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

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Abstract

Anomers of monovalent and divalent β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-D-gluco-pyranosides were synthesized under different glycosylation conditions, and evaluated for in vitro antimetastatic activity. Three compounds showed promising inhibitory effects on cancer cell attachment, spreading, migration, and invasion. © 2002 Elsevier Science Ltd. All rights reserved.

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1. 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→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.

2. Results and discussion

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-azido-2-deoxy-D-glucopyranosyl nitrate (**1**)[6] was treated with $NaNO_2$ and H_2O in 1,4-dioxane for 10 h at 80 °C to give hemiacetal **2**,[7] which then reacted with CCl_3CN and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) in dry CH_2Cl_2 for 3 h at 0 °C to give the imidate **3**. Imidate **3** reacted with the spacer-arm aglycons in CH_2Cl_2 at room temperature with Me_3SiOTf as promoter to afford the β-glycosides (**5** or **6**) in yields of 65–70%. Treating **1** with LiBr[2] afforded bromide **4**, which then reacted in the presence of tetrabutyl ammonium bromide (Bu_4NBr)[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 Me_3SiOTf, the asymmetric divalent glycosides (**9** and **10**) were mainly obtained. On the other hand, $BF_3{\cdot}OEt_2$, a weaker promoter than Me_3SiOTf, 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 Me_3SiOTf, but asymmetric divalent glycosides **9** or **10** were obtained when $BF_3{\cdot}OEt_2$ 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-

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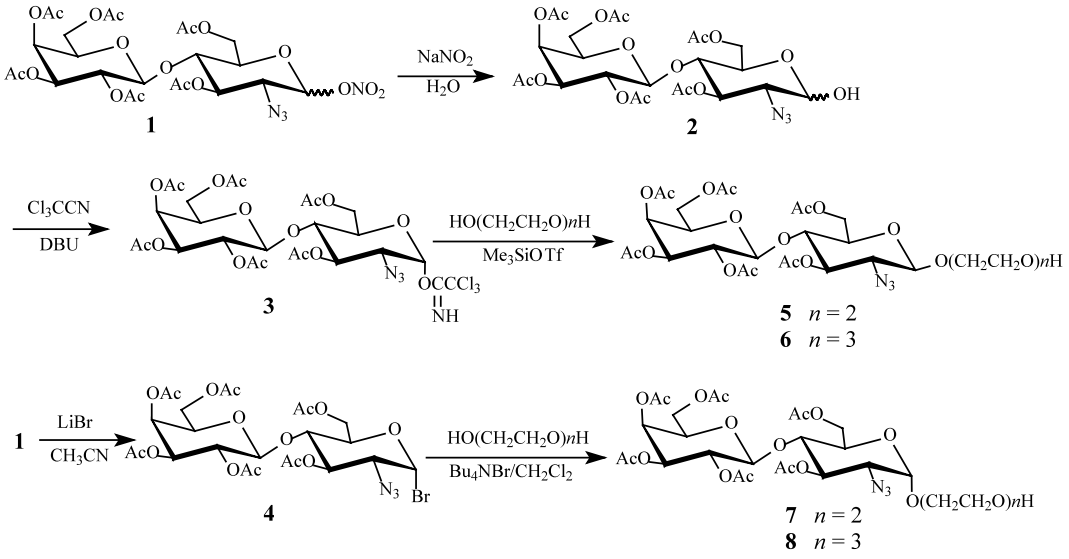
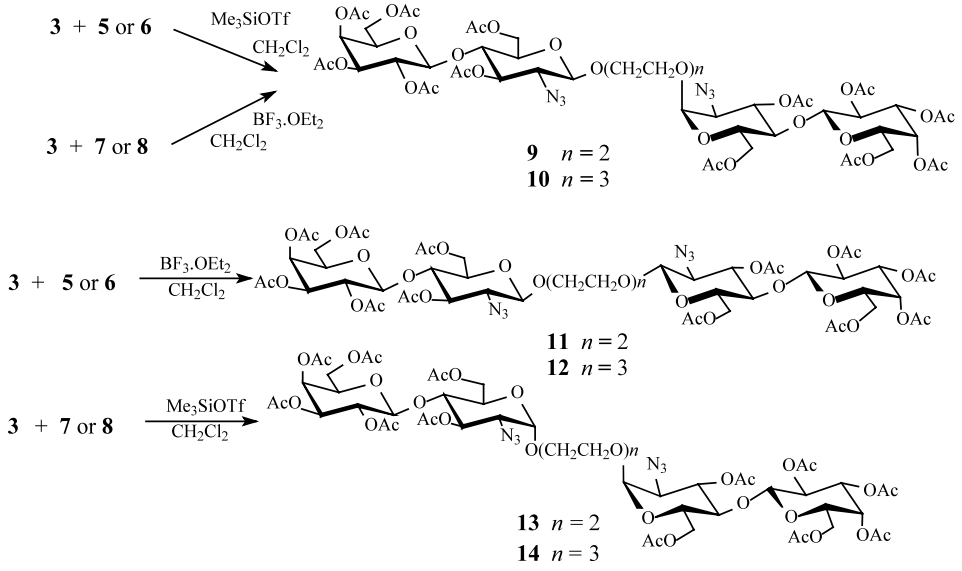


Scheme 1.



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 phosphaotase 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.

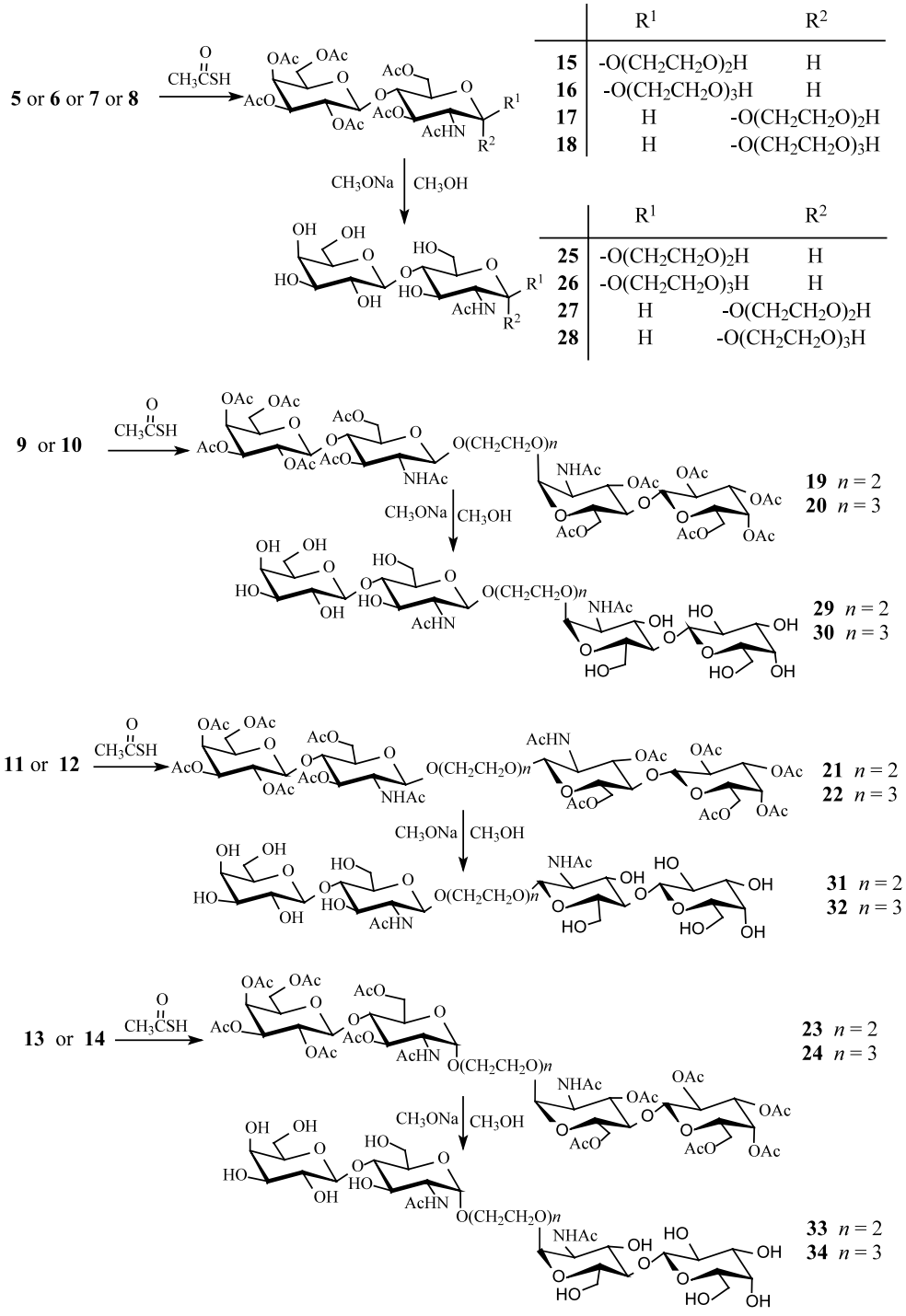
The results from Table 2 indicate that compound **26** is capable of inhibiting human hepatocellular carcinoma cell migration and invasion.

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*-acetyllactosamine derivatives, in an appropriate structure, might be developed as an anti-metastatic therapeutics.

3. Experimental

3.1. 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 $CDCl_3$, CD_3OD, and D_2O as solvents. Elemental analyses were performed with a Perkin–Elmer 240C instrument. Mass spectra were recorded with an IBI-MDS Sciexciex Qstar type of mass spectrometer. Purity of the products was verified by TLC on Silica Gel GF_{254}. Column chromatography was performed on Silica Gel H_{60}.

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 $NaNO_2$ (4 g) were added. The mixture was heated at 80 °C for 10 h with stirring, and then concentrated, and 50 mL of $CHCl_3$

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 glucosides).
[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 CH_2Cl_2 (12 mL), and then CCl_3CN (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%.

3.3. 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 CH_2Cl_2 (10 mL), Me_3SiOTf was added and the mixture was stirred at room temperature for 16 h. The mixture was then diluted with CH_2Cl_2 (20 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 to afford 0.32 g of **5** as a colorless syrup, yield 70%; $[\alpha]_D^{25}$ + 32.0° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): 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, CH_2O), 3.10 (dd, 1 H, H-2), 2.17–1.96 (6s, 18 H, $6 \times CH_3CO$); ^{13}C NMR ($CDCl_3$): δ 170.3–168.9 (6 C, CH_3CO), 102.1 (C-1), 100.9 (C-1′), 75.9 (C-4), 72.8 (CH_2O), 72.4 (CH_2O), 71.8 (C-3), 71.0 (C-3′), 70.7 (C-5), 70.1 (CH_2O), 69.5 (C-5′), 69.1 (C-2′), 66.6 (C-4′), 63.9 (C-2), 61.8 (C-6), 61.7 (CH_2O), 60.8 (C-6′), 20.8–20.5 (6 C, CH_3CO). Anal. Calcd for $C_{28}H_{41}N_3O_{18}$: C, 47.53; H, 5.84; N, 5.94. Found: C, 47.17; H, 5.59; N, 5.49.

3.4. 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° (*c* 1.35, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 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, CH_2O), 2.15–1.95 (6s, 18 H, $6 \times CH_3CO$); ^{13}C NMR ($CDCl_3$): δ 170.3–169.0 (6 C, CH_3CO), 101.9 (C-1), 100.9 (C-1′), 76.0 (C-4), 72.6 (CH_2O), 72.4 (CH_2O), 71.9 (C-3), 71.0 (C-3′), 70.7 (C-5), 70.5 (CH_2O), 70.3 (CH_2O), 69.1 (C-5′), 69.0 (C-2′), 67.7 (CH_2O), 66.7 (C-4′), 63.9 (C-2), 61.9 (C-6), 61.6 (CH_2O), 60.8 (C-6′), 20.9–20.5 (6 C, CH_3CO). Anal. Calcd for $C_{30}H_{45}N_3O_{19}$: C, 47.94; H, 6.03; N, 5.59. Found: C, 47.57; H, 5.88; N, 5.31.

3.5. 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 CH_3CN (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 CH_2Cl_2 (15 mL), were added Bu_4NBr (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%; $[\alpha]_D^{25}$ +61.9° (*c* 1.55, $CHCl_3$); ^{1}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, $6\times CH_3CO$); ^{13}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 $C_{28}H_{41}N_3O_{18}$: C, 47.53; H, 5.84; N, 5.94. Found: C, 47.70; H, 6.05; N, 5.51.

3.6. 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-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; $[\alpha]_D^{25}$ +80.0° (*c* 1.40, $CHCl_3$); ^{1}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, $6\times CH_3CO$); ^{13}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 $C_{30}H_{45}N_3O_{19}$: C, 47.94; H, 6.03; N, 5.59. Found: C, 47.76; H, 6.18; N, 5.80.

3.7. 1-[2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→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→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; $[\alpha]_D^{25}$ +57.1° (*c* 0.63, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.47 (dd, 1 H, H_α-3), 5.35 (dd, 2 H, H_α-4′, H_β-4′), 5.11–5.07 (m, 2 H, H_α-2′, H_β-2′), 5.05 (d, 1 H, $J_{1,2}$ 3.54 Hz, H_α-1), 4.98–4.95 (m, 3 H, H_β-3, H_α-3′, H_β-3′), 4.49 (d, 1 H, $J_{1,2}$ 7.99 Hz, 1 H, H_β-1), 4.47 (d, 2H, $J_{1',2'}$ 7.90 Hz, H_α-1′, H_β-1′), 4.45, 4.18–4.08 (m, 8 H, H_α-6a, 6b, H_α-6a′, 6b′, H_β-6a, 6b, H_β-6a′, 6b′), 3.98–3.76 (m, 6 H, H_α-4, 5, H_α-5′, H_β-4, 5, H_β-5′), 3.75–3.65 (m, 8 H, CH_2O), 3.45 (dd, 1 H, H_β-2), 3.12 (dd, 1 H, H_α-2), 2.17–1.96 (12s, 36 H, $12\times CH_3CO$); ^{13}C NMR ($CDCl_3$): δ 170.2–168.9 (12 C, CH_3CO), 101.9 (C_β-1), 101.1 (C_α-1′), 100.9 (C_β-1′), 97.8 (C_α-1), 76.5 (C_α-4), 75.9 (C_β-4), 72.6 (CH_2O), 71.9 (C_β-3), 71.0, 70.9 (2 C, C_α-3′, C_β-3′), 70.7, 70.6 (2 C, C_α-5′, C_β-5′), 70.5 (CH_2O), 70.2 (C_α-3), 70.1 (CH_2O), 69.3, 69.1 (2 C, C_α-2′, C_β-2′), 69.1, 68.4 (2 C, C_α-5, C_β-5), 67.4 (CH_2O), 66.6, 66.5 (2C, C_α-4′, C_β-4′), 63.9 (C_β-2), 61.9, 61.8 (2 C, C_α-6, C_β-6), 61.0, 60.8 (2 C, C_α-6′, C_β-6′), 60.7 (C_α-2), 20.9–20.4 (12 C, CH_3CO). Anal. Calcd for $C_{52}H_{72}N_6O_{33}$: C, 47.49; H, 5.56; N, 6.12. Found: C, 47.19; H, 5.49; N, 5.81.

3.8. 1-[2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→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→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; $[\alpha]_D^{25}$ +66.1° (*c* 2.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.47 (dd, 1 H, H_α-3), 5.35 (dd, 2 H, H_α-4′, H_β-4′), 5.10–5.09 (m, 2 H, H_α-2′, H_β-2′), 5.04 (d, 1 H, $J_{1,2}$ 3.35 Hz, H_α-1), 4.96–4.94 (m, 3 H, H_β-3, H_α-3′, H_β-3′), 4.49 (d, 1 H, $J_{1,2}$ 7.96 Hz, 1 H, H_β-1), 4.47 (d, 2 H, $J_{1',2'}$ 7.90 Hz, H_α-1′, H_β-1′), 4.45, 4.17–4.07 (m, 8 H, H_α-6a, 6b, H_α-6a′, 6b′, H_β-6a, 6b, H_β-6a′, 6b′), 3.98–3.72 (m, 6 H, H_α-4, 5, H_α-5′, H_β-4, 5, H_β-5′), 3.72–3.67 (m, 12 H, CH_2O), 3.42 (dd, 1 H, H_β-2), 3.11 (dd, 1 H, H_α-2), 2.18–1.97 (12s, 36 H, $12\times CH_3CO$); ^{13}C NMR ($CDCl_3$): δ 170.3–168.9 (12 C, CH_3CO), 102.0 (C_β-1), 101.1 (C_α-1′), 100.9 (C_β-1′), 98.1 (C_α-1), 76.5 (C_α-4), 76.0 (C_β-4), 72.7 (CH_2O), 72.6 (CH_2O), 71.9 (C_β-3), 71.0, 70.9 (2 C, C_α-3′, C_β-3′), 70.7, 70.3 (2 C, C_α-5′, C_β-5′), 70.2 (CH_2O), 70.1 (C_α-3), 70.0 (CH_2O), 69.4 (CH_2O), 69.3, 69.1 (2 C, C_α-2′, C_β-2′), 69.0, 68.4 (2 C, C_α-5, C_β-5), 67.7 (CH_2O), 66.6, 66.5 (2 C, C_α-4′, C_β-4′), 63.9 (C_β-2), 61.9, 61.0 (2 C, C_α-6, C_β-6), 60.8, 60.7 (2 C, C_α-6′, C_β-6′), 60.6 (C_α-2), 20.9–20.4 (12 C, CH_3CO). Anal. Calcd for $C_{54}H_{76}N_6O_{34}$: C, 47.93; H, 5.66; N, 6.21. Found: C, 47.73; H, 5.84; N, 5.92.

3.9. 3-Oxapent-1,5-diyl bis[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→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 CH_2Cl_2 (15 mL) in the presence of powered molecular sieves 4 Å (1 g) was cooled to 0 °C and $BF_3{\cdot}OEt_2$ (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 (Na_2SO_4) 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%); $[\alpha]_D^{25}$ +17.9° (*c* 2.68, $CHCl_3$); ^{1}H NMR ($CDCl_3$): 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, CH_2O), 3.43 (dd, 1 H, H-2), 2.17–1.98 (6s, 18 H, 6 × CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.3–168.9 (6 C, CH_3CO), 102.1 (C-1), 100.9 (C-1′), 76.0 (C-4), 72.9 (CH_2O), 72.0 (C-3), 70.8 (C-3′), 70.5 (C-5′), 70.2 (CH_2O), 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, CH_3CO). Anal. Calcd for $C_{52}H_{72}N_6O_{33}$: C, 47.49; H, 5.56; N, 6.12. Found: C, 47.70; H, 5.65; N, 6.36.

3.10. 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-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; $[\alpha]_D^{25}$ +8.9° (*c* 2.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$): 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, CH_2O), 3.42 (dd, 1 H, H-2), 2.18–1.98 (6s, 18 H, 6 × CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.3–169.0 (6 C, CH_3CO), 102.1 (C-1), 101.0 (C-1′), 76.0 (C-4), 72.6 (CH_2O), 71.8 (C-3), 71.0 (C-3′), 70.7 (C-5′), 70.3 (CH_2O), 70.0 (CH_2O), 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, CH_3CO). Anal. Calcd for $C_{54}H_{76}N_6O_{34}$: C, 47.93; H, 5.66; N, 6.21. Found: C, 48.00; H, 5.74; N, 6.18.

3.11. 3-Oxapent-1,5-diyl bis[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→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 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 the 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 **13** (0.23 g) as a colorless syrup (41%); $[\alpha]_D^{25}$ +52.2° (*c* 1.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$): 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, CH_2O), 3.10 (dd, 1 H, H-2), 2.17–1.97 (6s, 18 H, 6 × CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.2–169.0 (6 C, CH_3CO), 101.1 (C-1′), 98.1 (C-1), 76.6 (C-4), 71.1 (C-3′), 70.7 (C-5′), 70.4 (CH_2O), 70.2 (C-3), 69.2 (C-2′), 68.6 (C-5), 67.6 (CH_2O), 66.7 (C-4′), 62.0 (C-6), 61.1 (C-6′), 60.8 (C-2), 20.8–20.5 (6 C, CH_3CO). Anal. Calcd for $C_{52}H_{72}N_6O_{33}$: C, 47.49; H, 5.56; N, 6.12. Found: C, 47.23; H, 5.83; N, 6.34.

3.12. 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-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; $[\alpha]_D^{25}$ +65.4° (*c* 1.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$): 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, CH_2O), 3.13 (dd, 1 H, H-2), 2.16–1.97 (6s, 18 H, 6 × CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.3–169.0 (6 C, CH_3CO), 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 (CH_2O), 69.5 (CH_2O), 69.3 (C-2′), 68.5 (C-5), 67.8 (CH_2O), 66.8 (C-4′), 62.0 (C-6), 60.9 (C-6′), 60.8 (C-2), 20.9–20.4 (6 C, CH_3CO). Anal. Calcd for $C_{54}H_{76}N_6O_{34}$: C, 47.93; H, 5.66; N, 6.21. Found: C, 47.79; H, 5.56; N, 5.92.

3.13. 5-Hydroxy-3-oxapentyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→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 $CHCl_3$–MeOH to give **15** as a colorless syrup (0.16 g, 80%); $[\alpha]_D^{25}$ −12.8° (*c* 0.94, $CHCl_3$); ^{1}H NMR[1] H NMR ($CDCl_3$): 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, CH_2O), 2.15–1.97 (7s, 21 H, 6 × CH_3CO, C*H*$_3$CONH); ^{13}C NMR ($CDCl_3$): δ 170.6–169.3 (7 C, 6 × *C*OCH$_3$, CONH), 101.5 (C-1), 101.0 (C-1′), 75.8 (C-4), 72.8 (–CH_2O–), 72.7 (C-3), 72.2 (CH_2O), 71.1 (CH_2O), 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 (CH_2O), 60.7 (C-6′), 53.1 (C-2), 23.0 (*C*H$_3$CONH), 20.8–20.4 (6 C, *C*H$_3$CO). Anal. Calcd for $C_{30}H_{45}NO_{19}$: C, 49.79; H, 6.27; N, 1.94. Found: C, 49.43; H, 6.19; N, 1.76.

3.14. 8-Hydroxy-3,6-dioxaoctyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→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 $CHCl_3$–MeOH to afford a colorless syrup in 72% yield; $[\alpha]_D^{25}$ −11.1° (*c* 0.72, $CHCl_3$); ^{1}H NMR ($CDCl_3$): 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, CH_2O), 2.14–1.97 (7s, 21 H, 6 × CH_3CO, C*H*$_3$CONH); ^{13}C NMR ($CDCl_3$): δ 171.2 (NHCO), 170.6–169.2 (6 C, *C*OCH$_3$), 101.8 (C-1), 100.9 (C-1′), 76.2 (C-4), 73.8 (CH_2O), 72.4 (C-3), 71.5 (CH_2O), 70.9 (C-3′), 70.7 (C-5′), 70.5 (CH_2O), 70.1 (CH_2O), 69.2 (C-2′), 68.4 (C-5), 67.1 (CH_2O), 66.7 (C-4′), 62.4 (C-6), 61.2 (CH_2O), 60.8 (C-6′), 53.6 (C-2), 23.0 (*C*H$_3$CONH), 20.8–20.3 (6 C, *C*H$_3$CO). Anal. Calcd for $C_{32}H_{49}NO_{20}$: C, 50.06; H, 6.43; N, 1.82. Found: C, 49.89; H, 6.51; N, 1.69.

3.15. 5-Hydroxy-3-oxapentyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→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 chromatography with 40:1 $CHCl_3$–MeOH to afford a colorless syrup in 75% yield; $[\alpha]_D^{25}$ +62.3° (*c* 1.22, $CHCl_3$); ^{1}H NMR ($CDCl_3$): 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, CH_2O), 2.15–1.95 (7s, 21 H, 6 × CH_3CO, C*H*$_3$CONH); ^{13}C NMR ($CDCl_3$): δ 171.1 (CONH), 170.5–169.3 (6 C, *C*OCH$_3$), 101.2 (C-1′), 97.3 (C-1), 76.3 (C-4), 72.6 (CH_2O), 71.5 (C-3), 70.9 (C-3′), 70.6 (C-5′), 69.7 (CH_2O), 69.2 (C-2′), 68.6 (C-5), 67.4 (CH_2O), 66.6 (C-4′), 62.0 (C-6), 61.5 (CH_2O), 60.7 (C-6′), 52.0 (C-2), 23.0 (*C*H$_3$CONH), 20.9–20.4 (6 C, *C*H$_3$CO). Anal. Calcd for $C_{30}H_{45}NO_{19}$: C, 49.79; H, 6.27; N, 1.94. Found: C, 49.36; H, 6.01; N, 1.89.

3.16. 8-Hydroxy-3,6-dioxaoctyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→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 $CHCl_3$–MeOH to afford a colorless syrup in 70% yield; $[\alpha]_D^{25}$ +50.8° (*c* 0.63, $CHCl_3$); ^{1}H NMR ($CDCl_3$): 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, CH_2O), 2.15–1.95 (7s, 21 H, 6 × CH_3CO, C*H*$_3$CONH); ^{13}C NMR ($CDCl_3$): δ 170.6–169.2 (7C, 6 × *C*OCH$_3$, NHCO), 101.1 (C-1′), 97.4 (C-1), 76.6 (C-4), 72.7 (CH_2O), 71.6 (C-3), 71.0 (C-3′), 70.9 (CH_2O), 70.6 (C-5′), 70.3 (CH_2O), 69.9 (CH_2O), 69.3 (C-2′), 68.5 (C-5), 66.8 (CH_2O), 66.6 (C-4′), 62.0 (C-6), 61.8 (CH_2O), 60.7 (C-6′), 51.7 (C-2), 22.8 (*C*H$_3$CONH), 20.8–20.4 (6 C, *C*H$_3$CO). Anal. Calcd for $C_{32}H_{49}NO_{20}$: C, 50.06; H, 6.43; N, 1.82. Found: C, 50.03; H, 6.11; N, 1.71.

3.17. 1-[2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→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→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 $CHCl_3$–MeOH to give **19** as a colorless syrup (0.15 g, 59%); $[\alpha]_D^{25}$ +38.5° (*c* 0.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$): 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_α-2′, H_β-2′), 5.07 (1 H, H_β-3), 4.96–4.94 (m, 2H, H_α-3′, H_β-3′), 4.83 (d, 1 H, $J_{1,2}$ 4.00 Hz, H_α-1), 4.71 (d, 1 H, $J_{1,2}$ 8.50 Hz, 1 H, H_β-1), 4.58 (d, 1 H, $J_{1',2'}$ 8.00 Hz, 1 H, H_α-1′), 4.52 (d, 1 H, $J_{1',2'}$ 8.00 Hz, 1 H, H_β-1′), 4.50, 4.11–4.08 (m, 8 H, H_α-6a, 6b, H_α-6a′, 6b′, H_β-6a, 6b, H_β-6a′, 6b′), 4.27 (dd, 1 H, H_α-2), 4.07 (dd, 1 H, H_β-2), 3.91–3.79 (m, 6 H, H_α-4, 5, H_α-5′, H_β-4, 5, H_β-5′), 3.76–3.56 (m, 8 H, CH_2O), 2.19–1.96 (14s, 42 H, C$H_{3\alpha}$CONH, C$H_{3\beta}$CONH, 12 × CH_3CO); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.8 (2 C, CH_3CO_αNH, CH_3CO_βNH), 170.5–169.2 (12 C, CH_3CO), 101.2 (C_α-1′), 101.0 (C_β-1), 100.0 (C_β-1′), 97.3 (C_α-1), 76.3 (C_α-4), 76.0 (C_β-4), 72.7 (C_β-3), 72.5 (CH_2O), 71.8 (C_α-3), 71.2, 70.9 (2 C, C_α-3′, C_β-3′), 70.8, 70.6 (2 C, C_α-5′, C_β-5′), 70.5 (CH_2O), 69.3 (CH_2O), 69.2, 69.0 (2 C, C_α-2′, C_β-2′), 69.1, 68.2 (2 C, C_α-5, C_β-5), 67.6 (CH_2O), 66.5, 66.2 (2 C, C_α-4′, C_β-4′), 62.1, 61.8 (2 C, C_α-6, C_β-6), 60.7, 60.5 (2 C, C_α-6′, C_β-6′), 52.7, 52.4 (2 C, C_α-2, C_β-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.

3.18. 1-[2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1 → 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 → 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° (*c* 0.89, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 6.60, 6.51 (d, 2 H, NH_α, NH_β), 5.36 (dd, 2 H, H_α-4′, H_β-4′), 5.23 (dd, 1 H, H_α-3), 5.13–5.11 (m, 2 H, H_α-2′, H_β-2′), 5.05 (1 H, H_β-3), 4.97–4.95 (m, 2 H, H_α-3′, H_β-3′), 4.80 (d, 1 H, $J_{1,2}$ 3.50 Hz, H_α-1), 4.66 (d, 1 H, $J_{1,2}$ 8.00 Hz, H_β-1), 4.51 (d, 2H, $J_{1',2'}$ 8.00 Hz, H_α-1′, H_β-1′), 4.45, 4.12–4.10 (m, 8 H, H_α-6a, 6b, H_α-6a′, 6b′, H_β-6a, 6b, H_β-6a′, 6b′), 4.27 (dd, 1 H, H_α-2), 4.07 (dd, 1 H, H_β-2), 3.93–3.78 (m, 6 H, H_α-4, 5, H_α-5′, H_β-4, 5, H_β-5′), 3.77–3.62 (m, 12 H, CH_2O), 2.16–1.96 (14s, 42 H, C$H_{3\alpha}$CONH, C$H_{3\beta}$CONH, 12 × CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.9–169.2 (14 C, CH_3CO_αNH, CH_3CO_βNH, 12 × CH_3CO), 101.5 (C_α-1′), 101.2 (C_β-1), 101.1 (C_β-1′), 97.5 (C_α-1), 76.3 (C_α-4), 76.2 (C_β-4), 73.1 (CH_2O), 72.6 (C_β-3), 72.5 (CH_2O), 71.5 (C_α-3), 71.1, 71.0 (2 C, C_α-3′, C_β-3′), 70.9, 70.6 (2 C, C_α-5′, C_β-5′), 70.9 (CH_2O), 70.5 (CH_2O), 69.9 (CH_2O), 69.2, 69.0 (2 C, C_α-2′, C_β-2′), 68.5 (2 C, C_α-5, C_β-5), 67.2 (CH_2O), 66.5, 66.4 (2 C, C_α-4′, C_β-4′), 62.2, 61.9 (2 C, C_α-6, C_β-6), 60.7, 60.5 (2 C, C_α-6′, C_β-6′), 53.3, 51.7 (2 C, C_α-2, C_β-2), 23.1, 23.0 (2 C, $C_\alpha H_3$CONH, $C_\beta H_3$CONH), 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.

3.19. 3-Oxapent-1,5-diyl bis[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1 → 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° (*c* 2.28, $CHCl_3$); ^{1}H 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 × CH_3CO, NHCOCH_3); ^{13}C NMR ($CDCl_3$): δ 171.0–169.2 (7 C, 6 × $COCH_3$, 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.

3.20. 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-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° (*c* 0.98, $CHCl_3$); ^{1}H 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 × 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.

3.21. 3-Oxapent-1,5-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] (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° (*c* 1.03,

$CHCl_3$); ^1H NMR ($CDCl_3$): 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, CH_2O), 2.15–1.97 (7s, 21 H, 6 × CH_3CO, $NHCOCH_3$); ^{13}C NMR ($CDCl_3$): δ 170.9–169.1 (7 C, 6 × $COCH_3$, $NHCOCH_3$), 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 (CH_2O), 69.3 (C-2′), 68.7 (C-5), 67.1 (CH_2O), 66.7 (C-4′), 61.9 (C-6), 60.8 (C-6′), 52.0 (C-2), 23.0 (CH_3CONH), 20.9–20.4 (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, 50.08; H, 5.80; N, 1.83.

3.22. 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 $CHCl_3$–MeOH to afford a colorless syrup in 50% yield; $[\alpha]_D^{25}$ +34.3° (*c* 1.75, $CHCl_3$); ^1H NMR ($CDCl_3$): 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, CH_2O), 2.15–1.96 (7s, 21 H, 6 × CH_3CO, CH_3CONH); ^{13}C NMR ($CDCl_3$): δ 170.9–169.2 (7 C, 6 × $COCH_3$, $NHCOCH_3$), 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 (CH_2O), 69.9 (CH_2O), 69.1 (C-2′), 68.4 (C-5), 67.4 (CH_2O), 66.5 (C-4′), 61.9 (C-6), 60.6 (C-6′), 51.8 (C-2), 23.0 (CH_3CONH), 20.9–20.5 (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, 50.44; H, 6.35; N, 1.76.

3.23. 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%); $[\alpha]_D^{25}$ −83.9° (*c* 0.62, H_2O); ^1H NMR (D_2O): 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′, CH_2O), 2.09 (s, 3 H, $NHCOCH_3$); ^{13}C NMR (D_2O): 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′, CH_2O), 65.6 (C-4′), 58.0 (C-6), 57.2 (C-6′), 52.1 (C-2), 19.2 (CH_3CONH). ESI-TOFF-MS: m/z 472.2 $[M+1]^+$.

3.24. 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%; $[\alpha]_D^{25}$ −105.3° (*c* 0.76, H_2O); ^1H NMR (D_2O): 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′, CH_2O), 2.03 (s, 3 H, $NHCOCH_3$); ^{13}C NMR (D_2O): 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′, CH_2O), 64.9 (C-4′), 57.8 (C-6), 57.1 (C-6′), 52.3 (C-2), 19.7 (CH_3CONH). ESI-TOFF-MS: m/z 516.2 $[M+1]^+$.

3.25. 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%; $[\alpha]_D^{25}$ +70.6° (*c* 0.68, H_2O); ^1H NMR (CD_3OD): 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′, CH_2O), 3.57 (dd, 1 H, H-2′), 3.50 (dd, 1 H, H-3′), 1.98 (s, 3 H, $NHCOCH_3$); ^{13}C NMR (CD_3OD): 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, CH_2O), 72.6 (C-2′), 68.2 (C-4′), 62.5 (C-6), 62.0 (C-6′), 54.9 (C-2), 22.6 (CH_3CONH). ESI-TOFF-MS: m/z 472.2 $[M+1]^+$.

3.26. 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%; $[\alpha]_D^{25}$ +64.9° (*c* 0.37, H_2O); ^1H NMR (CD_3OD): 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′, CH_2O), 3.56 (dd, 1 H, H-2′), 3.50 (dd, 1 H, H-3′), 1.98 (s, 3 H, $NHCOCH_3$); ^{13}C NMR (CD_3OD): 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, CH_2O), 72.6 (C-2′), 68.1 (C-4′), 62.5 (C-6), 62.0 (C-6′), 54.9 (C-2), 22.6 (CH_3CONH). ESI-TOFF-MS: m/z 516.2 $[M+1]^+$.

3.27. 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 prepa-

ration of **25**. The yield was 97%; $[\alpha]_D^{25}$ +31.8° (*c* 0.63, H_2O); ^1H NMR (D_2O): 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′, CH_2O), 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 × NHCOC*H*$_3$); ^{13}C NMR (D_2O): 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, CH_2O), 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, *C*H$_3$CONH). ESI-TOFF-MS: *m*/*z* 837.3 $[M+1]^+$.

3.28. 1-[β-D-Galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyloxy-8-[β-D-galactopyranosyl-(1→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%; $[\alpha]_D^{25}$ +30.3° (*c* 0.66, H_2O); ^1H NMR (D_2O): 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′, CH_2O), 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 × NHCOC*H*$_3$); ^{13}C NMR (D_2O): 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, CH_2O), 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, *C*H$_3$CONH). ESI-TOFF-MS: *m*/*z* 881.4 $[M+1]^+$.

3.29. 3-Oxapent-1,5-diyl bis(β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside) (31)

Compound **31** was prepared as described for the preparation of **25**. The yield was 94%; $[\alpha]_D^{25}$ +26.7° (*c* 1.20, H_2O); ^1H NMR (CD_3OD): 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′, CH_2O), 2.02 (s, 3 H, NHCOC*H*$_3$); ^{13}C NMR (CD_3OD): 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, CH_2O), 68.2 (C-4′), 62.5 (C-6), 62.0 (C-6′), 55.1 (C-2), 22.5 (*C*H$_3$CONH). ESI-TOFF-MS: *m*/*z* 837.3 $[M+1]^+$.

3.30. 3,6-Dioxaoct-1,8-diyl bis[β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside] (32)

Compound **32** was prepared as described for the preparation of **25**. The yield was 98%; $[\alpha]_D^{25}$ +21.7° (*c* 0.92, H_2O); ^1H NMR (CD_3OD): 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′, CH_2O), 1.99 (s, 3 H, NHCOC*H*$_3$); ^{13}C NMR (CD_3OD): 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, CH_2O), 68.1 (C-4′), 62.4 (C-6), 61.8 (C-6′), 56.6 (C-2), 23.2 (*C*H$_3$CONH). ESI-TOFF-MS: *m*/*z* 903.3 $[M+Na]^+$.

3.31. 3-Oxapent-1,5-diyl bis[β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside] (33)

Compound **33** was prepared as described for the preparation of **25**. The yield was 95%; $[\alpha]_D^{25}$ +38.7° (*c* 1.24, H_2O); ^1H NMR (CD_3OD): 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′, CH_2O), 3.62 (dd, 1 H, H-2′), 3.54 (dd, 1 H, H-3′), 2.01 (s, 3 H, NHCOC*H*$_3$); ^{13}C NMR (CD_3OD): 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, CH_2O), 68.1 (C-4′), 62.4 (C-6), 61.8 (C-6′), 54.8 (C-2), 22.8 (*C*H$_3$CONH). ESI-TOFF-MS: *m*/*z* 859.3 $[M+Na]^+$.

3.32. 3,6-Dioxaoct-1,8-diyl bis[β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranoside] (34)

Compound **34** was prepared as described for the preparation of **25**. The yield was 93%; $[\alpha]_D^{25}$ +55.8° (*c* 0.86, H_2O); ^1H NMR (CD_3OD): 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′, CH_2O), 3.55 (dd, 1 H, H-2′), 3.49 (dd, 1 H, H-3′), 1.99 (s, 3 H, NHCOC*H*$_3$); ^{13}C NMR (CD_3OD): 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, CH_2O), 68.2 (C-4′), 62.5 (C-6), 62.0 (C-6′), 55.0 (C-2), 22.7 (*C*H$_3$CONH). ESI-TOFF-MS: *m*/*z* 881.4 $[M+1]^+$.

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