SUPPORTING MATERIAL

Stereoselective Synthesis of 2-Hyddroxy-α-Mannopyranosides from Glucal Donors

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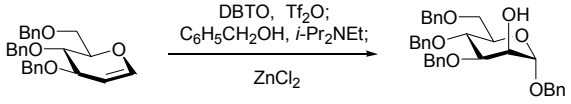
General Procedures. All reactions were performed in flame-dried modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper or rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. The appropriate glucal and the sulfoxide were dried by azeotropic removal of water with toluene (2ml/0.12 mmol scale) prior to initiation of the glycosylation reactions. Organic solutions were concentrated by rotary evaporation below 30 °C at *ca.* 25 Torr. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography (analytical and preparative) was performed using glass plates pre-coated to a depth of 0.25 mm with 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm).

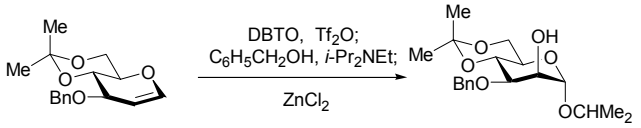
Materials. Dichloromethane, diisopropylethylamine, toluene, isopropyl alcohol, methyl alcohol, allyl alcohol and benzyl alcohol were distilled from calcium hydride at 760 Torr. Benzylamine was dried by storage under argon over 4 Å molecular sieves. Trifluoromethanesulfonic anhydride was triply distilled from phosphorous pentoxide.

Instrumentation. Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum BX spectrophotometer referenced to a polystyrene standard. Data are presented as frequency of absorption (cm^{-1}). Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR or ^{13}C NMR) spectra were recorded on a Varian 400, a Varian 500, or a Varian Inova 500 NMR spectrometer; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances), integration, coupling constant in Hertz (Hz) and assignment. Optical rotations were acquired on a Perkin Elmer-341 Digital Polarimeter. Melting points were recorded with a Buchi melting point apparatus and are uncorrected.

General Procedure for Oxidative Mannosylation:

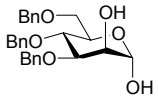


Benzyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside. To a solution of dibenzothiophene-5-oxide (240 mg, 1.2 mmol, 5 equiv) and 2,4,6-tri-*t*-butyl pyridine (30 mg, 0.12 mmol, 0.53 equiv) in 5 ml of dichloromethane at –78 °C was added trifluoromethanesulfonic anhydride (80 μL, 0.48 mmol, 2.0 equiv). The solution was stirred at –78 °C for 10 min, then at –45 ºC for 1 h before it was cooled back to –78 °C. A solution of 3,4,6-tri-*O*-benzyl-D-glucal (94 mg, 0.23 mmol, 1 equiv) in 5 ml of dichloromethane at –78 °C was added to the reaction vessel via cannula. The resulting solution was stirred at this temperature for 1 h before the sequential addition of benzyl alcohol (74 μL, 0.72 mmol, 3 equiv) and diisopropyl ethyl amine (250 μL, 1.4 mmol, 6 equiv). The reaction mixture was stirred at –78 °C for 15 min, then at -45 °C for 15 min, and finally at 0 °C for 20 min before a solution of $ZnCl_2$ in ether (1.0 *M*, 480 μL, 0.48 mmol, 2 equiv) was added to the solution. The reaction mixture was then stirred at 0 ºC for 25 min and then at 23 ºC for 16 h. The solution was partitioned between dichloromethane (15 mL) and water (15 mL), and the aqueous layer was further extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with water (3 x 10 mL) and dried (sodium sulfate). The filtrate was concentrated and the residue was purified by column chromatography (5% ethyl acetate in benzene) to afford benzyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (80 mg, 65%). R_f = 0.59 (35% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.26 (m, 18H), 7.20-7.18 (m, 2H), 5.03 (d, 1H, *J* = 1.5 Hz, H1), 4.85 (d, 1H, *J* = 10.75 Hz), 4.74 (d, 1H, *J* = 11.86 Hz), 4.72 (d, 1H, *J* = 11.3 Hz), 4.69 (d, 1H, *J* = 11.7 Hz), 4.69 (d, 1H, *J* = 12.6 Hz), 4.57 (d, 1H, *J* = 12.1 Hz), 4.53 (d, 1H, *J* = 10.9 Hz), 4.52 (d, 1H, *J* = 11.9 Hz), 4.1 (dd, 1H, *J* = 3.18, 1.79 Hz), 3.96 (dd, 1H, *J* = 8.69, 3.11 Hz), 3.92 (t, 1H, *J* = 9.70, 8.76 Hz), 3.88-3.86 (m, 1H), 3.79 (dd, 1H, *J* = 10.61, 4.21 Hz), 3.72 (dd, 1H, *J* = 10.74, 1.82 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ ; 164.67, 138.44, 138.42, 138.11, 138.00, 137.35, 128.72, 128.62, 128.56, 128.53, 128.27, 128.17, 128.11, 128.06, 128.02, 127.90, 127.77, 98.62, 80.46, 80.46, 77.52, 75.54, 75.36, 74.51, 74.48, 73.76, 73.64, 72.19, 71.63, 71.44, 69.26, 69.05, 68.58, 66.55; FTIR (neat film) 3452, 3063, 3031, 2916, 1644, 1496, 1454, 1364, 1209, 1056, 1028, 911, 801, 736, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{34}H_{36}O_6Na$ (M+Na) 563.2410, found 563.2408.

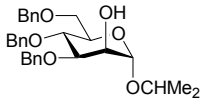


Isopropyl-3-*O*-benzyl-4,6-Di-*O*-isopropylidene-α-D-mannopyranoside. To a solution of dibenzothiophene-5-oxide (241 mg, 1.2 mmol, 5 equiv) and 2,4,6-tri-*t*-butyl pyridine (30 mg, 0.12 mmol, 0.53 equiv) in 5 ml of dichloromethane at –78 °C was added trifluoromethanesulfonic anhydride (80 μL, 0.48 mmol, 2 equiv). The solution was stirred at –78 °C for 10 min, then at –60 ºC for 1 h before it was cooled back to –78 °C. A solution of 3- *O*-

benzyl-4,6-di-*O*-isopropylidene-D-glucal (63 mg, 0.23 mmol, 1 equiv) in 5 ml of dichloromethane at –78 °C was added to the reaction vessel via cannula. The resulting solution was stirred at this temperature for 2 h before the sequential addition of isopropyl alcohol (54 μL, 0.72 mmol, 3.0 equiv) and diisopropyl ethyl amine (250 μL, 1.4 mmol, 6 equiv). The reaction mixture was stirred at –78 °C for 15 min, then at -45 °C for 15 min, and finally at 0 °C for 20 min before a solution of $ZnCl_2$ in ether (1.0 *M*, 482 μL, 0.48 mmol, 2 equiv) was added to the solution. The reaction mixture was then stirred at 0 ºC for 25 min and then at 23 ºC for 16 h. The solution was partitioned between dichloromethane (15 mL) and water (15 mL), and the aqueous layer was further extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with water (3 x 10 mL) and dried (sodium sulfate). The filtrate was concentrated and the residue was purified by column chromatography (30% ethyl acetate in benzene) to afford isopropyl-3-*O*-benzyl-4,6-Di-*O*-isopropylidene-α-D-mannopyranoside (63 mg, 78%). R_f = 0.59 (35% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 5H), 4.93(d, 1H, *J*=1.36 Hz, H1), 4.83 (d, 1H, *J*=11.95 Hz), 4.68 (d, 1H, *J*=11.71 Hz), 4.10 (t, 1H, *J*=9.59 Hz), 3.97 (dt, 1H, *J*=3.48, 1.37 Hz), 3.91 (hept, 1H, *J*=6.27 Hz), 3.85 (d, 1H, *J*=9.37 Hz), 3.82 (d, 1H, *J*=10.9 Hz), 3.77 (dd, 1H, *J*=9.4, 3.51 Hz), 3.75 (dt, 1H, *J*=9.44, 8.12 Hz), 2.6 (d, 1H, *J*=1.23 Hz), 1.516 (s, 3H), 1.44 (s, 3H), 1.20 (d, 3H, *J*=6.2 Hz), 1.14 (d, 3H, *J*=6.2 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ138.19, 128.11, 127.45, 127.29, 99.37, 97.61, 75.94, 72.59, 71.35, 70.30, 68.89, 63.77, 62.12, 29.02, 22.98, 20.90, 18.97; FTIR (neat film) 3468, 2973, 2924, 1497, 1455, 1382, 1316, 1267, 1200, 1173, 1117, 1088, 1044, 943, 916, 884, 857, 750, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{19}H_{29}O_6$ $(M+H)^+$ 353.1964 found 353.1964.

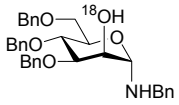


3,4,6-tri-*O*-benzyl-α-D-mannopyranose . R_f = 0.17 (35% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.28 (m, 13H), 7.20-7.18(m, 2H), 5.28 (d, 1H, *J*=1.5 Hz, H1), 4.87 (d, 1H, *J*=8.2 Hz), 4.83 (d, 1H, *J*=7.7 Hz), 4.71 (d, 1H, *J*=10.3 Hz), 4.68 (d, 1H, *J*=11.3 Hz) 4.55 (d, 1H, *J*=12.3 Hz), 4.49 (d, 1H, *J*=10.7 Hz), 4.07 (ddd, 1H, *J*=9.7, 5.1, 1.8 Hz), 4.04 (dd, 1H, *J*=3.1, 1.8 Hz), 3.95 (dd, 1H, *J*=9.2, 3.2 Hz), 3.75 (t, 1H, *J*=9.5 Hz), 3.70 (dd, 1H, *J*=10.5, 2.3 Hz), 3.66 (d, 1H, *J*=10.3, 5.9 Hz), 2.75 (br s, 2H); FTIR (neat film) 3411, 3088, 3063, 3031, 2919, 2869, 1953, 1813, 1586, 1605, 1496, 1454, 1316, 1259, 1209, 1094, 1028, 911, 841, 800, 737, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{27}H_{30}O_6Na$ $(M+Na)^+$ 473.1940 found 473.1939.

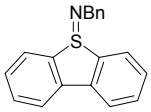


Isopropyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside. R_f = 0.72 (50% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.25 (m, 13H), 7.18-7.16(m, 2H), 5.02 (d, 1H, *J*=1.8 Hz, H1), 4.81 (d, 1H, *J*=10.7 Hz), 4.72 (d, 1H, *J*=11.5 Hz), 4.68 (d, 1H, *J*=11.5 Hz), 4.63 (d, 1H, *J*=12.1 Hz) 4.55 (d, 1H, *J*=12.3 Hz), 4.49 (d, 1H, *J*=10.7 Hz), 4.01-3.99 (m, 1H), 4.00 (dt, 1H, *J*=2.8, 1.7 Hz), 3.94 (hept, 1H, *J*=6.1 Hz), 3.92-3.84 (m, 3H), 3.79-3.75 (m, 1H), 3.69 (dd, 1H, *J*=10.6, 1.4 Hz), 2.42 (d, 1H, *J*=2.7 Hz), 1.18 (d, 3H, *J*=6.4 Hz), 1.13 (d, 3H, *J*=6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.33, 138.31, 138.06, 128.54, 128.39, 128.33, 128.05, 127.89,

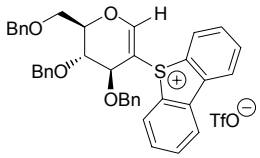
127.86, 127.79, 127.73, 127.56, 97.07, 80.40, 75.23, 74.49, 73.44, 71.93, 70.98, 68.95, 68.91, 68.86, 23.20, 21.21; FTIR (neat film) 3441, 3064, 3031, 2972, 2925, 2922, 1453, 1368, 1124, 1099, 1053, 737, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{30}H_{35}O_6$ (M-H) 491.2434 found 491.2435.



1-Benzylamino-3,4,6-tri-*O*-benzyl-1-deoxy-2-^{18}O-α-D-mannopyranoside. R_f = 0.47 (50% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.23 (m, 18H), 7.20-7.12 (m, 2H), 4.85 (d, 1H, *J*=10.9 Hz), 4.71 (d, 1H, *J*=11.64 Hz), 4.68 (d, 1H, *J*=13.8 Hz), 4.65 (d, 1H, *J*=11.6 Hz), 4.59 (d, 1H, *J*=12.25 Hz), 4.53 (d, 1H, *J*=10.9 Hz), 4.11 (d, 1H, *J*=13.13 Hz), 4.07 (dd, 1H, *J*=3.6, 0.8 Hz), 4.02 (d, 1H, *J*=1.1 Hz, H1), 3.908 (d, 1H, *J*=13.22 Hz), 3.82-3.78 (m, 2H), 3.73 (dd, 1H, *J*=10.7, 4.72 Hz), 3.57 (dd, 1H, *J*=8.73, 3.27 Hz), 3.35 (ddd, 1H, *J*=9.94, 4.84, 2.07 Hz), 2.68 (bs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.58, 138.09, 138.03, 137.41, 128.32, 128.24, 128.09, 128.07, 128.06, 127.75, 127.67, 127.63, 127.61, 127.43, 127.31, 126.68, 86.19, 82.58, 75.69, 74.76, 74.45, 73.25, 71.39, 68.98, 68.79, 48.85; FTIR (neat film) 3432, 3088, 3064, 3032, 2967, 1497, 1455, 1365, 1309, 1267, 1207, 1095, 737, 699 cm^{-1}; MS (FAB) *m/z*: Calcd for $C_{34}H_{38}O_4{}^{18}ON$ $(M+Na)^+$ 564.3, found 564.3.

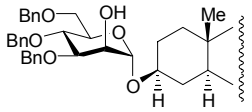


Dibenzothiophene-*N*-benzylsulfilimine. R_f = 0.13 (50% ethyl acetate in hexane with 1% triethyl amine); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (ddd, 2H, *J* = 7.75, 1.1, 0.7 Hz), 7.87 (ddd, 2H, *J* = 7.58, 0.97, 0.69 Hz), 7.59 (td, 2H, *J* = 7.47, 1.11 Hz), 7.46 (td, 2H, *J* = 7.64, 1.18 Hz), 7.18-7.08 (m, 5H), 3.48 (s, 2H, C*H*$_2$Ph); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.83, 139.89, 137.55, 131.13, 128.64, 127.66, 127.58, 126.45, 126.32, 125.85, 121.33, 52.59.

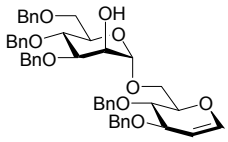


3,4,6-Tri-*O*-benzyl-2-dibenzothiophenium-D-glucal trifluoromethanesulfonate. R_f = 0.33 (10% acetone in ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, 1H, *J* = 7.3 Hz), 8.31 (s, 1H, H1), 8.30 (d, 1H, *J* = 7.8 Hz), 8.24(d, 2H, *J* = 8.1 Hz), 8.05 (dt, 1H, *J* = 7.6, 1.0 Hz), 7.82 (dt, 1H, *J* = 7.6, 1.1 Hz), 7.79 (dt, 1H, *J* = 7.7, 1.1 Hz), 7.63 (dt, 1H, *J* = 7.5, 1.1 Hz), 7.36-7.14 (m, 13H), 6.58-6.63 (m, 2H), 4.97-4.94 (m, 1H), 4.56 (d, 1H, *J* = 11.6 Hz), 4.48 (s, 2H), 4.39 (d, 1H, *J* = 11.6 Hz), 4.11-4.10(m, 1H), 3.91 (d, 1H, *J* = 11.0 Hz), 3.85 (dd, 1H, *J* = 11.0, 7.9 Hz), 3.66 (dd, 1H, *J* = 11.0, 4.2 Hz), 3.28 (dd, 1H, *J* = 3.0, 1.8 Hz), 3.20 (d, 1H, *J* = 10.8 Hz); ^{13}C NMR (126 MHz, Acetone$_6$) δ 163.50, 140.74, 139.44, 138.97, 138.28, 137.14, 135.23, 134.55, 132.10, 131.79, 129.18, 129.13, 129.04, 18.90, 128.70, 128.51, 128.47, 128.41, 128.35, 125.05,

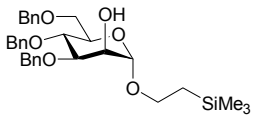
124.83, 123.73, 121.32, 120.54, 98.94, 80.11, 73.58, 72.37, 71.90, 71.33, 69.02, 68.09; FTIR (neat film) 3068, 3062, 3058, 2950, 2900, 1723, 1611, 1500, 1460, 1380, 1285, 1196, 1098, 1020 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{39}H_{35}O_4S$ (M^+) 599.2257, found 599.2256.



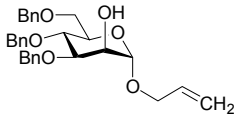
Dihydrocholesteryl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside. R_f 0.38 (15% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.25 (m, 13H), 7.18-7.16 (m, 2H), 5.06 (d, 1H, *J*=1.2 Hz, H1), 4.82 (d, 1H, *J*=10.7 Hz), 4.72 (d, 1H, *J*=11.5 Hz), 4.68 (d, 1H, *J*=10.9 Hz), 4.65 (d, 1H, *J*=12.0 Hz), 4.53 (d, 1H, *J*=12.1 Hz), 4.50 (d, 1H, *J*=10.8 Hz), 4.03-4.01 (m, 1H), 3.91 (dd, 1H, *J*=8.94, 3.19 Hz), 3.89-3.81 (m, 2H), 3.77 (dd, 1H, *J*=10.7, 4.4 Hz), 3.71 (dd, 1H, *J*=10.9, 1.8 Hz), 3.63-3.56 (m, 1H), 2.43 (d, 1H, *J*=2.7 Hz, OH), 1.98-1.94 (m, 1H) 1.85-1.77 (m, 2H), 1.72-1.68 (m, 1H), 1.64-1.45 (m, 6H), 31.36-0.94 (m, 21H), 0.90 (d, 3H, *J*=6.51 Hz), 0.87 (dd, 6H, *J*=6.6, 2.5 Hz), 0.78(s, 3H), 0.64(s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ138.35, 138.34, 138.07, 128.53, 128.38, 128.31, 127.99, 127.87, 127.81, 127.79, 127.69, 127.55, 97.06, 80.44, 75.99, 75.16, 74.54, 73.40, 71.91, 70.96, 69.07, 68.85, 56.47, 56.27, 54.29, 44.93, 42.59, 40.01, 39.51, 36.77, 36.16, 35.80, 35.56, 35.48, 32.04, 29.69, 28.69, 28.24, 28.00, 27.39, 24.21, 23.82, 22.81, 22.56, 21.21, 18.66, 12.26, 12.06; FTIR (neat film) 3460, 3064, 3031, 2930, 2866, 1497, 1466, 1454, 1382, 1370, 1211, 1101, 1064, 734, 676 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{54}H_{75}O_6$ (M-H) 819.5564 found 819.5567.



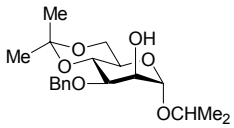
3,4,-Di-*O*-benzyl-glucalyl-(1 6)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside. R_f = 0.28 (20% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-6.99 (m, 15H), 6.18 (d, 1H, *J*=6.4 Hz), 5.08 (d, 1H, *J*=1.2 Hz, H1), 4.88 (d, 1H, *J*=11.1 Hz), 4.86 (d, 1H, *J*=11.6 Hz), 4.74 (d, 1H, *J*=11.6 Hz), 4.65 (dd, 1H, *J*=5.9, 2.4 Hz), 4.60 (d, 1H, *J*=11.6 Hz), 4.55 (d, 1H, *J*=11.9 Hz), 4.51 (d, 1H, *J*=12.1 Hz), 4.40 (d, 1H, *J*=11.9Hz), 4.43 (d, 1H, *J*=11.4), 4.29 (d, 1H, *J*=11.9Hz), 4.25 (d, 1H, *J*=11.6 Hz), 4.11 (dt, 1H, *J*=6.2, 1.4 Hz), 4.06 (dd, 1H, *J*=10.7, 4.7 Hz), 3.95 (dd, 1H, *J*=9.5, 3.1 Hz), 3.91 (dd, 1H, *J*=5.0, 2.1 Hz), 3.87 (dd, 1H, *J*=9.0, 5.9 Hz), 3.82 (dd, 1H, *J*=8.5, 6.6 Hz), 3.77 (q, 1H, *J*=3.2 Hz), 3.75-3.72 (m, 1H), 3.71-3.69 (m, 1H), 3.66 (dd, 1H, *J*=11.1, 1.9 Hz), 3.59 (dd, 1H, *J*=10.9, 0.9 Hz), 2.58 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.53, 138.78, 138.57, 138.41, 138.46, 138.23, 128.86, 128.77, 128.63, 128.49, 128.41, 128.20, 128.14, 127.99, 127.88, 127.82, 127.76, 127.69, 127.63, 127.61, 127.59, 100.23, 99.98, 99,76, 76.12, 75.98, 75.84, 74.23, 73.82, 73.08, 71.55, 70.75, 70.06, 65.89, 64.43, 62.51; FTIR (neat film) 3467, 3063, 3030, 2917, 1726, 1648, 1496, 1454, 1362, 1318, 1239, 1209, 110, 1028, 839, 736, 696 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{47}H_{50}O_9Na$ $(M+Na)^+$ 781.3353 found 781.3353.



Trimethylsilylethyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside. R_f = 0.41 (20% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.26 (m, 13H), 7.19-7.17 (m, 2H), 4.92 (d, 1H, *J* = 1.6 Hz, H1), 4.83 (d, 1H, *J* = 10.8 Hz), 4.86 (d, 1H, *J* = 11.5 Hz), 4.68 (d, 1H, *J* = 11.0 Hz), 4.67 (d, 1H, *J* = 12.2 Hz), 4.54 (d, 1H, *J* = 12.4 Hz), 4.50 (d, 1H, *J* = 11.0 Hz), 4.02 (dd, 1H, *J* = 3.2, 1.8 Hz), 3.90 (dd, 1H, *J* = 8.7, 3.2 Hz), 3.84 (t, 1H, *J* = 8.7 Hz), 3.83-3.74 (m, 3H), 3.71 (dd, 1H, *J* = 10.5, 6.4 Hz), 2.37 (br s, 1H), 0.96 (ddd, 1H, *J* = 13.8, 10.8, 6.4 Hz), 0.87 (ddd, 1H, *J* = 14.0,10.6, 5.7 Hz), 0.13-0 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.49, 138.18, 128.76, 128.58, 128.57, 128.55, 128.19, 128.14, 129.09, 128.08, 127.90, 127.78, 98.91, 80.52, 75.35, 74.61, 73.64, 72.15, 71.15, 69.18, 68.73, 65.10, 18.07, -1.15; FTIR (neat film) 3448, 3064, 3031, 2899, 1736, 1497, 1454, 1363, 1316, 1249, 1208, 1102, 1028, 859, 837, 735, 697cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{32}H_{42}O_6Na$ (M+Na) 573.2648, found 573.2649.

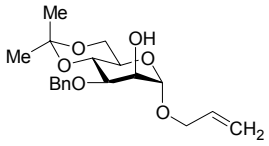


Allyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside. R_f = 0.33 (20% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.27 (m, 13H), 7.19-7.17 (m, 2H), 5.90 (dddd, 1H, *J*=17.2, 10.3, 6.1, 5.2 Hz), 5.28 (dq, 1H, *J*=17.3, 1.7 Hz), 5.19 (dq, 1H, *J*=10.4, 1.3 Hz), 4.97 (d, 1H, *J*=1.7 Hz, H1), 4.84 (d, 1H, *J*=10.7 Hz), 4.73 (d, 1H, *J*=11.5 Hz), 4.70 (d, 1H, *J*=11.2 Hz), 4.67 (d, 1H, *J*=12.3 Hz), 4.55 (d, 1H, *J*=12.1 Hz), 4.51 (d, 1H, *J*=10.8 Hz), 4.19 (ddt, 1H, *J*=12.9, 5.0, 1.5 Hz), 4.08 (dd, 1H, *J*=3.3, 1.8 Hz), 4.00 (ddt, 1H, *J*=12.9, 6.2, 1.3 Hz), 3.93 (dd, 1H, *J*=8.9, 3.2 Hz), 3.87 (t, 1H, *J*=9.6 Hz), 3.81 (ddd, 1H, *J*=8.9, 3.2, 1.9 Hz), 3.77 (dd, 1H, *J*=10.6, 4.4 Hz), 3.72 (dd, 1H, *J*=10.5, 1.8 Hz), 2.47 (bs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.52, 138.18, 133.94, 128.80, 128.63, 128.59, 128.22, 128.20, 128.12, 128.10, 127.96, 127.83, 117.78, 98.60, 80.47, 75.42, 74.52, 73.68, 72.24, 71.33, 69.11, 68.60, 68.19; FTIR (neat film) 344.7, 3064, 3031, 2914, 1954, 1724, 1647, 1604, 1497, 1454, 1364, 1316, 1270, 1209, 1097, 1059, 1028, 914, 844, 803, 737, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{30}H_{34}O_6Na$ $(M+Na)^+$ 513.2253 found 513.2251.

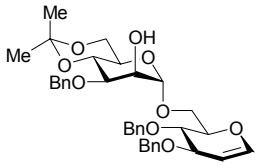


Isopropyl-3-*O*-benzyl-4,6-di-*O*-isopropylidene-α-D-mannopyranoside. R_f = 0.59 (35% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 5H), 4.93(d, 1H, *J*=1.36 Hz, H1), 4.83 (d, 1H, *J*=11.95 Hz), 4.68 (d, 1H, *J*=11.71 Hz), 4.10 (t, 1H, *J*=9.59 Hz), 3.97 (dt, 1H, *J*=3.48, 1.37 Hz), 3.91 (hept, 1H, *J*=6.27 Hz), 3.85 (d, 1H, *J*=9.37 Hz), 3.82 (d, 1H, *J*=10.9 Hz), 3.77 (dd, 1H, *J*=9.4, 3.51 Hz), 3.75 (dt, 1H, *J*=9.44, 8.12 Hz), 2.6 (d, 1H, *J*=1.23 Hz), 1.516 (s, 3H), 1.44 (s, 3H), 1.20 (d, 1H, *J*=6.2 Hz), 1.14 (d, 1H, *J*=6.2 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ138.19, 128.11, 127.45, 127.29, 99.37, 97.61, 75.94, 72.59, 71.35, 70.30, 68.89, 63.77, 62.12, 29.02, 22.98, 20.90, 18.97; FTIR (neat film) 3468, 2973, 2924, 1497, 1455, 1382,

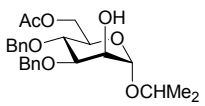
1316, 1267, 1200, 1173, 1117, 1088, 1044, 943, 916, 884, 857, 750, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{19}H_{29}O_6$ $(M+H)^+$ 353.1964 found 353.1964.



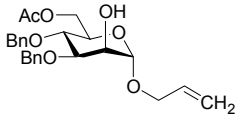
Allyl 3-*O*-benzyl-4,6-di-*O*-isopropylidene-α-D-mannopyranoside. R_f = 0.33 (20% ethyl acetate in benzene); ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 5.90 (dddd, 1H, *J*=17.1, 10.3, 6.2, 5.2 Hz), 5.29 (dq, 1H, *J*=17.1, 1.5 Hz), 5.22 (dq, 1H, *J*=10.3, 1.2 Hz), 4.88 (d, 1H, *J*=1.3 Hz, H1), 4.84 (d, 1H, *J*=11.8 Hz), 4.69 (d, 1H, *J*=12.0 Hz), 4.17 (ddt, 1H, *J*=12.9, 5.2, 1.4 Hz), 4.12 (t, 1H, *J*=9.6 Hz), 4.04 (dd, 1H, *J*=3.4, 1.4 Hz), 3.97 (ddt, 1H, *J*=12.8, 6.2, 2.3 Hz), 3.86 (s, 1H), 3.85 (d, 1H, *J*=1.3 Hz), 3.79 (dd, 1H, *J*=9.7, 3.5 Hz), 3.69 (dt, 1H, *J*=9.7, 8.0 Hz), 2.65 (bs, 1H), 1.53 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.64, 137.84, 128.89, 128.44, 128.42, 117.79, 99.94, 99.39, 98.97, 79.94, 72.21, 72.07, 71.72, 68.32, 68.28, 68.05, 66.13, 64.43, 62.61, 62.08; FTIR (neat film) 3440, 2994, 2923, 2086, 1644, 1497, 1455, 1370, 1320, 1267, 1200, 1173, 1114, 1088, 1071, 1035, 915, 856, 750, 698 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{19}H_{26}O_6Na$ $(M+Na)^+$ 373.1627 found 373.1627.



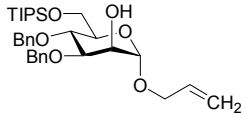
3,4,-Di-*O*-benzyl-glucalyl-(1 6)-3-*O*-benzyl-4,6-di-*O*-isopropylidene-α-D-mannopyranoside. R_f = 0.30 (20% ethyl acetate in benzene); ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.26 (m, 15H, ArH), 6.41 (dd, 1H, *J*=6.1, 1.0 Hz), 4.91 (dd, 1H, *J*=6.1, 2.6 Hz), 4.89 (d, 1H, *J*=1.4 Hz, H1), 4.87 (d, 1H, *J*=11.4 Hz), 4.84 (d, 1H, *J*=11.8 Hz), 4.82 (d, 1H, *J*=12.0 Hz), 4.67 (d, 1H, *J*=9.1 Hz), 4.65 (d, 1H, *J*=8.9 Hz), 4.56 (d, 1H, *J*=11.6 Hz), 4.23 (ddd, 1H, *J*=6.1, 3.0, 1.3 Hz), 4.12 (t, 1H, *J*=9.5 Hz), 4.04-4.00 (m, 2H), 3.96 (dd, 1H, *J*=11.5, 4.8 Hz), 3.83 (d, 1H, *J*=5.4 Hz), 3.82 (d, 1H, *J*=1.5 Hz), 3.79-3.71 (m, 3H), 3.69 (dd, 1H, *J*=10.5, 8.1 Hz), 2.6 (d, 1H, *J*=1.1 Hz), 1.52 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.79, 138.53, 138.38, 138.23, 128.71, 128.65, 128.18, 128.11, 128.03, 128.00, 127.94, 100.53, 100.07, 99.88, 76.36, 76.05, 75.86, 74.29, 73.87, 73.17, 71.61, 70.80, 70.10, 65.92, 64.50, 62.54, 29.51, 19.48; FTIR (neat film) 3468, 3064, 3031, 2993, 2921, 2877, 2248, 1725, 1649, 1606, 1497, 1454, 1383, 1370, 1322, 1267, 1239, 1201, 1089, 1030, 943, 913, 857, 736, 698, 649 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{36}H_{42}O_9Na$ $(M+H)^+$ 641.2727 found 641.2725.



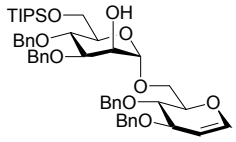
Isopropyl 6-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranoside. R_f = 0.43 (35% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.29 (m, 10H), 5.0 (d, 1H, *J*=1.5 Hz, H1), 4.89 (d, 1H, *J*=10.7 Hz), 4.74 (d, 1H, *J*=11.2 Hz), 4.70 (d, 1H, *J*=11.4 Hz), 4.59 (d, 1H, *J*=10.9 Hz), 4.43 (s, 1H), 4.32 (s, 1H), 4.02 (q, 1H, *J*=1.8 Hz), 3.95-3.90 (m, 2H), 3.77 (t, 1H, *J*=9.6 Hz), 2.49 (bs, 1H), 2.06 (s, 3H), 1.21 (d, 3H, *J*=6.1 Hz), 1.27 (d, 3H, *J*=6.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.15, 138.12, 138.02, 128.80, 128.74, 128.71, 128.43, 128.40, 128.21, 128.15, 128.03, 97.40, 80.61, 75.43, 74.26, 72.15, 69.65, 69.39, 68.91, 63.68, 23.30, 21.52, 21.08; FTIR (neat film) 3469, 3031, 2972, 2928, 1742, 1497, 1454, 1368, 1314, 1240, 1094, 1046, 978, 738, 699 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{25}H_{32}O_7Na$ $(M+Na)^+$ 467.2046 found 467.2946.



Allyl 6-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranoside. R_f = 0.49 (35% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.29 (m, 10H), 5.89 (dddd, 1H, *J*=17.4, 10.6, 6.2, 5.2 Hz), 5.28 (dq, 1H, *J*=17.2, 1.6 Hz), 5.21 (dq, 1H, *J*=10.6, 1.4 Hz), 4.94 (d, 1H, *J*=1.6 Hz, H1), 4.94 (d, 1H, *J*=10.9 Hz), 4.73 (d, 1H, *J*=11.5 Hz), 4.70 (d, 1H, *J*=11.4 Hz), 4.59 (d, 1H, *J*=10.9 Hz), 4.33-4.10 (m, 2H), 4.17 (ddt, 1H, *J*=12.9, 5.3, 1.4 Hz), 4.08 (dd, 1H, *J*=3.2, 1.8 Hz), 4.00 (ddt, 1H, *J*=13.0, 6.4, 1.3 Hz), 3.94 (dd, 1H, *J*=8.9, 3.3 Hz), 3.86 (ddd, 1H, *J*=9.9, 4.5, 2.7 Hz), 3.78 (dd, 1H, *J*=10.0, 9.0 Hz), 2.46 (bs, 1H), 2.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.16, 138.14, 137.94, 133.72, 128.85, 128.74, 128.73, 128.38, 128,37, 128.31, 128.18, 128.13, 118.03, 98.51, 80.50, 75.42, 74.08, 72.26, 69.55, 68.44, 68.33, 63.61, 21.13; FTIR (neat film) 3474, 3065, 3031, 2909, 1741, 1647, 1497, 1455, 1366, 1318, 1241, 981, 929, 839, 800, 737, 699cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{25}H_{30}O_7Na$ $(M+Na)^+$ 465.1889 found 465.1888.



Allyl-3,4-di-*O*-benzyl-6-*O*-triisopropylsilyl-α-D-mannopyranoside. R_f = 0.46 (10% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.29 (m, 10H), 5.89 (dddd, 1H, *J*=17.1, 10.4, 6.3, 5.2 Hz), 5.26 (dq, 1H, *J*=17.2, 1.6 Hz), 5.19 (dq, 1H, *J*=10.4, 1.3 Hz), 4.90 (d, 1H, *J*=1.3 Hz, H1), 4.89 (d, 1H, *J*=11.1 Hz), 4.73 (d, 1H, *J*=11.4 Hz), 4.70 (d, 1H, *J*=11.1 Hz), 4.65 (d, 1H, *J*=11.0 Hz), 4.19(ddt, 1H, *J*=12.8 5.3, 1.4 Hz), 4.06 (dd, 1H, *J*=3.2, 1.8 Hz), 4.01-3.92 (m, 3H), 3.89 (dd, 1H, *J*=10.9, 5.3 Hz), 3.78 (t, 1H, *J*=9.9 Hz), 3.69 (ddd, 1H, *J*=9.8, 5.3, 1.8 Hz), 2.38 (bs, 1H), 1.14-1.02 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.99, 128.76, 128.65, 128.28, 128.15, 128.12, 127.97, 117.75, 98.26, 80.61, 75.44, 74.51, 72.98, 72.28, 68.69, 67.81, 63.16, 18.25, 18.22, 17.93, 12,22; FTIR (neat film) 3468, 3065, 3031, 2942, 2866, 1648, 1497, 1455, 1383, 1365, 1315, 1246, 1210, 1107, 1057, 1029, 995, 920, 883, 839, 792, 749, 697 cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{32}H_{48}O_6NaSi$ $(M+Na)^+$ 579.3118 found 579.3115.



3,4,-Di-*O*-benzyl-glucalyl-(1 6)-3,4-di-*O*-benzyl-6-*O*-triisopropylsilyl-α-D-mannopyranoside. R_f = 0.40 (10% ethyl acetate in benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.28 (m, 15H), 6.39 (dd, 1H, *J*=6.6, 0.7 Hz), 4.91-4.88 (m, 2H), 4.88 (d, 1H, *J*=10.4 Hz), 4.87 (d, 1H, *J*=11.3 Hz), 4.72 (d, 1H, *J*=11.6 Hz), 4.67 (d, 1H, *J*=10.8 Hz), 4.68 (m, 2H), 4.61 (d, 1H, *J*=11.9 Hz), 4.68 (m, 2H), 4.61(d, 1H, *J*=11.9 Hz), 4.56 (d, 1H, *J*=11.6 Hz), 4.24 (ddd, 1H, *J*=6.3, 2.4, 1.5 Hz), 4.05 (sept, 1H, *J*=1.7 Hz), 4.02-3.95 (m, 2H), 3.89 (ddd, 1H, *J*=9.4, 3.1, 1.8 Hz), 3.87-3.75 (m, 4H), 3.66-3.61 (m, 1H), 2.31 (d, 1H, *J*=3.2 Hz), 1.08-0.93 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.87, 138.83, 138.82, 138.41, 138.31, 138.14, 128.72, 128, 67, 128.60, 128.55, 128.14, 128.10, 128.00, 127.95, 127.93, 127.90, 127.81, 100.06, 99.72, 99.97, 80.18, 76.56, 76.29, 76.27, 75.29, 74.57, 74.24, 73.93, 72.85, 72.16, 70.77, 68.46, 65.64, 19.04, 18.23, 18.19, 17.91, 17.86, 17.22, 12.77, 12.76, 12.19; FTIR (neat film) 3478, 3064, 3031, 2921, 2866, 1648, 1497, 1454, 1387, 1360, 1330, 1239, 1209, 1101, 1070, 1043, 1028, 883, 806, 735, 697cm^{-1}; HRMS (FAB) *m/z*: Calcd for $C_{49}H_{64}O_9NaSi$ $(M+Na)^+$ 847.4217 found 847.4216.