Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supplementary Information

Efficient *O*- and *S*-glycosylation with *ortho*-2,2-dimethoxycarbonylcyclopropylbenzyl thioglycoside donors by catalytic strain-release

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Supplemental Experimental Procedures

General information

All reactions were carried out under argon or nitrogen atmosphere with magnetic stirring unless otherwise indicated. All commercially obtained reagents were used as received, except where specified otherwise. $Sc(OTf)_3$ was purchased from Alfa and used without further purification. Tetrahydrofuran (THF) and toluene were distilled immediately from sodium-benzophenone ketyl before use. Dichloromethane (CH_2Cl_2), pyridine, and acetonitrile were refluxed over calcium hydride and distilled before use. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from Sigma-Aldrich and used without further purification. Flash column chromatography was performed on Silica Gel H (300–400 mesh, Qingdao, China). Analytical thin-layer chromatography was performed on Silicycle SiliaPlate glass-backed plates coated with silica gel (60 mesh pore size, F-254 indicator) and visualized by exposure to ultraviolet light and/or staining with 7% sulfuric acid in methanol. Optical rotations were determined with a JASCO P-1020 digital polarimeter. All NMR spectra were recorded with Bruker BBFO-400 (400 MHz) NMR spectrometer at room temperature using $CDCl_3$, CD_2Cl_2, or CD_3OD as solvent. The NMR spectra were calibrated by using residual undeuterated chloroform (δ_H = 7.26 ppm), $CDCl_3$ (δ_C = 77.16 ppm), residual undeuterated dichloromethane (δ_H = 5.32 ppm), CD_2Cl_2 (δ_C = 53.84 ppm) residual undeuterated methanol (δ_H = 3.31 ppm), CD_3OD (δ_C = 49.00 ppm) as internal references. ^{19}F NMR signals were referenced against $PhCF_3$ (δ = – 63.2 ppm) as an external standard. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet.

Synthesis of CCPB thioglycosides 3a-h

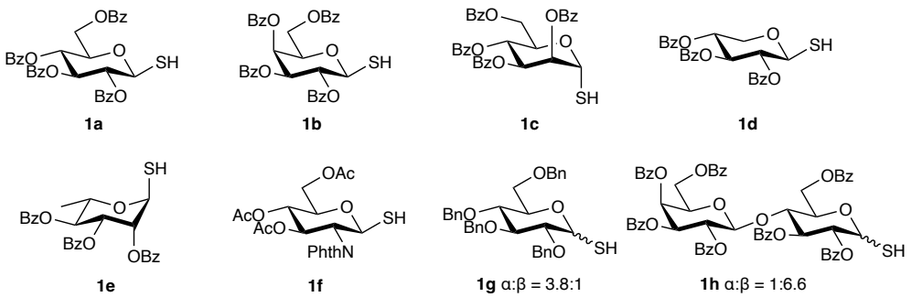
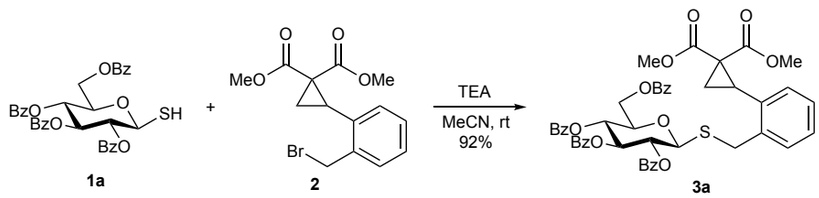


Figure S1. Anomeric thiols used in this project.

Thiols **1a-1e**,[1] **1f-1g**[2] and **1h**[1] were prepared following the reported procedures.

***ortho*-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,3′,4′,6′-tetra-*O*-benzoyl-1′-thio-β-D-glucopyranoside (3a)**



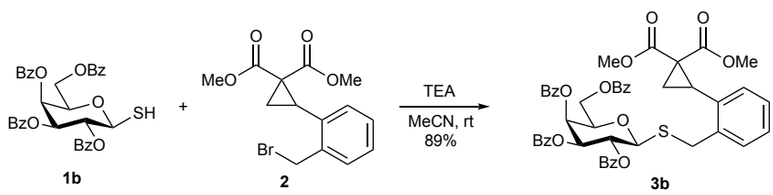
To a solution of thiol **1a** (1.68 g, 2.74 mmol) and **2** (3.3 mmol, 1.2 equiv) in anhydrous MeCN (10 mL) was added triethylamine (TEA, 4.11 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 1 h before it was then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane: EtOAc = 3:1) to afford the desired CCPB thioglycoside **3a** (2.17 g, 2.52 mmol, 92%, d.r. = 1:1) as a white foam.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.0 Hz, 2H), 8.01 (d, J = 7.0 Hz, 2H), 7.95 (d, J = 6.9 Hz, 2H), 7.90 – 7.79 (m, 10H), 7.55 – 7.45 (m, 6H), 7.42 – 7.28 (m, 17H), 7.25 – 7.11 (m, 7H), 7.10 – 7.01 (m, 2H), 5.89 (t, J = 9.5 Hz, 1H), 5.80 (t, J = 9.4 Hz, 1H), 5.75 – 5.70 (m, 1H), 5.70 – 5.65 (m, 1H), 5.62 – 5.55 (m, 2H), 4.84 (d, J = 10.0 Hz, 1H), 4.67 (dd, J = 12.2, 3.1 Hz, 1H), 4.62 – 4.50 (m, 4H), 4.20 (d, J = 12.9 Hz, 1H), 4.14 – 4.06 (m, 3H), 4.05 – 3.98 (m, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 3.39 (t, J = 8.7 Hz, 1H), 3.34 (t, J = 8.7 Hz, 1H), 3.27 (s, 3H), 3.26 (s, 3H), 2.24 (dd, J = 8.1, 5.2 Hz, 1H), 2.18 (dd, J = 8.2, 5.2 Hz, 1H), 1.65 (dd, J = 9.2, 5.2 Hz, 1H), 1.53 (dd, J = 9.2, 5.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.7, 167.1, 167.0, 166.3, 166.2, 165.9, 165.29, 165.25, 165.2, 137.4, 137.1, 133.53, 133.49, 133.4, 133.33, 133.26, 133.2, 130.03, 129.97, 129.95, 129.92, 129.90, 129.84, 129.83, 129.82, 129.7, 129.3, 129.2, 128.91, 128.88, 128.6, 128.50, 128.47, 128.44, 128.42, 128.38, 128.0, 127.9, 127.61, 127.59, 127.4, 84.1, 82.4, 77.4, 76.2, 76.1, 74.3, 70.8, 69.80, 69.78, 63.6, 63.5, 53.04, 52.96, 52.30, 52.26, 36.8, 36.5, 32.3, 32.1, 29.94, 29.92, 18.6, 18.2.

HRMS (ESI$^+$, m/z): calcd for $C_{48}H_{42}O_{13}SNa^+$ $(M+Na)^+$: 881.2238; Found: 881.2224.

***ortho*-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,3′,4′,6′-tetra-*O*-benzoyl-1′-thio-β-D-galactopyranoside (3b)**



Following the procedure for **3a**, **1b** (920 mg, 2.70 mmol) was coupled with **2** (3.24 mmol, 1.2 equiv) to afford donor **3b** (1.15 g, 2.40 mmol, 89%, d.r. = 1:1) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 3:1).

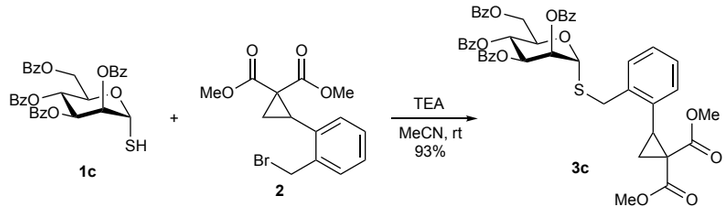
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 6H), 8.04 (d, J = 7.2 Hz, 2H), 7.97 (d, J = 7.8 Hz, 2H), 7.85

(d, *J* = 7.8 Hz, 2H), 7.81 – 7.75 (m, 4H), 7.64 – 7.33 (m, 22H), 7.24 – 7.12 (m, 8H), 7.07 (dd, *J* = 11.5, 6.5 Hz, 2H), 6.08 – 6.02 (m, 2H), 5.92 – 5.79 (m, 2H), 5.66 (dd, *J* = 9.9, 3.3 Hz, 1H), 5.54 (dd, *J* = 9.9, 3.3 Hz, 1H), 4.88 (d, *J* = 10.0 Hz, 1H), 4.76 – 4.68 (m, 2H), 4.61 (d, *J* = 10.1 Hz, 1H), 4.50 – 4.37 (m, 2H), 4.36 – 4.26 (m, 3H), 4.16 – 4.03 (m, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.45 (t, *J* = 8.7 Hz, 1H), 3.37 (t, *J* = 8.7 Hz, 1H), 3.30 (s, 3H), 3.27 (s, 3H), 2.29 (dd, *J* = 8.0, 5.3 Hz, 1H), 2.19 (dd, *J* = 8.1, 5.3 Hz, 1H), 1.69 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.53 (dd, *J* = 9.2, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.9, 169.7, 166.99, 166.97, 166.1, 166.0, 165.62, 165.55, 165.52, 165.46, 165.3, 137.2, 137.1, 133.68, 133.65, 133.4, 133.32, 133.27, 130.1, 130.04, 129.99, 129.94, 129.86, 129.83, 129.80, 129.79, 129.50, 129.48, 129.3, 129.22, 129.15, 129.1, 128.9, 128.8, 128.73, 128.71, 128.58, 128.56, 128.5, 128.39, 128.35, 128.3, 128.0, 127.9, 127.59, 127.56, 127.43, 84.37, 82.8, 74.91, 74.86, 72.8, 68.5, 68.34, 68.29, 68.2, 62.4, 61.9, 53.0, 52.9, 52.3, 52.2, 36.8, 36.5, 32.2, 29.9, 29.7, 18.5, 18.1.

HRMS (ESI$^+$, m/z): calcd for $C_{48}H_{42}O_{13}SNa^+$ $(M+Na)^+$: 881.2238; Found: 881.2231.

ortho-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,3′,4′,6′-tetra-_O_-benzoyl-1′-thio-α-D-mannopyranoside (3c)



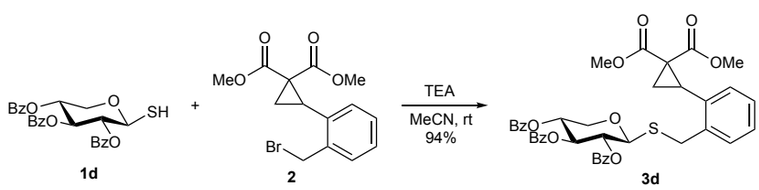
Following the procedure for **3a**, **1c** (612 mg, 1.00 mmol) was coupled with **2** (1.20 mmol, 1.2 equiv) to afford donor **3c** (815 mg, 0.95 mmol, 95%, d.r. = 1:1) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.17 – 8.12 (m, 4H), 8.07 – 8.02 (m, 4H), 8.00 – 7.95 (m, 4H), 7.85 – 7.79 (m, 4H), 7.61 – 7.55 (m, 4H), 7.54 – 7.48 (m, 2H), 7.44 – 7.34 (m, 15H), 7.30 – 7.27 (m, 2H), 7.25 – 7.18 (m, 7H), 7.16 – 7.06 (m, 2H), 6.25 – 6.16 (m, 2H), 5.90 – 5.78 (m, 4H), 5.48 (s, 1H), 5.42 (s, 1H), 4.93 – 4.87 (m, 1H), 4.84 – 4.78 (m, 1H), 4.75 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.69 (dd, *J* = 12.4, 2.5 Hz, 1H), 4.55 (dd, *J* = 12.4, 4.1 Hz, 1H), 4.49 (dd, *J* = 12.3, 3.7 Hz, 1H), 4.19 (d, *J* = 13.4 Hz, 1H), 4.13 (d, *J* = 13.3 Hz, 1H), 3.96 (d, *J* = 13.4 Hz, 1H), 3.91 – 3.86 (m, 4H), 3.84 (s, 3H), 3.55 (t, *J* = 8.7 Hz, 1H), 3.49 (t, *J* = 8.7 Hz, 1H), 3.32 – 3.26 (s, 6H), 2.38 – 2.28 (m, 2H), 1.85 – 1.76 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.10, 170.06, 167.09, 167.07, 166.3, 166.2, 165.53, 165.47, 165.22, 165.20, 137.0, 136.9, 133.5, 133.4, 133.3, 133.14, 133.13, 133.13, 133.10, 130.2, 130.11, 130.06, 130.0, 129.94, 129.90, 129.86, 129.85, 129.8, 129.5, 129.4, 129.1, 129.0, 128.7, 128.61, 128.57, 128.55, 128.5, 128.4, 128.0, 127.92, 127.89, 127.7, 127.6, 82.6, 81.5, 71.7, 71.6, 70.92, 70.88, 69.51, 69.46, 67.12, 67.05, 63.0, 62.8, 53.2, 53.1, 52.33, 52.31, 37.2, 36.8, 33.3, 32.4, 30.2, 30.1, 18.6, 18.5.

HRMS (ESI$^+$, m/z): calcd for $C_{48}H_{42}O_{13}SNa^+$ $(M+Na)^+$: 881.2238; Found: 881.2238.

ortho-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,3′,4′-tri-_O_-benzoyl-1′-thio-β-D-xylopyranoside (3d)



Following the procedure for **3a**, **1d** (380 mg, 0.79 mmol) was coupled with **2** (0.95 mmol, 1.2 equiv) to afford donor **3d** (540 mg, 0.743 mmol, 94%, d.r. = 1:1) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 4:1).

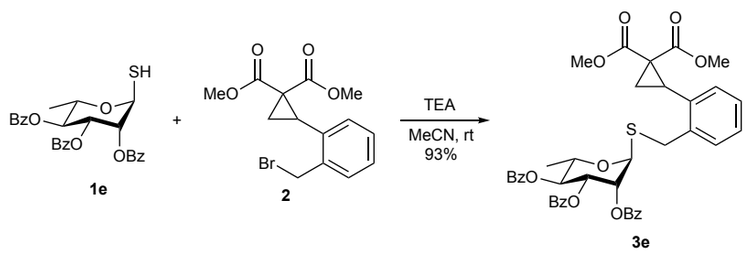
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.04 – 7.96 (m, 10H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.55 – 7.48 (m, 6H), 7.40 – 7.32 (m, 13H), 7.25 – 7.17 (m, 5H), 7.10 – 7.04 (m, 2H), 5.75 (t, *J* = 7.1 Hz, 1H), 5.69 (t, *J* = 6.8 Hz, 1H),

5.46 (t, *J* = 6.8 Hz, 1H), 5.39 (t, *J* = 6.6 Hz, 1H), 5.34 – 5.28 (m, 2H), 4.94 (d, *J* = 6.7 Hz, 1H), 4.88 (d, *J* = 6.5 Hz, 1H), 4.64 (dd, *J* = 12.2, 4.1 Hz, 1H), 4.58 (dd, *J* = 12.1, 4.2 Hz, 1H), 4.19 (d, *J* = 13.0 Hz, 1H), 4.08 (d, *J* = 13.4 Hz, 1H), 4.02 – 3.95 (m, 2H), 3.81 – 3.68 (m, 8H), 3.49 – 3.42 (m, 2H), 3.31 – 3.27 (m, 6H), 2.31 – 2.22 (m, 2H), 1.74 (dd, *J* = 9.3, 5.2 Hz, 1H), 1.67 – 1.63 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.9, 169.8, 167.0, 165.5, 165.31, 165.27, 165.2, 165.1, 137.5, 137.3, 133.44, 133.40, 133.35, 133.32, 133.25, 133.2, 130.1, 129.99, 129.96, 129.9, 129.3, 129.2, 129.0, 128.43, 128.37, 128.3, 127.90, 127.85, 127.7, 127.4, 127.3, 83.2, 82.2, 70.9, 70.6, 70.1, 70.0, 69.01, 68.95, 63.8, 63.4, 52.94, 52.86, 52.2, 36.8, 36.6, 32.5, 32.3, 30.14, 30.09, 18.5, 18.3.

HRMS (ESI$^+$, m/z): calcd for $C_{40}H_{36}O_{11}SNa^+$ (M+Na)$^+$: 747.1871; Found: 747.1876.

ortho-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,3′,4′-tri-*O*-benzoyl-1′-thio-α-L-rhamnopyranoside (3e)



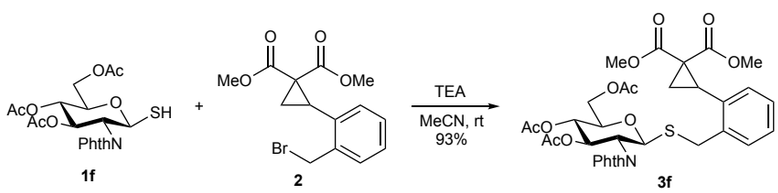
Following the procedure for **3a**, **1e** (510 mg, 1.03 mmol) was coupled with **2** (1.24 mmol, 1.2 equiv) to afford donor **3e** (712 mg, 0.96 mmol, 93%, d.r. = 1:1) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.12 – 8.05 (m, 4H), 8.02 – 7.96 (m, 4H), 7.83 – 7.77 (m, 4H), 7.63 – 7.57 (m, 2H), 7.54 – 7.45 (m, 6H), 7.43 – 7.35 (m, 7H), 7.32 – 7.28 (m, 1H), 7.26 – 7.18 (m, 8H), 7.17 – 7.13 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 5.81 – 5.66 (m, 6H), 5.37 (s, 1H), 5.34 (s, 1H), 4.66 – 4.57 (m, 1H), 4.57 – 4.79 (m, 1H), 4.17 (d, *J* = 13.7 Hz, 1H), 4.10 (d, *J* = 13.6 Hz, 1H), 3.92 (d, *J* = 7.1 Hz, 1H), 3.89 (d, *J* = 5.1 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.55 (t, *J* = 8.7 Hz, 1H), 3.49 (t, *J* = 8.7 Hz, 1H), 3.32 (s, 3H), 3.31 (s, 3H), 2.37 – 2.29 (m, 2H), 1.85 – 1.77 (m, 2H), 1.41 (d, *J* = 6.2 Hz, 3H), 1.35 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.1, 170.0, 167.13, 167.08, 165.87, 165.85, 165.5, 165.44, 165.42, 165.39, 137.5, 137.4, 133.5, 133.4, 133.3, 133.2, 133.0, 130.1, 130.0, 129.84, 129.76, 129.52, 129.50, 129.4, 129.19, 129.16, 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 127.54, 127.45, 82.3, 81.3, 72.2, 72.1, 70.74, 70.68, 67.6, 67.5, 53.08, 53.06, 52.3, 37.0, 36.7, 33.0, 32.2, 30.3, 30.2, 18.7, 18.5, 17.8, 17.6.

HRMS (ESI$^+$, m/z): calcd for $C_{41}H_{38}O_{11}SNa^+$ (M+Na)$^+$: 761.2027; Found: 761.2026.

ortho-2,2-Dimethoxycarbonylcyclopropylbenzyl 3′,4′,6′-tri-*O*-acetyl-2′-deoxy-2′-phthalimido-1′-thio-β-D-glucopyranoside (3f)



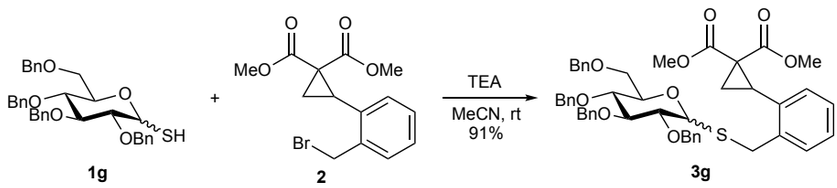
Following the procedure for **3a**, **1f** (500 mg, 1.11 mmol) was coupled with **2** (1.33 mmol, 1.2 equiv) to afford donor **3f** (720 mg, 1.03 mmol, 93%, d.r. = 1:1) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.84 – 7.70 (m, 8H), 7.19 – 7.08 (m, 6H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 5.81 – 5.75 (m, 1H), 5.71 (d, *J* = 9.6 Hz, 1H), 5.40 (d, *J* = 10.5 Hz, 1H), 5.21 – 5.12 (m, 3H), 4.41 – 4.34 (m, 2H), 4.32 – 4.24 (m, 2H), 4.17 (d, *J* = 12.3 Hz, 1H), 4.08 (d, *J* = 13.0 Hz, 1H), 4.01 (d, *J* = 12.3 Hz, 1H), 3.96 – 3.93 (m, 2H), 3.84 – 3.70 (m, 9H), 3.30 (t, *J* = 8.7 Hz, 1H), 3.24 – 3.18 (m, 7H), 2.22 (dd, *J* = 8.0, 5.4 Hz, 1H), 2.15 – 2.07 (m, 7H), 2.00 – 1.97 (m, 6H), 1.83 – 1.80 (m, 6H), 1.68 (dd, *J* = 9.3, 5.2 Hz, 1H), 1.50 (dd, *J* = 9.3, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.77, 170.76, 170.11, 170.09, 169.8, 169.7, 169.5, 167.6, 167.2, 167.0, 166.9, 137.7, 137.0, 134.4, 134.3, 133.1, 133.0, 131.7, 131.3, 129.9, 129.8, 128.4, 128.1, 127.8, 127.6, 127.5, 127.4, 123.8, 123.6, 81.1, 80.2, 75.9, 75.7, 71.6, 71.5, 69.0, 68.9, 62.4, 62.2, 53.72, 53.67, 53.0, 52.9, 52.2, 36.6, 36.5, 32.2, 32.1, 30.1, 29.9, 20.9, 20.8, 20.7, 20.5, 18.6, 18.3.

HRMS (ESI$^+$, m/z): calcd for $C_{34}H_{35}O_{13}SNNa^+$ $(M+Na)^+$: 720.1721; Found: 720.1723.

***ortho*-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,3′,4′,6′-tetra-*O*-benzyl-1′-thio-D-glucopyranoside (3g)**



Following the procedure for **3a**, **1g** (670 mg, 1.20 mmol) was coupled with **2** (1.44 mmol, 1.2 equiv) to afford donor **3g** (875 mg, 1.1 mmol, 91%, α/β = 3.8/1) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 6:1).

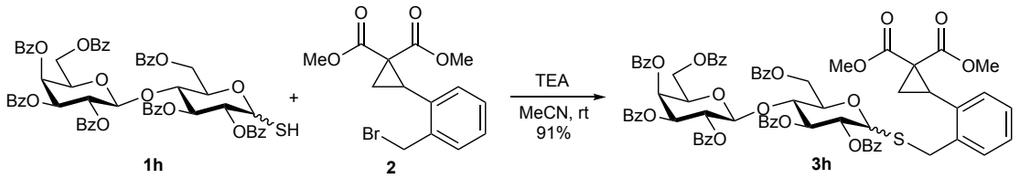
α anomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.04 (m, 60.6H), 5.43 (d, J = 4.4 Hz, 1H), 5.24 (d, J = 5.6 Hz, 1H), 4.93 (dd, J = 10.8, 4.8 Hz, 2H), 4.83 (dd, J = 10.8, 4.8 Hz, 2H), 4.75 (d, J = 10.8 Hz, 1H), 4.69 (d, J = 11.6 Hz, 1H), 4.63 (d, J = 12.4 Hz, 2H), 4.55 – 4.46 (m, 5H), 4.38 (brs, 2H), 4.23 – 4.08 (m, 2.54H), 4.03 – 3.98 (m, 1.28H), 3.91 (d, J = 13.6 Hz, 1H), 3.88 – 3.75 (m, 11H), 3.72 – 3.55 (m, 9H), 3.29 (brs, 7.56H), 2.30 (ddd, J = 13.6, 8.0, 5.2 Hz, 2H), 2.03 – 2.01 (m, 0.25H, β), 1.78 – 1.61 (m, 2.57H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 170.0, 167.20, 167.16, 138.9, 138.54, 138.52, 138.4, 138.2, 138.1, 138.0, 137.7, 133.4, 133.1, 130.3, 129.9, 128.49, 128.46, 128.4, 128.2, 128.1, 128.04, 127.96, 127.91, 127.88, 127.86, 127.81, 127.78, 127.74, 127.70, 127.5, 127.14, 127.10, 83.9, 83.0, 82.8, 82.1, 79.3, 79.2, 77.6, 75.9, 75.8, 75.2, 75.1, 73.6, 71.9, 71.8, 70.96, 70.95, 68.7, 68.4, 53.0, 52.30, 52.28, 36.9, 36.7, 31.7, 30.8, 30.3, 30.2, 29.8, 18.7, 18.5.

HRMS (ESI$^+$, m/z): calcd for $C_{48}H_{50}O_9SNa^+$ $(M+Na)^+$: 825.3068; Found: 825.3066.

***ortho*-2,2-Dimethoxycarbonylcyclopropylbenzyl 4′-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2′,3′,6′-tri-*O*-benzoyl-1′-thio-D-glucopyranoside (3h)**



Following the procedure for **3a**, **1h** (1.10 g, 1.01 mmol) was coupled with **2** (1.21 mmol, 1.2 equiv) to afford donor **3h** (1.21 g, 0.92 mmol, 91%, α/β = 1/6.6) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 2:1).

β anomer

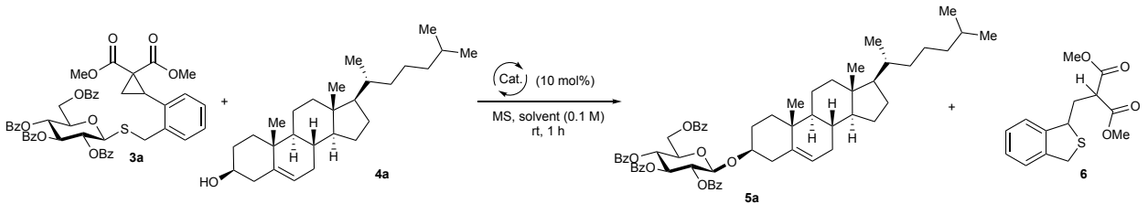
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 20H), 7.90 – 7.88 (m, 4H), 7.85 – 7.82 (m, 2H), 7.74 – 7.71 (m, 4H), 7.64 – 7.31 (m, 32H), 7.24 – 7.05 (m, 14H), 7.03 – 6.97 (m, 2H), 5.82 – 5.67 (m, 6H), 5.50 (td, J = 9.6, 3.2 Hz, 2H), 5.36 (ddd, J = 10.4, 3.2, 2.0 Hz, 2H), 4.88 (dd, J = 7.6, 2.0 Hz, 2H), 4.74 (d, J = 10.0 Hz, 1H), 4.64 (dd, J = 12.4, 1.6 Hz, 1H), 4.53 – 4.48 (m, 4H), 4.32 – 4.24 (m, 2H), 4.09 (d, J = 13.2 Hz, 1H), 3.97 – 3.85 (m, 5H), 3.81 – 3.69 (m, 9H), 3.67 (s, 3H), 3.33 – 3.25 (m, 2H), 3.23 (s, 3H), 3.20 (s, 3H), 2.16 (ddd, J = 18.0, 8.0, 5.2 Hz, 2H), 1.55 (dd, J = 9.6, 5.2 Hz, 1H), 1.49 (dd, J = 9.6, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.6, 166.91, 166.86, 165.8, 165.6, 165.39, 165.36, 165.3, 165.21, 165.16, 164.8, 137.3, 137.1, 133.5, 133.43, 133.38, 133.3, 133.20, 133.16, 133.13, 133.11, 129.98, 129.95, 129.9, 129.8, 129.74, 129.70, 129.66, 129.62, 129.58, 129.55, 129.4, 129.20, 129.17, 128.9, 128.8, 128.7, 128.63, 128.58, 128.5, 128.4, 128.31, 128.28, 128.2, 127.9, 127.7, 127.5, 127.4, 127.3, 101.01, 100.97,

84.1, 82.3, 76.9, 76.0, 75.8, 74.1, 71.8, 71.4, 70.7, 70.6, 69.94, 69.92, 67.5, 62.8, 62.6, 61.1, 52.9, 52.8, 52.14, 52.11, 36.7, 36.4, 32.6, 32.0, 29.8, 29.7, 18.4, 18.1.

HRMS (ESI$^+$, m/z): calcd for $C_{75}H_{64}O_{21}SNa^+$ $(M+Na)^+$: 1355.3553; Found: 1355.3558.

General procedure for reaction optimization



An oven-dried 5 mL round bottom flask was charged with **3a** (51.5 mg, 60.0 μmol) and **4a** (19.3 mg, 50.0 μmol). Anhydrous solvent (0.5 mL) was added to dissolve the donor and acceptor, followed by the addition of freshly activated molecular sieve (50 mg). The mixture was stirred at room temperature for 15 min before the catalyst (5.0 μmol, 0.1 equiv) was added quickly. The mixture was stirred at the indicated temperature until the reaction was completed. The reaction was quenched with triethylamine before the mixture was concentrated *in vauco*. The residue was purified by silica gel column chromatography to afford the glycoconjugate **5a** as a white solid and heterocycle **6** as a colorless oil.

Compound 5a

^{1}H NMR (400 MHz, CDCl3) δ 8.02 – 8.00 (m, 2H), 7.97 – 7.95 (m, 2H), 7.92 – 7.90 (m, 2H), 7.85 – 7.83 (m, 2H), 7.56 – 7.47 (m, 3H), 7.44 – 7.28 (m, 9H), 5.90 (t, *J* = 9.6 Hz, 1H), 5.63 (t, *J* = 9.6 Hz, 1H), 5.50 (t, *J* = 8.8 Hz, 1H), 5.23 (d, *J* = 3.6 Hz, 1H), 4.95 (d, *J* = 8.0 Hz, 1H), 4.61 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.53 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.17 (dd, *J* = 9.2, 4.8 Hz, 1H), 3.61 – 3.47 (m, 1H), 2.21 – 2.11 (m, 2H), 2.02 (dd, *J* = 10.0, 6.4 Hz, 1H), 1.94 – 1.90 (m, 2H), 1.87 – 1.76 (m, 1H), 1.72 (dd, *J* = 13.2, 4.0 Hz, 1H), 1.60 – 1.33 (m, 11H), 1.18 – 0.96 (m, 9H), 0.93 – 0.86 (m, 14H), 0.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.0, 165.4, 165.2, 140.5, 133.5, 133.31, 133.26, 133.2, 130.0, 129.90, 129.88, 129.85, 129.8, 129.6, 129.03, 128.97, 128.53, 128.49, 128.47, 128.4, 122.1, 100.3, 80.6, 73.2, 72.2, 70.3, 63.5, 56.9, 56.3, 50.3, 42.5, 39.9, 39.7, 39.0, 37.2, 36.8, 36.3, 35.9, 32.1, 32.0, 29.9, 29.7, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0.

The data are identical to the literature report.[3]

Compound 6

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 – 7.13 (m, 4H), 4.73 – 4.57 (m, 1H), 4.30 (d, *J* = 14.1 Hz, 1H), 4.13 (d, *J* = 14.1 Hz, 1H), 3.74 (s, 3H), 3.67 – 3.61 (m, 1H), 3.60 (s, 3H), 2.62 (ddd, *J* = 13.6, 8.9, 3.9 Hz, 1H), 2.28 (ddd, *J* = 14.2, 9.1, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 169.94, 169.90, 143.4, 140.9, 127.7, 127.3, 125.3, 124.9, 52.9, 52.8, 52.3, 50.2, 38.2, 37.2.

HRMS (ESI$^+$, m/z): calcd for $C_{14}H_{16}O_4SNa^+$ $(M+Na)^+$: 303.0662; Found: 303.0662.

Acceptor scope studies with CCPB thioglycoside 3a

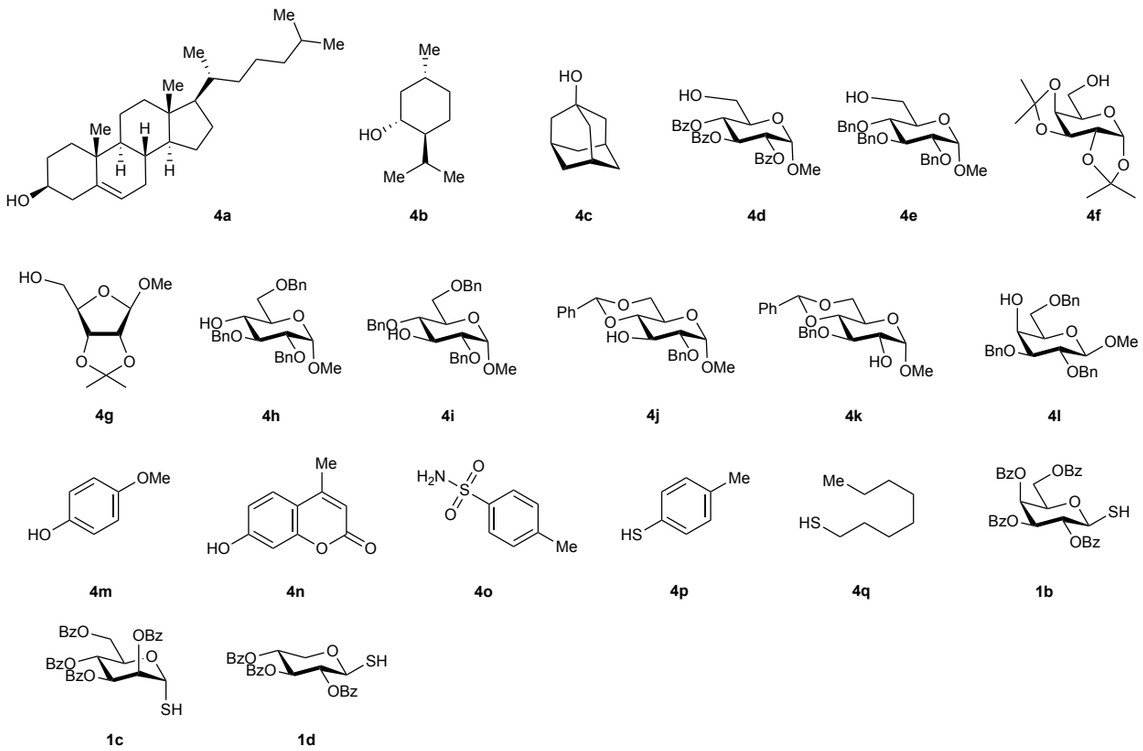
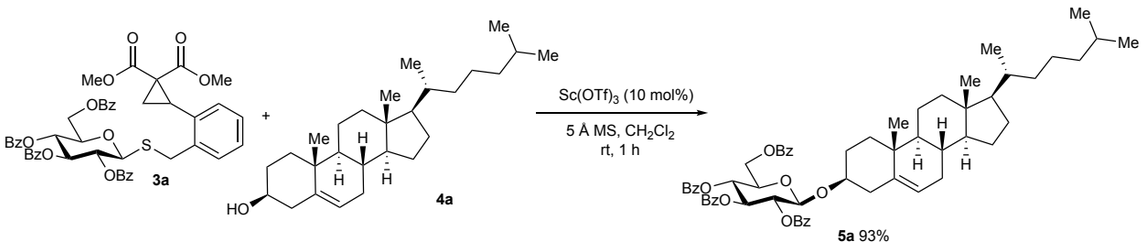


Figure S2. Acceptors used in this part.

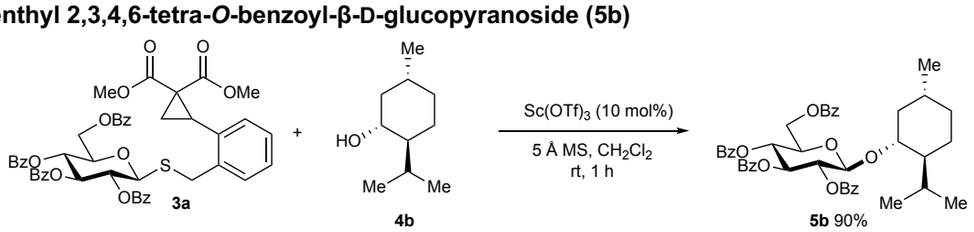
Acceptors **4a-c** and **m-q** are commercially available. Acceptors **4d**,[4] **4e**,[4] **4f**,[4] **4g**,[5] **4h**[6] **4i**,[7] **4j**,[8] **4k**,[8] **4l**[9] are prepared according to the literature reports.

(3β)-Cholest-5-en-3-yl 2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-glucopyranoside (5a)



An oven-dried 5 mL round bottom flask was charged with **3a** (51.5 mg, 60.0 μmol) and **4a** (19.3 mg, 50.0 μmol), anhydrous CH_2Cl_2 (0.5 mL) was added to dissolve the starting materials. Freshly activated 5 Å MS (50 mg) was added and the mixture was stirred at room temperature for 15 min before $Sc(OTf)_3$ (2.5 mg, 5.0 μmol) was added. The mixture was stirred at room temperature for another 1 h with the color changing from colorless to purple. After completion of the reaction as identified by thin layer chromatography (TLC), the reaction was quenched by triethylamine with the purple color faded. The mixture was concentrated *in vauco* and the residue was purified by silica gel column chromatography to afford the titled compound **5a** (45.0 mg, 46.5 μmol, 93%) as a white solid.

(–)-Menthyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (5b)



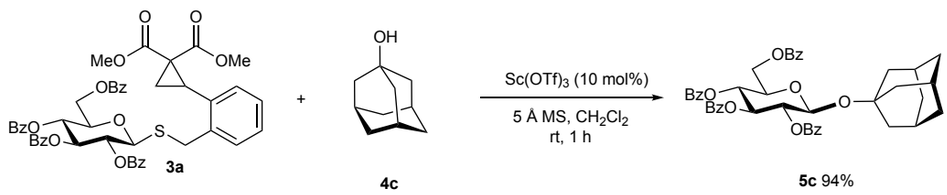
Following the procedure for **5a**, **3a** (51.5 mg, 60.0 μmol) was coupled with **4b** (7.8 mg, 50.0 μmol) to afford **5b** (33.2 mg, 45.0 μmol, 90%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.7 Hz, 2H), 7.96 (d, J = 7.8 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.56 – 7.46 (m, 3H), 7.45 – 7.26 (m, 9H), 5.89 (t, J = 9.7 Hz, 1H), 5.63 (t, J = 9.7 Hz, 1H), 5.49 (t, J = 8.8 Hz, 1H), 4.93 (d, J = 7.9 Hz, 1H), 4.62 (dd, J = 12.1, 3.2 Hz, 1H), 4.48 (dd, J = 12.0, 5.7 Hz, 1H), 4.18 – 4.09 (m, 1H), 3.48 (td, J = 10.7, 4.1 Hz, 1H), 2.32 – 2.19 (m, 1H), 1.94 (d, J = 12.4 Hz, 1H), 1.57 (d, J = 11.9 Hz, 2H), 1.22 (d, J = 33.2 Hz, 3H), 0.91 (dd, J = 14.1, 11.0 Hz, 1H), 0.82 (d, J = 7.1 Hz, 3H), 0.73 (dd, J = 15.4, 6.7 Hz, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.0, 165.4, 165.2, 133.5, 133.3, 133.21, 133.19, 130.0, 129.90, 129.86, 129.8, 129.7, 129.1, 129.0, 128.5, 128.4, 99.1, 79.2, 77.4, 73.4, 72.3, 72.2, 70.4, 63.6, 47.5, 40.9, 34.2, 31.5, 25.3, 23.2, 22.2, 20.9, 15.8.

The data are identical to the literature report.[10]

1-Adamantyl 2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-glucopyranoside (5c)



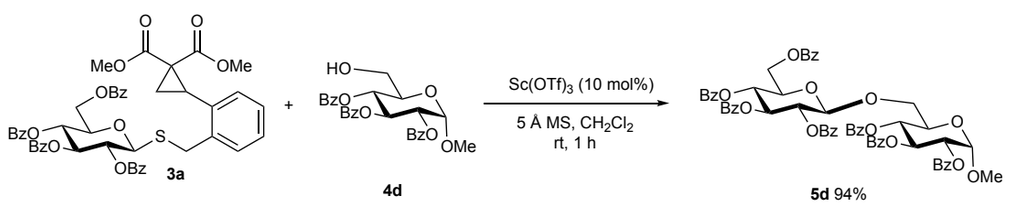
Following the procedure for **5a**, **3a** (51.5 mg, 60.0 μmol) was coupled with **4c** (7.6 mg, 50.0 μmol) to afford **5c** (34.5 mg, 47.0 μmol, 94%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.8 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.56 – 7.45 (m, 3H), 7.46 – 7.32 (m, 7H), 7.31 – 7.26 (m, 2H), 5.92 (t, J = 9.6 Hz, 1H), 5.55 (t, J = 9.7 Hz, 1H), 5.49 (dd, J = 9.7, 8.0 Hz, 1H), 5.13 (d, J = 7.9 Hz, 1H), 4.58 (dd, J = 11.9, 3.1 Hz, 1H), 4.49 (dd, J = 11.9, 7.1 Hz, 1H), 4.22 – 4.14 (m, 1H), 2.02 (s, 3H), 1.82 (d, J = 11.8 Hz, 3H), 1.65 (d, J = 11.8 Hz, 3H), 1.59 – 1.48 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.0, 165.5, 165.1, 133.6, 133.3, 133.20, 133.20, 130.0, 129.91, 129.85, 129.8, 129.7, 129.1, 129.0, 128.6, 128.5, 128.44, 128.41, 94.5, 76.0, 73.4, 72.3, 72.1, 70.5, 63.9, 45.5, 42.5, 36.2, 30.7.

The data are identical to the literature report.[3]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (5d)



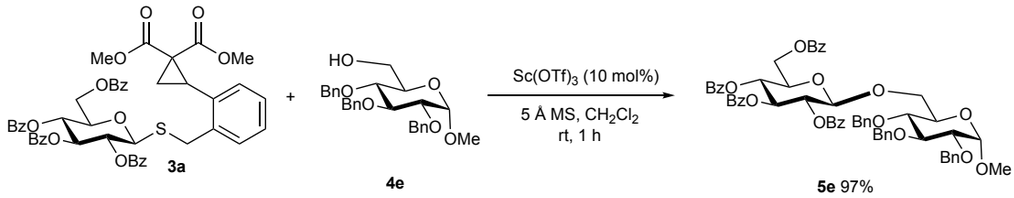
Following the procedure for **5a**, **3a** (51.5 mg, 60.0 μmol) was coupled with **4d** (25.3 mg, 50.0 μmol) to afford **5d** (51.4 mg, 47.0 μmol, 94%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.0 Hz, 2H), 7.99 – 7.96 (m, 2H), 7.94 (d, J = 7.0 Hz, 2H), 7.89 (d, J = 7.0 Hz, 2H), 7.86 (d, J = 7.0 Hz, 2H), 7.83 (d, J = 7.0 Hz, 2H), 7.79 (d, J = 7.2 Hz, 2H), 7.57 – 7.27 (m, 20H), 7.25 (d, J = 4.4 Hz, 1H), 6.08 (t, J = 9.8 Hz, 1H), 5.93 (t, J = 9.7 Hz, 1H), 5.66 (t, J = 9.7 Hz, 1H), 5.57 (dd, J = 9.8, 7.8 Hz, 1H), 5.32 (t, J = 9.9 Hz, 1H), 5.10 (dd, J = 10.2, 3.6 Hz, 1H), 4.98 (d, J = 7.9 Hz, 1H), 4.95 (d, J = 3.6 Hz, 1H), 4.62 (dd, J = 12.2, 3.2 Hz, 1H), 4.45 (dd, J = 12.2, 5.1 Hz, 1H), 4.26 – 4.19 (m, 1H), 4.18 – 4.13 (m, 1H), 4.11 (dd, J = 11.3, 2.0 Hz, 1H), 3.79 (dd, J = 11.3, 7.6 Hz, 1H), 3.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 165.83, 165.78, 165.6, 165.3, 133.6, 133.4, 133.3, 133.23, 133.15, 130.01, 129.98, 129.96, 129.89, 129.87, 129.8, 129.7, 129.5, 129.4, 129.2, 129.0, 128.92, 128.90, 128.53, 128.50, 128.45, 128.4, 128.3, 101.9, 96.6, 73.0, 72.4, 72.1, 72.0, 70.5, 69.82, 69.78, 69.1, 68.9, 63.2, 55.2.

The data are identical to the literature report.[3]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (5e)



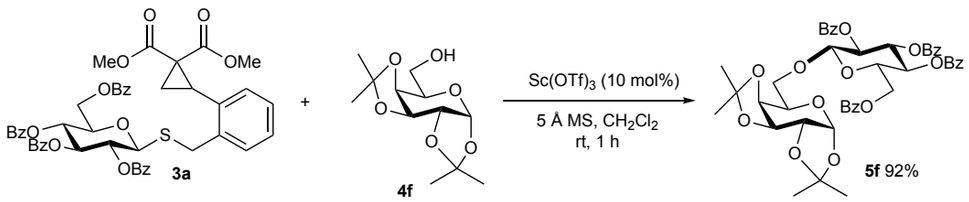
Following the procedure for **5a**, **3a** (51.5 mg, 60.0 μmol) was coupled with **4d** (23.2 mg, 50.0 μmol) to afford **5d** (50.8 mg, 48.5 μmol, 97%) as a white solid.

^{1}H NMR (400 MHz,d $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 2H), 7.92 – 7.87 (m, 4H), 7.83 (d, J = 7.8 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.43 – 7.20 (m, 24H), 7.10 – 7.04 (m, 2H), 5.90 (t, J = 9.6 Hz, 1H), 5.68 (t, J = 9.6 Hz, 1H), 5.60 (t, J = 8.7 Hz, 1H), 4.90 (d, J = 10.9 Hz, 1H), 4.83 (d, J = 7.8 Hz, 1H), 4.74 (d, J = 12.0 Hz, 1H), 4.69 (d, J = 11.0 Hz, 1H), 4.65 – 4.57 (m, 2H), 4.57 – 4.48 (m, 3H), 4.30 (d, J = 11.2 Hz, 1H), 4.15 (d, J = 9.7 Hz, 1H), 4.13 – 4.07 (m, 1H), 3.89 (t, J = 9.2 Hz, 1H), 3.79 – 3.69 (m, 2H), 3.44 (dd, J = 9.5, 3.4 Hz, 1H), 3.39 (t, J = 9.2 Hz, 1H), 3.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.0, 165.3, 165.0, 138.9, 138.33, 138.27, 133.5, 133.4, 133.3, 133.2, 129.93, 129.86, 129.8, 129.7, 129.3, 128.92, 128.88, 128.54, 128.52, 128.46, 128.44, 128.41, 128.38, 128.2, 128.0, 127.7, 127.6, 101.5, 98.1, 82.0, 79.9, 77.5, 75.6, 74.8, 73.5, 73.0, 72.3, 72.0, 69.9, 69.6, 68.5, 63.4, 55.1.

The data are identical to the literature report.[3]

6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5f)



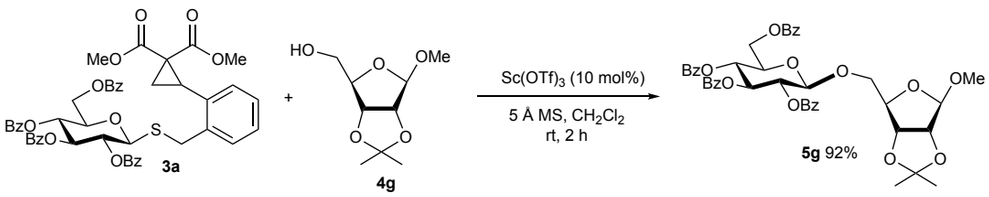
Following the procedure for **5a**, **3a** (67.0 mg, 78.0 μmol) was coupled with **4f** (17.0 mg, 65.0 μmol) to afford **5f** (50.2 mg, 60.5 μmol, 92%) as a colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.7 Hz, 2H), 7.97 (d, J = 7.7 Hz, 2H), 7.90 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.57 – 7.46 (m, 3H), 7.44 – 7.26 (m, 9H), 5.90 (t, J = 9.6 Hz, 1H), 5.68 (t, J = 9.7 Hz, 1H), 5.54 (t, J = 8.7 Hz, 1H), 5.42 (d, J = 5.0 Hz, 1H), 5.05 (d, J = 7.8 Hz, 1H), 4.65 (dd, J = 12.1, 3.1 Hz, 1H), 4.49 (dd, J = 12.2, 5.3 Hz, 1H), 4.43 (dd, J = 7.9, 2.1 Hz, 1H), 4.25 – 4.14 (m, 2H), 4.10 (d, J = 8.0 Hz, 1H), 4.02 (dd, J = 10.5, 3.7 Hz, 1H), 3.93 – 3.81 (m, 2H), 1.37 (s, 3H), 1.24 (s, 3H), 1.23 – 1.81 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.9, 165.33, 165.27, 133.5, 133.3, 133.2, 130.1, 130.0, 129.9, 129.8, 129.5, 129.02, 128.98, 128.52, 128.48, 128.4, 128.3, 109.4, 108.6, 101.4, 96.3, 73.2, 72.3, 72.0, 71.1, 70.7, 70.5, 70.0, 68.4, 67.7, 63.4, 26.0, 25.8, 25.0, 24.4.

The data are identical to the literature report.[3]

Methyl 2,3-*O*-isopropylidene-5-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-β-D-ribofuranoside (5g)



Following the procedure for **5a**, **3a** (51.5 mg, 60.0 μmol) was coupled with **4g** (10.2 mg, 50.0 μmol) to afford **5g** (36.2 mg, 46.0 μmol, 92%) as a colorless syrup.

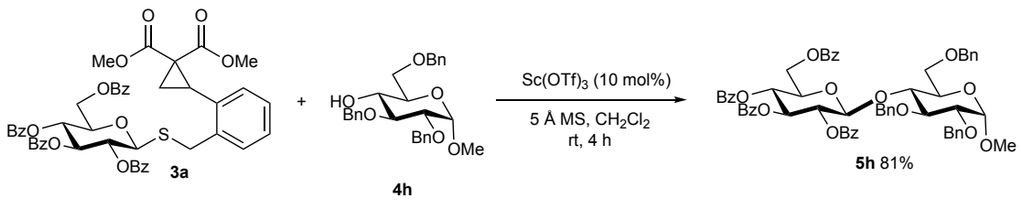
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.3 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.3 Hz, 2H),

7.82 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.46 (m, 3H), 7.46 – 7.26 (m, 9H), 5.90 (t, *J* = 9.6 Hz, 1H), 5.67 (t, *J* = 9.7 Hz, 1H), 5.54 (dd, *J* = 9.7, 7.9 Hz, 1H), 4.92 (d, *J* = 8.0 Hz, 1H), 4.87 (s, 1H), 4.65 (dd, *J* = 12.5, 3.1 Hz, 1H), 4.61 (d, *J* = 6.1 Hz, 1H), 4.55 – 4.45 (m, 2H), 4.27 (t, *J* = 7.3 Hz, 1H), 4.16 (dt, *J* = 9.1, 4.1 Hz, 1H), 3.85 (t, *J* = 9.4 Hz, 1H), 3.67 (dd, *J* = 10.3, 6.2 Hz, 1H), 3.18 (s, 3H), 1.36 (s, 3H), 1.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.3, 165.9, 165.3, 165.2, 133.6, 133.4, 133.3, 129.99, 129.98, 129.9, 129.7, 129.4, 128.93, 128.91, 128.6, 128.5, 128.43, 128.41, 112.37, 109.5, 100.9, 85.1, 84.7, 81.9, 73.1, 72.5, 71.8, 69.9, 63.2, 54.8, 29.9, 26.4, 24.9.

The data are identical to the literature report.[3]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside (5h)



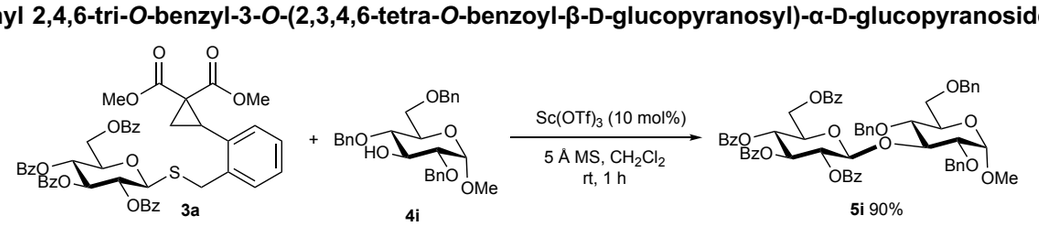
Following the procedure for **5a**, **3a** (73.2 mg, 85.0 μmol) was coupled with **4h** (33.0 mg, 71.0 μmol) to afford **5h** (60.3 mg, 57.5 μmol, 81%) as a colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.96 (d, *J* = 7.8 Hz, 2H), 7.90 – 7.85 (m, 4H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.55 – 7.26 (m, 21H), 7.25 – 7.13 (m, 6H), 5.62 (t, *J* = 9.5 Hz, 1H), 5.54 (t, *J* = 9.5 Hz, 1H), 5.46 (t, *J* = 8.8 Hz, 1H), 5.07 (d, *J* = 11.2 Hz, 1H), 4.84 – 4.69 (m, 4H), 4.58 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 3.6 Hz, 1H), 4.40 (dd, *J* = 12.1, 3.3 Hz, 1H), 4.34 (d, *J* = 12.2 Hz, 1H), 4.25 (dd, *J* = 12.0, 5.0 Hz, 1H), 3.96 (t, *J* = 9.4 Hz, 1H), 3.88 (t, *J* = 9.1 Hz, 1H), 3.75 – 3.67 (m, 2H), 3.52 – 3.40 (m, 3H), 3.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.1, 165.8, 165.2, 164.9, 139.4, 138.5, 138.0, 133.5, 133.4, 133.3, 133.1, 129.9, 129.80, 129.76, 129.3, 129.1, 129.00, 128.97, 128.6, 128.50, 128.45, 128.42, 128.38, 128.2, 127.9, 127.5, 127.3, 100.5, 98.6, 80.1, 79.0, 75.5, 73.74, 73.68, 73.3, 72.4, 72.0, 70.0, 69.6, 67.7, 63.3, 55.5.

The data are identical to the literature report.[11]

Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside (5i)



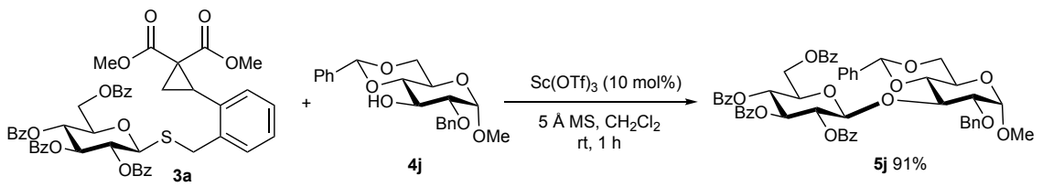
Following the procedure for **5a**, **3a** (68.7 mg, 80.0 μmol) was coupled with **4i** (30.8 mg, 66.0 μmol) to afford **5i** (61.8 mg, 59.4 μmol, 90%) as a colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.02 (d, *J* = 7.7 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.51 – 7.25 (m, 22H), 7.15 – 7.08 (m, 4H), 5.95 (t, *J* = 9.7 Hz, 1H), 5.72 (t, *J* = 9.7 Hz, 1H), 5.65 (t, *J* = 8.9 Hz, 1H), 5.52 (d, *J* = 8.0 Hz, 1H), 5.13 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 12.3 Hz, 1H), 4.57 – 4.48 (m, 3H), 4.47 – 4.34 (m, 3H), 4.30 (d, *J* = 3.4 Hz, 1H), 4.18 – 4.10 (m, 2H), 3.68 – 3.53 (m, 4H), 3.35 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.2, 166.0, 165.4, 165.3, 138.6, 138.1, 138.0, 133.5, 133.4, 133.3, 132.99, 129.97, 129.9, 129.83, 129.77, 129.6, 129.0, 128.60, 128.57, 128.5, 128.4, 128.3, 128.22, 128.18, 128.17, 128.1, 128.0, 127.8, 127.5, 101.1, 97.8, 81.0, 79.5, 77.4, 75.6, 75.0, 73.9, 73.6, 73.3, 72.7, 72.1, 70.1, 69.7, 68.6, 63.4, 55.1.

The data are identical to the literature report.[11]

Methyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside (5j)



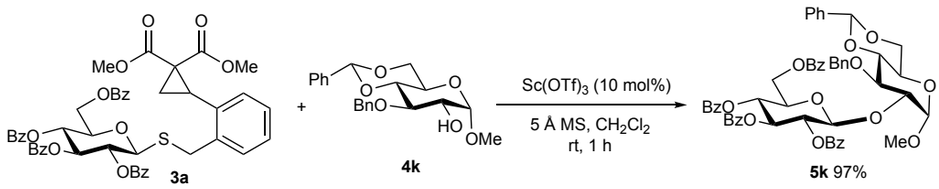
Following the procedure for **5a**, **3a** (51.5 mg, 60.0 μmol) was coupled with **4j** (18.6 mg, 50.0 μmol) to afford **5j** (43.5 mg, 45.5 μmol, 91%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 4H), 7.86 (d, J = 7.9 Hz, 2H), 7.80 (d, J = 7.8 Hz, 2H), 7.52 – 7.23 (m, 21H), 7.11 (dd, J = 5.7, 3.0 Hz, 2H), 5.88 (t, J = 9.6 Hz, 1H), 5.74 – 5.62 (m, 2H), 5.56 (s, 1H), 5.25 (d, J = 7.8 Hz, 1H), 4.59 (d, J = 12.6 Hz, 1H), 4.50 (dd, J = 12.2, 3.3 Hz, 1H), 4.35 – 4.16 (m, 5H), 3.96 (dt, J = 9.0, 4.1 Hz, 1H), 3.82 – 3.73 (m, 1H), 3.69 (t, J = 10.1 Hz, 1H), 3.61 (t, J = 9.2 Hz, 1H), 3.43 (dd, J = 9.3, 3.7 Hz, 1H), 3.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.0, 165.4, 165.3, 138.2, 137.4, 133.4, 133.30, 133.28, 133.0, 130.0, 129.9, 129.83, 129.76, 129.5, 129.1, 129.02, 128.99, 128.52, 128.49, 128.46, 128.38, 128.35, 128.3, 128.0, 127.9, 126.2, 101.5, 101.2, 99.0, 79.9, 79.6, 77.9, 74.2, 73.4, 72.5, 72.0, 70.0, 69.1, 63.4, 62.4, 55.4.

The data are identical to the literature report.[3]

Methyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside (5k)



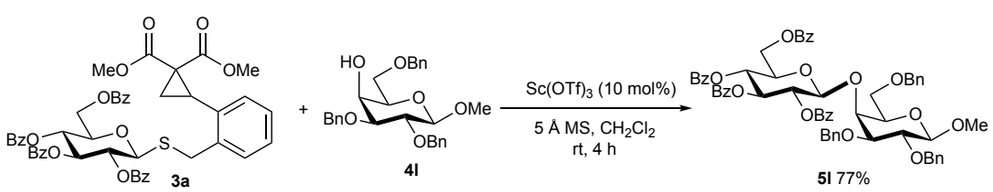
Following the procedure for **5a**, **3a** (51.5 mg, 60.0 μmol) was coupled with **4k** (18.6 mg, 50.0 μmol) to afford **5k** (46.1 mg, 48.5 μmol, 97%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.7 Hz, 2H), 7.94 (d, J = 7.7 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 7.8 Hz, 2H), 7.60 – 7.14 (m, 22H), 7.01 (d, J = 7.0 Hz, 2H), 5.93 (t, J = 9.6 Hz, 1H), 5.76 – 5.66 (m, 2H), 5.51 (s, 1H), 5.21 (d, J = 7.8 Hz, 1H), 4.98 (d, J = 3.5 Hz, 1H), 4.80 – 4.71 (m, 1H), 4.56 (d, J = 11.7 Hz, 1H), 4.47 (dd, J = 12.1, 5.3 Hz, 1H), 4.42 (d, J = 11.7 Hz, 1H), 4.27 (dd, J = 10.2, 4.7 Hz, 1H), 4.16 (dt, J = 9.0, 3.9 Hz, 1H), 3.94 (t, J = 9.3 Hz, 1H), 3.86 – 3.77 (m, 2H), 3.70 (t, J = 10.3 Hz, 1H), 3.55 (t, J = 9.3 Hz, 1H), 3.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.9, 165.3, 165.1, 138.5, 137.4, 133.6, 133.4, 133.3, 130.0, 129.92, 129.88, 129.8, 129.6, 129.3, 129.0, 128.88, 128.86, 128.6, 128.5, 128.4, 128.24, 128.18, 127.5, 127.4, 126.2, 102.5, 101.5, 100.4, 82.2, 80.9, 77.4, 74.9, 73.3, 72.5, 72.2, 69.7, 69.3, 62.9, 62.2, 55.6.

The data are identical to the literature report.[12]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-β-D-galactopyranoside (5l)



Following the procedure for **5a**, **3a** (62.8 mg, 73.0 μmol) was coupled with **4l** (28.5 mg, 61.0 μmol) to afford **5l** (52.1 mg, 56.7 μmol, 93%) as a colorless syrup.

$[\alpha]_D^{23}$ = +33.2 (c = 1.0, $CHCl_3$).

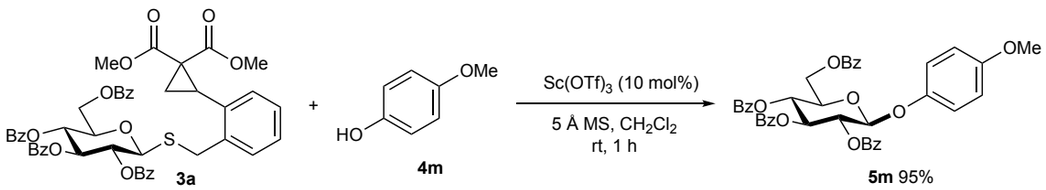
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 7.8 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.46 – 7.26 (m, 17H), 7.25 – 7.17 (m, 6H), 7.08 (d, J = 6.9 Hz, 2H), 5.91 (t, J = 9.7 Hz, 1H), 5.71 (t, J = 9.7 Hz, 1H), 5.57 (t, J = 8.9 Hz, 1H),

5.26 (d, *J* = 7.9 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.59 (dd, *J* = 12.6, 3.1 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 4.47 – 4.41 (m, 2H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.17 (d, *J* = 7.6 Hz, 1H), 4.08 – 3.99 (m, 2H), 3.80 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.75 (d, *J* = 10.9 Hz, 1H), 3.68 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.52 (t, *J* = 5.8 Hz, 1H), 3.47 (s, 3H), 3.42 (dd, *J* = 9.6, 2.5 Hz, 1H), 3.30 (t, *J* = 8.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.1, 166.0, 165.3, 165.0, 138.9, 138.6, 138.4, 133.5, 133.32, 133.27, 133.1, 130.2, 130.0, 129.92, 129.87, 129.72, 129.68, 129.1, 129.0, 128.7, 128.6, 128.52, 128.45, 128.4, 128.28, 128.25, 128.0, 127.8, 127.72, 127.67, 127.5, 104.6, 101.7, 81.4, 79.7, 74.83, 74.77, 73.7, 73.6, 73.5, 73.1, 72.2, 72.1, 69.79, 69.76, 62.8, 56.8.

HRMS (ESI$^+$, m/z): calcd for $C_{62}H_{58}O_{15}Na^+$ $(M+Na)^+$: 1065.3668; Found: 1065.3672.

4-Methoxyphenyl 2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-glucopyranoside (5m)



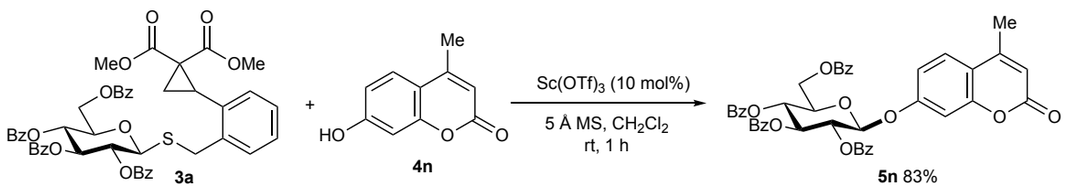
Following the procedure for **5a**, **3a** (51.5 mg, 60 μmol) was coupled with **4m** (6.2 mg, 50.0 μmol) to afford **5m** (33.4 mg, 47.5 μmol, 95%) as a light-yellow syrup.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.07 – 8.01 (m, 2H), 8.01 – 7.96 (m, 2H), 7.96 – 7.91 (m, 2H), 7.90 – 7.84 (m, 2H), 7.62 – 7.27 (m, 13H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 5.98 (t, *J* = 9.5 Hz, 1H), 5.78 (dd, *J* = 9.6, 7.9 Hz, 1H), 5.71 (t, *J* = 9.6 Hz, 1H), 5.27 (d, *J* = 7.8 Hz, 1H), 4.68 (dd, *J* = 12.1, 2.9 Hz, 1H), 4.55 (dd, *J* = 12.1, 6.6 Hz, 1H), 4.33 – 4.25 (m, 1H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.2, 165.9, 165.4, 165.2, 155.9, 151.1, 133.7, 133.4, 133.3, 130.01, 129.95, 129.9, 129.7, 129.3, 128.9, 128.8, 128.59, 128.55, 128.53, 128.46, 119.1, 114.6, 101.0, 73.0, 72.7, 71.9, 69.9, 63.4, 55.7.

The data are identical to the literature report.[13]

4-Methylumbelliferyl 2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-glucopyranoside (5n)



Following the procedure for **5a**, **3a** (51.5 mg, 60 μmol) was coupled with **4n** (8.8 mg, 50.0 μmol) to afford **5n** (31.3 mg, 41.5 μmol, 83%) as a white solid.

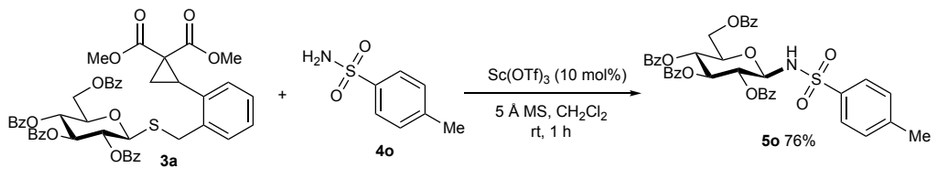
$[\alpha]_D^{23}$ = +32.6 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.04 (d, *J* = 7.0 Hz, 2H), 7.99 – 7.92 (m, 4H), 7.87 (d, *J* = 7.0 Hz, 2H), 7.58 – 7.44 (m, 6H), 7.40 – 7.30 (m, 7H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.16 (d, *J* = 1.3 Hz, 1H), 6.02 (t, *J* = 9.3 Hz, 1H), 5.83 (dd, *J* = 9.3, 7.5 Hz, 1H), 5.74 (t, *J* = 9.5 Hz, 1H), 5.54 (d, *J* = 7.5 Hz, 1H), 4.68 (dd, *J* = 12.2, 2.8 Hz, 1H), 4.54 (dd, *J* = 12.2, 6.8 Hz, 1H), 4.42 (ddd, *J* = 9.7, 6.8, 2.8 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.2, 165.9, 165.4, 165.2, 160.9, 159.4, 155.0, 152.2, 133.8, 133.7, 133.6, 133.5, 130.1, 129.97, 129.96, 129.9, 129.5, 129.0, 128.8, 128.71, 128.67, 128.65, 128.6, 128.5, 125.8, 115.7, 114.1, 113.4, 104.4, 98.9, 73.1, 72.7, 71.6, 69.4, 63.3, 18.7.

HRMS (ESI$^+$, m/z): calcd for $C_{44}H_{35}O_{12}^+$ $(M+H)^+$: 755.2129; Found: 755.2120.

***N*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-*para*-methylbenzenesulfonamide (5o)**



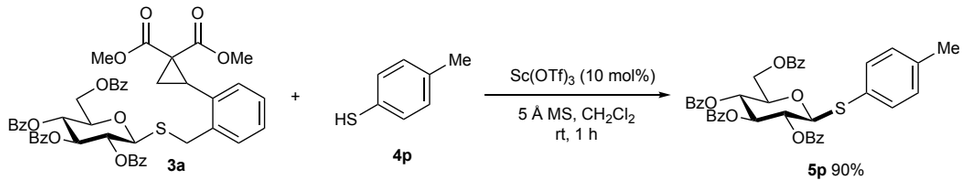
Following the procedure for **5a**, **3a** (51.5 mg, 60 µmol) was coupled with **4o** (8.6 mg, 50.0 µmol) to afford **5o** (28.5 mg, 38.0 µmol, 76%) as a colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.0 Hz, 2H), 7.88 (d, J = 7.0 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 7.0 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.58 – 7.47 (m, 4H), 7.44 – 7.32 (m, 8H), 6.94 (d, J = 8.2 Hz, 2H), 5.97 (t, J = 9.6 Hz, 1H), 5.86 (d, J = 9.3 Hz, 1H), 5.61 (t, J = 9.8 Hz, 1H), 5.33 (t, J = 9.5 Hz, 1H), 5.14 (t, J = 9.3 Hz, 1H), 4.45 (dd, J = 12.2, 3.0 Hz, 1H), 4.36 (dd, J = 12.2, 4.9 Hz, 1H), 4.18 (ddd, J = 10.0, 4.9, 3.0 Hz, 1H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.2, 165.8, 165.3, 143.7, 138.3, 133.9, 133.7, 133.5, 133.3, 130.2, 130.0, 129.9, 129.8, 129.7, 129.6, 128.7, 128.60, 128.55, 128.5, 128.3, 126.9, 83.4, 73.9, 72.9, 71.3, 69.3, 63.0, 21.5.

The data are identical to the literature.[3]

para-Tolyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (5p)



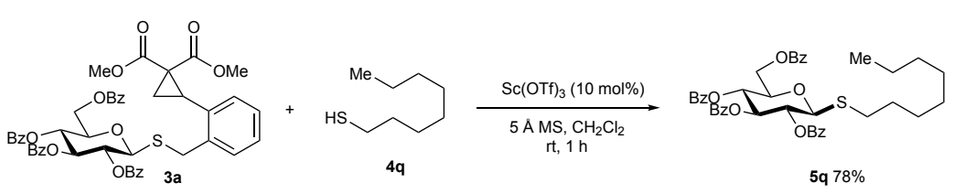
Following the procedure for **5a**, **3a** (51.5 mg, 60 µmol) was coupled with **4p** (6.2 mg, 50.0 µmol) to afford **5p** (31.6 mg, 45.0 µmol, 90%) as a colorless syrup.

^{1}H NMR (400 MHz, CDCl3) δ 8.05 (d, J = 6.9 Hz, 2H), 7.98 (d, J = 7.0 Hz, 2H), 7.90 (d, J = 7.0 Hz, 2H), 7.80 (d, J = 7.0 Hz, 2H), 7.62 – 7.32 (m, 12H), 7.29 – 7.24 (m, 3H), 6.94 (d, J = 7.9 Hz, 2H), 5.90 (t, J = 9.5 Hz, 1H), 5.60 (t, J = 9.8 Hz, 1H), 5.46 (t, J = 9.7 Hz, 1H), 4.99 (d, J = 10.0 Hz, 1H), 4.69 (dd, J = 12.2, 2.8 Hz, 1H), 4.48 (dd, J = 12.2, 5.7 Hz, 1H), 4.18 (ddd, J = 10.0, 5.7, 2.8 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.8, 165.2, 165.1, 138.7, 133.9, 133.5, 133.3, 133.23, 133.16, 129.90, 129.88, 129.86, 129.8, 129.69, 129.66, 129.3, 128.8, 128.7, 128.43, 128.40, 128.3, 127.6, 86.3, 76.3, 74.3, 70.5, 69.4, 63.1, 21.2.

The data are identical to the literature.[3]

Octyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (5q)



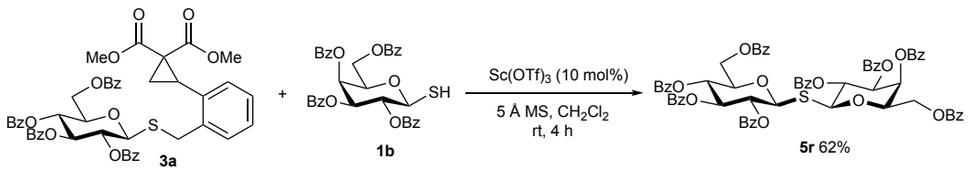
Following the procedure for **5a**, **3a** (51.5 mg, 60 µmol) was coupled with **4q** (8.0 µL, 50.0 µmol) to afford **5q** (28.3 mg, 39.0 µmol, 78%) as a colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 6.9 Hz, 2H), 7.95 (d, J = 6.9 Hz, 2H), 7.90 (d, J = 6.9 Hz, 2H), 7.82 (d, J = 7.0 Hz, 2H), 7.56 – 7.46 (m, 3H), 7.44 – 7.32 (m, 7H), 7.29 – 7.25 (m, 2H), 5.93 (t, J = 9.5 Hz, 1H), 5.67 (t, J = 9.8 Hz, 1H), 5.56 (t, J = 9.7 Hz, 1H), 4.85 (d, J = 10.0 Hz, 1H), 4.63 (dd, J = 12.2, 3.1 Hz, 1H), 4.50 (dd, J = 12.2, 5.4 Hz, 1H), 4.18 (ddd, J = 10.0, 5.5, 3.1 Hz, 1H), 2.81 – 2.65 (m, 2H), 1.61 – 1.54 (m, 2H), 1.30 – 1.17 (m, 10H), 0.86 (t, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.0, 165.4, 165.3, 133.6, 133.41, 133.36, 133.3, 130.01, 129.97, 129.9, 129.8, 129.4, 129.0, 128.9, 128.6, 128.5, 128.4, 84.2, 76.5, 74.3, 70.8, 69.8, 63.5, 31.9, 30.3, 29.8, 29.3, 29.2, 28.9, 22.8, 14.2.

The data are identical to the literature.[3]

2,3,4,6-Tetra-*O*-benzoyl-1-thio-1-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (5r)



Following the procedure for **5a**, **3a** (170 mg, 0.2 mmol) was coupled with **1b** (61.3 mg, 0.1 mmol) to afford **5r** (73.6 mg, 62.0 μmol, 62%) as a white foam.

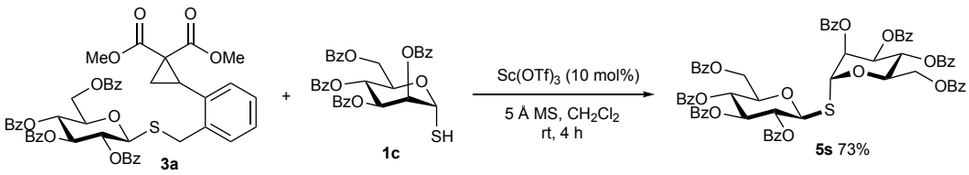
$[\alpha]_D^{23}$ = +57.4 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.16 – 8.10 (m, 4H), 8.01 (d, *J* = 7.0 Hz, 2H), 7.97 – 7.91 (m, 6H), 7.80 – 7.77 (m, 2H), 7.77 – 7.44 (m, 2H), 7.64 – 7.57 (m, 4H), 7.55 – 7.47 (m, 6H), 7.45 – 7.34 (m, 12H), 7.25 – 7.23 (m, 2H), 5.81 – 5.70 (m, 3H), 5.57 – 5.48 (m, 2H), 5.37 (dd, *J* = 9.9, 3.5 Hz, 1H), 5.19 – 5.13 (m, 2H), 4.62 – 4.54 (m, 2H), 4.50 (dd, *J* = 12.1, 3.1 Hz, 1H), 4.32 (dd, *J* = 11.5, 5.2 Hz, 1H), 3.88 – 3.77 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.0, 165.9, 165.8, 165.7, 165.5, 165.4, 165.2, 133.8, 133.7, 133.5, 133.4, 130.2, 130.13, 130.06, 130.00, 129.96, 129.90, 129.87, 129.82, 129.75, 129.7, 129.10, 129.05, 129.0, 128.91, 128.85, 128.8, 128.6, 128.5, 128.43, 128.41, 80.9, 80.5, 76.6, 75.4, 74.2, 72.9, 71.0, 69.8, 68.3, 63.3, 62.4.

HRMS (ESI$^+$, m/z): calcd for $C_{68}H_{55}O_{18}S^+$ $(M+H)^+$: 1191.3109; Found: 1191.3101.

2,3,4,6-Tetra-*O*-benzoyl-1-thio-1-*S*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-β-D-glucopyranoside (5s)



Following the procedure for **5a**, **3a** (170 mg, 0.2 mmol) was coupled with **1e** (61.3 mg, 0.1 mmol) to afford **5s** (87.2 mg, 73.0 μmol, 73%) as a white foam.

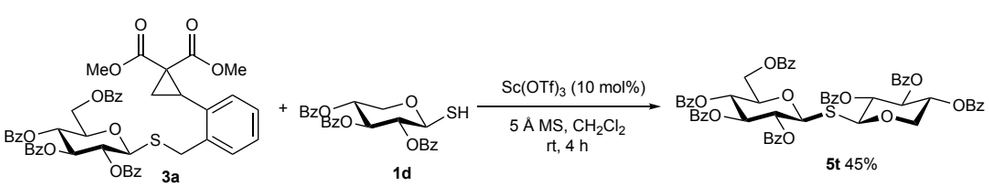
$[\alpha]_D^{23}$ = +1.8 (*c* = 3.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.15 (d, *J* = 6.9 Hz, 2H), 8.02 – 7.98 (m, 6H), 7.94 – 7.89 (m, 4H), 7.83 (d, *J* = 7.0 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.48 – 7.30 (m, 16H), 7.23 (t, *J* = 7.2 Hz, 6H), 6.28 (t, *J* = 10.1 Hz, 1H), 6.03 (s, 1H), 5.95 (t, *J* = 9.5 Hz, 1H), 5.83 – 5.75 (m, 4H), 5.19 (d, *J* = 9.9 Hz, 1H), 4.86 – 4.72 (m, 3H), 4.54 (dd, *J* = 12.5, 2.7 Hz, 1H), 4.47 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.31 – 4.25 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.11, 166.06, 165.8, 165.4, 165.3, 165.1, 133.54, 133.46, 133.34, 133.28, 133.0, 130.1, 130.0, 129.89, 129.86, 129.81, 129.78, 129.75, 129.5, 129.2, 129.0, 128.89, 128.87, 128.74, 128.73, 128.6, 128.54, 128.50, 128.47, 128.45, 128.4, 128.3, 83.1, 81.5, 76.9, 74.2, 71.9, 71.5, 70.6, 70.4, 69.0, 66.4, 62.6, 62.3.

HRMS (ESI$^+$, m/z): calcd for $C_{68}H_{55}O_{18}S^+$ $(M+H)^+$: 1191.3109; Found: 1191.3101.

2,3,4,6-Tetra-*O*-benzoyl-1-thio-1-*S*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-β-D-glucopyranoside (5t)



Following the procedure for **5a**, **3a** (170 mg, 0.2 mmol) was coupled with **1d** (47.9 mg, 0.1 mmol) to afford **5t** (47.7 mg, 45.0 μmol, 45%) as a white foam.

$[\alpha]_D^{23}$ = –18.4 (*c* = 1.0, $CHCl_3$).

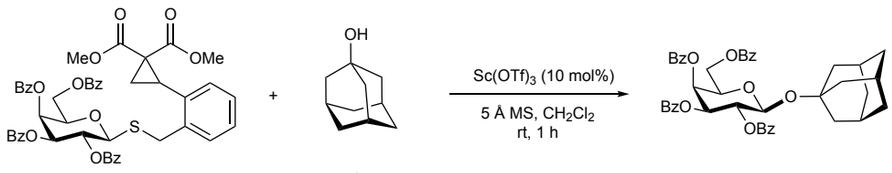
^1H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.93 (m, 10H), 7.93 – 7.89 (m, 2H), 7.83 (d, *J* = 7.0 Hz, 2H), 7.57 – 7.47 (m, 5H), 7.45 – 7.27 (m, 16H), 6.00 (t, *J* = 9.5 Hz, 1H), 5.73 – 5.67 (m, 1H), 5.67 – 5.62 (m, 2H), 5.60 (t, *J* = 4.7 Hz, 1H), 5.34 (t, *J* = 4.1 Hz, 1H), 5.24 (d, *J* = 10.2 Hz, 1H), 5.05 (q, *J* = 3.9 Hz, 1H), 4.64 (dd, *J* = 12.2, 3.0 Hz, 1H), 4.54 (dd, *J* = 12.2, 5.8 Hz, 1H), 4.44 (dd, *J* = 12.9, 3.0 Hz, 1H), 4.23 (ddd, *J* = 9.3, 5.8, 3.0 Hz, 1H), 3.69 (dd, *J* = 12.7, 4.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 165.5, 165.3, 165.2, 165.1, 164.73, 133.66, 133.6, 133.5, 133.4, 133.2, 130.2, 130.1, 130.0, 129.92, 129.85, 129.8, 129.7, 129.4, 129.1, 128.62, 128.58, 128.55, 128.50, 128.48, 128.46, 128.4, 81.7, 79.9, 76.6, 74.2, 70.9, 69.7, 69.3, 67.8, 67.7, 63.4, 61.0.

HRMS (ESI$^+$, m/z): calcd for $C_{60}H_{48}O_{16}SNa^+$ $(M+Na)^+$: 1079.2561; Found: 1079.2548.

Donor scope studies with CCPB thioglycosides 3b-h

1-Adamantyl 2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-galactopyranoside (7a)



3b **4c** **7a** 94%

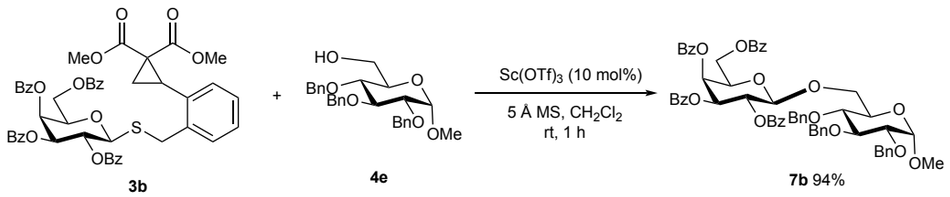
Following the procedure for **5a**, **3b** (51.5 mg, 60 μmol) was coupled with **4c** (7.6 mg, 50.0 μmol) to afford **7a** (34.3 mg, 47.0 μmol, 94%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 2H), 8.04 (d, J = 7.8 Hz, 2H), 7.96 (d, J = 7.8 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.65 – 7.34 (m, 10H), 7.27 – 7.20 (m, 2H), 5.97 (d, J = 3.4 Hz, 1H), 5.78 (dd, J = 10.3, 7.9 Hz, 1H), 5.61 (dd, J = 10.4, 3.5 Hz, 1H), 5.10 (d, J = 8.0 Hz, 1H), 4.61 (dd, J = 11.4, 7.7 Hz, 1H), 4.47 (dd, J = 11.4, 5.5 Hz, 1H), 4.33 (t, J = 6.6 Hz, 1H), 2.04 (s, 3H), 1.85 (d, J = 11.6 Hz, 3H), 1.69 (d, J = 11.5 Hz, 3H), 1.56 (p, J = 12.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 165.7, 165.2, 133.7, 133.3, 133.2, 130.3, 129.9, 129.84, 129.79, 129.76, 129.7, 129.2, 129.0, 128.7, 128.53, 128.48, 128.4, 94.8, 76.0, 72.3, 71.3, 70.1, 68.5, 62.7, 42.5, 36.2, 30.7.

The data are identical to the literature.[14]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (7b)



3b **4e** **7b** 94%

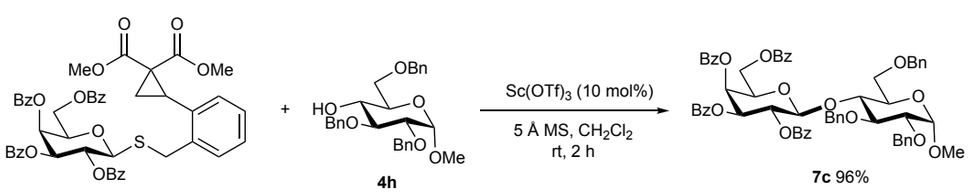
Following the procedure for **5a**, **3b** (70.1 mg, 82.0 μmol) was coupled with **4e** (31.8 mg, 68.0 μmol) to afford **7b** (66.8 mg, 47.0 μmol, 94%) as a colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.8 Hz, 2H), 8.03 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.65 – 7.38 (m, 9H), 7.33 – 7.22 (m, 16H), 7.14 (d, J = 7.0 Hz, 2H), 5.98 (d, J = 3.4 Hz, 1H), 5.86 (dd, J = 10.3, 8.0 Hz, 1H), 5.61 (dd, J = 10.4, 3.4 Hz, 1H), 4.91 (d, J = 10.9 Hz, 1H), 4.79 – 4.65 (m, 4H), 4.60 (d, J = 5.6 Hz, 1H), 4.57 (d, J = 4.8 Hz, 1H), 4.51 (d, J = 3.5 Hz, 1H), 4.45 – 4.36 (m, 2H), 4.26 (t, J = 6.6 Hz, 1H), 4.22 (d, J = 8.9 Hz, 1H), 3.94 – 3.88 (m, 1H), 3.80 – 3.74 (m, 2H), 3.44 – 3.35 (m, 2H), 3.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.73, 165.67, 165.2, 138.9, 138.4, 138.3, 133.7, 133.4, 133.2, 130.2, 129.9, 129.8, 129.5, 129.4, 129.1, 128.8, 128.7, 128.6, 128.54, 128.50, 128.47, 128.4, 128.2, 127.99, 127.97, 127.8, 127.7, 127.6, 102.1, 98.0, 82.0, 80.0, 77.6, 77.4, 75.6, 74.8, 73.5, 71.8, 71.5, 69.9, 69.7, 68.8, 68.2, 62.0, 55.1.

The data are identical to the literature.[14]

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (7c)



3b **4h** **7c** 96%

Following the procedure for **5a**, **3b** (65.0 mg, 76.0 μmol) was coupled with **4h** (29.1 mg, 63.0 μmol) to afford

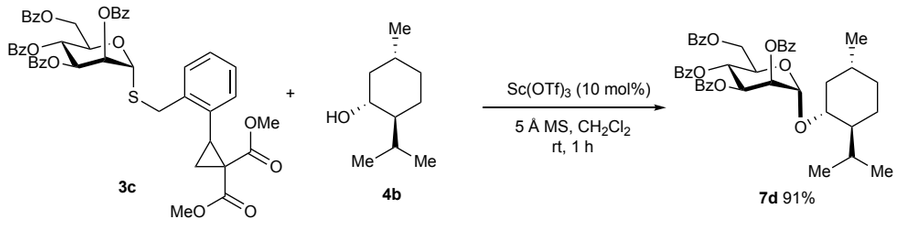
7c (63.1 mg, 60.5 μmol, 96%) as a colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.7 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.8 Hz, 2H), 7.60 – 7.27 (m, 23H), 7.24 – 7.14 (m, 4H), 5.86 (d, J = 3.4 Hz, 1H), 5.71 (dd, J = 10.3, 8.1 Hz, 1H), 5.32 (dd, J = 10.4, 3.4 Hz, 1H), 5.19 (d, J = 11.1 Hz, 1H), 4.92 (d, J = 11.1 Hz, 1H), 4.84 – 4.73 (m, 3H), 4.66 (d, J = 12.3 Hz, 1H), 4.59 (d, J = 3.6 Hz, 1H), 4.41 (dd, J = 11.2, 6.2 Hz, 1H), 4.33 (d, J = 12.2 Hz, 1H), 4.20 (dd, J = 11.2, 7.5 Hz, 1H), 4.04 (t, J = 9.4 Hz, 1H), 3.95 – 3.91 (m, 2H), 3.71 (dd, J = 10.9, 2.7 Hz, 1H), 3.59 – 3.48 (m, 2H), 3.45 (d, J = 10.7 Hz, 1H), 3.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.6, 165.0, 139.51, 138.48, 137.9, 133.5, 133.4, 133.3, 130.0, 129.9, 129.83, 129.78, 129.7, 129.3, 129.2, 129.0, 128.9, 128.7, 128.6, 128.53, 128.48, 128.42, 128.37, 128.2, 127.9, 127.34, 127.29, 100.5, 98.7, 80.0, 78.8, 75.4, 73.8, 73.7, 72.0, 71.1, 70.5, 69.7, 68.0, 67.7, 61.6, 55.5.

The data are identical to the literature.[14]

(–)-Menthyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (7d)



Following the procedure for **5a**, **3c** (51.5 mg, 60.0 μmol) was coupled with **4b** (7.8 mg, 50.0 μmol) to afford **7d** (33.6 mg, 45.5 μmol, 91%) as a white solid.

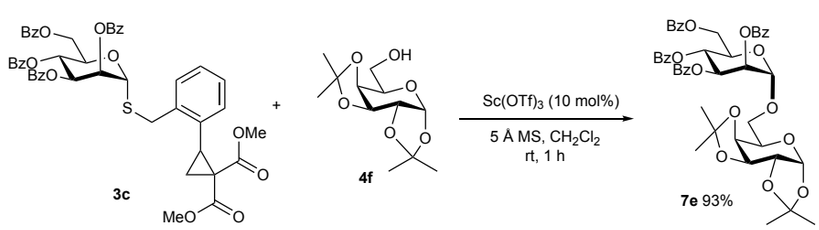
$[\alpha]_D^{23}$ = –66.4 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.05 (m, 4H), 7.99 (d, J = 7.7 Hz, 2H), 7.86 (d, J = 7.7 Hz, 2H), 7.64 – 7.33 (m, 10H), 7.32 – 7.26 (m, 2H), 6.07 (t, J = 10.0 Hz, 1H), 5.95 (dd, J = 10.1, 3.1 Hz, 1H), 5.64 (d, J = 3.0 Hz, 1H), 5.21 (s, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.60 (dd, J = 10.5, 5.3 Hz, 1H), 4.49 (dd, J = 12.0, 5.1 Hz, 1H), 3.51 (td, J = 10.6, 4.2 Hz, 1H), 2.29 – 2.21 (m, 2H), 1.73 – 1.62 (m, 2H), 1.44 – 1.38 (m, 2H), 1.27 – 1.15 (m, 1H), 1.09 – 0.94 (m, 4H), 0.93 – 0.82 (dd, J = 13.5, 6.6 Hz, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.7, 165.7, 133.5, 133.3, 133.2, 130.03, 129.97, 129.89, 129.87, 129.6, 129.3, 129.2, 128.7, 128.6, 128.5, 128.4, 99.4, 83.0, 71.2, 70.2, 69.2, 67.4, 63.5, 48.6, 43.0, 34.4, 31.8, 26.0, 23.4, 22.3, 21.2, 16.4.

HRMS (ESI$^+$, m/z): calcd for $C_{44}H_{46}O_{11}Na^+$ $(M+Na)^+$: 757.2983; Found: 757.2990.

6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (7e)



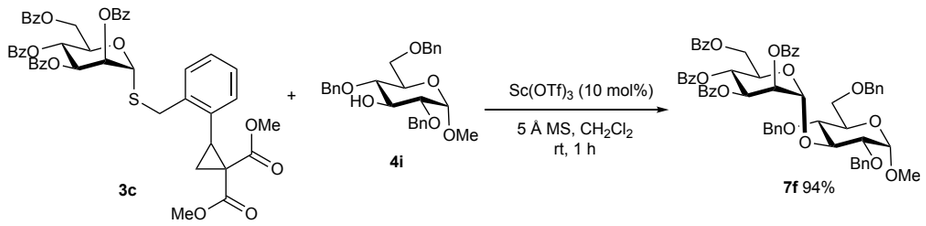
Following the procedure for **5a**, **3c** (56.7 mg, 66.0 μmol) was coupled with **4f** (17.0 mg, 55.0 μmol) to afford **7e** (43.0 mg, 51.2 μmol, 93%) as a colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 2H), 8.09 – 8.03 (m, 2H), 7.99 – 7.94 (m, 2H), 7.87 – 7.81 (m, 2H), 7.62 – 7.33 (m, 10H), 7.30 – 7.24 (m, 2H), 6.14 (t, J = 10.1 Hz, 1H), 5.92 (dd, J = 10.1, 3.2 Hz, 1H), 5.75 (s, 1H), 5.57 (d, J = 4.9 Hz, 1H), 5.17 (s, 1H), 4.73 – 4.64 (m, 2H), 4.64 – 4.56 (m, 1H), 4.50 (dd, J = 12.2, 3.9 Hz, 1H), 4.39 – 4.31 (m, 2H), 4.12 (t, J = 6.3 Hz, 1H), 3.97 (dd, J = 10.5, 6.3 Hz, 1H), 3.89 (dd, J = 10.5, 6.0 Hz, 1H), 1.63 (s, 3H), 1.43 (s, 3H), 1.40 – 1.33 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.6, 165.53, 165.46, 133.53, 133.48, 133.3, 133.1, 130.1, 130.0, 129.92, 129.90, 129.85, 129.5, 129.28, 129.25, 128.7, 128.6, 128.5, 128.4, 109.6, 108.9, 98.0, 96.5, 71.1,

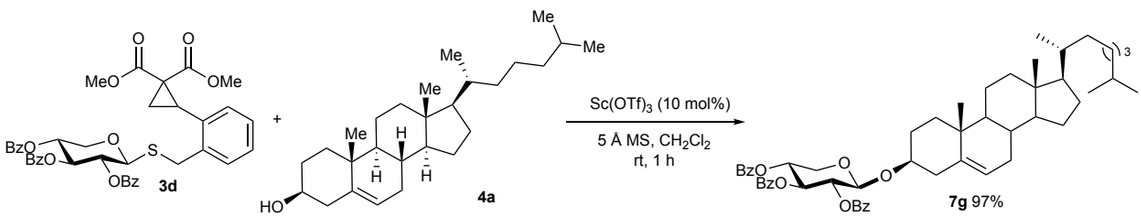
70.8, 70.5, 70.4, 69.0, 67.7, 67.0, 66.9, 63.0, 26.4, 26.1, 25.1, 24.6.
The data are identical to the literature.[15]

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7f)



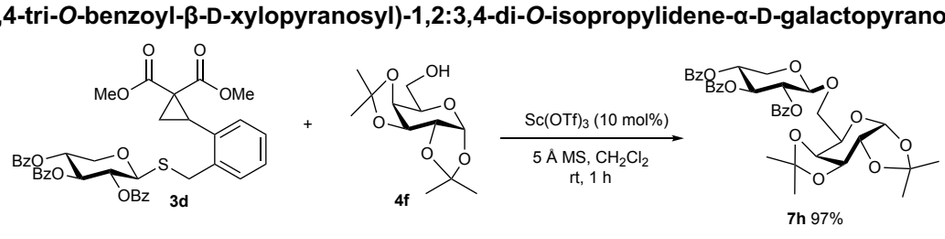
Following the procedure for **5a**, **3c** (94.2 mg, 0.11 mmol) was coupled with **4i** (42.4 mg, 91.0 μmol) to afford **7f** (89.4 mg, 85.5 μmol, 94%) as a colorless syrup.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.6 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.86 – 7.82 (m, 4H), 7.59 – 7.28 (m, 18H), 7.26 – 7.17 (m, 4H), 7.12 – 6.98 (m, 5H), 6.06 (t, J = 10.2 Hz, 1H), 5.96 (dd, J = 10.2, 3.2 Hz, 1H), 5.84 (d, J = 3.2 Hz, 1H), 5.58 (s, 1H), 4.89 (d, J = 10.1 Hz, 1H), 4.85 (d, J = 3.4 Hz, 1H), 4.81 – 4.69 (m, 3H), 4.66 (d, J = 12.0 Hz, 1H), 4.57 – 4.49 (m, 2H), 4.46 (dd, J = 12.4, 2.1 Hz, 1H), 4.33 (t, J = 9.3 Hz, 1H), 4.00 (dd, J = 12.5, 3.7 Hz, 1H), 3.84 (t, J = 9.1 Hz, 1H), 3.79 – 3.71 (m, 2H), 3.71 – 3.63 (m, 2H), 3.39 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.8, 165.4, 165.2, 137.8, 137.72, 137.68, 133.3, 133.2, 132.8, 130.4, 130.0, 129.9, 129.83, 129.79, 129.5, 129.3, 128.6, 128.54, 128.52, 128.44, 128.40, 128.36, 128.23, 128.20, 128.1, 127.9, 127.7, 127.6, 97.9, 97.4, 79.4, 78.0, 76.4, 74.8, 73.7, 72.5, 70.5, 70.0, 68.6, 68.4, 66.7, 62.7, 55.3.
The data are identical to the literature.[16]

(3β)-Cholest-5-en-3-yl 2′,3′,4′-tri-*O*-benzoyl-β-D-xylopyranoside (7g)



Following the procedure for **5a**, **3d** (43.5 mg, 60.0 μmol) was coupled with **4a** (19.3 mg, 50.0 μmol) to afford **7g** (40.3 mg, 48.5 μmol, 97%) as a white foam.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 6H), 7.56 – 7.46 (m, 3H), 7.43 – 7.31 (m, 6H), 5.77 (t, J = 7.4 Hz, 1H), 5.35 (t, J = 6.6 Hz, 1H), 5.33 – 5.26 (m, 2H), 4.96 (d, J = 5.6 Hz, 1H), 4.45 (dd, J = 12.2, 4.3 Hz, 1H), 3.69 (dd, J = 12.1, 7.3 Hz, 1H), 3.63 – 3.53 (m, 1H), 2.28 (dd, J = 13.7, 4.6 Hz, 1H), 2.16 (t, J = 12.5 Hz, 1H), 2.05 – 1.90 (m, 3H), 1.90 – 1.77 (m, 2H), 1.71 – 0.98 (m, 22H), 0.96 (s, 3H), 0.92 (d, J = 6.4 Hz, 3H), 0.87 (d, J = 6.6 Hz, 6H), 0.67 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 165.6, 165.3, 140.4, 133.5, 133.4, 133.3, 130.02, 129.95, 129.6, 129.41, 129.38, 128.54, 128.47, 122.2, 98.8, 79.0, 70.9, 70.7, 69.4, 61.5, 56.9, 56.3, 50.3, 42.5, 39.9, 39.7, 38.8, 37.4, 36.9, 36.3, 35.9, 32.1, 32.0, 29.7, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0.
The data are identical to the literature.[17]

6-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (7h)



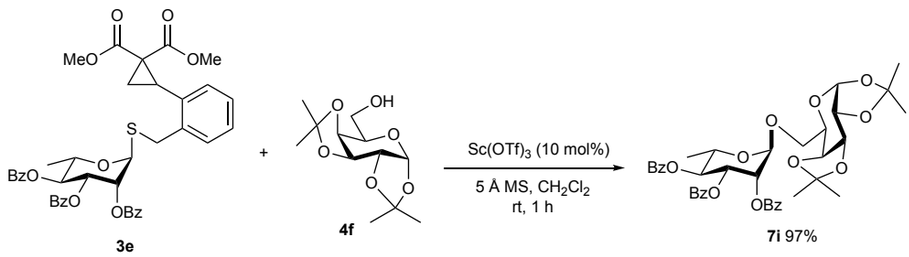
Following the procedure for **5a**, **3d** (46.2 mg, 64.0 μmol) was coupled with **4f** (13.8 mg, 53.0 μmol) to afford **7h** (36.5 mg, 51.4 μmol, 97%) as a colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 6H), 7.57 – 7.47 (m, 3H), 7.42 – 7.30 (m, 6H), 5.74 (t, J = 7.1 Hz, 1H), 5.47 (d, J = 5.0 Hz, 1H), 5.40 (t, J = 6.3 Hz, 1H), 5.35 – 5.27 (m, 1H), 4.96 (d, J = 5.2 Hz, 1H), 4.54 – 4.43 (m, 2H), 4.27 (dd, J = 5.0, 2.3 Hz, 1H), 4.21 (d, J = 7.9 Hz, 1H), 4.02 (dd, J = 10.3, 5.8 Hz, 1H), 3.95 (t, J = 6.2 Hz, 1H), 3.78 (dd, J = 10.3, 6.2 Hz, 1H), 3.72 (dd, J = 12.4, 6.9 Hz, 1H), 1.44 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 165.5, 165.3, 133.5, 133.4, 133.3, 130.1, 130.02, 130.00, 129.5, 129.40, 129.35, 128.53, 128.49, 128.4, 109.5, 108.7, 100.3, 96.4, 71.1, 70.7, 70.6, 70.5, 70.3, 69.3, 67.7, 67.1, 61.3, 26.1, 25.9, 25.0, 24.6.

The data are identical to the literature.[18]

6-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (7i)



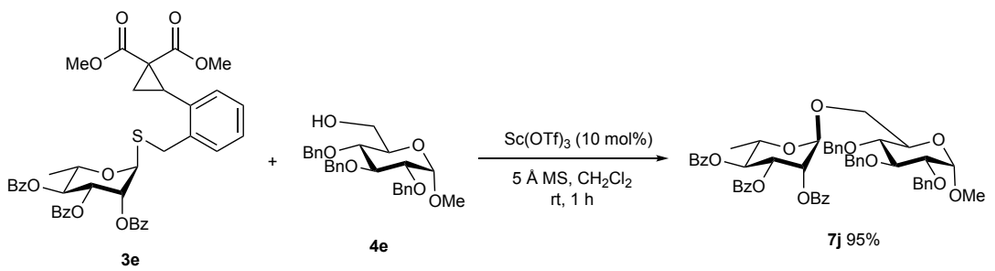
Following the procedure for **5a**, **3e** (46.1 mg, 62.0 μmol) was coupled with **4f** (13.4 mg, 52.0 μmol) to afford **7i** (36.8 mg, 51.0 μmol, 98%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.7 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 7.7 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.44 – 7.35 (m, 3H), 7.28 – 7.23 (m, 2H), 5.86 – 5.79 (m, 1H), 5.73 – 5.62 (m, 2H), 5.55 (d, J = 5.1 Hz, 1H), 5.08 (s, 1H), 4.70 (d, J = 7.9 Hz, 1H), 4.45 (d, J = 7.9 Hz, 1H), 4.42 – 4.31 (m, 2H), 4.18 – 4.09 (m, 1H), 4.00 (t, J = 8.7 Hz, 1H), 3.75 – 3.66 (m, 1H), 1.61 (s, 3H), 1.47 (s, 3H), 1.42 – 1.33 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.7, 165.6, 133.5, 133.4, 133.2, 130.1, 129.81, 129.78, 129.6, 129.5, 129.4, 128.7, 128.5, 128.4, 109.3, 108.9, 97.5, 96.4, 72.0, 70.94, 70.87, 70.81, 70.78, 70.3, 66.8, 66.2, 65.5, 26.3, 26.2, 25.1, 24.6, 17.6.

The data are identical to the literature.[18]

Methyl 6-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (7j)



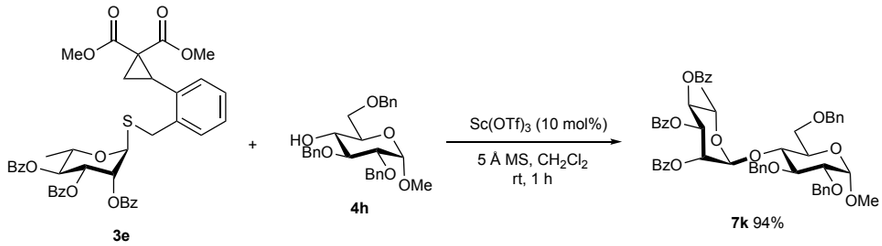
Following the procedure for **5a**, **3e** (81.6 mg, 0.11 mmol) was coupled with **4e** (42.8 mg, 92.0 μmol) to afford **7j** (81.0 mg, 87.4 μmol, 95%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.7 Hz, 2H), 7.98 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.43 – 7.23 (m, 20H), 5.83 (dd, J = 10.2, 3.4 Hz, 1H), 5.71 – 5.62 (m, 2H), 5.04 (d, J = 10.9 Hz, 1H), 5.01 – 4.94 (m, 2H), 4.91 – 4.80 (m, 2H), 4.75 – 4.61 (m, 3H), 4.24 – 4.14 (m, 1H), 4.07 (t, J = 9.2 Hz, 1H), 3.98 (d, J = 10.9 Hz, 1H), 3.89 (dd, J = 10.3, 5.6 Hz, 1H), 3.69 – 3.58 (m, 2H), 3.54 (t, J = 9.4 Hz, 1H), 3.48 (s, 3H), 1.33 (d, J = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.5, 138.8, 138.28, 138.26, 133.5, 133.4, 133.1, 130.0, 129.83, 129.75, 129.6, 129.4, 129.3, 128.7, 128.57, 128.55, 128.5, 128.3, 128.2, 128.1, 128.03, 128.00, 127.9, 127.7, 98.1, 98.0, 82.29, 80.28, 77.9, 75.9, 75.2, 73.5, 71.9, 70.8, 70.2, 70.0, 67.2, 66.8, 55.4, 17.7.

The data are identical to the literature.[18]

Methyl 4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (7k)



3e **4h** **7k** 94%

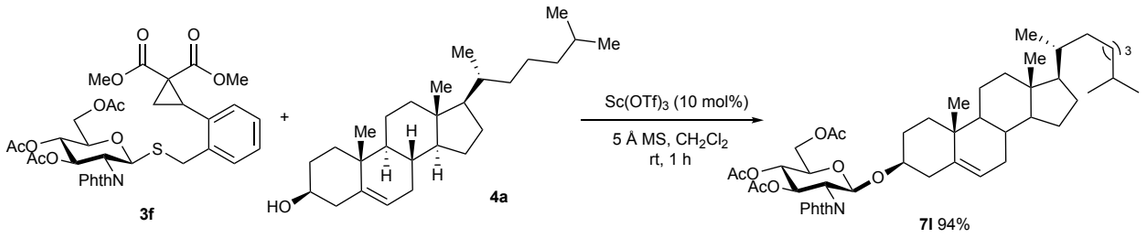
Following the procedure for **5a**, **3e** (81.6 mg, 0.11 mmol) was coupled with **4h** (42.1 mg, 91.0 μmol) to afford **7k** (79.3 mg, 85.5 μmol, 94%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.7 Hz, 2H), 7.91 (d, J = 7.7 Hz, 2H), 7.87 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.51 – 7.27 (m, 16H), 7.23 – 7.10 (m, 6H), 5.80 (dd, J = 10.2, 3.3 Hz, 1H), 5.67 – 5.55 (m, 2H), 5.27 – 5.18 (m, 2H), 4.87 (d, J = 11.1 Hz, 1H), 4.77 (d, J = 12.1 Hz, 1H), 4.68 – 4.63 (m, 2H), 4.61 (d, J = 11.8 Hz, 1H), 4.56 (d, J = 11.9 Hz, 1H), 4.43 – 4.34 (m, 1H), 4.07 – 3.96 (m, 2H), 3.95 – 3.82 (m, 2H), 3.75 (d, J = 11.0 Hz, 1H), 3.66 (dd, J = 8.9, 3.4 Hz, 1H), 3.42 (s, 3H), 0.91 (d, J = 6.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.8, 138.8, 138.1, 137.9, 133.6, 133.34, 133.26, 130.0, 129.81, 129.78, 129.6, 129.4, 128.7, 128.6, 128.5, 128.42, 128.36, 128.31, 128.27, 128.1, 128.0, 127.59, 127.55, 127.4, 98.1, 97.2, 80.5, 79.9, 75.6, 75.0, 73.5, 73.4, 71.9, 71.4, 70.2, 70.1, 68.4, 67.2, 55.4, 17.3.

The data are identical to the literature.[18]

(3β)-Cholest-5-en-3-yl 3′,4′,6′-tri-*O*-acetyl-2′-deoxy-2′-phthalimido-β-D-glucopyranoside (7l)



3f **4a** **7l** 94%

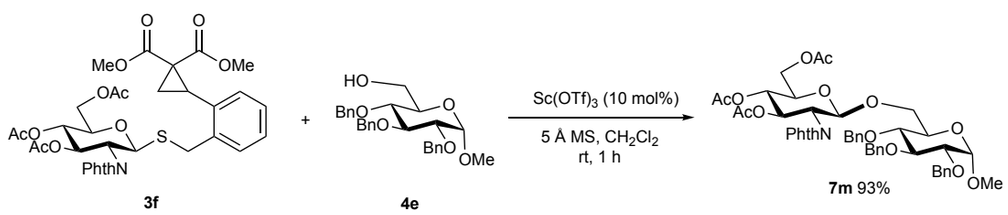
Following the procedure for **5a**, **3f** (41.9 mg, 60.0 μmol) was coupled with **4a** (19.3 mg, 50.0 μmol) to afford **7l** (37.8 mg, 47.0 μmol, 94%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H), 7.78 – 7.70 (m, 2H), 5.77 (t, J = 9.9 Hz, 1H), 5.47 (d, J = 8.4 Hz, 1H), 5.22 (d, J = 4.7 Hz, 1H), 5.15 (t, J = 9.6 Hz, 1H), 4.37 – 4.25 (m, 2H), 4.14 (dd, J = 12.4, 2.3 Hz, 1H), 3.90 – 3.80 (m, 1H), 3.53 – 3.40 (m, 1H), 2.10 (s, 3H), 2.07 – 1.75 (m, 13H), 1.60 – 0.82 (m, 35H), 0.63 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.3, 169.6, 140.3, 134.4, 131.5, 123.7, 122.2, 96.9, 79.6, 71.8, 71.0, 69.3, 62.3, 56.8, 56.3, 55.0, 50.2, 42.4, 39.9, 39.6, 38.7, 37.3, 36.7, 36.3, 35.9, 32.0, 31.9, 29.5, 28.3, 28.1, 24.4, 23.9, 22.9, 22.7, 21.1, 20.9, 20.8, 20.6, 19.4, 18.8, 12.0.

The data are identical to the literature.[19]

Methyl 6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (7m)



3f **4e** **7m** 93%

Following the procedure for **5a**, **3f** (65.5 mg, 94.0 μmol) was coupled with **4e** (34.0 mg, 78.0 μmol) to afford

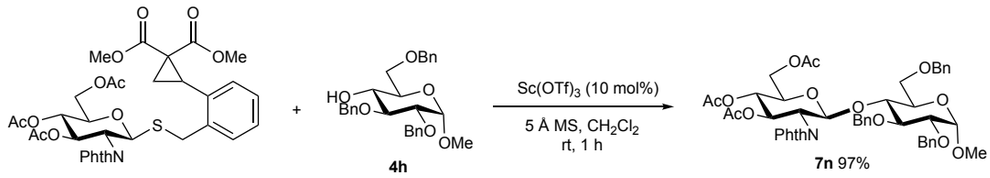
7m (66.8 mg, 75.7 μmol, 97%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.74 – 7.47 (m, 4H), 7.34 – 7.16 (m, 14H), 7.06 – 6.96 (m, 2H), 5.77 (t, *J* = 9.9 Hz, 1H), 5.41 (d, *J* = 8.4 Hz, 1H), 5.16 (t, *J* = 9.6 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 10.9 Hz, 1H), 4.55 (d, *J* = 12.1 Hz, 1H), 4.42 – 4.34 (m, 3H), 4.30 (dd, *J* = 12.3, 4.6 Hz, 1H), 4.15 (d, *J* = 12.0 Hz, 1H), 4.11 (d, *J* = 10.8 Hz, 1H), 4.07 (d, *J* = 9.2 Hz, 1H), 3.88 – 3.78 (m, 2H), 3.68 – 3.60 (m, 2H), 3.36 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.21 (t, *J* = 9.4 Hz, 1H), 3.15 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.8, 170.3, 169.5, 138.7, 138.2, 137.9, 134.2, 131.3, 128.5, 128.4, 128.2, 128.01, 127.98, 127.8, 127.7, 127.63, 123.57, 98.4, 98.0, 81.9, 79.8, 77.7, 75.7, 74.8, 73.4, 72.0, 70.8, 69.3, 69.1, 68.8, 62.2, 55.0, 54.6, 20.9, 20.7, 20.5.

The data are identical to the literature.[19]

Methyl 4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (7n)



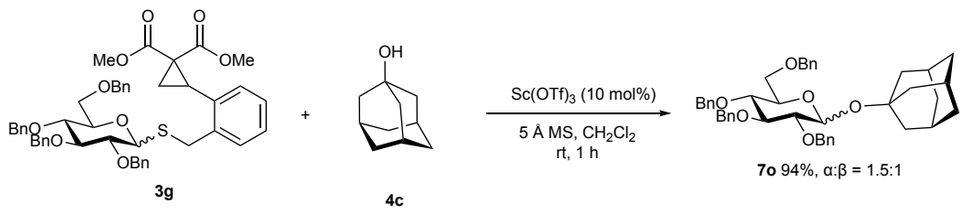
Following the procedure for **5a**, **3f** (48.6 mg, 70.0 μmol) was coupled with **4h** (27.2 mg, 58.0 μmol) to afford **7n** (47.8 mg, 53.9 μmol, 93%) as a white foam.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.86 – 7.77 (m, 2H), 7.71 – 7.65 (m, 2H), 7.44 – 7.40 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.20 (m, 12H), 5.69 (t, *J* = 9.9 Hz, 1H), 5.63 (d, *J* = 8.3 Hz, 1H), 5.11 (t, *J* = 9.6 Hz, 1H), 4.99 (d, *J* = 11.8 Hz, 1H), 4.92 (d, *J* = 11.8 Hz, 1H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 12.1 Hz, 1H), 4.50 (d, *J* = 3.6 Hz, 1H), 4.39 – 4.30 (m, 2H), 4.26 (t, *J* = 9.5 Hz, 1H), 4.07 (dd, *J* = 12.4, 3.7 Hz, 1H), 3.98 (t, *J* = 9.3 Hz, 1H), 3.88 (t, *J* = 9.1 Hz, 1H), 3.81 (d, *J* = 12.3 Hz, 1H), 3.55 (d, *J* = 10.0 Hz, 1H), 3.49 – 3.39 (m, 3H), 3.35 (d, *J* = 10.3 Hz, 1H), 3.26 (s, 3H), 2.00 – 1.93 (m, 6H), 1.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.8, 170.3, 169.5, 139.6, 138.4, 138.3, 134.4, 131.6, 128.5, 128.37, 128.35, 128.2, 127.9, 127.5, 127.4, 127.2, 127.0, 123.7, 98.2, 97.4, 80.3, 79.5, 75.7, 74.8, 73.5, 73.0, 71.7, 70.9, 69.5, 68.8, 68.4, 61.7, 55.5, 55.4, 20.8, 20.7, 20.5.

The data are identical to the literature.[20]

1-Adamantyl 2′,3′,4′,6′-tetra-*O*-benzyl-D-glucopyranoside (7o)



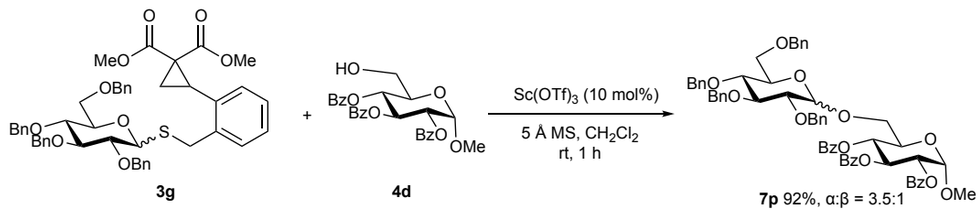
Following the procedure for **5a**, **3g** (59.7 mg, 74.0 μmol) was coupled with **4c** (9.5 mg, 62.0 μmol) to afford **7o** (39.4 mg, 58.3 μmol, 94%, α/β = 1.5/1) as a white foam.

^{1}H NMR (400 MHz, CDCl3) *δ* 7.38 – 7.14 (m, 33.92H), 5.29 (d, *J* = 3.6 Hz, 1H), 5.05 – 4.97 (m, 1.64H), 4.92 (d, *J* = 10.8 Hz, 0.66H), 4.86 – 4.79 (m, 3H), 4.77 – 4.70 (m, 3.57H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.59 – 4.54 (m, 2H), 4.50 – 4.43 (m, 2H), 4.05 – 4.00 (m, 2H), 3.80 – 3.72 (m, 1.63H), 3.68 – 3.61 (m, 3.33H), 3.56 – 3.42 (m, 3H), 2.18 – 2.13 (m, 5H), 1.98 – 1.81 (m, 10H), 1.65 – 1.61 (m, 9.66H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.2, 138.7, 138.51, 138.47, 138.4, 138.3, 128.50, 128.47, 128.43, 128.40, 128.35, 128.3, 128.10, 128.08, 128.02, 127.96, 127.9, 127.8, 127.7, 127.6, 96.4, 90.0, 85.3, 82.5, 82.2, 80.3, 78.4, 78.3, 75.8, 75.7, 75.4, 75.2, 75.1, 74.71, 74.67, 73.6, 73.5, 73.0, 69.8, 69.7, 68.9, 42.9, 42.6, 36.4, 30.9, 30.8.

The data are identical to the literature.[18]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (7p)



Following the procedure for **5a**, **3g** (39.6 mg, 49.0 μmol) was coupled with **4d** (21.0 mg, 41.0 μmol) to afford **7p** (38.8 mg, 37.7 μmol, 92%, α/β = 3.5/1) as a white foam.

α anomer

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.99 (d, *J* = 7.0 Hz, 2H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.87 (d, *J* = 7.0 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.45 – 7.27 (m, 21H), 7.26 – 7.18 (m, 5H), 7.17 – 7.11 (m, 2H), 6.15 (t, *J* = 9.5 Hz, 1H), 5.53 (t, *J* = 9.9 Hz, 1H), 5.27 – 5.18 (m, 2H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 11.0 Hz, 1H), 4.80 – 4.77 (m, 1H), 4.77 – 4.75 (m, 1H), 4.75 – 4.74 (m, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 12.1 Hz, 1H), 4.46 (d, *J* = 11.0 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 4.36 – 4.29 (m, 1H), 3.97 (t, *J* = 9.3 Hz, 1H), 3.89 – 3.82 (m, 2H), 3.67 – 3.64 (m, 1H), 3.63 – 3.61 (m, 1H), 3.59 (dd, *J* = 11.0, 2.2 Hz, 1H), 3.54 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.51 (dd, *J* = 10.6, 2.1 Hz, 1H), 3.44 (s, 3H).

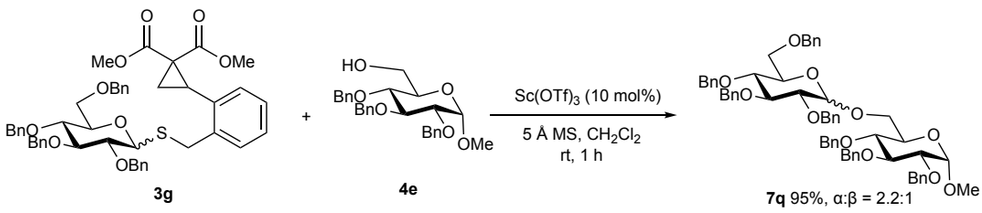
^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.0, 165.9, 165.4, 139.0, 138.7, 138.5, 138.1, 133.5, 133.2, 130.1, 129.8, 129.4, 129.3, 129.2, 128.53, 128.45, 128.4, 128.10, 128.06, 128.0, 127.9, 127.8, 127.62, 127.60, 97.4, 96.9, 81.9, 80.1, 77.7, 75.7, 74.9, 73.5, 73.2, 72.4, 70.8, 70.4, 69.8, 68.7, 68.4, 66.8, 55.7.

β anomer

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.97 (d, *J* = 6.9 Hz, 2H), 7.93 (d, *J* = 7.0 Hz, 2H), 7.86 – 7.83 (m, 2H), 7.52 – 7.48 (m, 2H), 7.44 – 7.27 (m, 22H), 7.26 – 7.21 (m, 4H), 7.17 – 7.12 (m, 2H), 6.17 (t, *J* = 9.8 Hz, 1H), 5.47 (t, *J* = 9.9 Hz, 1H), 5.25 (dd, *J* = 10.1, 3.6 Hz, 1H), 5.21 (d, *J* = 3.6 Hz, 1H), 5.05 (d, *J* = 10.8 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 1H), 4.68 (d, *J* = 10.8 Hz, 1H), 4.53 (d, *J* = 6.3 Hz, 1H), 4.50 (d, *J* = 4.9 Hz, 1H), 4.47 (d, *J* = 7.7 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 4.37 (dd, *J* = 10.0, 7.2 Hz, 1H), 4.12 (dd, *J* = 11.1, 2.2 Hz, 1H), 3.81 (dd, *J* = 11.0, 7.5 Hz, 1H), 3.66 – 3.56 (m, 4H), 3.49 – 3.40 (m, 2H), 3.38 (s, 3H).

The data are identical to the literature.[21]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (7q)



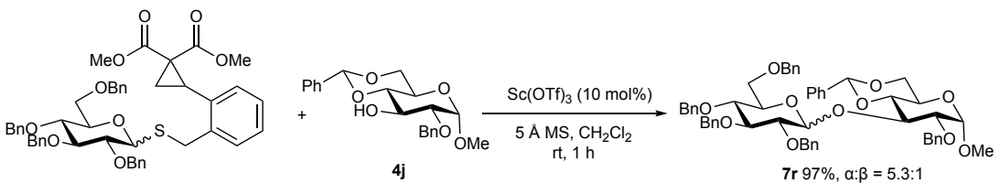
Following the procedure for **5a**, **3g** (45.3 mg, 56.0 μmol) was coupled with **4e** (21.7 mg, 47.0 μmol) to afford **7q** (43.7 mg, 44.7 μmol, 95%, α/β = 2.2/1) as a white foam.

^{1}H NMR (400 MHz, CDCl3) *δ* 7.38 – 7.14 (m, 51H), 5.02 – 4.92 (m, 5.9H), 4.87 – 4.79 (m, 5.6H), 4.76 – 4.69 (m, 5H), 4.66 – 4.53 (m, 6.8H), 4.50 – 4.43 (m, 2.4H), 4.38 (d, *J* = 7.8 Hz, 0.47H), 4.21 (dd, *J* = 10.8, 2.0 Hz, 0.42H), 4.04 – 3.96 (m, 2.7H), 3.87 – 3.44 (m, 16.8H), 3.38 (s, 3H), 3.35 (s, 1.33H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.0, 138.62, 138.59, 138.56, 138.5, 138.4, 138.3, 138.1, 128.6, 128.53, 128.51, 128.48, 128.45, 128.43, 128.39, 128.3, 128.13, 128.10, 128.08, 128.06, 128.03, 127.99, 127.96, 127.9, 127.83, 127.78, 127.76, 127.74, 127.70, 127.67, 127.65, 127.6, 103.9, 98.2, 98.1, 97.4, 84.9, 82.3, 82.1, 81.8, 80.3, 80.1, 79.9, 78.1, 78.0, 77.9, 77.8, 75.8, 75.6, 75.1, 75.0, 73.53, 73.49, 72.5, 70.5, 70.4, 70.0, 69.2, 68.6, 66.2, 55.32, 55.27.

The data are identical to the literature.[18]

Methyl 4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (7r)



Following the procedure for **5a**, **3g** (49.1 mg, 49.0 μmol) was coupled with **4j** (19.0 mg, 51.0 μmol) to afford **7r** (44.3 mg, 47.5 μmol, 97%, α/β = 5.3/1) as a white solid.

α anomer

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.42 – 7.26 (m, 18H), 7.26 – 7.14 (m, 8H), 7.13 – 7.07 (m, 4H), 6.96 – 6.91 (m, 2H), 5.60 (d, *J* = 3.6 Hz, 1H), 5.47 (s, 1H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 3.3 Hz, 1H), 4.80 (d, *J* = 3.6 Hz, 1H), 4.72 (d, *J* = 3.7 Hz, 1H), 4.66 (d, *J* = 11.2 Hz, 1H), 4.62 – 4.54 (m, 3H), 4.44 – 4.28 (m, 4H), 4.28 – 4.19 (m, 2H), 3.98 (t, *J* = 9.3 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.79 (t, *J* = 9.3 Hz, 1H), 3.75 – 3.63 (m, 3H), 3.54 – 3.46 (m, 3H), 3.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.1, 139.0, 138.2, 138.0, 137.6, 137.2, 129.5, 128.8, 128.6, 128.5, 128.40, 128.35, 128.26, 128.25, 128.1, 128.0, 127.73, 127.65, 127.6, 127.53, 127.48, 127.4, 126.5, 102.2, 98.7, 96.3, 83.1, 81.8, 78.9, 78.2, 77.6, 75.7, 74.9, 73.6, 73.5, 72.9, 71.3, 69.9, 69.4, 68.3, 61.9, 55.5.

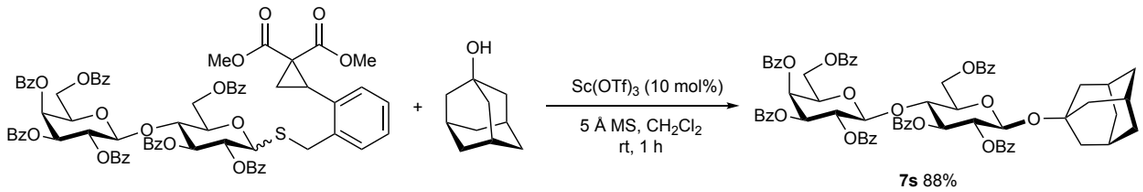
β anomer

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.44 – 7.40 (m, 2H), 7.38 – 7.26 (m, 18H), 7.26 – 7.20 (m, 9H), 7.17 – 7.14 (m, 2H), 5.47 (s, 1H), 5.07 (d, *J* = 11.2 Hz, 1H), 4.95 – 4.88 (m, 2H), 4.81 – 4.75 (m, 3H), 4.72 (d, *J* = 11.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 4.51 – 4.45 (m, 4H), 4.37 (t, *J* = 9.1 Hz, 1H), 4.21 (dd, *J* = 10.1, 4.6 Hz, 1H), 3.82 (td, *J* = 9.9, 4.6 Hz, 1H), 3.72 – 3.55 (m, 7H), 3.50 (t, *J* = 8.2 Hz, 1H), 3.36 (s, 3H), 3.28 – 3.22 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 139.0, 138.9, 138.6, 138.4, 138.2, 137.5, 129.0, 128.50, 128.46, 128.39, 128.36, 128.24, 128.15, 128.06, 128.05, 128.0, 127.8, 127.64, 127.55, 126.3, 102.7, 101.6, 98.9, 85.1, 83.1, 80.6, 80.5, 78.2, 76.0, 75.7, 75.1, 75.0, 74.9, 73.9, 73.7, 69.2, 68.8, 62.3, 55.5.

The data are identical to the literature.[22]

1-Adamantyl 4′-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2′,3′,6′-tri-*O*-benzoyl-β-D-glucopyranoside (7s)



Following the procedure for **5a**, **3h** (80.0 mg, 60.0 μmol) was coupled with **4c** (7.6 mg, 50.0 μmol) to afford **7s** (53.0 mg, 44.0 μmol, 88%) as a colorless syrup.

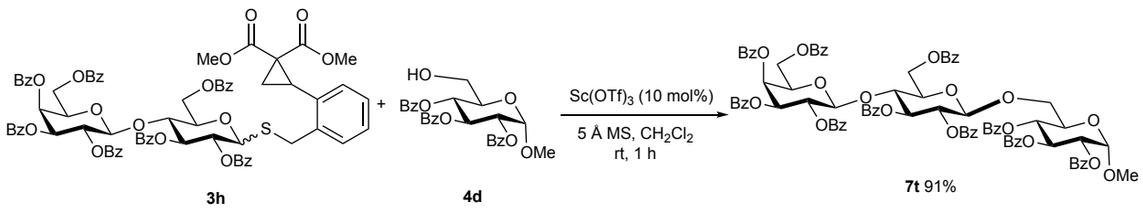
$[\alpha]_D^{23}$ = +47.7 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.05 – 7.89 (m, 12H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.46 (m, 8H), 7.43 – 7.26 (m, 9H), 7.24 – 7.18 (m, 2H), 7.16 – 7.10 (m, 2H), 5.80 (t, *J* = 9.4 Hz, 1H), 5.76 – 5.69 (m, 2H), 5.44 (d, *J* = 8.8 Hz, 1H), 5.41 – 5.36 (m, 1H), 5.00 (d, *J* = 8.0 Hz, 1H), 4.87 (d, *J* = 7.9 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.45 (dd, *J* = 11.8, 6.3 Hz, 1H), 4.14 (t, *J* = 9.4 Hz, 1H), 3.94 (t, *J* = 6.7 Hz, 1H), 3.86 (dd, *J* = 9.8, 6.4 Hz, 1H), 3.75 (dd, *J* = 11.5, 6.5 Hz, 1H), 3.64 (dd, *J* = 11.5, 6.7 Hz, 1H), 2.00 (s, 3H), 1.75 (d, *J* = 11.8 Hz, 3H), 1.64 – 1.41 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.91, 165.72, 165.56, 165.52, 165.34, 165.12, 164.91, 133.65, 133.51, 133.43, 133.35, 133.20, 133.13, 130.14, 129.90, 129.83, 129.78, 129.74, 129.68, 129.57, 129.02, 128.87, 128.80, 128.78, 128.70, 128.61, 128.54, 128.45, 128.37, 128.32, 101.19, 94.26, 76.95, 75.85, 73.49, 72.94, 72.01, 71.93, 71.55, 70.11, 67.73, 63.21, 61.31, 42.42, 36.14, 30.65.

HRMS (ESI$^+$, m/z): calcd for $C_{71}H_{64}O_{18}Na^+$ (M+Na)$^+$: 1227.3985; Found: 1227.3981.

Methyl 6-*O*-[4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (7t)



3h **4d** **7t** 91%

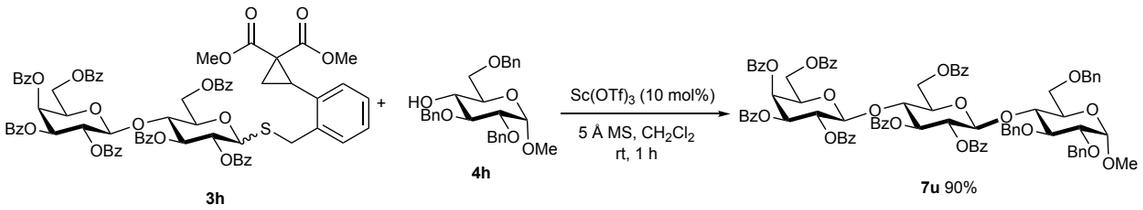
Following the procedure for **5a**, **3h** (80.0 mg, 60.0 μmol) was coupled with **4c** (25.3 mg, 50.0 μmol) to afford **7t** (71.1 mg, 45.5 μmol, 91%) as a white foam.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.94 (d, J = 8.2 Hz, 10H), 7.95 – 7.90 (m, 4H), 7.84 (d, J = 7.8 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 7.8 Hz, 2H), 7.66 – 7.28 (m, 26H), 7.25 – 7.11 (m, 6H), 6.06 (t, J = 9.8 Hz, 1H), 5.84 (t, J = 9.5 Hz, 1H), 5.79 – 5.70 (m, 2H), 5.52 (dd, J = 9.8, 8.0 Hz, 1H), 5.37 (dd, J = 10.3, 3.3 Hz, 1H), 5.28 (t, J = 9.9 Hz, 1H), 5.08 (dd, J = 10.2, 3.5 Hz, 1H), 4.94 (d, J = 3.5 Hz, 1H), 4.91 – 4.82 (m, 2H), 4.57 (d, J = 12.1 Hz, 1H), 4.48 (dd, J = 12.3, 4.1 Hz, 1H), 4.27 (t, J = 9.4 Hz, 1H), 4.18 (t, J = 9.0 Hz, 1H), 4.02 (d, J = 11.4 Hz, 1H), 3.92 – 3.80 (m, 2H), 3.77 – 3.64 (m, 3H), 3.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.8, 165.74, 165.65, 165.5, 165.44, 165.38, 165.3, 164.9, 133.6, 133.5, 133.39, 133.35, 133.3, 133.1, 130.1, 130.0, 129.9, 129.84, 129.78, 129.73, 129.70, 129.6, 129.53, 129.52, 129.3, 129.1, 129.0, 128.83, 128.79, 128.73, 128.68, 128.6, 128.5, 128.4, 128.34, 128.32, 128.30, 101.7, 101.0, 96.5, 76.0, 73.1, 72.9, 72.0, 71.91, 71.88, 71.5, 70.4, 70.0, 69.7, 68.9, 68.8, 67.6, 62.4, 61.2, 55.1.

The data are identical to the literature.[23]

Methyl 4-*O*-[4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl]-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (7u)



3h **4h** **7u** 90%

Following the procedure for **5a**, **3h** (131.2 mg, 98.0 μmol) was coupled with **4h** (38.1 mg, 82.0 μmol) to afford **7u** (112.5 mg, 73.8 μmol, 90%) as a colorless syrup.

$[\alpha]_D^{23}$ = +22.0 (c = 1.0, $CHCl_3$).

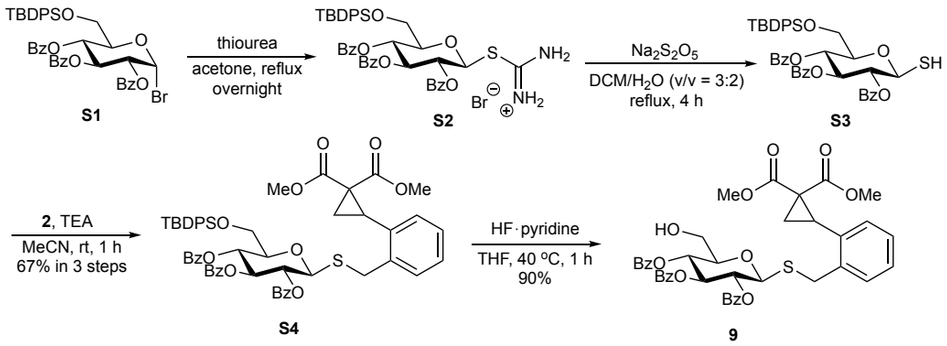
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.8 Hz, 2H), 8.03 (d, J = 7.6 Hz, 2H), 8.00 – 7.96 (m, 4H), 7.93 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 7.7 Hz, 2H), 7.75 (d, J = 7.8 Hz, 2H), 7.65 – 7.34 (m, 24H), 7.25 – 7.21 (m, 8H), 7.16 – 7.09 (m, 2H), 7.01 – 6.98 (m, 2H), 5.76 – 5.69 (m, 2H), 5.50 (t, J = 9.4 Hz, 1H), 5.41 (t, J = 9.0 Hz, 1H), 5.31 (dd, J = 10.4, 3.4 Hz, 1H), 5.02 (d, J = 11.4 Hz, 1H), 4.74 (d, J = 11.2 Hz, 1H), 4.72 – 4.66 (m, 3H), 4.58 (d, J = 7.9 Hz, 1H), 4.55 – 4.51 (m, 2H), 4.35 – 4.24 (m, 3H), 4.15 (t, J = 9.4 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.77 (t, J = 6.6 Hz, 1H), 3.73 – 3.60 (m, 3H), 3.47 (d, J = 8.1 Hz, 1H), 3.44 – 3.38 (m, 2H), 3.29 – 3.23 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.6, 165.5, 165.4, 165.3, 165.1, 164.9, 139.3, 138.4, 137.8, 133.6, 133.5, 133.40, 133.37, 133.3, 133.12, 130.08, 130.0, 129.9, 129.83, 129.75, 129.7, 129.63, 129.61, 129.56, 129.4, 129.0, 128.83, 128.79, 128.78, 128.74, 128.69, 128.66, 128.6, 128.4, 128.34, 128.26, 128.1, 128.0, 127.8, 127.1, 127.0, 100.8, 100.4, 98.5, 80.1, 78.7, 75.5, 75.2, 73.7, 73.6, 73.2, 72.7, 72.3, 71.9, 71.4, 69.9, 69.6, 67.7, 67.6, 62.6, 61.1, 55.4.

HRMS (ESI$^+$, m/z): calcd for $C_{89}H_{80}O_{23}Na^+$ (M+Na)$^+$: 1539.4983; Found: 1539.4988.

One-pot glycosylation studies

***ortho*-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,3′,4′-tri-*O*-benzoyl-1′-thio-β-D-glucopyranoside (9)**



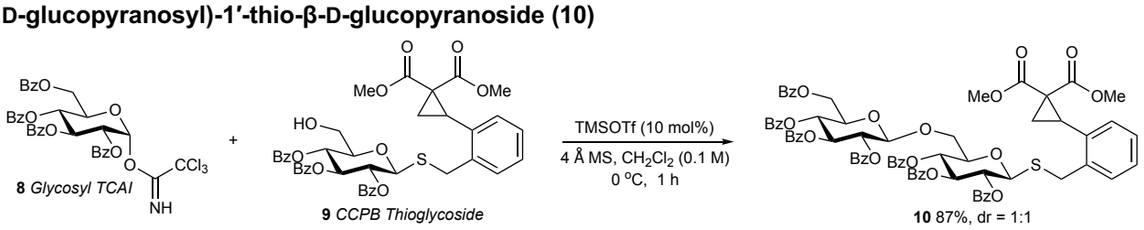
To a solution of bromide **S1**[24] (540 mg, 0.68 mmol) in anhydrous acetone (30 mL) was added thiourea (105 mg, 1.36 mmol). The mixture was refluxed overnight before it was cooled to room temperature and concentrated *in vauco* to afford **S2**. Compound **S2** obtained from last was suspended in a mixed solvent of CH_2Cl_2/H_2O (v/v = 3:2, 50 mL), and to this mixture was added $Na_2S_2O_5$ (194 mg, 1.02 mmol). The mixture was refluxed under the oil bath for 4 h before it was cooled to room temperature and diluted with CH_2Cl_2. Two phases were separated and the aqueous phase was extracted by CH_2Cl_2, the organic phases were combined, dried over Na_2SO_4, filtered and concentrated *in vauco* to afford compound **S3**. Following the procedure for **3a**, **S3** obtained from last step was coupled with **2** (268 mg, 0.82 mmol) to afford **S4** (452 mg, 0.455 mmol, 67% for 3 steps) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 5:1). To a solution of **S4** (452 mg, 0.455 mmol) in THF (5 mL) was added HF (70% in pyridine, 236 μL, 9.1 mmol) at room temperature dropwise. The mixture was heated to 40 °C and stirred at this temperature for another 1 h. The mixture was diluted with H_2O, and extracted with EtOAc. The organic phase was washed successively with H_2O, saturated $NaHCO_3$ solution and brine. The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane: EtOAc = 3:1) to afford **9** (310 mg, 0.41 mmol, 90%, d.r. = 1:1) as a white foam.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 8H), 7.84 – 7.79 (m, 4H), 7.53 – 7.48 (m, 4H), 7.42 – 7.35 (m, 10H), 7.29 – 7.26 (m, 4H), 7.26 – 7.23 (m, 2H), 7.22 – 7.16 (m, 4H), 7.08 – 7.03 (m, 2H), 5.92 – 5.84 (m, 2H), 5.64 (t, J = 9.7 Hz, 1H), 5.57 – 5.47 (m, 3H), 4.77 (d, J = 10.0 Hz, 1H), 4.68 (d, J = 9.9 Hz, 1H), 4.27 (d, J = 11.6 Hz, 1H), 4.19 (d, J = 12.6 Hz, 1H), 4.09 – 4.03 (m, 2H), 3.87 – 3.73 (m, 13H), 3.57 (t, J = 8.7 Hz, 1H), 3.49 – 3.37 (m, 2H), 3.31 (s, 3H), 3.29 (s, 3H), 2.33 (dd, J = 8.2, 5.3 Hz, 1H), 2.27 (dd, J = 8.2, 5.2 Hz, 1H), 1.73 – 1.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.4, 167.0, 166.9, 165.93, 165.87, 165.69, 165.65, 165.4, 165.2, 137.1, 137.0, 133.6, 133.41, 133.37, 133.3, 133.22, 133.18, 130.3, 130.1, 130.00, 129.98, 129.95, 129.8, 129.3, 129.2, 129.01, 128.95, 128.87, 128.85, 128.54, 128.46, 128.42, 128.38, 128.11, 128.09, 127.9, 127.6, 127.5, 83.3, 82.9, 79.6, 79.2, 74.30, 74.26, 70.9, 70.2, 69.5, 69.4, 61.9, 61.8, 53.4, 53.2, 52.4, 52.3, 37.2, 36.8, 32.4, 31.8, 30.5, 30.2, 29.7, 29.4, 18.54, 18.51.

HRMS (ESI$^+$, m/z): calcd for $C_{41}H_{38}O_{12}SNa^+$ $(M+Na)^+$: 777.1976; Found: 777.1987.

***ortho*-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,3′,4′-tri-*O*-benzoyl-6′-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1′-thio-β-D-glucopyranoside (10)**



A solution of glucosyl TCAI **8**[25] (88.9 mg, 0.12 mmol, 1.2 equiv) and **9** (75.5 mg, 0.1 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (1 mL) containing freshly activated 5 Å MS (50 mg) was stirred under the ice bath for 15

min before a solution of TMSOTf in CH_2Cl_2 (0.1 equiv) was added. The mixture was stirred under the ice bath for additional 1 h before the reaction was quenched with TEA. The mixture was concentrated *in vauco* and the residue was purified by silica gel column chromatography (toluene:EtOAc = 15:1) to afford the titled compound **10** (116 mg, 87.0 μmol, 87%, d.r. = 1:1) as a white foam.

isomer 1

$[\alpha]_D^{23}$ = –11.1 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.01 (d, *J* = 7.0 Hz, 2H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.91 – 7.87 (m, 4H), 7.85 (d, *J* = 7.0 Hz, 2H), 7.82 – 7.76 (m, 4H), 7.57 – 7.27 (m, 19H), 7.26 – 7.23 (m, 2H), 7.23 – 7.16 (m, 3H), 7.05 – 7.00 (m, 1H), 5.88 (t, *J* = 9.7 Hz, 1H), 5.74 (t, *J* = 9.5 Hz, 1H), 5.58 (t, *J* = 9.7 Hz, 1H), 5.53 – 5.46 (m, 2H), 5.37 (t, *J* = 9.7 Hz, 1H), 5.00 (d, *J* = 7.9 Hz, 1H), 4.61 (dd, *J* = 12.1, 3.2 Hz, 1H), 4.46 (d, *J* = 9.9 Hz, 1H), 4.40 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.17 (ddd, *J* = 9.9, 5.1, 3.2 Hz, 1H), 4.09 – 4.00 (m, 2H), 3.94 – 3.84 (m, 3H), 3.76 (s, 3H), 3.39 (t, *J* = 8.6 Hz, 1H), 3.32 (s, 3H), 2.23 (dd, *J* = 8.1, 5.2 Hz, 1H), 1.74 (dd, *J* = 9.2, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.3, 167.2, 166.3, 165.9, 165.8, 165.5, 165.4, 165.32, 165.27, 137.6, 133.6, 133.5, 133.4, 133.3, 133.2, 130.4, 130.03, 130.00, 129.95, 129.90, 129.86, 129.85, 129.8, 129.42, 129.36, 129.04, 129.02, 128.9, 128.6, 128.54, 128.50, 128.44, 128.40, 128.37, 127.9, 127.7, 127.4, 101.6, 83.2, 78.4, 74.2, 73.0, 72.2, 72.0, 70.4, 69.93, 69.86, 69.7, 68.9, 63.3, 53.9, 53.1, 52.4, 37.1, 31.9, 31.0, 30.1, 29.8, 29.4, 18.8.

HRMS (ESI$^+$, m/z): calcd for $C_{75}H_{64}O_{21}SNa^+$ $(M+Na)^+$: 1355.3553; Found: 1355.3558.

isomer 2

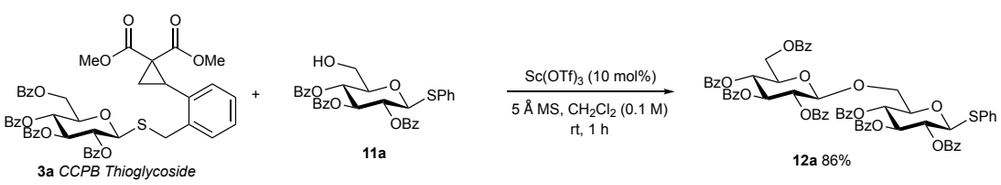
$[\alpha]_D^{23}$ = –29.9 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.99 (d, *J* = 7.0 Hz, 2H), 7.96 (d, *J* = 7.0 Hz, 2H), 7.89 (d, *J* = 7.0 Hz, 2H), 7.84 – 7.78 (m, 4H), 7.78 – 7.73 (m, 4H), 7.57 – 7.27 (m, 20H), 7.25 – 7.15 (m, 5H), 7.07 – 7.03 (m, 1H), 5.89 (d, *J* = 9.7 Hz, 1H), 5.64 (td, *J* = 9.5, 2.2 Hz, 2H), 5.56 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.43 (t, *J* = 9.7 Hz, 1H), 5.30 (t, *J* = 9.6 Hz, 1H), 4.93 (d, *J* = 7.8 Hz, 1H), 4.59 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.40 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.31 (d, *J* = 10.1 Hz, 1H), 4.12 (ddd, *J* = 9.8, 5.0, 3.2 Hz, 1H), 4.10 – 4.05 (m, 1H), 3.91 – 3.85 (m, 1H), 3.83 (d, *J* = 10.9 Hz, 1H), 3.77 (d, *J* = 9.0 Hz, 2H), 3.72 (s, 3H), 3.34 (d, *J* = 8.7 Hz, 1H), 3.30 (s, 3H), 2.19 (d, *J* = 5.1 Hz, 1H), 1.51 (dd, *J* = 9.2, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.8, 167.1, 166.2, 165.9, 165.8, 165.5, 165.3, 165.1, 137.3, 133.61, 133.57, 133.4, 133.30, 133.26, 133.2, 130.7, 130.04, 129.96, 129.89, 129.87, 129.8, 129.7, 129.32, 129.28, 129.0, 128.9, 128.8, 128.6, 128.40, 128.36, 127.7, 127.6, 101.4, 81.8, 77.8, 74.2, 73.1, 72.4, 72.0, 70.5, 69.9, 69.8, 69.0, 63.2, 53.9, 52.9, 52.3, 36.6, 31.9, 31.8, 30.0, 29.8, 29.4.

HRMS (ESI$^+$, m/z): calcd for $C_{75}H_{64}O_{21}SNa^+$ $(M+Na)^+$: 1355.3553; Found: 1355.3558.

Phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (12a)



Following the procedure for **5a**, **3a** (51.5 mg, 60.0 μmol) was coupled with **11a**[26] (29.3 mg, 50.0 μmol) to afford **12a** (50.1 mg, 43.0 μmol, 86%) as a white solid.

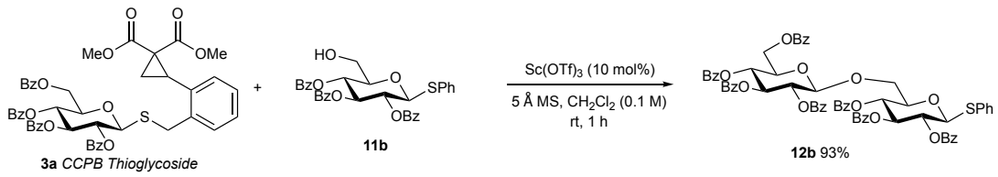
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.06 (d, *J* = 7.7 Hz, 2H), 7.97 – 7.90 (m, 6H), 7.87 – 7.81 (m, 4H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.59 – 7.26 (m, 26H), 5.89 – 5.77 (m, 2H), 5.61 (t, *J* = 9.7 Hz, 1H), 5.50 (dd, *J* = 9.7, 7.9 Hz, 1H), 5.37 (t, *J* = 9.7 Hz, 1H), 5.28 (t, *J* = 9.7 Hz, 1H), 4.98 (d, *J* = 7.8 Hz, 1H), 4.93 (d, *J* = 10.0 Hz, 1H), 4.61 (dd, *J* = 12.3, 2.9 Hz, 1H), 4.42 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.09 – 3.91 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.2, 165.9, 165.8, 165.4, 165.32, 165.28, 165.1, 133.60, 133.56, 133.4, 133.33, 133.29, 133.2, 131.9, 130.00, 129.98, 129.95, 129.9, 129.8, 129.7, 129.42, 129.38, 129.3, 129.01, 128.96, 128.8, 128.64, 128.60, 128.55, 128.50, 128.46, 128.42, 128.36, 101.2, 86.0, 78.7, 74.2, 73.1, 72.4,

72.0, 70.7, 69.8, 69.7, 68.4, 63.0.

The data are identical to the literature report.[3]

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (12b)



Following the procedure for **5a**, **3a** (51.5 mg, 60.0 μmol) was coupled with **11b**[27] (27.2 mg, 50.0 μmol) to afford **12b** (52.1 mg, 46.5 μmol, 93%) as a colorless syrup.

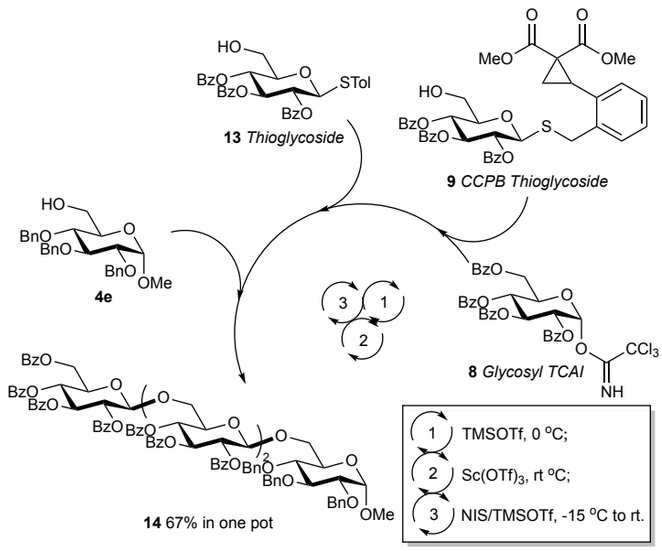
$[\alpha]_D^{23}$ = +7.4 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.03 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.46 – 7.24 (m, 26H), 7.15 – 7.10 (m, 2H), 5.84 (t, *J* = 9.6 Hz, 1H), 5.67 (t, *J* = 9.6 Hz, 1H), 5.57 (t, *J* = 8.8 Hz, 1H), 4.90 (d, *J* = 7.8 Hz, 1H), 4.88 – 4.81 (m, 2H), 4.74 (d, *J* = 11.0 Hz, 1H), 4.70 – 4.58 (m, 4H), 4.49 (dd, *J* = 12.1, 5.0 Hz, 1H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.14 (d, *J* = 11.4 Hz, 1H), 4.02 (dt, *J* = 9.0, 4.1 Hz, 1H), 3.86 (dd, *J* = 11.5, 5.0 Hz, 1H), 3.61 (t, *J* = 8.7 Hz, 1H), 3.48 (dd, *J* = 10.1, 4.6 Hz, 1H), 3.45 – 3.38 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.2, 166.0, 165.3, 165.1, 138.5, 138.1, 138.0, 133.6, 133.5, 133.3, 133.23, 133.19, 132.3, 130.0, 129.93, 129.89, 129.8, 129.4, 129.3, 129.0, 128.54, 128.50, 128.48, 128.4, 128.3, 128.0, 127.9, 127.83, 127.81, 127.76, 101.0, 87.4, 86.7, 80.7, 79.1, 77.6, 77.4, 75.7, 75.5, 75.0, 73.2, 72.3, 72.1, 69.9, 68.0, 63.3.

HRMS (ESI$^+$, m/z): calcd for $C_{67}H_{60}O_{14}SNa^+$ $(M+Na)^+$: 1143.3596; Found: 1143.3610.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-{2,3,4-tri-*O*-benzoyl-6-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranoside (14)



To a solution of glucosyl trichloroacetimidate **8** (66 mg, 88.0 μmol) and CCPB thioglycoside **9** (60.3 mg, 80.0 μmol) in anhydrous CH2Cl2 (1.5 mL) was added freshly activated 5 Å MS (200 mg). The mixture was stirred at room temperature for 30 min before it was cooled to 0 °C and treated with a solution of trimethylsilyl trifluoromethanesulfonate (TMSOTf) in anhydrous CH_2Cl_2 (0.08 M, 200 μL, 16.0 μmol). The mixture was stirred at 0 °C for another 2 h before it was warmed up to room temperature. To this solution was added thioglycoside **13**[28] (48.0 mg, 73.0 μmol) and the mixture was stirred for 10 min before $Sc(OTf)_3$ (7.2 mg, 15.0 μmol) was added. The mixture was stirred at room temperature for 1 h before it was re-chilled to –15 °C. Terminal acceptor **4e** (30.6 mg, 66.0 μmol), *N*-iodosuccinimide (NIS, 22.3 mg, 99.0 μmol) and a solution of TMSOTf in anhydrous CH_2Cl_2 (0.066 M, 200 μL, 13.2 μmol) were added sequentially. The mixture was

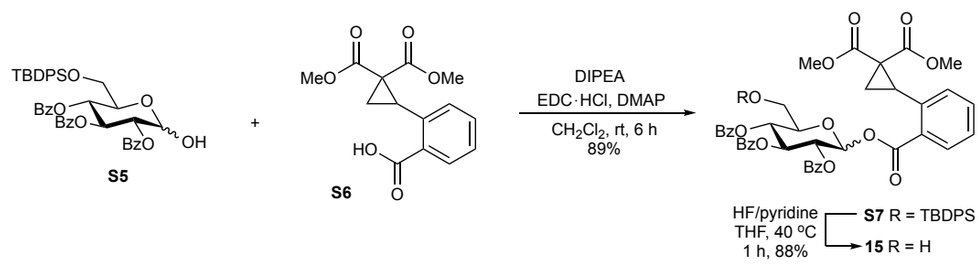
stirred at the same temperature for another 2 h before the reaction was quenched with triethylamine. The mixture was filtered with the assistance of Celite and concentrated *in vauco*. The residue was purified by silica gel column chromatography (toluene: EtOAc = 20:1) to afford the titled compound **14** (88 mg, 44.2 μmol, 67%) as a white foam.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 4H), 7.97 – 7.91 (m, 4H), 7.91 – 7.86 (m, 6H), 7.83 – 7.77 (m, 4H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.54 – 7.27 (m, 34H), 7.25 – 7.23 (m, 3H), 7.21 – 7.12 (m, 6H), 7.04 – 7.00 (m, 2H), 6.11 (t, *J* = 9.7 Hz, 1H), 5.81 (t, *J* = 9.6 Hz, 1H), 5.70 – 5.61 (m, 2H), 5.57 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.54 – 5.47 (m, 2H), 5.23 (dd, *J* = 9.8, 7.8 Hz, 1H), 5.14 – 5.06 (m, 2H), 4.90 (d, *J* = 11.0 Hz, 1H), 4.72 (d, *J* = 12.3 Hz, 1H), 4.68 (s, 1H), 4.66 – 4.53 (m, 5H), 4.48 – 4.42 (m, 2H), 4.31 – 4.23 (m, 2H), 4.06 – 3.94 (m, 3H), 3.88 – 3.76 (m, 4H), 3.67 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.58 – 3.52 (m, 1H), 3.46 (dd, *J* = 10.8, 3.5 Hz, 1H), 3.40 – 3.33 (m, 2H), 3.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 165.8, 165.7, 165.6, 165.4, 165.3, 165.03, 164.99, 139.1, 138.5, 138.3, 133.6, 133.4, 133.3, 133.2, 133.1, 130.1, 130.0, 129.93, 129.91, 129.89, 129.86, 129.83, 129.80, 129.78, 129.76, 129.52, 129.45, 129.4, 129.2, 129.04, 129.01, 128.97, 128.94, 128.86, 128.8, 128.6, 128.53, 128.45, 128.42, 128.39, 128.36, 128.34, 128.30, 128.2, 128.0, 127.9, 127.7, 127.51, 127.49, 101.4, 101.2, 101.0, 98.2, 82.0, 80.0, 75.5, 74.6, 74.3, 73.8, 73.5, 73.0, 72.8, 72.7, 72.3, 72.2, 72.1, 71.9, 70.7, 69.8, 69.7, 69.6, 68.8, 68.2, 67.9, 63.4, 55.4.

The data are identical to the literature.[17]

2′,3′,4′-Tri-*O*-benzoyl-D-glucopyranosyl *ortho*-2,2-dimethoxycarbonylcyclopropyl benzoate (15)



To a solution of **S5**[24] (730 mg, 1.0 mmol) and *ortho*-2,2-dimethoxycarbonylcyclopropylbenzoic acid **S6**[3] (418 mg, 1.5 mmol) in anhydrous CH_2Cl_2 (2.5 mL) were sequentially added 4-dimethylaminopyridine (DMAP, 25 mg, 0.2 mmol), *N*,*N*-diisopropylethylamine (DIPEA, 520 μL, 3.0 mmol), and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl, 480 mg, 2.5 mmol) under the ice bath. The ice bath was removed and the mixture was stirred at room temperature for 6 h. After completion of the reaction as indicated by TLC, the mixture was diluted with CH_2Cl_2 and washed sequentially with 1 M HCl solution, saturated $NaHCO_3$ solution, dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane: EtOAc = 5:1) to afford **S7** (886 mg, 0.89 mmol, 89%) as a white foam. Following the procedure for compound **9**, **S7** obtained from the last step was converted into **15** (586 mg, 0.78 mmol, 88%) as a white foam.

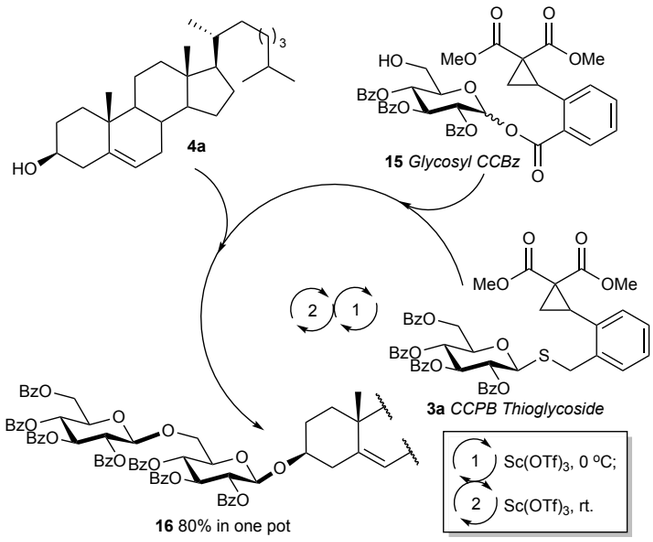
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.08 (m, 5.5H), 8.01 – 7.83 (m, 46H), 7.79 – 7.76 (m, 1H), 7.74 – 7.71 (m, 1H), 7.66 – 7.61 (m, 1.8H), 7.55 – 7.28 (m, 86H), 7.16 – 7.10 (m, 3.5H), 6.91 (d, *J* = 3.6 Hz, 1H), 6.82 (d, *J* = 3.6 Hz, 0.5H), 6.79 (d, *J* = 3.6 Hz, 1.8H), 6.40 – 6.26 (m, 5.9H), 6.22 (d, *J* = 8.4 Hz, 1.5H), 6.05 (td, *J* = 9.6 Hz and 4.8 Hz, 4H), 5.88 – 5.77 (m, 4H), 5.72 – 5.56 (m, 9.6H), 5.50 (t, *J* = 9.8 Hz, 1.5H), 4.36 – 4.21 (m, 3.8H), 4.12 – 4.01 (m, 4.3H), 3.97 – 3.72 (m, 47.8H), 3.32 (s, 4.6H), 3.29 (s, 4.3H), 3.00 (s, 9H), 2.93 (s, 2H), 2.23 – 2.04 (m, 10H), 1.90 – 1.73 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.50, 170.46, 170.2, 170.1, 167.30, 167.26, 167.1, 166.1, 165.84, 165.82, 165.79, 165.4, 165.3, 165.2, 164.9, 164.6, 164.2, 164.1, 137.7, 137.6, 137.5, 137.04, 133.97, 133.9, 133.80, 133.75, 133.6, 133.5, 133.4, 133.1, 133.0, 132.8, 132.6, 132.5, 131.8, 131.2, 130.7, 130.5, 130.4, 130.3, 130.11, 130.09, 130.06, 130.0, 129.93, 129.90, 129.86, 129.8, 129.68, 129.65, 129.5, 129.2, 129.1, 129.0, 128.94, 128.90, 128.86, 128.83, 128.80, 128.77, 128.63, 128.59, 128.57, 128.50, 128.46, 128.4, 128.1, 127.9, 127.7, 92.7, 92.6, 90.2, 90.0, 76.1, 75.5, 73.12, 73.06, 72.9, 72.8, 72.7, 71.1, 70.8, 70.7, 70.5, 70.1, 70.0, 69.7, 69.3, 69.1, 69.0, 62.2, 61.5, 61.0, 53.1, 53.01, 52.98, 52.9, 52.4, 52.2, 51.9, 51.6, 36.40, 36.36,

35.64, 35.61, 33.5, 32.7, 32.6, 20.3, 19.6.

HRMS (ESI$^+$, m/z): calcd for $C_{41}H_{36}O_{14}Na^+$ $(M+Na)^+$: 775.1997; Found: 775.1987.

(3β)-Cholest-5-en-3-yl 2′,3′,4′-tri-*O*-benzoyl-6′-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (16)



To a solution of donor **3a** (48.0 mg, 55.0 μmol) and **15** (37.6 mg, 50.0 μmol) in anhydrous CH_2Cl_2 (1.5 mL) was added freshly activated 5 Å MS (150 mg). The mixture was stirred at room temperature for 30 min before it was cooled to 0 °C and treated with $Sc(OTf)_3$ (2.5 mg, 5.0 μmol). The mixture was stirred at this temperature for 6 h before acceptor **4a** (21.5 mg, 55.0 μmol) and another portion of $Sc(OTf)_3$ (2.5 mg, 5.0 μmol) were added. The mixture was warmed up to room temperature and stirred at the same temperature overnight. After completion of the reaction, it was quenched with triethylamine. The mixture was filtered with the assistance of Celite and concentrated *in vauco*. The residue was purified by silica gel column chromatography (toluene: EtOAc = 20:1) to afford the titled compound **16** (57.5 mg, 40.0 μmol, 80%) as a white foam.

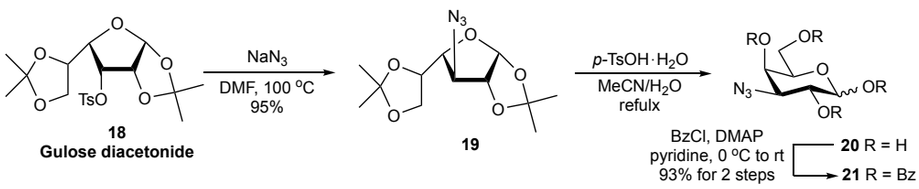
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.02 (d, *J* = 7.0 Hz, 2H), 7.96 – 7.93 (m, 2H), 7.93 – 7.91 (m, 2H), 7.87 (d, *J* = 7.0 Hz, 2H), 7.84 (d, *J* = 7.0 Hz, 2H), 7.80 (d, *J* = 6.8 Hz, 2H), 7.78 (d, *J* = 6.5 Hz, 2H), 7.58 – 7.26 (m, 21H), 5.86 – 5.80 (m, 1H), 5.80 – 5.74 (m, 1H), 5.59 (t, *J* = 9.6 Hz, 1H), 5.48 (dd, *J* = 9.7, 7.8 Hz, 1H), 5.37 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.31 (t, *J* = 9.5 Hz, 1H), 5.23 (d, *J* = 4.9 Hz, 1H), 5.04 (d, *J* = 7.8 Hz, 1H), 4.79 (d, *J* = 7.9 Hz, 1H), 4.57 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.41 (dd, *J* = 12.1, 5.1 Hz, 1H), 4.08 (ddd, *J* = 8.9, 5.0, 3.2 Hz, 1H), 4.04 – 3.90 (m, 3H), 3.51 – 3.41 (m, 1H), 2.12 – 1.74 (m, 7H), 1.61 – 0.83 (m, 48H), 0.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.2, 165.9, 165.7, 165.5, 165.3, 165.2, 140.5, 133.5, 133.3, 133.2, 130.0, 129.93, 129.89, 129.8, 129.71, 129.65, 129.5, 129.1, 129.0, 128.6, 128.54, 128.52, 128.48, 128.41, 128.38, 122.0, 101.0, 100.4, 80.8, 74.3, 73.1, 72.5, 72.2, 72.0, 70.1, 69.7, 68.2, 63.1, 56.9, 56.3, 50.1, 42.5, 40.0, 39.7, 39.2, 37.2, 36.8, 36.4, 35.9, 32.01, 31.97, 29.9, 29.8, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0.

The data are identical to the literature.[29]

Total synthesis of TD139

1,2,4,6-Tetra-*O*-benzoyl-3-deoxy-3-azido-D-galactopyranoside (21)



18
Gulose diacetonide

19

To a solution of gulose diacetonide **18**[30] (4.14 g, 10.0 mmol) in anhydrous DMF (100 mL) was added NaN_3 (1.95 g, 30.0 mmol). The mixture was heated to 100 °C and stirred at this temperature overnight. After completion of the reaction as indicated by TLC, the mixture was concentrated to about 20 mL *in vauco*. The mixture was diluted with EtOAc and washed sequentially with H_2O, saturated $NaHCO_3$ and brine. The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane: EtOAc = 11:1 to 9:1) to afford the 3-deoxy-3-azido-galactofuranose **19** (2.71 g, 9.50 mmol, 95%) as a colorless oil. To a solution of **9** obtained from the last step in a mixed solvent of MeCN/H_2O (v/v = 1:1, 20 mL) was added *p*-toluenesulfonic acid monohydrate (90.4 mg, 0.475 mmol). The mixture was heated to reflux for 5 h before the reaction was quenched with triethylamine. The mixture was concentrated *in vauco* to afford the galactopyranose **20**, which was used without further purification. To the suspension of compound **20** in anhydrous pyridine (100 mL) were sequentially added DMAP (22.4 mg, 0.2 mmol) and benzoyl chloride (BzCl, 6.62 mL, 57.0 mmol) dropwise under an ice bath. The mixture was allowed to warm up to room temperature naturally and stirred at room temperature overnight. After completion of the reaction as indicated by TLC, the mixture was concentrated *in vauco*. The residue was diluted with EtOAc and washed sequentially with 1 M HCl solution and saturated $NaHCO_3$ solution. The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane: EtOAc = 7:1) to afford **21α** (2.72 g, 4.38 mmol, 46%) as a white foam and **21β** (2.77 g, 4.46 mmol, 47%) as a colorless oil.

21α anomer

$[\alpha]_D^{23}$ = +158.5 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.3 Hz, 2H), 8.02 – 7.96 (m, 4H), 7.67 – 7.60 (m, 2H), 7.58 – 7.46 (m, 6H), 7.44 – 7.36 (m, 4H), 6.93 (d, *J* = 3.6 Hz, 1H), 6.07 (d, *J* = 1.9 Hz, 1H), 5.79 (dd, *J* = 10.9, 3.6 Hz, 1H), 4.71 (t, *J* = 6.3 Hz, 1H), 4.57 (dd, *J* = 11.4, 6.5 Hz, 1H), 4.52 (dd, *J* = 10.9, 3.3 Hz, 1H), 4.39 (dd, *J* = 11.4, 6.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.1, 165.5, 164.5, 134.0, 133.9, 133.8, 133.4, 130.2, 130.0, 129.91, 129.88, 129.4, 129.1, 128.9, 128.8, 128.74, 128.65, 128.54, 128.51, 90.2, 69.7, 69.2, 68.7, 62.1, 58.9.

HRMS (ESI$^+$, m/z): calcd for $C_{34}H_{27}O_9N_3Na^+$ $(M+Na)^+$: 644.1645; Found: 644.1630.

21β anomer

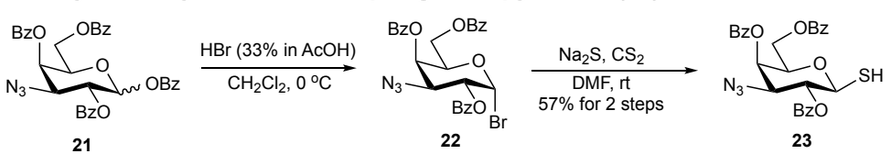
$[\alpha]_D^{23}$ = +54.7 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.20 (d, *J* = 7.0 Hz, 2H), 8.08 (d, *J* = 7.0 Hz, 2H), 8.04 (d, *J* = 6.9 Hz, 2H), 8.02 (d, *J* = 7.0 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.50 (m, 5H), 7.46 – 7.38 (m, 6H), 6.21 (d, *J* = 8.3 Hz, 1H), 6.00 (d, *J* = 4.4 Hz, 1H), 5.91 (dd, *J* = 10.5, 8.2 Hz, 1H), 4.61 (dd, *J* = 10.3, 5.5 Hz, 1H), 4.51 – 4.40 (m, 2H), 4.17 (dd, *J* = 10.5, 3.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.1, 165.5, 165.3, 164.8, 134.0, 133.9, 133.8, 133.4, 130.33, 130.30, 129.9, 129.5, 128.82, 128.78, 128.6, 128.54, 128.51, 93.2, 73.3, 69.6, 68.4, 62.5, 62.0.

HRMS (ESI$^+$, m/z): calcd for $C_{34}H_{27}O_9N_3Na^+$ $(M+Na)^+$: 644.1645; Found: 644.1630.

2,4,6-Tri-*O*-benzoyl-3-deoxy-3-azido-1-thio-β-D-galactopyranose (23)



21

22

23

To a solution of **21** (2.38 g, 3.82 mmol) in anhydrous CH_2Cl_2 (20 mL) was added dropwise HBr (33% in AcOH, 3.35 mL, 19.14 mmol) under an ice bath. The reaction was stirred under an ice bath for 30 min before the mixture was poured into water, the aqueous phase was extracted with CH_2Cl_2, the organic layers were combined, washed with saturated $NaHCO_3$ solution, and dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane: EtOAc = 6:1) to afford the glycosyl bromide **22** as a white foam, which was used immediately for the next step. To the solution of the bromide **22** obtained from the last step in anhydrous DMF (10 mL) was added Na_2S (596 mg, 7.64 mmol). The mixture was exposed to sonication to facilitate the dispersion of the salt, followed by the dropwise addition of CS_2 (346 μmol, 5.73 mmol) under an ice bath to form a purple solution. The mixture was removed from the ice bath and stirred at room temperature for 15 min before it was poured into 1 M HCl solution. The aqueous phase was extracted with EtOAc, and the combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane: EtOAc = 3:1) to afford compound **23** (1.16 g, 2.17 mmol, 57% for 2 steps) as a white foam.

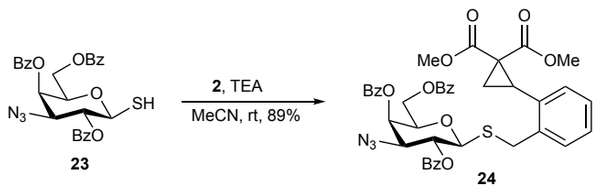
$[\alpha]_D^{23}$ = +200.1 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.16 (d, *J* = 6.9 Hz, 2H), 8.09 (d, *J* = 6.9 Hz, 2H), 8.05 (d, *J* = 6.9 Hz, 2H), 7.65 – 7.42 (m, 12H), 5.93 (dd, *J* = 3.4, 1.1 Hz, 1H), 5.56 (t, *J* = 9.9 Hz, 1H), 4.81 (t, *J* = 9.7 Hz, 1H), 4.58 (dd, *J* = 11.4, 6.6 Hz, 1H), 4.38 (dd, *J* = 11.5, 6.3 Hz, 1H), 4.27 – 4.21 (m, 1H), 3.99 (dd, *J* = 10.2, 3.3 Hz, 1H), 2.55 (d, *J* = 9.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.2, 165.6, 165.5, 133.9, 133.8, 133.5, 130.2, 130.0, 129.9, 129.5, 129.14, 129.07, 128.8, 128.7, 128.6, 79.8, 76.3, 72.9, 68.7, 63.5, 62.3.

HRMS (ESI$^+$, m/z): calcd for $C_{27}H_{23}O_7N_3NaS^+$ $(M+Na)^+$: 556.1154; Found: 556.1163.

ortho-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,4′,6′-tri-_O_-benzoyl-3′-deoxy-3′-azido-1′-thio-β-D-galactopyranoside (24)



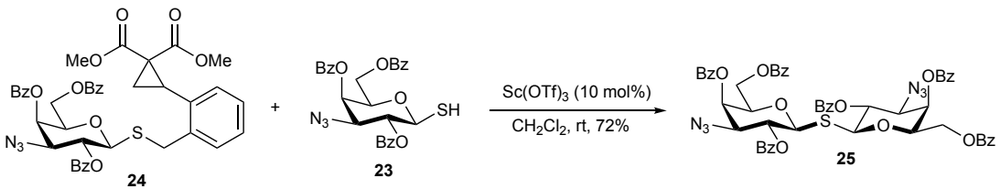
Following the procedure for **3a**, **23** (213 mg, 0.4 mmol) was transformed into donor **24** (275.2 mg, 0.35 mmol, 89%, d.r. = 1:1) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.18 – 8.13 (m, 4H), 8.10 – 8.03 (m, 6H), 7.94 (d, *J* = 7.0 Hz, 2H), 7.64 – 7.54 (m, 6H), 7.53 – 7.41 (m, 12H), 7.33 – 7.27 (m, 1H), 7.22 – 7.13 (m, 4H), 7.11 – 7.01 (m, 3H), 5.94 – 5.87 (m, 2H), 5.69 – 5.52 (m, 2H), 4.75 (d, *J* = 9.9 Hz, 1H), 4.67 – 4.56 (m, 2H), 4.48 (d, *J* = 9.9 Hz, 1H), 4.41 (dd, *J* = 11.5, 6.1 Hz, 1H), 4.33 (dd, *J* = 11.3, 7.1 Hz, 1H), 4.21 (d, *J* = 12.6 Hz, 1H), 4.18 – 4.10 (m, 2H), 4.09 – 4.01 (m, 3H), 3.99 (dd, *J* = 10.2, 3.2 Hz, 1H), 3.88 (dd, *J* = 10.1, 3.3 Hz, 1H), 3.77 – 3.67 (m, 6H), 3.40 (t, *J* = 8.6 Hz, 1H), 3.34 (d, *J* = 8.7 Hz, 1H), 3.27 (s, 3H), 3.25 (s, 3H), 2.25 (dd, *J* = 8.1, 5.2 Hz, 1H), 2.16 (dd, *J* = 8.2, 5.2 Hz, 1H), 1.64 (d, *J* = 5.1 Hz, 1H), 1.51 (dd, *J* = 9.2, 5.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.0, 169.7, 167.0, 166.19, 166.15, 165.6, 165.5, 165.4, 165.2, 137.3, 137.2, 133.9, 133.8, 133.7, 133.6, 133.5, 133.43, 133.37, 133.32, 130.31, 130.27, 130.12, 130.07, 130.03, 129.96, 129.92, 129.88, 129.6, 129.3, 129.2, 128.94, 128.85, 128.8, 128.64, 128.61, 128.58, 128.5, 128.00, 127.96, 127.6, 127.5, 127.4, 84.7, 83.0, 75.6, 75.5, 69.3, 69.2, 68.8, 68.6, 63.61, 63.57, 62.5, 62.0, 53.00, 52.95, 52.3, 52.2, 36.9, 36.5, 32.2, 32.1, 29.9, 29.7, 18.6, 18.2.

HRMS (ESI$^+$, m/z): calcd for $C_{41}H_{37}O_{11}N_3NaS^+$ $(M+Na)^+$: 802.2046; Found: 802.2067.

2,4,6-Tri-_O_-benzoyl-3-deoxy-3-azido-1-thio-1-_S_-(2,4,6-tri-_O_-benzoyl-3-deoxy-3-azido-β-D-galactopyranosyl)-β-D-galactopyranoside (25)



24 **23** **25**

Following the procedure for **5a**, **24** (93.6 mg, 0.12 mmol) was coupled with **23** (53.3 mg, 0.1 mmol) to afford **25** (74.4 mg, 77.0 μmol, 77%) as a white foam after purification by silica gel column chromatography (toluene: EtOAc = 20:1).

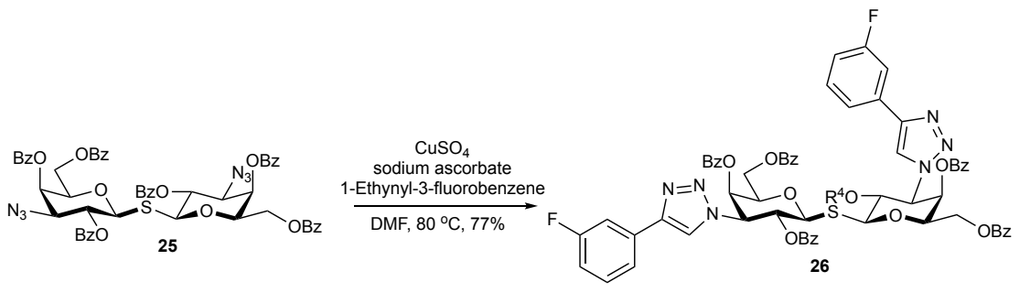
$[\alpha]_D^{23}$ = +69.3 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.12 (d, *J* = 7.0 Hz, 4H), 8.07 – 8.02 (m, 8H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.60 – 7.54 (m, 4H), 7.52 – 7.48 (m, 4H), 7.46 – 7.40 (m, 8H), 5.61 (d, *J* = 4.6 Hz, 2H), 5.43 (t, *J* = 10.0 Hz, 2H), 4.92 (d, *J* = 10.0 Hz, 2H), 4.60 (dd, *J* = 11.6, 7.7 Hz, 2H), 4.26 (dd, *J* = 11.6, 5.2 Hz, 2H), 3.90 – 3.80 (m, 2H), 3.45 (dd, *J* = 10.0, 3.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.82, 165.75, 165.3, 133.9, 133.8, 133.7, 130.32, 130.25, 130.1, 129.8, 129.1, 128.9, 128.8, 128.6, 81.6, 76.0, 69.3, 68.7, 63.7, 62.3.

HRMS (ESI$^+$, m/z): calcd for $C_{54}H_{44}O_{14}N_6NaS^+$ $(M+Na)^+$: 1055.2534; Found: 1055.2554.

2,4,6-Tri-*O*-benzoyl-3-deoxy-3-(4-*meta*-fluorophenyl-1,2,3-triazole-1-yl)-1-thio-1-*S*-[2,4,6-tri-*O*-benzoyl-3-deoxy-3-(4-*meta*-fluorophenyl-1,2,3-triazole-1-yl)-β-D-galactopyranosyl]-β-D-galactopyranoside (26)



25 **26**

To a solution of azide **25** (86.0 mg, 83.0 μmol) in a mixed solvent of DMF/H_2O (v/v = 4:1, 800 μL) were sequentially added 1-ethynyl-3-fluorobenzene (57.7 μL, 0.5 mmol), $CuSO_4$ (6.7 mg, 42.0 μmol) and sodium ascorbate (13.2 mg, 66.4 μmol). The reaction mixture was evacuated and backfilled with argon 3 times and was placed in an oil bath which was pre-heated to 80 °C. The mixture was stirred at 80 °C for another 4 h before it was cooled up to room temperature. The mixture was then directly concentrated *in vauco* and the residue was purified by silica gel column chromatography (hexane: EtOAc = 12:7) to afford the titled triazole **26** (81.3 mg, 63.9 μmol, 77%) as a white foam.

$[\alpha]_D^{23}$ = +161.2 (*c* = 1.0, $CHCl_3$).

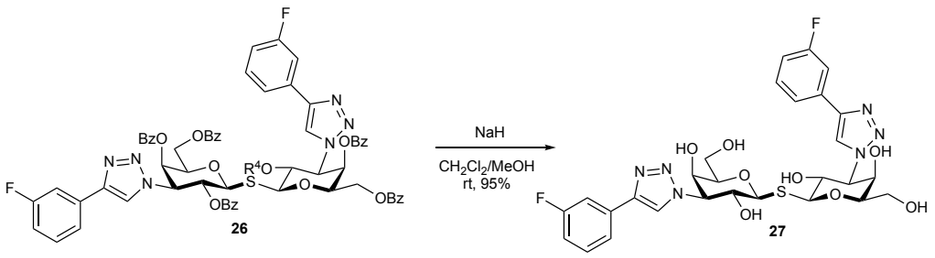
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.16 (d, *J* = 7.0 Hz, 4H), 7.95 (d, *J* = 7.0 Hz, 4H), 7.88 (d, *J* = 7.0 Hz, 4H), 7.72 – 7.68 (m, 2H), 7.67 (s, 2H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 4H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.9 Hz, 4H), 7.37 (t, *J* = 7.8 Hz, 4H), 7.20 – 7.14 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.06 – 7.01 (m, 2H), 6.92 – 6.86 (m, 2H), 5.96 – 5.89 (m, 2H), 5.77 (d, *J* = 3.3 Hz, 2H), 5.19 (d, *J* = 9.8 Hz, 2H), 5.16 (dd, *J* = 10.9, 3.2 Hz, 2H), 4.69 (dd, *J* = 11.6, 7.7 Hz, 2H), 4.31 (dd, *J* = 11.6, 5.3 Hz, 2H), 4.10 – 4.01 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.8, 165.4, 164.6, 164.3, 161.8, 147.1 (d, J_{C-F} = 2.9 Hz), 134.3, 134.2, 134.1, 132.1 (d, J_{C-F} = 8.5 Hz), 130.4, 130.3, 130.2, 130.1, 129.6, 129.1, 128.7, 128.3, 128.1, 121.4 (d, J_{C-F} = 2.8 Hz), 119.0, 115.2 (d, J_{C-F} = 21.2 Hz), 112.8 (d, J_{C-F} = 23.0 Hz), 82.1, 76.2, 69.6, 67.2, 63.6, 62.1.

^{19}F NMR (376 MHz, $CDCl_3$) *δ* -112.7 – -113.0 (m, 1F).

HRMS (ESI$^+$, m/z): calcd for $C_{70}H_{54}O_{14}N_6NaSF_2^+$ $(M+Na)^+$: 1295.3284; Found: 1295.3317.

TD139 (27)



To a solution of **26** (21.6 mg, 17.0 μmol) in a mixed solvent of CH_2Cl_2/MeOH (v/v = 1:1, 1 mL) was added NaH (60% in mineral oil, 1 mg, 25.0 μmol) under an ice bath. The mixture was warmed up to room temperature and stirred at the same temperature for 30 min before the reaction was quenched with AcOH. The mixture was concentrated *in vauco* and the residue was purified by silica gel column chromatography (CH_2Cl_2:MeOH = 9:1) to afford TD139 **27** (10.5 mg, 16.2 μmol, 95%) as a white solid.

^{1}H NMR (400 MHz, CD_3OD) δ 8.57 (s, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 9.8 Hz, 2H), 7.47 – 7.38 (m, 2H), 7.06 (td, J = 8.5, 2.6 Hz, 2H), 4.17 (d, J = 2.7 Hz, 2H), 3.91 (dd, J = 7.5, 4.2 Hz, 2H), 3.84 (dd, J = 11.3, 7.3 Hz, 2H), 3.73 (dd, J = 11.3, 4.1 Hz, 2H).

^{13}C NMR (100 MHz, CD_3OD) δ 165.9, 163.5, 147.2, 134.3 (d, $J_{C\text{-}F}$ = 8.5 Hz), 131.9 (d, $J_{C\text{-}F}$ = 8.5 Hz), 123.1 – 120.4 (m), 115.8 (d, $J_{C\text{-}F}$ = 21.5 Hz), 113.1 (d, $J_{C\text{-}F}$ = 23.2 Hz), 86.7, 81.4, 69.7, 68.8, 68.4, 62.9.

^{19}F NMR (376 MHz, CD_3OD) δ -113.80 – -113.57 (m, 1F).

The data are identical to the literature report.[31]

Comparison of the NMR spectra of synthetic TD139 with literature report.

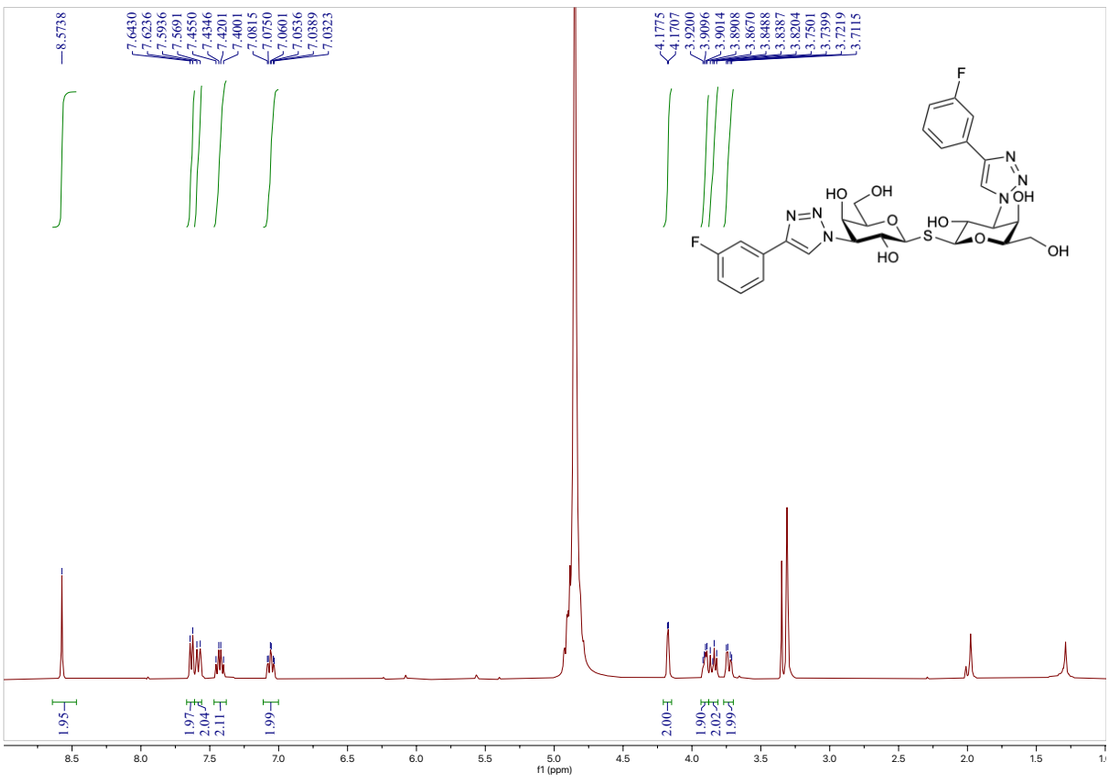


Figure S3. ^{1}H NMR spectrum of synthetic TD139.

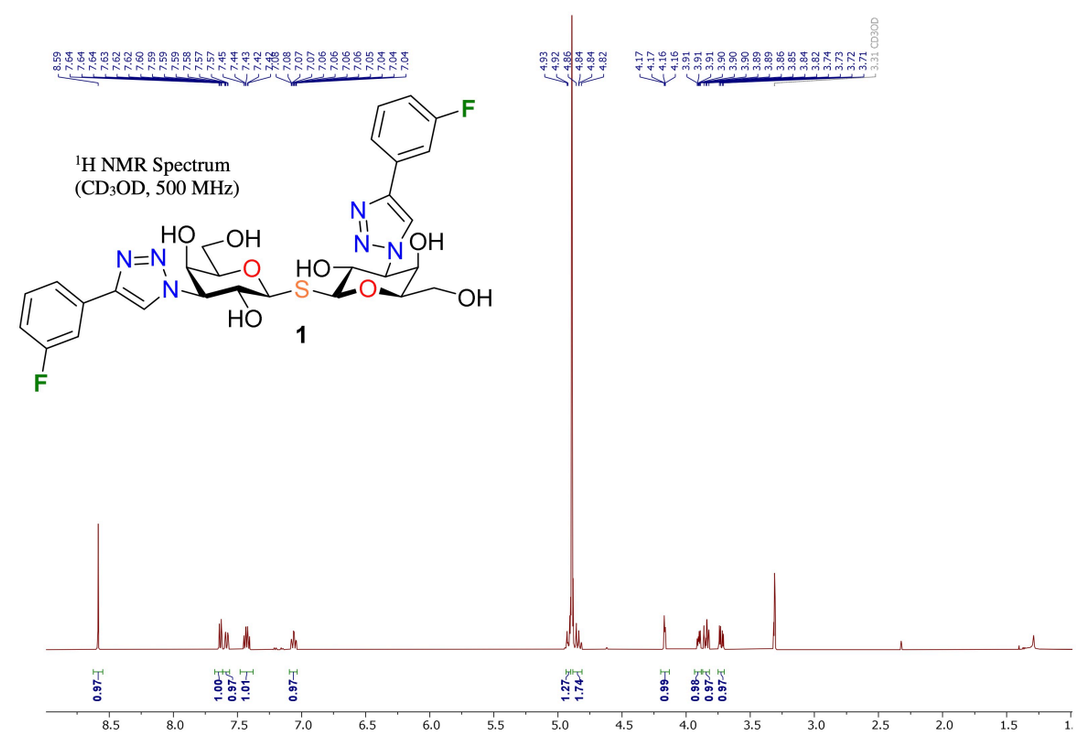


Figure S4. ^{1}H NMR spectrum of literature report (Giguère, D. (2020). Org. Biomol. Chem. *18*, 3903.).

Synthetic TD139: ^{13}C NMR spectrum

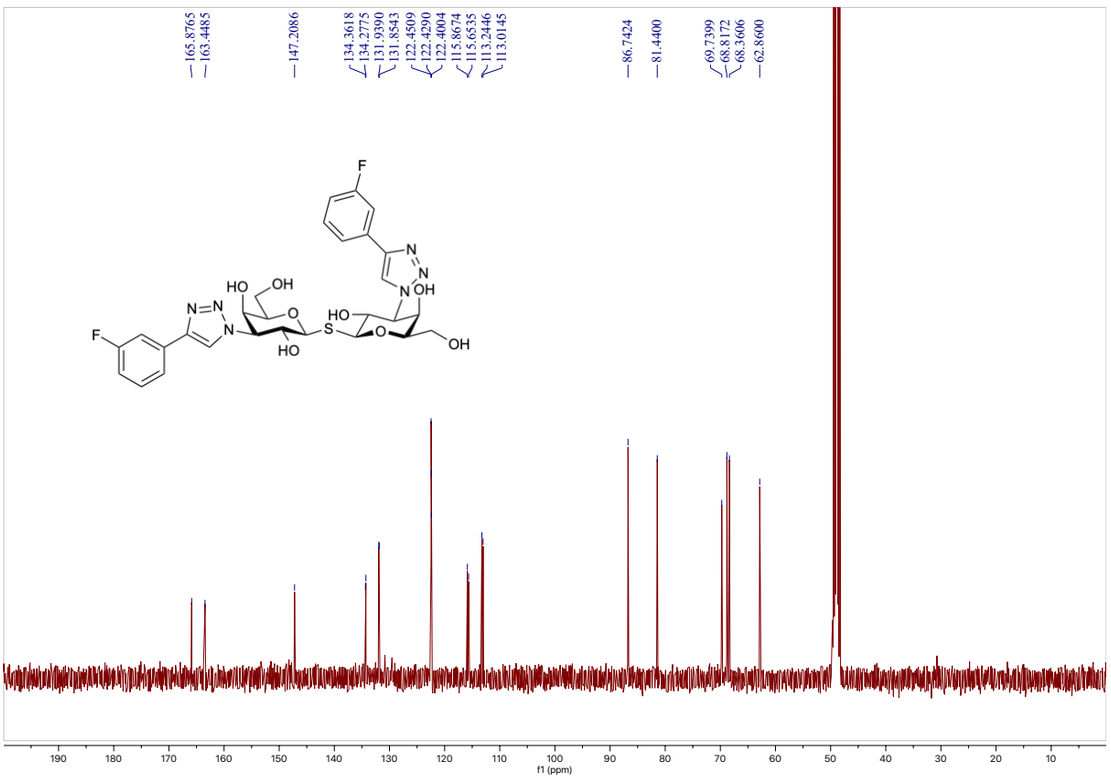


Figure S5. ^{13}C NMR spectrum of synthetic TD139.

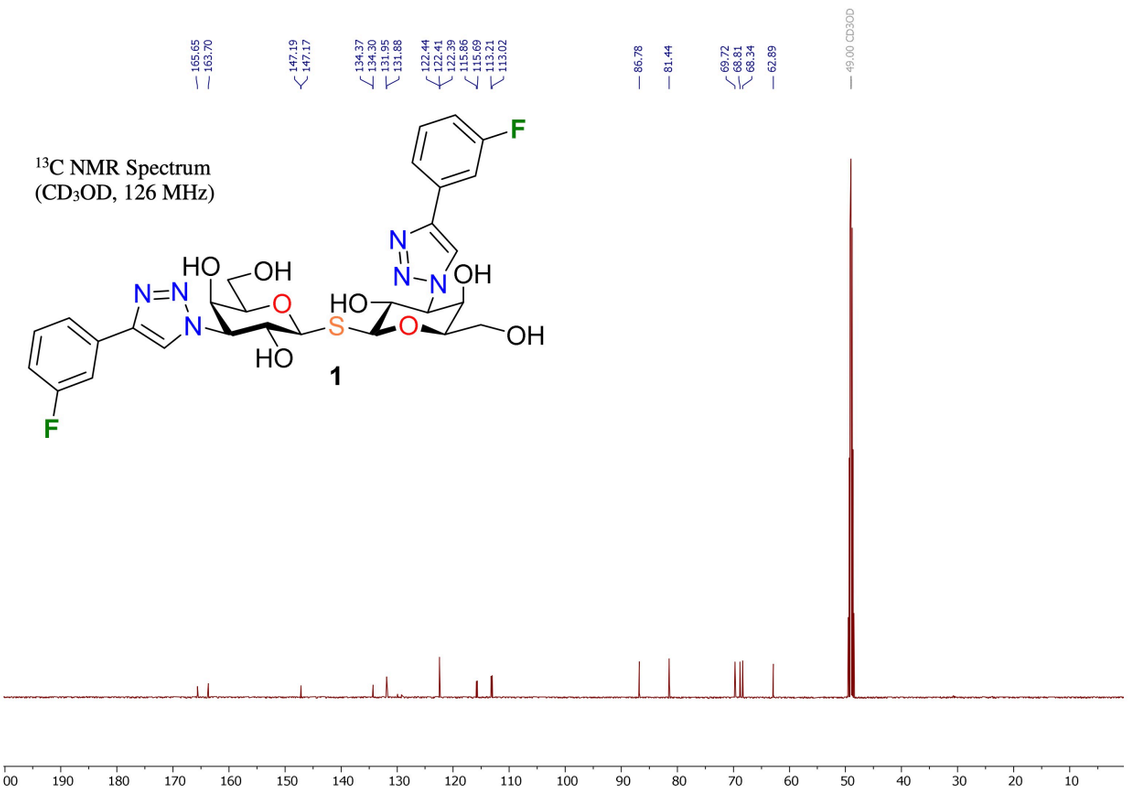
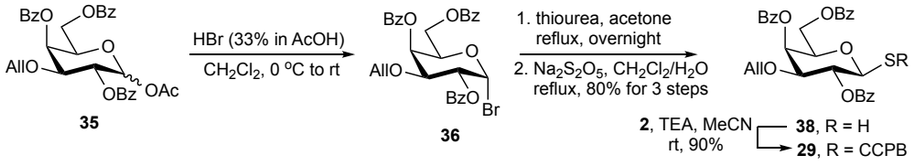


Figure S6. ^{13}C NMR spectrum of literature report (Giguère, D. (2020). Org. Biomol. Chem. *18*, 3903.).

One-pot synthesis of tetrasaccharide of polysaccharide of *Escherichia coli* O33

***ortho*-2,2-Dimethoxycarbonylcyclopropylbenzyl 2′,4′,6′-tri-*O*-benzoyl-3′-*O*-allyl-1′-thio-β-D-galactopyranoside (29)**



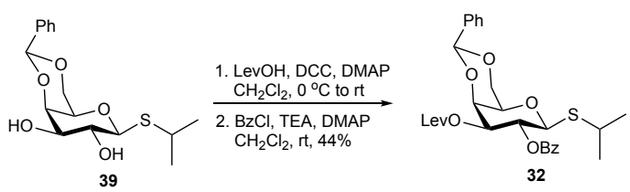
To a solution of acetate **35**[32] (1.71 g, 2.97 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (100 mL) was added a solution of 33% HBr in AcOH (10 mL) under an ice bath. The mixture was stirred at room temperature for 5 h before the mixture was poured into H_2O. The aqueous phase was extracted with CH_2Cl_2, the combined organic layers were washed sequentially with H_2O, sat. $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered, concentrated *in vauco* to afford glycosyl bromide **36***,* which was used directly without further purification. The residue was dissolved in anhydrous acetone (100 mL) and to the solution was added thiourea (452 mg, 5.94 mmol, 2.0 equiv). The suspension was heated to reflux overnight. After completion of the reaction, the mixture was concentrated *in vauco* and the residue was used directly without further purification. The adduct **37** obtained from the last step was dissolved in a mixed solvent of CH_2Cl_2/H_2O (v/v = 3:2, 100 mL). To the mixture was added $Na_2S_2O_5$ (2.82 g, 14.85 mmol, 5.0 equiv), and the mixture was heated to reflux for 4 h. Two layers were separated, and the aqueous phase was extracted with CH_2Cl_2, the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 4:1) to afford the glycosyl thiol **38** (1.29 g, 2.38 mmol, 80% for 3 steps) as a white foam. Following the procedure for **3a**, **38** (998 mg, 1.82 mmol, 1.0 equiv) was coupled with **2** (2.18 mmol, 1.2 equiv) to afford CCPB thioglycoside **29** (1.31 g, 1.64 mmol, 90%, d.r. = 1:1) as a white foam after purification by silica gel column chromatography (hexane: EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.04 (m, 10H), 7.93 (d, J = 7.6 Hz, 2H), 7.62 – 7.41 (m, 18H), 7.33 – 7.31 (m, 1H), 7.20 – 7.12 (m, 4H), 7.07 – 7.01 (m, 3H), 5.92 – 5.83 (m, 2H), 5.72 – 5.51 (m, 4H), 5.17 – 5.09 (m, 2H), 5.06 – 4.96 (m, 2H), 4.69 – 4.60 (m, 3H), 4.49 – 4.36 (m, 3H), 4.25 – 3.92 (m, 11H), 3.84 (dd, J = 9.6, 3.2 Hz, 1H), 3.76 – 3.69 (m, 7H), 3.44 – 3.33 (m, 2H), 3.29 – 3.23 (m, 6H), 2.25 (dd, J = 8.0, 5.2 Hz, 1H), 2.16 (dd, J = 8.0, 5.2 Hz, 1H), 1.67 (dd, J = 9.2, 5.2 Hz, 1H), 1.52 (dd, J = 9.2, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.7, 167.1, 166.3, 166.2, 165.9, 165.8, 165.4, 165.3, 137.5, 137.4, 134.2, 134.1, 133.50, 133.46, 133.43, 133.35, 133.3, 133.24, 133.18, 130.17, 130.14, 130.07, 129.94, 129.88, 129.85, 129.8, 129.7, 129.6, 129.5, 128.64, 128.61, 128.58, 128.5, 128.44, 128.40, 127.9, 127.5, 127.4, 127.3, 117.7, 117.6, 84.2, 82.5, 77.8, 75.1, 75.0, 70.8, 69.9, 69.7, 67.5, 67.3, 63.1, 62.5, 52.92, 52.89, 52.3, 52.2, 36.8, 36.5, 31.9, 31.8, 30.0, 29.9, 18.6, 18.1.

HRMS (ESI$^+$, m/z): calcd for $C_{44}H_{42}O_{12}NaS^+$ $(M+Na)^+$: 817.2289; Found: 817.2299.

Isopropyl 2-*O*-benzyl-3-*O*-levulinoyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (32)



To a solution of diol **39**[33] (3.26 g, 10.0 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (100 mL) was added sequentially DMAP (611 mg, 5.0 mmol, 0.5 equiv), LevOH (1.39 g, 12.0 mmol, 1.2 equiv) and dicyclohexylcarbodiimide (DCC, 3.09 g, 15.0 mmol, 1.5 equiv). The mixture was stirred at room temperature for 1 h before the mixture was filtered, the filtrate was concentrated *in vauco* to afford the inseparable O-3 monoacylated and diacylated product, which was directly exposed to the next benzoylation. To the solution of the mixture obtained from the last step in anhydrous CH_2Cl_2 (100 mL) was added DMAP (122 mg, 1.0 mmol, 0.1 equiv), BzCl (1.74 mL, 15.0 mmol, 1.5 equiv) and TEA (2.1 mL, 15.0 mmol, 1.5 equiv) under an

ice bath. The mixture was stirred at room temperature overnight. After completion of the reaction, the mixture was washed sequentially with 1 M HCl solution, sat. $NaHCO_3$ solution and brine. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in *vauco*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 2:1) to afford the titled compound **32** (1.65 g, 4.4 mmol, 44% for 2 steps) as a white foam.

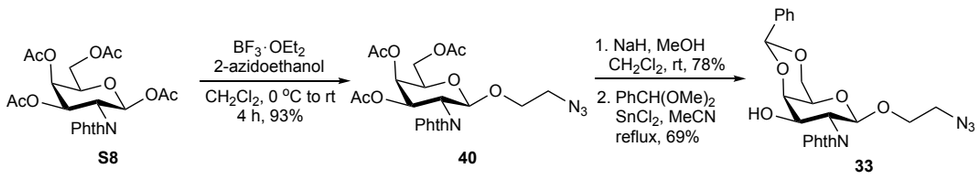
$[\alpha]_D^{23}$ = –13.4 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.59 – 7.52 (m, 3H), 7.47 – 7.36 (m, 5H), 5.72 (t, *J* = 10.0 Hz, 1H), 5.52 (s, 1H), 5.20 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.71 (d, *J* = 10.0 Hz, 1H), 4.43 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.36 (dd, *J* = 12.4, 1.6 Hz, 1H), 4.05 (dd, *J* = 12.4, 1.6 Hz, 1H), 3.63 – 3.56 (m, 1H), 3.39 – 3.29 (m, 1H), 2.64 – 2.42 (m, 4H), 1.90 (s, 3H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.25 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 172.2, 165.4, 137.8, 133.3, 130.0, 129.8, 129.2, 128.5, 128.3, 126.6, 101.4, 83.3, 73.9, 73.3, 70.0, 69.3, 67.8, 37.9, 34.8, 29.6, 28.4, 25.0, 23.7.

HRMS (ESI$^+$, m/z): calcd for $C_{28}H_{32}O_8NaS^+$ $(M+Na)^+$: 551.1710; Found: 551.1727.

2-Azidoethyl 4′,6′-*O*-benzylidene-2′-deoxy-2′-phthalimido-β-D-galactopyranoside (33)



To a solution of acetate **S8**[34] (3.17 g, 6.65 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (30 mL) was added sequentially 2-azidoethanol (1.16 g, 13.3 mmol, 2.0 equiv) and boron trifluoride-diethyl ether complex (2.46 mL, 20.0 mmol, 3.0 equiv) under an ice bath. The mixture was stirred at room temperature for 4 h before the reaction was quenched with H_2O. Two layers were separated, and the aqueous phase was extracted with CH_2Cl_2, the combined organic layers were washed with H_2O, sat. $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 3:2) to afford compound **40** (3.12 g, 6.18 mmol, 93%) containing a small portion of α-isomer, which was used without further purification. To a suspension of **40** in MeOH (50 mL) was added NaH (60% in mineral oil, 123.6 mg, 3.09 mmol, 0.5 equiv) under an ice bath. The mixture was stirred at room temperature for 30 min before the reaction was quenched with AcOH. The mixture was concentrated *in vauco* and the residue was purified by silica gel column chromatography (pure EtOAc) to afford pure β-anomer (1.82 g, 4.82 mmol, 78%). The triol was suspended in anhydrous MeCN (50 mL). To the mixture was added $PhCH(OMe)_2$ (1.45 mL, 9.64 mmol, 2.0 equiv) and $SnCl_2$ (91 mg, 0.48 mmol, 0.1 equiv). The mixture was heated to 80 °C and refluxed at this temperature for another 2 h before the reaction was quenched with TEA. The mixture was concentrated *in vauco* and the residue was purified by silica gel column chromatography (hexane:EtOAc = 1:1) to afford the titled compound **33** (1.55 g, 3.33 mmol, 69%) as a white gum.

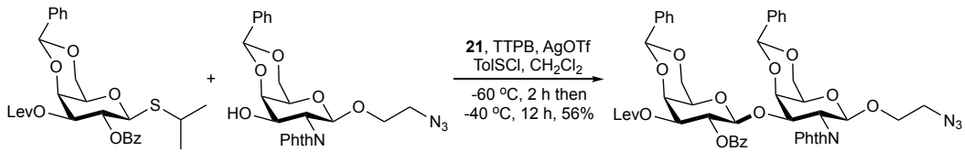
$[\alpha]_D^{23}$ = +23.3 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.72 – 7.68 (m, 2H), 7.58 – 7.54 (m, 2H), 7.44 – 7.39 (m, 3H), 5.62 (s, 1H), 5.36 (d, *J* = 7.8 Hz, 1H), 4.55 – 4.45 (m, 2H), 4.38 (dd, *J* = 12.4, 1.6 Hz, 1H), 4.30 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.14 (dd, *J* = 12.6, 2.0 Hz, 1H), 4.07 (ddd, *J* = 10.4, 4.8, 3.6 Hz, 1H), 3.68 – 3.63 (m, 2H), 3.46 – 3.35 (m, 1H), 3.23 – 3.13 (m, 1H), 2.52 (d, *J* = 10.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.5, 137.4, 134.1, 132.1, 132.0, 129.5, 128.5, 126.6, 123.7, 123.2, 101.7, 98.5, 75.2, 69.3, 68.2, 68.1, 67.0, 54.7, 50.6.

HRMS (ESI$^+$, m/z): calcd for $C_{23}H_{22}O_7N_4Na^+$ $(M+Na)^+$: 489.1381; Found: 489.1386.

2-Azidoethyl 4′,6′-*O*-benzylidene-3′-*O*-(2-*O*-benzyl-3-*O*-levulinoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-2′-deoxy-2′-phthalimido-β-D-galactopyranoside (41)



32 **33** **41**

To a solution of donor **32** (485 mg, 0.92 mmol, 1.2 equiv) and acceptor **33** (357 mg, 0.766 mmol, 1.0 equiv) and 2,4,6-tri-*tert*-butylpyridine (TTPB, 473.8 mg, 1.915 mmol, 2.5 mmol) in anhydrous CH_2Cl_2 (5 mL) containing freshly activated 4 Å MS (300 mg). The mixture was stirred at -60 °C for 1 h before AgOTf (492 mg, 1.915 mmol, 2.5 equiv) and TolSCl (146 mg, 0.92 mmol, 1.2 equiv) quickly. The mixture was stirred at -60 °C for another 2 h before it was warmed up to -40 °C and stirred at this temperature for 12 h. The reaction was quenched with sat. $NaHCO_3$ solution and diluted with CH_2Cl_2. Two phases were separated and the aqueous phase was extracted with CH_2Cl_2, the combined organic layers were washed with H_2O, dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane:EtOAc:CH_2Cl_2 = 1:1:1) to afford the titled compound **41** (394 mg, 0.429 mmol, 56%) as a colorless syrup.

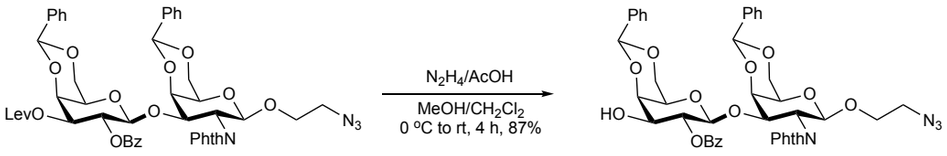
$[\alpha]_D^{23}$ = +27.9 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.66 – 7.60 (m, 3H), 7.57 – 7.38 (m, 8H), 7.37 – 7.27 (m, 6H), 7.18 (dd, *J* = 8.2, 7.4 Hz, 2H), 5.53 (dd, *J* = 10.3, 8.0 Hz, 1H), 5.45 (s, 1H), 5.44 (s, 1H), 5.23 (d, *J* = 8.5 Hz, 1H), 5.01 (dd, *J* = 10.3, 3.5 Hz, 1H), 4.93 – 4.86 (m, 2H), 4.71 (dd, *J* = 11.2, 8.4 Hz, 1H), 4.46 (d, *J* = 3.5 Hz, 1H), 4.33 – 4.25 (m, 2H), 4.06 (d, *J* = 12.3, 1H), 4.02 – 3.92 (m, 3H), 3.62 – 3.53 (m, 2H), 3.47 – 3.43 (m, 1H), 3.34 – 3.24 (m, 1H), 3.17 – 3.08 (m, 1H), 2.54 – 2.29 (m, 4H), 1.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 206.1, 172.0, 169.2, 167.3, 164.8, 137.8, 137.7, 133.9, 133.6, 132.9, 131.6, 131.5, 129.6, 129.2, 128.7, 128.4, 128.3, 128.09, 128.07, 126.7, 126.42, 123.37, 122.9, 101.3, 100.9, 100.7, 98.5, 75.7, 73.3, 72.1, 69.17, 69.15, 68.8, 67.4, 67.0, 66.5, 51.6, 50.6, 37.8, 29.4, 28.2.

HRMS (ESI$^+$, m/z): calcd for $C_{48}H_{46}O_{15}N_4Na^+$ $(M+Na)^+$: 941.2852; Found: 941.2848.

2-Azidoethyl 4′,6′-*O*-benzylidene-3′-*O*-(2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-2′-deoxy-2′-phthalimido-β-D-galactopyranoside (31)



41 **31**

To a solution of disaccharide **41** (383 mg, 0.417 mmol, 1.0 equiv) in a mixed solvent of CH_2Cl_2/MeOH (v/v = 1:1, 10 mL) was added dropwise a pre-mixed solution of AcOH (119 μL, 2.09 mmol, 5.0 equiv) and hydrazine monohydrate (~55% hydrazine, 118 μL, 2.09 mmol, 5.0 equiv) in MeOH (1 mL) under an ice bath. The mixture was allowed to warm up to room temperature and the mixture was stirred at room temperature for another 4 h. After completion of the reaction. The reaction was concentrated *in vauco*. The residue was diluted with CH_2Cl_2, washed with H_2O, dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel chromatography (hexane:EtOAc:CH_2Cl_2 = 1:1:1) to afford the titled acceptor **31** (298 mg, 0.363 mmol, 87%) as a colorless syrup.

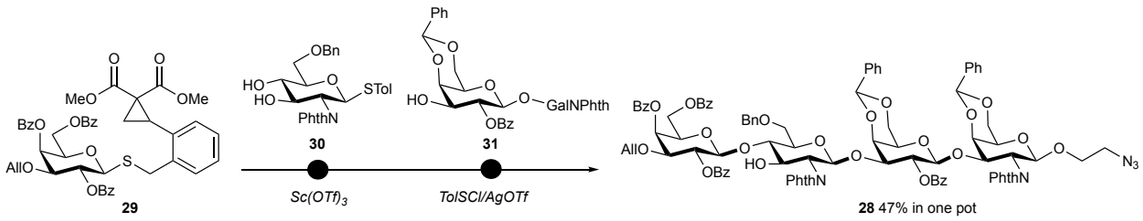
$[\alpha]_D^{23}$ = +30.2 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, CDCl3) *δ* 7.73 – 7.66 (m, 3H), 7.57 – 7.51 (m, 5H), 7.45 – 7.35 (m, 6H), 7.31 – 7.27 (m, 3H), 7.21 – 7.17 (m, 2H), 5.47 (s, 1H), 5.36 (s, 1H), 5.33 – 5.26 (m, 2H), 4.90 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.84 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.71 (dd, *J* = 11.2, 8.4 Hz, 1H), 4.40 (d, *J* = 3.6 Hz, 1H), 4.30 (d, *J* = 12.4 Hz, 1H), 4.12 (d, *J* = 3.6 Hz, 1H), 4.04 – 3.97 (m, 2H), 3.92 – 3.89 (m, 1H), 3.84 – 3.80 (m, 1H), 3.71 (br s, 1H), 3.62 – 3.57 (m, 2H), 3.40 – 3.38 (m, 1H), 3.39 – 3.29 (m, 1H), 3.21 – 3.12 (m, 1H), 2.59 – 2.39 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.2, 167.4, 166.0, 137.8, 137.6, 133.9, 133.6, 133.0, 131.8, 131.7, 129.7, 129.53, 129.48, 128.8, 128.5, 128.42, 128.35, 128.12, 128.10, 126.8, 126.5, 123.4, 123.0, 101.7, 101.1, 100.1, 98.5, 75.7, 75.5, 72.8, 72.5, 72.0, 69.2, 68.8, 67.5, 67.0, 66.7, 51.7, 50.7.

HRMS (ESI$^+$, m/z): calcd for $C_{43}H_{40}O_{13}N_4Na^+$ (M+Na)$^+$: 843.2484; Found: 843.2493.

2-Azidoethyl 4′,6′-*O*-benzylidene-3′-*O*-{2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-[6-*O*-benzyl-4-*O*-(2,4,6-tri-*O*-benzoyl-3-*O*-allyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-β-D-galactopyranosyl}-2′-deoxy-2′-phthalimido-β-D-galactopyranoside (28)



A solution of CCPB thioglycoside **29** (191 mg, 0.24 mmol, 1.2 equiv) and thioglycoside **30**[35] (104 mg, 0.22 mmol, 1.1 equiv) in anhydrous CH_2Cl_2 (2 mL) containing freshly activated 5 Å MS (200 mg) was stirred at -30 °C for 1 h before $Sc(OTf)_3$ (10.8 mg, 22 μmol, 0.11 equiv) was added quickly. The resulting mixture was stirred at -30 °C for 12 h before a solution of acceptor **31** (164 mg, 0.20 mmol, 1.0 equiv) and TTBP (199 mg, 0.8 mmol, 4.0 equiv) in anhydrous CH_2Cl_2 (0.5 mL) was added into the mixture by a syringe. The mixture was chilled to -60 °C and stirred at this temperature for 1 h before AgOTf (205 mg, 0.8 mmol, 4.0 equiv) and TolSCl (64 mg, 0.4 mmol, 2.0 equiv) were respectively added quickly. The mixture was stirred at -60 °C for 2 h before the mixture was warmed up to -30 °C and stirred at this temperature for another 12 h. After completion of the reaction as indicated by the TLC, the mixture was diluted with CH_2Cl_2 and poured into H_2O, two phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed sequentially with H_2O, sat. $NaHCO_3$ solution, dried over Na_2SO_4, filtered and concentrated *in vauco*. The residue was purified by silica gel column chromatography (hexane:EtOAc:CH_2Cl_2 = 1:1:1) to afford the titled compound **28** (144 mg, 0.084 mmol, 42%) as a white foam.

$[\alpha]_D^{23}$ = +49.7 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, CDCl3) δ 8.11 – 8.06 (m, 4H), 7.88 – 7.86 (m, 2H), 7.70 – 7.68 (m, 1H), 7.62 – 7.12 (m, 32H), 7.02 – 6.99 (m, 2H), 6.91 – 6.87 (m, 2H), 5.74 (d, *J* = 3.2 Hz, 1H), 5.67 – 5.58 (m, 1H), 5.52 (dd, *J* = 10.0, 8.0 Hz, 1H), 5.27 – 5.21 (m, 4H), 5.18 – 5.12 (m, 2H), 5.10 – 5.03 (m, 1H), 4.79 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.74 – 4.68 (m, 2H), 4.64 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.53 (dd, *J* = 11.0, 8.4 Hz, 1H), 4.36 (d, *J* = 1.6 Hz, 1H), 4.34 – 4.31 (m, 1H), 4.25 – 4.07 (m, 7H), 3.96 – 3.90 (m, 4H), 3.82 – 3.77 (m, 2H), 3.73 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.63 (dq, *J* = 8.0, 2.8 Hz, 1H), 3.57 – 3.51 (m, 2H), 3.50 – 3.36 (m, 5H), 3.29 – 3.23 (m, 1H), 3.12 – 3.06 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 167.4, 166.4, 165.7, 165.1, 164.5, 138.3, 138.2, 137.8, 133.9, 133.7, 133.5, 133.39, 132.43, 131.98, 131.95, 131.3, 130.2, 130.1, 129.9, 129.7, 129.3, 129.1, 129.04, 129.01, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.6, 126.7, 126.3, 123.5, 123.1, 118.4, 102.4, 101.1, 100.7, 99.8, 99.7, 98.4, 83.8, 79.6, 77.4, 76.5, 75.6, 75.2, 73.6, 73.1, 72.7, 71.3, 71.2, 71.1, 70.1, 69.9, 69.7, 69.1, 68.4, 67.4, 67.04, 67.00, 67.0, 63.3, 55.7, 51.9, 50.7.

HRMS (ESI$^+$, m/z): calcd for $C_{94}H_{85}O_{27}N_5Na^+$ (M+Na)$^+$: 1738.5324; Found: 1738.5319.

NMR spectra

^{1}H and ^{13}C NMR spectra of **3a**

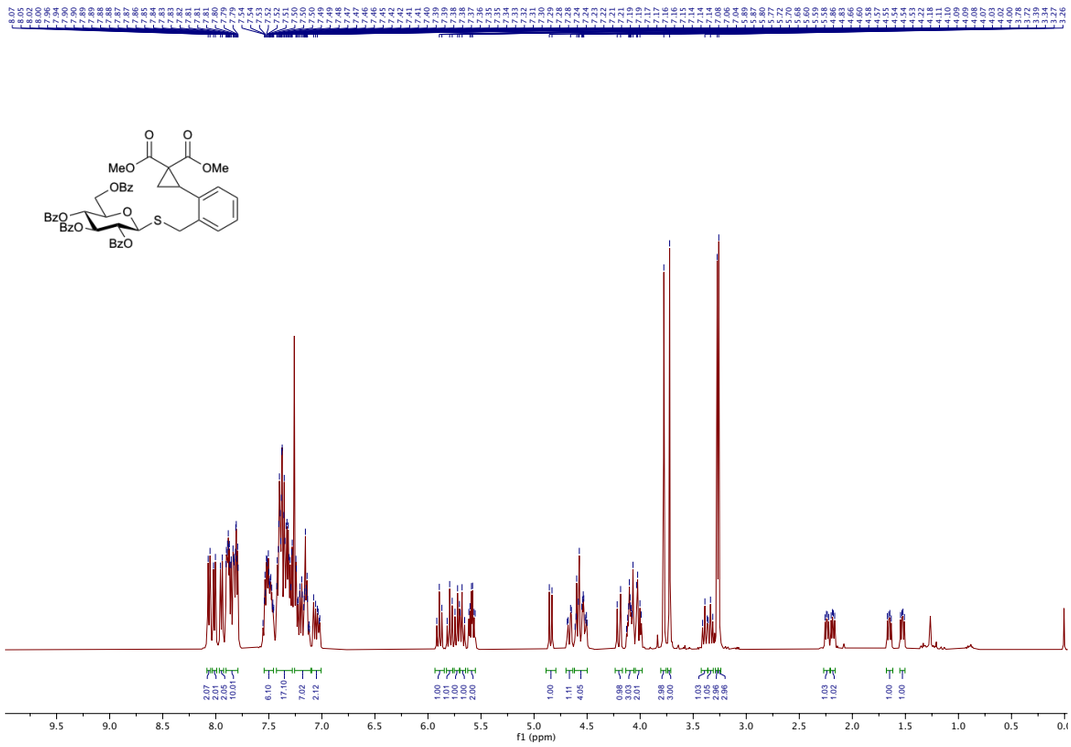


Figure S7. ^{1}H NMR spectrum of **3a** ($CDCl_3$, 400 MHz, 25 °C).

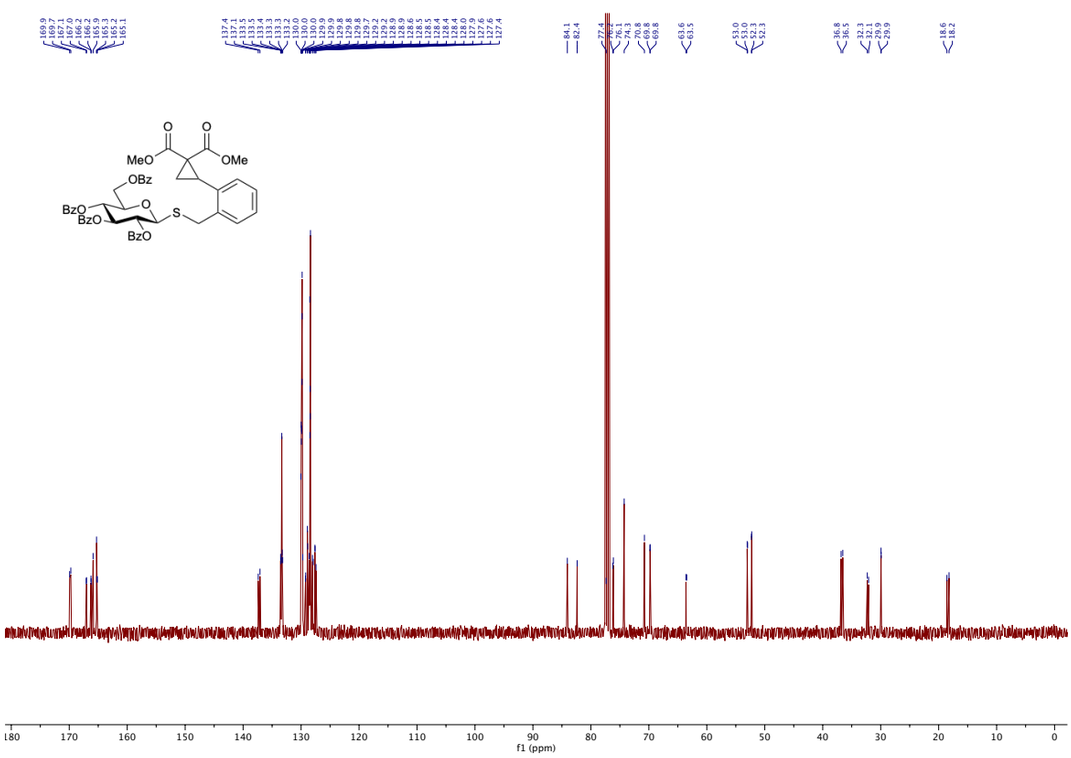


Figure S8. ^{13}C NMR spectrum of **3a** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **3b**

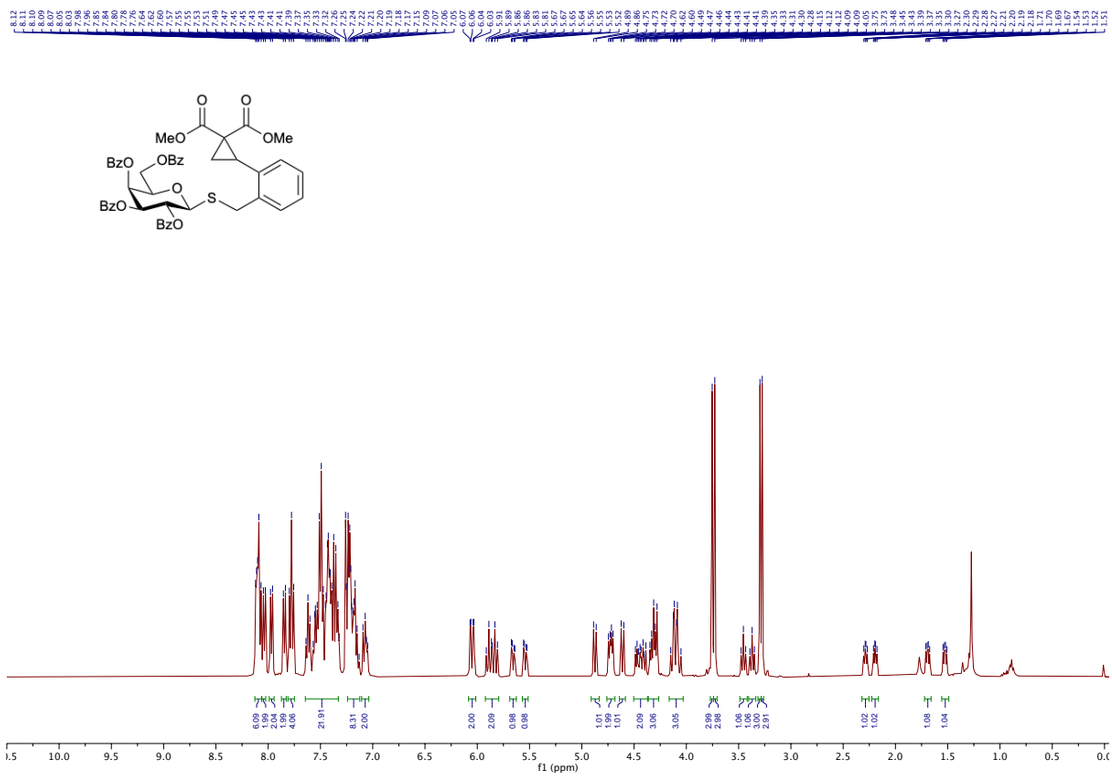


Figure S9. ^{1}H NMR spectrum of **3b** ($CDCl_3$, 400 MHz, 25 °C).

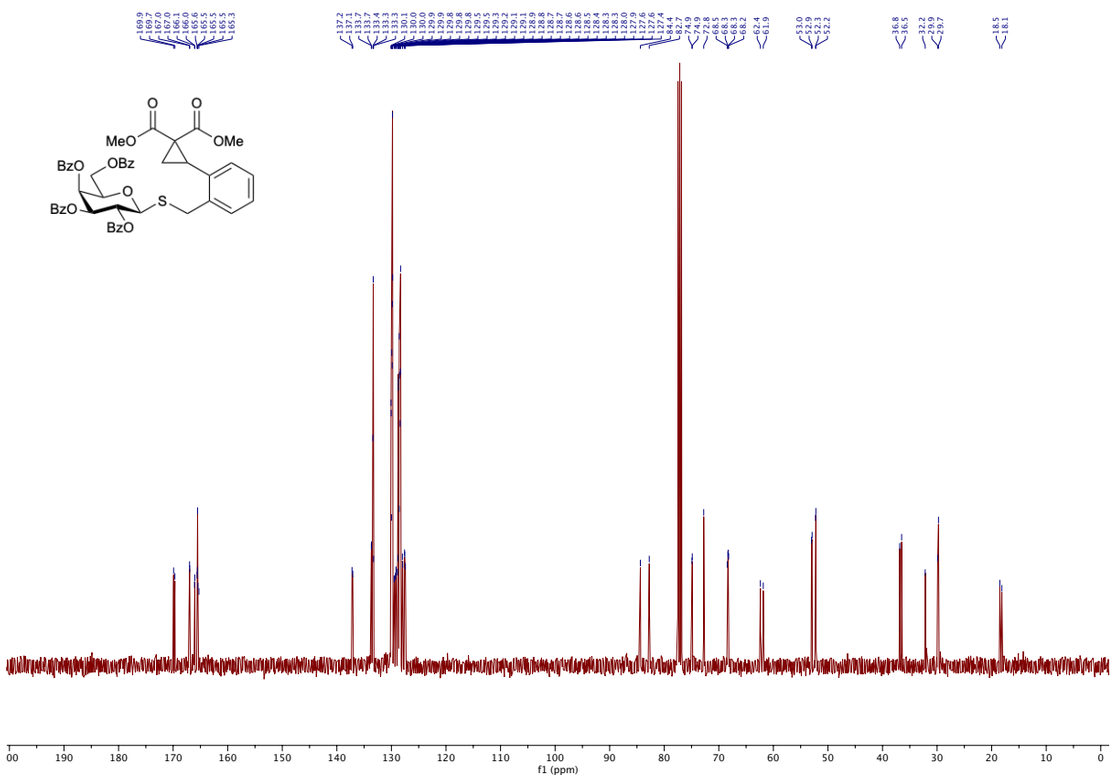


Figure S10. ^{13}C NMR spectrum of **3b** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **3c**

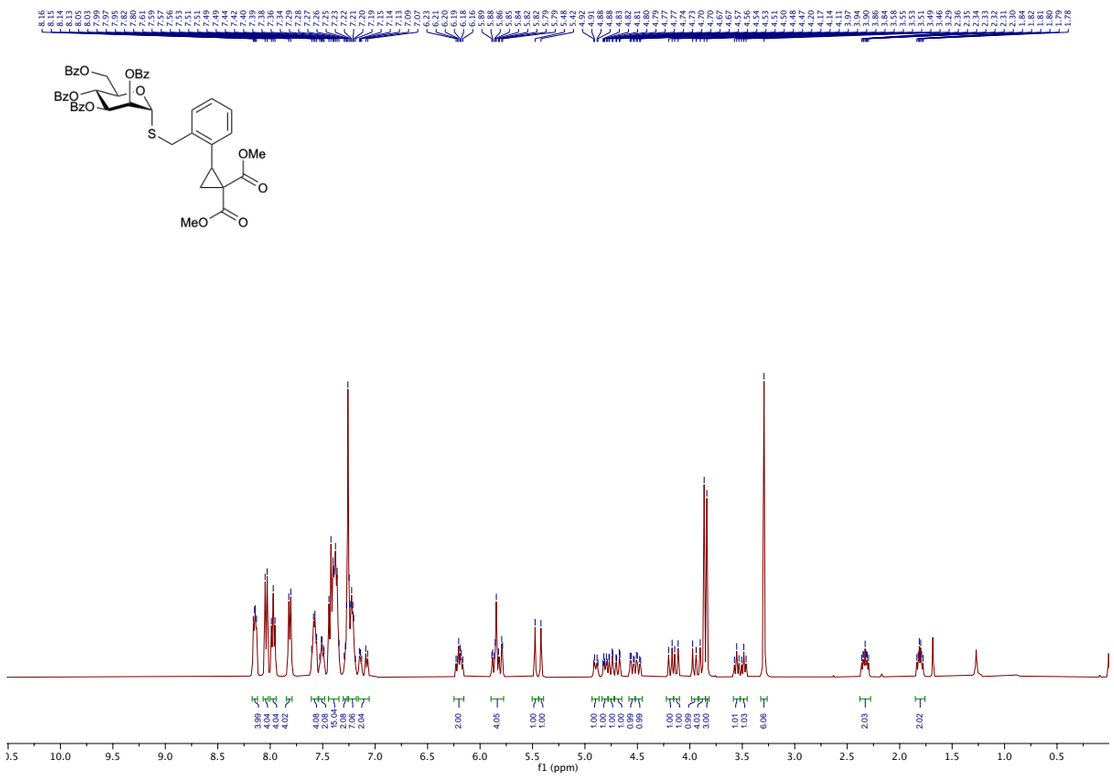


Figure S11. ^{1}H NMR spectrum of **3c** ($CDCl_3$, 400 MHz, 25 °C).

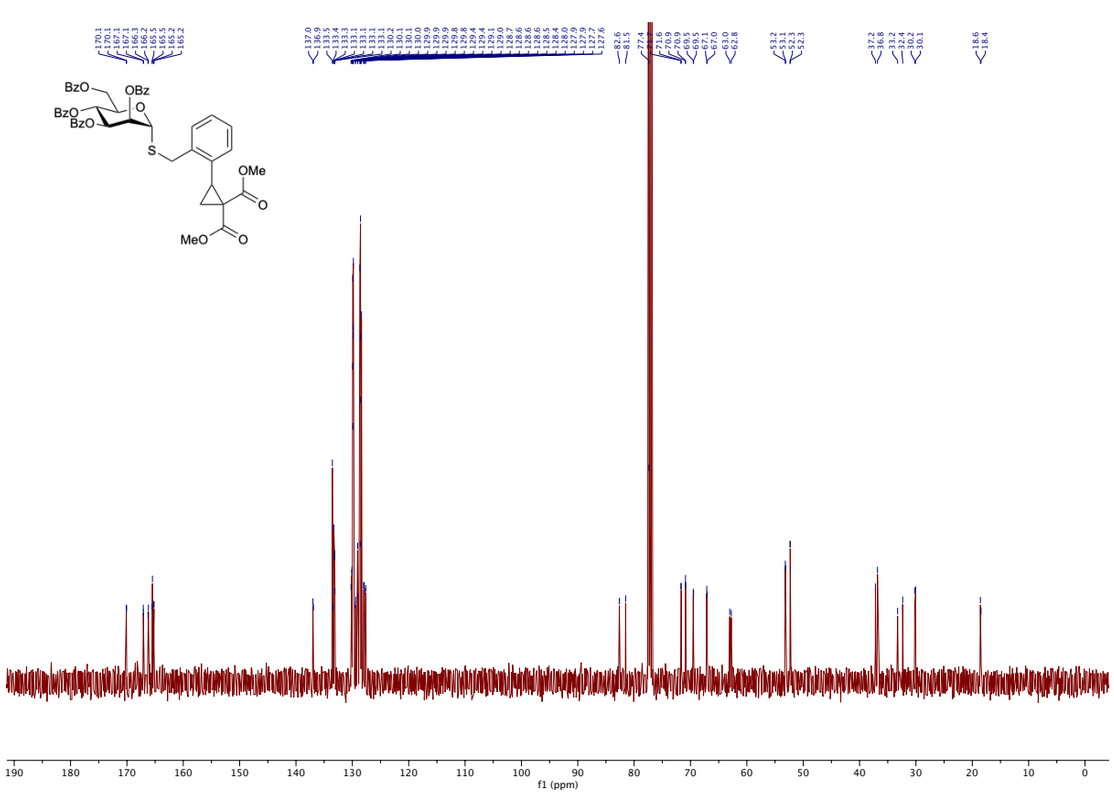


Figure S12. ^{13}C NMR spectrum of **3c** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **3d**

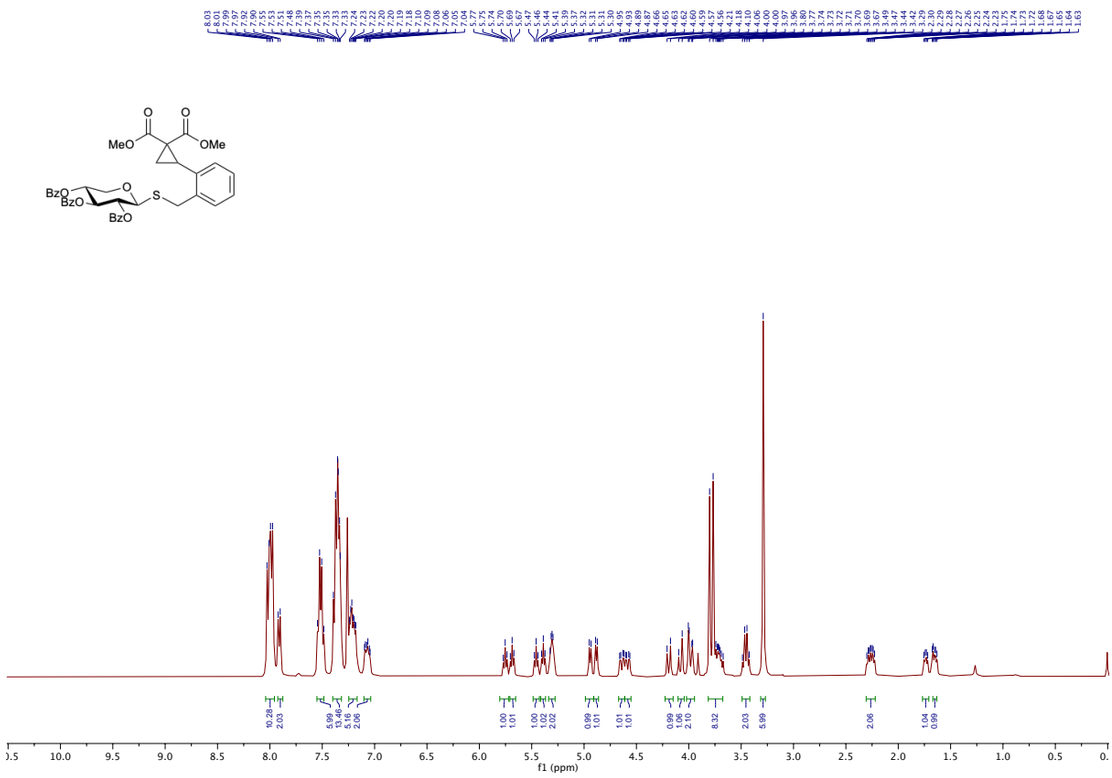


Figure S13. ^{1}H NMR spectrum of **3d** ($CDCl_3$, 400 MHz, 25 °C).

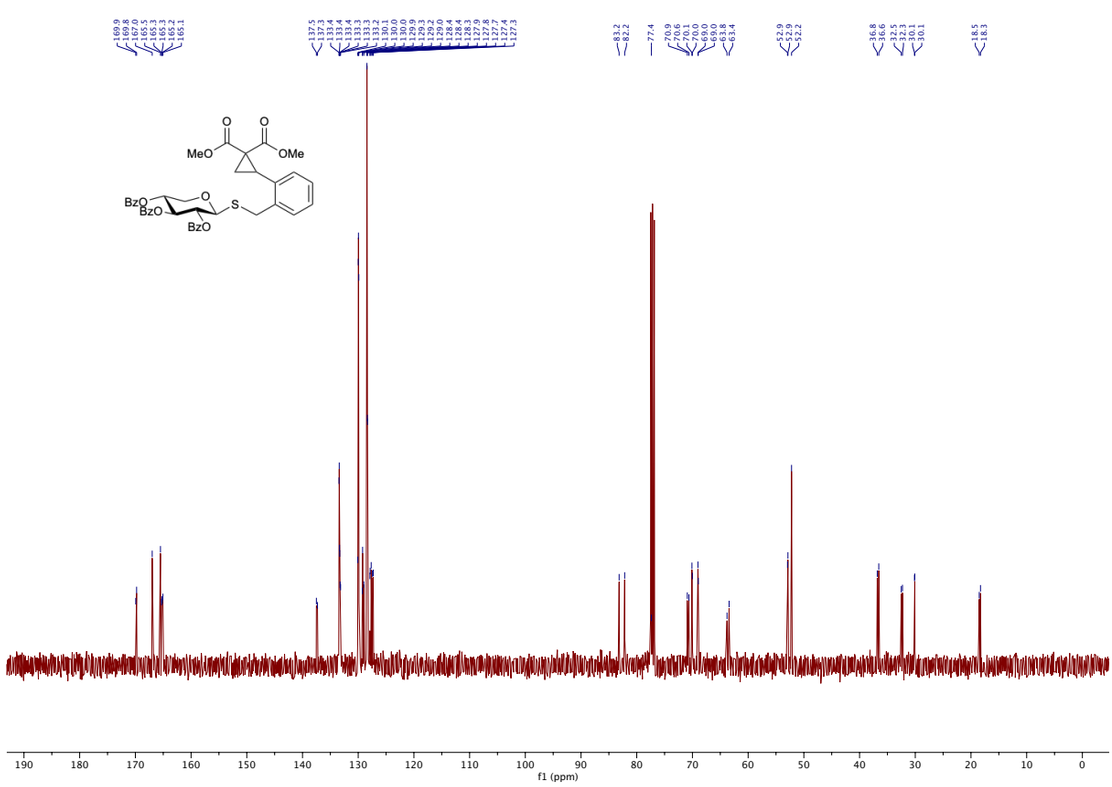


Figure S14. ^{13}C NMR spectrum of **3d** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **3e**

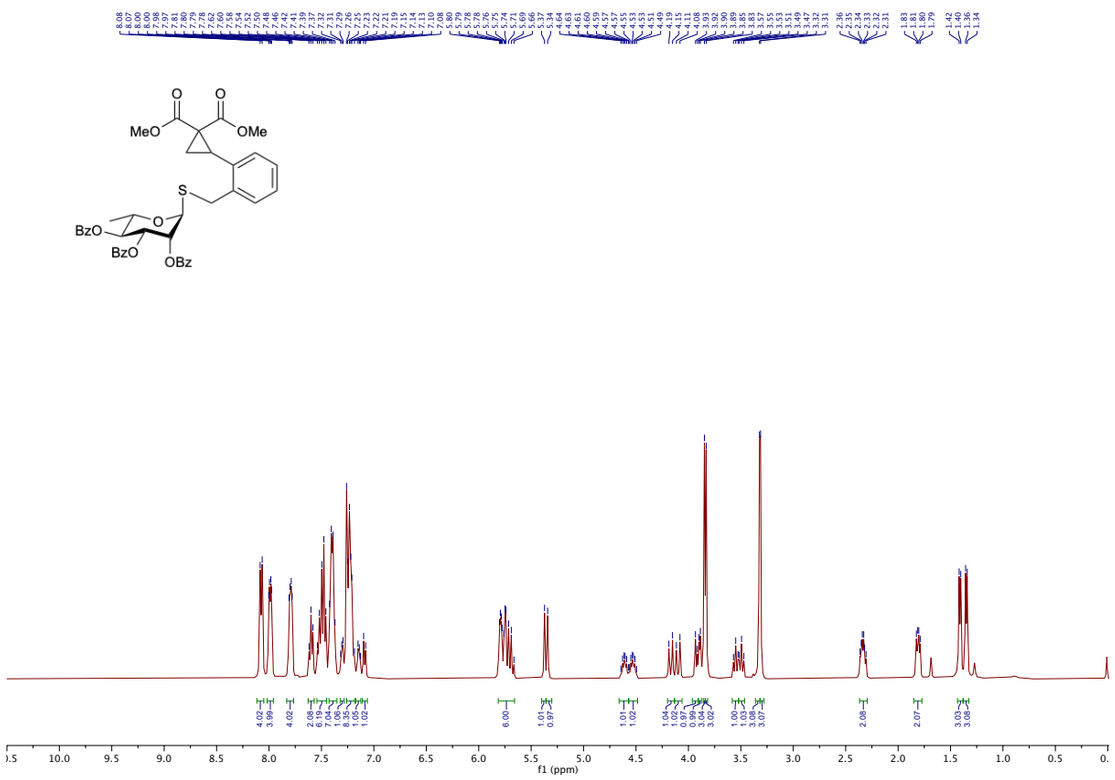


Figure S15. ^{1}H NMR spectrum of **3e** ($CDCl_3$, 400 MHz, 25 ºC).

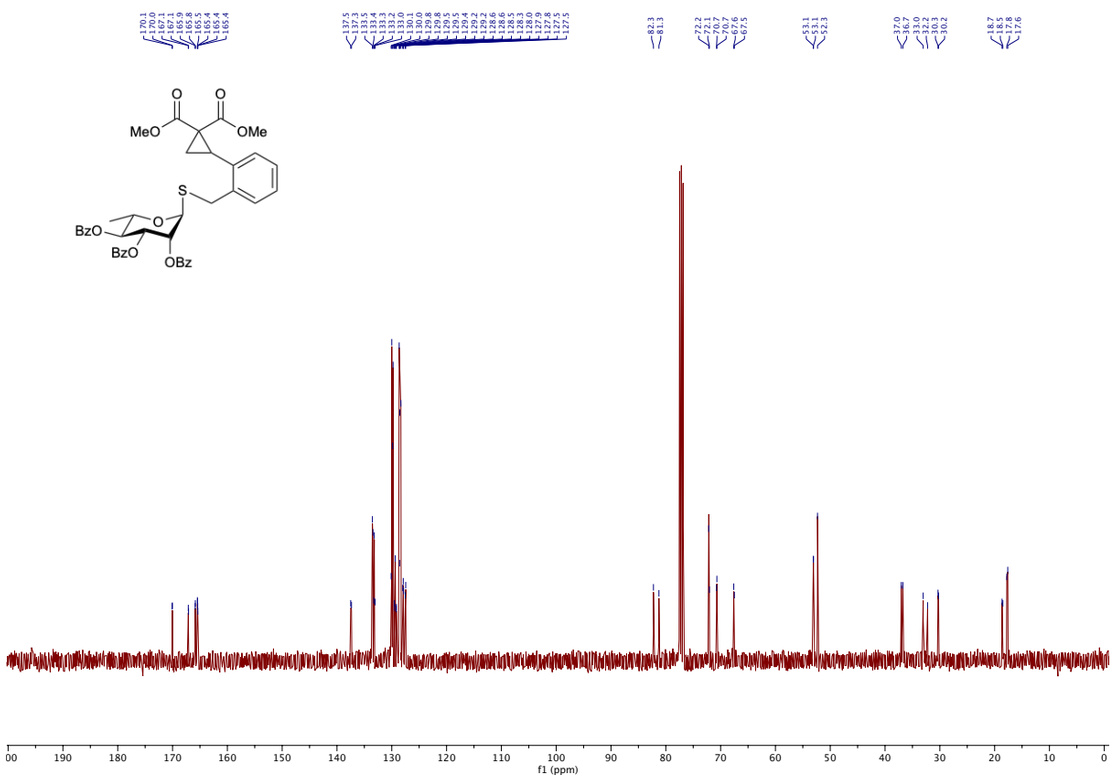


Figure S16. ^{13}C NMR spectrum of **3e** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **3f**

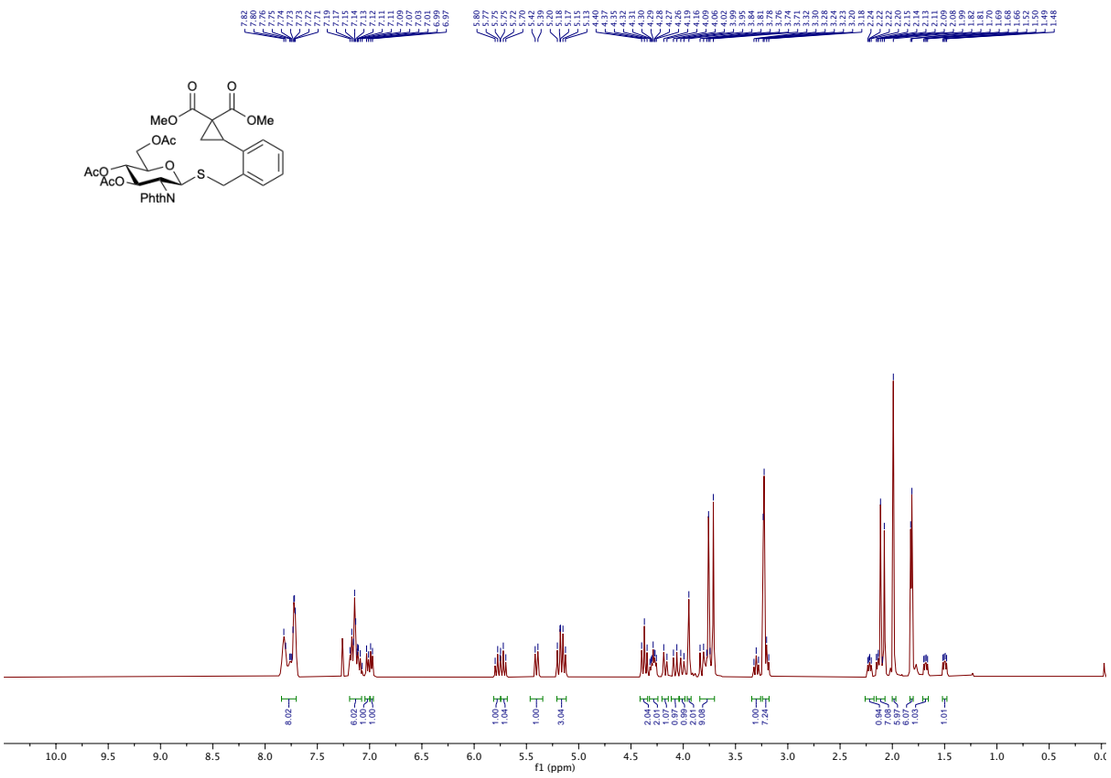


Figure S17. ^{1}H NMR spectrum of **3f** ($CDCl_3$, 400 MHz, 25 ºC).

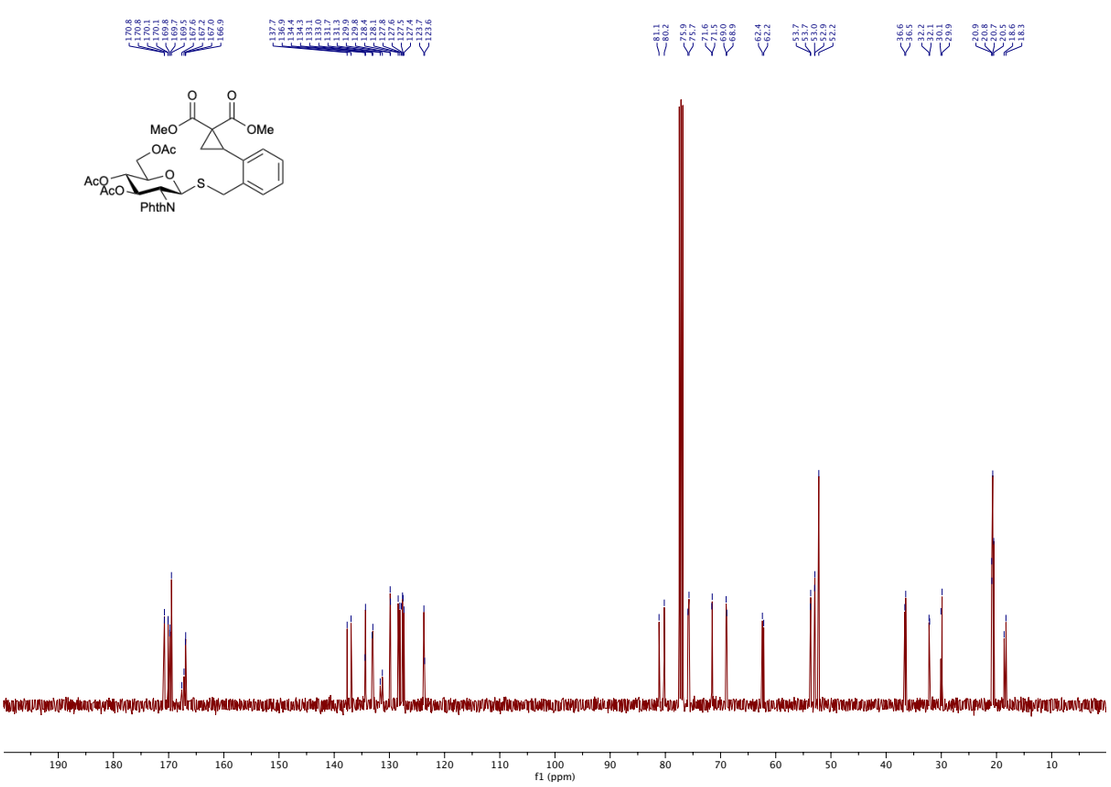


Figure S18. ^{13}C NMR spectrum of **3f** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **3g**

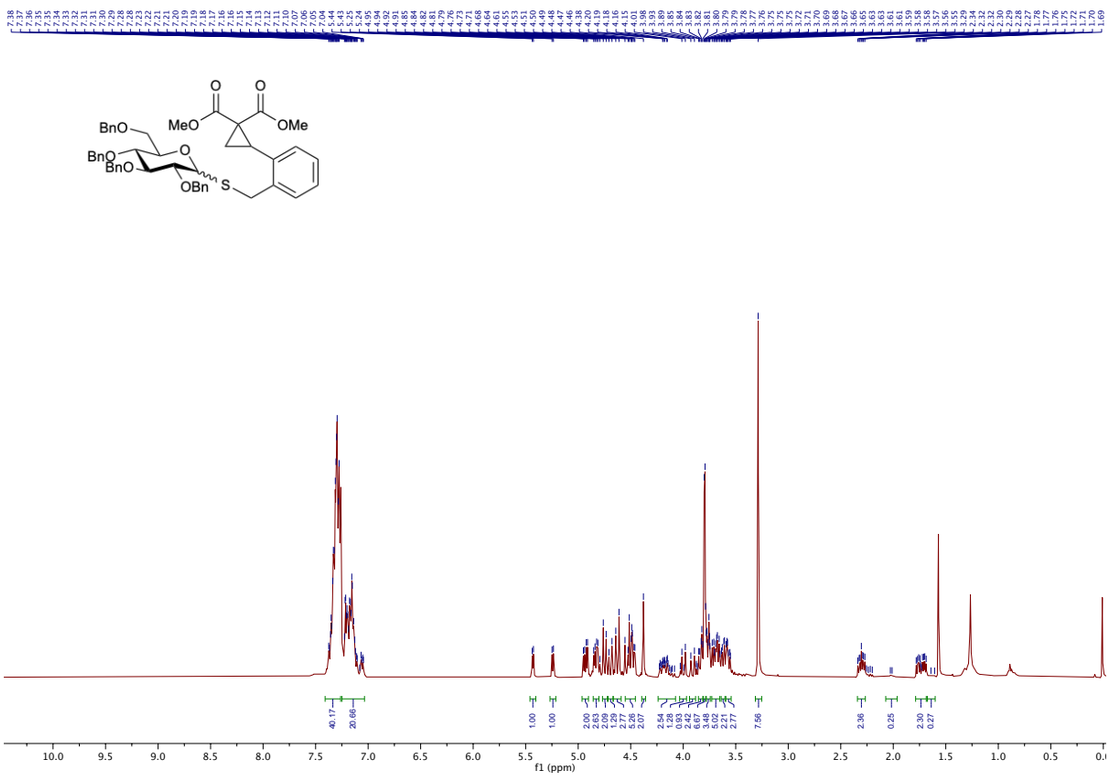


Figure S19. ^{1}H NMR spectrum of **3g** ($CDCl_3$, 400 MHz, 25 °C).

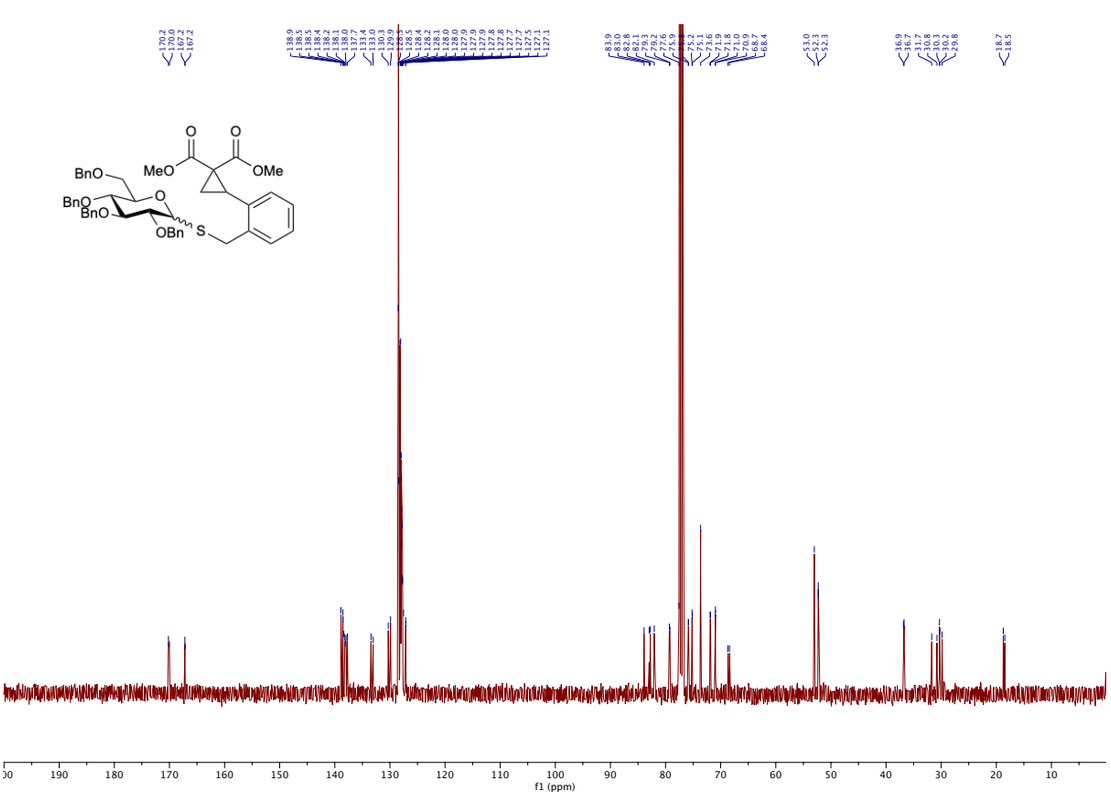


Figure S20. ^{13}C NMR spectrum of **3g** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **3h**

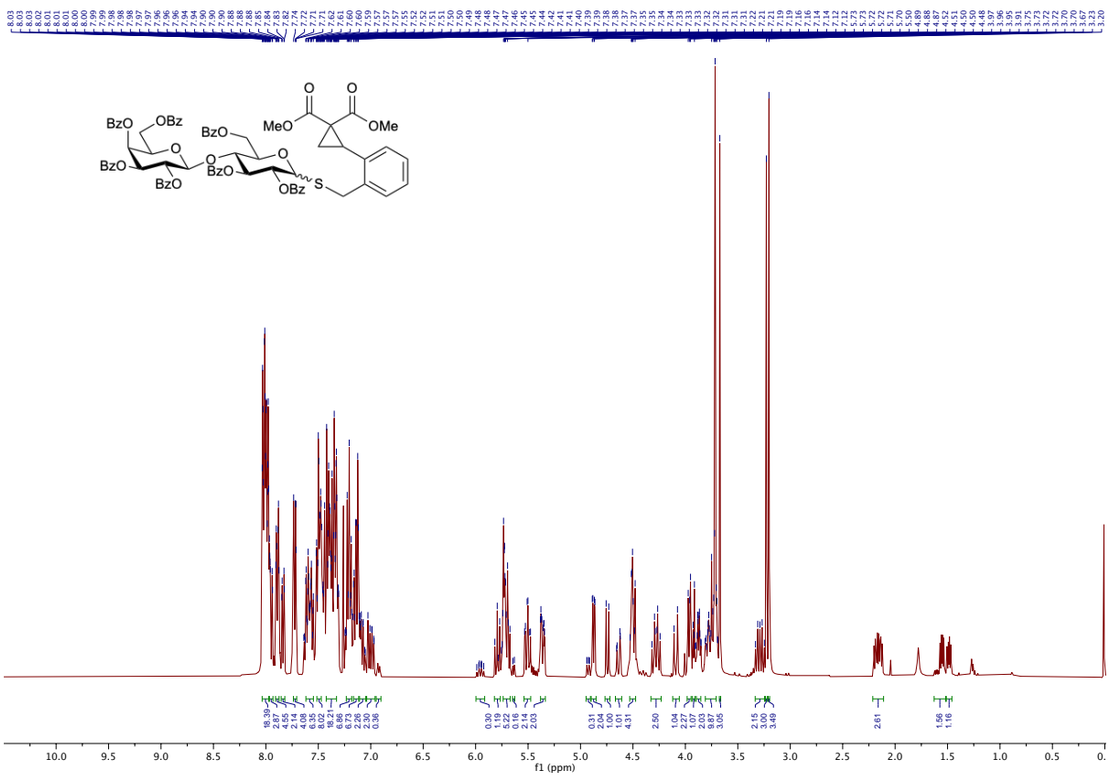


Figure S21. ^{1}H NMR spectrum of **3h** ($CDCl_3$, 400 MHz, 25 °C).

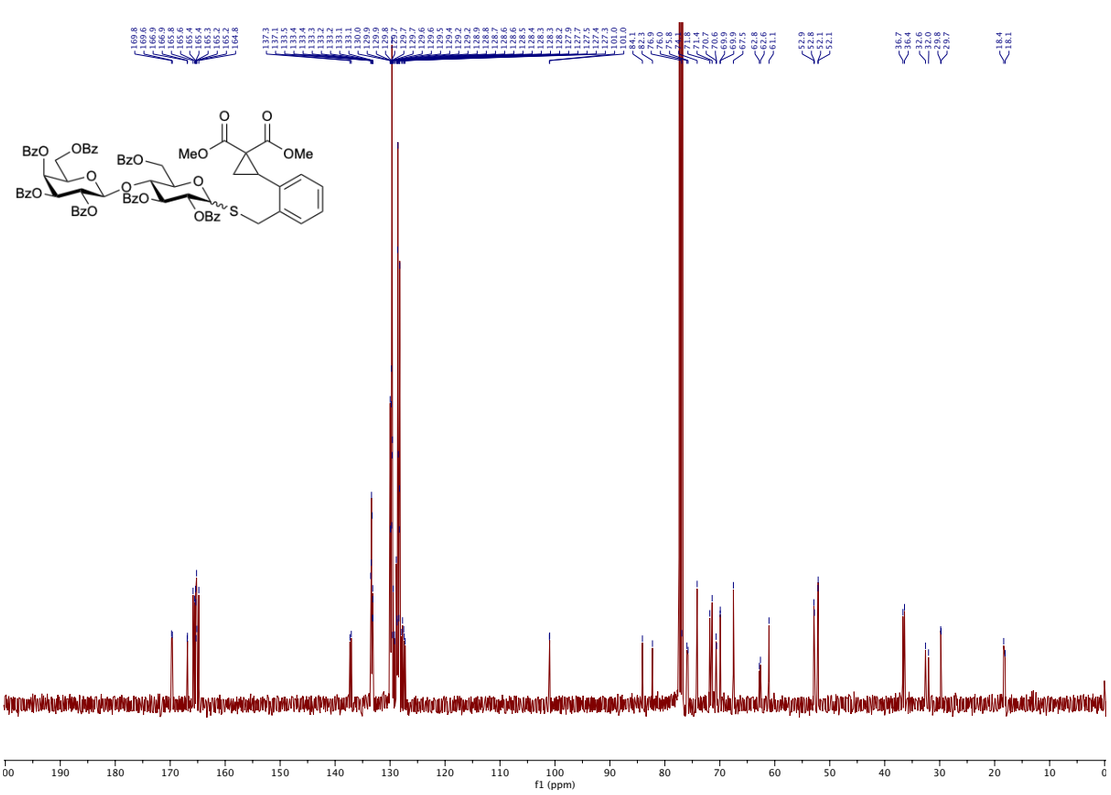


Figure S22. ^{13}C NMR spectrum of **3h** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **6**

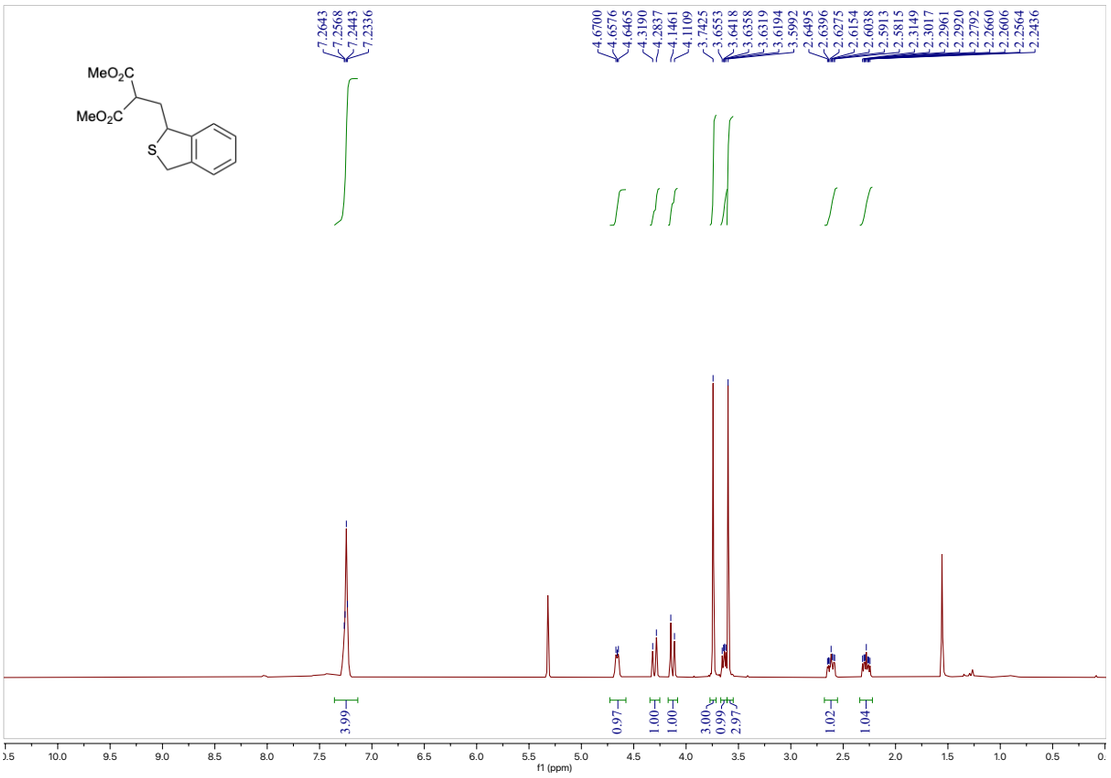


Figure S23. ^{1}H NMR spectrum of **6** (CD_2Cl_2, 400 MHz, 25 ºC).

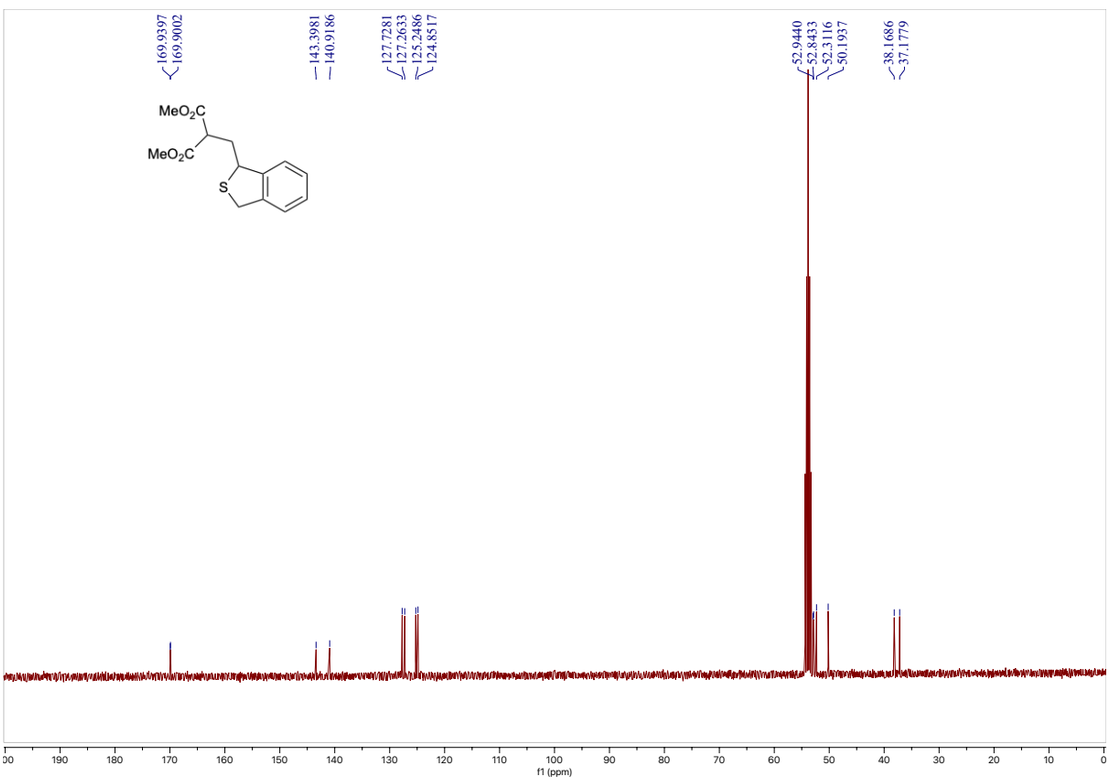


Figure S24. ^{13}C NMR spectrum of **6** (CD_2Cl_2, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **5a**

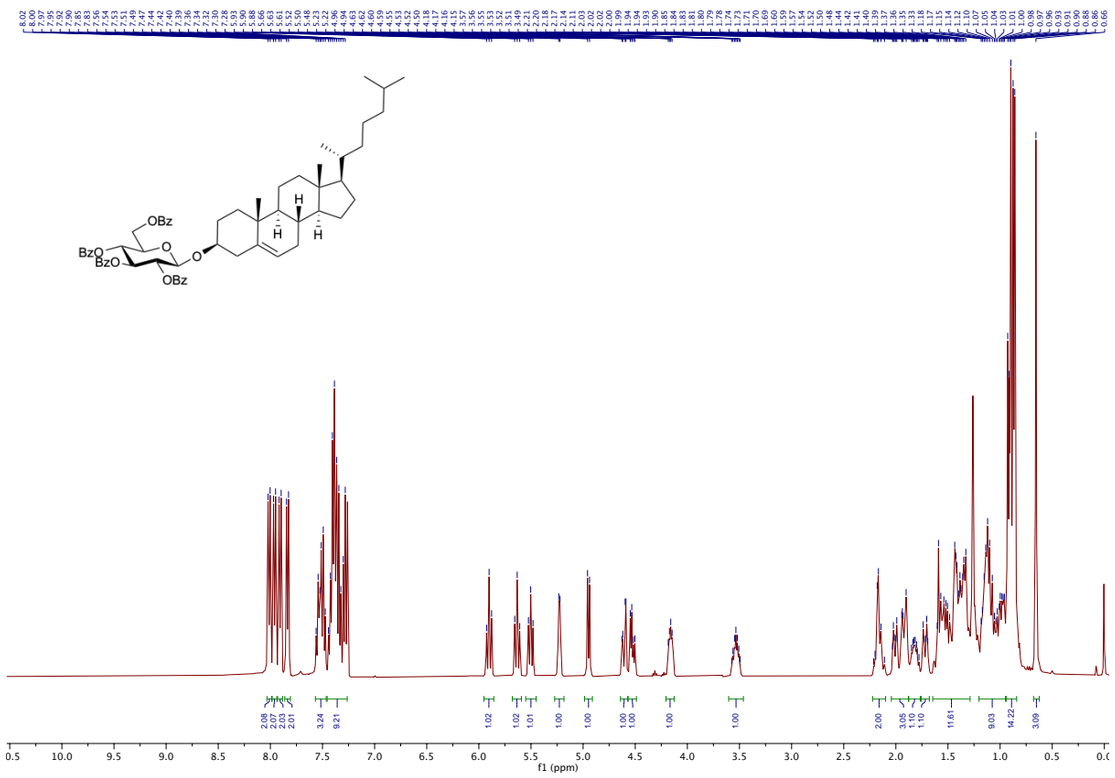


Figure S25. ^{1}H NMR spectrum of **5a** ($CDCl_3$, 400 MHz, 25 ºC).

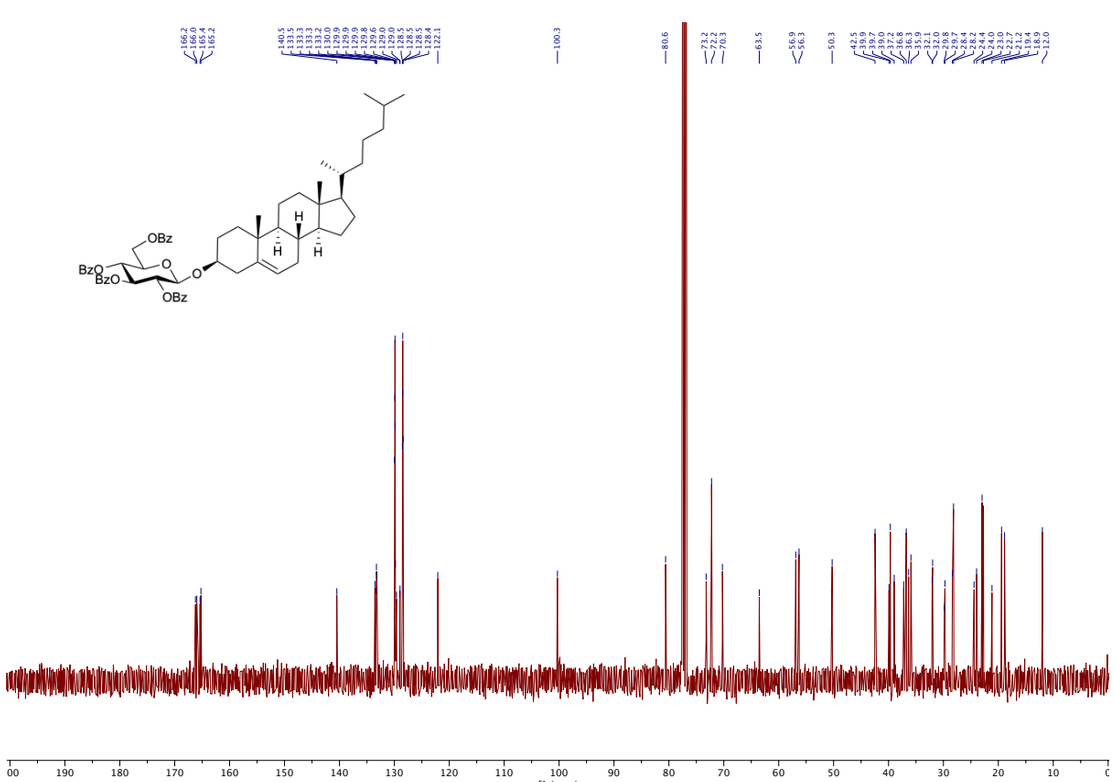


Figure S26. ^{13}C NMR spectrum of **5a** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **5b**

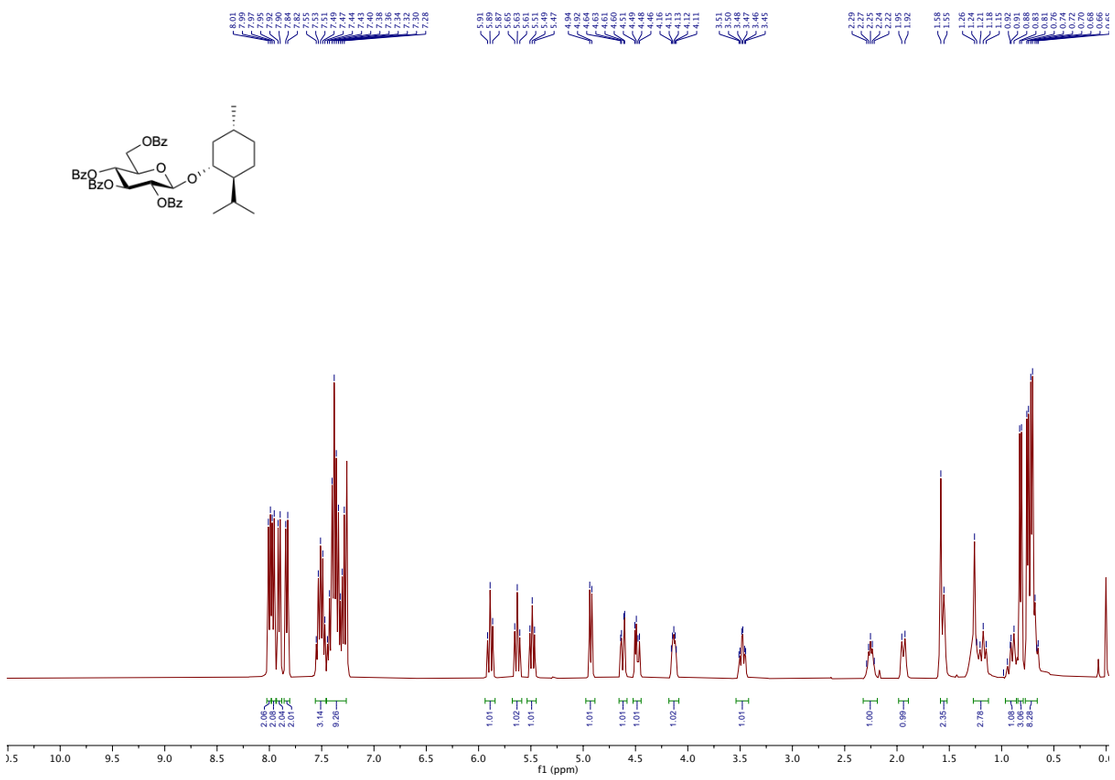


Figure S27. ^{1}H NMR spectrum of **5b** ($CDCl_3$, 400 MHz, 25 °C).

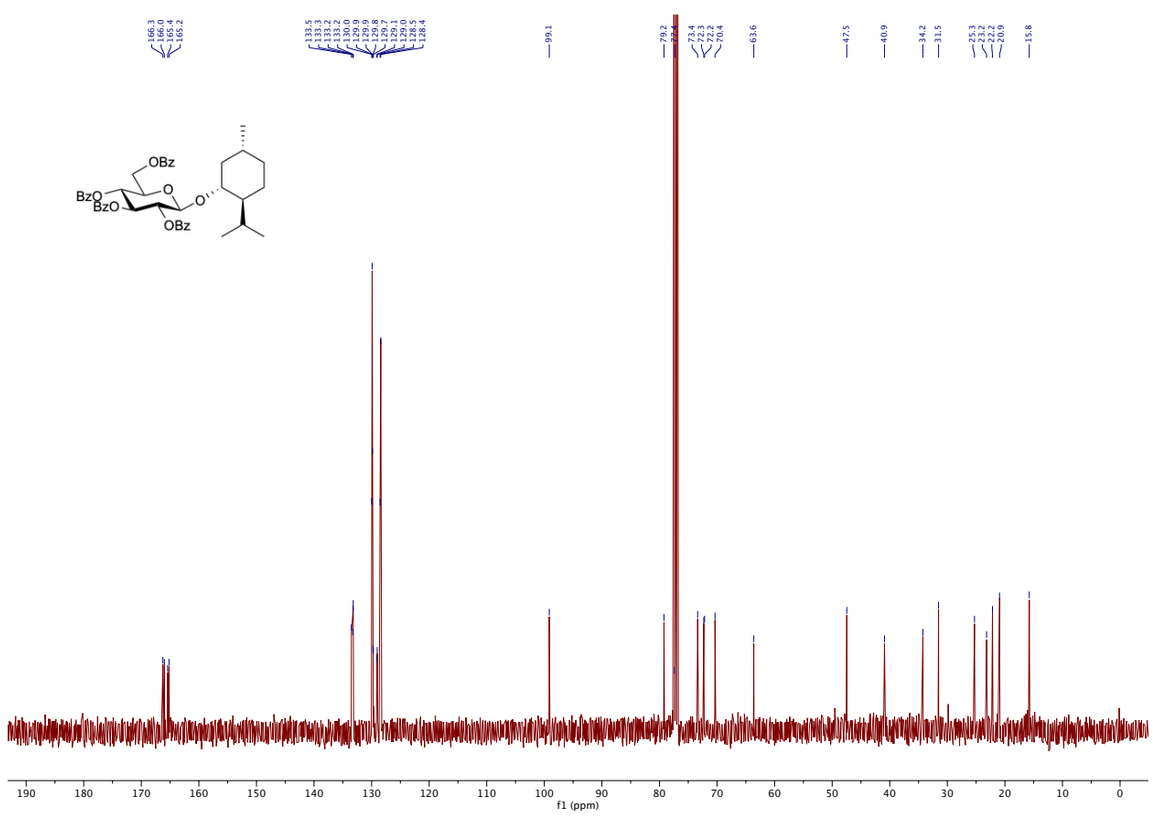


Figure S28. ^{13}C NMR spectrum of **5b** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5c**

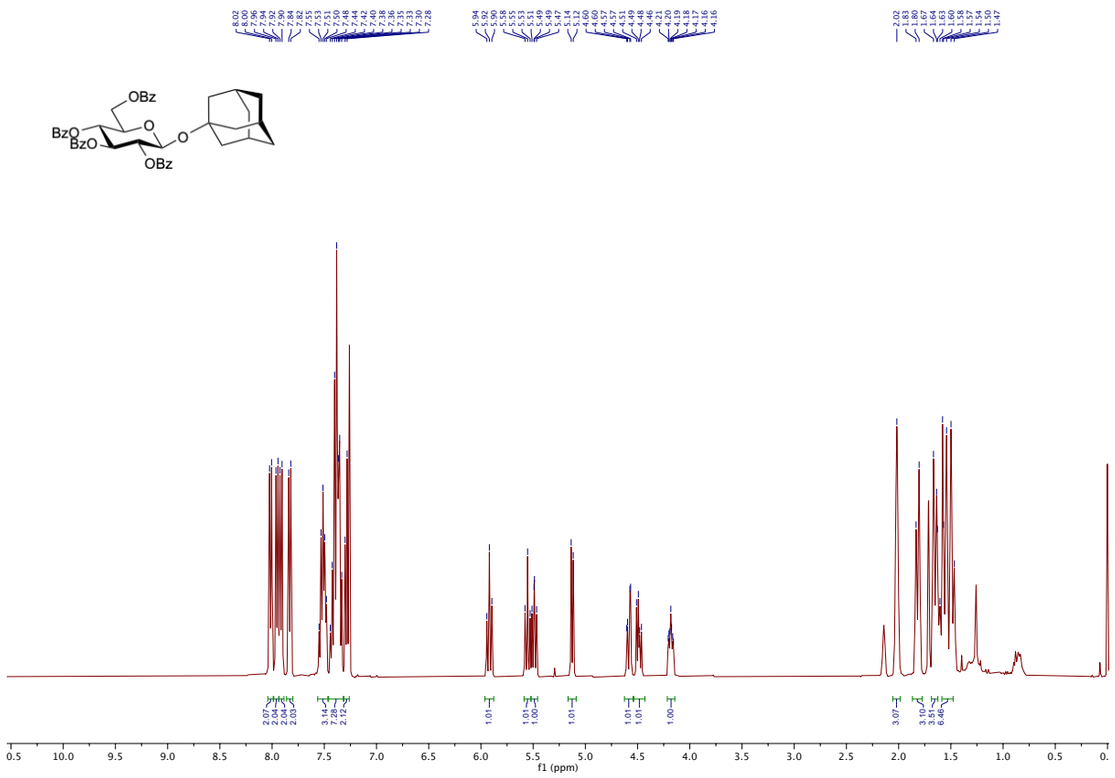


Figure S29. ^{1}H NMR spectrum of **5c** ($CDCl_3$, 400 MHz, 25 °C).

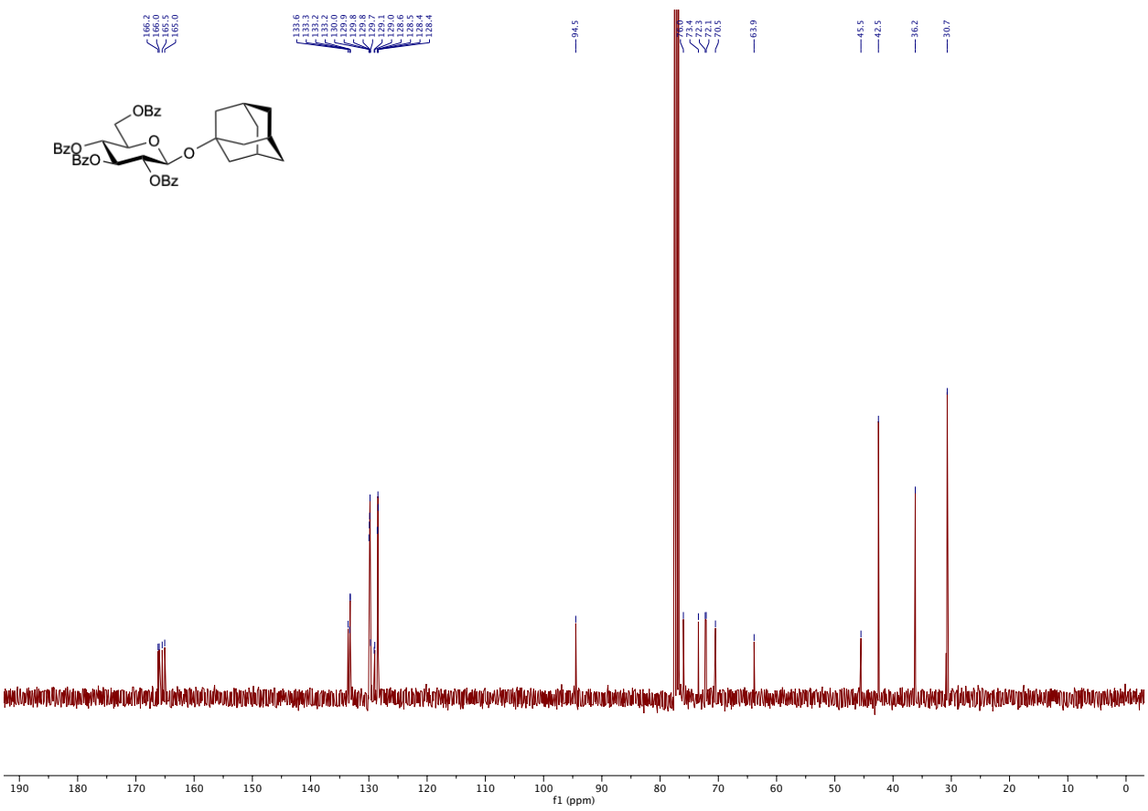


Figure S30. ^{13}C NMR spectrum of **5c** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5d**

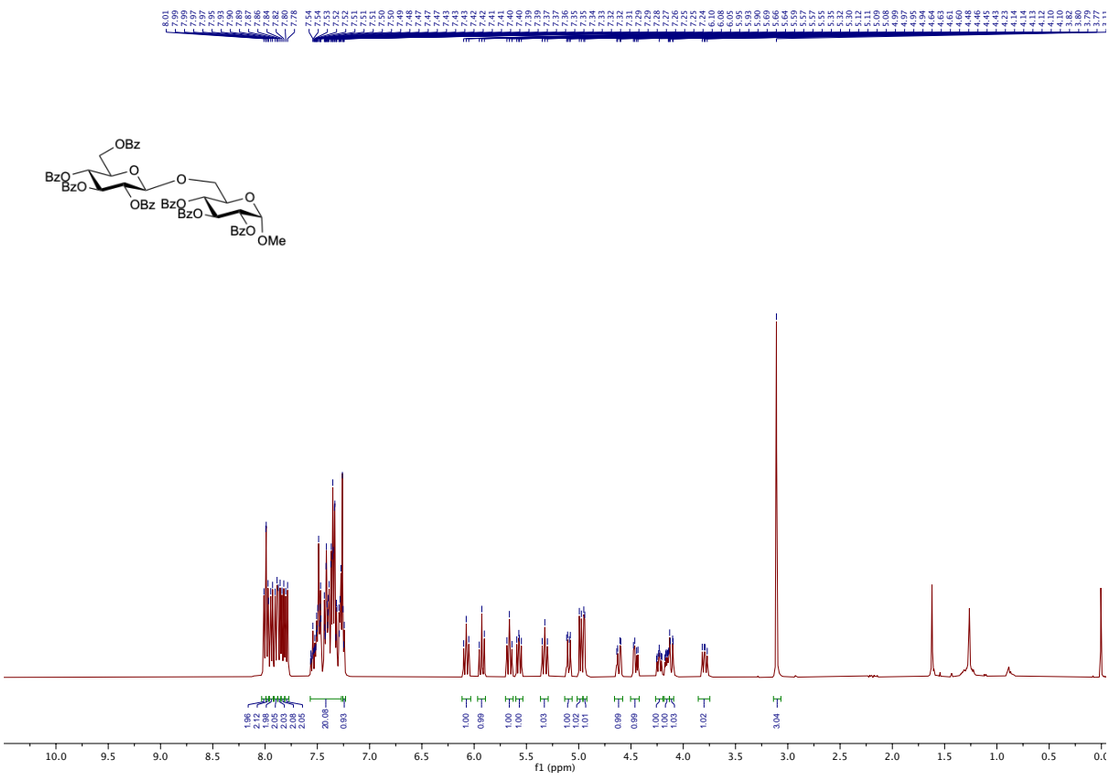


Figure S31. ^{1}H NMR spectrum of **5d** ($CDCl_3$, 400 MHz, 25 °C).

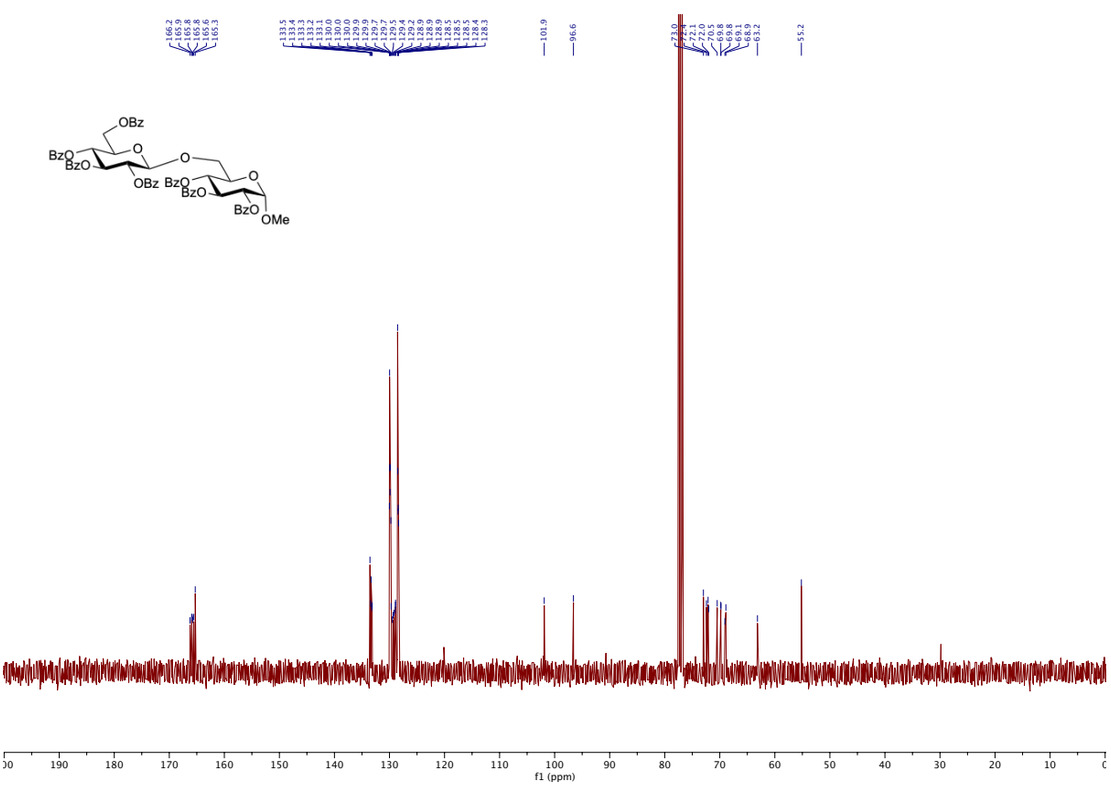


Figure S32. ^{13}C NMR spectrum of **5d** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5e**

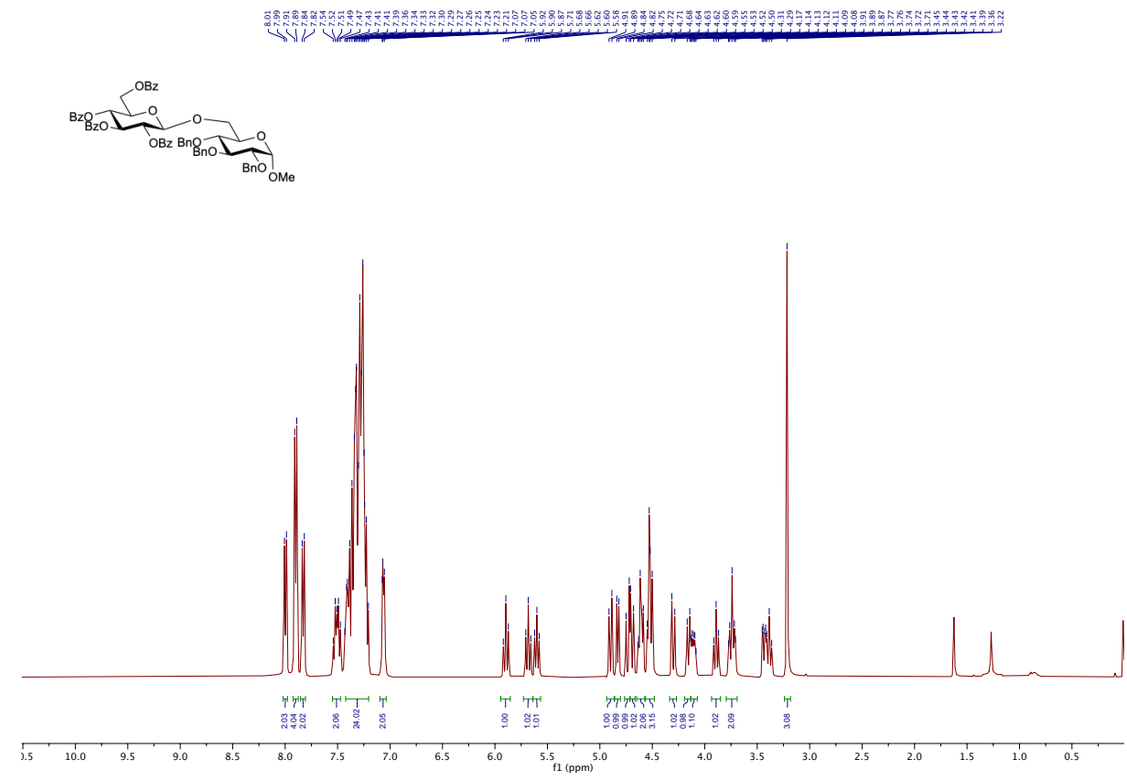


Figure S33. ^{1}H NMR spectrum of **5e** ($CDCl_3$, 400 MHz, 25 °C).

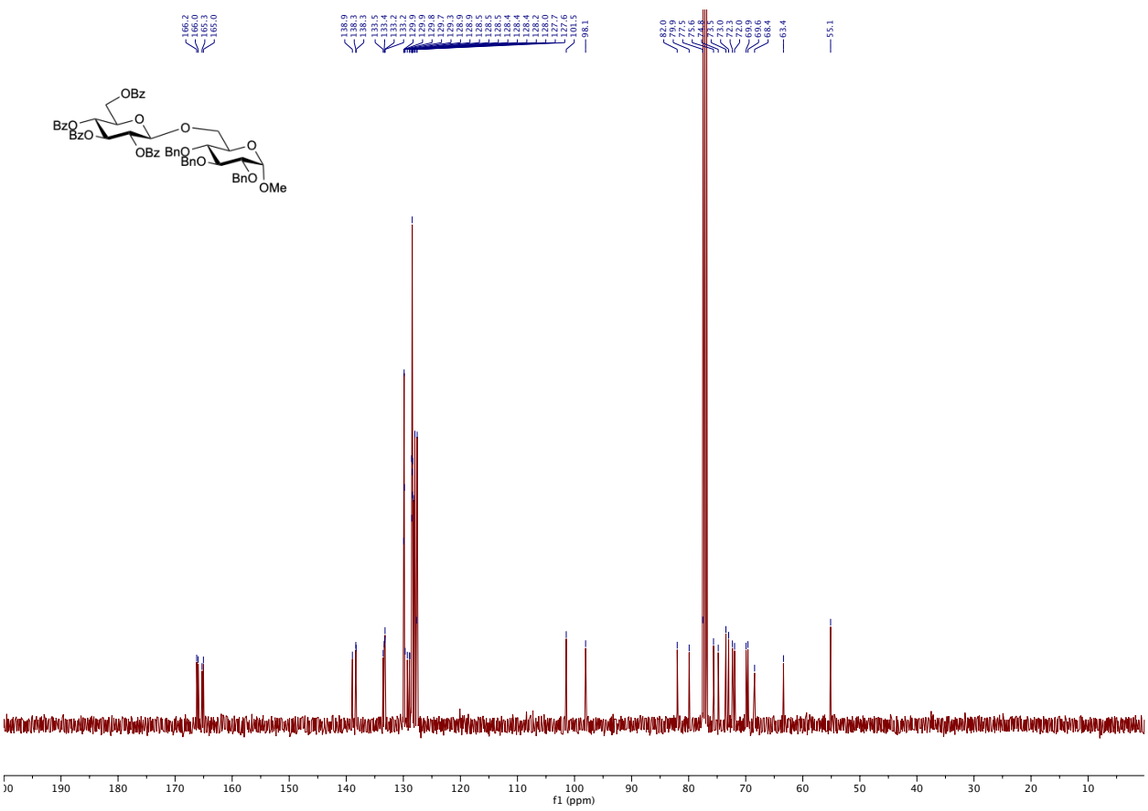


Figure S34. ^{13}C NMR spectrum of **5e** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5f**

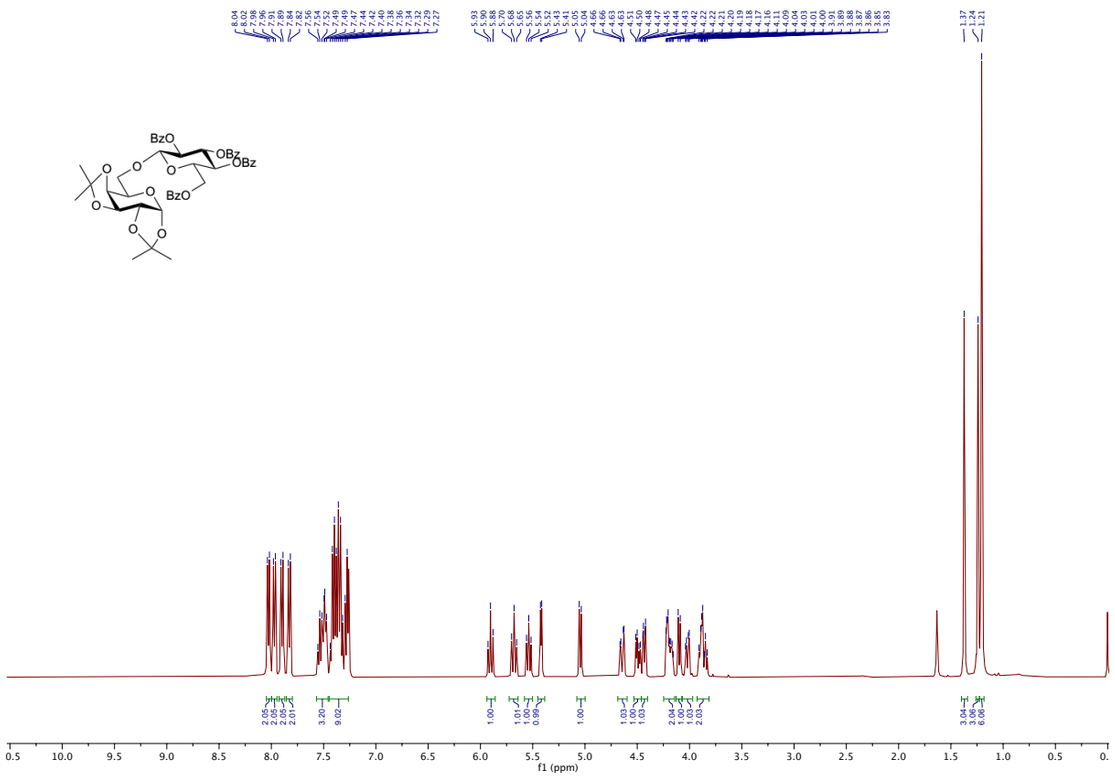


Figure S35. ^{1}H NMR spectrum of **5f** ($CDCl_3$, 400 MHz, 25 ºC).

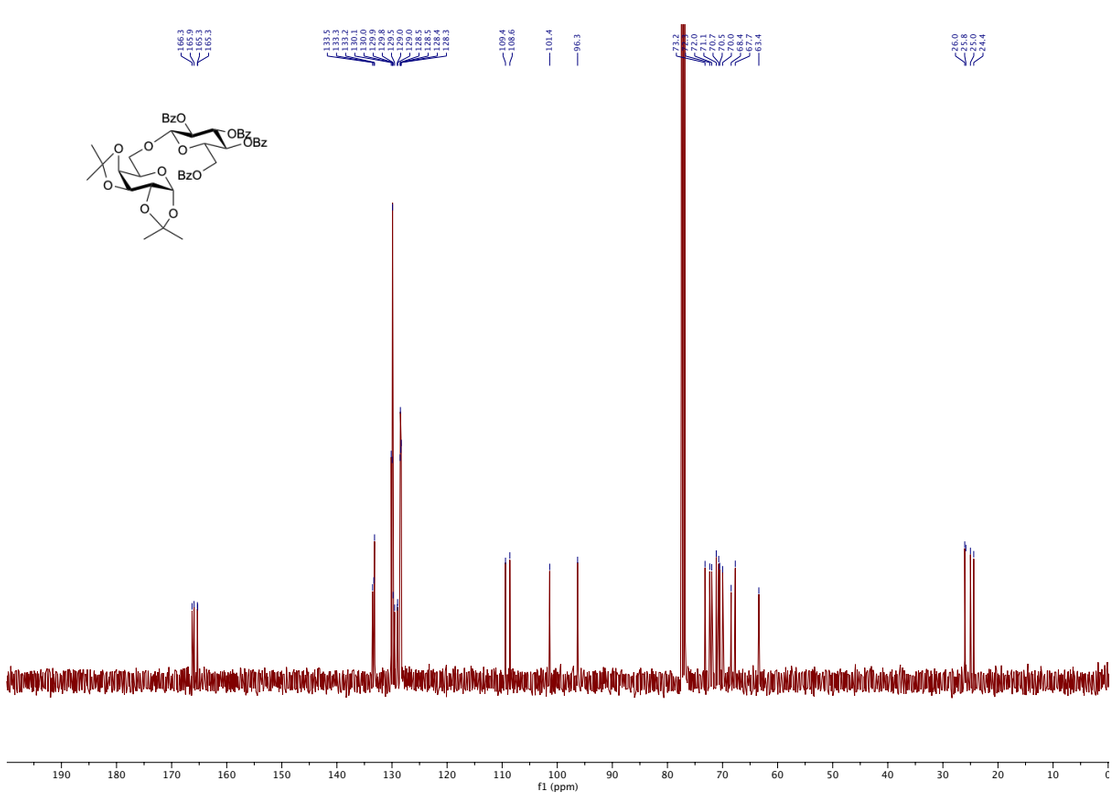


Figure S36. ^{13}C NMR spectrum of **5f** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **5g**

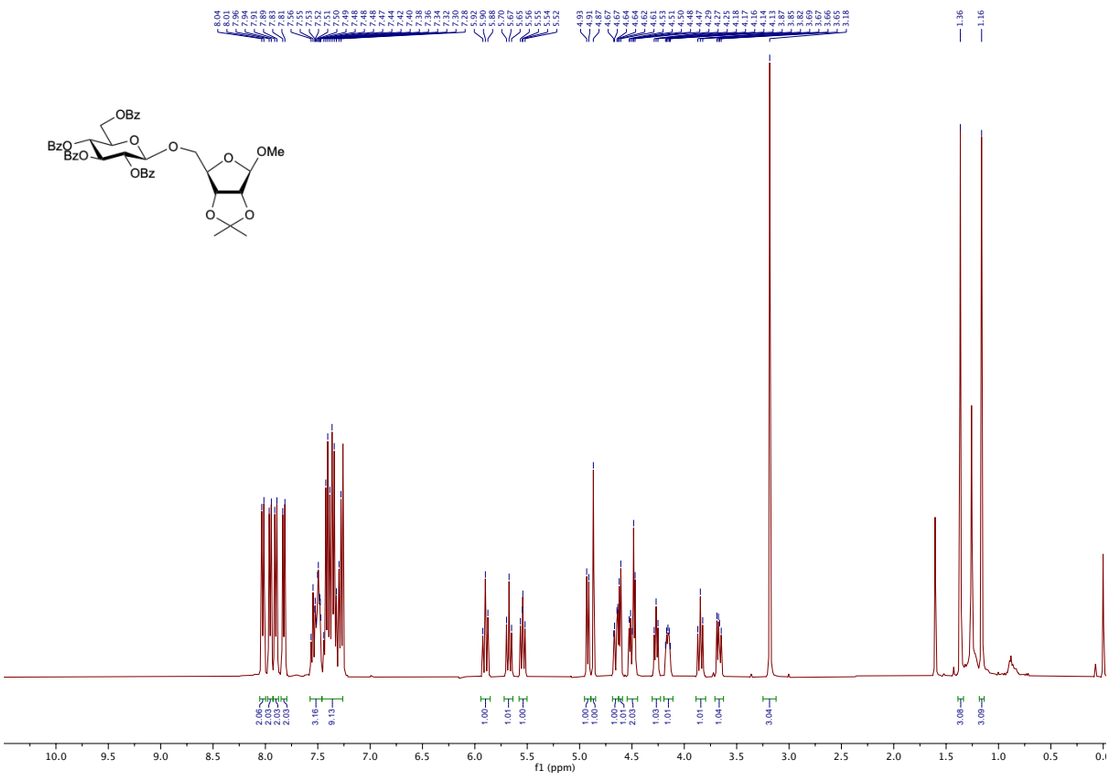


Figure S37. ^{1}H NMR spectrum of **5g** ($CDCl_3$, 400 MHz, 25 °C).

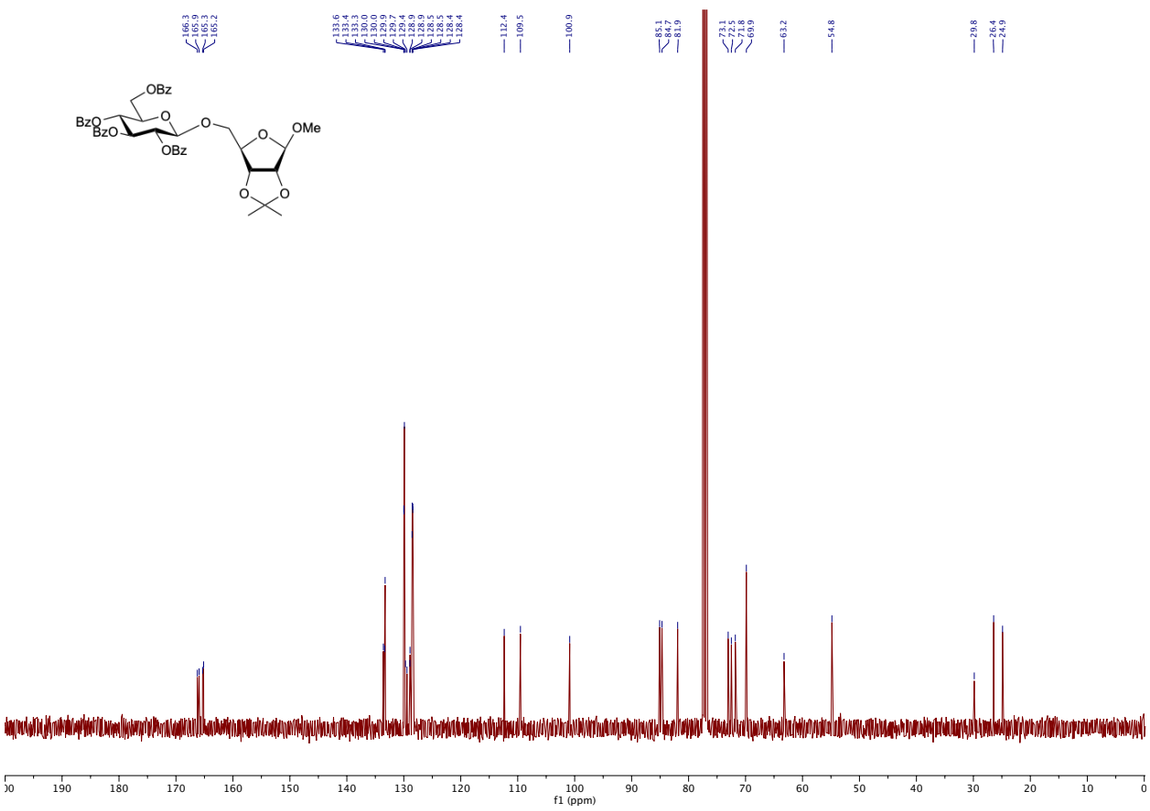


Figure S38. ^{13}C NMR spectrum of **5g** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5h**

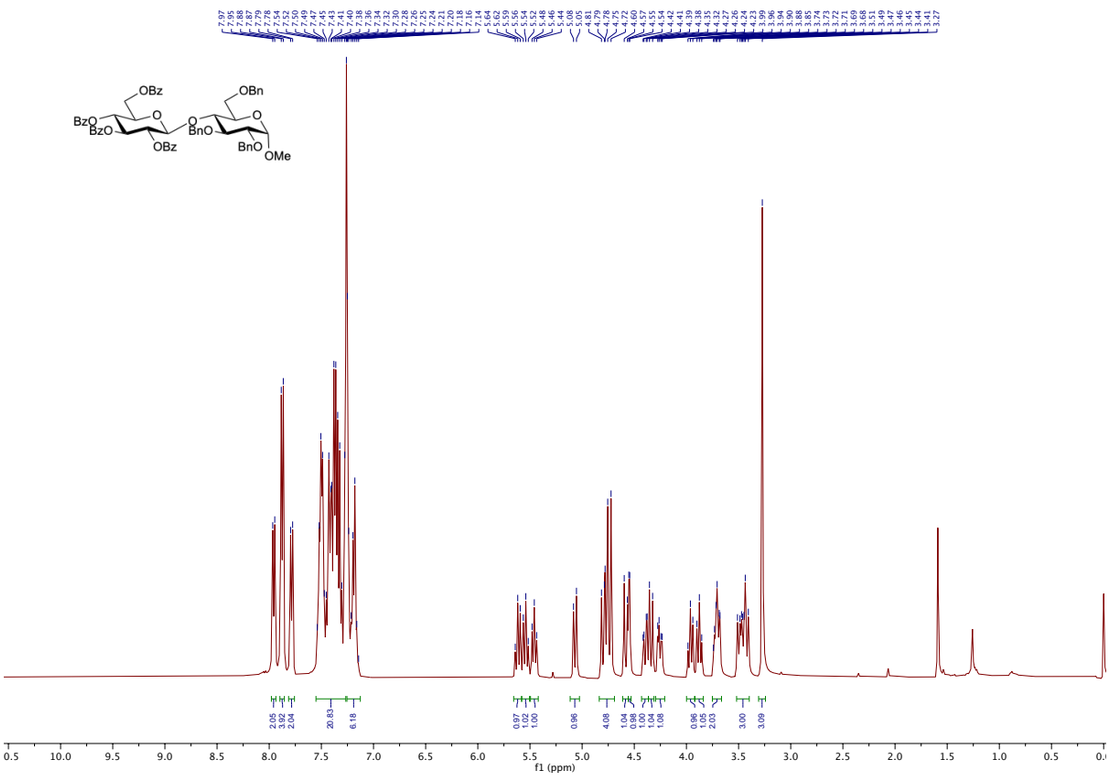


Figure S39. ^{1}H NMR spectrum of **5h** ($CDCl_3$, 400 MHz, 25 °C).

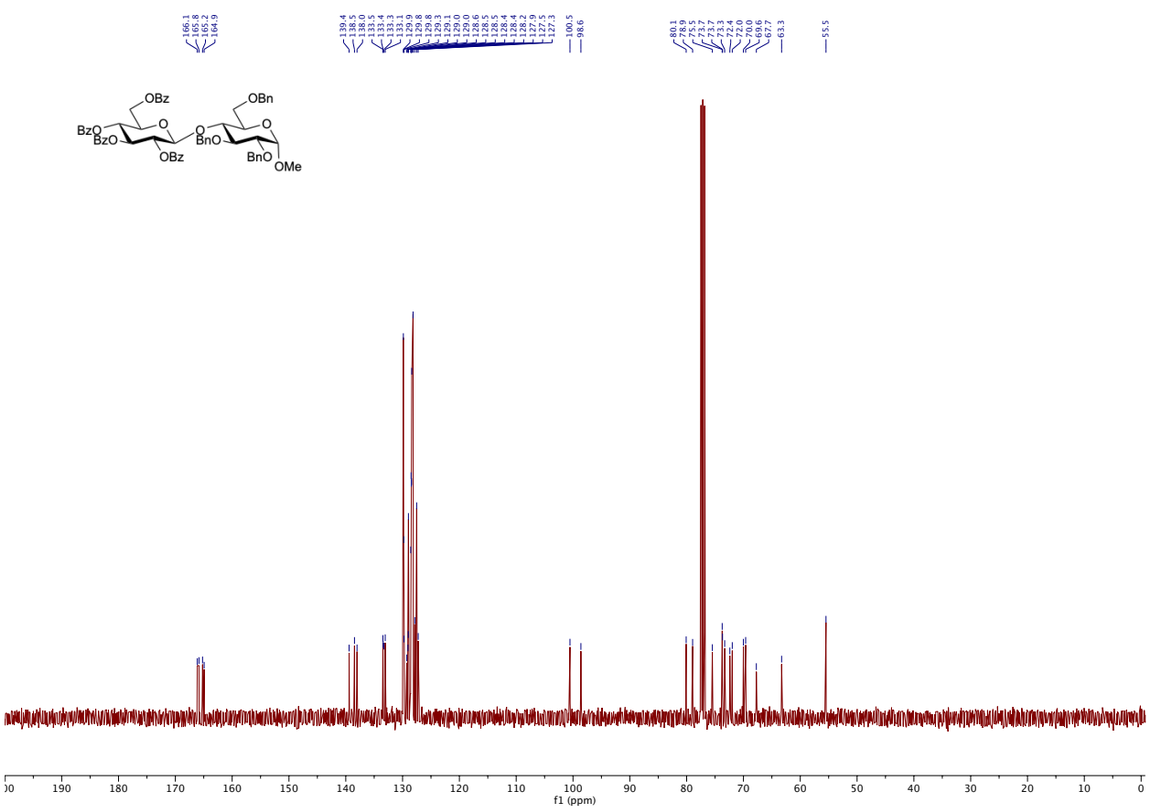


Figure S40. ^{13}C NMR spectrum of **5h** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5i**

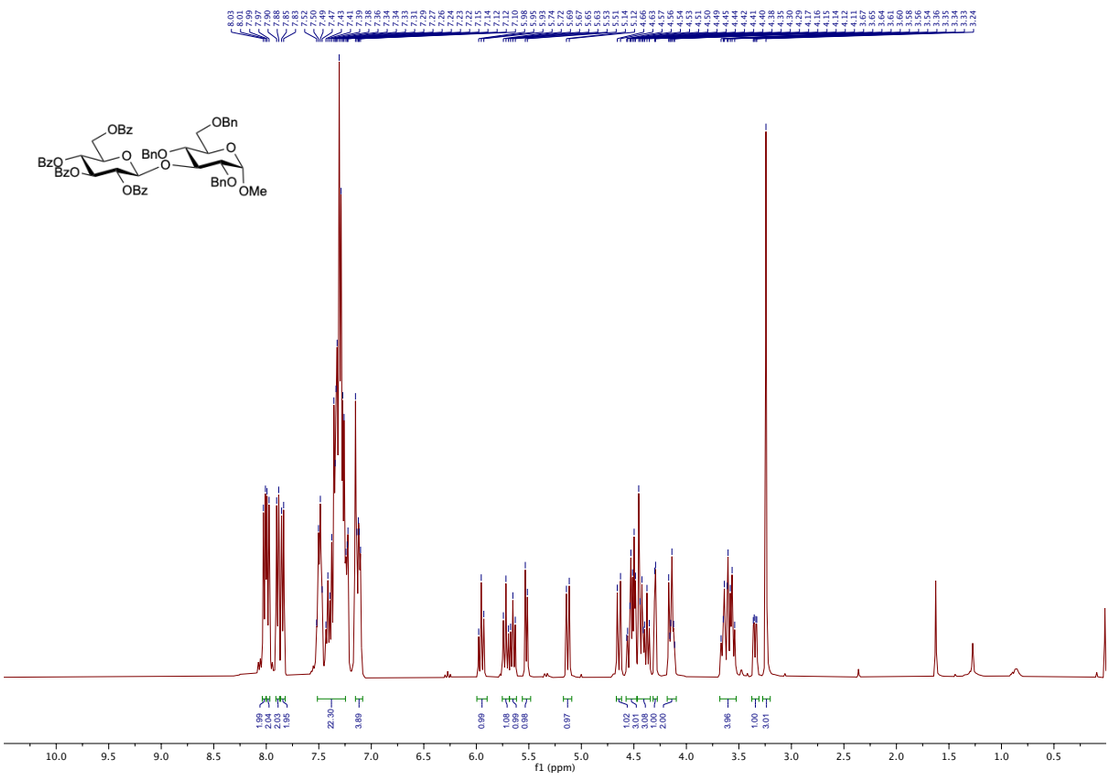


Figure S41. ^{1}H NMR spectrum of **5i** ($CDCl_3$, 400 MHz, 25 ºC).

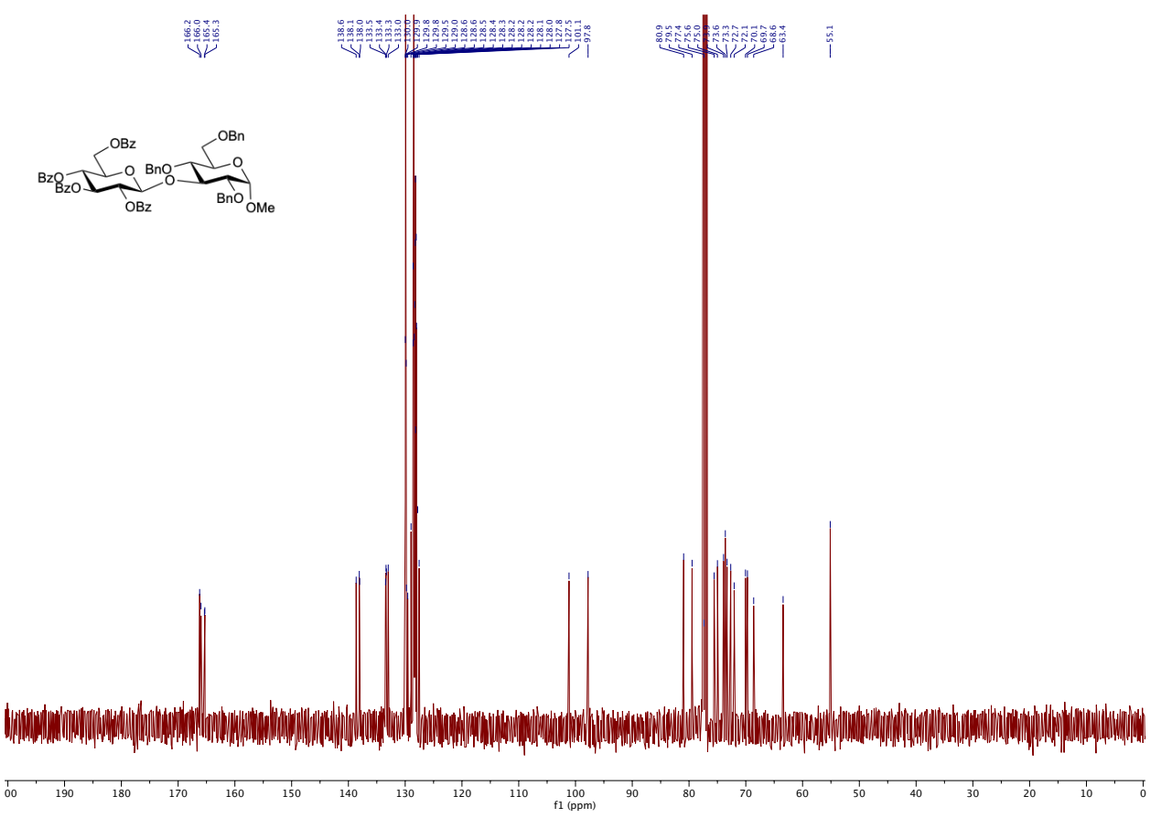


Figure S42. ^{13}C NMR spectrum of **5i** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **5j**

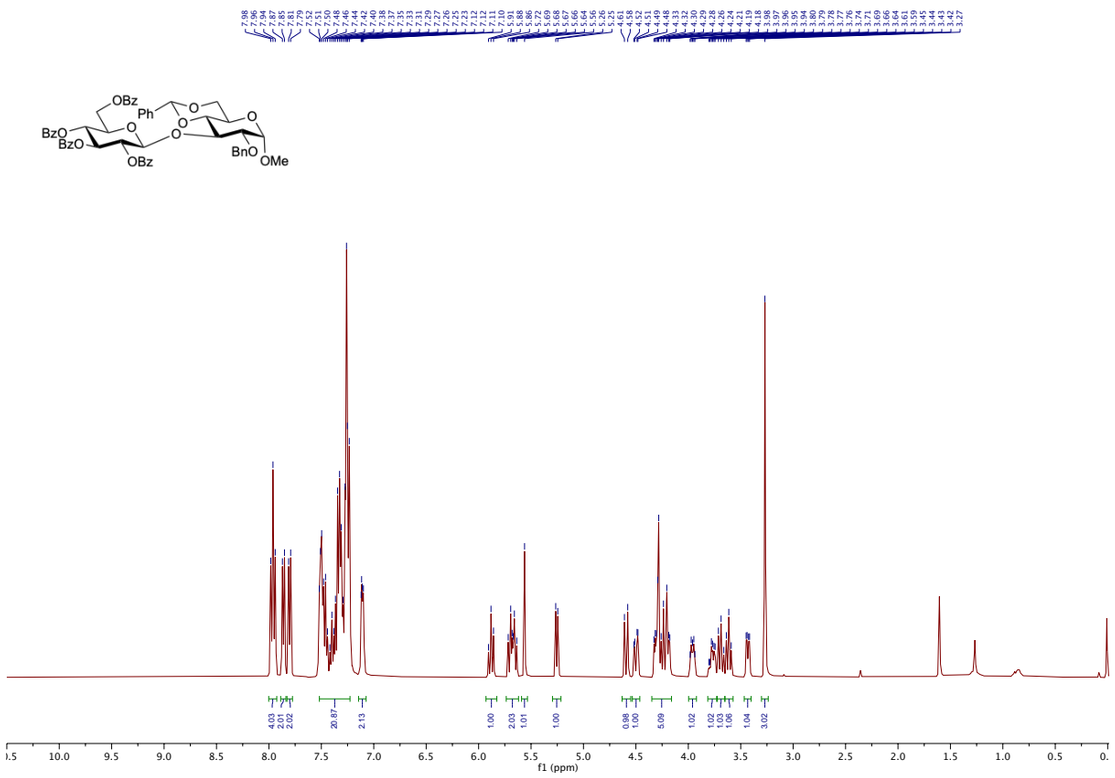


Figure S43. ^{1}H NMR spectrum of **5j** ($CDCl_3$, 400 MHz, 25 °C).

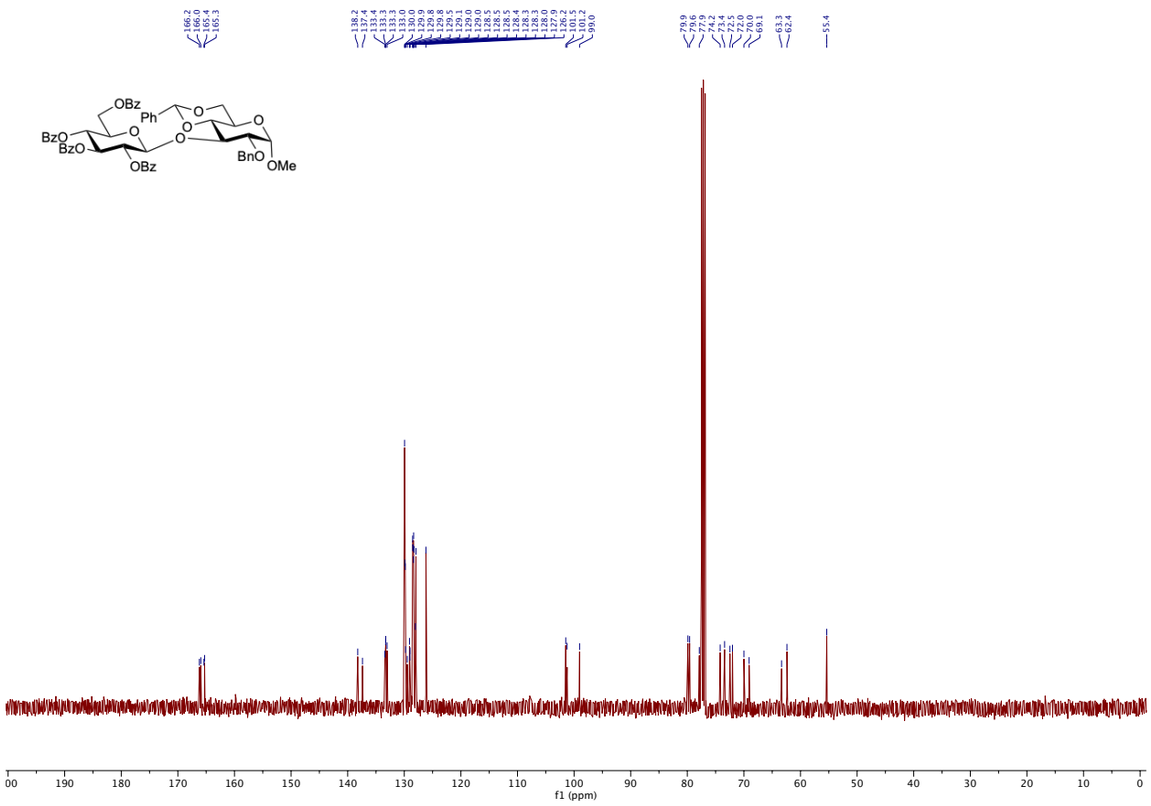


Figure S44. ^{13}C NMR spectrum of **5j** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5k**

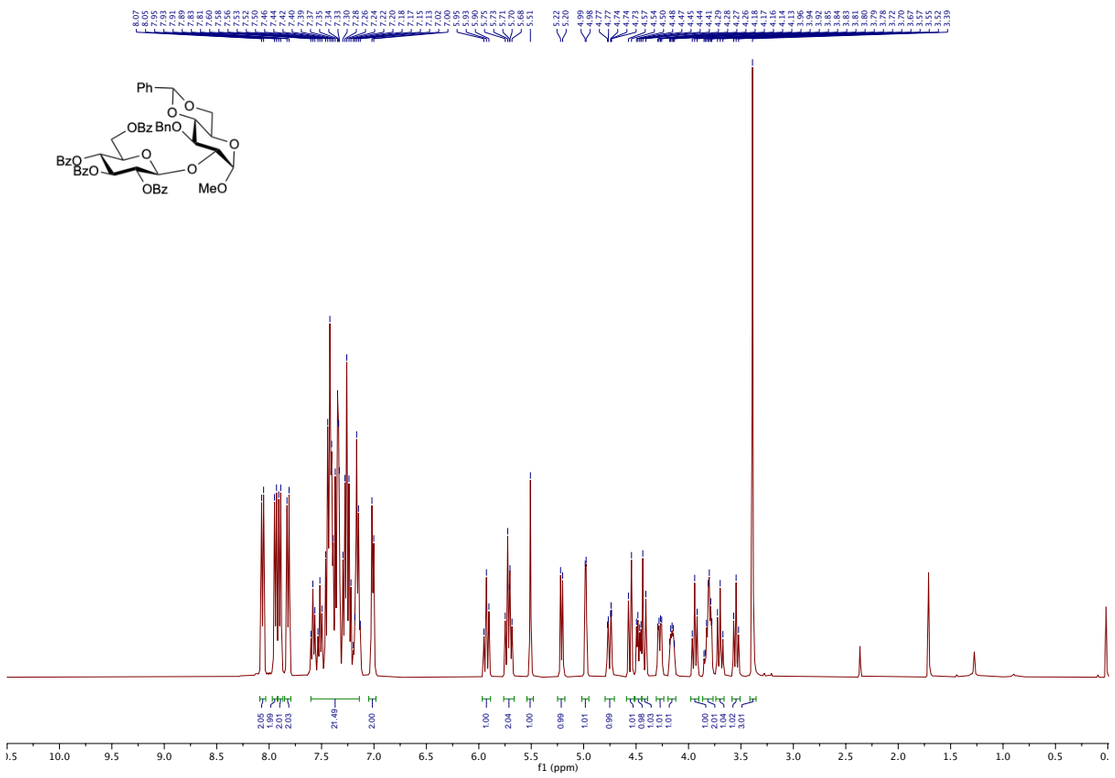


Figure S45. ^{1}H NMR spectrum of **5k** ($CDCl_3$, 400 MHz, 25 °C).

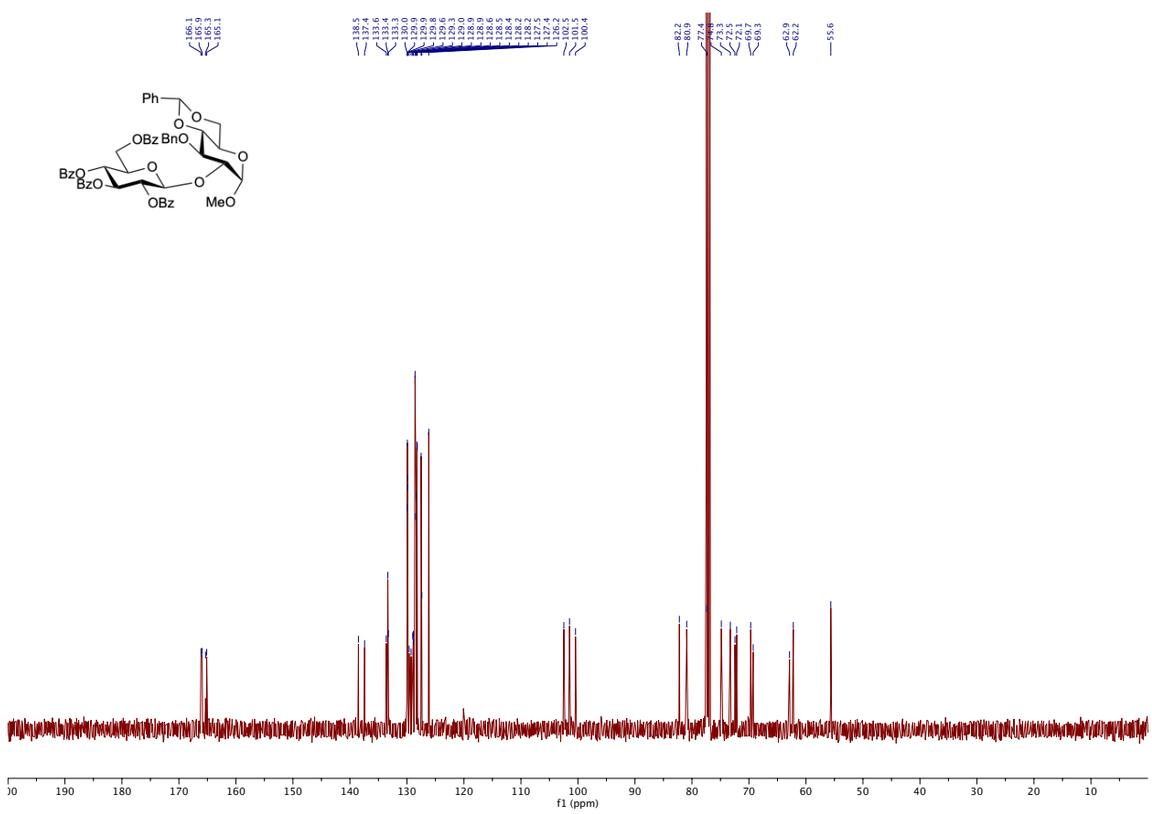


Figure S46. ^{13}C NMR spectrum of **5k** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5l**

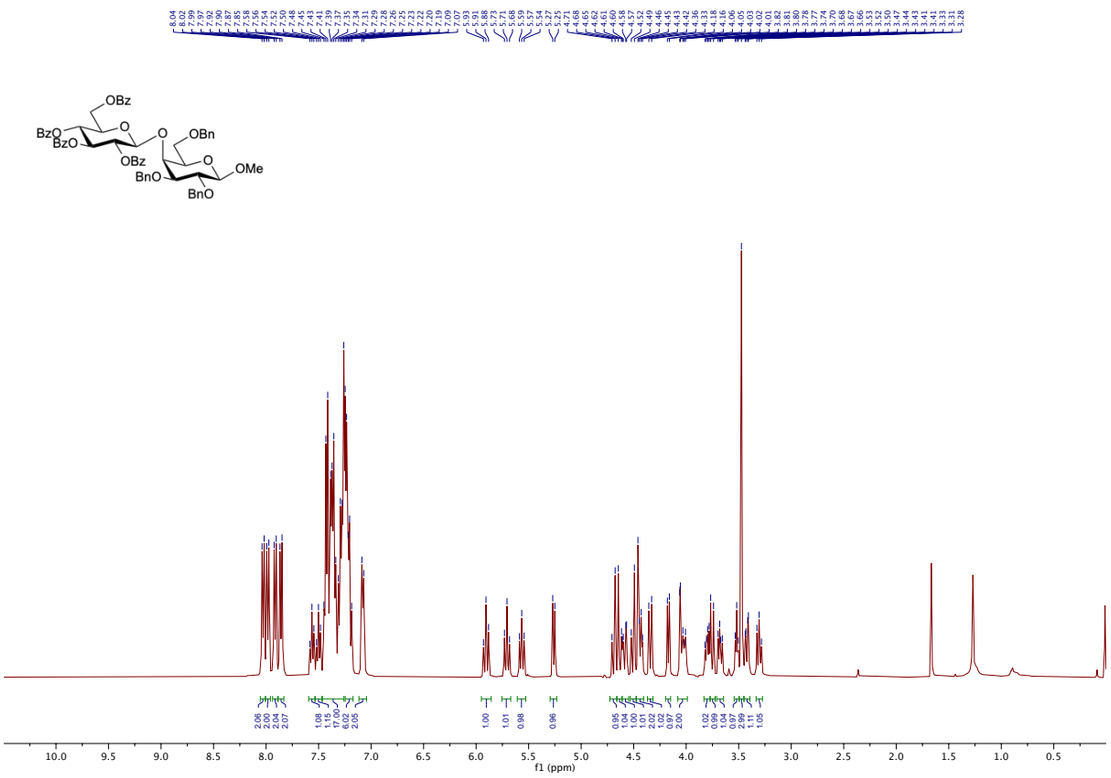


Figure S47. ^{1}H NMR spectrum of **5l** ($CDCl_3$, 400 MHz, 25 ºC).

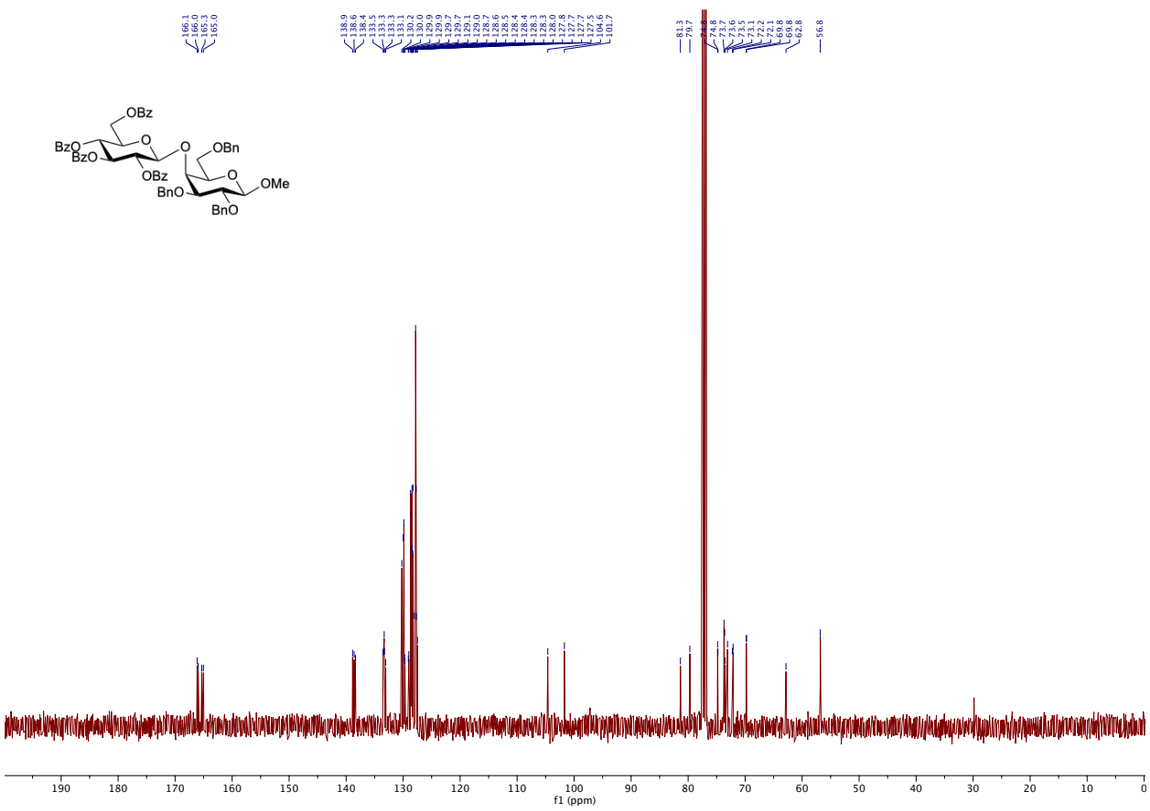


Figure S48. ^{13}C NMR spectrum of **5l** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **5m**

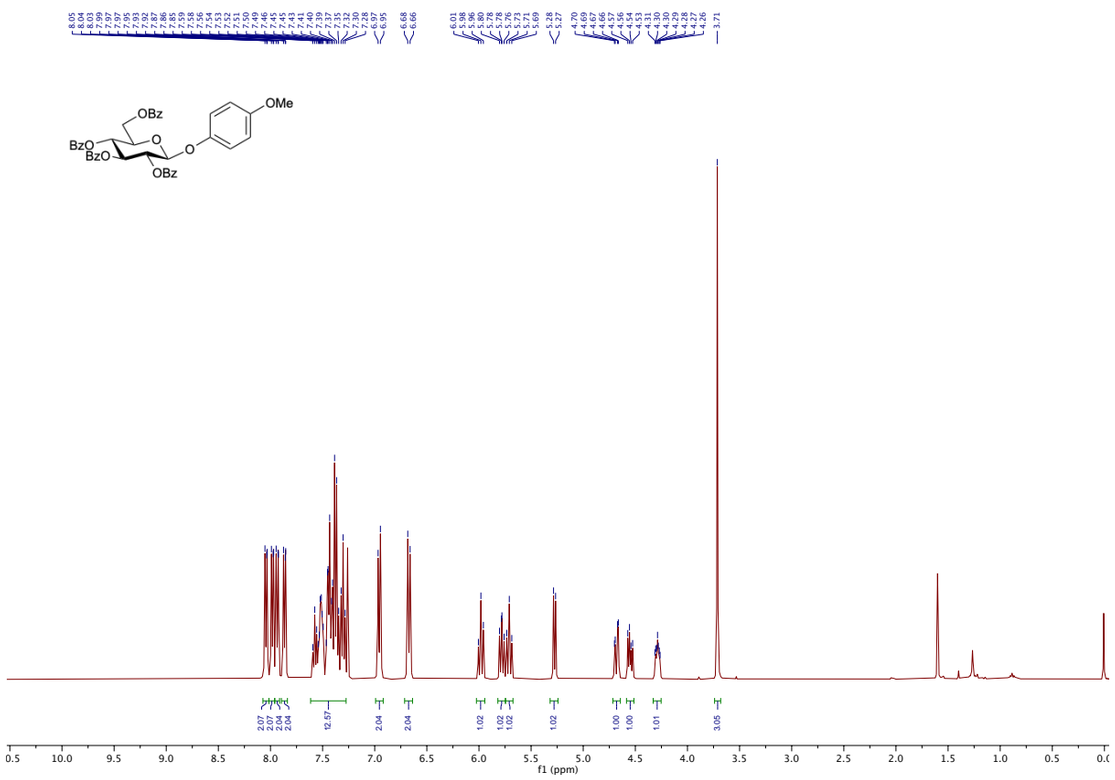


Figure S49. ^{1}H NMR spectrum of **5m** ($CDCl_3$, 400 MHz, 25 °C).

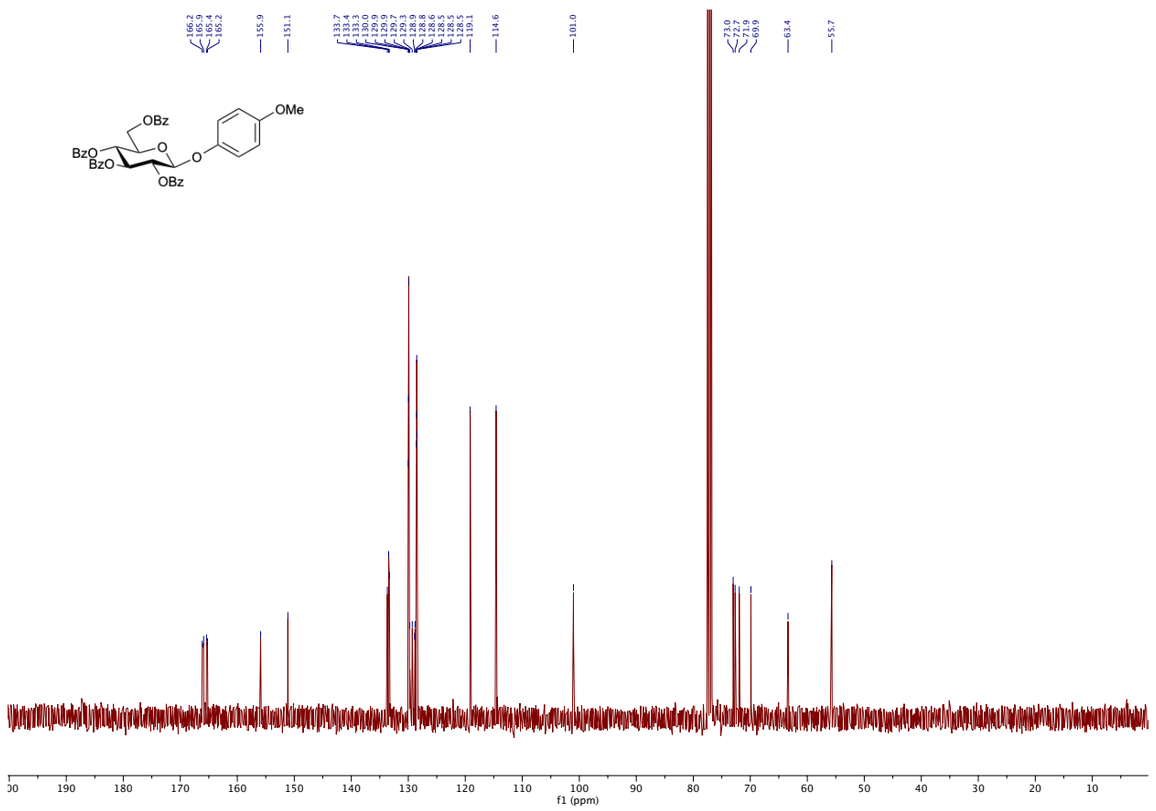


Figure S50. ^{13}C NMR spectrum of **5m** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5n**

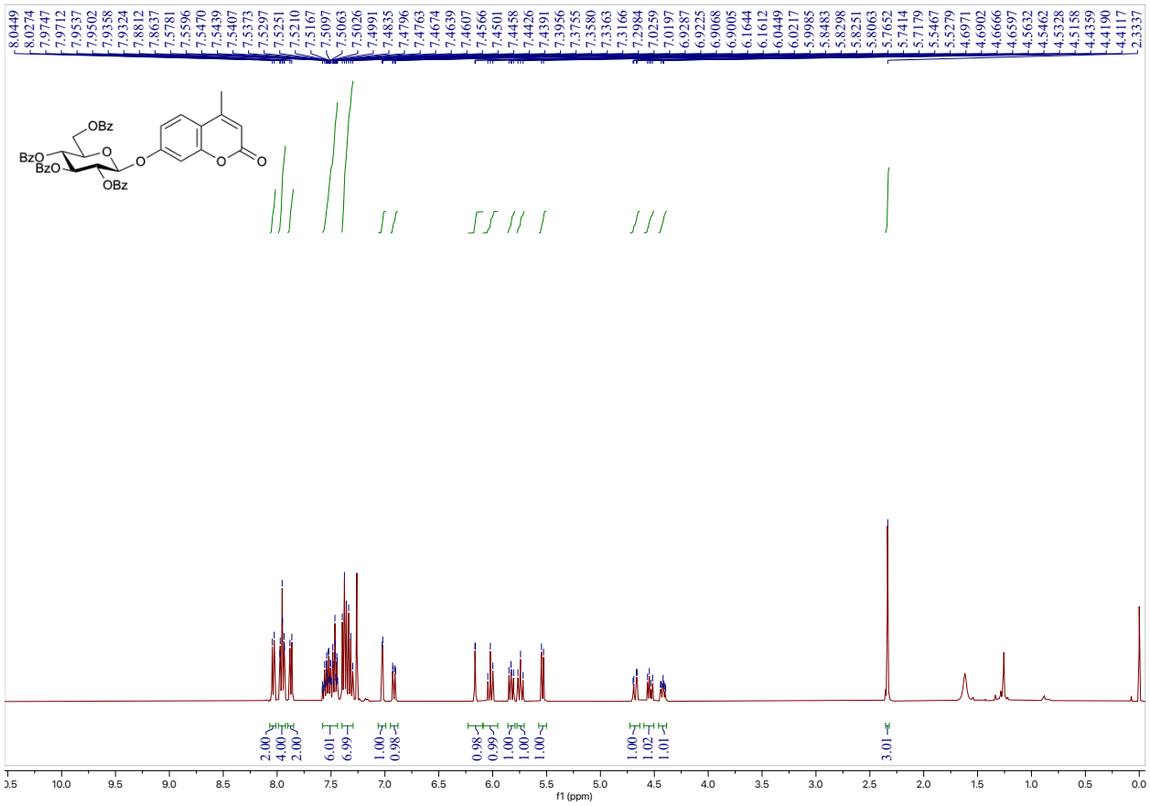


Figure S51. ^{1}H NMR spectrum of **5n** ($CDCl_3$, 400 MHz, 25 °C).

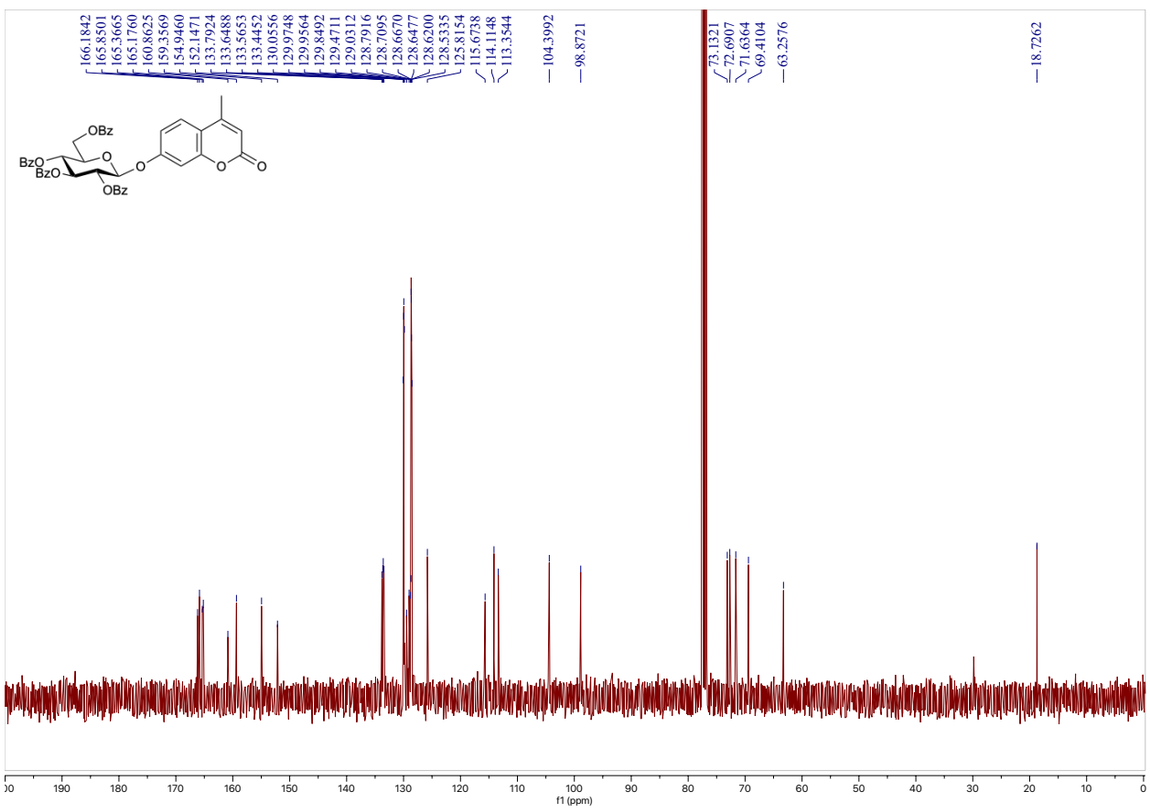


Figure S52. ^{13}C NMR spectrum of **5n** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5o**

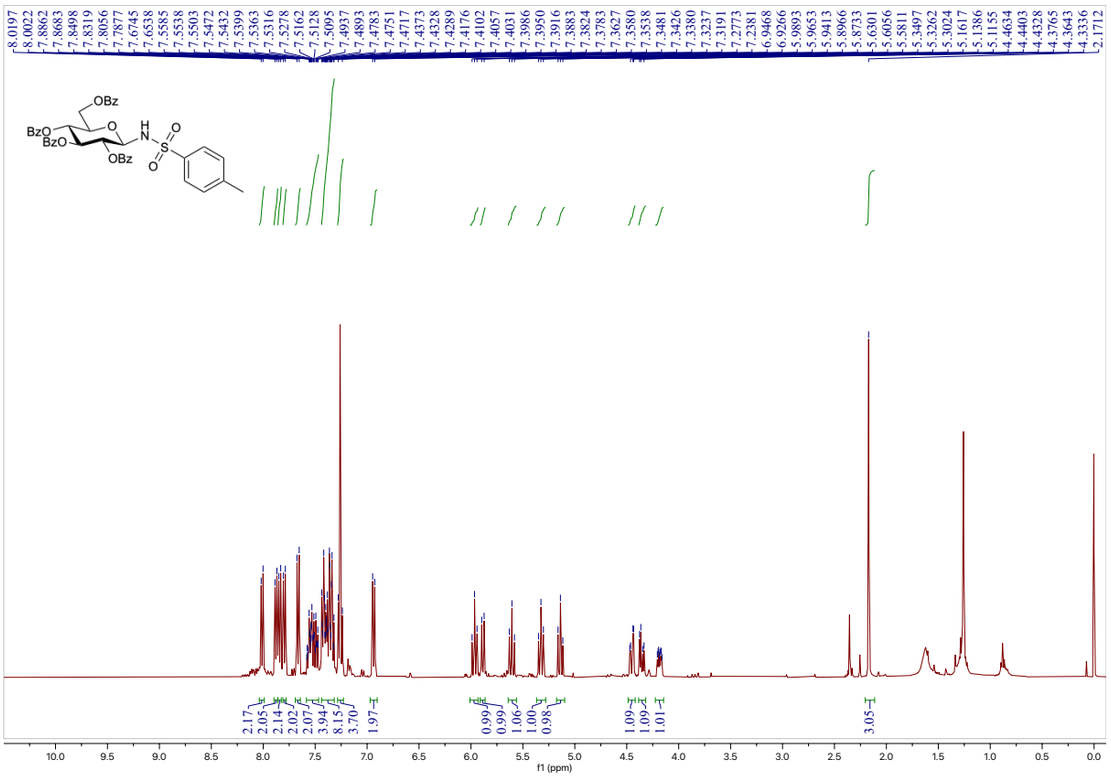


Figure S53. ^{1}H NMR spectrum of **5o** ($CDCl_3$, 400 MHz, 25 °C).

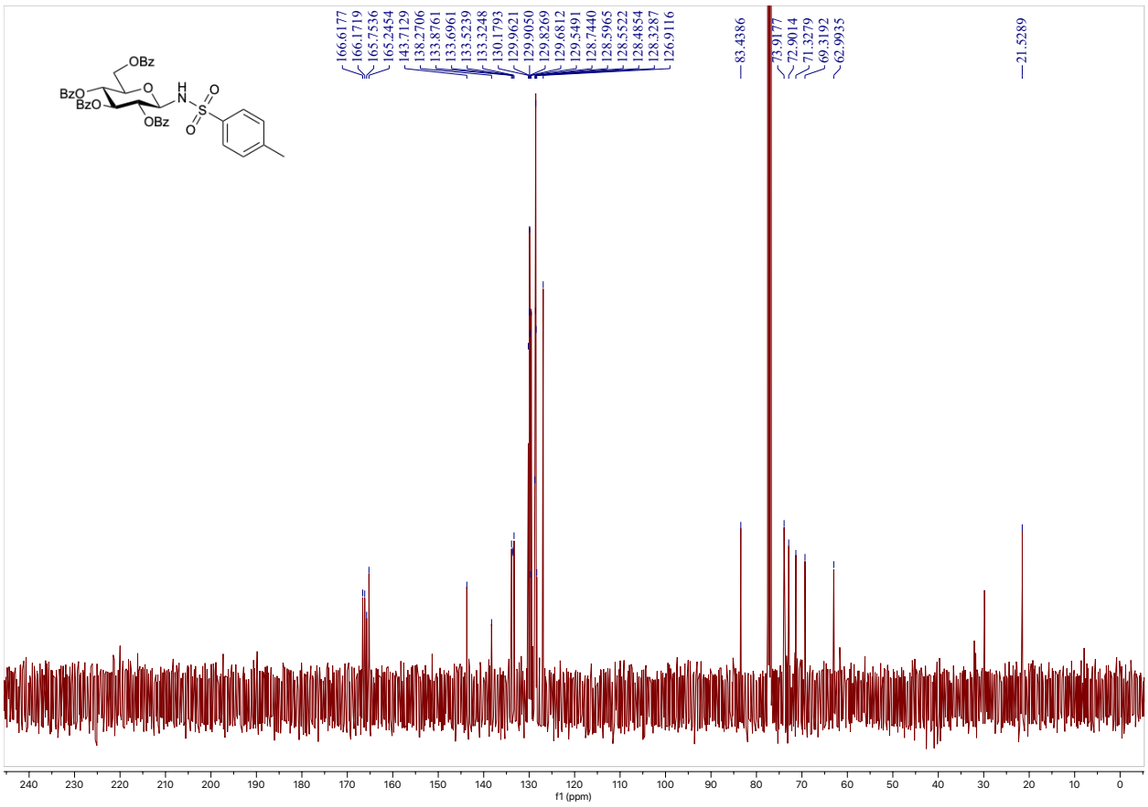


Figure S54. ^{13}C NMR spectrum of **5o** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5p**

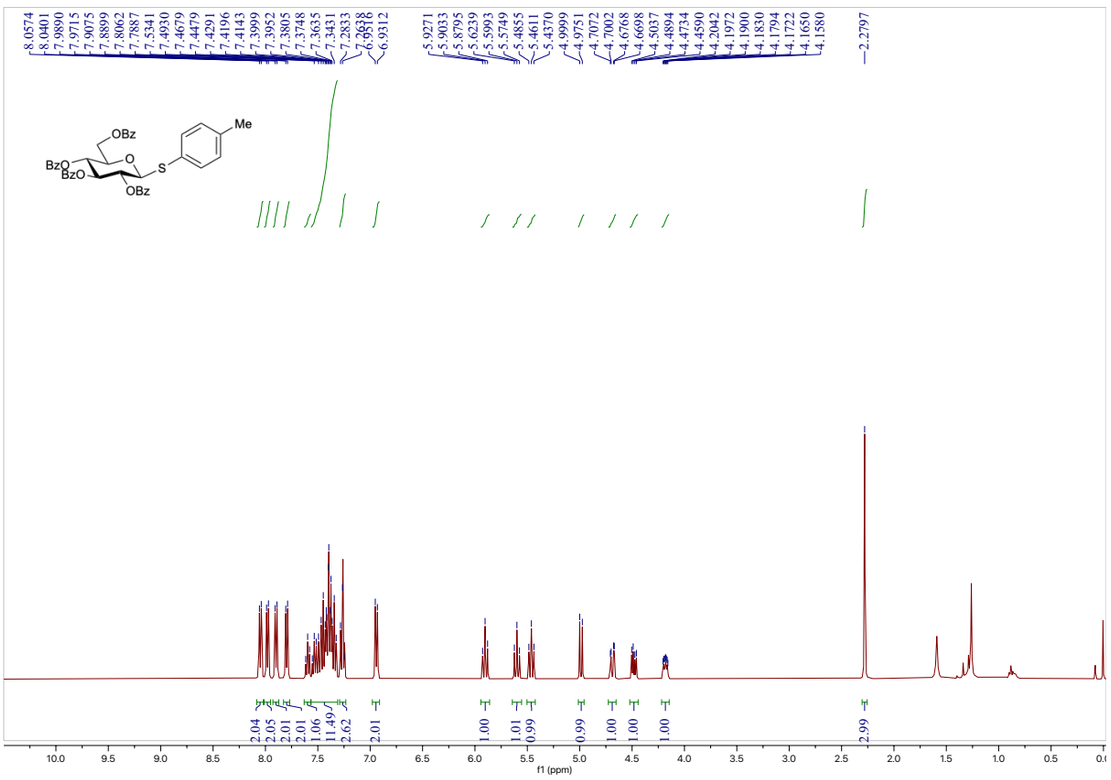


Figure S55. ^{1}H NMR spectrum of **5p** ($CDCl_3$, 400 MHz, 25 °C).

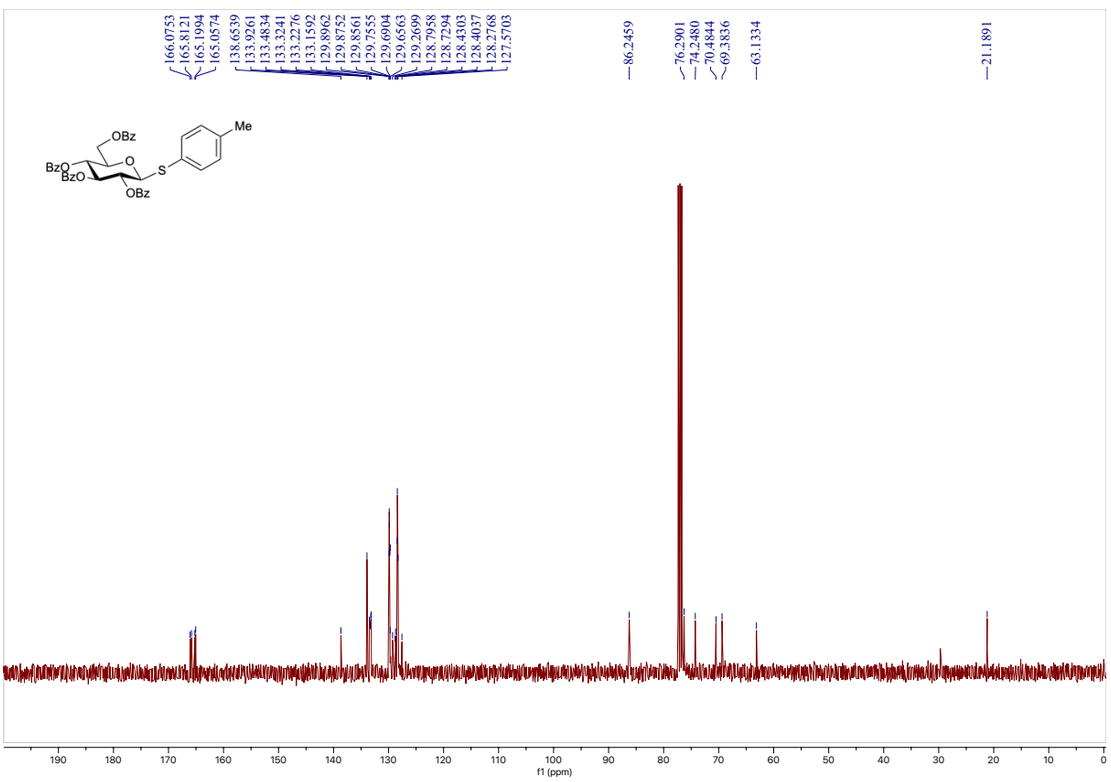


Figure S56. ^{13}C NMR spectrum of **5p** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5q**

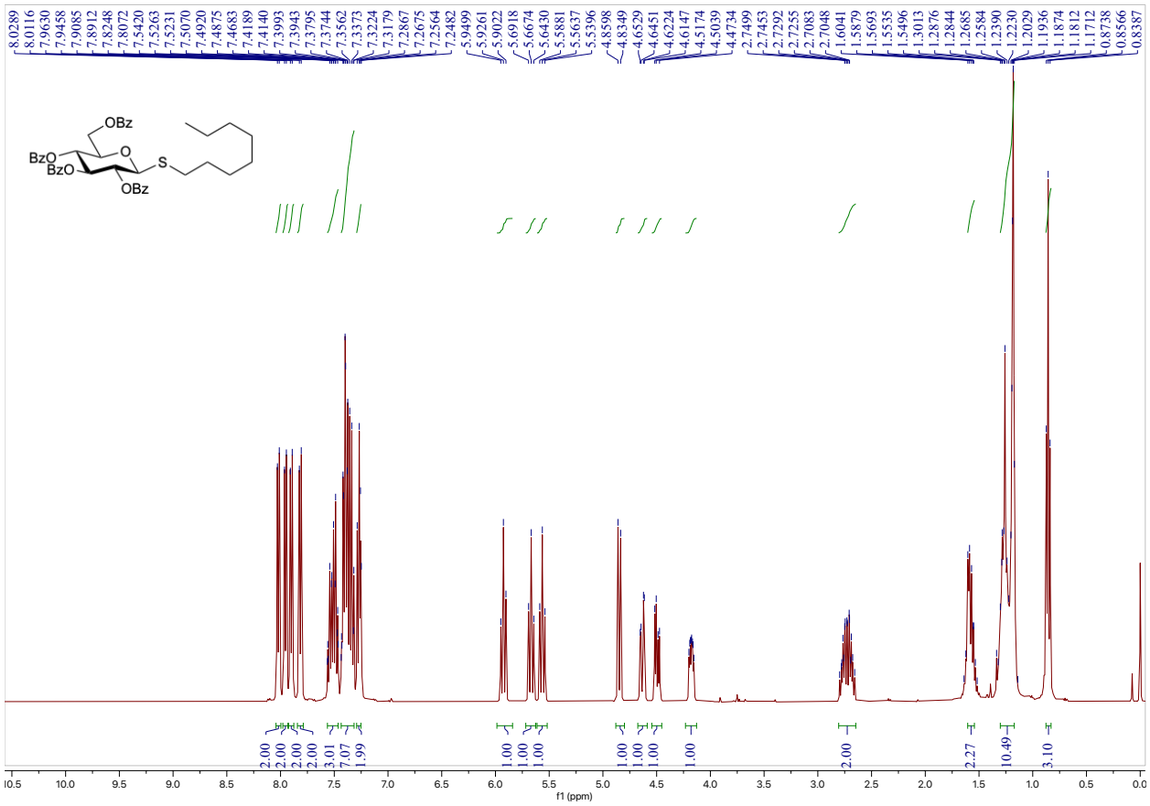


Figure S57. ^{1}H NMR spectrum of **5q** ($CDCl_3$, 400 MHz, 25 °C).

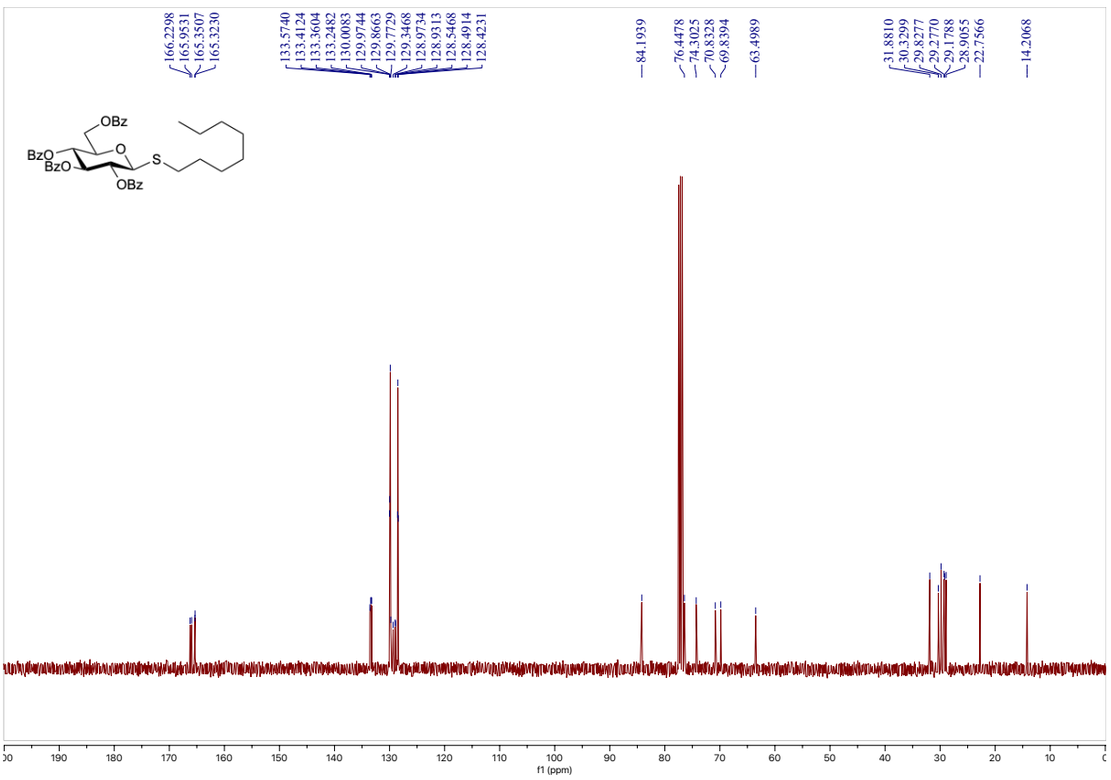


Figure S58. ^{13}C NMR spectrum of **5q** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5r**

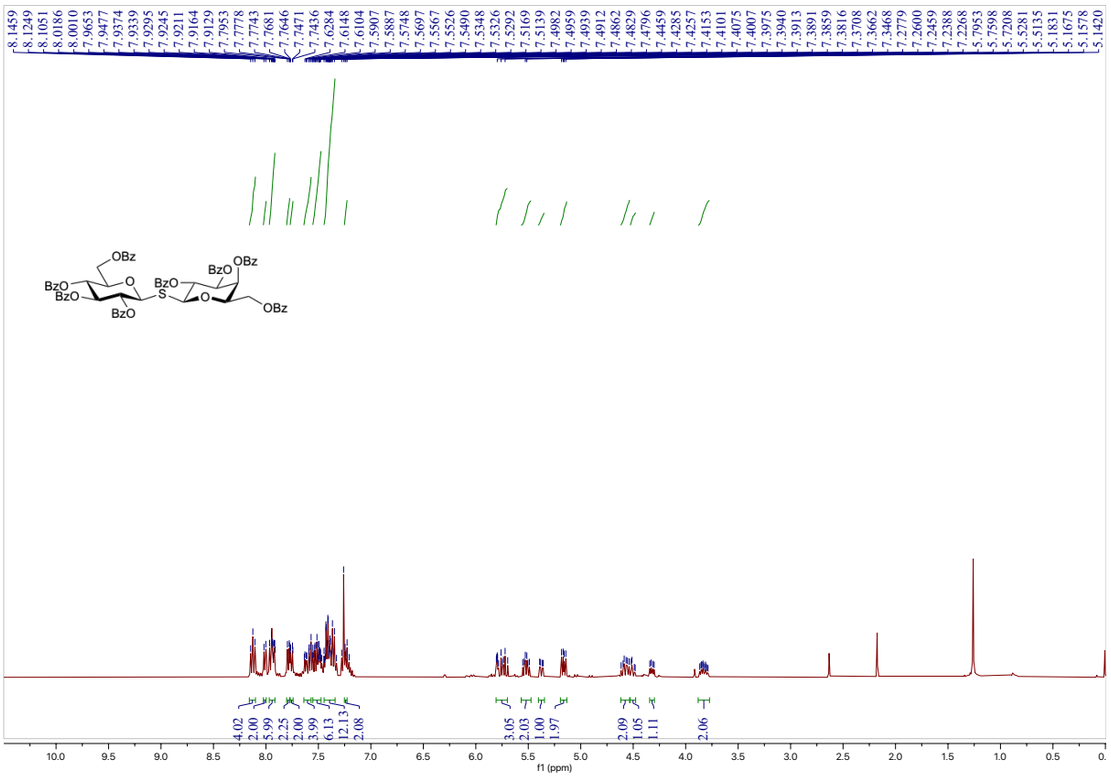


Figure S59. ^{1}H NMR spectrum of **5r** ($CDCl_3$, 400 MHz, 25 ºC).

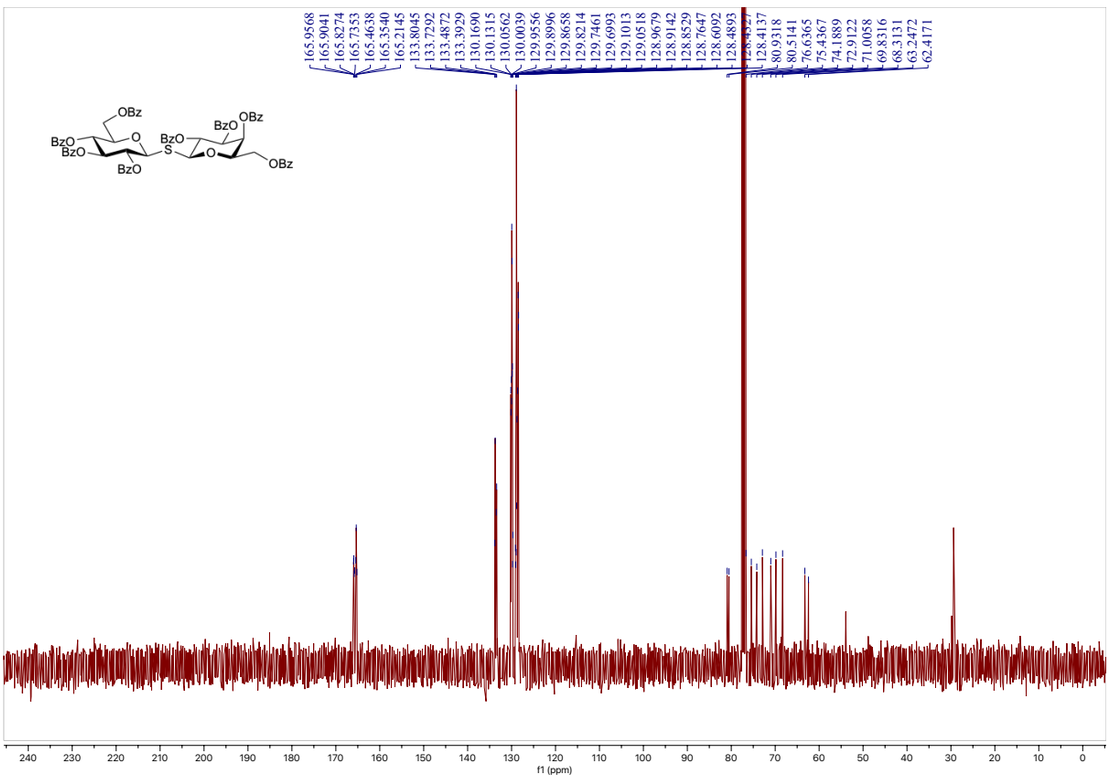


Figure S60. ^{13}C NMR spectrum of **5r** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **5s**

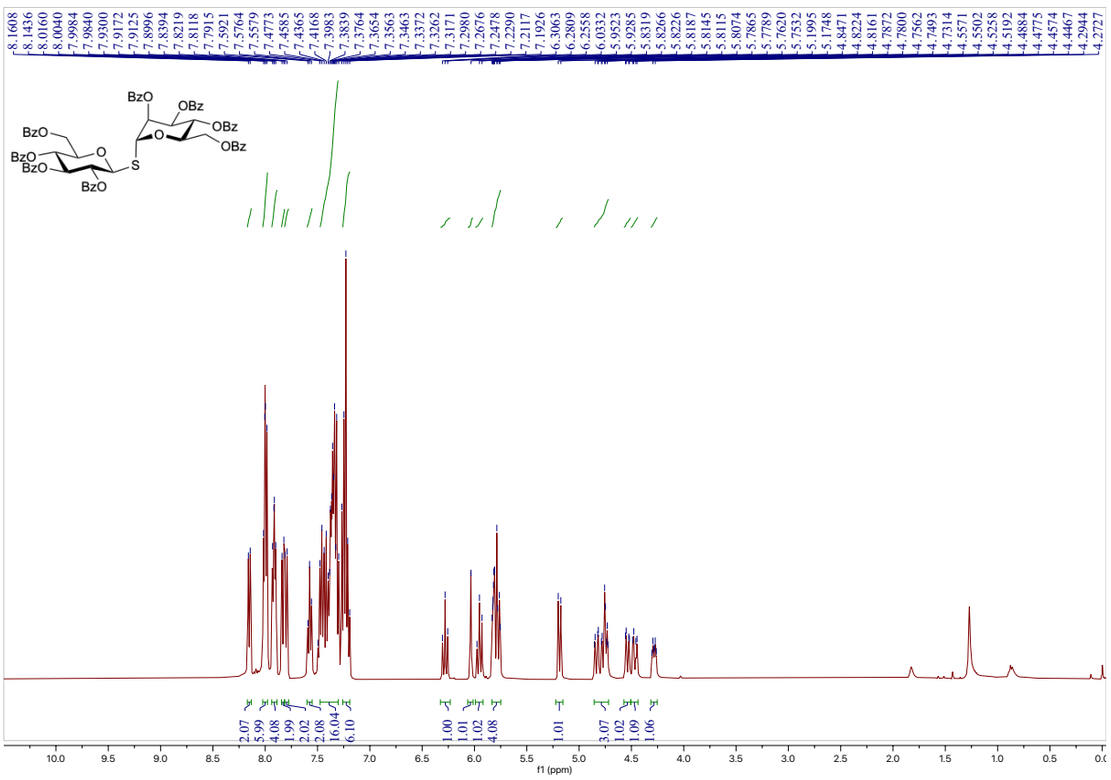


Figure S61. ^{1}H NMR spectrum of **5s** ($CDCl_3$, 400 MHz, 25 °C).

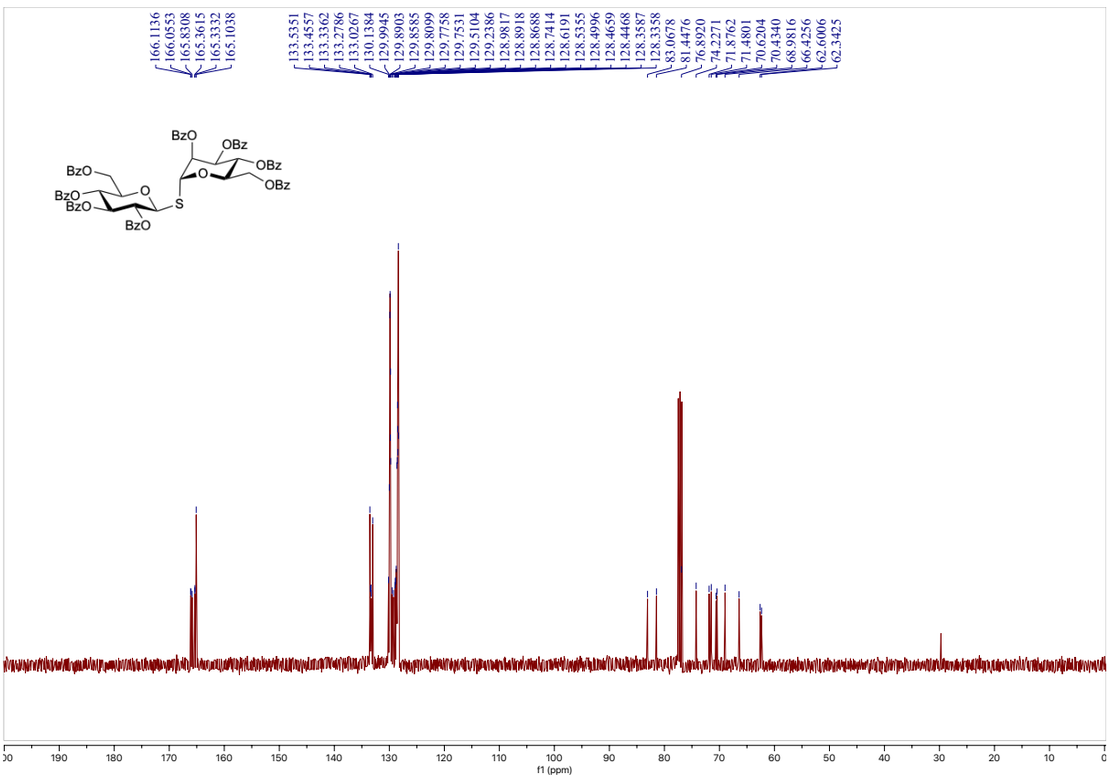


Figure S62. ^{13}C NMR spectrum of **5s** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **5t**

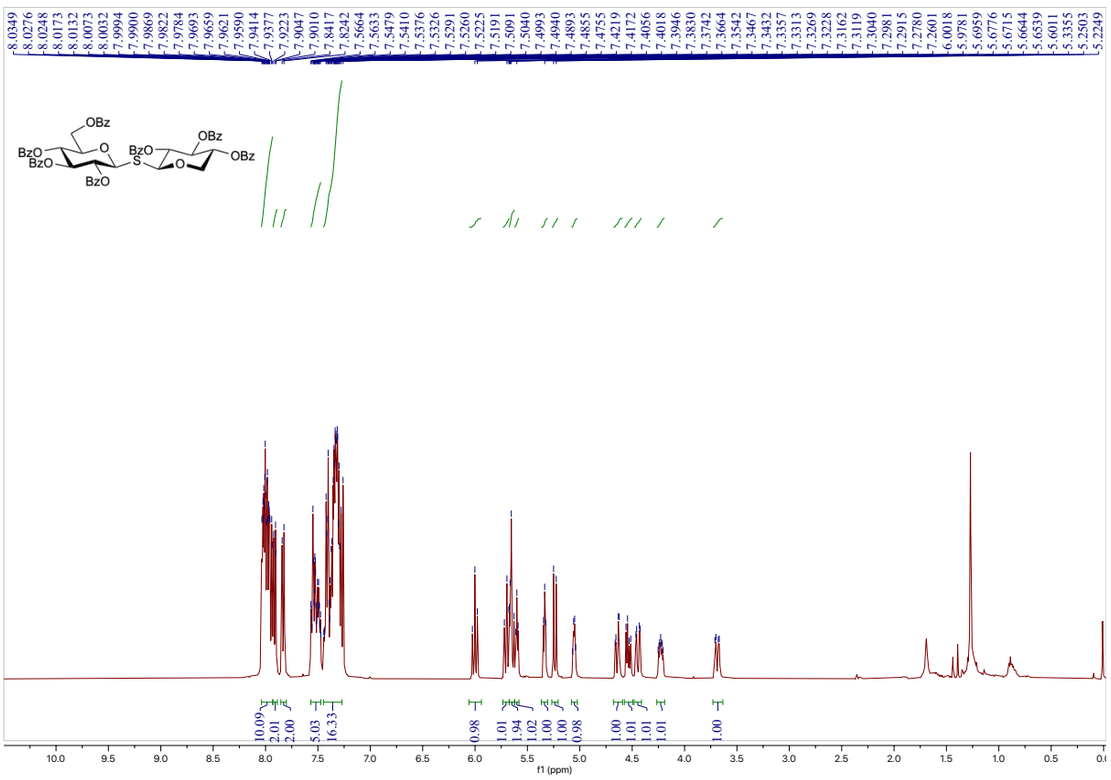


Figure S63. ^{1}H NMR spectrum of **5t** ($CDCl_3$, 400 MHz, 25 ºC).

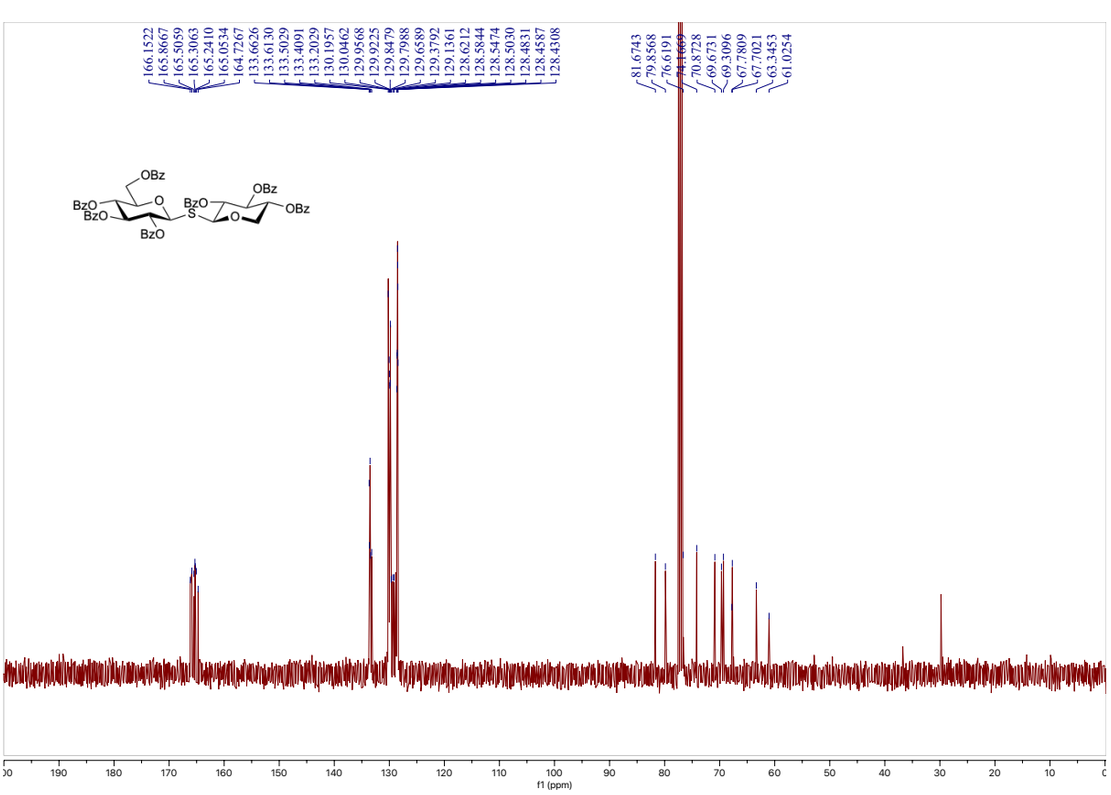


Figure S64. ^{13}C NMR spectrum of **5t** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **7a**

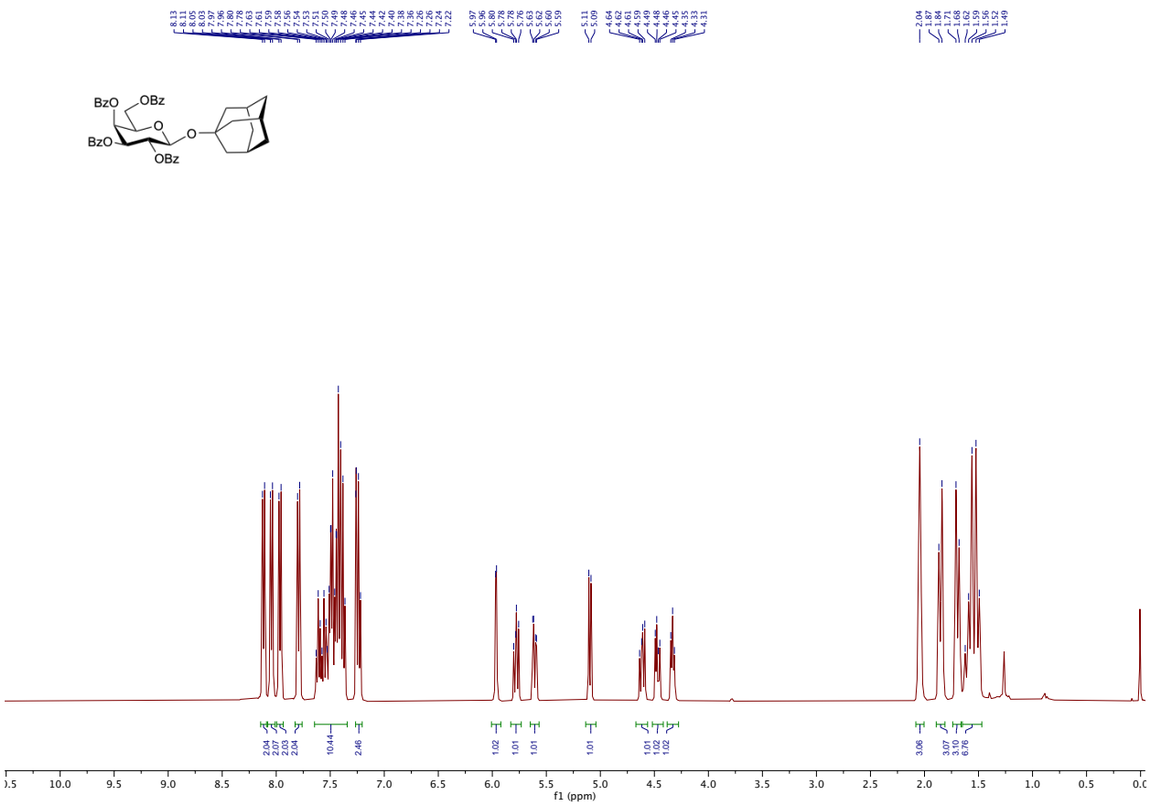


Figure S65. ^{1}H NMR spectrum of **7a** ($CDCl_3$, 400 MHz, 25 ºC).

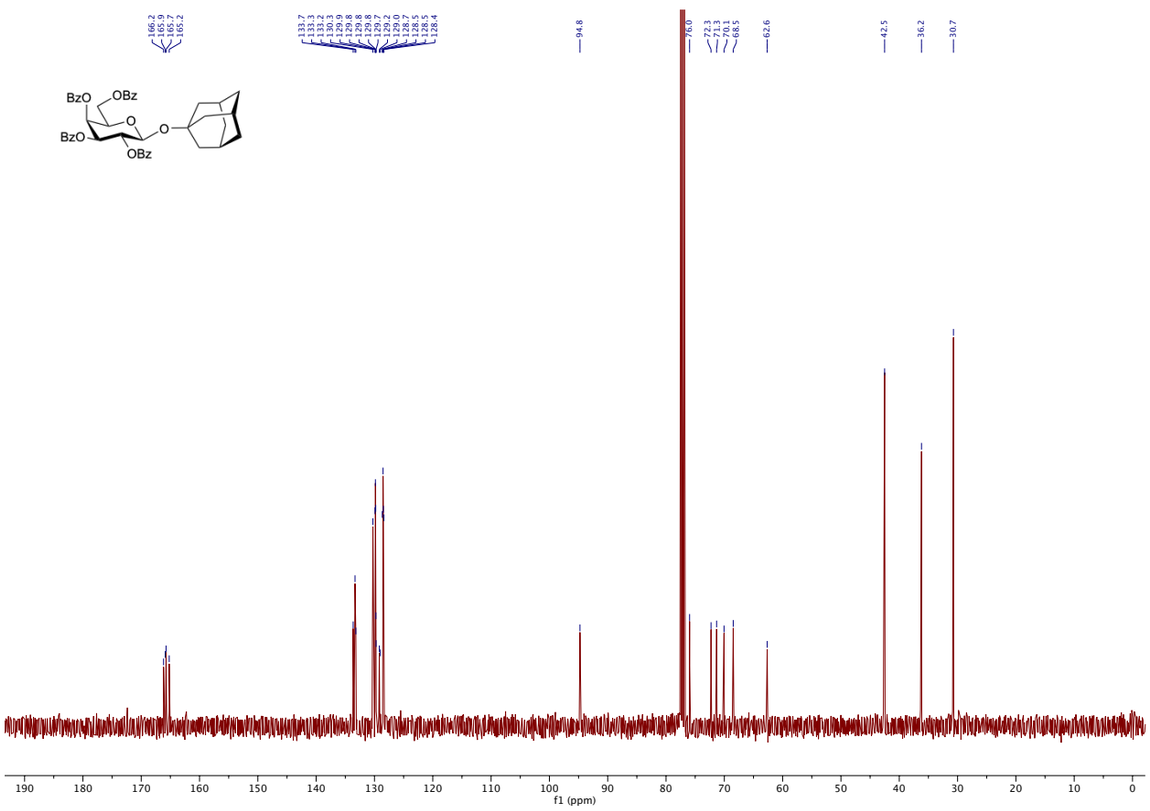


Figure S66. ^{13}C NMR spectrum of **7a** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **7b**

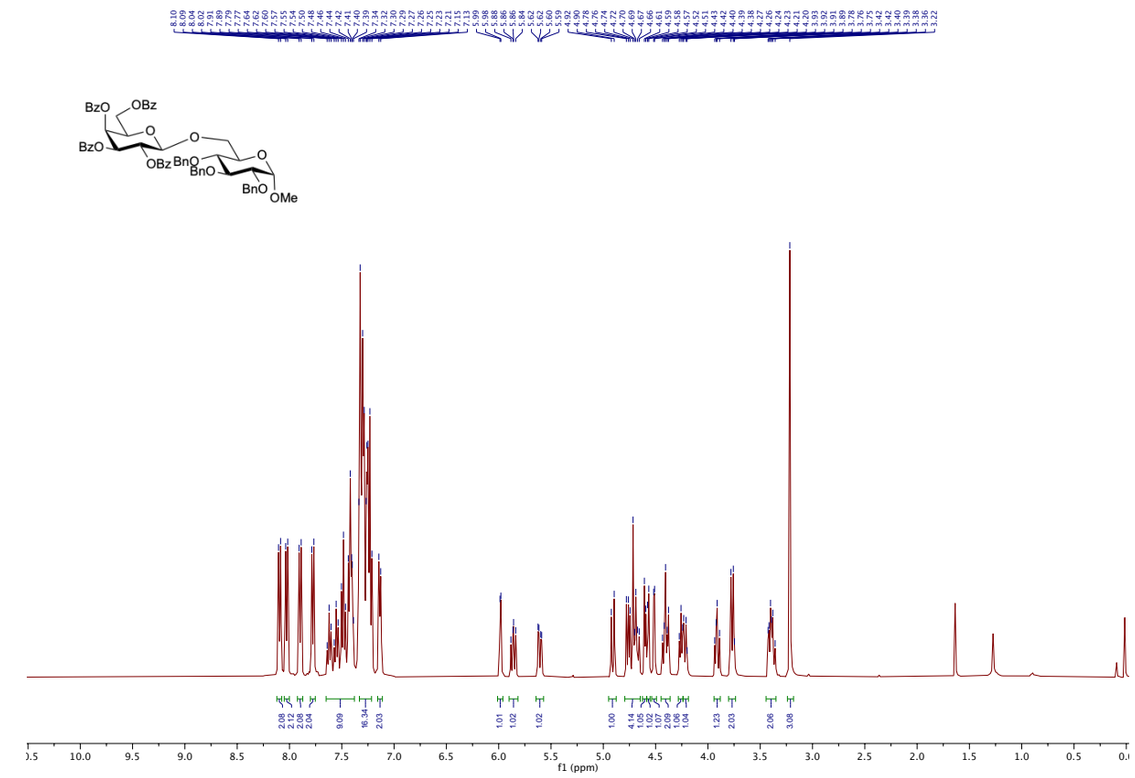


Figure S67. ^{1}H NMR spectrum of **7b** ($CDCl_3$, 400 MHz, 25 °C).

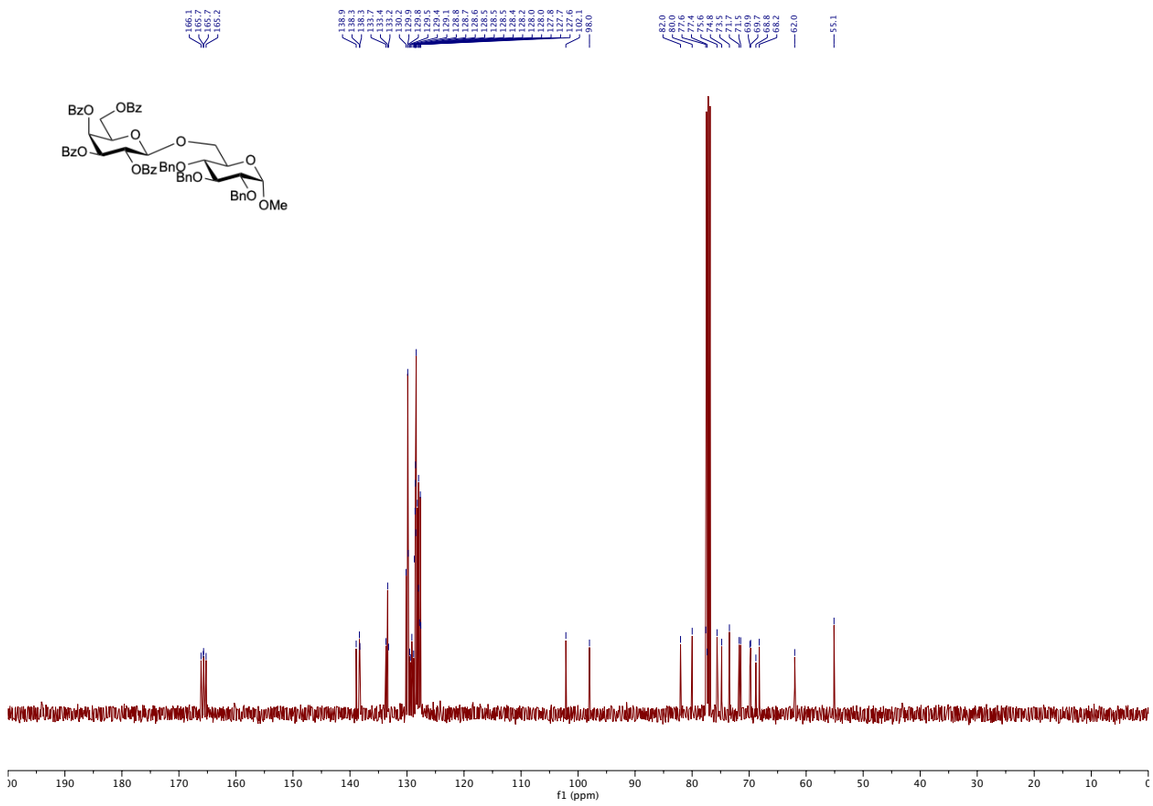


Figure S68. ^{13}C NMR spectrum of **7b** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7c**

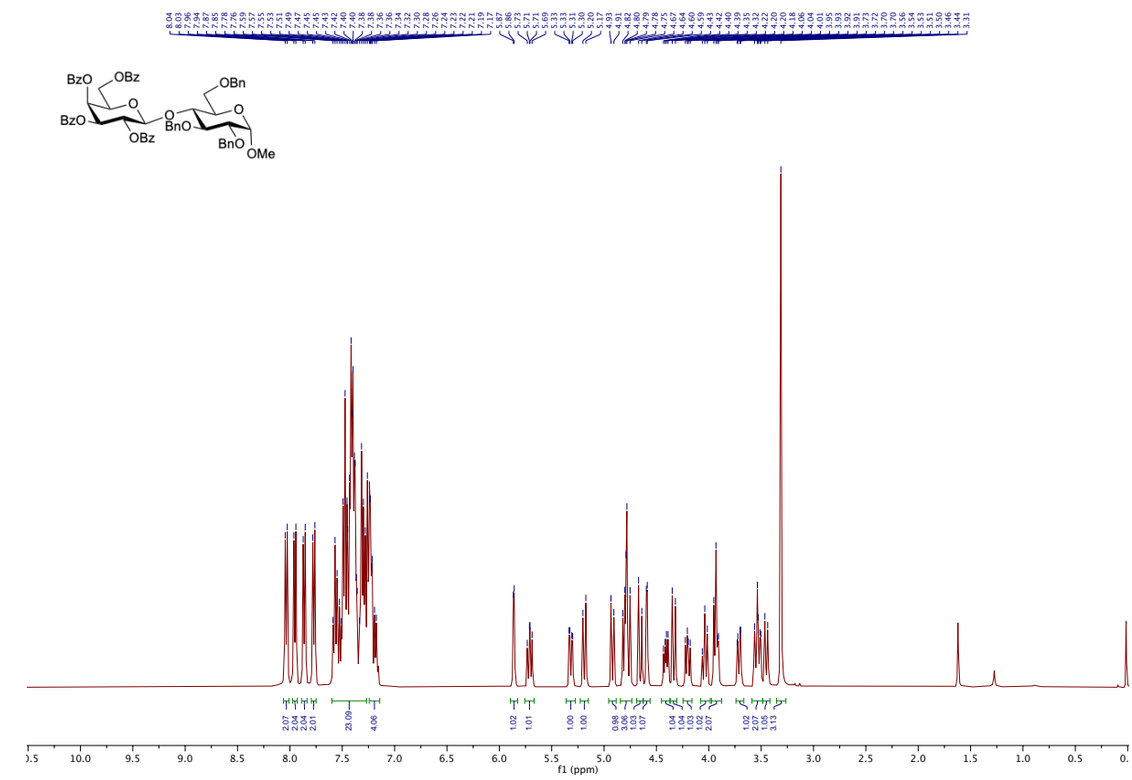


Figure S69. ^{1}H NMR spectrum of **7c** ($CDCl_3$, 400 MHz, 25 ºC).

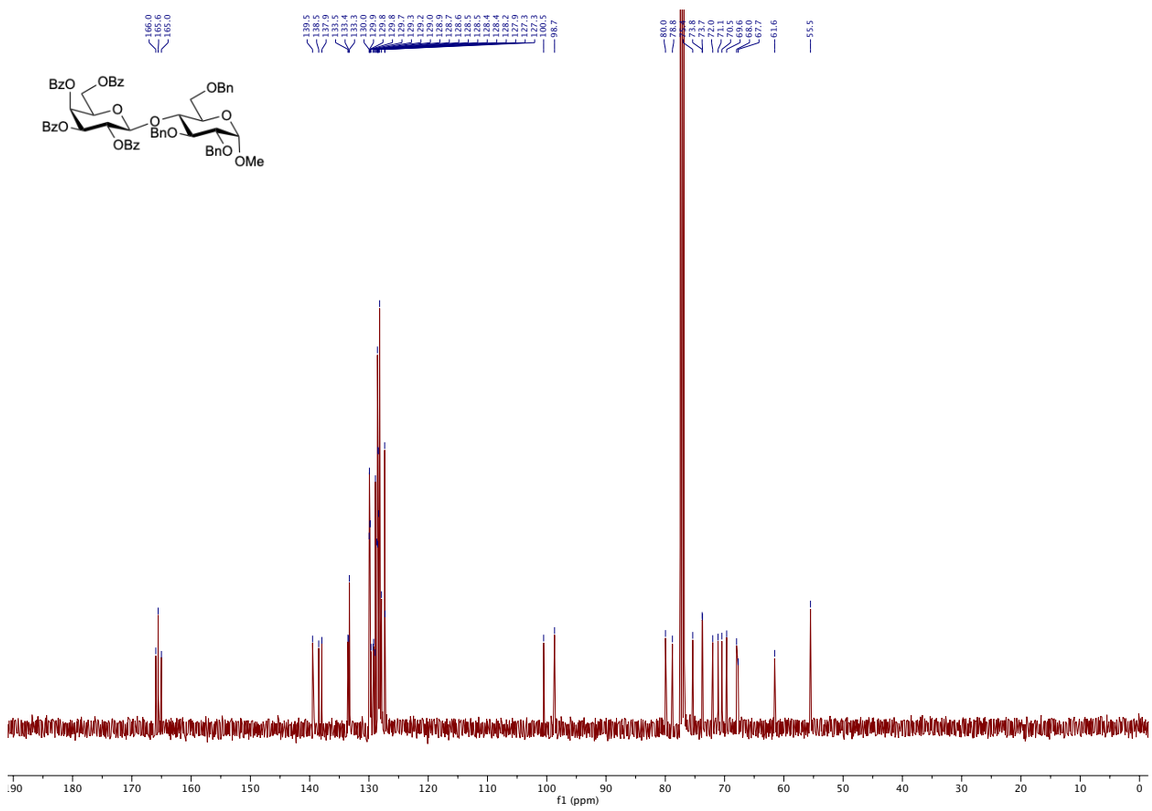


Figure S70. ^{13}C NMR spectrum of **7c** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **7d**

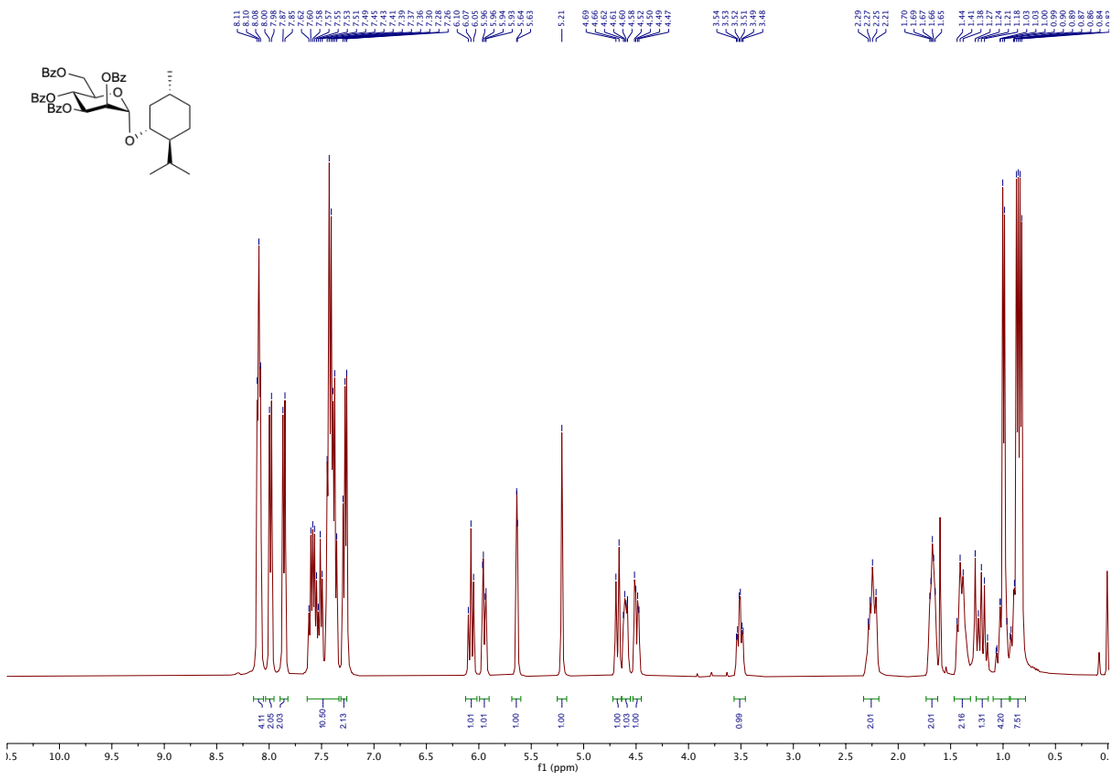


Figure S71. ^{1}H NMR spectrum of **7d** ($CDCl_3$, 400 MHz, 25 °C).

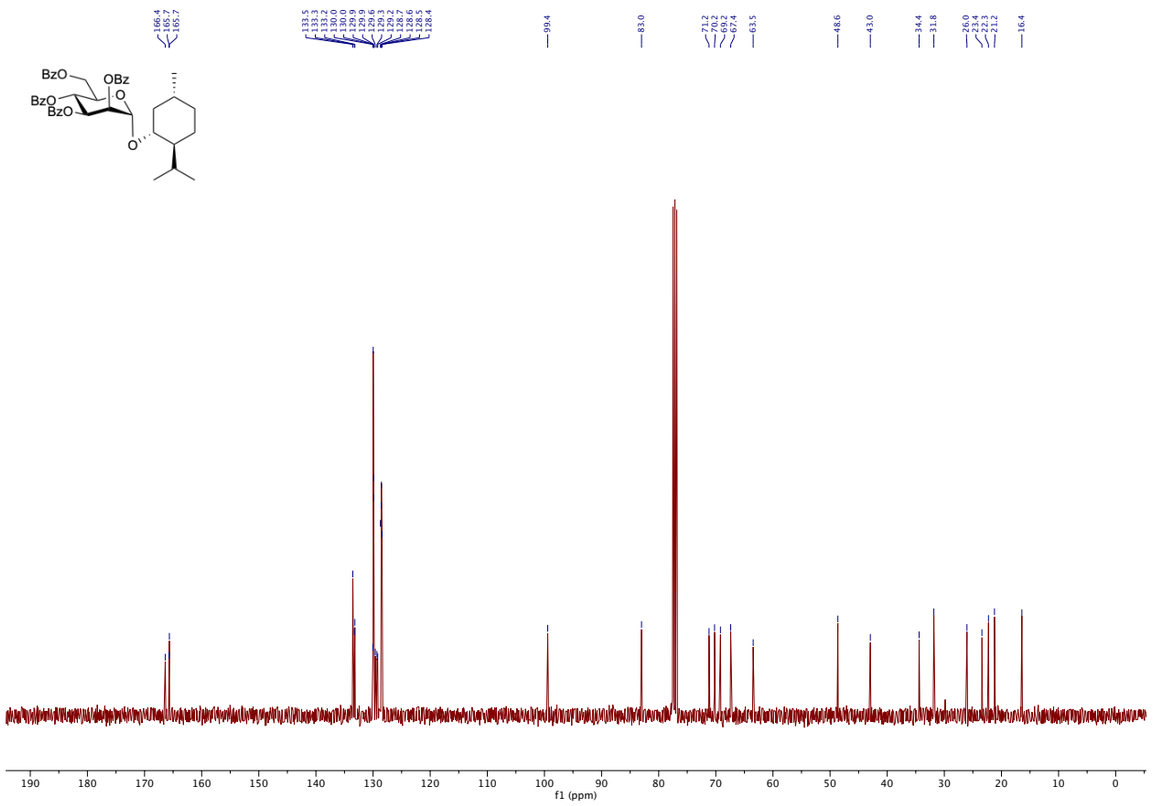


Figure S72. ^{13}C NMR spectrum of **7d** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7e**

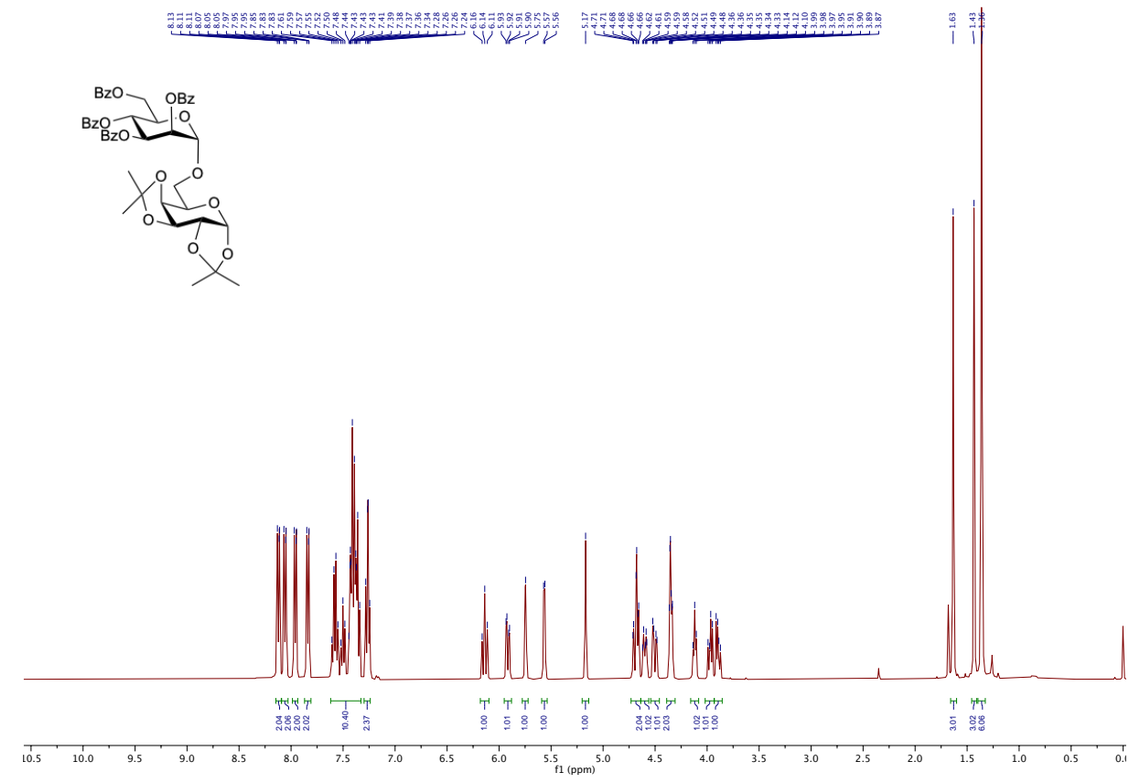


Figure S73. ^{1}H NMR spectrum of **7e** ($CDCl_3$, 400 MHz, 25 °C).

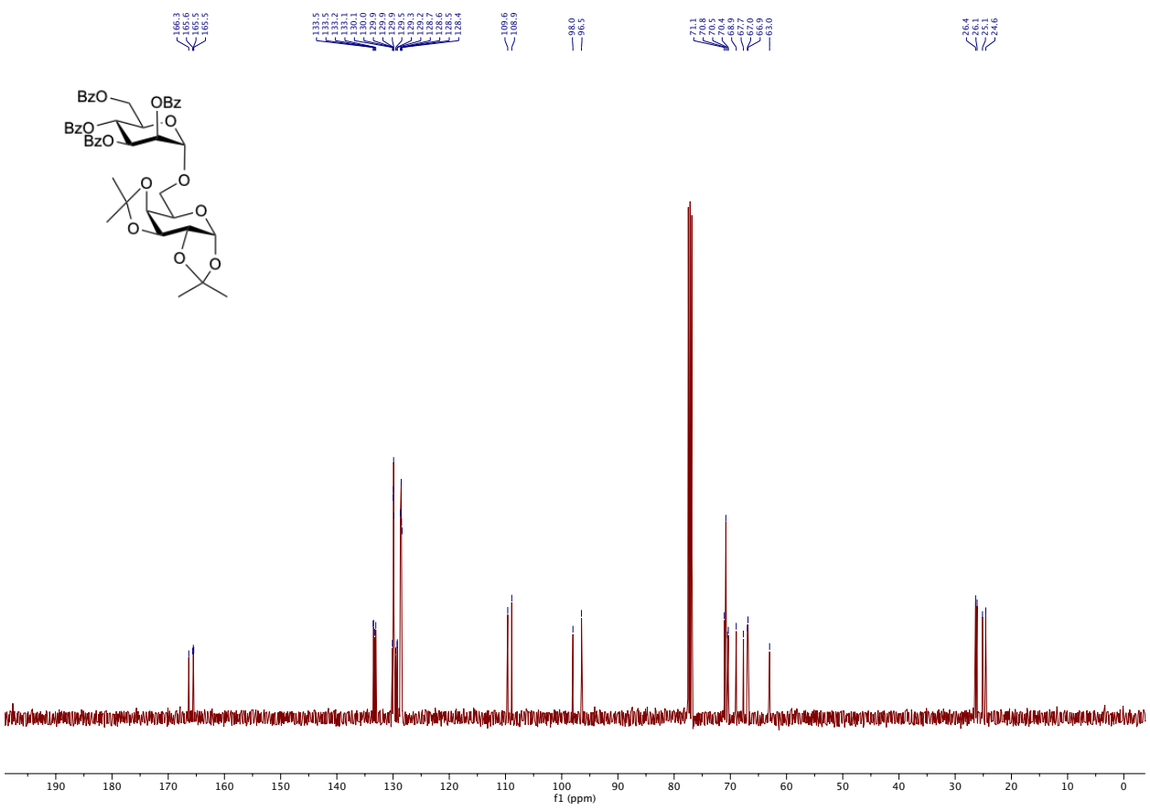


Figure S74. ^{13}C NMR spectrum of **7e** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7f**

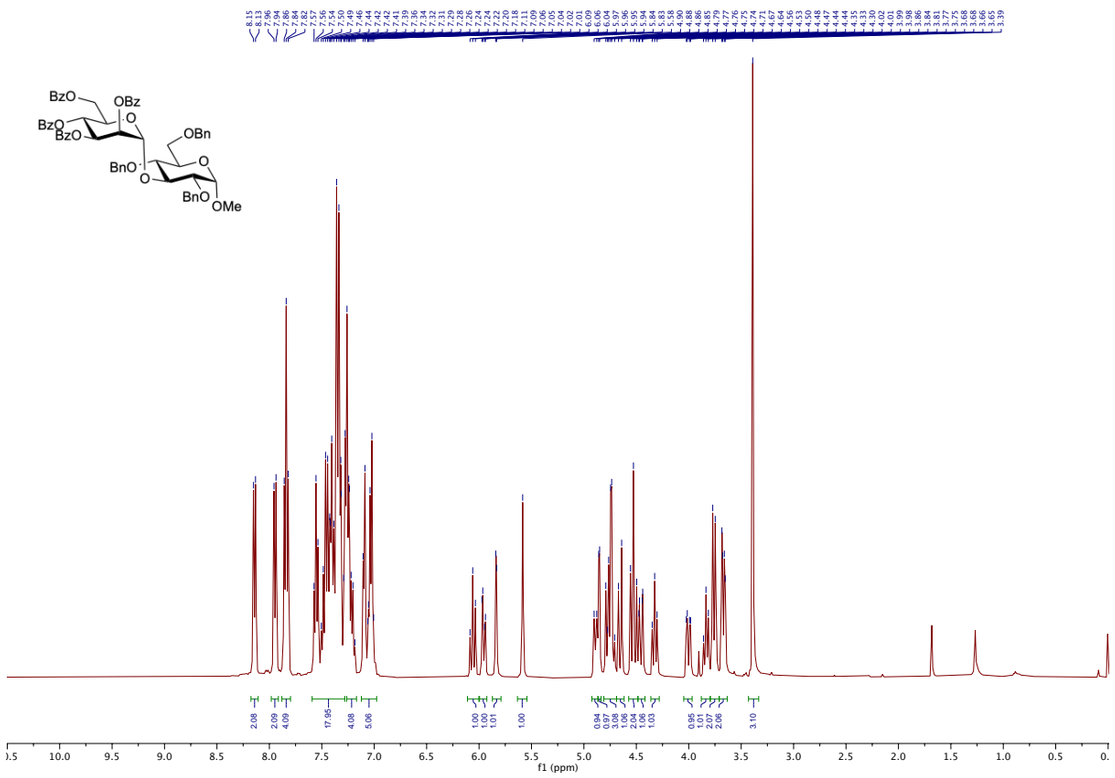


Figure S75. ^{1}H NMR spectrum of **7f** ($CDCl_3$, 400 MHz, 25 ºC).

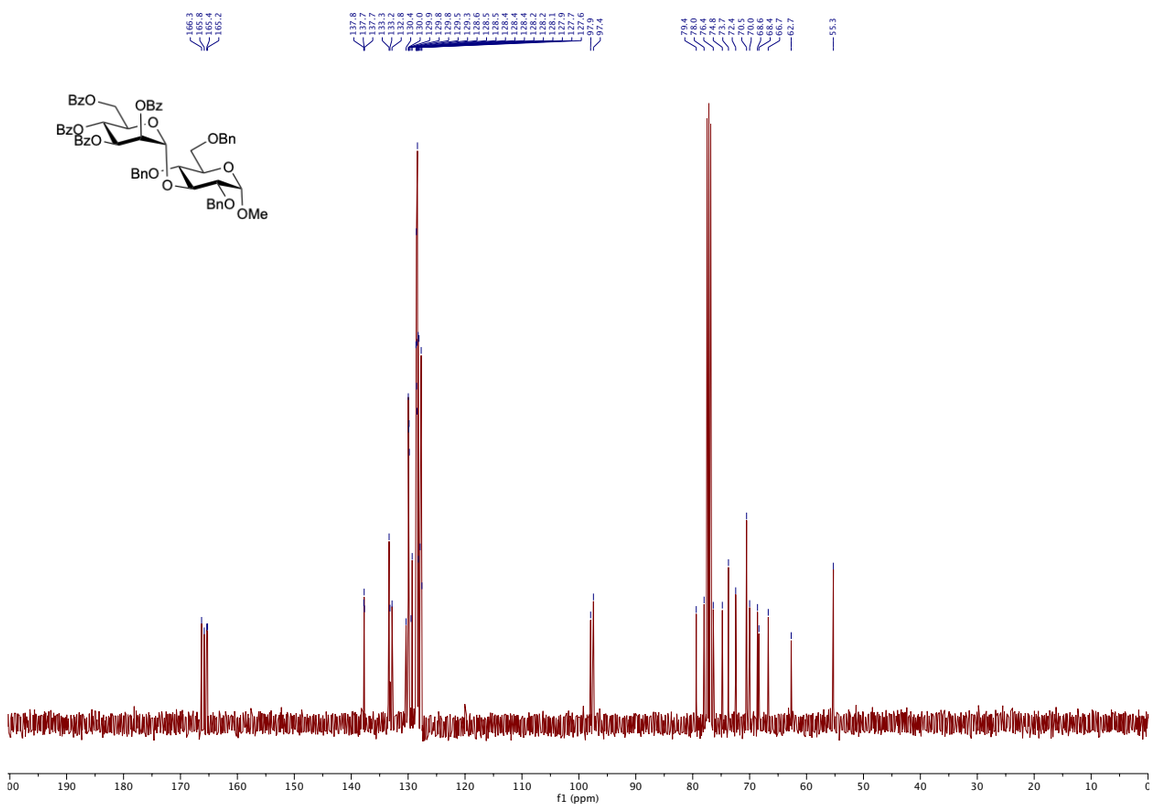


Figure S76. ^{13}C NMR spectrum of **7f** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **7g**

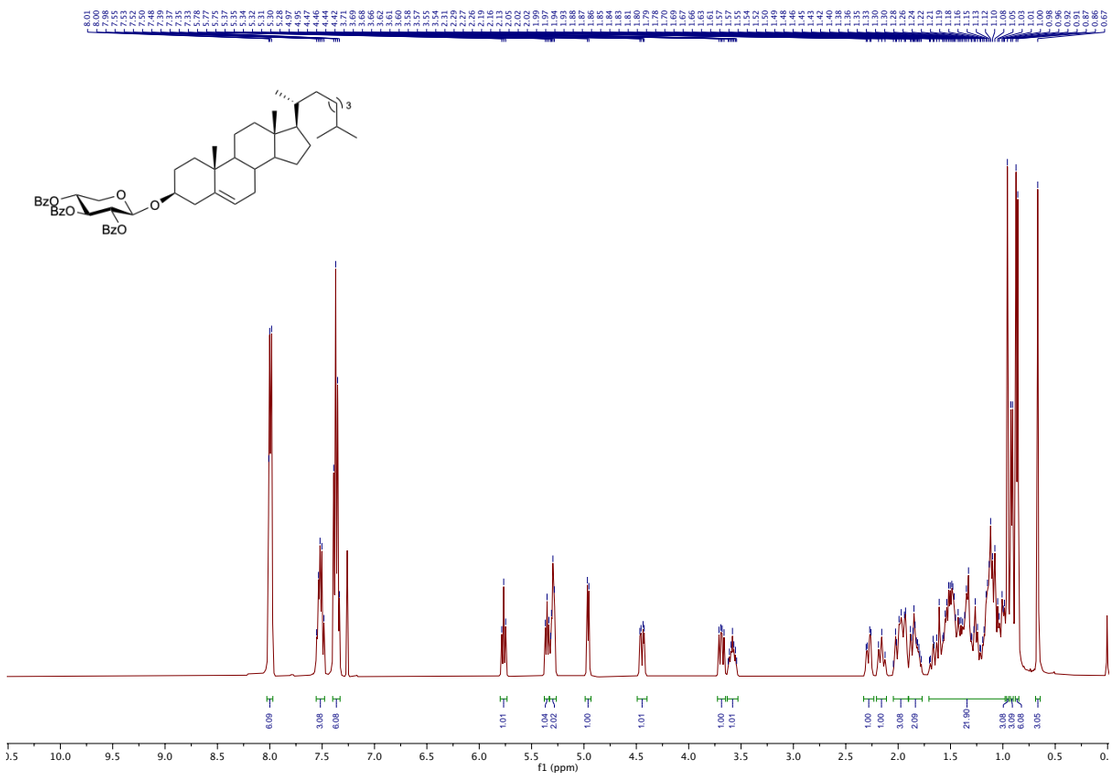


Figure S77. ^{1}H NMR spectrum of **7g** ($CDCl_3$, 400 MHz, 25 °C).

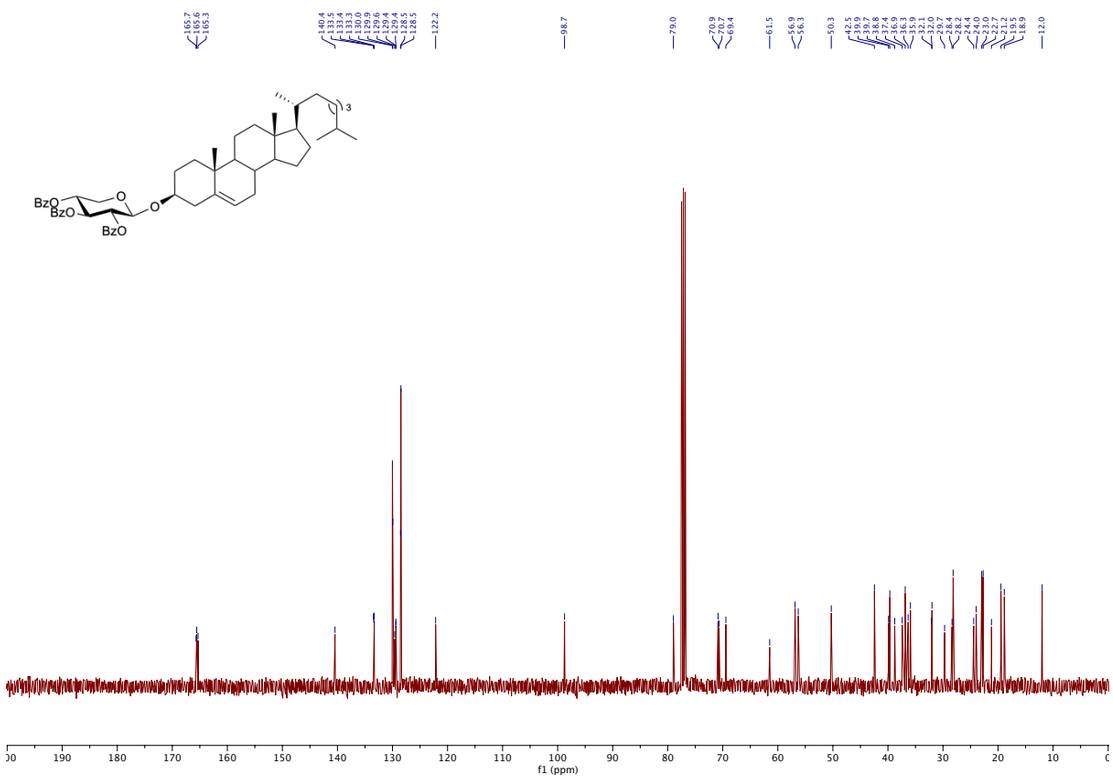


Figure S78. ^{13}C NMR spectrum of **7g** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7h**

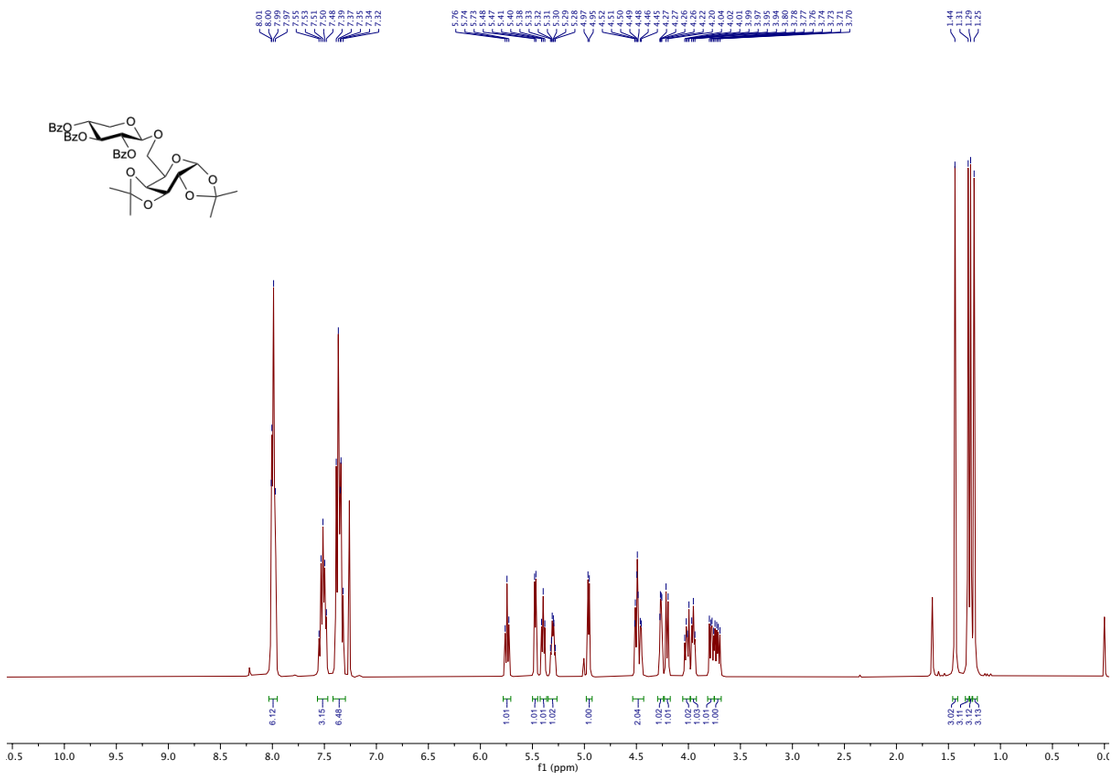


Figure S79. ^{1}H NMR spectrum of **7h** ($CDCl_3$, 400 MHz, 25 °C).

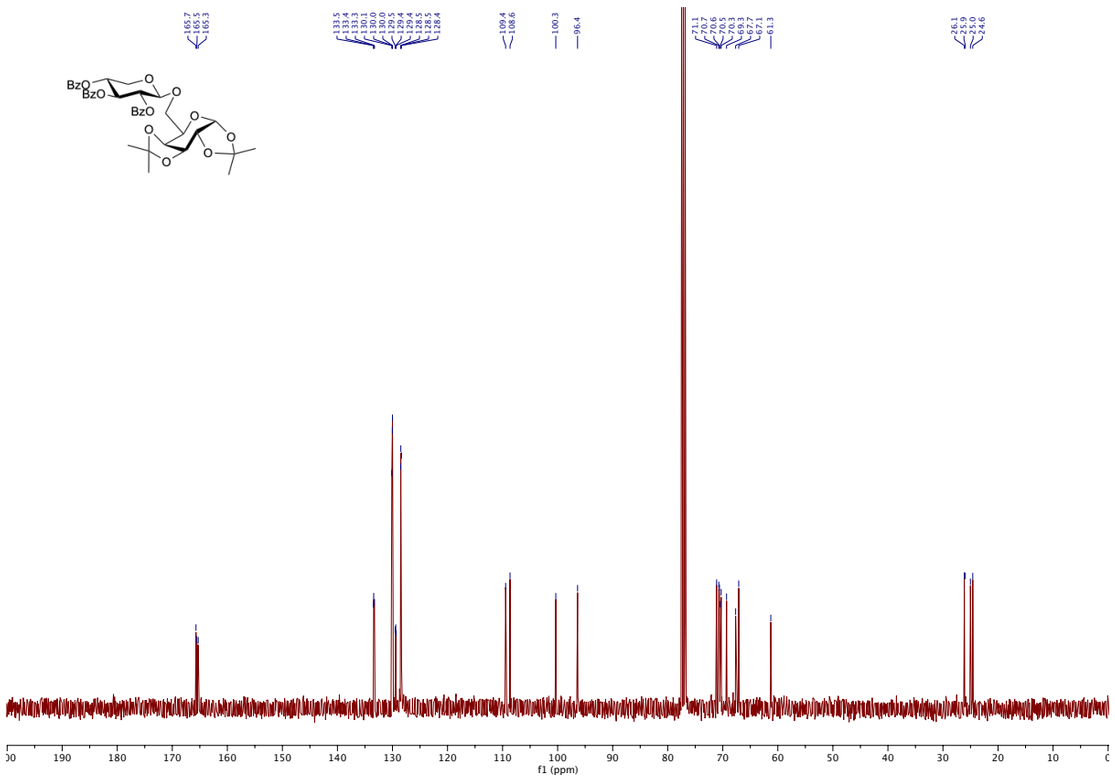


Figure S80. ^{13}C NMR spectrum of **7h** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7i**

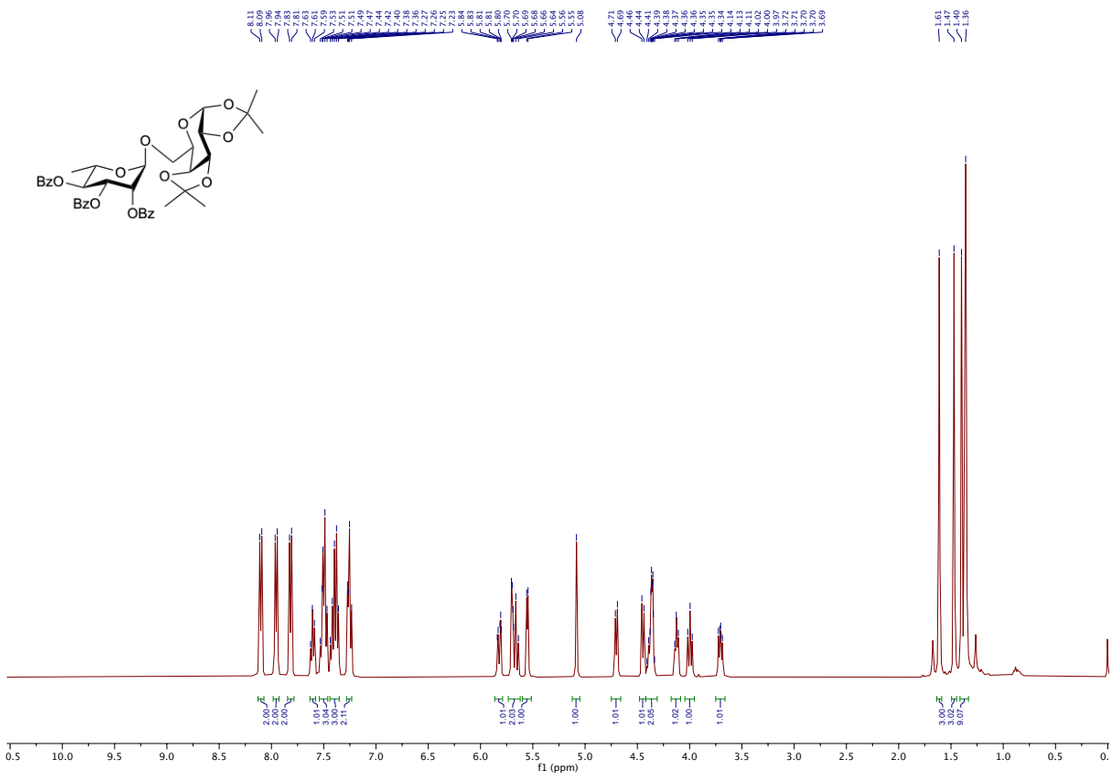


Figure S81. ^{1}H NMR spectrum of **7i** ($CDCl_3$, 400 MHz, 25 °C).

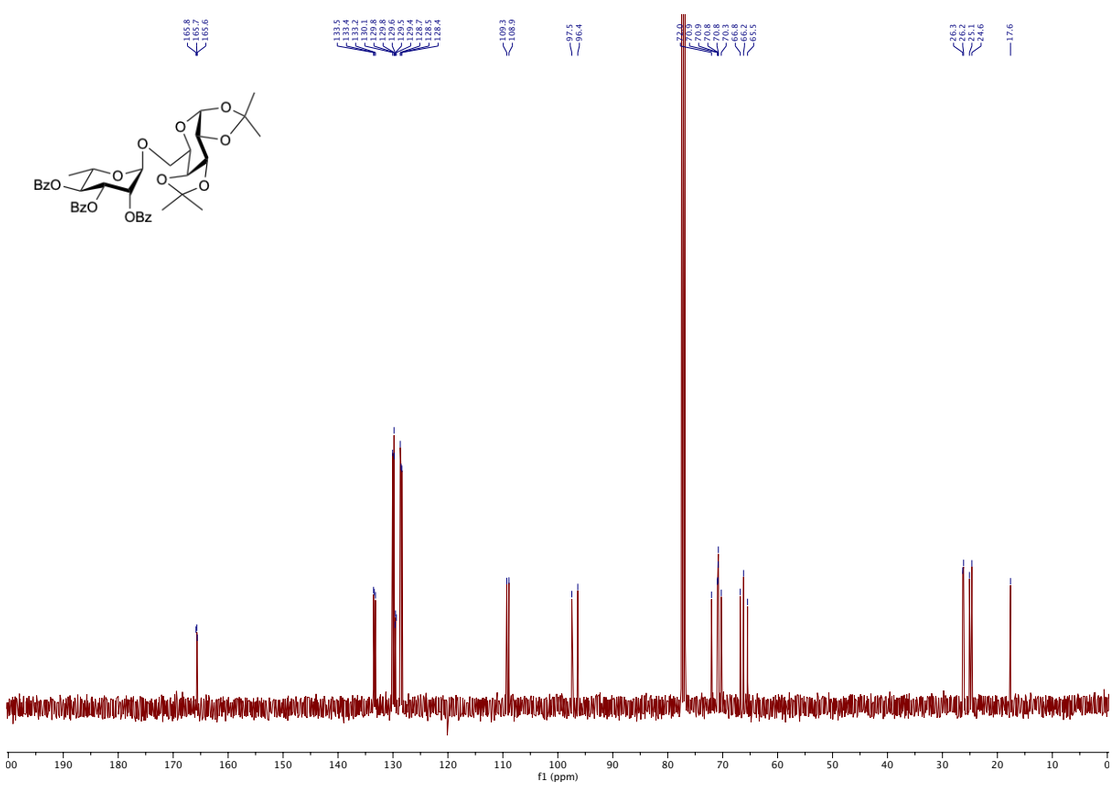


Figure S82. ^{13}C NMR spectrum of **7i** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7j**

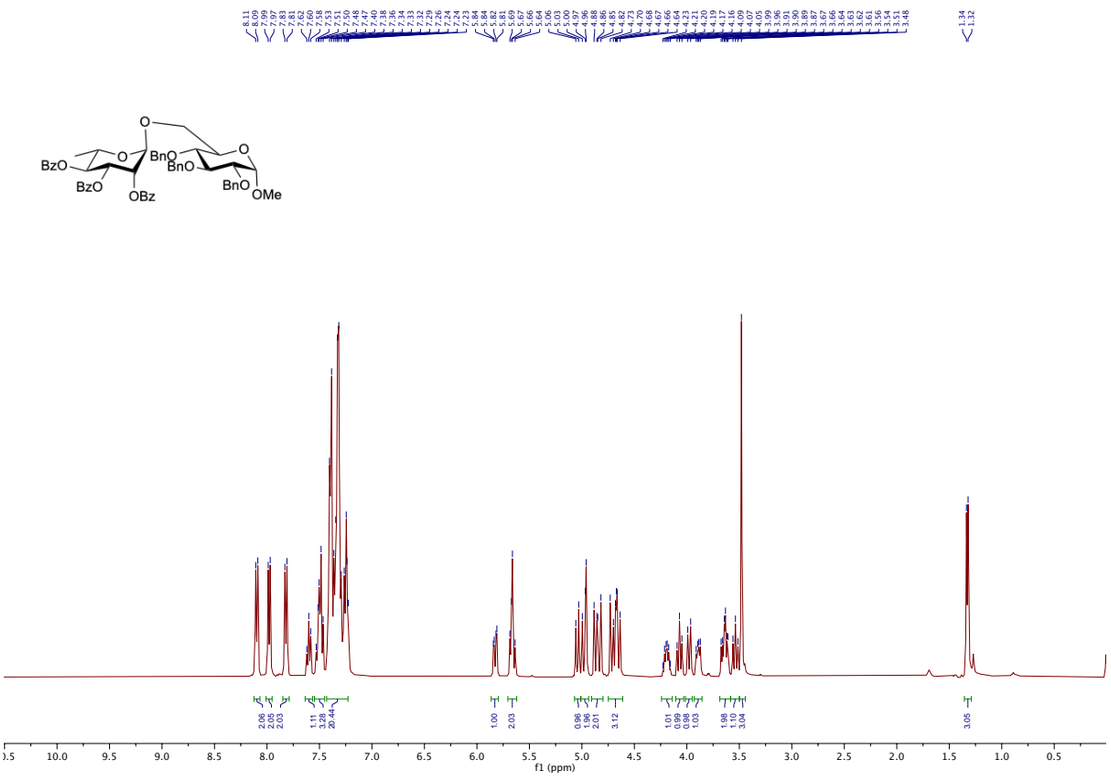


Figure S83. ^{1}H NMR spectrum of **7j** ($CDCl_3$, 400 MHz, 25 °C).

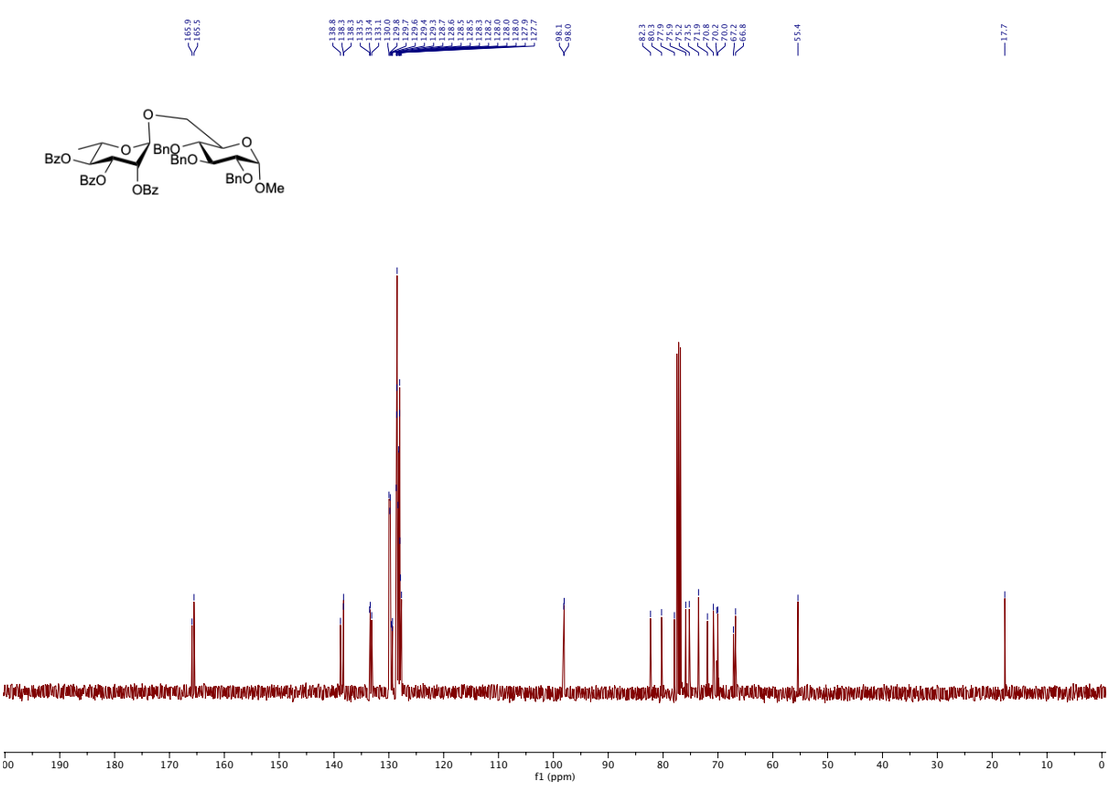


Figure S84. ^{13}C NMR spectrum of **7j** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7k**

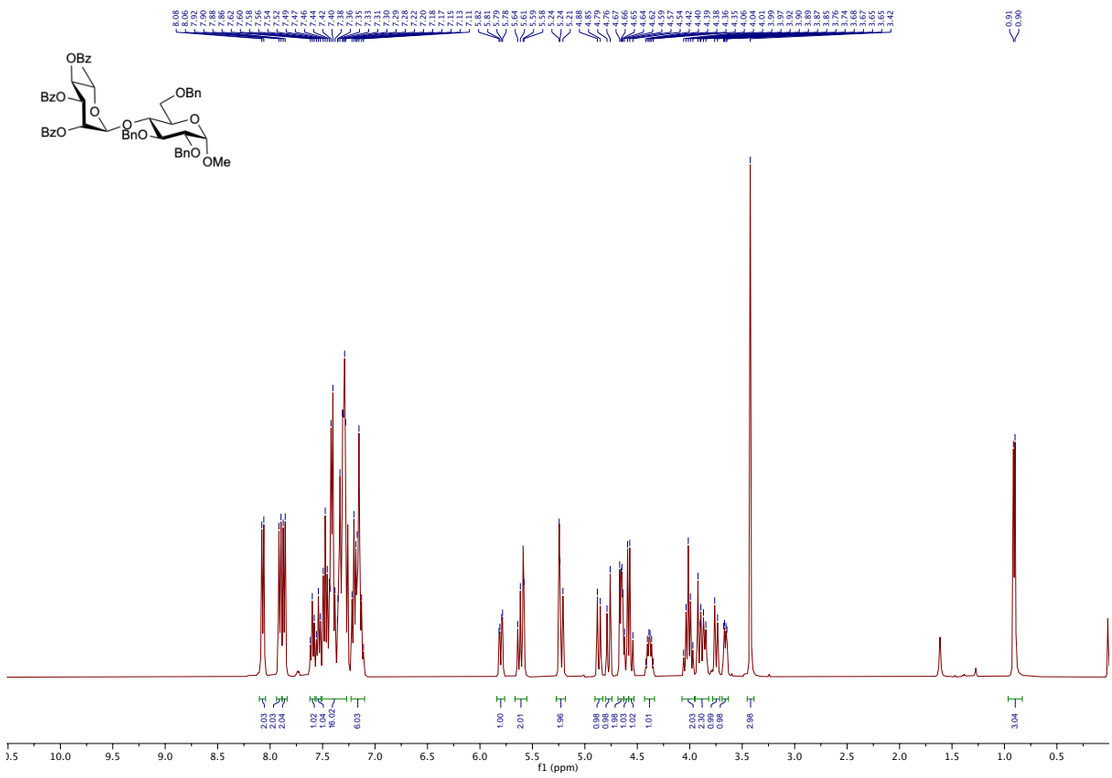


Figure S85. ^{1}H NMR spectrum of **7k** ($CDCl_3$, 400 MHz, 25 °C).

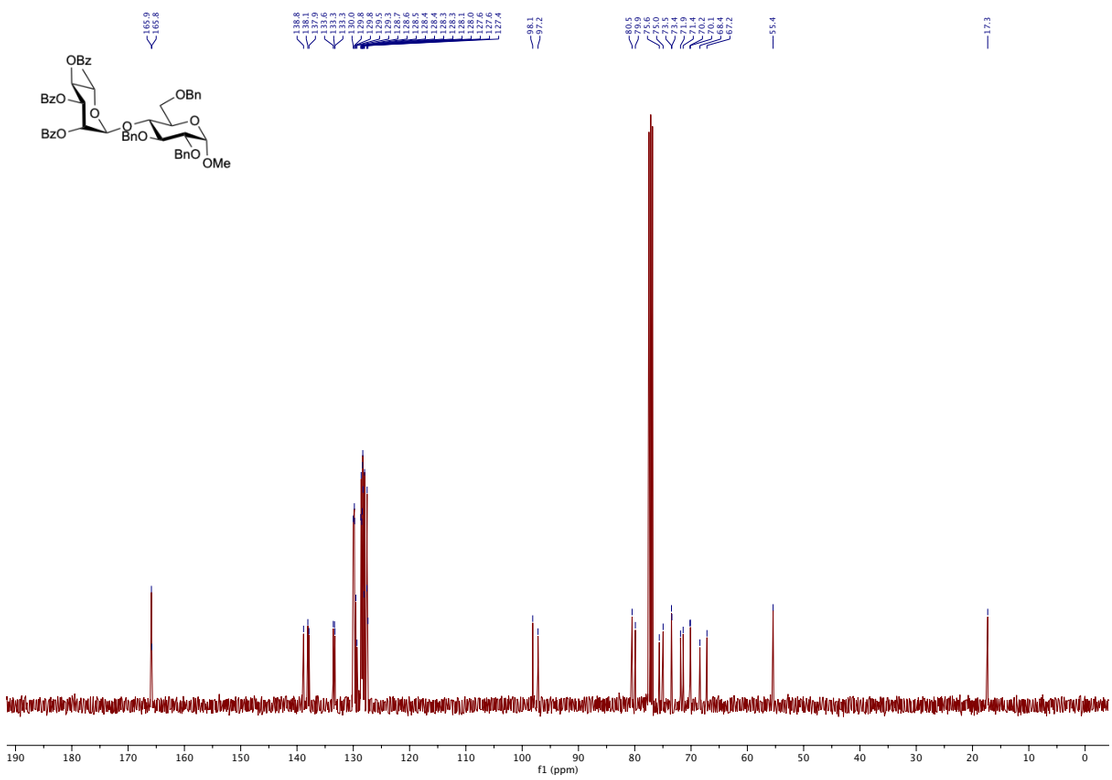


Figure S86. ^{13}C NMR spectrum of **7k** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7l**

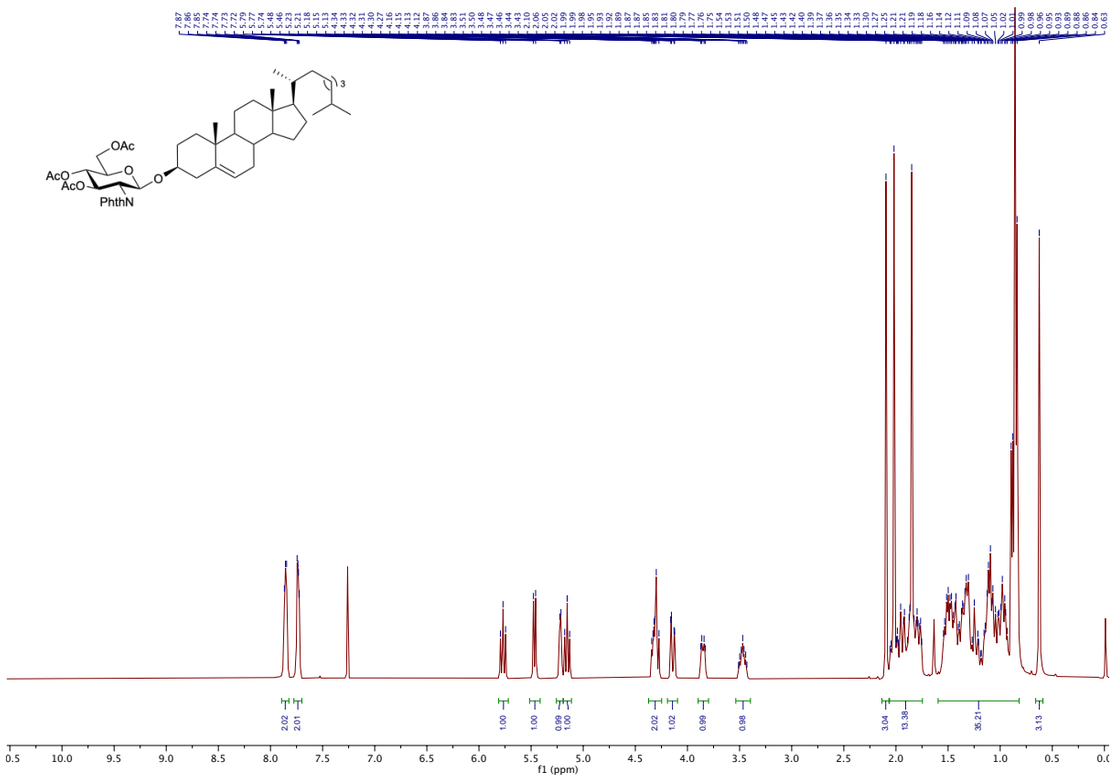


Figure S87. ^{1}H NMR spectrum of **7l** ($CDCl_3$, 400 MHz, 25 ºC).

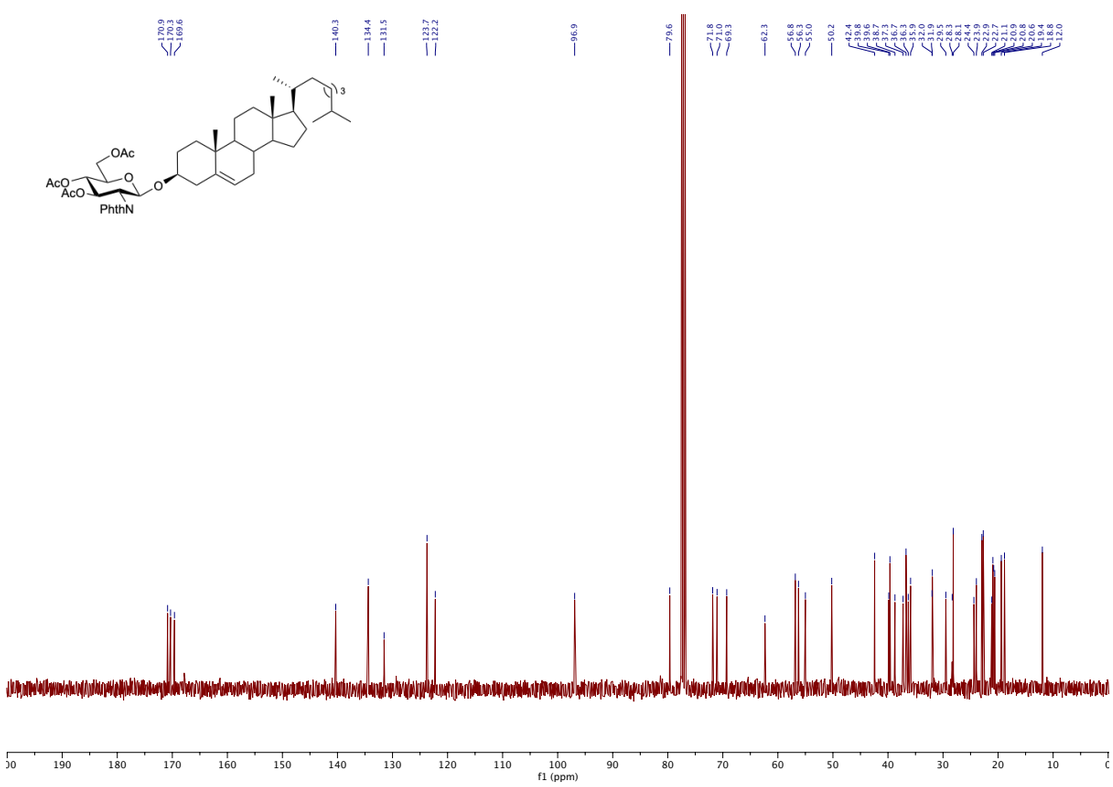


Figure S88. ^{13}C NMR spectrum of **7l** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **7m**

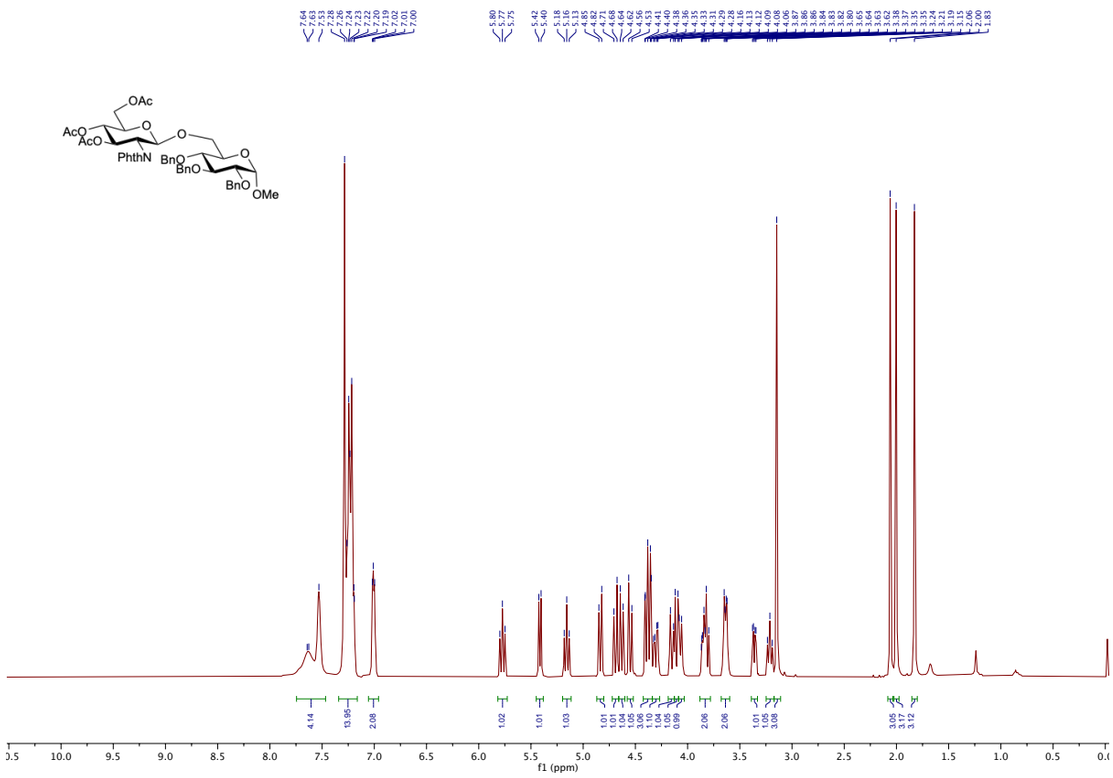


Figure S89. ^{1}H NMR spectrum of **7m** ($CDCl_3$, 400 MHz, 25 °C).

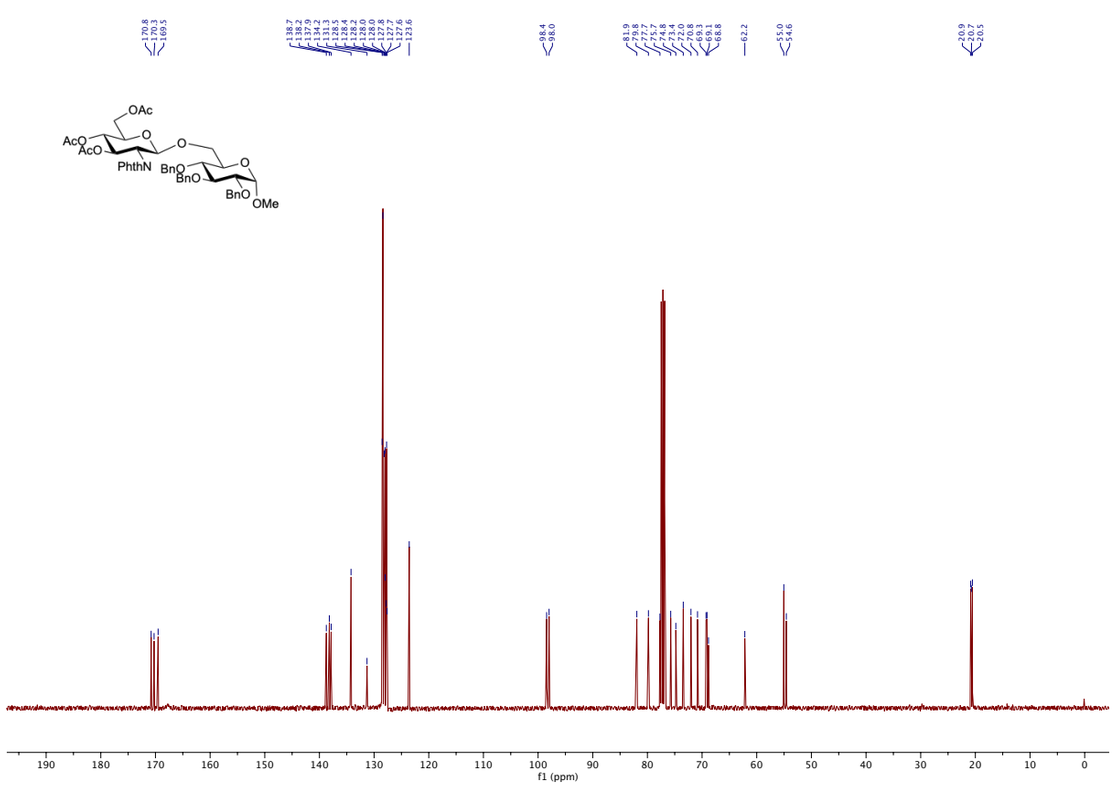


Figure S90. ^{13}C NMR spectrum of **7m** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7n**

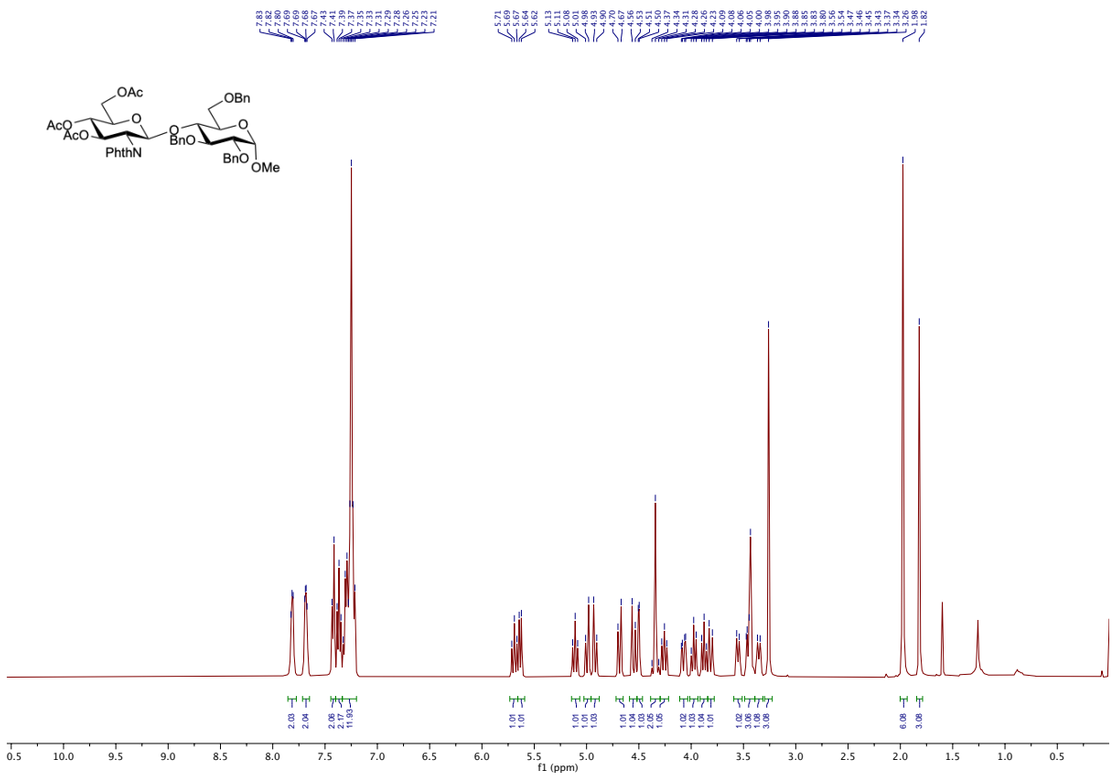


Figure S91. ^{1}H NMR spectrum of **7n** ($CDCl_3$, 400 MHz, 25 °C).

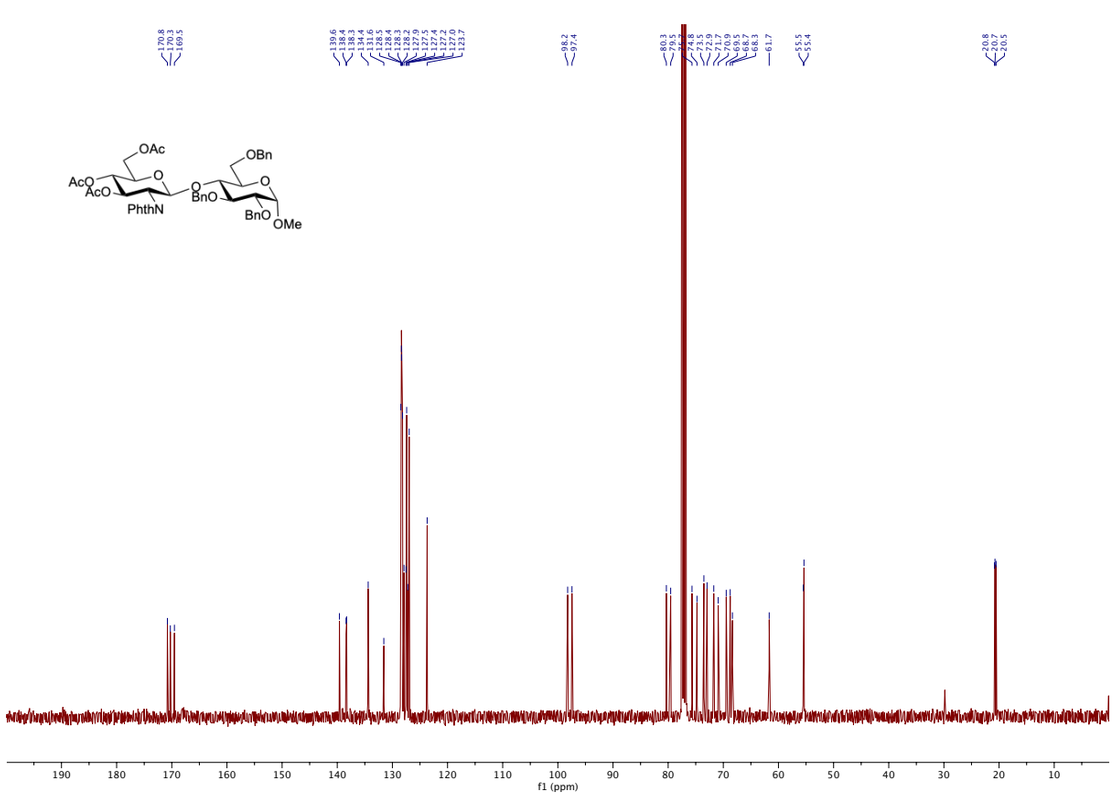


Figure S92. ^{13}C NMR spectrum of **7n** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7o**

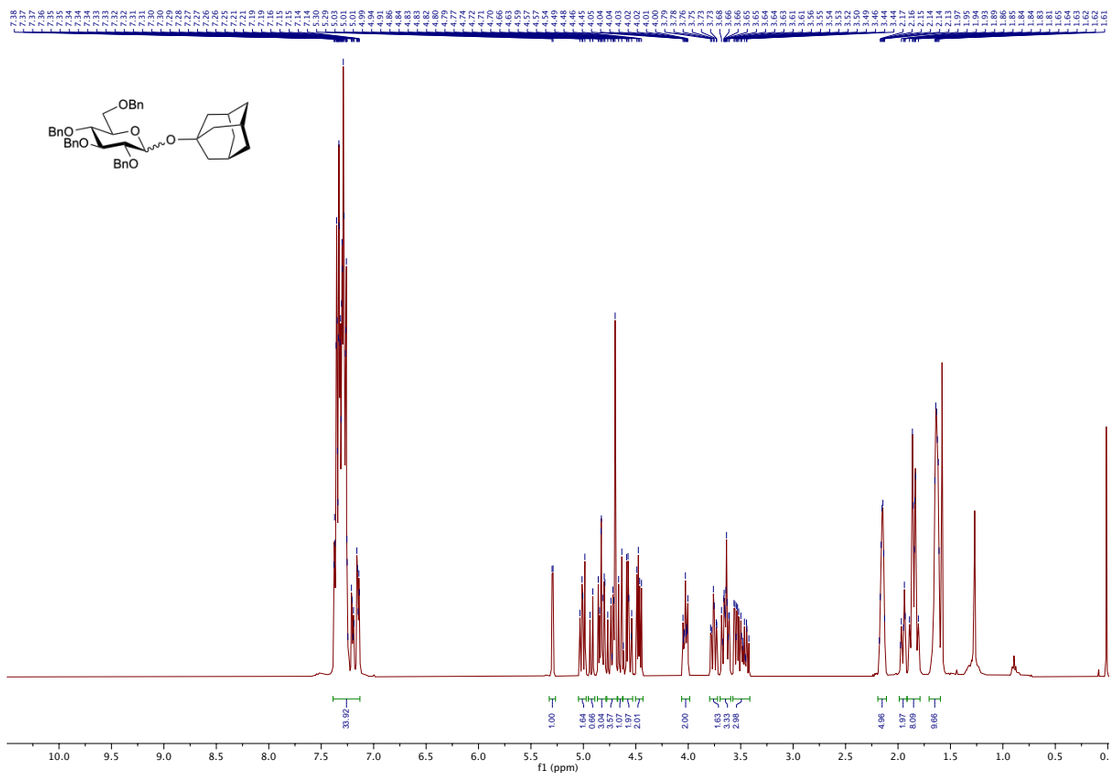


Figure S93. ^{1}H NMR spectrum of **7o** ($CDCl_3$, 400 MHz, 25 °C).

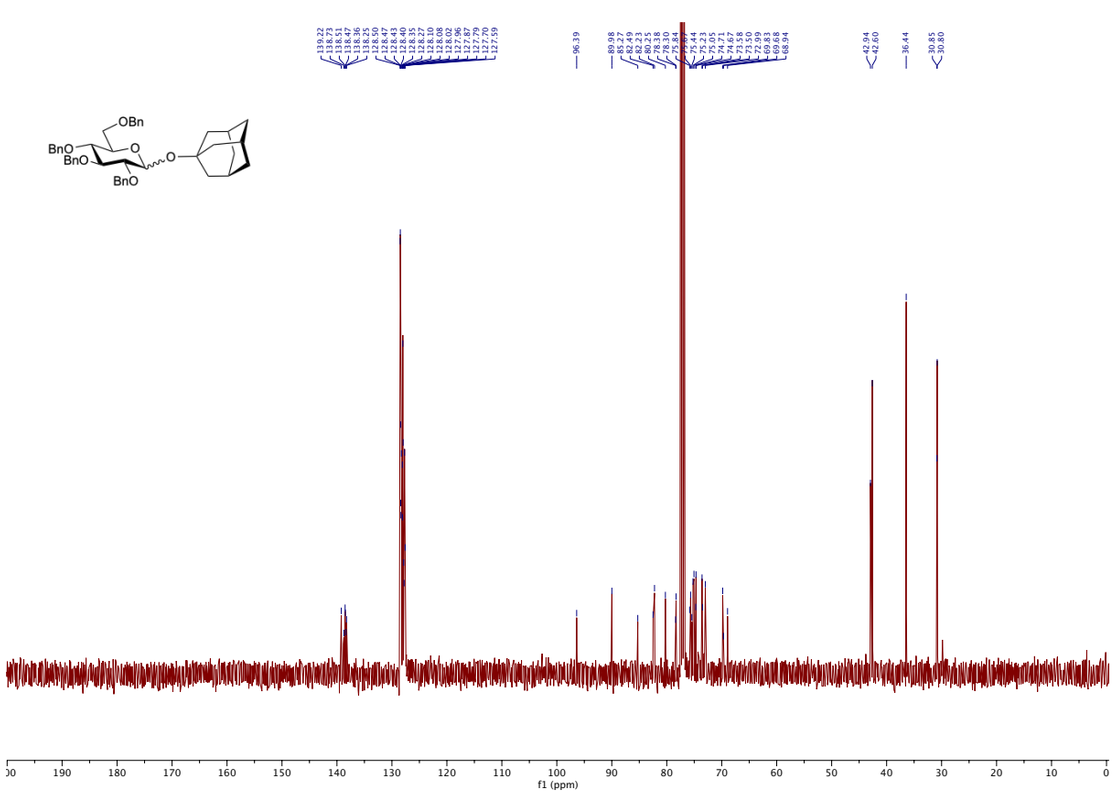


Figure S94. ^{13}C NMR spectrum of **7o** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7pα**

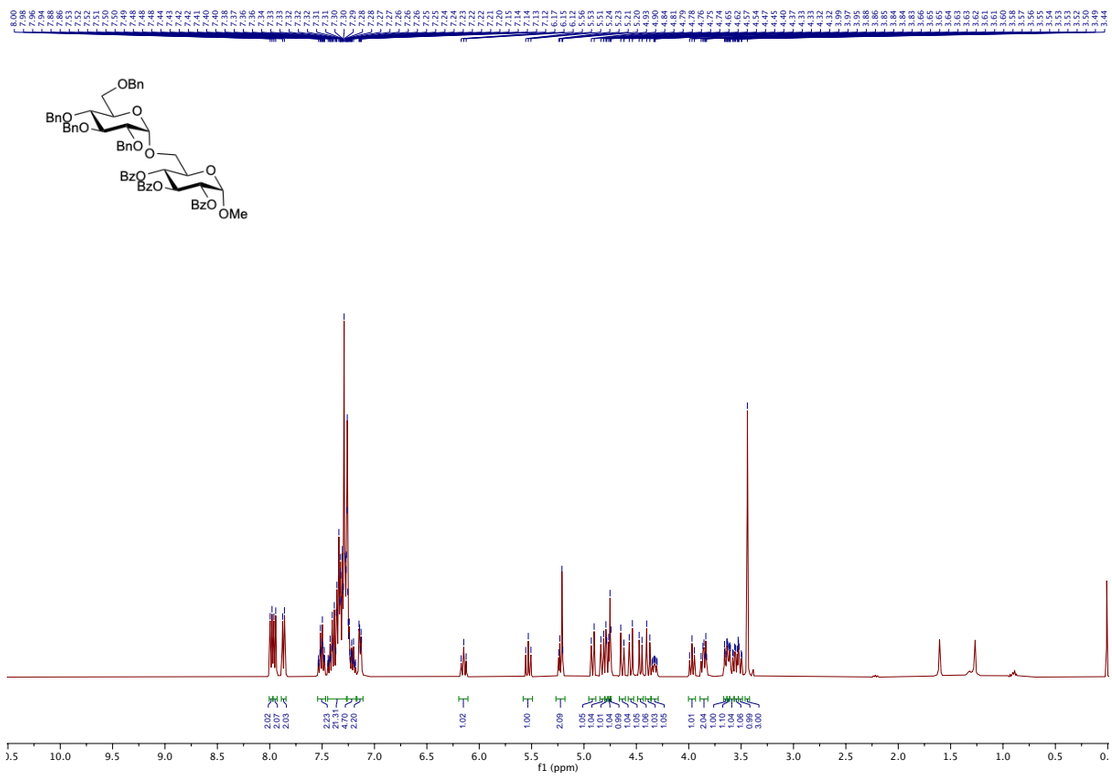


Figure S95. ^{1}H NMR spectrum of **7pα** ($CDCl_3$, 400 MHz, 25 °C).

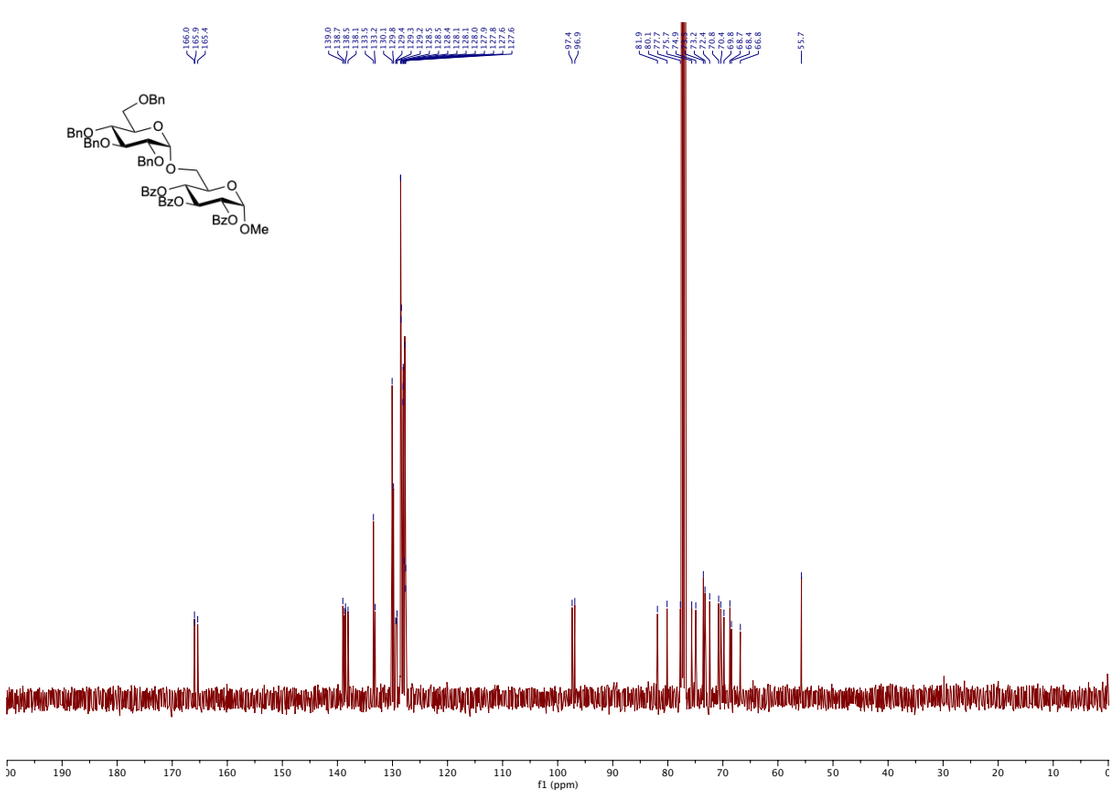


Figure S96. ^{13}C NMR spectrum of **7pα** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H NMR spectrum of **7pβ**

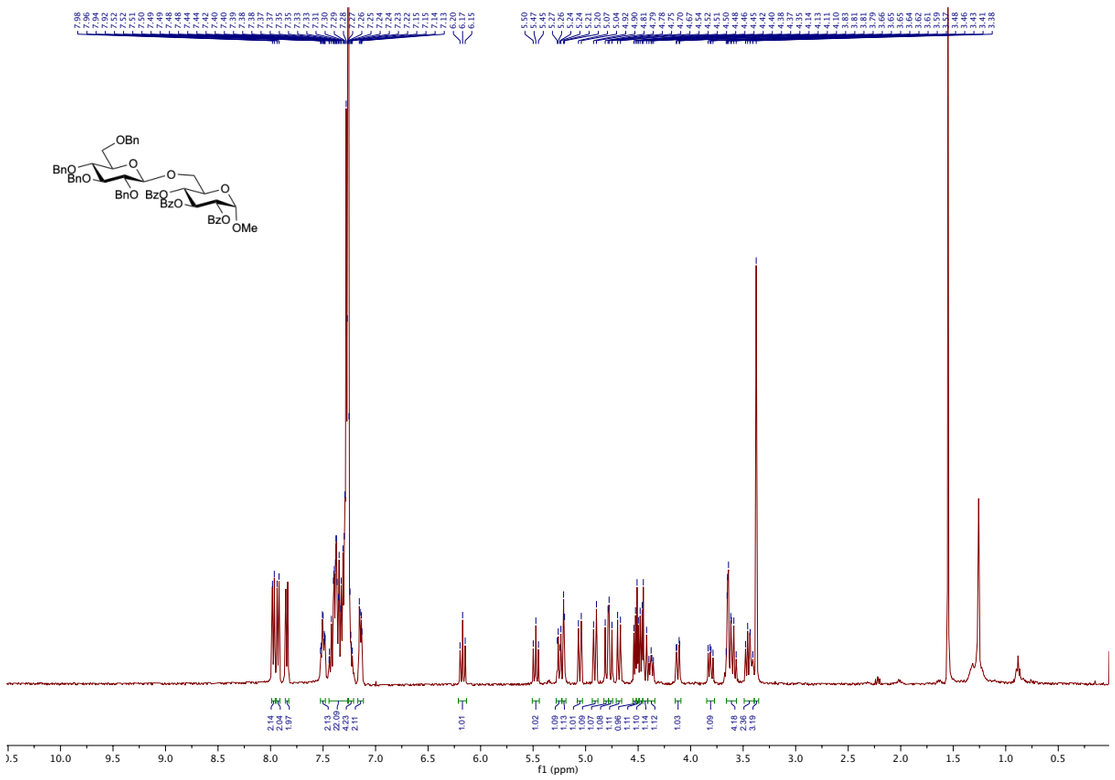


Figure S97. ^{1}H NMR spectrum of **7pβ** ($CDCl_3$, 400 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7q**

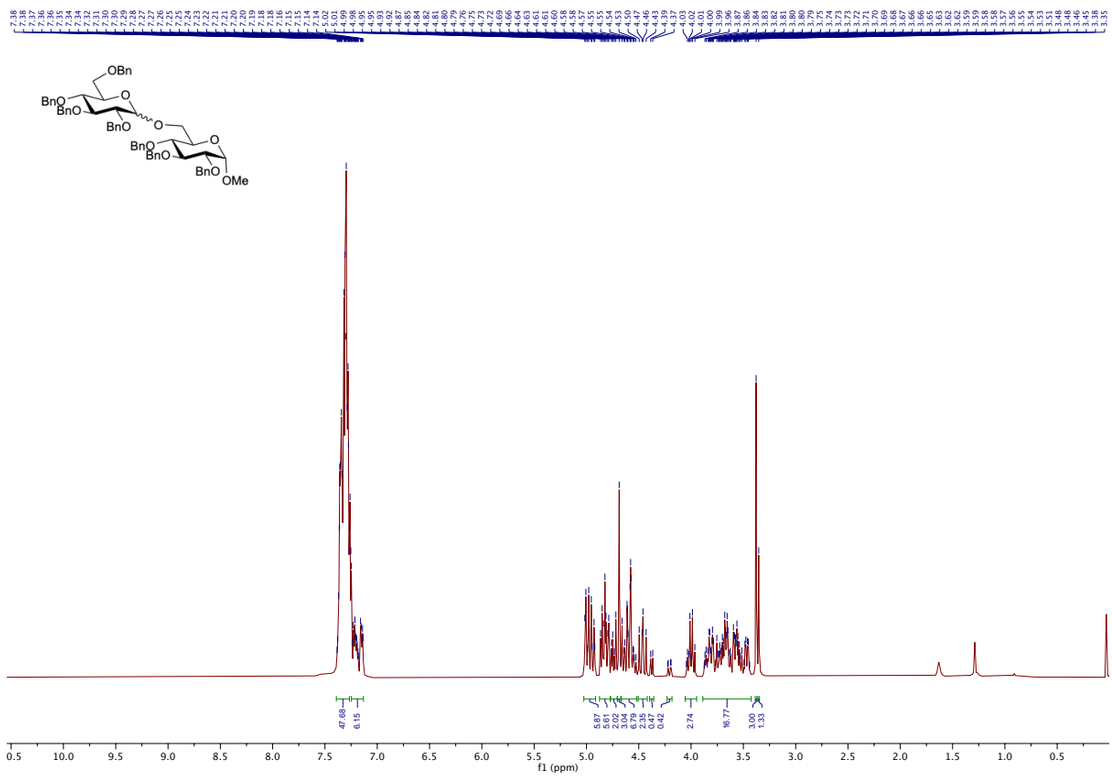


Figure S98. ^{1}H NMR spectrum of **7q** ($CDCl_3$, 400 MHz, 25 °C).

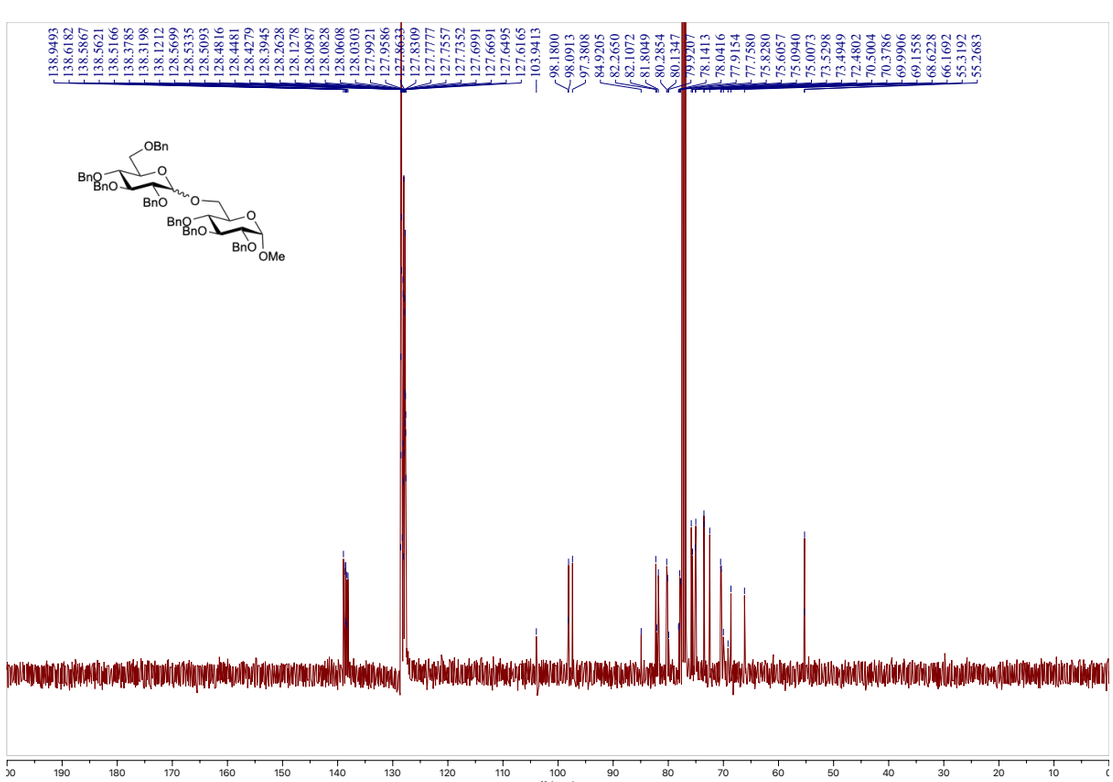


Figure S99. ^{13}C NMR spectrum of **7q** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7rα**

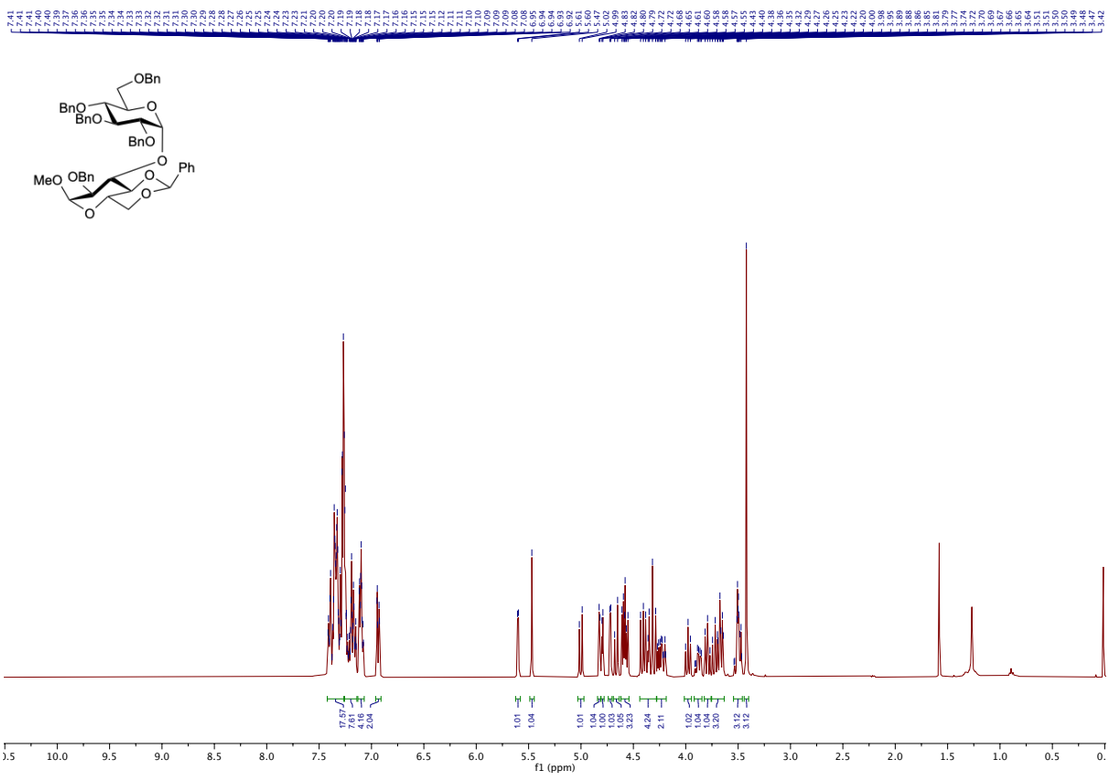


Figure S100. ^{1}H NMR spectrum of **7rα** ($CDCl_3$, 400 MHz, 25 ºC).

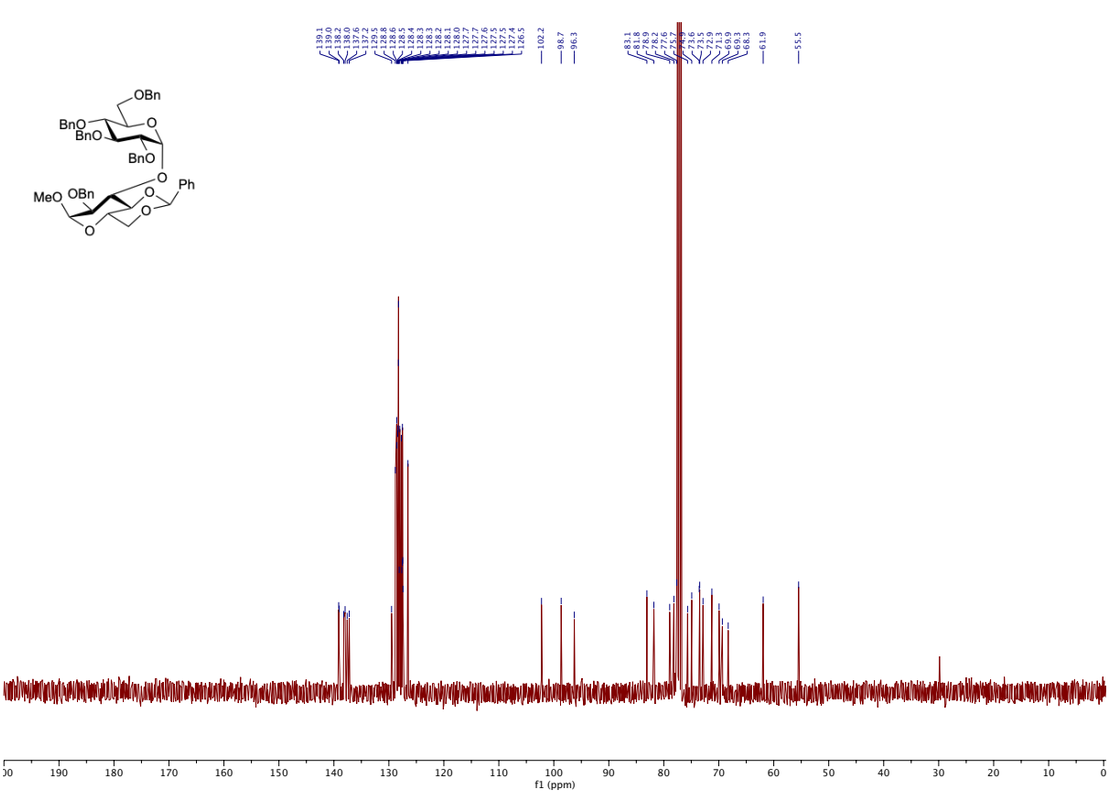


Figure S101. ^{13}C NMR spectrum of **7rα** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **7rβ**

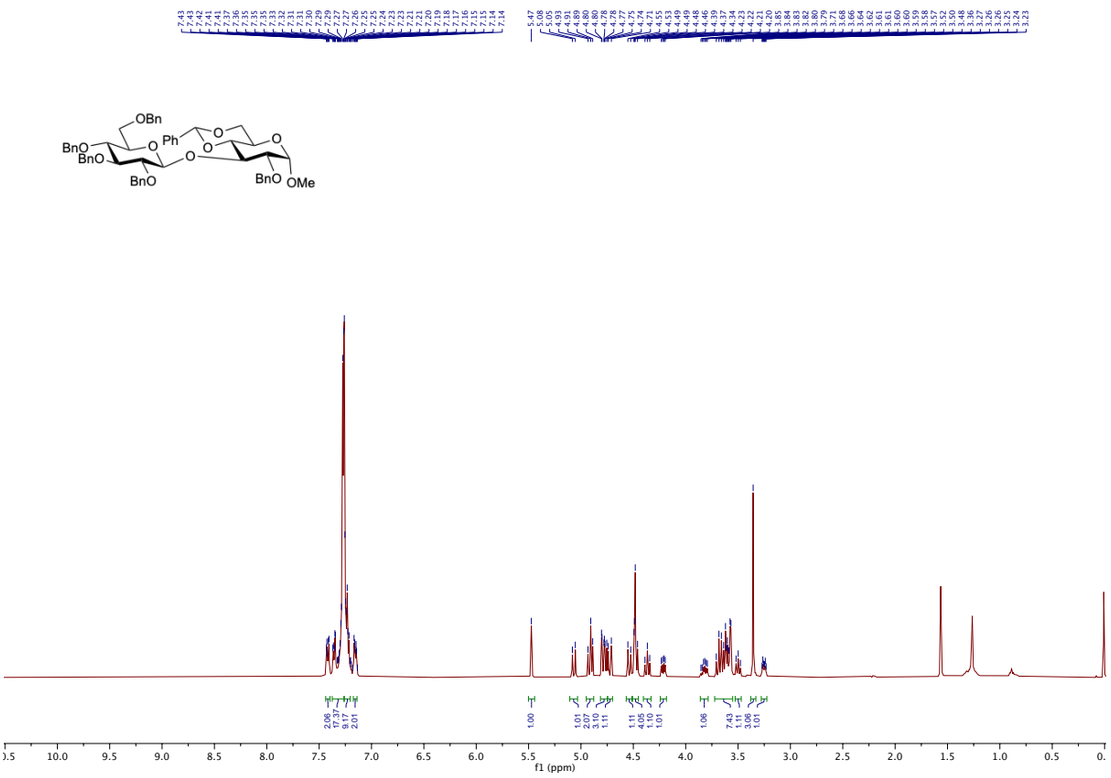


Figure S102. ^{1}H NMR spectrum of **7rβ** ($CDCl_3$, 400 MHz, 25 °C).

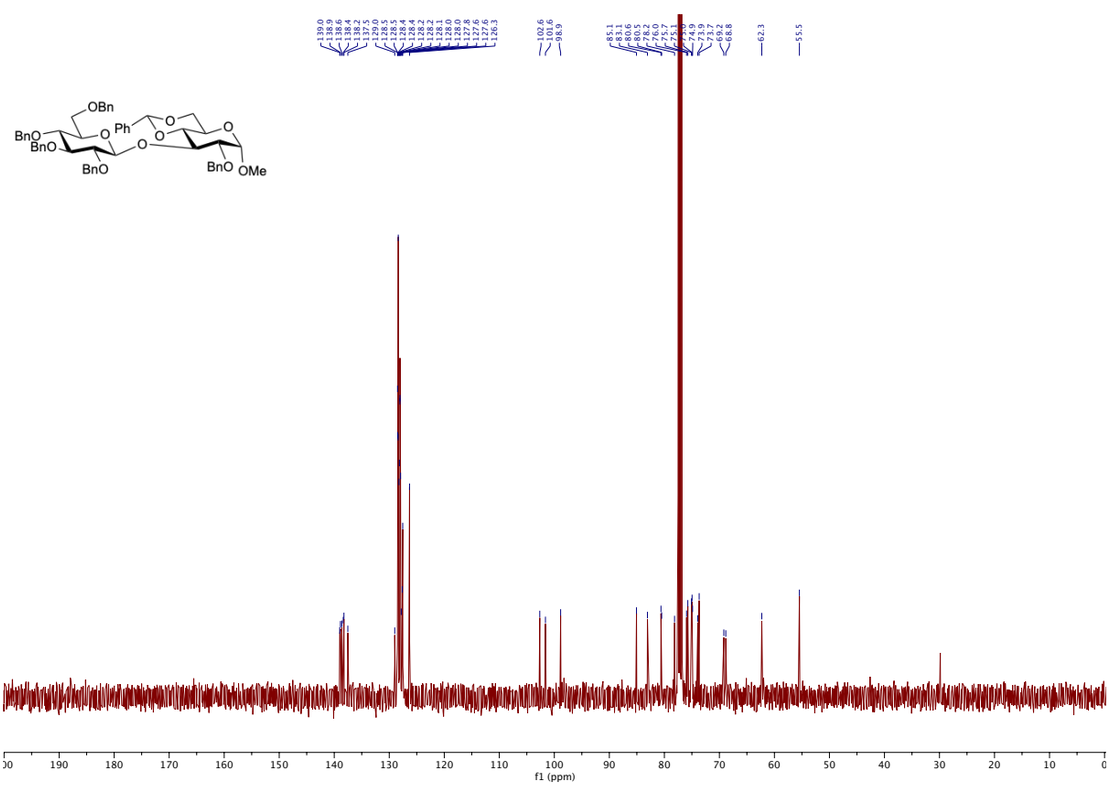


Figure S103. ^{13}C NMR spectrum of **7rβ** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7s**

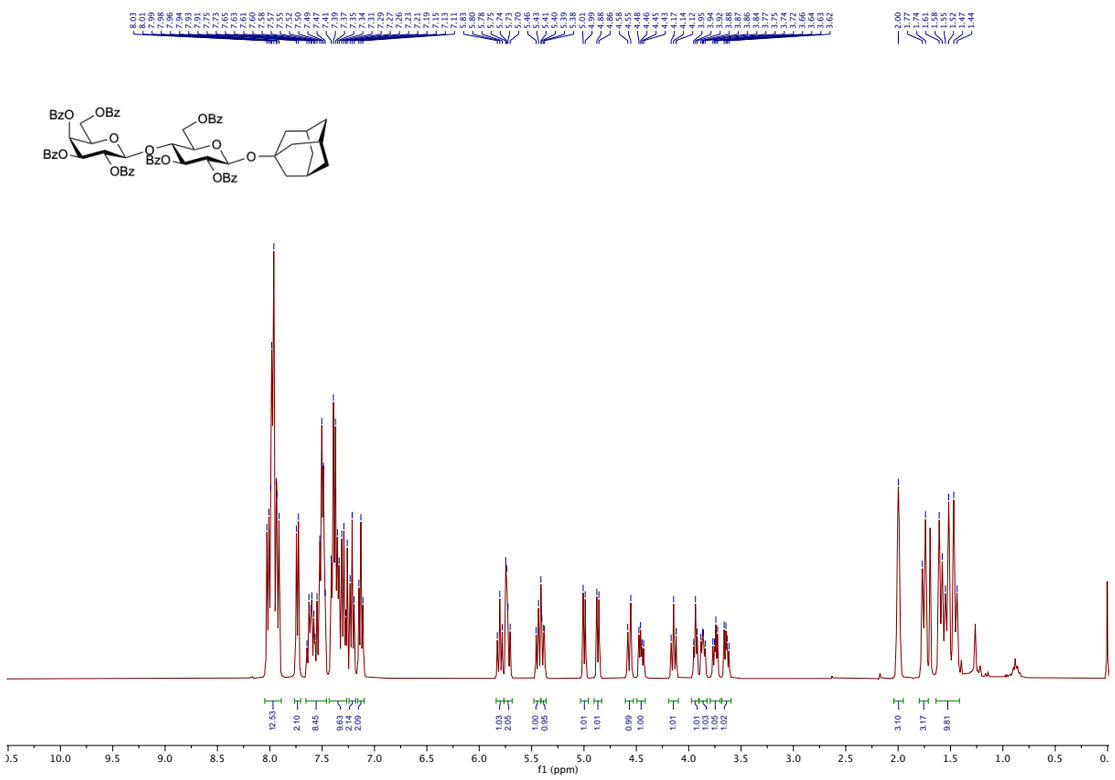


Figure S104. ^{1}H NMR spectrum of **7s** ($CDCl_3$, 400 MHz, 25 °C).

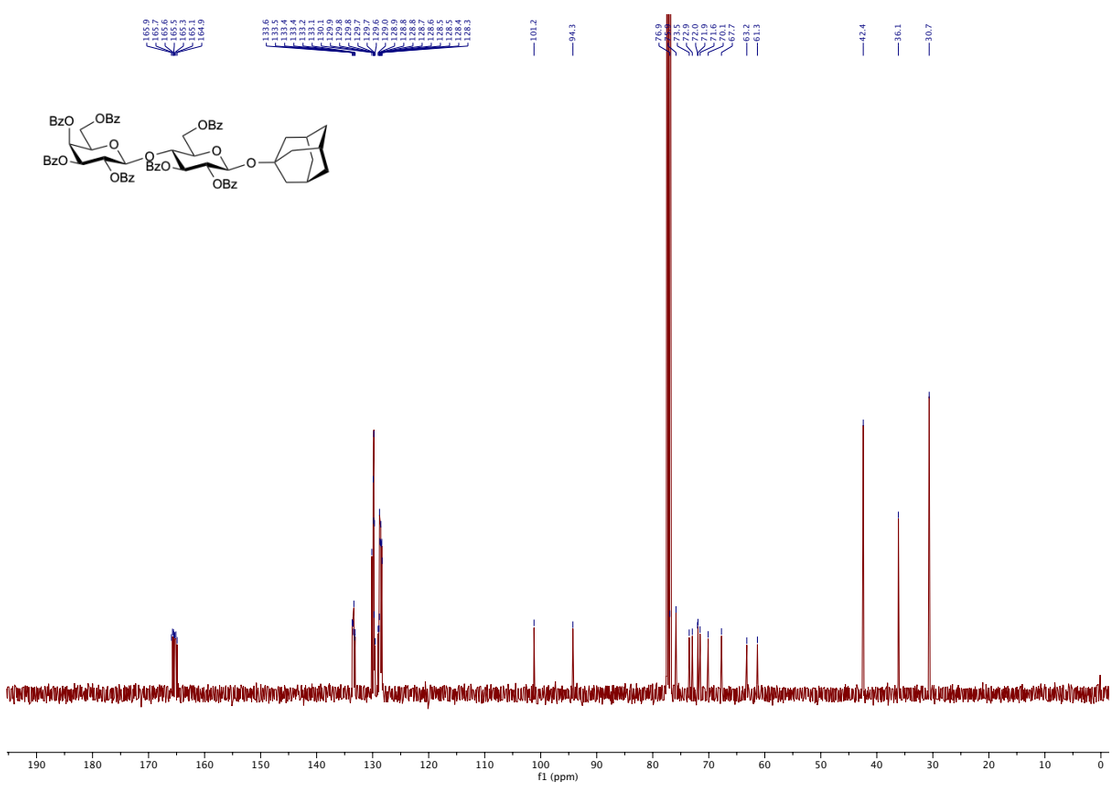


Figure S105. ^{13}C NMR spectrum of **7s** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7t**

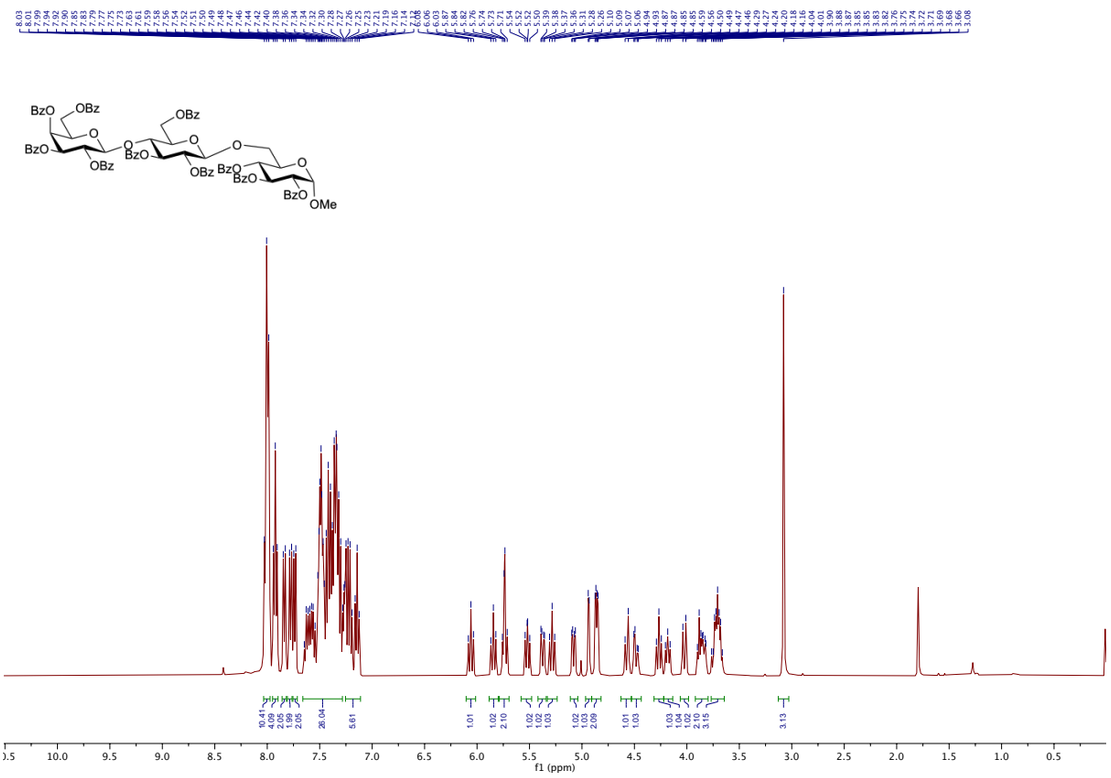


Figure S106. ^{1}H NMR spectrum of **7t** ($CDCl_3$, 400 MHz, 25 °C).

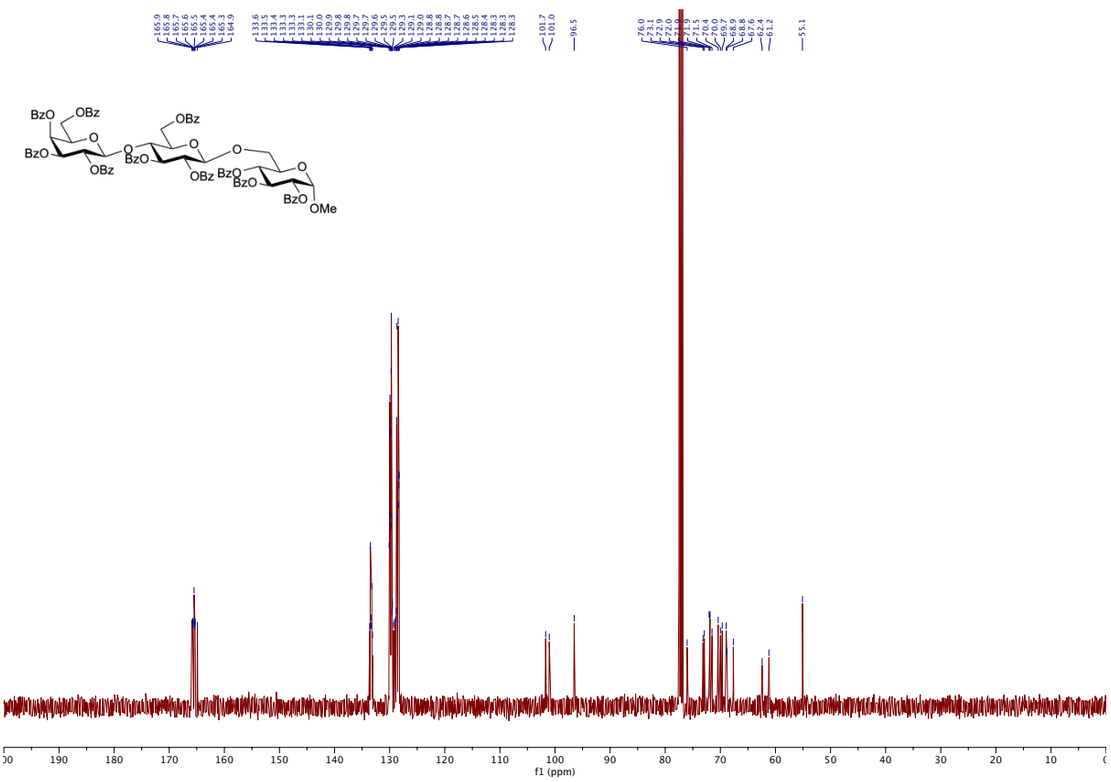


Figure S107. ^{13}C NMR spectrum of **7t** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **7u**

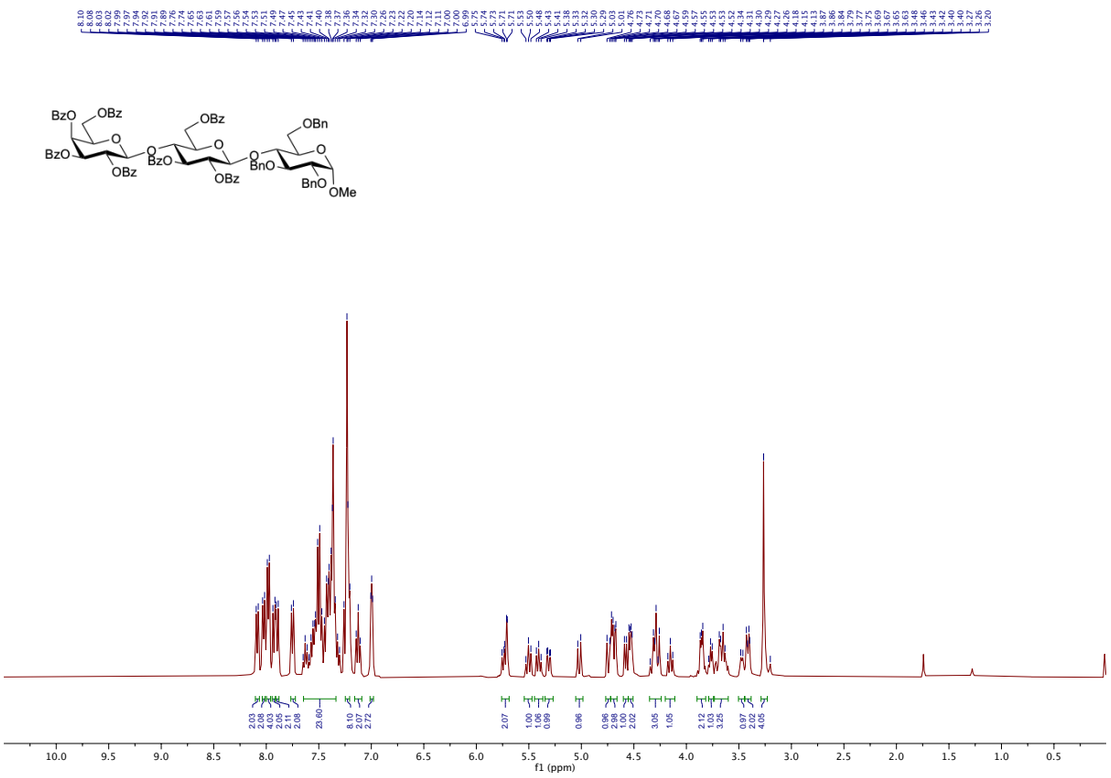


Figure S108. ^{1}H NMR spectrum of **7u** ($CDCl_3$, 400 MHz, 25 °C).

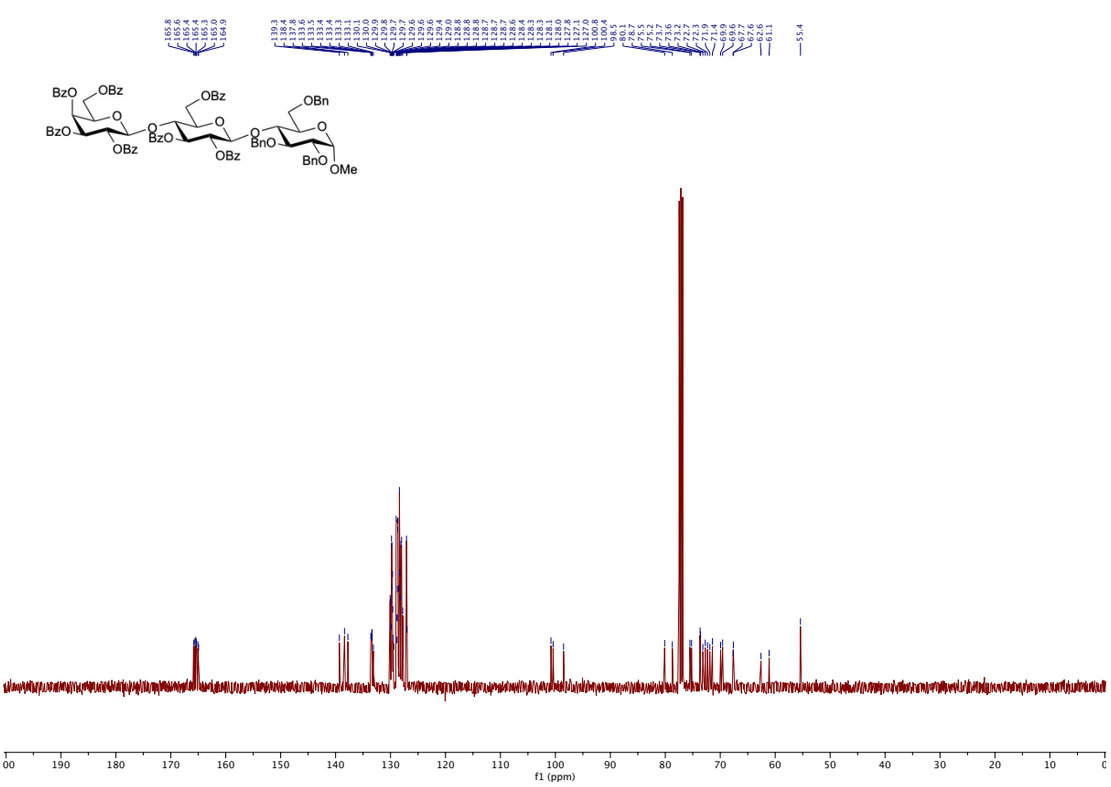


Figure S109. ^{13}C NMR spectrum of **7u** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **9**

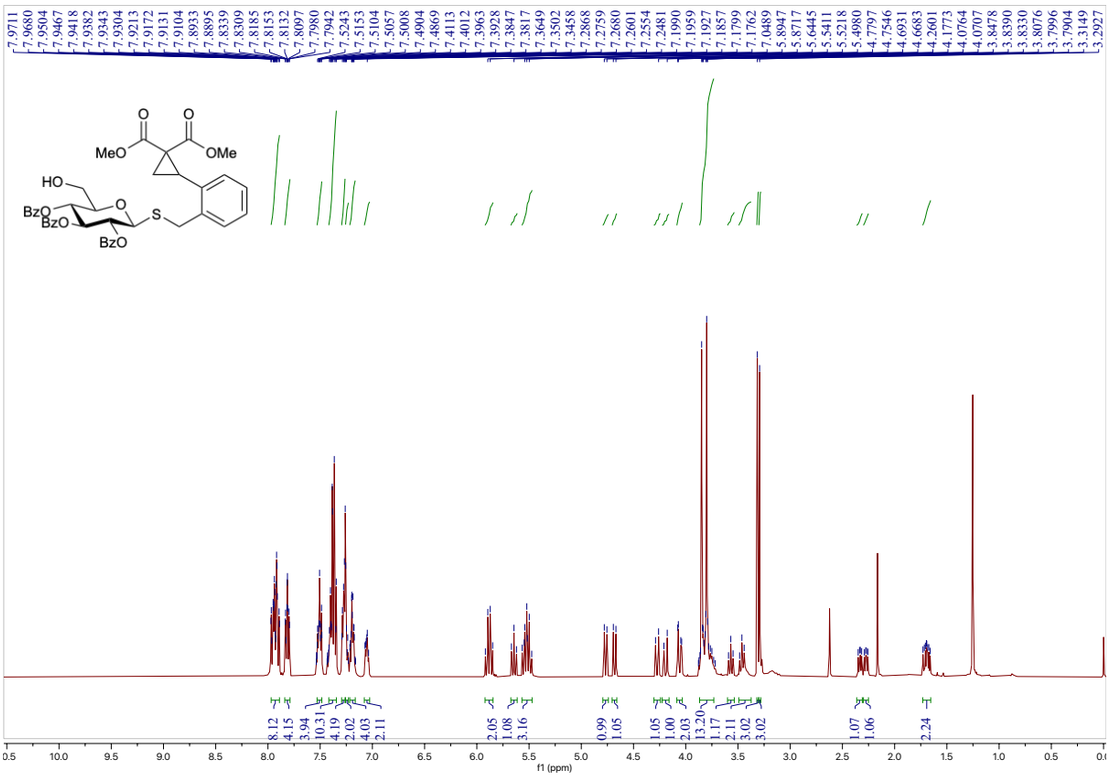


Figure S110. ^{1}H NMR spectrum of **9** ($CDCl_3$, 400 MHz, 25 ºC).

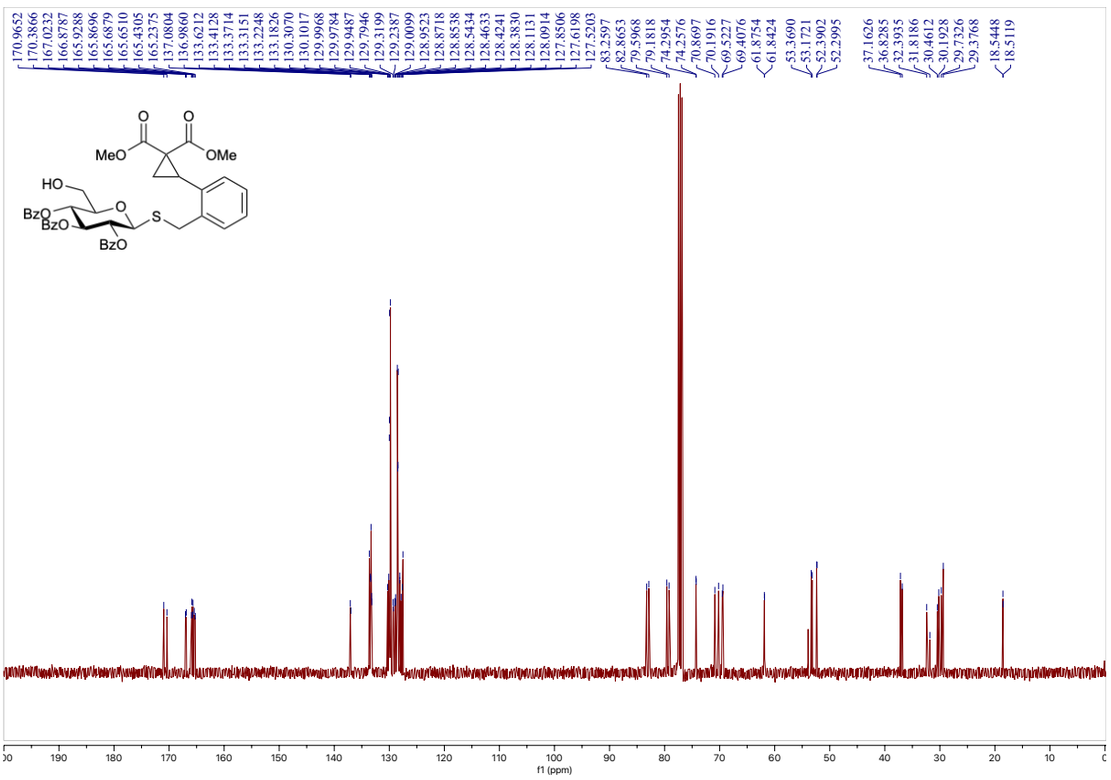


Figure S111. ^{13}C NMR spectrum of **9** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **10**

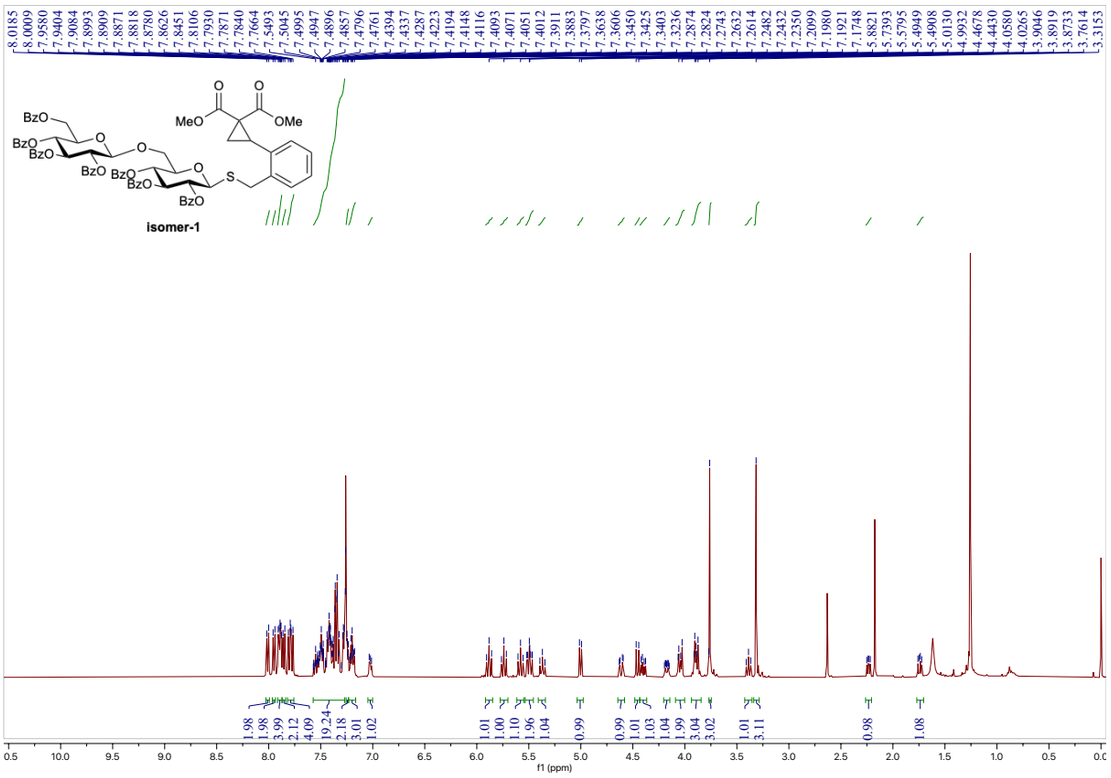


Figure S112. ^{1}H NMR spectrum of **10** ($CDCl_3$, 400 MHz, 25 °C).

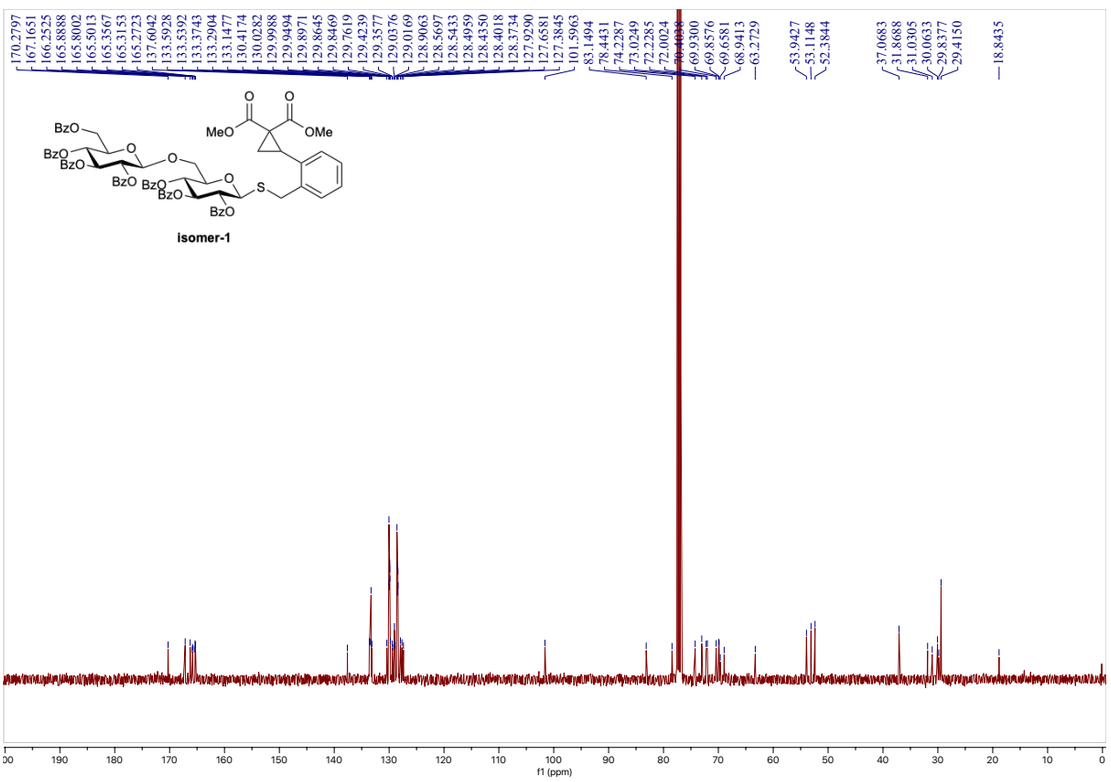


Figure S113. ^{13}C NMR spectrum of **10** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **10′**

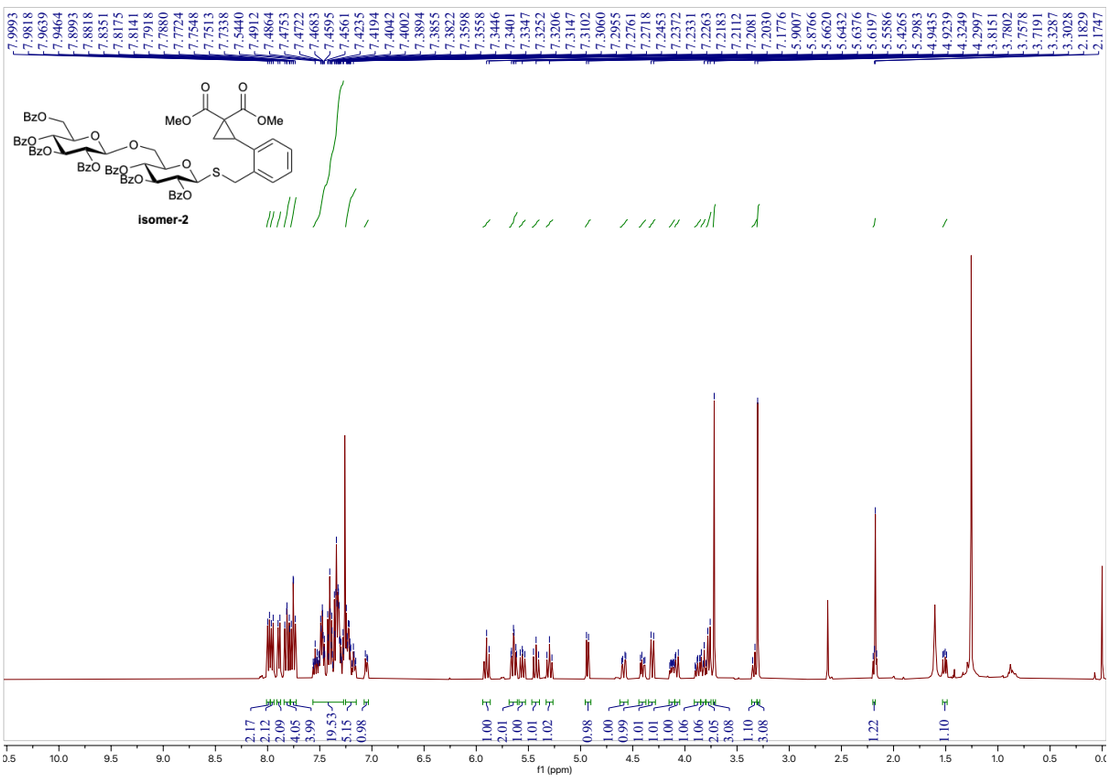


Figure S114. ^{1}H NMR spectrum of **10′** ($CDCl_3$, 400 MHz, 25 °C).

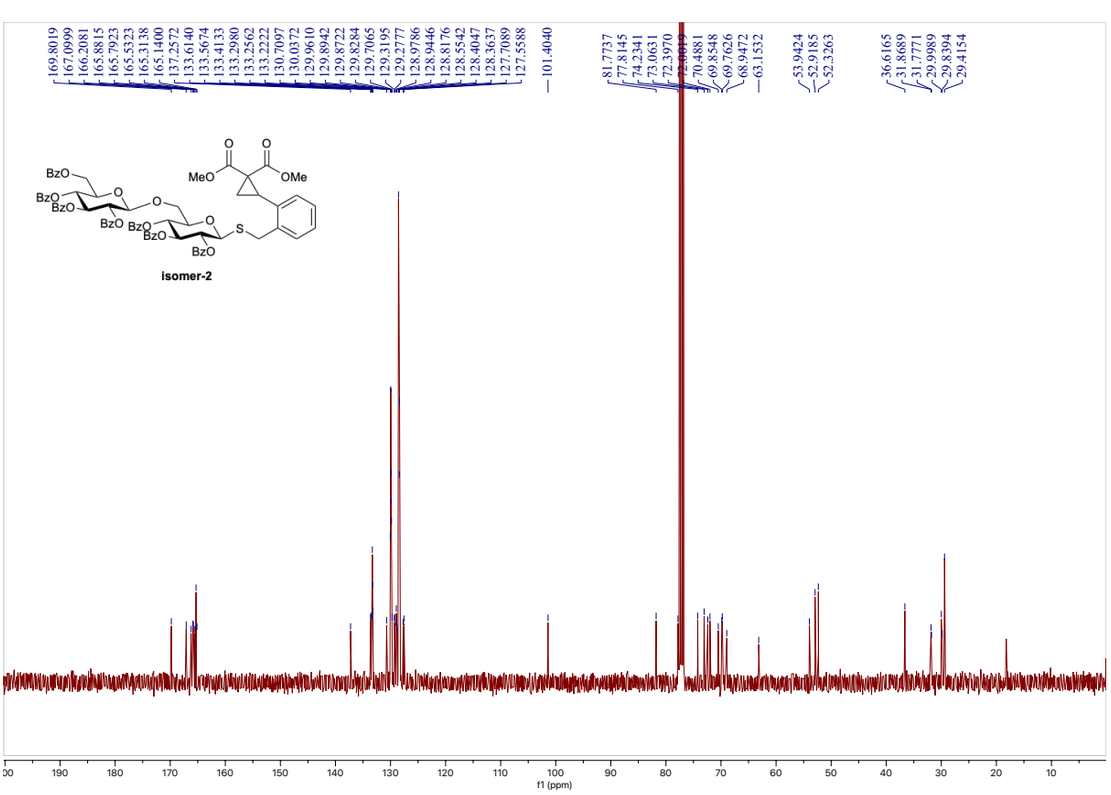


Figure S115. ^{13}C NMR spectrum of **10′** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **12a**

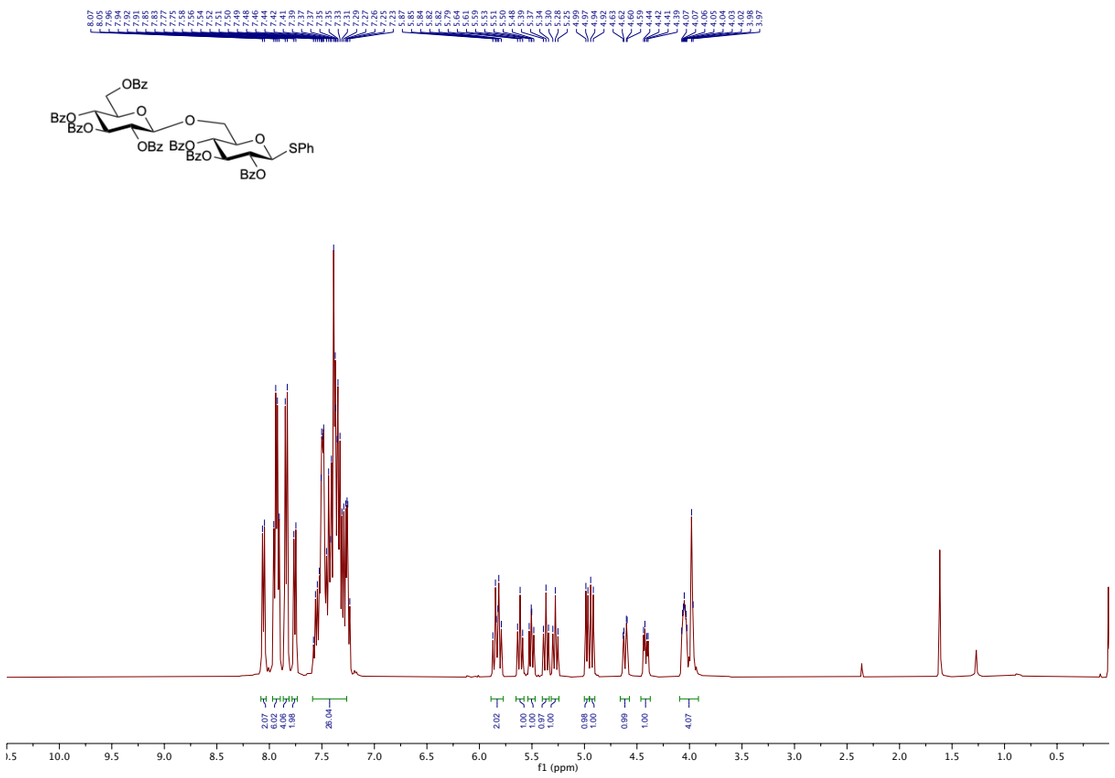


Figure S116. ^{1}H NMR spectrum of **12a** ($CDCl_3$, 400 MHz, 25 ºC).

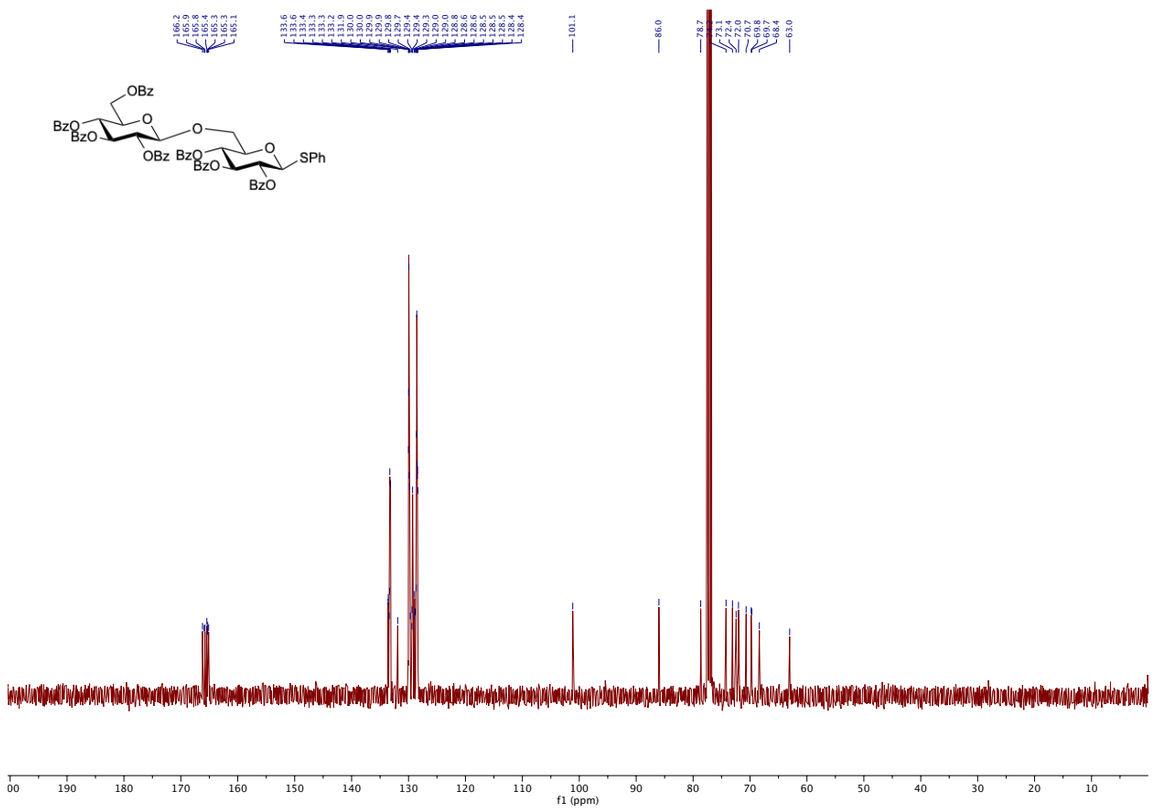


Figure S117. ^{13}C NMR spectrum of **12a** ($CDCl_3$, 100 MHz, 25 ºC).

^{1}H and ^{13}C NMR spectra of **12b**

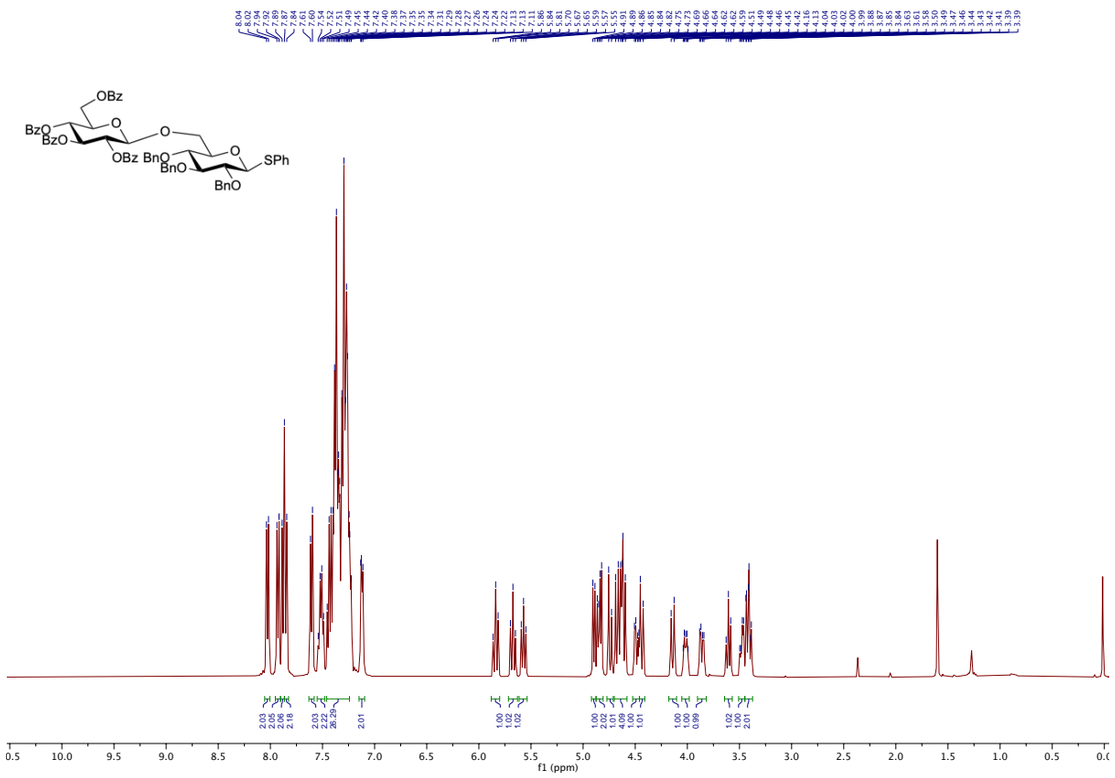


Figure S118. ^{1}H NMR spectrum of **12b** ($CDCl_3$, 400 MHz, 25 °C).

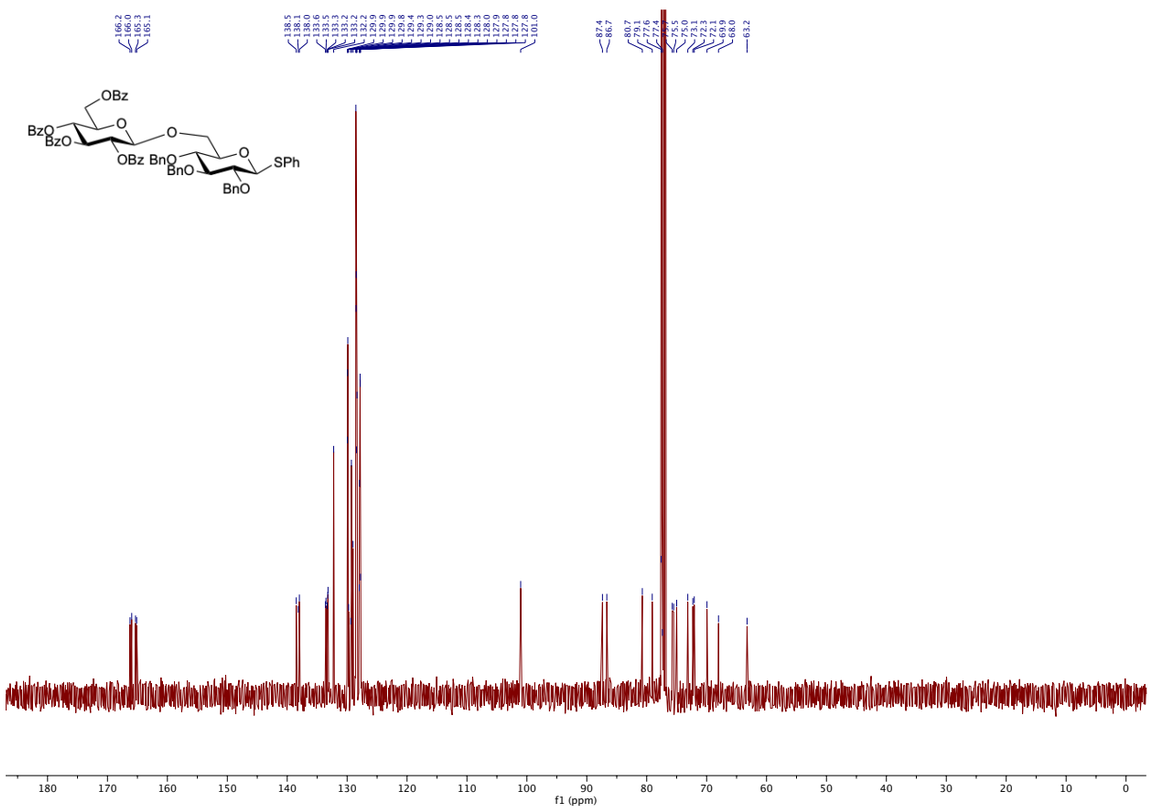


Figure S119. ^{13}C NMR spectrum of **12b** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **14**

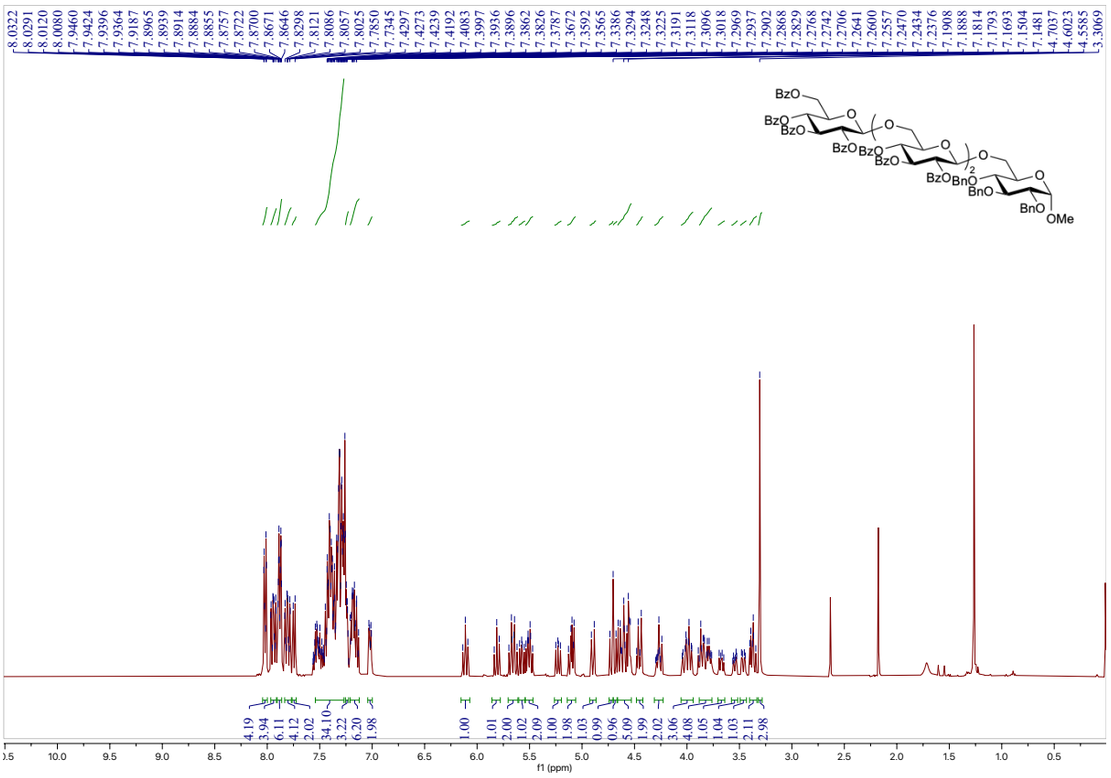


Figure S120. ^{1}H NMR spectrum of **14** ($CDCl_3$, 400 MHz, 25 °C).

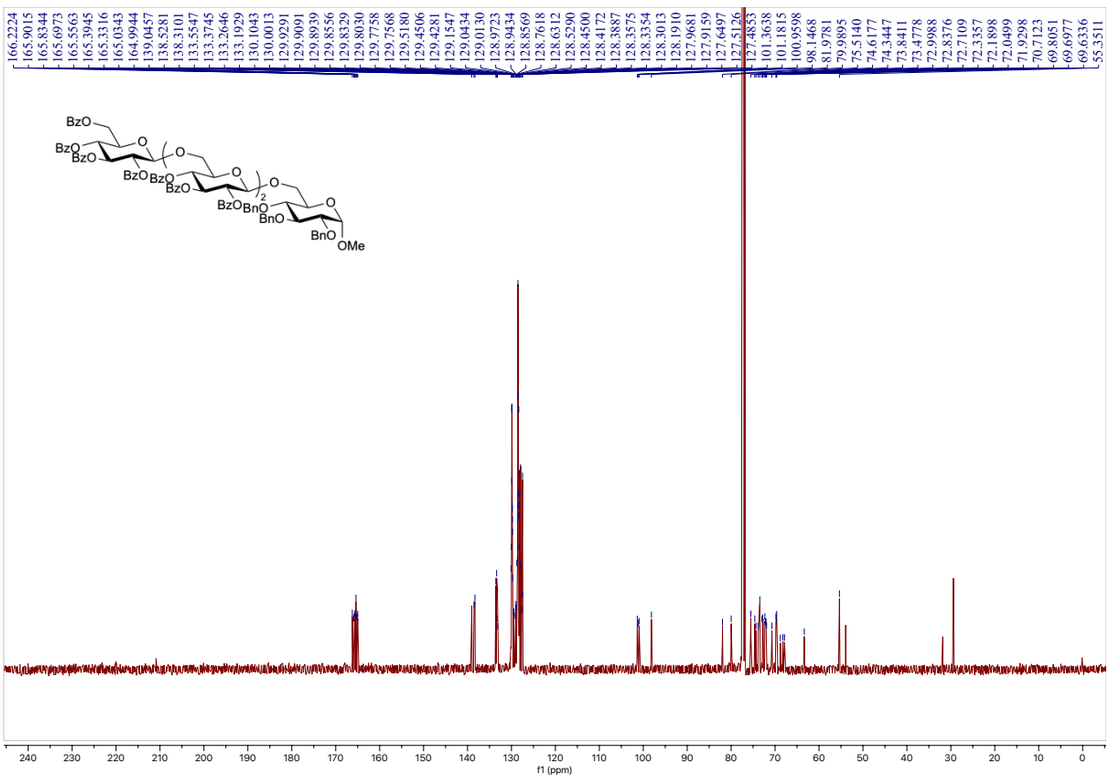


Figure S121. ^{13}C NMR spectrum of **14** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **15**

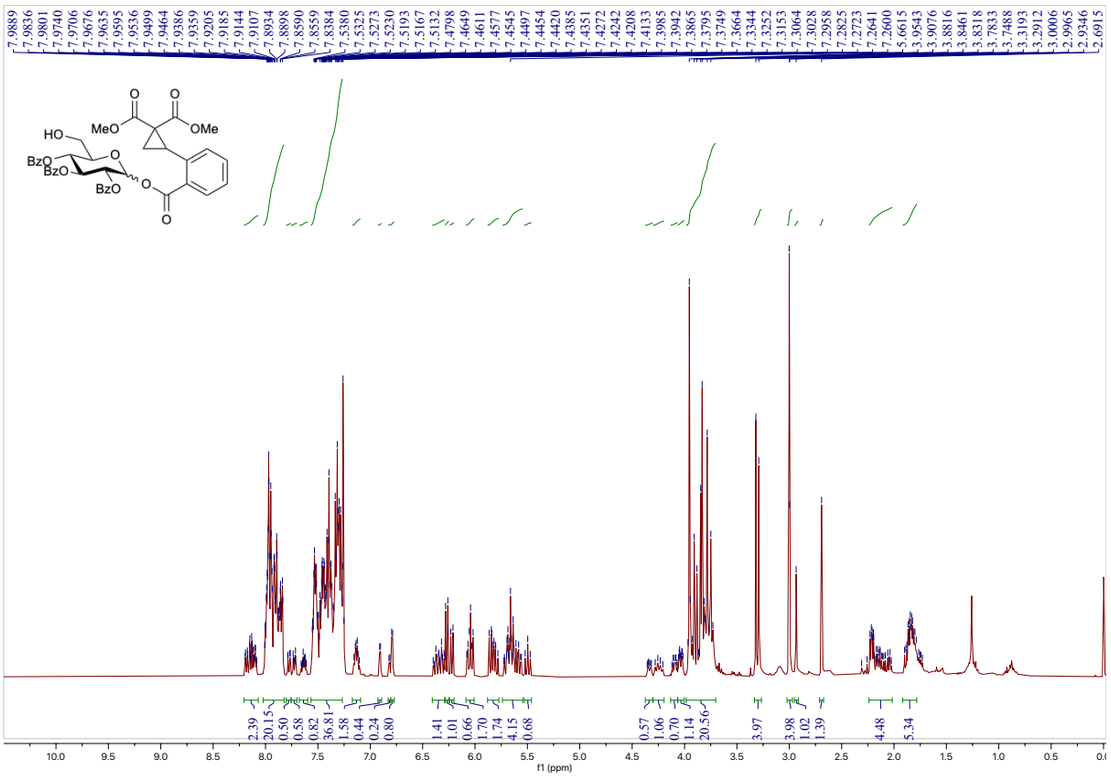


Figure S122. ^{1}H NMR spectrum of **15** ($CDCl_3$, 400 MHz, 25 °C).

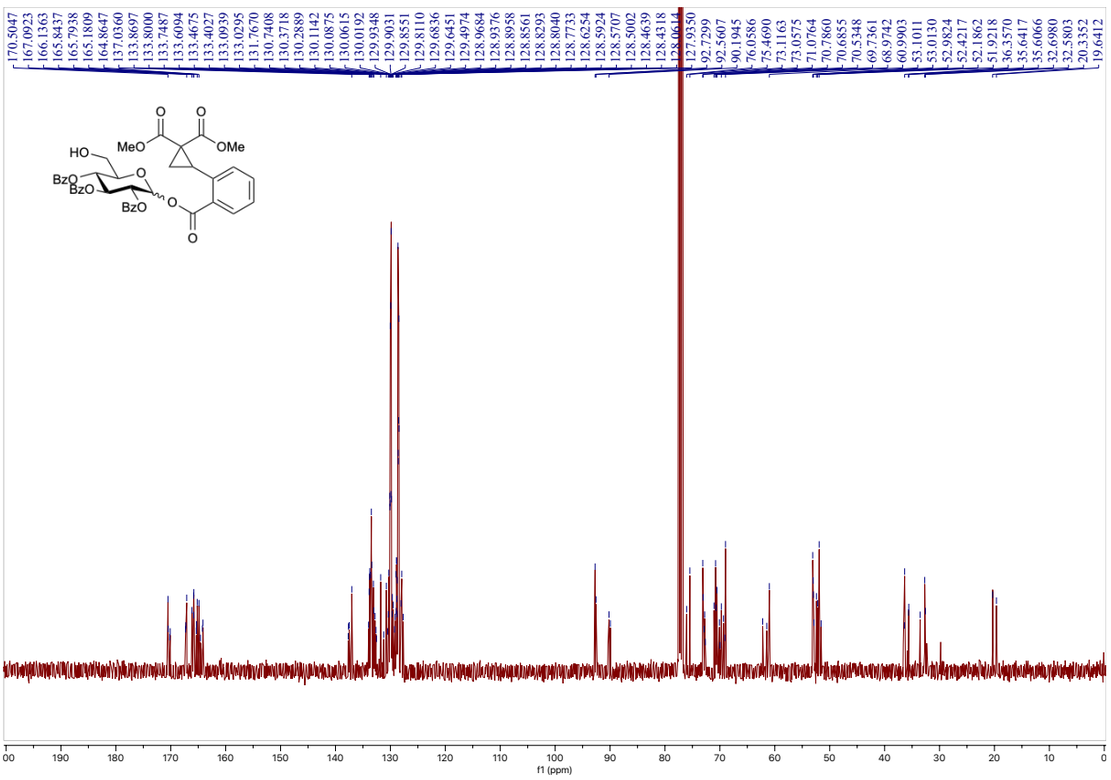


Figure S123. ^{13}C NMR spectrum of **15** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **16**

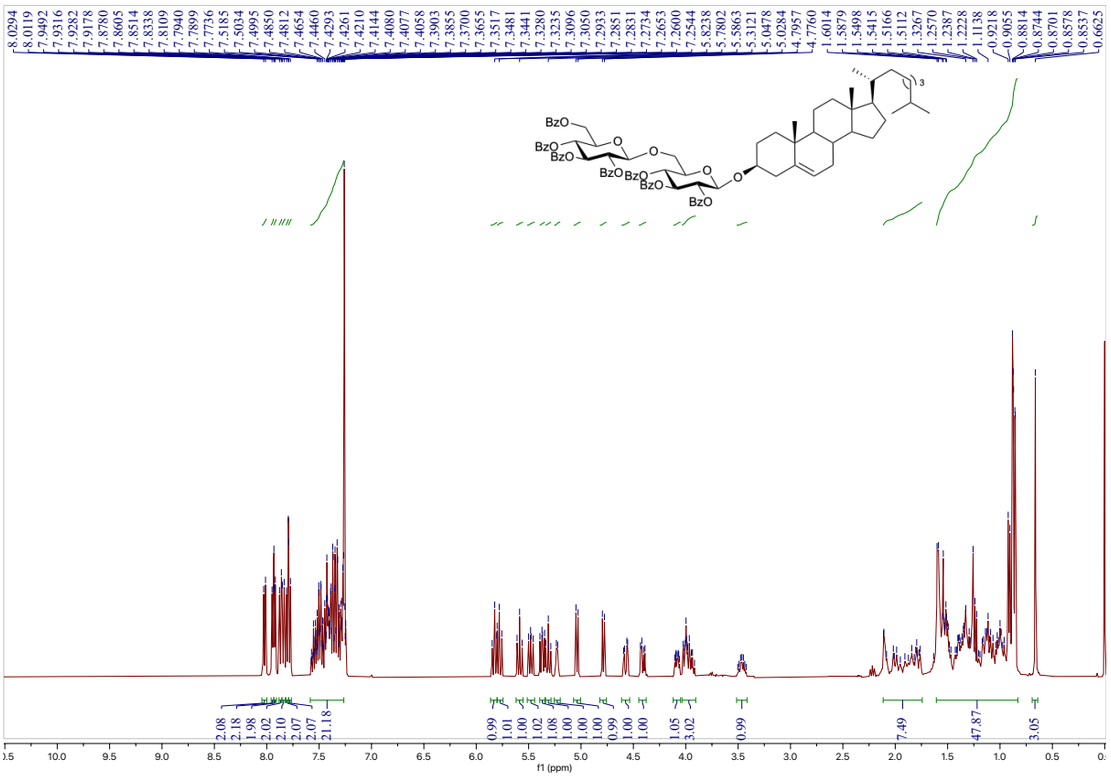


Figure S124. ^{1}H NMR spectrum of **16** ($CDCl_3$, 400 MHz, 25 °C).

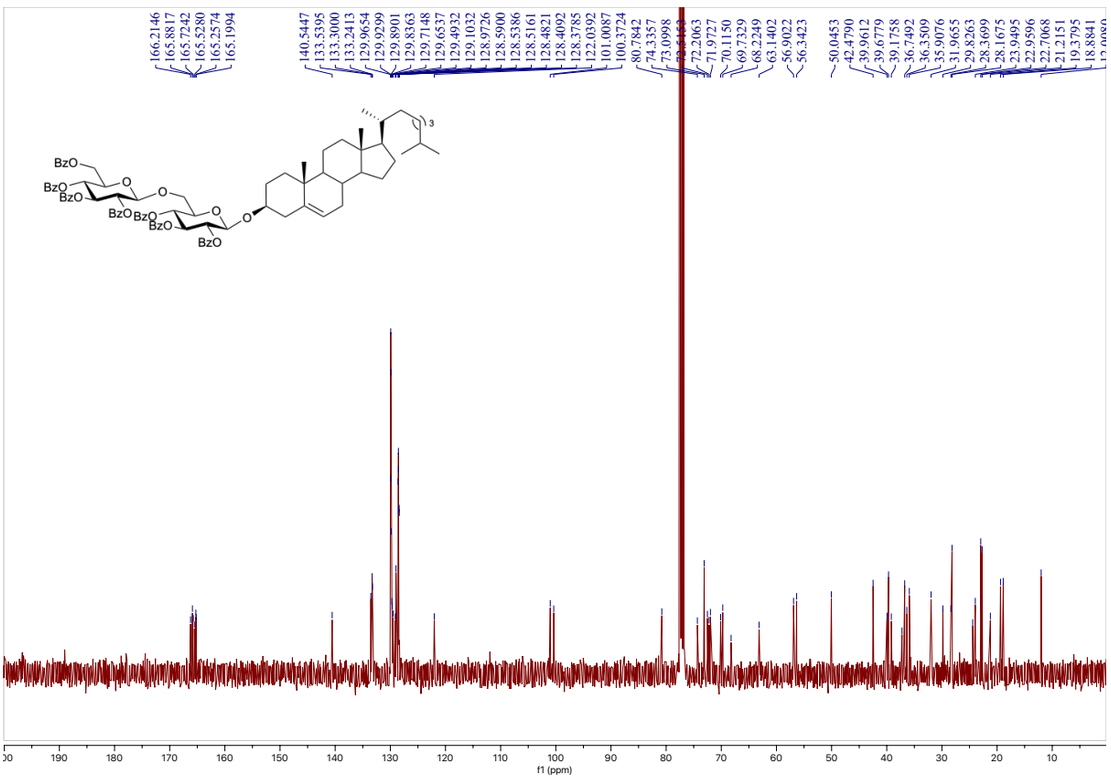


Figure S125. ^{13}C NMR spectrum of **16** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **21α**

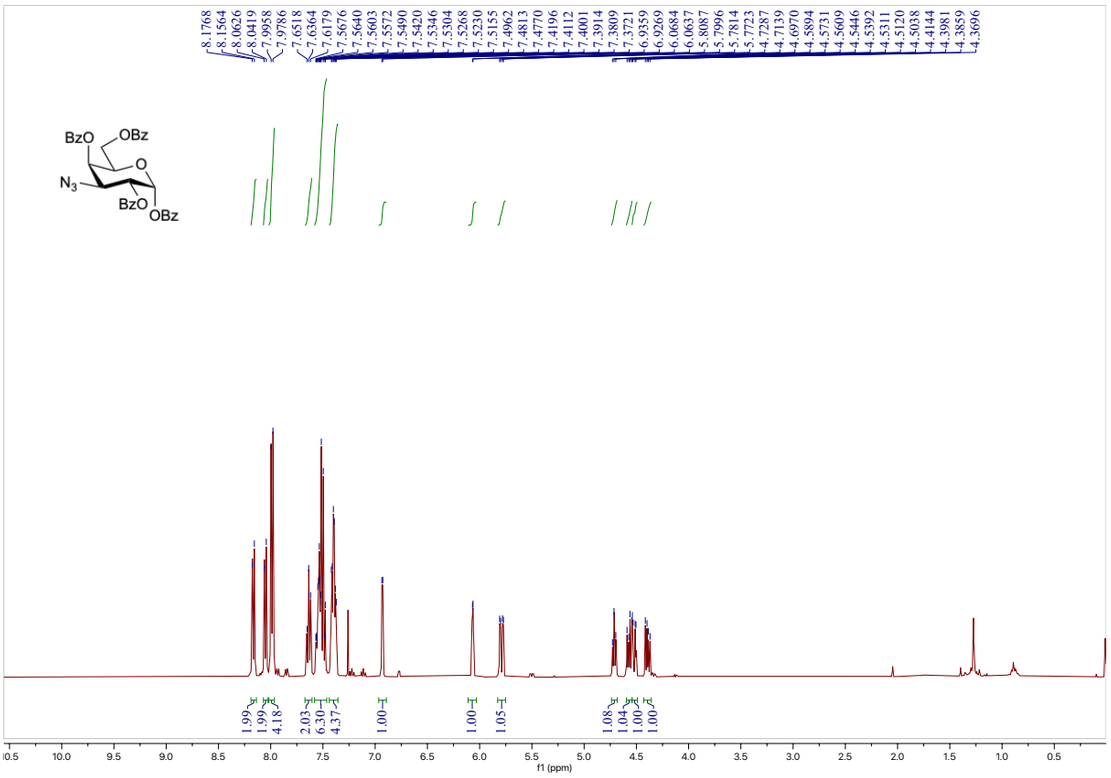


Figure S126. ^{1}H NMR spectrum of **21α** ($CDCl_3$, 400 MHz, 25 °C).

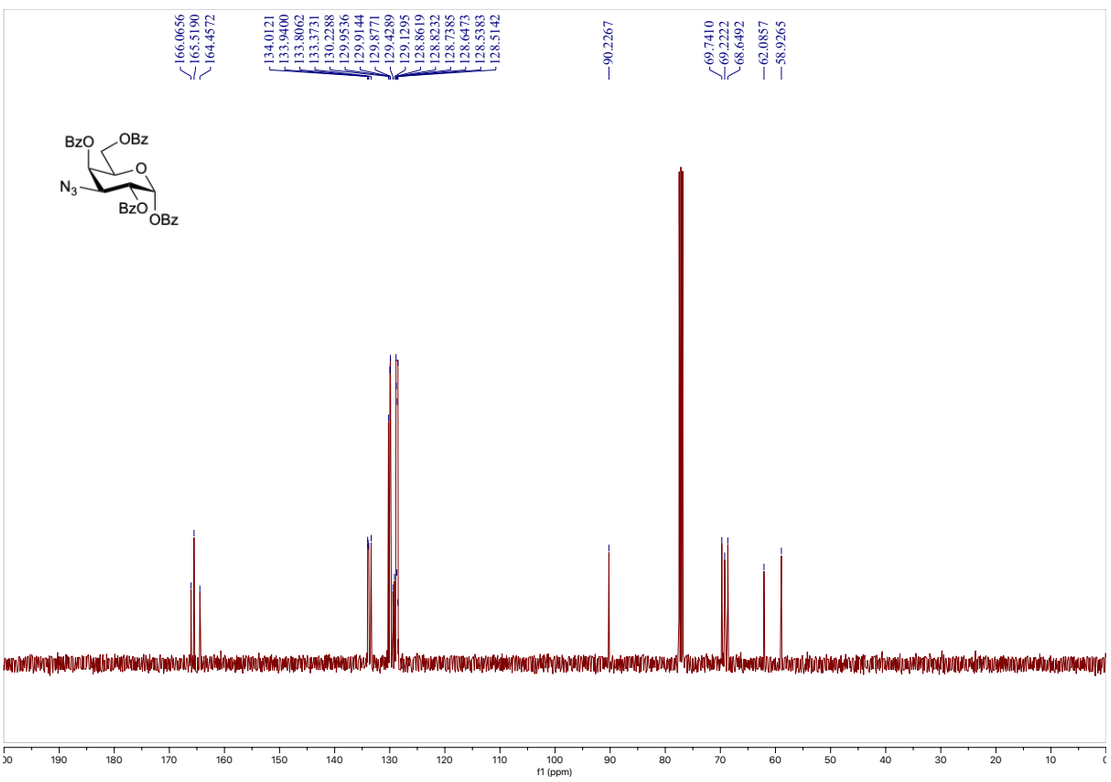


Figure S127. ^{13}C NMR spectrum of **21α** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **21β**

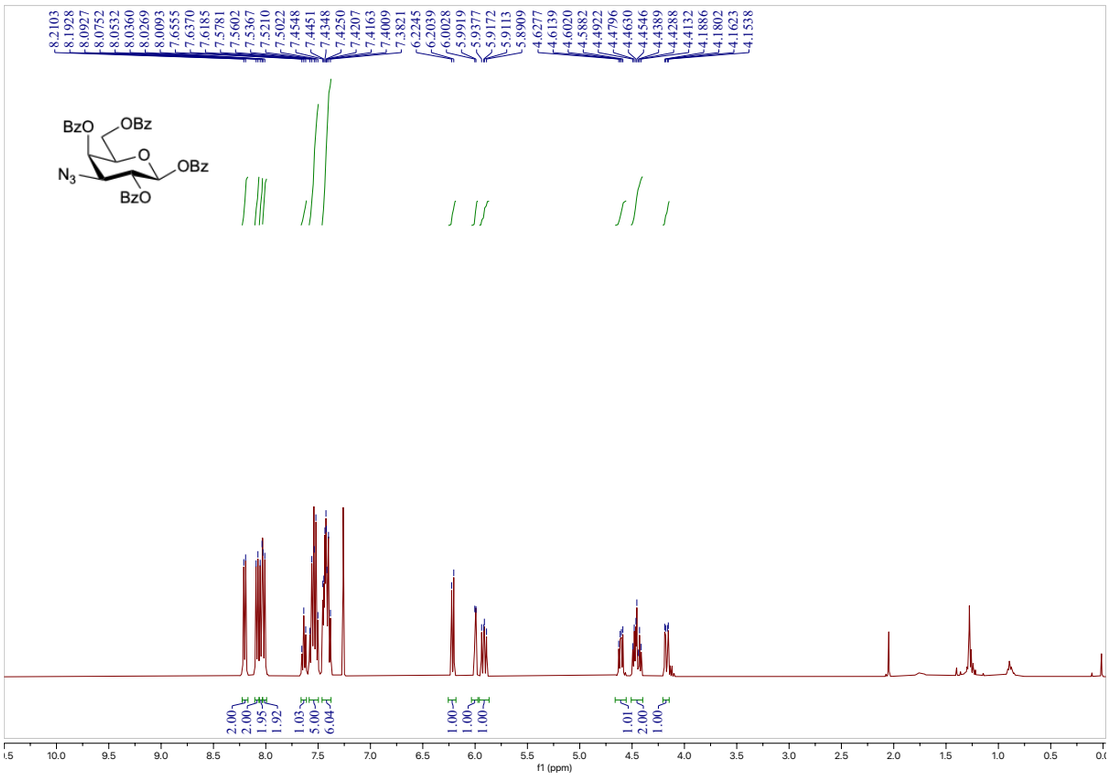


Figure S128. ^{1}H NMR spectrum of **21β** ($CDCl_3$, 400 MHz, 25 °C).

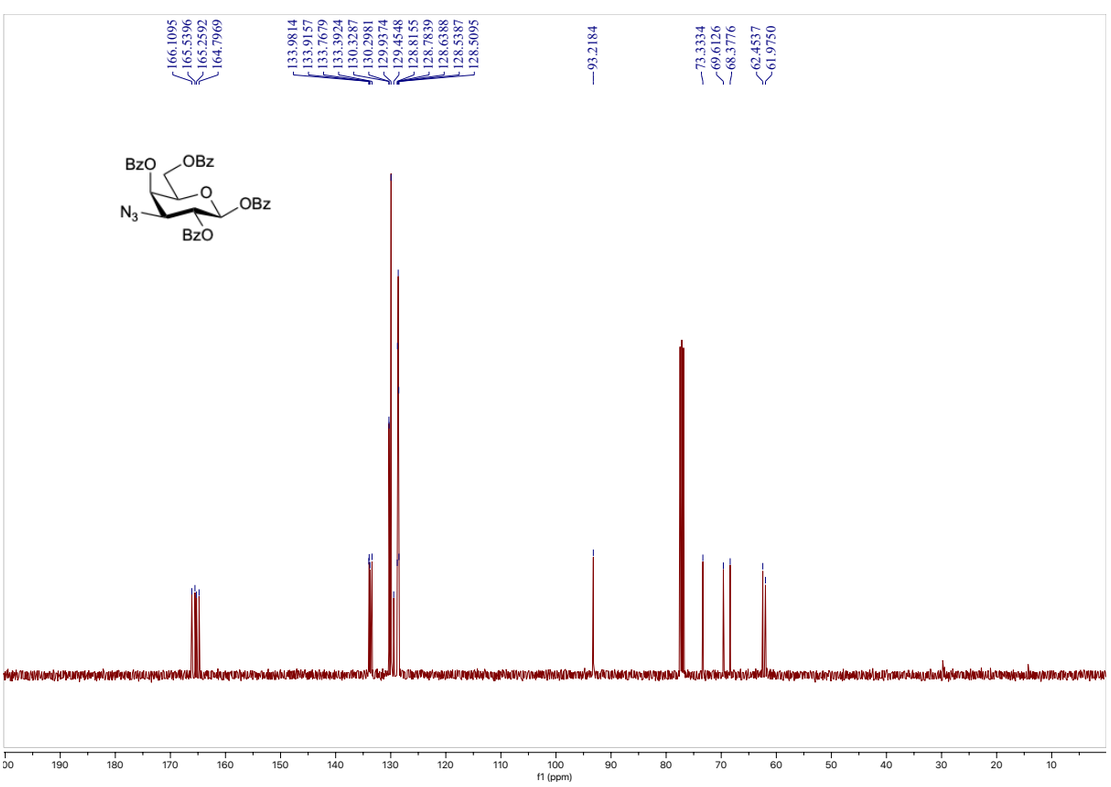


Figure S129. ^{13}C NMR spectrum of **21β** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **23**

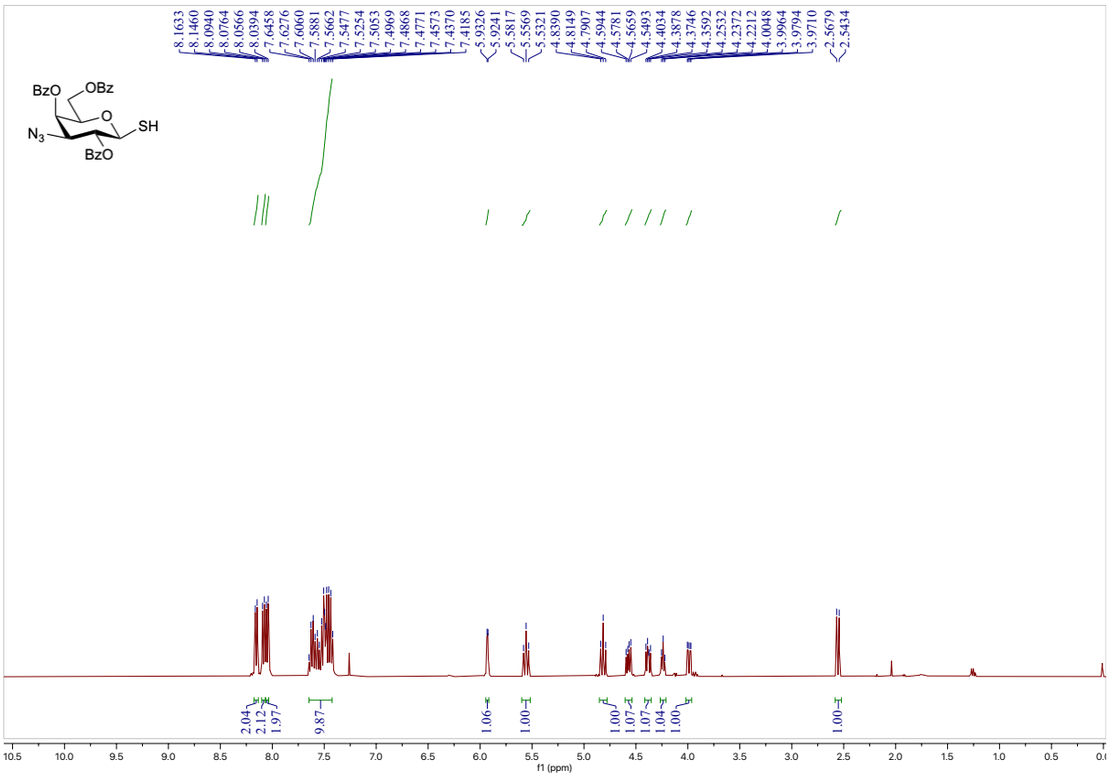


Figure S130. ^{1}H NMR spectrum of **23** ($CDCl_3$, 400 MHz, 25 °C).

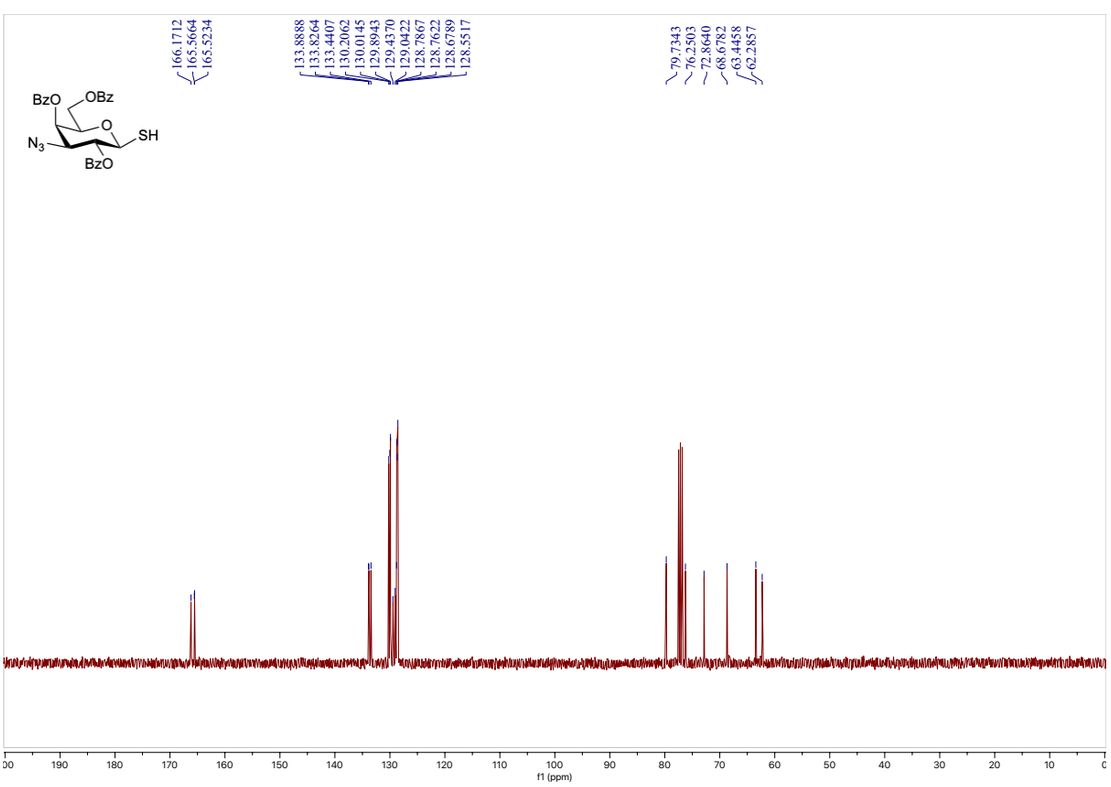


Figure S131. ^{13}C NMR spectrum of **23** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **24**

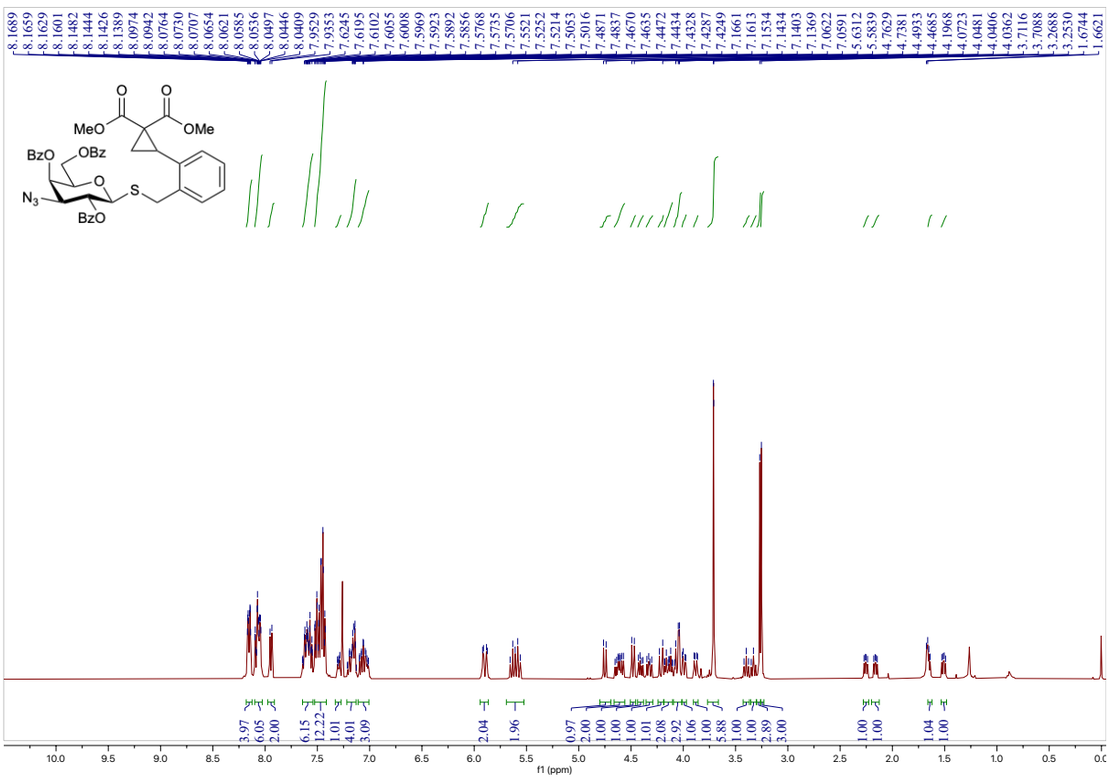


Figure S132. ^{1}H NMR spectrum of **24** ($CDCl_3$, 400 MHz, 25 °C).

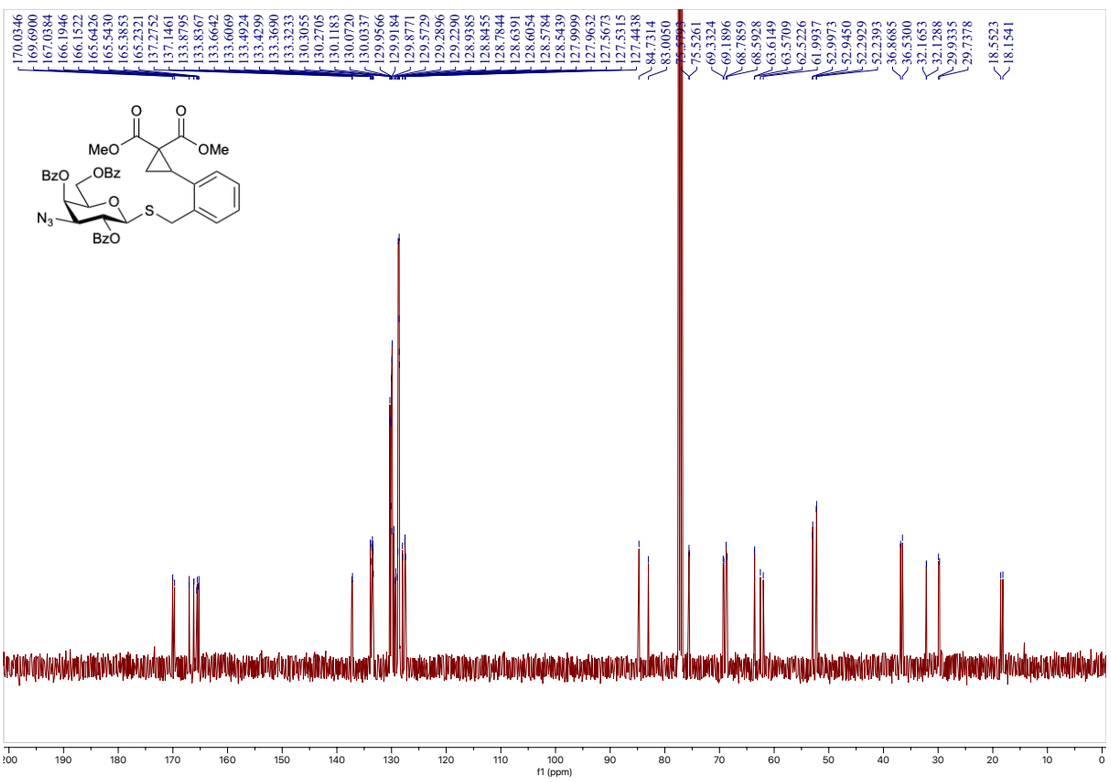


Figure S133. ^{13}C NMR spectrum of **24** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H and ^{13}C NMR spectra of **25**

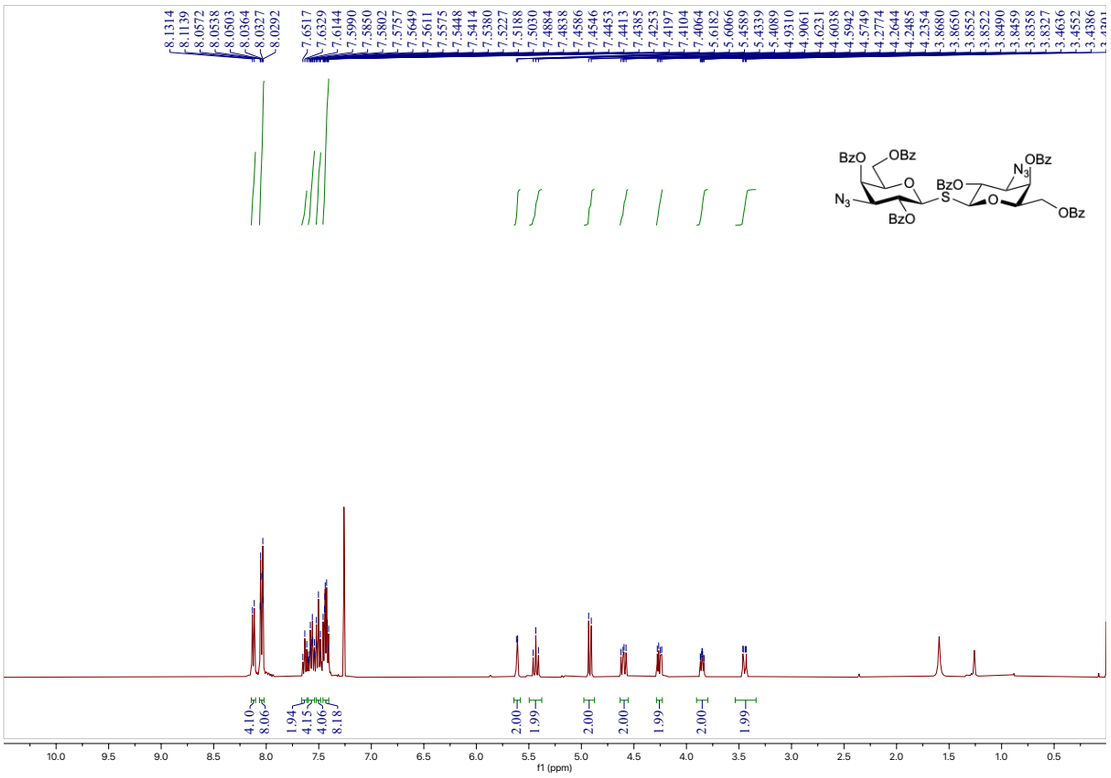


Figure S134. ^{1}H NMR spectrum of **25** ($CDCl_3$, 400 MHz, 25 °C).

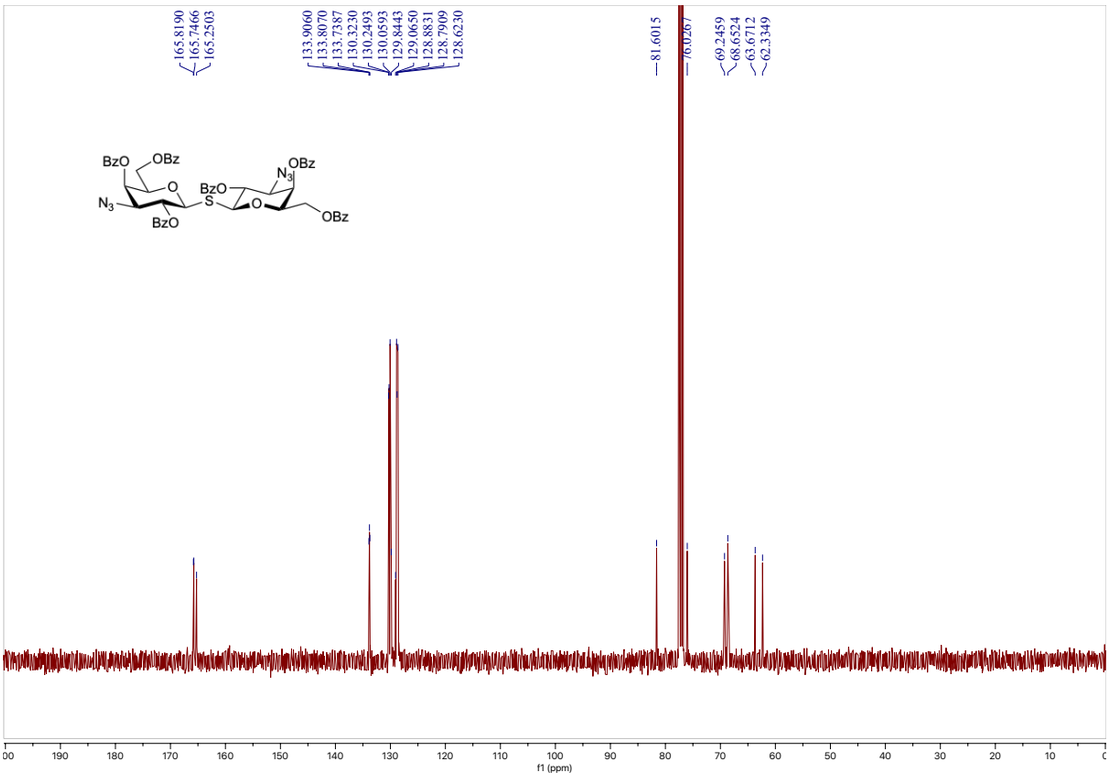


Figure S135. ^{13}C NMR spectrum of **25** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H, ^{13}C and ^{19}F NMR spectra of **26**

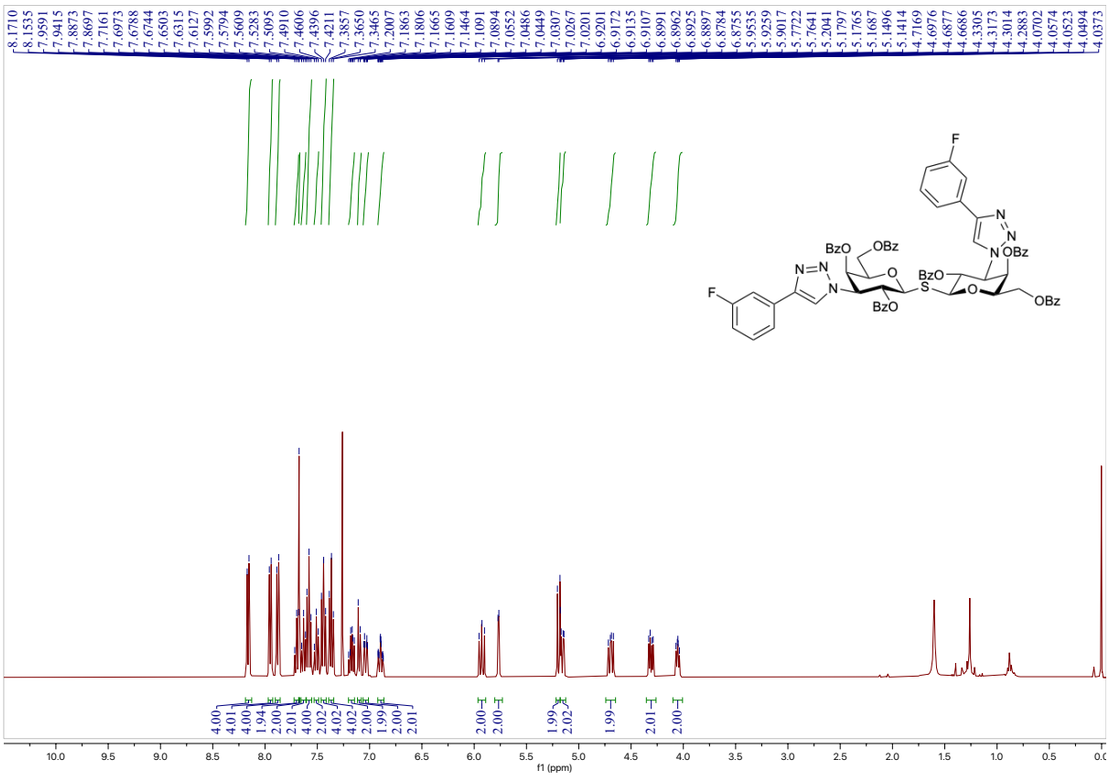


Figure S136. ^{1}H NMR spectrum of **26** ($CDCl_3$, 400 MHz, 25 °C).

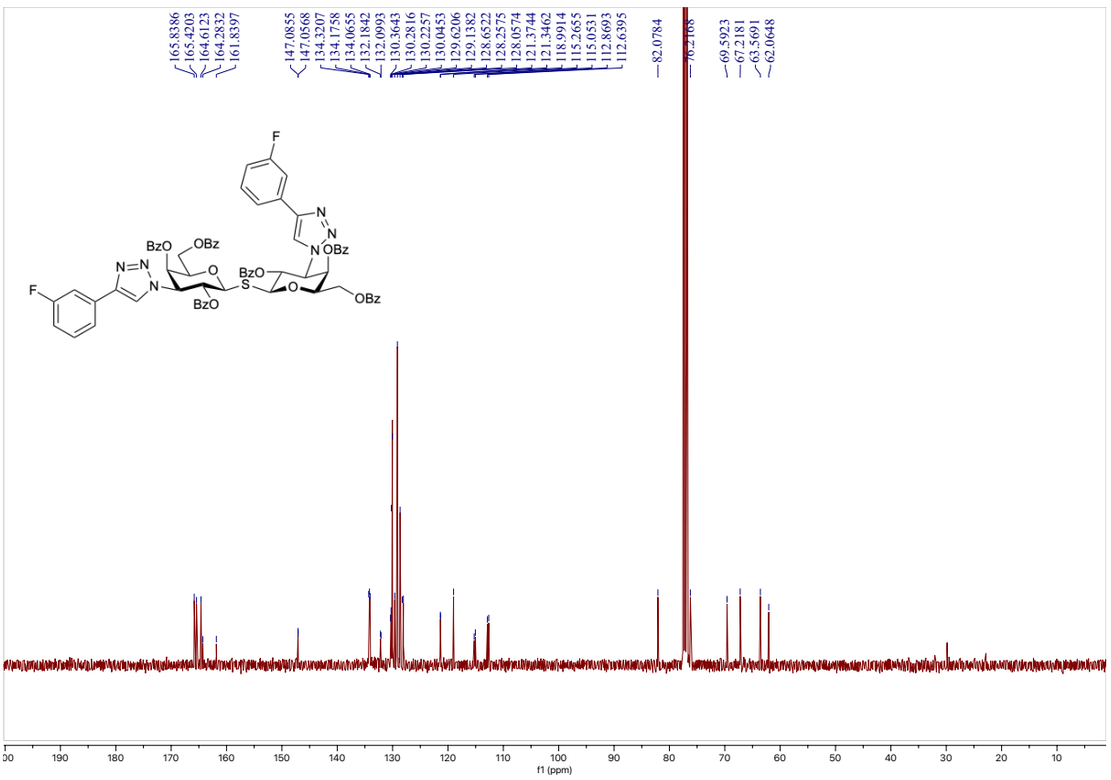


Figure S137. ^{13}C NMR spectrum of **26** ($CDCl_3$, 100 MHz, 25 °C).

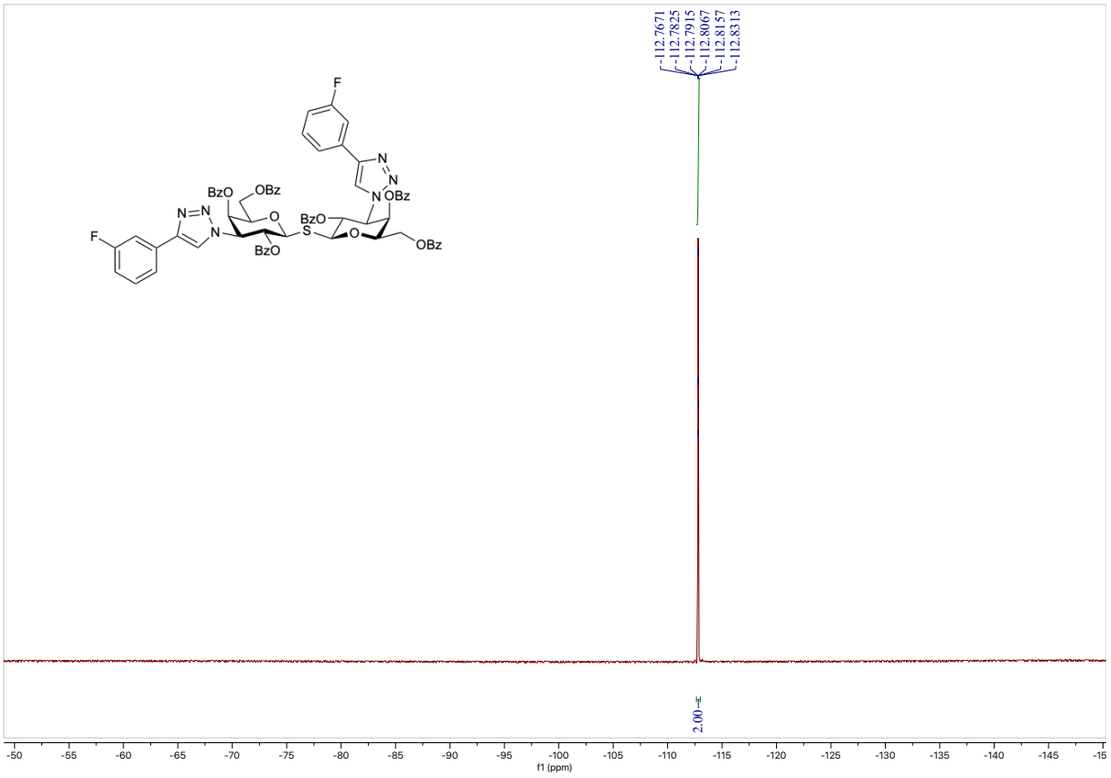


Figure S138. ^{19}F NMR spectrum of **26** ($CDCl_3$, 376 MHz, 25 ºC).

^{1}H, ^{13}C and ^{19}F NMR spectra of **27**

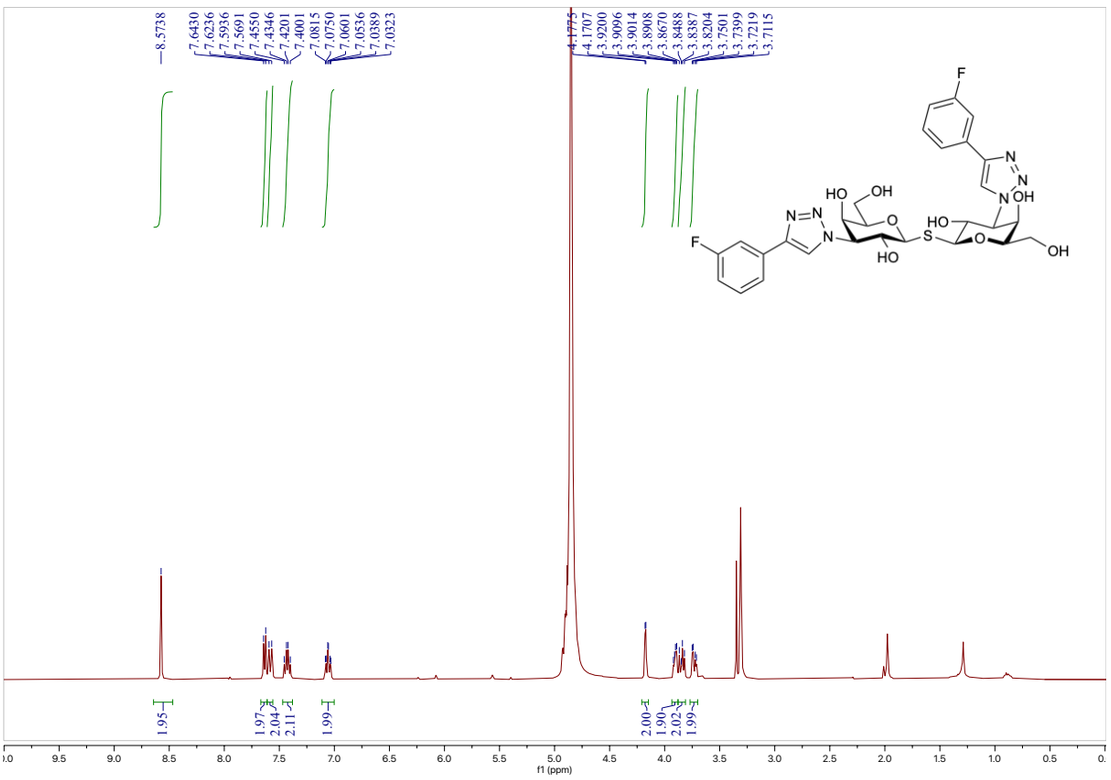


Figure S139. ^{1}H NMR spectrum of **27** (CD_3OD, 400 MHz, 25 ºC).

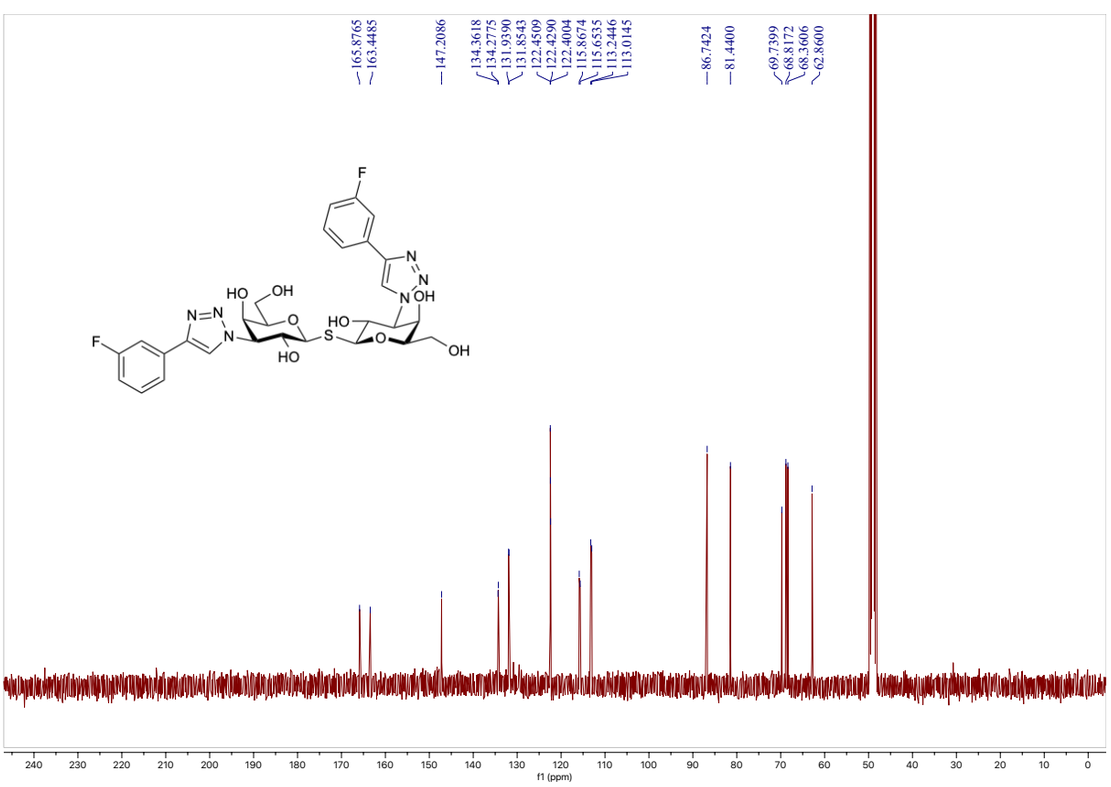


Figure S140. ^{13}C NMR spectrum of **27** (CD_3OD, 100 MHz, 25 ºC).

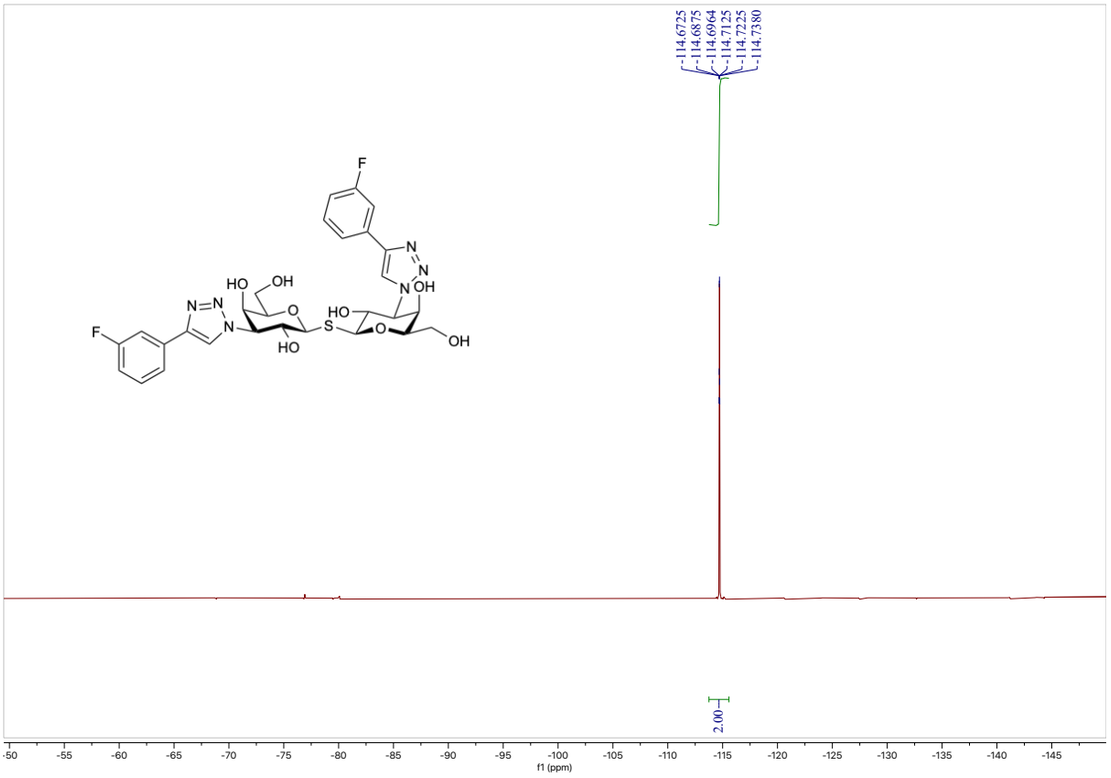


Figure S141. ^{13}C NMR spectrum of **27** (CD_3OD, 376 MHz, 25 °C).

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

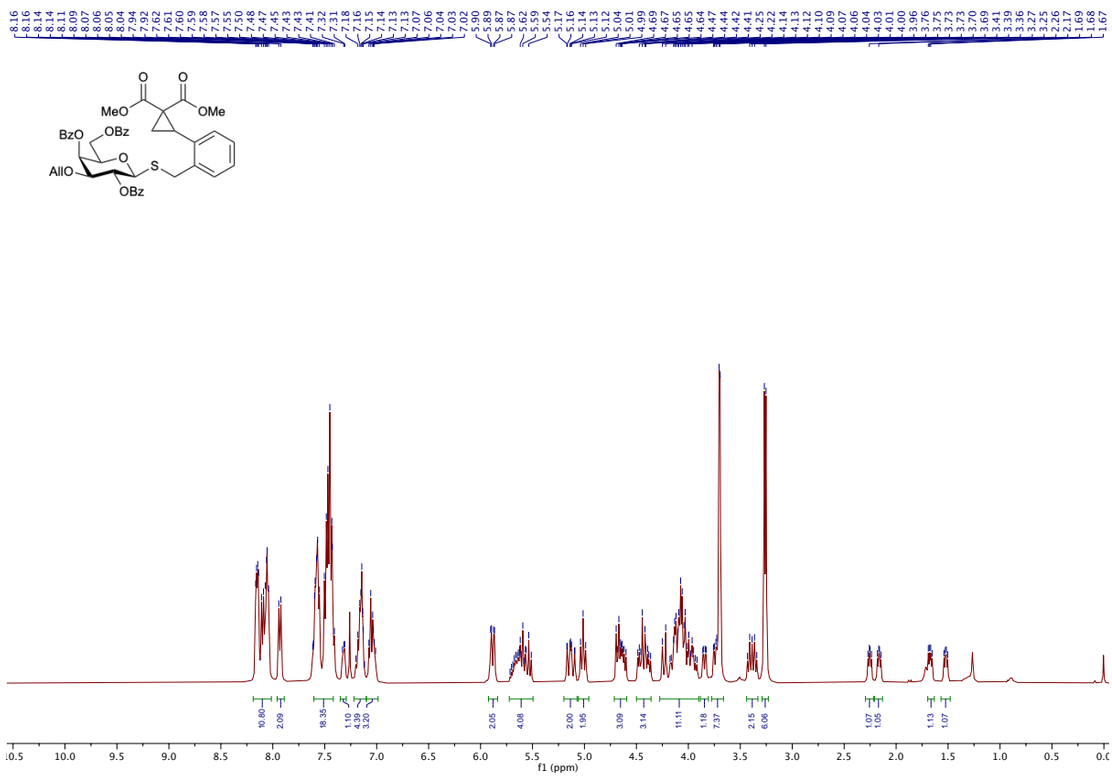


Figure S142. ^{1}H NMR spectrum of **29** ($CDCl_3$, 400 MHz, 25 °C).

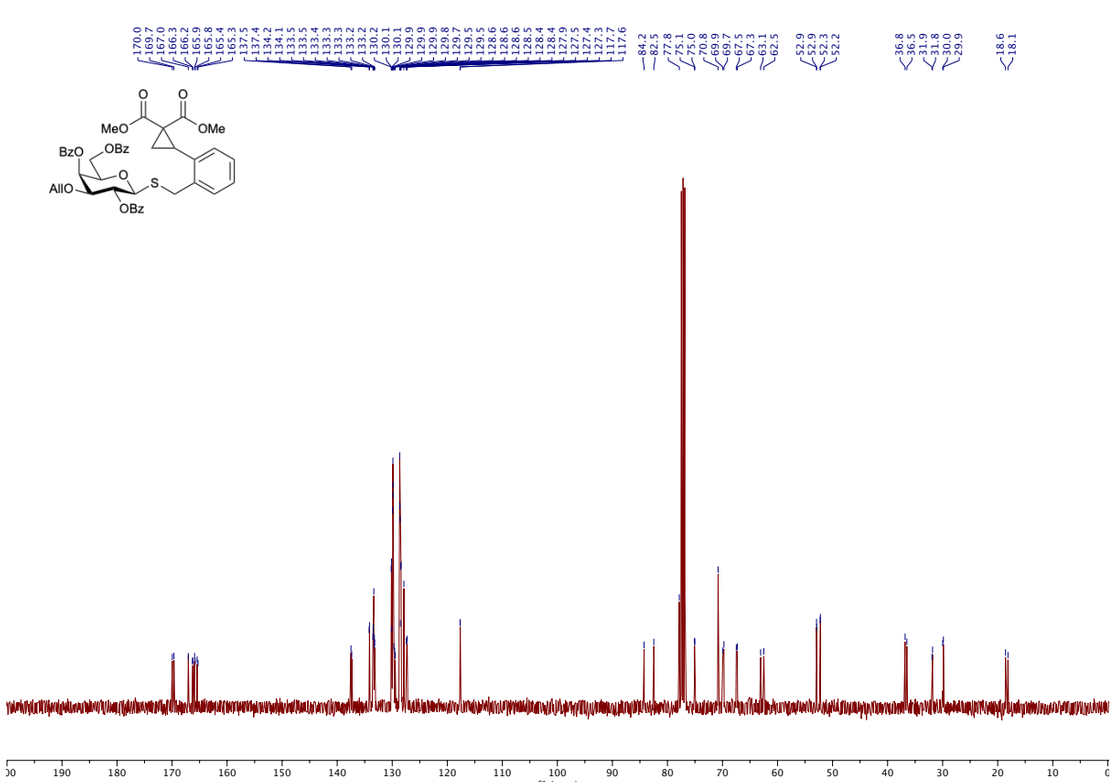


Figure S143. ^{13}C NMR spectrum of **29** ($CDCl_3$, 100 MHz, 25 °C).

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

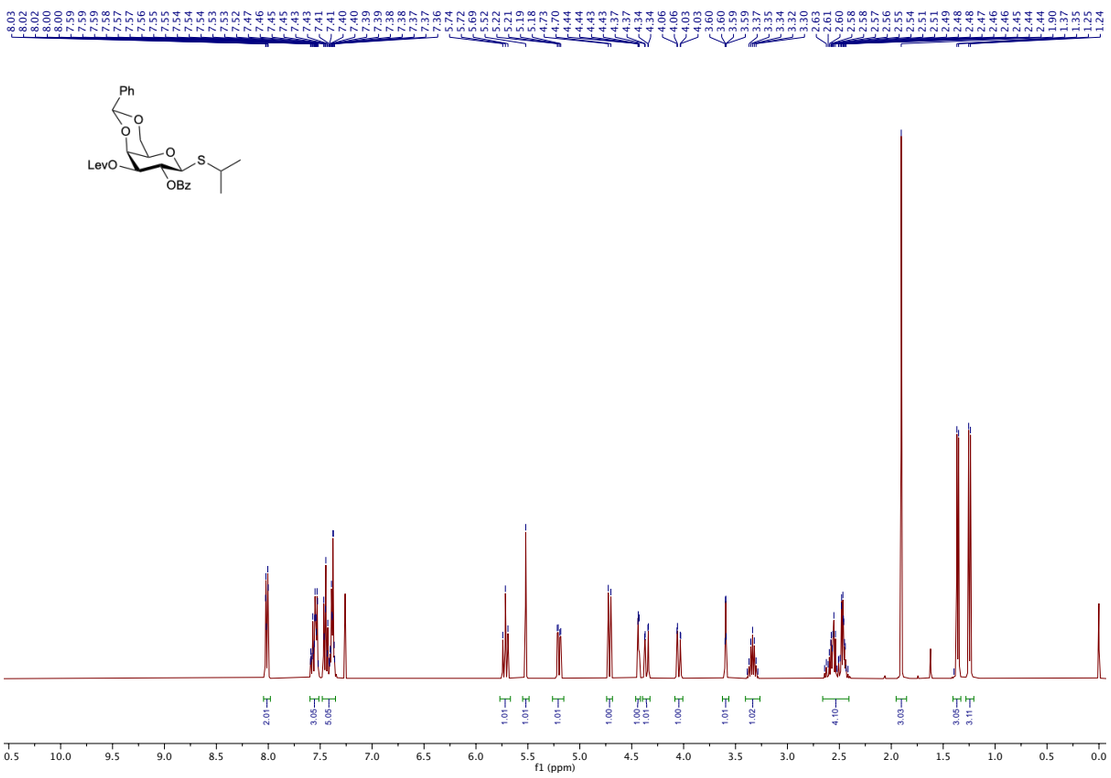


Figure S144. ^{1}H NMR spectrum of **32** ($CDCl_3$, 400 MHz, 25 °C).

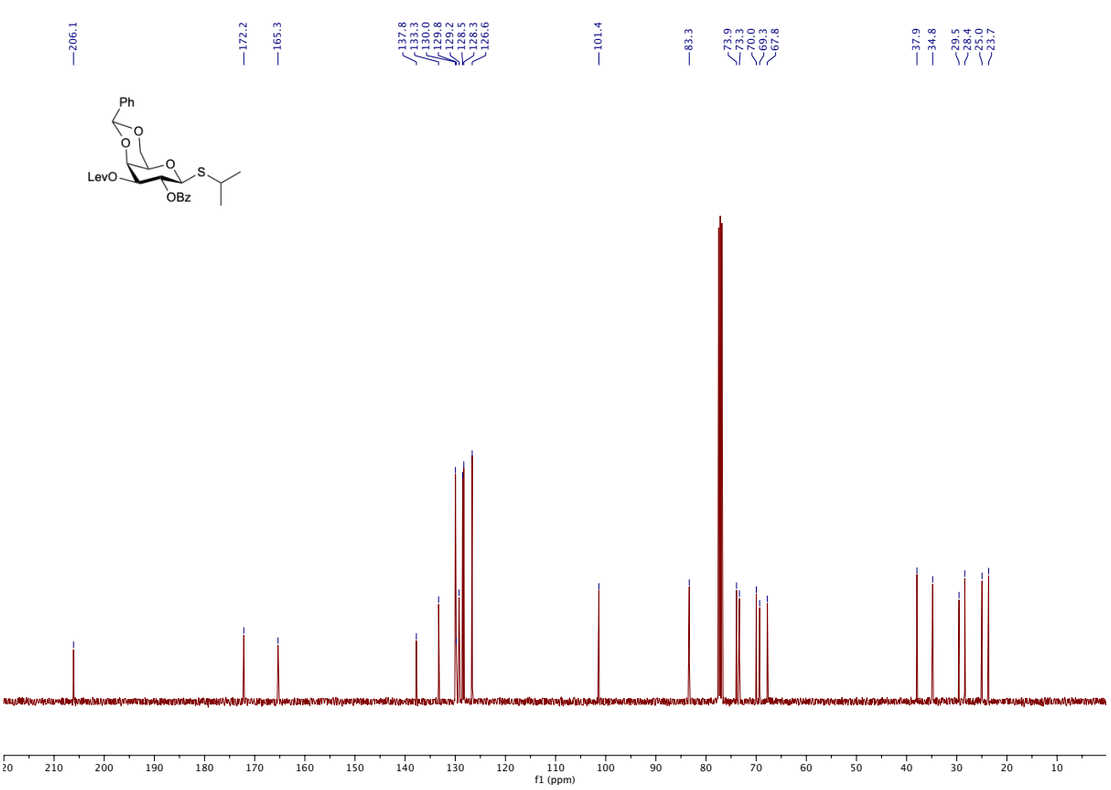


Figure S145. ^{13}C NMR spectrum of **32** ($CDCl_3$, 100 MHz, 25 °C).

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

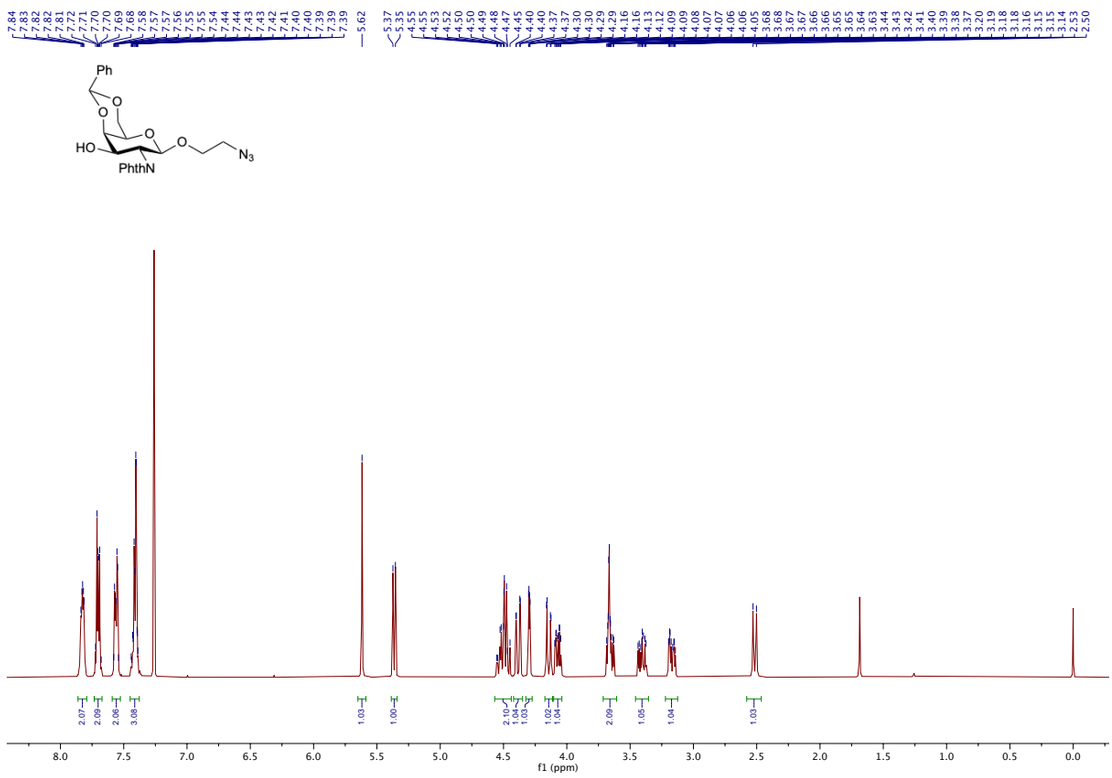


Figure S146. ^{1}H NMR spectrum of **33** ($CDCl_3$, 400 MHz, 25 °C).

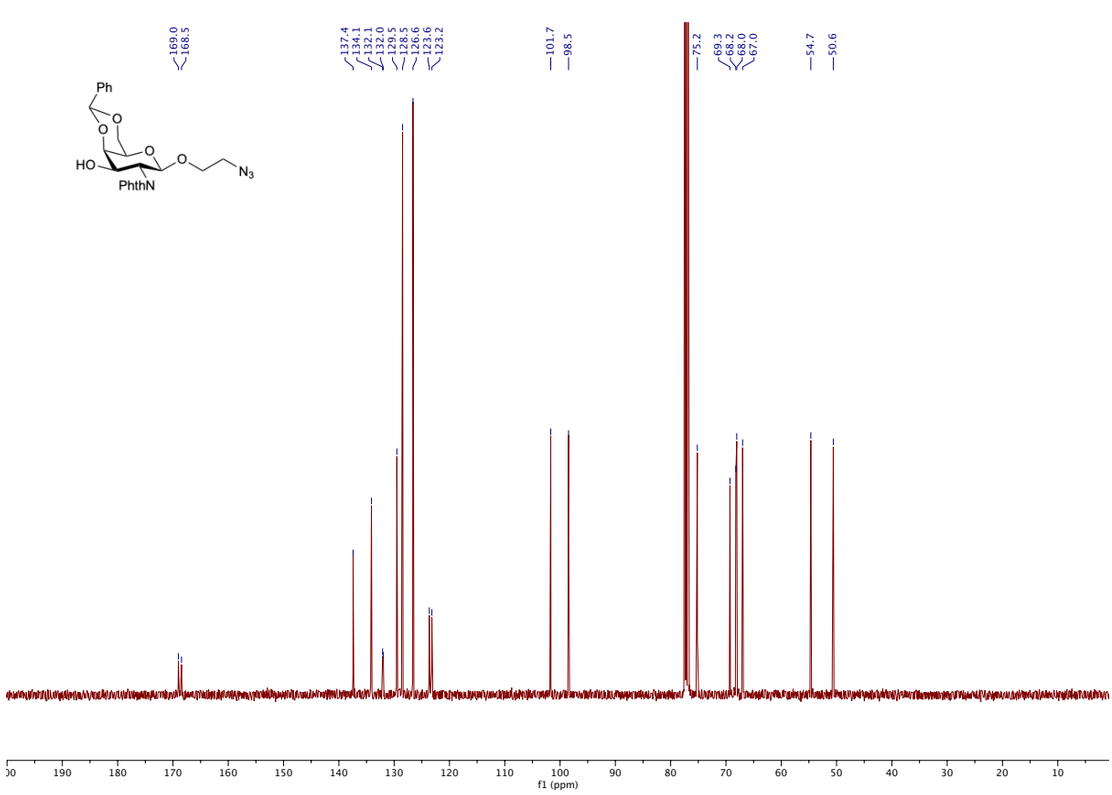


Figure S147. ^{13}C NMR spectrum of **33** ($CDCl_3$, 100 MHz, 25 °C).

^{1}H, ^{13}C, COSY and HSQC NMR spectra of **41**

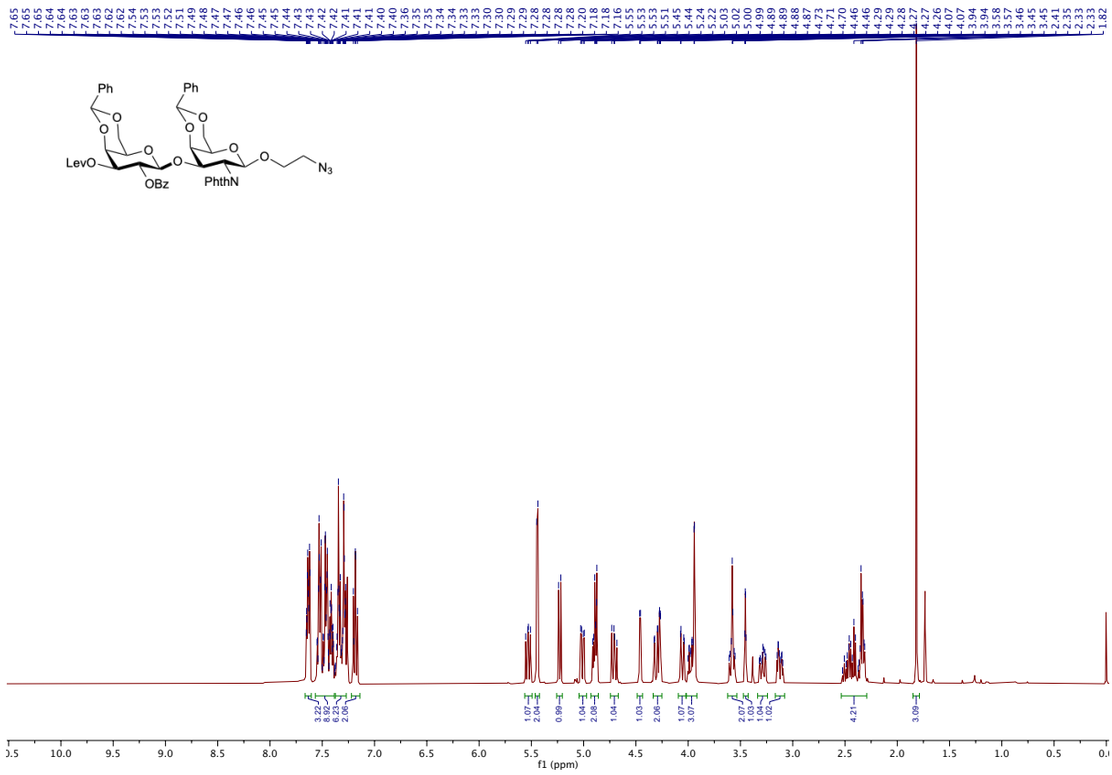


Figure S148. ^{1}H NMR spectrum of **41** ($CDCl_3$, 400 MHz, 25 °C).

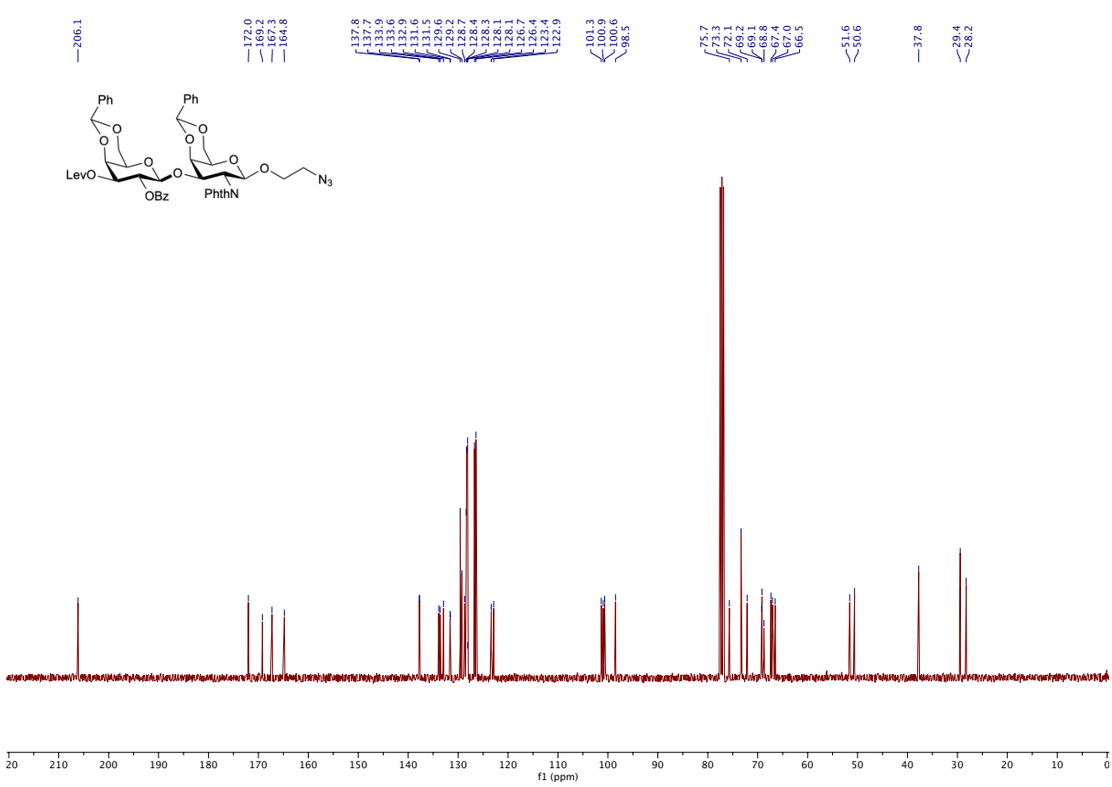


Figure S149. ^{13}C NMR spectrum of **41** ($CDCl_3$, 100 MHz, 25 °C).

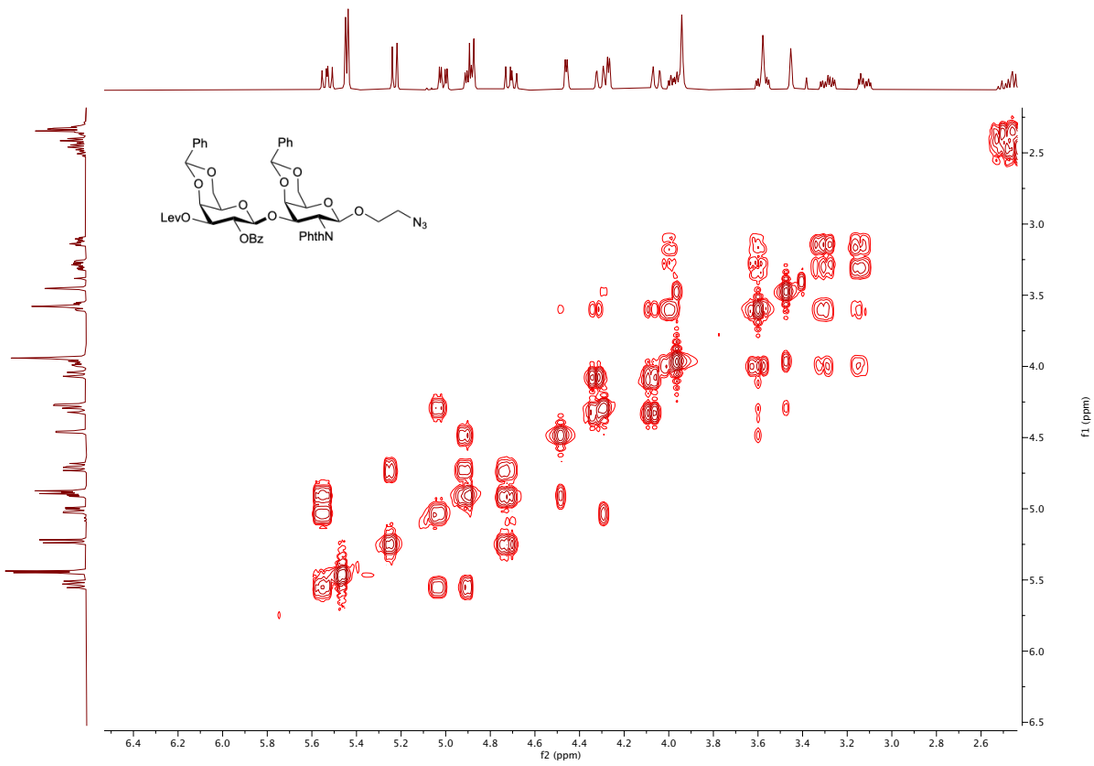


Figure S150. ^{1}H-^{1}H COSY spectrum of **41** ($CDCl_3$, 25 °C).

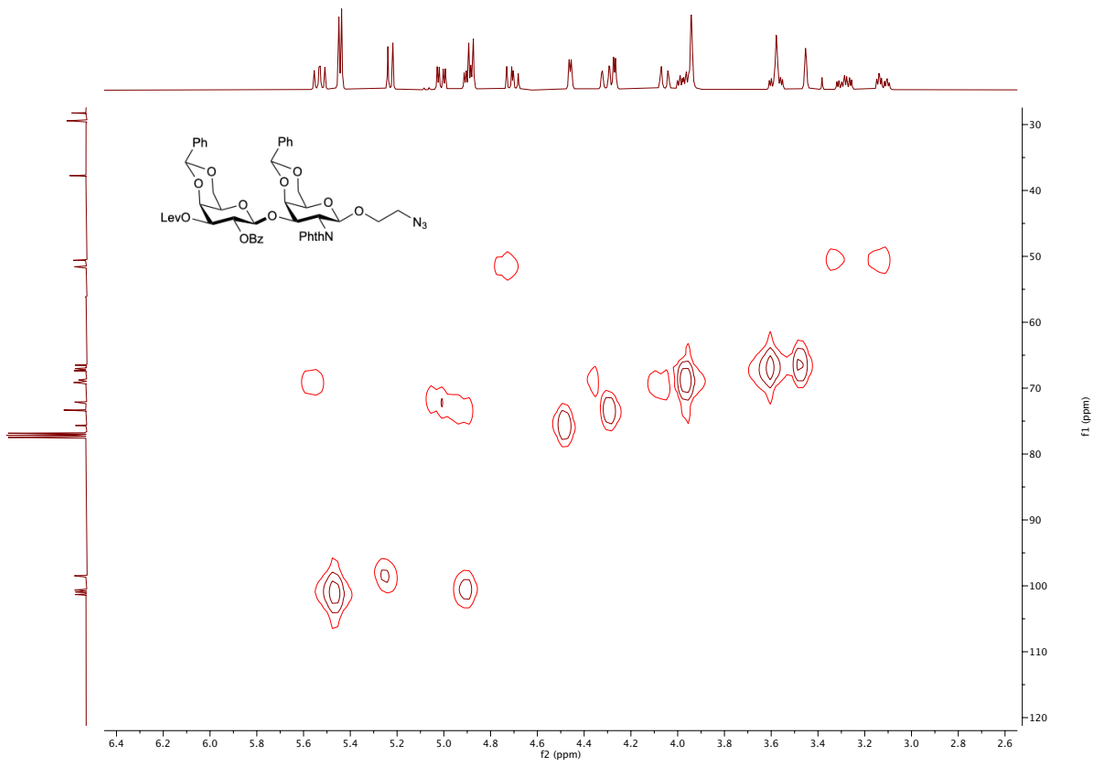


Figure S151. ^{1}H-^{13}C HSQC spectrum of **41** ($CDCl_3$, 25 °C).

^{1}H, ^{13}C, COSY and HSQC NMR spectra of **31**

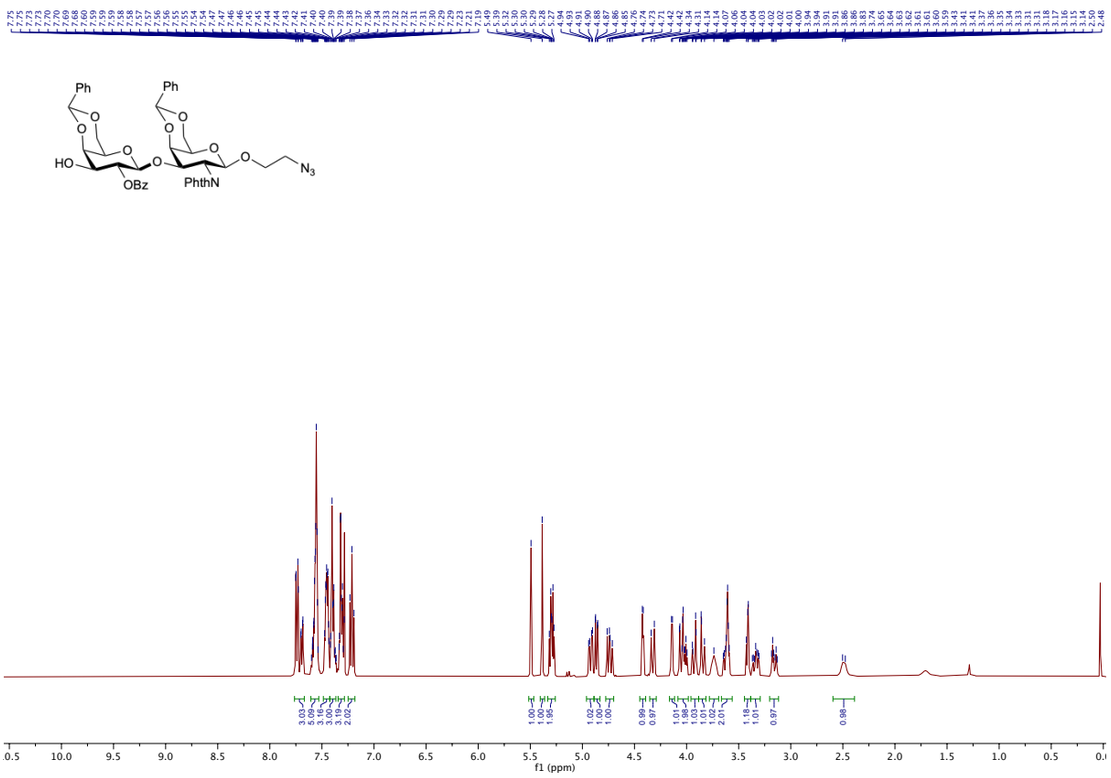


Figure S152. ^{1}H NMR spectrum of **31** ($CDCl_3$, 400 MHz, 25 °C).

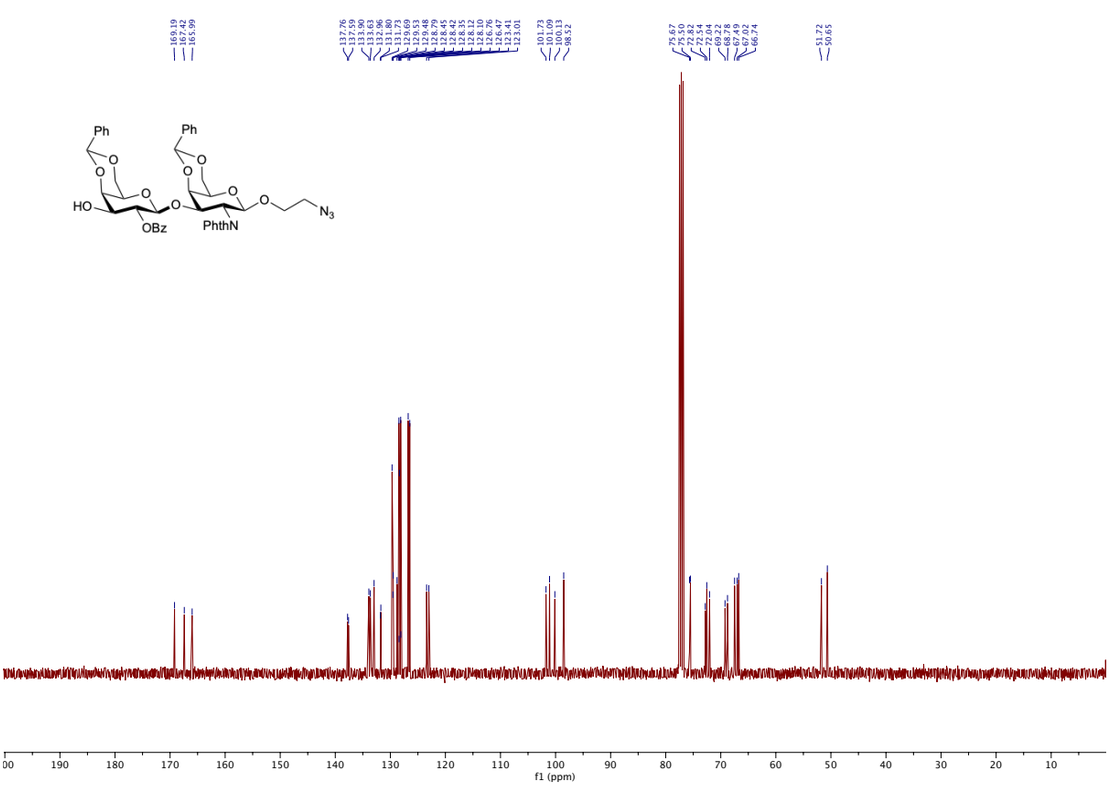


Figure S153. ^{13}C NMR spectrum of **31** ($CDCl_3$, 100 MHz, 25 °C).

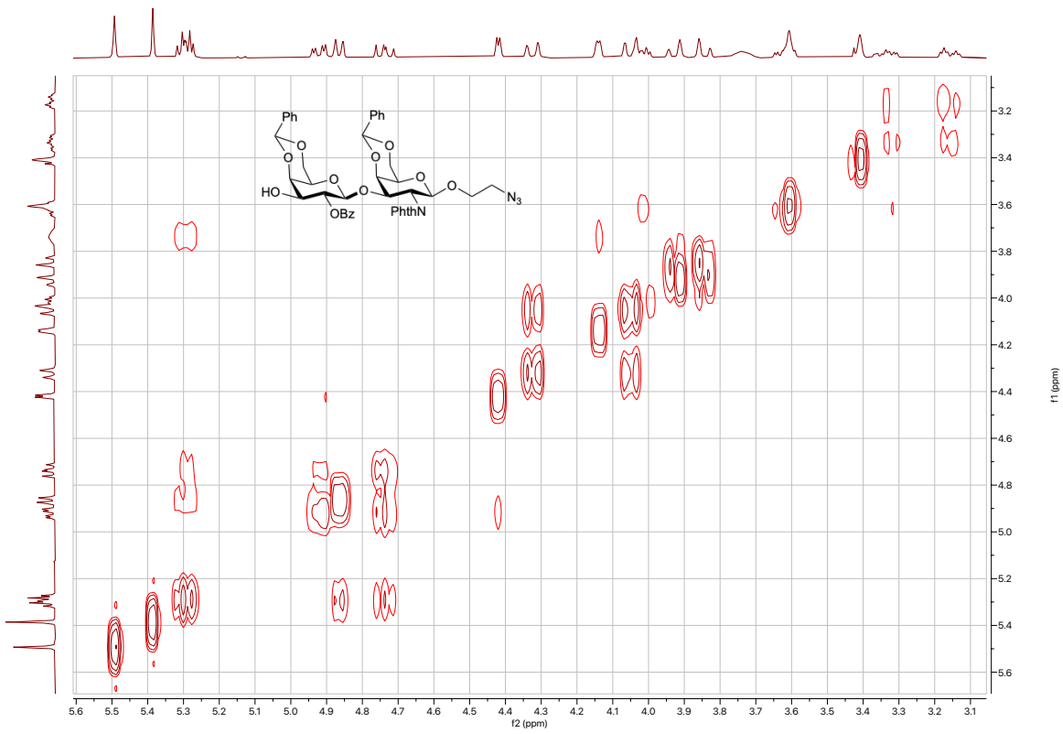


Figure S154. ^{1}H-^{1}H COSY spectrum of **31** ($CDCl_3$, 25 °C).

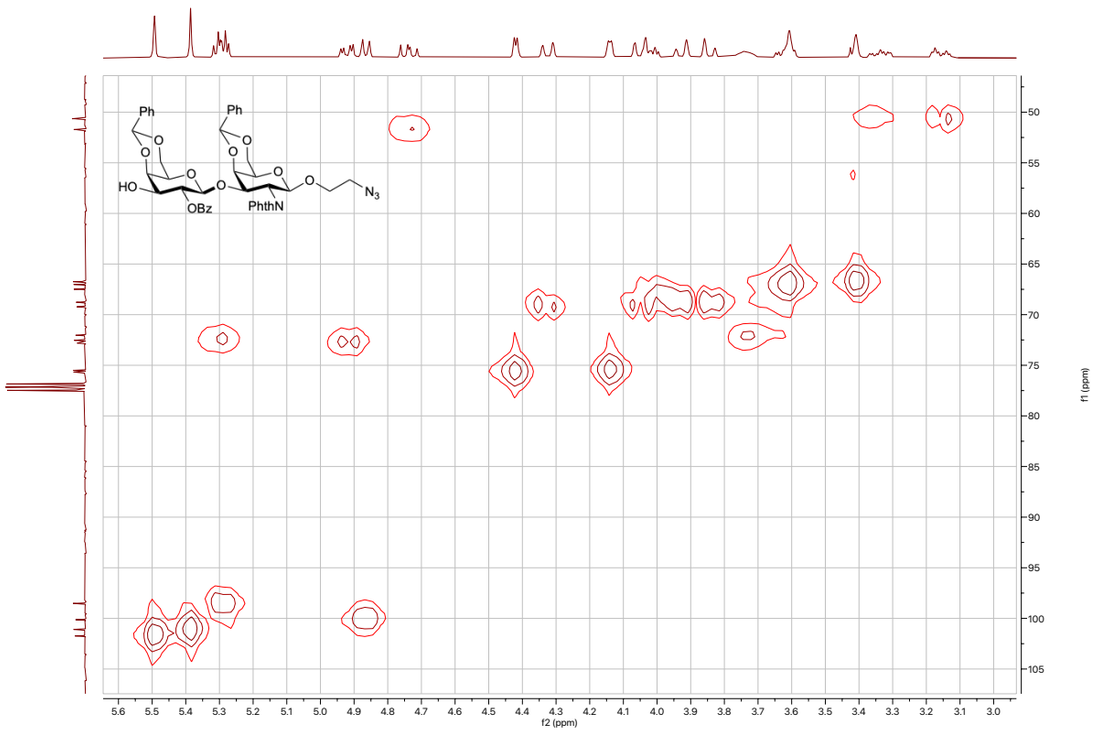


Figure S155. ^{1}H-^{13}C HSQC spectrum of **31** ($CDCl_3$, 25 °C).

^{1}H, ^{13}C, COSY and HSQC NMR spectra of **28**

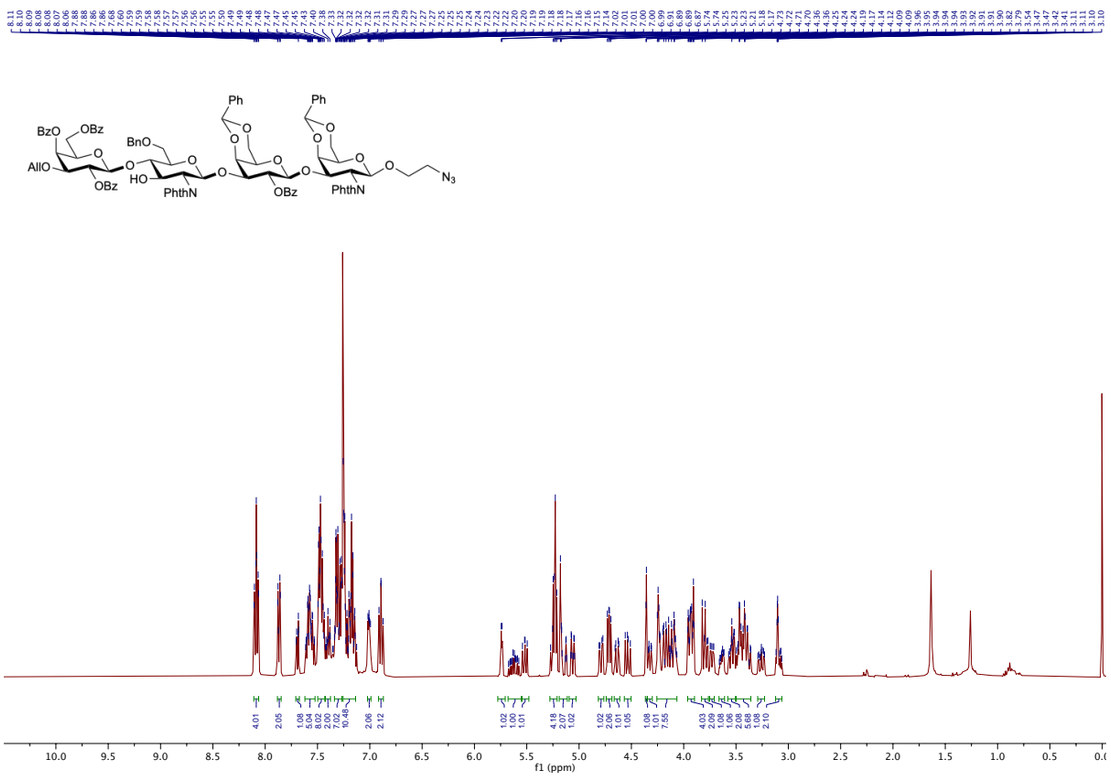


Figure S156. ^{1}H NMR spectrum of **28** ($CDCl_3$, 400 MHz, 25 °C).

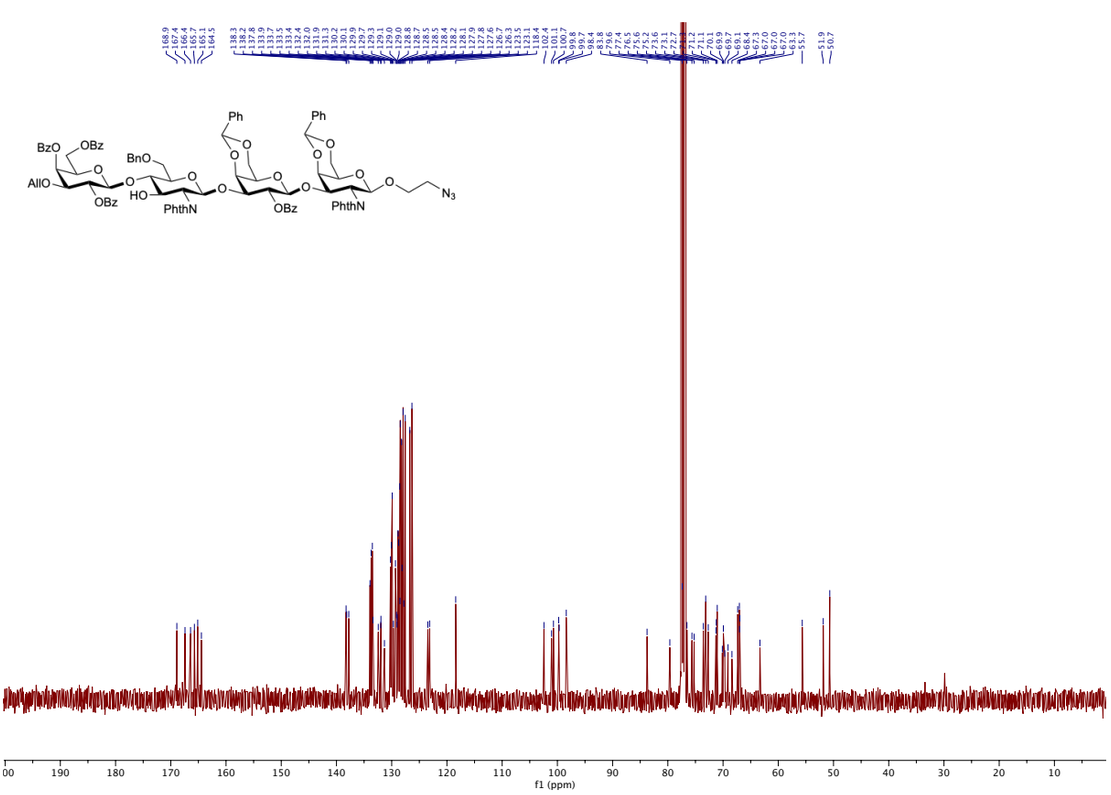


Figure S157. ^{13}C NMR spectrum of **28** ($CDCl_3$, 100 MHz, 25 °C).

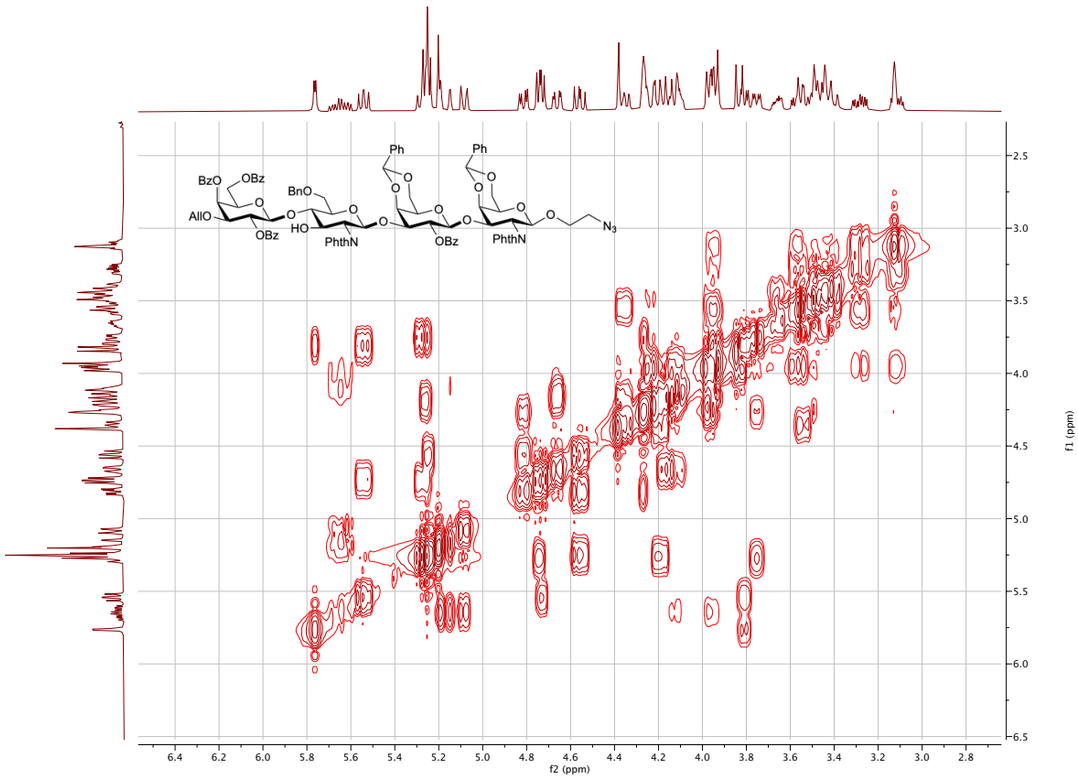


Figure S158. ^{1}H-^{1}H COSY spectrum of **28** ($CDCl_3$, 25 °C).

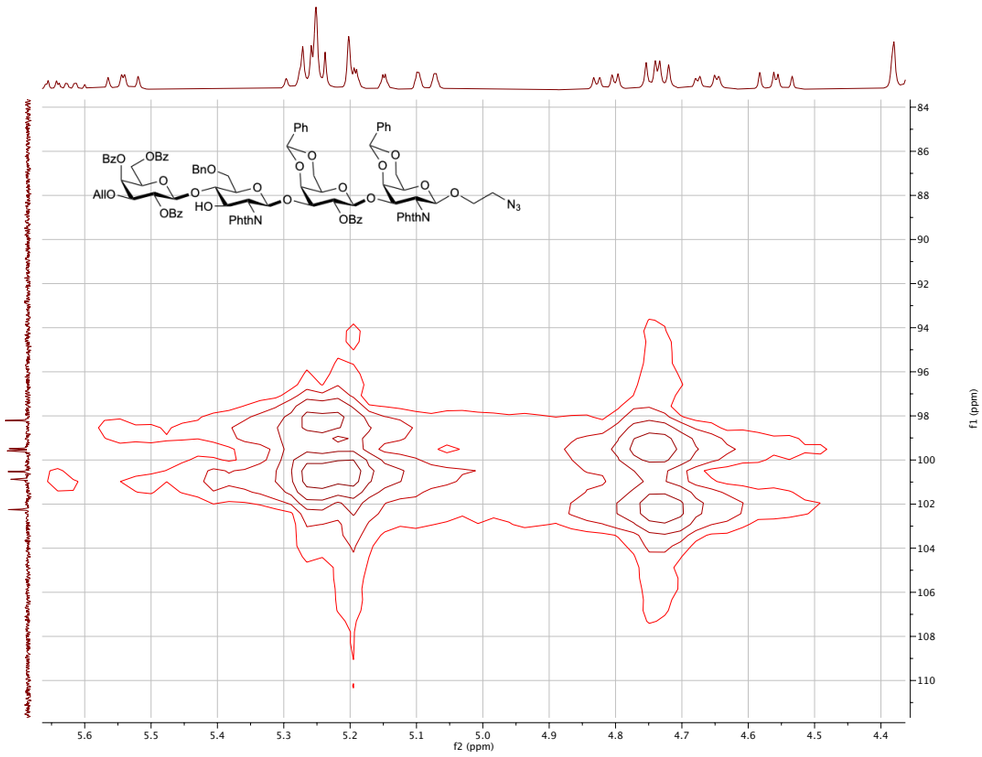


Figure S159. ^{1}H-^{13}C HSQC spectrum of **28** ($CDCl_3$, 25 °C).

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