ANGEWANDTE CHEMIE
A Journal of the Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z19309

69451 Weinheim, Germany

The Reactivity Based One-pot Synthesis of Lewis Y Carbohydrate Hapten: a Colon-rectal Cancer Antigen Determinant**

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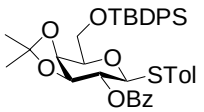
Supporting Information

General: All chemicals were purchased as reagent grade and used without further purification. Dichloromethane (CH_2Cl_2), toluene and acetonitrile (CH_3CN) were distilled over calcium hydride. Tetrahydrofuran (THF) and ether (Et_2O) were distilled over sodium metal/benzophenone ketyl. Anhydrous DMF was obtained form Aldrich. Molecular sieves (MS) for glycosylation were AW300 (from Aldrich) and activated prior to use. Reactions were monitored with analytical thin layer chromatography (TLC) on EM silica gel 60 F254 plates and visualized under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate. Flash column chromatography was performed on silica gel 60 Geduran (35–75 μm, EM Science). ^{1}H-NMR spectra were recorded on a Bruker DRX-500 (500 Hz) or 600 (600 Hz) spectrometer at 20 ^{o}C. Chemical shifts (δ ppm) were assigned according to the internal standard signal of tetramethylsilane in $CDCl_3$ (δ = 0 ppm) or spiked acetone in D_2O (δ = 2.04 ppm). ^{13}C NMR spectra were obtained using Attatched Proton Test (APT) on a Bruker DRX-500 or 600 (125 Hz) spectrometer and were reported in δ ppm scale using the signal of $CDCl_3$ (δ = 77.00 ppm) or spiked acetone in D_2O (δ = 29.8 ppm)as reference. Assignments of NMR signals were based on two-dimensional Double Quantum Filtered ^{1}H-^{1}H Correlation Spectroscopy (2D-DFQ-COSY) and Heteronuclear Multiple

Quantum ^{13}C-^{1}H Correlation Spectroscopy (2D-HMQC), which were recorded on the same Bruker DRX -series spectrometers mentioned above.

Le^{y} 1. To a solution of **14** (80 mg, 29 μmol) in acetic anhydride (Ac_2O) (2.5 ml) was added zinc dust (0.5 g). The reaction was stirred at room temperature for 10 h and the zinc dust was filtered off. The filtrate was then concentrated in vacuo to remove excess Ac_2O and the residue was purified with flash column chromatography (hexane/EtOAc, 1:3). The product was dissolved in CH_2Cl_2/MeOH (2 ml, 2:1), 25% NaOMe in MeOH (0.01 ml) was added and the reaction mixture was stirred for 18 h at room temperature. The reaction was then concentrated and the residue was co-evaporated with toluene (2x). The deacylated product was dissolved in MeOH/CH_2Cl_2/AcOH (2 ml, 3:1:1) and Pd-black (10 mg) was added. The reaction mixture was stirred under H_2 (1 atm) for 18 h at room temperature. After removal of the solvent in vacuo, the product was purified on a C-18 reverse phase column (LiChroprep RP-18, EM Science) with H_2O/MeOH elution (0% MeOH gradient to 60% MeOH). **1** Le^{y} (8 mg, 25%) was obtained as glassy white solid. For Le^{y} **1**: ^{1}H NMR (600 MHz, D_2O, 20 ^{o}C): δ = 1.05 (d, J = 6.6, 3H; fucosyl-CH_3), 1.08 (d, J = 6.6, 3H; fucosyl-CH_3), 1.11–1.17 (m, 2H; aglycon-CH_2), 1.35–1.45 (m, 4H; aglycon-CH_2), 1.84 (s, 6H; CH_3C=O), 2.21 (t, J = 7.3 Hz, 2H; aglycon-CH_2), 3.27 (m, 1H), 3.37–3.42 (m, 4H), 3.45–3.82 (m, 31H), 3.96 (d, J = 3.3 Hz, 1H), 4.06 (q, J = 6.2 Hz, 1H), 4.27 (d, J = 7.7 Hz, 1H; H^1), 4.33 (d, J = 7.7 Hz, 2H; H^1), 4.53 (d, J = 8.1 Hz, 1H; H^1), 4.69 (q, J = 6.8 Hz, 1H), 4.93 (d, J = 4.0 Hz, 1H; fucosyl-H^1), 5.08 (d, J = 3.3 Hz, 1H; fucosyl-H^1); ^{13}C NMR (125 MHz, D_2O , 20 ^{o}C): δ = 15.01, 15.03, 21.71, 21.84, 23.47, 24.22, 33.22, 51.65, 54.62, 59.34, 59.62, 60.48, 61.05, 66.37, 66.50, 67.26, 67.85, 68.32, 68.75, 69.29, 69.57, 69.82, 71.27, 71.51, 72.02, 72.62, 73.12, 74.31, 74.43, 74.93, 78.00, 81.58, 98.18, 99.00, 99.78, 100.60, 102.09, 102.46; HRMS (MALDI-FTMS) m/z calcd for $C_{47}H_{80}N_2O_{31}Na$ $[M + Na]^+$ 1191.4637, found 1191.4620.

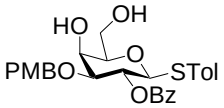
Compound 4.



p-Methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyanoside (15g, 33 mmol) in MeOH/CH_2Cl_2 (20 ml, 1:1) was deacetylated with 25% NaOMe in MeOH (0.5 ml) at 0 ^oC under Ar and the reaction was quenched with Amerlite IRC-50 (H^+ form). The crude product was obtained after filtering off the resin and concentration. To the deacetylated crude product (9 g, 31 mmol) and imidazole (3 g, 47 mmol) in anhydrous DMF (20 ml) at 0 ^oC was added TBDPSCl (10 ml, 38 mmol). After 3 h, MeOH was added to the mixture and the DMF was removed in vacuo. The C6-O silylated product (13 g, 25 mmol) was obtained by flash column chromatography purification (CH_2Cl_2/MeOH, 50:1 gradient to 20:1). The silylated compound from previous step was dissolved in acetone (20 ml) and camphorsulfonic acid (CSA) (0.6 g, 2.5 mmol) and 2,2-dimethoxypropane (6 ml, 49 mmol) were added. The reaction was stirred at room temperature for 3 h and the mixture was neutralized with triethylamine, followed by concentration in vacuum. The residue was dissolved in CH_2Cl_2 and was washed with saturated $NaHCO_3$, brine, dried ($MgSO_4$) and concentrated to give the crude isopropylidene acetal derivative (11.3 g, 20 mmol). The isopropylidene acetal product was dissolved in anhydrous CH_2Cl_2 (20 ml), to which pyridine (20 ml) and benzoyl chloride (3.5 ml, 30 mmol) were added. The reaction mixture was stirred at room temperature for 3 h and the mixture was diluted with CH_2Cl_2, which was washed with 0.1M HCl, brine, dried ($MgSO_4$) and concentrated for flash column chromatography purification (hexane/CH_2Cl_2/EtOAc, 4:1:0.2). The target compound **4** (11.4 g, 54% for 4 steps) was obtained as a colorless oily substance. For compound **4**: ^1H NMR (500 MHz, $CDCl_3$, 20 ^oC): δ = 1.07 (s, 9H; *t*-butyl), 1.33 (s, 3H; CH_3), 1.56 (s, 3H; CH_3), 2.28 (s, 3H; *p*-methyl), 3.95–4.02 (m, 3H; H-5 H-6), 4.32–4.34 (m, 2H; H-3; H-4), 4.71 (dd, *J* = 10.0, 1.0 Hz, 1H; H-1), 5.26 (dd, *J* = 10.0, 6.0 Hz, 1H; H-2), 7.01(d, *J* = 8.0 Hz, 2H; aromatic), 7.57 (t, *J* = 7.4 Hz, 1H; aromatic), 7.33–7.46 (m, 9H; aromatic), 7.72 (d, *J* = 7.7 Hz, 4H; aromatic), 8.07 (dd, *J* = 7.5, 1.1 Hz, 2 H; aromatic); ^{13}C NMR (125 MHz,

$CDCl_3$, 20 °C): δ = 19.21, 21.10, 26.34, 26.76, 27.71, 62.91, 72.24, 73.47, 77.03, 77.31, 86.56, 110.47, 127.65, 127.72, 128.30, 129.60, 129.72, 129.87, 129.90, 132.43, 133.09, 133.28, 135.64, 137.73, 164.38; HRMS *m*/*z* calcd for $C_{39}H_{44}O_6SSiNa$ $[M + Na]^+$ 691.2520, found 691.2511.

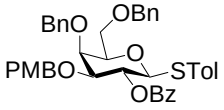
Compound 5.



Compound **4** (9.1 g, 13.6 mmol) was dissolved in CH_2Cl_2 (20 ml) to which 70% AcOH (20 ml) was added and the reaction was stirred at 80 °C for 4 h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2. The organic layer was washed with sat. $NaHCO_3$, H_2O, dried ($MgSO_4$) and concentrated for flash column chromatography purification (hexane/EtOAc, 3:1 gradient to 2:1). The product (6.9 g, 11 mmol) and dibutyl tin (II) oxide (3.5 g, 14 mmol) were suspended in anhydrous toluene/benzene (50 ml, 1:1) and refluxed with a Dean-Stark trap at 120 °C under Ar for 18 h. Solvent was reduced to approximately 30 ml by removal of benzene, the reaction temperature was cooled to 90 °C and then *p*-methoxybenzyl chloride (PMB) (3 ml, 22 mmol) and tetra-butyl ammonium iodide (Bu_4NI) (0.2 g, 0.55 mmol) were added. The solution was stirred for another 6 h and concentrated in vacuum for direct flash column chromatography purification (hexane/CH_2Cl_2/EtOAc, 3:1:0.75). The benzylated product was obtained as colorless oily substance, which was then desilylated with tetra-butyl ammonium fluoride TBAF (1M in THF, 10 ml) in CH_2Cl_2/THF (15 ml, 1:1). After 5 h, sat. NH_4Cl was added and the desilylated product was extracted with CH_2Cl_2 (3 x). The organic phase was combined and washed with brine, dried ($MgSO_4$) and concentrated for flash column chromatography purification (hexane/CH_2Cl_2/EtOAc, 1:1:2). Compound **5** (3.5 g, 60% from **4**) was obtained as a colorless oily substance. For compound **5**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 2.29 (s, 3H; *p*-methyl), 2.36 (br, 1H; OH), 2.80 (br, 1H; OH), 3.58 (t, *J* = 5.9 Hz, 1H; H-5), 3.64 (dd, *J* = 9.5, 3.3 Hz, 1H; H-3), 3.71 (s, 3H; *p*-OMe), 3.83 (d, *J* = 10.7 Hz, 1H; H-6), 4.01 (dd, *J* = 11.7, 6.9 Hz, 1H; H-6), 4.11 (d, *J* = 2.6 Hz, 1H; H-4), 4.43 (d, *J* =

12.1 Hz, 1H; benzyl), 4.58 (d, *J* = 12.1 Hz, 1H; benzyl), 4.69 (d, *J* = 10.2 Hz, 1H; H-1), 5.43 (t, *J* = 9.7 Hz, 1H; H-2), 6.64 (d, *J* = 8.4 Hz, 2H; aromatic), 7.05 (d, *J* = 9.0 Hz, 4H; aromatic), 7.33 (d, *J* = 8.1 Hz, 2H; aromatic), 7.46 (t, *J* = 8.0 Hz, 2H; aromatic), 7.60 (t, *J* = 7.3 Hz, 1H; aromatic), 8.00 (dd, *J* = 7.0, 1.1 Hz, 2H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ = 21.09, 26.52, 5512, 62.46, 66.69, 69.67, 71.01, 78.37, 78.66, 86.79, 113.77, 127.68, 128.32, 128.95, 129.03, 129.53, 129.61, 129.89, 132.87, 133.10, 134.77, 138.03, 159.35, 165.25; HRMS *m*/*z* calcd for $C_{28}H_{30}O_7SNa$ $[M + Na]^+$ 533.1604, found 533.1623.

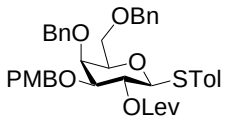
Compound 6.



Compound **5** (3.6 g, 6.8 mmol), in anhydrous DMF (15 ml) was added to DMF (5 ml) suspension of NaH (0.34g, 14.3 mmol), Bu_4NI (0.26 g, 0.7 mmol) and BnBr (2.44 ml, 20.4 mmol) at 0 °C under Ar. Reaction mixture was stirred at 0 °C to room temperature and quenched with MeOH. The reaction mixture was concentrated in vacuum, redissolved in CH_2Cl_2, and washed with dilute HCl (0.5 M), brine, dried ($MgSO_4$) and concentrated for flash column chromatography purification (hexane/CH_2Cl_2/EtOAc, 2:1:0.05 gradient 2:1:0.1), and compound **6** was obtained as a white solid (4.6 g, 90% from **5**). For compound **6**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 2.27 (s, 3H; *p*-methyl), 3.64–3.69 (m, 4H; H-3, H-5, H-6), 3.72 (s, 3H; *p*-OMe), 3.99 (d, *J* = 2.6 Hz, 1H; H-4), 4.40–4.48 (m, 3H; benzyl), 4.57 (d, *J* = 12.1 Hz, 1H; benzyl), 4.59 (d, *J* = 11.7 Hz, 1H; benzyl), 4.69 (d, *J* = 9.9 Hz, 1H; H-1), 4.98 (d, *J* = 11.7 Hz, 1H; benzyl), 5.61 (t, *J* = 9.6 Hz, 1H; H-2), 6.64 (d, *J* = 8.4 Hz, 2H; aromatic), 6.99 (d, *J* = 8.4 Hz, 2H; aromatic), 7.05 (d, *J* = 8.8 Hz, 2H; aromatic), 7.26–7.31 (m, 12H; aromatic), 7.45 (t, *J* = 7.7 Hz, 2H; aromatic), 7.59 (m, 1H; aromatic), 8.01 (dd, *J* = 8.4, 1.4 Hz, 2H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ = 21.10, 55.13, 68.86, 70.41, 71.35, 72.68, 73.59, 74.31, 77.66, 80.62, 87.22, 113.63,

127.45, 127.79, 127.91, 128.03, 128.15, 128.25, 128.41, 129.31, 129.44, 129.65, 129.72, 129.88, 130.17, 132.92, 137.58, 137.89, 138.51, 159.13, 165.21; HRMS *m*/*z* calcd for $C_{42}H_{42}O_7SNa$ $[M + Na]^+$ 713.2543, found 713.2546.

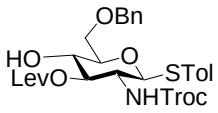
Compound 7.



To compound **6** (4.6 g, 6.7 mmol) in CH_2Cl_2/MeOH (10 ml) was added NaOMe (25% in MeOH, 0.5 ml) in MeOH/CH_2Cl_2 (15 ml, 1:1) and the reaction was stirred at room temperature and quenched with Amerlite IRC-50 (H^+ form). The crude product was obtained after filtration of resin and concentration in vacuum. Debenzoylated **6** from above was dissolved in anhydrous CH_2Cl_2 (10 ml), followed by the addition of 4-(dimethylamino) pyridine (DMAP) (0.5 g, 4.7 mmol), levulinic acid (1.2 g, 10 mmol) and 1-[3-(dimethylamino) propyl]-3-ethylcarbodiimide hydrochloride (EDC) (1.91 g, 10 mmol). The mixture was stirred at room temperature under Ar for 4 h, diluted with CH_2Cl_2, washed with 0.1 M HCl, H_2O, brine, dried ($MgSO_4$) and concentrated. Compound **7** was precipitated in hexane/Et_2O (2:1) as white solid (4.0 g, 90% for 2 steps). For compound **7**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 ^{o}C): δ = 2.18 (s, 3H; CH_3C=O), 2.28 (s, 3H; *p*-methyl), 2.59 (t, *J* = 6.1 Hz, 2H; lev-CH_2), 2.69–2.83 (m, 2H; lev-CH_2), 3.53 (dd, *J* = 9.5, 2.5 Hz, 1H; H-3), 3.56–3.66 (m, 3H; H-5, H-6), 3.80 (s, 3H; *p*-OMe), 3.92 (d, *J* = 2.5 Hz, 1H; H-4), 4.41 (dd, *J* = 22.7, 11.4 Hz, 2H; benzyl), 4.49 (d, *J* = 12.1 Hz, 1H; benzyl), 4.54 (d, *J* = 9.9 Hz, 1H; H-1), 4.55 (d, *J* = 12.1 Hz, 1H; benzyl), 4.55 (d, *J* = 12.1 Hz, 1H; benzyl), 4.60 (d, *J* = 11.7 Hz, 1H; benzyl), 5.35 (t, *J* = 9.5 Hz, 1H; H-2), 6.87 (d, *J* = 8.8 Hz, 2H; aromatic), 7.01 (d, *J* = 8.1, Hz, 2H; aromatic), 7.23–7.38 (m, 14H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 20 ^{o}C): δ = 21.10, 28.10, 29.89, 37.91, 55.24, 68.83, 70.14, 71.72, 72.88, 73.53, 74.25, 77.60, 80.88, 87.05, 113.76, 127.41, 127.75, 127.85, 127.98,

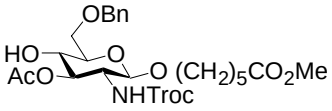
128.11, 128.38, 129.28, 129.47, 129.69, 130.97, 132.47, 137.57, 137.84, 159.26, 171.40, 206.37; HRMS *m*/*z* calcd for $C_{40}H_{44}O_8SNa$ $[M + Na]^+$ 707.2649, found 707.2624.

Compound 8.



For compound **8**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 ^{o}C): δ = 2.15 (s, 3H; CH_3C=O), 2.31 (s, 3H; *p*-methyl), 2.45–2.59 (m, 2H; lev-CH_2), 2.72–2.80 (m, 2H; lev-CH_2), 3.31 (d, *J* = 2.9 Hz, 1H; OH), 3.55–3.59 (m, 1H; H-5), 3.66–3.74 (m, 2H; H-4, H-2), 3.78 (dd, *J* = 5.1, 10.7 Hz, 1H; H-6), 3.84 (dd, J = 3.1, 10.7 Hz, 1H; H-6), 4.57 (dd, *J* = 11.7, 14.7 Hz, 2H; benzyl), 4.70 (d, *J* = 10.3 Hz, 1H; H-1), 4.77 (s, 2H; carbamate-CH_2), 5.07 (d, *J* = 9.7 Hz, 1H; H-3), 5.30 (d, *J* = 9.2 Hz, 1H; carbamate-NH), 7.04 (d, *J* = 8 Hz, 2H; aromatic), 7.28–7.37 (m, 7H; aromatic), 7.41 (d, *J* = 8 Hz, 2H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 20 ^{o}C): δ = 21.13, 28.16, 29.72, 38.34, 54.65, 69.93, 70.06, 73.63, 74.52, 76.81, 78.50, 87.14, 127.68, 127.71, 128.40, 128.82, 129.69, 132.97, 137.93, 138.15, 154.13, 173.27; HRMS *m*/*z* calcd for $C_{28}H_{32}Cl_3NO_8SNa$ $[M + Na]^+$ 670.0806, found 670.0816.

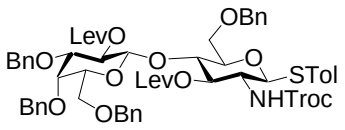
Compound 9.



For compound **9**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 ^{o}C): δ = 1.33–1.38 (m, 2H; aglycon-CH_2), 1.54–1.64 (m, 4H; aglycon-CH_2), 2.10 (s, 3H; CH_3C=O), 2.30 (t, *J* = 7.3 Hz, 2H; aglycon-CH_2), 3.08 (d, *J* = 2.9 Hz; OH), 3.44–3.49 (m, 1H; aglycon-CH_2), 3.52–3.55 (m, 1H; H-5), 3.63 (dd, *J* = 18.7, 9.5 Hz, 1H; H-2), 3.67 (s, 3H; CO_2Me), 3.72 (dt, *J* = 9.6, 3.3 Hz, 1H; H-4), 3.77–3.81 (m, 2H; H-6), 3.86 (dt, *J* = 9.5, 6.2 Hz, 1H; aglycon-CH_2), 4.49 (d, *J* = 8.1 Hz, 1H; H-1), 4.59 (dd, *J* = 23.5, 12.1 Hz, 2H; benzyl), 4.72 (dd, *J* = 54.3, 12.1 Hz, 2H; carbamate-CH_2), 5.09 (t, *J* = 9.9 Hz, 1H; H-3), 5.35 (d, *J* = 8.8 Hz, 1H; carbamate-NH), 7.36–7.28 (m, 5H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 20 ^{o}C): δ = 20.92, 24.37,

25.26, 28.97, 33.79, 51.53, 55.94, 69.48, 70.30, 71.09, 73.75, 73.88, 74.37, 74.89, 101.11, 127.73, 127.90, 128.47, 137.50, 154.27, 171.71, 174.23; HRMS *m*/*z* calcd for $C_{25}H_{34}Cl_3NO_{10}Na$ $[M + Na]^+$ 636.1140, found 636.1138.

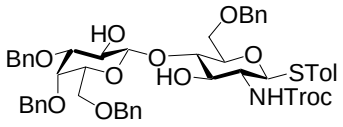
Compound 10.



Galactosyl donor **3** (0.22 g, 0.33 mmol), glucosaminyl acceptor **8** (0.14 g, 0.22 mmol) and MS (AW300) were suspended and stirred in anhydrous CH_2Cl_2 (2 ml) for 1 h under Ar. The mixture was cooled to –45 °C, and *N*-iodosuccinimde (NIS) (74 mg, 0.33 mmol) and 0.5 M triflic acid (TfOH) in ether (60 μl, 0.03 mmol). The reaction was stirred at –45 °C for 3 h and quenched with sat $NaHCO_3$ and solid $Na_2S_2O_3$. The reaction mixture was filtered and the filtrate was washed with sat. $Na_2S_2O_3$, sat. $NaHCO_3$, brine, dried ($MgSO_4$) and concentrated for flash column chromatography (hexane/EtOAc, 2.5:1). Compound **10** (0.10 g, 40%) was obtained as a glassy white substance. For compound **10**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 1.94 (s, 3H; CH_3C=O), 2.11 (s, 3H; CH_3C=O), 2.29 (s, 3H; *p*-methyl), 2.32–2.47 (m, 5H; lev-CH_2), 2.53–2.70 (m, 3H; lev-CH_2), 3.35 (dd, *J* = 2.6, 10.3 Hz, 1H; H'-3), 3.38 (dd, *J* = 5.0, 5.5 Hz, 1H; H'-5), 3.51–3.60 (m, 3H; H-5, H'-6), 3.68 (dt, *J* = 9.9 Hz, 1H; H-2), 3.74–3.80 (ddd, *J* = 3.3, 11.0, 19.1, 2H; H'-6), 3.86 (t, *J* = 9.2, 1H; H-4), 3.90 (d, *J* = 2.2 Hz, 1H; H'-4), 4.34 (d, *J* = 7.5 Hz, 1H; H'-1), 4.43–4.48 (m, 5H; benzyl), 4.61–4.67 (m, 3H; H-1, benzyl), 4.78 (dd, *J* = 12.1, 64.5 Hz, 2H; carbamate-CH_2), 4.88 (d, *J* = 11.3 Hz, 1H; benzyl), 5.02 (t, *J* = 9.1 Hz, 1H; H-3), 5.13 (dd, *J* = 8.1, 9.9 Hz, 1H; H'-2), 5.18 (d, *J* = 9.5 Hz, 1H; carbamate-NH), 7.04 (d, *J* = 8.1 Hz, 2H; aromatic), 7.22–7.41 (m, 22 H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ = 21.09, 27.78, 27.87, 29.58, 29.82, 37.68, 37.74, 54.98, 67.80, 67.98, 71.80, 71.91, 72.50, 73.05, 73.43, 73.47, 73.76, 73.80, 74.48, 79.04, 80.24, 87.00, 95.52, 100.28, 127.36, 127.46, 127.64, 127.67, 127.79, 127.88, 127.91, 128.17, 128.33, 128.35, 128.47, 128.63, 129.60, 133.21,

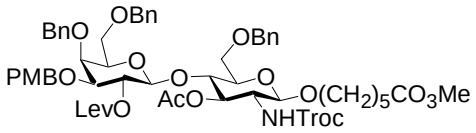
137.68, 137.90, 138.08, 138.10, 138.52, 154.04, 171.09, 172.46, 206.26, 206.55; HRMS *m*/*z* calcd for $C_{60}H_{66}Cl_3NO_{15}SNa$ [*M* + Na]$^+$ 1200.3111, found 1200.3120.

Compound 11.



Compound **10** (0.62 g, 0.52 mmol) was dissolved in pyridine (4 ml) and 4 M hydrazine hydrate ($NH_2NH_2 \cdot xH_2O$) in pyridine/AcOH (3:2) (1 ml, 4 mmol) was added. The reaction was stirred at room temperature for 3 h and quenched with penta-2, 4-dione. After removal of solvent, the residue was dissolved in CH_2Cl_2 and washed with 0.1 M HCl, brine, dried ($MgSO_4$) and concentrated for flash column chromatography (hexane/EtOAc, 5:3). Compound **11** (0.4 g, 79 %) was a white glassy solid. For compound **11**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 ^{o}C): δ = 2.28 (s, 3H; *p*-methyl), 3.12 (br, 1H), 3.33 (dd, *J* = 1.9, 9.9 Hz, 1H), 3.42–3.56 (m, 6H), 3.71–3.93 (m, 5H), 4.23 (d, *J* = 7.7 Hz, 1H; H'-1), 4.38 (dd, *J* = 11.5, 33.4 Hz, 2H; benzyl), 4.40–4.56 (m, 4H), 4.65–4.69 (m, 4H), 4.80–4.84 (m, 2H), 5.31 (br, 1H), 7.00 (d, *J* = 7.7 Hz, 2H; aromatic), 7.21–7.33 (m, 20H; aromatic), 7.38 (d, *J* = 7.7 Hz, 2H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 20 ^{o}C): δ = 21.05, 56.19, 68.36, 69.35, 70.91, 72.55, 72.59, 73.31, 73.51, 73.80, 74.42, 74.47, 77.47, 81.72, 82.65, 86.37, 95.54, 104.30, 127.43, 127.63, 127.69, 127.79, 127.84, 127.89, 127.95, 128.00, 128.13, 128.21, 128.24, 128.37, 128.41, 128.43, 128.46, 128.49, 128.86, 129.55, 133.00, 137.30, 137.87, 137.88, 137.92, 138.05, 154.00; HRMS *m*/*z* calcd for $C_{50}H_{54}Cl_3NO_{11}SNa$ [*M* + Na]$^+$ 1004.2375, found 1004.2343.

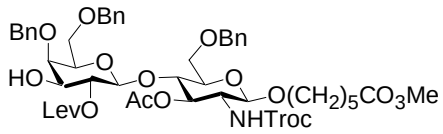
Compound 12.



Galactosyl building block **7** (0.84 g, 1.23 mmol), glucosaminyl building block **9** (0.58 g, 0.95 mmol) and MS (AW300) were suspended in anhydrous CH_2Cl_2 (8 ml) and stirred at room temperature under Ar for 2 h. The reaction mixture was then cooled to –45 ^oC followed by addition of NIS (0.28 g, 1.23 mmol) and 0.5 M TfOH (100 μl, 50 μmol). The reaction was stirred at –45 ^oC for 2 h and quenched with sat $NaHCO_3$ and solid $Na_2S_2O_3$. The reaction mixture was filtered and the filtrate was washed with sat. $Na_2S_2O_3$, sat. $NaHCO_3$, brine, dried ($MgSO_4$) and purified by flash column chromatography (toluene/ EtOAc, 2:1), target compound **12** (0.85 g, 77%) was obtained as glassy white solid. For compound **12**: ^1H NMR (500 MHz, $CDCl_3$, 20 ^oC): δ = 1.34 (q, *J* = 7.7 Hz, 2H; aglycon-CH_2), 1.52–1.63 (m, 4H; aglycon-CH_2), 1.87 (s, 3H; CH_3C=O), 2.13 (s, 3H; CH_3C=O), 2.28 (dt, *J* =7.4, 1.1 Hz, 2H; aglycon-CH_2), 2.40–2.44 (m, 2H; lev-CH_2), 2.58–2.70 (m, 2H; lev-CH_2), 3.32 (dd, *J* = 9.9, 2.5 Hz, 1H; H'-3), 3.38 (dd, *J* = 8.1, 5.7 Hz, 1H; H'-5), 3.44 (dt, *J* = 9.5, 6.6 Hz, 1H; aglycon-CH_2), 3.47–3.59 (m, 3H; H'-5, H-6), 3.65 (s, 3H; CO_2Me), 3.68–3.78 (m, 3H; H-2, H-6), 3.79 (s, 3H; *p*-OMe), 3.84–3.90(m, 3H; H-4, H'-4, aglycon-CH_2), 4.34 (d, *J* = 8.0 Hz, 1H; H'-1), 4.36 (d, *J* = 10.2 Hz, 1H; H-1), 4.39–4.42 (m, 3H; benzyl), 4.47 (d, *J* = 12.1 Hz, 1H; benzyl), 4.49 (d, *J* = 12.1 Hz, 1H; benzyl), 4.56 (d, *J* = 11.7 Hz, 1H; benzyl), 4.69 (d, *J* = 12.1 Hz, 1H; benzyl), 4.70 (dd, *J* = 40, 12.1 Hz, 2H; carbamate-CH_2), 4.90 (d, *J* = 11.7 Hz, 1H; benzyl), 5.01 (t, *J* = 9.5 Hz, 1H; H-3), 5.13 (dd, *J* = 9.9, 8.1 Hz, 1H; H'-2), 5.27 (d, *J* = 9.2 Hz, 1H; carbamate-NH), 6.88 (d, *J* = 8.4 Hz, 2H; aromatic), 7.36–7.20 (m, 17H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 20 ^oC): δ = 20.68, 24.37, 25.23, 27.76, 28.97, 29.82, 33.78, 37.64, 51.45, 55.18, 55.20, 55.95, 67.82, 67.95, 69.31, 71.38, 72.37, 72.57, 73.07, 73.38, 73.49, 74.26, 74.28, 74.31, 74.89, 79.90, 100.44, 101.46, 113.71, 127.35, 127.62, 127.74, 127.79, 127.82, 127.84, 128.09, 128.31, 128.43,

129.04, 129.98, 137.63, 138.09, 138.53, 154.27, 159.19, 170.67, 171.07, 174.11, 206.32; HRMS *m/z* calcd for $C_{58}H_{70}Cl_3NO_{18}Na$ $[M + Na]^+$ 1196.355, found 1196.3524.

Compound 13.



Compound **12** (1.2 g, 1.02 mmol) was dissolved in CH_2Cl_2/phosphate buffer (6 ml, 10:1) solution, followed by DDQ (0.8 g, 3 mmol) addition. After 1.5 h, the mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$, H_2O, brine, dried ($MgSO_4$), and concentrated for flash column chromatography purification (hexane/EtOAc, 1:1.5). The final product **13** (0.8 g, 75 %) was obtained as white glassy solid. For compound **13**: ^{1}H NMR (500 MHz, $CDCl_3$, 20 ^{o}C): δ = 1.34 (p, *J* = 7.3 Hz, 2H; aglycon-CH_2), 1.51–1.63 (m, 4H; aglycon-CH_2), 1.91 (s, 3H; CH_3C=O), 2.15 (s, 3H; MeC=O), 2.29 (dt, *J* = 7.3, 1.5 Hz, 2H; aglycon-CH_2), 2.43 (d, *J* = 9.2 Hz, 1H; OH), 2.48 (t, *J* = 6.6 Hz, 2H; lev-CH_2), 2.64–2.78 (m, 2H; lev-CH_2), 3.43–3.51 (m, 4H; H-3, H-5, H'-3, aglycon-CH_2), 3.55–3.60 (m, 2H; H-6), 3.66 (s, 3H; CO_2Me), 3.69–3.74 (m, 2H; H-2, H-6), 3.82–3.85 (m, 2H; H'-4, H-6), 3.86–3.88 (m, 1H; aglycon-CH_2), 3.91 (t, *J* = 9.2 Hz, 1H; H-4), 4.36 (d, *J* = 8.1 Hz, 1H; H'-1), 4.39 (d, *J* = 8.1 Hz 1H; H-1), 4.46 (dd, *J* = 15.8, 11.7 Hz, 2H; benzyl), 4.61 (dd, *J* = 118.5, 12.1 Hz, 2H; benzyl), 4.67 (dd, *J* = 41.1, 12.2 Hz, 2H; benzyl), 4.73 (dd, *J* = 48, 12.1 Hz, 2H; carbamate-CH_2), 4.83 (dd, *J* = 9.5, 8.1 Hz, 1H; H'-2), 5.04 (t, *J* = 9.8 Hz, 1H; H-3), 5.32 (d, *J* = 9.5 Hz, 1H; carbamate-NH), 7.25–7.36 (m, 15H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 20 ^{o}C): δ = 20.73, 24.33, 25.20, 27.83, 28.94, 29.75, 33.75, 37.91, 51.46, 55.99, 67.65, 69.31, 72.52, 72.93, 73.34, 73.90, 74.31, 74.59, 74.77, 75.03, 75.94, 95.55, 100.02, 101.38, 127.56, 127.68, 127.74, 127.82, 127.87, 128.34, 128.38, 128.43, 137.45, 137.99, 138.13, 154.26, 170.64, 172.33, 174.12, 206.73; HRMS *m*/z, calcd for $C_{50}H_{62}Cl_3NO_{17}Na$ $[M + Na]^+$ 1076.2975, found 1076.2943.