Efficient Synthesis of β-Cyanosugars Using Glycosyl Iodides Derived from Per-*O*-Silylated Mono- and Disaccharides.

Abhijit S. Bhat and Jacquelyn Gervay-Hague*.
Department of Chemistry, University of Arizona. Tucson AZ 85721.

Supplemental Information:

General Information: All chemicals purchased from commercial vendors and used without further purification, unless noted**. Tetrabutylammonium cyanide is highly toxic and appropriate precautions must be taken while handling this reagent**. It is important to note that, *tetrabutylammonium cyanide (TBACN; Aldrich) is hygroscopic and was azeotroped to dryness with benzene prior to use in cyanation reactions*. Pure TMSI (Fluka) is a clear and colorless liquid that slowly liberates iodine and turns red upon storage (TMSI was stored in the freezer over a bed of drierite), we have noted that the *reaction outcomes were adversely affected when TMSI that had turned dark red-brown and opaque was used*. Dichloromethane, triethylamine and TMSCl were distilled over CaH_2; benzene was distilled over potassium/benzophenone. HPLC was performed with a using a Waters Delta 600 HPLC system using either a Waters C18 Deltapack or a Vydac peptide C-18 column, peaks were monitored using Waters differential refractometer and Waters 2487 dual absorbance detector. ^{1}H spectra were recorded on a Bruker DRX at 600 or 500 MHz and ^{13}C NMR were recorded at 150 MHz or 125 MHz, respectively. Mass Spectra were obtained at UA Mass spectroscopy facility. Optical activity was recorded using a JASCO digital polarimeter; melting points were recorded in open capillaries on a MeltTemp II. All reactions were performed in oven dried glassware under an inert argon environment, unless otherwise noted.

General Procedure for the synthesis of persilylated carbohydrates:

To a solution of the free carbohydrate (1mmol) in DMF (0.2M solution), freshly distilled Et_3N (1.1 mmol for each free hydroxyl) was added and the resulting solution was cooled

to 0 °C in an ice bath. Freshly distilled TMSCl (1.1 mmol for each free hydroxyl) was added to the above solution and the reaction mixture was stirred at room temperature for 4h (8h for disaccharide). Pentane (50 mL) and crushed ice were added to the reaction mixture successively. The aqueous layer was extracted with pentane (3 x 25 mL) and the combined organics were washed with water (2 x 50 mL) and brine (3 x 50 mL), dried (Na_2SO_4) and concentrated to give the persilylated carbohydrate derivatives as either colorless oils (monosaccharides) or white solids (disaccharides).

1,2,3,4,6-Penta-*O*-trimethylsilyl-α-D-glucopyranose: Colorless oil (89%). ^{1}H NMR (CD_2Cl_2) δ 5.01 (d, *J* = 3.0 Hz, 1H), 3.74 (t, *J* = 8.9 Hz, 1H), 3.70-3.67 (m, 2H), 3.65-3.59 (m, 1H), 3.43 (t, *J* = 9.1 Hz, 1H), 3.35 (dd, *J* = 9.1, 3.1 Hz, 1H), 0.18-0.12 (m, 45H); ^{13}C NMR (CD_2Cl_2) δ 94.40, 74.69, 74.62, 73.05, 72.47, 62.51, 1.44, 1.08, 0.56, 0.27, -0.15. HRMS calcd. for $C_{21}H_{52}O_6Si_5$: 540.2610. Found: [M+H] 541.1019.

1,2,3,4,6-Penta-*O*-trimethylsilyl-α-D-galactopyranose: Colorless oil (90%) ^{1}H NMR (CD_2Cl_2) δ 5.01 (d, *J* = 2.2 Hz, 1H), 3.74 (t, *J* = 8.9 Hz, 1H), 3.70-3.67 (m, 2H), 3.65-3.59(m, 1H), 3.89-3.81 (m, 4H), 3.56 (dd, *J* = 9.75, 7.52 Hz, 1H), 3.41 (dd, *J* = 9.74, 7.96, 1H), 0.15-0.10 (m, 45 H); ^{13}C NMR (CD_2Cl_2) δ 95.12, 73.10, 72.88, 72.40, 71.45, 62.43, 0.91, 0.62, 0.44, 0.24, -0.11. HRMS calcd. for $C_{21}H_{52}O_6Si_5$: 540.2610. Found: [M+H] 541.1221.

1,2,3,4-Tetra-*O*-trimethylsilyl-α-L-fucopyranose: Colorless oil (94%) ^{1}H NMR (CD_2Cl_2) δ 4.98 (d, *J* = 2.8 Hz, 1H, H-1), 4.02 (q, *J* = 6.9 Hz, 1H, H-5), 3.85-3.77 (m, 2H, H-3, H-4), 3.61(d, *J* = 2.8 Hz, 1H, H-2), 1.07 (d, *J* = 6.0 Hz, 1H, H-6), 0.15-0.11 (m, 36 H); ^{13}C NMR (CD_2Cl_2) δ 95.05, 76.53, 71.15, 70.18, 67.03, 17.06, 0.81, 0.59, 0.48, 0.30. LRMS calcd for $C_{18}H_{44}O_5Si_4$: 452.23. Found MS: [M-H] 451.30.

1,2,3,4,6-Penta-*O*-trimethylsilyl-α-D-mannopyranose: Colorless oil (92%). ^{1}H NMR (CD_2Cl_2) δ 4.88 (d, *J* = 1.7 Hz, 1H), 3.80-3.79 (m, 2H), 3.72-3.71 (d, *J* = 1.2 Hz, 1H), 3.69-3.65 (m, 2H), 3.57-3.51 (m, 1H), 0.15-0.10 (m, 45H); ^{13}C NMR (CD_2Cl_2) δ 96.12,

75.96, 75.23, 72.87, 68.81, 62.94, 0.87, 0.76, 0.47, -0.09, -0.12. HRMS calcd. for $C_{21}H_{52}O_6Si_5$: 540.2610. Found:[M-H] 539.3810.

1,2,3,6,2',3',4',6'-Octa-*O*-trimethylsilyl-α-lactose: Sticky white solid (64%). ^{1}H NMR (CD_2Cl_2) δ 5.02 (d, *J* = 3.2 Hz, 1H), 4.30 (d, *J* = 7.6 Hz, 1H), 4.05 (d, *J* = 11.3 Hz, 1H), 3.88 (brs, 1H), 3.73-3.62 (m, 7H), 3.41-3.39 (m, 2H), 3.38 (m, 1H) 0.18-0.11 (m, 72H); ^{13}C NMR δ 102.41, 98.06, 75.32 75.00, 74.71, 74.08, 72.57, 72.03, 71.80, 72.57, 72.03, 71.80, 60.87, 60.48, 0.58, 0.53, 0.37, 0.26, 0.04, -.01. HRMS calcd. for $C_{36}H_{86}O_{11}Si_8$: 918.4324. Found [M-H] 917.7060.

1,2,3,6,2',3',4',6'-Octa-*O*-trimethylsilyl-β-cellobiose: White crystalline solid (79%). ^{1}H NMR (CD_2Cl_2) δ 4.45 (d, *J* = 7.4 Hz, 1H), 4.41 (d, *J* = 7.7 Hz, 1H), 3.92(dd, *J* = 11.1, 3.16 Hz, 1H), 3.84 (d, *J* = 9.3 Hz, 1H), 3.78 (d, *J* = 10.1 Hz, 1H), 3.73 (t, *J* = 9.5, 1H), 3.58 (dd, *J* = 11.0, 6.27 Hz, 1H), 3.43 (t, *J* = 9.0 Hz, 1H), 3.34 (t, *J* = 8.6 Hz, 1H), 3.27 (t, *J* = 8.9 Hz, 1H), 3.25-3.19 (m, 2H), 3.13-3.11 (m, 1H), 0.17-0.13 (m, 72H); ^{13}C NMR (CD_2Cl_2) δ 103.91, 99.34, 79.12, 78.95, 78.92, 78.12, 77.88, 76.94, 75.46, 73.22, 64.35, 62.33, 1.88, 1.54, 1.44, 1.06, 0.54, 0.42, -0.12,-0.14. HRMS calcd. for $C_{36}H_{86}O_{11}Si_8$: 918.4324. Found MS: [M+Na] 941.2234.

1,2,3,6,2',3',4',6'-Octa-*O*-trimethylsilyl-α/β-melibiose: White crystalline solid (85%). ^{1}H NMR ($CDCl_3$) 5.04 (d, *J* = 3.4 Hz, 1H), 4.94 (d, *J* = 3.4 Hz, H-7 of minor isomer, approx. ratio of major:minor 5:1), 4.40 (d, *J* = 3.0 Hz, 1H), 4.40 (d, *J* = 7.3 Hz, 1H, H-1 minor isomer), 3.88-3.78 (m, 4H), 3.77-3.52 (m, 10H), 3.35 (dd, *J* = 9.0, 3.1 Hz, 1H), 0.15-0.13 (m, 72H); ^{13}C NMR δ 100.15, 99.56, 98.06, 93.75, 78.26, 77.04, 76.85, 74.22, 74.20, 72.90, 72.31, 72.25, 71.71, 71.50, 71.16, 71.06, 70.96, 70.91, 69.38, 64.66, 63.19, 61.44, 61.32, 1.92, 1.42, 1.28, 1.03, 0.96, 0.65, 0.62, 0.54, 0.49, 0.40, 0.26, 0.23, 0.12, -0.41, -0.43. LRMS for $C_{36}H_{86}O_{11}Si_8$ calcd: 918.43. Found: [M+H] 919.66.

General procedure for cyanation reactions:

TMSI (0.55 mmol) was added to a 0.1 M solution of persilylated carbohydrate (0.5 mmol.) in dry CH_2Cl_2. The solution was stirred under argon at room temperature for 10 min. and concentrated *in vacuo*. The residue was azeotroped with freshly distilled benzene until the color of the benzene solution remained pale yellow. The residue was then dissolved in either dry CH_2Cl_2 or benzene and canulated into a stirring solution of TBACN (1.5 equiv.) over molecular sieves in the same solvent. The solution was stirred under argon for 1h, and concentrated *in vacuo*. EtOAc was added to the residue and cooled in an ice bath to precipitate tetrabutylammonium iodide, the solution was filtered, and the filtrate was washed with small portions of water, dried (Na_2SO_4) and concentrated. The residue was dissolved in 10 mL of MeOH. The methanolic solution was refluxed for 40 min., cooled and concentrated. It was found that stirring the methanolic solution with Amberjet 1200(H) ion exchange resin significantly reduced the tetrabutylammonium impurities from the reaction mixture. The residue, containing cyano carbohydrates with residual tetrabutylammonium salt impurities, could either be purified by RPHPLC to isolate the free cyano carbohydrates, or acylated to give the *per*-acyl cyanosugars. For acylation, the residue was dissolved in pyridine (10mL), Ac_2O (2mL) and DMAP (catalytic) were added and the reaction stirred for 8h. Pyridine was removed *in vacuo* by azeotroping with toluene and the residue was purified by flash chromatography (1:1 Hexanes/EtOAc). For isolation of unprotected cyanosugars, the residue was dissolved in water and purified by RPHPLC using water/acetonitrile gradient. HPLC was performed with a using a Waters Delta 600 HPLC system using either a Waters C18 Deltapack or a Vydac peptide C-18 column, peaks were monitored using Waters differential refractometer and Waters 2487 dual absorbance detector. The free sugars were eluted with 100% water (containing 0.1% TFA) and the column was

flushed with 100% acetonitrile after the sugars had eluted to remove organic impurities. The RI detector was baseline normalized with 100% water before each run.

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl cyanide:[4b] White solid. ^{1}H NMR ($CDCl_3$) δ 5.31 (t, *J* = 9.7 Hz, 1H, H-2), 5.17 (t, *J* = 9.4 Hz, 1H, H-3), 5.10 (t, *J* = 9.8 Hz, 1H, H-4), 4.34 (d, *J* = 10.2 Hz, 1H, H-1), 4.24 (dd, *J* = 12.7, 4.9 Hz, 1H, H-6), 4.14 (dd, *J* = 12.5, 1.7 Hz, 1H, H-6'), 3.73-3.70 (m, 1H, H-5), 2.11 (s, 6H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR 170.45, 170.00, 169.09, 168.68, 114.08, 76.74, 72.75, 68.88, 67.19, 66.40, 61.36, 20.60, 20.42, 20.32.

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl cyanide:[4b] White solid. ^{1}H NMR ($CDCl_3$) δ 5.45 (t, *J* = 9.9 Hz, 1H, H-3), 5.13 (d, *J* = 6.2 Hz, 1H, H-1), 5.08 (t, *J* = 10.0 Hz, 1H, H-4), 5.03 (dd, *J* = 10.1, 6.1 Hz, 1H, H-2), 4.32 (dd, *J* = 12.6, 4.3 Hz, 1H, H-6), 4.17 (d, *J* = 1.8 Hz, 1H, H-6'), 4.15-4.10 (m, 1H, H-5), 2.13 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H); ^{13}C NMR δ170.44, 169.62, 169.43, 169.42, 113.78, 73.64, 71.01, 67.98, 67.35, 65.22, 61.33, 20.67, 20.54, 20.42.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl cyanide:[4b] Pale yellow solid. ^{1}H NMR ($CDCl_3$) δ 5.53 (t, *J* = 10.2 Hz, 1H, H-2), 5.41 (dd, *J* = 3.5, 1.16 Hz, 1H, H-4), 5.01 (dd, *J* = 10.3, 3.5 Hz, 1H, H-3), 4.28 (d, *J* = 10.2 Hz, 1H, H-1), 4.12 (m, 2H, H-6, H-6'), 3.91 (t, *J* = 6.5 Hz, 1H, H-5); ^{13}C NMR δ 170.42, 170.03, 168.91, 114.53, 75.62, 70.93, 66.90, 66.89, 66.14, 61.18, 20.62, 20.43, 20.21.

2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl cyanide:[4b] ^{1}H NMR δ 5.53 (d, *J* = 3.5, 1.16 Hz, 1H, H-4), 5.31 (dd, *J* = 10.6, 2.9 Hz, 1H, H-3); 5.24 (dd, *J* = 10.6, 5.7 Hz, 1H, H-2), 5.18 (d, *J* = 5.7 Hz, 1H, H-1), 4.31 (t, *J* = 6.3 Hz, 1H, H-5), 4.13 (m, 2H, H-6, H-6'), 2.15 (s, 6H), 2.06 (s, 3H), 2.02 (s, 3H); ^{13}C NMR δ 170.21, 169.84, 169.54, 169.52, 114.14, 72.49, 68.21, 67.24, 65.34, 65.11, 61.20, 20.49, 19.21, 19.18.

2,3,4-Tri-*O*-acetyl-β-L-fucopyranosyl cyanide:[4b] White solid. ^{1}H NMR ($CDCl_3$) δ 5.40 (t, *J* = 10.1 Hz, 1H, H-2), 5.17 (d, *J* = 2.7 Hz, 1H, H-4), 4.93 (dd, *J* = 10.1, 3.2 Hz, 1H,

H-3), 4.21 (d, *J* = 10.2 Hz, 1H, H-1), 3.83-3.70 (m, 1H, H-5), 2.12 (s, 3H), 2.03 (s, 3H), 1.91 (s, 3H), 1.13 (d, *J* = 6.4 Hz, 1H, H-6); ^{13}C NMR δ 170.17, 169.66, 168.71, 114.68, 74.11, 71.09, 69.61, 66.55, 66.04, 20.35, 20.31, 20.28, 15.89.

2,3,4,6-Tetra-*O*-acetyl-*β*-D-mannopyranosyl cyanide:[4b] ^{1}H NMR δ 5.61 (m, 1H, H-2), 5.24 (t, *J* = 10.0 Hz, H-4), 5.05 (dd, *J* = 10.1, 3.4, 1H, H-3), 4.58 (d, *J* = 0.9 Hz, 1H, H-1), 4.26 (dd, *J* = 12.5, 5.8 Hz, 1H, H-6), 4.17 (dd, *J* = 12.6, 2.2, 1H, H-6), 3.70-3.67 (m, 1H, H-5), 2.25 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H); ^{13}C NMR δ 170.48, 169.84, 169.57, 169.31, 113.47, 77.12, 70.51, 67.52, 66.66, 64.81, 62.07, 20.64, 20.53, 20.45, 20.41.

2,3,4,6-Tetra-*O*-acetyl-*α*-D-mannopyranosyl cyanide:[4b] ^{1}H NMR δ 5.42 (m, 1H, H-2), 5.36 (dd, *J* = 9.9, 3.2 Hz, 1H, H-3), 3.18 (t, *J* = 9.8 Hz, 1H, H-4), 4.89 (d, *J* = 2.0 Hz, 1H, H-1), 4.33 (dd, *J* = 12.6, 5.4 Hz, 1H, H-6), 4.16 (dd, *J* = 12.6, 1.9 Hz, 1H, H-6'), 4.08-4.05 (m, 1H, H-5), 2.18 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H); ^{13}C NMR δ 170.38, 169.56, 169.43, 113.38, 74.26, 68.86, 68.68, 68.58, 65.04, 61.59, 20.61 (broad peak), 20.43.

2,3,6,2',3',4',6'-Hepta-*O*-acetyl-*β*-cyanocellobiose: Pale yellow solid. MP 198^{0}C $[\alpha]_D$ +40.50° (*c* 5.1, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 5.22 (t, *J* = 9.6 Hz, 1H, H-8), 5.16-5.12 (m, 1H, H-9), 5.05 (t, *J* = 9.8 Hz, 1H, H-10), 4.90 (dd, *J* = 9.2, 8.1 Hz, 1H, H-2), 4.51 (d, *J* = 7.9 Hz, H-1), 4.48 (dd, *J* = 2.4, 1.9 Hz, 1H, H-6), 4.36 (dd, *J* = 12.5, 4.4 Hz, 1H, H-12), 4.29 (d, *J* = 10.0 Hz, 1H, H-7), 4.09-4.04 (m, 2H, H-6', H-12'), 3.79 (t, *J* = 9.6 Hz, 1H, H-4), 3.68-3.65 (m, 1H, H-11), 3.62-3.60 (m, 1H, H-5), 2.14 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H); ^{13}C NMR 170.42, 170.14, 170.11, 169.61, 169.33, 169.01, 168.92, 114.25, 100.76, 75.41, 73.31, 72.75, 72.41, 72.06, 71.48, 69.05, 67.63, 66.29, 61.45, 61.38, 20.73, 20.61, 20.48, 20.39, 20.36. HRMS calcd. for $C_{27}H_{36}O_{17}N_1$:646.1983. Found: 646.1981.

2,3,6,2',3',4',6'-Hepta-*O*-acetyl-β-cyanolactose: White solid. MP 159 ^{0}C, $[\alpha]_D$ +81.51° (*c* 5.8, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 5.31 (d, *J* = 2.9 Hz, 1H, H-10), 5.17 (t, *J* = 9.4 Hz, 1H, H-2), 5.12 (t, *J* = 8.8 Hz, 1H, H-3), 5.05 (dd, *J* = 10.4, 7.9 Hz, H-8), 4.93 (dd, *J* = 10.4, 3.5 Hz, 1H, H-9), 4.45 (d, *J* = 7.8 Hz, 1H, H-7); 4.45-4.44 (dd, *J* = 12.3, 2.3 Hz, H-6'), 4.27 (d, *J* = 9.8 Hz, H-1), 4.10-4.02 (m, 3H, H-6, H-12, H-12'), 3.84 (t, *J* = 7.0 Hz, 1H, H-11), 3.77 (t, *J* = 9.6 Hz, 1H, H-4), 3.60-3.57 (m, 1H, H-5), 2.10 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.92 (s, 3H); ^{13}C NMR δ 170.26, 170.11, 169.99, 169.92, 169.54, 168.99, 168.92, 114.28, 100.99, 77.34, 75.14, 72.64, 70.76, 70.72, 69.08, 68.92, 66.49, 66.16, 61.47, 60.71, 20.68, 20.58, 20.52, 20.39, 20.32. HRMS calcd. for $C_{27}H_{36}O_{17}N_1$: 646.1983. Found: 646.1982.

1-β-Cyano-D-glucose (18): Amorphous white solid (HPLC: retention time: 10.2 min Vydac C18), ^{1}H NMR (D_2O) δ 4.33 (d, *J* = 10.1 Hz, 1H, H-1), 3.84 (dd, *J* = 12.6, 1.9 Hz, 1H), 3.67-3.63 (m, 2H), 3.44-3.36 (m, 3H); ^{13}C NMR (D_2O) δ 117.10, 80.51, 76.22, 71.06, 68.82, 68.41, 60.47. HRMS calcd. for $C_7H_{11}O_5N_1$: 189.0637. Found MS:189.1264.

1-β-Cyanocellobiose (19): (HPLC: retention time: 14.5 min Vydac C18)^{1}H NMR (D_2O) δ 4.24 (d, *J* = 10.0 Hz, 1H), 4.17 (d, *J* = 10.0 Hz, 1H), 3.93-3.62 (m, 13H), 3.56-3.48 (m, 4H) ;^{13}C NMR (D_2O) δ 118.14, 104.39, 81.14, 79.39, 78.02, 77.74, 76.46, 74.14, 73.17, 71.29, 69.89, 61.87, 61.24. HRMS calcd. for $C_{13}H_{21}O_{10}N_1$: 351.1165. Found: [M+H] 352.0845.

1-β-Cyanolactose (HPLC: retention time: 14.5 min Vydac C18) ^{1}H NMR (D_2O) δ 4.40 (d, *J* = 7.8 Hz, 1H), 4.37 (d, *J* = 10.1 Hz, 1H), 3.93-3.87 (m, 3H), 3.77-3.47 (m, 12H); ^{13}C NMR (D_2O) δ117.22, 102.85, 79.33, 77.28, 75.39, 74.85, 72.53, 70.94, 70.85, 68.58, 68.26, 61.05, 59.82. LRMS calcd. for $C_{13}H_{21}O_{10}N_1$: 351.12. Found: [M+H] 352.14.

General procedure for reduction of unprotected cyano sugars using $CoCl_2/NaBH_4$

$CoCl_2(H_2O)_6$ (0.1 mmol.) was added to a solution of the unprotected cyanosugar (1 mmol) in 3 mL of 2:1THF:H_20 and stirred for 5 min. $NaBH_4$ (2 mmol.) was added to the purple solution in small portions with vigorous stirring. Addition of $NaBH_4$ was accompanied by evolution of H_2 gas and formation of a black precipitate. The reaction mixture was stirred for 50 min. and another 2 equiv. of $NaBH_4$ were added and stirring continued for another hour. The reaction was quenched with 28% NH_4OH solution and the reaction mixture was centrifuged. The supernatant was separated and the lower layer washed with 2:1 THF/H_2O and recentrifuged. This process was repeated 4 times and both layers concentrated. The C-1 aminomethyl carbohydrates were isolated after lyophilization of the aqueous layer. The crude product was further purified by Ion-Exchange Chromatography. Thus, a solution of amine in water was loaded onto an Amberjet(H) column, the column washed with 6-10 column volumes of water. Glycosyl amines were eluted with 0.5N NH_4OH, fractions were spotted on TLC plates and stained with ninhydrin stain to identify amine containing fractions)to provide the aminomethyl carbohydrates as pale yellow solids. **Note**: The aminomethyl carbohydrates slowly decompose upon standing at room temperature, they are significantly more stable when stored at -20 °C.

***β*-D-galactopyranosyl-*C*-methyl amine (14):** Yellow solid, MP 189-91°C, $[\alpha]_D$ +30.46° (*c* 1.5, H_2O), ^{13}C (CD_3OD) δ 81.44, 80.45, 76.24, 71.04, 70.51, 63.23, 43.75. HRMS calcd. for $C_7H_{15}O_5N_1$: 193.0950. Found [M+H] 194.5120.

***β*-D-glucopyranosyl-*C*-methyl amine (20):** Yellow solid, MP 168°C $[\alpha]_D$ -6.34° (*c* 1.5, H_2O), ^{13}C (CD_3OD) δ 81.82, 81.55, 79.67, 73.52, 71.82, 63.41, 43.91. HRMS calcd. for $C_7H_{15}O_5N_1$: 193.0950. Found: [M+H] 194.1245.

***β*-Cellobiosyl-*C*-methylamine (21):** White solid, MP 235-37°C, $[\alpha]_D$ +29.45 (*c* 2.0, H_2O), ^{13}C NMR (D_2O) δ 105.45, 83.15, 81.21, 80.24, 78.56, 76.34, 75.11, 74.31, 73.25, 71.10, 64.31, 62.46, 44.89. LRMS calcd. for $C_{13}H_{25}O_{10}N_1$: 355.15. Found: 355.91.