Stereoselective β-Mannosylations and β-Rhamnosylations from Glycosyl Hemiacetals
Mediated by Lithium Iodide

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Donor and Acceptor Limitations

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References
General Experimental

The reagents and solvents used in the following experiments were bought commercially and used without further purification. Oxalyl chloride from a fresh bottle was immediately stored in a Young’s tube under a nitrogen atmosphere. In a glove-box, anhydrous lithium iodide beads were powdered. The powdered LiI was stored in capped vials on the bench for several weeks before use. It should be a free-flowing white solid. Dry solvents were obtained using equipment based on Grubb’s design[1] and stored in Strauss flask over 4 Å molecular sieves. A Karl Fischer Titrator was used to determine the amount of water in dry solvents. For air-sensitive reactions, solvents were added via syringe through rubber septa. Reactions were monitored by thin layer chromatography using silica-coated aluminium plates and the eluents outlined in the respective experiments; spots were detected under 254 nm UV light. Flash column chromatography was performed using silica gel [Davisil, 400–230 mesh (63–40 μm)]. ¹H NMR, ¹³C NMR and 2D NMR were carried out on 400 MHz, 500 MHz or 600 MHz spectrometers using deuterated chloroform (CDCl₃). Chemical shifts are reported in parts per million (ppm), coupling constants (J) are reported in Hertz (Hz) and multiplicities are abbreviated as; s (singlet), d (doublet), t (triplet) or m (multiplet) or combinations thereof. Chemical shifts were referenced to the residual proton of TMS for ¹H NMR spectra and to the ¹³C signal of deuterated chloroform (CDCl₃) for ¹³C NMR spectra. For compounds not reported in literature, NMR assignments have been made using COSY, HSQC and HMBC. Mass Spectra were recorded by the University College Dublin, School of Chemistry mass spectrometry service using ESI-MS and GCMS techniques.

4-Methoxyphenyl 2-azido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside 3h was purchased from Carbosynth.
Scheme 1 Syntheses of mannosyl donors.
1,2,3,4,6-Penta-O-acetyl-α/β-D-mannopyranose S1

A solution of D-mannose (1.0 g, 5.5 mmol) in pyridine (2 mL) was treated with acetic anhydride (5.2 mL, 55 mmol) and DMAP (67 mg, 0.55 mmol) and stirred at room temperature. TLC (1:1; cyclohexane/EtOAc) analysis after 3 h showed complete consumption of starting material. The reaction mixture was diluted with CH$_2$Cl$_2$ and washed with 1 M HCl, saturated NaHCO$_3$, and brine. The organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated in vacuo to give S1 as a colourless syrup (2.1 g, quantitative crude, α/β = 78:22). NMR data were consistent with literature data.[2]

The following were observed for α/β anomers:

**α-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): δ 2.06 (s, 3H, CH$_3$), 2.02 (s, 3H, CH$_3$).

**β-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): δ 6.05 (d, $J$ = 1.9 Hz, 1H, H-1), 5.34 – 5.29 (m, 2H, H-3, H-4), 5.24 – 5.22 (m, 1H, H-2), 4.25 (dd, $J$ = 12.4, 4.8 Hz, 1H, H-6a), 4.07 (dd, $J$ = 12.4, 2.5 Hz, 1H, H-6b), 4.05 – 3.99 (m, 1H, H-5), 2.15 (s, 3H, CH$_3$), 2.14 (s, 3H, CH$_3$), 1.975 (s, 3H, CH$_3$).

Ethyl 2,3,4,6-tetra-O-acetyl-1-thio-α-D-mannopyranoside S2

Under a N$_2$ atmosphere, a solution of pentaacetate mannose S1 (22 g, 56 mmol) and 4Å powdered molecular sieves in anhydrous CH$_2$Cl$_2$ (200 mL) was treated with ethanethiol (12.0 mL, 161 mmol) at room temperature. The reaction mixture was stirred at 0 ºC for 30 min after which BF$_3$.Et$_2$O (21.0 mL, 169 mmol) was slowly added. After stirring the reaction mixture at room temperature for 18 h, the
reaction was quenched with saturated NaHCO₃. The organic layer was washed with water and brine, dried over anhydrous MgSO₄ and concentrated in vacuo to give a yellow paste. Purification by column chromatography (2:1; cyclohexane/EtOAc) gave the title compound S2 as a white solid (15 g, 68% yield). ¹H NMR (500 MHz, Chloroform-d): δ 5.34 (dd, J = 3.2, 1.6 Hz, 1H, H-2), 5.32 (t, J = 9.9 Hz, 1H, H-4), 5.29 (d, J = 0.9 Hz, 1H, H-1), 5.27 (dd, J = 9.9, 3.3 Hz, 1H, H-3), 4.40 (ddd, J = 9.4, 5.3, 2.3 Hz, 1H, H-5), 4.32 (t, J = 9.9 Hz, 1H, H-6a), 4.28 (dd, J = 12.2, 2.4 Hz, 1H, H-6b), 2.74 – 2.55 (m, 2H, SCH₂CH₃), 2.17 (s, 3H, CH₃), 2.10 (s, 3H, CH₃), 1.99 (s, 3H, CH₃), 1.31 (t, J = 7.4 Hz, 3H, SCH₂CH₃). ¹³C NMR (126 MHz, Chloroform-d): δ 170.7 (C=O), 170.1 (C=O), 169.91 (C=O), 169.86 (C=O), 82.4 (C-1), 71.3 (C-2), 69.6 (C-3), 69.1 (C-4), 66.5 (C-5), 62.6 (C-6), 25.6 (SCH₂CH₃), 21.1 (CH₃), 20.86 (CH₃), 20.85 (CH₃), 20.78 (CH₃), 14.90 (SCH₂CH₃). NMR data were consistent with literature data.[3]

**Ethyl 4,6-O-benzylidene-1-thio-α-D-mannopyranoside S3**

![Structure](image)

A solution of S2 (10.9 g, 27.8 mmol) in methanol (100 mL) was treated with Na₂CO₃ (883 mg, 8.34 mmol) and stirred at room temperature for 4 h. The reaction mixture was neutralised with resin IR-120, filtered and concentrated in vacuo to give a brown syrup. A solution of the syrup in MeCN (100 mL) was treated with TsOH.H₂O (529 mg, 2.78 mmol), followed by benzaldehyde dimethyl acetal (5.0 mL, 34 mmol) and stirred at 60 °C for 8 h. The reaction mixture was concentrated in vacuo, re-dissolved in CH₂Cl₂, washed with saturated NaHCO₃ and brine, dried over anhydrous MgSO₄ and concentrated in vacuo. After purification by column chromatography (100:0 to 80:20; CH₂Cl₂/EtO), the title compound S3 was obtained as a white solid (2.4 g, 28% yield over 2 steps). ¹H NMR (500 MHz, Chloroform-d): δ 7.54 – 7.45 (m, 2H, ArCH), 7.44 – 7.31 (m, 3H, ArCH), 5.56 (s, 1H, PhCH), 5.36 (d, J = 1.1 Hz, 1H, H-1), 4.28 – 4.18 (m, 2H H-6a, H-3), 4.11 (dt, J = 3.1, 1.4 Hz, 1H, H-2), 4.05 (dt, J = 9.7, 3.3 Hz, 1H, H-5), 3.96 (t, J = 9.3 Hz, 1H, H-4), 3.89 – 3.79 (m, 1H, H-6b), 2.88 (d, J = 2.0 Hz, 1H, OH), 2.80 (d, J = 3.3 Hz, 1H, OH), 2.73 – 2.52 (m, 2H, SCH₂CH₃), 1.30 (t, J = 7.4 Hz, 3H, SCH₂CH₃). NMR data were consistent with literature data.[4]
Ethyl 2,3-di-O-benzyl-4,6-O-benzylidene-1-thio-α/β-D-mannopyranoside S4

Under a N₂ atmosphere, a solution of mannopyranoside S3 (2.4 g, 7.7 mmol) in anhydrous DMF (17 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (1.1 g, 27 mmol) was added. The reaction mixture was stirred at room temperature for 30 min after which it was again cooled down to 0 °C. Benzyl bromide (3.2 mL, 27 mmol) was added dropwise and the reaction mixture was left to stir at room temperature for 4 h. The reaction was quenched with MeOH and the mixture was concentrated in vacuo to give a yellow slurry. The slurry was diluted with CH₂Cl₂ (150 mL) and washed with 1 M HCl, followed by saturated NaHCO₃ and brine, dried over anhydrous MgSO₄ and concentrated in vacuo.

Purification by column chromatography (95:5 to 0:100; Pentane/Et₂O) gave S4 as clear yellowish syrup (3.1 g, 81% yield, α/β = 93:7).

The following were observed for α/β anomers:

**α-anomer**

1H NMR (500 MHz, Chloroform-d): δ 7.52 – 7.48 (m, 2H, ArCH), 7.41 – 7.26 (m, 13H, ArCH).

13C NMR (126 MHz, Chloroform-d): δ 138.6 (C), 138.1 (C), 137.8 (C), 129.0 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 126.2 (CH), 101.6 (PhCH), 83.7 (C-1), 79.4 (C-4), 78.3 (C-2), 76.6 (C-3), 73.3 (PhCH₂), 73.2 (PhCH₂), 68.8 (C-6), 64.8 (C-5), 25.5 (SCH₂CH₃), 15.1 (SCH₂CH₃). NMR data were consistent with literature data.[5]

**β-anomer**

1H NMR (500 MHz, Chloroform-d) selected signals: δ 5.62 (s, 1H, PhCH), 5.01 (d, J = 11.2 Hz, 1H, CH₂HPh), 4.86 (d, J = 12.4 Hz, 1H, CH₂HPh), 4.81 (d, J = 11.2 Hz, 1H, CH₂HPh), 4.72 (d, J = 12.4 Hz, 1H, CH₂HPh), 4.01 (d, J = 3.2, 1.2 Hz, 1H, H-2), 3.72 (dd, J = 9.9, 3.1 Hz, 1H, H-3), 3.40 (ddd, J = 10.1, 9.2, 5.0 Hz, 1H, H-5), 1.28 (t, J = 7.4 Hz, 3H, SCH₂CH₃).
Ethyl 2,3,6-tri-O-benzyl-1-thio-α-D-mannopyranoside S5

Based on the literature procedure,\[^6\] under a N\(_2\) atmosphere, a solution of \(\text{S}_4\) (2.0 g, 4.1 mmol) in anhydrous CH\(_2\)Cl\(_2\) (14 mL) was cooled to 0 °C and treated slowly with trifluoroacetic acid (1.9 mL, 25 mmol) followed by triethylsilane (4.0 mL, 25 mmol). The reaction mixture was warmed up to room temperature and stirred for 45 minutes. The reaction was diluted with CH\(_2\)Cl\(_2\) and quenched with saturated NaCHO\(_3\). The organic layer was washed with brine, dried over anhydrous MgSO\(_4\) and concentrated in vacuo to give a yellow syrup. Purification by column chromatography (3:1 to 2:1; Pentane/Et\(_2\)O) gave \(\text{S}_5\) as a yellowish syrup (1.7 g, 85% yield).

\[^1\]H NMR (500 MHz, Chloroform-d): \(\delta 7.41–7.21\) (m, 15H, ArCH), \(4.70\) (d, \(J = 12.2\) Hz, 1H, CHHPh), \(4.58\) (d, \(J = 12.2\) Hz, 1H, CHHPh), \(4.56\) (d, \(J = 12.1\) Hz, 1H, CHHPh), \(4.54\) (d, \(J = 11.7\) Hz, 1H, CHHPh), \(4.47\) (d, \(J = 11.7\) Hz, 1H, CHHPh), \(4.15 – 4.05\) (m, 2H, H-4, H-5), \(3.84\) (dd, \(J = 9.1, 3.1\) Hz, 1H, H-3), \(2.70 – 2.53\) (m, 2H, SCH\(_2\)CH\(_3\)), \(2.48\) (d, \(J = 1.8\) Hz, 1H, OH), \(1.26\) (t, \(J = 7.4\) Hz, 3H, SCH\(_3\)). \[^{13}\]C NMR (126 MHz, Chloroform-d): \(\delta 138.4\) (C), \(138.1\) (C), \(138.0\) (C), \(128.6\) (CH), \(128.5\) (CH), \(128.4\) (CH), \(128.1\) (CH), \(128.0\) (CH), \(127.9\) (CH), \(127.7\) (CH), \(127.6\) (CH), \(82.1\) (C-1), \(79.9\) (C-3), \(75.8\) (C-2), \(73.6\) (PhCH\(_2\)), \(72.2\) (PhCH\(_2\)), \(71.9\) (PhCH\(_2\)), \(71.8\) (C-5), \(70.3\) (C-6), \(68.0\) (C-4), \(25.5\) (SCH\(_2\)CH\(_3\)), \(15.1\) (SCH\(_3\)). NMR data were consistent with literature data.\[^4\]

Ethyl 6-O-triisopropylsilyl-1-thio-α/β-D-mannopyranoside S6

A solution of \(\text{S}_2\) (13 g, 33 mmol) in methanol (250 mL) was treated with Na\(_2\)CO\(_3\) (1.0 g, 9.9 mmol) and stirred at room temperature for 2 h. The reaction mixture was neutralised with resin IR-120, filtered and concentrated in vacuo to give a brown paste. Under a N\(_2\) atmosphere, a solution of the crude material and imidazole (6.7 g, 99 mmol) in anhydrous DMF (100 mL) was treated with triisopropylsilyl chloride (11 mL, 52 mmol) and left to stir at room temperature for 2 h. The reaction mixture was diluted with CH\(_2\)Cl\(_2\) and washed with water and brine, dried over anhydrous MgSO\(_4\) and concentrated in vacuo to give a brown syrup. Purification by column chromatography (100:0 to 95:5; CH\(_2\)Cl\(_2\)/MeOH) gave \(\text{S}_6\) as
a white solid (11 g, 85% yield over 2 steps, α/β = 90:10). ESI-HRMS for C_{17}H_{30}O_{3}SSiNa^{+} (M+Na)^{+} calculated: 403.1945; found: 403.1948.

α-anomer

$^1$H NMR (600 MHz, Chloroform-d): δ 5.30 (d, J = 1.4 Hz, 1H, H-1), 4.07 – 4.00 (m, 2H, H-2, H-5), 4.00 – 3.92 (m, 2H, H-6a, H-6b), 3.89 – 3.80 (m, 2H, H-3, H-4), 3.62 (s, 1H, OH), 3.02 (d, J = 3.8 Hz, 1H, OH), 2.80 (d, J = 3.5 Hz, 1H, OH), 2.66 (dq, J = 12.9, 7.4 Hz, 1H, SCH(CHOH)), 2.58 (dq, J = 13.0, 7.4 Hz, 1H, SCHHCH_{3}), 1.29 (t, J = 7.4 Hz, 3H, SCH_{2}C_{6}H_{5}), 1.08 (s, 12H, SiCH(CH_{3})_{2}), 1.07 (s, 6H, SiCH(CH_{3})_{2}). $^{13}$C NMR (151 MHz, Chloroform-d): δ 83.9 (C-1), 72.25 (C-3/4), 72.22 (C-3/4), 71.8 (C-2), 70.2 (C-5), 66.0 (C-6), 25.1 (SCH_{2}C_{6}H_{5}), 15.0 (SCH_{2}CH), 11.87 (SiCH(CH_{3})_{2}).

β-anomer

$^1$H NMR (600 MHz, Chloroform-d) selected signals: δ 4.68 (d, J = 1.0 Hz, 1H, H-1), 4.07 – 4.00 (m, 2H, H-2, H-6a), 4.00 – 3.92 (m, 1H, H-6b), 3.89 – 3.80 (m, 1H, H-4), 3.72 (s, 1H, OH), 3.62 (br s, 1H, H-3), 3.36 (ddd, J = 9.3, 7.1, 5.2 Hz, 1H, H-5), 2.73 (dq, J = 11.5, 7.4, 3.7 Hz, 2H, SCH_{2}CH_{3}). $^{13}$C NMR (151 MHz, Chloroform-d) selected signals: δ 83.8 (C-1), 77.9 (C-5), 75.2 (C-3), 71.7 (C-2 or C-4), 65.9 (C-6), 25.4 (SCH_{2}CH_{3}), 15.2 (SCH_{2}CH_{3}).

**Ethyl 2,3,4-tri-O-benzyl-6-O-triisopropylsilyl-1-thio-α-D-mannopyranoside S7**

Under a N₂ atmosphere, a solution of mannopyranoside S6 (2.00 g, 5.2 mmol) in anhydrous DMF (8.4 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (757 mg, 18.9 mmol) was added. The reaction mixture was stirred at room temperature for 30 min after which it was again cooled down to 0 °C. Benzyl bromide (2.2 mL, 19 mmol) was added dropwise and the reaction mixture was left to stir at room temperature for 2 h. The reaction was quenched with MeOH and diluted with pentane (150 mL). The aqueous layer was washed with pentane (2 x 40 mL). The organic layers were combined and neutralised with 1 M HCl. The organic layer was washed with water and brine, dried over anhydrous MgSO₄ and concentrated in vacuo to give a yellow syrup. Purification by column chromatography (98:2 to 95:5; Pentane/Et₂O) gave S7 as a clear colourless syrup (3.0 g, 88% yield). $^1$H NMR (600 MHz, Chloroform-d): δ 7.39 – 7.23 (m, 15H, ArCH), 5.33 (d, J = 1.5 Hz, 1H, H-1), 4.92 (d, J = 11.0 Hz, 1H, CHHPh), 4.66 (s, 2H, 2 x CHHPh), 4.65 – 4.60 (m, 2H, 2 x CHHPh), 4.58 (d, J = 11.7 Hz, 1H, CHHPh), 3.98 (ddd, J = 9.5, 4.5, 2.4 Hz, 1H, H-5), 3.96 – 3.91 (m, 3H, H-4, H-6a, H-6b), 3.86 (dd, J = 8.9, 3.2
C (CH))

Chloroform-\textsubscript{d}: δ 138.9 (C), 138.5 (C), 128.4 (C), 128.49 (CH), 128.46 (CH), 128.42 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 81.3 (C-3), 76.8 (C-2), 75.28 (PhCH\textsubscript{2}), 75.25 (C-4), 73.8 (C-5), 72.3 (PhCH\textsubscript{2}), 72.1 (PhCH\textsubscript{2}), 63.3 (C-6), 25.0 (SCH\textsubscript{2}CH\textsubscript{3}), 18.14 (SiCH(CH\textsubscript{2})\textsubscript{3}), 18.11 (SiCH(CH\textsubscript{3})\textsubscript{2}), 14.9 (SCH\textsubscript{2}CH\textsubscript{3}), 12.2 (SiCH(CH\textsubscript{3})\textsubscript{2}). ESI-HRMS for C\textsubscript{38}H\textsubscript{54}O\textsubscript{5}SiNa\textsuperscript{+} (M+Na\textsuperscript{+}) calculated: 673.3353; found: 673.3351.

**Ethyl 2,3,4-tri-O-(4-methylbenzyl)-6-O-triisopropylsilyl-1-thio-\alpha-D-mannopyranoside S8**

![Diagram](image)

Based on the literature procedure,\textsuperscript{[7]} under a N\textsubscript{2} atmosphere, a solution of mannopyranoside S\textsubscript{6} (1.2 g, 3.2 mmol) in anhydrous DMF (11 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (577 mg, 14.4 mmol) was added. The reaction mixture was stirred at room temperature for 30 min after which it was again cooled down to 0 °C. 4-Methylbenzyl bromide (2.66 g, 14.4 mmol) was added and the reaction mixture was left to stir at room temperature for 5 h. The reaction was quenched with MeOH and diluted with Et\textsubscript{2}O (100 mL). The aqueous layer was washed with Et\textsubscript{2}O (2 x 40 mL). The organic layers were combined and neutralised with 1 M HCl. The organic layer was washed with water and brine, dried over anhydrous MgSO\textsubscript{4} and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (99:1 to 95:5; Pentane/Et\textsubscript{2}O) gave S\textsubscript{8} as a clear colourless syrup (1.7 g, 77% yield). \textsuperscript{1}H NMR (600 MHz, Chloroform-\textsubscript{d}): δ 7.28 – 7.16 (m, 6H, ArCH), 7.14 – 7.07 (m, 6H, ArCH), 5.30 (d, J = 1.5 Hz, 1H, H-1), 4.86 (d, J = 10.7 Hz, 1H, CHHPh), 4.62 (s, 2H, 2 x CHHPh), 4.55 (d, J = 11.3 Hz, 2H, 2 x CHHPh), 4.52 (d, J = 11.5 Hz, 1H, CHHPh), 3.94 (ddd, J = 9.4, 5.7, 1.9 Hz, 1H, H-5), 3.91 – 3.83 (m, 3H, H-4, H-6a, H-6b), 3.82 (dd, J = 9.2, 3.1 Hz, 1H, H-3), 3.76 (dd, J = 3.1, 1.6 Hz, 1H, H-2), 2.60 (dq, J = 12.8, 7.3 Hz, 1H, SC/HCH\textsubscript{3}), 2.51 (dq, J = 12.9, 7.5 Hz, 1H, SC/HCH\textsubscript{3}), 2.343 (s, 3H, CH\textsubscript{3}), 2.341 (s, 3H, CH\textsubscript{3}), 2.33 (s, 3H, CH\textsubscript{3}), 1.21 (t, J = 7.4 Hz, 3H, SCH\textsubscript{2}CH\textsubscript{3}), 1.10 – 1.05 (m, 3H, SiCH(CH\textsubscript{3})\textsubscript{2}), 1.05 (s, 12H, SiCH(CH\textsubscript{3})\textsubscript{2}), 1.04 (s, 6H, SiCH(CH\textsubscript{3})\textsubscript{2}). \textsuperscript{13}C NMR (151 MHz, Chloroform-\textsubscript{d}): δ 137.37 (C), 137.35 (2 x C), 135.9 (C), 135.6 (C), 135.4 (C), 129.2 (CH), 129.13 (CH), 129.11 (CH), 128.3 (CH), 128.1 (CH), 81.2 (C-1), 80.5 (C-3), 76.4 (C-2), 75.1 (PhCH\textsubscript{2} and C-4), 73.8 (C-5), 72.1 (PhCH\textsubscript{2}), 71.9 (PhCH\textsubscript{2}), 63.3 (C-6), 24.9 (SCH\textsubscript{2}CH\textsubscript{3}), 21.34 (CH\textsubscript{3}), 21.33 (CH\textsubscript{3}), 21.31 (CH\textsubscript{3}), 18.13 (SiCH(CH\textsubscript{3})\textsubscript{2}), 18.11 (SiCH(CH\textsubscript{3})\textsubscript{2}), 14.9 (SCH\textsubscript{2}CH\textsubscript{3}), 12.1 (SiCH(CH\textsubscript{3})\textsubscript{2}). ESI-HRMS for C\textsubscript{41}H\textsubscript{54}O\textsubscript{5}SiNa\textsuperscript{+} (M+Na\textsuperscript{+}) calculated: 710.4269; found: 710.4268.
Ethyl 2,3,4-tri-O-benzyl-6-O-(4-methylbenzyl)-1-thio-α-D-mannopyranoside S9

Based on the literature procedure,[8] a solution of S7 (1.0 g, 1.5 mmol) in MeCN/H$_2$O (4:1, 15 mL) was treated with trifluoroacetic acid (0.94 mL, 12 mmol) at room temperature. After stirring for 16 h at room temperature, the reaction was quenched with saturated NaHCO$_3$ and diluted with CH$_2$Cl$_2$ (100 mL). The aqueous layer was washed with CH$_2$Cl$_2$ (2 x 100 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO$_4$ and concentrated in vacuo to give a clear syrup. The crude material was used in the next step without further purification. Based on the literature procedure,[7] under a N$_2$ atmosphere, a solution of the crude mannopyranoside in anhydrous DMF (5 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (154 mg, 3.85 mmol) was added. The reaction mixture was stirred at room temperature for 30 min after which it was again cooled down to 0 °C. 4-Methylbenzyl bromide (712 mg, 3.85 mmol) was added and the reaction mixture was left to stir at room temperature for 2 h. The reaction was quenched with MeOH and diluted with Et$_2$O (100 mL). The aqueous layer was washed with Et$_2$O (2 x 40 mL). The organic layers were combined and neutralised with 1 M HCl. The organic layer was washed with water and brine, dried over anhydrous MgSO$_4$ and concentrated in vacuo to give a yellow oil. Purification by column chromatography (90:10 to 60:40; Pentane/Et$_2$O) gave S9 as a yellowish syrup (850 mg, 92% yield over 2 steps). $^1$H NMR (500 MHz, Chloroform-d): δ 7.41 – 7.35 (m, 2H, ArCH), 7.34 – 7.20 (m, 13H, ArCH), 7.15 (dd, J = 7.5, 2.1 Hz, 2H, ArCH), 7.10 (d, J = 7.8 Hz, 2H, ArCH), 5.40 (d, J = 1.3 Hz, 1H, H-1), 4.86 (d, J = 10.8 Hz, 1H, CHPhH), 4.73 (d, J = 12.4 Hz, 1H, CHPhH), 4.68 – 4.61 (m, 2H, 2 x CHPhH), 4.58 (d, J = 11.8 Hz, 1H, CHPhH), 4.55 (d, J = 11.8 Hz, 1H, CHPhH), 4.47 (d, J = 10.8 Hz, 1H, CHPhH), 4.46 (d, J = 11.9 Hz, 1H, CHPhH), 4.11 (ddd, J = 9.8, 4.8, 1.9 Hz, 1H, H-5), 4.05 – 3.98 (m, 1H, H-4), 3.86 – 3.81 (m, 2H, H-2, H-3), 3.80 (dd, J = 10.8, 4.7 Hz, 1H, H-6a), 3.68 (dd, J = 10.8, 1.9 Hz, 1H, H-6b), 2.69 – 2.49 (m, 2H, SCH$_2$CH$_3$), 2.31 (s, 3H, CH$_3$), 1.24 (t, J = 7.4 Hz, 3H, SCH$_2$CH$_3$). $^{13}$C NMR (126 MHz, Chloroform-d): δ 138.7 (C), 138.4 (C), 138.3 (C), 137.2 (C), 135.4 (C), 129.1 (CH), 128.49 (CH), 128.48 (CH), 128.4 (CH), 128.09 (CH), 128.06 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.74 (CH), 127.65 (CH), 82.0 (C-1), 80.5 (C-2/3), 76.5 (C-2/3), 75.21 (PhCH$_3$), 75.19 (C-4), 73.3 (PhCH$_3$), 72.19 (PhCH$_3$), 72.15 (C-5), 72.07 (PhCH$_2$), 69.0 (C-6), 25.4 (SCH$_2$CH$_3$), 21.3 (CH$_3$), 15.1 (SCH$_2$CH$_3$). ESI-HRMS for C$_{37}$H$_{42}$O$_5$Na$^+$ (M+Na)$^+$ calculated: 621.2645; found: 621.2648.
Based on the literature procedure, a solution of S6 (4.00 g, 10.5 mmol) in acetone (11 mL) was treated with 2,2-dimethoxypropane (52 mL, 0.42 mol) followed by TsOH.H2O (400 mg, 2.10 mmol). After stirring the reaction mixture for 18 h at room temperature, the reaction was quenched with saturated NaHCO3 and the product was extracted with Et2O (3 x 150 mL). The combined organic layers were dried over anhydrous MgSO4 and concentrated in vacuo to give a yellow oil. Purification by column chromatography (90:10 to 80:20; Pentane/Et2O) gave S10 as a colourless syrup (3.7 g, 84% yield).

1H NMR (500 MHz, Chloroform-d): δ 5.53 (s, 1H, H-1), 4.16 (dd, J = 5.6, 1.0 Hz, 1H, H-2), 4.11 (dd, J = 7.3, 5.7 Hz, 1H, H-3), 3.99 – 3.89 (m, 3H, H-6a, H-6b, H-5), 3.80 (ddd, J = 9.4, 7.3, 2.3 Hz, 1H, H-4), 3.09 (d, J = 2.4 Hz, 1H, OH), 2.69 (dq, J = 13.0, 7.3 Hz, 1H, SCHHCH3), 2.54 (dq, J = 13.0, 7.5 Hz, 1H, SCHHCH3), 1.54 (s, 3H, O2C(CH3)2), 1.35 (s, 3H, O2C(CH3)2), 1.29 (t, J = 7.4 Hz, 3H, SCH2CH3), 1.18 – 1.09 (m, 3H, SiCH(CH3)2), 1.08 (s, 12H, SiCH(CH3)2), 1.07 (s, 6H, SiCH(CH3)2).

13C NMR (126 MHz, Chloroform-d): δ 109.7 (O2C(CH3)2), 79.5 (C-1), 78.3 (C-3), 76.3 (C-2), 72.9 (C-4), 69.1 (C-5), 65.3 (C-6), 28.3 (O2C(CH3)2), 26.5 (O2C(CH3)2), 24.3 (SCH2CH3), 18.0 (SiCH(CH3)2), 14.6 (SCH2CH3), 11.9 (SiCH(CH3)2). ESI-HRMS for C20H40O5SiNa+ (M+Na)+ calculated: 443.2258; found: 443.2258.

Based on the literature procedure, under a N2 atmosphere, a solution of mannopyranoside S10 (1.1 g, 2.6 mmol) in anhydrous DMF (5 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (208 mg, 5.21 mmol) was added. The reaction mixture was stirred at room temperature for 30 min after which it was again cooled down to 0 °C. 4-Methylbenzyl bromide (962 mg, 5.20 mmol) was added and the reaction mixture was left to stir at room temperature for 2 h. The reaction was quenched with MeOH and diluted with Et2O (100 mL). The aqueous layer was washed with Et2O (2 x 75 mL). The organic
layers were combined and neutralised with 1 M HCl. The organic layer was washed with water and brine, dried over anhydrous MgSO$_4$ and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (98:2 to 95:5; Pentane/Et$_2$O) gave S11 as a clear yellowish syrup (1.3 g, 93% yield). $^1$H NMR (500 MHz, Chloroform-*d*): δ 7.24 – 7.18 (m, 2H, ArCH), 7.13 (d, $J$ = 7.8 Hz, 2H, ArCH), 5.54 (s, 1H, H-1), 4.84 (d, $J$ = 11.3 Hz, 1H, CHPh), 4.57 (d, $J$ = 11.3 Hz, 1H, CHPh), 4.29 (dd, $J$ = 7.2, 5.7 Hz, 1H, H-3), 4.15 (dd, $J$ = 5.7, 0.9 Hz, 1H, H-2), 3.96 (qd, $J$ = 5.6, 1.9 Hz, 1H, H-5), 3.94 (dd, $J$ = 11.1, 1.8 Hz, 1H, H-6a), 3.80 (dd, $J$ = 11.0, 5.7 Hz, 1H, H-6b), 3.57 (dd, $J$ = 10.2, 7.2 Hz, 1H, H-4), 2.71 (dq, $J$ = 12.9, 7.3 Hz, 1H, SCHHCH$_3$), 2.51 (dq, $J$ = 12.9, 7.5 Hz, 1H, SCHHCH$_3$), 2.33 (s, 3H, CH$_3$), 1.52 (s, 3H, O2C(CH$_3$)2, 1.36 (s, 3H, O2C(CH$_3$)2), 1.26 (t, $J$ = 7.4 Hz, 3H, SCH$_2$CH$_3$), 1.13 – 1.02 (m, 21H, SiCH(CH$_3$)$_2$). $^{13}$C NMR (126 MHz, Chloroform-*d*): δ 137.4 (C), 135.5 (C), 129.1 (CH), 128.2 (CH), 109.4 (O2C(CH$_3$)2), 79.0 (C-3), 78.9 (C-1), 76.8 (C-2), 76.1 (C-4), 73.1 (PhCH$_2$), 70.7 (C-5), 63.2 (C-6), 28.2 (O2C(CH$_3$)2), 26.6 (O2C(CH$_3$)2), 23.8 (SCH$_2$CH$_3$), 21.3 (CH$_3$), 18.1 (SiCH(CH$_3$)$_2$), 14.4 (SCH$_2$CH$_3$), 12.1 (SiCH(CH$_3$)$_2$). ESI-HRMS for C$_{28}$H$_{48}$O$_5$SiNa$^+$ (M+Na)$^+$ calculated: 547.2884; found: 547.2884.

2,3,4,6-Tetra-*$O$-benzyl-$\alpha$/\$\beta$-D-mannopyranose 1a

![Diagram of the reaction](https://via.placeholder.com/150)

A solution of S2 (2.8 g, 7.1 mmol) in methanol (30 mL) was treated with Na$_2$CO$_3$ (222 mg, 2.09 mmol) and stirred at room temperature for 14 h. The reaction mixture was neutralised with resin IR-120, filtered and concentrated *in vacuo* to give a brown syrup. Under a N$_2$ atmosphere, a solution of the syrup in anhydrous DMF (18 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (1.6 g, 39 mmol) was added. The reaction mixture was stirred at room temperature for 30 min after which it was again cooled down to 0 °C. Benzyl bromide (4.7 mL, 39 mmol) was added dropwise and the reaction mixture was left to stir at room temperature for 4 h. The reaction was quenched with MeOH and the mixture was concentrated *in vacuo* to give a yellow slurry. The slurry was diluted with CH$_2$Cl$_2$ and washed with 1 M NaHCO$_3$, followed by saturated NaCl solution and brine, dried over anhydrous MgSO$_4$ and concentrated *in vacuo*. Purification by column chromatography (90:10 to 80:20; Pentane/Et$_2$O) gave S12 as a clear yellow oil (3.8 g, 90% yield, $\alpha$ only). $^1$H NMR (400 MHz, Chloroform-*d*): δ 7.41 – 7.22 (m, 18H, ArCH), 7.21 – 7.11 (m, 2H, ArCH), 5.40 (d, $J$ = 1.4 Hz, 1H, H-1), 4.88 (d, $J$ = 10.8 Hz, 1H, CHPh), 4.73 (d, $J$ = 12.4 Hz, 1H, CHPh), 4.66 (d, $J$ = 12.4 Hz, 2H, 2 x CHPh), 4.59 (d, $J$ = 11.9 Hz, 1H, CHPh), 4.55 (d, $J$ = 11.9 Hz, 1H, CHPh), 4.53 – 4.46 (m, 2H, 2 x CHPh), 4.13 (ddd, $J$ = 9.8, 4.8, 1.9 Hz, 1H, H-5), 4.06 – 3.99 (m, 1H, H-4), 3.87 – 3.78 (m, 3H, H-2, H-3, H-6a), 3.71 (dd, $J$ = 10.8, 1.9 Hz, 1H, H-6b)
2.70 – 2.48 (m, 2H, SCH₂CH₃), 1.24 (t, J = 7.4 Hz, 3H, SCH₂CH₃). ¹³C NMR (126 MHz, Chloroform-d): δ 138.7 (C), 138.5 (C), 138.4 (C), 138.3 (C), 128.49 (CH), 128.48 (CH), 128.42 (CH), 128.39 (CH), 128.1 (CH), 128.0 (CH), 127.93 (CH), 127.85 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 82.0 (C-1), 80.5 (C-), 76.5 (C-), 75.24 (PhCH), 75.20 (C-4), 73.4 (PhCH), 72.2 (PhCH), 72.14 (C-5), 72.09 (PhCH), 69.3 (C-6), 25.5 (SCH₂CH₃), 15.1 (SCH₂CH₃). NMR data were consistent with literature data.¹³

S12 was dissolved in 9:1 acetone/water (30 mL) and treated with NBS (3.5 g, 20 mmol) at room temperature. After 5 h the reaction was quenched with saturated Na₂S₂O₃ and diluted with CH₂Cl₂. The aqueous layer was washed with CH₂Cl₂. The combined organic layers were washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo to give a yellow syrup. Purification by column chromatography (2:1 to 1:1; Pentane/Et₂O) afforded the hydrolysed product 1a as a colourless syrup (3.1 g, 89% yield, α/β = 90:10).

¹H NMR (500 MHz, Chloroform-d): δ 7.40 – 7.20 (m, 18H, ArCH), 7.20 – 7.11 (m, 2H, ArCH), 5.24 (dd, J = 3.4, 1.9 Hz, 1H, H-1), 4.87 (d, J = 10.9 Hz, 1H, CHPH), 4.74 (d, J = 12.4 Hz, 1H, CHPH), 4.70 (d, J = 12.5 Hz, 1H, CHPH), 4.61 (s, 2H, 2 x CHPH), 4.58 (d, J = 12.2 Hz, 1H, CHPH), 4.52 (d, J = 12.2 Hz, 1H, CHPH), 4.49 (d, J = 10.9 Hz, 1H, CHPH), 4.03 (ddd, J = 9.9, 6.4, 2.1 Hz, 1H, H-5), 3.95 (ddd, J = 9.3, 3.0 Hz, 1H, H-3), 3.85 (t, J = 9.6 Hz, 1H, H-4), 3.79 (ddd, J = 3.0, 1.9 Hz, 1H, H-2), 3.71 (ddd, J = 10.5, 2.1 Hz, 1H, H-6a), 3.66 (ddd, J = 10.5, 6.4 Hz, 1H, H-6b), 3.23 (d, J = 3.4 Hz, 1H, OH).

2,3,4-Tri-O-benzyl-6-O-(4-methylbenzyl)-α/β-D-mannopyranose 1b

A solution of S9 (829 mg, 1.38 mmol) in 9:1 acetone/water (14 mL) and treated with NBS (737 mg, 4.14 mmol) at room temperature. After 2 h the reaction was quenched with saturated Na₂S₂O₃ and diluted with CH₂Cl₂. The aqueous layer was washed with CH₂Cl₂. The combined organic layers were washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo to give a colourless syrup. Purification by column chromatography (100:0 to 90:10; CH₂Cl₂/Et₂O) afforded the hydrolysed product 1b as a white solid (681 mg, 89% yield, α/β = 80:20). ESI-HRMS for C₃₅H₄₈O₆Na⁺ (M+Na)⁺ calculated: 577.2561; found: 577.2559.

The following were observed for α/β anomers:

¹H NMR (600 MHz, Chloroform-d): δ 7.39 – 7.05 (m, 19H, ArCH), 4.60 (s, 2H, 2 x CHPH), 2.31 (s, 3H, CH₃).

α-anomer
$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 5.24 (dd, $J = 3.4$, 1.9 Hz, 1H, OH), 4.86 (d, $J = 10.9$ Hz, 1H, CHPh), 4.73 (d, $J = 12.5$ Hz, 1H, CHPh), 4.70 (d, $J = 12.4$ Hz, 1H, CHPh), 4.54 (d, $J = 12.0$ Hz, 1H, CHPh), 4.48 (d, $J = 12.0$ Hz, 1H, CHPh), 4.47 (d, $J = 10.9$ Hz, 1H, CHPh), 4.02 (ddd, $J = 9.9$, 6.5, 2.1 Hz, 1H, H-5), 3.95 (dd, $J = 9.3$, 3.1 Hz, 1H, H-3), 3.87 – 3.81 (m, 1H, H-4), 3.78 (dd, $J = 3.1$, 1.9 Hz, 1H, H-2), 3.69 (dd, $J = 10.4$, 2.1 Hz, 1H, H-6a), 3.64 (dd, $J = 10.5$, 6.5 Hz, 1H, H-6b), 3.35 (d, $J = 3.4$ Hz, 1H, OH).

$^{13}$C NMR (151 MHz, Chloroform-$d$): $\delta$ 138.6 (C), 138.54 (C), 138.50 (C), 137.39 (C), 135.1 (C), 129.14 (CH), 128.47 (CH), 128.46 (CH), 128.30 (CH), 128.11 (CH), 127.98 (CH), 127.76 (CH), 127.72 (CH), 127.67 (CH), 92.9 (C-1), 79.9 (C-3), 75.38 (C-4), 75.2 (PhCH$_2$), 75.0 (C-2), 73.3 (PhCH$_2$), 72.8 (PhCH$_2$), 72.3 (PhCH$_2$), 71.7 (C-5), 69.5 (C-6), 21.31 (CH$_3$).

$\beta$-anomer

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 5.07 (d, $J = 11.7$ Hz, 1H, CHPh), 4.83 (d, $J = 10.7$ Hz, 1H, CHPh), 4.76 – 4.67 (m, 3H, 3 x CHPh), 4.64 (dd, $J = 11.5$, 1.4 Hz, 1H, H-1), 4.51 (d, $J = 10.7$ Hz, 1H, CHPh), 3.94 – 3.90 (m, 1H, H-4), 3.85 – 3.80 (m, 2H, H-2, OH), 3.71 (d, $J = 3.5$ Hz, 2H, H-6a-H-6b), 3.58 (dd, $J = 9.4$, 2.8 Hz, 1H, H-3), 3.43 (dt, $J = 9.5$, 3.5 Hz, 1H, H-5).

$^{13}$C NMR (151 MHz, Chloroform-$d$): $\delta$ 138.4 (C), 138.3 (C), 138.2 (C), 137.37 (C), 135.2 (C), 129.13 (CH), 128.7 (CH), 128.6 (CH), 128.45 (CH), 128.33 (CH), 128.32 (CH), 128.12 (CH), 128.06 (CH), 127.96 (CH), 127.80 (CH), 93.9 (C-1), 83.2 (C-3), 76.2 (C-2), 75.35 (C-5), 75.1 (PhCH$_2$), 74.8 (PhCH$_2$), 74.7 (C-4), 73.5 (PhCH$_2$), 73.0 (PhCH$_2$), 68.9 (C-6), 21.30 (CH$_3$).

2,3,6-Tri-$O$-benzyl-$4-O$-(4-methylbenzyl)-$\alpha$/$\beta$-$D$-mannopyranose 1c

Based on the literature procedure,[8] a solution of S$_{11}$ (1.3 g, 2.5 mmol) in MeCN/H$_2$O (4:1, 13 mL) was treated with trifluoroacetic acid (2.0 mL, 26 mmol) at room temperature. After stirring for 7 h at room temperature, the reaction was quenched with saturated NaHCO$_3$ and diluted with CH$_2$Cl$_2$ (150 mL). The aqueous layer was washed with CH$_2$Cl$_2$ (2 x 100 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO$_4$ and concentrated in vacuo to give a bright yellow oil. The crude material was used in the next step without further purification.

Under a N$_2$ atmosphere, a solution of crude mannopyranoside S$_{13}$ in anhydrous DMF (5 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (462 mg, 11.3 mmol) was added. The reaction mixture
was stirred at room temperature for 15 min after which it was again cooled down to 0 °C. Benzyl bromide (1.3 mL, 11 mmol) was added and the reaction mixture was left to stir at room temperature for 3 h. The reaction was quenched with MeOH and diluted with Et₂O (100 mL). The aqueous layer was washed with Et₂O (2 x 75 mL). The organic layers were combined and dried over anhydrous MgSO₄ and concentrated in vacuo to give a yellow oil.

A solution of crude S14 in 9:1 acetone/water (13 mL) and treated with NBS (1.3 g, 7.5 mmol) at room temperature. After 2.5 h the reaction was quenched with saturated Na₂S₂O₃ and diluted with CH₂Cl₂. The aqueous layer was washed with CH₂Cl₂ (2 x 100 mL). The combined organic layers were washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo to give a yellow syrup. Purification by column chromatography (100:0 to 90:10; CH₂Cl₂/MeOH) afforded the hydrolysed product 1c as a yellowish syrup (1.1 g, 79% yield over 3 steps, α/β = 85:15). ESI-HRMS for C₃5H₃₅O₆Na⁺ (M+Na)⁺ calculated: 577.2561; found: 577.2565.

**The following were observed for α/β anomers:**

1H NMR (500 MHz, Chloroform-d): δ 7.39 – 7.23 (m, 15H, ArCH), 7.11 – 6.96 (m, 4H, ArCH), 2.32 (s, 3H, CH₃). 13C NMR (126 MHz, Chloroform-d): δ 75.1 (PhCH₂), 21.3 (CH₃).

**α-anomer**

1H NMR (500 MHz, Chloroform-d): δ, 5.25 (dd, J = 3.4, 1.9 Hz, 1H, H-1), 4.83 (d, J = 10.6 Hz, 1H, CH₂Ph), 4.75 (d, J = 12.6 Hz, 1H, CH₂Ph), 4.70 (d, J = 12.6 Hz, 1H, CH₂Ph), 4.64 (d, J = 11.9 Hz, 1H, CH₂Ph), 4.60 (d, J = 11.9 Hz, 1H, CH₂Ph), 4.58 (d, J = 12.3 Hz, 1H, CH₂Ph), 4.53 (d, J = 12.3 Hz, 1H, CH₂Ph), 4.45 (d, J = 10.6 Hz, 1H, CH₂Ph), 4.01 (ddd, J = 9.8, 6.2, 2.1 Hz, 1H, H-5), 3.94 (dd, J = 9.3, 3.0 Hz, 1H, H-3), 3.85 (t, J = 9.6 Hz, 1H, H-4), 3.79 (dd, J = 3.0, 2.0 Hz, 1H, H-2), 3.71 (dd, J = 10.5, 2.2 Hz, 1H, H-6a), 3.66 (dd, J = 10.5, 6.3 Hz, 1H, H-6b), 2.92 (d, J = 3.3 Hz, 1H, OH). 13C NMR (126 MHz, Chloroform-d): δ 138.7 (C), 138.5 (C), 138.2 (C), 137.4 (C), 135.5 (C), 129.1 (CH), 128.48 (CH), 128.45 (CH), 128.28 (CH), 128.09 (CH), 127.97 (CH), 127.8 (CH), 127.71 (CH), 127.66 (CH), 92.9 (C-1), 79.9 (C-3), 75.2 (C-4), 75.0 (C-2), 73.5 (PhCH₂), 72.8 (PhCH₂), 72.4 (PhCH₂), 71.8 (C-5), 69.8 (C-6).

**β-anomer**

1H NMR (500 MHz, Chloroform-d): δ 5.09 (d, J = 11.8 Hz, 1H, CH₂Ph), 4.80 (d, J = 10.7 Hz, 1H, CH₂Ph), 4.74 – 4.66 (m, 3H, 3 x CH₂Ph), 4.66 – 4.60 (m, 3H, H-1, 2 x CH₂Ph), 4.50 (d, J = 10.9 Hz, 1H, CH₂Ph), 3.92 (t, J = 9.4 Hz, 1H, H-4), 3.84 – 3.82 (m, 1H, H-2), 3.80 – 3.74 (m, 1H, OH), 3.74 – 3.70 (m, 2H, H-6a, H-6b), 3.59 (dd, J = 9.4, 2.8 Hz, 1H, H-3), 3.43 (ddd, J = 9.5, 4.2, 2.9 Hz, 1H, H-5). 13C NMR (126 MHz, Chloroform-d): δ 138.34 (C), 138.29 (C), 137.6 (C), 135.3 (C), 129.2 (CH), 128.7 (CH), 128.6 (CH), 128.31 (CH), 128.05 (CH), 127.95 (CH), 127.1 (CH), 93.8 (C-1), 83.2 (C-3), 76.3 (C-2), 75.4 (C-5), 74.8 (PhCH₂), 74.6 (C-4), 73.7 (PhCH₂), 73.0 (PhCH₂), 69.2 (C-6).
2,3,4-Tri-O-benzyl-6-O-(4-methoxybenzyl)-α-D-mannopyranose 1d

Under a \( \text{N}_2 \) atmosphere, a solution of mannopyranoside \( \text{S6} \) (0.50 g, 1.3 mmol) in anhydrous DMF (2.6 mL) was cooled to 0°C and NaH (60% dispersion in mineral oil) (0.21 g, 5.2 mmol) was added followed by benzyl bromide (0.62 mL, 5.2 mmol). After stirring the reaction mixture for 11 h, it was quenched with MeOH and diluted with \( \text{Et}_2\text{O} \) (40 mL). The aqueous layer was washed with \( \text{Et}_2\text{O} \) (2 x 40 mL). The organic layers were combined and neutralised with 1 M HCl. The organic layer was washed with water and brine, dried over anhydrous MgSO\(_4\) and concentrated \textit{in vacuo} to give a yellow oil.

Based on the literature procedure\,[8] a solution of crude \( \text{S7} \) in MeCN/H\(_2\)O (4:1, 6.5 mL) was treated with trifluoroacetic acid (0.74 mL, 10 mmol) at room temperature. After stirring for 8 h at room temperature, the reaction was quenched with saturated NaHCO\(_3\) and diluted with CH\(_2\)Cl\(_2\) (50 mL). The aqueous layer was washed with CH\(_2\)Cl\(_2\) (2 x 50 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO\(_4\) and concentrated \textit{in vacuo} to give a yellow syrup. The crude material was used in the next step without further purification. Under a \( \text{N}_2 \) atmosphere, a solution of the crude mannopyranoside in anhydrous DMF (2.5 mL) was cooled to 0°C and NaH (60% dispersion in mineral oil) (130 mg, 3.25 mmol). After 15 minutes, 4-methoxylbenzyl bromide (0.45 mL, 3.3 mmol) was added and the reaction mixture was left to stir at room temperature for 2 h. The reaction was quenched with MeOH and diluted with \( \text{Et}_2\text{O} \) (100 mL). The aqueous layer was washed with \( \text{Et}_2\text{O} \) (2 x 40 mL). The organic layers were combined and neutralised with 1 M HCl. The organic layer was washed with water and brine, dried over anhydrous MgSO\(_4\) and concentrated \textit{in vacuo} to give a yellow oil.

A solution of \( \text{S15} \) in 9:1 acetone/water (13 mL) and treated with NBS (0.69 g, 3.9 mmol) at room temperature. After 2 h the reaction was quenched with saturated Na\(_2\)S\(_2\)O\(_3\) and diluted with CH\(_2\)Cl\(_2\). The aqueous layer was washed with CH\(_2\)Cl\(_2\). The combined organic layers were washed with water and brine, dried over anhydrous MgSO\(_4\), filtered and concentrated \textit{in vacuo} to give a colourless syrup. Purification by column chromatography (96:4; CH\(_2\)Cl\(_2\)/\( \text{Et}_2\text{O} \)) afforded the hydrolysed product along with an aromatic impurity. Trituration from Pentane/\( \text{Et}_2\text{O} \) (90:10) afforded pure \( \text{1d} \) as a white solid (471 mg, 63% yield over 4 steps, \( \alpha \)-only). \(^1\)H NMR (600 MHz, Chloroform-\( d \)): \( \delta \) 7.49 – 7.03 (m, 17H, ArCH), 6.82 (d, \( J = 8.1 \) Hz, 2H, ArCH), 5.30 – 5.13 (m, 1H, H-1), 4.86 (d, \( J = 10.9 \) Hz, 1H, CHPh), 4.74 (d, \( J = 12.5 \) Hz, 1H, CHPh), 4.70 (d, \( J = 12.6 \) Hz, 1H, CHPh), 4.60 (s, 2H, 2 x CHPh), 4.54 – 4.39 (m, 3H, 3 x CHPh), 4.02 (br t, \( J = 8.1 \) Hz, 1H, H-5), 3.94 (dd, \( J = 9.4, 3.1 \) Hz, 1H, H-3), 3.83 (t, \( J = 9.5 \) Hz, 3H, H-4).
Hz, 1H, H-4), 3.78 (s, 1H, H-2), 3.75 (s, 3H, OCH₃), 3.68 (d, J = 10.4 Hz, 1H, H-6a), 3.63 (dd, J = 10.4, 6.7 Hz, 1H, H-6b), 3.39 (d, J = 3.4 Hz, 1H, OH). ¹³C NMR (151 MHz, Chloroform-d): δ 159.3 (C), 138.6 (C), 138.54 (C), 138.51 (C), 130.2 (C), 129.8 (CH), 128.48 (CH), 128.46 (CH), 128.4 (CH), 128.1 (CH), 127.98 (CH), 127.76 (CH), 127.73 (CH), 127.72 (CH), 127.67 (CH), 113.9 (CH), 92.9 (C-1), 79.9 (C-3), 75.4 (C-4), 75.2 (PhCH₂), 75.0 (C-2), 73.0 (PhCH₂), 72.8 (PhCH₂), 72.3 (PhCH₂), 71.6 (C-5), 69.3 (C-6), 55.3 (OCH₃). NMR data were consistent with literature data.[¹⁰]

**2,3,4-Tri-O-benzyl-6-O-(2-naphthyl)-α/β-D-mannopyranose 1e**

Under a N₂ atmosphere, a solution of mannopyranoside S₆ (0.50 g, 1.3 mmol) in anhydrous DMF (2.6 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (0.21 g, 5.2 mmol) was added followed by benzyl bromide (0.62 mL, 5.2 mmol). After stirring the reaction mixture for 11 h, it was quenched with MeOH and diluted with Et₂O (40 mL). The aqueous layer was washed with Et₂O (2 x 40 mL). The organic layers were combined and neutralised with 1 M HCl. The organic layer was washed with water and brine, dried over anhydrous MgSO₄ and concentrated *in vacuo* to give a yellow oil.

Based on the literature procedure,[⁸] a solution of crude S₇ in MeCN/H₂O (4:1, 6.5 mL) was treated with trifluoroacetic acid (0.74 mL, 10 mmol) at room temperature. After stirring for 8 h at room temperature, the reaction was quenched with saturated NaHCO₃ and diluted with CH₂Cl₂ (50 mL). The aqueous layer was washed with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO₄ and concentrated *in vacuo* to give a yellow syrup. The crude material was used in the next step without further purification. Under a N₂ atmosphere, a solution of the crude mannopyranoside in anhydrous DMF (2.5 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (130 mg, 3.25 mmol). After 5 minutes, 2-(bromomethyl)naphthalene (719 mg, 3.25 mmol) was added and the reaction mixture was left to stir at room temperature for 1 h. The reaction was quenched with MeOH and diluted with Et₂O (100 mL). The aqueous layer was washed with Et₂O (2 x 40 mL). The organic layers were combined and neutralised with 1 M HCl. The organic layer was washed with water and brine, dried over anhydrous MgSO₄ and concentrated *in vacuo* to give a yellow oil.

A solution of S₁₆ in 9:1 acetone/water (13 mL) and treated with NBS (0.69 g, 3.9 mmol) at room temperature. After 2 h the reaction was quenched with saturated Na₂S₂O₃ and diluted with CH₂Cl₂. The aqueous layer was washed with CH₂Cl₂. The combined organic layers were washed with water and
brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo to give a colourless syrup. Purification by column chromatography (1:1 to 1:2; Pentane/Et₂O) afforded the hydrolysed product along with an aromatic impurity. Trituration from Pentane/Et₂O (90:10) afforded pure 1e as a white solid (523 mg, 68% yield over 4 steps, α/β = 87:13). ESI-HRMS for C₃₈H₃₈O₆Na⁺ (M+Na)⁺ calculated: 613.2561; found: 613.2559.

The following were observed for α/β anomers:

1H NMR (600 MHz, Chloroform-d): δ 7.82 – 7.72 (m, 4H, ArCH), 7.49 – 7.42 (m, 3H, ArCH), 7.39 – 7.22 (m, 10H, ArCH), 7.21 – 7.08 (m, 3H, ArCH), 7.05 (d, J = 7.1 Hz, 2H, ArCH), 4.76 – 4.67 (m, 4H, 4 x CH₂HPh).

α-anomer

1H NMR (600 MHz, Chloroform-d): δ 5.26 (dd, J = 3.4, 1.9 Hz, 1H, H-1), 4.85 (d, J = 10.9 Hz, 1H, CH₂HPh), 4.57 (s, 2H, 2 x CH₂HPh), 4.45 (d, J = 10.9 Hz, 1H, CH₂HPh), 4.07 (dd, J = 9.1, 6.6, 2.0 Hz, 1H, H-5), 3.94 (dd, J = 9.4, 2.9 Hz, 1H, H-3), 3.85 (t, J = 9.6 Hz, 1H, H-4), 3.78 (t, J = 2.5 Hz, 1H, H-2), 3.70 (dd, J = 10.5, 2.0 Hz, 1H, H-6a), 3.70 (dd, J = 10.5, 6.6 Hz, 1H, H-6b), 3.33 (d, J = 3.4 Hz, 1H, OH).

13C NMR (151 MHz, Chloroform-d): δ 138.6 (C), 138.5 (C), 138.4 (C), 135.6 (C), 133.37 (C), 133.15 (C), 128.5 (CH), 128.37 (CH), 128.30 (CH), 128.1 (CH), 128.04 (CH), 127.98 (CH), 127.83 (CH), 127.77 (CH), 127.74 (CH), 127.68 (CH), 127.67 (CH), 126.9 (CH), 126.18 (CH), 126.0 (CH), 92.9 (C-1), 79.9 (C-3), 75.4 (C-4), 75.18 (PhCH₂), 75.0 (C-2), 73.6 (PhCH₂), 72.8 (PhCH₂), 72.3 (PhCH₂), 71.7 (C-5), 69.8 (C-6).

β-anomer

1H NMR (600 MHz, Chloroform-d): δ 5.07 (d, J = 11.8 Hz, 1H, CH₂HPh), 4.82 (d, J = 10.7 Hz, 1H, CH₂HPh), 4.79 (d, J = 12.3 Hz, 1H, CH₂HPh), 4.65 (dd, J = 11.6, 1.4 Hz, 1H, H-1), 4.51 (d, J = 10.7 Hz, 1H, CH₂HPh), 3.96 – 3.91 (m, 1H, H-4), 3.82 (d, J = 11.4 Hz, 1H, OH), 3.81 (d, J = 2.2 Hz, 1H, H-2), 3.80 – 3.74 (m, 2H, H-6a, H-6b), 3.56 (dd, J = 9.4, 2.8 Hz, 1H, H-3), 3.46 (dd, J = 9.6, 4.5, 2.8 Hz, 1H, H-5).

13C NMR (151 MHz, Chloroform-d): δ 138.3 (C), 138.20 (C), 138.15 (C), 135.8 (C), 133.38 (C), 133.14 (C), 128.7 (CH), 128.6 (CH), 128.41 (CH), 128.26 (CH), 126.23 (CH), 125.9 (CH), 93.9 (C-1), 83.2 (C-3), 76.2 (C-2), 75.4 (C-5), 75.16 (PhCH₂), 74.8 (PhCH₂), 74.7 (C-4), 73.8 (PhCH₂), 72.9 (PhCH₂), 69.2 (C-6).
2,3,4-Tri-O-benzyl-6-O-tert-butyldiphenylsilyl-α/β-D-mannopyranose 1f

A solution of S2 (500 mg, 1.27 mmol) in methanol (10 mL) was treated with Na₂CO₃ (40 mg, 0.38 mmol) and stirred at room temperature for 1.5 h. The reaction mixture was neutralised with resin IR-120, filtered and concentrated *in vacuo* to give a brown paste. Under a N₂ atmosphere, a solution of the crude material and imidazole (259 mg, 3.81 mmol) in anhydrous DMF (2.5 mL) was treated with TBDPSCI (0.50 mL, 1.9 mmol) and left to stir at room temperature for 2.5 h. The reaction mixture was diluted with Et₂O and washed with water and brine, dried over anhydrous MgSO₄ and concentrated *in vacuo* to give a yellow syrup.

Under a N₂ atmosphere, a solution of crude mannopyranoside S17 in anhydrous DMF (2.5 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (228 mg, 5.72 mmol) was added. The reaction mixture was stirred at room temperature for 15 min after which it was again cooled down to 0 °C. Benzyl bromide (0.68 mL, 5.7 mmol) was added and the reaction mixture was left to stir at room temperature for 6 h. The reaction was quenched with MeOH and diluted with Et₂O (100 mL). The aqueous layer was washed with Et₂O (2 x 75 mL). The organic layers were combined and dried over anhydrous MgSO₄ and concentrated *in vacuo* to give a yellow oil.

A solution of crude S18 in 9:1 acetone/water (13 mL) and treated with NBS (678 mg, 3.81 mmol) at room temperature. After 50 minutes the reaction was quenched with saturated Na₂S₂O₃ and diluted with CH₂Cl₂. The aqueous layer was washed with CH₂Cl₂ (2 x 100 mL). The combined organic layers were washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated *in vacuo* to give a yellow syrup. Purification by column chromatography (3:1 to 0:1; Pentane/Et₂O) afforded the hydrolysed product 1f as a yellowish syrup (388 mg, 44% yield over 4 steps, α/β = 85:15).

The following were observed for α/β anomers:

**1H NMR (500 MHz, Chloroform-d):** δ 7.77 – 7.72 (m, 2H, ArCH), 7.72 – 7.66 (m, 2H, ArCH), 7.41 – 7.22 (m, 19H, ArCH), 7.20 – 7.12 (m, 2H, ArCH). **13C NMR (126 MHz, Chloroform-d):** δ 135.8 (CH), 19.49 (SiC(CH₃)₃).

**α-anomer**

**1H NMR (500 MHz, Chloroform-d):** δ 5.22 (dd, J = 3.3, 1.9 Hz, 1H, H-1), 4.92 (d, J = 10.8 Hz, 1H, CHPh), 4.81 (d, J = 12.4 Hz, 1H, CHPh), 4.69 – 4.64 (m, 3H, 3 x CHPh), 4.61 (d, J = 10.9 Hz, 1H, CHPh), 4.13 (t, J = 9.6 Hz, 1H, H-4), 4.01 (dd, J = 11.3, 4.6 Hz, 1H, H-6a), 3.97 (dd, J = 9.5, 3.1 Hz,
1H, H-3), 3.91 – 3.83 (m, 2H, H-6b, H-5), 3.79 (dd, J = 3.1, 1.9 Hz, 1H, H-2), 2.58 (d, J = 3.4 Hz, 1H, OH), 1.05 (s, 9H, SiC(CH$_3$)$_3$). $^{13}$C NMR (126 MHz, Chloroform-d): δ 138.8 (C), 138.74 (C), 138.73 (C), 136.08 (CH), 134.1 (C), 133.6 (C), 129.66 (CH), 129.64 (CH), 128.49 (CH), 128.43 (CH), 128.0 (CH), 127.86 (CH), 127.76 (CH), 127.63 (CH), 127.60 (CH), 92.9 (C-1), 79.8 (C-3), 75.7 (C-2), 75.23 (PhCH$_3$), 74.85 (C-4), 73.3 (C-5), 72.9 (PhCH$_3$), 72.4 (PhCH$_3$), 63.6 (C-6), 26.98 (SiC(CH$_3$)$_3$). NMR data were consistent with literature data.$^{[11]}$

β-anomer

$^1$H NMR (500 MHz, Chloroform-d) selected signals: δ 5.15 (d, J = 11.5 Hz, 1H, CHPh), 4.91 (d, J = 10.8 Hz, 1H, CHPh), 4.76 (s, 2H, 2 x CHPh), 4.68 – 4.63 (m, 1H, H-1), 4.18 (t, J = 9.3 Hz, 1H, H-4), 3.95 – 3.91 (m, 1H, H-6a), 3.88 – 3.84 (m, 1H, H-2), 3.66 – 3.61 (m, 2H, OH, H-3), 3.33 (ddd, J = 9.2, 3.7, 2.1 Hz, 1H, H-5), 1.04 (s, 9H, SiC(CH$_3$)$_3$). $^{13}$C NMR (126 MHz, Chloroform-d): δ 138.6 (C), 138.5 (C), 138.3 (C), 136.13 (CH), 134.0 (C), 133.4 (C), 128.7 (CH), 128.6 (CH), 128.51 (CH), 127.91 (CH), 127.82 (CH), 127.69 (CH), 93.6 (C-1), 83.1 (C-3), 77.1 (C-2), 76.2 (C-5), 75.21 (PhCH$_3$), 74.94 (PhCH$_3$), 74.4 (C-4), 73.0 (PhCH$_3$), 63.1 (C-6), 26.95 (SiC(CH$_3$)$_3$).

2,3,6-Tri-O-benzyl-4-O-tert-butyldimethylsilyl-α/β-D-mannopyranose 1g

Under a N$_2$ atmosphere, a solution of S5 (800 mg, 1.62 mmol), TBSCI (488 mg, 3.24 mmol), imidazole (441 mg, 6.48 mmol) and DMAP (20 mg, 0.16 mmol) in anhydrous DMF (2 mL) was stirred at room temperature for 15 h. The reaction mixture diluted with CH$_2$Cl$_2$ and washed with water and brine. The organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated in vacuo to give a colourless oil. The crude material was used in the next step without further purification. $^1$H NMR (500 MHz, Chloroform-d): δ 7.38 – 7.22 (m, 15H, ArCH), 5.39 (d, J = 1.8 Hz, 1H, H-1), 4.66 – 4.56 (m, 4H, 4 x CHPh), 4.53 (s, 2H, 2 x CHPh), 4.10 (ddd, J = 8.4, 6.1, 2.0 Hz, 1H, H-5), 4.07 – 4.00 (m, 1H, H-4), 3.81 – 3.75 (m, 2H, H-2, H-6a), 3.72 (dd, J = 10.7, 6.3 Hz, 1H, H-6b), 3.62 (dd, J = 8.6, 3.0 Hz, 1H, H-3), 2.73 – 2.54 (m, 2H, SCH$_2$CH$_3$), 1.28 (t, J = 7.4 Hz, 3H, SCH$_2$CH$_3$), 0.82 (s, 9H, SiC(CH$_3$)$_3$), 0.01 (s, 6H, 2 x SiCH$_3$). $^{13}$C NMR (126 MHz, Chloroform-d): δ 138.7 (C), 138.45 (C), 138.43 (C), 128.4 (CH), 128.353 (CH), 128.345 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 81.92 (C-1), 80.6 (C-3), 76.4 (C-2), 73.6 (C-5), 73.2 (PhCH$_3$), 72.2 (PhCH$_3$), 71.7 (PhCH$_2$), 69.9 (C-6), 68.5 (C-4), 26.1 (SiC(CH$_3$)$_3$), 25.3 (SCH$_2$CH$_3$), 18.3 (SiC(CH$_3$)$_3$), 15.1 (SCH$_2$CH$_3$), -3.7 (SiCH$_3$), -4.8 (SiCH$_3$).
The crude material S19 was dissolved in 9:1 acetone/water (10 mL) and treated with NBS (865 mg, 4.86 mmol) at room temperature. TLC analysis (2:1; Pentane/Et₂O) of the reaction after 2.5 h showed the hydrolysed product along with de-silylated hydrolysed product. The reaction was quenched with saturated Na₂S₂O₃ and diluted with CH₂Cl₂. The organic layer was washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography (3:1 to 1:1, Pentane/Et₂O) afforded the hydrolysed product 1g as a syrup (308 mg, 34% yield over 2 steps, α/β = 86:14). ESI-HRMS for C₃₃H₄₄O₆SiNa⁺ (M+Na)⁺ calculated: 587.2799; found: 587.2799.

The following were observed for α/β anomers:

**α-anomer**

1H NMR (500 MHz, Chloroform-d): δ 7.39 – 7.19 (m, 15H, ArCH). 13C NMR (126 MHz, Chloroform-d): 26.0 (SiC(CH₃)₃).

1H NMR (500 MHz, Chloroform-d): δ 5.26 (t, J = 2.5 Hz, 1H, H-1), 4.69 (d, J = 12.3 Hz, 1H, CHPh), 4.65 (d, J = 12.3 Hz, 1H, CHHPh), 4.64 (d, J = 12.3 Hz, 1H, CHHPh), 4.59 (d, J = 11.9 Hz, 1H, CHHPh), 4.55 (d, J = 12.0 Hz, 1H, CHHPh), 4.52 (d, J = 12.3 Hz, 1H, CHHPh), 4.01 (ddd, J = 9.7, 8.1, 2.0 Hz, 1H, H-5), 3.91 (t, J = 8.7 Hz, 1H, H-4), 3.79 – 3.75 (m, 2H, H-2, H-6a), 3.72 (dd, J = 8.8, 2.9 Hz, 1H, H-3), 3.58 (dd, J = 10.4, 6.7 Hz, 1H, H-6b), 3.48 (br s, 1H, OH), 0.79 (s, 9H, SiC(CH₃)₃), -0.03 (s, 3H, SiCH₃), -3.7 (SiCH₃), -4.8 (Si(CH₃)₂). 13C NMR (126 MHz, Chloroform-d): δ 138.63 (C), 138.59 (C), 138.2 (C), 128.47 (CH), 128.40 (CH), 128.3 (CH), 128.04 (CH), 127.8 (CH), 127.65 (CH), 127.63 (CH), 127.5 (CH), 93.0 (C-1), 79.9 (C-3), 74.8 (C-2), 73.4 (PhCH₂), 73.0 (C-5), 72.9 (PhCH₂), 71.8 (PhCH₂), 70.3 (C-6), 68.7 (C-4), 18.22 (SiC(CH₃)₃), -3.7 (SiCH₃), -4.8 (Si(CH₃)₂).

**β-anomer**

1H NMR (500 MHz, Chloroform-d) selected signals: δ 4.98 (d, J = 11.7 Hz, 1H, CHHPh), 4.77 – 4.72 (m, 1H, H-1), 3.97 (t, J = 8.7 Hz, 1H, H-4), 3.83 – 3.80 (m, 2H, H-2, H-6a), 3.62 (dd, J = 10.4, 6.7 Hz, 1H, H-6b), 3.47 (dd, J = 8.9, 6.4, 2.5 Hz, 1H, H-5), 3.41 (dd, J = 8.7, 2.7 Hz, 1H, H-3), 0.81 (s, 9H, SiC(CH₃)₃), 0.02 (s, 6H, 2 x SiCH₃). 13C NMR (126 MHz, Chloroform-d) selected signals: δ 128.6 (CH), 128.55 (CH), 128.42 (CH), 128.02 (CH), 127.9 (CH), 127.69 (CH), 93.8 (C-1), 83.2 (C-3), 76.9 (C-5), 75.6 (C-2), 74.5 (PhCH₂), 68.0 (C-4), 18.19 (SiC(CH₃)₃), -3.8 (SiCH₃), -4.7 (Si(CH₃)₂).
Based on the literature procedure, a solution of S7 (930 mg, 1.43 mmol) in MeCN/H$_2$O (4:1, 10 mL) was treated with trifluoroacetic acid (0.89 mL, 12 mmol) at room temperature. After stirring for 11 h at room temperature, the reaction was quenched with saturated NaHCO$_3$ and diluted with CH$_2$Cl$_2$ (100 mL). The aqueous layer was washed with CH$_2$Cl$_2$ (2 x 40 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO$_4$ and concentrated in vacuo to give a colourless syrup. The crude material was used in the next step without further purification.

Under a N$_2$ atmosphere, a solution of the crude material and DMAP (17 mg, 0.14 mmol) in anhydrous CH$_2$Cl$_2$ (2.9 mL) was treated with anhydrous pyridine (0.11 mL, 1.4 mmol) followed by benzoyl chloride (0.33 mL, 2.8 mmol) at room temperature. TLC (CH$_2$Cl$_2$) analysis of the reaction after 50 minutes showed complete consumption of starting material. The reaction was quenched with water and diluted with CH$_2$Cl$_2$. The organic layer was washed with 1 M HCl, saturated NaHCO$_3$ and brine. The organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated in vacuo to give a colourless oil.

The crude material was dissolved in 9:1 acetone/water (14 mL) and treated with NBS (1.02 g, 5.72 mmol) at room temperature. After 3 h the reaction was quenched with saturated Na$_2$S$_2$O$_3$ and diluted with CH$_2$Cl$_2$. The aqueous layer was washed with CH$_2$Cl$_2$. The combined organic layers were washed with water and brine, dried over anhydrous MgSO$_4$, filtered and concentrated in vacuo to give a colourless syrup. Purification by column chromatography (2:1 to 1:1; Pentane/Et$_2$O) afforded the hydrolysed product 1h as a colourless syrup (645 mg, 81% yield over 3 steps, $\alpha/\beta = 77:23$).

The following were observed for $\alpha/\beta$ anomers:

$^1$H NMR (500 MHz, Chloroform-d): $\delta$ 8.05 – 7.97 (m, 2H, ArCH), 7.55 – 7.47 (m, 1H, ArCH), 7.42 – 7.20 (m, 17H, ArCH), 4.62 (d, $J = 10.8$ Hz, 1H, CH/HPh). $^{13}$C NMR (126 MHz, Chloroform-d): $\delta$ 75.4 (PhCH$_3$), 63.9 (C-6).
α-anomer

$^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 5.27 (d, $J = 2.0$ Hz, 1H, H-1), 4.95 (d, $J = 10.8$ Hz, 1H, CH$_2$Ph), 4.77 (d, $J = 12.2$ Hz, 1H, CH$_2$Ph), 4.68 (s, 2H, 2 x CH$_2$Ph), 4.65 (d, $J = 12.2$ Hz, 1H, CH$_2$Ph), 4.58 (dd, $J = 11.9$, 1.6 Hz, 1H, H-6a), 4.52 (dd, $J = 12.0$, 3.4 Hz, 1H, H-6b), 4.16 – 4.10 (m, 2H, H-4, H-5), 4.06 – 4.01 (m, 1H, H-3), 3.83 (dd, $J = 3.0$, 2.0 Hz, 1H, H-2), 2.92 (br s, 1H, OH). $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 166.6 (C=O), 138.48 (C), 138.47 (C), 138.2 (C), 133.1(CH), 129.9 (CH), 128.55 (CH), 128.53 (CH), 128.46 (CH), 128.44 (CH), 128.29 (CH), 127.88 (CH), 127.73 (CH), 92.8 (C-1), 79.8 (C-3), 75.3 (C-2), 74.6 (C-4), 72.9 (PhCH$_2$), 72.4 (PhCH$_2$), 70.6 (C-5).

β-anomer

$^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 5.14 (d, $J = 11.5$ Hz, 1H, CH$_2$Ph), 4.91 (d, $J = 10.8$ Hz, 1H, CH$_2$Ph), 4.78 (s, 2H, 2 x CH$_2$Ph), 4.72 (d, $J = 1.3$ Hz, 1H, H-1), 4.67 (d, $J = 11.6$ Hz, 1H, CH$_2$Ph), 4.59 (dd, $J = 11.9$, 2.3 Hz, 1H, H-6a), 4.49 (dd, $J = 11.7$, 4.5 Hz, 1H, H-6b), 4.06 – 4.01 (m, 1H, H-4), 3.89 (dd, $J = 2.8$, 1.4 Hz, 1H, H-2), 3.69 (dd, $J = 9.3$, 2.7 Hz, 1H, H-3), 3.63 (ddd, $J = 9.5$, 4.6, 2.3 Hz, 1H, H-5). $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 166.5 (C=O), 138.3 (C), 137.92 (C), 137.86 (C), 130.2 (CH), 128.73 (CH), 128.71 (CH), 128.59 (CH), 128.32 (CH), 128.12 (CH), 128.06 (CH), 127.95 (CH), 127.82 (CH), 127.69 (CH), 93.8 (C-1), 83.2 (C-3), 76.6 (C-2), 75.0 (PhCH$_2$), 74.2 (C-4), 73.6 (C-5), 73.0 (PhCH$_2$). NMR data were consistent with literature data.$^{[12]}

4-O-Acetyl-2,3,6-tri-O-benzyl-α/β-D-mannopyranose S22

A solution of S5 (800 mg, 1.62 mmol), acetic anhydride (0.31 mL, 1.6 mmol) and DMAP (20 mg, 0.16 mmol) in pyridine (0.13 mL, 1.6 mmol) (little bit of CH$_2$Cl$_2$ was added to get a clear solution) was stirred at room temperature for 2 h. The reaction mixture was diluted with CH$_2$Cl$_2$ and washed with 1 M HCl, saturated NaHCO$_3$ and brine. The organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated in vacuo to give a yellowish syrup. The crude material was used in the next step without further purification. $^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.44 – 7.14 (m, 15H, ArCH), 5.38 (t, $J = 9.7$ Hz, 1H, H-4), 5.37 (s, 1H, H-1), 4.69 (d, $J = 12.4$ Hz, 1H, CH$_2$Ph), 4.66 (d, $J = 12.4$ Hz, 1H, CH$_2$Ph), 4.54 (d, $J = 11.9$ Hz, 1H, CH$_2$Ph), 4.53 (d, $J = 12.2$ Hz, 1H, CH$_2$Ph), 4.51 (d, $J = 12.0$ Hz, 1H, CH$_2$Ph), 4.43 (d, $J = 12.1$ Hz, 1H, CH$_2$Ph), 4.23 – 4.16 (m, 1H, H-5), 3.82 (dd, $J = 3.1$, 1.8 Hz, 1H, H-2), 3.76 (ddd, $J = 9.5$, 3.1 Hz, 1H, H-3), 3.62 (dd, $J = 10.8$, 6.1 Hz, 1H, H-6a), 3.55 (dd, $J = 10.8$, 3.1 Hz, 1H, H-6b), 2.70 – 2.52 (m, 2H, SCH$_2$CH$_3$), 1.92 (s, 3H, CH$_3$), 1.26 (t, $J = 7.4$ Hz, 3H, SCH$_2$CH$_3$). $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 17.0 (C=O), 138.3 (C), 138.2 (C), 138.1 (C), 128.49 (CH), 128.46 (CH), 26
128.4 (CH), 128.0 (CH), 127.81 (CH), 127.79 (CH), 127.75 (CH), 127.6 (CH), 82.14 (C-1), 77.4 (C-3), 76.0 (C-2), 73.5 (PhCH₂), 72.4 (PhCH₂), 71.9 (PhCH₂), 70.7 (C-5), 69.9 (C-6), 69.2 (C-4), 25.4 (SCH₂CH₃), 21.1 (CH₃), 15.0 (SCH₂CH₃). NMR data were consistent with literature data.⁴¹

The crude material S₂₁ was dissolved in 9:1 acetone/water (10 mL) and treated with NBS (865 mg, 4.86 mmol) at room temperature. After 5 h the reaction was quenched with saturated Na₂S₂O₃ and diluted with CH₂Cl₂. The organic layer was washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography (2:1 to 1:1, Pentane/Et₂O) afforded the hydrolysed product S₂₂ as a syrup (632 mg, 79% yield over 2 steps, α/β = 79:21).

The following were observed for α/β anomers:

α-anomer

¹H NMR (500 MHz, Chloroform-d): δ 7.41 – 7.16 (m, 15H, ArCH), 4.57 (d, J = 11.9 Hz, 1H, CH₂HPh), 4.52 (d, J = 12.0 Hz, 1H, CH₂HPh), 4.49 (d, J = 12.1 Hz, 1H, CH₂HPh). ¹³C NMR (126 MHz, Chloroform-d): 21.1 (CH₃).

β-anomer

¹H NMR (500 MHz, Chloroform-d): δ 5.28 (t, J = 9.8 Hz, 1H, H-4), 5.23 (d, J = 2.5 Hz, 1H, H-1), 4.75 (d, J = 12.4 Hz, 1H, CH₂HPh), 4.67 (d, J = 12.4 Hz, 1H, CH₂HPh), 4.46 (d, J = 12.2 Hz, 1H, CH₂HPh), 4.06 (ddd, J = 10.1, 7.5, 2.6 Hz, 1H, H-5), 3.86 (dd, J = 9.6, 3.0 Hz, 1H, H-3), 3.77 (ddd, J = 3.0, 2.1 Hz, 1H, H-2), 3.60 (dd, J = 10.5, 7.5 Hz, 1H, H-6a), 3.47 (dd, J = 10.5, 2.6 Hz, 1H, H-6b), 3.38 (d, J = 3.4 Hz, 1H, OH), 1.92 (s, 3H, CH₃). ¹³C NMR (126 MHz, Chloroform-d): δ 170.1 (C=O), 138.4 (C), 138.3 (C), 137.89 (C), 128.47 (CH), 128.45 (CH), 128.2 (CH), 128.0 (CH), 127.81 (CH), 127.77 (CH), 127.73 (CH), 127.6 (CH), 93.1 (C-1), 76.9 (C-3), 74.4 (C-2), 73.6 (PhCH₂), 73.0 (PhCH₂), 72.0 (PhCH₂), 70.4 (C-5), 70.2 (C-6), 69.2 (C-4).

NMR data were consistent with literature data.[¹³]
A solution of S7 (1.00 g, 1.54 mmol) in 9:1 acetone/water (15 mL) and treated with NBS (822 mg, 4.62 mmol) at room temperature. TLC (8:2; Pentane/Et2O) analysis of reaction after 3 minutes showed complete consumption of starting material and the desired hydrolysed product along with de-silylated hydrolysed product were observed. The reaction was immediately quenched with saturated Na2S2O3 and diluted with CH2Cl2. The aqueous layer was washed with CH2Cl2. The combined organic layers were washed with water and brine, dried over anhydrous MgSO4, filtered and concentrated in vacuo to give a colourless syrup. Purification by column chromatography (9:1 to 7:3; Pentane/Et2O) afforded the hydrolysed product S23 as a colourless syrup (564 mg, 60% yield, α/β = 72:28). ESI-HRMS for C36H50O6SiNa+ (M+Na)+ calculated: 629.3269; found: 629.3269.

The following were observed for α/β anomers:

H NMR (600 MHz, Chloroform-d): δ 7.40 – 7.25 (m, 15H, ArCH), 1.16 – 1.03 (m, 3H, SiC(CH3)2), 1.06 (s, 12H, SiCH(CH3)2), 1.05 (s, 6H, SiCH(CH3)2).

13C NMR (151 MHz, Chloroform-d): δ 18.2 (SiCH(CH3)2), 18.1 (SiCH(CH3)2).

α-anomer

H NMR (600 MHz, Chloroform-d): δ 5.23 (dd, J = 3.6, 2.0 Hz, 1H, H-1), 4.92 (d, J = 10.9 Hz, 1H, CHHPh), 4.75 (d, J = 12.5 Hz, 1H, CHHPh), 4.67 – 4.63 (m, 4H, 4 x CHHPh), 4.00 – 3.96 (m, 2H, H-6a), 3.91 (dd, J = 11.1, 2.1 Hz, 1H, H-6b), 3.87 – 3.81 (m, 1H, H-5), 3.78 (t, J = 2.4 Hz, 1H, H-2), 2.80 (d, J = 3.5 Hz, 1H, OH).

13C NMR (151 MHz, Chloroform-d): δ 138.9 (C), 138.8 (C), 138.7 (C), 128.47 (CH), 128.46 (CH), 128.4 (CH), 128.2 (CH), 127.86 (CH), 127.81 (CH), 127.79 (CH), 92.8 (C-1), 79.8 (C-3), 75.6 (C-2), 75.2 (PhCH2), 74.9 (C-4), 73.8 (C-5), 72.8 (PhCH2), 72.40 (PhCH2), 63.4 (C-6), 12.17 (SiCH(CH3)2).

β-anomer

H NMR (600 MHz, Chloroform-d): δ 5.11 (d, J = 11.6 Hz, 1H, CHHPh), 4.87 (d, J = 10.8 Hz, 1H, CHHPh), 4.79 – 4.74 (m, 2H, 2 x CHHPh), 4.73 (d, J = 10.9 Hz, 1H, CHHPh), 4.69 – 4.66 (m, 1H, H-1), 4.61 (d, J = 11.5 Hz, 1H, CHHPh), 4.08 (t, J = 9.2 Hz, 1H, H-4), 4.01 – 3.95 (m, 2H, H-6a, H-6b), 3.87 – 3.81 (m, 1H, H-2), 3.65 (d, J = 12.2 Hz, 1H, OH), 3.64 (dd, J = 9.3, 2.7 Hz, 1H, H-3), 3.31 (dt, J = 9.1, 3.0 Hz, 1H, H-5).

13C NMR (151 MHz, Chloroform-d): δ 138.5 (C), 138.3 (C), 128.6 (CH), 128.6 (CH), 128.53 (CH), 128.1 (CH), 127.94 (CH), 127.84 (CH), 127.68 (CH), 127.67 (CH), 127.6 (CH),
Following the literature procedure,[14,15] the penta-O-acetate mannose S1 (2.17 g, 5.55 mmol), and FeCl₃·6H₂O (749 mg, 2.77 mmol) were dissolved in bench MeCN (10 mL) and heated to 90 °C using MW 150W. TLC analysis (2:1; cyclohexane/EtOAc) after 30 min showed complete consumption of starting material. The reaction mixture was diluted with CH₂Cl₂ and washed with water, saturated NaHCO₃, and brine. The organic layer was dried over anhydrous MgSO₄, filtered and concentrated in vacuo. Purification by column chromatography (Rf = 0.4, 5:1; CH₂Cl₂/EtOAc) gave the product S24 as a yellow syrup (290 mg, 63% yield, α/β ≥ 95:5). ¹H NMR (500 MHz, Chloroform-d): δ 5.43 (dd, J = 10.0, 3.4 Hz, 1H, H-3), 5.31 (t, J = 10.0 Hz, 1H, H-4), 5.27 (dd, J = 3.4, 1.9 Hz, 1H, H-2), 5.25 (br s, 1H, H-1), 4.28 – 4.21 (m, 2H, H-6a, H-5), 4.17 – 4.12 (m, 1H, H-6b), 3.64 (br s, 1H, OH), 2.17 (s, 3H, CH₃), 2.11 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 2.01 (s, 3H, CH₃). ¹³C NMR (126 MHz, Chloroform-d): δ 171.0 (C=O), 170.3 (C=O), 170.2 (C=O), 169.9 (C=O), 92.3 (C-1), 70.14 (C-2), 68.9 (C-3), 68.6 (C-5), 66.3 (C-4), 62.71 (C-6), 21.0 (CH₃), 20.9 (CH₃), 20.85 (CH₃), 20.83 (CH₃). NMR data were consistent with literature data.[16]

6-O-Pivaloyl-2,3,4-tri-O-p-methylbenzyl-α/β-D-mannopyranose 1i

For the synthesis of 3i see p.54.
Under a N₂ atmosphere, 3i (200 mg, 0.37 mmol) was dissolved in anhydrous CH₂Cl₂ (3.7 mL) and the reaction was treated with anhydrous pyridine (0.11 mL, 1.4 mmol) followed by pivaloyl chloride (0.146 mL, 1.20 mmol) at room temperature. TLC (cyclohexane:EtOAc) analysis of the reaction after 1 h showed complete consumption of starting material. The reaction was quenched with water and diluted
with CH₂Cl₂. The organic layer was washed with 1 M HCl, saturated NaHCO₃ and brine. The organic layer was dried over anhydrous MgSO₄, filtered and concentrated in vacuo to give a colourless oil.

The crude material S25 was dissolved in 9:1 acetone/water (4 mL) and treated with NBS (214 mg, 1.20 mmol) at room temperature. After 5 minutes the reaction was quenched with saturated Na₂S₂O₃ and diluted with CH₂Cl₂. The aqueous layer was washed with CH₂Cl₂. The combined organic layers were washed with water and brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo to give a colourless syrup. Purification by column chromatography (2:1 to 1:1; Pentane/Et₂O) afforded the hydrolysed product 1i as a colourless syrup (176 mg, 83% yield over 2 steps, α/β = 71:29). ESI-HRMS for C₃₅H₄₄O₇NH₄⁺ (M+NH₄⁺) calculated: 594.3431; found: 594.3420.

The following were observed for α/β anomers:

α-anomer

¹H NMR (500 MHz, Chloroform-d): δ 7.29 – 7.07 (m, 17H, ArCH), 4.70 (d, J = 12.0 Hz, 2H 2 x CHHHPh), 4.61 – 4.51 (m, 5H, 5 x CHHHPh), 2.37 – 2.31 (m, 13H, CH₃).

β-anomer

¹H NMR (500 MHz, Chloroform-d): δ 5.17 (d, J = 1.6 Hz, 1H, H-1), 4.90 (d, J = 10.5 Hz, 1H, CHHHPh), 4.47 – 4.43 (m, 1H, H-6a), 4.23 (dd, J = 11.9, 3.1 Hz, 1H, H-6b), 3.99 – 3.90 (m, J = 3.7 Hz, 3H, H-2, H-3, H-4), 3.76 (br s, 1H, H-2), 3.10 (br s, 1H, OH), 1.19 (s, 9H, CH₃).
Acetyl 2,3,4,6-Tetra-O-benzyl-α/β-D-mannopyranose 8a

A solution of 1a (150 mg, 0.28 mmol) in pyridine (200 μL) was treated with acetic anhydride (200 μL, 2.00 mmol) and stirred at room temperature. TLC (4:1; cyclohexane/EtOAc) analysis after 3 h showed complete consumption of starting material. The reaction mixture was diluted with CH₂Cl₂ and washed with 1 M HCl, saturated NaHCO₃, and brine. The organic layer was dried over anhydrous MgSO₄, filtered and concentrated in vacuo to give 8a as a yellowish syrup (163 mg, quantitative yield, α/β = 89:11).

α-anomer

¹H NMR (500 MHz, Chloroform-d): δ 7.42 – 7.37 (m, 2H, ArCH), 7.36 – 7.22 (m, 16H, ArCH), 7.20 – 7.15 (m, 2H, ArCH), 6.22 (d, J = 2.1 Hz, 1H, H-1), 4.89 (d, J = 10.6 Hz, 1H, CHHPh), 4.78 (d, J = 12.3 Hz, 1H, CHHPh), 4.73 (d, J = 12.4 Hz, 1H, CHHPh), 4.66 (d, J = 12.1 Hz, 1H, CHHPh), 4.59 (d, J = 11.9 Hz, 1H, CHHPh), 4.58 – 4.50 (m, 3H, 3 x CHHPh), 4.08 (t, J = 9.6 Hz, 1H, H-4), 3.88 – 3.82 (m, 2H, H-3, H-5), 3.78 (dd, J = 11.0, 4.7 Hz, 1H, H-6a), 3.73 (dd, J = 3.2, 2.1 Hz, 1H, H-2), 3.71 (dd, J = 11.0, 1.9 Hz, 1H, H-6b), 2.01 (s, 3H, CH₃). ¹³C NMR (126 MHz, Chloroform-d): δ 169.1 (C=O), 138.4 (2 x C), 138.3 (C), 138.0 (C), 128.51 (CH), 128.45 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.89 (CH), 127.85 (CH), 127.84 (CH), 127.7 (CH), 92.0 (C-1), 79.3 (C-3), 75.4 (PhCH), 74.6 (C-5), 74.4 (C-4), 73.6 (PhCH), 73.5 (C-2), 72.6 (PhCH), 72.2 (PhCH), 69.0 (C-6), 21.2 (CH₃).

β-anomer

¹H NMR (500 MHz, Chloroform-d) selected signals: 5.59 (d, J = 1.1 Hz, 1H, H-1), 3.99 (t, J = 9.4 Hz, 1H, H-4), 3.94 (dd, J = 2.8, 1.1 Hz, 1H, H-2), 3.62 (dd, J = 9.3, 2.8 Hz, 1H, H-3), 3.56 (dt, J = 9.6, 3.6 Hz, 1H, H-5), 2.07 (s, 3H, CH₃). NMR data were consistent with literature data.[¹⁷]
Synthesis of Rhamnosyl Donors

Scheme 2. Syntheses of rhamnosyl donors
L-Rhamnose (5.00 g, 30.4 mmol) was added to acetic anhydride (70.0 mL, 735 mmol) giving a cloudy solution. Pyridine (70.0 mL, 863 mmol) was added, and the mixture was stirred at room temperature for 15 mins, after which the cloudy solution had turned clear. TLC analysis (cyclohexane: EtOAc; 6:4; \( R_f = 0.6 \)) showed full conversion of the starting material into a single product. The reaction was diluted with CH\(_2\)Cl\(_2\) (150 mL) and 1 M HCl (50 mL) was added and stirring was continued for 0.5 h. The organic layer was washed with saturated NaHCO\(_3\) solution (3 x 50 mL), water (3 x 50 mL), brine (1 x 50 mL), dried over anhydrous MgSO\(_4\) and filtered. The resulting solution was concentrated in vacuo to give the product S26 as a pale yellow oil (8.70 g, 26.2 mmol, 88\%, \( \alpha/\beta \) 84:16). \(^{1}H\) NMR (600 MHz, Chloroform-\(d\)) \( \delta \) 6.02 (d, \( J = 2.0 \) Hz, 1H), 5.32 – 5.29 (m, 1H), 5.25 (dd, \( J = 3.6, 2.0 \) Hz, 1H), 5.12 (t, \( J = 10.0 \) Hz, 1H), 3.94 (dq, \( J = 9.7, 6.2 \) Hz, 1H), 2.17 (s, 3H), 2.16 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.24 (d, \( J = 6.2 \) Hz, 3H). \(^{13}C\) NMR (151 MHz, Chloroform-\(d\)) \( \delta \) 170.0, 169.79, 169.77, 168.3, 90.6, 70.4, 68.74, 68.68, 68.6, 20.9, 20.8, 20.72, 20.65, 17.4. NMR data are consistent with the literature.\(^{[18]}\)

Under a N\(_2\) atmosphere, a solution of tetraacetate rhamnose S26 (8.70 g, 26.2 mmol) in anhydrous CH\(_2\)Cl\(_2\) (262 mL) was treated with ethanethiol (4.90 mL, 68.1 mmol) at room temperature. The reaction mixture was stirred at 0 \(^\circ\)C for 30 min after which BF\(_3\).Et\(_2\)O (16.2 mL, 131 mmol) was slowly added. After stirring the reaction mixture at room temperature for 20 h, TLC analysis (cyclohexane: EtOAc; 6:4; \( R_f = 0.7 \)) showed full conversion of the starting material into a single product. The reaction mixture was then carefully quenched with saturated NaHCO\(_3\). The organic layer was washed with water and brine, dried over anhydrous MgSO\(_4\) and concentrated in vacuo to give S27 as a yellow oil (9.0 g, 26.2 mmol, quant., \( \alpha/\beta \) 80:20). \(^{1}H\) NMR (500 MHz, Chloroform-\(d\)) \( \delta \) 5.34 (dd, \( J = 3.4, 1.6 \) Hz, 1H), 5.23 (dd, \( J = 10.1, 3.4 \) Hz, 1H), 5.20 (d, \( J = 1.5 \) Hz, 1H), 5.10 (t, \( J = 9.9 \) Hz, 1H), 4.29 – 4.18 (m, 1H), 2.69 – 2.57 (m, 2H), 2.16 (s, 3H), 2.06 (s, 3H), 1.99 (s, 3H), 1.30 (t, \( J = 7.4 \) Hz, 3H), 1.24 (d, \( J = 6.3 \) Hz, 3H). NMR data are consistent with the literature.\(^{[19]}\)

Thiorhamnoside S27 (9.0 g, 26.2 mmol) was dissolved in MeOH (300 mL). Na\(_2\)CO\(_3\) (0.5 g, 5.0 mmol) was added to the solution and the mixture was left to stir at room temperature for 2 h, after which TLC analysis (EtOAc; \( R_f = 0 \)) indicated that the reaction had gone to completion. The reaction mixture was neutralised with resin IR-120 and the mixture was filtered and was concentrated in vacuo to give S28 as a yellow oil, which was used in the next step without further purification.
Ethyl 2,3-O-isopropylidene-1-thio-L-rhamnoside S29

Thiorhamnoside S28 (3.00 g, 14.4 mmol) was dissolved in acetone (21 mL) and pTsOH.H2O (0.68 g, 2.64 mmol) was added to the reaction mixture. 2,2-Dimethoxypropane (31.8 mL, 259 mmol) was added and the reaction left to stir at room temperature overnight. TLC analysis (CH2Cl2:MeOH; 97:3; Rf = 0.7) indicated that the reaction had gone to completion. Et3N (2 mL) was added to quench the reaction mixture and the solvent was concentrated in vacuo. The crude residue was dissolved in CH2Cl2 (50 mL) and washed with water, dried over anhydrous Na2SO4, filtered and concentrated in vacuo. Purification by column chromatography (pentane: EtOAc; 95:5 to 80:20) led to separation of the two anomers of S29 (α anomer; 2.23 g, 8.99 mmol, 63%, β anomer; 0.35 g, 1.4 mmol, 16%).

α-anomer:
1H NMR (500 MHz, Chloroform-d) δ 5.52 (d, J = 0.9 Hz, 1H, H-1), 4.17 (dd, J = 5.5, 0.8 Hz, 1H, H-2), 4.05 (dd, J = 7.6, 5.5 Hz, 1H, H-3), 4.00 – 3.93 (m, 1H, H-5), 3.43 (ddd, J = 9.7, 7.6, 4.0 Hz, 1H, H-4), 2.91 (dd, J = 4.6, 1.9 Hz, 1H, OH), 2.67 (dq, J = 13.0, 7.4 Hz, 1H, SCH2CH3), 2.54 (dq, J = 13.0, 7.4 Hz, 1H, SCH2CH3), 1.54 (s, 3H, CH3), 1.35 (s, 3H, CH3), 1.33 – 1.28 (m, 6H, SCH2CH3, H-6). NMR data are consistent with the literature.[19]

β-anomer:
1H NMR (500 MHz, Chloroform-d) δ 4.83 (d, J = 2.2 Hz, 1H, H-1), 4.28 (dd, J = 5.5, 2.2 Hz, 1H, H-2), 3.99 (dd, J = 7.3, 5.4 Hz, 1H, H-3), 3.45 (ddd, J = 9.5, 7.3, 3.4 Hz, 1H, H-4), 3.30 – 3.23 (m, 1H, H-5), 2.96 – 2.89 (m, 1H, OH), 2.77 (q, J = 7.5 Hz, 2H, SCH2CH3), 1.55 (s, 3H, CH3), 1.38 (s, 3H, CH3), 1.36 – 1.30 (m, 6H, SCH2CH3, H-6). NMR data are consistent with the literature.[20]

2,3,4-Tri-O-benzyl-L-rhamnoside 1j

Under a N2 atmosphere, thiorhamnoside S28 (3.00 g, 14.4 mmol) was dissolved in anhydrous DMF (72 mL). The flask was cooled to 0 °C (50:50; ice/water), and NaH (60% dispersion in mineral oil) (2.60 g, 108 mmol) was added to the reaction flask. The ice bath was removed, and the reaction was left to stir
at room temperature for 30 min. The flask was again cooled to 0 °C, and BnBr (6.0 mL, 50.4 mmol) and TBAI (0.44 g, 1.2 mmol) were added to the reaction mixture. The ice bath was removed, and the reaction mixture was left to stir at room temperature overnight, after which TLC analysis (cyclohexane: EtOAc; 9:1; \( R_f = 0.5 \)) showed that the starting material had been consumed. The reaction was quenched with MeOH (5 mL), and the solvents were removed using rotary evaporation. The crude mixture was dissolved in \( \text{CH}_2\text{Cl}_2 \) (100 mL) and washed with 1 M HCl (2 × 50 mL), deionised water (1 × 50 mL), saturated NaHCO\(_3\) (2 × 50 mL), deionised H\(_2\)O (1 × 50 mL) and brine (1 × 50 mL). The organic layer was dried over anhydrous Na\(_2\)SO\(_4\), filtered off and concentrated in vacuo.

Crude rhamnoside S30 (~14.7 mmol) was dissolved in a 9:1 mixture of acetone:water (140 mL) and NBS (7.70 g, 44.1 mmol) was added. The reaction left to stir at room temperature for 2 h when TLC analysis (cyclohexane: EtOAc; 8:2; \( R_f = 0.3 \)) showed the complete conversion of the starting material to the desired product. The mixture was quenched with saturated Na\(_2\)S\(_2\)O\(_3\) (50 mL), concentrated in vacuo to remove acetone and diluted with \( \text{CH}_2\text{Cl}_2 \) (250 mL). The organic phase was then washed with saturated NaHCO\(_3\) (50 mL), deionised H\(_2\)O (50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na\(_2\)SO\(_4\), filtered off and concentrated in vacuo. Purification by column chromatography (pentane: EtOAc; 9:1 to 8:2) gave product 1j as a white solid (6.0 g, 13.8 mmol, 96%, \( \alpha/\beta \) 1:1).

Signals observed for both anomers:

\( ^1\text{H} \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 7.41 – 7.25 (m, 30H, Ar-CH), 5.10 (d, \( J = 11.6 \) Hz, 1H, PhCH\(_2\)), 4.94 (d, \( J = 10.9 \), 1H, PhCH\(_2\)), 4.93 (\( J = 10.8 \), 1H, PhCH\(_2\)), 4.81 – 4.62 (m, 9H, 9 x PhCH\(_2\)).

\( ^{13}\text{C} \) NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 138.60 (4º C), 138.56 (4º C), 138.33 (4º C), 138.28 (4º C), 138.07 (4º C), 138.05 (4º C), 128.63 (Ar-CH), 128.55 (Ar-CH), 128.43 (Ar-CH), 128.36 (Ar-CH), 128.2 (Ar-CH), 128.09 (Ar-CH), 128.06 (Ar-CH), 128.02 (Ar-CH), 128.01 (Ar-CH), 127.9 (Ar-CH), 127.8 (Ar-CH), 127.7 (Ar-CH), 127.63 (Ar-CH), 127.55 (Ar-CH), 75.43 (PhCH\(_2\)), 75.35 (PhCH\(_2\)), 74.9 (PhCH\(_2\)), 72.9 (PhCH\(_2\)), 72.3 (PhCH\(_2\)).

\( \alpha \)-anomer:

\( ^1\text{H} \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 5.15 (d, \( J = 1.9 \) Hz, 1H, H-1), 3.96 – 3.89 (m, 2H, H-3, H-5), 3.80 (dd, \( J = 3.1 \), 2.0 Hz, 1H, H-2), 3.63 (t, \( J = 9.4 \) Hz, 1H, H-4), 2.71 (s, 1H, OH), 1.31 (d, \( J = 6.2 \) Hz, 3H, H-6).

\( ^{13}\text{C} \) NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 93.0 (C-1), 80.5 (C-4), 79.7 (C-3), 75.0 (C-2), 68.1 (C-5), 18.1 (C-6).

\( \beta \)-anomer:

\( ^1\text{H} \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 4.61 (t, \( J = 4.5 \) Hz, 1H, H-1), 3.84 (d, \( J = 1.9 \) Hz, 1H, H-2), 3.59 – 3.54 (m, 2H, H-3, H-4), 3.40 – 3.32 (m, 1H, H-5), 1.34 (d, \( J = 6.2 \) Hz, 1H, H-6).

\( ^{13}\text{C} \) NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 93.4 (C-1), 83.1 (C-3), 78.0 (C-4), 76.55 (C-2), 71.61 (C-5), 17.9 (C-6).

NMR data are consistent with the literature.[21]
2,3-Di-O-benzyl-4-O-p-methylbenzyl-L-rhamnoside 1k

Under an N₂ atmosphere, thiorhamnoside S29 (1 g, 4 mmol) was dissolved in anhydrous DMF (20 mL, 0.5 M) and NaH (60% dispersion in mineral oil) (192 mg, 8.00 mmol) was added. The ice bath was removed, and the reaction was left to stir at room temperature for 30 min. The flask was again cooled to 0 °C, and pMeBnBr (0.93 g, 5.0 mmol) was added to the reaction mixture. The ice bath was removed, and the reaction mixture was left to stir at room temperature overnight, after which TLC analysis (cyclohexane:EtOAc; 4:1; \( R_f = 0.8 \)) showed that the starting material had been consumed. The reaction was quenched with MeOH (2 mL), and the solvents were removed using rotary evaporation. The crude mixture was dissolved in CH₂Cl₂ (100 mL) and washed with 1 M HCl (2 × 50 mL), deionised water (1 × 50 mL), saturated NaHCO₃ (2 × 50 mL), deionised H₂O (1 × 50 mL) and brine (1 × 50 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered off and concentrated in vacuo.

Crude thiorhamnoside S31 was dissolved in CH₂Cl₂ (12 mL) and H₂O (0.5 mL) was added. TFA (4.0 mL, 52 mmol) was then added and the reaction left to stir at RT overnight. TLC analysis (cyclohexane: EtOAc; 7:3; \( R_f = 0.3 \)) indicated that the reaction had gone to completion. The reaction mixture was quenched saturated NaHCO₃ (20 mL), diluted with CH₂Cl₂ (50 mL) and the two layers were separated. The aqueous phase was extracted with CH₂Cl₂ (100 mL) and the combined organic layers were washed with water (20 mL), brine (20 mL), dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The crude material was used in the next step without further purification. Under a N₂, the crude thiorhamnoside was dissolved in anhydrous DMF (20 mL, 0.2 M). The flask was cooled to 0 °C (50:50; ice/water), and NaH (60% dispersion in mineral oil) (384 mg, 16.0 mmol) was added to the reaction flask. The ice bath was removed, and the reaction was left to stir at room temperature for 30 min. The flask was again cooled to 0 °C, and BnBr (1.2 mL, 10 mmol) was added to the reaction mixture. The ice bath was removed, and the reaction mixture was left to stir at room temperature for 4 h, after which TLC analysis (cyclohexane: EtOAc; 4:1; \( R_f = 0.6 \)) showed that the starting material had been consumed. The reaction was quenched with MeOH (2 mL), and the solvents were removed using rotary evaporation. The crude mixture was dissolved in CH₂Cl₂ (100 mL) and washed with 1 M HCl (2 × 50 mL), deionised water (1 × 50 mL), saturated NaHCO₃ (2 × 50 mL), deionised H₂O (1 × 50 mL) and brine (1 × 50 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered off and concentrated in vacuo.
Crude rhamnoside S32 was dissolved in a 9:1 mixture of acetone:water (20 mL) and NBS (1.1 mg, 6.0 mmol) was added. The reaction left to stir at room temperature for 1 h when TLC analysis (cyclohexane:EtOAc; 6:4; \( R_f = 0.6 \)) showed the complete conversion of the starting material to the desired product. The crude mixture was dissolved in CH\(_2\)Cl\(_2\) (100 mL) and washed with saturated Na\(_2\)S\(_2\)O\(_3\) (50 mL), saturated NaHCO\(_3\) (50 mL), deionised H\(_2\)O (50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na\(_2\)SO\(_4\), filtered off and concentrated in vacuo. Purification by column chromatography (pentane: EtOAc; 9:1 to 8:2) gave product 1k as an off-white solid (757 mg, 1.75 mmol, 87%, \( \alpha/\beta \) 76:24). ESI-HRMS for C\(_{28}\)H\(_{32}\)O\(_5\)NH\(_4^+\) (M+NH\(_4^+\)) calculated: 466.2588; found: 466.2588.

Signals observed for both anomers:

\( ^1H \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 7.40 – 7.25 (m, 11H, Ar-CH), 7.21 (d, \( J = 7.8 \) Hz, 3H, Ar-CH), 7.16 – 7.10 (m, 3H, Ar-CH), 5.10 (d, \( J = 11.6 \) Hz, 0.5H, PhCH\(_2\)), 4.90 (d, \( J = 10.6, \) 1H, PhCH\(_2\)), 4.88 (d, \( J = 10.5, \) 0.5H, PhCH\(_2\)), 4.81 – 4.71 (m, 3H, 3 x PhCH\(_2\)), 4.69 (d, \( J = 11.1 \) Hz, 1H, PhCH\(_2\)), 4.66 – 4.63 (m, 2H, 2 x PhCH\(_2\)), 4.60 (d, \( J = 10.8 \) Hz, 1H, PhCH\(_2\)). \( ^{13}C \) NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 138.6 (4º C), 138.3 (4º C), 138.13 (4º C), 138.05 (4º C), 137.5 (4º C), 137.3 (4º C), 135.5 (4º C), 135.2 (4º C), 129.1 (Ar-CH), 129.0 (Ar-CH), 128.6 (Ar-CH), 128.5 (Ar-CH), 128.4 (Ar-CH), 128.3 (Ar-CH), 128.20 (Ar-CH), 128.15 (Ar-CH), 128.1 (Ar-CH), 128.0 (Ar-CH), 127.8 (Ar-CH), 127.67 (Ar-CH), 127.66 (Ar-CH), 127.62 (Ar-CH), 127.5 (Ar-CH), 75.3 (PhCH\(_2\)), 75.2 (PhCH\(_2\)), 74.9 (PhCH\(_2\)), 72.94 (PhCH\(_2\)), 72.90 (PhCH\(_2\)), 72.3 (PhCH\(_2\)).

\( \alpha \)-anomer:

\( ^1H \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 5.15 (dd, \( J = 3.4, \) 1.9 Hz, 1H, H-1), 3.95 – 3.86 (m, 2H, H-5, H-3), 3.80 (dd, \( J = 3.1, \) 1.9 Hz, 1H, H-2), 3.66 – 3.57 (m, 1H, H-4), 2.62 – 2.60 (m, 1H, OH), 2.33 (s, 3H, CH\(_3\)), 1.31 (d, \( J = 6.3 \) Hz, 3H, H-6). \( ^{13}C \) NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 93.0 (C-1), 80.4 (C-4), 79.6 (C-3), 75.1 (C-2), 68.3 (C-5), 21.2 (CH\(_3\)), 18.1 (C-6).

\( \beta \)-anomer:

\( ^1H \) NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 4.62 (s, 1H, H-1), 3.85 – 3.82 (m, 1H, H-2), 3.57 – 3.52 (m, 2H, H-3, H-4), 3.39 – 3.30 (m, 1H, H-5), 2.46 (d, \( J = 3.5 \) Hz, 1H, OH), 2.34 (s, 3H, CH\(_3\)), 1.33 (d, \( J = 6.2 \) Hz, 3H, H-6). \( ^{13}C \) NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 93.3 (C-1), 83.1 (C-3), 79.8 (C-4), 76.6 (C-2), 71.6 (C-5), 21.2 (CH\(_3\)), 17.9 (C-6).
2,3-Di-\(\text{O}\)-benzyl-4-\(\text{O}\)-benzoyl-L-rhamnoside 1l

![Chemical Structure](image)

Under an \(\text{N}_2\) atmosphere, thiorhamnoside \(\text{S29}\) (1 g, 4 mmol) was dissolved in anhydrous DMF (20 mL, 0.5 M) and BzCl (0.9 mL, 8.0 mmol) was added. Pyridine (1.29 mL, 16.0 mmol) was then added and the reaction left to stir at RT overnight. TLC analysis (cyclohexane: EtOAc; 4:1; \(R_f = 0.8\)) indicated that the reaction had gone to completion. The reaction mixture was diluted with CH\(_2\)Cl\(_2\) (100 mL) and washed with 1 M HCl (50 mL). The aqueous phase was extracted with CH\(_2\)Cl\(_2\) (100 mL) and the combined organic layers were washed with saturated NaHCO\(_3\) (50 mL), water (50 mL) and brine (50 mL). The organic phase was dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated in \textit{vacuo}.

Crude thiorhamnoside \(\text{S33}\) was dissolved in CH\(_2\)Cl\(_2\) (12 mL) and H\(_2\)O (0.5 mL) was added. TFA (4.0 mL, 52 mmol) was then added and the reaction left to stir at RT overnight. TLC analysis (cyclohexane:EtOAc; 7:3; \(R_f = 0.4\)) indicated that the reaction had gone to completion. The reaction mixture was quenched saturated NaHCO\(_3\) (20 mL), diluted with CH\(_2\)Cl\(_2\) (50 mL) and the two layers were separated. The aqueous phase was extracted with CH\(_2\)Cl\(_2\) (100 mL) and the combined organic layers were washed with water (20 mL), brine (20 mL), dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated in \textit{vacuo}. The crude material was used in the next step without further purification. Under a \(\text{N}_2\), the crude thiorhamnoside was dissolved in anhydrous DMF (20 mL). The flask was cooled to 0 °C (50:50; ice/water), and NaH (60% dispersion in mineral oil) (384 mg, 16.0 mmol) was added to the reaction flask. The ice bath was removed, and the reaction was left to stir at room temperature for 30 min. The flask was again cooled to 0 °C, and BnBr (1.2 mL, 10 mmol) was added to the reaction mixture. The ice bath was removed, and the reaction mixture was left to stir at room temperature for 4 h, after which TLC analysis (cyclohexane: EtOAc; 4:1; \(R_f = 0.6\)) showed that the starting material had been consumed. The reaction was quenched with MeOH (2 mL), and the solvents were removed using rotary evaporation. The crude mixture was dissolved in CH\(_2\)Cl\(_2\) (100 mL) and washed with 1 M HCl (2 × 50 mL), deionised water (1 × 50 mL), saturated NaHCO\(_3\) (2 × 50 mL), deionised H\(_2\)O (1 × 50 mL) and brine (1 × 50 mL). The organic layer was dried over anhydrous Na\(_2\)SO\(_4\), filtered off and concentrated in \textit{vacuo}.

Crude rhamnoside \(\text{S34}\) (~1.0 mmol) was dissolved in a 9:1 mixture of acetone:water (9:1 mL) and NBS (534 mg, 3 mmol) was added. The reaction left to stir at room temperature for 1 h when TLC analysis (cyclohexane: EtOAc; 6:4; \(R_f = 0.5\)) showed the complete conversion of the starting material to the desired product. The crude mixture was dissolved in CH\(_2\)Cl\(_2\) (50 mL) and washed with saturated Na\(_2\)S\(_2\)O\(_3\).
(25 mL), saturated NaHCO₃ (25 mL), deionised H₂O (25 mL) and brine (25 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered off and concentrated in vacuo. Purification by column chromatography (pentane:EtOAc; 9:1 to 8:2) gave product 1l as a yellowish syrup (251 mg, 0.56 mmol, 56%, α/β 80:20). ¹H NMR (500 MHz, Chloroform-d) δ 8.02 (d, J = 7.8 Hz, 3H, Ar-CH), 7.62 – 7.54 (m, 2H, Ar-CH), 7.48 – 7.15 (m, 10H, Ar-CH), 5.50 (t, J = 9.7 Hz, 1H, H-4), 5.24 (s, 1H, H-1), 4.83 (d, J = 12.3 Hz, 1H, PhCH₂), 4.75 – 4.70 (m, 1H, PhCH₂), 4.56 (d, J = 12.1 Hz, 1H, PhCH₂), 4.45 (d, J = 12.2 Hz, 1H, PhCH₂), 4.14 – 4.06 (m, 1H, H-5), 3.99 (dd, J = 9.7, 2.8 Hz, 1H, H-3), 3.87 (d, J = 2.4 Hz, 1H, H-2), 2.89 (d, J = 3.5 Hz, 1H, OH), 1.25 (d, J = 6.4 Hz, 3H, H-6). NMR data are consistent with the literature.²²

2,3,4-Tri-O-acetyl-L-rhamnoside S35

Crude rhamnoside S27 (1 g, 3 mmol) was dissolved in a 9:1 mixture of acetone:water (30 mL) and NBS (1.6 g, 9.0 mmol) was added. The reaction was left to stir at room temperature overnight. TLC analysis (cyclohexane:EtOAc; 1:1; Rf = 0.4) showed the complete conversion of the starting material to the desired product. Purification by column chromatography (pentane:EtOAc; 1:1) gave product S35 as a white solid (400 mg, 1.38 mmol, 46% α/β 89:11). ¹H NMR (500 MHz, Chloroform-d) δ 5.37 (dd, J = 10.1, 3.4 Hz, 1H, H-3), 5.26 (dd, J = 3.2, 2.0 Hz, 1H, H-2), 5.15 (br s, 1H, H-1), 5.07 (t, J = 10.0 Hz, 1H, H-4), 4.18 – 4.09 (m, 1H, H-5), 3.86 (s, 1H, OH), 2.17 – 2.15 (m, 3H, CH₃), 2.06 (s, 3H, CH₃), 2.01 (s, 3H, CH₃), 1.22 (d, J = 6.3 Hz, 3H, H-6). ¹³C NMR (151 MHz, Chloroform-d) δ 170.4 (C=O), 170.23 (C=O), 170.17 (C=O), 92.00 (C-1), 71.1 (C-4), 70.4 (C-2), 68.9 (C-3), 66.3 (C-5), 20.88 (CH₃), 20.8 (CH₃), 20.7 (CH₃), 17.4 (C-6). NMR data are consistent with the literature.²³
Synthesis of Acceptors

Methyl 2,3,4-tri-O-benzyl-α-D-glucopyranoside 3a

Under a N₂ atmosphere, methyl α-D-glucopyranoside (3.66 g, 18.9 mmol) was dissolved in anhydrous DMF (30 mL) and imidazole (3.86 g, 56.6 mmol) was added. TIPSCl (4.43 mL, 20.7 mmol) was added dropwise over a period of 15 minutes. After-stirring the reaction at RT for 24 h, it was diluted with water (100 mL) and extracted with CH₂Cl₂ (3 × 60 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo.

A solution of the crude product S36 was dissolved in anhydrous DMF (100 mL) and the flask was cooled to 0 ºC. NaH (60% dispersion in mineral oil) (3.77 g, 94.3 mmol) was added to the solution and the ice-bath was removed. The reaction was stirred at room temperature for 1 h, after which it was again cooled to 0 ºC and treated slowly with BnBr (11.2 mL, 94.3 mmol). The ice-bath was removed, and the reaction mixture was left to stir at room temperature. TLC analysis (cyclohexane:EtOAc; 9:1) after 12 h showed complete consumption of starting material. The reaction mixture was quenched with MeOH (10 mL) and was extracted with Et₂O (3 × 200 mL). The combined organic layer was washed with 1 M HCl (100 mL) followed by saturated NaHCO₃ (100 mL) and brine (30 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to give a yellow oil.

The crude product S37 was dissolved in MeOH (10 mL) and 1.25 M HCl in MeOH (10 mL) was added. The reaction was left to stir over the weekend, after which TLC analysis (cyclohexane:EtOAc; 9:1, Rf = 0.1) showed that the reaction had gone to completion. The reaction mixture was quenched with saturated NaHCO₃ (20 mL), diluted with CH₂Cl₂ (250 mL) and the two phases were separated. The organic phase was washed with saturated NaHCO₃ (50 mL), water (50 mL), brine (50 mL), dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to give a yellow oil. Purification by column chromatography (pentane:EtOAc; 98:2 to 90:10 to 80:20) afforded the desired product 3a as a white solid (6.0 g, 12.9 mmol, 68% over 3 steps).

Rf = 0.4 (pentane:EtOAc; 4:1; H₂SO₄ (15-20% EtOH) stain); ¹H NMR (500 MHz, Chloroform-d): δ 7.40 – 7.25 (m, 15H, Ar-CH), 4.99 (d, J = 10.9 Hz, 1H, PhCH₂), 4.91 – 4.77 (m, 3H, 3 x PhCH₂), 4.70 – 4.63 (m, 2H, 2 x PhCH₂), 4.57 (d, J = 3.5 Hz, 1H, H-1), 4.00 (t, J = 9.3 Hz, 1H, H-3), 3.80 – 3.62 (m, 3H, H-6a, H-6b, H-5), 3.56 – 3.47 (m, 2H, H-4, H-2), 3.37 (s, 1H, OCH₃), 1.64 (br s, 1H, OH). ¹³C NMR (126 MHz, Chloroform-d): δ 166.0 – 157.0 (C-aromatic), 72.6 (C-4), 70.9 (C-3 x PhCH₂), 69.4 (C-2 x PhCH₂), 68.2 (C-1), 66.2 (C-3), 65.1 – 64.4 (C-5, C-6a, C-6b), 61.0 (C-5), 44.1 (C-4), 37.5 (C-3 x PhCH₂), 32.1 (C-2 x PhCH₂), 31.4 (CH₃), 20.1 (CH₃).
Methyl 4,6-O-benzylidene-α-D-glucopyranoside S38

Under a N₂ atmosphere, a solution of methyl-α-D-glucopyranoside (5.0 g, 26 mmol) in anhydrous DMF (52 mL) was treated with TsOH.H₂O (0.25 g, 1.3 mmol), followed by benzaldehyde dimethyl acetal (4.6 mL, 31 mmol) and stirred at 60 °C for 18 h. The reaction mixture was concentrated in vacuo, re-dissolved in CH₂Cl₂, washed with saturated NaHCO₃ and brine, dried over anhydrous MgSO₄ and concentrated in vacuo to give a yellow slurry. After purification by column chromatography (95:5 to 90:10; CH₂Cl₂/MeOH), the title compound S38 was obtained as a white solid (5.0 g, 68% yield). ¹H NMR (500 MHz, Chloroform-d): δ 7.51 – 7.45 (m, 2H, ArCH), 7.43 – 3.31 (m, 3H, ArCH), 5.51 (s, 1H, PhCH), 4.74 (d, J = 3.9 Hz, 1H, H-1), 4.27 (dd, J = 9.9, 4.5 Hz, 1H, H-6a), 3.90 (td, J = 9.2, 2.0 Hz, 1H, H-3), 3.78 (td, J = 9.7, 4.5 Hz, 1H, H-5), 3.75 – 3.67 (m, 1H, H-6b), 3.59 (td, J = 9.0, 3.8 Hz, 1H, H-2), 3.46 (t, J = 9.4 Hz, 1H, H-4), 3.42 (s, 1H, OCH₃), 3.22 (d, J = 2.4 Hz, 1H, OH), 2.65 (d, J = 9.0 Hz, 1H, OH). ¹³C NMR (126 MHz, Chloroform-d): δ 137.2 (C), 129.4 (CH), 128.4 (CH), 126.5 (CH), 102.1 (PhCH), 99.9 (C-1), 81.1 (C-4), 72.9 (C-2), 71.7 (C-3), 69.0 (C-6), 62.5 (C-5), 55.7 (OCH₃). NMR data were consistent with literature data.[25]

Methyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside S39

Under a N₂ atmosphere, a solution of glucopyranoside S38 (5.0 g, 18 mmol) in anhydrous DMF (40 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil) (2.3 g, 58 mmol) was added. The reaction mixture was stirred at room temperature for 30 min after which it was again cooled down to 0
Benzyl bromide (6.4 mL, 54 mmol) was added dropwise to the reaction mixture. The reaction mixture was left to stir at room temperature for 9 h. The reaction was quenched with MeOH and the mixture was concentrated in vacuo to give a yellow slurry. The slurry was diluted with CH$_2$Cl$_2$ and washed with 1 M HCl, followed by saturated NaHCO$_3$ and brine, dried over anhydrous MgSO$_4$ and concentrated in vacuo. Purification by column chromatography (90:10; Pentane/Et$_2$O) gave S39 as a white solid (7.9 g, 95% yield).

$^1$H NMR (500 MHz, Chloroform-d): δ 7.52 – 7.46 (m, 2H, ArCH), 7.42 – 7.24 (m, 13H, ArCH), 5.55 (s, 1H, PhCH), 4.91 (d, $J$ = 11.3 Hz, 1H, CHHPh), 4.85 (d, $J$ = 12.2 Hz, 1H, CHHPh), 4.85 (d, $J$ = 11.3 Hz, 1H, CHHPh), 4.70 (d, $J$ = 12.2 Hz, 1H, CHHPh), 4.60 (d, $J$ = 3.7 Hz, 1H, H-1), 4.26 (dd, $J$ = 10.1, 4.8 Hz, 1H, H-6a), 4.05 (t, $J$ = 9.3 Hz, 1H, H-3), 3.83 (td, $J$ = 9.9, 4.8 Hz, 1H, H-5), 3.70 (t, $J$ = 10.3 Hz, 1H, H-6b), 3.60 (t, $J$ = 9.4 Hz, 1H, H-4), 3.56 (dd, $J$ = 9.3, 3.7 Hz, 1H, H-2), 3.40 (s, 1H, OCH$_3$).

$^{13}$C NMR (126 MHz, Chloroform-d): δ 138.9 (C), 138.3 (C), 137.5 (C), 129.0 (CH), 128.6 (CH), 128.44 (CH), 128.35 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.7 (CH), 126.2 (CH), 101.4 (PhCH), 99.4 (C-1), 82.3 (C-4), 79.3 (C-2), 78.7 (C-3), 75.5 (PhCH$_2$), 73.9 (PhCH$_2$), 69.2 (C-6), 62.5 (C-5), 55.5 (OCH$_3$). NMR data were consistent with literature data.[25]

**Methyl 2,3,6-tri-O-benzyl-α-D-glucopyranoside 3b**

Based on the literature procedure,[6] under a N$_2$ atmosphere, a solution of S39 (3.6 g, 7.8 mmol) in anhydrous CH$_2$Cl$_2$ (29 mL) was cooled to 0 °C and treated slowly with trifluoroacetic acid (3.6 mL, 47 mmol) followed by triethylsilane (7.4 mL, 47 mmol). The reaction mixture was warmed up to room temperature and stirred for 45 minutes. The reaction was diluted with CH$_2$Cl$_2$ and quenched with saturated NaCHO$_3$. The organic layer was washed with brine, dried over anhydrous MgSO$_4$ and concentrated in vacuo to give a yellow syrup. Purification by column chromatography (2:1; Pentane/Et$_2$O) gave 3b as a yellowish syrup (3.0 g, 83% yield). $^1$H NMR (500 MHz, Chloroform-d): δ 7.41 – 7.21 (m, 15H, ArCH), 5.00 (d, $J$ = 11.5 Hz, 1H, CHHPh), 4.77 (d, $J$ = 12.1 Hz, 1H, CHHPh), 4.73 (d, $J$ = 11.4 Hz, 1H, CHHPh), 4.66 (d, $J$ = 12.1 Hz, 1H, CHHPh), 4.63 (d, $J$ = 3.5 Hz, 1H, H-1), 4.59 (d, $J$ = 12.2 Hz, 1H, CHHPh), 4.54 (d, $J$ = 12.1 Hz, 1H, CHHPh), 3.78 (t, $J$ = 9.2 Hz, 1H, H-3), 3.73 – 3.68 (m, 1H, H-5), 3.68 – 3.65 (m, 2H, H-6a, H-6b), 3.60 (td, $J$ = 9.2, 2.4 Hz, 1H, H-4), 3.53 (dd, $J$ = 9.6, 3.5 Hz, 1H, H-2), 3.38 (s, 3H, OCH$_3$), 2.31 (t, $J$ = 2.4 Hz, 1H, OH). $^{13}$C NMR (126 MHz, Chloroform-d): δ 138.9 (C), 138.2 (C), 138.1 (C), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.12 (CH), 128.08 (CH), 128.0 (CH), 127.76 (CH), 127.75 (CH), 98.3 (C-1), 81.6 (C-3), 79.7 (C-2).
Methyl 2-benzyl-4-hydroxy-3,6-dideoxy-3-glucopyranoside 3d and Methyl 3-O-benzyl-4-hydroxy-3,6-dideoxy-3-glucopyranoside 40

A solution of glucopyranoside 38 (6.7 g, 24 mmol) in anhydrous CHCl₃ (240 mL) was treated with Bu₄NOH (4.1 g, 12 mmol) followed by benzyl bromide (3.4 mL, 29 mmol) and 1 M NaOH (80 mL) at room temperature. The reaction mixture was then left to stir at reflux for 41 h. The organic and aqueous layers were separated and the aqueous layer was washed with CHCl₃. The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo to give a white solid. Purification by column chromatography (90:10, Petroleum/EtOAc) gave 3d and 40 as white solids (6.6 g, 74% yield).

**NMR data**

| Compound | NMR (400 MHz, Chloroform-d₆) | NMR (101 MHz, Chloroform-d₆) |
|----------|------------------------------|------------------------------|
| S40 | δ 7.61 – 7.43 (4H, ArCH), 7.44 – 7.14 (4H, ArCH), 5.57 (s, HPh), 4.26 (d, J = 12.2 Hz, H), 4.15 (d, J = 9.3 Hz, H), 3.88 (s, 3H, OCH₃), 3.46 (t, J = 9.9 Hz, H), 3.04 (s, 3H, OCH₃), 2.98 (d, J = 7.4 Hz, H), 1.47 (d, J = 9.3 Hz, H), 1.32 (t, J = 11.6 Hz, H), 0.54 (s, 3H, OCH₃), 0.29 (s, 3H, OCH₃) | δ 179.6 (C), 126.2 (C), 121.4 (C), 137.5 (C), 129.2 (C), 128.5 (C), 128.4 (C), 128.1 (C), 127.9 (C), 126.8 (C), 101.4 (C), 100.01 (C), 82.1 (C), 79.0 (C), 75.0 (C), 69.2 (C), 62.2 (C), 55.6 (OCH₃), 55.5 |

**Notes**

NMR data were consistent with literature data. [25]
Methyl 3-O-acetyl-2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside S41 and Methyl 2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside S42

![Chemical Structures]

A solution of 3d and S40 (6.6 g, 18 mmol), acetic anhydride (3.4 mL, 36 mmol) and DMAP (22 mg, 0.18 mmol) in pyridine (1.4 mL, 18 mmol) (little bit of CH₂Cl₂ was added to get a clear solution) was stirred at room temperature for 4 h. The reaction mixture was diluted with CH₂Cl₂ and washed with 1 M HCl, saturated NaHCO₃, and brine. The organic layer was dried over anhydrous MgSO₄, filtered and concentrated in vacuo to give a white solid. The crude material was used in the next step without further purification.

**S41 (3-OAc)**

¹H NMR (600 MHz, Chloroform-d): δ 7.46 – 7.41 (m, 2H, ArCH), 7.40 – 7.28 (m, 8H, ArCH), 5.56 (t, J = 9.7 Hz, 1H, H-3), 5.45 (s, 1H, PhCH), 4.69 (d, J = 3.5 Hz, 1H, H-1), 4.66 (d, J = 12.4 Hz, 1H, C(H)Ph), 4.63 (d, J = 12.4 Hz, 1H, C(H)Ph), 4.26 (dd, J = 10.3, 4.9 Hz, 1H, H-6a), 3.89 (td, J = 10.0, 4.9 Hz, 1H, H-5), 3.70 (t, J = 10.3 Hz, 1H, H-6b), 3.57 (dd, J = 9.7, 3.6 Hz, 1H, H-2), 3.53 (t, J = 9.6 Hz, 1H, H-4), 3.402 (s, 3H, OCH₃), 2.04 (s, 3H, CH₃). ¹³C NMR (151 MHz, Chloroform-d): δ 169.8 (C=O), 138.0 (C), 137.2 (C), 129.1 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 126.3 (CH), 101.6 (PhCH), 98.9 (C-1), 79.7 (C-4), 77.8 (C-2), 73.14 (PhCH₂), 70.7 (C-3), 69.12 (C-6), 62.48 (C-5), 55.5 (OCH₃), 21.14 (CH₃). NMR data were consistent with literature data.¹²⁶

**S42 (2-OAc)**

¹H NMR (600 MHz, Chloroform-d): δ 7.51 – 7.47 (m, 2H, ArCH), 7.40 – 7.28 (m, 8H, ArCH), 5.59 (s, 1H, PhCH), 4.93 – 4.86 (m, 3H, H-1, H-2, C(H)Ph), 4.71 (d, J = 11.2 Hz, 1H, C(H)Ph), 4.30 (dd, J = 10.1, 4.7 Hz, 1H, H-6a), 4.03 (t, J = 9.4 Hz, 1H, H-3), 3.88 – 3.83 (m, 2H, H-5, H-6b), 3.75 – 3.68 (m, 1H, H-4), 3.396 (s, 3H, OCH₃), 2.08 (s, 3H, OCH₃). ¹³C NMR (151 MHz, Chloroform-d): δ 170.5 (C=O), 138.6 (C), 137.4 (C), 128.41 (CH), 128.37 (CH), 127.8 (CH), 127.7 (CH), 126.2 (CH), 101.5 (PhCH), 97.9 (C-1), 82.2 (C-4), 76.3 (C-3), 75.0 (PhCH₂), 73.12 (C-2), 69.08 (C-6), 62.45 (C-5), 55.4 (OCH₃), 21.05 (CH₃). NMR data were consistent with literature data.¹²⁷
Methyl 3-O-acetyl-2,6-di-O-benzyl-α-D-glucopyranoside S43 and Methyl 2-O-acetyl-3,6-di-O-benzyl-α-D-glucopyranoside S44

![Structural formula of S43 and S44](image)

Under a N₂ atmosphere, a solution of S41 and S42 (6.7 g, 16 mmol) in anhydrous CH₂Cl₂ (59 mL) was cooled to 0 °C and treated slowly with trifluoroacetic acid (7.4 mL, 96 mmol) followed by triethylsilane (15 mL, 96 mmol). The reaction mixture was warmed up to room temperature and stirred for 1 h. The reaction was diluted with CH₂Cl₂ and quenched with saturated NaCHO₃. The organic layer was washed with brine, dried over anhydrous MgSO₄ and concentrated in vacuo to give a yellowish syrup. Purification by column chromatography (3:1 to 1:1; Pentane/Et₂O) gave S43 as a colourless syrup (3.2 g, 48% yield) and S44 as a colourless syrup (0.98 g, 15% yield).

**S43 (3-OAc)**

1H NMR (500 MHz, Chloroform-d): δ 7.38 – 7.25 (m, 10H, ArCH), 5.23 (t, J = 9.5 Hz, 1H, H-3), 4.68 (d, J = 3.6 Hz, 1H, H-1), 4.66 (d, J = 12.4 Hz, 1H, CHPh), 4.62 (d, J = 12.4 Hz, 1H, CHPh), 4.60 (d, J = 12.1 Hz, 1H, CHPh), 4.56 (d, J = 12.1 Hz, 1H, CHPh), 3.77 – 3.67 (m, 3H, H-4, H-6a, H-6b), 3.64 (td, J = 9.3, 4.7 Hz, 1H, H-5), 3.53 (dd, J = 9.9, 3.6 Hz, 1H, H-2), 3.38 (s, 3H, OCH₃), 2.79 (d, J = 4.7 Hz, 1H, OH), 2.09 (s, 3H, CH₃). 13C NMR (126 MHz, Chloroform-d): δ 172.4 (C=O), 138.1 (C), 138.0 (C), 128.6 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 98.0 (C-1), 76.8 (C-2), 75.8 (C-3), 73.8 (PhCH₂), 73.2 (PhCH₂), 70.6 (C-5), 70.4 (C-4), 69.4 (C-6), 55.4 (OCH₃), 21.2 (CH₃). ESI-HRMS for C₂₃H₂₈O₇Na⁺ (M+Na)⁺ calculated: 439.1727; found: 439.1729.

**S44 (2-OAc)**

1H NMR (500 MHz, Chloroform-d): δ 7.37 – 7.26 (m, 10H, ArCH), 4.91 (d, J = 3.7 Hz, 1H, H-1), 4.85 (dd, J = 9.9, 3.7 Hz, 1H, H-2), 4.80 (d, J = 11.7 Hz, 1H, CHPh), 4.73 (d, J = 11.7 Hz, 1H, CHPh), 4.62 (d, J = 12.1 Hz, 1H, CHPh), 4.56 (d, J = 12.1 Hz, 1H, CHPh), 3.84 (dd, J = 9.9, 8.5 Hz, 1H, H-3), 3.78 – 3.67 (m, 4H, H-4, H-5, H-6a, H-6b), 3.39 (s, 3H, OCH₃), 2.49 (d, J = 2.5 Hz, 1H, OH), 2.07 (s, 3H, CH₃). 13C NMR (126 MHz, Chloroform-d): δ 170.4 (C=O), 138.7 (C), 138.0 (C), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.9 (CH), 127.80 (CH), 97.3 (C-1), 79.9 (C-3), 75.3 (PhCH₂), 73.8 (PhCH₂), 73.5 (C-2), 71.6 (C-4/5), 69.9 (C-4/5 and C-6), 55.3 (OCH₃), 21.1 (CH₃). NMR data were consistent with literature data.¹²⁻¹⁸
Methyl 2,4,6-tri-O-benzyl-α-D-glucopyranoside 3c

Under a N₂ atmosphere, a solution of glucopyranoside S43 (2.1 g, 5.0 mmol) in anhydrous DMF (17 mL) was cooled to 0 °C and benzyl bromide (0.72 mL, 6.1 mmol) was added. After 15 minutes, NaH (60% dispersion in mineral oil) (242 g, 6.05 mmol) was added in one portion and the reaction mixture was stirred at 0 °C for 30 minutes. The reaction mixture was warmed to room temperature and stirred for 3.5 h. The reaction was quenched with MeOH and the mixture was concentrated in vacuo to give a yellowish slurry. The slurry was diluted with CH₂Cl₂ and washed with 1 M HCl, followed by saturated NaHCO₃ and brine, dried over anhydrous MgSO₄ and concentrated in vacuo. A solution of the crude in MeOH was treated with MeONa (0.14 g, 2.5 mmol) and the mixture was left to stir at room temperature for 3 days. Purification by column chromatography (98:2 to 95:5; CH₂Cl₂/Et₂O) gave 3c as a colourless syrup (1.3 g, 56% yield over 2 steps). ¹H NMR (500 MHz, Chloroform-d): δ 7.38 – 7.25 (m, 13H, ArCH), 7.24 – 7.18 (m, 2H, ArCH), 4.83 (d, J = 11.1 Hz, 1H, CHHPh), 4.70 (d, J = 12.2 Hz, 1H, CHHPh), 4.67 (d, J = 12.1 Hz, 1H, CHHPh), 4.65 (d, J = 3.5 Hz, 1H, H-1), 4.61 (d, J = 12.1 Hz, 1H, CHHPh), 4.52 (d, J = 11.2 Hz, 1H, CHHPh), 4.49 (d, J = 12.2 Hz, 1H, CHHPh), 4.07 (dd, J = 9.5, 8.7, 2.2 Hz, 1H, H-3), 3.74 – 3.69 (m, 2H, H-5, H-6a), 3.67 – 3.62 (m, 1H, H-6b), 3.58 – 3.51 (m, 1H, H-4), 3.41 (dd, J = 9.6, 3.5 Hz, 1H, H-2), 3.33 (s, 3H, OCH₃), 2.42 (d, J = 2.2 Hz, 1H, OH). ¹³C NMR (126 MHz, Chloroform-d): δ 138.6 (C), 138.13 (C), 138.07 (C), 128.7 (CH), 128.52 (CH), 128.51 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 97.7 (C-1), 79.6 (C-2), 77.6 (C-4), 74.7 (PhCH₂), 73.8 (C-3), 73.7 (PhCH₂), 73.2 (PhCH₂), 69.8 (C-5), 68.7 (C-6), 55.3 (OCH₃). NMR data were consistent with literature data.[²⁹]

Methyl 4,6-O-benzylidene-α-D-galactopyranoside S45

Following the literature procedure,[³⁰] a solution of methyl α-D-galactopyranose (1.1 g, 5.7 mmol), benaldehyde dimethyl acetal (1.0 ml, 6.7 mmol) and pTsOH.H₂O (0.02 g, 0.1 mmol, 2 mol%) in anhydrous DMF (12 ml) was heated on a rotary-evaporator (50 °C, 250 mbar) for four hours. TLC
analysis (9:1; ethyl acetate/methanol; H₂SO₄ (10-15% EtOH)) of the reaction mixture against a sample of pure product showed the desired product had been formed ($R_f = 0.64$) and some starting material remained ($R_f = 0.49$, faint spot). The DMF was removed using rotary evaporation. The white solid obtained was dissolved in CH₂Cl₂ (20 ml) and washed with saturated NaHCO₃ solution (20 ml). The aqueous layer was extracted with CH₂Cl₂ (3 × 20 ml). The combined organic layers were washed with brine (20 ml) and dried over Na₂SO₄, filtered and concentrated in vacuo. Purification by column chromatography (95:5; dichloromethane/methanol) gave the desired product S45 as a white solid (0.87 g, 54% yield); $R_f = 0.24$ (95:5; CH₂Cl₂/MeOH), mp 172–174 °C (lit. 170.3–171.0 °C (cyclohexane/ethyl acetate)); $^1$H NMR (400 MHz, Chloroform-d) δ 7.58–7.44 (m, 2H, Ar-CH), 7.44–7.30 (m, 3H, Ar-CH), 5.54 (s, 1H, PhCH), 4.91 (d, $J = 3.1$ Hz, 1H, H-1), 4.27 (dd, $J = 12.5$, 1.6 Hz, 1H, H-6a), 4.24 (br d, $J = 2.0$ Hz, 1H, H-4), 4.06 (dd, $J = 12.6$, 1.8 Hz, 1H, H-6b), 3.99–3.83 (m, 2H, H-2, H-3), 3.67 (br s, 1H, H-5), 3.44 (s, 3H, OCH₃), 2.64 (d, $J = 7.3$ Hz, 1H, OH), 2.42 (d, $J = 6.3$ Hz, 1H, OH); $^{13}$C NMR (101 MHz, Chloroform-d) δ 137.7 (4 °C), 129.3 (Ar-CH), 128.4 (Ar-CH), 126.4 (Ar-CH), 101.4 (PhCH), 100.4 (C-1), 76.0 (C-4), 69.9, 69.8 (C-2, C-3), 69.4 (C-6), 62.8 (C-5), 55.8 (OCH₃); ESI-HRMS for C₁₄H₁₈NaO₆⁺ (M+Na) calculated: 305.1001; found: 305.0986. NMR data were consistent with the literature. Based on the literature procedure, $n$Bu₄NHSO₄ (16 g, 47 mmol) followed by aq. NaOH (150 mL, 1.2M) were added to a stirred solution of methyl 4,6-O-benzylidene-α-D-galactopyranoside S45 (13.5 g, 47.8 mmol) in CH₂Cl₂ (500 mL). The mixture was stirred for 30 min at room temperature. BnBr (7.0 mL, 59 mmol) was then added to the reaction mixture. The reaction was heated at reflux temperature for three days (time unoptimised). TLC analysis (9:1; dichloromethane/methanol) showed that some of the galactopyranoside starting material remained ($R_f = 0.45$) and two new spots were detected in the reaction mixture ($R_f = 0.82, 0.86$). The aqueous and organic layers were separated. The aqueous layer was extracted with CH₂Cl₂ (2 × 150 mL). The combined organic layers were washed with NaHCO₃ (200
mL), brine (200 mL), dried over MgSO₄, filtered and concentrated in vacuo. Column chromatography was performed (99:1 to 90:10; cyclohexane/ EtOAc) which afforded a mixture of methyl 2-O-benzyl-4,6-O-benzylidene-α-D-galactopyranoside S₄₆ and methyl 3-O-benzyl-4,6-O-benzylidene-α-D-galactopyranoside S₃j as a white solid (12 g, 67% yield). Based on the relative integrations of PhCH in the ¹H NMR spectrum the ratio of the two products was determined as 54:46 (S₄₆:S₃j, 3-OH/2-OH product). The mixture of S₄₆ and S₃j (12 g, 32 mmol) was added to a solution of acetic anhydride (12.0 mL, 127 mmol) and anhydrous pyridine (50 mL), under a N₂ atmosphere. The reaction mixture was stirred at room temperature for three days (time unoptimised). TLC analysis (EtOAc) showed that the starting materials had been consumed (Rᵣ = 0.53) and a new spot appeared (Rᵣ = 0.66). The reaction mixture was diluted with CH₂Cl₂ (200 mL) and washed with 1M HCl (2 × 100 mL), brine (100 mL), dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. Purification by column chromatography (95:5 to 60:40; cyclohexane/ EtOAc) afforded S₄₇ (3-OAc) as an amorphous white solid (6.9 g, 52% yield) and S₄₈ (2-OAc) as a white solid (3.4 g, 26% yield); 1.6 g (12% yield) remained as mixed fractions.

**Methyl 2-O-benzyl-3-O-acetyl-4,6-O-benzylidene-α-D-galactopyranoside S₄₇:**  Rᵣ = 0.3 (4:1; cyclohexane/ EtOAc); ¹H NMR (400 MHz, Chloroform-d) δ 7.52 – 7.45 (m, 2H, Ar-CH), 7.43 – 7.27 (m, 8H, Ar-CH), 5.50 (s, 1H, PhCH), 5.29 (dd, J = 10.5, 3.5 Hz, 1H, H-3), 4.80 (d, J = 3.5 Hz, 1H, H-1), 4.75 (d, J = 12.2 Hz, 1H, PhCH₂), 4.62 (d, J = 12.2 Hz, 1H, PhCH₂), 4.46 (dd, J = 3.6, 1.2 Hz, 1H, H-4), 4.23 (dd, J = 12.5, 1.6 Hz, 1H, H-6a), 4.09 (dd, J = 10.5, 3.5 Hz, 1H, H-2), 4.04 (dd, J = 12.5, 1.8 Hz, 1H, H-6b), 3.75 – 3.69 (m, 1H, H-5), 3.40 (s, 3H, OCH₃), 2.09 (s, 3H, (H₂C(C=O)O); ¹³C NMR (101 MHz, Chloroform-d) δ 170.8 (C=O), 138.4 (4 °C), 137.9 (4 °C), 129.1 (Ar-CH), 128.5 (Ar-CH), 128.3 (Ar-CH), 127.9 (Ar-CH), 126.3 (Ar-CH), 100.9 (PhCH), 99.3 (C-1), 74.4 (C-4), 73.7, 73.6 (C-2, PhCH₂), 71.0 (C-3), 69.4 (C-6), 62.2 (C-5), 55.7 (OCH₃), 21.3 (H₂C(C=O)O); ESI-HRMS for C₂₅H₂₆NaO₇⁺ (M+Na)⁺ calculated: 437.1576; found: 437.1561. NMR data were consistent with literature data.[30]

**Methyl 3-O-benzyl-2-O-acetyl-4,6-O-benzylidene-α-D-galactopyranoside S₄₈:**  Rᵣ = 0.27 (4:1; cyclohexane/ EtOAc); ¹H NMR (500 MHz, Chloroform-d) δ 7.61 – 7.47 (m, 2H, Ar-CH), 7.41 – 7.22 (m, 8H, Ar-CH), 5.48 (s, 1H, PhCH), 5.34 (dd, J = 10.5, 3.6 Hz, 1H, H-2), 5.06 (d, J = 3.6 Hz, 1H, H-1), 4.72 (d, J = 12.5 Hz, 1H, PhCH₂), 4.68 (d, J = 12.5 Hz, 1H, PhCH₂), 4.24 (dd, J = 12.4, 1.6 Hz, 1H, H-6a), 4.20 (br d, J = 3.3 Hz, 1H, H-4), 4.04 – 3.95 (m, 2H, H-3, H-6b), 3.63 – 3.56 (m, 1H, H-5), 3.38 (s, 3H, OCH₃), 2.09 (s, 3H, (H₂C(C=O)O); ¹³C NMR (126 MHz, Chloroform-d) δ 170.4 (C=O), 138.5 (4 °C), 137.8 (4 °C), 129.0 (Ar-CH), 128.4 (Ar-CH), 128.2 (Ar-CH), 127.7 (Ar-CH), 127.5 (Ar-CH), 126.4 (Ar-CH), 101.1 (PhCH), 98.0 (C-1), 74.3 (C-4), 73.7 (C-3), 71.9 (PhCH₂), 70.2 (C-2), 69.3 (C-6), 62.5 (C-5), 55.5 (OCH₃), 21.1 (H₂C(C=O)O); ESI-HRMS for C₂₅H₂₆NaO₇⁺ (M+Na)⁺ calculated: 437.1576; found: 437.1598.
Using Zemplén conditions,[31] S47 (1.5 g, 3.6 mmol) was dissolved in MeOH (36 mL) and NaOMe was added (0.08 g, 1.5 mmol). After 24 h TLC analysis (5:3; cyclohexane/ EtOAc) showed the starting material was consumed ($R_f = 0.35$) and a new spot had appeared ($R_f = 0.09$) in the reaction mixture. The mixture was neutralised with Amberlyst® IR 120, filtered and concentrated in vacuo. Purification by column chromatography (62:38 to 24:75; cyclohexane/ EtOAc) afforded the desired product S46 as a white foam (1.12 g, 84% yield).

Rf = 0.09 (5:3; cyclohexane/ EtOAc); 1H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.43 (m, 2H, Ar-CH), 7.41 – 7.25 (m, 8H, Ar-CH), 5.55 (s, 1H, PhCH), 4.81 (d, J = 12.3 Hz, 1H, PhCH2), 4.79 (d, J = 3.6 Hz, 1H, H-1), 4.66 (d, J = 12.1 Hz, 1H, PhCH2), 4.28 (dd, J = 3.9, 1.3 Hz, 1H, H-4), 4.25 (dd, J = 12.5, 1.6 Hz, 1H, H-6a), 4.14 (br dd, J = 10.1, 3.6 Hz, 1H, H-3), 4.07 (dd, J = 12.6, 1.9 Hz, 1H, H-6b), 3.82 (dd, J = 10.0, 3.5 Hz, 1H, H-2), 3.71 – 3.64 (m, 1H, H-5), 3.37 (s, 3H, OCH3), 2.41 (s, 1H, OH); 13C NMR (101 MHz, Chloroform-d) δ 138.4 (4° C), 137.7 (4° C), 129.3 (Ar-C), 128.6 (Ar-CH), 128.3 (Ar-CH), 128.2 (Ar-CH), 128.0 (Ar-CH), 126.4 (Ar-CH), 101.4 (PhCH), 99.1 (C-1), 76.9 (C-2), 76.2 (C-4), 73.5 (PhCH2), 69.5 (C-6), 68.7 (C-3), 62.5 (C-5), 55.7 (OCH3); ESI-HRMS for C21H24NaO6+ (M+Na)+ calculated: 395.1471; found: 395.1467. 1H NMR data were consistent with the literature.[30]

Methyl 3-O-benzyl-4,6-O-benzylidene-α-D-galactopyranoside 3j

Using Zemplén conditions,[31] S48 (1.5 g, 3.6 mmol) was dissolved in MeOH (36 mL) and NaOMe was added (0.09 g, 1.7 mmol). As the reaction proceeded a white precipitate formed. After 24 h this was filtered using Hirsch filtration. The filter cake was washed with cold MeOH. Desired product 3j was obtained as a white solid without further purification (0.8 g, 60% yield). A second crop was obtained
from the filtrate (0.4 g, 30% yield). mp 200–202 °C (lit.[32] 185–186 °C (CH₂Cl₂/hexane)); ¹H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.45 (m, 2H, Ar-CH), 7.44 – 7.21 (m, 8H, Ar-CH), 5.45 (s, 1H, PhCH₂), 4.95 (d, J = 3.8 Hz, 1H, H-1), 4.73 (s, 2H, 2 × PhCH₂), 4.26 (dd, J = 12.5, 1.6 Hz, 1H, H-6a), 4.23 – 4.16 (m, 2H, H-2, H-4), 4.02 (dd, J = 12.4, 1.8 Hz, 1H, H-6b), 3.79 (dd, J = 10.0, 3.5 Hz, 1H, H-3), 3.65 – 3.57 (m, 1H, H-5), 3.44 (s, 3H, OCH₃), 2.26 (d, J = 6.2 Hz, 1H, OH); ¹³C NMR (101 MHz, Chloroform-d) δ 138.5 (4 °C), 137.9 (4 °C), 129.0 (Ar-CH), 128.6 (Ar-CH), 128.3 (Ar-CH), 127.94 (Ar-CH), 127.92 (Ar-CH), 126.4 (Ar-CH), 101.1 (PhCH), 100.3 (C-1), 76.6 (C-3), 73.7 (C-4), 71.5 (PhCH₂), 69.6 (C-6), 68.1 (C-2), 62.9 (C-5), 55.7 (OCH₃); ESI-HRMS for C₂₇H₃₃NaO₅⁺ (M+Na)⁺ calculated: 395.1471; found: 395.1456. Proton NMR data were consistent with the literature data with the exception of the assignments for H-4 and H-5.[32]

**Ethyl 2,3,4-tri-O-(4-methylbenzyl)-1-thio-α-D-mannopyranoside 3i**

Based on the literature procedure,[8] a solution of S8 (0.69 g, 1.0 mmol) in MeCN/H₂O (4:1, 15 mL) was treated with trifluoroacetic acid (0.940 mL, 12.2 mmol) at room temperature. After stirring for 4 h at room temperature, the reaction was quenched with saturated NaHCO₃ and diluted with CH₂Cl₂ (100 mL). The aqueous layer was washed with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated in vacuo to give a bright yellow oil. Purification by column chromatography (9:1 to 1:1; pentane/Et₂O) gave 3i as a colourless syrup (0.54 g, quantitative yield). ESI-HRMS for C₃₂H₄₀O₅SN⁺ (M+NH₄)⁺ calculated: 554.2935; found: 554.2939. ¹H NMR (500 MHz, Chloroform-d): δ 7.27 – 7.18 (m, 6H, Ar-CH), 7.15 – 7.09 (m, 6H, Ar-CH), 5.26 (d, J = 1.3 Hz, 1H, H-1), 4.88 (d, J = 10.7 Hz, 1H, CHHPh), 4.67 (d, J = 12.2 Hz, 1H, CHHPh), 4.63 (d, J = 12.1 Hz, 1H, CHHPh), 4.58 (d, J = 10.7 Hz, 1H, CHHPh), 4.55 (d, J = 11.5 Hz, 1H, CHHPh), 4.52 (d, J = 11.6 Hz, 1H, CHHPh), 3.99 – 3.90 (m, 2H, H-4, H-5), 3.85 – 3.72 (m, 4H, H-2, H-3, H-6a, H-6b), 2.61 – 2.45 (m, 2H, SCH₂CH₃), 2.34 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 1.24 – 1.17 (m, 4H, SCH₂CH₃, OH). ¹³C NMR (126 MHz, Chloroform-d): δ 137.6 (C), 137.5 (C), 137.4 (C), 135.5 (C), 135.3 (C), 135.1 (C), 129.18 (CH), 129.16 (CH), 129.15 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 82.40 (C-1), 80.3 (C-3), 76.4 (C-2), 75.2 (PhCH₂), 75.0 (C-4), 72.5 (C-5), 72.4 (PhCH₂), 72.1 (PhCH₂), 62.5 (C-6), 25.4 (SCH₂CH₃), 21.29 (CH₃), 21.28 (CH₃), 21.27 (CH₃), 15.0 (SCH₂CH₃).
Methyl 2,3,4-tri-O-benzoyl-α-D-glucopyranoside S49

Methyl α-D-glucopyranoside (2.0 g, 10 mmol), was dissolved in anhydrous pyridine (34 mL) under a N2 atmosphere and treated with imidazole (1.40 g, 20.6 mmol) and TIPSCl (2.2 mL, 10 mmol). The reaction mixture was stirred at room temperature for 17 hours and monitored by TLC (9:1; CH2Cl2/methanol). When the starting material was consumed, BzCl (7.38 mL, 61.8 mmol) and catalytic DMAP (0.1 g, 1 mmol) were added and the reaction was stirred for 7.5 hours. The reaction mixture turned a yellow colour. TLC analysis (8:2; pentane/Et2O) showed complete conversion of intermediate. The reaction was quenched with water (5 mL), diluted with CH2Cl2 (200 mL) and the two phases separated. The organic layer was subsequently washed with 1 M HCl, water, saturated NaHCO3 and brine, dried over anhydrous MgSO4, filtered and concentrated in vacuo to give a light brown syrup. The crude material was dissolved in CH3CN and water (100 mL, 7:1) and treated with TFA (16 mL, 0.21 mol). The reaction mixture was stirred at room temperature for 21 hours and monitored by TLC analysis (8:2; pentane/Et2O). The reaction mixture was concentrated in vacuo and the residue was diluted with CH2Cl2 (200 mL), washed with brine, dried over anhydrous MgSO4 and concentrated in vacuo to give a light brown syrup. Purification by column chromatography (1:1 pentane/Et2O followed by 9:1 CH2Cl2/Et2O) afforded the product S49 (3.23 g, 48% yield) as a white crystalline solid. 1H NMR (400 MHz, Chloroform-d): δ 8.01 – 7.94 (m, 4H, ArCH), 7.90 – 7.85 (m, 2H, ArCH), 7.57 – 7.48 (m, 2H, ArCH), 7.45 – 7.34 (m, 5H, ArCH), 7.32 – 7.24 (m, 2H, ArCH), 6.23 (t, J = 9.7 Hz, 1H, H-3), 5.50 (t, J = 9.9 Hz, 1H, H-4), 5.32 – 5.24 (m, 2H, H-2, H-1), 4.04 (ddd, J = 10.1, 3.8, 2.3 Hz, 1H, H-5), 3.83 (ddd, J = 13.0, 8.7, 2.3 Hz, 1H, H-6a), 3.74 (ddd, J = 12.9, 5.5, 3.8 Hz, 1H, H-6b), 3.47 (s, 3H, OCH3), 2.68 (dd, J = 8.7, 5.6 Hz, 1H, OH). 13C NMR (101 MHz, Chloroform-d): δ 166.6 (C=O), 166.0 (C=O), 165.9 (C=O), 133.9 (C), 133.5 (C), 133.3 (C), 130.13 (CH), 130.05 (CH), 129.8 (CH), 129.3 (CH), 129.2 (CH), 128.72 (CH), 128.66 (CH), 128.6 (CH), 128.4 (CH), 97.3 (C-1), 72.2 (C-2), 70.2 (C-3), 69.9 (C-5), 69.7 (C-4), 61.2 (C-6), 55.8 (CH3). NMR data were consistent with literature data.[8]
**β-Mannosylations and β-Rhamnosylations**

**General Procedure A for Mannosylation Donor Scope**

A 25 mL crimp-top vial charged with a stir-bar, hemiacetal (0.10 mmol, 1 eq) and Ph₃PO (14 mg, 0.050 mmol, 0.5 eq) was placed under three cycles of vacuum and nitrogen. The solids were dissolved in anhydrous CHCl₃ (0.2 mL, 0.5 M), treated with oxalyl chloride (10 μL, 0.12 mmol, 1.2 eq) and left to stir at room temperature. After 1 h, the solvent and excess oxalyl chloride were removed by applying vacuum. Solid acceptor (0.07 mmol, 0.7 eq) and powdered LiI (53 mg, 0.40 mmol, 4 eq) were added to the vial and placed under three cycles of vacuum and nitrogen. The contents were re-dissolved in anhydrous CHCl₃ (0.25 mL, 0.4 M w.r.t. donor) and treated with iPr₂NEt (42 μL, 0.25 mmol, 2.5 eq). The reaction was stirred at 45 °C for 24 h or 30 °C for 36 h. The reaction mixture was diluted with CH₂Cl₂ (1 mL) and treated with 1 M HCl (1 mL). The aqueous layer was washed with CH₂Cl₂ (2 x 1 mL) and the combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo to give a yellow or brown syrup. The α/β ratio was determined by ¹H NMR spectroscopy of the crude reaction mixture.

**General Procedure B for Mannosylation Acceptor Scope**

A 25 mL crimp-top vial charged with a stir-bar, hemiacetal (0.10 mmol, 1 eq) and Ph₃PO (28 mg, 0.10 mmol, 1 eq) was placed under three cycles of vacuum and nitrogen. The solids were dissolved in anhydrous CHCl₃ (0.2 mL, 0.5 M), treated with oxalyl chloride (10 μL, 0.12 mmol, 1.2 eq) and left to stir at room temperature. After 30 minutes, the solvent and excess oxalyl chloride were removed by applying vacuum. Solid acceptor (0.07 mmol, 0.7 eq) and powdered LiI (53 mg, 0.40 mmol, 4 eq) were added to the vial and placed under three cycles of vacuum and nitrogen. The contents were re-dissolved in anhydrous CHCl₃ (0.25 mL, 0.4 M w.r.t. donor) and treated with iPr₂NEt (69 μL, 0.40 mmol, 4 eq). The reaction was stirred at 45 °C for 24 h. The reaction mixture was diluted with CH₂Cl₂ (1 mL) and treated with 1 M HCl (1 mL). The aqueous layer was washed with CH₂Cl₂ (2 x 1 mL) and the combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo to give a yellow or brown syrup. The α/β ratio was determined by ¹H NMR spectroscopy of the crude reaction mixture.

**General Procedure C for Mannosylation Acceptor Scope**

A 25 mL crimp-top vial charged with a stir-bar, hemiacetal (0.10 mmol, 1 eq) and Ph₃PO (28 mg, 0.10 mmol, 1 eq) was placed under three cycles of vacuum and nitrogen. The solids were dissolved in anhydrous CHCl₃ (0.2 mL, 0.5 M), treated with oxalyl chloride (10 μL, 0.12 mmol, 1.2 eq) and left to stir at room temperature. After 30 minutes, the solvent and excess oxalyl chloride were removed by applying vacuum. Powdered LiI (53 mg, 0.40 mmol, 4 eq) was added to the vial and placed under three cycles of vacuum and nitrogen. A stock solution of the acceptor in anhydrous CHCl₃ (0.4 M w.r.t. donor
or 0.28 M w.r.t acceptor) was added followed by iPr₂NEt (69 μL, 0.40 mmol, 4 eq). The reaction was stirred at 45 °C for 24 h. The reaction mixture was diluted with CH₂Cl₂ (1 mL) and treated with 1 M HCl (1 mL). The aqueous layer was washed with CH₂Cl₂ (2 x 1 mL) and the combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo to give a yellow or brown syrup. The α/β ratio was determined by ¹H NMR spectroscopy of the crude reaction mixture.

General procedure D for Rhamnosylation Donor Scope

A 25 mL crimp-top vial charged with a stir-bar, hemiacetal (0.10 mmol, 1 eq) and Ph₃PO (28 mg, 0.10 mmol, 1 eq) was placed under three cycles of vacuum and nitrogen. The solids were dissolved in anhydrous CHCl₃ (0.2 mL, 0.5 M), treated with oxalyl chloride (10 μL, 0.12 mmol, 1.2 eq) and left to stir at room temperature. After 30 minutes, the solvent and excess oxalyl chloride were removed by applying vacuum. Solid acceptor (0.07 mmol, 0.7 eq) and powdered LiI (53 mg, 0.40 mmol, 4 eq) were added to the vial and placed under three cycles of vacuum and nitrogen. The contents were re-dissolved in anhydrous CHCl₃ (0.25 mL, 0.4 M w.r.t. donor) and treated with iPr₂NEt (69 μL, 0.40 mmol, 4 eq). The reaction was stirred at 45 °C or 30 °C for 24 h. The reaction mixture was diluted with CH₂Cl₂ (15 ml) and washed with 1M HCl (2 × 5 ml), brine (10 ml), dried using Na₂SO₄, filtered and concentrated in vacuo. The α/β ratio was determined by ¹H NMR spectroscopy of the crude reaction mixture.

General procedure E for Rhamnosylation Acceptor Scope

A 25 mL crimp-top vial charged with a stir-bar, hemiacetal (0.10 mmol, 1 eq) and Ph₃PO (14 mg, 0.050 mmol, 0.5 eq) was placed under three cycles of vacuum and nitrogen. The solids were dissolved in anhydrous CHCl₃ (0.2 mL, 0.5 M), treated with oxalyl chloride (10 μL, 0.12 mmol, 1.2 eq) and left to stir at room temperature. After 1 h, the solvent and excess oxalyl chloride were removed by applying vacuum. Solid acceptor (0.07 mmol, 0.7 eq) and powdered LiI (53 mg, 0.40 mmol, 4 eq) were added to the vial and placed under three cycles of vacuum and nitrogen. The contents were re-dissolved in anhydrous CHCl₃ (0.25 mL, 0.4 M w.r.t. donor) and treated with iPr₂NEt (42 μL, 0.25 mmol, 2.5 eq). The reaction was stirred at 45 °C or 30 °C for 24 h. The reaction mixture was diluted with CH₂Cl₂ (15 ml) and washed with 1M HCl (2 × 5 ml), brine (10 ml), dried using Na₂SO₄, filtered and concentrated in vacuo. The α/β ratio was determined by ¹H NMR spectroscopy of the crude reaction mixture.
Methyl (2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside 2a

Following the general procedure A, hemiacetal 1a (54 mg, 0.10 mmol), Ph₃PO (28 mg, 0.10 mmol, 1 eq) and acceptor 3a (33 mg, 0.070 mmol) were used. The reaction was stirred at 45 °C for 18 h. ¹H NMR spectroscopy of the crude reaction mixture gave an α/β = 2:98. Purification by column chromatography (97:3; CH₂Cl₂/Et₂O) gave 2a as a white solid (55 mg, 80% yield).

1 mmol scale
In a slight modification of general procedure A, hemiacetal 1a (580 mg, 1.07 mmol), Ph₃PO (149 mg, 0.535 mmol, 0.05 eq) and acceptor 3a (348 mg, 0.750 mmol) were used. The reaction was stirred at 30 °C for 18 h. ¹H NMR spectroscopy of the crude reaction mixture gave an α/β = 4:96. Purification by column chromatography (85:15; Cyclohexane/EtOAc) gave 2a as a white solid (615 mg, 85% yield). Reaction was also performed at 45 °C leading to the desired product 2a as a white solid (α/β = 10:90, 90% yield).

β-anomer
¹H NMR (500 MHz, Chloroform-d): δ 7.48 – 7.05 (m, 35H, ArCH), 5.01 (d, J = 10.9 Hz, 1H, CHHPh), 4.93 (d, J = 12.5 Hz, 1H, CHHPh), 4.88 (d, J = 10.8 Hz, 1H, CHHPh), 4.83 (d, J = 10.9 Hz, 1H, CHHPh), 4.81 (d, J = 11.5 Hz, 1H, CHHPh), 4.81 – 4.75 (m, 2H, 2 x CHHPh), 4.66 (d, J = 12.1 Hz, 1H, CHHPh), 4.61 – 4.54 (m, 3H, H-1, 2 x CHHPh), 4.53 (d, J = 11.9 Hz, 1H, CHHPh), 4.52 (d, J = 10.7 Hz, 1H, CHHPh), 4.51 (d, J = 11.5 Hz, 1H, CHHPh), 4.47 (d, J = 11.9 Hz, 1H, CHHPh), 4.16 (dd, J = 10.5, 2.0 Hz, 1H, H-6a), 4.12 (s, 1H, H-1’), 4.02 (t, J = 9.2 Hz, 1H, H-3), 3.83 (t, J = 9.5 Hz, 1H, H-4’), 3.81 – 3.77 (m, 1H, H-5), 3.77 (dd, J = 10.9, 2.2 Hz, 1H, H-6a’), 3.75 – 3.68 (m, 2H, H-2’, H-6b’), 3.50 (dd, J = 9.7, 3.5 Hz, 1H, H-2), 3.49 – 3.41 (m, 2H, H-6b, H-4), 3.41 (dd, J = 9.4, 3.1 Hz, 1H, H-3’), 3.38 (dd, J = 9.7, 6.2, 2.1 Hz, 1H, H-5’), 3.32 (s, 3H, OCH₃). ¹³C NMR (126 MHz, Chloroform-d): δ 139.0 (C), 138.9 (C), 138.6 (C), 138.4 (2 x C), 138.3 (C), 138.2 (C), 128.6 (CH), 128.52 (CH), 128.49 (CH), 128.48 (CH), 128.46 (CH), 128.40 (CH), 128.39 (CH), 128.3 (CH), 128.21 (CH), 128.18 (CH), 128.1 (CH), 127.9 (CH), 127.79 (CH), 127.75 (CH), 127.73 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 101.6 (C-1’), 97.9 (C-1), 82.4 (C-3’), 82.3 (C-3), 80.0 (C-2), 77.8 (C-4), 76.1 (C-5’), 75.8 (PhCH₂), 75.3 (PhCH₂), 75.1 (C-4’), 74.9 (PhCH₂), 73.8 (PhCH₂), 73.7 (C-2’), 73.6 (PhCH₂), 73.5 (PhCH₂), 71.7 (PhCH₂), 69.91 (C-5), 69.88 (C-6’), 68.4 (C-6), 55.2 (OCH₃). NMR data were consistent with literature data. [33]
α-anomer

$^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 3.30 (s, 3H, OCH$_3$).

Optimisation reactions (isolated yields and $\alpha/\beta$ ratios)

| Donor | Ph$_3$PO 1 eq | Ph$_3$PO 1 eq | Ph$_3$PO 2 eq | Ph$_3$PO 0.5 eq |
|-------|---------------|---------------|---------------|---------------|
|       | 45 °C, 24 h   | 30 °C, 36 h   | 45 °C, 18 h   | 45 °C, 18 h   |
| 1b    | $\alpha/\beta = 21:79$ | $\alpha/\beta = 5:95$ | $\alpha/\beta = 5:95$ | 71%           |
|       | 71%           | 78%           |               | 93%           |
| 1c    | $\alpha/\beta = 19:81$ | $\alpha/\beta = 4:96$ | $\alpha/\beta = 4:97$ | 70%           |
|       | 70%           | 93%           |               | 90%           |
| 1d    | $\alpha/\beta = 14:86$ | $\alpha/\beta = 5:95$ | $\alpha/\beta = 3:97$ | 50% conv      |
|       | 50% conv      | 46%           |               | 71%           |
| 1e    | $\alpha/\beta = 11:89$ | $\alpha/\beta = 12:88$ | $\alpha/\beta = 59:41$ | 77%           |
|       | 77%           | 77%           | 67% conv      | 94%           |

Methyl (2,3,4-tri-O-benzyl-6-O-(4-methylbenzyl)-β-D-mannopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside 2b

Following the general procedure A, hemiacetal 1b (55 mg, 0.10 mmol) and acceptor 3a (33 mg, 0.070 mmol) were used. The reaction was stirred at 45 °C for 18 h. $^1$H NMR spectroscopy of the crude reaction mixture gave an $\alpha/\beta = 5:95$. Purification by column chromatography (97:3; CH$_2$Cl$_2$/Et$_2$O) gave 2b as a white solid (64 mg, 93% yield). ESI-HRMS for C$_{65}$H$_{88}$O$_{11}$Na$^+$ (M+Na)$^+$ calculated: 1023.4654; found: 1023.4659.

β-anomer

$^1$H NMR (600 MHz, Chloroform-$d$): $\delta$ 7.53 – 7.11 (m, 32H, ArCH), 7.07 (d, $J = 7.7$ Hz, 2H, ArCH), 5.01 (d, $J = 10.9$ Hz, 1H, CHHPh), 4.93 (d, $J = 12.5$ Hz, 1H, CHHPh), 4.87 (d, $J = 10.7$ Hz, 1H, CHHPh), 4.82 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.81 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.78 (d, $J = 12.5$ Hz, 1H, CHHPh), 4.78 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.66 (d, $J = 12.1$ Hz, 1H, CHHPh), 4.58 (d, $J = 3.5$ Hz, 1H, H-1), 4.55 (d, $J = 11.9$ Hz, 1H, CHHPh), 4.53 – 4.49 (m, 4H, 4 x CHHPh), 4.47 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.42 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.37 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.36 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.35 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.34 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.33 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.32 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.31 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.30 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.29 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.28 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.27 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.26 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.25 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.24 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.23 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.22 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.21 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.20 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.19 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.18 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.17 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.16 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.15 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.14 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.13 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.12 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.11 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.10 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.09 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.08 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.07 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.06 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.05 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.04 (d, $J = 11.4$ Hz, 1H, CHHPh), 4.03 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.02 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.01 (d, $J = 11.0$ Hz, 1H, CHHPh), 4.00 (d, $J = 11.4$ Hz, 1H, CHHPh), 3.99 (d, $J = 12.2$ Hz, 1H, CHHPh), 3.98 (d, $J = 11.7$ Hz, 1H, CHHPh).
4.16 (dd, J = 10.5, 2.0 Hz, 1H, H-6a), 4.11 (s, 1H, H-1’), 4.02 (t, J = 9.2 Hz, 1H, H-3), 3.82 (t, J = 9.5 Hz, 1H, H-4’), 3.80 – 3.77 (m, 1H, H-5), 3.75 (dd, J = 10.9, 1.9 Hz, 1H, H-6a’), 3.72 (d, J = 3.0 Hz, 1H, H-2’), 3.70 (dd, J = 10.8, 5.9 Hz, 1H, H-6b’), 3.50 (dd, J = 9.6, 3.5 Hz, 1H, H-2), 3.47 – 3.42 (m, 2H, H-6b, H-4), 3.40 (dd, J = 9.4, 3.0 Hz, 1H, H-3’), 3.37 (ddd, J = 9.6, 5.9 Hz, 1H, H-6b’), 3.33 (s, 3H, OCH3), 3.30 (s, 3H, CH3). 13C NMR (151 MHz, Chloroform-d): δ 139.0 (C), 138.9 (C), 138.43 (C), 138.42 (C), 138.3 (C), 138.2 (C), 137.2 (C), 135.5 (C), 129.1 (CH), 128.6 (CH), 128.51 (CH), 128.47 (CH), 128.42 (CH), 128.40 (CH), 128.28 (CH), 128.27 (CH), 128.20 (CH), 128.18 (CH), 128.10 (CH), 127.77 (CH), 127.76 (CH), 127.73 (CH), 127.71 (CH), 127.66 (CH), 127.5 (CH), 101.6 (C-1’, 1JCH = 154.0 Hz, from coupled HSQC), 97.9 (C-1, 1JCH = 170.0 Hz, from coupled HSQC), 82.4 (C-3’), 82.3 (C-3), 80.0 (C-2), 77.8 (C-4), 76.1 (C-5’), 75.8 (PhCH2), 75.3 (PhCH2), 75.1 (C-4’), 74.9 (PhCH2), 73.8 (PhCH2), 73.7 (C-2’), 73.46 (PhCH2), 73.45 (PhCH2), 71.7 (PhCH2), 69.9 (C-5), 69.6 (C-6’), 68.4 (C-6), 55.2 (OCH3), 21.3 (CH3).

α-anomer

1H NMR (600 MHz, Chloroform-d): δ 4.96 (d, J = 1.8 Hz, 1H, H-1’), 3.30 (s, 3H, OCH3).

13C NMR (151 MHz, Chloroform-d): δ 98.4 (C-1’, 1JCH = 170.0 Hz, from coupled HSQC).

β-anomer

Methyl (2,3,6-tri-O-benzyl-4-O-(4-methylbenzyl)-β-D-mannopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside 2c

Following the general procedure A, hemiacetal 1c (55 mg, 0.10 mmol) and acceptor 3a (32 mg, 0.069 mmol) were used. The reaction was stirred at 45 °C for 18 h. 1H NMR spectroscopy of the crude reaction mixture gave an α/β = 4:96. Purification by column chromatography (97:3; CH2Cl2/Et2O) gave 2c as a white solid (62 mg, 90% yield). ESI-HRMS for C63H68O11Na+ (M+Na)+ calculated: 1023.4654; found: 1023.4659.

β-anomer

1H NMR (500 MHz, Chloroform-d): δ 7.43 – 7.15 (m, 32H, ArCH), 7.07 (s, 2H, ArCH), 5.01 (d, J = 11.0 Hz, 1H, CHHPh), 4.93 (d, J = 12.5 Hz, 1H, CHHPh), 4.83 (d, J = 10.5 Hz, 1H, CHHPh), 4.82 (d, J = 10.9 Hz, 1H, CHHPh), 4.81 (d, J = 11.5 Hz, 1H, CHHPh), 4.78 (d, J = 12.5 Hz, 1H, CHHPh), 4.78 (d, J = 12.1 Hz, 1H, CHHPh), 4.66 (d, J = 12.1 Hz, 1H, CHHPh), 4.62 – 4.54 (m, 3H, 2 x CHHPh, H-1), 4.53 (d, J = 11.9 Hz, 1H, CHHPh), 4.51 (d, J = 11.5 Hz, 1H, CHHPh), 4.49 (d, J = 11.9 Hz, 1H, CHHPh), 4.48 (d, J = 10.5 Hz, 1H, CHHPh), 4.15 (dd, J = 10.5, 2.0 Hz, 1H, H-6a), 4.11 (d, J = 0.7 Hz,
1H, H-1‘), 4.01 (dd, J = 9.7, 8.8 Hz, 1H, H-3), 3.81 (t, J = 9.5 Hz, 1H, H-4‘), 3.81 – 3.74 (m, 2H, H-5, H-6a’), 3.73 – 3.67 (m, 2H, H-2‘, H-6b’), 3.50 (dd, J = 9.7, 3.5 Hz, 1H, H-2), 3.49 – 3.40 (m, 2H, H-6b, H-4), 3.40 (dd, J = 9.4, 3.0 Hz, 1H, H-3‘), 3.37 (ddd, J = 9.7, 6.1, 1.9 Hz, 1H, H-5‘), 3.32 (s, 3H, OCH3), 2.32 (s, 3H, CH3). 13C NMR (126 MHz, Chloroform-d): δ 139.0 (C), 138.9 (C), 138.6 (C), 138.42 (C), 138.35 (C), 138.2 (C), 137.5 (C), 129.1 (CH), 128.6 (CH), 128.52 (CH), 128.48 (CH), 128.39 (CH), 128.38 (CH), 128.37 (CH), 128.27 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.72 (CH), 127.67 (CH), 127.6 (CH), 127.5 (CH), 101.6 (C-1‘), 1JCH = 154.8 Hz, from coupled HSQC), 97.9 (C-1, 1JCH = 169.8 Hz, from coupled HSQC), 82.4 (C-3‘), 82.3 (C-3), 80.0 (C-2), 77.8 (C-4), 76.1 (C-5‘), 75.8 (PhCH2), 75.2 (PhCH2), 74.94 (C-4‘), 74.85 (PhCH2), 73.8 (PhCH2 and C-2‘), 73.6 (PhCH2), 73.5 (PhCH2), 71.7 (PhCH2), 69.91 (C-5), 69.87 (C-6‘), 68.4 (C-6), 55.2 (OCH3), 21.3 (CH3).

α-anomer
1H NMR (500 MHz, Chloroform-d): δ 4.95 (d, J = 1.9 Hz, 1H, H-1‘), 3.30 (s, 3H, OCH3).

13C NMR (126 MHz, Chloroform-d): δ 98.4 (C-1, 1JCH = 171.2 Hz, from coupled HSQC).

Following the general procedure A, hemiacetal 1d (57 mg, 0.10 mmol) and acceptor 3a (32 mg, 0.069 mmol) were used. The reaction was stirred at 45 °C for 18 h. 1H NMR spectroscopy of the crude reaction mixture gave an α/β = 3:97. Purification by column chromatography (97:3; CH2Cl2/Et2O) gave 2d as a white solid (49 mg, 71% yield). ESI-HRMS for C63H68O12Na+ (M+Na)+ calculated: 1039.4603; found: 1039.4613.

β-anomer
1H NMR (600 MHz, Chloroform-d): δ 7.45 – 7.14 (m, 32H, ArCH), 6.82 – 6.74 (m, 2H, ArCH), 5.01 (d, J = 10.9 Hz, 1H, CHPh), 4.93 (d, J = 12.5 Hz, 1H, CHPh), 4.87 (d, J = 10.7 Hz, 1H, CHPh), 4.82 (d, J = 10.9 Hz, 1H, CHPh), 4.81 (d, J = 11.4 Hz, 1H, CHPh), 4.78 (d, J = 12.5 Hz, 1H, CHPh), 4.78 (d, J = 12.1 Hz, 1H, CHPh), 4.66 (d, J = 12.1 Hz, 1H, CHPh), 4.58 (d, J = 3.5 Hz, 1H, H-1), 4.55 – 4.45 (m, 6H, 6 x CHPh), 4.17 (dd, J = 10.5, 2.0 Hz, 1H, H-6a), 4.12 (s, 1H, H-1‘), 4.02 (t, J = 9.2 Hz, 1H, H-3), 3.82 (t, J = 9.5 Hz, 1H, H-4‘), 3.80 (ddd, J = 10.1, 5.5, 1.9 Hz, 1H, H-5), 3.75 (s, 3H, OCH3), 3.75 – 3.73 (m, 1H, H-6a‘), 3.73 – 3.71 (m, 1H, H-2‘), 3.69 (dd, J = 10.9, 5.9 Hz, 1H, H-6b‘), 3.50 (dd, J = 9.7, 3.5 Hz, 1H, H-2), 3.46 (dd, J = 10.6, 5.4 Hz, 1H, H-6b), 3.44 (dd, J = 10.0, 8.8 Hz, 1H, H-1‘), 3.41 (t, J = 9.5 Hz, 1H, H-4‘), 3.37 (t, J = 9.5 Hz, 1H, H-4‘), 3.30 (s, 3H, OCH3), 2.32 (s, 3H, CH3).
1H, H-4), 3.41 (dd, J = 9.4, 3.0 Hz, 1H, H-3’), 3.36 (ddd, J = 9.8, 5.9, 2.0 Hz, 1H, H-5’), 3.33 (s, 3H, OCH3). 13C NMR (151 MHz, Chloroform-d): δ 159.2 (C), 139.0 (C), 138.9 (C), 138.43 (C), 138.42 (C), 138.3 (C), 138.2 (C), 130.6 (C), 129.6 (CH), 128.6 (CH), 128.51 (CH), 128.48 (CH), 128.43 (CH), 128.39 (CH), 128.3 (CH), 128.19 (CH), 128.18 (CH), 128.1 (CH), 128.78 (CH), 127.78 (CH), 127.73 (CH), 127.72 (CH), 127.67 (CH), 127.5 (CH), 113.8 (CH), 101.6 (C-1’), \(^1J_{CH} = 155.0\) Hz, from coupled HSQC), 97.90 (C-1, \(^1J_{CH} = 170.1\) Hz, from coupled HSQC), 82.4 (C-3’), 82.3 (C-3), 80.0 (C-2), 77.8 (C-4), 76.1 (C-5’), 75.8 (PhCH2), 75.3 (PhCH2), 75.1 (C-4’), 74.9 (PhCH2), 73.8 (PhCH2), 73.8 (C-2’), 73.5 (PhCH2), 72.22 (PhCH2), 71.7 (PhCH2), 69.9 (C-5), 69.4 (C-6’), 68.4 (C-6), 55.3 (OCH3), 55.2 (OCH3).

\(\alpha\)-anomer

\(^1\)H NMR (500 MHz, Chloroform-d): δ 4.96 (d, J = 1.7 Hz, 1H, H-1’), 3.30 (s, 3H, OCH3). 13C NMR (126 MHz, Chloroform-d) from HSQC: δ 98.3 (C-1’).

Methyl (2,3,4-tri-O-benzyl-6-O-(2-naphthyl)-\(\beta\)-D-mannopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-\(\alpha\)-D-glucopyranoside 2e

Following the general procedure A, hemiacetal 1e (59 mg, 0.10 mmol) and acceptor 3a (32 mg, 0.069 mmol) were used. The reaction was stirred at 45 °C for 18 h. \(^1\)H NMR spectroscopy of the crude reaction mixture gave an \(\alpha/\beta = 5:95\). Purification by column chromatography (97:3; CH2Cl2/Et2O) gave 2e as a white solid (68 mg, 94% yield). ESI-HRMS for C_{60}H_{88}O_{11}Na^+ (M+Na)^+ calculated: 1059.4654; found: 1059.4660.

\(\beta\)-anomer

\(^1\)H NMR (500 MHz, Chloroform-d): δ 7.86 – 7.70 (m, 4H, ArCH), 7.52 – 7.07 (m, 33H, ArCH), 5.01 (d, J = 10.9 Hz, 1H, CHHPh), 4.94 (d, J = 12.5 Hz, 1H, CHHPh), 4.87 (d, J = 10.8 Hz, 1H, CHHPh), 4.82 (d, J = 11.0 Hz, 1H, CHHPh), 4.80 (d, J = 11.5 Hz, 1H, CHHPh), 4.79 (d, J = 12.5 Hz, 1H, CHHPh), 4.78 (d, J = 12.0 Hz, 1H, CHHPh), 4.75 (d, J = 12.3 Hz, 1H, CHHPh), 4.72 (d, J = 12.3 Hz, 1H, CHHPh), 4.66 (d, J = 12.1 Hz, 1H, CHHPh), 4.58 (d, J = 3.5 Hz, 1H, H-1), 4.56 – 4.56 (m, 4H, 4 x CHHPh), 4.18 (dd, J = 10.5, 2.0 Hz, 1H, H-6a), 4.13 (s, 1H, H-1’), 4.02 (t, J = 9.2 Hz, 1H, H-3), 3.88 – 3.81 (m, 1H, H-4’), 3.83 – 3.78 (m, 2H, H-5, H-6a’), 3.75 (dd, J = 10.9, 6.0 Hz, 1H, H-6b’), 3.73 (d, J = 2.9 Hz, 1H, H-2’), 3.51 (dd, J = 9.6, 3.5 Hz, 1H, H-2), 3.50 – 3.37 (m, 4H, H-6b, H-4, H-3’, H-5’), 3.32 (s, 3H, OCH3). 13C NMR (126 MHz, Chloroform-d): δ 139.0 (C), 138.9 (C), 138.4 (C), 138.31 (C), 138.29 (C), 58
138.2 (C), 136.1 (C), 133.4 (C), 133.1 (C), 128.6 (CH), 128.51 (CH), 128.49 (CH), 128.47 (CH), 128.40 (CH), 128.3 (CH), 128.17 (CH), 128.15 (CH), 128.05 (CH), 128.02 (CH), 127.8 (CH), 127.74 (CH), 127.67 (CH), 127.5 (CH), 126.6 (CH), 126.1 (CH), 125.9 (CH), 101.7 (C-1’, 1JCH = 154.1 Hz, from coupled HSQC), 97.9 (C-1, 1JCH = 169.1 Hz, from coupled HSQC), 82.4 (C-3’), 82.3 (C-3), 80.0 (C-2), 77.8 (C-4), 76.1 (C-5’), 75.8 (PhCH2), 75.3 (PhCH2), 75.1 (C-4’), 74.8 (PhCH2), 73.82 (PhCH2), 73.72 (C-2’), 73.69 (PhCH2), 73.5 (PhCH2), 71.7 (PhCH2), 69.9 (C-5), 69.8 (C-6’), 68.4 (C-6), 55.2 (OCH3).

\( \alpha \)-anomer

\(^1\)H NMR (500 MHz, Chloroform-\( \text{d} \)): \( \delta 4.98 \) (d, \( J = 1.9 \) Hz, 1H, H-1’), 3.30 (s, 3H, OCH3). \(^{13}\)C NMR (126 MHz, Chloroform-\( \text{d} \)) from short HSQC: \( \delta 98.5 \) (C-1’).

Methyl (2,3,4-tri-O-benzyl-6-O-tert-butyldiphenylsilyl-\( \beta \)-D-mannopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-\( \alpha \)-D-glucopyranoside 2f

Following the general procedure A, hemiacetal 1f (69 mg, 0.10 mmol) and acceptor 3a (32 mg, 0.069 mmol) were used. The reaction was stirred at 45 °C for 18 h. \(^1\)H NMR spectroscopy of the crude reaction mixture gave an \( \alpha/\beta = 9:91 \). Purification by column chromatography (100:0 to 97:3; CH2Cl2/Et2O) gave 2f as a white solid (74 mg, 95% yield). ESI-HRMS for C71H82O11SiN+ (M+NH4)+ calculated: 1152.5652; found: 1152.5654.

\( \beta \)-anomer

\(^1\)H NMR (500 MHz, Chloroform-\( \text{d} \)): \( \delta 7.83 – 7.76 \) (m, 2H, ArCH), 7.77 – 7.66 (m, 2H, ArCH), 7.49 – 7.12 (m, 36H, ArCH), 5.03 (d, \( J = 10.9 \) Hz, 1H, CHHPh), 4.96 (d, \( J = 12.2 \) Hz, 1H, CHHPh), 4.93 (d, \( J = 10.8 \) Hz, 1H, CHHPh), 4.89 – 4.75 (m, 4H, 4 x CHHPh), 4.68 (d, \( J = 12.1 \) Hz, 1H, CHHPh), 4.64 – 4.53 (m, 5H, H-1, 4 x CHHPh), 4.19 (dd, \( J = 10.6, 2.0 \) Hz, 1H, H-6a), 4.15 (s, 1H, H-1’), 4.05 (t, \( J = 9.2 \) Hz, 1H, H-3), 4.02 (t, \( J = 9.5 \) Hz, 1H, H-4’), 3.98 (dd, \( J = 11.1, 4.8 \) Hz, 1H, H-6a’), 3.95 (dd, \( J = 11.1, 2.3 \) Hz, 1H, H-6b’), 3.82 (ddd, \( J = 10.0, 5.2, 2.0 \) Hz, 1H, H-5), 3.76 (d, \( J = 3.1 \) Hz, 1H, H-2’), 3.54 – 3.45 (m, 3H, H-2, H-4, H-6b), 3.46 (dd, \( J = 9.4, 2.9 \) Hz, 1H, H-3’), 3.37 (s, 3H, OCH3), 3.29 (ddd, \( J = 9.6, 4.9, 2.2 \) Hz, 1H, H-5’), 1.03 (s, 9H, SiC(CH3)3). \(^{13}\)C NMR (126 MHz, Chloroform-\( \text{d} \)): \( \delta 139.1 \) (C), 138.9 (C), 138.6 (C), 138.5 (C), 138.4 (C), 138.2 (C), 136.0 (CH), 135.7 (CH), 134.1 (C), 133.6 (C), 129.60 (CH), 129.55 (CH), 128.6 (CH), 128.51 (CH), 128.50 (CH), 128.45 (CH), 128.3 (CH), 128.19 (CH), 128.16 (CH), 128.10 (CH), 128.05 (CH), 127.76 (CH), 127.75 (CH), 127.73 (CH), 127.67 (CH), 59
Following the general procedure A, hemiacetal $1g$ (56 mg, 0.10 mmol), Ph$_3$PO (28 mg, 0.10 mmol, 1 eq) and acceptor $3a$ (32 mg, 0.069 mmol) were used. The reaction was stirred at 45 °C for 24 h. $^1$H NMR spectroscopy of the crude reaction mixture gave an $\alpha/\beta = 5:95$. Purification by column chromatography (97:3; CH$_2$Cl$_2$/Et$_2$O) gave $2g$ as a white solid (31 mg, 44% yield). ESI-HRMS for $C_{68}H_{101}O_SiNa^+$ (M+Na)$^+$ calculated: 1033.4893; found: 1033.4897.

**β-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.40 – 7.11 (m, 30H, ArCH), 5.00 (d, $J = 10.9$ Hz, 1H, CH$_3$Ph), 4.89 (d, $J = 12.4$ Hz, 1H, CH$_3$Ph), 4.82 (d, $J = 11.0$ Hz, 1H, CH$_3$Ph), 4.81 (d, $J = 11.2$ Hz, 1H, CH$_3$Ph), 4.78 (d, $J = 12.1$ Hz, 1H, CH$_3$Ph), 4.65 (d, $J = 12.1$ Hz, 1H, CH$_3$Ph), 4.64 (d, $J = 12.0$ Hz, 1H, CH$_3$Ph), 4.64 (d, $J = 12.3$ Hz, 1H, CH$_3$Ph), 4.57 (d, $J = 3.5$ Hz, 1H, H-1'), 4.51 (d, $J = 11.4$ Hz, 1H, CH$_3$Ph), 4.50 (d, $J = 12.1$ Hz, 1H, CH$_3$Ph), 4.49 (d, $J = 11.9$ Hz, 1H, CH$_3$Ph), 4.39 (d, $J = 11.9$ Hz, 1H, CH$_3$Ph), 4.23 (d, $J = 0.9$ Hz, 1H, H-1'), 4.18 (dd, $J = 10.5$, 2.0 Hz, 1H, H-6a), 4.01 (t, $J = 9.3$ Hz, 1H, H-3), 3.88 (t, $J = 9.1$ Hz, 1H, H-4'), 3.82 (dd, $J = 10.7$, 1.9 Hz, 1H, H-6a'), 3.81 – 3.76 (m, 1H, H-5), 3.71 (d, $J = 2.8$ Hz, 1H, H-2'), 3.62 (dd, $J = 10.7$, 7.4 Hz, 1H, H-6b'), 3.53 – 3.46 (m, 2H, H-2, H-6b), 3.44 (dd, $J = 10.0$, 8.9 Hz, 1H, H-4), 3.35 (ddd, $J = 9.3$, 7.4, 1.9 Hz, 1H, H-5'), 3.31 (s, 3H, OCH$_3$), 3.20 (dd, $J = 9.0$, 2.8 Hz, 1H, H-3'), 0.79 (s, 9H, SiC(CH$_3$)$_3$), -0.028 (s, 3H, SiCH$_3$), -0.035 (s, 3H, SiCH$_3$). $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 139.1 (C), 139.0 (C), 138.7 (C), 138.4 (C), 138.23 (C), 138.21 (C), 128.6 (CH), 128.53 (CH), 128.49 (CH), 128.4 (CH), 128.31 (CH), 128.30 (CH), 128.19 (CH), 128.16 (CH), 128.08 (CH), 128.06 (CH), 128.0 (CH), 127.79 (CH), 127.76 (CH), 127.7 (CH), 127.64 (CH), 127.55 (CH), 127.5 (CH), 127.4 (CH), 101.4 (C-1'), $^1$J$_{ICCH} = 155.4$ Hz, from coupled HSQC), 97.9 (C-1), $^1$J$_{ICH} = 170.2$ Hz. 

Methyl (2,3,6-tri-O-benzyl-4-O-tert-butyldimethylsilyl-β-D-mannopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside 2g

![structure of compound 2g](image-url)
Hz, from coupled HSQC), 82.4 (C-3’), 82.3 (C-3), 80.0 (C-2), 77.9 (C-4), 77.7 (C-5’), 75.9 (PhCH₂), 74.9 (PhCH₂), 74.02 (C-2’), 73.98 (PhCH₂), 73.6 (PhCH₂), 73.5 (PhCH₂), 71.2 (PhCH₂), 70.4 (C-6’), 70.0 (C-5), 68.4 (C-4’), 68.3 (C-6), 55.1 (OCH₃), 26.1 (SiC(CH₃)₃), 18.2 (SiC(CH₃)₃), -3.6 (SiCH₃), -4.8 (SiCH₃).

α-anomer

1H NMR (500 MHz, Chloroform-d): δ 3.30 (s, 3H, OCH₃).

Methyl (2,3,4-tri-O-benzyl-6-O-(benzoyl)-α/β-D-mannopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside 2h

Following the general procedure A, hemiacetal 1h (55 mg, 0.10 mmol), Ph₃PO (28 mg, 0.10 mmol, 1 eq) and acceptor 3a (32 mg, 0.069 mmol) were used. The reaction was stirred at 45 °C for 44 h. 1H NMR spectroscopy of the crude reaction mixture gave an α/β = 15:85. Purification by column chromatography (97:3; CH₂Cl₂/Et₂O) gave 2h as a white solid (23 mg, 37% yield).

β-anomer

1H NMR (500 MHz, Chloroform-d): δ 8.05 – 7.98 (m, 2H, ArCH), 7.52 – 7.46 (m, 1H, ArCH), 7.45 – 7.41 (m, 2H, ArCH), 7.39 – 7.11 (m, 30H, ArCH), 4.99 (d, J = 10.9 Hz, 1H, CHHPh), 4.94 (d, J = 12.3 Hz, 1H, CHHPh), 4.93 (d, J = 10.7 Hz, 1H, CHHPh), 4.80 (d, J = 10.9 Hz, 1H, CHHPh), 4.80 (d, J = 11.5 Hz, 1H, CHHPh), 4.78 (d, J = 12.3 Hz, 1H, CHHPh), 4.76 (d, J = 12.2 Hz, 1H, CHHPh), 4.64 (d, J = 12.1 Hz, 1H, CHHPh), 4.61 (dd, J = 11.7, 2.3 Hz, 1H, H-6a’), 4.59 (d, J = 10.7 Hz, 1H, CHHPh), 4.59 (d, J = 11.9 Hz, 1H, CHHPh), 4.55 (d, J = 3.6 Hz, 1H, H-1), 4.52 (d, J = 11.8 Hz, 1H, CHHPh), 4.49 (d, J = 11.5 Hz, 1H, CHHPh), 4.48 (dd, J = 11.7, 5.5 Hz, 1H, H-6b’), 4.19 (s, 1H, H-1’), 4.12 (dd, J = 10.5, 2.0 Hz, 1H, H-6a), 3.99 (t, J = 9.4 Hz, 1H, H-4’), 3.98 (t, J = 9.2 Hz, 1H, H-3), 3.81 – 3.76 (m, H-1, H-5), 3.78 (d, J = 3.0 Hz, 1H, H-2’), 3.52 (ddd, J = 9.6, 5.5, 2.3 Hz, 1H, H-5’), 3.50 – 3.43 (m, 3H, H-3’, H-2, H-6b), 3.39 (dd, J = 10.1, 8.8 Hz, 1H, H-4), 3.28 (s, 3H, OCH₃). 13C NMR (126 MHz, Chloroform-d): δ 166.5 (C=O), 138.92 (C), 138.85 (C), 138.3 (C), 138.2 (C), 138.13 (C), 138.10 (C), 133.0 (CH), 130.2 (C), 129.9 (CH), 128.60 (CH), 128.57 (CH), 128.56 (CH), 128.54 (CH), 128.51 (CH), 128.4 (CH), 128.34 (CH), 128.31 (CH), 128.29 (CH), 128.14 (CH), 128.10 (CH), 128.08 (CH), 127.88 (CH), 127.86 (CH), 127.79 (CH), 127.76 (CH), 127.5 (CH), 101.9 (C-1’), 97.9 (C-1), 82.2 (C-3 and C-3’), 80.0 (C-2), 77.9 (C-4), 75.9 (PhCH₂), 75.4 (PhCH₂), 74.9 (PhCH₂), 74.8 (C-4’), 73.9 (PhCH₂, C-2’).
and C-5’), 73.5 (PhCH$_2$), 71.7 (PhCH$_2$), 69.9 (C-5), 68.6 (C-6), 64.2 (C-6’), 55.1 (OCH$_3$). NMR data were consistent with literature data.

**α-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 3.31 (s, 3H, OCH$_3$).

Following general procedure A, hemiacetal 1i (58 mg, 0.10 mmol), iPr$_2$NEt (70 μL, 0.4 mmol) and acceptor 3a (33 mg, 0.07 mmol) were used. The reaction was stirred at 45 °C for 24 h. $^1$H NMR spectroscopy of the crude reaction mixture showed $\beta$-only product. Purification by column chromatography (6:4; pentane/ Et$_2$O) afforded the desired product 2i as a colourless syrup (72 mg, quantitative yield). $R_f$ = 0.5 (4:1; cyclohexane/ EtOAc); $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.39 – 7.08 (m, 27H, Ar-CH), 5.01 (d, $J$ = 10.8 Hz, 1H, PhCH$_2$), 4.92 – 4.70 (m, 6H, 4 x PhCH$_2$), 4.67 (d, $J$ = 12.1 Hz, 1H, PhCH$_2$), 4.60 – 4.57 (m, 1H, H-1), 4.53 – 4.43 (m, 4H, 4 x PhCH$_2$), 4.41 (d, $J$ = 11.8 Hz, 1H, H-6a’), 4.17 (dd, $J$ = 11.6, 6.9 Hz, 1H, H-6b’), 4.14 – 4.11 (m, 2H, H-6a, H-1’), 4.00 (t, $J$ = 9.3 Hz, 1H, H-3), 3.82 – 3.73 (m, 2H, H-4’, H-5’), 3.70 (br s, 1H, H-2’), 3.51 (ddd, $J$ = 9.7, 3.5, 1.6 Hz, 1H, H-2), 3.48 – 3.34 (m, 4H, H-6b, H-4, H-3’, H-5), 3.30 (s, 3H, OCH$_3$), 2.35 – 2.31 (m, 9H, CH$_3$), 1.15 (d, $J$ = 1.7 Hz, 9H, CH$_3$). $^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 178.2 (C=O), 138.8 (4ºC), 138.3 (4ºC), 138.1 (4ºC), 137.6 (4ºC), 137.4 (4ºC), 137.0 (4ºC), 135.6 (4ºC), 135.1 (4ºC), 135.0 (4ºC), 129.13 (Ar-CH), 129.09 (Ar-CH), 128.8 (Ar-CH), 128.50 (Ar-CH), 128.48 (Ar-CH), 128.42 (Ar-CH), 128.39 (Ar-CH), 128.3 (Ar-CH), 128.2 (Ar-CH), 128.1 (Ar-CH), 128.0 (Ar-CH), 127.8 (Ar-CH), 127.7 (Ar-CH), 127.7 (Ar-CH), 101.5 (C-1’, $^1$J$_{C,H}$ = 156.0 Hz, from coupled HSQC), 97.8 (C-1, $^1$J$_{C,H}$ = 170.5 Hz, from coupled HSQC), 82.2 (C-3), 82.1 (C-3’), 79.9 (C-2), 77.7 (C-4), 75.8 (PhCH$_2$), 75.2 (PhCH$_2$), 74.8 (C-4’, PhCH$_2$), 73.9 (C-5), 73.40 (PhCH$_2$), 73.36 (PhCH$_2$), 73.1 (C-2’), 71.5 (PhCH$_3$), 69.7 (C-5’), 68.1 (C-6), 63.7 (C-6’), 55.0 (OCH$_3$), 38.8 (C(CH$_3$)$_2$)), 27.2 (2 x CH$_3$), 21.2 (CH$_3$). ESI-HRMS for C$_{63}$H$_{74}$O$_{12}$Na$^+$ (M+Na)$^+$ calculated: 1045.5072; found: 1045.5074.
Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4-tri-O-benzyl-β-L-rhamnosyl)-α-D-glucopyranoside 2j

Following general procedure D, hemiacetal 1j (50 mg, 0.12 mmol), Ph₃PO (33.4 mg, 0.120 mmol), (COCl)₂ (12 μL, 0.14 mmol), LiI (64 mg, 0.48 mmol), iPr₂NEt (52 μL, 0.30 mmol) and acceptor 3a (40.0 mg, 0.084 mmol) were used. The reaction was stirred at 45 °C for 15 h. ¹H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (4:1; cyclohexane/ EtOAc) afforded the desired product 2i as a colourless syrup (74 mg, quantitative yield). Rf = 0.7 (7:3; cyclohexane/ EtOAc); ¹H NMR (600 MHz, Chloroform-d) δ 7.43 – 7.19 (m, 30H, Ar-CH), 4.98 – 4.93 (m, 3H, 3 × PhCH₂), 4.86 (d, J = 11.6 Hz, 2H, 2 × PhCH₂), 4.80 (d, J = 12.2 Hz, 1H, PhCH₂), 4.79 – 4.74 (m, 2H, 2 × PhCH₂), 4.66 (d, J = 12.2 Hz, 1H, PhCH₂), 4.62 (d, J = 10.9 Hz, 1H, PhCH₂), 4.60 (d, J = 3.5 Hz, 1H, H-1), 4.53 (d, J = 11.9 Hz, 1H, PhCH₂), 4.46 (d, J = 11.9 Hz, 1H, PhCH₂), 4.42 (s, 1H, H-1’), 4.28 (dd, J = 11.1, 3.2 Hz, 1H, H-6a), 3.98 (t, J = 9.3 Hz, 1H, H-3), 3.95 (d, J = 3.0 Hz, 1H, H-2’), 3.76 – 3.71 (m, 1H, H-5), 3.65 – 3.60 (m, 2H, H-4, H-6b), 3.58 (t, J = 9.3 Hz, 1H, H-4’), 3.48 (dd, J = 9.6, 3.5 Hz, 1H, H-2), 3.44 (dd, J = 9.4, 3.0 Hz, 1H, H-3’), 3.35 (s, 3H, OCH₃), 3.31 (dq, J = 9.2, 6.1 Hz, 1H, H-5’), 1.34 (d, J = 6.1 Hz, 3H, H-6’). ¹³C NMR (151 MHz, Chloroform-d) δ 138.9 (4ºC), 138.8 (4ºC), 138.6 (4ºC), 138.4 (4ºC), 138.23 (4ºC), 138.21 (4ºC), 128.5 (Ar-CH), 128.36 (Ar-CH), 128.35 (Ar-CH), 128.34 (Ar-CH), 128.31 (Ar-CH), 128.23 (Ar-CH), 128.16 (Ar-CH), 128.11 (Ar-CH), 128.09 (Ar-CH), 128.06 (Ar-CH), 127.89 (Ar-CH), 127.88 (Ar-CH), 127.67 (Ar-CH), 127.66 (Ar-CH), 127.58 (Ar-CH), 127.57 (Ar-CH), 127.54 (Ar-CH), 127.4 (Ar-CH), 101.4 (C-1’, JCH = 156.1 Hz, from coupled HSQC), 98.3 (C-1, JCH = 169.2 Hz, from coupled HSQC), 82.0 (C-3’), 81.8 (C-3), 80.2 (C-4), 79.9 (C-2), 77.8 (C-4’), 75.7 (PhCH₂), 75.4 (PhCH₂), 75.2 (PhCH₂), 74.3 (C-2’), 74.0 (PhCH₂), 73.5 (PhCH₂), 72.0 (C-5’), 71.3 (PhCH₂), 70.0 (C-5), 67.2 (C-6), 55.2 (OCH₃), 18.0 (C-6’). NMR data were consistent with the literature. ESI-HRMS for C₅₆H₆₀NO₁₀⁺ (M+NH₄)⁺ calculated: 898.4525; found: 898.4531.
Methyl 2,3,4-tri-O-benzyl-6-O-(2,3-di-O-benzyl-4-O-p-methylbenzyl-β-L-rhamnosyl)-α-D-glucopyranoside 2k

Following general procedure D, hemiacetal 1k (45 mg, 0.1 mmol), Ph₃PO (28 mg, 0.1 mmol), (COCl): (10 μL, 0.12 mmol), LiI (54 mg, 0.4 mmol), iPr₂NEt (44 μL, 0.25 mmol) and acceptor 3a (33 mg, 0.07 mmol) were used. The reaction was stirred at 30 °C for 20 h. ¹H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (9:1 to 6:4; pentane/ EtOAc) afforded the desired disaccharide 2j as a colourless syrup (64 mg, quantitative yield). Rₜ = 0.4 (4:1; cyclohexane/EtOAc); Reaction at 45 °C gave desired disaccharide 2j as an α:β anomic mixture (α/β 18:82). ¹H NMR (600 MHz, Chloroform-d) δ 7.45 – 7.40 (m, 2H, Ar-CH), 7.40 – 7.17 (m, 25H, Ar-CH), 7.12 (d, J = 7.8 Hz, 2H, Ar-CH), 4.97 (s, 1H, PhCH₂), 4.96 – 4.94 (m, 1H, PhCH₂), 4.90 (d, J = 10.6 Hz, 1H, PhCH₂), 4.86 (d, J = 11.6 Hz, 2H, 2 × PhCH₂), 4.80 (d, J = 12.1 Hz, 1H, PhCH₂), 4.78 – 4.76 (m, 2H, 2 × PhCH₂), 4.66 (d, J = 12.1 Hz, 1H, PhCH₂), 4.60 (d, J = 3.5 Hz, 1H, H-1), 4.57 (d, J = 10.6 Hz, 1H, PhCH₂), 4.53 (d, J = 11.9 Hz, 1H, PhCH₂), 4.47 (d, J = 11.9 Hz, 1H, PhCH₂), 4.42 (s, 1H, H-1‘), 4.27 (dd, J = 11.1, 3.2 Hz, 1H, H-6a), 3.98 (t, J = 9.3 Hz, 1H, H-3), 3.94 (d, J = 3.0 Hz, 1H, H-2‘), 3.73 (ddd, J = 10.1, 3.2, 1.9 Hz, 1H, H-5), 3.65 – 3.60 (m, 2H, H-4, H-6b), 3.58 (t, J = 9.3 Hz, 1H, H-4‘), 3.50 – 3.46 (m, 1H, H-2), 3.43 (dd, J = 9.4, 3.0 Hz, 1H, H-3‘), 3.34 (s, 3H, OCH₃), 3.29 (dq, J = 9.2, 6.2 Hz, 1H, H-5‘), 2.32 (s, 3H, CH₃), 1.34 (d, J = 6.1 Hz, 3H, H-6‘). ¹³C NMR (151 MHz, Chloroform-d) δ 138.9 (4°C), 138.8 (4°C), 138.4 (4°C), 138.3 (4°C), 138.2 (4°C), 137.4 (4°C), 135.5 (4°C), 129.0 (Ar-CH), 128.5 (Ar-CH), 128.37 (Ar-CH), 128.35 (Ar-CH), 128.31 (Ar-CH), 128.25 (Ar-CH), 128.22 (Ar-CH), 128.17 (Ar-CH), 128.12 (Ar-CH), 128.09 (Ar-CH), 127.90 (Ar-CH), 127.89 (Ar-CH), 127.7 (Ar-CH), 127.58 (Ar-CH), 127.56 (Ar-CH), 127.54 (Ar-CH), 127.4 (Ar-CH), 101.4 (C-1‘), 1JCH = 154.0 Hz, from coupled HSQC), 98.3 (C-1), 1JCH = 170.8 Hz, from coupled HSQC), 82.0 (C-3‘), 81.9 (C-3), 80.1 (C-4‘), 79.9 (C-2), 77.8 (C-4), 75.7 (PhCH₂), 75.3 (PhCH₂), 75.2 (PhCH₂), 74.4 (C-2‘), 74.0 (PhCH₂), 73.5 (PhCH₂), 72.0 (C-5‘), 71.4 (PhCH₂), 70.0 (C-5), 67.2 (C-6), 55.2 (OCH₃), 21.2 (CH₃), 18.0 (C-6‘). ESI-HRMS C₆₅H₆₆NO₁₀⁺ (M+NH₄)⁺ calculated: 912.4681; found: 913.4725.
Methyl 2,3,4-tri-O-benzyl-6-O-(2,3-di-O-benzyl-4-O-benzoyl-β-L-rhamnosyl)-α-D-glucopyranoside 2l

Following general procedure E, hemiacetal 1l (45 mg, 0.1 mmol), Ph₃PO (14 mg, 0.05 mmol), (COCl)₂ (10 μL, 0.12 mmol), LiI (54 mg, 0.4 mmol), iPr₂NEt (70 μL, 0.4 mmol) and acceptor 3a (33 mg, 0.07 mmol) were used. The reaction was stirred at 45 °C for 24 h. ¹H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (9:1 to 7:3; pentane/Et₂O) afforded the desired product 2k as a colourless syrup (27 mg, 43% yield). 

**¹H NMR** (500 MHz, Chloroform-d) δ 8.00 (dd, J = 8.3, 1.4 Hz, 2H, Ar-CH), 7.61 – 7.55 (m, 27H, Ar-CH), 5.43 (t, J = 9.6 Hz, 1H, H-4’), 4.99 – 4.95 (m, 2H, 2 × PhCH₂), 4.91 – 4.86 (m, 2H, 2 × PhCH₂), 4.83 – 4.73 (m, 3H, 3 × PhCH₂), 4.68 (d, J = 12.2 Hz, 1H, PhCH₂), 4.62 (d, J = 3.6 Hz, 1H, H-1), 4.51 (s, 1H, H-1’), 4.47 (d, J = 12.6 Hz, 1H, PhCH₂), 4.31 (dd, J = 11.1, 3.2 Hz, 1H, H-6a), 4.26 (d, J = 12.6 Hz, 1H, PhCH₂), 4.02 (d, J = 3.1 Hz, 1H, H-2’), 4.01 – 3.95 (m, H-3), 3.79 – 3.72 (m, 1H, H-5), 3.68 – 3.63 (m, 2H, H-4, H-6b), 3.54 – 3.45 (m, 3H, H-3’, H-2, H-5’), 3.36 (s, 3H, OCH₃), 1.26 (d, J = 6.2 Hz, 3H, H-6’). ¹³C NMR (126 MHz, Chloroform-d) δ 165.6 (C=O), 138.9 (4ºC), 138.6 (4ºC), 138.4 (4ºC), 138.2 (4ºC), 137.7 (4ºC), 133.1 (4ºC), 130.1 (4ºC), 129.8 (Ar-CH), 128.5 (Ar-CH), 128.38 (Ar-CH), 128.35 (Ar-CH), 128.31 (Ar-CH), 128.24 (Ar-CH), 128.18 (Ar-CH), 128.17 (Ar-CH), 128.13 (Ar-CH), 127.92 (Ar-CH), 127.89 (Ar-CH), 127.7 (Ar-CH), 127.63 (Ar-CH), 127.58 (Ar-CH), 127.57 (Ar-CH), 127.4 (Ar-CH), 101.3 (C-1’, ¹JCH = 155.0 Hz, from coupled HSQC), 98.4 (C-1, ¹JCH = 174.0 Hz, from coupled HSQC), 81.9 (C-3), 79.8 (C-2), 78.4 (C-3’), 77.8 (C-4), 75.7 (PhCH₂), 75.2 (PhCH₂), 74.1 (PhCH₂), 73.7 (C-2’), 73.49 (PhCH₂), 73.45 (C-4’), 70.9 (C-5’), 70.7 (PhCH₂), 70.0 (C-5), 67.2 (C-6), 55.2 (OCH₃), 17.7 (C-6’). ESI-HRMS for C₅₅H₆₂NO₁₁⁺ (M+NH₄)⁺ calculated: 912.4317; found: 912.4318.
Methyl (2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside 4b

Following the general procedure C, hemiacetal 1a (54 mg, 0.10 mmol) and acceptor 3b (32 mg, 0.069 mmol) were used. The reaction was stirred at 45 °C for 24 h. $^1$H NMR spectroscopy of the crude reaction mixture gave an $\alpha/\beta = 5:95$. Purification by column chromatography (97:3; CH$_2$Cl$_2$/Et$_2$O) gave 4b as a yellow oil (41 mg, 60% yield).

**β-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): δ 7.43 – 7.11 (m, 35H, ArCH), 5.14 (d, $J = 11.3$ Hz, 1H, CHPh), 4.85 (d, $J = 10.9$ Hz, 1H, CHPh), 4.84 (d, $J = 12.1$ Hz, 1H, CHPh), 4.81 (d, $J = 12.1$ Hz, 1H, CHPh), 4.77 (d, $J = 12.2$ Hz, 1H, CHPh), 4.75 (d, $J = 11.3$ Hz, 1H, CHPh), 4.60 (d, $J = 12.1$ Hz, 1H, CHPh), 4.58 (d, $J = 3.6$ Hz, 1H, H-1), 4.57 (d, $J = 12.1$ Hz, 1H, CHPh), 4.53 (d, $J = 10.8$ Hz, 1H, CHPh), 4.48 (d, $J = 11.9$ Hz, 1H, CHPh), 4.45 (d, $J = 11.8$ Hz, 1H, CHPh), 4.44 (d, $J = 12.1$ Hz, 1H, CHPh), 4.42 (s, 1H, H-1'), 4.37 (d, $J = 12.1$ Hz, 1H, CHPh), 4.36 (d, $J = 12.2$ Hz, 1H, CHPh), 3.93 – 3.89 (m, 2H, H-3, H-4), 3.87 (t, $J = 9.5$ Hz, 1H, H-4'), 3.76 – 3.69 (m, 1H, H-5), 3.70 (d, $J = 3.1$ Hz, 1H, H-2'), 3.67 (dd, $J = 11.2$, 1.8 Hz, 1H, H-6a'), 3.59 – 3.55 (m, 2H, H-6a, H-6b), 3.54 (dd, $J = 11.2$, 5.4 Hz, 1H, H-6b'), 3.49 – 3.43 (m, 1H, H-2), 3.37 (s, 3H, OCH$_3$), 3.31 – 3.24 (m, 1H, H-5'), 3.28 (dd, $J = 9.5$, 3.1 Hz, 1H, H-3'). $^{13}$C NMR (126 MHz, Chloroform-$d$): δ 139.8 (C), 139.04 (C), 138.98 (C), 138.7 (C), 138.48 (C), 138.46 (C), 137.9 (C), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.30 (CH), 128.25 (CH), 128.2 (CH), 128.13 (CH), 128.08 (CH), 128.06 (CH), 127.98 (CH), 127.95 (CH), 127.91 (CH), 127.85 (CH), 127.8 (CH), 127.73 (CH), 127.68 (CH), 127.6 (CH), 127.4 (CH), 127.3 (CH), 127.1 (CH), 101.0 (C-1'), 98.5 (C-1), 82.7 (C-3'), 80.5 (C-3), 79.3 (C-2), 77.3 (C-4), 76.3 (C-5'), 75.4 (PhCH$_2$), 75.2 (C-2'), 75.1 (PhCH$_2$), 75.0 (C-4'), 74.2 (PhCH$_2$), 73.8 (PhCH$_2$), 73.7 (PhCH$_2$), 73.6 (PhCH$_2$), 71.8 (PhCH$_2$), 69.8 (C-5), 69.7 (C-6'), 68.9 (C-6), 55.4 (OCH$_3$). NMR data were consistent with literature data.\[35\]

**α-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): δ 3.39 (s, 3H, OCH$_3$).
Methyl (2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-α-D-glucopyranoside 4c

Following the general procedure C, hemiacetal 1a (54 mg, 0.10 mmol), Ph₃PO (14 mg, 0.050 mmol, 0.5 eq) and acceptor 3c (32 mg, 0.069 mmol) were used. The reaction was stirred at 45 °C for 24 h. ¹H NMR spectroscopy of the crude reaction mixture gave an α/β = 1:99. Purification by column chromatography (97:3; CH₂Cl₂/Et₂O) gave 4c as a yellow oil (58 mg, 84% yield). ESI-MS for C₆₂H₆₆O₁₁Na⁺ (M+Na)⁺ calculated: 1009.4497; found: 1009.4496.

β-anomer

¹H NMR (500 MHz, Chloroform-d): δ 7.49 – 7.44 (m, 2H, ArCH), 7.33 – 7.06 (m, 33H, ArCH), 5.27 (d, J = 11.1 Hz, 1H, CHPh), 4.92 (s, 2H, 2 x CHPh), 4.85 (d, J = 10.7 Hz, 1H, CHPh), 4.79 (s, 1H, H-1’), 4.68 (d, J = 3.4 Hz, 1H, H-1), 4.55 (d, J = 12.2 Hz, 1H, CHPh), 4.54 (d, J = 10.8 Hz, 1H, CHPh), 4.51 – 4.43 (m, 3H, 3 x CHPh), 4.43 (s, 2H, 2 x CHPh), 4.41 – 4.36 (m, 3H, 3 x CHPh), 4.18 (dd, J = 9.6, 8.6 Hz, 1H, H-3), 3.97 (t, J = 9.6 Hz, 1H, H-4’), 3.77 (d, J = 2.9 Hz, 1H, H-2’), 3.75 – 3.66 (m, 4H, H-5, H-6a’, H-6b’, H-6a), 3.66 – 3.60 (m, 1H, H-6b), 3.55 (dd, J = 9.9, 8.6 Hz, 1H, H-4), 3.46 (dd, J = 9.7, 3.4 Hz, 1H, H-2), 3.39 – 3.32 (m, 2H, H-3’, H-5’), 3.35 (s, 3H, OCH₃). ¹³C NMR (126 MHz, Chloroform-d): δ 139.3 (C), 139.1 (C), 138.9 (C), 138.64 (C), 138.56 (C), 138.1 (C), 138.0 (C), 128.7 (CH), 128.48 (CH), 128.46 (CH), 128.4 (CH), 128.22 (CH), 128.20 (CH), 128.16 (CH), 128.13 (CH), 128.11 (CH), 128.0 (CH), 127.8 (CH), 127.74 (CH), 127.68 (CH), 127.4 (CH), 127.3 (CH), 102.6 (C-1’, ¹JCH = 158.3 Hz, from coupled HSQC), 97.5 (C-1’, ¹JCH = 170.0 Hz, from coupled HSQC), 83.0 (C-3’), 80.9 (C-2), 80.6 (C-3), 76.3 (C-4), 76.0 (C-5’), 75.3 (PhCH₃), 75.1 (C-4’), 75.0 (C-2’), 74.9 (PhCH₃), 74.0 (PhCH₂), 73.6 (PhCH₃), 73.5 (PhCH₂), 73.1 (PhCH₂), 72.0 (PhCH₃), 70.0 (C-5), 69.7 (C-6’), 68.8 (C-6), 55.2 (OCH₃).

α-anomer

¹H NMR (500 MHz, Chloroform-d): δ 3.31 (s, 3H, OCH₃).
Methyl (2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-(1→3)-2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside 4d

Following the general procedure B, hemiacetal 1a (54 mg, 0.10 mmol), acceptor 3d (26 mg, 0.070 mmol) and iPr₂NEt (84 μL, 0.50 mmol) were used. The reaction was stirred at 60 °C for 24 h. ¹H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (97:3; CH₂Cl₂/Et₂O) gave 4d as a yellowish oil (33 mg, 52% yield). ¹H NMR (600 MHz, Chloroform-d): δ 7.50 – 7.41 (m, 4H, ArCH), 7.32 – 7.12 (m, 26H, ArCH), 5.50 (s, 1H, PhCH), 4.93 (d, J = 12.2 Hz, 1H, CHHPh), 4.87 (d, J = 12.2 Hz, 1H, CHHPh), 4.82 (d, J = 10.7 Hz, 1H, CHHPh), 4.70 (s, 1H, H-1’), 4.57 (d, J = 11.7 Hz, 1H, CHHPh), 4.57 (d, J = 3.7 Hz, 1H, H-1), 4.52 (d, J = 10.7 Hz, 1H, CHHPh), 4.51 (s, 2H, 2 x CHHPh), 4.47 (d, J = 11.8 Hz, 1H, CHHPh), 4.44 (d, J = 11.9 Hz, 1H, CHHPh), 4.41 (d, J = 11.8 Hz, 1H, CHHPh), 4.22 (dd, J = 10.2, 4.8 Hz, 1H, H-6a), 4.19 (t, J = 9.3 Hz, 1H, H-3), 3.93 (t, J = 9.6 Hz, 1H, H-4’), 3.85 (d, J = 2.9 Hz, 1H, H-2’), 3.80 (td, J = 9.9, 4.7 Hz, 1H, H-5), 3.72 (dd, J = 11.3, 4.7 Hz, 1H, H-6a’), 3.70 – 3.66 (m, 2H, H-6b, H-6b’), 3.63 (t, J = 9.4 Hz, 1H, H-4), 3.53 (dd, J = 9.3, 3.7 Hz, 1H, H-2), 3.38 (dd, J = 9.5, 2.9 Hz, 1H, H-3’), 3.37 (s, 3H, OCH₃), 3.30 (ddd, J = 9.7, 4.7, 2.1 Hz, 1H, H-5’). ¹³C NMR (151 MHz, Chloroform-d): δ 139.4 (C), 138.9 (C), 138.6 (C), 138.5 (C), 138.0 (C), 137.5 (C), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.24 (CH), 128.20 (CH), 128.18 (CH), 128.14 (CH), 128.12 (CH), 128.09 (CH), 127.7 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 126.3 (CH), 102.1 (C-1’), 101.6 (PhCH), 98.7 (C-1), 82.8 (C-3’), 80.33 (C-2), 80.29 (C-4), 77.4 (C-3), 76.2 (C-5’), 75.2 (PhCH₂), 74.92 (C-2’), 74.88 (C-4’), 74.0 (PhCH₂), 73.7 (PhCH₂), 73.5 (PhCH₂), 71.8 (PhCH₂), 69.6 (C-6), 69.1 (C-6’), 62.6 (C-5), 55.5 (OCH₃). NMR data were consistent with literature data.[36]

Phenyl 2,3,4,6-tetra-O-benzyl-β-D-mannopyranoside 4e

Following the general procedure B, hemiacetal 1a (54 mg, 0.10 mmol), acceptor 3e (7 mg, 0.07 mmol) and iPr₂NEt (42 μL, 0.25 mmol) were used. The reaction was stirred at 25 °C for 24 h. ¹H NMR
spectroscopy of the crude reaction mixture gave an $\alpha/\beta = 3.97$. Purification by column chromatography (CH$_2$Cl$_2$) gave 4e as a white solid (39 mg, 91% yield).

Reaction at 30 °C gave $\alpha/\beta = 6.94$.

**β-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 7.58 – 7.43 (m, 2H, ArCH), 7.38 – 7.18 (m, 20H, ArCH), 7.08 – 6.92 (m, 3H, ArCH), 5.09 (d, $J = 12.3$ Hz, 1H, CHHPh), 5.00 (d, $J = 12.4$ Hz, 1H, CHHPh), 4.98 (d, $J = 0.8$ Hz, 1H, H-1), 4.93 (d, $J = 10.9$ Hz, 1H, CHHPh), 4.60 (d, $J = 11.9$ Hz, 1H, CHHPh), 4.59 (d, $J = 11.9$ Hz, 1H, CHHPh), 4.58 (d, $J = 10.9$ Hz, 1H, CHHPh), 4.55 (d, $J = 11.9$ Hz, 1H, CHHPh), 4.53 (d, $J = 11.9$ Hz, 1H, CHHPh), 4.09 (dd, $J = 3.0$, 0.8 Hz, 1H, H-2), 3.97 (t, $J = 9.4$ Hz, 1H, H-4), 3.87 (dd, $J = 10.9$, 2.0 Hz, 1H, H-6a), 3.77 (dd, $J = 10.9$, 6.2 Hz, 1H, H-6b), 3.64 – 3.58 (m, 1H, H-5), 3.60 (dd, $J = 9.2$, 3.0 Hz, 1H, H-3). $^{13}$C NMR (126 MHz, Chloroform-$d$): $\delta$ 157.4 (C), 138.7 (C), 138.6 (C), 138.4 (C), 138.2 (C), 129.58 (CH), 128.57 (CH), 128.55 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.84 (CH), 127.78 (CH), 127.7 (CH), 127.6 (CH), 122.5 (CH), 116.5 (CH), 99.5 (C-1), 82.3 (C-3), 76.3 (C-5), 75.3 (PhCH$_2$), 74.9 (C-4), 74.3 (PhCH$_2$ and C-2), 73.6 (PhCH$_2$), 71.9 (PhCH$_2$), 69.7 (C-6). NMR data were consistent with literature data.[37]

**α-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 5.59 (d, $J = 2.0$ Hz, 1H, H-1).

1-Naphthyl 2,3,4,6-tetra-$O$-benzyl-$\beta$-D-mannopyranoside 4f

Following the general procedure B, hemiacetal 1a (54 mg, 0.10 mmol), acceptor 3f (10 mg, 0.069 mmol) and iPr$_2$NEt (42 µL, 0.25 mmol) were used. The reaction was stirred at 25 °C for 24 h. $^1$H NMR spectroscopy of the crude reaction mixture gave an $\alpha/\beta = 1.99$. Purification by column chromatography (CH$_2$Cl$_2$) gave 4f as a white solid (38 mg, 83% yield). ESI-HRMS for C$_{44}$H$_{82}$O$_6$Na$^+$ (M+Na$^+$) calculated: 689.2874; found: 689.2880.

**β-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): $\delta$ 8.13 (dd, $J = 8.4$, 1.3 Hz, 1H, ArCH), 7.82 – 7.77 (m, 1H, ArCH), 7.60 – 7.56 (m, 2H, ArCH), 7.51 (d, $J = 8.2$ Hz, 1H, ArCH), 7.47 (ddd, $J = 8.2$, 6.8, 1.4 Hz, 1H, ArCH), 7.42 (ddd, $J = 8.2$, 6.8, 1.4 Hz, 1H, ArCH), 7.37 – 7.20 (m, 19H, ArCH), 7.15 (dd, $J = 7.8$, 1.0 Hz, 1H, ArCH), 5.24 (d, $J = 12.1$ Hz, 1H, CHHPh), 5.17 (d, $J = 0.9$ Hz, 1H, H-1), 5.09 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.93 (d, $J = 10.9$ Hz, 1H, CHHPh), 4.65 (d, $J = 11.8$ Hz, 1H, CHHPh), 4.61 (d, $J = 10.9$ Hz,
$^1$H, $^{13}$C NMR (126 MHz, Chloroform-$d$): δ 153.5 (C), 138.8 (C), 138.6 (C), 138.4 (C), 138.2 (C), 134.6 (C), 128.6 (CH), 128.5 (CH), 128.45 (CH), 128.43 (CH), 128.38 (CH), 128.2 (CH), 127.9 (CH), 127.8 (CH), 127.74 (CH), 127.69 (CH), 127.5 (CH), 126.4 (CH), 126.1 (CH), 125.6 (CH), 125.6 (CH), 122.2 (CH), 109.2 (CH), 100.0 (C-1), $^J_{IC} = 155.5$ Hz, from coupled HSQC ), 82.3 (C-3), 76.4 (C-5), 75.2 (PhCH$_2$ and C-2), 75.0 (C-4), 74.7 (PhCH$_2$), 73.6 (PhCH$_2$), 72.1 (PhCH$_2$), 69.7 (C-6).

**α-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): δ 5.76 (d, $J = 1.9$ Hz, 1H, H-1).

**p-Nitrophenyl 2,3,4,6-tetra-$O$-benzyl-$β$-D-mannopyranoside 4g**

Following the general procedure B, hemiacetal 1a (54 mg, 0.10 mmol), acceptor 3g (9.7 mg, 0.070 mmol) and iPr$_2$NEt (42 μL, 0.25 mmol) were used. The reaction was stirred at 45 °C for 24 h. $^1$H NMR spectroscopy of the crude reaction mixture gave an $α/β = 1:99$. Purification by column chromatography (CH$_2$Cl$_2$) gave 4g as a white solid (34 mg, 74% yield). ESI-HRMS for C$_{40}$H$_{39}$NO$_8$Na$^+$ (M+Na)$^+$ calculated: 684.2568; found: 684.2566.

**β-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): δ 8.16 – 8.09 (m, 2H, ArCH), 7.52 – 7.46 (m, 2H, ArCH), 7.40 – 7.17 (m, 18H, ArCH), 7.08 – 7.01 (m, 2H, ArCH), 5.06 (d, $J = 1.0$ Hz, 1H, H-1), 5.02 (d, $J = 12.2$ Hz, 1H, CHHPh), 4.97 (d, $J = 12.3$ Hz, 1H, CHHPh), 4.92 (d, $J = 10.9$ Hz, 1H, CHHPh), 4.63 (d, $J = 11.9$ Hz, 1H, CHHPh), 4.59 (d, $J = 11.7$ Hz, 1H, CHHPh), 4.58 (d, $J = 10.9$ Hz, 1H, CHHPh), 4.56 (d, $J = 11.8$ Hz, 1H, CHHPh), 4.50 (d, $J = 11.8$ Hz, 1H, CHHPh), 4.11 (dd, $J = 2.9$, 1.0 Hz, 1H, H-2), 3.96 (t, $J = 9.2$ Hz, 1H, H-4), 3.85 (dd, $J = 10.6$, 1.9 Hz, 1H, H-6a), 3.71 (dd, $J = 10.6$, 6.7 Hz, 1H, H-6b), 3.69 – 3.62 (m, 1H, H-5), 3.64 (dd, $J = 9.1$, 2.8 Hz, 1H, H-3). $^{13}$C NMR (126 MHz, Chloroform-$d$): δ 162.0 (C), 142.8 (C), 138.4 (C), 138.3 (C), 138.2 (C), 138.0 (C), 128.63 (CH), 128.56 (CH), 128.51 (CH), 128.47 (CH), 128.4 (CH), 128.2 (CH), 127.98 (CH), 127.97 (CH), 127.9 (CH), 127.8 (CH), 125.9 (CH), 116.5 (CH), 98.7 (C-1), $^J_{IC} = 159.0$ Hz, from coupled HSQC), 82.0 (C-3), 76.4 (C-5), 75.3 (PhCH$_2$), 74.7 (C-4), 74.6 (PhCH$_2$), 74.3 (C-2), 73.6 (PhCH$_2$), 72.3 (PhCH$_2$), 69.4 (C-6).

**α-anomer**

$^1$H NMR (500 MHz, Chloroform-$d$): δ 5.64 (d, $J = 2.2$ Hz, 1H, H-1).
**p-Methoxyphenyl (2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-(1→4)-2-azido-3,6-di-O-benzyl-β-D-glucopyranoside 4h**

Following the general procedure B, hemiacetal 1a (108 mg, 0.200 mmol), Ph$_3$PO (28 mg, 0.10 mmol), oxalyl chloride (20 μL, 0.24 mmol), LiI (107 mg, 0.800 mmol), acceptor 3h (49 mg, 0.10 mmol) and iPr$_2$NEt (0.14 mL, 0.80 mmol) were used. The reaction was stirred at 45 °C for 22 h. $^1$H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (90:10 to 75:25; cyclohexane/Et$_2$O) gave 4h as a colourless syrup (45 mg, 45% yield).

ESI-HRMS for C$_{62}$H$_{69}$N$_4$O$_{11}$+ (M+NH$_4$)$^+$ calculated: 1045.4957; found: 1045.4957.

$^1$H NMR (600 MHz, Chloroform-d): δ 7.41 – 7.38 (m, 2H, ArCH), 7.37 – 7.33 (m, 2H, ArCH), 7.33 – 7.13 (m, 26H, ArCH), 7.05 – 6.99 (m, 2H, ArCH), 6.83 – 6.77 (m, 2H, ArCH), 5.18 (d, $J = 11.3$ Hz, 1H, CH$_2$Ph), 4.86 (d, $J = 12.0$ Hz, 1H, CH$_2$Ph), 4.86 (d, $J = 10.9$ Hz, 1H, CH$_2$Ph), 4.83 (d, $J = 12.0$ Hz, 1H, CH$_2$Ph), 4.70 (d, $J = 11.3$ Hz, 1H, CH$_2$Ph), 4.67 (d, $J = 8.2$ Hz, 1H, H-1), 4.57 (d, $J = 12.1$ Hz, 1H, CH$_2$Ph), 4.53 (d, $J = 10.9$ Hz, 1H, CH$_2$Ph), 4.50 (s, 1H, H-1'), 4.50 (d, $J = 11.9$ Hz, 1H, CH$_2$Ph), 4.48 (d, $J = 11.9$ Hz, 1H, CH$_2$Ph), 4.45 (d, $J = 12.1$ Hz, 1H, CH$_2$Ph), 4.40 (d, $J = 12.1$ Hz, 1H, CH$_2$Ph), 4.37 (d, $J = 12.1$ Hz, 1H, CH$_2$Ph), 4.00 (dd, $J = 9.8$, 8.8 Hz, 1H, H-4'), 3.88 (t, $J = 9.5$ Hz, 1H, H-4'), 3.79 – 3.75 (m, 1H, H-2'), 3.77 (s, 3H, OCH$_3$), 3.73 – 3.67 (m, 2H, H-6a, H-6a'), 3.61 (dd, $J = 11.1$, 4.4 Hz, 1H, H-6b), 3.59 (dd, $J = 9.9$, 8.2 Hz, 1H, H-2'), 3.53 (dd, $J = 11.0$, 5.6 Hz, 1H, H-6b'), 3.49 (ddd, $J = 9.8$, 4.3, 2.4 Hz, 1H, H-5), 3.44 (dd, $J = 9.8$, 8.8 Hz, 1H, H-3), 3.36 (dd, $J = 9.4$, 2.9 Hz, 1H, H-3'), 3.32 (ddd, $J = 9.7$, 5.6, 1.8 Hz, 1H, H-5'). $^{13}$C NMR (151 MHz, Chloroform-d): δ 155.7 (C), 151.3 (C), 138.9 (C), 138.81 (C), 138.76 (C), 138.5 (C), 138.4 (C), 137.9 (C), 128.62 (CH), 128.53 (CH), 128.44 (CH), 128.35 (CH), 128.28 (CH), 128.2 (CH), 128.104 (CH), 128.096 (CH), 128.0 (CH), 127.9 (CH), 127.82 (CH), 127.78 (CH), 127.75 (CH), 127.65 (CH), 127.55 (CH), 127.47 (CH), 127.4 (CH), 118.9 (CH), 114.7 (CH), 101.7 (C-1, $^{13}$J$_{CH}$ = 163.4 Hz, from coupled HSQC), 101.0 (C-1', $^{13}$J$_{CH}$ = 155.2 Hz, from coupled HSQC), 82.8 (C-3'), 81.2 (C-3), 77.0 (C-4), 76.2 (C-5'), 75.18 (C-5, C-2', PhCH$_2$), 75.1 (PhCH$_2$), 74.9 (C-4'), 74.4 (PhCH$_2$), 73.7 (PhCH$_2$), 73.5 (PhCH$_2$), 71.9 (PhCH$_2$), 69.7 (C-6'), 68.8 (C-6), 65.9 (C-2), 55.8 (OCH$_3$).
Methyl 2,3,6-tri-O-benzyl-4-O-(2,3,4-tri-O-benzyl-β-D-rhamnosyl)-α-D-glucopyranoside 5b

Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph₃PO (14 mg, 0.05 mmol), (COCl): (10 μL, 0.12 mmol), LiI (54 mg, 0.4 mmol), iPr₂NEt (70 μL, 0.4 mmol) and acceptor 3b (33 mg, 0.07 mmol) were used. The reaction was stirred at 45 °C for 24 h. ¹H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (9:1 to 6:4; pentane/ EtOAc) afforded the desired product 5b as a colourless syrup (48.2 mg, 78% yield). Rᵣ = 0.6 (4:1; cyclohexane/ EtOAc); ¹H NMR (500 MHz, Chloroform-d) δ 7.44 – 7.39 (m, 2H, Ar-CH), 7.37 – 7.16 (m, 26H, Ar-CH), 7.16 – 7.12 (m, 2H, Ar-CH), 4.96 (d, J = 11.6 Hz, 1H, PhCH₂), 4.88 (d, J = 10.7 Hz, 1H, PhCH₂), 4.81 (s, 2H, 2 × PhCH₂), 4.73 (d, J = 12.1 Hz, 1H, PhCH₂), 4.66 (d, J = 3.5 Hz, 1H, H-1), 4.65 – 4.61 (m, 2H, 2 × PhCH₂), 4.61 (s, 1H, H-1’), 4.57 (d, J = 10.8 Hz, 1H, PhCH₂), 4.53 (d, J = 12.0 Hz, 1H, PhCH₂), 4.30 (d, J = 11.6 Hz, 1H, PhCH₂), 4.22 (d, J = 11.7 Hz, 1H, PhCH₂), 4.18 (d, J = 11.7 Hz, 1H, PhCH₂), 3.90 (dd, J = 10.6, 1.9 Hz, 1H, H-6a), 3.83 (t, J = 9.3 Hz, 1H, H-3), 3.80 – 3.70 (m, 2H, H-5, H-6b), 3.70 – 3.63 (m, 1H, H-4), 3.61 (d, J = 2.9 Hz, 1H, H-2’), 3.54 – 3.47 (m, 2H, H-2, H-4’), 3.44 (s, 3H, OCH₃), 3.23 – 3.14 (m, 1H, H-5’), 3.13 (dd, J = 9.5, 2.9 Hz, 1H, H-3’), 1.25 (d, J = 6.1 Hz, 3H, H-6’). ¹³C NMR (126 MHz, Chloroform-d) δ 138.84 (4ºC), 138.79 (4ºC), 138.6 (4ºC), 138.42 (4ºC), 138.35 (4ºC), 138.0 (4ºC), 128.49 (Ar-CH), 128.48 (Ar-CH), 128.44 (Ar-CH), 128.38 (Ar-CH), 128.30 (Ar-CH), 128.21 (Ar-CH), 128.17 (Ar-CH), 128.14 (Ar-CH), 128.13 (Ar-CH), 128.0 (Ar-CH), 127.7 (Ar-CH), 127.6 (Ar-CH), 127.53 (Ar-CH), 127.51 (Ar-CH), 127.50 (Ar-CH), 127.4 (Ar-CH), 127.3 (Ar-CH), 127.1 (Ar-CH), 102.4 (C-1’, ¹JCH = 159.0 Hz, from coupled HSQC), 97.9 (C-1, ¹JCH = 170.0 Hz, from coupled HSQC), 82.8 (C-3’), 82.1 (C-3), 80.0 (C-4’), 79.8 (C-2), 76.9 (C-4), 75.5 (PhCH₂), 75.4 (PhCH₂), 73.8 (C-2’), 73.7 (PhCH₂), 73.4 (PhCH₂), 73.1 (PhCH₂), 71.8 (C-5’), 71.5 (PhCH₂), 69.8 (C-5), 69.1 (C-6), 55.4 (OCH₃), 17.9 (C-6’). ESI-HRMS for C₃₃H₅₆NO₁₀⁺ (M+NH₄)⁺ calculated: 898.4525; found: 898.4567.
Methyl 2,4,6-tri-O-benzyl-3-O-(2,3,4-tri-O-benzyl-β-L-rhamnosyl)-α-D-glucopyranoside 5c

Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph3PO (28 mg, 0.1 mmol), (COCl)2 (10 μL, 0.12 mmol), Lii (54 mg, 0.4 mmol), iPr2NEt (70 μL, 0.4 mmol) and acceptor 3c (33 mg, 0.07 mmol) were used. The reaction was stirred at 45 °C for 20 h. 1H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (9:1 to 6:4; pentane/ Et2O) afforded the desired product 5c as a colourless syrup (54 mg, 88% yield). RF = 0.4 (4:1; cyclohexane/ EtOAc); 1H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.40 (m, 2H, Ar-CH), 7.40 – 7.17 (m, 26H, Ar-CH), 7.04 – 7.01 (m, 2H, Ar-CH), 4.99 (d, J = 12.6 Hz, 1H, PhCH2), 4.93 – 4.84 (m, 3H, 3 × PhCH2), 4.77 (d, J = 12.6 Hz, 1H, PhCH2), 4.65 – 4.64 (m, 2H, H-1’, PhCH2), 4.63 – 4.58 (m, 2H, H-1, PhCH2), 4.48 (d, J = 12.0 Hz, 1H, PhCH2), 4.44 (d, J = 11.8 Hz, 1H, PhCH2), 4.30 (d, J = 11.8 Hz, 1H, PhCH2), 4.26 – 4.19 (m, 2H, 2 × PhCH2), 4.09 (t, J = 9.3 Hz, 1H, H-3), 3.74 – 3.61 (m, 4H, H-2’, H-5, H-6a, H-6b), 3.60 – 3.44 (m, 3H, H-4’, H-4, H-2), 3.36 (s, 3H, OCH3), 3.25 (dd, J = 9.3, 6.1 Hz, 1H, H-5’), 3.20 (dd, J = 9.4, 2.9 Hz, 1H, H-3’), 1.35 (d, J = 6.1 Hz, 3H, H-6’). 13C NMR (126 MHz, Chloroform-d) δ 139.1 (4ºC), 139.0 (4ºC), 138.5 (4ºC), 138.4 (4ºC), 138.3 (4ºC), 137.8 (4ºC), 128.5 (4ºC), 128.40 (4ºC), 128.36 (4ºC), 128.3 (4ºC), 128.23 (4ºC), 128.18 (4ºC), 128.15 (4ºC), 128.14 (4ºC), 128.11 (4ºC), 128.06 (4ºC), 127.8 (4ºC), 127.7 (4ºC), 127.50 (4ºC), 127.49 (4ºC), 127.46 (4ºC), 127.40 (4ºC), 127.35 (4ºC), 126.5 (4ºC), 102.6 (4ºC), 1JCH = 156.0 Hz, from coupled HSQC, 99.2 (C-1), 1JCH = 171.0 Hz, from coupled HSQC, 83.0 (C-3’), 82.4 (C-3), 80.3 (C-4’), 78.6 (C-4), 77.1 (C-2), 75.5 (PhCH2), 74.6 (C-2’), 74.1 (PhCH2), 73.9 (PhCH2), 73.7 (PhCH2), 73.6 (PhCH2), 71.8 (C-5’), 71.5 (PhCH2), 69.6 (C-5), 68.5 (C-6), 55.2 (OCH3), 18.1 (C-6’). ESI-HRMS for C55H64NO10+ (M+NH4)+ calculated: 898.4525; found: 898.4529.
Methyl 2-O-benzyl-4,6-benzylidene-3-O-(2,3,4-tri-O-benzyl-β-L-rhamnosyl)-α-D-glucopyranoside 5d

Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph₃PO (28 mg, 0.1 mmol), (COCl)₂ (10 μL, 0.12 mmol), LiI (54 mg, 0.4 mmol), iPr₂NEt (70 μL, 0.4 mmol) and acceptor 3d (26 mg, 0.07 mmol) were used. The reaction was stirred at 45 °C for 24 h. ¹H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (9:1 to 6:4; pentane/Et₂O) afforded the desired product 5d as a colourless syrup (24.3 mg, 44% yield). Rᵢ = 0.6 (4:1; cyclohexane/EtOAc); Reaction gave similar results when 50 mol% Ph₃PO was used.

¹H NMR (500 MHz, Chloroform-d) δ 7.43 – 7.19 (m, 25H, Ar-CH), 5.26 (s, 1H, PhCH), 5.04 (d, J = 12.2 Hz, 1H, PhCH₂), 4.89 (d, J = 10.8 Hz, 1H, PhCH₂), 4.87 (s, 2H, 2 × PhCH₂), 4.77 (d, J = 12.3 Hz, 1H, PhCH₂), 4.63 (s, 1H, H-1'), 4.60 (d, J = 10.8 Hz, 1H, PhCH₂), 4.57 (d, J = 3.8 Hz, 1H, H-1), 4.29 – 4.13 (m, 4H, 2 × PhCH₂, H-6a, H-3), 3.95 (d, J = 2.6 Hz, 1H, H-2'), 3.78 (td, J = 10.0, 4.8 Hz, 1H, OCH₂), 3.38 (s, 3H, OCH₃), 3.33 – 3.25 (m, 3H, H-3', H-4, H-5'), 1.37 (d, J = 6.2 Hz, 3H, H-6').

¹³C NMR (126 MHz, Chloroform-d) δ 139.2 (4ºC), 138.7 (4ºC), 138.5 (4ºC), 138.3 (4ºC), 138.2 (4ºC), 129.22 (Ar-CH), 129.21 (Ar-CH), 128.4 (Ar-CH), 128.33 (Ar-CH), 128.30 (Ar-CH), 128.10 (Ar-CH), 128.09 (Ar-CH), 128.0 (Ar-CH), 127.69 (Ar-CH), 127.64 (Ar-CH), 127.59 (Ar-CH), 127.48 (Ar-CH), 127.46 (Ar-CH), 127.34 (Ar-CH), 126.0 (Ar-CH), 103.2 (C-1', J₁CH = 157.0 Hz, from coupled HSQC), 101.66 (PhCH₂), 99.78 (C-1, J₁CH = 171.0 Hz, from coupled HSQC), 83.0 (C-3'), 81.7 (C-4), 79.9 (C-4', C-3), 77.8 (C-2), 75.4 (PhCH₂), 74.18 (PhCH₂), 74.15 (C-2'), 73.8 (PhCH₂), 72.1 (C-5'), 71.4 (PhCH₂), 69.1 (C-6), 61.9 (C-5), 55.41 (OCH₃), 18.1 (C-6'). ESI-HRMS for C₄₄H₅₆NO₁₀⁺ (M+NH₄)⁺ calculated: 806.3899; found: 806.3920.

Phenyl 2,3,4-tri-O-benzyl-β-L-rhamnoside 5e

Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph₃PO (28 mg, 0.1 mmol), (COCl)₂ (10 μL, 0.12 mmol), LiI (54 mg, 0.4 mmol), iPr₂NEt (44 μL, 0.25 mmol) and acceptor 3e (0.007 mg,
0.07 mmol) were used. The reaction was stirred at rt for 20 h. $^1$H NMR spectroscopy of the crude reaction mixture gave an $\alpha/\beta = 2:98$. Purification by column chromatography (9:1; pentane/EtO) afforded the desired product 5f as a white solid (35.7 mg, quantitative yield). $R_f = 0.6$ (4:1; cyclohexane/EtOAc); Reaction gave anomeric mixture ($\alpha/\beta = 17:83$) when performed at 45 °C. $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.55 – 7.51 (m, 2H, Ar-CH), 7.38 – 7.20 (m, 15H, Ar-CH), 7.03 – 6.99 (m, 1H, Ar-CH), 6.99 – 6.96 (m, 2H, Ar-CH), 5.08 (d, $J = 12.4$ Hz, 1H, PhCH$_2$), 5.03 – 4.95 (m, 3H, 2 × PhCH$_2$, H-1), 4.70 – 4.66 (m, 1H, PhCH$_2$), 4.60 – 4.49 (m, 2H, 2 × PhCH$_2$), 4.07 (d, $J = 2.8$ Hz, 1H, H-2), 3.71 (t, $J = 9.3$ Hz, 1H, H-4), 3.55 (dd, $J = 9.4$, 3.0 Hz, 1H, H-3), 3.51 – 3.43 (m, 1H, H-5), 1.42 (d, $J = 6.2$ Hz, 3H, H-6). $^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 157.2 (4ºC), 138.6 (4ºC), 138.4 (4ºC), 138.1 (4ºC), 129.5 (Ar-CH), 128.5 (Ar-CH), 128.4 (Ar-CH), 128.2 (Ar-CH), 128.1 (Ar-CH), 127.8 (Ar-CH), 127.7 (Ar-CH), 127.64 (Ar-CH), 127.59 (Ar-CH), 122.4 (Ar-CH), 116.2 (Ar-CH), 99.1 (C-1, $^1J_{CH} = 156.0$ Hz, from coupled HSQC), 82.0 (C-3), 79.9 (C-4), 75.5 (PhCH$_2$), 74.34 (C-2), 74.29 (PhCH$_2$), 72.1 (C-5), 71.7 (PhCH$_2$), 18.1 (C-6). ESI-HRMS for C$_{33}$H$_{38}$NO$_5^+$ (M+NH$_4^+$) calculated: 528.2744; found: 528.2745.

Naphthyl 2,3,4-tri-O-benzyl-β-L-rhamnoside 5f

Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph$_3$PO (28 mg, 0.1 mmol), (COCl)$_2$: (10 μL, 0.12 mmol), LiI (54 mg, 0.4 mmol), iPr$_2$NEt (44 μL, 0.25 mmol) and acceptor 3f (10 mg, 0.07 mmol) were used. The reaction was stirred at rt for 20 h. $^1$H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (4:1; pentane/EtO) afforded the desired product 5f as a brown solid (40 mg, quantitative yield). $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 8.12 (d, $J = 8.3$ Hz, 1H, Ar-CH), 7.79 (d, $J = 8.0$ Hz, 1H, Ar-CH), 7.59 (d, $J = 7.0$ Hz, 1H, Ar-CH), 7.53 – 7.41 (m, 3H, Ar-CH), 7.39 – 7.24 (m, 15H, Ar-CH), 7.03 (d, $J = 7.5$ Hz, 1H, Ar-CH), 5.24 (d, $J = 12.2$ Hz, 1H, PhCH$_2$), 5.13 (s, 1H, H-1), 5.11 (d, $J = 12.2$ Hz, 1H, PhCH$_2$), 5.00 (d, $J = 10.8$ Hz, 1H, PhCH$_2$), 4.70 (d, $J = 10.8$ Hz, 1H, PhCH$_2$), 4.65 – 4.56 (m, 2H, 2 × PhCH$_2$), 4.25 (d, $J = 2.7$ Hz, 1H, H-2), 3.77 (t, $J = 9.3$ Hz, 1H, H-4), 3.62 (dd, $J = 9.4$, 2.9 Hz, 1H, H-3), 3.55 (dq, $J = 9.2$, 6.2 Hz, 1H, H-5), 1.46 (d, $J = 6.2$ Hz, 3H, H-6). $^{13}$C NMR (151 MHz, Chloroform-$d$) $\delta$ 153.3 (4ºC), 138.7 (4ºC), 138.4 (4ºC), 138.1 (4ºC), 134.5 (4ºC), 128.5 (Ar-CH), 128.43 (Ar-CH), 128.41 (Ar-CH), 128.3 (Ar-CH), 128.1 (Ar-CH), 127.8 (Ar-CH), 127.72 (Ar-CH), 127.65 (Ar-CH), 127.57 (Ar-CH), 126.3 (Ar-CH), 125.84 (Ar-CH), 125.80 (Ar-CH), 125.5 (Ar-CH), 122.2 (Ar-CH), 122.1 (Ar-CH), 108.6 (Ar-CH), 99.7 (C-1, $^1J_{CH} = 156.0$ Hz, from coupled HSQC), 82.3 (C-3), 78.0 (C-4), 75.5 (PhCH$_2$), 75.3 (C-2), 74.7 (PhCH$_2$),

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72.2 (C-5), 71.9 (PhCH₂), 18.2 (C-6). ESI-HRMS for C₃₇H₄₀NO₅⁺ (M+NH₄)⁺ calculated: 578.2901; found: 578.2907.

**p-Nitrophenyl 2,3,4-tri-O-benzyl-β-L-rhamnoside 5g**

Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph₃PO (28 mg, 0.1 mmol), (COCl)₂ (10 μL, 0.12 mmol), Lil (54 mg, 0.4 mmol), iPr₂NET (44 μL, 0.25 mmol) and acceptor 3g (9.7 mg, 0.07 mmol) were used. The reaction was stirred at 45 °C for 24 h. ¹H NMR spectroscopy of the crude reaction mixture gave an α/β = 4:96. Purification by column chromatography (4:1; pentane/Et₂O) afforded the desired product 5g as a white solid (34 mg, 87% yield). ¹H NMR (500 MHz, Chloroform-d) δ 8.18 (d, J = 9.3 Hz, 2H, Ar-CH), 7.53 – 7.49 (m, 2H, Ar-CH), 7.39 – 7.26 (m, 13H, Ar-CH), 6.99 (d, J = 9.3 Hz, 2H, Ar-CH), 5.06 – 5.05 (m, 1H, H-1), 5.04 – 4.97 (m, 3H, 3 x PhCH₂), 4.71 – 4.67 (m, 1H, PhCH₂), 4.65 – 4.56 (m, 2H, 2 x PhCH₂), 4.09 (d, J = 2.8 Hz, 1H, H-2), 3.72 (t, J = 9.2 Hz, 1H, H-4), 3.59 (dd, J = 9.3, 2.8 Hz, 1H, H-3), 3.52 (dq, J = 9.1, 6.2 Hz, 1H, H-5), 1.42 (d, J = 6.2 Hz, 3H, H-6). ¹³C NMR (126 MHz, Chloroform-d) δ 161.8 (4ºC), 142.6 (4ºC), 138.24 (4ºC), 138.21 (4ºC), 137.9 (4ºC), 128.49 (Ar-CH), 128.46 (Ar-CH), 128.45 (Ar-CH), 128.3 (Ar-CH), 128.1 (Ar-CH), 127.9 (Ar-CH), 127.83 (Ar-CH), 127.79 (Ar-CH), 127.70 (Ar-CH), 125.8 (Ar-CH), 116.1 (Ar-CH), 98.3 (C-1), 1, JCH = 156.0 Hz, from coupled HSQC), 81.8 (C-3), 79.6 (C-4), 75.6 (PhCH₂), 74.6 (PhCH₂), 74.3 (C-2), 72.4 (C-5), 72.1 (PhCH₂), 18.0 (C-6). ESI-HRMS for C₃₃H₃₃NO₇Na⁺ (M+Na)⁺ calculated: 578.2149; found: 578.2149.

**p-Methoxyphenyl 2-azido-3,6-di-O-benzyl-4-O-(2,3,4-tri-O-benzyl-β-L-rhamnosyl)-β-D-glucopyranoside 5h**

Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph₃PO (14 mg, 0.05 mmol), (COCl)₂ (10 μL, 0.12 mmol), Lil (54 mg, 0.4 mmol), iPr₂NET (70 μL, 0.4 mmol) and acceptor 3h (24.5 mg, 0.05...
mmol) were used. The reaction was stirred at 45 °C for 15 h. ¹H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (9:1; cyclohexane/Et₂O) afforded the desired product 5h as a colourless syrup (27 mg, 60% yield). R₁ = 0.5 (4:1; cyclohexane/EtOAc); ¹H NMR (500 MHz, Chloroform-d) δ 7.40 (dd, J = 7.6, 1.6 Hz, 2H, Ar-CH), 7.35 – 7.21 (m, 21H, Ar-CH), 7.18 (d, J = 6.8 Hz, 2H, Ar-CH), 7.12 – 7.09 (m, 2H, Ar-CH), 6.82 – 6.78 (m, 2H, Ar-CH), 4.89 (d, J = 11.0 Hz, 2H, 2 × PhCH₂), 4.79 – 4.77 (m, 2H, 2 × PhCH₂), 4.76 (d, J = 8.1 Hz, 1H, H-1), 4.62 – 4.54 (m, 3H, 3 × PhCH₂), 4.53 (s, 1H, H-1’), 4.31 (s, 2H, 2 × PhCH₂), 4.26 (d, J = 11.5 Hz, 1H, PhCH₂), 4.16 – 4.10 (m, 1H, H-6a), 3.77 (s, 3H, OCH₃), 3.68 – 3.61 (m, 4H, H-2, H-4, H-5, H-6b), 3.58 (d, J = 2.7 Hz, 1H, H-2’), 3.52 (t, J = 9.4 Hz, 1H, H-4’), 3.30 – 3.24 (m, 1H, H-3), 3.23 – 3.14 (m, 2H, H-3’, H-5’), 1.29 (d, J = 6.1 Hz, 3H, H-6’). ¹³C NMR (126 MHz, Chloroform-d) δ 155.5 (4ºC), 151.3 (4ºC), 138.7 (4ºC), 138.6 (4ºC), 138.4 (4ºC), 138.3 (4ºC), 138.0 (4ºC), 128.6 (Ar-CH), 128.5 (Ar-CH), 128.4 (Ar-CH), 128.3 (Ar-CH), 128.2 (Ar-CH), 127.9 (Ar-CH), 127.8 (Ar-CH), 127.7 (Ar-CH), 127.6 (Ar-CH), 127.5 (Ar-CH), 127.4 (Ar-CH), 127.2 (Ar-CH), 101.9 (C-1’, J_CCH = 157.0 Hz, from coupled HSQC), 101.5 (C-1, J_CCH = 167.0 Hz, from coupled HSQC), 83.4 (C-3), 82.7 (C-3’), 79.9 (C-4’), 76.3 (C-4), 75.5 (PhCH₃), 75.4 (PhCH₂), 75.0 (C-5), 74.0 (C-2’), 73.9 (PhCH₂), 73.4 (PhCH₂), 71.9 (C-5’), 71.8 (PhCH₂), 69.7 (C-6), 66.0 (C-2) 55.7 (OCH₃), 17.9 (C-6’). ESI-HRMS for C₅₂H₆₃N₄O₁₀ (M+Na)+ calculated: 944.4093; found: 944.2120.

**Ethyl 1-thiol 2,3,4-tri-O-benzyl-6-O-(2,3,4-tri-O-p-methylbenzyl-β-L-rhamnosyl)-α-D-mannopyranoside 5i**

![Diagram of the molecule](attachment:image.png)

Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph₃PO (14 mg, 0.05 mmol), (COCl)₂ (10 µL, 0.12 mmol), Lil (54 mg, 0.4 mmol), iPr₂NEt (44 µL, 0.25 mmol) and acceptor 3i (38 mg, 0.07 mmol) were used. The reaction was stirred at 45 °C for 15 h. ¹H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (9:1 to 7:3; cyclohexane/Et₂O) afforded the desired product 5i as a colourless syrup (65.6 mg, 98% yield). R₁ = 0.55 (4:1; cyclohexane/EtOAc); ¹H NMR (500 MHz, Chloroform-d) δ 7.46 – 7.42 (m, 2H, Ar-CH), 7.35 – 7.17 (m, 19H, Ar-CH), 7.14 (d, J = 7.7 Hz, 2H, Ar-CH), 7.10 (d, J = 7.7 Hz, 2H, Ar-CH), 7.03 (d, J = 7.7 Hz, 2H, Ar-CH), 5.33 (d, J = 1.6 Hz, 1H, H-1), 4.99 (d, J = 12.3 Hz, 1H, PhCH₂), 4.95 (d, J = 10.9 Hz, 1H, PhCH₂), 4.83 (d, J = 12.3 Hz, 1H, PhCH₂), 4.78 (d, J = 10.1 Hz, 1H, PhCH₂), 4.67 (d, J = 10.1 Hz, 1H, PhCH₂), 4.65 – 4.53 (m, 5H, 5 × PhCH₂), 4.52 (s, 1H, H-1’), 4.42 (d, J = 11.9 Hz, 1H, PhCH₂), 4.38 – 4.29 (m, 2H,
PhCH$_2$, H-6a), 4.14 (t, $J = 9.5$ Hz, 1H, H-4), 4.05 (ddd, $J = 9.7$, 3.6, 1.7 Hz, 1H, H-5), 3.99 (d, $J = 3.0$ Hz, 1H, H-2$^\prime$), 3.82 (dd, $J = 3.1$, 1.6 Hz, 1H, H-2), 3.79 (dd, $J = 9.3$, 3.1 Hz, 1H, H-3), 3.68 (dd, $J = 11.4$, 1.8 Hz, 1H, H-6b), 3.58 (t, $J = 9.3$ Hz, 1H, H-4$^\prime$), 3.42 (dd, $J = 9.4$, 3.1 Hz, 1H, H-3$^\prime$), 3.32 (dq, $J = 9.1$, 6.1 Hz, 1H, H-5$^\prime$), 2.63 – 2.44 (m, 2H, SCH$_2$CH$_3$), 2.35 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$), 2.25 (s, 3H, CH$_3$), 1.37 (d, $J = 6.2$ Hz, 3H, H-6$^\prime$), 1.19 (t, $J = 7.4$ Hz, 3H, SCH$_2$CH$_3$). $^{13}$C NMR (126 MHz, Chloroform-d) δ 139.0 (4°C), 138.7 (4°C), 138.4 (4°C), 137.30 (4°C), 137.28 (4°C), 137.2 (4°C), 135.7 (4°C), 135.5 (4°C), 135.2 (4°C), 129.00 (Ar-CH), 128.97 (Ar-CH), 128.85 (Ar-CH), 128.40 (Ar-CH), 128.35 (Ar-CH), 128.3 (Ar-CH), 128.1 (Ar-CH), 128.0 (Ar-CH), 127.8 (Ar-CH), 127.62 (Ar-CH), 127.59 (Ar-CH), 127.50 (Ar-CH), 127.2 (Ar-CH), 101.5 (C-1$^\prime$), $^{1}J_{	ext{CH}} = 155.6$ Hz, from coupled HSQC), 82.5 (C-1, $^{1}J_{	ext{CH}} = 164.0$ Hz, from coupled HSQC), 81.9 (C-3$^\prime$), 80.2 (C-4$^\prime$), 80.1 (C-3), 76.6 (C-2), 75.4 (PhCH$_2$), 75.2 (PhCH$_2$), 74.7 (C-4), 74.13 (PhCH$_3$), 74.10 (C-2$^\prime$), 72.3 (PhCH$_2$), 72.1 (PhCH$_2$, C-5), 71.9 (C-5$^\prime$), 70.9 (PhCH$_2$), 67.5 (C-6), 25.4 (SCH$_2$CH$_3$), 21.3 (CH$_3$), 21.23 (CH$_3$), 21.16 (CH$_3$), 18.11 (C-6$^\prime$), 15.05 (SCH$_2$CH$_3$). ESI-HRMS for C$_{30}$H$_{72}$NO$_3$S$^{+}$ (M+NH$_4$)$^+$ calculated: 970.4922; found: 970.4917.

Methyl 3-O-benzyl-4,6-benzylidene-2-O-(2,3,4-tri-O-benzyl-β-L-rhamnosyl)-α-D-galactopyranoside 5j

Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph$_3$PO (14 mg, 0.05 mmol), (COCl)$_2$: (10 μL, 0.12 mmol), LiI (54 mg, 0.4 mmol), iPr$_2$NET (70 μL, 0.4 mmol) and 3j (26 mg, 0.07 mmol) were used. The reaction was stirred at 45 °C for 24 h. $^1$H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (4:1 to 1:1; pentane/ Et$_2$O) afforded the desired product 5j as a colourless syrup (21.4 mg, 44% yield). $R_f = 0.3$ (7:3; cyclohexane/ EtOAc); $^1$H NMR (500 MHz, Chloroform-d) δ 7.56 – 7.51 (m, 2H, Ar-CH), 7.45 – 7.19 (m, 23H, Ar-CH), 5.45 (s, 1H, PhCH$_2$), 4.99 (d, $J = 12.3$ Hz, 1H, PhCH$_2$), 4.94 – 4.91 (m, 2H, H-1, PhCH$_2$), 4.90 – 4.84 (m, 2H, 2 × PhCH$_2$), 4.71 (d, $J = 12.3$ Hz, 1H, PhCH$_3$), 4.64 – 4.60 (m, 2H, PhCH$_3$, H-1), 4.53 (d, $J = 11.8$ Hz, 1H, PhCH$_3$), 4.47 (d, $J = 11.8$ Hz, 1H, PhCH$_3$), 4.42 (dd, $J = 10.1$, 3.5 Hz, 1H, H-2), 4.23 (dd, $J = 12.5$, 1.6 Hz, 1H, H-6a), 4.14 (dd, $J = 3.7$, 1.2 Hz, 1H, H-4), 4.01 (dd, $J = 12.5$, 1.8 Hz, 1H, H-6b), 3.97 (dd, $J = 10.1$, 3.6 Hz, 1H, H-3), 3.92 (d, $J = 3.0$ Hz, 1H, H-2$^\prime$), 3.63 – 3.58 (m, 2H, H-5, H-4$^\prime$), 3.46 (dd, $J = 9.4$, 2.9 Hz, 1H, H-3$^\prime$), 3.39 (s, 3H, OCH$_3$), 3.27 (dq, $J = 9.2$, 6.1 Hz, 1H, H-5$^\prime$), 1.35 (d, $J = 6.1$ Hz, 3H,
Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph₃PO (28 mg, 0.1 mmol), (COCl): (10 μL, 0.12 mmol), LiI (54 mg, 0.4 mmol), iPr₂NEt (70 μL, 0.4 mmol) and acceptor 3k (24 mg, 0.07 mmol) were used. The reaction was stirred at 45 °C for 24 h. ¹H NMR spectroscopy of the crude reaction mixture showed β-only product. Purification by column chromatography (9:1 to 7:3; pentane/ Et₂O) afforded the desired product 5k as a white solid (30 mg, 60% yield) along with hemiacetal 1j (15%). Rf = 0.6 (4:1; cyclohexane/ EtOAc); ¹H NMR (500 MHz, Chloroform-d) δ 7.52 (d, J = 6.9 Hz, 2H, Ar-CH), 7.39 – 7.26 (m, 13H, Ar-CH), 7.02 (d, J = 8.5 Hz, 2H, Ar-CH), 6.89 (d, J = 8.6 Hz, 2H, Ar-CH), 5.06 (d, J = 12.4 Hz, 1H, PhCH₂), 4.98 (d, J = 11.2 Hz, 2H, 2 × PhCH₂), 4.93 (s, 1H, H-1), 4.67 (d, J = 10.8 Hz, 1H, PhCH₂), 4.61 – 4.49 (m, 3H, CH, 2 × PhCH₂), 4.05 (d, J = 2.7 Hz, 1H, H-2), 3.68 (br s, 4H, H-4, OCH₃), 3.54 (dd, J = 9.4, 2.9 Hz, 1H, H-3), 3.52 – 3.42 (m, 1H, H-5), 3.09 – 2.96 (m, 2H, PhCH₂), 1.44 – 1.38 (m, 12H, H-6, Cl(CH₃)₃). ¹³C NMR (101 MHz, Chloroform-d) δ 172.3 (C=O), 156.3 (4°C), 138.5 (4°C), 138.4 (4°C), 130.0 (4°C), 132.93 (4°C), 129.53 (4°C), 128.46 (Ar-CH), 128.4 (Ar-CH), 128.3 (Ar-CH), 128.2 (Ar-CH), 128.1 (Ar-CH), 127.6 (Ar-CH), 116.3 (Ar-CH), 99.1 (C-1, ¹JCH = 154.9 Hz, from coupled HSQC), 82.0 (C-3), 80.0 (Cl(CH₃)₃), 79.9 (C-4), 75.5 (PhCH₂), 74.32 (C-2), 74.26 (PhCH₂), 72.1 (C-5), 71.7 (PhCH₂), 54.5 (CH), 52.2 (OCH₃), 37.5 (CH₂), 28.29 (Cl(CH₃)₃)), 18.06 (C-6). ESI-HRMS for C₄₂H₆₅N₃O₁₀⁺ (M+NH₄)⁺ calculated: 729.3746; found: 729.3749.
Following general procedure E, hemiacetal 1j (44 mg, 0.1 mmol), Ph₃PO (28 mg, 0.1 mmol), (COCl)₂ (10 μL, 0.12 mmol), LiI (54 mg, 0.4 mmol), iPr₂NEt (44 μL, 0.25 mmol) and cholesterol (27 mg, 0.07 mmol) were used. The reaction was stirred at rt for 24 h. ¹H NMR spectroscopy of the crude reaction mixture gave an α/β = 1:1. Purification by column chromatography (9:1; pentane/Et₂O) afforded the desired product S50 as a white solid (54 mg, quantitative yield). R_f = 0.8 (4:1; cyclohexane/EtOAc);

Reaction gave same anomeric mixture when performed at rt and when general procedure B was used.

Signals observed for both anomers:

¹H NMR (500 MHz, Chloroform-d) δ 7.50–7.46 (m, 2H, Ar-CH), 7.40–7.24 (m, 28H, Ar-CH), 5.01–4.87 (m, 3H, 3×PhCH₂), 4.78 (d, J = 12.3 Hz, 1H, PhCH₂), 4.73–4.69 (m, 1H, PhCH₂), 4.78 (d, J = 12.3 Hz, 1H, PhCH₂), 4.67–4.61 (m, 5H, 5×PhCH₂), 3.61 (td, J = 9.3, 2.0 Hz, 2H, H-4α, H-4β), 3.54 (dddd, J = 15.8, 11.2, 8.3, 3.4 Hz, 1H), 3.39 (ddd, J = 15.4, 7.7, 3.2 Hz, 1H), 2.53–2.43 (m, 1H), 2.13–1.91 (m, 7H), 1.90–1.77 (m, 7H), 1.63–1.42 (m, 22H), 1.40–1.29 (m, 5H), 1.29–1.20 (m, 4H), 1.19–1.04 (m, 17H), 1.03 (s, 3H), 1.00 (dd, J = 7.1, 3.6 Hz, 4H), 0.97 (s, 3H), 0.93–0.89 (m, 8H), 0.88–0.84 (m, 11H), 0.69–0.66 (m, 5H).

¹³C NMR (126 MHz, Chloroform-d) δ 140.9 (4ºC), 140.5 (4ºC), 138.9 (4ºC), 138.7 (4ºC), 138.63 (4ºC), 138.57 (4ºC), 138.5 (4ºC), 138.3 (4ºC), 138.2 (4ºC), 128.6 (Ar-CH), 128.37 (Ar-CH), 128.35 (Ar-CH), 128.33 (Ar-CH), 128.31 (Ar-CH), 128.12 (Ar-CH), 128.09 (Ar-CH), 128.0 (Ar-CH), 127.95 (Ar-CH), 127.64 (Ar-CH), 127.56 (Ar-CH), 127.54 (Ar-CH), 127.50 (Ar-CH), 127.47 (Ar-CH), 127.3 (Ar-CH), 78.3, 76.4, 75.4 (PhCH₃), 73.8 (PhCH₂), 72.8 (PhCH₂), 72.1 (PhCH₂), 71.3 (PhCH₂), 56.8, 56.7, 56.16, 56.15, 50.2, 50.1, 42.34, 42.32, 40.2, 39.81, 39.77, 39.5, 38.4, 37.3, 37.1, 36.74, 36.72, 36.32, 35.8, 31.95, 31.90, 31.89, 29.4, 28.2, 28.1, 28.0, 24.3, 23.8, 22.8, 22.6, 21.10, 21.05, 19.42, 19.36, 18.74, 18.73, 11.9. ESI-HRMS for C₅₄H₇₅O₅⁺ (M+H)⁺ calculated: 803.5609; found: 803.5616.

α-anomer:

¹H NMR (500 MHz, Chloroform-d) δ 5.33–5.29 (m, 1H, C=CH), 4.88 (d, J = 1.6 Hz, 1H, H-1), 3.88 (dd, J = 9.4, 3.1 Hz, 1H, H-3), 3.79–3.72 (m, 2H, H-5, H-2), 1.31 (d, J = 6.2 Hz, 3H, H-6). ¹³C NMR (126 MHz, Chloroform-d) δ 121.8 (C=CH), 96.0 (C-1, J_CCH = 169.0 Hz, from coupled HSQC), 80.8 (C-4), 80.3 (C-3), 75.5 (C-2), 68.0 (C-5), 18.0 (C-6).

β-anomer:

¹H NMR (500 MHz, Chloroform-d) δ 5.39–5.33 (m, 1H, C=CH), 4.47 (s, 1H, H-1), 3.84 (d, J = 3.0 Hz, 1H, H-2), 3.44 (dd, J = 9.4, 3.1 Hz, 1H, H-3), 3.29 (dq, J = 9.2, 6.1 Hz, 1H, H-5), 1.36 (d, J = 6.1
Donor and Acceptor Limitations

Peracetylated/4-OAc donors S22, S24 and S35, were disarmed and no glycosylation was observed. 6-OTIPS donor S23 led to the anhydro sugar. Benzylidene acceptors S40 and S46 were poor nucleophiles and no desired reaction was observed. Benzoylated acceptor S49 led to complex mixtures due to ester migration. We confirmed that ester migration occurred on benzyloylated acceptor S49 with iPr₂NEt in CHCl₃ at 45 °C in the absence of other reagents. Acceptor S43 gave a complex mixture in reactions with 1a; there were trace amounts of the desired β-product (as evidenced by HSQC), and the major product was the donor elimination product. We suspect there was also acyl migration but it was difficult to be sure because of the complex mixture generated. S43 is a poor nucleophile and so observation of elimination is not that surprising. Reaction with cholesterol gave the product S50 in a very high yield but with no selectivity. When S35 used as donor in the glycosylation reaction with acceptor 3a, transesterification was observed giving product S51 (see below).
Mechanistic Investigations

**Route A**

\[ \text{Ph}_3\text{PO} \] (CO\text{O})\text{I}_2 \quad \text{rt, 30 min} \quad \text{CHCl}_3 \quad \text{ROH, iPr}_2\text{NEt CHCl}_3, 45^\circ\text{C} \quad \text{no glycosylation} \\

**Route B**

\[ \text{TMSI} \quad \text{CHCl}_3, 45^\circ\text{C} \quad \text{ROH, iPr}_2\text{NEt CHCl}_3, 45^\circ\text{C} \quad \text{Detected by } ^1\text{H NMR spectroscopy (H-1, 6.91 ppm)} \\

**Route C**

\[ \text{Ph}_3\text{P, ICH}_2\text{CH}_2\text{I CHCl}_3, 45^\circ\text{C, 40 min} \quad \text{ROH} = \text{BnO} \text{HO} \text{BnO OMe} \text{BnO} \text{BnO} \text{BnO} \]
| Entry | Route | Deviation from standard procedure | \( \beta/\alpha \) |
|-------|-------|-----------------------------------|-----------------|
| 1     | A     | No \( \text{Ph}_3\text{PO} \)      | \( \geq 20:1 \) |
| 2     | A     | 0.5 eq \( \text{Ph}_3\text{PO} \)  | \( \geq 20:1 \) |
| 3     | A     | No LiI                             | No glycosylation |
| 4     | A     | NaI *in lieu* of LiI              | 1:1             |
| 5     | A     | Filtration of insoluble LiCl/LiI salts | 1:1         |
| 6     | A     | Filtration of insoluble LiCl/LiI salts; no \( \text{Ph}_3\text{PO} \) | \( \geq 20:1 \) |
| 7     | A     | 2 eq LiI in lieu of 4 eq LiI       | 2:3             |
| 8     | A     | 2 eq \( \text{Ph}_3\text{PO} \)   | 1:1             |
| 9     | A     | 2 eq \( \text{Ph}_3\text{PO} \), 8 eq LiI | 10:1        |
| 10    | A     | No \( \text{Ph}_3\text{PO} \), 4Å MS | \( \geq 20:1 \) |
| 11    | B     | 0.5 eq \( \text{Ph}_3\text{PO} \)  | 2:3             |
| 12    | B     | 4 eq LiI                          | 3:1             |
| 13    | B     | 4 eq LiCl                         | 2:3             |
| 14    | C     | -                                 | 2:3             |
| 15    | C     | 4 eq LiI                          | \( \geq 20:1 \) |

* Determined by \(^1\text{H} \) NMR spectroscopy of the reaction mixture. After synthesis of \( \text{6a} \), the \( \text{Ph}_3\text{PO} \) was removed by chromatography.

**Route A:**

Following the general procedure A, hemiacetal \( \text{1a} \) (378 mg, 0.700 mmol), \( \text{Ph}_3\text{PO} \) (195 mg, 0.500 mmol) and oxalyl chloride (64 \( \mu \)L, 0.77 mmol) were used. After 30 minutes, the solvent and excess oxalyl chloride were removed by applying vacuum. (For removal of \( \text{Ph}_3\text{PO} \): The crude mannosyl chloride was subjected to flash column chromatography (\( R_f = 0.9, 96:4; \) \( \text{CH}_2\text{Cl}_2/\text{Et}_2\text{O} \)) to obtain the isolated mannosyl chloride \( \text{6a} \) as a yellowish syrup. A stock solution of \( \text{6a} \) in anhydrous \( \text{CHCl}_3 \) (0.4 M) was prepared).

**Entry 1:** Acceptor (0.7 eq), powdered LiI (4 eq) and iPr\(_2\)NEt (2.5 eq) were used (reaction was also performed for 5 h).

**Entry 2:** \( \text{Ph}_3\text{PO} \) (0.5 eq), acceptor (0.7 eq), powdered LiI (4 eq) and iPr\(_2\)NEt (2.5 eq) were used.

**Entry 3:** \( \text{Ph}_3\text{PO} \) (1 eq), acceptor (0.7 eq) and iPr\(_2\)NEt (2.5 eq) were used.

**Entry 4:** \( \text{Ph}_3\text{PO} \) (1 eq), acceptor (0.7 eq), NaI (4 eq) and iPr\(_2\)NEt (2.5 eq) were used (reaction gave same glycosylation outcome in both \( \text{CHCl}_3 \) and MeCN).

**Entry 5:** \( \text{Ph}_3\text{PO} \) (1 eq), powdered LiI (4 eq) and iPr\(_2\)NEt (2.5 eq) were used and the reaction left to stir for 3 h (glycosyl iodide formation); syringe filtration was carried out and then acceptor (0.7 eq) added.

**Entry 6:** Isolated mannosyl chloride \( \text{6a} \) (1 eq), powdered LiI (4 eq) and iPr\(_2\)NEt (2.5 eq) were used and the reaction left to stir for 3 h (glycosyl iodide formation); syringe filtration was carried out and then acceptor (0.7 eq) added.
Entry 7: Acceptor (0.7 eq), powdered LiI (2 eq), iPr<sub>2</sub>NEt (2.5 eq) and were used (reaction was carried out with and without Ph<sub>3</sub>PO, leading to similar results in both cases).

Entry 8: Ph<sub>3</sub>PO (2 eq), acceptor (0.7 eq), LiI (4 eq) and iPr<sub>2</sub>NEt (2.5 eq) were used.

Entry 9: Ph<sub>3</sub>PO (2 eq), acceptor (0.7 eq), LiI (8 eq) and iPr<sub>2</sub>NEt (2.5 eq) were used.

Entry 10: Acceptor (0.7 eq), powdered LiI (4 eq), iPr<sub>2</sub>NEt (2.5 eq) and 4Å MS (30 mg) were used.

Route B:
In a solution of glycosyl acetate 8a (57 mg, 0.1 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (500 μL), freshly activated 4Å MS (59 mg) were added followed by the addition of TMSI (17 μL, 0.12 mmol). After 30 minutes, the solvent and excess reagent were removed by applying vacuum. The residue was redissolved in anhydrous CHCl<sub>3</sub> (250 μL).

Entry 11: Ph<sub>3</sub>PO (0.5 eq), acceptor (0.7 eq) and iPr<sub>2</sub>NEt (2.5 eq) were used.

Entry 12: Acceptor (0.7 eq), powdered LiI (4 eq) and iPr<sub>2</sub>NEt (2.5 eq) were used.

Entry 13: Acceptor (0.7 eq), powdered LiCl (4 eq) and iPr<sub>2</sub>NEt (2.5 eq) were used.

Route C:
Based on a modified literature procedure,[39] hemiacetal 1a (54 mg, 0.10 mmol), Ph<sub>3</sub>P (26 mg, 0.10 mmol) and 1,2-diiodoethane (28 mg, 0.10 mmol) were dissolved in anhydrous CHCl<sub>3</sub> (300 μL) and stirred at 45 °C for 40 minutes. Solvent was removed by applying vacuum and the residue was redissolved in anhydrous CHCl<sub>3</sub> (250 μL).

Entry 14: Acceptor (0.7 eq) and iPr<sub>2</sub>NEt (2.5 eq) were used.

Entry 15: Acceptor (0.7 eq), powdered LiI (4 eq) and iPr<sub>2</sub>NEt (2.5 eq) were used.

The reactions were stirred at 45 °C for 24 h. The α/β ratio was determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture.
Figure S1 Stacked $^1$H NMR spectra (CDCl$_3$, 500 MHz) of experiments to probe mechanism.

Figure S2 Stacked $^1$H NMR spectra (CDCl$_3$, 500 MHz) of experiments to probe mechanism.
Figure S3 Stacked $^1$H NMR spectra (CDCl$_3$, 500 MHz) of experiments to probe mechanism.
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