Supplementary Material For Communication

Targeted Glycosyl Donor Delivery for Site-Selective Glycosylation

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EXPERIMENTAL:

General Procedures

All NMR spectra were recorded at 25°C at 400 MHz (^{1}H) or 100 MHz (^{13}C) and chemical shifts are reported relative to internal TMS. Accurate mass measurements were made using FAB at 10K resolution, and elemental analyses were conducted at Atlantic microlab, Norcross, GA. All reactions were conducted under inert argon atmosphere. TLC plates (Riedel-de Haen, coated with silicagel 60F 254) were detected by UV. Silicagel (spectrum SIL 58, 230-400 mesh, grade 60) was used for column chromatography. Dichloromethane and toluene were distilled from CaH_2. N-Iodosuccinimide was crystallized from hot CH_2Cl_2.

1,3,4,5-Tetra-O-benzyl-2-O-(2,3,4-tri-O-benzyl-6-O-[t-butyldiphenylsilyl]-α-D-mannopyranosyl)-D-*myo*-inositol (**6**) and 1,3,4,5-Tetra-O-benzyl-6-O-(2,3,4-tri-O-benzyl-6-O-[t-butyldiphenylsilyl]-α-D-mannopyranosyl)-D-*myo*-inositol (**7a**). The diol **3** (50 mg, 0.092 mmol) and glycosyl donor **4a** (91 mg, 0.119 mmol) were together taken up in a small quantity of toluene, azeotroped to remove traces of water and then placed under high vaccum overnight. The mixture was dissolved in dry CH_2Cl_2 (2 mL) under Argon atmosphere. N-Iodosuccinimide (27 mg, 0.119 mmol) was added to the solution, after stirring for 3 minutes, TBDMSOTf (7 μL, 0.027 mmol) was added. The reaction was quenched after 10 minutes with 10% aq: sodium thiosulphate and saturated sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was separated, dried and the solvent was removed under reduced pressure. The crude residue on flash column chromatography (1:4 EtOAc-Hex) afforded **6** (44 mg, 0.03 mmol, 49%) as a major product. R*f* [1:2 EtOAc-Hex] 0.5, and **7a** (15 mg 16%).

Data for **6**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 - 6.92 (m, 45H, Ar), 5.35 (d, 1H, H-1, J=1.2), 4.95 - 4.41 (m, 14H, Bn), 4.37 (t, J=2.4, 1H), 4.28 - 4.23 (dd, J-10, 9.6, 1H), 3.98 - 3.85 (m, 3H), 3.79 - 3.71 (m, 3H), 3.58 - 3.56 (d, J=11.2, 1H, 3.32 - 3.25 (m, 2H), 3.19 - 3.16 (dd, J=9.6, 2, 1H), 2.39 (bs, 1H, OH) 1.02 (s, 9H, t-Bu).

^{13}C NMR: δ 138.99, 138.67, 138.57, 137.73, 137.43, 136.096, 135.64, 133.91, 133.61, 129.422, 129.36, 128.62, 128.47, 128.347, 128.29, 128.22, 128.18, 128.13, 128.06, 128.02, 127.96, 127.74, 127.56, 127.47, 127.36, 127.33, 127.17, 127.11, 127.06, 98.00 (C-1), 83.22, 80.85, 80.47, 79.38, 79.15, 75.78, 75.61, 75.21, 74.43, 72.90, 72.71, 72.16, 72.10, 70.08, 62.70, 26.80, 19.33.

FAB-MS m/z: 1209.6 (M^+-1).

Benzoylation of **6**. The mannoinositol **6** (30 mg, 0.025 mmol) was dissolved in pyridine (2 mL) at 0°C. To the solution was added DMAP (3 mg, 0.025 mmol) followed by benzoyl chloride (20 μL, 0.25 mmol) and stirred for 14h at room temperature. The reaction was

quenched with drops of water and solvent was removed under reduced pressure. The residue was flash chromatographed (1:4 EtOAc-Hexane) to afford the corresponding benzoate (31 mg, 0.0235 mmol, 94%) as a colorless paste. R*f* (1:4 EtOAc-Hexane) 0.5.

Data for **7a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 - 6.95 (m, Ar), 5.79 - 5.74 (dd, J=9.6, 10, 1H), 5.40 (bs, 1H), 4.99 - 4.41 (m, 15H), 4.30 - 4.25 (dd, J=10, 10, 1H), 4.02 - 3.86 (m, 4H), 4.79 - 3.76 (dd, J=11.2, 2.8, 1H), 3.60 - 3.51 (m, 2H), 3.44 - 3.41 (dd, J=10, 2, 1H), 3.32 - 3.29 (dd, J=10, 2.3, H), 1.03 (s, 9H).

FAB-MS m/z: 1312.45 (M^+-1), 1354.40 (M+$^+$K), 1447.42 (M^+-Cs).

Anal. cald for $C_{48}H_{86}O_{12}Si$: C, 76.68, H, 6.59. Found; C,76.76, H, 6.63.

Acetylation of **7a** The mannoinositol **7a** (10 mg, 0.0082 mmol) was dissolved in pyridine (1 mL) at 0°C. To the solution was added DMAP (1 mg, 0.0082 mmol) followed by acetic anhydride (3 μL, 0.033 mmol) and stirred for 3h, the temperature being slowing increased to room temperature. The reaction was quenched with drops of water and solvent was removed under reduced pressure. The residue was flash chromatographed tp afford the corresponding acetate (6 mg, 0.0048 mmol, 59%) as a colorless paste. R*f* (1:4 EtOAc-Hexane) 0.4.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 - 6.88 (m, Ar), 5.85 - 5.84 (dd, J=2.8, 2.4, 1H), 5.496 - 5.493 (d, J=1.2, 1H, 4.91 - 4.32 (m, 14H), 4.21 - 2.16 (dd, J=10, 10, 1H), 4.09 - 4.04 (dd, J=10, 9.6, 1H), 3.92 - 3.76 (m, 4H), 3.59 - 3.57 (m, 2H), 3.46 - 3.43 (dd, J=10, 2.8, 1H), 3.39 - 3.36 (dd, J=9.6, 2.4, 1H), 3.31 - 3.26 (dd, J=9.6, 9.6, 1H), 2.12 (s, 3H), 0.99 (s, 9H).

FABMS: m/z 1251.56 (m^+-1).

1,3,4,5-Tetra-O-benzyl-6-O-(2-O-benzoyl-3,4-di-O-benzyl-6-O-[t-butyldiphenylsilyl]-α-D-mannopyranosyl)-D-*myo*-inositol (**7b**) The diol **3** (50 mg, 0.092 mmol) and glycosyl donar **5a** (92 mg, 0.119 mmol) were together taken up in a small quantity of toluene, azeotroped to remove traces of water and then placed under high vaccum overnight. The mixture was dissolved in CH_2Cl_2 (2 mL) at 0°C under Argon atm. N-Iodosuccinimide (27 mg, 0.119 mmol) was added to the solution, after stirring for 3 minutes TBDMSOTf (6.3 μL, 0.027 mmol) was added. The reaction was quenched after 20 minutes with 10% aq: sodium thiosulphate and saturated aq: sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was separated, dried and solvent was removed under reduced pressure. The crude residue on flash column chromatography (1:4 EtOAc-Hex) afforded **7b** (80 mg, 0.065 mmol, 71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 - 6.84 (m, 45H, Ar-H), 5.79 - 5.78 (dd, J=1.6, 2 Hz, 1H), 5.605-5.601 (d, J=1.6 Hz, 1H, H-1), 4.90 - 4.55 (m, 12H, BnCH_2 s), 4.25 - 4.20 (dd, J=9.6, 10 Hz, 1H), 4.17 - 4.12 (m, 2H), 4.07 - 4.03 (dd, J=3.2, 10 Hz, 1H), 3.98 - 3.91 (m, 2H), 3.58 - 3.48 (m, 2H), 3.38 - 3.36 (dd, J=2.8, 3.2 Hz, 1H), 3.35 - 3.34 (dd, J=3.2, 3.2 Hz, 1H), 3.30 - 3.25 (dd, J=9.6, 9.2 Hz, 1H), 2.36 (bs, 1H, OH), 1.06 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.74 (C=O Ph), 139.09, 138.53, 138.25, 137.86, 137.16, 135.93, 135.64, 133.78, 133.31, 132.94, 130.00, 129.36, 128.57, 128.46, 128.39, 128.27, 128.22, 128.03, 127.96, 127.88, 127.55, 127.49, 127.09, 98.26 (C1), 81.34, 81.06, 80.61, 79.50, 78.41, 75.81, 75.51, 74.93, 74.92, 74.08, 72.63, 72.10, 71.47, 69.31, 66.44, 62.39, 26.84, 19.31.

Comparison of the reaction with corresponding 2-benzoyl pentenyl sugar

The diol **3**(50 mg, 0.092 mmol) and 2-benzoyl n-pentenyl glycoside corresponding to **5a** (92 mg, 0.119 mmol) were together taken up in a small quantity of toluene, azeotroped to remove traces of water and then placed under high vaccum overnight. The mixture was dissolved in CH_2Cl_2 (2 mL) at 0°C under Argon atm. N-Iodosuccinimide (27 mg, 0.119 mmol) was added to the solution, after stirring for 3 minutes TBDMSOTf (6.3 μL, 0.027 mmol) was added. The reaction was quenched after 30 minutes with 10% aq: sodium thiosulphate and saturated aq: sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was separated, dried and solvent was removed under

reduced pressure. The crude residue on flash column chromatography (1:4 EtOAc-Hex) afforded **7b** (65 mg, 58 %).

Acetylation of **7b** To a solution of alcohol **7b** (70 mg, 0.057 mmol) in pyridine (2 mL) at 0°C was added Ac_2O (22 µL, 0.22 mmol) and DMAP (7 mg, 0.057 mmol). The solution was stirred at room temperature for 1h. The reaction was quenched with drops of water and solvent was evaporated off under reduced pressure. The residue on flash column chromatography (1:4 EtOAc-Hex) afforded the acetate (57 mg, 0.045 mmol, 79%) as a colourless paste.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 - 6.83 (m, 45H, Ar-H), 5.85 - 5.84 (dd, J=2.8, 2.4 Hz, 1H), 5.81 - 5.80 (dd, J=1.6, 2 Hz, 1H), 5.602 - 5.599 (d, J=1.2 Hz, 1H, H-1) 4.01 - 4.47 (m, 12H, $BnCH_2$ s), 4.21 - 4.17 (dd, J=9.6, 10 Hz, 1H), 4.07 - 3.96 (m, 3H), 3.86 - 3.81 (dd, J=9.6, 9.6 Hz, 1H), 3.61 - 3.52 (m, 2H), 3.47 - 3.46 (dd, J=3.2, 3.2 Hz, 1H), 3.45 - 3.43 (dd, J=2.8, 3.2 Hz, 1H), 3.34 - 3.29 (dd, J=9.6, 9.6 Hz, 1H), 2.10 (s, 3H), 1.05 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.39 ($OCOCH_3$), 165.97 (OCOPh), 139.08, 138.49, 138.17, 137.65, 137.52, 136.82, 135.94, 135.66, 133.65, 133.36, 132.95, 130.01, 129.41, 129.29, 128.86, 128.48, 128.42, 128.22, 128.12, 128.02, 127.83, 127.60, 127.57, 127.43, 127.22, 127.12, 97.99 (C1), 81.68, 81.08, 78.72, 78.32, 78.12, 75.99, 75.76, 75.03, 74.66, 74.06, 72.17, 71.86, 71.42, 69.05, 65.93, 62.55, 26.83, 21.03, 19.27.

FABMS-m/z: 1265.56 (M^+-1)

Anal. cald. for $C_{79}H_{82}O_{13}Si$: C, 74.86; H, 6.52. Found: C,74.66; H, 6.59.

1,3,4,5-Tetra-O-benzyl-6-O-(2-benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (**7c**). The diol **3** (50 mg, 0.092 mmol) and glycosyl donor **5b** (75 mg, 0.12 mmol) were together taken up in a small quantity of toluene, azeotroped to remove traces of water and then placed under high vaccum overnight. The mixture was dissolved in CH_2Cl_2 (2 mL) at 0°C under Argon atmosphere. N-Iodosuccinimide (27 mg, 0.12 mmol) was added to the solution, after stirring for 3 minutes, TBDMSOTf (6.2 µL, 0.027 mmol) was added. The reaction was quenched after 20 minutes, with 10% aq: sodium thiosulphate and saturated sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was removed under reduced pressure. The crude residue on flash column chromatography (1:4 EtOAc-Hex) afforded **7c** (72 mg, 0.067 mmol, 73%) as a colorless paste.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 - 7.03 (m, 40H, Ar-H), 5.75 - 5.73 (dd, J=2, 2.4 Hz, 1H), 5.632 - 5.628 (d, J=1.6 Hz, 1H, H-1), 4.94 - 4.29 (m, 14H, $BnCH_2$ s), 4.22 - 3.99 (m, 6H), 3.49 - 3.35 (m, 4H), 3.33 - 3.28 (dd, J=9.6, 9.6 Hz, 1H), 2.36 (bs, 1H, -OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.60 (OCOPh) 138.93, 138.80, 138.55, 138.13, 137.99, 137.85, 136.98, 132.94, 129.95, 128.51, 128.46, 128.31, 128.20, 128.15, 128.10, 128.03, 127.99, 127.94, 127.86, 127.72, 127.52, 127.46, 127.35, 127.26, 127.19, 127.15, 98.00 (C1), 81.35, 81.08, 80.64, 79.51, 78.04, 75.83, 75.82, 75.02, 74.81, 74.29, 73.16, 72.55, 71.99, 71.52, 71.32, 69.01, 68.59, 66.28.

FAB-MS m/z: 1075.38 (M^+-1).

Acetylation of **7c** To a solution of alcohol **7c** (15 mg, 0.014 mmol) in pyridine (1 mL) at 0°C was added Ac_2O (6 µL, 0.055 mmol) and DMAP (2 mg, 0.014 mmol). The solution was stirred at room temperature for 1h. The reaction was quenched with drops of water and solvent was evaporated off under reduced pressure. The residue on flash column chromatography (1:4 EtOAc-Hex) afforded the acetate (13 mg, 0.0116 mmol, 83%) as colourless paste.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 - 7.00 (m, 40H, Ar-H), 5.86 - 5.84 (dd, J=2.8, 2.8 Hz, 1H), 5.78 - 5.77 (dd, J=2, 2.4 Hz, 1H), 5.635 - 5.631 (d, J=1.6 Hz, 1H) 4.96 - 4.28 (m, 14H, Bn CH_2 s), 4.13 - 4.03 (m, 4H), 3.92 - 3.87 (dd, J=9.6, 10 Hz, 1H), 3.51 - 3.41 (m, 4H), 3.38 - 3.33 (dd, J=9.6, 9.6 Hz, 1H), 2.11 (s, 3H).

FAB-MS-m/z: 1117.4 (M^+-1), 1011.4 $(MH\text{-}HOBn)^+$

1,3,4,5-Tetra-O-benzyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-D-*myo*-inositol (**9a**). The diol **3** (50 mg, 0.092 mmol) and glycosyl donor **8a** (79 mg, 0.119 mmol) were together taken up in a small quantity of toluene, azeotroped to remove traces of water and then placed under high vaccum overnight. The mixture was dissolved in CH_2Cl_2 (2 mL) at 0°C under Argon atmosphere. N-Iodosuccinimide (27 mg, 0.119 mmol) was added to the solution, after stirring for 3 minutes, TBDMSOTf (6.4 μL, 0.027 mmol) was added. The reaction was quenched after 20 minutes, with 10% aq: sodium thiosulphate and saturated sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was separated, dried and the solvent was removed under reduced pressure. The crude residue on flash column chromatography (3:7 EtOAc-Hex) afforded **9a** (78 mg, 0.070 mmol, 76%) as a colorless paste.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 - 7.17 (m, 40H, Ar-H), 5.88 - 5.83 (dd, J=10, 9.6 Hz, 1H), 5.67 - 5.62 (dd, J=9.6, 10 Hz, 1H), 5.61 - 5.57 (dd, J=8, 10 Hz, 1H), 5.49 - 5.47 (d, J=8.4 Hz, 1H, H-1), 4.99 - 4.88 (dd, J=12, 10.8 Hz, 2H), 4.72 - 4.37 (m, 10H), 4.10 - 3.96 (m, 2H), 3.33 - 3.27 (m, 3H), 2.46 (s, 1H, -OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.07, 165.74, 165.20, 138.50, 138.29, 137.78, 133.38, 133.11, 133.10, 129.79, 129.68, 128.78, 128.58, 128.32, 128.27, 127.92, 127.84, 127.71, 127.63, 127.58, 100.57 (C1), 83.19, 81.08, 79.12, 78.57, 75.68, 75.25, 73.43, 72.97, 72.44, 72.37, 71.98, 69.97, 68.74, 63.19.

FAB-MS m/z: 1119.6 (M^++1).

Acetylation of **9a** To a solution of alcohol **9a** (25 mg, 0.022 mmol) in pyridine (2 mL) at 0°C was added Ac_2O (0.2 mL) and DMAP (catalytic). The solution was stirred at room temperature for 14h. The reaction was quenched with drops of water and solvent was evaporated off under reduced pressure. The residue on flash column chromatography (1:4 EtOAc-Hex) afforded the acetate (21 mg, 82%) as colourless paste.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 - 7.15 (m, 40H, Ar-H), 5.85 - 5.81 (dd, J=9.6, 10 Hz, 1H), 5.74 - 5.72 (dd, J=2.8, 2.8 Hz, 1H), 5.67 - 5.63 (dd, J=9.6, 9.6 Hz, 1H), 5.61 - 5.56 (dd, J=8, 9.6 Hz, 1H), 5.45 - 5.43 (d, J=7.6 Hz, 1H, H-1), 4.85 - 4.36 (m, 10H), 4.32 - 4.28 (dd, J=9.2, 9.6 Hz, 1H), 3.93 - 3.88 (m, 1H), 3.80 - 3.76 (dd, J = 9.6, 9.6 Hz, 1H), 3.39 - 3.33 (m, 3H), 2.02 (s, 3H).

1,3,4,5-Tetra-O-benzyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-D-*myo*-inositol (**9b**). The diol **3** (50 mg, 0.092 mmol) and glycosyl donor **8b** (79 mg, 0.119 mmol) were together taken up in a small quantity of toluene, azeotroped to remove traces of water and then placed under high vaccum overnight. The mixture was dissolved in CH_2Cl_2 (2 mL) at 0°C under Argon atm. N-Iodosuccinimide (27 mg, 0.119 mmol) was added to the solution, after stirring for 3 minutes, TBDMSOTf (6.4 μL, 0.027 mmol) was added. The reaction was quenched after 20 minutes with 10% aq: sodium thiosulphate and saturated sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was separated, dried and the solvent was removed under reduced pressure. The crude residue on flash column chromatography (3:7 EtOAc-Hex) afforded **9b** (75 mg, 0.067 mmol, 73%) as a colorless paste.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 - 7.17 (m, 40H, Ar-H), 5.97 - 5.96 (dd, J=3.2, 0.4 Hz, 1H), 5.88 - 5.83 (dd, J=8, 10.4 Hz, 1H), 5.59 - 5.56 (dd, J=3.2, 10.4 Hz, 1H), 5.51 - 5.49 (d, J=8 Hz, 1H, H-1), 5.18 - 5.15 (d, J=11.2 Hz, 1H), 4.91 - 4.39 (m, 10H), 4.23 - 4.17 (m, 2H), 4.03 - 3.98 (dd, J=9.6, 9.6 Hz, 1H), 3.37 - 3.32 (m, 3H), 2.48 (bs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.92, 165.48, 165.39, 165.33, 138.55, 138.48, 138.31, 137.79, 133.34, 133.17, 133.11, 129.75, 129.67, 129.61, 128.53, 128.41, 128.34, 128.55, 128.20,

127.89, 127.87, 127.78, 127.68, 127.57, 127.49, 127.25, 100.71 (C1), 83.22, 81.09, 79.20, 78.07, 77.06, 75.72, 75.14, 73.39, 72.40, 71.67, 71.02, 70.51, 68.68, 68.18, 61.67.

FAB-MS m/z: 1117.3 (M^+-1), 1119.3 (M^++1).

Acetylation of **9b** To a solution of alcohol **9b** (20 mg, 0.018 mmol) in pyridine (2 mL) at 0°C was added Ac_2O (8.5 μL, 0.09 mmol) and DMAP (2 mg, 0.018 mmol). The solution was stirred at room temperature for 14h. The reaction was quenched with drops of water and the solvent was evaporated under reduced pressure. The residue on flash column chromatography (1:3 EtOAc-Hex) afforded the acetate (20 mg, 0.017 mmol, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 - 7.16 (m, 40H, Ar-H), 5.97 - 5.96 (dd, J=0.4, 3.6 Hz, 1H), 5.91 - 5.86 (dd, J=8, 10.4 Hz, 1H), 5.80 - 5.79 (dd, J=2.8, 2.8 Hz, 1H) 5.59 - 5.55 (dd, J=3.6, 10.8 Hz, 1H), 5.47 - 5.45 (d, J=8 Hz, 1H), 4.90 - 4.32 (m, 11H), 4.16 - 4.12 (dd, J=7.2, 6Hz, 1H), 3.84 - 3.80 (dd, J=9.6, 9.6 Hz, 1H), 3.44 - 3.37 (m, 3H), 2.07 (s, 3H).

FAB-MS-m/z: 1159.2 (M^+-1), 1161.2 (M^++1).

3,6-Di-O-allyl-1-O-methyl-2-O-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**11**).

The diol **10** (54.8 mg, 0.2 mmol) and glycosyl donor **4b** (158.08, 0.26 mmol) were taken together in a small quantity of toluene, azeotroped to remove traces of water and then placed under high vaccuum overnight. The mixture was dissolved in CH_2Cl_2 (4 mL) at O°C under Argon atmosphere. N-iodosuccinimide (58.5 mg, 0.26 mmol) was added to the solution, after stirring for 3 minutes, TBDMSOTf (13.78 μL, 0.06 mmol) was added. The reaction mixture was quenched after 20 minutes with 10% aq. sodium thiosulphate and saturated sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was separated, dried and the solvent was removed under reduced pressure. The crude residue on flash column chromatography (1:3 EtOAc-Hex) afforded **11** (34 mg, 0.043 mmol, 66%) as a colorless paste [yield is based on recovered acceptor **10** (37 mg, 0.13 mmol)].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 - 7.15 (m, 20H, Ar-H), 5.95 - 5.81 (m, 2H), 5.30 - 5.11 (m, 4H), 5.09 (bs, 1H, H-1), 4.88 - 4.46 (m, 12H), 4.10 - 3.35 (m, 21H), 3.24 (S, 3H).

FAB-MS-m/z: 795 (M^+-1)

Benzoylation of **11**

To a solution of alcohol **11** (24 mg, 0.03 mmol) in pyridine (2 mL) at 0°C was added benzoyl chloride (16 μL) and DMAP (catalytic). The solution was stirred at room temperature for overnight. The reaction was quenched with drops of water and solvent was evaporated off under reduced pressure. The residue on flash column chromatography (1:3 EtOAc-Hex) afforded the benzoate (25 mg, 92%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 - 8.04 (d, 2H, Ar-H), 7.64 - 7.14 (m, 23H, Ar-H), 5.85 - 5.06 (m, 2H), 5.40 - 5.33 (dd, J=9.6, 9.3 Hz, 1H), 5.19 (bs, 1H), 5.15 - 4.99 (m, 4H), 4.91 - 4.80 (m, 2H), 4.72 - 4.46 (m, 7H), 4.07 - 3.85 (m, 11H), 3.74 (bs, 2H), 3.55 (bs, 2H), 3.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.25 (OCOPH), 138.60, 138.59, 138.58, 134.72, 134.64, 134.00, 133.30, 130.41, 129.92,129.48,128.69, 128.61,128.55, 128.21, 128.11, 127.93, 127.70, 127.63, 117.45, 117.03, 100.01(C-1), 100.20(C-1), 79.64, 75.14, 75.08, 74.73, 74.46, 73.46, 72.69, 72.62, 72.37, 72.08, 71.59, 70.45, 70.15, 69.76, 55.11.

3,6-Di-O-allyl-1-O-methyl-4-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**12**). The diol **10** (25 mg, 0.091 mmol) and glycosyl donor **5b** (81 mg, 0.13 mmol) were together taken up in a small quantity of toluene, azeotroped to remove traces of water and then placed under high vaccum overnight. The mixture was dissolved in CH_2Cl_2 (2 mL) at 0°C under Argon atmosphere. N-Iodosuccinimide (29 mg, 0.13 mmol) was added to the solution, after stirring for 3 minutes, TBDMSOTf (7 μL, 0.03 mmol) was added. The reaction was

quenched after 20 minutes with 10% aq: sodium thiosulphate and saturated sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was separated, dried and the solvent was removed under reduced pressure. The crude residue on flash column chromatography (1:3 EtOAc-Hex) afforded **12** (51 mg, 0.063 mmol, 69%) as a colorless paste.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 - 7.19 (m, 20H, Ar-H), 6.04 - 5.85 (m, 2H), 5.68 - 5.67 (dd, J=2, 2.8 Hz, 1H), 5.422 - 5.418 (d, J=1.6 Hz, 1H, H-1), 5.33 - 5.09 (m, 4H), 4.89 - 4.73 (m, 4H), 4.59 - 4.52 (m, 3H), 4.14 - 3.88 (m, 10H), 3.78 - 3.63 (m, 5H), 3.39 (s, 3H), 2.42 (s, 1H, -OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.48, (OCOPh), 138.45, 138.04, 134.83, 134.02, 133.01, 129.92, 128.31, 128.27, 127.91, 127.56, 127.50, 118.33, 116.83, 99.98 (C1), 99.51 (C1'), 79.72, 78.15, 75.21, 74.15, 73.50, 73.13, 72.60, 72.44, 71.53, 70.46, 70.19, 69.33, 69.08, 67.54, 54.99.

FAB-MS m/z: 809.3 (M^+-1), 811.3 (M^++1).

Acetylation of **12** To a solution of alcohol **12** (10 mg, 0.012 mmol) in pyridine (1 mL) at 0°C was added Ac_2O (0.2 mL) and DMAP (catalytic). The solution was stirred at room temperature for 14h. The reaction was quenched with drops of water and solvent was evaporated off under reduced pressure. The residue on flash column chromatography (1:3 EtOAc-Hex) afforded the acetate (9 mg, 0.011 mmol, 88%) as a colourless paste.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 - 7.13 (m, 20H, Ar-H), 5.92 - 5.81 (m, 2H), 5.66 - 5.64 (dd, J=2.4, 2.8 Hz, 1H), 5.391 - 5.386 (d, J=2 Hz, 1H, H-1), 5.22 - 5.21 (d, J=1.2 Hz, 1H) 5.20 - 5.19 (dd, J=2, 3.2 Hz, 1H), 5.174 - 5.170 (d, J=1.6 Hz, 1H), 5.08 - 5.05 (m, 2H), 4.82 - 4.64 (m, 4H), 4.52 - 4.47 (m, 3H), 4.06 - 3.62 (m, 14H), 3.32 (s, 3H), 2.02 (s, 3H).

1,3,4,5-Tetra-O-benzyl-2-O-(2,3,4-tri-O-benzyl-6-O-[t-butyldiphenylsilyl]-α-D-mannopyranosyl-6-O-(2-O-benzoyl-2,4,6-tri-O-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol (**17**). The diol **3** (50 mg, 0.092 mmol) and glycosyl donors **4a** (75 mg, 0.12 mmol) and **5b** (90 mg. 0.12 mmol) were together taken up in a small quantity of toluene, azeotroped to remove traces of water. The mixture was dissolved in CH_2Cl_2 (3 mL) at 0°C under Argon atmosphere. N-Iodosuccinimide (54 mg, 0.24 mmol) was added to the solution. After stirring for 3 minutes, TBDMSOTf (12 μL, 0.054 mmol) was added. The reaction was quenched after 1h with 10% aqueous sodium thiosulphate and saturated sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was removed under reduced pressure. The crude residue on flash column chromatography (1:4 EtOAc-Hex) afforded the psuedo-trisaccharide **17** (62 mg, 0.036 mmol, 39%) as the major product along with **7c** (40 mg, 0.037 mmol, 40%).

Note: In order to confirm the regioselectivity, the pseudo-disaccharide **7c** was coupled with **4a** which afforded the same psuedo-trisaccharide **17** in 14% isolated yield. The unreacted acceptor **7c** was recovered.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 - 6.94 (m, 65H, Ar-H), 5.83 - 5.81 (dd, J=2.4, 2 Hz, 1H), 5.626 - 5.621 (d, J=2 Hz, 1H, H-1), 5.35 (s, 1H, H-1), 4.97 - 4.36 (m, 20H), 4.29 - 3.99 (m, 7H), 3.93 - 3.90 (dd, J=2.8, 9.6 Hz, 1H), 3.85 - 3.59 (m, 4H), 3.48 - 3.26 (m, 5H), 1.03 (s, 9H).

FAB-MS m/z: 1745.76 (M^+-1).

Anal. cald. for $C_{111}H_{114}O_{17}Si$: CX, 76.26; H, 6.57. Found: C, 76.00; H, 6.71.

3,6-Di-O-allyl-1-O-methyl-2-O-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-4-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-manno-pyranoside (**18**).

The diol **10** (27.4 mg, 0.1 mmol) the glycosyl donors **4b** (66.88 mg, 0.11 mmol) and **5b** (68.42, 0.11 mmol) were together taken up in a small quantity of toluene, azeotroped to remove traces of water. The mixture was dissolved in CH_2Cl_2 (3 mL) at 0°C under Argon atmosphere. N-iodosuccinimide (58.5 mg, 0.26 mmol) was added to the solution. After stirring for 3 minutes, TBDMSOTf (13.78 μL, 0.06 mmol) was added. The reaction mixture was quenched after 1 hour

with 10% aq. sodium thiosulphate and saturated sodium bicarbonate, and extracted with CH_2Cl_2. The organic layer was removed under reduced pressure. The crude residue on flash column chromatography (1:4 EtOAc-Hex) afforded the trisaccharide **18** (45 mg, 0.034 mmol, 54%) as the major product, along with the disaccharide **12** (20 mg, 0.025 mmol, 39%). Unreacted acceptor **10** (10 mg, 0.03 mmol) was recovered.

Note: Regioselectivity was confirmed by coupling disaccharide **12** with **4b** affording the same trisaccharide **18** in 36% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 - 8.06 (d, 2H, Ar-H), 7.58 - 7.06 (m, 38H, Ar-H), 5.94 - 5.84 (m, 2H), 5.70 (bs, 1H), 5.39 (bs, 1H), 5.26 - 4.99 (m, 5H), 4.95 - 4.46 (m, 15H), 4.12 - 3.61 (m, 21H), 3.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.31 (OCOPh), 138.59, 138.53, 138.45, 138.39, 138.27, 138.07, 135.01, 134.01, 134.32, 133.04, 130.03, 129.96, 129.92, 128.39, 128.30, 128.28, 128.24, 128.19, 128.04, 127.98, 127.96, 127.83, 127.81, 127.69, 127.59, 127.48, 117.68, 116.41, 99.81(C-1), 99.68(C-1), 97.80(C-1), 79.82, 79.43, 78.32, 75.26, 74.91, 74.76, 74.16, 74.00, 73.49, 73.36, 73.24, 72.56, 72.32, 72.27, 72.15, 71.55, 70.84, 70.70, 69.74, 69.48, 69.03, 54.81.

Anal. Cald. For $C_{80}H_{86}O_{17}$: C, 72.82; H, 6.57. Found C, 72.90; H. 6.66.