Supporting Information
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Supporting Information

An efficient synthesis of the pentasaccharide repeating unit of *Pseudomonas aeruginosa* Psl exopolysaccharide

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General Information

Materials Optical rotations were measured at room temperature on a Perkin–Elmer 241 automatic polarimeter. TLC analysis was performed on Kieselgel 60 F254 (Merck) silica–gel plates with visualization by immersing in a sulfuric-acid solution (5% in EtOH) followed by heating. Column chromatography was performed on silica gel 60 (Merck 0.063–0.200 mm) and Sephadex LH-20 (Sigma–Aldrich, bead size: 25–100 mm). Organic solutions were dried over MgSO4 and concentrated under vacuum. One- (1D) and two-dimensional (2D) 1H, 13C, COSY and HSQC spectra were recorded on Bruker Avance II 400 (1H: 400 MHz; 13C: 100.28 MHz) spectrometer at 25 °C. Chemical shifts are referenced to SiMe4 or sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS, d = 0.00 ppm for 1H nuclei) and to residual solvent signals (CDCl3: d = 77.00 ppm, CD3OD: d = 49.15 ppm for 13C nuclei). HRMS measurements were carried out on a maXis II UHR ESI-QTOF MS instrument (Bruker) in positive ionization mode. The following parameters were applied for the electrospray ion source: capillary voltage: 3.6 kV; end plate offset: 500 V; nebulizer pressure: 0.5 bar; dry gas temperature: 200 °C and dry gas flow rate: 4.0 L/min. Constant background correction was applied for each spectrum, the background was recorded before each sample by injecting the blank sample matrix (solvent). Na-formate calibrant was injected after each sample which enabled internal calibration during data evaluation. Mass spectra were recorded by otofControl version 4.1 (build: 3.5, Bruker) and processed by Compass DataAnalysis version 4.4 (build: 200.55.2969).

Phenyl 2,4-di-O-acetyl-1-thio-α-L-rhamnopyranoside (13)

To the solution of compound 12 (10.0 g, 0.039 mol) in CH2Cl2 (87 mL) triethyl orthoacetate (57 mL, 0.31 mol, 8 equiv.) and p-TsOH (742 mg, 3.90 mmol, 0.1 equiv.) were added and the reaction mixture was stirred for 24 h at room temperature. When the TLC (6:4 n-hexane/acetone; Rf = 0.65) indicated complete disappearance of the starting material, the reaction was quenched by addition of Et3N (9.5 mL) and all volatiles were evaporated. The crude product (12.7 g) was dissolved in CH2Cl2 (80 mL) and Ac2O (7.37 mL, 78 mmol, 2.0 equiv.), Et3N (16.3 mL, 117 mmol, 3.0 equiv.) and DMAP (476 mg) were added. When the TLC (7:3 n-hexane/acetone; Rf = 0.55) indicated complete disappearance of the starting material (1 h), the reaction mixture was diluted with CH2Cl2 (395 mL), washed with a saturated aqueous solution of NaHCO3 (2 x 150 mL) and water (2 x 150 mL), the organic phase was dried, filtered and concentrated. The crude product (14.4 g) was dissolved in 80% AcOH (286 mL) and the mixture was vigorously stirred for 10 min. After 10 min the reaction mixture was diluted with CH2Cl2 (200 mL), then aqueous solution of NaHCO3 (100 mL) and solid NaHCO3 was added. After the reaction mixture was extracted with CH2Cl2 (3 x 250 mL) then the organic layer was carefully washed with aqueous solution of NaHCO3 (2 x 250 mL) and water (2 x 250 mL) until neutral pH. The organic layer was then dried on MgSO4, filtrated and concentrated. The crude product was purified by crystallization from a mixture of acetone/n-hexane to give 13 (9.03 g, 68% for three steps) as white crystals. Rf = 0.52 (6:4 n-hexane/acetone); [α]D: −135.5 (c 0.20, CHCl3); M. p.: 210-212 °C (from acetone/n-hexane); 1H NMR (400 MHz, CDCl3) δ 7.47-7.25 (m, 5H, arom), 5.48 (d, J1,2 = 1.0 Hz, 1H, H-1), 5.33 (dd, J2,3 = 3.5 Hz, J1,2 = 1.4 Hz, 1H, H-2), 4.94 (t, J3,4 = J4,5 = 9.8 Hz, 1H, H-4), 4.31 (dq, J4,5
= 9.8 Hz, \( J_{5,CH_3} = 6.2 \) Hz, 1H, H-5), 4.02 (ddd, \( J_{3,4} = 9.7 \) Hz, \( J_{3,OH} = 8.4 \) Hz, \( J_{2,3} = 3.5 \) Hz, 1H, H-3), 2.60 (d, \( J_{3,OH} = 8.2 \) Hz, 1H, H-3-OH), 2.15 (s, 6H, 2 x Ac-CH\(_3\)), 1.24 (d, \( J = 6.2 \) Hz, 3H, CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.6, 170.6 (2C, 2 x Ac-CO), 133.6 (1C, C\(_3\) arom), 131.8-127.9 (5C, arom), 85.7 (1C, C-1), 74.9 (1C, C-4), 74.3 (1C, C-2), 69.2 (1C, C-3), 67.4 (1C, C-5), 21.1 (2C, 2 x Ac-CH\(_3\)), 17.4 (1C, 1 x CH\(_3\)) ppm; MS (UHR ESI-QTOF): \( m/z \) calcd for C\(_{14}H\(_20\)NaO\(_6\)S: 363.0873 [M+Na]; Found: 363.0872.

Phenyl [2-O-benzyl-4,6-O-benzylidene-3-O-(2-naphthyl)methyl-\( \beta \)-D-mannopyranosyl]-(1→3)-2,4-di-O-acetyl-1-thio-\( \alpha \)-L-rhamnopyranoside (14) and Phenyl [2-O-benzyl-4,6-O-benzylidene-3-O-(2-naphthyl)methyl-\( \beta \)-D-mannopyranosyl]-(1→3)-2,4-di-O-acetyl-1-thio-\( \alpha \)-L-rhamnopyranoside (15)

**Method I.** A solution of donor 6 (150 mg, 0.2541 mmol), BSP (21.3 g, 0.1016 mmol, 0.4 equiv.), TTBP (57 g, 0.2287 mmol, 0.9 equiv.) and activated 3 Å powdered molecular sieves in dried CH\(_2\)Cl\(_2\) (5.4 mL) was stirred at −60 °C under nitrogen atmosphere for 30 min, then was added Tf\(_2\)O (44 µL, 0.2617 mmol, 1.03 equiv.). After 10 min, acceptor 13 (121 mg, 0.3557 mmol, 1.4 equiv.) in dried CH\(_2\)Cl\(_2\) (2 mL) was added. The reaction mixture was stirred at −60 °C for further 3 h. After 3 h the reaction mixture was quenched by the addition of triethylphosphite (83 µL, 0.4828 mmol, 1.9 equiv.). The mixture was stirred at −60 °C for another 10 min, after which it was warmed up to room temperature. The molecular sieves were filtered off, and the organic layer was washed with saturated aqueous NaHCO\(_3\) solution, brine and dried Na\(_2\)SO\(_4\). The organic layer was concentrated under reduced pressure. The crude product was purified by silica gel chromatography (7:3 \( \rightarrow \) 55:45 n-hexane/EtOAc) to give 14 (62 mg, 31%) as a white foam, 6 (50 mg, 33%) as a white foam and 13 (46 mg, 38%) as a white foam.

**Method II.** A mixture of thiomannosyl donor 6 (1.5 g, 2.541 mmol), BSP (532 mg, 2.541 mmol, 1 equiv.), TTBP (1.26 n g, 5.082 mmol, 2.0 equiv.) and 4 Å molecular sieves (3.3 g) in CH\(_2\)Cl\(_2\) (34 mL) was stirred under an atmosphere of Argon for 1 h. The reaction was cooled (−60 °C) and Tf\(_2\)O (470 µL, 2.795 mmol, 1.1 equiv.) was added. After 30 min of stirring at −60 °C, a solution of the acceptor 13 (1.21 g, 3.554 mmol, 1.4 equiv.) in CH\(_2\)Cl\(_2\) (18.3 mL) was added. The reaction mixture was stirred for further 1 h at −60 °C. After 1 h the reaction mixture was quenched by the addition of triethylphosphite (828 µL, 4.828 mmol, 1.9 equiv.). The mixture was filtered, and the filtrate was washed with saturated NaHCO\(_3\) (100 mL) and brine (100 mL). The organic phase was dried (MgSO\(_4\)), filtered and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (7:3 n-hexane/EtOAc) to give 14 (827 mg, 40%) as a white foam.

**Method III.** A mixture of thiomannosyl donor 6 (270 mg, 0.457 mmol), BSP (96 mg, 0.4575 mmol, 1 equiv.), TTBP (227 mg, 0.915 mmol, 2.0 equiv.) and 4 Å molecular sieves (0.6 g) in CH\(_2\)Cl\(_2\) (6.2 mL) was stirred under an atmosphere of Argon for 1 h. The reaction was cooled (−60 °C) and Tf\(_2\)O (92 µL, 0.549 mmol, 1.2 equiv.) was added. After 30 min of stirring at −60 °C, a solution of the acceptor 13 (218 mg, 0.869 mmol, 1.4 equiv.) in CH\(_2\)Cl\(_2\) (3.3 mL) was
added. The reaction mixture was stirred for further 1 h at −60 °C. After 1 h the reaction mixture was quenched by the addition of triethylphosphate (149 µL, 0.869 mmol). The mixture was filtered, and the filtrate (100 mL) was washed with saturated NaHCO₃ (70 mL) and brine (60 mL). The organic phase was dried (MgSO₄), filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel chromatography (7:3 → 55:45 n-hexane/EtOAc) to give 14 (200 mg, 54%) as a colourless syrup and 15 (32 mg, 8.5%) as a colourless syrup.

Data of 14: [α]D²⁵ −34.5 (c 0.20, CHCl₃); Rf = 0.44 (7:3 n-hexane/EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.25 (m, 22H, arom), 5.63 (s, 1H, Hα), 5.48 (d, J₁₂ = 1.3 Hz, 1H, H-1), 5.39 (dd, J₂,₂ = 3.3 Hz, J₁,₂ = 1.6 Hz, 1H, H-2), 5.21 (t, J₃,₄ = J₄,₅ = 9.8 Hz, 1H, H-4), 4.95-4.70 (m, 4H, NAP-CH₂, Bn-CH₂), 4.54 (s, 1H, H-1'), 4.32 (dd, J = 10.5 Hz, J = 4.9 Hz, 1H, H-6'a), 4.26-4.09 (m, 2H, H-4', H-5), 4.03 (dd, J₃,₄ = 9.8 Hz, J₂,₃ = 3.4 Hz, 1H, H-3), 3.90 (t, J = 10.3 Hz, 1H, H-6'b), 3.75 (d, J₂,₃ = 3.1 Hz, 1H, H-2'), 3.55 (dd, J₂,₃ = 3.2 Hz, J₃,₄ = 9.9 Hz, 1H, H-3'), 3.32 (dd, J = 9.8 Hz, J = 4.9 Hz, 1H, H-5'), 2.00. 1.85 (2 x s, 6H, 2 x Ac-CH₃), 1.21 (d, J = 6.2 Hz, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 169.8 (2C, 2 x Ac-CO), 138.6, 137.7, 135.8, 133.5, 133.3, 133.1 (6C, 6 x C₅ arom), 131.8-125.8 (22C, arom), 103.6 (1C, J₁'-H₁' = 152.5 Hz, C-1'), 101.6 (1C, C₆₅₋), 85.5 (1C, C-1), 78.3 (1C, C-4'), 77.1 (1C, C-3'), 76.2 (1C, C-2'), 76.1 (1C, C-3), 74.7 (1C, Bn-CH₂), 73.9 (1C, C-2), 73.0 (1C, C-4), 72.3 (1C, Bn-CH₂), 68.6 (1C, C-6'), 67.9 (1C, C-5'), 67.8 (1C, C-5), 21.0, 20.8 (2C, 2 x Ac-CH₃), 17.5 (1C, 1 x CH₃) ppm; MS (UHR ESI-QTOF): m/z calcd for C₄₇H₄₈NaO₁₁S: 843.2810 [M+Na]; Found: 843.2810.

Data of 15: [α]D²⁵ −15.0 (c 0.20, CHCl₃); Rf = 0.53 (7:3 n-hexane/EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.25 (m, 22H, arom), 5.64 (s, 1H, Hα), 5.55 (dd, J₂,₂ = 2.9 Hz, J₁,₂ = 1.3 Hz, 1H, H-2), 5.40 (s, 1H, H-1), 5.07 (s, 1H, H-1'), 5.02 (t, J₃,₄ = J₄,₅ = 9.8 Hz, 1H, H-4), 4.82-4.65 (m, 4H, NAP-CH₂, Bn-CH₂), 4.32-4.27 (m, 2H, H-5, H-6'a), 4.25 (t, J₅,₄ = J₄,₅ = 9.7 Hz, 1H, H-4'), 4.08 (dd, J₃,₄ = 9.8 Hz, J₂,₃ = 3.3 Hz, 1H, H-3), 3.90 (t, J = 10.3 Hz, 1H, H-6'b), 3.81-3.75 (m, 2H, H-3', H-5'), 3.58-3.57 (m, 1H, H-2'), 2.02, 1.94 (2 x s, 6H, 2 x Ac-CH₃), 1.22 (d, J = 6.2 Hz, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 170.1 (2C, 2 x Ac-CO), 138.2, 137.8, 136.0, 133.4, 133.3, 133.0 (6C, 6 x C₅ arom), 131.8-125.8 (22C, arom), 101.9 (1C, C₆₅₋), 95.2 (1C, J₁'-H₁' = 171.4 Hz, C-1'), 86.1 (1C, C-1), 78.6 (1C, C-4'), 75.9 (1C, C-3'), 75.7 (1C, C-2'), 73.1, 73.0 (2C, 2 x Bn-CH₂), 71.7 (1C, C-4), 70.6 (1C, C-3), 69.0 (1C, C-2), 68.9 (1C, C-6'), 67.9 (1C, C-5), 64.8 (1C, C-5'), 21.1, 20.8 (2C, 2 x Ac-CH₃), 17.5 (1C, 1 x CH₃) ppm; MS (UHR ESI-QTOF): m/z calcd for C₄₇H₄₈NaO₁₁S: 843.2810 [M+Na]; Found: 843.2805.

4-Methoxyphenyl [2-O-benzyl-4,6-O-benzylidene-3-O-(2-naphtyl)methyl-β-D-mannopyranosyl]-(1→3)-[2,4-di-O-acetyl-α-L-rhamnopyranosyl]-(1→3)-2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (16)

To a solution of the acceptor 9 (377 mg, 0.812 mmol) and disaccharide donor 14 (1000 mg, 1.219 mmol, 1.5 equiv.) in dry CH₂Cl₂ (27.0 mL) 4 Å MS (50 pieces) were added and the reaction mixture was stirred at room temperature. After 30 min the stirred mixture was cooled to −20 °C under argon. After at this temperature, NIS (411 mg, 1.828 mmol, 1.5 equiv. to the donor) and TfOH (48.0 µL, 0.548 mmol, 0.3 equiv. to NIS) dissolved in dry THF (1.5 mL)
were added. The temperature was allowed to warm up to 0 °C and the reaction mixture was stirred for 3 h. Then reaction mixture was quenched with Et$_3$N (500 μL), diluted with CH$_2$Cl$_2$ (250 mL), filtered and the mixture was washed with saturated aqueous solution of Na$_2$S$_2$O$_3$ (2 x 50 mL), saturated aqueous solution of NaHCO$_3$ (50 mL) and H$_2$O (2 x 50 mL) until neutral pH. The organic layer was dried on MgSO$_4$ and concentrated. The crude product was purified by silica gel chromatography (97:3 CH$_2$Cl$_2$/EtOAc) to give 16 (1038 mg, 73%) as a colourless syrup. $[\alpha]_{D}^{25}$ = -45.5 (c 0.24, CHCl$_3$); $R_f = 0.29$ (97:3 CH$_2$Cl$_2$/EtOAc); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80-6.81 (m, 31H, arom), 5.62 (s, 1H, Hac), 5.52 (s, 1H, Hac), 5.36 (s, 1H, H-2'), 5.27 (s, 1H, H-1'), 5.05 (t, J$_{3',4'} = J_{4',5'} = 9.7$ Hz, 1H, H-4'), 4.99 (d, J$_{1,2} = 7.6$ Hz, 1H, H-1), 4.94-4.69 (m, 6H, NAP-CH$_2$, 2 x Bn-Ch$_2$), 4.49 (s, 1H, H-1''), 4.34 (dt, J = 10.0 Hz, J = 4.8 Hz, 2H, H-6a, H-6'a), 4.19 (t, J$_{3',4'} = J_{4',5'} = 9.3$ Hz, 1H, H-4''), 4.13-4.08 (m, 1H, H-5'), 4.03-3.97 (m, 2H, H-3, H-3'), 3.91 (t, J = 10.2 Hz, 1H, H-6'b), 3.79-3.73 (m, 6H, H-2, H-2', H-6b, OCH$_3$), 3.63 (t, J$_{3',4'} = J_{4',5'} = 9.4$ Hz, 1H, H-4), 3.52-3.46 (m, 2H, H-3', H-5), 3.32 (td, J = 9.4 Hz, J = 4.8 Hz, 1H, H-5''), 2.02, 1.97 (2 x s, 6H, 2 x Ac-Ch$_3$), 0.77 (d, J = 4.6 Hz, 3H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.8, 169.6 (2C, 2 x Ac-CO), 155.6, 150.9, 138.6, 137.7, 137.6, 137.1, 135.8, 133.2, 133.0 (9C, 9 x C$_q$ arom), 129.2-114.7 (31C, arom), 103.4 (1C, C-1'), 103.1 (1C, C-1), 101.8, 101.5 (2C, 2 x C$_a$), 97.6 (1C, C-1'), 82.2 (1C, C-2'), 79.0 (1C, C-4), 78.3 (1C, C-4'), 76.9 (1C, C-3'), 76.3, 76.1 (2C, C-2', C-3'), 75.8 (1C, C-3), 75.1, 74.6 (2C, 2 x Bn-Ch$_2$), 73.1 (1C, C-4'), 72.1 (1C, Bn-Ch$_2$), 71.8 (1C, C-2'), 68.8 (1C, C-6), 68.6 (1C, C-6'), 67.8 (1C, C-5''), 66.3 (1C, C-5), 66.0 (1C, C-5'), 55.7 (1C, OCH$_3$), 20.9, 20.7 (2C, 2 x Ac-Ch$_3$), 16.8 (1C, 1 x CH$_3$) ppm; MS (UHR ESI-QTOF): m/z calcd for C$_{68}$H$_{70}$NaO$_{18}$: 1179.4454 [M+Na]$^+$; Found: 1179.4444.

4-Methoxyphenyl [2-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl-(1→3)[2,4-di-O-acetyl-a-L-rhamnopyranosyl-(1→3)]2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (17)

Compound 16 (111 mg, 0.094 mmol) was dissolved in the mixture of CH$_2$Cl$_2$ (1.46 mL) and water (161 μL) then DDQ were added (32 mg, 0.1413 mmol,) and the reaction mixture was stirred for 1.5 h at room temperature. After 1.5 h the reaction mixture was diluted with CH$_2$Cl$_2$ (50 mL), washed with saturated aqueous solution of NaHCO$_3$ (2 x 20 mL) and with water (3 x 20 mL) until neutral pH. The organic phase was dried over MgSO$_4$, filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel chromatography (6:4 n-hexane/EtOAc) to give 17 (80 mg, 83 %) as a colourless syrup. $[\alpha]_{D}^{25}$ +59.6 (c 0.15, CHCl$_3$); $R_f = 0.36$ (6:4 n-hexane/EtOAc); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49-6.82 (m, 24H, arom), 5.57 (s, 1H, Hac), 5.51 (s, 1H, Hac), 5.39 (d, J$_{2,3} = 3.3$ Hz, 1H, H-2'), 5.27 (s, 1H, H-1'), 5.06 (t, J$_{3',4'} = J_{4',5'} = 9.9$ Hz, 1H, H-4'), 5.01 (d, J$_{1,2} = 7.6$ Hz, 1H, H-1), 4.97-4.88 (m, 3H, NAP-CH$_2$, Bn-Ch$_{2a}$), 4.65 (s, 1H, H-1''), 4.53 (d, J = 11.6 Hz, 1H, Bn-Ch$_{2a}$), 4.39-3.40 (m, 2H, H-6a, H-6'a), 4.17 (dd, J$_{3',5'} = 10.0$ Hz, J$_{5',3} = 6.2$ Hz, 1H, H-5'), 4.05 (dd, J$_{3',4'} = 10.2$ Hz, J$_{2',3'} = 3.0$ Hz, 1H, H-3'), 4.02 (t, J$_{2,3} = J_{3,4} = 9.2$ Hz, 1H, H-3), 3.86-3.71 (m, 9H, H-2, H-2', H-3', H-4', H-6b, H-6'b, OCH$_3$), 3.67 (t, J$_{3',4'} = J_{4',5'} = 9.5$ Hz, 1H, H-4), 3.52 (td, J = 9.7 Hz, J = 4.9 Hz, 1H, H-5), 3.32 (td, J = 9.6 Hz, J = 4.9 Hz, 1H, H-5'), 2.51 (d, J = 8.2 Hz, 1H, H-3''-OH), 1.98, 1.94 (2 x s, 6H, 2 x Ac-Ch$_3$), 0.80 (d, J = 6.2 Hz, 3H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.8, 169.7 (2C, 2 x Ac-CO), 155.7, 150.9, 138.2, 137.6, 137.3, 137.2 (6C, 6 x C$_q$ arom), 129.2-114.7 (24C, arom), 103.4 (1C, C-1''), 103.1 (1C, C-1), 102.0, 101.8 (2C, 2 x C$_a$), 97.6 (1C, C-1'), 82.2 (1C, C-2), 79.3 (1C, C-
4"), 79.0 (1C, C-4), 78.0 (1C, C-2"), 76.2 (1C, C-3"), 76.1 (1C, C-3), 75.1, 75.0 (2C, 2 x Bn-
CH₂), 72.9 (1C, C-4"), 71.8 (1C, C-2"), 70.4 (1C, C-3"), 68.8 (1C, C-6), 68.6 (1C, C-6'), 67.1 (1C, C-5"), 66.4 (1C, C-5), 66.0 (1C, C-5'), 55.7 (1C, OCH₃), 21.0, 20.9 (2C, 2 x Ac-CH₃),
16.8 (1C, 1 x CH₃) ppm; MS (UHR ESI-QTOF): m/z calc'd for C₅₇H₉₈NaO₁₈$: 1057.3828
[M+Na]$; Found: 1057.3829.

4-Methoxyphenyl [2-O-terc-butyldimethylsilyl-4,6-O-benzylidene-3-O-(2-
naphthyl)methyl-β-d-mannopyranosyl)-(1→3)][2-O-benzyl-4,6-O-benzylidene-β-d-
mannopyranosyl)-(1→3)][2,4-di-O-acetyl-a-l-rhamnopyanosyl][(1→3)-2-O-benzyl-4,6-
O-benzylidene-β-d-glucopyranoside (18)

A mixture of thiomannosyl donor 5 (665 mg, 1.083 mmol, 1.6 equiv.), BSP (272 mg, 1.299
mmol, 1.2 equiv.), TTBP (538 mg, 2.165 mmol, 2.0 equiv.) and 4 Å molecular sieves (1.5 g)
in dry CH₂Cl₂ (15.0 mL) was stirred under an atmosphere of Argon for 1 h. The reaction was
cooled (−60 °C) and Tf₂O (218 μL, 1.299 mmol, 1.2 equiv.) was added. After 30 min of
stirring at −60 °C, a solution of the acceptor 17 (700 mg, 0.677 mmol) in CH₂Cl₂ (5.0 mL)
was added. The reaction mixture was stirred for further 1 h at −60 °C. After 1 h the reaction
mixture was quenched by the addition of pyridine (2.67 mL). The mixture was filtered, and
the filtrate (100 mL) was washed with saturated aqueous solution of NaHCO₃ (70 mL) and
brine (60 mL). The organic phase was dried over MgSO₄, filtered and the filtrate was
concentrated under reduced pressure. The crude product was purified by silica gel
chromatography (7.3 n-hexane/EtOAc) to give 18 (819 mg, 79 %) as a white foam. [α]D
²⁵
−59.0 (c 0.12, CHCl₃); Rf = 0.39 (7.3 n-hexane/EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 7.82-
6.82 (m, 36H, arom), 5.57 (s, 2H, 2 x Hac), 5.50 (s, 1H, Hac), 5.38 (d, J₂,₃ = 3.4 Hz, 1H, H-
2'), 5.26 (s, 1H, H-1'), 5.08 (t, J₃,₄ = J₃,₅ = 9.8 Hz, 1H, H-4'), 5.01 (d, J₁,₂ = 7.6 Hz, 1H, H-
1), 4.97-4.78 (m, 5H, NAP-CH₂, Bn-CH₂, Bn-CH₂), 4.60 (s, 1H, H-1"), 4.57 (d, J = 12.4 Hz,
1H, Bn-CH₂), 4.39-4.32 (m, 2H, H-6a, H-6"a), 4.17-4.11 (m, 2H, H-5', H-6'a), 4.05 (dd,
J₃,₄ = J₃,₅ = 3.4 Hz, H-3' = 10.0 Hz, 1H, H-3''), 4.02-3.97 (m, 3H, H-3', H-4', H-4''), 3.94-3.88 (m,
3H, H-1'"), H-3'"), H-6'"b, 3.85-3.72 (m, 8H, H-2, H-2"), H-2'"), H-6b, H-6"b, OCH₃), 3.67 (t,
J₃,₄ = J₄,₅ = 9.4 Hz, 1H, H-4), 3.52 (td, J = 9.7 Hz, J = 5.0 Hz, 1H, H-5), 3.38 (td, J = 9.7 Hz, J
= 4.7 Hz, 1H, H-5'"), 3.23 (dd, J₂,₃ = 2.5 Hz, J₂,₄ = 9.6 Hz, 1H, H-3"), 2.96 (dd, J = 9.7 Hz, J
= 4.8 Hz, 1H, H-5'"), 1.97, 1.95 (2 x s, 6H, 2 x Ac-CH₃), 0.80-0.78 (m, 12H, 3 x t-Bu-CH₃,
CH₂), 0.06, -0.05 (2 x s, 6H, 2 x CH₂ TBS) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 169.7
(2C, 2 x Ac-CO), 155.7, 151.0, 138.3, 137.8, 137.7, 137.6, 137.2, 136.2, 133.4, 133.0 (10C,
10 x C₉ arom), 129.3-114.8 (36C, arom), 103.7 (1C, C-1"), 103.2 (1C, C-1), 102.1, 101.9,
101.7 (3C, 3 x Cac), 97.7 (1C, C-1"), 96.3 (1C, C-1"'), 82.2 (1C, C-2), 79.1 (1C, C-4), 78.9
(1C, C-3), 77.7 (1C, C-3"), 76.6 (1C, C-4"), 76.2 (1C, C-4"'), 76.0 (1C, C-3"), 75.2, 73.9 (2C,
2 x Bn-CH₂), 73.6 (1C, C-3'"), 73.3 (1C, C-4'), 73.0 (1C, C-2'"), 71.9 (1C, NAP-CH₂), 71.8
(1C, C-2"), 70.8 (1C, C-2'"), 69.0, 68.9, 68.7 (3C, 3 x C-6), 68.2 (1C, C-5"'), 67.7 (1C, C-5"),
66.5 (1C, C-5), 66.0 (1C, C-5'), 55.8 (1C, OCH₃), 26.0 (3C, 3 x t-Bu-CH₃), 21.0, 20.9 (2C, 2
x Ac-CH₃), 18.5 (1C, C₉ t-Bu), 16.9 (1C, 1 x CH₃), -4.3, -4.6 (2C, 2 x CH₃ TBS) ppm; MS (UHR
Compound 18 (805 mg, 0.523 mmol) was dissolved in dry THF (11 mL) and the reaction mixture was cooled to 0 °C. After 1M solution of TBAF in dry THF (1.046 mL, 2.0 equiv.) was added and the reaction mixture was stirred for 24 h at room temperature. After 24 h the reaction mixture was diluted with EtOAc (300 mL) washed with water (75 mL) and brine (75 mL). The crude product was purified by silica gel chromatography (6:4 n-hexane/acetonitrile) to give 19 (718 mg, 96%) as a white foam. [α]25D = −55.8 (c 0.12, CHCl3); Rf = 0.34 (6:4 n-hexane/acetonitrile); 1H NMR (400 MHz, CDCl3) δ 7.90-6.87 (m, 36H, arom), 5.61, 5.59, 5.48 (3 x s, 3H, 3 x Hα), 5.42 (d, J = 3.4 Hz, 1H, H-2”), 5.32 (s, 1H, H-1”), 5.13 (t, J = 9.3 Hz, 1H, H-4”), 5.06 (d, J = 11.7 Hz, 1H, H-1’), 5.01-4.84 (m, 5H, NAP-CH2, Bn-CH2, Bn-CH2α), 4.65 (s, 1H, H-1”), 4.63 (d, J = 12.8 Hz, 1H, Bn-CH2β), 4.44-4.38 (m, 2H, H-6a, H-6”a), 4.22-3.76 (m, 17H), 3.72 (t, J = 9.4 Hz, 1H, H-4’), 3.57 (td, J = 9.7 Hz, J = 5.0 Hz, 1H), 3.46-3.38 (m, 2H), 3.04 (td, J = 9.8 Hz, J = 4.9 Hz, 1H), 2.86 (s, 1H, H-2”-OAc), 2.05, 2.01 (2 x s, 6H, 2 x Ac-CH2), 0.85 (d, J = 6.1 Hz, 3H, CH3) ppm; 13C NMR (100 MHz, CDCl3) δ 169.8, 169.6 (2C, 2 x Ac-CO), 155.7, 151.0, 138.1, 137.7, 137.5, 137.3, 135.7, 133.4, 133.2 (10C, 10 x Cq arom), 129.2-114.8 (36C, arom), 103.4 (1C, C-1”), 103.2 (1C, C-1’), 101.9, 101.8, 101.5 (3C, 3 x Cac), 97.6 (1C, C-1”), 96.0 (1C, C-1”), 82.2, 79.1, 78.4, 76.5, 76.2, 76.0, 75.6, 73.6, 73.3, 71.8, 69.6, 67.9, 67.0, 66.4, 66.0 (16C, skeleton carbons), 75.2, 74.0, 72.1 (3C, 2 x Bn-CH2, NAP-CH2), 68.9, 68.7 (3C, 3 x C-6), 55.8 (1C, OCH3), 21.0 (2C, 2 x Ac-CH3), 16.9 (1C, 1 x CH3) ppm; MS (UHR ESI-QTOF): m/z calcd for C81H84NaO23: 1447.5296 [M+Na]+; Found: 1447.5298.

4-Methoxyphenyl [2,3,4,6-tetra-O-acetyl-α-L-rhamnopyranosyl]-[(1→2)-[4,6-O-benzylidene-3-O-(2-naphthyl)methyl-β-d-mannopyranosyl]-[(1→3)-[2-O-benzyl-4,6-O-benzylidene-β-d-mannopyranosyl]-[(1→3)-[2,4-di-O-acetyl-α-L-rhamnopyranosyl]-[(1→3)-2-O-benzyl-4,6-O-benzylidene-β-d-glucopyranoside (20)

Method I.: To a solution of acceptor 19 (615 mg, 0.4317 mmol, 1.0 equiv.) and donor 10 (314 mg, 0.712 mmol, 1.5 equiv.) in dry CH2Cl2 (16.5 mL) 4 Å MS (25 pieces) were added and the reaction mixture was stirred at room temperature. After 30 min the stirred mixture was cooled to −20 °C under argon. After at this temperature, NIS (240 mg, 1.068 mmol, 1.5 equiv. to the donor) was dissolved in dry THF (427 μL) and TfOH (19 μL, 0.2137 mmol, 0.3 equiv. to the donor) were added. The temperature was allowed to warm up to 0 °C and the reaction mixture was stirred for 4 h. After 4 h the reaction mixture was quenched with Et3N (1 mL), diluted with CH2Cl2 (250 mL), filtered and the mixture was extracted with saturated
aqueous solution of Na₂S₂O₃ (2 x 100 mL), saturated aqueous solution of NaHCO₃ (100 mL) and with H₂O (2 x 100 mL) until neutral pH. The organic layer was dried on MgSO₄ and concentrated. The crude product was purified by silica gel chromatography (65:35 n-hexane/acetoneto) to give 20 (0 mg, 0%) and 19 (600 mg, starting tetrasaccharide acceptor) as a colourless syrup.

**Method II.** To a solution of donor 11 (247 mg, 0.503 mmol, 1.5 equiv.) and acceptor 19 (398 mg, 0.280 mmol, 1.0 equiv.) in dry CH₂Cl₂ (7.6 mL) 4 Å MS were added then the reaction mixture was stirred at room temperature. After 30 min the stirred mixture was cooled to −20 °C under argon. After at this temperature, TMSOTf (22.8 µL, 0.1257 mmol, 0.25 equiv. to the donor) diluted with dry CH₂Cl₂ (188 µL) was added. The temperature was allowed to warm up to 0 °C and the reaction mixture was stirred for 4 h. After 4 h the reaction mixture was quenched with Et₃N (159 µL), and concentrated. The crude product was purified by silica gel chromatography (95:5 CH₂Cl₂/acetoneto) to give 20 (407 mg, 83%) as a colourless syrup. [α]D²⁵ 

\[ \text{H NMR (400 MHz, CDCl₃): } R_I = 0.58 \text{ (95:5 CH₂Cl₂/acetoneto)} \]

\[ \text{1H NMR (400 MHz, CDCl₃): } \delta 7.84-6.83 \text{ (m, 36H, arorn), } 5.69 \text{ (s, 1H, H₃ac), } 5.57 \text{ (s, 1H, H₄ac), } 5.56 \text{ (s, 2H, H₅ac, H-2-V.), } 5.39 \text{ (dd, } J_{1,2} = 1.5 \text{ Hz, } J_{2,3} = 3.3 \text{ Hz, 1H, H-2-II.), } 5.33 \text{ (dd, } J_{2,3} = 3.3 \text{ Hz, } J_{3,4} = 10.3 \text{ Hz, 1H, H-3-V.), } 5.29-5.26 \text{ (m, 2H, H-1-II., H-4-V.), } 5.23 \text{ (s, 1H, H-1-V.), } 5.09 \text{ (t, } J_{3,4} = 9.9 \text{ Hz, 1H, H-4-II.), } 5.02 \text{ (d, } J_{1,2} = 7.7 \text{ Hz, 1H, H-1-I.), } 5.01-4.62 \text{ (m, 6H, NAP-CH₂, 2 x Bn-CH₂), } 4.61-4.59 \text{ (m, 2H, H-1-III., H-5-V.), } 4.40-4.33 \text{ (m, 3H, H-6a-I., H-6a-III., H-6a-V.), } 4.22 \text{ (dd, } J = 4.8 \text{ Hz, } J = 10.5 \text{ Hz, 1H, H-6a-IV.), } 4.18-4.13 \text{ (m, 2H, H-4-IV., H-5-II.), } 4.08 \text{ (dd, } J_{3,4} = 3.1 \text{ Hz, } J_{2,3} = 9.4 \text{ Hz, 1H, H-3-II.), } 4.04-4.00 \text{ (m, 2H, H-3-I., H-6b-V.), } 3.98-3.91 \text{ (m, 4H, H-1-I., H-3-III., H-6b-III., H-6b-IV.), } 3.89 \text{ (d, } J = 9.8 \text{ Hz, 1H, H-4-III.), } 3.83-3.74 \text{ (m, 7H, H-2-I., H-2-II., H-2-IV., H-6b-I., OCH₃), } 3.68 \text{ (t, } J_{3,4} = 9.4 \text{ Hz, 1H, H-4-I.), } 3.53 \text{ (dd, } J = 9.6 \text{ Hz, } J = 5.0 \text{ Hz, 1H, H-5-I.), } 3.36 \text{ (dd, } J_{2,3} = 3.1 \text{ Hz, } J_{3,4} = 9.5 \text{ Hz, 1H, H-3-IV.), } 3.36-3.33 \text{ (m, 1H, H-5-III.), } 3.08 \text{ (td, } J = 9.7 \text{ Hz, } J = 5.0 \text{ Hz, 1H, H-5-IV.), } 2.09, 2.04, 1.98, 1.93, 1.35 \text{ (5 x s, 18H, 6 x Ac-CH₃), } 0.80 \text{ (d, } J = 6.2 \text{ Hz, 3H, } CH₃ \text{ ppm); } ^{13}C \text{ NMR (100 MHz, CDCl₃): } \delta 170.9, 170.0, 169.8, 169.7 \text{ (6C, 6 x Ac-CO), } 155.6, 150.9, 137.8, 137.6, 137.4, 137.3, 135.6, 133.2, 133.0 \text{ (10C, 10 x C₆ arorn), } 129.4-114.7 \text{ (36C, arorn), } 103.4 \text{ (1C, C-1-III.), } 103.1 \text{ (1C, C-1-I.), } 101.8, 101.5, 100.5 \text{ (3C, 3 x C₃₆), } 99.3 \text{ (1C, C-1-V.), } 97.5 \text{ (1C, C-1-II.), } 95.3 \text{ (1C, C-1-IV.), } 82.2 \text{ (1C, C-2-I.), } 79.0 \text{ (2C, C-4-I., C-4-IV.), } 77.6 \text{ (1C, C-3-IV.), } 76.0 \text{ (1C, C-3-I.), } 75.9 \text{ (2C, C-3-II., C-4-III.), } 75.1 \text{ (1C, Bn-CH₂), } 75.0 \text{ (1C, C-2-IV.), } 73.7 \text{ (1C, Bn-CH₂), } 73.6 \text{ (1C, C-3-III.), } 73.2 \text{ (1C, NAP-CH₂), } 73.1 \text{ (1C, C-4-II.), } 71.7 \text{ (1C, C-2-III.), } 71.6 \text{ (1C, C-2-II.), } 69.9 \text{ (1C, C-3-V.), } 69.4 \text{ (1C, C-2-IV.), } 68.8 \text{ (1C, C-6-I.), } 68.5 \text{ (1C, C-5-V.), } 68.4 \text{ (1C, C-6-IV.), } 68.3 \text{ (1C, C-6-III.), } 68.0 \text{ (1C, C-5-III.), } 67.4 \text{ (1C, C-5-IV.), } 66.4 \text{ (1C, C-5-I.), } 65.9 \text{ (1C, C-5-II.), } 65.1 \text{ (1C, C-4-V.), } 61.8 \text{ (1C, C-6-V.), } 55.7 \text{ (1C, OCH₃), } 21.1, 21.0, 20.9, 20.8, 20.7, 19.9 \text{ (6C, 6 x Ac-CH₃), } 16.8 \text{ (1C, 1 x CH₃) ppm; MS (UHR ESI-QTOF): m/z calc'd for C₉₈H₁₀₀NaO₂₅: } 1777.6246 \text{ [M+Na]⁺; Found: 1777.6245.} \]

**4-Methoxyphenyl α-d-mannopyranosyl-(1→2)-β-d-mannopyranosyl-(1→3)-β-d-mannopyranosyl-(1→3)-α-l-rhamnopyranosyl-(1→3)-β-d-glucopyranoside (8)**

[Diagram of the compounds and reaction scheme]

Compound 20 (396 mg, 0.226 mmol) was dissolved in MeOH (10 mL) then NaOMe was added (pH ≈ 10-12) and the reaction mixture was stirred for 24 h at room temperature. After 24 h the reaction mixture was neutralized by Amberlite IR-120 (H⁺) ion-exchange resin then it was filtered, washed with MeOH and concentrated. [α]D²⁵ 

\[ \text{[α]D²⁵ = -36.7 \text{ (c 0.25, CHCl₃); } R_I = 0.51 \text{ (9:1 CH₂Cl₂/MeOH); MS (UHR ESI-QTOF): m/z calc'd for C₈₃H₉₀NaO₂₆: } 1525.5613} \]
[M+Na]$^+$; Found: 1525.5622. The crude product was reacted further without purification. A mixture of the crude product (339 mg, 0.226 mmol), which was dissolved in EtOH (17.0 mL) /AcOH (96%, 1.0 mL), and Pd/C (10%, 235 mg) was stirred in an autoclave under a H$_2$ atmosphere (10 bar) for 24 h. The reaction mixture was diluted with MeOH, filtered through a pad of Celite$^6$ and the filtrate was concentrated. The crude product was purified by silica gel column chromatography (7:6:1 CH$_2$Cl$_2$/MeOH/H$_2$O) to give compound 8 (145 mg, 70% for two steps) as a white solid. [$\alpha$]$^{25}_D$ $-13.5$ ($c$ 0.14, MeOH); $R_f$ = 0.29 (7:6:1 CH$_2$Cl$_2$/MeOH/H$_2$O); $^1$H NMR (400 MHz, D$_2$O) $\delta$ 7.01-6.85 (m, 4H, arom), 5.08 (s, 2H, H-1-II., H-1-V.), 4.90 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1-I.), 4.76 (s, 2H, H-1-III., H-1-IV.), 4.21-4.19 (m, 2H, H-2-III., H-2-V.), 4.11-4.08 (m, 2H, H-2-IV., H-5-V.), 3.99-3.96 (m, 2H, H-2-II., H-5-II.), 3.87-3.83 (m, 2H, H-3-V., H-3-II.), 3.80-3.76 (m, 5H, H-3-III., 4 x H-6a), 3.69 (s, 3H, OCH$_3$), 3.66-3.44 (m, 13H, H-2-I., H-3-I., H-4-I., H-5-I., H-4-II., H-4-III., H-3-IV., H-4-IV., H-4-V., 4 x H-6b), 3.32-3.27 (m, 2H, H-5-III., H-5-IV.), 1.16 (d, $J$ = 6.2 Hz, 3H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 154.7, 150.8 (2C, 2 x C$_q$ arom), 118.2, 115.0 (4C, arom), 101.2 (1C, C-1-III.), 101.1 (1C, C-1-V.), 101.0 (1C, C-1-I.), 100.6 (1C, C-1-II.), 96.6 (1C, C-1-IV.), 81.8 (1C, C-3-I.), 79.4 (1C, C-3-V.), 79.1 (1C, C-3-III.), 76.8 (1C, C-5-IV.), 76.0 (1C, C-5-I.), 75.6 (1C, C-2-IV.), 71.0 (1C, C-4-V.), 70.3 (1C, C-2-V.), 70.2 (1C, C-3-III.), 70.0 (1C, C-2-II.), 68.8 (1C, C-5-II.), 67.8 (1C, C-4-I.), 67.6 (1C, C-2-III.), 66.8 (1C, C-4-IV.), 66.5 (1C, C-4-II.), 65.0 (1C, C-4-III.), 61.0, 60.9, 60.7, 60.5 (4C, 4 x C-6), 55.7 (1C, OCH$_3$), 16.5 (1C, 1 x CH$_3$) ppm; MS (UHR ESI-QTOF): m/z calcld for C$_{37}$H$_{58}$NaO$_{26}$: 941.3109 [M+Na]$^+$; Found: 941.3112.
$^1$H and $^{13}$C spectra of compound 8:
$^1$H and $^{13}$C spectra of compound 13:
$^1$H and $^{13}$C spectra of compound 14:
$^1$H and $^{13}$C spectra of compound 15:
$^1$H and $^{13}$C spectra of compound 16:
$^1$H and $^{13}$C spectra of compound 17:
$^{1}$H and $^{13}$C spectra of compound 18:
$^1$H and $^{13}$C spectra of compound 19:
$^1$H and $^{13}$C spectra of compound 20: