First Synthesis of 1,2,3-Triazolo-Linked (1,6)-α-D-Oligomannoses (Triazolomannoses) by Iterative Cu(I)-Catalyzed Alkyne-Azide Cycloaddition

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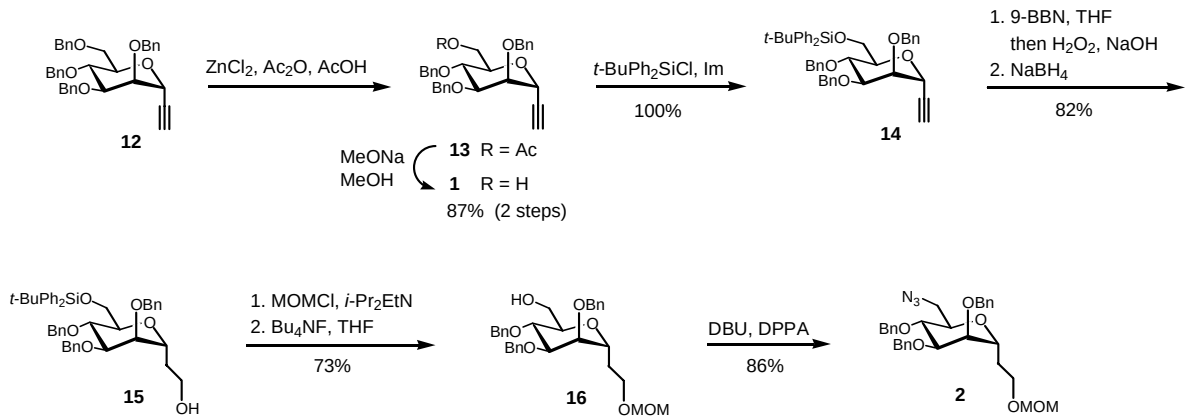
Electronic Supplementary Information

All moisture-sensitive reactions were performed under a nitrogen atmosphere using oven-dried glassware. Anhydrous solvents were dried over standard drying agents[19] and freshly distilled prior to use. Reactions were monitored by TLC on silica gel 60 F_{254} with detection by charring with sulfuric acid. Flash column chromatography[20] was performed on silica gel 60 (230-400 mesh). Optical rotations were measured at 20 ± 2 °C in the stated solvent; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. ^1H NMR (300 and 400 MHz) and ^{13}C NMR spectra (75 and 100 MHz) spectra were recorded for $CDCl_3$ solutions at rt unless otherwise specified; chemical shifts are in ppm (δ) from $SiMe_4$ (TMS) as internal standard; assignments were aided by homo- and heteronuclear two-dimensional experiments. MALDI-TOF mass spectra were acquired using 2,6-dihydroxy-benzoic acid as the matrix. The closed vessel MW experiments were performed using a Biotage Initiator apparatus; the reaction time was counted when the reaction mixture reached the preset temperature.

Preparation of building block 1 and platform 2



8-*O*-Acetyl-3,7-anhydro-4,5,6-tri-*O*-benzyl-1,2-dideoxy-D-*glycero*-D-*talo*-oct-1-ynitol (13).[21] To a stirred solution of known[16] tetra-*O*-benzyl derivative **12** (96 mg, 0.17 mmol) in a 2:1 mixture of acetic anhydride and acetic acid (3 cm^3), $ZnCl_2$ (238 mg, 1.75 mmol) was added. The resulting mixture was stirred at rt for 4 h, then diluted with AcOEt (30 cm^3), washed with H_2O (2 x 20 cm^3) and saturated aqueous $NaHCO_3$ (20 cm^3), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with 5:1 cyclohexane-AcOEt to give **13** (83 mg, 95%) as an

amorphous solid; $[\alpha]_D$ = +20.7 (*c* 1.0, $CHCl_3$). The ^1H NMR data of **13** were identical to those previously reported[21]. Anal. Calcd. for $C_{31}H_{32}O_6$: C, 74.38; H, 6.44;. Found: C, 74.10; H, 6.20.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-1,2-dideoxy-D-*glycero*-D-*talo*-oct-1-ynitol (1). To a stirred solution of known[16] tetra-*O*-benzyl derivative **12** (577 mg, 1.05 mmol) in a 2:1 mixture of acetic anhydride and acetic acid (15 cm^3), $ZnCl_2$ (1,43 g, 10.5 mmol) was added. The resulting mixture was stirred at rt for 7 h, then diluted with AcOEt (50 cm^3), washed with H_2O (2 x 30 cm^3) and saturated aqueous $NaHCO_3$ (30 cm^3), dried (Na_2SO_4), concentrated, and dried under high vacuum to give crude acetate **13**. To a solution of **13** in MeOH (20 cm^3) was added a 0.2 M solution of NaOMe in MeOH (3 cm^3, freshly prepared from Na and MeOH). The solution was kept at rt for 1 h, then neutralized with acetic acid, and concentrated. A solution of the residue in AcOEt (50 cm^3) was washed with H_2O (30 cm^3) and saturated aqueous $NaHCO_3$ (30 cm^3), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with 3:1 cyclohexane-AcOEt to afford alcohol **1** (420 mg, 87%) as an amorphous solid; $[\alpha]_D$ = +27.7 (*c* 1.0, $CHCl_3$). ^1H NMR: δ 7.45-7.23 (15 H, m, 3 Ph), 5.02-4.62 (7 H, m, PhC*H*$_2$ and 3-H), 4.11 (1 H, dd, $J_{4,5}$ = 2.5, $J_{5,6}$ = 9.0 Hz, 5-H), 4.01 (1 H, t, $J_{6,7}$ = 10.5 Hz, 6-H), 3.96-3.78 (4 H, m, 4-H, 7-H and 8-H), 2.58 (2 H, d, $J_{1,3}$ = 2.5 Hz, 1-H), 2.12 (1 H, br t, OH). ^{13}C NMR: δ 138.1 (*C*), 137.8 (*C*), 128.4 (*C*H), 128.1 (*C*H), 127.8 (*C*H), 127.7 (*C*H), 80.1 (*C*H_2), 78.4 (*C*), 77.5 (*C*H), 76.4 (*C*H), 75.3 (*C*H), 75.0 (*C*H_2), 74.6 (*C*H_2), 72.2 (*C*H), 66.3 (*C*H_2), 62.3 (*C*H). MALDI-TOF MS: 481.3 (M^+ + Na). Anal. Calcd. for $C_{29}H_{30}O_5$: C, 75.96; H, 6.59. Found: C, 75.76; H, 6.30.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-8-*O*-*tert*-butyldimethylsilyl-1,2-dideoxy-D-*glycero*-D-*talo*-oct-1-ynitol (14). To a stirred solution of alcohol **1** (310 mg, 0.68 mmol) in anhydrous DMF (5 cm^3) was added imidazole (460 mg, 6.80 mmol), followed by *tert*-butyldimethylsilyl chloride (510 mg, 3.38 mmol). The resulting solution was kept at rt for 3 h, then diluted with AcOEt (50 cm^3), washed with H_2O (2 x 30 cm^3) and brine (20 cm^3), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with 9:1 cyclohexane-AcOEt to afford **14** (387 mg, 100%) as a syrup; $[\alpha]_D$ = +13.7 (*c* 1.0, $CHCl_3$). ^1H NMR: δ 7.45-7.23 (15 H, m, 3 Ph), 5.02-4.62 (6 H, m, 3 PhC*H*$_2$), 4.80 (1 H, t, $J_{3,4}$ = 2.5 Hz, 3-H), 4.07 (2 H, m, 8-H), 4.01 (1 H, dd, $J_{4,5}$ = 4.0 Hz, $J_{5,6}$ = 11.5 Hz, 5-H), 3.95 (1 H, dd, $J_{6,7}$ = 1.7 Hz, 6-H), 3.84 (1 H, dd, 4-H), 3.82 (1 H, ddd, *J* = 1.7, 5.0, 5.0 Hz, 7-H), 2.53 (1 H, d, $J_{1,3}$ = 2.5 Hz, 1-H), 0.93 (9 H, s, C(C*H*$_3$)$_3$), 0.13 and 0.16 (6 H, 2 s, 2 C*H*$_3$). MALDI-TOF MS: 595.6 (M^+ + Na), 609.6 (M^+ + K). Anal. Calcd. for $C_{35}H_{44}O_5Si$: C, 73.39; H, 7.74. Found: C, 73.16; H, 7.50.

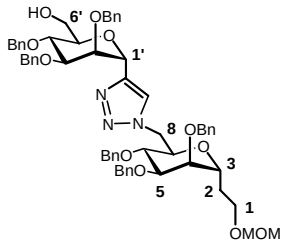
3,7-Anhydro-4,5,6-tri-*O*-benzyl-8-*O*-*tert*-butyldimethylsylil-2-deoxy-D-*glycero*-D-*talo*-octitol (15). To a stirred solution of **14** (118 mg, 0.21 mmol) in anhydrous THF (2 cm^3) was added dropwise 9-BBN (1.0 mmol, 2 cm^3 of a 0.5 M solution in THF). Stirring was continued at rt for18 h, then to the reaction mixture was added an alkaline solution of H_2O_2 (freshly prepared from 1 cm^3 of 6 M aqueous solution of NaOH and 400 mm^3 of a ca. 35% solution of H_2O_2 in water). The

reaction mixture was stirred at rt for 2 h, then cooled to 0 °C and treated with $NaBH_4$ (100 mg, 2.6 mmol). The mixture was stirred for an additional 30 min at rt, then diluted with acetic acid (0.5 cm^3) and AcOEt (30 cm^3), washed with H_2O (30 cm^3) and saturated $NaHCO_3$ (30 cm^3), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with 3:1 cyclohexane-AcOEt to give **15** (100 mg, 82%) as a syrup; $[\alpha]_D$ = +19.2 (*c* 1.4, $CHCl_3$). ^{1}H NMR selected data: δ 7.48-7.25 (15 H, m, 3 Ph), 4.68-4.50 (6 H, m, 3 PhC*H*$_2$), 4.18 (1 H, ddd, *J* = 3.5, 6.0, 10.0 Hz, 3-H), 2.82 (1 H, br t, OH), 1.98-1.70 (2 H, m, 2-H), 0.91 (9 H, s, C(C*H*$_3$)$_3$), 0.12 and 0.14 (6 H, 2 s, 2 C*H*$_3$). MALDI-TOF MS: 615.9 (M^+ + Na). Anal. Calcd. for $C_{35}H_{48}O_6Si$: C, 70.91; H, 8.16. Found: C, 70.77; H, 8.10.

3,7-Anhydro-4,5,6-tri-*O*-benzyl-2-deoxy-1-*O*-methoxymethyl-D-*glycero*-D-*talo*-octitol (16). To a stirred, cooled (0 °C) solution of alcohol **15** (90 mg, 0.15 mmol) in anhydrous CH_2Cl_2 (2 cm^3) was added *N,N*-diisopropylethylamine (150 mm^3, 0.86 mmol) and chloromethyl metyl ether (35 mm^3, 0.46 mmol). The mixture was stirred at rt for 3 h, then diluted with MeOH (0.5 cm^3) and concentrated. To a solution of the residue in THF (3 cm^3) was added tetrabutylammonium fluoride trihydrate (80 mg, 0.3 mmol). The reaction mixture was stirred at rt for 15 h, then concentrated. The residue was eluted from a column of silica gel with 1:1 cyclohexane-AcOEt to afford syrupy **16** (58 mg, 73%); $[\alpha]_D$ = +9.8 (*c* 1, $CHCl_3$). ^{1}H NMR: δ 7.45-7.23 (15 H, m, 3 Ph), 4.90-4.55 (8 H, m, PhC*H*$_2$ and OC*H*$_2$OMe), 4.21 (1 H, ddd, $J_{3,4}$ = 4.0 Hz, $J_{2,3}$ = 9.5 Hz, 3-H), 3.98-3.56 (8 H, m, 1,4,5,6,7,8-H), 3.36 (3 H, s, C*H*$_3$), 2.45 (1 H, br s, OH), 1.96-1.75 (2 H, m, 2-H). ^{13}C NMR: δ 138.4 (*C*), 128.7 (*C*H), 128.2 (*C*H), 128.1 (*C*H), 96.7 (*C*H$_2$), 78.0 (*C*H), 76.5 (*C*H), 75.4 (*C*H), 74.5 (*C*H) and (*C*H$_2$), 72.6 (*C*H$_2$), 72.1 (*C*H$_2$), 70.6 (*C*H), 64.3 (*C*H$_2$), 62.1 (*C*H$_2$), 55.6 (*C*H$_3$), 29.8 (*C*H$_2$). MALDI-TOF MS: 545.6 (M^+ + Na). Anal. Calcd. for $C_{31}H_{38}O_7$: C, 71.24; H, 7.33. Found: C, 70.96; H, 7.40.

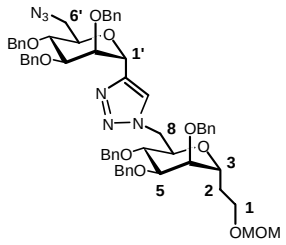
3,7-Anhydro-8-azido-4,5,6-tri-*O*-benzyl-1,2,8-trideoxy-1-*O*-methoxymethyl-D-*glycero*-D-*talo*-octitol (2). A mixture of alcohol **16** (218 mg, 0.42 mmol), diphenyl phosphoryl azide (270 mm^3, 1.25 mmol), 1,8-diazabicyclo[5.4.0.]undec-7-ene (125 mm^3, 0.84 mmol), and anhydrous DMF (2.5 cm^3) was stirred at 120 °C for 20 h, then cooled to room temperature, diluted with AcOEt (50 cm^3), washed with saturated aqueous Na_2CO_3 (30 cm^3), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with 3:1 cyclohexane-AcOEt to afford **2** (197 mg, 86%) as a syrup; $[\alpha]_D$ = + 6.0 (*c* 1, $CHCl_3$). ^{1}H NMR: δ 7.45-7.21 (15 H, m, 3 Ph), 4.90-4.55 (8 H, m, 3 PhC*H*$_2$ and OC*H*$_2$OMe), 4.21 (1 H, ddd, $J_{3,4}$ = 4.0 Hz, $J_{2,3}$ = 8.5 Hz, 3-H), 3.77 (1 H, m, 5-H), 3.70 (1 H, ddd, *J* = 3.1, 7.0 Hz, 7-H), 3.64 (1 H, dd, $J_{4,5}$ = 2.2 Hz, 4-H), 3.59 (1 H, m, 1-H), 3.55 (1 H, t, $J_{6,7}$ = 7.0 Hz, 6-H), 3.51 and 3.38 (2 H, 2 m, 8-H), 3.36 (3 H, s, C*H*$_3$), 1.97-1.70 (2 H, m, 2-H). ^{13}C NMR: δ 138.0 (*C*), 128.5 (*C*H), 128.4 (*C*H), 128.0 (*C*H), 127.7 (*C*H), 96.5 (*C*H$_2$), 77.6 (*C*H), 75.8 (*C*H), 75.6 (*C*H), 74.3 (*C*H$_2$), 73.3 (*C*H), 72.1 (*C*H$_2$), 71.7 (*C*H$_2$), 70.6 (*C*H), 64.0 (*C*H$_2$), 55.2 (*C*H$_3$), 51.3 (*C*H$_2$), 29.6 (*C*H$_2$). MALDI-TOF MS: 585.5 (M^+ + K). Anal. Calcd. for $C_{31}H_{37}N_3O_6$: C, 67.99; H, 6.81; N, 7.67. Found: C, 68.30; H, 6.93; N, 7.52.

8-[1-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-1*H*-1,2,3-triazol-4-yl]-3,7-anhydro-4,5,6-tri-*O*-benzyl-1,2,8-trideoxy-1-*O*-methoxymethyl-D-*glycero*-D-*talo*-octitol (3).



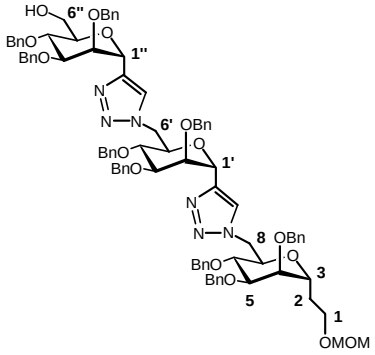
A mixture of sugar acetylene **1** (120 mg, 0.26 mmol), sugar azide **2** (129 mg, 0.24 mmol), *N*,*N*-diisopropylethylamine (170 mm^3, 1.00 mmol), CuI (10 mg, 0.05 mmol), and toluene (3 cm^3) was stirred in the dark at rt for 18 h, then diluted with AcOEt (50 cm^3), washed with saturated aqueous $NaHCO_3$ (30 cm^3), dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel with cyclohexane-AcOEt (from 2:1 to 1:1) to give first unreacted acetylene **1** (15 mg, 12%). Eluted second was **3** (190 mg, 80%) as an amorphous solid; $[\alpha]_D$ = +22.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR selected data: δ 7.68 (1 H, s, triazole 4-H), 5.24 (1 H, d, $J_{1',2'}$ = 1.8 Hz, 1'-H), 4.20 (1 H, ddd, *J* = 4.0, 4.0, 6.5 Hz, 3-H), 3.36 (3 H, s, CH_3), 2.39 (1 H, br s, OH), 1.97-1.70 (2 H, m, 2-H). ^{13}C NMR selected data: δ 144.6 (*C*, triazole 4-C), 123.9 (*C*H, triazole 5-C), 96.4 (O*C*H_2O), 71.1 (*C*H, 1'-C), 70.3 (*C*H, 3-C), 55.3 (*C*H_3), 29.7 (*C*H_2, 2-C). MALDI-TOF MS: 1027.8 (M^+ + Na). Anal. Calcd. for $C_{60}H_{67}N_3O_{11}$: C, 71.62; H, 6.71; N, 4.18. Found: C, 71.83; H, 6.66; N, 3.89.

8-[1-(6-azido-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-mannopyranosyl)-1*H*-1,2,3-triazol-4-yl]-3,7-anhydro-4,5,6-tri-*O*-benzyl-1,2,8-trideoxy-1-*O*-methoxymethyl-D-*glycero*-D-*talo*-octitol (4).



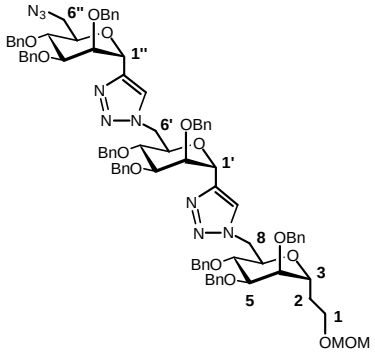
The replacement of the hydroxy group of **3** (180 mg, 0.18 mmol) with an azido group was performed as described for the synthesis of **2** to give, after column chromatography on silica gel (2:1 cyclohexane-AcOEt) azide **4** as an amophous solid (150 mg, 81%); $[\alpha]_D$ = +13.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR selected data: δ 7.73 (1 H, s, triazole 4-H), 5.23 (1 H, d, $J_{1',2'}$ = 1.8 Hz, 1'-H), 4.22 (1 H, ddd, *J* = 4.0, 4.0, 6.0 Hz, 3-H), 3.30 (3 H, s, CH_3), 1.97-1.70 (2 H, m, 2-H). ^{13}C NMR selected data: δ 144.5 (*C*, triazole 4-C), 124.1 (*C*H, triazole 5-C), 96.4 (O*C*H_2O), 70.9 (*C*H, 1'-C), 70.8 (*C*H, 3-C), 55.3 (*C*H_3), 29.6 (*C*H_2, 2-C). MALDI-TOF MS: 1070.2 (M^+ + H + K). Anal. Calcd. for $C_{60}H_{66}N_6O_{10}$: C, 69.88; H, 6.45; N, 8.15. Found: C, 70.11; H, 6.77; N, 8.43.

Trimannoside (5).



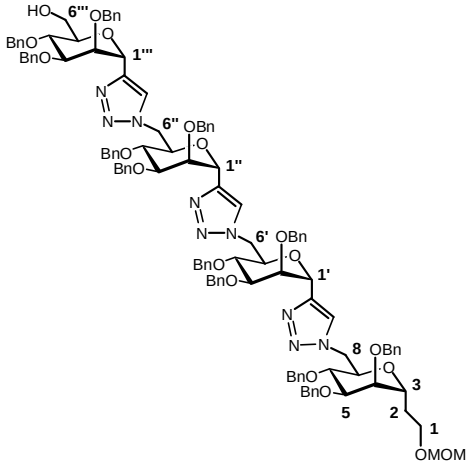
The coupling of azide **4** (120 mg, 0.12 mmol) with sugar acetylene **1** (60 mg, 0.13 mmol) was performed as described for the synthesis of **3** to give, after column chromatography on silica gel (from 3:2 to 1:1 cyclohexane-AcOEt), **5** as an amophous solid (150 mg, 87%); $[\alpha]_D$ = +18.5 (*c* 1, $CHCl_3$). ^{1}H NMR selected data: δ 7.83 and 7.52 (2 H, 2 s, triazole 4-H), 5.29 and 5.22 (2 H, 2 d, *J* = 1.7 Hz, 1'-H, 1''-H), 4.24 (1 H, ddd, *J* = 4.0, 4.0, 6.5 Hz, 3-H), 3.28 (3 H, s, CH_3), 2.33 (1 H, br t, OH), 1.83-1.70 (2 H, m, 2-H). ^{13}C NMR selected data: δ 144.6 and 143.9 (*C*, triazole 4-C), 124.2 and 124.0 (*C*H, triazole 5-C), 96.4 (O*C*H_2O), 71.4 and 70.6 (*C*H, 1'-C, 1''-C and 3-C), 55.2 (*C*H_3), 29.7 (*C*H_2, 2-C). MALDI-TOF MS: 1513.1 (M^+ + H + Na). Anal. Calcd. for $C_{89}H_{96}N_6O_{15}$: C, 71.75; H, 6.50; N, 5.64. Found: C, 71.90; H, 6.27; N, 5.37.

Trimannoside azide (6).



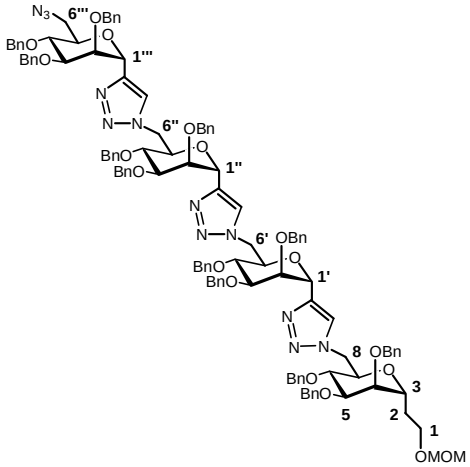
The replacement of the hydroxy group of **5** (110 mg, 0.074 mmol) with an azido group was performed as described for the synthesis of **2** to give, after column chromatography on silica gel (3:1 cyclohexane-AcOEt), azide **6** as an amophous solid (95 mg, 85%); $[\alpha]_D$ = +12.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR selected data: δ 7.91 and 7.56 (2 H, 2 s, triazole 4-H), 5.28 and 5.24 (2 H, 2 d, *J* = 1.7 Hz, 1'-H, 1''-H), 4.23 (1 H, ddd, *J* = 6.0, 6.0, 7.5 Hz, 3-H), 3.29 (3 H, s, CH_3), 1.80-1.70 (2 H, m, 2-H). ^{13}C NMR selected data: δ 144.5 and 143.9 (*C*, triazole 4-C), 124.5 and 124.2 (*C*H, triazole 5-C), 96.4 (O*C*H_2O), 71.0, 70.7 and 70.5 (*C*H, 1'-C, 1''-C and 3-C), 55.2 (*C*H_3), 29.7 (*C*H_2, 2-C). MALDI-TOF MS: 1537.9 (M^+ + H + Na). Anal. Calcd. for $C_{89}H_{95}N_9O_{14}$: C, 70.57; H, 6.32; N, 8.32. Found: C, 70.73; H, 6.11; N, 8.54.

Tetramannoside (7).



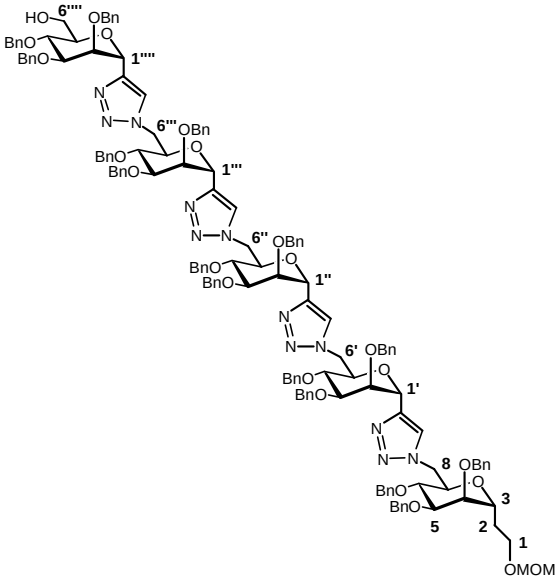
The coupling of azide **6** (80 mg, 0. 053 mmol) with sugar acetylene **1** (27 mg, 0.058 mmol) was performed as described for the synthesis of **3** to give, after column chromatography on silica gel (2:1 cyclohexane-AcOEt), **7** as an amophous solid (94 mg, 90%); $[\alpha]_D$ = +17.8 (*c* 1.0, $CHCl_3$). ^1H NMR selected data: δ 7.82, 7.71 and 7.46 (3 H, 3 s, triazole 4-H), 5.31, 5.28 and 5.24 (3 H, 3 d, *J* = 1.7 Hz, 1'-H, 1''-H, 1'''-H), 4.23 (1 H, ddd, *J* = 4.5, 4.5, 7.5 Hz, 3-H), 3.25 (3 H, s, CH_3), 2.33 (1 H, br t, OH), 1.80-1.67 (2 H, m, 2-H). MALDI-TOF MS: 1996.5 (M^+ + Na). Anal. Calcd. for $C_{118}H_{125}N_9O_{19}$: C, 71.82; H, 6.38; N, 6.39. Found: C, 71.54; H, 6.61; N, 6.73.

Tetramannoside azide (8).



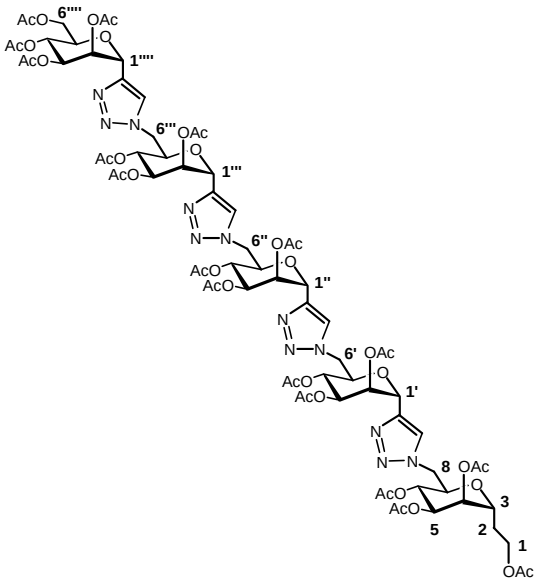
The replacement of the hydroxy group of **7** (50 mg, 0.025 mmol) with an azido group was performed as described for the synthesis of **2** to give, after column chromatography on silica gel (3:1 cyclohexane-AcOEt), azide **8** as an amophous solid (40 mg, 79%); $[\alpha]_D$ = +12.3 (*c* 1.0, $CHCl_3$). ^1H NMR selected data: δ 7.90, 7.73 and 7.45 (3 H, 3 s, triazole 4-H), 5.31 and 5.27 (3 H, 3 d, *J* = 1.8 Hz, 1'-H, 1''-H, 1'''-H), 4.23 (1 H, ddd, *J* = 4.5, 4.5, 7.5 Hz, 3-H), 3.25 (3 H, s, CH_3), 1.80-1.67 (2 H, m, 2-H). ^{13}C NMR selected data: δ 144.5 and 143.9 (*C*, triazole 4-C), 124.5 and 123.9 (*C*H, triazole 5-C), 96.4 (O*C*H_2O), 55.2 (*C*H_3), 29.6 (*C*H_2, 2-C). MALDI-TOF MS: 2021.4 (M^+ + Na). Anal. Calcd. for $C_{118}H_{124}N_{12}O_{18}$: C, 70.92; H, 6.25; N, 8.41. Found: C, 70.67; H, 6.19; N, 8.33.

Pentamannoside (9).



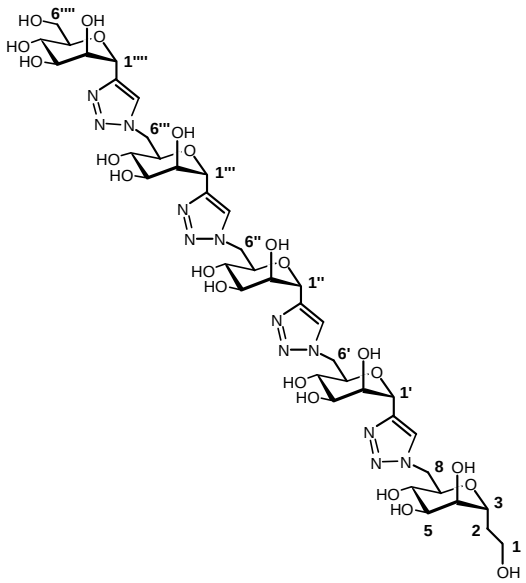
The coupling of azide **8** (28 mg, 0. 014 mmol) with sugar acetylene **1** (7 mg, 0.015 mmol) was performed as described for the synthesis of **3** to give, after column chromatography on silica gel (from 2:1 to 1:1 cyclohexane-AcOEt), **9** as an amophous solid (29 mg, 84%); $[\alpha]_D$ = +17.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR selected data: δ 7.84, 7.63, 7.60 and 7.44 (4 H, 4 s, triazole 4-H), 5.41, 5.39, 5.30 and 5.27 (4 H, 4 d, *J* = 1.7 Hz, 1'-H, 1"-H, 1'"-H, 1""-H), 4.24 (1 H, ddd, *J* = 4.5, 4.5, 7.5 Hz, 3-H), 3.22 (3 H, s, CH_3), 2.38 (1 H, br s, OH), 1.80-1.67 (2 H, m, 2-H). ^{13}C NMR selected data: δ 144.7 and 143.7 (*C*, triazole 4-C), 124.5, 124.3 and 123.9 (*C*H, triazole 5-C), 96.3 (O*C*H_2O), 71.5, 71.4, 71.2, 71.0 and 70.6 (*C*H, 1'-C, 1"-C, 1'"-C, 1""-C and 3-C), 55.1 (*C*H_3), 29.7 (*C*H_2, 2-C). MALDI-TOF MS: 1027.8 (M^+ + Na). Anal. Calcd. for $C_{147}H_{154}N_{12}O_{23}$: C, 71.86; H, 6.32; N, 6.84;. Found: C, 71.61; H, 6.27; N, 7.07.

Peracetylated pentamannoside (10).



To a solution of **9** (15 mg, 6 μmol) in anhydrous CH_2Cl_2 (2 cm^3) was added trifluoroacetic acid (100 mm^3). The solution was kept at rt for 3 h, then concentrated and dried under high vacuum. The ^1H NMR analysis of the crude product proved the absence of the methoxymethyl protecting group. To a stirred, cooled (–60 °C) solution of the residue in anhydrous CH_2Cl_2 (2 cm^3) was added a 1 M solution of BCl_3 in CH_2Cl_2 (480 mm^3, 0.48 mmol). The solution was stirred at –60 °C for 1 h and, after an additional 1 h stirring at 0 °C, diluted with MeOH (0.5 cm^3), stirred at 0 °C for 15 min, diluted with triethylamine (0.5 cm^3), concentrated, and dried under high vacuum to give a white solid. A suspension of the residue in pyridine (2 cm^3) and acetic anhydride (0.5 cm^3) was stirred at rt for 18 h, then diluted with MeOH (1 cm^3) and concentrated. The residue was eluted from a column of silica gel (3:1 CH_2Cl_2–AcOEt, then AcOEt) to give **10** (9 mg, 83%); $[\alpha]_D$ = +3.3 (*c* 0.8, $CHCl_3$). ^1H NMR selected data: δ 8.05, 7.81, 7.79, and 7.69 (4 H, 4 s, triazole 4-H), 5.86, 5.85, 5.78 and 5.77 (4 H, 4 d, *J* = 1.9 Hz, 1'-H, 1"-H, 1'"-H, 1""-H), 4.24 (1 H, ddd, *J* = 4.5, 7.5 Hz, 3-H), 1.64-1.58 (2 H, m, 2-H). ^{13}C NMR selected data: δ 142.6, 142.1 and 141.7 (*C*, triazole 4-C), 124.4 and 124.3 (*C*H, triazole 5-C), 68.4, 68.0, 67.7, 66.6 and 64.9 (*C*H, 1'-C, 1"-C, 1'"-C, 1""-C and 3-C), 29.7 (CH_2, 2-C). MALDI-TOF MS: 1798.9 (M^+ + H + Na). Anal. Calcd. for $C_{74}H_{94}N_{12}O_{39}$: C, 50.06; H, 5.34; N, 9.47. Found: C, 49.93; H, 5.41; N, 9.66.

Free hydroxy pentamannoside (11).



To a solution of **10** (9 mg, 0.005 mmol) in MeOH (1 cm^3) was added a ca. 0.2 M solution of NaOMe in MeOH (0.2 cm^3, prepared from Na and MeOH immediately before the use) and, after 1 h, H_2O (0.3 cm^3). The solution was kept at rt for an additional 1 h, then neutralized with Dowex 50X2-400 resin (H^+ form, activated and washed with H_2O and MeOH immediately before the use). The resin was washed with H_2O and MeOH, the solution was concentrated and dried under high vacuum to give **11** (5 mg, 93%) as an amorphous solid; $[\alpha]_D$ = +0.6 (*c* 0.5, H_2O). ^1H NMR (D_2O)

selected data: δ 8.00, 7.52, 7.32, and 7.20 (4 H, 4 s, triazole 4-H), 5.13, 5.11, 5.1 and 5.08 (4 H, 4 d, *J* = 1.9 Hz, 1'-H, 1''-H, 1'''-H, 1''''-H).

Typical procedure for microwave assisted coupling for the synthesis of compounds 3, 5, 7, 9. A mixture of sugar acetylene (0.1 mmol), sugar azide (0.1 mmol), *N*,*N*-diisopropylethylamine (0.2 mmol), CuI (5 mg, 0.026 mmol) and DMF (0.6 cm^3) in a vial sealed with a Teflon septum and aluminium crimp was subjected to microwave irradiation for 5 min at 100 °C. The work-up and purification were identical to the ones used in the conventional coupling procedure.

Typical procedure for microwave assisted alcohol-to-azide conversion for the synthesis of compounds 4, 6, 8. A mixture of sugar alcohol (0.1 mmol), diphenyl phosphoryl azide (0.3 mmol), 1,8-diazabicyclo[5.4.0.]undec-7-ene (0.2 mmol) and anhydrous DMF (0.6 cm^3) in a vial sealed with a Teflon septum and aluminium crimp was subjected to microwave irradiation for 2 h at 120 °C. The work-up and purification were identical to the ones used in the conventional alcohol-to-azide conversion procedure.

References

19 W. L. F Armarego, D. D. Perrin, *Purification of Laboratory Chemicals,* 4th ed., Butterworth-Heinemann: Oxford, 1996.

20 W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923-2925.

21 The compound **13** was already reported in the literature; however only its ^1H NMR data were described (T. Nishikawa, M. Ishikawa and M. Isobe, *Synlett*, 1999, 123-125.