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Synthesis and Potential Antimetastatic Activity of Monovalent and Divalent β -D-Galactopyranosyl-(1 \rightarrow 4)-2-Acetamido-2-Deoxy-D-Glucopyranosides

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Synthesis and potential antimetastatic activity of monovalent and divalent β -D-galactopyranosyl-(1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucopyranosides

Qing Li, Bin Su, Hui Li, Xiang-Bao Meng, Meng-Shen Cai, Zhong-Jun Li, Rou-Li Zhou, Ta-Lin Suo

Introduction

The repeating unit carbohydrate moiety of laminin, *N*-acetyllactosamine, might play a role in the prevention of tumor metastasis.¹ A precursor of *N*-acetyllactosamine, 2,3,4,6-tetra-*O*-acetyl- β -D-galacto-pyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy-D-glucopyranosyl nitrate was first prepared and purified,^{2–6} and then used as the starting material in a synthesis of *N*-acetyllactosamine and its derivatives.

Results and discussion

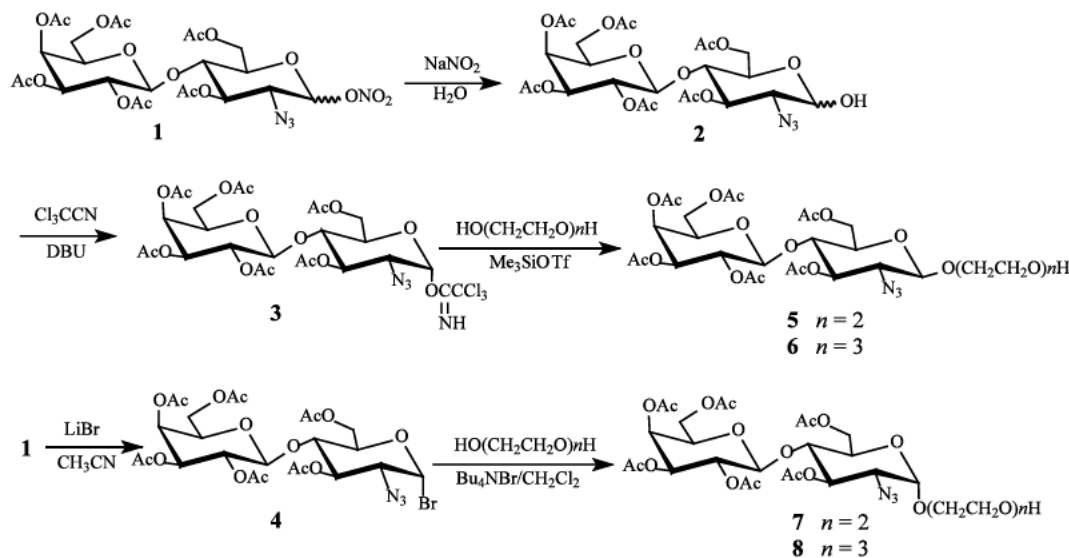
2,3,4,6-Tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy-D-glucopyranosyl nitrate (**1**)⁶ was treated with NaNO₂ and H₂O in 1,4-dioxane for 10 h at 80 °C to give hemiacetal **2**,⁷ which then reacted with CCl₃CN and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) in dry CH₂Cl₂ for 3 h at 0 °C to give the imidate **3**. Imidate **3** reacted with the spacer-arm aglycons in CH₂Cl₂ at room temperature with Me₃SiOTf as

promoter to afford the β -glycosides (**5** or **6**) in yields of 65–70%. Treating **1** with LiBr² afforded bromide **4**, which then reacted in the presence of tetrabutyl ammonium bromide (Bu₄NBr)^{8–10} with the spacer-arm aglycons to give the α -glycosides (**7** or **8**) in yields of 38–42% (Scheme 1).

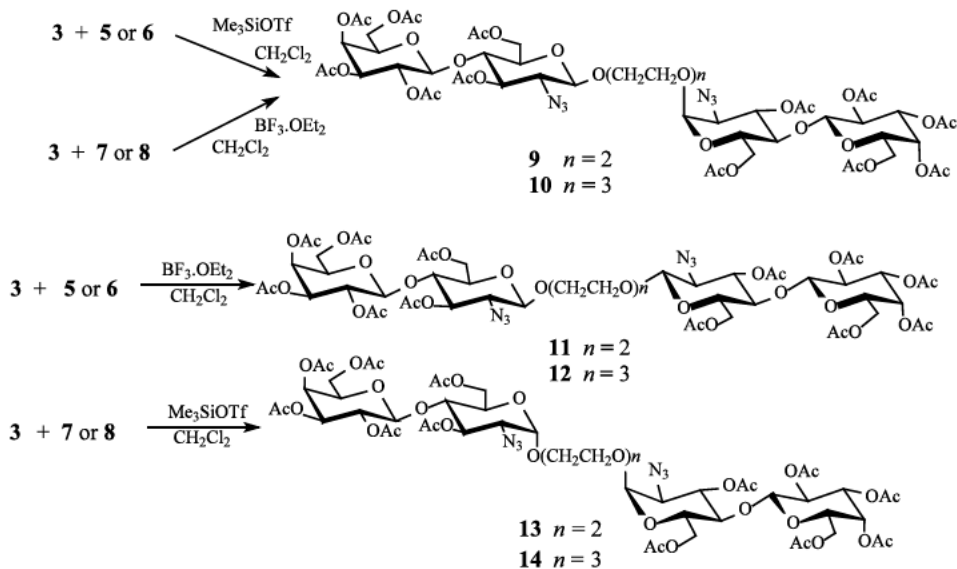
When imidate **3** reacted with **5** or **6** in the presence of Me₃SiOTf, the asymmetric divalent glycosides (**9** and **10**) were mainly obtained. On the other hand, BF₃·OEt₂, a weaker promoter than Me₃SiOTf, when used in the reaction of **3** and **5** or **6** gave the symmetric divalent glycosides (**11** and **12**) of β -configuration selectively. The α -symmetric divalent glycosides (**13** and **14**) were obtained selectively when **7** or **8** reacted with **3** in the presence of Me₃SiOTf, but asymmetric divalent glycosides **9** or **10** were obtained when BF₃·OEt₂ was used in these reactions (Scheme 2).

Treating the azides **5–14** with thioacetic acid^{11,12} for 30 h at room temperature gave the corresponding acetamides **15–24** in yields of 48–80%, and these were deprotected to give the target compounds **25–34** in yields of 93–98% (Scheme 3).

The potential antimetastatic activity of compounds **25–34** was determined by measurements of inhibitory effects on cancer-cell attachment, spreading, and migra-



Scheme 1.



Scheme 2.

tion to the LN-1 coated substrate, as well as invasion through Matrigel. The results are shown in Tables 1 and 2.

The inhibitory effects on cancer-cell attachment and spreading were determined by the conventional acidic phosphatase method.¹³

The data from Table 1 indicate that the tested compounds had some inhibitory effect at 7 mM for the monovalent glycosides and 3.5 mM for the divalent glycosides, and compounds 26, 33, 34 had significant inhibitory effects on cancer-cell attachment and spreading.

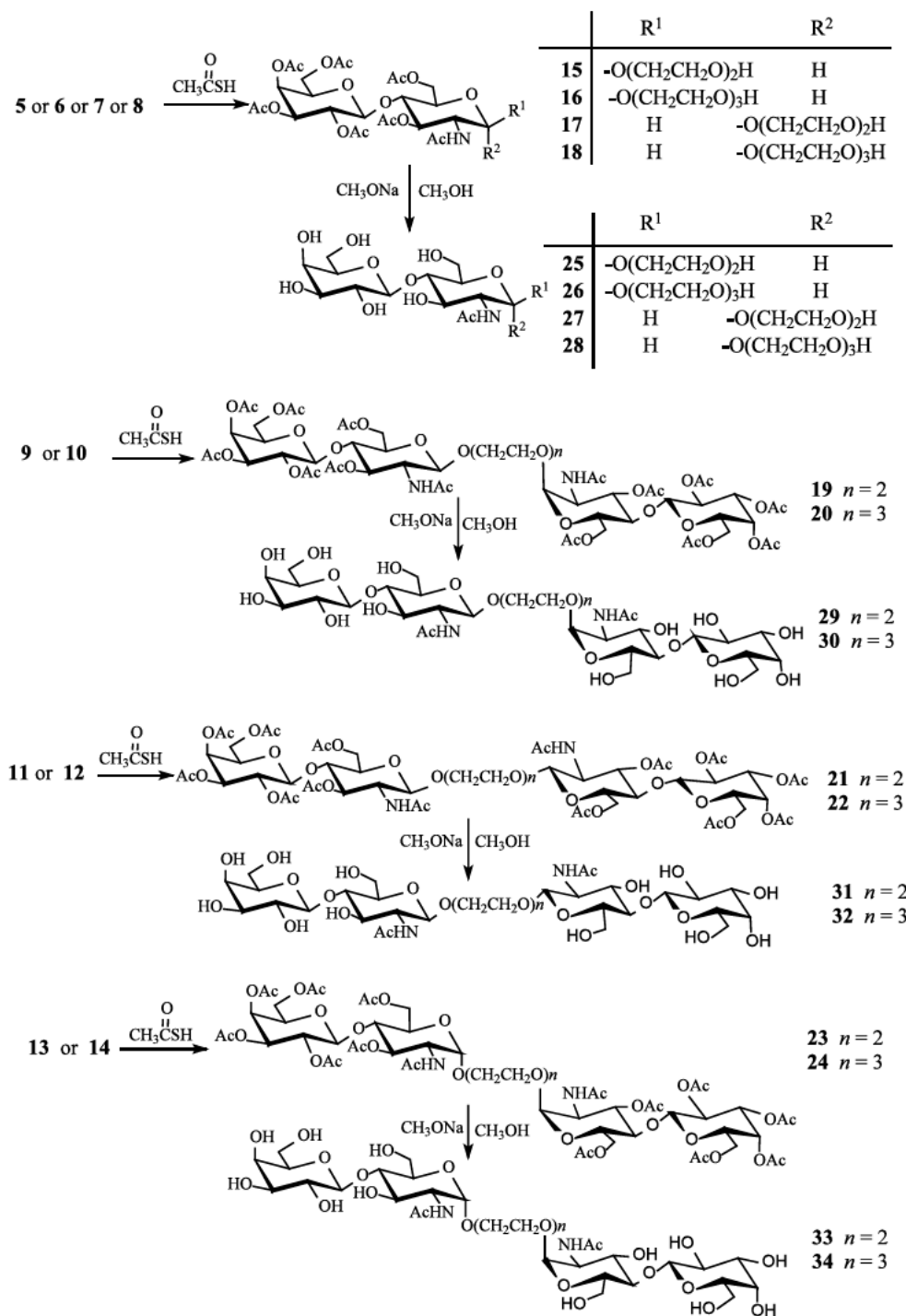
The results from Table 2 indicate that compound 26 is capable of inhibiting human hepatocellular carcinoma cell migration and invasion.

Cancer-cell attachment, spreading, migration, and invasion constitute metastasis-associated cell behavior. Certain synthetic lactosamine derivatives here showed some potential for inhibiting cancer-cell metastasis-associated behavior. It is therefore proposed that these *N*-acetylglucosamine derivatives, in an appropriate structure, might be developed as an anti-metastatic therapeutics.

Experimental

General methods

Optical rotations were recorded using an Optical Activity AA-10R type polarimeter. NMR spectra were



Scheme 3.

recorded with Bruker ARX-400, Varian VRX300, or Varian VRX500 spectrometers, with CDCl₃, CD₃OD, and D₂O as solvents. Elemental analyses were performed with a Perkin–Elmer 240C instrument. Mass spectra were recorded with an IBI-MDS Sciex Qstar type of mass spectrometer. Purity of the products was verified by TLC on Silica Gel GF₂₅₄. Column chromatography was performed on Silica Gel H₆₀.

3.2. 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy-D-glucopyranosyl trichloroacetimidate (3)

Compound 1 (3 g) was dissolved in 1,4-dioxane (50 mL), and then water (15 mL) and NaNO₂ (4 g) were added. The mixture was heated at 80 °C for 10 h with stirring, and then concentrated, and 50 mL of CHCl₃

Table 1
Cancer-cell attachment and spreading on LN-1 substrate

Entry	Cancer-cell attachment rate (%) ^a
Laminin + BSA(control)	100
Laminin + BSA + LacNAc	82.6
Laminin + BSA + compound 25	70.3
Laminin + BSA + compound 26	57.6 ^b
Laminin + BSA + compound 27	96.8
Laminin + BSA + compound 28	89.4
Laminin + BSA + compound 29	76.5
Laminin + BSA + compound 30	81.0
Laminin + BSA + compound 31	101
Laminin + BSA + compound 32	99.0
Laminin + BSA + compound 33	53.5 ^b
Laminin + BSA + compound 34	55.7 ^b

^a At concentration 2 (7 mM for monovalent glycosides and 3.5 mM for divalent glycosides).

^b These compounds showed a significant inhibitory effect.

Table 2
Migration of BEL-7402 human hepatocellular carcinoma cells and invasion analysis^a

	Number of migrating cells	Number of invading cells
In the absence of compound 26	35 ± 2.33	26.67 ± 4.19
In the presence of compound 26	13.6 ± 1.46 ^b	9.8 ± 1.86 ^b

^a Experimental method see Ref. 14.

^b $P < 0.01$ versus control group.

was added. The organic layer was washed with water, dried, and concentrated. The crude product was purified by chromatography (1:1 petroleum ether (60–90 °C)–EtOAc) to give **2** (2.4 g) as colorless syrup in 85% yield. Compound **2** (1 g) was dissolved in anhydrous CH₂Cl₂ (12 mL), and then CCl₃CN (1 mL) and DBU (0.2 mL) were added. The solution was stirred for 3 h at 0 °C, concentrated, and the crude product purified by chromatography [1:1 petroleum ether (60–90 °C)–EtOAc] to afford **3** (1 g) as a yellow syrup in yield of 81%.

5-Hydroxy-3-oxapentyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (5)

To a solution of **3** (0.5 g, 0.65 mmol) and diethylene glycol (0.5 mL) in dry CH₂Cl₂ (10 mL), Me₃SiOTf was added and the mixture was stirred at room temperature for 16 h. The mixture was then diluted with CH₂Cl₂ (20 mL) and washed with water, dried (Na₂SO₄) and evap-

orated under diminished pressure. The resulting oily brown residue was purified by flash chromatography with 2:5 petroleum ether (60–90 °C)–EtOAc as eluent to afford 0.32 g of **5** as a colorless syrup, yield 70%; $[\alpha]_D^{25} + 32.0^\circ$ (*c* 0.5, CHCl₃); ¹H NMR (CDCl₃): δ 5.35 (dd, 1 H, H-4'), 5.09 (dd, 1 H, H-2'), 4.99 (dd, 1 H, H-3), 4.94 (dd, 1 H, H-3'), 4.46 (d, 1 H, $J_{1,2}$ 8.08 Hz, H-1), 4.44 (d, 1 H, $J_{1',2'}$ 7.84 Hz, H-1'), 4.51, 4.18–4.06 (m, 4 H, H-6a, 6b, H-6a', 6b'), 4.03–3.80 (m, 3 H, H-4, 5, H-5'), 3.74–3.58 (m, 8 H, CH₂O), 3.10 (dd, 1 H, H-2), 2.17–1.96 (6s, 18 H, 6 × CH₃CO); ¹³C NMR (CDCl₃): δ 170.3–168.9 (6 C, CH₃CO), 102.1 (C-1), 100.9 (C-1'), 75.9 (C-4), 72.8 (CH₂O), 72.4 (CH₂O), 71.8 (C-3), 71.0 (C-3'), 70.7 (C-5), 70.1 (CH₂O), 69.5 (C-5'), 69.1 (C-2'), 66.6 (C-4'), 63.9 (C-2), 61.8 (C-6), 61.7 (CH₂O), 60.8 (C-6'), 20.8–20.5 (6 C, CH₃CO). Anal. Calcd for C₂₈H₄₁N₃O₁₈: C, 47.53; H, 5.84; N, 5.94. Found: C, 47.17; H, 5.59; N, 5.49.

8-Hydroxy-3,6-dioxaoctyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (6)

Compound **6** was prepared as described for the preparation of **5** and the crude product was purified by chromatography with 2:7 petroleum ether (60–90 °C)–EtOAc as eluent. A colorless syrup was obtained in 65% yield; $[\alpha]_D^{25} + 23.7^\circ$ (*c* 1.35, CHCl₃). ¹H NMR (CDCl₃): δ 5.33 (dd, 1 H, H-4'), 5.09 (dd, 1 H, H-2'), 5.00 (dd, 1 H, H-3), 4.94 (dd, 1 H, H-3'), 4.50 (d, 1 H, $J_{1,2}$ 8.06 Hz, H-1), 4.44 (d, 1 H, $J_{1',2'}$ 7.84 Hz, H-1'), 4.47, 4.15–3.82 (m, 6 H, H-5, H-5', H-6a, 6b, H-6a', 6b'), 3.41 (dd, 1 H, H-2), 3.73–3.59 (m, 13 H, H-4, CH₂O), 2.15–1.95 (6s, 18 H, 6 × CH₃CO); ¹³C NMR (CDCl₃): δ 170.3–169.0 (6 C, CH₃CO), 101.9 (C-1), 100.9 (C-1'), 76.0 (C-4), 72.6 (CH₂O), 72.4 (CH₂O), 71.9 (C-3), 71.0 (C-3'), 70.7 (C-5), 70.5 (CH₂O), 70.3 (CH₂O), 69.1 (C-5'), 69.0 (C-2'), 67.7 (CH₂O), 66.7 (C-4'), 63.9 (C-2), 61.9 (C-6), 61.6 (CH₂O), 60.8 (C-6'), 20.9–20.5 (6 C, CH₃CO). Anal. Calcd for C₃₀H₄₅N₃O₁₉: C, 47.94; H, 6.03; N, 5.59. Found: C, 47.57; H, 5.88; N, 5.31.

5-Hydroxy-3-oxapentyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranoside (7)

Compound **1** (1 g) was dissolved in anhydrous CH₃CN (10 mL), and then LiBr (1 g) and 4 Å molecular sieves (2 g) were added. The mixture was stirred for 6 h at room temperature, the sieves were filtered off and the filtrate concentrated to give **4** (0.8 g) as a yellow syrup.² To a solution of **4** and diethylene glycol (1 mL) in dry CH₂Cl₂ (15 mL), were added Bu₄NBr (0.5 g) and 4 Å molecular sieves (1 g), and the mixture was stirred at room temperature for 24 h, the mixture was then

diluted with CH_2Cl_2 (30 mL) and washed with water, dried (Na_2SO_4), and evaporated under diminished pressure. The resulting oily brown residue was purified by flash chromatography with 2:5 petroleum ether (60–90 °C)–EtOAc as eluent and 0.32 g of **7** was obtained as a colorless syrup. The total yield of two steps was 38%; $[\alpha]_{\text{D}}^{25} + 61.9^\circ$ (c 1.55, CHCl_3); $^1\text{H NMR}$ (CDCl_3): δ 5.46 (dd, 1 H, H-3), 5.36 (dd, 1 H, H-4'), 5.12 (dd, 1 H, H-2'), 5.02 (d, 1 H, $J_{1,2}$ 3.40 Hz, H-1), 4.97 (dd, 1 H, H-3'), 4.48 (d, 1 H, $J_{1',2'}$ 7.96 Hz, H-1'), 4.44, 4.19–4.09 (m, 4 H, H-6a, 6b, H-6a', 6b'), 4.06–3.83 (m, 3 H, H-4, 5, H-5'), 3.74–3.59 (m, 8 H, CH_2O), 3.13 (dd, 1 H, H-2), 2.18–1.96 (6s, 18 H, $6 \times \text{CH}_3\text{CO}$); $^{13}\text{C NMR}$ (CDCl_3): δ 170.4–169.2 (6 C, CH_3CO), 101.2 (C-1'), 98.0 (C-1), 76.5 (C-4), 72.6 (CH_2O), 71.0 (C-3'), 70.6 (C-5), 70.1 (CH_2O), 70.0 (C-3), 69.1 (C-2'), 68.5 (C-5'), 67.7 (CH_2O), 66.6 (C-4'), 62.0 (C-6), 61.8 (CH_2O), 61.1 (C-6'), 60.8 (C-2), 20.9–20.5 (6 C, CH_3CO). Anal. Calcd for $\text{C}_{28}\text{H}_{41}\text{N}_3\text{O}_{18}$: C, 47.53; H, 5.84; N, 5.94. Found: C, 47.70; H, 6.05; N, 5.51.

8-Hydroxy-3,6-dioxaoctyl 2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-O-acetyl-2-azido-2-deoxy- α -D-glucopyranoside (8)

Compound **8** was prepared as described for the preparation of **7** and the crude product was purified by chromatography with 2:7 petroleum ether (60–90 °C)–EtOAc as eluent to afford a colorless syrup in 42% yield; $[\alpha]_{\text{D}}^{25} + 80.0^\circ$ (c 1.40, CHCl_3); $^1\text{H NMR}$ (CDCl_3): δ 5.49 (dd, 1 H, H-3), 5.36 (dd, 1 H, H-4'), 5.12 (dd, 1 H, H-2'), 5.04 (d, 1 H, $J_{1,2}$ 3.52 Hz, H-1), 4.96 (dd, 1 H, H-3'), 4.49 (d, 1 H, $J_{1',2'}$ 7.88 Hz, H-1'), 4.47, 4.17–3.88 (m, 6 H, H-5, H-5', H-6a, 6b, H-6a', 6b'), 3.75–3.60 (m, 13 H, H-4, CH_2O), 3.10 (dd, 1 H, H-2), 2.17–1.97 (6s, 18 H, $6 \times \text{CH}_3\text{CO}$); $^{13}\text{C NMR}$ (CDCl_3): δ 170.4–169.2 (6 C, CH_3CO), 101.2 (C-1'), 98.1 (C-1), 76.5 (C-4), 72.5 (CH_2O), 71.1 (C-3'), 70.8 (C-5), 70.6 (CH_2O), 70.1 (C-3), 70.4 (CH_2O), 69.9 (CH_2O), 69.2 (C-2'), 68.4 (C-5'), 67.7 (CH_2O), 66.6 (C-4'), 62.0 (C-6), 61.8 (CH_2O), 61.0 (C-6'), 60.8 (C-2), 21.0–20.52 (6 C, CH_3CO). Anal. Calcd for $\text{C}_{30}\text{H}_{45}\text{N}_3\text{O}_{19}$: C, 47.94; H, 6.03; N, 5.59. Found: C, 47.76; H, 6.18; N, 5.80.

1-[2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-O-acetyl-2-azido-2-deoxy- β -D-glucopyranosyloxy-5-[2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-O-acetyl-2-azido-2-deoxy- α -D-glucopyranosyloxy-3-oxapentane (9)

A mixture of **3** (0.5 g, 0.65 mmol) and **5** (0.3 g, 0.42 mmol) in dry CH_2Cl_2 (15 mL) in the presence of powered molecular sieves 4 Å (1 g) was cooled to –20 °C and Me_3SiOTf (0.1 mL) was added dropwise with stirring. The mixture was kept for 1 h at –20 to 0 °C and 24 h at room temperature, then the mixture

was filtered and filtrate was washed with aqueous NaHCO_3 and water, dried (Na_2SO_4) and concentrated. The residue was subjected to chromatography on silica gel [4:5 petroleum ether (60–90 °C)–EtOAc] to give **9** (0.24 g) as a colorless syrup in 43% yield; $[\alpha]_{\text{D}}^{25} + 57.1^\circ$ (c 0.63, CHCl_3); $^1\text{H NMR}$ (CDCl_3): δ 5.47 (dd, 1 H, H $_{\alpha}$ -3), 5.35 (dd, 2 H, H $_{\alpha}$ -4', H $_{\beta}$ -4'), 5.11–5.07 (m, 2 H, H $_{\alpha}$ -2', H $_{\beta}$ -2'), 5.05 (d, 1 H, $J_{1,2}$ 3.54 Hz, H $_{\alpha}$ -1), 4.98–4.95 (m, 3 H, H $_{\beta}$ -3, H $_{\alpha}$ -3', H $_{\beta}$ -3'), 4.49 (d, 1 H, $J_{1,2}$ 7.99 Hz, 1 H, H $_{\beta}$ -1), 4.47 (d, 2H, $J_{1',2'}$ 7.90 Hz, H $_{\alpha}$ -1', H $_{\beta}$ -1'), 4.45, 4.18–4.08 (m, 8 H, H $_{\alpha}$ -6a, 6b, H $_{\alpha}$ -6a', 6b', H $_{\beta}$ -6a, 6b, H $_{\beta}$ -6a', 6b'), 3.98–3.76 (m, 6 H, H $_{\alpha}$ -4, 5, H $_{\alpha}$ -5', H $_{\beta}$ -4, 5, H $_{\beta}$ -5'), 3.75–3.65 (m, 8 H, CH_2O), 3.45 (dd, 1 H, H $_{\beta}$ -2), 3.12 (dd, 1 H, H $_{\alpha}$ -2), 2.17–1.96 (12s, 36 H, $12 \times \text{CH}_3\text{CO}$); $^{13}\text{C NMR}$ (CDCl_3): δ 170.2–168.9 (12 C, CH_3CO), 101.9 (C $_{\beta}$ -1), 101.1 (C $_{\alpha}$ -1'), 100.9 (C $_{\beta}$ -1'), 97.8 (C $_{\alpha}$ -1), 76.5 (C $_{\alpha}$ -4), 75.9 (C $_{\beta}$ -4), 72.6 (CH_2O), 71.9 (C $_{\beta}$ -3), 71.0, 70.9 (2 C, C $_{\alpha}$ -3', C $_{\beta}$ -3'), 70.7, 70.6 (2 C, C $_{\alpha}$ -5', C $_{\beta}$ -5'), 70.5 (CH_2O), 70.2 (C $_{\alpha}$ -3), 70.1 (CH_2O), 69.3, 69.1 (2 C, C $_{\alpha}$ -2', C $_{\beta}$ -2'), 69.1, 68.4 (2 C, C $_{\alpha}$ -5, C $_{\beta}$ -5), 67.4 (CH_2O), 66.6, 66.5 (2C, C $_{\alpha}$ -4', C $_{\beta}$ -4'), 63.9 (C $_{\beta}$ -2), 61.9, 61.8 (2 C, C $_{\alpha}$ -6, C $_{\beta}$ -6), 61.0, 60.8 (2 C, C $_{\alpha}$ -6', C $_{\beta}$ -6'), 60.7 (C $_{\alpha}$ -2), 20.9–20.4 (12 C, CH_3CO). Anal. Calcd for $\text{C}_{52}\text{H}_{72}\text{N}_6\text{O}_{33}$: C, 47.49; H, 5.56; N, 6.12. Found: C, 47.19; H, 5.49; N, 5.81.

1-[2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-O-acetyl-2-azido-2-deoxy- β -D-glucopyranosyloxy-8-[2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-O-acetyl-2-azido-2-deoxy- α -D-glucopyranosyloxy-3-dioxaoctane (10)

Compound **10** was prepared as described for the preparation of **9**. The crude product was purified by chromatography with 2:3 petroleum ether (60–90 °C)–EtOAc to afford a colorless syrup in 40% yield; $[\alpha]_{\text{D}}^{25} + 66.1^\circ$ (c 2.48, CHCl_3); $^1\text{H NMR}$ (CDCl_3): δ 5.47 (dd, 1 H, H $_{\alpha}$ -3), 5.35 (dd, 2 H, H $_{\alpha}$ -4', H $_{\beta}$ -4'), 5.10–5.09 (m, 2 H, H $_{\alpha}$ -2', H $_{\beta}$ -2'), 5.04 (d, 1 H, $J_{1,2}$ 3.35 Hz, H $_{\alpha}$ -1), 4.96–4.94 (m, 3 H, H $_{\beta}$ -3, H $_{\alpha}$ -3', H $_{\beta}$ -3'), 4.49 (d, 1 H, $J_{1,2}$ 7.96 Hz, 1 H, H $_{\beta}$ -1), 4.47 (d, 2 H, $J_{1',2'}$ 7.90 Hz, H $_{\alpha}$ -1', H $_{\beta}$ -1'), 4.45, 4.17–4.07 (m, 8 H, H $_{\alpha}$ -6a, 6b, H $_{\alpha}$ -6a', 6b', H $_{\beta}$ -6a, 6b, H $_{\beta}$ -6a', 6b'), 3.98–3.72 (m, 6 H, H $_{\alpha}$ -4, 5, H $_{\alpha}$ -5', H $_{\beta}$ -4, 5, H $_{\beta}$ -5'), 3.72–3.67 (m, 12 H, CH_2O), 3.42 (dd, 1 H, H $_{\beta}$ -2), 3.11 (dd, 1 H, H $_{\alpha}$ -2), 2.18–1.97 (12s, 36 H, $12 \times \text{CH}_3\text{CO}$); $^{13}\text{C NMR}$ (CDCl_3): δ 170.3–168.9 (12 C, CH_3CO), 102.0 (C $_{\beta}$ -1), 101.1 (C $_{\alpha}$ -1'), 100.9 (C $_{\beta}$ -1'), 98.1 (C $_{\alpha}$ -1), 76.5 (C $_{\alpha}$ -4), 76.0 (C $_{\beta}$ -4), 72.7 (CH_2O), 72.6 (CH_2O), 71.9 (C $_{\beta}$ -3), 71.0, 70.9 (2 C, C $_{\alpha}$ -3', C $_{\beta}$ -3'), 70.7, 70.3 (2 C, C $_{\alpha}$ -5', C $_{\beta}$ -5'), 70.2 (CH_2O), 70.1 (C $_{\alpha}$ -3), 70.0 (CH_2O), 69.4 (CH_2O), 69.3, 69.1 (2 C, C $_{\alpha}$ -2', C $_{\beta}$ -2'), 69.0, 68.4 (2 C, C $_{\alpha}$ -5, C $_{\beta}$ -5), 67.7 (CH_2O), 66.6, 66.5 (2 C, C $_{\alpha}$ -4', C $_{\beta}$ -4'), 63.9 (C $_{\beta}$ -2), 61.9, 61.0 (2 C, C $_{\alpha}$ -6, C $_{\beta}$ -6), 60.8, 60.7 (2 C, C $_{\alpha}$ -6', C $_{\beta}$ -6'), 60.6 (C $_{\alpha}$ -2), 20.9–20.4 (12 C, CH_3CO). Anal. Calcd for $\text{C}_{54}\text{H}_{76}\text{N}_6\text{O}_{34}$: C, 47.93; H, 5.66; N, 6.21. Found: C, 47.73; H, 5.84; N, 5.92.

3-Oxapent-1,5-diyl bis[2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy- β -D-glucopyranoside] (11)

A mixture of **3** (0.5 g, 0.65 mmol) and **5** (0.3 g, 0.42 mmol) in dry CH₂Cl₂ (15 mL) in the presence of powered molecular sieves 4 Å (1 g) was cooled to 0 °C and BF₃·OEt₂ (0.2 mL) was added dropwise with stirring. The mixture was kept for 1 h at –20 to 0 °C and 24 h at room temperature, then the mixture was filtered and filtrate was washed with aqueous sodium bicarbonate and water, dried (Na₂SO₄) and concentrated. The residue was subjected to chromatography on silica gel [4:5 petroleum ether (60–90 °C)–EtOAc] to give **11** (0.15 g) as a colorless syrup (27%); [α]_D²⁵ + 17.9° (*c* 2.68, CHCl₃); ¹H NMR (CDCl₃): δ 5.36 (dd, 1 H, H-4'), 5.12 (dd, 1 H, H-2'), 4.98 (dd, 1 H, H-3), 4.95 (dd, 1 H, H-3'), 4.50 (d, 1 H, *J*_{1,2} 8.00 Hz, H-1), 4.47 (d, 1 H, *J*_{1',2'} 8.00 Hz, 1 H, H-1'), 4.45, 4.20–4.05 (m, 4 H, H-6a, 6b, H-6a', 6b'), 4.01–3.81 (m, 3 H, H-4, 5, H-5'), 3.74–3.69 (m, 4 H, CH₂O), 3.43 (dd, 1 H, H-2), 2.17–1.98 (6s, 18 H, 6 \times CH₃CO); ¹³C NMR (CDCl₃): δ 170.3–168.9 (6 C, CH₃CO), 102.1 (C-1), 100.9 (C-1'), 76.0 (C-4), 72.9 (CH₂O), 72.0 (C-3), 70.8 (C-3'), 70.5 (C-5'), 70.2 (CH₂O), 69.4 (C-5), 69.2 (C-2'), 66.8 (C-4'), 64.0 (C-2), 62.0 (C-6), 60.9 (C-6'), 20.9–20.4 (6 C, CH₃CO). Anal. Calcd for C₅₂H₇₂N₆O₃₃: C, 47.49; H, 5.56; N, 6.12. Found: C, 47.70; H, 5.65; N, 6.36.

3,6-Dioxaoct-1,8-diyl bis[2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy- β -D-glucopyranoside] (12)

Compound **12** was prepared as described for the preparation of **11**. The crude product was purified by chromatography with 2:3 petroleum ether (60–90 °C)–EtOAc to afford a colorless syrup in 30% yield of; [α]_D²⁵ + 8.9° (*c* 2.25, CHCl₃); ¹H NMR (CDCl₃): δ 5.36 (dd, 1 H, H-4'), 5.09 (dd, 1 H, H-2'), 4.97 (dd, 1 H, H-3), 4.94 (dd, 1 H, H-3'), 4.48 (d, 1 H, *J*_{1,2} 8.06 Hz, H-1), 4.44 (d, 1 H, *J*_{1',2'} 8.00 Hz, H-1'), 4.42, 4.20–4.06 (m, 4 H, H-6a, 6b, H-6a', 6b'), 4.02–3.81 (m, 3 H, H-4, 5, H-5'), 3.75–3.65 (m, 6 H, CH₂O), 3.42 (dd, 1 H, H-2), 2.18–1.98 (6s, 18 H, 6 \times CH₃CO); ¹³C NMR (CDCl₃): δ 170.3–169.0 (6 C, CH₃CO), 102.1 (C-1), 101.0 (C-1'), 76.0 (C-4), 72.6 (CH₂O), 71.8 (C-3), 71.0 (C-3'), 70.7 (C-5'), 70.3 (CH₂O), 70.0 (CH₂O), 69.4 (C-5), 69.0 (C-2'), 66.6 (C-4'), 63.9 (C-2), 61.9 (C-6), 60.8 (C-6'), 20.9–20.5 (6 C, CH₃CO). Anal. Calcd for C₅₄H₇₆N₆O₃₄: C, 47.93; H, 5.66; N, 6.21. Found: C, 48.00; H, 5.74; N, 6.18.

3-Oxapent-1,5-diyl bis[2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy- α -D-glucopyranoside] (13)

A mixture of **3** (0.5 g, 0.65 mmol) and **7** (0.3 g, 0.42 mmol) in dry CH₂Cl₂ (15 mL) in the presence of powered molecular sieves 4 Å (1 g) was cooled to –20 °C and Me₃SiOTf (0.1 mL) was added dropwise with stirring. The mixture was kept for 1 h at –20 to 0 °C and 24 h at room temperature, then the mixture was filtered and the filtrate was washed with aqueous NaHCO₃ and water, dried (Na₂SO₄) and concentrated. The residue was subjected to chromatography on silica gel [4:5 petroleum ether (60–90 °C)–EtOAc] to give **13** (0.23 g) as a colorless syrup (41%); [α]_D²⁵ + 52.2° (*c* 1.15, CHCl₃); ¹H NMR (CDCl₃): δ 5.47 (dd, 1 H, H-3), 5.36 (dd, 1 H, H-4'), 5.11 (dd, 1 H, H-2'), 5.04 (d, 1 H, *J*_{1,2} 3.50 Hz, H-1), 4.96 (dd, 1 H, H-3'), 4.48 (d, 1 H, *J*_{1',2'} 7.50 Hz, 1 H, H-1'), 4.44, 4.21–4.04 (m, 4 H, H-6a, 6b, H-6a', 6b'), 3.99–3.82 (m, 3 H, H-4, 5, H-5'), 3.76–3.69 (m, 4 H, CH₂O), 3.10 (dd, 1 H, H-2), 2.17–1.97 (6s, 18 H, 6 \times CH₃CO); ¹³C NMR (CDCl₃): δ 170.2–169.0 (6 C, CH₃CO), 101.1 (C-1'), 98.1 (C-1), 76.6 (C-4), 71.1 (C-3'), 70.7 (C-5'), 70.4 (CH₂O), 70.2 (C-3), 69.2 (C-2'), 68.6 (C-5), 67.6 (CH₂O), 66.7 (C-4'), 62.0 (C-6), 61.1 (C-6'), 60.8 (C-2), 20.8–20.5 (6 C, CH₃CO). Anal. Calcd for C₅₂H₇₂N₆O₃₃: C, 47.49; H, 5.56; N, 6.12. Found: C, 47.23; H, 5.83; N, 6.34.

3,6-Dioxaoct-1,8-diyl bis[2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-azido-2-deoxy- α -D-glucopyranoside] (14)

Compound **14** was prepared as described for the preparation of **13**. The crude product was purified by chromatography with 2:3 petroleum ether (60–90 °C)–EtOAc to afford a colorless syrup in 39% yield; [α]_D²⁵ + 65.4° (*c* 1.04, CHCl₃); ¹H NMR (CDCl₃): δ 5.46 (dd, 1 H, H-3), 5.36 (dd, 1 H, H-4'), 5.11 (dd, 1 H, H-2'), 5.03 (d, 1 H, *J*_{1,2} 3.30 Hz, H-1), 4.95 (dd, 1 H, H-3'), 4.48 (d, 1 H, *J*_{1',2'} 7.50 Hz, H-1'), 4.43, 4.20–4.07 (m, 4 H, H-6a, 6b, H-6a', 6b'), 4.03–3.83 (m, 3 H, H-4, 5, H-5'), 3.76–3.65 (m, 6 H, CH₂O), 3.13 (dd, 1 H, H-2), 2.16–1.97 (6s, 18 H, 6 \times CH₃CO); ¹³C NMR (CDCl₃): δ 170.3–169.0 (6 C, CH₃CO), 101.1 (C-1'), 98.1 (C-1), 76.6 (C-4), 71.1 (C-3'), 70.7 (C-5'), 70.2 (C-3), 70.1 (CH₂O), 69.5 (CH₂O), 69.3 (C-2'), 68.5 (C-5), 67.8 (CH₂O), 66.8 (C-4'), 62.0 (C-6), 60.9 (C-6'), 60.8 (C-2), 20.9–20.4 (6 C, CH₃CO). Anal. Calcd for C₅₄H₇₆N₆O₃₄: C, 47.93; H, 5.66; N, 6.21. Found: C, 47.79; H, 5.56; N, 5.92.

5-Hydroxy-3-oxapentyl 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- β -D-glucopyranoside (15)

A solution of **5** (0.2 g) in thioacetic acid (3 mL) was stirred at room temperature for 36 h, then concentrated. The residue was eluted from a column of silica gel with 50:1 CHCl₃-MeOH to give **15** as a colorless syrup (0.16 g, 80%); $[\alpha]_D^{25} - 12.8^\circ$ (*c* 0.94, CHCl₃); ¹H NMR (CDCl₃): δ 6.72 (d, 1 H, NH), 5.36 (dd, 1 H, H-4'), 5.11 (dd, 1 H, H-2'), 5.05 (dd, 1 H, H-3), 4.97 (dd, 1 H, H-3'), 4.73 (d, 1 H, *J*_{1,2} 7.86 Hz, H-1), 4.50 (d, 1 H, *J*_{1,2'} 7.89 Hz, H-1'), 4.46, 4.15-4.11 (m, 4 H, H-6a, 6b, H-6a', 6b'), 4.08 (dd, 1 H, H-2), 3.90 (m, 1 H, H-5), 3.88 (m, 1 H, H-5'), 3.80 (m, 1 H, H-4), 3.77-3.60 (m, 8 H, CH₂O), 2.15-1.97 (7s, 21 H, 6 \times CH₃CO, CH₃CONH); ¹³C NMR (CDCl₃): δ 170.6-169.3 (7 C, 6 \times COCH₃, CONH), 101.5 (C-1), 101.0 (C-1'), 75.8 (C-4), 72.8 (-CH₂O-), 72.7 (C-3), 72.2 (CH₂O), 71.1 (CH₂O), 70.8 (C-3'), 70.7 (C-5'), 69.1 (C-2'), 68.5 (C-5), 66.6 (C-4'), 62.5 (C-6), 61.7 (CH₂O), 60.7 (C-6'), 53.1 (C-2), 23.0 (CH₃CONH), 20.8-20.4 (6 C, CH₃CO). Anal. Calcd for C₃₀H₄₅NO₁₉: C, 49.79; H, 6.27; N, 1.94. Found: C, 49.43; H, 6.19; N, 1.76.

8-Hydroxy-3,6-dioxaoctyl 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- β -D-glucopyranoside (16)

Compound **16** was prepared as described for the preparation of **15**. The crude product was purified by chromatography with 40:1 CHCl₃-MeOH to afford a colorless syrup in 72% yield; $[\alpha]_D^{25} - 11.1^\circ$ (*c* 0.72, CHCl₃); ¹H NMR (CDCl₃): δ 6.86 (d, 1 H, NH), 5.34 (d, 1 H, H-4'), 5.10 (dd, 1 H, H-2'), 5.03 (d, 1 H, H-3), 4.96 (dd, 1 H, H-3'), 4.69 (d, 1 H, *J*_{1,2} 8.10 Hz, H-1), 4.49 (d, 1 H, *J*_{1,2'} 7.80 Hz, H-1'), 4.46, 4.11-4.09 (m, 4 H, H-6a, 6b, H-6a', 6b'), 4.07 (dd, 1 H, H-2), 3.89 (m, 1 H, H-5), 3.87 (m, 1 H, H-5'), 3.82 (m, 1 H, H-4), 3.76-3.61 (m, 12 H, CH₂O), 2.14-1.97 (7s, 21 H, 6 \times CH₃CO, CH₃CONH); ¹³C NMR (CDCl₃): δ 171.2 (NHCO), 170.6-169.2 (6 C, COCH₃), 101.8 (C-1), 100.9 (C-1'), 76.2 (C-4), 73.8 (CH₂O), 72.4 (C-3), 71.5 (CH₂O), 70.9 (C-3'), 70.7 (C-5'), 70.5 (CH₂O), 70.1 (CH₂O), 69.2 (C-2'), 68.4 (C-5), 67.1 (CH₂O), 66.7 (C-4'), 62.4 (C-6), 61.2 (CH₂O), 60.8 (C-6'), 53.6 (C-2), 23.0 (CH₃CONH), 20.8-20.3 (6 C, CH₃CO). Anal. Calcd for C₃₂H₄₉NO₂₀: C, 50.06; H, 6.43; N, 1.82. Found: C, 49.89; H, 6.51; N, 1.69.

5-Hydroxy-3-oxapentyl 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- α -D-glucopyranoside (17)

Compound **17** was prepared as described for the preparation of **15**. The crude product was purified by chro-

matography with 40:1 CHCl₃-MeOH to afford a colorless syrup in 75% yield; $[\alpha]_D^{25} + 62.3^\circ$ (*c* 1.22, CHCl₃); ¹H NMR (CDCl₃): δ 6.39 (d, 1 H, NH), 5.35 (dd, 1 H, H-4'), 5.25 (dd, 1 H, H-3), 5.13 (dd, 1 H, H-2'), 4.97 (dd, 1 H, H-3'), 4.83 (d, 1 H, *J*_{1,2} 3.44 Hz, H-1), 4.52 (d, 1 H, *J*_{1,2'} 7.89 Hz, H-1'), 4.24 (dd, 1 H, H-2), 4.47, 4.12-4.06 (m, 4 H, H-6a, 6b, H-6a', 6b'), 3.94 (m, 1 H, H-5), 3.90 (m, 1 H, H-5'), 3.79 (m, 1 H, H-4), 3.77-3.62 (m, 8 H, CH₂O), 2.15-1.95 (7s, 21 H, 6 \times CH₃CO, CH₃CONH); ¹³C NMR (CDCl₃): δ 171.1 (CONH), 170.5-169.3 (6 C, COCH₃), 101.2 (C-1'), 97.3 (C-1), 76.3 (C-4), 72.6 (CH₂O), 71.5 (C-3), 70.9 (C-3'), 70.6 (C-5'), 69.7 (CH₂O), 69.2 (C-2'), 68.6 (C-5), 67.4 (CH₂O), 66.6 (C-4'), 62.0 (C-6), 61.5 (CH₂O), 60.7 (C-6'), 52.0 (C-2), 23.0 (CH₃CONH), 20.9-20.4 (6 C, CH₃CO). Anal. Calcd for C₃₀H₄₅NO₁₉: C, 49.79; H, 6.27; N, 1.94. Found: C, 49.36; H, 6.01; N, 1.89.

8-Hydroxy-3,6-dioxaoctyl 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- α -D-glucopyranoside (18)

Compound **18** was prepared as described for the preparation of **15**. The crude product was purified by chromatography with 40:1 CHCl₃-MeOH to afford a colorless syrup in 70% yield; $[\alpha]_D^{25} + 50.8^\circ$ (*c* 0.63, CHCl₃); ¹H NMR (CDCl₃): δ 7.32 (d, 1 H, NH), 5.34 (d, 1 H, H-4'), 5.27 (d, 1 H, H-3), 5.13 (dd, 1 H, H-2'), 4.96 (dd, 1 H, H-3'), 4.76 (d, 1 H, *J*_{1,2} 3.30 Hz, H-1), 4.54 (d, 1 H, *J*_{1,2'} 7.80 Hz, H-1'), 4.47, 4.12-4.07 (m, 4 H, H-6a, 6b, H-6a', 6b'), 4.29 (dd, 1 H, H-2), 3.90 (m, 1 H, H-5), 3.88 (m, 1 H, H-5'), 3.81 (m, 1 H, H-4), 3.77-3.62 (m, 12 H, CH₂O), 2.15-1.95 (7s, 21 H, 6 \times CH₃CO, CH₃CONH); ¹³C NMR (CDCl₃): δ 170.6-169.2 (7C, 6 \times COCH₃, NHCO), 101.1 (C-1'), 97.4 (C-1), 76.6 (C-4), 72.7 (CH₂O), 71.6 (C-3), 71.0 (C-3'), 70.9 (CH₂O), 70.6 (C-5'), 70.3 (CH₂O), 69.9 (CH₂O), 69.3 (C-2'), 68.5 (C-5), 66.8 (CH₂O), 66.6 (C-4'), 62.0 (C-6), 61.8 (CH₂O), 60.7 (C-6'), 51.7 (C-2), 22.8 (CH₃CONH), 20.8-20.4 (6 C, CH₃CO). Anal. Calcd for C₃₂H₄₉NO₂₀: C, 50.06; H, 6.43; N, 1.82. Found: C, 50.03; H, 6.11; N, 1.71.

1-[2,3,4,6-Tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- β -D-glucopyranosyloxy-5-[2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- α -D-glucopyranosyloxy-3-oxapentane (19)

A solution of **9** (0.25 g) in thioacetic acid (3 mL) was stirred for 50 h at room temperature, then concentrated. The residue was eluted from a column of silica gel with 40:1 CHCl₃-MeOH to give **19** as a colorless syrup (0.15 g, 59%); $[\alpha]_D^{25} + 38.5^\circ$ (*c* 0.52, CHCl₃); ¹H NMR (CDCl₃): δ 6.48, 6.35 (d, 2 H, NH _{α} , NH _{β}), 5.36 (dd, 2 H, H _{α} -4', H _{β} -4'), 5.22 (dd, 1 H, H _{α} -3), 5.12-5.10

(m, 2 H, $H_{\alpha-2'}$, $H_{\beta-2'}$), 5.07 (1 H, $H_{\beta-3}$), 4.96–4.94 (m, 2H, $H_{\alpha-3'}$, $H_{\beta-3'}$), 4.83 (d, 1 H, $J_{1,2}$ 4.00 Hz, $H_{\alpha-1}$), 4.71 (d, 1 H, $J_{1,2}$ 8.50 Hz, 1 H, $H_{\beta-1}$), 4.58 (d, 1 H, $J_{1',2'}$ 8.00 Hz, 1 H, $H_{\alpha-1'}$), 4.52 (d, 1 H, $J_{1',2'}$ 8.00 Hz, 1 H, $H_{\beta-1'}$), 4.50, 4.11–4.08 (m, 8 H, $H_{\alpha-6a}$, 6b, $H_{\alpha-6a'}$, 6b', $H_{\beta-6a}$, 6b, $H_{\beta-6a'}$, 6b'), 4.27 (dd, 1 H, $H_{\alpha-2}$), 4.07 (dd, 1 H, $H_{\beta-2}$), 3.91–3.79 (m, 6 H, $H_{\alpha-4}$, 5, $H_{\alpha-5'}$, $H_{\beta-4}$, 5, $H_{\beta-5'}$), 3.76–3.56 (m, 8 H, CH_2O), 2.19–1.96 (14s, 42 H, $CH_{3\alpha}CONH$, $CH_{3\beta}CONH$, $12 \times CH_3CO$); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.8 (2 C, $CH_3CO_{\alpha}NH$, $CH_3CO_{\beta}NH$), 170.5–169.2 (12 C, CH_3CO), 101.2 ($C_{\alpha-1'}$), 101.0 ($C_{\beta-1}$), 100.0 ($C_{\beta-1'}$), 97.3 ($C_{\alpha-1}$), 76.3 ($C_{\alpha-4}$), 76.0 ($C_{\beta-4}$), 72.7 ($C_{\beta-3}$), 72.5 (CH_2O), 71.8 ($C_{\alpha-3}$), 71.2, 70.9 (2 C, $C_{\alpha-3'}$, $C_{\beta-3'}$), 70.8, 70.6 (2 C, $C_{\alpha-5'}$, $C_{\beta-5'}$), 70.5 (CH_2O), 69.3 (CH_2O), 69.2, 69.0 (2 C, $C_{\alpha-2'}$, $C_{\beta-2'}$), 69.1, 68.2 (2 C, $C_{\alpha-5}$, $C_{\beta-5}$), 67.6 (CH_2O), 66.5, 66.2 (2 C, $C_{\alpha-4'}$, $C_{\beta-4'}$), 62.1, 61.8 (2 C, $C_{\alpha-6}$, $C_{\beta-6}$), 60.7, 60.5 (2 C, $C_{\alpha-6'}$, $C_{\beta-6'}$), 52.7, 52.4 (2 C, $C_{\alpha-2}$, $C_{\beta-2}$), 23.2, 22.9 (2 C, CH_3CONH), 20.9–20.5 (12 C, CH_3CO). Anal. Calcd for $C_{56}H_{80}N_2O_{35}$: C, 50.15; H, 6.01; N, 2.09. Found: C, 50.08; H, 5.80; N, 1.92.

1-[2,3,4,6-Tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- β -D-glucopyranosyloxy-8-[2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetamido-2-deoxy- α -D-glucopyranosyloxy-3-dioxaoctane (20)

Compound **20** was prepared as described for the preparation of **19**. The crude product was purified by chromatography with 35:1 $CHCl_3$ –MeOH to afford a colorless syrup in 56% yield; $[\alpha]_D^{25} + 13.5^\circ$ (c 0.89, $CHCl_3$); 1H NMR ($CDCl_3$): δ 6.60, 6.51 (d, 2 H, NH_{α} , NH_{β}), 5.36 (dd, 2 H, $H_{\alpha-4'}$, $H_{\beta-4'}$), 5.23 (dd, 1 H, $H_{\alpha-3}$), 5.13–5.11 (m, 2 H, $H_{\alpha-2'}$, $H_{\beta-2'}$), 5.05 (1 H, $H_{\beta-3}$), 4.97–4.95 (m, 2 H, $H_{\alpha-3'}$, $H_{\beta-3'}$), 4.80 (d, 1 H, $J_{1,2}$ 3.50 Hz, $H_{\alpha-1}$), 4.66 (d, 1 H, $J_{1,2}$ 8.00 Hz, $H_{\beta-1}$), 4.51 (d, 2H, $J_{1',2'}$ 8.00 Hz, $H_{\alpha-1'}$, $H_{\beta-1'}$), 4.45, 4.12–4.10 (m, 8 H, $H_{\alpha-6a}$, 6b, $H_{\alpha-6a'}$, 6b', $H_{\beta-6a}$, 6b, $H_{\beta-6a'}$, 6b'), 4.27 (dd, 1 H, $H_{\alpha-2}$), 4.07 (dd, 1 H, $H_{\beta-2}$), 3.93–3.78 (m, 6 H, $H_{\alpha-4}$, 5, $H_{\alpha-5'}$, $H_{\beta-4}$, 5, $H_{\beta-5'}$), 3.77–3.62 (m, 12 H, CH_2O), 2.16–1.96 (14s, 42 H, $CH_{3\alpha}CONH$, $CH_{3\beta}CONH$, $12 \times CH_3CO$); ^{13}C NMR ($CDCl_3$): δ 170.9–169.2 (14 C, $CH_3CO_{\alpha}NH$, $CH_3CO_{\beta}NH$, $12 \times CH_3CO$), 101.5 ($C_{\alpha-1'}$), 101.2 ($C_{\beta-1}$), 101.1 ($C_{\beta-1'}$), 97.5 ($C_{\alpha-1}$), 76.3 ($C_{\alpha-4}$), 76.2 ($C_{\beta-4}$), 73.1 (CH_2O), 72.6 ($C_{\beta-3}$), 72.5 (CH_2O), 71.5 ($C_{\alpha-3}$), 71.1, 71.0 (2 C, $C_{\alpha-3'}$, $C_{\beta-3'}$), 70.9, 70.6 (2 C, $C_{\alpha-5'}$, $C_{\beta-5'}$), 70.9 (CH_2O), 70.5 (CH_2O), 69.9 (CH_2O), 69.2, 69.0 (2 C, $C_{\alpha-2'}$, $C_{\beta-2'}$), 68.5 (2 C, $C_{\alpha-5}$, $C_{\beta-5}$), 67.2 (CH_2O), 66.5, 66.4 (2 C, $C_{\alpha-4'}$, $C_{\beta-4'}$), 62.2, 61.9 (2 C, $C_{\alpha-6}$, $C_{\beta-6}$), 60.7, 60.5 (2 C, $C_{\alpha-6'}$, $C_{\beta-6'}$), 53.3, 51.7 (2 C, $C_{\alpha-2}$, $C_{\beta-2}$), 23.1, 23.0 (2 C, $C_{\alpha}H_3CONH$, $C_{\beta}H_3CONH$), 20.9–20.5 (12 C, CH_3CO). Anal. Calcd for $C_{58}H_{84}N_2O_{36}$: C, 50.29; H, 6.11; N, 2.02. Found: C, 50.46; H, 6.39; N, 1.85.

3-Oxapent-1,5-diyl bis[2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- β -D-glucopyranoside] (21)

Compound **21** was prepared as described for the preparation of **19**. The crude product was purified by chromatography with 35:1 $CHCl_3$ –MeOH to afford a colorless syrup in 50% yield; $[\alpha]_D^{25} + 5.3^\circ$ (c 2.28, $CHCl_3$); 1H NMR ($CDCl_3$): δ 6.81 (d, 1 H, NH), 5.36 (d, 1 H, $H-4'$), 5.15 (dd, 1 H, $H-2'$), 5.07 (dd, 1 H, $H-3$), 4.98 (dd, 1 H, $H-3'$), 4.77 (d, 1 H, $J_{1,2}$ 8.00 Hz, $H-1$), 4.54 (d, 1 H, $J_{1',2'}$ 7.25 Hz, $H-1'$), 4.45, 4.16–4.07 (m, 4 H, $H-6a$, 6b, $H-6a'$, 6b'), 4.06 (dd, 1 H, $H-2$), 3.91 (m, 1 H, $H-5$), 3.86 (m, 1 H, $H-5'$), 3.82 (m, 1 H, $H-4$), 3.78–3.60 (m, 4 H, CH_2O), 2.19–1.95 (7s, 21 H, $6 \times CH_3CO$, $NHCOCH_3$); ^{13}C NMR ($CDCl_3$): δ 171.0–169.2 (7 C, $6 \times COCH_3$, $NHCOCH_3$), 101.5 (C-1), 101.1 (C-1'), 75.9 (C-4), 72.9 (CH_2O), 72.7 (C-3), 70.8 (C-3'), 70.6 (C-5'), 69.2 (C-2'), 68.4 (C-5), 67.5 (CH_2O), 66.5 (C-4'), 62.1 (C-6), 60.7 (C-6'), 52.7 (C-2), 22.9 (CH_3CONH), 20.9–20.5 (6 C, CH_3CO). Anal. Calcd for $C_{56}H_{80}N_2O_{35}$: C, 50.15; H, 6.01; N, 2.09. Found: C, 49.89; H, 6.26; N, 1.85.

3,6-Dioxaoct-1,8-diyl bis[2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- β -D-glucopyranoside] (22)

Compound **22** was prepared as described for the preparation of **19**. The crude product was purified by chromatography with 35:1 $CHCl_3$ –MeOH to afford a colorless syrup in 52% yield; $[\alpha]_D^{25} + 8.2^\circ$ (c 0.98, $CHCl_3$); 1H NMR ($CDCl_3$): δ 6.55 (d, 1 H, NH), 5.35 (d, 1 H, $H-4'$), 5.11 (dd, 1 H, $H-2'$), 5.04 (dd, 1 H, $H-3$), 4.96 (dd, 1 H, $H-3'$), 4.66 (d, 1 H, $J_{1,2}$ 8.00 Hz, $H-1$), 4.50 (d, 1 H, $J_{1',2'}$ 8.00 Hz, $H-1'$), 4.48, 4.13–4.07 (m, 4 H, $H-6a$, 6b, $H-6a'$, 6b), 4.04 (m, 1 H, $H-2$), 3.91 (m, 1 H, $H-5$), 3.86 (m, 1 H, $H-5'$), 3.83 (m, 1 H, $H-4$), 3.78–3.62 (m, 6 H, CH_2O), 2.17–1.97 (7s, 21 H, $6 \times CH_3CO$, CH_3CONH); ^{13}C NMR ($CDCl_3$): δ 171.1 ($NHCOCH_3$), 170.4–169.2 (6 C, $COCH_3$), 101.5 (C-1), 101.2 (C-1'), 76.2 (C-4), 73.1 (CH_2O), 72.8 (C-3), 71.0 (C-3'), 70.6 (C-5'), 70.5 (CH_2O), 69.4 (CH_2O), 69.3 (C-2'), 68.5 (C-5), 66.7 (C-4'), 62.4 (C-6), 60.8 (C-6'), 53.3 (C-2), 23.0 (CH_3CONH), 20.8–20.4 (6 C, CH_3CO). Anal. Calcd for $C_{58}H_{84}N_2O_{36}$: C, 50.29; H, 6.11; N, 2.02. Found: C, 50.54; H, 6.16; N, 1.71.

3-Oxapent-1,5-diyl bis[2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy- α -D-glucopyranoside] (23)

Compound **23** was prepared as described for the preparation of **19**. The crude product was purified by chromatography with 35:1 $CHCl_3$ –MeOH to afford a colorless syrup in 48% yield; $[\alpha]_D^{25} + 50.5^\circ$ (c 1.03,

CHCl₃); ¹H NMR (CDCl₃): δ 6.40 (d, 1 H, NH), 5.35 (d, 1 H, H-4'), 5.24 (dd, 1 H, H-3), 5.12 (dd, 1 H, H-2'), 4.96 (dd, 1 H, H-3'), 4.84 (d, 1 H, *J*_{1,2} 3.25 Hz, H-1), 4.52 (d, 1 H, *J*_{1',2'} 7.50 Hz, H-1'), 4.46, 4.13–4.07 (m, 4 H, H-6a, 6b, H-6a', 6b'), 4.26 (dd, 1 H, H-2), 3.90 (m, 1 H, H-5), 3.87 (m, 1 H, H-5'), 3.80 (m, 1 H, H-4), 3.77–3.64 (m, 4 H, CH₂O), 2.15–1.97 (7s, 21 H, 6 × CH₃CO, NHCOCH₃); ¹³C NMR (CDCl₃): δ 170.9–169.1 (7 C, 6 × COCH₃, NHCOCH₃), 101.3 (C-1'), 97.3 (C-1), 76.4 (C-4), 71.4 (C-3), 71.0 (C-3'), 70.7 (C-5'), 70.0 (CH₂O), 69.3 (C-2'), 68.7 (C-5), 67.1 (CH₂O), 66.7 (C-4'), 61.9 (C-6), 60.8 (C-6'), 52.0 (C-2), 23.0 (CH₃CONH), 20.9–20.4 (6 C, CH₃CO). Anal. Calcd for C₅₆H₈₀N₂O₃₅: C, 50.15; H, 6.01; N, 2.09. Found: C, 50.08; H, 5.80; N, 1.83.

3,6-Dioxaoct-1,8-diyl bis[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1 → 4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy-α-D-glucopyranoside] (24)

Compound **24** was prepared as described for the preparation of **19**. The crude product was purified by chromatography with 35:1 CHCl₃–MeOH to afford a colorless syrup in 50% yield; [α]_D²⁵ + 34.3° (*c* 1.75, CHCl₃); ¹H NMR (CDCl₃): δ 6.30 (d, 1 H, NH), 5.35 (d, 1 H, H-4'), 5.25 (dd, 1 H, H-3), 5.11 (dd, 1 H, H-2'), 4.98 (dd, 1 H, H-3'), 4.80 (d, 1 H, *J*_{1,2} 3.50 Hz, H-1), 4.52 (d, 1 H, *J*_{1',2'} 8.00 Hz, H-1'), 4.46, 4.13–4.09 (m, 4 H, H-6a, 6b, H-6a', 6b), 4.26 (m, 1 H, H-2), 3.95 (m, 1 H, H-5), 3.88 (m, 1 H, H-5'), 3.82 (m, 1 H, H-4), 3.77–3.62 (m, 6 H, CH₂O), 2.15–1.96 (7s, 21 H, 6 × CH₃CO, CH₃CONH); ¹³C NMR (CDCl₃): δ 170.9–169.2 (7 C, 6 × COCH₃, NHCOCH₃), 101.3 (C-1'), 97.4 (C-1), 76.4 (C-4), 71.5 (C-3), 71.0 (C-3'), 70.5 (C-5'), 70.4 (CH₂O), 69.9 (CH₂O), 69.1 (C-2'), 68.4 (C-5), 67.4 (CH₂O), 66.5 (C-4'), 61.9 (C-6), 60.6 (C-6'), 51.8 (C-2), 23.0 (CH₃CONH), 20.9–20.5 (6 C, CH₃CO). Anal. Calcd for C₅₈H₈₄N₂O₃₆: C, 50.29; H, 6.11; N, 2.02. Found: C, 50.44; H, 6.35; N, 1.76.

5-Hydroxy-3-oxapentyl β-D-galactopyranosyl-(1 → 4)-2-acetamido-2-deoxy-β-D-glucopyranoside (25)

A catalytic amount of sodium was added to a solution of compound **15** (0.1 g) in methanol (5 mL). The mixture was stirred at room temperature for 12 h, then neutralized with H⁺ cation exchange resin. The solution was filtered and concentrated and the residue was dissolved in 10 mL water and freeze-dried to give **25** as a white solid (0.062 g, 95%); [α]_D²⁵ – 83.9° (*c* 0.62, H₂O); ¹H NMR (D₂O): δ 4.64 (d, 1 H, *J*_{1,2} 8.10 Hz, H-1), 4.52 (d, 1 H, *J*_{1',2'} 7.50 Hz, H-1'), 4.06–3.69 (m, 20 H, H-2, 3, 4, 5, 6a, 6b, H-2', 3', 4', 5', 6a', 6b', CH₂O), 2.09 (s, 3 H, NHCOCH₃); ¹³C NMR (D₂O): δ 171.5 (NHCO), 99.9 (C-1'), 98.0 (C-1), 75.6 (C-4), 72.4, 71.8, 69.6, 69.5, 68.8, 68.0, 66.6, 66.0, 57.4 (9 C, C-3,

C-5, C-2', C-3', C-5', CH₂O), 65.6 (C-4'), 58.0 (C-6), 57.2 (C-6'), 52.1 (C-2), 19.2 (CH₃CONH). ESI-TOFF-MS: *m/z* 472.2 [M + 1]⁺.

8-Hydroxy-3,6-dioxaoctyl β-D-galactopyranosyl-(1 → 4)-2-acetamido-2-deoxy-β-D-glucopyranoside (26)

Compound **26** was prepared as described for the preparation of **25**. The yield was 97%; [α]_D²⁵ – 105.3° (*c* 0.76, H₂O); ¹H NMR (D₂O): δ 4.58 (d, 1 H, *J*_{1,2} 7.80 Hz, H-1), 4.46 (d, 1 H, *J*_{1',2'} 7.50 Hz, H-1'), 3.96–3.64 (m, 24 H, H-2, 3, 4, 5, 6a, 6b, H-2', 3', 4', 5', 6a', 6b', CH₂O), 2.03 (s, 3 H, NHCOCH₃); ¹³C NMR (D₂O): δ 171.2 (NHCO), 99.3 (C-1'), 97.5 (C-1), 75.7 (C-4), 72.7, 72.0, 70.7, 69.8, 68.5, 68.0, 66.6, 66.3, 64.9, 57.8, 57.3 (11 C, C-3, C-5, C-2', C-3', C-5', CH₂O), 64.9 (C-4'), 57.8 (C-6), 57.1 (C-6'), 52.3 (C-2), 19.7 (CH₃CONH). ESI-TOFF-MS: *m/z* 516.2 [M + 1]⁺.

5-Hydroxy-3-oxapentyl β-D-galactopyranosyl-(1 → 4)-2-acetamido-2-deoxy-α-D-glucopyranoside (27)

Compound **27** was prepared as described for the preparation of **25**. The yield was 96%; [α]_D²⁵ + 70.6° (*c* 0.68, H₂O); ¹H NMR (CD₃OD): δ 4.82 (d, 1 H, *J*_{1,2} 3.60 Hz, H-1), 4.36 (d, 1 H, *J*_{1',2'} 7.50 Hz, H-1'), 3.93–3.60 (m, 18 H, H-2, 3, 4, 5, 6a, 6b, H-4', 5', 6a', 6b', CH₂O), 3.57 (dd, 1 H, H-2'), 3.50 (dd, 1 H, H-3'), 1.98 (s, 3 H, NHCOCH₃); ¹³C NMR (CD₃OD): δ 173.6 (NHCO), 105.2 (C-1'), 98.6 (C-1), 81.5 (C-4), 77.1 (C-5'), 74.9 (C-3'), 73.6, 72.3, 71.2, 71.1, 70.3, 62.2 (6 C, C-3, C-5, CH₂O), 72.6 (C-2'), 68.2 (C-4'), 62.5 (C-6), 62.0 (C-6'), 54.9 (C-2), 22.6 (CH₃CONH). ESI-TOFF-MS: *m/z* 472.2 [M + 1]⁺.

8-Hydroxy-3,6-dioxaoctyl β-D-galactopyranosyl-(1 → 4)-2-acetamido-2-deoxy-α-D-glucopyranoside (28)

Compound **28** was prepared as described for the preparation of **25**. The yield was 98%; [α]_D²⁵ + 64.9° (*c* 0.37, H₂O); ¹H NMR (CD₃OD): δ 4.81 (d, 1 H, *J*_{1,2} 3.30 Hz, H-1), 4.37 (d, 1 H, *J*_{1',2'} 7.80 Hz, H-1'), 3.98–3.62 (m, 22 H, H-2, 3, 4, 5, 6a, 6b, H-4', 5', 6a', 6b', CH₂O), 3.56 (dd, 1 H, H-2'), 3.50 (dd, 1 H, H-3'), 1.98 (s, 3 H, NHCOCH₃); ¹³C NMR (CD₃OD): δ 173.6 (NHCO), 105.1 (C-1'), 98.6 (C-1), 81.4 (C-4), 77.1 (C-5'), 74.9 (C-3'), 73.7, 72.3, 71.6, 71.4, 71.2, 71.1, 70.3, 62.2 (8 C, C-3, C-5, CH₂O), 72.6 (C-2'), 68.1 (C-4'), 62.5 (C-6), 62.0 (C-6'), 54.9 (C-2), 22.6 (CH₃CONH). ESI-TOFF-MS: *m/z* 516.2 [M + 1]⁺.

1-β-D-Galactopyranosyl-(1 → 4)-2-acetamido-2-deoxy-β-D-glucopyranosyloxy-5-β-D-galactopyranosyl-(1 → 4)-2-acetamido-2-deoxy-α-D-glucopyranosyloxy-3-oxapentane (29)

Compound **29** was prepared as described for the prepara-

ration of **25**. The yield was 97%; $[\alpha]_{\text{D}}^{25} + 31.8^\circ$ (c 0.63, H₂O); ¹H NMR (D₂O): δ 4.82 (d, 1 H, $J_{1,2}$ 3.50 Hz, H _{α} -1), 4.52 (d, 1 H, $J_{1,2}$ 8.00 Hz, H _{β} -1), 4.41 (d, 2 H, $J_{1',2'}$ 7.50 Hz, H _{α} -1', H _{β} -1'), 3.94–3.65 (m, 28 H, H _{α} -2, 3, 4, 5, 6a, 6b, H _{α} -4', 5', 6a', 6b', H _{β} -2, 3, 4, 5, 6a, 6b, H _{β} -4', 5', 6a', 6b', CH₂O), 3.61 (dd, 2 H, H _{α} -2', H _{β} -2'), 3.48 (dd, 2 H, H _{α} -3', H _{β} -3'), 1.98 (s, 6 H, 2 × NHCOCH₃); ¹³C NMR (D₂O): δ 175.0, 174.9 (2 C, NHCO), 103.4 (C _{α} -1'), 103.2 (C _{β} -1'), 101.6 (C _{β} -1), 97.4 (C _{α} -1), 79.2, 78.9 (2 C, C _{α} -4, C _{β} -4), 75.9, 75.3 (2 C, C _{α} -5', C _{β} -5'), 73.3, 73.0 (2 C, C _{α} -3', C _{β} -3'), 71.5, 71.2 (2 C, C _{α} -2', C _{β} -2'), 70.4, 70.3, 70.2, 69.6, 69.5, 67.4 (6 C, C _{α} -3, C _{β} -3, C _{α} -5, C _{β} -5, CH₂O), 69.1, 68.9 (2 C, C _{α} -4', C _{β} -4'), 61.6, 60.6 (2 C, C _{α} -6, C _{β} -6), 60.4, 60.3 (2 C, C _{α} -6', C _{β} -6'), 55.6, 53.7 (2 C, C _{α} -2, C _{β} -2), 22.7, 22.4 (2 C, CH₃CONH). ESI-TOFF-MS: m/z 837.3 [M + 1]⁺.

1- β -D-Galactopyranosyl-(1 \rightarrow 4)-2-acetamido-2-deoxy- β -D-glucopyranosyloxy-8- β -D-galactopyranosyl-(1 \rightarrow 4)-2-acetamido-2-deoxy- α -D-glucopyranosyloxy]-3,6-dioxaoctane (30)

Compound **30** was prepared as described for the preparation of **25**. The yield was 98%; $[\alpha]_{\text{D}}^{25} + 30.3^\circ$ (c 0.66, H₂O); ¹H NMR (D₂O): δ 4.83 (d, 1 H, $J_{1,2}$ 3.30 Hz, H _{α} -1), 4.53 (d, 1 H, $J_{1,2}$ 8.00 Hz, H _{β} -1), 4.41 (d, 2 H, $J_{1',2'}$ 7.50 Hz, H _{α} -1', H _{β} -1'), 3.94–3.65 (m, 28 H, H _{α} -2, 3, 4, 5, 6a, 6b, H _{α} -4', 5', 6a', 6b', H _{β} -2, 3, 4, 5, 6a, 6b, H _{β} -4', 5', 6a', 6b', CH₂O), 3.62 (dd, 2 H, H _{α} -2', H _{β} -2'), 3.49 (dd, 2 H, H _{α} -3', H _{β} -3'), 1.98 (s, 6 H, 2 × NHCOCH₃); ¹³C NMR (D₂O): δ 175.1, 174.9 (2 C, NHCO), 103.4 (C _{α} -1'), 103.2 (C _{β} -1'), 101.6 (C _{β} -1), 97.4 (C _{α} -1), 79.2, 78.9 (2 C, C _{α} -4, C _{β} -4), 75.9, 75.3 (2 C, C _{α} -5', C _{β} -5'), 73.3, 73.0 (2 C, C _{α} -3', C _{β} -3'), 71.5, 71.2 (2 C, C _{α} -2', C _{β} -2'), 70.4, 70.2, 70.1, 69.6, 69.5, 67.3, 67.1 (7 C, C _{α} -3, C _{β} -3, C _{α} -5, C _{β} -5, CH₂O), 69.1, 68.9 (2 C, C _{α} -4', C _{β} -4'), 61.6, 60.6 (2 C, C _{α} -6, C _{β} -6), 60.4, 60.2 (2 C, C _{α} -6', C _{β} -6'), 55.6, 53.7 (2 C, C _{α} -2, C _{β} -2), 22.7, 22.5 (2 C, CH₃CONH). ESI-TOFF-MS: m/z 881.4 [M + 1]⁺.

3-Oxapent-1,5-diyl bis(β -D-galactopyranosyl-(1 \rightarrow 4)-2-acetamido-2-deoxy- β -D-glucopyranoside) (31)

Compound **31** was prepared as described for the preparation of **25**. The yield was 94%; $[\alpha]_{\text{D}}^{25} + 26.7^\circ$ (c 1.20, H₂O); ¹H NMR (CD₃OD): δ 4.51 (d, 1 H, $J_{1,2}$ 8.00 Hz, H-1), 4.38 (d, 1 H, $J_{1',2'}$ 7.50 Hz, H-1'), 3.97–3.48 (m, 16 H, H-2, 3, 4, 5, 6a, 6b, H-2', 3', 4', 5', 6a', 6b', CH₂O), 2.02 (s, 3 H, NHCOCH₃); ¹³C NMR (CD₃OD): δ 174.0 (NHCO), 105.1 (C-1'), 102.6 (C-1), 81.6 (C-4), 77.2 (C-5'), 74.9 (C-3'), 72.6 (C-2'), 72.3, 71.5, 71.2, 70.4 (4 C, C-3, C-5, CH₂O), 68.2 (C-4'), 62.5 (C-6), 62.0 (C-6'), 55.1 (C-2), 22.5 (CH₃CONH). ESI-TOFF-MS: m/z 837.3 [M + 1]⁺.

3,6-Dioxaoct-1,8-diyl bis(β -D-galactopyranosyl-(1 \rightarrow 4)-2-acetamido-2-deoxy- β -D-glucopyranoside) (32)

Compound **32** was prepared as described for the preparation of **25**. The yield was 98%; $[\alpha]_{\text{D}}^{25} + 21.7^\circ$ (c 0.92, H₂O); ¹H NMR (CD₃OD): δ 4.53 (d, 1 H, $J_{1,2}$ 8.00 Hz, H-1), 4.39 (d, 1 H, $J_{1',2'}$ 7.50 Hz, H-1'), 3.96–3.54 (m, 18 H, H-2, 3, 4, 5, 6a, 6b, H-2', 3', 4', 5', 6a', 6b', CH₂O), 1.99 (s, 3 H, NHCOCH₃); ¹³C NMR (CD₃OD): δ 174.2 (NHCO), 104.8 (C-1'), 102.6 (C-1), 81.0 (C-4), 76.9 (C-5'), 74.5 (C-3'), 72.5 (C-2'), 72.2, 71.4, 71.1, 70.1, 69.9 (5 C, C-3, C-5, CH₂O), 68.1 (C-4'), 62.4 (C-6), 61.8 (C-6'), 56.6 (C-2), 23.2 (CH₃CONH). ESI-TOFF-MS: m/z 903.3 [M + Na]⁺.

3-Oxapent-1,5-diyl bis(β -D-galactopyranosyl-(1 \rightarrow 4)-2-acetamido-2-deoxy- α -D-glucopyranoside) (33)

Compound **33** was prepared as described for the preparation of **25**. The yield was 95%; $[\alpha]_{\text{D}}^{25} + 38.7^\circ$ (c 1.24, H₂O); ¹H NMR (CD₃OD): δ 4.85 (d, 1 H, $J_{1,2}$ 3.50 Hz, H-1), 4.39 (d, 1 H, $J_{1',2'}$ 7.50 Hz, H-1'), 3.97–3.68 (m, 14 H, H-2, 3, 4, 5, 6a, 6b, H-4', 5', 6a', 6b', CH₂O), 3.62 (dd, 1 H, H-2'), 3.54 (dd, 1 H, H-3'), 2.01 (s, 3 H, NHCOCH₃); ¹³C NMR (CD₃OD): δ 174.0 (NHCO), 104.9 (C-1'), 98.5 (C-1), 81.2 (C-4), 77.0 (C-5'), 74.7 (C-3'), 72.6 (C-2'), 72.2, 71.3, 71.0, 70.2 (4 C, C-3, C-5, CH₂O), 68.1 (C-4'), 62.4 (C-6), 61.8 (C-6'), 54.8 (C-2), 22.8 (CH₃CONH). ESI-TOFF-MS: m/z 859.3 [M + Na]⁺.

3,6-Dioxaoct-1,8-diyl bis(β -D-galactopyranosyl-(1 \rightarrow 4)-2-acetamido-2-deoxy- α -D-glucopyranoside) (34)

Compound **34** was prepared as described for the preparation of **25**. The yield was 93%; $[\alpha]_{\text{D}}^{25} + 55.8^\circ$ (c 0.86, H₂O); ¹H NMR (CD₃OD): δ 4.84 (d, 1 H, $J_{1,2}$ 3.50 Hz, H-1), 4.37 (d, 1 H, $J_{1',2'}$ 7.50 Hz, H-1'), 3.97–3.63 (m, 16 H, H-2, 3, 4, 5, 6a, 6b, H-4', 5', 6a', 6b', CH₂O), 3.55 (dd, 1 H, H-2'), 3.49 (dd, 1 H, H-3'), 1.99 (s, 3 H, NHCOCH₃); ¹³C NMR (CD₃OD): δ 173.5 (NHCO), 105.2 (C-1'), 98.7 (C-1), 81.5 (C-4), 77.2 (C-5'), 75.0 (C-3'), 72.7 (C-2'), 72.3, 71.6, 71.4, 71.2, 70.4 (5 C, C-3, C-5, CH₂O), 68.2 (C-4'), 62.5 (C-6), 62.0 (C-6'), 55.0 (C-2), 22.7 (CH₃CONH). ESI-TOFF-MS: m/z 881.4 [M + 1]⁺.

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