Supplementary Material

A General Approach for the Chemoenzymatic Synthesis of Asymmetrically Branched *N*-Glycans

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1. Chemical Synthesis

Materials and Methods

^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz, 600 MHz, or 800 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) relative to trimethylsilane (TMS) as the internal standard. NMR data is presented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration. All NMR signals were assigned on the basis of ^{1}H NMR, gCOSY, gHSQC, gHMQC, and ^{13}C experiments. Mass spectra were recorded on an Applied Biosystems SCIEX MALDI TOF/TOF 5800 mass spectrometer. The matrix used was 2,5-dihydroxy-benzoic acid (DHB). Column chromatography was performed on silica gel G60 (Silicycle, 60-200 μm, 60Å). TLC-analysis was conducted on Silicagel 60 F_{254} (EMD Chemicals inc.) with detection by UV-absorption (254nm) were applicable, and by spraying with 20% sulfuric acid in ethanol followed by charring at ~150°C or by spraying with a solution of Hanessian's stain followed by charring at ~150°C. CH_2Cl_2 was freshly distilled from calcium hydride under nitrogen prior to use. Molecular sieves (4Å) were flame activated under vacuum prior to use.

NMR nomenclature

The residues of the oligosaccharides have been labeled as depicted in **Fig. S1**. Starting from the reducing sugar, GlcNAc-1, GlcNAc-2, the β-mannoside is labeled as Man-3, the α-3 mannoside as Man-4, the α-6 mannoside as Man-4', followed by the *N*-acetylglucosamine residues as GlcNAc-5, -7, and -7' and the galactosides as Gal-6 and -8.

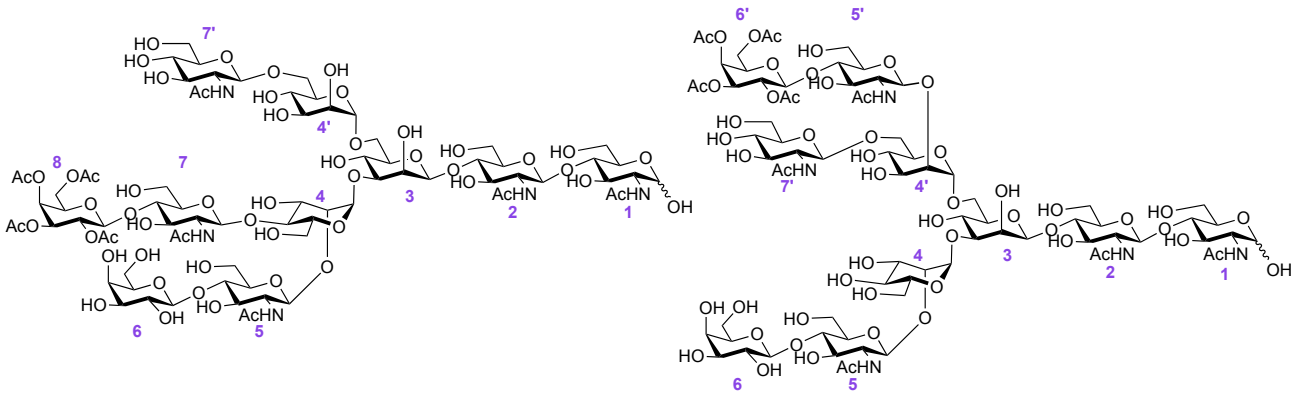


Fig. S1. Oligosaccharide residue labels.

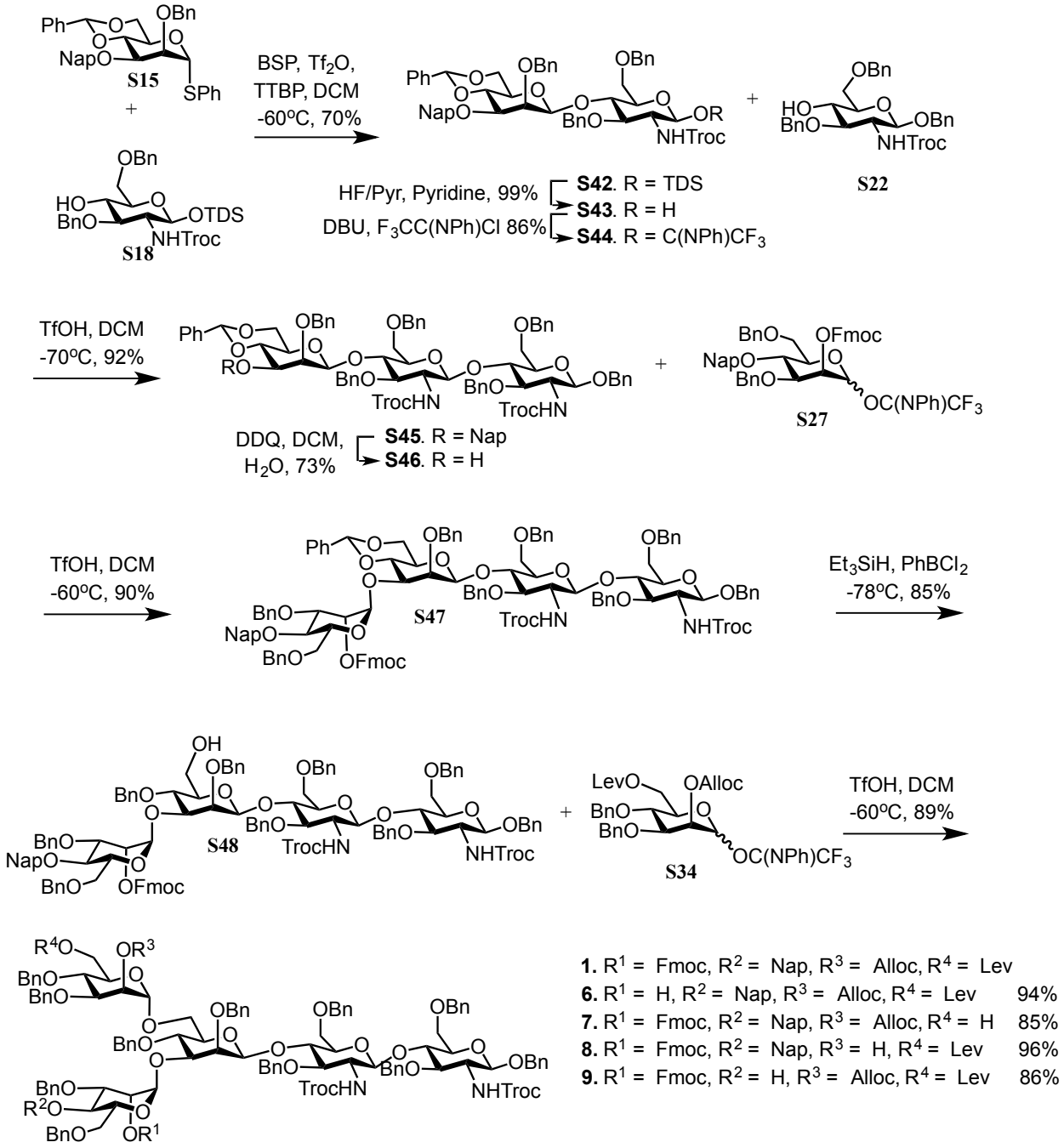


Fig. S2. Chemical synthesis of orthogonally protected core pentasaccharide **1**

Pentasaccharide **1** was prepared from monosaccharide building blocks **S15**, **S18**, **S22**, **S27**, and **S34** (**Fig. S2**). Thus, treatment of mannosyl donor **S15** with 1-benzenesulfinyl piperidine (BSP) (*41*) resulted in the formation of an intermediate α-triflate that was displaced by alcohol **S18** to provide mainly β-mannoside **S42**. The anomeric dimethylthexylsilyl ether (TDS) group of **S42** was removed with HF in pyridine to give lactol **S43**, which was converted into a *N*-phenyl-trifluoroacetimidate **S44** by treatment with *N*-phenyltrifluoroacetimidoyl chloride in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (*25*, *26*). A triflic acid (TfOH) catalyzed glycosylation of **S44** with **S22** gave trisaccharide **S45** in an excellent yield as only the β-anomer. The Nap ether (*42*) was removed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and the resulting alcohol **S46** was coupled with **S27** using TfOH as the activator resulting in the formation of tetrasaccharide **S47**. The benzylidene acetal of **S47** was regioselectively opened using triethylsilane and $PhBCl_2$ to provide glycosyl acceptor **S48**, which was coupled with **S34** to give target compound **1**.

The Fmoc group of **1** could be selectively removed by the non-nucleophilic base triethylamine to give **6** whereas treatment with the nucleophilic base hydrazine acetate led to cleavage of the Lev ester to provide **7** without affecting the other base sensitive protecting groups. Treatment of **1** with $Pd(PPh_3)_4$ affected only the Alloc protecting group providing the corresponding hydroxyl **8** and oxidation with DDQ resulted in the removal of the Nap ether to give **9** in high yield.

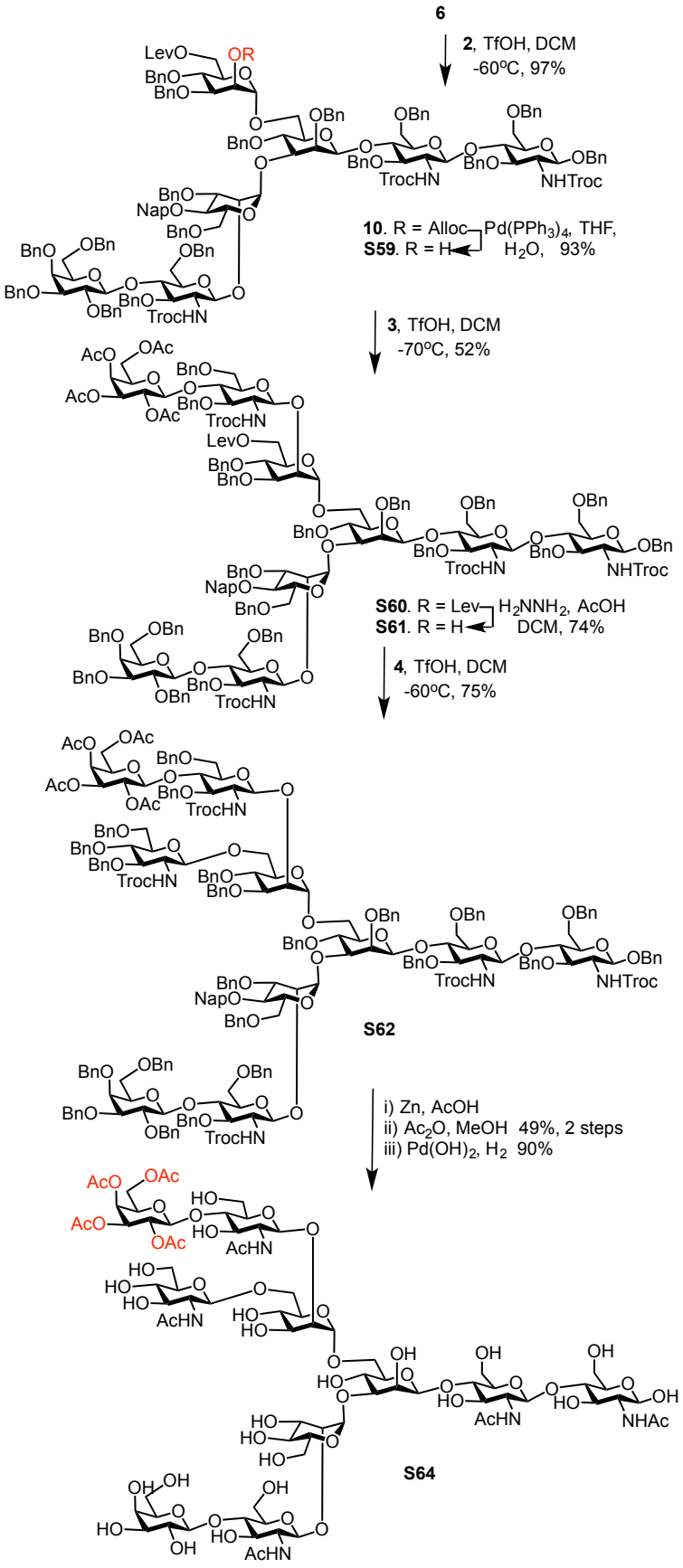


Fig. S3. Chemical Synthesis of decasaccharide **S64** which is a positional isomer of decasaccharide **15.**

In addition to decasaccharide **15**, pentasaccharide **1** is an appropriate starting material for the chemical synthesis of other bi-, tri-, and tetra-antennary precursor oligosaccharides by changing the number and sites of attachment of the appendages (**2-5**). For example, a positional isomer of decasaccharide **15** was readily prepared by sequential removal and glycosylations of the Fmoc, Alloc and Lev groups of **1** with glycosyl donors **2**, **3**, and **4**, respectively (**Fig. S3**)

Experimental Procedures

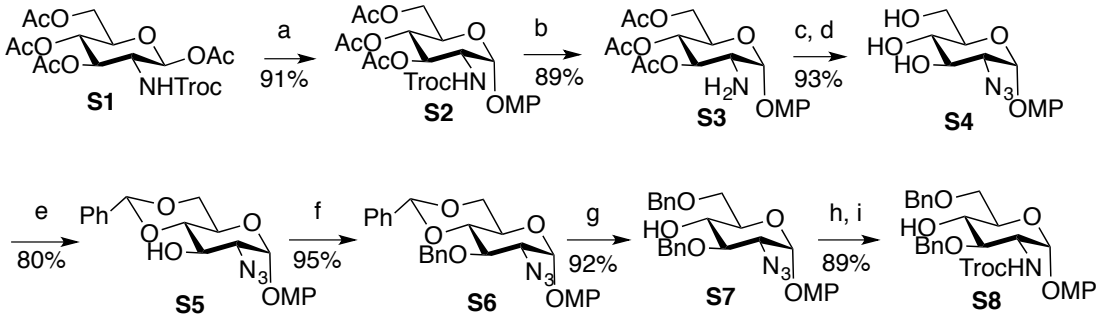


Fig. S4. Synthesis of glucosamine acceptor **S8.**
a) p-methoxyphenol, BF_3 etherate, DCM, rt, overnight; b) Zn dust, AcOH, DCM, MeOH, rt, 1 h;
c) NaOMe, MeOH, DCM, rt, 2 h; d) K_2CO_3, $ZnCl_2$, TfN_3, DCM, MeOH, H_2O, rt, overnight;
e) $PhCH(OCH_3)_2$, CSA, toluene, rt, 2 h; f) NaH, BnBr, DMF, 2 h; g) Et_3SiH, TfOH, DCM, -78 °C, 1 h;
h) PMe_3(1 M), NaOH, THF, H_2O, rt, overnight; i) TrocCl, solid $NaHCO_3$, THF, 4 h.

***p*-Methoxyphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-α-D-glucopyranoside (S2).** Boron trifluoride diethyl etherate (15.9 ml, 126.3 mmol) was added to a cooled (0 °C) solution of glucopyranoside **S1** (22 g, 42.1 mmol) and *p*-methoxylphenol (6 g, 48.4 mmol) in DCM (200 mL). The reaction mixture was stirred overnight, after which it was diluted with DCM (200 mL) and washed with a saturated solution of $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:2, v:v) to afford **S2** (22.5 g, 91%) as an amorphous white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.05 (s, 6H, CH_3CO), 2.06 (s, 3H, CH_3CO), 3.78 (s, 3H, OCH_3), 4.07-4.15 (dd, J = 12.3, 1.6 Hz, 1H, H-6b), 4.11 (ddd, J = 10.1, 4.4, 1.8 Hz, 1H, H-5), 4.21 (m, 2H, H-6a, H-2), 4.63 (d, J = 12.0 Hz, 1H, troc C*H*H), 4.82 (d, J = 12.0 Hz, 1H, troc C*H*H), 5.20 (*t*, J = 10.0 Hz, 1H, H-4), 5.43-5.52 (m, 3H, H-3, H-1, NH), 6.83-6.85 (d, J = 9.0 Hz, 2H, 2x aromatic CH), 7.02-7.04 (d, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5, 20.6 (×2), 54.0, 55.5, 61.7, 68.0, 68.2, 70.7, 74.5, 95.2, 96.7, 114.6, 117.8, 149.8, 154.2, 155.5, 169.3, 170.4, 170.9. $^1J_{C1,H1}$ = 174.4 Hz. MALDI-MS: $[M+Na]^+$ $C_{22}H_{26}Cl_3NNaO_{11}$, calcd 608.0469, obsd 608.0116.

***p*-Methoxyphenyl 4,6-*O*-benzylidene-2-deoxy-2-azido-α-D-glucopyranoside (S5).** Zn powder (24.1 g, 369 mmol) was added slowly to a cooled (0 °C) solution of *p*-methoxyphenyl glucopyranoside **S2** (12 g, 20.5 mmol) in MeOH (45 mL), AcOH (24 mL), and DCM (24 mL) and the reaction mixture was stirred under an atmosphere of N_2 at room temperature for 1 h. The

reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The resulting residue was diluted with DCM (300 mL), washed with a saturated aqueous solution of $NaHCO_3$ until a neutral pH was achieved and then the organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (DCM:MeOH, 6:1, v:v) to afford the glucosamine **S3** as an amorphous white solid (7.52 g, 89%). NaOMe (9.9 mL, 52.5 mmol, 5.33 M in MeOH) was added to a solution of compound **S3** (7.52 g, 17.5 mmol) in MeOH (35 mL) and DCM (35 mL). The resulting reaction mixture was stirred for 2 h at room temperature and neutralized with conc. HCl and concentrated *in vacuo*. The resulting residue, K_2CO_3 (4.8 g, 35 mmol) and a catalytic amount of $ZnCl_2$ (120 mg, 0.9 mmol) were dissolved in MeOH (40 mL) and H_2O (10 mL). Freshly prepared TfN_3 (50 mL in DCM, 52.5 mmol) was added to the solution and the reaction mixture was stirred overnight at room temperature. The solvent was concentrated under reduced pressure and the resulting residue was diluted with EtOAc (200 mL), neutralized with conc. HCl and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (DCM:MeOH, 10:1, v:v) to give **S4** (5.05 g, 93% over two steps) as an amorphous white solid. Compound **S4** (5 g, 16.1 mmol), camphorsulfonic acid (1.12 g, 4.83 mmol) and benzaldehyde dimethylacetal (2.89 mL, 19.3 mmol) were dissolved in anhydrous toluene (100 mL) and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with EtOAc (200 mL), washed with a saturated aqueous solution of $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane:EtOAc, 2:1, v:v) to afford compound **S5** (5.13 g, 80%) as an amorphous white solid. . ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.17 (s, 1H, OH), 3.41 (dd, J = 10.0 Hz, 3.5 Hz, 1H, H-2), 3.61 (t, J = 9.5 Hz, 1H, H-4), 3.75-3.79 (t, J = 10.3 Hz, 1H, H-6b), 3.82 (s, 3H, OCH_3), 4.08 (td, J = 9.9, 4.9 Hz, 1H, H-5), 4.28 (dd, J = 10.3, 5.0 Hz, 1H, H-6a), 4.41 (*t*, J = 10.0 Hz, 1H, H-3), 4.45 (d, J = 3.5 Hz, 1H, H-1), 5.58 (s, 1H, benzylidene CH), 6.88-6.91 (m, 2H, 2x aromatic CH), 7.05-7.08 (d, 2H, 2x aromatic CH), 7.41-7.44 (d, 3H, 3x aromatic CH), 7.53-7.55 (m, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6, 62.9, 63.0, 68.6, 68.7, 81.7, 98.3, 102.1, 114.7, 118.2, 126.3, 128.4, 129.4, 136.8, 150.3, 155.5; MALDI-MS: $[M+Na]^+$ $C_{20}H_{21}N_3NaO_6$, calcd 422.1328, obsd 422.0684.

***p*-Methoxyphenyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-deoxy-2-azido-α-D-glucopyranoside (S6).** Benzyl bromide (1.07 mL, 9 mmol) and NaH (0.36 g, 60% NaH in mineral oil, 9 mmol) were added to a cooled (0 °C) solution of compound **S5** (3 g, 7.51 mmol) in DMF (50 mL). The

reaction mixture was stirred at room temperature under an atmosphere$_2$ for 2 h and then concentrated *in vacuo*. The resulting residue was diluted with EtOAc (100 mL), washed with saturated $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexane:EtOAc, 3:1, v:v) to afford **S6** (3.5 g, 95%) as an amorphous white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.54 (dd, J = 10.0 Hz, 3.5 Hz, 1H, H-2), 3.79-3.86 (m, 5H, H-4, H-6b, OCH_3), 4.14 (td, J = 9.9, 4.9 Hz, 1H, H-5), 4.29-4.34 (m, 2H, H-3, H-6a), 4.90 (d, J = 11.0 Hz, 1H, CH*H*Ph), 5.05 (d, J = 11.0 Hz, 1H, C*H*HPh), 5.47 (d, J = 3.5 Hz, 1H, H-1), 5.65 (s, 1H, benzylidene CHPh), 6.88 (d, J = 9.0 Hz, 2H, 2x aromatic CH), 7.06 (d, J = 9.0 Hz, 2H, 2x aromatic CH), 7.29-7.46 (m, 8H, 8x aromatic CH), 7.53-7.55 (m, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 62.9, 63.3, 68.8, 75.1, 76.0, 82.7, 98.3, 101.5, 114.7, 118.2, 126.0, 127.9, 128.2, 128.3, 128.5, 129.1, 137.1, 137.8, 150.3, 155.5; MALDI-MS: $[M+Na]^+$ $C_{27}H_{27}N_3NaO_6$, calcd 512.1798, obsd 512.1291.

***p*-Methoxyphenyl 3,6-di-O-benzyl-2-deoxy-2-azido-α-D-glucopyranoside (S7).** Triethylsilane (2.1 mL, 13.1 mmol) and TfOH (1.05 mL, 11.9 mmol) were sequentially added to a cooled (-78 °C) solution of compound **S6** (2 g, 4.09 mmol) in DCM (200 mL). The reaction mixture was stirred at -78 °C for 1 h and then quenched with MeOH (2 mL), Et_3N (2 mL). The resulting mixture was washed with saturated aqueous $NaHCO_3$, water, (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 3:1:1, v:v:v) to afford compound **S7** (1.84 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.88 (d, J = 3.3 Hz, 1H, OH), 3.48 (dd, J = 10.2, 3.4 Hz, 1H, H-2), 3.73-3.82 (m, 5H, H-6a, H-6b, OCH_3), 3.88 (td, J = 9.2, 3.1 Hz, 1H, H-4), 4.05 (dt, J = 9.4, 4.5 Hz, 1H, H-5), 4.12 (t, J = 9.4 Hz, 1H, H-3), 4.58 (d, J = 11.9 Hz, 1H, C*H*HPh), 4.64 (d, J = 12.0 Hz, 1H, CH*H*Ph), 4.97 (d, J = 11.1 Hz, 1H, C*H*HPh), 5.05 (d, J = 11.1 Hz, 1H, CH*H*Ph), 5.49 (d, J = 3.4 Hz, 1H, H-1), 6.90 (d, J = 9.1 Hz, 2H, 2x aromatic CH), 7.15 (d, J = 6.4 Hz, 2H, 2x aromatic CH), 7.34-7.42 (m, 5H, 5x aromatic CH), 7.46 (t, J = 7.5 Hz, 2H, 2x aromatic CH), 7.52 (d, J = 7.3 Hz, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 62.5, 63.3, 69.4, 70.6, 71.8, 73.5, 75.0, 79.5, 97.8, 114.5, 118.2, 127.5, 127.7, 127.9, 128.0, 128.3, 128.5, 137.6, 138.0, 150.4, 155.3; MALDI-MS: $[M+Na]^+$ $C_{27}H_{29}N_3NaO_6$, calcd 514.1954, obsd 514.1327.

***p*-Methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-α-D-glucopyranoside (S8).** PMe_3 (6.6 mL, 6.6 mmol, 1 M in THF) and NaOH (3.4 mL, 3.4 mmol, 1

M) were added to a solution of compound **S7** (0.65 g, 1.32 mmol) in THF (40 mL) and H_2O (10 mL) and stirred overnight at room temperature. The reaction mixture was concentrated *in vacuo* and the resulting residue was diluted with DCM (100 mL), neutralized with conc. HCl and concentrated *in vacuo*. The resulting residue was passed through a short silica gel column (DCM:MeOH, 10:1, v:v) and fractions containing product were combined and concentrated under reduced pressure. The resulting residue was dissolved in THF (16 mL), to which, solid $NaHCO_3$ (0.22 g, 2.64 mmol) and 2,2,2-trichloroethyl chloroformate (0.21 mL, 1.58 mmol) were added. The reaction mixture was stirred at room temperature under an atmosphere of N_2 for 4 h and then filtered. The filtrate was concentrated, diluted with DCM (50 mL), and washed with water and brine. The organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 7:1, v:v) to afford compound **S8** (0.75 g, 89% for two steps) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.00 (d, *J* = 2.5 Hz, 1H, OH), 3.73-3.81 (m, 5H, H-6a, H-6b, OCH_3), 3.85 (t, *J* = 9.5 Hz, 1H H-3), 3.91 (td, *J* = 9.2, 3.1 Hz, 1H, H-4), 4.01 (dt, *J* = 9.3, 4.5 Hz, 1H, H-5), 4. 16-4.21 (m, 1H, H-2), 4.56 (d, *J* = 11.9 Hz, 1H, CH*H*Ph), 4.62 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.70 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.89 (m, 3H, troc CH_2, CH*H*Ph), 5.35 (d, *J* = 9.6 Hz, 1H, NH), 5.48 (d, *J* = 3.5 Hz, 1H, H-1), 6.86 (d, *J* = 9.1 Hz, 2H, 2x aromatic CH), 7.05-7.07 (m, 2H, 2x aromatic CH), 7.32-7.42 (m, 10H, 10x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 54.4, 55.5, 69.7, 70.7, 71.9, 73.5, 74.4, 74.6, 79.7, 95.3, 97.5, 114.6, 118.2, 127.5, 127.7 (×2), 127.8 (×2), 128.3, 128.5, 137.7, 138.1, 150.1, 154.2, 155.3; MALDI-MS: $[M+Na]^+$ $C_{30}H_{32}Cl_3NNaO_8$, calcd 662.1091, obsd 622.0419.

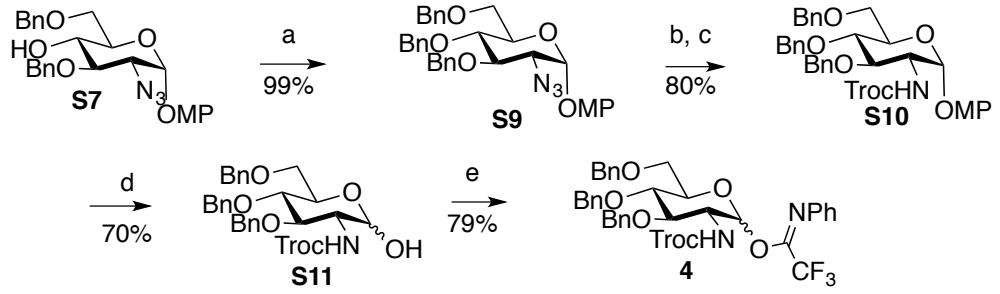


Fig. S5. Synthesis of glucosamine donor **4.**
a) BnBr, NaH, DMF, rt, 2 h; b) PMe_3(1 M), NaOH, THF, H_2O, rt, overnight; c) TrocCl, solid $NaHCO_3$, THF, 4 h; d) CAN, CH_3CN, H_2O, rt, 2 h; e) $CF_3C(NPh)Cl$, DBU, DCM, rt, 1 h.

***p*-Methoxyphenyl 3,4,6-*O*-benzyl-2-azido-2-deoxy-α-D-glucopyranoside (S9).**

Benzyl bromide (0.15 mL, 1.2 mmol) and NaH (49 mg, 60% NaH in mineral oil, 13.8 mmol) were added to a solution of *p*-Methoxyphenyl 3,6-di-*O*-benzyl-2-deoxy-2-azido-α-D-glucopyranoside **S7** (400 mg, 0.81 mmol) in DMF (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 2 h, after which it was diluted with EtOAc (100 mL) and washed with saturated $NaHCO_3$ and water. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane:EtOAc, 7:1, v:v) to afford compound **S9** (470 mg, 99%) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.64 (dd, *J* = 10.2, 2.7 Hz, 1H, H-2), 3.79 (d, *J* = 10.8 Hz, 1H, H-6b), 3.86 (s, 3H, OCH_3), 3.92 (dd, *J* = 10.7, 2.7 Hz, 1H, H-6a), 3.98 (t, *J* = 9.4 Hz, 1H, H-4), 4.17 (d, *J* = 9.7 Hz, 1H, H-5), 4.37 (t, *J* = 9.5 Hz, 1H, H-3), 4.59 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.72 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.99 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 5.09 (q, *J* = 8.4 Hz, 2H, CH_2Ph), 5.61 (d, *J* = 2.8 Hz, 1H, H-1), 6.96 (d, *J* = 8.4 Hz, 2H, 2x aromatic CH), 7.22 (d, *J* = 8.4 Hz, 2H, 2x aromatic CH), 7.33 (d, *J* = 7.0 Hz, 2H, 2x aromatic CH), 7.40-7.50 (m, 11H, 11x aromatic CH), 7.55 (d, *J* = 7.4 Hz, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 55.4, 63.1, 68.1, 71.1, 73.3, 74.9, 75.3, 78.0, 80.0, 97.6, 114.5, 118.0, 127.6 (×2), 127.7 (×3), 127.9, 128.0, 128.2, 128.3 (×2), 137.6, 137.8 (×2), 150.3, 155.2; MALDI-MS: $[M+Na]^+$ $C_{34}H_{35}N_3NaO_6$, calcd 604.2424, obsd 604.1910.

***p*-Methoxyphenyl 3,4,6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-D-α−glucopyranoside (S10).** PMe_3 in THF (5.2 mL, 5.2 mmol, 1 M) and NaOH (2.68 mL, 2.7 mmol, 1 M) were added to a solution of compound **S9** (600 mg, 1.03 mmol) in THF (40 mL) and H_2O (10 mL). The reaction mixture was stirred at room temperature overnight, after which it was concentrated under reduced pressure, diluted with DCM (100 mL), neutralized by conc. HCl and

was concentrated *in vacuo.* 2,2,2-Trichloroethyl chloroformate (0.167 mL, 1.24 mmol) was added to a solution of the resulting residue and solid $NaHCO_3$ (170 mg, 2.06 mmol) in THF (15 mL). The reaction mixture was stirred at room temperature under an atmosphere of N_2 for 4 h and filtered. The filtrate was concentrated under reduced pressure, diluted with DCM (50 mL) and washed with water and brine. The organic layers were combined, dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (5:1:1 hexanes:EtOAc –DCM) to afford compound **S10** (610 mg, 80% for two steps) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.74 (d, *J* = 10.2 Hz, 1H, H-6b), 3.82 (s, 3H, OCH_3), 3.86 (dd, *J* = 10.9, 3.7 Hz, 1H, H-6a), 3.94 (t, *J* = 9.3 Hz, 1H, H-5), 4.01 (t, *J* = 9.6 Hz, 1H, H-4), 4.06 (d, *J* = 8.9 Hz, 1H, H-3), 4.26 (td, *J* = 10.0, 3.3 Hz, 1H, H-2), 4.55 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.64 (d, *J* = 10.8 Hz, 1H, CH*H*Ph), 4.71 (dd, *J* = 11.7, 9.9 Hz, 2H, 2xC*H*HPh), 4.87-4.92 (m, 3H, C*H*HPh, troc CH_2), 4.99 (d, *J* = 11.3 Hz, 1H, CH*H*Ph), 5.28 (d, *J* = 9.6 Hz, 1H, NH), 5.54 (d, *J* = 3.4 Hz, 1H, H-1), 6.88 (d, *J* = 8.9 Hz, 2H, 2x aromatic CH), 7.08 (d, *J* = 8.9 Hz, 2H, 2x aromatic CH), 7.27 (d, *J* = 6.7 Hz, 2H, 2x aromatic CH), 7.33-7.43 (m, 13H, 13x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 55.0, 55.5, 68.2, 71.4, 73.3, 74.6, 75.0, 75.2, 78.1, 80.1, 95.3, 97.4, 114.6, 118.0, 127.7, 127.8 (×3), 128.0, 128.3 (×2), 128.4, 137.8 (×2), 138.0, 150.0, 154.2, 155.3; MALDI-MS: $[M+Na]^+$ $C_{37}H_{38}Cl_3NNaO_8$, calcd 752.1561, obsd 752.1502.

(*N*-Phenyl)-2,2,2-trifluoroacetimidate 3,4,6-tri-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy) carbonylamino-D-glucopyranoside (4). Ceric ammonium nitrate (225 mg, 0.408 mmol) was added to a solution of compound **S10** (100 mg, 0.136 mmol) in a mixture of CH_3CN:H_2O (4 mL:1 mL) at 0 °C. The reaction mixture was stirred at room temperature under an atmosphere of N_2 for 2 h, after which it was concentrated under reduced pressure. The resulting residue was diluted with DCM (50 mL) washed with H_2O, dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:1, v:v) to afford the corresponding hemiacetal **S11** (60.2 mg, 70%). DBU (9.6 µL, 64 µmol) was added to a solution of hemiacetal **S11** (40 mg, 64 µmol) and *N*-phenyltrifluoroacetimidoyl chloride (52 µL, 0.32 mmol) in DCM (5 mL) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:1, v:v) to afford

the corresponding imidate donor **4** (40.3 mg, 79%) as an amorphous white solid. The glycosyl donor was used for the preparation of compound **14**.

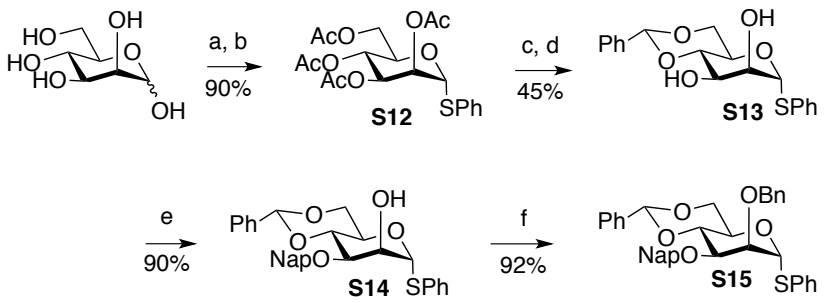


Fig. S6. Synthesis of compound **S15.**
a) Ac_2O, pyridine, rt, overnight; b) PhSH, BF_3 etherate, DCM, rt, 20 h; c) NaOMe, MeOH, rt, 4 h; d) $PhCH(OMe)_2$, CSA, DMF, 70 °C, overnight; e) Bu_2SnO, Toluene, reflux, 3 h, then NapBr, CsF, DMF, rt, overnight; f) NaH, BnBr, DMF, rt, 2 h

Phenyl 4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-thio-α-D-mannopyranoside (S14). A solution of D-mannose (20 g, 0.11 mol) in pyridine (250 mL) was cooled down to 0 °C, followed by slow addition of acetic anhydride (105 mL, 1.1 mol). The reaction mixture was stirred at room temperature overnight and quenched with ethanol (100 mL) at 0 °C, followed by concentration under reduced pressure. The resulting residue was diluted with DCM (500 mL), washed with a saturated solution of $NaHCO_3$, 10% aq. HCl and water, dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* Boron trifluoride diethyl etherate (42 ml, 0.33 mol) was added to a solution of the resulting residue and thiophenol (13.9 ml, 0.13 mol) in DCM (250 mL) at 0 °C. The reaction mixture was stirred at room temperature for 20 h and diluted with DCM (200 mL). The resulting solution was washed with a saturated solution of $NaHCO_3$ and water, dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:2, v:v) to afford compound **S12** (44 g, 90% for 2 steps) as white amorphous solid. Compound **S12** (36 g, 81.7 mmol) was dissolved in MeOH (500 mL) and to this, sodium (0.94 g, 41 mmol) was added in portions and the mixture was stirred for 4 h at room temperature after which it was neutralized with Amberlite IR-120, filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was dissolved in anhydrous DMF (100 mL), to which benzaldehyde dimethylacetal (8.1 mL, 0.13 mol) and camphorsulfonic acid (2.3 g, 9.8 mmol) were added and the reaction mixture was stirred at 70 °C overnight, after which the reaction was quenched with Et_3N, diluted with DCM (500 mL) and washed with a saturated solution of $NaHCO_3$, water and then dried (Na_2SO_4),

filtered, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 4:1, v:v) to afford **S13** (10.6 g, 45%) as white amorphous solid. Compound **S13** (5.85g, 16.2 mmol), dibutyltin oxide (4.24 g, 17 mmol) and toluene (110 mL) were refluxed for 3 h, followed by concentration under reduced pressure. The resulting solid, cesium fluoride (2.59 g, 16.2 mmol), 2-(bromomethyl)naphthalene (3.77 g, 16.2 mmol), and DMF (50 mL) were stirred at room temperature overnight. DMF was removed by concentration under reduced pressure and the residue was diluted with DCM (200 mL). The resulting solution was washed with a saturated solution of $NaHCO_3$ and water, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:1, v:v) to afford compound **S14** (7.3 g, 90%) as white amorphous solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.10 (d, *J* = 8.8 Hz, 1H, OH), 3.91 (t, *J* = 10.3 Hz, 1H, H-6b), 4.06 (dd, *J* = 9.5, 3.3 Hz, 1H, H-3), 4.27 (dq, *J* = 10.1, 5.1 Hz, 2H, H-6a, H-4), 4.35 (d, *J* = 1.6 Hz, 1H, H-2), 4.39 (td, *J* = 9.8, 4.9 Hz, 1H, H-5), 4.95 (d, *J* = 12.1 Hz, 1H, C*H*Hnap), 5.06 (d, *J* = 12.1 Hz, 1H, CH*H*nap), 5.64 (s, 1H, H-1), 5.68 (s, 1H, benzylidene CHPh), 7.28-7.36 (m, 3H, 3x aromatic CH), 7.42-7.50 (m, 5H, 5xCH, Aromatic), 7.50-7.56 (m, 3H, 3x aromatic CH), 7.58 (dd, *J* = 6.9, 2.4 Hz, 2H, 2x aromatic CH), 7.80 (t, *J* = 4.6 Hz, 1H, aromatic CH), 7.88 (d, *J* = 4.4 Hz, 3H, 3x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 64.6, 68.5, 71.3, 73.1, 75.7, 78.9, 87.8, 101.7, 125.6, 126.1 (×2), 126.2, 126.7, 127.6, 127.7, 127.9, 128.2, 128.3, 129.0, 129.1, 131.7, 133.1, 133.2 (×2), 135.1, 137.4. $^1J_{C1,H1}$ = 170.0 Hz. MALDI-MS: $[M+Na]^+$ $C_{30}H_{28}NaO_5S$ calcd 523.1555, obsd 523.0720.

Phenyl 4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-2-*O*-benzyl-thio-α-D-mannopyranoside (S15). Benzyl bromide (1.99 mL, 16.8 mmol) and NaH (60% NaH in mineral oil, 0.67 g, 16.8 mmol) were added to a cooled (0 °C) solution of compound **S14** (7.0 g, 14 mmol) in DMF (100 mL). The mixture was stirred at room temperature under an atmosphere of N_2 for 2 h, followed by quenching with MeOH, after which it was concentrated under reduced pressure. The resulting residue was diluted with EtOAc (200 mL) and washed with saturated $NaHCO_3$ and water, and the organic layer was dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 8:1, v:v) to afford compound **S15** (7.6 g, 92%) as an amorphous white solid. ^{1}H NMR (600 MHz; $CDCl_3$): δ 4.02 (t, *J* = 10.2 Hz, 1H, H-6b), 4.18 (dd, *J* = 9.7, 3.2 Hz, 1H, H-3), 4.21-4.22 (m, 1H, H-2), 4.36 (dd, *J* = 10.2, 4.7 Hz, 1H, H-6a), 4.45 (tt, *J* = 9.4, 4.6 Hz, 1H, H-5), 4.51 (t, *J* = 9.6 Hz, 1H, H-4), 4.87-

4.83 (m, 2H, Nap CH_2), 4.93 (d, *J* = 12.5 Hz, 1H, C*H*HPh), 5.07 (d, *J* = 12.5 Hz, 1H, CH*H*Ph), 5.66-5.67 (s, 1H, H-1), 5.79 (s, 1H, benzylidene CHPh), 7.33-7.45 (m, 6H, 6x aromatic CH), 7.46 -7.52 (m, 7H, 7x aromatic CH), 7.55-7.59 (m, 3H, 3x aromatic CH), 7.67-7.70 (m, 2H, 2x aromatic CH), 7.84 (dq, *J* = 6.2, 3.2 Hz, 1H, aromatic CH), 7.90-7.94 (m, 3H, 3x aromatic CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 65.4, 68.4, 72.8, 72.9, 76.1, 77.9, 78.9, 86.9, 101.5, 125.5, 125.7, 125.9, 126.1 (×2), 127.5 (×2), 127.7, 127.8, 128.0, 128.1, 128.3, 128.8, 129.0, 131.5, 132.8, 133.2, 133.6, 135.7, 137.5, 137.6. MALDI-MS: $[M+Na]^+$ $C_{37}H_{34}NaO_5S$ calcd 613.2025, obsd 613.1689.

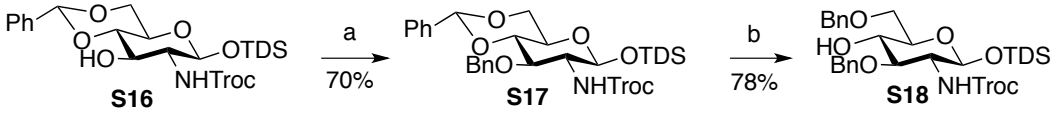


Fig. S7. Synthesis of Glucoamine acceptor **S18**.
a) BnBr, Ag_2O, MS4Å, rt, 30 h; b) Et_3SiH, TfOH, DCM, -78 °C, 1 h

Dimethylthexylsilyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S17). Benzyl bromide (13.2 mL, 0.11 mol) and freshly prepared silver(II) oxide (20.6 g, 2 eq, 89 mmol) were added to a solution of dimethylthexylsilyl 4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside **S16** (*43*) (26 g, 44.5 mmol) and acid washed 4Å molecular sieves in DCM (200 mL) and stirred in dark at room temperature for 30 h. The mixture was filtered through Celite to remove the silver(II) oxide and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (Hexanes:EtOAc, 4:1,v:v) to afford compound **S17** (21 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.05 (s, 3H, TDS Si-CH_3), 0.08 (s, 3H, TDS Si-CH_3), 0.77 (s, 6H, 2x TDS C-CH_3), 0.79 (d, *J* = 2.9 Hz, 3H, TDS CH-C*H*$_3$), 0.80 (d, *J* = 3 Hz, 3H, TDS CH-C*H*$_3$), 1.54 (dd, *J* = 13.6, 6.7 Hz, 1H, TDS C*H*-CH_3), 3.25 (m, 1H, H-2), 3.39 (m, 1H, H-5), 3.67 (t, *J* = 9.2 Hz, 1H, H-4), 3.73 (t, *J* = 10.3 Hz, 1H, H-6b), 3.92 (m, 1H, H-3), 4.23 (dd, *J* = 10.5 Hz, 5.0 Hz, 1H, H-6a), 4.61 (t, *J* = 15 Hz, 3H, C*H*HPh, troc CH_2), 4.83 (d, *J* = 11.8 Hz, 1H, CH*H*Ph), 4.86 (d, *J* = 7.5 Hz, 1H, H-1), 4.97 (d, *J* = 6.2 Hz, 1H, NH), 5.5 (s, 1H, benzylidene CHPh), 7.18-7.25 (m, 5H, 5x aromatic CH), 7.30-7.35 (m, 3H, 3x aromatic CH), 7.43 (dd, *J* = 7.6, 1.7 Hz, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ -3.4, -1.8, 18.5 (×2), 20.0 (×2), 24.8, 34.0, 60.1, 66.0, 68.8, 74.3, 74.6, 76.4, 82.7, 95.4, 95.9, 101.2, 126.1, 127.8, 128.2, 128.3, 128.4,

129.0, 137.4, 138.2, 153.8. MALDI-MS: $[M+Na]^+$ $C_{31}H_{42}Cl_3NNaO_7Si$, calcd 696.1694, obsd 696.1413.

Dimethylthexylsilyl *O*-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S18). Triethylsilane (4.54 mL, 28.5 mmol) and TfOH (2.3 mL, 25.8 mmol) were sequentially added to a cooled (-78 °C) solution of compound **S17** (6.0 g, 8.9 mmol) in DCM (200 mL). The reaction mixture was stirred at -78 °C for 1 h and then quenched by addition of MeOH (5 mL) and Et_3N (5 mL). The resulting mixture was washed with saturated aqueous $NaHCO_3$ and water, dried (MgSO4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (Hexanes:EtOAc, 4:1,v:v) to afford dimethylthexylsilyl 3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside **S18** (4.7 g, 78%). ^{1}H NMR (500 MHz; $CDCl_3$): δ 0.00 (s, 3H, TDS Si-CH_3), 0.04 (s, 3H, TDS Si-CH_3), 0.71 (s, 3H, TDS C-CH_3), 0.71 (s, 3H, TDS C-CH_3), 0.73 (d, J = 2.7 Hz, 3H, TDS CH-CH_3), 0.75 (d, J = 2.7 Hz, 3H, TDS CH-CH_3), 1.49 (dt, J = 13.7, 6.9 Hz, 1H, TDS CH-CH_3), 3.00 (s, 1H, OH), 3.23 (d, J = 7.2 Hz, 1H, H-2), 3.31 (s, 1H, H-5), 3.54 (m, 2H, H-4, H-3), 3.57 (d, J = 4.7 Hz, 2H, H-6a, H-6b), 4.43 (q, J = 9.4 Hz, 2H, troc CH_2), 4.51 -4.66 (m, 5H, H-1, 2x CH_2Ph), 5.02 (d, J = 8.0 Hz, 1H, NH), 7.13-7.22 (m, 10H, 10x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ -3.5, -1.9, 18.4, 18.5, 19.9, 20.0, 24.7, 33.9, 59.0, 70.3, 72.3, 73.5, 74.0, 74.4, 80.4, 95.3, 95.5, 127.5, 127.6, 127.7, 127.9, 128.3, 128.4, 137.8, 138.3, 153.9. MALDI-MS: $[M+Na]^+$ $C_{31}H_{44}Cl_3NNaO_7Si$, calcd 698.1850, obsd 698.1365.

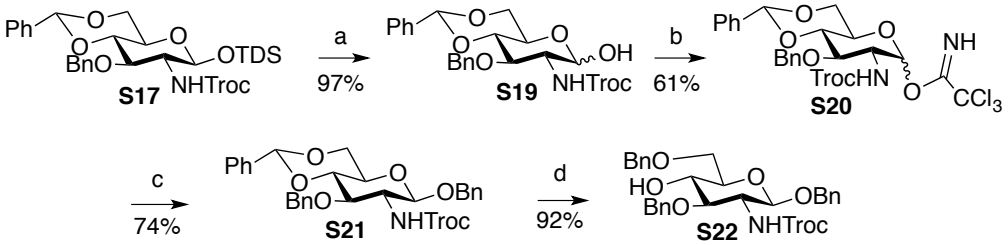


Fig. S8. Synthesis of Glucoamine acceptor **S22**.
a) HF/pyridine, pyridine, rt, overnight; b) Cl_3CCN, DBU, DCM, rt, 1 h;
c) BnOH, TfOH, DCM, MS4Å, -70 ºC to -20 ºC, 1 h; d) Et_3SiH, TfOH, DCM, -78 ºC, 1 h

Benzyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S21). HF (35 mL, 65-70% in pyridine) was added to a cooled (0 °C) solution of compound **S17** (5 g, 7.4 mmol) in pyridine (70 mL). The reaction mixture was stirred at room

temperature, overnight, after which it was diluted with EtOAc (200 mL), washed with 10% aq. $CuSO_4$, saturated aq. $NaHCO_3$ and H_2O. The organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (Hexanes:EtOAc, 6:1,v:v) to afford compound **S19** (3.84 g, 97%) as an amorphous white solid. Trichloroacetonitrile (7.15 mL, 71.4 mmol) and DBU (0.11 mL, 0.71 mmol) were added to a solution of compound **S19** (1.9 g, 3.57 mmol) in DCM (100 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and was then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexanes:EtOAc, 6:1,v:v) to afford the corresponding imidate **S20** (1.47 g, 61%) as an amorphous white solid. The trichloroacetimidate **S20** (1.47 g, 2.17 mmol), benzyl alcohol (0.45 mL, 4.34 mmol), molecular sieve MS-4Å, and DCM (100 mL) were stirred at room temperature for 30 min. The reaction mixture was cooled to −70 °C, followed by addition of TfOH (38 µL, 0.43 mmol) and was stirred for 1 h allowing the temperature to rise from −70 °C to −20 °C and was then quenched with Et_3N (0.2 mL). The resulting mixture was diluted with DCM (300 mL), washed with a saturated solution of $NaHCO_3$ and H_2O, dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (Hexanes:EtOAc:DCM, 5:1:1, v:v:v) to give compound **S21** (1 g, 74%) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.46 (m, 2H, H-2, H-5), 3.76 (t, J = 9.2 Hz, 1H, H-4), 3.85 (t, J = 10.3 Hz, 1H, H-6b), 4.00 (t, J = 8.5 Hz, 1H, H-3), 4.40 (dd, J = 10.5, 5.0 Hz, 1H, H-6a), 4.60 (d, J = 12.0 Hz, 1H, C*H*HPh), 4.69 (m, 3H, CH*H*Ph, troc CH_2), 4.79 (d, J = 8.2 Hz, 1H, H-1), 4.90 (dd, J = 11.8, 2.3 Hz, 2H, 2x(C*H*HPh)), 5.04 (s, 1H, NH), 5.60 (s, 1H, benzylidene CHPh), 7.27-7.37 (m, 10H, 10x aromatic CH), 7.41 (m, 3H, 3x aromatic CH), 7.51 (d, J = 6.2 Hz, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 58.1, 66.1, 68.8, 71.2, 74.5, 76.5, 82.6, 85.1, 99.8, 101.3, 126.0, 127.9, 128.0, 128.3 (×2), 128.4, 128.5, 129.1, 136.9, 137.3, 138.0, 153.9. MALDI-MS: $[M+Na]^+$ $C_{30}H_{30}Cl_3NNaO_7$, calcd 644.0986, obsd 644.0748.

Benzyl 3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S22). Triethylsilane (0.82 mL, 5.1 mmol) and TfOH (0.41 mL, 4.7 mmol) were sequentially added to a cooled (-78 °C) solution of compound **S21** (1 g, 1.6 mmol) in DCM (100 mL). The reaction mixture was stirred under an atmosphere of N_2 at -78 °C for 1 h and quenched upon addition of MeOH (1 mL) and Et_3N (1 mL). The resulting mixture was washed with saturated aq. $NaHCO_3$ and H_2O, dried (Na_2SO_4), filtered, and the filtrate was concentrated

in vacuo. The resulting residue was purified by silica gel column chromatography (Hexanes:EtOAc:DCM, 4:1:1, v:v:v) to give benzyl 3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside **S22** (0.92 g, 92%). ^{1}H NMR (300 MHz; $CDCl_3$): δ 2.78 (s, 1H, OH), 3.39-3.49 (m, 2H, H-5, H-2), 3.75 (m, 4H, H-4, H-3, H-6a, H-6b), 4.59 (m, 3H, 3x C*H*HPh), 4.65-4.73 (m, 3H, H-1, troc CH_2), 4.76 (d, *J* = 12.0 Hz, 2H, CH_2Ph), 4.88 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 5.06 (d, *J* = 7.2 Hz, 1H, NH), 7.26-7.39 (m, 15H, 15x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 57.4, 70.5, 70.7, 73.1, 73.7, 73.8, 74.3, 74.5, 80.5, 99.2, 127.8, 127.9 (×2), 128.1, 128.4, 128.5, 128.6, 137.2, 137.7, 138.2, 154.0. MALDI-MS: $[M+Na]^+$ $C_{30}H_{32}Cl_3NNaO_7$, calcd 646.1142, obsd 646.0339.

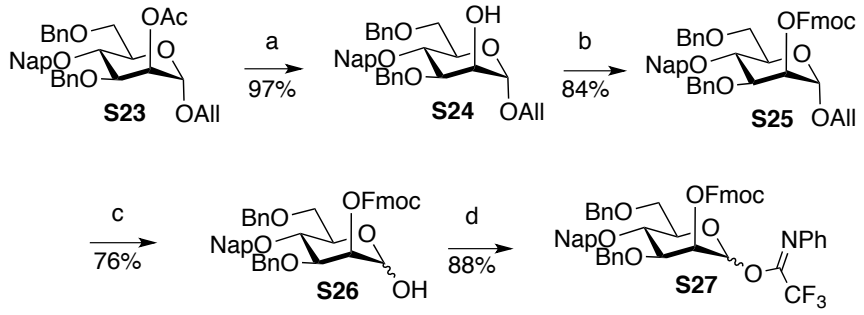


Fig. S9. Synthesis of compound **S27.**
a) NaOMe, MeOH, DCM, rt, 2 h; b) FmocCl, pyridine, DCM, rt, 4 h; c) $PdCl_2$, NaOAc, DCM, AcOH, H_2O, rt, overnight; d) $CF_3C(NPh)Cl$, 60% NaH, DCM, rt, 1 h.

Allyl 3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-α-D-mannopyranoside (S24). NaOMe (30%, 0.32 mL, 5.66 mmol) was added to a solution of compound **S23** (*44*) (1.65 g, 2.83 mmol) in a mixture of DCM (20 mL) and MeOH (20 mL). The reaction mixture was stirred for 2 h under an atmosphere of N_2 and was neutralized with conc. HCl and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:1, v:v) to afford compound **S24** (1.49 g, 97%) as white amorphous solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 2.45 (s, 1H, OH), 3.63-3.75 (m, 3H, H-6b, H-5, H-6a), 3.83-3.88 (m, 2H, H-3, H-4), 3.92 (dd, *J* = 12.9, 6.1 Hz, 1H, allyl C*H*H), 4.00 (s, 1H, H-2), 4.11 (dd, *J* = 12.9, 5.1 Hz, 1H, allyl C*H*H), 4.43 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.57-4.66 (m, 4H, 3x C*H*HPh, nap C*H*H), 4.89 (d, *J* = 10.5 Hz, 2H, nap C*H*H, H-1), 5.10 (d, *J* = 10.4 Hz, 1H, allyl CH=C*H*H), 5.19 (dd, *J* = 17.2, 1.4 Hz, 1H, allyl CH=C*H*H), 5.81 (ddt, *J* = 16.8, 11.0, 5.6 Hz, 1H, allyl C*H*=CHH), 7.15-7.29 (m, 11H, 11x aromatic CH), 7.36-7.40 (m, 2H, 2x aromatic CH), 7.53 (s, 1H, aromatic CH), 7.67 (d, *J* = 8.6 Hz, 2H, 2x aromatic CH), 7.73 (t, *J* = 4.6 Hz, 1H, aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 68.0, 68.4, 68.9, 71.1, 72.0, 73.4, 74.3, 75.2, 80.3, 98.4, 117.5, 119.2, 125.8,

126.0 (×2), 126.5, 127.6 (×2), 127.8, 127.9 (×2), 128.0 128.3, 128.5, 132.9, 133.3, 133.7, 135.8, 137.9, 138.2. MALDI-MS: $[M+Na]^+$ $C_{34}H_{36}NaO_6$, calcd 563.2410, obsd 563.2203.

Allyl 3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranoside (S25) Fluorenylmethoxycarbonyl chloride (0.78g, 3.04 mmol) and pyridine (1.22 mL, 15.2 mmol) were sequentially added to a solution of compound **S24** (0.82 g, 1.52 mmol) in DCM (30 mL) and the reaction mixture was stirred for 4 h at room temperature under an atmosphere of N_2, after which it was diluted with DCM (100 mL) and the organic phase was washed with saturated $NaHCO_3$ and then dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 7:1, v:v) to afford compound **S25** (0.98 g, 84%) as white amorphous solid. . ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.88 (d, *J* = 10.4 Hz, 1H, H-6b), 3.97 (dd, *J* = 10.7, 4.6 Hz, 1H, H-6a), 4.01 (dd, *J* = 9.3, 3.8 Hz, 1H, H-5), 4.14 (m, 2H, H-4, allyl C*H*H), 4.21 (dd, *J* = 9.3, 2.9 Hz, 1H, H-3), 4.32 (dd, *J* = 12.9, 5.2 Hz, 1H, allyl C*H*H), 4.37 (t, *J* = 7.6 Hz, 1H, fmoc CH), 4.43 (dd, *J* = 10.1, 8.1 Hz, 1H, fmoc C*H*H), 4.55 (dd, *J* = 10.2, 7.3 Hz, 1H, fmoc C*H*H), 4.64 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.73 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.81 (dd, *J* = 11.5, 6.8 Hz, 2H, C*H*HPh, nap C*H*H), 4.90 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 5.16 (m, 2H, H-1, nap C*H*H), 5.30 (d, *J* = 10.4 Hz, 1H, allyl CH=C*H*H), 5.37-5.41 (m, 2H, H-2, allyl CH=C*H*H), 6.00 (ddt, *J* = 16.8, 11.0, 5.6 Hz, 1H, allyl C*H*=CHH), 7.27-7.49 (m, 15H, 15x aromatic CH), 7.53-7.57 (m, 2H, 2x aromatic CH), 7.72 (d, *J* = 3.8 Hz, 2H, 2x aromatic CH), 7.76 (d, *J* = 7.5 Hz, 1H, aromatic CH), 7.85 (d, *J* = 8.3 Hz, 4H, 4x aromatic CH), 7.90 (t, *J* = 4.6 Hz, 1H, aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 46.6, 68.1, 68.9, 70.2, 71.6, 71.8, 72.7, 73.4, 74.4, 75.3, 78.3, 96.6, 117.8, 119.9, 120.0, 125.2, 125.4, 125.8, 125.9, 126.5, 127.1, 127.5, 127.6 (×2), 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 132.9, 133.2, 133.3, 135.8, 137.9, 138.2, 141.1, 141.2, 143.2, 143.5, 154.8. MALDI-MS: $[M+Na]^+$ $C_{49}H_{46}NaO_8$, calcd 785.3090, obsd 785.1928.

(*N*-Phenyl)-2,2,2-trifluoroacetimidate 3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2-*O*-(9-fluorenylmethyloxycarbonyl)-D-mannopyranoside (S27). NaOAc (1.07 g, 13.1 mmol) and $PdCl_2$ (0.77 g, 4.36 mmol) were added to s solution of compound **S25** (1.66 g, 2.18 mmol) in a mixture of DCM (20 mL), MeOH (20 mL) and H_2O (1 mL). The reaction mixture was stirred overnight under an atmosphere of N_2 and then was concentrated under reduced pressure. The residue was diluted with DCM (200 mL) and the organic phase was washed with H_2O and then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting residue was purified by silica

gel column chromatography (hexanes:EtOAc, 3:1, v:v) to afford the corresponding hemiacetal **S26** (1.2 g, 76%) as a colorless gel. NaH (60%, 66 mg, 1.66 mmol) was added to a cooled (0 °C) solution of the hemiacetal **S26** (1.2 g, 1.66 mmol) and *N*-phenyltrifluoroacetimidoyl chloride (1.35 mL, 8.3 mmol) in DCM (80 mL) and stirred at room temperature for 1 h, followed by concentration *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 8:1, v:v) to afford the corresponding *N*-phenyl-trifluoroacetimidate **S27** (1.3 g, 88%) as an amorphous white solid. The mannosyl donor was used for the preparation of compound **S47**.

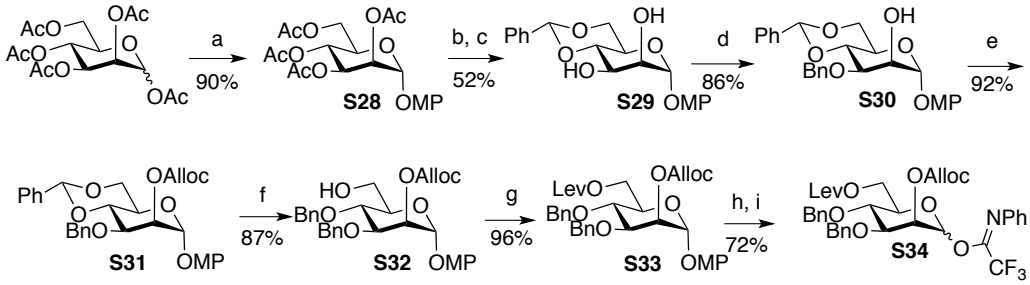


Fig. S10. Synthesis of mannose donor **S34.**
a) p-methoxyphenol, BF_3 etherate, DCM, rt, overnight; b) NaOMe, MeOH, DCM, rt, 2 h;
c) $PhCH(OMe)_2$, CSA, DMF, 70 °C, overnight; d) Bu_2SnO, Toluene, reflux, 3 h, then BnBr, CsF, DMF, rt, overnight;
e) AllocCl, TMEDA, rt, 4 h; f) Et_3SiH, $PhBCl_2$, DCM, -78 °C, 1 h; g) LevOH, EDC.HCl, DMAP, DCM, rt, overnight;
h) CAN, CH_3CN, H_2O, rt, 2 h; i) $CF_3C(NPh)Cl$, 60% NaH, DCM, rt, 1 h;

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (S28).** Boron trifluoride diethyl etherate (19.3 ml, 153.7 mmol) was added to a cooled (0 °C) solution of D-Mannose pentaacetate (20 g, 51.2 mmol) and *p*-methoxylphenol (7.3 g, 58.9 mmol) in DCM (200 mL). The reaction mixture was stirred overnight, after which, it was diluted with DCM (300 mL) and washed with a saturated solution of $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:2, v:v) to afford compound **S28** (21.1 g, 90%) as white amorphous solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 1.96 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 3.69 (s, 3H, OCH_3), 4.02 (dd, J = 12.1, 2.3 Hz, 1H, H-5), 4.08 (ddd, J = 10.1, 5.4, 2.2 Hz, 1H, H-6b), 4.21 (dd, J = 12.2, 5.4 Hz, 1H, H-6a), 5.29 (t, J = 10.1 Hz, 1H, H-4), 5.35 (d, J = 1.6 Hz, 1H, H-1), 5.37 (dd, J = 3.4, 1.8 Hz, 1H, H-2), 5.48 (dd, J = 10.0, 3.5 Hz, 1H, H-3), 6.74-6.78 (m, 2H, 2x aromatic CH), 6.94-6.97 (m, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.4 (×2), 20.6, 55.3, 62.0, 65.8, 68.7, 68.8, 69.2,

96.4, 114.4, 117.6, 149.4, 155.2, 169.5, 169.6, 169.7, 170.2. $^{1}J_{C1,H1}$ = 179.1 Hz. MALDI-MS: $[M+Na]^+$ $C_{21}H_{26}NaO_{11}$, calcd 477.1373, obsd 477.1067.

***p*-Methoxyphenyl 4,6-*O*-benzylidene-3-*O*-benzyl-α-D-mannopyranoside (S30).** NaOMe (30%, 5.4 mL, 96.8 mmol) was added to a solution of compound **S28** (11 g, 24.2 mmol) in a mixture of DCM (100 mL) and MeOH (100 mL). The reaction mixture was stirred for 2 h under an atmosphere of N_2 and then neutralized with conc. HCl, after which it was concentrated under reduced pressure. The resulting residue (6.7 g, 23.4 mmol), camphorsulfonic acid (1.09 g, 4.68 mmol), and benzaldehyde dimethylacetal (3.86 mL, 25.7 mmol) were dissolved in DMF (80 mL) and stirred at 70 °C overnight, followed by quenching with Et_3N (5 mL) and concentration under reduced pressure. The residue was diluted with DCM (500 mL) and washed with a saturated solution of $NaHCO_3$ and water, and the organic layer was dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford compound **S29** (4.68 g, 52% for 2 steps) as an amorphous white solid. Compound **S29** (3.6 g, 9.62 mmol) and di-butyltin oxide (2.5 g, 10.1 mmol) were dissolved in toluene (100 mL) and refluxed for 3 h, followed by concentration under reduced pressure. The resulting solid was dissolved in DMF (50 mL), cesium fluoride (1.53 g, 10.1 mmol), and benzyl bromide (1.2 mL, 10.1 mmol) were added to the solution and stirred at room temperature overnight. DMF was removed by concentration under reduced pressure. The residue was diluted with DCM (200 mL) and washed with a saturated solution of $NaHCO_3$ and water, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:1, v:v) to afford compound **S30** (3.8 g, 86%) as white amorphous solid. . ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.26 (s, 1H, OH), 3.81 (s, 3H, OCH_3), 3.89 (t, *J* = 10.3 Hz, 1H, H-6b), 4.06 (td, *J* = 9.8, 4.8 Hz, 1H, H-5), 4.17 (dd, *J* = 9.6, 3.3 Hz, 1H, H-3), 4.22 (d, *J* = 1.2 Hz, 1H, H-2), 4.26 (t, *J* = 8.8 Hz, 2H, H-4, H-6a), 4.82 (d, *J* = 11.7 Hz, 1H, CH*H*Ph), 4.98 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 5.51 (s, 1H, H-1), 5.68 (s, 1H, benzylidene CHPh), 6.89 (d, *J* = 9.1 Hz, 2H, 2x aromatic CH), 7.03 (t, *J* = 6.3 Hz, 2H, 2x aromatic CH), 7.34-7.47 (m, 8H, 8x aromatic CH), 7.57-7.58 (m, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 55.5, 63.9, 68.6, 69.8, 73.2, 75.5, 78.7, 98.8, 101.5, 114.6, 117.6, 126.0, 127.8, 127.9, 128.1, 128.4, 128.8, 137.4, 137.9, 149.7, 155.0. MALDI-MS: $[M+Na]^+$ $C_{27}H_{28}NaO_7$, calcd 487.1733, obsd 487.0863.

***p*-Methoxyphenyl 4,6-*O*-benzylidene-3-*O*-benzyl-2-*O*-allyloxycarbonyl-α-D-mannopyranoside (S31).** Allylchloroformate (0.51 mL, 4.78 mmol) and tetramethylethylenediamine (0.89 mL, 5.97 mmol) were added to a solution of compound **S30** (1.85 g, 3.98 mmol) in DCM (50 mL) and the resulting mixture was stirred at room temperature for 4 h, after which it was diluted with DCM (200 mL) and washed with saturated $NaHCO_3$ and water. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford compound **S31** as white amorphous solid (2.01 g, 92%). ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.80 (s, 3H, OCH_3), 3.90 (t, *J* = 10.2 Hz, 1H, H-6b), 4.10 (td, *J* = 9.7, 4.7 Hz, 1H, H-5), 4.23-4.32 (m, 3H, H-3, H-4, H-6a), 4.73 (d, *J* = 5.8 Hz, 2H, alloc CH_2), 4.87 (d, *J* = 12.7 Hz, 2H, CH_2Ph), 5.33 (dd, *J* = 10.4, 1.0 Hz, 1H, alloc CH=C*H*H), 5.44 (dd, *J* = 17.2, 1.2 Hz, 1H, alloc CH=C*H*H), 5.48 (d, *J* = 1.5 Hz, 1H, H-2), 5.58 (s, 1H, H-1), 5.69 (s, 1H, benzylidene CHPh), 5.96-6.04 (m, 1H, alloc C*H*=CHH), 6.89 (d, *J* = 9.1 Hz, 2H, 2x aromatic CH), 7.03 (t, *J* = 6.3 Hz, 2H, 2x aromatic CH), 7.27-7.48 (m, 8H, 8x aromatic CH), 7.57 (d, *J* = 6.7 Hz, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 55.5, 64.4, 68.4, 68.9, 72.4, 75.5, 73.7, 78.1, 97.5, 101.5, 114.6, 117.8, 119.1, 126.0, 127.5 (×2), 128.1, 128.2, 128.8, 131.2, 137.3, 138.0, 149.5, 154.4, 155.3. MALDI-MS: $[M+Na]^+$ $C_{31}H_{32}NaO_9$, calcd 571.1944, obsd 571.0970.

***p*-Methoxyphenyl 3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-α-D-mannopyranoside (S32).** Triethylsilane (0.31 mL, 1.91 mmol) and dichlorophenylborane (0.28 mL, 2.16 mmol) were added sequentially to a cooled (-78 °C) solution of compound **S31** (0.7 g, 1.27 mmol) in DCM (50 mL). The reaction mixture was stirred at -78 °C for 1 h and then quenched with MeOH (0.5 mL) and Et_3N (0.5 mL). The resulting mixture was washed with saturated aq. $NaHCO_3$. The reaction mixture was extracted with DCM (2 x 20 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford compound **S32** (0.61 g, 87%). ^{1}H NMR (500 MHz; $CDCl_3$): δ 2.05 (t, *J* = 6.6 Hz, 1H, OH), 3.78 (s, 3H, OCH_3), 3.82 (m, 2H, H-6a, H-6b), 3.89 (dd, *J* = 9.9, 2.7 Hz, 1H, H-5), 4.01 (t, *J* = 9.6 Hz, 1H, H-4), 4.24 (dd, *J* = 9.4, 3.0 Hz, 1H, H-3), 4.68-4.72 (m, 4H, 2x C*H*HPh, alloc CH_2), 4.87 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.98 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 5.30 (d, *J* = 10.4 Hz, 1H, alloc CH=C*H*H), 5.41 (t, *J* = 8.6 Hz, 2H, H-2, alloc CH=C*H*H), 5.55 (s, 1H, H-1), 5.97 (ddt, *J* = 16.9, 11.1, 5.7 Hz, 1H, alloc C*H*=CHH), 6.85 (d, *J* = 9.0 Hz, 2H, 2x aromatic CH), 7.00 (d, *J* = 9.0 Hz,

2H, 2x aromatic CH), 7.27-7.39 (m, 8H, 8x aromatic CH), 7.43 (d, *J* = 7.2 Hz, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 61.8, 68.9, 72.0, 72.3, 72.6, 73.9, 75.4, 77.8, 96.8, 114.6, 117.9, 119.2, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 131.3, 137.9, 138.2, 149.6, 154.5, 155.3. MALDI-MS: $[M+Na]^+$ $C_{31}H_{34}NaO_9$, calcd 573.2101, obsd 573.2120.

***p*-Methoxyphenyl 6-*O*-levulinoyl-3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-α-D-mannopyranoside (S33).** Levulinic acid (0.13 g, 1.25 mmol), *N*-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (0.27 g, 1.42 mmol) and 4-(dimethylamino)pyridine (11 mg, 0.09 mmol) were added to a solution of **S32** (0.49 g, 0.89 mmol) in DCM (20 mL). After stirring overnight at room temperature, the reaction mixture was washed with $NaHCO_3$ and extracted with DCM (2 x 50 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:1, v:v) to afford compound **S33** as white amorphous solid (0.56 g, 96%). ^{1}H NMR (500 MHz; $CDCl_3$): δ 2.19 (s, 3H, lev CH_2COCH_3), 2.59 (td, *J* = 6.7, 3.3 Hz, 2H, lev $COOCH_2$), 2.73 (dt, *J* = 8.7, 6.8 Hz, 2H, lev CH_2COCH_3), 3.80 (s, 3H, OCH_3), 3.88 (t, *J* = 9.6 Hz, 1H, H-4), 4.02 (ddd, *J* = 10.0, 4.6, 2.5 Hz, 1H, H-5), 4.23 (dd, *J* = 9.2, 3.3 Hz, 1H, H-3), 4.32-4.38 (m, 2H, H-6a, H-6b), 4.64 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.69-4.71 (m, 3H, C*H*HPh, alloc CH_2), 4.86 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.97 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 5.31 (dd, *J* = 10.4, 1.0 Hz, 1H, alloc CH=C*H*H), 5.38-5.43 (m, 2H, H-2, alloc CH=C*H*H), 5.53 (d, *J* = 1.6 Hz, 1H, H-1), 5.98 (ddt, *J* = 17.0, 10.7, 6.0 Hz, 1H, alloc C*H*=CHH), 6.84-6.87 (m, 2H, 2x aromatic CH), 7.00-7.03 (m, 2H, 2x aromatic CH), 7.29-7.43 (m, 10H, 10x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.9, 29.7, 378, 55.6, 63.1, 68.9, 70.3, 72.0, 72.2, 73.8, 75.3, 77.9, 96.5, 114.6, 117.8, 119.2, 127.8 (×2), 127.9, 128.1, 128.4 (×2), 131.3, 137.7, 137.9, 149.7, 154.5, 155.2, 172.3, 206.4. MALDI-MS: $[M+Na]^+$ $C_{36}H_{40}NaO_{11}$, calcd 671.2468, obsd 671.2477.

(*N*-Phenyl)-2,2,2-trifluoroacetimidate 6-*O*-levulinoyl-3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-D-mannopyranoside (S34). Ceric ammonium nitrate (2.54 g, 4.62 mmol) was added to a solution of compound **S33** (1.0 g, 1.54 mmol) in a mixture of CH_3CN (30 mL) and H_2O (7.5 mL) at 0 °C. After stirring at room temperature under an atmosphere of N_2 for 2 h, the mixture was concentrated under reduced pressure and the residue was dissolved in DCM (100 mL) and washed with H_2O. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:2, v:v) to afford the corresponding hemiacetal (0.74 g, 1.36 mmol). NaH

(60%, 54 mg, 1.36 mmol) was added to a cooled (0 °C) solution of the obtained hemiacetal and *N*-phenyltrifluoroacetimidoyl chloride (1.1 mL, 6.8 mmol) in DCM (70 mL) and the mixture was stirred at room temperature for 1 h, after which it was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 4:1, v:v) to afford the corresponding *N*-phenyl trifluoroacetimidate **S34** (790 mg, 72% for 2 steps) as an amorphous white solid. The mannosyl donor was used for the preparation of compound **1**.

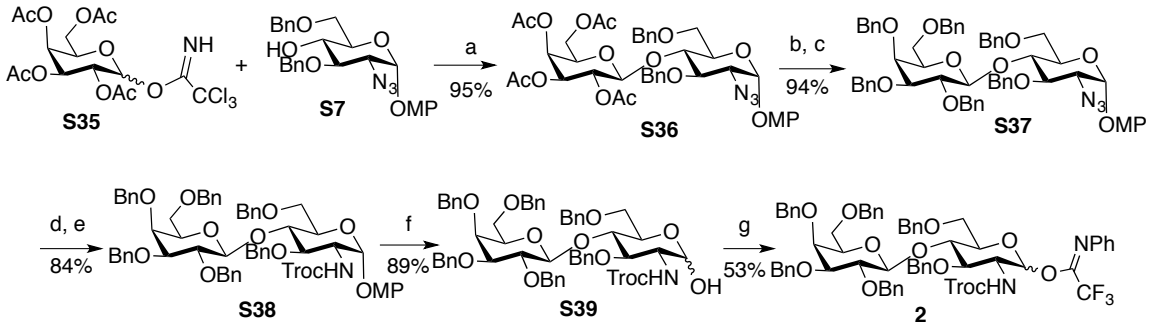


Fig. S11. Synthesis of lactosamine donor **2.**
a) TfOH, DCM, MS4Å, -70 °C to -20 °C, 1 h; b) NaOMe, DCM, MeOH, rt, 2h; c) BnBr, NaH, DMF, rt, 2 h;
d) PMe_3(1 M), NaOH, THF, H_2O, rt, overnight; e) TrocCl, solid $NaHCO_3$, THF, 4 h;
f) CAN, CH_3CN, H_2O, rt, 2 h; e) $CF_3C(NPh)Cl$, DBU, DCM, rt, 1 h.

***p*-Methoxyphenyl [2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-azido-*α*-D-glucopyranoside (S36).** Trichloroacetimidate donor **S35** (*45*) (644 mg, 1.31 mmol) and azido-glucose acceptor **S7** (450 mg, 0.92 mmol) were dissolved in DCM (40 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−70 °C), followed by addition of TfOH (23 µL, 0.26 mmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise from −70 °C to −20 °C, before quenching with Et_3N (0.05 mL). The reaction mixture was washed with $NaHCO_3$ and extracted with DCM (2 x 50 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford **S36** (716 mg, 95%) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 1.96 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 3.50 (dd, *J* = 10.0, 3.6 Hz, 1H, GlcN H-2), 3.57 (t, *J* = 7.1 Hz, 1H, Gal H-5), 3.62-3.64 (m, 1H, Gal H-6b), 3.77-3.81 (m, 4H, Gal H-6a, OCH_3), 3.88 (dd, *J* = 11.2, 5.9 Hz, 2H, GlcN H-5 & H-6b), 4.01 (dd, *J* = 11.2, 8.0 Hz, 1H, GlcN H-6a), 4.08-4.17 (m, 2H, GlcN H-4 & H-3), 4.43 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.47 (d, *J* = 8.0

Hz, 1H, Gal H-1), 4.78-4.82 (m, 3H, H-4', 2x C*H*HPh), 5.14 (dt, *J* = 10.4, 4.0 Hz, 2H, Gal H-2, C*H*HPh), 5.28 (d, *J* = 3.3 Hz, 1H, H-3'), 5.46 (d, *J* = 3.5 Hz, 1H, H-1), 6.84-6.87 (m, 2H, 2x aromatic CH), 7.06-7.09 (m, 2H, 2x aromatic CH), 7.29-7.44 (m, 8H, 8x aromatic CH), 7.49 (d, *J* = 7.3 Hz, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 20.8 (×2), 21.0, 55.8, 60.7, 62.9, 67.0, 67.5, 69.7, 70.7, 71.2 (×2), 73.9, 75.3, 77.8, 77.9, 97.7, 100.2, 114.9, 118.1, 127.9, 128.2, 128.4, 128.5, 128.6, 129.0, 137.6, 138.5, 150.7, 155.6, 169.3, 170.2, 170.3, 170.4. MALDI-MS: $[M+Na]^+$ $C_{41}H_{47}N_3NaO_{15}$, calcd 844.2905, obsd 844.2606.

***p*-Methoxyphenyl [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-azido-*α*-D-glucopyranoside (S37).** NaOMe (30%, 0.29 mL, 5.2 mmol) was added to a solution of compound **S36** (710 mg, 0.86 mmol) in a mixture of DCM (10 mL) and MeOH (10 mL). The reaction mixture was stirred for 2 h under an atmosphere of N_2, after which it was neutralized with conc. HCl and concentrated under reduced pressure. To a cooled (0 ^{o}C) solution of the resulting residue in DMF (20 mL), NaH (210 mg, 60% NaH in mineral oil, 5.2 mmol) and benzyl bromide (0.51 mL, 4.3 mmol) were added .The mixture was stirred at room temperature for 2 h, followed by quenching with EtOH. The reaction mixture was washed with $NaHCO_3$ and extracted with EtOAc (2 x 100 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 5:1, v:v) to afford compound **S37** (820 mg, 94% for 2 steps) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.46-3.51 (m, 3H, Gal H-6a, Gal H-5, Gal H-3), 3.57 (dd, *J* = 10.0, 3.5 Hz, 1H, GlcN H-2), 3.65 (dd, *J* = 11.6, 6.4 Hz, 2H, Gal H-6b, GlcN H-6b), 3.88 (s, 3H, OCH_3), 3.93 (dd, *J* = 9.5, 7.9 Hz, 1H, Gal H-2), 4.02 (dd, *J* = 8.9, 5.6 Hz, 2H, GlcN H-6a, GlcN H-5), 4.05 (d, *J* = 2.7 Hz, 1H, Gal H-4), 4.22 (td, *J* = 18.8, 9.1 Hz, 2H, GlcN H-3, GlcN H-4), 4.37 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.46-4.50 (m, 3H, 2x C*H*HPh, Gal H-1), 4.69 (dd, *J* = 11.7, 5.6 Hz, 2H, 2x C*H*HPh), 4.81-4.87 (m, 3H, C*H*HPh, CH_2Ph), 4.94 (q, *J* = 14.3 Hz, 2H, CH_2Ph), 5.13 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 5.34 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 5.52 (d, *J* = 3.5 Hz, 1H, GlcN H-1), 6.96 (dd, *J* = 7.3, 5.3 Hz, 2H, 2x aromatic CH), 7.20-7.22 (m, 2H, 2x aromatic CH), 7.28-7.49 (m, 28H, 28x aromatic CH), 7.55 (d, *J* = 7.1 Hz, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 62.6, 67.6, 68.0, 69.7, 71.2, 72.5, 73.0, 73.2, 73.3, 73.6, 74.7, 75.2, 75.3, 76.4, 76.6, 79.9, 82.3, 97.7, 102.7, 114.6, 118.1, 127.2, 127.3, 127.4, 127.5 (×3), 127.6, 127.7, 127.8, 127.9, 128.1 (×2), 128.2, 128.3 (×2), 137.9, 138.0, 138.4

(×2), 138.6, 138.9, 150.6, 155.3. MALDI-MS: $[M+Na]^+$ $C_{61}H_{63}N_3NaO_{11}$, calcd 1036.4360, obsd 1036.3352.

***p*-Methoxyphenyl [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl]- (1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-α-D-glucopyranoside (S38).** PMe_3 in THF (3.94 mL, 3.95 mmol, 1 M) and NaOH (2.1 mL, 2.1 mmol, 1 M) were added to a solution of compound **S37** (800 mg, 0.79 mmol) in THF (40 mL) and H_2O (10 mL), and the resulting mixture was stirred overnight at room temperature. The mixture was concentrated under reduced pressure and the resulting residue was diluted with DCM (100 mL) and neutralized with conc. HCl and the mixture was concentrated *in vacuo*. The resulting residue was dissolved in THF (16 mL), to which, solid $NaHCO_3$ (130 mg, 1.58 mmol) and 2,2,2-trichloroethyl chloroformate (0.127 mL, 0.95 mmol) were added. The reaction mixture was stirred at room temperature under an atmosphere of N_2 for 4 h and then filtered. The filtrate was concentrated, diluted with DCM (100 mL), and washed with water and brine. The organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 4:1, v:v) to afford compound **S38** (769 mg, 84% for two steps) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.27 (m, 3H, Gal H-3, Gal H-5, Gal H-6a), 3.38 (t, *J* = 10.0 Hz, 1H, Gal H-6b), 3.46 (d, *J* = 9.9 Hz, 1H, GlcN H-6b), 3.66-3.71 (m, 5H, OCH_3, GlcN H-3, Gal H-2), 3.76 (m, 2H, GlcN H-6a, GlcN H-5), 3.82 (s, 1H, Gal H-4), 3.98-4.04 (m, 2H, GlcN H-2, GlcN H-4), 4.15 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.23-4.29 (m, 3H, Gal H-1, 2x C*H*HPh), 4.43-4.46 (m, 2H, 2x C*H*HPh), 4.53-4.75 (m, 7H, troc CH_2, 5x C*H*HPh), 4.87 (d, *J* = 11.5 Hz, 1H, C*H*HPh), 5.01 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 5.07 (d, *J* = 9.2 Hz, 1H, NH), 5.36 (d, *J* = 3.3 Hz, 1H, GlcN H-1), 6.72 (d, *J* = 8.9 Hz, 2H, 2x aromatic CH), 6.93 (d, *J* = 8.9 Hz, 2H, 2x aromatic CH), 7.18 (ddt, *J* = 28.5, 14.5, 7.3 Hz, 30H, 30x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 54.7, 55.6, 67.8, 68.1, 71.4, 72.5, 73.0, 73.1, 73.4, 73.6, 74.4, 74.6 (×2), 75.3, 77.9, 80.0, 82.4, 95.4, 97.3, 102.8, 114.6, 127.2, 118.1, 127.2, 127.3, 127.4, 127.5 (×2), 127.6, 127.7, 127.8 (×2), 128.0, 128.1, 128.3 (×2), 128.4, 138.0, 138.1, 138.4, 138.7, 138.9, 139.0, 150.4, 154.2, 155.3. MALDI-MS: $[M+Na]^+$ $C_{64}H_{66}Cl_3NNaO_{13}$, calcd 1184.3497, obsd 1184.2256.

(*N*-Phenyl)-2,2,2-trifluoroacetimidate [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl]-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-D-glucopyranoside (2). Ceric ammonium nitrate (1.55 g, 2.85 mmol) was added to a cooled (0 °C)

solution of compound **S38** (1.1 g, 0.95 mmol) in a mixture of CH_3CN (30 mL) and H_2O (7.5 mL). The reaction mixture was stirred under an atmosphere of N_2 for 2 h at room temperature. The mixture was concentrated under reduced pressure and the residue was dissolved in DCM (100 mL) and washed with H_2O. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2.5:1, v:v) to afford the corresponding hemiacetal **S39** (890 mg, 89%). *N*-phenyltrifluoroacetimidoyl chloride (0.68 mL, 4.22 mmol) and DBU (126 µL, 0.95 mmol) were added to a cooled (0 °C) solution of compound **S39** in DCM (40 mL). The reaction mixture was stirred at room temperature for 1 h and was then concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:1, v:v) to afford the corresponding *N*-phenyltrifluoroacetimidate **2** (550 mg, 53%) as an amorphous white solid. The disaccharide donor was used for the preparation of compound **10**.

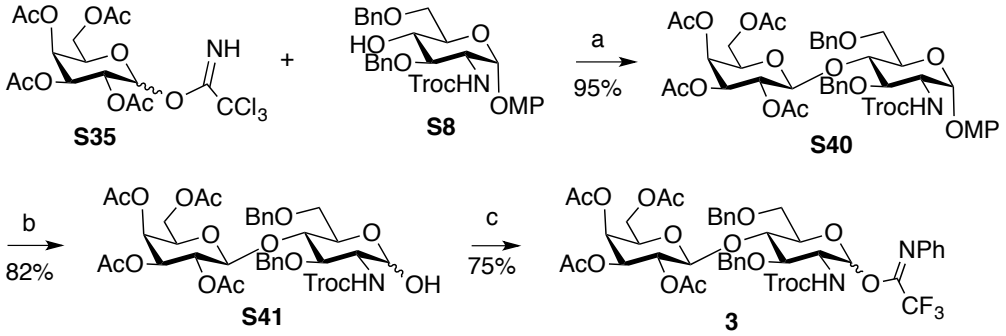


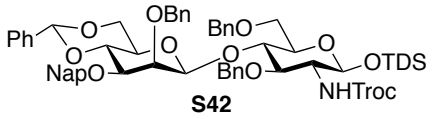
Fig. S12. Synthesis of lactosamine donor **3.**
a) TfOH, DCM, MS4Å, -70 ºC to -20 ºC, 1 h; b) CAN, CH_3CN, H_2O, rt, 2 h;
c) $CF_3C(NPh)Cl$, DBU, DCM, rt, 1 h.

***p*-Methoxyphenyl [2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl]-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*α*-D-glucopyranoside (S40).**
Trichloroacetimidate donor **S35** (0.88 g, 1.62 mmol) and acceptor **S8** (0.73 g, 1.1 mmol) were dissolved in DCM (40 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−70 °C), followed by addition of TfOH (29 µL, 0.32 mmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise from −70 °C to −20 °C, before quenching with Et_3N (0.05 mL). The reaction mixture was washed with $NaHCO_3$ and extracted with DCM (2 x 100 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:2, v:v) to

afford disaccharide **S40** (1.05 g, 95%) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 1.96 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 3.60 (m, 2H, GlcNH-6b, Gal H-5), 3.77-3.83 (m, 6H, OCH_3, GlcN H-6a & H-5), 3.87 (dd, *J* = 11.1, 6.1 Hz, 1H, Gal H-6b), 3.94 (t, *J* = 9.3 Hz, 1H, Gal H-6a), 4.09-4.16 (m, 2H, GlcN H-2 & H-4), 4.44 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.50 (d, *J* = 8.0 Hz, 1H, Gal H-1), 4.63 (d, *J* = 12.0 Hz, 1H, troc C*H*H), 4.70 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.79 (dd, *J* = 19.3, 11.8 Hz, 3H, troc C*H*H, C*H*HPh, Gal H-3), 5.03 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 5.13 (t, *J* = 9.1 Hz, 1H, Gal H-2), 5.22 (d, *J* = 9.2 Hz, 1H, NH), 5.27 (s, 1H, Gal H-4), 5.49 (d, *J* = 3.2 Hz, 1H, GlcN H-1), 6.83 (d, *J* = 9.0 Hz, 2H, 2x aromatic CH), 7.00 (d, *J* = 8.9 Hz, 2H, 2x aromatic CH), 7.28 (t, *J* = 6.9 Hz, 1H, aromatic CH), 7.43-7.33 (m, 9H, 9x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 20.4 (×2), 20.5, 20.6, 20.9, 54.6, 55.5, 60.2, 60.5, 66.7, 67.1 69.4, 70.3, 70.8, 71.0, 73.5, 74.3, 74.4, 76.4, 77.4, 95.2, 96.9, 100.0, 114.5, 117.6, 127.4 (×2), 128.1, 128.5, 137.4, 138.4, 150.1, 154.1, 155.1, 169.1, 169.8, 170.0 (×2). $^{1}J_{C1,H1}$ = 174.8, 163.1 Hz. MALDI-MS: $[M+Na]^+$ $C_{44}H_{50}Cl_3NNaO_{17}$, calcd 992.2042, obsd 992.2042.

(*N*-Phenyl)-2,2,2-trifluoroacetimidate [2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl]- (1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranoside (3). Ceric ammonium nitrate (1.69 g, 3.09 mmol) was added to a cooled (0 °C) solution of disaccharide **S40** (1.0 g, 1.03 mmol) in a mixture of CH_3CN (30 mL) and H_2O (7.5 mL), and the reaction mixture was stirred under an atmosphere of N_2 for 2 h at room temperature. The mixture was concentrated under reduced pressure and the residue was diluted with DCM (100 mL), washed with H_2O and dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:2, v:v) to afford the corresponding hemiacetal **S41** (730 mg, 82%). *N*-phenyltrifluoroacetimidoyl chloride (0.68 mL, 4.2 mmol) and DBU (127 μL, 0.95 mmol) were added to a cooled (0 °C) solution of compound **S41** in DCM (50 mL). The reaction mixture was stirred at room temperature for 1 h and was then concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford the disaccharide donor **3** (650 mg, 75%) as an amorphous white solid. The disaccharide donor was used for the preparation of compound **12**.

Dimethylthexylsilyl [4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-2-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranoside (S42).

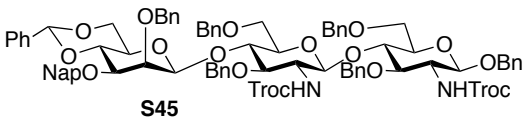


S42

A mixture of glycosyl donor **S15** (500 mg, 0.85 mmol) and activated molecular sieves (4Å) (500 mg) in DCM (20 mL) were stirred for 30 min under an atmosphere of N_2 at room temperature, after which the mixture was cooled (−60 °C), followed by addition of 1-benzenesulfinyl piperidine (190 mg, 0.89 mmol) and 2,4,6-Tri-*tert*-butylpyrimidine (0.42 g, 1.7 mmol). The mixture was stirred for 5 min at −60 °C and then Tf_2O (0.15 mL, 0.89 mmol) was added and vigorously stirred for 10 min at −60 °C, followed by addition of a solution of acceptor **S18** (544 mg, 0.81mmol) in DCM (5 mL). The reaction mixture was stirred for 1 h at −60 °C and was quenched with Et_3N (1 mL). The reaction mixture was washed with $NaHCO_3$ and extracted with DCM (2 x 75 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 15:1:1, v;v:v) to afford disaccharide **S42** (690 mg, 70%) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 0.13 (s, 3H, TDS CH_3), 0.18 (s, 3H, TDS CH_3), 0.85 (s, 3H, TDS CH_3), 0.85 (s, 3H, TDS CH_3), 0.87 (d, *J* = 2.9 Hz, 3H, TDS CHC*H*$_3$), 0.88 (d, *J* = 2.9 Hz, 3H, TDS CHC*H*$_3$), 1.62 (q, *J* = 6.9 Hz, 1H, TDS C*H*(CH_3)), 3.18 (td, *J* = 9.7, 4.8 Hz, 1H, Man-3 H-5), 3.26 (d, *J* = 8.6 Hz, 1H, GlcN-2 H-2), 3.43 (dt, *J* = 9.1, 2.8 Hz, 1H, GlcN-2 H-5), 3.51-3.65 (m, 4H, GlcN-2 (H-6b, H-6a), Man-3 (H-3, H-6b)), 3.84 (d, *J* = 2.9 Hz, 1H, Man-3 H-2), 3.89-3.91 (m, 1H, GlcN-2 H-3), 3.98 (t, *J* = 8.8 Hz, 1H, GlcN-2 H-4), 4.15 (m, 2H, Man-3 (H-6a, H-4)), 4.40 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.55-4.61 (m, 3H, Man-3 H-1, 2x C*H*HPh), 4.67 (s, 2H, troc CH_2), 4.76 (d, *J* = 12.7 Hz, 1H, C*H*HPh), 4.87 (d, *J* = 12.8 Hz, 1H, C*H*HPh), 4.90-4.94 (m, 3H, GlcN-2 H-1, nap CH_2), 5.04 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 5.12 (s, 1H, NH), 5.59 (s, 1H, benzylidene CHPh), 7.19-7.50 (m, 21H, 21x aromatic CH), 7.52 (dt, *J* = 5.3, 2.0 Hz, 2H, 2x aromatic CH), 7.70 (dd, *J* = 5.8, 3.5 Hz, 1H, aromatic CH), 7.79-7.85 (m, 3H, 3x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* -3.4, -1.9, 18.5, 18.6, 20.0, 20.1,24.8, 34.0, 59.6, 67.4, 68.6, 68.9, 72.4, 73.5, 74.2, 74.5, 74.7, 75.0, 76.6, 78.2, 78.3, 78.7, 95.2, 95.4, 101.4, 101.7, 125.5, 125.8, 126.0, 126.1, 126.2, 126.9, 127.1, 127.4, 127.5, 127.6 (×2), 127.7, 127.8 (×2), 127.9 (×2) , 128.0, 128.1, 128.2 (×2), 128.3 (×2), 128.4, 128.9, 132.9, 133.3, 135.9, 137.7, 137.8, 138.6, 138.9,

153.8. $^{1}J_{C1,H1}$ = 160.5 Hz, 157.5 Hz. MALDI-MS: $[M+Na]^+$ $C_{62}H_{72}Cl_3NNaO_{12}Si$, calcd 1178.3787, obsd 1178.3632.

Benzyl [4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-2-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S45).

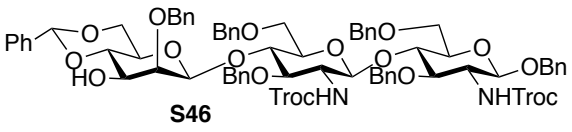


S45

To a cooled (0 °C) solution of disaccharide **S42** (4.5 g, 3.88 mmol) in pyridine (68 mL), HF (34 mL, 65-70% in pyridine) was added. The resulting mixture was stirred overnight at room temperature, after which it was diluted with EtOAc (200 mL), washed with 10% of $CuSO_4$, saturated aq. $NaHCO_3$ and H_2O. The organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford the corresponding hemiacetal (3.94 g, 99%) as an amorphous white solid. The resulting solid (3.9 g, 3.84 mmol) was dissolved in DCM (150 mL) and the mixture was cooled (0 °C). *N*-phenyltrifluoroacetimidoyl chloride (3.1 mL, 19.2 mmol) and DBU (0.58 mL, 3.84 mmol) were added to the mixture and stirred at room temperature for 1 h. The reaction mixture was then concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 4:1, v:v) to afford the corresponding *N*-phenyltrifluoroacetimidate disaccharide donor **S44** (3.9 g, 86%) as an amorphous white solid. Donor **S44** (1.9 g, 1.6 mmol) and acceptor **S22** (950 mg, 1.52 mmol) were dissolved in DCM (120 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−70 °C), followed by addition of TfOH (28 μL, 0.32 mmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise from −70 °C to −20 °C, before quenching with Et_3N (0.1 mL). The molecular sieves were filtered and the filtrate was washed with $NaHCO_3$ and extracted with DCM (2 x 100 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 3:1:1, v:v:v) to afford trisaccharide **S45** (2.4 g, 92%) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 3.04 (d, *J* = 4.8 Hz, 1H, Man-3 H-5), 3.15 (d, *J* = 9.4 Hz, 1H, GlcN-2 H-5), 3.21-3.25 (m, 1H, GlcN-2 H-3), 3.34-3.37 (m, 2H, GlcN-1 H-5, GlcN-2 H-6b), 3.40 (dd, *J* = 9.9, 3.1 Hz, 1H, Man-3 H-3), 3.45-3.52 (m, 4H, GlcN-1 H-2, GlcN-2 H-6a,

Man-3 H-6b, GlcN-2 H-2), 3.61-3.65 (m, 2H, GlcN-1 H-3, GlcN-1 H-6b), 3.73 (d, *J* = 2.9 Hz, 1H, Man-3 H-2), 3.76 (dd, *J* = 10.8, 4.1 Hz, 1H, GlcN-1 H-6a), 3.89 (t, *J* = 8.9 Hz, 1H, GlcN-2 H-4), 3.97 (t, *J* = 8.4 Hz, 1H, GlcN-1 H-4), 4.02 (dd, *J* = 10.5, 4.8 Hz, 1H, Man-3 H-6a), 4.08 (t, *J* = 9.6 Hz, 1H, Man-3 H-4), 4.12 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.30 (d, *J* = 12.1 Hz, 1H, CH*H*Ph), 4.34 (d, *J* = 11.6 Hz, 1H, NH), 4.37 (d, *J* = 8.1 Hz, 1H, GlcN-2 H-1), 4.40 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.45 (s, 1H, Man-3 H-1), 4.47 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.52-4.61 (m, 6H, GlcN-1 H-1, C*H*HPh, 2x troc CH_2), 4.69 (d, *J* = 12.6 Hz, 2H, 2x C*H*HPh), 4.75 (d, *J* = 12.0 Hz, 1H, CH*H*Ph), 4.81 (d, *J* = 12.7 Hz, 1H, CH*H*Ph), 4.86 (d, *J* = 12.1 Hz, 2H, CH*H*Ph), 4.89 (s, 2H, CH_2, nap), 5.01 (t, *J* = 9.9 Hz, 2H, NH, CH*H*Ph), 5.51 (s, 1H, CH, benzylidene), 7.07-7.11 (m, 3H, 3x aromatic CH), 7.14-7.39 (m, 32H, 32x aromatic CH), 7.42-7.47 (m, 6H, 6x aromatic CH), 7.64-7.66 (m, 1H, aromatic CH), 7.74-7.81 (m, 3H, 3x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.6, 57.3, 60.3, 67.2, 67.9, 68.3, 68.5, 70.4, 72.2, 72.6, 73.2 (×2) , 73.4, 73.9, 74.2, 74.3, 74.9, 76.5, 76.6, 77.5, 77.8, 78.0, 78.5, 78.6, 79.4, 95.4, 95.5, 99.5, 100.3, 101.3, 101.4, 125.3, 125.8, 125.9 (×2), 126.0 (×2), 126.3, 126.6, 127.2, 127.3, 127.5 (×3), 127.6 (×2), 127.7 (×2), 127.9, 128.0, 128.1 (×2), 128.2, 128.3, 128.4, 128.6, 128.8, 128.9, 132.8, 133.1, 135.8, 137.2, 137.5 (×2), 137.8, 138.4, 138.5, 138.6, 138.8, 153.8, 153.9. $^{1}J_{C1,H1}$ = 162.5 Hz, 159.8 Hz, 164.6 Hz. MALDI-MS: $[M+Na]^+$ $C_{84}H_{84}Cl_6N_2NaO_{18}$, calcd 1641.3748, obsd 1641.2380.

Benzyl [4,6-*O*-benzylidene-2-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S46).

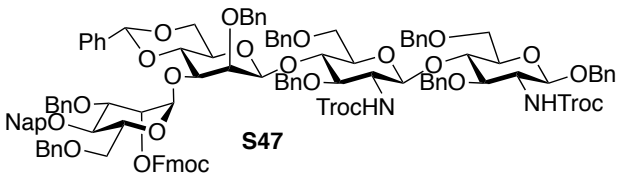


S46

To a cooled (0 °C) solution of compound **S45** (1.6 g, 990 μmol) in a mixture of DCM (35 mL) and H_2O (3.5 mL), 2,3-dichloro-5,6-dicyano-p-benzoquinone (0.27 g, 1.19 mmol) was added and the resulting mixture was stirred at room temperature for 3 h. After which it was filtered, diluted with DCM (100 mL), and the organic phase was washed with H_2O until the solution became colorless. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 3:2, v:v) to afford compound **S46** (1.07 g, 73%) as an amorphous white solid. ^{1}H NMR (500 MHz; $CDCl_3$): δ 2.30 (d, *J* = 8.4 Hz, 1H, OH), 2.97 (td, *J* = 9.6, 4.9 Hz, 1H, Man-3 H-5), 3.10 (d, *J* = 9.5 Hz, 1H, GlcN-2 H-5), 3.18 (t, *J* = 7.9 Hz, 1H, GlcN-2 H-3), 3.30-3.51 (m, 7H, GlcN-1 H-5, Man-3 H-6b, GlcN-2 H-2, Man-3 H-3, GlcN-2 H-6b, GlcN-1 H-2, GlcN-2 H-6a), 3.57-3.63 (m, 4H, GlcN-1 H-3, GlcN-1

H-6b, Man-3 H-2, Man-3 H-4), 3.72 (dd, *J* = 10.7, 3.1 Hz, 1H, GlcN-1 H-6a), 3.88 (t, *J* = 9.0 Hz, 1H, GlcN-2 H-4), 3.95 (m, 2H, GlcN-1 H-4, Man-3 H-6a), 4.20 (d, *J* = 12.0 Hz, 1H C*H*HPh), 4.25 (d, *J* = 5.8 Hz, 1H, NH), 4.37 (m, 4H, C*H*HPh, GlcN-2 H-1, CH*H*Ph, C*H*HPh), 4.47-4.70 (m, 10H, 2x troc CH_2, Man-3 H-1, GlcN-1 H-1, C*H*HPh, C*H*HPh, C*H*HPh, CH*H*Ph), 4.80 (d, *J* = 12.1 Hz, 1H, CH*H*Ph), 4.85 (d, *J* = 12.1 Hz, 1H, CH*H*Ph), 4.93 (d, *J* = 11.5 Hz, 3H, NH, CH*H*Ph, CH*H*Ph), 5.34 (s, 1H, benzylidene CHPh), 7.10-7.30 (m, 29H, 29x aromatic CH), 7.32-7.33 (m, 4H, 4x aromatic CH), 7.37 (dd, *J* = 7.5, 1.8 Hz, 2H, 2x aromatic CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.8, 57.3, 66.8, 68.0, 68.3, 68.5, 70.6, 70.8 73.5 (×2) , 74.1, 74.2, 74.3, 74.4, 75.6, 77.9, 78.6, 78.8, 79.0, 79.6, 95.4, 95.6, 99.5, 100.3, 101.6, 101.9, 126.2, 127.3, 127.4 (×2), 127.6, 127.7, 127.8, 127.9 (×2), 128.0, 128.1, 128.2 (×2), 128.3, 128.5 (×2), 128.7, 128.9, 129.1, 137.2 (×2), 137.5, 137.9, 138.1, 138.7 (×2), 153.9 (×2). MALDI-MS: $[M+Na]^+$ $C_{73}H_{76}Cl_6N_2NaO_{18}$, calcd 1501.3122, obsd 1501.1051.

Benzyl [3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl]-(1→3)-[4,6-*O*-benzylidene-2-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (S47).

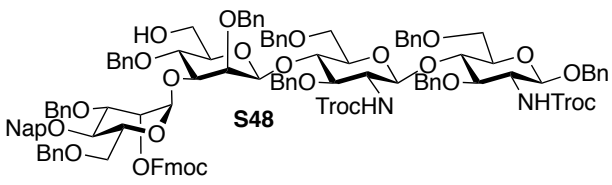


S47

N-Phenyl trifluoroacetimidate donor **S27** (97 mg, 110 μmol) and trisaccharide acceptor **S46** (80 mg, 55 μmol) were dissolved in DCM (10 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−60 °C), followed by addition of TfOH (1.9 μL, 22 μmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise from −60 °C to −20 °C, before quenching with solid $NaHCO_3$ (20 mg). The reaction mixture was washed with aq. $NaHCO_3$ and extracted with DCM (2 x 25 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 4:1:1, v:v:v) to afford **S47** (110 mg, 90%) as an amorphous white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.13 (td, *J* = 9.4, 5.0 Hz, 1H, Man-3 H-5), 3.29 (d, *J* = 9.3 Hz, 1H, GlcN-2 H-5), 3.40 (d, *J* = 7.7 Hz, 1H, GlcN-2 H-3), 3.51 (t, *J* = 5.4 Hz, 2H, GlcN-1 H-5, GlcN-2 H-6a), 3.59 (dt, *J* = 18.7, 9.4 Hz, 2H, Man-3 H-6a, GlcN-2 H-2), 3.69 (dd, *J* = 19.1, 9.8

Hz, 2H, GlcN-1 H-2, GlcN-2 H-6a), 3.78 (d, *J* = 10.1 Hz, 2H, GlcN-1 H-3, GlcN-1 H6a), 3.85 (d, *J* = 10.1 Hz, 1H, Man-4 H-6b), 3.90-3.93 (m, 4H, Man-4 H-6a, GlcN-1 H-6b, Man-3 H-2, Man-3 H-3), 4.02 (t, *J* = 6.3 Hz, 1H, Man-4 H-5), 4.07 (d, *J* = 8.9 Hz, 1H, GlcN-2 H-4), 4.10-4.23 (m, 6H, GlcN-1 H-4, Man-4 H-4, Man-4 H-3, Man-3 H-6b, Man-3 H-4), 4.30-4.37 (m, 3H, C*H*HPh, C*H*HPh), 4.47-4.55 (m, 5H, CH*H*Ph, CH*H*Ph, C*H*HPh, GlcN-2 H-1), 4.65 (dt, *J* = 20.42, 10.81 Hz, 6H, C*H*HPh, C*H*HPh, C*H*HPh, Man-3 H-1, GlcN-1 H-1, C*H*HPh), 4.76 (t, *J* = 12.6 Hz, 5H, C*H*HPh, CH*H*Ph), 4.86 (td, *J* = 17.5, 11.5 Hz, 4H, Nap CH*H,* CH*H*Ph, CH*H*Ph), 5.00 (dq, *J* = 20.4, 10.2 Hz, 4H, CH*H*Ph, CH*H*Ph), 5.17 (dd, *J* = 31.4, 11.2 Hz, 3H, NH, CH*H*Ph, Nap C*H*H), 5.56-5.57 (m, 2H, Man-4 H-1, Man-4 H-2), 5.61 (s, 1H, benzylidene CHPh), 7.23-7.59 (m, 52H, 52x aromatic CH), 7.73 (dd, *J* = 19.0, 9.3 Hz, 3H, 3x aromatic CH), 7.86-7.90 (m, 4H, 4x aromatic CH), 7.94 (t, *J* = 4.6 Hz, 1H, aromatic CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 20.9, 46.4, 56.7, 57.3, 60.3, 64.2, 66.8, 67.9, 68.2, 68.3, 69.1, 70.1, 70.5, 71.5, 72.1, 72.3, 73.2, 73.4, 73.5, 74.0, 74.1, 74.2, 74.3, 74.5, 75.2, 75.3, 75.5, 77.3, 77.4, 77.8, 78.3, 78.5, 78.6, 79.4, 95.4, 95.5, 98.3, 99.5, 100.3, 101.0, 101.1, 119.9 (×2), 125.1, 125.3, 125.8 (×2), 125.9, 126.0, 126.4, 127.1, 127.3, 127.4, 127.5, 127.6 (×2), 127.7 (×3), 127.8, 127.9 (×2), 128.0, 128.1, 128.2 (×2), 128.3(×2), 128.5, 128.7, 128.9, 132.8, 133.1, 135.8, 137.1, 137.2, 137.6, 137.7, 137.8, 138.0, 138.3, 138.6, 138.7, 141.1 (×2), 143.2, 143.4, 153.8, 153.9, 154.5. $^{1}J_{C1,H1}$ = GlcN-1 164 Hz, GlcN-2 161 Hz, Man-3 160 Hz, Man-4 177 Hz. MALDI-MS: $[M+Na]^+$ $C_{119}H_{116}Cl_6N_2NaO_{25}$, calcd 2205.5896, obsd 2205.4729.

Benzyl [3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl]-(1→3)-[2,4-di-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (S48).

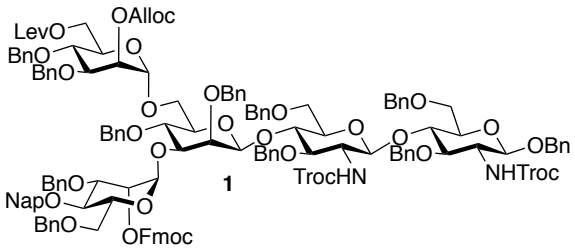


S48

Triethylsilane (11 μL, 68.56 μmol) and dichlorophenylborane (10.2 μL, 77.7 μmol) were added sequentially to a cooled (−78 °C) solution of tetrasaccharide **S47** (100 mg, 45.7 μmol) in DCM (8 mL). The resulting mixture was stirred under an atmosphere of N_2 at −78 °C for 40 min and quenched upon addition of solid $NaHCO_3$ and MeOH. The resulting mixture was washed with saturated aq. $NaHCO_3$ and H_2O, dried (Na_2SO_4), filtered, and the filtrate was

concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 3:1:1, v:v:v) to afford tetrasaccharide acceptor **S48** (85.1 mg, 85%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.03 (dd, *J* = 6.6, 2.5 Hz, 1H, Man-3 H-5), 3.21 (d, *J* = 6.9 Hz, 2H, GlcN-2 H-5, GlcN-2 H-3), 3.36-3.39 (m, 1H, Man-3 H-6a), 3.43-3.47 (m, 2H, GlcN-1 H-5, GlcN-2 H-6a), 3.52-3.57 (m, 1H, GlcN-2 H-2), 3.59-3.65 (m, 4H, GlcN-1 H-2, GlcN-2 H-6b, Man-3 H-6b, Man-3 H-3), 3.69-3.78 (m, 4H, GlcN-1 H-6a, GlcN-1 H-3, Man-4 H-6a, Man-4 H-6b), 3.85-3.90 (m, 3H, GlcN-1 H6b, Man-3 H-4, Man-3 H-2), 3.95 (t, *J* = 9.1 Hz, 1H, GlcN-2 H-4), 3.99-4.07 (m, 4H, Man-4 H-5, Man-4 H-4, GlcN-1 H-4, Man-4 H-3), 4.28 (dt, *J* = 12.0, 5.8 Hz, 3H, NH, C*H*HPh), 4.33 (d, *J* = 7.9 Hz, 1 H), 4.39 (d, *J* = 8.4 Hz, 1H, GlcN-2 H-1), 4.42-4.49 (m, 4H, CH*H*Ph, C*H*HPh, C*H*HPh), 4.52 (dt, *J* = 8.6, 4.1 Hz, 3H, C*H*HPh, C*H*HPh, Man-3 H-1), 4.56 (d, *J* = 3.7 Hz, 1H, C*H*HPh), 4.61 (d, *J* = 12.3 Hz, 3H, C*H*HPh, GlcN-1 H-1), 4.66 (dd, *J* = 11.6, 4.9 Hz, 5H, CH*H*Ph, C*H*HPh), 4.73 (dd, *J* = 11.2, 8.3 Hz, 2H, Nap C*H*H, CH*H*Ph), 4.75-4.83 (m, 3H, CH*H*Ph, CH*H*Ph), 4.86 (d, *J* = 14.2 Hz, 1H, C*H*HPh), 4.91 (d, *J* = 9.5 Hz, 1H, CH*H*Ph), 4.96 (d, *J* = 12.6 Hz, 2H, CH*H*Ph), 5.05 (ddd, *J* = 31.7, 20.0, 10.1 Hz, 4H, NH, CH*H*Ph, CH*H*Ph, Nap CH*H*), 5.35 (s, 1H, Man-4 H-1), 5.37 (d, *J* = 2.4 Hz, 1H, Man-4 H-2), 7.17-7.24 (m, 9H, 9x aromatic CH), 7.25-7.37 (m, 30H, 30x aromatic CH), 7.40 (t, *J* = 7.6 Hz, 3H, 3x aromatic CH), 7.44-7.49 (m, 7H, 7x aromatic CH), 7.53 (dq, *J* = 6.3, 3.2 Hz, 2H, 2x aromatic CH), 7.68 (q, *J* = 8.3 Hz, 3H, 3x aromatic CH), 7.78-7.84 (m, 5H, 5x aromatic CH), 7.88 (dd, *J* = 6.0, 3.4 Hz, 1H, aromatic CH). ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 14.1, 21.0, 46.5, 56.7, 57.3, 60.3, 61.7, 68.0, 68.3, 69.2, 70.3, 70.6, 71.8, 72.5, 72.6, 73.3, 73.4, 73.6, 74.1 (×2), 74.3, 74.4, 74.6, 74.8, 74.9, 75.1, 75.6, 76.6, 77.5, 77.6, 77.9, 78.1, 78.6, 79.7, 80.4, 95.5 (×2), 99.3, 99.6, 100.5 (×2) , 120.0 (×2), 125.2, 125.4, 125.8, 125.9, 126.0, 126.3, 126.9, 127.0, 127.1, 127.3, 127.5 (×2), 127.6, 127.7 (×2), 127.8 (×2), 127.9 (×2), 128.1, 128.2 (×2), 128.3(×2) ,128.4, 128.5, 128.7, 128.8, 129.1, 132.9, 133.2, 133.9, 135.8, 137.2, 137.6, 137.7, 137.8 (×2), 138.0, 138.6 (×2), 138.7, 141.2 (×2), 143.2, 143.5, 154.1, 154.6. MALDI-MS: $[M+Na]^+$ $C_{119}H_{118}Cl_6N_2NaO_{25}$, calcd 2207.6053, obsd 2207.1960.

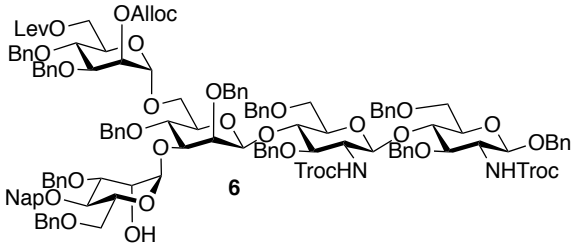
Benzyl [3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl-(1→3)]-[6-*O*-levulinoyl-3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-α-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (1).



N-Phenyl trifluoroacetimidate donor **S34** (0.65 g, 910 μmol), tetrasaccharide acceptor **S48** (1.0 g, 460 μmol) were dissolved in DCM (120 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−60 °C), followed by addition of TfOH (1.9 μL, 22 μmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise from −60 °C to −20 °C, before quenching with solid $NaHCO_3$. The reaction mixture was washed with aq. $NaHCO_3$ and extracted with DCM (2 x 25 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 2.5:1:1, v:v:v) to afford pentasaccharide **1** (1.1 g, 89%) as an amorphous white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.02 (s, 3H, Lev CH_2COCH_3), 2.38 (t, *J* = 6.7 Hz, 2H, Lev $COOCH_2CH_2$), 2.51-2.55 (m, 2H, Lev $COOCH_2CH_2$), 3.02 (d, *J* = 9.4 Hz, 1H, GlcN-2 H-5), 3.07 (dd, *J* = 9.2, 2.4 Hz, 1H, Man-3 H-5), 3.23 (d, *J* = 8.3 Hz, 1H, GlcN-2 H-3), 3.32 (dt, *J* = 16.4, 6.1 Hz, 3H, GlcN-2 H-2, Man-4 H-5, GlcN-2 H-6a), 3.44-3.51 (m, 4H, GlcN-2 H-6b, GlcN-1 H-2, Man-3 H-6a, Man-3 H-3), 3.54-3.65 (m, 8H, Man-4 H-6a, Man-4' H-4, GlcN-1 H-3, Man-4' H-5, Man-3 H-6b, Man-4 H-6b), 3.77 (dt, *J* = 5.2, 3.5 Hz, 2H, Man-3 H-4, Man-4' H-3), 3.82 (d, *J* = 2.1 Hz, 1H, Man-3 H-2), 3.86 (dd, *J* = 17.3, 8.1 Hz, 4H, GlcN-2 H-4, Man-4 H-4), 3.94-4.05 (m, 3H, Man-4 H-3, Man-4' H-6a, Man-4' H-6b), 4.13-4.23 (m, 5H, C*H*HPh, NH), 4.27-4.39 (m, 9H, GlcN-2 H-1, C*H*HPh, C*H*HPh, C*H*HPh, C*H*HPh, alloc *H*HC-C=CH, C*H*HPh), 4.41-4.47 (m, 7H, alloc H*H*C-C=CH, C*H*HPh, GlcN-1 H-1, Man-3 H-1, C*H*HPh, CH*H*Ph), 4.52 (dt, *J* = 12.7, 6.8 Hz, 6H, CH*H*Ph, CH*H*Ph, C*H*HPh), 4.60 (dd, *J* = 11.8, 5.0 Hz, 3H, Nap C*H*H, CH*H*Ph, C*H*HPh), 4.66 (d, *J* = 11.4 Hz, 1H, CH*H*Ph), 4.72-4.80 (m, 5H, CH*H*Ph, C*H*HPh, Man-4' H-1, CH*H*Ph), 4.93 (dt, *J* = 23.6, 11.9 Hz, 4H, CH*H*Ph, CH*H*Ph, NH, Nap CH*H*), 5.06 (s, 1H, Man-4' H-2), 5.13 (d, *J* = 10.4 Hz, 1H, alloc HC=CH*H*), 5.18-5.24 (m, 3H, Man-4 H-1, alloc HC=C*H*H, Man-4 H-2), 5.76 (dd, *J* = 17.1, 10.5 Hz, 1H,

alloc *H*C=CH_2), 7.01-7.25 (m, 57H, 57x aromatic CH), 7.34 (q, *J* = 7.9 Hz, 4H, 4x aromatic CH), 7.38-7.40 (m, 2H, 2x aromatic CH), 7.54 (q, *J* = 8.9 Hz, 3H, 3x aromatic CH), 7.64-7.71 (m, 4H, 4x aromatic CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 27.8, 29.7, 37.8, 46.5, 48.6, 52.4, 56.4, 57.4, 60.3, 63.1, 66.6, 68.1, 68.4, 68.6, 69.2, 69.9, 70.3, 70.5, 71.3, 71.8, 71.9, 72.5, 72.6, 73.2, 73.4, 73.7, 74.3, 74.1, 74.2, 74.3 (×2), 74.5, 74.8, 75.1 (×2), 76.3, 77.3, 77.7, 78.0, 78.1, 78.6, 81.1, 95.5, 95.6, 97.4, 99.3, 99.5 (×2), 100.3, 101.3, 118.9 , 119.9, 120.0 (×2), 125.1, 125.4, 125.8, 125.9, 126.0, 126.3, 127.1, 127.3, 127.4, 127.5, 127.6, 127.7 (×3), 127.8, 127.9, 128.0 (×2), 128.2 (×3), 128.3(×3), 128.4, 128.5 (×2), 131.4, 132.9, 133.2, 135.8, 137.2, 137.7, 137.8, 137.9, 138.0, 138.2, 138.6, 138.8, 139.0, 141.2 (×2), 143.2, 143.5, 153.8 (×2), 154.2, 154.6, 171.1, 206.5. $^{1}J_{C1,H1}$ = GlcN-1 164 Hz, GlcN-2 164 Hz, Man-3 159 Hz, Man-4 176 Hz, Man-4' 175 Hz. MALDI-MS: $[M+Na]^+$ $C_{148}H_{150}Cl_6N_2NaO_{34}$, calcd 2731.8099, obsd 2731.4468.

Benzyl [3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-α-D-mannopyranosyl-(1→3)]-[6-*O*-levulinoyl-3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-α-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (6).

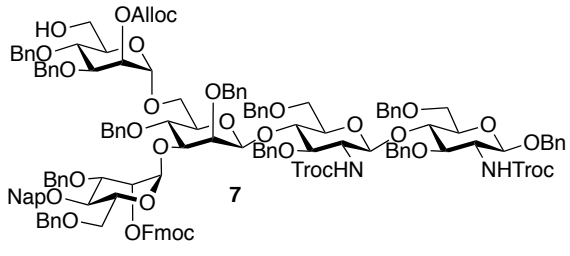


6

To a solution of pentasaccharide **1** (20 mg, 7.37 μmol) in DCM (2 mL), Et_3N (0.5 mL) was added and the resulting mixture was stirred at room temperature under an atmosphere of N_2 for 4 h, after which it was concentrated *in vacuo* and the residue was azeotropically dried with toluene (3x5 mL). The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 1.5:1:1, v:v:v) to afford compound **6** (17.3 mg, 94%). ^{1}H NMR (600 MHz; $CDCl_3$): δ 2.04 (s, 3H, lev CH_2COCH_3), 2.39 (t, *J* = 6.6 Hz, 2H, lev $COOCH_2CH_2$), 2.52-2.55 (m, 2H, lev $COOCH_2CH_2$), 3.00 (d, *J* = 9.4 Hz, 1H, GlcN-2 H-5), 3.07 (td, *J* = 4.7, 3.3 Hz, 1H, Man-3 H-5), 3.20 (s, 1H, GlcN-2 H-3), 3.29 (m, 2H, GlcN-2 H-2, Man-4 H-5), 3.33 (dd, *J* = 11.0, 3.4 Hz, 1H, GlcN-2 H-6a), 3.44-3.50 (m, 5H, Man-3 H-3, GlcN-2 H-6b, GlcN-1 H-2, Man-3 H-6a), 3.53-3.61 (m, 9H, Man-4 H-6a, Man-4' H-4, GlcN-1 H-3, Man-4' H-5, Man-3 H-6b), 3.63 (dd, *J* = 10.7, 3.6 Hz, 1H, Man-4 H-6a), 3.73 (t, *J* = 9.5 Hz, 1H, Man-3 H-4), 3.77-3.89 (m, 10H, Man-4' H-3, Man-3 H-2, Man-4 H-4, Man-4 H-3, GlcN-2 H-4, Man-4 H-2), 3.99 (d, *J* =

11.3 Hz, 1H, Man-4' H-6a), 4.04 (dd, *J* = 11.9, 4.1 Hz, 1H, Man-4' H-6b), 4.20 (t, *J* = 11.1 Hz, 3H, C*H*HPh, NH, C*H*HPh), 4.26 (d, *J* = 7.8 Hz, 1H, GlcN-2 H-1), 4.32 (dd, *J* = 18.3, 6.3 Hz, 3H, C*H*HPh, CH*H*Ph, C*H*HPh), 4.36-4.41 (m, 3H, C*H*HPh, C*H*HPh), 4.45 (dt, *J* = 12.8, 5.9 Hz, 7H, CH*H*Ph, GlcN-1 H-1, CH*H*Ph, Man-3 H-1, C*H*HPh), 4.48-4.54 (m, 7H, C*H*HPh, C*H*HPh, C*H*HPh, CH*H*Ph), 4.56-4.62 (m, 4H, Nap C*H*H, CH*H*Ph, CH*H*Ph), 4.73-4.80 (m, 5H, CH*H*Ph, C*H*HPh, CH*H*Ph, Man-4' H-1, CH*H*Ph), 4.89-4.95 (m, 4H, Nap CH*H*, CH*H*Ph, NH, CH*H*Ph), 5.06 (s, 2H, Man-4 H-1, Man-4' H-2), 5.13 (dd, *J* = 10.5, 1.1 Hz, 1H, alloc CH=C*H*H), 5.22 (dt, *J* = 17.2, 1.4 Hz, 1H, alloc CH=CH*H*), 5.77 (ddt, *J* = 16.9, 10.7, 6.0 Hz, 1H, alloc C*H*=CH_2), 7.01 (t, *J* = 7.4 Hz, 1H, aromatic CH), 7.07-7.25 (m, 53H, 53x aromatic CH), 7.36-7.41 (m, 4H, 4x aromatic CH), 7.53 (s, 1H, aromatic CH), 7.64-7.68 (m, 2H, 2x aromatic CH), 7.75 (dd, *J* = 6.0, 3.4 Hz, 1H, aromatic CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 27.8, 29.7, 37.8, 46.5, 48.6, 52.4, 56.4, 57.4, 60.3, 63.1, 66.6, 68.1, 68.4, 68.6, 69.2, 69.9, 70.3, 70.5, 71.3, 71.8, 71.9, 72.5, 72.6, 73.2, 73.4, 73.7, 74.3, 74.1, 74.2, 74.3 (×2), 74.5, 74.8, 75.1 (×2), 76.3, 77.3, 77.7, 78.0, 78.1, 78.6, 81.1, 95.5, 95.6, 97.4, 99.3, 99.5, 100.3, 101.4 (×2), 119.0 ,125.8, 125.9, 126.0, 126.3, 127.2, 127.3 (×2), 127.4 (×2), 127.5 (×2), 127.7 (×3), 127.8 (×2), 127.9 (×2), 128.0, 128.1 (×2), 128.2, 128.3(×2), 128.4, 128.5 (×2), 128.6 (×2), 128.7, 131.4, 132.9, 133.2, 135.9, 137.3, 137.8 (×3), 137.9, 138.0, 138.2, 138.9, 139.0, 153.9 (×2), 154.3, 172.3, 206.6. MALDI-MS: $[M+Na]^+$ $C_{133}H_{140}Cl_6N_2NaO_{32}$, calcd 2509.7418, obsd 2509.4609.

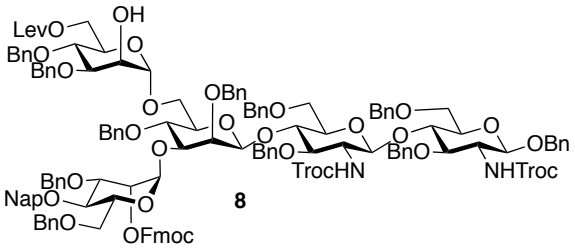
Benzyl [3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl-(1→3)]-[3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-α-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (7).



Hydrazine acetate (1.22 mg, 13.3 µmol) was added to a solution of pentasaccharide **1** (30 mg, 11.1 µmol) in a mixture of DCM (3 mL) and MeOH (0.3 mL) and the resulting mixture was stirred at room temperature for 5 h. The mixture was concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 2.5:1:1, v:v:v) to afford compound **7** (24.5 mg, 85%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.31 (s, 1H, OH), 3.03 (d, *J* = 9.7 Hz, 1H, GlcN-2 H-5), 3.08 (dd,

J = 8.9, 5.9 Hz, 1H, Man-3 H-5), 3.27-3.31 (m, 3H, Man-3 H-6a, GlcN-2 H-2, GlcN-2 H-6a), 3.37 (d, *J* = 9.6 Hz, 2H, GlcN-2 H-6b, GlcN-1 H-5), 3.47-3.55 (m, 7H, GlcN-2 H-3, Man-3 H-6b, GlcN-1 H-2, Man-3 H-3), 3.57-3.64 (m, 6H, GlcN-1 H-3, GlcN-1 H-6a, Man-4' H-4, Man-3 H-4, Man-4 H-5), 3.66 (dd, *J* = 10.7, 3.9 Hz, 1H, GlcN-1 H-6b), 3.73 (dd, *J* = 9.4, 2.8 Hz, 1H, Man-4' H-3), 3.80 (d, *J* = 2.5 Hz, 1H, Man-3 H-2), 3.86-3.91 (m, 2H, Man-4 H-4), 3.93 (dd, *J* = 14.0, 6.0 Hz, 1H, GlcN-1 H-4), 3.96 (dd, *J* = 8.7, 3.3 Hz, 1H, Man-4 H-3), 4.07 (t, *J* = 9.0 Hz, 1H, GlcN-2 H-4), 4.21 (ddq, *J* = 49.7, 19.5, 9.7 Hz, 4H, C*H*HPh), 4.32-4.40 (m, 6H, C*H*HPh, C*H*HPh, C*H*HPh), 4.45 (ddt, *J* = 16.7, 11.2, 5.4 Hz, 7H, C*H*HPh, C*H*HPh, Man-3 H-1, alloc *H*HC-C=CH, C*H*HPh, C*H*HPh, GlcN-1 H-1), 4.51-4.62 (m, 11H, CH*H*Ph, CH*H*Ph, GlcN-2 H-1, alloc H*H*C-C=CH, CH*H*Ph, Nap C*H*H, C*H*HPh, CH*H*Ph, CH*H*Ph), 4.68 (d, *J* = 11.2 Hz, 1H, CH*H*Ph), 4.72-4.80 (m, 3H, C*H*HPh, CH*H*Ph, CH*H*Ph), 4.82-4.85 (m, 1H, NH), 4.96 (dd, *J* = 23.0, 11.6 Hz, 4H, CH*H*Ph, CH*H*Ph, Nap CH*H*, Man-4' H-2), 5.05 (d, *J* = 13.8 Hz, 1H, Man-4' H-1), 5.09-5.10 (m, 1H, NH), 5.13 (d, *J* = 10.5 Hz, 1H, alloc CH=C*H*H), 5.20 (s, 1H, Man-4 H-1), 5.24-5.26 (m, 2H, alloc CH=CH*H,* Man-4 H-2), 5.80 (ddt, *J* = 16.9, 11.0, 5.7 Hz, 1H, alloc C*H*=CHH), 7.05-7.27 (m, 56H, 56x aromatic CH), 7.33 (ddd, *J* = 6.6, 6.3, 4.7 Hz, 4H, 4x aromatic CH), 7.40 (dd, *J* = 6.2, 3.2 Hz, 2H, 2x aromatic CH), 7.52 (s, 2H, 2x aromatic CH), 7.56 (d, *J* = 7.5 Hz, 1H, aromatic CH), 7.65 (dt, *J* = 6.1, 3.3 Hz, 1H, aromatic CH), 7.68 (d, *J* = 8.5 Hz, 1H, aromatic CH), 7.70 (d, *J* = 7.6 Hz, 2H, 2x aromatic CH), 7.75 (dd, *J* = 5.7, 3.6 Hz, 1H aromatic CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.7, 46.5, 56.5, 57.8, 61.3, 67.1, 67.9, 68.4, 68.8, 69.2, 69.9, 70.3, 70.5, 71.5 (×2), 71.9, 72.2, 72.5, 72.6, 72.7, 73.3 (×2), 73.4, 73.9, 74.0, 74.3 (×2), 74.5, 74.9 (×2), 75.0, 75.1, 75.4, 76.5, 77.4, 77.8, 78.0 (×2), 78.4, 81.2, 95.6, 97.2, 99.5 (×2), 100.0, 101.0, 119.2 , 120.0 (×2), 125.2, 125.4, 125.8, 125.9, 126.0, 126.3, 127.2, 127.3, 127.4 (×2), 127.5, 127.6 (×2), 127.7 (×4), 127.8 (×3), 127.9 (×2), 128.0 (×2), 128.1 (×2), 128.2, 128.3(×2), 128.4 (×2), 128.5, 128.6 (×2), 131.4, 132.9, 133.2, 135.9, 137.3, 137.5, 137.6, 137.8, 138.0 (×2), 138.1, 138.5, 138.6, 139.0, 141.2, 141.3, 143.2, 143.5, 153.8, 153.9, 154.2, 154.7. MALDI-MS: $[M+Na]^+$ $C_{143}H_{144}Cl_6N_2NaO_{32}$, calcd 2633.7731, obsd 2633.6345.

Benzyl [3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl-(1→3)]-[6-*O*-levulinoyl-3,4-di-*O*-benzyl)-α-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (8).

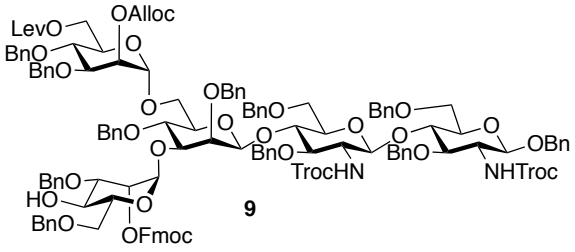


8

Tetrakis(triphenylphosphine) palladium (6.4 mg, 5.6 μmol) was added to a solution of pentasaccharide **1** (30 mg, 11.1 μmol) in a mixture of THF (3 mL) and H_2O (0.3 mL) and the resulting mixture was stirred at room temperature overnight, after which it was concentrated *in vacuo* and the residue was azeotropically dried with toluene (3x5 mL). The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 3:2:1, v:v:v) to afford compound **8** (27.8 mg, 96%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.02 (s, 3H, lev CH_2COCH_3), 2.16 (s, 1H, OH), 2.38 (t, *J* = 6.6 Hz, 2H, lev $COOCH_2CH_2$), 2.52 (t, *J* = 6.6 Hz, 2H, lev $COOCH_2CH_2$), 3.03 (d, *J* = 5.9 Hz, 2H, Man-3 H-5, GlcN-2 H-5), 3.13 (s, 1H, GlcN-2 H-3), 3.29-3.30 (m, 1H, Man-4 H-5), 3.34 (dd, *J* = 10.9, 3.0 Hz, 1H, GlcN-2 H-6a), 3.37 (d, *J* = 9.0 Hz, 1H, GlcN-2 H-2), 3.46-3.68 (m, 13H, GlcN-2 H-6b, GlcN-1 H-2, Man-3 H-3, Man-3 H-6a, Man-4 H-6a, Man-4' H-5, Man-4' H-4, Man-3 H-6b, GlcN-1 H-3, Man-4' H-3, Man-4 H-6b), 3.76-3.81 (m, 3H, Man-4' H-2, Man-3 H-4, Man-3 H-2), 3.87 (dd, *J* = 17.6, 8.6 Hz, 4H, Man-2 H-4, Man-4 H-4, Man-1 H-4), 3.95 (dd, *J* = 8.7, 2.8 Hz, 1H, Man-4 H-3), 3.99-4.01 (m, 1H, Man-4' H-6a), 4.07 (dd, *J* = 11.9, 4.0 Hz, 1H, Man-4' H-6b), 4.13-4.20 (m, 4H, C*H*HPh), 4.24 (d, *J* = 8.1 Hz, 1H, GlcN-2 H-1), 4.31 (dd, *J* = 10.8, 4.3 Hz, 4H, C*H*HPh, CH*H*Ph), 4.33-4.39 (m, 4H, C*H*HPh, C*H*HPh, C*H*HPh), 4.41 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.42-4.50 (m, 6H, Man-3 H-1, C*H*HPh, GlcN-1 H-1, C*H*HPh, C*H*HPh), 4.52 (d, *J* = 12.2 Hz, 3H, CH*H*Ph), 4.58 (t, *J* = 9.0 Hz, 3H, CH*H*Ph, Nap C*H*H), 4.64 (t, *J* = 12.3 Hz, 2H, CH*H*Ph, CH*H*Ph), 4.74 (dd, *J* = 11.4, 5.8 Hz, 2H, CH*H*Ph, C*H*HPh), 4.78-4.81 (m, 3H, CH*H*Ph, Man-4' H-1, CH*H*Ph), 4.95 (dd, *J* = 22.4, 11.7 Hz, 4H, CH*H*Ph, CH*H*Ph, NH, Nap CH*H*), 5.19 (s, 1H, Man-4 H-1), 5.25 (s, 1H, Man-4 H-2), 7.02-7.23 (m, 55H, 55x aromatic CH), 7.26 (d, *J* = 7.4 Hz, 2H, 2x aromatic CH), 7.34 (dd, *J* = 16.1, 7.7 Hz, 4H, 4x aromatic CH), 7.38-7.40 (m, 2H, 2x aromatic CH), 7.53 (d, *J* = 6.8 Hz, 2H, 2x aromatic CH), 7.56 (d, *J* = 7.5 Hz, 1H, aromatic CH), 7.64 (t, *J* = 4.7 Hz, 1H, aromatic CH), 7.67 (d, *J* = 8.4 Hz, 1H, aromatic CH), 7.70 (d, *J* = 7.6 Hz, 2H, 2x aromatic CH), 7.74-7.75 (m, 1H, aromatic CH). ^{13}C NMR (125 MHz, $CDCl_3$): *δ*

27.8, 29.7, 29.8, 37.8, 46.5, 56.5, 57.2, 60.4, 63.2, 66.2, 67.6, 68.1, 68.4, 69.1, 69.7, 70.3, 70.5, 71.2, 71.8, 72.5, 72.6, 73.3, 73.5 (×2), 73.7 (×2) , 73.9, 74.3, 74.4, 74.5, 74.7, 74.8, 75.0, 75.2, 76.6, 77.5, 77.7, 78.0, 78.1, 78.6, 79.4 (×2), 80.9, 95.6 (×2), 99.3, 99.6 (×2), 100.5, 101.0, 120.0 (×2), 125.2, 125.4, 125.8, 125.9, 126.4, 127.2, 127.3 (×2), 127.5, 127.6 (×4), 127.7 (×2), 127.8 (×3), 127.9 (×3), 128.1, 128.2 (×3), 128.3(×3), 128.4 (×2), 128.6 (×2), 128.8, 132.9, 133.2, 135.8, 137.2, 137.7, 137.8 (×3), 138.0, 138.2, 138.7, 138.8, 141.2 (×3), 143.5, 153.9, 154.0, 154.6, 172.4, 206.7. MALDI-MS: $[M+Na]^+$ $C_{144}H_{146}Cl_6N_2NaO_{32}$, calcd 2647.7888, obsd 2647.4988.

Benzyl [3,6-di-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl-(1→3)]-[6-*O*-levulinoyl-3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-α-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (9).

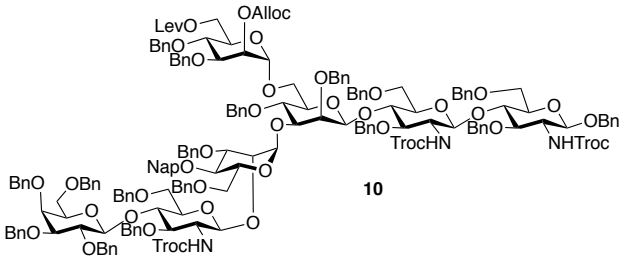


9

DDQ (3.0 mg, 13.3 μmol) was added to a cooled (0 °C) solution of pentasaccharide **1** (30 mg, 11.1 μmol) in a mixture of DCM (3 mL) and H_2O (0.3 mL). The resulting mixture was stirred at room temperature for 3 h. The mixture was diluted with DCM (30 mL) and the organic phase was washed with H_2O until the solution became colorless. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 2.5:1:1, v:v:v) to afford compound **9** (24.6 mg, 86%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.03 (s, 3H, lev CH_2COCH_3), 2.39 (t, J = 6.7 Hz, 2H, $COOCH_2CH_2$), 2.54 (q, J = 6.2 Hz, 2H, $COOCH_2CH_2$), 3.00 (d, J = 9.4 Hz, 1H, GlcN-2 H-5), 3.06 (dd, J = 9.3, 2.5 Hz, 1H, Man-3 H-5), 3.22 (s, 1H, GlcN-2 H-3), 3.31 (dt, J = 11.5, 5.8 Hz, 3H, GlcN-2 H-2, GlcN-1 H-5, GlcN-2 H-6a), 3.43-3.51 (m, 4H, GlcN-2 H-6b, GlcN-1 H-2, Man-3 H-6a, Man-3 H-3), 3.55-3.65 (m, 7H, GlcN-1 H-6a, GlcN-1 H-3, Man-4' H-4, Man-3 H-6b, Man-4' H-5, GlcN-1 H-6b), 3.69 (td, J = 8.7, 2.8 Hz, 2H, Man-4 H-3), 3.77 (dq, J = 8.6, 3.2 Hz, 2H, Man-4' H-3, Man-3 H-4), 3.81-3.89 (m, 5H, Man-3 H-2, GlcN-2 H-4, GlcN-1 H-4), 3.97-3.99 (m, 1H, Man-4' H-6a), 4.04 (dd, J = 11.8, 3.8 Hz, 1H, Man-4' H-6b), 4.12-4.21 (m, 5H, NH, C*H*HPh, C*H*HPh), 4.28 (dd, J = 10.1, 7.3 Hz, 2H, GlcN-2 H-1), 4.33 (td, J = 7.9, 3.7 Hz, 3H, CH*H*Ph, C*H*HPh, C*H*HPh), 4.38 (dt, J = 11.8, 6.0 Hz, 3H, C*H*HPh, C*H*HPh, , alloc *H*HC-

C=CH), 4.42-4.47 (m, 7H, C*H*HPh, alloc H*H*C-C=CH, CH*H*Ph, C*H*HPh, GlcN-1 H-1, Man-3 H-1), 4.49-4.56 (m, 6H, C*H*HPh, CH*H*Ph), 4.61 (dd, *J* = 11.9, 3.2 Hz, 2H, CH*H*Ph, CH*H*Ph), 4.66 (d, *J* = 11.4 Hz, 1H, CH*H*Ph), 4.73-4.80 (m, 5H, CH*H*Ph, C*H*HPh, CH*H*Ph, Man-4' H-1), 4.92 (dd, *J* = 27.7, 12.2 Hz, 3H, CH*H*Ph, NH, CH*H*Ph), 5.07 (s, 1H, Man-4' H-2), 5.13 (dd, *J* = 10.4, 0.8 Hz, 1H, alloc HC=CH*H*), 5.16 (s, 1H, Man-4 H-1), 5.19 (t, *J* = 2.1 Hz, 1H, Man-4 H-2), 5.22 (dd, *J* = 17.2, 1.3 Hz, 1H, HC=C*H*H), 5.76 (td, *J* = 11.2, 5.8 Hz, 1H, alloc C*H*=CHH), 7.04 (q, *J* = 8.0 Hz, 2 H, 2x aromatic CH), 7.11-7.27 (m, 54H, 54x aromatic CH), 7.34 (t, *J* = 7.5 Hz, 2H, 2x aromatic CH), 7.37 (d, *J* = 7.5 Hz, 2H, 2x aromatic CH), 7.52 (dd, *J* = 13.1, 7.5 Hz, 2H, 2x aromatic CH), 7.70 (d, *J* = 7.6 Hz, 2H, aromatic CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27., 29.7, 37.9, 46.6, 57.4, 63.2, 66.6, 67.2, 68.1, 68.4, 68.7, 69.9, 70.1, 70.4, 70.5, 71.3, 71.7, 71.8, 71.9, 72.3, 73.2, 73.5, 73.6, 73.7, 73.8, 74.4, 74.5 (×2), 74.6, 74.8 75.2, 77.4, 77.8, 78.1, 78.2, 78.6, 81.1, 95.6, 97.5, 99.5, 99.6, 100.3, 101.3, 104.3, 119.0, 120.0 (×2), 125.2, 125.3, 127.2 (×3), 127.3, 127.4, 127.5 (×2), 127.6, 127.7 (×2), 127.8 (×2), 127.9 (×2), 128.0, 128.1 (×2), 128.2 (×2), 128.3(×2), 128.4 (×3), 128.5, 128.6 (×3), 131.4, 137.2, 137.5, 137.7, 137.8 (×2), 137.9, 138.0, 138.2, 138.6, 138.9, 139.0, 141.2 (×2), 143.2, 143.4, 153.9 (×2), 154.3, 154., 172.3, 206.6. MALDI-MS: $[M+Na]^+$ $C_{137}H_{142}Cl_6N_2NaO_{34}$, calcd 2591.7473, obsd 2591.4341.

Benzyl [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-*α*-D-mannopyranosyl-(1→3)]-[6-*O*-levulinoyl-3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (10).



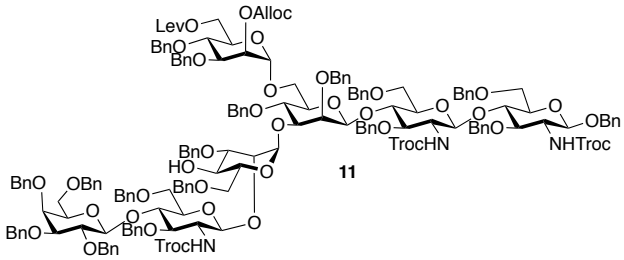
10

N-Phenyl trifluoroacetimidate donor **2** (468 mg, 380 μmol), pentasaccharide acceptor **6** (475 mg, 190 μmol), were dissolved in DCM (45 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−60 °C), followed by addition of TfOH (6.7 μL, 76 μmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise

from −60 °C to −20 °C, before quenching with Et_3N (10 µL). The reaction mixture was washed with aq. $NaHCO_3$ and extracted with DCM (2 x 50 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 2.5:1:1, v:v:v) to afford **10** (650 mg, 97%) as an amorphous white solid. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.01 (s, 3H, lev CH_2COCH_3), 2.36 (t, *J* = 6.8 Hz, 2H, lev $COOCH_2CH_2$), 2.50-2.53 (m, 2H, lev $COOCH_2CH_2$), 2.96 (d, *J* = 7.3 Hz, 1H), 3.00 (d, *J* = 9.5 Hz, 2H, GlcN-2 H-5, Man-3 H-5), 3.21 (s, 1H, GlcN-2 H-3), 3.25-3.32 (m, 8H, GlcN-2 H-6a, GlcN-2 H-2, GlcN-1 H-5, Gal-6 H-3, GlcN-5 H-2), 3.39-3.55 (m, 14H, GlcN-2 H-6b, GlcN-1 H-2, GlcN-1 H-3, Man-4' H4, Man-4' H-5, GlcN-1 H6a, Man-3 H-3), 3.63 (dt, *J* = 6.9, 3.6 Hz, 2H, GlcN-1 H-6b), 3.69-3.74 (m, 4H, Man-3 H-4, Man-4 H-4, Gal-6 H-2, Man-4' H-3), 3.76-3.88 (m, 7H, Man-3 H-2, Gal-6 H-4, Man-4 H-3, GlcN-2 H-4, GlcN-1 H-4), 3.97-3.99 (m, 3H, Man-4 H-2, Man-4' H-6a, Man-4' H-6b), 4.10-4.17 (m, 4H, GlcN-5 H-1, C*H*HPh, C*H*HPh, C*H*HPh), 4.22-4.55 (m, 31H, NH, CH*H*Ph, GlcN-2 H-1, CH*H*Ph, CH*H*Ph, C*H*HPh, Gal-6 H-1, C*H*HPh, C*H*HPh, C*H*HPh, C*H*HPh, alloc CH*H*-CH=CH_2, CH*H*Ph, CH*H*Ph, alloc C*H*H-CH=CH_2, C*H*HPh, C*H*HPh, GlcN-1 H-1, Man-3 H-1, C*H*HPh, C*H*HPh, Nap CH*H*), 4.60 (dd, *J* = 12.4, 8.1 Hz, 4H, CH*H*Ph, CH*H*Ph), 4.64-4.66 (m, 2H, CH*H*Ph), 4.70 (d, *J* = 11.7 Hz, 2H, CH*H*Ph), 4.73-4.79 (m, 7H, C*H*HPh, CH*H*Ph, Man-4' H-1, CH*H*Ph, CH*H*Ph, NH), 4.84-4.88 (m, 4H, CH*H*Ph, CH*H*Ph, CH*H*Ph), 4.91 (d, *J* = 16.3 Hz, 2H, Nap C*H*H, NH), 4.97 (s, 1H, Man-4 H-1), 5.02 (s, 1H, Man-4' H-2), 5.12 (dd, *J* = 10.5, 1.0 Hz, 1H, alloc CH=CH*H*), 5.21 (dd, *J* = 17.2, 1.3 Hz, 1H, alloc CH=C*H*H), 5.75 (dd, *J* = 17.1, 10.6 Hz, 1H, alloc C*H*=CH_2), 6.99-7.25 (m, 84H, 84x aromatic CH), 7.31 (d, *J* = 7.5 Hz, 2H, 2x aromatic CH), 7.37 (dt, *J* = 6.4, 3.2 Hz, 2H, 2x aromatic CH), 7.51 (s, 1H, aromatic CH), 7.64 (dd, *J* = 9.1, 2.9 Hz, 2H, 2x aromatic CH), 7.72 (dd, *J* = 6.0, 3.4 Hz, 1H, aromatic CH). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 27.8, 29.7, 37.8, 56.3, 56.6, 57.4, 60.3, 63.1, 66.7, 68.1, 68.2, 68.3, 68.4, 68.6, 69.8, 70.0, 70.5, 70.8, 71.2, 71.8, 72.5, 72.7, 72.9, 73.0, 73.1 (×2), 73.4 (×2), 73.5, 73.6 (×2), 73.8, 74.2 (×2), 74.3 (×2), 74.5, 74.6, 74.8 (×2), 75.1, 76.2, 76.5, 77.7, 77.8, 78.1, 78.4, 78.6, 79.8, 80.3, 82.3, 95.5, 95.6, 95.7, 97.3, 99.5, 99.6, 99.9, 100.2, 101.1, 102.7, 118.9, 125.6, 125.9, 126.0 126.2, 126.3, 127.1, 127.3 (×3), 127.4 (×2), 127.5 (×2), 127.6 (×4), 127.7 (×2), 127.8 (×3), 127.9 (×2), 128.0 (×3), 128.1 (×2), 128.2 (×3), 128.3(×3), 128.4, 128.5, 128.6, 131.4, 132.8, 133.2, 136.1, 137.2, 137.8 (×2), 137.9, 138.0, 138.1 (×2), 138.2, 138.4 (×2), 138.6, 138.7 (×2), 138.9, 153.8 (×2), 154.2, 172.2, 206.7. $^1J_{C1,H1}$ = GlcN-1 165 Hz, GlcN-2 164 Hz, Man-3 158 Hz, Man-4

174 Hz, Man-4' 174 Hz, GlcN-5 161 Hz, Gal-6 165 Hz.. MALDI-MS: $[M+Na]^+$ $C_{190}H_{198}Cl_9N_3NaO_{43}$, calcd 3547.0494, obsd 3548.6545.

Benzyl [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→3)]-[6-*O*-levulinoyl-3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (11).

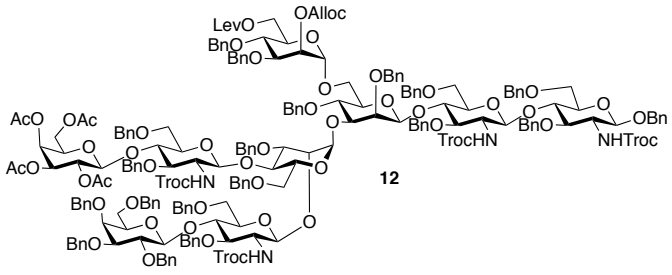


11

DDQ (7.7 mg, 34 μmol) was added to a cooled (0 °C) solution of heptasaccharide **10** (100 mg, 28.3 μmol) in a mixture of DCM (6 mL) and H_2O (0.6 mL). The resulting mixture was stirred at room temperature for 3 h. The mixture was diluted with DCM (30 mL) and the organic phase was washed with H_2O until the solution became colorless. The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 2.5:1:1, v:v:v) to afford acceptor **11** (72.7 mg, 76%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.02 (s, 3H, lev CH_2COCH_3), 2.37 (t, *J* = 6.8 Hz, 2H, lev $COOCH_2CH_2$), 2.50-2.54 (m, 2H, lev $COOCH_2CH_2$), 2.92 (td, *J* = 4.7, 3.3 Hz, 1H), 2.99 (d, *J* = 6.7 Hz, 2H, GlcN-2 H-5), 3.25-3.33 (m, 9H, GlcN-2 H-3, GlcN-2 H-6a, GlcN-2 H-2, GlcN-5 H-2, GlcN-1 H-5), 3.39-3.59 (m, 15H, GlcN-2 H-6b, GlcN-1 H-2, Man-4 H-3, Man-4' H-4, GlcN-1 H-6a, GlcN-1 H-3, Man-4' H-5), 3.63 (dt, *J* = 11.5, 6.1 Hz, 1H, GlcN-1 H-6b), 3.66-3.74 (m, 6H, Man-4 H-4, Gal-6 H-2, Man-4' H-3), 3.77-3.81 (m, 3H, Man-3 H-2), 3.83 (dd, *J* = 17.7, 8.9 Hz, 1H, GlcN-2 H-4), 3.88 (t, *J* = 7.9 Hz, 1H, GlcN-1 H-4), 3.94 (s, 1H, Man-4 H-2), 3.97-4.00 (m, 3H, GlcN-5 H-1, Man-4' H-6a, Man-4' H-6b), 4.04 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.14-4.21 (m, 5H, C*H*HPh, C*H*HPh, C*H*HPh, CH*H*Ph), 4.22-4.32 (m, 7H, C*H*HPh, CH*H*Ph, GlcN-2 H-1, NH, Gal-6 H-1, CH*H*Ph), 4.34-4.52 (m, 19H, C*H*HPh, C*H*HPh, CH*H*Ph, C*H*HPh, alloc CH_2-CH=CH_2, Man-3 H-1, GlcN-1 H-1, C*H*HPh, C*H*HPh, C*H*HPh, C*H*HPh), 4.58-4.63 (m, 6H, CH*H*Ph, CH*H*Ph), 4.66-4.73 (m, 4H, CH*H*Ph, CH*H*Ph, C*H*HPh), 4.77 (dt, *J* = 11.7, 5.9 Hz, 5H, CH*H*Ph, Man-4' H-1, CH*H*Ph), 4.86 (td, *J* = 12.6, 3.6 Hz, 4H, CH*H*Ph, CH*H*Ph, CH*H*Ph), 4.96 (s, 1H, Man-4 H-1), 5.02 (s, 1H, Man-4' H-2), 5.12 (dd, *J* = 10.4, 1.1 Hz, 1H, alloc CH=CH*H*), 5.21 (dd, *J* = 17.2, 1.4 Hz, 1H,

alloc CH=C*H*H), 5.75 (dd, *J* = 17.1, 10.5 Hz, 1H, alloc C*H*=CH_2), 6.98-7.01 (m, 3H, 3x aromatic CH), 7.03-7.09 (m, 9H, 9x aromatic CH), 7.09-7.25 (m, 71H, 71x aromatic CH), 7.33 (t, *J* = 7.2 Hz, 2H, 2x aromatic CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.9, 29.8, 37.9, 56.4, 56.6, 57.5, 63.1, 66.8, 68.2, 68.3, 68.4, 68.5, 68.7, 69.9, 70.2, 70.5, 70.9, 71.3, 71.9, 72.6, 72.7, 73.0, 73.1, 73.4, 73.5, 73.6, 73.7, 73.9, 74.2, 74.3, 74.4, 74.6 (×3), 74.8, 75.1 (×2), 75.2, 76.2, 76.7, 76.8, 77.7, 77.9, 78.5, 79.9, 80.0, 82.4, 95.6, 95.7, 97.4, 99.6, 99.9, 100.3, 101.0, 102.9, 119.0, 126.1, 127.2, 127.3, 127.4 (×5), 127.5 (×3), 127.7 (×3), 127.8, 127.9, 128.0 (×3), 128.1, 128.2 (×3), 128.3(×4), 128.4 (×2), 128.5 (×2), 128.6 (×2), 131.4, 137.3, 137.9 (×3), 138.0 (×3), 138.2, 138.3, 138.4, 138.5, 138.6, 138.7, 138.9 (×2), 139.0 (×2), 153.9 (×2), 154.3, 172.2, 206.7; MALDI-MS: $[M+Na]^+$ $C_{179}H_{190}Cl_9N_3NaO_{43}$, calcd 3406.9868, obsd 3406.6396.

Benzyl [[2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)]-[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→4)]-3,6-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→3)]-[6-*O*-levulinoyl-3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (12).

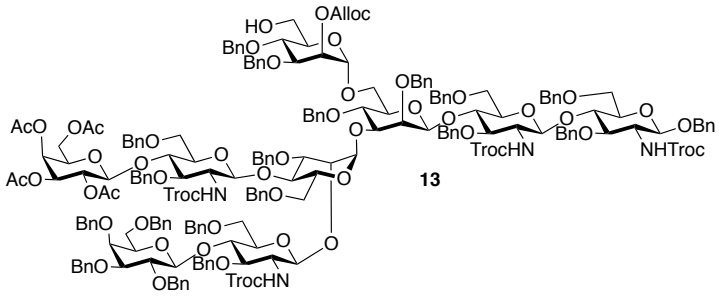


12

N-Phenyl trifluoroacetimidate donor **3** (33 mg, 31.8 μmol), heptasaccharide acceptor **11** (54 mg, 15.9 μmol), were dissolved in DCM (10 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−60 °C), followed by addition of TfOH (0.56 μL, 6.36 μmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise from −60 °C to −20 °C, before quenching with Et_3N (10 μL). The reaction mixture was washed with aq. $NaHCO_3$ and extracted with DCM (2 x 50 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 2:1:1, v:v:v) to afford nonasaccharide **12** (63.2 mg, 94%) as an amorphous white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.89 (t, *J* = 12.7 Hz, 9H, 3x

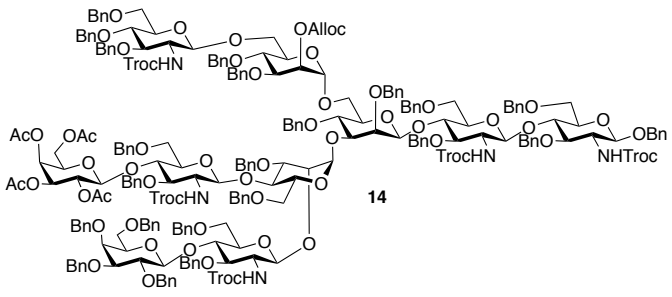
$COCH_3$), 1.99 (d, J = 0.5 Hz, 6H, $COCH_3$, lev CH_2COCH_3), 2.37 (t, J = 6.7 Hz, 2H, lev $COOCH_2CH_2$), 2.51-2.54 (m, 2H, lev $COOCH_2CH_2$), 2.86-2.89 (m, 1H, Man-3 H-5), 2.92-2.94 (m, 1H), 3.02-3.08 (m, 1H, GlcN-2 H-5), 3.14-3.29 (m, 10H, GlcN-2 H-3, GlcN-2 H-2, Gal-6 H-3, GlcN-1 H-5), 3.33-3.37 (m, 3H, GlcN-2 H-6a), 3.39-3.61 (m, 13H, Gal-8 H-5, GlcN-2 H-6b, GlcN-1 H-2, Man-3 H-3, GlcN-1 H-6a, GlcN-1 H-3), 3.61-3.69 (m, 3H, GlcN-1 H-6b, Gal-6 H-2, GlcN-5 H-2), 3.69-3.93 (m, 15H, Man-3 H-4, Man-4' H-3, Gal-8 H-6a, Man-4 H-3, Man-3 H-2, Gal-8 H-6b, GlcN-2 H-4, GlcN-1 H-4, Man-4 H-2), 3.96-4.07 (m, 3H, GlcN-5 H-1), 4.14-4.21 (m, 3H, C*H*HPh, C*H*HPh, NH), 4.21-4.56 (m, 34H, CH*H*Ph, Gal-6 H-1, C*H*HPh, C*H*HPh, GlcN-2 H-1, Gal-8 H-1, C*H*HPh, CH*H*Ph, NH, C*H*HPh, CH*H*Ph, alloc CH_2-CH=CH_2, C*H*HPh, C*H*HPh, GlcN-1 H-1, GlcN-7 H-1, Man-3 H-1, C*H*HPh, C*H*HPh), 4.58-4.81 (m, 18H, CH*H*Ph, CH*H*Ph, Gal-8 H-3, CH*H*Ph, CH*H*Ph, C*H*HPh, Man-4' H-1, CH*H*Ph, CH*H*Ph), 4.82-4.98 (m, 8H, CH*H*Ph, Man-4 H-1, CH*H*Ph, NH, Gal-8 H-2), 5.02 (s, 1H, Man-4' H-2), 5.11-5.16 (m, 2H, alloc CH=C*H*H, Gal-8 H-4), 5.21 (d, J = 17.1 Hz, 1H, alloc CH=CH*H*), 5.73-5.78 (m, 1H, alloc C*H*=CH_2), 6.94-7.29 (m, 93H, 93x aromatic CH), 7.39 (d, J = 7.5 Hz, 2H, 2x aromatic CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.5, 20.6, 20.9, 27.8, 29.6 29.8, 37.8, 56.3, 57.0, 57.4, 57.7, 60.5, 63.1, 66.7, 67.4, 68.1, 68.3, 68.6, 69.2, 69.8, 70.3, 70.5, 70.7, 71.3, 71.8, 71.9, 72.5, 72.7, 72.9, 73.1 (×2), 73.2, 73.3, 73.4, 73.5, 73.6, 73.7, 74.1, 74.2, 74.3, 74.4, 74.5, 74.6, 74.8, 75.1 (×2), 75.4, 76.6, 77.9, 78.3, 78.4, 78.6, 78.8, 79.9, 82.2, 95.6, 95.7, 97.3, 99.5 (×2), 100.2, 100.8, 101.1, 102.7, 118.9, 126.1, 127.0, 127.1, 127.2, 127.3 (×2), 127.4, 127.5 (×2), 127.6 (×2), 127.7 (×2), 127.8 (×2), 127.9, 128.0 (×2), 128.1 (×3), 128.2 (×3), 128.3 (×2), 128.4 (×2), 128.5 (×2), 128.6 (×2), 128.9, 129.4, 131.4, 137.2, 137.8 (×2), 138.0, 138.2 (×2), 138.3, 138.4, 138.6 (×2), 138.7, 139.0 (×2), 153.8 (×2), 154.2, 169.4, 170.0, 170.1 (×2), 172.2, 206.6. $^1J_{C1,H1}$ = GlcN-1 164 Hz, GlcN-2 163 Hz, Man-3 158 Hz, Man-4 172 Hz, Man-4' 175 Hz, Gal-6 168 Hz, Gal-8 170 Hz. MALDI-MS: $[M+Na]^+$ $C_{216}H_{232}Cl_{12}N_4NaO_{58}$, calcd 4252.1488, obsd 4252.9712.

Benzyl [[2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)]-[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→4)]-3,6-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→3)]-[3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (13).



Hydrazine acetate (1.3 mg, 14.2 μmol) was added to a solution of nonasaccharide **12** (50 mg, 11.8 μmol) in a mixture of DCM (5 mL) and MeOH (0.5 mL) and the resulting mixture was stirred at room temperature for 5 h. The mixture was concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography (hexanes:EtOAc:DCM, 2.5:1:1, v:v:v) to afford acceptor **13** (41.3 mg, 85%). ^{1}H NMR (800 MHz, $CDCl_3$): δ 1.95 (s, 3H, Ac), 1.96 (s, 3H, Ac), 1.97 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.95-3.02 (m, 2H), 3.12-3.13 (m, 1H), 3.26-3.30 (m, 5H), 3.35-3.68 (m, 24H), 3.72-3.77 (m, 3H), 3.81-3.95 (m, 11H), 4.00-4.12 (m, 2H), 4.14-4.27 (m, 2H), 4.30-4.33 (m, 4H), 4.38-4.57 (m, 27H), 4.65-4.74 (m, 11H), 4.76-4.87 (m, 10H), 4.91-4.95 (m, 3H), 4.99-5.05 (m, 5H), 5.13 (br, 1H), 5.20-5.23 (m, 2H), 5.26-5.34 (m, 1H), 5.86-5.90 (m, 1H, Alloc), 7.03 (br, 2H), 7.08-7.35 (m, 91H), 7.45-7.46 (m, 2H); MALDI-MS: $[M+Na]^+$ $C_{211}H_{226}C_{l12}N_4NaO_{56}$, calcd 4154.1120, obsd 4153.8813.

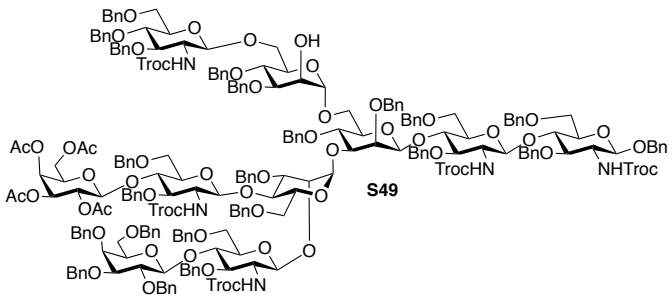
Benzyl [[2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)]-[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→4)]-3,6-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→3)]-[3,4,6-tri-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-*O*-allyloxycarbonyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (14).



Glucosamine donor **4** (46.2 mg, 58.0 μmol), nonasaccharide acceptor **13** (120 mg, 29 μmol), were dissolved in DCM (8 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−60 °C), followed by addition of TfOH (1 μL, 11.6 μmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise from −60 °C to −20 °C, before quenching with Et_3N (10 μL). The reaction mixture was washed with aq. $NaHCO_3$ and extracted with DCM (2 x 50 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford decasaccharide **14** as an amorphous white solid (108 mg, 78%). ^{1}H NMR (CDCl3, 600 MHz): δ 1.95 (t, *J* = 8.5 Hz, 9H, 3x $COCH_3$), 2.07 (s, 3H, $COCH_3$), 2.97 (dd, *J* = 21.9, 7.2 Hz, 2H, Man-3 H-5), 3.07-3.08 (m, 1H, GlcN-2 H-5), 3.22-3.59 (m, 27H, GlcN-2 H-3, Man-3 H-6a, GlcN-2 H-2, Gal-6 H-3, Man-3 H-6b, GlcN-5 H-2, GlcN-2 H-6a, Gal-8 H-5, GlcN-1 H-2, GlcN-2 H-6b, Man-3 H-3), 3.65-3.74 (m, 6H, GlcN-1 H-3, Man-4' H-4, Gal-6 H-2), 3.81-3.93 (m, 15H, Gal-8 H-6a, Man-4' H-3, GlcN-7' H-2, Man-4 H-3, Gal-6 H-4, Man-3 H-2, Man-3 H-4, Gal-8 H-6b, GlcN-2 H-4), 3.98 (s, 1H, Man-4 H-2), 4.13 (t, *J* = 2.0 Hz, 2H, GlcN-5 H-1), 4.18-4.24 (m, 5H, C*H*HPh, C*H*HPh), 4.30-4.38 (m, 10H, GlcN-2 H-1, NH, C*H*HPh, CH*H*Ph, Gal-6 H-1, Gal-8 H-1, C*H*HPh, C*H*HPh), 4.40-4.85 (m, 52H, GlcN-7' H-1, C*H*HPh, CH*H*Ph, GlcN-1 H-1, GlcN-7 H-1, C*H*HPh, C*H*HPh, CH*H*Ph, Man-3 H-1, C*H*HPh, CH*H*Ph, CH*H*Ph, C*H*HPh, CH*H*Ph, Gal-8 H-3, CH*H*Ph, Man-4' H-1, C*H*HPh), 4.89-

5.04 (m, 8H, CH*H*Ph, NH, CH*H*Ph, CH*H*Ph, Man-4 H-1, CH*H*Ph, Gal-8 H-2), 5.08 (s, 1H, Man-4' H-2), 5.17 (d, *J* = 10.5 Hz, 1H, alloc CH=CH*H*), 5.22 (d, *J* = 3.2 Hz, 1H, Gal-8 H-4), 5.28 (dd, *J* = 17.2, 1.1 Hz, 1H, alloc CH=C*H*H), 5.79-5.84 (m, 1H, alloc C*H*=CH_2), 7.00-7.35 (m, 107H, 107x aromatic CH), 7.46 (d, *J* = 7.5 Hz, 2H, 2x aromatic CH), 7.52 (dd, *J* = 5.7, 3.3 Hz, 0.5H, 0.5x aromatic CH), 7.70 (dd, *J* = 5.7, 3.3 Hz, 0.5H, 0.5x aromatic CH). ^{13}C NMR (200 MHz, $CDCl_3$): δ 20.5, 20.6, 20.9, 29.7, 56.3, 57.0, 57.3, 57.5, 57.8, 60.5, 66.6, 66.7, 67.4, 67.6, 68.1, 68.3, 68.6, 68.9, 69.3, 69.7, 70.3, 70.5, 70.8, 71.2, 71.7, 72.0, 72.5, 72.8, 72.9, 73.1, 73.4, 73.9, 74.0, 74.2, 74.4, 74.5, 74.6, 74.8, 75.1, 75.5, 76.3, 76.6, 78.1, 78.3, 78.6, 78.9, 79.9, 80.5, 82.2, 95.6, 95.7, 97.4, 99.5 (×2), 97.3, 100.4, 100.9, 101.2, 102.7, 119.0, 127.1, 127.0, 127.1, 127.3 (×2), 127.4 (×2), 127.5, 127.6 (×2), 127.7 (×2), 127.8 (×2), 127.9, 128.0 (×2), 128.1 (×2), 128.2 (×2), 128.3 (×2), 128.4 (×2), 128.5 (×2), 128.6, 128.7, 131.4, 137.3, 137.8, 138.0 (×2), 138.2 (×2), 138.4, 138.6, 138.8, 139.0, 139.1, 153.8 (×2), 154.3, 169.4, 170.0, 170.1, 170.2. $^{1}J_{C1,H1}$ = GlcN-1 163 Hz, GlcN-2 163 Hz, Man-3 160 Hz, Man-4 173 Hz, Man-4' 177 Hz, GlcN-5 158 Hz, Gal-6 167 Hz, GlcN-7 157 Hz, Gal-8 169 Hz, GlcN-7' 163 Hz. MALDI-MS: $[M+Na]^+$ $C_{241}H_{256}Cl_{15}N_5NaO_{62}$, calcd 4759.2258, obsd 4761.1192.

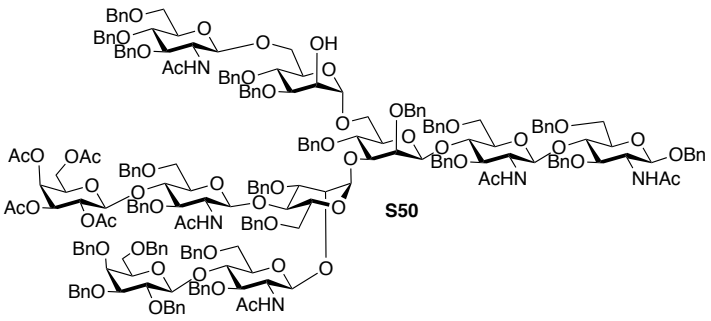
Benzyl [[2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)]-[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→4)]-3,6-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→3)]-[3,4,6-tri-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S49).



Tetrakis(triphenylphosphine) palladium (12.2 mg, 10.6 μmol) was added to a solution of decasaccharide **14** (100 mg, 21.1 μmol) in a mixture of THF (20 mL) and H_2O (2 mL) and the resulting mixture was stirred at room temperature overnight, after which it was concentrated *in vacuo* and the residue was azeotropically dried with toluene

(3x5 mL). The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford **S49** (94 mg, 96%) as an amorphous white solid. ^{1}H NMR (CDCl3, 600 MHz): δ 1.88 (t, *J* = 6.4 Hz, 9H, 3x $COCH_3$), 1.99 (s, 3H, $COCH_3$), 2.20 (m, 1H, OH), 2.88-2.93 (m, 2H), 3.03-3.04 (m, 1H, GlcN-2 H-5), 3.12-3.28 (m, 11H, GlcN-2 H-3, Gal-6 H-3, GlcN-5 H-2, GlcN-1 H-5), 3.32-3.53 (m, 17H, GlcN-2 H-2, GlcN-2 H-6a, Gal-8 H-5, GlcN-1 H-2, GlcN-2 H-6b, Man-3 H-3, GlcN-1 H-6a, GlcN-1 H-3), 3.58-3.60 (m, 4H), 3.66 (t, *J* = 9.3 Hz, 4H, GlcN-1 H-6b, Gal-6 H-2), 3.70-3.91 (m, 16H, Gal-8 H-6a, Man-4' H-2, Man-3 H-2, Man-4 H-3, Gal-8 H-6b, GlcN-2 H-4, GlcN-1 H-4, Man-4 H-2), 4.02-4.16 (m, 6H, NH, GlcN-5 H-1, C*H*HPh, C*H*HPh), 4.21-4.33 (m, 10H, GlcN-2 H-1, C*H*HPh, CH*H*Ph, Gal-6 H-1, C*H*HPh, GlcN-7' H-1, Gal-8 H-1, C*H*HPh, C*H*HPh, CH*H*Ph), 4.35-4.62 (m, 32H, C*H*HPh, CH*H*Ph, C*H*HPh, GlcN-1 H-1, C*H*HPh, C*H*HPh, C*H*HPh, GlcN-7 H-1, CH*H*Ph, Man-3 H-1, CH*H*Ph, C*H*HPh, CH*H*Ph), 4.69 (td, *J* = 23.5, 9.8 Hz, 13H, CH*H*Ph, Gal-8 H-3, CH*H*Ph, CH*H*Ph, Man-4' H-1, CH*H*Ph, C*H*HPh), 4.78 (d, *J* = 12.1 Hz, 2H, CH*H*Ph), 4.83-4.98 (m, 7H, CH*H*Ph, NH, Man-4 H-1, CH*H*Ph, Gal-8 H-2), 5.03-5.04 (m, 1H, NH), 5.15 (d, *J* = 3.4 Hz, 1H, Gal-8 H-4), 6.94-7.27 (m, 108H, 8x aromatic CH), 7.39 (d, *J* = 7.5 Hz, 2H, 2x aromatic CH).MALDI-MS: $[M+Na]^+$ $C_{237}H_{252}Cl_{15}N_5NaO_{60}$, calcd 4675.2047, obsd 4676.5065.

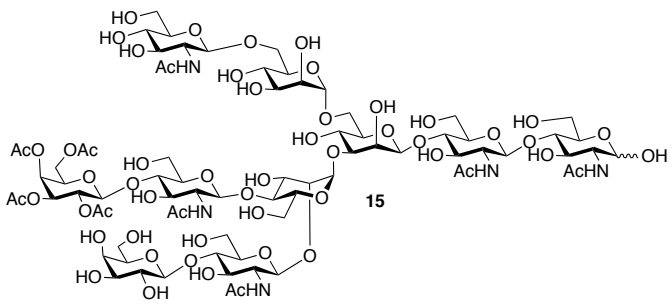
Benzyl [[2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-acetamido-*β*-D-glucopyranosyl-(1→2)]-[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-acetamido-*β*-D-glucopyranosyl-(1→4)]-3,6-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→3)]-[3,4,6-tri-*O*-benzyl-2-deoxy-2-acetamido-*β*-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-acetamido-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-acetamido-*β*-D-glucopyranoside (S50).



Zn powder (0.25 g, 3.86 mmol) was added, slowly, to a cooled (0 °C) solution of compound **S49** (90 mg, 19.3 μmol) in MeOH (6 mL), AcOH (3 mL) and DCM (3 mL) and the mixture was stirred under an atmosphere of N_2 at room temperature for 2 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The resulting residue was diluted with DCM (50 mL), washed with a

saturated aqueous solution of $NaHCO_3$ until a neutral pH was achieved and then the organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The mixture of the obtained solid, MeOH (6 mL) and Ac_2O (99 μL, 0.97 mmol) was stirred overnight at room temperature and was quenched by adding one drop of water. After which it was concentrated *in vacuo* and the residue was azeotropically dried with toluene (3x5 mL). The resulting residue was purified by silica gel column chromatography (toluene:acetone, 3:2, v:v) to afford the desired compound **S50** (40 mg, 52% for 2 steps), which was used in the next step.

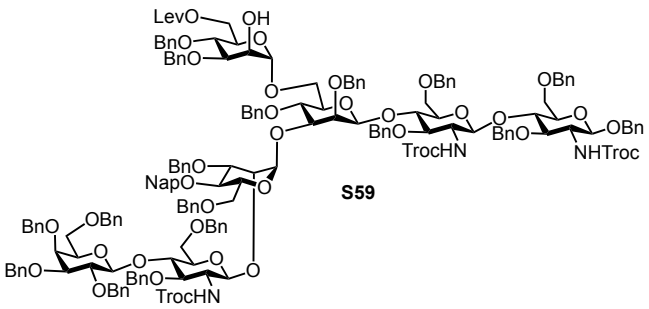
[[*β*-D-*N*-Acetyllactosamine(1→2)]-[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-*β*-D-*N*-acetyl glucosamine-(1→4)]-*α*-D-mannopyranosyl-(1→3)]-[-*β*-D-glucopyranosyl-(1→6)-*α*-D-mannopyranosyl-(1→6)]-[-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-2-acetamido-*β*-D-glucopyranosyl]-(1→4)-2-deoxy-2-acetamido-*β*-D-glucopyranoside (15).



To a solution of compound **S50** (27 mg) in MeOH (8 mL) and H_2O (1 mL), $Pd(OH)_2$ (50 mg) was added and the resulting mixture was stirred under H_2 at room temperature for 36 h, after which it was filtered and the filtrate was concentrated *in vacuo*. The resulting residue was diluted with H_2O (15 mL) and washed with DCM (5 mL×3) and EtOAc (5 mL×3) and the aqueous phase was lyophilized. The residue was re-constituted in H_2O (3 mL) and lyophilized to afford decasaccharide **15** (12.5 mg, 92%) as an amorphous white solid. ^{1}H NMR (D_2O, 900 MHz): δ 2.02 (s, 3H, $COCH_3$), 2.03-2.05 (m, 9H, 3x $COCH_3$), 2.07 (s, 6H, 2x $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.16 (s, 3H, $COCH_3$), 2.22 (d, J = 5.2 Hz, 3H, $COCH_3$), 3.43-3.47 (m, 2H, GlcNAc-7' H-5), 3.50-3.52 (m, 1H, GlcNAc-1β H-4), 3.53-3.58 (m, 5H, Gal-6 H-2, GlcNAc-7' H-4, GlcNAc-7 H-5, GlcNAc-5 H-5, Man-4 H-6a), 3.60-3.69 (m, 9H, Gal-6 H-3, GlcNAc-2 H-4, GlcNAc-1β H-3, Man-3 H-4, Man-4 H-4, Man-4' H-4, GlcNAc-1α H-3, GlcNAc-1β H-2), 3.69-3.79 (m, 26H, GlcNAc-5 H-3, GlcNAc-7 H-4, GlcNAc-7' H-3, GlcNAc-7' H-2, GlcNAc-2 H-3, GlcNAc-5 H-2, GlcNAc-7 H-3, Gal-6 H-5, Man-3 H-3, Man-4' H-6a, Man-4' H-5, Man-4 H-5, GlcNAc-2 H-2, GlcNAc-7 H-2), 3.80-3.90 (m, 10H, Man-4 H-6b, Man-4' H-3, Gal-6 H-4, GlcNAc-1α H-2), 3.92 (d, J = 3.4 Hz, 2H), 3.93-3.97 (m, 3H, Man-4' H-2), 4.03 (dd, J = 9.2, 3.0 Hz, 1H, Man-4 H-3), 4.16 (d, J = 9.6 Hz, 1H, Man-4' H-6b), 4.22 (dt, J = 11.8, 6.3 Hz, 3H, Man-3 H-2, Man-4 H-2, Gal-8 H-6a), 4.27 (td, J = 12.0, 5.3 Hz, 2H, Gal-8

H-6b, Gal-8 H-5), 4.45 (d, *J* = 7.8 Hz, 1H, Gal-6 H-1), 4.54 (td, *J* = 17.0, 8.4 Hz, 3H, GlcNAc-7 H-1, GlcNAc-7' H-1, GlcNAc-5 H-1), 4.60 (t, *J* = 7.8 Hz, 1H, GlcNAc-2 H-1), 4.69 (d, *J* = 7.8 Hz, 0.4H, GlcNAc-1β H-1), 4.76 (s, 1H, Man-3 H-1), 4.87 (s, 1H, Man-4' H-1), 4.94 (d, *J* = 8.0 Hz, 1H, Gal-8 H-1), 5.11-5.14 (m, 2H, Man-4 H-1, Gal-8 H-3), 5.18 (d, *J* = 2.5 Hz, 0.5 H, GlcNAc-1α H-1), 5.26 (dd, *J* = 10.3, 3.3 Hz, 1H, Gal-8 H-2), 5.48 (d, *J* = 3.3 Hz, 1H, Gal-8 H-4). MALDI-MS: $[M+Na]^+$ $C_{78}H_{125}N_5NaO_{55}$, calcd 2034.7036, obsd 2034.5044.

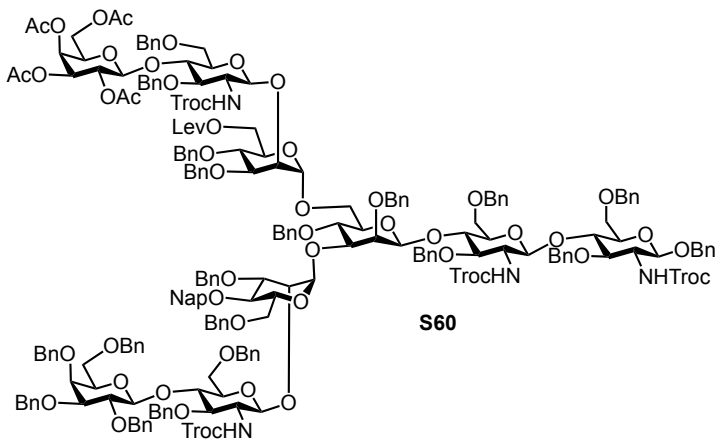
Benzyl [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-*α*-D-mannopyranosyl-(1→3)]-[6-*O*-levulinoyl-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S59).



Tetrakis(triphenylphosphine) palladium (32.7 mg, 28.4 μmol) was added to solution of heptasaccharide **10** (100 mg, 28.3 μmol) in a mixture of THF (20 mL)and H_2O (2 mL). The resulting mixture was stirred at room temperature overnight, after which it was concentrated *in vacuo* and the residue was azeotropically dried with toluene (3x5 mL). The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford compound **S59** (182 mg, 93%) as an amorphous white solid. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.99 (d, *J* = 6.5 Hz, 3H, lev CH_2COCH_3), 2.16 (s, 1H, OH), 2.34 (t, *J* = 6.6 Hz, 2H, lev $COOCH_2CH_2$), 2.49 (t, *J* = 6.7 Hz, 2H, lev COO CH_2CH_2), 2.96-3.01 (m, 3H, Gal-6 H-5, GlcN-2 H-5), 3.11 (s, 1H, GlcN-2 H-3), 3.25-3.41 (m, 8H, GlcN-2 H-6a, Gal-6 H-3, GlcN-5 H-2, GlcN-2 H-2), 3.42-3.67 (m, 15H, GlcN-1 H-2, Gal-6 H-6a, Man-3 H-3, Man-4 H-4, GlcN-1 H-3, Man-4' H-3, Gal-6 H-6b), 3.69-3.74 (m, 4H, Gal-6 H-2, Man-4' H-2), 3.80 (t, *J* = 4.9 Hz, 3H, Man-3 H-2), 3.83-3.88 (m, 4H, Gal-6 H-4, GlcN-2 H-4, GlcN-2 H-6b), 3.98 (d, *J* = 9.6 Hz, 2H, Man-4 H-2), 4.02 (d, *J* = 3.7 Hz, 1H, Man-4 H-3), 4.11 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.16 (d, *J* = 11.7 Hz, 2H, GlcN-5 H-1, C*H*HPh), 4.21 (d, *J* = 12.0 Hz, 2H, GlcN-2 H-1, C*H*HPh), 4.24-4.29 (m, 5H, CH*H*Ph, CH*H*Ph, CH*H*Ph), 4.33 (dt, *J* = 13.9, 6.9 Hz, 5H, Gal-6 H-1, C*H*HPh, C*H*HPh), 4.38-4.52 (m, 15H, CH*H*Ph, C*H*HPh, C*H*HPh, Man-3 H-1, GlcN-1 H-1, C*H*HPh), 4.56-4.66 (m, 7H,

C*H*HPh, C*H*HPh, CH*H*Ph, CH*H*Ph), 4.71-4.79 (m, 8H, C*H*HPh, CH*H*Ph, Man-4' H-1, CH_2 Nap), 4.86 (dd, *J* = 17.7, 8.7 Hz, 3H, CH*H*Ph, CH*H*Ph, CH*H*Ph), 4.94-4.98 (m, 3H, CH*H*Ph, NH, Man-4 H-1), 7.02 (ddt, *J* = 14.1, 5.1, 4.0 Hz, 8H, 8x aromatic CH), 7.04-7.25 (m, 76H, 76x aromatic CH), 7.32 (d, *J* = 7.5 Hz, 2H, 2x aromatic CH), 7.36 (dq, *J* = 6.3, 3.2 Hz, 2H, 2x aromatic CH), 7.50 (s, 1H, aromatic CH), 7.62-7.63 (m, 2H, 2x aromatic CH), 7.71 (dd, *J* = 6.0, 3.4 Hz, 1H, aromatic CH). $^1J_{C1,H1}$ = GlcN-1 164 Hz, GlcN-2 164 Hz, Man-3 158 Hz, Man-4 174 Hz, Man-4' 174 Hz, GlcN-5 162 Hz, Gal-6 163 Hz. MALDI-MS: $[M+Na]^+$ $C_{186}H_{194}Cl_9N_3NaO_{41}$, calcd 3463.0282, obsd 3469.1376.

Benzyl [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-*α*-D-mannopyranosyl-(1→3)]-[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)-6-*O*-levulinoyl-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S60).

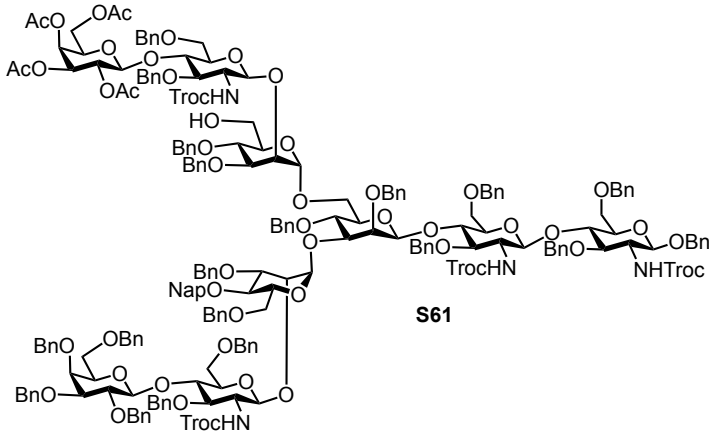


S60

N-Phenyl trifluoroacetimidate donor **3** (90 mg, 87 µL), heptasaccharide acceptor **S59** (150 mg, 43.5 µL), were dissolved in DCM (10 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−70 °C), followed by addition of TfOH (1.54 µL, 17.4 µmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise from −70 °C to −20 °C, before quenching with Et_3N (50 µL). The reaction mixture was washed with aq. $NaHCO_3$ and extracted with DCM (2 x 50 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford nonasaccharide **S60** (97 mg, 52%) as an amorphous white solid. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.03 (s, 9H, 3x $COCH_3$), 2.15

(d, *J* = 11.4 Hz, 6H, $COCH_3$, lev CH_2COCH_3), 2.45 (t, *J* = 5.8 Hz, 2H, lev $COOCH_2CH_2$), 2.63 (t, *J* = 6.6 Hz, 2H, lev $COOCH_2CH_2$), 3.04 (d, *J* = 8.1 Hz, 1H, Gal-6 H-5), 3.09-3.14 (m, 2H, GlcN-2 H-3), 3.31 (d, *J* = 1.1 Hz, 1H, GlcN-5' H-2), 3.38-3.45 (m, 8H, GlcN-2 H-2, GlcN-5 H-4, GlcN-5 H-2, Gal-6 H-3), 3.48-3.65 (m, 14H, Gal-6' H-5, Gal-6 H-6a, GlcN-1 H-2), 3.72-3.76 (m, 4H, Gal-6 H-6b, GlcN-1 H-3, GlcN-2 H-5), 3.82-3.85 (m, 4H, Man-4' H-3, Gal-5' H-3, Gal-6 H-2), 3.88-4.03 (m, 12H, Gal-6' H-6b, Man-3 H-2, GlcN-2 H-4, Gal-6 H-4, GlcN-5 H-3, Man-4 H-4, Gal-6' H-6a), 4.08 (s, 3H, Man-4 H-3, Man-4 H-2, Man-4' H-2), 4.17-4.25 (m, 4H, GlcN-5 H-1, NH, C*H*HPh, C*H*HPh), 4.28 (d, *J* = 11.7 Hz, 2H, C*H*HPh, C*H*HPh), 4.33-4.45 (m, 10H, GlcN-2 H-1, CH*H*Ph, CH*H*Ph, CH*H*Ph, C*H*HPh, Gal-6 H-1), 4.50-4.64 (m, 22H, GlcN-1 H-1, GlcN-5' H-1, Gal-6' H-1, Man-3 H-1, C*H*HPh, C*H*HPh, C*H*HPh), 4.71-4.79 (m, 10H, C*H*HPh, CH*H*Ph, CH*H*Ph, Man-4' H-1), 4.85 (dt, *J* = 10.0, 4.8 Hz, 3H, Gal-6' H-3, C*H*HPh, CH*H*Ph), 4.91 (dd, *J* = 17.6, 10.1 Hz, 7H, CH*H*Ph, CH_2 Nap), 5.00 (q, 12.0 Hz, 4H, CH*H*Ph, CH*H*Ph, NH), 5.09 (s, 1H, Man-4 H-1), 5.17 (dd, *J* = 10.2, 8.1 Hz, 1H, Gal-6' H-2), 5.29 (d, *J* = 3.3 Hz, 1H, Gal-6' H-4), 5.58 (t, *J* = 0.6 Hz, 1H, NH), 7.10-7.17 (m, 10H, 10x aromatic CH), 7.18-7.42 (m, 87H, 87x aromatic CH), 7.48 (dq, *J* = 6.3, 3.2 Hz, 2H, 2x aromatic CH), 7.62 (s, 1H, aromatic CH), 7.74-7.75 (m, 2H, 2x aromatic CH).;). $^1J_{C1,H1}$ = GlcN-1 163 Hz, GlcN-2 162 Hz, Man-3 159 Hz, Man-4 175 Hz, Man-4' 173 Hz, GlcN-5 154 Hz, Gal-6 164 Hz, GlcN-5' 156 Hz, Gal-6' 162 Hz. MALDI-MS: $[M+Na]^+$ $C_{223}H_{236}Cl_{12}N_4NaO_{56}$, calcd 4308.1902, obsd 4310.9014.

Benzyl [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-*α*-D-mannopyranosyl-(1→3)]-[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S61).

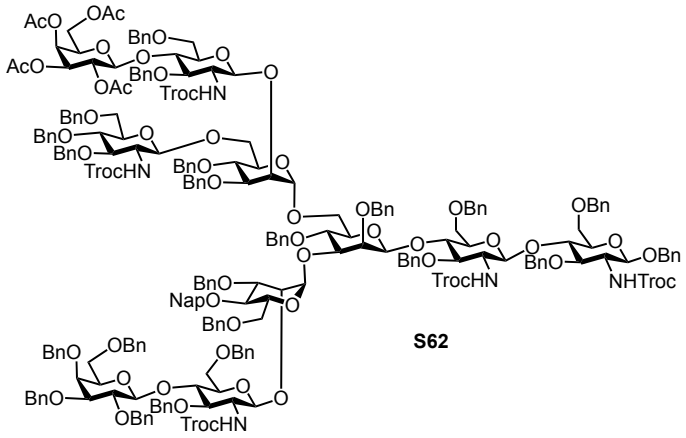


S61

Hydrazine acetate (2.3 mg, 24.6 μmol) was added to a solution of nonasaccharide **S60** (88 mg, 20.5 μmol) in a mixture of DCM (5 mL) and MeOH (0.5 mL) and the resulting mixture was stirred at room temperature for 5 h. The mixture was concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford acceptor **S61** (63.8 mg, 74%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.88 (s, 9H, 3x $COCH_3$), 2.00 (d, J = 0.6 Hz, 3H, $COCH_3$), 2.39 (td, J = 2.1, 1.1 Hz, 1H, OH), 2.91-2.97 (m, 3H, Gal-6 H-5, GlcN-2 H-5, GlcN-5 H-5), 3.08-3.09 (m, 1H, GlcN-2 H-3), 3.26-3.42 (m, 16H, GlcN-5' H-4, GlcN-5 H-4, GlcN-2 H-2, Gal-6 H-3, GlcN-5' H-2, GlcN-1 H-4, GlcN-5 H-2, Man-4' H6a, Man-4' H6b), 3.45 (t, J = 7.0 Hz, 4H, Gal-6' H-5, GlcN-1 H-2, Gal-6 H-6a), 3.53 (dt, J = 26.0, 13.9 Hz, 6H, GlcN-5' H-5), 3.62 (d, J = 6.4 Hz, 3H, GlcN-1 H-3, Gal-6 H-6b), 3.69-3.90 (m, 16H, Gal-6 H-2, Gal-6' H-6b, Man-3 H-2, Man-4 H-3, GlcN-5' H-3, Gal-6 H-4, Gal-6' H-6a, GlcN-5 H-3, GlcN-2 H-4, Man-4' H-2), 3.97 (s, 1H, Man-4 H-2), 4.00-4.08 (m, 2H, GlcN-5 H-1, NH), 4.15 (dq, J = 34.8, 11.1 Hz, 7H, GlcN-5' H-1, C*H*HPh, GlcN-2 H-1, C*H*HPh, C*H*HPh), 4.24-4.34 (m, 8H, CH*H*Ph, CH*H*Ph, CH*H*Ph, Gal-6 H-1, C*H*HPh), 4.38-4.67 (m, 30H, C*H*HPh , CH*H*Ph, C*H*HPh, C*H*HPh, C*H*HPh, GlcN-1 H-1, C*H*HPh, Man-3 H-1, Gal-6' H-1, CH*H*Ph, Man-4' H-1, CH*H*Ph, CH*H*Ph, CH*H*Ph), 4.73-4.89 (m, 15H, Man-6' H-3, C*H*HPh, C*H*HPh, CH_2 Nap, CH*H*Ph, CH*H*Ph, CH*H*Ph, NH), 4.97 (s, 1H, Man-4 H-1), 5.04-5.08 (m, 1H, Gal-6' H-2), 5.17 (d, J = 3.1 Hz, 1H, Gal-6' H-4), 6.90-7.29 (m, 97H, 97x aromatic CH), 7.35-7.38 (m, 2H, 2x aromatic CH), 7.49 (s, 1H, aromatic CH), 7.62-

7.63 (m, 2H, aromatic CH). $^{1}J_{C1,H1}$ = GlcN-1 164 Hz, GlcN-2 162 Hz, Man-3 159 Hz, Man-4 174 Hz, Man-4' 174 Hz, GlcN-5 156 Hz, Gal-6 163 Hz, GlcN-5' 160 Hz, Gal-6' 164 Hz. MALDI-MS: $[M+Na]^+$ $C_{218}H_{230}Cl_{12}N_4NaO_{54}$, calcd 4210.1534, obsd 4214.0688.

Benzyl [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-*α*-D-mannopyranosyl-(1→3)]-[[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)]-[3,4,6-tri-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy) carbonylamino-*β*-D-glucopyranosyl-(1→6)]-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside (S62).

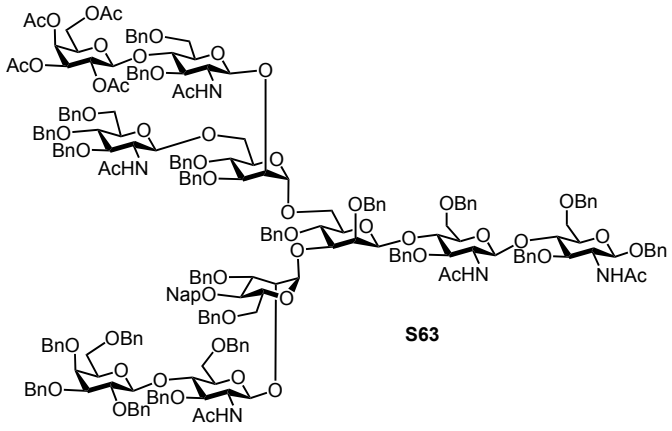


S62

Glucosamine donor **4** (22.8 mg, 28.6), nonasaccharide acceptor **S61** (60 mg, 14.3 μmol), were dissolved in DCM (8 mL), followed by addition of molecular sieves (4Å) and stirring at room temperature for 30 min, after which the reaction mixture was cooled (−60 °C), followed by addition of TfOH (5.72 μL, 0.5 μmol). The reaction mixture was stirred for 1 h, allowing the temperature to rise from −60 °C to −20 °C, before quenching with Et_3N (20 μL). The reaction mixture was washed with aq. $NaHCO_3$ and extracted with DCM (2 x 50 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (hexanes:EtOAc, 2:1, v:v) to afford decasaccharide **S62** as an amorphous white solid (52.3 mg, 76%). ^{1}H NMR (CDCl3, 500 MHz): δ 1.88 (t, *J* = 5.6 Hz, 9H, 3x $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.91-3.32 (m, 17H, Gal-6 H-3, GlcN-2 H-2), 3.37-3.96 (m, 41H, GlcN-1 H-2, Gal-6' H-5, Gal-6 H-2, Man-4 H-4, Man-4' H-3, Gal-6' H-6a, Man-3 H-2, Man-4 H-3, Gal-6 H-4, Man-2 H-2, Gal-6' H-6b), 4.04-4.17 (m, 7H, Man-4' H-2, NH, C*H*HPh, C*H*HPh, C*H*HPh, C*H*HPh), 4.28 (ddd, *J* = 21.2, 16.8, 10.4 Hz, 10H, C*H*HPh, CH*H*Ph, GlcN-2 H-1, CH*H*Ph, CH*H*Ph, C*H*HPh, C*H*HPh,

Gal-6 H-1), 4.38-4.66 (m, 39H, CH*H*Ph, GlcN-1 H-1, C*H*HPh, C*H*HPh, C*H*HPh, C*H*HPh, C*H*HPh, CH*H*Ph, C*H*HPh, Man-3 H-1, C*H*HPh, CH*H*Ph, CH*H*Ph, Gal-6' H-1, CH*H*Ph, CH*H*Ph, C*H*HPh, CH*H*Ph, CH*H*Ph, Man-4' H-1), 4.73-4.81 (m, 9H, C*H*HPh, Gal-6' H-3, CH_2 Nap, CH*H*Ph, CH*H*Ph, CH*H*Ph, CH*H*Ph), 4.85-4.92 (m, 5H, CH*H*Ph, NH, CH*H*Ph), 4.97 (s, 1H, Man-4 H-1), 5.04-5.08 (m, 1H, Gal-6' H-2), 5.18 (d, *J* = 2.8 Hz, 1H, Gal-6' H-4), 6.99-7.23 (m, 107H, 107x aromatic CH), 7.29 (d, *J* = 7.4 Hz, 2H, 2x aromatic CH), 7.33 (d, *J* = 7.3 Hz, 2H, 2x aromatic CH), 7.37 (dd, *J* = 5.2, 4.0 Hz, 2H, 2x aromatic CH), 7.50 (s, 1H, aromatic CH), 7.61-7.63 (m, 2H, 2x aromatic CH), 7.72 (t, *J* = 4.5 Hz, 1H, aromatic CH). MALDI-MS: $[M+Na]^+$ $C_{248}H_{260}Cl_{15}N_5NaO_{60}$, calcd 4815.2673, obsd 4819.6006.

Benzyl [2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-deoxy-2-acetamido-*β*-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-*α*-D-mannopyranosyl-(1→3)]-[[2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-deoxy-3,6-di-*O*-benzyl-2-(2,2,2-trichloroethoxy)-carbonylamino-*β*-D-glucopyranosyl-(1→2)]-[3,4,6-tri-*O*-benzyl-2-deoxy-2-acetamido-*β*-D-glucopyranosyl-(1→6)]-3,4-di-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)]-[2,4-di-*O*-benzyl-*β*-D-mannopyranosyl]-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-acetamido-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-acetamido-*β*-D-glucopyranoside (S63).

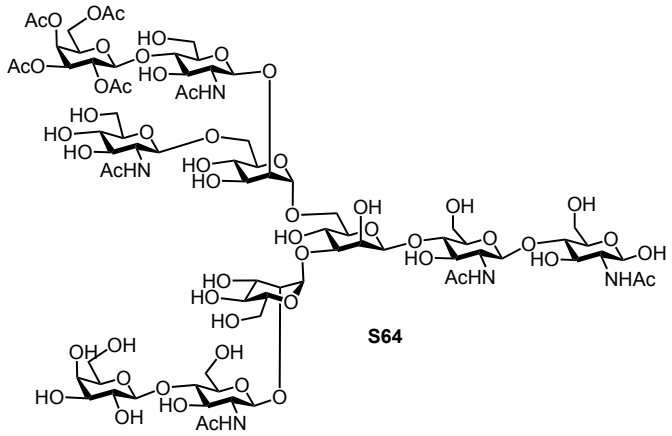


S63

Zn powder (68 mg, 1.04 mmol) was added, slowly, to a cooled (0 °C) solution of compound **S62** (50 mg, 10.4 μmol) in MeOH (3 mL), AcOH (1.5 mL) and DCM (1.5 mL) and the mixture was stirred under an atmosphere of N_2 at room temperature for 2 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The resulting residue was diluted with DCM (30 mL), washed with a saturated aqueous solution of $NaHCO_3$ until a neutral pH was achieved and then the organic layer was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The mixture of the obtained solid, MeOH (3 mL) and Ac_2O (49 μL, 0.52 mmol) was stirred overnight at room temperature and was quenched by adding one drop of water. After which it was concentrated *in vacuo* and the residue was azeotropically dried with toluene

(3x5 mL). The resulting residue was purified by silica gel column chromatography (toluene:acetone, 3:2, v:v) to afford the desired compound **S63** (21 mg, 49% for 2 steps), which was used in the next step.

[*β*-D-*N*-Acetyllactosamine-(1→2)-*α*-D-mannopyranosyl-(1→3)]-[[*β*-D-*N*-Acetyllactosamine-(1→2)]-[-*β*-D-glucopyranosyl-(1→6)]-*α*-D-mannopyranosyl-(1→6)]-[-*β*-D-mannopyranosyl]-(1→4)-[2-deoxy-2-acetamido-*β*-D-glucopyranosyl]-(1→4)-2-deoxy-2-acetamido-*β*-D-glucopyranoside (S64).



To a solution of compound **S63** (16.5 mg) in MeOH (5 mL) and H_2O (0.6 mL), $Pd(OH)_2$ (30 mg) was added and the resulting mixture was stirred under H_2 at room temperature for 36 h, after which it was filtered and the filtrate was concentrated *in vacuo*. The resulting residue was diluted with H_2O (10 mL) and washed with DCM (5 mL×3) and EtOAc (5 mL×3) and the aqueous phase was lyophilized. The residue was re-constituted in H_2O (2 mL) and lyophilized to afford decasaccharide **S64** (7.6 mg, 95%) as an amorphous white solid. ^{1}H NMR (D_2O, 800 MHz): δ 1.99-2.02 (m, 15H, 5x $COCH_3$), 2.05-2.06 (m, 6H, 2x $COCH_3$), 2.14 (s, 3H, $COCH_3$), 2.19 (s, 3H, $COCH_3$), 3.37 (t, *J* = 9.8 Hz, 1H, Man-4' H-4), 3.40-3.43 (m, 2H, GlcNAc-7' H-4, GlcNAc-7' H-5), 3.44-3.49 (m, 3H, GlcNAc-5' H-3, Man-4 H-4, GlcNAc-1b H-4), 3.50-3.60 (m, 9H, Gal-6 H-2, Man-4' H-6a, GlcNAc-7' H-3, Man-3 H-5, Man-4 H-6a, Gal-6 H-5, GlcNAc-2 H-4, GlcNAc-1a/b H-3), 3.61-3.66 (m, 4H, Gal-6 H-3, GlcNAc-1b H-2), 3.67-3.77 (m, 23H, GlcNAc-7' H-2, Man-4' H-5, GlcNAc-5' H-2, GlcNAc-5' H-5, GlcNAc-2 H-3, Man-3 H-4, Man-4 H-6a, Man-4 H-6b, Man-4 H-5, GlcNAc-5 H-2, GlcNAc-7' H-6a, Man-3 H-3, GlcNAc-2 H-2), 3.80-3.87 (m, 8H, Man-3 H-6a, Man-4' H-3, GlcNAc-5' H-4, GlcNAc-1a H-2), 3.88-3.92 (m, 5H, Man-4 H-3, Gal-6 H-4, GlcNAc-7' H-6b), 3.94 (dd, *J* = 11.9, 1.7 Hz, 1H, Man-3 H-6b), 4.06 (t, *J* = 1.5 Hz, 1H, Man-4' H-2), 4.16-4.21 (m, 4H, Man-4 H-2, Man-4' H-6b, Gal-6' H-6b, Man-3 H-2), 4.25 (td, *J* = 12.0, 5.4 Hz, 2H, Gal-6' H-6a, Gal-6' H-5), 4.43 (d, *J* = 7.8 Hz, 1H, Gal-6 H-1), 4.50 (d, *J* = 8.4 Hz, 1H, GlcNAc-7' H-1), 4.54 (dd, *J* = 10.4, 8.1 Hz, 2H, GlcNAc-5' H-1, GlcNAc-5 H-1), 4.58 (t, *J* = 7.4 Hz, 1H, GlcNAc-2 H-1), 4.66 (d, *J* = 7.9 Hz, 0.4H, GlcNAc-1b H-1), 4.73 (s, 1H, Man-3

H-1), 4.83 (s, 1H, Man-4' H-1), 4.92 (d, *J* = 8.0 Hz, 1H, Gal-6' H-1), 5.09-5.11 (m, 2H, Man-4 H-1, Gal-6' H-2), 5.16 (d, *J* = 2.7 Hz, 1H, GlcNAc-1a H-1), 5.24 (dd, *J* = 10.3, 3.4 Hz, 1H, Gal-6' H-3), 5.46 (d, *J* = 3.3 Hz, 1H, Gal-6' H-4). $^{1}J_{C1,H1}$ = GlcNAc-1α 172 Hz, GlcNAc-1β 162 Hz, GlcNAc-2 164 Hz, Man-3 161 Hz, Man-4 171 Hz, Man-4' 170 Hz, GlcNAc-5 161 Hz, Gal-6 163 Hz, GlcNAc-5' 161 Hz, Gal-6' 166 Hz, GlcNAc-7' 161 Hz. MALDI-MS: $[M+Na]^+$ $C_{78}H_{125}N_5NaO_{55}$, calcd 2034.7036, obsd 2034.8636.

2. Enzymatic Synthesis

Methods

All enzymatic reactions were performed in aqueous buffered system with the appropriate pH for each enzyme. Water was purified by NANOpure Diamond^{TM} water system (Barnstead D3750 Hollow Fibre Filter). The reactions were monitored by mass spectrometry recorded on an Applied Biosystems SCIEX MALDI TOF/TOF 5800 using dihydroxybenzoic acid as matrix and by thin layer chromatography (TLC) performed on glass plates coated with HPTLC Silica gel 60 F_{254}. TLCs were developed with appropriate eluents (EtOH:H_2O:EtOAC:AcOH, 5:2:2:0.1, v:v:v:v) or (*i*PrOH:H_2O:NH_4OH, 4:1:3, v:v:v), and the spots were visualized by UV light for nucleotides and/or dipping in 10% sulfuric acid in ethanol, followed by charring to detect sugars. Gel filtration chromatography was performed using a column (50 cm × 1 cm) packed with Sephadex^{TM} G-25 Superfine (GE Healthcare), eluted with 0.1 M NH_4HCO_3 (aq) eluent.

Mass spectrometry (MS) profiles of permethylated glycans were recorded with an Applied Biosystems SCIEX MALDI TOF/TOF 5800 using dihydroxybenzoic acid as the matrix.

All nuclear magnetic resonance (NMR) spectra were acquired on 800 MHz or 900 MHz Varian/Agilent Direct Drive spectrometers operating at 25 ^{o}C. Data were collected using standard pulse programs from the spectrometer library. Samples were dissolved into 99.96% D_2O. Chemical shifts are referenced to internal DSS at 0 ppm for compound 29, and thereafter to the GlcNAc-1 H1α set to 5.182 ppm.

For integration of 1D proton spectra, data were acquired with recycling delays of 10 seconds and a small tip angle. The residual HDO signal was suppressed by a low-power presaturation pulse.

Typically, 2D homonuclear spectra were collected as a 1750 X 512 complex point data set with a spectral width of 7.8 ppm. The “zTOCSY” sequence was run with an 80 msec dipsi-2 mixing sequence; the NOESY mixing time was 300ms. The “HSQCAD” sequence was used for the carbon-proton correlated spectra. Typically, the carbon spectral width was 80 ppm, centered at 80 ppm, and collected with 256 points.

Data was processed with iNMR (Mestrelab Research) and Mnova (Mestrelab Inc.) software with standard zero filling, linear prediction and squared cosine or Gaussian apodization functions.

Materials

The recombinant enzymes, *Helicobacter pylori* β1-3-*N*-acetylglucosaminyltransferase (β3GlcNAcT) (*46*) and *H. pylori*-α1,3-fucosyltransferase (HPα1-3FucT) (*30*) used in this study were produced and purified as described previously. ST3Gal-IV (α2-3sialyltransferase) and ST6Gal-I (α2-6sialyltransferase) were provided by Dr. K. W. Moremen (Complex Carbohydrate Research Center, Athens, GA). GalT-1 (β1-4Galactosyltransferase from bovine milk) was purchased from Sigma-Aldrich. Alkaline Phosphatase from calf intestine (CIAP) was purchased from Calbiochem EMD Millipore. Uridine 5'-diphospho-N-acetylglucosamine (UDP-GlcNAc), Uridine 5'-diphosphogalactose (UDP-Gal), Cytidine 5'-monophospho-*N*-acetylneuraminic (CMP-Neu5Ac) acid, and Guanosine 5'-diphospho-L-fucose (GDP-Fuc) were purchased from Carbosynth Limited.

NMR nomenclature

The residues of the oligosaccharides have been labeled as depicted in the **Fig. S13**. Starting from the reducing sugar, GlcNAc-1, GlcNAc-2, the β-mannoside is labeled as Man-3, the α-3 mannoside as Man-4, the α-6 mannoside as Man-4', followed by the *N*-acetylglucosamine residues as GlcNAc-5, -7, -7', and -ext, the galactosides as Gal-6, -8, -8', and -ext, the two fucosides are labeled as Fuc-1 and Fuc-2 and the sialic acids as Neu5Ac (α-3 or α-6, depending on the linkage).

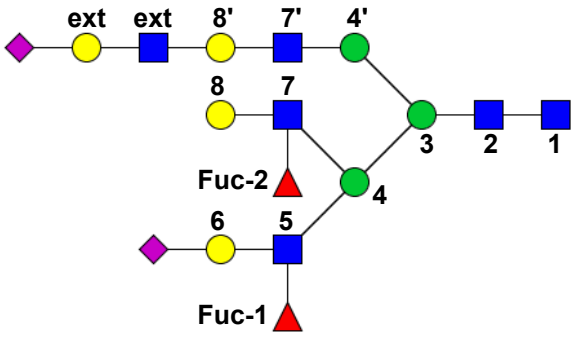


Fig. S13. Oligosaccharide residue labels.

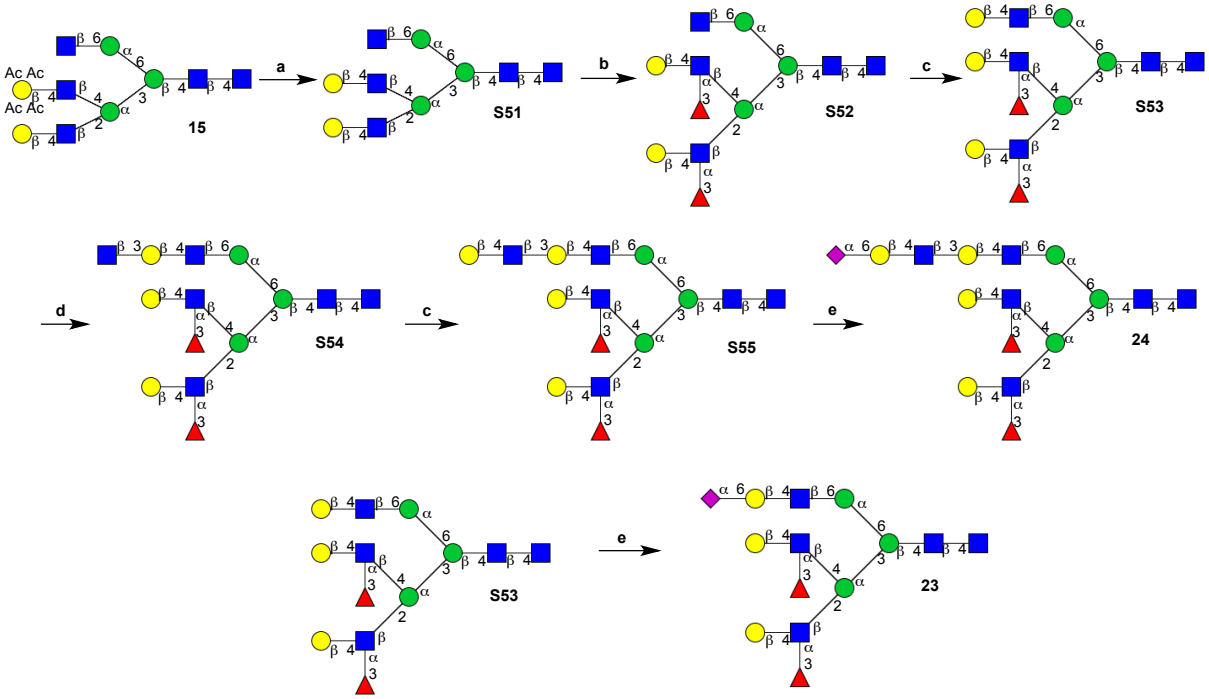


Fig. S14. Synthesis of compounds **23** and **24.**
a) NH_4OH,H_2O; b) HPα1-3FucT, GDP-Fuc; c) Gal-T1, UDP-Gal; d) β1-3GlcNAcT, UDP-GlcNAc; e) ST6Gal-I, CMP-Neu5Ac.

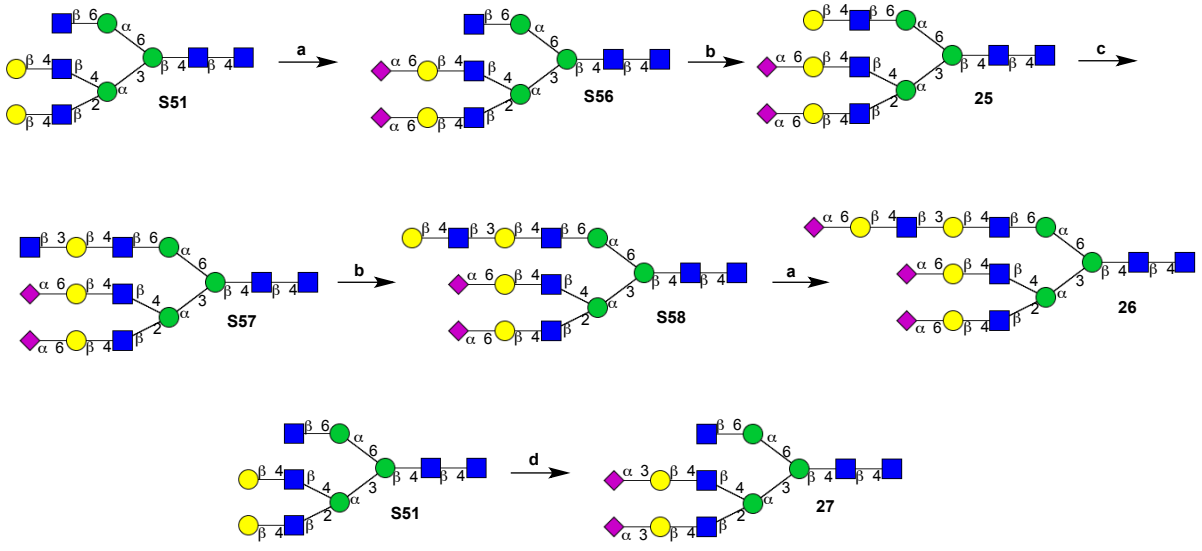


Fig. S15. Synthesis of compounds **25, 26** and **27.**
a) ST6Gal-I, CMP-Neu5Ac; b) H Gal-T1, UDP-Gal; c) β1-3GlcNAcT, UDP-GlcNAc; d) ST3Gal-IV, CMP-Neu5Ac.

General Experimental Procedures

General method for the removal of acetyl esters. Glycan (**16** or **15**) was dissolved in a mixture of H_2O and 28%-30% NH_4OH (10% in volume) to achieve a 341 μM final concentration of glycan. The reaction mixture was shaken at room temperature for 2 h. Upon completion, as indicated by MALDI, the reaction mixture was lyophilized and the residue was reconstituted in water and subjected to gel filtration over Sephadex G-25 (eluent 0.1M NH_4HCO_3). Fractions containing product were combined and lyophilized to give the respective products (**17** or **S51**) as an amorphous white solid.

General method for (α2-3) sialylation. Glycan (**15** or **S51**) and CMP-Neu5Ac (2 eq per sialic acid) were dissolved in sodium cacodylate buffer (50 mM, pH 7.6) containing BSA (0.1%). CIAP (10 mU) and ST3Gal-IV (3.3 mU/μmol substrate for mono-sialylation or 6.6 mU/μmol substrate for bis-sialylation) were added to achieve a final concentration of glycan ranging from 4-7 mM. The resulting reaction mixture was incubated at 37 ^oC for 18 h. In case TLC showed remaining starting material, additional CMP-Neu5Ac (1 or 2 eq), CIAP (10 mU), and ST3Gal-IV (3.3 mU/μmol substrate for mono-sialylation or 6.6 mU/μmol substrate for bis-sialylation) were added and incubated at 37 ^oC until no starting material could be detected. The reaction mixture was centrifuged and the supernatant subjected to gel filtration over Sephadex G-25 (eluent 0.1 M NH_4HCO_3). Fractions containing product as detected by MALDI-TOF MS, were combined and lyophilized to give the respective products (**16** or **27**) as amorphous white solids.

General method for (α2-6) sialylation. Glycan (**S51**, **21**, **S53**, **S55**, or **S58**) and CMP-Neu5Ac (2 eq per sialic acid) were dissolved in sodium cacodylate buffer (50mM, pH 7.6) containing BSA (0.1%). CIAP (10 mU) and ST6Gal-I (18.8 mU/μmol substrate for bis-sialylation or 9.4 mU/μmol substrate for mono-sialylation) were added to achieve a final concentration of glycan ranging from 3-7 mM and the resulting reaction mixture was incubated at 37 ^oC for 18 h. In case TLC showed remaining starting material, additional CMP-Neu5Ac (1 or 2 eq), CIAP (10 mU), and ST6Gal-I (18.8 mU/μmol substrate for bis-sialylation or 9.4 mU/μmol substrate for mono-sialylation) were added and incubated at 37 ^oC until no starting material could be detected. The reaction mixture was centrifuged and the supernatant subjected to gel filtration over Sephadex G-

25 (eluent 0.1 M NH_4HCO_3). Fractions containing product were combined and lyophilized to give (**S56, 22, 23, 24**, or **26**) as amorphous white solids.

General method for (α1-3) fucosylation. Glycan (**17** or **S51**) and GDP-Fucose (2 eq per fucose) were dissolved in Tris buffer (50 mM, pH 7.5) with $MnCl_2$ (10 mM). CIAP (10 mU) and HPα1-3FucT (6.6 mU/μmol of substrate) were added to achieve a final concentration of glycan ranging from 2-5 mM. The resulting mixture was incubated at 37 ^oC for 18 h. In case TLC or MS analysis showed starting material or mono-fucosylated intermediate, additional GDP-Fucose (2 eq), CIAP (10 mU), and HPα1-3FucT (6.6 mU/μmol substrate) were added and incubated at 37 ^oC until no starting material or mono-fucosylated intermediate could be detected. The reaction mixture was centrifuged and the supernatant subjected to gel filtration over Sephadex G-25 (eluent 0.1 M NH_4HCO_3). Fractions containing product were combined and lyophilized to give the respective products (**18** or **S52**) as amorphous white solids.

General method for (β1-4) galactosylation. Glycan (**18**, **20**, **S52**, **S54**, **S56**, or **S57**) and UDP-galactose (2 eq) were dissolved in Tris buffer (50 mM, pH 7.5) containing BSA (0.1%) and $MnCl_2$ (20 mM). CIAP (10 mU) and GalT-1 (3.4 mU/μmol substrate) were added to achieve a final concentration of glycan ranging from 2-5 mM. The resulting reaction mixture was incubated at 37 ^oC for 10 h. The reaction mixture was centrifuged and the supernatant subjected to gel filtration over Sephadex G-25 (eluent 0.1 M NH_4HCO_3). Fractions containing the product were combined and lyophilized to give the respective products (**19**, **21**, **S53**, **S55**, **25**, or **S58**) as amorphous white solids.

General method for installation of (β1-3) *N*-acetylglucosamine moieties. Glycan (**19**, **S53**, or **25**) and UDP-GlcNAc (1.5 eq) were dissolved in HEPES buffer (50 mM, pH 7.3) containing KCl (25 mM), $MgCl_2$ (2 mM), and dithiothreitol (1 mM). To this, CIAP (10 mU) and HP-39 (β1-3GlcNAc Transferase) (5.5 mU/μmol substrate) were added to achieve a final concentration of glycan ranging from 2-5 mM. The resulting reaction mixture was incubated at 37 ^oC for 6h. The reaction mixture was centrifuged and the supernatant subjected to gel filtration over Sephadex G-25 (eluent 0.1 M NH_4HCO_3). Fractions containing product were combined and lyophilized to give the respective products (**20**, **S54**, or **S57**) as amorphous white solids.

Permethylation Analysis

Mass spectrometry (MS) profiles of permethylated glycans are provided in **Table S1.** All glycans were permethylated using the procedure below.

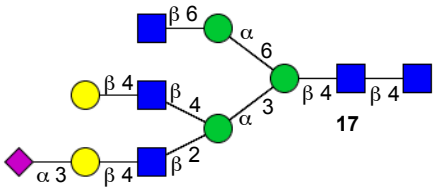
Preparation of base. DMSO (1.5 mL) was added to 50% aq. NaOH (100 µL) and MeOH (200 µL) in a pyrex tube. The tube was vortexed and then centrifuged to bring the gel to the bottom of the tube. The top layer solution was removed and the gel was washed with DMSO (x5). To the clean gel, DMSO (1 mL) was added and the gel was broken (vortex).

Permethylation. Iodomethane (125 µL) and the broken gel (350 µL) were added to the glycan (~8 µg) dissolved in DMSO (200 µL). The tube was purged with N_2 and vortexed continuously for 10 min, after which water (1.5 mL) was added. The excess iodomethane was removed by a flow of N_2, and the permethylated glycan was extracted with DCM (x2). The extracted DCM layers were combined and washed with water (x5). The clean DCM extract was transferred to another pyrex tube and was dried using a flow of N_2. MeOH (20 µL) was added to the tube, vortexed and used for attaining the mass spectra.

Table S1. MS profiles of permethylated glycans.

Residue	$[M+Na]^+$	Calculated Mass	Observed Mass
17	$C_{118}H_{208}N_6NaO_{59}$	2676.3358	2676.1235
18	$C_{134}H_{236}N_6NaO_{67}$	3024.5142	3024.3752
19	$C_{143}H_{252}N_6NaO_{72}$	3228.6140	3229.9102
20	$C_{154}H_{271}N_7NaO_{77}$	3473.7403	3473.7217
21	$C_{163}H_{287}N_7NaO_{82}$	3677.8401	3678.7620
22	$C_{179}H_{314}N_8NaO_{90}$	4039.0137	4039.1436
S51	$C_{102}H_{181}N_5NaO_{51}$	2315.1621	2315.2039
S52	$C_{118}H_{209}N_5NaO_{59}$	2663.3405	2663.6631
S53	$C_{127}H_{225}N_5NaO_{64}$	2867.4403	2867.4248
23	$C_{143}H_{252}N_6NaO_{72}$	3228.6140	3228.6877
S54	$C_{138}H_{244}N_6NaO_{69}$	3112.5666	3112.5461
S55	$C_{147}H_{260}N_6NaO_{74}$	3316.6664	3316.7107
24	$C_{163}H_{287}N_7NaO_{82}$	3677.8401	3677.5269
S56	$C_{134}H_{235}N_7NaO_{67}$	3037.5094	3037.5730
25	$C_{143}H_{251}N_7NaO_{72}$	3241.6092	3241.2322
S57	$C_{154}H_{270}N_8NaO_{77}$	3486.7355	3486.3799
S58	$C_{163}H_{286}N_8NaO_{82}$	3690.8353	3690.5249
26	$C_{179}H_{313}N_9NaO_{90}$	4052.0090	4051.9392
27	$C_{134}H_{235}N_7NaO_{67}$	3037.5094	3037.6360

NMR Analysis



Full ^{1}H NMR assignments are provided in **Table S2**. GlcNAc-5 was identified from a crosspeak between its H1 and Man4-H2 in a NOESY spectrum, (**Fig. S16**) as well as a crosspeak between GlcNAc-5 H1 and Man-4 C2 in the HMBC spectrum. Also a strong NOE crosspeak is observed between GlcNAc-5 H1 and Man4 H1, which is often seen for 1-2 linkages. The complete spin system could be traced from the COSY, TOCSY, and HSQC-TOCSY spectra, although protons H2, 3, and 4 have overlapped signals. GlcNAc-7' was identified from the linkage to the 6-position of Man-4' from the NOE crosspeak GlcNAc-7' H1 to Man-4'-H6, and a crosspeak from GlcNAc-7' H1 to Man-4' C6 in the HMBC spectrum. H2, 3, and 4 could be identified from the TOCSY and HSQC-TOCSY spectra.

GlcNAc-7 was then assigned by elimination. H2, 3, 4, 5 and 6 could be traced from COSY, TOCSY, and HSCQ-TOCSY spectra, however as with GlcNAc-5, H2, 3, and 4 signals overlap.

The linkage to the C4 position of Man-4 was confirmed by crosspeaks from GlcNAc-7 C1 to Man-4 H4 and GlcNAc-7 H1 to Man-4 C4 in the HMBC spectrum. H1-H4 NOE crosspeaks could not be distinguished because of overlapped signals, however crosspeaks from GlcNAc-7 H1 to Man-4-H3 and Man-4-H6 support the 1-4 linkage.

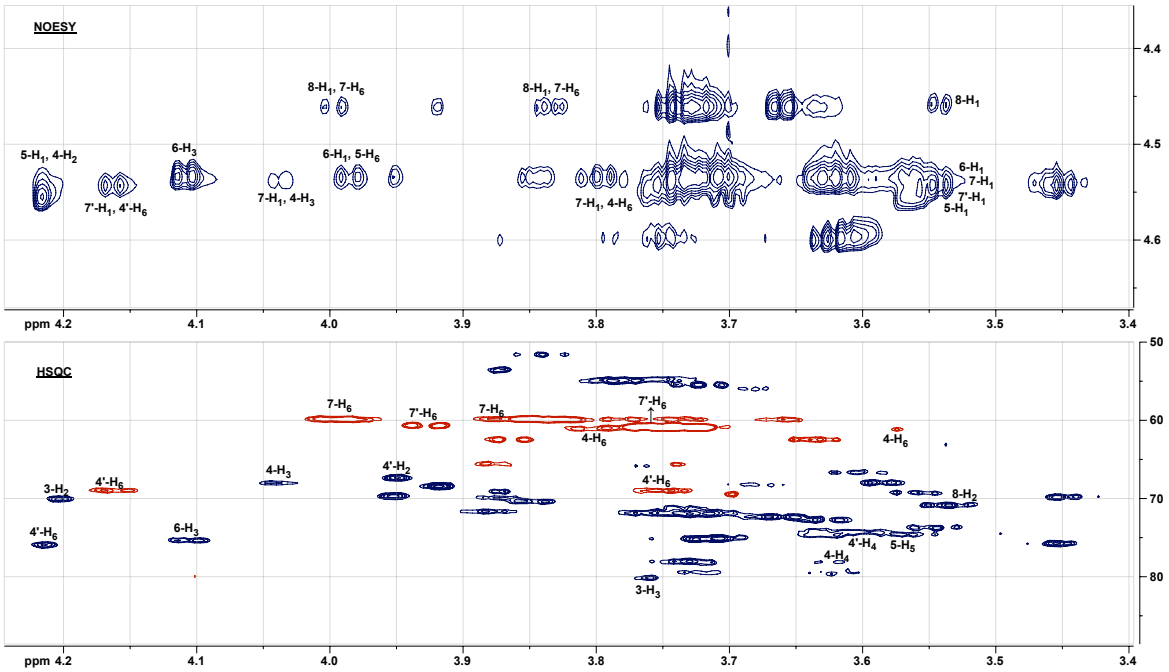


Fig. S16. NOESY and HSQC of compound **17**.

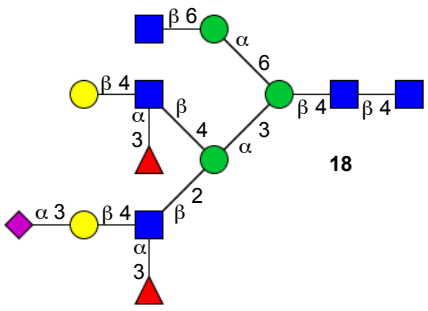
Gal-6 has the Neu5Ac linked to the 3-position, which causes significant downfield shift of Gal-6-H3 whereas Gal-8 is expected to have standard peak positions (e.g. H3 at 3.60, H4 at 3.9).

Gal-8-H1, 2, 3, 4 was easy to find in the TOCSY spectrum, as its anomeric was distinct from the other β-residues. A direct linkage between H1 of Gal-8 and H4 of GlcNAc-7 could not be confirmed because of overlapping signals (see above), however NOE crosspeaks between H1 of Gal-8 and H6, H6' of GlcNAc-7 are consistent with the 1-4 linkage.

Gal-6 H1 closely overlapped with most of the GlcNAcs, but H3 was located in the TOCSY spectrum at 4.049, and so H1, 2, and 4 could also be assigned. These shifts confirm that it is substituted at position 3 by Neu5Ac. As with Gal-8, the direct linkage to GlcNAc-5 H4 was not confirmed due to signal overlap, but NOE crosspeaks between H1 of Gal-6 and H6 and H6' of GlcNAc-5 are consistent with the 1-4 linkage.

Table S2. ^{1}H NMR of compound **17**.

17	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**
GlcNAc-1α	5.182	3.871	3.625	NA	NA	NA
Man-4	5.11	4.214	4.036	3.616	3.752	3.802, 3.575
Man-4'	4.872	3.953	3.85	3.605	3.739	4.162, 3.75
Man-3	4.757	4.201	3.7607	3.635	3.879	NA
GlcNAc-1β	4.687	3.691	3.67	3.615	3.507	3.825,3.643
GlcNAc-2	4.604,4.594	3.791,3.779	3.72-3.75	3.72-3.75	3.601	NA
GlcNAc-5	4.558	3.743	3.70-3.74	3.70-3.74	3.564	3.983,3.842
GlcNAc-7	4.535	3.788	3.71-3.74	3.71-3.74	3.629	3.983,3.835
GlcNAc-7'	4.544	3.725	3.545	3.441	3.46	3.928, 3.752
Gal-6	4.534	3.56	4.108	3.951	NA	NA
Gal-8	4.461	3.536	3.658	3.917	NA	NA
Neu5Ac(α-3)	NA	NA	2.75 1.792	3.68	3.841	3.626



Full ^{1}H NMR assignments are provided in **Table S3**. The spectra confirm the presence of 2 additional fucose residues. Below is the 1D proton spectrum (**Fig. S17**) showing 3 anomeric peaks at 5.10 ppm (2 fucose plus 1 mannose), fucose H5 signals at 4.83 ppm, and fucose H6 signals at 1.17 ppm.

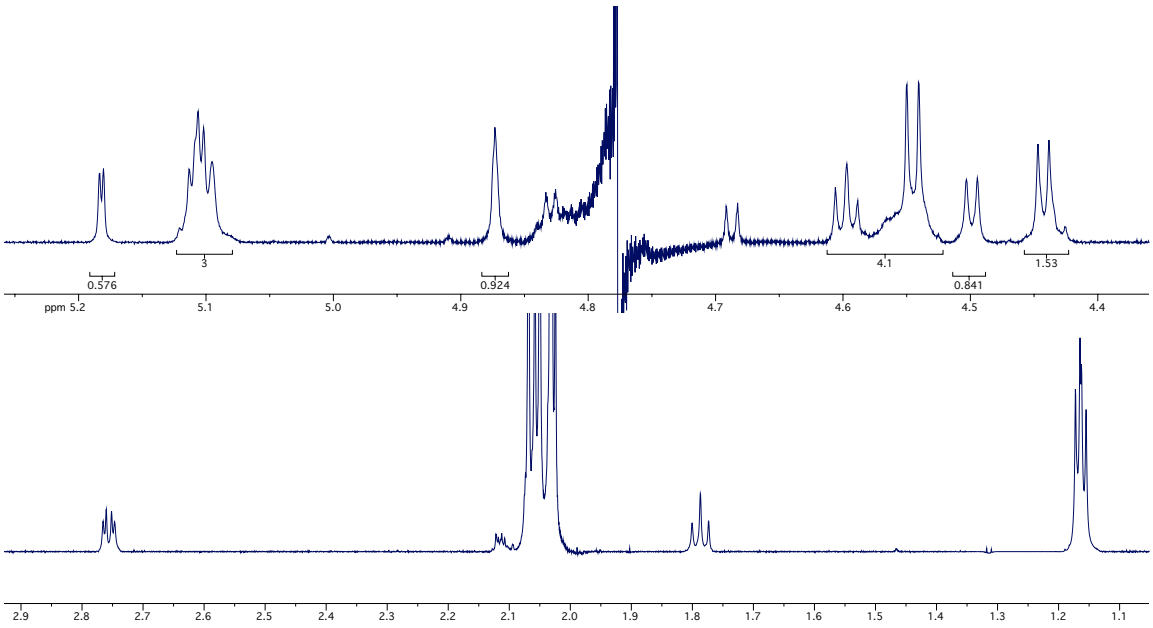


Fig. S17. ^{1}H NMR spectra of compound **18**.

There are also shifts in GlcNAc-5, Gal-6 and GlcNAc-7, Gal-8 anomeric signals (**Fig. S18**: lower panel), whereas GlcNAc-7' is unchanged from compound **17** (**Fig. S18**: upper panel).

The intensities of GlcNAc-5 H1 and GlcNAc-7 H1 are reduced in the 2D spectra from broadening of the signals by the addition of the fucosyl residues.

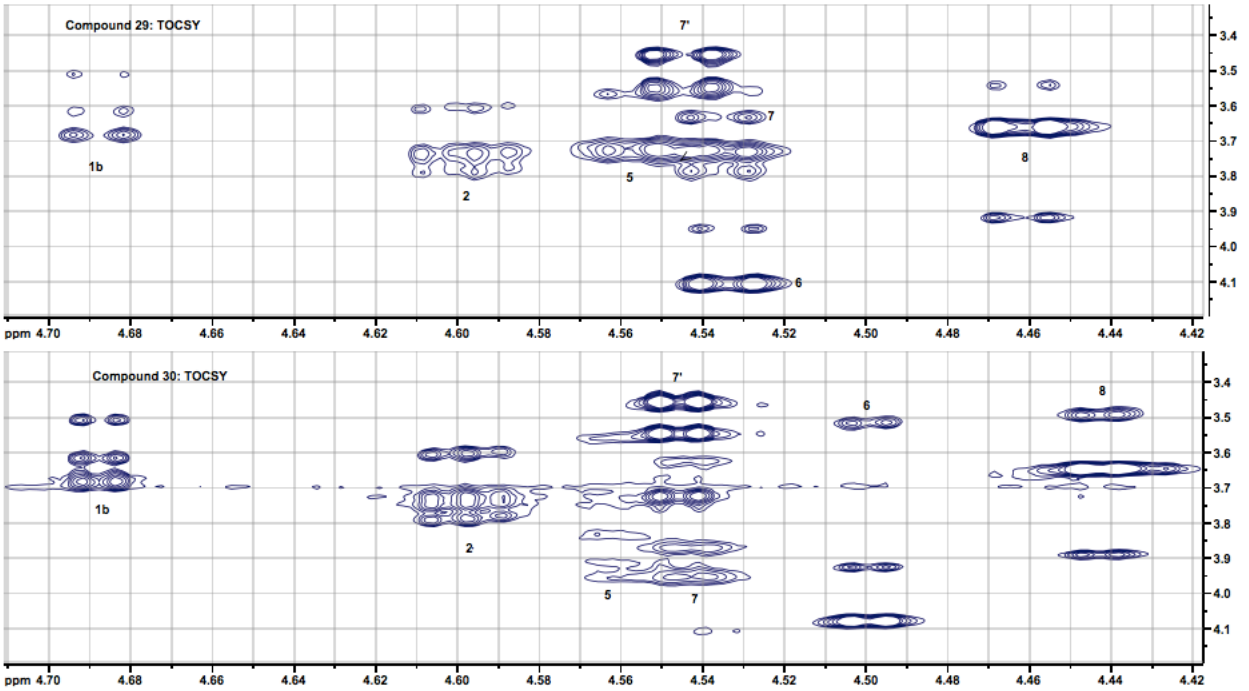


Fig. S18. TOCSY spectra of compounds **17** and **18**.

From the NOESY (**Fig. S19**) there are crosspeaks between Fuc1 and GlcNAc-5 H2, as well as between Fuc-2 H1 and GlcNAc H2 and H4. The expected crosspeaks between Fuc-H1 and GlcNAc-H3, usually observed for glycosidic linkages, are not seen due to the weak signals of GlcNAc-H3 and interference from spectral artifacts arising from contaminating glycerol. The presence of both GlcNAc-H2 and H4 suggests that the fucosyl residues have a limited orientation placing their H1s on the side of the GlcNAc opposite to its H3.

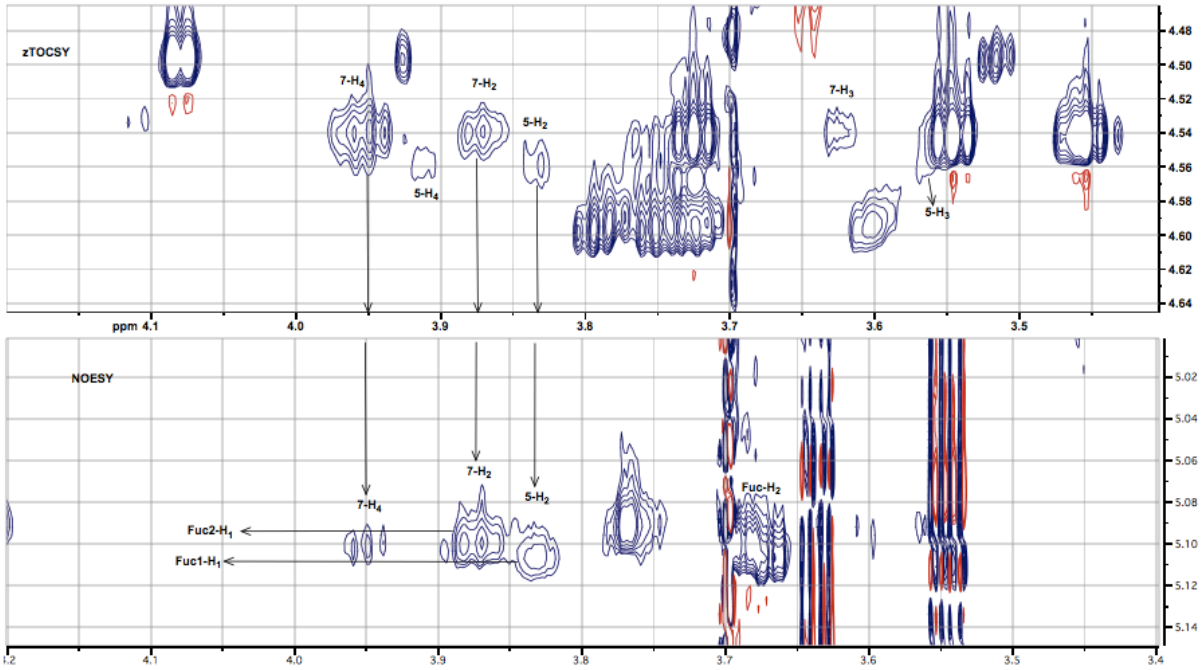
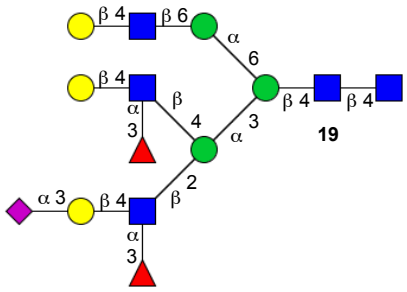


Fig. S19. TOCSY and NOESY spectra of compound **18**.

Table S3. ^{1}H NMR of compound **18**.

18	H1	H2	H3	H4	H5	H6	Fuc CH_3
GlcNAc-1α	5.182	3.871	3.627	NA	NA	NA	-
Man-4	5.096	4.211	4.035	3.598	3.753	NA	-
Man-4'	4.873	3.952	3.85	3.55	3.738	NA	-
Man-3	4.754	4.203	3.766	3.637	NA	NA	-
GlcNAc-1β	4.687	3.695	3.673	3.615	3.507	NA	-
GlcNAc-2	4.603, 4.593	3.793, 3.782	3.72-3.75	3.72-3.75	3.601	NA	-
GlcNAc-5	4.56	3.724	NA	NA	NA	NA	-
GlcNAc-7	4.543	3.724	NA	NA	NA	NA	-
GlcNAc-7'	4.546	3.724	3.545	3.444	NA	NA	-
Gal-6	4.499	3.515	4.079	3.926	NA	NA	-
Gal-8	4.443	3.491	3.648	3.889	NA	NA	-
Neu5Ac (α-3)	NA	NA	2.756, 1.787	3.677	3.844	3.65	-
Fuc-1	5.111	3.671	3.891	3.77	4.809	-	1.164
Fuc-2	5.103	3.689	3.891	3.782	4.83	-	1.164



Full ^{1}H NMR assignments are provided in **Table S4**. The anomeric region of the Tocsy spectrum (**Fig. S20**) of **18** and **19** shows the additional anomeric peak (Gal-8') with crosspeaks consistent with a galactosyl residue, compared to compound **18** (below, upper panel).

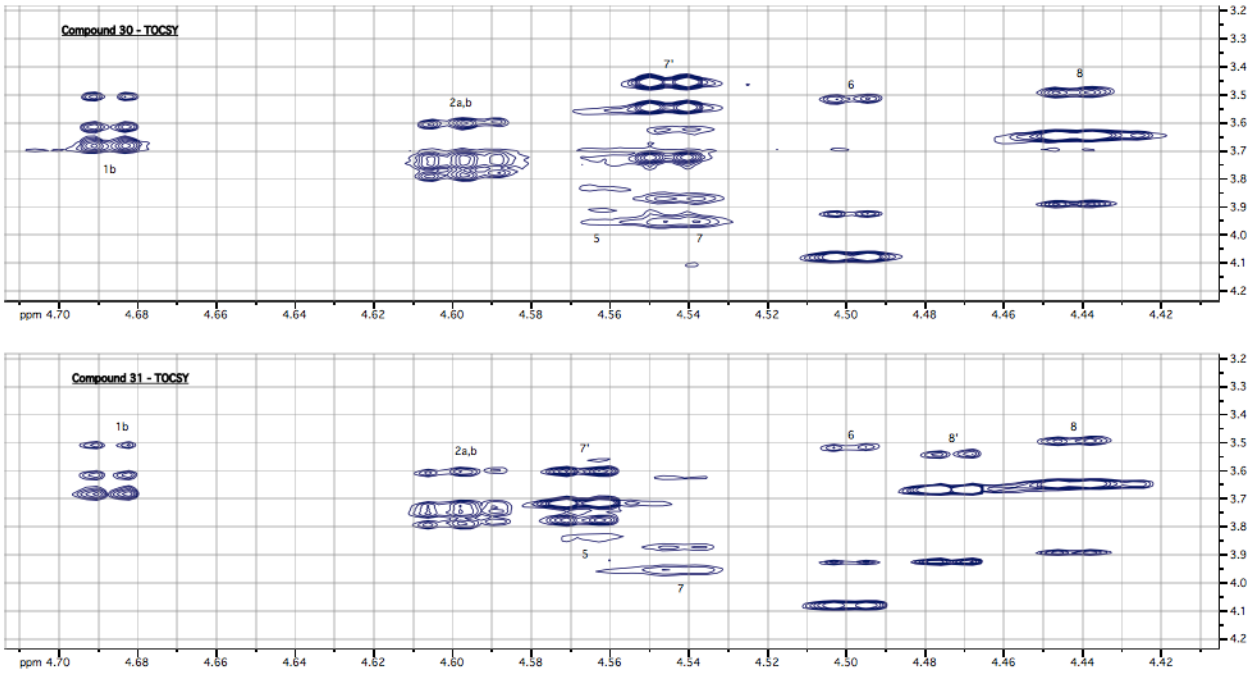


Fig. S20. TOCSY spectra of compounds **18** and **19**.

The NOESY spectrum (**Fig. S21**) also shows a crosspeak between Gal-8' H1 and the GlcNAc-7' H4.

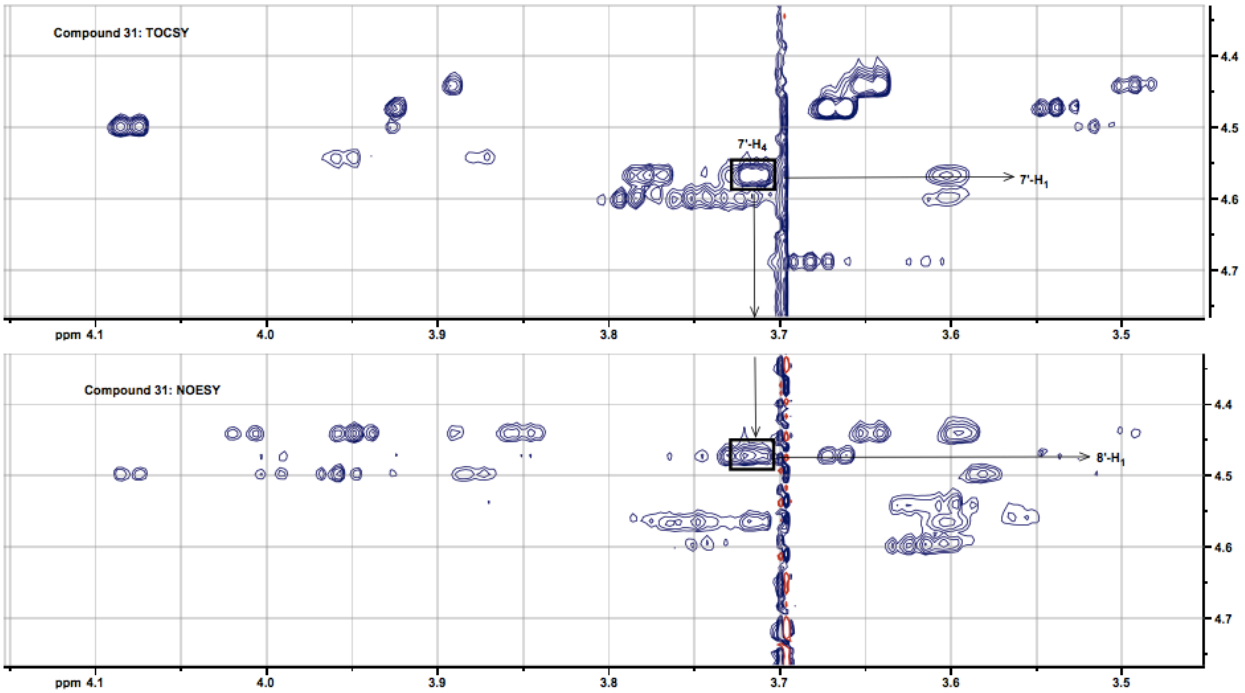
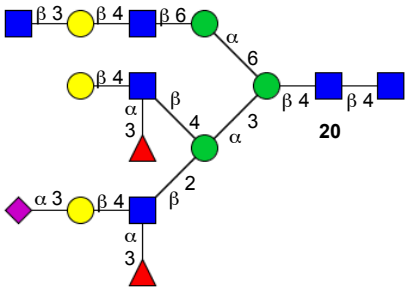


Fig. S21. TOCSY and NOESY spectra of compound **19**.

Table S4. ^{1}H NMR of compound **19**.

19	H1	H2	H3	H4	H5	H6	Fuc CH_3
GlcNAc-1α	5.182	3.866	3.6286	NA	NA	NA	-
Man-4	5.095	4.211	4.035	3.597	3.751	3.562,3.79	-
Man-4'	4.875	3.954	3.852	3.603	NA	NA	-
Man-3	4.756	4.206	3.77	3.638	3.876	NA	-
GlcNAc-1β	4.688	3.692	3.617	3.509	NA	NA	-
GlcNAc-2	4.604,4.593	3.798,3.779	3.72-3.75	3.72-	3.6	NA	-
GlcNAc-5	4.564	3.84	3.561	3.913	NA	NA	-
GlcNAc-7	4.541	3.87	3.625	3.957	NA	NA	-
GlcNAc-7'	4.567	3.778	3.72	3.72	3.6	NA	-
Gal-6	4.499	3.516	4.081	3.927	NA	NA	-
Gal-8	4.442	3.493	3.646	3.891	NA	NA	-
Gal-8'	4.474	3.537	3.667	3.925	NA	NA	-
Neu5Ac (α-3)	NA	NA	2.756, 1.789	3.678	3.846	3.65	-
Fuc-1	5.111	3.671	3.895	3.771	4.818	-	1.163
Fuc-2	5.104	3.688	3.887	3.786	4.836	-	1.166



Full ^{1}H NMR assignments are provided in **Table S5**. The anomeric region shows the addition of a GlcNAc (**Fig. S22**: below, lower panel, "GlcNAc-ext") compared to compound **19** (below, upper panel).

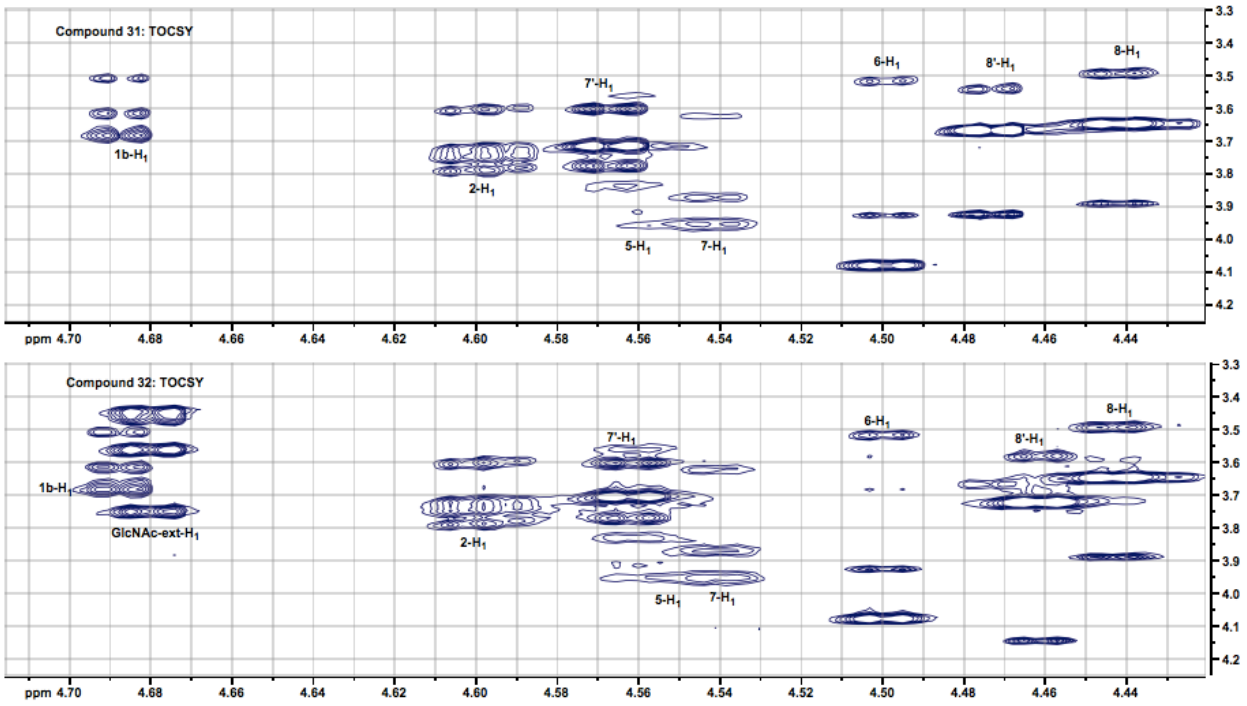


Fig. S22. TOCSY spectra of compounds **19** and **20**.

In addition, the NOESY spectrum (**Fig. S23)** shows a crosspeak between GlcNAc-ext H1 and gal-8' H3.

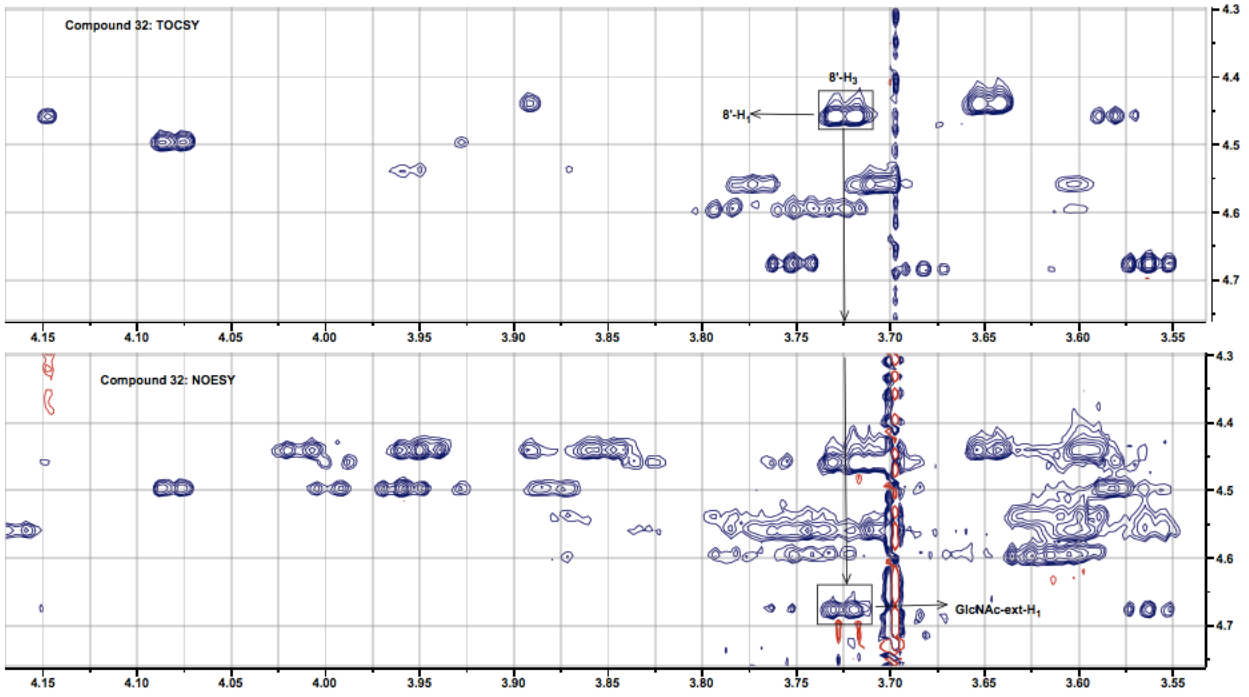


Fig. S23. TOCSY and NOESY spectra of compound **20**.

Table S5. ^{1}H NMR of compound **20**.

20	H1	H2	H3	H4	H5	H6	Fuc CH_3
GlcNAc-1α	5.182	3.872	3.63	NA	NA	NA	-
Man-4	5.097	4.209	4.034	3.599	3.749	3.564, 3.788	-
Man-4'	4.873	3.953	3.852	3.624	NA	NA	-
Man-3	4.756	4.205	3.766	NA	NA	NA	-
GlcNAc-1β	4.688	3.682	3.615	3.509	NA	NA	-
GlcNAc-2	4.602,	3.793, 3.782	3.72-3.75	3.72-3.75	3.6	NA	-
GlcNAc-5	4.562	3.83	3.56	3.91	NA	NA	-
GlcNAc-7	4.541	3.872	3.63	3.95	NA	NA	-
GlcNAc-7'	4.562	3.773	3.72	3.72	3.602	3.832, 3.994	-
GlcNAc-ext	4.679	3.752	3.563	3.464	3.444	3.757, 3.891	-
Gal-6	4.499	3.516	4.08	3.927	NA	NA	-
Gal-8	4.443	3.491	3.647	3.892	NA	NA	-
Gal-8'	4.461	3.581	3.725	4.147	NA	NA	-
Neu5Ac (α-3)	NA	NA	2.756, 1.789	3.679	3.844	3.65	-
Fuc-1	5.111	3.67	3.891	3.769	4.809	-	1.16
Fuc-2	5.103	3.687	3.891	3.785	4.83	-	1.168

Table S6. ^{1}H NMR of compound **21**.

21	H1	H2	H3	H4	H5	H6	Fuc CH_3
GlcNAc-1α	5.182	3.874	3.63	NA	NA	NA	-
Man-4	5.095	4.209	4.035	3.6	3.748	3.79, 3.56	-
Man-4'	4.875	3.953	3.849	3.623	NA	NA	-
Man-3	4.755	4.202	3.774	NA	NA	NA	-
GlcNAc-1β	4.688	3.694	3.614	3.505	NA	NA	-
GlcNAc-2	4.603, 4.595	3.795,3.780	3.72-3.75	3.72-3.75	3.604	NA	-
GlcNAc-5	4.561	3.83	3.56	3.9	NA	NA	-
GlcNAc-7	4.541	3.868	3.63	3.96	NA	NA	-
GlcNAc-7'	4.561	3.771	3.705	3.602	3.829	NA	-
GlcNAc-ext	4.698	3.802	3.72-3.73	3.72-3.73	3.583	3.845, 3.945	-
Gal-6	4.499	3.516	4.081	3.927	NA	NA	-
Gal-8	4.443	3.493	3.646	3.89	NA	NA	-
Gal-8'	4.459	3.579	3.722	4.153	NA	NA	-
Gal-ext	4.473	3.538	3.661	3.919	NA	NA	-
Neu5Ac (α-3)	NA	NA	2.756,	3.679	3.844	3.65	-
Fuc-1	5.11	3.689	3.891	3.77	4.829	-	1.17
Fuc-2	5.105	3.671	3.891	3.786	4.812	-	1.161

Table S7. ^{1}H NMR of compound **22**.

22	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.182	3.87	3.63	NA	NA	NA	-
Man-4	5.095	4.208	4.038	3.59	3.747	3.788, 3.568	-
Man-4'	4.876	3.952	3.849	3.612	NA	NA	-
Man-3	4.755	4.205	3.769	3.639	NA	NA	-
GlcNAc-1β	4.687	3.694	3.616	3.51	NA	NA	-
GlcNAc-2	4.602, 4.592	3.794, 3.782	3.734	3.605	NA	NA	-
GlcNAc-5	4.561	3.78	3.706	3.605	3.83	NA	-
GlcNAc-7	4.541	NA	3.953	3.62	3.871	NA	-
GlcNAc-7'	4.561	3.78	3.706	3.605	3.83	NA	-
GlcNAc-ext	4.726	3.805	3.66	3.603	NA	NA	-
Gal-6	4.5	3.515	4.08	3.927	NA	NA	-
Gal-8	4.443	3.49	3.647	3.893	NA	NA	-
Gal-8'	4.462	3.586	3.732	4.155	NA	NA	-
Gal-ext	4.447	3.531	3.665	3.92	NA	NA	-
Neu5Ac (α-3)	-	-	2.756, 1.789	3.678	3.856	3.65	-
Neu5Ac (α-6)	-	-	2.665, 1.716	3.647	3.803	3.696	-
Fuc-1	5.111	3.668	3.891	3.777	4.81	-	1.164
Fuc-2	5.104	3.687	3.891	3.787	4.83	-	1.164

Table S8. ^{1}H NMR of compound **S51**.

S51	H1	H2	H3	H4	H5	H6
GlcNAc-1α	5.182	3.87	3.621	NA	NA	NA
Man-4	5.111	4.216	4.04	3.619	3.757	3.803,
Man-4'	4.872	3.953	3.847	3.605	3.739	NA
Man-3	4.763	4.205	3.759	3.637	NA	NA
GlcNAc-1β	4.688	3.691	3.672	3.615	3.508	3.645,
GlcNAc-2	4.6	3.785	3.745	3.603	NA	NA
GlcNAc-5	4.546	3.723	3.547	3.442	NA	NA
GlcNAc-7	4.537	3.786	3.729	3.631	NA	NA
GlcNAc-7'	4.563	3.744	3.711	3.571	NA	NA
Gal-6	4.458	3.533	3.655	3.919	NA	NA
Gal-8	4.458	3.533	3.655	3.919	NA	NA

Table S9. ^{1}H NMR of compound **23**.

23	H1	H2	H3	H4	H5	H6	Fuc CH_3
GlcNAc-1α	5.182	3.868	3.624	NA	NA	NA	-
Man-4	5.097	4.213	4.043	3.601	3.759	NA	-
Man-4'	4.876	3.954	3.851	3.555	3.745	NA	-
Man-3	4.757	4.205	3.772	3.638	NA	NA	-
GlcNAc-1β	4.687	3.694	3.62	3.51	NA	NA	-
GlcNAc-2	4.603	3.799	3.738	3.627	NA	NA	-
GlcNAc-5	4.595	3.773	3.738	3.627	NA	NA	-
GlcNAc-7	4.564	3.939	3.749	3.560	NA	NA	-
GlcNAc-7'	4.55	3.949	3.872	3.627	NA	NA	-
Gal-6	4.442	3.494	3.647	3.891	NA	NA	-
Gal-8	4.432	3.494	3.647	3.891	NA	NA	-
Gal-8'	4.45	3.536	3.666	3.92	NA	NA	-
Neu5Ac (α-6)	-	-	2.665,1.714	3.651	3.795	3.695	-
Fuc-1	5.12	3.682	3.9	3.783	4.829	-	1.169
Fuc-2	5.105	3.689	3.89	3.786	4.829	-	1.169

Table S10. ^{1}H NMR of compound **24**.

24	H1	H2	H3	H4	H5	H6	Fuc CH3
GlcNAc-1α	5.182	3.869	3.625	NA	NA	NA	-
Man-4	5.099	4.204	4.046	3.6	3.747	NA	-
Man-4'	4.873	3.954	3.85	3.555	3.751	NA	-
Man-3	4.757	4.203	3.77	3.632	NA	NA	-
GlcNAc-1β	4.688	3.68	3.613	3.508	NA	NA	-
GlcNAc-2	4.599	3.779	3.741	3.6	NA	NA	-
GlcNAc-5	4.561	3.77	3.706	3.603	3.837	NA	-
GlcNAc-7	4.545	NA	3.949	3.623	3.872	NA	-
GlcNAc-7'	4.561	3.77	3.706	3.603	3.837	NA	-
GlcNAc-ext	4.724	3.795	3.658	3.6	NA	NA	-
Gal-6	4.441	3.492	3.652	3.892	NA	NA	-
Gal-8	4.428	3.482	3.639	3.892	NA	NA	-
Gal-8'	4.461	3.584	3.728	4.1507	NA	NA	-
Gal-ext	4.449	3.53	3.664	3.917	NA	NA	-
Neu5Ac (α-6)	-	-	2.665, 1.714	3.648	3.802	3.694	-
Fuc-1	5.119	3.68	3.895	3.783	4.825	-	1.169
Fuc-2	5.104	3.687	3.888	3.783	4.825	-	1.169

Table S11. ^{1}H NMR of compound **25**.

25	H1	H2	H3	H4	H5	H6
GlcNAc-1α	5.182	3.862	3.626	NA	NA	NA
Man-4	5.120	4.222	4.041	3.631	3.766	3.93, 3.818
Man-4'	4.875	3.954	3.858	3.608	3.744	NA
Man-3	4.756	4.218	3.763	3.638	NA	NA
GlcNAc-1β	4.685	3.691	3.611	3.508	NA	NA
GlcNAc-2	4.598	3.796	3.741	3.608	NA	NA
GlcNAc-5	4.588	3.745	3.641	3.589	NA	NA
GlcNAc-7	4.563	3.783	3.715	3.602	NA	NA
GlcNAc-7'	4.563	3.783	3.757	3.657	NA	NA
Gal-6	4.432	3.529	3.66	3.919	NA	NA
Gal-8	4.432	3.529	3.66	3.919	NA	NA
Gal-8'	4.472	3.537	3.666	3.921	NA	NA
Neu5Ac (α-6)	-	-	2.658, 1.716	3.656	3.803	3.705

Table S12. ^{1}H NMR of compound **26**.

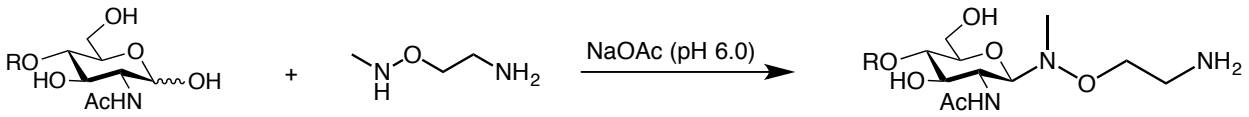
26	H1	H2	H3	H4	H5	H6
GlcNAc-1α	5.182	3.862	3.636	3.554	NA	NA
Man-4	5.121	4.22	4.039	3.629	NA	NA
Man-4'	4.876	3.953	3.857	3.608	3.761	NA
Man-3	4.756	4.212	3.762	3.637	NA	NA
GlcNAc-1β	4.685	3.685	3.614	3.51	NA	NA
GlcNAc-2	4.598	3.793	3.736	3.608	NA	NA
GlcNAc-5	4.589	3.744	3.641	3.59	NA	NA
GlcNAc-7	4.557	3.784	3.711	3.658	3.604	NA
GlcNAc-7'	4.557	3.784	3.711	3.658	3.604	NA
GlcNAc-ext	4.722	3.801	3.66	3.602	NA	NA
Gal-6	4.458	3.584	3.73	4.152	3.755	NA
Gal-8	4.435	3.53	3.661	3.917	3.813	3.865, NA
Gal-8'	4.435	3.53	3.661	3.917	3.813	3.865, NA
Gal-ext	4.435	3.53	3.661	3.917	3.813	3.865, NA
Neu5Ac (α-6)	-	-	2.661, 1.707	3.644	3.803	3.696

Table S13. ^{1}H NMR of compound **27**.

27	H1	H2	H3	H4	H5	H6
GlcNAc-1α	5.182	3.8642	3.6287	NA	NA	NA
Man-4	5.1085	4.2123	4.037	3.613	3.753	3.804, 3.568
Man-4'	4.872	3.952	3.8495	3.595	3.7323	NA
Man-3	4.7535	4.204	3.755	3.629	NA	NA
GlcNAc-1β	4.686	3.691	3.613	3.505	NA	NA
GlcNAc-2	4.6, 4.592	3.793, 3.783	3.724	3.626	NA	NA
GlcNAc-5	4.554	3.74	3.714	3.565	NA	NA
GlcNAc-7	4.544	3.724	3.544	3.442	NA	NA
GlcNAc-7'	4.535	3.785	3.717	3.634	NA	NA
Gal-6	4.5365	3.562	4.0851	3.9504	NA	NA
Gal-8	4.5365	3.562	4.0851	3.9504	NA	NA
Neu5Ac (α-3)	-	-	2.748, 1.793	3.678	3.842	3.627

3. Microarray

General Procedure for Linkering



22-27

R = sugar

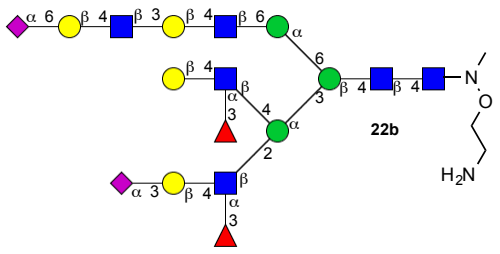
bi-functional spacer

22b-27b

R = sugar

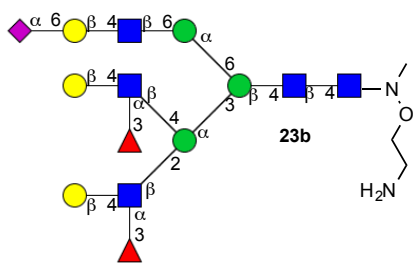
Free reducing glycan (0.2 mg) and bi-functional spacer (20 equiv.) were dissolved in 0.1 M acetate aqueous buffer (pH 6.0). The glycan concentration was 2 mM. The mixture was incubated at 37 °C for 48 h and monitored by MALDI-TOF MS. The reaction mixture was loaded over Sephadex G-25 Superfine gel filtration column (50 cm x 1 cm) with 0.1 M NH_4HCO_3 (aq) eluent to remove off excess spacer and salt. Fractions were lyophilized. The final product was characterized by MALDI-TOF MS and ^{1}H NMR. It's worthy to note that this linkering reaction may not be completed. But the material without the bi-functional spacer couldn't print on the NHS-activated glass slides.

Compound **22b**.



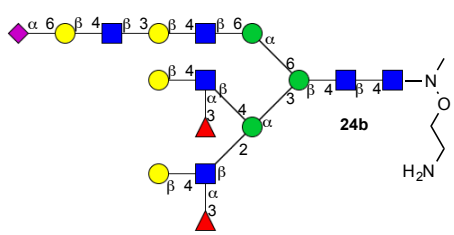
^{1}H NMR (600 MHz, D_2O) 5.10 (s, 3H, Man-4 H-1, Fuc-1 H-1, Fuc-2 H-1), 4.87 (overlapped with H_2O, 1H, Man-4' H-1), 4.75 (s, 1H, Man-3 H-1), 4.71 (d, J = 7.9 Hz, 1H, GlcNAc-1 H-1), 4.59 (d, J = 7.9 Hz, 1H, GlcNAc-ext H-1), 4.57-4.51 (m, 3H, GlcNAc-2 H-1, GlcNAc-5 H-1, GlcNAc-7' H-1), 4.49 (d, J = 8.0 Hz, 1H, GlcNAc-7 H-1), 4.48-4.41 (m, 4H, Gal-6 H-1, Gal-8 H-1, Gal-8' H-1, Gal-ext H-1), 4.22-4.13 (m, 6H, Man-3 H-2, Man-4 H-2, Man-4' H-2, Gal-6 H-3, Gal-6 H-4, Gal-8' H-4), 4.11-3.45 (m, 96 H), 3.25-3.16 (m, 2H, $CH_2CH_2NH_2$), 2.76 (s, 3H, -NCH_3), 2.76-2.72 (m, 1H, α-3Neu5Ac H-3e), 2.69-2.63 (m, 1H, α-6Neu5Ac H-3e), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03(9) (s, 3H), 2.03 (s, 6H), 2.02 (s, 6H), 1.79 (t, J = 12.4 Hz, 1H, α-3Neu5Ac H-3a), 1.72 (t, J = 12.2 Hz, 1H, α-6Neu5Ac H-3a), 1.16 (d, J = 6.0 Hz, 3H, Fuc-1 CH_3), 1.15 (d, J = 6.0 Hz, 3H, Fuc-2 CH_3).

Compound **23b**.



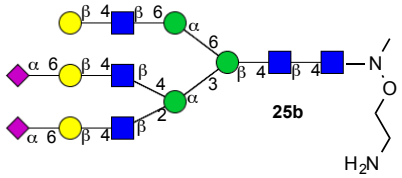
^{1}H NMR (600 MHz, D_2O) 5.14-5.07 (m, 3H, Man-4 H-1, Fuc-1 H-1, Fuc-2 H-1), 4.87 (s, 1H, Man-4' H-1), 4.75 (overlapped, 1H, Man-3 H-1), 4.71 (Overlapped, 1H, GlcNAc-1 H-1), 4.62-4.52 (m, 4H, GlcNAc-2 H-1, GlcNAc-5 H-1, GlcNAc-7 H-1, GlcNAc-7' H-1), 4.47-4.41 (m, 3H, Gal-6 H-1, Gal-8 H-1, Gal-8' H-1), 4.24-4.14 (m, 4H, Man-3 H-2, Man-4 H-2, Man-4' H-2), 4.08-3.45 (m, 79 H), 3.23-3.17 (m, 2H, $CH_2CH_2NH_2$), 2.76 (s, 3H, -NCH_3), 2.66 (dd, J = 4.2, 12.0 Hz, 1H, α-6Neu5Ac H-3e), 2.07 (s, 6H), 2.05 (s, 3H), 2.03 (s, 6H), 2.02 (s, 3H), 1.71 (t, J = 12.3 Hz, 1H, α-6Neu5Ac H-3a), 1.16 (d, J = 6.0 Hz, 6H, Fuc-1 CH_3, Fuc-2 CH_3).

Compound **24b**.



^{1}H NMR (600 MHz, D_2O) 5.13-5.08 (m, 3H, Man-4 H-1, Fuc-1 H-1, Fuc-2 H-1), 4.87 (s, 1H, Man-4' H-1), 4.75 (Overlapped, 1H, Man-3 H-1), 4.71 (Overlapped, 1H, GlcNAc-1 H-1), 4.62-4.50 (m, 5H, GlcNAc-2 H-1 GlcNAc-5 H-1 GlcNAc-7 H-1 GlcNAc-7' H-1 GlcNAc-ext H-1), 4.48-4.41 (m, 4H, Gal-6 H-1, Gal-8 H-1, Gal-8' H-1, Gal-ext H-1), 4.22-4.12 (m, 5H, Man-3 H-2, Man-4 H-2, Man-4' H-2, Gal-6 H-3, Gal-8' H-4), 4.06-3.45 (m, 90H), 3.25-3.15 (m, 2H, $CH_2CH_2NH_2$), 2.76 (s, 3H, -NCH_3), 2.66 (dd, J = 4.5, 12.4 Hz, 1H, α-6Neu5Ac H-3e), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03(8) (s, 3H), 2.03 (s, 6H), 2.02 (s, 3H), 1.71 (t, J = 12.1 Hz, 1H, α-6Neu5Ac H-3a), 1.16 (d, J = 6.3 Hz, 6H, Fuc-1 CH_3, Fuc-2 CH_3).

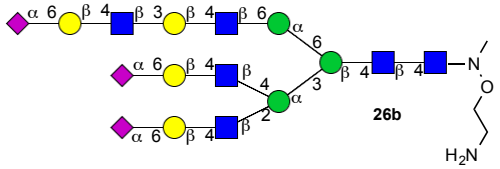
Compound **25b**.



^{1}H NMR (600 MHz, D_2O) 5.11 (s, 1H, Man-4 H-1), 4.87 (s, 1H, Man-4' H-1), 4.76 (overlapped, 1H, Man-3 H-1), 4.72 (Overlapped, 1H, GlcNAc-1 H-1), 4.62-4.52 (m, 4H, GlcNAc-2 H-1 GlcNAc-5 H-1 GlcNAc-7 H-1 GlcNAc-7' H-1), 4.47 (d, J = 7.7 Hz, 1H, Gal-8' H-1), 4.44 (d, J = 7.5 Hz, 1H, Gal-6 H-1), 4.43 (d, J = 7.5 Hz, 1H, Gal-8 H-1), 4.25-4.13 (m, 4H, Man-3 H-2, Man-4 H-2, Man-4' H-2), 4.07-3.45 (m, 78 H), 3.24-3.15 (m, 2H, $CH_2CH_2NH_2$), 2.76 (s, 3H, -NCH_3), 2.65

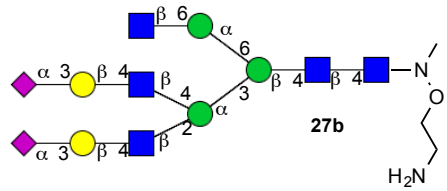
(dd, J = 4.3, 12.4 Hz, 2H, α-6Neu5Ac H-3e), 2.09 (s, 3H), 2.06 (s, 3H), 2.05(7) (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 6H), 1.74-1.66 (m, 2H, α-6Neu5Ac H-3a).

Compound **26b**.



^{1}H NMR (600 MHz, D_2O) 5.11 (s, 1H, Man-4 H-1), 4.87 (Overlapped, 1H, Man-4' H-1), 4.75 (s, 1H, Man-3 H-1), 4.70 (d, J = 7.7 Hz, 1H, GlcNAc-1 H-1), 4.62-4.52 (m, 5H, GlcNAc-2 H-1, GlcNAc-5 H-1, GlcNAc-7 H-1, GlcNAc-7' H-1, GlcNAc-ext H-1), 4.48-4.41 (m, 4H, Gal-6 H-1, Gal-8 H-1, Gal-8' H-1, Gal-ext H-1), 4.24-4.13 (m, 5H, Man-3 H-2, Man-4 H-2, Man-4' H-2, Gal-6 H-4, Gal-8' H-4), 4.08-3.45 (m, 96 H), 3.25-3.15 (m, 2H, $CH_2CH_2NH_2$), 2.76 (s, 3H, -NCH_3), 2.69-2.61 (m, 3H, α-6Neu5Ac H-3e), 2.10 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 6H), 2.03 (s, 3H), 2.01 (s, 9H), 1.77-1.65 (m, 3H, α-6Neu5Ac H-3a).

Compound **27b**.



^{1}H NMR (600 MHz, D_2O) 5.11 (s, 1H, Man-4 H-1), 4.87 (s, 1H, Man-4' H-1), 4.76 (overlapped, 1H, Man-3 H-1), 4.72 (Overlapped, 1H, GlcNAc-1 H-1), 4.59 (d, J = 7.7 Hz, 1H, GlcNAc-2 H-1), 4.57-4.52 (m, 5H, GlcNAc-5 H-1, GlcNAc-7 H-1, GlcNAc-7' H-1, Gal-6 H-1, Gal-8 H-1), 4.23-3.42 (m, 76 H), 3.24-3.15 (m, 2H, $CH_2CH_2NH_2$), 2.76 (s, 3H, -NCH_3), 2.76-2.72 (m, 2H, α-3Neu5Ac H-3e), 2.06 (s, 6H), 2.04 (s, 3H), 2.03 (s, 6H), 2.02 (s, 6H), 1.79 (t, J = 12.1 Hz, 2H, α-3Neu5Ac H-3a).

Glycan Array Production Methods

Glycan arrays were custom printed on a MicroGridII (Digilab) contact microarray robot equipped with StealthSMP4B microarray pins (Telechem) as previously described. Briefly, samples of each glycan were diluted to 100 μM and, subsequently to 10 μM, in 150 NaPO4 buffer, pH 8.4. Aliquots of 10 μL were loaded in 384-well plates and imprinted onto NHS activated glass slides (SlideH, Schott/Nexterion) with 7 arrays, each containing 6 replicates of each sample at both concentrations. Printed slides were humidified post-print for 1 h and desiccated overnight. Remaining NHS-ester residues were quenched by immersing slides in 50 mM Ethanolamine in 50 mM borate buffer, pH 9.2, for 1 h. Blocked slides were washed with water, spun dry, and stored at room temperature until used.

Genes, expression vectors, protein expression, purification and glycan array binding of HA.

Codon optimized H1 and H5 encoding cDNAs (Genscript, USA) of A/Cal/05/09 (Accession; ACP41926.1), A/Kentucky/07 (Accession; CY028163), A/reassortant/NIBRG-14 (Viet Nam/1194/2004 x Puerto Rico/8/1934) (Accession; ACU65077.1), were cloned into the pCD5 expression as described previously (*47, 48*). The HA proteins were expressed in HEK293S GnT1(-) cells and purified from the cell culture supernatants as described previously. Binding of HA to the glycan array was assessed similarly as described previously. Briefly, purified, soluble trimeric HA was pre-complexed with horseradish peroxidase (HRP)-linked anti-Strep-tag mouse antibody and with Alexa488-linked anti-mouse IgG (4:2:1 molar ratio) prior to incubation.

Glycan Array Screening and Analyses

For analyses using lectins, lectins were diluted to 10 μg/mL lectin + 2 μg/mL Streptavidin or 1 μg/mL of lectin + 0.2 μg/mL Streptavidin. Recombinant HA analyses were performed using HA-antibody complexes prepared by mixing recombinant HA, mouse anti-Strep2 (AbCam), and anti-mouse-IgG Alexa Fluor 488 (Invitrogen) in a molar ratio of 4:2:1, respectively. Antibody analyses were prepared using 10 μg/mL of antibody mixed with 5 μg/mL of the appropriate detection antibody. Antibody complexes were anti-LeX (Seikagaku) + anti-mouse-IgM-R-PE (Jackson), CD15/anti-LeX-FITC (BioLegend) + anti-mouse-IgM-AlexaFluor488 (Invitrogen), anti-SLeX (Seikagaku) + anti-mouse-IgM-R-PE (Jackson) and CD15s/anti-SLeX + anti-mouse-IgM-R-PE (Jackson). E-selectin-Fc chimera recombinant protein (R&D Systems) was tested at 50 μg/mL and 25 μg/mL, pre-complexed with anti-human-IgG-R-PE at 25 μg/mL and 12.5

μg/mL, respectively. These prepared mixtures of complexes were incubated for 15 min on ice, diluted to 100 μl in TSM buffer (20 mM Tris, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 1% BSA, and 0.05% Tween-20) and incubated on the array surface in a humidified chamber for 1 h. Slides were subsequently washed by successive rinses with PBS-T, PBS, and deionized H_2O. Washed arrays were dried by centrifugation and immediately scanned for FITC and R-PE signal on a Perkin-Elmer ProScanArray Express confocal microarray scanner. Fluorescent signal intensity was measured using Imagene (Biodiscovery) and mean intensity minus mean background were calculated and graphed using MS Excel. For each glycan, the mean signal intensity is calculated from 6 replicates spots as follows. The highest and lowest signal of the 6 replicates are removed and the remaining 4 replicates are used to calculate the mean signal, standard deviation (SD), and standard error measurement (SEM). Bar graphs represent the averaged mean signal minus background for each glycan sample and error bars are the SEM value.

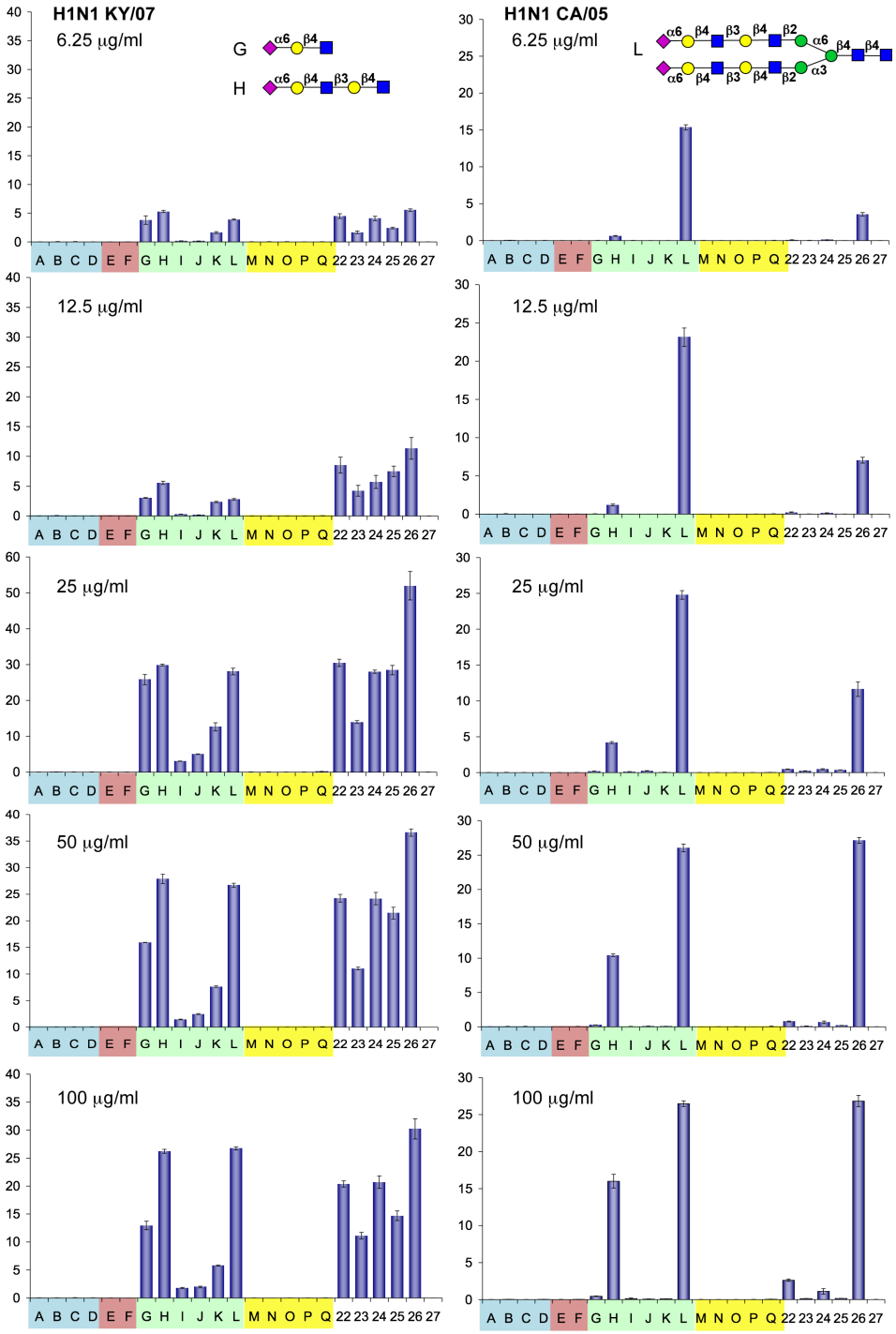


Fig. S24. Analysis of the receptor binding specificity of H1 hemagglutinins (HA) from seasonal and pandemic influenza viruses. Recombinant HA proteins from a representative seasonal, A/Kentucky/UR06-0258/2007 (LEFT), and pandemic, A/California/05/09 (RIGHT), H1N1 influenza viruses were used to interrogate the glycan microarray for binding specificity. Strep2-tagged HAs were premixed with mouse anti-Strep2 and anti-mouse-AlexaFluor647 (Invitrogen) in a molar ratio of 4:2:1, respectively, and allowed to pre-complex on ice. After 30 min, protein mixtures were serially diluted to achieve 5 samples at 6.25, 12.5, 25, 50, and 100 μg/mL. HA complexes were incubated on the array surface for 90 min and then washed. Washed arrays were scanned and evaluated for AlexaFluor647 signal. Shown is the mean signal and standard error of the fluorescence intensity ($x10^{-3}$) calculated for six independent replicates on the array.

Table S14. Compounds Printed on the Microarray.