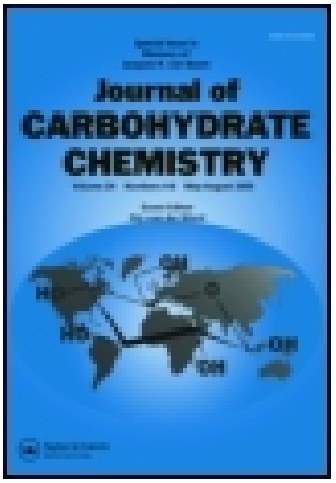

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Mimics of the Structural Elements of Type III Group B Streptococcus Capsular Polysaccharide. Part II: Synthesis of a Carboxylate-Containing Hexasaccharide with a Short Spacer

Wei Zou [a] & Harold J. Jennings [a]
[a] Institute for Biological Sciences, National Research Council of Canada , Ottawa, Canada , K1A 0R6
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MIMICS OF THE STRUCTURAL ELEMENTS OF TYPE III GROUP B *STREPTOCOCCUS* CAPSULAR POLYSACCHARIDE. PART II: SYNTHESIS OF A CARBOXYLATE-CONTAINING HEXASACCHARIDE WITH A SHORT SPACER

Wei Zou and Harold J. Jennings*

Institute for Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

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ABSTRACT

3-Aminopropyl *O*-(β-D-galactopyranosyl)-(1→4)-*O*-(β-D-glucopyranosyl)-(1→6)-*O*-{3-*O*-[(*S*)-1-carboxyethyl]-β-D-galactopyranosyl-(1→4)-*O*}-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (**18**) was synthesized by block condensations from suitably protected acceptors and donors, namely 3-azidopropyl 4-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**5**), phenyl 3-*O*-benzyl-4,6-di-*O*-isopropylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**7**), 2,4,6-tri-*O*-acetyl-3-*O*-[(*S*)-1-(methoxycarbonyl)ethyl]-α-D-galactopyranosyl trichloroacetimidate (**11**), and 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**14**). Compound **18** contains structural elements of type III group B *Streptococcus* capsular polysaccharide in which terminal sialic acid is replaced by an (*S*)-1-carboxyethyl group, and has a short spacer for the conjugation with peptide or protein.

INTRODUCTION

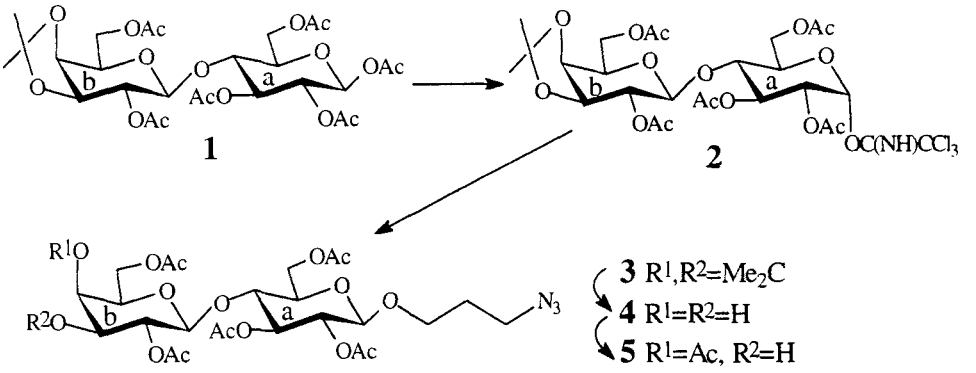
Group B *Streptococcus* (GBS) is a major cause of neonatal sepsis and meningitis.[1,2] GBS are classified into serotypes on the basis of their type-specific capsular polysaccharides,[2] and type III polysaccharide (GBS III) is responsible for more than 60% of all GBS infections.[1] On the basis of its unusual length dependence[3] it was proposed that the epitope of GBS III polysaccharide was conformational in nature,[3,4] and that the conformation of this epitope was dependent on the presence of the carboxylate groups of non-immunogenic sialic acid residues.[3,4] Therefore, a lactic acid-ether group was chosen as the surrogate anionic group[5] to mimic the function of sialic acid, since when attached to 3-*O* position of the terminal β-D-galactopyranosyl residue of desialylated GBS III it puts a carboxylate group in the same position as it is in the GBS III polysaccharide.

In the previous paper,[5] we have reported the synthesis of a basal carboxylate-containing methyl pentasaccharide that contains a complete repeating unit of the polysaccharide in which a terminal sialic acid residue was replaced by an (*S*)-1-carboxyethyl group. Here we describe the synthesis of another carboxylate-containing hexasaccharide with a 3-aminopropyl spacer at the reducing end, which would enable us to conjugate this oligosaccharide to a peptide or protein.

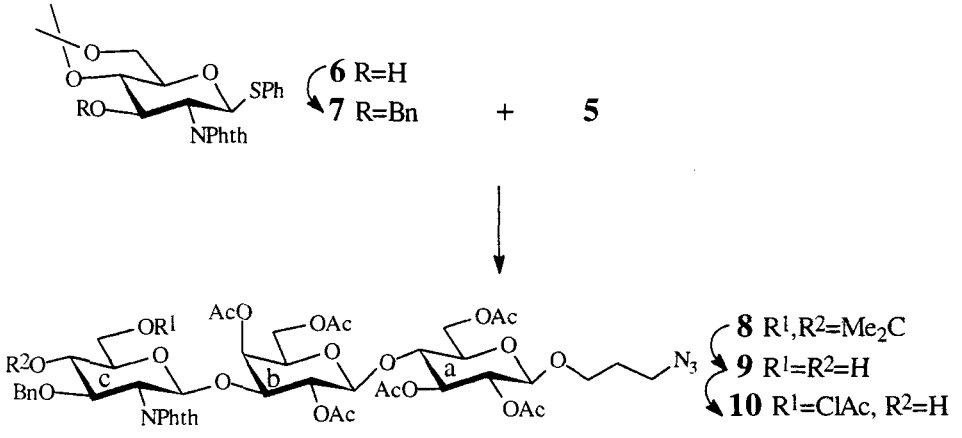
RESULTS AND DISCUSSION

Compound **1** was synthesized from lactose according to the method described by Baer and Abbas.[6] Treatment of **1** with hydrazine acetate in DMF removed its 1-*O*-acetyl group, and the following reaction with trichloroacetonitrile and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) gave 4-*O*-(2,6-di-*O*-acetyl-3,4-di-*O*-isopropylidene-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**2**) in 72% yield. 3-Azidopropyl 4-*O*-(2,6-di-*O*-acetyl-3,4-di-*O*-isopropylidene-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**3**) was then prepared in 92% yield by coupling **2** with 3-azidopropyl alcohol[7] in dichloromethane, using boron trifluoride diethyl etherate as a promoter. The 3^b,4^b-di-*O*-isopropylidene group of **3** was removed by treatment with 90% CF_3CO_2H/CH_2Cl_2 (1:10) at 0 °C to afford 3-azidopropyl 4-*O*-(2,6-di-*O*-acetyl-β-D-

galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**4**) as a crystalline solid in 81% yield. The regioselective acetylation of **4** at the axial 4^b-OH was achieved in 87% yield by a two step protocol:[8] formation of a cyclic orthoester intermediate with $MeC(OMe)_3$/TsOH and the subsequent stereoselective opening of the orthoester ring with 20% acetic acid, leading to disaccharide **5** as glycosyl acceptor.

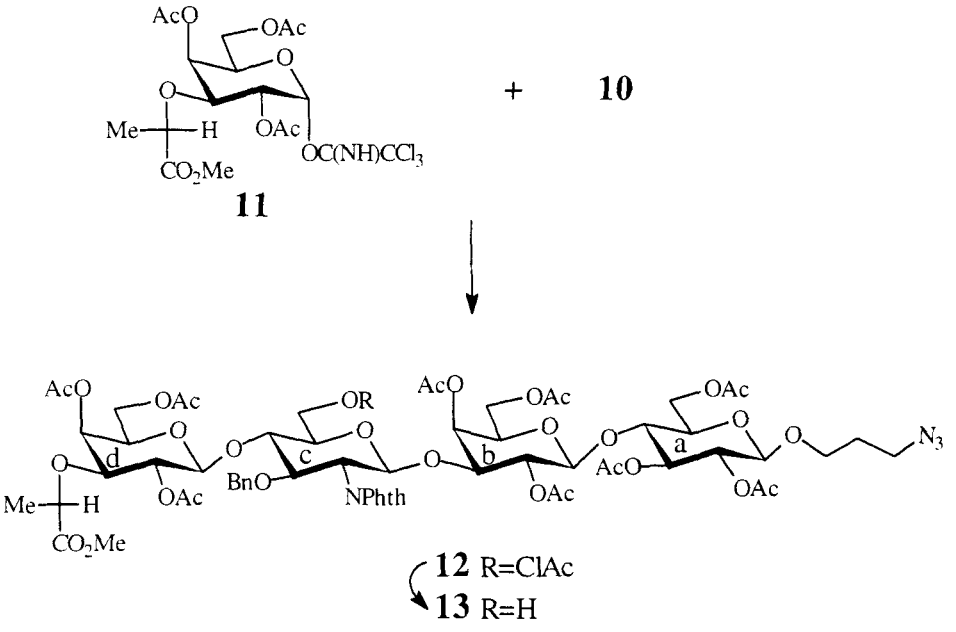


Compound **6** was prepared in 88% yield from phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[5,9,10] by a two step procedure: de-*O*-acetylation with



NaOMe/MeOH followed by isopropylidenation with 2,2-dimethoxypropane[11,12] in acetonitrile. Benzylation of **6** with BnBr/DMF/NaH afforded compound **7** in 66% yield. As

previously reported with a similar compound,[13] the anomeric proton (H-1) resonance (5.553 ppm) of compound **7** in the ^{1}H NMR spectrum showed a multiplet pattern instead of the expected doublet. Compound **7** was coupled with **5** in dichloromethane using NIS/TfOH at -45 °C to furnish trisaccharide **8** in 58% yield. Compound **9** was then obtained from **8** in 93% yield by the same method as described in the transformation of **3** to **4**, and regioselective chloroacetylation of **9** at its 6^c-*O*-position with one equivalent of chloroacetic anhydride gave 3-azidopropyl *O*-(3-*O*-benzyl-6-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**10**) in 56% yield.

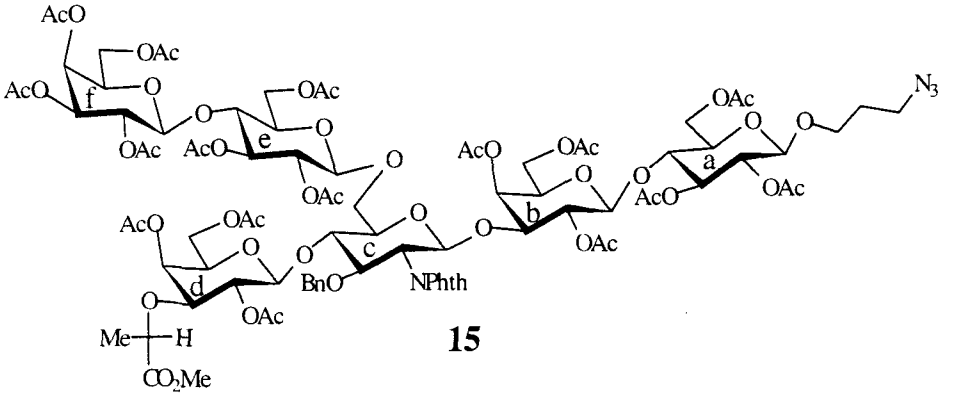


Tetrasaccharide derivative **12** was synthesized in 50% yield by condensation of **10** with glycosyl donor **11**[5] in dichloromethane, using trimethylsilyl triflate as a promoter, at -45 °C. The 6^c-*O*-chloroacetyl group was then removed by treatment with thiourea and 2,6-lutidine in dichloromethane/methanol (1:1)[14-16] giving a quantitative yield of compound **13**.

A noteworthy feature of the ^{1}H NMR spectra of compounds **8**, **9**, **10**, **12**, and **13** is that the chemical shift of one of the acetyl groups is greatly affected by the substituent at the 6^c-*O*-position. The chemical shifts of the acetyl group were at higher field in **9** (1.30 ppm)

and **13** (1.23 ppm) than they were in **8**, **10**, and **12** (≈ 1.70 ppm). This could be explained by the shielding effect of phthalimido group on the acetyl group in **9** and **13**.

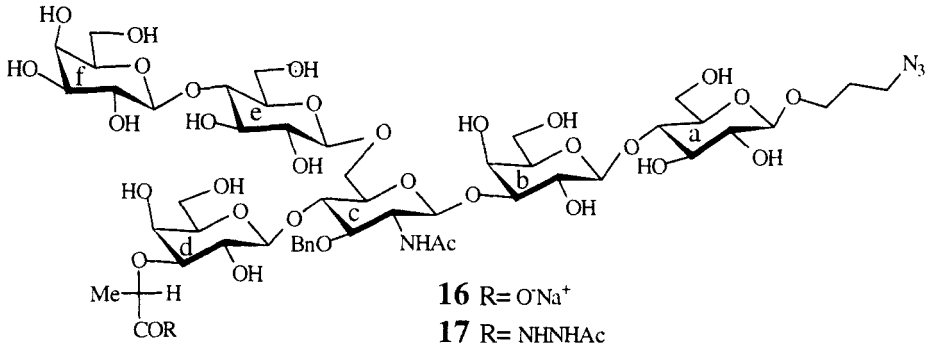
13 + **14**



15

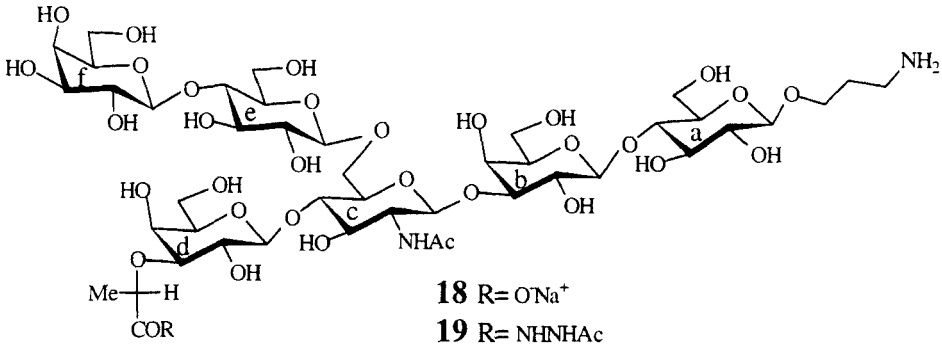
Compound **13** was condensed with lactosyl trichloroacetimidate **14**[11] by the method described in the synthesis of **12** to afford hexasaccharide derivative **15** in 55% yield. Six anomeric carbon signals in the ^{13}C NMR spectrum of **15** were observed at 97.88, 100.33, 100.57, 101.21(2C), and 101.50 ppm. Removal of *O*-acetyl groups and saponification of the methyl ester were performed in one step by treatment with 0.1N NaOH/MeOH (1:4).[5,17] Hydrazinolysis of the phthalimido group followed by *N*-acetylation with acetic anhydride in methanol[5,17] yielded a mixture of 3-azidopropyl *O*-(β-D-galactopyranosyl)-(1→4)-*O*-(β-D-glucopyranosyl)-(1→6)-*O*-{3-*O*-[(*S*)-1-carboxyethyl]-β-D-galactopyranosyl-(1→4)-*O*}-(2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (**16**) and its hydrazide derivative **17** with a ratio about 2:1 according to the relative intensity of the lactyl methyl groups in the ^{1}H NMR spectrum. The separation of **16** (44%) and **17** (19%) was achieved by chromatography on DEAE Sephadex by the procedures previously described.[5] Catalytic hydrogenation of compound **16** led to compound **18** in 92% yield. Similarly, compound **19** was obtained in 95% from **17** by the same procedure.

In the ^{1}H and ^{13}C NMR spectra of **18** and **19**, the anomeric regions showed great similarity. The ^{1}H NMR spectrum of **18** (see Figure 1) showed resonances of six anomeric protons at 4.714 (H-1^{c}, β-GlcNAc) 4.566 (H-1^{d} and H-1^{e}, β-Gal and β-Glc), 4.503 (H-1^{a}, β-Glc), 4.463 (H-1^{f}, β-Gal), and 4.436 (H-1^{b}, β-Gal) ppm. In the ^{13}C NMR spectrum of **18**, anomeric carbon signals were observed at 103.39, 103.87, 103.93, 104.27 (3C) ppm. FAB mass spectroscopy analysis also confirmed the structures of both **18** and **19**.



16 R= $O^{-}Na^{+}$

17 R= NHNHAc



18 R= $O^{-}Na^{+}$

19 R= NHNHAc

EXPERIMENTAL

General methods. Melting points are uncorrected. Optical rotations were measured at room temperature with a Perkin-Elmer 243 polarimeter, using a 10-cm 1-mL cell. ^{1}H and

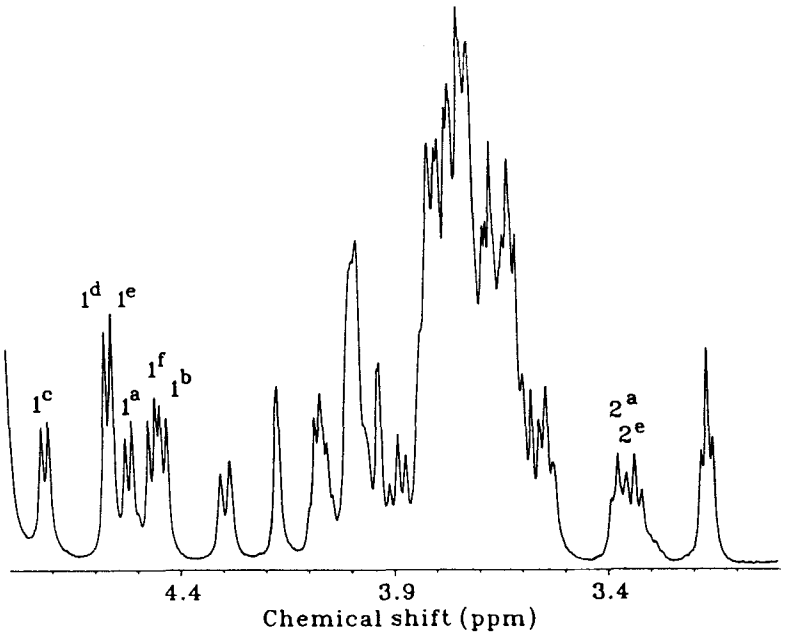


Figure 1. 500 MHz ^{1}H NMR spectrum (3.0-4.8 ppm) of compound **18** recorded in D_2O at 293 K.

^{13}C NMR spectra were recorded at 500 MHz and 125 MHz, respectively, with a Bruker AMX 500 instrument at 300 K unless otherwise noted. Chemical shifts are given relative to the signal of internal Me_4Si or indirectly to the solvent signal 7.25 ($CDCl_3$) and 4.76 (D_2O) for ^{1}H NMR spectra, and to the solvent signals 76.9 ($CDCl_3$), 31.55 (internal acetone) for ^{13}C NMR spectra. The ^{1}H NMR resonances of oligosaccharides were assigned on the basis of 2D ^{1}H-homonuclear chemical-shift correlated (^{1}H-COSY) experiments. FAB mass spectroscopic analyses were performed with a JEOL JMS-AX505H mass spectrometer.

Column chromatography was performed on Silica gel 60 (Merck, 230-400 mesh) and fractions were monitored by TLC on Silica gel 60 F_{254} (Merck). Detection was effected by examination under UV light and by charring with 5% sulphuric acid solution in ethanol. Solutions were concentrated at or below 40 °C and dried with anhydrous Na_2SO_4.

4-*O*-(2,6-Di-*O*-acetyl-3,4-di-*O*-isopropylidene-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (2). To a solution of 4-*O*-(2,6-di-*O*-

acetyl-3,4-di-*O*-isopropylidene-β-D-galactopyranosyl)-1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose (**1**) (6.0 g, 9.46 mmol) in DMF (60 mL) was added hydrazine acetate (1.0 g, 10.87 mmol) and the mixture was stirred at 60 °C for 2 h. Ethyl acetate (200 mL) was added and the solution was washed with aq NaCl and water, dried, and concentrated to a syrup. To the solution of above syrup in dichloromethane (70 mL) and trichloroacetonitrile (10 mL) was added DBU (1.6 mL) at 0 °C. The mixture was stirred at 0 °C for another 1 h. The solution was then concentrated and the residue was purified by chromatography (CH_2Cl_2/CH_3COCH_3 9:1) to give **2** (5.0 g, 72%) as an amorphous solid: $[\alpha]_D$ +84° (*c* 0.43, MeOH); ^{1}H NMR ($CDCl_3$) δ 1.295 and 1.516 (s and s, 3H each, Me_2C), 1.986, 2.048, 2.057, 2.072, 2.114 (5s, 3H each, 5 x OAc), 6.463 (d, 1H, H-1^a, $J_{1,2}$ = 3.5 Hz), 8.622 (s, 1H, NH).

3-Azidopropyl 4-*O*-(2,6-Di-*O*-acetyl-3,4-di-*O*-isopropylidene-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (3). To a solution of **2** (2.5 g, 3.4 mmol) in dry dichloromethane (10 mL) were added 3-azidopropyl alcohol (0.7 g, 6.9 mmol) and 4Å molecular sieves (2.0 g). After stirring at rt for 2 h the mixture was cooled to 0 °C and boron trifluoride diethyl etherate (250 μL) was slowly added. The mixture was further stirred at 0 °C for 2 h, neutralized with triethylamine (300 μL), and then diluted with dichloromethane (50 mL) and filtered. The filtrate was washed subsequently with water, aq $NaHCO_3$, and water, dried, and then concentrated to a residue. Purification by chromatography (dichloromethane/acetone 9:1) gave amorphous **3** (2.1 g, 92%): ^{1}H NMR ($CDCl_3$) δ 1.293 and 1.511 (s and s, 3H each, Me_2C), 1.795 (m, 2H, $OCH_2CH_2CH_2N_3$), 2.021(2), 2.026, 2.056, 2.101 (4s, 5 x OAc), 3.331 (m, 2H, $OCH_2CH_2CH_2N_3$), 4.334 (d, 1H, H-1^b, $J_{1,2}$ = 7.6 Hz), 4.443 (d, 1H, H-1^a, $J_{1,2}$ = 8.2 Hz), 4.879 (dt, 2H, H-2^a, H-2^b), 5.161 (t, 1H, H-3^a).

3-Azidopropyl 4-*O*-(2,6-Di-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (4). To a solution of **3** (2.1 g, 3.1 mmol) in dichloromethane (50 mL) at 0 °C was added 90% trifluoroacetic acid (5 mL). The mixture was stirred at 0 °C until the TLC indicated that the reaction was complete (1 h). The dichloromethane solution was then washed subsequently with cold water, aq $NaHCO_3$, and water, dried, and concentrated to give crystals of **4** (1.6 g, 81%): mp 112-113 °C (EtOAc/hexane); $[\alpha]_D$ +6.4° (*c* 0.84, MeOH); ^{1}H NMR ($CDCl_3$) δ 1.807 (m, 2H, $OCH_2CH_2CH_2N_3$), 2.023(2),

2.089(2), 2.106 (3s, 5 x OAc), 2.802 (d, 1H, 3^b-OH, J = 3.4 Hz), 3.235 (d, 1H, 4^b-OH, J = 6.8 Hz), 3.334 (m, 2H, $OCH_2CH_2CH_2N_3$), 3.731 (t, 1H, H-4^a, $J_{3,4} = J_{4,5} = 9.3$ Hz), 3.818 (bs, 1H, H-4^b), 4.339 (d, 1H, H-1^b, $J_{1,2} = 7.6$ Hz), 4.448 (d, 1H, H-1^a, $J_{1,2} = 8.0$ Hz), 4.811 (dd, 1H, H-2^a, $J_{2,3} = 9.3$), 4.886 (dd, 1H, H-2^b, $J_{2,3} = 8.0$ Hz), 5.152 (t, 1H, H-3^a, $J_{2,3} = J_{3,4} = 9.3$ Hz); HRFABMS Calcd for $C_{25}H_{37}N_3O_{16}Li$ (M+Li): 642.2334. Found: 642.2343.

Anal. Calcd for $C_{25}H_{37}N_3O_{16}$: C, 47.2; H, 5.9; N, 6.6. Found: C, 47.4; H, 5.8; N, 6.4.

3-Azidopropyl 4-*O*-(2,4,6-Tri-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (5). To a solution of **4** (1.5 g, 2.36 mmol) in dichloromethane (20 mL) were added trimethyl orthoacetate (2 mL) and *p*-toluenesulfonic acid monohydrate (15 mg). The solution was stirred at rt for 20 min until the starting material was completely consumed. Acetic acid (20%, 10 mL) was then added and the mixture was vigorously stirred overnight. Dichloromethane (50 mL) was added to the mixture and the solution was washed subsequently with water, aq $NaHCO_3$, and water, dried, and concentrated to a residue. Purification by chromatography (dichloromethane/acetone 9:1) gave a solid **5** (1.4 g, 87%): $[\alpha]_D$ +14° (*c* 0.59, MeOH); ^{1}H NMR ($CDCl_3$) δ 1.810 (m, 2H, $OCH_2CH_2CH_2N_3$), 2.015, 2.027, 2.060, 2.098, 2.106, 2.153 (6s, 3H each, 6 x OAc), 2.466 (d, 1H, 3^b-OH), 3.337 (m, 2H, $OCH_2CH_2CH_2N_3$), 4.411 (d, 1H, H-1^b, $J_{1,2} = 7.8$ Hz), 4.458 (d, 1H, H-1^a, $J_{1,2} = 7.8$ Hz), 4.830 (dd, 1H, H-2^a, $J_{2,3} = 9.2$ Hz), 4.879 (dd, 1H, H-2^b, $J_{2,3} = 8.7$ Hz), 5.166 (t, 1H, H-3^a, $J_{2,3} = J_{3,4} = 9.2$ Hz), 5.276 (bs, 1H, H-4^b); ^{13}C NMR ($CDCl_3$) δ 20.78 (6 x CH_3CO), 28.94 ($OCH_2CH_2CH_2N_3$), 47.91 ($CH_2CH_2CH_2N_3$), 61.37, 62.08, 66.45, 69.14 (2 x C-6), 100.61, 100.77 (2 x C-1), 169.60-171.16 (6 x CH_3CO); HRFABMS Calcd for $C_{27}H_{39}N_3O_{17}Li$ (M+Li): 684.2440. Found: 684.2451.

Phenyl 2-Deoxy-4,6-di-*O*-isopropylidene-2-phthalimido-1-thio-β-D-glucopyranoside (6). A solution of phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (5.0 g, 9.5 mmol) in 0.02M NaOMe/MeOH (100 mL) was stirred at rt for 1 h. The solution was neutralized with Dowex-50 (H^+) ion-exchange resin, and the filtrate was concentrated to a residue. To a solution of above residue in acetonitrile (100 mL) was added α,α-dimethoxypropane (4 mL) and *p*-toluenesulfonic acid monohydrate (0.1 g). The mixture was stirred for 16 h, neutralized with triethylamine (0.5 mL), and

concentrated to a residue. Purification by chromatography (EtOAc/hexane 1:1) gave **6** (3.7 g, 88%): mp 185-186 °C (EtOAc/hexane); $[\alpha]_D$ +49° (*c* 1.03, MeOH); ^{1}H NMR ($CDCl_3$) δ 1.402 and 1.498 (s and s, 3H each, Me_2C), 2.264 (d, 1H, 3-OH, J = 2.9 Hz), 3.503 (m, 1H, H-5), 3.612 (t, 1H, H-4, $J_{3,4} = J_{4,5} = 9.1$ Hz), 3.807 (t, 1H, H-6a, $J_{5,6a} = J_{6a,6b} = 10.4$ Hz), 3.966 (dd, 1H, H-6b, $J_{5,6b} = 5.1$ Hz), 4.270 (dd, 1H, H-2, $J_{2,3} = 9.1$ Hz), 4.452 (dt, 1H, H-3, $J_{2,3} = J_{3,4} = 9.1$ Hz, $J_{3,OH} = 2.9$ Hz), 5.645 (d, 1H, H-1, $J_{1,2} = 10.5$ Hz), 7.233-7.340 (m, 5H, SPh), 7.732-7.882 (m, 4H, Phth); HRFABMS Calcd for $C_{23}H_{23}NO_6SLi$ (M+Li): 448.1406. Found: 448.1406.

Anal. Calcd for $C_{23}H_{23}NO_6S$: C, 62.6; H, 5.2; N, 3.2. Found: C, 62.7; H, 5.3; N, 2.9.

Phenyl 3-*O*-Benzyl-2-deoxy-4,6-di-*O*-isopropylidene-2-phthalimido-1-thio-β-D-glucopyranoside (7). To a solution of **6** (1.0 g, 2.3 mmol) in dry DMF (25 mL) was added 50% NaH (0.12 g, 2.5 mmol). The mixture was stirred at rt for 0.5 h, and then benzyl bromide (0.35 mL, 2.9 mmol) was added. After stirring overnight the mixture was diluted with cold water (100 mL) and extracted with ethyl acetate (100 mL). The organic solution was washed subsequently with water, 0.1N HCl, and water, dried, and concentrated to a crystalline solid. Recrystallization from EtOAc/hexane gave prisms of **7** (0.8 g, 66%): mp 170-171 °C; $[\alpha]_D$ +104° (*c* 0.81, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.430 and 1.508 (s and s, 3H each, Me_2C), 3.505 (m, 1H, H-5), 3.811 (m, 2H, H-4, 6a), 3.976 (dd, 1H, H-6b, $J_{5,6b} = 5.4$ Hz, $J_{6a,6b} = 10.7$ Hz), 4.224 (m, 2H, H-2, 3), 4.451 and 4.709 (2d, 1H each, CH_2Ph, J = 12.3 Hz), 5.553 (m, 1H, H-1), 6.858-6.974 (m, 5H, Ph), 7.202-7.309 (m, 5H, SPh), 7.623-7.829 (m, 4H, Phth); HRFABMS Calcd for $C_{30}H_{29}NO_6SLi$ (M+Li): 538.1876. Found: 538.1866.

Anal. Calcd for $C_{30}H_{29}NO_6S$: C, 67.8; H, 5.5; N, 2.6. Found: C, 67.5; H, 5.7; N, 2.5.

3-Azidopropyl *O*-(3-*O*-Benzyl-2-deoxy-4,6-di-*O*-isopropylidene-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (8). To a solution of **5** (0.35 g, 0.52 mmol), **7** (0.32 g, 0.60 mmol), and NIS (0.33 g, 1.47 mmol) in dichloromethane (4 mL) were added 4Å molecular sieves (0.5 g). The mixture was stirred at rt for 1 h, cooled to -45 °C, and triflic acid (30 μL) was added to the mixture under nitrogen. The stirring was continued

at that temperature for another 1 h and the reaction was then quenched by the addition of a solution of 2,6-lutidine (1 mL) in dichloromethane (20 mL). The filtrate was washed subsequently with cold water, 1N HCl, and water, dried, and concentrated to a solid residue. Purification by chromatography (EtOAc/hexane 1:1) gave amorphous **8** (0.33 g, 58%): $[\alpha]_D$ +26° (*c* 0.37, MeOH); ^{1}H NMR ($CDCl_3$) δ 1.424 and 1.499 (s and s, 3H each, Me_2C), 1.707 (s, 3H, OAc), 1.772 (m, 2H, $OCH_2CH_2CH_2N_3$), 1.934, 1.982, 2.050, 2.054, 2.096 (5s, 3H each, 5 x OAc), 3.302 (m, 2H, $OCH_2CH_2CH_2N_3$), 3.626 (t, 1H, H-4^a, $J_{3,4}$ = $J_{3,5}$ = 9.5 Hz), 4.167 (t, 1H, H-3^c, $J_{2,3}$ = $J_{3,4}$ = 9.1 Hz), 4.216 (d, 1H, H-1^b, $J_{1,2}$ = 8.1 Hz), 4.393 (d, 1H, H-1^a, $J_{1,2}$ = 8.0 Hz), 4.418 and 4.665 (2d, 1H each, CH_2Ph, J = 12.4 Hz), 4.760 (dd, 1H, H-2^b, $J_{2,3}$ = 9.4 Hz), 4.804 (dd, 1H, H-2^a, $J_{2,3}$ = 9.2 Hz), 5.019 (t, 1H, H-3^a, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz), 5.097 (d, 1H, H-1^c, $J_{1,2}$ = 8.2 Hz), 5.267 (d, 1H, H-4^b, $J_{3,4}$ = 2.9 Hz), 6.886-6.961 (m, 5H, Ph), 7.679 (m, 4H, Phth); HRFABMS Cacld for $C_{51}H_{62}N_4O_{23}Li$ (M+Li): 1105.3965. Found: 1105.3976.

3-Azidopropyl *O*-(3-*O*-Benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (9). Compound **8** (0.3 g, 0.27 mmol) was converted to **9** (0.27 g, 93%) as described in the synthesis of **4**: $[\alpha]_D$ +29° (*c* 0.43, MeOH); ^{1}H NMR ($CDCl_3$) δ 1.354 (s, 3H, OAc), 1.773 (m, 2H, $OCH_2CH_2CH_2N_3$), 1.946, 1.988, 2.047, 2.054, 2.154 (5s, 3H each, 5 x OAc), 2.234 (d, 1H, 4^c-OH, J = 3.7 Hz), 3.139 (dd, 1H, 6^c-OH), 3.304 (m, 2H, $OCH_2CH_2CH_2N_3$), 4.244 (d, 1H, H-1^b, $J_{1,2}$ = 8.0 Hz), 4.371 (d, 1H, H-1^a, $J_{1,2}$ = 7.9 Hz), 4.452 and 4.599 (2d, 1H each, CH_2Ph, J = 12.2 Hz), 4.775-4.824 (m, 2H, H-2^a, H-2^b), 5.046 (t, 1H, H-3^a, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz), 5.208 (d, 1H, H-1^c, $J_{1,2}$ = 8.2 Hz), 5.489 (d, 1H, H-4^b), 6.987 (m, 5H, Ph), 7.685 (m, 4H, Phth); ^{13}C NMR ($CDCl_3$) δ 19.75-20.88 (6 x CH_3CO), 28.95 ($OCH_2CH_2CH_2N_3$), 47.92 ($OCH_2CH_2CH_2N_3$), 55.32 (C-2^c), 61.28, 61.38, 61.90 (3 x C-6), 98.91, 100.53, 100.64 (3 x C-1), 168.15, 169.55, 169.60, 170.33, 170.43, 170.91 (6 x CH_3CO); HRFABMS Cacld for $C_{48}H_{58}N_4O_{23}Li$ (M+Li): 1065.3652. Found: 1065.3650.

3-Azidopropyl *O*-(3-*O*-Benzyl-6-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (10). To a solution of **9** (0.25 g, 0.236 mmol) and 2,6-lutidine (0.5 mL) in dichloromethane (10 mL) at 0 °C was added dropwise a solution of

chloroacetic anhydride (45 mg, 0.255 mmol) in dichloromethane (2 mL). The solution was then stirred at rt overnight and then washed subsequently with water, 1N HCl, and water, dried, and concentrated to a residue. Purification by chromatography (EtOAc/hexane 2:1) gave solid **10** (0.15 g, 56%): $[\alpha]_D$ +32° (*c* 0.46, MeOH); ^{1}H NMR ($CDCl_3$) δ 1.727 (s, 3H, OAc), 1.774 (m, 2H, $OCH_2CH_2CH_2N_3$), 1.939, 1.984, 2.063, 2.081(2) (4s, 5 x OAc), 2.383 (d, 1H, 4^c-OH, J = 3.6 Hz), 3.295 (m, 2H, $OCH_2CH_2CH_2N_3$), 4.219 (d, 1H, H-1^b, $J_{1,2}$ = 7.6 Hz), 4.481 and 4.602 (2d, 1H each, CH_2Ph, J = 12.5 Hz), 4.725 (dd, 1H, H-2^b, $J_{2,3}$ = 9.6 Hz), 4.776 (dd, 1H, H-6a^c, $J_{6a,6b}$ = 11.8 Hz), 4.811 (dd, 1H, H-2^a, $J_{2,3}$ = 9.4 Hz), 5.027 (t, 1H, H-3^a, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz), 5.107 (d, 1H, H-1^c, $J_{1,2}$ = 8.2 Hz), 5.263 (d, 1H, H-4^b, $J_{3,4}$ = 2.9 Hz), 6.957-7.024 (m, 5H, Ph), 7.682 (m, 4H, Phth); ^{13}C NMR ($CDCl_3$) δ 20.30-20.79 (5 x CH_3CO), 28.95 ($OCH_2CH_2CH_2N_3$), 40.94 ($ClCH_2CO$), 47.92 ($OCH_2CH_2CH_2N_3$), 55.44 (C-2^c), 61.71, 61.94, 62.80 (3 x C-6), 97.90, 100.55(2) (3 x C-1), 127.64, 127.73, 123.37, 137.82 (Ph), 131.64, 133.87 (Phth), 167.70, 168.46, 169.54, 169.70, 169.80, 170.43, 170.65 (6 x CH_3CO, $ClCH_2CO$).

3-Azidopropyl *O*-{2,4,6-Tri-*O*-acetyl-3-*O*-[(*S*)-1-(methoxycarbonyl)ethyl]-β-D-galactopyranosyl}-(1→4)-*O*-(3-*O*-benzyl-6-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (12). To a solution of **11** (0.15 g, 0.28 mmol) and **10** (0.14 g, 0.12 mmol) in dichloromethane (5 mL) were added 4Å molecular sieves (0.3 g). The mixture was stirred at rt for 1 h, cooled to -45 °C, and trimethylsilyl triflate (50 μL) was added to the mixture. Stirring was continued at that temperature for another 2 h and the reaction was then quenched by the addition of a solution of 2,6-lutidine (0.5 mL) in dichloromethane (10 mL). The filtrate was washed subsequently with cold water, 1N HCl, and water, dried, and concentrated to a solid residue. Purification by chromatography (EtOAc/hexane 2:1) gave amorphous **12** (90 mg, 50%): $[\alpha]_D$ +42° (*c* 0.31, MeOH); ^{1}H NMR ($CDCl_3$) δ 1.314 (d, 3H, $MeCHCO_2Me$, J = 6.5 Hz), 1.673 (s, 3H, OAc), 1.772 (m, 2H, $OCH_2CH_2CH_2N_3$), 1.932, 1.981, 1.996, 2.045, 2.057, 2.071, 2.086, 2.116 (8s, 3H each, 8 x OAc), 3.304 (m, 2H, $OCH_2CH_2CH_2N_3$), 3.697 (s, 3H, CO_2Me), 4.209 (d, 1H, H-1^b, $J_{1,2}$ = 8.2 Hz), 4.346 (d, 1H, H-1^a, $J_{1,2}$ = 8.9 Hz), 4.592 (d, 1H, H-1^d, $J_{1,2}$ = 8.0 Hz), 4.690 (dd, 1H, H-2^b), 4.805 (dd, 1H, H-2^a, $J_{2,3}$ = 9.4 Hz), 5.020 (t, 1H, H-3^a, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz), 5.082 (d, 1H, H-1^c, $J_{1,2}$ = 8.3 Hz), 5.173 (dd, 1H, H-2^d), 5.227 (d,

1H, H-4[b]), 5.470 (d, 1H, H-4[d]), 6.834-6.960 (m, 5H, Ph), 7.640 (m, 4H, Phth); ^{13}C NMR ($CDCl_3$) δ 18.03 (*Me*CHCO$_2$Me), 20.23-20.87 (9 x *C*H$_3$CO), 28.95 (OCH$_2$*C*H$_2$CH$_2$N$_3$), 40.93 (ClCH$_2$CO), 47.92 (OCH$_2$CH$_2$*C*H$_2$N$_3$), 52.07 (OMe), 55.58 (C-2[c]), 61.42, 61.67, 61.81, 61.93 (4 x C-6), 97.76, 100.50, 100.54, 101.20 (4 x C-1), 127.11, 127.48, 127.92, 138.31 (Ph), 131.62, 133.65 (Phth), 167.09-172.17 (9 x CH$_3$*C*O, ClCH$_2$*C*O).

3-Azidopropyl *O*-{2,4,6-Tri-*O*-acetyl-3-*O*-[(*S*)-1-(methoxycarbonyl)ethyl]-β-D-galactopyranosyl}-(1→4)-*O*-(3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (13). To a solution of **12** (80 mg, 0.053 mmol) in dichloromethane/methanol (1:1, 4 mL) was added thiourea (78 mg) and 2,6-lutidine (0.5 mL), and the mixture was stirred overnight. Ethyl acetate (50 mL) was added and the solution was washed subsequently with water, 1N HCl, and water, dried, and concentrated to give amorphous **13** in a quantitative yield: $[\alpha]_D$ +22° (*c* 0.46, MeOH); ^{1}H NMR ($CDCl_3$) δ 1.298 (bs, 6H, *Me*CHCO$_2$Me and OAc), 1.769 (m, 2H, OCH$_2$C*H*$_2$CH$_2$N$_3$), 1.942, 1.981(2), 2.035, 2.040, 2.055, 2.117, 2.164 (7s, 8 x OAc), 3.208 (dd, 1H, 6[c]-OH), 3.301 (m, 2H, OCH$_2$CH$_2$C*H*$_2$N$_3$), 3.695 (s, 3H, CO$_2$Me), 4.235 (d, 1H, H-1[b], $J_{1,2}$ = 8.2 Hz), 4.368 (d, 1H, H-1[a], $J_{1,2}$ = 8.9 Hz), 4.611 (d, 1H, H-1[d], $J_{1,2}$ = 8.0 Hz), 4.756-4.819 (m, 3H, H-2[a], H-2[b], one of C*H*$_2$Ph), 5.039 (t, 1H, H-3[a], $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz), 5.173 (dd, 1H, H-2[d], $J_{2,3}$ = 9.4 Hz), 5.177 (d, 1H, H-1[c], $J_{1,2}$ = 8.5 Hz), 5.455 (d, 1H, H-4[d]), 5.476 (d, 1H, H-4[b]), 6.834-6.960 (m, 5H, Ph), 7.640 (m, 4H, Phth); ^{13}C NMR ($CDCl_3$) δ 18.03 (*Me*CHCO$_2$Me), 20.23-20.87 (9 x *C*H$_3$CO), 28.95 (OCH$_2$*C*H$_2$CH$_2$N$_3$), 47.91 (OCH$_2$CH$_2$*C*H$_2$N$_3$), 52.03 (OMe), 55.51 (C-2[c]), 60.16, 61.33, 61.38, 61.90 (4 x C-6), 98.65, 100.51, 100.60, 101.34 (4 x C-1), 168.05-171.02 (9 x CH$_3$*C*O).

3-Azidopropyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[(*S*)-1-(methoxycarbonyl)ethyl]-β-D-galactopyranosyl-(1→4)-*O*}-(3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (15). To a solution of **13** (70 mg, 0.049 mmol) and **14** (70 mg, 0.090 mmol) in dichloromethane (2.5 mL) were added 4Å molecular sieves (0.11 g). The mixture was stirred at rt for 1 h, cooled to -45 °C, and trimethylsilyl triflate (13 μL) was added to the mixture. Stirring was continued at that

temperature for another 2 h and the reaction was then quenched by the addition of a solution of 2,6-lutidine (0.5 mL) in dichloromethane (10 mL). The filtrate was washed subsequently with cold water, 1N HCl, and water, dried, and concentrated to a solid residue. Purification by chromatography (EtOAc/hexane 5:1) gave amorphous **15** (55 mg, 55%): $[\alpha]_D$ +15° (*c* 1.5, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.289 (d, 3H, *Me*$CHCO_2Me$, J = 6.5 Hz), 1.769 (m, 2H, $OCH_2CH_2CH_2N_3$), 1.862, 1.923(2), 1.965(3), 2.004, 2.036(3), 2.056, 2.079(2), 2.093, 2.105, 2.121, 2.127 (11s, 17 x OAc), 3.300 (m, 2H, $OCH_2CH_2CH_2N_3$), 3.687 (s, 3H, CO_2Me), 5.328 (bs, 2H, H-4^b, H-4^f), 5.457 (d, 1H, H-4^d), 6.784-6.935 (m, 5H, Ph), 7.629 (m, 4H, Phth); ^{13}C NMR ($CDCl_3$) δ 97.88, 100.33, 100.57, 101.21(2), 101.50 (6 x C-1); FABMS for $C_{90}H_{114}N_4O_{50}$ (2050.7): *m/z* 2074.4 $[M+Na]^+$, 2051.0 $[M]^+$ (positive mode); 2050.9 $[M]^-$ (negative mode).

3-Azidopropyl *O*-(β-D-Galactopyranosyl)-(1→4)-*O*-(β-D-glucopyranosyl)-(1→6)-*O*-{3-*O*-[(*S*)-1-carboxyethyl]-β-D-galactopyranosyl-(1→4)-*O*}-(2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (16) and 3-Azidopropyl *O*-(β-D-Galactopyranosyl)-(1→4)-*O*-(β-D-glucopyranosyl)-(1→6)-*O*-{3-*O*-[(*S*)-1-(*N*-acetylhydrazidocarbonyl)ethyl]-β-D-galactopyranosyl-(1→4)-*O*}-(2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (17). To a solution of **15** (50 mg, 0.024 mmol) in methanol (3 mL) was added 1N NaOH (0.1 mL). The mixture was stirred at rt for 20 h and then neutralized by the addition of Dowex-50 ion-exchange resin (H^+). The filtrate was concentrated to a residue. To a solution of above residue in 95% ethanol (3 mL) was added hydrazine hydrate (0.5 mL) and the mixture was refluxed for 20 h. After evaporation of solvent, the residue was dissolved in methanol (3 mL) and treated with acetic anhydride (0.5 mL) at rt for 40 h. The solvent was then evaporated, and the residue was purified by chromatography on Sephadex LH-20 with methanol as eluent to afford a mixture of **16** and **17**. The separation of **16** from **17** was achieved by chromatography on a Sephadex DEAE column. Compound **17** was eluted with 0.01M tris buffer (pH 7.5), and **16** was then eluted by same buffer with 0.5M NaCl. The two fractions were separately desalted by passage through a column of Sephadex G-10, and lyophilized to afford pure **16** (14 mg, 44%) and **17** (6 mg, 19%).

For **16**: $[\alpha]_D$ +30° (*c* 0.25, H_2O); ^1H NMR (D_2O, 293 K) δ 1.436 (d, 3H, *Me*$CHCO_2Na$, J = 6.5 Hz), 1.893 (s, 3H, NAc) 1.942 (m, 2H, $OCH_2CH_2CH_2N_3$), 3.324

(dd, 1H, H-2^e, $J_{2,3}$ = 8.2 Hz), 3.391 (t, 1H, H-2^a, $J_{2,3}$ = 7.9 Hz), 3.479 (t, 2H, $OCH_2CH_2CH_2N_3$, J = 6.5 Hz), 4.431 (d, 1H, H-1^b, $J_{1,2}$ = 7.8 Hz), 4.470 (d, 1H, H-1^f, $J_{1,2}$ = 7.8 Hz), 4.497 (d, 1H, H-1^a, $J_{1,2}$ = 7.9 Hz), 4.565 (d, 1H, H-1^e, $J_{1,2}$ = 7.8 Hz), 4.615 (d, 1H, H-1^d, $J_{1,2}$ = 7.8 Hz), 4.698 (d, 1H, H-1^c, $J_{1,2}$ = 7.8 Hz), 4.720 and 4.999 (2d, 1H each, CH_2Ph, J = 11.5 Hz), 7.405-7.458 (m, 5H, Ph); ^{13}C NMR (D_2O, 293 K) δ 19.35 (*Me*$CHCO_2Na$), 22.78 (CH_3CON), 28.89 ($OCH_2CH_2CH_2N_3$), 48.51 ($OCH_2CH_2CH_2N_3$), 55.31 (C-2^e), 102.77, 103.17, 103.32, 103.42, 103.59(2) (6 x C-1), 128.97, 129.28, 129.37, 138.24 (Ph), 175.10 (CH_3CON), 182.91 (CO_2Na); FABMS for $C_{51}H_{79}N_4O_{33}Na$ (1298.5): *m/z* 1300.0 $[M+H]^+$ (positive mode); 1276.1 $[M-Na]^-$ (negative mode).

For **17**: $[\alpha]_D$ +28° (*c* 0.31, H_2O); ^{1}H NMR (D_2O, 293 K) δ 1.488 (d, 3H, *Me*CHCONHNH, J = 6.5 Hz), 1.906 (m, 5H, NAc, $OCH_2CH_2CH_2N_3$), 2.090 (s, 3H, NHNH*Ac*), 3.315 (dd, 1H, H-2^e, $J_{2,3}$ = 8.2 Hz), 3.387 (dd, 1H, H-2^a, $J_{2,3}$ = 7.9 Hz), 3.470 (t, 2H, $OCH_2CH_2CH_2N_3$, J = 6.5 Hz), 4.439 (d, 1H, H-1^b, $J_{1,2}$ = 9.0 Hz), 4.477 (d, 1H, H-1^f, $J_{1,2}$ = 7.9 Hz), 4.504 (d, 1H, H-1^a, $J_{1,2}$ = 8.0 Hz), 4.580 (d, 1H, H-1^e, $J_{1,2}$ = 7.7 Hz), 4.626 (d, 1H, H-1^d, $J_{1,2}$ = 7.4 Hz), 4.725 (d, 1H, H-1^c, $J_{1,2}$ = 9.0 Hz), 4.707 and 5.006 (2d, 1H each, CH_2Ph, J = 11.0 Hz), 7.414-7.444 (m, 5H, Ph); ^{13}C NMR (D_2O, 293 K) δ 18.31 (CH*Me*CONHNH), 20.40 ($CH_3CONHNH$), 22.78 (CH_3CON), 28.89 ($OCH_2CH_2CH_2N_3$), 48.51 ($OCH_2CH_2CH_2N_3$), 102.77, 103.07, 103.12, 103.42, 103.59(2) (6 x C-1), 173.74 (MeCHCONHNH), 175.11 and 175.55 (CH_3CON, $CH_3CONHNH$); FABMS for $C_{53}H_{84}N_6O_{33}$ (1333.3): *m/z* 1355.6 $[M+Na]^+$ (positive mode); 1332.1 $[M-H]^-$ (negative mode).

3-Aminopropyl *O*-(β-D-Galactopyranosyl)-(1→4)-*O*-(β-D-glucopyranosyl)-(1→6)-*O*-{3-*O*-[(*S*)-1-carboxyethyl]-β-D-galactopyranosyl-(1→4)-*O*}-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (18). To a solution of **16** (12 mg, 9.2 μmol) in water/acetic acid (8:2, 3 mL) was added 10% Pd-on-carbon (50% wet, 10 mg). The mixture was stirred under hydrogen for 20 h. The filtrate was then lyophilised to give compound **18** (10 mg, 92%): $[\alpha]_D$ +1.3° (*c* 0.38, H_2O); ^{1}H NMR (D_2O, 293 K) δ 1.396 (d, 3H, CH*Me*CO_2Na, J = 6.8 Hz), 2.034 (s and m, 5H, NAc, $OCH_2CH_2CH_2NH_2$), 3.157 (t, 2H, $OCH_2CH_2CH_2NH_2$, J = 6.8 Hz), 3.327-3.383 (m, 2H, H-2^e, H-2^a), 4.436 (d, 1H, H-1^b, $J_{1,2}$ = 7.9 Hz), 4.463 (d, 1H, H-1^f, $J_{1,2}$ = 7.8 Hz), 4.503 (d, 1H, H-1^a, $J_{1,2}$ = 8.0 Hz), 4.566 (d, 2H, H-1^d and H-1^e, $J_{1,2}$

= 7.8 Hz), 4.714 (d, 1H, H-1^{c}, $J_{1,2}$ = 8.3 Hz); ^{13}C NMR (D_2O, 293 K) δ 19.99 (CH*Me*CO_2Na), 23.49 (*C*H_3CON), 28.00 (OCH_2*C*$H_2CH_2NH_2$), 38.89 (OCH_2CH_2*C*H_2NH_2), 55.46 (C-2^{c}), 103.39, 103.87, 103.93, 104.27(3) (6 x C-1), 176.23 (CH_3*C*ON), 183.48 (CO_2Na); FABMS for $C_{44}H_{75}N_2O_{33}Na$ (1182.4): *m/z* 1205.4 $[M+Na]^+$, 1183.6 $[M+H]^+$ (positive mode); 1159.3 $[M-Na]^-$ (negative mode).

3-Aminopropyl *O*-(β-D-Galactopyranosyl)-(1→4)-*O*-(β-D-glucopyranosyl)-(1→6)-*O*-{3-*O*-[(*S*)-1-(*N*-acetylhydrazidocarbonyl)ethyl]-β-D-galactopyranosyl-(1→4)-*O*}-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside (19). To a solution of **17** (4.5 mg, 3.37 μmol) in water/acetic acid (8:2, 2 mL) was added 10% Pd-on-carbon (50% wet, 6 mg). The mixture was stirred under hydrogen for 16 h. The filtrate was then lyophilised to give compound **19** (3.9 mg, 95%): $[\alpha]_D$ +12.4° (*c* 0.24, H_2O); ^{1}H NMR (D_2O, 293 K) δ 1.474 (d, 3H, CH*Me*CO, J = 6.3 Hz), 2.034 (s and m, 5H, NAc, $OCH_2CH_2CH_2NH_2$), 2.077 (s, 3H, NHNH*Ac*), 3.157 (t, 2H, $OCH_2CH_2CH_2NH_2$, J = 6.3 Hz), 3.310-3.372 (m, 2H, H-2^{e}, H-2^{a}), 4.436 (d, 1H, H-1^{b}, $J_{1,2}$ = 7.9 Hz), 4.464 (d, 1H, H-1^{f}, $J_{1,2}$ = 7.8 Hz), 4.503 (d, 1H, H-1^{a}, $J_{1,2}$ = 7.6 Hz), 4.571 (d, 2H, H-1^{d} and H-1^{e}, $J_{1,2}$ = 7.8 Hz), 4.717 (d, 1H, H-1^{c}, $J_{1,2}$ = 7.7 Hz); ^{13}C NMR (D_2O, 293 K) δ 19.02 (CH*Me*CO), 21.03 (*C*H_3CONHNH), 23.48 (*C*H_3CON), 27.98 (OCH_2*C*$H_2CH_2NH_2$), 38.88 (OCH_2CH_2*C*H_2NH_2), 56.49 (C-2^{c}), 103.38, 103.72, 103.88, 104.25(3) (6 x C-1), 174.57 (CHMe*C*ONHNH), 176.24 and 176.32 (CH_3*C*ON and CH_3*C*ONHNH); FABMS for $C_{46}H_{80}N_4O_{33}$ (1216.5): *m/z* 1239.4 $[M+Na]^+$ (positive mode); 1216.2 $[M]^-$ (negative mode).

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