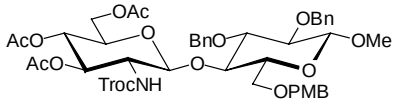
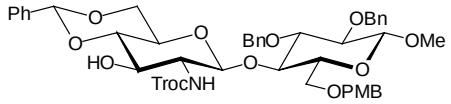
Experimental Section

General Materials and Methods. All spectral data were obtained on either a Varian Unity-Plus spectrometer (^{1}H resonance frequency of 500 MHz), a Varian INOVA spectrometer (^{1}H resonance frequency of 500 MHz), or a Varian INOVA spectrometer (^{1}H resonance frequency of 750 MHz) and samples internally referenced as indicated. Reagents and solvents were reagent grade and used as received unless otherwise noted. THF and benzene were distilled from sodium benzoquinone ketal before use, dichloromethane and acetonitrile were distilled from CaH_2 and methanol distilled from Mg shavings. Tf_2O was distilled from P_2O_5. TLC were performed on glass plates with fluorescent indicator (Merck Silica gel 60 F_{254}) and were visualized using a mixture of *p*-anisaldehyde and ceric ammonium sulfate-molybdate stain. Normal phase flash chromatography following the method of Still and co-workers[1] was employed throughout.



6

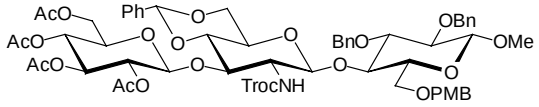
Methyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-*β*-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (6). TMSOTf (4 μL, 22.4 μmol) was added to a stirred slurry of **4** (111 mg, 0.224 mmol), **5** (402 mg, 0.642 mmol) and 4 Å MS in dry CH_2Cl_2 (1.3 mL) at -30 °C. The reaction was stirred under Ar for 1 h and warmed to r.t. After 3 h the reaction was quenched with Et_3N, filtered through Celite®, concentrated *in vacuo* and purified by flash chromatography (3:2, hexanes:EtOAc) to afford **6** (196 mg, 87%) as a white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (2H, AA'XX', $J_{AX} = J_{A'X'} = 7.7$ Hz, $J_{AA'} = J_{XX'} = 3.0$ Hz, $J_{AX'} = J_{A'X} = 0.5$ Hz), 7.30 (10H, m), 7.05 (2H, AA'XX', $J_{AX} = J_{A'X'} = 7.7$ Hz, $J_{AA'} = J_{XX'} = 3.0$ Hz, $J_{AX'} = J_{A'X} = 0.5$ Hz), 4.99 (1H, AB_q, $J_{AB} = 11.4$ Hz, $\nu_A = 4.98$, $\nu_B = 4.75$), 4.97 (1H, t, $J = 9.5$ Hz), 4.89 (1H, t, $J = 10.1$ Hz), 4.83 (1H, AB_q, $J_{AB} = 11.8$ Hz, $\nu_A = 4.80$, $\nu_B = 4.65$), 4.75 (1H, AB_q, $J_{AB} = 11.4$ Hz, $\nu_A = 4.98$, $\nu_B = 4.75$), 4.75 (1H, AB_q, $J_{AB} = 11.6$ Hz, $\nu_A = 4.70$, $\nu_B = 4.40$), 4.71 (2H, bs), 4.65 (1H, AB_q, $J_{AB} = 11.8$ Hz, $\nu_A = 4.80$, $\nu_B = 4.65$), 4.64 (1H, bd,), 4.53 (1H, bd, $J = 8.2$ Hz), 4.42 (1H, AB_q, $J_{AB} = 11.6$ Hz, $\nu_A = 4.70$, $\nu_B = 4.40$), 4.27 (1H, d, $J = 7.7$ Hz), 4.12 (1H, dd, $J = 12.2$, 4.3 Hz), 3.91 (1H, bt, $J = 9.6$ Hz), 3.86 (3H, s), 3.84 (1H, bd, $J = 9.7$ Hz), 3.76 (1H, dd, $J = 11.0$, 1.4 Hz), 3.59 (3H, m), 3.57 (3H, s), 3.56 (1H, t, J = 9.1 Hz), 3.39 , 3.37 , 2.02 (3H, s), 2.01 (3H, s), 1.95 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 170.5, 169.6, 159.9, 154.2, 139.4, 138.6, 130.5, 129.8, 128.4, 128.3, 128.2, 127.7, 127.4, 127.3, 114.4, 104.9, 100.6, 82.7, 81.7, 77.4, 75.1, 74.8, 74.5, 74.1, 73.2, 72.7, 71.4, 68.5, 67.9, 57.3, 56.6, 55.4, 20.7. HRFABMS calculated for $C_{44}H_{51}Cl_3NO_{16}$ (M+H) 954.2273, found 954.2270.



7

Methyl *O*-(4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-*β*-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (7). A stock solution of guanidine/guanidinium nitrate[2] (4 mL) was added to a flask containing **6** (383 mg, 0.400 mmol) at r.t. The solution was stirred under dry N_2 for 20 min. The reaction was neutralized with Dowex 50W-X8 cation exchange resin. The resin was filtered and the filtrate concentrated to yield the triol as a white foam. The residue was dissolved in CH_2Cl_2 (20 mL) and washed with 10% aqueous $NaHCO_3$ (40 mL). The layers were separated and the aqueous phase extracted with CH_2Cl_2 (2 x 20 mL). The organic phases were combined and dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford the triol as a white foam (315 mg, 95%).

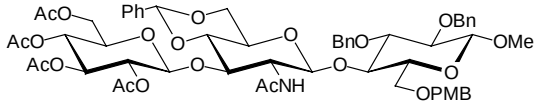
Catalytic *p*-toluenesulfonic acid monohydrate was added to a solution of the triol (315 mg, 0.379 mmol) and benzaldehyde dimethyl acetal (780 μL, 5.20 mmoL) in dry CH_3CN (4.5 mL). The reaction was stirred under N_2 at r.t. for 30 min, then neutralized with Et_3N and purified by flash chromatography (2:1, hexanes:EtOAc) to afford **7** (267 mg, 76%) as a clear syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (2H, m), 7.32 (15H, m), 6.98 (2H, AA'XX', $J_{AX} = J_{A'X'} = 7.7$ Hz, $J_{AA'} = J_{XX'} = 3.0$ Hz, $J_{AX'} = J_{A'X} = 0.5$ Hz), 5.42 (1H, s), 4.88 (1H, AB_q, $J_{AB} = 10.9$ Hz, $\nu_A = 4.83$, $\nu_B = 4.81$), 4.86 (1H, AB_q, $J_{AB} = 13.7$ Hz, $\nu_A = 4.74$, $\nu_B = 4.72$), 4.85 (1H, AB_q, $J_{AB} = 11.1$ Hz, $\nu_A = 4.78$, $\nu_B = 4.76$), 4.84 (NH, bs), 4.77 (1H, AB_q, $J_{AB} = 10.9$ Hz, $\nu_A = 4.83$, $\nu_B = 4.81$), 4.75 (1H, AB_q, $J_{AB} = 11.7$ Hz, $\nu_A = 4.56$, $\nu_B = 4.53$), 4.69 (1H, AB_q, $J_{AB} = 11.1$ Hz, $\nu_A = 4.78$, $\nu_B = 4.76$), 4.61 (1H, AB_q, $J_{AB} = 13.7$ Hz, $\nu_A = 4.74$, $\nu_B = 4.72$), 4.35 (1H, AB_q, $J_{AB} = 11.7$ Hz, $\nu_A = 4.56$, $\nu_B = 4.53$), 4.33 (1H, bd, $J = 8.6$ Hz), 4.26 (1H, d, $J = 7.7$ Hz), 4.03 (1H, dd, $J = 10.1$, 4.3 Hz), 3.87 (1H, t, J = 9.3 Hz), 3.80 (1H, dd, $J = 10.8$, 2.8 Hz), 3.79 (3H, s), 3.58 (1H, dd, $J = 11.0$, 3.0 Hz), 3.56 (3H, s), 3.51 (1H, t, $J = 8.9$ Hz), 3.46 (2H, m), 3.41 (1H, m), 3.39 (1H, dd, $J = 9.2$, 7.6 Hz), 3.32 (1H, dt, $J = 9.7$, 2.3 Hz), 3.30 (1H, t, $J = 10.5$ Hz), 3.13 (1H, td, $J = 9.6$, 5.0 Hz), 3.10 (1H, bs). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 155.2, 139.4, 138.7, 137.2, 131.0, 129.8, 129.5, 128.5, 128.4, 128.3, 128.2, 127.8, 127.5, 126.5, 114.4, 104.9, 101.9, 101.3, 82.8, 81.8, 81.3, 78.3, 75.1, 74.9, 74.8, 74.2, 73.5, 72.3, 68.6, 67.9, 66.0, 58.7, 57.3, 55.6. HRFABMS calculated for $C_{45}H_{50}Cl_3NO_{13}$ (M+Na) 940.2245, found 940.2257.



9

Methyl *O*-(2,3,4-tri-*O*-acetyl-*β*-D-glucopyranosyl)-(1→3)-(4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-*β*-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (9). TMSOTf (22 μL, 0.121 mmol) was added to a solution of **8** (1.10 g, 2.23 mmol) and 4 Å MS in dry CH_2Cl_2 (3.5 mL) at -30 °C under Ar. After 20 min, a solution of **7** (1.11 g, 1.21 mmol) in dry CH_2Cl_2

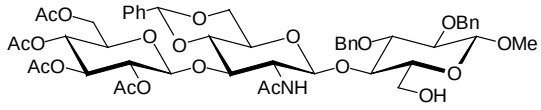
(2 mL) was added dropwise to the solution of **8**. The reaction was stirred at -30 °C for an additional 30 min and allowed to warm to r.t. over 12 h. The reaction was neutralized with Et_3N and filtered through Celite® and concentrated *in vacuo*. The residue was purified by flash chromatography (3.5:2 to 1:1 hexanes:EtOAc) to afford **9** (1.27g, 84%) as a white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (2H, m), 7.41 (2H, AA'XX', J_{AX} = $J_{A'X'}$ = 7.7 Hz, $J_{AA'}$ = $J_{XX'}$ = 3.0 Hz, $J_{AX'}$ = $J_{A'X}$ = 0.5 Hz), 7.39-7.24 (13H, m), 7.05 (2H, AA'XX', J_{AX} = $J_{A'X'}$ = 7.7 Hz, $J_{AA'}$ = $J_{XX'}$ = 3.0 Hz, $J_{AX'}$ = $J_{A'X}$ = 0.5 Hz), 5.45 (1H, s), 5.14 (1H, t, *J* = 9.6 Hz), 5.07 (1H, t, *J* = 9.8 Hz), 4.97 (1H, dd, *J* = 9.6, 8.0 Hz), 4.89 (1H, AB_q, J_{AB} = 12.1 Hz, ν_A = 4.76, ν_B = 4.74), 4.86 (1H, AB_q, J_{AB} = 10.5 Hz, ν_A = 4.82, ν_B = 4.79), 4.85 (1H, AB_q, J_{AB} = 11.5 Hz, ν_A = 4.79, ν_B = 4.77), 4.84 (1H, AB_q, J_{AB} = 12.0 Hz, ν_A = 4.59, ν_B = 4.57), 4.75 (1H, AB_q, J_{AB} = 10.5 Hz, ν_A = 4.82, ν_B = 4.79), 4.71 (1H, AB_q, J_{AB} = 11.5 Hz, ν_A = 4.79, ν_B = 4.77), 4.60 (1H, AB_q, J_{AB} = 12.1 Hz, ν_A = 4.76, ν_B = 4.74), 4.53 (1H, d, *J* = 8.0 Hz), 4.36 (1H, d, *J* = 8.2 Hz), 4.32 (1H, AB_q, J_{AB} = 12.0 Hz, ν_A = 4.59, ν_B = 4.57), 4.26 (1H, d, *J* = 7.8 Hz), 4.14 (1H, m), 4.08 (1H, dd, *J* = 10.5, 4.8 Hz), 4.03 (1H, m), 3.93 (1H, t, *J* = 9.4 Hz), 3.92 (1H, m), 3.91 (3H, s), 3.75 (2H, m), 3.58 (3H, s), 3.57-3.50 (4H, m), 3.49 (1H, t, *J* = 9.3 Hz), 3.44 (1H, dd, *J* = 9.2, 1.4 Hz), 3.34 (1H, t, *J* = 10.2 Hz), 3.27 (1H, bd, *J* = 9.6 Hz), 3.16 (1H, td, *J* = 9.6, 4.9 Hz), 2.04 (3H, s), 2.03 (3H, s), 2.02 (3H, s), 2.01 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 170.4, 169.5, 169.4,159.5, 153.9, 139.3, 138.7, 137.3, 131.5, 130.0, 129.2, 128.4, 128.3, 128.2, 128.1, 127.6, 127.5, 127.4, 126.1, 127.5, 127.4, 126.1, 105.0, 101.1, 100.9, 100.5, 95.7, 82.8, 81.8, 79.2, 78.8, 77.1, 75.5, 74.9, 74.7, 74.3, 73.2, 72.9, 71.7, 71.4, 68.5, 68.4, 67.2, 66.2, 62.2, 57.9, 57.3, 55.6, 20.9, 20.7. HRFABMS calculated for $C_{59}H_{68}C_{l3}NO_{22}$ (M+Na) 1270.3170, found 1270.3195.



10

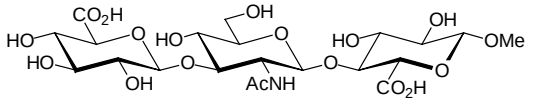
Methyl *O*-(2,3,4-tri-*O*-acetyl-*β*-D-glucopyranosyl)-(1→3)-(4,6-*O*-benzylidene-2-acetamido-2-deoxy-(*β*-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (10). Cadmium dust (374 mg, 3.33 mmol) was added to a solution of **9** (208 mg, 0.166 mmol) in DMF:AcOH (2:1.5, 3.5 mL) and the reaction was stirred at r.t. under N_2. After 12 h the reaction mixture was filtered through Celite®, rinsed with DMF (5 mL) then azeotroped with toluene (5 x 20 mL). The residue was treated with acetic anhydride in pyridine:CH_2Cl_2 (1:1) for 4 h at r.t., then quenched with MeOH (1mL). The reaction was concentrated *in vacuo* and the residue redissolved in CH_2Cl_2 (50 mL) then washed with a 2:1 solution of 10% $(NH_4)_2SO_3$ / 10% HCl, H_2O (1 x 60 mL), saturated aqueous $NaHCO_3$ (1 x 60 mL), and brine (1 x 60 mL) then dried (Na_2SO_4). The organic extract was filtered, concentrated *in vacuo* and purified by flash chromatography (3.5:1, EtOAc:hexanes) to afford **10** (160 mg, 86%) as a clear foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (2H, m), 7.49-7.22 (17H, m), 6.96 (2H, AA',XX', J_{AX} = $J_{A'X'}$ = 7.7 Hz, $J_{AA'}$ = $J_{XX'}$ = 3.0 Hz, $J_{AX'}$ = $J_{A'X}$ = 0.5 Hz), 5.41 (1H,s), 5.13 (1H, t, *J* = 9.4 Hz), 5.04 (1H, t, *J* = 9.7 Hz), 4.95 (1H, m), 4.93 (1H, dd, *J* = 9.6, 8.4 Hz), 4.84 (1H, AB_q, J_{AB} = 11.1 Hz, ν_A = 4.82, ν_B = 4.80), 4.83 (1H, m), 4.82 (1H, AB_q, J_{AB} = 11.2 Hz, ν_A = 4.76, ν_B = 4.74), 4.77 (1H, AB_q, J_{AB} = 12.1 Hz, ν_A = 4.76, ν_B = 4.74), 4.71 (1H, AB_q, J_{AB}

= 12.0 Hz, ν_A = 4.586, ν_B = 4.56), 4.66 (1H, AB_q, J_{AB} = 11.2 Hz, ν_A = 4.76, ν_B = 4.74), 4.60 (1H, d, *J* = 8.0 Hz), 4.42 (1H, AB_q, J_{AB} = 12.0 Hz, ν_A = 4.58, ν_B = 4.56), 4.26 (1H, d, *J* = 7.7 Hz), 4.11 (1H, dd, *J* = 12.2, 4.4 Hz), 4.02-3.99 (2H, m), 3.90 (1H, t, *J* = 8.9 Hz), 3.84 (3H, s), 3.65 (1H, dd, *J* = 10.9, 2.3 Hz), 3.64 (1H, dd, *J* = 10.6, 3.6 Hz), 3.58 (1H, dq, *J* = 9.8, 2.3 Hz), 3.56 (3H, s), 3.54-3.49 (2H, m), 3.41-3.33 (4H, m), 3.19 (1H, td, *J* = 9.7, 5.1 Hz), 1.99 (3H, s), 1.93 (6H, s), 1.85 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.5, 170.0, 169.6, 169.5, 159.5, 139.3, 138.7, 137.4, 130.6, 130.5, 129.3, 128.4, 128.3, 128.2, 128.1, 127.7, 127.5, 127.3, 126.3, 114.2, 104,8, 101.3, 100.2, 99.9, 83.1, 81.9, 79.9, 77.7, 76.8, 75.4, 74.9, 74.5, 73.3, 73.1, 71.7, 68.7, 68.3, 67.9, 66.1, 62.1, 57.6, 57.3, 55.6, 23.6, 20.9, 20.8, 20.6. HRFABMS calculated for $C_{58}H_{69}NO_{21}$ (M+Na) 1138.4260, found 1138.4256.



11

Methyl *O*-(2,3,4-tri-*O*-acetyl-*β*-D-glucopyranosyl)-(1→3)-(4,6-*O*-benzylidene-2-acetamido-2-deoxy-(*β*-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-benzyl)-*β*-D-glucopyranoside (11). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (36 mg, 0.157 mmol) was added to a stirred solution of **10** (160 mg, 0.143 mmol) in MeCN:H_2O (10:1, 2 mL) at 0 °C. After 12 h the reaction was diluted with CH_2Cl_2 (20 mL), washed with saturated aqueous $NaHCO_3$ (1 x 30 mL), then dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (7:2:1, EtOAc:hexanes:*i*PrOH) to afford **11** (119 mg, 84%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.26 (15H, m), 6.10 (1H bs,), 5.39 (1H, s), 5.32 (1H, d, *J* = 8.2 Hz), 5.08 (1H, t, *J* = 9.5 Hz), 5.02 (1H, d, *J* = 9.8 Hz), 4.91 (1H, dd, *J* = 9.2, 8.1 Hz), 4.90 (1H, AB_q, J_{AB} = 11.9 Hz, ν_A = 4.82, ν_B = 4.80), 4.82 (1H, AB_q, J_{AB} = 10.9 Hz, ν_A = 4.74, ν_B = 4.72), 4.82 (1H, d, *J* = 10.9 Hz), 4.70 (1H, AB_q, J_{AB} = 11.9 Hz, ν_A = 4.82, ν_B = 4.80), 4.63 (1H, AB_q, J_{AB} = 10.9 Hz, ν_A = 4.74, ν_B = 4.72), 4.56 (1H, t, *J* = 9.6 Hz), 4.33 (1H, d, *J* = 7.8 Hz), 4.01 (1H, dd, *J* = 12.4, 3.6 Hz), 3.93 (1H, dd, *J* = 12.5, 2.4 Hz), 3.89-3.83 (3H, m), 3.74 (1H, dd, *J* = 12.1, 3.7 Hz), 3.58 (1H, t, *J* = 8.9 Hz), 3.57 (1H, t, *J* = 9.1 Hz), 3.55 (3H,s), 3.45 (1H, t, *J* = 10.2 Hz), 3.37 (1H, dd, *J* = 8.9, 7.9 Hz), 3.34-3.31 (2H, m), 3.30 (1H, td, *J* = 9.5, 5.1 Hz), 3.14 (1H, dt, *J* = 9.8, 7.6 Hz), 2.01 (3H, s), 2.00 (3H, s), 1.96 (3H, s), 1.95 (3H, s), 1.94 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 170.9, 170.4, 169.7, 169.6, 139.2, 138.4, 137.3, 129.6, 128.5, 128.3, 127.9, 127.5, 126.7, 126.4, 105.0, 101.7, 100.2, 99.8, 83.3, 82.3, 80.2, 76.9, 76.8, 75.1, 75.0, 73.1, 71.9, 71.7, 68.7, 68.1, 65.9, 61.7, 61.4, 60.6, 59.1, 57.5, 23.8, 20.9, 20.8, 20.7. HRFABMS calculated for $C_{50}H_{61}NO_{20}$ (M+Na) 1018.3685, found 1018.3683.

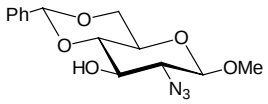


2

Methyl *O*-(*β*-D-glucopyranosyluronic acid)-(1→3)-2-acetamido-2-deoxy-(*β*-D-glucopyranosyl)-(1→4)-*β*-D-glucopyranosiduronic acid (2). Catalytic Na° was added

to a solution of **11** (89 mg, 0.089 mmol) in dry MeOH (5 mL) and stirred at r.t. for 12 h under N_2. The reaction was neutralized with Dowex 50W-X8 cation exchange resin, filtered and concentrated *in vacuo* to afford **12** as a white solid in quantitative yield. The residue was used in the subsequent oxidation step without further purification.

A saturated solution of aqueous $NaHCO_3$ (0.5 mL) and a 5% solution of NaOCl (0.65 mL) was added to a solution of **12**, NaBr (2 mg, 19.4 μmol), tetrabutylammonium bromide (2mg, 6.20 μmol), and TEMPO (2 mg, 12.8 μmol) in (1:1) CH_2Cl_2:H_2O (2 mL) at 0 °C. After 12 h the reaction was quenched with MeOH (0.5 mL), neutralized with 10% HCl and concentrated *in vacuo*. The residue was redissolved in (1:1) MeOH:H_2O (10 mL) and $Pd(OH)_2$ (20 weight percent) on carbon (100 mg) added. The suspension was vigorously stirred under H_2 (60 psi) for 48 h. The reaction was filtered through Celite® then passed though a short column of Sephadex LH-20 (water/MeOH) and purified on a Sephadex G-10 column using water as an eluent to afford **2** as a white foam. ^{1}H NMR (750 MHz, D_2O) δ 4.55 (1H, d, *J* = 8.3 Hz), 4.44 (1H, d, *J* = 8.0 Hz), 4.35 (1H, d, *J* = 8.2 Hz), 3.90 (1H, dd, *J* = 12.4, 2.1 Hz), 3.82 (1H, dd, *J* = 10.1, 8.4 Hz), 3.76 (1H, dd, *J* = 12.5, 5.3 Hz), 3.72 (1H, t, *J* = 9.3 Hz), 3.71 (1H, t, *J* = 9.2 Hz), 3.70 (1H, dd, *J* = 8.6, 1.7 Hz), 3.67 (1H, d, *J* = 9.9 Hz), 3.56 (1H, t, *J* = 9.3 Hz), 3.53 (3H, s), 3.52 (1H, t, *J* = 9.9 Hz), 3.49-3.47 (2H, m), 3.46 (1H, ddd, *J* = 9.8, 5.4, 2.3 Hz), 3.30 (1H, dd, *J* = 9.4, 8.0 Hz), 3.29 (1H, m), 1.89 (3H, s). ^{13}C NMR (188 MHz, D_2O, CH_3CN as a reference) δ 184.8, 183.6, 102.7, 102.3, 99.9, 82.3, 79.5, 74.8, 74.7, 73.2, 72.1, 71.2, 67.9, 59.9, 56.7, 53.6, 21.9. HRFABMS calculated for $C_{21}H_{31}NO_{18}Na_2$ (M+Na) 654.1234, found 654.1226.

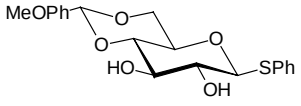


16

Methyl 2-azido-2deoxy-4,6-*O*-benzylidene-*β*-D-glucopyranoside (16). A solution of tri-*O*-acetyl-D-glucal (**13**) (3.07 g, 11.3 mmol) in wet CH_3CN (56 mL) was added dropwise to a dry mixture of NaN_3 (1.10 g, 16.9 mmol) and ceric (IV) ammonium nitrate (CAN, 18.58 g, 33.9 mmol) at –30 °C. The suspension was stirred vigorously under N_2 for 8 h. (5:1 toluene:EtOAc). Upon warming to 0 °C, the reaction was poured into water (0 °C) and extracted with EtOAc (3 x 200 mL). The organic extracts were combined then washed with water (1 x 300 mL) and brine (1 x 300 mL) then dried (Na_2SO_4). The filtrate was concentrated *in vacuo*, then azeotroped with benzene (5 x 20 mL) to afford **14** (4.48 g, quantitative) as a clear syrup. Na° (1.56 g, 67.8 mmol) was added to a stirred solution of **14** in dry MeOH (60 mL) at 0 °C. After 30 min the reaction was neutralized with Dowex 50W-X8 cation exchange resin, filtered and concentrated *in vacuo*. The syrup was redissolved in MeOH:acetone (1:3) and cooled to –20 °C to precipitate $NaNO_3$. The precipitate was removed and the filtrate concentrated *in vacuo* to afford **15** as a clear syrup.

The mixture of **15** (2.47 g, 1.13 mmol) was azeotroped with benzene (3 x 25 mL) and dissolved in dry MeCN (113 mL) to which benzaldehyde dimethyl acetal (2.5 mL, 16.9 mmol) and catalytic *p*-toluenesulfonic acid monohydrate was added. The reaction was stirred under N_2 at r.t. for 6 h then neutralized with Et_3N. The desired isomer was

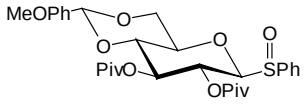
separated by flash chromatography (3:1, hexanes:EtOAc) to afford **16** (424 mg, 12%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (2H, m), 7.38 (3H, m), 5.53 (1H, s), 4.35 (1H, dd, *J* = 10.5, 5.1 Hz), 4.31 (1H, d, *J* = 8.1 Hz), 3.78 (1H, t, *J* = 10.5 Hz), 3.66 (1H, dt, *J* = 2.1, 9.4 Hz), 3.59 (3H, s), 3.54 (1H, t, *J* = 9.2 Hz), 3.39 (1H, dt, *J* = 5.1, 10.5 Hz), 3.38 (1H, dd, *J* = 9.0, 8.9 Hz), 2.78 (1H, bd *J* = 2.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 129.6, 128.6, 126.4, 103.7, 102.2, 80.8, 77.0, 72.2, 68.7, 66.6, 66.3, 57.7. HRFABMS calculated for $C_{14}H_{18}N_3O_5$ (M+H) 308.1246, found 308.1247.



19

Phenyl 4,6-*O*-(4-methoxybenzylidene)-1-thio-*β*-D-glucopyranoside (19). A solution of catalytic Na° dissolved in dry MeOH (5mL) was added to a stirred suspension **18**[3] (1.02 g, 2.31 mmoL) in dry MeOH (30 mL) at r.t. under N_2. After 5 min the suspension cleared and stirred an additional 3 h. The reaction was neutralized with Dowex 50W-X8 cation exchange resin, filtered and concentrated *in vacuo* to afford the tetraol as a white solid (625 mg, 99%). The tetraol was azeotroped with benzene (3 x 5 mL) and used in the subsequent step without further purification.

Catalytic *p*-toluenesulfonic acid monohydrate was added to a solution of the tetraol (625 mg, 2.29 mmol) and *p*-methoxybenzaldehyde dimethyl acetal (433 μL, 2.52 mmol), in dry DMF (4 mL). The reaction was heated at 50 °C on a rotary evaporator under water aspirator pressure (~ 22 mmHg) for 2 h. The temperature was increased to 70 °C and the mixture concentrated to a volume 2 mL. The remaining solution was poured into a stirred slurry of ice (4g), saturated aqueous $NaHCO_3$ (20 mL), and hexanes (20 mL) and an off-white, sticky solid formed immediately and was rinsed with hexanes. The solid was recrystallized from EtOAc/hexanes to afford **19** (848 mg, 88%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (2H, m), 7.40 (2H, AA'XX', $J_{AX} = J_{A'X'} = 7.7$ Hz, $J_{AA'} = J_{XX'} = 3.0$ Hz, $J_{AX'} = J_{A'X} = 0.5$ Hz), 7.34 (3H, m), 6.88 (2H, AA'XX', $J_{AX} = J_{A'X'} = 7.7$ Hz, $J_{AA'} = J_{XX'} = 3.0$ Hz, $J_{AX'} = J_{A'X} = 0.5$ Hz), 5.49 (1H, s), 4.64 (1H, d, *J* = 9.8 Hz), 4.37 (1H, dd, *J* = 10.4, 3.9 Hz), 3.86 (1H, td, *J* = 8.8, 2.3 Hz), 3.80 (3H, s), 3.77 (1H, t, *J* = 10.1 Hz), 3.53-3.45 (3H, m), 2.74 (1H, bs), 2.63 (1H, bs). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 133.3, 131.5, 129.6, 129.4, 128.8, 127.8, 113.9, 102.1, 88.9, 80.4, 74.8, 72.8, 70.8, 68.8, 55.5. HRFABMS calculated for $C_{20}H_{22}O_6S$ (M+H) 391.1215, found 391.1213.

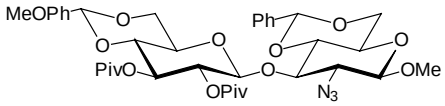


20

Phenyl 2,3-di-*O*-pivaloyl-4,6-*O*-(4-methoxybenzylidene)-1-thio-*β*-D-glucopyranosyl sulfoxide (20). To a flask containing **19** (788 mg, 2.02 mmol) in dry pyridine (20 mL) was added trimethylacetyl chloride (PivCl) (994 μL, 8.08 mmol) followed by a catalytic amount of DMAP. The reaction was refluxed 12 h under N_2 and after cooling to r.t., quenched with MeOH (5 mL) and concentrated *in vacuo*. The syrup

was redissolved in CH_2Cl_2 (40 mL) and washed with a 2:1 solution of 10% $(NH_4)_2SO_3$ and 10% HCl (1 x 60 mL), saturated $NaHCO_3$ (1 x 60 ml), and brine (1x 60 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo*, then recrystallized from EtOAc/hexanes to afford the sulfide precursor, phenyl 2,3-di-*O*-pivaloyl-4,6-*O*-(4-methoxybenzylidene)-1-thio-*β*-D-glucopyranoside (1.04 g, 92 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (2H, m), 7.35 (4H, m), 6.92 (2H, m), 5.47 (1H, s), 5.37 (1H, t, *J* = 9.5 Hz), 5.07 (1H, t, *J* = 9.6 Hz), 4.82 (1H, d, *J* = 10.2 Hz), 4.37 (1H, dd, *J* = 10.4, 4.9 Hz), 3.79 (1H, t, *J* = 10.3 Hz), 3.78 (3H, s), 3.68 (1H, t, *J* = 9.6 Hz), 3.57 (1H, dt, *J* = 9.8, 5.0 Hz), 1.22 (9H, s), 1.14 (9H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 176.6, 160.0, 132.8, 132.3, 129.4, 129.1, 128.3, 127.2, 113.6, 101.1, 87.2, 78.5, 72.3, 70.6, 69.8, 68.4, 55.25, 38.8, 38.7, 27.1, 27.0. HRFABMS calculated for $C_{30}H_{38}O_8S$ (M+Na) 581.2185, found 581.2184.

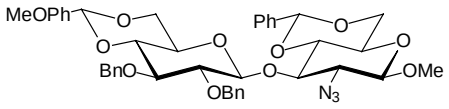
A solution *m*-chloroperoxybenzoic acid (490 mg, 2.84 mmol) in dry CH_2Cl_2 (2.5 mL) was added to a solution of the sulfide (1.51 g, 2.71 mmol) in dry CH_2Cl_2 (25 mL) at –78 °C. After 20 min, the mixture was poured into saturated $NaHCO_3$ (100 mL) and washed with saturated $NaHCO_3$ (2 x 100 mL) then dried (Na_2SO_4), filtered and concentrated *in vacuo*, and purified by flash chromatography (8:2, hexanes:EtOAc) to afford a white solid corresponding to **20** (1.08 g, 69%) as a mixture of diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (1H, m), 7.74 (1H, m), 7.65-7.55 (8H, m), 7.28 (2H, m), 7.27 (2H, m), 6.84 (4H, m), 5.59 (1H, dd, *J* = 9.8, 9.1 Hz), 5.45 (1H, s), 5.44 (1H, t, *J* = 9.5 Hz), 5.42-5.37 (1H, m), 5.08 (1H, dd, *J* = 10.3, 8.8 Hz), 4.68 (1H, d, *J* = 10.3 Hz), 4.62 (1H, m), 4.37 (1H, dd, *J* = 10.3, 4.7 Hz), 4.32 (1H, m), 4.22 (1H, d, *J* = 9.9 Hz), 4.12 (1H, dd, *J* = 5.1, 2.1 Hz), 3.79 (6H, s), 3.78 (1H, t, *J* = 10.5 Hz), 3.76 (1H, t, *J* = 9.8 Hz), 3.65-3.55 (1H,m), 3.53-3.39 (2H,m), 1.27 (18H, s), 1.19 (9H, s), 1.15 (9H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 177.3, 176.8, 176.3, 160.3, 160.2, 139.3, 135.1, 134.8, 131.8, 130.7, 129.3, 129.2, 129.1, 127.4, 127.3, 125.4, 113.8, 113.7, 101.4, 101.3, 91.8, 89.9, 78.0, 77.7, 72.4, 72.2, 71.2, 70.7, 67.6, 67.0, 55.4, 39.0, 31.7, 27.4, 27.3, 27.2. HRFABMS calculated for $C_{30}H_{38}O_9S$ (M+Na) 597.2134, found 597.2133.



21

Methyl *O*-(2,3-di-*O*-pivaloyl-4,6-*O*-(4-methoxybenzylidene)-*β*-D-glucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-*β*-D-glucopyranoside (21). Trifluoromethanesulfonic anhydride (122 μL, 0.725 mmol) was added to a solution of **20** (834 mg, 1.45 mmol) in dry CH_2Cl_2 (30 mL) at –78 °C then warmed to –60 °C. After 20 min, a solution of **16** (285 mg, 0.926 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (951 mg, 4.63 mmol) in dry CH_2Cl_2 (10 mL) was added via cannula. After an additional 20 min at –60 °C the mixture was warmed to -30 °C over 1 h. The reaction was quenched with saturated $NaHCO_3$ (10 mL), and washed with saturated $NaHCO_3$ (1 x 50 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo* and purified by flash chromatography (5:1, petroleum ether:EtOAc) to afford **21** (573 mg, 83%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (2H, m), 7.41-7.32 (3H, m), 7.29 (2H, AA'XX', $J_{AX} = J_{A'X'} = 6.5$ Hz, $J_{AA'} = J_{XX'} = 2.5$ Hz, $J_{AX'} = J_{A'X} = 0.4$ Hz), 6.84 (2H,

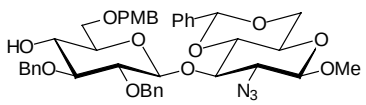
AA'XX', $J_{AX} = J_{A'X'} = 6.5$ Hz, $J_{AA'} = J_{XX'} = 2.5$ Hz, $J_{AX'} = J_{A'X} = 0.4$ Hz), 5.53 (1H, s), 5.35 (1H, s), 5.27 (1H, t, *J* = 9.5 Hz), 5.10 (1H, dd, *J* = 9.0, 7.7 Hz), 4.92 (1H, d, *J* = 7.8 Hz), 4.34 (1H, dd, *J* = 10.4, 4.8 Hz), 4.29 (1H, d, *J* = 8.0 Hz), 4.15 (1H, dd, *J* = 10.5, 5.1 Hz), 3.79 (1H, t, *J* = 7.8 Hz), 3.78 (3H, s), 3.70-3.61 (4H, m), 3.56 (3H, s), 3.40-3.34 (3H, m), 1.21 (9H, s), 1.14 (9H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 176.8, 160.1, 137.2, 129.6, 129.5, 128.5, 127.4, 126.1, 113.7, 103.8, 101.5, 101.2, 101.1, 79.7, 78.7, 78.2, 72.3, 71.6, 68.7, 68.6, 66.5, 66.4, 66.1, 57.7, 55.4, 39.0, 38.9, 27.3, 27.2. HRFABMS calculated for $C_{38}H_{49}N_3O_{13}$ (M+Na) 778.3163, found 778.3166.



22

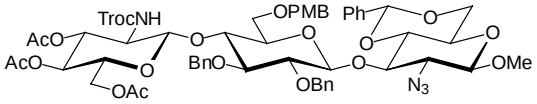
Methyl *O*-(2,3-di-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-*β*-D-glucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-*β*-D-glucopyranoside (22). Lithium hydroxide monohydrate (185 mg, 4.41 mmol) was added to a solution stirred of **21** (667 mg, 0.882 mmol) in 3:2:1 MeOH:THF:H_2O (50 mL) under N_2 then warmed to 60 °C for 24 h. The reaction was diluted with CH_2Cl_2 and neutralized with 1M HCl. The organic layer was washed with saturated $NaHCO_3$ (2 x 60 mL), brine (1 x 60 mL) then dried (Na_2SO_4) and concentrated *in vacuo* to afford the corresponding diol (442 mg) as a white solid.

Benzyl bromide (0.360 mL, 3.01 mmol) was added to a solution of the diol in dry DMF (5 mL) and NaH (144 mg, 60% dispersion in mineral oil) at 0 °C under N_2. After 6 h the reaction was quenched with MeOH (5mL) and diluted with CH_2Cl_2 (50 mL). The organic layer was washed with saturated $NaHCO_3$ (1 x 60 mL), brine (1 x 60 mL) then dried (Na_2SO_4) filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (2:1, hexanes:EtOAc) to afford **22** (474 mg, 82%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (2H, m), 7.30 (16H, m), 6.9 (2H, AA'XX', $J_{AX} = J_{A'X'} = 6.5$, $J_{AA'} = J_{XX'} = 2.5$ Hz, $J_{AX'} = J_{A'X} = 0.4$ Hz), 5.55 (1H, s), 5.39 (1H, s), 4.93 (1H, AB_q, $J_{AB} = 11.0$ Hz, $\nu_a = 4.93$, $\nu_b = 4.81$), 4.87 (1H, AB_q, $J_{AB} = 11.6$ Hz, $\nu_a = 4.87$, $\nu_b = 4.74$), 4.86 (1H, d, *J* = 7.3 Hz), 4.81 (1H, AB_q, $J_{AB} = 11.0$ Hz, $\nu_a = 4.93$, $\nu_b = 4.81$), 4.75 (1H, AB_q, $J_{AB} = 11.6$ Hz, $\nu_a = 4.87$, $\nu_b = 4.74$), 4.35 (1H, dd, *J* = 9.1, 5.1 Hz), 4.34 (1H, d, *J* = 7.8 Hz), 4.13 (1H, dd, *J* = 10.4, 5.0 Hz), 3.82 (3H, s), 3.82 (1H, t, *J* = 10.3 Hz), 3.81 (1H, t, *J* = 9.4 Hz), 3.74 (1H, t, *J* = 7.8 Hz), 3.61 (3H, s), 3.54 (1H, t, J = 7.5 Hz), 3.47 (1H, dd, 9.6, 8.8 Hz), 3.41 (1H, td, *J* = 9.9, 5.2 Hz), 3.28 (1H, td, 9.4, 5.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 138.7, 138.5, 137.2, 130.0, 129.5, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7, 127.5, 126.2, 113.7, 103.9, 103.2, 101.6, 101.1, 82.2, 81.4, 81.2, 79.6, 78.6, 75.2, 74.9, 68.9, 68.7, 66.5, 66.4, 66.0, 57.7, 55.4. HRFABMS calculated for $C_{42}H_{46}N_3O_{11}$ (M+H) 768.3132, found 768.3132.



23

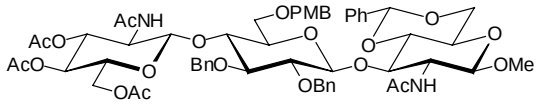
Methyl *O*-(2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-β-D-glucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (23). A solution of trifluoroacetic acid (287 μL, 3.73 mmol) in dry DMF (1.5 mL) at 0 °C was added via cannula to a stirred mixture of **22** (287 mg, 0.373 mmol), sodium cyanoborohydride (117 mg, 1.87 mmol) and 3 Å MS (200 mg) in dry DMF (3.5 mL). After 8 h the mixture was filtered through Celite® and poured into an ice-cold solution of saturated $NaHCO_3$ (20 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL) and the combined extracts were washed with saturated $NaHCO_3$ (2 x 30 mL) and brine (1 x 30 mL), then dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (2.5:1 to 2:1, hexane:EtOAc) to afford **23** (262 mg, 91%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (5H, m), 7.31 (10H, m), 7.20 (2H, AA'XX', $J_{AX} = J_{A'X'} = 6.5$ Hz, $J_{AA'} = J_{XX'} = 2.5$ Hz, $J_{AX'} = J_{A'X} = 0.4$ Hz), 6.87 (2H, AA'XX', $J_{AX} = J_{A'X'} = 6.5$ Hz, $J_{AA'} = J_{XX'} = 2.5$ Hz, $J_{AX'} = J_{A'X} = 0.4$ Hz), 5.47 (1H, s), 5.02 (1H, AB_q, $J_{AB} = 10.7$ Hz $\nu_a = 5.02$, $\nu_b = 4.76$), 4.89 (1H, AB_q, $J_{AB} = 11.4$ Hz, $\nu_a = 4.89$, $\nu_b = 4.72$), 4.76 (1H, AB_q, $J_{AB} = 10.7$ Hz, $\nu_a = 5.02$, $\nu_b = 4.76$), 4.75 (1H, d, $J = 7.5$ Hz), 4.73 (1H, AB_q, $J_{AB} = 11.4$ Hz, $\nu_a = 4.89$, $\nu_b = 4.72$), 4.37 (2H, AB_q, $J_{AB} = 11.4$ Hz, $\nu_a = 4.38$, $\nu_b = 4.36$), 4.32 (1H, d, $J = 8.1$ Hz), 4.31 (1H, dd, $J = 10.3$, 4.9 Hz), 3.83 (1H, t, $J = 9.3$ Hz), 3.81 (3 H, s), 3.75 (1H, t, $J = 9.1$ Hz), 3.74 (1H, t, $J = 10.5$ Hz), 3.61 (3H, s), 3.56 (2H, m), 3.51 (1H, dd, $J = 9.4$, 1.4 Hz), 3.48 (1H, t, $J = 5.1$ Hz), 3.43 (1H, m), 3.42 (1H, t, $J = 7.6$ Hz), 3.37 (1H, td, $J = 9.6$, 4.8 Hz), 3.20 (1H, dt, $J = 9.1$, 4.9 Hz), 2.54 (1H, bd, 2.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 138.9, 138.7, 137.3, 130.1, 129.1, 129.3, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 126.4, 114.0, 103.8, 102.6, 101.6, 84.5, 82.1, 79.7, 78.5, 75.7, 75.0, 73.6, 73.5, 72.2, 70.5, 68.7, 66.6, 66.5, 57.7, 55.5. We were unable to obtain any mass spectrometry data for this intermediate.



24

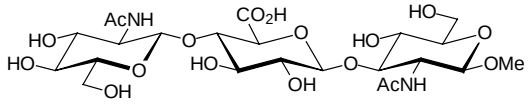
Methyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-β-D-glucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (24). A 0.5 M solution of TMSOTf in dry CH_2Cl_2 (11 μL) was added to a flask containing **5** (219 mg, 0.350 mmol), **23** (117 mg, 0.152 mmol) and 4 Å MS (150 mg) in dry CH_2Cl_2 (2.2 mL) at 0 °C under a Ar. The reaction was stirred for 2 h at 0 °C and warmed to r.t. over 1 h then neutralized with Et_3N, filtered through Celite® and concentrated *in vacuo*. The residue was purified by flash chromatography (10:1 to 7:1, $CHCl_3$:EtOAc) to afford **24** (162 mg, 86%) as a white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (2H, m), 7.37-7.22 (15H, m), 6.98 (AA'XX', 2H, $J_{AX} = J_{A'X'} = 6.5$ Hz, $J_{AA'} = J_{XX'} = 2.5$ Hz, $J_{AX'} = J_{A'X} = 0.4$ Hz), 6.61 (1H, bs), 6.06 (1H, bs), 5.48 (1H, s), 4.97 (1H, AB_q, $J_{AB} = 11.3$ Hz, $\nu_a = 4.91$, $\nu_b = 4.78$), 4.93 (1H, AB_q, $J_{AB} = 9.3$ Hz, $\nu_a = 4.83$, $\nu_b = 4.81$), 4.91 (1H, m), 4.90 (1H, m), 4.75 (1H, AB_q, $J_{AB} = 11.1$ Hz, $\nu_a = 4.68$, $\nu_b = 4.66$), 4.74-4.72 (2H, m), 4.71 (1H, AB_q, $J_{AB} = 9.3$ Hz, $\nu_a = 4.83$, $\nu_b = 4.81$), 4.71 (1H, AB_q, $J_{AB} = 11.3$ Hz, $\nu_a = 4.91$, $\nu_b = 4.78$), 4.59 (1H, AB_q, $J_{AB} = 11.1$ Hz, $\nu_a = 4.68$, $\nu_b = 4.66$), 4.52 (1H, m), 4.51 (1H, AB_q, $J_{AB} = 11.4$ Hz, $\nu_a = 4.38$, $\nu_b = 4.36$), 4.35 (1H, d, $J = 8.7$ Hz),

4.34 (1H, dd, J = 10.5, 3.7 Hz), 4.24 (1H, AB_q, J_{AB} = 11.4 Hz, ν_a = 4.38, ν_b = 4.36), 4.05 (1H, dd, J = 12.5, 4.5 Hz), 3.81 (3H, s), 3.84-3.78 (3H, m), 3.80 (1H, dd, J = 11.2, 9.3 Hz), 3.72 (1H, t, J = 9.2 Hz), 3.63 (3H, s), 3.58-3.51 (4H, m), 3.49 (1H, dd, J = 9.4, 8.0 Hz), 3.47-3.39 (3H, m), 3.31 (1H, bd, J = 8.4 Hz), 3.19 (1H, bd, J = 9.2 Hz), 2.00 (3H, s), 1.99 (3H, bs), 1.94 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.6, 169.7, 159.9, 154.2, 139.4, 138.6, 137.4, 130.5, 129.9, 129.4, 128.5, 128.4, 128.3, 128.2, 127.7, 127.4, 127.2, 126.4, 114.3, 103.9, 102.7, 101.7, 100.5, 83.1, 82.1, 79.7, 78.4, 77.9, 75.1, 75.0, 74.6, 74.2, 73.2, 72.8, 71.6, 68.7, 68.6, 68.2, 66.6, 66.5, 61.9, 57.7, 56.7, 55.4, 20.7. HRFABMS calculated for $C_{57}H_{65}Cl_3N_4O_{20}$ (M+Na) 1253.3155, found 1253.3156.



25

Methyl *O*-(3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→4)-(2,3-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-*β*-D-glucopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-acetamido-2-deoxy–*β*-D-glucopyranoside (25). Cadmium dust (792 mg, 7.05 mmol) was added to a solution of **24** (290mg, 0.235 mmol) in 1:1 AcOH:DMF (1 mL). The reaction was stirred for 8 h at r.t. then diluted with CH_2Cl_2 and filtered through Celite®. The filtrate was concentrated *in vacuo* and azeotroped with toluene (5 x 10 mL). The residue was redissolved in dry pyridine (5 mL) and thioacetic acid (336 μL, 4.70 mmol) added and the reaction stirred at r.t. After 12 h, acetic anhydride was added and the reaction stirred for an additional 30 min then quenched with MeOH and concentrated *in vacuo*. The residue was redissolved in CH_2Cl_2 (20 mL) and washed with saturated $NaHCO_3$ (then dried ($MgSO_4$). The residue was purified by flash chromatography (20:1, CH_2Cl_2:MeOH) to afford **25** (288 mg, 90%) as a clear syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (2H, m), 7.37-7.18 (15H, m), 6.97 (2H, AA'XX', J_{AX} = $J_{A'X'}$ = 7.7 Hz, $J_{AA'}$ = $J_{XX'}$ = 2.7 Hz, $J_{AX'}$ = $J_{A'X}$ = 0.4 Hz), 5.52 (1H, s), 5.36 (1H, d, J = 7.2 Hz), 5.08 (1H, d, J = 8.2 Hz), 5.01 (1H, AB_q, J_{AB} = 11.5 Hz, ν_a = 4.86, ν_b = 4.84), 4.99 (1H, d, J = 9.3 Hz), 4.97 (1H, t, J = 9.8 Hz), 4.85 (1H, dd, J = 10.4, 9.4 Hz), 4.77 (1H, AB_q, J_{AB} = 11.7 Hz, ν_a = 4.70, ν_b = 4.69), 4.68 (1H, AB_q, J_{AB} = 11.5 Hz, ν_a = 4.86, ν_b = 4.84), 4.62 (1H, AB_q, J_{AB} = 11.7 Hz, ν_a = 4.706, ν_b = 4.69), 4.56 (1H, t, J = 9.5 Hz), 4.47 (1H, d, J = 8.5 Hz), 4.46 (1H, AB_q, J_{AB} = 11.5 Hz, ν_a = 4.22, ν_b = 4.20), 4.32 (1H, dd, J = 10.4, 4.8 Hz), 4.26 (1H, d, J = 7.8 Hz), 4.07 (1H, dd, J = 12.3, 4.4 Hz), 3.96 (1H, AB_q, J_{AB} = 11.5 Hz, ν_a = 4.22, ν_b = 4.20), 3.93 (1H, t, J = 9.4 Hz), 3.91 (1H, t, J = 8.9 Hz), 3.88-3.85 (1H, m), 3.84 (3H, s), 3.83-3.82 (1H, m), 3.76 (1H, t, J = 10.2 Hz), 3.60 (1H, t, J = 9.0 Hz), 3.53 (1H, td, J = 9.8, 5.2 Hz), 3.46 (3H, s), 3.41-3.36 (4H, m), 3.22 (1H, dt, J = 9.8, 3.0 Hz), 2.85 (1H, dt, J = 8.6, 8.2 Hz), 2.00 (3H, s), 1.98 (3H, s), 1.92 (3H, s), 1.66 (3H, s), 1.59 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 171.0, 170.9, 170.4, 169.6, 160.0, 149.3, 139.3, 138.7, 137.9, 136.8, 130.7, 129.8, 129.2, 128.8, 128.4, 128.3, 128.2, 127.9, 127.5, 127.4, 126.7, 124.2, 114.4, 103.6, 101.7, 100.7, 100.5, 83.4, 81.9, 80.2, 78.0, 77.9, 75.3, 75.2, 74.0, 73.6, 73.2, 71.7, 69.0, 68.9, 68.6, 66.3, 62.1, 59.7, 57.4, 55.5, 54.5, 21.1, 20.7. HRFABMS calculated for $C_{58}H_{70}N_2O_{20}$ (M+H) 1115.4600, found 1115.4600.



3

Methyl *O*-(2-acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→4)-(*β*-D-glucopyranosyluronic acid)-(1→3)-2-acetamido-2-deoxy–*β*-D-glucopyranoside (3). Ceric (IV) ammonium nitrate (234 mg, 0.431 mmol) was added to a stirred solution of **25** (240 mg, 0.216 mmol) in 9:1 CH_2Cl_2:H_2O (2 mL) at 0 °C. After 1 h, the reaction was diluted with CH_2Cl_2 (20 mL) and washed with H_2O (1 x 20 mL) and saturated aqueous $NaHCO_3$ (1 x 20 mL) then dried ($MgSO_4$).

A saturated solution of aqueous $NaHCO_3$ (0.5 mL) and a 5% solution of NaOCl (0.65 mL) was added to a stirred solution of the alcohol, NaBr (1 mg, 9.7 μmol), tetrabutylammonium bromide (1mg, 3.1 μmol), and TEMPO (1 mg, 6.4 μmol) in (6:1) CH_2Cl_2:H_2O (3.5 mL) at 0 °C. After 20 min the reaction was quenched with MeOH (0.5 mL), the acidified with 1M HCl. The aqueous layer was repeatedly extracted with CH_2Cl_2 (3 x 10 mL). The organic extracts were combined and dried ($MgSO_4$) then concentrated *in vacuo*.

The residue was redissolved in 10:1 MeOH:H_2O (5 mL), then $Pd(OH)_2$ (20 weight percent) on carbon (100 mg) was added and the reaction placed under H_2 (60 psi) for 48 hours at r.t. The hydrogenolysis product was filtered through Celite® and concentrated *in vacuo* then redissolved in 2:1 H_2O:THF. Lithium hydroxide monohydrate was added and the reaction stirred under N_2. After 12 h, the reaction was neutralized with Dowex 50W-X8 cation exchange resin and concentrated *in vacuo*. The residue was purified by size-exclusion chromatography on a Sephadex G-10 column using water as an eluent and afforded **3** (76 mg, 57%) was a white solid. 1H NMR (750 MHz, D_2O) δ 4.51 (1H, d, *J* = 8.4 Hz), 4.48 (1H, d, *J* = 7.9 Hz), 4.43 (1H, d, *J* = 8.5 Hz), 3.95 (1H, dd, *J* = 12.4, 3.7 Hz), 3.94 (1H, dd, *J* = 10.9, 3.3 Hz), 3.85 (1H, t, *J* = 8.7 Hz), 3.80 (1H, dd, *J* = 10.4, 8.7 Hz), 3.75 (1H, t, *J* = 8.8 Hz), 3.73 (1H, dd, *J* = 12.4, 5.5 Hz), 3.70 (1H, dd, *J* = 10.4, 8.8 Hz), 3.67 (1H, dd, *J* = 10.6, 8.6 Hz), 3.60 (1H, t, *J* = 9.4 Hz), 3.51 (1H, dd, *J* = 10.2, 8.4 Hz), 3.50 (1H, t, *J* = 7.0 Hz), 3.47 (3H, s), 3.46-3.42 (4H, m), 3.34 (1H, dd, *J* = 9.4, 8.2 Hz), 2.01 (3H, s), 1.98 (3H, s). ^{13}C NMR (188 MHz, D_2O, CH_3CN as a reference) δ 174.2, 102.6, 101.3, 100.7, 82.3, 79.6, 75.4, 73.2, 73.1, 71.8, 69.2, 68.2, 60.3, 60.1, 56.7, 54.9, 53.9, 21.9, 21.8. HRFABMS calculated for $C_{23}H_{38}LiN_2O_{17}$ (M+Li) 621.2330, found 621.2330.

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(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(2) A stock solution of guanidine/guanidinium nitrate was prepared according to reference 8. Briefly, 1M NaOMe in methanol (1 mL) was added to a solution of guanidinium nitrate (622 mg, 5 mmol) in MeOH/CH_2Cl_2 (50 mL, 9:1).
(3) Compound **18** was prepared according to Tropper, F.D.; Andersson, F.O.; Grand-Maitre, C.; Roy, R. *Synthesis* **1991**, 734.