Electronic Supplementary Information.

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

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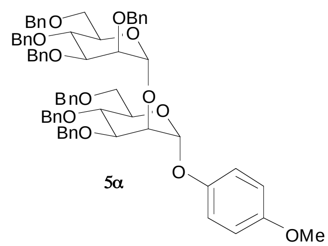
***para*-Methoxyphenyl (2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside 5α**

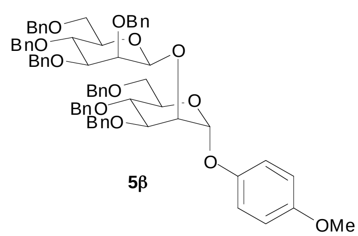


5α

para-Methoxyphenyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside **4** (33 mg, 0.06 mmol), phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyranoside **3** (41 mg, 0.065 mmol) and 2,4,6-tri-*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 ^{o}C. Dimethylthiosulfonium triflate (260 μL of a 0.4 M solution in DCM) was added and the reaction mixture was stirred at -78 ^{o}C under an atmosphere of argon. After 1 h, t.l.c (4:1, petrol:ethyl acetate) indicated formation of a product (R_f 0.4) with complete consumption of the starting materials (R_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-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside **5α** (43 mg, 67 %) as a colourless oil; $[\alpha]_D^{7}$ +41.3 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film) no significant peaks; δ_H (500 MHz, $CDCl_3$)

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, $J_{5,6'}$ 3.8 Hz, $J_{6,6'}$ 11.4 Hz, H-6'), 3.87 (1H, as, H-2b), 3.89-4.00 (5H, m, H-3b, H-4a, H-4b, H-5a, H-5b), 4.14 (1H, dd, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 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, $J_{1,2}$ 1.6 Hz, H-1b), 5.59 (1H, d, $J_{1,2}$ 1.8 Hz, H-1a), 6.75 (2H, d, *J* 9.1 Hz, 2 x Ar-H_{PMP}), 6.99 (2H, d, 2 x Ar-H_{PMP}), 7.16-7.59 (35H, m, 35 x Ar-H); δ_C (125 MHz, $CDCl_3$) 55.6 (q, OMe), 69.2, 69.4 (2 x t, C-6a, C-6b), 72.2 (t, CH_2), 72.4 (d, C-4a, C-4b), 72.6, 73.2 (2 x t, 2 x CH_2), 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 CH_2), 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-C_{PMP}), 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-C_{PMP}); *m/z* (ESI^+) 1137 ($M+MeCN+NH_4^+$, 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%).

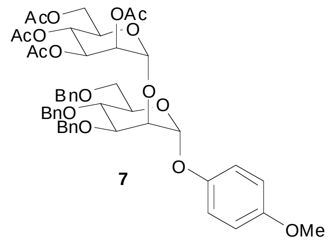
***para*-Methoxyphenyl (2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside 5β**



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; $[\alpha]_D^{22}$ -15.5 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film) no significant peaks; δ_H (400 MHz, $CDCl_3$) 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 $Ar\text{-}H_{PMP}$), 7.03 (2H, d, 2 x $Ar\text{-}H_{PMP}$), 7.19-7.57 (35H, m, 35 x Ar-H); δ_C (100 MHz, $CDCl_3$) 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 CH_2), 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 $Ar\text{-}C_{PMP}$), 127.3-128.6 (d, Ar-C), 138.1-138.9 (s, Ar-C), 150.3, 155.5 (s, $Ar\text{-}C_{PMP}$); *m/z* (ESI^+) 1137 ($M+MeCN+NH_4^+$, 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**

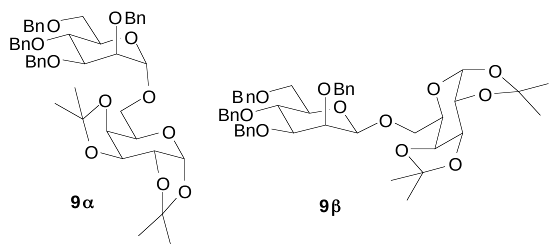


7

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 ^{o}C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 ^{o}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 ^{o}C. The mixture was stirred at -78 ^{o}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; $[\alpha]_D^{9}$ +64.6 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film) 1752 (s, C=O) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.90, 2.00, 2.03, 2.14 (12H, 4 x s, 4 x OAc), 3.71 (1H, dd, $J_{5,6}$ 2.3 Hz, $J_{6,6'}$ 11.3 Hz, H-6a), 3.76 (3H, s, OMe), 3.77 (1H, dd, $J_{5,6'}$ 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, C<u>H</u>H'a), 4.55 (1H, d, *J* 10.9 Hz, C<u>H</u>H'b), 4.63 (1H, d, CH<u>H</u>'a), 4.71 (1H, d, *J* 11.9 Hz, C<u>H</u>H'c), 4.81 (1H, d, CH<u>H</u>'c), 4.87 (11H, d, CH<u>H</u>'b), 5.02 (1H, d, $J_{1,2}$ 1.7 Hz, H-1b), 5.25 (1H, at, *J* 9.9 Hz, H-4b), 5.45 (1H, dd, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 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, $CDCl_3$) 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 CH_2), 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 $_{PMP}$), 127.4-128.9 (d, Ar-C), 138.3, 150.1, 155.5 (s, Ar-C), 169.7, 169.8, 169.9, 170.7 (4 x s, 4 x C=O); *m/z* (ESI^+) 945 ($M+MeCN+NH_4^+$, 100%); HRMS (ESI^+) calcd. for $C_{48}H_{54}O_{16}Na$ ($M+Na^+$) 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

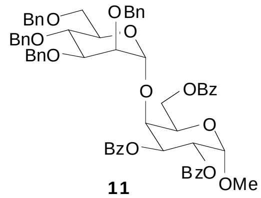


1,2:3,4-Diisopropylidene-D-galactose **8** (19 mg, 0.072 mmol), phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyranoside **3** (50 mg, 0.08 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (145 mg, 0.56 mmol) were dried in a desiccator overnight. The reagents were dissolved in DCM (2 mL) and transferred 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 dimethyldisulfide (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 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 0.5) with complete consumption of the starting materials (R_f 0.6, 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 (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: $[\alpha]_D^{25}$ -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: $[\alpha]_D^{25}$ -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, $J_{5,6}$ 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, $J_{5,6}$ 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 $C_{46}H_{58}NO_{11}$ ($M+NH_4^+$) 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

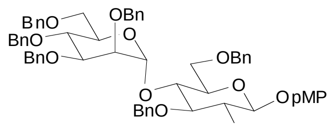


11

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 ^{o}C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 ^{o}C. To this flask was added dimethyldisulfide (59 μL, 0.66 mmol) and trifluoromethylsulfonic anhydride (111 μL, 0.66 mmol). After 2 min, the solution was transferred to the flask containing the sugar reagents at -78 ^{o}C. The mixture was stirred at -78 ^{o}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 0.2, 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-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside **11** (85 mg, 75 %) as a colourless oil;

$[\alpha]_D^{25}$ +67.1 (*c*, 2.0 in $CHCl_3$); ν_{max} (thin film) 1723 (s, C=O) cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.66 (1H, dd, $J_{5,6}$ 1.6 Hz, $J_{6,6'}$ 11.0 Hz, H-6b), 3.10 (1H, dd, $J_{5,6'}$ 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, $J_{1,2}$ 1.6 Hz, H-1b), 5.24 (1H, d, $J_{1,2}$ 3.7 Hz, H-1a), 5.51 (1H, dd, $J_{2,3}$ 10.8 Hz, H-2a), 5.72 (1H, dd, $J_{3,4}$ 3.2 Hz, H-3a), 7.09-7.63 (35H, m, 35 x Ar-H); δ_C (125 MHz, $CDCl_3$) 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, CH_2), 74.2 (d, C-3b), 74.6 (d, C-2b), 74.7 (d, C-4a), 74.9 (t, CH_2), 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 ($M+NH_4^+$, 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%).

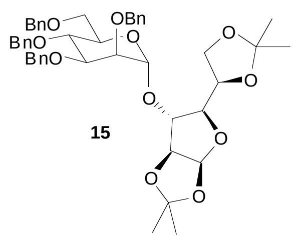
para-Methoxyphenyl (2,3,4,6-tetra-_O_-benzyl-α-D-mannopyranosyl)-(1→4)-2,6-di-_O_-benzyl-2-_N_-phthalimido–β-D-glucopyranoside 13



13

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-mannopyranoside **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 ^oC. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 ^oC. 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 ^oC. The mixture was stirred at -78 ^oC under an atmosphere of argon. After 1 h, t.l.c (2:1, petrol:ethyl acetate) indicated formation of a product (R_f 0.4) with complete consumption of the starting materials (R_f 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-mannopyranosyl)-(1→4)-2,6-di-*O*-benzyl-2-*N*-phthalimido–β-D-glucopyranoside **13** (61 mg, 78 %, α anomer only) as a colourless oil; $[\alpha]_D^{25}$ +47.7 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film) 1715 (s, C=O) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.68 (1H, dd, $J_{5,6}$ 10.6 Hz, $J_{6,6'}$ 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, $J_{6,6'}$ 2.8 Hz, $J_{5,6}$ 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); δ_C (100 MHz, $CDCl_3$) 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, CH_2), 73.1 (d, C-5b), 73.3, 73.4, 74.5 (3 x t, 3 x CH_2), 74.9 (d, C-4b), 75.0 (t, CH_2), 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 ($M+NH_4^+$, 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-mannopyranosyl-(1→3)-1,2:5,6-diisopropylidene-D-glucopyranose 15

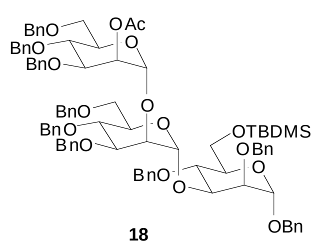


15

1,2:5,6-Diisopropylidene-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 in $CHCl_3$); ν_{max} (thin film) no significant peaks; δ_H (500 MHz, $CDCl_3$) 1.23, 1.33, 1.41, 1.49 (12H, 4 x s, 4 x CH_3), 3.78 (1H, at, *J* 2.8 Hz, H-2b), 3.80-3.85 (4H, m, H-6b, H-6'b, H-5a, H-5b), 3.99-4.03 (2H, m, H-3b, H-6a), 4.06-4.11 (3H, m, H-4a, H-4b, H-6'a), 4.28 (1H, d, *J* 1.5 Hz, H-3a), 4.51 (1H, d, *J* 10.7 Hz, CH), 4.55 (1H, d, *J* 11.6 Hz, CH), 4.56 (1H, d, *J* 12.0 Hz, CH), 4.60 (1H, d, *J* 11.7 Hz, CH), 4.66-4.69 (3H, m, 2 x CH, H-2a), 4.76 (1H, d, 12.6 Hz, CH), 4.89 (1H, d, *J* 10.4 Hz, CH), 5.24 (1H, d, $J_{1,2}$ 1.6 Hz, H-1b), 5.81(1H, d, $J_{1,2}$ 3.8 Hz, H-1a), 7.17-7.40 (20H, m, 20 x Ar-H); δ_C (125 MHz, $CDCl_3$) 25.5, 26.1, 26.8, 26.9 (4 x q, 4 x Me), 67.7 (t, C-6a), 69.2 (t, C-6b), 72.1, 72.2 (2 x t, 2 x CH_2), 72.5 (d, C-4b), 72.6 (d, C-5b), 73.5 (t, CH_2), 74.2 (d, C-2b), 74.7 (d, C-3b), 75.3 (t, CH_2), 79.6 (d, C-5a), 80.6 (d, C-3a), 81.3 (d, C-4a), 83.7 (d, C-2a), 98.9 (d, C-1b), 105.2 (d, C-1a), 109.3, 111.9 (2 x s, 2 x $C(CH_3)_2$), 127.5-128.4 (d, Ar-C), 138.1, 138.2, 138.3 (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 805.3560.

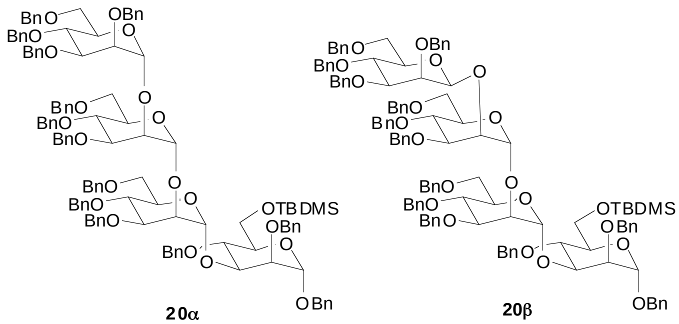
Benzyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranoside 18



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 ^{o}C. DCM (2 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 ^{o}C. To this flask was added dimethyldisulfide (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 ^{o}C. The mixture was stirred at -78 ^{o}C under an atmosphere of argon. After 1 h, t.l.c (5:1, petrol:ethyl acetate) indicated formation of a product (R_f 0.5) with complete consumption of the starting materials (R_f 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; $[\alpha]_D^{21}$ +15.3 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film) 1758 (br, C=O) cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.06, 0.07 (6H, 2 x s, 2 x CH_3), 0.91 (9H, s, $C(CH_3)_3$), 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, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 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, $J_{1,2}$ 1.4 Hz, H-1a), 5.06 (1H, d, $J_{1,2}$ 1.5 Hz, H-1c), 5.2 (1H, d, $J_{1,2}$ 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); δ_C (125 MHz, $CDCl_3$) -5.3, -5.1, (q, 2 x CH_3), 18.4 (s, $\underline{C}(CH_3)_3$), 26.0 (q, $C(\underline{C}H_3)_3$), 62.6 (t, C-6b), 68.4 (t, C-6a), 68.7 (t, CH_2), 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 CH_2), 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→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*-butylpyrimidine (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 ^{o}C. DCM (1 mL) was added to a flame dried flask containing 4Å molecular sieves and stirred for 1 h then cooled to 0 ^{o}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 ^{o}C. The mixture was stirred at -78 ^{o}C under an atmosphere of argon. After 1 h, t.l.c (5:1, petrol:ethyl acetate) indicated formation of a product (R_f 0.5) with complete consumption of the starting materials (R_f 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-butyldimethylsilyl-α-D-mannopyranoside **20β** (40 mg, 47 %) as a colourless oil.

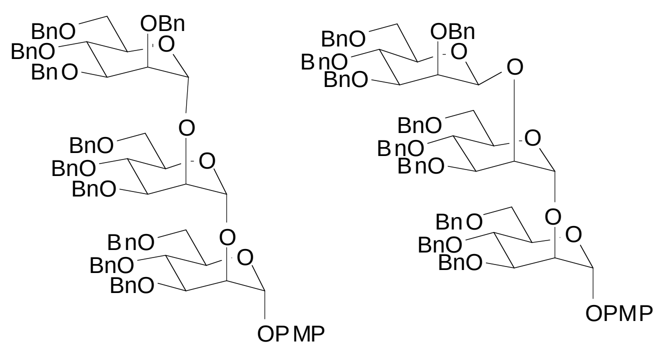
Conditions B:

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*-butyldimethylsilyl-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 ^{o}C. Dimethylthiosulfonium triflate (50 mg, 0.194 mmol) was added and the reaction mixture was stirred at -78 ^{o}C under an atmosphere of argon. After 1 h, t.l.c (5:1, petrol:ethyl acetate) indicated formation of a product (R_f 0.5) with complete consumption of the starting materials (R_f 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-butyldimethylsilyl-α-D-mannopyranoside **20** (35 mg, 41 %, α:β, 2.5:1, inseparable mixture) as a colourless oil.

20β: $[\alpha]_D^{17}$ +2.2 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film) no significant peaks; δ_H (500 MHz, $CDCl_3$) 0.10, 0.11 (2 x s, 2 x CH_3), 0.96 (9H, s, $C(CH_3)_3$), 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, $J_{5,6}$ 1.4 Hz, $J_{6,6'}$ 10.6 Hz, H-6c), 3.60 (1H, dd, $J_{5,6'}$ 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, $J_{2,3}$ 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, $J_{1,2}$ 1.2 Hz, H-1a), 5.12 (1H, d, *J* 11.8 Hz, CH), 5.21 (1H, d, $J_{1,2}$ 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, $CDCl_3$) -5.3, -5.1 (2 x q, 2 x CH_3), 18.4 (s, $\underline{C}(CH_3)_3$), 25.9 (q, $C(\underline{C}H_3)_3$), 62.6 (t, C-6a), 68.5 (t, C-6c), 68.7 (t, CH_2), 69.6 (t, C-6b), 69.9 (t, C-6d), 70.3, 70.5 (2 x t, 2 x CH_2), 71.6 (d, C-5c), 71.9 (t, CH_2), 72.1 (d, C-2c), 72.7 (d, C-5b), 72.8, 73.1, 73.3 (3 x t, 3 x CH_2), 73.3 (d, C-5a), 73.4 (t, CH_2), 73.8 (d, C-2d, C-4c), 74.2, 74.4 (2 x t, 2 x CH_2), 74.7, 74.7 (2 x d, C-2b, C-4a, C-4d), 74.8, 74.8 (2 x t, 2 x CH_2), 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**



22α **22β**

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 (R_f 0.45, 0.5) with complete consumption of the starting materials (R_f 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. Dimethylthiosulfonium 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 (R_f 0.5) with complete consumption of the starting materials (R_f 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.

22α: R_f 0.5 (4:1, petrol:ethyl aceate); $[\alpha]_D^{25}$ +17.3 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film) no significant peaks; δ_H (500 MHz, $CDCl_3$) 3.28 (1H, ddd, *J* 1.9 Hz, *J* 5.3 Hz, *J* 7.6 Hz, H-5c), 3.32 (1H, dd, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 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, $J_{2,3}$ 2.9 Hz, $J_{3,4}$ 7.9 Hz, H-3b), 4.14 (1H, dd, $J_{2,3}$ 2.8 Hz, $J_{3,4}$ 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, $J_{1,2}$ 1.9 Hz, H-1b), 5.58 (1H, d, $J_{1,2}$ 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); δ_C (125 MHz, $CDCl_3$) 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, CH_2), 71.7, 72.3 (d, C-2b, C-5a, C-5b), 72.9, 73.2, 73.3 (t, CH_2), 74.0 (d, C-2c), 74.2 (d, C-2a), 74.3, 74.3 (t, CH_2), 74.6 (d, C-4b), 74.8 (d, C-4c), 74.9 (d, C-4a), 75.0 (t, CH_2), 75.2 (t, CH_2), 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 ($M+NH_4^+$, 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%).

22β: R_f 0.45 (4:1, petrol:ethyl aceate); $[\alpha]_D^{25}$ -3.1 (*c*, 2.0 in $CHCl_3$); ν_{max} (thin film) no significant peaks; δ_H (500 MHz, $CDCl_3$) 3.60 (1H, dd, $J_{5,6}$ 1.6 Hz, $J_{6,6'}$ 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, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 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, $J_{1,2}$ 1.3 Hz, H-1b), 5.15 (1H, d, $J_{1,2}$ 1.6 Hz, H-1c), 5.63 (1H, d, $J_{1,2}$ 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); δ_C (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%).