Supporting Information

A Synthetic Glycan Array Containing GXM Capsular Polysaccharide Fragments Allows Mapping of Protective Epitopes in Cryptococcus neoformans

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Contents

General Procedures

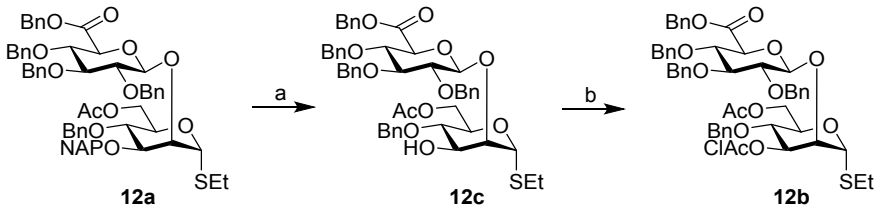
2-Naphthylmethyl Removal

DDQ (2 equiv.) was added to a vigorously stirred solution of compound (1eq) in CH_2Cl_2/PBS (100 mM, pH 7.5) (0.02M, 85:15) at 5–10 °C, in the dark. The progress of the reaction was carefully monitored by TLC, and quenched upon completion, by adding 10 %aq. $Na_2S_2O_3$solution and $NaHCO_3$(1:1, v/v). The resulting mixture was extracted CH_2Cl_2, and the organic layer was washed sequentially with sat. $NaHCO_3$ solution, brine, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography.

DMTST Mediated Glycosylation

A mixture of thioglycoside donor (1.5eq), acceptor (1eq), and crushed 4 Å molecular sieves in dry Et_2O (0.01M) was stirred at 20 °C for 60 min. The reaction mixture was cooled to 0 °C, DMTST (3eq) was added, and the reaction mixture was stirred at 0 °C for 60 min. The reaction was allowed to rise to room temperature. If required, the reaction was pushed to completion by an additional amount of DMTST (3eq). Stirring was continued until the reaction was complete (ca. 4–8 h). The reaction quenched with Et_3N at 0 °C.The solution was filtered through a pad of Celite®, and the filtratewas concentrated in vacuo. Purification by flash column chromatog-raphy

Building Block Synthesis



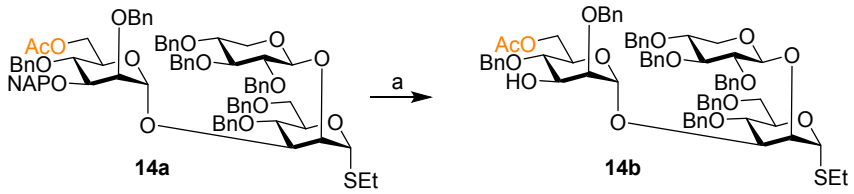
Scheme 1. Reagents and conditions: (a) DDQ, CH_2Cl_2/H_2O (10:1), 20°C, 60 min, 61%; (b) Chloroacetyl chloride, CH_2Cl_2/pyridine (15:1), 0°C, 60 min, 96%.

Ethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-1-thio-α-D-mannopyranoside (12c)

DDQ (95 mg, 0.42 mmol) was added to a vigorously stirred solution of compound **12a** (270 mg, 0.26 mmol) in CH_2Cl_2/H_2O (16.5 mL, 10:1) at 20°C. An additional amount of DDQ (71 mg, 0.31 mmol) was added after 20 min. More DDQ (71 mg, 0.31 mmol) was added after 40 min. After 60 min, the reaction was quenched by adding 10% aq. $Na_2S_2O_3$-solution (30 mL). The resulting mixture was extracted once with CH_2Cl_2 (100 mL), the layers were separated, and the organic layer was washed sequentially with sat. $NaHCO_3$-solution (3 x 100 mL), and brine (1 x 100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, 100 mL, 4.5 cm, toluene→toluene-EtOAc, 96:4→93:7→90:10→87:13→84:16→78:22) to give **12c** (142 mg, 61%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.34; $[\alpha]_D^{20}$ +56.6 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.22 (m, 23H), 7.14-7.09 (m, 2H), 5.32 (bs, 1H), 5.19-5.13 (ABq, 2H), 5.02 (d, *J* 11.1 Hz, 1H), 4.98 (d, *J* 10.2 Hz, 1H), 4.92 (d, *J* 11.2 Hz, 1H), 4.79 (d, *J* 11.0 Hz, 1H), 4.73-4.68 (m, 2H), 4.63 (d, *J* 11.0 Hz, 1H), 4.51-4.47 (m, 2H), 4.35-4.30 (m, 2H), 4.18 (dt, *J* 3.4 Hz, *J* 9.7 Hz, 1H), 4.07 (dd, *J* 1.2 Hz, *J* 3.3 Hz, 1H), 4.01-3.97 (m, 2H), 3.85 (t, *J* 9.2 Hz, 1H), 3.67-3.63 (m, 2H), 3.56-3.52 (m, 1H), 2.62-2.49 (m, 2H), 1.83 (s, 3H), 1.23 (t, *J* 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 168.1, 138.4, 138.4, 137.8, 137.7, 135.0, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.3, 128.2, 127.1, 128.0, 127.9, 127.9, 103.4, 83.7, 82.7, 82.4, 81.1, 79.2, 76.4, 75.9, 75.2, 75.2, 75.0, 74.7, 71.9, 69.8, 67.8, 63.5, 25.5, 20.8, 15.1. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{51}H_{56}O_{12}NaS$, 915.3390; found, 915.3397.

Ethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-1-thio-α-D-mannopyranoside (12b)

Chloroacetyl chloride (106 μL, 1.33 mmol) was added to a solution of compound **12c** (298 mg, 0.33 mmol) in CH_2Cl_2/pyridine (16 mL, 15:1) at 0 °C. On adding chloroacetyl chloride, the colourless reaction mixture turned bright yellow. The progress of the reaction was monitored by TLC (toluene-EtOAc, 6:1). After 10 min, the reaction mixture was diluted with toluene, concentrated *in vacuo* to a syrup, and then re-dissolved and co-evaporated with toluene (3 x 10 mL) (water bath temperature of rotary evaporator: < 30 °C). Purification by flash column chromatography (SiO_2, 100 mL, 4.5 cm, toluene→toluene-EtOAc, 96:4→93:7→90:10→87:13→84:16→78:22) gave **12b** (311 mg, 96%) as a colourless syrup; R_f (toluene-EtOAc, 6:1) 0.64; $[\alpha]_D^{20}$ +16.4 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-7.03 (m, 25H), 5.30 (bs, 1H), 5.18-5.12 (ABq, 2H), 5.10 (dd, *J* 3.3 Hz, *J* 9.6 Hz, 1H), 5.03 (d, *J* 9.8 Hz, 1H), 4.92 (d, *J* 11.0 Hz, 1H), 4.82-4.77 (m, 2H), 4.70 (d, *J* 10.8 Hz, 1H), 4.66 (d, *J* 9.8 Hz, 1H), 4.63 (d, *J* 11.2 Hz, 1H), 4.43 (d, *J* 10.8 Hz, 1H), 4.38-4.29 (m, 5H), 4.09-4.03 (m, 2H), 4.00-3.96 (m, 1H), 3.85 (d, *J* 9.8 Hz, 1H), 3.80 (t, *J* 9.1 Hz, 1H), 3.65 (t, *J* 8.9 Hz, 1H), 3.56 (m, 1H), 2.63-2.53 (m, 2H), 1.78 (s, 3H), 1.25 (t, *J* 7.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.7, 168.8, 166.9, 138.4, 137.9, 137.8, 137.6, 134.8, 129.0, 128.9, 128.8, 128.7, 128.6, 128.6, 128.6, 128.5, 128.3, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 103.2, 83.7, 82.3, 81.3, 79.5, 77.3, 75.9, 75.6, 75.3, 75.2, 75.2, 74.4, 72.7, 69.8, 67.9, 63.0, 41.0, 25.6, 20.7, 14.9. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{53}H_{57}O_{13}NaSCl$, 991.3106; found, 991.3109.

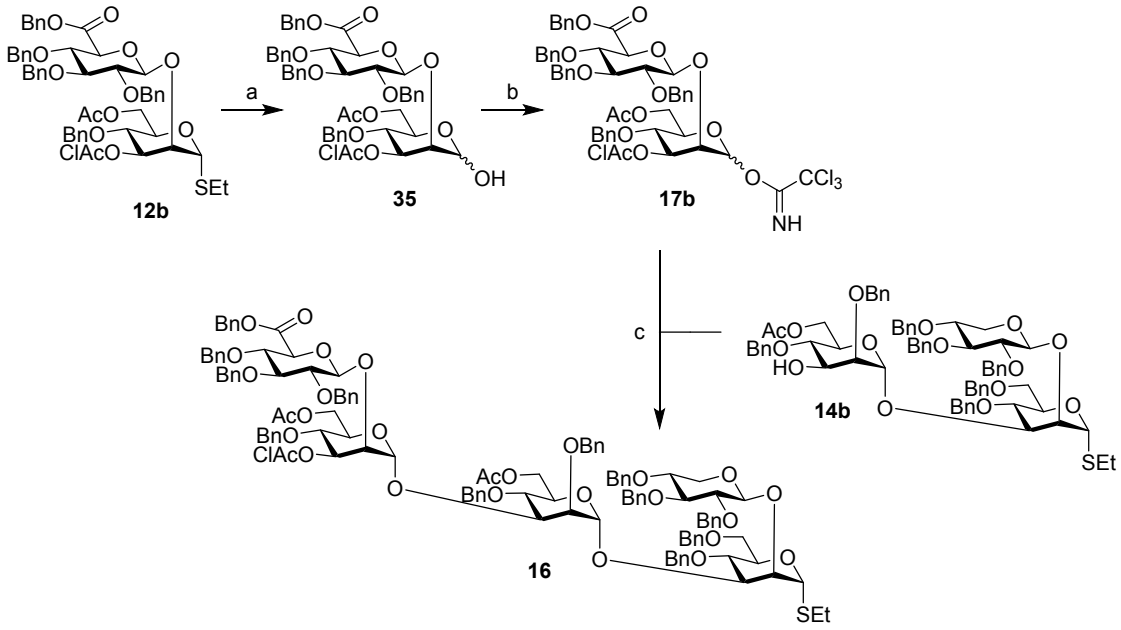


Scheme 2. Reagents and conditions: (a) DDQ, DCM/H_2O (10:1), 20°C, 60 min, 68%.

Ethyl 6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylo-pyranosyl-(1→2)]-4,6-di-*O*-benzyl-1-thio-α-D-mannopyranoside (14b)

For method see general procedure for 2-Naphthylmethyl removal.

R_f 0.49 (toluene/EtOAc 84:16); $[\alpha]_D^{20}$ +36.0 (*c* 1.00, $CHCl_3$);**^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.43-7.11 (m, 35H), 5.39 (s, 1H), 5.25 (s, 1H), 5.07 (d, *J* 10.1 Hz, 1H), 4.93 (d, *J* 11.2 Hz, 1H), 4.87-4.78 (m, 3H), 4.68 (d, *J* 11.8 Hz, 1H), 4.60-4.55 (m, 2H), 4.47-4.38 (m, 3H), 4.36-4.22 (m, 6H), 4.20-4.17 (bs, 1H), 4.12-4.03 (m, 5H), 4.00 (dd, *J* 4.8 Hz, *J* 11.7 Hz, 1H), 3.79 (dd, *J* 4.1 Hz, *J* 10.8 Hz, 1H), 3.73 (dd, *J* 1.1 Hz, *J* 3.6 Hz, 1H), 3.68 (dd, *J* 1.3 Hz, *J* 10.7 Hz, 1H), 3.57-3.47 (m, 3H), 3.44 (t, *J* 8.2 Hz, 1H), 3.09 (dd, *J* 9.8 Hz, *J* 11.5 Hz, 1H), 2.63-2.51 (m, 2H), 2.28 (d, *J* 10.0 Hz, 1H), 2.11 (s, 3H), 1.23 (t, *J* 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 171.1, 138.9, 138.8, 138.6, 138.6, 138.2, 138.1, 137.7, 128.9, 128.5, 128.4, 128.3, 128.3, 128.3, 127.9, 127.9, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 126.6, 104.1, 99.0, 83.9, 82.5, 81.1, 80.6, 78.9, 77.9, 77.7, 77.1, 75.6, 75.4, 75.1, 74.7, 74.5, 73.4, 72.7, 72.3, 72.1, 71.7, 69.4, 69.4, 64.5, 63.6, 25.3, 21.2, 15.0. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{70}H_{78}O_{15}NaS$, 1213.4959; found, 1213.4962.



Scheme 3. Reagents and conditions: (a) NIS, TFA, DCM/H_2O (20:1), 0 °C, 1 h, 92% (α;β, 3:1); (b) Cl_3CCN, DBU, DCM, 0 °C, 60 min, > 99% (crude yield); (c) TMSOTf, Et_2O, 4 Å MS, −40 °C→10 °C, 2 h, 76% (α-only).

Benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-D-mannopyranose (35)

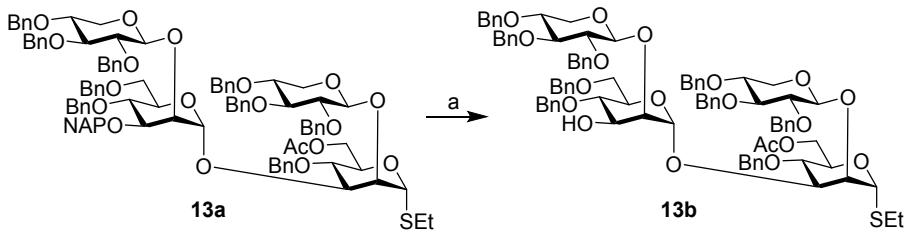
NIS (30 mg, 0.13 mmol) and TFA (10 μL, 0.13 mmol) were added to a vigorously stirred solution of thioglycoside **12b** (120 mg, 0.12 mmol) in CH_2Cl_2/H_2O (2.1 mL, 20:1) at 20 °C. After 1 h, the reaction was quenched by adding 10% aq. $Na_2S_2O_3$-solution (10 mL). The resulting mixture was extracted once with CH_2Cl_2 (15 mL), the layers were separated, and the organic layer was washed sequentially with sat. $NaHCO_3$-solution (3 x 10 mL), and brine (1 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash column chromatography (RevererisX1, 40 gram column, toluene-EtOAc, 98:2→70:30) gave an anomeric mixture of the **35** (106 mg, 92%, α:β, 3:1) as a colourless syrup; $\mathbf{R}_f$ (cyclohexane-EtOAc, 8:2) 0.38; **^{1}H NMR** (500 MHz, $CDCl_3$) selected signals **35*a*** 5.25 (dd, *J* 3.6 Hz, *J* 9.6 Hz, 1H), 5.21 (dd, *J* 1.6 Hz, *J* 3.5 Hz, 1H), 4.26 (dd, *J* 1.9 Hz, *J* 3.4 Hz, 1H), 3.18 (d, *J* 3.6 Hz, 1H), 1.77 (s, 3H);*δ* 4.94 (d, *J* 10.0 Hz, 1H), 4.47 (d, *J* 7.9 Hz, 1H), 4.21 (d, *J* 3.3 Hz, 1H), 1.77 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) selected signals **35*a*** *δ* 170.8, 168.8, 167.0, 138.4, 138.0, 137.8, 137.7, 134.8, 103.5, 92.7, 83.6, 81.4, 79.5, 75.9, 75.7, 75.3, 75.2, 75.1, 74.8, 74.4, 72.5, 69.6, 68.0, 63.1, 41.1, 20.7; ^{1}H NMR (500 MHz, $CDCl_3$) selected signals **35*β*** *δ* 4.94 (d, *J* 10.0 Hz, 1H), 4.47 (d, *J* 7.9 Hz, 1H), 4.21 (d, *J* 3.3 Hz, 1H), 1.95 (s, 3H); ^{13}C NMR

(125 MHz, $CDCl_3$) selected signals **35*β*** δ 170.7, 168.7, 167.1, 138.1, 137.8, 137.4, 136.5, 134.7, 104.8, 93.8, 84.0, 81.3, 79.8, 78.2, 77.0, 76.3, 75.8, 75.3, 75.2, 74.6, 73.1, 72.4, 68.0, 63.1, 41.0, 20.9. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{51}H_{53}O_{14}NaCl$, 947.3022; found, 947.3033.

Ethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-1-thio-α-D-mannopyranoside (16)

Trichloroacetonitrile (100 μL, 1.0 mmol) and DBU (10 μL, 66 μmol) were added to an ice-cooled solution of hemiacetal **35** (120 mg, 0.13 mmol) in dry CH_2Cl_2 (50 mL) in an atmosphere of nitrogen. After complete consumption of the starting material (2 h), the mixture was concentrated *in vacuo* to a brown oil. Filtration on silica (cyclohexane-EtOAc+0.1% Et_3N) to remove DBU afforded donor **17b** (126 mg) that was used in the next glycosylation without further purifications.
A catalytic amount of TMSOTf (10 μL, 55.2 μmol) was added to a solution of acceptor **14b** (108 mg, 90.7 μmol) in dry Et_2O (4.0 mL) containing 4 Å molecular sieves kept at −40 °C in an atmosphere of nitrogen. A solution of donor **7** in dry Et_2O (3 mL) was added dropwise over 1 h to the reaction vessel. The temperature was then allowed to rise to −10 °C in 2 h. The reaction mixture was neutralised with Et_3N, the solids were removed by filtration, and the filtrate was concentrated *in vacuo* to a yellowish oil. Purification by automated flash column chromatography (RevererisX1, 40 gram column, cyclohexane-EtOAc, 90:10→70:30) gave **16** (144 mg, 76%) as a colourless, amorphous solid. $\mathbf{R}_f$ (cyclohexane-EtOAc 8:2) 0.45; $[\alpha]_D^{20}$ −2.8 (*c* 1.00, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.01 (m, 60H), 5.41 (s, 1H), 5.24-5.20 (m, 2H), 5.17-5.10 (m, 4H), 4.99 (d, *J* 10.4 Hz, 1H), 4.87-4.83 (m, 2H), 4.81-4.72 (m, 3H), 4.70-4.45 (m, 9H), 4.44-4.30 (m, 7H), 4.26-4.18 (m, 4H), 4.14-3.93 (m, 11H), 3.91-3.77 (m, 5H), 3.69-3.63 (m, 2H), 3.52-3.48 (m, 3H), 3.43-3.38 (m, 2H), 3.24 (t, *J* 9.1 Hz, 1H), 3.13-3.06 (m, 1H), 2.64-2.53 (m, 2H), 2.10 (s, 3H), 1.66 (s, 3H), 1.24 (t, *J* 9.1 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.1, 170.5, 168.8, 166.9, 139.2, 138.7, 138.66, 138.6, 138.5, 138.2, 138.2, 138.1, 138.0, 137.9, 137.6, 134.8, 129.0, 128.9, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 126.7, 126.5, 103.9 ($J_{C,H}$ 155 Hz), 103.2 ($J_{C,H}$ 160 Hz), 100.2 ($J_{C,H}$ 170 Hz), 99.7 ($J_{C,H}$ 170 Hz), 83.9, 83.2, 82.4 ($J_{C,H}$ 165 Hz), 81.3, 81.2, 80.5, 80.4, 79.5, 79.4, 78.4, 78.3, 75.5 (2C), 75.4, 75.3, 75.2, 75.1, 75.1, 75.0, 74.8, 74.8, 74.7, 74.5, 74.1, 73.5, 73.1, 72.2, 72.1, 71.8, 69.9, 69.9, 69.4, 67.8, 64.1, 63.7, 62.8, 41.1, 25.5,

21.2, 20.7, 15.0. **HRMS (ESI):** $[M+Na]^+$ calcd for $C_{121}H_{129}O_{28}NaSCl$, 2119.7977; found, 2119.7947.

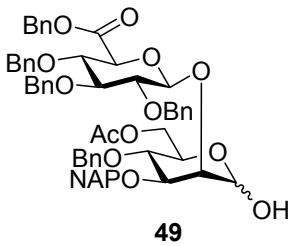


Scheme 4. Reagents and conditions: (a) DDQ, DCM/H_2O (10:1), 20 °C, 60 min, 68%.

Ethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-1-thio-α-D-mannopyranoside (13b)

For method see general procedure for 2-Naphthylmethyl removal.

R_f 0.49 (toluene/EtOAc 84:16); $[\alpha]_D^{20}$ +38.0 (*c* 1.00, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.13 (m, 45H), 5.27 (s, 1H), 5.16 (s, 1H), 5.02 (d, *J* 10.0 Hz, 1H), 4.97 (d, *J* 11.3 Hz, 1H), 4.92 (d, *J* 10.8 Hz, 1H), 4.89-4.80 (m, 5H), 4.70 (d, *J* 11.8 Hz, 1H), 4.65 (d, *J* 10.0 Hz, 1H), 4.62-4.48 (m, 6H), 4.35 (d, *J* 11.5 Hz, 1H), 4.33-4.26 (m, 5H), 4.23-4.17 (m, 2H), 4.07-4.01 (m, 2H), 3.97-3.90 (m, 2H), 3.82-3.74 (m, 4H), 3.66 (dd, *J* 5.8 Hz, *J* 10.6 Hz, 1H), 3.58-3.35 (m, 6H), 3.29-3.25 (m, 1H), 3.06-2.97 (m, 2H), 2.86 (t, *J* 11.0 Hz, 1H), 2.55-2.44 (m, 2H), 1.83 (s, 3H), 1.20 (t, *J* 7.4 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.7, 139.3, 139.0, 138.8, 138.7, 138.5, 138.3 (2C), 138.2 (2C), 128.8, 128.8, 128.7, 128.6, 128.4, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 126.9, 104.3, 104.0, 101.1, 83.9, 83.4, 82.9, 81.5, 80.9, 80.8, 80.7, 78.9, 77.8, 77.4, 77.3, 75.6 (2C), 75.1, 74.9, 74.9, 74.7 (2C), 73.6, 73.5, 72.8, 71.9, 70.9, 70.3, 69.9, 64.1, 63.6, 63.3, 25.7, 20.7, 15.1. **HRMS (ESI):** $[M+Na]^+$ calcd for $C_{70}H_{78}O_{15}NaS$, 1525.6321; found, 1525.6383.

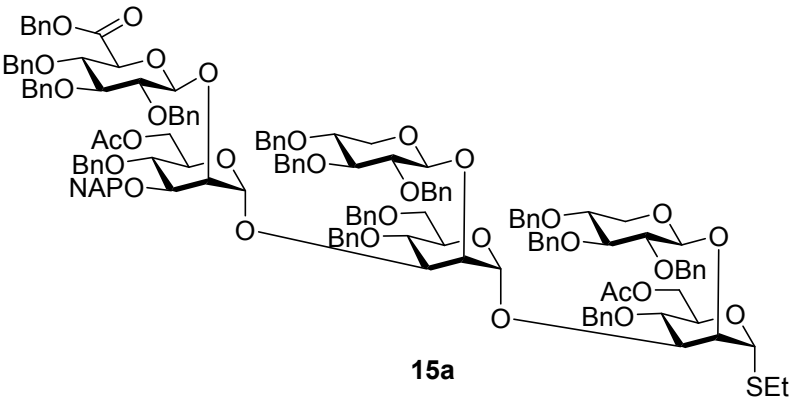


49

Benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-D-mannopyranose (49)

NIS (87 mg, 0.38 mmol) and TFA (30 μL, 0.38 mmol) were added to a vigorously stirred solution of thioglycoside **12a** (400 mg, 0.38 mmol) in DCM/H_2O (21 mL, 20:1) at 20°C TLC (toluene-EtOAc, 5:1). After 90 min, the reaction was quenched by adding of 10% aq. $Na_2S_2O_3$-solution (50 mL). The resulting mixture was extracted once with DCM (100 mL), the layers were separated, and the organic layer was washed sequentially with sat. $NaHCO_3$-solution (3 x 100 mL) and brine (1 x 100 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 100 mL, 4.5 cm, toluene→toluene-EtOAc, 93:7→90:10→87:13→84:16→81:19→75:25) gave an anomeric mixture (α:β, 3:1) of the *title compound* **49** (305 mg, 80%) as a colourless, amorphous solid. Two anomers: $\mathbf{R}_f$ (toluene-EtOAc, 5:1) = 0.38; $\mathbf{R}_f$ (toluene-EtOAc, 5:1) = 0.25. Data for the **α-anomer 94**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.76 (m, 4H), 7.52-7.12 (m, 28H), 5.35 (s, 1H), 5.12 (d, 1H, J_{gem} = 11.0 Hz), 5.08 (ABq, 2H), 4.97 (d, 1H, J_{gem} = 10.5 Hz), 4.94-4.90 (m, 2H), 4.78 (d, 1H, J_{gem} = 11.0 Hz), 4.77 (d, 1H, J_{gem} = 10.0 Hz), 4.60-4.50 (m, 5H), 4.30 (m, 2H), 4.26 (m, 1H), 4.06-4.02 (m, 2H), 3.97-3.96 (m, 3H), 3.72-3.65 (m, 2H), 2.74 (d, 1H, J = 3.5 Hz), 1.68 (s, 3H, C(=O)CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.7 (*C*(=O)CH_3), 167.9, 138.5, 138.3, 138.0, 137.9, 135.4, 134.9, 133.3, 133.1, 129.0, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 126.7, 125.9, 125.8, 103.4, 92.6, 84.0, 81.3, 78.9, 77.2, 75.7, 75.2, 75.1, 74.8, 74.6, 73.8, 70.9, 69.9, 67.4, 63.4, 20.5. Selected data for the **β-anomer**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.07-5.01 (ABq, 2H), 4.78 (m, 1H), 4.64 (m, 1H), 4.35-4.34 (m, 2H), 4.14 (dd ≈ d, 1H, J = 3.0 Hz), 4.00-3.98 (m, 2H), 3.89 (dd ≈ t, 1H, J = 9.5 Hz), 3.72-3.70 (m, 2H), 3.64-3.63 (m, 1H), 3.50-3.47 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.6, 167.7, 138.2, 137.7, 136.6, 135.0, 134.8, 133.2, 133.1, 105.3, 94.6, 84.3, 81.6, 79.7, 79.2, 77.8, 76.4, 75.2, 75.0, 73.5, 73.4, 70.9, 67.5, 63.3, 20.7. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{60}H_{60}O_{13}Na$, 1011.3932; found, 1011.3967; **Anal.** Calcd for $C_{60}H_{60}O_{13}$: C, 72.86; H, 6.11. Found: C, 72.49; H, 6.12 %.

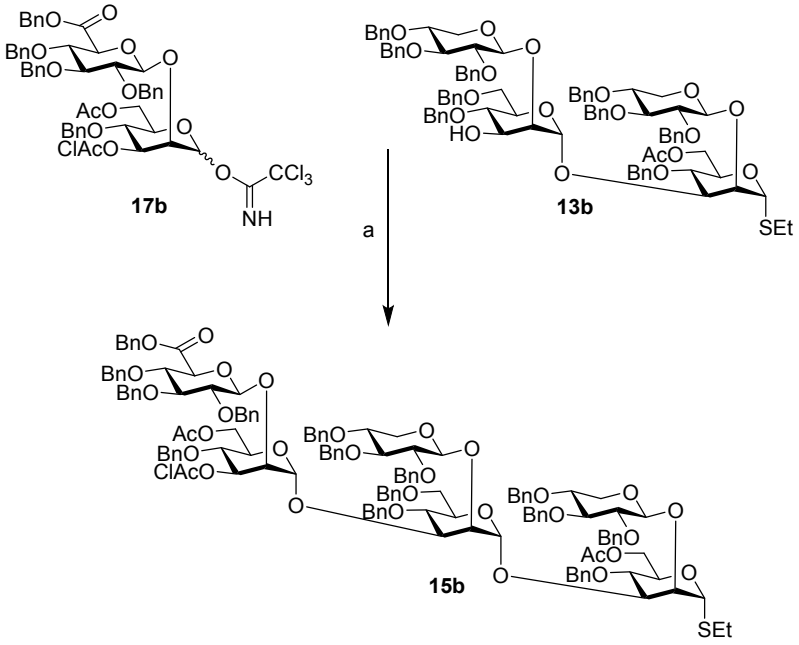
Ethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-1-thio-α-D-mannopyranoside (15a)



15a

Trichloroacetonitrile (41 μL, 0.41 mmol) and DBU (1 μL, 6.7 μmol) were added to an ice-cooled solution of hemiacetal **49** (67 mg, 0.067 mmol) in dry DCM (4 mL) in an atmosphere of nitrogen (TLC, toluene-EtOAc, 5:1). After 60 min, the solution was filtered through a short pad of silica (cyclohexane-EtOAc+0.1% Et_3N) to remove DBU afforded donor and the filtrate was concentrated *in vacuo* to give the **17a** as a colorless foam. Donor **17a** was prepared immediately prior to use in the inverse glycosylation with acceptor. A catalytic amount of TMSOTf (4 μL, 20 μmol) was added to a solution of acceptor **13b** (97 mg, 65 μmol) in dry toluene (2.0 mL) containing crushed molecular sieves (AW-300) kept at −78 °C in an atmosphere of nitrogen. A solution of donor **17a** (73 mg, 65 μmol) in dry toluene (0.5 mL) was added dropwise over 1 h to the reaction vessel using a syringe pump (rate of addition: 0.5 mL per hour). The temperature was then allowed to rise to 20 °C overnight (TLC, toluene-EtOAc, 6:1).The reaction mixture was neutralised with Et_3N, the solids were removed by filtration, and the filtrate was concentrated *in vacuo* to a yellowish oil. Purification by flash column chromatography (SiO_2, 70 mL, 2.3 cm, toluene→toluene-EtOAc, 98:2→96:4→94:6→92:8→90:10 →88:12→86:14→84:16) gave the *title compound* **15a** (96 mg, 60%) as a colourless, amorphous solid. $\mathbf{R}_f$ (toluene-EtOAc, 9:1) = 0.45; $\mathbf{R}_f$ (toluene-EtOAc, 6:1) = 0.65; $[\alpha]_D^{20}$ −15.0 (*c* 0.59, $CHCl_3$) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74-7.73 (m, 2H, H_{ar}), 7.70 (d, 1H, H_{ar}), 7.66 (d, 1H, H_{ar}), 7.46-7.05 (m, 73H, H_{ar}), 5.29 (s, 1H), 5.23 (s, 1H,), 5.14 (s, 1H), 5.11-5.04 (m, 4H), 5.01 (d, 1H, J_{gem} = 10.8 Hz), 4.96 (d, 1H, J_{gem} = 10.8 Hz), 4.87-4.75 (m, 6H), 4.71-4.59 (m, 5H), 4.56-4.36 (m, 10H), 4.31-4.26 (m, 5H), 4.25 (dd ≈m, 1H), 4.22-4.16 (m, 6H), 4.11 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.6 Hz), 4.08 (dd ≈ d, 1H, J = 10.2 Hz), 4.01 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.6 Hz), 3.98-3.87 (m, 7H), 3.78-3.73 (m, 2H), 3.71 (dd ≈ t, 1H, J = 9.9 Hz), 3.63 (dd ≈ d, 1H, J = 9.0 Hz), 3.58 (dd, 1H, $J_{5,6b}$ = 5.4 Hz, $J_{6a,6b}$ = 10.8 Hz), 3.55-3.49 (m, 3H), 3.42 (dd ≈ t, 1H, J = 9.0

Hz), 3.33-3.25 (m, 4H), 3.17 (dd ≈ t, 1H, J = 9.0 Hz), 3.03 (dd ≈ t, 1H, J = 10.8 Hz), 2.67-2.63 (ddd ≈ m, 1H), 2.55-2.46 (m, 2H, SCH_2CH$_3$), 1.84 (s, 3H, C(=O)CH_3), 1.60 (s, 3H, C(=O)CH_3), 1.21 (t, 3H, J = 7.5 Hz, SCH$_2$CH_3); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.6 (2C, C(=O)CH$_3$), 168.0, 139.0, 138.9, 138.7, 138.6, 138.5, 138.4, 138.3, 138.1, 138.0, 135.5, 135.0, 133.2, 133.0, 129.2, 128.7-127.3, 126.9, 126.7, 125.9, 125.80, 125.75 (C_{ar}), 103.8 ($J_{C,H}$ = 160 Hz), 103.5 ($J_{C,H}$ = 160 Hz), 103.0 ($J_{C,H}$ = 165 Hz), 101.4 ($J_{C,H}$ = 175 Hz), 99.5 ($J_{C,H}$ = 175 Hz), 83.8, 83.34, 83.30, 82.7 ($J_{C,H}$ = 170 Hz), 81.4, 81.3, 81.1, 80.7, 80.6, 78.7, 78.3, 78.1, 77.61, 77.57, 76.5, 75.4, 75.3, 75.2, 75.1, 75.0, 74.9, 74.6, 74.4, 74.3, 74.2, 73.8, 73.6, 73.0, 72.3, 71.7, 70.2, 69.8, 69.7, 67.2, 63.5, 63.3, 63.2, 63.1, 25.6 (SCH$_2$CH$_3$), 20.6 (C(=O)CH$_3$), 20.5 (C(=O)CH$_3$), 15.0 (SCH$_2$$CH_3$); **HRMS (ESI)**: [M+Na]$^+$ *m/z* Calcd for $C_{149}H_{156}O_{31}NaS$, 2496.0249; found, 2496.0227; **Anal.** Calcd for $C_{149}H_{156}O_{31}S$: C, 72.31; H, 6.35. Found: C, 70.62; H, 6.28 %.

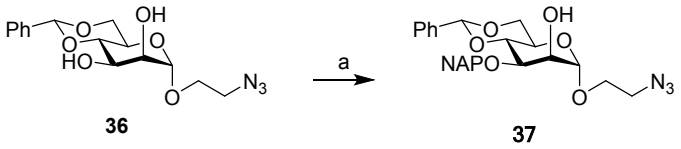


Scheme 5. Reagents and conditions: (a) TMSOTf, Et_2O, AW-300 MS, −40 °C→0 °C, 2 h, 70% (α–only).

Ethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-1-thio-α-D-mannopyranoside (15b)

A catalytic amount of TMSOTf (10 μL, 55 μmol) was added to a solution of acceptor **13b** (246 mg, 0.164 mmol) in dry Et_2O (8.0 mL) containing crushed molecular sieves (AW-300) kept at −40 °C in an atmosphere of nitrogen. A solution of donor **17b** (218 mg, 1.73 mmol) in dry toluene (0.5 mL) was added dropwise. After 20 min, the temperature was allowed to rise to 0 °C. After further 2h, the reaction mixture was neutralised with Et_3N, the solids were removed by filtration, and the filtrate was concentrated *in vacuo*. Purification by flash column chromatography (RevererisX1, 40 gram column, toluene-EtOAc, 98:2→70:30) gave **15b** (276 mg, 70%) as a colourless, amorphous solid; $\mathbf{R}_f$ (cyclohexane-EtOAc, 8:2) 0.26; $[\alpha]_D^{20}$ −14.6 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47-7.02 (m, 70H), 5.36 (dd, *J* 3.3 Hz, *J* 9.8 Hz, 1H), 5.30 (bs, 1H), 5.19-5.01 (m, 7H), 4.89-4.73 (m, 7H), 4.71-4.68 (m, 2H), 4.66-4.60 (m, 3H), 4.59-4.55 (m, 3H), 4.54-4.41 (m, 4H), 4.39-4.18 (m, 13H), 4.14-4.11 (m, 2H), 4.08-3.91 (m, 8H), 3.87 (t, *J* 9.8 Hz, 1H), 3.77 (dd, *J* 5.2 Hz, *J* 11.5 Hz, 1H), 3.73-4.68 (m, 2H), 3.67-3.59 (m, 2H), 3.55-3.47 (m, 3H), 3.46-3.35 (m, 4H), 3.32 (d, *J* 9.9 Hz, 1H), 3.20 (t, *J* 9.2 Hz, 1H), 3.07-3.01 (m, 1H), 2.69 (t, *J* 10.7 Hz, 1H), 2.56-2.43 (m, 2H), 1.84 (s, 3H), 1.67 (s, 3H), 1.21 (t, *J* 7.4 Hz, 1H); **^{13}C NMR** (500 MHz, $CDCl_3$) δ 170.7, 170.6, 168.8, 166.9, 139.0, 139.0, 139.0, 138.7, 138.5, 138.5 (2C), 138.3, 138.3, 138.2, 138.1, 138.1, 138.0, 134.9, 129.2, 129.1, 129.1, 128.9, 128.8, 128.7, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.4, 126.8, 126.2, 125.4, 103.9 ($J_{C,H}$ 155 Hz), 103.1 ($J_{C,H}$ 160 Hz), 103.0 ($J_{C,H}$ 160 Hz), 101.2 ($J_{C,H}$ 170 Hz), 100.2 ($J_{C,H}$ 170 Hz), 83.9, 83.4, 83.1, 82.8, 81.4, 81.4, 81.1, 80.8 (2C, $J_{C,H}$ 165 Hz), 79.4, 78.5, 78.4, 77.9 (2C), 77.4, 75.7, 75.5, 75.5, 75.4, 75.2, 75.2, 75.1, 75.1, 74.9, 74.8, 74.8, 74.2 (2C), 74.0, 73.6, 73.1, 72.8, 72.6, 71.9, 70.3, 69.8, 69.5, 67.8, 63.5, 63.3, 63.2, 62.9, 41.2, 25.7, 20.7, 20.7, 15.1. **HRMS (ESI):** $[M+Na]^+$ calcd for $C_{140}H_{149}O_{32}NaSCl$, 2431.9339; found, 2431.9270.

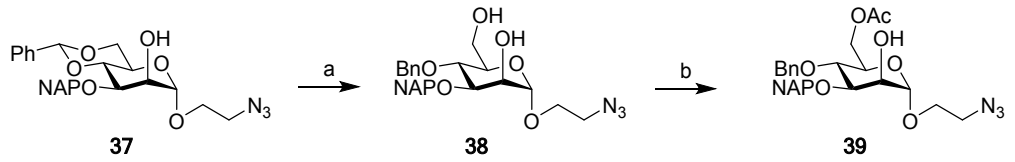
Synthesis of Small Spacer Equipped Structures



Scheme 6. Reagents and conditions: (a) Bu_2SnO, toluene, reflux, o/n; 2. NAPBr, Bu_4NI, toluene, reflux, 3 h, 88%.

2-Azidoethyl 4,6-*O*-benzylidene-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (37)

A solution of diol **36** (10.0 g, 29.65 mmol) and dibutyltin oxide (9.96 g, 40.02 mmol) in anhydrous toluene (320 mL) was heated under reflux overnight with removal of water (Dean-Stark trap). The mixture was concentrated to half-volume, tetrabutylammonium iodide (14.78 g, 40.02 mmol), 2-(bromomethyl)naphthalene (7.21 g, 32.62 mmol) were added, and the reaction mixture was refluxed for another 3 h (TLC, toluene-EtOAc, 1:1). The reaction mixture was diluted with EtOAc (400 mL), and the organic layer was washed sequentially with water (3 x 200 mL), 10% aq. KF-solution (3 x 200 mL), and brine (2 x 200 mL), dried over $MgSO_4$, and concentrated *in vacuo* to a yellow oily residue. Purification by flash column chromatography (SiO_2, 600 mL, 7.5 cm, pentane→pentane-Et_2O, 50:50→35:65→25:75→15:85) gave the title compound **37** (12.50 g, 88%) as a pale yellow syrup. $[\alpha]_D^{20}$ +28.0 (*c* 1.0, $CHCl_3$), **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.84-7.78 (m, 3H), 7.74-7.71 (m, 1H), 7.53-7.43 (m, 5H), 7.40-7.35 (m, 3H), 5.63 (s, 1H), 4.99 (d, *J* 12.1 Hz, 1H), 4.93-4.88 (m, 2H), 4.30-4.24 (m, 1H), 4.16-4.11 (m, 2H), 3.99 (dd, *J* 3.4 Hz, *J* 9.6 Hz, 1H), 3.90-3.82 (m, 3H), 3.60 (ddd, *J* 3.7 Hz, *J* 6.8 Hz, *J* 10.6 Hz, 1H), 3.42-3.32 (m, 2H), 2.75 (d, *J* 1.3 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 137.7, 135.5, 133.4, 133.2, 129.1, 128.4, 128.4 (2C), 128.1, 127.8, 126.8, 126.3 (2C), 126.3, 126.1, 125.9, 101.9, 100.4 (anomeric), 78.8, 75.6, 73.2, 69.9, 69.0, 66.9, 63.8, 50.5. **HRMS (ESI):** Calcd for $C_{26}H_{28}N_3O_6$ $[M+H]^+$ 478.1978, found 478.1972.



Scheme 7. Reagents and conditions: (a) 1M BH_3 in THF, 1M Bu_2BOTf in CH_2Cl_2, 0 °C, 2h, 72%; (b) 2,4,6-trimethylpyridine, AcCl, CH_2Cl_2, 2h, 70%.

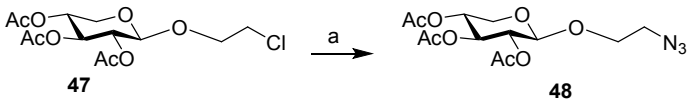
2-Azidoethyl 4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (38)

Compound **37** (850 mg, 1.78 mmol) was dissolved in dry THF (20 mL) under N_2 atmosphere and the solution was cooled to 0 °C before adding 1M BH_3 in THF (18 mL, 18 mmol) and after 5 min 1M Bu_2BOTf in CH_2Cl_2 (1.8 mL, 1.8 mmol) drop wise. After 2 h, Et_3N was carefully added followed by drop wise addition of MeOH until gas evolution. The solution was co-evaporated three times with MeOH and the crude was purified by automated flash chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 70:30→10:90) to give pure **38** (612 g, 72%) as a syrup; R_f 0.07 (7:3 toluene-EtOAc); $[\alpha]_D^{20}$ + 22.1 (*c* 1.0, $CHCl_3$), **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.83-7.73 (m, 4H), 7.51-7.44 (m, 3H), 7.33-7.25 (m, 5H), 4.92-4.89 (m, 2H), 4.87-4.81 (m, 2H), 4.68 (d, *J* 11.0 Hz, 1H), 4.08 (s, 1H), 3.97 (dd, *J* 3.2 Hz, *J* 9.3 Hz, 1H), 3.91 (t, *J* 9.4 Hz, 1H), 3.86-3.77 (m, 3H), 3.68 (dt, *J* 3.2 Hz, *J* 9.3 Hz, 1H), 3.54 (ddd, *J* 3.4 Hz, *J* 6.9 Hz, *J* 10.5 Hz, 1H), 3.34 (ddd, *J* 3.4 Hz, *J* 6.9 Hz, *J* 10.3 Hz, 1H), 3.54 (ddd, *J* 3.5 Hz, *J* 5.8 Hz, *J* 13.3 Hz, 1H), 2.94 (s, 1H), 2.40 (s, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 138.4, 135.3, 133.4, 133.2, 128.6 (2C), 128.5, 128.1, 128.0 (2C), 127.9, 127.8, 127.0, 126.3, 126.2, 126.0, 99.5 (anomeric), 79.9, 75.3, 73.9, 72.4, 72.1, 68.4, 66.8, 62.0, 50.5. **HRMS (ESI):** Calcd for $C_{26}H_{29}N_3O_6Na$ $[M+Na]^+$ 502.1954, found 502.1948.

2-Azidoethyl 6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (39)

Compound **38** (500 mg, 1.04 mmol) was dissolved in dry CH_2Cl_2 (10 mL) under N_2 atmosphere and the solution was cooled to −78 °C before adding 2,4,6-trimethylpyridine (0.2 mL, 1.3 mmol) and AcCl (64 μL, 0.89 mmol). After 2 h, the reaction was quenched adding H_2O (5 mL), the mixture was allowed to attain room temperature. The mixture was extracted with CH_2Cl_2 (3 x 30 mL), the layers were separated, and the organic layer was dried ($MgSO_4$), filtered and concentrated. The crude was purified by silica gel chromatography (8:2 cyclohexane-EtOAc) to give pure **39** (543 mg, 70%) as a syrup; R_f 0.11 (6:4 cyclohexane-EtOAc); $[\alpha]_D^{20}$ +16.7 (*c* 1.1, $CHCl_3$), **^{1}H-NMR** (500

MHz, $CDCl_3$) δ 7.84-7.74 (m, 4H), 7.49-7.45 (m, 3H), 7.33-7.26 (m, 5H), 4.92-4.88 (m, 2H), 4.87-4.81 (m, 2H), 4.61 (d, *J* 10.9 Hz, 1H), 4.34 (d, *J* 11.9 Hz, 1H), 4.29 (dd, *J* 4.7 Hz, *J* 11.9 Hz, 1H), 4.09-4.07 (m, 1H), 3.98 (dd, *J* 3.2 Hz, *J* 8.8 Hz, 1H), 3.87-3.78 (m, 3H), 3.60-3.56 (m, 1H), 3.39-3.29 (m, 2H), 2.62 (bs, 1H), 2.04 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 170.9, 138.0, 135.1, 133.3, 133.2, 128.6 (2C), 128.5, 128.2 (2C), 128.0, 128.0, 127.8, 127.0, 126.3, 126.2, 125.9, 99.5 (anomeric), 80.1, 75.2, 73.8, 72.3, 69.8, 68.2, 66.8, 63.4, 50.5, 21.0. **HRMS (ESI)**: Calcd for $C_{28}H_{31}N_3O_7Na$ $[M+Na]^+$ 544.2060, found 544.2056.

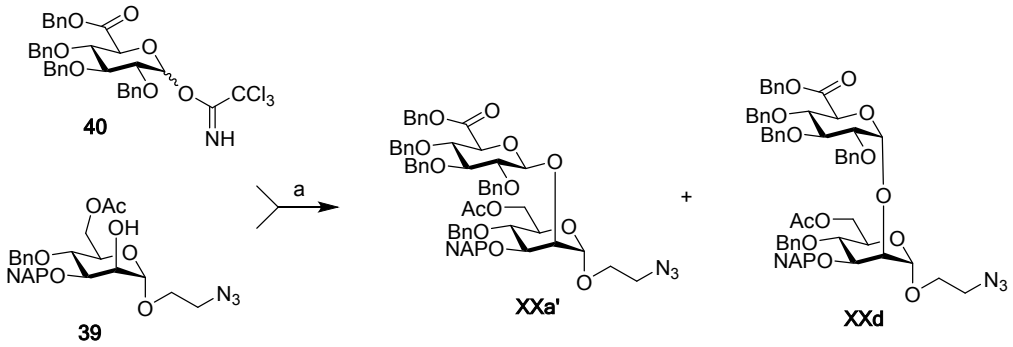


47 48

Scheme 8. Reagents and conditions: (a) NaN_3, dry. DMF, 80 °C, 4 h, 96%.

2-Azidoethyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (48)

NaN_3 (1.23 g, 18.9 mmol) was added portionwise to a solution of sugar **47** (1.60 g, 4.7 mmol) in dry DMF (73 mL) kept at 80 °C. After complete addition, heating was continued until no starting material was detected by TLC analysis. After 4 h, the reaction mixture was poured into ice-water (100 mL) under vigorous stirring. The product was extracted once with EtOAc (200 mL). The layers were separated, and the organic layer was washed sequentially with water (1 x 200 mL) and brine (1 x 200 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 90:10→70:30) gave **48** (1.56 g, 96%) as a colourless, crystalline solid (needles). $\mathbf{R}_f$ (toluene-EtOAc, 7:3) 0.43; $[\alpha]_D^{20}$ −87.5 (*c* 1.0, $CHCl_3$), **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 5.17 (t, *J* 8.4 Hz, 1H), 4.97-4.93 (m, 2H), 4.57 (d, *J* 6.7 Hz, 1H), 4.15 (dd, *J* 0.5 Hz, *J* 11.9 Hz, 1H), 3.99 (ddd, *J* 3.4 Hz, *J* 5.5 Hz, *J* 10.7 Hz, 1H), 3.67 (ddd, *J* 3.3 Hz, *J* 7.8 Hz, *J* 10.8 Hz, 1H), 3.46 (ddd, *J* 3.4 Hz, *J* 7.8 Hz, *J* 13.3 Hz, 1H), 3.40 (dd, *J* 8.6 Hz, *J* 11.9 Hz, 1H), 3.33 (ddd, *J* 3.3 Hz, *J* 5.4 Hz, *J* 13.4 Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 170.2, 169.9, 169.6, 100.6 (anomeric), 71.3, 70.6, 68.9, 68.2, 68.1, 50.7. **HRMS (ESI):** Calcd for $C_{13}H_{19}N_3O_8Na$ $[M+Na]^+$ 368.1070, found 368.1075.



Scheme 9. Reagents and conditions: (a) $BF_3{\cdot}Et_2O$, dry CH_2Cl_2, 4 Å MS, −78 °C, 1 h, 17% (α:β, 1:3).

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (12a') and **2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (12d)**

A solution of **40** (460 mg, 0.65 mmol) and **39** (250 mg, 0.48 mmol) in dry CH_2Cl_2 (7 mL) and trimethylacetonitrile (3.5 mL) containing 4 Å molecular sieves was cooled under N_2 atmosphere to −78 °C before adding 2.5 mL of a 0.02 M solution of $BF_3{\cdot}Et_2O$ in dry CH_2Cl_2. After 1 h, the reaction was quenched by addition of Et_3N (1 mL), the mixture was allowed to attain room temperature, filtered through a pad of Celite® and concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→90:10) gave pure **12d** (20 mg, 4%) and pure **12a'** (70 mg, 13%).

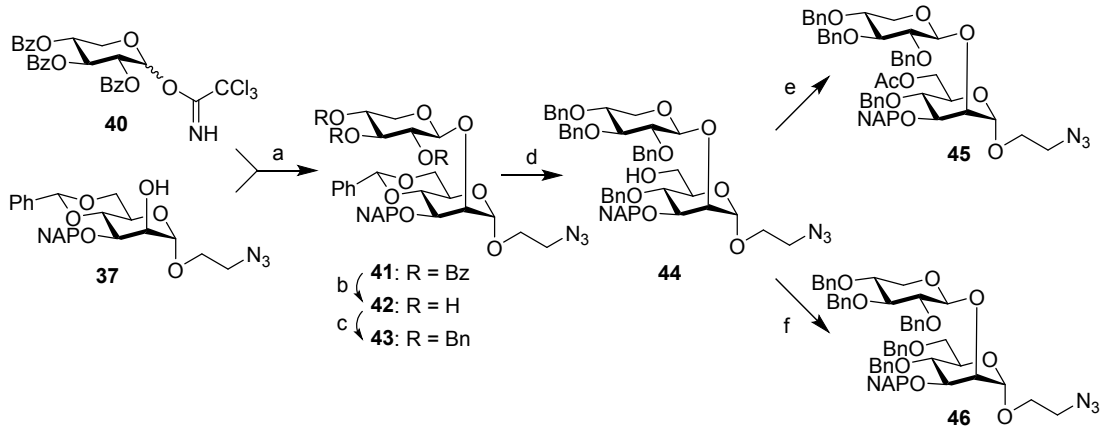
Compound **12a'**

R_f (toluene-EtOAc, 95:5) 0.46; $[\alpha]_D^{20}$ +0.8 (*c* 1.0, $CHCl_3$), **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.80-7.76 (m, 4H), 7.53-7.11 (m, 28H), 5.12 (d, *J* 9.9 Hz, 1H), 5.10-5.05 (m, 2H), 4.99-4.89 (m, 4H), 4.81-4.76 (m, 2H), 4.62 (d, *J* 9.9 Hz, 1H), 4.58-4.51 (m, 4H), 4.36 (dd, *J* 3.9 Hz, *J* 12 Hz, 1H), 4.31-4.28 (m, 2H), 4.03-3.95 (m, 4H), 3.86-3.82 (m, 2H), 3.74-3.65 (m, 2H), 3.56 (ddd, *J* 3.6 Hz, *J* 6.8 Hz, *J* 10.6 Hz, 1H), 3.39-3.28 (m, 2H), 1.69 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 170.7, 168.0, 138.5, 138.3, 138.0, 137.9, 135.4, 134.9, 133.2, 129.1 (2C), 128.8 (2C), 128.6 (2C), 128.6, 128.5 (2C), 128.5 (2C), 128.5 (2C), 128.4 (2C), 128.2, 128.2 (2C), 128.2 (2C), 128.0 (2C), 127.9, 127.9 (2C), 127.8, 127.8, 127.7, 127.6, 126.8, 126.1, 126.0, 103.6 ($J_{C,H}$ 169 Hz), 98.1 ($J_{C,H}$ 162 Hz),

84.1, 81.4, 78.9, 77.7, 75.9, 75.3, 75.3, 75.2, 74.9, 74.5, 73.6, 71.0, 70.1, 67.5, 66.7, 63.3, 50.5, 20.6. **HRMS (ESI):** Calcd for $C_{62}H_{63}N_3O_{13}Na$ $[M+Na]^+$ 1080.4259, found 1080.4280.

Compound **12d**

R_f (toluene-EtOAc, 95:5) 0.54; $[\alpha]_D^{20}$ +17.0 (*c* 1.0, $CHCl_3$), **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.83-7.67 (m, 4H), 7.49-7.01 (m, 28H), 5.44 (d, *J* 3.6 Hz, 1H), 5.21 (d, *J* 12.2 Hz, 1H), 5.14 (d, *J* 12.2 Hz, 1H), 4.97 (d, *J* 10.9 Hz, 1H), 4.92 (d, *J* 1.7 Hz, 1H), 4.85 (d, *J* 11.1 Hz, 1H), 5.44 (d, *J* 3.6 Hz, 1H), 4.79 (d, *J* 2.5 Hz, 1H), 4.77-4.70 (m, 4H), 4.48-4.44 (m, 2H), 4.40-4.34 (m, 2H), 4.32 (dd, *J* 2.2 Hz, *J* 11.8 Hz, 1H), 4.25 (dd, *J* 4.6 Hz, *J* 11.8 Hz, 1H), 4.19 (t, *J* 2.2 Hz, 1H), 4.06-3.99 (m, 2H), 3.95 (t, *J* 9.6 Hz, 1H), 3.81-3.73 (m, 3H), 3.58 (dd, *J* 3.6 Hz, *J* 9.6 Hz, 1H), 3.45 (ddd, *J* 4.0 Hz, *J* 6.2 Hz, *J* 10.5 Hz, 1H), 3.32-3.24 (m, 2H), 1.97 (s, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 171.1, 169.5, 138.6, 138.2, 138.2, 137.0, 128.7 (2C), 128.6 (2C), 128.6, 128.5 (2C), 128.5 (2C), 128.4, 128.4 (2C), 128.3 (2C), 128.1, 128.0 (2C), 127.9 (2C), 127.9 (2C), 127.8 (2C), 127.8, 127.8, 127.5, 127.2, 127.2 (2C), 126.3, 126.3, 126.2, 99.0 ($J_{C,H}$ 174 Hz), 98.0 ($J_{C,H}$ 174 Hz), 81.0, 80.0, 79.4, 79.3, 75.8, 75.3, 75.1, 74.4, 73.8, 73.1, 71.8, 71.1, 70.8, 67.5, 66.8, 63.3, 50.5, 20.9. **HRMS (ESI)**: Calcd for $C_{62}H_{63}N_3O_{13}Na$ $[M+Na]^+$ 1080.4259, found 1080.4294.



Scheme 10. Reagents and conditions: (a) TBDMSOTf, DCM, AW-300 MS, −78 °C→20 °C, o/n, 86%; (b) NaOMe, MeOH, 20 °C; 2. Dowex® H^+ ion-exchange resin, 86%; (c) NaH, BnBr, DMF, 0 °C→20 °C, 3 h, 90%; (d) Bu_2BOTf, BH_3 (1 M in THF), DCM, 0 °C, 90 min, 76%; (e) Ac_2O, pyridine, 20 °C, 3 h, 93%; (f) NaH, BnBr, DMF, 0 °C→20 °C, 2 h, 95%.

2-Azidoethyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (41)

A catalytic amount of TBDMSOTf (335 μL, 1.46 mmol) was added to a solution of donor **40** (8.89 g, 14.66 mmol) and acceptor **37** (7.00 g, 14.66 mmol) in dry DCM (125 mL) containing crushed molecular sieves (AW-300) kept at −78 °C in an atmosphere of nitrogen. The temperature was then allowed to rise to 20 °C overnight (TLC, toluene-EtOAc, 6:1). The reaction mixture was neutralised with Et_3N (1.23 mL, 8.79 mmol), the solids were removed by filtration, and the filtrate was concentrated *in vacuo* to a yellowish foam. Purification by flash column chromatography (SiO_2, 350 mL, 7.5 cm, toluene→toluene-EtOAc, 98:2→96:4→94:6→92:8→90:10→88:12→86:14) gave the *title compound* **41** (11.70 g, 86%) as a colourless, amorphous solid. $[\alpha]_D^{20}$ −48.8 (*c* 1.0, $CHCl_3$), **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* 8.24-8.21 (m, 2H), 8.09-8.06 (m, 2H), 7.98-7.95 (m, 2H), 7.87 (m, 1H), 7.82-7.78 (m, 2H), 7.72-7.69 (m, 1H), 7.59-7-47 (m, 5H), 7.46-7.35 (m, 10 H), 7.28-7.23 (m, 2H), 5.61 (t, *J* 4.0 Hz, 1H), 5.33-5.32 (m, 1H), 5.16-5.13 (m, 1H), 5.11 (s, 1H), 5.09 (d, *J* 2.1 Hz, 1H), 5.06-4.98 (ABq, 2H), 4.95 (dd, *J* 2.5 Hz, *J* 12.9 Hz, 1H), 4.87 (d, *J* 1.0 Hz, 1H), 4.30 (dd, *J* 1.5 Hz, *J* 3.2 Hz, 1H), 4.10-4.05 (m, 2H), 3.99 (t, *J* 9.7 Hz, 1H), 3.82-3.78 (m, 2H), 3.73 (dt, *J* 4.8 Hz, *J* 9.9 Hz, 1H), 3.56-3.46 (m, 2H), 3.37-2.27 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) *δ* 165.7, 165.4, 165.0, 137.8, 136.0, 133.6, 133.5, 133.4, 133.4, 133.1, 130.5, 130.2, 130.1, 129.7, 129.4, 129.4, 129.2, 129.1, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.0, 127.8, 126.4, 126.3, 126.2, 125.9, 125.8, 101.6, 98.2, 96.7, 78.6, 74.9, 74.6, 73.2, 68.7, 68.4, 68.0, 67.4, 66.8, 64.6, 59.5, 50.5; **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{52}H_{47}N_3O_{13}Na$, 944.3007; found, 944.2960.

2-Azidoethyl β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (42)

A catalytic amount of sodium methoxide (68 mg, 1.27 mmol) was added to a solution of disaccharide **41** (11.70 g, 12.69 mmol) in dry methanol (250 mL). The mixture was swirled at 20 °C overnight (TLC, DCM-MeOH, 9:1). After complete conversion, Dowex® (H^+) acidic ion exchange resin was added for neutralization, the resin was filtered off, washed with methanol and the filtrate was concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 200 mL, 4.5 cm, DCM→DCM-MeOH, 99:1→98:2→97:3→96:4→95:5) gave the *title compound* **42** (11.70 g, 86%) as a colourless, amorphous solid. R_f (CH_2Cl_2-MeOH, 9:1) = 0.39; $[\alpha]_D^{20}$ −1.8 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* 7.82-7.77 (m, 3H), 7.76-7.72 (m, 1H), 7.52-7.49 (m, 2H), 7.48-7.43 (m, 3H), 7.40-7.36 (m, 3H), 5.66 (s, 1H), 5.05 (d, *J* 11.7 Hz, 1H), 4.88 (d, *J* 11.7 Hz, 1H), 4.85 (d, *J*

1.4 Hz, 1H), 4.55-4.50 (m, 1H), 4.27 (dd, *J* 3.4 Hz, *J* 9.1 Hz, 1H), 4.21-4.16 (m, 2H), 4.08 (dd, *J* 3.4 Hz, *J* 10.0 Hz, 1H), 4.05-4.01 (m, 2H), 3.89-3.81 (m, 3H), 3.66-3.57 (m, 2H), 3.51-3.46 (m, 2H), 3.39-3.35 (m, 2H), 3.26 (dd, *J* 9.1 Hz, *J* 11.7 Hz, 1H), 3.17 (bs, 1H), 2.67 (bs, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.6, 134.8, 133.4, 133.3, 129.1, 128.5, 128.4, 128.2, 127.8, 127.6, 126.3, 126.3, 126.2, 126.2, 101.8, 101.4, 100.2, 79.5, 75.0, 74.6, 74.6, 71.7, 69.9, 69.6, 68.9, 66.8, 65.4, 64.3, 50.4. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{31}H_{35}N_3O_{10}Na$, 632.2220; found, 632.2195.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (43)

Sodium hydride (3.81 g, 95.61 mmol, 60% oil dispersion) was washed with pentane (3 x 100 mL) prior to use. Sodium hydride was added portionwise to a solution of triol **42** (12.96 g, 21.24 mmol) in dry DMF (200 mL) kept at 0 °C under an atmosphere of nitrogen. After 15 min, benzyl bromide (10.09 mL, 84.96 mmol) was added dropwise at 0 °C under vigorous stirring. The temperature was then allowed to rise to 20 °C over 3 h (TLC, toluene-EtOAc, 6:1). After complete consumption of the starting material, residual sodium hydride was quenched with MeOH, and then with H_2O (300 mL). The resulting mixture was extracted once with EtOAc (600 mL), the layers were separated, and the organic layer was washed with brine (1 x 400 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 350 mL, 7.5 cm, toluene→toluene-EtOAc, 98:2→96:4→94:6→92:8→90:10→88:12) gave the *title compound* **43** (16.87 g, 90%) as a colourless syrup. R_f (toluene-EtOAc, 6:1) = 0.55; $[\alpha]_D^{20}$ −8.0 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.82-7.79 (m, 1H), 7.76-7.74 (m, 1H), 7.68-7.66 (m, 1H), 7.52-7.27 (m, 23H), 5.61 (s, 1H), 4.98 (d, *J* 10.5 Hz, 1H), 4.95 (d, *J* 1.3 Hz, 1H), 4.93-4.85 (m, 4H), 4.73-4.69 (m, 2H), 4.61 (d, *J* 11.6 Hz, 1H), 4.45 (d, *J* 7.2 Hz, 1H), 4.28 (dd, *J* 3.0 Hz, *J* 8.5 Hz, 1H), 4.22-4.17 (m, 2H), 4.04-3.98 (m, 2H), 3.86-3.78 (m, 3H), 3.66 (td, *J* 5.2 Hz, *J* 9.0 Hz, 1H), 3.61-3.49 (m, 3H), 3.35 (ddd, *J* 3.5 Hz, *J* 7.1 Hz, *J* 13.2 Hz, 1H), 3.30-3.22 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.9, 138.5, 138.3, 137.8, 136.1, 133.5, 133.1, 129.0, 128.6, 128.6, 128.5, 128.3, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.7, 126.4, 126.3, 126.0, 125.9, 125.7, 104.1, 101.8, 99.2, 84.0, 81.6, 78.6, 77.9, 76.3, 75.7, 75.3, 74.3, 73.5, 72.0, 69.1, 66.8, 64.7, 64.3, 50.5. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{52}H_{53}N_3O_{10}Na$, 902.3629; found, 902.3613.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (44)

A 1 M solution of BH_3 in THF (23.6 mL, 23.6 mmol) was added to a solution of acetal **43** (2.08 g, 2.36 mmol) in dry DCM (40 mL) kept at 0 °C under an atmosphere of nitrogen. After 5 min, a 1 M solution of BuBOTf (2.36 mL, 2.36 mmol) was added dropwise at 0 °C, and the reaction mixture was stirred for 90 min (TLC, toluene-EtOAc, 6:1). After complete consumption of the starting material, the reaction was quenched with Et_3N (10 mL), followed by dropwise addition of MeOH at 0°C. The mixture was concentrated *in vacuo*, and the residue was re-dissolved and co-evaporated with MeOH (3 x 50 mL). The syrupy residue was re-dissolved in MeOH, the solution was filtered through a short pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 200 mL, 4.5 cm, toluene→toluene-EtOAc, 97:3→94:6→91:9→88:12→85:15→82:18→79:21) gave the *title compound* **44** (1.59 g, 76%) as a colourless syrup. R_f (toluene-EtOAc, 9:1) = 0.07; R_f (toluene-EtOAc, 6:1) = 0.16; $[\alpha]_D^{20}$ +6.2 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 7.77-7.74 (m, 1H), 7.72-7.69 (m, 1H), 7.53-7.50 (m, 1H), 7.48-7.43 (m, 2H), 7.38-7.25 (m, 20H), 5.01-4.97 (m, 2H), 4.95-4.91 (m, 2H), 4.88-4.83 (m, 2H), 4.76-4.70 (m, 3H), 4.62-4.59 (m, 2H), 4.42 (d, *J* 7.4 Hz, 1H), 4.16 (dd, *J* 1.9 Hz, *J* 3.2 Hz, 1H), 4.00-3.96 (m, 2H), 3.90 (t, *J* 9.5 Hz, 1H), 3.82-3.75 (m, 2H), 3.72-3.63 (m, 3H), 3.58 (t, *J* 8.9 Hz, 1H), 3.55-3.48 (m, 2H), 3.34 (ddd, *J* 3.4 Hz, *J* 7.3 Hz, *J* 13.2 Hz, 1H), 3.29-3.21 (m, 2H), 1.62 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.9, 138.7, 138.6, 138.3, 135.7, 133.4, 133.2, 128.6, 128.5, 128.5, 128.4, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.3, 126.6, 126.1, 125.9 103.9, 98.3, 84.0, 81.4, 78.2, 77.7, 75.6, 75.3, 75.0, 74.9, 74.6, 73.5, 72.5, 71.7, 66.7, 64.3, 62.7, 50.5. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{52}H_{55}N_3O_{10}Na$, 904.3785; found, 904.3763.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (45)

Acetic anhydride (2.44 mL, 25.76 mmol) was added to a solution of compound **44** (2.84 g, 1.47 mmol) in dry pyridine (50 mL) at 20 °C, and the mixture was stirred for 3 h (TLC, toluene-EtOAc, 9:1). The reaction mixture was concentrated *in vacuo*, and then re-dissolved and co-evaporated with toluene (3 x 100 mL). Purification by flash column chromatography (SiO_2, 200 mL, 4.5 cm, toluene→toluene-EtOAc, 97:3→94:6→91:9→88:12→85:15) gave the *title compound* **45** (2.76 g, 93%) as a colourless syrup. R_f (toluene-EtOAc, 9:1) = 0.25; R_f (toluene-

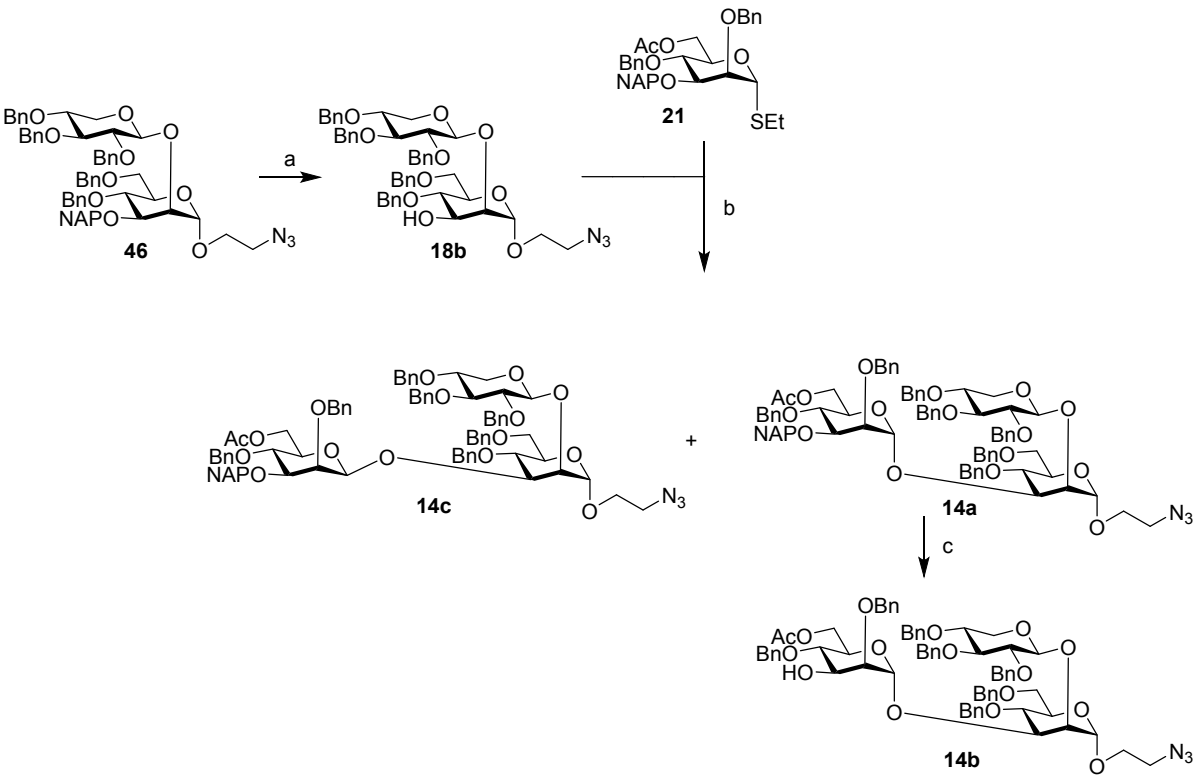
EtOAc, 6:1) = 0.40; $[\alpha]_D^{20}$ +11.0 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.77-7.75 (m, 1H), 7.73-7.69 (m, 2H), 7.53-7.51 (m, 1H), 7.48-7.44 (m, 2H), 7.40-7.25 (m, 20H), 5.06 (d, *J* 10.1 Hz, 1H), 4.99 (d, *J* 10.8 Hz, 1H), 4.96-4.93 (m, 2H), 4.90-4.84 (ABq, 2H), 4.76-4.71 (m, 2H), 4.64-4.60 (m, 2H), 4.56 (d, *J* 10.8 Hz, 1H), 4.40 (d, *J* 7.1 Hz, 1H), 4.34-4.29 (m, 2H), 4.16 (dd, *J* 1.9 Hz, *J* 2.9 Hz, 1H), 4.02-3.93 (m, 3H) 3.84-3.79 (m, 2H), 3.70-3.65 (m, 1H), 3.58-3.51 (m, 3H), 3.35 (ddd, *J* 3.5 Hz, *J* 7.0 Hz, *J* 13.1 Hz, 1H), 3.31-3.20 (m, 2H), 1.75 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 138.9, 138.4, 138.4, 138.3, 135.6, 133.4, 133.2, 129.0, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 128.0, 128.0, 127.4, 126.7, 126.1, 126.0, 104.3, 98.4, 84.1, 81.5, 78.3, 77.6, 75.7, 75.3, 75.3, 75.2, 74.0, 73.6, 71.7, 70.4, 66.8, 64.3, 63.4, 50.5, 20.7. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{54}H_{57}N_3O_{11}Na$, 946.3891; found, 946.3876

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranoside (46)

Sodium hydride (155 mg, 3.88 mmol, 60% oil dispersion) was washed with pentane (3 x 10 mL) prior to use. Sodium hydride was added portionwise to a solution of compound **44** (0.98 g, 1.11 mmol) in dry DMF (40 mL) kept at 0 °C under an atmosphere of nitrogen. After 15 min, benzyl bromide (395 μL, 3.33 mmol) was added dropwise at 0 °C under vigorous stirring. The temperature was then allowed to rise to 20 °C over 2 h (TLC, toluene-EtOAc, 6:1). After complete consumption of the starting material, residual sodium hydride was quenched with MeOH, and then with H_2O (80 mL). The resulting mixture was extracted once with EtOAc (160 mL), the layers were separated, and the organic layer was washed with brine (1 x 100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 200 mL, 4.5 cm, toluene→toluene-EtOAc, 98:2→96:4→94:6→92:8→90:10) gave the *title compound* **46** (1.03 g, 95%) as a colourless syrup. R_f (toluene-EtOAc, 9:1) = 0.38; R_f (toluene-EtOAc, 6:1) = 0.55; $[\alpha]_D^{20}$ +7.8 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 7.76-7.73 (m, 1H), 7.70-7.67 (m, 1H), 7.53-7.50 (m, 1H), 7.47-7.42 (m, 2H), 7.41-7.37 (m, 2H), 7.36-7.13 (m, 23H), 5.06 (d, *J* 10.4 Hz, 1H), 4.98-4.93 (m, 3H), 4.90-4.82 (ABq, 2H), 4.76-4.70 (m, 2H), 4.61 (d, *J* 11.7 Hz, 1H), 4.55-4.51 (m, 2H), 4.42 (bs, 2H), 4.40 (d, *J* 7.3 Hz, 1H), 4.15 (bs, 1H), 4.03-3.96 (m, 3H), 3.84 (ddd, *J* 5.0 Hz, *J* 7.9 Hz, *J* 12.3 Hz, 1H), 3.81-3.77 (m, 1H), 3.75-3.64 (m, 3H), 3.57-3.49 (m, 3H), 3.35 (ddd, *J* 3.5 Hz, *J* 7.2 Hz, *J* 13.1 Hz, 1H), 3.29-3.20 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.0, 138.8, 138.7, 138.4, 138.3, 135.8, 133.5, 133.2, 129.0, 128.6, 128.4, 128.3, 128.3, 128.1, 128.1, 128.1, 128.0, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.3, 126.7, 126.0, 125.9, 104.2, 98.3, 84.1, 81.3,

78.4, 77.6, 75.7, 75.3, 75.3, 75.1, 74.5, 73.6, 73.4, 72.3, 71.7, 69.7, 66.7, 64.3, 50.6. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{59}H_{61}N_3O_{10}Na$, 994.4255; found, 994.4252

Synthesis of Large Spacer-Equipped Saccharides of Serotype D



Scheme 11. Reagents and conditions: (a) DDQ, DCM/H_2O (10:1), 20 °C, 2.5 h, 72%; (b) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 2 h, 85% (α:β, 3:1); (c) DDQ, DCM/H_2O (10:1), 20 °C, 3 h, from 77%.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl–α-D-mannopyranoside (18b)

DDQ (924 mg, 4.07 mmol) was added to a vigorously stirred solution of compound **46** (1.4 g, 1.44 mmol) in CH_2Cl_2/t-BuOH (28.6 mL, 10:1) at 20 °C. After 2.5 h, the reaction was quenched by adding 10% aq. $Na_2S_2O_3$-solution (50 mL). The layers were separated, and the organic layer was washed sequentially with sat. $NaHCO_3$-solution (3 x 50 mL), and brine (1 x 50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 95:5→70:30) to give **18b** (860 mg, 72%) as a colourless syrup; R_f (cyclohexane-EtOAc, 8:2) 0.29; $[\alpha]_D^{20}$ +24.4 (*c* 1.1,

$CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.19 (m, 25H), 4.97-4.93 (m, 2H), 4.91-4.84 (m, 2H), 4.71 (d, *J* 11.7 Hz, 1H), 4.66 (d, *J* 10.7 Hz, 1H), 4.59 (t, *J* 11.3 Hz, 1H), 4.52 (ABq, *J* 11.2 Hz, 2H), 4.34 (d, *J* 7.7 Hz, 1H), 4.02 (td, *J* 3.4 Hz, *J* 9.2 Hz, 1H), 3.97-3.92 (m, 2H), 3.85-3.81 (m, 1H), 3.78-3.66 (m, 4H), 3.64-3.50 (m, 3H), 3.41-3.33 (m, 2H), 3.29 (ddd, *J* 3.6 Hz, *J* 5.8 Hz, *J* 13.2 Hz, 1H), 3.24-3.16 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.7, 138.7, 138.5, 138.3, 138.1, 128.6, 128.4, 128.4, 128.4, 128.4, 128.4, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 104.6, 98.5, 83.7, 81.1, 80.7, 77.5, 76.7, 75.7, 75.0, 75.0, 73.6, 73.4, 71.8, 70.8, 69.5, 66.4, 64.3, 50.5. HRMS (ESI): $[M+Na]^+$ *m/z* Calcd for $C_{48}H_{53}N_3O_{10}Na$, 854.3629; found, 854.3635.

2-Azidoethyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-β-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (14c) and **2-Azidoethyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (14a)**

A mixture of thioglycoside donor **21** (184 mg, 0.31 mmol), acceptor **18b** (173.4 mg, 0.20 mmol) and crushed molecular sieves (4 Å) in dry Et_2O (30 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (154 mg, 0.60 mmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 2 h. The reaction was and quenched with Et_3N (300 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by silica column chromatography (cyclohexane-EtOAc, 70:30) gave **14a** (181 mg, 64%) and **14c** (60 mg, 21%) as a colourless syrups.

Compound **14c**

R_f (cyclohexane-EtOAc, 8:2) 0.12; $[\alpha]_D^{20}$ −22.6 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69-7.65 (m, 4H), 7.48-7.13 (m, 38H), 5.05-4.89 (m, 5H), 4.85 (d, *J* 11.0 Hz, 1H), 4.69-4.56 (m, 5H), 4.53 (d, *J* 11.7 Hz, 1H), 4.50-4.39 (m, 2H), 4.35-4.28 (m, 2H), 4.11 (bs, 2H), 3.96 (t, *J* 9.4 Hz, 1H), 3.91-3.81 (m, 3H), 3.76 (dd, *J* 4.7 Hz, *J* 11.5 Hz, 1H), 3.67 (bs, 2H), 3.59-3.46 (m, 5H), 3.44-3.35 (m, 2H), 3.28-3.23 (m, 1H), 3.16 (t, *J* 10.7 Hz, 1H), 1.94 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.0, 139.2, 138.8, 138.6, 138.4, 138.3, 138.2, 138.1, 135.5, 133.3, 132.0, 128.8, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.3, 126.2, 126.2, 125.9, 125.5, 103.5 ($J_{C\text{-}H}$ 155 Hz), 99.5 ($J_{C\text{-}H}$ 150 Hz), 98.3 ($J_{C\text{-}H}$ 175 Hz), 83.8, 82.5, 81.4, 77.8, 76.6, 75.6, 75.2, 74.9, 74.4 (2C), 74.4, 74.0, 73.8, 73.7 (2C), 73.4, 73.3, 71.6, 71.1, 69.7, 66.7, 64.1, 63.8, 50.5, 20.9. **HRMS (ESI):** $[M-H]^+$ *m/z* Calcd for $C_{81}H_{84}N_3O_{16}$, 1354.5852; found, 1354.5913.

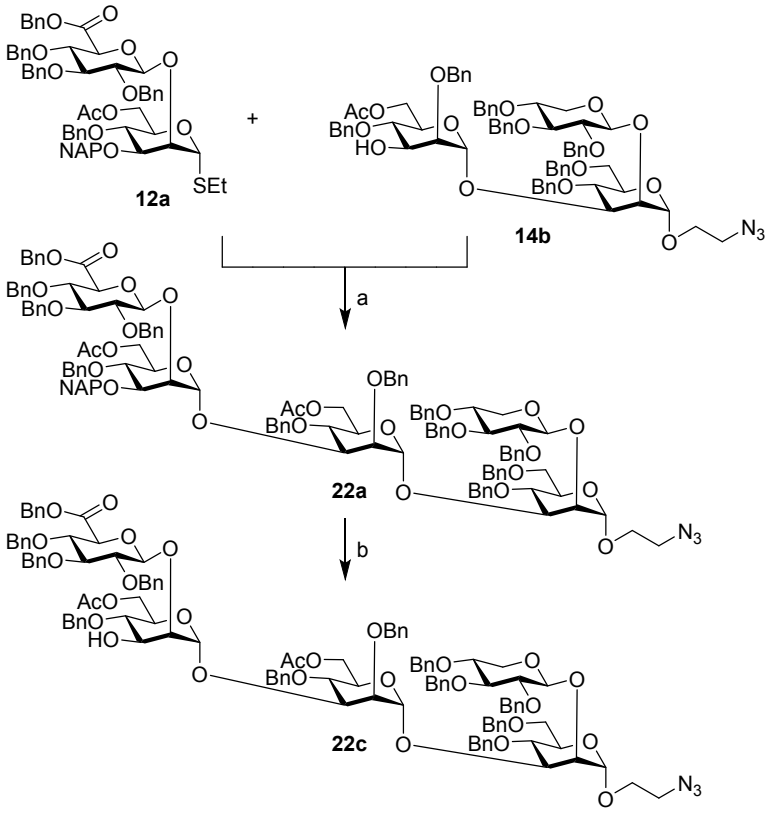
Compound **14a**

R_f (cyclohexane-EtOAc, 8:2) 0.23; $[\alpha]_D^{20}$ −5.8 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79-7.71 (m, 4H), 7.42-7.10 (m, 38H), 5.19 (d, *J* 0.5 Hz, 1H), 5.04 (d, *J* 10.3 Hz, 1H), 4.98 (d, *J* 11.0 Hz, 1H), 4.91 (d, *J* 1.2 Hz, 1H), 4.84 (q, *J* 11.0 Hz, 2H), 4.77 (d, *J* 11.8 Hz, 1H), 4.67 (d, *J* 11.9 Hz, 1H), 4.64-4.59 (m, 2H), 4.48-4.26 (m, 12H), 4.14-4.10 (m, 2H), 4.01 (dd, *J* 1.7 Hz, *J* 1.7 Hz, 1H), 3.97 (dd, *J* 1.7 Hz, *J* 3.2 Hz, 1H), 3.95-3.89 (m, 2H), 3.82 (ddd, *J* 3.9 Hz, *J* 6.2 Hz, *J* 10.4 Hz, 1H), 3.79-3.76 (m, 1H), 3.71-3.68 (m, 2H), 3.64 (dd, *J* 1.6 Hz, *J* 10.7 Hz, 1H), 3.54 (ddd, *J* 3.3 Hz, *J* 5.1 Hz, *J* 6.6 Hz, 1H), 3.51-3.45 (m, 2H), 3.41 (dd, *J* 5.1 Hz, *J* 11.6 Hz, 1H), 3.39-3.30 (m, 2H), 3.10 (dd, *J* 9.9 Hz, *J* 11.6 Hz, 1H), 2.06 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.1, 138.9, 138.8, 138.6, 138.6, 138.4, 138.2, 138.1, 136.1, 133.4, 133.0, 128.9, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.6, 127.5, 127.4, 126.8, 126.5, 126.2, 126.0, 104.5 ($J_{C\text{-}H}$ 155 Hz), 99.9 ($J_{C\text{-}H}$ 175 Hz), 98.4 ($J_{C\text{-}H}$ 170 Hz), 83.9, 81.4, 80.1, 78.7, 77.5, 76.4, 75.9, 75.7, 75.1 (2C), 75.1, 75.0, 74.4, 73.5, 72.8, 72.6, 72.4, 72.4, 70.4, 69.3, 66.4, 64.0, 63.6, 50.5, 21.0. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{81}H_{85}N_3O_{16}Na$, 1378.5828; found, 1378.5828.

2-Azidoethyl 6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (14b)

DDQ (165.6 mg, 0.72 mmol) was added to a vigorously stirred solution of compound **14a** (509 mg, 0.37 mmol) in CH_2Cl_2/MeOH (8.8 mL, 10:1) at 20 °C. An additional amount of DDQ (182 mg, 0.80 mmol) was added after 20 min. After 3 h, the reaction was quenched by adding 10% aq. $Na_2S_2O_3$-solution (40 mL). The resulting mixture was extracted once with CH_2Cl_2 (40 mL), the layers were separated, and the organic layer was washed sequentially with sat. $NaHCO_3$-solution (3 x 40 mL), and brine (1 x 40 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 95:5→70:30) to give **14b** (353 mg, 77%) as a colourless syrup; R_f (cyclohexane-EtOAc, 6:1) 0.48; $[\alpha]_D^{20}$ −1.2 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.12 (m, 35H), 5.25 (s, 1H), 5.02 (d, *J* 10.3 Hz, 1H), 4.94-4.89 (m, 2H), 4.85-4.77 (m, 3H), 4.66 (d, *J* 11.8 Hz, 1H), 4.60-4.56 (m, 2H), 4.48-4.27 (m, 9H), 4.15 (dd, *J* 3.3 Hz, *J* 9.6 Hz, 1H), 4.11-3.97 (m, 5H), 3.84-3.80 (m, 2H), 3.76-3.67 (m, 3H), 3.58-3.47 (m, 4H), 3.4-3.31 (m, 3H), 3.12-3.05 (m, 1H), 2.27 (d, *J* 9.9 Hz, 1H), 2.06 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 139.0, 138.7, 138.7, 138.6, 138.2, 138.2, 137.8, 128.9, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 127.9, 127.9, 127.9, 127.7, 127.7, 127.6, 127.6, 127.6, 126.7, 104.5, 99.2, 98.4, 83.9, 81.3, 79.1, 78.8, 77.8, 77.3, 76.9, 75.6, 75.1,

75.0, 74.7, 74.5, 73.5, 72.8, 72.4 (2C), 71.8, 69.4, 69.3, 66.3, 6410, 63.6, 50.5, 20.9. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{70}H_{77}N_3O_{16}Na$, 1238.5202; found, 1238.5211.



Scheme 12. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 2 h, 94% (α-only); (b) DDQ, DCM/H_2O (10:1), 20 °C, 1 h, 45%.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (22a)

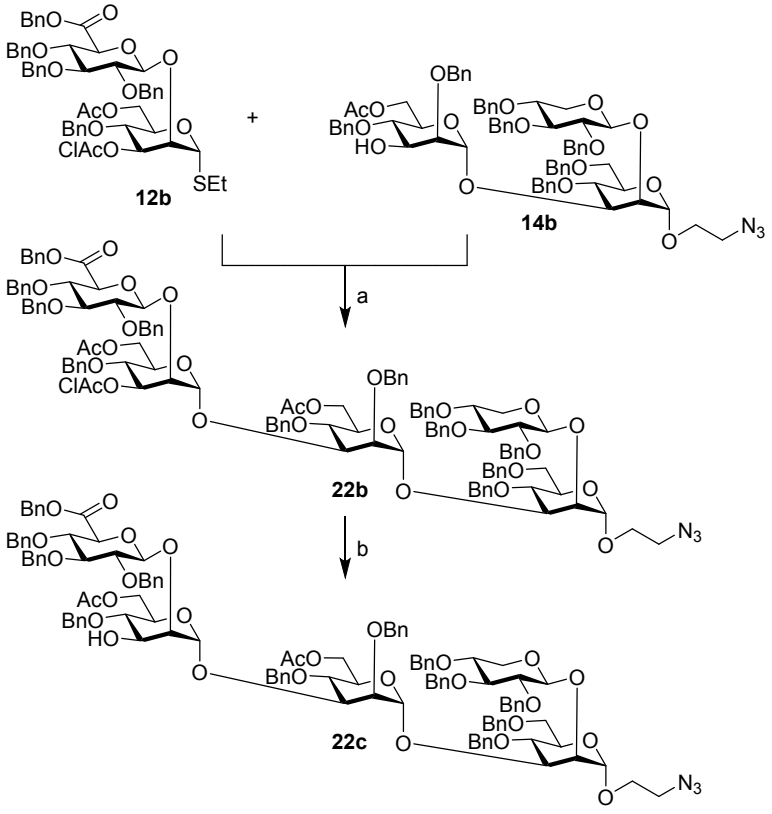
A mixture of thioglycoside donor **12a** (306.2 mg, 0.3 mmol), acceptor **14b** (245 mg, 0.2 mmol) and crushed molecular sieves (4 Å) in dry Et_2O (25 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (234 mg, 0.9 mmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 2 h. The reaction was and quenched with Et_3N (1.5 mL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by silica flash column chromatography (cyclohexane-

EtOAc, 75:25) gave **22a** (414 mg, 94%) as a colourless syrup; R_f (cyclohexane-EtOAc, 75:25) 0.45; $[\alpha]_D^{20}$ −16.2 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75-7.60 (m, 4H), 7.45 -7.02 (m, 60H), 5.25 (s,1H), 5.19 (s,1H), 5.12-5.02(m, 4H), 4.98 (d, *J* 11.0 Hz, 1H), 4.93 (s, 1H), 4.80 (q, *J* 11.3 Hz, 2H), 4.76-4.67 (m, 4H), 4.63-4.58 (m, 2H), 4.56-4.41 (m, 9H), 4.37-4.27 (m, 4H), 4.26-4.17 (m, 5H), 4.15-3.91 (m, 10H), 3.89-3.77 (m, 5H), 3.74-3.65 (m, 3H), 3.58-3.45 (m, 6H), 3.41-3.26 (m, 3H), 3.07 (t, *J* 10.7 Hz, 1H), 2.05 (s, 1H), 1.58 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 170.6, 168.1, 139.1, 138.7, 138.6, 138.6, 138.5, 138.5, 138.3, 138.2, 138.2 (2C), 137.9, 135.4, 135.0, 133.3, 133.1, 129.2, 129.0, 128.8, 128.8, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 126.9, 126.9, 126.2, 126.0, 125.9, 104.4 ($J_{C\text{-}H}$ 160 Hz), 103.2 ($J_{C\text{-}H}$ 160 Hz), 100.1 ($J_{C\text{-}H}$ 170 Hz), 99.6 ($J_{C\text{-}H}$ 175 Hz), 98.2 ($J_{C\text{-}H}$ 170 Hz), 83.9, 83.5, 81.3, 81.3, 79.1, 79.0, 78.8, 78.7, 78.4, 78.4, 77.8, 75.6, 75.4, 75.3, 75.3 (2C), 75.1, 75.0, 74.8 (2C), 74.6, 74.6, 73.9, 73.6, 73.5, 73.1, 72.3, 72.0, 71.4, 70.3, 69.6, 69.4, 67.4, 66.4, 63.7, 63.7, 63.3, 50.5, 20.9, 20.6. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{130}H_{135}N_3O_{28}Na$, 2208.9130; found, 2208.9050.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (22c)

DDQ (59 mg, 0.26 mmol) was added to a vigorously stirred solution of compound **22a** (280 mg, 0.13 mmol) in CH_2Cl_2/H_2O (3 mL, 10:1) at 20 °C. After 60 min, the reaction was quenched by adding 10% aq. $Na_2S_2O_3$-solution (20 mL). The resulting mixture was extracted once with CH_2Cl_2 (20 mL), the layers were separated, and the organic layer was washed sequentially with sat. $NaHCO_3$-solution (3 x 20 mL), and brine (1 x 20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→70:30) to give **22c** (118 mg, 45%) as a colourless syrup; **R_f** (toluene-EtOAc, 8:2) 0.65; $[\alpha]_D^{20}$ +0.4 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 -7.02 (m, 60H), 5.20 (bs, 2H), 5.16-5.06 (m, 3H), 4.98 (d, *J* 11.2 Hz, 1H), 4.94-4.89 (m, 2H), 4.81 (q, *J* 11.2 Hz, 2H), 4.77-4.72 (m, 3H), 4.66-4.56 (m, 7H), 4.49-4.44 (m, 1H), 4.43-4.36 (m, 5H), 4.34-4.21 (m, 6H), 4.17-4.10 (m, 2H), 4.07-3.96 (m, 5H), 3.89-3.77 (m, 6H), 3.73-3.66 (m, 4H), 3.61 (t, *J* 9.5 Hz, 1H), 3.57-3.48 (m, 5H), 3.41-3.29 (m, 4H), 3.11 (dd, *J* 9.9 Hz, 11.3 Hz, 1H), 2.97 (d, *J* 9.7 Hz, 3H), 2.06 (s, 1H), 1.70 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 170.7, 168.1, 139.1, 138.7, 138.7, 138.6, 138.4, 138.3, 138.2, 138.2, 137.9, 137.9, 137.8, 135.0, 129.0, 128.9, 128.9, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.1, 127.9, 127.8,

127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.3, 126.9, 126.4, 104.3, 103.1, 100.2 (2C), 98.2, 84.0, 83.1, 81.4, 80. 7, 80.4, 79.5, 79.0 (2C), 78.6, 78.4, 78.4, 75.8, 75.6, 75.5, 75.5, 75.3, 74.9, 74.9, 74.6, 74.2, 73.54 73.2, 72.3, 72.1, 71.0, 69.9, 69.81 69.4, 67.7, 66.4, 63.7, 63.3 50.5 21.0, 20.8. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{119}H_{127}N_3O_{28}Na$, 2068.8504; found, 2068.8606.



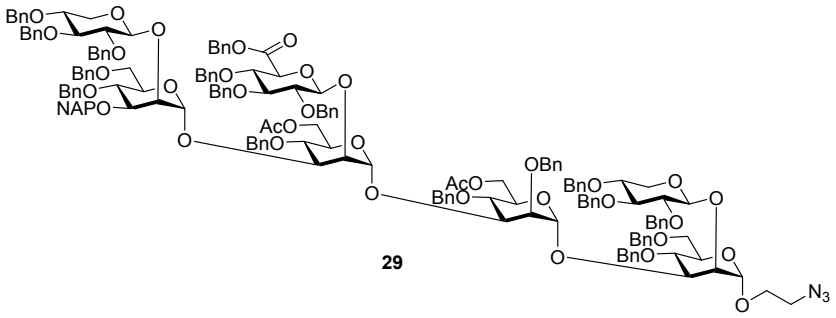
Scheme 13. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 7 h, 74% (α-only); (b) thiourea, $NaHCO_3$, TBAI, dry. THF, 65 ºC, 92%.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-−mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (22b)

A mixture of thioglycoside donor **12b** (227 mg, 0.23 mmol), acceptor **14b** (185.5 mg, 0.15 mmol) and crushed molecular sieves (4 Å) in dry Et_2O (13 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (121.4 mg, 0.47 mmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 7 h. The reaction was and quenched with Et_3N (1.3 mL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography

(RevelerisX1, 40 gram column, toluene-EtOAc, 99:1→70:30) gave **22b** (240 mg, 74%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.28; $[\alpha]_D^{20}$ −2.8 (1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 -7.01 (m, 60H), 5.24-5.20 (m, 2H), 5.16-5.01 (m, 3H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.98 (d, *J* 10.4 Hz, 1H), 4.93 (bs, 1H), 4.86-4.72 (m, 5H), 4.69 (d, *J* 11.1 Hz, 1H), 4.65-4.50 (m, 7H), 4.48-4.39 (m, 4H), 4.37-4.26 (m, 5H), 4.24-4.19 (m, 2H), 4.17-4.10 (m, 4H), 4.05-3.87 (m, 9H), 3.85-3.78 (m, 4H), 3.73 (dd, *J* 4.3 Hz, *J* 10.7 Hz, 1H), 3.70-3.62 (m, 2H), 3.55 (ddd, *J* 4.0 Hz, *J* 6.3 Hz, *J* 10.7 Hz, 1H), 3.51-3.46 (m, 3H), 3.43-3.32 (m, 4H), 3.24 (t, *J* 9.1 Hz, 1H), 3.10 (dd, *J* 8.3 Hz, 12.5 Hz, 1H), 2.06 (s, 1H), 1.65 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.0, 170.5, 168.9, 167.0, 139.1, 138.7, 138.7, 138.5, 138.5, 138.2 (2C), 138.2, 138.0, 138.0, 137.7, 134.9, 129.0, 129.0, 128.8, 128.7, 128.7, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 127.3, 126.8, 126.6, 104.3 ($J_{C,H}$ 160 Hz), 103.2 ($J_{C,H}$ 160 Hz), 100.2 ($J_{C,H}$ 170 Hz), 99.8 ($J_{C,H}$ 170 Hz), 98.2 ($J_{C,H}$ 170 Hz), 83.9, 83.2, 81.3, 81.2, 80.5, 79.4, 78.9, 78.6, 78.3 (2C), 75.6 (2C), 75.5, 75.3, 75.2, 75.1, 74.9, 74.9, 74.8, 74.7, 74.6, 74.4, 74.1, 73.5, 73.1, 72.3, 72.2, 71.8, 69.9, 69.9, 69.4, 67.9, 66.4, 63.7 (2C), 62.8, 50.5, 41.1, 21.0, 20.7. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{121}H_{128}N_3O_{29}NaCl$, 2144.8220; found, 2144.8254.

2-Azidoethyl (2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl)-(1→2)]-3-*O*-(2-naphthalenylmethyl)-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate]-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (29)



29

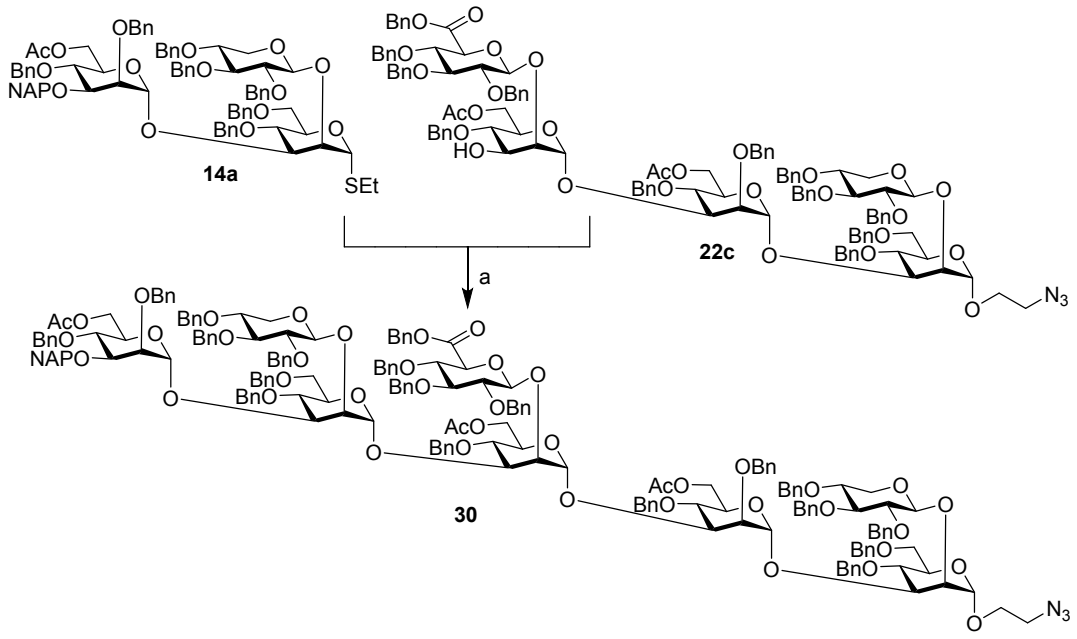
A mixture of thioglycoside donor **11a** (36.9 mg, 39 μmol), acceptor **22c** (48 mg, 23.5 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (5 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (19 mg, 73.6 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 1.5 h. The reaction was and quenched with Et_3N (100 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40

gram column, toluene-EtOAc, 97:3→80:20) gave **29** (57 mg, 83%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.77; $[\alpha]_D^{20}$ −15.8 (*c* 1.0, $CHCl_3$); ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.79 (m, 1H), 7.73 (d, *J* 8.2 Hz, 2H), 7.56 (d, *J* 8.3 Hz, 1H), 7.46-6.90 (m, 86H), 5.30 (s, 1H), 5.28-5.24 (m, 2H), 5.12 (d, *J* 10.3 Hz, 1H), 5.08 (d, *J* 10.1 Hz, 1H), 5.00 (d, *J* 11.3 Hz, 1H), 4.97-4.92 (m, 3H), 4.90-4.84 (m, 2H), 4.80-4.71 (m, 6H), 4.67-4.46 (m, 14H), 4.43 (s, 2H), 4.36 (d, *J* 11.7 Hz, 1H), 4.33-4.22 (m, 8H), 4.20 (m, 2H), 4.17-4.10 (m, 5H), 4.05-3.99 (m, 5H), 3.94-3.79 (m, 11H), 3.75-3.64 (m, 4H), 3.56-3.42 (m, 9H), 3.40-3.33 (m, 3H), 3.27 (t, *J* 9.1 Hz, 1H), 3.15 (t, *J* 9.0 Hz, 1H), 3.07 (dd, *J* 9.5 Hz, *J* 11.2 Hz, 1H), 2.57 (t, *J* 9.5 Hz, 1H), 2.01 (s, 3H), 1.61 (s, 3H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 170.9, 170.4, 167.8, 139.1, 139.1, 139.0, 139.0, 138.7, 138.7, 138.6, 138.5, 138.5, 138.5, 138.4, 138.2, 138.2, 138.1, 138.1, 137.8, 136.5, 135.5, 133.4, 133.1, 129.2, 129.0, 128.8, 128.7, 128.7, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 127.4, 127.4, 127.3, 127.1, 127.1, 126.8, 126.7, 126.4, 125.8, 125.7, 125.4, 104.4 ($J_{C,H}$ 160 Hz), 103.5 ($J_{C,H}$ 155 Hz), 102.6 ($J_{C,H}$ 160 Hz), 100.7 ($J_{C,H}$ 170 Hz), 100.0 ($J_{C,H}$ 170 Hz), 99.9($J_{C,H}$ 170 Hz), 98.3 ($J_{C,H}$ 170 Hz), 83.9, 83.5, 83.3, 81.7, 81.3, 80.7, 80.3, 79.3, 79.2, 79.1, 78.7, 78.7, 78.5, 78.3, 77.4, 76.1, 75.9, 75.6 (2C), 75.4, 75.4 (2C), 75.3, 75.0, 74.9, 74.8, 74.6, 74.6, 74.5 (2C), 74.4, 73.9, 73.6, 73.2, 73.2, 73.1, 73.0, 72.3, 72.3, 71.8, 70.4, 69.7, 69.6, 69.4, 67.1, 66.4, 63.9, 63.8, 63.6, 63.1, 50.5, 20.9, 20.7. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{176}H_{183}N_3O_{37}Na$, 2953.2428; found, 2953.2444.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (22c)

Preparation of **22c** from following Scheme (cleavage of the choloroacetate):

Compound **22b** (240 mg, 0.11 mmol) was dissolved in THF (1.2 mL). Thiourea (26.6 mg, 0.35 mmol), $NaHCO_3$ (32.7 mg, 0.39 mmol), and *n*-Bu_4NI (8.7 mg, 23.5 μmol) were added, and the suspension was heated at 65 °C. After 20 h, the reaction mixture was cooled to ambient temperature and diluted with CH_2Cl_2. The solids were removed by filtration, and the filtrate was concentrated *in vacuo*. Purification by flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 99:1→80:20) gave **22c** (214 mg, 92%) as a colourless syrup.

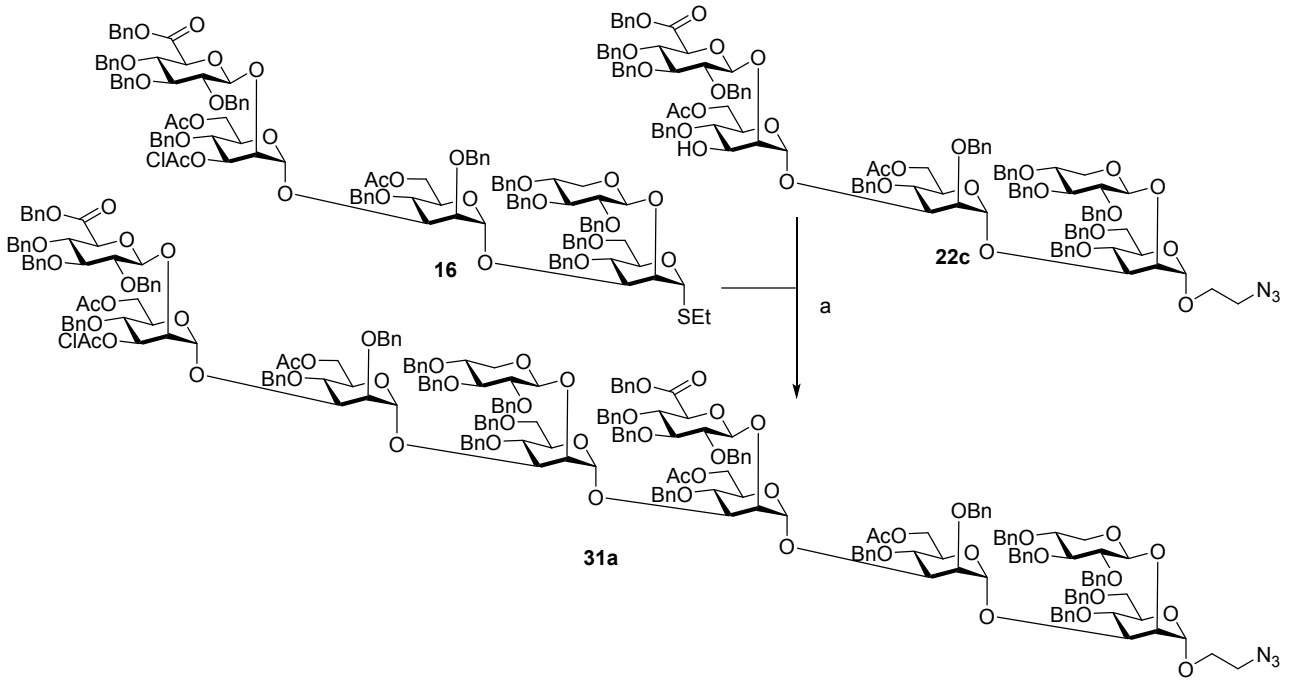


Scheme 14 Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 1.5 h, 79% (α-only).

2-Azidoethyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (30)[1]

A mixture of thioglycoside donor **14a** (53 mg, 39.8 μmol), acceptor **22c** (50 mg, 24.4 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (5 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (21 mg, 81.3 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 1.5 h. The reaction was and quenched with Et_3N (100 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 99:1→70:30) gave **30** (64 mg, 79%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.23; $[\alpha]_D^{20}$ − 23.9 (*c* 1.2, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73-7-64 (m, 4H), 7.40-6.93 (m, 98H), 5.36 (s, 1H), 5.30 (s, 1H), 5.26 (s, 1H), 5.24 (s, 1H), 5.15 (d, *J* 10.5 Hz, 1H), 5.09 (d, *J* 10.2 Hz, 1H), 4.99 (d, *J* 11.2 Hz, 1H), 4.96-4.93 (m, 2H), 4.86 (d, *J* 12.2 Hz, 1H), 4.80-4.71 (m, 8H), 4.67-4.62 (m, 3H), 4.60-4.55 (m, 4H), 4.54-4.42 (m, 11H), 4.41-4.36 (m, 2H), 4.34-4.20 (m, 10H), 4.18-4.07 (m, 10H), 4.07-4.00 (m, 5H), 3.99-3.94 (m, 3H), 3.93-3.79 (m,

9H), 3.76-3.61 (m, 5H), 3.57-3.41 (m, 6H), 3.41-3.33 (m, 3H), 3.31-3.24 (m, 4H), 3.18 (t, *J* 9.0 Hz, 1H), 3.08-3.02 (m, 1H), 2.29 (t, *J* 10.7 Hz, 1H), 2.09 (s, 3H), 2.02 (s, 3H), 1.59 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.1, 170.9, 170.5, 167.6, 139.1, 139.0, 139.0, 138.9, 138.8, 138.7, 138.6, 138.6, 138.6, 138.5, 138.5, 138.4, 138.4, 138.3, 138.3, 138.2, 138.1, 137.7, 136.2, 135.4, 133.3, 132.9, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.4, 127.3, 127.1, 126.9, 126.7, 126.4, 126.2, 126.2, 125.9, 104.4 ($J_{C,H}$ 160 Hz), 103.0 ($J_{C,H}$ 160 Hz), 102.43 ($J_{C,H}$ 160 Hz), 101.1 ($J_{C,H}$ 170 Hz), 100.1 ($J_{C,H}$ 170 Hz), 99.8 (2C, $J_{C,H}$ 170 Hz), 98.3 ($J_{C,H}$ 170 Hz), 83.9, 83.5, 83.2, 81.5, 81.3, 81.2, 80.4, 79.9, 79.3 (2C), 78.8, 78.7, 78.3, 78.1 (2C), 78.0, 77.5, 77.4, 76.0, 75.4, 75.4, 75.4, 75.3 (2C), 75.0, 74.9, 74.8, 74.7, 74.6, 74.6 (2C), 74.5, 74.5, 74.0, 73.6, 73.2, 73.0, 72.7, 72.6, 72.4, 72.3, 72.0, 71.7, 70.3, 70.2, 69.6, 69.4, 69.4, 67.0, 66.4, 63.8, 63.6, 63.5, 63.1, 63.0, 50.5, 21.2, 20.9, 20.6. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{198}H_{207}N_3O_{43}Na$, 3337.4001; found, 3337.4077.

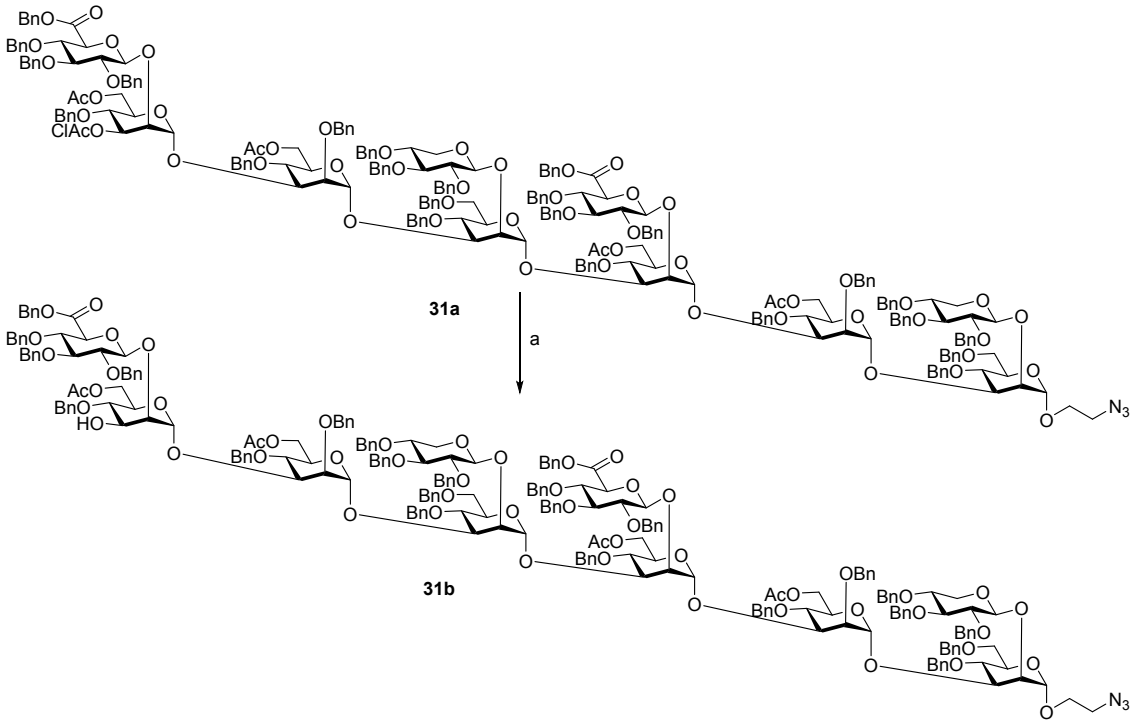


Scheme 15. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 1.5 h, 82% (α-only).

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-

acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (31a)

A mixture of thioglycoside donor **16** (90 mg, 42.9 μmol), acceptor **22c** (58 mg, 28.3 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (5 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (33 mg, 127 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 1.5 h. The reaction was and quenched with Et_3N (100 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→70:30) gave **31a** (95 mg, 82%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.36; $[\alpha]_D^{20}$ −23.2 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44-6.83 (m, 120H), 5.49 (s, 1H), 5.30 (s, 2H), 5.27 (s, 1H), 5.21 (dd, *J* 9.8, 3.2 Hz, 1H), 5.18-5.11 (m, 4H), 5.09-5.04 (m, 2H), 4.94 (s, 1H), 4.91 (d, *J* 10.5 Hz, 1H), 4.89-4.82 (m, 2H), 4.81-4.44 (m, 33H), 4.38-3.69 (m, 49H), 3.65-3.59 (m, 2H), 3.58-3.52 (m, 2H), 3.51-3.44 (m, 4H), 3.42-3.29 (m, 8H), 3.27-3.20 (m, 2H), 3.14 (t, *J* 9.0 Hz, 1H), 3.08-3.01 (m, 1H), 2.21 (t, *J* 10.7 Hz, 1H), 2.10 (s, 3H), 2.03 (s, 3H), 1.57 (2s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.1, 170.1, 170.5, 170.3, 168.9, 167.8, 166.9, 139.1, 139.1, 139.0, 138.8, 138.7, 138.6, 138.5 (2C), 138.5, 138.5, 138.5, 138.4, 138.3, 138.2 (2C), 138.2, 138.2, 138.1, 138.0, 138.0, 137.9, 137.7, 135.3, 134.9, 129.0, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 127.1, 126.9, 126.7, 126.5, 125.6, 104.4 ($J_{C,H}$ 160 Hz), 103.2 ($J_{C,H}$ 155 Hz), 102.9 ($J_{C,H}$ 160 Hz), 102.5 ($J_{C,H}$ 160 Hz), 100.5 ($J_{C,H}$ 170 Hz), 100.3 ($J_{C,H}$ 170 Hz), 100.1 ($J_{C,H}$ 170 Hz), 99.9 ($J_{C,H}$ 170 Hz), 99.8 ($J_{C,H}$ 170 Hz), 98.3 ($J_{C,H}$ 170 Hz), 83.9, 83.5, 83.2, 83.1, 81.5, 81.3, 81.3, 81.0, 80.9, 80.5, 80.2, 79.4, 79.3, 78.8, 78.6, 78.3 (2C), 78.2, 77.9, 77.4, 75.7, 75.6, 75.4, 75.4, 75.4, 75.3, 75.2 (2C), 75.1, 75.0 (2C), 74.9, 74.8, 74.8 (2C), 74.7, 74.7, 74.6, 74.5, 74.5, 74.4, 74.2, 74.2, 74.0, 73.9, 73.6, 73.2, 73.0, 72.9, 72.7, 72.3, 72.1, 71.7, 71.6, 70.3, 69.8, 69.7, 69.6, 69.4 (2C), 67.8, 67.0, 66.4, 63.8, 63.6, 63.2, 63.1, 63.0, 62.7, 50.5, 41.1, 21.2, 20.9, 20.6 (2C). **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{238}H_{250}N_3O_{56}NaCl$, 4103.6393; found, 4103.6377.

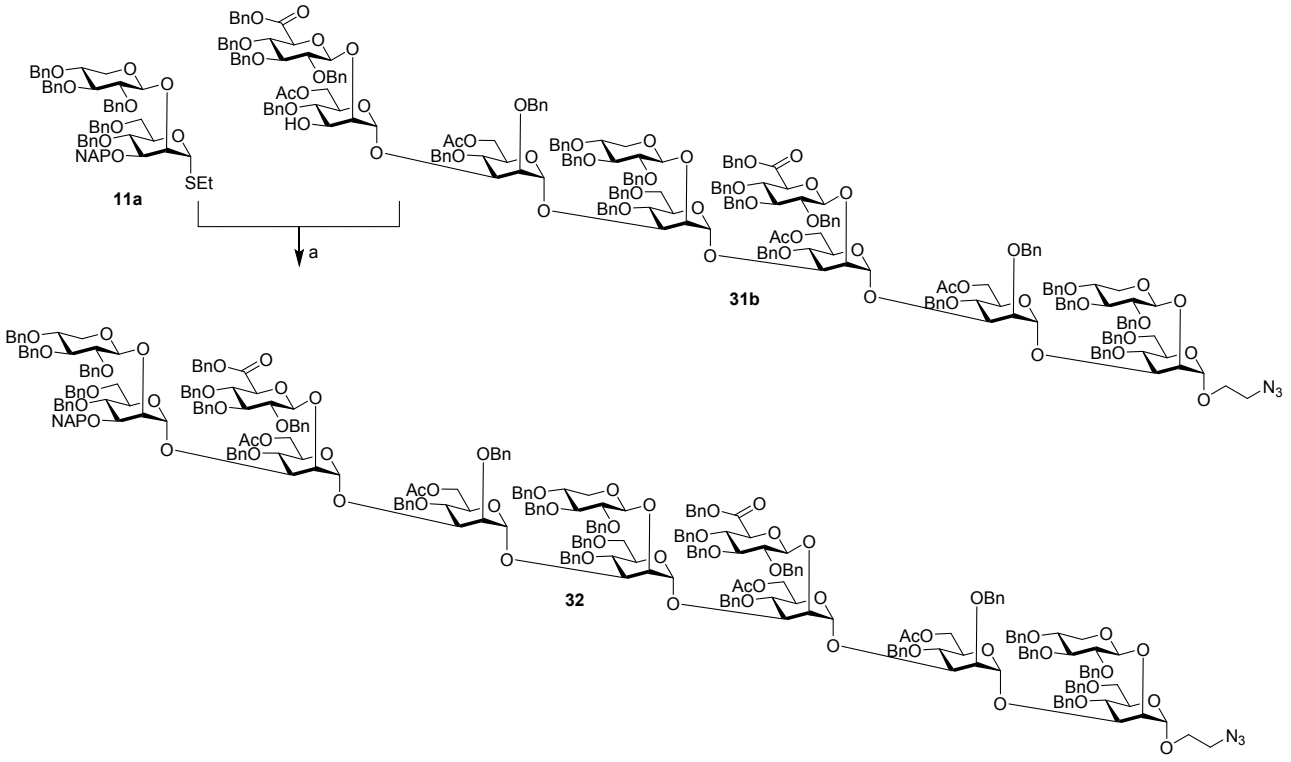


Scheme 16. Reagents and conditions: (a) thiourea, $NaHCO_3$, TBAI, dry. THF, 65 ºC, 16 h, 89%.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (31b)

Compound **31a** (96 mg, 23.5 μmol) was dissolved in THF (0.9 mL). Thiourea (5.4 mg, 70.9 μmol), $NaHCO_3$ (6.5 mg, 77.3 μmol), and *n*-Bu_4NI (2 mg, 5.4 μmol) were added, and the suspension was heated at 65 °C. After 16 h, the reaction mixture was cooled to ambient temperature and diluted with DCM. The solids were removed by filtration, and the filtrate was concentrated *in vacuo*. Purification by flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→70:30) gave **31b** (84 mg, 89%) as a colourless syrup; R_f (toluene-EtOAc, 85:15) 0.22; $[\alpha]_D^{20}$ −11.8 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44-6.85 (m, 120H), 5.46 (s, 1H), 5.32-5.28 (m, 2H), 5.27 (s, 1H), 5.19-5.04 (m, 6H), 4.97-4.93 (m, 2H), 4.89-4.34 (m, 36H), 4.33-3.96 (m, 30H), 3.94-3.79 (m, 11H), 3.75-3.51 (m, 11H), 3.49-3.41 (m, 4H), 3.39-3.29 (m, 9H), 3.39-3.29 (m, 9H), 3.14 (t, *J* 9.0 Hz, 1H), 3.08-3.01 (m, 1H), 2.93 (d, *J* 9.7 Hz, 1H), 2.21 (t, *J* 10.7 Hz, 1H), 2.10

(s, 3H), 2.03 (s, 3H), 1.60-1.55 (2s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.0, 170.9, 170.5, 170.4, 168.1, 167.8, 139.1 (2C), 139.0, 138.8 (2C), 138.7, 138.6, 138.5, 138.5, 138.5, 138.4, 138.3, 138.2, 138.2, 138.2, 138.1, 137.9, 137.8, 137.7, 135.3, 135.0, 129.0, 128.8, 128.7, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 127.1, 126.9, 126.7, 126.4, 126.0, 104.4, 103.2, 102.8, 102.5, 100.6, 100.4, 100.2, 99.9, 99.7, 98.3, 83.9, 83.5, 83.2, 83.0, 81.5, 81.3 (2C), 81.0, 80.5 (2C), 79.4 (2C), 79.1, 78.9, 78.8, 78.6, 78.3, 78.3, 78.2, 78.0, 77.9, 77.4, 75.7, 75.6, 75.4, 75.4, 75.4, 75.3, 75.3, 75.2, 74.9 (2C), 74.8 (2C), 74.7 (2C), 74.6 (2C), 74.5, 74.5, 74.2, 74.1, 73.9, 73.5, 73.2, 73.0, 72.9, 72.8, 72.3, 71.7, 71.7, 70.9, 70.3, 69.8, 69.7, 69.6, 69.4 (2C), 67.6, 67.0, 66.4, 63.8, 63.6, 63.2, 63.1 (2C), 63.1, 50.5, 21.2, 20.9, 20.7, 20.6. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{236}H_{249}N_3O_{55}Na$, 4027.6677; found, 4027.6865.

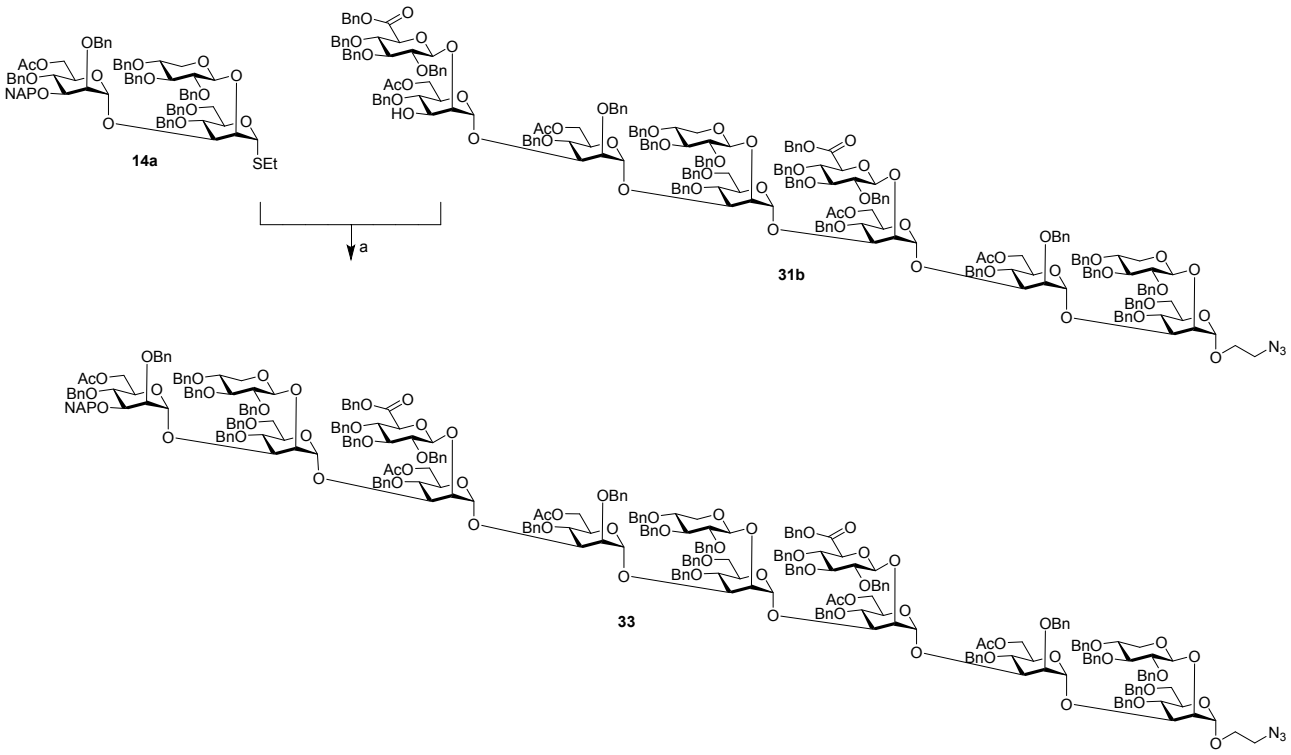


Scheme 17. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 2 h, 86% (α-only).

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (32)

A mixture of thioglycoside donor **11a** (14 mg, 14.7 μmol), acceptor **31b** (41 mg, 10.2 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (2 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (12 mg, 56 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 2 h. The reaction was and quenched with Et_3N (100 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 99:1→70:30) gave **32** (43 mg, 86%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.23; $[\alpha]_D^{20}$ −18.6 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.78 (d, *J* 8.8 Hz, 1H), 7.71 (m, 2H), 7.54 (d, *J* 8.4 Hz, 1H), 7.45-6.78 (m, 147H), 5.51 (s, 1H), 5.30 (s, 3H), 5.26 (s, 2H), 5.17 (d, *J* 10.3 Hz, 1H), 5.05 (m, 4H), 4.93 (m, 3H), 4.90-4.60 (m, 20H), 4.60-4.38 (m, 22H), 4.26 (m, 18H), 4.16-3.93 (m, 20H), 3.93-3.80 (m, 12H), 3.79-3.60 (m, 8H), 3.60-3.19 (m, 22H), 3.16 (t, *J* 9.0 Hz, 1H), 3.10 (t, *J* 9.0 Hz, 1H), 3.08-3.02 (m, 1H), 2.18 (t, *J* 10.8 Hz, 1H), 2.03 (s, 3H), 2.00 (s, 3H), 1.57 (s, 3H), 1.51 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.0, 170.9, 170.5, 170.2, 167.8, 167.8, 139.1, 139.1, 139.1, 139.1, 139.1, 139.0, 138.7 (2C), 138.6, 138.6 (2C), 138.6, 138.5, 138.5 (2C), 138.5, 138.5, 138.4, 138.4, 138.2, 138.2 (3C), 138.2, 138.1, 138.1, 137.7, 136.5, 135.6, 135.3, 133.4, 133.1, 129.0, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 127.4, 127.4, 127.3, 127.3, 127.1, 127.0, 126.9, 126.7, 126.7, 126.5, 126.0, 125.8, 125.7, 104.4 ($J_{C,H}$ 156 Hz), 103.5 ($J_{C,H}$ 156 Hz), 103.1 ($J_{C,H}$ 156 Hz), 102.7 ($J_{C,H}$ 162 Hz), 102.5 ($J_{C,H}$ 156 Hz), 100.8 ($J_{C,H}$ 171 Hz), 100.7 ($J_{C,H}$ 171 Hz), 100.3 ($J_{C,H}$ 171 Hz), 100.0 (2C, $J_{C,H}$ 170 Hz), 99.8 ($J_{C,H}$ 170 Hz), 98.3 ($J_{C,H}$ 171 Hz), 83.9, 83.5, 83.5, 83.4, 83.1, 81.6, 81.6, 81.3, 81.2, 81.0, 80.7, 80.6, 79.9, 79.4, 79.3, 79.1 (2C), 78.8, 78.7, 78.5, 78.4, 78.3, 78.0, 77.9, 76.5, 75.9, 75.6, 75.6, 75.5, 75.4, 75.4, 75.4, 75.4, 75.2, 75.1 (2C), 75.0 (2C), 74.9, 74.8 (2C), 74.7, 74.7, 74.6, 74.6 (2C), 74.5 (3C), 74.5, 74.2, 74.1 (2C), 74.0, 73.9, 73.6 (2C), 73.2, 73.2 (2C), 73.2, 73.1, 73.0 (2C), 72.9, 72.6, 72.4, 72.3,

71.7, 71.5, 70.3 (2C), 69.6, 69.6, 69.5, 69.5, 67.1, 67.1, 66.4, 63.9 (2C), 63.6, 63.4, 63.1, 63.0, 63.0, 50.5, 21.1, 20.9, 20.6, 20.6. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{293}H_{305}N_3O_{64}Na$, 4912.0602; found, 4912.0537.

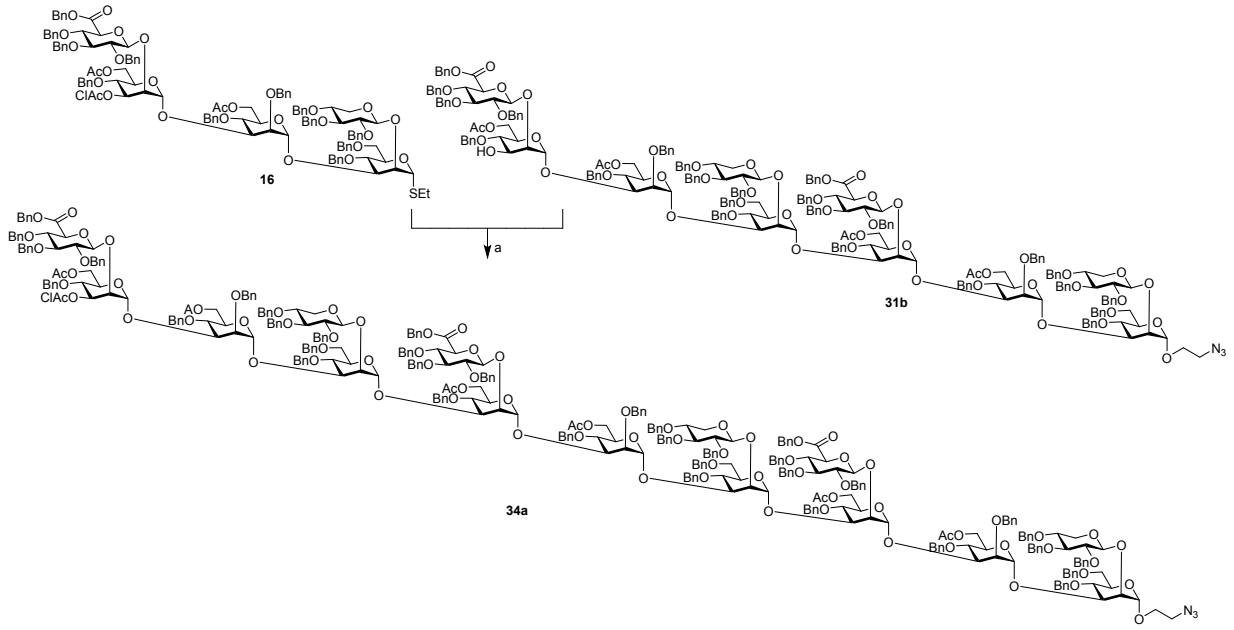


Scheme 18. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 2.5 h, 78% (α-only).

2-Azidoethyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (33)

A mixture of thioglycoside donor **14a** (22 mg, 16.5 μmol), acceptor **31b** (44 mg, 10.9 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (5 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (12.7 mg, 49 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 2.5 h. The reaction was and quenched with Et_3N (60 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→70:30) gave **33** (45 mg, 78%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.17; $[\alpha]_D^{20}$ −14.8 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74-7.67 (m, 3H), 7.65 (d, *J* 8.2 Hz, 1H), 7.43-6.84 (m, 158H), 5.53 (s, 1H), 5.34 (s, 1H), 5.32-5.27 (m, 3H), 5.26 (s, 1H), 5.23 (s, 1H), 5.17 (d, *J* 10.4 Hz, 1H), 5.10-5.03 (m, 3H), 4.98 (d, *J* 11.1 Hz, 1H), 4.95-4.92 (m, 2H), 4.89-4.38 (m, 46H), 4.36-3.80 (m, 59H), 3.80-3.60 (m, 9H), 3.58-3.53 (m, 1H), 3.53-3.43 (m, 6H), 3.42-3.21 (m, 12H), 3.18 (t, *J* 9.0 Hz, 1H), 3.10 (t, *J* 9.0 Hz, 1H), 3.07-3.02 (m, 1H), 2.32 (t, *J* 10.6 Hz, 1H), 2.17 (t, *J* 10.5 Hz, 1H), 2.06 (s, 3H), 2.02 (2s, 6H), 1.57 (s, 3H), 1.48 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.1, 171.0, 170.9, 170.5, 170.3, 167.8, 167.6, 139.1, 139.1, 139.1, 139.1, 139.0, 139.0, 138.8, 138.7, 138.7, 138.6, 138.6, 138.6, 138.6 (2C), 138.5, 138.5 (2C), 138.5, 138.5, 138.4, 138.3, 138.3, 138.3, 138.2 (2C), 138.2, 138.2, 138.0, 137.7, 136.2, 135.4, 135.3, 133.4, 133.0, 129.2, 129.0, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 128.0, 128.0, 127.8, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5, 127.4, 127.4, 127.4, 127.4, 127.3, 127.3, 127.3, 127.1, 126.9, 126.8, 126.7, 126.4, 126.3, 126.2, 126.0, 125.9, 125.9, 125.4, 104.4 ($J_{C,H}$ 156 Hz), 103.1 ($J_{C,H}$ 152 Hz), 103.0 ($J_{C,H}$ 158 Hz), 102.5 (2C, $J_{C,H}$ 160 Hz, $J_{C,H}$ 159 Hz), 101.3 ($J_{C,H}$ 170 Hz), 100.6 ($J_{C,H}$ 171 Hz), 100.2 ($J_{C,H}$ 171 Hz), 100.1 ($J_{C,H}$ 171 Hz), 99.9 ($J_{C,H}$ 170 Hz), 99.8 (2C, $J_{C,H}$ 170 Hz, $J_{C,H}$ 170 Hz), 98.3 ($J_{C,H}$ 170 Hz),, 83.9, 83.5, 83.4, 83.3, 83.1, 81.6, 81.4, 81.3, 81.2, 81.2, 81.0, 80.5, 80.2, 80.0, 79.4, 79.2, 78.8, 78.7, 78.6, 78.5, 78.3 (2C), 78.2, 78.1, 78.0, 77.9, 77.6, 77.1, 76.1, 75.5 (2C), 75.4, 75.4, 75.3, 75.2, 75.1 (2C),

75.0, 75.0, 74.9, 74.8 (3C), 74.7 (2C), 74.6 (2C), 74.6 (2C), 74.5 (2C), 74.3, 74.3, 74.1, 74.1, 73.9, 73.6 (2C), 73.2, 73.2, 73.0, 72.9, 72.7, 72.6, 72.6, 72.4, 72.4, 72.0, 71.7, 71.5, 70.3, 70.3, 70.2, 69.6, 69.5, 69.5 (2C), 69.3, 67.1, 67.0, 66.4, 63.8, 63.6, 63.5, 63.3, 63.1, 63.0 (3C), 50.5, 21.2, 21.2, 20.9, 20.6, 20.5. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{315}H_{329}N_3O_{70}Na$, 5296.2175; found, 5296.2114.

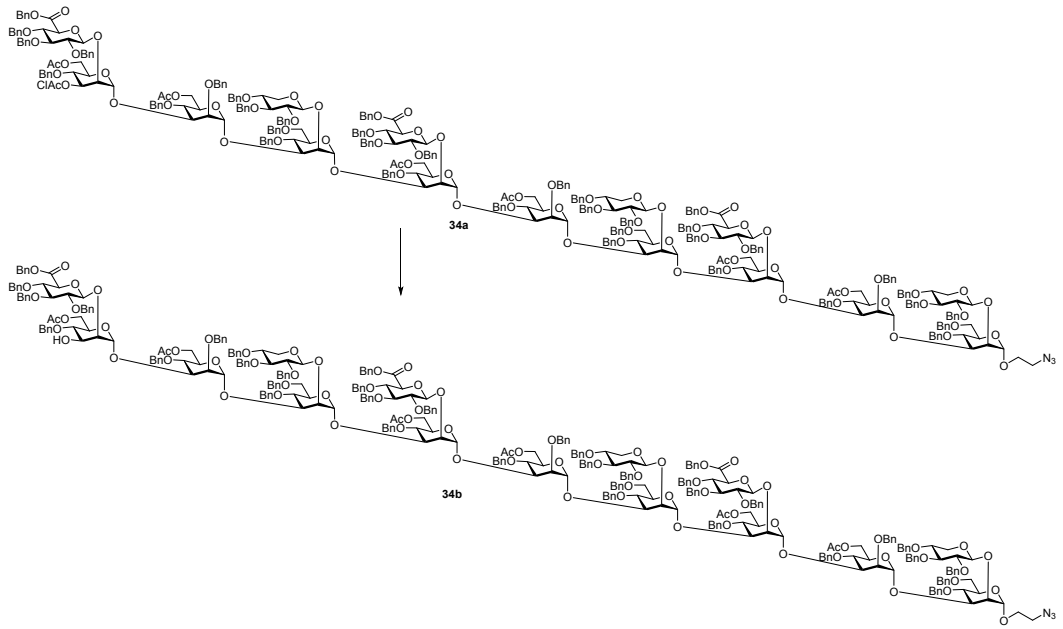


Scheme 19. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 3 h, 82% (α-only).

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (34a)

A mixture of thioglycoside donor **16** (32 mg, 15.5 μmol), acceptor **31b** (44 mg, 10.4 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (4 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (12.0 mg, 46.5 μmol) was added. The

cooling bath was removed and stirring was continued at 20 °C for 3 h. The reaction was and quenched with Et_3N (60 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→70:30) gave **34a** (52 mg, 82%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.25; $[\alpha]_D^{20}$ −27.8 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53-6.71 (m, 180H), 5.53 (s, 1H), 5.46 (s, 1H), 5.30 (s, 5H), 5.26 (s, 1H), 5.21 (dd, *J* 3.1 Hz, 9.7 Hz,1H), 5.19-5.02 (m, 8H), 4.98-4.38 (m, 51H), 4.38-3.65 (m, 76H), 3.65-3.18 (m, 26H), 3.17-3.09 (m, 2H), 3.07-3.00 (m, 1H), 2.28-2.14 (m, 2H), 2.08 (s, 3H), 2.02 (s, 6H), 1.57 (s, 6H), 1.47 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.0 (2C), 170.9, 170.5, 170.3, 170.3, 168.9, 167.8 (2C), 166.9, 139.2, 139.1, 139.1, 139.1, 138.9, 138.7, 138.6, 138.6, 138.6, 138.5, 138.5, 138.5, 138.4, 138.4, 138.3, 138.3, 138.2, 138.2, 138.2, 138.2, 138.0, 138.0, 138.0, 137.7, 135.4, 135.3, 134.9, 129.0, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 127.1, 126.9, 126.7, 126.5, 126.1, 104.4 ($J_{C,H}$ 158 Hz), 103.3 ($J_{C,H}$ 161 Hz), 103.0 (2C, $J_{C,H}$ 162 Hz), 102.5 (2C, $J_{C,H}$ 160 Hz), 100.7 (2C, $J_{C,H}$ 171 Hz), 100.2 ($J_{C,H}$ 171 Hz), 100.2 (2C, $J_{C,H}$ 171 Hz, 172 Hz), 99.9 (3C, $J_{C,H}$ 171 Hz, 171 Hz, 171 Hz), 98.3 ($J_{C,H}$ 170 Hz), 83.9, 83.5, 83.4, 83.2, 83.1 (2C), 81.6, 81.4, 81.3, 81.2 (2C), 81.1, 80.9, 80.7, 80.5, 80.3 (2C), 79.4 (2C), 79.3, 79.2, 78.8, 78.7, 78.6, 78.4 (2C), 78.3 (2C), 78.0, 78.0, 77.9, 77.8, 77.6, 77.2, 75.7, 75.6, 75.5 (2C), 75.4, 75.3 (3C), 75.3, 75.2, 75.1 (4C), 75.0 (2C), 74.9, 74.8 (2C), 74.8, 74.7 (3C), 74.7, 74.6 (2C), 74.5 (3C), 74.4, 74.3, 74.2, 74.2, 74.1, 74.1, 73.9 (2C), 73.6 (2C), 73.2, 73.2, 73.0, 72.9, 72.8, 72.7, 72.6, 72.4, 72.2, 71.7, 71.6, 71.5, 70.3, 70.2, 69.8, 69.7, 69.6, 69.5 (2C), 69.3, 67.8, 67.1, 67.0, 66.4, 63.8, 63.6, 63.3, 63.2, 63.1, 63.1, 63.0 (2C), 62.8, 50.5, 41.1, 21.1 (2C), 20.9, 20.6 (2C), 20.5. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{355}H_{372}N_3O_{83}NaCl$, 6062.4567; found, 6062.4761



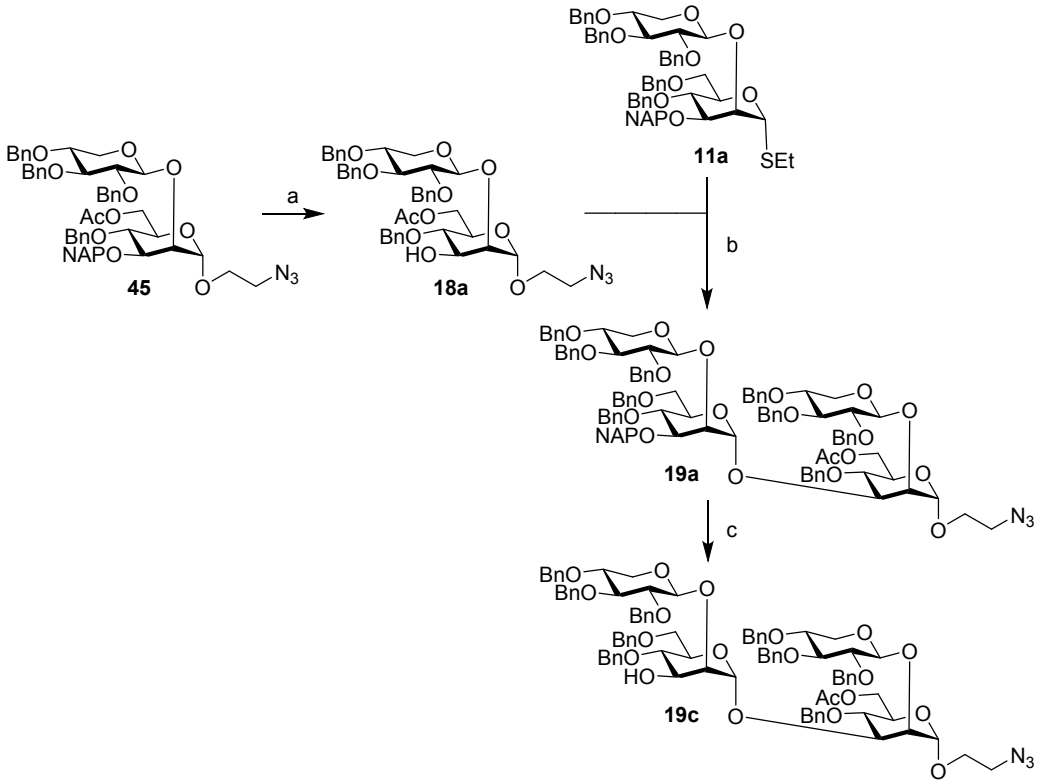
Scheme 20. Reagents and conditions: (a) thiourea, $NaHCO_3$, TBAI, dry. THF, 70 ºC, 16 h, 89%.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-6-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranoside (34b)

Compound **34a** (51 mg, 8.4 μmol) was dissolved in THF (0.3 mL). Thiourea (2 mg, 26.3 μmol), $NaHCO_3$ (2.3 mg, 27.3 μmol), and *n*-Bu_4NI (0.6 mg, 1.6 μmol) were added, and the suspension was heated at 65 °C. After 16 h, the reaction mixture was cooled to ambient temperature and diluted with DCM. The solids were removed by filtration, and the filtrate was concentrated *in vacuo*. Purification by flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→80:20) gave **34b** (45 mg, 89%) as a colourless syrup; R_f (toluene-EtOAc, 8:2) 0.47; $[\alpha]_D^{20}$ −17.9 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43-6.83 (m, 180H), 5.54 (s, 1H), 5.44 (s, 1H), 5.33-5.25 (m, 5H), 5.20-5.03 (m, 8H), 4.99-4.92 (m, 2H), 4.89-4.35 (m, 50H), 4.33-3.61 (m,

75H), 3.60-3.23 (m, 24H), 3.15 (t, *J* 9.0 Hz, 1H), 3.11 (t, *J* 9.0 Hz, 1H), 3.08-3.02 (m, 1H), 2.94 (d, *J* 9.7 Hz, 1H), 2.25 (t, *J* 10.6 Hz, 1H), 2.18 (t, *J* 10.1 Hz, 1H), 2.09 (s, 3H), 2.03 (s, 6H), 1.61 (s, 3H), 1.57 (s, 3H), 1.47 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.0 (2C), 170.9, 170.5, 170.5, 170.3, 168.1, 167.8, 167.8, 139.1 (2C), 139.1, 139.1, 139.0, 138.8, 138.7 (2C), 138.6, 138.6, 138.6 (2C), 138.5 (3C), 138.5 (2C), 138.5, 138.4, 138.4 (2C), 138.3, 138.3, 138.2, 138.2 (4C), 138.2, 138.0, 137.9, 137.8, 137.7, 135.3, 135.3, 135.0, 129.0, 128.9, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 127.1, 126.9, 126.9, 126.7, 126.4, 126.1, 104.4, 103.2, 103.0, 102.9, 102.5 (2C), 100.6, 100.6, 100.5, 100.2, 100.2, 99.9, 99.9 (2C), 98.3, 83.9, 83.5, 83.4, 83.2, 83.1, 83.0, 81.6, 81.4, 81.3, 81.3, 81.2, 80.9, 80.5 (2C), 80.3, 79.4 (2C), 79.3, 79.2, 79.0, 78.8, 78.7, 78.6, 78.4, 78.4, 78.3 (2C), 78.1, 78.0, 77.9, 77.3, 77.2, 75.7, 75.6, 75.5 (3C), 75.4 (3C), 75.3, 75.3 (2C), 75.1 (3C), 75.0, 74.9 (2C), 74.8 (3C), 74.8, 74.7 (3C), 74.7, 74.6 (4C), 74.5 (4C), 74.3, 74.2, 74.2, 74.1 (2C), 73.9 (2C), 73.6, 73.2, 73.2, 73.0, 72.9, 72.8, 72.8, 72.6, 72.4, 71.7 (2C), 71.5, 70.9, 70.3, 70.2, 69.8, 69.7, 69.6, 69.5, 69.5 (2C), 69.3, 67.6, 67.1, 67.0, 66.4, 63.8, 63.6, 63.3, 63.2, 63.1 (2C), 63.0, 50.5, 21.2, 21.1, 20.9, 20.7, 20.6, 20.5. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{353}H_{370}N_3O_{82}Na$, 5985.4773; found, 5985.4893.

Synthesis of Large Spacer-Equipped Saccharides of Serotype A



Scheme 21. Reagents and conditions: (a) DDQ, DCM/H_2O (10:1), 20 °C, 2 h, from 68 to 73%; (b) DMTST, Et_2O, 4 Å MS , 0 °C→20 °C, 4 h, 89%; (c) DDQ, DCM/H_2O (10:1), 20 °C, 2 h, from 64 to 80%.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl–α-D-mannopyranoside (18a)

For method see general procedure for 2-Naphthylmethyl removal.

R_f (toluene-EtOAc, 6:1) = 0.26; $[\alpha]_D^{20}$ +42.0 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37-7.24 (m, 20H), 4.99 (d, *J* 11.1 Hz, 1H), 4.92 (d, *J* 10.5 Hz, 1H), 4.89-4.87 (m, 2H), 4.86 (d, *J* 1.3 Hz, 1H), 4.73 (d, *J* 11.7 Hz, 1H), 4.70 (d, *J* 10.4 Hz, 1H), 4.65-4.61 (m, 2H), 4.37 (dd, *J* 2.1 Hz, *J* 11.9 Hz, 1H), 4.34 (d, *J* 7.7 Hz, 1H), 4.27 (dd, *J* 4.8 Hz, *J* 11.9 Hz, 1H), 4.03 (td, *J* 3.3 Hz, *J* 9.2 Hz, 1H), 3.99-3.94 (m, 2H), 3.84-3.78 (m, 2H), 3.66-3.50 (m, 4H), 3.42-3.36 (m, 2H), 3.32 (ddd, *J* 3.6 Hz, *J* 6.0 Hz, *J* 13.2 Hz, 1H), 3.23 (dd, *J* 10.5 Hz, *J* 11.5 Hz, 1H), 3.17 (d, *J* 9.4 Hz, 1H), 1.87 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 138.7, 138.4, 138.2, 138.1, 128.6, 128.6, 128.6, 128.5, 128.5, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 104.5, 98.5, 83.7, 81.4, 80.6, 77.5, 76.2, 75.8, 75.2, 75.0, 73.6, 70.9, 69.9, 66.6, 64.3, 63.5, 50.5, 20.8. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{43}H_{49}N_3O_{11}Na$, 806.3265; found, 806.3230.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylo-pyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (19a)

For method see general procedure for DMTST Mediated Glycosylation.

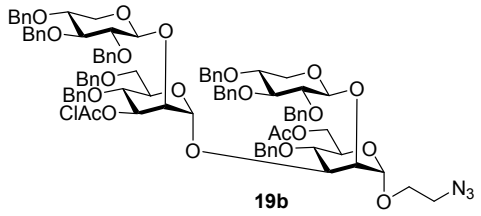
R_f (toluene-EtOAc, 6:1) = 0.48; $[\alpha]_D^{20}$ +3.5 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.66 (m, 4H), 7.51-7.46 (m, 1H), 7.43-7.11 (m, 47H), 5.19 (s, 1H), 5.06 (d, *J* 10.7 Hz, 1H), 5.01 (d, *J* 11.0 Hz, 1H), 4.97 (d, *J* 10.1 Hz, 1H), 4.86-4.75 (m, 7H), 4.69 (d, *J* 11.9 Hz, 1H), 4.64 (d, *J* 10.1 Hz, 1H), 4.59-4.53 (m, 3H), 4.49 (d, *J* 10.7 Hz, 1H), 4.46-4.38 (m, 3H), 4.34-4.20 (m, 6H), 4.14-4.07 (m, 3H), 3.98-3.91 (m, 4H), 3.83-3.68 (m, 6H), 3.58-3.52 (m, 1H), 3.48-3.26 (m, 7H), 3.19 (ddd, *J* 3.9 Hz, *J* 6.2 Hz, *J* 13.1 Hz, 1H), 3.09-3.03 (m, 1H), 2.77 (t, *J* 10.8 Hz, 1H), 1.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.6, 139.3, 139.0, 138.9, 138.9, 138.7, 138.6, 138.4, 138.2, 138.1, 136.0, 133.4, 133.1, 128.9, 128.7, 128.7, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.5, 127.5, 127.4, 127.2, 126.9, 126.7, 126.0, 125.9, 104.3 ($J_{C,H}$ 160 Hz), 103.7 ($J_{C,H}$ 155 Hz), 100.3 ($J_{C,H}$ 170 Hz), 98.4 ($J_{C,H}$ 170 Hz), 83.9, 83.5, 81.7, 81.0, 78.6 (3C), 77.7 (2C), 75.9, 75.7, 75.4, 75.2, 75.1, 75.0, 74.8, 74.5, 73.5, 73.2, 72.6, 72.2, 70.4, 70.0, 66.6, 64.0, 63.5, 63.2, 50.3, 20.7. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{100}H_{105}N_3O_{20}Na$, 1690.7189; found, 1690.7153.

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylo-pyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (19c)

For method see general procedure for 2-Naphthylmethyl removal.

R_f (toluene-EtOAc, 6:1) = 0.25; $[\alpha]_D^{20}$ +13.6 (*c* 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.12 (m, 45H), 5.19 (s, 1H), 4.99-4.96 (m, 2H), 4.94 (d, *J* 10.9 Hz, 1H), 4.88-4.79 (m, 6H), 4.69 (d, *J* 11.8 Hz, 1H), 4.66-4.59 (m, 5H), 4.51 (s, 2H), 4.36-4.24 (m, 6H), 4.13-4.05 (m, 3H), 3.99 (dd, *J* 5.2 Hz, *J* 11.7 Hz, 1H), 3.90 (t, *J* 9.4 Hz, 1H), 3.85-3.68 (m, 7H), 3.60 (t, *J* 9.6 Hz, 1H), 3.56-3.35 (m, 6H), 3.30-3.20 (m, 3H), 3.10-3.01 (m, 2H), 2.85 (t, *J* 11.0 Hz, 1H), 1.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.7, 139.3, 138.9, 138.8 (2C), 138.6, 138.4, 138.3, 138.3, 138.2, 128.8, 128.8, 128.7, 128.6, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 126.9, 104.5,

104.2, 101.0, 98.5, 83.9, 83.3, 81.6, 80.9, 80.8, 79.0, 77.9 (2C), 77.4, 77.2, 75.6, 75.6, 75.2, 74.8, 74.8, 74.7, 74.5, 73.5, 73.5, 72.8, 72.0, 70.90, 70.5, 69.9, 66.7, 64.1, 63.6, 63.3, 50.4, 20.8. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{89}H_{97}N_3O_{20}Na$, 1550.6563; found, 1550.6541.

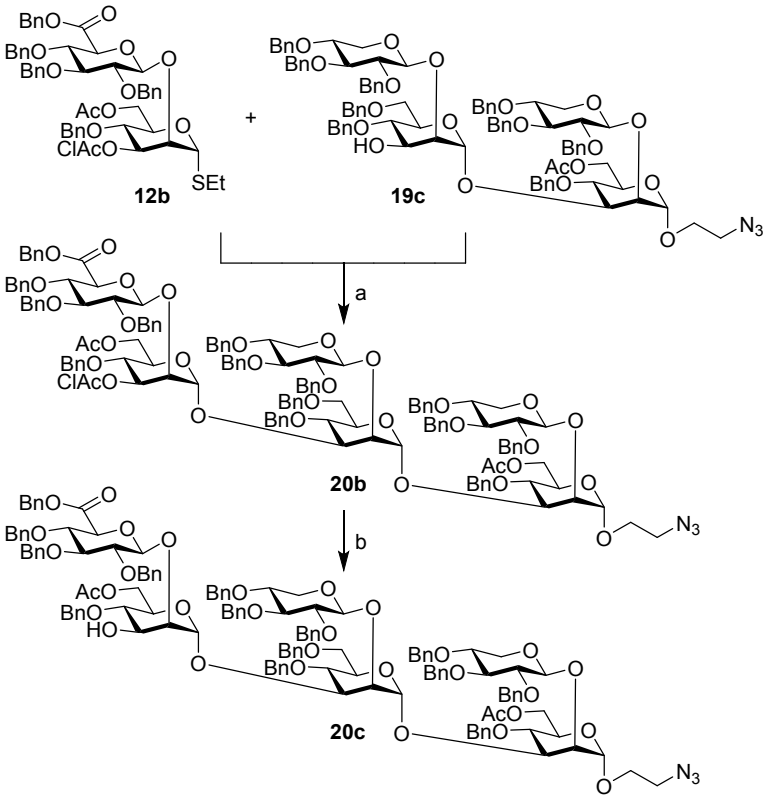


19b

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-3-*O*-chloroacetyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylo-pyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (19b)

A mixture of thioglycoside donor **11b** (85 mg, 96 μmol), acceptor **18a** (51 mg, 64 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (6 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C, freshly prepared DMTST (50 mg, 192 μmol) was added, and the reaction mixture was stirred at 0 °C for 60 min. The progress of the reaction was monitored by TLC (toluene-EtOAc, 6:1). The cooling bath was removed, an additional amount of DMTST was added (50 mg, 192 μmol), and stirring was continued at 20 °C for 2 h. The reaction was quenched with Et_3N (135 μL, 960 μmol) at 0 °C, the solids were removed by filtration, and the filtrate was concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 70 mL, 2.3 cm, toluene→toluene-EtOAc, 96:4→93:7→90:10 →87:13→84:16→80:20) gave the *title compound* **19b** (98 mg, 95%) as a colourless foam. $\mathbf{R}_f$ (toluene-EtOAc, 9:1) = 0.24; $\mathbf{R}_f$ (toluene-EtOAc, 6:1) = 0.47; $[\alpha]_D^{20}$ −10.9 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.15 (m, 45H, H_{ar}), 5.34 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 10.0 Hz), 5.17 (d ≈ s, 1H), 4.98 (d, 1H), 4.97 (d, 1H), 4.86-4.76 (m, 6H), 4.72-4.53 (m, 7H), 4.50-4.30 (m, 7H), 4.25 (dd, 1H, $J_{5,6b}$ = 4.0 Hz, $J_{6a,6b}$ = 12.0 Hz), 4.15 (dd, 1H, *J* = 1.0 Hz, *J* = 3.0 Hz), 4.10 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz), 4.06-4.02 (m, 2H), 4.00-3.90 (m, 4H), 3.84-3.71 (m, 5H), 3.65 (dd, 1H, $J_{4,5a}$ = 5.5 Hz, $J_{5a,5b}$ = 11.5 Hz), 3.63-3.58 (m, 1H), 3.51-3.43 (m, 4H), 3.36-3.32 (m, 1H), 3.29-3.23 (m, 3H), 3.07 (dd ≈ t, 1H, *J* = 10.8 Hz), 2.71 (dd ≈ t, 1H, *J* = 11.3 Hz1.82 (s, 3H, C(=O)CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.6 (*C*(=O)CH_3), 166.6 (*C*(=O)CH_2Cl), 138.9, 138.8, 138.6 (2C), 138.4, 138.3 (2C), 138.2, 138.0 ($C_{ar,quart}$), 128.6, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.4, 127.3, 126.9 (C_{ar}), 104.0, ($J_{C,H}$ 160 Hz), 103.7 ($J_{C,H}$ = 160 Hz), 100.4 ($J_{C,H}$ = 175 Hz), 98.2 ($J_{C,H}$ = 175 Hz), 83.6, 83.2, 81.5, 80.8, 77.9, 77.7, 77.5, 75.8, 75.4, 75.3, 75.14, 75.11, 74.8,

74.6, 74.2 , 73.5, 73.4, 73.2, 72.7, 71.8, 70.4, 69.2, 66.6 ($OCH_2CH_2N_3$), 63.9, 63.3, 63.1, 50.3 ($OCH_2CH_2N_3$), 41.1 ($C(=O)CH_2Cl$), 20.6 ($C(=O)CH_3$); **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{91}H_{98}N_3O_{21}NaCl$, 1626.6279; found, 1626.6224; **Anal.** Calcd for $C_{91}H_{98}ClN_3O_{21}$: C, 68.09; H, 6.15; Cl, 2.21; N, 2.62. Found: C, 68.05; H, 5.85; Cl, 2.38; N, 2.62 %.



Scheme 22. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 6 h, 74% (α-only); (b) thiourea, TBAI, dry. THF, 65 ºC, 16 h, 91%.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (20b)

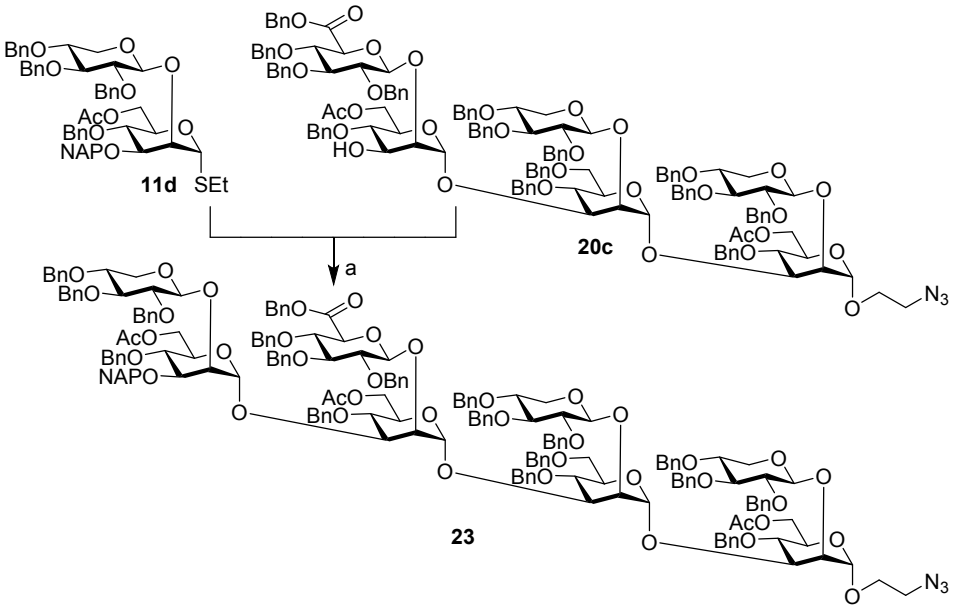
A mixture of thioglycoside donor **12b** (302 mg, 0.31 mmol), acceptor **19c** (316 mg, 0.20 mmol) and crushed molecular sieves (4 Å) in dry Et_2O (17 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (161.5 mg, 0.62 mmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 6 h. The reaction was and quenched with Et_3N (1.1 mL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1,

40 gram column, toluene-EtOAc, 98:2→80:20) gave **20b** (375 mg, 74%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.41; $[\alpha]_D^{20}$ −17.4 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44-7.01 (m, 70H), 5.37 (dd, *J* 2.2 Hz, *J* 9.8 Hz, 1H), 5.21-5.11 (m, 4H), 5.06-5.00 (m, 3H), 4.92-4.73 (m, 8H), 4.72-4.68 (m, 2H), 4.67-4.61 (m, 3H), 4.60-4.55 (m, 3H), 4.52-4.47 (m, 2H), 4.46-4.27 (m, 10H), 4.27-4.20 (m, 3H), 4.17-4.11 (m, 4H), 4.09-3.89 (m, 8H), 3.87-3.83 (m, 1H), 3.79-3.71 (m, 4H), 3.68-3.62 (m, 2H), 3.53-3.30 (m, 10H), 3.24-3.16 (m, 2H), 3.07 (t, *J* 10.7 Hz, 1H), 2.67 (t, *J* 10.7 Hz, 1H), 1.85 (s, 3H), 1.69 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.7, 170.6, 168.8, 166.9, 139.2 (2C), 139.0, 138.8, 138.5 (2C), 138.4, 138.4, 138.3, 138.2, 138.1, 138.0, 138.0, 134.9, 129.1, 128.9, 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.2, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5, 126.8, 126.2, 104.5 ($J_{C,H}$ 165 Hz), 103.1 ($J_{C,H}$ 160 Hz), 102.8 ($J_{C,H}$ 160 Hz), 100.9 ($J_{C,H}$ 175 Hz), 100.2 ($J_{C,H}$ 175 Hz), 98.4 ($J_{C,H}$ 175 Hz), 83.9, 83.3, 83.1, 81.5, 81.4, 81.1, 79.6, 79.4, 79.0, 78.4, 78.4, 77.9, 77.4, 75.7, 75.5 (2C), 75.3, 75.3, 75.1, 75.1, 75.0, 74.9, 74.8, 74.7 (2C), 74.3, 74.0, 73.9, 73.6, 73.1, 72.7, 72.6, 71.9, 70.5, 69.7, 69.4, 67.7, 66.7, 63.6, 63.2, 63.2, 62.9, 50.3, 41.2, 20.8, 20.7. **HRMS (ESI):** $[M+Na]^+$ *m/z* Calcd for $C_{140}H_{148}N_3O_{33}ClNa$, 2456.9581; found, 2456.9690.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (20c)

Compound **20b** (375 mg, 0.15 mmol) was dissolved in THF (2 mL). Thiourea (35.6 mg, 0.47 mmol), $NaHCO_3$ (43.2 mg, 0.51 mmol), and *n*-Bu_4NI (11.5 mg, 31.1 μmol) were added, and the suspension was heated at 65 °C. After 16 h, the reaction mixture was cooled to ambient temperature and diluted with CH_2Cl_2. The solids were removed by filtration, and the filtrate was concentrated *in vacuo*. Purification by flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→70:30) gave **20c** (330 mg, 91%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.26; $[\alpha]_D^{20}$ −5.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.01 (m, 70H), 5.25 (s, 1H), 5.18 (s, 1H), 5.12 (q, *J* 12.2 Hz, 2H), 5.06-4.99 (m, 3H), 4.97 (d, *J* 10.8 Hz, 1H), 4.91-4.69 (m, 9H), 4.68-4.55 (m, 7H), 4.50 (dd, *J* 4.0 Hz, *J* 9.9 Hz, 1H), 4.44 (s, 2H), 4.42-4.11 (m, 11H), 4.17-4.10 (m, 4H), 4.02-3.90 (m, 5H), 3.87-3.80 (m, 3H), 3.77-3.64 (m, 6H), 3.58-3.22 (m, 12H), 3.11-3.06 (m, 1H), 2.84 (d, *J* 9.6 Hz, 1H), 2.66 (t, *J* 10.8 Hz, 1H), 1.84 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 170.7, 168.0, 139.0, 139.0, 138.9 (2C), 138.8, 138.5, 138.4, 138.4, 138.3, 138.2, 138.1, 138.0, 138.0, 135.0, 129.1, 129.0, 128.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5,

128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 126.8, 126.0, 125.4, 104.4, 103.4, 103.0, 101.1, 100.2, 98.3, 83.9, 83.3, 83.0, 81.5, 81.2, 80.5, 80.1, 79.5, 78.9 (2C), 78.4, 78.0, 77.8, 77.5, 76.0, 75.5 (2C), 75.5, 75.4, 75.3, 74.9, 74.8, 74.7, 74.6, 74.5, 74.1 (2C), 73.9, 73.5, 73.1, 72.6, 71.9, 70.8, 70.5, 69.7, 69.4, 67.5, 66.7, 63.6, 63.2, 63.2 (2C), 50.3, 20.8, 20.7. HRMS (ESI): $[M+Na]^+$ *m/z* Calcd for $C_{138}H_{147}N_3O_{32}Na$, 2380.9865; found, 2380.9897.

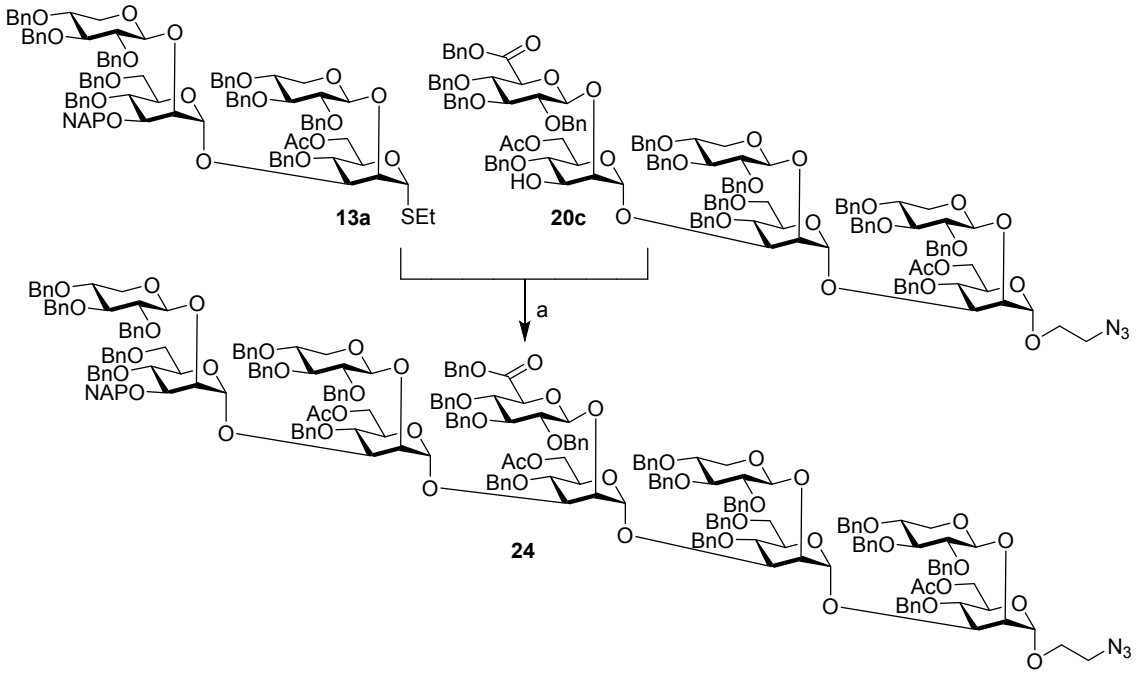


Scheme 23. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 2 h 30 min, 89% (α-only).

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (23)

A mixture of thioglycoside donor **11d** (27 mg, 30.0 μmol), acceptor **20c** (47 mg, 19.9 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (4 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (16.0 mg, 62.0 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 2 h. The reaction was and quenched with Et_3N (60 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→80:20) gave **23** (57 mg, 89%) as a colourless syrup;

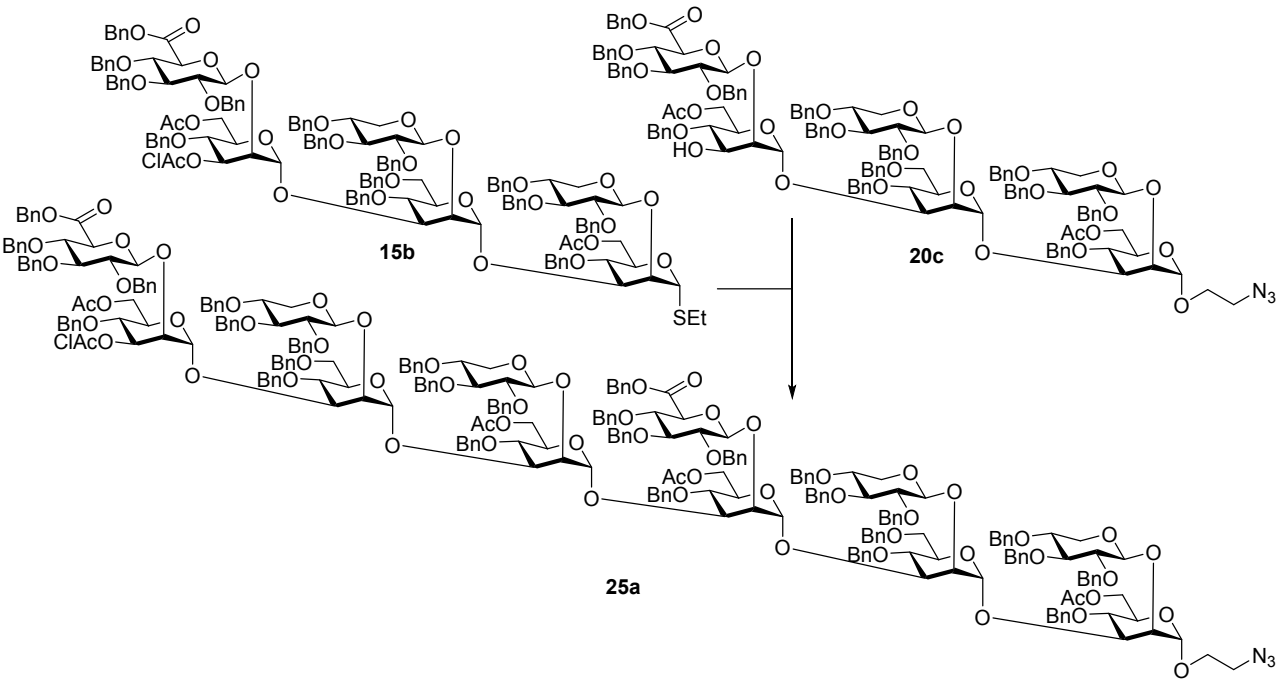
R_f (toluene-EtOAc, 9:1) 0.46; $[\alpha]_D^{20}$ −22.0 (*c* 1.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.82-7.78 (m, 1H), 7.74 (m, 2H), 7.58 (d, *J* 8.3 Hz, 1H), 7.48-6.94 (m, 93H), 5.28 (s, 2H), 5.24-5.15 (m, 2H), 5.11 (d, *J* 10.4, 1H), 5.03 (m, 3H), 4.96 (m, 2H), 4.89-4.76 (m, 7H), 4.75-4.70 (m, 2H), 4.69-4.48 (m, 15H), 4.44-3.87 (m, 34H), 3.87-3.81 (m, 1H), 3.79-3.66 (m, 5H), 3.63 (dd, *J* 5.1, 10.5 Hz, 1H), 3.55-3.37 (m, 10H), 3.37-3.29 (m, 3H), 3.23 (ddd, *J* 3.9, 6.1, 13.1 Hz, 1H), 3.15 (t, *J* 9.0 Hz, 1H), 3.05 (t, *J* 10.7Hz, 1H), 2.70-2.53 (m, 2H), 1.85 (s, 3H), 1.60 (s, 3H), 1.55 (s, 3H); **^{13}C NMR** NMR (125 MHz, $CDCl_3$) δ 170.7, 170.7, 170.5, 168.0, 139.2, 139.0, 139.0, 138.9, 138.8, 138.7, 138.7, 138.6, 138.5, 138.5 (2C), 138.5, 138.4, 138.3, 138.2, 138.1, 138.1, 136.3, 135.5, 133.4, 133.1, 129.1, 129.0, 128.8, 128.8, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 127.4, 127.4, 127.1, 126.7, 126.4, 126.3, 125.9, 125.8, 104.5 ($J_{C,H}$ 156 Hz), 103.4 ($J_{C,H}$ 162 Hz), 103.2 ($J_{C,H}$ 161 Hz), 102.5 ($J_{C,H}$ 160 Hz), 101.0 ($J_{C,H}$ 170 Hz), 100.7 ($J_{C,H}$ 170 Hz), 100.4 ($J_{C,H}$ 170 Hz), 98.4 ($J_{C,H}$ 171 Hz), 83.9, 83.5, 83.5, 83.4, 81.9, 81.5, 81.4, 81.1, 79.9 (2C), 79.4, 79.0 (2C), 78.4, 78.3, 78.0, 77.4, 77.0, 75.6 (2C), 75.5, 75.4, 75.4, 75.3, 75.3, 75.3, 75.2, 74.9, 74.8, 74.8, 74.7, 74.6, 74.5, 74.3, 73.9, 73.8, 73.6, 73.2 (2C), 73.1, 72.9, 72.2, 71.8, 70.6, 70.5, 69.8, 69.7, 67.3, 66.7, 63.9, 63.6, 63.4, 63.4, 63.3, 63.2, 50.4, 20.8, 20.7, 20.7. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{190}H_{199}N_3O_{42}Na$, 3217.3426; found, 3217.3440.



Scheme 24. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 2 h, 89% (α-only).

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylo-pyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (24)

A mixture of thioglycoside donor **13a** (57.5 mg, 34.9 μmol), acceptor **20c** (49 mg, 20.7 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (5 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (16.3 mg, 46.5 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 2 h. The reaction was and quenched with Et_3N (60 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→80:20) gave **24** (73 mg, 89%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.54; $[\alpha]_D^{20}$ −28.5 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.69 (d, *J* 7.8 Hz, 1H), 7.64 (m, 2H), 7.50-6.88 (m, 118H), 5.37 (s, 1H), 5.32 (s, 1H), 5.23-5.18 (m, 3H), 5.13-5.07 (m, 2H), 5.06-4.94 (m, 4H), 4.87-4.48 (m, 30H), 4.43-3.62 (m, 51H), 3.61-3.17 (m, 20H), 3.06 (t, *J* 10.8 Hz, 1H), 2.85 (t, *J* 10.7 Hz, 1H), 2.65-2.53 (m, 2H), 1.85 (s, 3H), 1.57 (s, 3H), 1.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.7, 170.6 (2C), 167.9, 139.4, 139.3, 139.2, 139.1 (2C), 139.0, 138.9, 138.8, 138.7, 138.7, 138.5, 138.5, 138.5, 138.4, 138.4, 138.4, 138.4, 138.3, 138.2, 138.1, 138.0, 136.1, 135.4, 133.3, 133.0, 129.0, 129.0, 129.0, 128.9, 128.9, 128.8, 128.8, 128.8, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5, 127.4, 127.3, 127.3, 127.1, 126.9, 126.7, 126.7, 126.2, 126.0, 125.8, 104.4 ($J_{C,H}$ 158 Hz), 103.4 ($J_{C,H}$ 158 Hz), 103.4 ($J_{C,H}$ 162 Hz), 102.8 ($J_{C,H}$ 158 Hz), 102.5 ($J_{C,H}$ 161 Hz), 101.9 ($J_{C,H}$ 170 Hz), 101.2 ($J_{C,H}$ 170 Hz), 100.2 ($J_{C,H}$ 170 Hz), 99.8 ($J_{C,H}$ 173 Hz), 98.4 ($J_{C,H}$ 171 Hz), 83.9, 83.6, 83.5, 83.4, 81.7, 81.6, 81.5, 81.2, 80.8, 80.3, 80.1, 79.6, 79.4, 79.0, 78.4 (2C), 78.2, 78.1, 77.7, 77.5, 77.4, 77.0, 75.6, 75.5, 75.4 (2C), 75.4, 75.3, 75.2, 75.1, 75.1, 75.1, 74.8, 74.7, 74.7, 74.5, 74.5 (2C), 74.4, 74.2, 74.2, 73.8, 73.6, 73.3, 73.2, 73.1, 72.9, 72.6, 72.3, 72.2 (2C), 71.8, 70.5, 70.2, 69.9, 69.7, 69.1, 67.3, 66.7, 64.0, 63.7, 63.4, 63.3 (2C), 63.1, 63.1, 50.3, 20.8, 20.7, 20.6. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{236}H_{247}N_3O_{51}Na$, 3961.6724; found, 3961.6921.

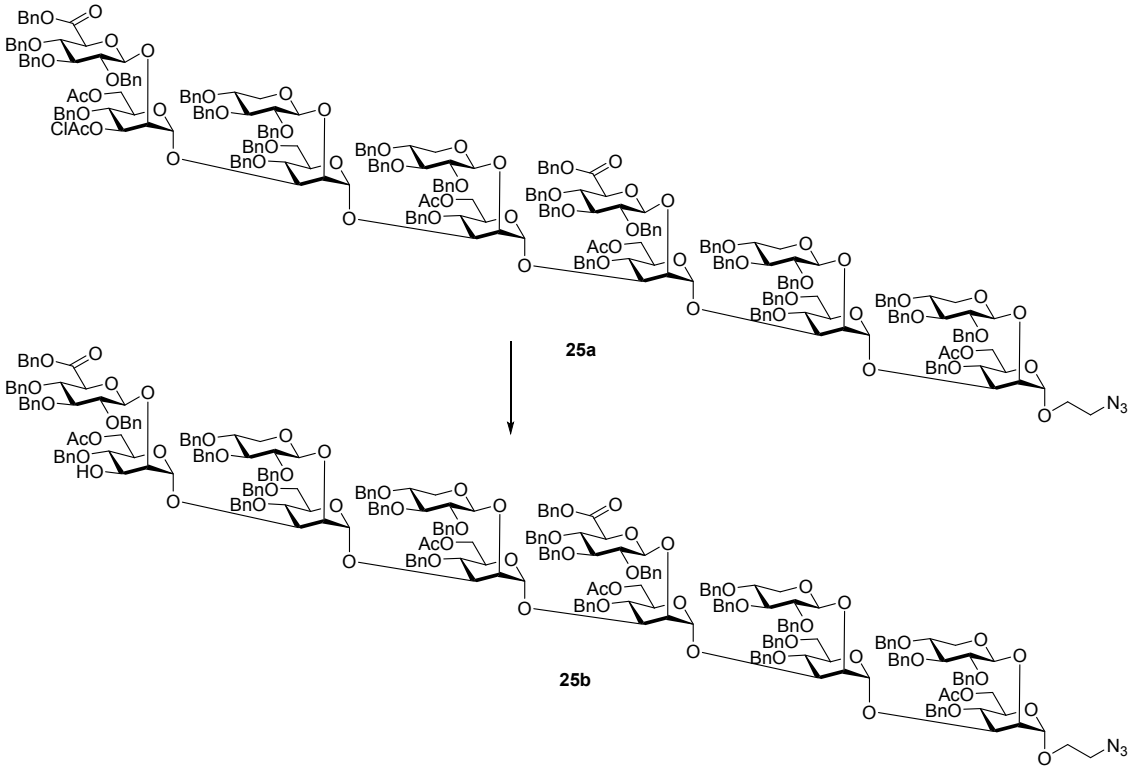


Scheme 25. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 3 h, 78% (α-only).

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (25a)

A mixture of thioglycoside donor **15b** (181 mg, 75.1 μmol), acceptor **20c** (118 mg, 50.0 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (12 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (58.0 mg, 224.0 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 3 h. The reaction was and quenched with Et_3N (200 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, tolene-acetone, 98:2→70:30) gave **25a** (183 mg, 78%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.36; $[\alpha]_D^{20}$ −34.6 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44-6.90 (m, 140H), 5.42 (s, 1H), 5.38 (dd, *J* 3.2 Hz, 9.8 Hz, 1H), 5.33 (s, 1H), 5.30 (s, 1H), 5.26-5.19 (m, 2H), 5.18-5.08 (m, 6H), 5.04 (d, *J* 10.0 Hz, 1H), 4.99-4.94 (m, 2H), 4.91-4.48 (m, 33H), 4.47-3.87

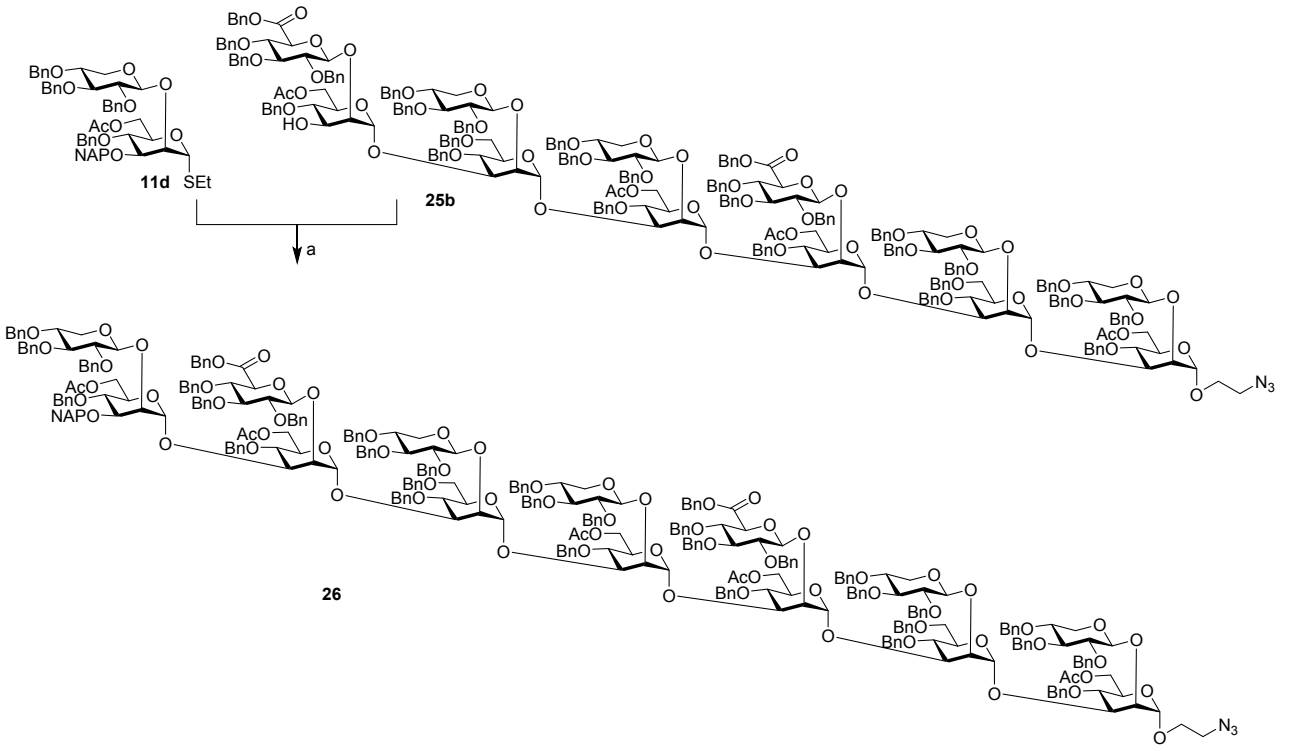
(m, 53H), 3.86-3.58 (m, 11H), 3.57-3.19 (m, 21H), 3.16 (t, *J* 9.1 Hz, 1H), 3.05 (t, *J* 10.8 Hz, 1H), 2.81 (t, *J* 10.6 Hz, 1H), 2.66-2.57 (m, 2H), 1.84 (s, 3H), 1.63 (s, 3H), 1.59 (s, 3H), 1.55 (s, 3H);**^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.7, 170.6, 170.5, 170.5, 168.8, 167.9, 166.9, 139.2, 139.2, 139.2 (2C), 139.1, 139.0, 138.9, 138.7, 138.7, 138.6, 138.5, 138.5, 138.5, 138.5, 138.5 (2C), 138.4, 138.3, 138.3, 138.3, 138.2, 138.2, 138.1, 138.1, 138.0, 138.0, 135.3, 134.9, 129.1, 129.1, 129.0, 128.9, 128.8, 128.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5, 127.4, 127.4, 127.3, 127.3, 126.8, 126.7, 126.3, 126.2, 104.4 ($J_{C,H}$ 160 Hz), 103.3 ($J_{C,H}$ 162 Hz), 103.2 ($J_{C,H}$ 160 Hz), 103.1 ($J_{C,H}$ 154 Hz), 102.5 ($J_{C,H}$ 155 Hz), 102.4 ($J_{C,H}$ 160 Hz), 101.5 ($J_{C,H}$ 169 Hz), 101.1 ($J_{C,H}$ 170 Hz), 100.5 ($J_{C,H}$ 170 Hz), 100.4 ($J_{C,H}$ 171 Hz), 100.2 ($J_{C,H}$ 171 Hz), 98.4 ($J_{C,H}$ 172 Hz), 83.9, 83.5, 83.4, 83.4, 83.4, 83.1, 81.7, 81.5, 81.5, 81.3, 81.3, 80.9, 80.1, 79.6, 79.5, 79.4, 79.4, 78.9, 78.4, 78.4, 78.3, 78.3 (2C), 78.2, 78.0, 78.0, 77.4, 76.5, 75.9, 75.6, 75.5, 75.4 (2C), 75.3, 75.3, 75.3 (2C), 75.2, 75.1, 75.1, 75.0, 74.9 (2C), 74.8 (4C), 74.7, 74.6, 74.6 (2C), 74.5, 74.4, 74.3, 74.3, 74.0 (2C), 73.8, 73.6, 73.3, 73.1, 72.8, 72.8, 72.7, 72.6, 71.8, 70.5, 70.4, 69.9, 69.6, 69.5, 68.8, 67.8, 67.3, 66.7, 63.6, 63.4, 63.3 (4C), 63.2, 62.9, 50.3, 41.2, 20.8, 20.7, 20.7, 20.6. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{276}H_{290}N_3O_{64}NaCl$, 4727.9116; found, 4727.8965.



Scheme 26. Reagents and conditions: (a) thiourea, $NaHCO_3$, TBAI, dry. THF, 65 ºC, 16 h, 88%.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (25b)

Compound **25a** (183 mg, 38.9 μmol) was dissolved in THF (2 mL). Thiourea (8.9 mg, 116 μmol), $NaHCO_3$ (11 mg, 131 μmol), and *n*-Bu_4NI (2.7 mg, 7.3 μmol) were added, and the suspension was heated at 65 °C. After 16 h, the reaction mixture was cooled to ambient temperature and diluted with DCM. The solids were removed by filtration, and the filtrate was concentrated *in vacuo*. Purification by flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→80:20) gave **25b** (158 mg, 88%) as a colourless syrup; R_f (toluene-EtOAc, 8:2) 0.26; $[\alpha]_D^{20}$ −28.2 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49-6.89 (m, 140H), 5.40 (s, 1H), 5.34 (s, 1H), 5.30 (s, 1H), 5.26-5.20 (m, 3H), 5.16-5.07 (m, 5H), 5.04 (d, *J* 10.0 Hz, 1H), 4.98 (m, 2H), 4.94-4.49 (m, 32H), 4.47-3.58 (m, 63H), 3.59-3.16 (m, 22H), 3.06 (t, *J* 10.8 Hz, 1H), 2.80 (m, 2H), 2.68-2.56 (m, 2H), 1.85 (s, 3H), 1.67 (s, 3H), 1.59 (s, 3H), 1.56 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.7, 170.6, 170.6, 170.5, 168.0, 167.9, 139.2, 139.2, 139.2 (2C), 139.0, 139.0, 139.0, 138.9, 138.7, 138.7, 138.5, 138.5, 138.5 (3C), 138.4, 138.4, 138.4, 138.3, 138.3 (2C), 138.1, 138.1, 138.0 (2C), 137.9, 135.3, 135.0, 129.0, 129.0, 129.0, 128.9, 128.8, 128.8, 128.7, 128.7, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5, 127.4, 127.4, 127.4, 127.4, 127.3, 127.3, 126.8, 126.7, 126.2, 126.0, 104.4, 103.3, 103.0, 103.0, 102.8, 102.5, 101.5, 101.1, 100.7, 100.4, 100.2, 98.3, 83.9, 83.5, 83.4, 83.4, 83.3, 83.0, 81.7, 81.5, 81.5, 81.2, 81.2, 80.3, 80.2, 80.0, 79.8, 79.5, 79.4, 78.9, 78.9, 78.4, 78.4 (2C), 78.3, 78.1, 78.0, 78.0, 77.4, 77.2, 75.9, 75.6, 75.5, 75.3, 75.3 (3C), 75.2, 75.2, 75.2 (2C), 75.1, 74.9, 74.8, 74.7, 74.6 (2C), 74.5 (3C), 74.3 (2C), 74.2, 74.2, 73.9, 73.8, 73.7, 73.6 (2C), 73.2, 73.0, 72.8 (2C), 72.5, 71.8, 71.7, 70.8, 70.5, 70.3, 69.8, 69.6, 69.3, 68.9, 67.5, 67.3, 66.7, 63.6, 63.4, 63.3 (4C), 63.2, 63.2, 50.3, 20.8, 20.7, 20.6. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{274}H_{289}N_3O_{63}Na$, 4651.9399; found, 4651.9854.

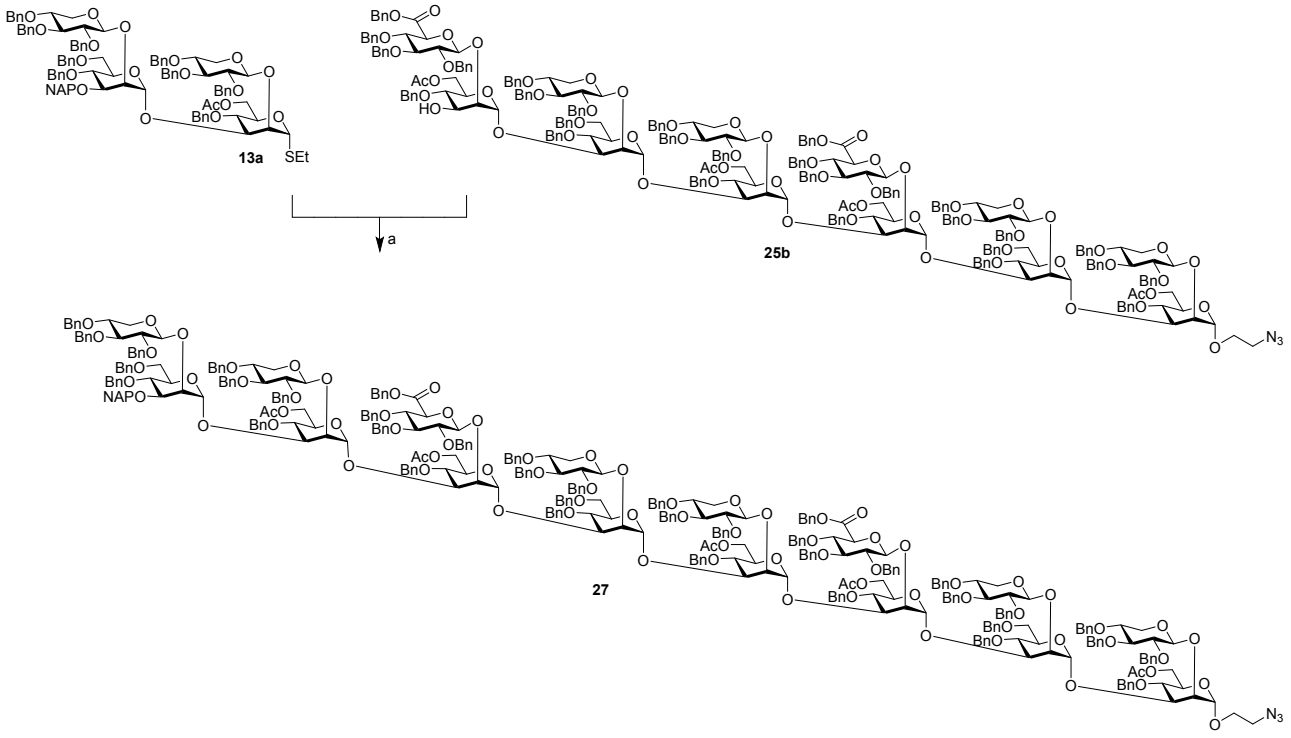


Scheme 27. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 1.5 h, 92% (α-only).

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-manno-pyranosyl-(1→3)-(benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (26)

A mixture of thioglycoside donor **11d** (11.8 mg, 13.1 μmol), acceptor **25b** (40.6 mg, 8.8 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (4 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (10.2 mg, 46.5 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 1.5 h. The reaction was and quenched with Et_3N (40 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40 gram column, toluene-EtOAc, 98:2→70:30) gave **26** (44.3 mg, 92%) as a colourless syrup;

R_f (toluene-EtOAc, 9:1) 0.47; $[\alpha]_D^{20}$ −33.1 (*c* 1.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.81-7.76 (m, 1H), 7.76-7.71 (m, 2H), 7.57 (d, *J* 8.4 Hz, 1H), 7.48-6.87 (m, 162H), 5.43 (s, 1H), 5.33 (s, 1H), 5.30-5.22 (m, 4H), 5.21-5.07 (m, 5H), 5.074.46 (m, 48H), 4.44-3.82 (m, 62H), 3.80-3.59 (m, 9H), 3.56-3.19 (m, 23H), 3.14 (t, *J* 9.0 Hz, 1H), 3.04 (t, *J* 10.7 Hz, 1H), 2.76 (t, *J* 10.5 Hz, 1H), 2.61 (m, 3H), 1.84 (s, 3H), 1.59 (s, 3H), 1.56 (s, 3H), 1.54 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.7, 170.7, 170.6, 170.5, 170.4, 168.0, 167.9, 139.4, 139.2, 139.2 (2C), 139.1, 139.0, 138.9 (2C), 138.8, 138.8, 138.7, 138.6, 138.6 (2C), 138.5, 138.5 (3C), 138.5, 138.4, 138.4, 138.3, 138.3, 138.3, 138.2, 138.2, 138.1 (2C), 138.0, 136.3, 135.5, 135.4, 133.4, 133.1, 129.2, 129.1, 129.0, 129.0, 128.9, 128.8, 128.8, 128.8, 128.7, 128.7, 128.7, 128.7, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 127.2, 127.1, 127.0, 126.8, 126.3, 125.9, 125.8, 125.4, 104.4 ($J_{C,H}$ 155 Hz), 103.4 ($J_{C,H}$ 155 Hz), 103.3 ($J_{C,H}$ 160 Hz), 103.2 ($J_{C,H}$ 159 Hz), 102.8 ($J_{C,H}$ 161 Hz), 102.6 (2C, $J_{C,H}$ 161 Hz, $J_{C,H}$ 158 Hz), 101.8 ($J_{C,H}$ 171 Hz), 101.1 ($J_{C,H}$ 170 Hz), 100.6 ($J_{C,H}$ 171 Hz), 100.5 (3C, $J_{C,H}$ 169 Hz, $J_{C,H}$ 172 Hz, $J_{C,H}$ 173 Hz), 98.4 ($J_{C,H}$ 170 Hz), 83.9, 83.6 (2C), 83.5 (3C), 83.4, 81.8, 81.7, 81.6, 81.5, 81.4, 81.3, 81.0, 80.2 (2C), 79.9, 79.6, 79.5, 79.4, 79.0, 78.9, 78.5, 78.5, 78.4 (3C), 78.3 (2C), 78.0, 77.4 (overlap with residual $CHCl_3$), 77.4, 77.2 (overlap with residual $CHCl_3$), 75.6 (2C), 75.6, 75.5, 75.4 (4C), 75.3 (2C), 75.2, 75.2, 75.1, 75.1, 74.8 (2C), 74.8 (2C), 74.7 (2C), 74.6, 74.5 (2C), 74.4, 74.3 (2C), 74.1, 73.9, 73.8 (3C), 73.7 (2C), 73.3 (2C), 73.2 (2C), 73.1 (2C), 72.8 (2C), 72.7 (2C), 72.1, 71.8, 71.7, 70.6, 70.5, 70.3, 69.9, 69.6 (2C), 69.0, 67.3, 67.3, 66.7, 63.9, 63.7, 63.5, 63.4 (2C), 63.3 (2C), 63.2, 50.4, 20.8, 20.7, 20.7, 20.6, 20.6. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{326}H_{341}N_3O_{73}Na$, 5488.2959; found, 5488.4702.

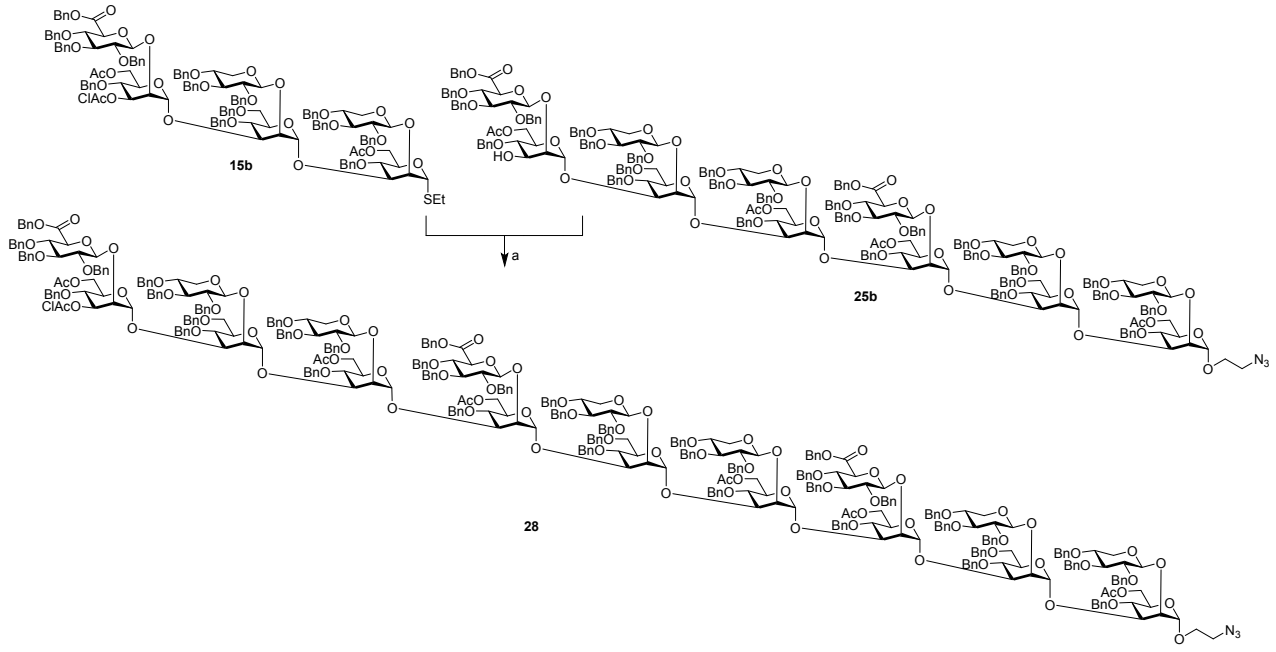


Scheme 28. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 1.5 h, 85% (α-only).

2-Azidoethyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)-4,6-di-*O*-benzyl-3-*O*-(2-naphthalenylmethyl)-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (27)

A mixture of thioglycoside donor **13a** (21.1 mg, 12.8 μmol), acceptor **25b** (39.9 mg, 8.6 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (4 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (10.0 mg, 38.7 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 1.5 h. The reaction was and quenched with Et_3N (40 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40

gram column, toluene-EtOAc, 98:2→70:30) gave **27** (45.6 mg, 85%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.51; $[\alpha]_D^{20}$ −23.7 (*c* 1.2, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.69 (d, *J* 7.9 Hz, 1H), 7.67-7.60 (m, 2H), 7.50-6.87 (m, 188H), 5.42 (s, 1H), 5.36 (s, 1H), 5.33 (s, 1H), 5.30 (s, 2H), 5.25 (d, *J* 10.1 Hz, 1H), 5.22-5.14 (m, 4H), 5.14-5.07 (m, 4H), 5.06-4.91 (m, 6H), 4.90-4.47 (m, 51H), 4.46-3.60 (m, 93H), 3.60-3.48 (m, 7H), 3.47-3.16 (m, 26H), 3.04 (t, *J* 10.7 Hz, 1H), 2.85 (t, *J* 10.7 Hz, 1H), 2.76 (t, *J* 10.3 Hz, 1H), 2.67-2.51 (m, 3H), 1.83 (s, 3H), 1.59 (s, 3H), 1.56 (s, 3H), 1.55 (s, 3H), 1.49 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.7, 170.6, 170.5 (2C), 170.4, 168.0, 167.9, 139.5, 139.4, 139.3, 139.3, 139.2 (2C), 139.1 (2C), 139.0, 139.0, 138.9, 138.8 (3C), 138.7, 138.5 (4C), 138.5 (3C), 138.4 (4C), 138.4, 138.3, 138.3 (2C), 138.3 (2C), 138.1 (2C), 138.0, 136.2, 135.4, 135.4, 133.3, 133.0, 129.2, 129.1, 129.0, 129.0, 128.9, 128.9, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.9, 126.8, 126.7, 126.3, 126.1, 126.0, 125.8, 104.4 ($J_{C,H}$ 161 Hz), 103.5 ($J_{C,H}$ 161 Hz), 103.3 ($J_{C,H}$ 159 Hz), 103.2 ($J_{C,H}$ 155 Hz), 103.0 ($J_{C,H}$ 160 Hz), 102.8 ($J_{C,H}$ 158 Hz), 102.6 (2C, $J_{C,H}$ 158 Hz, $J_{C,H}$ 156 Hz), 101.8 ($J_{C,H}$ 171 Hz), 101.7 ($J_{C,H}$ 171 Hz), 101.1 ($J_{C,H}$ 172 Hz), 100.7 ($J_{C,H}$ 170 Hz), 100.5 ($J_{C,H}$ 169 Hz), 100.4 ($J_{C,H}$ 169 Hz), 99.9 ($J_{C,H}$ 173 Hz), 98.4 ($J_{C,H}$ 172 Hz), 83.9, 83.6 (2C), 83.5, 83.5, 83.4 (3C), 81.8, 81.7, 81.5, 81.5, 81.3 (2C), 80.8, 80.4, 80.3, 80.2, 80.1, 79.9, 79.8, 79.4 (2C), 79.0, 78.6, 78.5, 78.4, 78.4, 78.3 (3C), 78.0, 77.7, 77.6, 77.6, 77.5, 77.2, 75.6 (2C), 75.5, 75.4 (3C), 75.4 (2C), 75.3, 75.3, 75.2 (2C), 75.1 (3C), 75.1 (2C), 74.8 (2C), 74.8, 74.7, 74.6 (2C), 74.5 (2C), 74.5, 74.4 (2C), 74.3 (3C), 74.3, 74.2 (2C), 74.0, 73.8, 73.8, 73.7 (2C), 73.4, 73.3, 73.3, 73.2, 73.1, 72.8 (2C), 72.7, 72.5, 72.3, 72.2, 71.8, 71.6, 70.5, 70.4, 70.2, 69.9, 69.6 (2C), 69.0 (2C), 67.3 (2C), 66.7, 64.0 (3C), 63.7, 63.4, 63.3 (3C), 63.2, 63.1, 50.4, 20.8, 20.7, 20.7, 20.6, 20.6. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{372}H_{389}N_3O_{82}Na$, 6232.6260; found, 6232.4678.



Scheme 29. Reagents and conditions: (a) DMTST, Et_2O, MS 4 Å, 0 °C→20 °C, 3 h, 82%.

2-Azidoethyl (benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate)-(1→2)-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-(1→3)-[benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranosyluronate-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-4,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (28)

A mixture of thioglycoside donor **15b** (32.1 mg, 13.3 μmol), acceptor **25b** (41.1 mg, 8,9 μmol) and crushed molecular sieves (4 Å) in dry Et_2O (4 mL) was stirred at 20 °C for 30 min. The reaction mixture was cooled to 0 °C and freshly prepared DMTST (10.3 mg, 39.9 μmol) was added. The cooling bath was removed and stirring was continued at 20 °C for 3 h. The reaction was and quenched with Et_3N (60 μL). The solution was filtered through a pad of Celite®, and the filtrate was concentrated *in vacuo*. Purification by automated flash column chromatography (RevelerisX1, 40

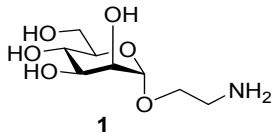
gram column, toluene-EtOAc, 98:2→70:30) gave **28** (50.7 mg, 82%) as a colourless syrup; R_f (toluene-EtOAc, 9:1) 0.45; $[\alpha]_D^{20}$ −37.6 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54-6.67 (m, 210H), 5.43, 5.41 (2s, 2H), 5.37 (dd, *J* 3.1 Hz, 9.8 Hz, 1H), 5.34 -5.27 (m, 4H), 5.25 (d, *J* 10.1, 1H), 5.23-5.06 (m, 11H), 5.03 (d, *J* 10.0, 1H), 4.99-4.92 (m, 3H), 4.90-4.45 (m, 49H), 4.45-3.57 (m, 95H), 3.56-3.12 (m, 31H), 3.04 (t, *J* 10.7 Hz, 1H), 2.81 (t, *J* 10.5 Hz, 1H), 2.74 (t, *J* 10.6 Hz, 1H), 2.67-2.56 (m, 2H), 1.84 (s, 3H), 1.62 (s, 3H), 1.58 (2s, 6H), 1.55 (s, 3H), 1.49 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) 170.8, 170.6 (2C), 170.5 (2C), 170.4, 168.8, 168.0, 167.9, 166.9, 139.4, 139.3 (2C), 139.2 (2C), 139.2 (2C), 139.1, 139.0, 138.9 (2C), 138.8 (3C), 138.6, 138.6 (2C), 138.5 (3C), 138.5, 138.5 (3C), 138.4, 138.4, 138.4, 138.3 (3C), 138.3, 138.2 (2C), 138.2, 138.1 (2C), 138.1, 138.1, 138.0, 135.4 (2C), 135.0, 129.1, 129.0, 128.9, 128.9, 128.8, 128.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 127.2, 127.0, 126.8, 126.8, 126.3, 126.2, 126.2, 104.4 ($J_{C,H}$ 161 Hz), 103.3 ($J_{C,H}$ 161 Hz), 103.2 ($J_{C,H}$ 162 Hz), 103.2 ($J_{C,H}$ 158 Hz), 103.0 ($J_{C,H}$ 155 Hz), 102.9 ($J_{C,H}$ 158 Hz), 102.6 ($J_{C,H}$ 162 Hz), 102.6 ($J_{C,H}$ 162 Hz), 102.4 ($J_{C,H}$ 159 Hz), 101.7 ($J_{C,H}$ 171 Hz), 101.4 ($J_{C,H}$ 171 Hz), 101.1 ($J_{C,H}$ 171 Hz), 100.6 ($J_{C,H}$ 173 Hz), 100.6 (3C, $J_{C,H}$ 172 Hz, $J_{C,H}$ 172 Hz, $J_{C,H}$ 173 Hz), 100.2 ($J_{C,H}$ 172 Hz), 98.4 ($J_{C,H}$ 170 Hz), 83.9, 83.6, 83.6, 83.5, 83.4, 83.4 (3C), 83.1, 81.8, 81.6, 81.6, 81.5 (2C), 81.3, 81.3 (2C), 80.9, 80.3, 80.2 (2C), 79.9, 79.6, 79.5, 79.5, 79.4, 78.9, 78.5, 78.4 (2C), 78.4 (2C), 78.3, 78.3, 78.2, 78.2, 78.0, 78.0, 77.6, 77.4, 75.9, 75.6, 75.6, 75.5, 75.4, 75.4 (3C), 75.3 (2C), 75.2 (2C), 75.2 (2C), 75.1, 75.0, 75.0, 75.0, 74.9 (2C), 74.8 (4C), 74.8 (4C), 74.6 (3C), 74.5, 74.5, 74.4 (2C), 74.3 (2C), 74.3, 74.2, 74.1 (3C), 73.8 (2C), 73.7, 73.7 (2C), 73.4, 73.3, 73.1, 72.8 (2C), 72.8, 72.7 (2C), 72.6, 71.8, 71.8, 71.6, 70.5, 70.4, 70.4, 69.9, 69.6, 69.6, 69.5, 69.1, 68.8, 67.8, 67.3, 67.3, 66.7, 63.7, 63.4 (4C), 63.3 (5C), 62.9, 50.4, 41.2, 20.8, 20.7, 20.7 (2C), 20.6, 20.6. **MALDI-MS:** $[M+Na]^+$ *m/z* Calcd for $C_{412}H_{432}N_3O_{95}NaCl$, 6998.8652; found, 6999.1968.

Deprotected Structures

General Procedure for deprotection

10% w Pd/C (20 mg, 18.1 μmol) was added to a solution of **19** (29 mg, 9.0 μmol) in AcOEt/H_2O/AcOH (4:2:1, 1.75 mL). The mixture was hydrogenolysed in a high-pressure reactor (Berghof) at 20 °C (p = 25 bar). After 24 h, the solids were removed by filtration using a 'sandwich filter' (3 frits stacked on top of each other in the following order: 20 μm, 10 μm, 5 μm), rinsed with H_2O (3 × 2 mL) and EtOH (3 × 2 mL), and the filtrate was concentrated *in vacuo*. 10% w Pd/C (20 mg, 18.1 μmol) was added to a solution of the crude in a 1:1 mixture of THF and H_2O (2 mL). The reaction mixture was hydrogenolysed again in a high-pressure reactor (Berghof) at 20 °C (p = 25 bar). After 48 h, the solids were removed by filtration using a 'sandwich filter' (3 frits stacked on top of each other in the following order: 20 μm, 10 μm, 5 μm), rinsed with H_2O (3 × 2 mL) and EtOH (3 × 2 mL), and the filtrate was concentrated *in vacuo*. Purification by reversed-phase chromatography (C-18, H_2O-MeOH, 9:1→8:2→7:3→6:4→2:8→0:10), followed by freeze-drying gave desired compound as a colourless, amorphous solid.

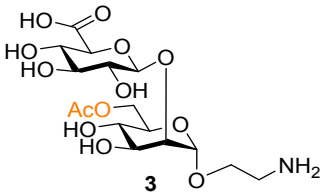
2-Aminoethyl α-D-mannopyranoside (1)



1

96 mg (> 99%) as a colourless, amorphous solid. **^{1}H NMR** (500 MHz, D_2O) δ 4.81 (d ≈ s br, 1H, H-1), 3.90-3.88 (m, 1H, H-2), 3.83-3.75 (m, 3H, H-3, H-6a, OCH^a_2CH_2NH_2), 3.70-3.66 (m, 1H, H-6b), 3.60-3.52 (m, 3H, H-4, H-5, OCH^b_2CH_2NH_2), 2.97-2.90 (m, 2H, OCH_2CH^a_2NH_2, OCH_2CH^b_2NH_2); **^{13}C NMR** (125 MHz, D_2O) δ 99.9 (C-1), 72.8 (C-5), 70.5 (C-3), 69.9 (C-2), 66.8 (2C, C-4, O*C*H_2CH_2NH_2), 60.9 (C-6), 39.6 (OCH_2*C*H_2NH_2); **HRMS (ESI)**: $[M+H]^+$ *m/z* Calcd for $C_8H_{18}NO_6$, 224.1134; found, 224.1127.

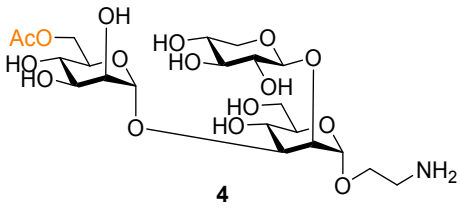
2-Aminoethyl β-D-glucopyranosyluronic acid-(1→2)-6-*O*-acetyl-α-D-mannopyranoside (3)



3

18 mg (38%) as a colourless, amorphous solid $[\alpha]_D^{20}$ − 22.6 (*c* 1.0, H_2O). **^{1}H NMR** (500 MHz, Deuterium Oxide) δ 5.04 (s, 1H), 4.54 (d, *J* = 7.7 Hz, 1H), 4.39 (d, *J* = 3.7 Hz, 3H), 4.21 (d, *J* = 3.9 Hz, 1H), 4.09 – 3.66 (m, 9H), 3.59 – 3.21 (m, 6H), 2.16 (s, 5H). **^{13}C NMR** (126 MHz, Deuterium Oxide) δ 174.0, 101.3, 98.0, 76.9, 75.2, 72.4, 72.3, 71.6, 70.4, 69.4, 66.7, 63.5, 63.3, 38.9, 20.1. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{16}H_{28}NO_{13}$, 442.1561; found, 442.1576.

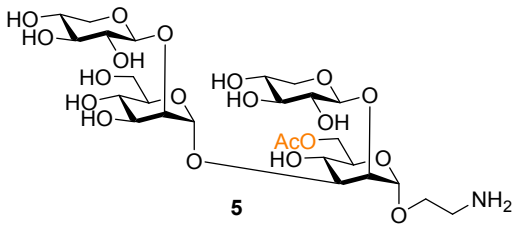
2-Aminoethyl 6-*O*-acetyl–α-D-mannopyranosyl-(1→3)-[β-D-xylo-pyranosyl-(1→2)]-α-D-mannopyranoside (4)



4

Colorless, amorphous solid 18 mg (85%). $[\alpha]_D^{20}$ +14.4 (*c* 1.0, H_2O). **^{1}H NMR** (500 MHz, Deuterium Oxide) δ 5.08 (s, 1H), 5.04 (s, 1H), 4.52 (d, *J* = 10.1 Hz, 1H), 4.39 (d, *J* = 7.7 Hz, 1H), 4.34 – 4.16 (m, 2H), 4.16 – 3.93 (m, 6H), 3.90 – 3.56 (m, 8H), 3.43 (s, 1H), 3.37 – 3.16 (m, 4H), 2.16 (s, 3H). **^{13}C NMR** (126 MHz, Deuterium Oxide) δ 103.1, 97.8, 63.9, 103.1, 63.9, 70.7, 69.7, 77.8, 63.6, 64.9, 77.4, 60.1, 70.1, 65.7, 63.6, 66.5, 73.1, 69.1, 75.4, 72.5, 39.1, 65.0, 20.2. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{21}H_{38}NO_{16}$, 560.2191; found, 560.2172.

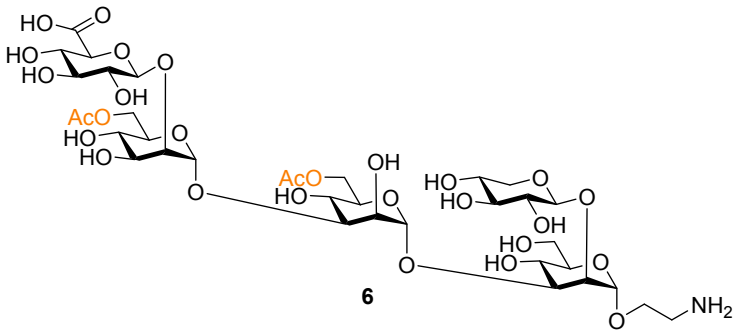
2-Aminoethyl β-D-xylopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[β-D-xylo-pyranosyl-(1→2)]-6-*O*-acetyl-α-D-mannopyranoside (5)



5

Colorless, amorphous solid 5 mg (60%). **^{1}H NMR** (500 MHz, Deuterium Oxide) δ 5.10 (s, 1H), 4.86 (s, 1H), 4.37 – 4.11 (m, 4H), 4.16 – 3.45 (m, 19H), 3.42 – 2.93 (m, 7H), 2.02 (s, 2H). **^{13}C NMR** δ 103.4, 102.4, 77.3, 75.5, 75.4, 72.6, 72.5, 72.4, 69.3, 69.1, 66.7, 66.2, 65.1, 65.0, 61.4, 60.7, 47.4, 28.3, 27.8, 27.7. **HRMS (ESI)**: $[M+H]^+$ *m/z* Calcd for $C_{26}H_{46}NO_{20}$ 692.2615; found, 692.2615

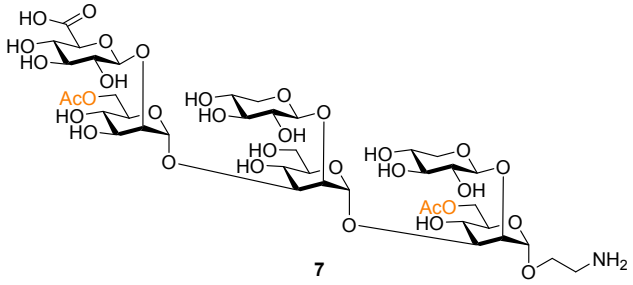
2-Aminoethyl β-D-glucopyranosyluronic acid-(1→2)-6-*O*-acetyl-α-D-mannopyranosyl-(1→3]-6-*O*-acetyl α-D-mannopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→2)]-α-D-mannopyranoside (6)



6

Colorless, amorphous solid 12.6 mg (60%). **^{1}H NMR** (500 MHz, Deuterium Oxide) δ 5.27 (s, 1H), 5.09 (s, 1H), 5.04 (s, 1H), 4.67 – 4.20 (m, 8H), 4.20 – 3.62 (m, 15H), 3.58 – 3.51 (m, 2H), 3.48 – 3.16 (m, 5H), 2.23 – 2.11 (m, 6H). **^{13}C NMR** (126 MHz, Deuterium Oxide) δ 100.5, 102.6, 97.8, 101.5, 63.6, 63.6, 63.3, 103.1, 63.7, 77.5, 70.7, 70.2, 70.0, 69.5, 77.6, 70.6, 63.9, 63.4, 64.2, 76.7, 64.6, 65.0, 64.3, 78.7, 78.8, 69.4, 60.1, 65.8, 65.2, 66.7, 63.3, 60.4, 63.4, 75.9, 73.1, 69.1, 68.5, 72.3, 71.6, 75.1, 75.4, 72.3, 72.5, 73.0, 39.0, 65.0, 20.2.

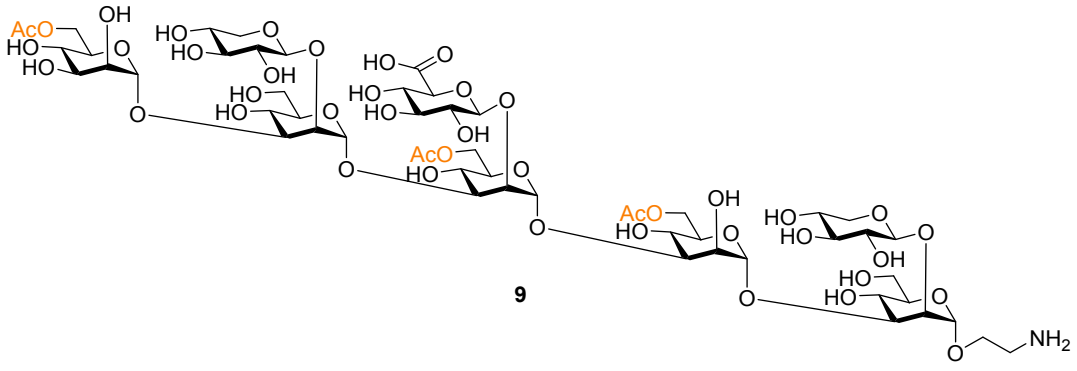
2-Aminoethyl β-D-glucopyranosyluronic acid-(1→2)-6-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→2)]-α-D-mannopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-α-D-mannopyranoside (7)



7

17.5 mg (65%) as a colourless, amorphous solid. $[\alpha]_D^{20}$ +4.1 (*c* 0.8, H_2O). **^{1}H NMR** (500 MHz, Deuterium Oxide) δ 5.29 (s, 1H), 5.24 (s, 1H), 5.00 (d, *J* = 1.8 Hz, 1H), 4.56 – 4.32 (m, 9H), 4.31 – 3.19 (m, 39H), 2.22 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (126 MHz, Deuterium Oxide) δ 174.0, 173.9, 103.3, 101.7, 99.7, 98.3, 78.1, 77.7, 77.4, 76.8, 75.4, 75.1, 74.2, 73.4, 72.7, 72.5, 72.3, 71.6, 70.6, 70.5, 69.5, 69.2, 69.1, 66.8, 66.5, 66.2, 65.0, 63.5, 46.6, 38.9, 22.3, 20.4, 20.1. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{40}H_{66}NO_{32}$, 1072.3606; found, 1072.3568.

2-Aminoethyl α-6-*O*-acetyl-D-mannopyranosyl-(1→3)-[(β-D-xylopyranosyl)-(1→2)]- acetyl-α-D-α-mannopyranosyl-(1→3)-[β-D-glucopyranosyluronic acid-(1→2)]-6-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→2)]-α-6-*O*-acetyl-D-mannopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→2)]-α-D-mannopyranoside (9)

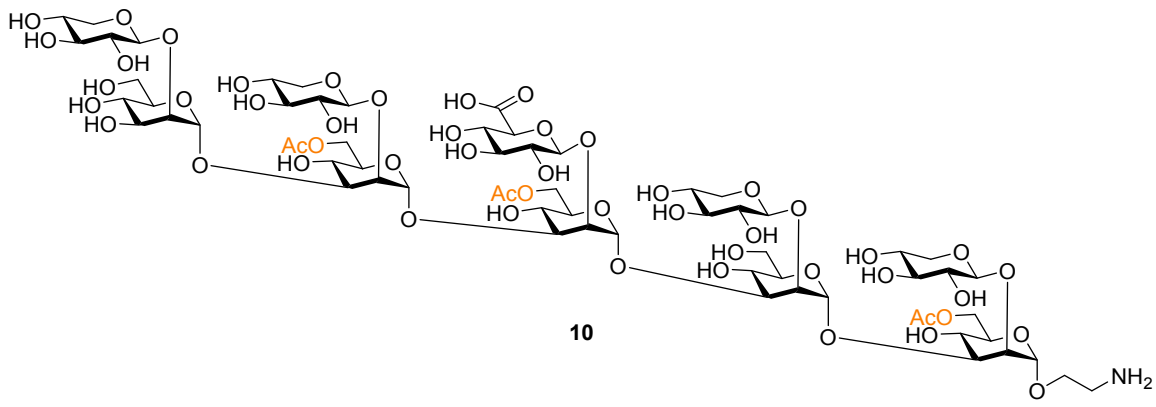


9

17 mg (60%) as a colourless, amorphous solid. **^{1}H NMR** (500 MHz, Deuterium Oxide) δ 5.31 – 5.18 (m, 3H), 5.10 (s, 1H), 5.04 (s, 1H), 4.59 – 3.96 (m, 22H), 3.92 – 3.19 (m, 22H), 2.26 – 2.12 (m, 9H). **^{13}C NMR** (126 MHz, Deuterium Oxide) δ 100.3, 100.6, 102.7, 102.6, 97.8, 101.6, 63.6, 63.1, 103.0, 103.1, 76.9, 63.6, 70.7, 69.5, 70.5, 78.2, 76.2, 69.7, 77.6, 70.8, 73.1, 77.1, 76.1, 77.2,

63.6, 65.0, 78.7, 66.3, 70.0, 65.8, 60.1, 65.8, 66.5, 63.6, 73.1, 76.9, 66.8, 69.1, 71.4, 75.3, 75.4, 72.4, 72.5, 65.0, 20.3, 20.7, 20.2. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{54}H_{87}NO_{43}Na$, 1460.4507; found, 1460.4550.

2-Aminoethyl β-D-xylopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[(β-D-xylopyranosyl)-(1→2)]-6-*O*-acetyl-α-D-α-mannopyranosyl-(1→3)-[β-D-glucopyranosyluronic acid-(1→2)]-6-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→2)]-α-D-mannopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→2)]-6-*O*-acetyl-α-D-mannopyranoside (10)



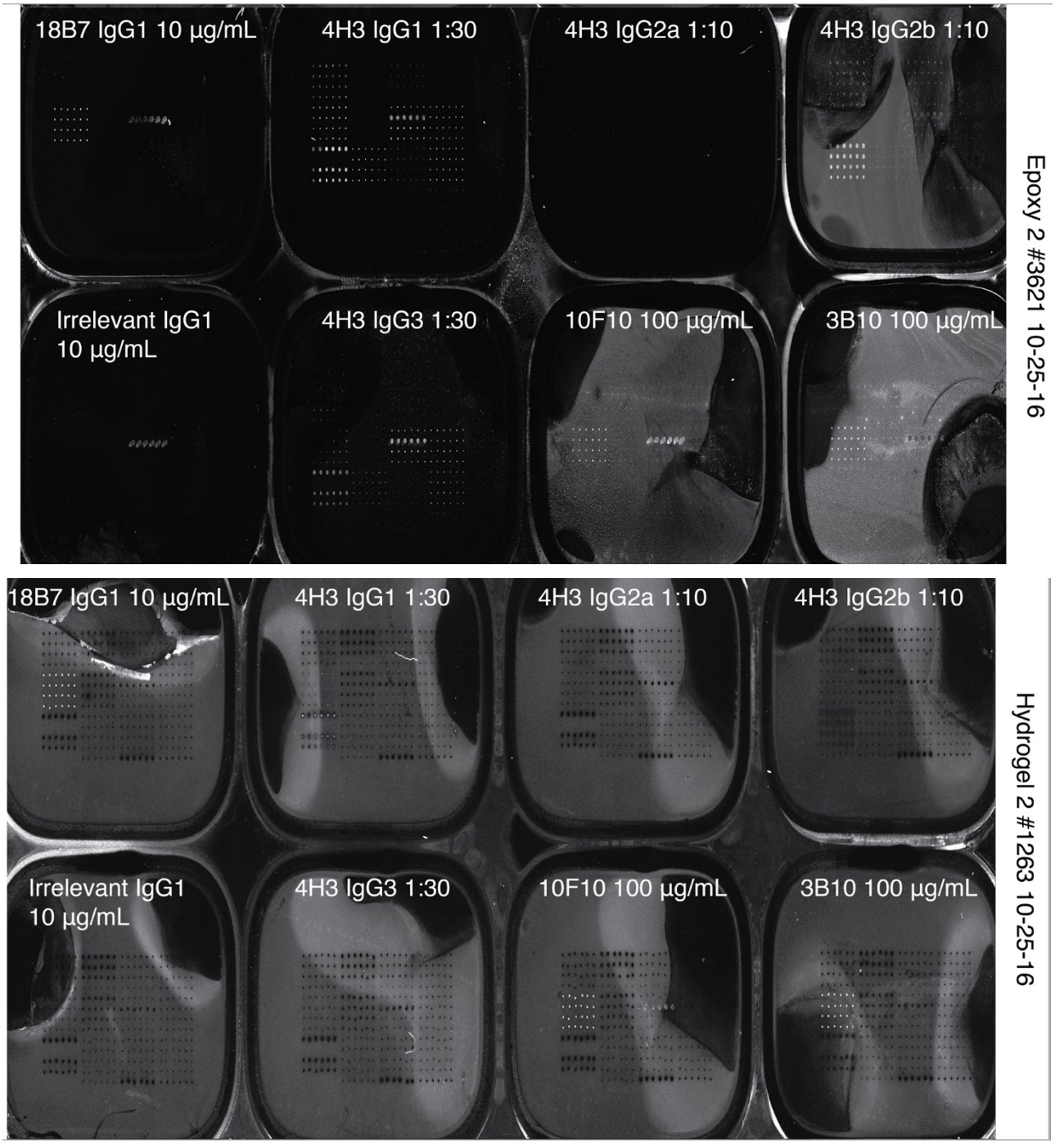
10

31 mg (37%) as a colourless, amorphous solid. **^{1}H NMR** (600 MHz, Deuterium Oxide) δ 5.18 (s, 1H), 5.13 (s, 1H), 5.11 (s, 1H), 5.02 (s, 1H), 4.84 (s, 1H), 4.43 – 3.42 (m, 44H), 2.07 (s, 2H), 2.04 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (151 MHz, Deuterium Oxide) δ 100.2, 100.0, 99.8, 101.6, 98.3, 102.4, 102.2, 63.2, 103.4, 63.1, 103.2, 63.0, 103.7, 78.6, 70.3, 77.6, 77.7, 70.5, 77.8, 75.7, 74.2, 75.2, 77.6, 73.2, 63.8, 65.0, 73.4, 73.4, 66.4, 70.6, 60.4, 69.3, 66.3, 66.4, 60.9, 63.8, 67.2, 66.9, 77.2, 69.2, 71.4, 75.4, 72.2, 75.4, 65.1, 72.7, 65.0, 38.9, 20.4, 20.4, 20.1. **HRMS (ESI)**: $[M+Na]^+$ *m/z* Calcd for $C_{64}H_{103}NO_{51}Na$, 1724.5395; found, 1724.5369.

Glycan Array Printing and Screening

Glycan printing followed published procedures.[1] Microarrays were constructed by piezoelectric non-contact printing (sciFLEXARRAYER S3, Scienion Inc) of the glycans on activated glass slides (Nexterion Slide H, Nexterion Slide E, Schott Inc). Compounds (300 μM, 250 μM, 200 μM, 125 μM) were printed (drop volume ~300 pL, 6 drop per spot), in replicates of 6 in sodium phosphate (200 mM), pH 8.5 buffer with on each slide. Overnight the slides were incubated in a humidity chamber, and the remaining activated esters were blocked with ethanolamine (50 mM) in TRIS (100 mM), pH 9.0. Next, slides were rinsed with MilliQ water, dried by centrifugation, and stored at 4 ºC. Hybridization of arrays was performed as described previously.[1] Briefly, printed slides were blocked in a humidity chamber at 26 ºC for 2 hours with 2% BSA in PBS, pH 7.4 with 50 mM ethanolamine, then washed 3 times for 2 minutes with PBS, pH 7.4, 0.1% Tween-20 (PBS-T) and once for 3 minutes with PBS. Primary anti-GXM mAbs or control Abs were prepared from stocks to the necessary concentration in 3% BSA in PBS-T. Biotinylated goat anti-mouse kappa chain Abs (Southern Biotech, Cat No. 1050-08) were used as secondary reagents for all primary antibodies except for 4H3 mAbs, which has a lambda light chain (Southern Biotech, Cat. No. 1060-08). Biotinylated goat anti-mouse heavy chain antibodies were used instead for each 4H3 isotype. Secondary antibodies were prepared at 1 μg/mL in PBS-T. Detection was performed with the streptavidin-conjugated SureLight P3 fluorophore (Cayman Chemical Company, Ann Arbor, MI) at 5 μg/mL in PBS-T. Hybridization was performed first with the primary Ab, then the secondary Ab, then the fluorophore, with washes between each step. All hybridization steps were performed using the Agilent 8-well gasket system in a humidity-controlled rotating hybridization oven at 26 ºC for 1 hour. Washes consisted of 3 times 2 minutes in tris-buffered saline, pH 7.6, 0.1% Tween 20 (TBS-T) and once for 3 minutes in TBS. Scanning was performed in an Agilent SureScan Dx microarray scanner with red wavelength emission detection. The data was processed on Mapix software. The mean fluorescent intensities (corrected for mean background) and standard deviations (SD) were calculated (n=6). Data were fitted using Prism software (GraphPad Software, Inc). Bar graphs represent the mean ± SD for each compound.

Representative Examples of Microarray Scans for Hydrogel and Epoxy Surfaces.



References for known compounds

Compounds **12a**, **14a**, **19a**, **21**, **11a** known from previous paper (GlcA and large donors)

Compound **47**: Jiang, Z.-H.; Schmidt, R. R. *Liebigs Ann. Chem.* **1992**, *1992*, 975.

Compound **40**: Coles, H. W.; Dodds, M. L.; Bergeim, F. H. *J. Am. Chem. Soc.* **1938**, *60*, 1020.

Compound **36**: Alpe, M.; Oscarson, S.; Svahnberg, P. *J. Carbohydr. Chem.* **2003**, *22*, 565

References for array printing

(1) Kilcoyne, M.; Gerlach, J. Q.; Gough, R.; Gallagher, M. E.; Kane, M.; Carrington, S. D.; Joshi, L. Construction of a Natural Mucin Microarray and Interrogation for Biologically Relevant Glyco-Epitopes. *Anal. Chem* **2012**, *84*, 2020.