Electronic Supplementary Information.

**Reagent Switchable Stereoselective \(\beta(1,2)\) Mannoside Mannosylation:**  
**OH-2 of Mannose is a Privileged Acceptor.**

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**para-Methoxyphenyl (2,3,4,6-tetra-\(\text{O}\)-benzyl-\(\alpha\)-\(\text{d}\)-mannopyranosyl)-(1\(\rightarrow\)2)-3,4,6-tri-\(\text{O}\)-benzyl-\(\alpha\)-\(\text{d}\)-mannopyranoside 5\(\alpha\)**

*para-Methoxyphenyl 3,4,6-tri-\(\text{O}\)-benzyl-\(\alpha\)-\(\text{d}\)-mannopyranoside* 4 (33 mg, 0.06 mmol), *phenyl 2,3,4,6-tetra-\(\text{O}\)-benzyl-1-thio-\(\alpha\)-\(\text{d}\)-mannopyranoside* 3 (41 mg, 0.065 mmol) and 2,4,6-tri-\text{tert}-butylpyrimidine (76 mg, 0.30 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (1 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. Dimethylthiosulfonium triflate (260 \(\mu\)L of a 0.4 M solution in DCM) was added and the reaction mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (4:1, petrol:ethyl acetate) indicated formation of a product (R\(\text{f}\) 0.4) with complete consumption of the starting materials (R\(\text{f}\) 0.1, 0.7). The reaction mixture was quenched with triethylamine (0.5 mL) and filtered through celite®. The filtrate was concentrated *in vacuo* and the residue purified by flash column chromatography (petrol→5:1, petrol:ethyl acetate) to afford *para-methoxyphenyl (2,3,4,6-tetra-\(\text{O}\)-benzyl-\(\alpha\)-\(\text{d}\)-mannopyranosyl)-(1\(\rightarrow\)2)-3,4,6-tri-\(\text{O}\)-benzyl-\(\alpha\)-\(\text{d}\)-mannopyranoside* 5\(\alpha\) (43 mg, 67 %) as a colourless oil; \([\alpha]_D^{\text{CHCl}_3} +41.3 \ (c, 1.0 \text{ in CHCl}_3)\); \(\nu_{\text{max}}\) (thin film) no significant peaks; \(\delta_H\) (500 MHz, CDCl\(_3\))

# Supplementary Material (ESI) for Organic & Biomolecular Chemistry  
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3.69 (1H, ad, J 11.2 Hz, H-6), 3.74-3.75 (2H, m, H-6, H-6'), 3.75 (3H, s, OMe), 3.80 (1H, dd, J5.6 3.8 Hz, J6.6 11.4 Hz, H-6'), 3.87 (1H, as, H-2b), 3.89-4.00 (5H, m, H-4a, H-4b, H-5a, H-5b), 4.14 (1H, dd, J2.3,1.3 Hz, J3.4 9.0 Hz, H-3a), 4.27 (1H, at, J 2.6 Hz, H-2a), 4.47-4.52 (5H, m, 5 x CH), 4.54 (1H, d, J 12.4 Hz, CH), 4.59 (1H, d, J 12.5 Hz, CH), 4.60 (1H, d, J 12.4 Hz, CH), 4.62 (1H, d, J 10.6 Hz, CH), 4.66 (1H, d, J 12.0 Hz, CH), 4.72 (1H, d, J 11.3 Hz, CH), 4.76 (1H, d, J 11.3 Hz, CH), 4.87 (1H, d, J 10.9 Hz, CH), 4.90 (1H, d, J 10.8 Hz, CH), 5.25 (1H, d, J1.2 1.6 Hz, H-1b), 5.59 (1H, d, J1.2 1.8 Hz, H-1a), 6.75 (2H, d, J 9.1 Hz, 2 x Ar-Hpmp), 6.99 (2H, d, 2 x Ar-Hpmp), 7.16-7.59 (35H, m, 35 x Ar-H); δC (125 MHz, CDCl3) 55.6 (q, OMe), 69.2, 69.4 (2 x t, C-6a, C-6b), 72.2 (t, CH2), 72.4 (d, C-4a, C-4b), 72.6, 73.2 (2 x t, 2 x CH2), 74.3 (d, C-2a), 74.4, 74.9 (2 x d, C-2b, C-5a, C-5b), 75.0, 75.1 (2 x t, 2 x CH2), 79.7 (d, C-3a, C-3b), 97.8 (d, C-1a), 99.7 (d, C-1b), 114.5, 117.8 (2 x d, 2 x Ar-Cpmp), 127.4-128.5 (d, 35 x Ar-C), 138.2, 138.3, 138.4,138.5, 138.6 (s, Ar-C), 150.1, 154.9 (2 x s, 2 x Ar-Cpmp); m/z (ESI+) 1137 (M+MeCN+NH4+, 100%), (M+Na+) peaks measured: 1101.5 (100%), 1102.5 (75%), 1103.5 (30%), 1104.5 (9%), 1105.5 (2%), peaks calculated: 1101.5 (100%), 1102.5 (71%), 1103.5 (23%), 1104.5 (4%), 1105.5 (1%).

**para-Methoxyphenyl (2,3,4,6-tetra-O-benzyl-β-D-mannopyanosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 5β**

![Diagram of compound 5β]

**para-Methoxyphenyl 3,4,6-tri-O-benzyl-α-D-mannopyranoside 4** (74 mg, 0.13 mmol), phenyl 2,3,4,6-tetra-O-benzyl-1-thio-α-D-mannopyranoside 3 (101 mg, 0.16 mmol) and 2,6-di-tert-butyl-4-methylpyridine (216 mg, 0.85 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (2 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 °C. To this flask was added
dimethyldisulfide (70 µL, 0.78 mmol) and trifluoromethylsulfonic anhydride (136 µL, 0.78 mmol). After 2 min, the solution was transferred to the flask containing the sugar reagents at -78 °C. The mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (4:1, petrol:ethyl acetate) indicated formation of a product ($R_f$ 0.3) with complete consumption of the starting materials ($R_f$ 0.1, 0.5). The reaction mixture was quenched with triethylamine (1 mL) and filtered through celite®. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (petrol→4:1, petrol:ethyl acetate) to afford para-methoxyphenyl (2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 5β (98 mg, 70 %) as a colourless oil; $\delta^2_{22}D$−15.5 (c, 1.0 in CHCl₃); $\nu$max (thin film) no significant peaks; $\delta_H$ (400 MHz, CDCl₃) 3.47-3.55 (2H, m, H-3b, H-5b), 3.65 (1H, d, $J_{5,6}$ 1.8 Hz, $J_{6,6'}$ 10.7 Hz, H-6), 3.69-3.78 (3H, m, H-6, 2 x H-6'), 3.77 (3H, s, OMe), 3.88-3.93 (2H, m, H-5a, H-4b), 4.00 (1H, at, $J$ 9.6 Hz, H-4a), 4.09 (1H, d, $J_{2,3}$ 3.0 Hz, H-2b), 4.17 (1H, dd, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 8.8 Hz, H-3a), 4.29 (1H, d, $J$ 10.8 Hz, CH), 4.39 (1H, d, $J$ 12.0 Hz, CH), 4.40 (1H, d, $J$ 11.9 Hz, CH), 4.47 (2H, ad, $J$ 12.8 Hz, 2 x CH), 4.53 (1H, d, $J$ 10.8 Hz, CH), 4.54 (1H, d, $J$ 10.9 Hz, CH), 4.58-4.62 (3H, m, H-2a, 2 x CH), 4.66 (1H, s, H-1b), 4.79 (1H, d, $J$ 10.8 Hz, CH), 4.88 (1H, d, $J$ 11.7 Hz, CH), 4.93 (1H, d, $J$ 10.9 Hz, CH), 5.08 (1H, d, $J$ 11.0 Hz, CH), 5.16 (1H, d, $J$ 11.7 Hz, CH), 5.56 (1H, d, $J_{1,2}$ 1.9 Hz, H-1a), 6.81 (2H, d, $J$ 9.0 Hz, 2 x Ar-HPMP), 7.03 (2H, d, 2 x Ar-HPMP), 7.19-7.57 (35H, m, 35 x Ar-H); $\delta_C$ (100 MHz, CDCl₃) 55.6 (q, OMe), 68.7, 70.0 (2 x t, C-6a, C-6b), 70.3, 70.9, 73.2, 73.4, 74.4, 74.9, 75.2 (7 x t, 7 x CH₂), 71.6 (d, C-2a), 73.9, 74.0 (2 x d, C-4a, C-4b, C-2b), 74.8 (d, C-5a), 74.8 (d, C-5b), 77.8 (d, C-3a), 81.7 (d, C-3b), 96.3 (d, C-1a), 99.5 (d, C-1b), 114.6, 117.7 (2 x d, 2 x Ar-CPMP), 127.3-128.6 (d, Ar-C), 138.1-138.9 (s, Ar-C), 150.3, 155.5 (s, Ar-CPMP); $m/z$ (ESI⁺) 1137 (M+MeCN+NH₄⁺, 100%), (M+Na⁺) peaks measured: 1101.5 (100%), 1102.5 (74%), 1103.5 (28%), 1104.5 (7%), 1105.5 (2%), peaks calculated: 1101.5 (100%), 1102.5 (71%), 1103.5 (23%), 1104.5 (4%), 1105.5 (1%).

**para-Methoxyphenyl (2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 7**
para-Methoxyphenyl 3,4,6-tri-O-benzyl-α-D-mannopyranoside 4 (54 mg, 0.10 mmol), phenyl 2,3,4,6-tetra-O-acetyl-1-thio-α-D-mannopyranoside 6 (64 mg, 0.15 mmol) and 2,6-di-tert-butyl-4-methylpyridine (205 mg, 0.8 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (2 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 °C. To this flask was added dimethyldisulfide (67 µL, 0.75 mmol) and trifluoromethylsulfonic anhydride (126 µL, 0.75 mmol). After 2 min, the solution was transferred to the flask containing the sugar reagents at -78 °C. The mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (2:1, petrol:ethyl acetate) indicated formation of a product (R_f 0.25) with complete consumption of the starting materials (R_f 0.2, 0.3). The reaction mixture was quenched with triethylamine (1 mL) and filtered through celite®. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (petrol→4:1, petrol:ethyl acetate) to afford para-methoxyphenyl (2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 7 (49 mg, 55%) as a colourless oil; [α]_D^20 +64.6 (c, 1.0 in CHCl_3); ν_max (thin film) 1752 (s, C=O) cm⁻¹; δ_H (400 MHz, CDCl₃) 1.90, 2.00, 2.03, 2.14 (12H, 4 x s, 4 x OAc), 3.71 (1H, dd, J₅,₆ 2.3 Hz, J₆,₆' 11.3 Hz, H-6a), 3.76 (3H, s, OMe), 3.77 (1H, dd, J₅,₆' 3.0 Hz, H-6'a), 3.94-4.03 (2H, m, H-5a, H-4a), 4.07-4.14 (3H, m, H-2a, H-3a, H-6b), 4.20-4.27 (2H, m, H-5b, H-6'b), 4.50 (1H, d, J 12.1 Hz, CHH'a), 4.55 (1H, d, J 10.9 Hz, CHH'b), 4.63 (1H, d, CHH'a), 4.71 (1H, d, J 11.9 Hz, CHH'c), 4.81 (1H, d, CHH'c), 4.87 (11H, d, CHH'b), 5.02 (1H, d, J₉,₉' 1.7 Hz, H-1b), 5.25 (1H, at, J 9.9 Hz, H-4b), 5.45 (1H, dd, J₀,₀ 3.4 Hz, J₀,₀' 9.9 Hz, H-3b), 5.50-5.51 (2H, m, H-1a, H-2b), 6.79 (2H, d, J 9.1 Hz, 2 x Ar-H_PMP), 7.01 (2H, d, J 9.1 Hz, 2 x Ar-H_PMP), 7.19-7.38 (15H, m, 15 x Ar-H); δ_C (100 MHz, CDCl₃) 20.5, 20.7, 20.7, 20.9 (4 x q, 4 x OAc), 55.6 (q, OMe), 62.7 (t, C-6b), 66.2 (d, C-4b), 68.9 (t, C-
6a), 69.0 (2 x d, C-5b, C-3b), 69.4 (d, C-2b), 72.1, 74.6 (2 x d, C-5a, C-4a), 72.6, 73.0, 75.3 (3 x t, 3 x CH₂), 76.3, 79.3 (2 x d, C-2a, C-3a), 97.9 (d, C-1a), 99.4 (d, C-1b), 114.6, 118.1 (2 x d, 2 x Ar-C<sub>PMP</sub>), 127.4-128.9 (d, Ar-C), 138.3, 150.1, 155.5 (s, Ar-C), 169.7, 169.8, 170.7 (4 x s, 4 x C=O); m/z (ESI<sup>+</sup>) 945 (M+MeCN+NH₄<sup>+</sup>, 100%); HRMS (ESI<sup>+</sup>) calcd. for C₄₈H₅₄O₁₆Na (M+Na<sup>+</sup>) 909.3304. Found 909.3321.

2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-1,2:3,4-diisopropylidene-D-galactopyranose 9α and 2,3,4,6-Tetra-O-acetyl-β-D-mannopyranosyl-(1→6)-1,2:3,4-diisopropylidene-D-galactopyranose 9β

1,2:3,4-Diisopropylidene-D-galactose 8 (19 mg, 0.072 mmol), phenyl 2,3,4,6-tetra-O-benzyl-1-thio-α-D-mannopyranoside 3 (50 mg, 0.08 mmol) and 2,6-di-tert-butyl-4-methylpyridine (145 mg, 0.56 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (2 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 °C. To this flask was added dimethylsulfide (39 μL, 0.43 mmol) and trifluoromethylsulfonic anhydride (73 μL, 0.43 mmol). After 2 min, the solution was transferred to the flask containing the sugar reagents at -78 °C. The mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (2:1, petrol:ethyl acetate) indicated formation of a product (R<sub>f</sub> 0.5) with complete consumption of the starting materials (R<sub>f</sub> 0.6, 0.2). The reaction mixture was quenched with triethylamine (0.5 mL) and filtered through celite. The filtrate was concentrated <i>in vacuo</i> and the residue purified by flash column chromatography (petrol→6:1, petrol:ethyl acetate) to afford 2,3,4,6-tetra-O-acetyl-D-mannopyranosyl-(1→6)-1,2:3,4-diisopropylidene-D-galactopyranose 9 (36 mg, 53%, α:β 3:1) as a colourless oil.
9α: [α]_D^{25} -10.9 (c, 1.0 in CHCl_3); ν_max (thin film) no significant peaks; δ_H (400 MHz, CDCl_3) 1.34, 1.44, 1.51 (12H, 3 x s, 4 x Me), 3.46-3.82 (5H, m, H-5b, H-6a, H-6’a, H-6b, H-6’b), 3.84 (1H, dd, J_{1,2} 1.9 Hz, J_{2,3} 2.8 Hz, H-2b), 3.93 (1H, dd, J_{3,4} 9.5 Hz, H-3b), 3.97 (1H, m, H-5a), 4.03 (1H, at, J 9.1 H-4b), 4.17 (1H, dd, J_{2,3} 1.8 Hz, J_{3,4} 8.1 Hz, H-4a), 4.33 (1H, dd, J_{1,2} 5.0 Hz, H-2a), 4.51-4.62 (5H, m, H-3a, 4 x CH), 4.68-4.77 (3H, m, 3 x CH), 4.88 (1H, d, J 10.7 Hz, CH), 5.03 (1H, d, H-1b), 5.54 (1H, d, H-1a), 7.16-7.40 (20H, m, 20 x Ar-H); δ_C (100 MHz, CDCl_3) 24.6, 24.9, 26.0, 26.1 (4 x q, 4 x Me), 65.2 (d, C-5a), 65.3, 69.1 (2 x t, C-6a, C-6b), 70.6 (2 x d, C-2a, C-3a), 70.9 (d, C-4a), 72.0 (d, C-5b), 72.1, 72.3, 73.3, 75.1 (4 x t, 4 x CH_2), 74.6 (d, C-2b), 74.8 (d, C-4b), 80.0 (d, C-3b), 96.3 (d, C-1a), 97.2 (d, C-1b), 108.5, 109.3 (2 x s, 2 x C(CH_3)$_2$), 127.4-128.3 (d, Ar-C), 138.4, 138.5, 138.6 (s, Ar-C); m/z (ESI*) 800 (M+NH$_4^+$, 100%); HRMS (ESI*) calcd. for C$_{46}$H$_{54}$NaO$_{11}$ (M+Na$^+$) 805.3558. Found 805.3550.

9β: [α]_D^{25} -38.3 (c, 0.4 in CHCl_3); ν_max (thin film) no significant peaks; δ_H (500 MHz, CDCl_3) 1.33, 1.34, 1.45, 1.48 (12H, 4 x s, 4 x CH$_3$), 3.43 (1H, dd, J$_{5,6}$ 2.2 Hz, J$_{5,5}$ 5.0 Hz, J$_{4,5}$ 9.4 Hz, H-5b), 3.48 (1H, dd, J$_{2,3}$ 3.1 Hz, J$_{3,4}$ 9.4 Hz, H-3b), 3.63 (1H, dd, J$_{3,8}$ 8.2 Hz, J$_{6,6'}$ 10.7 Hz, H-6a), 3.76 (1H, dd, J$_{6,6'}$ 10.7 H-6’b), 3.80 (1H, dd, H-6’b), 3.90 (1H, at, J 9.8 Hz, H-4b), 4.01 (1H, d, J 3.2 Hz, H-2b), 4.11-4.13 (1H, m, H-5a), 4.21-4.25 (2H, m, H-4a, H-6a), 4.34 (1H, dd, J$_{1,2}$ 4.7 Hz, J$_{2,3}$ 2.2 Hz, H-2a), 4.35 (1H, d, J 11.0 Hz, CH), 4.45 (1H, d, J 12.0 Hz, CH), 4.47 (1H, s H-1b), 4.51 (1H, d, J 11.1 Hz, CH), 4.57 (1H, d, J 12.3 Hz, CH), 4.62 (1H, dd, J$_{3,4}$ 8.2 Hz, H-3a), 4.65 (1H, d, J 12.3 Hz, CH), 4.91 (1H, d, J 10.8 Hz, CH), 4.93 (1H, d, J 12.7 Hz, CH), 5.02 (1H, d, J 12.3 Hz, CH), 5.61 (1H, d, H-1a), 7.16-7.52 (20H, m, 20 x Ar-H); δ_C (125 MHz, CDCl$_3$, from HSQC) 24.6, 25.8 (2 x q, 2 x Me), 67.9 (d, C-5a), 69.3 (d, C-6b), 69.8 (t, C-6a), 70.3 (d, C-2a), 70.6 (d, C-3a), 70.9 (t, CH$_2$), 71.5 (d, C-4a), 72.5 (d, C-2b), 73.4, 73.4 (2 x t, 2 x CH$_2$), 74.6 (d, C-4b), 75.0 (t, CH$_2$), 75.7 (d, C-5b), 81.8 (d, C-3b), 96.2 (d, C-1a), 102.3 (d, C-1b), 127.7-128.1 (d, Ar-C); m/z (ESI*) 800 (M+NH$_4^+$, 100%); HRMS (ESI*) calcd. for C$_{46}$H$_{58}$NaO$_{11}$ (M+Na$^+$) 800.4004. Found 800.4017.

Methyl-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl-(1→4)-2,3,6-tri-O-benzoyl-α-D-galactopyranoside 11
2,3,6-Tri-O-benzoyl-α-D-galactopyranoside 10 (56 mg, 0.11 mmol), phenyl 2,3,4,6-tetra-O-benzyl-1-thio-α-D-mannopyranoside 3 (77 mg, 0.12 mmol) and 2,6-di-tert-butyl-4-methylpyridine (199 mg, 0.77 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (2 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 °C. To this flask was added dimethyl disulfide (59 µL, 0.66 mmol) and trifluoromethylsulfonyl anhydride (111 µL, 0.66 mmol). After 2 min, the solution was transferred to the flask containing the sugar reagents at -78 °C. The mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (4:1, petrol:ethyl acetate) indicated formation of a product (Rf 0.3) with complete consumption of the starting materials (Rf 0.2, 0.7). The reaction mixture was quenched with triethylamine (1 mL) and filtered through celite®. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (petrol→5:1, petrol:ethyl acetate) to afford methyl-(2,3,4,6-tetra-O-benzyl-α-D-mannopyanosyl-(1→4)-2,3,6-tri-O-benzoyl-α-D-galactopyranoside 11 (85 mg, 75 %) as a colourless oil;

[α]D 25 +67.1 (c, 2.0 in CHCl3); v max (thin film) 1723 (s, C=O) cm⁻¹; δH (500 MHz, CDCl3) 2.66 (1H, dd, J5,6 1.6 Hz, J6,6' 11.0 Hz, H-6b), 3.10 (1H, dd, J5,6' 3.6 Hz, H-6'b), 3.42 (3H, s, OMe), 3.90-3.95 (2H, m, H-2b, H-5b), 3.99-4.04 (2H, m, H-3b, CH), 4.09-4.15 (2H, m, H-4b, H-6a), 4.33 (1H, at, J 6.9 Hz, H-5a), 4.37-4.49 (4H, m, H-4a, H-6'a, 2 x CH), 4.65 (1H, d, J 12.7 Hz, CH), 4.73 (1H, d, J 11.7 Hz, CH), 4.74-4.80 (2H, m, 2 x CH), 4.82 (1H, d, J 11.0 Hz, CH), 4.91 (1H, d, J1,2 1.6 Hz, H-1b), 5.24 (1H, d, J1,2 3.7 Hz, H-1a), 5.51 (1H, dd, J2,3 10.8 Hz, H-2a), 5.72 (1H, dd, J3,4 3.2 Hz, H-3a), 7.09-7.63 (35H, m, 35 x Ar-H); δC (125 MHz, CDCl3) 55.5 (q, OMe), 62.2 (t, C-6a), 67.8 (t, C-6b), 67.8 (d, C-5b), 69.1 (d, C-2a), 69.7 (d, C-3a), 73.6 (d, C-5b), 72.7, 72.8, 73.2 (t, CH2), 74.2 (d, C-3b), 74.6 (d, C-2b), 74.7 (d, C-4a), 74.9 (t, CH2), 79.8 (d, C-4b), 97.3 (d, C-1a), 100.0 (d, C-1b), 127.3-129.9 (d, Ar-C), 133.5, 133.2, 138.2, 138.5, 138.7 (s, Ar-C), 166.0 (s,
C=O); m/z (ESI⁺) 1046 (M+NH₄⁺, 100%); (M+Na⁺) peaks measured: 1051.4 (100%), 1052.4 (65%), 1053.4 (21%), 1054.4 (6%), calculated peaks: 1051.4 (100%), 1052.4 (67%), 1053.4 (22%), 1054.4 (5%).

**para-Methoxyphenyl (2,3,4,6-tetra-O-benzyl-α-d-mannopyanosyl)-(1→4)-2,6-di-O-benzyl-2-N-phthalimido-β-d-glucopyranoside 13**

![Diagram of chemical structure]

para-Methoxyphenyl 2,6-di-O-benzyl-2-N-phthalimido-β-d-glucopyranoside 12 (60 mg, 0.10 mmol), phenyl 2,3,4,6-tetra-O-benzyl-1-thio-α-d-mannopyanoside 3 (69 mg, 0.11 mmol) and 2,6-di-tert-butyl-4-methylpyridine (181 mg, 0.70 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (2 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 °C. To this flask was added dimethyldisulfide (55 µL, 0.60 mmol) and trifluoromethylsulfonic anhydride (101 µL, 0.60 mmol). After 2 min, the solution was transferred to the flask containing the flask containing the sugar reagents at -78 °C. The mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (2:1, petrol:ethyl acetate) indicated formation of a product (Rf 0.4) with complete consumption of the starting materials (Rf 0.7, 0.2). The reaction mixture was quenched with triethylamine (0.5 mL) and filtered through celite. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (3:1, petrol:ethyl acetate→2:1, petrol:ethyl acetate) to afford para-methoxyphenyl (2,3,4,6-tetra-O-benzyl-α-d-mannopyanosyl)-(1→4)-2,6-di-O-benzyl-2-N-phthalimido-β-d-glucopyranoside 13 (61 mg, 78 %, α anomer only) as a colourless oil; [α]₀⁺²⁵ +47.7 (c, 1.0 in CHCl₃); νₘₐₓ (thin film) 1715 (s, C=O) cm⁻¹; δ_H (400 MHz, CDCl₃) 3.68 (1H, dd, J₅₆ 10.6 Hz, J₆₅₆’ 1.5 Hz, H-6b), 3.71 (3H, s, OMe), 3.73-3.79 (2H, m, H-5a, H-6’b), 3.82 (1H, bs, H-2b), 3.85 (1H, dd, J₆₅₆’ 2.8 Hz, J₅₆ 7.9 Hz, H-6a), 3.90-3.98 (4H, m, H-4a, H-6a, H-3b, H-5b), 4.05 (1H, at, J 9.4 Hz, H-4b), 4.23 (1H, d, J 12.1 Hz, CH), 4.40 (1H, at, J 10.9 Hz, H-2a), 4.44-4.49 (2H, m, H-3a, CH), 4.51-4.69 (9H, m,
9 x CH), 4.90 (1H, d, J 10.9 Hz, CH), 5.37 (1H, d, J_{1,2} 2.0 Hz, H-1b), 5.59 (1H, d, J_{1,2} 8.1 Hz, H-1a), 6.79 (2H, d, J 9.1 Hz, 2 x Ar-H_{PMP}), 6.85 (2H, d, 2 x Ar-H_{PMP}), 6.93 (2H, at, J 7.8 Hz, 2 x Ar-H_{Phth}), 7.00 (2H, d, J 7.1 Hz, 2 x Ar-H_{Phth}), 7.18-7.68 (30H, 30 x Ar-H); δC (100 MHz, CDCl₃) 55.6 (q, OMe), 55.6 (d, C-2a), 69.3, 69.4 (2 x t, C-6a, C-6b), 72.3, 72.4 (2 x t, CH₂), 73.1 (d, C-5b), 73.3, 73.4, 74.5 (3 x t, 3 x CH₂), 74.9 (d, C-4b), 75.0 (t, CH₂), 75.1 (d, C-2b), 75.6 (d, C-5a), 78.5 (d, C-4a), 79.7 (d, C-3b), 80.5 (d, C-3a), 97.4 (d, C-1a), 100.3 (d, C-1b), 114.3, 118.6 (2 x d, Ar-H_{PMP}), 123.4 (d, Ar-C_{Phth}), 127.3-128.4 (d, Ar-C_{Bn}), 133.9 (d, Ar-C_{Phth}), 138.2-138.5 (s, Ar-C), 150.9, 155.3 (s, C=O); m/z (ESI⁺) 1135 (M+NH₄⁺, 100%); (M+Na⁺) peaks measured: 1140.4 (100%), 1141.5 (73%), 1142.5 (27%), 1143.5 (7%), calculated peaks: 1140.5 (100%), 1141.5 (76%), 1142.5 (31%), 1143.5 (9%).

2,3,4,6-Tetra-O-benzyl-α-D-mannopyanosyl-(1→3)-1,2:5,6-diisopropylidene-β-D-glucopyranose 15

![Diagram of 15]

1,2:5,6-Diisopropylidene-β-D-glucose 14 (25 mg, 0.096 mmol), phenyl 2,3,4,6-tetra-O-benzyl-1-thio-α-D-mannopyranoside 3 (73 mg, 0.11 mmol) and 2,6-di-tert-butyl-4-methylpyridine (148 mg, 0.576 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (2 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 °C. To this flask was added dimethyldisulfide (43 µL, 0.48 mmol) and trifluoromethylsulfonic anhydride (84 µL, 0.48 mmol). After 2 min, the solution was transferred to the flask containing the flask containing the sugar reagents at -78 °C. The mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (2:1, petrol:ethyl acetate) indicated formation of a product (R_f 0.7) with complete consumption of the starting materials (R_f 0.2, 0.8). The reaction mixture was quenched
with triethylamine (1 mL) and filtered through celite®. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (petrol → 5:1, petrol:ethyl acetate) to afford 2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl-(1→3)-1,2:5,6-diisopropylidene-D-glucopyranose 15 (48 mg, 64%) as a colourless oil; 

\[ [\alpha]_D^{25} +9.4 (c, 1.0 \text{ in CHCl}_3); \nu_{\text{max}} \text{ (thin film) no significant peaks; } \delta_\text{H} \text{ (500 MHz, CDCl}_3) 1.23, 1.33, 1.41, 1.49 \text{ (12H, 4 x s, 4 x CH}_3), 3.78 \text{ (1H, at, } J 2.8 \text{ Hz, H-2b), 3.80-3.85 \text{ (4H, m, H-6b, H-6’b, H-5a, H-5b), 3.99-4.03 \text{ (2H, m, H-3b, H-6a), 4.06-4.11 \text{ (3H, m, H-4b, H-6’a), 4.28 \text{ (1H, d, } J 1.5 \text{ Hz, H-3a), 4.51 \text{ (1H, d, } J 10.7 \text{ Hz, CH), 4.55 \text{ (1H, d, } J 11.6 \text{ Hz, CH), 4.56 \text{ (1H, d, } J 12.0 \text{ Hz, CH), 4.60 \text{ (1H, d, } J 11.7 \text{ Hz, CH), 4.66-4.69 \text{ (3H, m, 2 x CH, H-2a), 4.76 \text{ (1H, d, } 12.6 \text{ Hz, CH), 4.89 \text{ (1H, d, } J 10.4 \text{ Hz, CH), 5.24 \text{ (1H, d, J}_{1,2} 1.6 \text{ Hz, H-1b), 5.81(1H, d, } J_{1,2} 3.8 \text{ Hz, H-1a), 7.17-7.40 \text{ (20H, m, 20 x Ar-H); } \delta_\text{C} \text{ (125 MHz, CDCl}_3) 25.5, 26.1, 26.8, 26.9 \text{ (4 x q, 4 x Me), 67.7 (t, C-6a), 69.2 (t, C-6b), 72.1, 72.2 \text{ (2 x t, 2 x CH}_2), 72.5 \text{ (d, C-4b), 72.6 \text{ (d, C-5b), 73.5 \text{ (t, CH}_2), 74.2 \text{ (d, C-2b), 74.7 \text{ (d, C-3b), 75.3 \text{ (t, CH}_2), 79.6 \text{ (d, C-5a), 80.6 \text{ (d, C-3a), 81.3 \text{ (d, C-4a), 83.7 \text{ (d, C-2a), 98.9 \text{ (d, C-1b), 105.2 \text{ (d, C-1a), 109.3, 111.9 \text{ (2 x s, 2 x C(CH}_3)_2), 127.5-128.4 \text{ (d, Ar-C), 138.1, 138.2, 138.3 \text{ (s, Ar-C); } m/z \text{ (ESI}^+) \text{ 800 (M+NH}_4^+, 100\%); HRMS (ESI}^+) \text{ calcd. for } C_{46}H_54NaO_{11} \text{ (M+Na}^+) \text{ 805.3558. Found 805.3560.}}

\[ \text{Benzyl} \text{ (2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→3)-2,4-di-O-benzyl-6-O-tert-butyldimethylsilyl-α-D-mannopyranoside 18} \]

Benzyl 2,4-di-O-benzyl-6-O-tert-butyldimethylsilyl-α-D-mannopyranoside 17 (77 mg, 0.14 mmol), ethyl 2-O-acetyl-3,4,6-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-thio-α-D-mannopyranoside 16 (160 mg, 0.16 mmol) and 2,6-di-tert-butyl-4-methylpyridine (235 mg, 0.95 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (2 mL) and transferred using a cannula to a flame dried flask
containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 °C. To this flask was added dimethylsulfide (73 µL, 0.816 mmol) and trifluoromethylsulfonic anhydride (137 µL, 0.816 mmol). After 2 min, the solution was transferred to the flask containing the sugar reagents at -78 °C. The mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (5:1, petrol:ethyl acetate) indicated formation of a product (Rf 0.5) with complete consumption of the starting materials (Rf 0.6, 0.3). The reaction mixture was quenched with triethylamine (0.5 mL) and filtered through celite. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (petrol→6:1, petrol:ethyl acetate) to afford benzyl 2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→3)-2,4-di-O-benzyl-6-O-tert-butyldimethylsilyl-α-D-mannopyranoside 18 (136 mg, 68%) as a colourless oil; [α]_D +15.3 (c, 1.0 in CHCl3); νmax (thin film) 1758 (br, C=O) cm⁻¹; δH (500 MHz, CDCl3) 0.06, 0.07 (6H, 2 x s, 2 x CH3), 0.91 (9H, s, C(CH3)3), 2.13 (3H, s, Ac), 3.46 (1H, d, J 10.5 Hz, H-6a), 3.68-4.00 (14H, m, H-2a, H-3b/c, H-4a/b/c, H-5a/b/c, H-6b/c, H-6’a/b/c), 4.03 (1H, m, H-2b), 4.15 (1H, dd, J2,3 3.1 Hz, J3,4 9.5 Hz, H-3a), 4.31 (1H, d, J 12.2 Hz, CH), 4.40 (1H, d, J 10.9 Hz, CH), 4.42-4.46 (2H, m, 2 x CH), 4.51 (1H, d, J 12.1 Hz, CH), 4.53-4.68 (10H, m, 10 x CH), 4.76 (1H, d, J 11.7 Hz, CH), 4.82 (1 H, d, J 10.9 Hz, CH), 4.88 (1H, d, J 11.2 Hz, CH), 4.90 (1H, d, J1,2 1.4 Hz, H-1a), 5.06 (1H, d, J1,2 1.5 Hz, H-1c), 5.2 (1H, d, J1,2 1.3 Hz, H-1b), 5.54 (1H, at, J 2.2 H, H-2c), 7.14-7.36 (45H, m, 45 x Ar-H); δC (125 MHz, CDCl3) -5.3, -5.1, (q, 2 x CH3), 18.4 (s, C(CH3)3), 26.0 (q, C(CH3)3), 62.6 (t, C-6b), 68.4 (t, C-6a), 68.7 (t, CH2), 68.8 (d, C-2c), 69.5 (C-6c), 71.9, 72.1, 73.2, 73.4, 74.8, 74.9, 75.0 (t, 8 x CH2), 72.6, 73.4, 74.2, 74.8, 75.1, 77.2, 78.1 (d, C-2a/b, C-3b/c, C-4a/b/c, C-5a/b/c), 78.1 (d, C-3a), 96.1 (d, C-1a), 99.3 (d, C-1c), 100.9 (d, C-1b), 127.3-128.5 (d, 45 x Ar-C), 137.5-138.7 (s, 9 x Ar-C), 170.1 (s, C=O); m/z (ESI⁺) 1493 (M+Na⁺, 100 %); (M+Na⁺) peaks observed: 1451.7 (100%), 1452.7 (98%), 1453.7 (47%), 1454.7 (15%), 1555.7 (5%), peaks calculated: 1451.7 (99%), 1452.7 (100%), 1453.7 (56%), 1454.7 (22%), 1555.7 (7%).
Benzyl 2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-
mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-O-
benzyl-6-O-tert-butyldimethylsilyl-α-D-mannopyranoside 20β and Benzyl 2,3,4,6-
tetra-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-O-
benzyl-6-O-tert-butyldimethylsilyl-α-D-mannopyranoside 20α

Conditions A:
Benzyl (3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-
mannopyranosyl)-(1→3)-2,4,di-O-benzyl-6-O-tert-butyldimethylsilyl-α-D-
mannopyranoside 19 (63 mg, 0.044 mmol), phenyl 2,3,4,6-tetra-O-benzyl-1-thio-α-D-
mannopyranoside 3 (42 mg, 0.066 mmol) and 2,4,6-tri-tert-butylypyrimidine (90 mg, 
0.35 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM 
(1 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular 
sieves. The mixture was stirred for 1 h and cooled to -78 °C. DCM (1 mL) was added to a 
flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 °C. 
To this flask was added dimethyldisulfide (30 µL, 0.33 mmol) and trifluoromethylsulfonic anhydride (57 µL, 0.33 mmol). After 2 min, the solution was 
transferred to the flask containing the sugar reagents at -78 °C. The mixture was stirred at 
-78 °C under an atmosphere of argon. After 1 h, t.l.c (5:1, petrol:ethyl acetate) indicated 
formation of a product (Rf 0.5) with complete consumption of the starting materials (Rf 
0.1, 0.6). The reaction mixture was quenched with triethylamine (0.5 mL) and filtered 
through celite®. The filtrate was concentrated in vacuo and the residue purified by flash 
column chromatography (petrol→6:1, petrol:ethyl acetate) to afford benzyl 2,3,4,6-tetra-
O-benzyl-β-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-
3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-O-benzyl-6-O-tert-butylidimethylsilyl-α-D-mannopyranoside 20β (40 mg, 47 %) as a colourless oil.

**Conditions B:**
Benzyl (3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→3)-2,4-di-O-benzyl-6-O-tert-butylidimethylsilyl-α-D-mannopyranoside 19 (63 mg, 0.044 mmol), phenyl 2,3,4,6-tetra-O-benzyl-1-thio-α-D-mannopyranoside 3 (36 mg, 0.057 mmol) and 2,4,6-tri-tert-butylpyrimidine (57 mg, 0.22 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (1 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. Dimethylthiosulphonium triflate (50 mg, 0.194 mmol) was added and the reaction mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (5:1, petrol:ethyl acetate) indicated formation of a product (Rf 0.5) with complete consumption of the starting materials (Rf 0.1, 0.6). The reaction mixture was quenched with triethylamine (0.5 mL) and filtered through celite®. The filtrate was concentrated *in vacuo* and the residue purified by flash column chromatography (petrol→5:1, petrol:ethyl acetate) to afford benzyl 2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-O-benzyl-6-O-tert-butylidimethylsilyl-α-D-mannopyranoside 20 (35 mg, 41 %, α:β, 2.5:1, inseparable mixture) as a colourless oil.

20β: [α]⁺ +2.2 (c, 1.0 in CHCl₃); νₑₓₜ (thin film) no significant peaks; δH (500 MHz, CDCl₃) 0.10, 0.11 (2 x s, 2 x CH₃), 0.96 (9H, s, C(CH₃)₃), 3.23-3.26 (1H, m, H-5d), 3.31 (1H, dd, J 3.1 Hz, J 9.3 Hz, H-3d), 3.43 (1H, dd, J₅₆ 1.4 Hz, J₆ 10.6 Hz, H-6c), 3.60 (1H, dd, J₅₆ 3.6 Hz, H-6’c), 3.65-3.81 (7H, m, H-5a, H-6a, H-6’a, H-6b, H-6’b, H-6d, H-6’d), 3.83-3.85 (1H, m, H-4b), 3.87-3.97 (5H, m, H-2d, H-4a, H-4c, H-4d, H-5c), 4.02-4.07 (4H, m, H-2a, H-3b, H-3c, H-5b), 4.20 (1H, d, J₂₃ 2.4 Hz, H-2b), 4.22-4.28 (2H, m, 2 x CH), 4.24 (1H, s, H-3a), 4.35 (1H, s, H-1d), 4.47 (1H, s, H-2c), 4.38 -4.77 (18H, m, 18 x CH), 4.85-5.01 (5H, m, 5 x CH), 4.95 (1H, d, J₁₂ 1.2 Hz, H-1a), 5.12 (1H, d, J 11.8 Hz, CH), 5.21 (1H, d, J₁₂ 2.1 Hz, H-1c), 5.30 (1H, s, H-1b), 7.09-7.57 (65H, m, 65 x Ar-
H; δ_C (125 MHz, CDCl₃) -5.3, -5.1 (2 x q, 2 x CH₃), 18.4 (s, C(CH₃)₃), 25.9 (q, C(CH₃)₃), 62.6 (t, C-6a), 68.5 (t, C-6c), 68.7 (t, CH₂), 69.6 (t, C-6b), 69.9 (t, C-6d), 70.3, 70.5 (2 x t, 2 x CH₂), 71.6 (d, C-5c), 71.9 (t, CH₂), 72.1 (d, C-2c), 72.7 (d, C-5b), 72.8, 73.1, 73.3 (3 x t, 3 x CH₂), 73.3 (d, C-5a), 73.4 (t, CH₂), 73.8 (d, C-2d, C-4c), 74.2, 74.4 (2 x t, 2 x CH₂), 74.7, 74.7 (2 x d, C-2b, C-4a, C-4d), 74.8, 74.8 (2 x t, 2 x CH₂), 75.2 (d, C-4b), 75.6 (d, C-5d), 77.7 (d, C-3c), 78.0 (d, C-2a), 80.2 (d, C-3a, C-3b), 81.4 (d, C-3d), 96.0 (d, C-1a), 99.4 (d, C-1c, C-1d), 101.1 (d, C-1b), 127.2-128.9 (d, 65 x Ar-C), 137.5-138.7 (s, 13 x Ar-C); m/z (ESI⁺) 1975 (M+Na⁺, 100%); (M+Na⁺) peaks measured: 1973.9 (58%), 1974.9 (100%), 1975.9 (64%), 1976.9 (23%), 1977.9 (6%), 1978.9 (2%), 1979.9 (1%), peaks calculated: 1973.9 (72%), 1974.9 (100%), 1975.9 (74%), 1976.9 (39%), 1977.9 (16%), 1978.9 (5%), 1979.9 (2%).

**para-Methoxyphenyl (2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside**

**22β** and **para-Methoxyphenyl (2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 22α**

**Conditions A:**

**para-Methoxyphenyl** (3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 21 (82 mg, 0.083 mmol), phenyl 2,3,4,6-tetra-O-benzyl-1-thio-α-D-mannopyranoside 3 (66 mg, 0.10 mmol) and 2,4,6-tri-tert-butylpyrimidine (154 mg, 0.60 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (2 mL) and transferred using a cannula to a flame dried flask containing 4Å
molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 °C. To this flask was added dimethyldisulfide (45 μL, 0.50 mmol) and trifluoromethylsulfonic anhydride (87 μL, 0.50 mmol). After 2 min, the solution was transferred to the flask containing the flask containing the sugar reagents at -78 °C. The mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (4:1, petrol:ethyl acetate) indicated formation of 2 products (Rf 0.45, 0.5) with complete consumption of the starting materials (Rf 0.1, 0.6). The reaction mixture was quenched with triethylamine (1 mL) and filtered through celite®. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (petrol→8:1, petrol:ethyl acetate) to afford para-methoxyphenyl (2,3,4,6-tetra-O-benzyl-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 22 (105 mg, 84 %, α:β, 1:11) as a colourless oil.

Conditions B:
para-Methoxyphenyl (3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 21 (85 mg, 0.086 mmol), phenyl 2,3,4,6-tetra-O-benzyl-1-thio-α-D-mannopyranoside 3 (65 mg, 0.10 mmol) and 2,4,6-tri-tert-butylpyrimidine (111 mg, 0.43 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (1 mL) and transferred using a cannula to a flame dried flask containing 4Å molecular sieves. The mixture was stirred for 1 h and cooled to -78 °C. Dimethylthiosulphonium triflate (89 mg, 0.34 mmol) was added and the reaction mixture was stirred at -78 °C under an atmosphere of argon. After 1 h, t.l.c (5:1, petrol:ethyl acetate) indicated formation of a product (Rf 0.5) with complete consumption of the starting materials (Rf 0.1, 0.6). The reaction mixture was quenched with triethylamine (0.5 mL) and filtered through celite®. The filtrate was concentrated in vacuo and the residue purified by flash column chromatography (petrol→5:1, petrol:ethyl acetate) to afford para-methoxyphenyl (2,3,4,6-tetra-O-benzyl-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 22 (98 mg, 75 %, α:β, 3:1) as a colourless oil.
**22a**: Rf 0.5 (4:1, petrol:ethyl acetate); [α]D25 +17.3 (c, 1.0 in CHCl3); νmax (thin film) no significant peaks; δH (500 MHz, CDCl3) 3.28 (1H, ddd, J 1.9 Hz, J 5.3 Hz, J 7.6 Hz, H-5c), 3.32 (1H, dd, J2,3 3.1 Hz, J3,4 9.4 Hz, H-3c), 3.63 (2H, d, J 3.5 Hz, H-6b, H-6’b), 3.68-3.80 (5H, m, H-4b, H-6a, H-6’a, H-6c, H-6’c), 3.75 (3H, s, OMe), 3.87 (1H, at, J 9.6 Hz, H-4c), 3.90-3.97 (5H, m, H-2c, H-4a, H-4b, H-5a, H-5b), 4.03 (1H, dd, J2,3 2.9 Hz, J3,4 7.9 Hz, H-3b), 4.14 (1H, dd, J2,3 2.8 Hz, J3,4 8.8 Hz, H-3a), 4.21 (1H, d, J 11.0 Hz, CH), 4.31 (1H, at, J 1.9 Hz, H-2a), 4.34-4.39 (2H, m, 2 x CH), 4.41-4.42 (2H, m, H-1c, CH), 4.45-4.48 (3H, m, 3 x CH), 4.50-4.56 (4H, m, 3 x CH, H-2b), 4.60 (1H, d, J 11.1 Hz, CH), 4.63 (1H, d, J 12.0 Hz, CH), 4.70 (2H, d, J 11.7 Hz, 2 x CH), 4.78 (1H, s, J 11.3 Hz, CH), 4.84 (1H, d, J 11.9 Hz, CH), 4.90-4.99 (3H, m, 3 x CH), 5.08 (1H, d, J 12.0 Hz, CH), 5.28 (1H, d, J1,2 1.9 Hz, H-1b), 5.58 (1H, d, J1,2 1.6 Hz, H-1a), 6.76 (2H, d, J 9.1 Hz, 2 x Ar-H PMP), 7.00 (2H, d, 2 x Ar-H PMP), 7.04-7.52 (50H, m, 50 x Ar-H); δC (125 MHz, CDCl3) 55.6 (q, OMe), 69.2, 69.2 (2 x t, C-6a, C-6c), 69.8 (t, C-6b), 70.6, 70.7 (t, CH2), 71.7, 72.3 (d, C-2b, C-5a, C-5b), 72.9, 73.2, 73.3 (t, CH2), 74.0 (d, C-2c), 74.2 (d, C-2a), 74.3, 74.3 (t, CH2), 74.6 (d, C-4b), 74.8 (d, C-4c), 74.9 (d, C-4a), 75.0 (t, CH2), 75.2 (t, CH2), 75.7 (d, C-3c), 77.7 (d, C-3b), 80.0 (d, C-3a), 81.5 (d, C-5c), 97.9 (d, C-1a), 99.5 (d, C-1c), 99.7 (d, C-1b), 114.5, 117.8 (d, Ar-C PMP), 127.2-128.6 (d, Ar-C), 138.0-139.1 (s, Ar-C), 150.1, 154.9 (2 x s, Ar-C PMP); m/z (ESI+) 1529 (M+NH4+, 100%); (M+Na+) peaks measured: 1533.6 (98%), 1534.6 (100%), 1535.6 (53%), 1536.6 (17%), 1537.6 (5%) calculated peaks: 1533.6 (96%), 1534.6 (100%), 1535.6 (55%), 1536.6 (21%), 1537.6 (6%).

**22b**: Rf 0.45 (4:1, petrol:ethyl acetate); [α]D25 -3.1 (c, 2.0 in CHCl3); νmax (thin film) no significant peaks; δH (500 MHz, CDCl3) 3.60 (1H, dd, J5,6 1.6 Hz, J6,6’ 10.8 Hz, H-6c), 3.66-3.71 (5H, m, H-6a, H-6’a, H-6b, H-6’c, H-5c), 3.73 (3H, s, OMe), 3.79-3.81 (2H, m, H-2a, H-6’b), 3.86-3.94 (5H, m, H-3a, H-3b, H-4b, H-4c, H-5a), 3.97-4.02 (2H, m, H-4a, H-5b), 4.06 (1H, dd, J2,3 3.1 Hz, J3,4 8.8 Hz, H-3c), 5.15-6.16 (2H, m, H-2a, H-2c), 4.36 (1H, d, J 11.9 Hz, CH), 4.45-4.59 (13H, m, 13 x CH), 4.61-4.66 (3H, m, 3 x CH), 4.82 (1H, d, J 11.1 Hz, CH), 4.87 (2H, d, J 10.7 Hz, 2 x CH), 5.16 (1H, d, J1,2 1.3 Hz, H-1b), 5.15 (1H, d, J1,2 1.6 Hz, H-1c), 5.63 (1H, d, J1,2 1.9 Hz, H-1a), 6.72 (2H, d, J 9.2 Hz, 2 x Ar-H PMP), 6.96 (2H, d, 2 x Ar-H PMP), 7.15-7.37 (50H, m, 50 x Ar-H); δC (125 MHz,
CDCl$_3$) 55.6 (q, OMe), 69.1 (t, C-6b), 69.3 (t, C-6a), 69.4 (t, C-6c), 71.9 (t, CH$_2$), 72.1 (2 x d, C-4b, C-4c), 72.1 (t, CH$_2$), 72.2 (d, C-4a), 72.4, 72.5, 73.2, 73.3 (t, CH$_2$), 74.6 (2 x d, C-5a C-2b), 74.9 (2 x d, C-5c, C-5b), 75.0, 75.0 (2 x t, CH$_2$), 75.1 (2 x d, C-2a, C-2c), 79.1 (d, C-3c), 79.6, 79.6 (2 x d, C-3a, C-3b), 97.6 (d, C-1a), 99.5 (d, C-1c), 101.0 (d, C-1b), 114.5, 117.8 (d, Ar-C$_{PMP}$), 127.3-128.5 (d, Ar-C), 132.8-138.6 (s, Ar-C), 150.1, 154.8 (2 x s, Ar-C$_{PMP}$); $m/z$ (ESI$^+$) 1529 (M+NH$_4^+$, 100%); (M+Na$^+$) peaks measured: 1533.6 (98%), 1534.6 (100%), 1535.6 (53%), 1536.6 (17%), 1537.6 (5%) calculated peaks: 1533.6 (96%), 1534.6 (100%), 1535.6 (55%), 1536.6 (21%), 1537.6 (6%).