Supporting Information for

Protection against experimental melioidosis with a synthetic manno-heptopyranose hexasaccharide glycoconjugate

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NMR of key intermediates

Compound 5      Compound S13      Compound 13      Compound 27
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Compound S9      Compound 10      Compound 23      Compound 32
Compound S10     Compound 11      Compound 25      Compound S23
Compound 8      Compound 12      Compound 26      Compound 34

Animal care
General methods

All non-aqueous reactions were carried out under an atmosphere of nitrogen in dried glassware with magnetic stirring unless otherwise stated. Non-anhydrous solvents such as dichloromethane (DCM), diethyl ether (Et2O), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), methanol (MeOH), ethanol (EtOH), tert-butyl methyl ether (TBME), hexanes, n-heptane and toluene were ACS grade. Anhydrous solvents such as DCM, THF, DMF and MeOH were DriSolv® brand purchased from EMD and used as received. All reagents were ACS grade or better. Naphthalene flakes (“moth balls”) were purchased from Home Depot. 4-Acetoxy-2,2-dimethylbutyryl chloride (ADMB-Cl) was synthesized according to the method of Ensley [30] and stored in the freezer until used.

Flash chromatography was performed on Silicycle SiliaFlash® F60, 40-63 μm, 60Å silica gel (230-400 mesh). Analytical thin layer chromatography (TLC) was performed on glass-backed silica-coated high performance (HPTLC) plates (250 μm thickness, 60 Å pore size, F-254 indicator) and visualized by exposure to ultraviolet light and/or staining with p-anisaldehyde solution (p-anisaldehyde/HOAc/H2SO4/200 Proof EtOH; 23/9/31/825). 1H and 13C NMR spectra were recorded on a Varian MR-400 (400 MHz) spectrometer at 25 °C, unless otherwise stated. Chemical shifts are reported in parts per million from CDCl3 or D2O internal standard (7.26 or 4.79 ppm, respectively for 1H NMR spectra; 77.0 ppm for 13C in CDCl3). For 13C spectra measured in D2O 1,4-dioxane was used as the internal standard (67.19 ppm). Data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of doublets,ddd = doublet of doublet of doublets, br = broad; coupling constant(s) in Hz; integration). Optical rotations were measured using a digital polarimeter at 20 °C in the solvent specified. Low resolution matrix-assisted laser desorption/ionization (MALDI) mass spectra were obtained on an Applied Biosystems Voyager DE MALDI-TOF instrument by HT Labs (San Diego, CA). High-resolution mass spectra were obtained by Prof. Stephen J. Eyles at the University of Massachusetts Mass Spectrometry Center (Amherst, MA, USA) using an Orbitrap Fusion mass spectrometer (Thermo Scientific).
Individual reactions

Diol 5 (160.86g, 0.493 mol) was dissolved in DCM (1L) and Bu$_2$SnO (2.47g, 9.9 mmol) was added. The mixture was stirred, and triethylamine (69 ml, 0.495 mol) and p-toluenesulfonyl chloride (93.8g, 0.492 mol) were added. The reaction mixture was stirred at room temperature under N$_2$ overnight. The mixture was filtered through Celite; washed with DCM, and concentrated (bath at 20$^\circ$C. The residue was taken up in EtOAc (1L); washed with brine (1x), 1M HCl, brine (2x), NaHCO$_3$ (1x), and brine (2x) (checked pH; neutral); dried over MgSO$_4$, filtered, and concentrated to give 257 g of crude S1 as a foaming syrup which was used as is in the next step. TLC: 1:1 heptane:EtOAc, R$_f$ 0.60.

Compound 5 (diol) [α]$^20_D$ (c 2.13, CHCl$_3$) +209.4

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 (d, $J$ = 8.0 Hz, 2H), 7.13 (d, $J$ = 8.2 Hz, 2H), 5.72 (s, 1H, H-1), 4.33 (dd, $J$ = 5.6, 0.4 Hz, 1H), 4.16 (dd, $J$ = 8.0, 6.0 Hz, 1H), 4.06 (dt, $J$ = 10.0, 4.4 Hz, 1H), 3.71 – 3.79 (m, 3H), 2.33 (s, 3H, CH$_3$), 1.52 (s, 3H, CH$_3$), 1.36 (s, 3H, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.31, 132.90, 129.94, 128.79, 109.83, 84.10, 78.39, 76.12, 70.43, 70.37, 62.21, 28.09, 26.33, 21.10.
DMSO (5L) was added to KCN (115g) under N\textsubscript{2} and heated to 40-50 °C with mechanical stirring. S1 (256 g crude, 0.493 mol assumed) in DCM (300 mL) was added and stirred for 42 hours (internal temperature = 45.3 °C). The mixture was diluted with EA (8L), washed with brine (2x), dried over MgSO\textsubscript{4}/charcoal, filtered through silica, and washed with TBME. The resulting emulsion was back-extracted with EtOAc. The dried extract was concentrated, and the crude product was taken up in DCM, loaded onto silica (1kg) pre-eluted with heptane:TBME 2:1, and eluted with heptane:TBME 2:1, then with DCM:TBME (1:1) to obtain the product S2 (100g after recrystallization). The mother liquor was rechromatographed using heptane:EA 4:1, and the product was recrystallized from DCM:heptane 1:1 by slow evaporation of the DCM to yield another crop of S2 (9g). Total S2 yield: 109g, 0.325 mol, 66 %, two-step yield. TLC: 2:1 heptane:EtOAc, Rf = 0.39.

HRMS m/z: Calc.: 358.1083 (M+Na\textsuperscript{+}), Found: 358.1080.

\([\alpha]^{20}_D\) (c 2.21, CHCl\textsubscript{3}) +185.5

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.39 (d, \(J = 8.0\) Hz, 2H), 7.14 (d, \(J = 8.0\) Hz, 2H), 5.71 (s, 1H, H-1), 4.37 (d, \(J = 5.6\) Hz, 1H, H-2), 4.25 (ddd, \(J = 10.0, 7.6, 6.4\) Hz, 1H, H-5), 4.11 (dd, \(J = 7.6, 5.6\) Hz, 1H, H-3), 3.63 (dd, \(J = 10.0, 7.6\) Hz, 1H, H-4), 2.69 (ABX, \(J = 17.0, 6.4, 3.8\) Hz, 2H, H-6,6\textsuperscript{'}), 2.33 (s, 3H), 1.53 (s, 3H), 1.37 (s, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 138.45, 132.76, 130.02, 126.10, 116.62, 110.17, 84.58, 78.07, 76.28, 72.57, 66.22, 28.08, 26.29, 21.09, 20.53
To S2 (106g, 0.316 mol) was added hydrido(dimethylphosphinous acid-kP)[hydrogen bis(dimethylphosphinito-kP)] platinun (II) catalyst (1.5g, 0.0035 mol), followed by EtOH (400 ml) and H2O (200 ml). The mixture was heated to 80 °C and maintained overnight. The hot solution was poured into a beaker, one volume of H2O was added, and the mixture cooled in an ice water bath. The solid was filtered, air-dried, and then dried to a constant weight in a vacuum oven to give S3 (106g, 0.301 mol, 95.2 % yield). TLC: 10:1 DCM:MeOH, Rf 0.57.

HRMS m/z: Calc.: 376.1189 (MNa⁺), Found: 376.1186.

[α]D (c 0.52*, CHCl₃) +186.5 *This compound required significant dilution in CHCl₃ to achieve a clear solution.

1H NMR (400 MHz, CD₃OD) δ 7.35 (d, J = 7.0 Hz, 2H), 7.12 (d, J = 7.0 Hz, 2H), 5.60 (s, 1H, H-1), 4.37 (d, J = 5.5 Hz, 1H, H-2), 4.32 (m, 1H, H-5), 4.04 (dd, J = 7.4, 5.8 Hz, 1H, H-3), 3.42 (dd, J = 9.6, 7.4 Hz, 1H, H-4), 3.30 (bs, 1H, NH), 2.66 (dd, J = 7.0, 3.9 Hz, 1H, H-6), 2.30 (dd, J = 7.0, 3.9 Hz, 1H, H-6’), 2.29 (s, 3H), 1.72 (bs, 1H, NH), 1.47 (s, 3H), 1.36 (s, 3H).

13C NMR (100 MHz, CDCl₃) δ 172.69, 138.19, 132.50, 129.98, 128.91, 109.82, 84.26, 77.97, 76.14, 72.83, 67.96, 38.36, 28.08, 26.34, 21.07

S3 (106g, 0.301 mol) was dissolved in a solution of anhydrous MeOH (1L) and DMF-Dimethyl acetal (214 ml). The reaction mixture was stirred at room temperature overnight, then was diluted with EtOAc; washed with brine (1x), 1N HCl, brine (1x), NaHCO₃ (1x), and brine (1x); dried over Na₂SO₄, filtered, and concentrated to give S4 as a crude syrup (108 g, 97 % yield), which was used directly in the next step. TLC: 10:1 DCM:MeOH, Rf 0.69.
HRMS m/z: Calc.: 391.1186 (MNa⁺), Found: 391.1182.

¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.67 (s, 1H, H-1), 4.42 (dt, J = 8.8, 4.0, 1H, H-5), 4.34 (d, J = 5.6 Hz, 1H, H-2), 4.11 (dd, J = 6.8, 6.4 Hz, 1H, H-3), 3.56 (dd, J = 10.0, 7.6 Hz, 1H, H-4), 3.52 (s, 3H, OCH₃), 2.81 (dd, J = 15.3, 4.1 Hz, 1H, H-6), 2.47 (dd, J = 15.3, 8.1 Hz, 1H, H-6'), 2.29 (s, 3H), 1.50 (s, 3H), 1.34 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.48, 141.51, 137.56, 131.93, 129.71, 128.91, 109.77, 84.16, 78.28, 76.48, 73.09, 68.14, 51.66, 37.15, 28.04, 26.30, 21.02.

Crude S₄ (107.5g, approximately 0.293 mol) was azeotroped with toluene (3x). THF (1L) was added at room temperature under N₂. LiAlH₄ pellets (25g, 0.66 mol) were added one at a time and stirred until TLC showed complete reaction. The reaction was quenched carefully with EtOAc dropwise (64 ml), then 1N NaOH (125 ml) dropwise. After the mixture cooled the resulting emulsion was filtered through Celite and the filtrate was extracted with THF and concentrated. The Celite cake was suspended in THF, heated to approximately 60 °C, then filtered. The filtrate was concentrated, combined with the first extract residue, and concentrated again to give crude S₅ (93 g), which was used as is in the next step. TLC: 10:1 DCM:MeOH, Rf 0.43.

HRMS m/z: Calc.: 363.1237 (MNa⁺), Found: 363.1234.

[α]²⁰_D (c 2.39, CHCl₃) +218.0

¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.72 (s, 1H, H-1), 4.31 (d, J = 5.6 Hz, 1H, H-2), 4.09 (dd, J = 6.8, 6.0 Hz, 1H, H-3), 4.01 (m, 1H, H-5), 3.62 (bs, 2H,
OH), 3.54 (m, 1H, H-4), 3.51 (m, 2H, H-7, H-7’), 2.27 (s, 3H), 1.95 (m, 1H, H-6), 1.67 (m, 1H, H-6’), 1.49 (s, 3H), 1.32 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.88, 132.14, 129.91, 129.24, 109.63, 83.79, 78.23, 76.18, 73.22, 69.63, 59.43, 34.40, 28.10, 26.38, 21.08.

KOH (500g, 8.91 mol) was dissolved in H$_2$O (1L) with mechanical stirring. When the temperature stabilized at 54 °C, tetra-$n$-butylammonium bromide (TBAB) (1.4g, 4.3 mmol) was added. A solution of crude S5 (93g, approximately 0.27 mol) in toluene (1 L) was added, followed by dropwise addition of benzyl bromide (BnBr) (181 mL, 1.52 mol, 5.6 eq.). After addition of approximately 10 mL of BnBr, no further temperature increase was observed, thus the temperature was increased to 95 °C. The reaction was stirred for 18 hours before additional BnBr (56 mL) was added dropwise. The toluene layer was separated, washed with brine (0.5 L), dried over MgSO$_4$, filtered, and concentrated. The crude material was purified on a 1-kg silica column using a step gradient of 100:0 (5 L) $\rightarrow$ 70:30 (9 L) $\rightarrow$ 50:50 (2 L) heptane:EtOAc. After concentrating the relevant fractions the di-benzylated product was suspended in a minimum of heptane, cooled, filtered and dried in a vacuum oven. The heptane mother liquor was concentrated, and the residue was heated at 150 °C under vacuum (0.5 Torr) to remove dibenzyl ether. Upon cooling the resulting solid was dried and combined with the previously dried product to yield S6 (75g, 46 % four-step yield) of desired product. 17.4g of the mono-benzylated product also was isolated. TLC: DCM:MeOH, $R_f$ 0.79.
Naphthalene (380g, 2.96 mol) was dried by washing with THF and passing a N₂ stream over the solid overnight. THF (2.8 L) was added to the naphthalene followed by lithium wire (20 g, 2.9 mol), and the mixture was stirred until the Li completely dissolved (5 hours). S6 (112g, 0.216 mol) was azeotroped with toluene (3x), dissolved in THF (1L), and cooled to -70 °C. The lithium naphthalide solution was added slowly under Ar via syringe pump. The reaction mixture became dark green and when TLC (heptane:EtOAc 2:1) showed complete consumption of starting material the reaction mixture was allowed to warm to room temperature before being quenched with brine. The THF layer was washed with brine, dried over MgSO₄, filtered, and concentrated at room temperature. The solids obtained were suspended in heptane (1L) at room temperature then chilled to 0 °C and filtered. The heptane filtrate was loaded onto a silica column (1kg) and eluted with heptane (5L) then heptane:TBME 4:1 (1L fractions). The product-containing fractions (fractions 10-17) were concentrated at room temperature to give 7 (52g, 0.153 mol, 71 %).

HRMS m/z: Calc.: 363.1567 (MNa⁺), Found: 363.1563.

[α]²⁰_D (c 1.85, CHCl₃) +5.95

¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.35 (m, 10H), 6.31 (d, J = 6.0 Hz, 1H), 4.76 (AB, J = 11.6, 18.4 Hz, 2H, CH₂Ph), 4.70 (dd, J = 6.0, 2.4 Hz, 1H), 4.50 (s, 2H, CH₂Ph), 4.33 (bs, 1H), 3.97 (dt, J = 9.2, 3.2 1H), 3.62 (m, 2H), 3.37 (dd, J = 8.8, 8.0 1H), 2.27 (m, 1H, H-6), 1.89 (m, 1H, H-6’), 1.62 (bs, 1H, OH).

¹³C NMR (100 MHz, CDCl₃) δ 144.45, 128.52, 128.33, 127.90, 127.86, 127.64, 127.52, 102.90, 80.52, 74.55, 73.81, 73.01, 69.58, 66.35, 31.22.
Glycal 7 (52g, 0.153 mol) was added to a suspension of NaH (14.0 g, 0.58 mol, 50 % dispersion) in THF/NMP (500 mL) at room temperature under N₂. p-Methoxybenzyl chloride (PMB-Cl, 53 mL, 0.39 mol) was added dropwise, and the reaction mixture was stirred at room temperature overnight. The solution was quenched carefully with MeOH (100 mL) and stirred at room temperature for 1 hour. H₂O was added and the upper THF layer was separated, washed with brine (200 mL), dried over MgSO₄/charcoal, filtered through Celite, and concentrated. The concentrate was taken up in CH₃CN (200 mL), and washed with heptane (2 x 100 mL) to remove residual mineral oil from the NaH reagent. The CH₃CN layer was concentrated and the concentrate was stirred in the freezer overnight. The resulting solid S7 was used as is in the next step. TLC: 2:1 heptane:EtOAc, Rₜ 0.54.

Crude S7 was added to a THF/H₂O solution (10:1, 440 mL total). OsO₄ (1.0 g, 3.9 mmol) was added, and the reaction mixture was stirred at room temperature in the dark. After approximately 3 hours, TLC showed all the starting material was consumed. Thus, saturated sodium thiosulfate solution (~500 mL) was added, and the mixture was stirred for 1 hour. The upper THF layer was separated, washed with brine (200 mL), and filtered. The crude syrup (S8) was added to a pyridine/Ac₂O solution (1:1, 600 mL total) and stirred at room temperature overnight. At 18 hours, TLC (heptane:EtOAc 3:1) showed complete reaction. The reaction mixture was concentrated, the residue taken up in DCM and loaded onto a silica column (1 kg, pre-eluted with heptane:TBME 20:1). The material was eluted using a step gradient of 20:0:1 (2 L) → 10:0:1 (2 L) → 4:1:0 (4 L) → 1:1:0 (4 L) Heptane:EtOAc:TBME to give the desired product S9 (75 g, 0.13 mol, 85 % from 7), which eluted as
a 4:1 mixture of anomers in the late 4:1 and early 1:1 heptane:EtOAc fractions. TLC: 1:1 Hept:EA, 
R_f 0.38.

HRMS m/z: Calc.: 601.2408 (MNa^+), Found: 601.2404.

[α]^20_D (c 1.03, CHCl₃) +40.78

^1^H NMR (400 MHz, CDCl₃) δ 7.14 – 7.38 (m, 12H), 6.80 – 6.91 (m, 2H), 6.19 (d, J = 4.0 Hz, 0.8H, H-1α), 5.57 (d, J = 8.0 Hz, 0.2H, H-1β), 5.05 (m, 0.2H), 4.99 (dd, J = 10.0, 4.8 Hz, 0.8H), 4.86 (m, 1H), 4.58 – 4.78 (m, 4H), 4.38 – 4.56 (m, 4H), 3.95 (t, J = 9.6 Hz, 1H), 3.80 (s, 0.6H, OCH₃), 3.78 (s, 2.4H, OCH₃), 3.52 – 3.68 (m, 3H), 2.18 (m, 1H, H-6), 2.07 (s, 0.6H, CH₃), 2.04 (s, 2.4H, CH₃), 2.00 (s, 2.4H, CH₃), 1.96 (s, 0.6H, CH₃), 1.71 (m, 1H, H-6′).

^1^C NMR (100 MHz, CDCl₃) δ 169.86, 169.16, 159.30, 138.54, 137.97, 130.48, 129.48, 129.36, 129.27, 129.21, 128.42, 128.30, 128.28, 127.94, 127.89, 127.83, 127.70, 127.66, 127.47, 113.84, 113.80, 92.29, 89.60, 81.38, 81.33, 79.78, 75.36, 75.13, 75.03, 74.79, 73.11, 73.07, 72.95, 72.21, 71.45, 69.89, 65.98, 55.26, 31.66, 31.55, 20.80, 20.69.

S9 (69.8 g, 0.120 mol) was dissolved in THF (100 mL) at room temperature under N₂. The solution was stirred and triethylamine (16.8 mL) was added. The reaction mixture was stirred for 1 minute before benzylamine (BnNH₂, 12.9 mL, 0.118 mol) was added and the reaction mixture was stirred for 4 days. The solution was concentrated at room temperature and the crude product was taken up in a DCM/heptane solution and loaded onto a 1-kg silica column pre-eluted with 10:1 heptane:EtOAc. The mixture was eluted using a step gradient of 10:1 (2 L) → 4:1 (4 L) → 2:1 (2 L) → 1:1 (6 L) of Heptane:EtOAc to give the desired product S10 (50.3 g, 78 %), which eluted as a 3:1 mixture of
anomers in the 1:1 fractions. TLC: 2:1 heptane:EtOAc, R<sub>f</sub> 0.34. In addition, 13.0g of recovered starting material was isolated.

HRMS m/z: Calc.: 559.2302 (MNa<sup>+</sup>), Found: 559.2297.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 – 7.38 (m, 12H), 6.86 (d, J = 8.4 Hz, 2H), 5.26 (d, J = 3.2 Hz, 0.75H, H-1α), 4.64 – 4.90 (m, 5H), 4.41- 4.53 (m, 2.4H), 4.05 (m, 1.5H), 3.79 (s, 3H, OCH<sub>3</sub>), 3.50 – 3.69 (m, 3.3H), 3.34 (m, 1H), 2.19 (m, 1H, H-6), 2.07 (s, 2.25H, CH<sub>3</sub>), 2.05 (s, 0.75H, CH<sub>3</sub>), 1.71 (m, 1H, H-6').

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.19, 170.40, 159.34, 159.25, 138.47, 138.39, 138.26, 138.05, 130.74, 130.37, 129.40, 129.31, 128.43, 128.39, 128.36, 127.88, 127.82, 127.72, 127.62, 127.56, 113.89, 113.86, 95.53, 90.12, 82.31, 82.02, 81.80, 79.56, 76.08, 75.10, 75.05, 74.82, 74.13, 72.79, 72.59, 72.26, 67.43, 66.25, 66.11, 55.27, 31.63, 31.39, 20.97.

Trichloroacetonitrile (TCAN, 300 mL) was added to S10 (50.3g, 0.094 mol) and stirred until a clear solution resulted. Powdered K<sub>2</sub>CO<sub>3</sub> (100g, 325-mesh) was then added at room temperature and the reaction mixture was stirred overnight. The mixture was filtered through Celite, washed with DCM (100 mL), passed through a 200-g silica plug, concentrated, and used as is in the next step. Product yield: 61g crude S11. TLC: 2:1 heptane:EtOAc, R<sub>f</sub> 0.49.
Crude S11 (~ 0.094 mol assumed) was azeotroped with toluene (3x). DCM (200 mL) and allyl alcohol (200 mL) were added at room temperature under N₂. Neat TMSOTf (2 mL, 11 mmol, 0.12 eq) was added dropwise. After the reaction mixture was stirred for 5 minutes TLC showed the reaction was complete. It was quenched with Et₃N (50 mL) and concentrated at room temperature. The reaction mixture became a solid, so it was dissolved in more DCM (200 mL) with stirring. The mixture was taken up to 600 mL total volume with heptane at room temperature, and stirred to allow the trichloroacetamide (TCA) to crystallize out (obtained 9.0g of TCA). The mother liquor was concentrated to obtain 57.6g of crude S12. TLC: heptane:TBME:DCM 2:1:1, Rf 0.59.

HRMS m/z: Calc.: 599.2615 (MNa⁺), Found: 599.2612.

¹H NMR (400 MHz, CDCl₃) δ 7.17 – 7.35 (m, 12H), 6.83 (d, J = 8.8 Hz, 2H), 5.81 (dddd, J = 16.0, 10.3, 5.2, 5.2 Hz, 1H, =CH), 5.12 – 5.28 (m, 2H), 4.96 (dd, J = 9.2, 8.4 Hz, 1H), 4.84 (m, 1H), 4.42 – 4.74 (m, 5H), 4.34 (d, J = 8.0 Hz, 1H), 4.19 (dd, J = 9.2, 2.3 Hz, 1H), 3.98 (m, 1H), 3.78 (s, 3H, CH₃), 3.53 – 3.66 (m, 3H), 3.47 (dt, 1H, H-6), 3.34 (m, 1H), 3.16 (m, 1H), 2.21 (m, 1H, H-6), 1.99 (s, 3H, CH₃), 1.71 (m, 1H, H-6’).

¹³C NMR (100 MHz, CDCl₃) δ 169.50, 159.28, 138.47, 138.03, 133.85, 130.35, 129.47, 128.39, 127.92, 127.88, 127.78, 127.54, 116.91, 113.83, 99.88, 82.71, 81.87, 75.11, 74.62, 73.51, 72.88, 71.88, 69.65, 66.09, 55.25, 31.70.

Crude S12 (57.6 g) was dissolved in THF (200 mL). MeOH (100 mL) and NaOMe/MeOH solution (40 mL, 25 % by weight) were added. The reaction mixture was stirred at room temperature overnight. The mixture was diluted with THF (200 mL) and washed with brine (200 mL). The upper
THF layer was separated. A small amount of charcoal and silica gel were added, filtered through Celite, and concentrated to a crude syrup. The crude syrup was purified on a 500-g silica column using a step gradient of 9:1 (2 L) → 4:1 (4 L) → 3:1 (12 L) of heptane:EtOAc to give 8. (35g, 0.065 mol, 70 %, 3-step yield from S10). TLC: 2:1 heptane:EtOAc, Rf 0.41.

HRMS m/z: Calc.: 557.2510 (MNa⁺), Found: 557.2506.

1H NMR (400 MHz, CDCl3) δ 7.26 – 7.38 (m, 12H), 6.87 (d, J = 8.4 Hz, 2H), 5.89 (dddd, J = 16.8, 10.0, 5.6, 5.6 Hz, 1H, =CH), 5.22 – 5.34 (m, 2H, =CH₂), 4.91 – 4.96 (m, 2H, CH₂Ph), 4.68 (½AB, J = 10.9 Hz, 1H, CH₂Ph), 4.54 (AB, J = 36.4, 12.0 Hz, 2H, CH₂Ph), 4.31 (d, J = 7.3 Hz, 1H, H-1), 4.18 (ABX, J = 65.1, 12.6, 6.4 Hz, 2H, CH₃-CH=CH₂), 3.86 (m, 2H), 3.80 (s, 3H, OCH₃), 3.65 – 3.77 (m, 2H), 3.61 (dd, J = 9.1, 7.3 Hz, 1H, H-2), 3.53 (t, J = 9.1 Hz, 1H, H-4), 3.33 (t, J = 9.1 Hz, 1H, H-3), 2.26 (m, 1H, H-6), 1.71 (m, 1H, H-6').

13C NMR (100 MHz, CDCl3) δ 159.31, 159.26, 138.51, 138.44, 138.33, 138.25, 133.91, 133.66, 130.93, 130.82, 129.66, 129.62, 128.40, 128.37, 128.34, 127.93, 127.89, 127.75, 127.71, 127.69, 127.58, 127.54, 117.83, 117.80, 113.92, 113.88, 101.73, 97.08, 84.32, 83.18, 81.81, 81.65, 75.10, 75.06, 74.91, 74.82, 73.31, 72.95, 72.89, 72.01, 70.29, 68.08, 67.77, 66.62, 66.25, 55.26, 31.91, 31.73.

8 (21.6g, 0.04 mol) was dissolved in pyridine (30 mL), and ADMB-Cl (12 mL) was added followed by DMAP (10 mg). The reaction mixture was heated at 80 °C for 21.5 hours, at which point more ADMB-Cl (5 mL) was added, and stirring was continued at 80 °C for another 12 hours. The reaction was quenched by the addition of MeOH (10 mL) and stirring for 15 minutes. The mixture was
concentrated and the residue partitioned between EtOAc (150 mL) and H₂O (100 mL). The EtOAc layer was washed with NH₄Cl (100 mL) and brine (100 mL), dried over Na₂SO₄/charcoal, filtered, and concentrated. The crude material was purified by silica gel chromatography using a step gradient of 9:1 (5 L) → 4:1 (5 L) → 2:1 (10 L) of heptane:EtOAc to give S13 (23.9g, 0.035 mol, 86 % yield).

HRMS m/z: Calc.: 713.3296 (MNa⁺), Found: 713.3292.

¹H NMR (400 MHz, CDCl₃) δ 7.12 – 7.38 (m, 12H), 6.82 (d, J = 8.4 Hz, 2H), 5.82 (dddd, J = 16.4, 10.8, 5.6, 5.6 Hz, 1H, =CH), 5.00 – 5.24 (m, 3H), 4.38 – 4.85 (m, 6H), 3.83 – 4.24 (m, 6H), 3.77 (s, 3H), 3.47 – 3.74 (m, 3H), 3.37 (t, J = 9.2 0.5H), 3.30 (t, J = 9.6 0.5H), 2.20 (m, 1H, H-6), 1.77 – 2.02 (m, 5H), 1.71 (m, 1H, H-6′), 1.24 (s, 3H), 1.21 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 176.63, 175.49, 170.83, 159.18, 138.46, 138.41, 138.21, 138.05, 133.66, 133.62, 130.61, 130.26, 129.03, 128.93, 128.40, 128.35, 128.33, 128.30, 128.08, 127.83, 127.76, 127.72, 127.64, 127.54, 127.47, 117.40, 117.37, 113.79, 99.98, 94.49, 82.88, 82.11, 81.80, 79.78, 75.11, 75.01, 74.51, 74.44, 73.65, 72.89, 71.90, 69.87, 68.06, 67.43, 66.51, 66.11, 61.40, 61.3255.23, 40.99, 40.85, 38.32, 31.73, 31.60, 25.50, 25.07, 25.04, 20.89, 20.86.

8 (16.18g, 0.03 mol) was dissolved in pyridine (30 mL). DMAP (10 mg) and benzoyl chloride (5.0 mL, 0.04 mol) were added. The reaction mixture was stirred capped at room temperature for 1 hour at which point excess MeOH (5 mL) was added and stirred. The mixture was diluted with EtOAc (100 mL), washed with H₂O (2 x 100 mL), 1N HCl (100 mL), brine (100 mL), NaHCO₃ (100 mL), and brine (100 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated. The partially crystallized crude material was recrystallized from hot aqueous ethanol. The first crop of crystals was dried in a vacuum oven. The mother liquor was concentrated and purified by silica gel
chromatography using the same method used for S13 to give an additional amount of S14. Total yield of S14: 19.8g, 29.8 mmol, 99 % yield. TLC: 2:1 heptane:EtOAc, R_f 0.38.

HRMS m/z: Calc.: 661.2772 (MNa^+), Found: 661.2768.

^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.27 – 7.39 (m, 10H), 7.06 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 5.76 (dddd, J = 16.4, 11.2, 5.2, 5.2 Hz, 1H, =CH), 5.28 (t, J = 8.8 Hz, 1H), 5.06 – 5.20 (m, 2H), 4.91 (d, J = 11.2 Hz, 2H), 4.74 – 4.76 (m, 6H), 4.21 (dd, J = 13.6, 4.8 Hz, 1H), 4.01 (dd, J = 13.6, 6.0 Hz, 1H), 3.82 (t, J = 9.2 Hz, 1H), 3.56 – 3.72 (m, 6H), 3.46 (t, J = 8.8 Hz, 1H), 2.29 (m, 1H, H-6), 1.78 (m, 1H, H-6’).

^13C NMR (100 MHz, CDCl_3) δ 165.17, 159.17, 138.55, 138.14, 133.85, 132.95, 130.18, 130.10, 129.79, 129.74, 129.67, 129.51, 128.37, 128.32, 127.95, 127.89, 127.79, 127.67, 127.57, 117.05, 113.67, 99.96, 82.62, 82.01, 75.13, 74.67, 74.11, 72.94, 71.99, 69.72, 66.17, 55.09, 31.79.

S14 (16.3g, 0.026 mol) was dissolved in a CH_3CN/H_2O solution (9:1 v/v, 300 mL) at room temperature and the reaction mixture was cooled to 5-8 °C. Ceric ammonium nitrate (CAN, 29 g, 0.052 mol) was added in one portion and stirred. After 3 hours, TLC showed the reaction was approximately 80 % complete; therefore, more CAN (5 g, 9 mmol) was added. After 30 minutes, one more aliquot of CAN (5 g, 9 mmol) was added and stirred for an additional one hour. Celite (10g) and EtOAc (300 mL) were added and the suspension was stirred while Et_3N (100 mL) was added slowly and stirred for 5 minutes. The mixture was filtered through a Celite pad, washed with brine (2 x 200 mL), filtered, dried over MgSO_4, and filtered again. The solution was concentrated and stored under high vacuum overnight. The crude material was purified on a silica column using a step
Step 1: **S13** (22.9g, 0.033 mol) was dissolved in a CH$_3$CN/H$_2$O solution (9:1 v/v, 200 mL) and the mixture was cooled to 0 °C in an ice bath. CAN (40 g, 0.073 mol) was added in one portion and stirred. After 20 minutes, an additional portion of CAN (5 g, 9 mmol) was added. After 2.5 hours Celite (40 g) was added and the suspension stirred. EtOAc (400 mL) was added followed by the slow addition of Et$_3$N (100 mL). The reaction mixture was filtered through Celite, washed with brine (2 x 100 mL), and dried over Na$_2$SO$_4$/MgSO$_4$. The mixture was filtered and concentrated to yield crude product, which was purified on by silica gel chromatography using a step-gradient of 9:1 (650 mL).
7:1 (650 mL)  \rightarrow  4:1 (650 mL)  \rightarrow  2:1 (1.2 L) of heptane:EtOAc to give S15 as an anomeric mixture (16.9g, 0.03 mol, 90 \% yield); TLC 2:1 heptane:EtOAc Rf = 0.26.

HRMS m/z: Calc.: 593.2721 (MNa\(^+\)), Found: 593.2718.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.25 – 7.34 (m, 10H), 5.79 (dddd, \(J = 17.2, 11.2, 6.0, 5.6\) Hz, 1H, =CH), 5.08 – 5.21 (m, 2H, =CH\(_2\)), 4.89 – 4.95 (m, 1.5H), 4.79 (dd, \(J = 9.2, 7.6\) Hz, 0.5H), 4.70 (d, \(J = 11.6\) Hz, 1H, CH\(_2\)Ph), 4.64 (dd, \(J = 10.0, 3.6\) Hz, 0.5H), 4.25 – 4.54 (m, 2H), 4.37 (d, \(J = 8.4\) Hz, 0.5H), 4.15 – 4.25 (m, 2H), 3.92 – 4.09 (m, 2H), 3.72 – 3.84 (m, 1.5H), 3.58 – 3.63 (m, 2H), 3.45 (dt, \(J = 9.6, 2.0\) Hz, 0.5H), 3.22 – 3.29 (m, 2H), 2.22 (m, 1H, H-6), 1.94 – 2.02 (m, 4H, H-6\', CH\(_3\)), 1.85 (m, 1H), 1.72 (m, 1H), 1.21 – 1.24 (m, 6H, gem-CH\(_3\)).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.65, 176.56, 138.31, 138.23, 133.67, 132.24, 128.39, 128.32, 128.06, 127.98, 127.77, 127.63, 117.29, 113.72, 99.57, 94.30, 82.00, 76.05, 74.95, 74.88, 74.63, 72.89, 71.76, 69.91, 68.01, 67.15, 66.59, 66.17, 61.45, 40.88, 40.76, 38.61, 31.82, 31.71, 26.30, 25.87, 24.74, 24.47, 20.93.

Step 2: S15 (16.9g, 0.03 mol) was dissolved in pyridine (40 mL). Benzoyl chloride (7.0 mL, 0.056 mol) were added. The reaction mixture was stirred capped at room temperature overnight at which point excess MeOH was added and stirred. The mixture was concentrated \textit{in vacuo} and the residue was taken up in EtOAc (150 mL), washed with brine (100 mL), saturated NH\(_4\)Cl solution (100 mL) and brine (100 mL). The organic layer was dried over Na\(_2\)SO\(_4\), filtered, and concentrated. The crude material (20.3 g) was purified by silica gel chromatography using the same protocol used for the purification of S15 to give S16: 18.9 g, 29 mmol, 99+ \% yield. TLC: 2:1 heptane:EtOAc, Rf 0.28.

HRMS m/z: Calc.: 697.2983 (MNa\(^+\)), Found: 697.2978.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (d, \(J = 8.4\) Hz, 2H), 7.81 (d, \(J = 9.2\) Hz, 2H), 7.55 (t, \(J = 7.2\) Hz, 1H), 7.42 (t, \(J = 8.4\) Hz, 2H), 7.25 – 7.37 (m, 6H), 6.98 (d, \(J = 6.8\) Hz, 2H), 5.76 (dddd, \(J = 16.8, 11.2, 6.0, 4.8\) Hz, 1H, =CH), 5.17 (d, \(J = 19.2\) Hz, 1H, =CH\(_2\)), 5.05 – 5.09 (m, 3H, H-2, =CH\(_2\)), 4.90
(d, J = 11.2 Hz, 1H), 4.70 (d, J = 11.2 Hz, 1H), 4.44 – 4.56 (m, 3H), 4.20 (dd, J = 13.2, 4.8 Hz, 1H), 4.00 (dd, J = 13.4, 6.4 Hz, 1H), 3.91 (t, J = 9.2 Hz, 1H), 3.61 – 3.79 (m, 2H), 3.52 (dt, J = 9.2, 2.4 Hz 1H), 3.34 (t, J = 8.8 Hz, 1H), 3.13 (bs, 1H, OH), 2.28 (m, 1H, H-6), 1.77 (m, 1H, H-6’).

Catalyst preparation: H₂ was bubbled through a solution of (1,5-Cyclooctadiene) bis(methyldiphenylphosphine)iridium(I) hexafluorophosphate (Felkin’s catalyst) (2.0 g, 0.025 mmol) in THF (500 mL) until all solids dissolved, then the solution was purged with argon for 30 minutes.

Allyl isomerization: The activated, purged Felkin’s catalyst solution was added to a solution of S16 (18.9 g, 0.029 mol) in THF. When the starting material was consumed (TLC heptane:TBME:DCM, 4:1:1 v/v/v, developed 3x), a 50 % NMO aqueous solution (200 mL) was added, followed by OsO₄ (200 mg). The mixture was stirred at room temperature in the dark overnight. TLC (2:1 v/v heptane:EtOAc) showed the reaction was complete, thus saturated sodium thiosulfate solution (200 mL) was added and stirred for 1 hour. Brine was added, and the reaction solution separated into 2 layers. The upper THF layer was washed with brine (2 x 100 mL) and concentrated. The residue was taken up in DCM, and H₂O was added. The lower DCM layer was loaded onto a silica column pre-eluted with heptane:EtOAc 9:1 (1L) then heptane (100 mL) and eluted using a step gradient of 9:1 → 7:1 → 4:1 → 1:1 of heptane:EtOAc to give the desired product S17 as a 1.5:1 mixture of anomers (17.7g, 0.028 mol, 96.2 % two-step yield), which eluted in the 1:1 heptane:EtOAc fractions.

HRMS m/z: Calc.: 657.2670 (MNa⁺), 617.2745 (M-OH, oxocarbenium ion), Found: 657.2668, 617.2743.
\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.99 (m, 2H), 7.55 (m, 1H), 7.42 (t, \(J = 8.0\) Hz, 2H), 7.26 – 7.34 (m, 5H), 7.11 – 7.20 (m, 5H), 5.94 (t, \(J = 10.0\) Hz, 0.67H), 5.58 (dd, \(J = 10.4, 9.2\) Hz, 0.33H), 5.36 (t, \(J = 4\) Hz, 0.67H), 4.98 (dd, \(J = 10.0, 8.0\) Hz, 0.33H), 4.91 (dd, \(J = 9.2, 2.8\) Hz, 0.67H), 4.71 (t, \(J = 8.0\) Hz, 0.67H), 4.54 – 4.62 (m, 2H), 4.49 (AB, \(J = 12.4, 11.6\) Hz, 2H, CH\(_2\)Ph), 4.30 (d, \(J = 3.6\) Hz, 0.67H), 4.22 (dt, \(J = 9.6, 2.4\) Hz, 0.67H), 3.87 – 4.06 (m, 2H), 3.54 – 3.69 (m, 3H), 2.24 (m, 1H, H-6), 1.94 (s, 1H, CH\(_3\) minor anomer), 1.92 (s, 2H, CH\(_3\) major anomer), 1.73 – 1.89 (m, 3H), 1.27 (m, 2H), 1.00 – 1.08 (m, 6H, gem-CH\(_3\)).

The lactol S17 (17.7g, 27.9 mmol, 1 eq) was dissolved in Cl\(_3\)CCN (100 mL). Once the mixture became a homogeneous solution K\(_2\)CO\(_3\) (20g, 145 mmol, 325 mesh) was added under N\(_2\). The reaction mixture was capped tightly and stirred overnight at room temperature. The mixture was filtered through Celite, washed with DCM, concentrated to a syrup and plugged through silica (5 cm high x 10 cm diameter) using 1:1 heptane:EtOAc. The trichloroacetimidate (TCl) donor 4 was obtained as a pale yellow oil (21.2g, 97.5 %), which was used directly in the next step. TLC: 2:1 heptane:EtOAc, R\(_f\) 0.36.
The TCl donor 4 (21.2g, 27.9 mmol, 1.16 eq) and acceptor 3 (12.5g, 24.1 mmol, 1 eq) were dissolved in anhydrous DCM (30 mL), combined, and concentrated. The mixture was azeotroped with toluene (3 x 10 mL) and dissolved in dry DCM (50 mL) under N₂. Separately, in a dry box, a solution of TMSOTf in DCM (600 µL TMSOTf, 400 µL DCM, 3.3M solution) was prepared. 400 µL of the TMSOTf solution was added to the DCM solution of the donor and acceptor over 1 minute, whereupon the reaction mixture turned darker. After stirring an additional 10 minutes the reaction was quenched with saturated NaHCO₃ (100 mL) and EtOAc (200 mL). The EtOAc layer was washed with brine (150 mL), dried over Na₂SO₄, filtered, and concentrated. The mixture was chromatographed on silica (11 cm diameter x 12 cm high), eluted with heptane:EtOAc (6:1, 1.1L → 4:1, 1.5L → 3:1, 2.5L → 2:1, 0.6L) to give homogeneous coupling product 9 plus additional impure fractions enriched in the desired coupling product. These impure fractions were combined and re-chromatographed to give an additional quantity of homogeneous desired product 9, which was combined with the initially purified product to give 25.9g (94.6 % yield) of 9 as a thick white paste.

TLC: 2:1 heptane:EtOAc (3x), Rₛ 0.34.

HRMS m/z: Calc.: 1157.4869 (MNa⁺), Found: 1157.4869.

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.26 – 7.44 (m, 20H), 7.15 (m, 2H), 7.07 (m, 1H), 5.76 (dddd, J = 16.4, 10.4, 6.0, 5.2 Hz, 1H, =CH), 5.24 (t, J = 9.2 Hz, 1H, H-2), 5.16 (dd, J = 9.0, 7.8 Hz, 1H, H-2), 4.98 – 5.13 (m, 4H), 4.75 (d, J = 7.6 Hz, 1H), 4.41 – 4.63 (m, 7H), 4.36 (d, J = 8.0 Hz, 1H), 4.24 (t, J = 8.8 Hz, 1H), 4.14 (dd, J = 13.2, 4.8 Hz, 1H), 3.88 – 3.95 (m, 3H), 3.44 – 3.72 (m, 7H), 3.34 (t, J = 6.8 Hz, 1H), 2.24 (m, 2H, H-6), 1.96 (s, 3H, CH₃), 1.59 – 1.93 (m, 4H), 0.99 (s, 3H, CH₃), 0.93 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 176.09, 170.81, 165.42, 164.69, 138.66, 138.54, 138.52, 137.13, 133.67, 133.41, 133.22, 129.71, 129.67, 129.54, 129.41, 128.69, 128.60, 128.41, 128.33, 128.29, 128.19, 128.13, 128.12, 127.85, 127.67, 127.53, 127.50, 116.96, 99.73, 99.05, 80.35, 79.65, 78.52,
Allyl disaccharide 9 (25.8g, 22.8 mmol, 1 eq) was dissolved in DCM (50 mL) in a 2-L round-bottom flask and cooled under N₂ in an ice bath. In a separate flask, anhydrous MeOH (400 mL) was cooled in an ice bath to an internal temperature of less than 5 °C. Acetyl chloride (AcCl, 30 mL) was added at a rate that kept the internal temperature below 5 °C and the mixture was then cooled to approximately 3 °C. The MeOH/AcCl solution was added to the 9/DCM solution, and the reaction mixture was capped. The ice bath was allowed to slowly warm to room temperature overnight. The reaction mixture was poured into a saturated bicarbonate / EtOAc mixture (1L total) and was carefully agitated to quench the HCl. The EtOAc was washed with brine (500 mL), dried over Na₂SO₄, filtered, concentrated and placed under high vacuum on a rotary evaporator to remove the ADMB lactone by-product (theoretical yield of lactone = 2.6g). The disaccharide alcohol 10 remained as a yellow syrup (19.78g, 89 % yield), which was used in the next step. TLC: 2:1 heptane:EtOAc, Rₜ 0.39.

HRMS m/z: Calc.: 1001.4083 (MNa⁺), Found: 1001.4076.

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 8.4 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.27 – 7.48 (m, 21H), 7.16 (m, 2H), 7.09 (m, 1H), 5.75 (dddd, J = 16.4, 10.4, 6.0, 5.6 Hz, 1H, =CH), 5.26 (dd, J = 9.6, 8.4 Hz, 1H, =CH₂), 5.19 (d, J = 1.6 Hz, 1H), 5.01 – 5.15 (m, 3H), 4.42 – 4.64 (m, 7H), 4.34 (½ AB, J = 12.0 Hz, 1H, CH₂Ph), 4.19 (dd, J = 13.2, 5.2 Hz, 1H), 3.94 – 4.01 (m,
2H), 3.34 – 3.69 (m, 9H), 2.47 (bs, 1H, OH), 2.28 (m, 1H, H-6), 2.14 (m, 1H, H-6), 1.72 (m, 1H, H-6’), 1.53 (m, 1H, H-6’).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.15, 165.93, 138.76, 138.58, 138.53, 137.39, 133.73, 133.29, 133.03, 130.01, 129.88, 129.83, 129.77, 129.72, 128.53, 128.37, 128.31, 128.24, 128.16, 128.12, 128.08, 128.02, 127.99, 127.74, 127.68, 127.59, 127.55, 127.51, 127.46, 117.25, 103.28, 99.33, 81.74, 80.30, 80.01, 74.75, 74.64, 74.13, 73.09, 72.95, 72.71, 71.76, 69.74, 66.16, 66.02, 31.86, 31.79.

Step 1: Disaccharide alcohol 10 (19.7g, 20.1 mmol, 1 eq) was azeotroped with toluene (3 x 10 mL), put under N$_2$, and dissolved in anhydrous DCM (100 mL). Anhydrous pyridine (100 mL) was added, and the reaction mixture was cooled in an ice bath. Triflic anhydride (Tf$_2$O, 20.0 mL, 128 mmol, 6 eq) was added via syringe in 0.5-mL aliquots over 45 minutes (the internal temperature went from 2.8 °C to 11 °C. Once the temperature returned to less than 3 °C, the next aliquot was added). Within 10-15 minutes of the addition of Tf$_2$O, the reaction was complete by TLC (2:1 heptane:EtOAc; pre-treated plates with Et$_3$N). The reaction mixture was poured into saturated NaHCO$_3$ (100 mL), extracted with EtOAc (200 mL), dried with brine (100 mL) and Na$_2$SO$_4$, filtered, and concentrated without external heat applied to the bath to give the crude intermediate triflate TLC: 2:1 Hep:EA, $R_f$ 0.32. The reaction mixture was azeotroped with toluene (3 x 10 mL).

Step 2: The crude triflate from Step 1 immediately was dissolved in toluene (500 mL), and tetra-n-butylammonium acetate (TBAA, 84g, 278 mmol, 14 eq) was added. The reaction mixture was sonicated whereupon the mixture darkened and went from cloudy to clear. After sonicating for 4 hours the reaction mixture was concentrated in vacuo and passed through a silica plug (14 cm
diameter x 8 cm high), eluting with heptane:EtOAc (7:1, 800 mL → 5:1, 1200 mL → 4:1, 1000 mL → 2:1, 2400 mL), collecting 800-mL fractions. Upon concentration of the homogeneous fractions disaccharide 11 was isolated as pale yellow oil (15.8g, 77 %), which was used as is in the next step. TLC: 2:1 heptane:EtOAc, Rf 0.45.

HRMS m/z: Calc.: 1043.4188 (MNa+), Found: 1043.4185.

1H NMR (400 MHz, CDCl3) δ 8.03 (d, J = 7.2 Hz, 2H), 7.87 (d, J = 7.2 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.25 – 7.53 (m, 21H), 7.20 (m, 2H), 7.18 (m, 1H), 5.76 (dddd, J = 16.4, 10.4, 6.0, 5.2 Hz, 1H, =CH), 5.48 (d, J = 2.2 Hz, 1H, H-1), 5.30 – 5.06 (m, 4H), 5.04 (dd, J = 9.5, 5.6 Hz, 1H), 4.83 (s, 1H), 4.41 – 4.63 (m, 8H), 4.21 (dd, J = 13.6, 7.6 Hz, 1H), 4.19 (t, J = 8.8 Hz, 1H), 4.00 (dd J = 13.6, 5.6 Hz, 1H), 3.58 – 3.80 (m, 5H), 3.50 (m, 2H), 3.39 (t, J = 9.2 Hz, 1H), 2.33 (m, 2H, H-6), 2.04 (s., 3H, CH3), 1.78 (m, 1H, H-6').

13C NMR (100 MHz, CDCl3) δ 169.58, 165.16, 164.92, 138.78, 138.45, 137.28, 133.78, 133.59, 133.22, 133.12, 129.88, 129.85, 129.66, 129.45, 128.34, 128.31, 128.21, 128.08, 127.99, 127.94, 127.87, 127.79, 127.74, 127.68, 117.48, 99.60, 97.94, 80.55, 79.78, 77.75, 75.19, 74.93, 74.75, 74.53, 73.00, 74.17, 72.96, 72.22, 72.16, 70.27, 69.84, 66.60, 66.14, 31.93, 31.85, 20.71.

13C NMR (100 MHz, CDCl3, 1H-coupled) δ 99.60 (1Jc1,h1 = 162.0 Hz, □), 97.94 (1Jc1,h1 = 159.05 Hz, β).

Disaccharide 11 (15.8g, 15.5 mmol, 1 eq) was dissolved in THF (60 mL). MeOH (30 mL) was added, followed by a NaOMe/MeOH solution (25 % by weight, 5 mL). The reaction mixture was purged with N2, capped, and stirred overnight at room temperature. It was diluted with THF (500
mL) and washed with saturated NH₄Cl solution (400 mL) and brine (400 mL), dried over Na₂SO₄, filtered, concentrated, and azeotroped with toluene (4 x 20 mL) to give an oily solid (16.2 g). The aqueous layer was back-extracted with EtOAc (2 x 300 mL), dried, filtered, and concentrated (200mg product). The 1H NMR spectrum of the THF extract showed two compounds, one of which was the desired compound 12.

HRMS m/z: Calc.: 793.3558 (MNa⁺), Found: 793.3554.

1H NMR (400 MHz, CDCl₃) δ 7.22 – 7.34 (m, 20H), 5.87 (dddd, J = 16.8, 11.6, 6.0, 5.2 Hz, 1H, =CH), 5.28 – 5.16 (m, 2H, =CH₂), 4.81 – 4.90 (m, 3H, incl. H-1), 4.66 (½AB, J = 10.8 Hz, 1H, CH₂Ph), 4.61 (½AB, J = 10.4 Hz, 1H, CH₂Ph), 4.49 (AB, J = 24.0, 12.0 Hz, 2H, CH₂Ph), 4.37 (AB, J = 12.8, 12.8 Hz 2H, CH₂Ph), 4.16 – 4.23 (m, 2H, incl. H-1’), 4.05 (d, J = 3.6 Hz, 1H), 4.00 (dd J = 12.4, 6.4 Hz, 1H), 3.48 – 3.77 (m, 10H), 3.32 (m, 1H), 3.24 (d, J = 6.8 Hz, 1H, OH), 2.20 – 2.37 (m, 3H), 1.78 (m, 1H, H-6’), 1.68 (m, 1H, H-6’).

13C NMR (100 MHz, CDCl₃) δ 138.54, 138.49, 138.36, 138.02, 133.81, 128.41, 128.29, 128.12, 128.05, 127.88, 127.63, 127.56, 117.99, 101.34, 99.85, 81.40, 80.77, 79.94, 74.91, 74.11, 73.98, 72.78, 72.35, 71.91, 70.30, 66.60, 66.31, 31.80.

The mixture containing disaccharide 12, acetone (200 mL), 2,2-dimethoxypropane (50 mL), and pTsOH•H₂O (100mg) were combined and stirred at room temperature for 2 hours. Saturated NaHCO₃ (50 mL) was added, and the mixture was concentrated to remove most of the organic volatiles. The residue was partitioned between EtOAc (300 mL) and saturated NaHCO₃ (200 mL). The aqueous layer was washed with EtOAc (200 mL), and the combined organics were washed with
brine (200 mL), dried over Na₂SO₄, filtered, and concentrated. The mixture was chromatographed on silica gel (13 cm diameter x 10 cm high) pre-eluted with DCM/Et₃N (99:1) then eluted with DCM/Et₃N (99:1, 6 x 900 mL) → DCM/MeOH/Et₃N (95:5:1, 4 x 1L) to give acetonide 13 (10.3 g, 82 %) and a more polar running material identified as the gluco-gluco triol isomer (2.7 g, 22 %). TLC of 13: 20:1 DCM:MeOH, Rf 0.37.

¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.35 (m, 20H), 5.89 (dddd, J = 12.0, 10.4, 6.8, 5.6 Hz, 1H, =CH), 5.25 (dd, J = 16.0, 3.2, 1.2 Hz, 1H, =CH₂), 5.18 (dd, 2.4, 1.2 Hz, 0.5H, ½ =CH₂), 5.16 (m, 2H, ½ =CH₂, H-1), 5.03 (½ AB, J = 12.0 Hz, 1H, ½ CH₂Ph), 4.81 (½ AB, J = 12.0 Hz, 1H, ½ CH₂Ph), 4.58 (½ AB, J = 12.0 Hz, 1H, ½ CH₂Ph), 4.57 (½ AB, J = 12.0 Hz, 1H, ½ CH₂Ph), 4.48 (AB, J = 37.2, 12.0 Hz, 2H, CH₂Ph), 4.33 – 4.39 (m, 3H), 4.29 (t, J = 6.0 Hz, 1H), 4.21 (ddt, J = 6.4, 5.6, 1.6 Hz, 1H), 4.18 (d, J = 7.6 Hz, 1H), 4.01 (ddt, J = 6.4, 6.0, 1.2 Hz, 1H), 3.75 (t, J = 8.8 Hz, 1H), 3.30 – 3.65 (m, 9H), 3.11 (bs, 1H, OH), 2.12 – 2.28 (m, 2H), 1.66 (m, 2H), 1.51 (s, 3H, CH₃), 1.41 (s, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃) δ 138.57, 138.51, 138.45, 138.02, 133.77, 128.35, 128.30, 128.29, 128.19, 128.04, 127.89, 127.68, 127.56, 127.38, 118.02, 110.55, 101.26, 99.29, 83.34, 79.96, 79.80, 79.00, 74.56, 74.22, 74.03, 72.87, 72.75, 72.52, 71.99, 71.83, 70.29, 66.48, 66.20, 32.46, 31.86, 27.76, 26.29.

Step 1: Acetonide 13 (14.9 g, 18.4 mmol, 1 eq) was azeotroped with toluene (3 x 10 mL) then dissolved in anhydrous pyridine (25 mL). ADMB-Cl (10.6 g, 3 eq) was added with stirring, followed by DMAP (10 mg). The reaction mixture was purged with N₂, capped tightly, and put in an oil bath at 80 °C for 24 hours. The reaction mixture was concentrated in vacuo and the residue partitioned
between EtOAc (200 mL) and saturated NH₄Cl (200 mL). The EtOAc layer was washed with brine, saturated NaHCO₃ solution, and brine again (100 mL each). It was dried over Na₂SO₄/charcoal/silica gel, filtered through a silica pad, and concentrated to give crude 14. TLC of major product 14: 2:1 heptane:EtOAc, Rₚ 0.59.

**Step 2:** Crude 14 from Step 1 was dissolved in a HOAc/H₂O solution (4:1, 100 mL) and placed in a heating bath at 63 °C for 1 hour. The mixture was concentrated *in vacuo* and azeotroped with toluene (3 x 20 mL) and hexanes (2 x 20 mL) to give crude diol 15, which was used as is in the next step. TLC of 15: 2:1 hexane:EtOAc, Rₚ 0.13.

**Step 3:** The crude diol 15 was dissolved in pyridine (75 mL), and Ac₂O (75 mL) was added. The reaction mixture was purged with N₂, capped, and stirred overnight at room temperature. The reaction mixture was concentrated *in vacuo*, azeotroped with toluene (3 x 20 mL), and placed on the vacuum-line overnight. The mixture was purified by silica column (6 cm diameter x 16 cm high), eluted with hexane:EtOAc (5:1, 700 mL → 4:1, 600 mL → 3:1, 600 mL → 2:1, 600 mL → 3:2, 500 mL) to give disaccharide 2 (14.91 g, 80 % three-step yield from 13). TLC: 2:1 hexane:EtOAc, Rₚ 0.42.

HRMS m/z: Calc.: 1033.4556 (MNa⁺), Found: 1033.4548. [α]°D (c 1.9, CHCl₃) -10.00

H NMR (400 MHz, CDCl₃) δ 7.24 – 7.39 (m, 20H), 5.78 (dddd, J = 15.6, 10.4, 6.0, 5.2 Hz, 1H, =CH), 5.34 (d, J = 3.2Hz, 1H), 5.19 (dd, J = 3.2, 1.6 Hz, 1H, =CH₂), 5.14 (dd, 3.2, 1.6 Hz, 1H, =CH₂), 5.05 (½AB, J = 10.8 Hz, 1H, CH₂Ph), 4.87 – 4.94 (m, 2H), 4.72 (s, 1H, H-1), 4.63 (AB, J = 11.2, 9.2 Hz, 2H, CH₂Ph), 4.50 (½AB, J = 10.8 Hz, 1H, CH₂Ph), 4.48 (AB, J = 22.4, 12.0 Hz, 2H, CH₂Ph), 4.37 (AB, J = 26.4, 12.0 Hz, 2H, CH₂Ph), 4.09 – 4.17 (m, 5H), 3.88 (ddt, J = 13.2, 6.4, 1.6 Hz, 1H), 3.81 (dd, J = 9.6, 8.4 Hz, 1H), 3.43 – 3.62 (m, 5H), 3.32 (dt, J = 9.6, 2.4 Hz, 1H), 3.22 (t, J = 8.4 Hz, 1H), 2.21 (m, 2H), 2.06 (s, 3H, CH₃), 2.00 (s, 3H, CH₃), 1.94 (s, 3H, CH₃), 1.89 (m, 2H), 1.66 (m, 2H), 1.28 (2, 3H, CH₃), 1.25 (s, 3H, CH₃).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.15, 170.97, 169.78, 169.76, 138.68, 138.61, 138.42, 137.82, 133.50, 128.46, 128.34, 128.13, 127.91, 127.73, 127.71, 127.61, 127.58, 127.43, 127.35, 117.43, 99.51, 98.37, 81.01, 79.56, 77.22, 75.22, 74.61, 74.16, 73.62, 72.94, 72.69, 72.21, 71.70, 69.77, 69.60, 66.13, 66.01, 61.21, 40.95, 38.34, 31.79, 31.59, 25.40, 25.17, 24.65, 20.98, 20.88, 20.74.

Disaccharide 2 (9.83g, 9.72 mmol, 1 eq) was placed in a 500-mL round-bottom flask, azeotroped with toluene (3 x 15 mL) and brought into a dry box. In the dry box Felkin’s catalyst (1.25g, 1.48 mmol, 0.15 eq) was weighed into an empty 200-mL round-bottom flask, and anhydrous THF (100 mL) was added to each flask. The flasks were sealed with septa connected by a cannula and brought out of the dry box. H$_2$ was bubbled through the catalyst suspension with the exit port in the same flask. The substrate flask was kept under positive N$_2$ flow. H$_2$ was bubbled until all catalyst was dissolved and the color faded to a pale orange. The entire system was purged with N$_2$ for 15 minutes. The catalyst solution was transferred to the substrate solution via N$_2$ pressure through the cannula. The reaction mixture was stirred at room temperature for 30 minutes (TLC: 2:1:1 Hep:DCM:TBME, R$_f$ 0.46). A 50 % NMO aqueous solution (50 mL) and OsO$_4$ (3 mg) were added to the reaction mixture whereupon it darkened within a few seconds. It was left to stir at room temperature in the dark for 2.5 hours. Saturated Na$_2$S$_2$O$_3$ solution (100 mL) was added and stirred at room temperature for 1 hour. THF (200 mL) and brine (200 mL) were added, and the layers were separated. The aqueous layer was washed with THF (200 mL), and the combined THF layers were washed with brine. The THF was dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was chromatographed on silica gel (6 cm diameter x 14 cm high), eluting with hexanes:EtOAc 4:1 (500
mL) → 3:1 (600 mL) → 2:1 (1200 mL) → 1:1 (600 mL) to give the lactol 16 as a yellow syrup (7.75 g, 82.1% yield). TLC: 2:1 heptane:EtOAc, Rf 0.24.

HRMS m/z: Calc.: 933.4243 (MNa⁺), Found: 933.4234.

H NMR (400 MHz, CDCl₃) δ 7.24 – 7.42 (m, 20H), 5.46 (d, J = 3.4 Hz, 1H), 5.35 (d, J = 3.2 Hz, 1H), 5.12 (½AB, J = 11.2 Hz, 1H, CH₂Ph), 4.94 (m, 1H), 4.31 – 4.82 (m, 8H), 4.18 (m, 2H), 4.01 (t, J = 8.8 Hz, 1H), 3.61 (m, 6H), 3.24 (t, J = 9.0 Hz, 1H), 2.08 (s, 3H, CH₃), 1.99 (s, 3H, CH₃), 1.95 (s, 3H, CH₃), 1.88 – 2.26 (m, 6H), 1.73 (m, 2H, H-6”), 1.68 (m, 1H, H-6”), 1.28 (s, 3H, CH₃), 1.27 (s, 3H, CH₃).

C NMR (100 MHz, CDCl₃) δ 176.44, 171.29, 169.99, 169.79, 138.88, 138.67, 138.60, 138.54, 137.98, 128.44, 128.32, 128.21, 128.14, 128.02, 127.92, 127.89, 127.74, 127.71, 127.61, 127.52, 127.44, 127.40, 98.52, 95.44, 89.26, 79.77, 78.03, 77.06, 75.13, 75.15, 74.61, 74.30, 73.07, 72.74, 72.71, 72.33, 69.74, 67.27, 66.51, 66.21, 61.16, 40.72, 38.76, 31.94, 31.57, 25.43, 25.03, 20.91, 20.81, 20.70.

The lactol 16 (7.75 g, 7.98 mmol, 1 eq) was azeotroped with toluene (3 x 10 mL) and dissolved in Cl₃CCN (100 mL). Powdered K₂CO₃ (20 g) was added, and the reaction mixture was stirred at room temperature under N₂ for 4.5 hours. The mixture was poured through Celite and washed with DCM. The filtrate was passed through a short silica pad and washed with hexane/EtOAc (2:1 → 1:1). The filtrate was concentrated to give donor 17 as a pale yellow foam (9.0 g, quant.). TLC: 2:1 heptane:EtOAc, Rf 0.31.
6-Amino-1-hexanol (100g, 117.19 g/mol, 0.853 mol, 1.0 eq) was added to CH₂Cl₂ (1L). Benzaldehyde (94.9 mL, 0.939 mol, 1.1 eq) was added, followed by Na₂SO₄ (121.2g, 0.853 mol, 1.0 eq). The reaction mixture was stirred at room temperature overnight during which it became a clear, pale yellow solution. The reaction mixture was filtered through Celite and concentrated in vacuo to give S18.

Imine S18 (~ 0.853 mol, 1.0 eq) was dissolved in EtOH (600 mL) and the resulting mixture was stirred at 0 °C. NaBH₄ (12.09g, 0.320 mol, 1.5 eq) was added in 3-gram portions over 1 hour. The reaction mixture was allowed to warm to room temperature for 18 hours at which point additional NaBH₄ (6g) was added and stirring continued for 1 hour more. The reaction mixture was concentrated and redissolved in EtOAc (500 mL), washed with brine (2 x 150 mL), dried over Na₂SO₄, filtered and concentrated to give crude S19, which was used without further purification. TLC: 1:9 MeOH:CH₂Cl₂, Rf 0.35 (visualized with anisaldehyde (faint) and ninhydrin (very strong).

S19 (200g, 0.854 mol, 1 eq) was dissolved in CH₂Cl₂ (800 mL) and cooled to 0 °C over 30 minutes. Et₃N (37 ml, 2 eq) was added and the mixture was again stirred at 0 °C for 30 minutes. Cbz-Cl (125 ml, 1.1 eq) was added dropwise at 0 °C over 3 hours. The reaction mixture was allowed to warm to room temperature under N₂ for 18 hours to produce a white suspension. The reaction mixture was diluted with EtOAc, and the organics were washed with H₂O (3 x 800 mL), 1M HCl (2 x 500 mL), brine (800 mL), and dried over Na₂SO₄, filtered, and concentrated. The mixture was purified on a 400-mL silica plug (pre-washed with 5 % MeOH/CH₂Cl₂), eluting with 5 % MeOH/CH₂Cl₂ (1L) and concentrated to a viscous oil to give the crude linker 11, which was stored in the freezer. A portion of the crude 18 was purified to homogeneity by silica gel chromatography (6 cm diameter x 15 cm
high), eluted with hexanes:EtOAc (5:1, 600 mL → 4:1, 600 mL → 2:1, 1200 mL) to provide pure 18 as a colorless oil. Rf 0.35.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.16 – 7.37 (m, 10H), 5.17 (d, $J = 10.4$ Hz, 2H), 4.49 (d, $J = 8.0$ Hz, 2H), 3.59 (m, 2H), 3.23 (t, $J = 6.8$ Hz, 1H), 3.19 (t, $J = 6.8$ Hz, 1H), 1.14 – 1.53 (m, 8H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.45, 137.91, 128.52, 128.44, 127.92, 127.85, 127.25, 67.17, 62.81, 62.64, 50.43, 50.06, 46.83, 46.13, 32.54, 32.10, 27.57, 27.02, 26.47, 26.25, 25.33.

TCI donor 17 (9.0g, 8.1 mmol, 1 eq) and linker acceptor 18 (3.04g, 8.9 mmol, 1.1 eq) were combined and azeotroped with toluene (3 x 15 mL). The mixture placed under vacuum then brought into a dry box. Anhydrous DCM (40 mL) was added, and TMSOTf (147 µl, 0.81 mmol, 0.1 eq,) was added dropwise over 5 minutes. The reaction mixture was removed from the dry box and checked by TLC and quenched by the simultaneous addition of EtOAc (150 mL) and saturated NaHCO$_3$ (150 mL). The EtOAc layer was washed with brine (150 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. The crude residue was purified on a silica column (6 cm diameter x 10 cm high), eluting with hexanes:EtOAc 5:1 (600 mL) → 4:1 (600 mL) → 3:1 (600 mL) → 2:1 (1200 mL) to give the disaccharide 19 as a colorless oil (9.14g, 87 % yield). TLC: 2:1 hexanes:EtOAc, Rf 0.33.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.16 – 7.39 (m, 30H), 5.34 (d, $J = 3.2$ Hz, 1H), 5.16 (d, $J = 12.0$ Hz, 2H), 5.04 (d, $J = 10.8$ Hz, 1H), 4.84 – 4.91 (m, 2H), 4.72 (s, 1H), 4.63 (AB, $J = 11.2$, 9.2 Hz, 2H, CH$_2$Ph), 4.43 – 4.53 (m, 5H), 4.37 (AB, $J = 23.6$, 12.2 Hz, 2H, CH$_2$Ph), 4.05 – 4.18 (m, 3H), 2.21 (m, 1H), 2.06 (s, 3H, CH$_3$), 1.98 (s, 3H, CH$_3$), 1.94 (s, 3H, CH$_3$), 1.90 (m, 2H), 1.71 (m, 1H), 1.64 (m, 2H), 1.24 (m, 3H), 1.25 (s, 3H, CH$_3$), 1.23 (s, 3H, CH$_3$).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.12, 170.90, 169.81, 169.78, 156.77, 156.19, 138.80, 138.70, 138.54, 138.00, 137.9136.96, 136.85, 128.57, 128.51, 128.39, 128.25, 128.19, 128.13, 127.96, 127.85, 127.79, 127.69, 127.66, 127.59, 127.50, 127.45, 127.35, 127.22, 100.58, 98.47, 81.10, 79.61, 77.16, 75.26, 74.63, 74.26, 73.80, 72.93, 72.73, 72.24, 71.67, 69.66, 69.37, 67.14, 66.14, 66.02, 61.20, 50.49, 50.1647.18, 46.25, 40.96, 38.37, 34.71, 31.85, 31.63, 29.60, 29.10, 28.13, 27.70, 26.63, 25.80, 25.49, 25.33, 25.27, 22.70, 20.99, 20.92, 20.78, 14.22.

Under N$_2$ disaccharide 19 (9.08g, 7.01 mmol, 1 eq) was taken up in anhydrous THF (50 mL). Anhydrous MeOH (50 mL) was added, followed by a NaOMe solution (25 % by weight, 10 mL). The reaction mixture was stirred overnight at room temperature then diluted with THF (200 mL) and quenched with saturated NH$_4$Cl (200 mL). The organic layer was washed with brine (200 mL), and the aqueous layer was back-extracted with THF (2 x 100 mL). The organics were combined, dried over Na$_2$SO$_4$, filtered, and concentrated. The product was azeotroped with hexanes (3 x 20 mL). An oily solid was obtained, which was partitioned between DCM (100 mL) and brine (100 mL). The DCM layer was dried with Na$_2$SO$_4$, filtered (very slow), and concentrated. The slow filtration was a result of the desired triol adhering to the filter paper and Na$_2$SO$_4$ solids. Thus, the filter cake and filter paper were washed with MeOH until no more desired compound was present. The MeOH extracts were combined, concentrated and combined with the DCM extracted material to give crude triol 20 (6.45g). TLC: 1:1 hexanes:EtOAc, R$_f$ 0.18.

Compound 20: C$_{63}$H$_{75}$NO$_{13}$Na; LRMS Calc.: m/z = 1076.5; Found: m/z = 1077.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.18 – 7.40 (m, 30H), 5.19 (m, 2H), 4.94 (dd, $J = 10.8$, 2.8 Hz, 2H), 4.89 (s, 1H), 4.68 ($\frac{1}{2}$AB, $J = 11.2$ Hz, 1H, CH$_2$Ph), 4.64 ($\frac{1}{2}$AB, $J = 10.4$ Hz, 1H, CH$_2$Ph), 4.51 (m, 3H), 4.50 (AB, $J = 32.0$, 12.0 Hz, 2H, CH$_2$Ph), 4.39 (s, 1H), 4.12 (m, 2H), 3.18 – 3.75 (m, 18H), 2.26 (m, 2H), 1.83 (m, 1H), 1.70 (m, 1H), 1.54 (m, 4H), 1.20 – 1.39 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.81, 156.33, 138.53, 138.46, 138.37, 137.84, 136.88, 136.66, 128.59, 128.50, 128.47, 128.40, 128.33, 128.23, 128.13, 127.99, 127.87, 127.82, 127.67, 127.64, 127.61, 127.45, 127.33, 127.22, 102.46, 100.40, 80.98, 79.58, 75.16, 75.01, 74.14, 73.94, 72.88, 72.82, 72.47, 71.74, 69.90, 67.27, 66.67, 66.08, 50.45, 49.97, 46.65, 46.16, 31.95, 31.82, 30.36, 29.56, 29.32, 27.95, 27.28, 26.63, 26.21, 25.75, 25.57, 24.24, 14.20.

Step 1: Triol 20 (6.46g, 6.13 mmol, 1 eq) was azeotroped with acetone (3 x 20 mL). Acetone/2,2-dimethoxypropane (4:1, 100 mL) was added, followed by pTsOH•H$_2$O (50 mg). The reaction mixture was stirred at room temperature for 20 minutes and then diluted with EtOAc (250 mL). The mixture was washed with saturated NaHCO$_3$ (100 mL), followed by brine (100 mL). The mixture was then dried over Na$_2$SO$_4$, filtered, and concentrated. The product was chased with hexane and placed under vacuum to yield (6.5 g) product 21 as a syrup which was used as is in the next step. TLC: 1:1 heptane:EtOAc.

Step 2: The substrate 21 from Step 1 (6.1 mmol, 1 eq) was azeotroped with toluene (3 x 10 mL) then dissolved in anhydrous DCM (150 mL) under N$_2$. Dess-Martin periodinane (5.17g, 12.2 mmol, 2 eq) was added in 3 portions over 5 minutes. The reaction mixture was stirred at room temperature and became homogeneous within 2 minutes of the addition of each aliquot. After 1.5 hours, wet DCM (1
was added and after 2-3 minutes a small amount of white precipitate began to form. More wet DCM (10 mL) was added dropwise. The reaction mixture was stirred at room temperature for 16 hours. The mixture was diluted with DCM (200 mL), filtered through a Celite pad, washed with DCM (100 mL) and brine (200 mL), dried over Na₂SO₄, filtered, and concentrated. The crude ketone was used as is in the next step. TLC: 1:1 hexanes:EtOAc, Rₜ 0.62.

Step 3: The crude ketone from Step 2 was taken up in a DCM/MeOH solution (1:1, 150 mL), and NaBH₄ (1.04g, 27.5 mmol, 4.5 eq) was added under N₂ sweep. The reaction mixture was stirred at room temperature for 10 minutes and then concentrated in vacuo to dryness. The residue was partitioned between EtOAc (200 mL) and saturated NH₄Cl (200 mL). The organic layer was washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated. The crude product 22 was used as is in the next step. TLC: 1:1 hexanes:EtOAc, Rₜ 0.33.

Step 4: The crude alcohol 22 from Step 3 was taken up in pyridine (24 mL) and cooled to 0 °C in an ice bath. BzCl (2.4 mL, 20.7 mmol) was added, followed by DMAP (10 mg). The mixture was stirred overnight under N₂ and allowed to come to room temperature. Precipitate formed within 15 minutes. The reaction mixture was diluted with EtOAc (200 mL); quickly washed with HCl solution (pH 3, 2 x 100 mL), saturated NaHCO₃ (100 mL), and brine (200 mL); dried over Na₂SO₄, filtered, and concentrated. The residue was chased with water (1 x 10 mL) and hexanes (4 x 10 ml) to remove the residual pyridine and EtOAc before proceeding directly to the next step. TLC: 1:1 hexanes:EtOAc, Rₜ 0.82.

Step 5: The Step 4 residue was taken up in 80 % HOAc (80 mL) and heated to 50 °C overnight. The mixture was concentrated in vacuo to dryness and the residue was partitioned between EtOAc (200 mL) and saturated NaHCO₃ (100 mL), washed with saturated NaHCO₃ (100 mL), brine (100 mL), dried over Na₂SO₄, filtered, and concentrated. The product was purified on a silica column (6 cm diameter x 14 cm high), eluting with heptane:EtOAc 4:1 (700 mL) → 3:1 (600 mL) → 2:1 (600 mL) → 1:1 (1200 mL). Concentration of the relevant fractions gave diol 23 as an off-white waxy solid (3.92g, 3.39 mmol, 55 % 5-step yield). TLC: 1:1 heptane:EtOAc, Rₜ 0.35.
Compound 23: C\textsubscript{70}H\textsubscript{79}NO\textsubscript{14}Na; LRMS Calc.: m/z = 1180.5; Found m/z = 1180.

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.09 (d, \(J = 7.6\) Hz, 2H), 7.58 (tt, \(J = 7.6, 1.2\) Hz, 1H), 7.17 – 7.46 (m, 22H), 5.63 (d, \(J = 3.6\) Hz, 1H, H-2 (OBz)), 5.18 (s, 2H), 4.83 (AB, \(J = 84.8, 10.8\) Hz, 2H, CH\textsubscript{3}Ph), 4.78 (AB, \(J = 125, 10.8\) Hz, 2H, CH\textsubscript{3}Ph), 4.75 (s, 1H, H-1), 4.60 (½AB, \(J = 12.0\) Hz, 1H, CH\textsubscript{3}Ph), 4.41 – 4.52 (m, 6H, incl. H-1’), 4.09 (dd, \(J = 9.2, 3.6\) Hz, 1H), 3.87 (bs, 1H), 3.30 – 3.77 (m, 10H), 3.22 (m, 1H), 3.14 (m, 1H), 2.62 (d, \(J = 8.8\) Hz, 1H), 2.26 – 2.42 (m, 3H), 1.90 (m, 1H), 1.80 (m, 1H), 1.47 (m, 4H), 1.22 (m, 4H).

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.48, 156.74, 156.18, 138.65, 138.52, 138.42, 138.33, 137.95, 136.82, 133.23, 130.05, 129.89, 128.55, 128.48, 128.40, 128.32, 128.17, 128.08, 127.94, 127.89, 127.85, 127.82, 127.76, 127.73, 127.62, 127.58, 127.53, 127.50, 127.26, 127.19, 98.66, 97.02, 79.73, 77.99, 77.50, 77.34, 74.91, 74.78, 74.52, 72.96, 72.71, 72.13, 72.05, 71.07, 69.69, 69.22, 67.14, 66.52, 66.30, 50.44, 50.12, 47.11, 46.16, 32.10, 31.92, 31.88, 29.39, 27.99, 27.61, 26.53, 25.71, 22.74, 14.20.

Disaccharide donor 17 (3.4g, 3.10 mmol, 0.95 eq) and diol acceptor 23 (3.77g, 3.25 mmol, 1 eq) were combined in a 500-mL flask and azeotroped with toluene (3 x 10 mL). The mixture was placed under vacuum for 30 minutes then brought into a dry box. The mixture was dissolved in anhydrous DCM (25 mL), capped, removed from the dry box and cooled to -20 °C. TMSOTf (56 µL, 0.31 mmol) in DCM (0.5 mL) was added dropwise. Precipitate formed within 5 minutes and the reaction
was quenched concurrently with saturated NaHCO$_3$ solution (100 mL) and EtOAc (150 mL). The EtOAc layer was washed with brine (150 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. The product was purified by silica column (10 cm diameter x 11 cm height), eluting with heptane:EtOAc 4:1, 1000 mL → 3:1, 800 mL → 2:1, 900 mL → 3:2, 1500 mL to give the tetrasaccharide 25 (5.63g, 86%). TLC: 1:1 heptane:EtOAc, R$_f$ 0.37.

Compound 25: C$_{124}$H$_{143}$NO$_{29}$Na; LRMS Calc.: m/z = 2132.96; Found m/z = 2133.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, J = 7.6 Hz, 2H), 7.58 (tt, J = 7.6, 1.2 Hz, 1H), 7.17 – 7.55 (m, 52H), 5.65 (d, J = 3.2 Hz, 1H, H-2 (OBz)), 5.43 (d, J = 3.2 Hz, 1H, H-2 (OAc)), 5.20 (s, 2H), 5.11 (m, 2H), 5.03 (m, 2H), 4.98 (dd, J = 9.6, 3.0 Hz, 1H), 4.80 (s, 1H, H-1), 4.36 – 4.75 (m, 18H), 4.09 (m, 1H), 3.96 (m, 1H), 3.87 (m, 2H), 3.46 – 3.79 (m, 15H), 3.37 (m, 1H), 3.24 (m, 1H), 3.16 (m, 1H), 2.54 (d, J = 5.6 Hz, 1H), 2.23 – 2.46 (m, 4H), 2.13 (s, 3H, CH$_3$), 2.00 (s, 3H, CH$_3$), 1.88 (s, 3H, CH$_3$), 1.72 – 2.08 (m, 8H), 1.47 (m, 3H), 1.15 – 1.40 (m, 8H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.50, 171.21, 169.81, 169.78, 166.23, 156.73, 156.16, 139.01, 138.83, 138.74, 138.67, 138.60, 138.56, 138.00, 137.91, 136.86, 133.04, 130.15, 130.01, 128.56, 128.53, 128.49, 128.41, 128.37, 128.24, 128.21, 128.19, 128.06, 127.98, 127.96, 127.87, 127.79, 127.73, 127.65, 127.61, 127.54, 127.48, 127.45, 127.41, 127.28, 127.21, 98.72, 98.39, 96.83, 95.59, 81.05, 79.58, 78.72, 78.02, 77.44, 77.01, 76.52, 75.29, 74.72, 74.66, 74.19, 72.93, 72.77, 72.64, 72.43, 72.38, 72.19, 72.13, 69.64, 69.06, 67.14, 66.99, 66.61, 66.39, 66.08, 61.99, 50.45, 50.12, 47.13, 46.16, 41.14, 38.46, 32.15, 31.94, 31.83, 31.71, 29.42, 29.09, 27.99, 27.63, 26.53, 25.89, 25.21, 22.76, 20.92, 20.89, 20.78, 14.24.
Tetrasaccharide alcohol 25 (5.50 g, 2.60 mmol, 1 eq) was dissolved in DCM (20 mL). Pyridine (20 mL) and DMAP (5 mg) were added, and the solution was cooled in an ice bath for 5 minutes under \( \text{N}_2 \). BzCl (2.4 mL, 21 mmol) was added in 200-\( \mu \text{L} \) aliquots over 4 minutes under \( \text{N}_2 \). The ice bath was removed, and the solution was stirred at room temperature while the DCM was evaporated using a stream of \( \text{N}_2 \). After overnight stirring the reaction was diluted with EtOAc (200 mL) and washed with saturated \( \text{NH}_4\text{Cl} \) (2 x 100 mL), saturated \( \text{NaHCO}_3 \) (150 mL), and brine (150 mL). The mixture was dried over \( \text{Na}_2\text{SO}_4 \), filtered, and concentrated under low and high vacuum to remove the residual pyridine. The crude residue was purified by silica chromatography (6 cm diameter x 12 cm high), eluting with heptane:EtoAc (4:1, 500 mL \( \rightarrow \) 3:1, 400 mL \( \rightarrow \) 2:1, 1200 mL) to give 26 (4.74 g) as a colorless syrup. TLC: 1:1 heptane:EtoAc, \( R_f \) 0.54.

Compound 26: \( C_{131}H_{147}NO_{30} \text{Na} \); LRMS \( m/z \) Calc.: 2238 (MNa\(^+\)), Found \( m/z = 2239 \).

HRMS \( m/z \): Calc.: 1129.9896, 1130.4913, 1130.9930, 1131.4946, 1131.9963 (MNa\(^{2+}\), \( z = 2 \)), Found: 1129.9892, 1130.4912, 1130.9927, 1131.4941, 1131.9956.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.12 (d, \( J = 7.6 \) Hz, 2H), 7.86 (d, \( J = 7.2 \) Hz, 1H), 7.23 – 7.57 (m, 54H), 7.12 (t, \( J = 8.0 \) Hz, 2H), 5.71 (d, \( J = 3.0 \) Hz, 1H, H-2 (OBz)), 5.66 (d, \( J = 3.2 \) Hz, 1H, H-2 (OBz)), 5.39 (d, \( J = 3.2 \) Hz, 1H, H-2 (OAc)), 5.24 (s, 2H), 5.21 (m, 1H), 5.12 (m, 2H), 4.97 (dd, \( J = 9.6, 3.2 \) Hz, 1H), 4.90 (s, 1H, H-1), 4.87 (m, 1H), 4.47 – 4.79 (m, 17H), 4.09 (m, 1H), 3.91 (m, 4H), 3.64 – 3.82 (m, 12H), 3.40 – 3.60 (m, 4H), 3.28 (m, 1H), 3.19 (m, 1H), 2.57 (m, 1H), 2.45 (m, 1H), 2.35 (m, 2H), 2.14 (s, 3H, CH\(_3\)), 2.00 (s, 3H, CH\(_3\)), 1.99 (s, 3H, CH\(_3\)), 1.72 – 2.08 (m, 8H), 1.47 (m, 3H), 1.10 – 1.92 (m, 8H), 1.01 (s, 3H, CH\(_3\)), 0.99 (s, 3H, CH\(_3\)).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.99, 170.34, 169.40, 169.35, 166.13, 164.75, 156.39, 155.83, 138.73, 138.51, 138.44, 138.36, 138.34, 138.21, 138.11, 137.74, 137.71, 137.63, 136.57, 132.81, 132.69, 132.41, 130.12, 129.71, 129.63, 129.54, 129.37, 129.16, 128.22, 128.14, 128.12, 128.09, 128.05, 128.01, 127.96, 127.93, 127.88, 127.63, 127.57, 127.54, 127.41, 127.37, 127.22, 127.19, 127.13, 98.35, 97.85, 95.40, 93.92, 81.51, 79.37, 78.44, 77.06, 76.52, 74.86, 74.70, 74.61, 74.32, 74.22, 73.95, 73.78, 72.71, 72.66, 72.55, 72.51, 72.34, 72.19, 72.15, 71.70, 69.38, 69.32, 68.23, 66.93, 66.87, 66.82, 66.24, 66.08, 60.04, 50.13, 49.78, 46.79, 45.82, 40.41, 37.36, 31.67, 31.60, 31.52, 31.32, 29.09, 28.75, 27.65, 27.29, 26.18, 25.41, 25.01, 24.71, 24.62, 24.36, 24.19, 22.43, 22.39, 20.61, 20.57, 20.53, 20.41, 13.96.

Tetrasaccharide 26 (4.7 g, 2.12 mmol, 1 eq) was azeotroped with toluene (3 x 10 mL) then dissolved in anhydrous THF (15 mL) under N$_2$. Anhydrous MeOH (60 mL) and Mg(OMe)$_2$ solution (18 mL, 13.6 mmol, 6-10 % by wt. in MeOH) were added under N$_2$. The reaction mixture was stirred at room temperature (17 °C) for 9 hours. The mixture became cloudy upon complete addition of Mg(OMe)$_2$ therefore THF (5 mL) was added to make the mixture homogeneous. The reaction was quenched by adding saturated NH$_4$Cl (50 mL) and concentrating in vacuo. The residue was partitioned between DCM (200 mL) and brine (150 mL). The brine layer was back-extracted with DCM (100 mL) and the combined organics were dried over Na$_2$SO$_4$, filtered, and concentrated. Chromatography on silica gel (6 cm diameter x 12 cm height), eluting with heptane/EtOAc (3:1, 850 mL → 2:1, 1150 mL → 3:2, 1000 mL) gave triol 27 (3.13 g, 75 % yield) plus a small amount of recovered starting material (0.31 g, 6.6 %). TLC 27: 1:1 heptane:EtOAc, R$_f$ 0.24.
Compound 27: C_{119}H_{131}NO_{25}Na; LRMS m/z: Calc.: 1997.9, Found: 1997.

HRMS m/z: Calc.: 1009.9397, 1010.4414, 1010.9443 (MNa^{2+}, z = 2), Found: 1009.9317, 1010.4414, 1010.9431, 1011.4448.

^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.12 (d, \( J = 7.6 \) Hz, 2H), 7.86 (d, \( J = 7.2 \) Hz, 1H), 7.23 – 7.57 (m, 54H), 7.12 (t, \( J = 8.0 \) Hz, 2H), 5.71 (d, \( J = 3.0 \) Hz, 1H, H-2 (OBz)), 5.66 (d, \( J = 3.2 \) Hz, 1H, H-2 (OBz)), 5.39 (d, \( J = 3.2 \) Hz, 1H, H-2 (OAc)), 5.24 (s, 2H), 5.21 (m, 1H), 5.12 (m, 2H), 4.97 (dd, \( J = 9.6, 3.2 \) Hz, 1H), 4.90 (s, 1H, H-1), 4.87 (m, 1H), 4.47 – 4.79 (m, 17H), 4.09 (m, 1H), 3.91 (m, 4H), 3.64 – 3.82 (m, 12H), 3.40 – 3.60 (m, 4H), 3.28 (m, 1H), 3.19 (m, 1H), 2.57 (m, 1H), 2.45 (m, 1H), 2.35 (m, 2H), 2.14 (s, 3H, CH\textsubscript{3}), 2.00 (s, 3H, CH\textsubscript{3}), 1.99 (s, 3H, CH\textsubscript{3}), 1.72 – 2.08 (m, 8H), 1.47 (m, 3H), 1.10 – 1.92 (m, 8H), 1.01 (s, 3H, CH\textsubscript{3}), 0.99 (s, 3H, CH\textsubscript{3}).

^1^C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 167.38, 167.00, 156.79, 156.23, 138.78, 138.74, 138.68, 138.61, 138.58, 138.14, 138.04, 136.98, 136.86, 133.51, 133.29, 130.09, 130.01, 129.94, 129.23, 128.62, 128.51, 128.45, 128.41, 128.31, 128.29, 128.24, 128.15, 128.01, 127.92, 127.84, 127.78, 127.75, 127.70, 127.63, 127.53, 127.49, 127.33, 127.25, 104.01, 100.70, 98.67, 95.20, 82.92, 81.23, 80.51, 79.81, 78.77, 77.55, 76.78, 75.07, 74.93, 74.72, 74.21, 74.06, 72.99, 72.90, 72.81, 72.47, 72.35, 72.14, 72.08, 69.72, 69.59, 68.74, 67.20, 66.80, 66.43, 66.36, 66.13, 50.52, 50.18, 47.19, 46.22, 32.17, 32.10, 32.05, 31.98, 31.68, 29.46, 29.14, 28.08, 27.70, 26.58, 25.79, 22.82, 14.33.

Triol 27 (3.37g, 1.71 mmol) was azeotroped with acetone (3 x 10 mL). An acetone/2,2-DMP solution (4:1, 50 mL) was added, followed by pTSOH•H\textsubscript{2}O (25 mg, 0.13 mmol). The reaction mixture was stirred at room temperature (15 °C), concentrated to near dryness then partitioned between EtOAc.
(200 mL) and saturated NaHCO₃ (100 mL). It was washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated to give 28, which was used as is in the next step. TLC: 1:1 heptane:EtOAc, Rₜ 0.61.

HRMS m/z: Calc.: 1029.9554, 1030.4571, 1030.9587, 1031.4604 (MNa₂⁺, z = 2), Found: 1029.9552, 1030.4569, 1030.9587, 1031.4605.

The crude starting material 28 was azeotroped with toluene (3 x 5 mL) and dissolved in anhydrous DCM (20 mL). Dess-Martin periodinane (1.45 g, 3.42 mmol, 2 eq) was added in one portion under N₂ with stirring. The reaction mixture was stirred at room temperature for 1 hour during which the mixture became homogeneous. Wet DCM (2 mL) was then added and stirred at room temperature for 20 hours before diluting with DCM (150 mL). The solution turned milky-white and was washed with a saturated Na₂S₂O₃/NaHCO₃ solution (1:1, 100 mL), brine (100 mL), then dried over Na₂SO₄, filtered through Celite, and concentrated. The product was used as is in the next step. TLC: 4:1 toluene:EtOAc, Rₜ 0.48

The crude ketone was taken up in a DCM/MeOH solution (1:1, 50 mL) and cooled to 0 °C in an ice bath. NaBH₄ (300 mg, 8 mmol) was added and after 10 minutes the mixture was concentrated to dryness. The residue was partitioned between EtOAc (150 mL) and saturated NH₄Cl (100 mL), and the organic layer was washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated. By TLC, reduction was estimated at approximately 10:1 selectivity for manno versus gluco configuration. The mixture was purified by silica gel chromatography on a Grace Reveleris purification system using a SiliaSep HP 120g column and a heptane:EtOAc gradient (10 % EA → 50 % EA in 5 % steps with 5-minute plateaus and 3-minute step-ups, ELSD, UV1, UV2 detection, 40
mL/min). The products eluted at 50 % heptane:EtOAc: High R_f spot, 750mg, gluco 28), and 29 (major lower spot, 1.79g, manno). TLC: 1:1 heptane:EtOAc, R_f 0.68 (gluco isomer 28); 0.62 (manno isomer 29).

HRMS m/z: Calc.: 1030.4571 (MNa$_2^{+2}$, z = 2), Found: 1030.4572.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J$ = 7.2 Hz, 2H), 7.93 (d, $J$ = 7.6 Hz, 2H), 7.30 – 7.61 (m, 54H), 7.20 (t, $J$ = 7.6 Hz, 2H), 5.75 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.73 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.28 (s, 2H), 5.19 (½AB, $J$ = 11.2 Hz, 1H, CH$_2$Ph), 5.16 (½AB, $J$ = 10.8 Hz, 1H, CH$_2$Ph), 5.15 (d, $J$ = 2.0 Hz, 1H, H-1), 5.04 (s, 1H, H-1), 4.98 (½AB, $J$ = 10.4 Hz, 1H, CH$_2$Ph), 4.93 (½AB, $J$ = 11.6 Hz, 1H, CH$_2$Ph), 4.86 (s, 1H, H-1), 4.47 – 4.76 (m, 14H), 4.38 (m, 4H), 4.20 (m, 1H), 4.14 (m, 2H), 3.62 – 3.93 (m, 13H), 3.54 (m, 2H), 3.47 (m, 1H), 3.33 (m, 1H), 3.24 (m, 1H), 2.55 (m, 1H), 2.43 (m, 2H), 2.33 (m, 1H), 1.84 – 2.11 (m, 4H), 1.64 (s, 3H, CH$_3$), 1.47 (m, 3H), 1.40 (s, 3H CH$_3$), 1.18 – 1.66 (m, 10H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.36, 165.14, 156.35, 155.79, 138.54, 138.50, 138.40, 138.37, 138.28, 138.23, 137.87, 137.66, 136.53, 132.60, 132.52, 129.86, 129.67, 129.42, 128.21, 128.13, 128.00, 127.99, 127.91, 127.89, 127.86, 127.74, 127.67, 127.66, 127.60, 127.51, 127.38, 127.35, 127.25, 127.21, 127.15, 127.10, 127.05, 126.85, 110.12, 98.33, 96.66, 95.08, 93.80, 79.36, 78.68, 78.52, 78.21, 77.57, 76.39, 76.26, 74.34, 74.27, 74.23, 73.94, 72.55, 72.52, 72.45, 72.36, 72.27, 72.09, 71.99, 71.70, 71.13, 69.21, 68.77, 68.38, 67.10, 66.79, 66.51, 66.27, 66.13, 65.98, 50.17, 49.80, 46.79, 45.84, 32.55, 31.90, 31.68, 31.57, 29.07, 28.76, 28.71, 27.66, 27.29, 27.15, 26.15, 25.70, 25.36, 22.40, 13.91.
The alcohol 29 (2.15 g, 1.07 mmol, 1 eq) was taken up in pyridine (10 mL) and cooled to 0 °C. BzCl (1.0 mL, 8.6 mmol) was added, followed by DMAP (1mg). The reaction mixture was stirred overnight at room temperature then concentrated under high vacuum. The residue was partitioned between EtOAc (150 mL) and pH 3 HCl (100 mL). The mixture was washed with brine (100 mL), dried over Na₂SO₄, filtered, concentrated, and used as is in the next step. TLC: 2:1 heptane:EtOAc, Rf 0.34.

The crude material was taken up in 80 % HOAc (25 mL) and heated to 60 °C for 4 hours. The mixture was concentrated in vacuo and chased with hexanes. The residue was partitioned between EtOAc (150 mL) and saturated NaHCO₃ (100 mL), washed with brine, dried over Na₂SO₄, filtered, and concentrated. The crude mixture was purified by automated silica gel chromatography using a Grace Reveleris system (120g column, gradient 15→60 % EtOAc in heptane over 55 minutes) to give diol 30 (1.50 g, 77 %). TLC: 2:1 heptane:EtOAc, Rf: 0.13.

Compound 30: C₁₂₆H₁₃₅NO₂₆Na; LRMS m/z Calc.: 2101.9 (MNa⁺); Found 2102.

HRMS m/z: Calc.: 1062.4545 (MNa₂⁺, z = 2), Found: 1062.4540.

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 7.2 Hz, 2H), 7.89 (dt, J = 8.0, 1.2 Hz, 3H), 7.58 (dt, J = 7.2, 1.6 Hz, 1H), 7.27 – 7.48 (m, 56H), 7.18 (m, 3H), 5.71 (d, J = 3.2 Hz, 1H, H-2 (OBz)), 5.67 (d, J = 3.2 Hz, 1H, H-2 (OBz)), 5.58 (d, J = 3.2 Hz, 1H, H-2 (OBz)), 5.24 (s, 2H), 4.99 (m, 6H), 4.80 (s, 1H, H-1), 4.75 (½AB, J = 11.2 Hz, 1H, CH₂Ph), 4.67 (½AB, J = 10.8 Hz, 1H, CH₂Ph), 4.64 (s, 1H, H-1), 4.55 – 4.60 (m, 1H), 4.24 – 4.37 (m, 3H), 4.23 (m, 1H), 4.17 (m, 2H), 3.88 – 3.94 (m, 3H), 3.65 – 3.82 (m, 11H), 3.55 (m, 5H), 3.42 (m, 1H), 3.29 (m, 1H), 3.20 (m, 1H), 2.70 (bs, 2H, OH), 2.52 (m, 1H), 2.39 (m, 2H), 2.12 (m, 1H), 1.84 – 2.00 (m, 4H), 1.52 (m, 4H), 1.18 – 1.43 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 166.80, 165.98, 165.72, 156.79, 156.22, 138.77, 138.73, 138.65, 138.60, 138.58, 138.05, 136.94, 133.07, 132.99, 132.83, 130.19, 130.06, 129.81, 129.72, 129.65, 128.61, 128.51, 128.48, 128.44, 128.35, 128.26, 128.20, 128.12, 128.07, 128.00, 127.91, 127.82, 127.75, 127.60, 127.58, 127.56, 127.51, 127.48, 127.37, 127.26, 98.72, 96.92, 95.35, 93.30, 79.63,
The donor 17 (780mg, 0.70 mmol, 1 eq) and diol acceptor 30 (1.45g, 0.70 mmol, 1 eq) were combined in a flask, azeotroped with toluene (3 x 5 mL) then brought into a dry box. The mixture was dissolved in anhydrous DCM (10 mL), stoppered, removed from the dry box and cooled to -20 °C. TMSOTf (13 µL, 0.07 mmol in 0.5 mL anhydrous DCM) was added over 3 minutes and the solution stirred for an additional 15 minutes before being quenched with saturated NaHCO₃ (100 mL) and EtOAc (150 mL). The EtOAc layer was washed with brine (100 mL), dried over Na₂SO₄, filtered, and concentrated to a foam. The crude mixture was purified by silica gel chromatography using a Grace Reveleris system same conditions as those used for purification of 29 to give the desired hexasaccharide 31 (1.17g) in 50 % absolute yield. Unreacted diol acceptor 30 (580mg, 0.28 mmol, 40 %) was isolated during chromatography, which gave a corrected yield of 83 %. TLC of 31: 1:1 heptane:EtOAc, Rf 0.43.

Compound 31: C₁₈₀H₁₉₉NO₄₁Na; LRMS m/z Calc.: 3053.3 (MNa⁺); Found 3052.

1H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 7.6 Hz, 2H), 7.76 (m, 4H), 7.50 (t, J = 7.6 Hz, 1H), 7.15 – 7.44 (m, 74H), 7.06 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 8.0 Hz, 2H), 5.63 (d, J = 3.6 Hz, 1H, H-2 (OBz)), 5.59 (d, J = 3.0 Hz, 1H, H-2 (OBz)), 5.52 (d, J = 3.2 Hz, 1H, H-2 (OBz)), 5.37 (d, J = 3.0 Hz, 1H, H-2 (OAc)), 5.19 (s, 2H), 4.83 – 5.09 (m, 8H), 4.75 (s, 1H, H-1), 4.04 – 4.71 (m, 26H), 3.81 (m, 4H),...
3.27 – 3.73 (m, 24H), 3.23 (m, 1H), 3.14 (m, 1H), 2.44 (m, 1H), 2.39 (m, 2H), 2.32 (m, 3H), 2.20 (m, 2H), 2.09 (s, 3H, CH₃), 1.65 – 2.07 (m, 8H), 1.97 (s, 3H, CH₃), 1.84 (s, 3H, CH₃), 1.46 (m, 4H), 1.10 – 1.38 (m, 8H), 1.23 (s, 3H, CH₃), 1.18 (s, 3H, CH₃).

$^{13}$C NMR (100 MHz, CDCl₃) δ 175.45, 171.08, 169.75, 169.71, 166.69, 165.72, 165.29, 156.73, 156.15, 139.08, 138.97, 138.83, 138.77, 138.71, 138.66, 138.64, 138.61, 138.55, 137.97, 137.88, 136.90, 132.96, 132.70, 132.62, 130.11, 129.99, 129.78, 129.69, 128.63, 128.53, 128.48, 128.39, 128.36, 128.33, 128.29, 128.25, 128.23, 128.17, 128.16, 128.11, 128.09, 127.99, 127.96, 127.93, 127.84, 127.74, 127.68, 127.66, 127.63, 127.57, 127.53, 127.47, 127.43, 127.39, 127.35, 127.31, 98.66, 98.33, 96.55, 95.76, 95.27, 95.15, 81.01, 79.52, 78.78, 78.37, 78.25, 77.67, 77.45, 77.33, 77.13, 76.89, 76.81, 76.74, 76.40, 75.23, 74.69, 74.61, 74.56, 74.11, 73.03, 72.89, 72.74, 72.67, 72.62, 72.50, 72.42, 72.23, 72.08, 72.10, 69.62, 68.95, 68.66, 68.46, 67.13, 66.91, 66.86, 66.52, 66.45, 66.40, 66.13, 61.79, 50.47, 50.15, 47.11, 46.18, 41.06, 38.32, 34.71, 32.28, 32.07, 32.01, 31.91, 31.66, 31.62, 29.73, 29.42, 29.10, 29.05, 27.99, 27.62, 26.53, 25.71, 25.06, 22.73, 22.69, 20.86, 20.84, 20.73, 14.17.

The hexasaccharide alcohol 31 (1.06g, 0.35 mmol) was dissolved in a pyridine/DCM solution (5:2, 7 mL) and cooled to 0 °C. BzCl (1.0 mL) was added, followed by DMAP (1 mg) and the resulting mixture stirred at room temperature for 20 hours before concentrating in vacuo. The residue was partitioned between EtOAc (100 mL) and pH 3 HCl (100 mL). The EtOAc layer was washed with saturated NaHCO₃ (100 mL) and brine (100 mL), dried over Na₂SO₄, filtered, and concentrated. The
crude mixture was purified by silica gel chromatography using a Grace Reveleris system same conditions as those used for purification of 29 to give the desired hexasaccharide S20 (1.15 g, quant.). TLC: 2:1:1 heptane:DCM:TBME, Rf 0.37.

HRMS m/z: Calc.: 1067.7819, 1068.4508, 1068.7852, 1069.1197 (MNa$_3^{3+}$, z = 3), Found: 1067.7810, 1068.4508, 1068.7851, 1069.1193.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J$ = 7.0 Hz, 2H), 7.74 (m, 6H), 7.13 – 7.52 (m, 76H), 7.04 (m, 6H), 7.02 (t, $J$ = 8.0 Hz, 2H), 5.61 (d, $J$ = 3.6 Hz, 1H, H-2 (OBz)), 5.60 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.51 (d, $J$ = 3.2 Hz, 2H, H-2 (OBz)), 5.27 (d, $J$ = 3.6 Hz, 1H, H-2 (OAc)), 5.18 (s, 2H), 5.08 (d, $J$ = 10.4 Hz, 1H), 4.81 – 5.00 (m, 8H), 4.66 – 4.71 (m, 5H), 4.01 – 4.57 (m, 20H), 1.65 – 2.07 (m, 7H), 1.92 (s, 3H, CH$_3$), 1.84 (s, 3H, CH$_3$), 1.04 – 1.71 (m, 13H), 1.31 (s, 3H, CH$_3$), 1.28 (s, 3H, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.28, 170.66, 169.73, 169.62, 166.67, 165.72, 165.61, 164.93, 156.68, 156.10, 139.10, 138.85, 138.74, 138.72, 138.64, 138.61, 138.54, 137.94, 132.90, 132.69, 132.41, 130.15, 130.08, 129.99, 129.79, 129.67, 129.64, 129.60, 129.49, 128.51, 128.42, 128.35, 128.32, 128.24, 128.18, 128.16, 128.13, 128.09, 128.00, 127.94, 127.88, 127.83, 127.69, 127.66, 127.60, 127.55, 127.46, 127.43, 127.38, 127.34, 127.14, 98.65, 98.05, 95.47, 95.39, 95.04, 94.16, 80.73, 79.53, 78.51, 78.45, 78.09, 77.32, 77.23, 77.12, 76.94, 75.13, 74.89, 74.85, 74.55, 74.44, 74.15, 74.02, 72.95, 72.93, 72.87, 72.71, 72.46, 72.24, 72.05, 69.68, 69.58, 68.70, 68.45, 68.36, 67.27, 67.14, 66.92, 66.76, 66.51, 66.47, 66.37, 61.10, 50.46, 50.13, 47.19, 46.16, 40.66, 37.56, 36.10, 34.70, 34.55, 32.32, 32.10, 31.91, 31.72, 31.62, 29.40, 29.09, 29.05, 28.99, 28.00, 27.60, 26.52, 25.69, 25.31, 24.77, 24.58, 22.72, 22.69, 20.93, 20.83, 20.74, 20.67, 14.21.
S20 (1.10g, 0.351 mmol, 1 eq) was azeotroped with toluene (3 x 5 mL) then dissolved under N\textsubscript{2} in anhydrous THF (3 mL). MeOH anhydrous (10 mL) was added, followed by a Mg(OMe)\textsubscript{2} solution (3 mL, 6-10 % by wt in MeOH). It was stirred under N\textsubscript{2} at room temperature for 29 hours before being quenched with saturated NH\textsubscript{4}Cl (50 mL) and concentrated to dryness. The residue was partitioned between DCM (200 mL) and brine (100 mL). The DCM layer was washed with brine, and the brine was back-extracted with DCM, dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated (1.02g foam). Purification was effected by silica gel chromatography on a Grace Reveleiris system (80g column, 30 mL/min, heptane: EtOAc step gradient 10 → 50 % in EtOAc) to yield the desired triol S21 (790 mg, 78 %) yield, a small amount of a faster eluting partially deprotected intermediate (80 mg, < 10 %), and some recovered starting material (110 mg, 10 %). TLC of S21: 1:1 heptane:EtOAc, R\textsubscript{f} 0.32.

Compound S21: C\textsubscript{175}H\textsubscript{187}NO\textsubscript{37}Na; Low LRMS: Calc.: m/z = 2917.3; Found m/z = 2917.

HRMS m/z: Calc.: 987.7486, 988.0831, 988.7520, 989.0864 (M\textsubscript{Na}\textsuperscript{3+}, z = 3), Found: 987.7475, 988.0825, 988.7513, 989.0857.
Step 1: Triol S21 (780 mg, 0.27 mmol, 1 eq) was azeotroped with acetone (3 x 5 mL). An acetone/2,2-DMP solution (10 mL) was added, followed by pTSOH•H2O (5 mg). The reaction mixture was stirred at room temperature for 15 minutes then concentrated in vacuo to dryness. The residue was partitioned between EtOAc (100 mL) and saturated NaHCO3 (75 mL), washed with brine (75 mL), dried over Na2SO4, filtered, and concentrated, and used as is in the next step. TLC: 1:1 heptane:EtOAc, Rf 0.62.

Step 2: The crude acetonide from Step 1 (700 mg, 0.239 mmol, 1 eq) was azeotroped with toluene (3 x 5 mL) then taken up in anhydrous DCM (5 mL) under N2. Dess-Martin periodinane (202 mg, 0.478 mmol, 2 eq) was added in one portion and stirred at room temperature (monitored by TLC: 2:1:1 heptane:TBME:DCM). After 2.5 hours, wet DCM (4 drops) was added, and at 5.5 hours an additional 10 drops of wet DCM were added. After stirring overnight a final aliquot of wet DCM (1 mL) was added to drive the reaction to completion. Once complete, the reaction mixture was diluted with a MeOH/DCM solution (1:1, 20 mL total) and cooled in an ice bath.

Step 3: An excess of NaBH4 (25 mg, approximately 3 eq) was added to the cooled ketone solution from Step 2. The reaction mixture was stirred in ice for 15 minutes then concentrated to dryness. The residue was partitioned between saturated NH4Cl (100 mL) and EtOAc (100 mL). The EtOAc layer was washed with brine (100 mL), dried over Na2SO4, filtered, and concentrated. Purification was effected by silica gel chromatography using a Grace Reveleris system (80g column, 30 mL/min, heptane:EtOAc step gradient), which gave the desired manno-configured hexasaccharide S22 (400 mg, 50 % from S21) and the gluco isomer (120 mg, 15 %) formed during the reduction. The gluco-isomer was re-subjected to the oxidation-reduction sequence (5 mL anhydrous DCM, 50 mg Dess-Martin, overnight then MeOH/DCM solution (1:1, 10 mL), NaBH4 (10mg) 0 °C), which after similar purification gave an additional amount of S22 (60 mg, 7.5 %) and some gluco-isomer (20 mg, 2.5 %). TLC: 2:1:1 heptane:TBME:DCM, Rf 0.43 (gluco-isomer); 0.30 (manno-isomer S22).
The alcohol **S22** (450 mg, 0.153 mmol) was dissolved in DCM and pyridine (3 mL), BzCl (1 mL), and DMAP (1 mg) were added. The reaction mixture was capped and stirred for 17 hours then concentrated in vacuo. The residue was partitioned between EtOAc (100 mL) and pH 3 solution (100 mL). The EtOAc layer was washed with brine (100 mL), saturated NaHCO$_3$ (100 mL), and brine (50 mL) again. It was dried over Na$_2$SO$_4$, filtered, and concentrated. The product was used directly in the next step. TLC: 1:1 heptane:EtOAc, R$_f$ 0.66.

The crude material from the benzoylation reaction was taken up in 80% HOAc (10 mL) and stirred at 54 $^\circ$C for 22 hours before concentrating in vacuo and chasing with hexanes (2 x 15 mL). The residue was partitioned between EtOAc (100 mL) and saturated NaHCO$_3$. The EtOAc layer was washed with brine (75 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. Silica gel chromatography (40 g column) using a heptane:EtOAc step gradient (10-50% EtOAc) gave pure diol **32** (320 mg, 70% from S22) and a lower R$_f$ by-product (20 mg), which was identified by MALDI-MS and NMR as the desired product less one benzoate ester. TLC: 1:1 heptane:EtOAc, R$_f$ 0.60.

**Compound 32**: C$_{182}$H$_{190}$NO$_{38}$Na; LRMS m/z Calc.: 3020.3 (MNa$^+$); Found 3020.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J$ = 7.2 Hz, 2H), 7.81 (m, 6H), 7.53 (m, 1H), 7.20 – 7.43 (m, 80H), 7.13 (m, 6H), 5.66 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.63 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.57 (d, $J$ = 3.2 Hz, 2H, H-2 (OBz)), 5.52 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.48 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.21 (s, 2H), 4.87 – 5.00 (m, 10H), 4.73 (m, 2H), 4.39 – 4.64 (m, 16H), 4.08 – 4.33 (m, 9H), 3.34 – 3.89 (m, 28H), 3.25 (m, 1H), 3.17 (m, 1H), 2.59 (m, 2H), 2.37 (m, 6H), 2.08 (m, 1H), 1.96 (m, 3H), 1.85 (m, 2H), 1.48 (m, 4H), 1.29 (m, 4H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.72, 165.88, 165.85, 165.69, 165.73, 156.14, 138.78, 138.75, 138.70, 138.67, 138.58, 138.54, 138.52, 138.01, 132.98, 132.94, 132.73, 130.19, 130.02, 129.79, 129.77, 129.71, 129.60, 128.57, 128.48, 128.41, 128.38, 128.34, 128.32, 128.21, 128.16, 128.11, 128.07, 128.05, 128.04, 128.01, 127.96, 127.79, 127.76, 127.71, 127.68, 127.57, 127.55, 127.52, 127.48, 127.46, 127.39, 98.69, 98.01, 95.32, 95.25, 79.60, 78.53, 78.41, 76.76, 74.94, 74.75, 74.63, 74.46, 73.02, 72.99, 72.93, 72.82, 72.77, 72.52, 72.48, 72.27, 72.11, 70.98, 69.66, 69.62, 68.71, 68.61, 67.17, 66.91, 66.87, 66.84, 66.55, 66.43, 53.53, 50.48, 50.16, 47.17, 46.21, 32.31, 32.19, 32.09, 32.01, 31.95, 29.45, 28.01, 27.63, 26.56, 25.71, 22.76, 14.23.

Hexasaccharide diol 32 (320 mg, 0.107 mmol, 1 eq) was dissolved in a DCM/MeCN solution (1:1, 4 mL total). $\pm$-Camphorsulfonic acid (CSA) (8 mg) was added, followed by trimethylorthobenzoate (TMOB) (366 µL, 2.13 mmol, 20 eq). The mixture was stirred at room temperature for 4 hours before H$_2$O (1 mL) was added, and the stirring continued for 1 hour. The reaction mixture was diluted with EtOAc (100 mL) and saturated NaHCO$_3$ (100 mL), washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated. The crude mixture was purified on the Grace Reveleris system (40g silica column, 25 mL/min using a heptane:EtOAc step gradient) to give the desired 2-O-Bz regioisomer S23 (225 mg, 67%), the undesired 3-O-Bz regioisomer (55 mg, 16%), and recovered diol 32 (58 mg, 17%). TLC of the intermediate orthobenzoate 4:1 toluene:EtOAc, R$_f$ 0.51; S23: 4:1 toluene:EtOAc, R$_f$ 0.32.
Compound S23: C$_{189}$H$_{195}$NO$_{39}$Na; LRMS: Calc.: m/z = 3125.3; Found: m/z = 3127.

HRMS m/z: Calc.: 1057.0994, 1057.7683, 1058.1028, 1058.4372, 1058.7717 (MNa$_3^{3+}$), Found: 1057.0984, 1057.7680, 1058.1026, 1058.4369, 1058.7707.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J$ = 7.6 Hz, 2H), 7.78 (m, 8H), 7.50 (m, 1H), 7.20 – 7.41 (m, 81H), 7.09 (m, 8H), 5.62 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.58 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.53 (d, $J$ = 3.2 Hz, 2H, H-2 (OBz)), 5.50 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.48 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.41 (d, $J$ = 3.2 Hz, 1H, H-2 (OBz)), 5.18 (s, 2H), 4.83 – 4.93 (m, 10H), 4.70 (m, 1H), 4.28 – 4.54 (m, 16H), 4.02 – 4.28 (m, 10H), 3.34 – 3.81 (m, 28H), 3.22 (m, 1H), 3.14 (m, 1H), 2.34 (m, 6H), 2.07 (m, 1H), 1.93 (m, 3H), 1.84 (m, 2H), 1.45 (m, 4H), 1.24 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.70, 166.04, 165.85, 165.82, 165.80, 165.76, 156.73, 156.19, 138.77, 138.63, 138.40, 137.96, 132.95, 132.78, 132.66, 132.54, 130.13, 129.98, 129.85, 129.73, 128.46, 128.34, 128.01, 127.92, 127.83, 127.69, 127.44, 98.66, 95.28, 95.22, 95.18, 79.60, 78.43, 78.39, 78.33, 77.32, 76.89, 75.03, 74.59, 73.91, 72.96, 72.90, 72.86, 72.74, 72.58, 72.40, 72.23, 72.08, 69.60, 68.69, 68.56, 68.43, 67.14, 66.89, 66.82, 66.53, 66.41, 50.35, 50.22, 47.54, 46.18, 32.16, 31.92, 29.74, 29.42, 29.06, 26.53, 25.68, 22.73, 14.18.
Hexasaccharide alcohol S23 (200 mg, 0.064 mmol, 1 eq) was azeotroped with toluene (3 x 2 mL) then taken up in cyclohexane/DCM 2:1 (3 mL) under N\textsubscript{2}. TMSOTf/DCM solution (90 µl TMSOTf in 4.91 mL DCM, 0.1M) was prepared and added to the hexasaccharide solution. Benzyl 2,2,2-trichloroacetimidate (200 µL, 1.1 mmol, 17 eq) was added in one portion at room temperature, and after stirring overnight the reaction mixture was diluted to 100 mL with EtOAc, washed with NaHCO\textsubscript{3} (100 mL) and brine (100 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated. The crude material was purified on a Grace Reveleris system (12g silica column) using a heptane:EtOAc step gradient to give mostly homogeneous 33 (110 mg) with trace impurities by TLC. The material was used without further purification.

Step 1: Hexasaccharide 33 (100 mg, 0.031 mmol, 1 eq) was taken up in anhydrous THF (3 mL). Anhydrous MeOH (3 mL) and then a NaOMe/MeOH solution (100 µL, 25 % by wt.) were added. The mixture was stirred under N\textsubscript{2} overnight. The solution was concentrated then partitioned between EtOAc (100 mL) and saturated NH\textsubscript{4}Cl (100 mL). The aqueous layer was washed with DCM (100 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated. \textsuperscript{1}H/\textsuperscript{13}C NMR analysis of the crude material showed a complete loss of Bz groups and a persistence of linker with Cbz group intact. MALDI MS revealed trace amounts of a material consistent with a mono-de-O-benzyl derivative in addition to the desired product.
Step 2: The crude polyol was taken up in DCM (1 mL). Pyridine (3 mL) was added, followed by Ac₂O (1 mL) and DMAP (1 mg), and the solution stirred at room temperature for 17 hours. The reaction mixture was concentrated *in vacuo* to dryness and chased with hexane (2 x 5 mL). The residue was partitioned between EtOAc (100 mL) and pH 3 H₂O (100 mL). The organic layer was washed with saturated NaHCO₃ (100 mL) and brine (100 mL), dried over Na₂SO₄, filtered, and concentrated. Purification on a Grace Reveleris system (12 g silica column, 10 %-50 % Heptane in EtOAc over 18 minutes) gave the desired hexasaccharide 34 (50 mg, 57 % from 33).

Compound 34: C₁₆₆H₁₈₉NO₃₉Na; LRMS m/z Calc.: 2844.3 (MNa⁺); Found 2844.

HRMS m/z: Calc.: 1433.1311, 1433.6327, 1434.1344, 1434.6361, 1435.1378 (MNa₂²⁺, z = 2), Found: 1433.1283, 1433.6311, 1434.1346, 1434.6349, 1435.1369.

¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.41 (m, 75H), 5.45 (d, J = 2.8 Hz, 1H, H-2), 5.31 (d, J = 2.8 Hz, 1H, H-2), 5.28 (d, J = 2.8 Hz, 2H, H-2), 5.24 (m, 3H, H-2), 5.15 (m, 2H), 4.89 – 5.01 (m, 6H), 4.58 – 4.72 (m, 7H), 4.34 – 4.53 (m, 19H), 4.23 (s, 1H), 3.88 (m, 6H), 3.16 – 3.69 (m, 27H), 2.24 (m, 6H), 2.08 (s, 3H, CH₃), 2.04 (s, 3H, CH₃), 1.98 (s, 3H, CH₃), 1.97 (s, 3H, CH₃), 1.92 (s, 3H, CH₃), 1.88 (s, 3H, CH₃), 1.61 – 1.98 (m, 8H), 1.45 (m, 4H), 1.24 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 171.17, 170.89, 170.73, 170.70, 170.13, 156.68, 156.14, 138.67, 138.58, 138.51, 138.46, 138.42, 137.92, 137.66, 128.88, 128.51, 128.38, 128.35, 128.31, 128.21, 128.17, 128.03, 127.86, 127.79, 127.69, 127.65, 127.60, 127.51, 127.47, 127.45, 127.43, 127.39, 127.35, 98.41, 95.20, 94.90, 94.85, 94.81, 94.78, 80.27, 78.02, 77.90, 77.83, 77.23, 76.83, 75.13, 74.60, 74.53, 72.86, 72.79, 72.59, 72.39, 72.08, 72.03, 71.90, 71.33, 69.95, 68.08, 67.99, 67.88, 67.11, 66.79, 66.68, 66.59, 66.41, 66.26, 50.43, 50.18, 47.13, 46.19, 32.06, 31.92, 31.84, 29.69, 29.39, 28.02, 27.62, 26.60, 25.70, 20.95, 20.90, 20.78, 20.76, 20.71, 22.73, 14.18.
34 (48 mg, 17.0 µmol, 1 eq) was dissolved in THF (6 mL, inhibitor-free, anhydrous) and transferred to a hydrogenator flask. H₂O (3 mL, Omni Trace Ultra) was added with stirring. The solution became cloudy. 1N HCl (17 µL, 1 eq.) was added, and the reaction mixture was purged with N₂. 10 % Pd•C (100 mg) was added. The flask was secured to a hydrogenation manifold and purged free of O₂ by repeated evacuation and filling with N₂ followed by the saturation of H₂ using evacuation and filling. The reaction mixture was stirred at an initial H₂ pressure of 30 psi for 23 hours, then filtered through an Acrodisc CR (25 mm, 0.45 µm PTFE membrane), concentrated, and analyzed by ¹H NMR. Nearly all aromatic signals were gone, but approximately one Bn group equivalent remained. The reaction mixture was resubjected to the hydrogenation conditions for another 20 hours, filtered through a 0.45 µm PTFE Acrodisc, washing with H₂O (5 mL). The filtrate was concentrated in vacuo and chased with hexane. Final purification was achieved via size exclusion chromatography using Sephadex G-10 (2.5 cm diameter x 14 cm high, eluted with pH 4 H₂O, 4 mL fractions). Carbohydrate-containing fractions were combined and lyophilized to give the desired hexasaccharide antigen 1 as an amorphous white cake (16.2 mg, 67 %).

Compound 1: C₆₀H₉₉NO₃₇; LRMS m/z Calc.: 1426.7 (MH⁺), 1448.6 (MNa⁺); Found 1427, 1449.

HRMS m/z: Calc.: 724.7930 (MNa²⁺, z = 2), Found: 724.7929; Calc.: 1448.5788 (MNa⁺, z = 1), Found: 1488.5764.
$^1$H NMR (400 MHz, D$_2$O) $\delta$ 5.36 (bs, 2H), 5.19 (m, 4H), 5.08 (m, 1H), 4.80 (m, 5H), 3.85 (m, 6H), 3.66 (m, 16H), 3.49 – 3.57 (m, 5H), 3.36 (m, 12H), 2.86 (m, 2H), 1.96 – 2.04 (m, 27H), 1.46 – 1.61 (m, 14H), 1.25 (m, 5H).

$^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 173.48, 173.41, 173.39, 173.36, 173.34, 97.97, 97.82, 96.02, 95.99, 95.80, 78.73, 78.68, 78.60, 78.58, 72.83, 72.52, 72.24, 72.10, 71.10, 70.53, 70.21, 69.43, 69.31, 69.14, 68.99, 68.89, 68.80, 67.40, 61.44, 57.85, 57.79, 57.74, 39.35, 33.47, 33.38, 33.31, 32.60, 28.37, 27.77, 26.53, 25.23, 24.56, 22.84, 20.19, 20.09, 20.05.
NMR of key intermediates
Sample: 73-374
Sample ID: a_0_01
File: /home/walkup/Bill/73_374_Carbon_01.fid

Pulse Sequence: s2pul
Solvent: odol3
Temp. 26.0 °C / 299.1 K
Operator: Bill
File: 73_374_Carbon_01
VNMRS-400 “nme”

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
64 repetitions

OBSERVE C13, 100.3763456 MHz
DECouple H1, 398.1967584 MHz
Power 39 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
Sample: 72-288
Sample ID: s_0_01
File: /home/wallup/Bill1/72_288_Proton_01
Automation directory: /home/wallup/vnmrsys/data/auto_2011.03.22

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 72_288_Proton_01
VNMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 4096.4 Hz
8 repetitions

OBSERVE H1, 599.1897624 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 31 sec
Sample: 72-288
Sample ID: s_0_01
File: /home/walkup/BILL/72_288_Carbon_01.fid

Pulse sequence: a2pul
Solvent: dcd13
Temp. 26.0 C / 299.1 K
Operator: BILL
File: 72_288_Carbon_01
VNMRS-400 "mnr"

Relax delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
64 repetitions

COUPLING C13, 100.3763456 MHz
DECoupling H1, 399.1917584 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
Sample: 72-290L
Sample ID: s_0.01
File: /home/walkup/Bill/72_290L_Proton_01
Automation directory: /home/walkup/vnmrsys/data/auto_2011.03.23

Pulse Sequence: s2pul
Solvent: odo13
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 72_290L_Proton_01
VNMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 4006.4 Hz
8 repetitions
OBSERVE H1, 399.1897624 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 31 sec
Sample: 72-390L
Sample ID: a_0_01
File: /home/walkup/Bill/72_390L_Carbon_01.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 29.0 °C / 299.1 K
Operator: Bill
File: 72_390L_Carbon_01
VNMRS-400 "nmr" 

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24.097.8 Hz
64 repetitions

OBSERVE CI3, 100.3763456 MHz
DECOUPLE H1, 199.1917504 MHz
Power 39 dB
continuously on
WALZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec

S2
Sample: 40
Sample ID: a_001
File: /home/walkup/Bill1/76-100_Proton_01
Automation directory: /home/walkup/nnmsys/data/acro_2011.09.15

Pulse Sequence: s2pol
Solvent: cd3od
Temp. 24.0°C / 299.1 K
Operator: Bill1
File: 76-100_Proton_01
VNMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 4096.4 Hz
0 repetitions
OBSERVE H1, 399.1742506 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 31 sec

![Chemical Structure](Image)
Sample: s00
Sample ID: s_0_01
File: /home/walkup/Bl11/76-100_Carbon_01
Automation directory: /home/walkup/vnmrsys/data/auto_2011.09.15

Pulse Sequence: a2pul
Solvent: cd2d
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 76-100_Carbon_01
VnmrS-400  "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24809.8 Hz
256 repetitions
OBSERVE C15, 100.372452 MHz
DECOUPLE H1, 399.1761465 MHz
Power 39 dB
continuously on
WXL/YZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FFT size 65536
Total time 9 min, 51 sec
Gradient Shimming

Sample Name: 76-177
Data Collected on: wormhole-vnmxs400
Archive directory: /home/walkup/vnmrys/data/Bill
Sample directory: 76-177_20111201_01
FidFile: PROTON_01

Pulse Sequence: PROTON (s2pu1)
Solvent: odec13
Data collected on: Dec 1 2011

Temp. 26.0 C / 299.1 K
Operator: Bill

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 4006.4 Hz
8 repetitions
OBSERVE H1, 399.1728012 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 24 sec
Sample Name: 76-177
Data Collected on: wormhole-vmnr400
Archive directory: /home/wallop/vnrays/data/Bill
Sample directory: 76-177_20111201_01
FidFile: CARBON_01
Pulse Sequence: CARBON (a2pul)
Solvent: cdcl3
Data collected on: Dec 1 2011

Temp. 26.0 C / 299.1 K
Operator: Bill

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
256 repetitions
OBSERVE C13, 100.3720739 MHz
DECOUPLE H1, 399.1747702 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min 45 sec
Sample: 46-214-1
Sample ID: 8.0.01
File: /home/walkup/Bill/46_214_1_Proton_01
Automation directory: /home/walkup/vnmrsys/data/auto_2008.10.29_01

Pulse Sequence: sigpul
Solvent: dodo13
Ambient temperature
Operator: Bill
File: 46_214_1_Proton_01
VNMRS-400 "nme"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 4006.4 Hz
16 repetitions

OBsERVE H1, 399.2879045 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 51 sec
Sample: 46-214-1
Sample ID: a_0.01
File: /home/walkup/Bill/46_214_1_Carbon_01
Automation directory: /home/walkup/vmsreys/data/auto_2008.10.39_01

Pulse Sequence: z2pul
Solvent: odcl3
Ambient temperature
Operator: Bill
File: 46_214_1_Carbon_01
VNMRS-400 "nmr=

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
256 repetitions

OBSERVE C13, 100.3934799 MHz
DECOUPLE H1, 399.2599008 MHz
Power 33 dB
continuously on
NWMT-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 45536
Total time 9 min, 81 sec

BnO
BnO
O

7
Sample: 72-206
Sample ID: a_0.01
File: /home/walkup/Bill/72_206_Proton_01
Automation directory: /home/walkup/vnmrsys/data/auto_2011.03.02

Pulse Sequence: spul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 72_206_Proton_01
VNMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 4006.4 Hz
8 repetitions

OBSERVE H1, 399.1897624 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 31 sec
Sample: 72-304
Sample ID: s_0_01
File: /home/walkup/bill/72_304_Carbon_01
Automation directory: /home/walkup/vnmrsys/data/auto_2011.03.02

Pulse Sequence: aipul
Solvent: cdol3
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 72_304_Carbon_01
VNMRS-400 "nme"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24508.8 Hz
256 repetitions
OBSERVE C13, 100.3763456 MHz
DECOUPLE H1, 399.1917584 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 5 min, 51 sec

\[ \text{S9} \]
Sample: 72-213gww
Sample ID: s_0_03
File: /home/walkup/Bill/72_213gww_Proton_01
Automation directory: /home/walkup/vnmrsys/data/auto_2011.03.07_01

Pulse Sequence: s2pul
Solvent: odo13
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 72_213gww_Proton_01
VMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 4006.6 Hz
8 repetitions
OBSERVE H1, 399.1897624 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 31 sec
Sample: 72-213
Sample ID: s_0.0.03
File: /home/walkup/Bill/72_213ccv_Carbon_01
Automation directory: /home/walkup/vnmrs/data/auto_2011.03.07.01

Pulse Sequence: z2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: Bill
File: 72_213ccv_Carbon_01
VNMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 1.300 sec
Width 24589.8 Hz
256 repetitions
OBSERVE C13, 100.376456 MHz
DECOUPLE H1, 399.1917584 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
Sample: 54-124
Sample ID: a_0_02
File: /home/walkup/Bill/54_124_Carbon_02.fid

Pulse Sequence: s1p1
Solvent: cdcl3
Ambient temperature
Operator: Bill
File: 54_124_Carbon_02
VNMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
64 repetitions

OBSERVE C13, 100.3896080 MHz
DECOUPLE H1, 399.2445021 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.8 Hz
FT size 65536
Total time 9 min, 51 sec
Sample: 72-246
Sample ID: w_0_01
File: /home/walkup/Bill/72_246_Proton_01
Automation directory: /home/walkup/vnmrsys/data/auto_2011.03.14_01

Pulse Sequence: sispul
Solvent: dcd13
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 72_246_Proton_01

Note: S13
Sample: 72-346
Sample ID: a_0_01
File: /home/walkup/Bill/72_346_Carbon_01.fid

Pulse Sequence: sispul
Solvent: ddo13
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 72_346_Carbon_01
VNMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
64 repetitions
OBSERVE C13, 100.376456 MHz
DECcouple H1, 399.1517544 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 8 min, 51 sec

S13
Sample: 72-244beta
Sample ID: s_0_03
File: /home/walkup/Bill/72_244beta_Proton_01
Automation directory: /home/walkup/vnmrsys/data/auto_2011.03.14_01

Pulse Sequence: s1pul
Solvent: cdc13
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 72_244beta_Proton_01

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 4006.4 Hz
8 repetitions

S14

39.41 1.86 45.94 2.34 0.21 7.26 2.99
Sample: 72-344beta
Sample ID: s_0_03
File: /home/walkup/Bill/72_344beta_Carbon_01.fid

Pulse Sequence: s2pul
Solvent: dcl3
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 72_344beta_Carbon_01
VNMRS-400 "nrm"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
64 repetitions
OBSERVE C13, 100.3763456 MHz
DECOUPLE H1, 399.1917584 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.8 Hz
PT size 65536
Total time 9 min, 51 sec
Gradient Shimming

Sample Name: 72-264
Data Collected on: 72-264_20120915_01
Archive directory: /home/telmap/vnmr/vnmrj/data/RIH1
Sample directory: 72-264_20120915_01
FidFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 25 2012
Temp. 22.2 C / 295.4 K
Operator: Bill

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 4006.4 Hz
8 repetitions

OBSE RVE H1, 399.8860634 MHz
DATA PROCESSING
PT size 16384
Total time 0 min 24 sec
Sample Name: 72-264
Data Collected on: nmr.AncoraPharma.local-vnms400
Archive directory: /home/walkup/vnms400/data/Bill
Sample directory: 72-264_20130925_01
File: CARBON

Pulse Sequence: CARBON (se1pul)
Solvent: odc13
Data collected on: Sep 25 2012

Temp. 22.3 °C / 295.4 K
Operator: Bill

Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
64 repetitions

OBSERVE C13, 100.5514306 MHz
DECOUPLE H1, 399.8880628 MHz
Power 41 dB
continuously on

NATIV1-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 18 min

\[
\begin{array}{c}
\text{BnO} \\
\text{BnO} \\
\text{HO} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{BzO}
\end{array}
\]
Gradient Shimming

Sample Name: 79-209A
Data Collected on: 
nmr.AncoraPharma.local-vmnrs400
Archive directory: /home/walkup/vnmrj55/data/Bill
Sample directory: 79-209A_20131101_01
Fid file: PROTON_01

Pulse Sequence: PROTON (a2pul)
Solvent: cdcl3
Data collected on: Oct 1 2012

Temp. 20.6 C / 293.6 K
Operator: Bill

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.045 sec
Width 4006.4 Hz
16 repetitions

Observe H1, 399.8860kHz MHz
DATA PROCESSING
FT size 16384
Total time 0 min 49 sec
Sample Name: 79-209B
Data Collected on: 79-209B
Archive directory: /usr.AncoraPharma.local-vnmrs400
Sample directory: 79-2098.20120202_01
P14File: CARBON
Pulse Sequence: CARBON (e2pul)
Solvent: oel13
Data collected on: Oct 2 2012

Temp. 22.3 C / 295.4 K
Operator: Hill

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
384 repetitions

OBSERVE C13, 100.5914306 MHz
DECOUPLE H1, 399.8880628 MHz
Power 41 dB
continuously on

NMR T-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min

S16
Gradient Shimming

Sample Name: 79-216

Data Collected on: nam.AmcorPharma.local-vmnrs6400

Archive directory: /home/walkup/vmnrsys/data/Bill

Sample directory: 79-216_20121003_01

Pulse file: PROTON_01

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Oct 3 2012

Temp. 20.8 C / 293.9 K

Operator: Bill

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.045 sec

Width 4004.4 Hz

16 repetitions

NMR, 399.8860634 MHz

DATA PROCESSING

FT size 16384

Total time 0 min 49 sec

BnO

BnO

BzO

OH

OAc

S17

0 ppm

1 2 3 4 5 6 7 8 9 10
Sample Name: 79-216
Data Collected on: 79-216
Archive directory: /home/walkup/vnmrs/data/Bill
Sample directory: 79-216, 20121003_01
Pulse Sequence: CARBON (s2pul)
Solvent: cdc13
Data collected on: Oct 3 2012

Temp. 21.0 C / 294.1 K
Operator: Bill

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions

OBSERVE CH3, 50.5514306 MHz
DECOUPLE H1, 399.8880628 MHz
Power 41 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min
Sample: 72-299
Sample ID: #_0_01
File: /home/walkup/Bill/72_299_Carbon_01.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 29.0 C / 299.1 K
Operator: Bill
File: 72_299_Carbon_01
VNMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
256 repetitions
OBSERVE C13, 100.3763456 MHz
DECOUPLE H1, 399.1917584 MHz
Power 39 dB continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min. 51 sec

\[ 10 \]

\[ \text{Structure Image} \]
Sample: 76-001B
Sample ID: a_0_01
File: /home/walkup/Bill/76_001B_Proton_01
Automation directory: /home/walkup/vnmrj/vnmrj/data/auto_2011.03.29

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 298.0 C / 299.1 K
Operator: Bill
File: 76_001B_Proton_01
VNMRS-600 "mmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 406.4 Hz
8 repetitions

OBSERVED H1, 399.1897634 MHz
DATA PROCESSING
Baseline enhancement -0.3 Hz
FT size 65536
Total time 0 min, 31 sec
Sample: 76-001B
Sample ID: s_0.01
File: /home/walkup/Bill/76_001B_Carbon_01
Automation directory: /home/walkup/vnmrsys/data/auto_2011.03.29

Pulse Sequence: zpul
Solvent: ocd\textsubscript{13}
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 76_001B_Carbon_01
VNMRS-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
256 repetitions

OBSERVE C13, 100.3763456 MHz
DECouple H1, 399.1917584 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
Sample: 76-006A
Sample ID: 0.01
File: /home/wallmap/W1176_006A_Proton_01
Automation directory: /home/wallmap/vnmrj/knl/data/auto_2011_04.01

Pulse Sequence: s2pulse
Solvent: d6-dl3
Temp: 26.0 C / 299.1 K
Operator: B111
File: 76_006A_Proton_01
Vnmrj-400 "nmr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.040 sec
Width 4000.4 Hz
8 repetitions
OBSERVE H1, 399.1897624 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 31 sec

12
Sample: 76-006A
Sample ID: s_0.01
File: /home/walkup/Bill/76_006A_Carbon_01
Automation directory: /home/walkup/vnmrsys/data/auto_2011.04.01

Pulse Sequence: 3pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: Bill
File: 76_006A_Carbon_01
VnmrS-460 "nrMr"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
256 repetitions

OBSERVE C13, 100.37634856 MHz
DECOUPLE H1, 399.1917584 MHz
Power 39 dB
continuously on

WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
Sample: 76-006A
Sample ID: s_0.0
File: /home/walkup/76_006A_setup_01.fid
Pulse Sequence: gHMBC
Solvent: ddo13
Temp: 25.0 °C / 298.1 K
Operator: Mill
File: 76_006A_setup_01
VMR=400 "nmn"

Relax. delay 1.000 sec
Acq. time 0.128 sec
Width 2476.5 Hz
2D Width 14521.6 Hz
4 repetitions
2 x 128 increments
OBSERVE 1H, 195.189763 MHz
DECOUPLE 213, 101.386339 MHz
Power 33 dB
on during acquisition
off during delay
1H_P000844 modulated
DATA PROCESSING
Gauss apodization 0.059 sec
F1 DATA PROCESSING
Gauss apodization 0.007 sec
FT size 2048 x 2048
Total time 20 min, 10 sec
Gradient Shimming

Sample Name: 81-089-A
Data Collected on: nmr.AnacorPharma.local-vnmrs.40
Archive Directory: /home/wallcup/vnmrsays/data/Stewart
Sample directory: 81-089-A_20121206_01
FiSpFile: PROTON_01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 6 2012

Operator: Stewart
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 1097.7 Hz
8 repetitions
OBSERVE H1, 399.8780044 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 38 sec
Sample Name: 81-089-A
Data Collected on: 81-089-A
Archive directory: nmr.AncoraPharma.local-vnmrs400
Sample directory: 81-089-A_20121206_01
Pulse Sequence: CARBON (s2pul)
Solvent: cdc13
Data collected on: Dec 6 2012
Operator: Stewart
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 35000.0 Hz
SNR repetitions
SNR 12
SNR 10.5496193 MHz
DDECouple H1, 399.8806538 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 19 min
Gradient Shimming

Sample Name: 81-093-C
Data Collected on: mmr.ancorapharma.local-vnmrs60
Archive directory: /home/wallup/vnmrsy/data/Stewart
Sample directory: 81-093-C_20121212_01
FidFile: PROTON_01
Pulse Sequence: PROTON (a2pul)
Solvent: dcd13
Data collected on: Dec 12 2012

Operator: Stewart
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 4807.7 Hz
8 repetitions
OBSERVE H1, 399.8780644 MHz
DATA PROCESSING
PT size 32768
Total time 0 min 38 sec
Sample Name: 81-093-C
Data Collected on: 81-093-C
Archive directory: /home/val1/nuc/nmr/data/Stewart
Sample directory: 81-093-C_20131212_01
Pulse Sequence: CARBON (s2pal)
Solvent: dcl3
Data collected on: Dec 12 2013
Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 28000.0 Hz
1000 repetitions

Observe C13, 100.5149193 MHz
decouple H1, 399.8800618 MHz
Power 41 dB
continuously on

DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 38 min
Gradient Shimming

Sample Name: 81-097 lactol
Data Collected on: nem.AnacorPharma.local-vmrse400
Archive directory: /home/wellkup/vnmrsys/data/Stewart
Sample directory: 81-097_lactol_20121217_01
FidFile: PROTON_01

Pulse Sequence: PROTON (a2pul)
Solvent: cdc13
Data collected on: Dec 17 2012

Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 4807.7 Hz
8 repetitions

DATA PROCESSING
PT size 32768
Total time 0 min 35 sec
Gradient Shimming

Sample Name: B1-097 lactol
Data Collected on: numer.AncoraPharma.local-vnmrs400
Archive directory: /home/walkup/vnmrsys/data/Stewart
Sample directory: B1-097_lactol_20121217_02
FidFile: CARBON_01

Pulse Sequence: CARBON (s2pu1)
Solvent: odc13
Data collected on: Dec 17 2012

Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
128 repetitions

OBSEIVER C13, 100.6464193 MHz
DECORREL H1, 399.6800638 MHz
Power 41 dB continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 4 min 56 sec
Gradient: Shimming

Sample Name:
81-094

Data Collected on:
nmr.ancoraPharma.local-vnmr400

Archive directory:
/home/walkup/vnmrsys/data/Stewart

Sample directory:
81-094_20121213_01

FidFile: PROTON_01

Pulse Sequence: PROTON (z2pul)

Solvent: odo13

Data collected on: Dec 15 2012

Operator: Stewart

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 3.408 sec

Width 4807.7 Hz

16 repetitions

Observes H1, 399.8790644 MHz

DATA PROCESSING

FT size: 32768

Total time 1 min 11 sec
Sample Name: 81-094

Data Collected on: 
nmr.AnacorPharma.local-vnms400
Archive directory: 
/home/wellup/vnms4ys/data/Stewart
Sample directory:  
81-094_20121213_01

Pulse Sequence: CARBN (s2pul)
Solvent: dcm13
Data collected on: Dec 13 2012

Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
512 repetitions

OBSERVE C13, 100.5494193 MHz
DECOUPLE H1, 399.8800638 MHz
Power 41 dB
continuously on

WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 19 min
Gradient Shimming

Sample Name: 81-100-A
Data collected on: nmr.AncoraPharma.local-vnmrs400
Archive directory: /home/walkup/vnmrs/data/Stewart
Sample directory: 81-100-A_20121219_01
FidFile: PROTON_01

Pulse Sequence: PROTON (sp2pul)
Solvent: cdcl3
Data collected on: Dec 19 2012

Operator: Stewart

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 3.400 sec
Width 4607.7 Hz
16 repetitions
OBSERVE HL, 399.8780444 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 11 sec
Gradient Shimming

Sample Name: 81-100-A
Data Collected on: mnr.AncoraPharma.local-vnmrs400
Archive directory: /home/waj/kup/vnmrsys/data/Stewart
Sample directory: 81-100-A_20131215_02
PfdFile: C000001

Pulse Sequence: C000001 [32pul]
Solvant: dcal3
Data collected on: Dec 19 2013

Operator: Stewart
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
1000 repetitions
OBSERVE C13, 100.5494193 MHz
DECOUPLE H1, 399.8800638 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min
Gradient Shimming

Sample Name:
81-101-MeCH_extract
Data Collected on:
nmr.AncoraPharma.local-vmnr-00
Archive directory:
/home/walkup/vnmrsym/data/Stewart
Sample directory:
81-101-MeCH_extract_20121220_01
FidFile: PROTON_01
Pulse Sequence: PROTON [s2pu1]
Solvent: cdcl3
Data collected on: Dec 10 2012

Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 4807.7 Hz
8 repetitions
OBSERVE H1, 399.8700614 MHz
DATA PROCESSING
PT size 32768
Total time 0 min 35 sec
Gradient Shimming

Sample Name: 81-101-MeOH_extract
Data Collected on: 
/home/AcmePharma.local-vmmrc400
Archive directory:
/home/valkgs/vnmrc400/data/Stewart
Sample directory: 81-101-MeOH_extract_20131220_02
File: CARBON_01

Pulse Sequence: CARBON (x2pul)
Solvent: cdcl3
Data collected on: Dec 20 2013

Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
256 repetitions

OBSERVE C13, 100.5494193 MHz
DECouple H1, 399.8800638 MHz
Power 41 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.0 Hz
PT size 65536
Total time 9 min 52 sec
Sample Name: 81-107-17
Data Collected on: nmr.AncoraPharma.local-vnmr400
Archive directory: /home/walkup/vnmrays/data/Stewart
Sample directory: 81-107-17_20130110_01
Fidfile: CARBON_01
Pulse Sequence: CARBON (z2pul)
Solvent: odo13
Data collected on: Jan 10 2013
Operator: Stewart
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
2000 repetitions
OBSERVE C13, 100.5454193 MHz
DECouple H1, 399.8806399 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 17 min
Gradient Shimming

Sample Name: 109
Data Collected on: 109
Archive directory: /home/walkup/vnmrs/data/Stewart
Sample directory: 109
FidFile: 109

Pulse Sequence: PROTON (s2pul)
Solvent: odo13
Data collected on: Jan 21 2013

Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 4807.7 Hz
16 repetitions
OBSeve H1, 399.4780644 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 11 sec
Sample Name: 81-111-17
Data Collected on: mmu.AgnesPharma.local-vnmrs400
Archive directory: /home/walkup/vnmrs/data/Stewart
Sample directory: 81-111-17_20130121_01
File: CARNON_01

Pulse Sequence: CARNON (ms2pul)
Solvent: dcd13
Data collected on: Jan 21 2013

Operator: Stewart

Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 28000.0 Hz
5000 repetitions

OBSERVE C13, 100.5494193 MHz
DECOUPLE H1, 399.8804628 MHz
Power 41 dB
continuously on

WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.6 Hz
FT size 65536
Total time 3 hr, 12 min
Sample Name: 81-113-B
Data Collected on: nmr.AncooraPharma.local-vnmrs400
Archive Directory: /home/walkup/vnmrays/data/Stewart
Sample directory: 81-113-B_20130123_01
FidFile: CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 23 2013

Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
2000 repetitions
OBSERVE C13, 100.5494570 MHz
DECouple NH, 399.8821791 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 17 min
Sample Name: 81-118-B
Data Collected on: nmr.AncoraPharma.local-vnmrs400
Archive directory: /home/walkup/vnmrsys/Data/Stewart
Sample directory: 81-118-B_20130123_01
Pdfile: gCOSY_01

Pulse Sequence: gCOSY
Solvent: d2o13
Data collected on: Jan 23 2013

Operator: Stewart

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4223.0 Hz
2D Width 4223.0 Hz
Single scan
128 increments
OBSERVE H1, 399.878644 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.030 sec
FT size 2048 x 2048
Total time 3 min 10 sec
Sample Name: 81-118-B
Data Collected on: mnr.AncoraPharma.local-vnmrs400
Archive directory: /home/walkup/vnmrsys/data/Stewart
Sample directory: 81-118-B_30130133_01
PdFile: gOSY_01
Pulse Sequence: gOSY
Solvent: dcd13
Data collected on: Jan 23 2013
Operator: Stewart
Relax. delay 1.000 sec
Avg. time 0.150 sec
Width 4233.0 Hz
2D Width 4233.0 Hz
Single scan
128 increments

DEGREE 399.8780644 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.030 sec
FT size 2048 x 2048
Total time 3 min 10 sec
Sample Name: 81-114-3
Data Collected on: nmr.AncorePharma.local-vmnr400
Archive directory: /home/walkup/vmmrsys/data/Stewart
Sample directory: 81-114-B_20130123_01
Fidfile: BBQCAD_01
Pulse Sequence: BBQCAD
Solvent: cdcl3
Data collected on: Jan 23 2013
Operator: stewart
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 6410.3 Hz
3D Width 2010.6 Hz
2 repetitions
2 x 96 increments
OBSERVE E1, 399.9780644 MHz
DECouple G13, 100.5984686 MHz
Power 34 dB
on during acquisition
off during delay
WQ0 AutoX_PC080944 modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Line broadening 0.3 Hz
Gauss apodization 0.004 sec
FT size 1048 x 2048
Total time 8 min 18 sec
Sample Name: 81-118-B
Data Collected on: 20130204 07
File Name: CARBON_01
Pulse Sequence: CARBON (a2pul)
Solvent: cdc13
Data collected on: Feb 4 2013

Operator: Stewart
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 28000.0 Hz
1000 repetitions
OBSERVE C13, 100.5494193 MHz
DECOUPLE H1, 399.8800638 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
PT size 65536
Total time 38 min
Sample Name: 81-122-C
Data Collected on:
/home/walkup/vmmsys/data/Stewart
Sample directory:
81-122-C_20110208_01
Pulse sequence: PROTON (a2pu1)
Solvent: cdc13
Temperature: 25.0 C / 298.1 K
Operator: Stewart
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.402 sec
Width 4807.7 Hz
5 repetitions
OBSERVE H1, 399.8694179 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 35 sec
Sample Name: 81-122-C
Data Collected on: mmr.AmcorPharma.local-vnmr400
Archive directory: /home/valky/vnmr400/data/stewart
Sample directory: 81-122-C_20130208_01
필드: CARBONE_01

Pulse Sequence: CARBONE (s2pul)
Solvent: cdcl3
Data collected on: Feb 8 2013

Temp. 25.0 C / 298.1 K
Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 28600.0 Hz
912 repetitions
Observe 61, 100.8472956 MHz
Decoupler H1, 399.8716172 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min
Sample Name: 81-112-C
Data Collected on: nmr.licom.iPharma.local-vmsra06
Archive directory: /home/walkup/vnmrsy/data/Stewart
Sample directory: 81-112-C_20130228_01
ProjFile: HSCQCAD_01
Pulse Sequence: HSCQCAD
Solvent: d2o13
Data collected on: Feb 8 2013
Temp. 25.0 C / 298.1 K
Operator: Stewart
Relax. delay 1.000 sec
Avg. time 0.150 sec
Width 4007.7 Hz
2D Width 2010.6 Hz
2 repetitions
2 x 96 increments
RESOLVE H1, 399.8606179 MHz
ZDECouple G13, 100.0563446 MHz
Power 74 dB
on during acquisition
off during delay
W40 AutoX_8008944 modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.004 sec
FT size 2048 x 2048
Window times 8 x 16 16 sec
Sample Name: 81-126-B
Data Collected on: nmr.AncorePharma.local-vnmrs400
Archive directory: /home/walkup/vnmrsys/data/Stewart
Sample directory: 81-126-B_20130217_01
File: CARBON_01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 17 2013

Temp. 25.0 C / 298.1 K
Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
1000 repetitions
OBSERVE C13, 100.6172 MHz
DECOUPLE HL, 399.814172 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 38 min
Sample Name: 81-126-B
Data Collected on: /usr.Local-vnmra400
Archive directory: /home/walkup/vnmra400/Data/Stewart
Sample directory: /usr.Local-vnmra400/Data/Stewart
File name: 81-126-B_20130217_01
Pulse Sequence: gCOSY
Solvent: ocdOl3
Data collected on: Feb 17 2013
Temp. 25.0 C / 398.1 K
Operator: Stewart
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4629.6 Hz
2D Width 4629.6 Hz
Single scan
128 increments
H1, 399.8656179 MHz
DATA PROCESSING
Sq. size bell 0.075 sec
FI DATA PROCESSING
Sq. size bell 0.026 sec
FT size 2048 x 2048
Total time 3 min 10 sec
Sample Name:
81-126-8

Data Collected on:
mpr.ancoraPharma.local-vmmrs400

Archive directory:
/home/valcup/vmmrsys/data/Stewart

Sample directory:
81-126-8_20130217_01

File: NSQCAD_01

Pulse Sequence: NSQCAD

Solvent: cdcl3

Data collected on: Feb 17 2013

Temp. 25.0 C / 298.1 K

Operator: Stewart

Relax. delay 1.000 sec

Acq. time 0.150 sec

Width 4807.7 Hz

2D Width 2010.6 Hz

2 repetitions

3 x 95 increments

Observe H1, 599.8656179 MHz

Decouple C13, 100.6563446 MHz

Power 34 dB

during acquisition

during delay

W40_Spectrum.mpr modulated

Data Processing

Gaussian apodization 0.069 sec

F1 DATA PROCESSING

Gaussian apodization 0.096 sec

FT size 2048 x 2048

Total time 6 min 18 sec
Sample Name: 81-132-D
Data Collected on:
/home/total/total-seq/data/Stewart
Sample directory:
81-132-D_20130219_01
FidFile: PROTON_01
Pulse Sequence: PROTON (s)pull
Solvent: dcm
Data collected on: Feb 19 2013

Temp. 25.0 C / 298.1 K
Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Aqo. time 3.408 sec
Width 4807.7 Hz
8 repetitions

RESERVE 399.695179 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 35 sec
Sample Name: 81-132-D
Data Collected on: nmr.AncoraPharma.local-vnmrs400
Archive directory: /home/walgp/vnmrs4e4/Data/Stewart
Sample directory:
81-132-D.20130219.01
FidFile: CARBON_01
Pulse Sequence: CARBON (a2pul)
Solvent: cdcl3
Data collected on: Feb 19 2013

Temp. 25.0 °C / 298.1 K
Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
1000 repetitions
OBSERVE CI3, 100.5472854 MHz
DECcouple CH3, 299.8716172 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 38 min
Sample Name: S1-116-A
Data Collected on: nmr.AnconaPharma.local-vnmrs400
Archive directory: /home/watkins/vnmrsys/data/Stewart
Sample directory: S1-116-A_20130226_11
Filetype: gOSY_01
Pulse Sequence: gOSY
Solvent: acdl3
Data collected on: Feb 26 2013

Temp. 25.0 °C / 298.1 K
Operator: Stewart
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4644.3 Hz
2D width 4644.3 Hz
Single scan
128 increments
OBSERVE 81.399.8694179 MHz
DATA PROCESSING
Sp. size bell 0.075 sec
F1 DATA PROCESSING
Sp. size bell 0.027 sec
FT size 2048 x 2048
Total time 3 min 10 sec
Sample Name: 81-136-A
Data Collected on:
/home/AndreaPharma.local-vmmra406
Archive directory: /home/wallop/vmmreys/data/Stewart
Sample directory:
81-136-A_20110225_01
FieldFile: HRQCAD_01
Pulse Sequence: HRQCAD
Solvent: odoll
Temp: 25.0°C / 298.1 K
Operator: Stewart
Ramp delay 1.000 sec
Acq. time 0.100 sec
Width 4807.7 Hz
2D Width 20110.6 Hz
3 repetitions
3 N 94 increments
OBSERVE M1, 399.8696179 MHz
DECOUPLE C13, 100.5563446 MHz
Power 34 dB
on during acquisition
call during delay
W40_AUTOC_P000844 modulated
DATA PROCESSING
Owes e modulation 0.069 sec
F1 DATA PROCESSING
Owes e modulation 0.046 sec
FT size 2048 x 2048
Total time 6 min 10 sec
Sample Name: 81-143-B
Data Collected on: 20130320_02
Sample directory: 81-143-B_20130320_02
FidFile: CARBON_01

Pulse Sequence: CARBON [s2pu1]
Solvent: odc13
Data collected on: Mar 20 2013

Temp. 25.0 C / 298.1 K
Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
1000 repetitions

OBSERVE C13, 100.5472954 MHz
DECOUPLE H1, 399.8716172 MHz
Power 41 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 30 min
Sample Name: 81-148-B
Data Collected on: mmr.AmcorPharma.local-vmmre00
Archive directory: /home/va/kd/vnmrays/data/Stewart
Sample directory: 81-148-B_20130328_01
FidFile: PROTON_01
Pulse Sequence: PROTON (a2ps1)
Solvent: cdcl3
Data collected on: Mar 28 2013

Temp. 25.0 C / 298.1 K
Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.408 sec
Width 4007.7 Hz
# repetitions

OBSERVE H1, 399.866178 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 35 sec
Sample Name: 81-145-B
Data Collected on: nmr.AmcorPharma.local-nmr600
Archive directory: /home/walkup/vnmrsy/data/Stewart
Sample directory: 81-145-B_20130330_01
PipFile: CARBON_01
Pulse Sequence: CARBON (s2pul)
Solvent: ddd3
Data collected on: Mar 28 2013

Temp. 28.0°C / 298.1 K
Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 2500.0 Hz
1000 repetitions
OBSERVE C13, 100.6472954 MHz
DECOUPLE H1, 399.8716172 MHz
Power 41 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 38 min
Sample Name: S1-188-A
Data Collected on: mmr.AnacorPharma.local-vnmrs400
Archive directory: /home/walkup/vnmrsys/data/Stewart
Sample directory: S1-188-A_20130301_01
FidFile: CARBON_01
Pulse Sequence: CARBON (x2pul)
Solvent: cdc13
Data collected on: May 1 2013

Temp. 25.0 C / 298.1 K
Operator: Stewart

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 28000.0 Hz
9000 repetitions
OBsERVE C13, 100.5472954 MHz
DECOUPLE n1, 399.8716172 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 46 min
**Animal care**

Studies were performed using female BALB/cAnNCrl mice (BALB/c; Charles River UK) implanted with a sub-cutaneous Pico transponder (Uno BV, Netherlands) to allow individual mice to be tracked through the study. Mice used in vaccine studies were 6 - 8 weeks of age and 18g (+/- 2g) at the start of procedures. On arrival in the conventional animal unit and on transfer of mice into containment level 3 animal facilities, mice were acclimatised to their new surroundings for five days before any procedures were performed. All mice were randomly allocated into cages of five and were housed in polypropylene cages with a stainless steel mesh cover with integral water bottle holder and diet hopper which conform to the Code of Practice for the housing of animals bred, supplied or used for scientific purposes (December 2014). Mice were under a 12 hour light/dark cycle (350 to 400 Lux during the day, 10 Lux during the night with a ramp up and ramp down period at ‘dawn’ and ‘dusk’) at 19 to 23 °C and 45 to 65 % relative humidity. Cages contained 8/10 and 10/14 grade corn cob (International Product Supplies, UK) as a nesting material with a range of environmental enrichment added throughout studies (e.g irradiated aspen wood wool, cellulose dome home, hemp stem ‘Happi Mats’; International Product Supplies) and there was free access to food (Labdiet certified rodent diet 5002 and Labdiet EUrodent 22 % diet 5LF5; International Product Supplies) and water throughout the study. During immunisation and the subsequent rest period, mice were housed in a conventional animal unit in rooms supplied with rough filtered air giving 20 to 25 air changes per hour. For infection with *B. pseudomallei*, mice were housed in an ACDP containment level 3 animal facility within a rigid-wall half suit isolator (Howorth Air Technology, UK) supplied with an inward flow of HEPA-filtered air giving 35 to 45 air changes per hour where the room was supplied with double HEPA-filtered air giving 20 to 25 air changes per hour in the room. Mice were checked at least twice daily following challenge and clinical signs for each mouse recorded. Humane end-points were used throughout these studies to minimise suffering, with culls performed via cervical dislocation at the end-point.