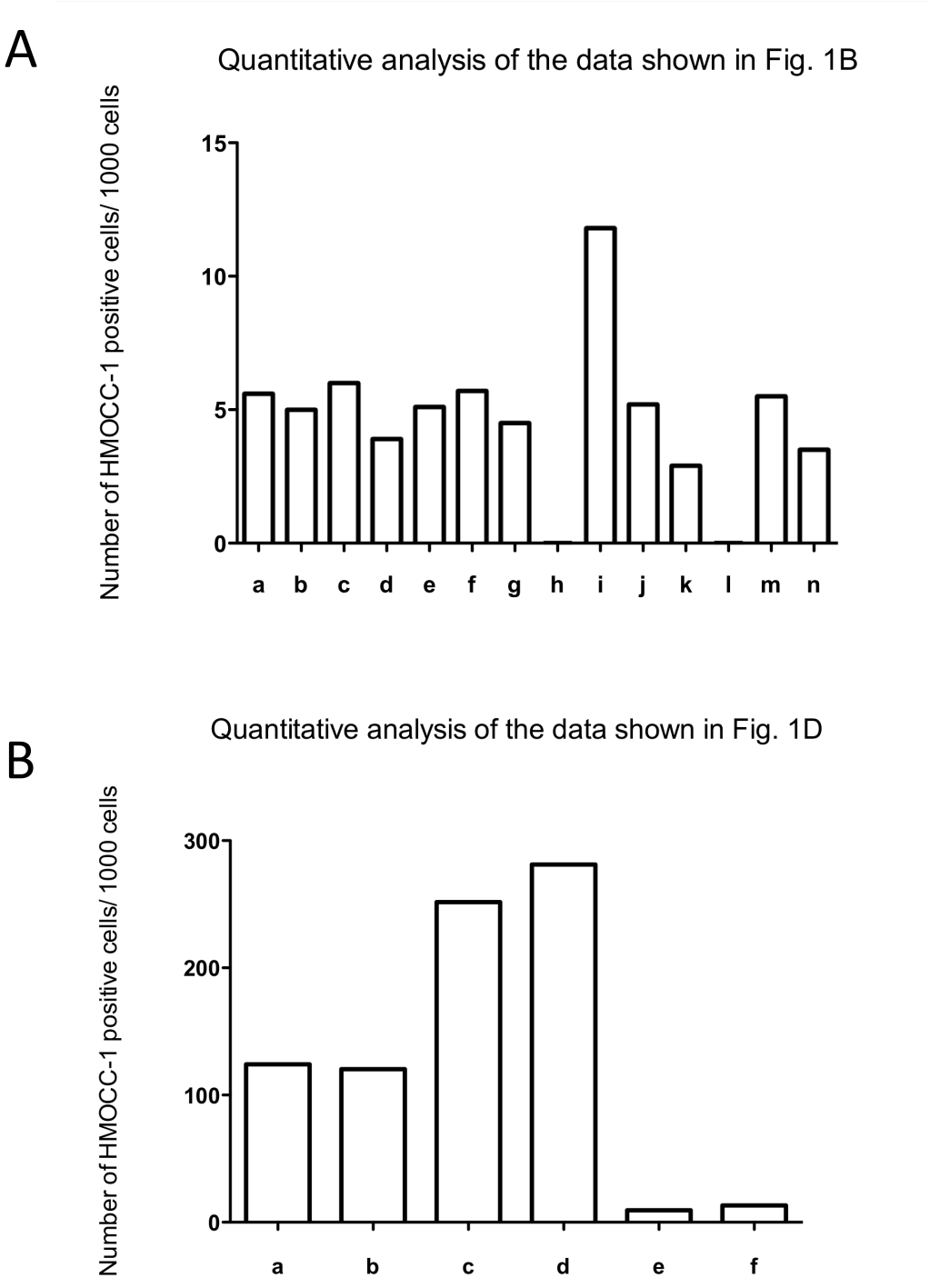
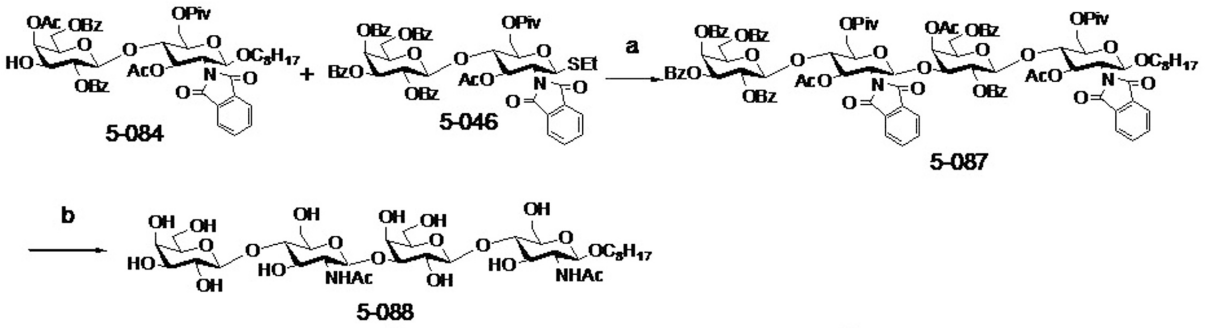


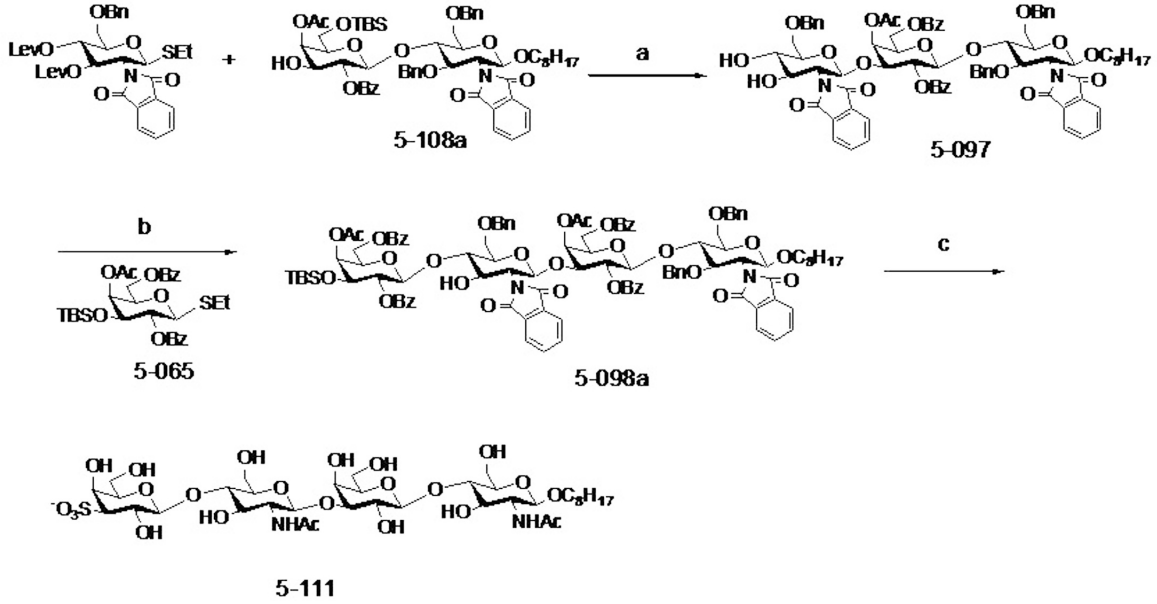
Fig. S1. Quantitative analyses of immunohistochemistry data presented in Fig. 1B and Fig. 1D.

A



conditions: a) NIS/TfOH, CH_2Cl_2, -40 °C, 61%; b) 1. n-BuOH, $NH_2CH_2CH_2NH_2$, 90 °C; 2. Py/Ac_2O; 3. NaOMe, CH_2Cl_2/MeOH; 4.$Pd(OH)_2$/C, MeOH, H_2, four steps 82%.

B



conditios: a) 1. NIS/TfOH, CH_2Cl_2, -40 °C, 2. Py/AcOH, NH_2NH_2-H_2O, 76%; b) NIS/AgOTf, CH_2Cl_2, -30 °C, 92%; c) 1. n-BuOH, $NH_2CH_2CH_2NH_2$, 90 °C; 2. Py/Ac_2O; 3. HF/Py, THF; 4. SO_3-NMe_3, DMF, 50 °C; 4. NaOMe, CH_2Cl_2/MeOH; 5.$Pd(OH)_2$/C, MeOH, H_2, five steps 71%.

Fig. S2. Chemical synthesis of unsulfated (**A**) and mono-sulfated (**B**) *N*-acetyl lactosaminyl tetrasaccahride octyls. Unsulfated tetrasaccharide (A) was designated as PW5-088b, and monosulfated oligosaccahride (B) was designated as PW5-111.

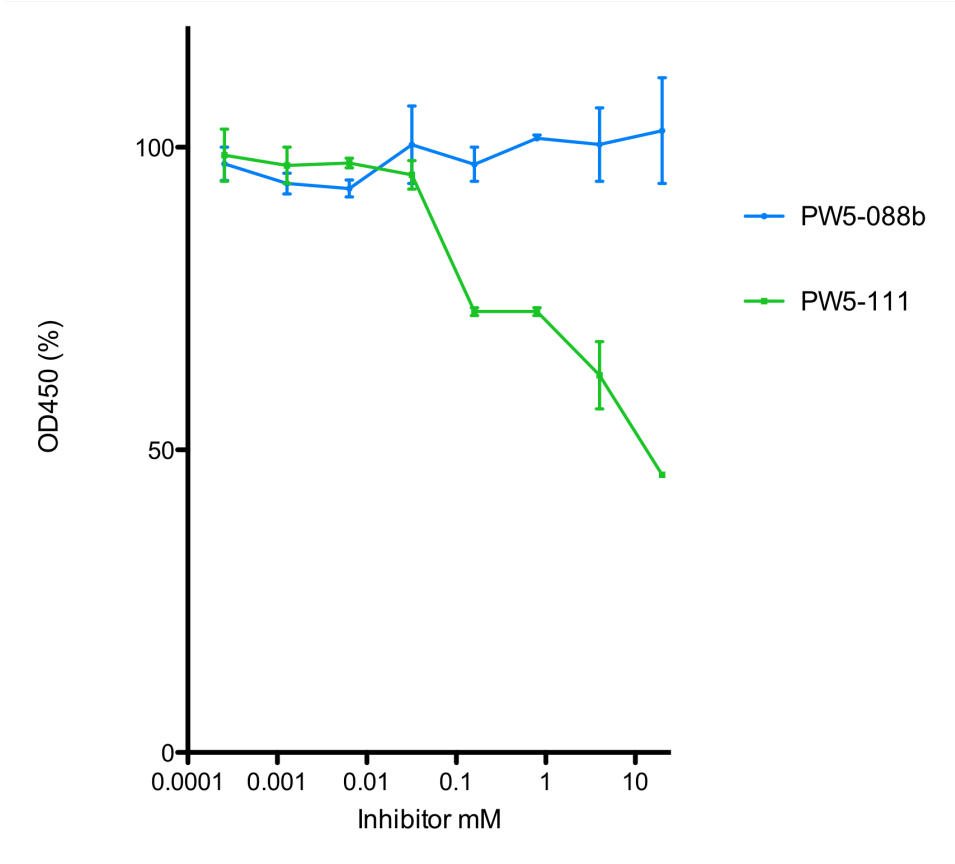


Fig. S3. ELISA inhibition assay by synthetic oligosaccharide-octyls. See Fig. S2 for the oligosaccharide structures.

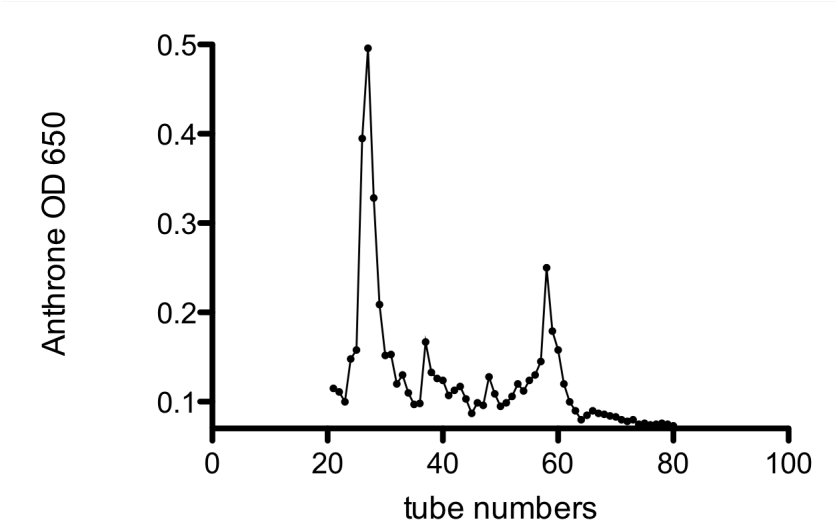


Fig. S4. Sephadex G-50 gel filtration chromatographies of glycans prepared from RMG-I cells. RMG-I cells (1 ml cells pellet) was digested by protease K. The soluble materials obtained after the digestion was treated with 0.5N-NaOH/1m M NaBH4 at 37C for 24 hours. After neutralization, the sample was treated with 0.1N H2SO4 at 90C for 1 hour to remove sialic acid. The sample was neutralized with TrisHCl and desalted by Sephadex G-15 equilibrated with water, lyophilized, and applied to Sephadex G-50 equilibrated with 0.2M NaCl. Fractions were monitored for neutral sugars by Anthrone color reaction. Materials eluted between 24 and 34 showed HMOCC-1 antigenic activity by ELISA inhibition assay, and were pooled as polylactosaminyl N-glycans.

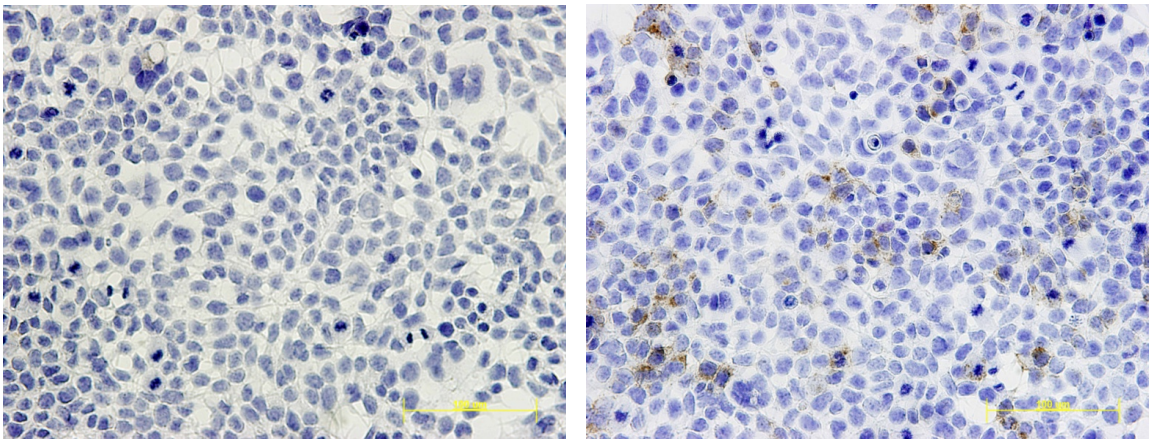


Fig. S5. Immunocytochemistry of HEK293T cells transfected by mammalian expression vectors for B3GNT2 and GAL3ST3. Transfected cells were stained by HMOCC-1 followed by peroxidase-conjugated anti-humans IgM antibody and peroxidase color reaction using DAB as a substrate. Hematoxylin was used for a counter stain.

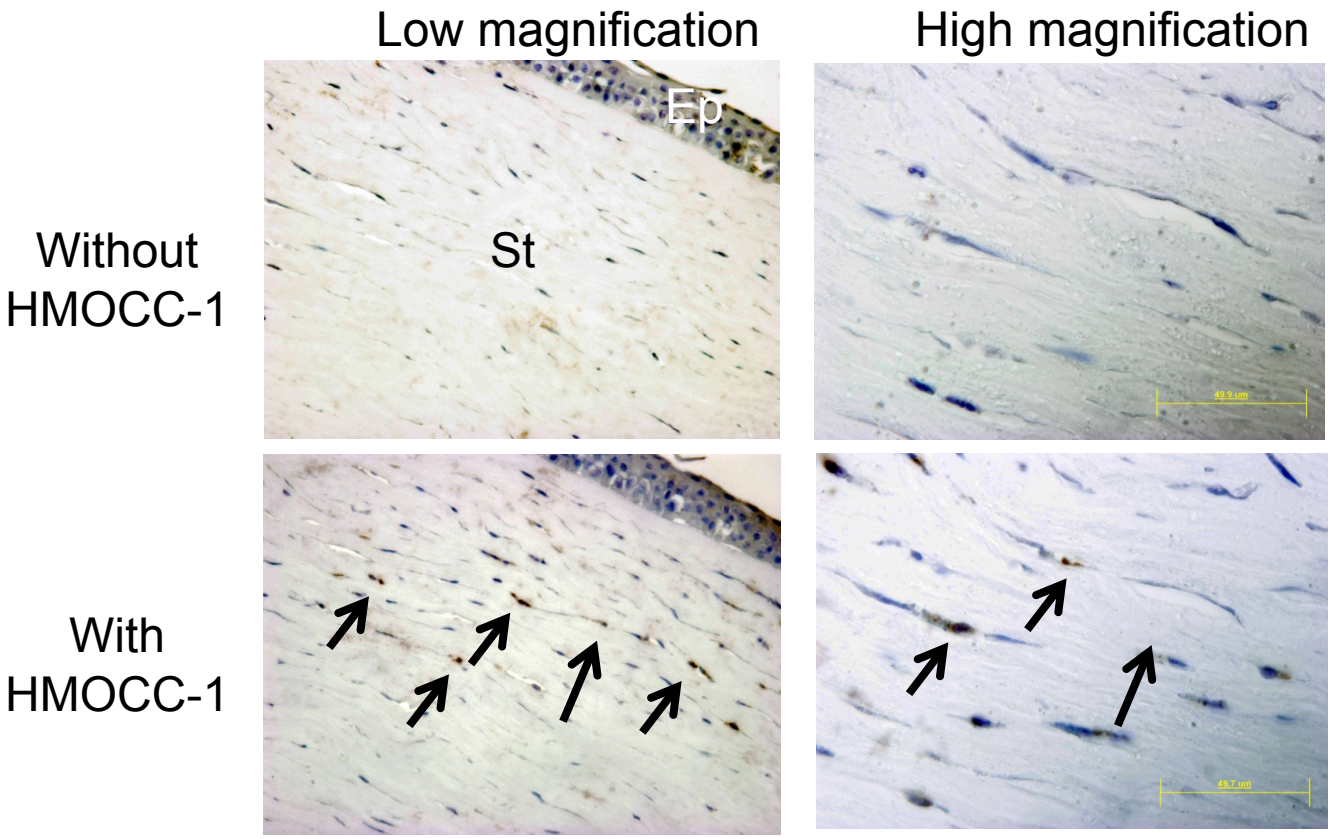


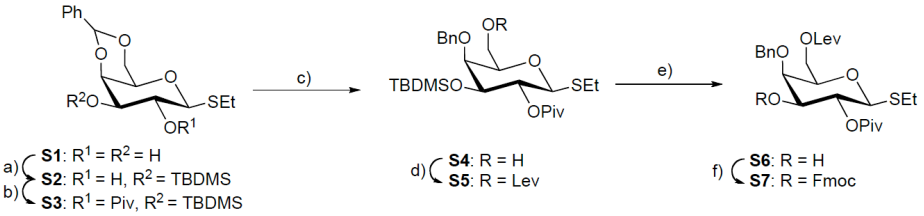
Fig. S6. Immunohistochemistry of human cornea with HMOCC-1. Paraffin section of human cornea was stained by HMOCC-1 followed by peroxidase-conjugated anti-human IgM antibody. Peroxidase color reaction was performed by DAB, and counter stain was by hematoxylin. Ep: corneal epithelia; St, stroma.

Supplemental Methods

(General)
Reactions were performed under an Ar-atmosphere except where noted. Analytical thin layer chromatography (TLC) was performed on Merk silica gel 60 F_{254} plates (0.25mm). Compounds were visualized by UV irradiation and by dipping the plate in a 5% (v/v) H_2SO_4 in methanol followed by heating. Flash column chromatography was carried out using forced flow of the indicated solvent on Fluka Kieselgel 60 (230-400 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL ECX (400 MHz, 100 MHz) or a Varian-VXR (400MHz, 100 MHz) spectrometer and are reported in ppm relative to the resonance of the solvent or tetramethylsilane as a standard (δ 0.0). ESI high-resolution mass spectra were performed by the MS-service at the Laboratory for Organic Chemistry (Free University of Berlin) or by the Scripps Center for Mass Spectrometry, and are given in *m/z*. ESI mass spectra were recorded on an Agilent ESI-TOF spectrometer, and are given in *m/z*.

.
(Abbreviation)
AIBN: azobisisobutyronitrile, Bn: benzyl, Bz: benzoyl, Cbz: benzyloxycarbonyl, DDQ: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, DIPC: *N*,*N*′-diisopropylcarbodiimide, DMAP: *N*,*N*′-dimethylaminopyridine, Fmoc: fluorenylmethyloxycarbonyl, Lev: levulinyl, NIS: *N*-iodosuccinimide, NPth: *N*-phthalimide, Piv: trimethylacetyl, PMB: *p*-methoxybenzyl, TBAF: tetra-*n*-butylammonium fluoride, TBDMS: *t*-butyldimethylsilyl, TCA: trichloroacetyl, TEAB: triethylammonium bicarbonate, Tf: trifluoromethanesulfonyl, TMS: trimethylsilyl, Ts: *p*-toluenesulfonyl.

Scheme 1. Synthesis of protected monosaccharides



a) TBDMSCl, imidazole, CH_2Cl_2, rt, 45 h, 84%; b) PivCl, pyridine, 70 °C, 45 h, 75%; c) BH_3·THF, $Cu(OTf)_2$, 0 °C to rt, 18 h; e) LevOH, DIPC, DMAP, CH_2Cl_2, rt, 2 h, 77% from **S3**; e) TBAF·$3H_2O$, AcOH, THF, 45 °C, 28 h, 80% f) FmocCl, pyridine, rt, 20 h, 80%.

Ethyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactopyranoside (S2).
To a solution of **S1**[S1] (1.29 g, 4.1 mmol) in anhydrous CH_2Cl_2 (40 mL), were added TBDMSCl (795 mg, 5.3 mmol) and imidazole (395 mg, 5.8 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 45 h and quenched with addition of sat. aq. $NaHCO_3$ (20 ml). The organic layer was washed with sat. aq. $NaHCO_3$ (20 ml). The aqueous layers were combined and back extracted with CH_2Cl_2 (1 x 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography (ethylacetate–hexane = 1:1, v/v) to give **S2** as colorless oil (1.48 g, 84%). ^{1}H NMR ($CDCl_3$) δ 7.39–7.37 (m, 2H), 7.25–7.20 (m, 3H), 5.37 (s, 1H), 4.22 (d, 1H, J = 9.0 Hz), 4.21, 3.88 (ABq, 2H, J_{AB} = 13 Hz), 3.95 (dd, 1H, J = <1 Hz, 3.6 Hz), 3.76 (t, 1H, J = 9.0 Hz), 3.59 (dd, 1H, J = 9.0 Hz, 3.6 Hz), 3.34 (d, 1H, J = <1 Hz), 2.74–2.56 (m, 2H), 2.24 (s, 1H), 1.19 (t, 3H, J = 7.5 Hz), 0.71 (s, 9H), 0.01 (s, 3H), –0.01 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 138.0, 128.7, 128.0, 125.1, 100.9, 85.2, 76.9, 75.5, 70.2, 69.4, 68.8, 25.7, 23.1, 19.2, 15.2, –4.4, –4.6. HRMS (ESI) *m/z* calcd. $[M+Na]^+$ 449.1788, found 449.1770.

Ethyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (S3).
To a solution of **S2** (4.27g, 10 mmol) in anhydrous pyridine (20 mL), was added PivCl (7.40 mL, 30 mmol) at 0 °C. The reaction mixture was stirred at 70 °C for 45 h, concentrated, diluted to CH_2Cl_2 (25 mL) and washed with brine (25 mL x 2) then sat. aq. $NaHCO_3$ (25 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel columnn chromatography (toluene–ethylacetate = 20:1, v/v) to give **S3** as a crystalline solid (3.84 g, 75%). ^{1}H NMR ($CDCl_3$) δ 7.54-7.51 (m, 2H), 7.39–7.35 (m, 3H), 5.50 (s, 1H), 5.34 (t, 1H, J = 10 Hz), 4.39 (d, 1H, J = 10 Hz), 4.37 (ABX, 1H, J_{AB} = 13 Hz, J_{AX} = <1 Hz), 4.12 (dd, 1H, J= 3.8 Hz, <1 Hz), 4.02 (ABX, 1H, J_{AB} = 13 Hz, J_{BX} = <1 Hz), 3.93 (dd, J=10 Hz, 3.8 Hz), 3.49 (br, 1H), 2.90–2.82 (m, 1H), 2.73–2.65 (m, 1H), 1.26 (t, 1H, J= 7.8 Hz), 1.24 (s, 9H), 0.86 (s, 9H), 0.08 (s, 3H), 006 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 176.8, 137.8, 128.8, 128.1, 126.2, 101.1, 82.8, 76.6, 73.3, 70.0, 69.4, 69.0, 38.8, 27.4, 25.6, 22.5, 18.0, 14.8, –4.1, –4.5. HRMS (ESI) *m/z* calcd. $[M+Na]^+$ 533.2364, found 533.2359.

Ethyl 4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-6-*O*-levulinyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (S5).

To a solution of **S3** (511 mg, 1.0 mmol) in 1 M BH_3·THF solution (10 mL), was added $Cu(OTf)_2$ (18.0 mg, 50 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 18 h, quenched with the addition of Et_3N (5 mL) and MeOH (5 mL) and concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate = 3:1, v/v) to give **S4** as colorless oil (423 mg, a mixture with small quantity of impurity). **S4** was used without further purification. ^{1}H NMR (selected signals, $CDCl_3$) δ 7.18–7.05 (m, 5H), 5.39 (t, 1H, J = 9.2 Hz), 5.07 (d, 1H, J = 11Hz), 4,54 (d, 1H, J = 11Hz), 4.34 (d, 1H, J = 9.2 Hz), 3.89–3.78 (m, 2H), 3.73 (dd, 1H, J = <1, 3.0), 3.57–3.51 (m, 2H), 1.74 (dd, 1H, J = 4.1 Hz, 8.2 Hz), 1.24 (s, 9H), 1.18 (t, 3H, J = 7.5 Hz), 0.90 (s, 9H), 0.18 (s 3H), 0.12 (s, 3H). ^{13}C NMR (selected signals, $CDCl_3$) δ 176.4, 137.8, 127.6, 127.1, 126.9, 83.1, 78.0, 76.4, 74.7, 74.0, 69.6, 61.4, 38.1, 26.8, 24.9, 22.7, 17.1, 13.9, –4.1, –5.7.

To a solution of **S4** and DMAP (57.0 mg, 0.47 mmol) in anhydrous CH_2Cl_2 (10 mL), were added levulinic acid (200 μL, 1.9 mmol) and DIPC (300 μL, 0.20 mmol) portion wise at room temperature. Reaction mixture was stirred at room temperature for 2 h and concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate = 7:1 to 5:1, v/v) to give **S5** as a colorless solid (468 mg, 77% from **S3**). ^{1}H NMR ($CDCl_3$) δ 7.25–7.11 (m, 5H), 5.25 (t, 1H, J = 9.5 Hz), 4.96, 4.41 (ABq, 2H, J_{AB} = 11 Hz), 4.22 (d, 1H, J = 9.5 Hz), 4.12 (A**B**X, 1H, J_{AB} = 11 Hz, J_{AX} = 6.4 Hz), 4.06 (A**B**X, 1H, J_{AB} = 11 Hz, J_{BX} = 5.9 Hz), 3.75 (dd, 1H, J = 2.6 Hz, 9.5 Hz), 3.63 (d, 1H, J = 2.6 Hz), 3.58 (AB**X**, J_{AX} = 6.4 Hz, J_{BX} = 5.9 Hz), 2.70–2.47 (m, 4H), 2.40 (t, 2H, J = 6.3), 2.06 (s, 3H), 1.14 (t, 3H, J = 8.1 Hz), 1.11 (s, 9H), 0.78 (s, 9H), 0.07 (s, 3H), –0.01 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 206.4, 177.0, 172.0, 138.5, 128.3, 127.6, 127.5, 83.7, 77.2, 75.9, 75.2, 75.0, 70.2, 63.5, 38.9, 37.9, 29.8, 27.9, 27.5, 25.7, 23.5, 17.9, 14.7, –3.4, –5.1. HRMS (ESI) *m/z* calcd. $[M+Na]^+$ 633.2888, found 633.2909.

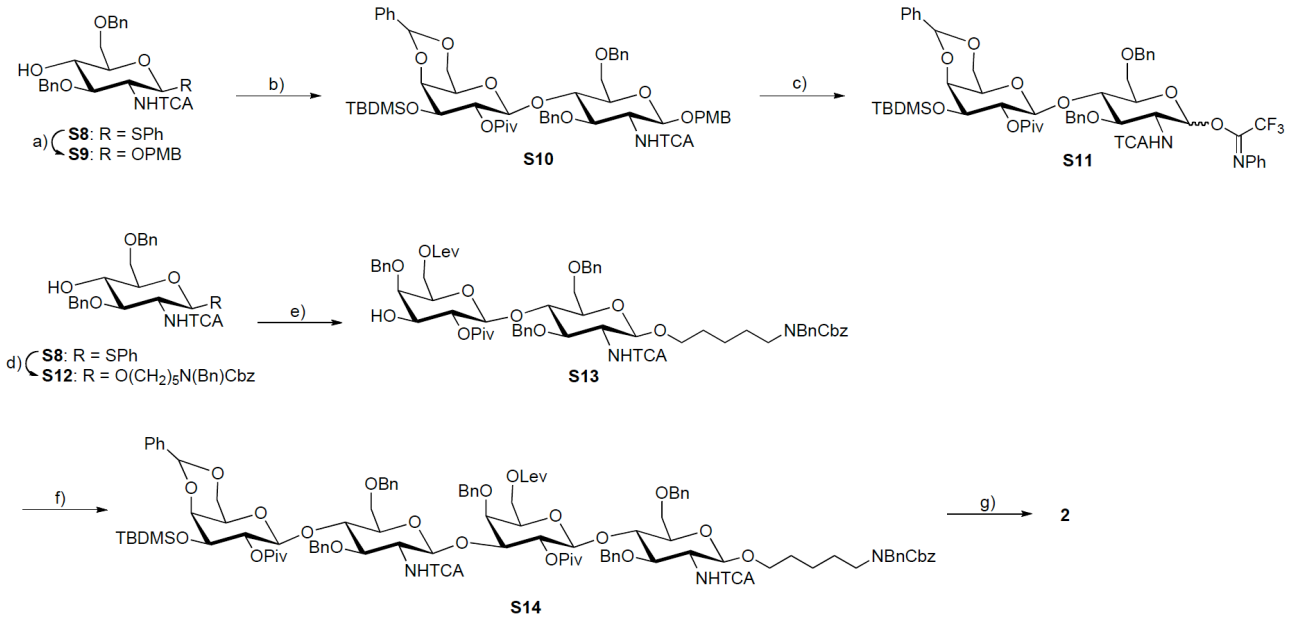
Ethyl 4-*O*-benzyll-6-*O*-levulinyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (S6).

S5 was dissolved to a mixture of acetic acid (1.2 mL) and TBAF (1 M in THF, 15.0 mL). The reaction mixture was stirred at 45 °C for 28 h, diluted with ethylacetate (150 mL) and washed with 0.5 M aq. HCl (50 mL). The aqueous layer was back extracted with ethylacetate (50 mL × 2). The organic layers were combined, washed with brine (50 mL) and sat. aq. $NaHCO_3$ (50 mL), dried under Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate = 2.5:1, v/v) to give **S6** as a colorless crystalline solid (305 mg, 80%). ^{1}H NMR ($CDCl_3$) δ 7.38–7.28 (m, 5H), 5.04 (t, 1H, J = 9.8 Hz), 4.75 (s, 2H), 4.42 (d, 1H, J = 9.8 Hz), 4.33 (A**B**X, 1H, J_{AB} = 11 Hz, J_{AX} = 6.5 Hz), 4.16 (A**B**X, 1H, J_{AB} = 11 Hz, J_{BX} =6.3 Hz), 3.87 (dd, 1H, J = <1 Hz, 3.4 Hz), 3.70–3.67 (m, 2H), 2.77-2.60 (m, 4H), 2.55 (t, 2H, J = 6.6 Hz), 2.32 (br, 1H), 2.19 (s, 3H), 1.26 (t, 3H, J = 7.5 Hz), 1.23 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 206.3, 178.5, 172.3, 137.7, 128.6, 128.0, 128.0, 83.3, 76.5, 76.0, 75.6, 74.3, 71.2, 62.8, 38.8, 37.9, 29.8, 27.8, 27.0, 23.9, 15.0. HRMS (ESI) *m/z* calcd. $[M+Na]^+$ 519.2023, found 519.2034.

Ethyl 4-*O*-benzyl-3-*O*-(fluorenylmethyloxycarbonyl)-6-*O*-levulinyl-2-*O*-pivaloyl-1-thio-β-D-galactopyranoside (S7).

To a solution of **S6** (885 mg, 1.8 mmol) in anhydrous pyridine (25 mL), was added FmocCl (1.55 g, 6.0 mmol) at room temperature. The reaction mixture was stired at room temperature for 20 h, concentrated, diluted with CH_2Cl_2 (30 mL) and washed with brine (20 mL × 3). The aqueous layers were combined, and back extracted with CH_2Cl_2 (20 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate = 3:1) and crystallization from EtOH to give **S7** as a colorless solid (1.02 g, 80%). ^{1}H NMR ($CDCl_3$) δ 7.67 (dt, 2H, J = 1.2 Hz, 7.6 Hz), 7.52 (d, 2H, J = 7.6 Hz), 7.34–7.16 (m, 10 H), 5.39 (t, 1H, J = 10 Hz), 4.86 (dd, 1H, J = 2.9 Hz, 9.8 Hz), 4.74, 4.46 (ABq, 2H, J_{AB} = 11 Hz), 4.38 (d, 1H, J = 10 Hz), 4.36–4.27 (m, 2H), 4.20 (A**B**X, 1H, J_{AB} = 11 Hz, J_{AX} = 6.4 Hz), 4.16 (t, J = 7.3 Hz), 4.06 (A**B**X, 1H, J_{AB} = 11 Hz, J_{BX} = 6.5 Hz), 3.91 (dd, 1H, J = <1 Hz, 2.9 Hz), 3.68 (AB**X**, 1H, J_{AX} = 6.4 Hz, J_{BX} = 6.5 Hz), 2.70–2.55 (m, 4H), 2.44 (t, 2H, J = 6.4 Hz), 2.11 (s, 3H), 1.17 (t, 3H, J = 7.0 Hz), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 206.4, 176.7, 177.3, 154.5, 143.1, 143.0, 141.3, 141.2, 137.4, 128.4, 128.3, 128.0, 127.9, 127.2, 125.1, 125.1, 120.1, 120.1, 83.7, 79.9, 75.8, 74.9, 73.5, 70.3, 67.2, 62.6, 46.6, 38.7, 37.8, 29.7, 27.7, 26.9, 23.8, 14.8. HRMS (ESI) *m/z* calcd. $[M+Na]^+$ 741.2704, found 741.2725.

Scheme 2. Synthesis of 2



a) *p*-methoxybenzylalcohol, NIS, TfOH, CH_2Cl_2, 0 °C, 62%; b) **S3**, NIS, TfOH, MS4Å, CH_2Cl_2, -40 °C to -20 °C, 40 min, 88%; c) (i) DDQ, CH_2Cl_2–H_2O (20:1, v/v), rt, 5 h; (ii) $CF_3C(NPh)Cl$, K_2CO_3, Acetone, 0 °C to rt, 4 h, 53% from **S10**; d) *N*-(Benzyl)-benzyloxycarbonyl-5-aminopentan-1-ol, NIS, TfOH, CH_2Cl_2, -40 °C to -20 °C, 40 min, 95%; e) (i) **S7**, NIS, TfOH, MS4Å, CH_2Cl_2, -40 °C to -20 °C, 40 min; (ii) Et_3N, CH_2Cl_2, rt, 3 h, 64% from **S12**; f) **S11**, TMSOTf, MS4Å, CH_2Cl_2, -78 °C to -20 °C, 45 min, 53 %; g) (i) Bu_3SnH, AIBN, xylene, 90 °C, 5 h; (ii) HF·pyridine, pyridine, rt, 16 h; (iii) $NH_2NH_2·H_2O$, AcOH, pyridine, rt, 3 h; (iv) SO_3·pyridine, pyridine, rt, 12 h; (v) NaOMe, MeOH, 45 °C, 3 h; (vi) Pd/C, AcOH, MeOH-H_2O (2:1, v/v), 48% from **S14**.

***p*-Methoxybenzyl 3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S9).**

S8 was synthesized from phenyl 4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-1-thio-β-D-glucopyranoside[S2] in a reported method[S3]. ^{1}H NMR ($CDCl_3$) δ 7.51–7.47 (2H), 7.37–7.22 (m, 13H), 6.83 (d, 1H, J = 8.0 Hz), 5.15 (d, 1H, J = 10 Hz), 4.76, 4.72 (ABq, 2H, J_{AB} = 11 Hz), 4.59, 4.56 (ABq, 2H, J_{AB} = 12 Hz), 3.96 (dd, 1H, J = 8.6, 10 Hz), 3.81 (ABX, 1H, J_{AB} = 10 Hz, J_{AX} = 4.9 Hz), 3.76 (ABX, 1H, J_{AB} = 10 Hz, J_{BX} = 4.7 Hz) 3.69 (dt, 1H, J = 2.6 Hz, 8.6 Hz), 3.59–3.54 (m, 1H), 3.49 (dt, 1H, J = 8.0 Hz, 10 Hz), 2.73 (d, 1H, J = 2.6 Hz). ^{13}C NMR ($CDCl_3$) δ 161.5, 137.7, 137.6, 133.1, 131.8, 129.0, 128.6, 128.5, 128.3, 128.1, 128.1, 127.9, 127.7, 84.7, 81.1, 77.9, 75.0, 73.8, 73.2, 70.5, 56.6. HRMS (ESI) *m/z* calcd. $[M+Na]^+$ 618.0646, found 618.0667. To a solution of **S8** (923 mg, 1.6 mmol) and *p*-methoxybenzylalchol (520 mg, 3,8 mmol) in CH_2Cl_2 (20 mL), was added NIS (526 mg, 2.3 mmol) and TfOH (10 µL, 0.11 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min, quenched with the addition of sat. aq. $NaHCO_3$ (20 mL) and sodium thiosulfate (1.5 g), washed with sat. aq. $NaHCO_3$ (20 mL). The aqueous layer was back extracted with $CHCl_3$ (20 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate = 5:1 to 2:1, v/v) to give **S9** as a colorless solid (600 mg, 62%). ^{1}H NMR ($CDCl_3$) δ 7.42–7.20 (m), 6.91–6.77 (m, 3H), 4.89 (d, 1H, J = 7.9 Hz), 4.79 (d, 1H, J = 11 Hz), 4.76, 4.74 (ABq, 2H, J_{AB} = 11 Hz), 4.64, 4.58 (ABq, 2H, J_{AB} = 11 H), 4.52 (d, 1H, J = 11 Hz), 3.98 (dd, 1H, J = 8.6 Hz, 10 Hz), 3.83–3.70 (m, 6H), 3.57-3.48 (m, 2H), 2.64 (br, 1H). ^{13}C NMR ($CDCl_3$) δ 161.7, 159.4, 137.9, 137.5, 129.8, 128.9, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 113.8, 97.8, 79.6, 74.7, 73.8, 73.6, 73.5, 70.7, 70.5, 58.2, 55.2. MS (ESI) *m/z* calcd. $[M+Na]^+$ 646.1137, found 646.1136.

***p*-Methoxybenzyl 4,6-*O*-benzylideneacetal-2-*O*-pivaloyl-3-O-*tert*-butyldimethylsilyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S10).**

S3 and **S9** were azeotroped with toluene (3 mL × 3) prior to use. To a solution of **S3** (0.15 g, 0.30 mmol) and **S9** (64 mg, 0.10 mmol) in anhydrous CH_2Cl_2 (dried over MS4Å prior to use, 4 mL), were added NIS (90 mg, 0.40 mmol) and MS4A (0.1 g). The reaction mixture was stirred for 30 min at –40 °C then TfOH (2.5 µL, 28 µmol) was added. The reaction mixture was stirred for 10 min at –40 °C, 30 min at -20 °C then quenched with the addition of sodium thiosulfate (1 g) and sat. aq. $NaHCO_3$ (15 mL). The mixture was diluted with CH_2Cl_2 (20 mL). The organic layer was separated and washed with sat. aq. $NaHCO_3$ (15 mL). The aqueous layers were combined and back extracted with CH_2Cl_2 (10 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography (toluene–ethylacetate = 1:0 to 4:1, v/v) to give **S10** as a colorless foam (97 mg, 88%).^{1}H NMR ($CDCl_3$) δ 7.40–7.00 (m, 17 H), 6.88 (d, 1 H, J = 8.5 Hz), 6.76 (dt, 2 H, J = <1 Hz, 8.5 Hz), 5.39 (s, 1 H), 5.15 (dd, 1H, J = 8.4 Hz, 9.3 Hz), 4.99 (d, 1 H, J = 11 Hz), 4.81 (d, 1 H, J = 7.1 Hz), 4.74 (d, 1 H, J = 11 Hz), 4.71 (d, 1 H, J = 11 Hz), 4.52 (d, 1 H, J = 11 Hz), 4.44 (d, 1 H, J = 11 Hz), 4.41 (d, 1 H, J = 11 Hz), 4.40 (d,

1 H, *J* = 8.0 Hz), 4.20 (d, 1 H, *J* = 12 Hz), 4.09 (t, 1 H, *J* = 7.9 Hz), 3.93–3.86 (m, 3 H), 3.90-3.79 (m, 2 H), 3.71 (s, 3 H), 3.66–3.63 (m, 2 H), 3.42–3.41 (m, 1 H), 3.05 (s, 1 H), 1.15 (s, 9H), 0.79 (s, 9H), 0.00 (s, 3 H), 0.00 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 176.5, 161.5, 159.3, 139.1, 137.7, 129.6–126.1, 113.6, 100.9, 99.7, 98.3, 77.6, 76.2, 75.1, 75.0, 74.6, 73.5, 72.0, 71.8, 70.6, 68.8, 68.5, 66.5, 56.7, 55.2, 38.7, 27.4, 25.6, 17.9, –4.0, –4.5. MS (ESI) *m/z* calcd. $[M+Na]^+$ 1094.3, found 1094.1.

_N_-Phenyl-trifluoroacetoimidoyl 4,6-_O_-benzylidene-3-_O_-_tert_-butyldimethylsilyl-2-_O_-pivaloyl-β-D-galactopyranosyl-(1→4)-3,6-di-_O_-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S11).

To a solution of **S10** (70 mg, 65 mmol) in anhydrous CH_2Cl_2 (2.0 mL), were added phosphate buffer (pH 7) and DDQ (45 mg, 0.20 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 5 h, then diluted with CH_2Cl_2 (15 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (10 mL × 3). The aqueous layers were combined, back extracted with CH_2Cl_2 (10 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated.

The crude product was passed through a pad of silica gel to remove remaining starting material, dried under vacuum and used in the next reaction without further purification. To a solution of the crude product in anhydrous acetone (5.0 mL) was added K_2CO_3 (54 mg, 0.39 mmol) and $CF_3C(NPh)Cl$ (60 mg, 0.29 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 4 h then concentrated. The crude product was purified by silica gel column chromatography (toluene–ethylacetate = 1:0 to 5:1, v/v) to give **S11** as colorless foam (39 mg, 53% form **S10**).

(major isomer) ^{1}H NMR ($CDCl_3$) δ 7.42–7.03 (m), 6.71 (d, 2 H, *J* = 7.8), 6.48 (d, 1H, *J* = 6.5 Hz), 5.42 (s, 1H), 5.23 (dd, 1 H, *J* = 8.4 Hz, 9.5 Hz), 5.15 (d, 1 H, *J* = 11 Hz), 4.77 (d, 1 H, *J* = 11 Hz), 4.67 (d, 1 H, *J* = 11 Hz), 4.41 (d, 1 H, *J* = 11 Hz), 4.36 (d, 1 H *J* = 8.2 Hz), 4.34–4.25 (1H), 4.14–4.05 (1H), 3.98–3.90 (m, 2 H), 3.87–3.59 (m, 5 H), 3.11 (s, 1 H), 1.16 (s, 9 H), 0.81 (s, 9H), 0.05 (s, 3 H), 0.04 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 119.3 (C-1), 100.9 (CHPh), 99.4 (C-1^{II}), 92.7 (CCl_3). MS (ESI) *m/z* calcd. $[M+Na]^+$ 1145.3, found 1145.2.

_N_-(Benzyl)-(benzyloxycarbonyl)-5-aminopentyl 3,6-di-_O_-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S12).

S8 and *N*-Benzyl-(benzyloxycarbonyl)-5-aminopentan-1-ol[S4] were azeotroped with anhydrous toluene (3 mL × 3) and dried under vacuum prior to use. To a solution of **S8** (0.20 g, 0.37 mmol) and *N*-(Benzyl)-benzyloxycarbonyl-5-aminopentan-1-ol (0.19 g, 0.56 mmol) in anhydrous CH_2Cl_2 (15 mL), were added MS4Å (ca. 0.2 g) and NIS (0.11 g, 0.48 mmol) at –40 °C. The reaction mixture was stirred at –40 °C for 15 min. To the reaction mixture was added TfOH (3 μL, 34 μmol). The reaction mixture was stirred at –40 °C for 10 min, at –20 °C for 30 min then quenched with the addition of sat. aq. $NaHCO_3$ (20 mL) and sodium thiosulfate (1 g). The organic phase was washed with sat. aq. $NaHCO_3$ (20 mL). The aqueous layers were combined and back extracted with CH_2Cl_2 (20 mL). The organic layers were combined, and filtered through a pad of cotton, and concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate, 1:0 to 3:1, v/v) and precipitation with hexane to give **S12** as a colorless powder (0.29 mg, 95%). ^{1}H NMR ($CDCl_3$) δ 7.38–7.02 (m, 20H), 5.06 (br, 2H), 4.84–4.62 (m, 3H), 4.59–4.35 (m, 4H), 3.96 (br, 1H), 3.86–3.00 (m, 9H), 1.54–1.30 (m, 4H), 1.29–1.09 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 162.8, 157.2, 138.0, 137.8, 137.5, 128.6–127.7, 127.3, 127.2, 99.2, 79.6, 74.7, 73.8, 73.6, 73.5, 70.5, 69.8, 67.1, 58.5, 50.2, 47.2, 29.5, 28.0, 23.5. MS (ESI) *m/z* Calcd. $[M+Na]^+$ 835.2290, found 835.2273.

_N_-Benzyl-(benzyloxycarbonyl)-5-aminopentyl 4-_O_-benzyl-6-_O_-levulinyl-2-_O_-pivaloyl-β-D-galactopyranosyl-(1→4)-3,6-di-_O_-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S13).

S7 and **S12** were azeotroped with anhydrous toluene (3 mL × 3) and dried under vacuum prior to use. To a solution of **S7** (0.11 g, 0.15 mmol) and **S12** (41 mg, 50 μmol) in CH_2Cl_2 (2 mL), were added MS4Å (0.1 g) and NIS (46 mg, 0.20 mmol) at –40 °C. The reaction mixture was stirred at –40 °C for 30 min then TfOH (2.5 μL, 28 μmol) was added. The reaction mixture was stirred at –40 °C for 10 min, –20 °C for 30 min, quenched with the addition of sat. aq. $NaHCO_3$ (10 mL) and sodium thiosulfate (0.5 g), and diluted to CH_2Cl_2 (10 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (10 mL). The aqueous layers were combined and back extracted with CH_2Cl_2 (10 mL). The organic layers were combined, dried under Na_2SO_4, filtered and concentrated. The residue was dissolved to a solution of CH_2Cl_2–Et_3N (10:1, v/v, 10 mL). The solution was stirred at room temperature for 3 h and concentrated. The obtained crude product was purified by silica gel column chromatography (toluene–ethylacetate, 1:0 to 7:3, v/v) to give **S13** as a colorless foam (41 mg, 64%). ^{1}H NMR ($CDCl_3$) δ 7.41–7.09 (m, 26H), 5.16 (br, 2H, J = 13Hz), 4.92 (t, 1H, *J* = 8.1 Hz), 4.90 (d, 1H, *J* = 11Hz), 4.83 (br, 1H), 4.74 (d, 1H, *J* = 11Hz), 4.71 (d, 1H, *J* = 12 Hz), 4.68 (d, 1H, *J* = 12 Hz), 4.55 (d, 1H, *J* = 11 Hz), 4.48 (br, 2H), 4.43 (d, 1H, *J* = 12 Hz), 4.39 (d, 1H, *J* = 8.1 Hz), 4.22–3.98 (m, 4H), 3.84–3.72 (m, 4 H), 3.59–3.33 (m, 5H), 3.19 (br, 2H), 2.71 (t, 2H, *J* = 7.0 Hz), 2.51 (t, 2H, *J* = 7.0 Hz), 2.17 (s, 3H), 1.59–1.41 (br, 4 H), 1.36–1.21 (m, 2 H), 1.21 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 206.5, 178.8, 172.2, 161.7, 156.2, 137.9, 137.8, 137.7, 128.6–127.2, 99.4, 99.2, 92.5, 76.4, 75.7, 75.4, 74.9, 74.3, 73.6, 73.6, 73.4, 72.0, 69.9, 68.2, 67.1, 64.2, 62.3, 57.1, 50.4, 46.6, 38.8, 37.9, 29.8, 29.1, 27.8, 27.2, 23.2. MS (ESI) *m/z* calcd. $[M+Na]^+$ 1269.4, found 1269.4.

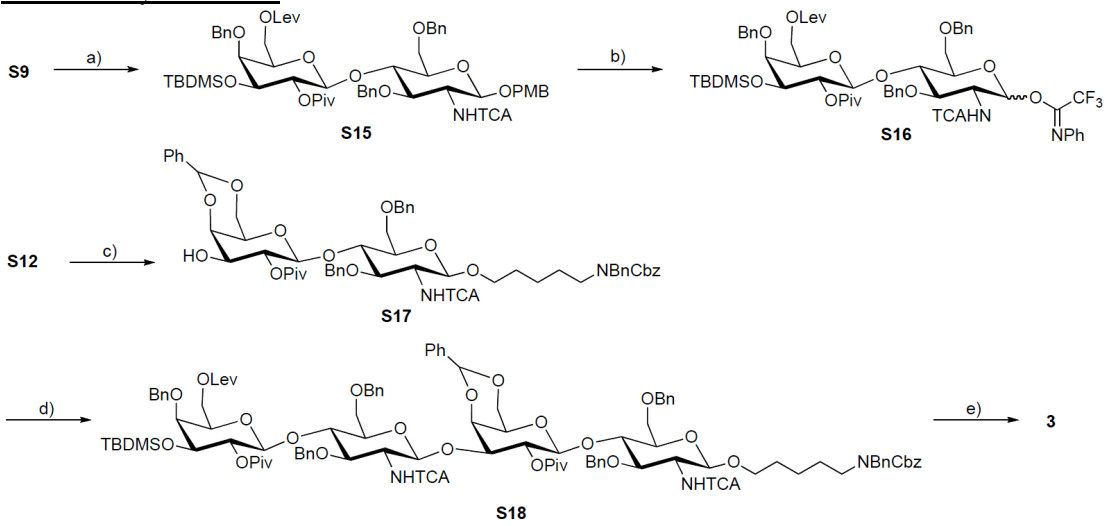
***N*-Benzyl-(benzyloxycarbonyl)-5-aminopentyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-*O*-pivaloyl-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1 → 3)-4-*O*-benzyl-6-*O*-levulinyl-2-*O*-pivaloyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S14).**

S11 and **S13** were azeotroped with anhydrous toluene (3 mL × 3) and dried under vacuum prior to use. To a solution of **S11** (39 mg, 34 mmol), **S13** (26 mg, 22 mmol) and MS4Å (30 mg) in CH_2Cl_2 (0.9 mL), was added TMSOTf (1.0 μL, 5.5 mmol) at -78 °C. The reaction mixture was stirred at –78 °C for 15 min, at –20 °C for 30 min, quenched with the addition of Et_3N (0.1 mL) and MeOH (50 μL) and concentrated. The crude product was purified by silica gel column chromatography (toluene–ethylacetate, 1:1 to 5:1, v/v) to give **S14** as a colorless oil (25 mg, 53%). ^{1}H NMR ($CDCl_3$) δ 7.39–6.99 (m, 42H), 5.38 (s, 1H), 5.16 (t, 1H, *J* = 8.5 Hz), 5.14 (t, 1H, *J* = 9.0 Hz), 5.09 (br, 2H), 4.96 (d, 1H, *J* = 11Hz), 4.87 (d, 1H, *J* = 11Hz), 4.74–4.30 (m, 13H), 4.25 (d, 1H, *J* = 8.5 Hz), 4.15 (d, 1H, *J* = 12 Hz), 4.12 (t, 1H, *J* = 7.5 Hz), 4.04–3.59 (m, 17H), 3.53–3.22 (m, 9H), 2.56 (t, 2H, *J* = 6.5 Hz), 2.32 (t, 2H, *J* = 6.5 Hz), 2.04 (s, 3H), 1.52–1.28 (m, 4H), 1.25–1.02 (m, 2H), 1.15 (s, 9H), 1.09 (s, 9H), 0.78 (s, 9H), 0.01 (s, 3H), –0.01 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 206.6, 176.5, 176.3, 172.1, 161.9, 161.7, 157.6, 138.2, 138.0, 137.9, 137.9, 137.2, 128.6–127.4, 125.2, 100.9, 100.0, 99.9, 99.7, 99.5, 92.4, 92.2, 77.9, 76.1, 75.7, 75.7, 75.5, 75.4, 75.3, 74.9, 74.9, 74.3, 74.2, 73.9, 73.5, 73.5, 73.5, 72.2, 72.1, 71.9, 69.5, 68.7, 68.5, 67.1, 67.1, 66.6, 62.8, 56.9, 56.2, 50.2, 47.1, 38.7, 38.6, 37.7, 29.8, 29.1, 27.7, 27.5, 27.3, 27.1, 25.6, 23.1, 18.0, –4.0, –4.5. MS (ESI) *m/z* calcd. $[M+Na]^+$ 2202.7, found 2202.4.

5-Aminopentyl 3-*O*-sulfo-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy–β-D-glucosaminopyranosyl-(1→3)-6-*O*-sulfo-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy–β-D-glucosaminopyranoside (2).

S14 (18 mg, 8.0 μmol) was dissolved to a solution of *n*-Bu_3SnH (0.14 mL, 0.52 mmol) in anhydrous xylene (1.7 mL). After bubbling Argongas for 10 min through the solution, AIBN (4.8 mg, 29 μmol) was added. The reaction mixture was stirred at 90 °C for 5 h then loaded onto silica gel column chromatography (hexane–ethylacetate, 1:0 to 1:2, v/v). Fractions eluted with hexane–ethylacetate (1:2, v/v) were concentrated, and dissolved to a solution of HF·pyridine (ca. 70%)–anhydrous pyridine (1:4, v/v, 1 mL) at 0 °C. The reaction mixture was stirred at room temperature for 16 h, quenched with sat. aq. $NaHCO_3$ (10 mL) and diluted to CH_2Cl_2 (10 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (10 mL). The aqueous layers were combined and back extracted with CH_2Cl_2 (10 mL). The organic layers were combined, dried under Na_2SO_4, filtered and concentrated. The crude product was dissolved to a solution of acetic acid–hydrazine monohydrate–anhydrous pyridine (2:3:50, v/v/v, 5.5 mL) at 0 °C. The reaction mixture was stirred at room temperature for 3 h, concentrated, and diluted to CH_2Cl_2 (10 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (10 mL). The aqueous layer was back extracted with CH_2Cl_2 (10 mL, 2 times). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was dissolved to anhydrous pyridine (1 mL). SO_3·pyridine (≥45%, 42 mg) was added to the solution at 0 °C. The reaction mixture was stirred at room temperature for 12 h, quenched with the addition of Et_3N (100 μL) and MeOH (50 μL), diluted to CH_2Cl_2 (10 mL) and washed with 1 M aq. TEAB (10 mL). The aqueous layer was back extracted with CH_2Cl_2 (10 mL× 2). The organic layers were combined, filtered with cotton and concentrated. The crude product was loaded onto silica gel column chromatography (CH_2Cl_2–MeOH–Et_3N = 100:0:1 to 100:5:1). Fractions containing product were combined, washed with 1 M aq. TEAB (10 mL) and concentrated. The product was dissolved to 0.5 M NaOMe in MeOH (1 mL). The reaction mixture was stirred at 45 °C for 3 h, and quenched with the addition of acetic acid (50 μL) and concentrated. The residue was diluted with $CHCl_3$ (10 mL), and washed with H_2O (5 mL). The aqueous layer was back extracted with $CHCl_3$ (10 mL × 5). The organic layers were combined, filtered through a pad of cotton and concentrated. The crude product was precipitated in toluene (1 mL), filtered and washed with toluene (1 mL × 3), purified by LH20 (MeOH) and passed through a pad of Dowex50WX8 (Na^+ form). The resultant residue was dissolved to MeOH–H_2O–acetic acid (2:1:0.02, v/v, 3 mL). After bubbling Argon gas for 15 min through the solution, Pd/C (16 mg) was added. The reaction mixture was bubbled with H_2 gas, stirred under H_2 at room temperature for 16 h, filtered through 0.45 μ PTFE membrane, and concentrated. The residue was lyophilized to give **2** as a colorless solid (5.5 mg, 48% from **S14**). ^{1}H NMR (D_2O) δ 4.56 (d, 1H, *J* = 7.8 Hz), 4.44 (d, 1H, *J* = 7.7 Hz), 4.37 (d, 1H, *J* = 7.7 Hz), 4.35 (d, 1H, *J* = 8.5 Hz), 4.19 (m, 1H), 4.14 (br, 1H), 4.10–4.04 (m, 3H), 3.89–3.40 (m, 22H), 2.84 (t, 2H, *J* = 7.5 Hz), 1.91 (s, 3H), 1.88 (s, 3H), 1.59–1.40 (m, 4H), 1.30–1.21 (m, 2H). ^{13}C NMR (D_2O) δ 180.5, 180.4, 101.9, 101.8, 101.6, 100.2, 81.1, 79.1, 78.3, 77.2, 74.0, 73.9, 73.8, 73.7, 71.6, 71.3, 71.2, 69.2, 68.9, 68.2, 66.4, 66.0, 60.1, 59.4, 58.9, 54.3, 54.3 38.5, 27.2, 25.4, 22.1, 21.3, 21.3. MS (ESI) *m/z* calcd. $[M+H]^+$ 994.2850, found 994.2889.

Scheme 3: Synthesis of 3



a) **S5**, NIS, TfOH, MS4Å, CH_2Cl_2, -40 °C to -20 °C, 40 min, 74%; b) (i) DDQ, CH_2Cl_2–H_2O (20:1, v/v), rt, 8 h; (ii) $CF_3C(NPh)Cl$, K_2CO_3, acetone, 0 °C to rt, 4 h, 38% from **S15**; c) (i) **S3**, NIS, TfOH, MS4Å, CH_2Cl_2, -40 °C to -20 °C, 40 min; (ii) TBAF·$3H_2O$, AcOH, THF, 45 °C, 20 h, 28% from **S12**; d) **S16**,TMSOTf, MS4Å, CH_2Cl_2, -78 °C to -20 °C, 45 min, 64 %. e) (i) Bu_3SnH, AIBN, xylene, 90 °C, 5 h; (ii) TBAF·$3H_2O$, AcOH, THF, 45 °C, 20 h; (iii) NH_2NH_2·H_2O, AcOH, pyridine, rt, 3 h; (iv) SO_3·pyridine, pyridine, rt, 12 h; (v) NaOMe, MeOH, 45 °C, 3 h; (vi) Pd/C, AcOH, MeOH-H_2O (2:1, v/v), 28% from **S18**.

***p*-Methoxybenzyl 4-*O*-benzyl-3-O-*tert*-butyldimethylsilyl-6-*O*-levulinyl-2-*O*-pivaloyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S15).**

S5 and **S9** were azeotroped with toluene (5 mL × 3) prior to use. To a solution of donor (0.37 g, 0.60 mmol) and acceptor (0.13 g, 0.20 mmol) in anhydrous CH_2Cl_2 (dried over MS4Å prior to use, 8 mL), were added NIS (0.18 g, 0.80 mmol) and MS4Å (powder, 0.2 g). The reaction mixture was stirred for 30 min at –40 °C then TfOH (8 µL) was added. The reaction mixture was stirred for 10 min at –40 °C, 30 min at –20 °C then quenched with the addition of sodium thiosulfate (2.5 g) and sat. aq. $NaHCO_3$ (15 mL). The mixture was diluted to CH_2Cl_2 (15 mL). The organic layer was separated and washed with sat. aq. $NaHCO_3$ (20 mL). The aqueous layers were combined and back extracted with CH_2Cl_2 (10 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography (toluene–ethylacetate = 7:1 to 3:1, v/v) to give **S15** as a colorless foam (0.17 g, 74%). ^{1}H NMR ($CDCl_3$) δ 7.29–6.90 (m, 18H), 6.69 (d, 2H, *J* = 8.2 Hz), 5.17 (dd, 1H, *J* = 8.1 Hz, 9.4 Hz), 4.93 (d, 1H, *J* = 11Hz), 4.71 (d, 1H, *J* = 10 Hz), 4.71 (d, 1H, *J* = 7.2 Hz), 4.66 (d, 1H, *J* = 11 Hz), 4.58 (d, 1H, *J* = 12 Hz), 4.43 (d, 1H, *J* = 11Hz), 4.38 (d, 1H, *J* = 12 Hz), 4.35 (d, 1H, *J* = 10 Hz), 4.34 (d, 1H, *J* = 11Hz), 4.26 (d, 1H, *J* = 8.1 Hz), 4.02–3.91 (m, 3H), 3.81 (t, 1H, *J* = 7.5 Hz), 3.73–3.60 (m, 6H), 3.58–3.52 (m, 2H), 3.45–3.39 (m, 2H), 2.58 (t, 2 H, *J* = 6.5), 2.35 (t, 2H, *J* = 6.5), 2.03 (s, 3H), 1.08 (s, 9H), 0.77 (s, 9H), 0.04 (s, 3H), -0.02 (s, 3H). ^{13} C NMR ($CDCl_3$) δ 206.8, 176.7, 172.3, 161.7, 159.3, 138.6, 138.1, 138.0, 129.5, 129.2, 128.5, 128.3, 128.3, 128.1, 127.9, 127.8, 127.5, 127.4, 113.8, 100.0, 98.3, 92.4, 77.1, 75.2, 75.2, 74.7, 73.9, 73.7, 73.5, 72.4, 72.0, 70.5, 68.8, 63.0, 56.1, 55.3, 38.9, 37.9, 29.8, 27.8, 27.6, 25.7, 17.8, –3.4, –5.0. MS (ESI) *m/z* calcd. $[M+Na]^+$ 1194.4, found 1193.9.

***N*-Phenyl-trifluoroacetoimidoyl 4-*O*-benzyl-3-O-*tert*-butyldimethylsilyl-6-*O*-levulinyl-2-*O*-pivaloyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S16).**

To a solution of **S15** (65 mg, 55 µmol) in anhydrous CH_2Cl_2 (4.0 mL), were added phosphate buffer (pH 7, 0.2 mL) and DDQ (39 mg, 0.17 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 8 h then diluted to CH_2Cl_2 (10 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (10 mL × 3). The aqueous layers were combined, back extracted with CH_2Cl_2 (10 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was passed through a pad of silica gel to remove remaining starting material, dried under vacuum and used to next reaction without further purification.

To a solution of the crude product in anhydrous acetone (3.0 mL) was added K_2CO_3 (38 mg, 0.28 mmol) and $CF_3C(NPh)Cl$ (38 mg, 0.18 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, at room temperature for 4 h, then concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate = 7:1 to 4:1, v/v) to give **S16** as colorless foam (26 mg, 38% from **S15**). (major isomer) ^{1}H NMR ($CDCl_3$) δ 7.30–6.94 (m), 6.65 (d, 2 H, J = 8.0), 6.49 (d, 1H, J = 7.1 Hz), 5.26 (dd, 1 H, J = 8.1 Hz, 9.5 Hz), 4.98 (d, 1 H, J = 11 Hz), 4.87 (d, 1 H, J = 11 Hz), 4.68 (d, 1 H, J = 12 Hz), 4.53 (d, 1 H, J = 11 Hz), 4.38 (d, 1 H, J = 11 Hz), 4.35 (d, 1H, J = 12

Hz), 4.20–3.95 (m), 3.78–3.49 (m), 3.42 (t, 2H, J = 6 Hz), 2.63 (t, 2H, J = 6.2 Hz), 2.42 (t, 2H, J = 6.2 Hz), 1.10 (s, 9 H), 0.79 (s, 9H), 0.11 (s, 3 H), 0.03 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 119.3 (C-1), 99.4 (C-1^{II}), 92.7 ($\underline{C}Cl_3$). MS (ESI) *m/z* calcd. $[M+Na]^+$ 1245.4, found 1245.0.

_N_-Benzyl-(benzyloxycarbonyl)-5-aminopentyl 4,6-_O_-benzylidene-2-_O_-pivaloyl-β-D-galactopyranosyl-(1 → 4)-3,6-di-_O_-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S17).

S3 and **S12** were azeotroped with anhydrous toluene (3 mL × 3) and dried under vacuum prior to use. To a solution of **S3** (0.18 g, 0.30 mmol) and **S12** (81 mg, 0.10 mmol) in anhydrous CH_2Cl_2 (4.0 mL), were added MS4Å (0.5 g) and NIS (90 mg, 0.40 mmol) at –40 °C. The reaction mixture was stirred at –40 °C for 30 min then TfOH (4.0 μL) was added. The reaction mixture was stirred at –40 °C for 10 min, –20 °C for 30 min, quenched with the addition of sat. aq. $NaHCO_3$ (20 mL) and sodium thiosulfate (2.0 g), and diluted to CH_2Cl_2 (15 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (20 mL). The aqueous layers were combined and back extracted with CH_2Cl_2 (10 mL). The organic layers were combined, dried under Na_2SO_4, filtered, and concentrated. The residue was dissolved to anhydrous THF (5.0 mL). To the solution were added acetic acid (30 μL) and TBAF·$3H_2O$ (0.23 g, 0.73 mmol) at room temperature. The reaction mixture was stirred at 45 °C for 12 h. TBAF·$3H_2O$ (0.49 g, 1.5 mmol) was added portion wise while reaction was stirred at 45 °C for additional 48 h. The reaction mixture was diluted to ethylacetate (25 mL), washed with 0.1 M HCl aq. (20 mL), brine (20 mL), sat. aq. $NaHCO_3$ (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate, 5:0 to 1:1, v/v) to give **S17** as colorless foam (32 mg, 28%). ^{1}H NMR ($CDCl_3$) δ 7.53–7.06 (m, 26H), 5.49 (s, 1H), 5.14 (br, 2H), 5.09 (d, 1H, *J* = 11 Hz), 5.03 (dd, 1H, *J* = 8.1 Hz, 10 Hz), 4.84 (br, 1H), 4.75 (d, 1H, *J* = 12 Hz), 4.56 (d, 1H, *J* = 11 Hz) 4.46 (d, 1H, *J* = 8.1 Hz), 4.45 (br, 2H), 4.40 (d, 1H, *J* = 12 Hz), 4.23 (ABX, 1H, *J* = 12 Hz, < 1 Hz), 4.13–4.02 (m, 3H), 3.94 (ABX, 1H, *J* = 12 Hz, 1.3 Hz), 3.87 (ABX, 1H, *J* = 10 Hz, 2.7 Hz), 3.80 (br, 1H), 3.76 (ABX, 1H, *J* = 10 Hz, 2.0 Hz), 3.54–3.29 (m, 4 H), 3.30–3.06 (m, 3H), 2.32 (br, 1H), 1.56–1.38 (br, 4 H), 1.32–1.14 (m, 2 H), 1.20 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 177.9, 161.6, 157.0, 138.1, 138.0, 137.9, 137.7, 129.2-127.8, 126.4, 101.4, 99.5, 99.2, 92.7, 77.6, 76.1, 75.6, 75.1, 74.9, 73.5, 72.4, 71.9, 69.7, 68.7, 68.1, 67.1, 66.5, 60..4, 57.8, 50.3, 46.1, 38.8, 29.2, 27.4, 27.3, 23.2. MS (ESI) *m/z* calcd. $[M+Na]^+$ 1169.4, found 1169.1.

_N_-Benzyl-(benzyloxycarbonyl)-5-aminopentyl 4-_O_-benzyl-3-_O_-_tert_-butyldimethylsilyl-6-_O_-levulinyl-2-_O_-pivaloyl-β-D-galactopyranosyl-(1 → 4)-3,6-di-_O_-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl-(1 → 3)-4,6-_O_-benzylidene-2-_O_-pivaloyl-β-D-galactopyranosyl-(1→4)-3,6-di-_O_-benzyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranoside (S18).

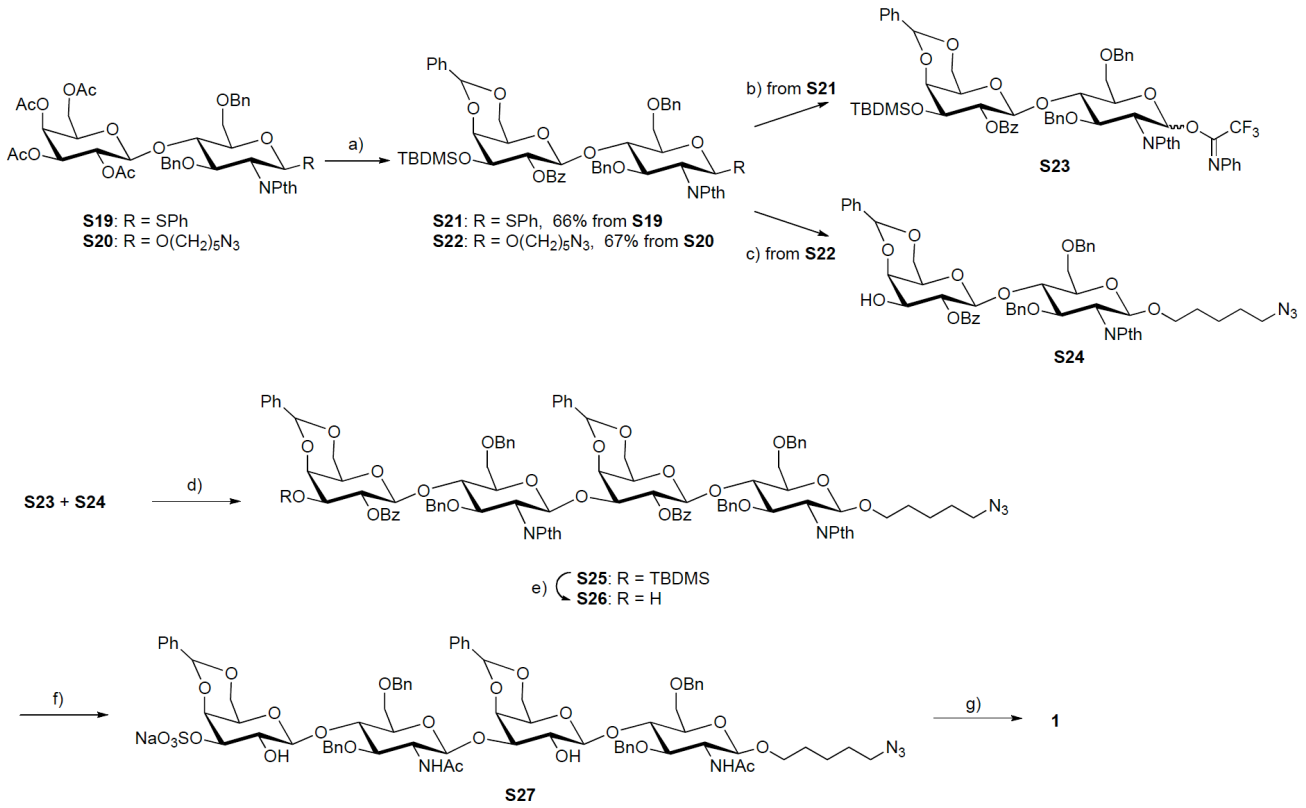
S16 and **S17** were azeotroped with anhydrous toluene (3 mL × 3) and dried under vacuum prior to use. To a solution of **S16** (37 mg, 30 μmol), **S17** (18 mg, 15 μmol) and MS4Å (0.2 mg) in CH_2Cl_2 (0.6 mL), was added TMSOTf (1.0 μL, 5.5 μmol) at –78 °C. The reaction mixture was stirred at –78 °C for 15 min, at –20 °C for 30 min, quenched with the addition of Et_3N (0.1 mL) and MeOH (50 μL) and concentrated. The crude product was purified by silica gel column chromatography (toluene–ethylacetate, 1:1 to 5:1, v/v) to give **S18** as a colorless oil (21 mg, 64%). ^{1}H NMR ($CDCl_3$) δ 7.37–6.95 (m, 42H), 5.37 (s, 1H), 5.23 (dd, 1H, *J* = 7.9 Hz, 10 Hz), 5.19 (dd, 1H, *J* = 7.9 Hz, 10 Hz), 5.08 (br, 2H), 4.96 (d, 1H, *J* = 11 Hz), 4.93 (d, 1H, *J* = 12 Hz), 4.85 (s, 2H), 4.70 (br, 1H), 4.70 (d, 1H, *J* = 12 Hz), 4.63 (d, 1H, *J* = 12 Hz), 4.57–4.47 (m, 3H), 4.42-4.33 (m, 4H), 4.30 (d, 1H, J = 7.9 Hz), 4.23 (d, 1H, *J* = 7.9 Hz), 4.18–3.31 (m, 23H), 3.10 (br, 2H), 3.00 (s, 1H), 2.60 (t, 2H, *J* = 6.4 Hz), 2.37 (t, 2H, J = 6.4 Hz), 2.05 (s, 3H), 1.49–1.34 (m, 4H), 1.24–1.06 (m, 2H), 1.15 (s, 9H), 1.13 (s, 9H), 0.83 (s, 9H), 0.11 (s, 3H), 0.05 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 206.6, 176.7, 176.5, 172.3, 161.8, 161.7, 156.2, 138.2, 138.0, 137.9, 137.8, 137.7, 128.6-127.4, 126.4, 101.5, 100.7, 99.8, 99.6, 99.4, 92.5, 92.2, 78.3, 77.7, 76.9, 75.4, 75.3, 75.2, 75.1, 75.0, 74.9, 74.6, 74.5, 74.4, 74.3, 73.8, 73.5, 72.8, 72.1, 72.0, 70.0, 69.6, 68.6, 68.6, 67.2, 66.5, 62.8, 56.7, 56.7, 50.2, 46.1, 38.9, 38.8, 37.9, 29.8, 29.1, 27.8, 27.6, 27.6, 27.4, 25.6, 23.3, 17.8, –3.4, –5.0. MS (ESI) *m/z* calcd. $[M-H]^-$ 2178.7, found 2179.3.

5-Aminopentyl 3,6-di-_O_-sulfo-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy–β-D-glucosaminopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy–β-D-glucosaminopyranoside (3).

S18 (20 mg, 9.0 μmol) was dissolved to a solution of *n*-Bu_3SnH (0.14 mL, 0.52 mmol) in xylene (1.7 mL). To a solution, was bubbled Argon gas for 10 min, then was added AIBN (4.8 mg, 29 μmol). The reaction mixture was stirred at 90 °C for 5 h then loaded onto silica gel column chromatography (hexane-ethylacetate, 1:0 to 1:2, v/v). Fractions eluted with hexane–ethylacetate (1:2, v/v) were concentrated, and dissolved to a solution of acetic acid (0.10 mL) in anhydrous THF (2.0 mL) at room temperature. To the solution was added 1M TBAF·$3H_2O$ in THF (3.0 mL, 3.0 mmol) at room temperature. The reaction mixture was stirred at 40 °C for 20 h, diluted with ethylacetate (25 mL), washed with 0.1 M HCl aq. (20 mL) and brine (20 mL). The organic phase was dried under Na_2SO_4, filtered and concentrated. The crude product was dissolved to a solution of acetic acid–hydrazine monohydrate–anhydrous pyridine (2:3:50, v/v/v, 5.5 mL) at 0 °C. The reaction mixture was stirred at room temperature for 3 h, concentrated,

and diluted to CH_2Cl_2 (10 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (10 mL). The aqueous layer was back extracted with CH_2Cl_2 (10 mL × 2). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was dissolved to anhydrous pyridine (1.0 mL). SO_3·pyridine (≥45%, 42 mg) was added to the solution at 0 °C. The reaction mixture was stirred at room temperature for 12 h, quenched with the addition of Et_3N (0.10 mL), MeOH (50 mL), diluted with CH_2Cl_2 (10 mL) and washed with 1 M TEAB aq. (10 mL). The aqueous layer was back extracted with CH_2Cl_2 (10 mL × 2). The organic layers were combined, filtered through a pad of cotton and concentrated. The crude product was passed through a silica gel column chromatography (CH_2Cl_2–MeOH–Et_3N = 100:0:1 to 100:5:1). Fractions containing product were combined, washed with 1 M TEAB aq. (10 mL) and concentrated. The product was dissolved to a solution of NaOMe (0.5 M) in MeOH (1.0 mL). The reaction mixture was stirred at 45 °C for 3h, and quenched with the addition of acetic acid (50 μL) and concentrated. The residue was diluted with $CHCl_3$ (10 mL), and washed with H_2O (5 mL). The aqueous layer was back extracted with $CHCl_3$ (10 mL × 5). The organic layers were combined, filtered through a pad of cotton and concentrated. The crude product was precipitated in toluene (1 mL), filtered and washed with toluene (1 mL × 3), dissolved to MeOH, passed through a pad of Dowex50WX8 (Na^+ form) and concentrated. The resultant residue was dissolved to MeOH–H_2O–acetic acid (2:1:0.02, v/v, 3 mL). After bubbling Argon gas through the solution for 15 min, Pd/C (16 mg) was added. Reaction mixture was bubbled with H_2 gas, stirred under H_2 at room temperature for 16 h, filtered through 0.45 μ PTFE membrane, and concentrated. The residue was lyophilized to give **3** as a colorless solid (4.8 mg, 28% from **S18**). ^{1}H NMR (D_2O) δ 4.54 (d, 1H, *J* = 8.0 Hz), 4.50 (d, 1H, *J* = 8.1 Hz), 4.36 (d, 1H, *J* = 7.6 Hz), 4.30 (d, 1H, *J* = 7.9 Hz), 4.19 (s, 1H), 4.08–4.04 (m, 3H), 4.00 (d, 1H, *J* = 3.0 Hz), 3.90–3.40 (m, 22H), 2.83 (t, 2H, *J* = 7.5 Hz), 1.91 (s, 6H), 1.59–1.40 (m, 4H), 1.30–1.21 (m, 2H). ^{13}C NMR (D_2O) δ 180.6, 180.5, 102.2, 102.0, 101.9, 100.3, 81.9, 79.9, 78.1, 77.6, 75.1, 74.0, 73.9, 72.3, 71.5, 71.1, 69.2, 69.1, 67.6, 67.5, 67.4, 66.1, 60.1, 59.4, 59.2, 54.2, 38.5, 27.2, 25.5, 22.1, 21.3, 21.2. MS (ESI) *m/z* calcd. $[M+H]^+$ 994.2850, found $[M+H]^+$ 994.2699

Scheme 4



a) (i) NaOMe, MeOH, rt then Dowex 50WX8 (H^+); (ii) $PhCH(OMe)_2$, TsOH, MeCN, rt; (iii) TBDMSCl, imidazole, CH_2Cl_2, 0 °C to rt; (vi) BzCl, pyridine, 66% for **S21**, 67% for **S22**; b) (i) NIS, TfOH, H_2O, CH_2Cl_2, 0 °C; (ii) $CF_3C(NPh)Cl$, acetone, K_2CO_3, 0 °C, 60% from **S21**; c) HF·py, pyridine-THF (1:1, v/v), 64% from **S22**; d) TMSOTf, CH_2Cl_2, -78 °C to 0 °C, 46%; e) TBAF, AcOH, THF, rt, 72 h, 67%; f) (i) SO·pyridine, pyridine, rt, 12 h; (ii) $NH_2NH_2{\cdot}H_2O$, *n*-BuOH, 90 °C, 12 h; (iii) Ac_2O, Et_3N, MeOH, 0 °C to rt, 2 h; (iv) Dowex50WX8 (Na^+ form), 68% from **S26**; g) Pd/C, AcOH, MeOH-H_2O (2:1, v/v) rt, 12 h, 90%

Phenyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-benzyl-2-deoxy-2-pthalimide-1-thio-β-D-glucopyranoside (S21).

To a 25 mM solution of 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[S5] (40 mL, 1.0 mmol), were added 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl 2,2,2-Trichloroacetimidate[S6] (0.66 g, 1.4 mmol) and MS4Å at room temperature. The solution was cooled to –78 °C, then TMSOTf (25 µL, 0.14 mmol) was added. The reaction mixture was stirred at –78 °C for 10 min, at 0 °C for 20 min then quenched with the addition of Et_3N (0.5 mL) and MeOH (0.2 mL). The solution was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–ethylacetate, 2:1 to 1:1, v/v) to give phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-pthalimide-1-thio-β-D-glucopyranoside (**S19**) as colorless foam (0.61 g, 67%). ^1H NMR ($CDCl_3$) δ 7.81–6.84 (m), 5.46 (d, 1H, *J* = 9.8 Hz), 5.25 (d, 1H, *J* = 3.0 Hz), 5.12 (dd, 1H, *J* = 7.9 Hz, 9.8 Hz), 4.84 (dd, 1H, *J* = 3.0 Hz, 7.9 Hz), 4.75 (d, 1H, *J* = 12 Hz), 4.74 (d, 1H, *J* = 12 Hz), 4.59 (d, 1H, *J* = 8.0 Hz), 4.49 (d, 1H, *J* = 12 Hz), 4.40 (d, 1H, *J* = 12 Hz), 4.27–4.17 (m, 2H), 4.03 (t, 1H, *J* = 9.2 Hz), 3.99–3.89 (m, 2H), 3.81–3.72 (m, 2H), 3.64 (t, 1H, *J* = 7.3 Hz), 3.55 (m, 1H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H).

To a solution of **S19** (0.61 g, 0.67 mmol) in anhydrous MeOH (5 mL), was added NaOMe (20 mg, 0.37 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 h, passed through a pad of Dowex50WX8 (H^+ form) and concentrated. The resultant residue was azeotroped with toluene (5 mL × 3), dried under vacuum and dissolved to anhydrous MeCN (15 mL). To the solution, were added $PhCH(OMe)_2$ (0.3 mL, 2.0 mmol) and $TsOH{\cdot}H_2O$ (19 mg, 0.1 mmol) at room temperature. The reaction mixture was stirred at room temperature for 30 min, quenched with the addition of Et_3N (0.5 mL) and concentrated. The residue was loaded onto a silica gel column chromatography (hexane–ethylacetate, 2:1 to 1:2, v/v). Fractions eluted with hexane–ethylacetate (1:2, v/v) were collected, concentrated, dried under vacuum and dissolved to anhydrous CH_2Cl_2 (15 mL). TBDMSCl (225 mg, 1.5 mmol) and imidazole (300 mg, 4.4 mmol) were added to the solution at room temperature. The reaction mixture was stirred at room temperature for 18 h and washed with sat. aq. $NaHCO_3$ (15 mL). The aqueous layer was back extracted with CH_2Cl_2 (20 mL). The organic layers were combined, dried over Na_2SO_4, filterted and concentrated.

The resultant residue was azeotroped with pyridine (5 mL × 3) and dissolved to anhydrous pyrdine (10 mL). To the solution, were added BzCl (0.25 mL, 2.1 mmol) and DMAP (28 mg, 0.23 mmol) at room temperature. The reaction mixture was stirred at room temperature for 15 h, diluted to toluene (20 mL) and washed with sat. aq. $NaHCO_3$ (20 mL × 3). The aqueous layers were combined and back extracted with toluene (20 mL × 2). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (hexane–ethylacetate, 3:1 to 2:1, v/v) to give **S21** (0.46 g, 66% from **S19**) as a colorless solid. ^{1}H NMR ($CDCl_3$) δ 8.01 (d, 2H, *J* = 9.0 Hz), 7.78 (d, 1H, *J* = 7.4 Hz), 7.72–7.06 (m, 21H), 6.99–6.93 (m, 2H), 6.77–6.67 (m, 3H), 5.49 (t, 1H, *J* = 8.5 Hz), 5.46 (s, 1H), 5.39 (d, 1H, *J* = 9.8 Hz), 5.01 (d, 1H, *J* = 12 Hz), 4.75 (d, 1H, *J* = 7.9 Hz), 4.65 (d, 1H, *J* = 12 Hz), 4.56 (d, 1H, *J* = 12 Hz), 4.39–4.17 (m, 4H), 4.09 (t, 1H, *J* = 8.5 Hz), 4.00–3.93 (m, 2H), 3.83 (dd, 1H, *J* = 2.4 Hz, 11.3 Hz), 3.72 (dd, 1H, *J* = 2.4 Hz, 11.3 Hz), 3.57 (d, 1H, *J* = 11.3 Hz), 3.42 (d, 1H, *J* = 8.5 Hz), 3.28 (s, 1H), 0.71 (s, 9H), 0.02 (s, 3H), -0.13 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 168.4, 164.7, 138.9, 138.8, 137.9, 133.8–126.4, 123.7, 101.1, 100.6, 83.4, 79.2, 78.3, 76.5, 75.3, 73.4, 72.8, 72.4, 68.9, 68.3, 68.1, 66.5, 54.9, 25.6, –4.5, –4.8.

5-Azidepenthyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-pthalimide-β-D-glucopyranoside (S22).

To a solution of **S20**[S7] (0.17 g, 0.18 mmol) in anhydrous MeOH (8 mL), was added NaOMe (8 mg, 0.15 mmol) at room temperature. The reaction mixture was stirred at room temperature for 5 h, passed through a pad of Dowex50WX8 (H^+ form) and concentrated. The resultant residue was azeotroped with MeCN (3 mL × 3), dried under vacuum and dissolved to anhydrous MeCN (5 mL). To the solution, were added $PhCH(OMe)_2$ (40 μL, 0.26 mmol) and $TsOH{\cdot}H_2O$ (4.1 mg, 22 μmol) at room temperature. The reaction mixture was stirred at room temperature for 30 min, quenched with the addition of Et_3N (0.1 mL) and concentrated. The residue was loaded onto a silica gel column chromatography (hexane–ethylacetate, 2:1 to 1:2, v/v). Fractions eluted with hexane–ethylacetate (1:2, v/v) were collected, concentrated, dried under vacuum and dissolved to anhydrous CH_2Cl_2 (5 mL). TBDMSCl (46 mg, 0.31 mmol) and imidazole (31 mg, 0.46 mmol) were added to the solution at room temperature. The reaction mixture was stirred at room temperature for 24 h and washed with sat. aq. $NaHCO_3$ (10 mL). The aqueous layer was back extracted with CH_2Cl_2 (10 mL). The organic layers were combined, dried over Na_2SO_4, filterted and concentrated. The resultant residue was azeotroped with pyridine (5 mL × 3) and dissolved to anhydrous pyrdine (5 mL). To the solution, were added BzCl (0.10 mL, 0.86 mmol) and DMAP (18 mg, 0.15 mmol) at room temperature. The reaction mixture was stirred at room temperature for 15 h and concentrated. The resultant residue was diluted to CH_2Cl_2 (20 mL) and washed with sat. aq. $NaHCO_3$ (10 mL × 3). The aqueous layers were combined and back extracted with CH_2Cl_2 (20 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (hexane–ethylacetate, 3:1 to 2:1, v/v) to give **S22** (0.13 g, 67% from **S20**) as a colorless solid. ^{1}H NMR ($CDCl_3$) δ 8.01 (d, 2H, *J* = 8.5 Hz), 7.80–7.17 (m, 17H), 7.00–6.96 (m, 2H), 6.72–6.78 (m, 3H), 5.48 (t, 1H, *J* = 9.8 Hz), 5.45 (s, 1H), 5.02 (d, 1H, *J* = 13 Hz), 4.97 (d, 1H, *J* = 7.9 Hz), 4.74–4.69 (m, 2H), 4.56 (d, 1H, *J* = 13 Hz), 4.38–4.32 (m, 2H), 4.26–4.19 (m, 1H), 4.15–4.07 (m, 2H), 4.00–3.94 (m, 2H), 3.80 (dd, 1H, *J* = 3.7 Hz, 9.8 Hz), 3.76–3.65 (m, 2H), 3.53 (d, 1H, *J* = 11 Hz), 3.35 (d, 1H, *J* = 9.8 Hz), 3.26 (br, 2H), 2.90–2.78 (m, 2H), 1.39–1.22 (m, 4H), 1.09–1.00 (m, 2H), 0.71 (s, 9H), 0.03 (s, 3H), -0.13 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 167.8, 167.7, 164.7, 139.0, 138.9, 138.5, 133.8, 133.1, 131.1, 129.9–126.3, 123.1, 101.0, 100.6, 98.2, 78.3, 76.5, 75.3, 74.8, 73.5, 72.4, 69.1, 69.0, 68.3, 68.0, 66.5, 56.0, 51.2, 28.8, 28.4, 25.5, 23.1, –4.3, –4.5. MS (ESI) *m/z* Calcd. $[M+Na]^+$ 1091.4, found 1091.2.

***N*-Phenyl-trifluoroacetoimidoyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-pthalimide-β-D-glucopyranoside (S23).**

To a solution of **S21** (0.46 g, 0.44 mmol) in anhydrous CH_2Cl_2 (10 mL), were added H_2O (0.10 mL) and NIS (0.23 g, 1.0 mmol) and TfOH (10 μL, 0.11 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min then quenched with the addition of sat. aq. $NaHCO_3$ (20 mL) and sodium thiosulfate (0.8 g). The organic layer was washed with sat. aq. $NaHCO_3$ (20 mL). The aqueous layers were combined, back extracted with CH_2Cl_2 (20 mL × 2). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was passed through a pad of silica gel to remove remaining starting material, dried under vacuum and used to next reaction without further purification. To a solution of the crude product in anhydrous acetone (10 mL) were added K_2CO_3 (74 mg, 0.54 mmol) and $CF_3C(NPh)Cl$ (0.15 g, 0.72 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, at room temperature for 8 h, then concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate = 3:1 to 1:1, v/v) to give **S23** as colorless foam (0.30 g, 60% from **S21**). (major isomer) ^{1}H NMR (selected signals, $CDCl_3$) δ 7.97 (d, 2H, J = 7.9Hz), 7.74–6.70 (m), 6.57 (br), 5.51–5.40 (m, 2H), 5.03 (d, 1H, *J* = 12 Hz), 4.76 (d, 1H, *J* = 12 Hz), 4.68 (d, 1H, *J* = 8.3 Hz), 4.56 (d, 1H, *J* = 12 Hz), 4.40 (d, 1H, *J* = 12 Hz), 4.38–4.12 (m, 5H), 4.03–3.94 (m, 2H), 3.78 (dd, 1H, *J* = 3.7 Hz, 9.6 Hz), 3.67 (br, 1H), 3.46 (br, 1H), 3.28 (s, 1H), 0.72 (s, 9H), 0.03

(s, 3H), –0.13 (s, 3H). ^{13}C NMR (selected signals, $CDCl_3$) δ 167.8, 167.4, 164.7, 119.2 (br, C-1^{I}), 101.0 (CHPh), 100.5 (C-1^{II}). MS (ESI) *m/z* Calcd. $[M+Na]^+$ 1151.4, found 1151.1.

5-Azidepenthyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-benzyl-2-deoxy-2-pthalimide-β-D-glucopyranoside (S24).

To a solution of **S22** (0.27 g, 0.25 mmol) in anhydrous pridine–THF (1:1, v/v, 10 mL), was added HF·pyridine (ca. 20%, 1.5 mL) at room temperature. The reaction mixture was stirred at room temperature for 40 h, then diluted to CH_2Cl_2 (30 mL) and quenched with the addition of sat. aq. $NaHCO_3$ (20 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (20 mL). The aqueous layers were combined and back extracted with CH_2Cl_2 (15 mL × 2). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography (hexane–ethylacetate = 2:1 to 1:2, v/v) to give **S24** as a colorless solid (0.15 g, 64% from **S22**).^{1}H NMR ($CDCl_3$) δ 8.02 (d, 2H, *J* = 7.3 Hz), 7.83–7.21 (m, 17H), 7.03–7.02 (m, 2H), 6.78–6.77 (m, 3H), 5.50 (s, 1H), 5.35 (dd, 1 H, *J* = 8.8 Hz, 8.9 Hz), 5.04–4.98 (m, 2 H), 4.74–4.73 (m, 2H), 4.58 (d, 1H, *J* = 12 Hz), 4.39 (d, 1H, *J* = 12 Hz), 4.33 (d, 1H, *J* = 12 Hz), 4.28–4.10 (m, 4H), 3.97 (d, 1H, *J* = 12 Hz), 3.77 (dd, 1H, *J* = 3.1 Hz, 11 Hz), 3.76–3.64 (m, 2H), 3.60 (d, 1H, *J* = 11 Hz), 3.39 (m, 1H), 3.33–3.23 (m, 2H), 2.91–2.79 (m, 2H), 1.75–1.24 (m, 6H). ^{13}C NMR (CDCl3) δ 167.8, 165.8, 138.9, 138.4, 137.4, 133.7, 133.4, 131.1, 130.0–126.5, 123.3, 101.6, 100.4, 98.3, 78.4, 75.5, 75.1, 74.7, 73.5, 73.4, 71.8, 69.1, 68.9, 68.2, 67.0, 66.4, 56.0, 51.2, 38.9, 29.0, 28.7, 23.0. MS (ESI) *m/z* Calcd. $[M+Na]^+$ 977.4, found 977.2.

5-Azidepenthyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-pthalimide-β-D-glucopyranosyl-(1 → 3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-pthalimide-β-D-glucopyranoside (S25).

S23 and **S24** were azeotoroped in with anhydrous toluene (3 mL × 3) prior to use. To a solution of **S23** (0.16 g, 0.16 mmol), **S24** (0.18 g, 0.16 mmol) and MS4Å in anhydrous CH_2Cl_2 (6.0 mL), was added TMSOTf (5 μL, 28 μmol) at –78 °C. The reaction mixture was stirred at –78 °C for 10 min, at 0 °C for 20 min then quenched with the addition of Et_3N (0.10 mL) and MeOH (50 μL). The solution was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–ethylacetate, 2:1, v/v) to give **S25** as colorless foam (0.14 g, 46%). ^{1}H NMR ($CDCl_3$) δ 8.21 (d, 2H, *J* = 8.3 Hz), 7.80–7.23 (m, 36H), 7.02-6.95 (m, 4H), 6.88–6.77 (m, 6H), 5.63 (dd, 1H, *J* = 8.3 Hz, 10 Hz), 5.56 (s, 1H), 5.43 (s, 1H), 5.41 (dd, 1H, *J* = 8.3 Hz, 10 Hz), 5.30 (d, 1H, *J* = 8.2 Hz), 5.08 (s, 1H, *J* = 12 Hz), 5.00 (d, 1H, *J* = 12 Hz), 4.97 (d, 1H, *J* = 8.0 Hz), 4.88 (d, 1H, *J* = 8.3 Hz), 4.74 (d, 1H, *J* = 12 Hz), 4.61–4.51 (m, 3H), 4.39–4.25 (m, 7H), 4.16–3.98 (m, 7H), 3.84–3.63 (m, 5H), 3.62–3.52 (m, 2H), 3.40–3.26 (m, 3H), 3.18 (br, 1H), 3.15 (d, br, 1H, J = 10 Hz), 2.94 (m, 2H), 1.52–1.05 (m, 6H), 0.85 (s, 9H), 0.15 (s, 3H), 0.00 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 167.8 (br), 167.5 (br), 164.8, 163.9, 138.8, 138.6, 138.3, 138.2, 137.9, 137.8, 133.5, 133.1, 133.0, 132.5, 130.1, 129.7, 129.5, 129.2, 128.6–127.5, 126.6, 126.6, 126.3, 126.2, 123.0 (br), 122.6 (br), 101.0, 100.9, 100.7, 100.4, 99.6, 98.0, 78.9, 78.8, 77.6, 77.4, 76.9, 76.3, 75.6, 74.9, 74.9, 74.5, 74.4, 73.4, 73.2, 73.0, 72.3, 70.6, 69.2, 68.9, 68.8, 68.5, 67.3, 66.4, 66.3, 55.7, 55.5, 51.0, 29.7, 28.6, 28,.2, 25.3, 22.9, –4.5, –4.7. MS (ESI) *m/z* calcd. $[M+Na]^+$ 1916.7, found 1916.2.

5-Azidepenthyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-benzyl-2-deoxy-2-pthalimide-β-D-glucopyranosyl-(1 → 3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-benzyl-2-deoxy-2-pthalimide-β-D-glucopyranoside (S26).

S25 (0.14 g, 73 μmol) was dissolved to a solution of TBAF (1 M) and acetic acid (0.55 mL) in THF (8.0 mL). The reaction mixture was stirred at room temperature for 72 h, then diluted to ethylacetate (20 mL) and washed with 0.1 M HCl aq. (20 mL) and brine (20 mL). The aqueous layers were combined and back extracted with ethylacetate (20 mL). The organic layers were combined, washed with sat. aq. $NaHCO_3$ (30 mL), dried over $MgSO_4$ and concentrated. The crude residue was purified by silica gel column chromatography (hexane–ethylacetate, 2:1 to 0:1, v/v) to give **S26** as colorless oil (87 mg, 67%). ^{1}H NMR ($CDCl_3$) δ 8.27 (d, 2H, *J* = 8.3 Hz), 7.82–7.31 (m, 36 H), 7.09–7.20 (m, 4H), 6.92–6.82 (m, 6H), 5.64 (s, 1H), 5.54 (dd, 1H, *J* = 8.3 Hz, 9.9 Hz), 5.49 (s, 1H), 5.47 (dd, 1H, *J* = 8.3 Hz, 10 Hz), 5.37 (d, 1H, *J* = 8.3 Hz), 5.12 (d, 1H, *J* = 12 Hz), 5.06 (d, 1H, *J* = 12 Hz), 5.02 (d, 1H, *J* = 8.0 Hz), 4.95 (d, 1H, *J* = 8.3 Hz), 4.79 (d, 1H, *J* = 12 Hz), 4.66 (d, 1H, *J* = 12 Hz), 4.63–4.56 (m, 3H), 4.44–4.30 (m, 8H), 4.22–4.04 (m, 5H), 3.98–3.72 (m, 6H), 3.66 (dd, 1H, *J* = 3.4 Hz, 10 Hz), 3.59 (dd, 1H, *J* = 3.2 Hz, 11 Hz), 3.45–3.30 (m, 3H), 3.26 (br, 1H), 3.21 (br, 1H), 2.98 (m, 2H), 1.54–1.32 (m, 4H), 1.25–1.11 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 167.9 (br), 167.5 (br), 165.8, 163.9, 138.7, 138.4, 138.3, 138.0, 137.8, 137.4, 133.5, 133.3, 133.1, 132.4, 129.8, 129.7, 129.4, 129.2, 129.1, 128.5-127.5, 126.8, 126.6, 126.3, 126.2, 123.0 (br), 122.7 (br), 101.3, 100.7, 100.7, 100.4, 99.6, 98.6, 78.9, 78.8, 77.5, 77.4, 76.9, 75.6, 75.4, 74.9, 74.8, 74.4, 74.4, 73.5, 73.4, 73.2, 71.7, 70.6, 69.0, 68.8, 68.7, 68.5, 67.3, 66.4, 66.3, 55.6, 55.4, 50.0, 28.6, 28.2, 22.9. MS (ESI) *m/z* calcd. $[M+Na]^+$ 1802.6, found 1802.4.

5-Azidepenthyl 4,6-*O*-benzylidene-3-*O*-sulfo-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-benzyl-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-benzyl-2-acetamido-2-deoxy-β-D-glucopyranoside (S27).

To a solution of **S26** (80 mg, 45 μmol) in anhydrous pyridine (4.5 mL), was added SO_3·pyridine (74 mg, 0.45 mmol). The reaction mixture was stirred at room temperature for 12 h, quenched with the addition of Et_3N (0.1 mL) and MeOH (50 μL) and concentrated. The residue was dissolved to $CHCl_3$ (15 mL) and washed with 1 M aq. TEAB (15 mL). The organic layer was filtered through a pad of cotton and concentrated. The resultant residue was dissolved to a solution of *n*-BuOH–hydrazine monohydrate (4:1, v/v, 2.5 mL). The mixture was stirred at 90 °C for 12 h, then concentrated and azeotroped with toluene (1 mL × 3). The resultant solid was precipitated in toluene (2 mL), filtered, washed with toluene (2 mL × 2), dried under vacuum and dissolved to anhydrous MeOH (2.0 mL). Ac_2O (0.5 mL) and Et_3N (1 mL) were added to the solution at 0 °C. The reaction mixture was stirred at room temperature for 2 h then concentrated. The crude residue was purified by silica gel column chromatography (CH_2Cl_2-MeOH-Et_3N = 100:1:0.5 to 100:3:1) to give **S27** (45 mg, 68% from **S26**). ^{1}H NMR (CD_3OD) δ 7.47–6.99 (m. 30 H), 5.46 (s, 1 H), 5.34 (s, 1H), 5.08 (d, 1 H, *J* = 11 Hz), 5.06 (d, 1H, *J* = 11 Hz), 4.65 (d, 1 H, *J* = 8.1 Hz), 4.58–4.32 (m, 10 H), 4.25–4.32 (m, 2 H), 4.05–3.58 (m, 19H), 3.45–3.36 (m, 3H), 3.17–3.14 (m, 2H), 3.07 (br, 1H), 1.78 (s, 3H), 1.77 (s, 3 H), 1.54–1.43 (m, 4H), 1.38–1.26 (m, 2H). ^{13}C NMR (CD_3OD) δ 173.5, 173.1, 140.4, 140.3, 139.9, 139.9, 139.8, 139.7, 129.5, 129.5, 129.5, 129.5, 129.1, 129.1, 129.1, 129.0, 128.8, 128.8, 128.8, 128.3, 128.3, 127.6, 127.6, 104.4, 104.4, 104.1, 102.6, 102.1, 102.1, 82.5, 82.5, 82.5, 79.9, 78.9, 78.5, 78.4, 77.1, 76.3, 76.2, 76.0, 75.9, 75.8, 74.4, 74.3, 71.2, 70.9, 70.3, 69.9, 69.6, 67.9, 67.9, 56.7, 56.5, 52.5, 51.9, 30.1, 29.6, 24.4, 23.2, 23.0. MS (ESI) *m/z* calcd. $[M]^-$ 1474.5, found 1474.3.

5-Aminopentyl 3-*O*-sulfo-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy–β-D-glucosaminopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucosaminopyranoside (1).

To a solution of **S27 in** MeOH–H_2O–acetic acid (2:1:0.05, v/v, 3.0 mL), was bubbled Argon gas for 15 min. Then 5% Pd/C (18 mg) was added to the solution. H_2 gas was bubbled in the reaction mixture for 15 min. The reaction mixture was stirred at room temperature for 12 h and filtered. The filtrate was concentrated and dried by lyophilization to give **1** as a colorless powder (25 mg, 90%). ^{1}H NMR (D_2O) δ 4.55 (d, 1H, *J* = 9.2 Hz), 4.45 (d, 1H, *J* = 8.5 Hz), 4.37 (br, 1H), 4.31 (d, 1H, *J* = 8.0 Hz), 4.19 (dd, 1H, *J* = 9.7 Hz), 4.14 (br, 1H), 4.01 (br, 1H), 3.87–3.46 (m), 2.84 (t, 2H, *J* = 7.9 Hz), 1.89 (s, 3H), 1.88 (s, 3H), 1.57–1.39 (m, 6H). ^{13}C NMR (D_2O) δ 174.3, 174.3, 102.8, 102.7, 102.4, 101.1, 82.1, 79.8, 78.5, 77.6, 74.8, 74.8, 74.7, 74.5, 72.3, 72.2, 72.1, 70.0, 69.1, 68.2, 65.9, 60.8, 60.8, 59.9, 59.7, 55.1, 55.0, 39.3, 28.0, 26.3, 22.1, 22.1, 21.3. MS (ESI) *m/z* calcd. $[M+H]^+$ 914.3282, 914.3295.

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