Supporting information

Experimental procedures

2,3,5,6-Tetra-*O*-benzoyl-α,β-D-galactofuranose (5). To dry 1,2,3,5,6-penta-*O*-benzoyl-α,β-D-galactofuranose (**4**, 1.3 g, 1.85 mmol), 32 % HBr in glacial AcOH (2.5 mL) was added and the suspension was stirred at room temperature, in the dark. After 2 h, the solution was concentrated under vacuo and the residue was coevaporated with toluene (5 x 5 mL). The resulting syrup was dissolved in acetone (3 mL), water (0.2 mL, 11.1 mmol) was added and stirred for 5 min. After addition of Ag_2CO_3 (0.40 g, 1.45 mmol), the suspension was vigorously stirred at 40 °C for 40 min, then filtered over celite and concentrated. The residue was purified by silica gel column chromatography (20 :1 toluene-EtOAc) to afford 0.99 g of **5** as a foamy product (90 %). R_f 0.23, 10:1 toluene-EtOAc; $[\alpha]_D$ 24.2° (*c* 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.84 (d, 0.3H, *J* = 4.8 Hz, H-1α), 5.70 (br s, 0.7H, H-1β); 5.66 (dd, 0.7 H, *J* = 1.0, 4.7 Hz, H-3β), 5.51 (d, 0.7H, *J* = 1 Hz, H-2β). Anal. Calcd. for $C_{56}H_{51}NO_{15}$: C, 68.77; H, 5.26. Found: C, 68.76; H, 5.22.

Benzyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (8). To a stirred solution of **7** (0.565 g, 0.58 mmol) in HOAc (6 mL) at 85 °C, H_2O (2.5 mL) was slowly added and heating continued for 2 h. The mixture was cooled and concentrated, and the residue subjected to successive co-evaporation with water (4 x 5 mL) and then with toluene (2 x 3mL). The remaining solid was purified by column chromatography (1:1 toluene-EtOAc) to afford 0.422 g of **8** as a white solid (82 % ; R_f 0.17, 2:1 toluene-EtOAc). Recrystallization from EtOH gave mp 196-197°C; $[\alpha]_D$ +48.6° (*c* 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.15-7.15 (m, 25H), 6.00 (d, 1H, *J* = 8.4 Hz, N*H*), 5.93 (br q, 1H, *J* = 5.12 Hz, H-5'), 5.74 (dd, 1H, *J* = 5.5, 1.5 Hz, H-3'), 5.34 (s, 2H, H-1', H-2'), 5.06 (d, 1H, *J* = 3.7 Hz, H-1), 4.86 (t, 1H, *J* = 5.2 Hz, H-4'), 4.80 (dd, 1H, *J* = 12.1, 5.1 Hz, H-6'a), 4.71, 4.49 (2d, 2H, *J* = 11.7 Hz, PhCH_2), 4.65 (dd, 1H, *J* = 12.1, 6.2

Hz, H-6'b), 4.24 (ddd, 1H, *J*= 3.7, 8.4, 9.9 Hz, H-2), 3.85-3.6 (m, 7H, H-3, 4, 5, 6a, 6b, 2OH), 2.03 (s, 3H, CH_3). 2D-COSY ^{1}H NMR allowed the assigment of the ^{1}H signals.
Anal. Calcd for $C_{49}H_{47}NO_{15}$: C, 66.13; H, 5.32. Found: C, 66.37; H, 5.25.

Benzyl β-D-galactofuranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (9). To 0.422 g (0.47 mmol) of compound **8**, 0.5 M sodium methoxide in MeOH (8 mL) at 0 °C, was added. After vigorously stirring for 1.5 h, water (0.5 mL) was added, and the solution passed through a column (1.5 cm x 5 cm) containing Amberlite IR-120 (H^+) resin. The solvent was evaporated and the remaining methyl benzoate was eliminated by five successive coevaporations with water, to afford **9** as a white solid (0.219 g, 98 %), Rf 0.78 (7:1:1 nPrOH-EtOH-H_2O). Crystallization from EtOH-EtOAc gave: mp 193-195 °C; $[\alpha]_D$ +25.5° (c 1, H_2O); ^{1}H NMR (200 MHz, D_2O): anomeric region δ 4.97 (bs, 1H, Gal*f*), 4.82 (d, 1H, *J* = 3.3 Hz, GlcNAc).
Anal. Calcd for $C_{21}H_{31}NO_{11}$._H_2O: C, 52.28; H, 6.68. Found: C, 52.17; H, 6.89.

β-D-Galactofuranosyl-(1→3)-2-acetamido-2-deoxy-α,β-D-glucopyranose (1). To a solution of **9** (0.151 g, 0.319 mmol) in MeOH (4 mL), 10 % Pd/C (50 mg) and ammonium formate (0.150 g, 2.4 mmol) were added. The mixture was heated in a 65 °C water bath for 20 min, then filtered and concentrated. The remaining syrup was further heated at 50°C in vacuo to give compound **1** (0.120 g, 98 %). Rf 0.62 and 0.58 (7:1:1 nPrOH-EtOH-H_2O) for the α and β anomers. Crystallization from MeOH gave mp 170-172 °C, $[\alpha]_D$ -64.8° (*c* 1, H_2O); ^{1}H NMR (200 MHz, D_2O): anomeric region δ 5.14 (d, 0.7 H, *J* = 3.7 Hz, α-GlcNAc), 5.05 (bs, 0.7H, β-Gal*f* of α anomer), 5.02 (bs, 0.3H, β-Gal*f* of β anomer), 4.73 (d, 0.3H, *J* = 8.4 Hz, β-GlcNAc).
Anal. Calcd. for $C_{14}H_{25}NO_{11}$ C, 43.86; H, 6.57. Found: C, 44.15; H, 6.51.

β-D-Galactofuranosyl-(1→3)-2-acetamido-2-deoxy-D-glucitol (10). To a solution of **1** (39 mg, 0.102 mmol) in 9:1 MeOH-H_2O (4 mL), $NaBH_4$ (50 mg, 1.32 mmol) was added, and the mixture stirred overnight at room temperature. The solution was eluted through a

column of Amberlite IR-120 (H^+ form) resin, concentrated and boric acid eliminated by five successive evaporations with MeOH. Filtration through a C-8 cartridge and further lyophylization of the sample afforded **10** (38 mg) as an amorphous solid (97 %): R_f 0.48 (7:1:1 nPrOH-EtOH-H_2O); $[\alpha]_D$ -71.9 (*c* 1, H_2O); ^1H NMR (200 MHz, D_2O): anomeric region δ 5.07 (s, 1H, Gal*f*).

Benzyl β-D-galactofuranosyl-(1→6)-2-acetamido-2-deoxy-α-D-glucopyranoside (13). - To 0.450 g (0.45 mmol) of compound **12**, 0.5 M sodium methoxide in MeOH (5 mL, 2.5 mmol) was added at room temperature. After stirring for 2.5 h , water (0.5 mL) was added and the solution passed through a column (1.5 cm x 5 cm) containing Amberlite IR-120 (H^+ form) resin. After concentration of the solution the remaining methyl benzoate was eliminated by successive coevaporations with water (3 x 5mL), to afford **13** as a crystalline solid (0.212 g, 99 %), R_f 0.68 (7:1:1 nPrOH-EtOH-H_2O). Recrystallization from MeOH-EtOH gave: mp 107-108 °C; $[\alpha]_D$ +74.4° (*c* 1, H_2O); ^1H NMR (200 MHz, D_2O): anomeric region δ 4.98 (bs, 1H, Gal*f*), 4.86 (d, 1H, *J* = 3.2 Hz, GlcNAc).
Anal. Calcd for $C_{21}H_{31}NO_{11}$._H_2O: C, 52.28; H, 6.68. Found: C, 52.06; H, 6.60.

β-D-Galactofuranosyl-(1→6)-2-acetamido-2-deoxy-α,β-D-glucopyranose (2). To a solution of **13** (0.103 g, 0.218 mmol) in MeOH (4 mL), 10 % Pd/C (50 mg) and ammonium formate (40 mg, 0.63 mmol) were added. The mixture was heated in a 65 °C water bath for 15 min, then filtered and concentrated. Further heating in vacuo at 50°C afforded compound **2** (82 mg, 98 %) as an amorphous solid with R_f 0.52 and 0.40 (7:1:1 nPrOH-EtOH-H_2O) for the α and β anomers. Crystallization from MeOH gave mp 159-160 °C, $[\alpha]_D$ -27.6 °C (*c* 0.6, H_2O); ^1H NMR (200 MHz, D_2O): anomeric region δ 5.11 (d, 0.7H, *J* = 3.3 Hz, α-GlcNAc), 4.96 (bs, 1H, β-Gal*f*). The signal for the β-anomer of GlcNAc was overlapped with the DHO signal.
Anal. Calcd. for $C_{14}H_{25}NO_{11}.H_2O$: 41.90; H, 6.78. Found: C, 42.03; H, 6.53.

β-D-Galactofuranosyl-(1→6)-2-acetamido-2-deoxy-D-glucitol (14). To a solution of **2** (42 mg, 0.11 mmol) in MeOH (2 mL), $NaBH_4$ (30 mg, 0.8 mmol) was added, and the mixture stirred at room temperature. After 16h, water (0.4 mL) was added and the solution was decationized by elution through a column of Dowex 50W-X8-400 (2 x 0.5 cm) H^+ form resin. The solution was concentrated and boric acid eliminated by five successive evaporations with MeOH to afford **14** as a very hygroscopic syrup (42 mg, 99 %): R_f 0.40 (7:1:1 nPrOH-EtOH-H_2O); $[\alpha]_D$ -56.6° (*c* 1, H_2O); ^1H NMR (200 MHz, D_2O): anomeric region δ 5.02 (s, 1H, Gal*f*).