Supporting Information For:

One-Pot Synthesis of Glucosamine Oligosaccharides

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General Techniques. ^{1}H NMR spectra were routinely recorded on a Bruker AM-400 spectrometer and a Bruker AM-200 spectrometer. Chemical shifts reported (in ppm) relative to internal Me_4Si (δ=0.0) with $CDCl_3$ as solvent. ^{1}H NMR spectra of trisaccharides **6**, **7**, **9** and of tetrasaccharide **12** were recorded on a Bruker AMX-600 spectrometer (Bar-Ilan University, Ramat-Gan, Israel). ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer at 100.61 MHz, and the chemical shifts reported (in ppm) relative to the residual solvent signal for $CDCl_3$ (δ=77.00). Mass spectra were obtained on a TSQ-70B mass spectrometer (Finnigan Mat) under fast-atom bombardment (FAB) conditions in glycerol matrices or by negative or positive chemical ionization (NCI or PCI) in isobutane. Reactions were monitored by TLC on Silica Gel 60 F_{254} (0.25 mm, Merck), and spots were visualized by charring with a yellow solution containing $(NH_4)Mo_7O_{24}{\cdot}4H_2O$ (120 g) and $(NH_4)_2Ce(NO_3)_6$ (5 g) in 10% H_2SO_4 (800 mL). Flash column chromatography was performed on Silica Gel 60 (70-230 mesh). All reactions were carried out under an argon atmosphere with anhydrous solvents, unless otherwise noted. All chemicals were obtained from commercial sources.

***p*-Methoxyphenyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-β-D-glucopyranosyl)-(1$\rightarrow$6)-(3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1$\rightarrow$6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β -D-glucopyranoside (6).** A solution of donor **2** (100 mg, 0.175 mmol) and acceptor-donor **4** (76 mg, 0.125 mmol) in CH_2Cl_2 (6 mL) was stirred in the presence of powdered flame dried 4Å molecular sieves (0.8 g). After being stirred for 30 min at room temperature, the mixture was cooled to -25^{o}C and treated with NIS (30.9 mg, 0.137 mmol). After about 10 min, TfOH (10 µL) was added and the stirring was continued until TLC (EtOAc/hexane 1:1.3) indicated about the completion of the reaction (40 min). To this mixture was added acceptor **5** (121.6 mg, 0.199 mmol) followed by addition of NIS (38 mg, 0.169 mmol) and TfOH (10 µL). The reaction was allowed to warm to 0^{0}C and after being stirred at this temperature for 2 h the TLC (EtOAc/hexane 1:1.3) indicated the completion of the reaction. The reaction was diluted with EtOAc (50 mL) and filtered through Celite. After thorough washing of the Celite with EtOAc, the washes were combined and extracted with saturated $Na_2S_2O_3$ (20 mL), saturated $NaHCO_3$ (2x30 mL), brine (20 mL), dried over $MgSO_4$ and concentrated. Silica gel chromatography of the crude (hexane $\rightarrow$ hexane/EtOAc 3:2) afforded the triglucosamine **6** as a white powder (136 mg, 69% yield). ^{1}H NMR (600 MHz, $CDCl_3$) data of **6** is summarized in the attached Table 1S. ^{13}C NMR (100.61 MHz) δ 20.61, 29.59, 54.65 (C_A-2), 55.55 (MeO), 56.21, 62.04 (C_C-6), 68.30 (C_A-6), 68.48 (C_B-6), 68.92 (C_C-4), 69.98 (C_B-4), 70.91 (C_A-3), 71.00

(C_A-4), 71.18 (C_B-3), 71.85 (C_B-5), 72.48 (C_C-3), 73.20 (C_C-5), 73.49 (C_A-5), 74.35, 95.78, 96.96 (C_C-1), 97.45 (C_B-1), 101.42 (C_A-1), 114.58, 118.43, 123.47, 123.53, 128.20, 128.38, 128.44, 128.59, 128.69, 129.02, 129.62, 129.71, 129.84, 129.93, 131.35, 131.45, 133.12, 133.41, 133.48, 133.87, 134.11, 150.31, 154.35, 155.56, 165.42, 165.49, 169.35, 170.30, 170.51; negative CIMS *m/z* 1583.1 (M^-, $C_{78}H_{68}O_{27}Cl_3N_3$ requires 1583.0).

***p*-Methoxyphenyl (3,4-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl)-(1→6)-(3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-2-deoxy-2-phthalimido-β-D-glucopyranoside (7).** Similar to the above procedure for the preparation of **6**, the donor **3** (215.4 mg, 0.241 mmol) and donor-acceptor **4** (140 mg, 0.229 mmol) in CH_2Cl_2 (10 mL) were coupled by promotion of NIS (51.7 mg, 0.230 mmol) and TfOH (10 μL) at –35°C. After completion of the reaction (15 min) acceptor **5** (286.4 mg, 0.46 mmol), NIS (77.6 mg, 0.345 mmol) and TfOH (10 μL) were added. The temperature was allowed to rise to 0^0C and the stirring was continued for an additional 30 min. Repetition of the workup and purification procedure used for **6** afforded the trisaccharide **7** (359 mg, 81%) as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$) data of **7** are summarized in the attached Table 2S. ^{13}C NMR (100.61 MHz) δ20.61, 29.59, 54.65, 55.55 (C_A-2), 56.20 (MeO), 62.03, 68.30, 68.92 (C_B-6), 69.98 (C_C-4), 70.91, 71.00, 71.18, 71.85, 72.48, 73.19, 73.49, 74.36, 95.77, 96.96 (C_A-1), 97.45 (C_B-1), 101.42 (C_C-1), 114.58, 118.43, 123.47, 123.53, 128.20, 128.38, 128.44, 128.59, 128.68, 129.02, 129.20, 129.62, 129.72, 129.84, 129.92, 131.35, 131.45, 133.12, 133.41, 133.48, 133.87, 134.11, 150.31, 154.35, 155.56, 165.42, 165.49, 169.35, 170.30, 170.51. FABMS *m/z* 1904.6 ($C_{102}H_{88}O_{26}Cl_3N_3Si$ requires 1905.5).

***p*-Methoxyphenyl (3,4-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl)-(1→6)-(3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-2-deoxy-2-phthalimido-β-D-glucopyranoside (9**)**.** Like the above, the donor **3** (161 mg, 0.181 mmol) and donor-acceptor **4** (100 mg, 0.164 mmol) in CH_2Cl_2 (7 mL) were coupled by promotion of NIS (41 mg, 0.182 mmol) and TfOH (10 μL) at –35°C. After completion of the reaction (15 min) acceptor **8** (296.6 mg, 0.476 mmol), NIS (82 mg, 0.361 mmol) and TfOH (10 μL) were added. The temperature was allowed to rise to 4^0C and the stirring was continued for 12 hr. Repetition of the workup and purification procedure used for **6** provided the trisaccharide **9** (157 mg, 50%) as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$) data of **9** are summarized in the attached Table 3S. ^{13}C NMR (150.92 MHz) δ26.60, 54.93 (C_A-2), 55.12 (C_B-2), 55.51 (MeO), 62.82 (C_A-6), 63.03 (C_C-6), 69.53 (C_C-4), 69.64 (C_B-4), 71.06 (C_B-3), 72.69 (C_A-3), 73.04 (C_C-3), 75.10 (C_C-5), 75.96 (C_A-4), 81.48, 97.22 (C_B-1), 97.63 (C_A-1), 101.28 (C_C-1), 114.34, 119.09, 123.65, 127.56, 127.62, 128.25, 128.31, 128.42, 128.84, 129.54, 129.63, 129.70, 129.79, 129.92, 130.04, 133.26, 134.09, 135.45, 135.53; negative CIMS *m/z* 1905.2 (M^-, $C_{102}H_{88}O_{26}Cl_3N_3Si$ requires 1905.5).

***p*-Methoxyphenyl(3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-β-D-glucopyranosyl)-(1→6)-(3,4-di-*O*-benzoyl-2-deoxy-2-(2,2,2-trichloroethyloxycarbonylamino)-β-D-glucopyranosyl)-(1→6)-(3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β -D-glucopyranoside (12)**. A solution of donor **10** (143.7 mg, 0.22 mmol) and donor-acceptor **11** (80 mg, 0.157 mmol) in dry Et_2O (5 mL) was stirred in the presence of powdered flame dried 4Å molecular sieves (0.6 g). After being stirred for 10 min at room temperature, the mixture was cooled to -20°C and treated with NIS (35.4 mg, 0.157 mmol). After about 10 min, TfOH (10 µL) was added and the stirring was continued until TLC (EtOAc/hexane 1:1.3) indicated the completion of the reaction (about 35 min). The reaction mixture was further cooled at –40°C and treated with **4** (95.9 mg, 0.157 mmol) dissolved in CH_2Cl_2 (7 mL), solid NIS (35.4 mg, 0.157 mmol), and TfOH (10 µL). The temperature was allowed to rise to –20°C and stirring was continued until TLC indicated the completion of the coupling step (20 min). The temperature of the reaction mixture was again lowered to –40°C and treated with **5** (195.5 mg, 0.314 mmol), solid NIS (35.4 mg, 0.157 mmol), and TfOH (10 µL). The mixture was allowed to warm at room temperature and the stirring was continued until the completion of the reaction (30 min). A similar workup and purification as described for compound **6** gave the tetrasaccharide **12** (200 mg, 63%) as a white solid. Attempts to record high quality ^{1}H NMR (600 MHz) spectrum of the product, either in $CDCl_3$, DMSO, or CD_3OD resulted largely broadened picks may be due to the aggregation of the compound. Addition of 10% CD_3OD in $CDCl_3$ significantly improved the resolution of the spectrum. The ^{1}H, ^{13}C, 2D-COSYand HMQC NMR in $CDCl_3/CD_3OD$ (9:1 v/v) along with mass spectroscopic properties of the purified **12** were consistent with the expected structure. Data for **12**: ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$ 9:1 v/v) δ2.03 (s, 6H, 2AcO), 2.04 (s, 3H, AcO), 3.52-3.61 (m, 2H), 3.62-3.73 (m, 4H, H_A-6, H_D-5, H_B-5), 3.89 (s, 4H, MeO + H_D-2), 3.94-4.10 (m, 3H, H_A-6), 4.20 (m, 2H, H_A-5), 4.32 (m, 1H, H_C-2), 4.41 (t, 1H, J = 10.2 Hz, H_B-2), 4.54-4.65 (m, 3H), 4.68 (d, 1H, J = 8.0 Hz, H_D-1), 4.72-4.81 (m, 2H, H_A-2), 4.83-4.87(m, 2H, NHCO*C*H_2Cl3), 4.97 (t, 1H, J = 9.8 Hz), 5.02 (t, 1H, J = 9.7 Hz, H_D-4), 5.31 (m, 2H, H_B-4, H_D-3), 5.54 (m, 1H, H_A-4), 5.57 (d, 1H, J = 8.4 Hz, H_C-1), 5.62 (d, 1H, J = 8.4 Hz, H_B-1), 6.04-6.10 (m, 2H, H_B-3, H_A-1), 6.25 (t, 1H, J = 9.7 Hz, H_A-3), 6.80 (d, 2H, J = 8.8 Hz, MeO*Ph*), 6.89 (d, 2H, J = 8.0 Hz, MeO*Ph*), 7.26-7.98 (m, 38H, aromatic protons); ^{13}C NMR (100.61 MHz, $CDCl_3/CD_3OD$ 9:1 v/v) δ20.56, 29.75, 54.75, 54.90, 55.53, 55.76, 62.23, 69.07, 70.06, 70.98, 71.25, 71.37, 71.70, 71.85, 72.62, 73.12, 73.49, 95.76, 95.94, 97.21, 97.58, 101.36, 114.78, 118.56, 123.67, 127.63, 128.37, 128.47, 128.54, 128.94, 129.10, 129.85, 129.97, 131.33, 133.53, 134.31, 150.51, 154.90, 165.92, 168.01, 170.00, 170.79, 171.19. FABMS *m/z* 2130.6 ($C_{101}H_{88}O_{35}Cl_6N_4$ requires 2130.5).