Supporting Information

General Remarks

Unless stated otherwise, chemicals were obtained from commercial sources and used without further purification. Solvents were purchased from Biosolve (Valkenswaard, The Netherlands). TLC was performed on Merck precoated Silica 60 plates. Spots were visualized by UV light and by 10% H_2SO_4 in MeOH. Microwave reactions were carried out in a dedicated microwave oven, i.e. the Biotage Initiator. The microwave power was limited by temperature control once the desired temperature was reached. A sealed vessel of 2 – 5 mL was used. Analytical HPLC runs were performed on a Shimadzu automated HPLC system with a reversed phase column (Alltech, Adsorbosphere C8, 90 Å, 5μm, 250x4.6 mm) equipped with an evaporative light scattering detector (PL-ELS 1000, Polymer Laboratories) and a UV/VIS detector operating at 220 and 254 nm. Preparative HPLC runs were performed on a Applied Biosystems workstation. Elution was effected using a gradient of 5% MeCN and 0.1% TFA in H_2O to 5% H_2O and 0.1% TFA in MeCN. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) were performed on a Varian G-300 spectrometer. Exact masses were measured by nanoelectrospray time-of-flight mass spectrometry on a Micromass LC ToF mass spectrometer at a resolution of 5000 fwhm. Gold-coated capillaries were loaded with 1 μL of sample (concentration 2 μM) dissolved in a 1:1 (v/v) mixture of CH_3CN-H_2O with 0.1% formic acid. NaI or poly(ethylene glycol) (PEG) was added as internal standard. The capillary voltage was set between 1100 and 1350 V, and the cone voltage was set at 30 V. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI ToF) MS were recorded on a Shimadzu Axima-CFR with α-cyano-4-hydroxycinnamic acid or sinapic acid as a matrix. Insulin and adrenocorticotropin fragment 18-39 (Acth) were used for calibration.

H-$(OCH_2CH_2)_5$-OTrityl (2)

To a solution of penta ethylene glycol **1** (6.35 mL, 30 mmol) in dry pyridine (100 mL) was added trityl chloride (2.79 g, 10 mmol) and the mixture was stirred for 70 h. The reaction mixture was concentrated to dryness at 60 °C, taken up in EtOAc (250 mL) and washed with H_2O (100 mL), NaOH (1M, 100 mL) and brine (100 mL). The organic phase was dried over Na_2SO_4, filtered and concentrated. Silica gel chromatography (EtOAc / MeOH, 1/0 → 19/1) yielded **3** as clear oil (3.45 g, 72 % based on trityl chloride). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 – 7.44 and 7.31 – 7.18 (5 and 10H, 2 x m, CH_{arom}), 3.70 – 3.63 (16H, m, OCH_2), 3.58 –

3.54 (2H, m, CH_2OH) and 3.23 (2H, t, CH_2OTrt, J = 5.4 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.0, 128.6, 127.6 and 126.8 (C_{arom}), 86.4 ($OCPh_3$), 72.4, 70.5 and 70.2 (OCH_2), 63.2 (CH_2OTrt) and 61.6 (CH_2OH). HRMS for $C_{29}H_{36}O_6$ (M, 480.2512) M + Na found 503.3338, calcd. 503.2410.

Br-($C_{11}H_{22}$)-(OCH_2CH_2)$_5$-OTrityl

A solution of **(3)** (3.45 g, 7.2 mmol) in dry DMF (25 mL) at 0 ˚C was treated with NaH (60% in oil, 400 mg, 21.6 mmol) and stirred for 30 min. This solution added in 15 min to a solution of 1,11-dibromoundecane in DMF (25 mL) at 0 ˚C. The final solution was slowly warmed to rt and stirred for 18 h. The reaction mixture was concentrated at 60 ˚C, taken up in EtOAc (200 mL) and washed with H_2O (100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. Silica gel chromatography (hex/EtOAc, 3/1 → 1/1) yielded **4** as a clear oil (3.12 g, 61% based on X). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48 – 7.44 and 7.30 – 7.17 (5 and 10H, 2 x m, CH_{arom}), 3.68 - 3.60 (16H, m, OCH_2), 3.59 – 3.53 (2H, m, $CH_2OC_{11}H_{22}Br$), 3.43 (2H, t, $OCH_2CH_2CH_2$, J = 6.9 Hz), 3.36 (2H,t, CH_2Br, J = 6.9 Hz), 3.25 (2H, t, CH_2OTrt, J = 5.1 Hz), 1.87 – 1.78 (2H, m, CH_2CH_2Br), 1.59 – 1.54 (2H, m, $OCH_2CH_2CH_2$) and 1.27 (14H, s, C_7H_{14}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.0, 128.5, 127.6 and 126.7 (C_{arom}), 86.3 ($OCPh_3$), 71.3, 70.4 and 69.9 (OCH_2), 63.2 (CH_2OTrt), 33.8, 32.6, 29.5, 29.3, 28.5, 28.0 and 25.9 ($C_{11}H_{22}Br$). HRMS for $C_{40}H_{57}O_6Br$ (M, 712.3339) M + Na found 735.4650, calcd. 735.3237.

Br-($C_{11}H_{22}$)-(OCH_2CH_2)$_5$-OH (3)

A solution of Br-($C_{11}H_{22}$)-(OCH_2CH_2)$_5$-OTrityl (2.79 g, 3.9 mmol) and *p*-toluene sulphonic acid in MeOH (40 mL) was stirred for 18 h. The reaction mixture was neutralised with aqueous $NaHCO_3$ and concentrated. **3** was obtained after silica gel chromatography (CH_2Cl_2/MeOH, 1/0 → 19/1) as clear oil (1.75 g, 95 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.71 - 3.55 (16H, m, OCH_2), 3.46 – 3.38 (4H, m, $OCH_2CH_2CH_2$, CH_2Br,), 3.21 (1H, bs, CH_2OH), 1.87 – 1.80 (2H, m, CH_2CH_2Br), 1.59 – 1.54 (2H, m, $OCH_2CH_2CH_2$) and 1.27 (14H, s, C_7H_{14}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 72.3, 71.1, 70.2, 69.9 and 69.7 (OCH_2), 61.2 (CH_2OH), 33.6, 32.4, 29.2, 28.4, 27.8 and 25.7 ($C_{11}H_{22}$). HRMS for $C_{21}H_{43}O_6Br$ (M, 470.2243) M + Na found 493.3121, calcd. 493.2141.

Br-($C_{11}H_{22}$)-(OCH_2CH_2)$_5$ 2,3,4,6-tri-O-acetyl-β-D-galactopyranoside

A solution of **3** (136 mg, 0.67 mmol) and 2,3,4,6-tri-O-acetyl-α-D-galactosyl trichloro acetimidate **4** (492 mg, 1 mmol) in dry toluene (10 mL) was stirred at 0 ˚C under a N_2 flow for 15 min. $BF_3.Et_2O$ (170 µL, 1.34 mmol) was added and the reaction was stirred at 0 ˚C for 1 h. After neutralisation with Et_3N the mixture was concentrated and subjected to silica gel chromatography (hex/EtOAc, 1/3 → 0/1). The product was obtained as clear oil (236 mg, 44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.39 (1H, d, H-4, $J_{3,4}$ = 3.6 Hz), 5.20 (1H, dd, H-2, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.2 Hz), 5.02 (1H, dd, H-3, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.6 Hz), 4.58 (1H, d, H-1, $J_{1,2}$ = 8.1 Hz), 4.15 (2H, dd, H-6ab, J = 2.4 Hz, J = 6.6 Hz), 3.98 – 3.90 (2H, m, CH*H*O$_{Gal}$ and H-5), 3.78 – 3.72 (1H, m, CH*H*O$_{Gal}$), 3.65 - 3.56 (18H, m, OCH_2), 3.48 – 3.39 (4H, m, O*C*$H_2$$CH_2$$CH_2$, CH_2Br,), 2.15, 2.06, 2.05 and 1.98 (4 x 3H, 4 x s, C(O)CH_3), 1.88 – 1.80 (2H, m, C*H*$_2$$CH_2Br$), 1.59 – 1.54 (2H, m, OCH_2C*H*$_2$$CH_2$) and 1.28 (14H, s, C_7H_{14}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.3, 170.0 and 169.4 (*C*(O)CH_3), 101.2 (C-1), 71.0, 68.6, 67.1 and 66.8 (C-2, C-3, C-4, C-5), 71.4, 70.5, 69.9 and 69.0 (OCH_2), 61.2 (C-6), 34.0, 32.7, 29.4, 28.6, 28.1 and 26.0 ($C_{11}H_{22}$) and 20.7 (C(O)*C*H_3). HRMS for $C_{35}H_{61}O_{15}Br$ (M, 800.3194) M + H found 801.4191, calcd. 801.3272.

azido-($C_{11}H_{22}$)-(OCH_2CH_2)$_5$ 2,3,4,6-tri-O-acetyl-β-D-galactopyranoside

A solution of Br-($C_{11}H_{22}$)-(OCH_2CH_2)$_5$ 2,3,4,6-tri-O-acetyl-β-D-galactopyranoside (264 mg, 0.33 mmol) and NaN_3 (107 mg, 1.65 mmol) was stirred in dry DMF at 100 ˚C for 20 h. The solution was concentrated at 60 ˚C, taken up in CH_2Cl_2 and filtered. Silica gel chromatography (hex/EtOAc, 1/7 → 0/1) yielded the azide (211 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.39 (1H, d, H-4, $J_{3,4}$ = 3.3 Hz), 5.20 (1H, dd, H-2, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 10.5 Hz), .02 (1H, dd, H-3, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.6 Hz), 4.59 (1H, d, H-1, $J_{1,2}$ = 8.1 Hz), 4.16 (2H, dd, H-6ab, J = 2.4 Hz, J = 6.9 Hz), 3.98 – 3.90 (2H, m, CH*H*O$_{Gal}$ and H-5), 3.79 – 3.73 (1H, m, CH*H*O$_{Gal}$), 3.66 - 3.57 (18H, m, OCH_2), 3.46 (2H, t, O*C*$H_2$$CH_2$$CH_2$, J = 6.9 Hz), 3.27 (2H, t, CH_2N_3, J = 6.9 Hz), 2.15, 2.06, 2.05 and 1.98 (4 x 3H, 4 x s, C(O)CH_3), 1.62 – 1.55 (2H, m, OCH_2C*H*$_2$$CH_2$) and 1.28 (14H, s, C_8H_{16}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.1, 170.0, 169.9 and 169.3 (*C*(O)CH_3), 101.1 (C-1), 70.9, 68.5, 67.0 and 66.7 (C-2, C-3, C-4, C-5), 71.3, 70.4, 69.9 and 68.9 (OCH_2), 61.1 (C-6), 51.3

(CH_2N_3), 29.2, 28.9, 28.7, 26.5 and 25.9 ($C_{11}H_{22}$) and 20.5 (C(O)*C*H_3). HRMS for $C_{35}H_{61}O_{15}N_3$ (M, 763.4103) M + H found 786.5811, calcd. 764.8779.

azido-($C_{11}H_{22}$)-($OCH_2CH_2)_5$ β-D-galactopyranoside (1)

A solution of azido-($C_{11}H_{22}$)-($OCH_2CH_2)_5$ 2,3,4,6-tri-O-acetyl-β-D-galactopyranoside (200 mg, 0.26 mmol) in MeOH was treated with NaOMe (30% wt in MeOH, 50 μL). After 2 h the solution was neutralised with Dowex-H^+, filtered, concentrated and silica gel chromatography (CH_2Cl_2/MeOH, 9/1 → 4/1) was used as final purification to yield **5a** was clear oil (119 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.52 (bs, 1H), 4.22 (1H, bd, H-1, $J_{1,2}$ = 7.2 Hz), 3.95 (1H, bs), 3.73 – 3.63 (2H, m), 3.58 - 3.46 (18H, m, OCH_2), 3.37 (2H, t, OC*H*$_2$$CH_2CH_2$, *J* = 6.9 Hz), 3.19 (2H, t, CH_2N_3, *J* = 7.2 Hz), 1.55 – 1.29 (2H, m, OCH_2C*H*$_2$$CH_2$) and 1.21 (14H, s, C_8H_{16}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 103.4 (C-1), 74.5, 73.4, 71.0 and 68.6 (C-2, C-3, C-4, C-5), 71.4, 70.3 and 68.4 (OCH_2), 61.1 (C-6), 51.3 (CH_2N_3), 29.3, 29.0, 28.7, 26.6 and 25.9 ($C_{11}H_{22}$). HRMS for $C_{27}H_{53}N_3O_{11}$ (M, 595.3680) M + Na found 618.3063, calcd. 618.3578.

Divalent galactose dendrimer (6b)

A solution of **6a** (30 mg, 29 μmol), **5a** (51 mg, 86 μmol), $CuSO_4.5H_2O$ (7.1 mg, 29 μmol) and sodium ascorbate (5.6 mg, 29 μmol) was heated in DMF/H_2O (1/1, v/v, 5 mL) under microwave irradiation at 80 ˚C for 20 min. The reaction mixture was concentrated at 60 ˚C and subjected to HPLC purification. Divalent dendrimer **6b** was obtained as oil (44.5 mg, 70%). ^{1}H NMR (H_2O/D_2O, 9/1, v/v, 500 MHz): δ = 8.51 (2H, bt, C(O)NH), 8.30 (2H, bt, C(O)NH), 7.97 (2H, bt, C(O)NH), 7.79 (2H, s, $CH_{triazole}$), 7.11 (2H, s, CH_{arom}-2,6), 6.77 (1H, s, CH_{arom}-4), 4.42 (2H, d, H-1, $J_{1,2}$ = 6.0 Hz), 4.33 (4H, t, OC*H*$_2$$C_{10}H_{20}$), 4.12 and 4.07 (2 x 4H, 2 x s, OCH_2C(O)), 3.94 – 3.50 (50H, m), 3.45 (4H, t, CH_2NHC(O)), 3.40 (4H, t, C*H*$_2$NHC(O)), 3.30 (4H, bd, $CH_2N_{triazole}$), 3.18 (4H, t, C*H*$_2$NHC(O)), 2.99 and 2.58 (2 x 4H, 2 x t, C*H*$_2$C*H*$_2$$C_{triazole}$), 1.77 (8H, m, OCH_2C*H*$_2$$CH_2$NH), 1.66 (4H, t, OCH_2C*H*$_2$$C_9H_{18}$), 1.51 (4H, t, C_9H_{18}C*H*$_2$$CH_2N_{triazole}$) and 1.25 - 1.10 (28H, m, C_7H_{14}). ^{13}C NMR (D_2O, 75.5 MHz): δ = 174.9, 172.3 and 171.8 (C(O)NH), 168.4 (*C*(O)OCH_3), 160.4 (C_{arom}-3,5), 146.9 ($C_{triazole}$-4), 132.2 (C_{arom}-1), 123.7 ($C_{triazole}$-5), 109.2 (CH_{arom}-2,6), 107.3 (CH_{arom}-4), 103.8 (C-1), 76.0 73.6 71.6 (C-2, C-3, C-4, C-5), 71.9, 70.5, 69.4 and 69.2 (OCH_2), 67.5 (O*C*$H_2$$CH_2$NH), 61.8 (C-6), 51.0 (C(O)O*C*H_3), 39.2 and 37.1 (OCH_2*C*H_2NH and *C*H_2NHC(O)) 36.0

($CH_2CH_2C_{triazole}$), 29.7, 29.3, 28.5, 26.7 and 26.3 ($CH_2CH_2CH_2$) and 22.0 ($CH_2CH_2C_{triazole}$). MALDI ToF for $C_{104}H_{184}N_{12}O_{40}$ (M, 2241.2733) M + Na found 2265.16, calcd 2265.6199.

Tetravalent galactose dendrimer (7b)

A solution of **7a** (20 mg, 9 μmol), **5a** (31 mg, 52 μmol), $CuSO_4.5H_2O$ (4.4 mg, 17 μmol) and sodium ascorbate (3.5 mg, 17 μmol) was heated in DMF/H_2O (1/1, v/v, 3 mL) under microwave irradiation at 80 ˚C for 20 min. The reaction mixture was concentrated at 60 ˚C and subjected to HPLC purification. Tetravalent dendrimer **7b** was obtained as oil (31.7 mg, 78%). ^{1}H NMR (H_2O/D_2O, 9/1, v/v, 500 MHz): δ = 8.68 (2H, t, C(O)NH), 8.50 (4H, t, C(O)NH), 8.30 (4H, t, C(O)NH), 7.97 (4H, t, C(O)NH), 7.76 (4H, s, $CH_{triazole}$), 7.03 (2H, s, CH_{arom}-2,6), 7.00 (4H, s, CH_{arom}-2',6'), 6.67 (3H, bs, CH_{arom}-4, 4'), 4.42 (4H, d, H-1, $J_{1,2}$ = 6.0 Hz), 4.28 (8H,bs t, $OCH_2C_{10}H_{20}$), 4.10 and 4.06 (2 x 4H, 2 x s, $OCH_2C(O)$), 3.94 – 3.73 (16H, m), 3.72 – 3.61 (44H, m), 3.60 – 3.52 (32H, m), 3.50 (8H, bs, $CH_2N_{triazole}$), 3.46 – 3.36 (12H, m $CH_2NHC(O)$), 3.28 (8H, bs, $CH_2NHC(O)$), 3.18 (8H, bd, $CH_2NHC(O)$), 2.97 and 2.57 (2 x 8H, bs and bt, $CH_2CH_2C_{triazole}$), 1.78 – 1.70 (16H, m, $OCH_2CH_2CH_2NH$), 1.66 (8H, t, $OCH_2CH_2C_9H_{18}$), 1.48 (8H, t, $C_9H_{18}CH_2CH_2N_{triazole}$) and 1.20 – 1.05 (56H, m, C_7H_{14}). ^{13}C NMR (D_2O, 75.5 MHz): δ = 174.7, 172.1 and 171.6 (C(O)NH), 169.0 ($C(O)OCH_3$), 160.5 (C_{arom}-3',5'), 146.9 ($C_{triazole}$-4), 118.2 (CH_{arom}) 103.8 (C-1), 76.0, 73.6, 71.6 and 69.5 (C-2, C-3, C-4 and C-5), 71.9, 70.5 and 69.4 (OCH_2), 67.4 (OCH_2CH_2NH), 61.8 (C-6), 51.1 ($C(O)OCH_3$), 39.2 and 37.2 (OCH_2CH_2NH and $CH_2NHC(O)$) 36.0 ($CH_2CH_2C_{triazole}$), 29.9, 29.4, 28.5, 26.8 and 26.4 ($CH_2CH_2CH_2$) and 22.0 ($CH_2CH_2C_{triazole}$). MALDI ToF for $C_{218}H_{378}N_{26}O_{82}$ (M, 4672.6208) M + Na found 4698.12, calcd 4698.45.

Octavalent Galactose dendrimer (8b)

A solution of **8a** (20 mg, 4 μmol), **5a** (30 mg, 50 μmol), $CuSO_4.5H_2O$ (4.2 mg, 17 μmol) and sodium ascorbate (3.3 mg, 17 μmol) was heated in DMF/H_2O (1/1, v/v, 3 mL) under microwave irradiation at 80 ˚C for 20 min. The reaction mixture was concentrated at 60 ˚C and subjected to HPLC purification. Octavalent dendrimer **8b** was obtained as oil (31 mg, 77%). ^{1}H NMR (H_2O/D_2O, 9/1, v/v, 500 MHz): δ = 8.66 (4H, bs, C(O)NH), 8.49 (8H, bs, C(O)NH), 8.30 (8H, bs, C(O)NH), 8.06 (2H, bs, C(O)NH), 7.97 (8H, bs, C(O)NH), 7.75 (8H, s, $CH_{triazole}$), 6.96 (14H, bs, CH_{arom}-2,6, 2',6', 2'',6''), 6.64 (7H, bs, CH_{arom}-4, 4', 4''), 4.42

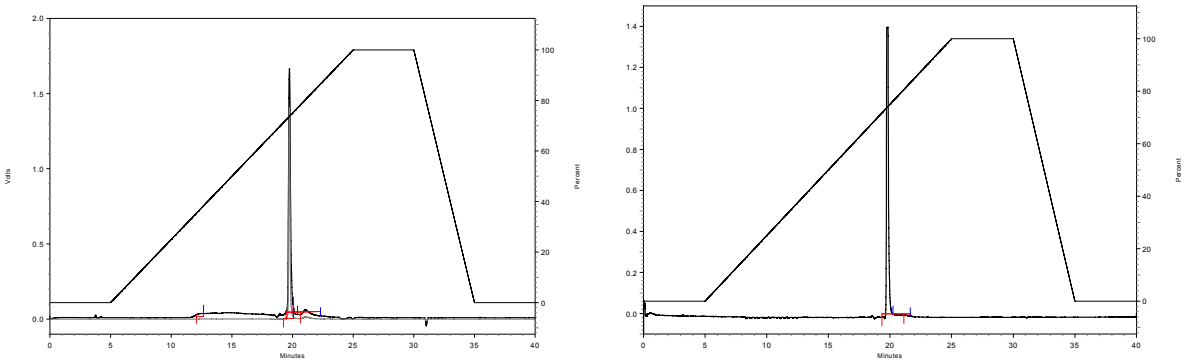
(8H, d, H-1, $J_{1,2}$ = 6.0 Hz), 4.27 (16H,bs, OC*H*$_2$C$_{10}$H$_{20}$), 4.12 and 4.02 (16H, m, OCH$_2$C(O)), 3.93 – 3.72 (16H, m), 3.72 – 3.61 (82H, m), 3.61 – 3.50 (60H, m), 3.48 (16H, bs, CH$_2$N$_{triazole}$), 3.46 – 3.36 (28H, m C*H*$_2$NHC(O)), 3.26 (16H, bs, C*H*$_2$NHC(O)), 3.16 (8H, bs, C*H*$_2$NHC(O)), 2.96 and 2.56 (2 x 8H, 2 x bs, CH$_2$CH$_2$C$_{triazole}$), 1.74 (32H, bs, OCH$_2$C*H*$_2$CH$_2$NH), 1.64 (16H, bt, OCH$_2$C*H*$_2$C$_9$H$_{18}$), 1.46 (16H, bs, C$_9$H$_{18}$C*H*$_2$CH$_2$N$_{triazole}$) and 1.20 – 1.05 (112H, m, C$_7$H$_{14}$). ^{13}C NMR (D$_2$O, 75.5 MHz): δ = 174.4, 171.9 and 171.4 (C(O)NH), 168.4 (*C*(O)OCH$_3$), 160.3 (C$_{arom}$-3'',5''), 103.6 (C-1), 75.8 73.4 and 71.4 (C-2, C-3, C-4, C-5), 71.7, 70.3, 69.2 and 69.1 (OCH$_2$), 61.6 (C-6), 50.8 (*C*H$_2$N$_{triazole}$), 37.0 (*C*H$_2$NHC(O)) 29.7, 29.2, 26.8 and 26.3 (CH$_2$*C*H$_2$CH$_2$) and 21.9 (CH$_2$*C*H$_2$C$_{triazole}$). MALDI ToF for C$_{446}$H$_{766}$N$_{54}$O$_{166}$ (M, 9558.3056) M + Na found 9561.58, calcd 9562.11.

Monovalent Galactose reference (5b)

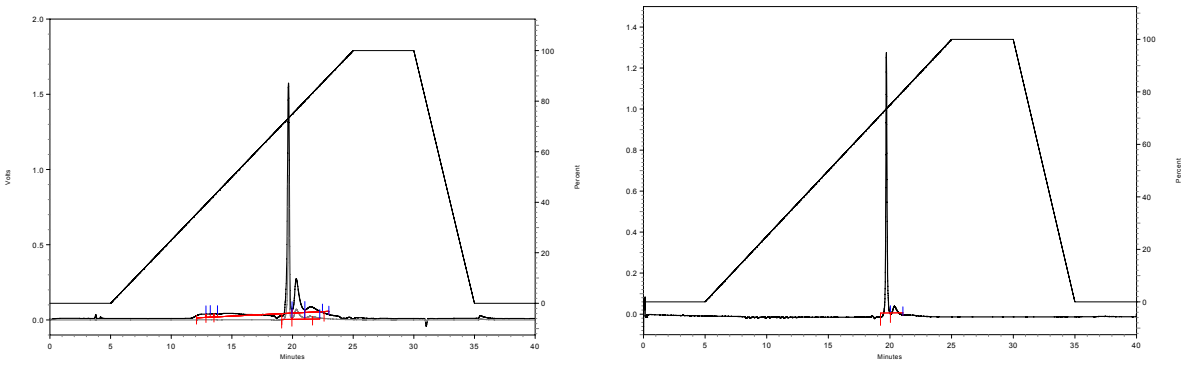
A solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranoside (3.90 g, 10.0 mmol) and tetraethylene glycol (6.91 mL, 40 mmol) in dry CH$_2$Cl$_2$ (50 mL) was cooled to 0 °C and BF$_3$.Et$_2$O (6.34 mL, 50 mmol) was added in 2 min. The mixture was stirred overnight, neutralized with Et$_3$N, diluted with CH$_2$Cl$_2$ (200 mL), washed with aqueous NaHCO$_3$ (5%, 125 mL), H$_2$O (125 mL) and brine (125 mL). The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated. Silica gel chromatography (CH$_2$Cl$_2$/MeOH, 19/1) of the residue gave the desired compound a slightly yellow syrup (3.24 g, 62%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.39 (1H, dd, H-4, $J_{3,4}$ = 3.6 Hz, $J_{4,5}$ = 1.2 Hz), 5.20 (1H, dd, H-2, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.5 Hz), 5.03 (1H, dd, H-3, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.3 Hz), 4.59 (1H, d, H-1, $J_{1,2}$ = 7.8 Hz), 4.16 (2H, dd, H-6ab, *J* = 3.6 Hz, *J* = 6.9 Hz), 3.98 – 3.91 (2H, m, CH*H*O$_{Gal}$ and H-5), 3.79 – 3.60 (15H, m, CH*H*O$_{Gal}$, OCH$_2$), 2.80 (1H, bs, OH), 2.15, 2.07, 2.05 and 1.98 (4 x 3H, 4 x s, C(O)CH$_3$). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 170.2, 170.1, 170.0 and 169.3 (*C*(O)CH$_3$), 101.1 (C-1), 70.7, 68.7 and 66.9 (C-2, C-3, C-4, C-5), 72.3, 70.5, 70.4, 70.1, 68.8 and 63.4 (OCH$_2$), 61.5 (CH$_2$OH), 61.1 (C-6), 20.6 and 20.5 (C(O)*C*H$_3$). HRMS for C$_{22}$H$_{36}$O$_{14}$ (M, 524.2105) M + Na found 547.1472, calcd. 547.2003. Obtained galactoside (1.05 g, 2.0 mmol) was stirred in MeOH (10 mL) and NaOMe (50 µL, 30% wt in MeOH) was added. After 1 h the reaction mixture was neutralized with Dowex-H$^+$, filtered and concentrated. Small impurities were removed by silica gel chromatography (EtOAc/MeOH/H2O, 5/2/1) to give **12** (531 mg, 75%). ^{1}H NMR (300 MHz, CD$_3$OD): δ = 4.26 (1H, d, H-1, $J_{1,2}$ = 6.9 Hz), 4.05 – 3.98 (1H, m), 3.83 (1H, s, H-4), 3.79 – 3.60 (15H, m, OCH$_2$) and 3.58 – 3.50 (5H, m). ^{13}C NMR (75.5 MHz, CD$_3$OD): δ = 105.1 (C-1), 76.7, 74.9, 72.6 and 70.3 (C-2, C-3, C-4, C-

5), 73.7, 71.5 and 69.7 (OCH_2), 62.6 and 62.3 (CH_2OH, C-6). HRMS for $C_{14}H_{28}O_{10}$ (M, 356.1682) M + Na found 379.1194, calcd. 379.1580.

HPLC of **6b**, UV and ELSD detection



HPLC of **7b**, UV and ELSD detection



HPLC of **8b**, UV and ELSD detection