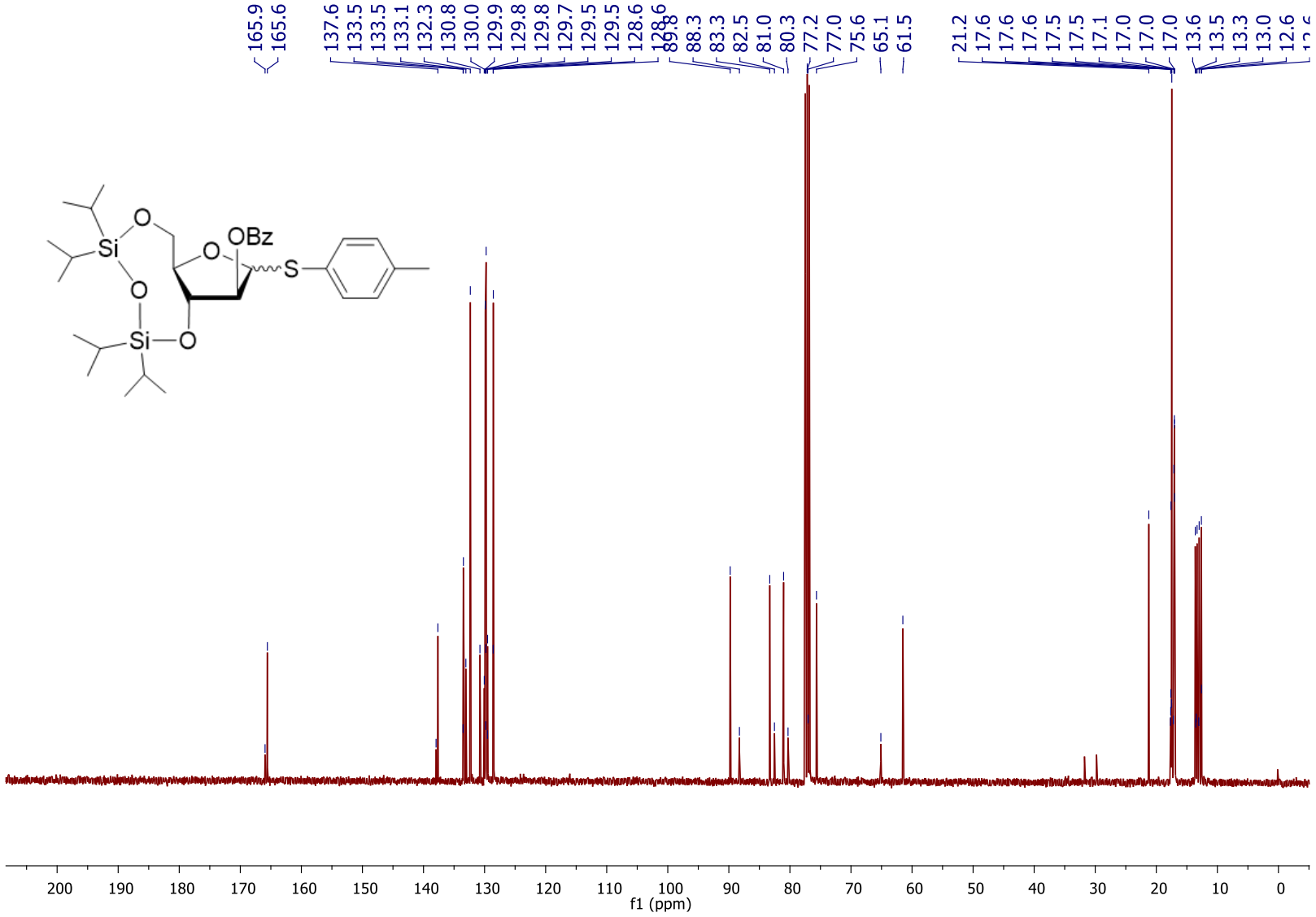
DEPT-135 NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **S5**



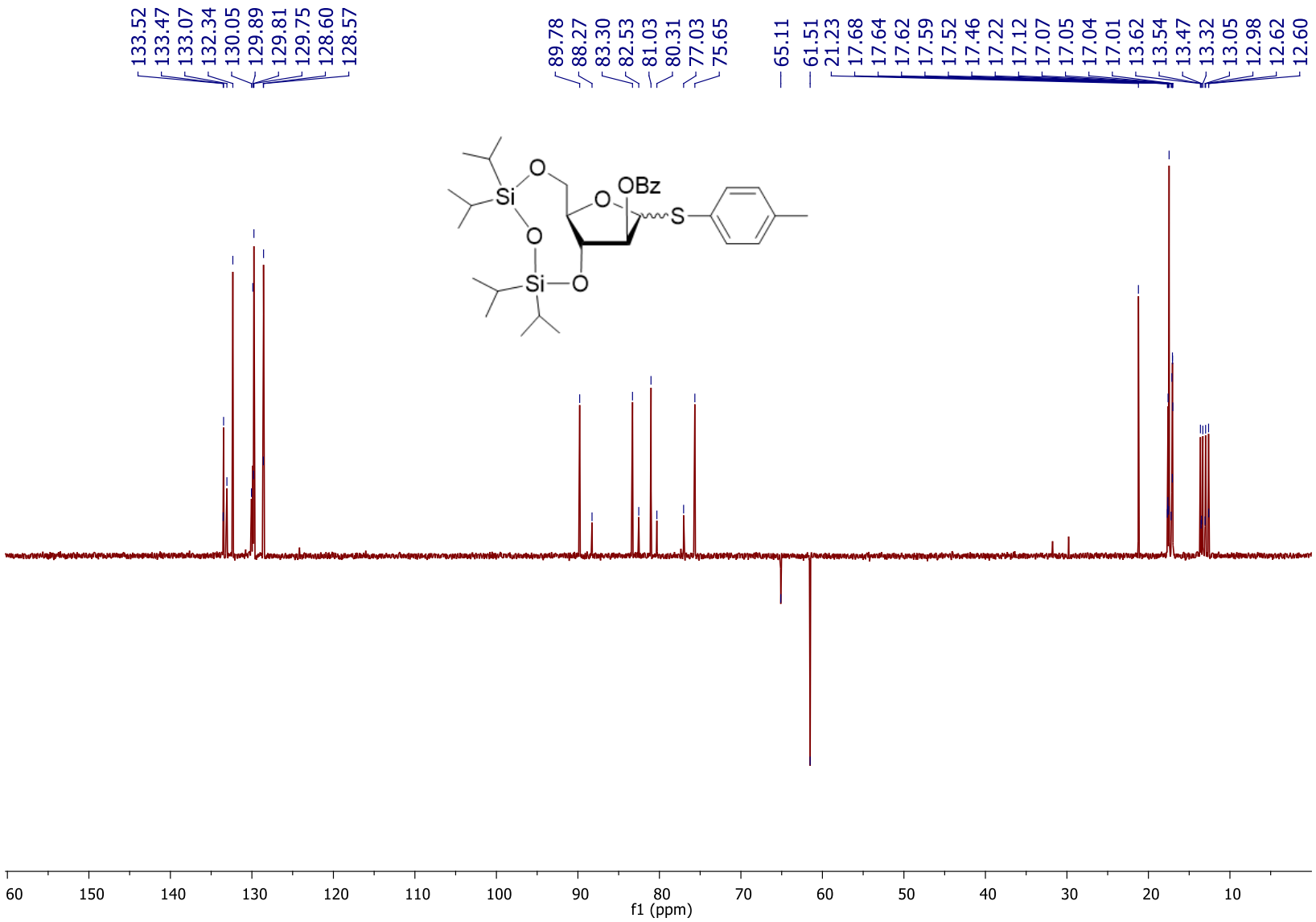
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **S6**



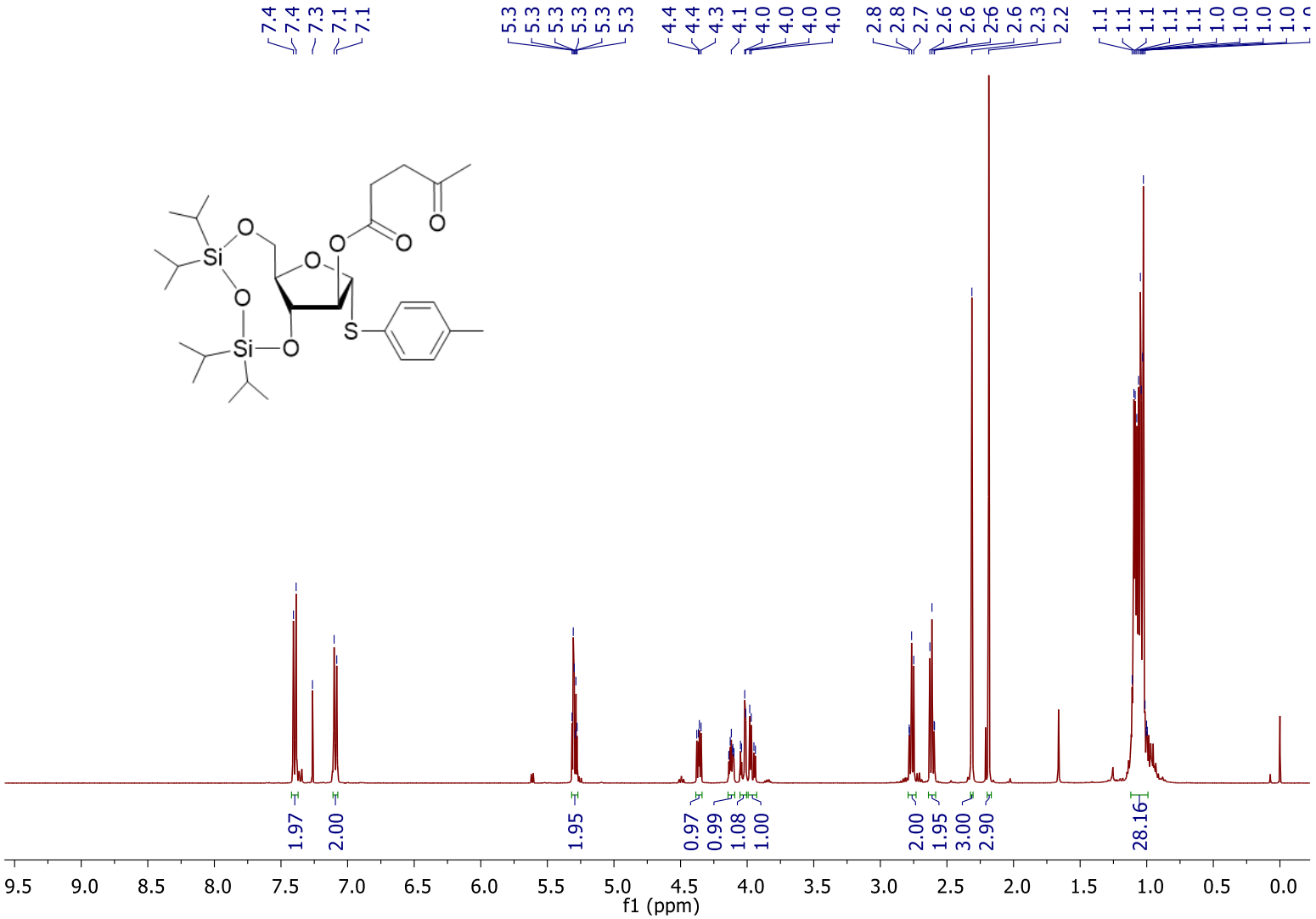
^{13}C NMR Spectrum (100.67 MHz, $CDCl_3$) of Compound **S6**



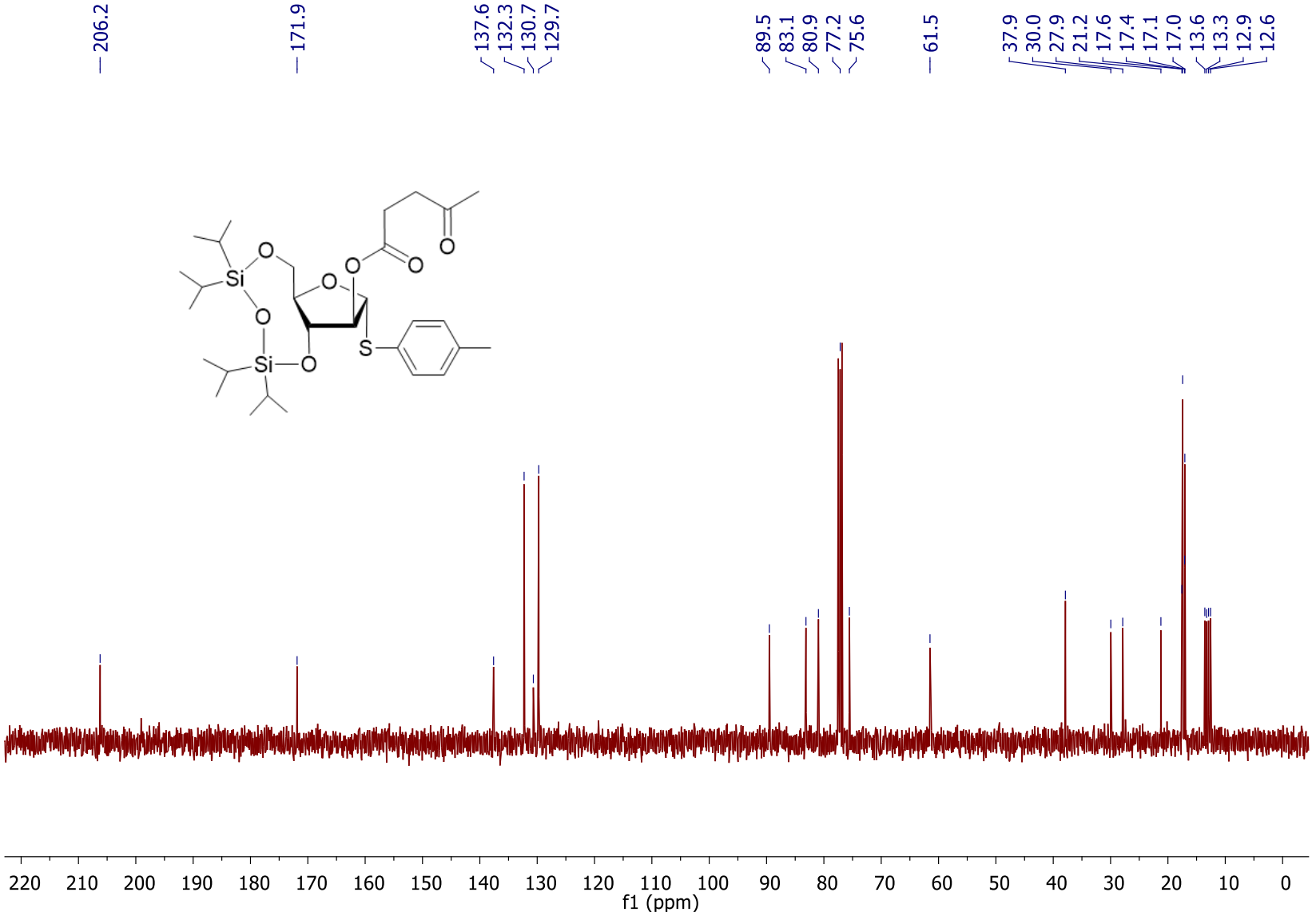
DEPT-135 NMR Spectrum (100.67 MHz, $CDCl_3$) of Compound **S6**



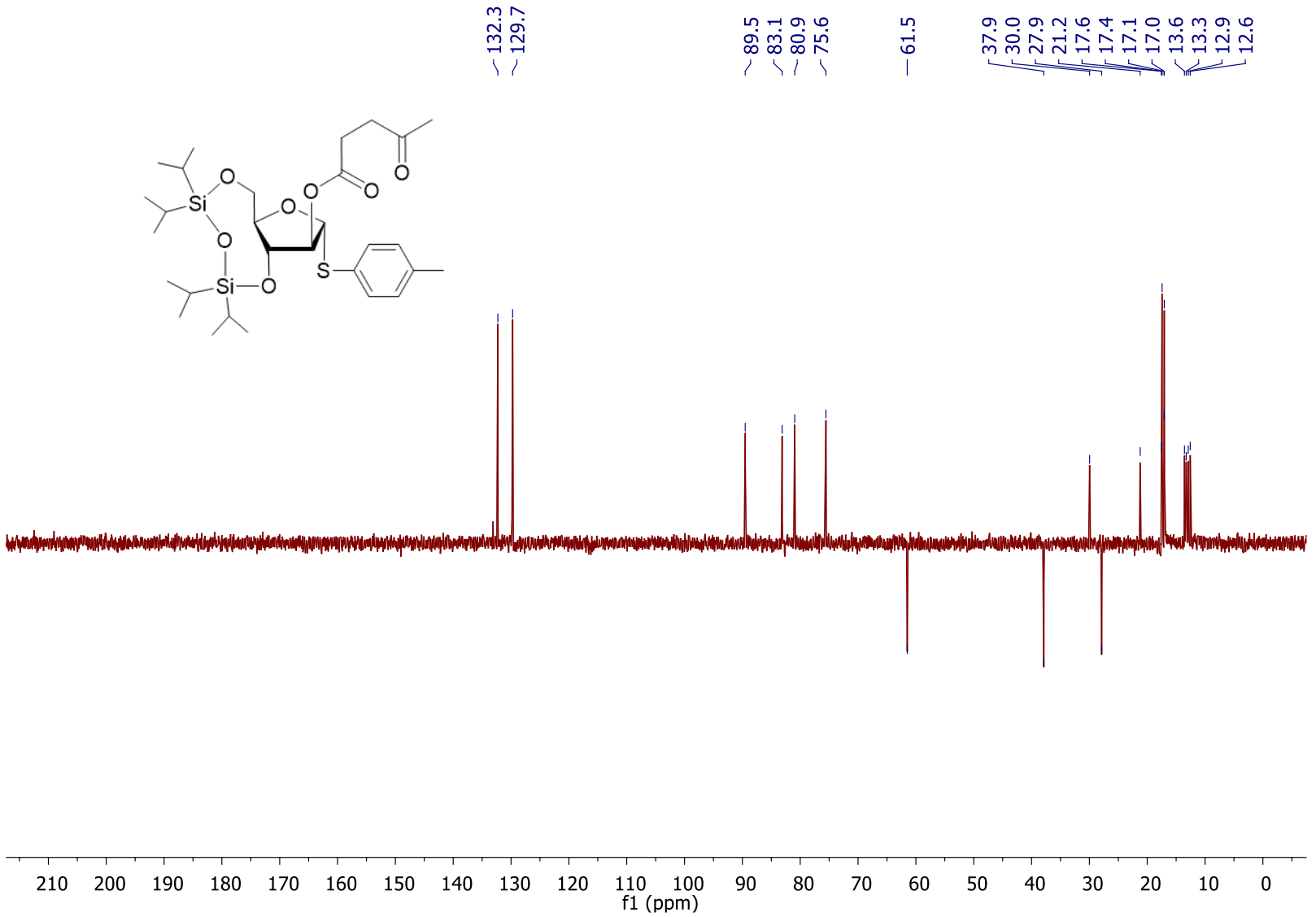
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **S7**



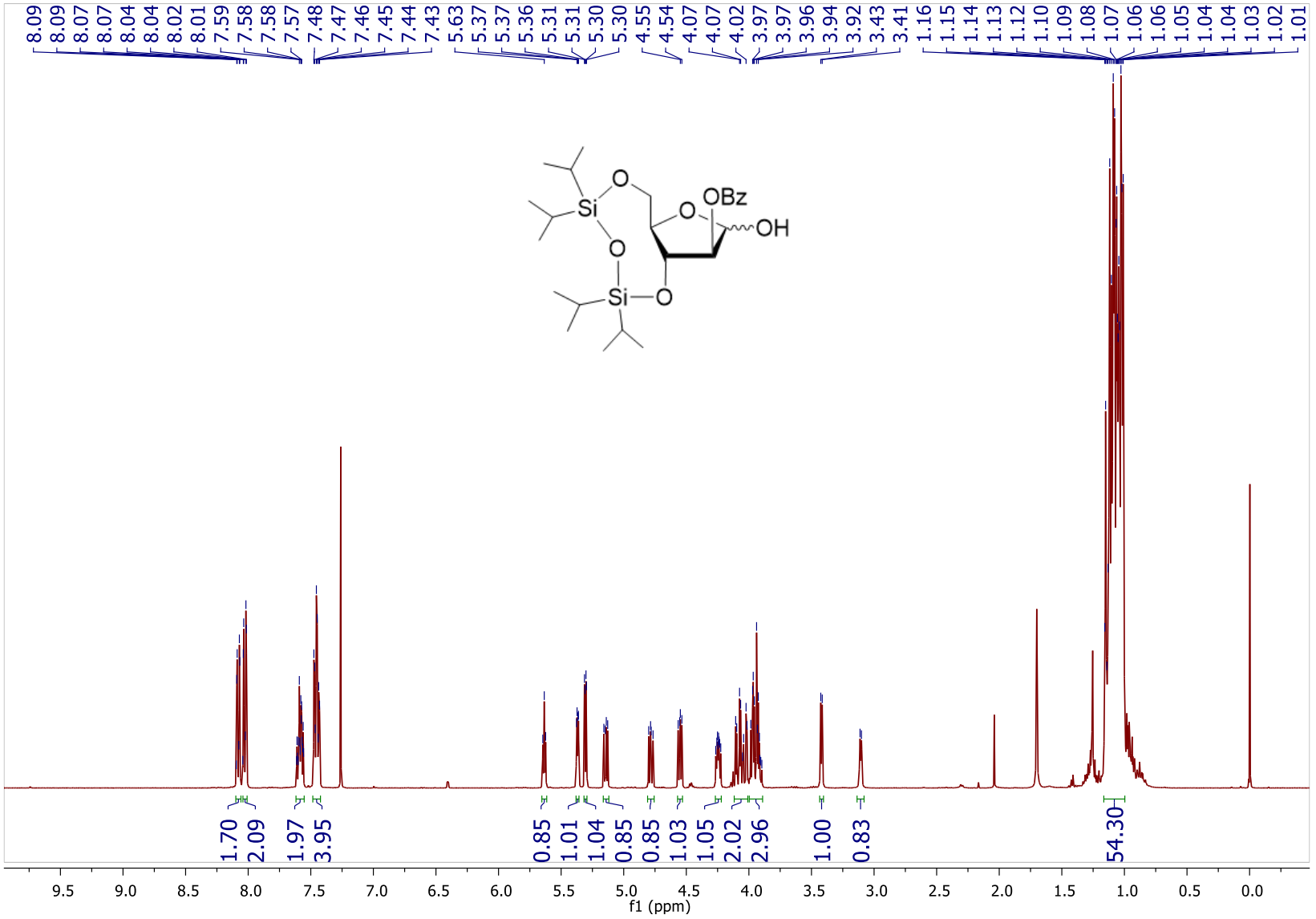
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **S7**



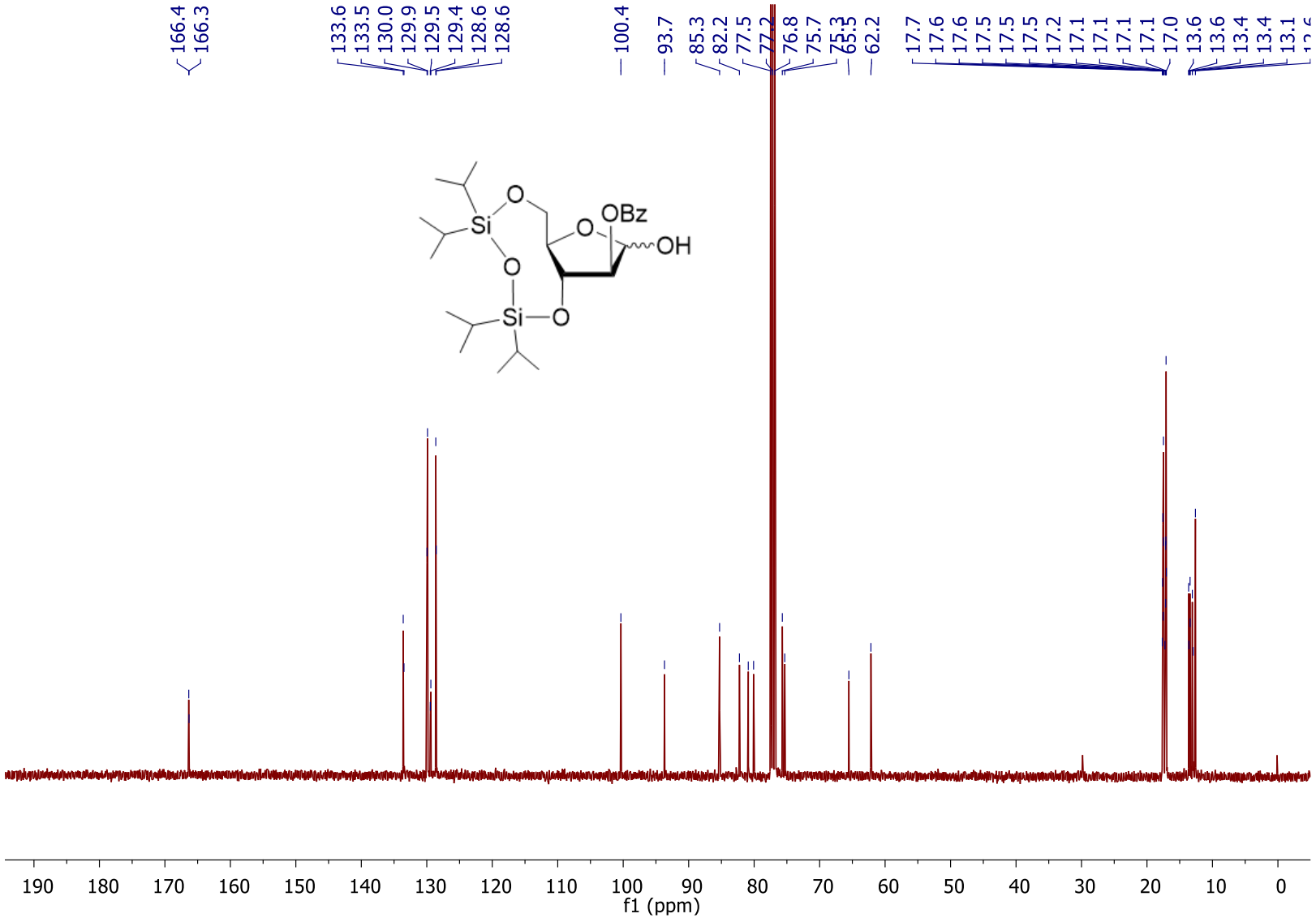
DEPT-135 NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **S7**



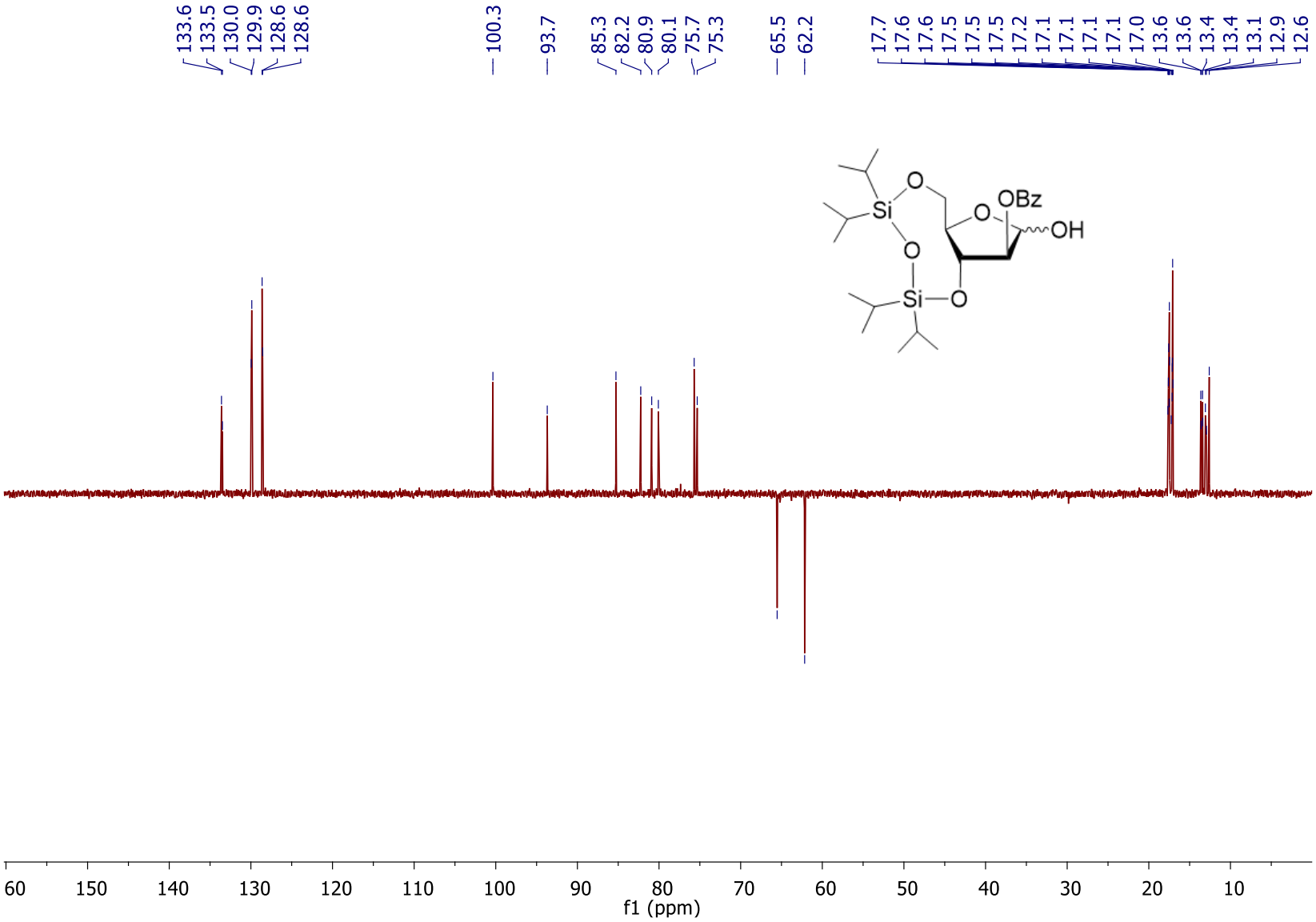
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **S6a**



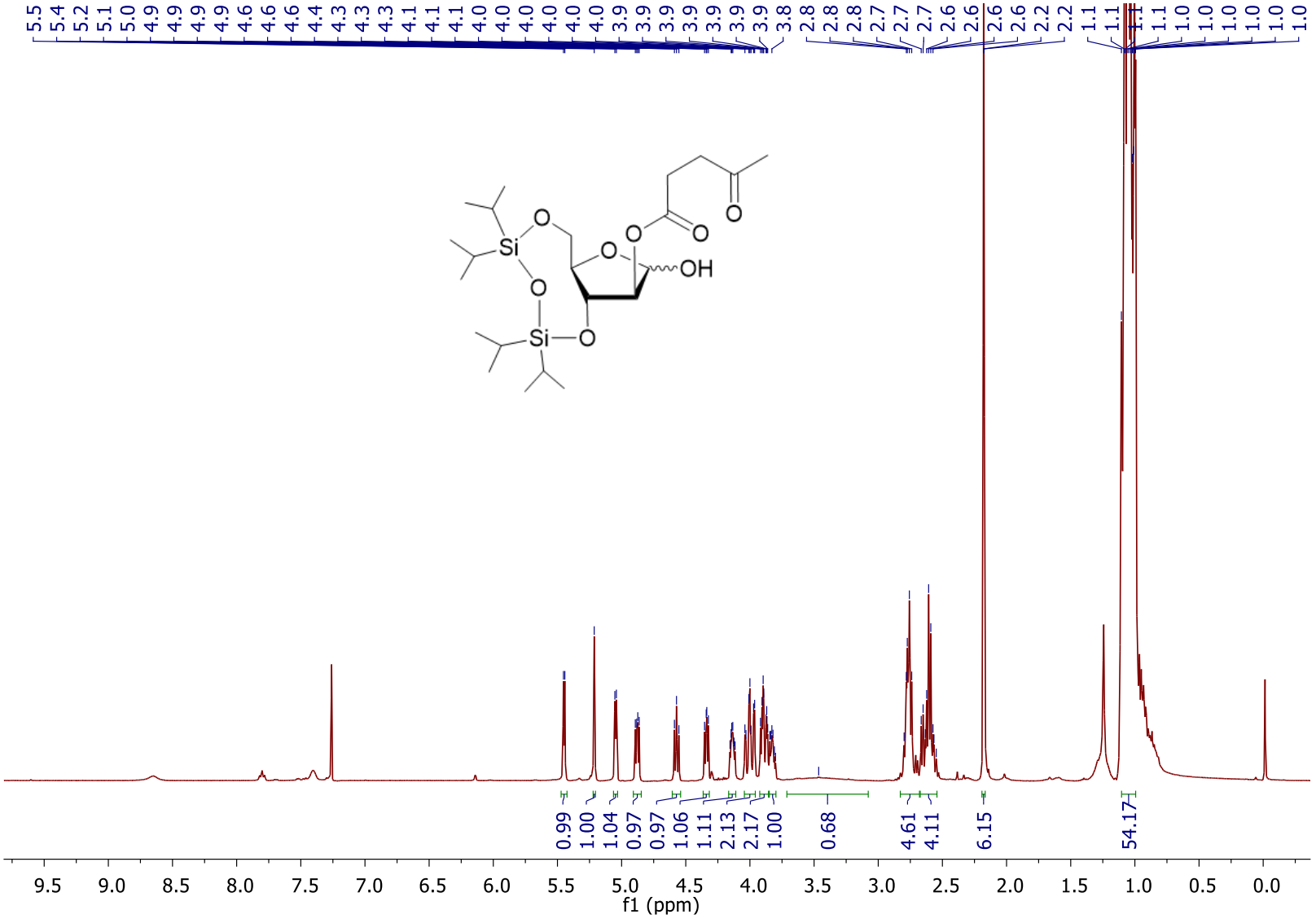
^{13}C NMR Spectrum (100.67 MHz, $CDCl_3$) of Compound **S6a**



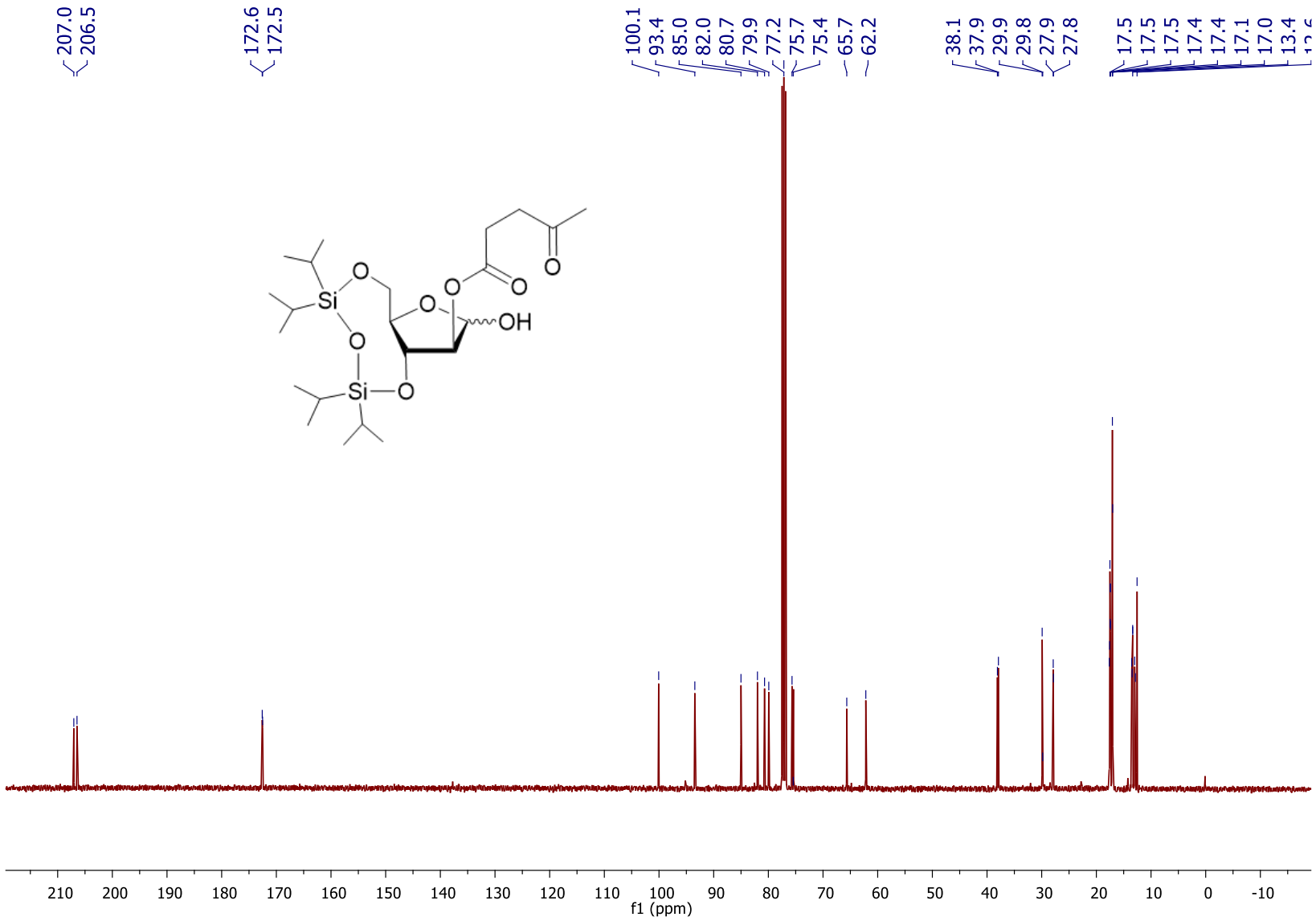
DEPT-135 NMR Spectrum (100.67 MHz, $CDCl_3$) of Compound **S6a**



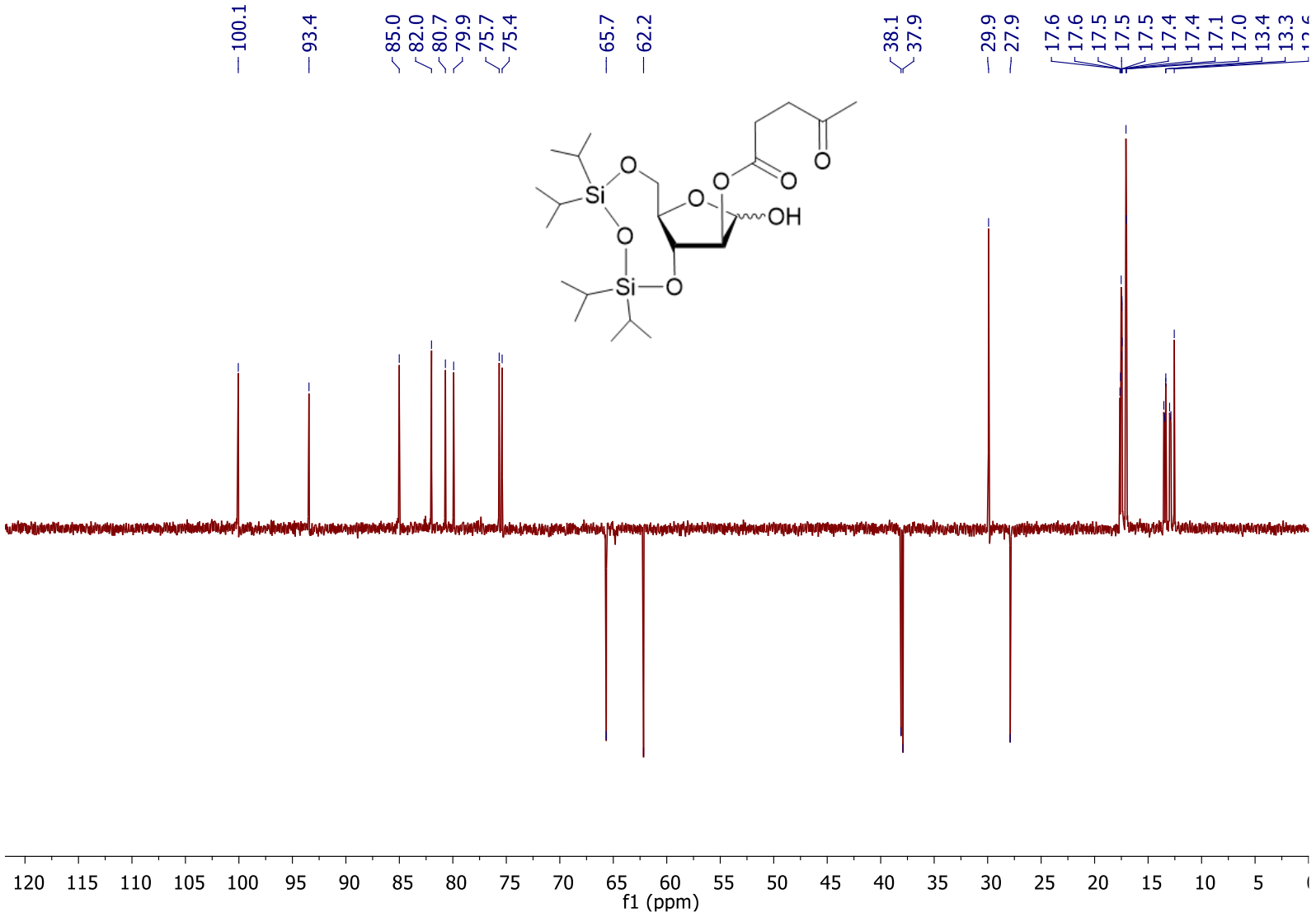
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **S7a**



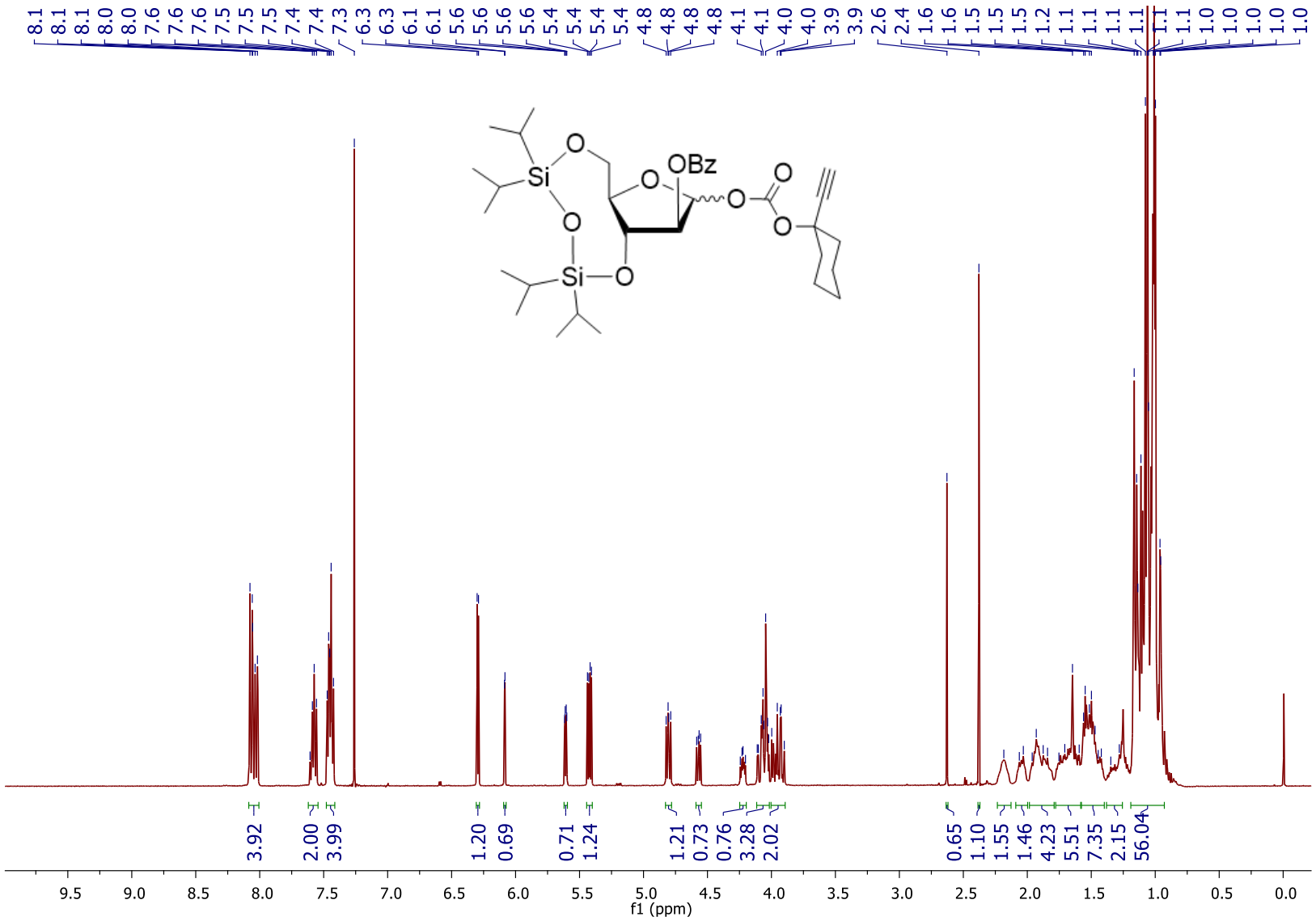
^{13}C NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **S7a**



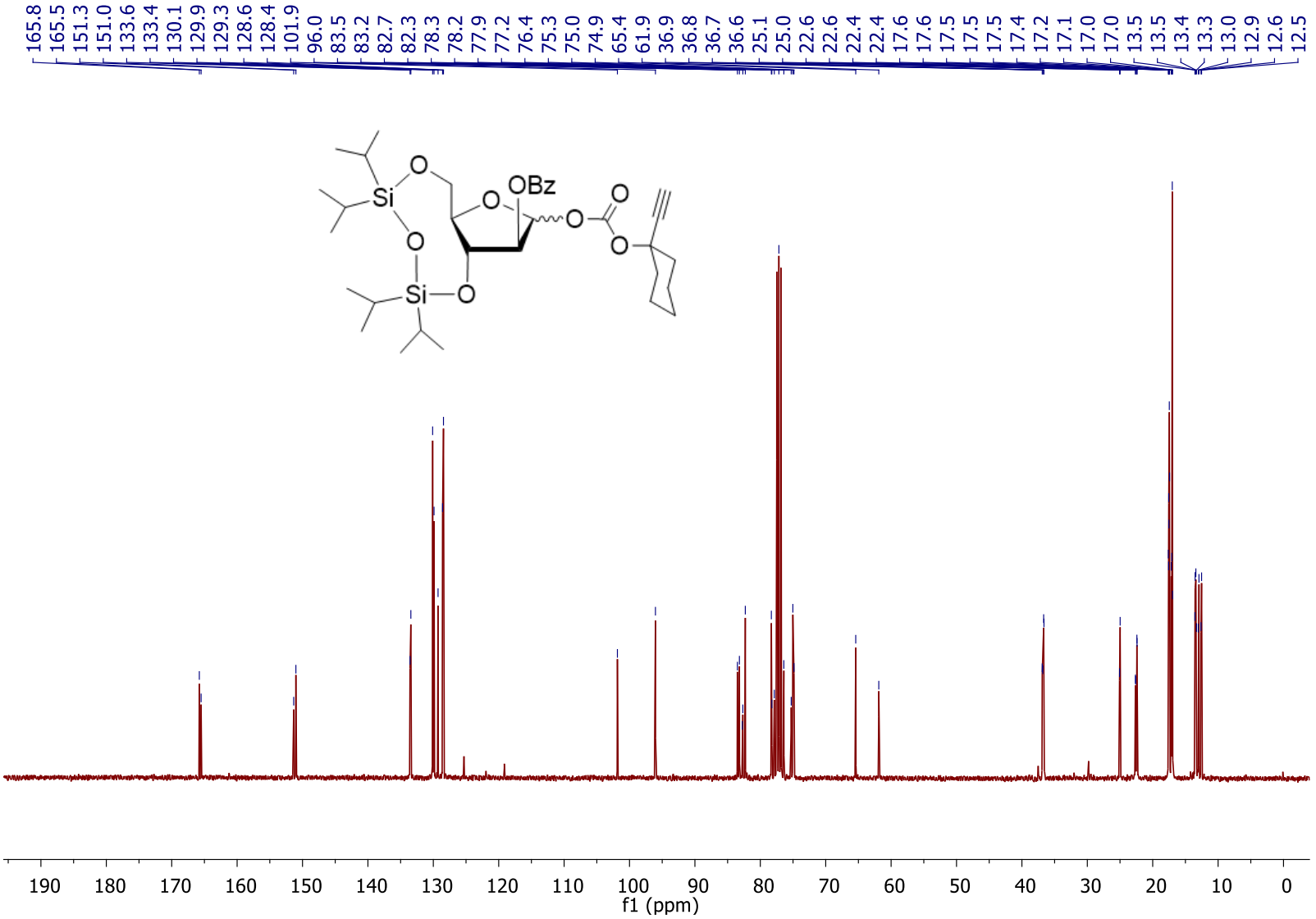
DEPT-135 NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **S7a**



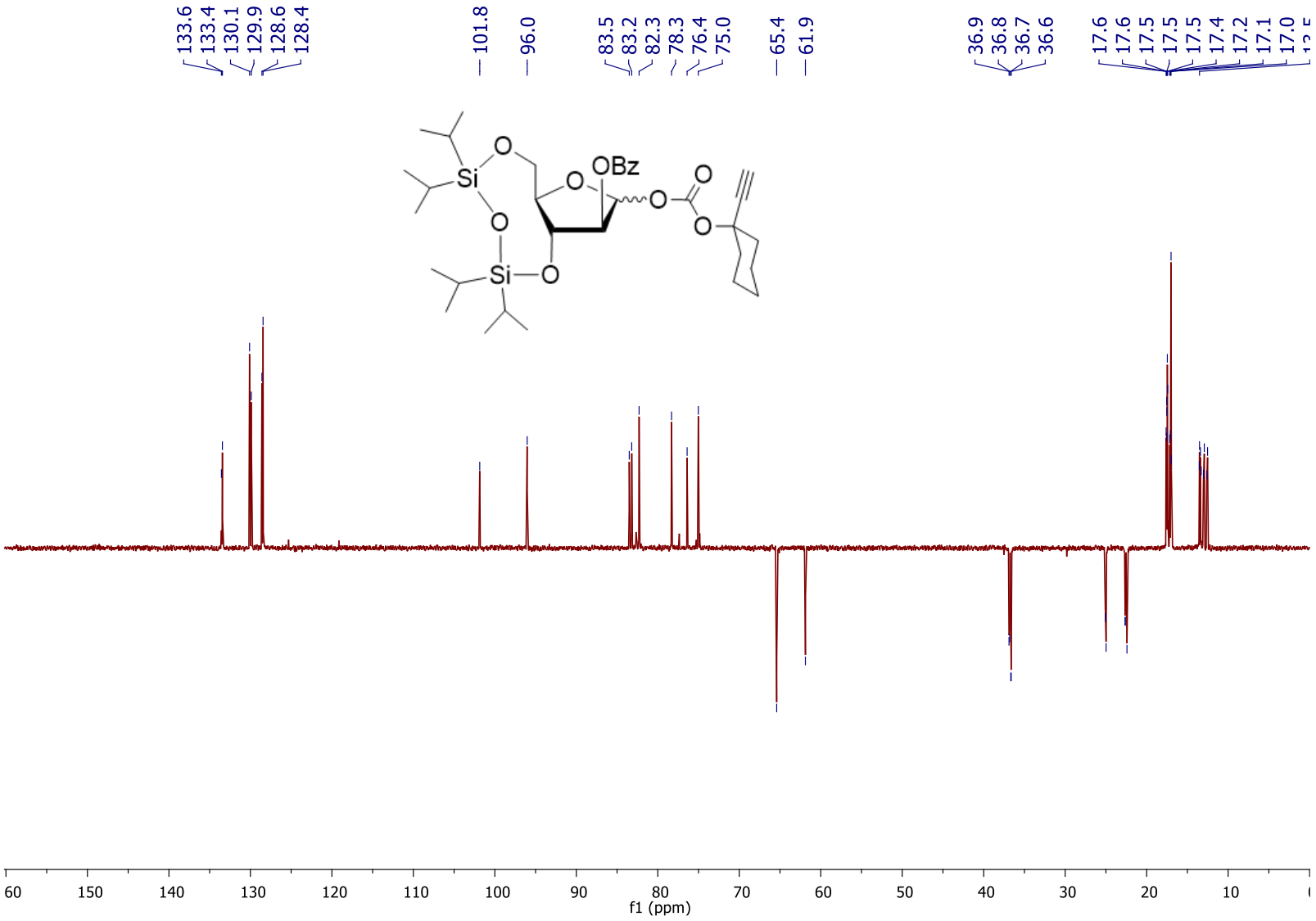
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **4**



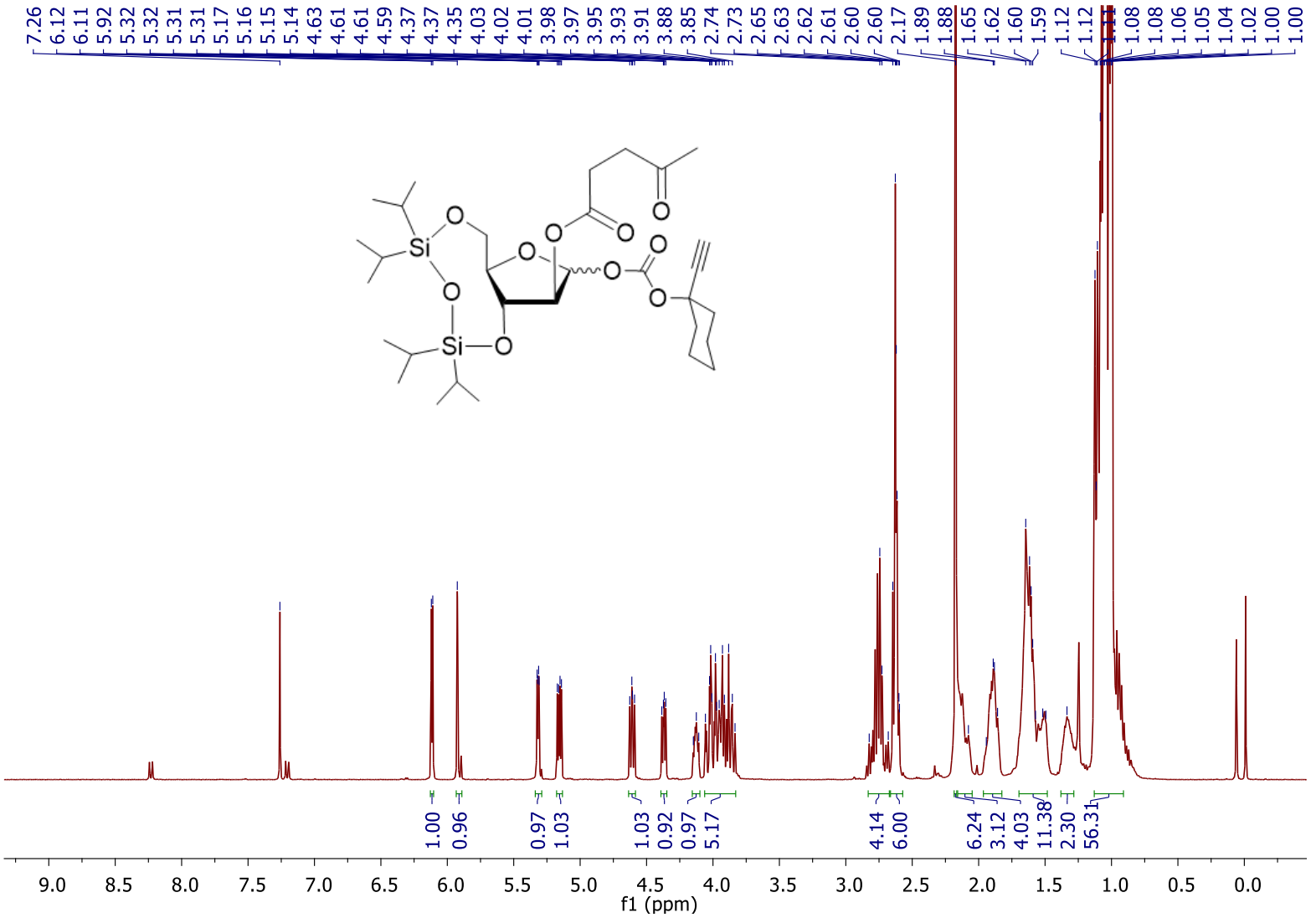
^{13}C NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **4**



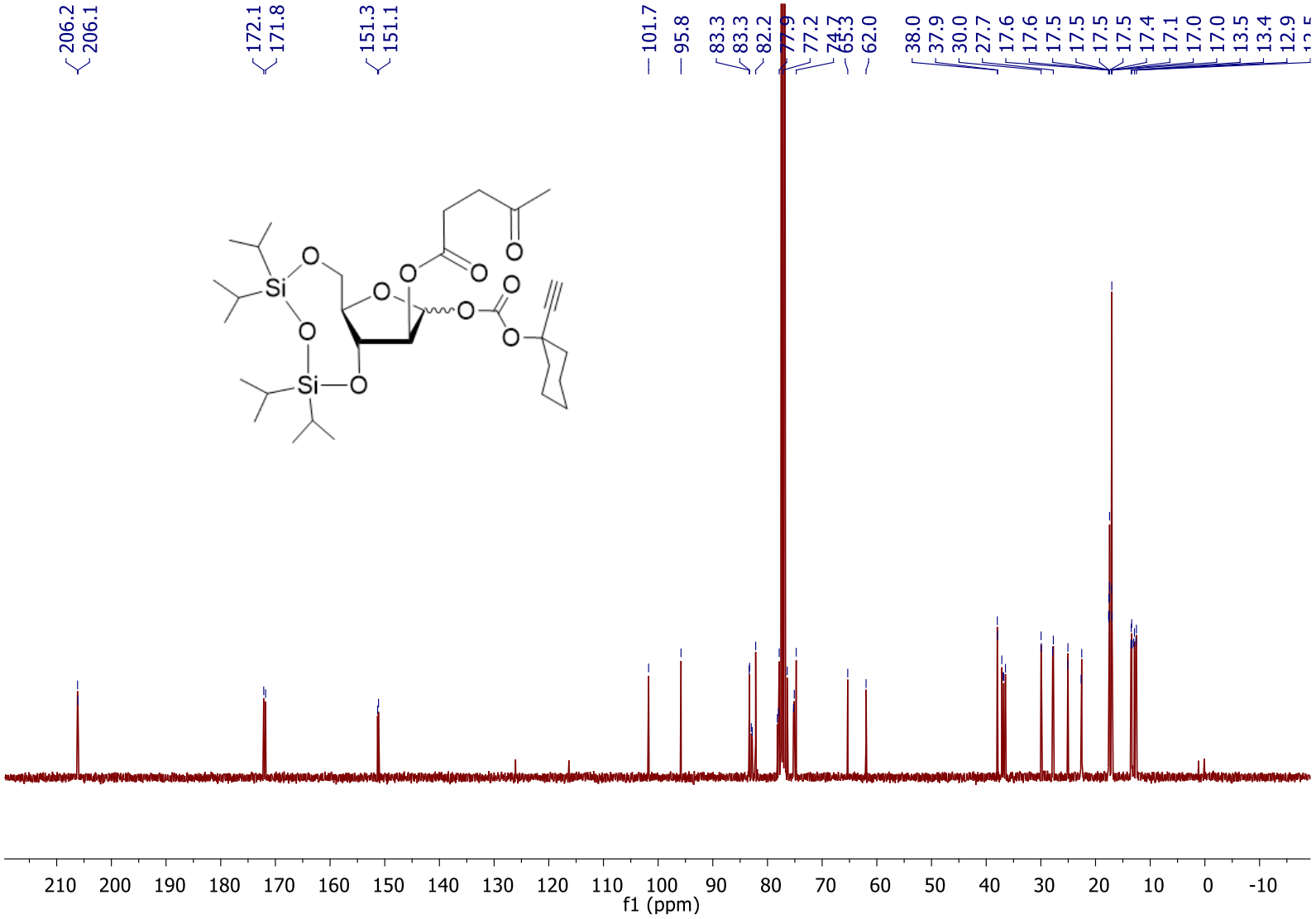
DEPT-135 NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **4**



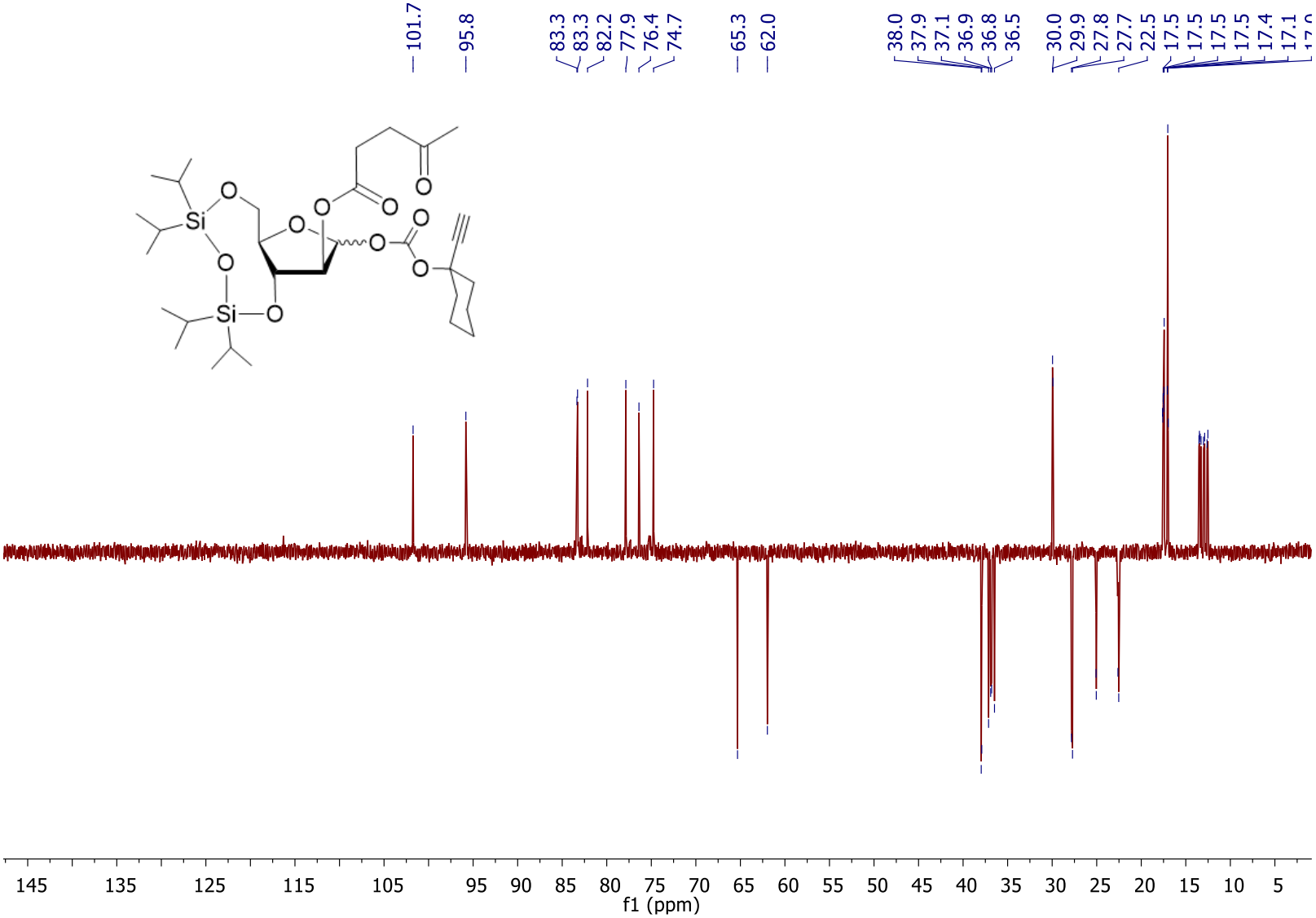
^{1}H NMR Spectrum (400.31MHz, $CDCl_3$) of Compound **5**



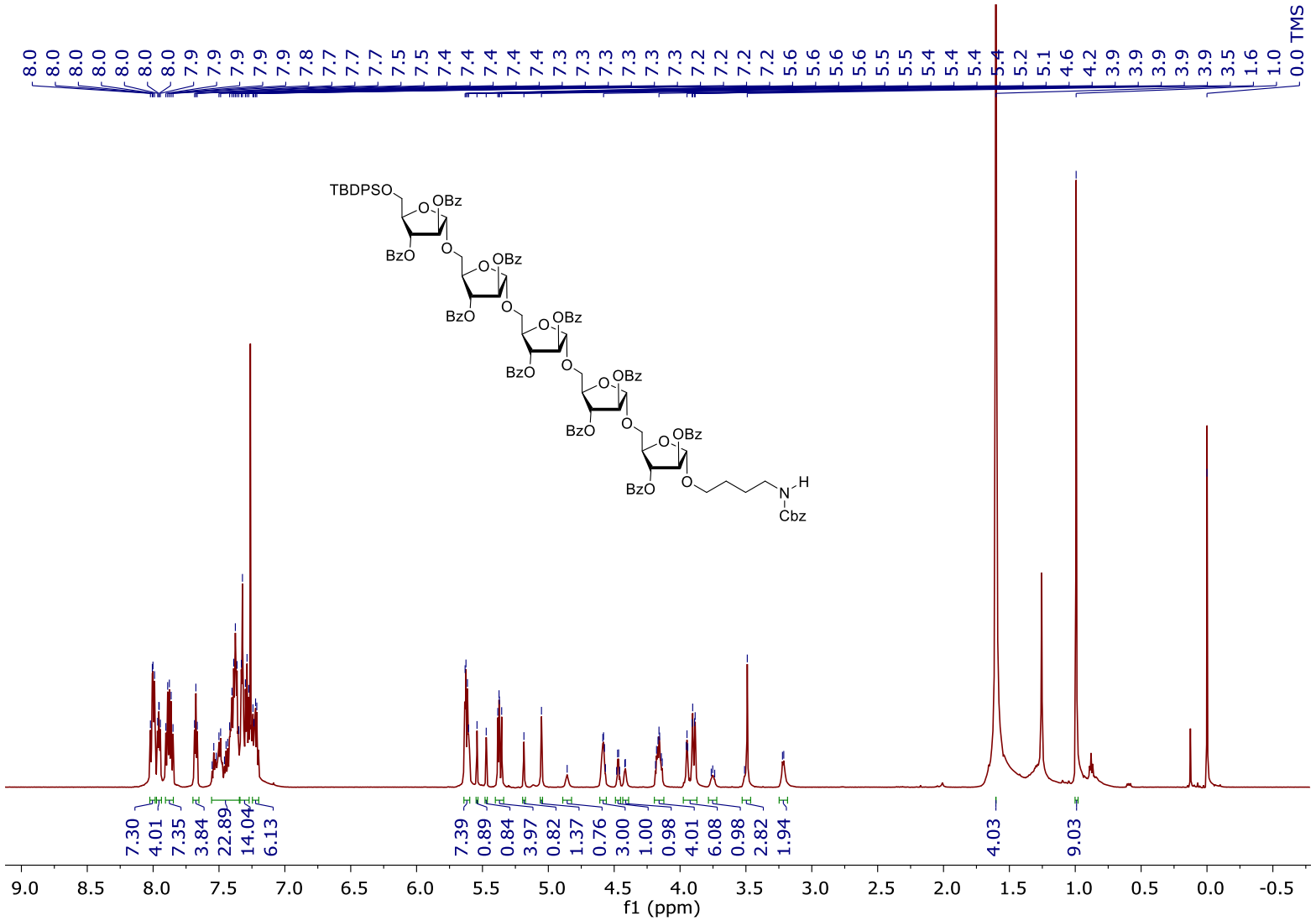
^{13}C NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **5**



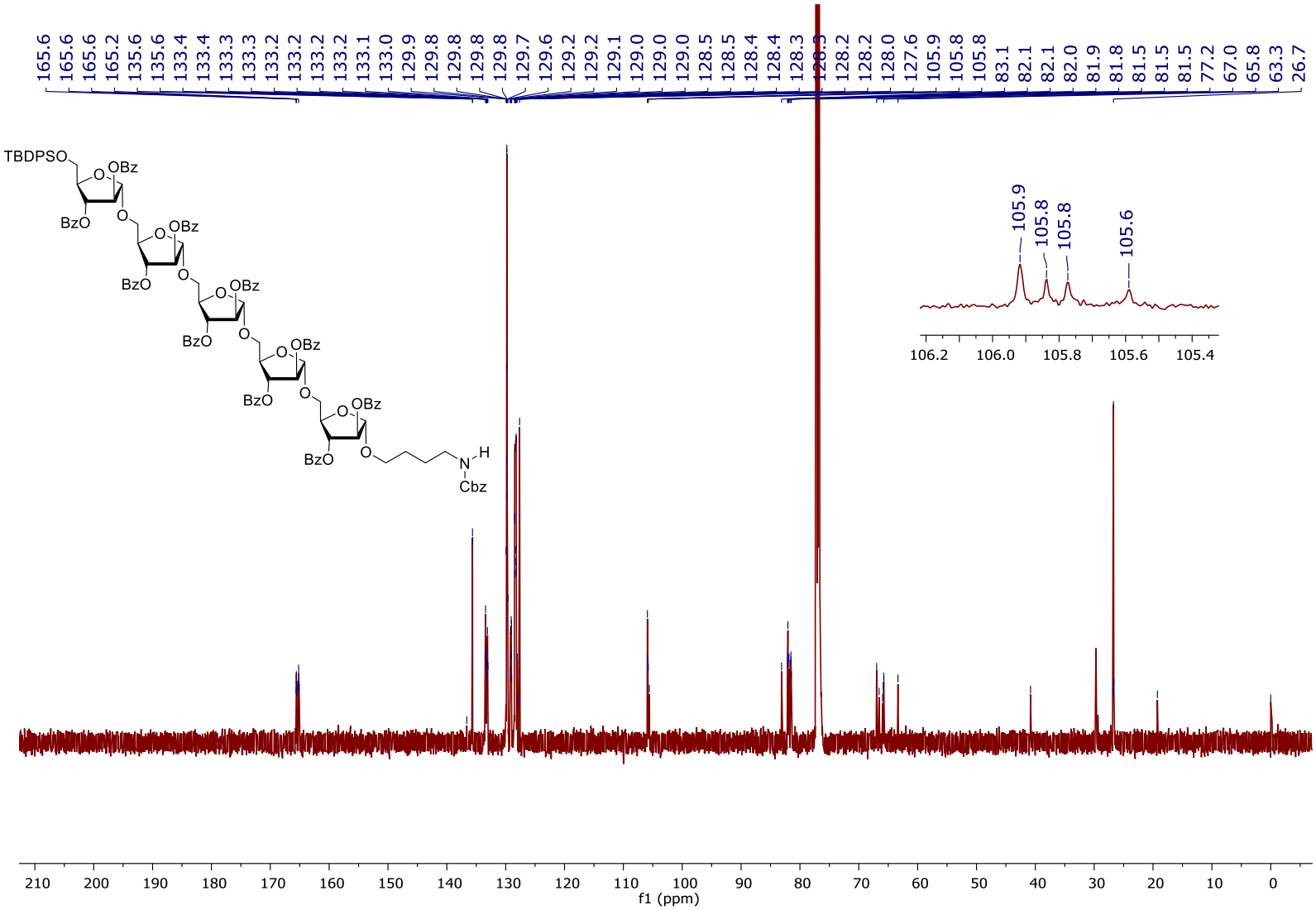
DEPT-135 NMR Spectrum (100.66 MHz, $CDCl_3$) of Compound **5**



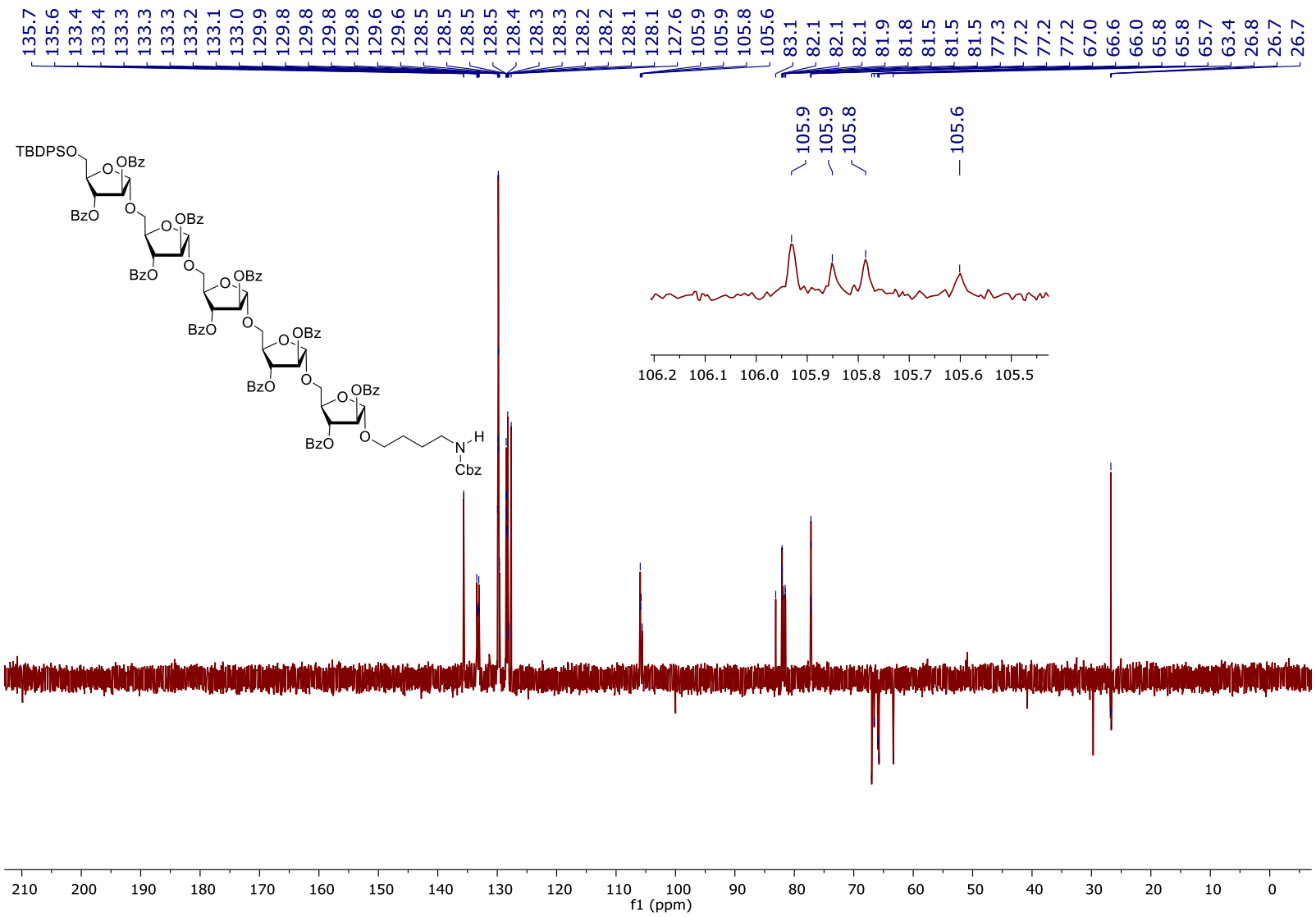
^{1}H NMR Spectrum (600.40 MHz, $CDCl_3$) of Compound **14**



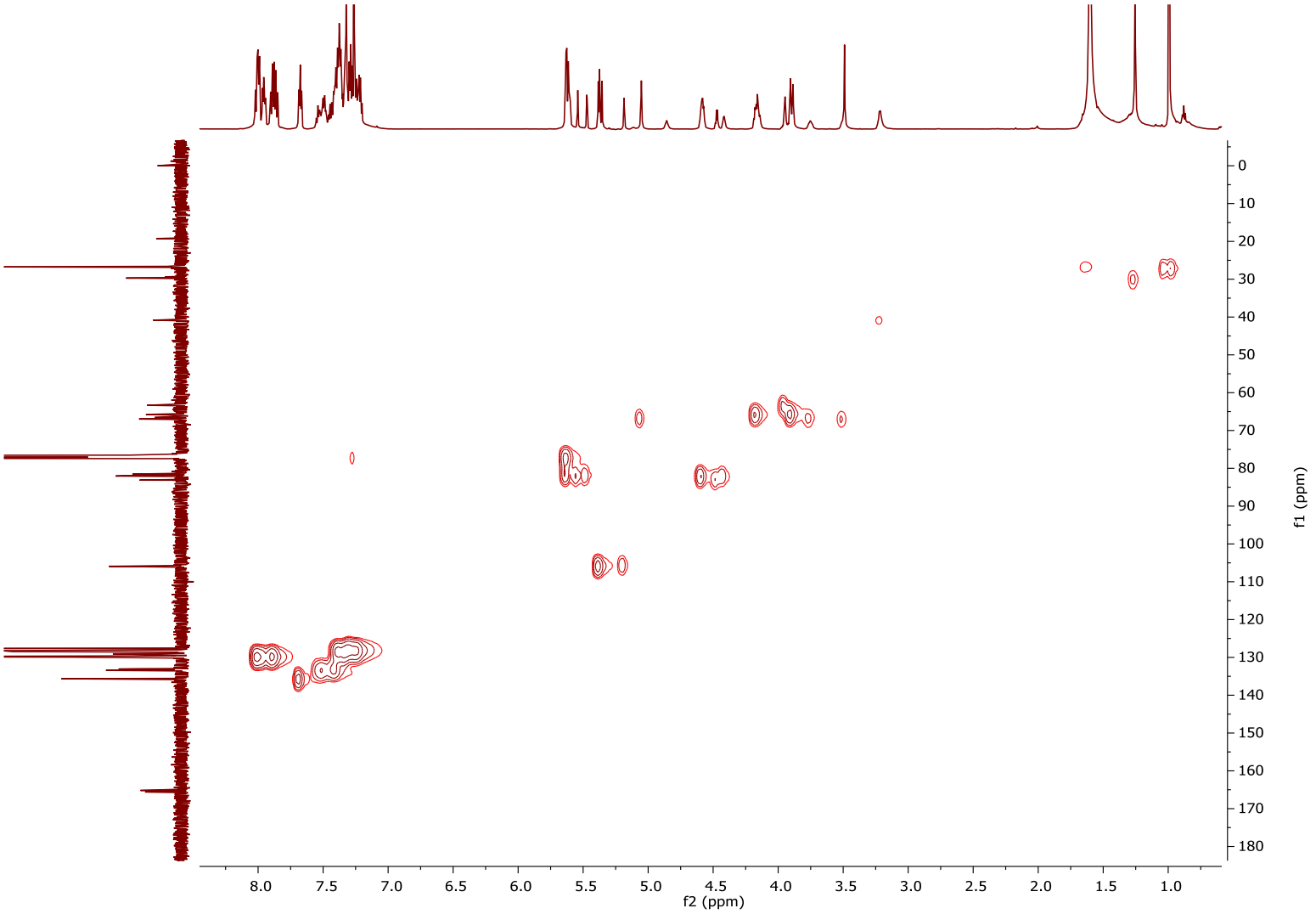
^{13}C NMR Spectrum (150.99 MHz, $CDCl_3$) of Compound **14**



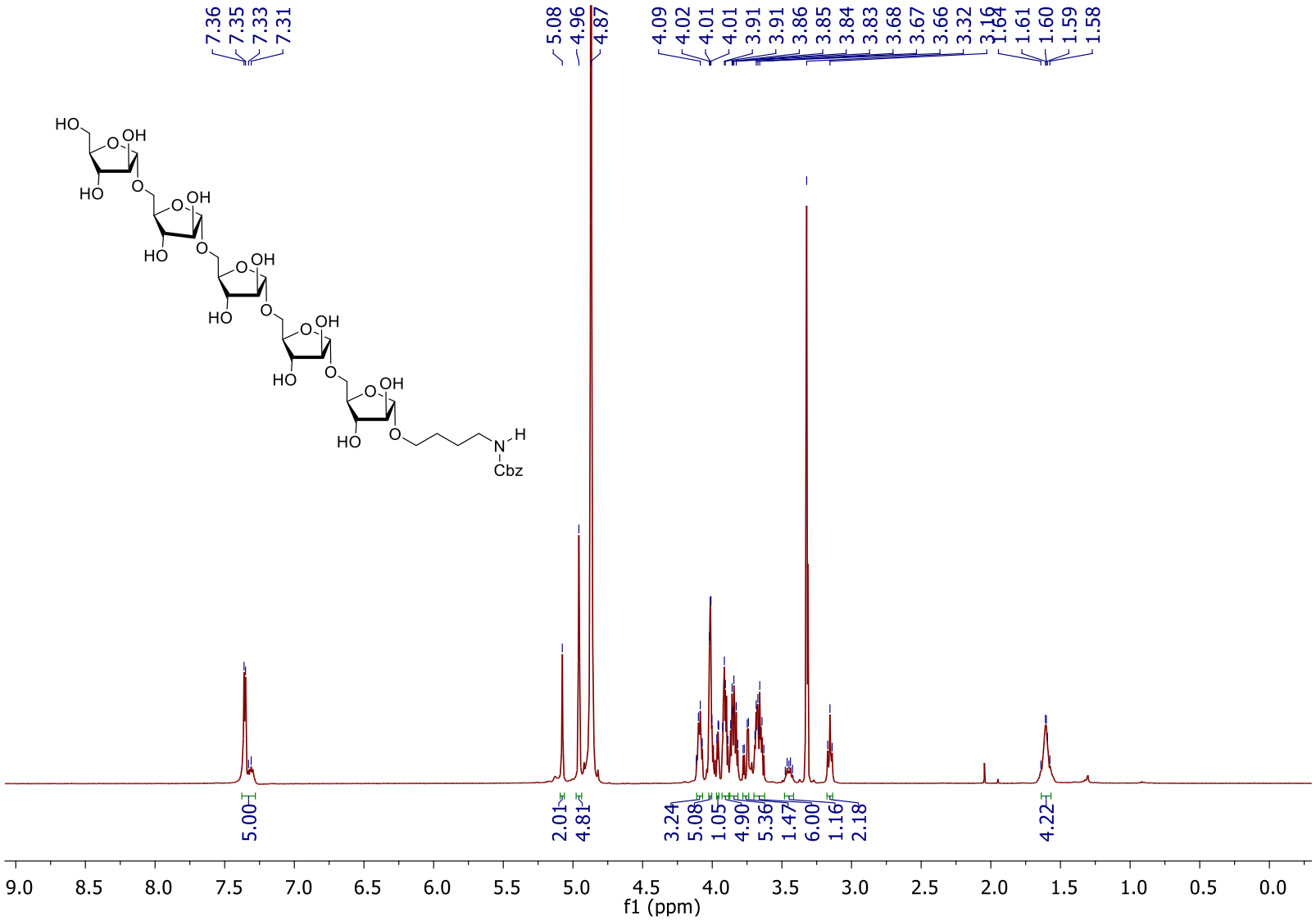
DEPT-135 NMR Spectrum (150.99 MHz, $CDCl_3$) of Compound **14**



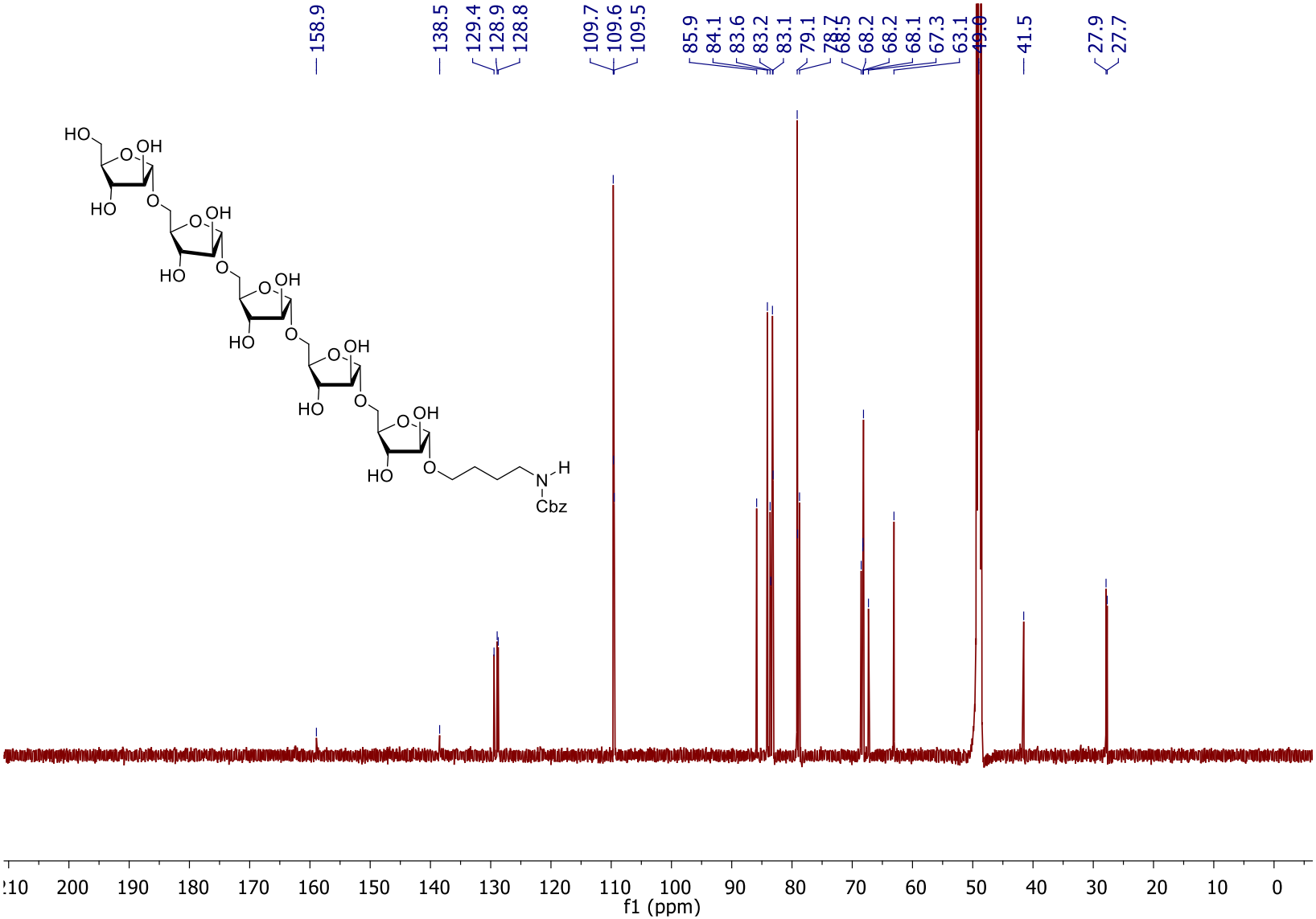
HSQC ^{13}C decoupled NMR spectrum of compound **14**



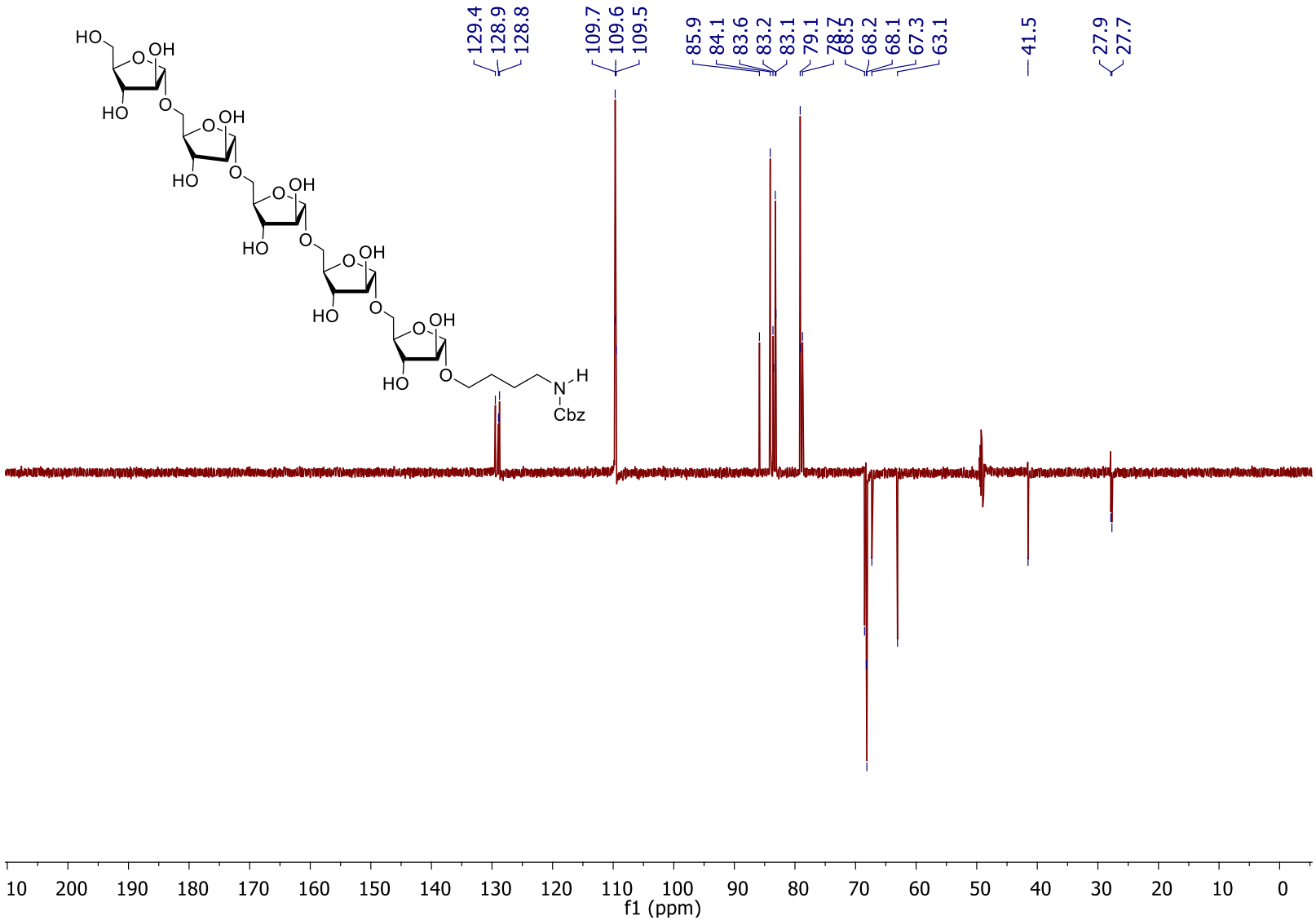
^{1}H NMR Spectrum (400.31MHz, CD_3OD) of Compound **1**



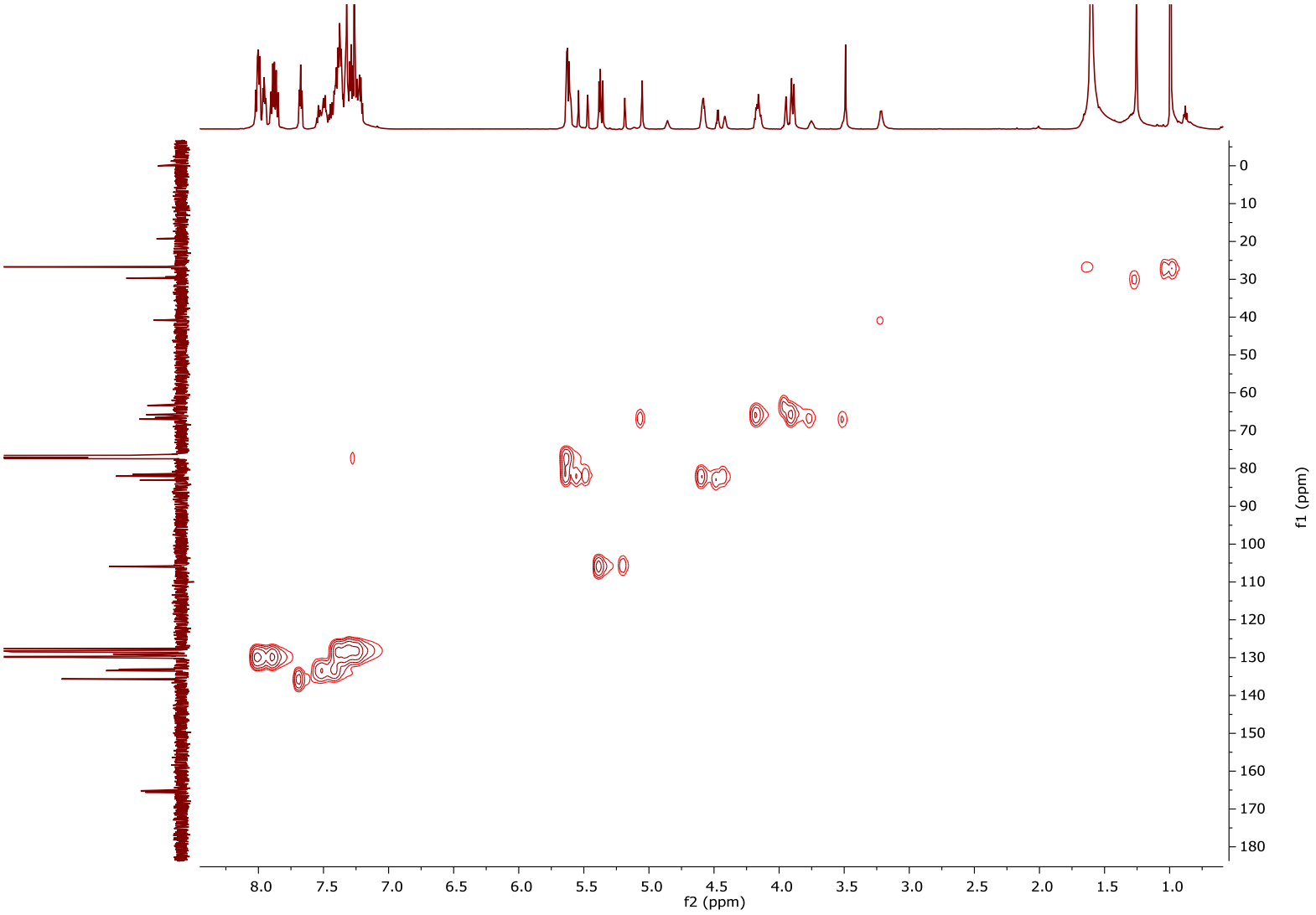
^{13}C NMR Spectrum (150.99 MHz, CD_3OD) of Compound **1**



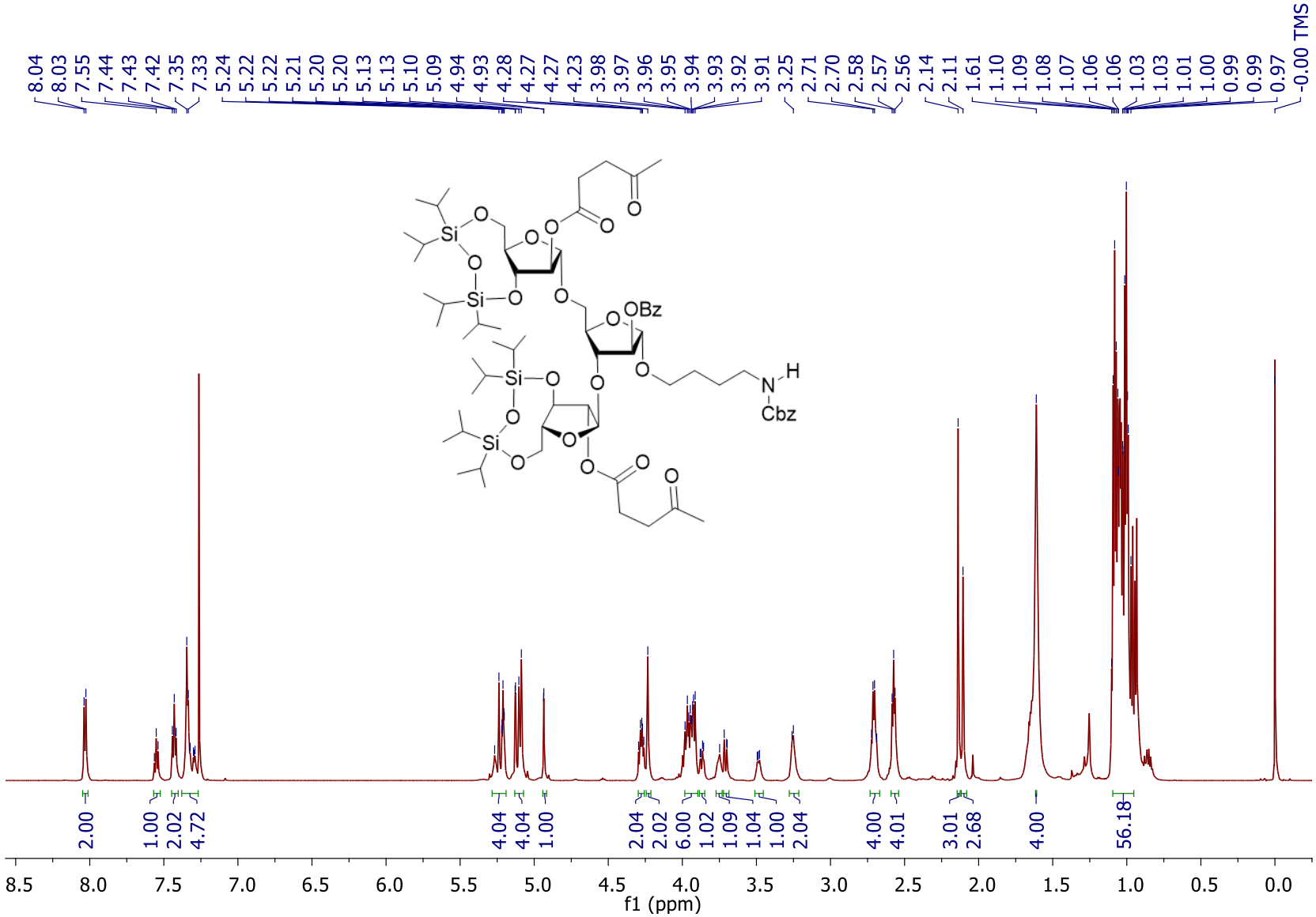
DEPT-135 NMR Spectrum (150.99 MHz, CD_3OD) of Compound **1**



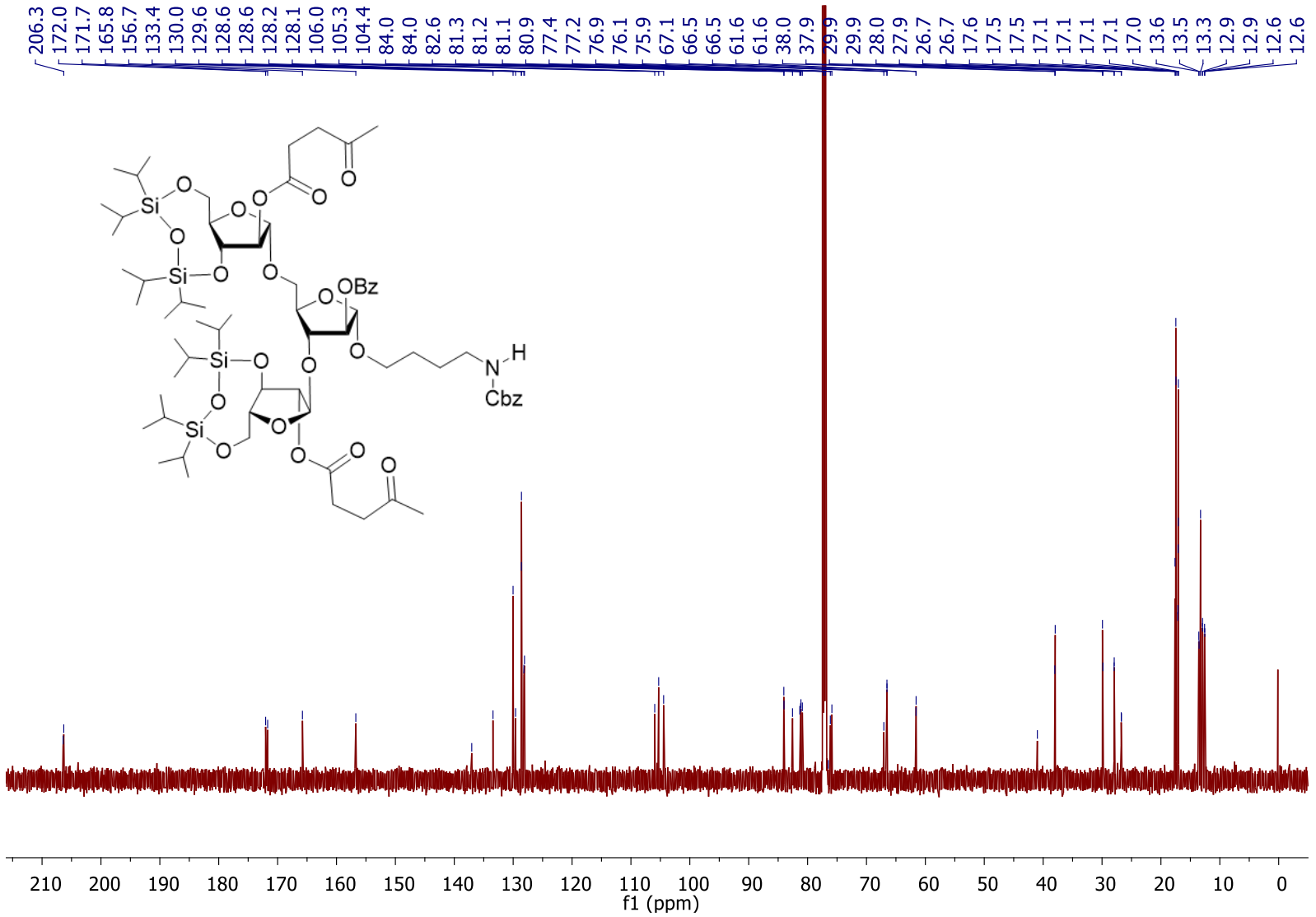
HSQC ^{13}C decoupled NMR spectrum of compound **1**



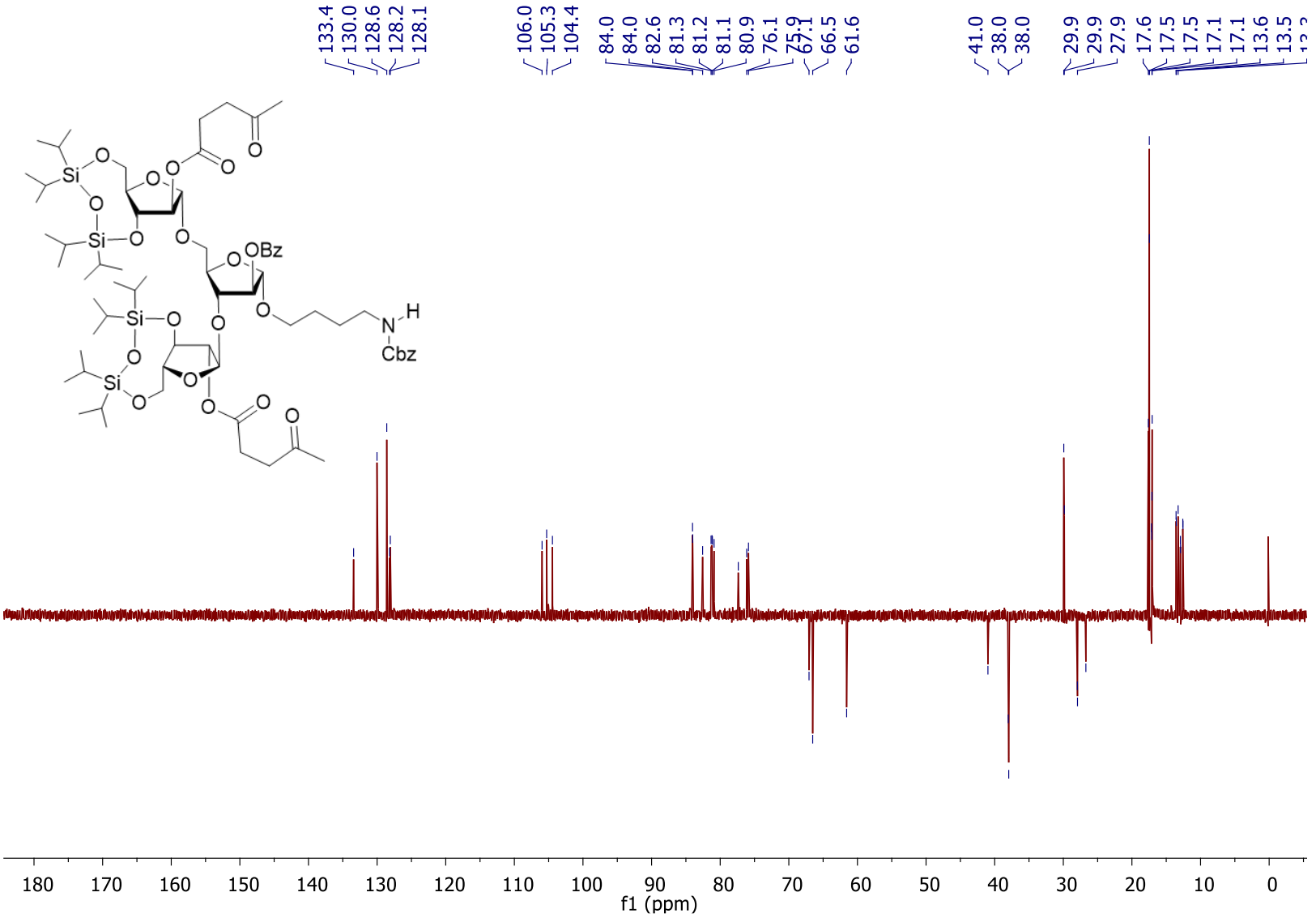
^{1}H NMR Spectrum (600.40 MHz, $CDCl_3$) of Compound **16**



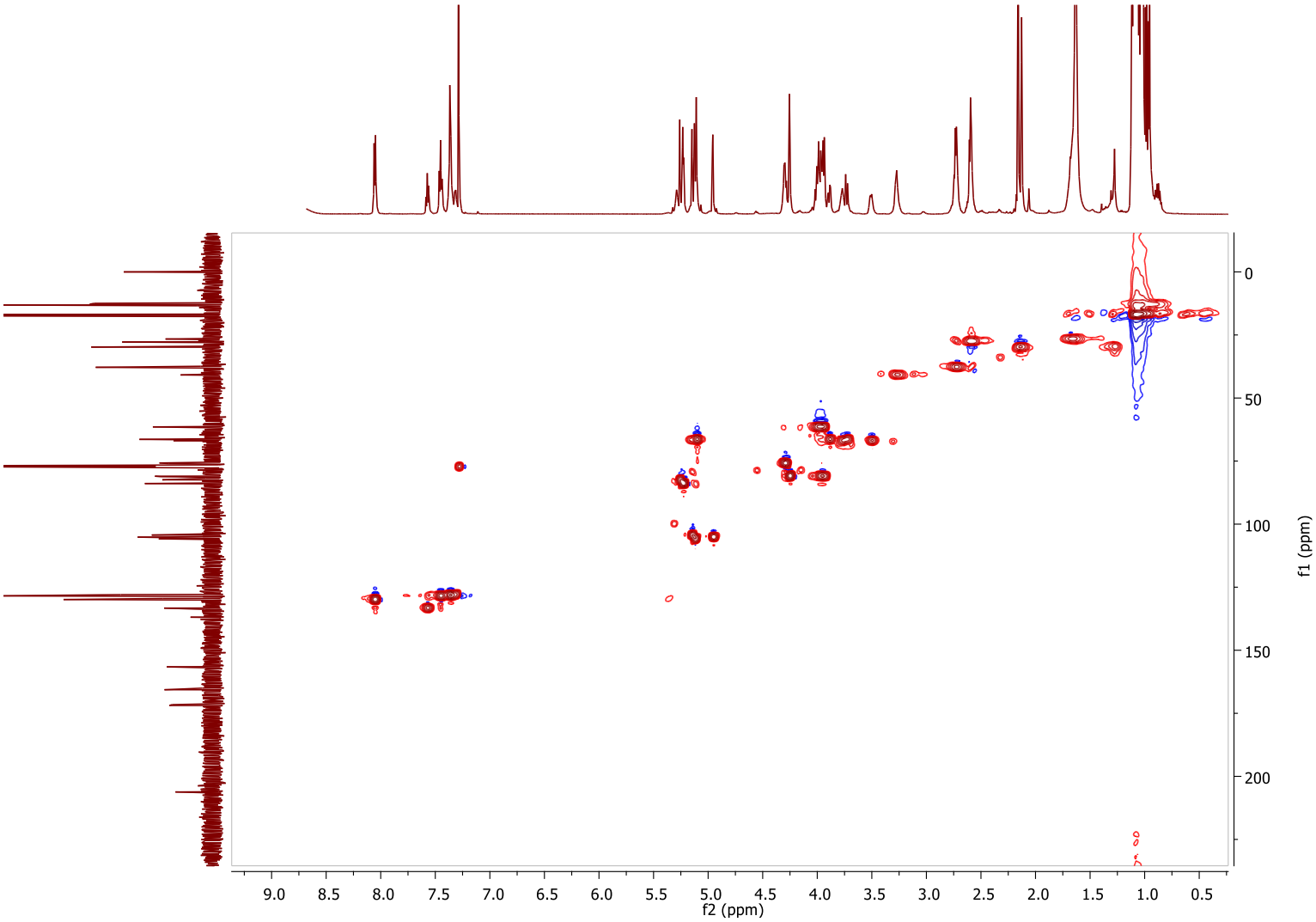
^{13}C NMR Spectrum (150.97 MHz, $CDCl_3$) of Compound **16**



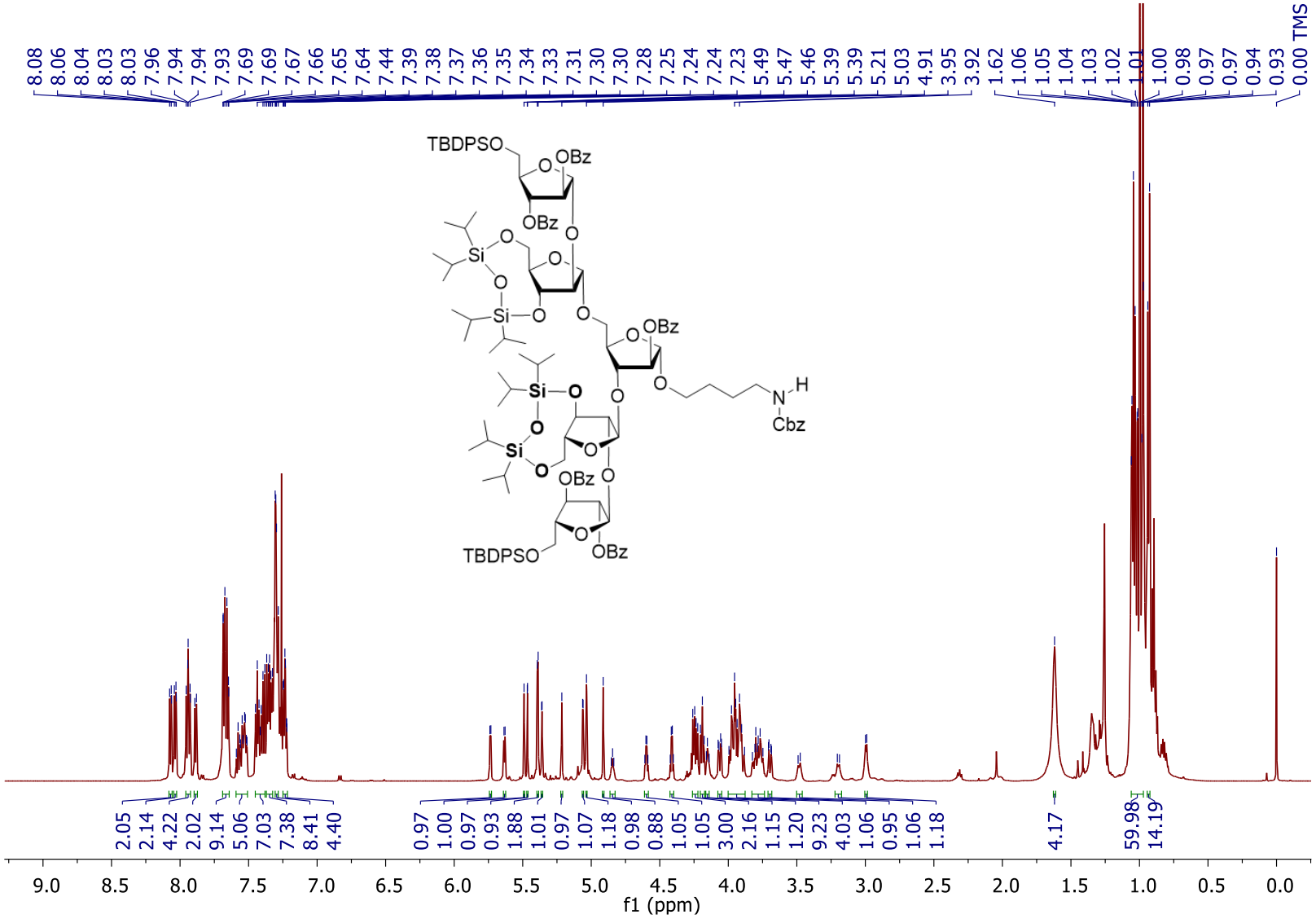
DEPT-135 NMR Spectrum (150.97 MHz, $CDCl_3$) of Compound **16**



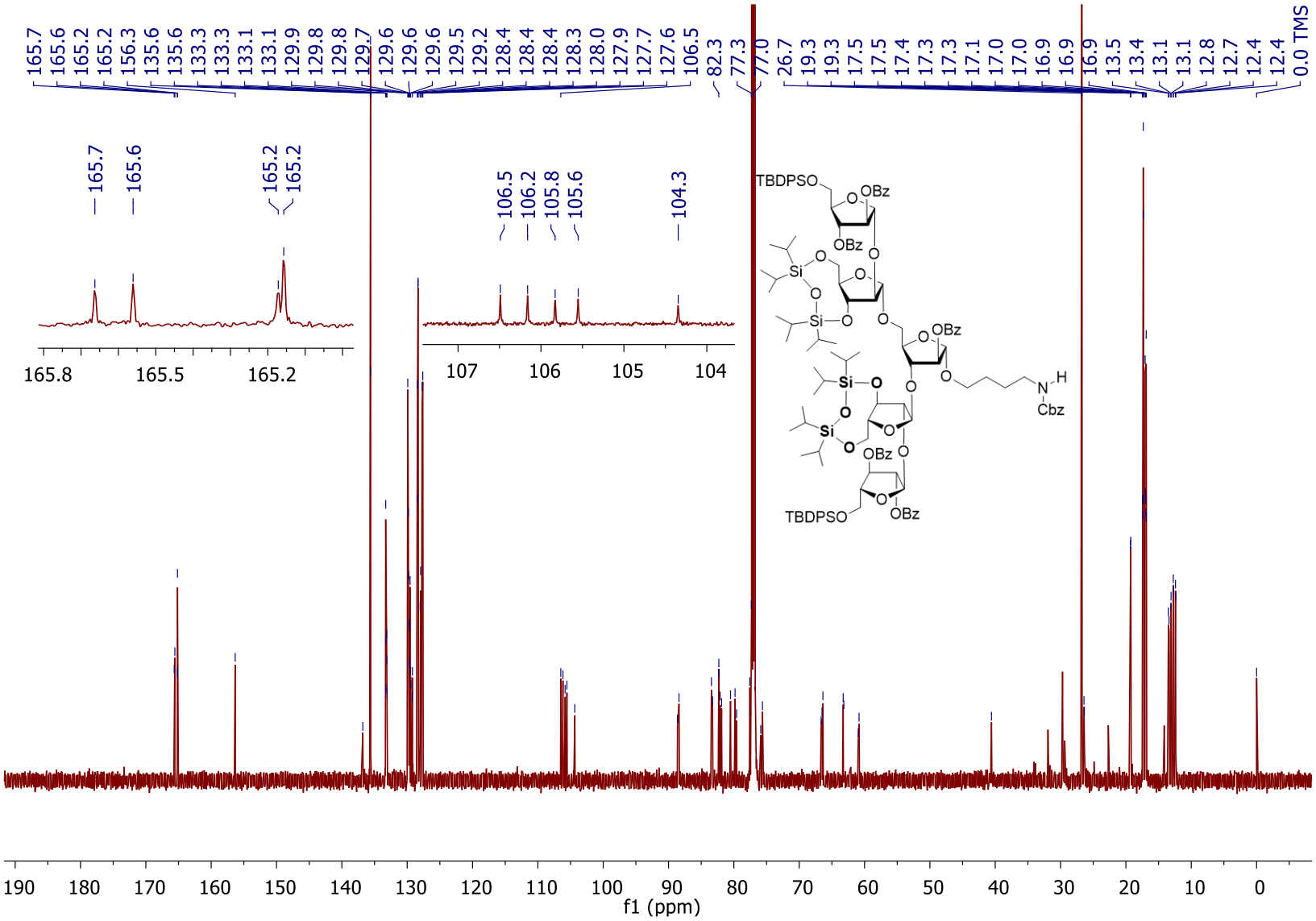
HSQC ^{13}C decoupled NMR spectrum of compound **16**



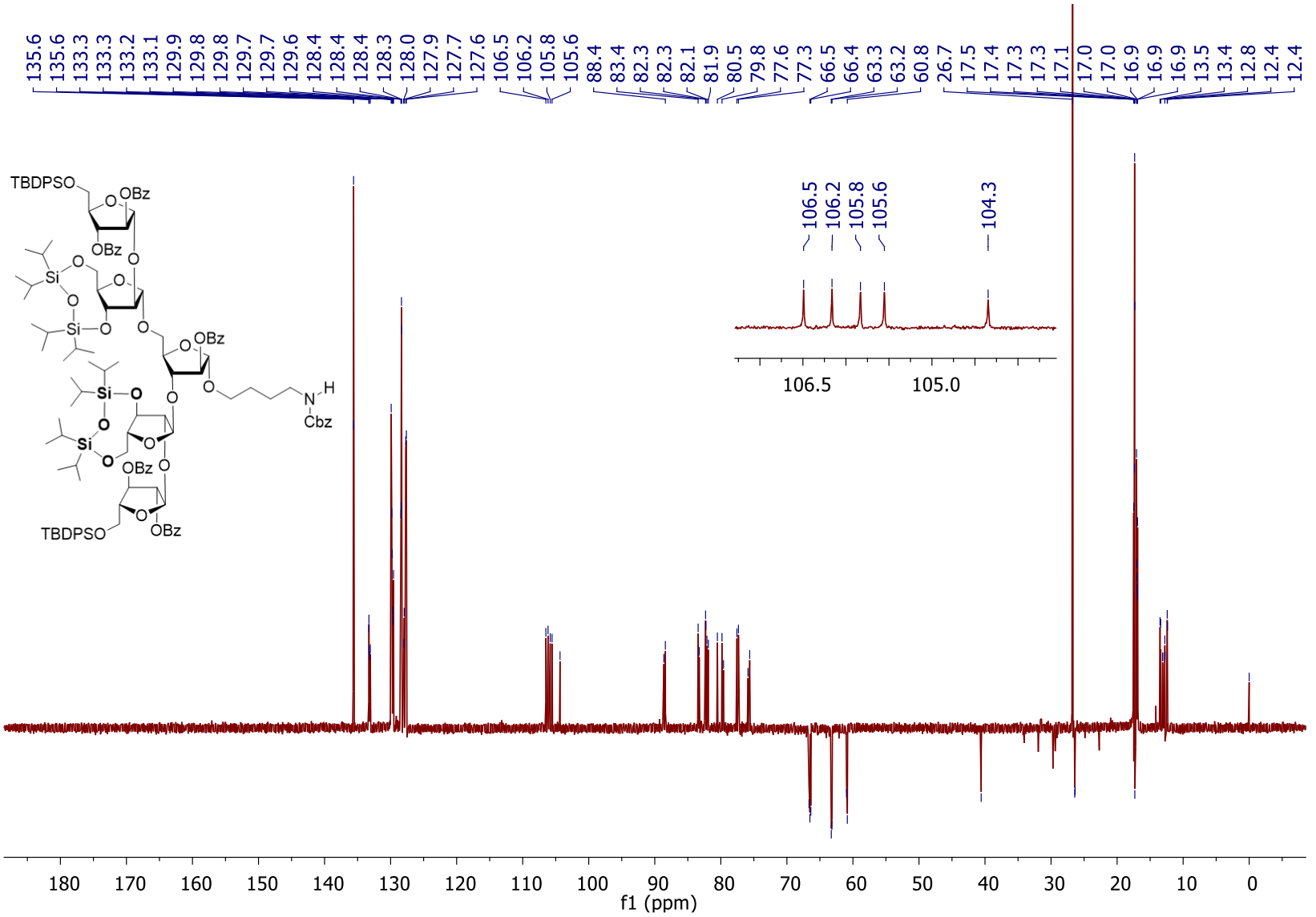
^{1}H NMR Spectrum (600.40 MHz, $CDCl_3$) of Compound **18**



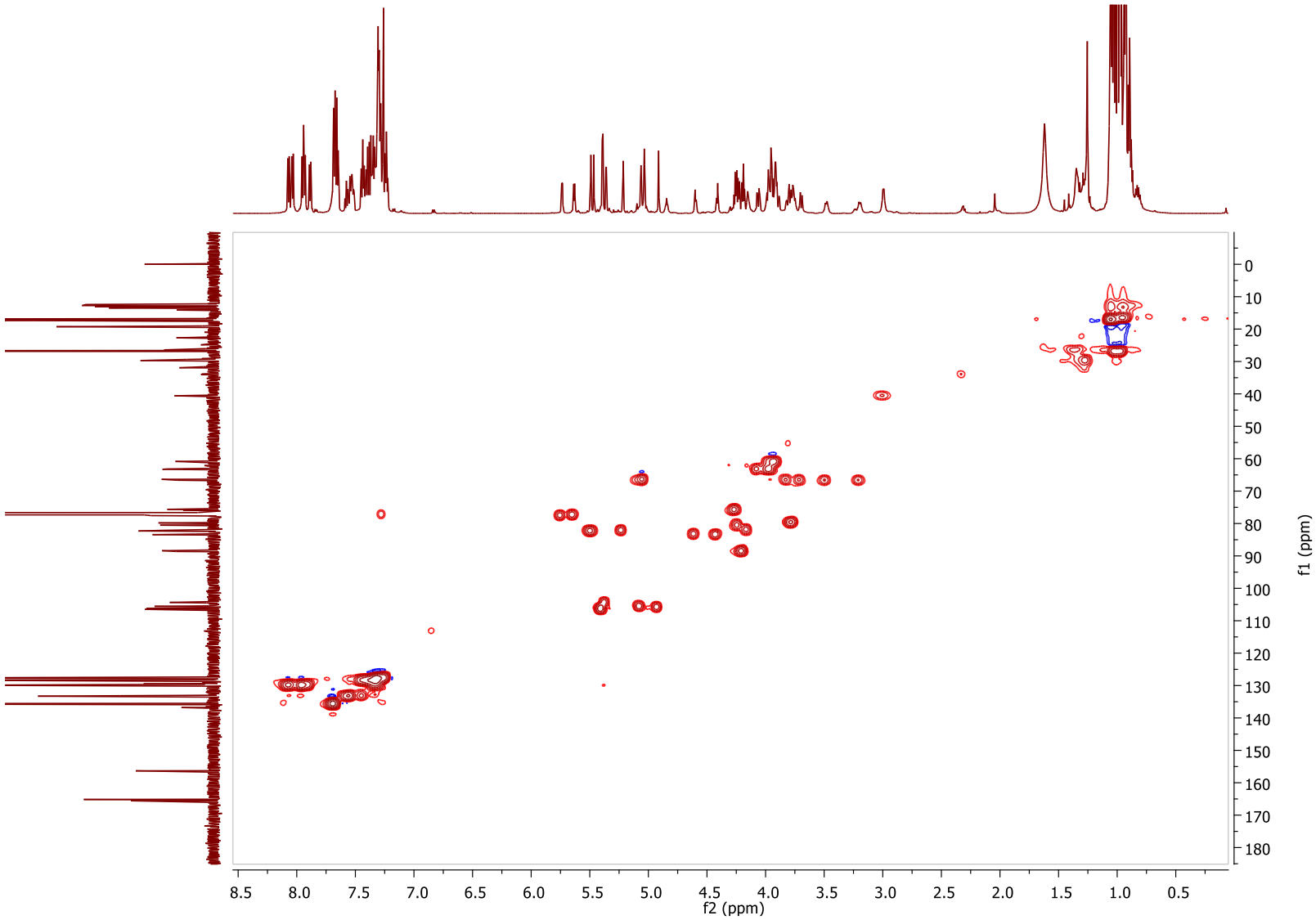
^{13}C NMR Spectrum (150.97 MHz, $CDCl_3$) of Compound **18**



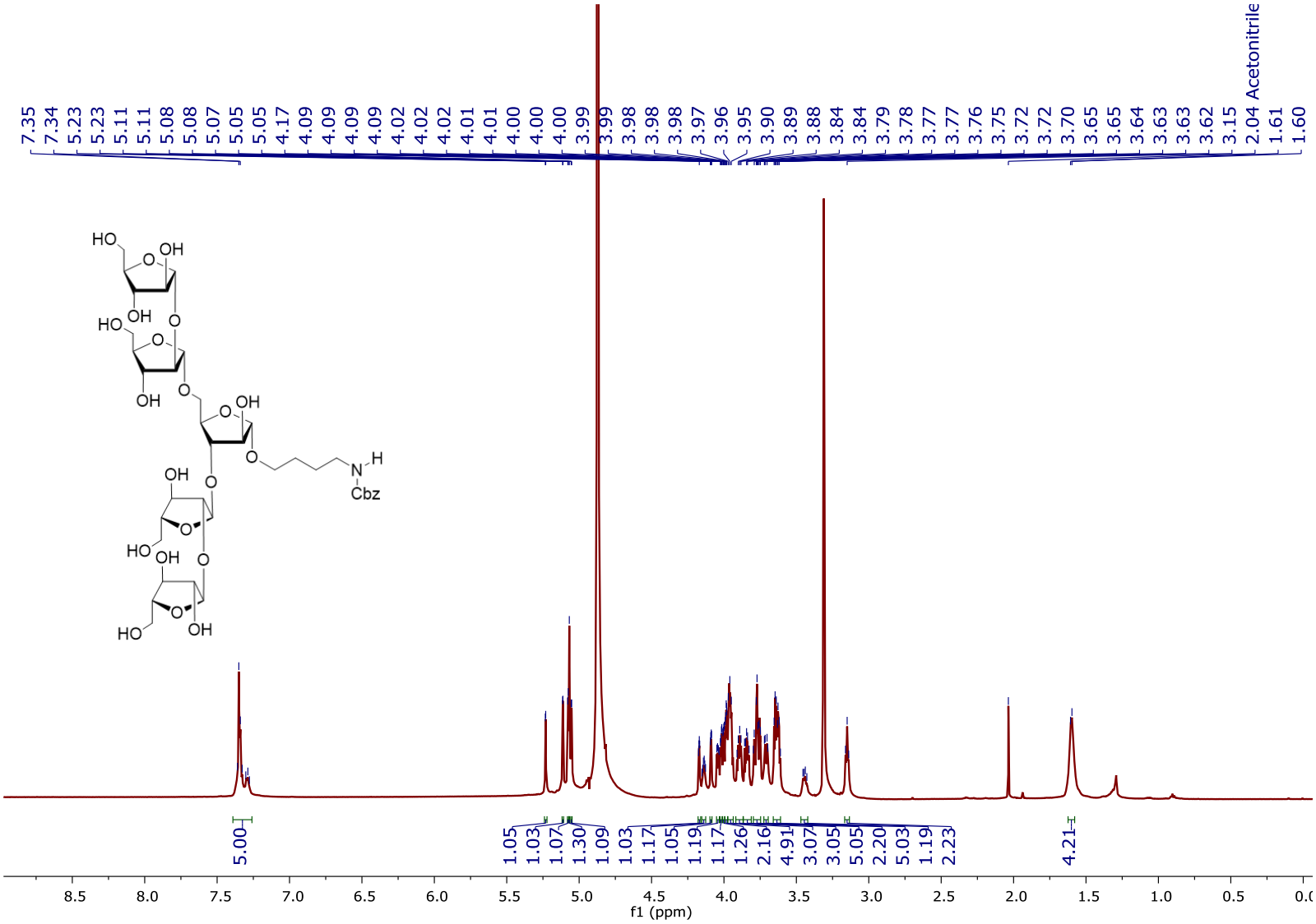
DEPT-135 NMR Spectrum (150.97 MHz, $CDCl_3$) of Compound **18**



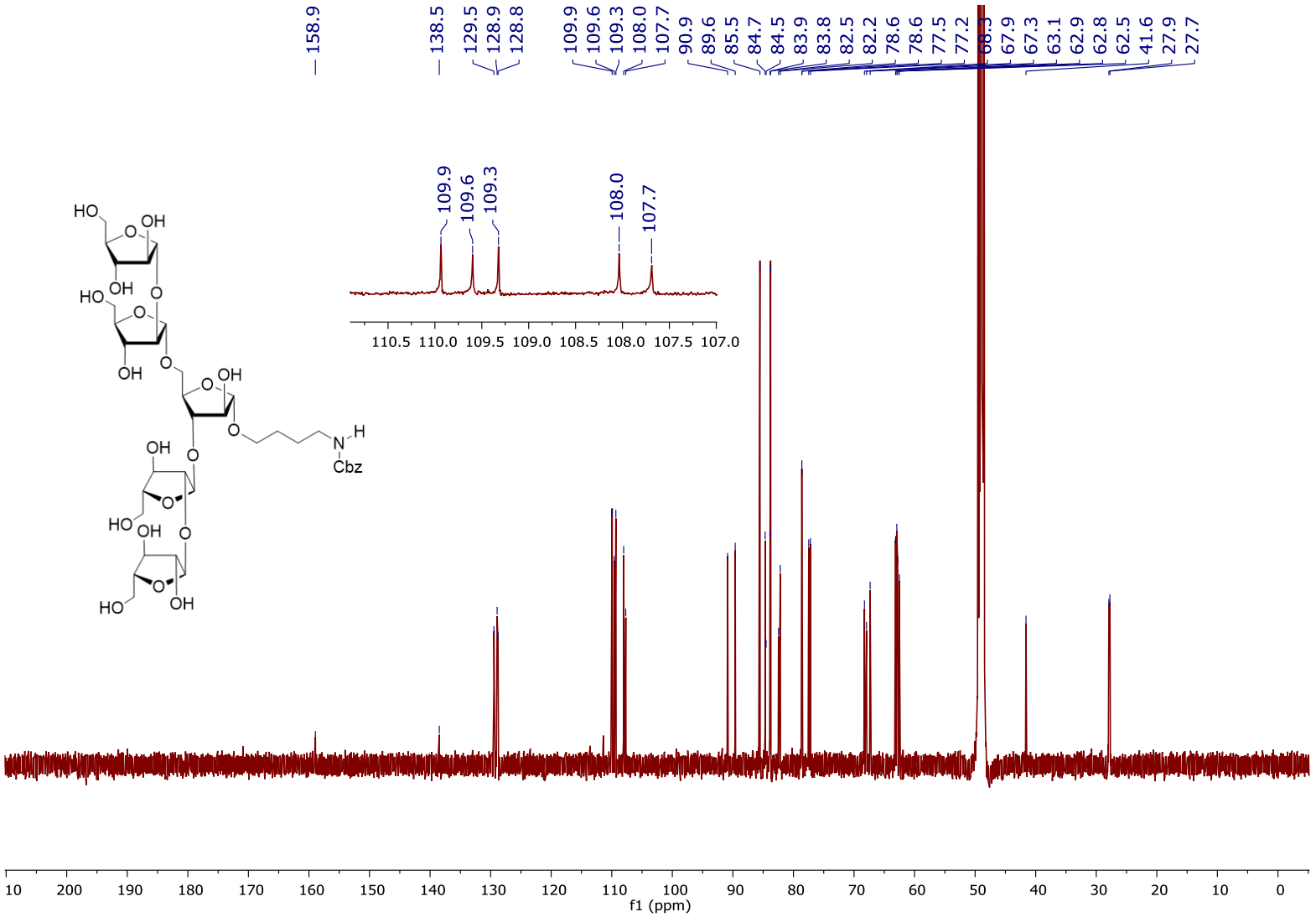
HSQC ^{13}C decoupled NMR spectrum of compound **18**



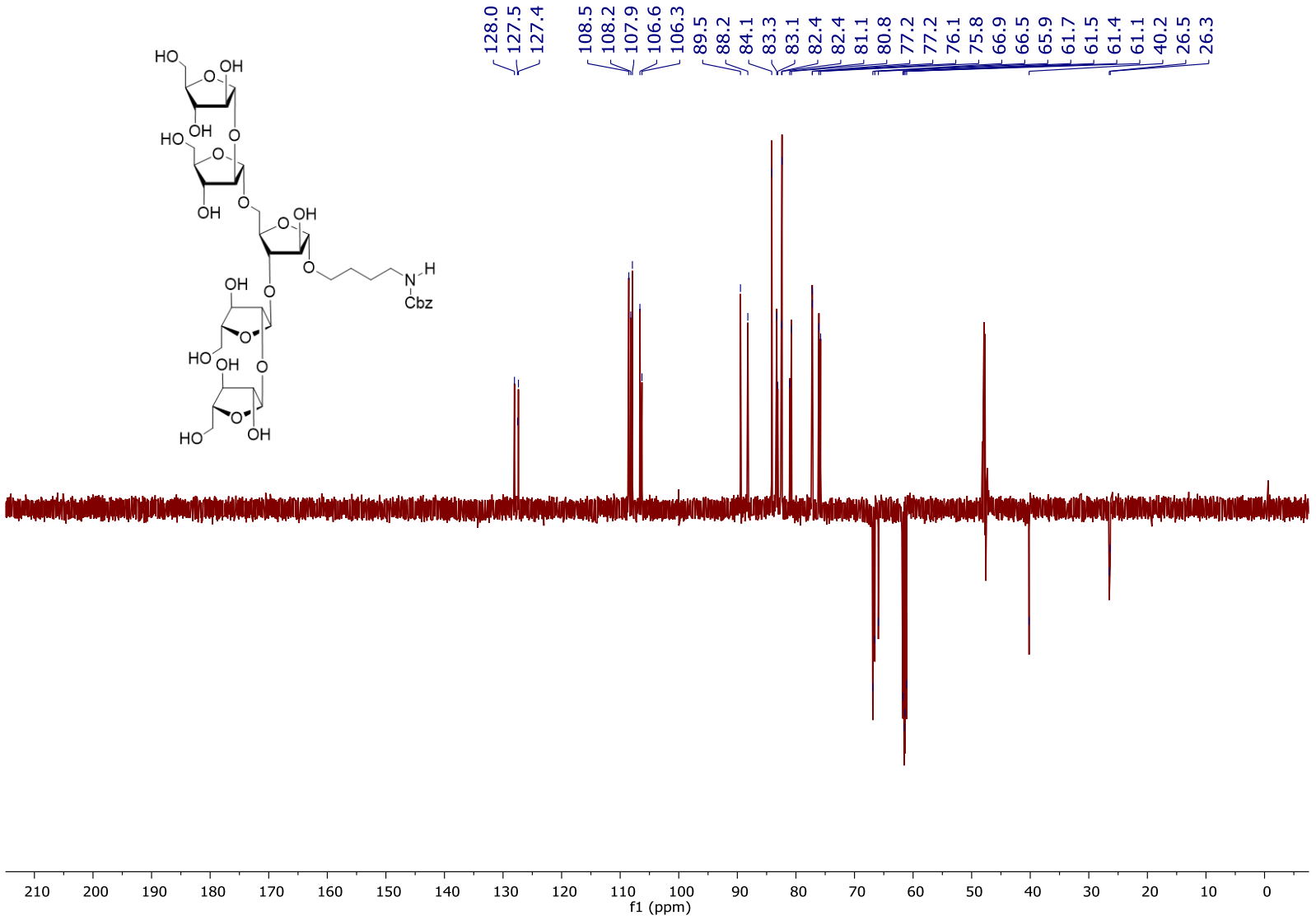
^{1}H NMR Spectrum (600.40 MHz, CD_3OD) of Compound **2**



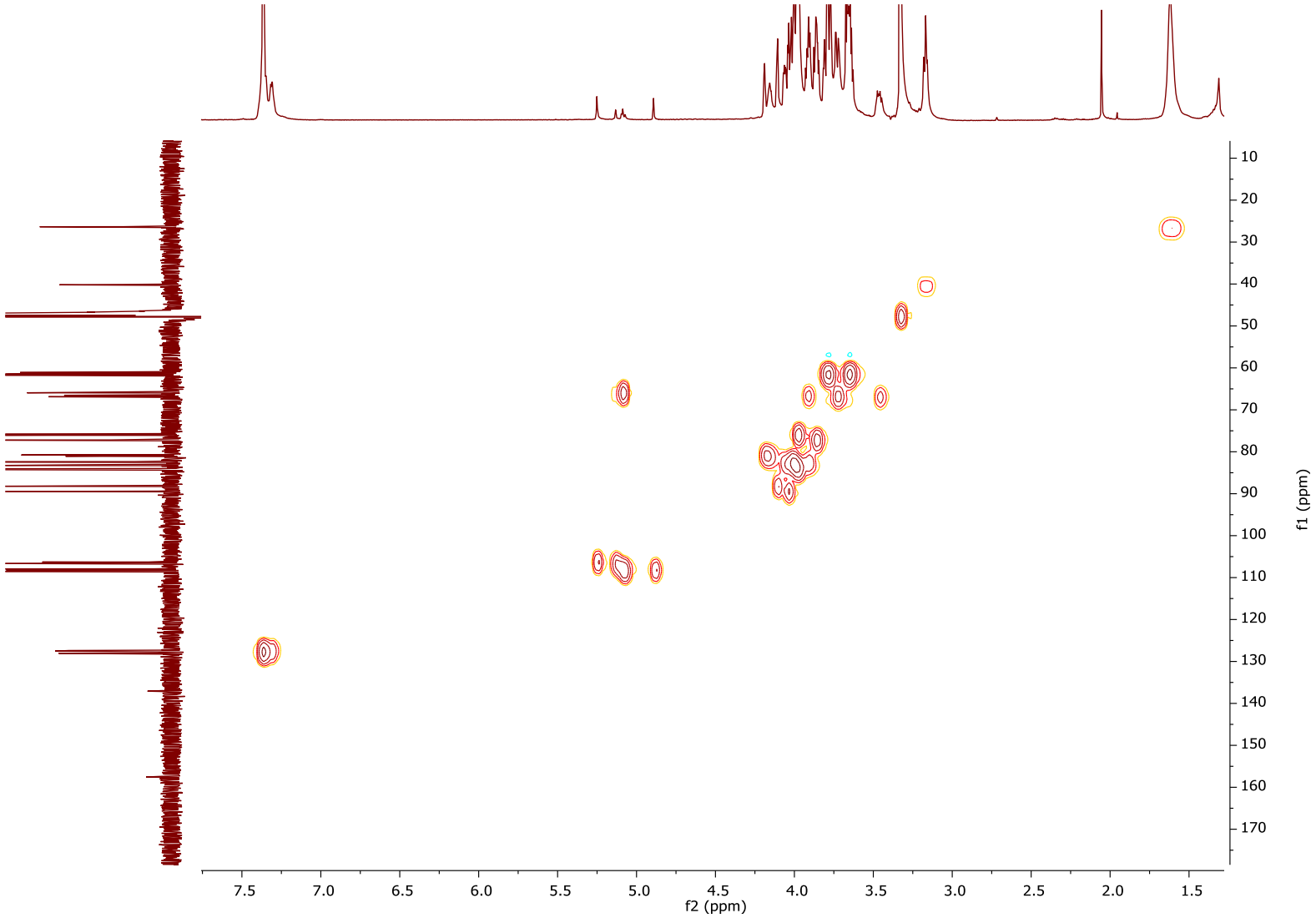
^{13}C NMR Spectrum (150.99 MHz, CD_3OD) of Compound **2**



DEPT-135 NMR Spectrum (150.99 MHz, CD_3OD) of Compound **2**

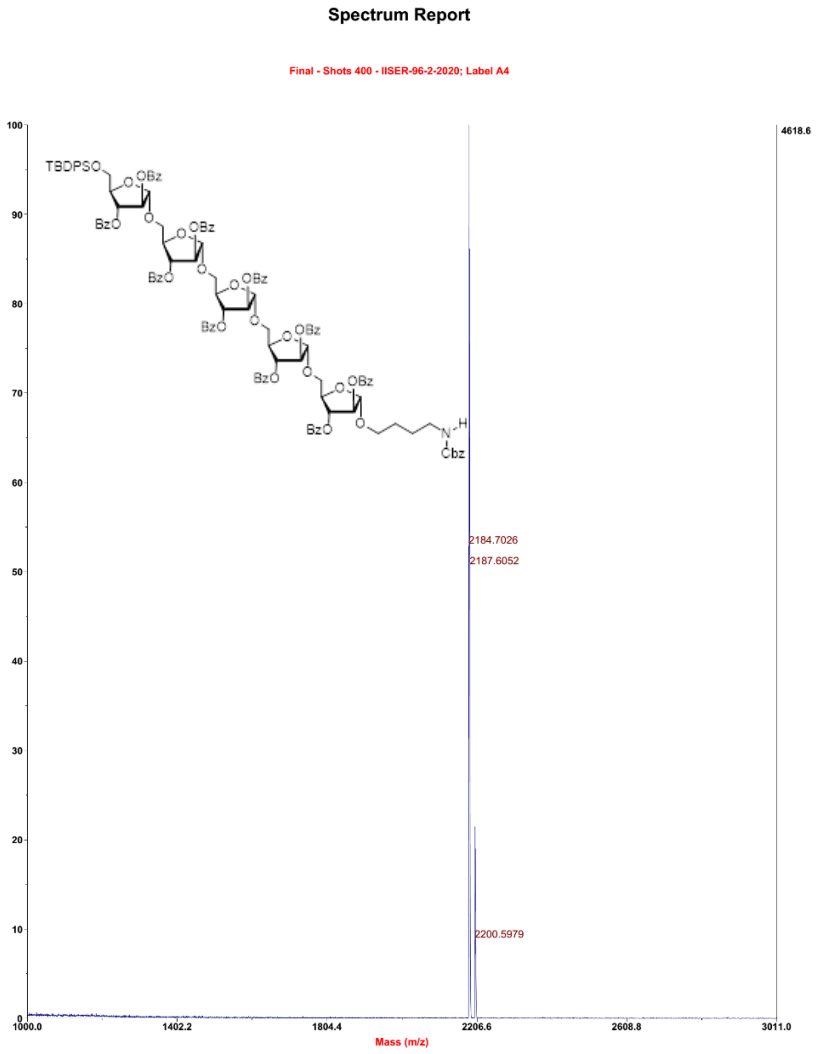


HSQC ^{13}C decoupled NMR spectrum of compound **2**

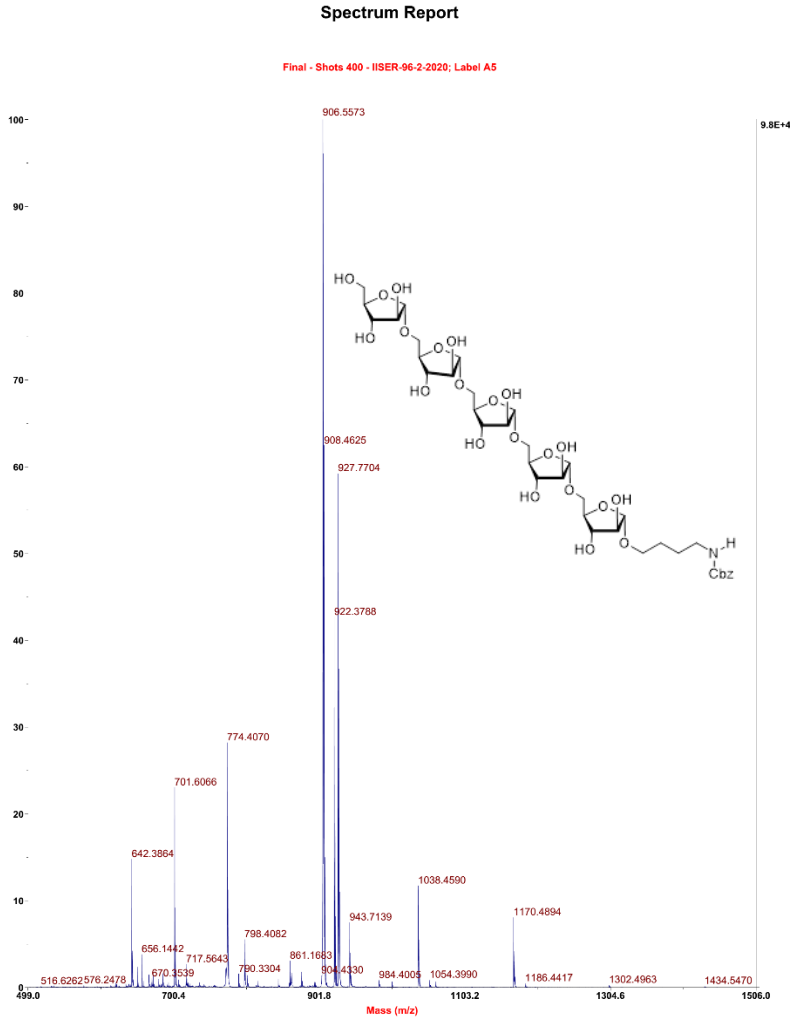


11.0 MALDI-TOF Mass spectral charts of compounds

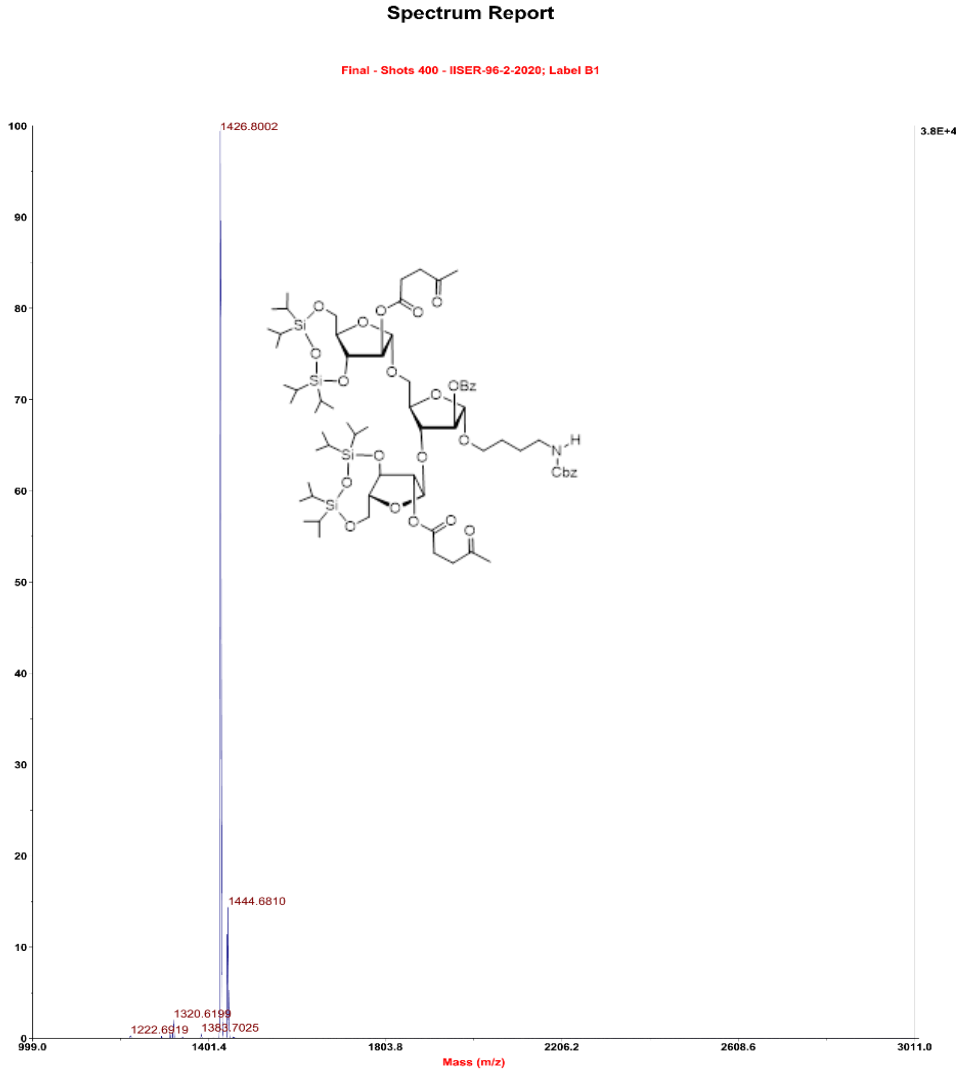
MALDI-TOF Mass Spectrum of Compound **14**



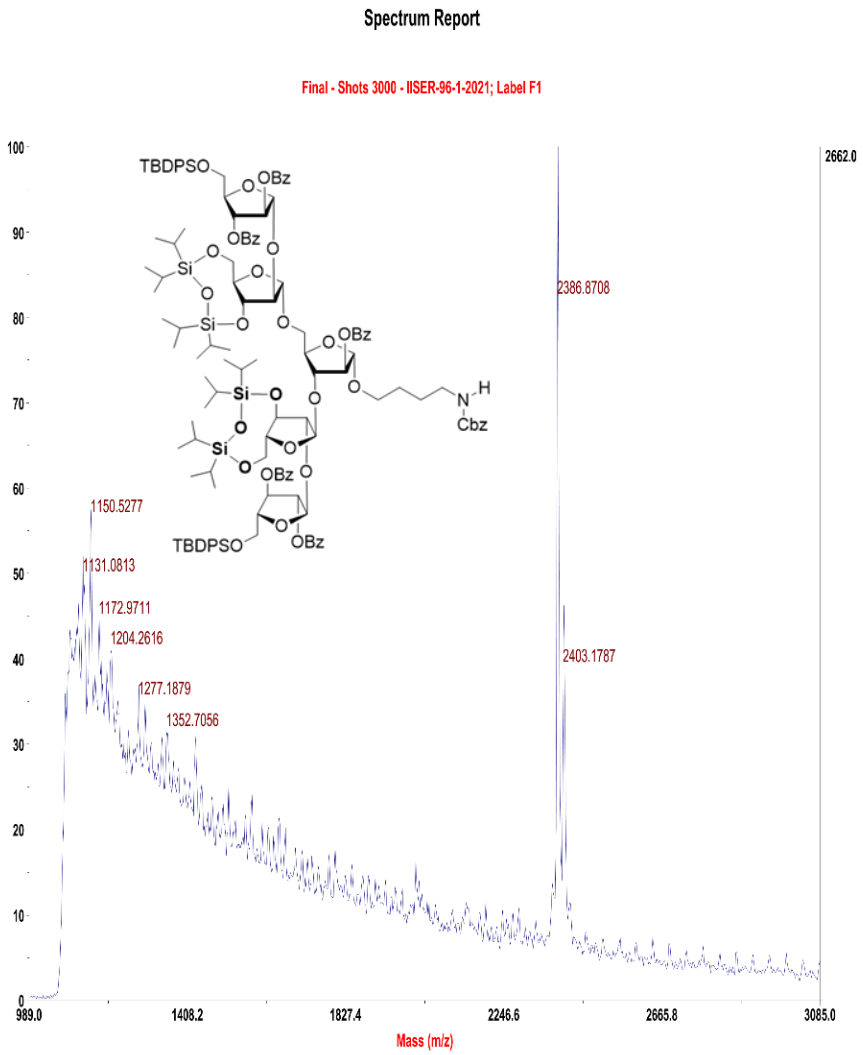
MALDI-TOF Mass Spectrum of Compound **1**



MALDI-TOF Mass Spectrum of Compound **16**



MALDI-TOF Mass Spectrum of Compound **18**



MALDI-TOF Mass Spectrum of Compound **2**