Stereocontrolled Glycoside Synthesis by Activation of Glycosyl Sulfone Donors with Scandium(III) triflate

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Experimental Details

General

Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F_{254} plates and visualized under UV (254 nm) and/or by staining with $KMnO_4$ or vanillin. Silica gel SDS 60 ACC 35-70 mm was used for column chromatography. Preparative TLC was done using Merck 60 F_{254} 0.5 mm. NMR spectra were recorded with AM 300, AVANCE 300 and AVANCE 500 Brüker spectrometers. Chemical shifts are given in parts per million, referenced to the solvent peak of $CDCl_3$, defined at 77.23 ppm (^{13}C NMR) and 7.26 ppm (^{1}H NMR). Microwave reactions were carried out with an Anton Paar Monowave 300 instrument. Melting points (uncorrected) were determined with the aid of a Büchi B-540 apparatus. IR spectra were recorded on a Perkin-Elmer Spectrum BX instrument with an FT-IR system. Optical rotations were measured on an Anton Paar MCP300 polarimeter using a cell of 1 dm-length path. All the reagent grade chemicals obtained from commercial sources were used as received.

The ratio α/β were determined by Reversed phase (RP)-UPLC-MS analyses. The instrument used for all the analysis was an UPLC system equipped with a PDA and a triple quadrupole mass spectrometer detector (Acquity UPLC-TQD, Waters). RP-UPLC (HSS T3 column, 1.8 μm, 2.1 mm × 100 mm) with 0.1% formic acid in CH_3CN and 0.1% formic acid in water as eluents at a flow rate of 0.6 mL/min. The detection was performed by PDA and using the TQD mass spectrometer operated in electrospray ionization positive mode at 3.2 kV capillary voltage.

Compounds **6, 4, 10**, **20, 22** are commercially available. Compound **3** was described in the literature[1]. Compounds **16**[2], **14**[3], **8**[4], **18**[5], **24**[6], **26**[7], **36**[8], **37**[9], **41**[10] and **43**[11] were prepared according to known procedures.

General procedure for oxidation of thioglycosides

A solution of thioglycoside (1 equiv.) in CH_2Cl_2 (0.2M) was treated at 0 °C with $NaHCO_3$ (8.2 equiv.) and 3-chloroperoxybenzoic acid (75 %, 2.5 equiv.) and was stirred for 1 hour at room temperature. The resulting mixture was diluted with CH_2Cl_2 and successively washed with saturated aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$. The organic layer was washed with brine, dried over Na_2SO_4, filtered and the solvents were removed under reduced pressure.

(2-Methyl-5-*tert*-butylphenyl) 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl sulfone 1: The General oxidation Procedure was followed using (2-methyl-5-*tert*-butylphenyl) 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyranoside **36**[8] (1.82 g, 2.59 mmol, 1 equiv.), $NaHCO_3$ (1.78 g, 21.12

mmol), *m*CPBA (1.52 g, 6.60 mmol) in CH_2Cl_2 (9 mL). The crude product was purified by chromatography on silica gel (heptane/EtOAc 9:1 to 8:2) to afford pure product **1** (1.47 g, 78 %, white amorphous solid). $[\alpha]_D^{20} = +40.3$ (*c* = 1.0, $CHCl_3$). IR: ν = 3064 and 3030 (=C-H), 2962 and 2865 (C-H) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 2.0 Hz, 1H, H_{aro} (SMbp)), 7.50 (dd, *J* = 8.0 Hz and *J* = 2.0 Hz, 1H, H_{aro} (SMbp)), 7.37-7.20 (m, 20H, H_{aro}), 7.16-7.12 (m, 1H, H_{aro} (SMbp)), 4.91 (d, $J_{1,2}$ = 2.0 Hz, 1H, *H1*), 4.81 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.74 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.67-4.65 (m, 2H, CH_2Ph), 4.61 (dd, $J_{2,3}$ = 3.5 Hz and $J_{2,1}$ = 2.0 Hz, 1H, *H2*), 4.48 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.43 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.42-4.37 (m, 1H, *H5*), 4.32 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.26 (dd, $J_{3,4}$ = 8.5 Hz and $J_{3,2}$ = 3.5 Hz, 1H, *H3*), 4.04 (dd, $J_{4,3} = J_{4,5}$ = 8.5 Hz, 1H, *H4*), 3.64 (dd, $J_{6,6'}$ = 11.0 Hz and $J_{6,5}$ = 4.0 Hz, 1H, *H6*), 3.46 (dd, $J_{6',6}$ = 11.0 Hz and $J_{6',5}$ = 2.0 Hz, 1H, *H6'*), 2.52 (s, 3H, ArCH_3), 1.28 (s, 9H, ArC(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 150.1 (Cq_{aro}, SMbp), 138.6 (Cq_{aro}), 138.5 (Cq_{aro}), 138.3 (Cq_{aro}), 137.8 (Cq_{aro}), 136.0 (Cq_{aro}, SMbp), 135.0 (Cq_{aro}, SMbp), 133.0 (CH$_{aro}$, SMbp), 131.5 (CH$_{aro}$, SMbp), 128.9 (2×CH$_{aro}$), 128.8 (2×CH$_{aro}$), 128.7 (4×CH$_{aro}$), 128.6 (2×CH$_{aro}$), 128.3 (4×CH$_{aro}$), 128.2 (4×CH$_{aro}$), 128.1 (CH$_{aro}$), 128.1 (2×CH$_{aro}$), 128.0 (CH$_{aro}$), 127.9 (CH$_{aro}$), 91.2 (*C1*), 79.8 (*C3*), 76.8 (*C5*), 75.0 (CH$_2$Ph), 74.0 (*C4*), 73.6 (CH$_2$Ph), 73.5 (CH$_2$Ph), 73.0 (CH$_2$Ph), 71.8 (*C2*), 69.0 (*C6*), 35.0 (ArC(CH$_3$)$_3$), 31.5 (ArC(CH$_3$)$_3$), 20.4 (ArCH$_3$). HRMS **(**ESI): calcd. for $C_{45}H_{50}O_7NaS$ $[M+Na]^+$: 757.3175. Found: 757.3204.

***Iso*-propyl 2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranoside 2b**[12]: phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-**α-D**-mannopyranoside[13] (250 mg, 0.463 mmol), and molecular sieves (4 Å, 400 mg) were stirred in dry CH_2Cl_2 (9.3 mL) at room temperature for 30 min. The reaction mixture was cooled to –60 °C and 1-benzenesulfinyl piperidine (106 mg, 0.509 mmol, 1.1 equiv.) and 2,4,6-tri-*tert*-butylpyrimidine (230 mg, 0.926 mmol, 2 equiv.) were added followed by the addition of Tf_2O (176 µL, 1.046 mmol, 1.2 equiv). After activation of donor (10 min), a solution of isopropanol (53 µL, 0.694 mmol, 1.5 equiv.) in CH_2Cl_2 (4.6 mL) was added. The reaction was stirred for 60 min at –60 °C. The reaction was then quenched with triethylamine (100 µL), and the resulting mixture was warmed to room temperature, filtered and washed with saturated aqueous $NaHCO_3$. The aqueous phase was extracted twice with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (heptane/EtOAc 95:5 to 90:10) gave the desired *iso*-propyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside[14] as a colorless oil (160 mg, 71%). A solution of this latter (160 mg, 0.326 mmol, 1 equiv.) in water

(53 µL) and TFA (100 µL) was stirred for 2 h at room temperature. After neutralisation with NEt_3 (0.3 mL), water (10 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL), the combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting precipitate was washed with pentane (3 x 10 mL) to lead to the corresponding diol (phenyl 2,3-di-*O*-benzyl-1-thio-**α-D**-mannopyranoside) (0.115 g, 88%), which was benzylated using (BnBr, NaH) in DMF to give after chromatography on silica gel (heptane/EtOAc 95:5 to 8:2) the corresponding compound **2b** as a colorless oil (0.125 g, 75%).

(2-Methyl-5-*tert*-butylthiophenyl) 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl sulfone 28: (2-Methyl-5-*tert*-butylthiophenyl) 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside[15] (1.9 g, 4.4 mmol) was benzylated using (BnBr, NaH) in DMF to give after chromatography on silica gel (heptane/EtOAc 100:0 to 8:2) the corresponding compound as a colorless oil (2.3 g, 3.8 mmol, 86%). The General oxidation Procedure was then followed using $NaHCO_3$ (2.6 g, 31 mmol), *m*CPBA (2.1 g, 9.5 mmol) in CH_2Cl_2 (19 mL). The crude product was purified (heptane/EtOAc 8:2) to afford the desired product **28** (2 g, 3.1 mmol, 83%) as a white solid. Mp = 135-136 °C (after recristallisation in heptane/EtOAc 6:4) $[\alpha]_D^{22}$ = +38.2 (*c* = 1.0, $CHCl_3$). IR: ν = 3092 and 3064 (=C-H), 2966, 2902 and 2871 (C-H) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.85 (d, *J* = 2.0 Hz, 1H, H_{aro}), 7.47-7.35 (m, 3H, H_{aro}), 7.32-7.09 (m, 14H, H_{aro}), 5.49 (s, 1H, PhC*H*O_2), 4.78 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.74-4.67 (m, 2H, OCH_2Ph and *H1*), 4.60 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.57-4.51 (m, 2H, OCH_2Ph and *H2*), 4.42-4.28 (m, 2H, *H5* and *H3*), 4.15 (t, *J* = 10.0 Hz, 1H, *H4*), 3.89 (dd, *J* = 4.5, 10.0 Hz, 1H, *H6*), 3.53 (t, *J* = 10.0 Hz, 1H, *H6*), 2.39 (s, 3H, CH_3) 1.23 (s, 9H, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz, α-anomer): δ 150.1 (Cq_{aro}), 138.7 (Cq_{aro}), 138.4 (Cq_{aro}), 137.3 (Cq_{aro}), 137.2 (Cq_{aro}), 135.6 (Cq_{aro}), 134.2 (Cq_{aro}), 132.8 (CH$_{aro}$), 131.3 (CH$_{aro}$), 129.0 (CH$_{aro}$), 128.6 (CH$_{aro}$), 128.4 (CH$_{aro}$), 128.2 (CH$_{aro}$), 128.1 (CH$_{aro}$), 128.0 (CH$_{aro}$), 127.8 (CH$_{aro}$), 127.7 (CH$_{aro}$), 126.1 (CH$_{aro}$), 101.7 (Ph*C*HO_2), 92.1 (*C1*), 77.8 (*C4*), 76.8 (*C3*), 74.3 (O*C*H$_2$Ph), 73.7 (O*C*H$_2$Ph), 72.6 (*C2*), 68.6 (*C5*), 68.5 (*C6*), 34.7 (*C*(CH_3)$_3$), 31.2 (*C*H_3), 19.9 (CH(*C*H_3)$_2$). HRMS **(**ESI): calcd. for $C_{38}H_{42}O_7NaS$ $[M + Na]^+$ 665.2549; found 665.2571.

Phenyl tetra-2,3,4,6-*O*-benzyl-α-D-mannopyranosyl sulfone 30: The General oxidation Procedure was followed using phenyl-2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyranoside **36**[16] (1.18 g, 1.87 mmol), $NaHCO_3$ (1.28 g, 15.3 mmol), *m*CPBA (1.6 g, 7 mmol, 3.7 equiv.) in CH_2Cl_2 (7 mL). The crude product was purified by chromatography on silica gel

(heptane/EtOAc 9:1 to 8:2) to afford pure product **30** (0.72 g, 58 %, colorless oil). $[\alpha]_D^{22}$ = +41.4 (*c* = 1.1, $CHCl_3$). IR: ν = 3088**,** 3063 and 3030 (=C-H), 2865 (C-H) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.5 Hz, 2H, H_{aro}), 7.60 (t, *J* = 7.5 Hz 1H, H_{aro}), 7.46-7.19 (m, 22H, H_{aro}), 4.88-4.80 (m, 2H, *H1* and CH_2Ph), 4.73-4.67 (m, 4H, CH_2Ph), 4.66-4.58 (m, 2H, 2H, *H2* and *H5*), 4.54 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.48 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.40 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.27 (dd, $J_{3,4}$ = 8.5 Hz and $J_{3,2}$ = 3.0 Hz, 1H, *H3*), 3.93 (dd, $J_{4,3}$ = 8.5 Hz and $J_{4,5}$ = 9.5 Hz, 1H, *H4*), 3.68-3.62 (m, 2H, *H6*). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 138.2 (Cq_{aro}), 138.1 (Cq_{aro}), 137.3 (Cq_{aro}), 136.9 (Cq_{aro}), 134.0 (CH$_{aro}$), 129.1 (CH$_{aro}$), 129.0 (CH$_{aro}$), 128.4 (CH$_{aro}$), 128.3 (CH$_{aro}$), 128.0 (CH$_{aro}$), 127.8 (CH$_{aro}$), 127.7 (CH$_{aro}$), 127.6 (CH$_{aro}$), 127.5 (CH$_{aro}$), 91.3 (*C1*), 79.2 (*C3*), 76.3 (*C5*), 74.5 (CH$_2$Ph), 74.0 (*C4*), 73.3 (CH$_2$Ph), 72.7 (CH$_2$Ph), 71.6 (*C2*), 69.6 (*C6*). HRMS **(**ESI): calcd. for $C_{40}H_{40}O_7NaS$ $[M+Na]^+$: 687.2392. Found: 687.2402.

(2-Methyl-5-*tert*-butylphenyl) 2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl sulfone 31: To a solution of **1** (0.285 g, 0.39 mmol, 1 equiv.) in TFA (0.4 mL) was added Ac_2O (1.6 mL, 17 mmol, 45 equiv.) at 0 °C and the mixture was allowed to react at rt for 2 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (10 mL) and the aqueous layer was extracted with AcOEt (3 x 10 mL). The combined organic layer were washed with a saturated solution of NaCl (15 mL) and dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the product was directly used in the next step. To the residue obtained (0.266 g, 0.39 mmol, 1 equiv.) was added a solution of Na (10 mg, 0.39 mmol, 1 equiv.) in dry MeOH (4 mL) at 0 °C. After 15 min at rt, the solution was concentrated under vacuum and the product was purified by flash chromatography on silica gel (heptane/EtOAc 9:1 to 7:3) to afford **31** (0.173 g, 0.27 mmol, 69 %) as a colorless oil. $[\alpha]_D^{22}$ = +50.2 (*c* = 0.4, $CHCl_3$). IR: ν = 3488 (OH), 3063 and 3030 (=C-H), 2963 and 2869 (C-H) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.55 (dd, *J* = 2.5 and 8.0 Hz, 1H, H_{aro}), 7.42-7.22 (m, 15H, H_{aro}), 4.91-4.83 (m, 2H, OCH_2Ph and *H1*), 4.78 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.74 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.69 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.65 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.63-4.56 (m, 2H, OCH_2Ph and *H2*), 4.33-4.23 (m, 2H, *H5* and *H3*), 3.96 (dd, *J* = 8.5 and 9.5 Hz, 1H, *H4*), 3.61 (d, *J* = 4.0, 2H, *H6*), 2.53 (s, 3H, CH_3) 1.33 (s, 9H, C$(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.0 (Cq_{aro}), 138.1 (Cq_{aro}), 137.4 (Cq_{aro}), 137.3 (Cq_{aro}), 135.4 (Cq_{aro}), 134.4 (Cq_{aro}), 132.7 (CH$_{aro}$), 131.3 (CH$_{aro}$), 128.6 (CH$_{aro}$), 128.5 (CH$_{aro}$), 128.4 (CH$_{aro}$), 128.3 (CH$_{aro}$), 128.1 (CH$_{aro}$), 128.0 (CH$_{aro}$), 127.8 (CH$_{aro}$), 90.7 (*C1*), 79.3 (*C3*), 77.0 (*C5*), 74.7 (*C2*), 73.7 and 73.6 (OCH$_2$Ph and *C*4), 72.8 (OCH$_2$Ph), 71.7 (OCH$_2$Ph), 62.1 (*C6*), 34.7 ($C(CH_3)_3$), 31.1 (CH_3), 19.9 (CH(CH_3)$_2$). HRMS **(**ESI): calcd. for $C_{38}H_{45}O_7S$ $[M + H]^+$ 645.2886; found 645.2905.

(2-Methyl-5-*tert*-butylphenyl) 3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside 32: (2-Methyl-5-*tert*-butylphenyl) 2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[17] (4.05 g, 8.06 mmol) was benzylated using (BnBr, NaH) in DMF to give after recristallization in heptane/EtOAc (9:1) the pure compound **32** as a white solid (3.60 g, 56%). Mp = 145 °C (after recristallisation in heptane/EtOAc 9:1). $[\alpha]_D^{22}$ = +79.5 (*c* = 1.1, $CHCl_3$). IR: ν = 3063 and 3030 (=C-H), 2961 and 2867 (C-H), 1776 and 1714 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (brd, *J* = 6.5 Hz, 1H, H_{aro}), 7.71-7.58 (m, 3H, H_{aro}), 7.49 (d, *J* = 2.0 Hz, 1H, H_{aro} (SMbp)), 7.36-7.21 (m, 10H, H_{aro}), 7.13 (dd, *J* = 8.0, 2.0 Hz, 1H, H_{aro} (SMbp)), 7.02-6.97 (m, 3H, H_{aro}), 6.91-6.84 (m, 3H, H_{aro}), 5.46 (d, $J_{1,2}$ = 10.0 Hz, 1H, *H1*), 4.84 (d, *J* = 10.5 Hz, 1H, CH_2Ph), 4.79 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.66 (d, *J* = 10.0 Hz, 1H, CH_2Ph), 4.64 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.56 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.44 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.39 (dd, $J_{3,2}$ = 10.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, *H3*), 4.33 (dd, $J_{2,1}$ = $J_{2,3}$ = 10.0 Hz, 1H, *H2*), 3.82 (dd, $J_{4,5}$ = 10.0 Hz, $J_{4,3}$ = 8.5 Hz, 1H, *H4*), 3.79-3.76 (m, 2H, *H6* and *H6'*), 3.65 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 6.0 Hz, $J_{5,6'}$ = 2.5 Hz, 1H, *H5*), 2.11 (s, 3H, ArCH_3), 1.23 (s, 9H, ArC(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1 (C=0), 167.5 (C=O), 149.6 (Cq_{aro}, SMbp), 138.3 (Cq_{aro}), 138.2 (Cq_{aro}), 138.1 (Cq_{aro}), 137.0 (Cq_{aro}), 134.0 (CH_{aro}), 133.9 (CH_{aro}), 132.0 (Cq_{aro}), 131.9 (Cq_{aro}), 131.8 (Cq_{aro}), 130.3, 129.9, 128.6, 128.5, 128.2, 128.11, 128.06, 128.0, 127.8, 127.5, 125.1, 123.6, 123.4 (20×CH_{aro}), 84.5 (*C1*), 80.6 (*C3*), 79.6 (*C4*), 79.5 (*C5*), 75.2 (CH_2Ph), 75.1 (CH_2Ph), 73.7 (CH_2Ph), 69.0 (*C6*), 55.3 (*C2*), 34.5 (ArC(CH_3)$_3$), 31.4 (ArC(CH_3)$_3$), 20.4 (ArCH_3). HRMS (ESI): calcd. for $C_{46}H_{47}NO_6SNa$ $[M + Na]^+$ 764.3022; found 764.3040.

(2-Methyl-5-*tert*-butylphenyl) (3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl sulfone 33: A solution of **32** (41 mg, 0.055 mmol, 1 equiv.), **31** (53 mg, 0.083 mmol, 1.5 equiv.) and molecular sieves (4 Å, 150 mg) were stirred in dry CH_2Cl_2 (0.25 mL) at room temperature for 30 min. The reaction mixture was cooled to –40 °C and NIS (31 mg, 0.138 mmol, 2.5 equiv.) and a solution of TfOH in CH_2Cl_2 (1M, 8 µL, 0.008 mmol, 0.15 equiv.) were successively added. After stirring for 60 min at –40 °C, the reaction was filtered over a pad of Celite® then quenched with saturated aqueous $NaHCO_3$ (10 mL). The aqueous phase was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were washed with saturated aqueous $Na_2S_2O_3$ (10 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by

chromatography on silica gel (heptane/EtOAc 95:5 to 8:2) to afford pure product **33** (55 mg, 82 %, colorless oil). $[\alpha]_D^{22}$ = +53.6 (*c* = 0.5, $CHCl_3$). IR: ν = 3064 and 3031 (=C-H), 2931 and 2867 (C-H), 1776 and 1713 (C=O) cm^{-1}. ^1H NMR (CD_3CN, 300 MHz): *δ* 7.83 (d, *J* = 2.0 Hz, 1H, H_{aro}), 7.71-7.52 (brm, 4H, H_{aro}), 7.43-7.15 (m, 26H, H_{aro}), 7.02-6.94 (m, 2H, H_{aro}), 6.93-6.83 (m, 4H, H_{aro}), 5.13 (d, 1H, *J* = 8.5 Hz, *H1B*), 4.87 (d, 1H, *J* = 1.5 Hz, *H1A*), 4.80 (d, 1H, *J* = 11.0 Hz, OCH_2Ph), 4.80 (d, 1H, *J* = 11.0 Hz, OCH_2Ph), 4.73 (d, 1H, *J* = 12.0 Hz, OCH_2Ph), 4.61 (d, 1H, *J* = 11.0 Hz, OCH_2Ph), 4.59-4.44 (m, 6H, OCH_2Ph), 4.45-4.41 (m, 1H, *H*2A), 4.35 (d, 1H, *J* = 12.0 Hz, OCH_2Ph), 4.27-4.16 (m, 3H, OCH_2Ph, *H*3B, *H*5B), 4.00 (dd, 1H, *J* = 3.5 and 8.5 Hz, *H*3A), 3.98-3.91 (m, 2H, OCH_2Ph, *H*2B), 3.76 (dd, *J* = 11.0 and 1.5 Hz, 1H, *H*6A or *H*6B), 3.74-3.60 (m, 5H, *H*4A, *H*4B, *H*6A, *H*6B), 3.60-3.55 (m, 1H, *H*5A), 2.48 (s, 3H, ArCH_3), 1.27 (s, 9H, ArC(CH_3)$_3$). ^{13}C NMR (CD_3CN, 125 MHz): *δ* 169.3 (*C*=O), 168.9 (*C*=O), 151.4, 139.9, 139.7, 139.6, 139.4, 139.0 (Cq_{aro}), 137.3 (CH_{aro}), 135.9 (Cq_{aro}), 135.6 (CH_{aro}), 134.4 (CH_{aro}), 132.6 (Cq_{aro}), 129.9, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, (CH_{aro}), 124.6 (CH_{aro}), 99.2 (*C*1B), 91.8 (*C*1A), 81.0 (*C*4A), 80.4 (*C*3B), 80.1 (*C*3A), 76.7 (*C*5B), 76.2 (*C*5A), 75.9, 75.8 75.5 (O*C*H_2Ph), 73.3 (O*C*H_2Ph and *C*4B), 73.9, 72.8 (O*C*H_2Ph), 72.1 (*C*2A), 70.0, 68.4 (*C6A* and *C6B*), 57.0 (*C2B*), 35.8 (*C*$(CH_3)_3$), 31.8 (C(*C*H_3)$_3$), 20.7 (*C*H_3); HRMS **(**ESI): calcd. for $C_{73}H_{75}NO_{13}Na$ $[M + Na]^+$ 1228.4857; found 1228.4855.

(2-Methyl-5-*tert*-butylphenyl) 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl sulfoxide 35: To a stirred solution of **36**[16] (500 mg, 0.71 mmol, 1 equiv.) and $NaHCO_3$ (209 mg, 2.49 mmol, 3.5 equiv.) in dry CH_2Cl_2 (4.5 mL), at – 78 °C under argon, was added dropwise along the sides of the flask a solution of 3-chloroperoxybenzoic acid 75% (197 mg, 0.85 mmol, 1.2 equiv.) in CH_2Cl_2 (5.5 mL). After stirring at – 78 °C for 1 hour and then at – 20 °C overnight, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and successively washed with saturated aqueous $Na_2S_2O_3$ (20 mL), saturated aqueous $NaHCO_3$ (20 mL) and brine (60 mL). The organic layer was separated and was dried over Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by chromatography on silica gel (heptane/EtOAc 9:1 to 6:4) to afford one major diastereoisomer of product **35** (399 mg, 78%, colorless oil). $[\alpha]_D^{22}$ = –17.6 (*c* = 1.7, $CHCl_3$). IR: ν = 3064 and 3030 (=C-H), 2962 and 2866 (C-H) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.79 (d, *J* = 2.0 Hz, 1H, SMbp), 7.37 (dd, *J* = 8.0 Hz and *J* = 2.0 Hz, 1H, SMbp), 7.33-7.12 (m, 20H, Ph), 7.09 (d, *J* = 8.0 Hz, 1H, SMbp), 4.87 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.77 (d, $J_{1,2}$ = 1.5 Hz, 1H, *H1*), 4.60 (s, 2H, CH_2Ph), 4.56 (d, *J* = 12.0 Hz, 1H, CH_2Ph), 4.52 (s, 2H, CH_2Ph), 4.47 (d, *J* = 10.5 Hz, 1H, CH_2Ph), 4.44-4.39 (m, 2H, *H2* and

CH_2Ph), 4.23 (dd, $J_{3,4}$ = 9.0 Hz and $J_{3,2}$ = 3.0 Hz, 1H, *H3*), 4.12 (m, 1H, *H5*), 4.04 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.0 Hz, 1H, *H4*), 3.74-3.65 (m, 2H, *H6* and *H6'*), 2.30 (s, 3H, ArCH_3), 1.28 (s, 9H, ArC(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.9 (C, SMbp), 140.5 (C, SMbp), 138.6 (C, Ph), 138.5 (C, Ph), 138.4 (C, Ph), 138.0 (C, Ph), 133.7 (C, SMbp), 131.1 (CH, SMbp), 128.7 (3×CH, SMbp and Ph), 128.7 (4×CH, Ph), 128.7 (2×CH, Ph), 128.3 (2×CH, Ph), 128.2 (2×CH, Ph), 128.1 (2×CH, Ph), 128.1 (2×CH, Ph), 128.1 (CH, Ph), 128.0 (2×CH, Ph), 127.9 (CH, Ph), 120.6 (CH, SMbp), 96.0 (*C1*), 80.3 (*C3*), 78.2 (*C5*), 75.4 (*C*H$_2$Ph), 74.1 (*C4*), 73.8 (*C*H$_2$Ph), 73.0 (*C*H$_2$Ph), 72.4 (*C*H$_2$Ph), 71.6 (C2), 69.5 (*C6*), 35.3 (Ar*C*(CH$_3$)$_3$), 31.6 (ArC(*C*H$_3$)$_3$), 18.5 (Ar*C*H$_3$). HRMS **(**ESI): calcd. for $C_{45}H_{50}O_6NaS$ $[M + Na]^+$ 741.3226; found 741.3233.

Phenyl 3,4-di-*O*-benzyl-2-*O*-methyl-α-D-rhamnopyranosyl sulfone 38: To a stirred solution of described phenyl 2-*O*-methyl-α-D-rhamnothiopyranoside[18] (175 mg, 0.65 mmol) in anhydrous DMF (6.5 mL), under argon atmosphere, was added at 0 °C NaH (116 mg, 2.91 mmol, 4.5 equiv., 60% dispersion in oil). After stirring for 30 min, benzyl bromide (0.31 mL, 2.59 mmol, 4 equiv.) was added dropwise and the resulting suspension was allowed to reach r.t. and stirred overnight. The reaction mixture was quenched at 0 °C with water (15 mL) and diluted with EtOAc. The layers were separated, the aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic extracts were washed with water (3 x 15 mL), brine (15 mL), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography (heptane/EtOAc 1:0 to 7:3) to give the corresponding benzylated product (3,4-di-*O*-benzyl-2-*O*-methyl-α-D-rhamnothiopyranoside) (252 mg, 0.56 mmol, 86%) as a colorless oil. $[\alpha]^{22}_D$ = +92.8 (*c* = 1.0, $CHCl_3$). IR: ν = 3031 (=C-H), 2879 (C-H) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48-7.25 (m, 15H, H_{aro}), 5.55 (d, *J* = 1.5 Hz, 1H, *H1*), 4.96 (d, *J* = 11.0 Hz, 1H, OCH_2Ph), 4.77 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.72 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.65 (d, *J* = 11.0 Hz, 1H, OCH_2Ph), 4.15 (dq, *J* = 9.5, 6.0 Hz, 1H, *H5*), 3.83 (dd, *J* = 9.5, 3.0 Hz, 1H, *H3*), 3.74 (dd, *J* = 3.0, 1.5 Hz, 1H, *H2*), 3.60 (ap. t, *J* = 9.5 Hz, 1H, *H4*), 3.48 (s, 3H, OCH_3), 1.34 (d, *J* = 6.0 Hz, 3H, CH(CH_3)). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.1 (Cq_{aro}), 136.0 (Cq_{aro}), 135.8 (Cq_{aro}), 131.1 (2×*C*H$_{aro}$), 129.0 (2×*C*H$_{aro}$), 128.5 (2×*C*H$_{aro}$), 128.4 (2×*C*H$_{aro}$), 128.1 (2×*C*H$_{aro}$), 128.0 (2×*C*H$_{aro}$), 127.8 (*C*H$_{aro}$), 127.7 (*C*H$_{aro}$), 127.2 (*C*H$_{aro}$), 84.9 (*C1*), 80.5 (*C4*), 79.9 (*C3*), 79.8 (*C2*), 75.5 (O*C*H$_2$Ph), 72.4 (O*C*H$_2$Ph), 69.1 (*C5*), 58.5 (O*C*H$_3$), 17.8 (CH(*C*H$_3$)). HRMS **(**ESI): calcd. for $C_{27}H_{30}O_4NaS$ $[M + Na]^+$ 473.1763; found 473.1761.

The General oxidation Procedure was followed using phenyl 3,4-di-*O*-benzyl-2-*O*-methyl-α-D-rhamnothiopyranoside (223 mg, 0.49 mmol), $NaHCO_3$ (341 mg, 4.05 mmol), *m*CPBA (305 mg, 1.24 mmol) in CH_2Cl_2 (2.5 mL). The crude product was purified by chromatography on silica

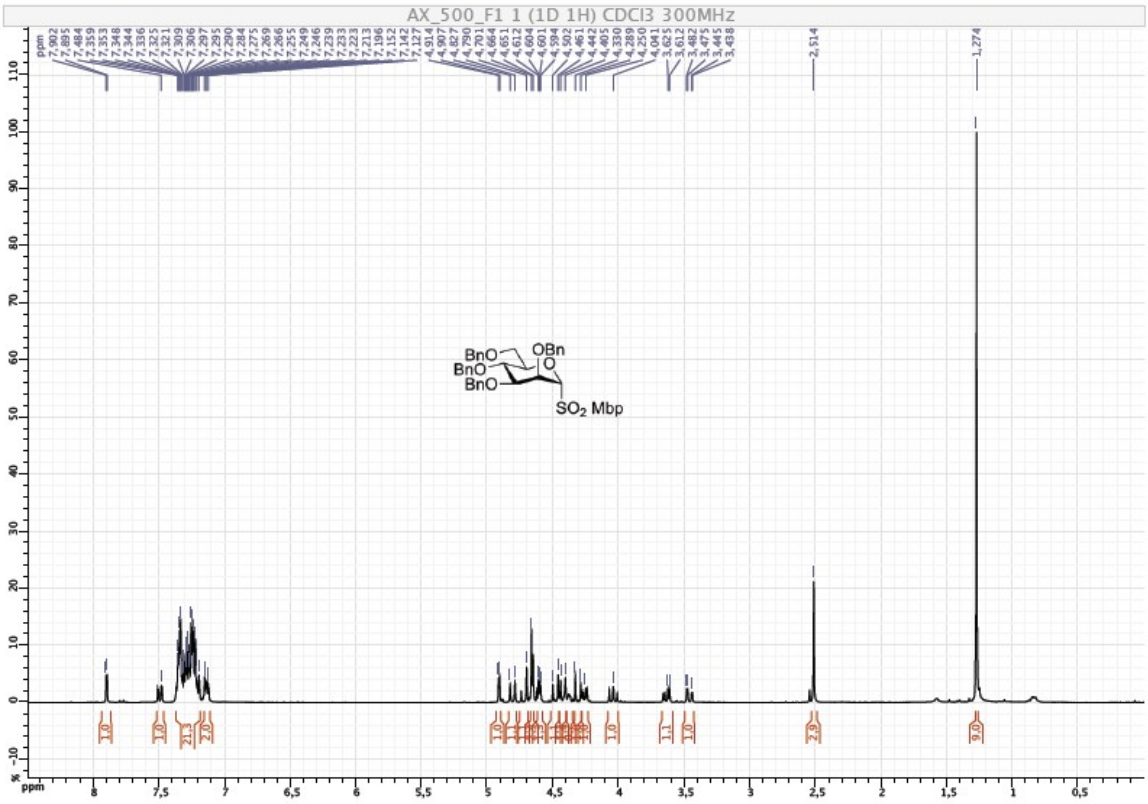
gel (heptane/EtOAc 1:0 to 6:4) to afford the desired product **38** (220 mg, 0.45 mmol, 92%) as a colorless oil. $[\alpha]^{22}_D$ = +80.4 (*c* = 0.7, $CHCl_3$). IR: ν = 3032 (=C-H), 2234 (C-H) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): *δ* 7.88 (m, 2H, H_{aro}), 7.69 (m, 1H, H_{aro}), 7.58 (m, 2H, H_{aro}), 7.45-7.29 (m, 10H, H_{aro}), 4.90 (d, *J* = 11.0 Hz, 1H, OCH_2Ph), 4.79 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.78 (d, *J* = 1.5 Hz, 1H, *H1*), 4.76 (d, *J* = 12.0 Hz, 1H, OCH_2Ph), 4.59 (d, *J* = 11.0 Hz, 1H, OCH_2Ph), 4.36 (dq, *J* = 9.0, 6.0 Hz, 1H, *H5*), 4.28 (br. s, 1H, *H2*), 4.26 (ap. t, *J* = 3.5 Hz, 1H, *H3*), 3.59-3.50 (m, 1H, *H4*), 3.47 (s, 3H, OCH_3), 1.20 (d, *J* = 6.0 Hz, 3H, CH(CH_3)). ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 138.3 (Cq_{aro}), 138.0 (Cq_{aro}), 137.0 (Cq_{aro}), 134.1 (CH$_{aro}$), 129.1 (2×CH$_{aro}$), 128.8 (2×CH$_{aro}$), 128.5 (2×CH$_{aro}$), 128.4 (2×CH$_{aro}$), 128.2 (2×CH$_{aro}$), 127.9 (CH$_{aro}$), 127.8 (2×CH$_{aro}$), 127.7 (CH$_{aro}$), 91.0 (*C1*), 79.3 (*C4*), 79.0 (*C3*), 74.9 (OCH$_2$Ph), 74.4 (*C2*), 73.0 (OCH$_2$Ph), 72.9 (*C5*), 59.0 (OCH$_3$), 18.4 (CH(CH$_3$)). HRMS (ESI): calcd. for $C_{27}H_{30}O_6NaS$ $[M + Na]^+$ 505.1661; found 505.1660.

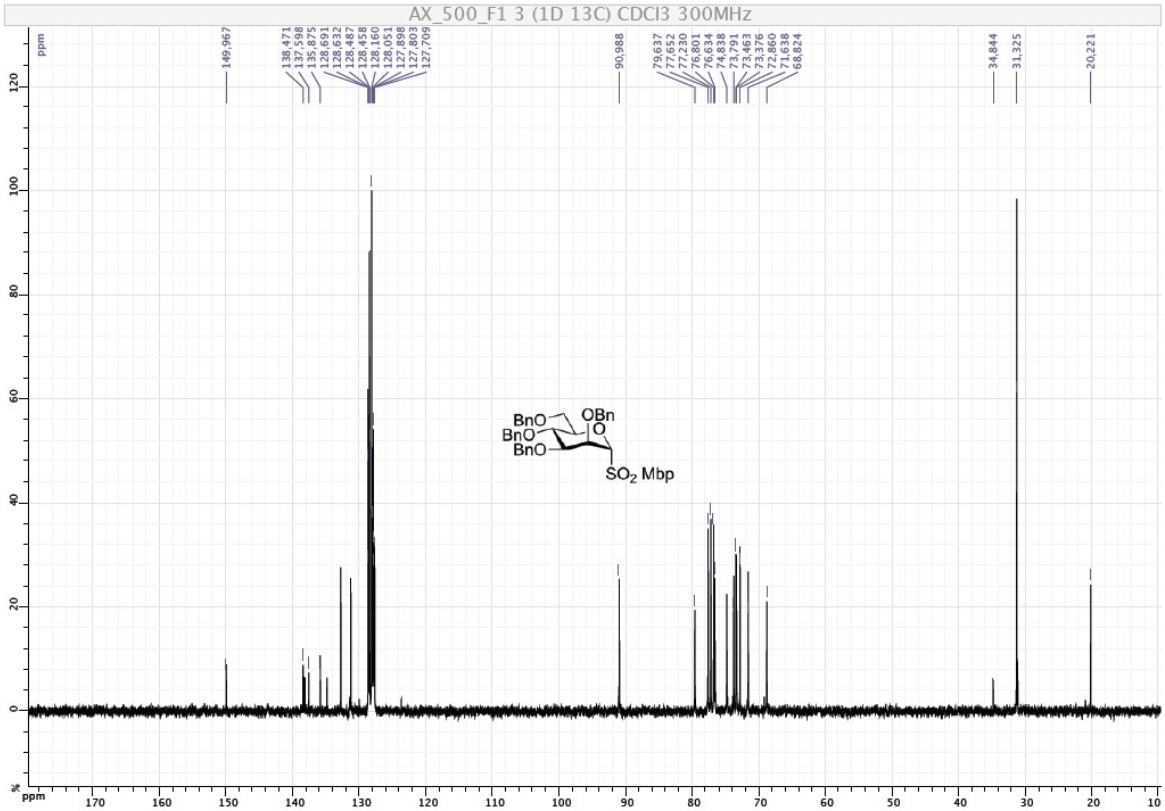
(2-Methyl-5-*tert*-butylphenyl) 3,4,6-tri-*O*-benzyl-2-trichloroacetamido-2-deoxy-β-D-glucopyranosyl sulfone 45: (2-Methyl-5-*tert*-butylphenyl) 2-trichloroacetamido-2-deoxy-1-thio-β-D-glucopyranoside[17] (785 mg, 1.62 mmol) was benzylated using (BnBr, NaH) in DMF to give after chromatography on silica gel (heptane/EtOAc 100:0 to 8:2) the pure 2-Methyl-5-*tert*-butylphenyl) 3,4,6-tri-*O*-benzyl-2-trichloroacetamido-2-deoxy-1-thio-β-D-glucopyranoside as a colorless oil (324 mg, 26%). The General oxidation Procedure was followed using 3,4,6-tri-*O*-benzyl-2-trichloroacetamido-2-deoxy-1-thio-β-D-glucopyranoside (324 mg, 0.42 mmol, 1 equiv.), $NaHCO_3$ (292 mg, 3.44 mmol, 8.2 equiv.), *m*CPBA 75% (292 mg, 1.05 mmol, 2.5 equiv.) in CH_2Cl_2 (5 mL). The crude product was purified by chromatography on silica gel (heptane/EtOAc 100:0 to 8:2) to afford pure product **45** (170 mg, 51%, white amorphous solid). $[\alpha]_D^{22}$ = +10.2 (*c* = 0.4, $CHCl_3$). IR: ν = 3350 (N-H), 3065 and 3032 (=C-H), 2909 and 2866 (C-H), 1698 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.89 (d, *J* = 2.0 Hz, 1H, H_{aro} (SMbp)), 7.42 (dd, *J* = 8.0 Hz and *J* = 2.0 Hz, 1H, H_{aro} (SMbp)), 7.31 (d, *J* = 7.0 Hz and $J_{2,NH}$ = 2.0 Hz, 1H, N*H*), 7.27-7.07 (m, 16H, H_{aro}), 5.12 (d, $J_{1,2}$ = 9.5 Hz, 1H, *H1*), 4.72 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.67 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.64 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.50 (d, *J* = 11.0 Hz, 1H, CH_2Ph), 4.36 (dd, $J_{3,2}$ = 9.5 Hz and $J_{3,4}$ = 8.5 Hz, 1H, *H3*), 4.28 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 4.16 (d, *J* = 11.5 Hz, 1H, CH_2Ph), 3.94 (dd, $J_{2,1}$ = 9.5 Hz, $J_{2,3}$ = 9.5 Hz and $J_{2,NH}$ = 7.0 Hz, 1H, *H2*), 3.59 (dd, $J_{4,3} = J_{4,5}$ = 8.5 Hz, 1H, *H4*), 3.56-3.42 (m, 3H, *H5*, *H6* and *H6'*), 2.56 (s, 3H, ArCH_3), 1.21 (s, 9H, ArC(CH_3)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 162.2 (C=0), 149.9 (Cq_{aro}), 138.0 (Cq_{aro}), 137.9 (Cq_{aro}), 137.8 (Cq_{aro}), 137.3 (Cq_{aro}), 134.3 (Cq_{aro}), 132.7, 131.6

(2×*C*H$_{aro}$), 128.7, 128.54, 128.47, 128.1, 128.0, 127.9, (16×*C*H$_{aro}$), 100. 2 (*C*Cl$_3$), 87.6 (*C1*), 80.1, 80.0 (*C3* and *C5*), 77.9 (*C4*), 75.8 (*C*H$_2$Ph), 74.9 (*C*H$_2$Ph), 73.8 (*C*H$_2$Ph), 68.9 (*C6*), 54.0 (*C2*), 34.9 (Ar*C*(CH$_3$)$_3$), 31.3 (ArC(*C*H$_3$)$_3$), 20.6 (Ar*C*H$_3$). HRMS **(**ESI): calcd. for $C_{40}H_{44}NO_7SCl_3Na$ [M + Na]$^+$ 810.1802; found 810.1802.

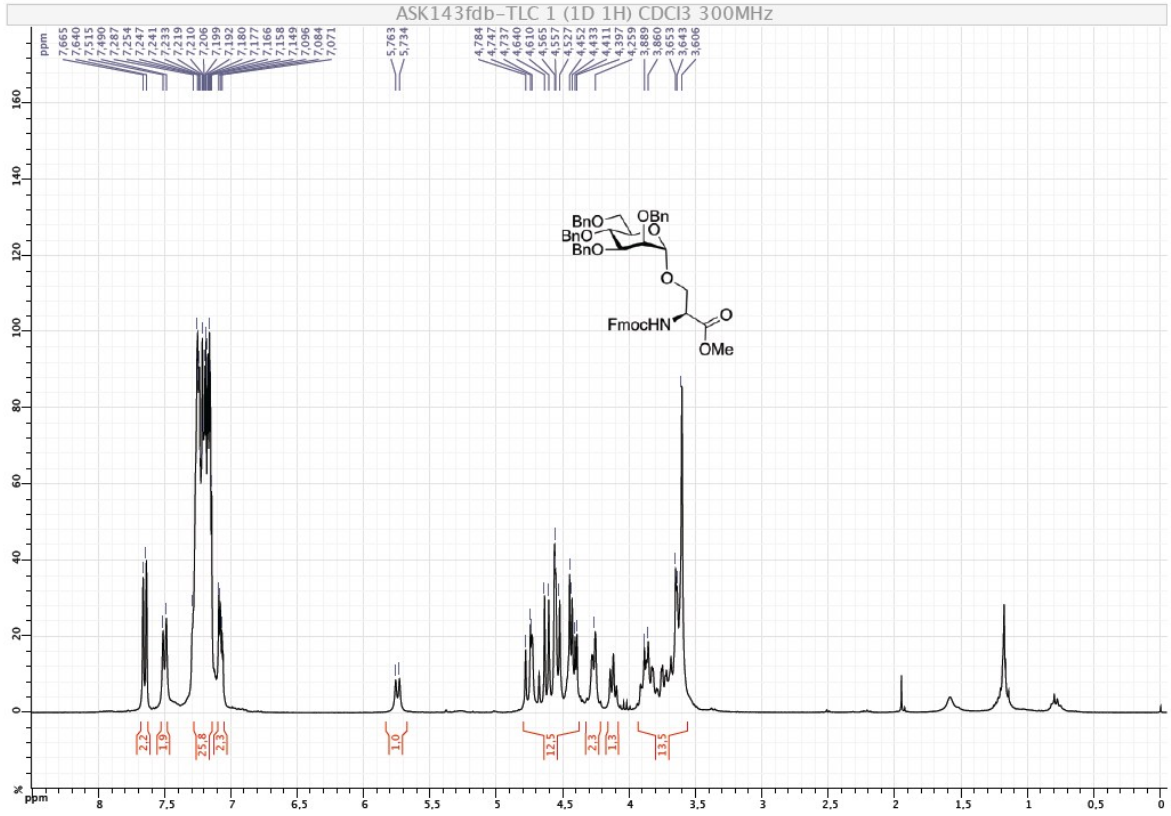
(2-Methyl-5-*tert*-butylphenyl) 3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl sulfone 47: The General oxidation Procedure was followed using **32** (0.5 g, 0.67 mmol, 1 equiv.), $NaHCO_3$ (0.46 g, 5.46 mmol, 8.2 equiv.), *m*CPBA 75% (0.43 g, 1.67 mmol, 2.5 equiv.) in CH_2Cl_2 (3 mL). The crude product was purified by chromatography on silica gel (heptane/EtOAc 100:0 to 8:2) to afford pure product **47** (225 mg, 43%, white amorphous solid). $[\alpha]_D^{22}$ = +31.3 (*c* = 0.2, $CHCl_3$). IR: ν = 3064 and 3030 (=C-H), 2964 and 2869 (C-H), 1778 and 1713 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 2.0 Hz, 1H, *H*$_{aro}$ (SMbp)), 7.80 (brd, *J* = 8.0 Hz and *J* = 2.0 Hz, 1H, *H*$_{aro}$), 7.68-7.61 (m, 3H, *H*$_{aro}$), 7.42 (dd, *J* = 8.0, 2.0 Hz, 1H, *H*$_{aro}$ (SMbp)), 7.35-7.25 (m, 6H, *H*$_{aro}$), 7.22-7.16 (m, 4H, *H*$_{aro}$), 7.11 (d, *J* = 8.0 Hz, 1H, *H*$_{aro}$ (SMbp)), 6.99-6.95 (m, 2H, *H*$_{aro}$), 6.90-6.82 (m, 3H, *H*$_{aro}$), 5.40 (d, $J_{1,2}$ = 10.0 Hz, 1H, *H1*), 4.79 (d, *J* = 11.0 Hz, 1H, C*H*$_2$Ph), 4.75 (d, *J* = 12.0 Hz, 1H, C*H*$_2$Ph), 4.62 (dd, $J_{21} = J_{23}$ = 10.0 Hz, 1H, *H2*), 4.60 (d, *J* = 11.0 Hz, 1H, C*H*$_2$Ph), 4.42 (d, *J* = 12.0 Hz, 1H, C*H*$_2$Ph), 4.39 (d, *J* = 12.0 Hz, 1H, C*H*$_2$Ph), 4.33 (dd, $J_{3,2}$ = 10.0 Hz and $J_{3,4}$ = 9.0 Hz, 1H, *H3*), 4.27 (d, *J* = 12.0 Hz, 1H, C*H*$_2$Ph), 3.73 (dd, $J_{4,3} = J_{4,5}$ = 9.0 Hz, 1H, *H4*), 4.33 (dd, $J_{6,6'}$ = 12.0 Hz and $J_{6,5}$ = 4.5 Hz, 1H, *H6*), 3.64-3.58 (m, 2H, *H6'* and *H5*), 2.76 (s, 3H, ArC*H*$_3$), 1.25 (s, 9H, ArC(C*H*$_3$)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4 (*C*=0), 166.7 (*C*=O), 149.5 (*Cq*$_{aro}$, SMbp), 137.9 (*Cq*$_{aro}$, SMbp), 137.7 (*Cq*$_{aro}$), 137.5 (*Cq*$_{aro}$), 137.3 (*Cq*$_{aro}$), 134.0 (*Cq*$_{aro}$, SMbp), 133.8 (*C*H$_{aro}$), 133.6 (*C*H$_{aro}$), 132.4 (*C*H$_{aro}$, SMbp), 131.8 (*Cq*$_{aro}$), 131.7 (*Cq*$_{aro}$), 131.2 (*C*H$_{aro}$, SMbp), 128.4, 128.3, 128.1, 127.9, 127.7, 127.5 (16×*C*H$_{aro}$), 123.6 (*C*H$_{aro}$), 123.4 (*C*H$_{aro}$), 86.7 (*C1*), 79.9, 79.8 (*C3* and *C5*), 78.6 (*C4*), 75.2 (*C*H$_2$Ph), 75.1 (*C*H$_2$Ph), 73.6 (*C*H$_2$Ph), 68.6 (*C6*), 50.3 (*C2*), 34.7 (Ar*C*(CH$_3$)$_3$), 31.1 (ArC(*C*H$_3$)$_3$), 20.4 (Ar*C*H$_3$). HRMS **(**ESI): calcd. for $C_{46}H_{47}NO_8NaS$ [M + Na]$^+$ 796.2920; found 796.2938.

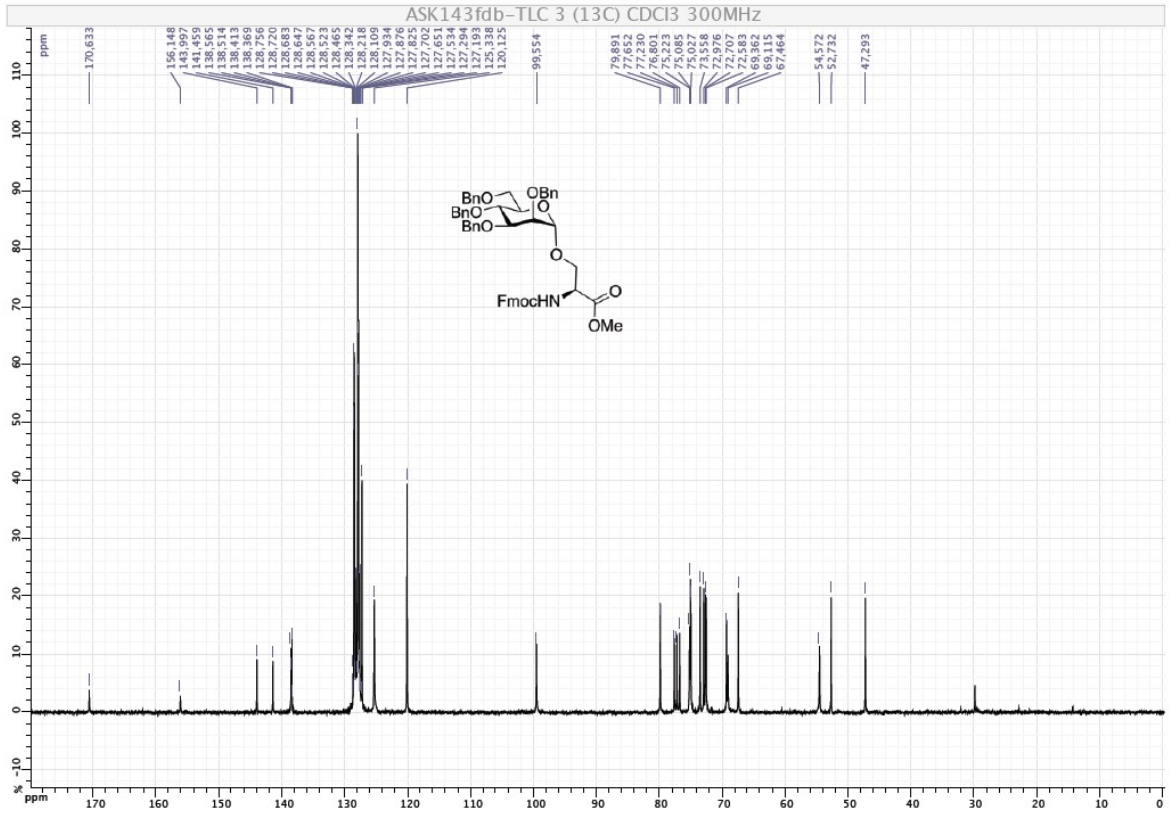
^{1}H and ^{13}C NMR spectra for compound **1**



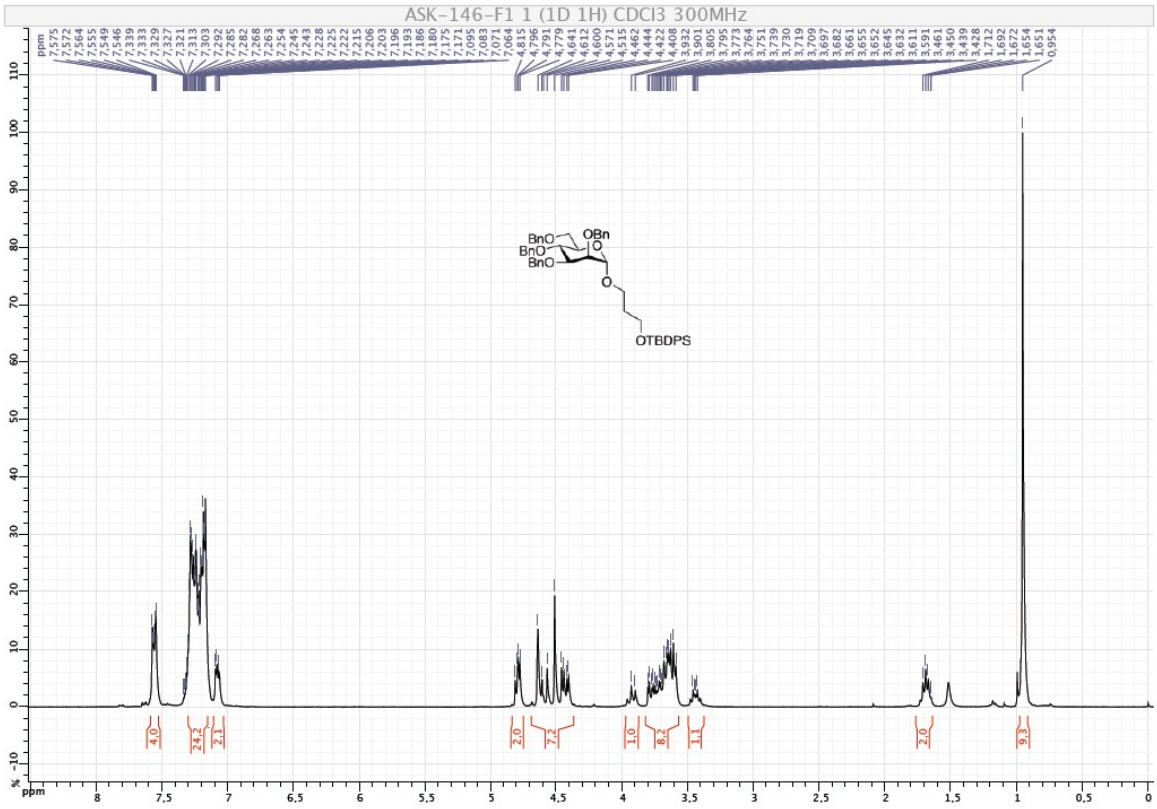


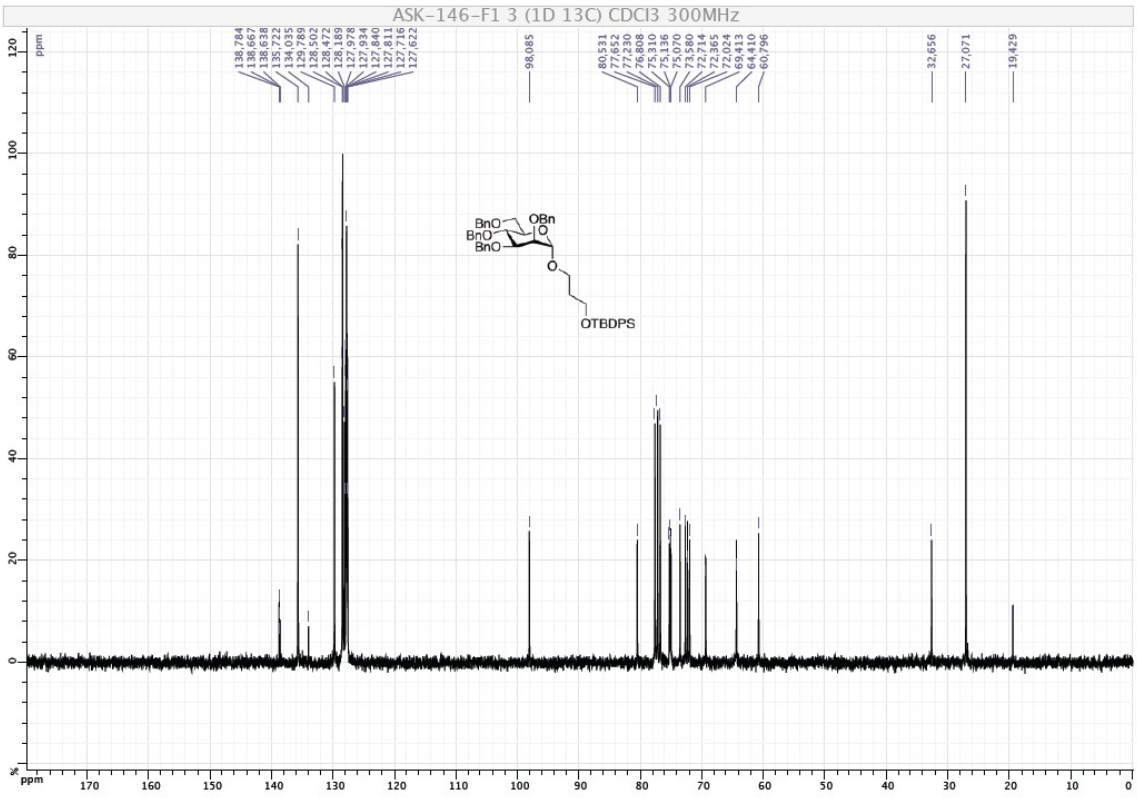
^{1}H and ^{13}C NMR spectra for compound **7α**



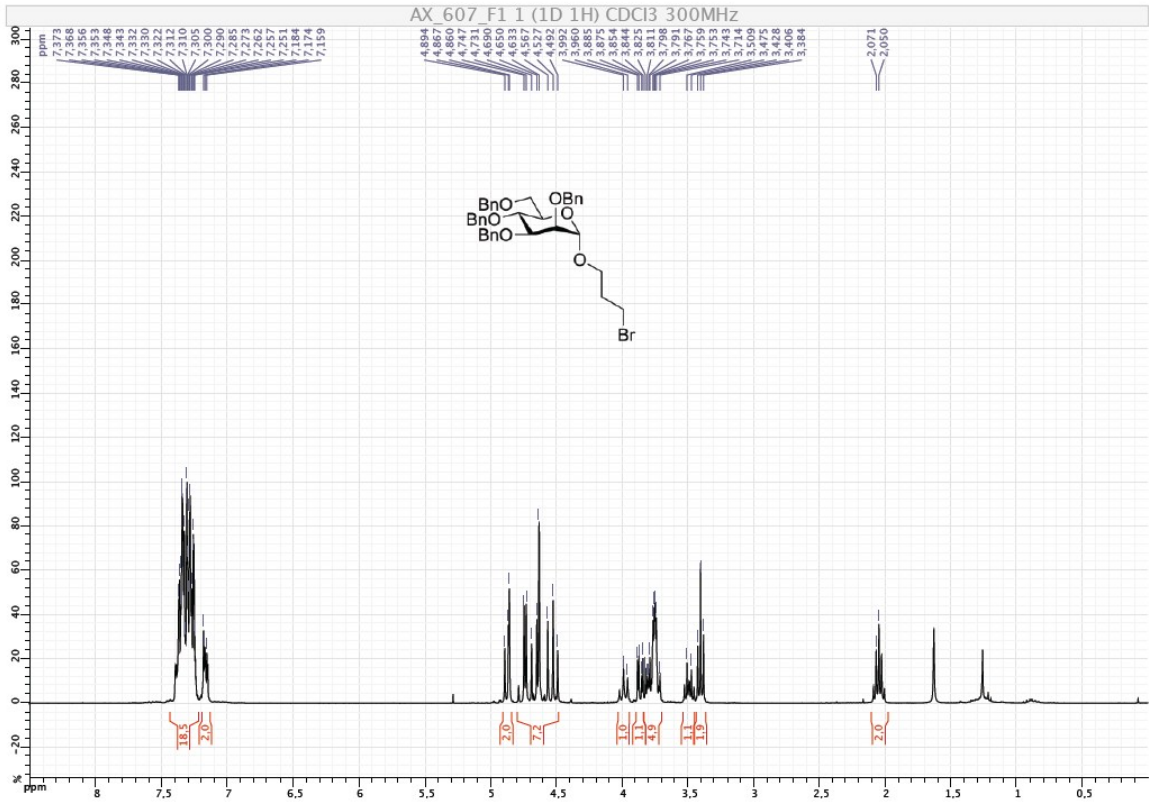


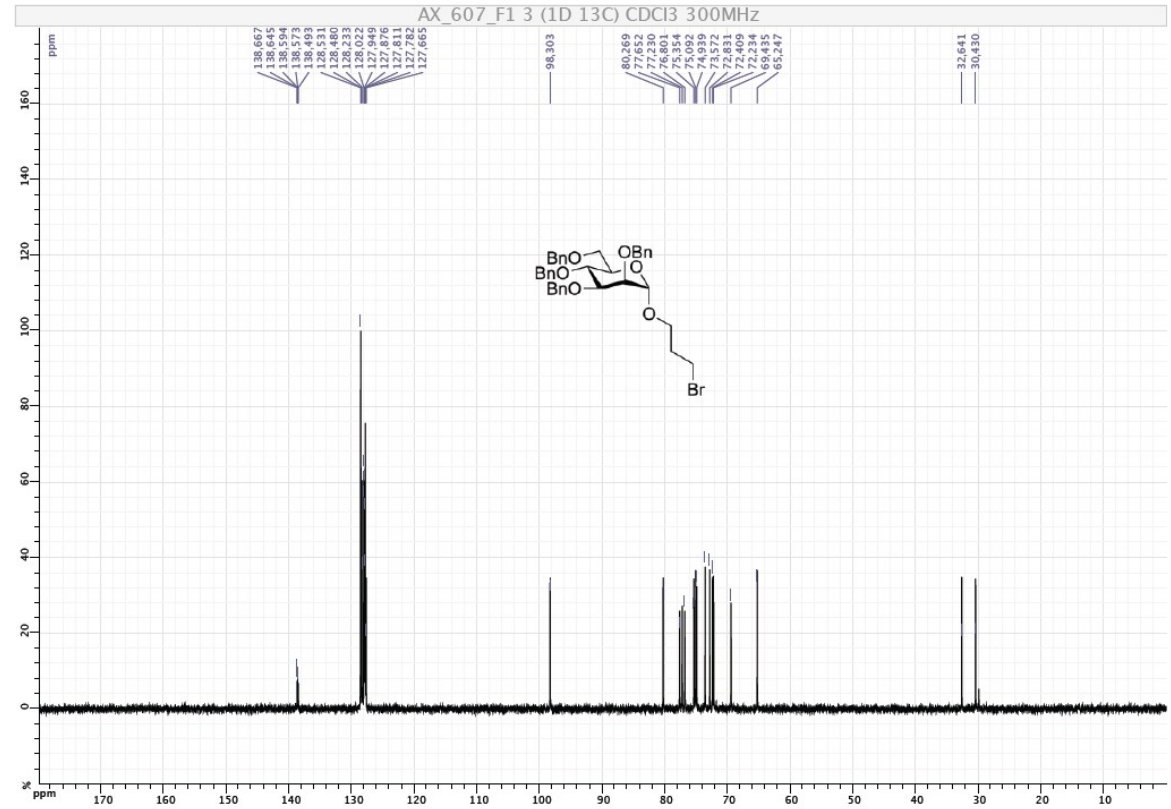
^{1}H and ^{13}C NMR spectra for compound **9α**



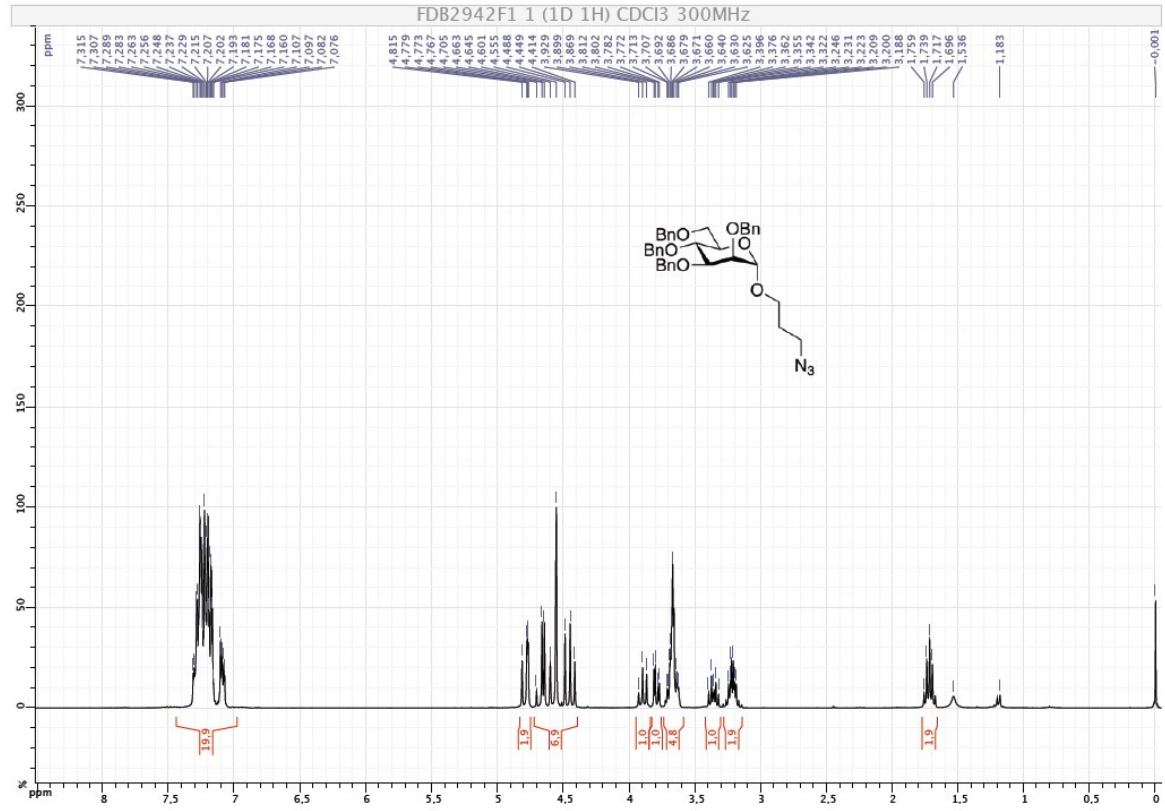


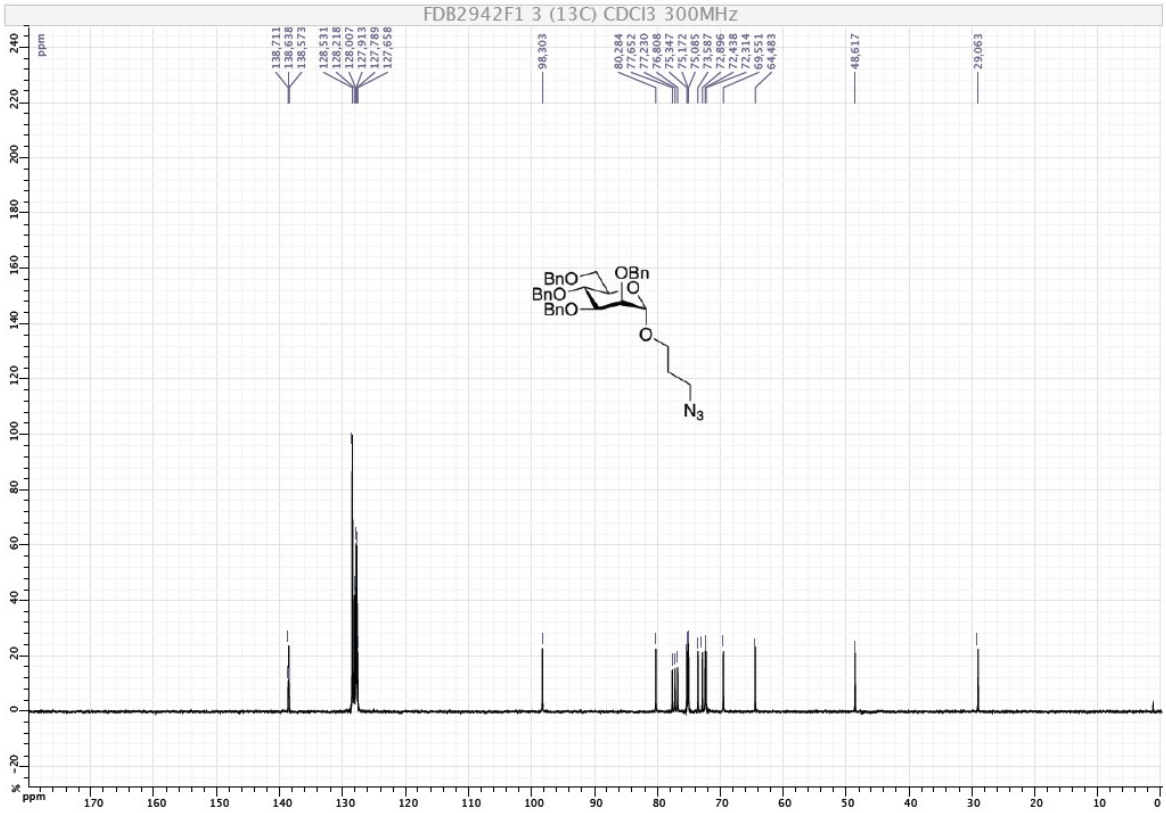
^{1}H and ^{13}C NMR spectra for compound **11α**



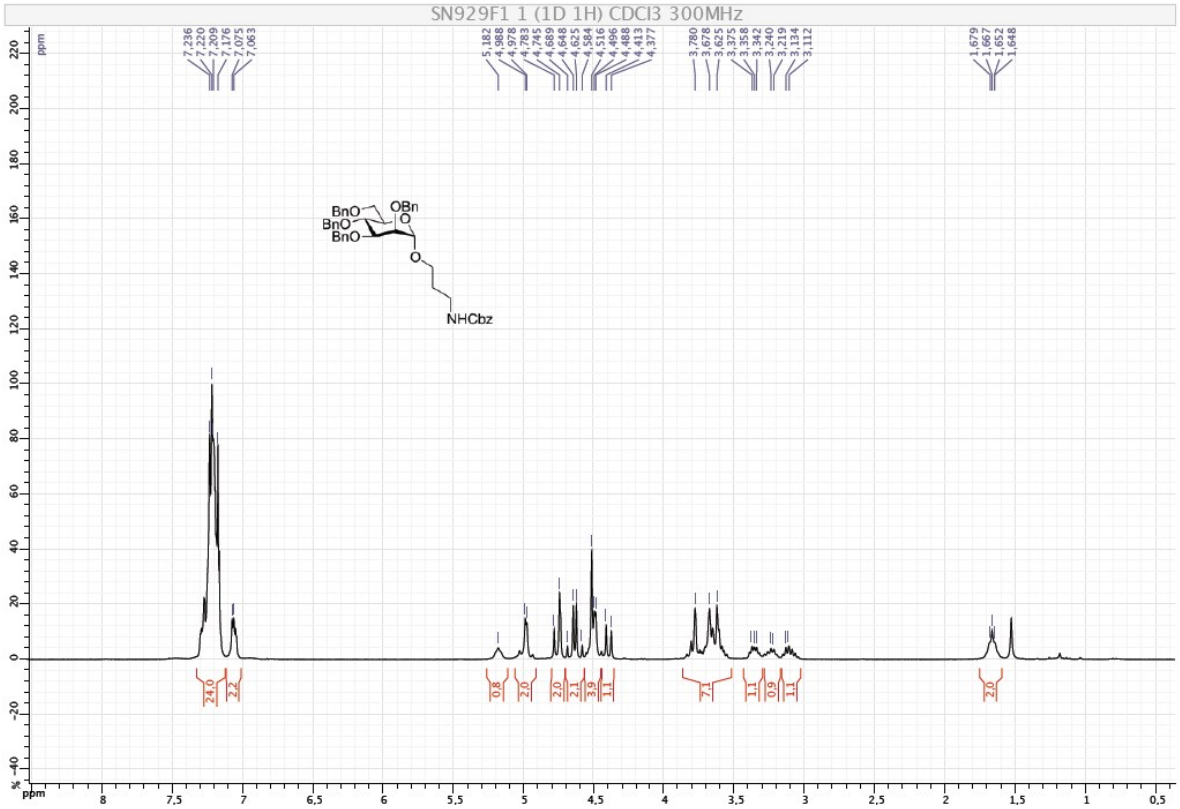


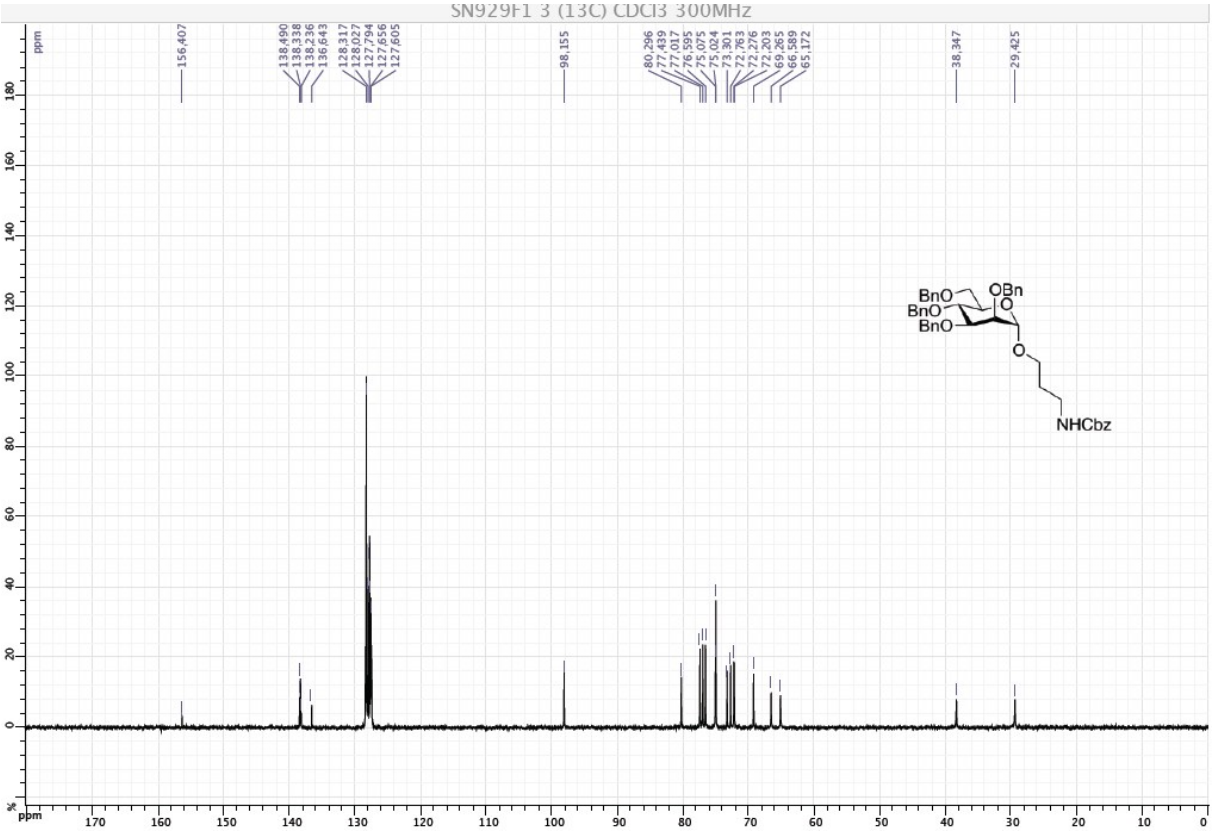
^{1}H and ^{13}C NMR spectra for compound **15α**



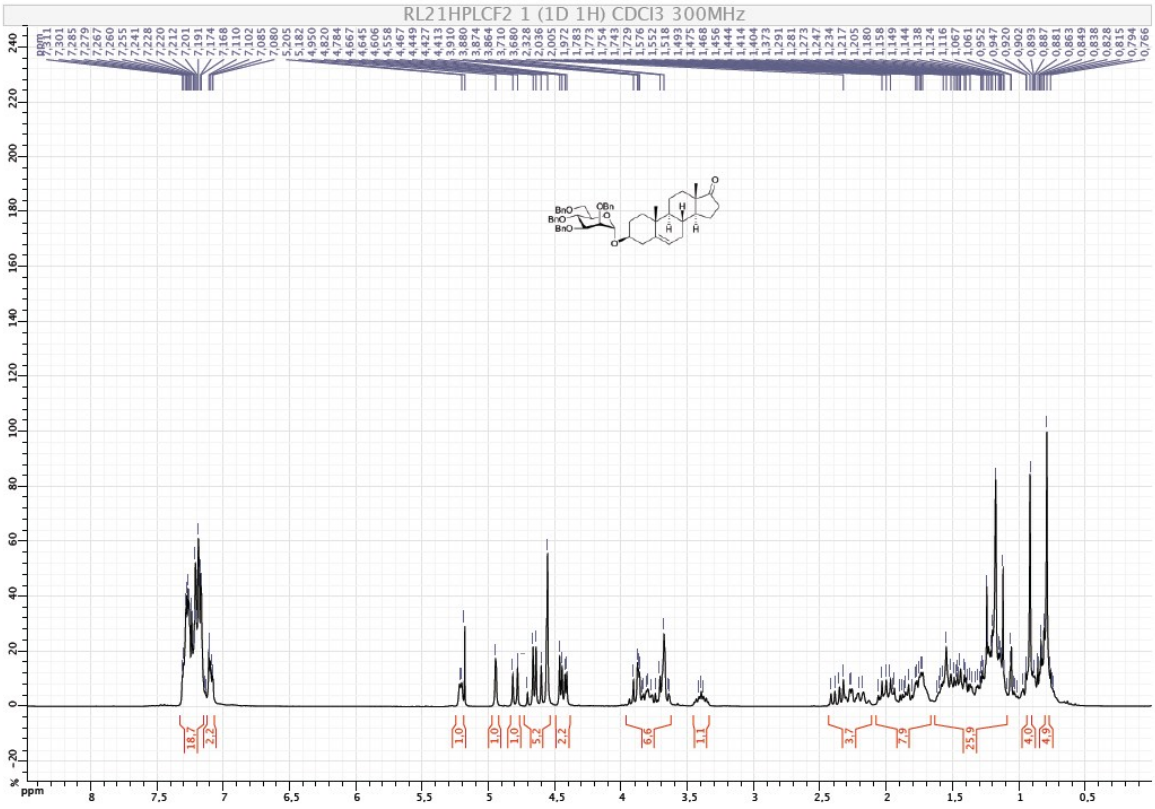


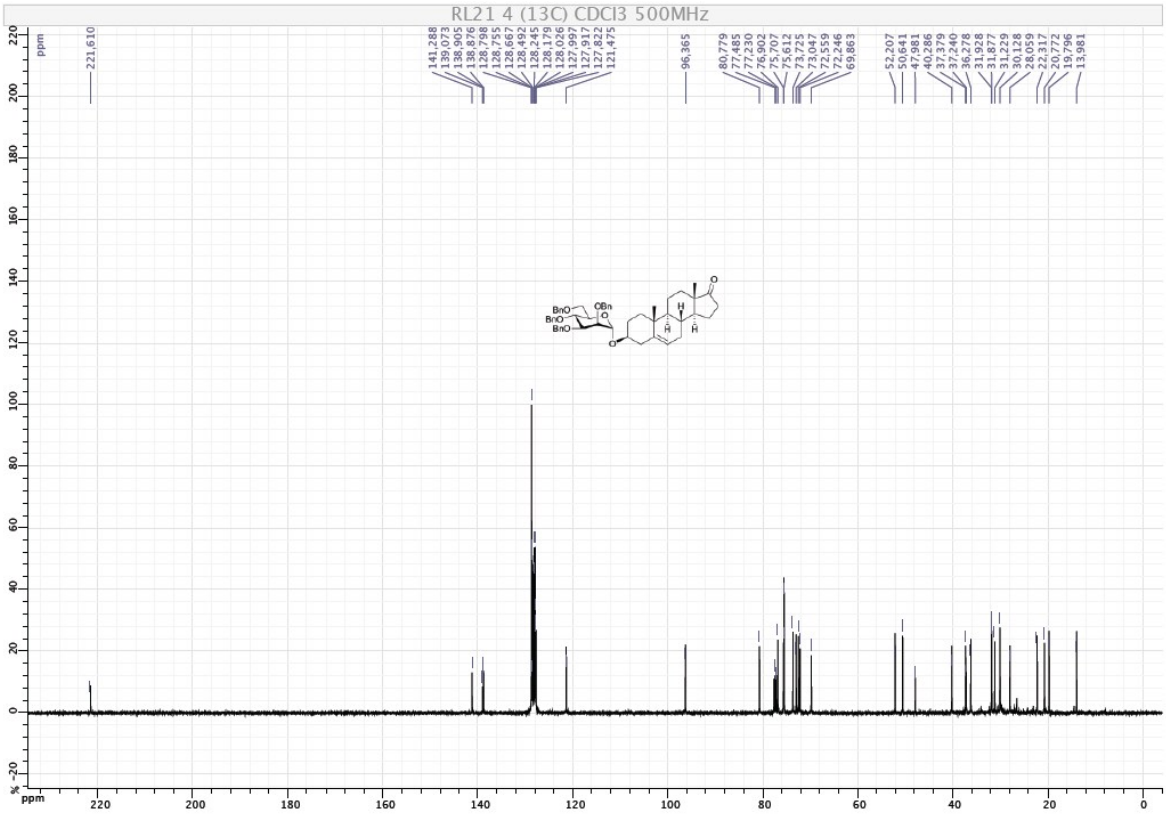
^{1}H and ^{13}C NMR spectra for compound **17α**



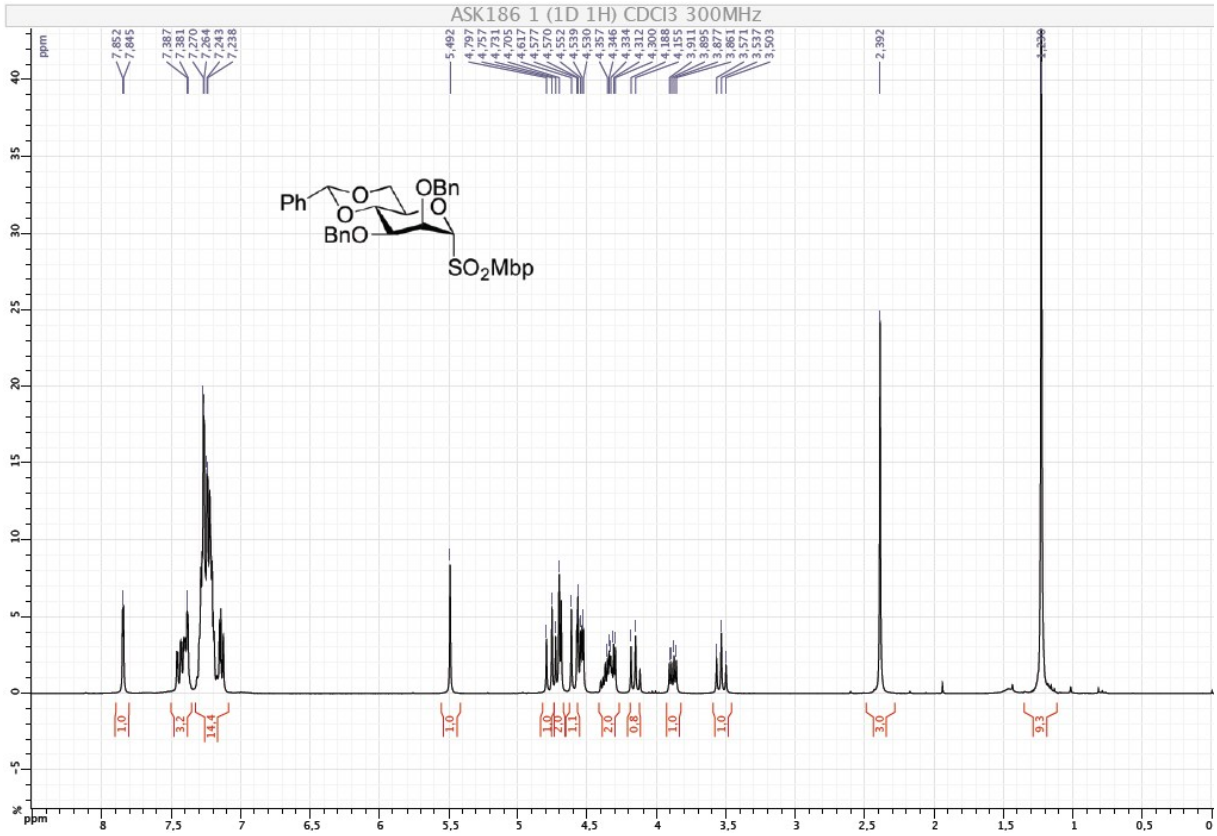


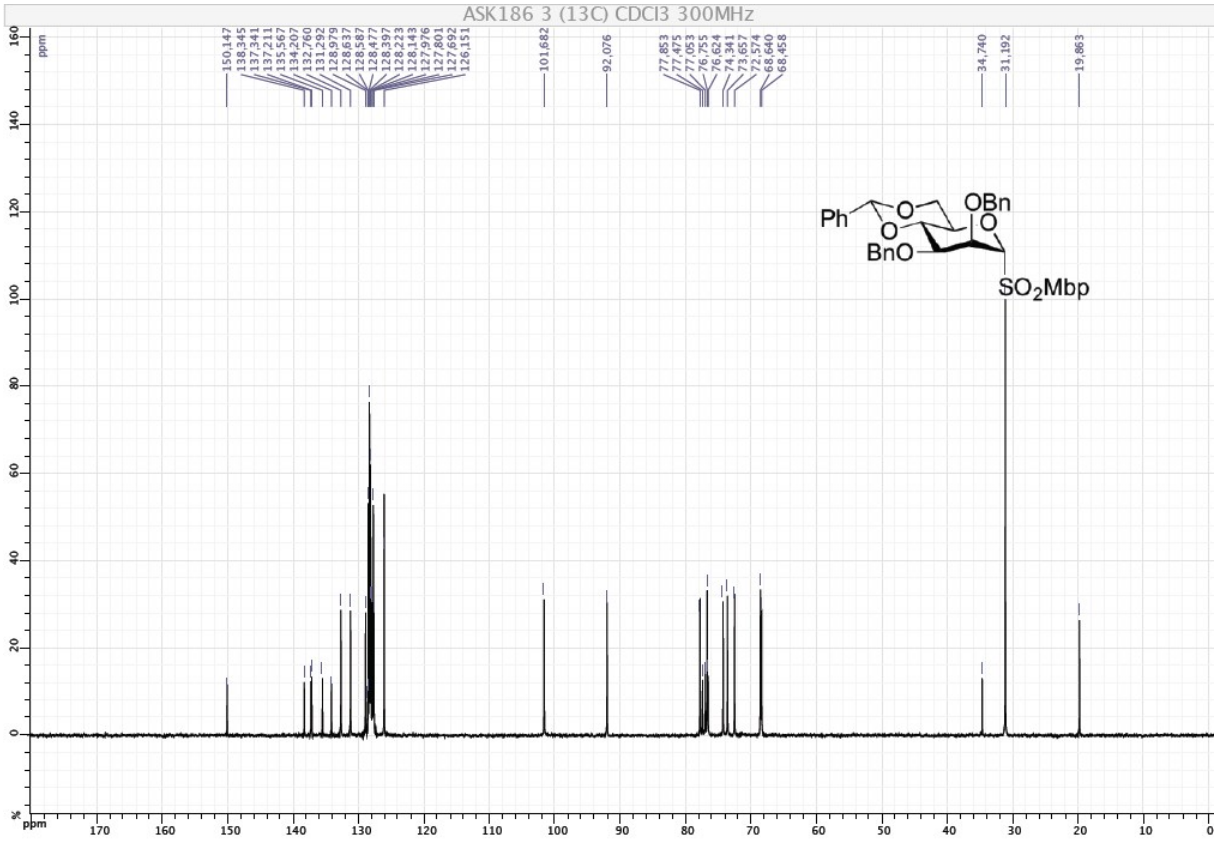
^{1}H and ^{13}C NMR spectra for compound **23α**



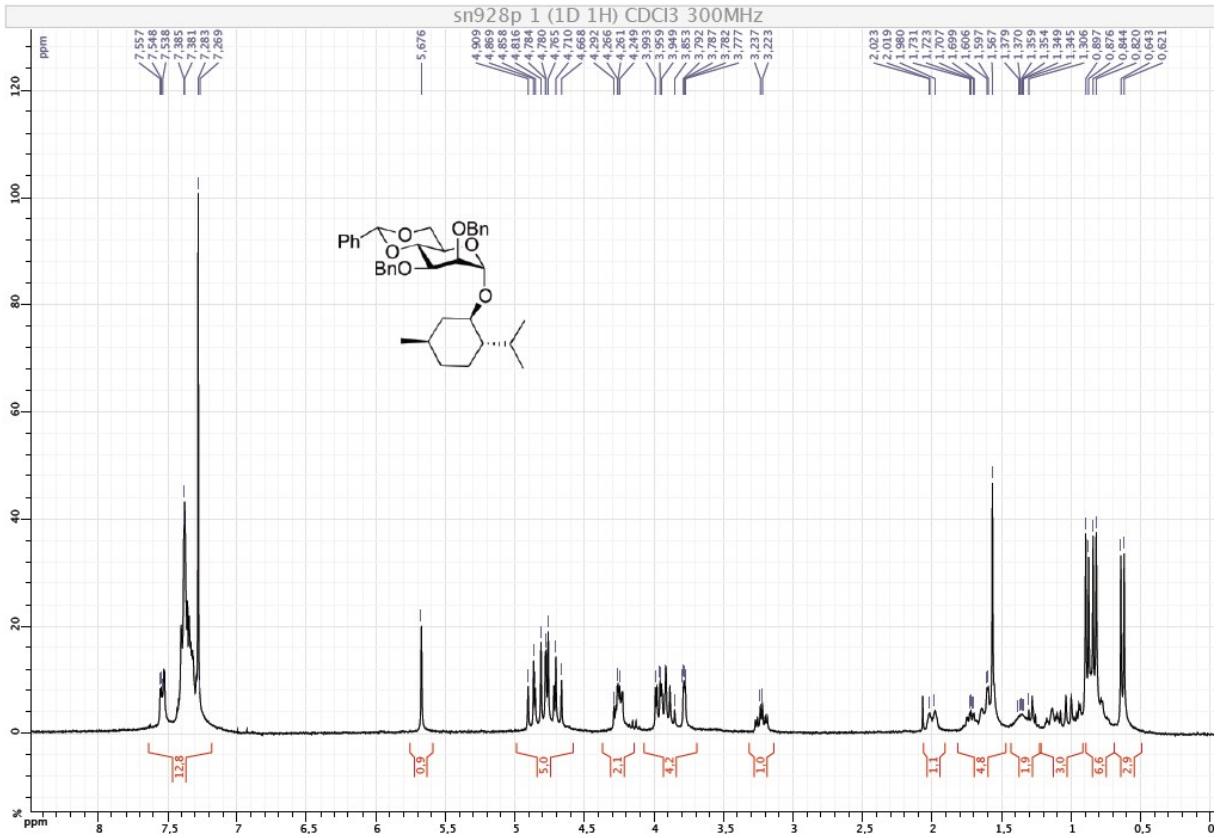


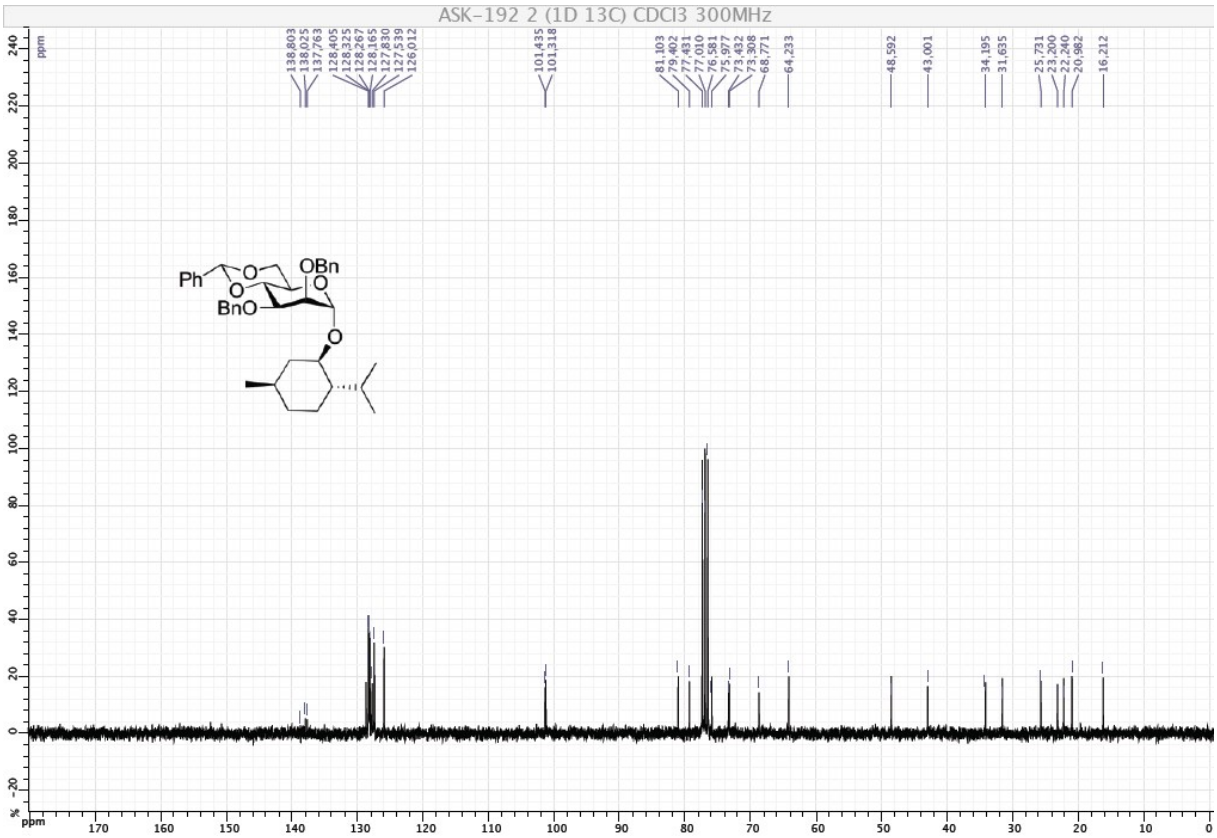
^{1}H and ^{13}C NMR spectra for compound **28**



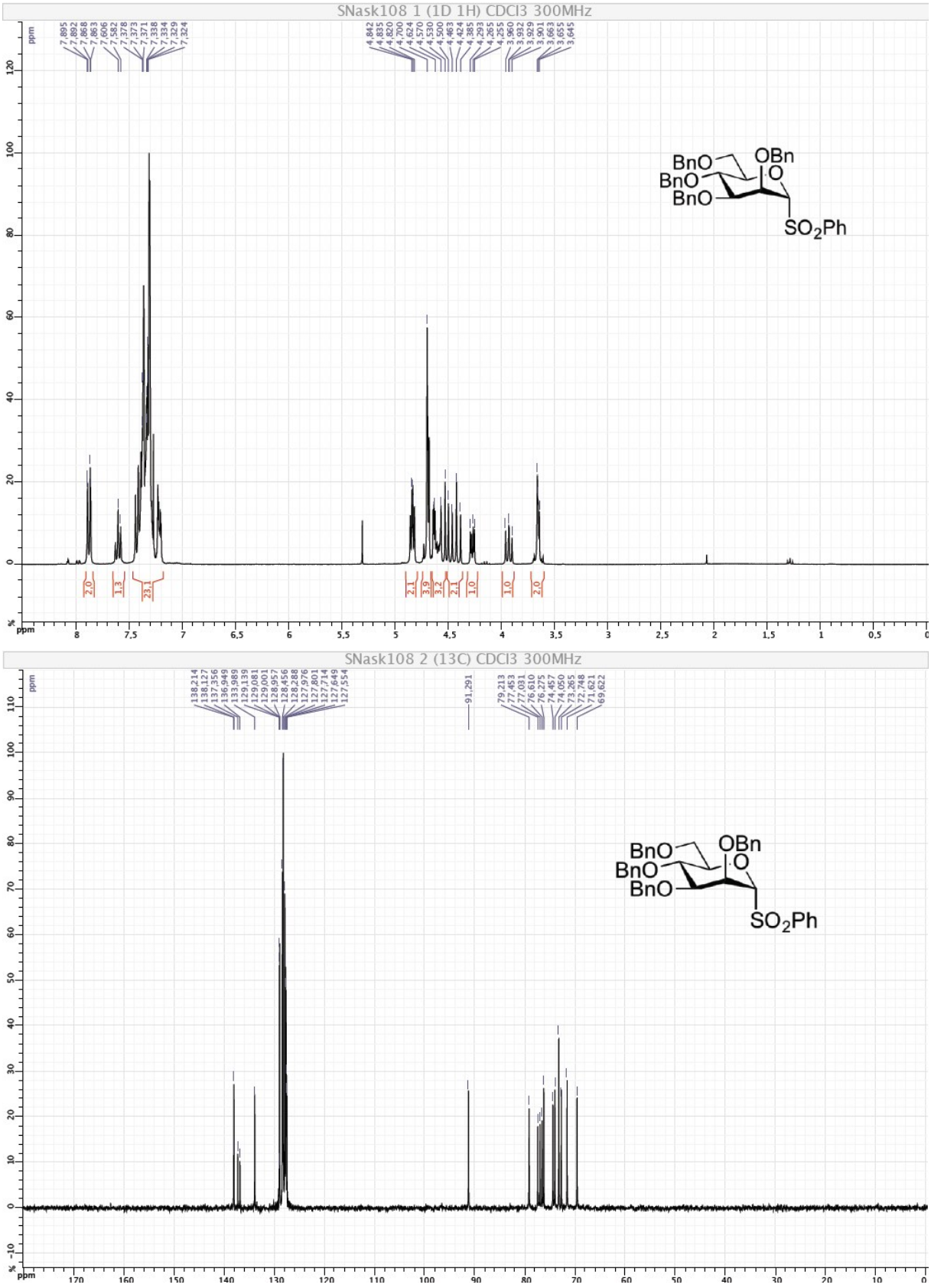


^{1}H and ^{13}C NMR spectra for compound **29**

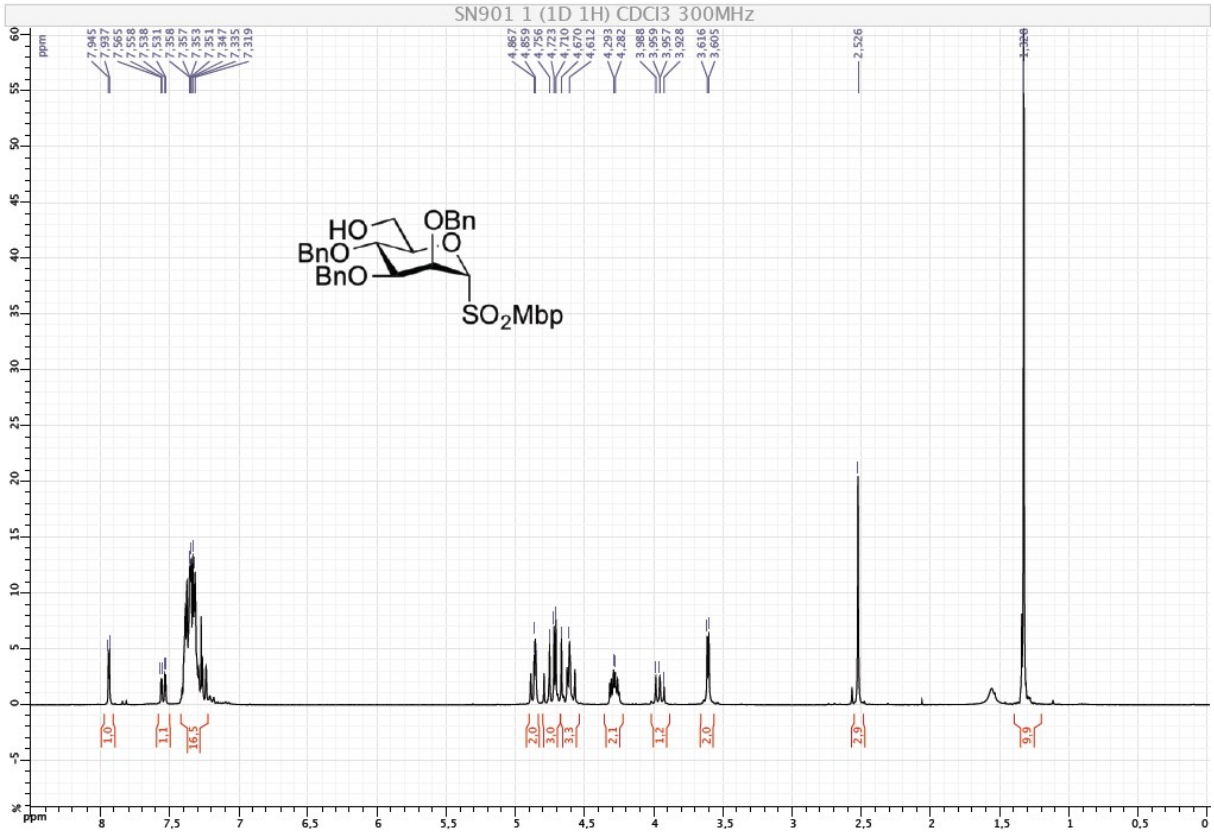


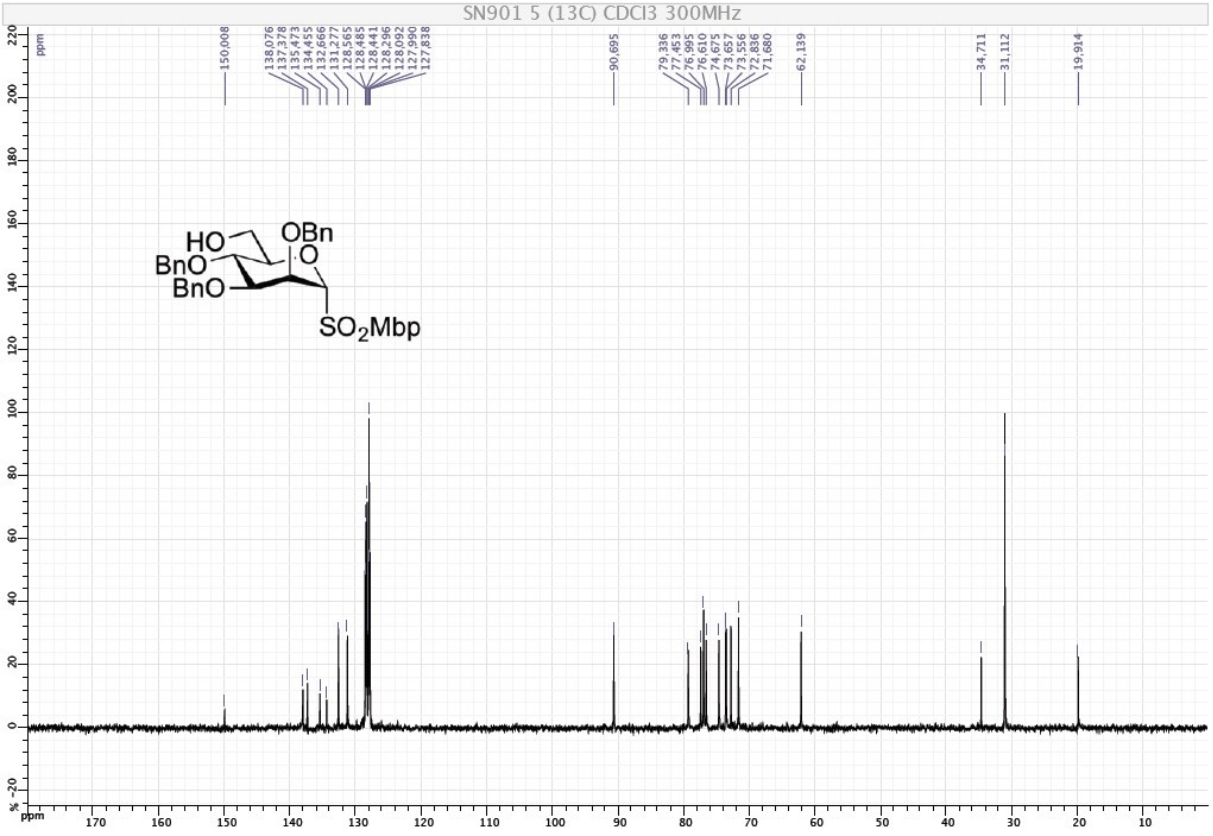


^{1}H and ^{13}C NMR spectra for compound **30**

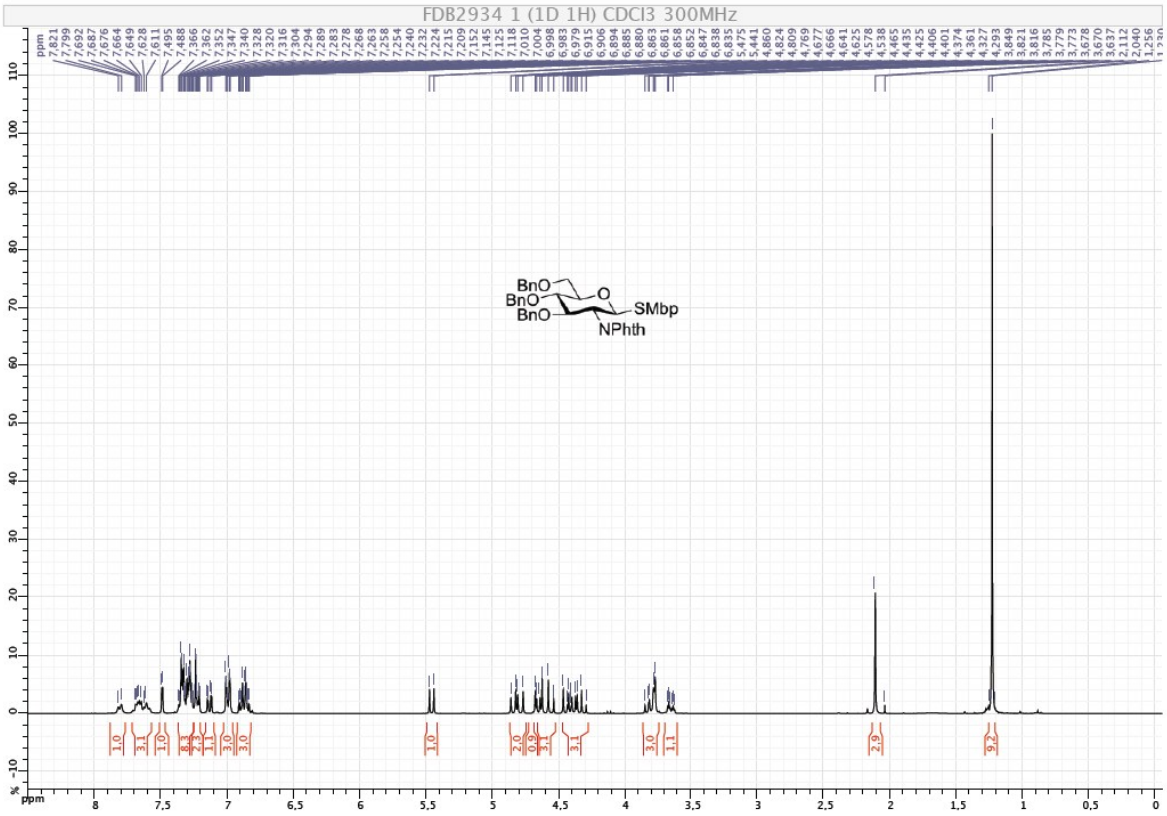


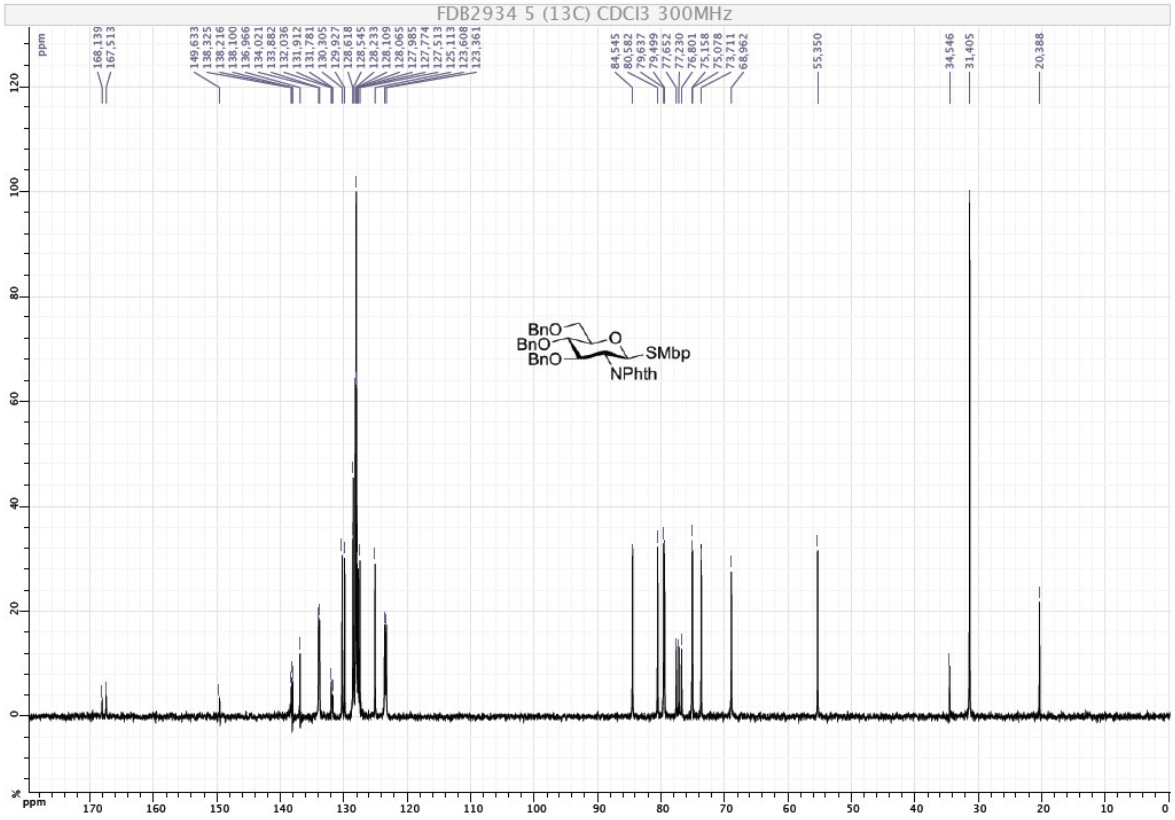
^{1}H and ^{13}C NMR spectra for compound **31**



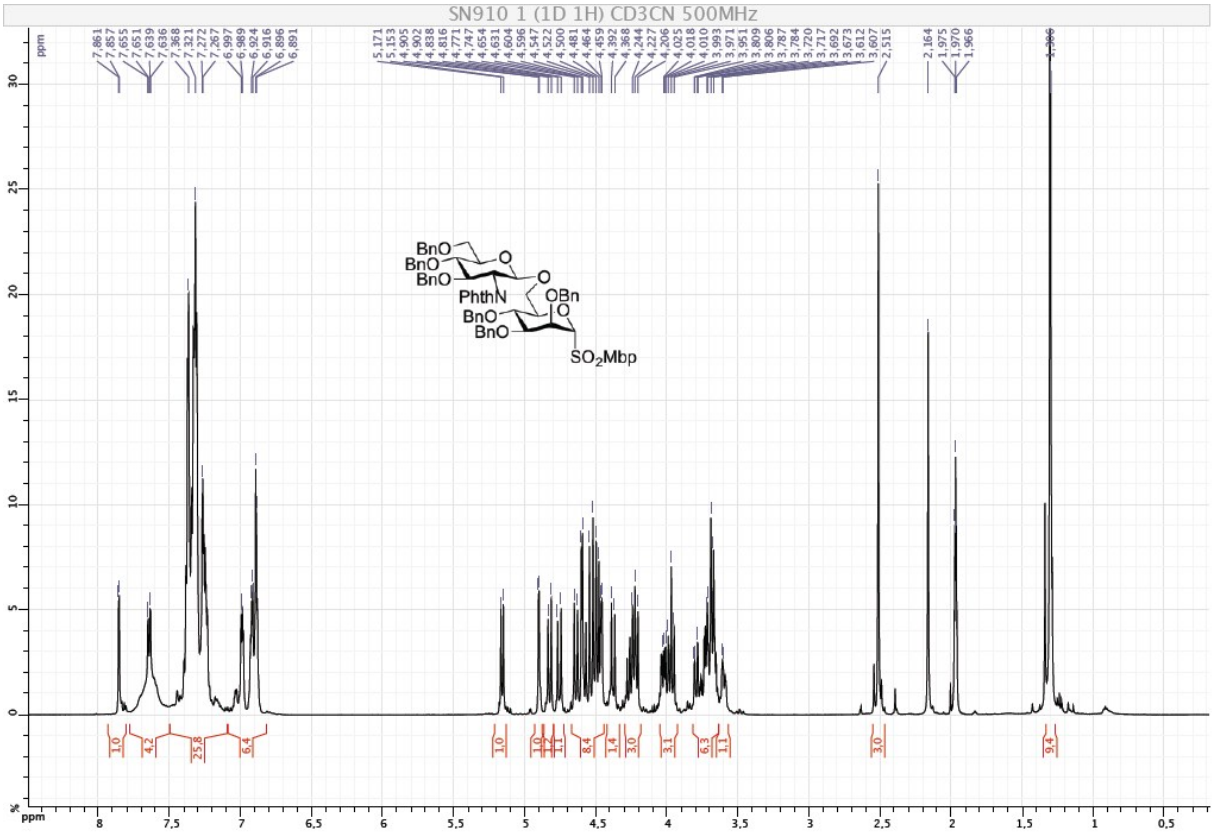


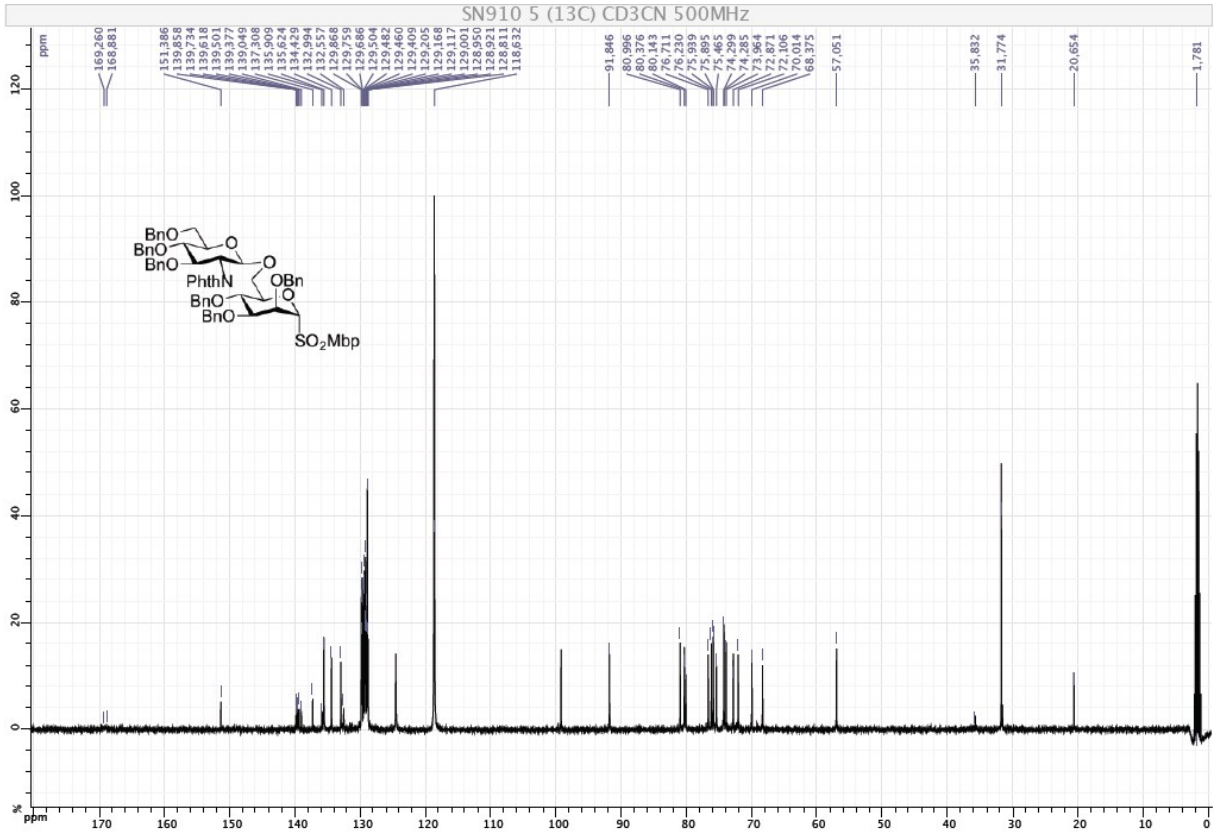
^{1}H and ^{13}C NMR spectra for compound **32**



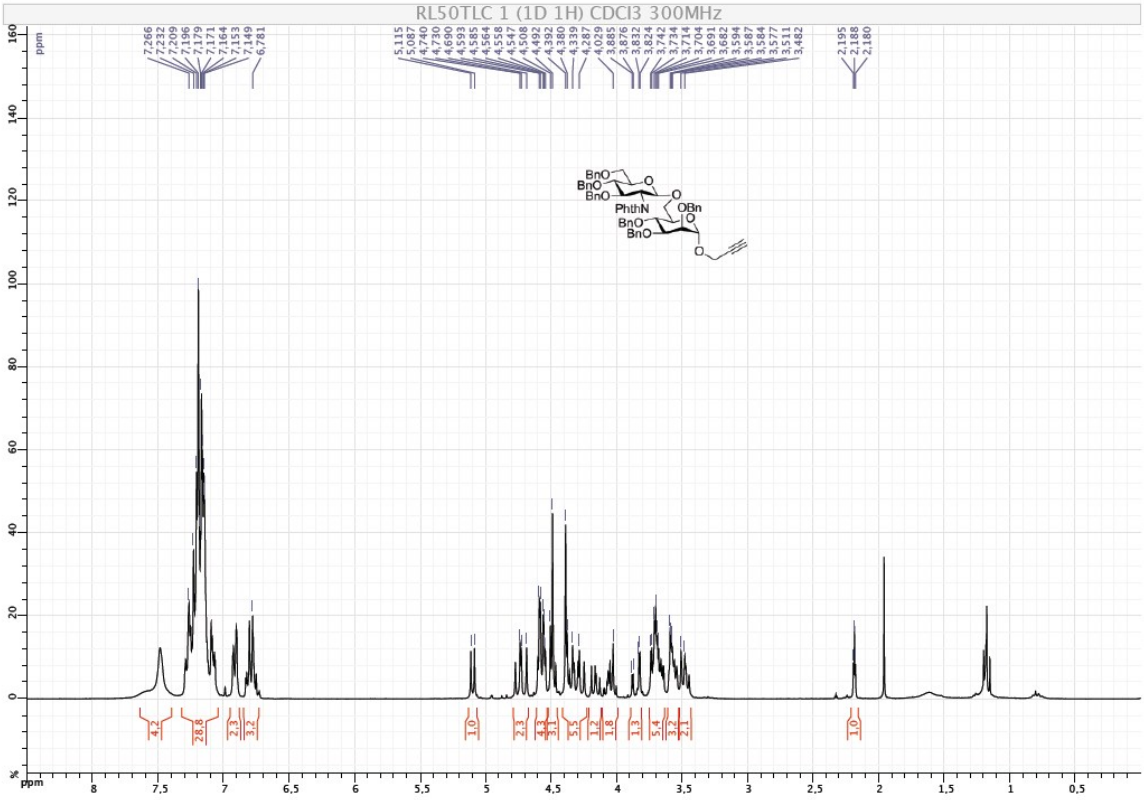


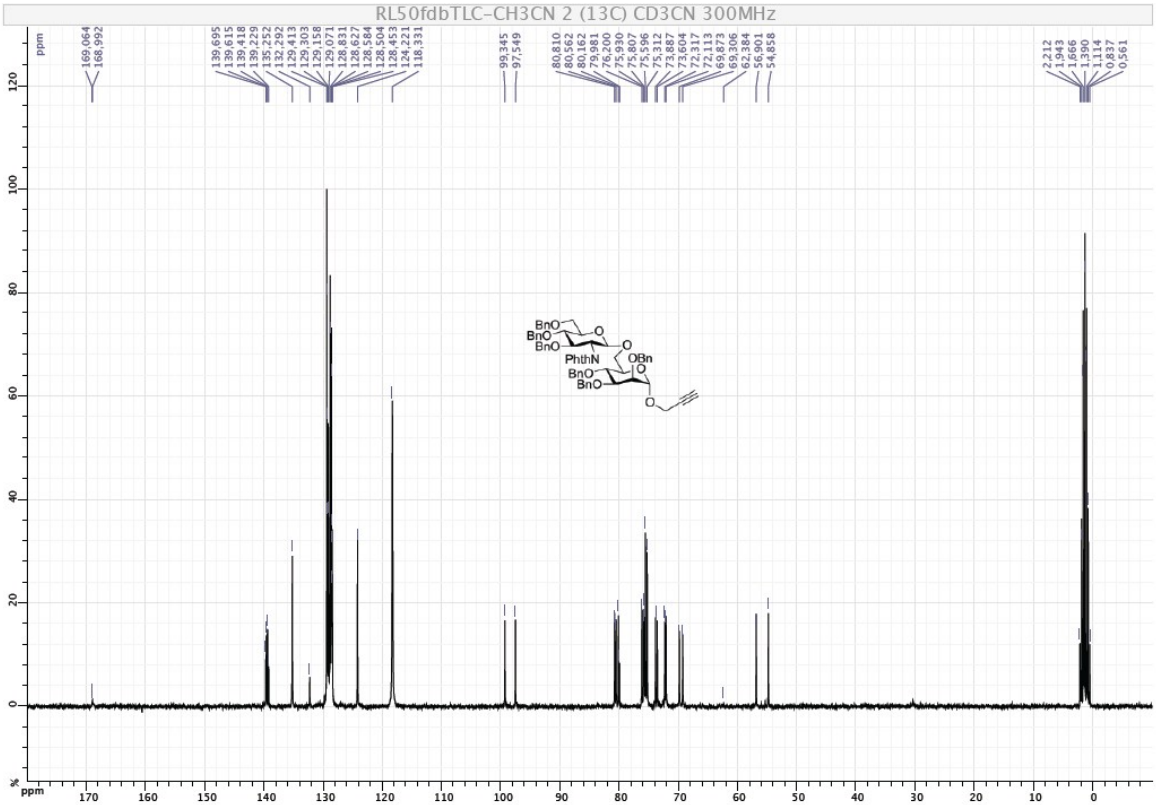
^{1}H and ^{13}C NMR spectra for compound **33**



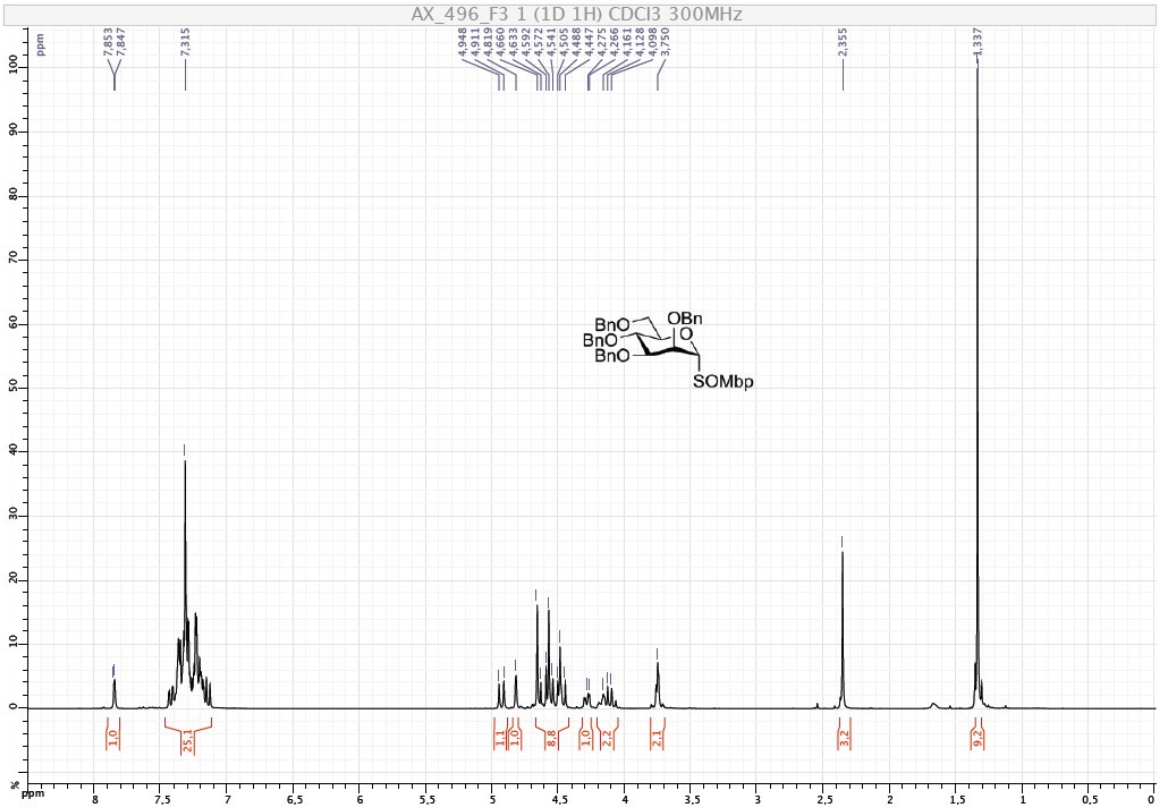


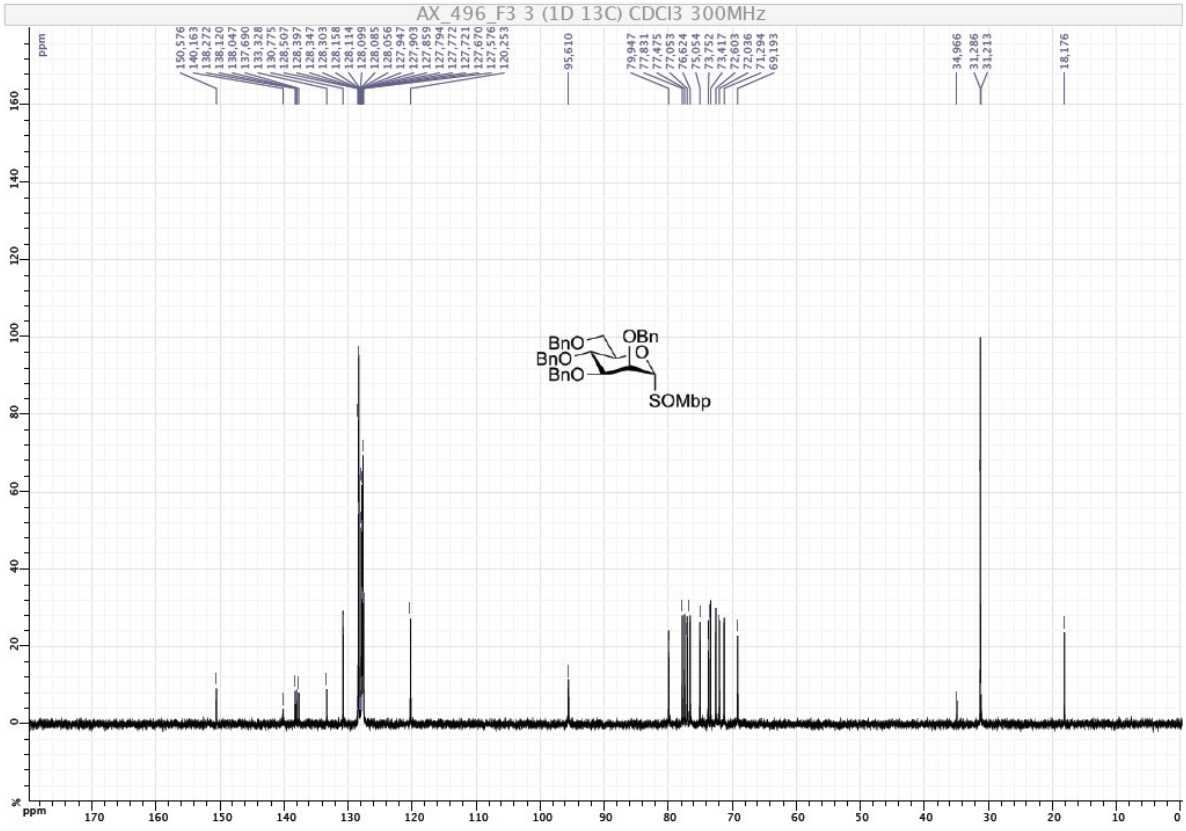
^{1}H and ^{13}C NMR spectra for compound **34α**



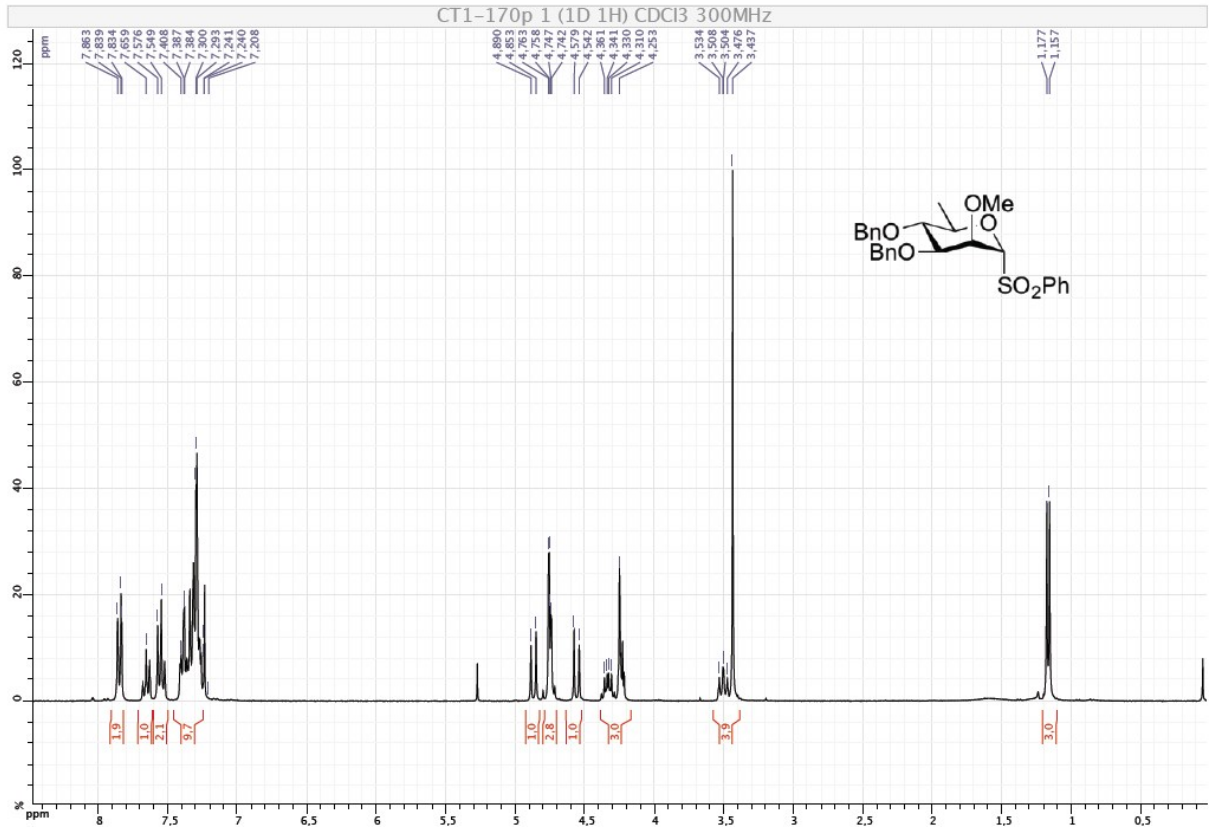


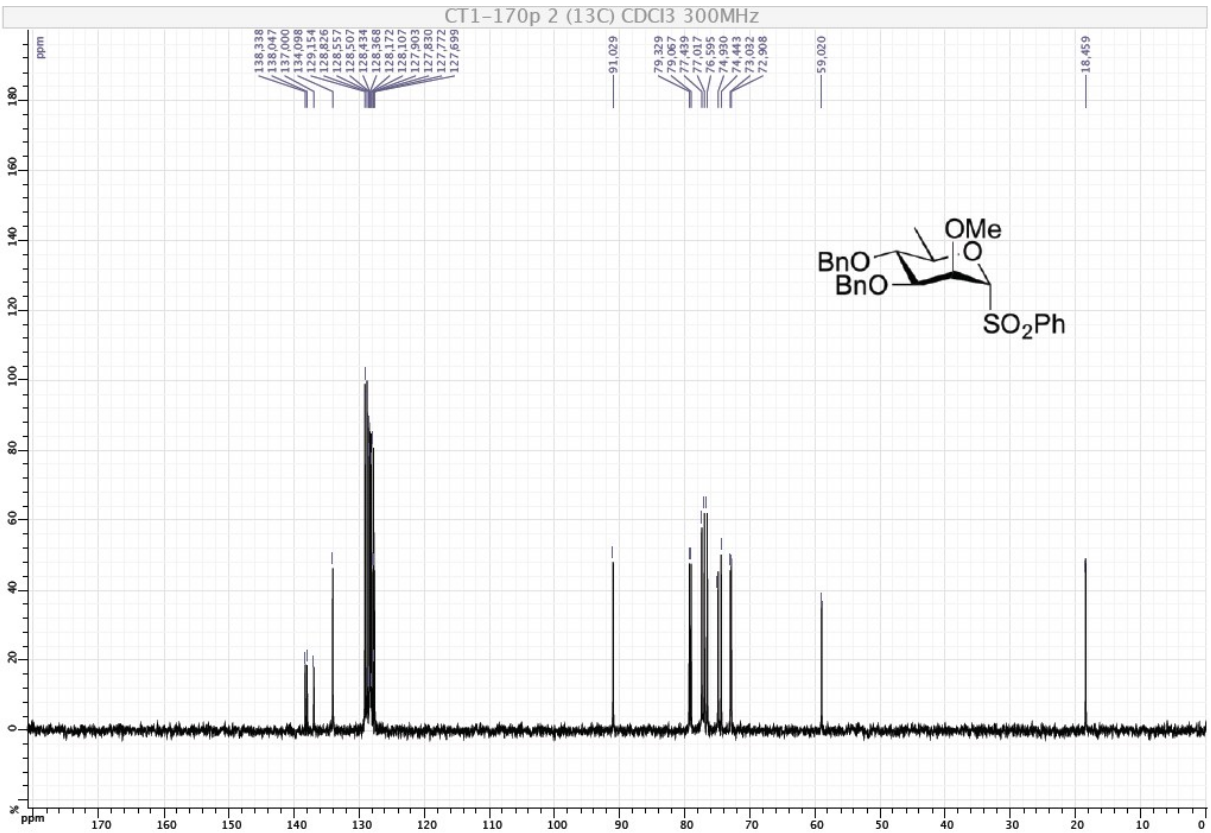
^{1}H and ^{13}C NMR spectra for compound **35**



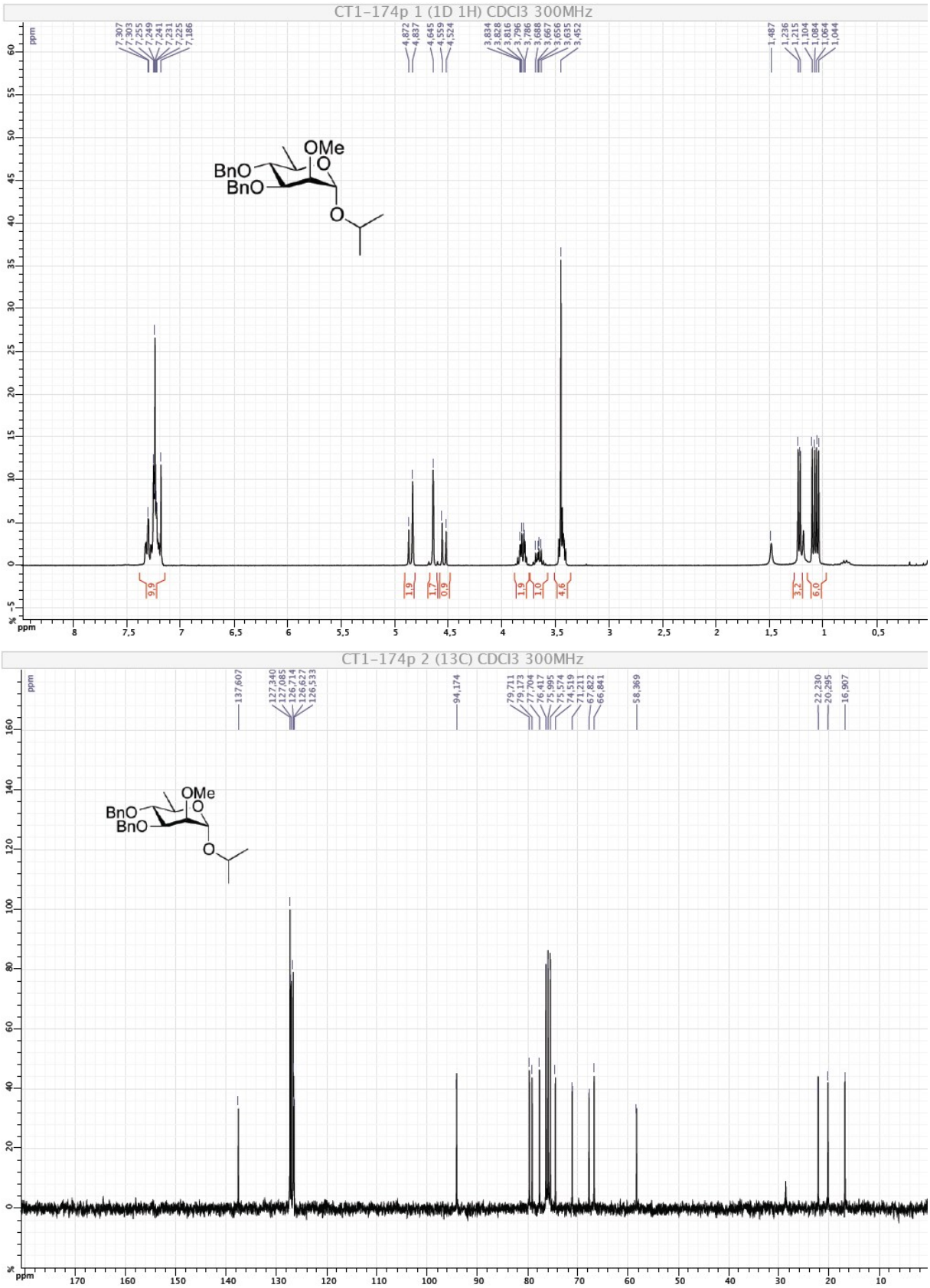


^{1}H and ^{13}C NMR spectra for compound **38**

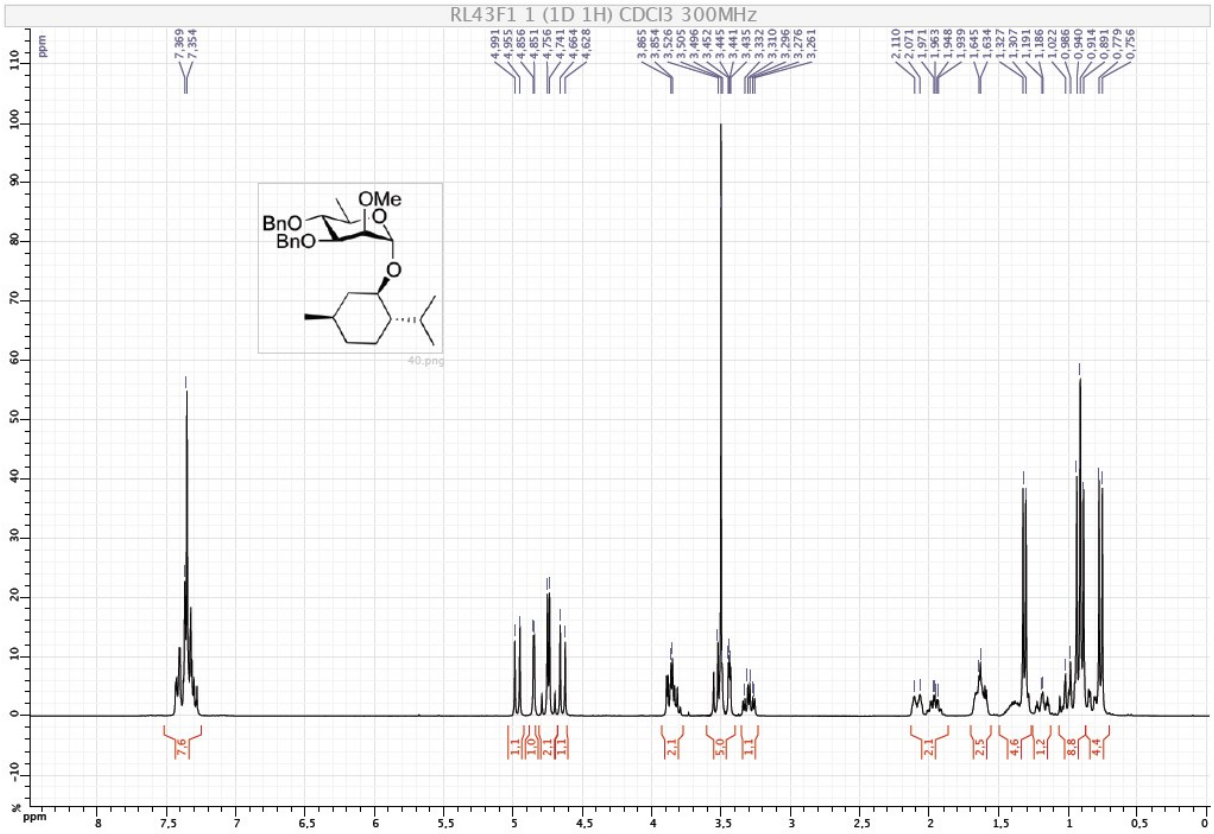


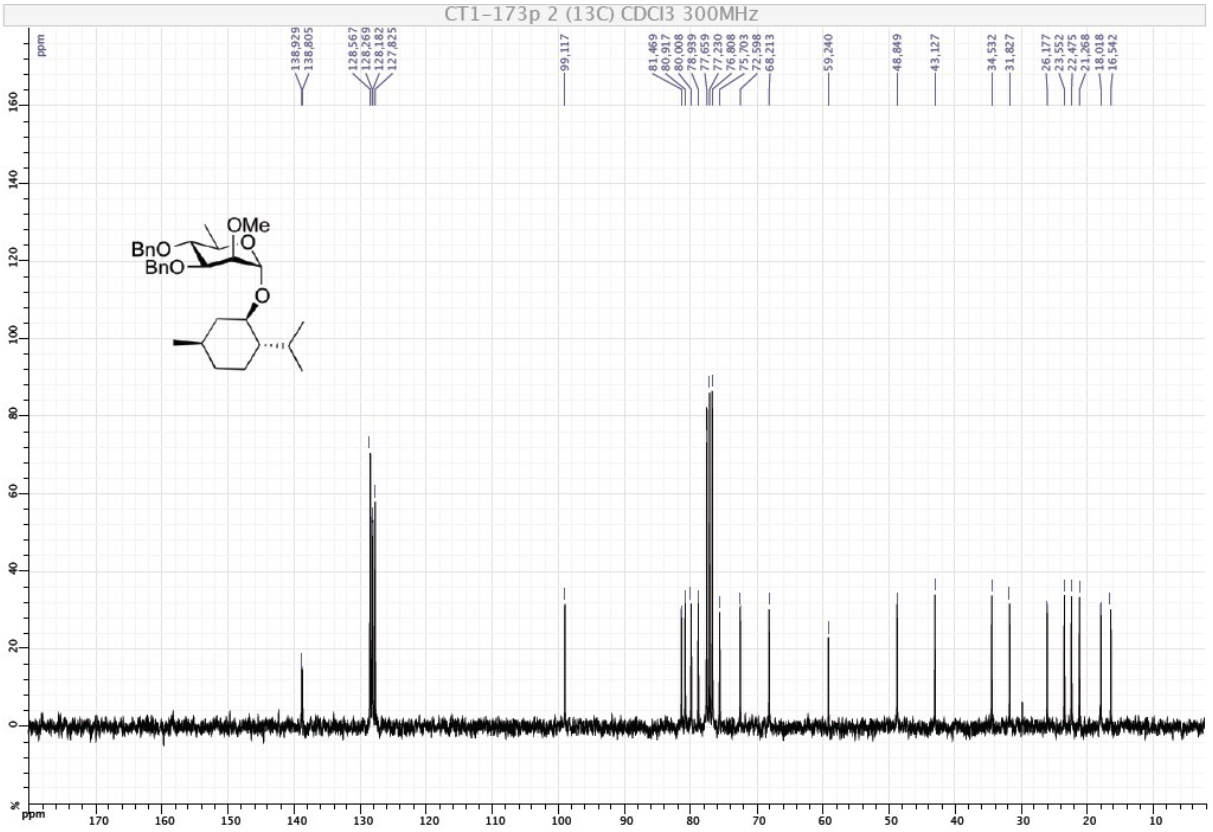


^{1}H and ^{13}C NMR spectra for compound **39**

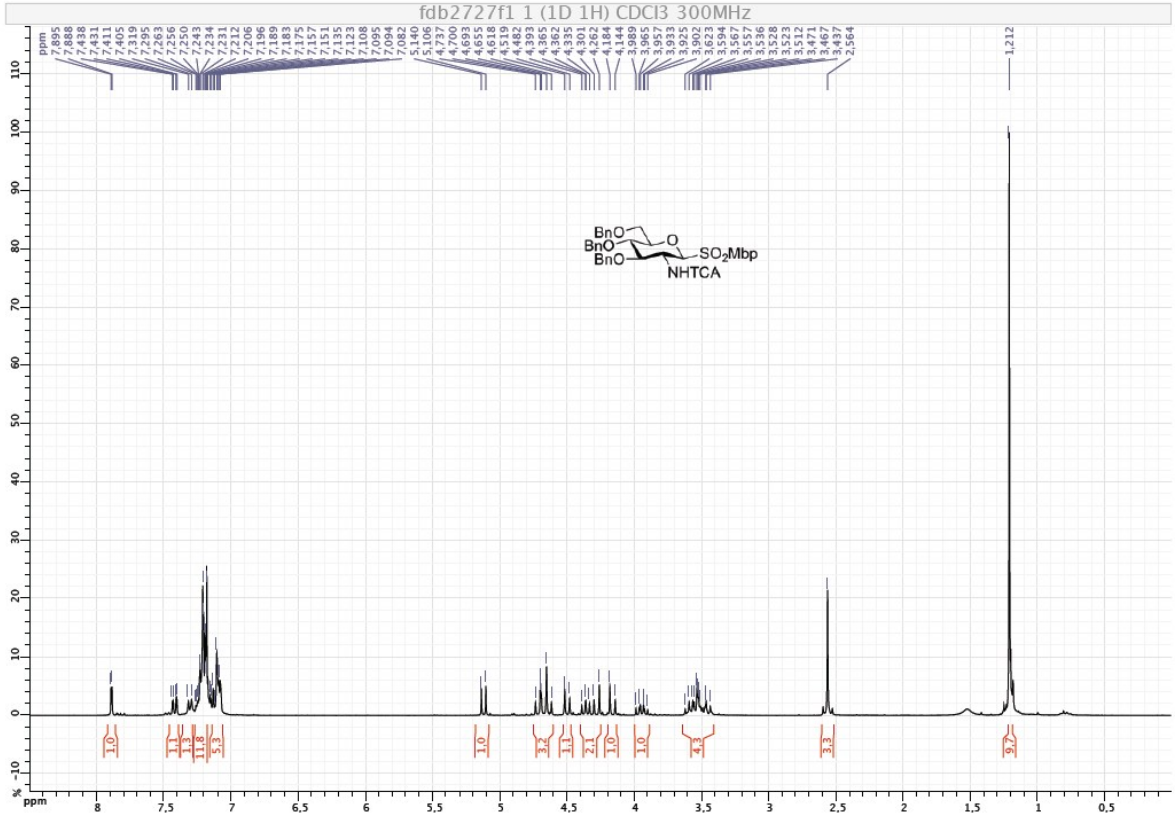


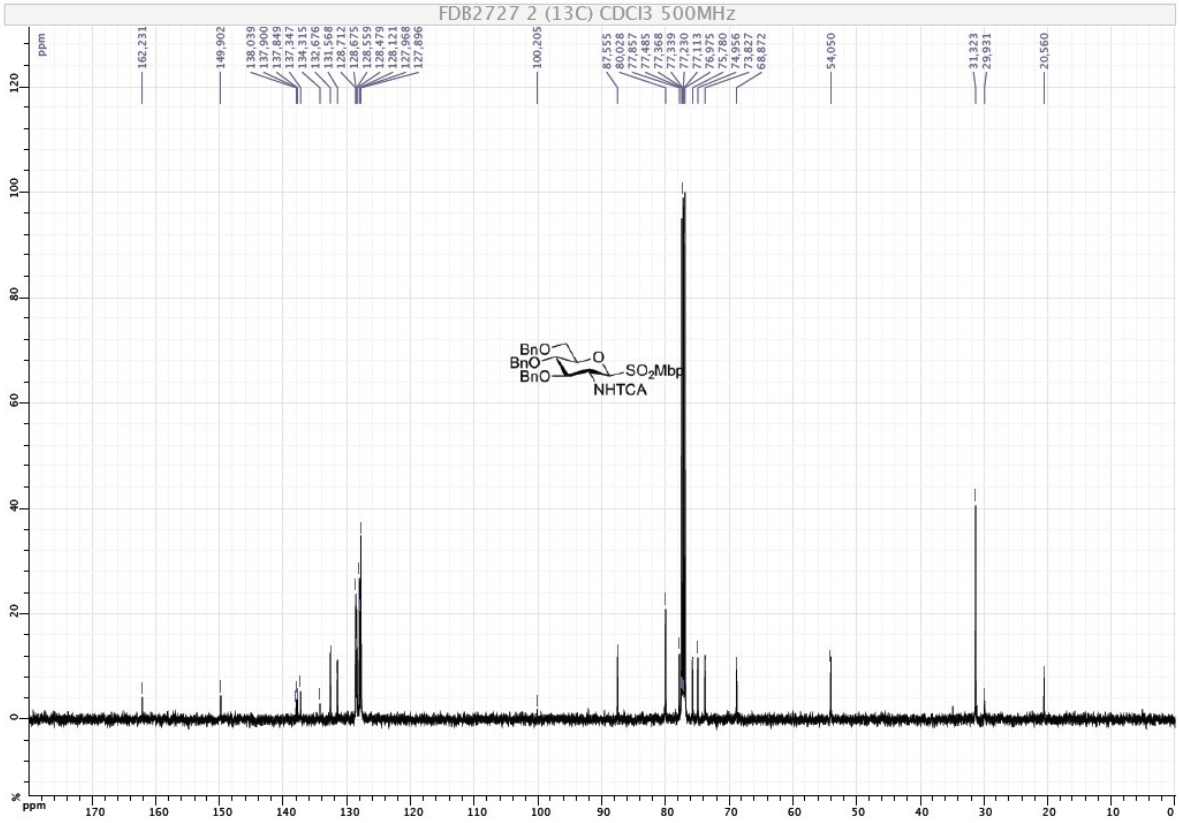
^{1}H and ^{13}C NMR spectra for compound **40**



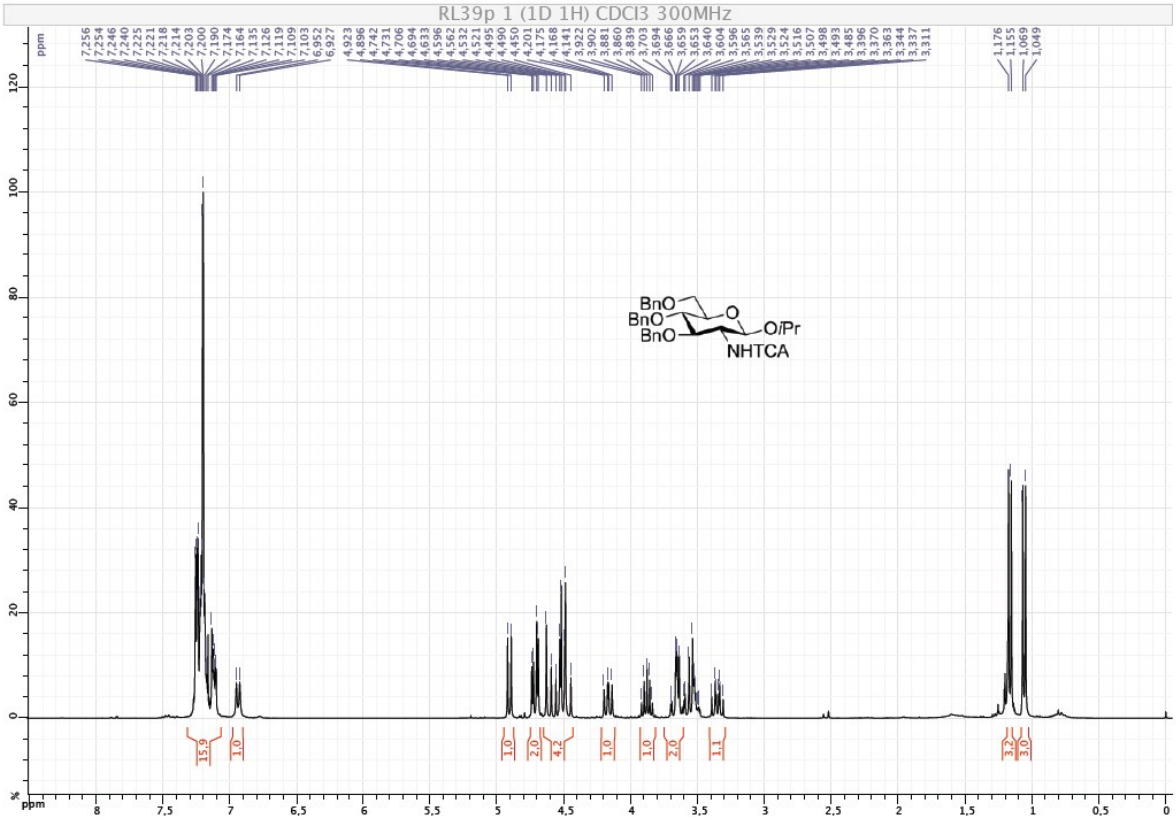


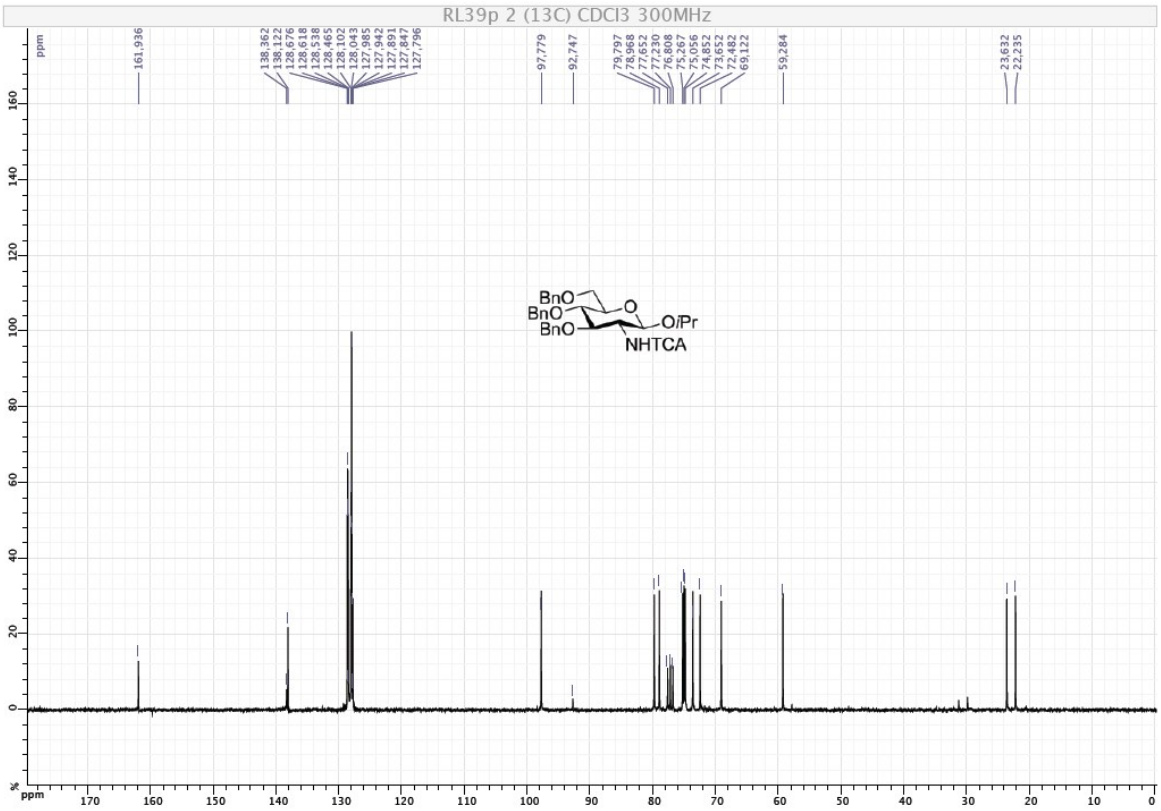
^{1}H and ^{13}C NMR spectra for compound **45**



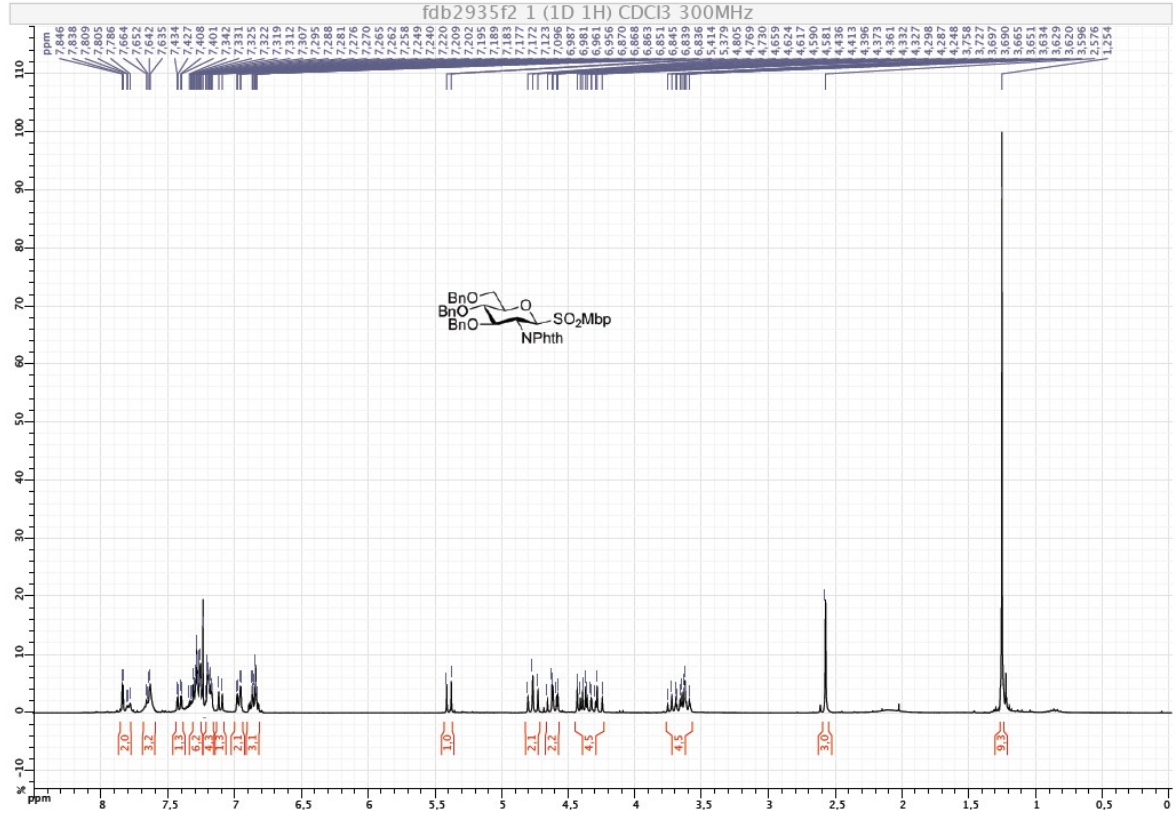


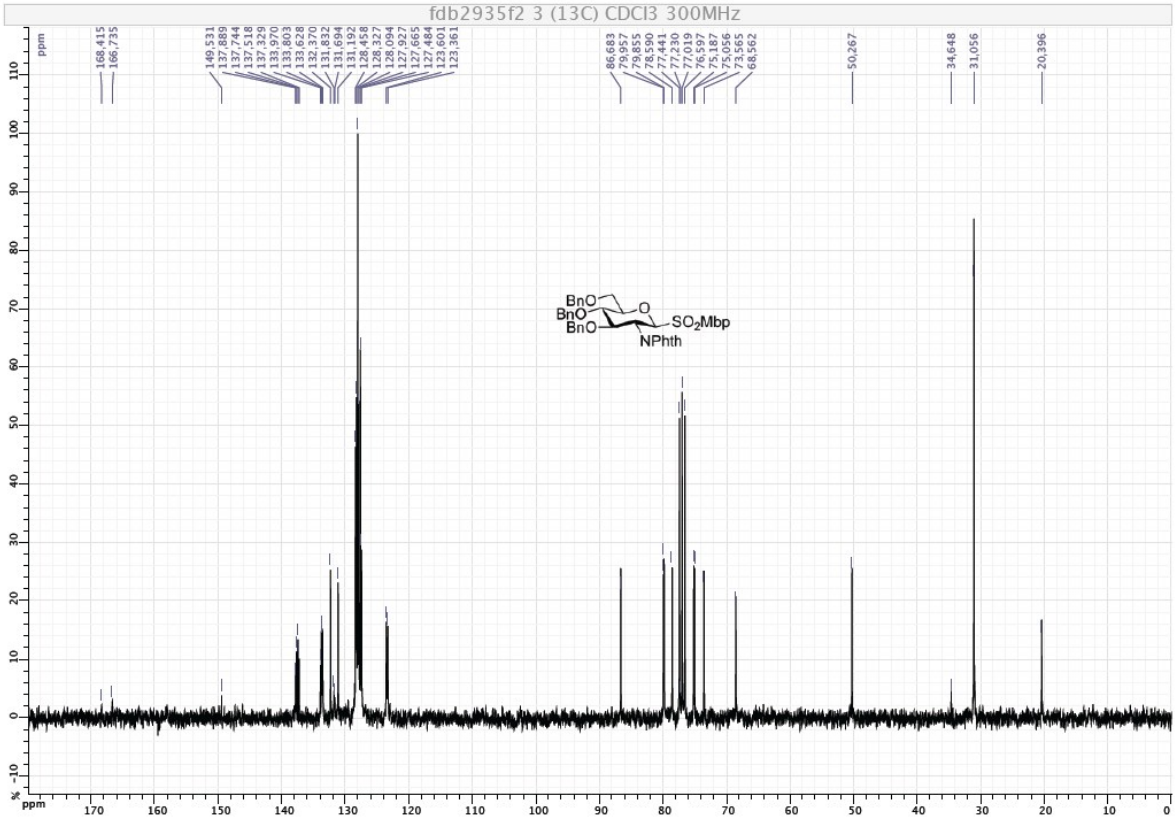
^{1}H and ^{13}C NMR spectra for compound **46β**



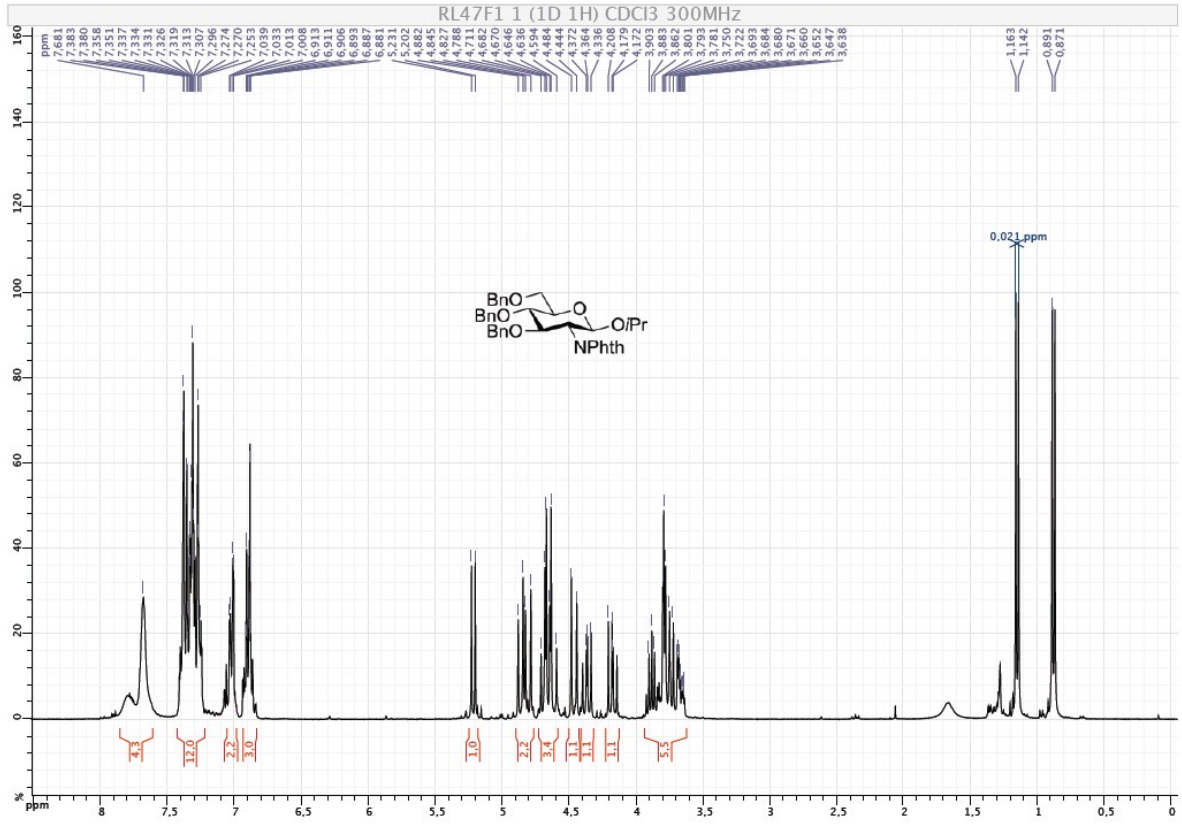


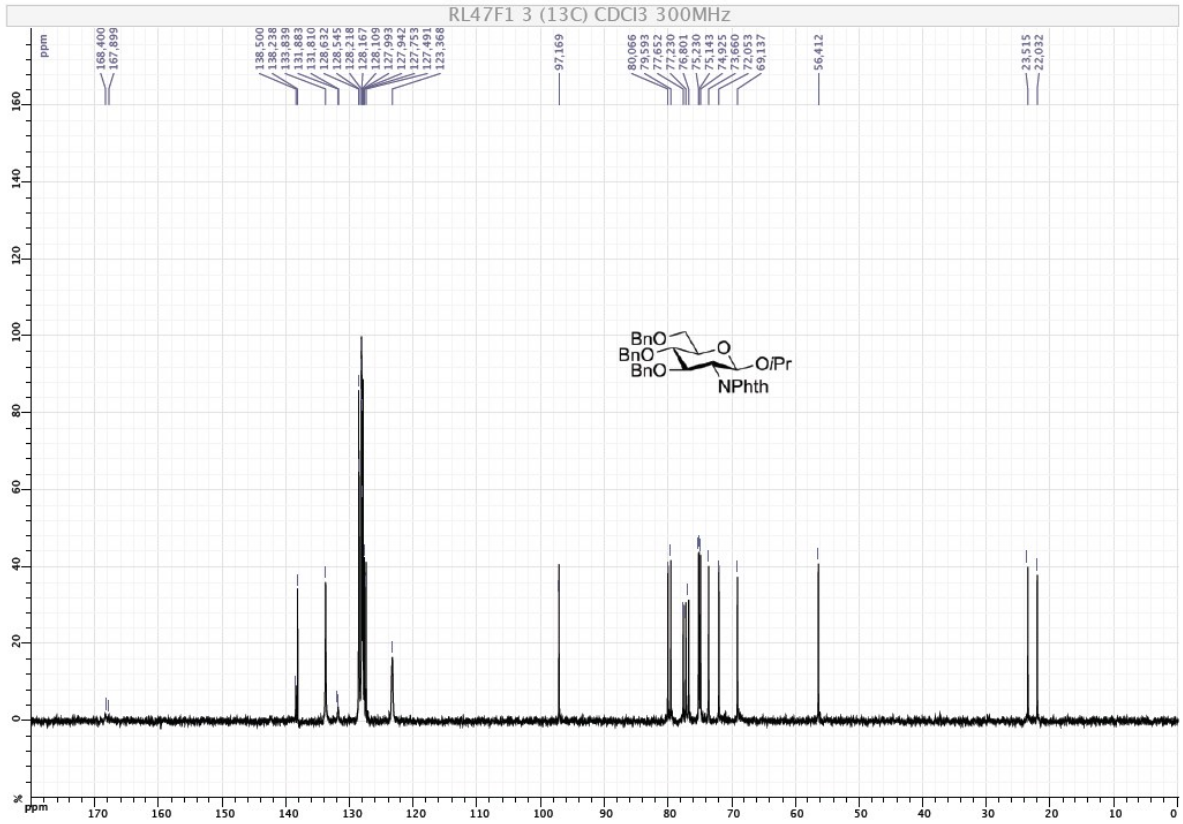
^{1}H and ^{13}C NMR spectra for compound **47**





^{1}H and ^{13}C NMR spectra for compound **48β**





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