Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Catalytic Stereoselective Synthesis of 2-Deoxy *α*-glycosides Using Glycosyl *Ortho*-[1-(*p*-MeOPhenyl)Vinyl]Benzoates (PMPVB) Donors

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Table of Contents

General Information

All solvents purchased were of commercial grade and reagents were purchased from Sigma-Aldrich, Merck, Carbosynth, Spectrochem, Alfa Aesar, Avra and used without further purification for reactions.

Analysis

Reactions were monitored by TLC on Kieselgel 60 F254 (Merck). Detection was done by examination under UV light (254 nm) and by charring with 10% sulfuric acid in water. Purification was performed by both Ultra High Performance Liquid Chromatography (UHPLC) using column [Particle size: (µ) 12, Dim: (mm) 250 x 10] in reverse phase and in normal phase using silica gel [Merck, 60-120 mesh] and Flash column chromatography (Combiflash $^{(R)}$ NextGen 300). Extracts were concentrated in vacuo using both Büchi rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) and 0.7 mmHg (oil pump), at rt. ^{1}H- and ^{13}C NMR were recorded on a Bruker 600 MHz ,500 MHz, and 400 MHz spectrometer using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent as the internal standard ($CDCl_3$: δ 7.26 for ^{1}H, δ 77.16 for ^{13}C). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublets, dt = doublet of triplet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet) etc., coupling constants J (Hz), and integration. High-resolution mass measurements were performed using Agilent technologies mass spectrometer (QTOF-ESI mode). The diastereomeric ratios were calculated from crude NMR. Specific rotation was recorded in Autopol II S2, the units of the specific rotation is (deg·mL)/(g·dm) and concentration *c* is given in g/100 ml.

Hemiacetals used in this study:

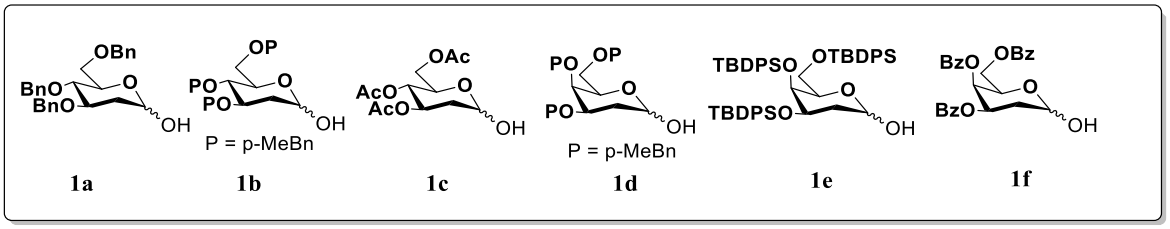


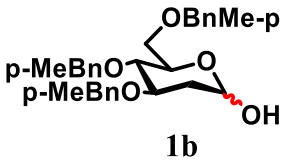
Figure 1.

1a, **1c**, **1e**, **1f** were synthesized following literature procedures[1,2].

General procedure 1

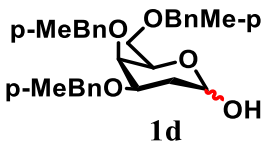
3,4,6-tri-para-methyl-*O*-benzyl-D-glycal (110 mg, 0.24 mmol, 1eqv.) was dissolved in 2 ml of 90:10:1 THF: water: 8(M) HCl and was stirred for 24 h[1]. The reaction mixture was then concentrated and extracted with DCM three times. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude was purified by Flash column chromatography in Ethyl acetate/Hexane solvent system.

Synthesis of 3,4,6-Tri- para-methyl-*O*-benzyl-2-deoxy-α/β-D-glucopyranose (1b)



1b was synthesized according to general procedure **1** (white solid, 85.7 mg, 75 %, α: β = 2.6:1, R_f = 0.30 (Hexane/EtOAc, 3:2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.02 (m, 15H), 5.39 (s, 1H), 4.88 – 4.72 (m, 2H), 4.67 – 4.53 (m, 4H), 4.50-4.42 (m, 3H), 4.04-3.96 (m, 2H), 3.70-3.60 (m, 3H), 3.50 – 3.41 (m, 2H), 3.21 (s, 1H), 2.64 (s, 1H), 2.43-2.35 (m, 1H)2.33 (s, 12H), 2.26 (dd, *J* = 12.8, 4.1 Hz, 1H), 1.71 – 1.63 (m, 1H), 1.53 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.33, 136.22, 134.66, 134.50, 134.30, 134.26, 133.99, 128.11, 128.04, 128.03, 127.98, 127.94, 127.11, 127.07, 126.83, 126.78, 93.17, 91.20, 77.98, 77.44, 76.62, 75.86, 74.03, 73.71, 72.33, 70.74, 70.43, 69.92, 68.11, 68.04, 37.03, 34.51, 20.13. HRMS (ESI) calcd for $C_{30}H_{40}NO_5$ $[M+NH_4]^+$ 494.2906, found 494.2910. $[\alpha]_D^{35}$= 0.32 (*c* 0.01, $CHCl_3$).

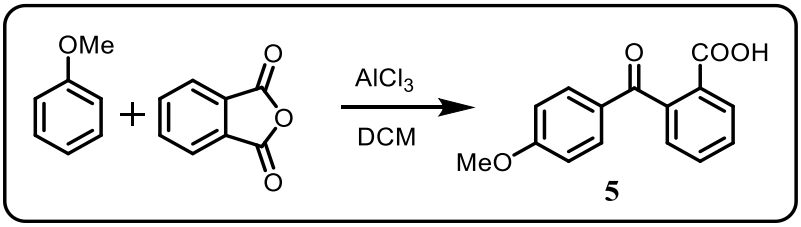
Synthesis of 3,4,6-Tri- para-methyl-*O*-benzyl-2-deoxy-α/β-D-galactopyranose (1d)



1d was synthesized according to general procedure **1** (White solid, 86.9 mg, 76 %, α: β = 3.3:1, R_f = 0.31 (Hexane/EtOAc, 3:2, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.06 (m, 12H), 5.39 (s, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.57 – 4.51 (m, 3H), 4.44 (d, *J* = 11.8 Hz, 1H), 4.34 (d, *J* = 11.7 Hz, 1H), 4.07 (t, *J* = 5.8 Hz, 1H), 3.93 (d, *J* = 10.8 Hz, 1H), 3.78 (s, 1H),

3.53 (t, *J* = 8.2 Hz, 1H), 3.39 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.27 (s, 1H), 2.33 (s, 6H), 2.31 (s, 3H), 2.16 (t, *J* = 12.4 Hz, 1H), 1.94 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.35, 136.15, 136.11, 134.77, 134.53, 133.89, 128.05, 128.01, 127.84, 127.45, 127.08, 126.41, 91.57, 73.21, 72.86, 72.27, 71.82, 69.33, 69.07, 69.03, 30.10, 20.13, 20.12. HRMS (ESI) calcd for $C_{30}H_{40}NO_5$ $[M+NH_4]^+$ 494.2906, found 494.2906. $[\alpha]_D^{35}$= 0.66 (*c* 0.016, $CHCl_3$).

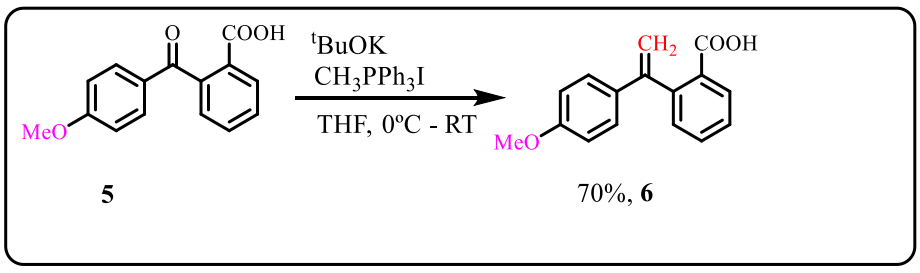
Synthesis of 2-(4-methoxybenzoyl)benzoic acid (5)



Scheme 1

To a solution of phthalic anhydride (4 g, 27 mmol,) in dichloromethane (100 mL) was added anisole (14.7 mL,135 mmol,). The solution was cooled in an ice bath and was added Aluminum chloride (7.2 g, 54 mmol) in portion wise. The ice bath was removed after 20 min and the reaction mixture was allowed to reach to room temperature. Then, the reaction mixture was refluxed for overnight. After completion of reaction, the reaction mixture was cooled to room temperature, and poured carefully into a stirred solution of ice/1N HCl (150 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3x150 mL). The combined organic layer was extracted with cold aqueous 1N NaOH (300 mL). The aqueous layer was extracted with dichloromethane (3x100 mL). The organic layers were discarded and the cold aqueous basic layer was acidified with concentrated HCl to make the pH reach 6, resulting in a milky white suspension. This was extracted with dichloromethane (3x200 mL), dried (by Na_2SO_4), and the organic layers were concentrated to provide compound **5** (4.5 g, 65 %) as a white solid.

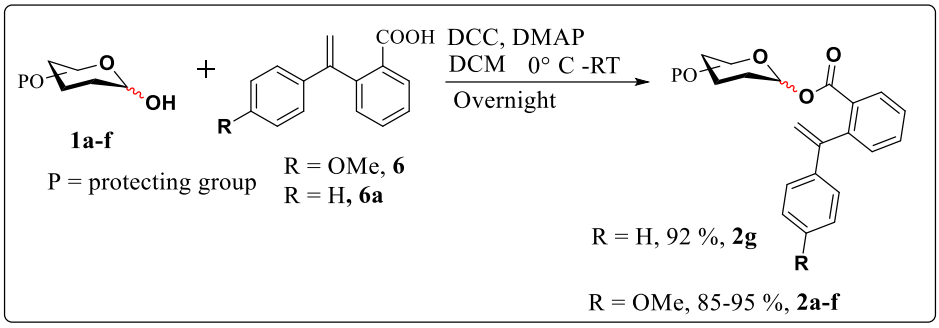
Synthesis of *ortho*-[1-(p-methoxy phenyl)vinyl]benzoic acid (6)



Scheme 2.

To a suspension of methyl triphenylphosphonium iodide (7.14 g, 20.0 mmol) in THF (100 mL) was added potassium *tert*-butoxide (3.36 g, 30.0 mmol) at 0 ºC. The mixture was then stirred for 30 min. Then 2-(4-methoxybenzoyl) benzoic acid (**5)** (10.0 mmol) was added to the reaction mixture at 0 ºC. The mixture was allowed to warm to room temperature, and stirred for 24 h. After completion of the reaction, THF was evaporated and the mixture was treated with 10%

NaOH (100 mL). The aqueous layer was washed with DCM (50 mL) and acidified with 1N HCl to make the pH reach 6. The aqueous layer was extracted with ethyl acetate (350 mL). The combined extracts were washed with brine (100 mL), dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by recrystallization from petroleum ether/ethyl acetate to give the product as a white solid, *ortho*-[1-(p-methoxy phenyl) vinyl]benzoic acid (**6**)[3].The compound **6a** were synthesized by following literature procedures[3].



Scheme 3.

General procedure 2

To a solution of **Sugar** (1.0 equiv. **1a-f**) and benzoic acid (**6, 6a**) (1.2 equiv.) in dry DCM was added 4-dimethylaminopyridine (DMAP) (0.2 equiv.) and *N*,*N*'-Dicyclohexylcarbodiimide (DCC) was added at 0 °C. The resulting mixture was allowed to reach room temperature and stirred for overnight. After completion of the reaction, the mixture was diluted with CH_2Cl_2, and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by Flash column chromatography to afford the glycosyl donors (**2a-g**).[4]

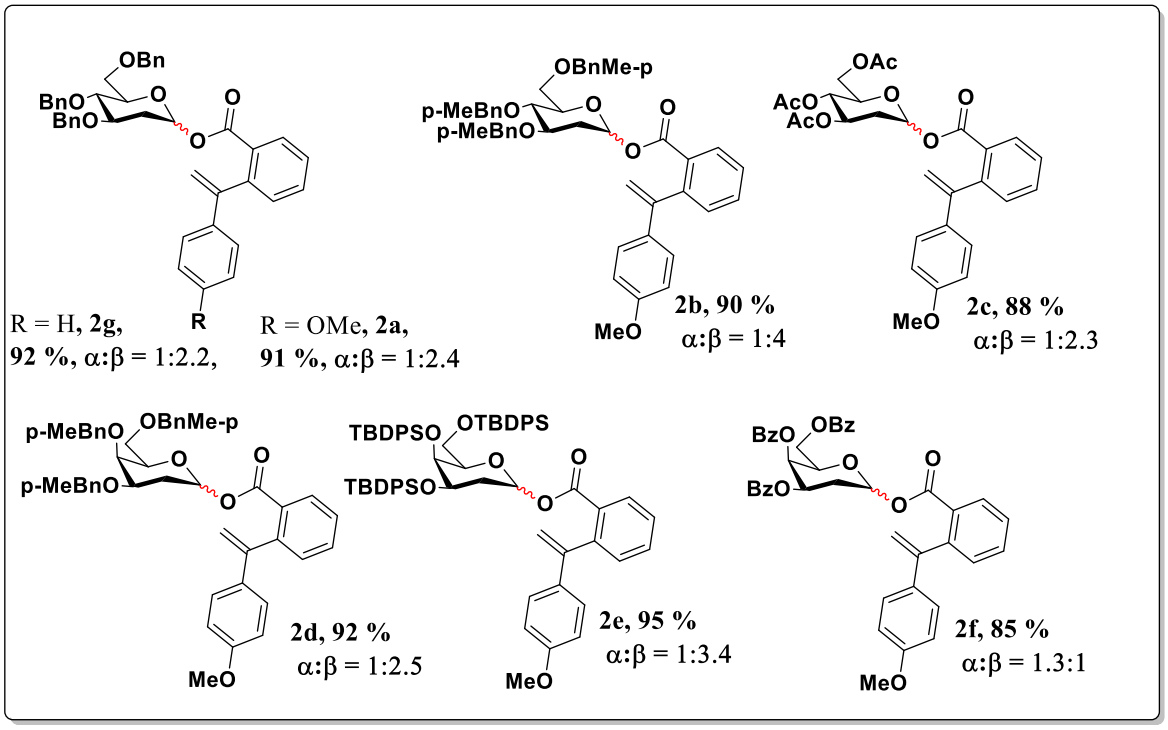
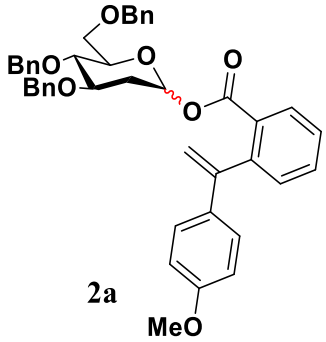


Figure 2. Glycosyl Donors used for this study

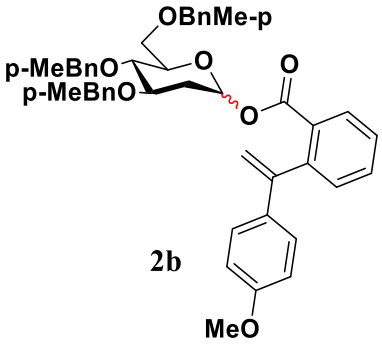
Synthesis of 3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (2a)



2a

Compound **2a** was prepared from **1a** (434.5 mg, 1 mmol) according to **General procedure 2**. The crude product was purified by Flash column chromatography to afford **2a** (610.4 mg, 91 %, α: β = 1:2.4) as a white solid, R*f* = 0.52 (Hexane/EtOAc, 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 10.8, 4.2 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.42 – 7.37 (m, 2H), 7.35 – 7.22 (m, 19H), 7.17 (t, *J* = 8.9 Hz, 6H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 1H), 6.24 (d, *J* = 2.0 Hz, 1H), 5.61 (s, 1H), 5.59 (d, *J* = 1.7 Hz, 1H), 5.57 (s, 1H), 5.12 (s, 1H), 5.02 (s, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.63 – 4.57 (m, 3H), 4.53 (d, *J* = 3.0 Hz, 1H), 4.52 (d, *J* = 1.9 Hz, 1H), 4.49 (d, *J* = 12.1 Hz, 2H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.39 (q, 11.6 Hz, 1H), 3.74 (d, *J* = 4.0 Hz, 1H), 3.72 (s, 4H), 3.70 (d, *J* = 1.4 Hz, 1H), 3.68 (dd, *J* = 6.1, 2.4 Hz, 1H), 3.65 (dd, *J* = 9.0, 3.9 Hz, 1H), 3.63 (d, *J* = 4.4 Hz, 1H), 3.61 (s, *J* = 5.8 Hz, 2H), 3.59 (d, *J* = 9.2 Hz, 1H), 3.56 (d, *J* = 9.6 Hz, 1H), 3.51 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.48 – 3.44 (m, 1H), 2.14 (dd, *J* = 13.1, 3.3 Hz, 1H), 2.12 – 2.07 (m, 1H), 1.77 – 1.70 (m, 1H), 1.55 (q, *J* = 11.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.47, 165.47, 159.36, 159.21, 148.53, 148.26, 143.39, 142.83, 138.65, 138.59, 138.30, 138.23, 138.17, 138.09, 133.30, 132.74, 132.07, 131.74, 131.33, 131.02, 130.99, 130.23, 130.19, 130.09, 128.48, 128.41, 128.39, 128.37, 128.31, 128.12, 128.01, 127.97, 127.95, 127.77, 127.76, 127.73, 127.70, 127.66, 127.64, 127.62, 127.54, 127.50, 113.72, 113.56, 112.57, 112.13, 93.14, 92.97, 78.89, 77.47, 75.93, 74.98, 74.84, 73.63, 73.53, 73.50, 71.73, 71.46, 68.68, 68.37, 55.25, 55.12, 34.88, 34.28.HRMS (ESI) calcd for $C_{43}H_{46}NO_7$ $[M+NH_4]^+$ 688.3274, found 688.3274. $[\alpha]_D^{35}$= 0.88 (*c* 0.015, $CHCl_3$)

Synthesis of 3,4,6-tri- para-methyl- *O*-benzyl-2-deoxy-D-glucopyranosyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (2b)

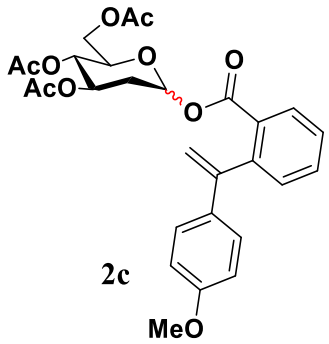


2b

Compound **2b** was prepared from **1b** (476.6 mg, 1 mmol) according to **General procedure 2**. The crude product was purified by Flash column chromatography to afford **2b** (641.6 mg, 90 %, α: β = 1:4) as a colourless syrup, R*f* = 0.52 (Hexane/EtOAc, 4:1, v/v). ^{1}H NMR (600 MHz,

$CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 7.3, 3.8 Hz, 4H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.61 (s, 1H), 5.55 (d, *J* = 8.8 Hz, 1H), 5.11 (s, 1H), 4.79 (d, *J* = 10.5 Hz, 1H), 4.59 – 4.54 (m, 2H), 4.49 (d, *J* = 11.4 Hz, 1H), 4.43 (d, *J* = 11.2 Hz, 2H), 3.74 (s, 3H), 3.69 (dd, *J* = 10.8, 3.8 Hz, 1H), 3.65 (d, *J* = 10.0 Hz, 1H), 3.57 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.53 (t, *J* = 9.0 Hz, 1H), 3.42 (d, *J* = 9.0 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 2.32 (s, 3H), 2.07 (dd, *J* = 11.4, 3.8 Hz, 1H), 1.56 – 1.49 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.43, 159.16, 148.49, 143.36, 137.40, 137.36, 137.27, 135.26, 135.19, 135.04, 133.26, 131.99, 131.27, 130.22, 130.07, 129.11, 129.00, 128.98, 128.14, 127.92, 127.81, 127.48, 113.51, 112.50, 92.95, 78.66, 77.09, 75.91, 74.78, 73.30, 71.36, 68.34, 55.22, 34.90, 21.19, 21.17. HRMS (ESI) calcd for $C_{46}H_{52}NO_7$ $[M+NH_4]^+$ 730.3744, found 730.3746. $[\alpha]_D^{35}$= 0.86 (*c* 0.014, $CHCl_3$).

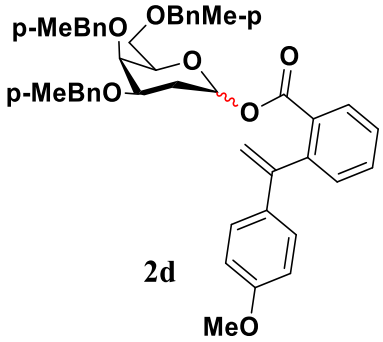
Synthesis of 3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (2c)



Compound **2c** was prepared from **1c** (290.3 mg, 1 mmol) according to **General procedure 2**. The crude product was purified by Flash column chromatography to afford **2c** (463.4 mg, 88 %, α: β = 1:2.3) as a yellow syrup, R*f* = 0.4 (Hexane/EtOAc, 3:1, v/v). The α anomer,^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.25 (m, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.25 (d, *J* = 2.7 Hz, 1H), 5.77 (s, 1H), 5.11 (s, 1H), 5.06-5.00 (m, 1H), 4.93 (t, *J* = 9.8 Hz, 1H), 4.08 (dd, *J* = 12.5, 3.7 Hz, 1H), 3.80 (dd, *J* = 12.8, 1.4 Hz, 1H), 3.78 (s, 3H), 3.51 (d, *J* = 10.1 Hz, 1H), 2.10 (dd, *J* = 13.3, 5.3 Hz, 1H), 2.05 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.89 – 1.83 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.67, 169.02, 168.66, 165.21, 158.42, 146.89, 141.83, 131.45, 131.00, 130.01, 129.63, 129.21, 126.98, 126.58, 112.77, 111.46, 90.77, 69.17, 67.61, 67.46, 60.63, 54.18, 32.84, 19.87, 19.66, 19.51. HRMS (ESI) calcd for $C_{28}H_{34}NO_{10}$ $[M+NH_4]^+$ 544.2183, found 544.2184. $[\alpha]_D^{35}$= 0.18 (*c* 0.01, $CHCl_3$

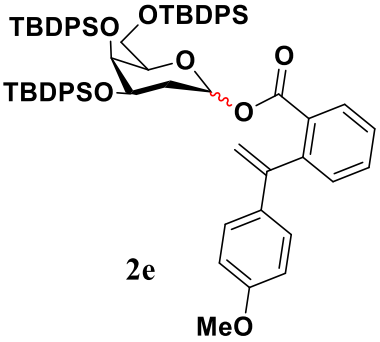
The β anomer, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 5.68 (d, *J* = 9.2 Hz, 1H), 5.62 (s, 1H), 5.11 (s, 1H), 4.97 (d, *J* = 5.1 Hz, 2H), 4.27 (dd, *J* = 12.0, 3.9 Hz, 1H), 4.04 (d, *J* = 12.2 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 1H), 2.14-2.08 (m, 1H), 2.06 (s, 3H), 2.03 (s, 6H), 1.69 – 1.62 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.73, 170.03, 169.78, 165.11, 159.22, 148.39, 143.48, 133.16, 132.25, 131.35, 130.14, 129.59, 127.90, 127.54, 113.52, 112.65, 91.84, 91.74, 91.68, 72.76, 70.11, 68.34, 62.03, 55.23, 34.31, 20.84, 20.75, 20.71. HRMS (ESI) calcd for $C_{28}H_{34}NO_{10}$ $[M+NH_4]^+$ 544.2183, found 544.2177. $[\alpha]_D^{35}$= 0.50 (*c* 0.014, $CHCl_3$)

Synthesis of 3,4,6-tri- para-methyl- *O*-benzyl-2-deoxy-D-galactopyranosyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (2d)



Compound **2d** was prepared from **1d** (476.6 mg, 1 mmol) according to **General procedure 2**. The crude product was purified by Flash column chromatography to afford **2d** (655.8 mg, 92 %, α: β = 1:2.5) as a white solid, R*f* = 0.55 (Hexane/EtOAc, 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.50 (dt, *J* = 14.6, 7.4 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.05 (m, 21H), 6.77 (dd, *J* = 8.4, 4.4 Hz, 3H), 6.28 (d, *J* = 2.0 Hz, 1H), 5.60 (s, 1H), 5.55 (s, 1H), 5.52 (d, , *J* = 6.0 Hz, 1H), 5.12 (s, 1H), 5.00 (s, 1H), 4.85 (d, *J* = 11.4 Hz, 1H), 4.79 (d, *J* = 11.3 Hz, 1H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.48 (d, *J* = 10.6 Hz, 3H), 4.43 – 4.37 (m, 2H), 4.33 (d, *J* = 6.0 Hz, 1H), 4.31 (d, *J* = 6.0 Hz, 1H) , 4.30-4.29 (m, 1H), 4.22 (d, *J* = 11.5 Hz, 1H), 3.79 (d, *J* = 10.8 Hz, 2H), 3.73 (m,4H), 3.69 (s, 1H), 3.56 (t, *J* = 9.8 Hz, 1H), 3.51 (d, *J* = 2.5 Hz, 2H), 3.50 (d, *J* = 5.2 Hz, 2H), 3.47 (d, *J* = 8.0 Hz, 1H), 3.41 (dd, *J* = 9.0, 5.5 Hz, 1H), 2.37 – 2.29 (m, 13H), 2.25 – 2.19 (m, 1H), 2.06 – 1.98 (m, 1H), 1.80 (d, *J* = 11.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.79, 165.36, 159.32, 159.07, 148.59, 148.12, 143.40, 142.60, 137.50, 137.45, 137.43, 137.28, 137.22, 137.19, 135.70, 135.65, 135.30, 135.01, 134.95, 134.80, 133.34, 132.67, 132.07, 131.58, 131.32, 131.27, 130.84, 130.32, 130.29, 129.91, 129.17, 129.10, 129.07, 128.92, 128.88, 128.46, 128.33, 128.17, 128.12, 128.09, 127.87, 127.50, 127.33, 113.64, 113.52, 112.55, 112.14, 93.66, 93.30, 76.46, 74.79, 74.20, 74.14, 74.08, 73.34, 73.31, 72.55, 71.87, 70.91, 70.14, 70.07, 68.56, 68.35, 55.22, 55.19, 31.09, 29.87, 21.24. HRMS (ESI) calcd for $C_{46}H_{52}NO_7$ $[M+NH_4]^+$ 730.3744, found 730.3743. $[\alpha]_D^{35}$= - 1.479 (*c* 0.02, $CHCl_3$).

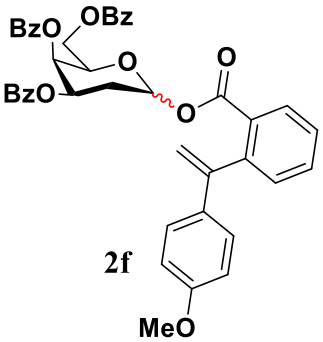
Synthesis of 3,4,6-tri-*O*-tertiary-butyldiphenylsilyl-2-deoxy-D-galactopyranosyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (2e)



Compound **2e** was prepared from **1e** (439.7 mg, 0.5 mmol) according to **General procedure 2**. The crude product was purified by Flash column chromatography to afford **2e** (530 mg, 95 %, α: β = 1:3.4) as a white solid, R_f = 0.8 (Hexane/EtOAc, 5:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 6.9 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.1 Hz, 3H), 7.55 – 7.49 (m, 6H), 7.47 – 7.37 (m, 8H), 7.36 – 7.31 (m, 6H), 7.31 – 7.26 (m,

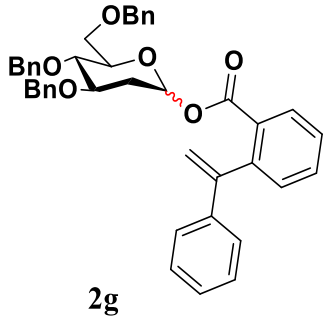
5H), 7.25 – 7.18 (m, 9H), 7.18 – 7.13 (m, 8H), 7.05 (t, *J* = 7.4 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 1H), 6.06 (bs, 1H), 5.53 (s, 1H), 5.44 (s, 1H), 5.25 (d, *J* = 9.1 Hz, 1H), 5.03 (s, 1H), 4.92 (s, 1H), 4.06 (s, 1H), 3.96 (d, *J* = 9.8 Hz, 1H), 3.81 (s, 1H), 3.70 (s, 3H), 3.69 (s, 1H),, 3.56 (m, 1H), 3.50 (m, 2H), 3.45 (m, 1H), 3.22 (d, *J* = 6.8 Hz, 1H), 3.10 (d, *J* = 7.1 Hz, 1H), 3.03 (bs, 1H), 2.50 (t, *J* = 11.1 Hz, 1H), 2.19 (dd, *J* = 11.3, 9.1 Hz, 1H), 1.46 (d, *J* = 10.8 Hz, 1H), 1.34 – 1.27 (m, 1H), 1.04 (s, 3H), 1.00 (s, 9H), 0.98 (s, 12H), 0.85 (s, 9H), 0.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.86, 164.57, 159.04, 158.88, 148.39, 148.37, 143.61, 143.25, 136.52, 136.47, 136.22, 135.94, 135.90, 135.82, 135.79, 135.73, 135.56, 135.50, 135.42, 133.79, 133.68, 133.67, 133.65, 133.52, 133.38, 133.32, 133.29, 133.07, 132.54, 131.77, 131.53, 131.16, 131.10, 130.69, 130.30, 129.97, 129.91, 129.77, 129.60, 129.58, 129.41, 129.33, 129.17, 127.89, 127.83, 127.70, 127.68, 127.61, 127.59, 127.55, 127.52, 127.47, 127.38, 127.29, 127.19, 127.13, 113.44, 113.34, 112.58, 112.28, 92.83, 92.50, 78.06, 76.40, 72.35, 71.57, 70.81, 69.89, 64.47, 64.32, 55.19, 55.12, 33.23, 32.45, 29.76, 27.19, 27.16, 27.11, 26.78, 26.75, 20.01, 18.93, 18.86. HRMS (ESI) calcd for $C_{70}H_{82}NO_7Si_3$ $[M+NH_4]^+$ 1132.5399, found 1132.5415. $[\alpha]_D^{35}$= + 0.40 (*c* 0.01, $CHCl_3$)

Synthesis of 3,4,6-tri-*O*-benzoyl-2-deoxy-D-galactopyranosyl-2-(1-(4-methoxyphenyl)vinyl)benzoate (2f)



Compound **2f** was prepared from **1f** (476.5 mg, 1 mmol) according to **General procedure 2**. The crude product was purified Flash column chromatography to afford **2f** (605.8 mg, 85 %, α: β = 1.3:1) as a white solid, R_f = 0.45 (Hexane/EtOAc, 3:1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.06 (m, 2H), 8.04 – 7.95 (m, 6H), 7.95 – 7.91 (m, 2H), 7.85 – 7.82 (m, 4H), 7.64 – 7.35 (m, 19H), 7.34 – 7.27 (m, 7H), 7.23 – 7.17 (m, 2H), 6.80-6.74 (m, 4H), 6.50 (d, *J* = 2.5 Hz, 1H), 5.89 – 5.85 (m, 2H), 5.78 (d, *J* = 2.7 Hz, 1H), 5.65 (d, *J* = 6 Hz, 1H), 5.63 (s, 1H), 5.40 – 5.36 (m, 1H), 5.36 – 5.32 (m, 1H), 5.15 (s, 1H), 5.13 (s, 1H), 4.55 (dd, *J* = 11.3, 6.5 Hz, 1H), 4.40 – 4.37 (m, 1H), 4.36 – 4.33 (m, 1H), 4.22 (dd, *J* = 6.9, 6.4 Hz, 1H), 4.17 (dd, *J* = 11.2, 6.9 Hz, 1H), 4.00 (t, *J* = 6.7 Hz, 1H), 3.67 (s, 3H), 3.55 (s, 3H), 2.36 (td, *J* = 12.9, 3.6 Hz, 1H), 2.09 (m, 2H), 2.00 – 1.95 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.70, 164.18, 164.06, 163.73, 163.69, 163.55, 163.46, 163.43, 157.67, 157.50, 146.63, 146.18, 141.59, 141.00, 131.63, 131.58, 131.44, 131.40, 131.33, 131.30, 131.28, 130.38, 130.30, 130.23, 129.50, 129.28, 128.93, 128.56, 128.26, 128.22, 128.09, 127.99, 127.95, 127.91, 127.84, 127.81, 127.73, 127.61, 126.76, 126.75, 126.58, 126.50, 126.48, 126.22, 126.06, 125.80, 125.76, 111.99, 111.76, 110.97, 110.47, 90.88, 90.69, 70.51, 67.75, 67.15, 65.03, 65.00, 64.27, 60.39, 60.36, 53.32, 53.19, 29.03, 27.72. HRMS (ESI) calcd for $C_{43}H_{40}NO_{10}$ $[M+NH_4]^+$ 730.2652, found 730.2653. $[\alpha]_D^{35}$= + 0.26 (*c* 0.01, $CHCl_3$).

Synthesis of 3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl-2-(1-phenyl)vinyl)benzoate (2g)



2g

Compound **2g** was prepared from **1a** (434.5 mg, 1 mmol) according to **General procedure 2**. The crude product was purified by Flash column chromatography to afford **2a** (589.5 mg, 92 %, α: β = 1:2.2) as a colorless syrup, R_f = 0.53 (Hexane/EtOAc, 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 0.8 Hz, H), 7.82 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.54 (td, *J* = 7.5, 1.2 Hz, 1H), 7.50 (td, *J* = 7.5, 1.2 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.37 – 7.19 (m, 29H), 7.19 – 7.15 (m, 4H), 6.21 (d, *J* = 2.2 Hz, 1H), 5.72 (s, 1H), 5.68 (s, 1H), 5.54 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.23 (s, 1H), 5.15 (s, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 11.0 Hz, 1H), 4.61 – 4.56 (m, 3H), 4.54 – 4.49 (m, 3H), 4.48 (d, *J* = 4.5 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.40 (q, *J* = 11.6 Hz, 1H), 3.72 (dd, *J* = 10.9, 4.0 Hz, 1H), 3.69 (d, *J* = 1.9 Hz, 1H), 3.66 (dt, *J* = 6.3, 2.7 Hz, 1H), 3.64 – 3.60 (m, 2H), 3.57 (dd, *J* = 16.7, 7.5 Hz, 2H), 3.51 (dd, *J* = 10.8, 1.4 Hz, 1H), 3.45 (ddd, *J* = 9.1, 3.7, 2.0 Hz, 1H), 2.13 – 2.09 (m, 1H), 2.05 (ddd, *J* = 12.5, 4.6, 2.1 Hz, 1H), 1.76 – 1.70 (m, 1H), 1.52 (dd, *J* = 22.6, 10.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.21, 165.33, 149.15, 148.91, 143.12, 142.63, 140.53, 140.10, 138.61, 138.54, 138.30, 138.21, 138.15, 138.09, 132.14, 131.82, 131.46, 131.12, 130.90, 130.29, 130.21, 129.99, 128.49, 128.42, 128.38, 128.36, 128.30, 128.20, 128.00, 127.95, 127.92, 127.83, 127.77, 127.76, 127.72, 127.69, 127.65, 127.63, 127.58, 127.52, 126.86, 126.74, 114.37, 114.06, 93.13, 93.00, 78.86, 77.43, 75.91, 74.97, 74.82, 73.62, 73.51, 73.50, 71.71, 71.50, 68.66, 68.37, 34.83, 34.23. HRMS (ESI) calcd for $C_{42}H_{44}NO_6$ $[M+NH_4]^+$ 658.3163, found 658.3167. $[\alpha]_D^{35}$ = + 0.38 (*c* 0.01, $CHCl_3$).

Acceptors used in this study:

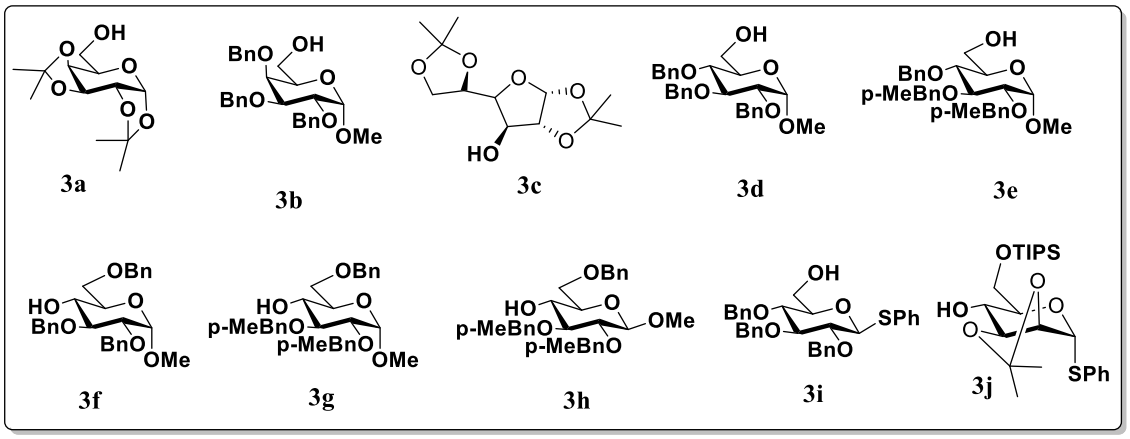
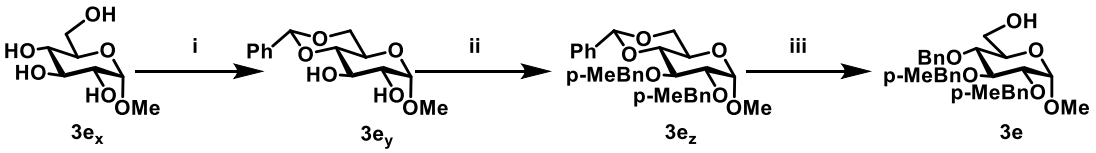


Figure 3.

3a-d,**3i**, were synthesized by following literature procedures.[1,2]

Synthesis of Methyl 2,3-di-*O*-para-methylbenzyl-4-*O*-benzyl-α-D-glucopyranoside (3e)



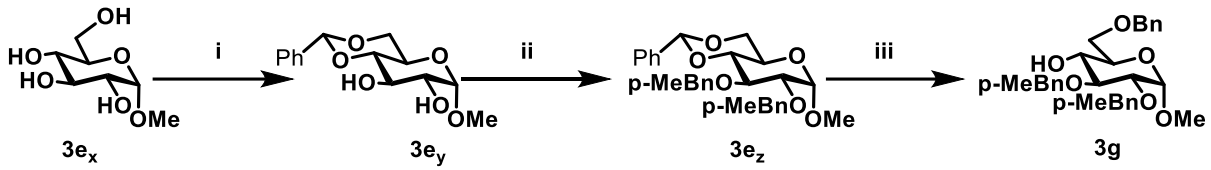
i) CSA, $PhCH(OMe)_2$, ACN ii) NaH, p-Me-BnBr, DMF iii) LAH, $AlCl_3$, Et_2O, DCM

A catalytic amount of camphorsulfonic acid (pH = 2) was added to a CH_3CN solution (100.0 mL) of methyl α-D-glucopyranoside (5.0 g, 25.7 mmol, **3e$_x$**) and $PhCH(OMe)_2$ (11.6 mL, 77.1 mmol). The resulting solution was stirred at RT for 48 h, then neutralized with TEA and concentrated *in vacuo*. The crude was washed with water, brine, dried over Na_2SO_4, concentrated in vacuo. The crude reaction mixture, dissolved in DMF, was treated with NaH, followed by Para methyl-benzyl bromide (p-Me-BnBr) at 0 °C. The resulting solution was stirred at room temperature for overnight. After completion of the reaction, MeOH was added to quench excess NaH. The reaction mixture was concentrated *in* vacuo*;* then the crude was diluted with H_2O and extracted with CH_2Cl_2 (3 x 50.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated *in vacuo*, and purified by flash column chromatography (hexane/AcOEt = 8:2) to get Methyl 2,3-di-paramethyl-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside **(3e$_z$)** as a white solid (8.2 g, 65 % yield over two steps).

Methyl 2,3-di-para-methyl-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (2g, 4.08 mmol, **3e$_z$**) was dissolved in CH_2Cl_2/Et_2O (1:1, 20 mL) and stirred at RT under a N_2 atm. After 10 min., $LiAlH_4$ (1.08 g, 28.56 mmol) was added at 0 °C and the mixture was heated to reflux. After an additional 10 min, $AlCl_3$ (2.72 g, 20.40 mmol) dissolved in Et_2O (1.0 mL) at 0 °C and the mixture was heated to reflux. After 1.5 h, the mixture was removed from the heat and excess $LiAlH_4$ was quenched with EtOAc. The mixture was diluted with Et_2O and washed once with water. The water phase was extracted once with Et_2O and the combined organic phases were washed three times with water, dried over Na_2SO_4 and concentrated. The crude was purified by flash column chromatography (Hexane/AcOEt = 8:2) to yield compound **3e** as a white solid (1.65 g, 82 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.29 (d, *J* = 6.0 Hz, 3H),

7.25 (dd, *J* = 7.9, 2.2 Hz, 4H), 7.14 (d, *J* = 7.4 Hz, 4H), 4.94 (d, *J* = 10.6 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.79 (d, *J* = 3.9 Hz, 1H), 4.77 (d, *J* = 5.4 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 2H), 4.51 (d, *J* = 3.5 Hz, 1H), 3.98 (t, *J* = 9.3 Hz, 1H), 3.77 – 3.72 (m, 1H), 3.67 (m, 1H), 3.65 – 3.61 (m, 1H), 3.50 (d, *J* = 9.4 Hz, 1H), 3.48 – 3.44 (m, 1H), 3.35 (s, 3H), 2.34 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.18, 137.69, 137.36, 135.71, 135.10, 129.18, 129.12, 128.50, 128.28, 128.20, 128.08, 127.89, 98.28, 81.83, 79.70, 77.37, 75.68, 75.04, 73.34, 70.64, 61.90, 55.21, 21.24. HRMS (ESI) calcd for $C_{30}H_{40}NO_6$ $[M+NH_4]^+$ 510.2856, found 510.2855. $[\alpha]_D^{35}$= + 0.16 (*c* 0.01, $CHCl_3$).

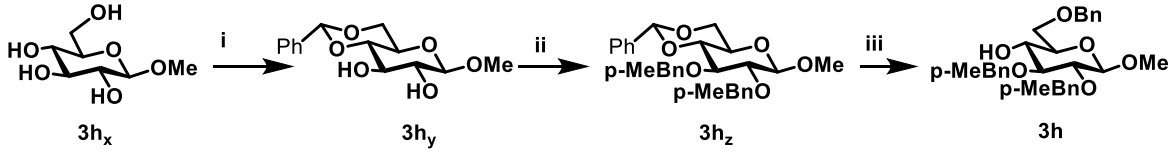
Synthesis of Methyl 2,3-di-*O*-para-methylbenzyl-6-*O*-benzyl-α-D-glucopyranoside (3g)



i) CSA, $PhCH(OMe)_2$, ACN ii) NaH,p-Me-BnBr, DMF iii) Et_3SiH, TFA, DCM

To a cooled solution (0 °C) of **3e$_z$** (2 g, 4.08 mmol) and Et_3SiH (3.26 mL, 20.4 mmol) in dry CH_2Cl_2 (40.0 mL), trifluoroacetic acid (1.56 mL, 20.4 mmol) was slowly added (15 min). The resulting solution was stirred at RT for three hours, and then the mixture was diluted with CH_2Cl_2 and neutralized with a saturated aqueous solution of $NaHCO_3$. The two phases were separated, the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude was purified by flash column chromatography (Hexane/AcOEt = 8:2) to yield compound **3g** as a white solid (1.53 g, 76 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 4H), 7.26 (t, *J* = 7.2 Hz, 5H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.96 (d, *J* = 11.3 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 11.3 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.60 – 4.55 (m, 2H), 4.53 (d, *J* = 12.2 Hz, 1H), 3.74 (t, *J* = 9.2 Hz, 1H), 3.70-3.67 (m, 1H), 3.66 – 3.63 (m, 2H), 3.56 (t, *J* = 9.3 Hz, 1H), 3.50 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.37 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.07, 137.73, 137.67, 135.78, 135.03, 129.35, 129.19, 128.38, 128.31, 128.23, 127.64, 98.28, 81.24, 79.33, 75.26, 73.57, 73.05, 70.48, 69.93, 69.42, 55.27, 21.25, 21.23. HRMS (ESI) calcd for $C_{30}H_{40}NO_6$ $[M+NH_4]^+$ 510.2856, found 510.2856. $[\alpha]_D^{35}$= + 0.30 (*c* 0.01, $CHCl_3$)

Synthesis of Methyl 2,3-di-*O*-para-methylbenzyl-6-*O*-benzyl-α-D-glucopyranoside (3h)

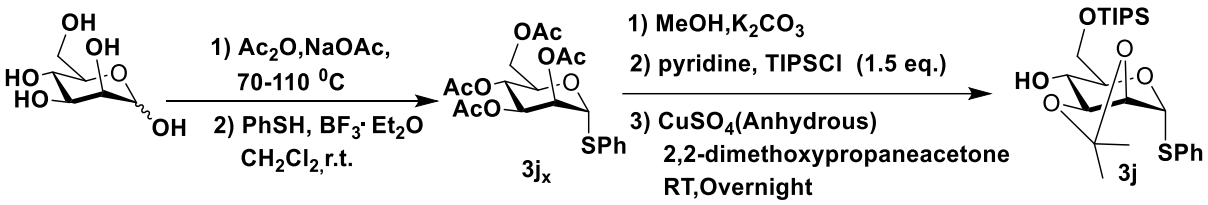


i) CSA, $PhCH(OMe)_2$, ACN ii) NaH,p-Me-BnBr, DMF iii) Et_3SiH, TFA, DCM

A catalytic amount of camphorsulfonic acid (pH = 2) was added to a CH_3CN solution (100.0 mL) of methyl β-D-glucopyranoside (5.0 g, 25.7 mmol, **3h$_x$**) and $PhCH(OMe)_2$ (11.6 mL, 77.1 mmol). The resulting solution was stirred at RT for 48 h, then neutralized with TEA and concentrated *in vacuo*. The crude was washed with water, brine, dried over Na_2SO_4, concentrated in vacuo. The crude reaction mixture, dissolved in DMF, was treated with NaH, followed by p-methyl-benzyl bromide (p-Me-BnBr) at 0 °C. The resulting solution was stirred at room temperature for overnight. After completion of the reaction, MeOH was added to

quench excess NaH. The reaction mixture was concentrated *in vacuo*; then the crude was diluted with H_2O and extracted with CH_2Cl_2 (3 x 50.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated *in vacuo,* and purified by flash column chromatography (hexane/AcOEt = 8:2) to get Methyl 2,3-di-paramethyl-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**3h$_z$)** as a white solid (7.85 g, 60 % over two steps). To a cooled solution (0 °C) of **3h$_z$** (2 g, 4.08 mmol) and Et_3SiH (3.26 mL, 20.4 mmol) in dry CH_2Cl_2 (40.0 mL), trifluoroacetic acid (1.56 mL, 20.4 mmol) was slowly added (15 min). The resulting solution was stirred at RT for three hours, and then the mixture was diluted with CH_2Cl_2 and neutralized with a saturated aqueous solution of $NaHCO_3$. The two phases were separated, the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude was purified by flash column chromatography (Hexane/AcOEt = 8:2) to yield compound **3h** as a white solid (1.46 g, 73 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 4.3 Hz, 4H), 7.30-7.24 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 4H), 4.90 – 4.85 (m, 2H, benzylic), 4.67 (d, *J* = 8.6 Hz, 1H), 4.65 (d, *J* = 9.3 Hz, 1H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.31 (d, *J* = 7.3 Hz, 1H), 3.77 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.68 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.57 (s, 3H), 3.54 (t, *J* = 9.0 Hz, 1H), 3.45 – 3.36 (m, 3H), 2.46 (s, 1H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.07, 137.73, 137.67, 135.78, 135.03, 129.35, 129.19, 128.38, 128.31, 128.23, 127.64, 98.28, 81.24, 79.33, 75.26, 73.57, 73.05, 70.48, 69.93, 69.42, 55.27, 21.25, 21.23. HRMS (ESI) calcd for $C_{30}H_{40}NO_6$ $[M+NH_4]^+$ 510.2856, found 510.2850. $[\alpha]_D^{35}$= + 0.1 (*c* 0.01, $CHCl_3$).

Phenyl 2,3-*O*-isopropylidene-6-*O*-triisopropylsilyl-1-thio-*α*-D-mannopyranoside (3j)



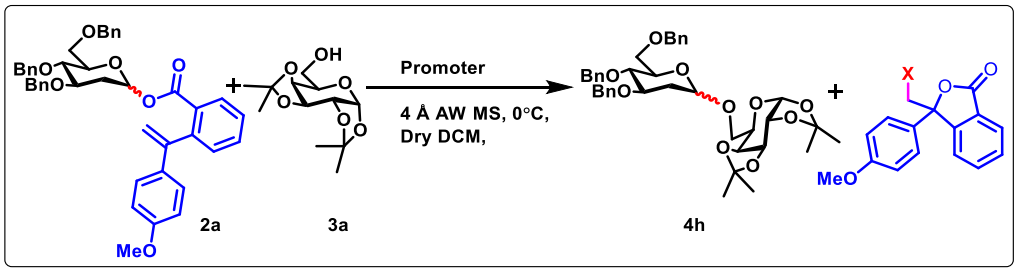
To a 100 mL flask was added Ac_2O (20 mL), followed by the addition of anhydrous NaOAc (5.0 g). The mixture was stirred at 70 ℃ for 30 min. After that D-mannose (5.0 g, 2.7 mmol) was added into the flask portion wise over 30 minutes. After vigorously stirred at 70 ℃ for another 30 min then the reaction mixture was heated at 110 ℃ for 6 h. After cooled down to room temperature, the mixture was poured into ice water (30 mL) and stirred vigorously for 1 hour. The resulting mixture was extracted by CH_2Cl_2 (40 mL × 3). The combined CH_2Cl_2 layer was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was dried under vacuum before dissolved by anhydrous CH_2Cl_2 (80 mL). To the solution was added thiophenol (3.8 g), followed by the addition of BF_3 •Et_2O (5.2 ml). The mixture was stirred at ambient temperature overnight and quenched by saturated $NaHCO_3$ solution (20 mL). The organic layer was washed with saturated Na_2CO_3 aqueous solution and brine, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated and purified by flash column chromatography to give compound **3j$_x$**.

To a solution of **3j$_x$** (4.7 g, 10.6 mmol) in methanol (20 mL) was added K_2CO_3 (100 mg). After stirred at room temperature for 3 h, the mixture was filtered and the filtrate was concentrated. The residue was dissolved in anhydrous pyridine (20 mL), followed by the addition of TIPSCl

(2.2 mL). The reaction mixture was stirred for 6 h after completion of reaction the mixture was diluted with CH_2Cl_2 (200 mL) and washed by 1M HCl solution, saturated $NaHCO_3$ solution and brine sequentially. The organic layer was dried over anhydrous Na_2SO_4 and concentrated and the residue was dissolved in anhydrous acetone (100 mL), followed by the addition of anhydrous CuSO4 (10.0 g) and 2,2-dimethoxypropane. The mixture was stirred overnight and then filtered. The filtrate was concentrated and purified by flash column chromatography to give **3j** (3.5 g, 7.56 mmol, 70%) as colorless syrup. *Rf* = 0.6 (Hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.32 – 7.24 (m, 3H), 5.75 (s, 1H), 4.33 (dd, *J* = 5.8, 0.6 Hz, 1H), 4.21 – 4.17 (m, 1H), 4.03 (ddd, *J* = 10.1, 5.8, 4.7 Hz, 1H), 3.92 – 3.85 (m, 2H), 3.82 (dd, *J* = 10.3, 6.1 Hz, 1H), 3.32 (d, *J* = 1.5 Hz, 1H), 1.54 (s, 3H), 1.37 (s, 3H), 1.09 – 1.02 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.32, 130.82, 127.96, 126.55, 108.76, 82.79, 77.11, 74.93, 71.46, 68.62, 63.99, 27.02, 25.36, 16.87, 16.85, 10.77. HRMS (ESI) calcd for $C_{24}H_{40}NaO_5SSi$ $[M+NH_4]^+$ 491.2263, found 491.2273. $[\alpha]_D^{35}$= + 0.68 (*c* 0.025, $CHCl_3$).

Optimization study.

For optimization of the reaction conditions, a solution of glycosyl donor **2a** (0.06 mmol) and acceptor **3a** (0.072 mmol) in dry CH_2Cl_2 (0.03 M) was stirred at room temperature for 60 min in the presence of activated acid washed (AW) 4Å MS (180 mg) under Ar atmosphere. Then the vessel was chilled to 0 °C followed by the addition of promoters at this temperature. In case of triflamide ($(CF_3SO_2)_2NH$), upon loading of 30 mol%, reaction was completed within 5 min, yielding 83 % with ratio 1.7: 1 (α: β) (**Table 1. Entry 1**). Upon using NIS (1.1 equiv) and TMSOTf (30 mol%), the reaction was completed within 20 min, giving 79% yield (1.7: 1/α: β) (**Table 1. Entry 2**). Then, we have taken triflic acid as promoter (30 mol%) which led to 85% yield with a ratio of 5.4: 1 (α: β) anomers (**Table 1. Entry 3**). There was no reaction when we have taken 10 mol% of triflic acid and attempted this reaction at 0 °C even after 24h, whereas with 15 mol% of catalyst loading, product formed in 64 % yield with an isomeric ratio 2.7: 1 (α: β) based on recovery of starting material after 5h (**Table 1. Entry 6**). With 20 mol% of triflic acid, the reaction led to 80 % of product with an anomeric ratio of 3.6 :1 (α: β) (**Table 1. Entry 7**). Then we raised the catalyst loading to 25 mol%, which led to reaction completion within 15 min yielding 81 % of product with ratio of anomers 4.5 :1 (α: β) (**Table 1. Entry 8**). To check reactivity our PMPVB donor, we did another experiment where **2g** donor were used instead of **2a** which resulted 18 % yield with anomeric ratio 2.2 :1 (α :β) after 12 h (**Table 1. Entry 9**).



Entry	Promoter	Amount of catalyst (mole %)	Time	Yield (%)	α: β
1	$(CF_3SO_2)_2NH$	30	5 min	83	1.7: 1
2	NIS (1.1 equiv.), TMSOTf	30	20 min	79	1.7: 1
3	TfOH	30	5 min	85	5.4: 1
4	TfOH	5	24 h	No reaction	--
5	TfOH	10	24 h	No reaction	--
6	TfOH	15	5 h	64*	2.7: 1
7	TfOH	20	30 min	80	3.6: 1
8	TfOH	25	15 min	81	4.5: 1
9	TfOH	30	12 h	18**	2.2 :1

* Based on recovery of starting material. ** **2g** donor were used.

Table 1. Optimization study

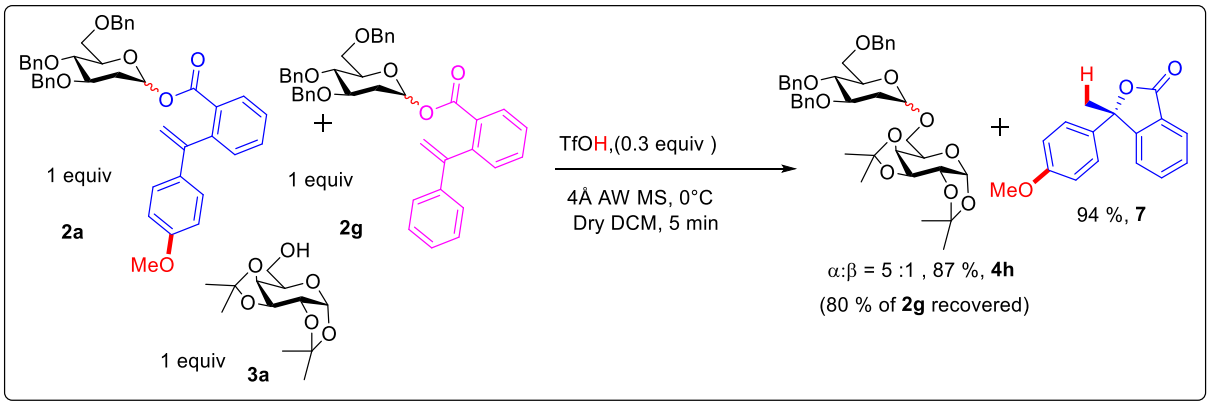
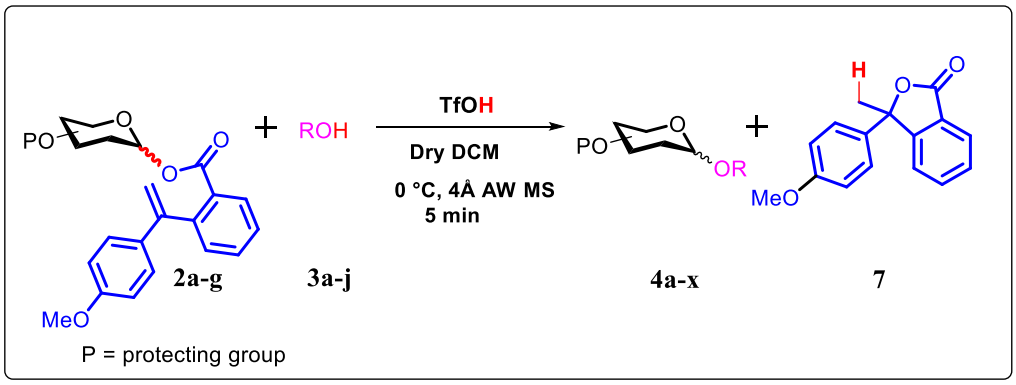


Figure 4: **Comparative study.**

A solution of glycosyl donor **2a** (40.2 mg, 0.06 mmol) and **2g** (38.5 mg, 0.06 mmol), and acceptor **3f** (15.6 mg, 0.06 mmol) in dry CH_2Cl_2 (0.03 M) was stirred at room temperature for 60 min in the presence of activated acid washed (AW) 4Å MS (250 mg) under Ar atmosphere. Then the vessel was chilled to 0 °C, to which TfOH (1.6 µl, 30 mol%) were added. The reaction mixture was stirred for 5 min at 0 °C. Then, Et_3N was added to quench the reaction. The crude reaction mixture was worked up with water, washed with brine, dried by Na_2SO_4, concentrated in rotavapor. The resulting crude reaction mixture was purified through Flash column chromatography to afford the glycosylated products **4h** (35.3 mg, 87 %, α: β = 5:1), **2g** (30.8 mg, 80 % recovered), and cyclized adduct **7** (14.3 mg, 94 %). Spectral data for **7,** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.66 (td, *J* = 7.6, 1.0 Hz, 1H), 7.52 (td, *J* = 7.6, 0.7

Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.31 (m, 2H), 6.89 – 6.84 (m, 2H), 3.79 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.03, 159.54, 154.39, 134.28, 132.56, 129.06, 126.68, 125.85, 125.19, 122.05, 113.96, 87.62, 55.32, 27.19. HRMS (ESI) calcd for $C_{16}H_{15}O_3$ $[M+H]^+$ 255.1021, found 255.1025. $[\alpha]_D^{35}$= - 0.60 (*c* 0.01, $CHCl_3$).

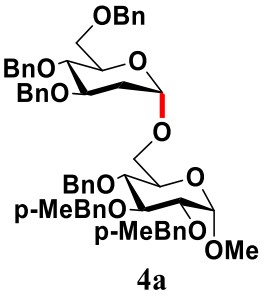


Scheme 4: General scheme for *O*-glycosylation

General procedure 3

A solution of glycosyl donor **2a-g** (1 equiv.) and acceptor **3a-j** (1.2 equiv.) in dry CH_2Cl_2 (0.03 M) was stirred at room temperature for 60 min in the presence of activated acid washed (AW) 4 Å MS (3.0 g/mmol) under Ar atmosphere. Then the vessel was chilled to 0 °C, to which triflic acid (30 mol%) were added. The reaction mixture was stirred for 5 min and TLC were checked. After completion of the reaction within 5 min, the temperature gradually rises to room temperature. Then Et_3N was added to quench the reaction. The crude reaction mixture was worked up with water, washed with brine, dried by Na_2SO_4, concentrated in rotavapor. The resulting crude reaction mixture was purified through Flash column chromatography to afford the glycosylated product.

Synthesis of Methyl 2,3-di–para-methyl-*O*-benzyl-4-*O*-benzyl -6-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (4a)

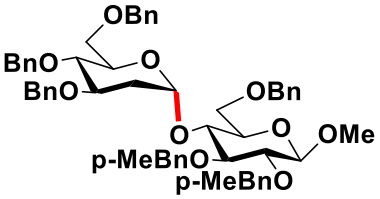


4a

Glycosylation of **2a** (40.2 mg, 0.06 mmol) with **3e** (35.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4a** (49 mg, 90 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.55 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.2 Hz, 3H), 7.29 -7.20 (m, 19H), 7.13 (dd, *J* = 10.9, 8.0 Hz, 6H), 4.99 (d, *J* = 2.2 Hz, 1H), 4.93 (t, *J* = 11.8 Hz, 2H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.75 (dd, *J* = 10.9, 8.8 Hz, 2H), 4.64 (dd, *J* = 11.7, 8.2 Hz, 2H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.56 (d, *J* = 7.4 Hz, 1H), 4.56 - 4.51 (m, 2H), 4.47 (d, *J* = 11.0 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 3.96 (t, *J* = 9.1 Hz, 1H), 3.94 – 3.90 (m, 1H), 3.80 (dd, *J* = 11.3, 4.3 Hz, 1H), 3.72 (dd, *J*

= 9.9, 3.3 Hz, 1H), 3.66 (d, *J* = 9.7 Hz, 1H), 3.59 (t, *J* = 9.2 Hz, 2H), 3.55 (d, *J* = 11.2 Hz, 1H), 3.51 - 3.44 (m, 3H), 3.33 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 2.29 (dd, *J* = 12.9, 4.9 Hz, 1H), 1.68 (td, *J* = 12.7, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.71, 137.58, 137.39, 137.13, 136.59, 136.29, 134.67, 134.15, 128.12, 128.05, 127.34, 127.29, 127.26, 127.20, 127.17, 127.15, 126.84, 126.75, 126.71, 126.53, 126.47, 126.41, 97.00, 96.75, 81.06, 78.79, 77.14, 76.73, 76.23, 74.62, 73.81, 73.78, 72.37, 72.13, 70.69, 69.86, 68.71, 67.70, 64.69, 54.06, 34.26, 20.16. HRMS (ESI) calcd for $C_{57}H_{68}NO_{10}$ $[M+NH_4]^+$ 926.4843, found 926.4842. $[\alpha]_D^{35}$= + 0.30 (*c* 0.01, $CHCl_3$).

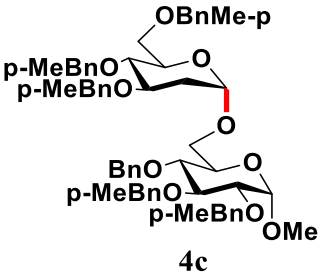
Synthesis of Methyl 2,3-di–para-methyl-*O*-benzyl-6-*O*-benzyl -4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-β-D-glucopyranoside (4b)



4b

Glycosylation of **2a** (40.2 mg, 0.06 mmol) with **3h** (35.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4b** (45.8 mg, 84 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.6 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 18H), 7.20 (t, *J* = 8.4 Hz, 3H), 7.16 (d, *J* = 6.9 Hz, 2H), 7.13 – 7.09 (m, 5H), 5.40 (d, *J* = 2.6 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.88 – 4.81 (m, 2H), 4.61 (d, *J* = 10.7 Hz, 1H), 4.56 (d, *J* = 12.4 Hz, 2H), 4.54 – 4.50 (m, 3H), 4.48 (dd, *J* = 11.4, 6.9 Hz, 2H), 4.38 (d, *J* = 12.2 Hz, 1H), 4.29 (d, *J* = 7.7 Hz, 1H), 3.84 – 3.79 (m, 1H), 3.77 (d, *J* = 10.3 Hz, 1H), 3.67 (d, *J* = 9.6 Hz, 1H), 3.61 (dd, *J* = 10.2, 5.8 Hz, 3H), 3.57 (s, 3H), 3.56 – 3.49 (m, 2H), 3.43 (d, *J* = 10.2 Hz, 2H), 3.41 – 3.37 (m, 1H), 2.32 (s, 3H), 2.32 (s, 3H), 2.04 (dd, *J* = 12.8, 4.5 Hz, 1H), 1.53 (d, *J* = 3.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.77, 137.66, 137.51, 137.26, 136.32, 136.20, 134.48, 134.46, 128.03, 127.32, 127.29, 127.26, 127.24, 126.92, 126.85, 126.58, 126.54, 126.51, 126.42, 103.58, 98.09, 83.79, 81.26, 77.20, 74.95, 74.12, 73.79, 73.76, 73.43, 72.50, 72.40, 70.85, 70.64, 68.99, 67.83, 55.96, 34.67, 20.13, 20.11. HRMS (ESI) calcd for $C_{57}H_{68}NO_{10}$ $[M+NH_4]^+$ 926.4843, found 926.4843. $[\alpha]_D^{35}$= + 0.4 (*c* 0.01, $CHCl_3$).

Synthesis of Methyl 2,3-di –para-methyl-*O*-benzyl-4-*O*-benzyl -6-*O*-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (4c)

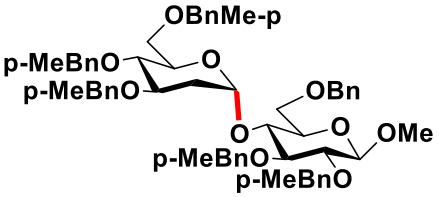


4c

Glycosylation of **2b** (42.8 mg, 0.06mmol) with **acceptor 3e** (35.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4c** (50.2 mg, 88 %, α only) as a colorless syrup. The crude

product was purified through flash column chromatography, R_f = 0.5.6 (Hexane: EtOAc = 4: 1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 11H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.12 (dd, *J* = 11.1, 8.0 Hz, 4H), 7.10 – 7.05 (m, 6H), 7.01 (d, *J* = 7.7 Hz, 2H), 4.98 (d, *J* = 2.2 Hz, 1H), 4.94 (d, *J* = 10.5 Hz, 1H), 4.91 (d, *J* = 11.1 Hz, 1H), 4.80 (d, *J* = 10.7 Hz, 1H), 4.76 (d, *J* = 5.1 Hz, 1H), 4.74 (d, *J* = 3.4 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.58 (q, *J* = 11.6 Hz, 2H), 4.53 (dd, *J* = 11.1, 7.9 Hz, 3H), 4.39 (d, *J* = 10.7 Hz, 1H), 4.34 (d, *J* = 12.0 Hz, 1H), 3.96 (t, *J* = 9.2 Hz, 1H), 3.92 – 3.87 (m, 1H), 3.78 (dd, *J* = 11.3, 4.4 Hz, 1H), 3.71 (dd, *J* = 9.9, 3.5 Hz, 1H), 3.63 (d, *J* = 9.7 Hz, 1H), 3.58 (dd, *J* = 10.7, 3.4 Hz, 1H), 3.57 – 3.53 (m, 2H), 3.48 (dd, *J* = 9.9, 3.7 Hz, 1H), 3.45 (d, *J* = 9.7 Hz, 2H), 3.32 (s, 3H), 2.34 (s, 3H), 2.33 (s, 6H), 2.30 (s, 3H), 2.29 (s, 3H), 2.26 (dd, *J* = 12.9, 4.9 Hz, 1H), 1.65 (td, *J* = 12.8, 3.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.39, 136.56, 136.25, 136.18, 136.14, 136.00, 134.73, 134.71, 134.61, 134.18, 134.08, 128.11, 128.04, 127.99, 127.94, 127.83, 127.29, 127.17, 127.14, 127.04, 126.90, 126.82, 126.49, 96.96, 96.76, 81.07, 78.87, 77.00, 76.80, 74.61, 73.83, 73.62, 72.21, 72.14, 70.60, 69.88, 68.75, 67.44, 64.66, 54.01, 34.31, 20.15, 20.11, 20.08. HRMS (ESI) calcd for $C_{60}H_{74}NO_{10}$ $[M+NH_4]^+$ 968.5313, found 968.5313. $[\alpha]_D^{35}$= + 0.28 (*c* 0.01, $CHCl_3$).

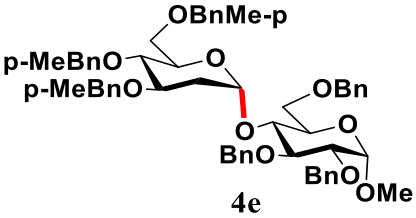
Synthesis of Methyl 2,3-di –para-methyl-*O*-benzyl-6-*O*-benzyl -4-*O*-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-β-D-glucopyranoside (4d)



4d

Glycosylation of **2b** (42.8 mg, 0.06 mmol) with **acceptor 3h** (35.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4d** (48.5 mg, 85 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.59 (Hexane/EtOAc = 4:1, v/v) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (dt, *J* = 12.7, 6.2 Hz, 4H), 7.25 (d, *J* = 13.2 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 3H), 7.18 (t, *J* = 7.0 Hz, 4H), 7.13 – 7.07 (m, 11H), 7.03 (d, *J* = 7.6 Hz, 2H), 5.38 (d, *J* = 1.3 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.85 (d, *J* = 10.7 Hz, 1H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.61 (d, *J* = 10.7 Hz, 1H), 4.54 (d, *J* = 11.7 Hz, 2H), 4.51 (dd, *J* = 10.5, 3.8 Hz, 3H), 4.49 – 4.46 (m, 1H), 4.38 (d, *J* = 10.5 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.29 (d, *J* = 7.6 Hz, 1H), 3.82 – 3.75 (m, 2H), 3.65 (d, *J* = 9.6 Hz, 1H), 3.62 – 3.58 (m, 3H), 3.57 (s, 3H), 3.50 (t, *J* = 8.2 Hz, 2H), 3.41 (dd, *J* = 11.9, 6.8 Hz, 2H), 3.38 (d, *J* = 9.2 Hz, 1H), 2.32 (s, 9H), 2.31 (s, 3H), 2.30 (s, 3H), 2.02 (dd, *J* = 12.9, 4.3 Hz, 1H), 1.54 (td, *J* = 12.9, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.46, 136.32, 136.21, 136.19, 136.16, 136.13, 134.72, 134.57, 134.41, 134.37, 134.07, 128.02, 127.99, 127.96, 127.89, 127.26, 127.23, 127.08, 127.07, 126.66, 126.58, 126.50, 126.40, 103.50, 98.14, 83.75, 81.21, 76.93, 76.06, 74.95, 74.14, 73.65, 73.43, 72.34, 72.30, 70.79, 70.59, 68.93, 67.37, 55.99, 34.70, 20.15, 20.13, 20.12. HRMS (ESI) calcd for $C_{60}H_{74}NO_{10}$ $[M+NH_4]^+$ 968.5313, found 968.5312. $[\alpha]_D^{35}$= + 0.48 (*c* 0.01, $CHCl_3$).

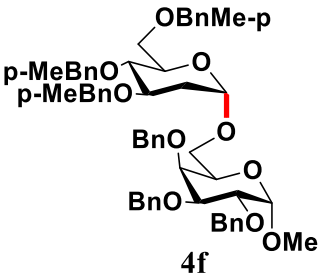
Synthesis of Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (4e)



4e

Glycosylation of **2b** (42.8 mg, 0.06 mmol) with **3f** (33.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4e** (47.11 mg, 85 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.6 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 13.4, 6.1 Hz, 5H), 7.29-7.24 (m, 9H), 7.22 – 7.20 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.12 – 7.05 (m, 6H), 7.02 (d, *J* = 7.7 Hz, 2H), 5.40 (d, *J* = 2.3 Hz, 1H), 5.01 (d, *J* = 11.1 Hz, 1H), 4.78 (d, *J* = 10.6 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.61 (dd, *J* = 9.6, 2.7 Hz, 3H), 4.54 – 4.46 (m, 4H), 4.43 (d, *J* = 12.1 Hz, 1H), 4.38 (d, *J* = 10.6 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 3.86 (t, *J* = 9.1 Hz, 1H), 3.84 – 3.79 (m, 1H), 3.71 – 3.61 (m, 5H), 3.57 (dd, *J* = 10.4, 3.0 Hz, 1H), 3.53 – 3.48 (m, 2H), 3.38 (s, 3H), 3.37 (s, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H), 2.05 (dd, *J* = 12.8, 4.5 Hz, 1H), 1.57 – 1.52 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.57, 138.34, 138.02, 137.25, 137.19, 137.18, 135.70, 135.60, 135.01, 129.04, 128.98, 128.91, 128.46, 128.42, 128.26, 128.14, 128.14, 128.07, 127.94, 127.73, 127.57, 127.51, 127.43, 127.41, 99.50, 97.75, 82.14, 80.09, 77.92, 77.11, 76.25, 75.45, 74.66, 73.31, 73.25, 73.21, 71.81, 71.67, 69.76, 69.46, 68.34, 55.23, 35.88, 21.20, 21.17, 21.16. HRMS (ESI) calcd for $C_{58}H_{70}NO_{10}$ $[M+NH_4]^+$ 940.5000, found 940.4990. $[\alpha]_D^{35}$= + 0.52 (*c* 0.015, $CHCl_3$).

Synthesis of Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-α-D-galactopyranoside (4f)

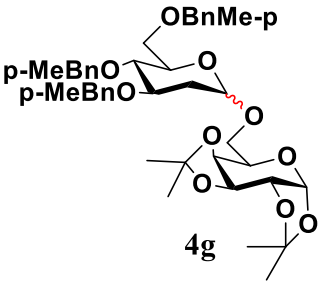


4f

Glycosylation of **2b** (42.8 mg, 0.06 mmol) with **3b** (33.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4f** (48.8 mg, 88 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.5 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.34 (m, 4H), 7.33 – 7.24 (m, 9H), 7.22 (d, *J* = 7.6 Hz, 4H), 7.11 (t, *J* = 7.7 Hz, 4H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 4.95 – 4.92 (m, 1H), 4.89 (d, *J* = 11.7 Hz, 1H), 4.85 – 4.81 (m, 1H), 4.79 (d, *J* = 10.5 Hz, 1H), 4.76 (d, *J* = 11.7 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.64 (d, *J* = 3.7 Hz, 2H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.58 (t, *J* = 5.6 Hz, 3H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 10.4 Hz, 1H), 4.02 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.92 (dd, *J* = 10.0, 2.4 Hz, 1H), 3.86 – 3.80 (m, 2H), 3.76 – 3.70 (m, 2H), 3.63 (d, *J* = 9.9 Hz, 1H), 3.61 – 3.53 (m, 3H), 3.34 – 3.30 (m, 1H), 3.29 (s, 3H), 2.32 (s, 3H), 2.31 (s, 6H), 2.01 (dd, *J* = 12.7, 4.7 Hz, 1H), 1.61 – 1.56 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.83, 138.45, 137.39, 137.35, 137.29, 135.63, 135.41, 134.91, 129.08, 129.06, 129.01, 128.54, 128.46, 128.39, 128.34, 128.23, 128.15, 127.77, 127.76,

127.59, 127.53, 98.62, 97.24, 79.25, 77.81, 77.14, 76.53, 74.88, 74.57, 74.54, 73.61, 73.53, 73.32, 71.70, 70.70, 68.62, 68.15, 65.51, 55.31, 55.24, 35.40, 21.25, 21.23. HRMS (ESI) calcd for $C_{58}H_{70}NO_{10}$ $[M+NH_4]^+$ 940.5000, found 940.4993. $[\alpha]_D^{35}$= + 0.40 (*c* 0.01, $CHCl_3$).

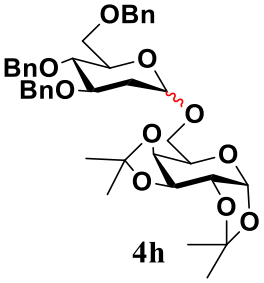
Synthesis of 1,2;3,4-di-*O*-isopropylidene-6-*O*-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-D-glucopyranosyl)-α-D-galactopyranose (4g)



4g

Glycosylation of **2b** (42.8 mg, 0.06 mmol) with **3a** (18.7 mg, 0.072 mmol) according to **General procedure 3** afforded **4g** (37.5 mg, 87 %, α: β = 6:1) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.54 (Hexane/EtOAc = 4:1, v/v. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.7 Hz, 4H), 7.12 (t, *J* = 7.4 Hz, 4H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 5.51 (d, *J* = 4.9 Hz, 1H), 5.00 (d, *J* = 2.3 Hz, 1H), 4.81 (d, *J* = 10.6 Hz, 1H), 4.60 (q, *J* = 12.4 Hz, 4H), 4.43 (t, *J* = 11.5 Hz, 2H), 4.30 (dd, *J* = 4.6, 1.9 Hz, 1H), 4.21 (d, *J* = 7.9 Hz, 1H), 3.98 – 3.91 (m, 2H), 3.79 – 3.68 (m, 3H), 3.65 (dd, *J* = 10.3, 7.1 Hz, 1H), 3.61 (d, *J* = 9.4 Hz, 2H), 2.33 (s, 3H), 2.32 (s, 3H), 2.32 (s, 3H), 2.30 – 2.27 (m, 1H), 1.73 – 1.67 (m, 1H), 1.51 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.27, 137.21, 137.14, 135.78, 135.55, 135.07, 129.03, 129.02, 128.95, 128.15, 128.12, 127.73, 109.28, 108.55, 97.29, 96.32, 78.02, 77.43, 74.81, 73.32, 71.75, 70.97, 70.94, 70.67, 70.63, 68.36, 65.61, 65.28, 35.45, 26.17, 26.00, 24.93, 24.57, 21.18. HRMS (ESI) calcd for $C_{42}H_{58}NO_{10}$ $[M+NH_4]^+$ 736.4061, found 736.4069. $[\alpha]_D^{35}$= + 0.30 (*c* 0.01, $CHCl_3$).

Synthesis of 1,2;3,4-di-*O*-isopropylidene-6-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-α-D-galactopyranose (4h)

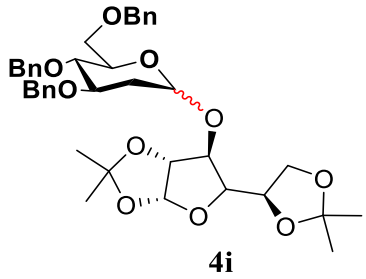


4h

Glycosylation of **2a** (40.2 mg, 0.06 mmol) with **3a** (18.7 mg, 0.072 mmol) according to **General procedure 3** afforded **4h** (34.4 mg, 85 %, α: β = 5:1) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.55 (Hexane/EtOAc = 4:1, v/v). For α anomer, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 10H), 7.28 – 7.24 (m, 3H), 7.18 (d, *J* = 7.4 Hz, 2H), 5.51 (d, *J* = 4.9 Hz, 1H), 5.02 (d, *J* = 2.4 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.69 – 4.62 (m, 3H), 4.59 (dd, *J* = 11.7, 3.5 Hz, 1H), 4.56 – 4.47 (m, 2H), 4.32 – 4.28 (m, 1H), 4.22 (d, *J* = 7.9 Hz, 1H), 4.03 – 3.97 (m, 1H), 3.95 (dd, *J* = 11.7, 4.9 Hz, 1H), 3.79 (dd, *J* = 7.3, 3.4 Hz, 2H), 3.74 – 3.71 (m, 1H), 3.66 (dd, *J* = 11.6, 5.2 Hz, 3H), 2.32 (dd, *J* =

13.0, 4.9 Hz, 1H), 1.72 (td, *J* = 13.0, 3.3 Hz, 1H), 1.51 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.78, 137.59, 137.19, 127.33, 127.31, 127.28, 126.92, 126.88, 126.59, 126.55, 126.53, 126.47, 108.29, 107.53, 96.26, 95.33, 77.25, 76.55, 73.92, 72.46, 70.77, 69.99, 69.66, 67.80, 64.71, 64.40, 34.43, 25.13, 24.98, 23.91, 23.57. ^{1}HRMS (ESI) calcd for $C_{39}H_{52}NO_{10}$ $[M+NH_4]^+$ 694.3591, found 694.3587. $[\alpha]_D^{35}$= + 0.36 (*c* 0.01, $CHCl_3$).

Synthesis of 1,2;4,6-di-*O*-isopropylidene-3-*O*-(2,3,4-tri-*O*-benzyl-D-glucopyranosyl)-α-D- glucofuranose (4i)

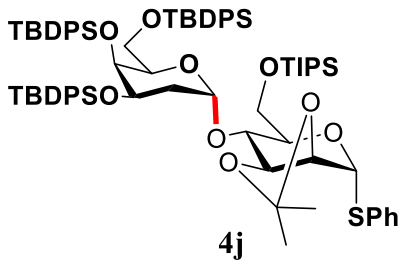


4i

Glycosylation of **2a** (40.2 mg, 0.06 mmol) with **3c** (18.7 mg, 0.072 mmol) according to **General procedure 3** afforded **4i** (33.3 mg, 82 %, α: β = 7:1) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.57 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 12.1, 7.5 Hz, 10H), 7.27 (dd, *J* = 13.7, 7.8 Hz, 3H), 7.18 (d, *J* = 6.7 Hz, 2H), 5.82 (d, *J* = 3.3 Hz, 1H), 5.24 (d, *J* = 2.3 Hz, 1H), 4.89 (d, *J* = 10.6 Hz, 1H), 4.64 (dd, *J* = 12.4, 5.1 Hz, 4H), 4.52 (dd, *J* = 11.1, 8.7 Hz, 2H), 4.24 (d, *J* = 2.1 Hz, 1H), 4.14 (dd, *J* = 13.9, 5.7 Hz, 1H), 4.11 – 4.08 (m, 1H), 4.06 (dd, *J* = 8.4, 2.2 Hz, 1H), 3.97 (dd, *J* = 8.4, 5.8 Hz, 1H), 3.95 – 3.91 (m, 1H), 3.81 – 3.76 (m, 2H), 3.73 (d, *J* = 8.9 Hz, 1H), 3.60 (t, *J* = 9.2 Hz, 1H), 2.27 (dd, *J* = 12.8, 4.7 Hz, 1H), 1.75 – 1.69 (m, 1H), 1.47 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.49, 138.25, 138.04, 128.43, 128.42, 128.38, 128.06, 127.92, 127.76, 127.68, 127.66, 111.85, 109.16, 105.26, 98.70, 83.74, 81.33, 80.25, 78.12, 77.19, 75.17, 73.57, 72.48, 71.86, 71.72, 68.94, 67.71, 35.20, 26.83, 26.12, 25.45. HRMS (ESI) calcd for $C_{39}H_{52}NO_{10}$ $[M+NH_4]^+$ 694.3591, found 694.3589.

$[\alpha]_D^{35}$= + 0.12 (*c* 0.01, $CHCl_3$).

Phenyl 2,3-*O*-isopropylidene-6-*O*-triisopropylsilyl-4-(3,4,6-tri-*O*-tertiary-butyldiphenylsilyl-2-deoxy-α-D-galactopyranosyl)-*α*-D-thiomannopyranoside (4j)

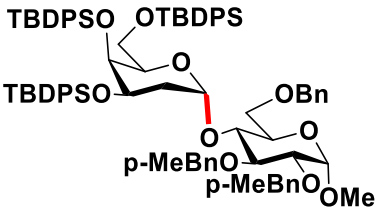


4j

Glycosylation of **2e** (55.8 mg, 0.05 mmol) with **3j** (27.9 mg, 0.06 mmol) according to **General procedure 3** afforded **4j** (59.9 mg, 90 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.8 (Hexane/EtOAc = 7:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.47 (m, 7H),

7.42 – 7.29 (m, 11H), 7.28 – 7.22 (m, 5H), 7.19 (dd, *J* = 13.5, 6.4 Hz, 4H), 7.15 (t, *J* = 7.5 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 2H), 5.69 (s, 1H), 5.43 (bs, 1H), 4.26 (d, *J* = 5.4 Hz, 1H), 3.98 – 3.94 (m, 1H), 3.93 (d, *J* = 8.6 Hz, 1H), 3.87-3.82 (m, 2H), 3.72 (d, *J* = 10.0 Hz, 1H), 3.68 – 3.56 (m, 3H), 3.45 (d, *J* = 6.5 Hz, 1H), 2.93 (d, *J* = 9.3 Hz, 1H), 2.34 (dt, *J* = 11.7, 9.3 Hz, 1H), 1.42 (s, 3H), 1.32 (s, 3H), 1.29-1.26 (m, 1H), 1.03 (s, 9H), 0.99 (s, 9H), 0.89 – 0.81 (m, 30H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.53, 136.22, 136.09, 135.80, 135.78, 135.47, 134.53, 133.82, 133.79, 133.71, 133.51, 133.44, 132.34, 131.47, 129.74, 129.55, 129.50, 129.26, 129.24, 129.04, 128.78, 127.69, 127.56, 127.51, 127.42, 127.19, 127.04, 109.39, 95.87, 84.33, 78.64, 76.46, 74.83, 72.61, 71.92, 71.52, 69.55, 65.48, 64.03, 33.54, 27.92, 27.20, 26.75, 26.55, 19.99, 18.85, 18.77, 17.90, 17.86, 11.70. HRMS (ESI) calcd for $C_{78}H_{108}NO_9SSi_4$ $[M+NH4]^+$ 1346.6822, found 1346.6822. $[\alpha]_D^{35}$= + 0.84 (*c* 0.025, $CHCl_3$).

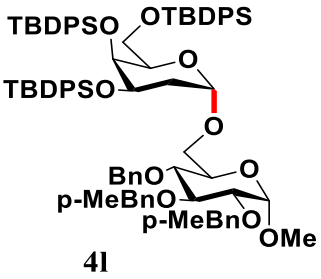
Synthesis of Methyl 2,3-di-para-methyl-*O*-benzyl-6-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-tertiary-butyldiphenylsilyl-2-deoxy-α-D-galactopyranosyl)-α-D-glucopyranoside (4k)



4k

Glycosylation of **2e** (55.8 mg, 0.05 mmol) with **3g** (29.6 mg, 0.06 mmol) according to **General procedure 3** afforded **4k** (56.9 mg, 84 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.75 (Hexane/EtOAc = 7:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.44 (m, 9H), 7.43 – 7.37 (m, 4H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.24 – 7.17 (m, 13H), 7.09 – 7.06 (m, 4H), 6.94 (t, *J* = 7.4 Hz, 2H), 6.89 (t, *J* = 7.2 Hz, 2H), 6.86 – 6.82 (m, 1H), 5.39 (d, *J* = 2.5 Hz, 1H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 3.3 Hz, 1H), 4.34 (d, *J* = 10.0 Hz, 1H), 4.32 (d, *J* = 8.3 Hz, 1H), 4.15 (d, *J* = 12.1 Hz, 1H), 3.68 (d, *J* = 10.9 Hz, 1H), 3.60 – 3.54 (m, 3H), 3.45 (s, 3H), 3.40-3.32 (m, 3H), 3.31 (d, *J* = 9.5 Hz, 1H), 3.17 (dd, *J* = 10.1, 8.1 Hz, 1H), 3.01 (d, *J* = 6.9 Hz, 1H), 2.75 (d, *J* = 9.3 Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H), 2.22 (td, *J* = 12.2, 3.3 Hz, 1H), 1.32 – 1.28 (m, 1H), 1.03 (s, 9H), 0.98 (s, 9H), 0.86 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.10, 137.65, 137.25, 136.63, 136.16, 136.06, 135.92, 135.63, 135.61, 134.96, 133.87, 133.81, 133.53, 133.37, 132.44, 129.77, 129.59, 129.29, 129.26, 129.13, 129.08, 128.99, 128.37, 127.98, 127.96, 127.82, 127.59, 127.55, 127.46, 127.35, 127.04, 97.71, 82.22, 79.56, 74.96, 74.35, 73.20, 73.07, 72.59, 72.38, 69.82, 69.70, 69.62, 65.49, 55.03, 33.78, 27.23, 27.18, 26.91, 21.29, 21.21, 20.02, 18.85, 18.82. HRMS (ESI) calcd for $C_{84}H_{104}NO_{10}Si_3$ $[M+NH4]^+$ 1370.6968, found 1370.6963. $[\alpha]_D^{35}$= + 1.14 (*c* 0.04, $CHCl_3$).

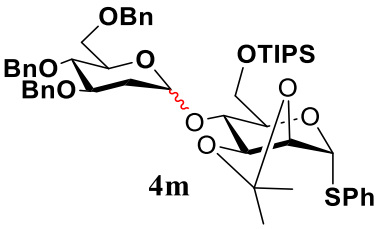
Synthesis of Methyl 2,3-di-para-methyl-*O*-benzyl-4-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-tertiary-butyldiphenylsilyl-2-deoxy-α-D-galactopyranosyl)-α-D-glucopyranoside (4l)



4l

Glycosylation of **2e** (55.8 mg, 0.05 mmol) with **3e** (29.6 mg, 0.06 mmol) according to **General procedure 3** afforded **4l** (61.5 mg, 91 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.7 (Hexane/EtOAc = 7:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 4H), 7.46 (d, *J* = 6.5 Hz, 4H), 7.42 – 7.34 (m, 5H), 7.32 – 7.25 (m, 9H), 7.23-7.18 (m, 7H), 7.17 – 7.06 (m, 12H), 7.02 (t, *J* = 7.4 Hz, 2H), 4.98 (d, *J* = 2.3 Hz, 1H), 4.94 (d, *J* = 10.7 Hz, 1H), 4.74 (merge d, 2H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.61 (d, *J* = 10.9 Hz, 1H), 4.51 (d, *J* = 3.2 Hz, 1H), 4.18 (d, *J* = 10.9 Hz, 1H), 4.00 (d, *J* = 10.0 Hz, 1H), 3.88 (t, *J* = 9.3 Hz, 1H), 3.75 (s, 1H), 3.71 (dd, *J* = 11.6, 3.9 Hz, 1H), 3.58 – 3.54 (m, 1H), 3.52 (dd, *J* = 9.8, 3.0 Hz, 1H), 3.46 (d, *J* = 11.5 Hz, 1H), 3.39 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.36 (d, *J* = 5.2 Hz, 1H), 3.20 (s, 3H), 3.16 (t, *J* = 9.5 Hz, 1H), 2.86 (dd, *J* = 10.4, 2.3 Hz, 1H), 2.41 – 2.36 (m, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 1.69 – 1.63 (m, 1H), 1.00 (s, 9H), 0.97 (s, 9H), 0.84 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.48, 136.51, 136.04, 135.43, 135.14, 135.12, 134.95, 134.77, 134.71, 134.48, 134.23, 132.94, 132.65, 131.69, 128.83, 128.58, 128.40, 128.24, 128.12, 128.05, 127.93, 127.22, 127.15, 126.94, 126.54, 126.44, 126.40, 126.35, 126.12, 97.02, 96.84, 80.94, 78.37, 76.82, 74.44, 73.95, 72.71, 71.92, 71.16, 69.22, 69.06, 64.08, 53.85, 32.54, 26.28, 26.19, 25.76, 20.16, 18.97, 18.05, 17.84. HRMS (ESI) calcd for $C_{84}H_{104}NO_{10}Si_3$ $[M+NH_4]^+$ 1370.6968, found 1370.6974. $[\alpha]_D^{35}$= + 0.50 (*c* 0.01, $CHCl_3$).

Phenyl 2,3-*O*-isopropylidene-6-*O*-triisopropylsilyl-4-(3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranosyl)-*α*-D-thiomannopyranoside (4m)



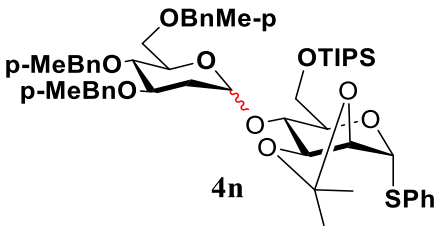
4m

Glycosylation of **2a** (40.2 mg, 0.06 mmol) with **3j** (33.8 mg, 0.072 mmol) according to **General procedure 3** afforded **4m** (44 mg, 83 %, α: β = 14:1) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.7 (Hexane/EtOAc = 4:1, v/v).The α anomer, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.8 Hz, 2H), 7.35 – 7.23 (m, 16H), 7.18 (d, *J* = 6.9 Hz, 2H), 5.77 (s, 1H), 5.59 (d, *J* = 1.8 Hz, 1H), 4.90 (d, *J* = 11.2 Hz, 1H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.62 (dd, *J* = 11.9, 6.0 Hz, 2H), 4.54 (d, *J* = 11.2 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 4.31 (d, *J* = 5.5 Hz, 1H), 4.27 – 4.24 (m, 1H), 4.06 – 4.02 (m, 1H), 3.94 – 3.88 (m, 2H), 3.86 – 3.80 (m, 2H), 3.77 – 3.72 (m, 2H), 3.72 – 3.68 (m, 1H), 3.58 (d, *J* = 9.1 Hz, 1H), 2.31 (dd, *J* = 12.8, 4.4 Hz, 1H), 1.76 (td, *J* = 12.9, 3.3 Hz, 1H), 1.52 (s, 3H), 1.33 (s, 3H), 1.00 – 0.93 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.93, 138.66, 138.02, 133.71, 131.61, 128.90, 128.41, 128.31, 128.15, 127.97, 127.64, 127.61, 127.56, 127.46, 127.40, 127.27, 109.71, 95.67, 83.90, 78.60, 77.95, 77.53, 76.37, 74.62, 73.55, 71.95, 71.55, 70.82, 70.60, 68.46, 62.68, 35.58,

27.87, 26.66, 18.00, 17.96, 11.94. HRMS (ESI) calcd for $C_{51}H_{72}NO_9SSi$ $[M+NH_4]^+$ 902.4697, found 902.4698. $[\alpha]_D^{35}$= + 0.38 (*c* 0.01, $CHCl_3$).

The β anomer ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.22 (m, 16H), 7.20 – 7.17 (m, 2H), 5.77 (s, 1H), 4.87 (d, *J* = 10.7 Hz, 1H), 4.76 (d, *J* = 8.6 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 10.7 Hz, 1H), 4.50 (d, *J* = 12.2 Hz, 1H), 4.36 – 4.32 (m, 1H), 4.30 (d, *J* = 5.5 Hz, 1H), 4.08 (dd, *J* = 9.5, 7.6 Hz, 1H), 3.94 (d, *J* = 9.6 Hz, 1H), 3.82 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.75 (dd, *J* = 10.7, 4.4 Hz, 1H), 3.72 (dd, *J* = 11.6, 1.8 Hz, 1H), 3.67 (dd, *J* = 10.4, 1.3 Hz, 1H), 3.60 (dd, *J* = 10.6, 4.8 Hz, 2H), 3.36 (d, *J* = 3.0 Hz, 1H), 2.30 (dd, *J* = 12.4, 1.9 Hz, 1H), 1.73 – 1.68 (m, 1H), 1.46 (s, 3H), 1.33 (s, 3H), 1.08 – 0.96 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.33, 138.31, 133.89, 131.15, 128.90, 128.45, 128.38, 128.30, 128.19, 127.91, 127.73, 127.70, 127.52, 127.17, 109.41, 99.30, 83.89, 79.59, 77.95, 76.76, 76.37, 75.04, 74.42, 73.32, 71.51, 70.99, 69.08, 61.78, 36.86, 27.86, 26.52, 17.99, 17.93, 11.84. HRMS (ESI) calcd for $C_{51}H_{72}NO_9SSi$ $[M+NH_4]^+$ 902.4697, found 902.4698. $[\alpha]_D^{35}$= + 0.28 (*c* 0.01, $CHCl_3$).

Phenyl 2,3-*O*-isopropylidene-6-*O*-triisopropylsilyl-4-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-D-glucopyranosyl)-*α*-D-thiomannopyranoside (4n).

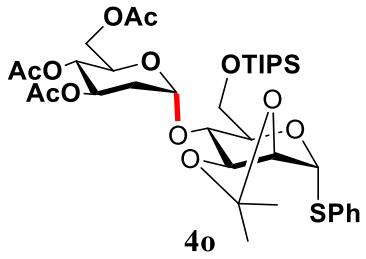


Glycosylation of **2b** (42.8 mg, 0.06 mmol) with **3j** (33.8 mg, 0.072 mmol) according to **General procedure 3** afforded **4n** (47.9 mg, 86 %, α: β = 14:1) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.71 (Hexane/EtOAc = 4:1, v/v)). The α anomer ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.9 Hz, 2H), 7.26 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 4H), 7.04 (d, *J* = 7.9 Hz, 2H), 5.77 (s, 1H), 5.57 (d, *J* = 2.1 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.59 (m, 3H), 4.45 (d, *J* = 10.9 Hz, 1H), 4.42 (d, *J* = 12.1 Hz, 1H), 4.30 (d, *J* = 5.4 Hz, 1H), 4.25 (t, *J* = 6.2 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.91 – 3.86 (m, 2H), 3.84 (dd, *J* = 11.2, 1.7 Hz, 1H), 3.81 (dd, *J* = 11.2, 4.7 Hz, 1H), 3.71 (m, 2H), 3.65 (t, *J* = 9.3 Hz, 1H), 3.53 (d, *J* = 9.0 Hz, 1H), 2.33 (s, 6H), 2.30 (s, 3H), 2.29 – 2.25 (m, 1H), 1.74 (td, *J* = 12.9, 3.4 Hz, 1H), 1.52 (s, 3H), 1.34 (s, 3H), 1.00 – 0.94 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.14, 136.09, 135.72, 135.04, 134.78, 134.09, 132.87, 130.60, 128.00, 127.93, 127.84, 127.71, 127.05, 126.71, 126.53, 126.31, 108.65, 94.80, 83.04, 77.57, 76.94, 76.36, 75.42, 73.39, 72.37, 70.84, 70.75, 70.08, 69.91, 67.40, 61.84, 34.66, 26.81, 25.58, 20.12, 20.10, 16.97, 16.94, 10.98. HRMS (ESI) calcd for $C_{54}H_{78}NO_9SSi$ $[M+NH_4]^+$ 944.5167, found 944.5167. $[\alpha]_D^{35}$= + 1.88 (*c* 0.035, $CHCl_3$).

For β anomer, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 4H), 7.13 (t, *J* = 8.5 Hz, 4H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 5.76 (s, 1H), 4.80 (d, *J* = 10.4 Hz, 1H), 4.73 (d, *J* = 8.7 Hz, 1H), 4.60 (t, *J* = 11.9 Hz, 2H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.44 (t, *J* = 10.4 Hz, 2H), 4.35 – 4.31 (m, 1H), 4.29 (d, *J* = 5.5 Hz, 1H), 4.06 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.93 (d, *J* = 9.6 Hz, 1H), 3.81 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.71 (dd, *J* = 10.3, 3.9 Hz, 2H), 3.64 – 3.60 (m, 1H), 3.58 – 3.53(m, 2H), 3.31 (d, *J* = 3.4 Hz,

1H), 2.34 (s, 3H), 2.33 (s, 6H), 2.29 – 2.24 (m, 1H), 1.71 – 1.64 (m, 1H), 1.45 (s, 3H), 1.31 (s, 3H), 1.04 – 0.95 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.27, 136.06, 134.50, 134.42, 134.38, 133.04, 130.25, 128.06, 127.95, 127.92, 127.85, 127.25, 127.01, 126.80, 126.13, 108.34, 98.42, 83.12, 78.45, 76.91,75.82, 75.36, 74.21, 73.76, 73.49, 72.20, 70.41, 70.20, 67.98, 60.96, 35.94, 28.68, 26.80, 25.43, 20.13, 16.95, 16.90, 10.92. HRMS (ESI) calcd for $C_{54}H_{78}NO_9SSi$ $[M+NH_4]^+$ 944.5167, found 944.5171. $[\alpha]_D^{35}$= + 0.40 (*c* 0.01, $CHCl_3$).

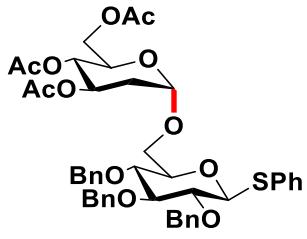
Phenyl 2,3-*O*-isopropylidene-6-*O*-triisopropylsilyl-4-(3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl)-*α*-D-thiomannopyranoside (4o).



4o

Glycosylation of **2c** (31.6 mg, 0.06 mmol) with **3j (**33.8 mg, 0.072 mmol) according to **General procedure 3** afforded **4o** (36.5 mg, 82 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.4.5 (Hexane: EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.9 Hz, 2H), 7.31 – 7.26 (m, 3H), 5.82 (s, 1H), 5.64 (d, *J* = 2.0 Hz, 1H), 5.29 – 5.24 (m, 1H), 5.05 (t, *J* = 9.8 Hz, 1H), 4.32 (dd, *J* = 12.2, 4.3 Hz, 2H), 4.30 – 4.28 (m, 1H), 4.08 – 4.03 (m, 2H), 4.02 – 3.95 (m, 2H), 3.93 (dd, *J* = 11.3, 3.4 Hz, 1H), 3.80 (dd, *J* = 11.2, 1.3 Hz, 1H), 2.27 (dd, *J* = 12.6, 4.9 Hz, 1H), 1.84 (td, *J* = 12.8, 3.4 Hz, 1H), 1.53 (s, 3H), 1.35 (s, 3H), 1.03-0.99 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.89, 170.29, 169.89, 133.32, 131.66, 128.96, 127.48, 109.80, 94.36, 83.70, 78.38, 76.34, 70.03, 70.00, 69.07, 68.88, 68.20, 62.30, 62.22, 35.01, 27.87, 26.62, 21.10, 20.87, 20.73, 18.00, 17.91, 11.95. HRMS (ESI) calcd for $C_{36}H_{60}NO_{12}SSi$ $[M+NH_4]^+$ 758.3605, found 758.3608. $[\alpha]_D^{35}$= + 0.60 (*c* 0.01, $CHCl_3$).

Phenyl 2,3,4-tri-*O*-benzyl-6-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-β-D-thioglucopyranoside (4p).

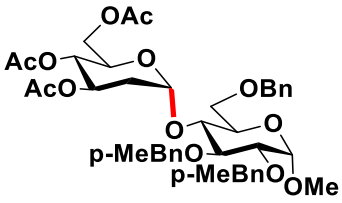


4p

Glycosylation of **2c** (31.6 mg, 0.06 mmol) with **3i** (39 mg, 0.072 mmol) according to **General procedure 3** afforded **4p** (41.6 mg, 85 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.38 (Hexane/EtOAc = 4:1, v/v) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.36-7.24 (m, 16H), 5.34-5.27 (m, 1H), 5.02 – 4.97 (m, 2H), 4.95 – 4.90 (m, 3H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.75 (d, *J* = 10.3 Hz, 1H), 4.65 (t, *J* = 11.8 Hz, 2H), 4.20 (d, *J* = 8.9 Hz, 1H), 3.97 (d, *J* = 11.1 Hz, 2H), 3.78 (d, *J* = 11.7 Hz, 1H), 3.72 (d, *J* = 10.8 Hz, 2H), 3.54 – 3.47 (m, 3H), 2.29 (dd, *J* =

12.9, 5.1 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.84 – 1.77 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.69, 169.07, 168.83, 137.26, 137.01, 136.97, 132.98, 130.48, 128.05, 127.45, 127.41, 127.19, 126.86, 126.83, 126.77, 126.71, 126.59, 126.44, 96.37, 86.64, 85.73, 79.95, 77.27, 76.79, 74.79, 74.45, 73.98, 68.15, 66.85, 65.59, 61.15, 33.87, 19.97, 19.73, 19.63. HRMS (ESI) calcd for $C_{45}H_{54}NO_{12}S$ $[M+NH_4]^+$ 832.3367, found 832.3369. $[\alpha]_D^{35}$= + 1.0 (*c* 0.015, $CHCl_3$).

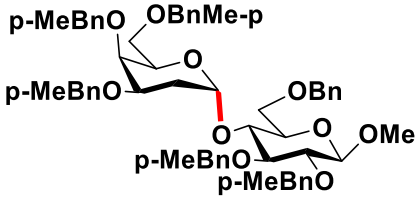
Synthesis of Methyl 2,3-di–para-methyl-*O*-benzyl-6-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (4q)



4q

Glycosylation of **2c** (31.6 mg, 0.06 mmol) with) with **3g** (35.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4q** (36.7 mg, 80 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.45 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.29 – 7.25 (m, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 8.1, 1.8 Hz, 4H), 5.42 (d, *J* = 2.8 Hz, 1H), 5.22 – 5.17 (m, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.90 (t, *J* = 9.8 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.3 Hz, 1H), 4.60-4.56 (m, 2H), 4.55 (d, *J* = 3.3 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.11 (dd, *J* = 12.3, 3.9 Hz, 1H), 3.90 (t, *J* = 9.2 Hz, 1H), 3.84-3.80 (m, 1H), 3.79 – 3.75 (m, 1H), 3.74 ((dd, *J* = 12.3, 1.6 Hz, 1H), 3.66 (dd, *J* = 9.7, 7.4 Hz, 2H), 3.64 – 3.60 (m, 1H), 3.49 (dd, *J* = 9.7, 3.4 Hz, 1H), 3.41 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 2.04-2.01 (m, 7H), 2.00 (s, 3H). 1.63 – 1.59 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.61, 169.09, 168.74, 137.10, 136.69, 136.19, 134.58, 133.93, 128.14, 128.02, 127.38, 127.24, 126.66, 126.59, 126.44, 97.49, 96.85, 80.70, 78.93, 75.30, 74.21, 72.33, 72.07, 68.59, 68.34, 68.28, 67.86, 67.61, 61.21, 54.27, 34.22, 20.14, 20.12, 19.92, 19.69. HRMS (ESI) calcd for $C_{42}H_{56}NO_{13}$ $[M+NH_4]^+$ 782.3752, found 782.3752. $[\alpha]_D^{35}$= + 0.26 (*c* 0.01, $CHCl_3$).

Synthesis of Methyl 2,3-di–para-methyl-*O*-benzyl-6-*O*-benzyl-4-*O*-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-β-D-glucopyranoside (4r)



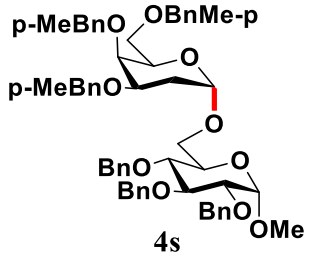
4r

Glycosylation of **2d** (42.8 mg, 0.06mmol) with **3h** (35.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4r** (47.4 mg, 83 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.60 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 4.3 Hz, 4H), 7.24 – 7.17 (m, 7H), 7.16 – 7.08

(m, 14H), 5.45 (d, *J* = 2.9 Hz, 1H), 4.89 (d, *J* = 10.5 Hz, 1H), 4.85 (d, *J* = 10.7 Hz, 1H), 4.82 (d, *J* = 11.5 Hz, 1H), 4.62 (d, *J* = 10.7 Hz, 1H), 4.54 (d, *J* = 11.3 Hz, 2H), 4.50 (d, *J* = 12.4 Hz, 2H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.28 (t, *J* = 9.9 Hz, 2H), 3.81 (bs, 1H), 3.78 (d, *J* = 7.2 Hz, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 3.74 – 3.70 (m, 1H), 3.60 – 3.55 (m, 5H), 3.52 (t, *J* = 9.0 Hz, 1H), 3.45- 3.41 (m, 3H), 3.38 (t, *J* = 8.4 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.31 (merged s, 9H), 2.11 (td, *J* = 12.5, 3.7 Hz, 1H), 1.82 (dd, *J* = 12.3, 3.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.59, 136.30, 136.26, 136.23, 136.15, 136.09, 134.83, 134.51, 134.48, 134.22, 134.12, 128.06, 128.03, 128.00, 127.84, 127.39, 127.22, 127.20, 126.95, 126.75, 126.59, 126.39, 126.35, 103.54, 98.31, 83.75, 81.24, 74.54, 74.24, 73.79, 73.47, 73.38, 72.95, 72.35, 72.21, 71.41, 69.77, 69.25, 69.19, 68.47, 55.96, 30.53, 20.13, 20.12. HRMS (ESI) calcd for $C_{60}H_{74}NO_{10}$ $[M+NH_4]^+$ 968.5313, found 968.5310.

$[\alpha]_D^{35}$= + 0.5 (*c* 0.01, $CHCl_3$).

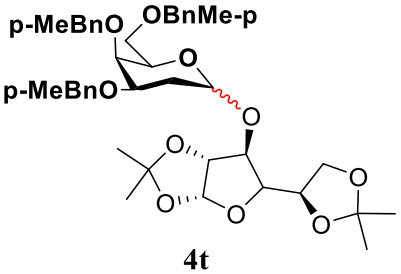
Synthesis of Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-α-D-glucopyranoside (4s)



4s

Glycosylation of **2d** (42.8 mg, 0.06 mmol) with **3d** (33.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4s** (49.33 mg, 89 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.6 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.17 (m, 20H), 7.13 – 7.07 (m, 7H), 5.01 (d, *J* = 2.5 Hz, 1H), 4.98 (d, *J* = 10.7 Hz, 1H), 4.85 (d, *J* = 6.0 Hz, 1H), 4.83 (d, *J* = 5.3 Hz, 1H), 4.81 (d, *J* = 6.4 Hz, 1H), 4.79 (d, *J* = 7.8 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 3.4 Hz, 1H), 4.55 (d, *J* = 11.3 Hz, 1H), 4.53-4.49 (m, 3H), 4.36 (d, *J* = 11.6 Hz, 1H), 4.28 (d, *J* = 11.5 Hz, 1H), 3.98 (t, *J* = 9.3 Hz, 1H), 3.86 – 3.78 (m, 4H), 3.71 (dd, *J* = 9.9, 3.1 Hz, 1H), 3.60 (d, *J* = 10.4 Hz, 1H), 3.52 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.50 – 3.44 (m, 3H), 3.30 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H), 2.18 (td, *J* = 12.3, 3.0 Hz, 1H), 1.98 (dd, *J* = 12.4, 3.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.76, 137.26, 137.19, 136.20, 136.17, 136.03, 134.89, 134.39, 134.14, 128.03, 127.96, 127.82, 127.44, 127.37, 127.32, 127.01, 126.87, 126.80, 126.71, 126.65, 126.60, 126.49, 97.27, 96.83, 81.13, 79.11, 76.99, 74.78, 73.96, 73.03, 73.01, 72.27, 72.17, 71.58, 69.10, 69.05, 68.86, 68.30, 64.96, 53.94, 30.04, 20.13, 20.06. HRMS (ESI) calcd for $C_{58}H_{70}NO_{10}$ $[M+NH4]^+$ 940.5000, found 940.5003. $[\alpha]_D^{35}$= + 0.34 (*c* 0.01, $CHCl_3$).

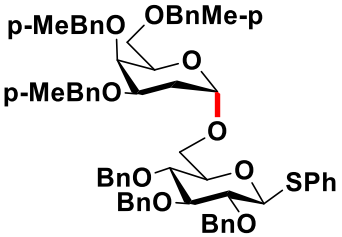
Synthesis of 1,2;4,6-di-*O*-isopropylidene-3-*O*-(3,4,6-tri-para-methyl-2-deoxy-D-galactopyranosyl)-α-D- glucofuranose (4t)



4t

Glycosylation of **2d** (42.8 mg, 0.06 mmol) with **3c** (18.7 mg, 0.072 mmol) according to **General procedure 3** afforded **4t** (35.4 mg, 82 %, α: β = 6:1) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.58 (Hexane/EtOAc = 4:1, v/v) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.09 (m, 12H), 5.82 (d, *J* = 3.4 Hz, 1H), 5.22 (d, *J* = 2.8 Hz, 1H), 4.87 (d, *J* = 11.4 Hz, 1H), 4.69 (d, *J* = 3.4 Hz, 1H), 4.57 (d, *J* = 4.9 Hz, 1H), 4.56 – 4.53 (m, 2H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.5 Hz, 1H), 4.20 (d, *J* = 2.5 Hz, 1H), 4.19 – 4.14 (m, 1H), 4.10 – 4.05 (m, 2H), 3.95 (dd, *J* = 8.4, 5.7 Hz, 1H), 3.89 – 3.85 (m, 2H), 3.84 – 3.80 (m, 1H), 3.57 (dd, *J* = 9.4, 6.4 Hz, 1H), 3.49 (dd, *J* = 9.4, 6.1 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H), 2.21 (td, *J* = 12.4, 3.6 Hz, 1H), 1.96 (dd, *J* = 12.5, 3.9 Hz, 1H), 1.47 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.34, 136.29, 136.16, 134.76, 134.34, 134.03, 128.08, 128.04, 127.87, 127.32, 126.91, 126.44, 110.76, 108.04, 104.29, 98.57, 82.50, 80.31, 79.99, 73.26, 73.00, 72.45, 71.69, 71.62, 69.99, 69.31, 68.87, 66.56, 30.08, 25.84, 25.74, 25.10, 24.37, 20.13. HRMS (ESI) calcd for $C_{42}H_{58}NO_{10}$ $[M+NH4]^+$ 736.4061, found 736.4061. $[\alpha]_D^{35}$= + 0.48 (*c* 0.01, $CHCl_3$).

Phenyl 2,3,4-tri-*O*-benzyl-6-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-α-D-galactopyranosyl)-β-D-thioglucopyranoside (4u)

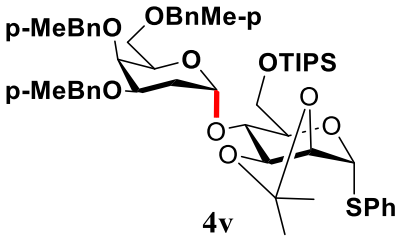


4u

Glycosylation of **2d** (42.8 mg, 0.06 mmol) with **3i** (39 mg, 0.072 mmol) according to **General procedure 3** afforded **4u** (55.3 mg, 92 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.61 (Hexane: EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.37-7.29 (m, 8H), 7.29 – 7.19 (m, 12H), 7.16 – 7.08 (m, 8H), 5.07 (d, *J* = 2.6 Hz, 1H), 4.91 (d, *J* = 10.4 Hz, 1H), 4.88 (d, *J* = 8.9 Hz, 1H), 4.84 (d, *J* = 10.2 Hz, 2H), 4.80 (d, *J* = 10.7 Hz, 1H), 4.74 (d, *J* = 10.2 Hz, 1H), 4.64 (d, *J* = 9.8 Hz, 1H), 4.56 (d, *J* = 11.1 Hz, 1H), 4.55 – 4.52 (m, 2H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 11.6 Hz, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 3.88 (t, *J* = 6.4 Hz, 1H), 3.86 – 3.82 (m, 2H), 3.80 (dd, *J* = 11.5, 4.9 Hz, 1H), 3.74 – 3.71 (m, 1H), 3.70 (d, *J* = 8.8 Hz, 1H), 3.52 (dd, *J* = 11.1, 7.6 Hz, 2H), 3.50 – 3.44 (m, 3H), 2.33 (s, 3H), 2.32 (s, 3H), 2.29 (s, 3H), 2.22 (td, *J* = 12.3, 3.3 Hz, 1H), 1.99 – 2.23(m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.40, 137.05, 137.00, 136.18, 136.16, 136.04, 134.93, 134.48, 134.25, 132.68, 131.04, 128.08, 127.97, 127.83, 127.43, 127.40, 127.32, 127.17, 126.81, 126.70, 126.46, 126.44, 97.36, 86.13,

85.74, 79.87, 77.53, 77.08, 74.82, 74.36, 74.04, 73.43, 73.04, 72.13, 71.68, 69.21, 69.00, 68.39, 65.14, 30.13, 29.86, 20.13, 20.07. HRMS (ESI) calcd for $C_{63}H_{72}NO_9S$ $[M+NH4]^+$ 1018.4928, found 1018.4933. $[\alpha]_D^{35}$= + 0.38 (*c* 0.01, $CHCl_3$).

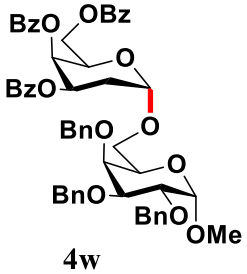
Phenyl 2,3-*O*-isopropylidene-6-*O*-triisopropylsilyl-4-(3,4,6-tri-para-methyl-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-*α*-D-thiomannopyranoside (4v)



4v

Glycosylation of **2d** (42.8 mg, 0.06 mmol) with **3j** (33.8 mg, 0.072 mmol) according to **General procedure 3** afforded **4v** (49.6 mg, 89 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.71 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.28 – 7.20 (m, 5H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 4H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 5.76 (s, 1H), 5.56 (d, *J* = 2.6 Hz, 1H), 4.84 (d, *J* = 11.3 Hz, 1H), 4.57 – 4.49 (m, 3H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.34 – 4.29 (m, 2H), 4.24 (t, *J* = 6.3 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.92 (s, 1H), 3.89 (d, *J* = 6.8 Hz, 1H), 3.84 (d, *J* = 11.1 Hz, 3H), 3.80 (dd, *J* = 10.9, 5.6 Hz, 1H), 3.60 (t, *J* = 8.3 Hz, 1H), 3.45 (dd, *J* = 8.4, 5.5 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.28 – 2.22 (m, 1H), 1.98 (dd, *J* = 12.3, 4.0 Hz, 1H), 1.48 (s, 3H), 1.32 (s, 3H), 1.01 – 0.96 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.11, 135.94, 135.02, 134.53, 134.19, 133.07, 130.48, 128.04, 127.91, 127.82, 127.78, 127.25, 126.77, 126.41, 126.25, 108.64, 95.14, 83.14, 77.54, 75.51, 73.50, 73.12, 72.26, 71.71, 70.35, 70.04, 69.52, 69.28, 67.93, 62.06, 30.25, 28.68, 26.76, 25.59, 20.12, 16.97, 16.93, 10.93. HRMS (ESI) calcd for $C_{54}H_{78}NO_9SSi$ $[M+NH4]^+$ 944.5167, found 944.5165. $[\alpha]_D^{35}$= - 0.34 (*c* 0.01, $CHCl_3$).

Phenyl 2,3,4-tri-*O*-benzyl-6-(3,4,6-tri-*O*-benzoyl-2-deoxy-α-D-galactopyranosyl)-α-D-galactopyranoside (4w)

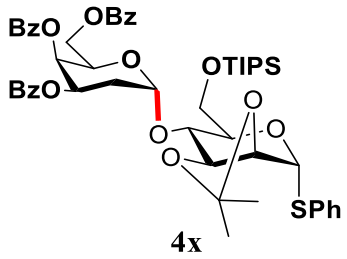


4w

Glycosylation of **2f** (42.9 mg, 0.06 mmol) with **3b** (33.5 mg, 0.072 mmol) according to **General procedure 3** afforded **4w** (46.1 mg, 83%, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.49 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.3 Hz, 2H), 8.00 (d, *J* = 7.3 Hz, 2H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.46 (m, 4H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.27 (m, 13H), 5.79 (d, *J* = 1.9 Hz, 1H), 5.62 – 5.57 (m, 1H), 4.95 (d, *J* = 11.9 Hz, 1H), 4.91 (d, *J* = 11.6 Hz, 1H), 4.82 (d, *J* = 8.7 Hz, 2H), 4.80 (d, *J* = 8.7 Hz, 1H), 4.69 – 4.65 (m, 2H),

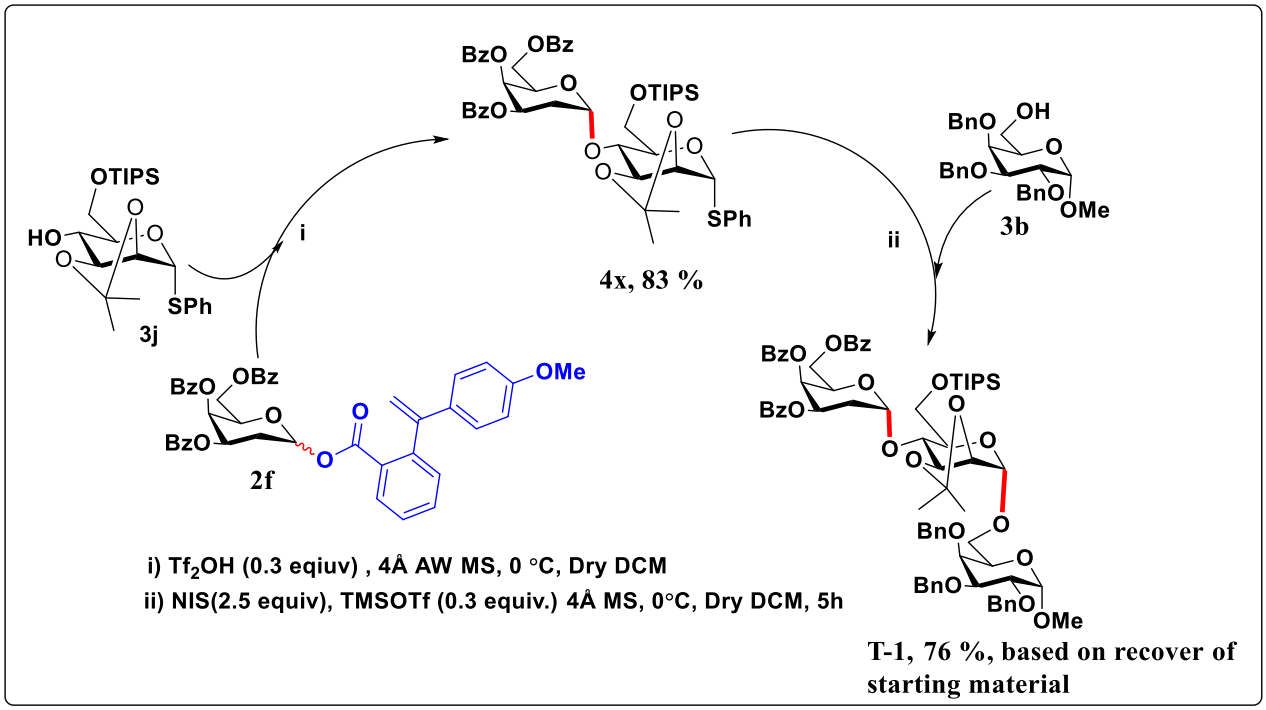
4.62 (d, *J* = 11.9 Hz, 1H), 4.52 – 4.49 (m, 1H), 4.46 (dd, *J* = 11.0, 7.5 Hz, 1H), 4.38 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.01 – 3.97 (m, 2H), 3.93 (bs, 1H), 3.86 (t, *J* = 6.2 Hz, 1H), 3.78 (dd, *J* = 9.1, 6.1 Hz, 1H), 3.38 (dd, *J* = 9.1, 6.8 Hz, 1H), 3.36 (s, 3H), 2.23 (td, *J* = 12.5, 3.3 Hz, 1H), 1.93 (dd, *J* = 12.5, 4.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.13, 164.65, 164.48, 137.82, 137.59, 137.52, 132.34, 132.04, 132.01, 128.82, 128.71, 128.67, 128.63, 127.53, 127.47, 127.39, 127.35, 127.32, 127.30, 127.26, 127.02, 126.67, 126.58, 126.54, 97.73, 96.17, 78.25, 75.61, 73.70, 73.47, 72.60, 72.52, 67.94, 66.63, 66.37, 66.12, 65.26, 62.45, 54.32, 29.63. HRMS (ESI) calcd for $C_{55}H_{58}NO_{13}$ $[M+NH4]^+$ 940.3908, found 940.3906. [α] $^{35}_{D}$= + 0.42 (*c* 0.01, $CHCl_3$).

Phenyl 2,3-*O*-isopropylidene-6-*O*-triisopropylsilyl-4-(3,4,6-tri-*O*-benzoyl-2-deoxy-α-D-galactopyranosyl)-*α*-D-thiomannopyranoside (4x)



4x

Glycosylation of **2f** (42.9 mg, 0.06 mmol) with **3j** (33.8 mg, 0.072 mmol) according to **General procedure 3** afforded **4x** (46.3 mg, 83 %, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.51 (Hexane/EtOAc = 4:1, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 2H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.50 (m, 3H), 7.47 (dd, *J* = 15.6, 7.7 Hz, 3H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.25 (m, 5H), 5.91 (bs, 1H), 5.86 (d, *J* = 1.8 Hz, 1H), 5.84 (s, 1H), 5.70 – 5.66 (m, 1H), 4.59 (t, *J* = 7.0 Hz, 1H), 4.49 (dd, *J* = 11.0, 6.1 Hz, 1H), 4.38-4.34 (m, 2H), 4.33 (dd, *J* = 10.9, 8.3 Hz, 1H), 4.16 – 4.08 (m, 2H), 4.00 (dd, *J* = 11.2, 3.8 Hz, 1H), 3.88 (d, *J* = 10.4 Hz, 1H), 2.41 (td, *J* = 12.5, 3.3 Hz, 1H), 2.22 (dd, *J* = 12.5, 4.7 Hz, 1H), 1.53 (s, 3H), 1.38 (s, 3H), 1.00 – 0.93 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.98, 165.69, 165.44, 133.49, 133.38, 133.15, 133.08, 131.71, 129.89, 129.72, 129.69, 129.65, 129.42, 128.97, 128.56, 128.41, 128.31, 127.49, 109.84, 95.26, 83.85, 78.50, 76.45, 70.80, 70.43, 67.53, 67.20, 67.03, 62.60, 62.43, 30.86, 27.89, 26.62, 17.93, 17.85, 11.95. HRMS (ESI) calcd for $C_{51}H_{66}NO_{12}SSi$ $[M+NH4]^+$ 944.4075, found 944.4071. [α] $^{35}_{D}$= + 0.18 (*c* 0.01, $CHCl_3$).



Scheme 5. Synthesis of trisaccharide (T-1).

A solution of glycosyl donor **4x** (27.8 mg, 0.03 mmol) and acceptor **3b** (16.7 mg, 0.036 mmol) in dry CH_2Cl_2 (0.03 M) was stirred at room temperature for 60 min in the presence of activated 4Å MS (80 mg) under Ar atmosphere. Then the vessel was chilled to 0 °C, to which NIS (16.9 mg, 0.075 mmol) and TMSOTf (1.6 µL, 30 mol%) were added. The reaction mixture was stirred for 5h min at 0 °C. Then, Et_3N was added to quench the reaction. The crude reaction mixture was worked up with water, washed with brine, dried by Na_2SO_4, concentrated in rotavapor. The resulting crude reaction mixture was purified through Flash column chromatography to afford the trisaccharide **T-1** (18.7 mg, 76 %, based on recovered donor **4x**, α only) as a colorless syrup. The crude product was purified through flash column chromatography, R_f = 0.25 (Hexane/EtOAc = 3:1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 8.00 – 7.96 (m, 2H), 7.85 – 7.82 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.43 – 7.34 (m, 8H), 7.33 – 7.26 (m, 11H), 5.86 (d, *J* = 2.4 Hz, 1H), 5.80 (d, *J* = 2.6 Hz, 1H), 5.65 – 5.60 (m, 1H), 4.96 (d, *J* = 11.7 Hz, 1H), 4.90 (d, *J* = 11.7 Hz, 1H), 4.83 (d, *J* = 12.1 Hz, 1H), 4.78 (d, *J* = 11.7 Hz, 1H), 4.75 (s, 1H), 4.70 (d, *J* = 6.4 Hz, 1H), 4.69 (d, *J* = 1.7 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.48 (q, *J* = 6.4 Hz, 2H), 4.33 (dd, *J* = 13.2, 9.4 Hz, 1H), 4.23 – 4.19 (m, 1H), 4.07 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.00 (d, *J* = 9.3 Hz, 1H), 3.97 (dd, *J* = 10.1, 2.7 Hz, 1H), 3.92 – 3.87 (m, 2H), 3.87 – 3.83 (m, 2H), 3.82 (d, *J* = 6.8 Hz, 1H), 3.78 (dd, *J* = 9.1, 5.5 Hz, 1H), 3.64 – 3.59 (m, 1H), 3.44 – 3.39 (m, 1H), 3.37 (s, 3H), 2.37 (td, *J* = 12.5, 3.6 Hz, 1H), 2.17 (dd, *J* = 12.0, 5.6 Hz, 1H), 1.49 (s, 3H), 1.35 (s, 3H), 1.04 – 0.97 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.94, 165.66, 165.39, 138.84, 138.49, 138.41, 133.34, 133.11, 133.03, 129.87, 129.72, 129.69, 129.66, 129.45, 128.53, 128.41, 128.40, 128.36, 128.29, 128.27, 128.11, 127.86, 127.72, 127.54, 127.51, 109.56, 98.85, 96.47, 95.32, 79.39, 78.71, 76.51, 75.62, 74.34, 74.02, 73.59, 73.55, 71.12, 69.15, 68.50, 67.66, 67.28, 67.05, 65.13, 63.20, 62.61, 55.47, 30.89, 29.71, 27.86, 26.50, 17.95, 17.89, 11.96. HRMS (ESI) calcd for $C_{73}H_{92}NO_{18}Si$ $[M+NH_4]^+$ 1298.6084, found 1298.6082. $[\alpha]_D^{35}$= + 0.18 (*c* 0.01, $CHCl_3$).

Reference

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2) Mukherji, A.; Kancharla, P. K. *O*rg.*Lett*. 2020, **22**, 2191−2195

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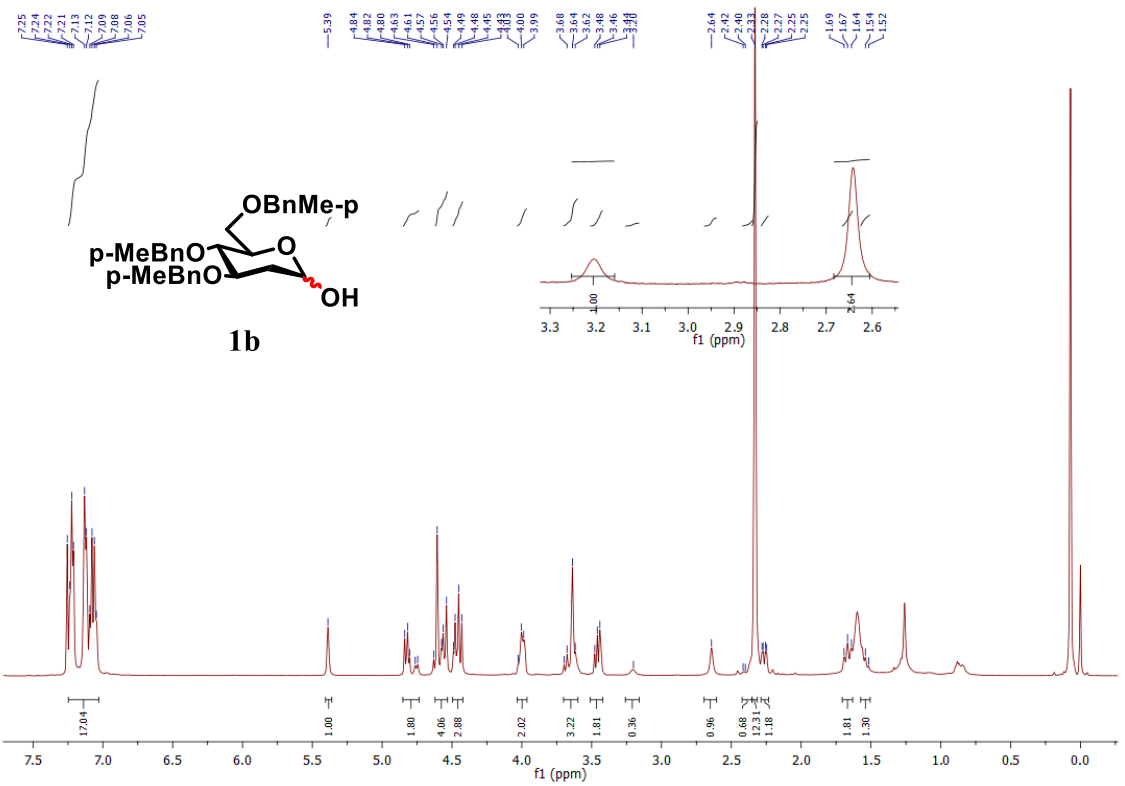
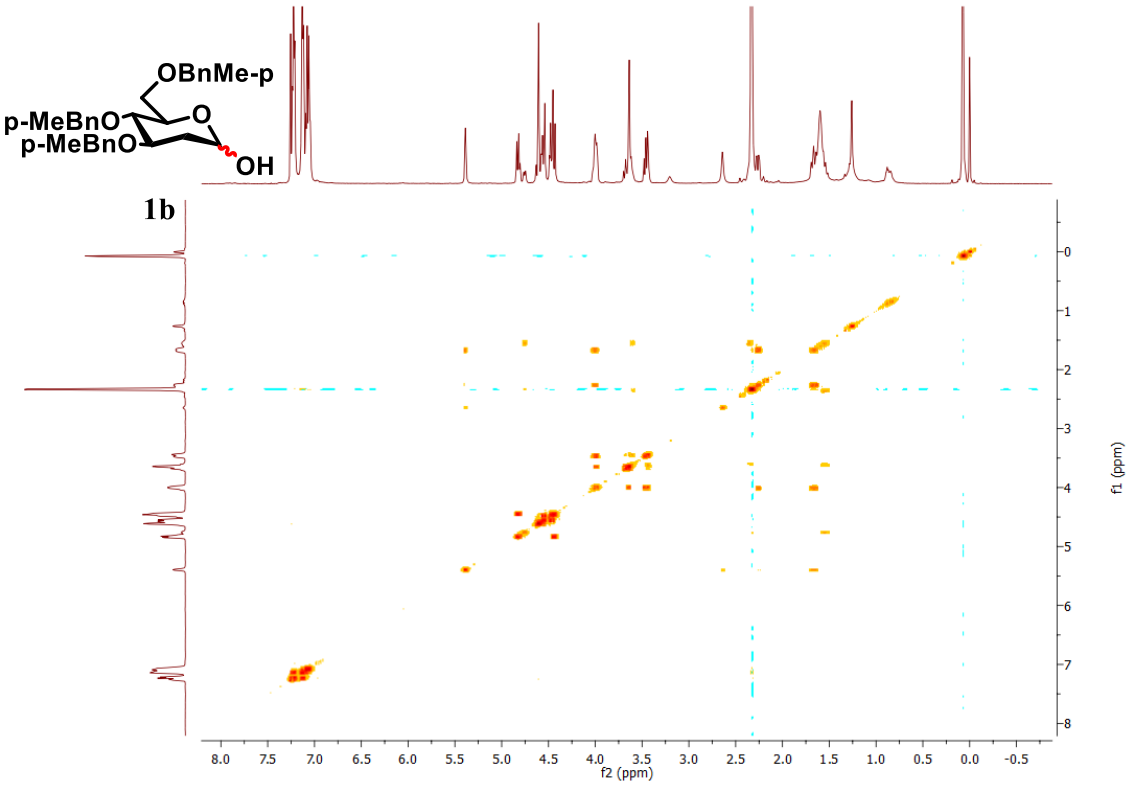
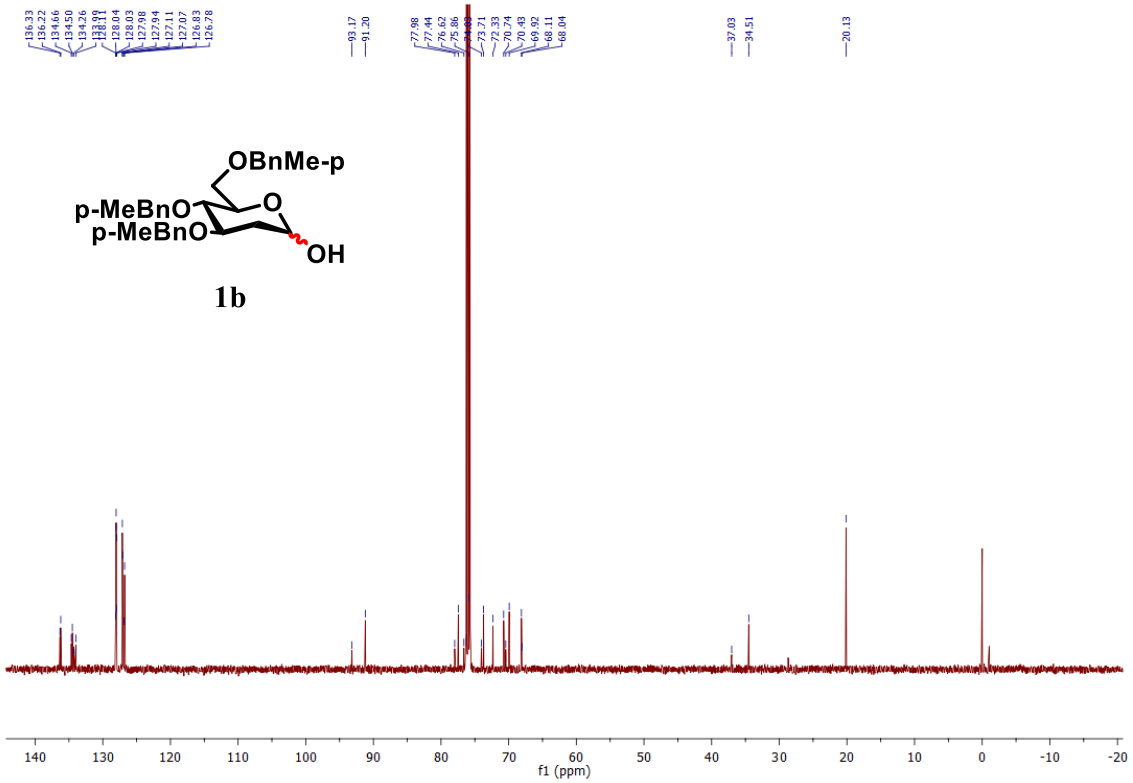
^{1}H NMR spectrum of compound 1b



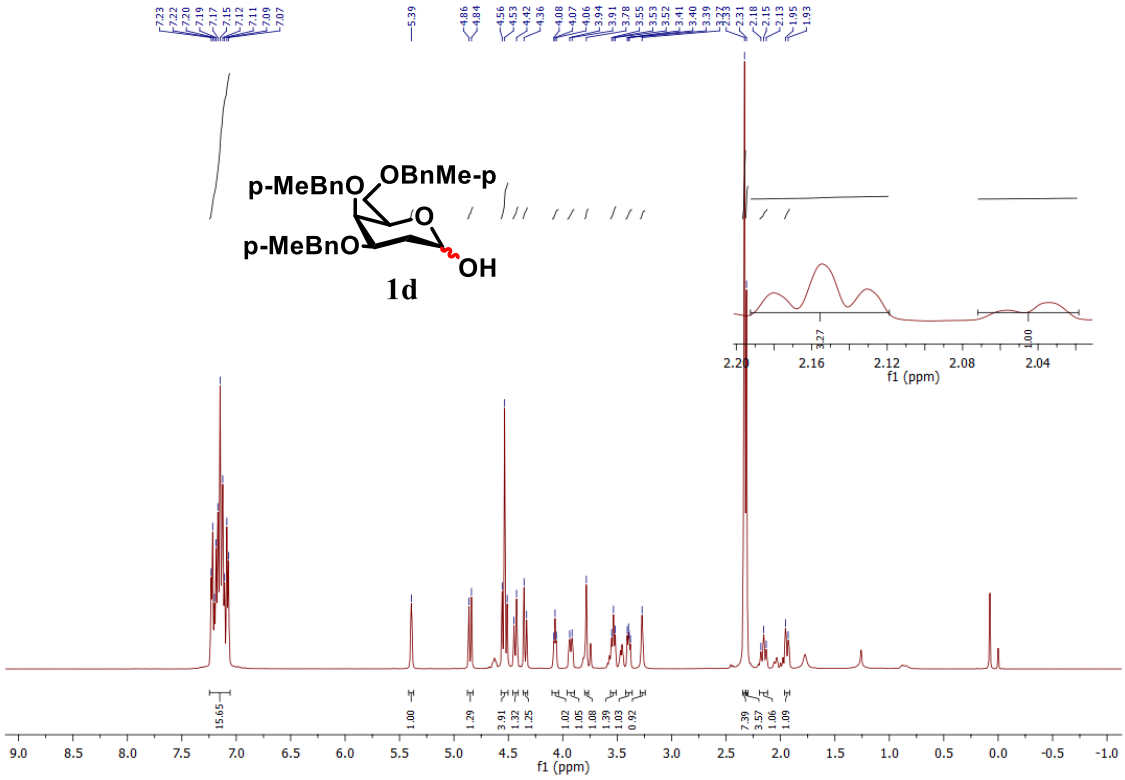
COSY NMR spectrum of compound 1b



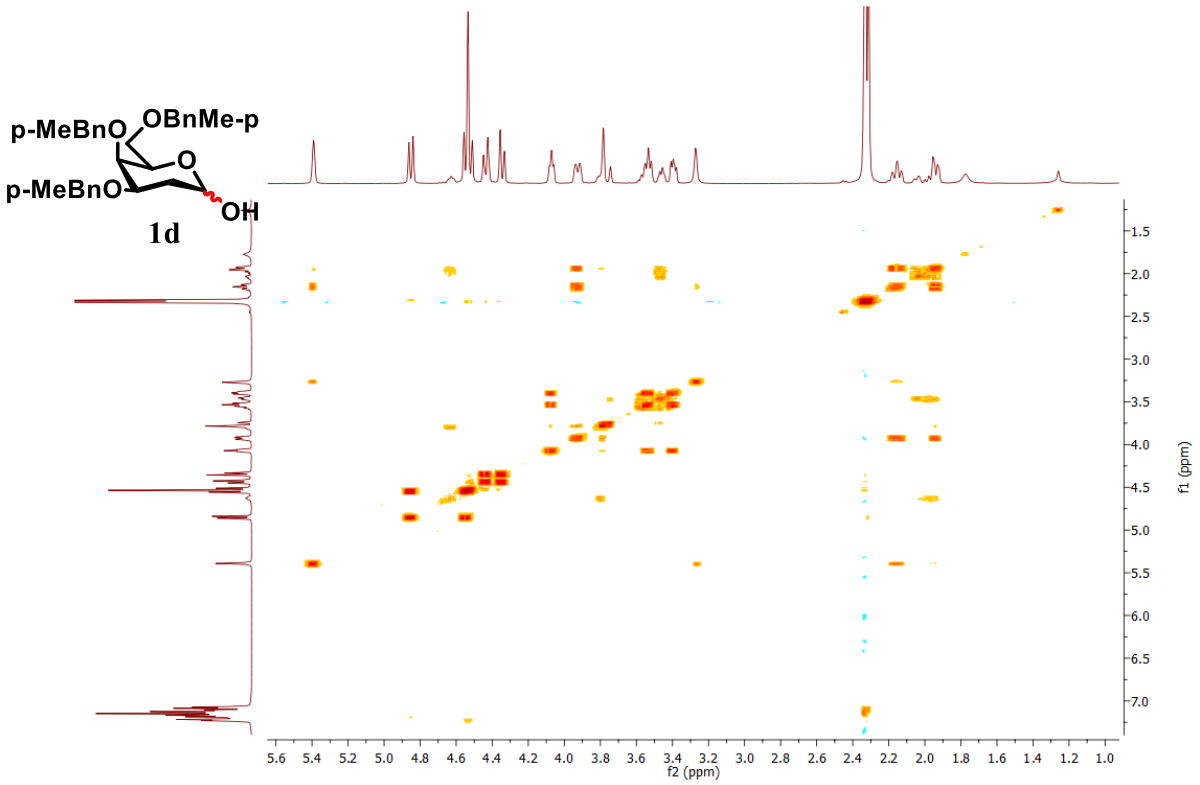
^{13}C NMR spectrum of compound 1b



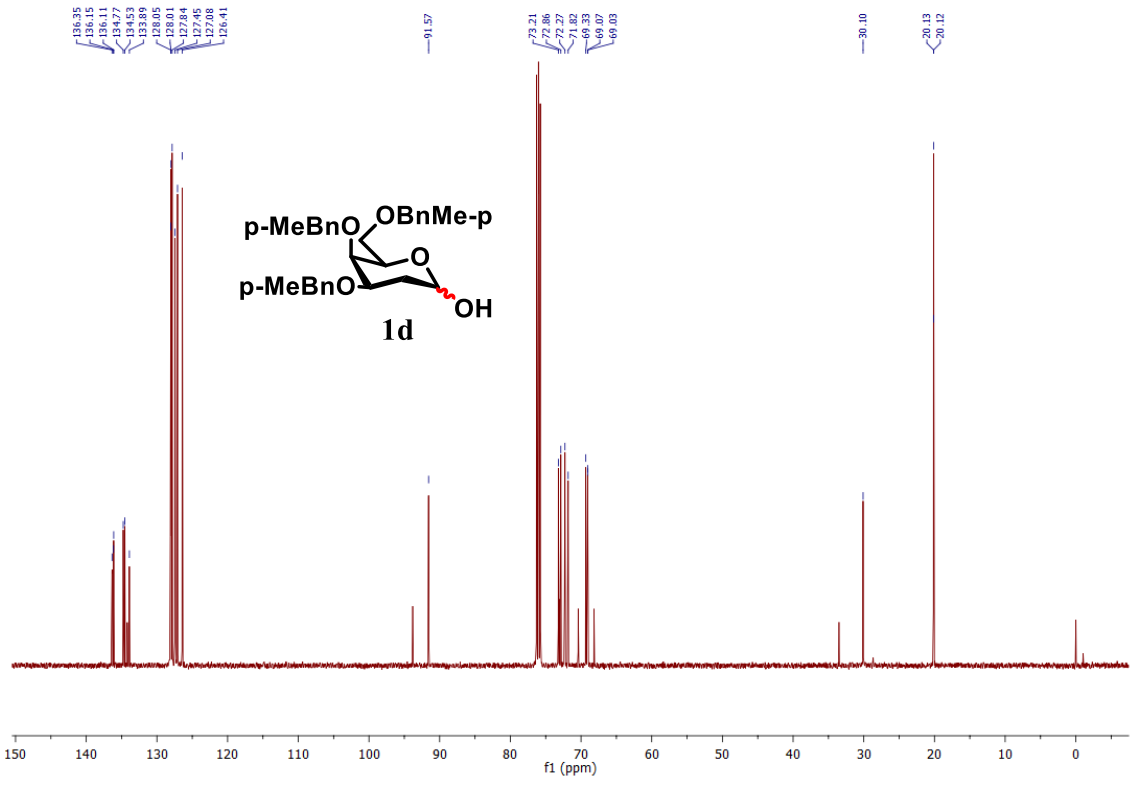
^{1}H NMR spectrum of compound 1d



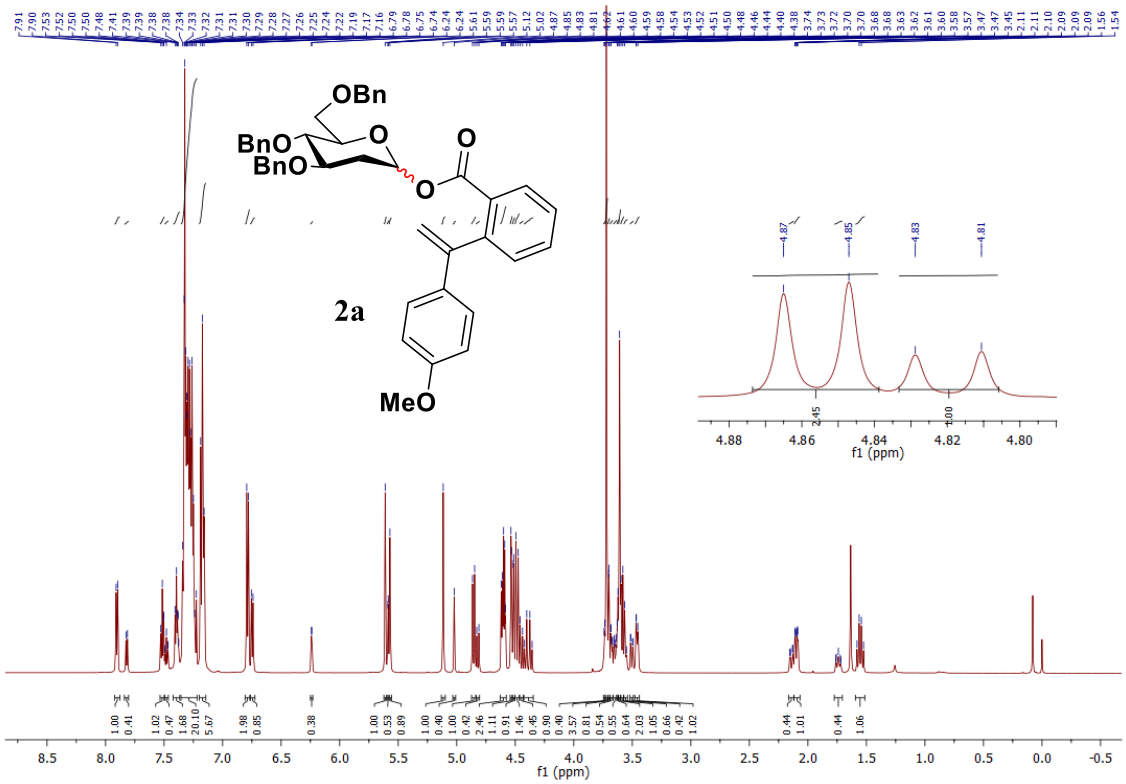
COSY NMR spectrum of compound 1d



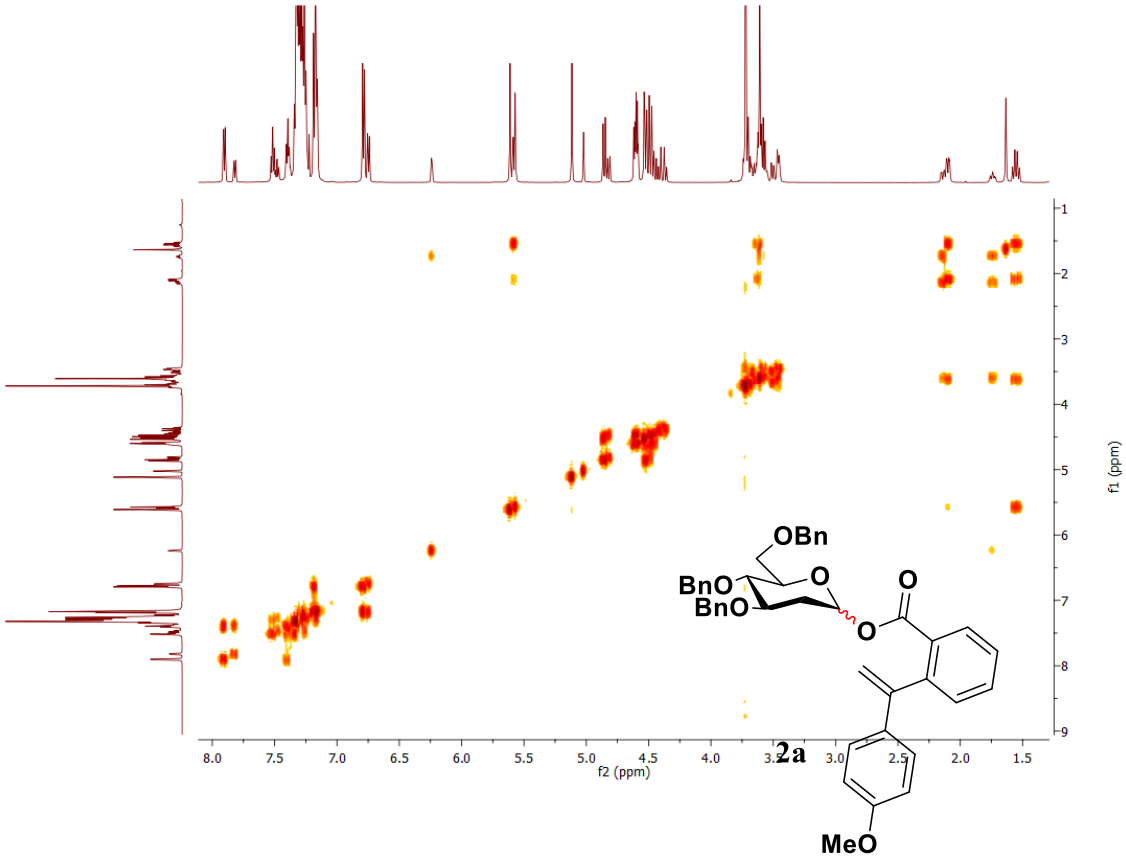
^{13}C NMR spectrum of compound 1d



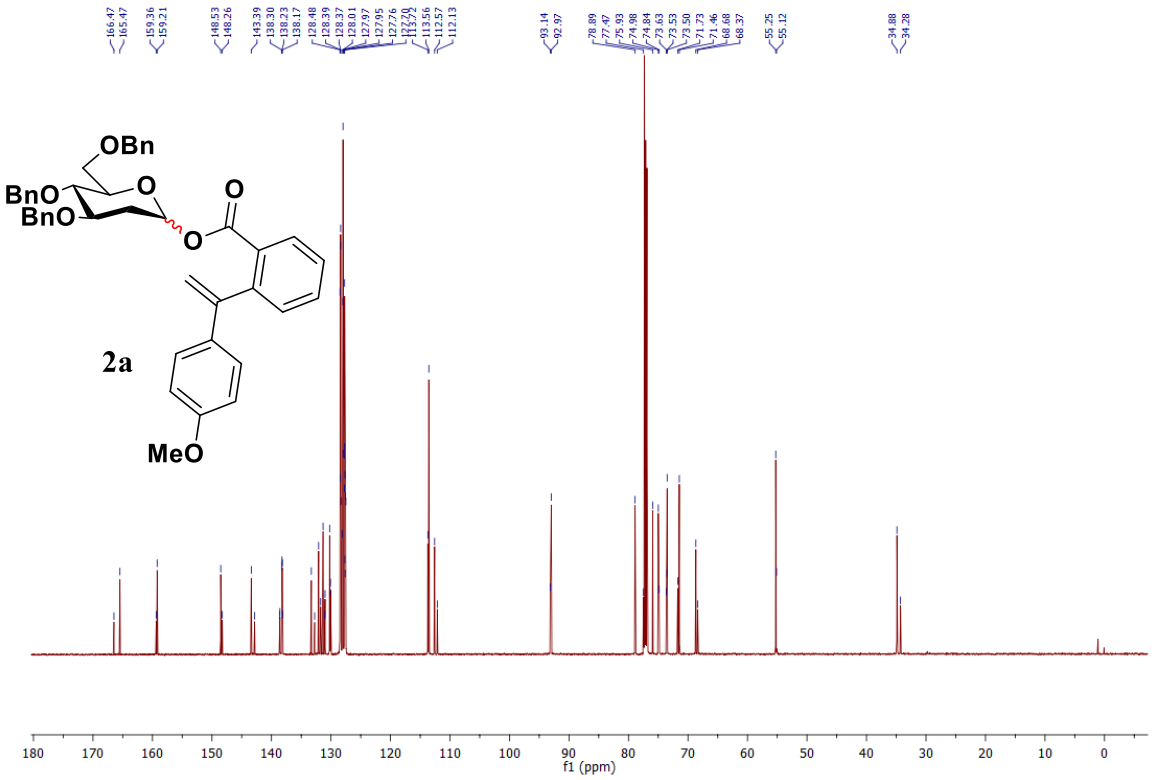
^{1}H NMR spectrum of compound 2a



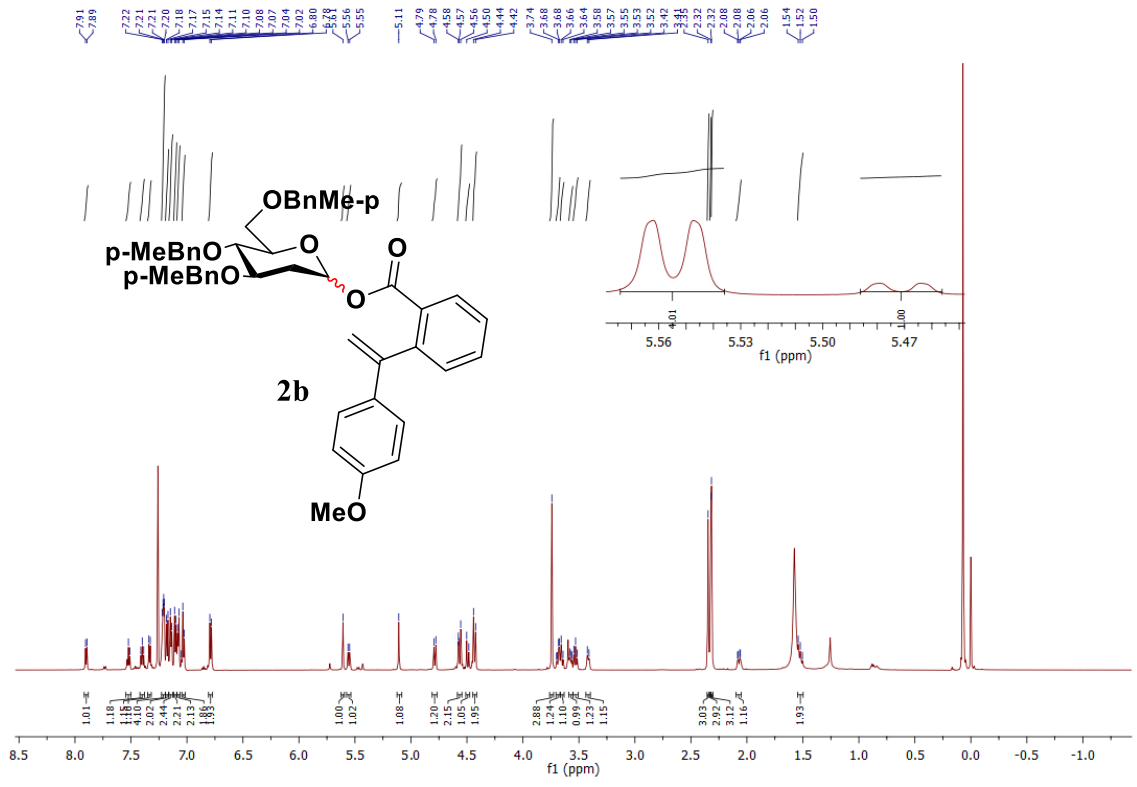
COSY NMR spectrum of compound 2a



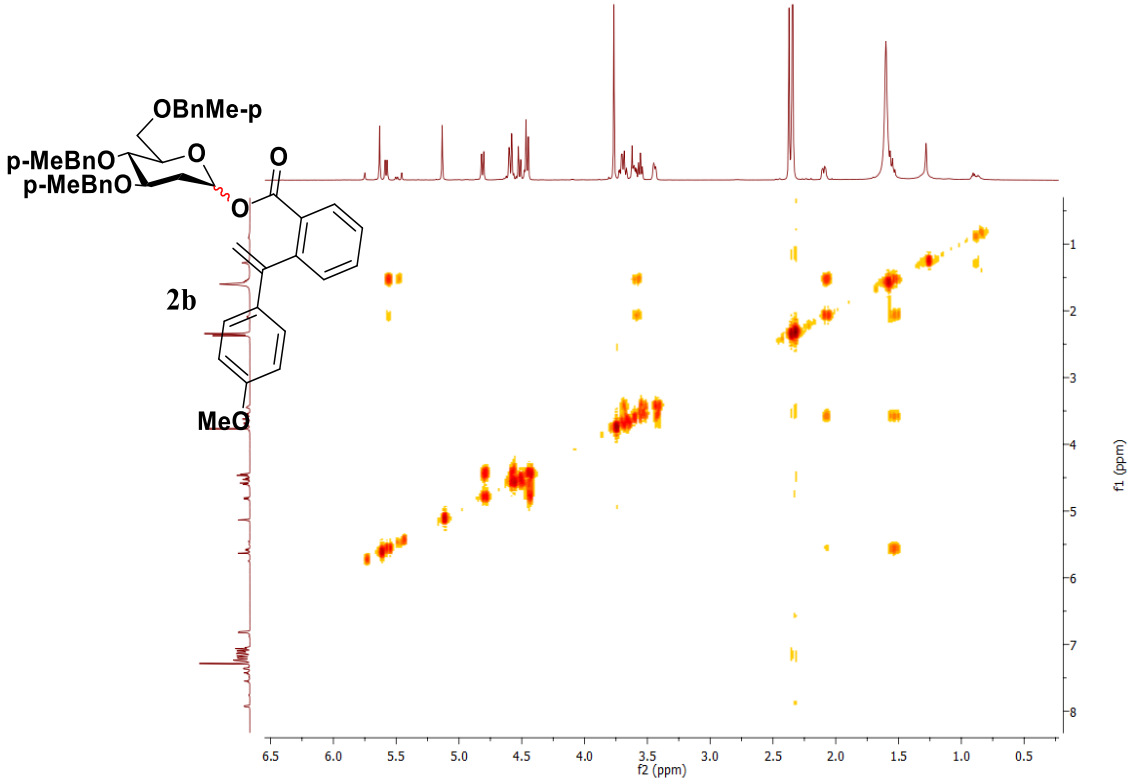
^{13}C NMR spectrum of compound 2a



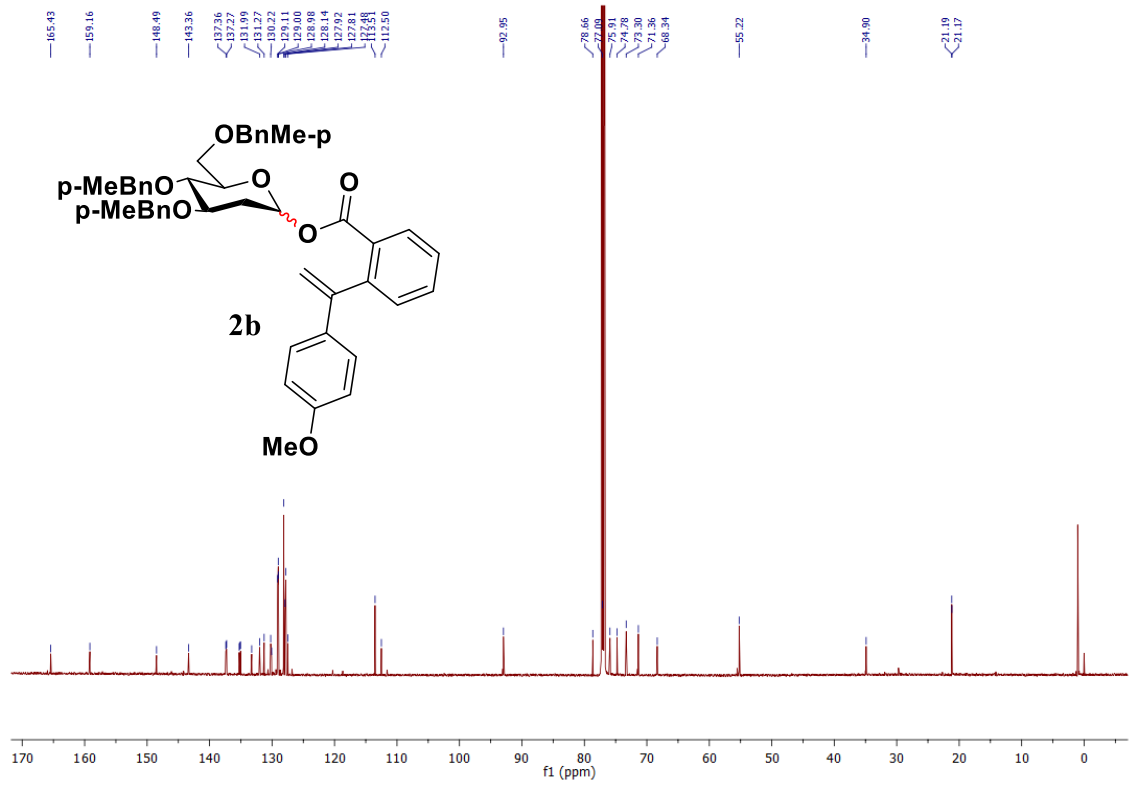
^{1}H NMR spectrum of compound 2b



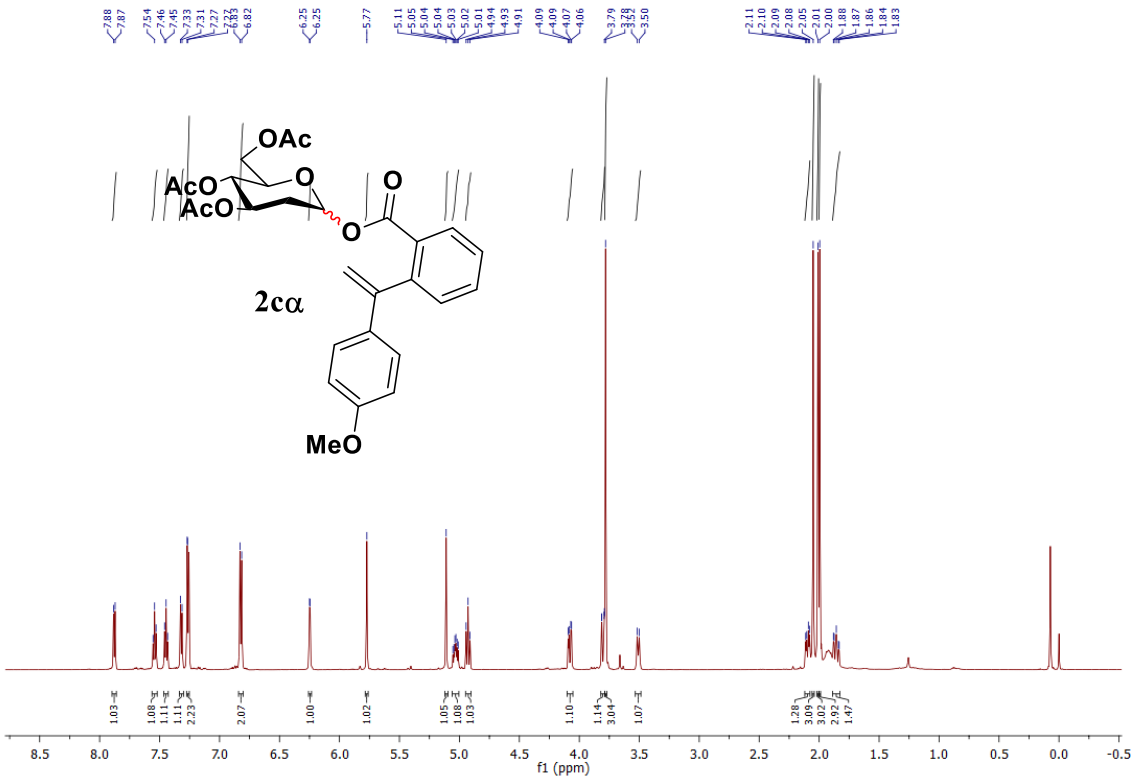
COSY NMR spectrum of compound 2b



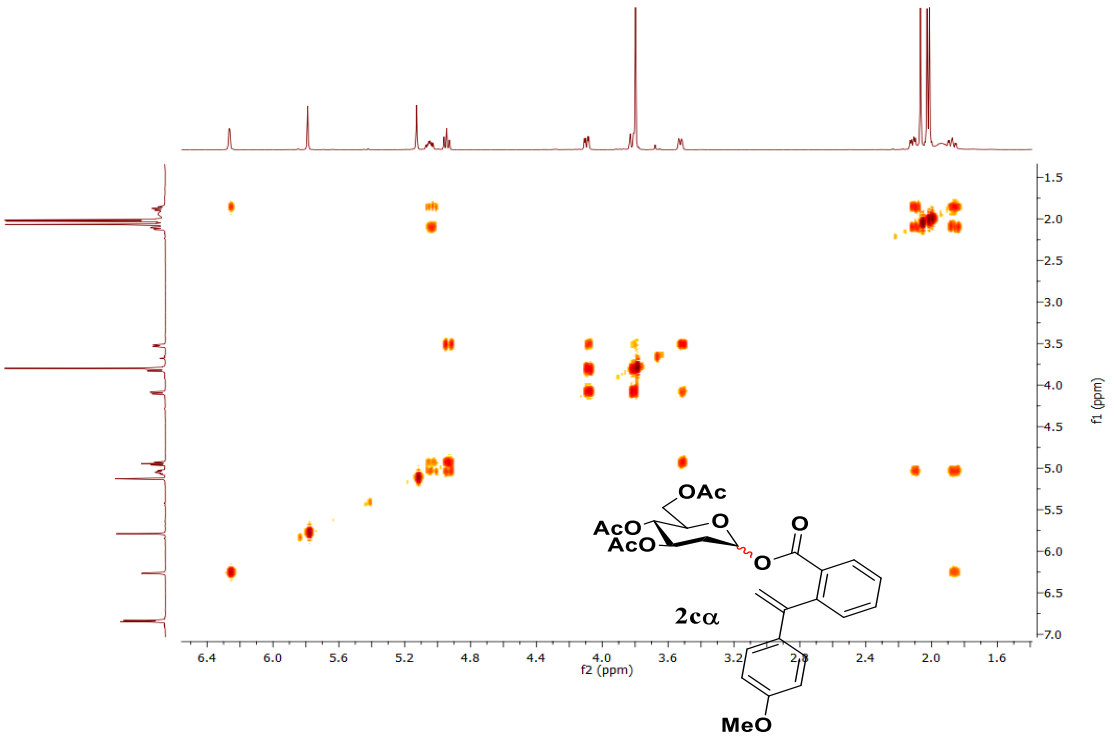
^{13}C NMR spectrum of compound 2b



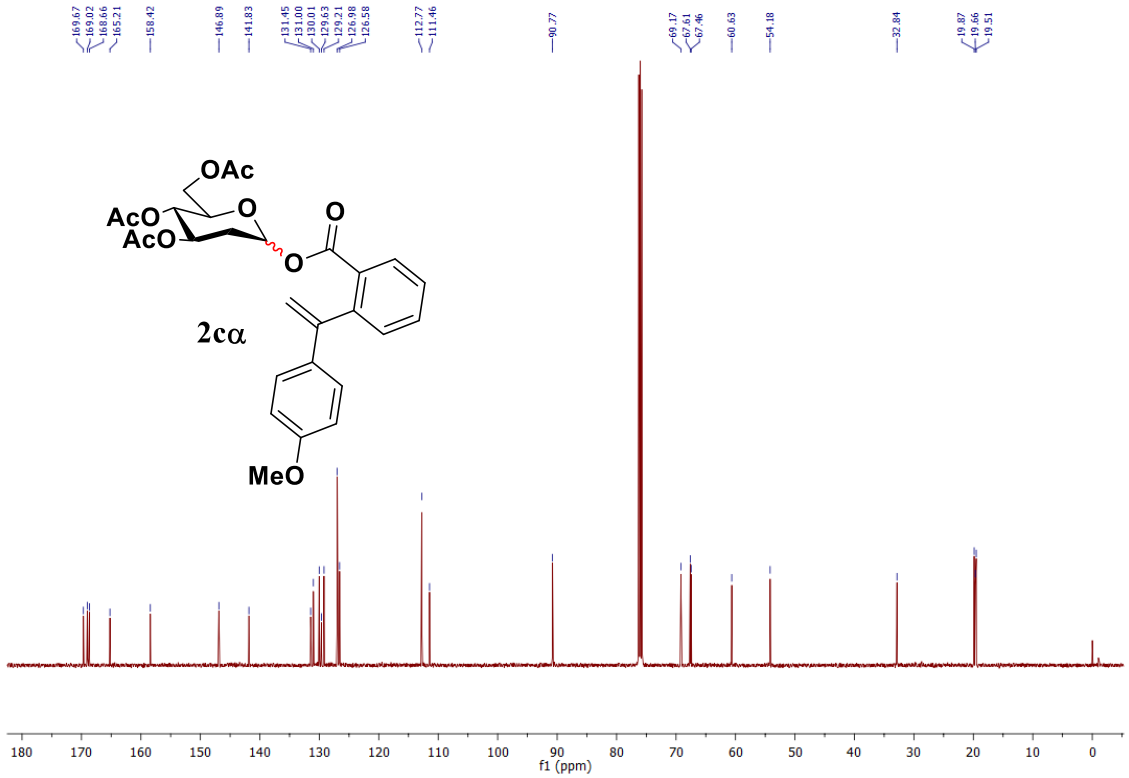
^{1}H NMR spectrum of compound 2cα



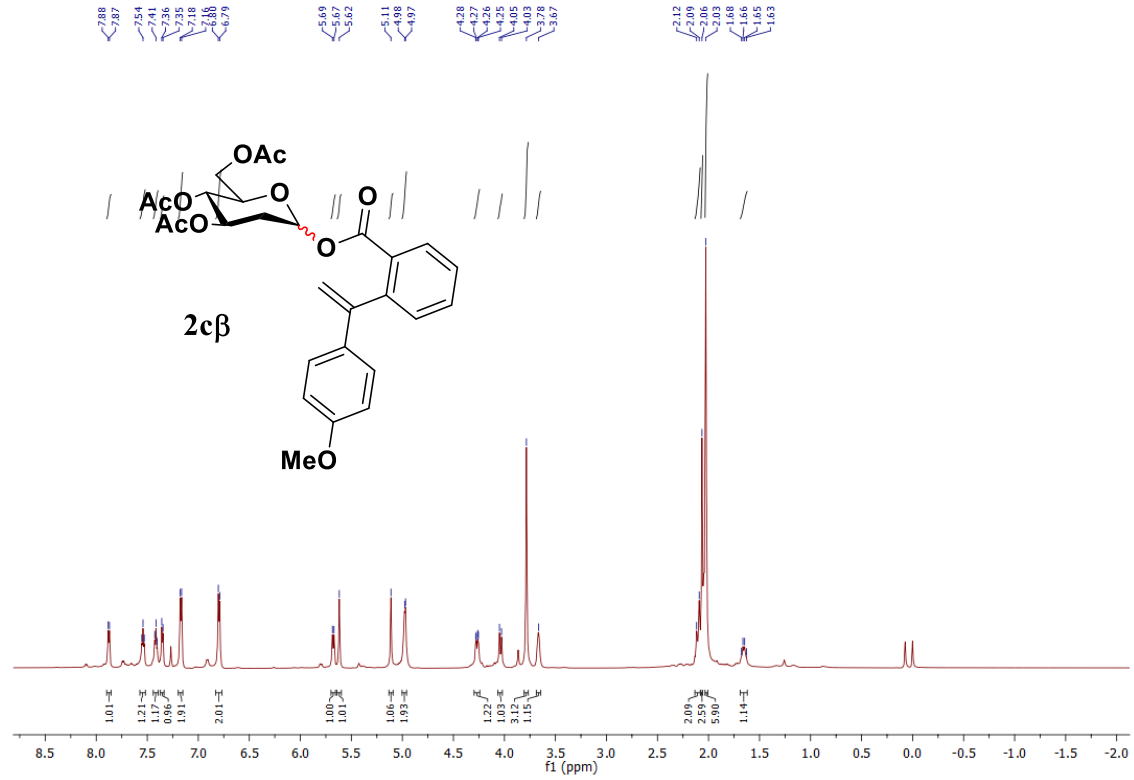
COSY NMR spectrum of compound 2cα



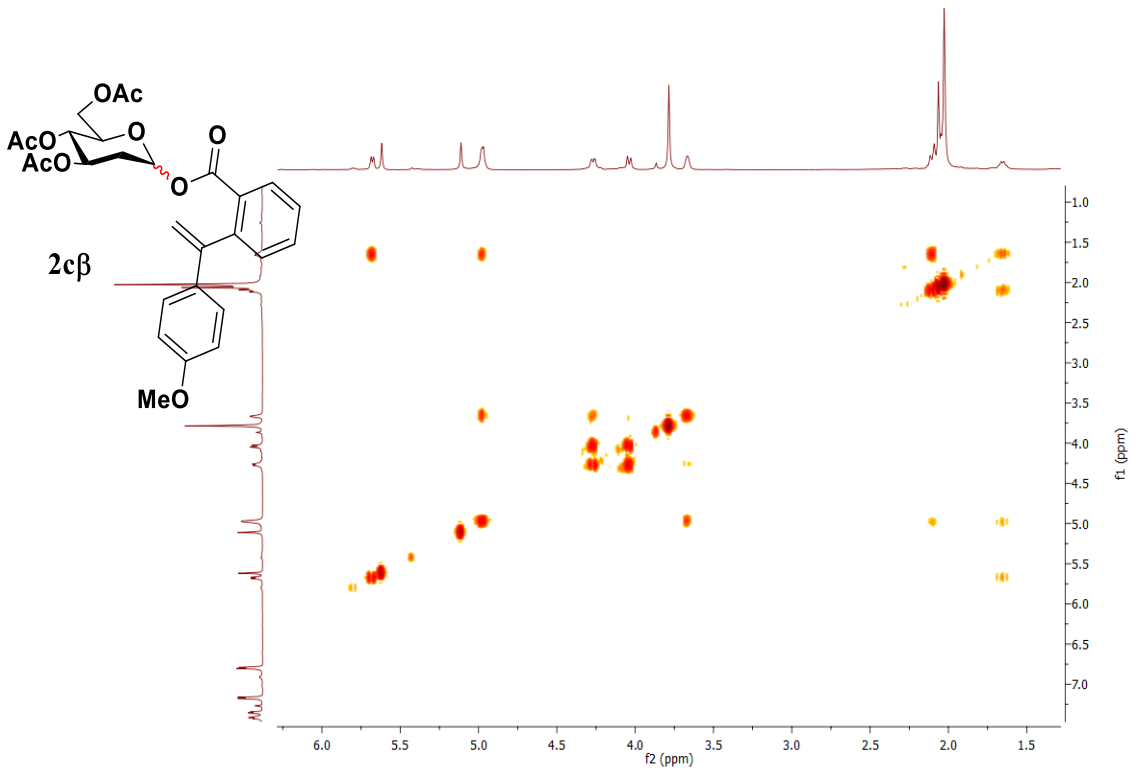
^{13}C NMR spectrum of compound 2cα



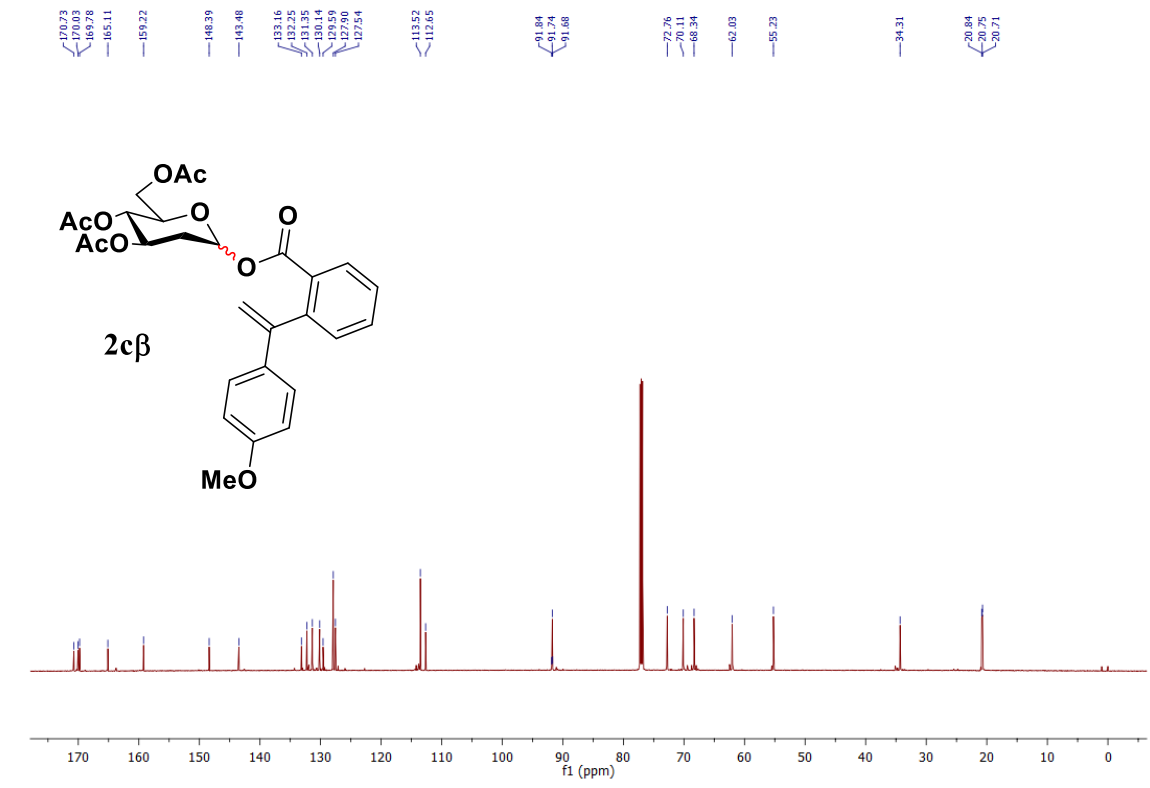
^{1}H NMR spectrum of compound 2cβ



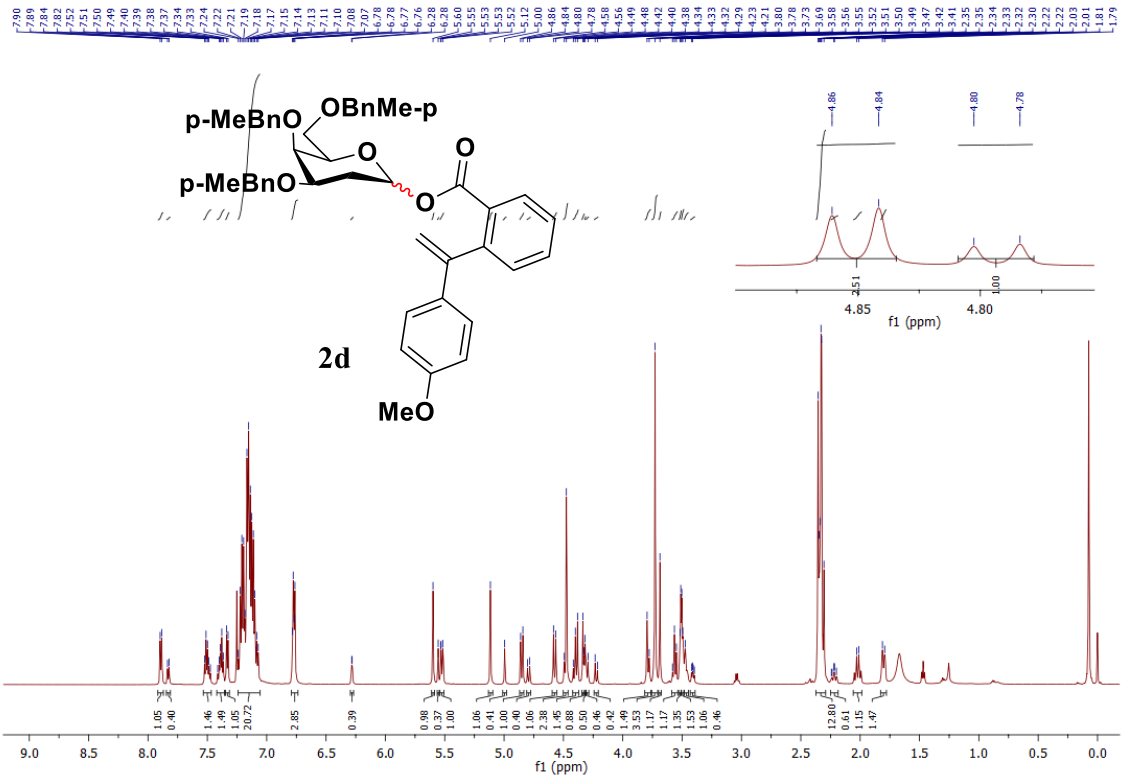
COSY NMR spectrum of compound 2cβ



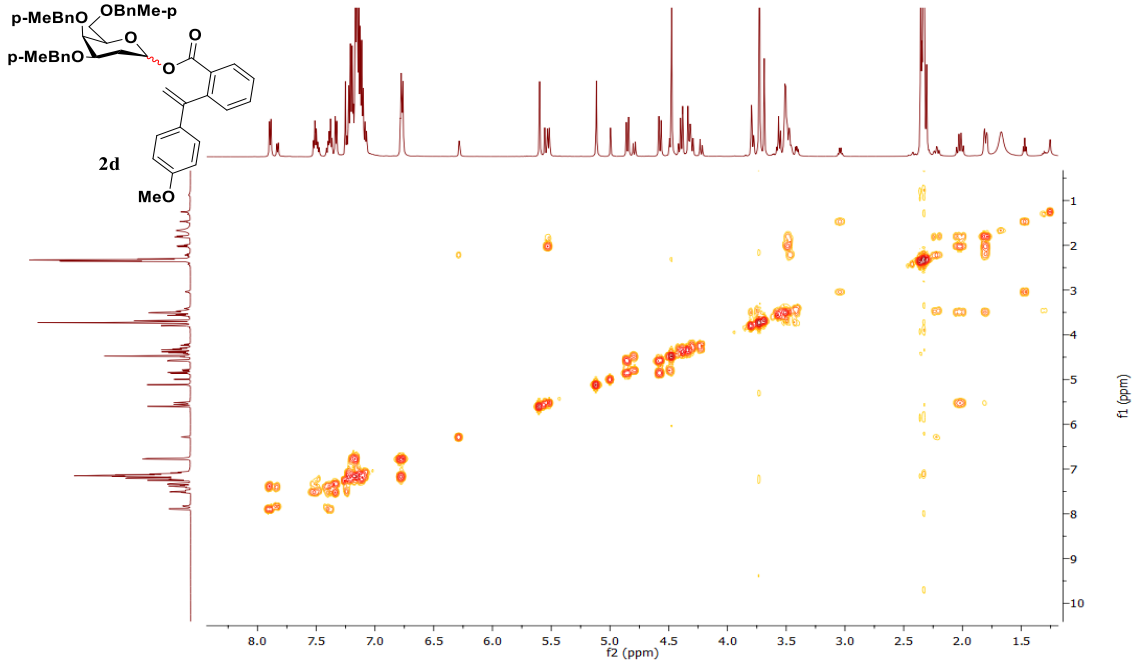
^{13}C NMR spectrum of compound 2cβ



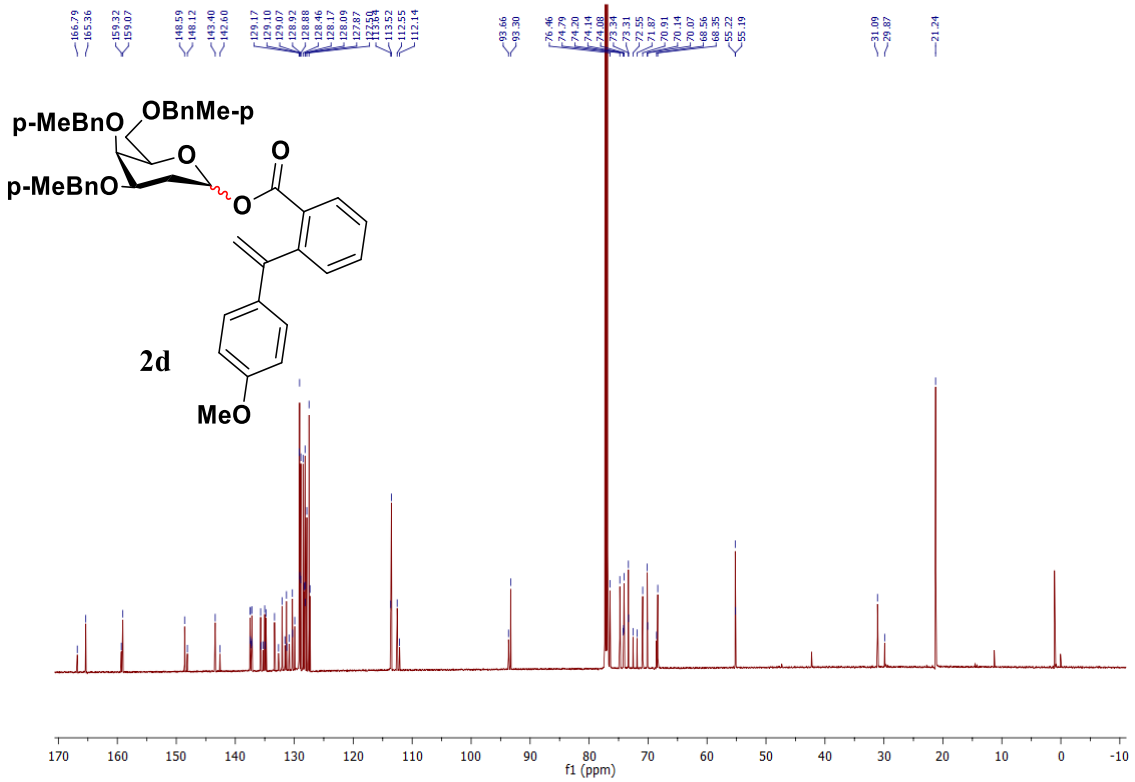
^{1}H NMR spectrum of compound 2d



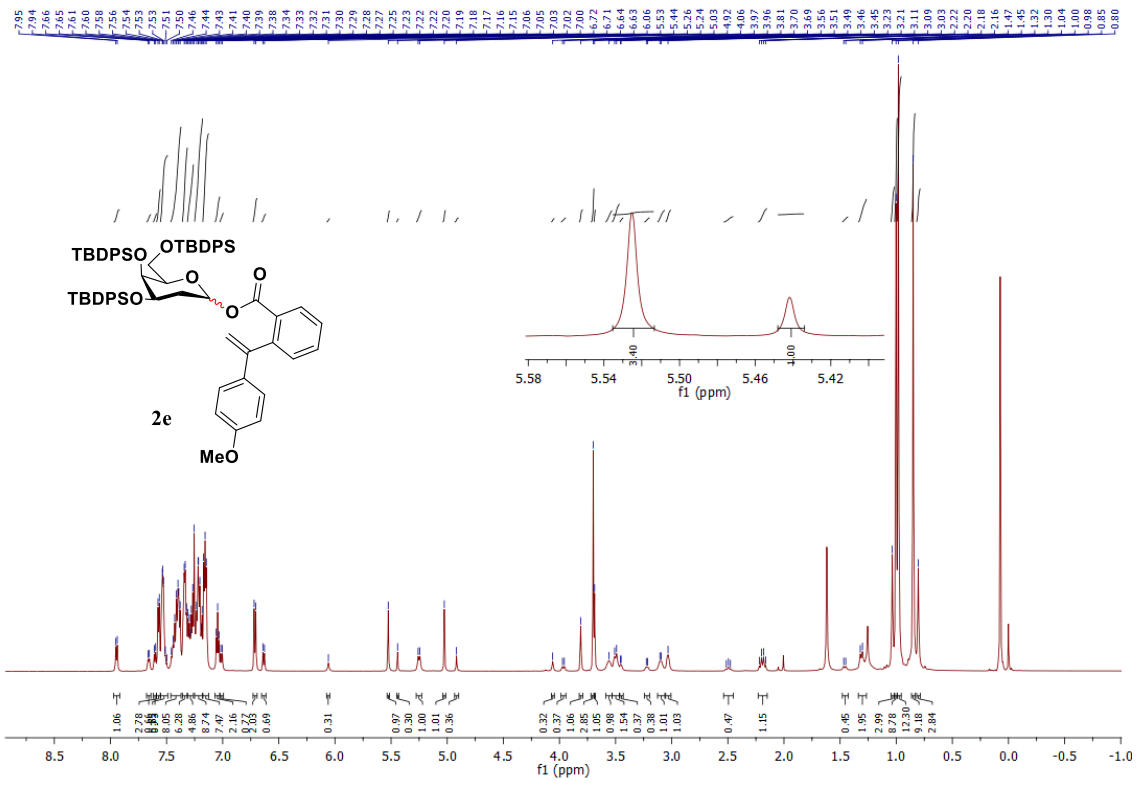
COSY NMR spectrum of compound 2d



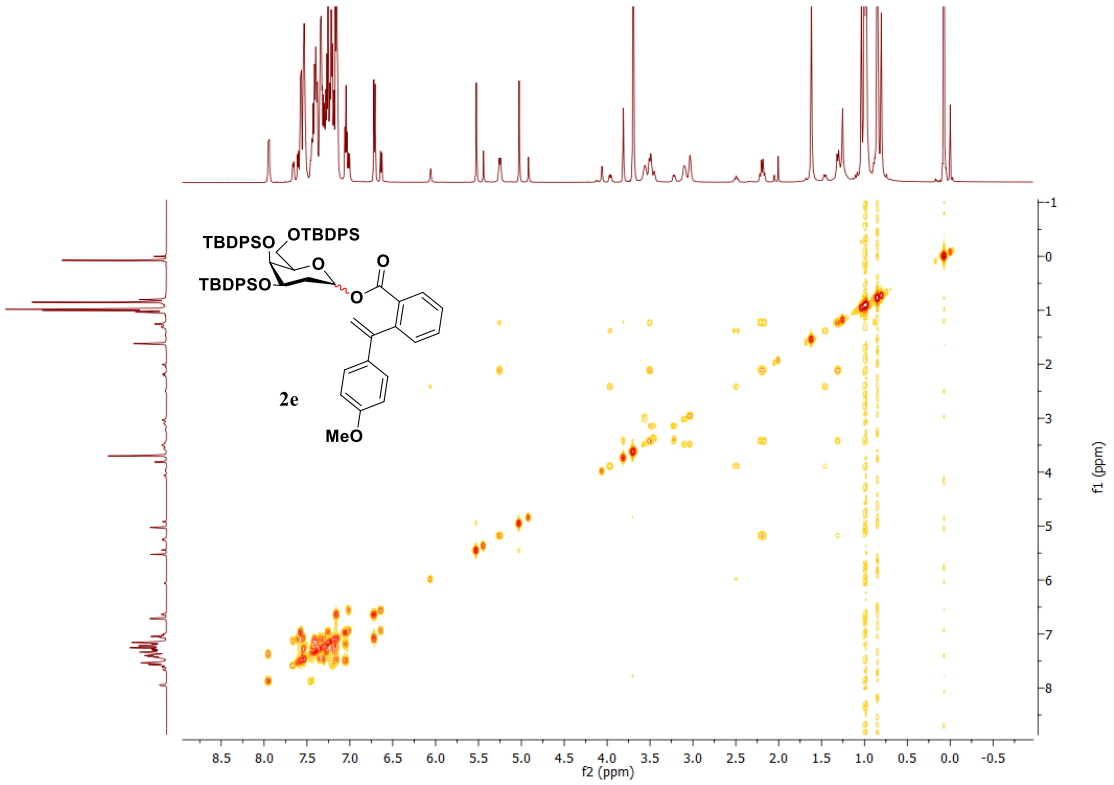
^{13}C NMR spectrum of compound 2d



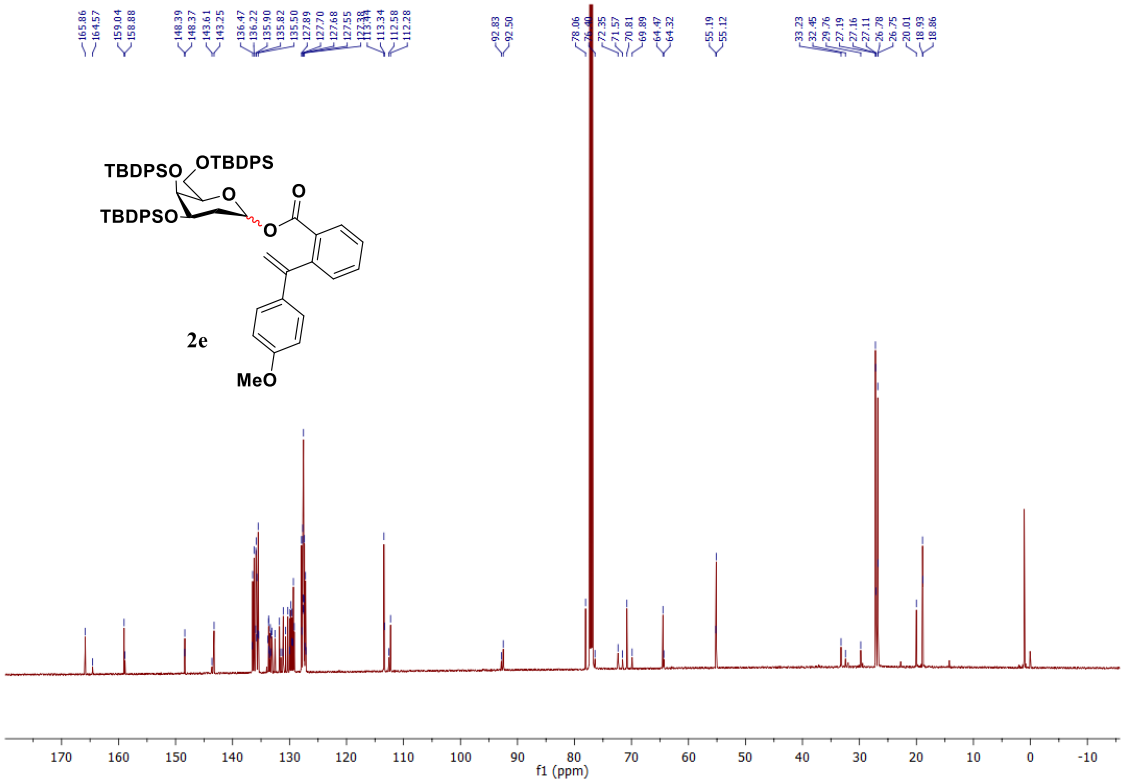
^{1}H NMR spectrum of compound 2e



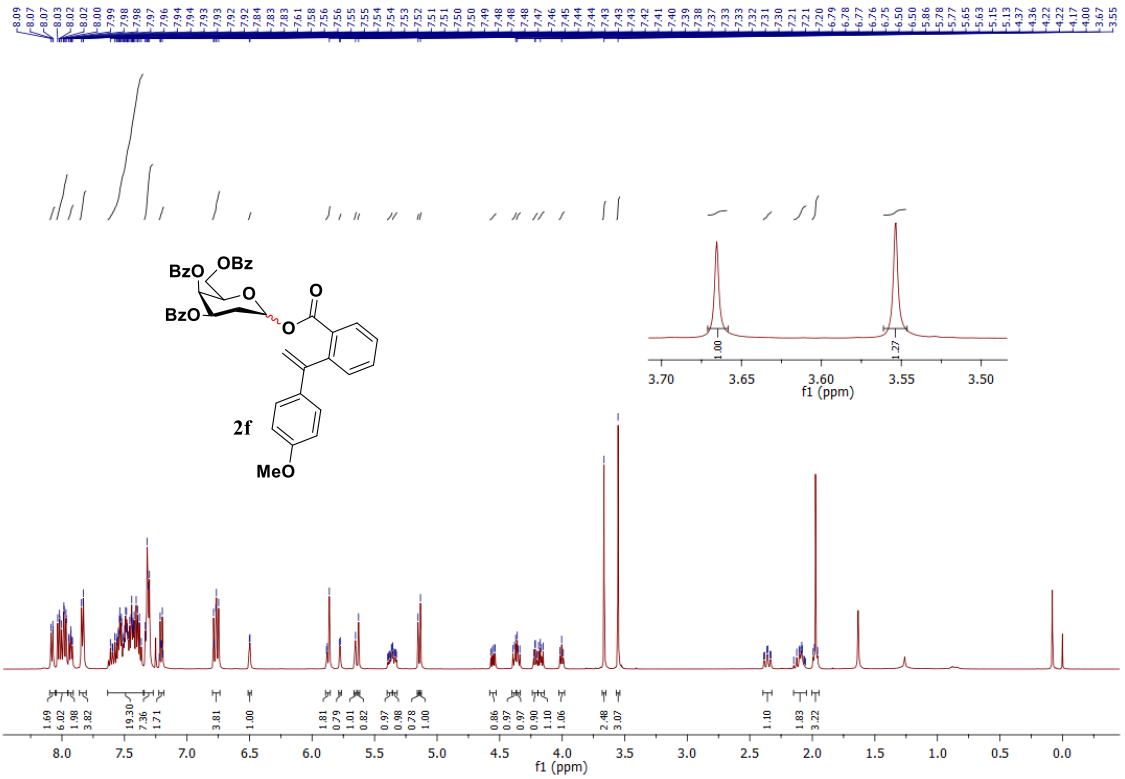
COSY NMR spectrum of compound 2e



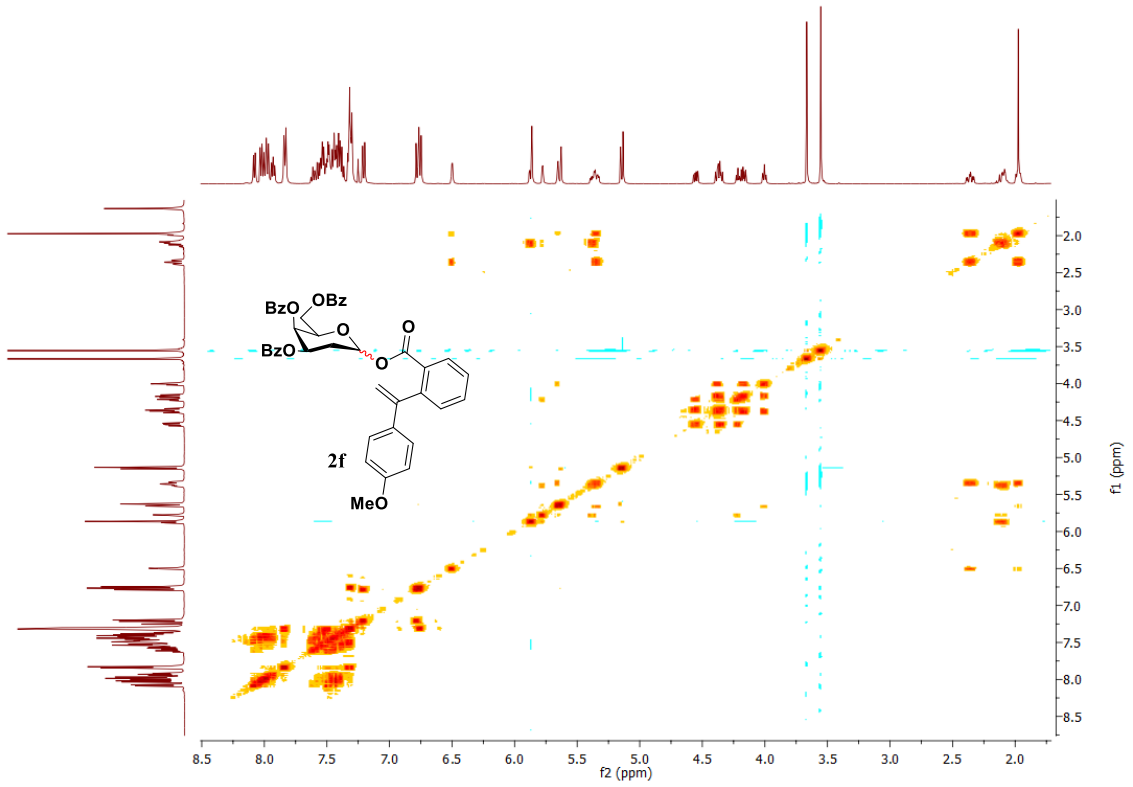
^{13}C NMR spectrum of compound 2e



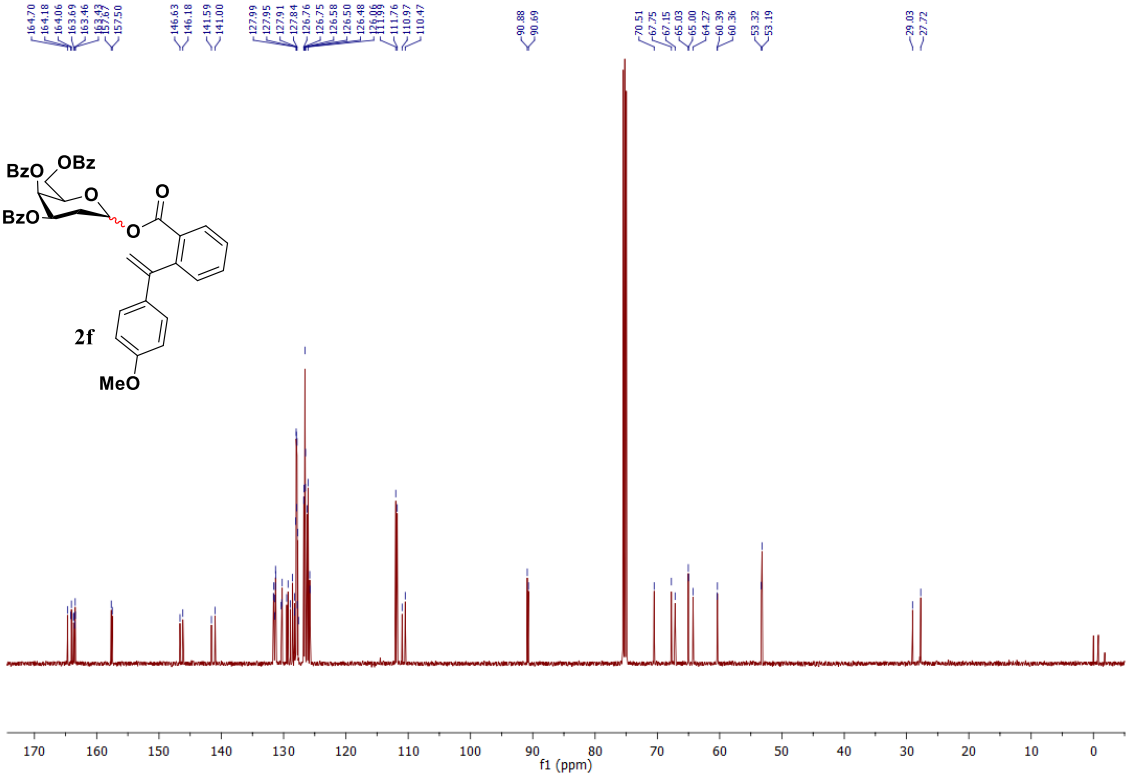
^{1}H NMR spectrum of compound 2f



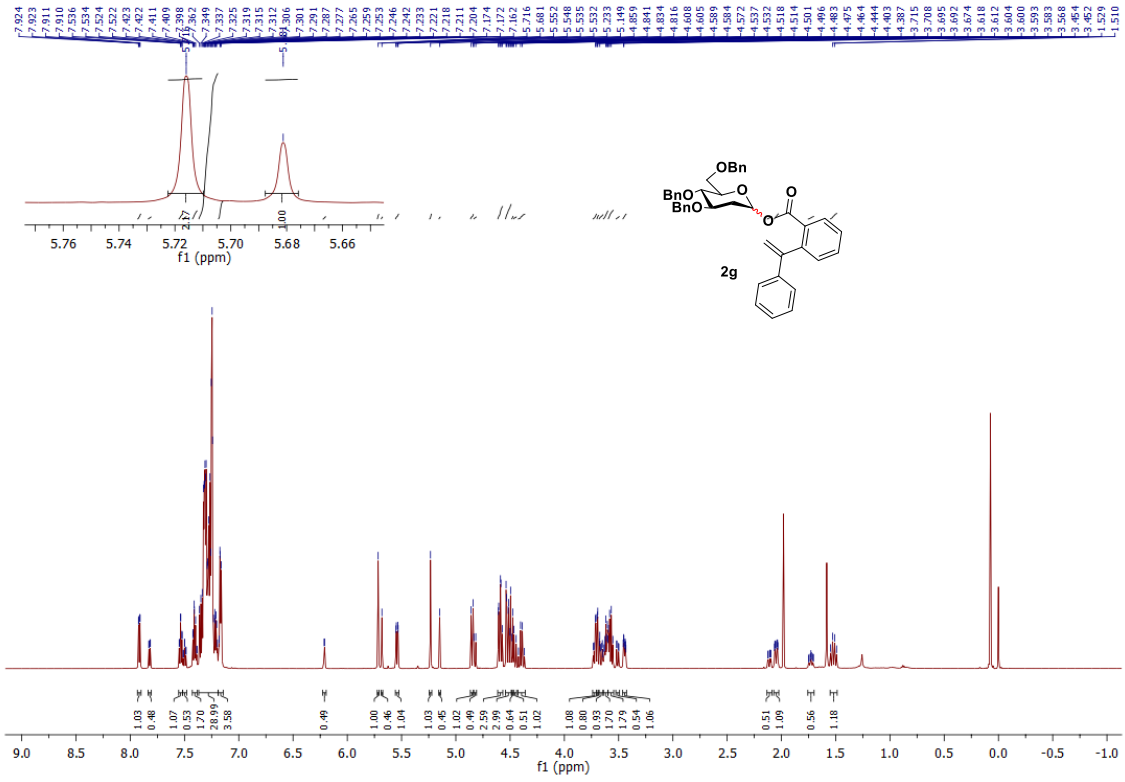
COSY NMR spectrum of compound 2f



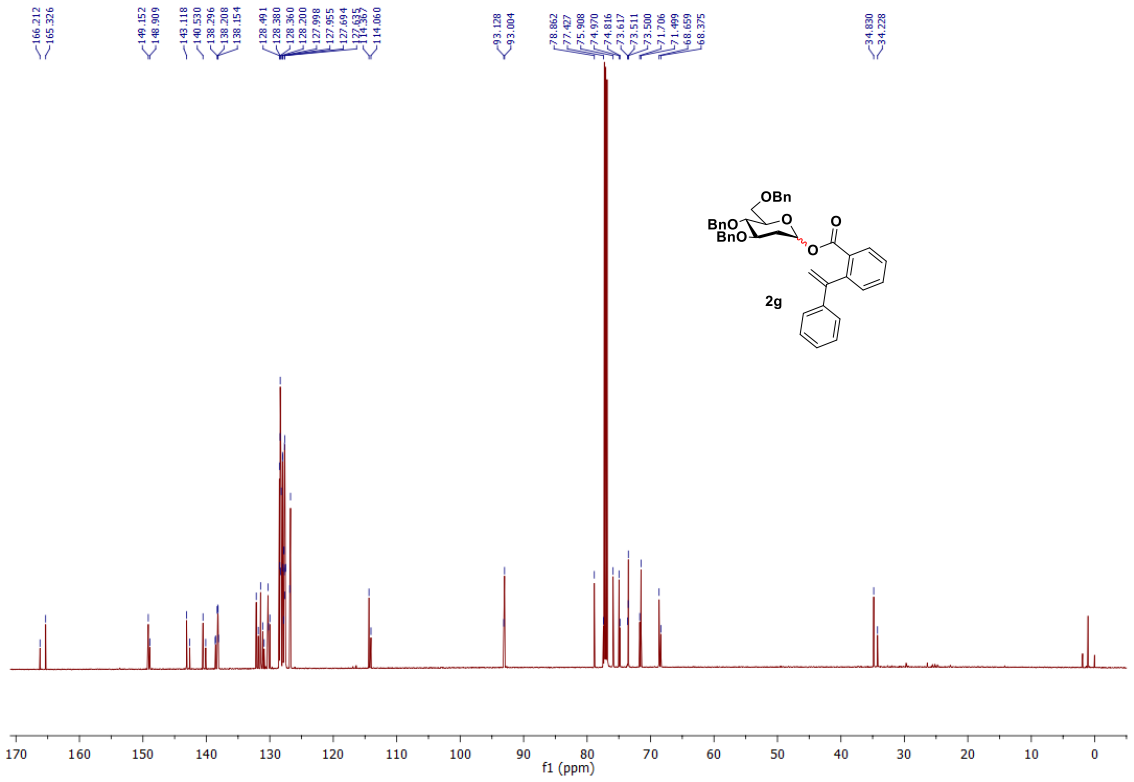
^{13}C NMR spectrum of compound 2f



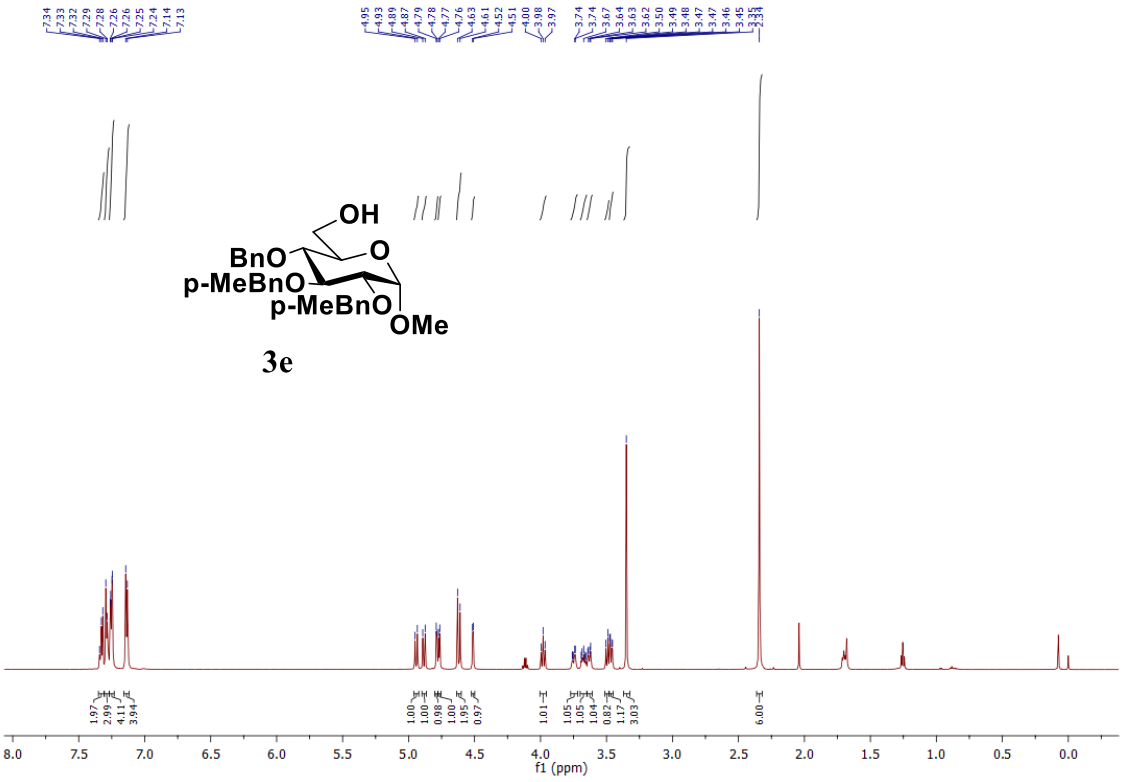
^{1}H NMR spectrum of compound 2g



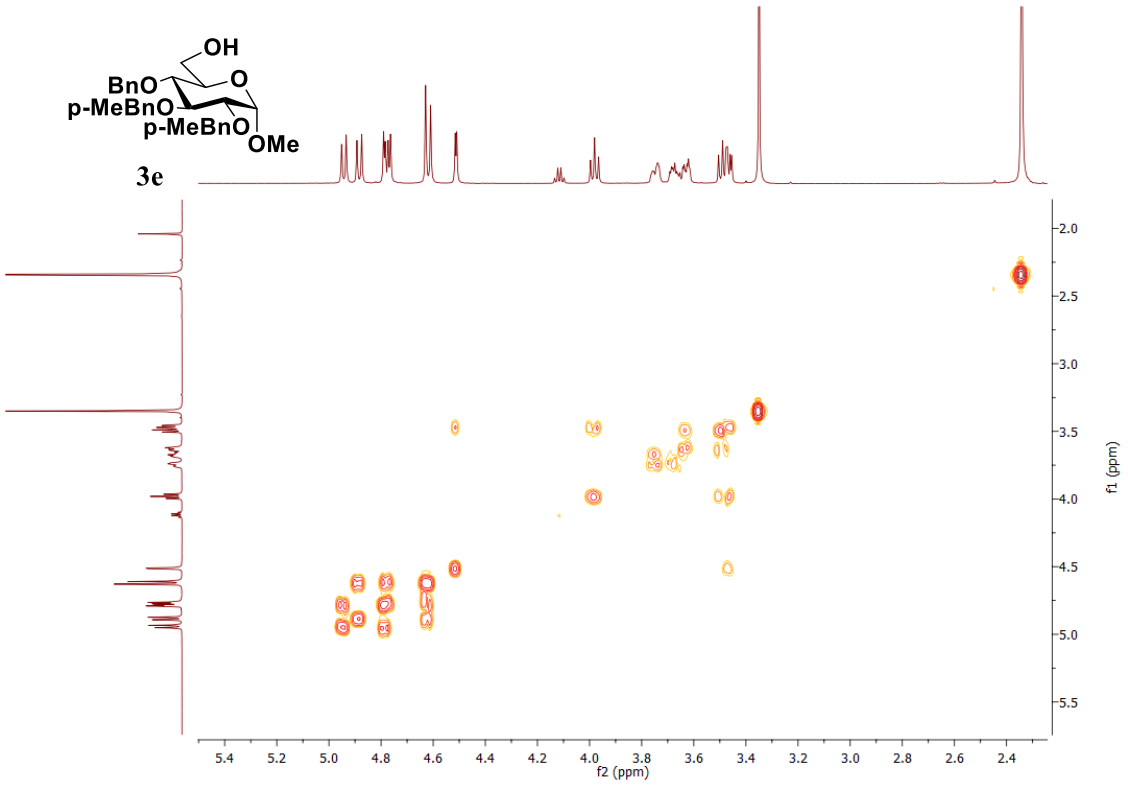
^{13}C NMR spectrum of compound 2g



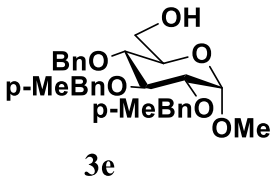
^{1}H NMR spectrum of compound 3e

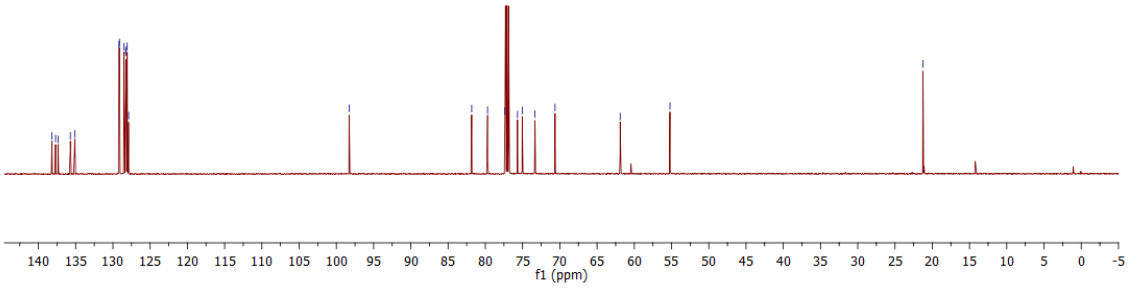


COSY NMR spectrum of compound 3e

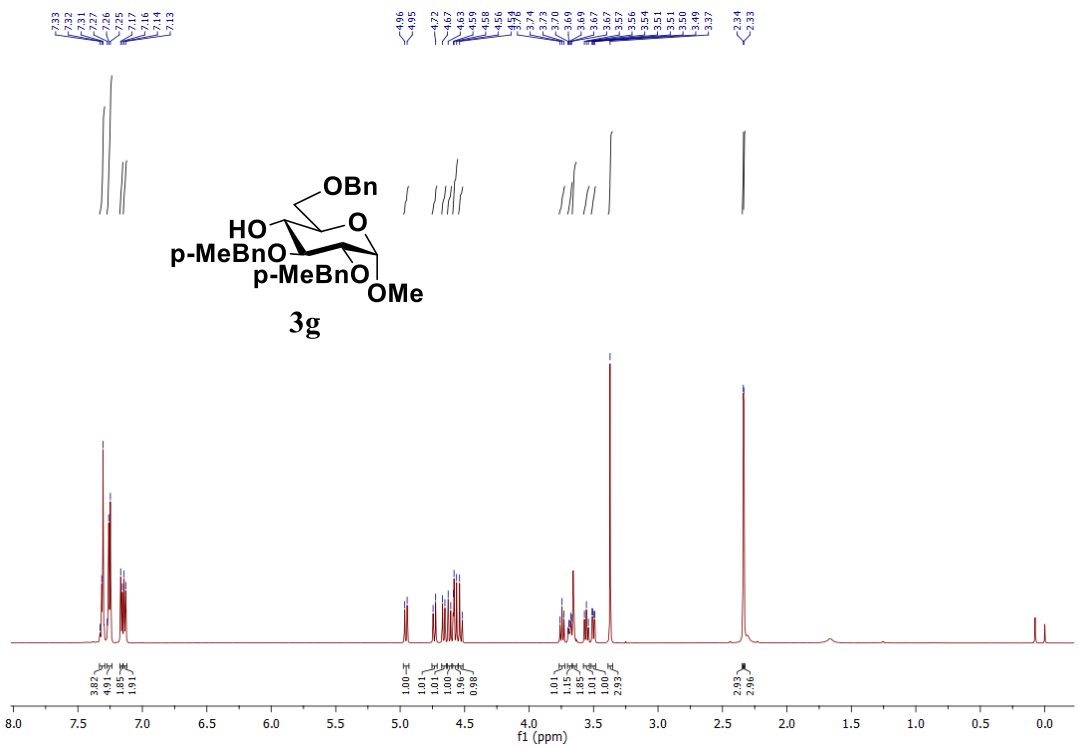


^{13}C NMR spectrum of compound 3e

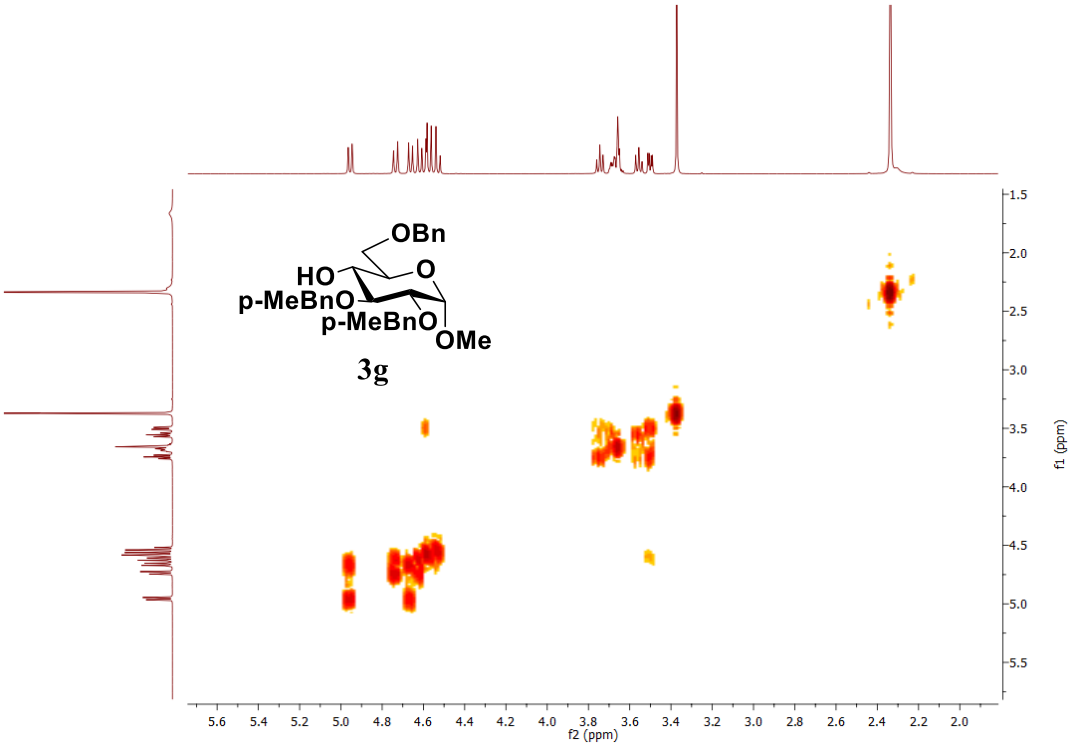




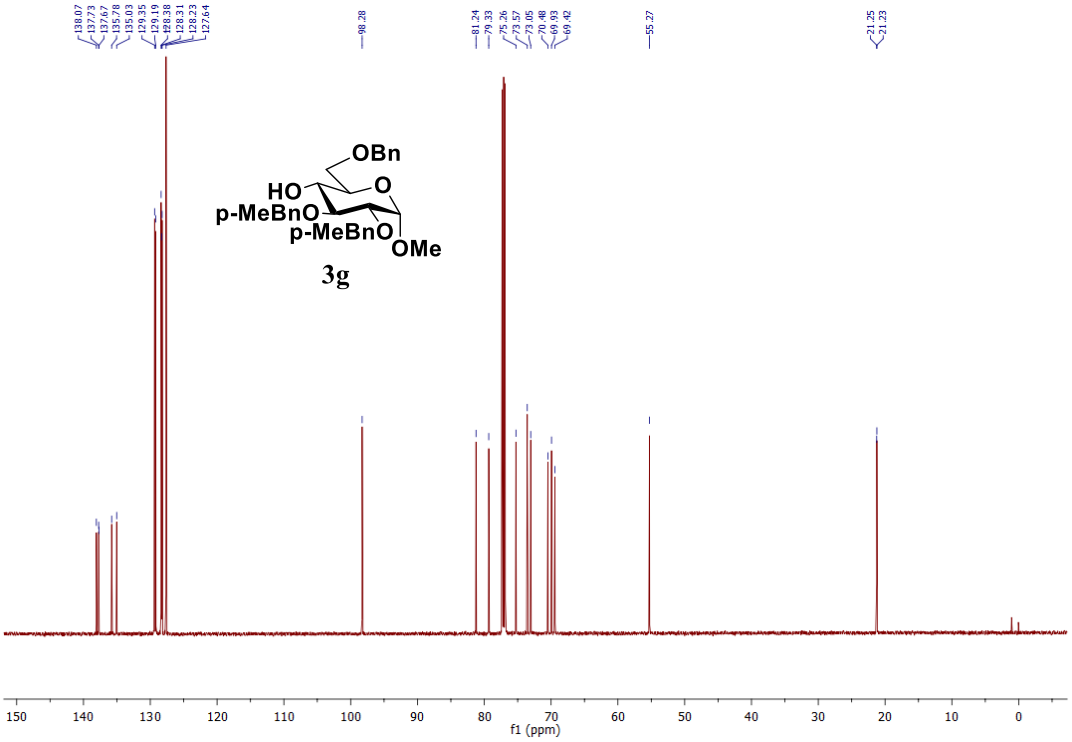
^{1}H NMR spectrum of compound 3g



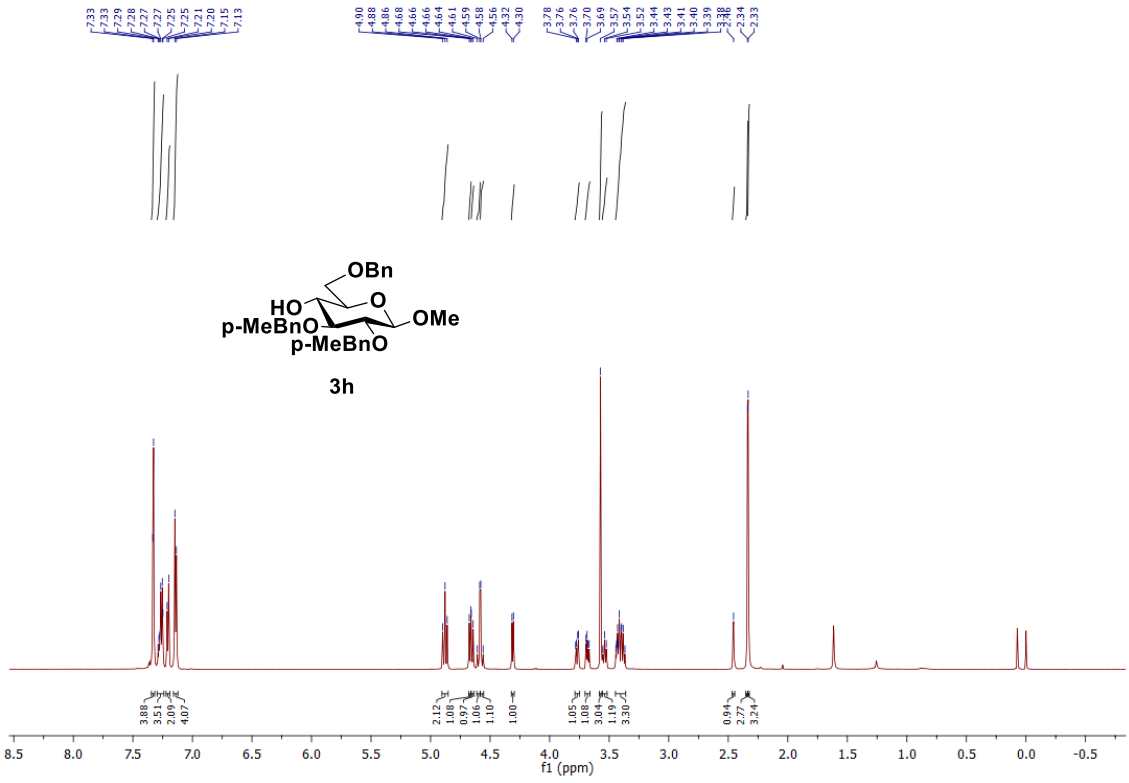
COSY NMR spectrum of compound 3g



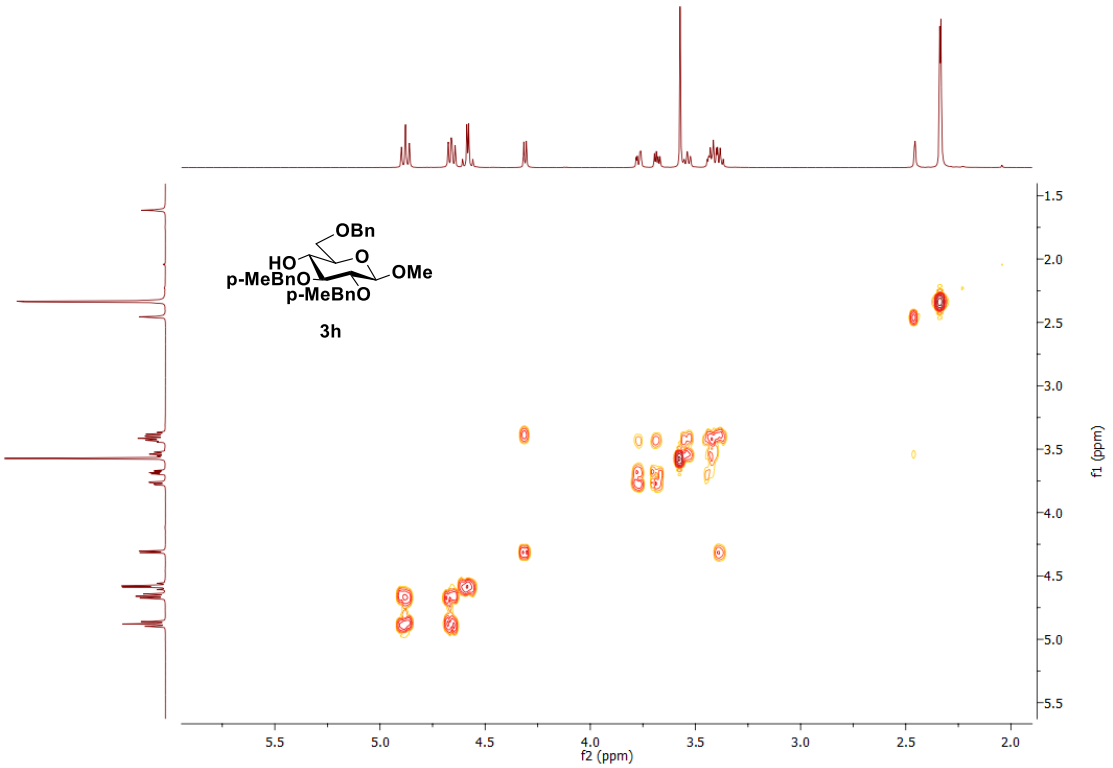
^{13}C NMR spectrum of compound 3g



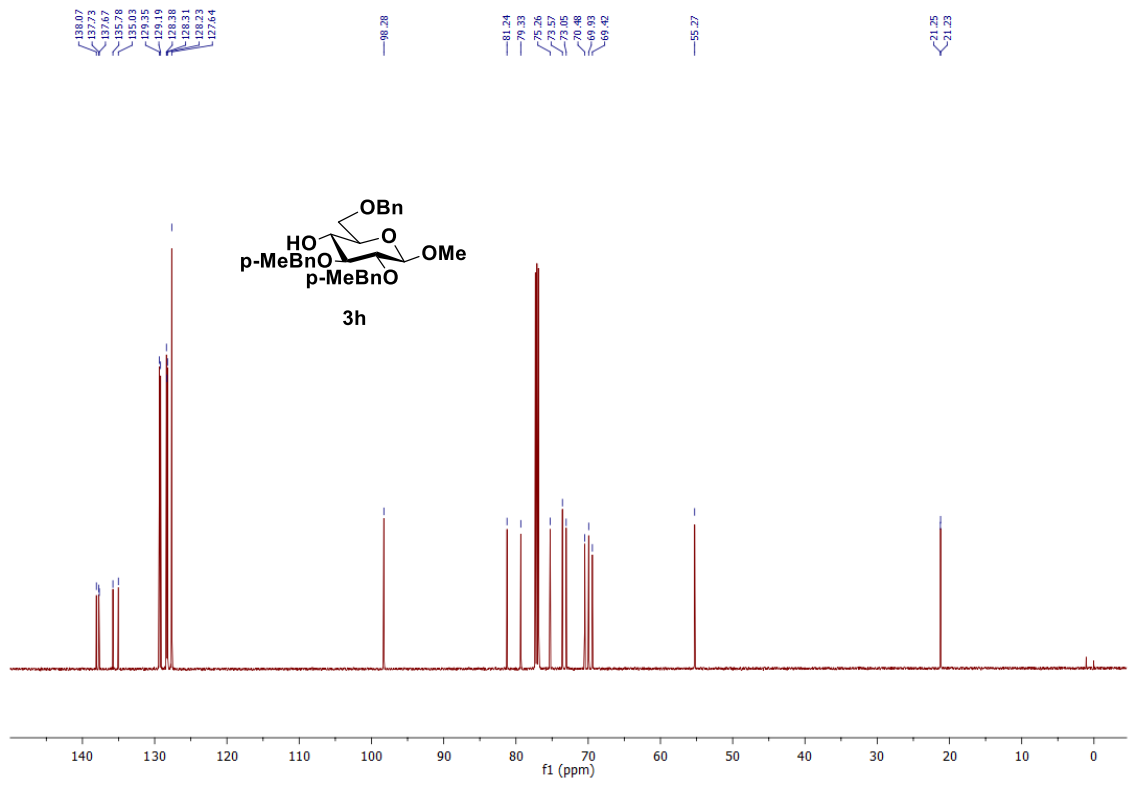
^{1}H NMR spectrum of compound 3h



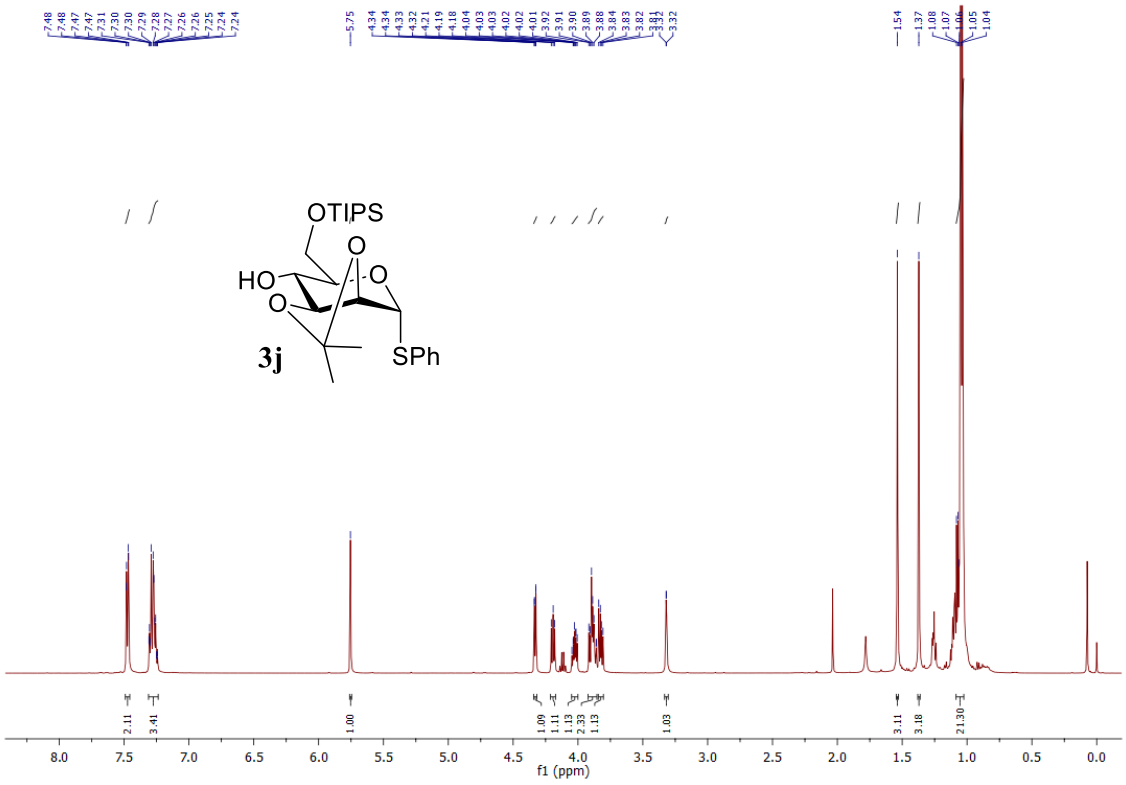
COSY NMR spectrum of compound 3h



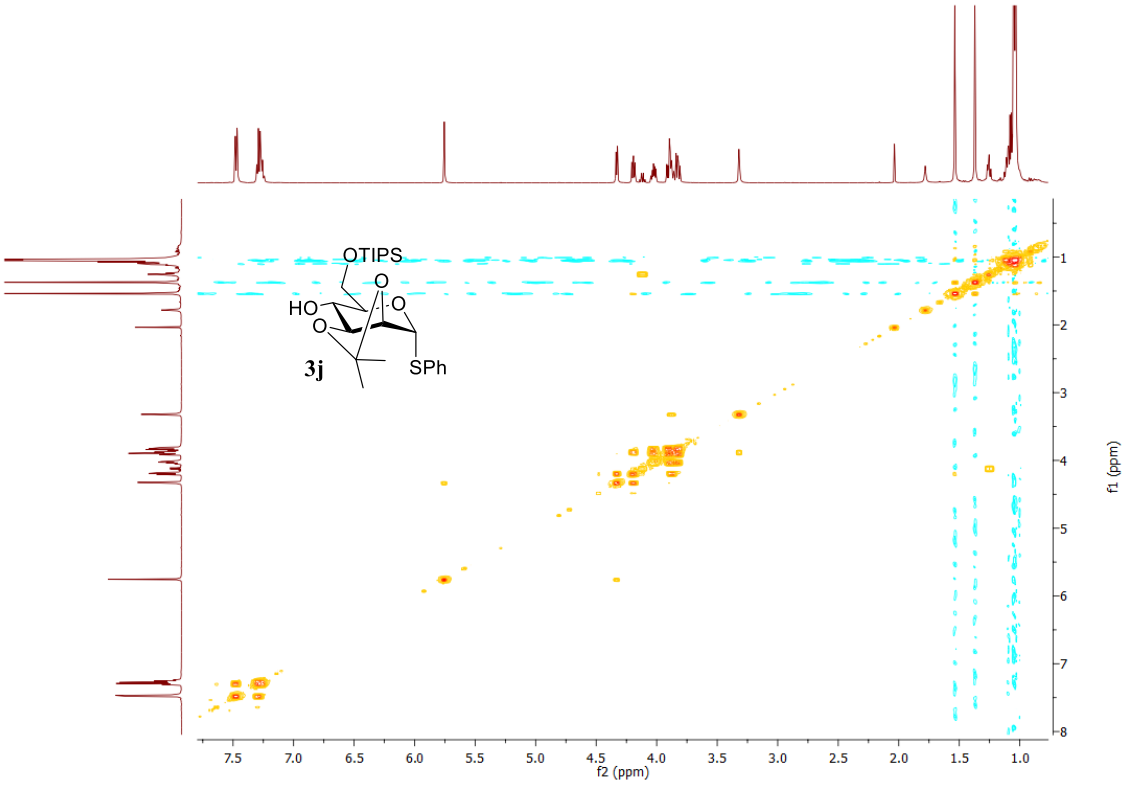
^{13}C NMR spectrum of compound 3h



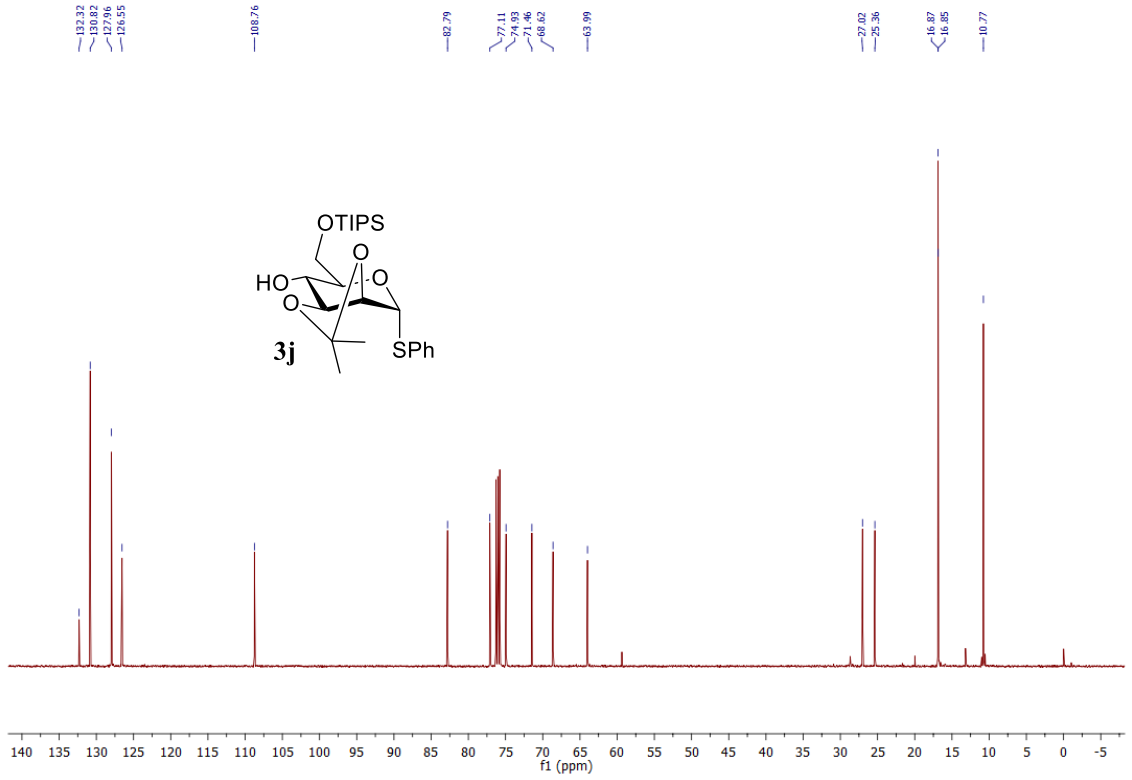
^{1}H NMR spectrum of compound 3j



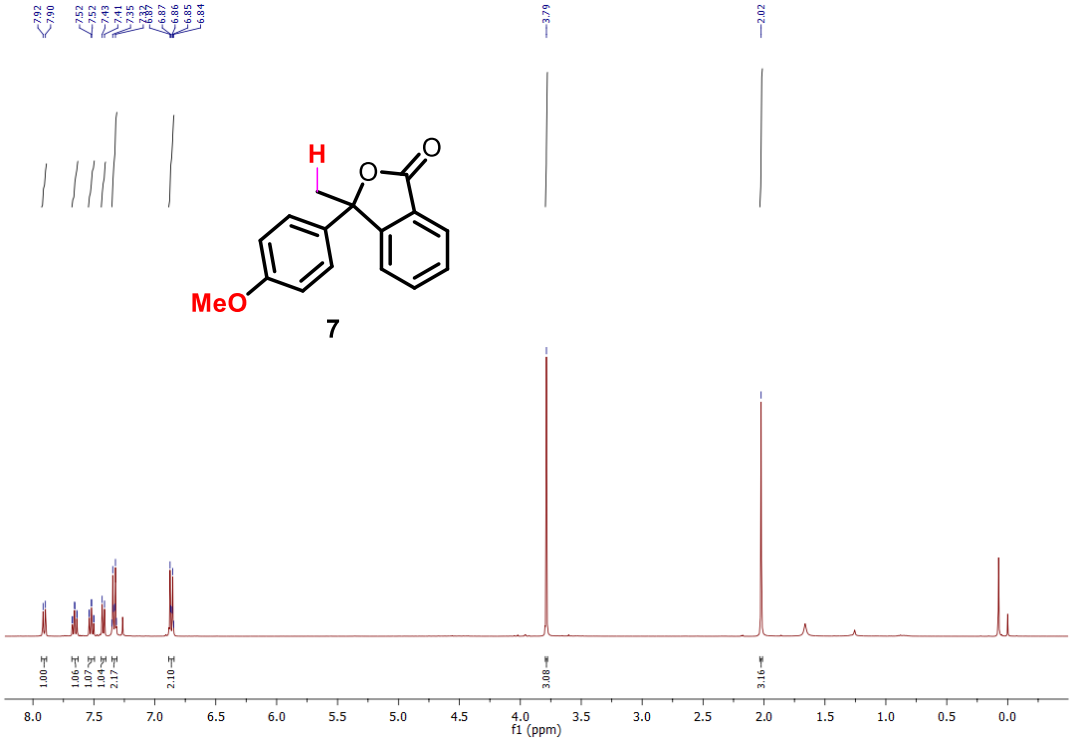
COSY NMR spectrum of compound 3j



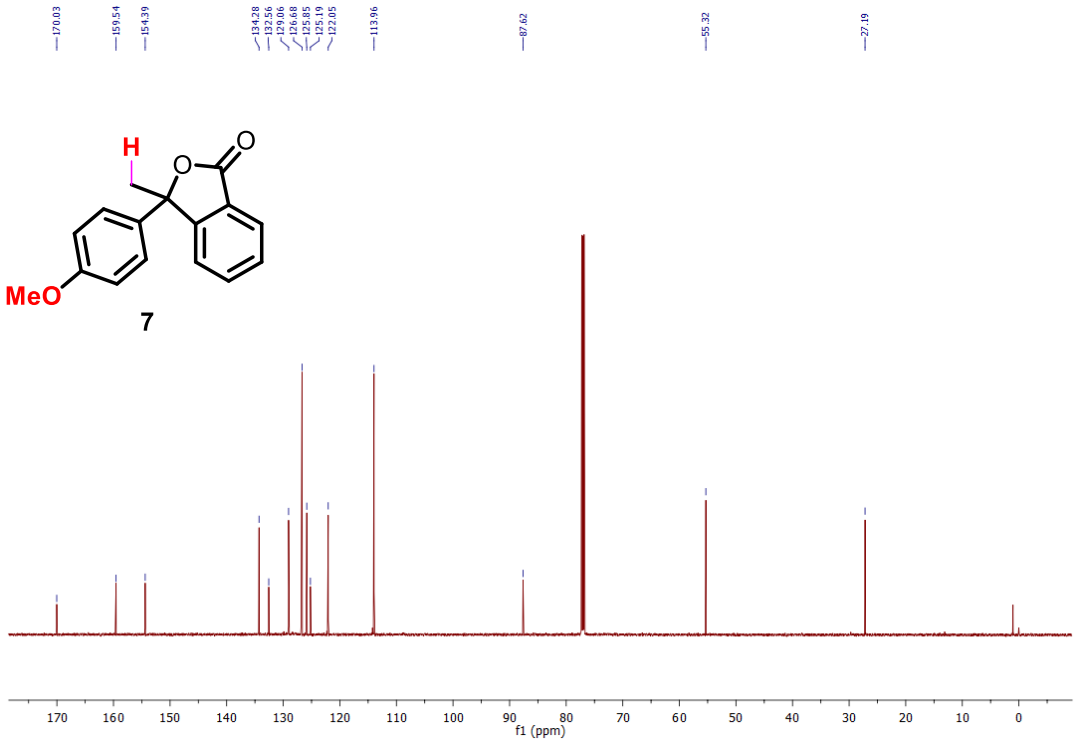
^{13}C NMR spectrum of compound 3j



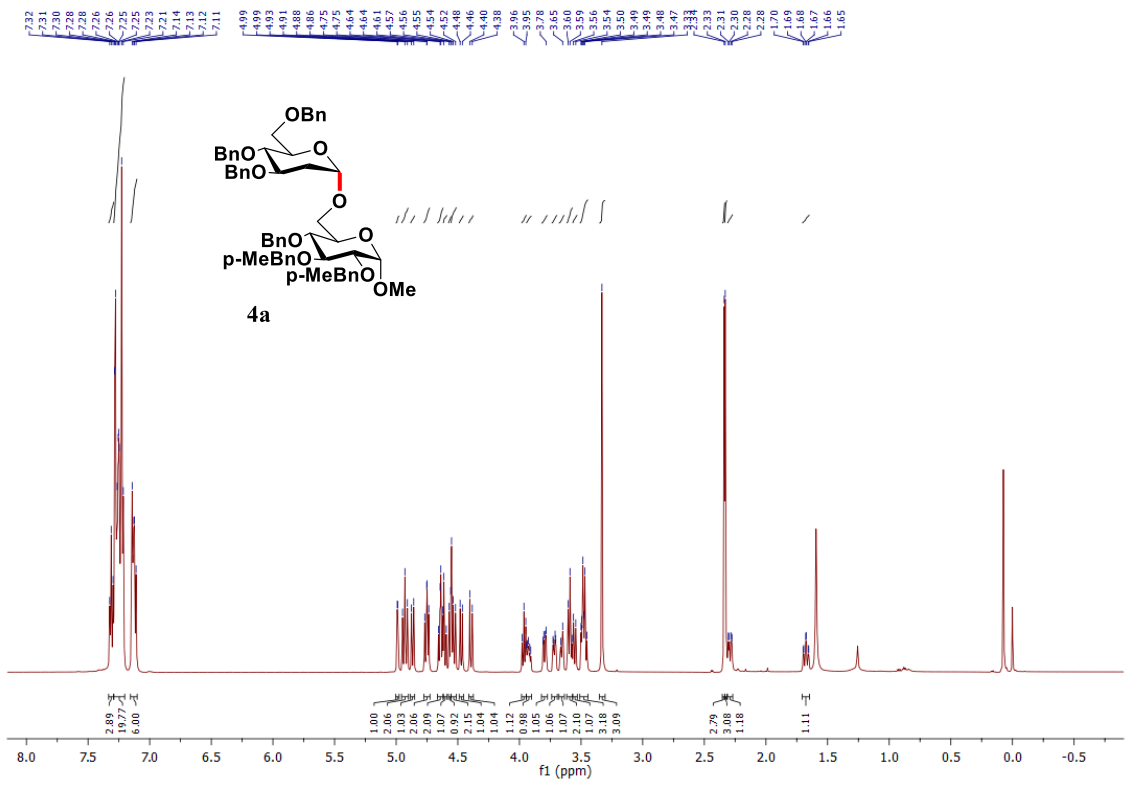
^{1}H NMR spectrum of compound 7



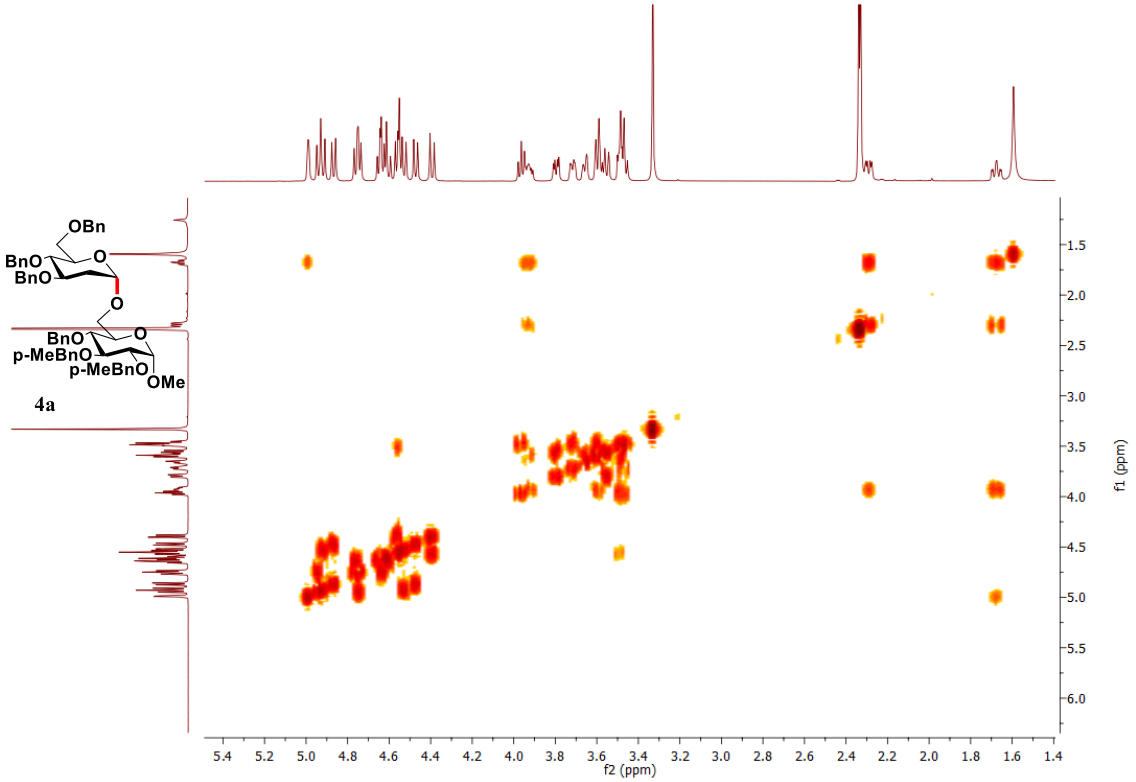
^{13}C NMR spectrum of compound 7



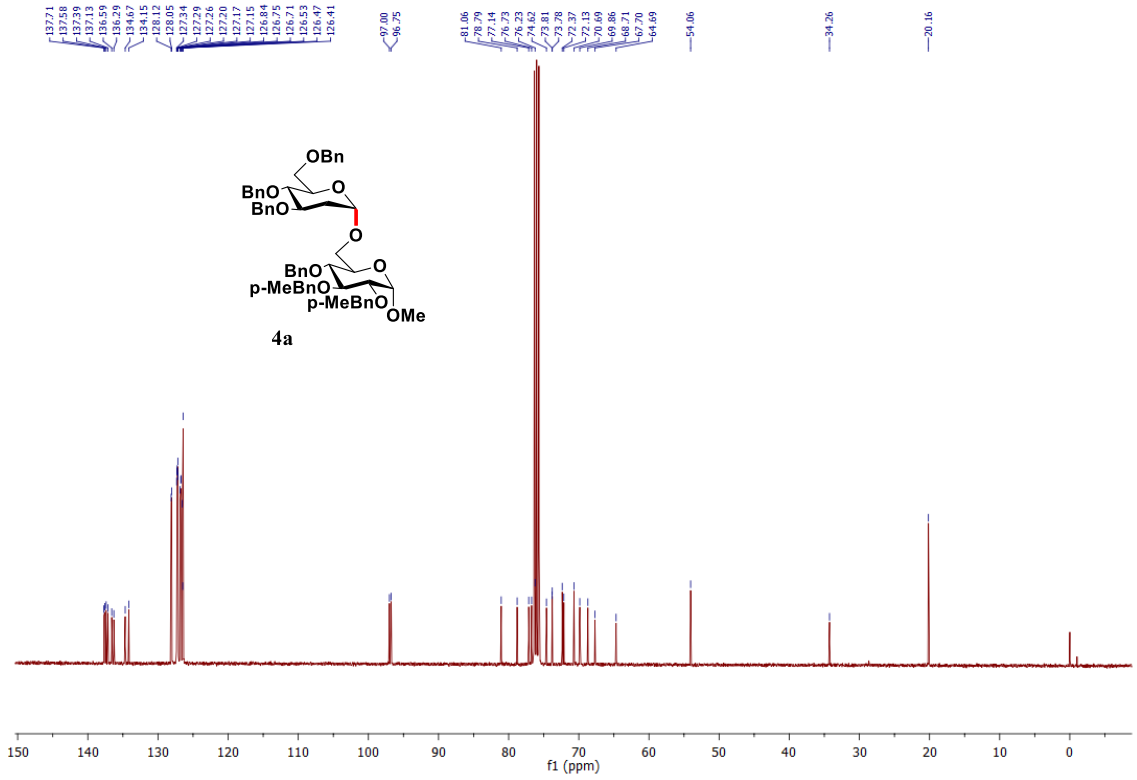
^{1}H NMR spectrum of compound 4a



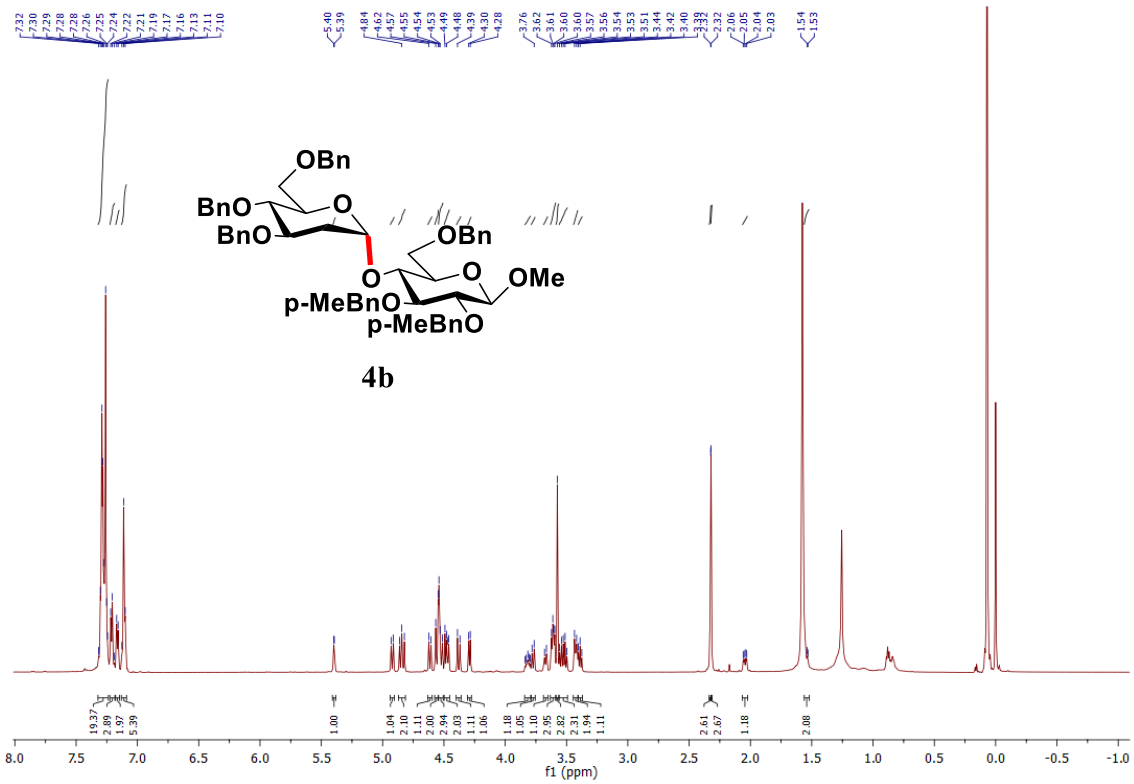
COSY NMR spectrum of compound 4a



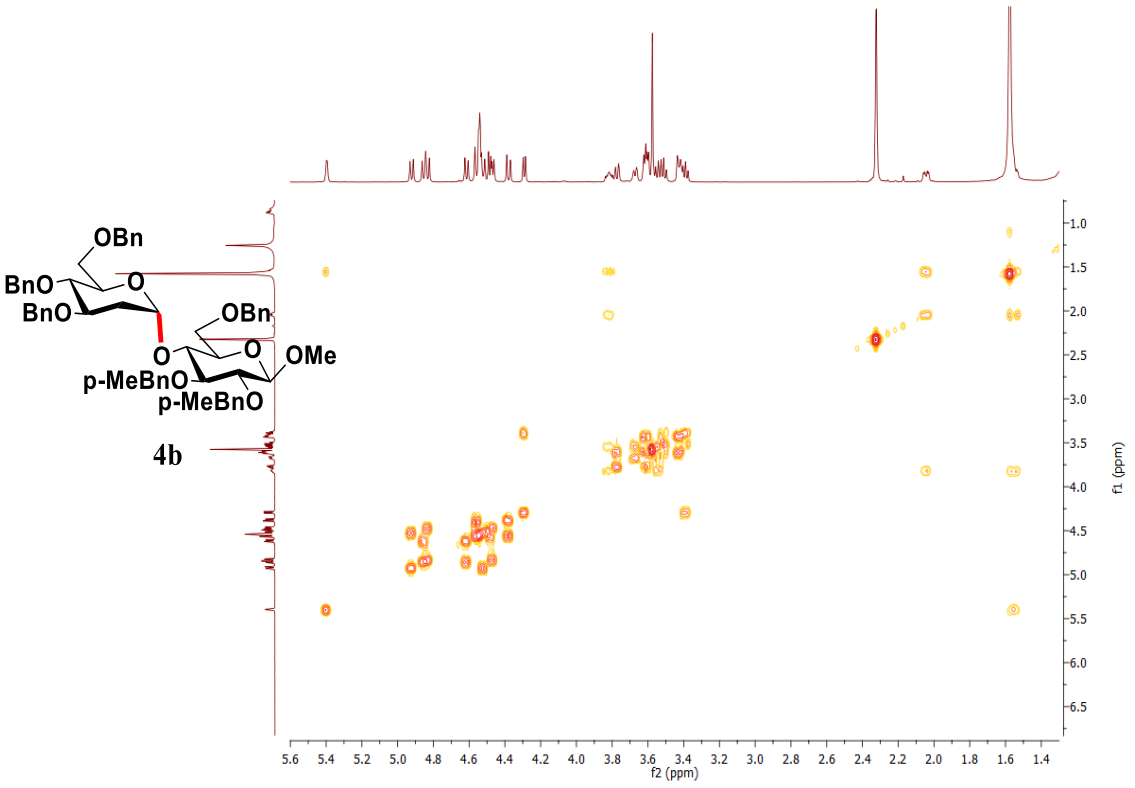
^{13}C NMR spectrum of compound 4a



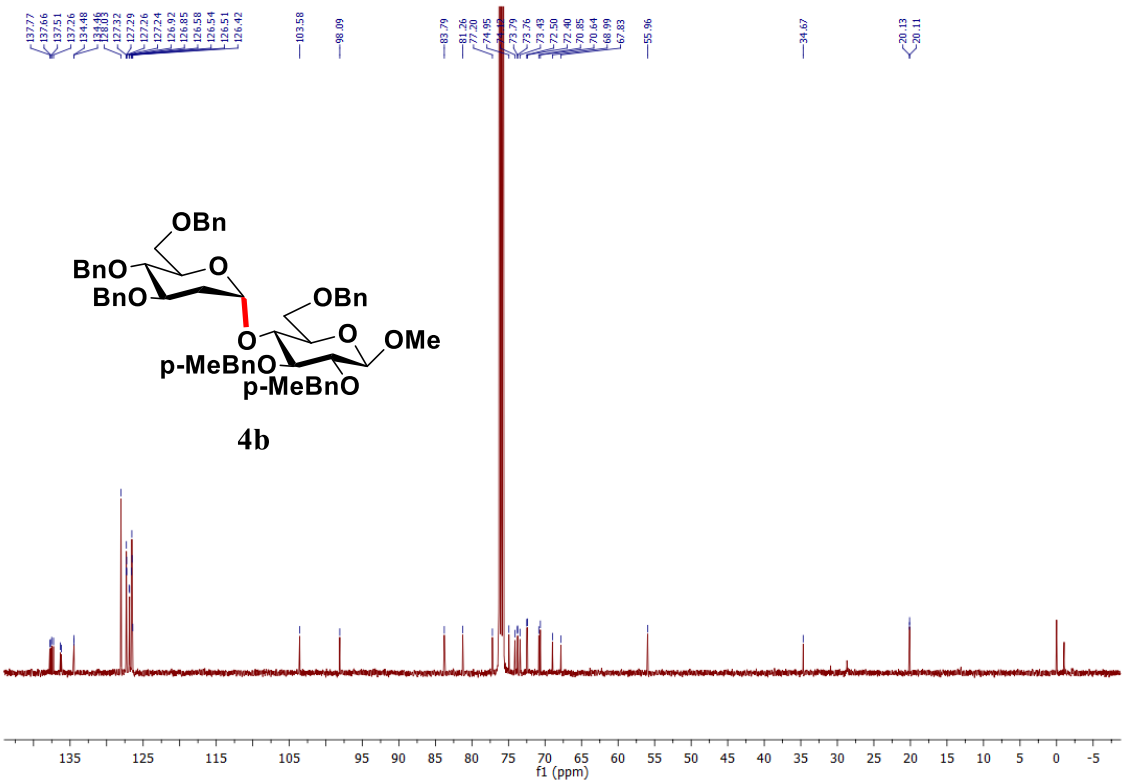
^{1}H NMR spectrum of compound 4b



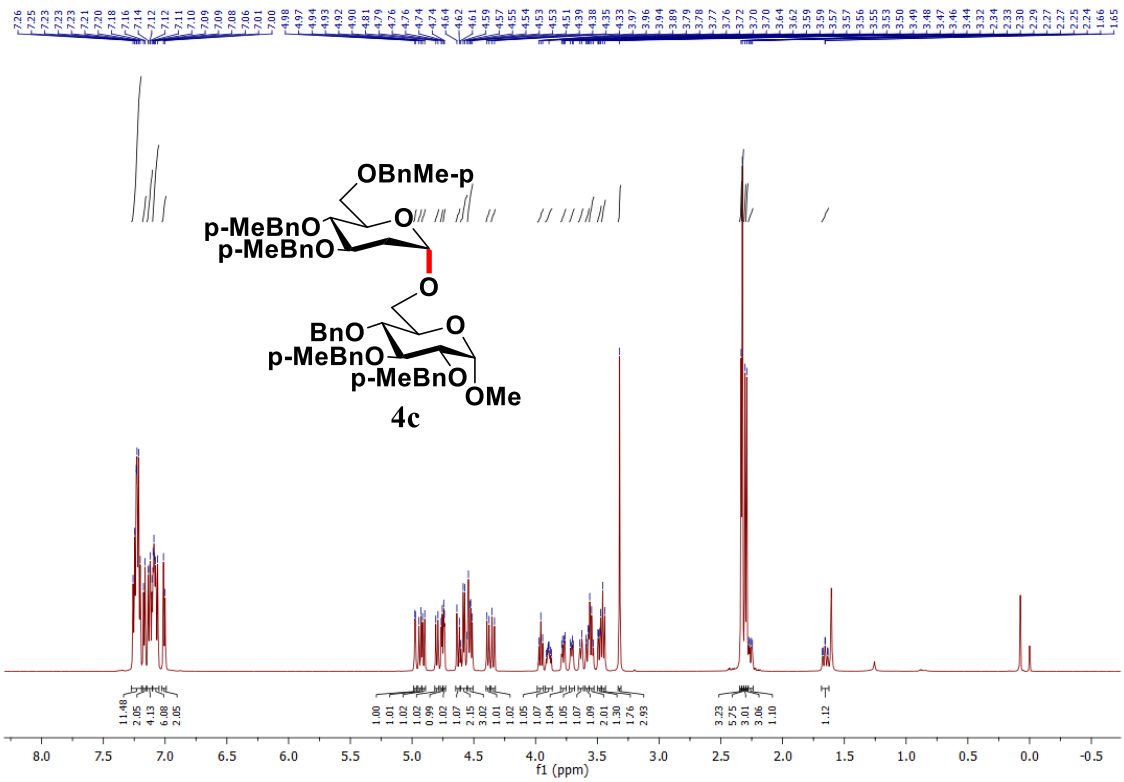
COSY NMR spectrum of compound 4b



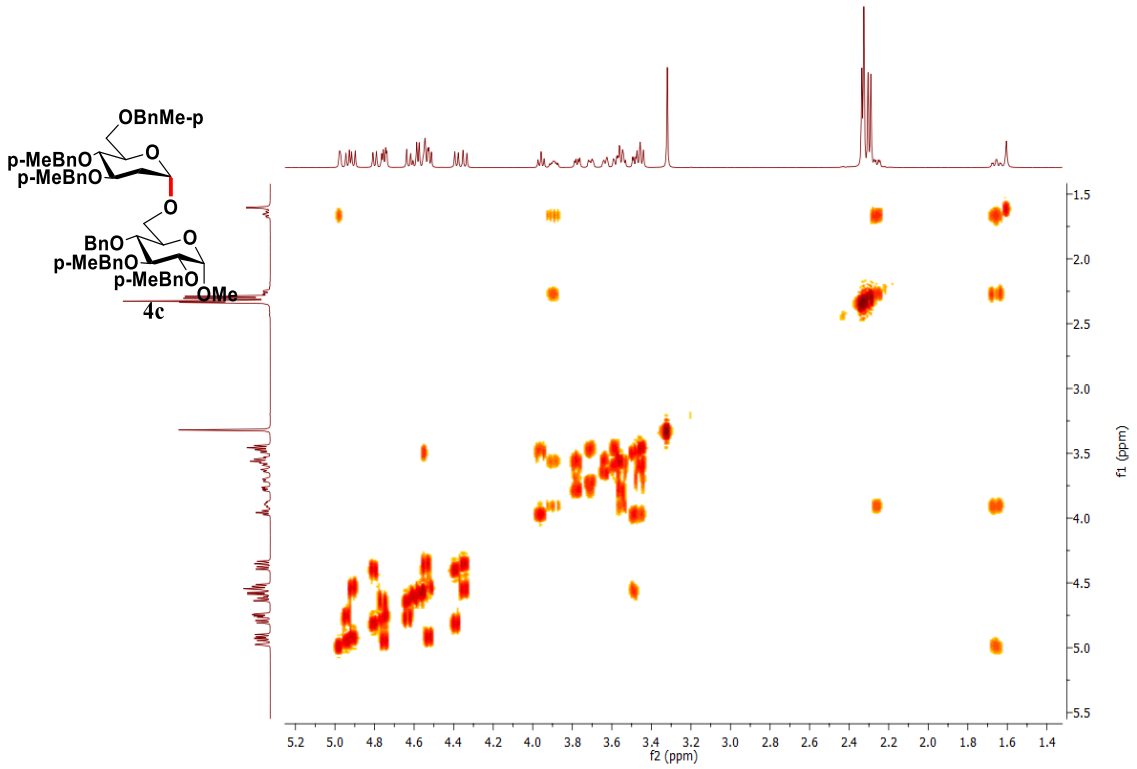
^{13}C NMR spectrum of compound 4b



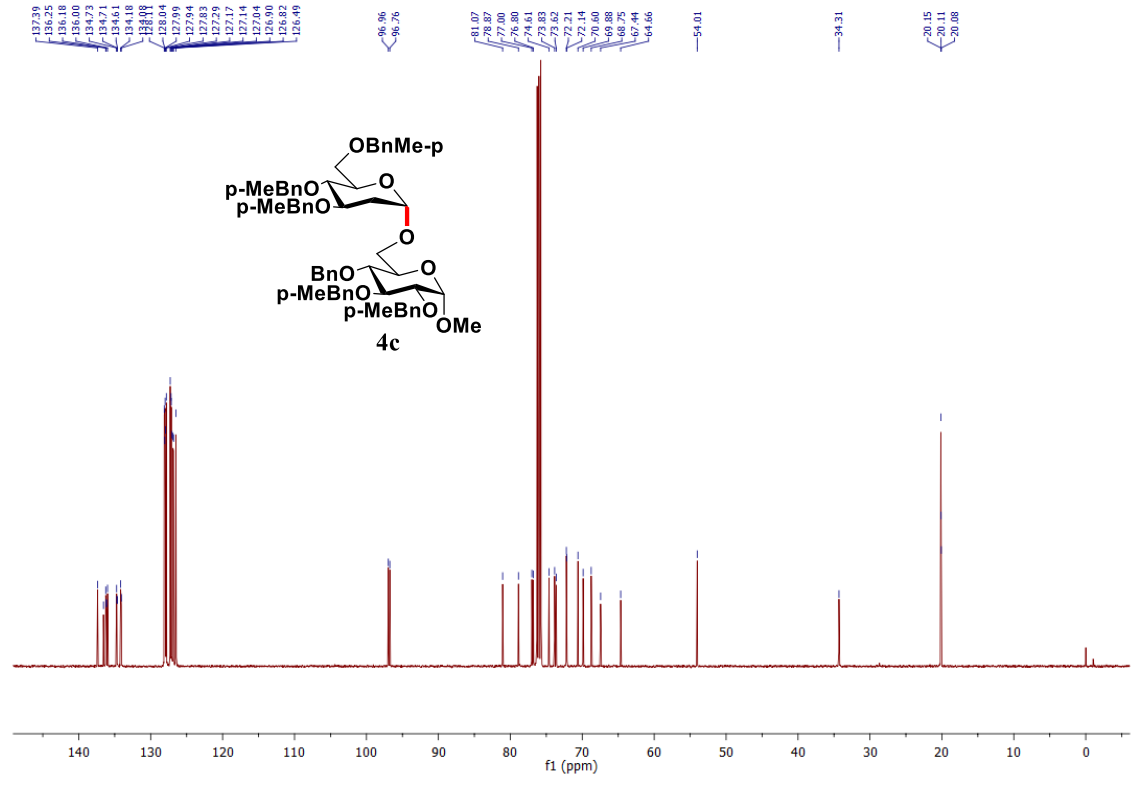
^{1}H NMR spectrum of compound 4c



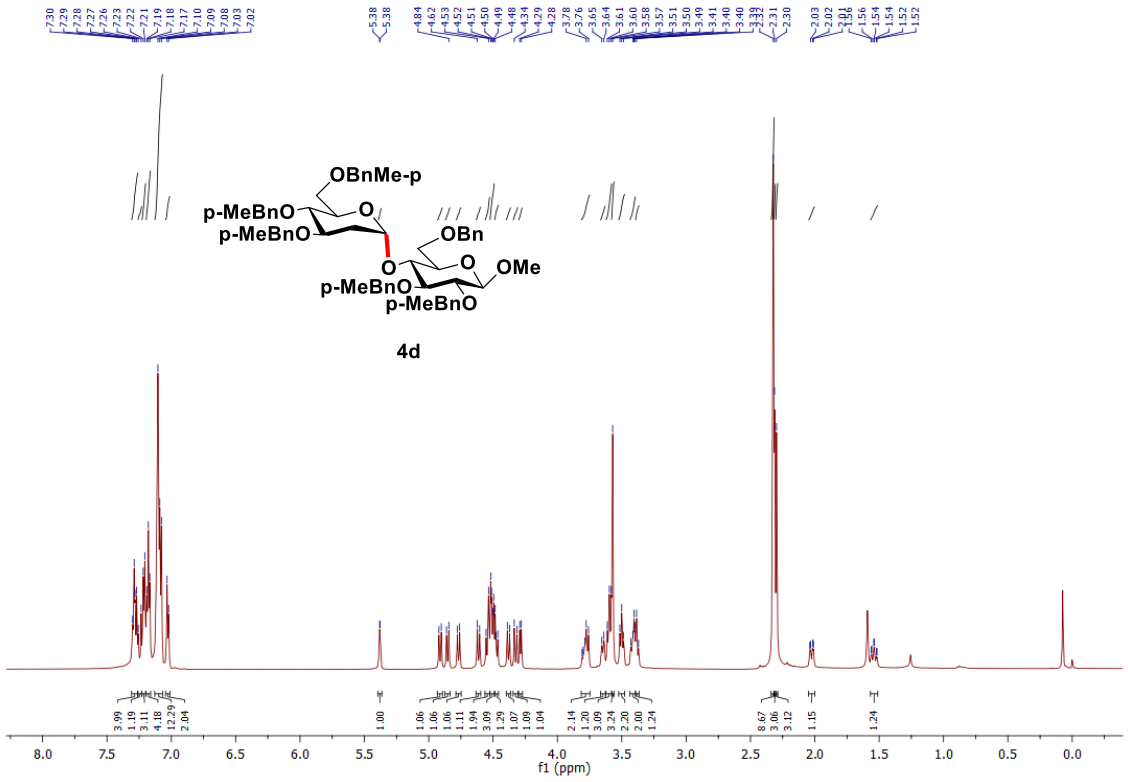
COSY NMR spectrum of compound 4c



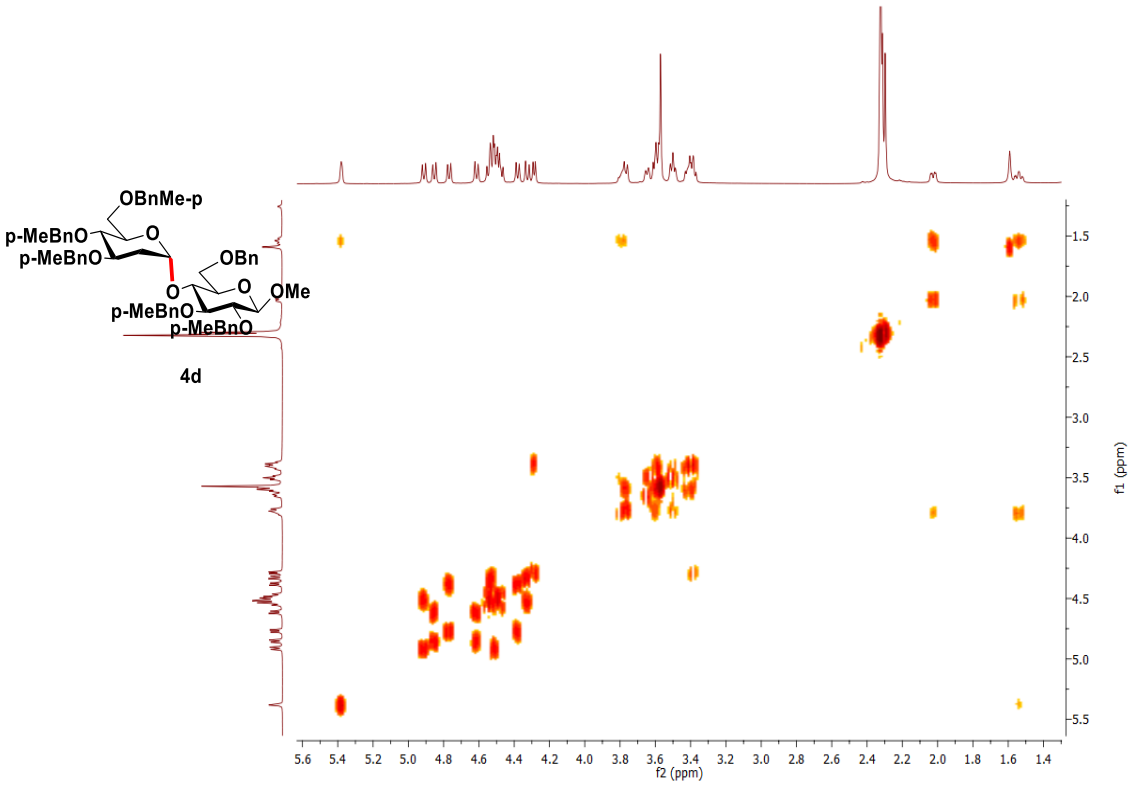
^{13}C NMR spectrum of compound 4c



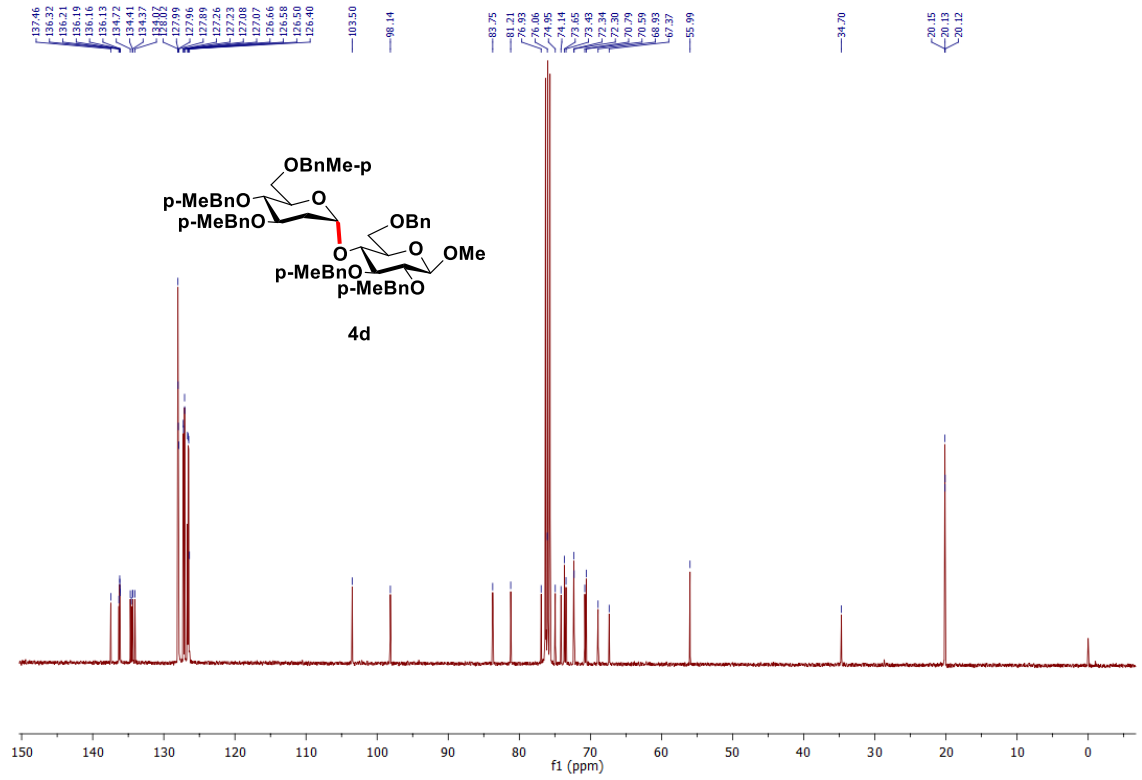
^{1}H NMR spectrum of compound 4d



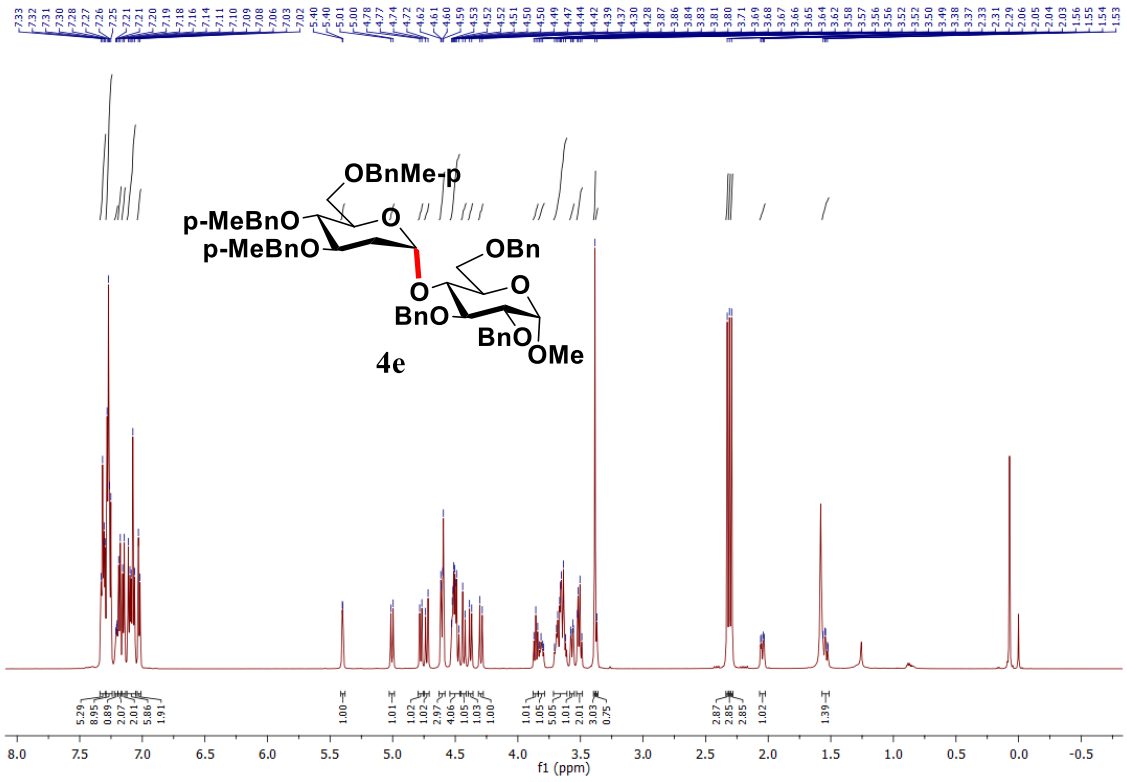
COSY NMR spectrum of compound 4d



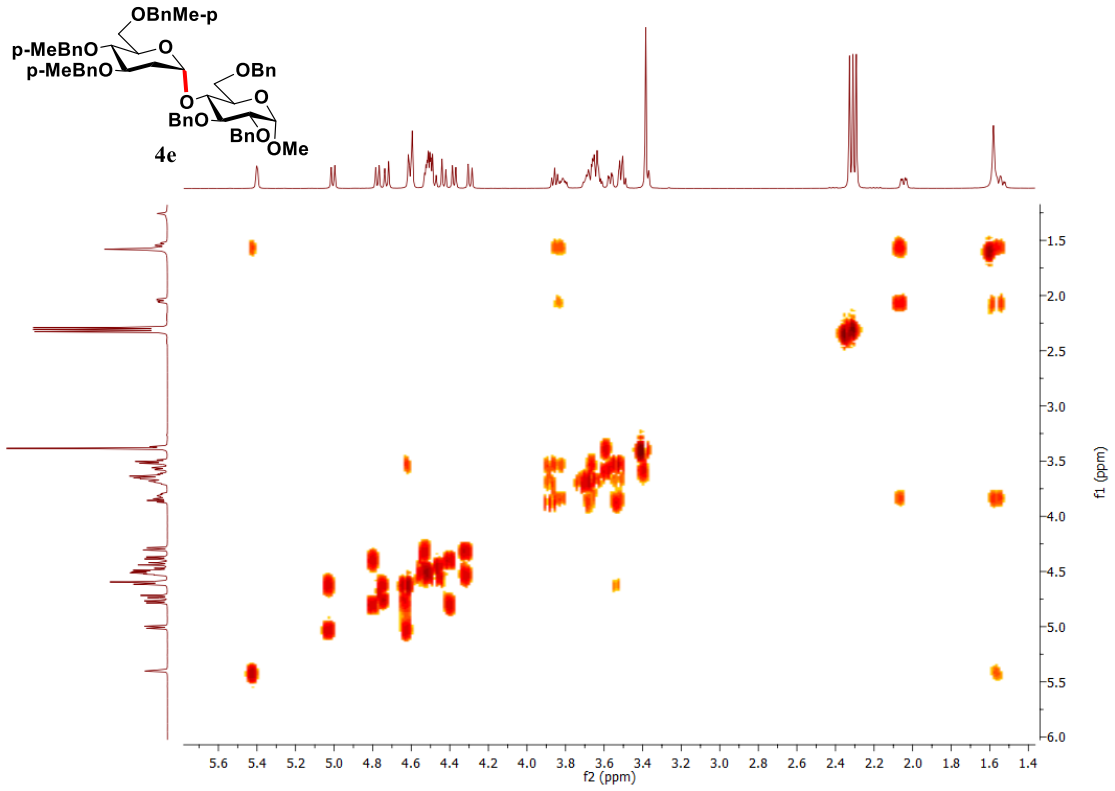
^{13}C NMR spectrum of compound 4d



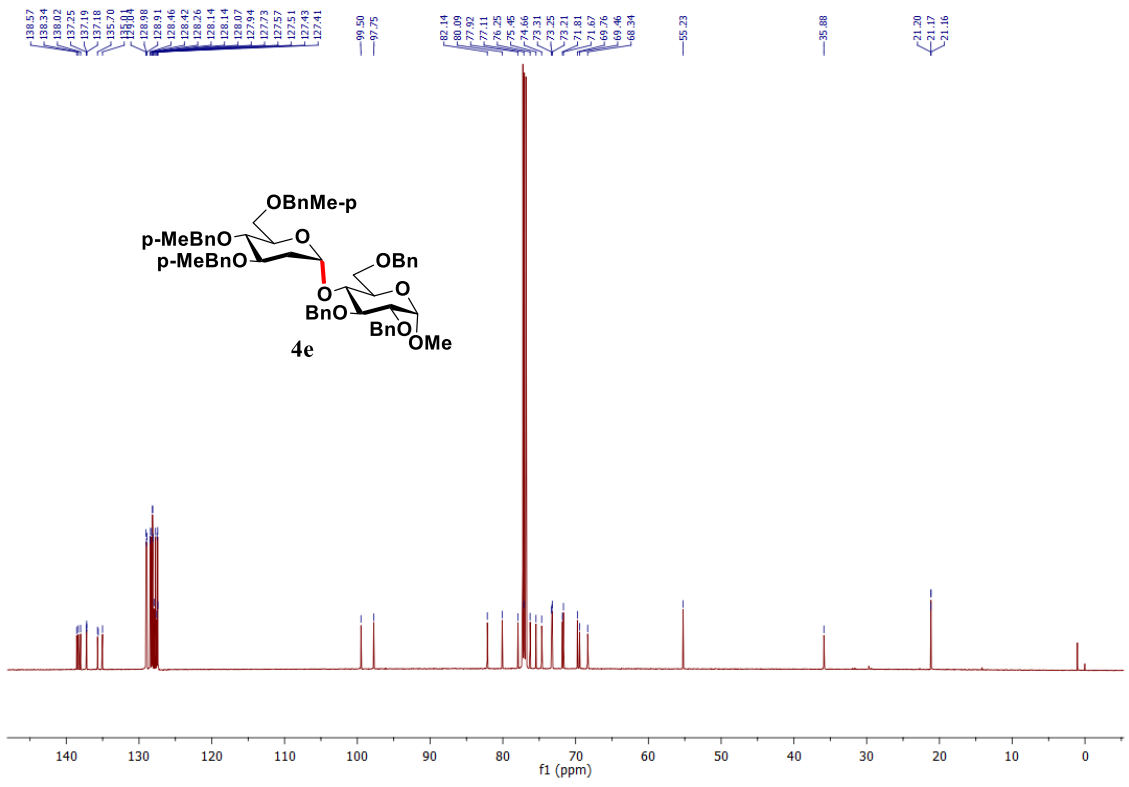
^{1}H NMR spectrum of compound 4e



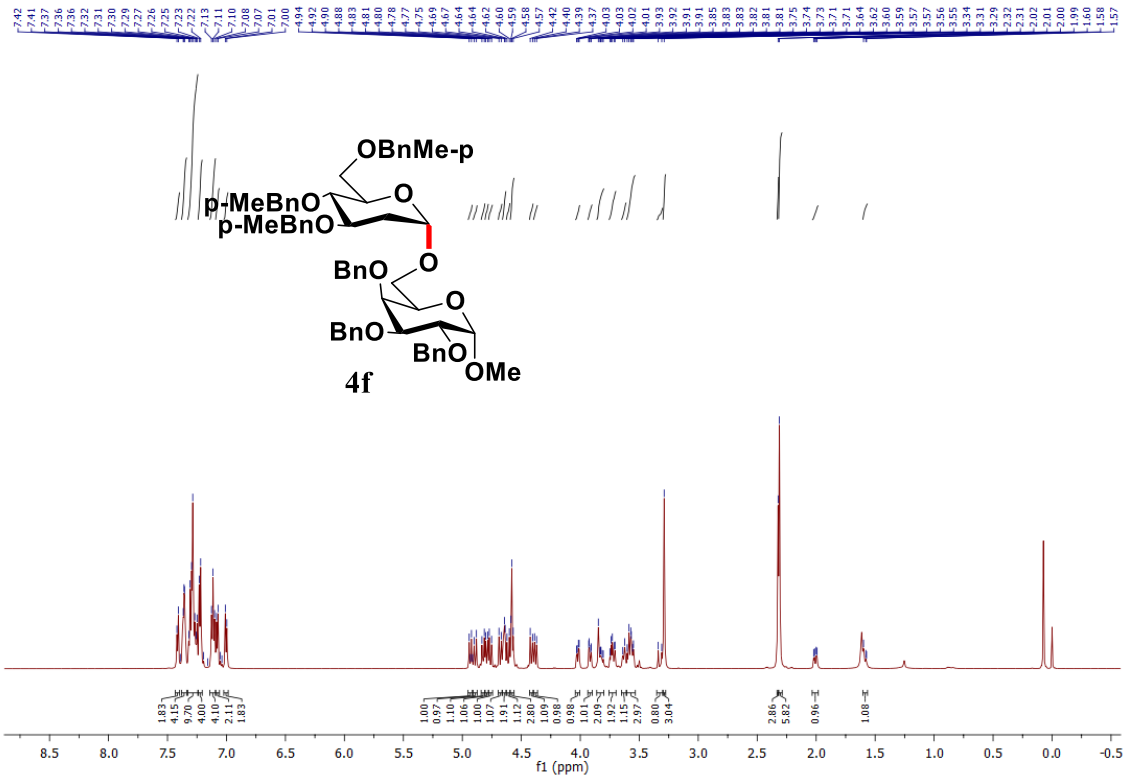
COSY NMR spectrum of compound 4e



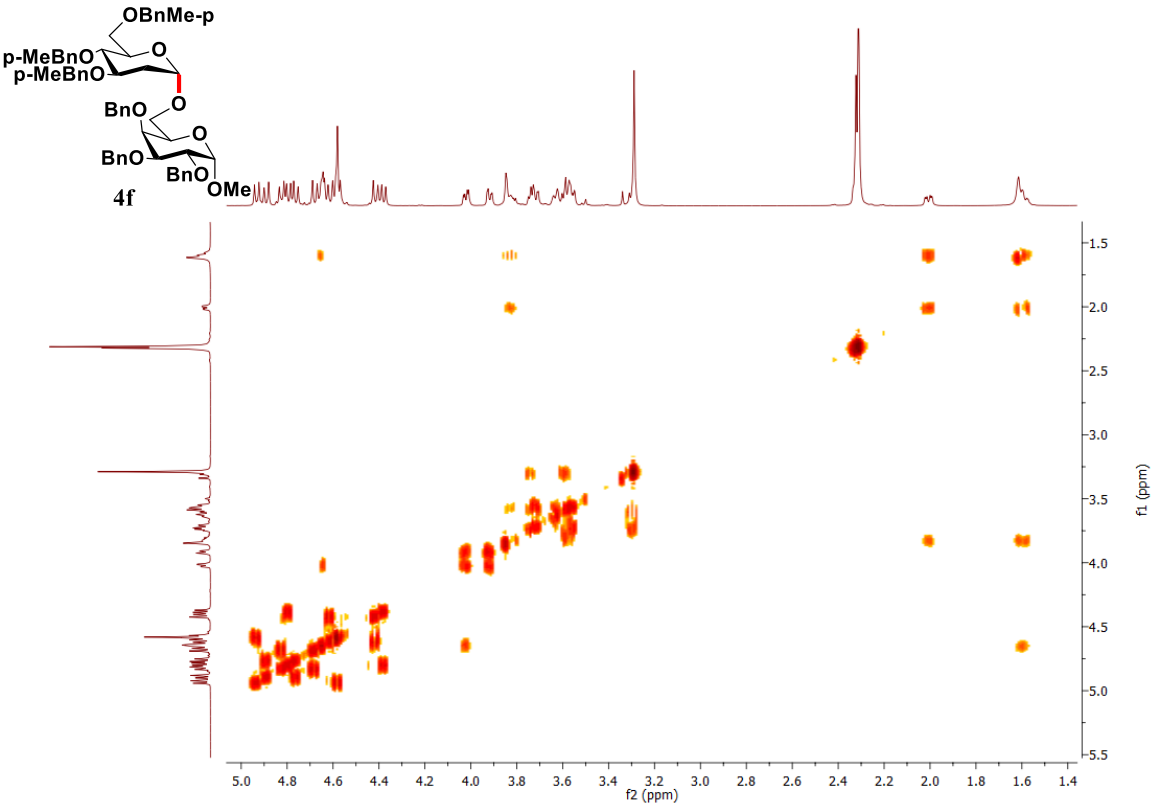
^{13}C NMR spectrum of compound 4e



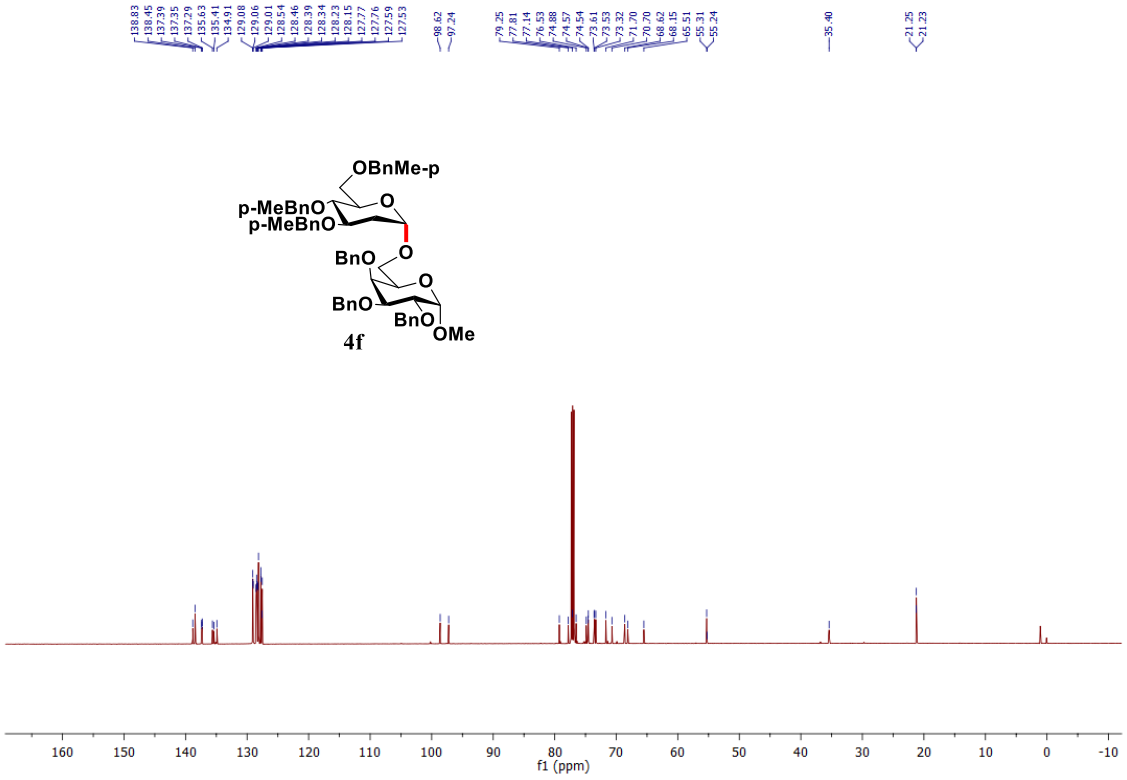
^{1}H NMR spectrum of compound 4f



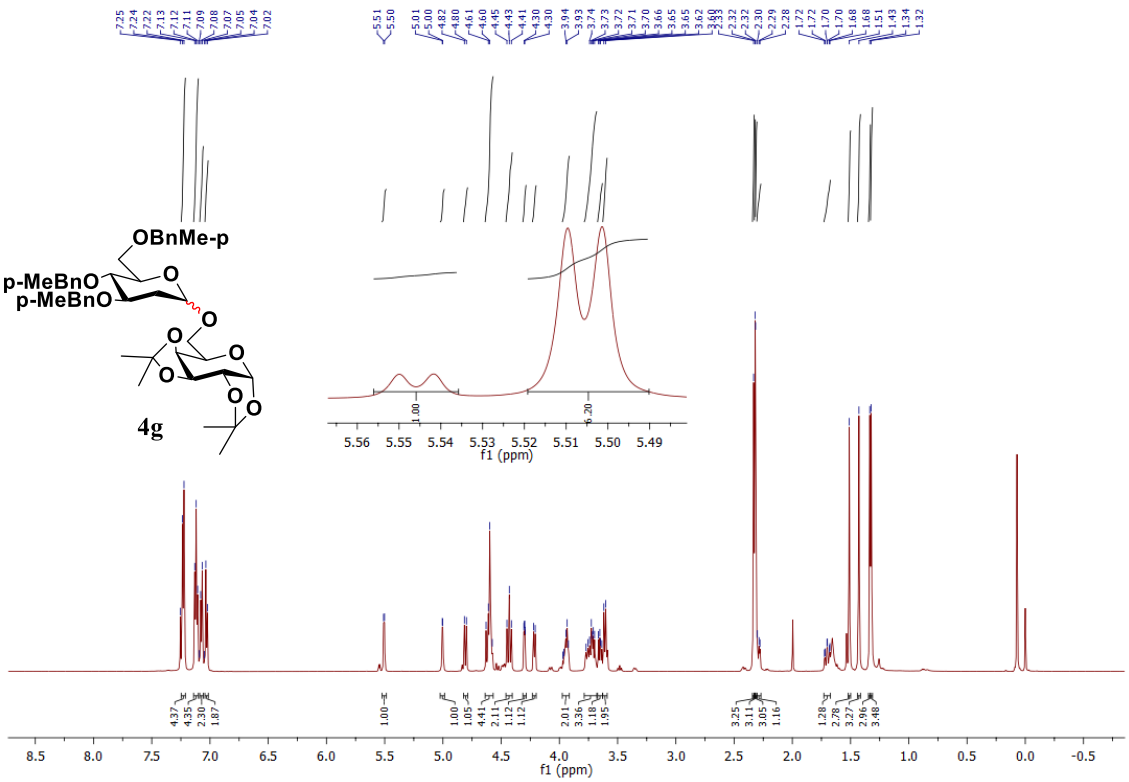
COSY NMR spectrum of compound 4f



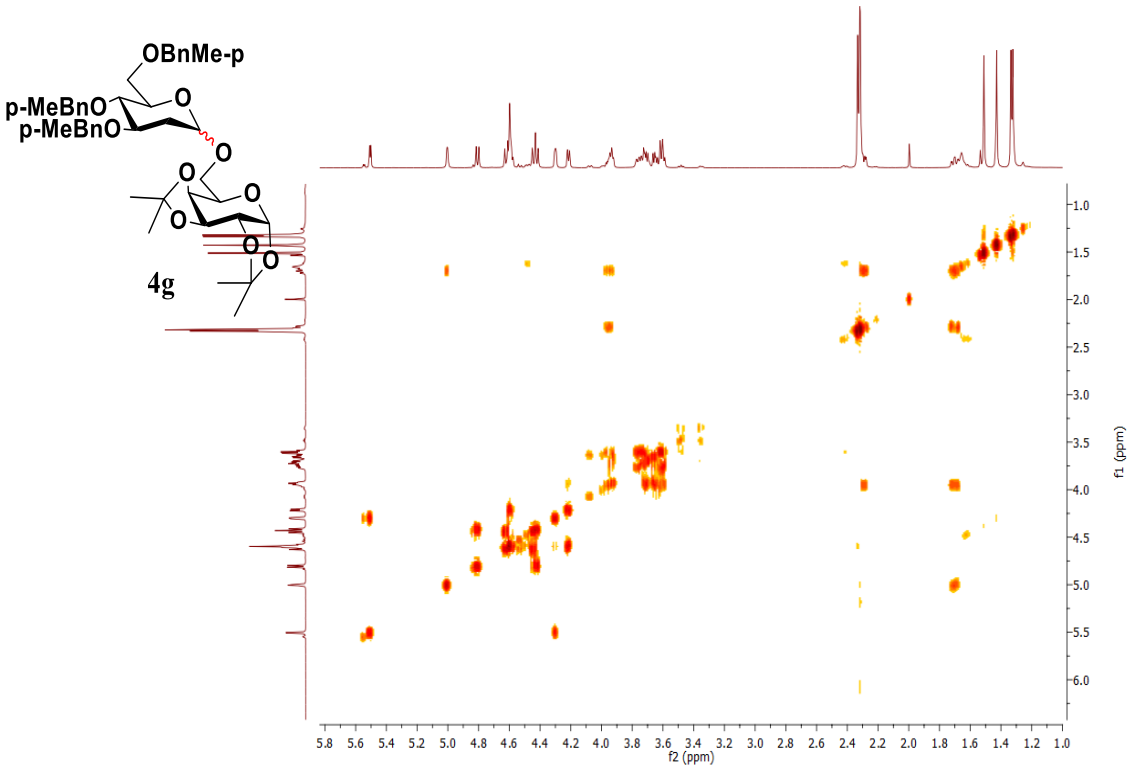
^{13}C NMR spectrum of compound 4f



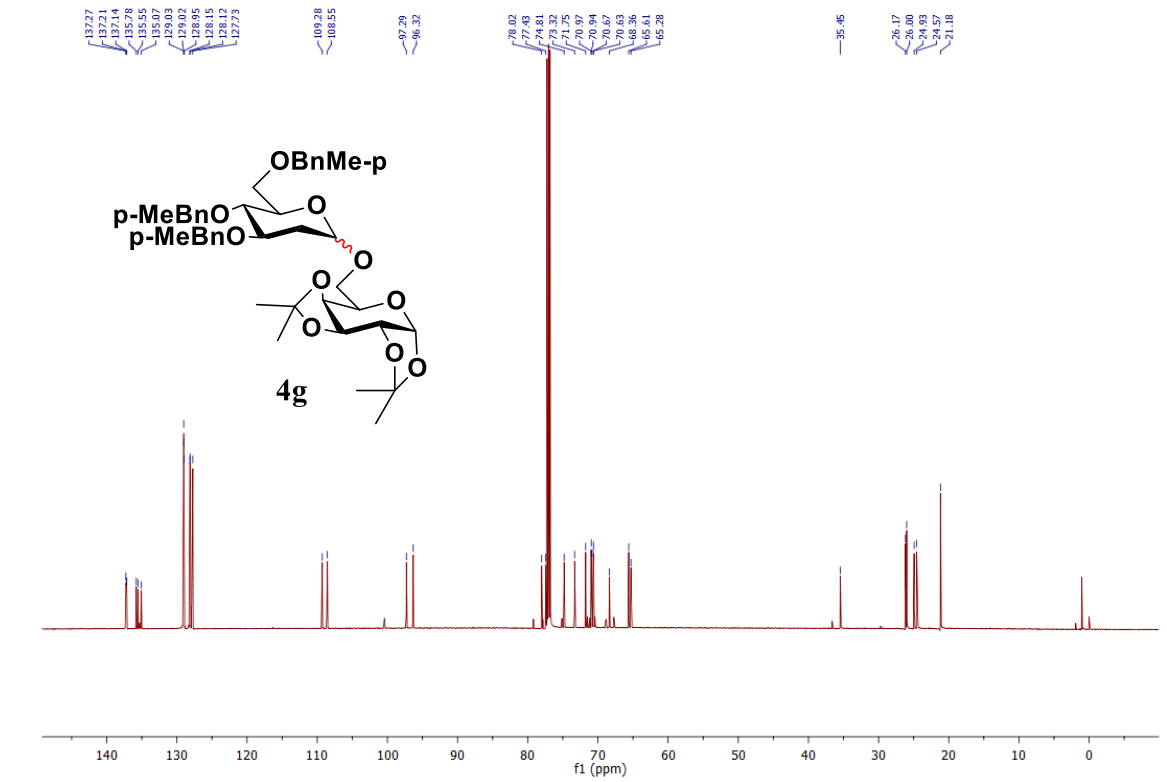
^{1}H NMR spectrum of compound 4g



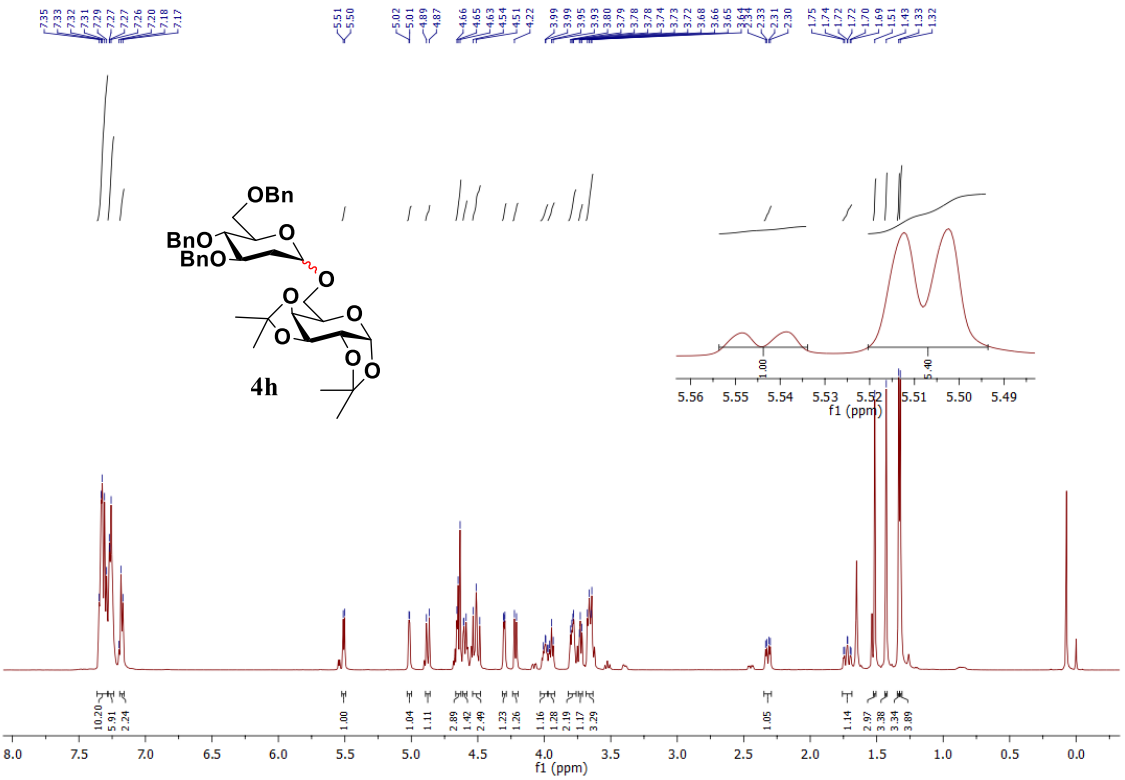
COSY NMR spectrum of compound 4g



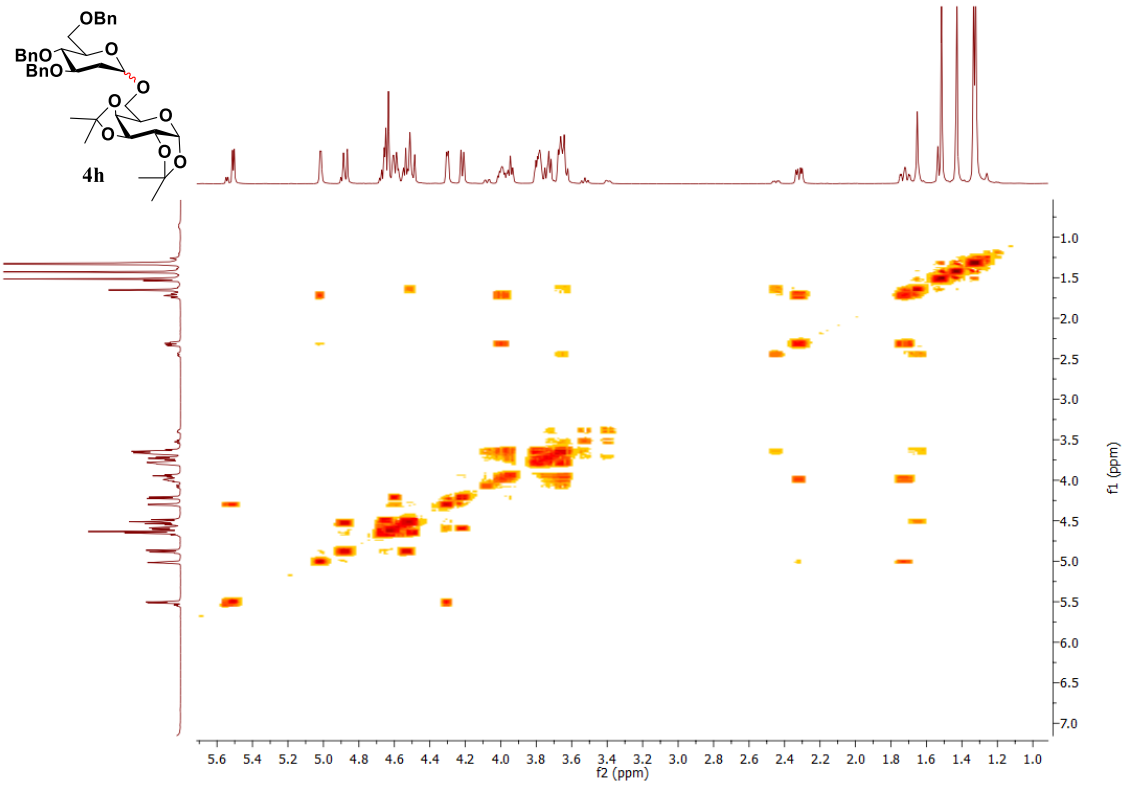
^{13}C NMR spectrum of compound 4g



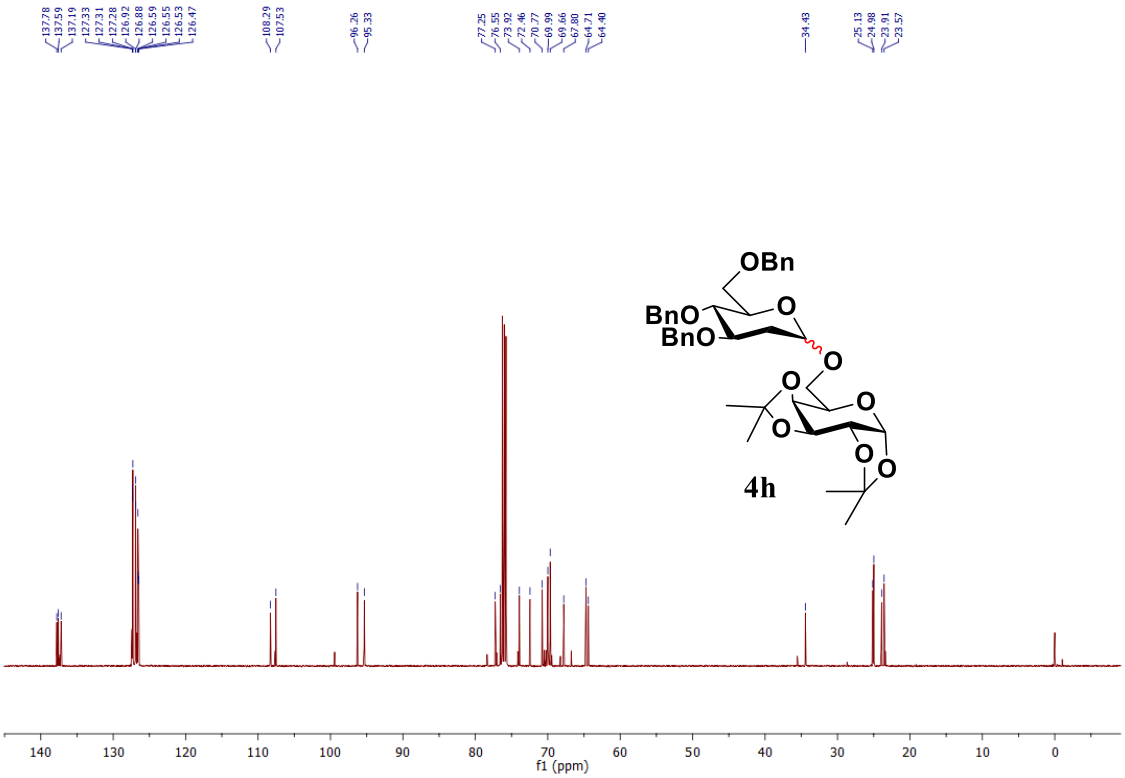
^{1}H NMR spectrum of compound 4hα



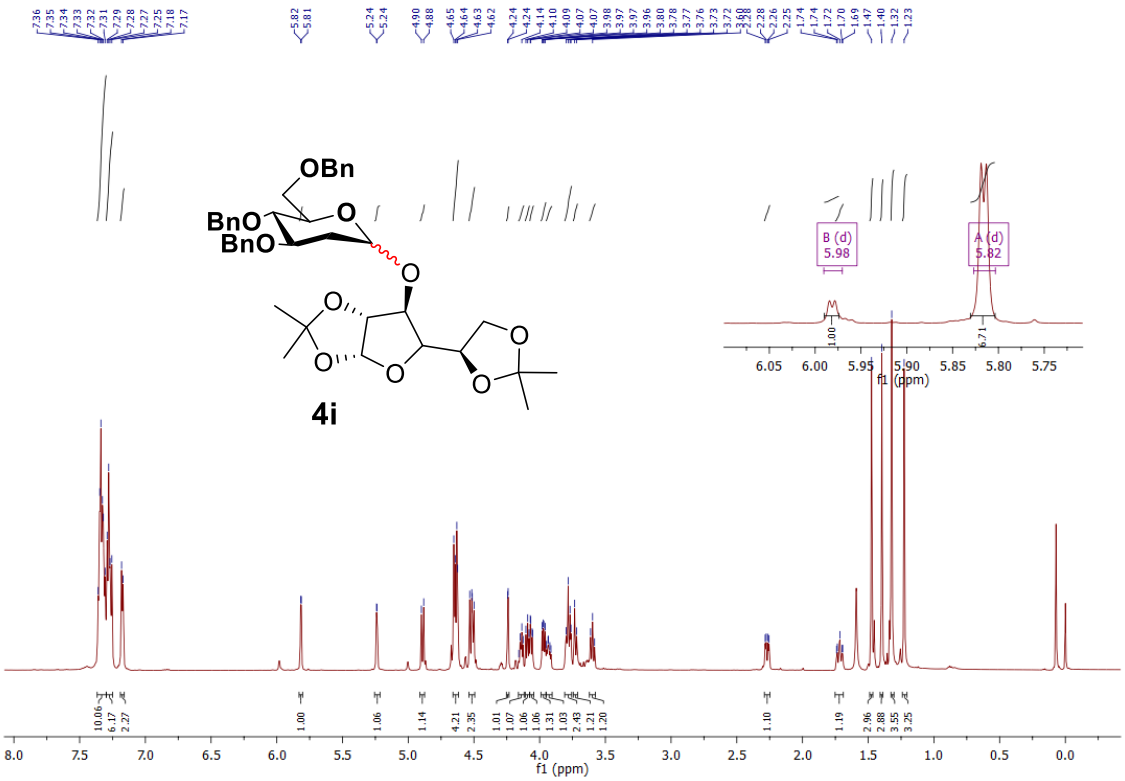
COSY NMR spectrum of compound 4hα



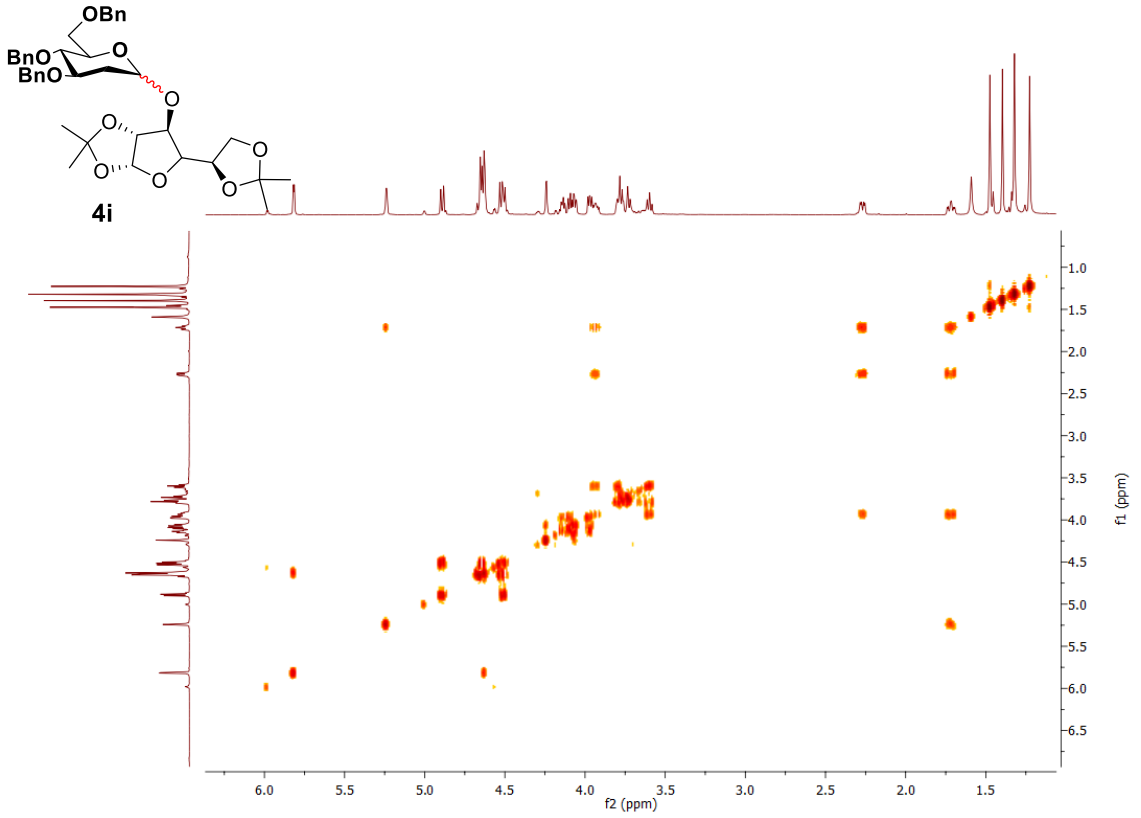
^{13}C NMR spectrum of compound 4hα



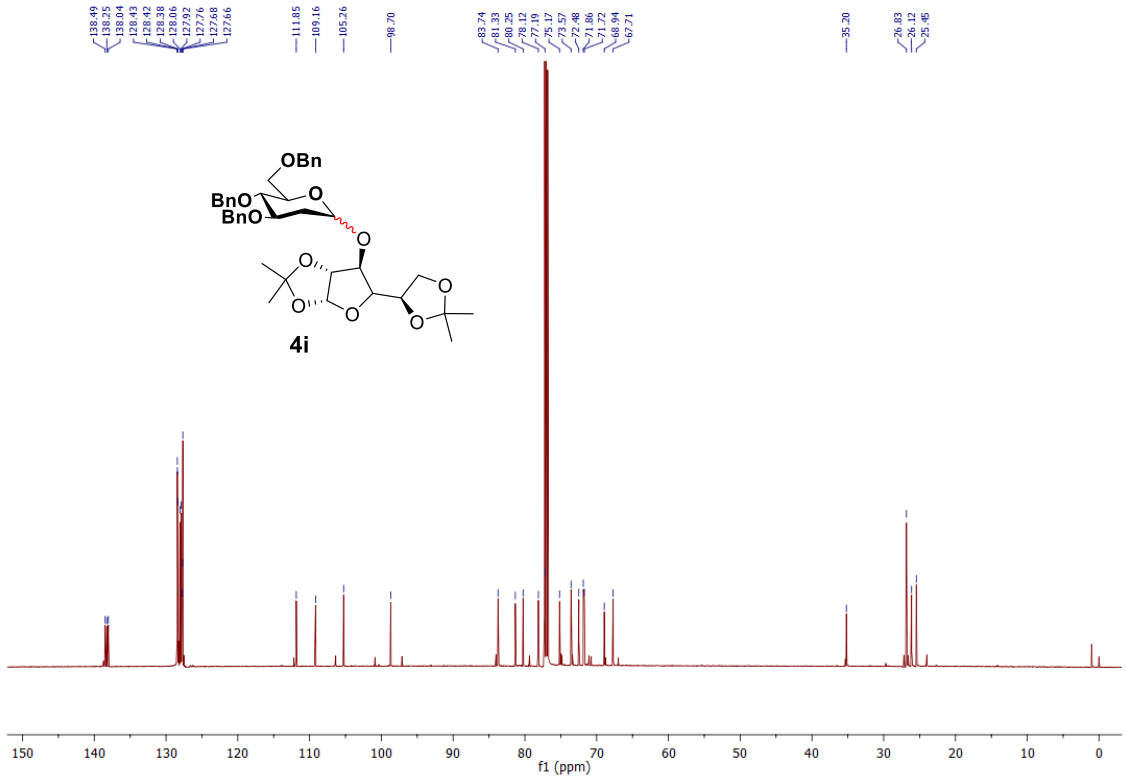
^{1}H NMR spectrum of compound 4i



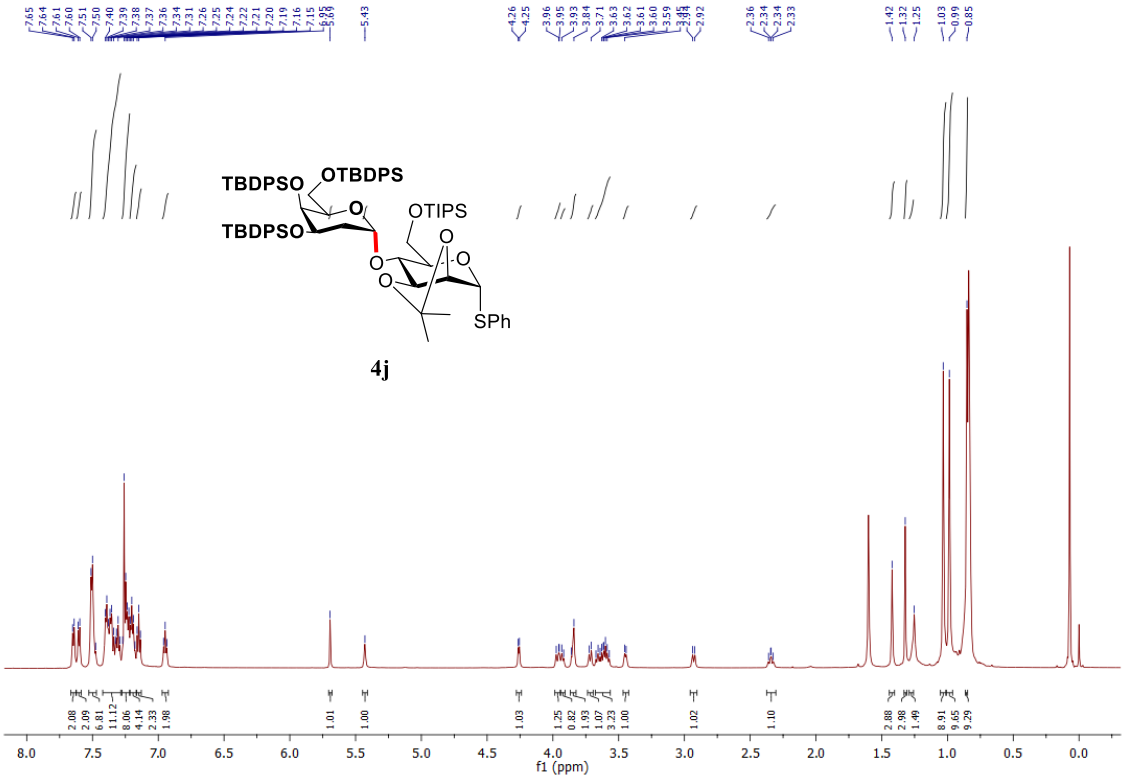
COSY NMR spectrum of compound 4i



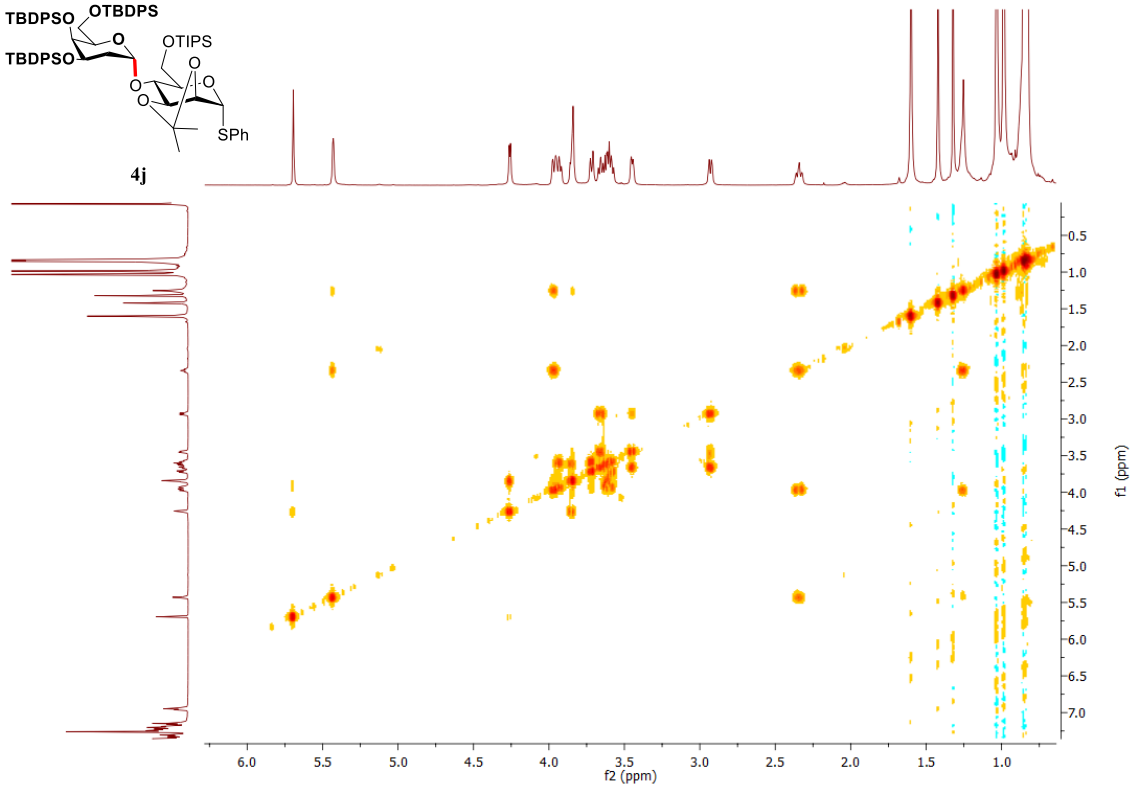
^{13}C NMR spectrum of compound 4i



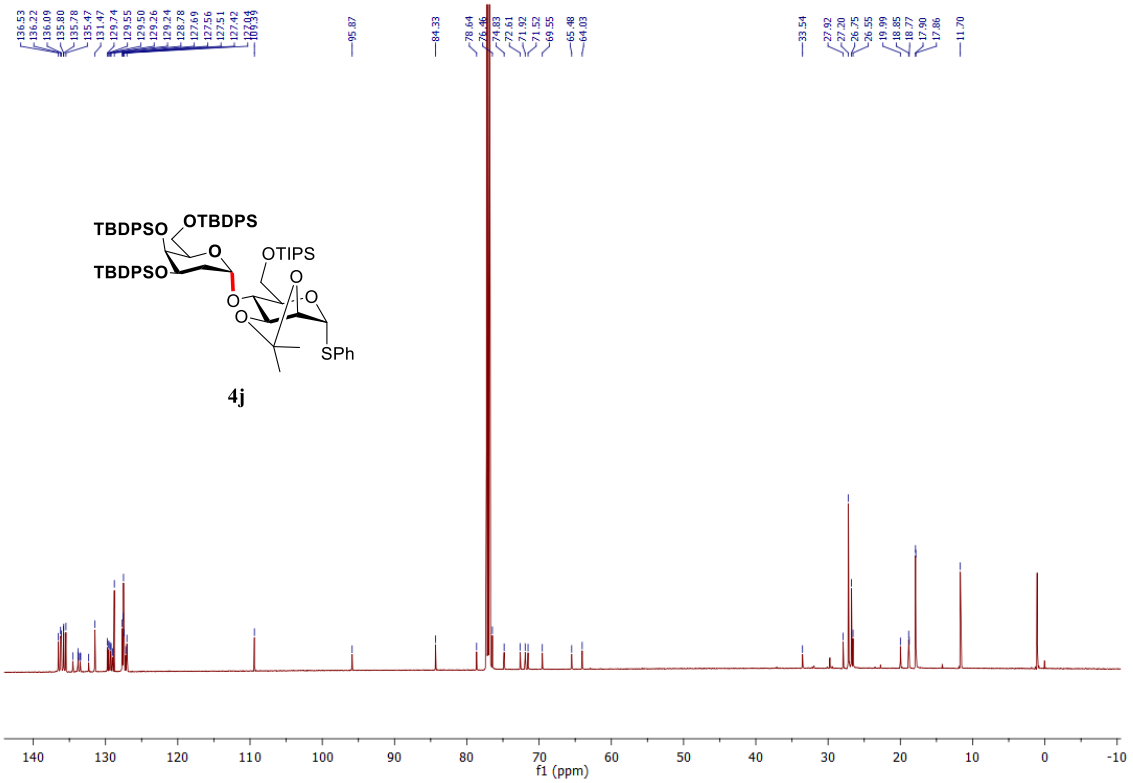
^{1}H NMR spectrum of compound 4j



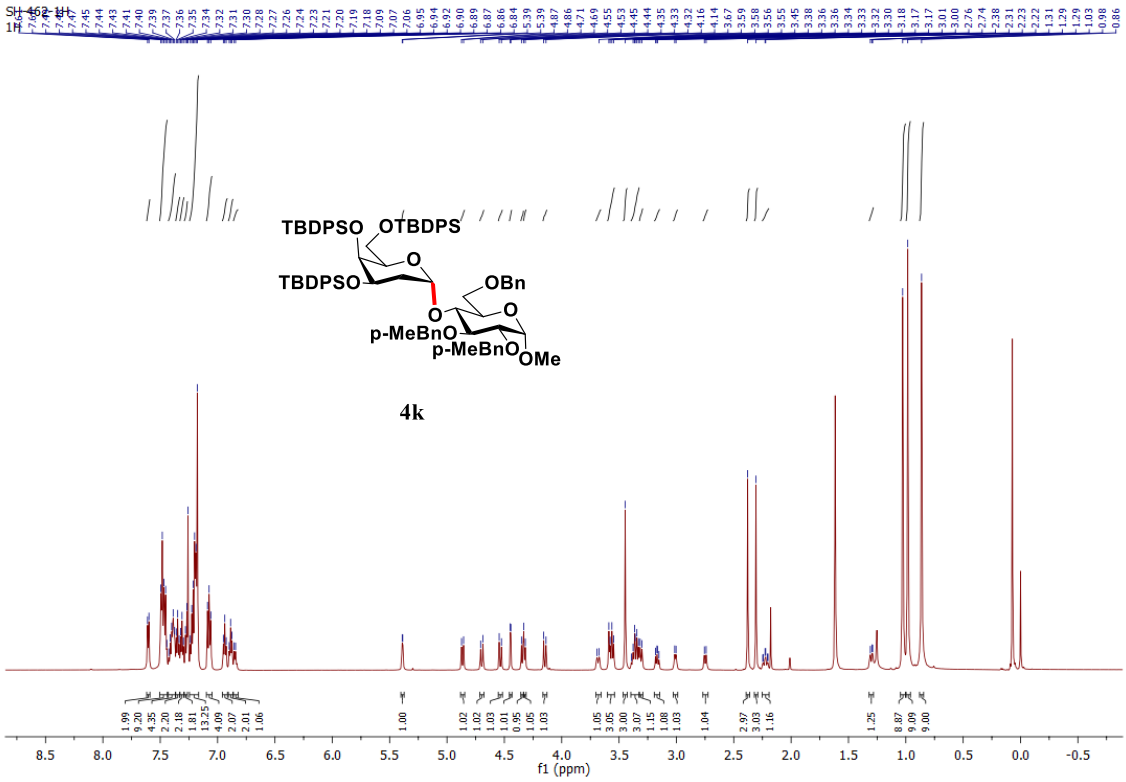
COSY NMR spectrum of compound 4j



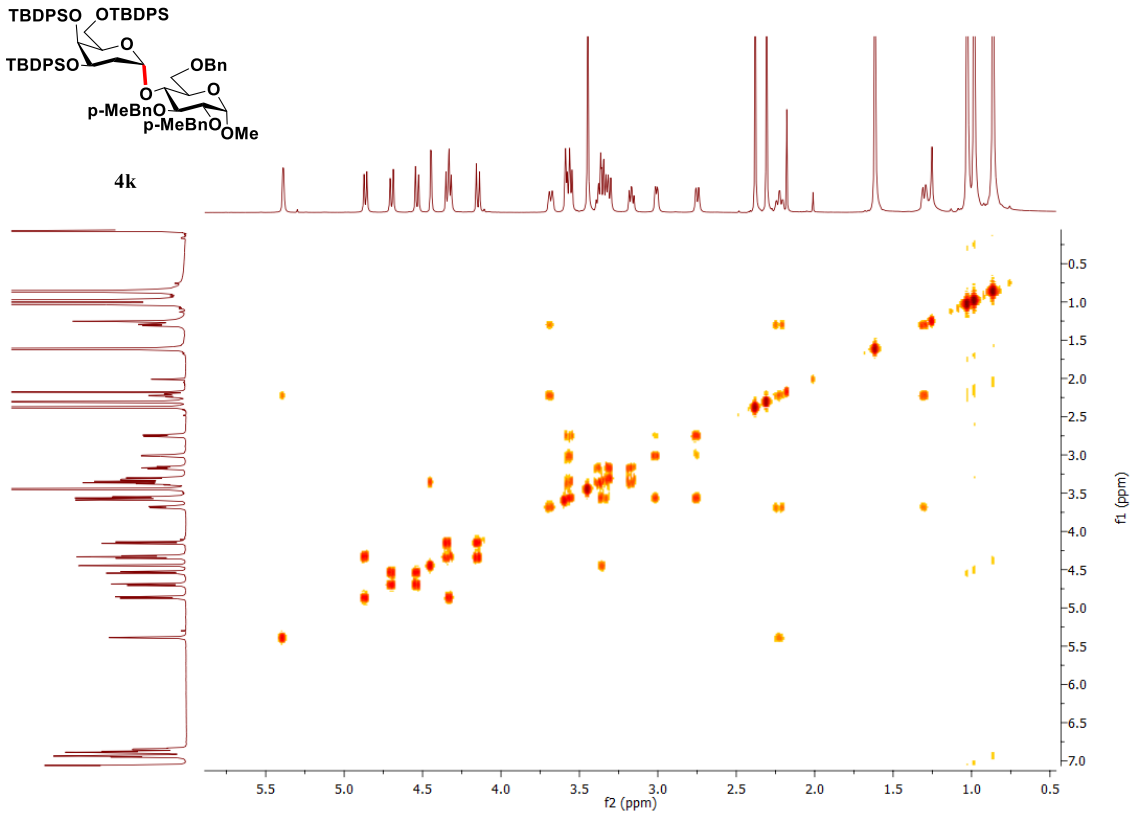
^{13}C NMR spectrum of compound 4j



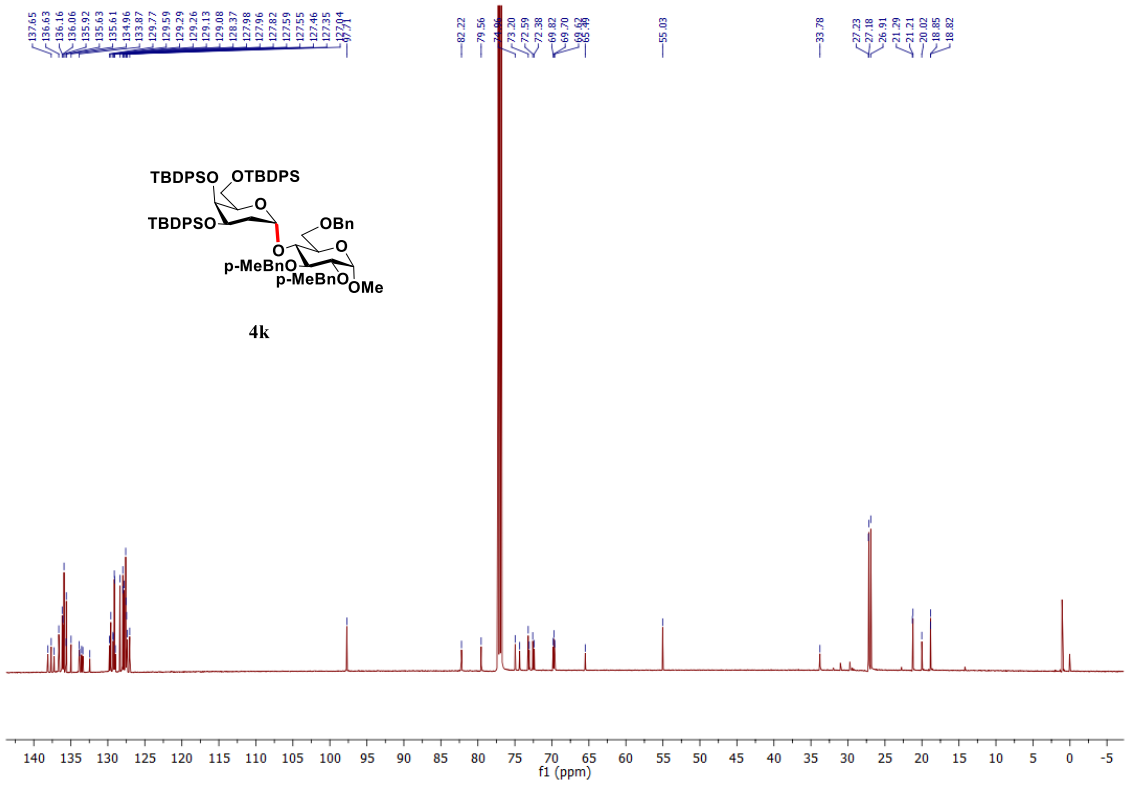
^{1}H NMR spectrum of compound 4k



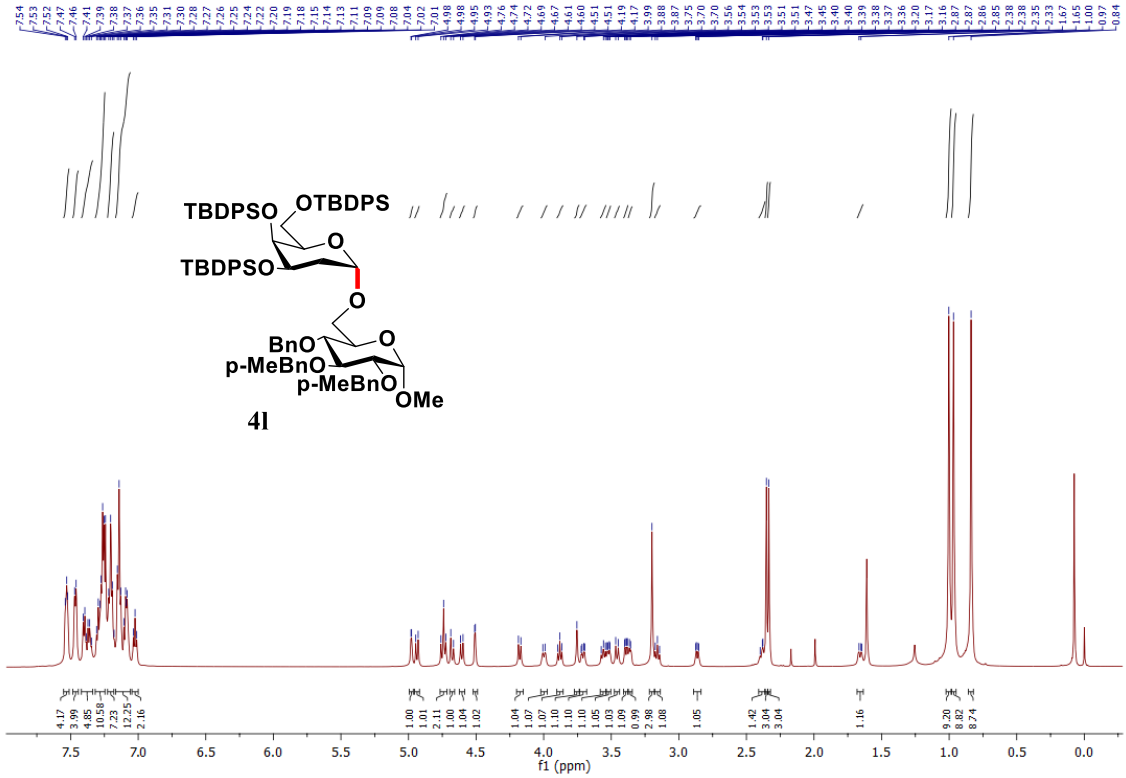
COSY NMR spectrum of compound 4k



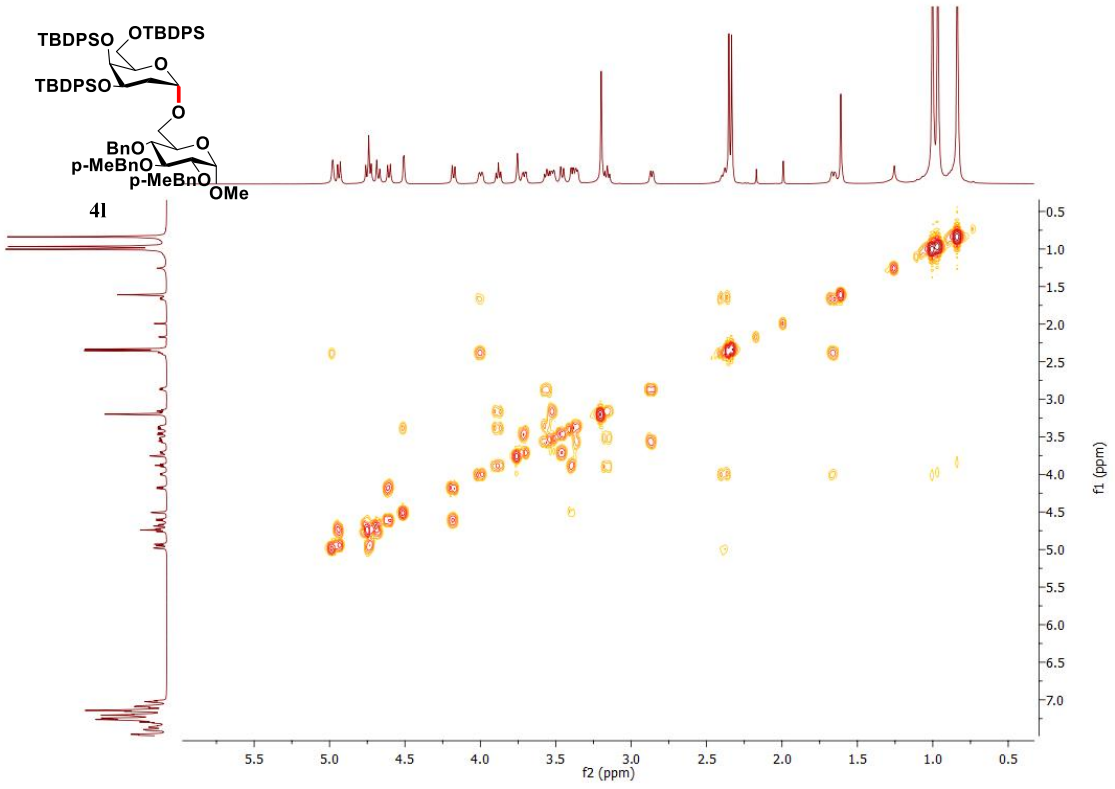
^{13}C NMR spectrum of compound 4k



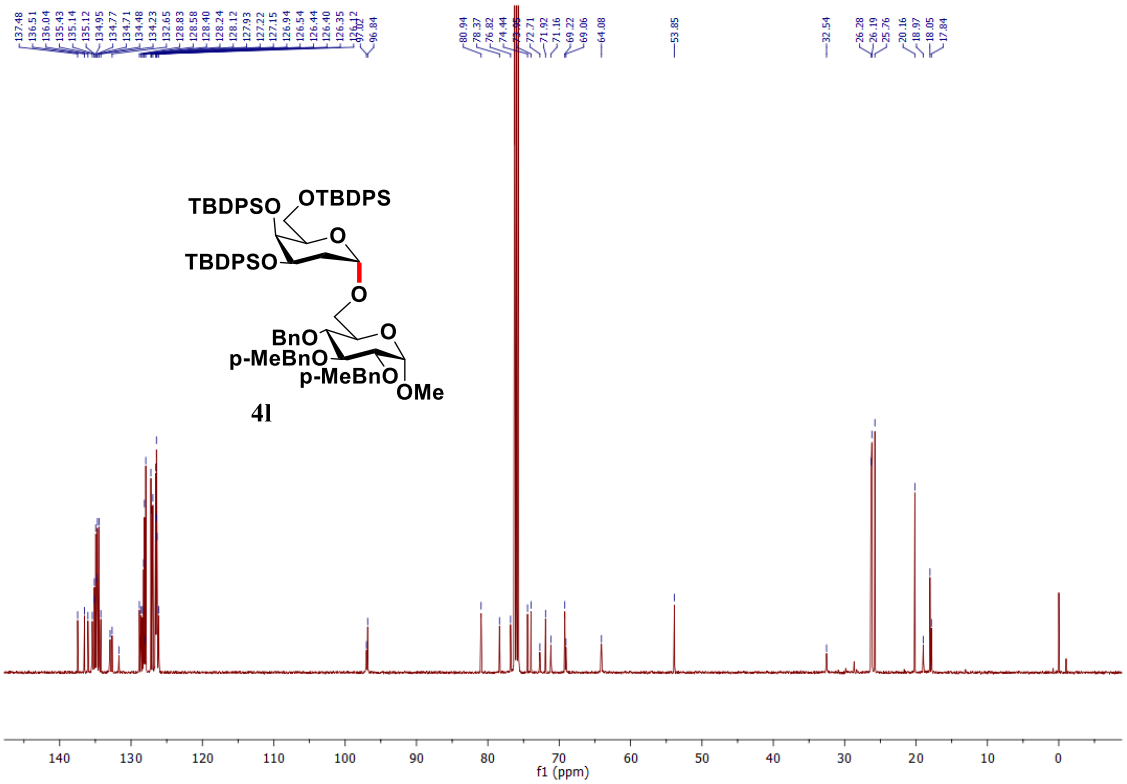
^{1}H NMR spectrum of compound 4l



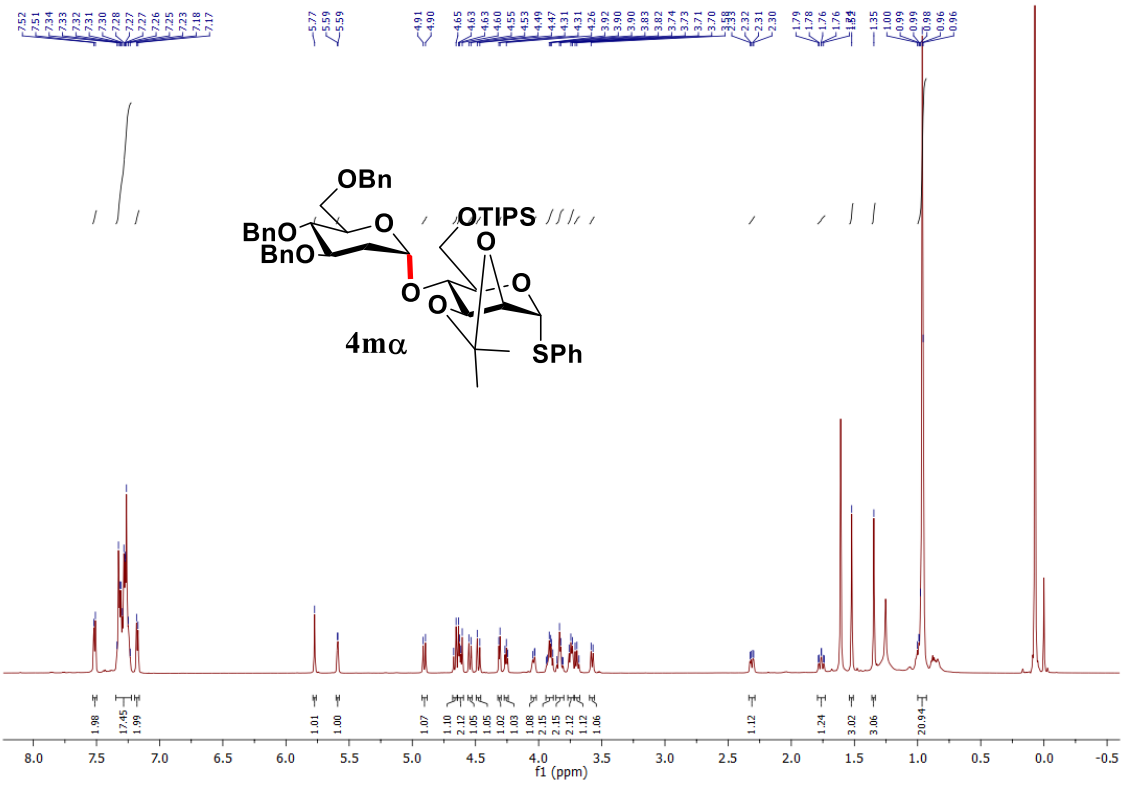
COSY NMR spectrum of compound 4l



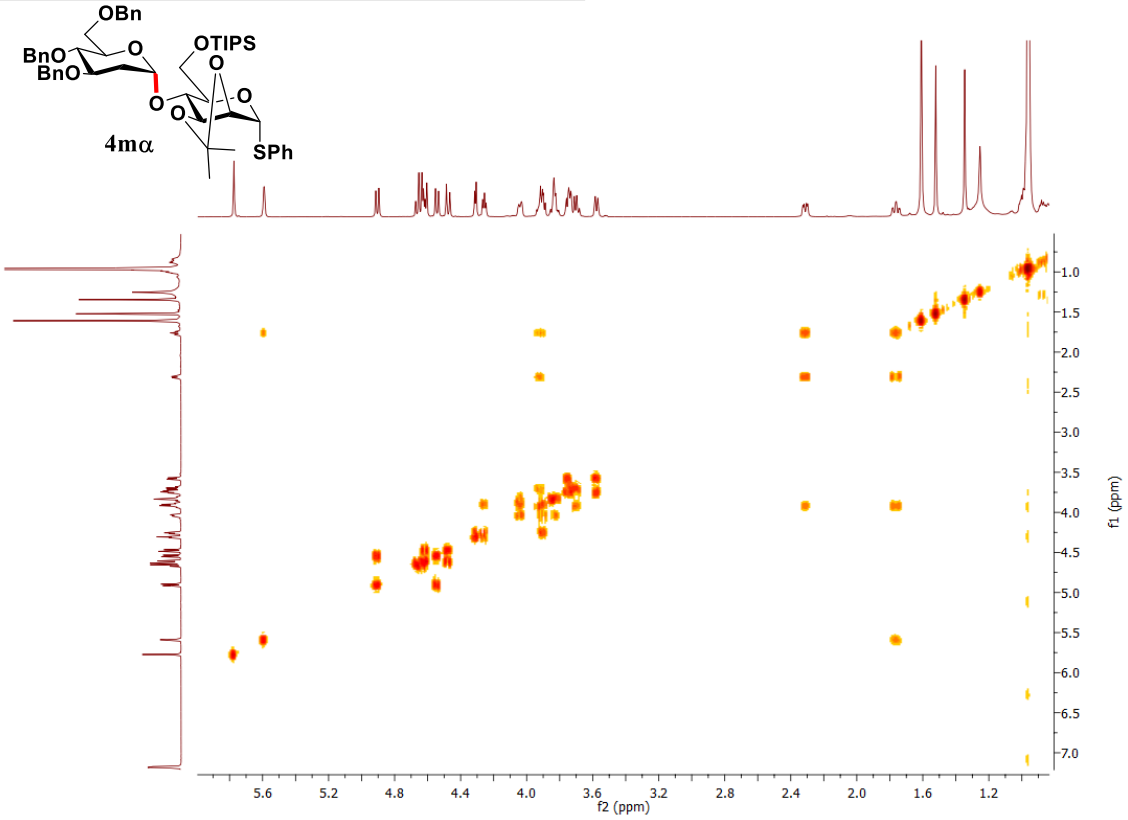
^{13}C NMR spectrum of compound 4l



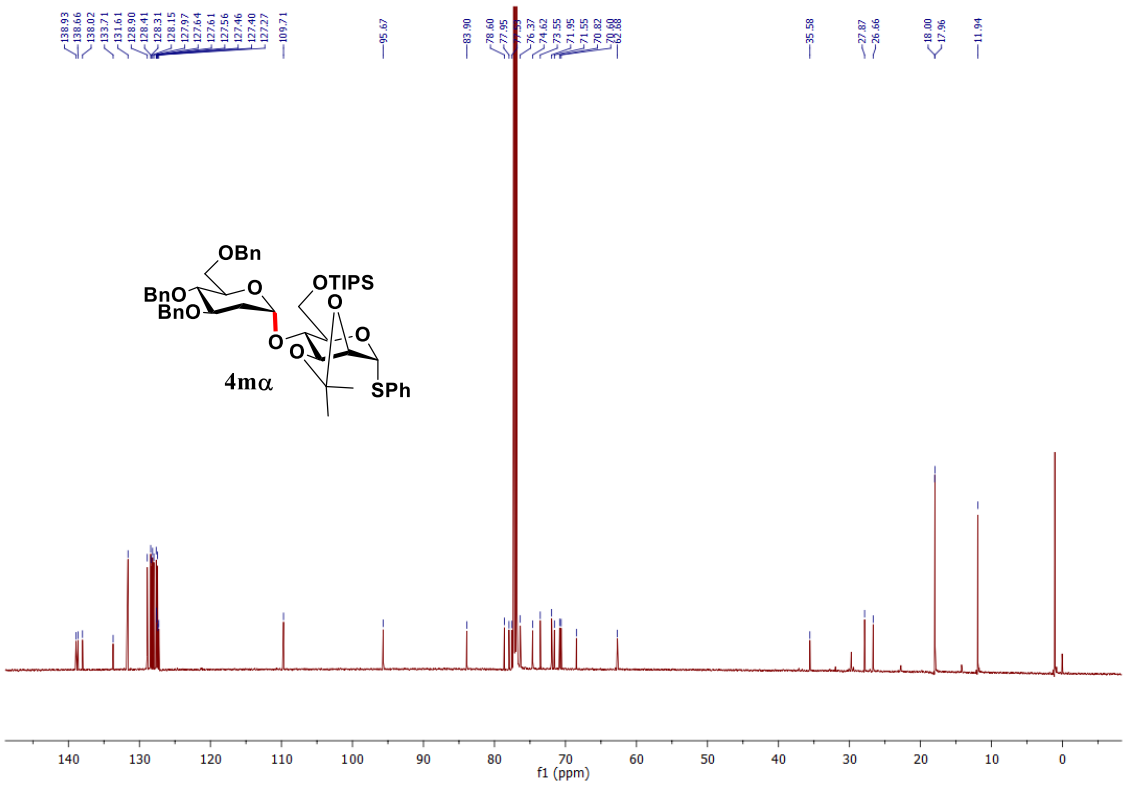
^{1}H NMR spectrum of compound 4mα



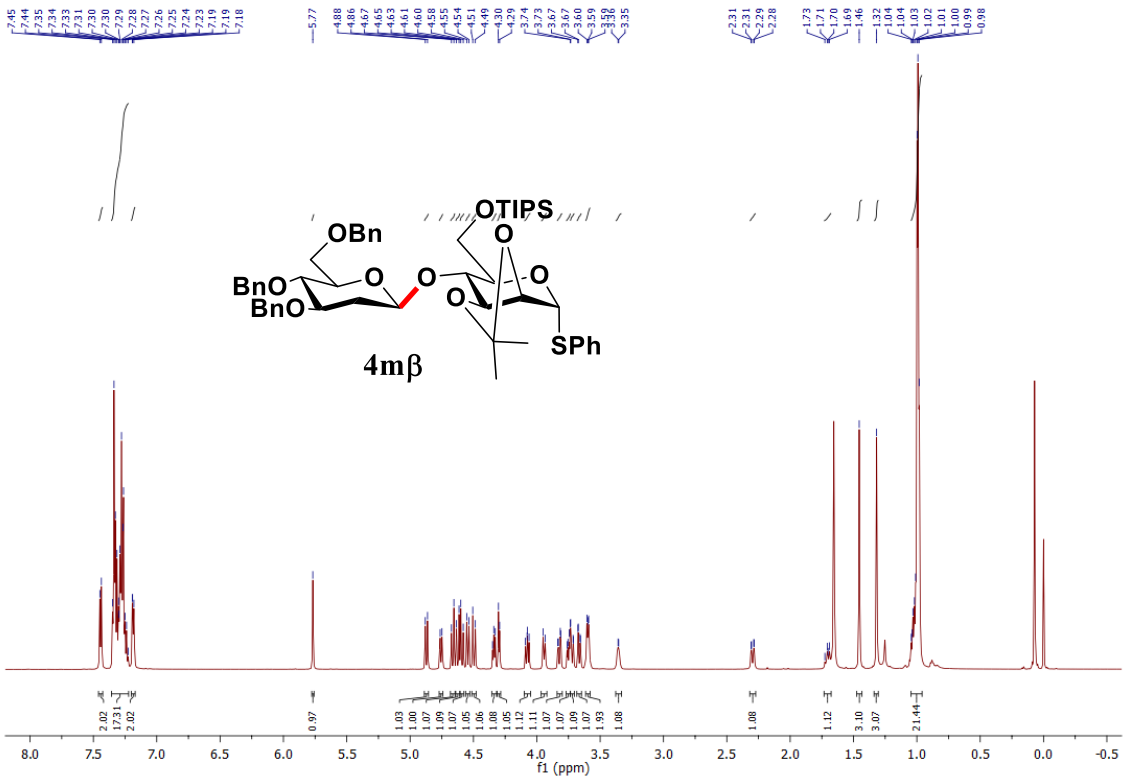
COSY NMR spectrum of compound 4mα



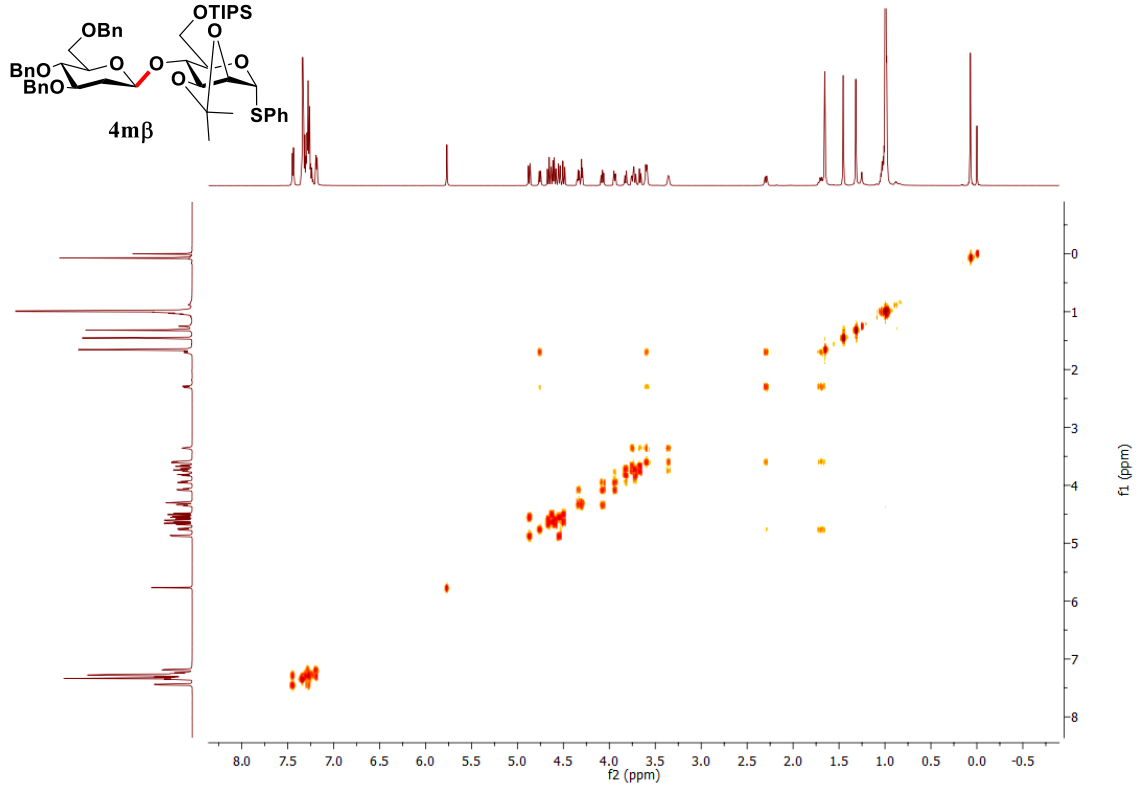
^{13}C NMR spectrum of compound 4mα



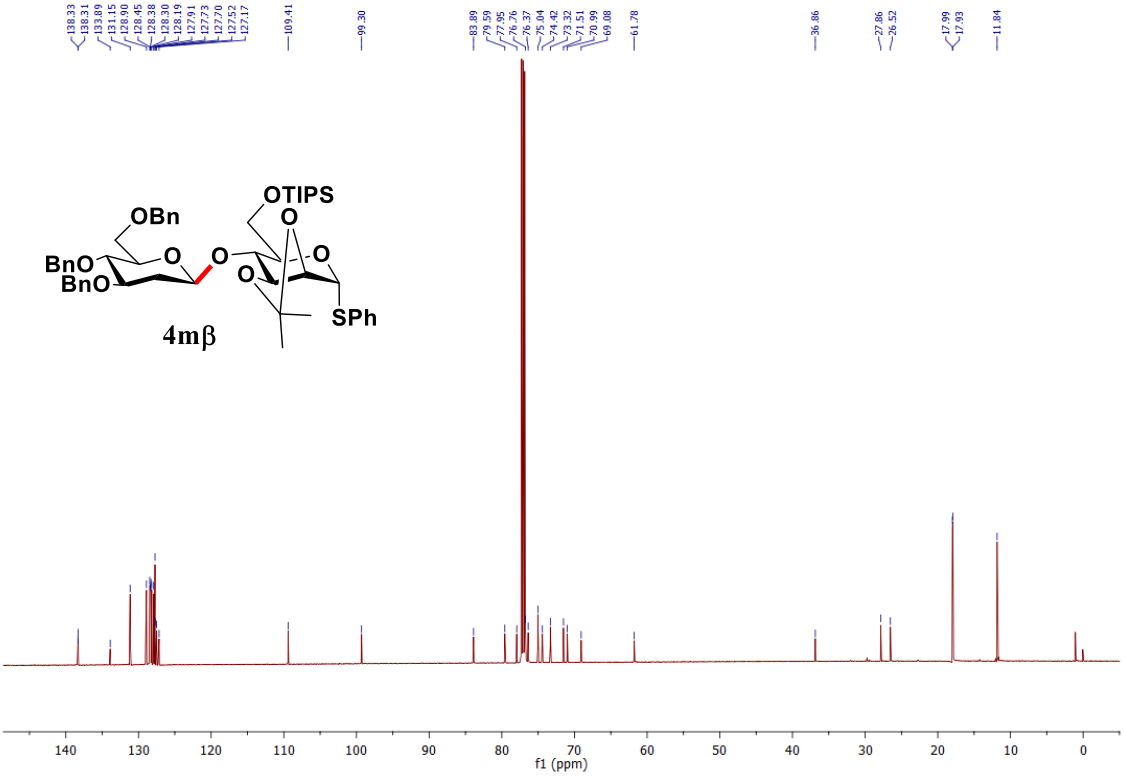
^{1}H NMR spectrum of compound 4mβ



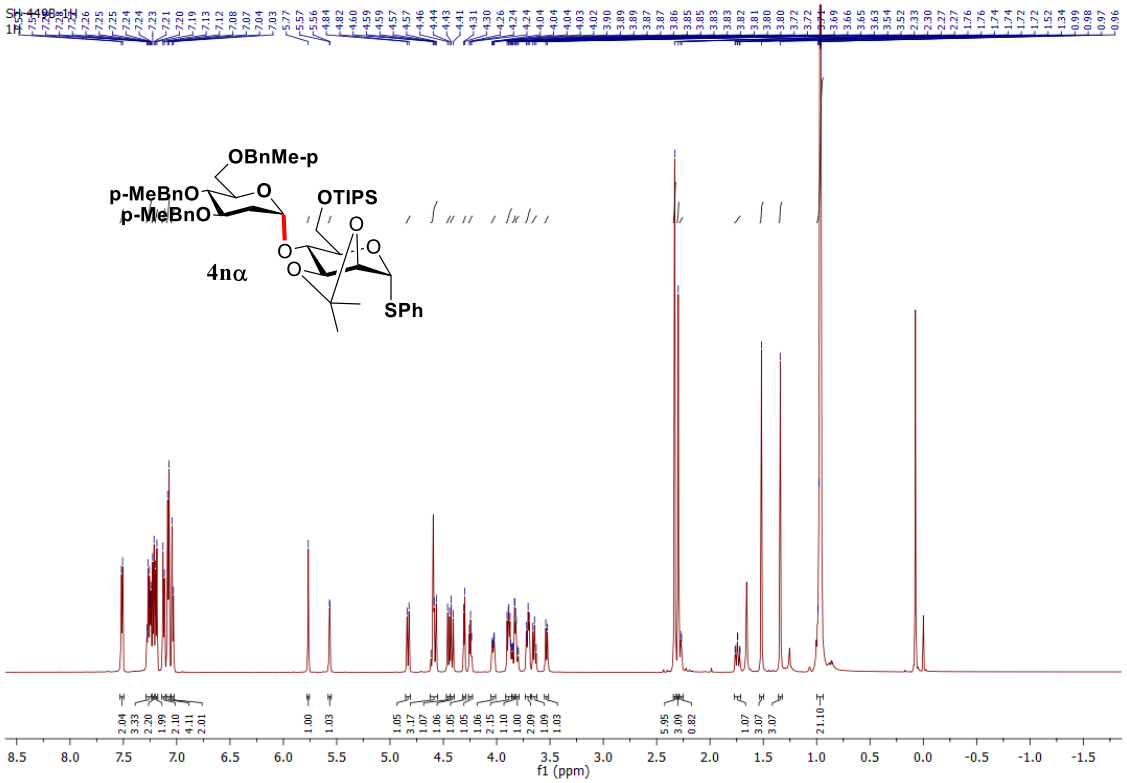
COSY NMR spectrum of compound 4mβ



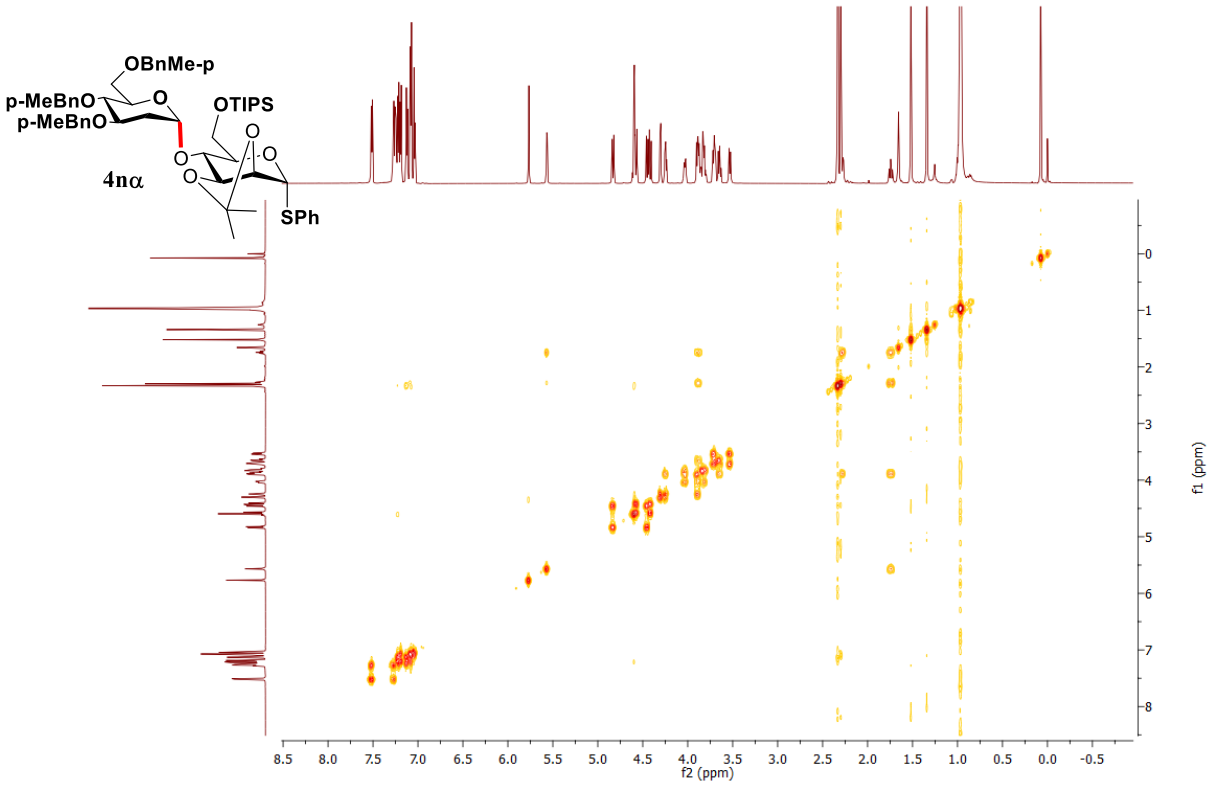
^{13}C NMR spectrum of compound 4mβ



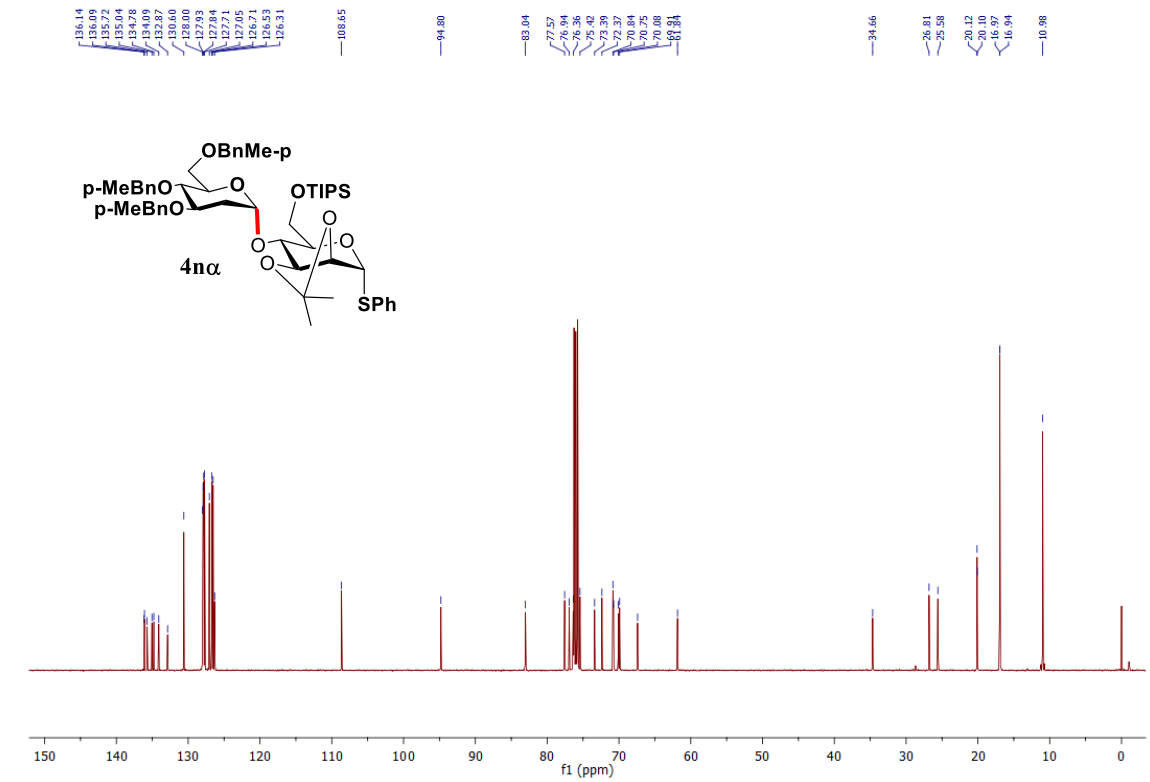
^{1}H NMR spectrum of compound 4nα



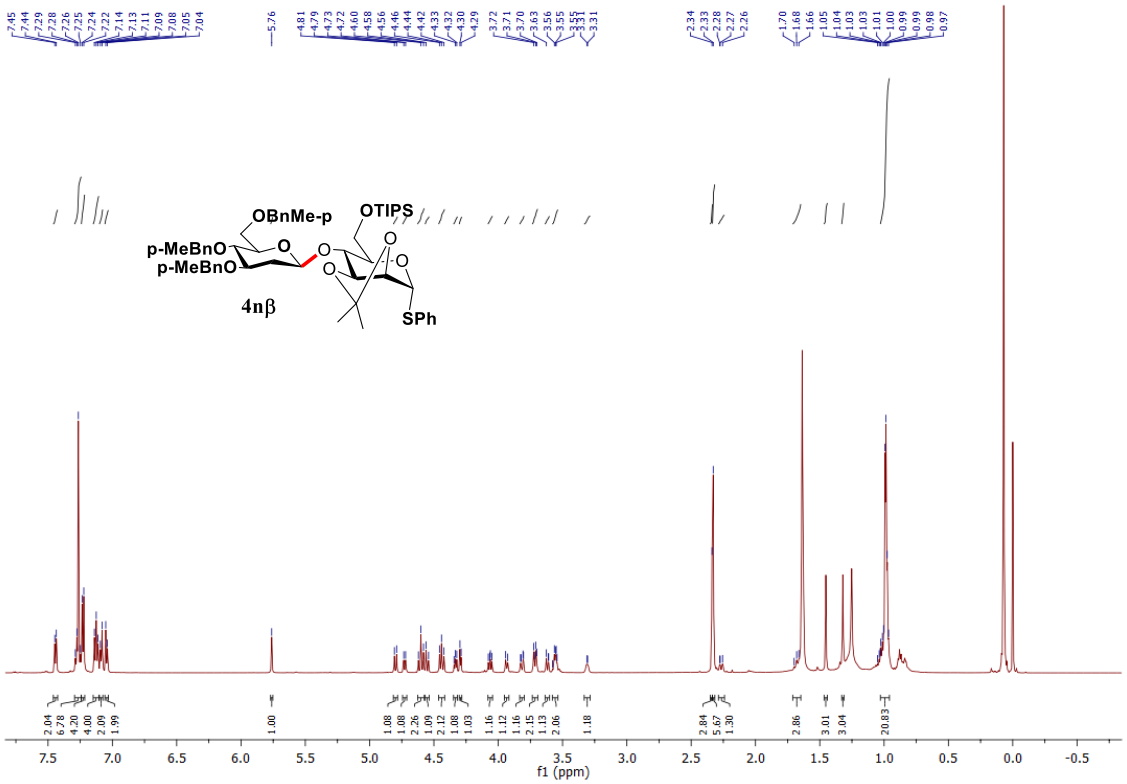
COSY NMR spectrum of compound 4nα



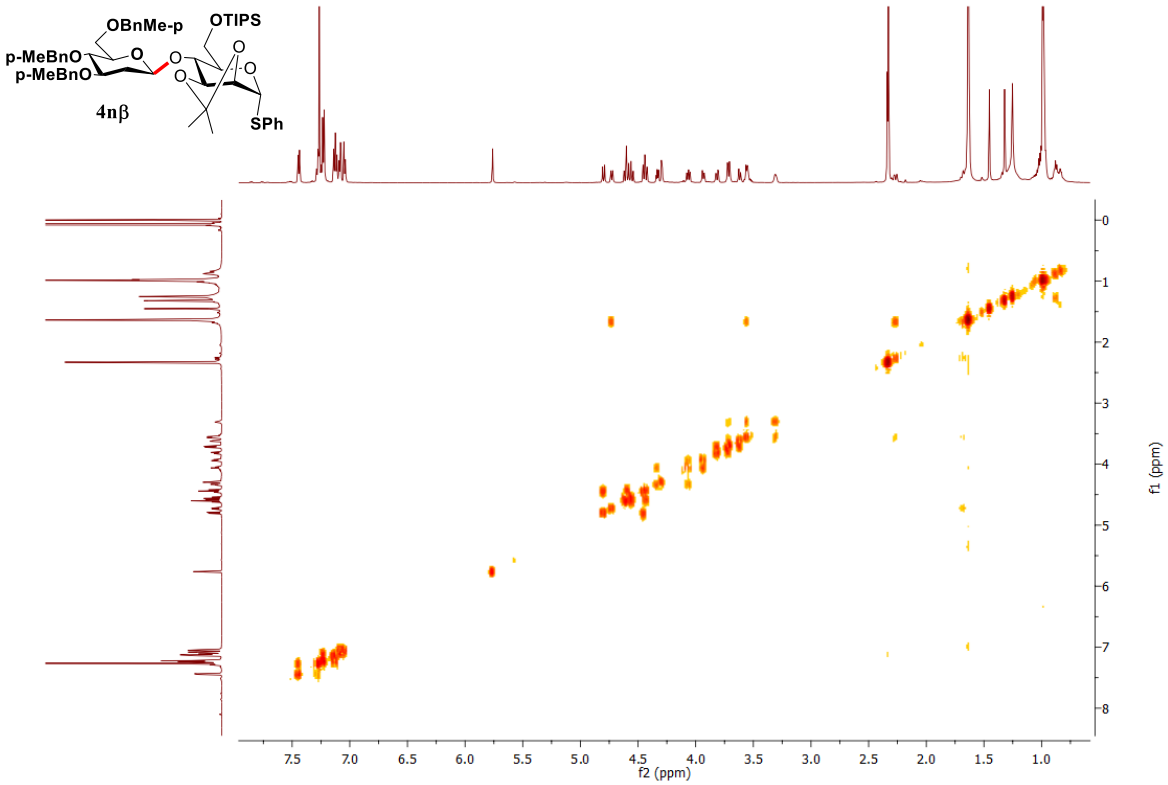
^{13}C NMR spectrum of compound 4nα



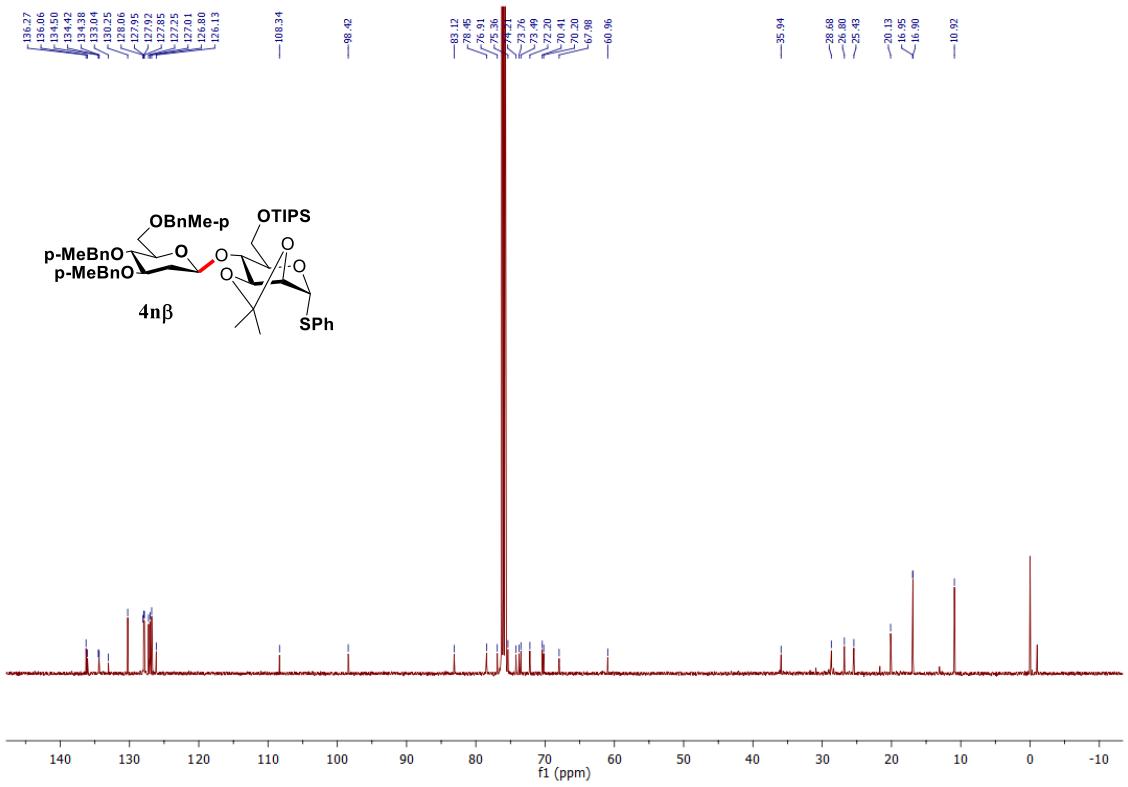
^{1}H NMR spectrum of compound 4nβ



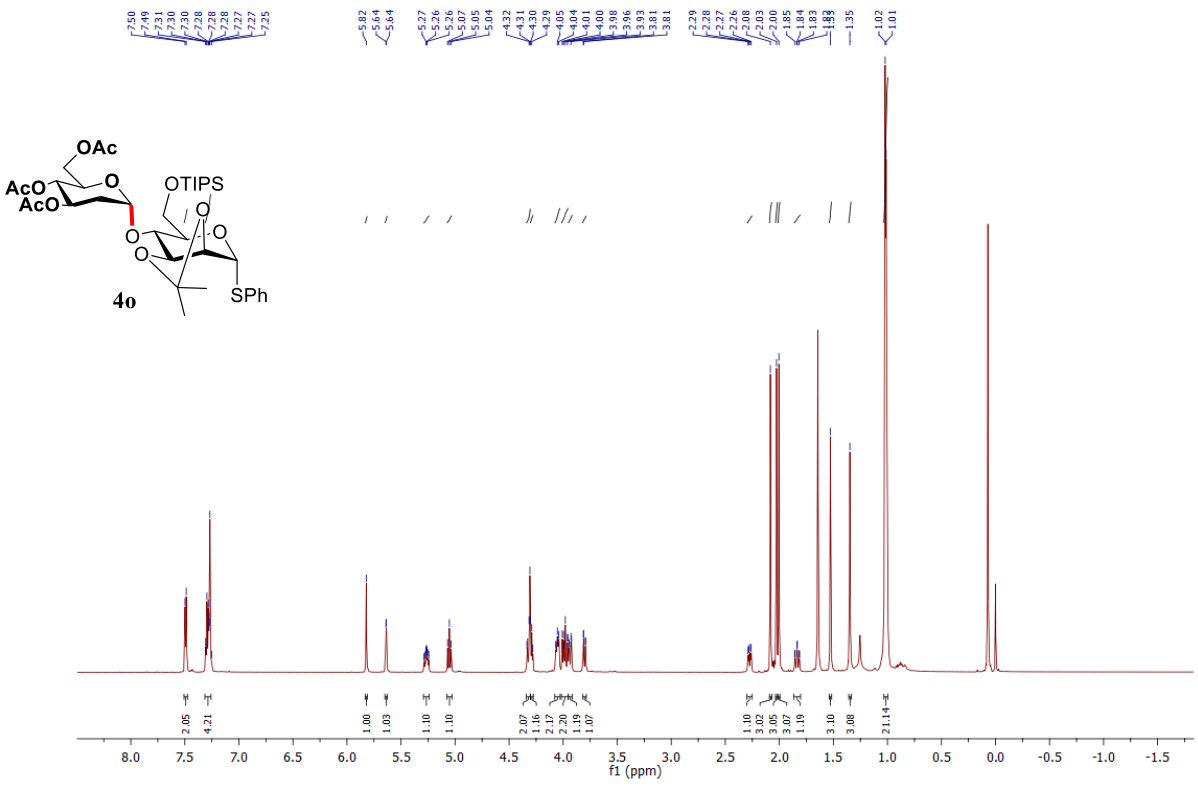
COSY NMR spectrum of compound 4nβ



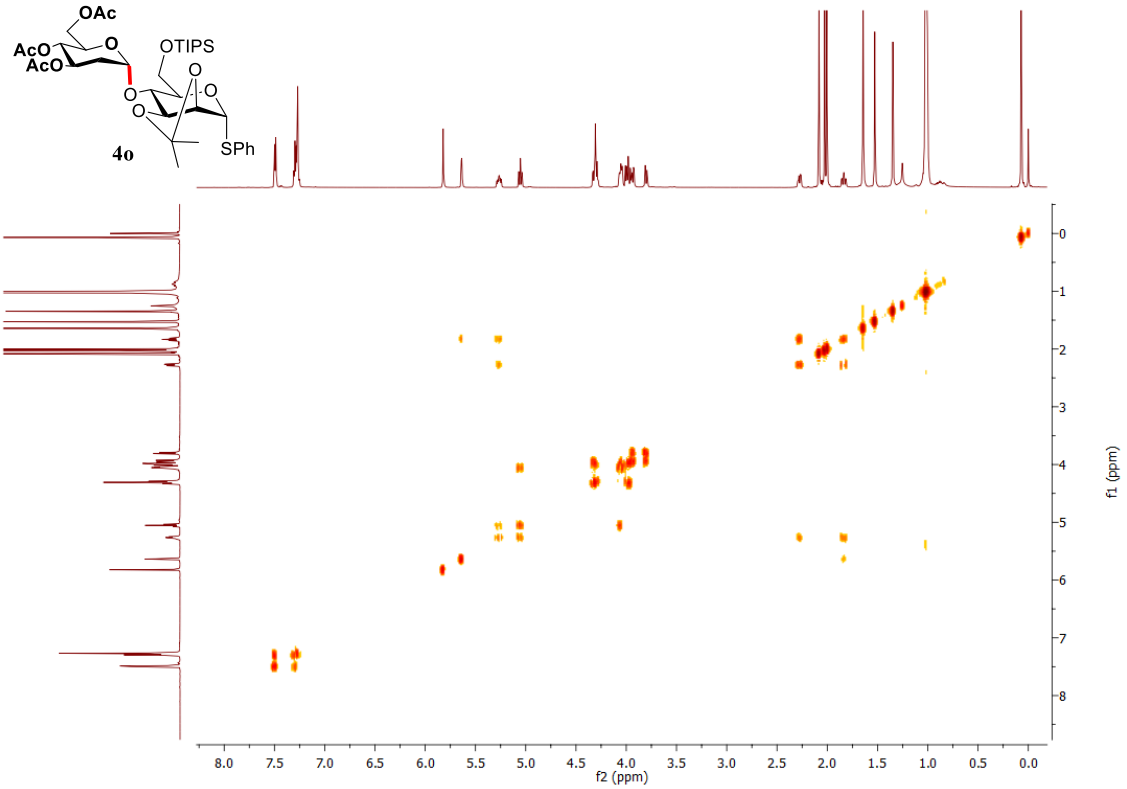
^{13}C NMR spectrum of compound 4nβ



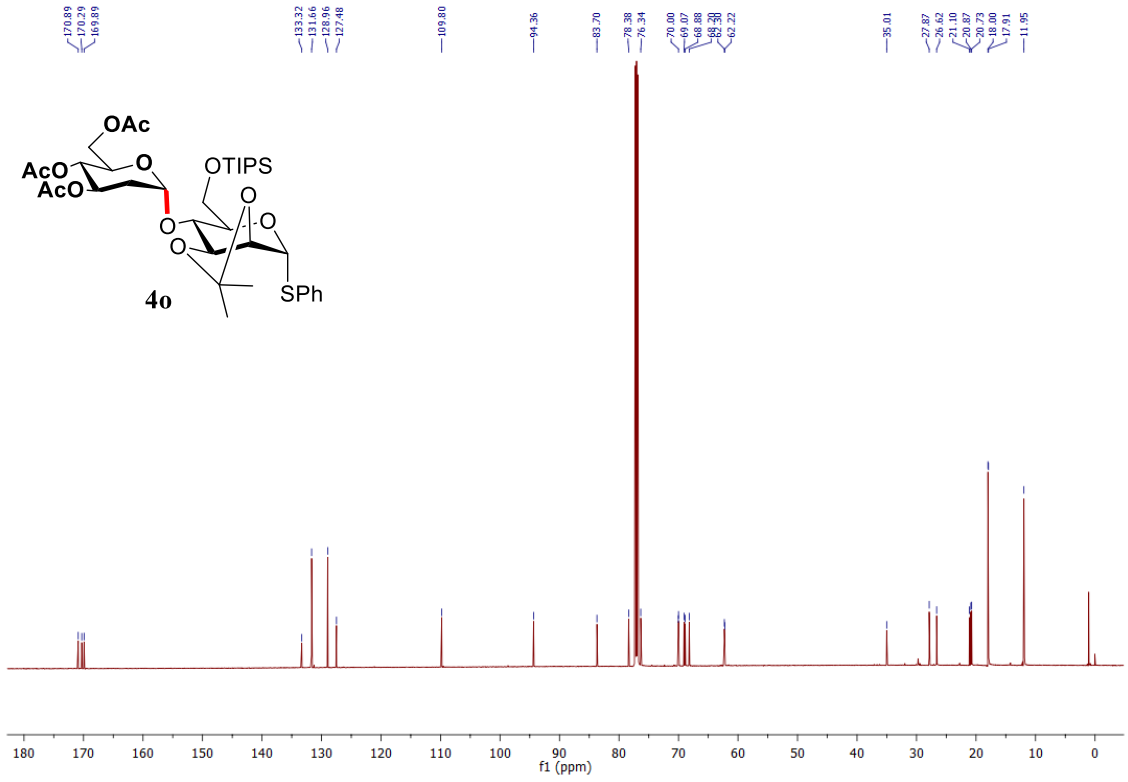
^{1}H NMR spectrum of compound 4o



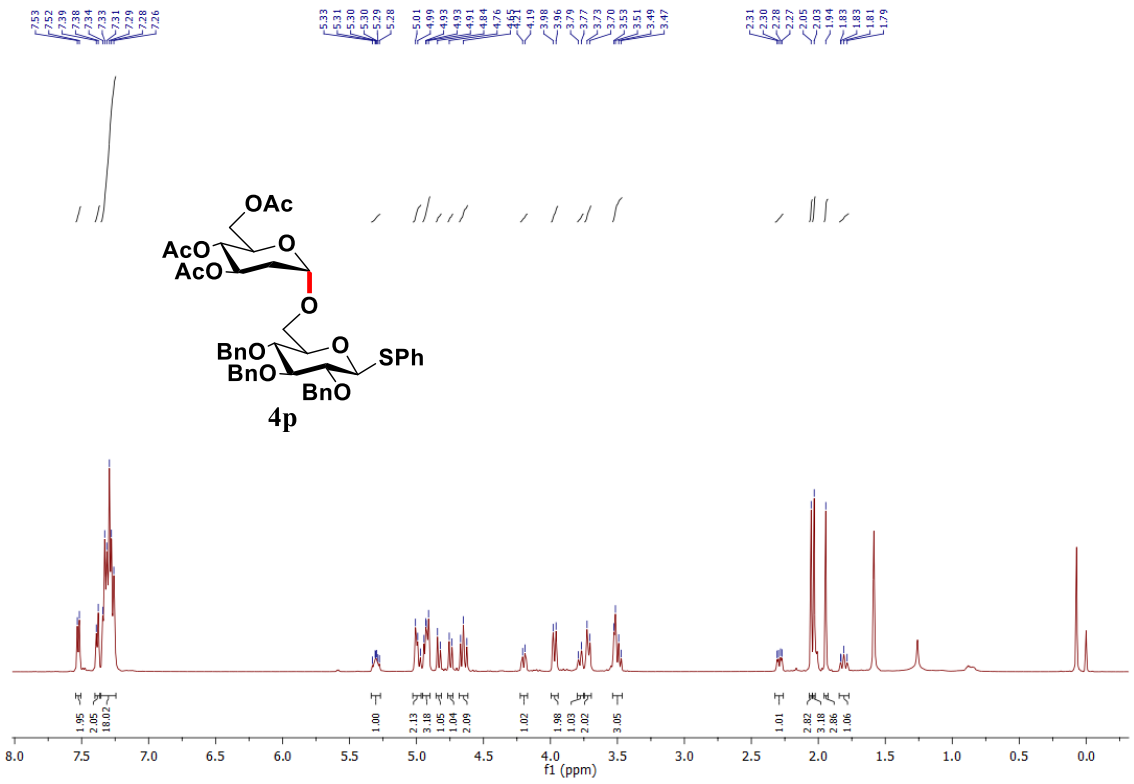
COSY NMR spectrum of compound 4o



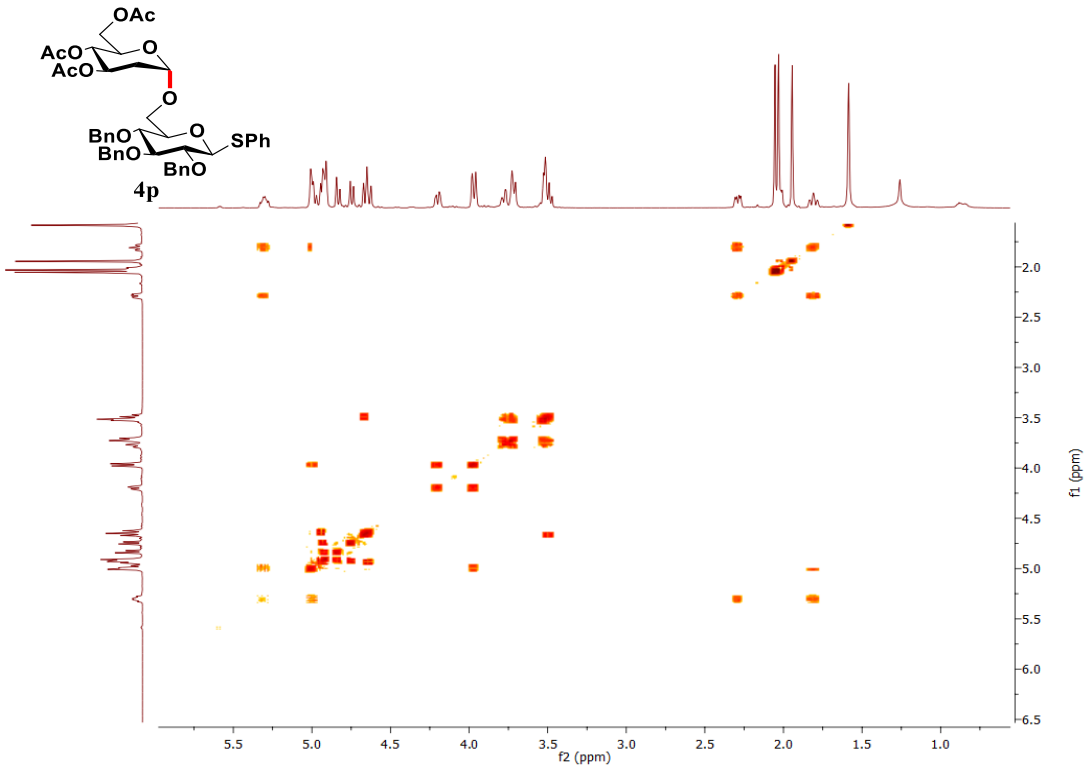
^{13}C NMR spectrum of compound 4o



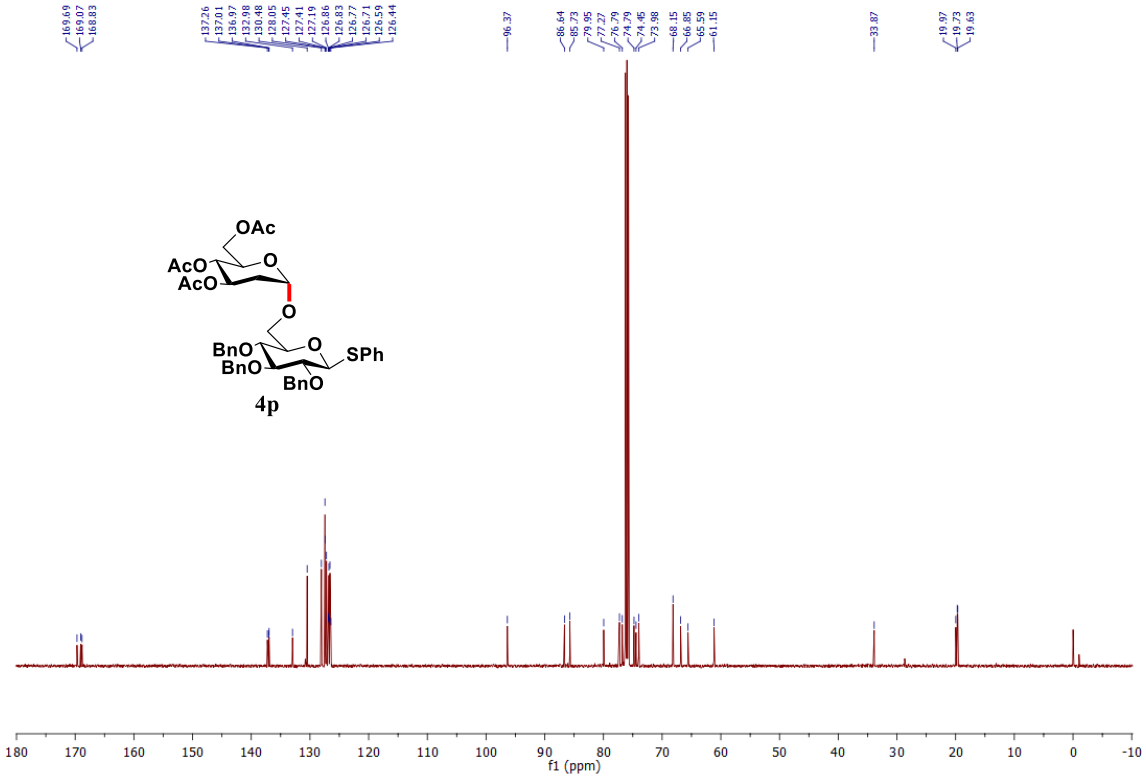
^{1}H NMR spectrum of compound 4p



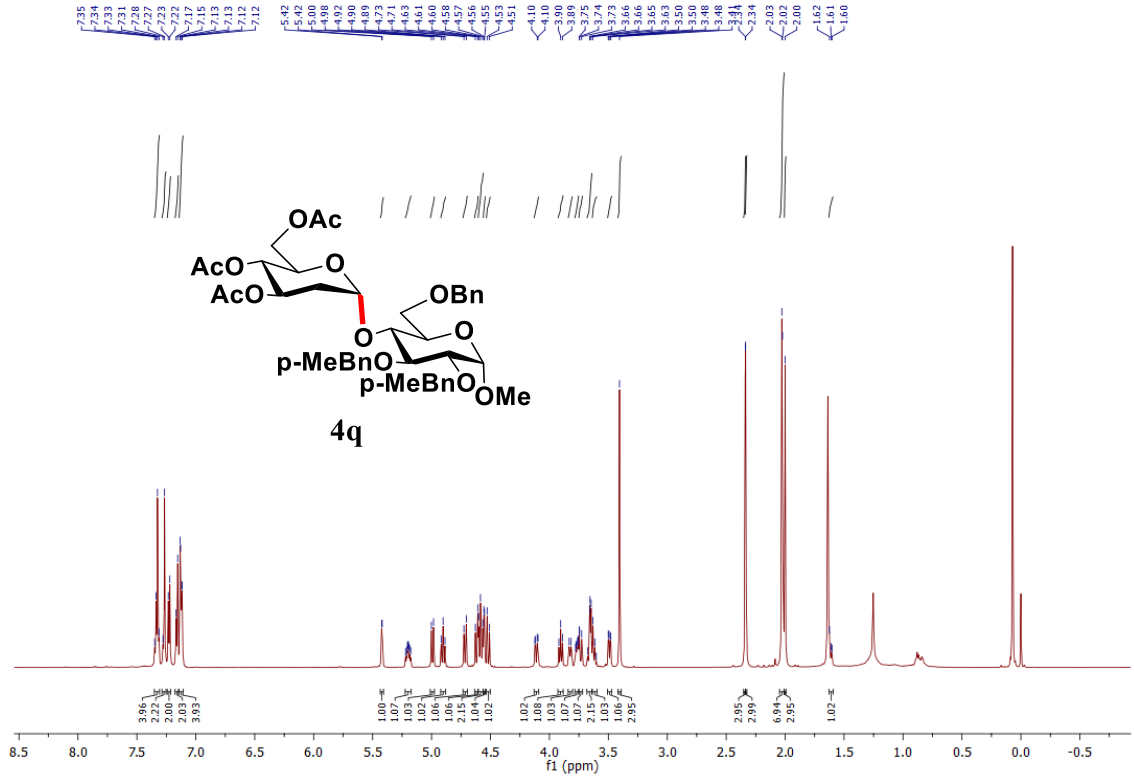
COSY NMR spectrum of compound 4p



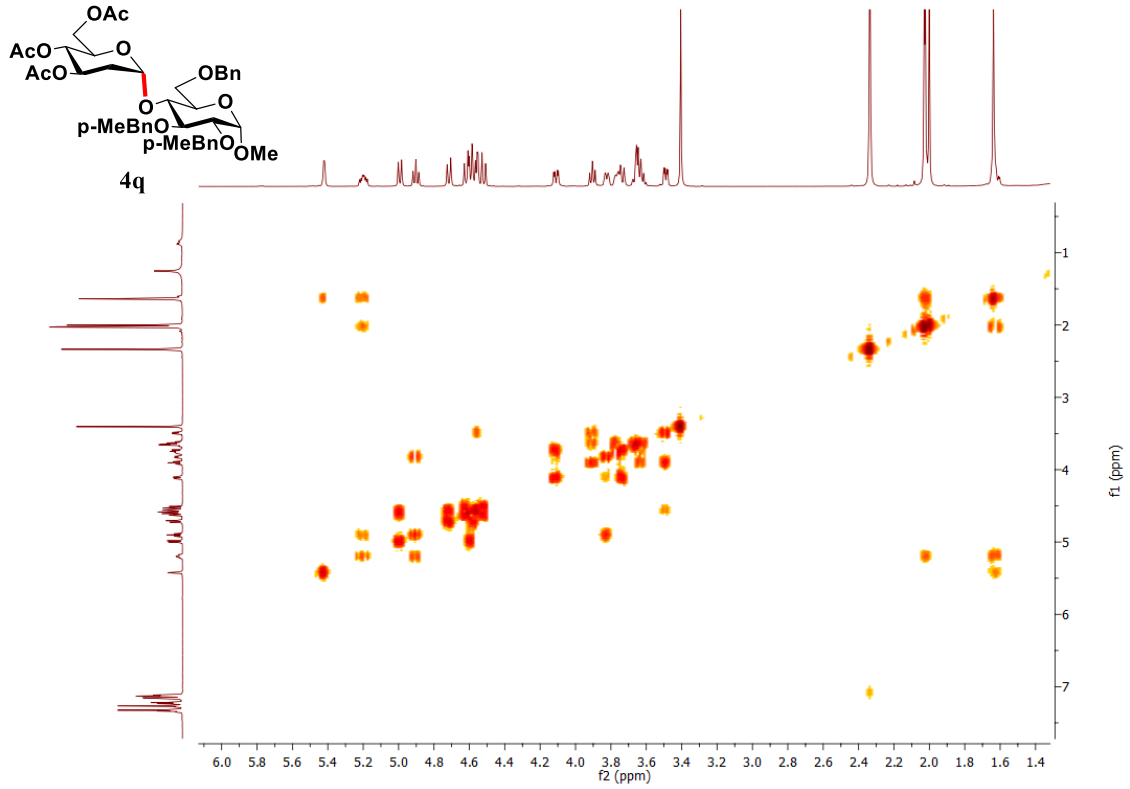
^{13}C NMR spectrum of compound 4p



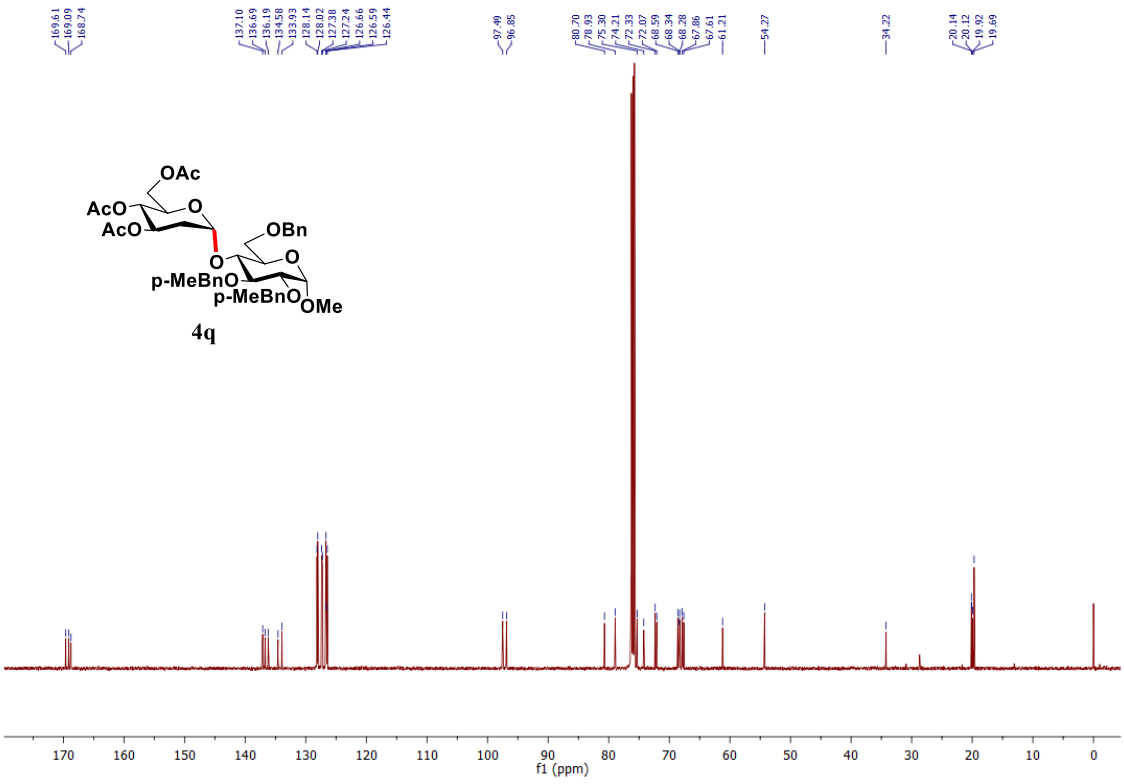
^{1}H NMR spectrum of compound 4q



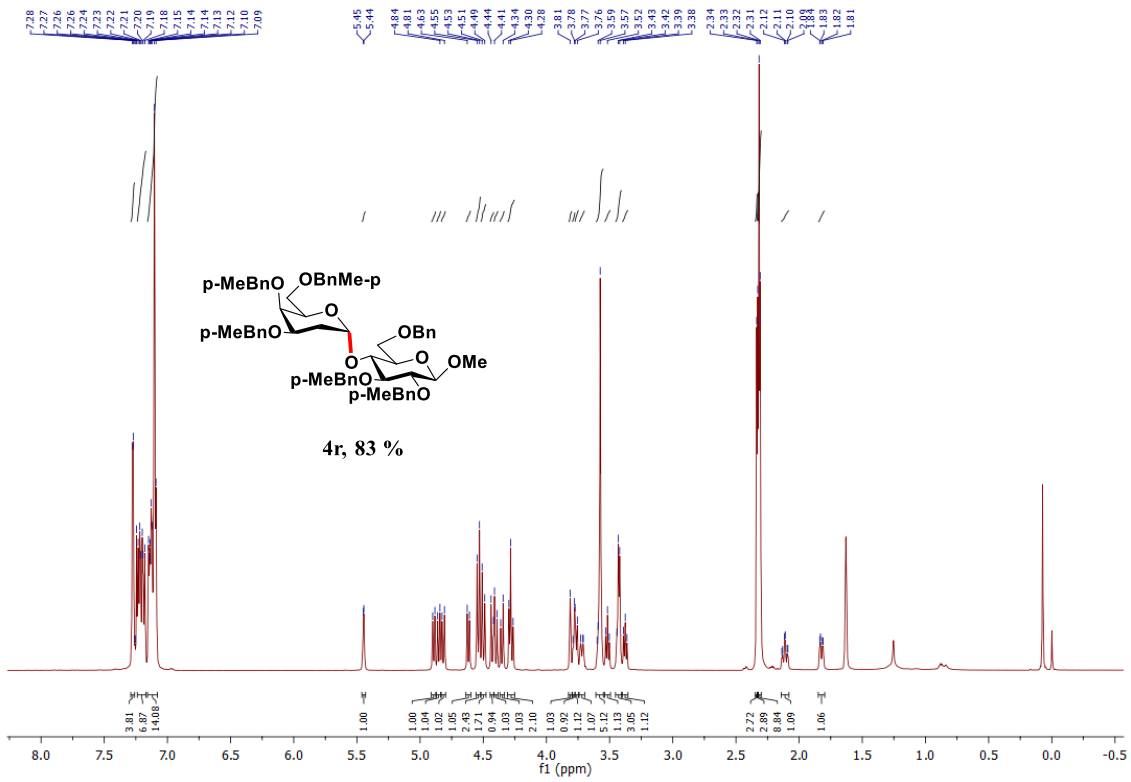
COSY NMR spectrum of compound 4q



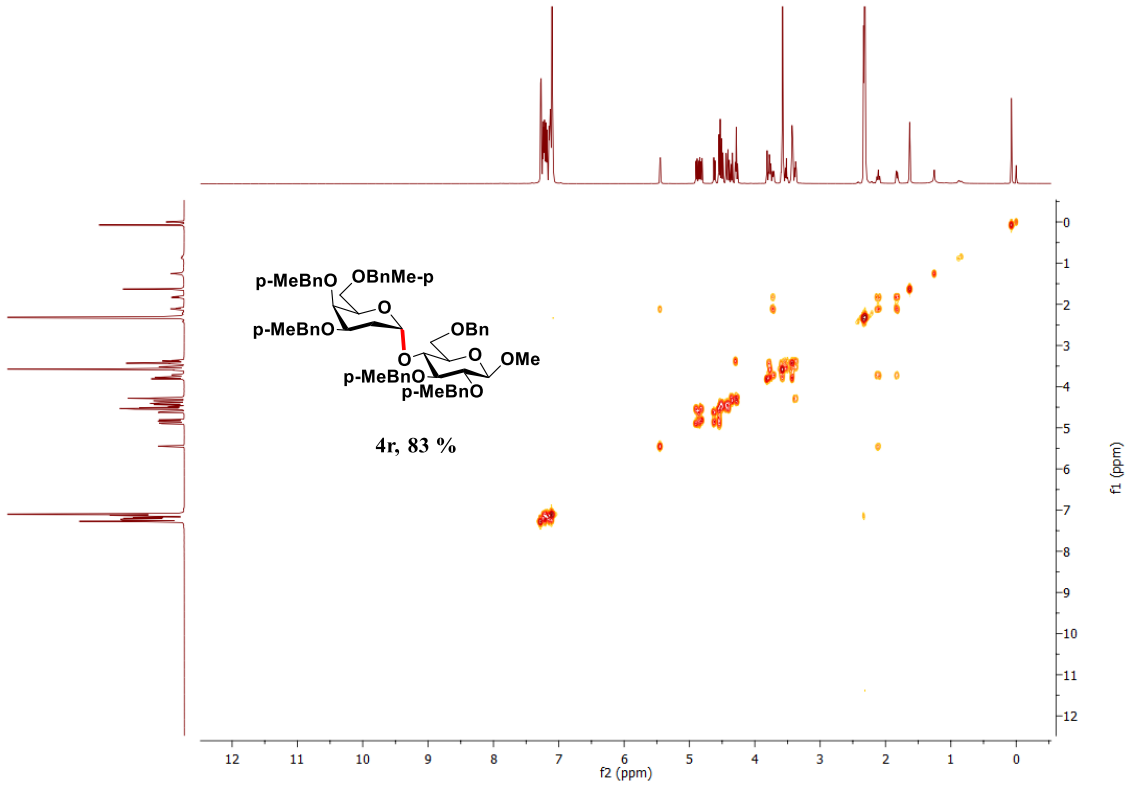
^{13}C NMR spectrum of compound 4q



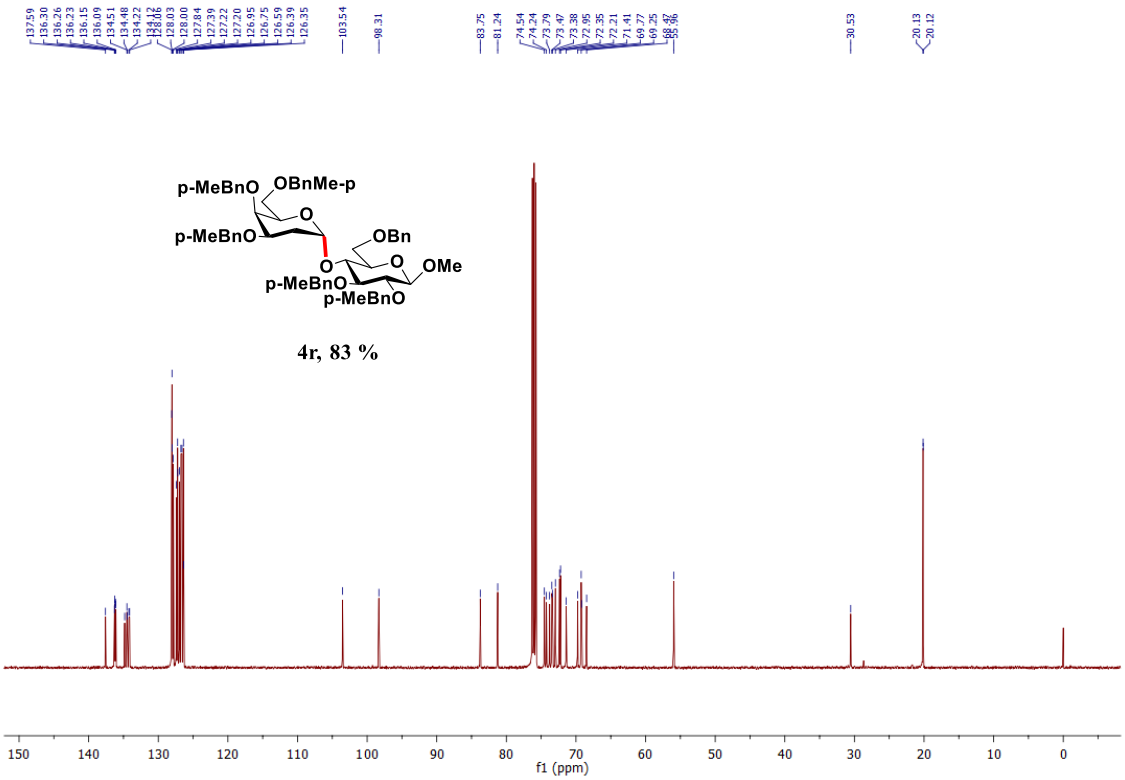
^{1}H NMR spectrum of compound 4r



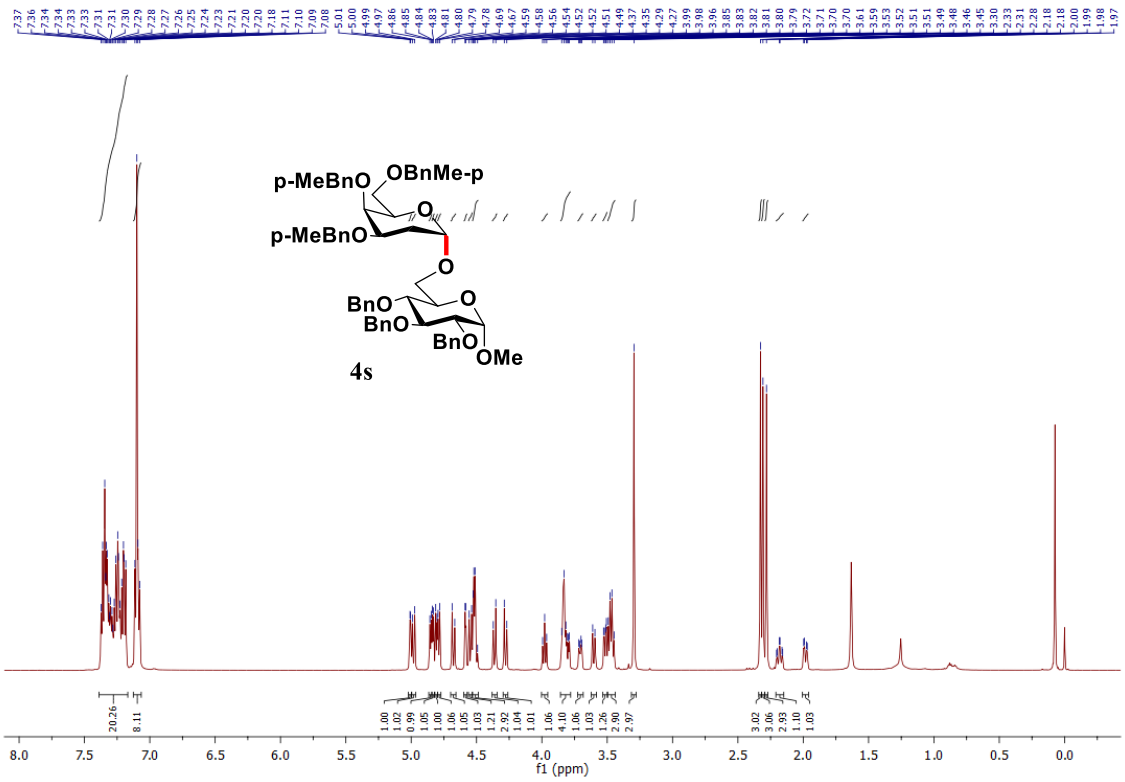
COSY NMR spectrum of compound 4r



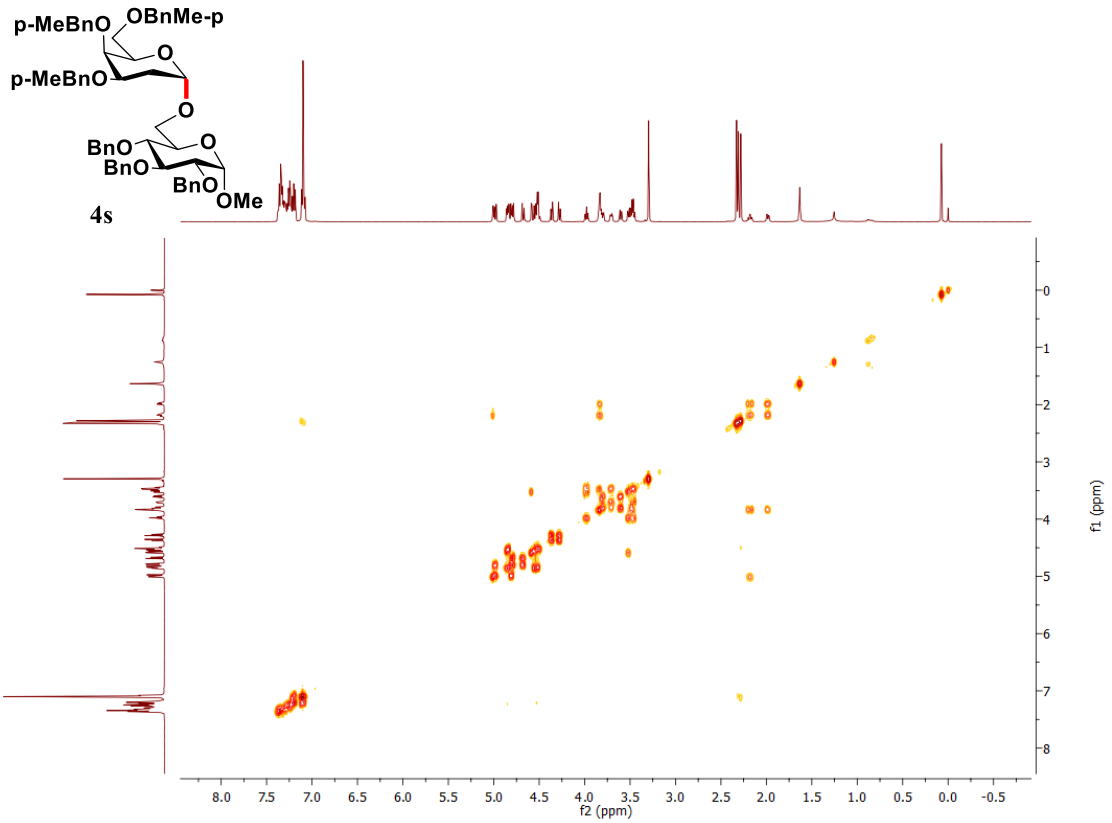
^{13}C NMR spectrum of compound 4r



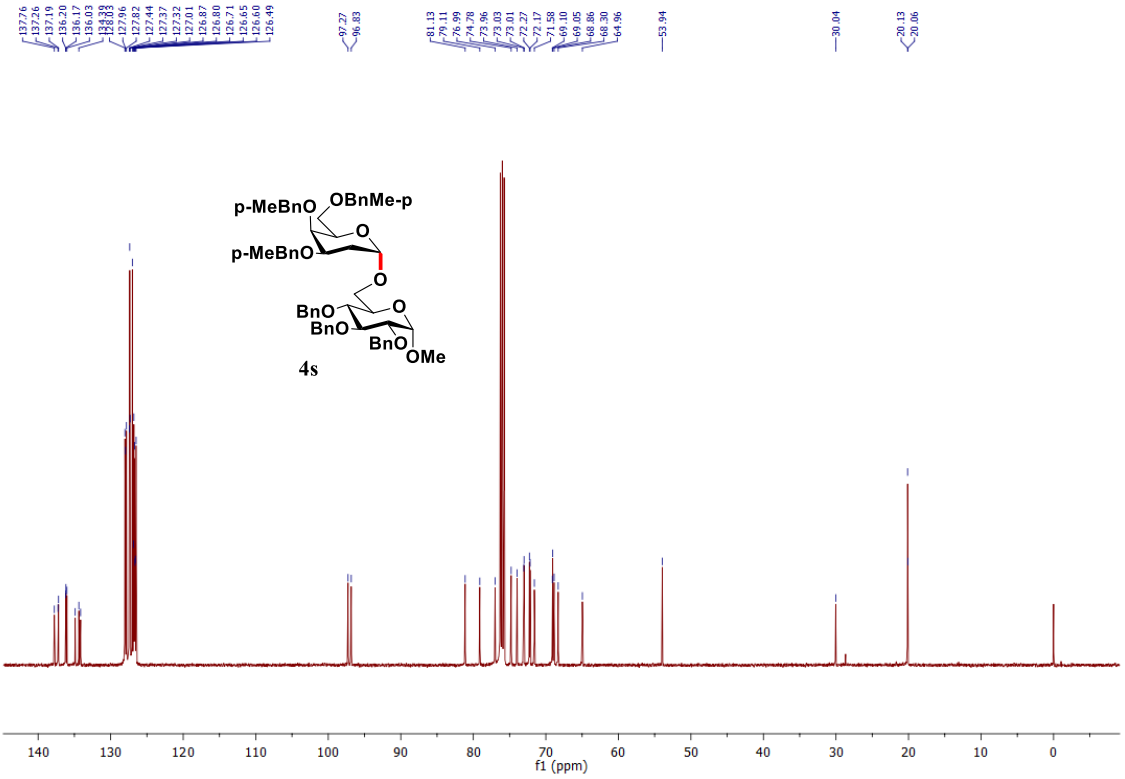
^{1}H NMR spectrum of compound 4s



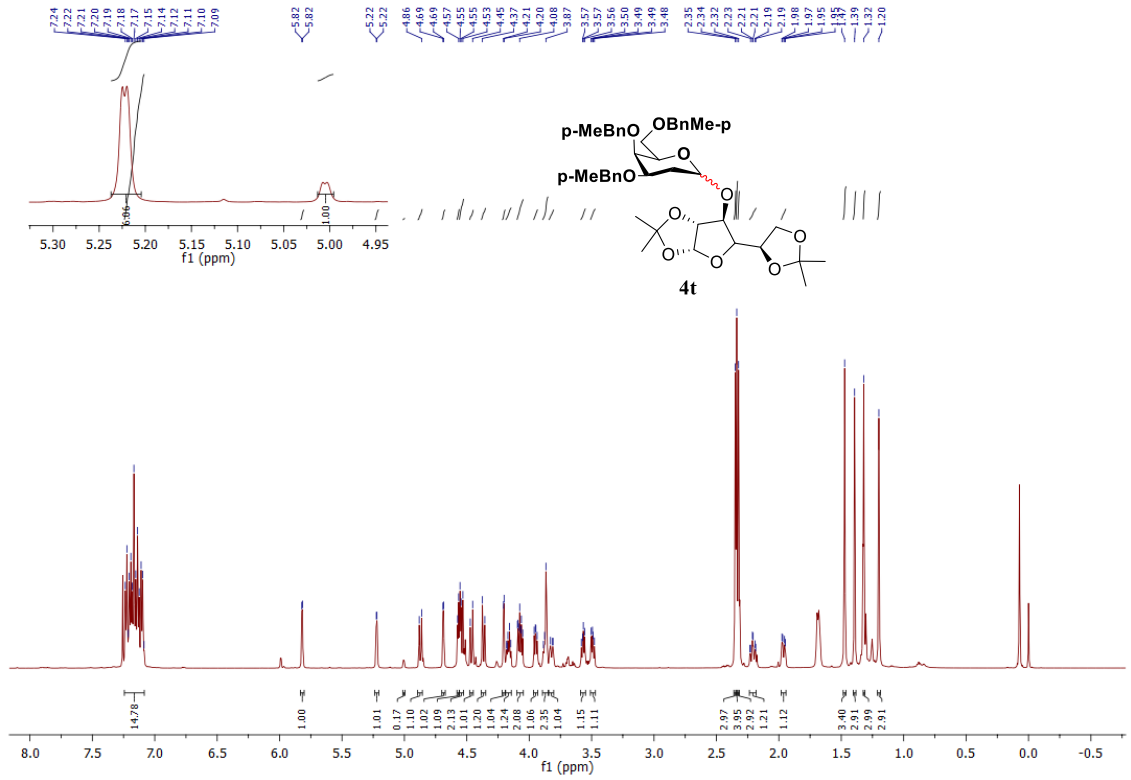
COSY NMR spectrum of compound 4s



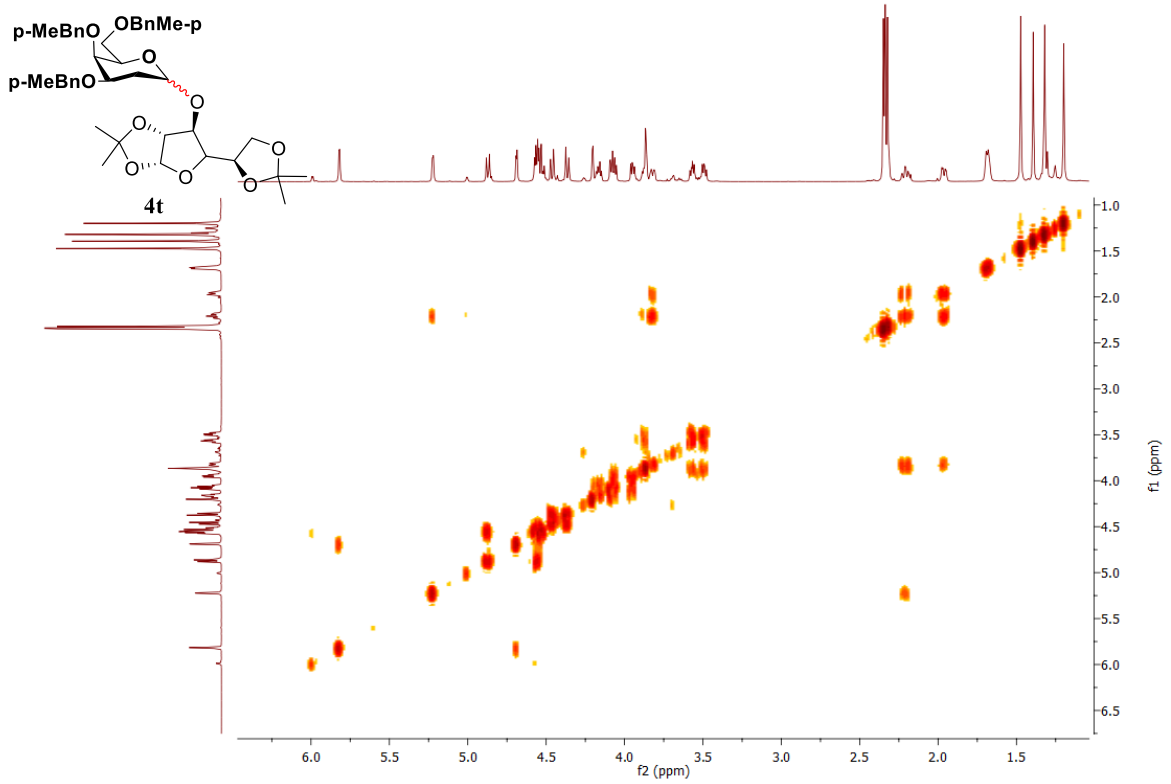
^{13}C NMR spectrum of compound 4s



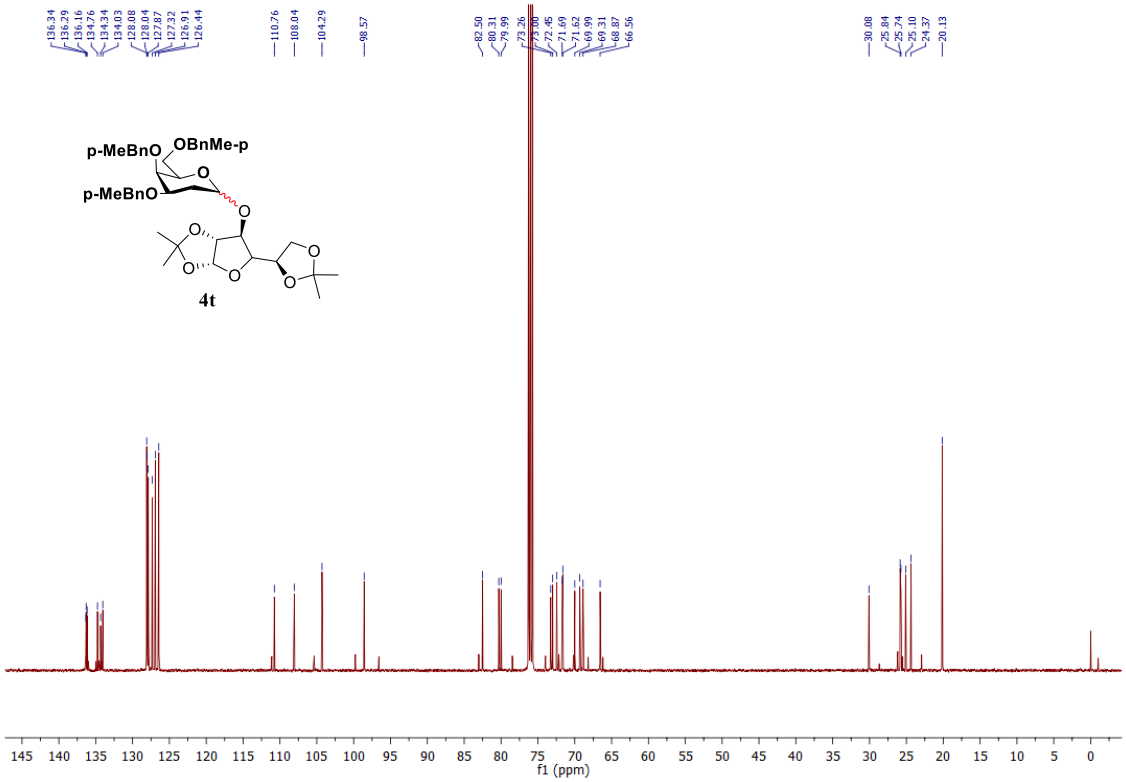
^{1}H NMR spectrum of compound 4t



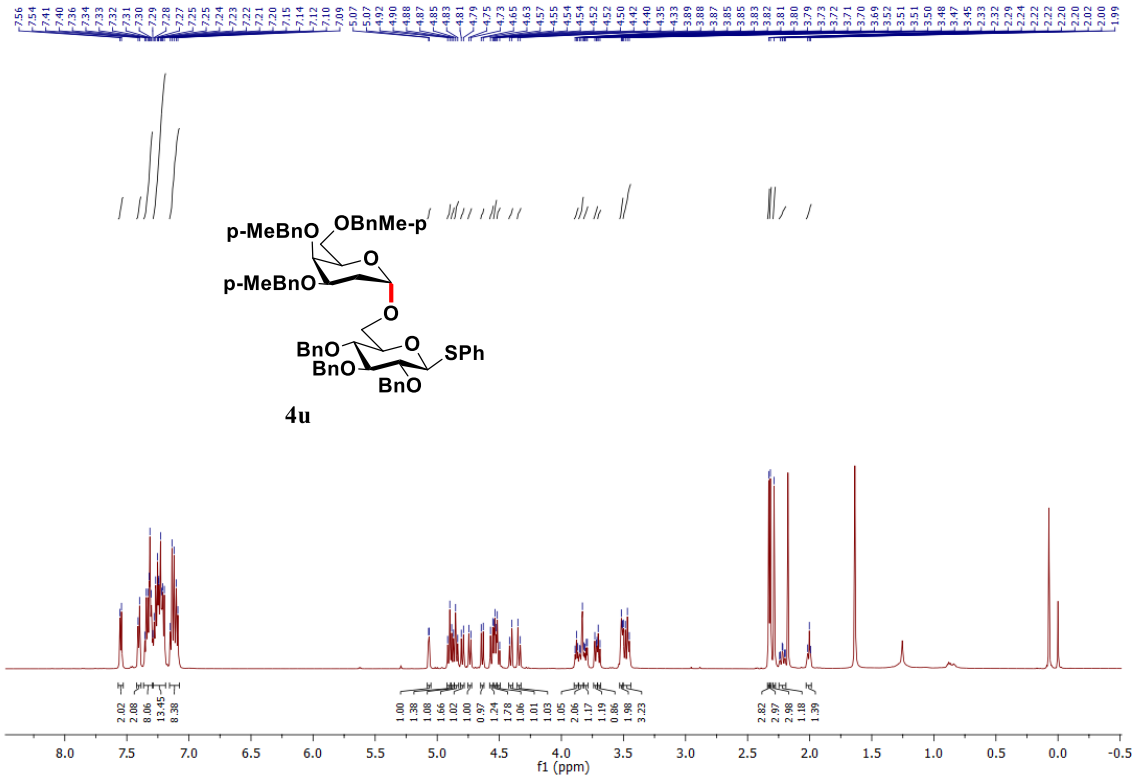
COSY NMR spectrum of compound 4t



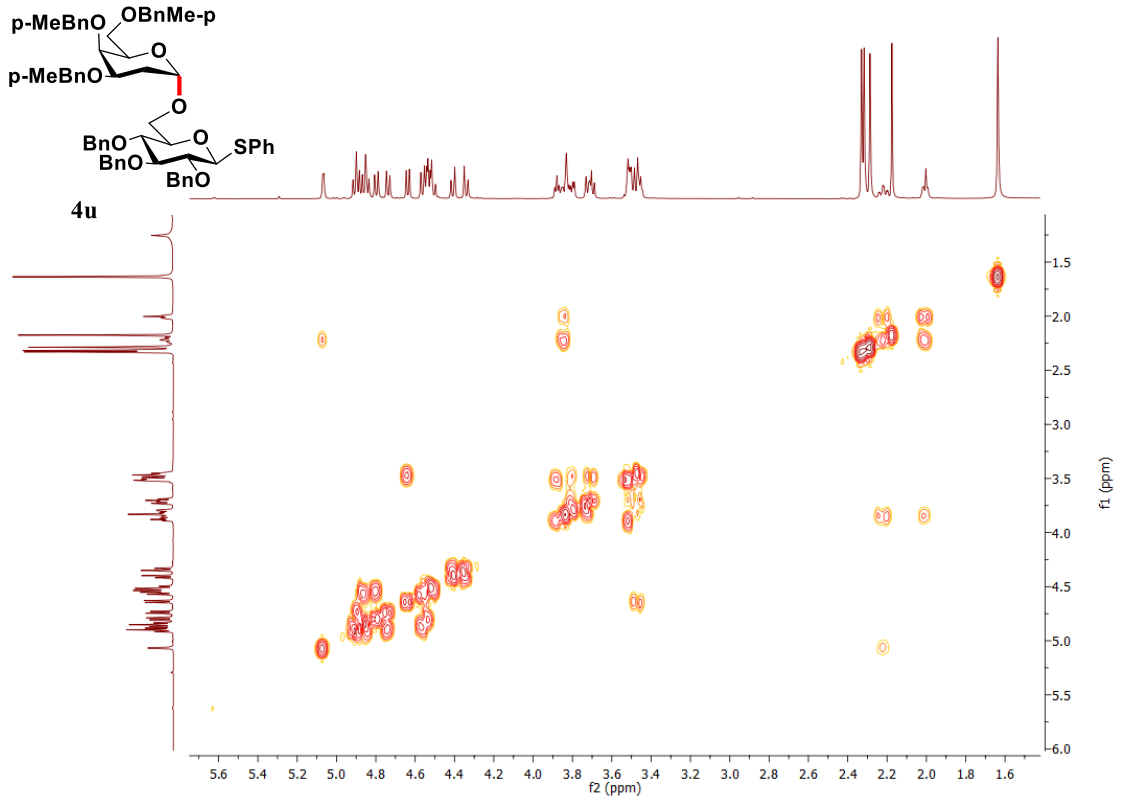
^{13}C NMR spectrum of compound 4t



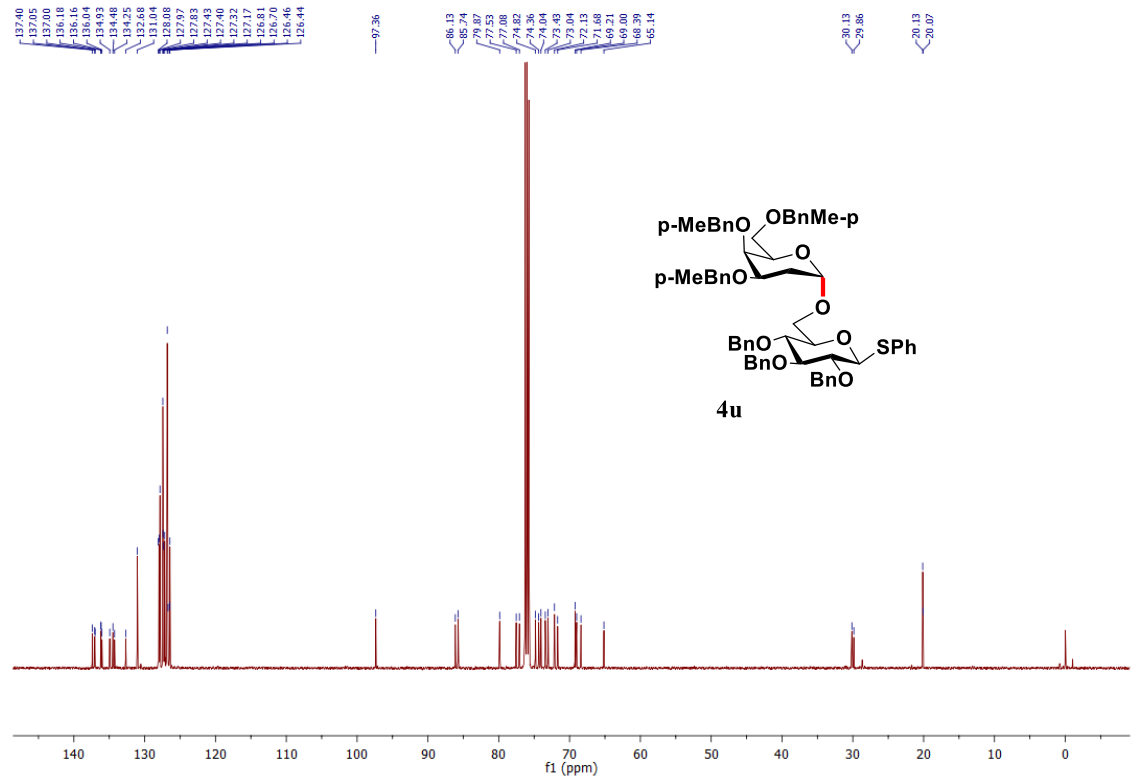
^{1}H NMR spectrum of compound 4u



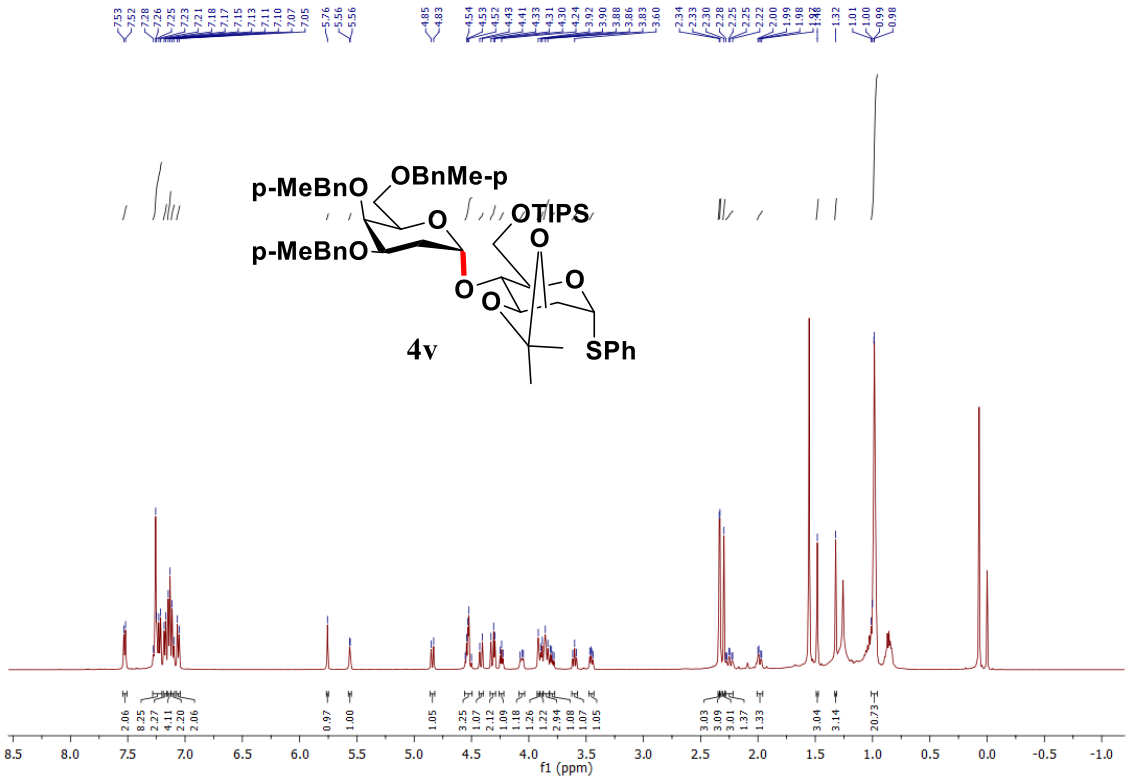
COSY NMR spectrum of compound 4u



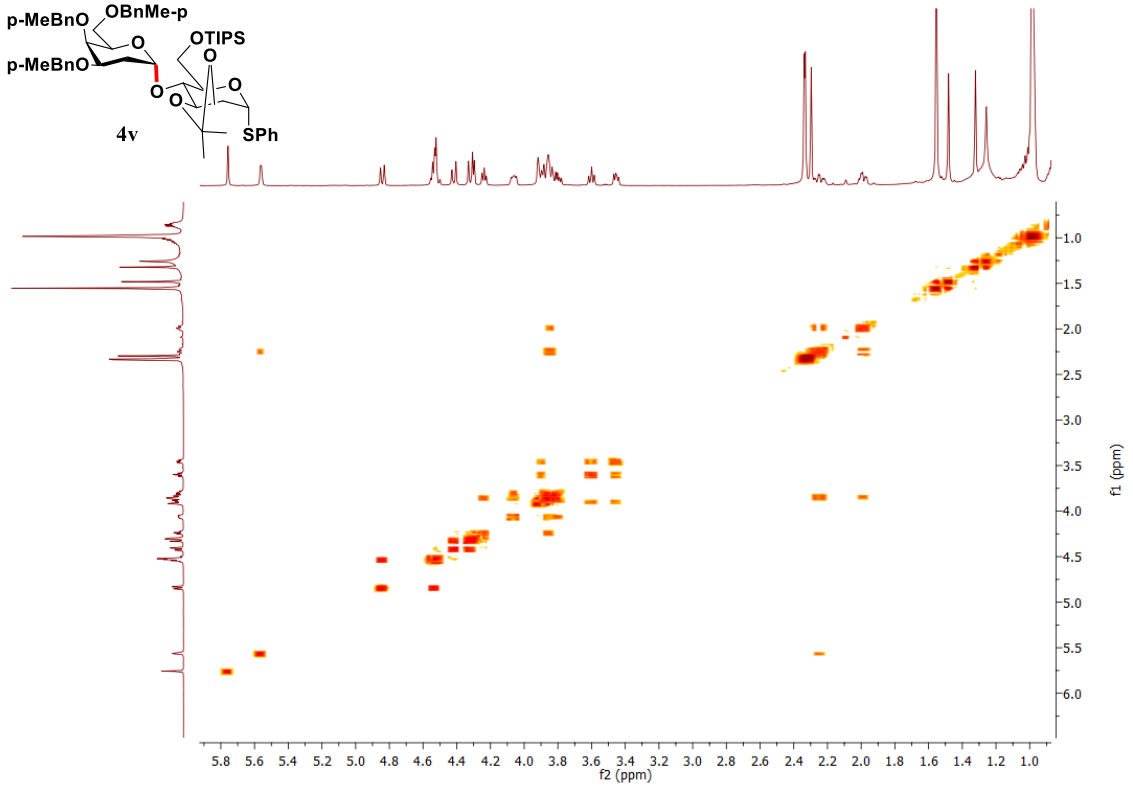
^{13}C NMR spectrum of compound 4u



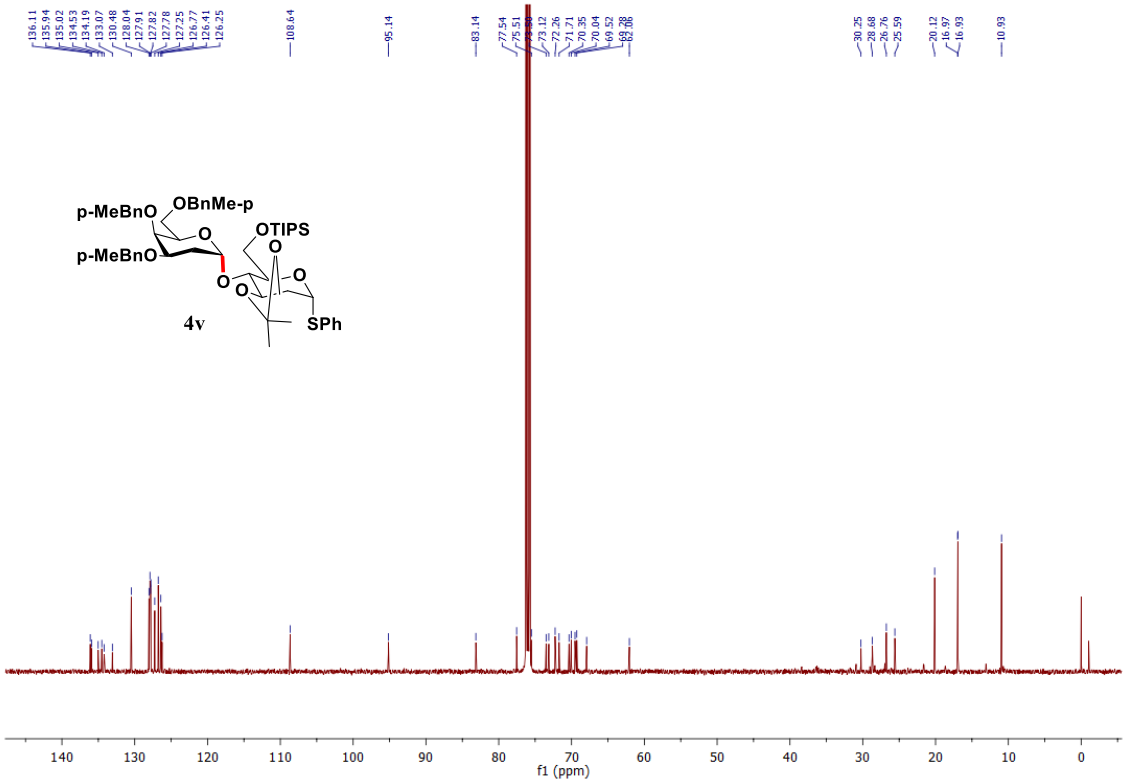
^{1}H NMR spectrum of compound 4v



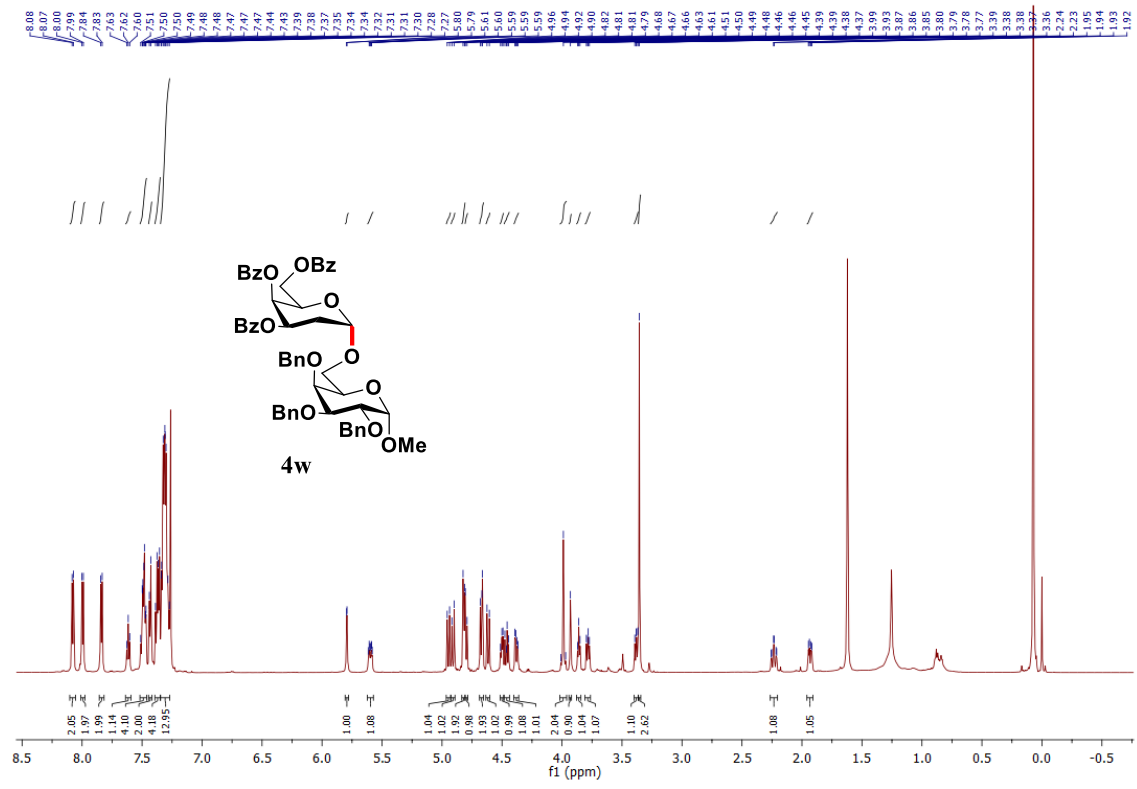
COSY NMR spectrum of compound 4v



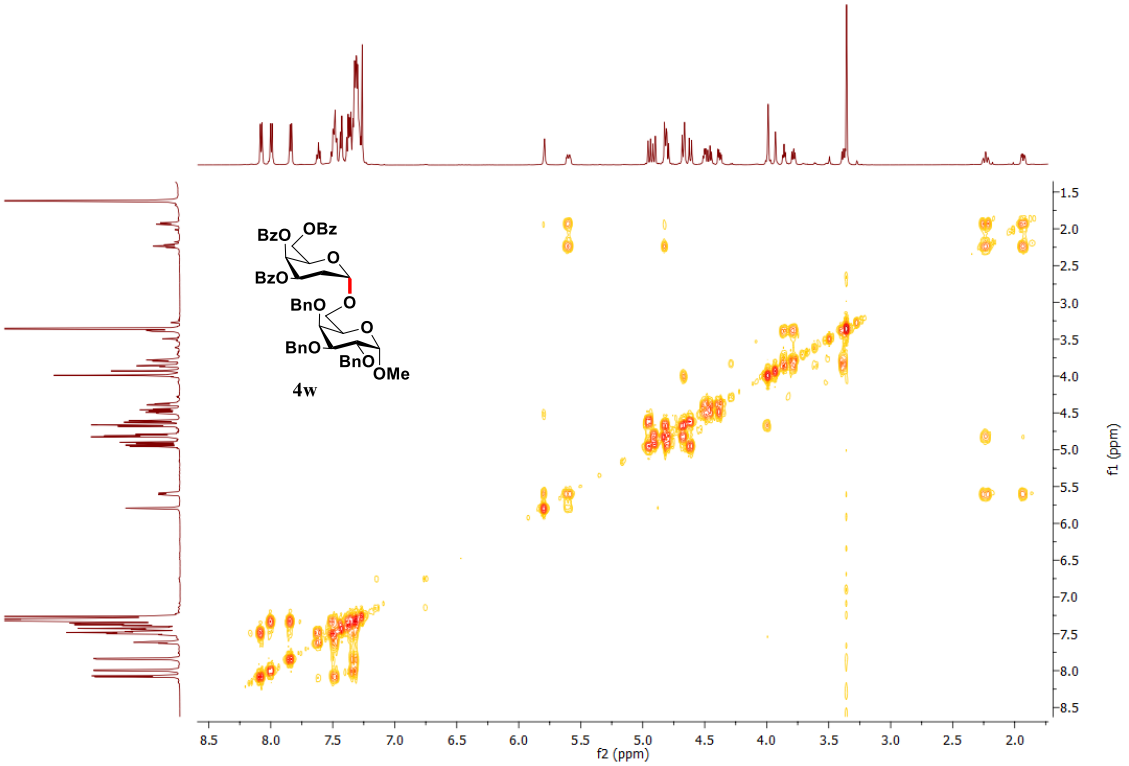
^{13}C NMR spectrum of compound 4v



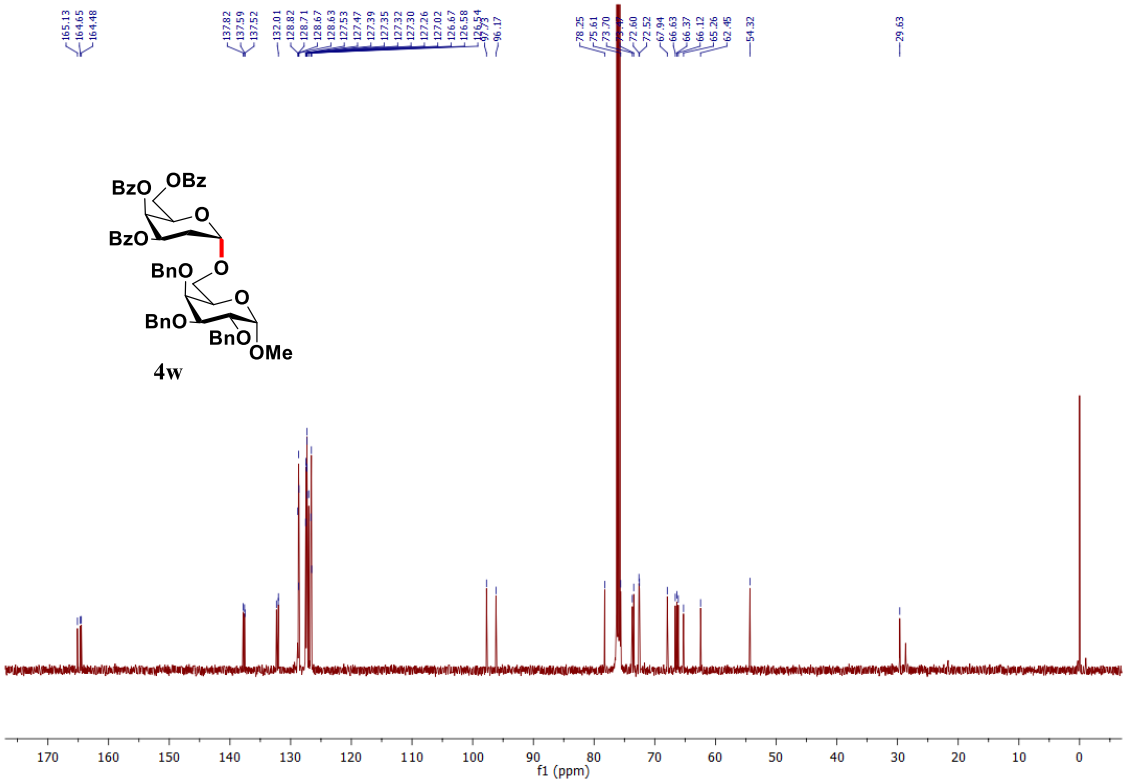
^{1}H NMR spectrum of compound 4w



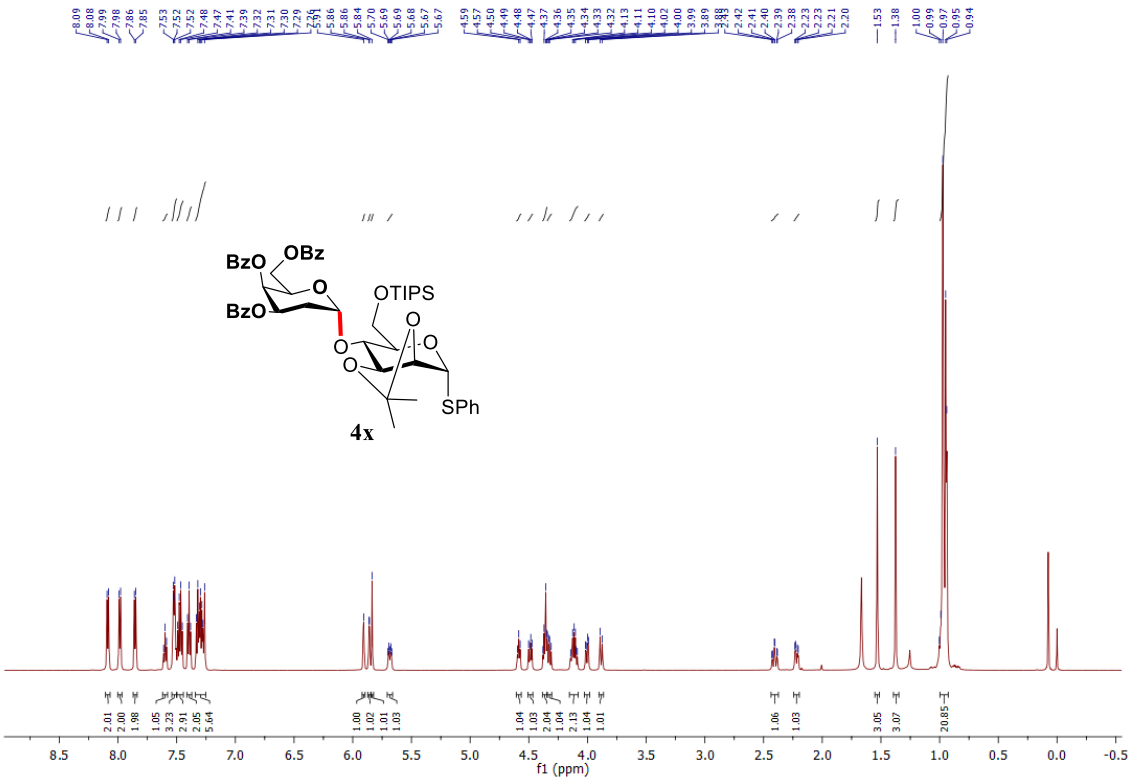
COSY NMR spectrum of compound 4w



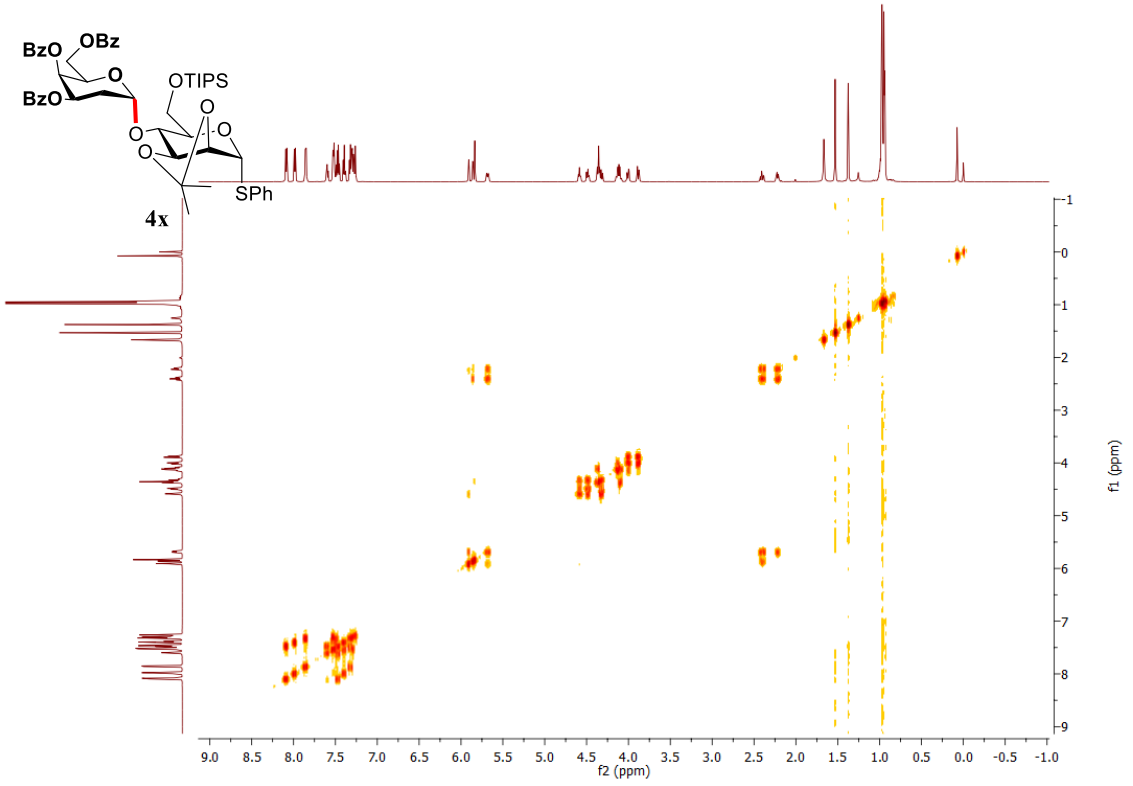
^{13}C NMR spectrum of compound 4w



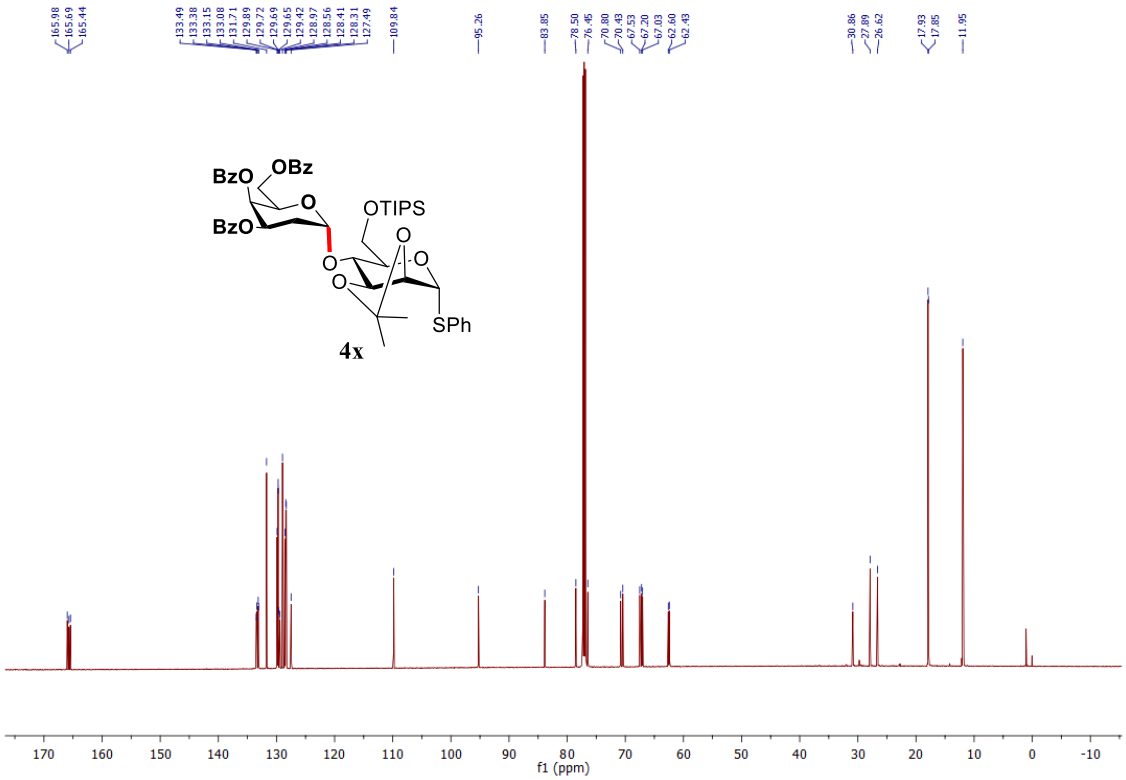
^{1}H NMR spectrum of compound 4x



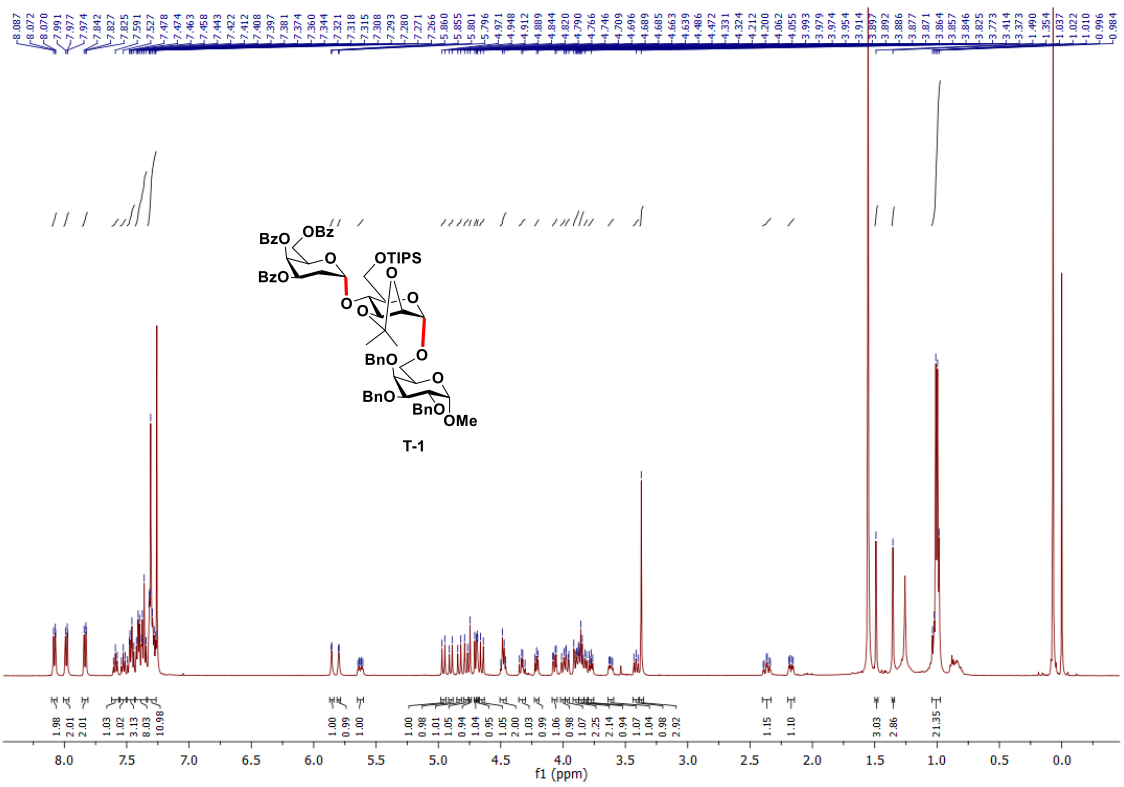
COSY NMR spectrum of compound 4x



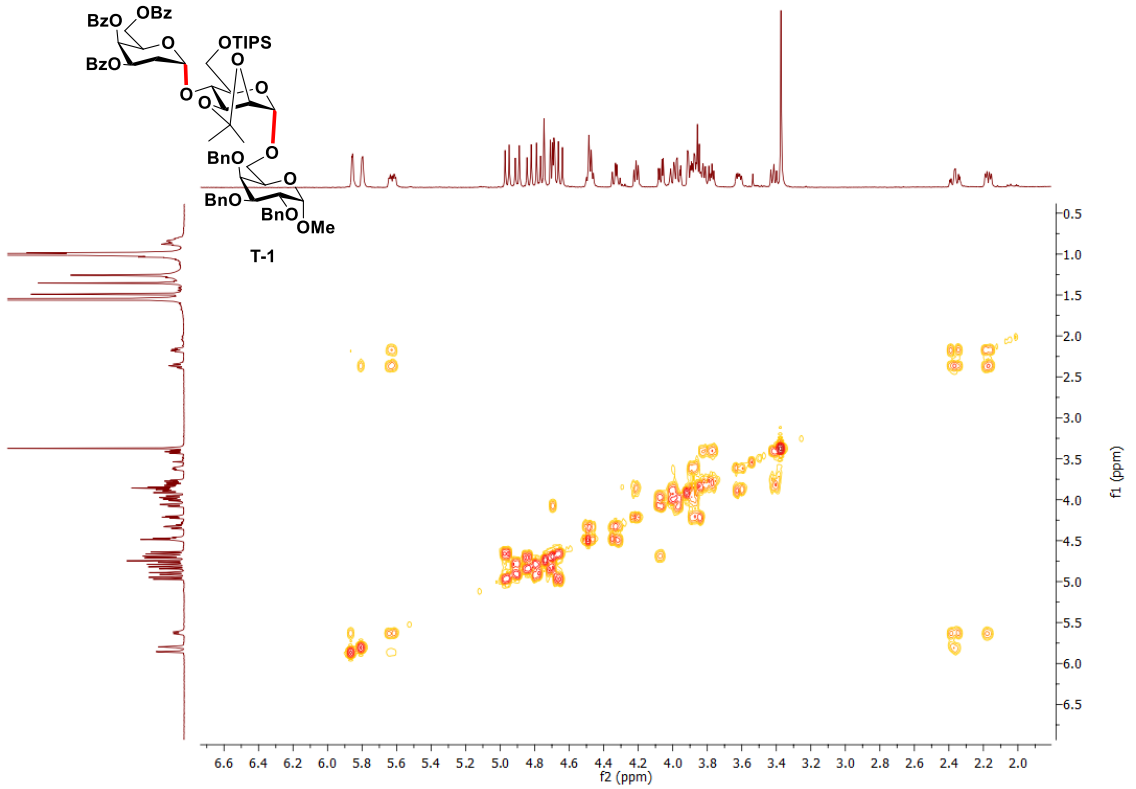
^{13}C NMR spectrum of compound 4x



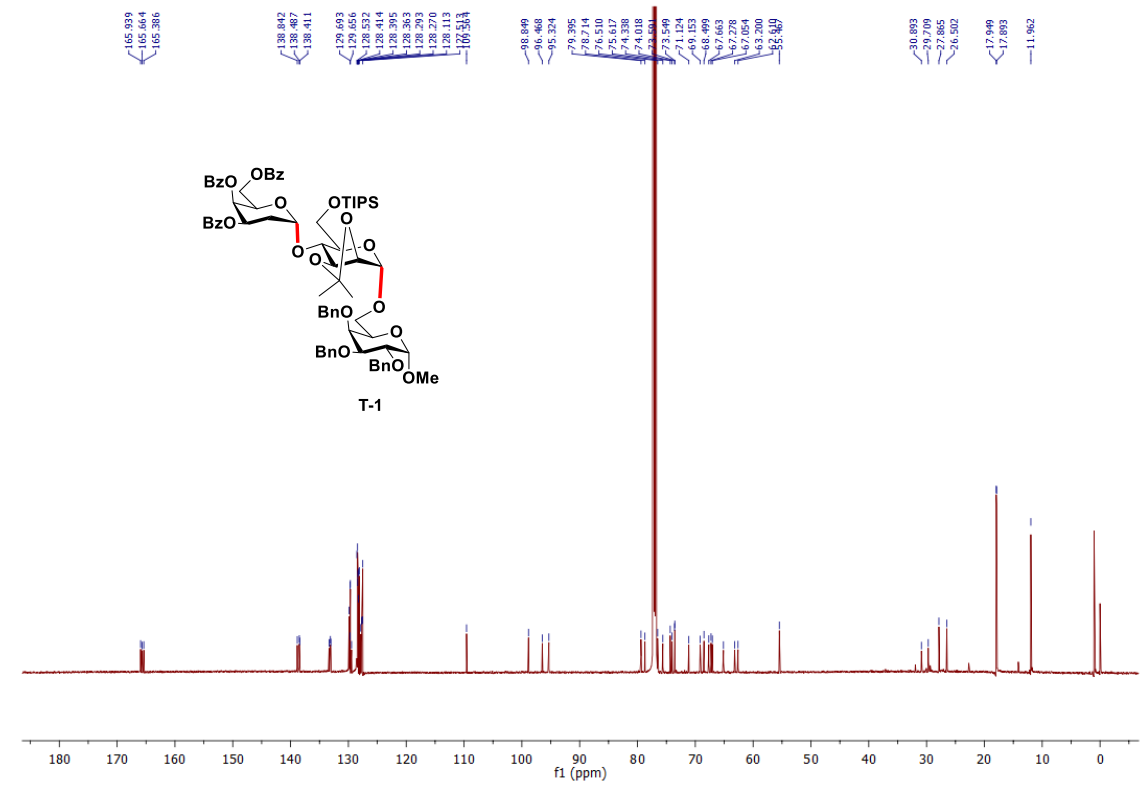
^{1}H NMR spectrum of compound T-1



COSY NMR spectrum of compound T-1



^{13}C NMR spectrum of compound T-1



HSQC NMR spectrum of compound T-1