Supporting Information for:

Towards the synthesis of a *Yersinia pestis* cell wall polysaccharide: Enantioselective synthesis of an L-glycero-D-manno-heptose building block

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Experimental Section

**General Information for Chemical Synthesis:** All chemicals used were reagent grade and used as supplied except where noted. All reactions were performed in oven-dried glassware under an inert atmosphere unless noted otherwise. Reagent grade *N*, *N*-dimethylformamide (DMF) was dried over activated molecular sieves prior to use. Pyridine, triethylamine (NEt₃) and acetonitrile (MeCN) were distilled over CaH₂ prior to use. Dichloromethane (CH₂Cl₂), toluene and tetrahydrofuran (THF) were purified by a Cycle-Tainer Solvent Delivery System unless noted otherwise. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (0.25mm). Compounds were visualized by UV irradiation or dipping the plate in a cerium sulfate-ammonium molybdate (CAM) solution. Flash column chromatography was carried out using forced flow of the indicated solvent on Fluka Kieselgel 60 (230-400 mesh). Purification by size exclusion recycling HPLC was carried out using JAI LC 9101 equipped with JAIGEL-1H and 2-H column in a series (CHCl₃). ¹H, ¹³C spectra were recorded on a Varian Mercury 300 (300 MHz), Bruker ECX (400 MHz), Bruker DRX500 (500 MHz), or, Bruker DRX700 (700 MHz) spectrometer in CDCl₃ with chemical shifts
referenced to internal standards CDCl₃ (7.26 ppm ¹H, 77.0 ppm ¹³C) unless otherwise stated. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet for ¹H NMR data. NMR chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hz. High resolution mass spectral (HRMS) analyses were performed by the MS-service at the Laboratory for Organic Chemistry (LOC) at ETH Zürich and the MS-service at Department of Organic Chemistry at Free University Berlin. High-resolution MALDI and ESI mass spectra were run on an IonSpec Ultra instrument. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. Optical rotations were measured using a Perkin-Elmer 241 and Unipol L1000 polarimeter.

**Synthetic Procedures:**

![Chemical Structures](Image)

**3,5-O-Isopropylidene-4-O-tert-butyldimethylsilyl-L-lyxose dimethyl acetal (8):**

To a solution of 3,5-O-Isopropylidene-2,4-di-O-tert-butyldimethylsilyl-L-lyxose dimethyl acetal 7 (18.88 g, 54 mmol) in THF (290 mL) was carefully added L-Selectride (1M in hexane, 76 mL) dropwise at -78 °C and the resulting solution was stirred at -78 °C for 3 h and further stirred at rt for 16 h. Upon complete consumption of compound 7, sat. aq. NH₄Cl was added to the resulting solution and the reaction mixture was extracted with EtOAc, and the organic phase was washed with sat. aq. NH₄Cl, brine, dried over MgSO₄, filtered and concentrated to give an oil that was purified by flash chromatography (15:1 to 10:1 cyclohexane / EtOAc) to provide 8 as colorless oil (14.95 g, 79%). [α]D = +11.50 (c = 1.09, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 4.42 (d, J = 2.0, 1H, H-1), 4.03 – 3.65 (m, 5H, H-2/3/4/5), 3.51 (s, 3H, OCH₃), 3.46 (s, 3H, OCH₃), 2.39 (d, J = 5.1, 1H, OH), 1.40 (s, 6H, C(CH₃)₂), 0.93 (s, 9H, Si(CH₃)₃), 0.09 (s, 6H, Si(CH₃)₂). ¹³C NMR (75 MHz, CDCl₃) δ 104.1, 98.5, 71.3, 70.6, 70.0, 65.7, 64.5, 56.9, 55.5, 28.6, 25.8, 19.6, 18.2, -4.6, -4.8. IR (cm⁻¹) 2930, 1463, 1379, 1137, 1080. ESI-HRMS m/z calcld. for C₁₆H₃₄NaO₆Si⁺: 373.2017, obsd. 373.2055 [M+Na]⁺.

**3,5-O-Isopropylidene-2-O-para-bromobenzyl-L-lyxose dimethyl acetal (10):**

To a solution of alcohol 8 (14.49 g, 42.3 mmol) in DMF (10 mL) was added para-bromobenzyl bromide (21.17 g, 84.7 mmol) and NaH (60% in oil, 5.08 g, 127 mmol) at 0 °C and the resulting solution was stirred at rt for 18 h. The reaction mixture was quenched by water and extracted with EtOAc and the organic phase was washed with brine, and dried over MgSO₄, filtered and concentrated to give an oil that was purified by
flash chromatography (9:1 cyclohexane / EtOAc) to provide 9 as colorless oil (22.05 g).
To a solution of 9 (524 mg, 1.00 mmol) in THF (10 mL) was added tetrabutylammonium
fluoride trihydrate (636 mg, 2.01 mmol) at rt and the resulting solution was stirred at rt
for 20 h. The reaction mixture was concentrated and was purified by flash
chromatography (4:1 to 1:1 cyclohexane / EtOAc) to provide 10 as colorless oil (331 mg,
82%, over two steps). $\left[\alpha\right]_D^{\text{rt}} = +21.24 \, (c = 0.89, \text{CHCl}_3)$. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$
7.43 (d, $J = 6.3$ Hz, 2H, CBr-(C$_6$H$_4$)$_2$), 7.25 (d, $J = 6.3$ Hz, 2H, CBr-(CH)$_2$-(CH)$_2$), 4.81 (d,
$J = 11.3$ Hz, 1H, OCH$_2$(C$_6$H$_4$Br)), 4.66 (d, $J = 11.3$, 1H, OCH$_2$(C$_6$H$_4$Br)), 4.42 (d, $J =$
3.0, 1H, H-1), 4.05 – 3.62 (m, 5H, H-2/3/4/5), 3.50 (s, 3H, OCH$_3$), 3.44 (s, 3H, OCH$_3$),
3.08 (d, $J = 8.7$ Hz, 1H, OH), 1.44 (s, 3H, CCH$_3$), 1.43 (s, 3H, CCH$_3$). $^{13}$C NMR (75
MHz, CDCl$_3$) $\delta$ 137.4, 131.3, 129.8, 121.5, 104.9, 98.9, 78.5, 74.5, 70.8, 65.9, 63.2, 56.9,
50.0, 29.6, 18.4. IR (cm$^{-1}$) 3486, 2937, 1380, 1199, 1068. ESI-HRMS m/z calcd. for
C$_{17}$H$_{25}$BrNaO$_6$: 427.0727, obsd. 427.0737 [M+Na]$^+$. 

4-O-Benzyl-3,5-O-isopropylidene-2-O-para-bromobenzyl-L-lyxose dimethyl acetal (11):
To a solution of alcohol 10 (11.9 g, 29.3 mmol) in DMF (90 mL) was added benzyl
bromide (7 mL, 58.6 mmol) and NaH (60% in oil, 2.46 g, 61.5 mmol) at 0 °C and the
resulting solution was stirred at rt for 23 h. The reaction mixture was quenched with
water and extracted with EtOAc and the organic phase was washed with brine, and dried
over MgSO$_4$, filtered and concentrated to give an oil which was purified by flash
chromatography (5:1 to 4:1 cyclohexane / EtOAc) to provide 11 as colorless oil (13.79 g,
95%). $\left[\alpha\right]_D^{\text{rt}} = +59.7 \, (c = 0.45, \text{CHCl}_3)$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
7.73 – 7.20 (m, 7H, Ar), 7.10 (d, $J = 8.7$ Hz, 2H, CBr-(CH)$_2$-(CH)$_2$), 4.91 (d, $J = 11.4$, 1H, OCH$_2$Ar),
4.65 (d, $J = 12.3$ Hz, 1H, OCH$_2$Ar), 4.50 (d, $J = 1.5$, 1H, H-1), 4.44 – 4.30 (m, 2H,
OCH$_2$Ar), 4.16 – 3.82 (m, 4H, H-2/3/4/5), 3.54 (s, 3H, OCH$_3$), 3.49 (dd, $J = 1.8$ Hz, 3.6
Hz, 1H, H-4), 3.47 (s, 3H, OCH$_3$), 1.45 (s, 6H, C(CH$_3$)$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$
138.2, 137.9, 131.1, 129.2, 128.3, 127.7, 127.6, 121.0, 105.6, 98.6, 76.9, 73.8, 70.8, 70.6,
69.3, 61.3, 57.4, 56.6, 29.2, 18.9. IR (cm$^{-1}$) 2933, 1488, 1379, 1130, 1068. ESI-HRMS m/z calcd. for
C$_{24}$H$_{31}$BrNaO$_6$: 517.1196, obsd. 517.1204 [M+Na]$^+$. 

4-O-Benzyl-2-O-para-bromobenzyl-5-O-tert-butyldiphenylsilyl-L-lyxose dimethyl acetal (12):
To a solution of acetal 11 (4.83 g, 9.77 mmol) in MeOH (105 mL) $dl$-camphorsulfonic
acid (113 mg, 0.45 mmol) was added at rt and the resulting solution was stirred at rt for 1
h. After checking the consumption of starting material, to the reaction mixture sat. aq.
NaHCO$_3$ (100 mL) and EtOAc (700 mL) was added and stirred vigorously to be
neutralized. After that, the organic layer was collected and washed with water, dried over MgSO₄, filtered and evaporated to give the diol as a crude product. The diol intermediate was dissolved with dichloromethane (50 mL) and imidazole (798 mg, 11.7 mmol) and tert-butyldiphenylsilyl chloride (3.07 mL, 11.7 mmol) and DMAP (407 mg, 2.93 mmol) was added and stirred at rt for 20 min. After checking for complete consumption of the diol, the reaction mixture was quenched with sat. aq. NaHCO₃ and the resulting solution was worked up with EtOAc. The organic layer was washed with brine and dried over MgSO₄, filtered, and concentrated to give an oil that was purified by flash chromatography (9:1 to 4:1 cyclohexane / EtOAc) to provide 12 as colorless oil (6.275 g, 93%). \[ \alpha \text{D}_{\text{rt}} = +48.39 \, (c = 1.11, \text{CHCl}_3). \]

\( ^1 \text{H NMR (300 MHz, CDCl}_3 \delta 7.67–7.11 \, (m, 19\text{H, Ar}), 4.74 \, (d, J = 12, 1\text{H, OCH}_2\text{Ar}), 4.64 \, (d, J = 11.7, 1\text{H, OCH}_2\text{Ar}), 4.56 \, (d, J = 3.3, 1\text{H, H-1}), 4.27 \, (d, J = 11.7, 1\text{H, OCH}_2\text{Ar}), 4.25 \, (d, J = 12, 1\text{H, OCH}_2\text{Ar}), 3.89-3.54 \, (m, 5\text{H, H-2/3/4/5}), 3.51 \, (s, 3\text{H}, \text{OCH}_3), 3.44 \, (s, 3\text{H, OCH}_3), 2.97 \, (d, J = 5.9, 1\text{H, OH}), 1.06 \, (s, 9\text{H}, \text{SiC(CH}_3)_3). \]

\( ^{13} \text{C NMR (75 MHz, CDCl}_3 \delta 138.3, 137.7, 135.5, 133.1, 133.0, 131.2, 129.7, 129.2, 128.2, 127.7, 127.7, 127.6, 121.1, 106.1, 78.8, 77.1, 72.9, 72.2, 70.9, 63.8, 56.5, 56.0, 26.8, 19.1. \)

IR (cm\(^{-1}\)) 3499, 2931, 1427, 1104, 1068, 740, 700. ESI-HRMS m/z calcd. for C\(_{37}\)H\(_{45}\)BrNaO\(_6\)Si\(_{3}\): 715.2061, obsd. 715.2073 [M+Na\(^{+}\)].

\( \quad \)

4-O-Benzyl-2-O-para-bromobenzyl-3-O-tert-butylidiphenylsilyl-5-O-tert-butyldiphenylsilyl-L-lyxose dimethyl acetal (13):

To a solution of alcohol 12 (3.163 g, 4.56 mmol) in dichloromethane (50 mL) was added 2,6-lutidine (2.7 mL, 23.1 mmol) and tert-butyldimethylsilyl trifluoromethanesulfonate (5.2 mL, 23.1 mmol) at -78 °C and the reaction mixture was stirred at -78 °C for 40 min. After checking for complete consumption of 12, the reaction mixture was quenched with sat. aq. NaHCO₃ and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, and dried over MgSO₄, filtered, and concentrated to give an oil that was purified by flash chromatography (20:1 cyclohexane / EtOAc) to provide 13 as colorless oil (3.59 g, 97%). \[ \alpha \text{D}_{\text{rt}} = 3.74 \, (c = 0.54, \text{CHCl}_3). \]

\( ^1 \text{H NMR (400 MHz, CDCl}_3 \delta 7.70 – 7.02 \, (m, 19\text{H, Ar}), 4.69 \, (d, J = 12.0, 1\text{H, OCH}_2\text{Ar}), 4.63 \, (d, J = 12.0, 1\text{H, OCH}_2\text{Ar}), 4.57 – 4.48 \, (m, 3\text{H, OCH}_2\text{Ar}/\text{H-1}), 4.24 \, (d, J = 5.8, 2.1, 1\text{H, H-2}), 3.98-3.50 \, (m, 4\text{H, H-3/4/5}), 3.35 \, (s, 3\text{H, OCH}_3), 2.97 \, (s, 3\text{H, OCH}_3), 1.11(s, 9\text{H, SiC(CH}_3)_3), 0.76 \, (m, 9\text{H, SiC(CH}_3)_3), 0.04 \, (s, 3\text{H, SiC(CH}_3)_3), 0.00 \, (s, 3\text{H, SiCH}_3). \]

\( ^{13} \text{C NMR (101 MHz, CDCl}_3 \delta 139.1, 137.9, 135.7, 135.6, 133.8, 133.7, 131.1, 129.5, 129.1, 128.1, 127.6, 127.5, 127.2, 120.9, 105.2, 83.2, 83.0, 73.8, 72.8, 72.4, 64.6, 55.8, 55.5, 26.9, 25.9, 19.2, 18.1, -4.7, -4.8. \)

IR (cm\(^{-1}\)) 2930, 2856, 1488, 1471, 1428, 1389, 1361, 1253, 1072, 1011, 836, 776, 739, 701. MALDI-HRMS m/z calcd. for C\(_{43}\)H\(_{59}\)BrO\(_6\)Si\(_2\)Na\(^{+}\): 829.2926, obsd. 829.2928 [M+Na\(^{+}\)].
4-O-Benzyl-2-O-para-bromobenzyl-3-O-tert-butylidemethylsilyl-5-O-tert-butylidiphenysilyl-L-lyxose (3):

To a solution of dimethyl acetal 13 (6.82 g, 8.43 mmol) in acetone (120 mL) was added pTsOH·H2O (160 mg, 0.83 mmol) and the reaction mixture was stirred at rt for 17 h. The reaction mixture was poured into EtOAc and sat. aq. NaHCO3 and vigorously stirred. The organic layer was collected and washed with brine, and dried over MgSO4, filtered, and concentrated to provide 3 as colorless oil (6.24 g, 97%). The aldehyde was used in the next reaction without purification. 1H NMR (300 MHz, CDCl3) δ 9.60 (d, J = 1.5, 1H, O=CH), 7.70 –7.04 (m, 19H, Ar), 4.61 (m, 2H, OCH2Ar), 4.50 (d, J = 11.9, 1H, OCH2Ar), 4.39 (d, J = 11.9, 1H, OCH2Ar), 4.22 – 3.57 (m, 5H, H-2/3/4/5), 1.04 (s, 9H, SiC(CH3)3), 0.80 (s, 9H, SiC(CH3)3), 0.02 (s, 3H, SiCH3), -0.03 (s, 3H, SiCH3). MALDI-HRMS m/z calcld. for C41H53BrNaO5Si2+: 783.2507, obsd. 783.2517 [M+Na]+.

Methyl 6-O-benzyl-4-O-para-bromobenzyl-2,5-di-O-tert-butylidemethylsilyl-7-O-tert-butylidiphenysilyl-L-glycero-D-mannoate (14):

Silyl enolether 4 (5.60 g, 20.2 mmol) was dissolved in toluene (40 mL) and MgBr2·OEt2 (5.23 g, 20.2 mmol) was added. The solution was stirred for 20 min at rt and cooled to -78 °C. Aldehyde 3 (3.09 g, 4.05 mmol) in dichloromethane (40 mL) was added dropwise and stirred at -78 °C for 2 h. The reaction mixture was quenched with sat. aq. NaHCO3 and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, dried over MgSO4, filtered, and concentrated to give an oil that was purified by flash chromatography (20:1 to 10:1 cyclohexane / EtOAc) to provide 14 as colorless oil (4.99 g, 61%). [α]D = +3.85 (c = 0.85, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.60 – 6.99 (m, 19H, Ar), 4.77 (d, J = 12.0, 1H, OCH2Ar), 4.65 (d, J = 12.0, 1H, OCH2Ar), 4.64 (d, J = 11.8, 1H, OCH2Ar), 4.37 (d, J = 11.8, 1H, OCH2Ar), 4.19 (d, J = 8.2, 1H, H-2), 4.10 – 3.81 (m, 6H, H-3/4/5/6/7), 3.72 (s, 3H, OCH3), 1.05 (s, 9H, SiC(CH3)3), 0.83 (s, 9H, SiC(CH3)3), 0.82 (s, 9H, SiC(CH3)3), 0.01 (s, 3H, SiCH3), -0.02 (s, 3H, SiCH3), -0.05 (s, 3H, SiCH3), -0.07 (s, 3H, SiCH3). 13C NMR (101 MHz, CDCl3) δ 173.1, 138.1, 137.5, 135.6, 135.6, 133.4, 131.2, 129.6, 129.6, 128.5, 128.4, 127.8, 127.7, 127.6, 127.6, 120.9, 81.8, 78.9, 74.4, 73.3, 73.1, 73.0, 72.8, 64.5, 61.7, 51.8, 26.9, 25.8, 25.8, 25.7, 19.2, 18.0, 18.0, -4.8, -4.9, -5.1, 5.3. IR (cm⁻¹) 2929, 1751, 1472, 1252, 1110, 836, 777, 700. ESI-HRMS m/z calcld. for C50H73BrNaO8Si3+: 987.3694, obsd. 987.3718 [M+Na]+.
To a solution of ester 14 (10.61 g, 8.19 mmol) in dichloromethane (150 mL) was added trifluoroacetic acid (10 mL) at rt and the solution was stirred at rt for 24 h. The reaction mixture was quenched with sat. aq. NaHCO₃ and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, dried over MgSO₄, filtered, and concentrated to give an oil which was purified by flash chromatography (15:1 to 10:1, then 1:1 cyclohexane / EtOAc) to provide the titled compounds 15 (3.78 g, 56%) and 16 (1.15 g, 20%).

**15**

$\alpha$D<sub>rt</sub> = +36.0 (c = 0.93, CHCl₃). 1H NMR (400 MHz, CDCl₃) δ 7.73 – 7.07 (m, 19H, Ar), 4.55 (d, J = 11.9, 1H, OCH₂Ar), 4.54 (d, J = 11.9, 1H, OCH₂Ar), 4.47 (d, J = 4.2, 1H, H-2), 4.41 (dd, J = 9.1, 2.2, 1H, H-5), 4.25 (d, J = 11.9, 1H, OCH₂Ar), 4.11 (d, J = 11.9, 1H, OCH₂Ar), 3.96 – 3.68 (m, 5H, H-3/4/6/7), 2.76 (s, 1H, OH), 1.05 (s, 9H, SiC(CH₃)₃), 0.93 (s, 9H, SiC(CH₃)₃), 0.23 (s, 3H, SiCH₃), 0.12 (m, 3H, SiCH₃).

13C NMR (101 MHz, CDCl₃) δ 169.6, 137.9, 136.3, 135.6, 135.5, 134.8, 133.0, 131.6, 129.9, 129.7, 129.4, 128.4, 128.0, 127.8, 127.8, 127.8, 127.7, 121.9, 76.1, 76.0, 75.7, 73.2, 72.9, 70.7, 69.3, 61.7, 26.9, 26.6, 25.7, 19.2, 18.4, -4.5, -5.6. IR (cm⁻¹) 2929, 1778, 1590, 1471, 1427, 1206, 1112, 1069, 701. MALDI-HRMS m/z calcd. for C₄₃H₅₅BrNaO₇Si⁺: 841.2562, obsd. 841.2578 [M+Na]⁺.

**16**

$\alpha$D<sub>rt</sub> = +65.62 (c = 1.16, CHCl₃). 1H NMR (700 MHz, CDCl₃) δ 7.73 – 7.07 (m, 19H, Ar), 4.52 (d, J = 11.8, 1H, OCH₂Ar), 4.51 (d, J = 11.8, 1H, OCH₂Ar), 4.45 – 4.35 (m, 1H, H-5), 4.27 (d, J = 3.0, 1H, H-2), 4.16 (d, J = 11.9, 1H, OCH₂Ar), 3.98 – 3.60 (m, 5H, H-3/4/6/7), 3.07 (s, 1H, OH), 1.06 (s, 9H, SiC(CH₃)₃). 13C NMR (176 MHz, CDCl₃) δ 172.6, 137.5, 136.0, 135.5, 135.5, 133.0, 132.9, 131.5, 129.9, 129.4, 128.4, 128.2, 127.9, 127.8, 121.9, 76.3, 76.0, 75.6, 72.7, 70.8, 70.5, 68.3, 61.1, 26.8, 19.1. IR (cm⁻¹) 3426, 2930, 1761, 1427, 1206, 1112, 1069, 701. ESI-HRMS m/z calcd. for C₃₇H₄₁BrNaO₇Si⁺: 727.1703, obsd. 727.1745 [M+Na]⁺.
6-O-Benzyl-4-O-para-bromobenzyl-3-O-tert-butyldimethylsilyl-7-O-tert-butyldiphenylsilyl-L-glycero-α/β-D-manno-heptopyranose (17) and 6-O-Benzyl-4-O-para-bromobenzyl-2-O-tert-butyldimethylsilyl-7-O-tert-butyldiphenylsilyl-L-glycero-α/β-D-manno-heptopyranose (18):

To a solution of lactone 15 (3.609 g, 4.4 mmol) in THF (72 mL) was added lithium tri-tert-butoxyalumin hydride (2.538 g, 9.68 mmol) at -15 °C and the reaction mixture was stirred at -15 °C for 1 h. The reaction mixture was quenched with aqueous solution of Rochelle salt and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, and dried over MgSO₄, filtered and concentrated to give an oil which was purified by flash chromatography (10:1 to 4:1 cyclohexane / EtOAc) to provide lactol 17 (1.68 g, 47%) and lactol 18 (1.36 g, 38%).

17 \([\alpha]_D^{25} = +39.8 \text{ (c = 0.53, CHCl}_3)\). \(^1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.74 – 7.07 (m, 19H, Ar), 5.16 (s, 1H, H-1), 4.72 – 4.61 (m, 2H, H-5/OC\(_2\)H\(_2\)Ar), 4.28 (d, \(J = 12.1\) 1H, OCH\(_2\)Ar), 4.17 – 3.61 (m, 8H, H-2/3/4/6/7/OC\(_2\)H\(_2\)Ar), 2.05 (s, 1H, OH), 1.07 (s, 9H, SiC(CH\(_3\))\(_3\)), 0.90 (s, 9H, SiC(CH\(_3\))\(_3\)), 0.10 (s, 3H, SiCH\(_3\)), 0.03 (s, 3H, SiCH\(_3\)). \(^{13}\)C NMR (176 MHz, CDCl\(_3\)) \(\delta\) 138.4, 138.3, 138.0, 137.8, 135.7, 135.6, 133.5, 133.4, 131.3, 131.2, 129.8, 129.8, 129.7, 128.3, 128.2, 127.9, 127.8, 127.8, 127.7, 127.5, 127.6, 127.5, 127.5, 127.5, 120.8, 93.6, 76.6, 76.3, 76.0, 75.2, 74.7, 73.4, 73.3, 73.2, 72.3, 72.1, 71.7, 69.8, 62.2, 61.9, 29.6, 25.8, 25.8, 25.7, 19.2, 19.2, 18.0, 17.9, -4.6, -4.6, -4.6. IR (cm\(^{-1}\)) 3447, 2930, 1427, 1254, 1110, 1069, 837, 702. MALDI-HRMS m/z calcld. for C\(_{43}\)H\(_{57}\)BrNaO\(_7\)Si\(_2\)^+: 843.2718, obsd. 843.2721 [M+Na]^+.

18 \([\alpha]_D^{25} = +24.2 \text{ (c = 0.5, CHCl}_3)\). \(^1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.74 – 7.11 (m, 19H, Ar), 4.99 (s, 1H, H-1), 4.79 – 4.65 (m, 2H, H-5/OCH\(_2\)Ar), 4.31 (d, \(J = 11.9\) 1H, OCH\(_2\)Ar), 4.20 (d, \(J = 11.9\) 1H, OCH\(_2\)Ar), 4.05 – 3.72 (m, 7H, H-2/3/4/6/7/OCH\(_2\)Ar), 1.96 (s, 1H, OH), 1.06 (d, \(J = 6.4\) 9H, SiC(CH\(_3\))\(_3\)), 0.94 (s, 9H SiC(CH\(_3\))\(_3\)), 0.11 (s, 3H, SiCH\(_3\)), 0.08 (s, 3H, SiCH\(_3\)). \(^{13}\)C NMR (176 MHz, CDCl\(_3\)) \(\delta\) 138.8, 137.9, 137.9, 135.7, 135.7, 135.6, 135.6, 133.5, 131.5, 131.3, 129.8, 129.7, 129.2, 129.1, 128.4, 128.2, 128.2, 127.8, 127.8, 127.7, 127.7, 127.3, 127.2, 121.2, 110.0, 94.7, 94.3, 75.9, 74.9, 74.6, 73.8, 73.8, 73.2, 73.1, 72.9, 72.2, 72.2, 71.9, 71.7, 69.8, 62.4, 62.0, 29.6, 26.9, 26.9, 26.0, 25.8, 25.7, 19.2, 18.4, 18.1, -4.3, -4.5, -4.6, -5.0. IR (cm\(^{-1}\)) 3450, 2930, 1428, 1255, 1120, 836, 702. MALDI-HRMS m/z calcld. for C\(_{43}\)H\(_{57}\)BrNaO\(_7\)Si\(_2\)^+: 843.2718, obsd. 843.2702 [M+Na]^+.

Supplementary Material (ESI) for Chemical Communications
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2-O-Acetyl-6-O-benzyl-4-O-para-bromobenzyl-3-O-tert-butylidemethylsilyl-7-O-tert-butylidiphenylsilyl-L-glycero-αβ-D-manno-heptopyranosyl acetate (19):

To a solution of diol 17 (383 mg, 0.47 mmol) in dichloromethane (5 mL) was added triethylamine (0.36 mL, 2.58 mmol), acetic anhydride (0.22 mL, 2.3 mmol) and DMAP (11 mg, 0.09 mmol) at rt. After stirring for 19 h, the reaction mixture was quenched with water and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, and dried over MgSO₄, filtered and concentrated to give an oil that was purified by flash chromatography (8:1 cyclohexane / EtOAc) to provide 19 (423 mg, quant.) as a white foam. [α]D²⁰ = +41.98 (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.07 (m, 19H, Ar), 6.12 (d, J = 2.0, 1H, H-1), 5.11 – 4.99 (m, 1H, H-2), 4.75 (d, J = 12.1, 1H, OCH₂Ar), 4.58 (d, J = 12.1, 1H, OCH₂Ar), 4.24 – 3.71 (m, 8H, H-3/4/5/6/7), 2.14 (s, 3H, C(O)CH₃), 2.01 (s, 3H, C(O)CH₃), 1.05 (s, 9H, SiC(CH₃)₃), 0.88 (s, 9H, SiC(CH₃)₃), 0.10 (s, 3H, SiCH₃), 0.03 (s, 3H, SiCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 170.0, 168.1, 138.3, 137.8, 135.6, 135.5, 133.3, 133.2, 131.3, 129.8, 128.3, 128.3, 128.1, 127.8, 127.7, 127.6, 121.0, 91.1, 76.3, 75.1, 73.4, 72.2, 72.1, 71.4, 71.3, 61.3, 26.8, 25.7, 20.9, 20.8, 19.2, 17.8, -4.7, -4.8. IR(cm⁻¹) 2930, 1750, 1368, 1216, 1106, 837, 701. MALDI-HRMS m/z calcld. for C₄₇H₆₁BrNaO₉Si₂⁺: 929.2919, obsd. 929.2916 [M+Na]⁺.

2-O-Acetyl-6-O-benzyl-4-O-para-bromobenzyl-3-O-tert-butylidemethylsilyl-7-O-tert-butylidiphenylsilyl-L-glycero-αβ-D-manno-heptopyranose (20):

To a solution of diacetate 19 (55 mg, 0.06 mmol) in DMF (0.5 mL) was added hydrazine acetate (22 mg, 0.238 mmol). After stirring for 13 h, the reaction mixture was quenched with sat. aq. NaHCO₃ and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, and dried over MgSO₄, filtered and concentrated to give an oil which was purified by flash chromatography (5:1 cyclohexane / EtOAc) to provide 20 (46mg, 89%) as a colorless oil. [α]D²⁰ = +28.7 (c = 1.01, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.08 (m, 19H, Ar), 5.09 – 5.06 (m, 1H, H-1), 5.03 – 4.97 (m, 1H, H-2), 4.77 (d, J = 12.2, 1H, OCH₂Ar), 4.69 (d, J = 12.0, 1H, OCH₂Ar), 4.27 (d, J = 12.0, 1H, OCH₂Ar), 4.19 (dd, J = 9.0, 3.4, 1H, H-5), 4.10 (d, J = 12.2, 1H, OCH₂Ar), 4.02– 3.69 (m, 5H, H-3/4/6/7), 2.29 (d, J = 3.7, 1H, OH), 2.13 (s, 3H, C(O)CH₃), 1.08 (s, 9H, SiC(CH₃)₃), 0.86 (s, 9H, SiC(CH₃)₃), 0.10 (s, 3H, SiCH₃), 0.01 (s, 3H, SiCH₃). ¹³C NMR (176 MHz, CDCl₃) δ 170.5, 138.5, 138.0, 135.7, 135.8, 133.4, 133.4, 131.3, 131.2, 129.8, 128.2, 128.1, 127.8, 127.7, 127.6, 120.8, 92.2, 76.7, 75.5, 73.3, 72.7, 72.5, 70.9, 70.1, 62.2, 26.9, 25.7, 21.0, 19.2, 17.8, -4.7, -4.9. IR(cm⁻¹) 3417, 3417, 2930, 1748, 1472, 1239, 1112, 1069, 837, 701. ESI-HRMS m/z calcld. for C₄₅H₅₇BrNaO₈Si₂⁺: 887.2809, obsd. 887.2812 [M+Na]⁺.
2-O-Acetyl-6-O-benzyl-4-O-para-bromobenzyl-3-O-tert-butyldimethylsilyl-7-O-tert-butyldiphenylsilyl-L-glycero-α/β-D-manno-heptopyranosyl N-phenyl trifluoroacetimidate (1):

To a solution of lactol 20 (46 mg, 0.053 mmol) in dichloromethane (0.8 mL) was added N-phenyl-trifluoroacetimidoyl chloride (33 mg, 0.158 mmol) and Cs₂CO₃ (35 mg, 0.107 mmol) at rt. After stirring for 1 h, the reaction mixture was concentrated. The residue was purified by flash SiO₂ chromatography (9:1 cyclohexane / EtOAc) to provide 1 (53 mg, 96%) as a colorless oil. [α]Drt = +55 (c = 1.2, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.72 –6.67 (m, 24H, Ar), 6.15 (s, 1H, H-1), 5.19 (s, 1H, H-2), 4.70 (d, J = 12.1, 1H, OC₂H₂Ar), 4.55 (d, J = 12.1, 1H, OC₂H₂Ar), 4.26 – 3.70 (m, 8H, H-3/4/5/6/7/OC₂H₂Ar), 2.12 (d, J = 10.9, 3H, C(O)CH₃), 1.03 (s, 9H, SiC(CH₃)₃), 0.83 (s, 9H, SiC(CH₃)₃), 0.08 (s, 3H, SiCH₃), 0.00 (s, 3H, SiCH₃). ¹³C NMR (101 MHz, CDCl₃) δ 170.4, 170.0, 143.3, 138.5, 137.7, 135.6, 133.4, 133.3, 133.2, 131.3, 129.9, 129.8, 129.7, 129.4, 128.7, 128.3, 128.2, 128.2, 127.8, 127.8, 127.6, 127.5, 127.5, 124.3, 121.0, 120.4, 119.3, 94.8, 94.1, 76.6, 76.5, 75.3, 74.8, 73.7, 73.5, 73.4, 72.9, 72.1, 71.2, 70.9, 69.8, 62.5, 62.4, 26.9, 26.8, 25.7, 25.6, 20.8, 20.7, 19.2, 19.1, 17.8, 17.8, -4.7, -4.9, -5.0. IR(cm⁻¹) 2931, 1752, 1718, 1598, 1209, 1112, 701. MALDI-HRMS m/z calcld. for C₅₃H₆₃BrF₃NNaO₈Si₂⁺:1058.3112, obsd. 1058.3119 [M+Na]⁺.

6-O-Benzyl-3-O-levulinoyl-4-O-para-bromobenzyl-2-O-tert-butyldimethylsilyl-7-O-tert-butyldiphenylsilyl-L-glycero-α/β-D-manno-heptopyranosyl levulinoate (18):

Levulinic acid (104 mg, 0.90 mmol) was dissolved in dichloromethane (3 mL) and the solution was cooled to 0 °C. N,N-diisopropylcarbodiimide (113 mg, 0.90 mmol) and DMAP (109 mg, 0.90 mmol) was successively added and the solution was stirred at 0 °C for 10 min. To this solution was added diol 18 (147 mg, 0.179 mmol) in dichloromethane (2 mL) and the resulting reaction mixture was stirred at rt for 19 h. Upon complete consumption of compound 18, water was added to the resulting solution and the reaction mixture was extracted with EtOAc. The organic phase was washed with brine, dried over MgSO₄, filtered and concentrated to give an oil that was purified by flash chromatography (7:3 cyclohexane / EtOAc) to provide 21 as colorless oil (160 mg, 88%). [α]Drt = +37.5 (c = 1.00, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.70 –7.06 (m, 19H, Ar), 5.95 (d, J = 2.3, 1H, H-1), 5.20 (dd, J = 9.2, 2.9, 1H, H-3), 4.67 (d, J = 12.1, 1H, OCH₂Ar), 4.47 (d, J = 11.9, 1H, OCH₂Ar), 4.26 – 3.81 (m, 8H, H-2/4/5/6/7/OC₂H₂Ar), 4.06 (s, 1H), 4.04 – 3.99 (m, 1H), 3.97 – 3.86 (m, 2H), 3.81 (t, J = 6.6, 1H), 2.75 – 2.34 (m, 8H, C(O)CH₂), 2.15 (s, 3H, C(O)CH₃), 2.11 (s, 3H, C(O)CH₃), 1.05 (s, 9H, ...
SiC(CH$_3$)$_3$, 0.92 (s, 9H, SiC(CH$_3$)$_3$), 0.08 (s, 3H, SiCH$_3$), 0.06 (s, 3H, SiCH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 206.0, 205.8, 172.1, 170.8, 138.7, 137.5, 135.6, 135.5, 133.4, 133.6, 131.3, 129.8, 129.7, 129.0, 128.2, 127.8, 127.4, 127.3, 121.3, 94.4, 76.5, 74.5, 73.1, 72.9, 72.6, 71.9, 69.1, 61.7, 37.7, 29.8, 29.7, 28.1, 27.9, 26.8, 25.7, 19.2, 18.0, -4.7, -5.2.

IR (cm$^{-1}$) 2930, 2857, 1741, 1719, 1359, 1135, 1105, 956, 835. MALDI-HRMS m/z calcld. for C$_{53}$H$_{69}$BrNaO$_{11}$Si$_2$: 1039.3454, obsd. 1041.3449 [M+Na]$^+$. 

$N$-Benzyl-benzyloxycarbonyl-5-aminopentyl 2,7-O-di-acetyl-6-O-benzyl-3-O-levulinoyl-4-O-para-bromobenzyl-L-glycero-$\alpha$-D-manno-heptopyranoside (22):

To a solution of levulinoate 21 (46 mg, 0.045 mmol) and $N$-(benzyl)benzyloxycarbonyl-5-amino-pentane-1-ol (18 mg, 0.055 mmol) in dichloromethane (0.5 mL) was added borontrifluoride diethylether complex (11 μL, 0.089 mmol) at 0 °C. After stirring for 11 h at rt, the reaction mixture was quenched with water, sat. aq. NaHCO$_3$ and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, filtered and concentrated to give an oil. Without purification, the residue was dissolved in THF (1 mL) and 70% HF-pyridine (0.1 mL) was added at rt. After stirring for 6 days, the reaction mixture was carefully quenched with sat. aq. NaHCO$_3$ and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, and dried over MgSO$_4$, filtered and concentrated to give the corresponding 2,7-diol as an oil. And without purification, the diol was treated with acetic anhydride (0.1 mL) and pyridine (0.5 mL) and the reaction mixture was stirred at rt for 16h. The reaction mixture was quenched with sat. aq. NaHCO$_3$ and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, dried over MgSO$_4$, filtered and concentrated to give an oil which was purified by flash chromatography (7:3 to 1:1 cyclohexane / EtOAc) to provide 22 (33 mg, 76%, 3 steps). [α]$_D^n$ = +40.3 (c = 1.00, CHCl$_3$). $^1$H NMR (700 MHz, CDCl$_3$) δ 7.53 – 6.96 (m, 19H), 5.36 (dd, $J$ = 9.7, 2.8 Hz, 1H, H-2), 5.25 – 5.11 (m, 4H, H-1/3/7), 4.84 (d, $J$ = 11.9, 1H, OCH$_2$Ar), 4.80 (brs, 1H, OCH$_2$Ar), 4.61 – 4.42 (m, 5H, OCH$_2$Ar), 4.28 – 3.15 (m, 5H, H-4/5/6/OCH$_2$C), 2.81 – 2.54 (m, 2H, NCH$_2$C), 2.34 – 1.75 (m, 13H, OCH$_3$, C(O)CH$_2$), 1.60 – 1.16 (m, 6H, CCH$_2$C). $^{13}$C NMR (176 MHz, CDCl$_3$) δ 206.1, 206.0, 171.8, 171.6, 170.4, 170.0, 156.6, 156.0, 137.8, 137.7, 137.1, 136.8, 131.4, 131.3, 128.9, 128.9, 128.8, 128.7, 128.4, 128.3, 127.9, 127.7, 127.1, 121.4, 97.4, 90.6, 73.4, 73.4, 73.2, 73.1, 72.9, 72.8, 72.5, 72.4, 72.3, 72.1, 72.1, 70.5, 69.8, 68.5, 67.8, 67.0, 62.4, 62.3, 50.5, 50.1, 46.9, 46.0, 37.6, 37.6, 29.7, 29.7, 29.6, 29.6, 28.9, 27.8, 27.7, 27.7, 27.4, 23.3, 20.9, 20.7, 20.7, 14.0. IR (cm$^{-1}$) 2936, 1745, 1697, 1366, 1229, 1069, 751. ESI-HRMS m/z calcld. for C$_{50}$H$_{58}$BrNaO$_{13}$+: 982.2984, obsd. 982.2951 [M+Na]$^+$. 

S10
**N-Benzyl-benzyloxy carbonyl-5-aminopentyl 2,7-O-di-acetyl-6-O-benzyl-4-O-para-bromobenzyl-L-glycero-α-D-manno-heptopyranoside (2):**

To a solution of 22 (33 mg, 0.034 mmol) in DMF (0.7 mL) was added hydrazine acetate (3.5 mg, 0.038 mmol) at rt. After stirring for 19 h at rt, the reaction mixture was quenched with sat. aq. NaHCO₃ and the resulting solution was worked up with EtOAc. The organic layer was washed with brine, dried over MgSO₄, filtered and concentrated to give an oil, which was purified by flash chromatography (7:3 to 1:1 cyclohexane / EtOAc) to provide 2 (25 mg, 85%). [α]_D^{rt} = +52.4 (c = 0.20, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.07 (m, 19H), 5.16 (m, 2H, H-1/2), 5.03 (bs, 2H, H-7), 4.83 (s, 1H, OCH₂Ar), 4.81 (d, J = 15.0, 1H, OCH₂Ar), 4.74 (d, J = 15.0, 1H, OCH₂Ar), 4.55 – 3.10 (m, 11H, H-3/4/5/6/ OCH₂C/OC₃H₂Ar), 2.81 – 2.54 (m, 2H, NCH₂C), 2.34 – 1.75 (m, 6H, OCH₃), 1.65 – 1.17 (m, 6H, CCH₂C). ¹³C NMR (101 MHz, CDCl₃) δ 171.0, 170.6, 170.5, 169.9, 138.0, 137.9, 137.4, 136.8, 131.5, 129.1, 129.0, 128.9, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.3, 121.5, 97.3, 75.4, 73.7, 73.6, 72.8, 72.6, 71.1, 70.5, 67.8, 67.2, 62.8, 50.5, 50.4, 47.1, 46.2, 31.9, 29.7, 29.0, 26.9, 23.4, 22.7, 21.1, 20.9. IR(cm⁻¹) 2924, 1743, 1698, 1234, 1070, 699. ESI-HRMS m/z calcd. for C₄₅H₅₂BrNNaO₁₁⁺: 884.2616, obsd. 884.2612 [M+Na]⁺.

**N-Benzyl-benzyloxy carbonyl-5-aminopentyl (2-O-acetyl-6-O-benzyl-4-O-para-bromobenzyl-L-glycero-α-D-manno-heptopyranosyl)-(1→3)-2,7-di-O-acetyl-6-O-benzyl-4-O-para-bromobenzyl-L-glycero-α-D-manno-heptopyranoside (23):**

To a solution of alcohol 2 (16 mg, 0.0185 mmol) and imidate 1 (25 mg, 0.024 mmol) in dichloromethane (0.2 mL) was added TMSOTf (2 μL, 0.01 mmol) at -20 °C and the temperature of the solution was warmed up to 0 °C over 30 min. The reaction mixture was quenched with triethylamine, concentrated and the residue was purified by flash chromatography (5:1 to 1:1 cyclohexane / EtOAc) to provide the crude product (31 mg). The crude product was dissolved in THF (0.5 mL) and 70 % HF-pyridine (43 μL, 0.367 mmol) was added at rt. After stirring for 18h, the reaction mixture was neutralized with sat. aq. NaHCO₃ carefully and the solution was extracted with EtOAc. The organic layer
was washed with brine, dried over MgSO$_4$, filtered and concentrated to give an oil, that was purified by size exclusion recycling HPLC (CHCl$_3$, eluting solvent) to provide disaccharide 23 (7 mg, 28%). $[\alpha]_D^{24} = +35.6$ (c = 0.33, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.51 – 6.80 (m, 28H), 5.26 – 5.00 (m, 4H), 4.91 – 4.72 (m, 3H), 4.63 – 4.30 (m, 6H), 4.29 – 3.50 (m, 13H), 3.44 – 3.02 (m, 3H), 2.19 – 1.95 (m, 9H), 1.65 – 1.11 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 170.6, 170.5, 170.2, 137.8, 137.4, 137.0, 136.9, 131.6, 131.5, 131.4, 131.3, 129.0, 128.9, 128.9, 128.8, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9, 127.9, 127.7, 127.7, 127.3, 127.2, 121.6, 121.4, 98.1, 97.3, 73.9, 73.4, 73.3, 72.8, 72.8, 72.6, 72.1, 71.9, 71.3, 70.9, 69.3, 67.6, 67.3, 62.6, 62.6, 50.1, 47.0, 29.7, 29.1, 27.5, 23.3, 21.1, 20.9. IR(cm$^{-1}$) 2929, 1743, 1696, 1233, 1069, 752. MALDI-HRMS m/z calcld. for C$_{68}$H$_{77}$Br$_2$NNaO$_{18}$+: 1378.3390, obsd. 1378.3396 [M+Na]$^+$. 

5-Aminopentyl-L-glycero-$\alpha$-D-manno-heptopyranosyl-L-glycero-$\alpha$-D-manno-heptopyranoside (SI-1):

For analytical purposes, disaccharide 21 (2.5 mg, 1.8µmol) was dissolved in a solution of NaOMe in methanol (1.6µM, 1.5mL) and stirred overnight. The reaction was then diluted in with 9:1 dichloromethane/methanol, neutralized with amberlite IR-120 and filtered through a pad of silica. Solvents were removed in vacuo and the crude residue was dissolved in 2:1:1 MeOH/THF/water (2 mL). AcOH was added (20µL) followed by Pd/C (8mg). The suspension was sonicated under argon flow for 30 minutes then under H$_2$ flow for 30 minutes and stirred at rt for two days. The suspension was filtered through a pad of celite and lyophilized. The crude residue was purified by HPLC, 0 $\rightarrow$ 20% acetonitrile (0,1% TFA), water (0.1% TFA) on a Pyramid C-18 Nucleodur column affording deprotected disaccharide SI-1. $^1$H NMR (600 MHz, d$_2$O) $\delta$ 4.01 – 3.96 (m, 3H), 3.94 (s, 1H), 3.91 (d, $J = 10.0$ Hz, 1H), 3.84 – 3.80 (m, $J = 12.1, 6.7$ Hz, 3H), 3.70 – 3.63 (m, $J = 17.8, 10.9, 5.2$ Hz, 3H), 3.63 – 3.58 (m, $J = 7.1, 5.3, 2.2$ Hz, 3H), 3.54 (d, $J = 9.4$ Hz, 1H), 3.49 – 3.42 (m, 3H), 2.94 (t, 2H), 1.68 – 1.55 (m, 4H), 1.45 – 1.34 (m, 2H). ESI-HRMS m/z calcld. for C$_{19}$H$_{37}$NNaO$_{13}$+: 510.2157, obsd. 510.2179 [M+Na]$^+$. 

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TBDPSO
BnO
PBBO
TBSO

1
OC(=NPh)CF₃

150 160 170 180 190 200 160 170 180 190 200
SI-1

Supplementary Material (ESI) for Chemical Communications
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SI-1

NH₂