Supplementary data

Novel Synthetic (1→6)-α-D-Mannodisaccharide Substrates Support Processive Mannosylation Catalysed by the Mycobacterial Cell Envelope Enzyme Fraction.

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Experimental

Glycoside 1, 2, 3, or 4 (3 mmol, 1 eq) was dissolved in pyridine (7 mL), and triphenylmethyl chloride (2 eq) was added. The solution was stirred at 55 °C for 24 h. After cooling, the pyridine was evaporated and the residue was co-evaporated with toluene (2 × 20 mL). The crude product was purified by column chromatography (hexane:EtOAc 5:1→0:1) to give 6-O-protected compounds 5-8 as an oil.

Octyl 6-O-triphenylmethyl-α-d-mannopyranoside (5). (1.22 g, 76%); [α]D +19 (c 1, methanol); lit2 [α]D +16.9 (c 1.3, CHCl3); 1H NMR (300 MHz, CD3OD): δ 7.49-7.46 (m, 5H, Ar), 7.30-7.19 (m, 10H, Ar), 4.79 (d, 1H, J1,2 = 1.1 Hz, H-1), 3.95 (dt, 1H, J= 6.9 Hz, J = 9.4 Hz, OCH2C6H15), 3.84-3.77 (m, 2H, H-2, H-5), 3.65 (dd, 1H, J2,3 = 3.4 Hz, J3,4 = 9.3 Hz, H-3), 3.54 (dt, 1H, J= 6.3 Hz, J = 9.5 Hz, OCH2C6H15), 3.51-3.42 (m, 2H, H-4, H-6a), 3.24 (dd, 1H, J5,6b = 7.8 Hz, J6a,6b = 9.6 Hz, H-6b), 1.73-1.69 (m, 2H, OCH2CH2C6H13), 1.50-1.22 (m, 10H, O(CH2)2(CH2)3CH3), 0.85 (t, 3H, J = 6.9 Hz, O(CH2)2CH3). 13C NMR (75 MHz, CD3OD): δ 145.7, 130.0, 128.7, 128.0 (Ar), 101.5 (C-1), 87.8 (C(Ph)3), 73.8, 72.2 (C-2, C-5), 73.0 (C-3), 69.3 (C-4), 68.5 (OCH2C6H15), 65.4 (C-6), 33.0, 30.8, 30.6, 30.5, 27.6, 23.8 (OCH2(CH2)6CH3), 14.5 (O(CH2)2CH3). HRMS (MALDI): m/z 557.2868 MNa⁺; calcd 557.2879 for C33H42O6Na.

Cyclohexylmethyl 6-O-triphenylmethyl-α-d-mannopyranoside (6). (1.27 g, 82%); [α]D +20 (c 1, methanol); 1H NMR (400 MHz, CD3OD): δ 7.52-7.50 (m, 5H, Ar), 7.32-7.24 (m, 10H, Ar), 4.80 (d, 1H, J1,2 = 1.3 Hz, H-1), 3.88-3.80 (m, 3H, H-2, H-5, OCH2C6H11), 3.68 (dd, 1H, J2,3 = 3.5 Hz, J3,4 = 9.4 Hz, H-3), 3.48-3.43 (m, 2H, H-4, H-6a), 3.37 (dd, 1H, J= 5.9 Hz, J = 9.3 Hz, OCH2C6H11), 3.26 (dd, 1H, J5,6b = 8.0 Hz, J6a,6b = 9.4 Hz, H-6b), 1.84-1.08 (m, 11H, OCH2C6H11). 13C NMR (100 MHz, CD3OD): δ 145.8, 130.1, 128.8, 128.1 (Ar), 101.5 (C-1), 87.8 (C(Ph)3), 74.0(2x), 72.3 (C-2, C-5, OCH2C6H11), 73.2 (C-3), 69.4 (C-4), 65.5 (C-6), 39.3, 31.7, 31.4, 27.9, 27.2, 27.1 (OCH2C6H11). HRMS (MALDI): m/z 541.2605 MNa⁺; calcd 541.2566 for C32H38O6Na.

2-Cyclohexylethyl 6-O-triphenylmethyl-α-d-mannopyranoside (7). (1.18 g, 74%); [α]D +21 (c 1, methanol); 1H NMR (600 MHz, CD3OD): δ 7.51-7.49 (m, 5H, Ar), 7.31-7.23 (m,
n mineral oil, 5 eq) was added during stirring. After 15 min, benzyl bromide (4 eq) was added and the resulting mixture was brought to rt and the stirring was continued for 16 h. The reaction was quenched with methanol (2-3 mL). The reaction mixture was diluted with CH₂Cl₂ (30 mL), washed with water (10 mL). The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic phases were again washed with water (10 mL), dried (Na₂SO₄), filtered and concentrated. The crude product was purified by column chromatography (hexane:EtOAc 10:1→6:1) and desired products 9-12 were obtained in oil forms.

Octyl-6-O-triphenylmethyl-1-thio-α-d-mannopyranoside (8). (1.21 g, 73%); [α]D +93 (c 1, methanol); ¹H NMR (400 MHz, CD₃OD): δ 7.51-7.48 (m, 6H, Ar), 7.32-7.22 (m, 9H, Ar), 5.33 (dd, 1H, J₁,₂ = 0.9 Hz, H-1), 4.20 (dd, 1H, J₂,₃ = 3.4 Hz, H-2), 3.69 (dd, 1H, J₃,₄ = 9.3 Hz, H-3), 3.54 (t, 1H, J₄,₅ = 9.6 Hz, H-4), 3.48 (dd, 1H, J₅,₆ₐ = 1.8 Hz, J₆ₐ,₆ₐ = 9.8 Hz, H-6a), 3.29 (dd, 1H, J₅,₆ₐ = 7.5 Hz, H-6b), 2.88 (dd, 1H, J = 6.3 Hz, J = 8.3 Hz, J = 12.9 Hz, SCH₂C₇H₁₅), 2.74 (ddd, 1H, J = 6.8 Hz, J = 8.4 Hz, J = 12.8 Hz, SCH₂C₇H₁₅), 1.80-1.71 (m, 2H, SCH₂CH₂C₆H₁₃), 1.46-1.40 (m, 2H, S(CH₂)₂CH₂C₆H₁₁), 1.33-1.19 (m, 8H, S(CH₂)₃(CH₂)₆CH₃), 0.86 (t, 3H, J = 7.0 Hz, S(CH₂)₇CH₃). ¹³C NMR (100 MHz, CD₃OD): δ 145.7, 130.1, 128.8, 128.1 (Ar), 87.9 (C-1), 85.8 (C(Ph)₃), 74.1 (C-5), 73.6(2x) (C-2, C-3), 69.6 (C-4), 65.4 (C-6), 33.1, 31.6, 31.0, 30.6, 30.5, 30.3, 23.8 (S(CH₂)₇CH₃), 14.6 (S(CH₂)₇CH₃). HRMS (MALDI): m/z 573.2659 MNa⁺; calcld 573.2651 for C₃₃H₄₀O₆Na.

General procedure for the protection of secondary hydroxyl groups. Synthesis of compounds 9-12.

Partially protected mannopyranoside 5, 6, 7, or 8 (1 mmol, 1 eq) was dissolved in DMF (7 mL), the solution was cooled to 0 °C, and sodium hydride (60% in mineral oil, 5 eq) was added during stirring. After 15 min, benzyl bromide (4 eq) was added and the resulting mixture was brought to rt and the stirring was continued for 16 h. The reaction was quenched with methanol (2-3 mL). The reaction mixture was diluted with CH₂Cl₂ (30 mL), washed with water (10 mL). The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic phases were again washed with water (10 mL), dried (Na₂SO₄), filtered and concentrated. The crude product was purified by column chromatography (hexane:EtOAc 10:1→6:1) and desired products 9-12 were obtained in oil forms.
Octyl 2,3,4-tri-O-benzyl-6-O-triphenylmethyl-α-D-mannopyranoside (9). (0.67 g, 83%); [α]D +15 (c 1, CHCl3); lit2 [α]D +18.7 (c 0.3, CHCl3); 1H NMR (300 MHz, CDCl3): δ 7.57-7.16 (m, 28H, Ar), 6.88 (m, 2H, Ar), 4.90 (d, 1H, J1,2 = 1.3 Hz, H-1), 4.82 (d, 1H, J = 12.5 Hz, PhCH2), 4.73-4.65 (m, 4H, 2x PhCH2), 4.26 (d, 1H, J = 10.4 Hz, PhCH2), 4.00 (dd, 1H, J3,4 = 9.5 Hz, J4,5 = 9.5 Hz, H-4), 3.89 (dd, 1H, J2,3 = 3.0 Hz, H-3), 3.82-3.79 (m, 2H, H-2, H-5), 3.74 (dt, 1H, J =6.9 Hz, J = 9.5 Hz, OCH2C6H13), 3.51 (dd, 1H, J5,6α = 1.3 Hz, J6α,6b = 9.7 Hz, H-6α), 3.41 (dt, 1H, J =6.6 Hz, J = 9.5 Hz, OCH2C6H13), 3.26 (dd, 1H, J5,6β = 5.3 Hz, H-6b), 1.59-1.50 (m, 2H, OCH2C6H13), 1.33-1.18 (m, 10H, O(CH2)2(CH2)5CH3), 0.86 (t, 3H, J = 7.0 Hz, O(CH2)2CH3). 13C NMR (75 MHz, CDCl3): δ 144.2, 138.8, 138.7, 138.2, 128.9-126.8 (Ar), 97.6 (C-1), 86.2 (C(Ph)3), 80.4, 75.8, 75.2, 75.1, 72.7, 72.3, 71.9, 67.4 (C-2, C-3, C-4, C-5, 3x PhCH2, OCH2C6H13), 63.1 (C-6), 31.8, 29.5, 29.4, 29.2, 26.2, 22.6 (OCH2(CH2)6CH3), 14.1 (O(CH2)7CH3). HRMS (MALDI): m/z 827.4269 MNa+; calcd 827.4287 for C53H60O6Na.

Cyclohexylmethyl 2,3,4-tri-O-benzyl-6-O-triphenylmethyl-α-D-mannopyranoside (10). (0.67 g, 85%); [α]D +22 (c 1, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.52-7.14 (m, 28H, Ar), 6.88 (m, 2H, Ar), 4.86 (d, 1H, J1,2 = 1.3 Hz, H-1), 4.83 (d, 1H, J = 12.5 Hz, PhCH2), 4.73-4.65 (m, 4H, 2x PhCH2), 4.27 (d, 1H, J = 10.5 Hz, PhCH2), 3.95 (dd, 1H, J3,4 = 9.5 Hz, J4,5 = 9.6 Hz, H-4), 3.88 (dd, 1H, J2,3 = 3.0 Hz, H-3), 3.83-3.78 (m, 2H, H-2, H-5), 3.59 (dd, 1H, J =7.3 Hz, J = 9.3 Hz, OCH2C6H11), 3.48 (dd, 1H, J5,6α = 1.3 Hz, J6α,6b = 9.7 Hz, H-6α), 3.27-3.19 (m, 2H, H-6b, OCH2C6H11), 1.77-0.90 (m, 11 H, OCH2C6H11). 13C NMR (100 MHz, CDCl3): δ 145.8, 138.9, 138.8, 138.4, 129.1-127.0 (Ar), 97.9 (C-1), 86.5 (C(Ph)3), 80.7, 76.0, 75.5, 75.4, 73.1, 72.9, 72.6, 72.3 (C-2, C-3, C-4, C-5, 3x PhCH2, OCH2C6H11), 63.4 (C-6), 38.1, 30.5, 30.2, 26.8, 26.1, 26.0 (OCH2C6H11). HRMS (MALDI): m/z 811.3986 MNa+; calcd 811.3975 for C53H58O6Na.

2-Cyclohexylethyl 2,3,4-tri-O-benzyl-6-O-triphenylmethyl-α-D-mannopyranoside (11). (0.69 g, 86%); [α]D +21 (c 1, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.52-7.17 (m, 28H, Ar), 6.89 (m, 2H, Ar), 4.89 (d, 1H, J1,2 = 1.5 Hz, H-1), 4.83 (d, 1H, J = 12.5 Hz, PhCH2), 4.72-4.65 (m, 4H, 2x PhCH2), 4.27 (d, 1H, J = 10.5 Hz, PhCH2), 3.97 (dd, 1H, J3,4 = 9.3 Hz, J4,5 = 9.4 Hz, H-4), 3.89 (dd, 1H, J2,3 = 3.0 Hz, H-3), 3.84-3.78 (m, 3H, H-2, H-5, OCH2CH2C6H11), 3.49 (dd, 1H, J5,6α = 1.5 Hz, J6α,6b = 9.8 Hz, H-6α), 3.44 (dt, 1H, J =7.0 Hz, J = 9.7 Hz,
OCH₂CH₂C₆H₁₁), 3.25 (dd, 1H, J₅,₆b = 5.6 Hz, H-6b), 1.71-0.86 (m, 13 H, OCH₂CH₂C₆H₁₁). ¹³C NMR (100 MHz, CDCl₃): δ 144.4, 138.9, 138.8, 138.5, 138.4, 129.1-127.0 (Ar), 97.8 (C-1), 86.5 (C(Ph₃)), 80.5, 75.9, 75.5, 75.3, 72.9, 72.5, 72.2 (C-2, C-3, C-4, C-5, 3x PhCH₂), 65.7 (OCH₂CH₂C₆H₁₁), 63.5 (C-6), 37.1, 34.9, 33.6, 33.5, 26.8, 26.5(2x) (OCH₂CH₂C₆H₁₁).

HRMS (MALDI): m/z 825.4133 MNaN⁺; calcd 825.4131 for C₅₄H₅₈O₆Na.

Octyl 2,3,4-tri-O-benzyl-6-O-triphenylmethyl-1-thio-α-d-mannopyranoside (12). (0.65 g, 79%); [α]D +49 (c 1, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.52-7.17 (m, 28H, Ar), 6.90-6.88 (m, 2H, Ar), 5.41 (s, 1H, H-1), 4.79 (d, 1H, J = 12.2 Hz, PhCH₂), 4.74-4.61 (m, 4H, 2x PhCH₂), 4.27 (d, 1H, J = 10.8 Hz, PhCH₂), 4.14-4.07 (m, 2H, H-4, H-5), 3.86-3.83 (m, 2H, H-2, H-3), 3.49 (dd, 1H, J₅,₆a = 1.5 Hz, J₆a,₆b = 9.9 Hz, H-6a), 3.28 (dd, 1H, J₅,₆b = 4.6 Hz, H-6b), 2.70-2.54 (m, 2H, S(CH₂)₂C₆H₁₅), 1.63-1.56 (m, 2H, S(CH₂)₂C₆H₁₅), 1.32-1.23 (m, 10H, S(CH₂)₂(CH₂)₂CH₃), 0.86 (t, 3H, J = 7.0 Hz, S(CH₂)₂CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 144.4, 138.7, 138.5, 138.4, 129.1-127.0 (Ar), 86.5 (C(Ph₃)), 81.9 (C-1), 80.6, 77.4, 75.5, 75.4, 72.5, 72.4(2x) (C-2, C-3, C-4, C-5, 3x PhCH₂), 63.1 (C-6), 32.0, 31.3, 29.8, 29.5, 29.4, 29.2, 22.9 (S(CH₂)₂CH₃), 14.3 (S(CH₂)₂CH₃). HRMS (MALDI): m/z 843.4014 MNaN⁺; calcd 843.4059 for C₅₄H₆₀O₃SNa.


Compound 9, 10, 11 or 12 (0.6 mmol, 1 eq) was dissolved in CH₂Cl₂:MeOH (2:1, 6 mL), and p-TsOH (0.89 eq) was added. The reaction mixture was stirred at rt until TLC indicated that reaction is complete (~35 min). The reaction mixture was diluted with CH₂Cl₂ (30 mL), washed with satd. NaHCO₃ (2 × 10 mL) and water (10 mL), then dried (Na₂SO₄), filtered and concentrated. Purification by column chromatography (hexane:EtOAc 4:1→2:1) gave the acceptors 13-16 as an oil.

Octyl 2,3,4-tri-O-benzyl-α-d-mannopyranoside (13). (0.29 g, 86%); [α]D +32 (c 1, CHCl₃); lit [α]D +27.6 (c 0.7, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.26 (m, 15H, Ar), 4.93 (d, 1H, J = 10.9 Hz, PhCH₂), 4.79 (d, 1H, J = 12.3 Hz, PhCH₂), 4.78 (d, 1H, J₁₂ = 1.6 Hz, H-1), 4.70-4.64 (m, 4H, 2x PhCH₂), 3.98 (dd, 1H, J₃,₄ = 9.3 Hz, J₄,₅ = 9.4 Hz, H-4), 3.92 (dd, 1H, J₂₃ = 2.7 Hz, H-3), 3.83 (dd, 1H, J₅,₆a = 2.8 Hz, J₆a,₆b = 11.7 Hz, H-6a), 3.79-3.75 (m, 2H, H-2, H-6b), 3.63 (m, 1H, H-5), 3.58 (dt, 1H, J = 6.8 Hz, J = 9.5 Hz, OCH₂C₆H₁₅), 3.31 (dt, 1H, J = 6.5 Hz, J = 9.6 Hz, OCH₂C₆H₁₅), 1.52-1.48 (m, 2H, OCH₂CH₂C₆H₁₅), 1.30-1.23 (m,
10H, O(CH$_2$)$_2$(CH$_2$)$_3$CH$_3$), 0.88 (t, 3H, J = 6.5 Hz, O(CH$_2$)$_2$CH$\_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.7, 138.6, 138.5, 129.6-127.8 (Ar), 98.4 (C-1), 80.5, 75.5, 75.3, 75.2, 73.2, 72.5, 72.3, 68.0 (C-2, C-3, C-4, C-5, 3x PhCH$_2$, OCH$_2$C$_2$H$_3$), 62.7 (C-6), 32.0, 29.6(2x), 29.4, 26.3, 22.9 (OCH$_2$(CH$_2$)$_3$CH$_3$), 14.3 (O(CH$_2$)$_2$CH$\_3$). HRMS (MALDI): m/z 585.3220 MNa$^+$; calcd 585.3192 for C$_{35}$H$_{46}$O$_6$Na.

Cyclohexylmethyl 2,3,4-tri-O-benzyl-α-D-mannopyranoside (14). (0.29 g, 89%); [α]$_D$ +36 (c 1, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.38-7.26 (m, 15H, Ar), 4.93 (d, 1H, J = 10.9 Hz, PhCH$_2$), 4.79 (d, 1H, J = 12.3 Hz, PhCH$_2$), 4.74 (d, 1H, J$_{1,2}$ = 1.5 Hz, H-1), 4.69-4.63 (m, 4H, 2x PhCH$_2$), 3.97 (dd, 1H, J$_{3,4}$ = 9.3 Hz, J$_{4,5}$ = 9.4 Hz, H-4), 3.91 (dd, 1H, J$_{2,3}$ = 2.8 Hz, H-3), 3.83 (dd, 1H, J$_{5,6a}$ = 3.0 Hz, J$_{6a,6b}$ = 11.6 Hz, H-6a), 3.78-3.74 (m, 2H, H-2, H-6b), 3.64-3.60 (m, 1H, H-5), 3.40 (dd, 1H, J = 7.0 Hz, J = 9.3 Hz, OCH$_2$C$_6$H$_5$), 3.12 (dd, 1H, J = 6.0 Hz, J = 9.4 Hz, OCH$_2$C$_6$H$_5$), 1.70-0.84 (m, 11H, OCH$_2$C$_6$H$_5$). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.7, 138.6(2x), 129.6-127.8 (Ar), 98.5 (C-1), 80.5, 75.3, 75.2(2x), 73.4, 73.1, 72.5, 72.3 (C-2, C-3, C-4, C-5, 3x PhCH$_2$, OCH$_2$C$_6$H$_5$), 62.7 (C-6), 38.0, 30.3, 30.0, 26.7, 26.0(2x) (OCH$_2$C$_6$H$_5$). HRMS (MALDI): m/z 569.2855 MNa$^+$; calcd 569.2879 for C$_{34}$H$_{48}$O$_6$Na.

2-Cyclohexylethyl 2,3,4-tri-O-benzyl-α-D-mannopyranoside (15). (0.28 g, 85%); [α]$_D$ +34 (c 1, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.37-7.22 (m, 15H, Ar), 4.93 (d, 1H, J = 10.9 Hz, PhCH$_2$), 4.79 (br d, 2H, H-1, PhCH$_2$), 4.70-4.64 (m, 4H, 2x PhCH$_2$), 3.97 (dd, 1H, J$_{3,4}$ = 9.3 Hz, J$_{4,5}$ = 9.4 Hz, H-4), 3.91 (dd, 1H, J$_{2,3}$ = 2.9 Hz, H-3), 3.83 (dd, 1H, J$_{5,6a}$ = 2.9 Hz, J$_{6a,6b}$ = 11.6 Hz, H-6a), 3.78-3.74 (m, 2H, H-2, H-6b), 3.67-3.62 (m, 2H, H-5, OCH$_2$CH$_2$C$_6$H$_5$), 3.35 (dt, 1H, J = 6.8 Hz, J = 9.6 Hz, OCH$_2$CH$_2$C$_6$H$_5$), 1.69-0.83 (m, 13H, OCH$_2$CH$_2$C$_6$H$_5$). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.7, 138.6(2x), 129.6-127.9 (Ar), 98.4 (C-1), 80.4, 75.5, 75.2 (2x), 73.1, 72.5, 72.3 (C-2, C-3, C-4, C-5, 3x PhCH$_2$), 65.9 (OCH$_2$CH$_2$C$_6$H$_5$), 62.7 (C-6), 37.0, 34.8, 33.6, 33.5, 26.7, 26.4(2x) (OCH$_2$CH$_2$C$_6$H$_5$). HRMS (MALDI): m/z 583.3048 MNa$^+$; calcd 583.3036 for C$_{35}$H$_{46}$O$_6$Na.

Octyl 2,3,4-tri-O-benzyl-1-thio-α-D-mannopyranoside (16). (0.27 g, 79%); [α]$_D$ +65 (c 1, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.38-7.26 (m, 15H, Ar), 5.26 (d, 1H, J$_{1,2}$ = 0.7 Hz, H-1), 4.94 (d, 1H, J = 10.9 Hz, PhCH$_2$), 4.69 (d, 1H, J = 10.9 Hz, PhCH$_2$), 4.68-4.57 (m, 4H, 2x PhCH$_2$), 4.02-3.97 (m, 2H, H-3, H-5), 3.86-3.74 (m, 4H, H-2, H-4, H-6a, H-6b), 2.58-2.46 (m, 2H, SCH$_2$C$_7$H$_5$), 1.57-1.52 (m, 2H, SCH$_2$CH$_2$C$_6$H$_3$), 1.36-1.21 (m, 10H,
S(CH$_2$)$_2$(CH$_2$)$_3$CH$_3$), 0.88 (t, 3H, $J$ = 6.9 Hz, S(CH$_2$)$_2$CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.6, 138.4, 138.3, 128.6-127.9 (Ar), 82.9 (C-1), 80.6, 76.8, 75.5, 75.2, 72.6(2x), 72.4 (C-2, C-3, C-4, C-5, 3x PhCH$_2$), 62.6 (C-6), 32.0, 31.7, 29.8, 29.3(2x), 29.0, 22.9 (S(CH$_2$)$_2$CH$_3$), 14.3 (S(CH$_2$)$_2$CH$_3$). HRMS (MALDI): $m/z$ 601.2981 MNa$^+$; calcd 601.2964 for C$_{35}$H$_{46}$O$_5$SNa.

**Synthesis of disaccharides 18-21. General procedure for coupling of the donor 17 with acceptors 13-16.**

Donor 17 (0.55 mmol, 1.5 eq), acceptor 13, 14, 15 or 16 (0.36 mmol, 1 eq) and 4Å MS (0.5 g) in CH$_2$Cl$_2$ (6 mL) were cooled at 0 °C and stirred under inert atmosphere for 15 min. After BF$_3$OEt$_2$ (0.55 mmol, 1.5 eq) was added, the reaction mixture was stirred at 0 °C until TLC indicated total consumption of starting material (30 min.). The reaction mixture was poured into satd NaHCO$_3$:CH$_2$Cl$_2$ (1:1, 30 mL) under stirring. The organic phase was separated, washed with satd NaHCO$_3$ (10 mL), water (10 mL), dried (Na$_2$SO$_4$), filtered and concentrated. Purification by column chromatography (hexane:EtOAc 1:1→3:1) yielded disaccharides 18-21 as an oil.

**Octyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (18).** (0.26 g, 83%); [α]$_D$ +32 (c 1, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.37-7.26 (m, 15H, Ar), 5.35 (dd, 1H, $J_{3,4'}$ = 10.0 Hz, H-3'), 5.29 (dd, 1H, $J_{2,3'}$ = 3.4 Hz, H-2'), 5.25 (t, 1H, $J_{4,5'}$ = 10.0 Hz, H-4'), 4.98 (d, 1H, $J$ = 11.2 Hz, PhCH$_2$), 4.92 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1'), 4.77 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.72 (d, 1H, $J$ = 11.5 Hz, PhCH$_2$), 4.69 (d, 1H, $J$ = 12.5 Hz, PhCH$_2$), 4.60 (m, 3H, PhCH$_2$, ½ PhCH$_2$), 4.18 (dd, 1H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6'a), 4.13-4.06 (m, 2H, H-5', H-6'b), 3.91 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.1 Hz, H-3), 3.85-3.73 (m, 5H, H-2, H-4, H-5, H-6'a, H-6b), 3.63 (dt, 1H, $J$ =6.7 Hz, $J$ = 9.7 Hz, OCH$_2$C$_7$H$_{15}$), 3.34 (dt, 1H, $J$ =6.5 Hz, $J$ = 9.7 Hz, OCH$_2$C$_7$H$_{15}$), 2.13, 2.05, 2.02, 1.96 (each s, each 3H, 4x CH$_3$CO), 1.57-1.51 (m, 2H, OCH$_2$CH$_2$C$_6$H$_{13}$), 1.30-1.21 (m, 10H, O(CH$_2$)$_2$(CH$_2$)$_2$CH$_3$), 0.88 (t, 3H, $J$ =6.6 Hz, O(CH$_2$)$_2$CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 171.0, 170.0 (2x), 169.8 (4x CH$_3$CO), 138.6, 128.6-127.8 (Ar), 97.8 (C-1), 97.6 (C-1'), 80.7 (C-3), 75.2 (PhCH$_2$), 75.0(2x) (C-2, C-4), 72.9 (PhCH$_2$), 72.3 (PhCH$_2$), 71.4 (C-5), 69.8 (C-2'), 69.3 (C-3'), 68.6 (C-5'), 67.8 (OCH$_2$C$_7$H$_{15}$), 67.2 (C-6), 66.5 (C-4'), 62.6 (C-6'), 32.1, 29.6(2x), 29.5, 26.4, 22.9 (OCH$_2$(CH$_2$)$_6$CH$_3$), 21.1, 20.9(2x), 20.8 (4xCH$_3$CO), 14.3 (O(CH$_2$)$_2$CH$_3$). HRMS (MALDI): $m/z$ 915.4146 MNa$^+$; calcd 915.4143 for C$_{49}$H$_{60}$O$_{13}$Na.
Cyclohexylmethyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyanosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (19). (0.28 g, 90%); [α]D +43 (c 1, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.37-7.25 (m, 15H, Ar), 5.34 (dd, 1H, J3,4 = 10.0 Hz, H-3'), 5.30 (dd, 1H, J2,3' = 3.3 Hz, H-2'), 5.25 (t, 1H, J4,5 = 10.0 Hz, H-4'), 4.97 (d, 1H, J = 11.2 Hz, PhCH2H), 4.91 (d, 1H, J1,2' = 1.6 Hz, H-1'), 4.76 (d, 2H, H-1, PhCH2), 4.68 (d, 1H, J = 12.5 Hz, PhCH2), 4.61 (m, 3H, PhCH2, ½ PhCH2), 4.18 (dd, 1H, J5,6a = 5.3 Hz, J6a,6'b = 12.3 Hz, H-6'a), 4.14-4.06 (m, 2H, H-5', H-6'b), 3.89 (dd, 1H, J2,3 = 3.0 Hz, J3,4 = 9.1 Hz, H-3), 3.85-3.71 (m, 5H, H-2, H-4, H-6a, H-6b), 3.43 (dd, 1H, J = 7.1 Hz, J = 9.4 Hz, OCH2C6H11), 3.14 (dd, 1H, J = 5.9 Hz, J = 9.4 Hz, OCH2C6H11), 2.13, 2.04, 2.02, 1.96 (each s, each 3H, 4x CH3CO), 1.71-0.86 (m, 11H, OCH2C6H11). 13C NMR (100 MHz, CDCl3): δ 171.0, 170.0 (2x), 169.7 (4x CH3CO), 138.6, 128.6-127.8 (Ar), 98.0 (C-1), 97.6 (C-1'), 80.6 (C-3), 75.3 (PhCH2), 75.0(2x) (C-2, C-4), 73.3 (OCH2C6H11), 72.9 (PhCH2), 72.4 (PhCH2), 71.4 (C-5), 69.8 (C-2'), 69.3 (C-3'), 68.6 (C-5'), 67.3 (C-6), 66.4 (C-4'), 62.6 (C-6'), 38.0, 30.3, 30.0, 26.7, 26.1, 26.0 (OCH2C6H11), 21.1, 20.9(2x), 20.8 (4xCH3CO). HRMS (MALDI): m/z 899.3815 MNa+; calcd 899.3829 for C49H60O15Na.

2-Cyclohexylethyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyanosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (20). (0.26 g, 81%); [α]D +46 (c 1, CHCl3); 1H NMR (400 MHz, CDCl3): δ 7.39-7.25 (m, 15H, Ar), 5.34 (dd, 1H, J3,4 = 9.9 Hz, H-3'), 5.30 (dd, 1H, J2,3' = 3.3 Hz, H-2'), 5.25 (t, 1H, J4,5 = 9.9 Hz, H-4'), 4.98 (d, 1H, J = 11.2 Hz, PhCH2), 4.91 (d, 1H, J1,2' = 1.5 Hz, H-1'), 4.76 (d, 1H, J1,2 = 1.7 Hz, H-1), 4.72 (d, 1H, J = 11.2 Hz, PhCH2), 4.69 (d, 1H, J = 12.5 Hz, PhCH2), 4.60 (m, 3H, PhCH2, ½ PhCH2), 4.18 (dd, 1H, J5,6a = 5.3 Hz, J6a,6'b = 12.3 Hz, H-6'a), 4.15-4.06 (m, 2H, H-5', H-6'b), 3.90 (dd, 1H, J2,3 = 3.0 Hz, J3,4 = 9.1 Hz, H-3), 3.85-3.72 (m, 5H, H-2, H-4, H-5, H-6a, H-6b), 3.68 (dt, 1H, J = 6.9 Hz, J = 9.7 Hz, OCH2CH2C6H11), 3.36 (dt, 1H, J = 6.7 Hz, J = 9.8 Hz, OCH2CH2C6H11), 2.13, 2.05, 2.02, 1.96 (each s, each 3H, CH3CO), 1.68-0.86 (m, 13H, OCH2CH2C6H11). 13C NMR (100 MHz, CDCl3): δ 171.0, 170.0 (2x), 169.7 (4x CH3CO), 138.6, 128.6-127.8 (Ar), 97.8 (C-1), 97.7 (C-1'), 80.6 (C-3), 75.2 (PhCH2), 75.0(2x) (C-2, C-4), 72.9 (PhCH2), 72.4 (PhCH2), 71.4 (C-5), 69.8 (C-2'), 69.3 (C-3'), 68.6 (C-5'), 67.3 (C-6), 66.4 (C-4'), 65.7 (OCH2CH2C6H11), 62.6 (C-6'), 37.0, 34.7, 33.6, 33.4, 26.8, 26.9(2x) (OCH2CH2C6H11), 21.1, 20.9(2x), 20.8 (4xCH3CO). HRMS (MALDI): m/z 913.4010 MNa+; calcd 913.3986 for C49H62O13Na.
Synthesis of disaccharide 22.
To a stirred and cooled at 0 °C solution containing disaccharide 21 (0.22 mmol, 1 eq) in CH₂Cl₂ (5 mL), mCPBA (0.66 mmol, 3 eq) was added. The reaction mixture was stirred at rt for 2 h, then diluted with CH₂Cl₂ (20 mL), washed with satd NaHCO₃ (2 × 20 mL) and water (20 mL). The organic phase was dried (Na₂SO₄), filtered and concentrated. The crude product was purified by flash chromatography (hexane:EtOAc 3:1→1.5:1). To a stirred and at 0 °C precooled solution containing compound (21) (0.22 mmol, 1 eq) in CH₂Cl₂ (5 mL) mCPBA (0.66 mmol, 3eq, based on 77% peroxide content) was added. The reaction mixture was stirred at rt for 2 h, diluted with CH₂Cl₂ (20 mL), washed with satd NaHCO₃ (2 × 15 mL) and water (20 mL). The organic phase was dried (Na₂SO₄), filtered and concentrated. The crude product was purified by flash chromatography (hexane:EtOAc 3:1→1.5:1).

Octyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranosyl sulfone (22). (0.17 g, 49% over 2 steps); [α]D +48 (c 1, CHCl₃); 1H NMR (400 MHz, CDCl₃): δ 7.31-7.17 (m, 15H, Ar), 5.24-5.15 (m, 3H, H-2', H-3', H-4'), 4.81 (br d, 2H, H-1', PhCH₂), 4.77 (d, 1H, J₁₂ = 2.0 Hz, H-1), 4.62 (d, 1H, J = 11.8 Hz, PhCH₂), 4.57 (d, 1H, J = 12.2 Hz, PhCH₂), 4.54 (d, 1H, J = 12.1 Hz, PhCH₂), 4.50 (d, 1H, J = 11.8 Hz, PhCH₂), 4.46 (d, 1H, J = 11.5 Hz, PhCH₂), 4.40 (dd, 1H, J₂₃ = 3.3 Hz, H-2), 4.30 (m, 1H, H-5), 4.11-4.06 (m, 2H, H-3, H-6′a), 4.00 (dd, 1H, J₅₆̵₆₅ = 2.2 Hz, J₆₆₅₆₆ = 12.2 Hz, H-6′b), 3.87 (m, 1H, H-5′), 3.78 (t, 1H, J₃₄ = 9.0 Hz, J₄₅ = 9.0 Hz, H-4), 3.69 (dd, 1H, J₅₆ = 5.8 Hz, J₆₆ = 11.3 Hz, H-6a), 3.61 (dd, J₅₆₆ = 1.4 Hz, H-6b), 3.06-2.93 (m, 2H, SO₂CH₂CH₂CH₃), 2.07, 1.95(2x), 1.89 (each s, each 3H, 4x CH₃CO), 1.78-1.66 (m, 2H, S O₂CH₂CH₂CH₂CH₃), 1.36-1.19 (m, 10H, SO₂CH₂CH₂CH₃), 0.81 (t, 3H, J = 6.3 Hz, SO₂CH₂CH₃). 13C NMR (100 MHz, CDCl₃): δ 170.9, 170.0, 169.9, 169.7 (4x CH₃CO), 138.2, 138.1, 137.5, 128.7-127.9 (Ar), 97.9 (C-1′), 88.5 (C-1), 79.4 (C-3), 75.7 (C-5), 74.6 (PhCH₂), 73.5(2x) (PhCH₂, C-4), 72.9 (PhCH₂), 70.9 (C-2), 69.7 (C-2′), 69.1 (C-3′), 68.8 (C-5′), 67.4 (C-6), 66.3 (C-4′), 62.5 (C-6′), 50.6 (SO₂CH₂CH₂CH₃), 31.9, 29.3, 29.2, 28.7, 22.8, 21.7 (SO₂CH₂CH₂CH₂CH₃), 21.1, 20.9(2x), 20.8 (4×CH₃CO), 14.3 (SO₂CH₂CH₂CH₃). HRMS (MALDI): m/z 963.3804 MNa⁺; calcld 963.3813 for C₄₉H₆₆O₁₆SNa.

To a solution of protected disaccharide 18, 19, 20 or 22 (0.17 mmol) in MeOH:CH₂Cl₂ (17:1, 4.75 mL) was added 1M MeONa (0.25 mL). After stirring overnight (16 h), the solution was
neutralized with Dowex 50 H⁺-form, filtered and concentrated. The crude product was purified by column chromatography (CH₂Cl₂:MeOH 9:1→5:1) to give partially deprotected disaccharides 23-26 as an oil.

Octyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (23). (0.11 g, 95%); [α]D +46 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CD₃OD): δ 7.39-7.25 (m, 15H, Ar), 4.89 (d, 1H, J₁:₂ = 1.2 Hz, H-1'), 4.88 (d, 1H, J = 11.0 Hz, PhCH₂), 4.81 (d, 1H, J₁:₂ = 1.4 Hz, H-1), 4.70-4.62 (m, 3H, PhCH₂), 4.58 (d, 1H, J = 11.6 Hz, PhCH₂), 4.54 (d, 1H, J = 11.6 Hz, PhCH₂), 3.93-3.58 (m, 13H, H-2, H-3, H-4, H-5, 6a, H-6b, H-2', H-3', H-4', H-5', H-6'a, H-6'b, OCH₂C₆H₁₅), 3.37 (dt, 1H, J = 6.1 Hz, J = 9.7 Hz, OCH₂C₆H₁₅), 1.57-1.51 (m, 2H, OCH₂CH₂C₆H₁₅), 1.38-1.24 (m, 10H, O(CH₂)₂(CH₂)₃CH₃). ¹³C NMR (100 MHz, CD₃OD): δ 140.0, 139.8, 132.5, 130.0-128.8 (Ar), 102.1 (C-1'), 99.1 (C-1), 81.3, 76.4, 76.1(2x), 74.6, 73.8, 73.1, 72.9, 72.8, 72.2, 69.2 (C-2, C-3, C-4, C-5, C-2', C-3', C-4', C-5', 3x PhCH₂), 68.8 (OCH₂C₆H₁₅), 67.5 (C-6), 62.6 (C-6'), 33.1, 30.6(2x), 30.5, 27.5, 23.9 (OCH₂(CH₂)₃CH₃), 14.6 (O(CH₂)₇CH₃). HRMS (MALDI): m/z 747.3695 MNa⁺; calcd 747.3720 for C₄₁H₅₂O₁₁Na.

Cyclohexylmethyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (24). (0.11 g, 90%); [α]D +50 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CD₃OD): δ 7.38-7.26 (m, 15H, Ar), 4.89 (d, 1H, J₁:₂ = 1.3 Hz, H-1'), 4.88 (d, 1H, J = 10.9 Hz, PhCH₂), 4.76 (d, 1H, J₁:₂ = 1.5 Hz, H-1), 4.69 (d, 1H, J = 12.2 Hz, PhCH₂), 4.65-4.62 (m, 2H, PhCH₂), 4.58 (d, 1H, J = 11.6 Hz, PhCH₂), 4.54 (d, 1H, J = 11.7 Hz, PhCH₂), 3.90-3.59 (m, 12H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-2', H-3', H-4', H-5', H-6'a, H-6'b), 3.44 (dd, 1H, J = 6.9 Hz, J = 9.4 Hz, OCH₂C₆H₁₅), 3.16 (dd, 1H, J = 5.9 Hz, J = 9.4 Hz, OCH₂C₆H₁₅), 1.73-0.89 (m, 11H, OCH₂C₆H₁₅). ¹³C NMR (100 MHz, CD₃OD): δ 139.9, 139.8, 139.7, 133.6, 132.5, 129.5-128.8 (Ar), 101.9 (C-1'), 99.1 (C-1), 81.2, 76.3, 76.1(2x), 74.6, 74.3, 73.8, 73.1, 72.8(2x), 72.2, 68.5 (C-2, C-3, C-4, C-5, C-2', C-3', C-4', C-5', 3x PhCH₂, OCH₂C₆H₁₅), 67.5 (C-6), 62.8 (C-6'), 39.2, 31.2, 31.1, 27.7, 27.1, 27.0 (OCH₂C₆H₁₅). HRMS (MALDI): m/z 731.3395 MNa⁺; calcd 731.3407 for C₄₀H₅₂O₁₁Na.

2-Cyclohexylethyl α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (25). (0.11 g, 91%); [α]D +54 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CD₃OD): δ 7.40-7.24 (m, 15H, Ar), 4.89 (br d, 2H, H-1', PhCH₂), 4.79 (d, 1H, J₁:₂ = 1.6 Hz, H-1), 4.72-4.62 (m, 3H,
PhCH₂), 4.59 (d, 1H, J = 11.7 Hz, PhCH₂), 4.54 (d, 1H, J = 11.7 Hz, PhCH₂), 3.91-3.57 (m, 13H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-2', H-3', H-4', H-5', H-6'a, H-6'b, OCH₂CH₂C₆H₁₁), 3.39 (dd, 1H, J₁ = 6.9 Hz, J₂ = 9.4 Hz, OCH₂CH₂C₆H₁₁), 1.74-0.86 (m, 13H, OCH₂CH₂C₆H₁₁).¹³C NMR (100 MHz, CD₃OD): δ 140.0, 139.8 (2x), 133.7, 132.5, 129.6-128.8 (Ar), 102.1 (C-1'), 99.1 (C-1), 81.2, 76.4, 76.1 (2x), 74.6, 73.8, 73.0 (2x), 72.8, 72.2, 68.6 (C-2, C-3, C-4, C-5, C-2', C-3', C-4', C-5'), 67.6 (C-6), 66.7 (OCH₂CH₂C₆H₁₁), 62.9 (C-6'), 38.1, 36.0, 34.7, 34.4, 27.8, 27.6, 27.5 (OCH₂CH₂C₆H₁₁). HRMS (MALDI): m/z 745.3569 MNa⁺; calcd 745.3564 for C₄₁H₅₆O₁₁Na.

Octyl α-d-mannopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-d-mannopyranosyl sulfone (26).

(0.12 g, 89%); [α]D +52 (c 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.70 (m, 2H, Ar), 7.53 (m, 2H, Ar), 7.36-7.19 (m, 11H, Ar), 4.85 (s, 1H, H-1'), 4.79 (d, 1H, J = 11.4 Hz, PhCH₂), 4.76 (d, 1H, J₁₂ = 2.7 Hz, H-1), 4.65-4.58 (m, 4H, 2x PhCH₂), 4.47-4.44 (m, 2H, H-2, PhCH₂), 4.31 (m, 1H, H-5), 4.11 (d, 1H, J₂,₃ = 3.2 Hz, J₃,₄ = 7.8 Hz, H-3), 3.92-3.89 (m, 2H, H-2', H-4'), 3.85-3.76 (m, 4H, H-4, H-6a, H-3', H-6'a), 3.65-3.60 (m, 2H, H-6b, H-6'b), 3.45 (m, 1H, H-5'), 3.01-2.97 (m, 2H, SO₂CH₂C₆H₁₅), 1.77-1.65 (m, 2H, SO₂CH₂CH₂C₆H₁₃), 1.41-1.26 (m, 10H, SO₂(CH₂)₂(CH₂)₅CH₃), 0.92 (t, 3H, J = 7.1 Hz, SO₂(CH₂)₇CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 138.2, 138.0, 137.4, 132.6, 131.1, 129.0-127.8 (Ar), 100.3 (C-1'), 88.5 (C-1), 78.9 (C-3), 75.9 (C-5), 74.3 (PhCH₂), 73.9 (C-4), 73.4 (PhCH₂), 72.9 (PhCH₂), 72.4 (C-5'), 71.8 (C-3'), 71.1, 70.9 (C-2, C-2'), 66.8 (C-6), 66.5 (C-4'), 61.1 (C-6'), 50.1 (SO₂CH₂(CH₂)₅CH₃), 31.9, 29.3, 29.2, 28.7, 22.8, 21.7 (SO₂CH₂(CH₂)₃CH₃), 14.3 (SO₂CH₂(CH₂)₅CH₃). HRMS (MALDI): m/z 795.3394 MNa⁺; calcd 795.3390 for C₄₁H₅₆O₁₂SNa.

Figure S1. LC-MS analysis of the enzymatic reaction mixture of 28. Panel (A) - HPLC profile. Panel (B) - ESI mass spectra obtained from peaks 1-4 in figure (a); all peaks are as [M+Na]^+.
Figure S2. LC-MS analysis of the enzymatic reaction mixture of 30. Panel (a) – HPLC profile.

Panel (b) - ESI mass spectra obtained from peaks 1-5 in figure (a); all peaks are as [M+Na]⁺.
**Figure S3.** MALDI-MS spectra recorded from the enzymatic sample of reference 27 after SPE fractionation. Peaks corresponding to consecutive mannose attachment are in a blue color and are detected as [M+Na]+. Unlabeled peaks originated from membrane protein of ManT.
Figure S4. MALDI-MS spectra recorded from the sample 28 after SPE (a) and after additional microscale ZipTip fractionation (b). Peaks corresponding to consecutive mannose attachment are in a blue color and are detected as [M+Na]+. Unlabeled peaks originated from the cell membrane protein of ManT.
Figure S5. MALDI-MS spectra recorded from the enzymatic sample 30 after SPE fractionation (inset represents a spectrum obtained after additional ZipTip-C18 fractionation). Peaks corresponding to consecutive mannose attachment are in a blue color and are detected as [M+Na]$^+$. Unlabeled peaks originated from membrane protein of ManT.
Figure S6. MALDI-MS spectra recorded from the sample 29: (a) before treatment with mannosidase; (b) after incubation with mannosidase for 2h; and (c) after 8h incubation. All peaks are as [M+Na]^+. Peaks corresponding to saccharide adducts are in blue color.
Figure S7. MALDI-MS spectra recorded from the sample 30: (a) before treatment with mannosidase, (b) after incubation with mannosidase for 2h; and (c) after 8h incubation. All peaks are as [M+Na]+. Peaks corresponding to saccharide adducts are in blue color.