Supporting Information for

Concise assembly of linear α(1→6)-linked octamannan fluorescent probe

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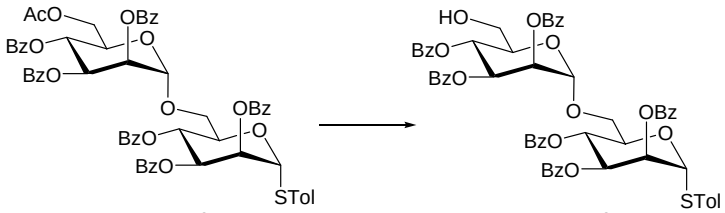
General Methods.

The reactions were performed under a dry argon atmosphere and reaction temperatures were measured externally. Anhydrous solvents over molecular sieves were purchased from Fluka and used as such in reactions. Whenever necessary, compounds and starting materials were dried by azeotropic removal of water with toluene under reduced pressure. The reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel ($60F_{254}$) plates (0.25 mm) from E. Merck and visualized using UV light (254 nm) and/or heating after spray with $(NH_4)_2SO_4$ solution (150 g ammonium sulfate, 30 mL H_2SO_4, 750 mL H_2O). All solvents used for work-up and chromatography were reagent grade from Fischer. Flash column chromatography was carried out on silica gel 60 (230-400 Mesh). ^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively on JEOL300 Eclipse spectrometer. The coupling constants (*J*) are reported in Hz and chemical shifts (δ) are in ppm relative to a residual solvent peak ($CDCl_3$) or an internal standard (TMS). The FABMS and HR-ESIMS spectra were recorded at Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign on Waters 70E-SE-4F, Waters Q-Tof Ultima API and Voyager-DE STR instruments respectively.

Synthesis of compounds **5**, **6**, **7**, **8** and **9** were carried out as earlier described by us and their analytical and spectral data were found similar.[1]

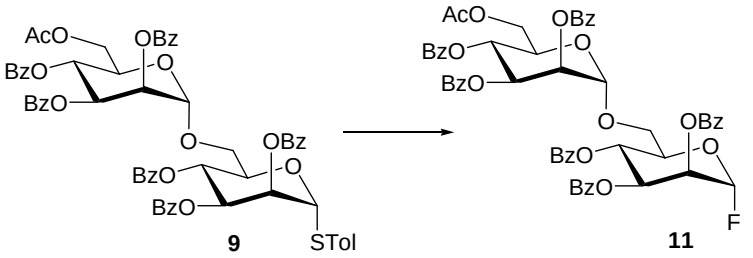
p-Thiotolyl 2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (10)



Acetyl chloride (0.6 mL) was added to a solution of disaccharide **9** (6.00 g, 5.38 mmol) in dry CH_2Cl_2 (60 mL) and dry MeOH (60 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum, and the resulting residue was purified by silica gel 60 column chromatography using mobile phase cyclohexane-EtOAc (3:1) to furnish pure disaccharide **10** (5.28 g, quantitative yield) as a white foam. m.p. 85-88 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.17 (2H, m, Ar), 8.04 (6H, m, Ar), 7.87 (4H, m, Ar), 7.50 (14H, m, Ar), 7.29 (6H, m, Ar) 7.19 (2H, d, *J* = 8.2 Hz, Ar), 6.16 (1H, t, *J* = 9.9 Hz), 6.04 (2H, m), 5.89 (1H, dd, *J* = 3.0, 10.2 Hz), 5.81 (2H, m), 5.73 (1H, s, H-1), 5.14 (1H, s, H-1′), 4.94 (1H, dd, *J* = 3.0, 10.0 Hz), 4.13 (1H, dd, *J* = 4.7, 11.0 Hz), 3.94 (1H, dd, *J* = 2.7, 9.9 Hz), 3.78 (1H, dd, *J* = 1.6, 11.0 Hz), 3.53 (2H, m), 2.34 (3H, s, $PhCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.75, 165.66, 165.58, 165.25 (C=O), 138.58, 133.79, 133.61, 133.35, 133.22, 132.78, 130.28, 130.11, 130.02, 129.96, 129.79, 129.41, 129.35, 129.23, 129.06, 129.99, 128.89, 128.70, 128.62, 128.43 (Ar), 98.20 (C-1′), 86.75 (C-1), 72.09, 71.05, 70.71, 70.60, 70.38, 69.80, 67.25, 67.16, 67.01, 61.06, 21.22 ($PhCH_3$). HR-ESIMS: *m/z* 1095.2874 $[M+Na]^+$ calcd for $C_{61}H_{52}O_{16}SNa$, found 1095.2871.

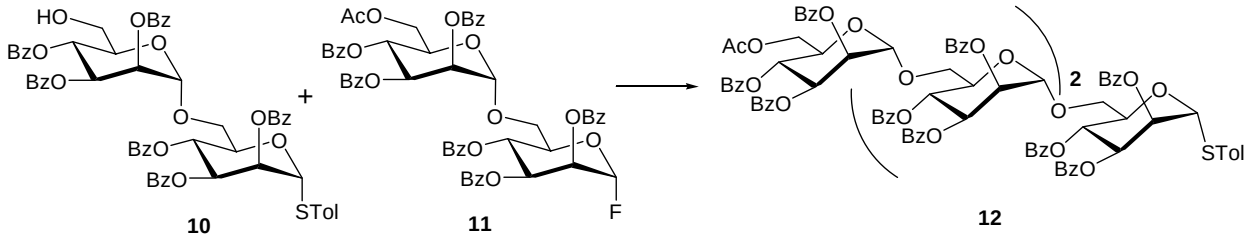
[1]Pathak, A. K.; Yerneni, C. K.; Young, Z.; Pathak, V. *Org. Lett.* **2008**, *10*, 145-148.

6-*O-Acetyl-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl fluoride (11)*



DAST (1.06 mL, 8.74 mmol) was added to a solution of **9** (6.50 g, 5.82 mmol) in 60 mL dry CH_2Cl_2 at 0 ^oC, followed by the addition of NBS (1.55 g, 8.74 mmol). The reaction mixture was stirred overnight, during which time it was allowed to rise to room temperature. The solvent was removed under vacuum, and the resulting residue was dissolved in EtOAc. The solution was washed with saturated aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel 60 column chromatography using mobile phase cyclohexane-EtOAc (3:1) to furnish pure fluoride **11** (5.35 g, 91% yield) as a white foam. m.p. 90-93 ^oC. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.18 (2H, m, Ar), 8.03 (6H, m, Ar), 7.86 (4H, m, Ar), 7.44 (18H, m, Ar), 6.22 (1H, dd, J = 9.9, 10.2 Hz, H-4), 5.92 (5H, m), 5.80 (1H, dd, J = 1.9, 3.0 Hz), 5.14 (1H, d, J = 1.4 Hz, H-1'), 4.54 (1H, m), 4.14 (4H, m), 3.84 (1H, dd, J = 1.9, 11.2 Hz), 1.90 (3H, s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.52, 165.68, 165.55, 165.46, 165.39, 165.35, 165.28 (C=O), 138.81, 133.65, 133.57, 133.44, 133.22, 130.21, 130.02, 129.96, 129.89, 129.79, 129.39, 129.34, 129.12, 128.99, 128.89, 128.83, 128.67, 128.56, 128.46, 128.43 (Ar), 105.21 (C-1, d, $J_{C,F}$ = 222.1 Hz), 98.11 (C-1′), 71.78, 70.12 (C-3, d, $J_{C,F}$ = 9.70 Hz), 69.39, 68.88 (C-5), 68.34, 66.40 (C-4), 66.27 (C-2, d, $J_{C,F}$ = 71.0 Hz), 62.60, 20.56 (CH_3). HR-ESIMS: *m/z* 1033.2695 $[M+Na]^+$ calcd for $C_{56}H_{47}O_{17}FNa$, found 1033.2705.

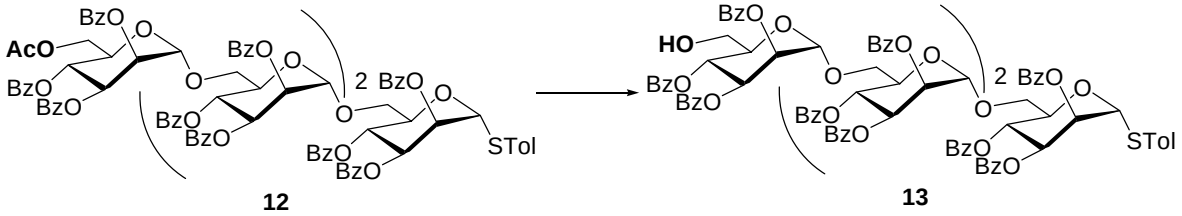
p-Thiotolyl 6-O-acetyl-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (12)



$AgClO_4$ (1.82 g, 8.82 mmol) and $SnCl_2$ (1.67 g, 8.82 mmol) were added to a stirred suspension of freshly activated 4 Å molecular sieves (500 mg) in 60 mL dry CH_2Cl_2. The mixture was cooled to 0 ^oC before a solution of thioglycoside **10** (4.73 g, 4.41 mmol), glycosyl fluoride **11** (4.90 g, 4.85 mmol) and 2,6-lutidine (0.51 mL, 4.41 mmol) in dry CH_2Cl_2 (10 mL) were added through a cannula. The reaction mixture was stirred overnight during which time it was allowed to rise to room temperature. The mixture was filtered through a Celite pad, solvent was removed under vacuum, and the resulting residue was dissolved in EtOAc. The solution was washed with a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel 60 column chromatography using mobile phase cyclohexane-EtOAc (2:1) to furnish **12** (7.14 g, 80% yield) as a white foam. m.p. 137-140 ^oC. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.21 (6H, m, Ar), 8.08 (10H, m, Ar), 7.94 (6H, d, *J* = 7.9 Hz, Ar), 7.87 (2H, m, Ar), 7.53 (25H, m, Ar),7.31 (16H, m, Ar), 7.16 (2H, d, *J* = 7.9 Hz), 6.42 (1H, dd, *J* = 9.7, 10.3 Hz), 6.18 (1H, dd, *J* = 9.9, 10.2 Hz), 6.12 (3H, m), 5.97 (5H, m), 5.79 (2H, m), 5.70 (1H, m), 5.25 (1H, s), 5.15 (1H, m), 5.02 (1H, s), 4.85 (1H, s), 4.40 (1H, dd, *J* = 3.9, 11.1 Hz), 4.21 (4H, m), 3.93 (4H, m), 3.46 (2H, m), 2.25 (3H, s, $PhCH_3$), 1.92 (3H, s, OAc). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.52 ($OCOCH_3$), 165.79, 165.72, 165.62, 165.48, 165.33, 165.24, 165.21

(OCOPh), 138.49, 133.65, 133.57, 133.50, 133.31, 133.17, 132.90, 130.26, 130.16, 130.04, 129.97, 129.93, 129.81, 129.44, 129.38, 128.95, 128.84, 128.68, 128.62, 128.42 (Ar), 98.36, 97.99, 97.79 (C-1′, C-1″, C-1‴), 86.91 (C-1), 77.40, 72.14, 71.07, 70.72, 70.60, 70.41, 70.25, 70.18, 69.52, 69.45, 68.77, 67.00, 66.79, 66.70, 66.48, 66.00, 62.50, 31.01, 21.22 ($PhCH_3$), 20.59 (CH_3). FABMS: *m/z* 2085.5 $[M+Na]^+$ calcd for $C_{117}H_{98}O_{33}SNa$, found 2085.0

p-Thiotolyl 2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (13)

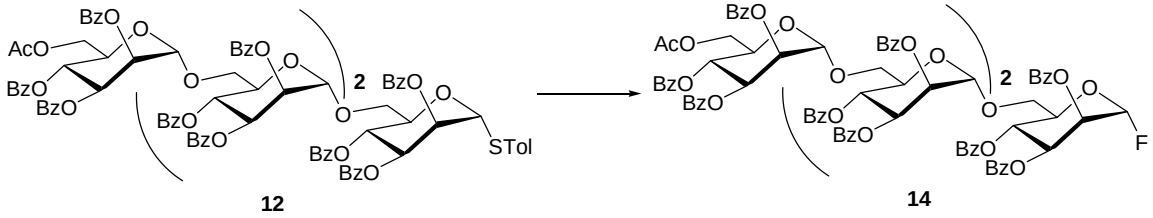


12 **13**

Acetyl chloride (0.56 mL) was added to the solution of tetrasaccharide **12** (3.00 g, 1.46 mmol) in dry CH_2Cl_2 (40 mL) and dry MeOH (40 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum and the resulting residue was purified by Silica gel 60 column chromatography using mobile phase cyclohexane-EtOAc (2:1) to furnish pure tetrasaccharide **13** (2.72 g, 96% yield) as a white foam. m.p. 142-145 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (6H, m, Ar), 8.07 (8H, m, Ar), 7.93 (10H, m, Ar), 7.41 (38H, m, Ar), 7.14 (2H, d, *J* = 8.3 Hz, Ar), 6.39 (1H, t, *J* = 10.0 Hz), 6.15 (1H, t, *J* = 10.0 Hz), 6.07 (4H, m), 5.95 (3H, m), 5.78 (2H, m), 5.77 (1H, s, H-1), 5.68 (1H, m), 5.22 (1H, s, H-1′), 5.12 (1H, dd, *J* = 2.5, 10.2 Hz), 5.01 (1H, s, H-1″), 4.81 (1H, s, H-1‴), 4.37 (1H, dd, *J* = 4.1, 11.3 Hz), 4.23 (2H, m), 3.92 (2H, m), 3.81 (2H, m), 3.43 (4H, m), 2.60 (1H, br s), 2.23 (3H, s, $PhCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.87, 165.76, 165.71, 165.59, 165.46, 165.34, 165.22 (C=O), 138.46, 133.80,

133.63, 138.48, 133.28, 133.12, 132.89, 130.15, 130.02, 129.92, 129.78, 129.42, 129.23, 129.13, 128.92, 128.82, 128.70, 128.61, 128.41 (Ar), 98.30, 98.18, 97.78 (C-1′, C-1″, C-1‴), 86.86 (C-1), 72.10, 70.98, 70.64, 70.56, 70.35, 69.75, 69.46, 67.17, 66.92, 66.75, 66.42, 66.03, 65.94, 60.92 (CH_2OH), 21.19 ($PhCH_3$). FABMS: (*m/z*): 2043.5 $[M+Na]^+$ calcd for $C_{115}H_{96}O_{32}SNa$, found 2043.3.

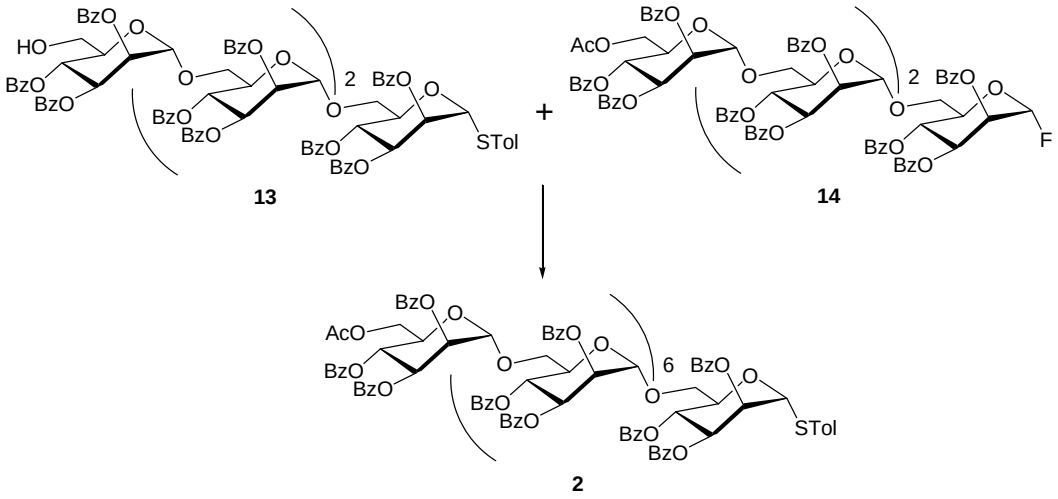
6-O-Acetyl-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl fluoride (14)



Tetrasaccharide **12** (3.00 g, 1.46 mmol) was dissolved in 40 mL of dry CH_2Cl_2 and DAST (0.26 mL, 2.18 mmol) was added followed by NBS (388 mg, 2.18 mmol) at 0 ^oC. The reaction mixture was stirred overnight, during which time it was allowed to rise to room temperature. The solvent was removed under vacuum and the resulting residue was dissolved in EtOAc. The solution was washed with saturated aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated and the residue was purified by silica gel 60 column chromatography using mobile phase cyclohexane-EtOAc (2.5:1) to furnish **14** (2.40 g, 84% yield) as a white foam. m.p. 137-140 ^oC. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.07 (14H, m, Ar), 7.88 (8H, m, Ar), 7.41 (38H, m, Ar), 6.42 (1H, t, *J* = 9.9 Hz), 5.99 (10H, m), 5.73 (1H, dd, *J* = 1.9, 3.0 Hz), 5.54 (1H, dd, *J* = 1.6, 3.0 Hz), 5.24 (1H, d, *J* = 1.4 Hz, H-1′), 4.99 (1H, d, *J* = 1.6 Hz, H-1″), 4.83 (1H, d, *J* = 1.3 Hz, H-1‴), 4.73 (1H, d, *J* = 10.1 Hz), 4.29 (3H, m), 4.14 (2H, m), 3.93 (4H, m), 3.50 (1H, d, *J* = 9.6 Hz), 3.43 (1H, d, *J* = 9.1 Hz), 1.89 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.52, 165.72,

165.62, 165.58, 165.51, 165.46, 165.23 (C=O), 133.76, 133.63, 133.53, 133.37, 133.17, 130.27, 130.03, 129.90, 129.81, 129.52, 129.45, 129.39, 129.21, 129.02, 128.93, 128.80, 128.66, 128.61, 128.43 (Ar), 105.39 (C-1, d, $J_{C,F}$ = 223.0 Hz), 98.38 (C-1′), 97.92 (C-1″), 97.56 (C-1‴), 70.01, 70.46, 70.39, 70.26, 70.20 (C-3, d, J = 8.6 Hz), 69.75, 69.43, 69.99, 68.78, 68.46, 67.01, 66.70, 66.08, 66.05 (C-2, d, J = 75.5 Hz), 62.52, 20.58 (CH_3). FABMS: *m/z* 1981.5 $[M+Na]^+$ calcd for $C_{110}H_{91}O_{33}FNa$, found 1981.7.

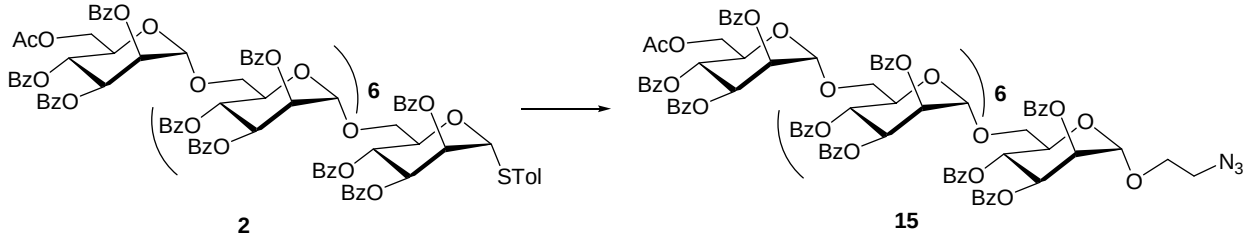
p-Thiotolyl 6-O-acetyl-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (2)



A dry CH_2Cl_2 (25 mL) solution of thioglycoside **13** (2.50 g, 1.24 mmol) and mannosyl fluoride **14** (2.91 g, 1.49 mmol) with freshly activated 4 Å molecular sieves (600 mg) were cooled to 0^oC. Cp_2HfCl_2 (15 mg, 0.05 mmol) was added to this mixture, followed by AgOTf (24 mg, 0.10 mmol). The reaction mixture was stirred overnight during which time it was allowed to rise to room temperature. The mixture was filtered through a Celite pad, the solvent was removed under vacuum, and the resulting residue was dissolved in chloroform. The solution was washed with

saturated aqueous $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel 60 column chromatography using mobile phase cyclohexane-EtOAc (1.5:1) to furnish **2** (2.98 g, 61% yield) as a white foam. m.p. 138-141 ^oC. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.14 (32H, m, Ar), 7.89 (15H, m, Ar), 7.42 (75H, m, Ar), 7.15 (2H, d, *J* = 8.2 Hz, Ar), 6.42 (1H, dd, *J* = 9.9, 10.2 Hz), 6.22 (5H, m), 6.10 (2H, m), 5.96 (10H, m), 5.78 (1H, s), 5.77 (1H, m), 5.73 (1H, m), 5.27 (1H, s), 5.14 (1H, m), 5.07 (1H, s), 5.01 (1H, s), 5.00 (1H, s), 4.99 (1H, s), 4.96 (1H, d, *J* = 1.4 Hz), 4.83 (1H, s), 4.39 (1H, dd, *J* = 4.1, 11.3 Hz), 4.19 (8H, m), 3.86 (7H, m), 3.56 (1H, d, *J* = 10.4 Hz), 3.38 (4H, m), 2.23 (3H, s, $PhCH_3$), 1.91 (3H, s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.52, 165.80, 165.72, 165.67, 165.58, 165.47, 165.37, 165.26, 165.20 (C=O), 138.50, 133.64, 133.44, 138.28, 133.08, 132.95, 130.60, 130.25, 130.18, 130.03, 129.97, 129.80, 129.55, 129.48, 129.41, 129.35, 129.31, 129.15, 128.95, 128.79, 128.61, 128.40 (Ar), 98.41, 97.99 (Anomeric C's), 86.89 (C-1), 72.10, 71.09, 70.66, 70.22, 69.58, 69.32, 68.73, 66.91, 66.68, 66.62, 66.38, 65.97, 65.84, 62.42, 21.21 ($PhCH_3$), 20.57 (CH_3). MALDI-TOF: *m/z* 3983.9 $[M+Na]^+$ calcd for $C_{225}H_{186}O_{65}SNa$, found 3983.4.

1-Azidoethyl 6-O-acetyl-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (15)

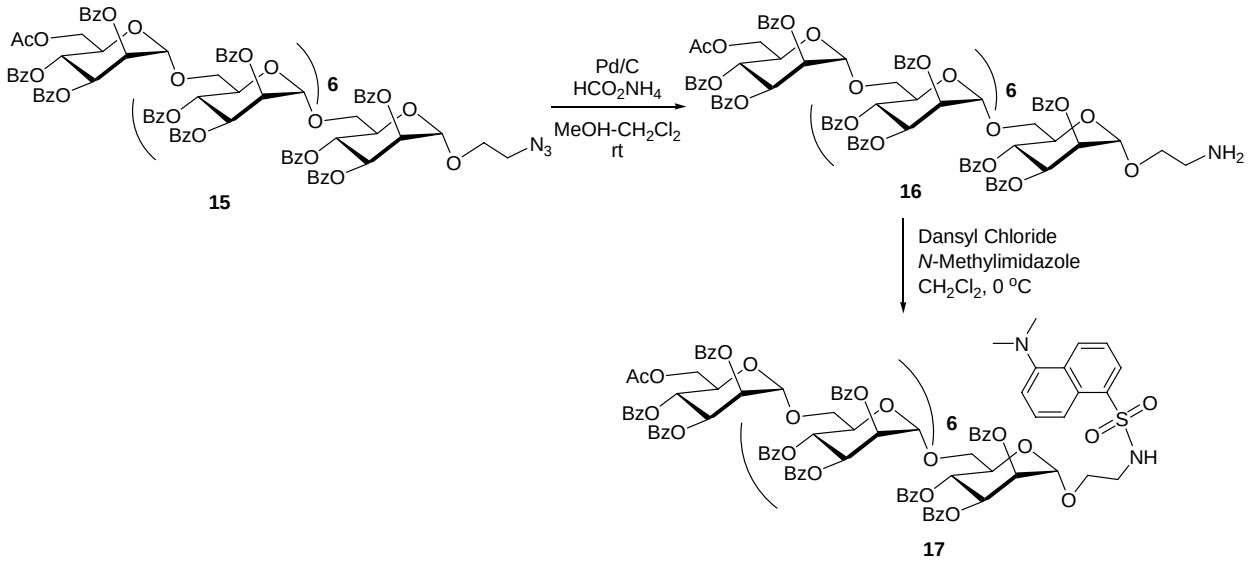


2 **15**

To a solution of thiooctasaccharide **2** (500 mg, 0.13 mmol) in dry CH_2Cl_2 (10 mL) were added 1-azidoethanol[2] (0.01 mL, 0.18 mmol) and 100 mg of 4Å molecular sieves. The mixture was stirred for 5 minutes at room temperature and the solution was cooled to -4 °C. NIS (38.0 mg, 0.15 mmol) and neat TfOH (0.002 mL, 0.03 mmol) were added and the reaction was stirred for 45 minutes at -4 °C. The temperature of the reaction mixture was raised to 0° C and 20 mL of saturated aqueous $NaHCO_3$ was added. It was extracted with 2x15 mL of $CHCl_3$. The organic layer was washed with saturated aqueous sodium thiosulfate solution. The organic layer was dried over Na_2SO_4 and concentrated to syrup. The residue was purified by silica gel 60 column chromatography using mobile phase cyclohexane-EtOAc (1.5:1) to furnish **15** (450 mg, 89% yield) as a colorless solid. m.p. 163-165 ^oC. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.16 (34H, m, Ar), 7.91 (16H, m, Ar), 7.44 (70H, m, Ar), 6.29-5.91 (23H, m, Ar), 5.79 (2H, m), 5.32 (1H, s), 5.27 (1H, s), 5.01 (12H, m), 4.65 (1H, m), 4.09 (10H, m), 3.52 (10H, m), 1.93 (3H, s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.52, 165.87, 165.69, 165.59, 165.51, 165.41, 165.28, 165.20 (C=O), 138.65, 133.48, 133.62, 130.19, 129.99, 129.81, 129.57, 129.42, 129.38, 129.16, 128.93, 128.63, 128.42 (Ar), 98.41, 98.07, 77.42, 70.73, 70.52, 70.27, 70.01, 69.84, 69.60, 69.36, 68.78, 67.33, 66.84, 66.67, 66.45, 66.34, 65.87, 62.46, 50.60 (CH_2N_3), 20.59 (CH_3). MALDI-TOF: *m/z* 3947.7 $[M+Na]^+$ calcd for $C_{220}H_{183}N_3O_{66}Na$, found 3947.1.

[2] Smith, R. H.; Mehl, A. F.; Shantz Jr., D. L.; Chmurny, G. N.; Michejda, C. J. *J. Org. Chem.* **1988**, *53*, 1467-1471.

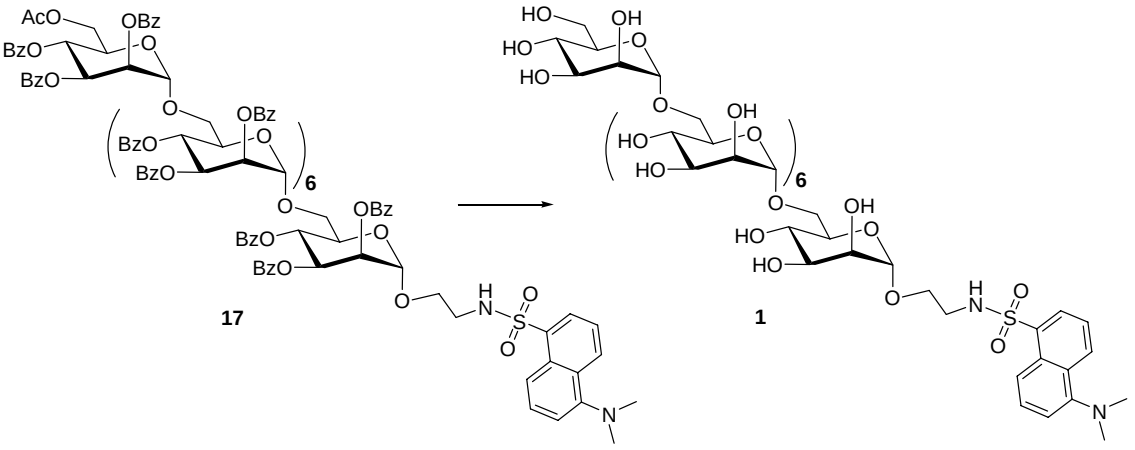
(5-N,N-Dimethylaminonaphthalene-1-sulfonamidoethyl) 6-O-acetyl-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (17)



To a solution of 1-azidoethyl octasacharide **15** (450 mg, 0.11 mmol) in dry MeOH-CH_2Cl_2 (9:1, 15 mL) was added Pd/C (98 mg, 0.91 mmol) and HCO_2NH_4 (28.91 mg, 0.45 mmol). The reaction mixture was allowed to stir 4 h at room temperature. TLC [$CHCl_3$:MeOH (9:1)] indicated the formation of one new major compound with lower R_f then starting material. It was then filtered through celite pad and washed with 20 mL of MeOH. The solvent was evaporated and the residue was dissolved in 20 mL of $CHCl_3$. The $CHCl_3$ solution was washed with water and dried over Na_2SO_4. It was concentrated and the residue **16** (380 mg, 82% yield) was used in next step without purification. To the solution of crude 1-aminoethyl octasaccharide **16** (360 mg, 0.09 mmol) in dry CH_2Cl_2 (15 mL) was added *N*-methylimidazole (0.14 µL, 0.18 mmol). The reaction mixture was cooled to 0 ^oC and dansyl chloride (38 mg, 0.14 mmol) was added in the dark. The reaction vessel was stirred overnight at 0 ^oC in dark. TLC [cyclohexane:EtOAc (1:1)]

indicated the formation of one new major fluorescent compound and 5 mL deionized water was added to quench the reaction. The organic layer was separated, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel 60 using mobile phase cyclohexane–EtOAc (2:1) to furnish **17** (262 mg, 69% yield) as light green solid. m.p. 158-160 ^oC. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.54 (2H, d, *J* = 8.5 Hz, Ar), 8.39 (2H, d, *J* = 8.8 Hz, Ar), 8.33 (2H, d, *J* = 7.4 Hz, Ar), 8.12 (46H, m, Ar), 7.93 (24H, m, Ar), 7.44 (50H, m), 7.02 (2H, d, *J* = 7.7 Hz, Ar), 6.20 (9H, m, Ar), 6.02 (12H, m), 5.85 (13H, m), 5.67 (1H, m), 5.18 (1H, s), 4.98 (7H, m), 4.66 (1H, s), 4.21 (16H, m), 3.84 (8H, m), 3.58 (3H, m), 3.38 (9H, m), 2.79 [6H, s, $N(CH_3)_2$], 1.90 (3H, s, CH_3), ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.48, 166.05, 165.91, 165.76, 165.70, 165.62, 165.55, 165.46, 165.35, 165.23, 165.17 (C=O), 152.01, 135.29, 133.58, 133.42, 133.31, 133.19, 133.06, 130.61, 130.16, 129.95, 129.79, 129.66, 129.57, 129.41, 129.17, 128.90, 128.67, 128.58, 128.38, 123.43, 118.80, 115.39 (Ar), 98.38, 98.11, 97.98, 97.81 (anomeric C's), 70.70, 70.61, 70.56, 70.49, 70.43, 70.23, 69.86, 69.64, 69.52, 69.39, 69.31, 68.73, 66.80, 66.65, 66.39, 66.29, 65.85, 62.43, 45.39 [$N(CH_3)_2$], 42.67 (CH_2NH), 20.55 (CH_3). MALDI-TOF: *m/z* 4155.1 $[M+Na]^+$ calcd for $C_{232}H_{196}N_2O_{68}SNa$, found 4155.8.

(5-N,N-Dimethylaminonaphthalene-1-sulfonamidoethyl)α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranoside (1)



To the solution of protected dansylated octamannan **17** (250 mg, 0.06 mmol) in dry CH_2Cl_2 (5 mL) was added saturated solution of NH_3 in MeOH (15 mL) and the reaction mixture was stirred overnight at room temperature. TLC [$CHCl_3$:MeOH:H_2O (65:35:10, lower layer)] indicated the formation of one new major fluorescent compound. The reaction mixture was concentrated and the syrup obtained was washed several times with CH_2Cl_2 followed by EtOAc. The residue was purified by column chromatography on Sephadex LH-20 using MeOH as mobile phase to furnish **1** (68 mg, 71% yield) as light green syrup. ^{1}H NMR (D_2O, 300 MHz): δ 8.86 (1H, m, Ar), 8.21 (2H, d, *J* = 7.1 Hz, Ar), 7.86 (3H, m, Ar), 5.28 (1H, s), 5.05 (1H, s), 4.37–4.08 (8H, m), 3.85–3.55 (19H, m), 3.45–3.39 (6H, m), 3.11 (2H, m), 2.29 [6H, s, $N(CH_3)_2$]. ^{13}C NMR (75 MHz, D_2O): δ 136.57, 132.04, 129.41, 129.32, 119.79, 116.88 (Ar), 100.22, 99.71, 99.55, 98.28, 98.17, 71.36, 71.20, 70.98, 70.56, 70.40, 70.43, 70.25, 69.85, 67.18, 66.11, 65.99, 64.88, 46.82 [$N(CH_3)_2$], 43.56 (CH_2NH). FABMS: (*m/z*) 1613.5 $[M+Na]^+$ calcd for $C_{62}H_{98}N_2O_{43}SNa$, found 1613.1.