Supplemental Material

Fmoc-Lys(tert-Boc)-Gly-Gly-OBn (4):

Trifluoroacetic acid (5 mL) was added to a solution of t-Boc-Gly-Gly-OBn (1.8 g , 5.59 mmoles) in dry CH₂Cl₂ (20 mL). The solution was stirred for one hour and the solvent was removed under reduced pressure. The residue (1.8 g) was re-dissolved in CH₂Cl₂ and added to a solution containing Finoc-Lys(t-Boc)-OH (2.25g , 4.8 mmoles), 1,1'-carbonyldiimidazole (850 mg, 5.2 mmoles) and N,N-diisopropylamine (3.8g, 30mmoles) which had been stirred together for one hour. The entire solution was stirred overnight under a nitrogen atmosphere at room temperature and then washed successively with 20 mL of 5% aqueous HCl, water and brine. The solution was then dried over MgSO₄ and concentrated to afford 2.8 g (87% yield) of 4: m.p. 67-70 °C; IR (neat) 1743.6, 1682.1, 3312 cm⁻¹; ¹H NMR (360 MHz, CDCl₃) δ 7.61 (2H, d, J= 7.5 Hz), 7.45 (2H, m), 7.27 (9H, m), 6.1 (1H, br. d, J= 5.8 Hz), 4.90 (2H, s), 4.79 (1H, br. s), 4.18 (2H, m), 3.97 (2H, m) 3.89 (2H, br. s); 2.95 (2H, br. s), 1.72 (2H, br. s), 1.59 (2H, br. s), 1.31 (11H, s); ¹³C NMR (90 MHz, CDCl₃) δ 172.8, 169.6, 169.4, 156.6, 156.2, 143.7, 141.1, 135.0, 128.4, 128.3, 128.0, 127.6, 126.9, 124.9, 119.8, 78.9, 66.9, 55.1, 46.9, 42.8, 41.1, 39.8, 31.6, 29.4, 28.3, 22.5; LRMS (electrospray, H₂O, positive ion mode, m/z) calcd for C₃₇H₄₄N₄O₈ (M¹) 672.25; found 695.31 (M¹ + Na).

Fmoc-L-Lys[2-(2.3.4.6-tetra-O-acetyl-α-D-galactopyranosyl)acetamide]-Gly-Gly-OBn (6):

Compound 4 (1.25 g, 1.86 mmoles) was dissolved in dry CH_2Cl_2 (20 mL) and treated with trifluoroacetic acid (10 mL) for one hour after which time the solution was concentrated under reduced pressure and the residue was then re-dissolved in CH_2Cl_2 .

In a separate flask, a solution of 2-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)acetic acid (650 mg, 1.67 mmoles), 1,1'-carbonyldiimidazole (300 mg, 1.85 mmoles) and N, N-diisopropylethylamine (3.0 g, 23 mmoles) in dry CH₂Cl₂ (20 mL) was stirred for an hour under a nitrogen atmosphere. This mixture was then added in a dropwise fashion to the solution described in the above paragraph and the reaction mixture was stirred at room temperature overnight. The solvent was then removed under reduced pressure and the residue was re-dissolved in ethylacetate. The organic layer was then washed successively with 20% aqueoeus HCl, saturated NaHCO3, water and brine, dried over MgSO4 and concentrated to afford a white crystalline solid which was then purified by flash chromatography (CH2Cl3/CH3OH; 30:1) to give 1.1 g (70% purified yield) of pure 6: 1R (neat) 1743.6, 1656.4, 3384.6 cm⁻¹; ¹H NMR (360 MHz, CDCl₃) 8 7.7 (2H, d, J=7.5 Hz), 7.53 (2H, m), 7.27 (9H, m) 6.70 (1H, br. s) 6.25 (1H, br. d, J=5.8 Hz), 5.36 (1H, br. s), 5.26 (1H, dd, J= 9.1, 5.0 Hz), 5.15 (1H, dd, J= 9.3, 3.3 Hz), 5.00 (2H, s), 4.70 (1H, m), 4.30 (2H, m), 4.15 (5H, m), 4.00 (6H, m), 3.20 (2H, br. s), 2.60 (1H, dd, J=15, 9.5 Hz), 2.40 (1H, dd, J=15, 4.7 Hz), 2.00 (3H, s), 1.97 (3H, s), 1.95 (6H, s), 1.80 (1H, br. s), 1.70 (1H, br. s) 1.50 (2H, br. s), 1.40 (2H, br. s); ¹³C NMR (90 MHz, CDCl3) & 172.7, 170.5, 169.9, 169.5, 169.46, 169.3, 156.5, 143.6,141.0, 135.0, 128.4, 128.3, 128.0, 127.6, 126.9, 124.9, 119.8, 69.2, 68.8, 67.8, 67.6, 67.1, 66.9, 61.2, 54.9, 46.9, 42.6, 41.0, 38.6, 34.0, 31.3, 28.6, 22.3, 20.5; LRMS (electrospray, H₂O, positive ion mode) calcd for C₄₈H₅₆N₄O₁₆ (M⁺) 944.34; found 967.23 ($M^+ + Na$).

Fmoc-L-Lys[2-(2.3.4.6-tetra-O-acetyl-α-D-galactopyranosyl)acetamidel-Gly-Gly-OH (7):

To a solution of 6 (1.0 g, 1.06 numoles) in methanol (50 mL) was added a catalytic amount of Pd/C. The flask was evacuated and a hydrogen-filled balloon was attached and the solution stirred overnight at room temperature. The reaction mixture was filtered and concentrated to afford 890 mg (98% yield) of 7: m.p. 143-145 °C; IR (neat) 3406, 1743, 1648 cm⁻¹; ¹H NMR (360 MHz, CDCl3) δ 7.70 (2H, d, J = 7.3 Hz), 7.50 (2H, d, J = 7.5 Hz), 7.30 (2H, br. s), 7.20 (2H, br. s), 6.90 (1H, br. s), 6.40 (1H, br. s), 5.35 (1H, br. s), 5.22 (1H, br. s), 5.16 (1H, br. s), 4.7 (1H, br. s), 4.3 (2H, m), 4.13 (5H, m), 4.00 (6H, m), 3.20 (2H, br. s), 2.60 (1H, br. s), 2.40 (1H, br. s), 2.03 (3H, s), 1.97 (3H, s), 1.95 (3H, s), 1.93 (3H, s), 1.75 (1H, br. s), 1.60 (1H, br. s), 1.40 (2H, br. s), 1.30 (2H, br. s); ¹³C NMR (90 MHz, CDCl₃) δ 173.4, 172.6, 170.8, 170.4, 170.1, 170.0, 169.8, 156.7, 143.5, 141.1, 127.7, 127.0, 125.0, 119.9, 69.4, 68.9, 67.9, 67.3, 67.1, 61.5, 55.1, 46.9, 42.8, 41.6, 39.1, 34.1, 31.7, 28.8, 22.7, 20.7.

Fmoc-Tris-[L-Lys-[2-(2.3.4.6-tetra-O-acetyl-α-D-galactopyranosyl)acctamide|-Gly-Gly|-Gly-OH (8):

The solid phase synthesis was performed on Fmoc-Gly-Wang resin from Nova Biochem. Fmoc-Gly-Wang resin (100 mg, 0.075 mmoles) was swollen in DMF for 1ht and then treated with 20% piperidine in DMF for 1hr to remove the Frace protecting group. The flask was then charged with DMF (5 mL), 7 (193 mg, 0.225 mmoles), N,N-Diisopropylethylamine (0.04 mL, 0.225 mmoles) and HATU (86 mg, 0.225 rumoles). This solution was allowed to stir until a negative Kaiser and TNBS tests were obtained. The reaction sequence described above was repeated three times. After completion of the third coupling a 20% piperidine in DMF solution was added and the solution stirred for 30 mins. The resin was then washed successively with DMF, 4% acetic acid, dichloromethane and methanol and dried over KOH under vacuum for 14 hrs. Cleavage of the glyco-peptide from the resin was accomplished by treatment with a 1:1 mixture of trifluoroacetic acid and dichloromethane for 30 minutes. The solution was then filtered off and the resin washed with trifluoroscetic acid. Diethyl other was then added to the filtrate and a white precipitate resulted. Filtration afforded 70 mg (43% yield) of 8: m.p. 100-103 °C; IR (neat) 3302, 1743, 1656 cm⁻¹; ¹H NMR (360 MHz, CDCl₃) δ 7.80 (2H, d), 7.67 (2H, t), 7.40 (2H, t), 7.33 (2H, d), 5.40 (3H, br. s), 5.25 (3H, br. s), 5.10 (3H, br. s), 4.68 (3H, br. s), 4.24-3.94 (29H, m), 3.19 (6H, br. s), 2.66 (3H, br. s), 2.52 (3H, br, s), 2.11-1.94 (36H, m), 1.5-1.28 (18H, m); ¹²C NMR (90 MHz, CDCl₃) δ 172.85, 172.2, 171.9, 171.5, 171.4, 142.6, 128.9, 128.0, 126.3, 121.1, 71.3, 70.0, 69.3, 69.0, 62.5, 43.9, 43.4, 41.8, 40.2, 35.0,

© 1999 American Chemical Society, Org. Lett., Ben ol 991025+ Supporting Info Page 3

31.7. 29.9, 24.2, 20.7, 20.6; LRMS (MALDI, m/z) calcd for $C_{95}H_{129}N_{13}O_{43}$ (M+) 2139.82; found 2161.12 (M⁺ + Na).

Fmoc-Tris-[L-Lys-[2-(α-D-galactopyranosyl)acetamide]-Gly-Gly|-Gly-Off (9):

Compound 8 (70 mg, 0.03 immole) was dissolved in 5 mL of methanol. A catalytic amount of sodium metal was added and the reaction mixture was stirred overnight. The solvent was removed under reduced pressure and the sample was lyophilized to furnish 38 mg of 9 (90% yield) as a pale yellow solid: 1 H NMR (360 MHz, D₂O) δ 4.6 (3H, br. s), 4.05 (17H, m), 3.85 (3H, br. d, J = 5.9 Hz), 3.78 (9H, m), 3.72 (6H, d, J = 5.2 Hz), 3.23 (6H, br. s); 2.70 (3H, dd, J = 2 and 11.2 Hz), 2.60 (3H, d, J = 9.8 Hz), 1.90 (6H, br. s), 1.56 (6H, br. s), 1.36 (6H, br. s); 13 C NMR (90 MHz, D₂O) δ 77.8, 77.3, 74.5, 73.6, 72.5, 65.7, 58.7, 53.7, 47.5, 47.2, 45.9, 44.0, 43.8, 37.2, 35.2, 32.7, 27.3, 24.9; LRMS (electrospray, H₂O, negative ion mode) calcd for $C_{56}H_{95}N_{13}O_{29}$ (M $^{+}$) 1413.64; found 1452.50 (M $^{+}$ + K).