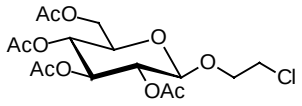
Experimental Section:

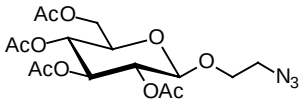
General Experimental Methods. NMR spectra were recorded on a Varian Unity-400, Varian Unity-500 or a Varian Inova-500 FT NMR spectrometer. Proton chemical shifts are reported in parts per million (ppm) with reference to $CHCl_3$ in the internal solvent (7.27 ppm) unless noted otherwise. Coupling constants are reported in hertz (Hz). Carbon chemical shifts are reported in parts per million (ppm) with reference to internal solvent $CDCl_3$ (77.23 ppm) unless noted otherwise. Splitting patterns as designated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broadened (br). All mass spectrometry data were obtained by the University of Illinois Mass Spectroscopy Lab. CH_2Cl_2, Et_3N, CH_3CN and pyridine were distilled from CaH_2 prior to use as reaction solvents. Benzene and THF were distilled from sodium benzophenone ketyl.

Analytical thin layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates with a fluorescent indicator. Visualization was accomplished by UV illumination, *p*-anisaldehyde solution followed by heat, and ceric ammonium molybdate solution followed by heat. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Merck.



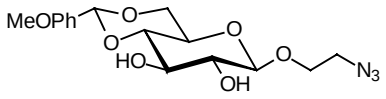
5

(2-chloroethyl)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (5).[1] To a stirred solution of tricholoroacetimidate **4** (11.4 g, 23.2 mmole), 4Å MS, and 2-chloroethanol (3.6 mL, 52.7 mmol) in 300 mL CH_2Cl_2 at -76 °C was added a solution of $BF_3{\cdot}OEt_2$ in 100 mL CH_2Cl_2 at -76 °C by cannula transfer. The reaction mixture was stirred for 1 h at -76 °C and then allowed to warm to rt. Sat'd $NaHCO_3$ (30 mL) was added and the reaction mixture was then filtered through celite. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to yield a yellow oil which was purified by flash chromatography (43% EtOAc in hexane) to afford the 2-chloroethyl glycoside **5** (7.81 g, 82%) as a white solid: R_f = 0.42 (50% EtOAc in hexane); ^{13}C NMR ($CDCl_3$, 126 MHz)[2] δ 170.50, 170.09, 169.33, 169.31, 100.97, 72.51, 71.80, 70.95, 69.86, 68.27, 61.78, 42.47, 20.61, 20.55, 20.48; ^1H NMR ($CDCl_3$, 500 MHz) δ 5.22 (t, 1H, J = 9.5 Hz), 5.09 (t, 1H, J = 9.7 Hz), 5.02 (dd, 1H, J = 9.7, 8.1 Hz), 4.57 (d, 1H, J = 7.8 Hz), 4.26 (dd, 1H, J = 12.2, 4.8 Hz), 4.14 (dd, 1H, J = 12.2, 2.3 Hz), 4.11 (dt, 1H, J = 11.2, 5.3 Hz), 3.77 (ddd, 1H, J = 11.1, 7.0, 6.0 Hz), 3.71 (ddd, 1H, J = 10.1, 4.7, 2.4 Hz), 3.63 (ddd, 1H, J = 11.0, 7.0, 5.3 Hz), 3.62 (ddd, 1H, J = 11.0, 6.0, 5.3), 2.09 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H); FABMS calcd for $C_{16}H_{23}ClO_{10}Na$ $(M+Na)^+$, 433.0877; found 433.0878.



6

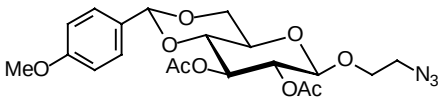
(2-azidoethyl)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (6). To a solution of 2-chloroethyl glycoside **5** (6.88 g, 16.75 mmol) in 500 mL DMF was added NaN_3 (10.1 g, 155.36 mmol). The reaction mixture was stirred at 50-60 °C for 3 days, then diluted with 500 mL $CHCl_3$ and washed with sat'd $NaHCO_3$, water (2×) and brine. The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure to yield an off-white solid that was purified by flash chromatography (50% EtOAc in hexane) to afford the 2-azidoethyl glycoside **6** (6.66 g, 95%) as a white solid: R_f = 0.35 (50% EtOAc in hexane); ^{13}C NMR ($CDCl_3$, 126 MHz)[3] δ 170.38, 169.97, 169.22, 169.17, 100.42, 72.58, 71.67, 70.87, 68.47, 68.14, 61.66, 50.31, 20.53, 20.48, 20.39; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.22 (t, 1H, J = 9.4 Hz), 5.10 (t, 1H, J = 9.7 Hz), 5.03 (dd, 1H, J = 9.7, 8.0 Hz), 4.60 (d, 1H, J = 7.9 Hz), 4.25 (dd, 1H, J = 12.3, 4.7 Hz), 4.16 (dd, 1H, J = 12.4, 2.5 Hz), 4.04 (ddd, 1H, J = 10.8, 4.8, 3.3 Hz), 3.71 (ddd, 1H, J = 10.0, 4.8, 2.6 Hz), 3.69 (ddd, 1H, J = 10.8, 8.5, 3.4 Hz), 3.50 (ddd, 1H, J = 13.4, 8.4, 3.4 Hz), 3.28 (ddd, 1H, J = 13.5, 4.8, 3.3 Hz), 2.09 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H); FABMS calcd for $C_{16}H_{23}N_3O_{10}Na$ $(M+Na)^+$, 440.1281; found 440.1282.



7

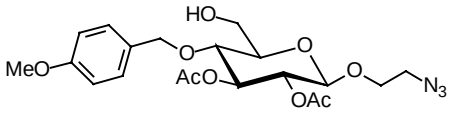
(2-azidoethyl)-4,6-*O*-*p*-methoxybenzylidene-β-D-glucopyranoside (7). A solution of 2-azidoethyl glycoside **6** (1.01 g, 2.43 mmol) in methanol (15 mL) was treated with methanolic NaOMe (Zemplén deacetylation conditions). The mixture was allowed to stir for 1 h at rt and then neutralized with acidic cation exchange resin (Dowex 50W-X8). The resin was removed by filtration, and the solvent was evaporated under reduced pressure to afford the tetraol as a clear syrup which was used without further purification.

To a solution of the tetraol in 4 mL distilled DMF was added benzaldehyde dimethyl acetal (0.54 mL, 3.14 mmol) and a catalytic amount of $TsOH{\cdot}H_2O$. The solution was maintained under reduced pressure at 50 °C for 2 h. A few drops of Et_3N were added and the reaction mixture was then concentrated under reduced pressure to yield a clear syrup which was purified by flash chromatography (67% EtOAc in $CHCl_3$) to **7** (0.84 g, 95%) as a white solid: R_f = 0.25 (67% EtOAc in $CHCl_3$); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 160.44, 129.60, 127.83, 113.88, 103.47, 102.00, 80.52, 74.61, 73.19, 69.02, 68.70, 66.60, 55.48, 50.89; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41 (AA'BB', 2H, $J_{AA'} = J_{BB'} = 2.3$ Hz, $J_{AB} = J_{A'B'} = 8.7$ Hz, $\nu_A = \nu_{A'} = 3702.0$ Hz, $\nu_B = \nu_{B'} = 3438.8$ Hz), 6.88 (AA'BB', 2H, as above), 5.47 (s, 1H), 4.40 (d, 1H, J = 7.6 Hz), 4.30 (dd, 1H, J = 10.5, 5.0 Hz), 4.03 (ddd, 1H, J = 10.7, 5.6, 3.6 Hz), 3.79 (s, 3H), 3.78-3.72 (m, 3H), 3.54-3.47 (m, 3H), 3.41 (td, 1H, J = 9.6, 5.0 Hz), 3.39 (ddd, 1H, J = 13.3, 5.7, 3.5 Hz), 3.26 (d, 1H, J = 3.0 Hz), 3.25 (d, 1H, J = 2.4 Hz); FABMS calcd for $C_{16}H_{22}N_3O_7$ $(M+H)^+$, 368.1458; found 368.1459.



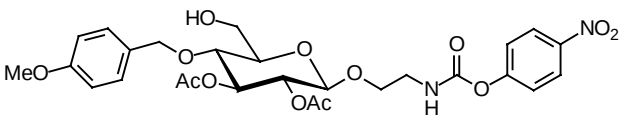
8

(2-azidoethyl)-2,3-Di-*O*-acetyl-4,6-*O*-*p*-methoxybenzylidene-β-D-glucopyranoside (8). To a solution of diol **7** (1.35 g, 3.67 mmol) in 20 mL pyridine was added Ac_2O (2.2 mL, 23.32 mmol). The reaction mixture was stirred at rt for 11 h, and then evaporated under reduced pressure. The residue was purified by flash chromatography (20% EtOAc in $CHCl_3$) to give **8** (1.64 g, 99%) as a white solid: R_f = 0.47 (20% EtOAc in $CHCl_3$); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.39, 169.88, 160.40, 129.43, 127.69, 113.81, 101.71, 101.45, 78.41, 72.30, 72.00, 68.88, 68.63, 66.66, 55.48, 50.73, 20.98, 20.92; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 (AA'BB', 2H, $J_{AA'} = J_{BB'}$ = 2.5 Hz, $J_{AB} = J_{A'B'}$ = 8.8 Hz, $J_{AB'} = J_{A'B}$ = 0.2 Hz, $\nu_A = \nu_{A'}$ = 3677.8 Hz, $\nu_B = \nu_{B'}$ = 3436.6 Hz), 6.88 (AA'BB', 2H, as above), 5.46 (s, 1H), 5.31 (t, 1H, J = 9.4 Hz), 5.02 (dd, 1H, J = 9.4, 7.9 Hz), 4.66 (d, 1H, J = 7.9 Hz), 4.34 (dd, 1H, J = 10.4, 5.0), 4.02 (ddd, 1H, J = 10.7, 5.1, 3.4 Hz), 3.80 (s, 3H), 3.79 (t, 1H, J = 10.2 Hz), 3.70 (ddd, 1H, J = 10.8, 7.8, 3.3 Hz), 3.69 (t, 1H, J = 9.5 Hz), 3.53 (td, 1H, J = 9.7, 4.9), 3.47 (ddd, 1H, J = 13.4, 8.1, 3.5 Hz), 3.31 (ddd, 1H, J = 13.3, 5.1, 3.3 Hz), 2.07 (s, 3H), 2.04 (s, 3H); FABMS calcd for $C_{20}H_{26}N_3O_9$ $(M+H)^+$, 451.1669; found 451.1670.



9

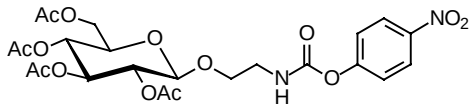
(2-azidoethyl)-2,3-di-*O*-acetyl-4-*O*-*p*-methoxybenzyl-β-D-glucopyranoside (9) was prepared from **8** (1.41 g, 3.12 mmol) by selective reductive opening of the *p*-methoxybenzylidene acetal according to conditions reported by Johansson and Samuelsson[4] with the following modification: The reaction was stirred at rt for 21 h. Purification by flash chromatography (50% EtOAc in hexane) afforded the alcohol **9** (1.20 g, 85%) as a white solid: R_f = 0.15 (50% EtOAc in hexane); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.32, 169.96, 159.72, 129.91, 129.80, 114.16, 100.88, 75.57, 75.07, 74.60, 71.97, 68.81, 61.62, 55.49, 50.73, 21.04, 20.93; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.19 (AA'BB', 2H, $J_{AA'} = J_{BB'}$ = 2.5 Hz, $J_{AB} = J_{A'B'}$ = 8.6 Hz, $J_{AB'} = J_{A'B}$ = 0.3 Hz, $\nu_A = \nu_{A'}$ = 3594.0 Hz, $\nu_B = \nu_{B'}$ = 3430.9 Hz), 6.86 (AA'BB', 2H, as above), 5.22 (t, 1H, J = 9.6 Hz), 4.89 (dd, 1H, J = 9.8, 7.9 Hz), 4.57 (d, 1H, J = 7.8 Hz), 4.55 (s, 2H), 4.00 (ddd, 1H, J = 10.9, 5.3, 3.3 Hz), 3.87 (dd, 1H, J = 12.4, 2.3 Hz), 3.79 (s, 3H), 3.73 (dd, 1H, J = 12.2, 3.9 Hz), 3.72 (t, 1H, J = 9.5 Hz), 3.69 (ddd, 1H, J = 10.9, 7.8, 3.2 Hz), 3.47-3.41 (m, 2H), 3.28 (ddd, 1H, J = 13.5, 5.3, 3.2 Hz), 2.03 (s, 3H), 1.97 (s, 3H); FABMS calcd for $C_{20}H_{27}N_3O_9Na$ $(M+Na)^+$, 476.1645; found 476.1644.



1

2-(*p*-nitrophenyl carbamate)-ethyl-2,3-di-*O*-acetyl-4-*O*-*p*-methoxybenzyl-β-D-glucopyranoside (1). To a solution of azide **9** (0.92 g, 2.03 mmol) and $TsOH{\cdot}H_2O$ (0.46 g, 2.42 mmol) in MeOH (100mL), in a Fisher-Porter bottle, was added a catalytic amount of Raney Ni. The reaction mixture was evacuated and stirred rigorously at rt, under a H_2 atmosphere of 60 psi for 1.5 h. The catalyst was removed by filtration through celite, and the solvent was evaporated under reduced pressure to afford the amine, which was used without further purification.

The amine was stirred in a solution of solid $NaHCO_3$ (1.80 g, 21.43 mmol) and *p*-nitrophenyl chloroformate (1.32 g, 6.54 mmol) in 80 mL CH_3CN at rt for 14 h. The reaction mixture was then filtered, concentrated under reduced pressure, and flash chromatographed (29% hexane in EtOAc) to afford the *p*-nitrophenyl carbamate **1** (0.94 g, 79%) as a white foam: R_f = 0.18 (29% hexane in EtOAc); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.30, 170.13, 159.79, 156.01, 153.36, 145.04, 129.98, 129.63, 125.38, 122.17, 114.19, 101.24, 75.71, 74.97, 74.84, 74.60, 72.12, 69.10, 61.61, 55.50, 41.45, 21.05, 20.95; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.25 (AA'BB', 2H, $J_{AA'} = J_{BB'} = 2.8$ Hz, $J_{AB} = J_{A'B'} = 9.1$ Hz, $J_{AB'} = J_{A'B} = 0.3$ Hz, $\nu_A = \nu_{A'} = 4121.5$ Hz, $\nu_B = \nu_{B'} = 3655.9$ Hz), 7.31 (AA'BB', 2H, as above), 7.20 (AA'BB', 2H, $J_{AA'} = J_{BB'} = 2.5$ Hz, $J_{AB} = J_{A'B'} = 8.5$ Hz, $J_{AB'} = J_{A'B} = 0.5$ Hz, $\nu_A = \nu_{A'} = 3595.5$ Hz, $\nu_B = \nu_{B'} = 3435.0$ Hz), 6.87 (AA'BB', 2H, as above), 5.67 (t, 1H, J = 5.8 Hz), 5.25 (t, 1H, J = 9.6 Hz), 4.90 (dd, 1H, J = 9.7, 8.2 Hz), 4.55 (AB_q, 2H, J_{AB} = 11.0 Hz, ν_A = 2281.2, ν_B = 2270.3, $\Delta\nu$ = 10.9 Hz), 4.55 (d, 1H, J = 7.9 Hz), 3.93-3.87 (m, 2H), 3.80 (s, 3H), 3.79-3.71 (m, 2H), 3.70 (t, 1H, J = 9.5 Hz), 3.55-3.42 (m, 3H), 2.06 (s, 3H), 2.00 (s, 3H); FABMS calcd for $C_{27}H_{32}N_2O_{13}Na$ $(M+Na)^+$, 615.1802; found 615.1800.

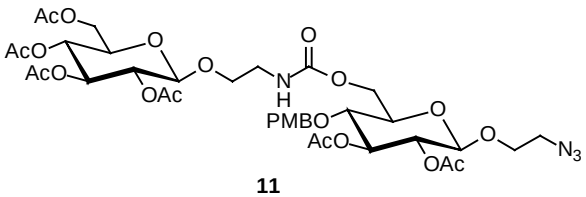


10

2-(*p*-nitrophenyl carbamate)-ethyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (10). To a solution of azide **6** (1.51 g, 3.62 mmol) and $TsOH{\cdot}H_2O$ (0.68 g, 3.60 mmol) in MeOH (80mL), in a Fisher-Porter bottle, was added a catalytic amount of Raney Ni. The reaction mixture was evacuated and stirred rigorously at rt, under a H_2 atmosphere of 60 psi for 2 h. The catalyst was removed by filtration through celite, and the solvent was evaporated under reduced pressure to afford the amine as a white foam, which was used without further purification.

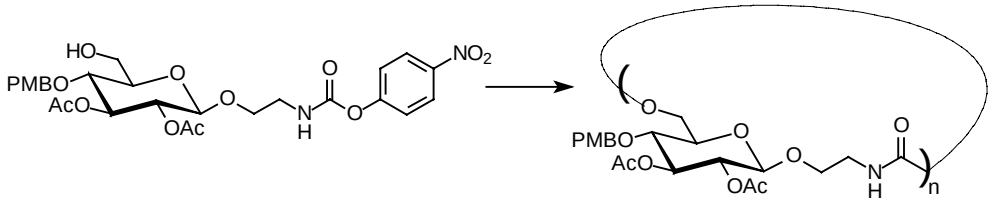
The amine was stirred in a solution of solid $NaHCO_3$ (2.64 g, 31.44 mmol) and *p*-nitrophenyl chloroformate (1.33 g, 6.58 mmol) in 100 mL CH_3CN at rt for 11 h. The reaction mixture was then filtered, concentrated under reduced pressure, and flash chromatographed (40% hexane in EtOAc) to afford the *p*-nitrophenyl carbamate **1** (1.87 g, 93%) as a white foam: R_f = 0.22 (50% hexane in EtOAc); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.84, 170.44, 169.74, 169.65, 156.05, 153.37, 125.36, 122.18, 101.19, 72.71, 72.18, 71.40, 69.13, 68.42, 62.01, 41.35, 20.89, 20.88, 20.77, 20.76; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.24 (AA'BB', 2H, $J_{AA'} = J_{BB'} = 2.6$ Hz, $J_{AB} = J_{A'B'} = 9.1$ Hz, $J_{AB'} = J_{A'B} = 0$ Hz, $\nu_A = \nu_{A'} = 4116.1$ Hz, $\nu_B = \nu_{B'} = 3652.4$ Hz), 7.31 (AA'BB', 2H, as above), 5.65 (br. t, 1H, J = 5.1 Hz), 5.22 (t, 1H, J = 9.7 Hz), 5.09 (t, 1H, J = 9.7 Hz), 5.02 (dd, 1H, J = 9.6, 7.9 Hz), 4.55 (d, 1H, J = 7.9 Hz), 4.25 (dd, 1H, J = 12.4, 4.8 Hz), 4.19 (dd, 1H, J = 12.5, 2.3 Hz), 3.91 (ABXX', 1H, ν_A = 1955.5, ν_B = 1897.7, ν_X = 1744.8, $\nu_{X'}$ = 1733.0, J_{AB} =

10.5, J_{AX} = 5.5, $J_{AX'}$ = 4.5, J_{BX} = 4.5, $J_{BX'}$ = 5.3, $J_{XX'}$ = 5.3 Hz), 3.80 (AB<u>X</u>XX', 1H, as above), 3.74 (ddd, 1H, J = 10.0, 4.8, 2.4 Hz), 3.49 (AB<u>X</u>X', 1H, as above), 3.47 (ABX<u>X</u>', 1H, as above), 2.07 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H); HRFABMS calcd for $C_{23}H_{29}N_2O_{14}$ $(M+H)^+$, 557.1619; found 557.1613.



11

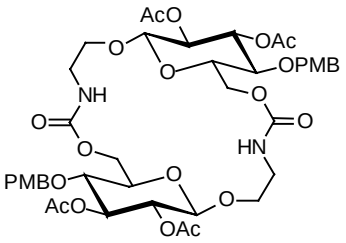
(11) To a solution of alcohol **9** (33.8 mg, 0.075 mmol), activated carbamate **10** (45.5 mg, 0.082 mmol), and NaH (20 mg of 60% disp. in paraffin, 0.5 mmol) in 2 mL CH_2Cl_2 was added Et_3N (30μL, 0.22 mmol). The reaction mixture was stirred for 1 h at 40 °C. The precipitate was filtered through celite, washed with sat'd $NaHCO_3$, dried ($MgSO_4$), and evaporated under reduced pressure. The resulting clear oil was flash chromatographed (33% hexane in EtOAc) to afford the carbamate **11** (59.5 mg, 92%) as a white solid: R_f = 0.21 (33% hexane in EtOAc); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.88, 170.45, 170.27, 169.97, 169.63, 159.76, 156.15, 129.99, 129.50, 114.16, 101.28, 100.71, 75.38, 75.15, 74.61, 73.60, 72.82, 72.12, 71.85, 71.41, 69.70, 68.77, 68.43, 63.15, 61.99, 55.47, 50.70, 41.12, 21.03, 20.91, 20.85, 20.76; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.18 (<u>AA</u>'BB', 2H, $J_{AA'} = J_{BB'}$ = 2.5 Hz, $J_{AB} = J_{A'B'}$ = 8.3 Hz, $J_{AB'} = J_{A'B}$ = 0.5 Hz, $\nu_A = \nu_{A'}$ = 3586.4 Hz, $\nu_B = \nu_{B'}$ = 3426.7 Hz), 6.86 (AA'<u>BB</u>', 2H, as above), 5.22 (t, 1H, J = 9.2 Hz), 5.21 (br. m, 1H), 5.19 (t, 1H, J = 9.4 Hz), 5.06 (t, 1H, J = 9.7 Hz), 4.98 (dd, 1H, J = 9.4, 7.9 Hz), 4.88 (dd, 1H, J = 9.6, 8.1 Hz), 4.53 (d, 1H, J = 7.9 Hz), 4.50 (AB_q, 2H, J_{AB} = 10.7 Hz, ν_A = 2253.9, ν_B = 2243.2, Δν = 10.8 Hz), 4.49 (d, 1H, J = 7.9 Hz), 4.36 (dd, 1H, J = 11.5, 1.7 Hz), 4.25 (dd, 1H, J = 12.2, 4.6 Hz), 4.24 (dd, 1H, J = 11.9, 4.4 Hz), 4.16 (dd, 1H, J = 12.2, 2.5 Hz), 4.00 (ddd, 1H, J = 10.8, 5.0, 3.4 Hz), 3.87-2.82 (m, 1H), 3.78 (s, 3H), 3.71-3.65 (m, 3H), 3.63 (t, 1H, J = 9.5 Hz), 3.55 (ddd, 1H, J = 9.9, 4.3, 2.2 Hz), 3.47 (ddd, 1H, J = 13.3, 8.3, 3.4 Hz), 3.41-3.45 (m, 2H), 3.26 (ddd, 1H, J = 13.4, 4.9, 3.4 Hz), 2.08 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H); HRFABMS calcd for $C_{37}H_{50}N_4O_{20}Na$ $(M+Na)^+$, 893.2916; found 893.2916.



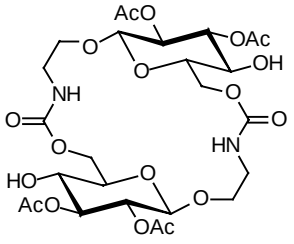
Synthesis of cyclized oligomers (3). To a solution of monomer **1** (50.7 mg, 0.086 mmol) and NaH (145 mg of 60% disp. in paraffin, 3.63 mmol) in 3 mL CH_2Cl_2 was added Et_3N (50 μL, 0.36 mmol). The reaction mixture was stirred at 43 °C for 26 h in a sealed tube. The reaction mixture was diluted with 5 mL CH_2Cl_2, then filtered through celite, washed with sat'd $NaHCO_3$ (3×, until the aqueous layer no longer turned yellow), dried ($MgSO_4$), and concentrated under reduced pressure. Cyclized oligomers **3** were precipitated from $CHCl_3$/hexane (and collected by

filtration through 0.45 μm nylon filter paper) as a white solid (30.4 mg, 78%).[5] The oligomers were flash chromatographed (14% hexane in EtOAc) to give the cyclized 2-mer **(3b)** (20%), cyclized 3-mer **(3c)** (9%) and cyclized 4-mer **(3d)** (3%) and the higher oligomers were washed off the column with 10% MeOH in $CHCl_3$.

Deprotection of cyclized oligomers (3). Cyclized oligomeric mixture **3** (9.8 mg, 0.022 mmol monomer units) was stirred in 5 mL of a 10% TFA/CH_2Cl_2 solution at rt for 1.5 h. The reaction mixture was then neutralized by shaking in sat'd $NaHCO_3$, dried ($MgSO_4$), concentrated under reduced pressure, and precipitated from $CHCl_3$/hexane (and filtered through 0.45 μm nylon filter paper) to afford the C4-deprotected cyclic oligomers **12** (3.6 mg, 50%). Deacetylation of **12** (7.8 mg, 0.0234 mmol monomer units) was accomplished by stirring in methanolic NaOMe for 4 h at rt. The reaction mixture was then neutralized with acidic cation exchange resin (Dowex 50W-X8). The resin was removed by filtration, and the solvent was evaporated under reduced pressure to afford the fully deprotected cyclic oligomers **13** (5.7 mg, 98%).

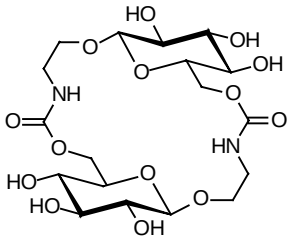


Cyclic 2-mer (3b). R_f = 0.31 (14% hexane in EtOAc); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.13, 170.01, 159.77, 156.16, 129.94, 129.26, 114.16, 101.87, 75.79, 75.00, 74.68, 73.24, 73.12, 72.17, 64.64, 55.51, 42.79, 21.05, 20.95; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (AA'BB', 2H, $J_{AA'} = J_{BB'}$ = 2.6 Hz, $J_{AB} = J_{A'B'}$ = 8.4 Hz, $J_{AB'} = J_{A'B}$ = 0.3 Hz, $\nu_A = \nu_{A'}$ = 2874.1 Hz, $\nu_B = \nu_{B'}$ = 2749.7 Hz), 6.87 (AA'BB', 2H, as above), 6.20 (dd, 1H, J = 8.7, 3.7 Hz), 5.24 (t, 1H, J = 9.4 Hz), 4.88 (dd, 1H, J = 9.8, 7.9 Hz), 4.51 (AB_q, 2H, J_{AB} = 10.8 Hz, ν_A = 1809.5, ν_B = 1799.4, $\Delta\nu$ = 10.1 Hz), 4.46 (d, 1H, J = 8.0 Hz), 4.31 (dd, 1H, J = 11.2, 1.8 Hz), 4.13 (dd, 1H, J = 11.1, 7.9 Hz), 4.03 (br. d, 1H, J = 12.1 Hz), 3.80 (s, 3H), 3.69-3.57 (m, 3H), 3.51 (t, 1H, J = 9.4 Hz), 3.15-3.06 (m, 1H), 2.04 (s, 3H), 1.99 (s, 3H); HRFABMS calcd for $C_{42}H_{54}N_2O_{20}Na$ $(M+Na)^+$, 929.3168; found 929.3172.

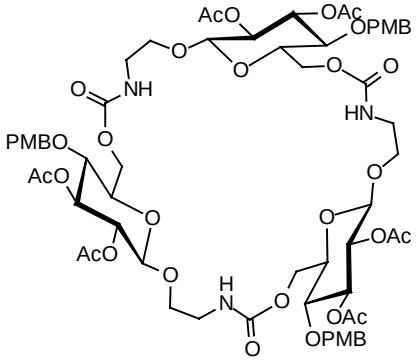


C4-deprotected cyclic 2-mer (12b). Cyclized 2-mer (19.1 mg, 0.021 mmol) was stirred in 6.5 mL of a 10% TFA/CH_2Cl_2 solution at rt for 30 min. The reaction mixture was then neutralized by shaking in sat'd $NaHCO_3$, dried ($MgSO_4$), and flash chromatographed (5% MeOH in $CHCl_3$) to

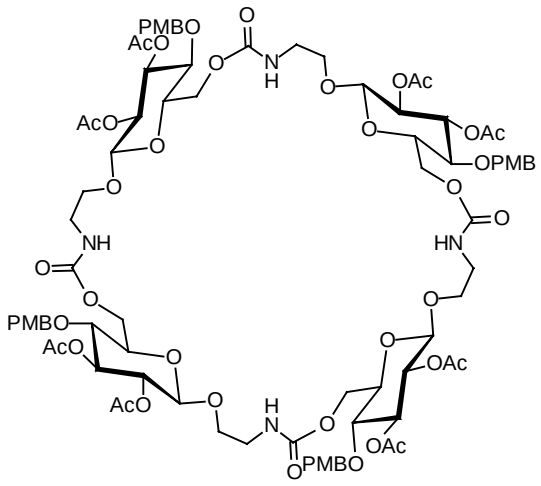
afford the C4-deprotected cyclic 2-mer **12b** (12.9 mg, 92%) as a white solid: R_f = 0.10 (14% hexane in EtOAc); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 171.09, 169.79, 157.44, 100.75, 74.87, 74.14, 71.83, 69.51, 67.95, 62.50, 42.23, 21.01, 20.94; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.48 (dd, 1H, J = 6.1, 2.6 Hz), 5.11 (t, 1H, J = 9.4 Hz), 5.03 (dd, 1H, J = 9.7, 7.7 Hz), 4.74 (dd, 1H, J = 12.5, 2.9 Hz), 4.56 (d, 1H, J = 7.7 Hz), 4.15-4.10 (m, 1H), 4.08 (dd, 1H, J = 12.6, 2.3 Hz), 3.78 (d, 1H, J = 4.5 Hz), 3.65 (ddd, 1H, J = 12.3, 10.1, 2.3 Hz), 3.58 (td, 1H, J = 9.6, 4.2 Hz), 3.48 (dt, 1H, J = 9.8, 2.6 Hz), 3.38-3.27 (m, 2H), 2.08 (s, 3H), 2.06 (s, 3H); HRFABMS calcd for $C_{26}H_{39}N_2O_{18}$ $(M+H)^+$, 667.2198; found 667.2195.



Fully deprotected cyclic 2-mer (13b). Deacetylation of **12b** (12.3 mg, 0.018 mmol) was accomplished by stirring in methanolic NaOMe for 1 h at rt. The reaction mixture was then neutralized with acidic cation exchange resin (Dowex 50W-X8). The resin was removed by filtration, and the solvent was evaporated under reduced pressure to afford the fully deprotected cyclic 2-mer **13b** (9.0 mg, 98%) as a white film: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.91 (t, 1H, J = 5.8 Hz), 4.75-4.26 (br. s, 3H), 4.18 (br. d, 1H, J = 11.6 Hz), 4.13 (d, 1H, J = 7.6 Hz), 4.03 (dd, 1H, J = 11.6, 7.2 Hz), 3.64-3.50 (m, 2H), 3.32 (br. t, 1H, J = 8.2 Hz), 3.24-3.11 (m, 3H), 3.08 (t, 1H, J = 9.2 Hz), 2.98 (t, 1H, J = 8.3 Hz); HRFABMS calcd for $C_{18}H_{30}N_2O_{14}Na$ $(M+Na)^+$, 521.1595; found 521.1593.



Cyclic 3-mer (3c). R_f = 0.19 (14% hexane in EtOAc); ^{1}H NMR ($CDCl_3$, 50 °C, 500 MHz) δ 7.19 (AA'BB', 2H, $J_{AA'} = J_{BB'}$ = 2.5 Hz, $J_{AB} = J_{A'B'}$ = 8.5 Hz, $J_{AB'} = J_{A'B}$ = 0.3 Hz, $\nu_A = \nu_{A'}$ = 3594.2 Hz, $\nu_B = \nu_{B'}$ = 3432.9 Hz), 6.87 (AA'BB', 2H, as above), 5.43 (br. s, 1H), 5.23 (t, 1H, J = 9.2 Hz), 4.89 (dd, 1H, J = 9.6, 7.9 Hz), 4.53 (br. s, 2H), 4.49 (d, 1H, J = 7.7 Hz), 4.38 (br. s, 1H), 4.29 (br. s, 1H), 3.79 (s, 3H), 3.79 (br. s, 1H), 3.74 (br. s, 1H), 3.63 (br. s, 1H), 3.59 (br. s, 1H), 3.41 (br. s, 1H), 3.33 (br. s, 1H), 2.02 (s, 3H), 2.00 (s, 3H); HRFABMS calcd for $C_{63}H_{82}N_3O_{30}$ $(M+H)^+$, 1360.4983; found 1360.4987.



Cyclic 4-mer (3d). R_f = 0.12 (14% hexane in EtOAc); ^{1}H NMR ($CDCl_3$, 50 °C, 500 MHz) δ 7.19 (AA'BB', 2H, $J_{AA'} = J_{BB'} = 2.2$ Hz, $J_{AB} = J_{A'B'} = 8.4$ Hz, $J_{AB'} = J_{A'B} = 0.5$ Hz, $\nu_A = \nu_{A'} = 3595.6$ Hz, $\nu_B = \nu_{B'} = 3432.6$ Hz), 6.86 (AA'BB', 2H, as above), 5.54 (br. s, 1H), 5.22 (t, 1H, J = 9.2 Hz), 4.88 (dd, 1H, J = 9.6, 7.9 Hz), 4.53 (br. s, 2H), 4.50 (br. s, 1H), 4.48 (d, 1H, J = 8.0 Hz), 4.23 (br. s, 1H), 3.81-3.78 (m, 4H), 3.74 (br. s, 1H), 3.60 (br. s, 2H), 3.38 (br. s, 1H), 3.34 (br. s, 1H), 2.02 (s, 3H), 1.98 (s, 3H); HRFABMS calcd for $C_{84}H_{109}N_4O_{40}$ $(M+H)^+$, 1835.6438; found 1835.6447.

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[1] This known compound (see ref. 2) was prepared in good yield using Schmidt's trichloroacetimidate glycosylation procedure (representative reference: Schmidt, R. R.; Kinzy, W. *Adv. Carb. Chem. Biochem.* **1994**, *50*, 21-123).

[2] The NMR data is in close agreement with that presented in the following reference: Miethchen, R.; Fehring, V. *Liebigs Ann./ Recueil* **1997**, 553-561.

[3] The NMR data is in close agreement with that presented in the references: (a) Tagmose, T.M.; Bols, M. *Chem. Eur. J.* **1997**, *3*, 453-462. (b) Chernyak, A.Y.; Sharma, V.M.; Kononov, L.O.; Krishna, P.R.; Levinsky, A.B.; Kochetkov, N.K.; Rao, A.R. *Carbohydrate Res.* **1992**, *223*, 303-309.

[4] Johansson, R.; Samuelsson, B. *J. Chem. Soc. Perkin. Trans. 1*; **1984**, 2371.

[5] Oligomers as seen by MALDI are unchanged by aqueous workup or by precipitation.