Intramolecular glycosylation under neutral conditions for synthesis of 1,4-linked disaccharides

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SUPPORTING INFORMATION

EXPERIMENTAL PROCEDURES

General Procedures: Melting points were uncorrected. CH_3NO_2 was purified by vacuum distillation to remove the water/CH_3NO_2 azeotrop, followed by drying with $CaSO_4$, and stored at 4°C in dark bottles over 4Å molecular sieves. Water contents (< 20 ppm) were measured by Karl-Fischer titration. All other solvents were distilled and/or stored over 3Å or 4Å molecular sieves as appropriate. ^{1}H NMR spectra were recorded on either a Varian Mercury 300 operating at 300.06 MHz equipped with a 4-nuclei probe or a Varian Unity Inova 500 operating at 499.87 MHz equipped with a z- (single axis) PFG inverse detection C-H-P probe. ^{13}C-NMR were recorded on a Varian Mercury 300 operating at 75.46 MHz. Chemical shift (δ) values are in ppm, coupling constants (*J*) are in Hz. All assignments were supported by 2D homonuclear chemical-shift correlation spectroscopy (gCOSY) and heteronuclear single quantum correlated spectroscopy (gHSQC) experiments. Thin-layer chromatography was performed on Merck Silica Gel 60 F_{254} plates and spots were visualized by UV light at 254 nm and/or spraying with 10% aq. H_2SO_4 followed by heating. Vacuum liquid chromatography was carried on Merck Silica Gel 60H. HPLC analyses were conducted with a Waters system (600 control unit, 996 photodiode array (PDA) detector, 717 Plus autosampler, Millenium32 control software) on a Waters Nova-Pak C18 column (3.9×5.0 mm cartridge; 4 μm particle size) using a linear gradient of 0.1% aq. TFA (A) and 0.1% TFA in CH_3CN (B): 0 min: 0% B, 2 min: 0% B, 5 min: 50% B, 12 min: 95% B, 13 min: 95% B, 13.5 min: 0% B, 20 min: 0% B. Monitoring was from 200 to 400 nm, integrations were performed at 215 and 265 nm, and individual peaks were analyzed by their UV-spectra. The purity of compounds was determined from integrations at 215 nm. MS analyses were performed on a Micromass LCT mass spectrometer.

Synthesis of esters 3 and 9: 2-Fluoro-3,5-dinitrobenzoic acid **1** was dissolved in dry CH_2Cl_2 (2 mL/mmol **1**) and dry DMF (0.1 equiv.) was added. An argon atmosphere was established and oxalyl chloride (1.0 equiv.) was added slowly. The reaction mixture was stirred for 15 min. at r.t. (dilution of 1 drop of the reaction mixture with MeOH, followed by TLC, indicated full conversion). The reaction

mixture was neutralized by addition of 2,6-lutidine (2.5 equiv.) under cooling on ice (dark red slurry). The alcohol (**2** or **8**, 1.0 equiv.) was added and the stirring continued for an additional 2 h. The product was purified by column chromatography (eluting with CH_2Cl_2 or EtOAc-hexane) to give **3** as slightly yellow crystals (mp. 146-149.5°C) in 78% yield or **9** as yellow crystals (mp. 55-59°C) in 63% yield, respectively.

Synthesis of aryl glycosides 5, 11, and 12 (Table 1): 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose **4** or -mannopyranose **10** (l equiv.), ester **3** or **9** (1.2 equiv.) and Li_2CO_3 (2.0 equiv.) were suspended in dry CH_2Cl_2 (10 mL/mmol **4**/**10**) under an argon atmosphere. The soluble base (DMAP, 0.3 equiv. dissolved in CH_2Cl_2, 0.5 mL, or 1,4-dimethylpiperazine, 0.6 equiv.) was added from a syringe in 5 portions over 25 min. The reactions were stirred at r.t. for the time indicated (Table 1) and monitored by analytical HPLC or TLC. The reaction mixture was purified by column chromatography (eluting with CH_2Cl_2-Et_2O) to give **5** in 90% yield (α/β ratio 8:1, mp. 56-66°C), **11** in 67% yield (α/β ratio 1:9.5, mp. 60-62°C), or **12** in 53% yield (α/β ratio 0:1, mp. 55-61°C), respectively.

Synthesis of 6: Aryl glycoside **5** (259 mg, 0.25 mmol) was dissolved in a mixture of HCOOH (6 mL, 0.16 mol), Et_2O (4 mL) and toluene (4 mL) and stirred for 45 min. The solution was extracted with water (6 × 4.5 mL), until pH ~ 5-6 of the aqueous phase, and the organic phase was dried over Na_2SO_4 and concentrated to a small volume. The crude product was purified by column chromatography (eluting with EtOAc-hexane) to yield title compound **6** as an oil in 46%.

General method for model intramolecular glycosylation (glycosyl transfer) and HPLC analysis (Table 2): The initial evaluation of conditions for the glycosylation was performed by dissolving the tethered glycoside **6**, **11**, or **12** (typically 0.01 mmol) in the solvent indicated (600 μL), adding the promoter indicated and mixing on an Eppendorf Thermomixer 5436 (combined heater/shaker). After shaking for the indicated period, a sample (40 μL) was diluted in acetonitrile (0.6 mL) and analyzed by analytical HPLC. Reported yields are based on integrated areas (215 nm).

Intramolecular glycosylation (glycosyl transfer): Up-scaled synthesis of glycosides 7, 13, and 14: Aryl glycosides **6**, **11** and **12** were dissolved in dry CH_3NO_2 (1.5 mL/mmol) under argon. The reactions were stirred at 60°C for the time indicated in Table 2 and monitored by analytical HPLC. Products were isolated as oils after purification by chromatography (silica gel column, eluting with EtOAc-hexane, or prep. HPLC). **7** was isolated in 39% yield (α/β ratio 2.7:1), **13** in 24% yield (α/β ratio 1:1.3) and **14** in 49% yield (α/β ratio 3.7:1), respectively.

Synthesis of 15 and 16: Esters **13** and **14** were dissolved in MeOH saturated with NaOMe. The reaction mixtures were stirred for 5 min. at r.t. and neutralized with dry ice. Products were purified by column chromatography (eluting with EtOAc-hexane) as oils in 95% (**15**) and 93% (**16**) yield, respectively.

SPECTROSCOPIC AND ANALYTICAL DATA

In the following NMR assignment, the carbohydrate moiety acting as the acceptor in glycosylation reactions is referred to as the A-ring, whereas the donor moiety is referred to as the B-ring.

3: ^{1}H NMR ($CDCl_3$) δ: 3.5 (t, 2H), 4.6 (t, 2H), 7.2-7.5 (m, 15H), 9.07 (dd, 1H, J = 3Hz, J = 6Hz), 9.11 (dd, 1H, J = 3Hz, J = 5Hz). ^{13}C NMR ($CDCl_3$), δ: 61.4 (1C, CH_2), 66.5 (1C, CH_2), 86.8 (1C, CPh_3), 123.3-131.8 (19C, Trt-2-6, C-1,3,4,6) 143.5 (3C, Trt-1), 156.7 (C-5), 159.0 (C-2), 160.7 (Ar-CO_2R). ES-MS, calcd. for $C_{28}H_{21}FN_2O_7$: 516,13. Found: *m/z* 243.1 $[Trt]^+$.

α5: ^{1}H NMR (Acetone-d_6), δ: 3.57 (dd, 1H, H-6, J = 1.7, J = 11.0), 3.68 (dd, 1H, H-6', J = 3.6, J = 11), 3.69 (dd, 1H, H-4, J = 9.2, J = 10), 3.70 (dd, 1H, H-2, J = 3.2, J = 9.4), 3.66-3.51 (2 × m, 2H, C$\underline{H}_2$OTrt), 3.94 (ddd, 1H, H-5, J = 1.7, J = 3.6, J = 10), 4.04 (dd, 1H, H-3, J = 9.2, J = 9.4), 4.6 (broad t, 2H, C$\underline{H}_2$OCO), 4.4-5.0 (m, 8H, C$\underline{H}_2$-Bn), 5.76 (d, 1H, H-1, J = 3.2), 7.0-7.4 (m, 35H, Ar-$\underline{H}$), 8.68 (d, 1H, Ar-3, J = 3.0), 8.72 (d, 1H, Ar-5, J = 3.0). ^{13}C NMR (Acetone-d_6), δ: 62.6-66.6 (2C, -O-$\underline{C}H_2$), 69.2, 73.8, 74.4, 74.9, 75.5, 76.1, 77.6, 82.1, 82.3 (9C, 4 × C$\underline{H}_2$-Bn, 5 × sugar-$\underline{C}$), 87.5 (1C, $\underline{C}$-Trt), 104.5 (1C, $\underline{C}$-1), 124.4 (1C, $\underline{Ar}$-CO_2R), 127.9-149.8 (46C, 42 × Bn/Trt, 2 × $\underline{Ar}$-H, 2 × $\underline{Ar}$-NO_2), 154.6 (1C, $\underline{Ar}$-Glc), 163.6 (1C, $\underline{C}$=O). ES-MS, calcd. for $C_{62}H_{56}N_2O_{13}$: 1036.38. Found: *m/z* 243.1 $[Trt]^+$. Anal. Calcd. for $C_{62}H_{56}N_2O_{13}$: C 71.80; H 5.44; N 2.70. Found: C 71.77; H 5.57; N 2.70.

α6: ^{1}H NMR (Acetone-d_6), δ: 3.71 (dd, 1H, H-4, J = 9.3, J = 10), 3.72 (dd, 1H, H-6, J = 1.8, J = 11), 3.78 (dd, 1H, H-6', J = 3.8, J = 11), 3.78 (dd, 1H, H-2, J = 3.2, J = 9.6), 3.89 (t, 2H, C$\underline{H}_2$OH, J = 4.7, J = 4.7), 3.96 (ddd, 1H, H-5, J = 1.8, J = 3.8, J = 10), 4.06 (dd, 1H, H-3, J = 9.4, J = 9.6), 4.5 (t, 2H, C$\underline{H}_2$OCO, J = 4.7, J = 4.7), 4.4-5.0 (m, 8H, C$\underline{H}_2$-Bn), 5.90 (d, 1H, H-1, J = 3.2), 7.1-7.4 (m, 20H, Ar-$\underline{H}$ on Bn), 8.66 (d, 1H, Ar-3, J = 2.9), 8.71 (d, 1H, Ar-5, J = 2.9). ^{13}C NMR (Acetone-d_6), δ: 60.5-60.7 (2C, CH_2), 69.5 (1C, C-4), 74.0 (1C, C-5), 74.5 (1C, C-3), 75.2 (1C, C-6), 75.7 (1C, C-2), 76.3-82.4 (4C, $\underline{C}H_2$-Bn), 103.9 (1C, C-1), 124.4 (1C, Ar-5), 128.2 (1C, Ar-2), 128.4 – 128.7 (4C, Bn-4), 128.9 – 129.1 (8C, Bn-3,5), 129.2 – 129.3 (8C, Bn-2,6), 130.5 (1C, Ar-3), 138.7 – 140.1 (4C, Bn-1), 142.4 (1C, Ar-6), 145.8 (1C, Ar-4), 154.2 (1C, Ar-1), 164.5 (1C, $\underline{C}$=O).

α7: ^{1}H NMR (Acetone-d_6), δ: 3.55 (dd, 1H, H-4, J = 9.0, J = 10.2), 3.56 (dd, 1H, H-2, J = 3.42, J = 9.4), 3.71 (d, 2H, 2 × H-6, J = 3.4), 3.86 (ddd, 1H, H-5, J = 3.4, J = 3.4, J = 10.2), 3.92 (dd, 1H, H-3, J = 9.0, J = 9.4), 3.96 (ddd, 1H, Ether-CH_2-a, J = 3.0, J = 5.5, J = 9.0), 4.15 (ddd, 1H, Ether-CH_2-b, J = 3.0, J = 6.0, J = 9.4), 4.51 (d, 1H, C$\underline{H}_2$-Bn, J = 12), 4.57 (d, 1H, C$\underline{H}_2$-Bn, J = 12), 4.58 (d, 1H, C$\underline{H}_2$-Bn, J = 11), 4.71 (d, 2H, C$\underline{H}_2$-Bn, J = 3.8), 4.79 (t, 2H, Ester-CH_2, 2 × J = ~9), 4.82 (d, 1H, C$\underline{H}_2$-Bn, J = 11), 4.91 (d, 1H, C$\underline{H}_2$-Bn, J = 11), 4.96 (d, 1H, C$\underline{H}_2$-Bn, J = 11), 5.11 (d, 1H, H-1, J = 3.4), 7.1-7.4 (m, 20H, Bn-H), 8.80 (d, 1H, Ar-2, J = 2.9), 8.87 (s, 1H, Ar-O$\underline{H}$), 8.92 (d, 1H, Ar-2, J = 2.9). ^{13}C NMR (Acetone-d_6), δ: 66.6 (1C, Ester-$\underline{C}H_2$), 66.0 (1C, Ether-$\underline{C}H_2$), 70.1 (1C, C-4), 71.7 (1C, C-5), 72.8 (1C, C-3), 73.8 (1C, C-6), 75.4 (1C, C-2), 75.9-82.7 (4C, $\underline{C}H_2$-Bn), 97.5 (1C, C-1), 102.4 (1C, Ar-1), 126.9 (1C, Ar-4), 128.0-128.2 (4C, Bn-4), 128.4-128.6 (8C, Bn-3,5), 128.7-129.0 (8C, Bn-2,6), 130.7 (1C, Ar-6), 139.7 (1C, Ar-3), 139.7 (1C, Ar-5), 138.7-140.1 (4C, Bn-1), 140.2 (1C, Ar-2), 163.8 (1C, $\underline{C}$=O). ES-MS, calcd. for $C_{43}H_{42}N_2O_{13}$: 794.27. Found: *m/z* 817.2 $[M + Na]^+$, 607.2 [M - (3,5-dinitro-2-hydroxybenzoyl) + H + $Na]^+$.

9: ^{1}H NMR ($CDCl_3$), δ: 3.41 (s, 3H, OCH_3), 3.50 (dd, 1H, H-4, J = 10, J = 8.9), 3.54 (dd, 1H, H-2, J = 3.8, J = 9.4), 3.81 (dd, 1H, H-3, J = 9.4, J = 9.1), 3.92 (ddd, 1H, H-5, J = 2.1, J = 5.2, J = 9.8), 4.58 (dd, 1H, H-6, J = 5.2, J = 12), 4.62 (d, 1H, H-1, J = 3.6), 4.67 (d, 1H, Ph-CH_2(a), J = 12), 4.69 (d, 1H, H-6', J = 2.1, J = 12), 4.71 (d, 1H, Ph-CH_2(b), J = 11), 4.79 (d, 1H, Ph-CH_2(a'), J = 12), 5.04 (d, 1H, Ph-

CH_2(b'), J = 11), 7.1-7.4 (m, 10H, Ph-H), ~9.0 (m, 2H, Ar-H4, Ar-H6). ^{13}C NMR ($CDCl_3$), δ: 55.6 (1C, OCH_3), 66.2 (1C, C-6), 69.0 (1C, C-5), 70.2 (1C, C-4), 73.5 (1C, Ph-CH_2), 75.7 (1C, Ph-CH_2), 79.9 (1C, C-2), 81.3 (1C, C-3), 98.5 (1C, C-1α), 121 (1C, Ar-1), 125.4 (1C, Ar-4), 128.3-128.9 (10C, 10 × Ph-H), 132.1 (2C, Ar-3, Ar-6), 138.1-138.7 (2C, Ph-C), 156 (1C, Ar-5), 159 (1C, Ar-2), 161 (1C, C=O). ES-MS, calcd. for $C_{28}H_{27}FN_2O_{11}$: 586.16. Found: *m/z* 609.1 $[M + Na]^+$.

β**11**: ^{1}H NMR ($CDCl_3$), δ: A-RING: 3.36 (s, 3H, OCH_3), 4.7 (d, 1H, H-1, J = 3.4), 3.49 (dd, 1H, H-2, J = 3.4, J = 9.4), 3.77 (dd, 1H, H-3, J = 9.4, J = 9.4), 3.48 (dd, 1H, H-4, J = 9.4, J = 9.4), 3.78 (m, 1H, H-5), 4.49 (m, 2H, 2 × H-6), B-RING: 5.19 (d, 1H, H-1', J = 7.7), 3.82 (dd, 1H, H-2', J = 7.7, J = 8.5), 3.68 (dd, 1H, H-3', J = 8.5, J = 8), 3.70 (dd, 1H, H-4', J = 9, J = 9), 3.35 (ddd, 1H, H-5', J = 1.7, J = 4.7, J = 9), 3.55 (dd, 1H, H-6', J = 1.7, J = 11), 3.62 (dd, 1H, H'-6', J = 4.7, J = 11), 4.98 (d, 1H, Bn-CH_2(a'), J = 11), 4.70 (d, 1H, Bn-CH_2(a), J = 10.5), 4.69 (d, 1H, Bn-CH_2(b), J = 11), 4.96 (d, 1H, Bn-CH_2(b'), J = 11), 4.79 (d, 1H, Bn-CH_2(c), J = 10), 4.92 (d, 1H, Bn-CH_2(c'), J = 10), 4.56 (d, 1H, Bn-CH_2(d), J = 11), 4.79 (d, 1H, Bn-CH_2(d'), J = 11), 4.57 (d, 1H, Bn-CH_2(e), J = 12), 4.65 (d, 1H, Bn-CH_2(e'), J = 12), 4.38 (d, 1H, Bn-CH_2(f), J = 12), 4.49 (d, 1H, Bn-CH_2(f'), J = 12), 7.1-7.4 (m, 30H, Ar-H), 8.7 (d, 1H, Ar-H4/6), 8.8 (d, 1H, Ar-H4/6). ^{13}C NMR ($CDCl_3$), δ: 55.4 (1C, OCH_3), 65.6 (1C, C-6), 68.5 (1C, C-5'), 68.8 (1C, C-5), 70.0 (1C, C-4), 73.0-75.8 (8C, CH_2-Ph, C-6', C-4'), 79.8 (1C, C-2), 81.2 (1C, C-3'), 82.1 (1C, C-2'), 84.2 (1C, C-3), 98.0 (1C, C-1), 104.5 (1C, C-1'), 122.6 (1C, Ar-1), 127.7-128.6 (31C, Ph-H, Ar-4), 129.0 (1C, Ar-6), 131.0 (1C, Ar-3), 137.8-138.6 (6C, Ph-C), 143.0 (1C, Ar-5), 151.1 (1C, Ar-2), 163.4 (1C, C=O). Anal. Calcd. for $C_{62}H_{62}N_2O_{17}$: C 67.26; H 5.64; N 2.53. Found: C 66.88; H 5.85; N 2.78.

α**12**: ^{1}H NMR ($CDCl_3$), δ: A-RING: 3.40 (s, 3H, OCH_3), 4.6 (d, 1H, H-1, J = 3.8), 3.50 (dd, 1H, H-2, J = 3.8, J = 9.8), 3.79 (dd, 1H, H-3, J = 9.4, J = 9.0), 3.53 (dd, 1H, H-4, J = 9.0, J = 9.0), 3.88 (m, 1H, H-5), 4.62 (m, 2H, 2 × H-6), B-RING: 5.65 (d, 1H, H-1', J = small, $^1J[^{13}CH(1)]$ = 196.5), 4.25 (dd, 1H, H-2', J = 2, J = 2.5), 3.98 (dd, 1H, H-3', J = 2.5, J = 8.5), 3.65 (dd, 1H, H-4', J = 9, J = 9), 3.70 (ddd, 1H, H-5', J = 9, J = 4.5, J = ~2), 3.49 (d, 1H, H-6', J = 12), 3.40 (d, 1H, H'-6', J = 12), 4.85 (d, 1H, Bn-CH_2(a), J = 12), 5.0 (d, 1H, Bn-CH_2(a'), J = 12), 4.75 (d, 1H, Bn-CH_2(b), J = 12), 5.0 (d, 1H, Bn-CH_2(b'), J = 12), 4.75 (d, 1H, Bn-CH_2(c), J = 11), 5.0 (d, 1H, Bn-CH_2(c'), J = 11), 4.55 (d, 1H, Bn-CH_2(d), J = 11), 4.88 (d, 1H, Bn-CH_2(d'), J = 11), 4.45 (d, 1H, Bn-CH_2(e), J = 12), 4.78 (d, 1H, Bn-CH_2(e'), J = 12), 4.42 (d, 1H, Bn-CH_2(f), J = 12), 4.6 (d, 1H, Bn-CH_2(f'), J = 12), 7.1-7.4 (m, 30H, Ar-H on Bn), 8.65 (d, 1H, Ar-H4/6), 8.75 (d, 1H, Ar-H4/6). ^{13}C NMR ($CDCl_3$), δ: 56 (1C, OCH_3), 69 (2C, C-6, C-5'), 69.5 (1C, C-5), 70 (1C, C-4), 72-77 (8C, CH_2-Ph, C-4', C-6'), 79 (1C, C-2), 80 (1C, C-3'), 81 (1C, C-2'), 82 (1C, C-3), 98 (1C, C-1), 105 (1C, C-1'), 123 (1C, Ar-3), 127-129 (32C, Ph-H, Ar-1, Ar-6), 129.5 (1C, Ar-4), 137.8-138.6 (6C, Ph-C), 142 (1C, Ar-5), 153 (1C, Ar-2), 163 (1C, C=O). ES-MS, calcd. for $C_{62}H_{62}N_2O_{17}$: 1106.4049. Found: *m/z* 1129.1 $[M + Na]^+$, 1124.2 $[M + H_2O + H]^+$, 563.1 $[(BnO)_4Glc + Na]^+$.

α**13**: ^{1}H NMR ($CDCl_3$), δ: A-RING: 3.40 (s, 3H, OCH_3), 4.65 (d, 1H, H-1, J = 2.6), 3.55 (dd, 1H, H-2, J = 2.6, J = 9.0), 4.10 (dd, 1H, H-3, J = 9.0, J = 9.0), 3.83 (dd, 1H, H-4, J = 9.0, J = 9.8), 4.08 (ddd, 1H, H-5, J = 9.8, 2 × J = small), 4.7 (2 × d, 2H, 2 × H-6, 2 × J = small), B-RING: 5.54 (d, 1H, H-1', J = 3.8), 3.51 (dd, 1H, H-2', J = 3.8, J = 9.4), 3.96 (dd, 1H, H-3', J = 9.4, J = 9.4), 3.54 (dd, 1H, H-4', J = 9.4, J = 9.8), 3.76 (ddd, 1H, H-5', J = 9.8, 2 × J = 2-5), 3.5 (m, 2H, 2 × H-6'), 4.84 (d, 1H, Bn-CH_2(a), J = 12), 4.98 (d, 1H, Bn-CH_2(a'), J = 12), 4.8 (d, 1H, Bn-CH_2(b), J = 11), 4.9 (d, 1H, Bn-CH_2(b'), J = 11), 4.46 (d, 1H, Bn-CH_2(c), J = 11), 4.82 (d, 1H, Bn-CH_2(c'), J = 11), 4.65 (d, 1H, Bn-CH_2(d), J = 12), 4.78 (d, 1H, Bn-CH_2(d'), J = 12), 4.58 (d, 1H, Bn-CH_2(e), J = 12), 4.70 (d, 1H, Bn-CH_2(e'), J = 12), 4.52 (d, 1H, Bn-CH_2(f), J = 12), 4.64 (d, 1H, Bn-CH_2(f'), J = 12), 7.1-7.4 (m, 30H, Ar-H på Bn), 8.7 (d, 1H, Ar-H4/6), 8.92 (d, 1H, Ar-H4/6). ^{13}C NMR ($CDCl_3$), δ: 55.5 (1C, OCH_3), 66.7 (1C, C-6), 67.8 (1C, C-5'),

68.9 (1C, C-5), 71.9 (1C, C-4), 73.5-75.1 (6C, CH$_2$-Ph), 75.5 (1C, C-6'), 77.9 (1C, C-4'), 79.2 (1C, C-2), 80.0 (1C, C-3'), 81.0 (1C, C-2'), 81.7 (1C, C-3), 97.7-97.8 (2C, C-1, C-1'), 115.8 (1C, Ar-1), 126.5-128.5 (31C, 30 × Ph-H, Ar-4), 130.0 (1C, Ar-6), 137.7-138.8 (7C, 6 × Ph-C, Ar-3), 159.5 (1C, Ar-5), 167.3 (1C, Ar-2), 167.5 (1C, C=O).

β**13**: ^{1}H NMR ($CDCl_3$), δ: A-RING: 3.39 (s, 3H, OCH_3), 4.47 (d, 1H, H-1, J = 4.3), 3.47 (dd, 1H, H-2, J = 4.3, J = 9.0), 3.95 (dd, 1H, H-3, J = 9.0, J = 9.8), 3.78 (dd, 1H, H-4, J = 9.8, J = 9.0), 3.88 (ddd, 1H, J = 9.0, 2 × J = small, H-5), 4.40 (d, 1H, J = 12, H-6), 4.74 (d, 1H, H'-6), B-RING: 4.47 (d, 1H, H-1', J = 8.1), 3.44 (dd, 1H, H-2', J = 8.1, J = 9.4), 3.69 (dd, 1H, H-3', J = 9.0, J = 9.0), 3.55 (dd, 1H, H-4', J = 9.0, J = 9.0), 3.46 (ddd, 1H, H-5', J = 9.0, 2 × J = small), 3.58-3.67 (2 × d, 2H, 2 × H-6'), 4.85 (d, 1H, Bn-CH$_2$(a), J = 12), 5.02 (d, 1H, Bn-CH$_2$(a'), J = 12), 4.83 (d, 1H, Bn-CH$_2$(b), J = 11), 4.89 (d, 1H, Bn-CH$_2$(b'), J = 11), 4.76 (d, 1H, Bn-CH$_2$(c), J = 11), 4.87 (d, 1H, Bn-CH$_2$(c'), J = 11), 4.50 (d, 1H, Bn-CH$_2$(d), J = 12), 4.78 (d, 1H, Bn-CH$_2$(d'), J = 12), 4.58 (d, 1H, Bn-CH$_2$(e), J = 12), 4.76 (d, 1H, Bn-CH$_2$(e'), J = 12), 4.32 (d, 1H, Bn-CH$_2$(f), J = 12), 4.35 (d, 1H, Bn-CH$_2$(f'), J = 12), 7.0-7.4 (m, 30H, Ar-H on Bn), 8.7 (d, 1H, Ar-H4/6), 9.0 (d, 1H, Ar-H4/6). ^{13}C NMR ($CDCl_3$), δ: 55.5 (1C, OCH_3), 65.6, 66.3, 68.7, 69.0 (4C, 4 × sugar-C), 73.6-76.1 (6C, CH$_2$-Ph), 77.4 (1C, C-6'), 77.9 (1C, C-4), 78.2 (1C, C-3'), 80.0 (1C, C-3), 83.0 (1C, sugar-C), 86.0 (1C, C-4'), 98.2 (1C, C-1), 103.4 (1C, C-1'), 116.4 (1C, Ar-1), 126.6 (1C, Ar-4), 127.6-128.7 (30C, Ph-H), 130.3 (1C, Ar-6), 137.7-138.8 (7C, 6 × Ph-C, Ar-3), 148.4 (1C, Ar-5), 159.6 (1C, Ar-2), 166.9 (1C, C=O). ES-MS, calcd. for $C_{62}H_{62}N_2O_{17}$: 1106.40. Found: *m/z* 1129.2 $[M + Na]^+$.

α**14**: ^{1}H NMR ($CDCl_3$), δ: A-RING: 3.4 (s, 3H, OCH_3), 4.57 (d, 1H, H-1, J = 3.4), 3.54 (dd, 1H, H-2, J = 3.4, J = 9.8), 3.89 (dd, 1H, H-3, J = 9.4, J = 9.0), 3.63 (dd, 1H, H-4, J = 9.4, J = 9.8), 4.08 (ddd, 1H, H-5, J = 9.8, J = 2, J = 5), 4.82 (dd, 1H, H'-6, J = 1.7, J = 12), 4.60 (d, 1H, H-6, J = 12), B-RING: 5.28 (d, 1H, H-1', J = 2.1), 3.70 (dd, 1H, H-2', J = 2.1, J = 2.6), 3.88 (dd, 1H, H-3', J = 2.6, J = 7.5), 3.58 (dd, 1H, H-4', J = 7.5, J = 6.8), 3.86 (m, 1H, H-5'), 3.66 (m, 2H, 2 × H-6'), 4.59 (d, 1H, Bn-CH$_2$(a), J = 12), 5.06 (d, 1H, Bn-CH$_2$(a'), J = 12), 4.60 (d, 1H, Bn-CH$_2$(b), J = 12), 4.71 (d, 1H, Bn-CH$_2$(b'), J = 12), 4.60 (d, 1H, Bn-CH$_2$(c), J = 12), 4.66 (d, 1H, Bn-CH$_2$(c'), J = 12), 4.45 (d, 1H, Bn-CH$_2$(d), J = 12), 4.80 (d, 1H, Bn-CH$_2$(d'), J = 11), 4.39 (d, 1H, Bn-CH$_2$(e), J = 11), 4.46 (d, 1H, Bn-CH$_2$(e'), J = 12), 4.20 (d, 1H, Bn-CH$_2$(f), J = 12), 4.30 (d, 1H, Bn-CH$_2$(f'), J = 12), 7.1-7.4 (m, 30H, Ar-H on Bn), 8.86 (d, 1H, Ar-H4/6, J = 2.6), 8.92 (d, 1H, Ar-H4/6, J = 2.6). ^{13}C NMR ($CDCl_3$), δ: 55.5 (1C, OCH_3), 66.0 (1C, C-6), 66.5 (1C, C-5'), 68.1 (1C, C-5), 69.9 (1C, C-4), 72.3-76.5 (8C, CH$_2$-Ph, C-6', C-4'), 78.5 (1C, C-2), 79.2 (1C, C-3'), 79.9 (1C, C-2'), 81.2 (1C, C-3), 97.8 (1C, C-1), 101.0 (1C, C-1'), 115.9 (1C, Ar-1), 126.5 (1C, Ar-4), 127.0-128.6 (30C, Ph-H), 130.2 (1C, Ar-6), 137.5-138.4 (8C, 6 × Ph-C, Ar-3, Ar-5), 159.5 (1C, Ar-2), 167.2 (1C, C=O). ES-MS, calcd. for $C_{62}H_{62}N_2O_{17}$: 1106.4049. Found: *m/z* 1129.2 $[M + Na]^+$.

β**14** ^{1}H NMR ($CDCl_3$), δ: A-RING: 3.46 (s, 3H, OCH_3), 4.69 (d, 1H, H-1, J = 3.4), 3.64 (dd, 1H, H-2, J = 3.8, J = 9.4), 4.03 (dd, 1H, H-3, J = 9.4, J = 9.4), 5.35 (dd, 1H, H-4, J = 9.8, J = 9.8), 4.00 (broad d, 1H, H-5, J = ~10), 3.78 (dd, 1H, H'-6, J = 3, J = 12), 3.50 (broad d, 1H, H-6, J = 12), B-RING: 4.84 (d, 1H, H-1', J = ~2), 3.82 (dd, 1H, H-2', J = ~2, J = ~2), 3.87 (dd, 1H, H-3', J = ~3, J = 9.4), 3.71 (dd, 1H, H-4', J = 9.4, J = 9.4), 3.48 (m, 1H, H-5'), 3.57 (broad d, 1H, H-6', J = 12), 3.41 (broad d, 1H, H'-6', J = 12), 4.53 (d, 1H, Bn-CH$_2$(a), J = 12), 4.89 (d, 1H, Bn-CH$_2$(a'), J = 12), 4.73 (d, 1H, Bn-CH$_2$(b), J = 12), 4.86 (d, 1H, Bn-CH$_2$(b'), J = 12), 4.51 (d, 1H, Bn-CH$_2$(c), J = 11), 4.84 (d, 1H, Bn-CH$_2$(c'), J = 11), 4.67 (d, 1H, Bn-CH$_2$(d), J = 12), 4.73 (d, 1H, Bn-CH$_2$(d'), J = 12), 4.63 (d, 1H, Bn-CH$_2$(e), J = 11), 4.65 (d, 1H, Bn-CH$_2$(e'), J = 11), 4.20 (d, 1H, Bn-CH$_2$(f), J = 12), 4.26 (d, 1H, Bn-CH$_2$(f'), J = 12), .7.1-7.4 (m, 30H, Ar-H on Bn), 8.1 (d, 1H, Ar-H4/6), 8.6 (d, 1H, Ar-H4/6). ES-MS, calcd. for $C_{62}H_{62}N_2O_{17}$: 1106.40. Found: *m/z* 1129.1 $[M + Na]^+$, 1124.2 $[M + H_2O + H]^+$.

α**15**: ^{1}H NMR ($CDCl_3$), δ: A-RING: 3.38 (s, 3H, OCH_3), 4.60 (d, 1H, H-1, J = 3.4), 3.57 (dd, 1H, H-2, J = 3.4, J = 9.4), 4.10 (dd, 1H, H-3, J = 9.4, J = 9.0), 4.03 (dd, 1H, H-4, J = 8.5, J = 9.8), 3.74 (ddd, 1H, H-5, J = 9.8, 2 × J = small), 3.94 (dd, 1H, H-6, J = 11, J = small), 3.76 (dd, 1H, H'-6, J = 11, J = small), B-RING: 5.76 (d, 1H, H-1', J = 3.8), 3.48 (dd, 1H, H-2', J = 3.8, J = 9.8), 3.92 (dd, 1H, H-3', J = 9.8, J = 9.0), 3.42 (dd, 1H, H-4', J = 9.0, J = 9.4), 3.82 (ddd, 1H, H-5', J = 9.4, 2 × J = 2-5), 3.66 (dd, 1H, H-6', J = 10, J = small), 3.52 (dd, 1H, H'-6', J = 10, J = small), 4.78 (d, 1H, Bn-C$\underline{H}_2$(a), J = 12), 5.02 (d, 1H, Bn-C$\underline{H}_2$(a'), J = 12), 4.78 (d, 1H, Bn-C$\underline{H}_2$(b), J = 11), 4.87 (d, 1H, Bn-C$\underline{H}_2$(b'), J = 11), 4.56 (d, 1H, Bn-C$\underline{H}_2$(c), J = 12), 4.80 (d, 1H, Bn-C$\underline{H}_2$(c'), J = 12), 4.42 (d, 1H, Bn-C$\underline{H}_2$(d), J = 11), 4.77 (d, 1H, Bn-C$\underline{H}_2$(d'), J = 11), 4.56 (d, 1H, Bn-C$\underline{H}_2$(e), J = 12), 4.66 (d, 1H, Bn-C$\underline{H}_2$(e'), J = 12), 4.48 (d, 1H, Bn-C$\underline{H}_2$(f), J = 12), 4.60 (d, 1H, Bn-C$\underline{H}_2$(f'), J = 12), 7.1-7.4 (m, 30H, Ar-$\underline{H}$ on Bn). ES-MS, calcd. for $C_{55}H_{60}O_{11}$: 896.41. Found: *m/z* 919.4 $[M + Na]^+$.

α**16**: ^{1}H NMR ($CDCl_3$), δ: A-RING: 3.38 (s, 3H, OCH_3), 4.60 (d, 1H, H-1, J = 3.4), 3.57 (dd, 1H, H-2, J = 3.4, J = 9.4), 3.90 (dd, 1H, H-3, J = 9.4, J = 9.0), 3.92 (dd, 1H, H-4, J = 8.5, J = 9.8), 3.68 (m, 1H, H-5), 3.8-3.95 (2 × dd, 2H, 2 × H-6), B-RING: 5.38 (d, 1H, H-1', J = 1-2), 3.48 (m, 1H, H-2', 2 × J = 1-5), 3.94 (dd, 1H, H-3', J = 2-5, J = 9.8), 3.53 (dd, 1H, H-4', J = 9.0, J = 9.8), 3.83 (m, 1H, H-5'), 3.64-3.72 (2 × dd, 2H, 2 × H-6'), 4.63 (d, 1H, Bn-C$\underline{H}_2$(a), J = 12), 5.08 (d, 1H, Bn-C$\underline{H}_2$(a'), J = 12), 4.61 (d, 1H, Bn-C$\underline{H}_2$(b), J = 11), 4.78 (d, 1H, Bn-C$\underline{H}_2$(b'), J = 11), 4.52 (d, 1H, Bn-C$\underline{H}_2$(c), J = 12), 4.68 (d, 1H, Bn-C$\underline{H}_2$(c'), J = 12), 4.42 (d, 1H, Bn-C$\underline{H}_2$(d), J = 12), 4.65 (d, 1H, Bn-C$\underline{H}_2$(d'), J = 12), 4.56 (d, 1H, Bn-C$\underline{H}_2$(e), J = 12), 4.63 (d, 1H, Bn-C$\underline{H}_2$(e'), J = 12), 4.22 (d, 1H, Bn-C$\underline{H}_2$(f), J = 12), 4.15 (d, 1H, Bn-C$\underline{H}_2$(f'), J = 12), 7.1-7.4 (m, 30H, Ar-$\underline{H}$ on Bn). ^{13}C NMR ($CDCl_3$), δ: 55 (1C, OCH_3), 71.4, 71.6, 72.9, 73.1 (4C, 4 × sugar-C), 73.7-76.2 (6C, $\underline{C}H_2$-Ph), 77.8, 78.5, 79.2, 80.7, 81.1, 82.5 (6C, 6 × sugar-C), 98, 99 (2C, C-1, C-1'), 127.5-129.1 (30C, $\underline{Ph}$-H), 137-140 (6C, $\underline{Ph}$-C). ES-MS, calcd. for $C_{55}H_{60}O_{11}$: 896.41. Found: *m/z* 919.4 $[M + Na]^+$, 915.4 $[M + H_2O + H]^+$.