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Synthesis of the Forssman pentasaccharide and terminal tetra-, tri-, and di-saccharide fragments

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ABSTRACT

The 2-(trimethylsilyl)ethyl (TMSEt) β-glycosides of the Forssman pentasaccharide [α-D-GalNAc-(1 → 3)-β-D-GalNAc-(1 → 3)-α-D-Gal-(1 → 4)-β-D-Gal-(1 → 4)-D-Glc] and the terminal tetrasaccharide, as well as the methyl glycosides **1** and **2** of the terminal di- and tri-saccharides, were synthesised by silver trifluoromethanesulfonate-promoted α-glycosylation of suitably protected mono-, di-, tri-, and tetra-saccharide alcohols with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl bromide, followed by removal of protecting groups. The anomeric TMSEt group of the Forssman pentasaccharide and terminal tetrasaccharide was removed with trifluoroacetic acid–dichloromethane, to give the corresponding hemiacetal sugars **4** and **6**.

INTRODUCTION

Antigens of the globoseries of glycolipids, in conjunction with the various proteins that bind to the oligosaccharide part of these antigens[1], constitute a useful model system for the study of molecular recognition between carbohydrate and protein. The interaction between the pilus-associated PapG adhesin protein of uropathogenic *Escherichia coli*[2] and galabiose [α-D-Gal-(1 → 4)-α,β-D-Gal] has been thoroughly investigated in our laboratory[3]. Since different strains of *E. coli* recognise slightly different epitopes of the globoseries glycolipids[4], we decided to synthesise the Forssman pentasaccharide as well as all corresponding di-, tri-, and tetra-saccharide fragments **1–6** for use in various bioassays and NMR investigations (Fig. 1).

The preceding paper describes the synthesis of glycosides of globotetraose and its terminal di- and tri-saccharide fragments while this paper is concerned with the synthesis of the TMSEt glycoside of the Forssman pentasaccharide and the

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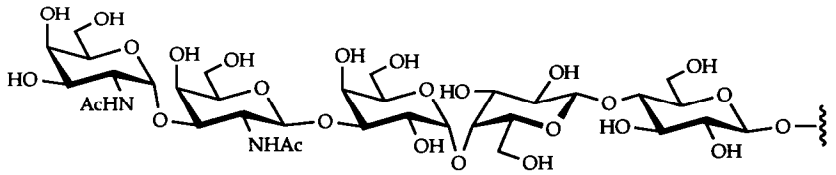


α-D-Galp-NAc-(1→3)-β-D-Galp-NAc-1-OMe (**1**)
α-D-Galp-NAc-(1→3)-β-D-Galp-NAc-(1→3)-α-D-Galp-1-OMe (**2**)
α-D-Galp-NAc-(1→3)-β-D-Galp-NAc-(1→3)-α-D-Galp-(1→4)-β-D-Galp-1-OTMSEt (**3**)
α-D-Galp-NAc-(1→3)-β-D-Galp-NAc-(1→3)-α-D-Galp-(1→4)-αβ-D-Galp-1-OH (**4**)
α-D-Galp-NAc-(1→3)-β-D-Galp-NAc-(1→3)-α-D-Galp-(1→4)-β-D-Galp-(1→4)-β-D-Glcp-1-OTMSEt (**5**)
α-D-Galp-NAc-(1→3)-β-D-Galp-NAc-(1→3)-α-D-Galp-(1→4)-β-D-Galp-(1→4)-αβ-D-Glcp-1-OH (**6**)

TMSEt = 2-(Trimethylsilyl)ethyl

Fig. 1. Synthetic fragments of the Forssman pentasaccharide.

terminal tetrasaccharide and the methyl glycosides of the terminal di- and tri-saccharides. A preliminary account of this work has been published[5]. The use of the TMSEt group as anomeric protecting group permitted the use of a wide range of protection, deprotection, and anomeric activation strategies[6]. The synthesis of the Forssman pentasaccharide[7] as well as the entire Forssman glycolipid[8] has been accomplished by others.

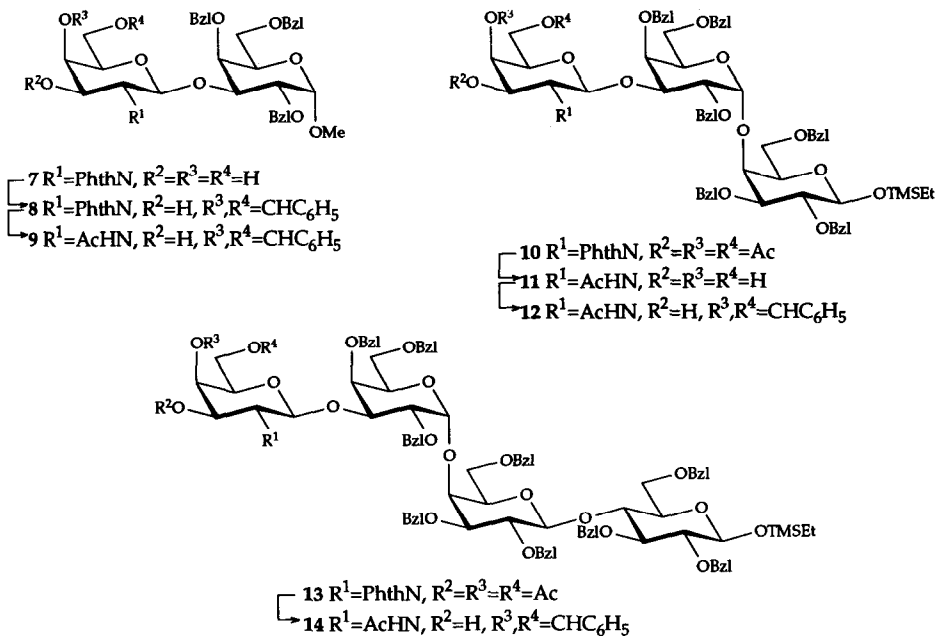
The synthetic strategy was based on the use of intermediates from the synthesis of the globotetraose tetrasaccharide and the corresponding fragments[1]. They were transformed into di-, tri-, and tetra-saccharide glycosyl acceptors, which were then α-glycosylated with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactosyl bromide[9], followed by removal of protecting groups from the products, thus yielding compounds **1–6**.

RESULTS AND DISCUSSION

The di-, tri-, and tetra-saccharide acceptors **9**, **12**, and **14** were prepared as follows (Scheme 1). Hydrazinolysis, acetylation, and *O*-deacetylation of **7** (ref 1), followed by 4,6-*O*-benzylidenation, using α,α-dimethoxytoluene and *p*-toluenesulfonic acid in acetonitrile, gave a disappointingly low yield of **9** (33%) due to several side-reactions in the benzylidenation reaction, including cleavage of the inter-glycosidic bond. Instead, benzylidenation of **7** with α,α-dimethoxytoluene and *p*-toluenesulfonic acid in acetonitrile to give **8** (82%), followed by hydrazinolysis, acetylation, and *O*-deacetylation afforded **9** (88%; 72% overall yield from **7**).

Hydrazinolysis and *N*-acetylation of **10** (ref 1) (α/β mixture at the terminal GalNPhth-residue, 8:92), and separation of the α/β mixture on a silica gel column furnished pure **11** (78%). Benzylidenation of **11**, as described for **7**, gave the trisaccharide alcohol **12** (77%).

Deacetylation, benzylidenation, hydrazinolysis, acetylation, and *O*-deacetylation of compound **13** (ref 1) gave the globotetraoside **14** (80% overall yield).

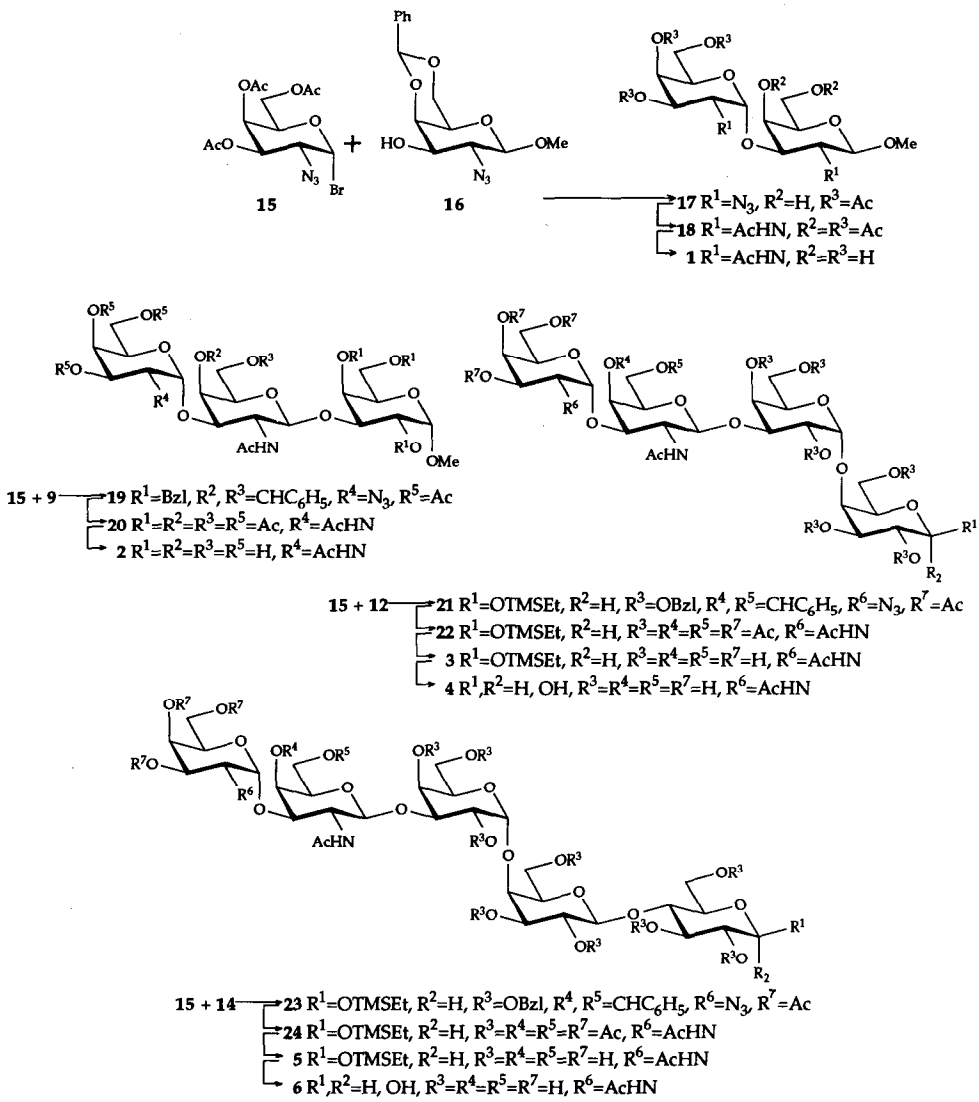


Scheme 1.

With the mono-, di-, tri-, and tetra-saccharide alcohols **16** (ref 10), **9**, **12**, and **14**, in hand, silver trifluoromethanesulfonate-promoted glycosylations with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl bromide[9] (**15**) were attempted (Scheme 2). Glycosylation of the monosaccharide alcohol **16** gave an anomeric mixture (71%, α/β 9:2), which was separable on silica gel after solvolysis of the benzylidene acetal to afford **17** (44%) and the corresponding β-glycoside (5%). Surprisingly, the glycosylation with the disaccharide alcohol **9** was rather sluggish and gave only a modest yield of **19** (41%), together with the corresponding β-glycoside (15%). In contrast, glycosylation of the tri- and tetra-saccharide alcohols **12** and **14** proceeded smoothly to furnish the tetra- and penta-saccharides **21** (79%) and **23** (83%), respectively; no β anomers were detected.

Acetylation of **17** with acetic anhydride–pyridine, followed by reductive acetylation of the azido group, using thioacetic acid[11], gave the fully acetylated derivative **18** (62%), which upon treatment with methanolic sodium methoxide afforded the disaccharide **1**. Sodium borohydride–nickel chloride-reduction[12] of the azido group in **19**, **21**, and **23**, followed by acetylation, hydrogenolysis of benzyl ethers, and acetylation, furnished the fully acetylated compounds **20** (76%), **22** (67%), and **24** (51%). *O*-Deacetylation gave the tri-, tetra-, and penta-saccharides **2** (94%), **3** (81%), and **5** (99%), respectively.

The TMSEt protecting group of the tetra- and penta-saccharides **3** and **5** was selectively cleaved with trifluoroacetic acid–dichloromethane[6a] to give the hemiacetal sugars **4** (76%) and **6** (88%).



Scheme 2.

EXPERIMENTAL

General methods.—See ref 1.

Methyl 3-O-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-β-D-galactopyranoside (**1**).—Compound **18** (24.3 mg, 37.5 μmol) was *O*-deacetylated in methanolic NaOMe (4 mL, 0.001 M). After 2.5 h, the mixture was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. Column chromatography (65 : 35 : 5 CH_2Cl_2–MeOH–H_2O) of the residue gave **1** (14.3 mg, 90%), $[\alpha]_D^{25}$ + 178° (*c* 0.40, H_2O). ^1H NMR data (D_2O): δ 5.02 (d, 1 H, *J* 3.7 Hz, H-1′), 4.42 (d, 1 H, *J* 8.5 Hz,

H-1), 4.17 (dd, 1 H, *J* 3.7, 11.2 Hz, H-2′), 3.98 (dd, 1 H, *J* 8.5, 10.9 Hz, H-2), 3.49 (s, 3 H, OMe), 2.01, 1.99 (2 s, 3 H each, Ac).

Methyl 3-O-[2-acetamido-3-O-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-2-deoxy-β-D-galactopyranosyl]-α-D-galactopyranoside (**2**).—Compound **20** (117.1 mg, 0.125 mmol) was *O*-deacetylated in methanolic NaOMe (2.5 mL, 0.04 M). After 5 h, water (1 mL) was added to dissolve the gel that was formed. The mixture was neutralised with Duolite (H^+) resin, filtered, and concentrated. Column chromatography (65:35:5 CH_2Cl_2–MeOH–H_2O) of the residue gave **2** (70.8 mg, 94%), $[\alpha]_D^{25}$ + 216° (*c* 1, H_2O). ^1H NMR data (D_2O): δ 5.03 (d, 1 H, *J* 3.7 Hz, H-1″), 4.73 (br s, 1 H, H-1), 4.67 (d, 1 H, *J* 8.6 Hz, H-1′), 4.18 (dd, 1 H, *J* 3.7, 10.8 Hz, H-2″), 4.16 (br d, 1 H, *J* 3.2 Hz, H-4), 4.06 (dd, 1 H, *J* 8.6, 10.8 Hz, H-2′), 3.37 (s, 3 H, OMe), 2.01, 2.00 (2 s, 3 H each, Ac). ^{13}C NMR data (D_2O): δ 175.7, 175.4, 103.5, 100.4, 94.3, 80.1, 75.7, 75.5, 72.1, 71.2, 69.9, 69.1, 68.5, 68.0, 64.4, 62.0, 61.8, 61.7, 55.8, 51.8, 50.2, 23.1, 22.8.

2-(Trimethylsilyl)ethyl 4-O-{3-O-[2-acetamido-3-O-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-2-deoxy-β-D-galactopyranosyl]-α-D-galactopyranosyl}-β-D-galactopyranoside (**3**).—Compound **22** (52.0 mg, 0.040 mmol) was treated with methanolic NaOMe (1 mL, 0.05 M) for 4 h 15 min, and the mixture was neutralised with Duolite (H^+) resin, filtered, and concentrated. Column chromatography (65:35:5 CH_2Cl_2–MeOH–H_2O) of the residue gave **3** (27.2 mg, 81%), $[\alpha]_D^{25}$ + 136° (*c* 1, H_2O). ^1H NMR data (D_2O): δ 5.03 (d, 1 H, *J* 3.7 Hz, H-1‴), 4.90 (d, 1 H, *J* 3.7 Hz, H-1′), 4.66 (d, 1 H, *J* 8.5 Hz, H-1″), 4.43 (d, 1 H, *J* 7.8 Hz, H-1), 4.36 (br t, 1 H, *J* 6.3 Hz, H-5′), 4.23 (br d, 1 H, *J* 2.2 Hz, H-4′), 4.17 (dd, 1 H, *J* 3.7, 11.7 Hz, H-2‴), 3.48 (dd, 1 H, *J* 7.8, 9.7 Hz, H-2), 2.01, 1.99 (2 s, 3 H each, Ac), 0.98 (m, 2 H, CH_2CH_2Si), −0.02 (s, 9 H, $SiMe_3$). ^{13}C NMR data (D_2O): δ 175.7, 175.4, 103.7, 103.0, 101.1, 94.4, 80.1, 77.7, 75.75, 75.69, 75.5, 73.3, 72.2, 71.8, 71.1, 69.7, 69.1, 69.1, 68.5, 68.4, 64.4, 61.8, 61.7, 61.2, 60.7, 51.7, 50.2, 23.1, 22.8, 18.5, −1.6.

4-O-{3-O-[2-Acetamido-3-O-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-2-deoxy-β-D-galactopyranosyl]-α-D-galactopyranosyl}-α,β-D-galactopyranose (**4**).—Compound **3** (27.2 mg, 32.1 mmol) was dissolved in dry CH_2Cl_2 (105 mL) and CF_3CO_2H (0.21 mL) under N_2[6a]. After 32 min, propyl acetate (1.2 mL) and toluene (2 mL) were added and the solution was concentrated. Column chromatography (5:5:1 CH_2Cl_2–MeOH–H_2O) of the residue gave **4** (18.3 mg, 76%), $[\alpha]_D^{25}$ + 229° (*c* 0.48, H_2O). ^1H NMR data for the α anomer (D_2O): δ 5.26 (d, 1 H, *J* 3.5 Hz, H-1), 5.02 (d, 1 H, *J* 3.7 Hz, H-1‴), 4.89 (d, 1 H, *J* 3.5 Hz, H-1′), 4.66 (d, 1 H, *J* 8.7 Hz, H-1″), 4.33 (br t, 1 H, *J* 6.8 Hz, H-5′), 4.22 (br s, 1 H, H-4′), 4.17 (dd, 1 H, *J* 3.7, 11.1 Hz, H-2‴), 2.01, 1.99 (2s, 6 H, Ac). ^1H NMR data for the β anomer (D_2O): δ 5.02 (d, 1 H, *J* 3.7 Hz, H-1‴), 4.89 (d, 1 H, *J* 3.5 Hz, H-1′), 4.66 (d, 1 H, *J* 8.7 Hz, H-1″), 4.61 (d, 1 H, *J* 7.9 Hz, H-1), 4.33 (br t, 1 H, *J* 6.8 Hz, H-5′), 4.22 (br s, 1 H, H-4′), 4.17 (dd, 1 H, *J* 3.7, 11.1 Hz, H-2‴), 2.01, 1.99 (2 s, 3 H each, Ac). The α,β-mixture had: ^{13}C NMR data (D_2O): δ 175.7, 175.5, 103.6, 101.2, 97.5, 94.4, 80.0, 78.2, 75.9, 75.7, 75.6, 73.3, 72.8, 72.2, 71.2, 69.8, 69.2, 68.53, 68.50, 67.6, 64.5, 61.9, 61.7, 61.3, 61.1, 51.8, 50.3, 23.1, 22.9.

2-(Trimethylsilyl)ethyl 4-O-(4-O-{3-O-[2-acetamido-3-O-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-2-deoxy-β-D-galactopyranosyl]-α-D-galactopyranosyl}-β-D-galactopyranosyl)-β-D-glucopyranoside (**5**).—Compound **24** (37.2 mg, 0.024 mmol) was treated with methanolic NaOMe (1 mL, 0.05 M) for 18 h, and the mixture was neutralised with Duolite (H^+) resin, filtered, and concentrated. Column chromatography (65:35:5 CH_2Cl_2–MeOH–H_2O) of the residue gave **5** (24.1 mg, 99%), $[\alpha]_D^{25}$ + 63° (*c* 0.6, H_2O). ^1H NMR data (D_2O): δ 5.06 (d, 1 H, *J* 3.7 Hz, H-1‴), 4.91 (d, 1 H, *J* 3.7 Hz, H-1″), 4.70 (d, 1 H, *J* 8.5 Hz, H-1‴), 4.50 (d, 1 H, *J* 7.3 Hz, H-1′), 4.47 (d, 1 H, *J* 7.1 Hz, H-1), 4.37 (br t, 1 H, *J* 6.3 Hz, H-5″), 4.24 (br d, 1 H, H-4″), 4.20 (dd, 1 H, *J* 3.7, 11.0 Hz, H-2‴), 3.27 (br t, 1 H, *J* 8.2 Hz, H-2), 2.03, 2.00 (2 s, 3 H each, Ac), 1.01 (m, 2 H, CH_2CH_2Si), 0.01 (s, 9 H, $SiMe_3$). ^{13}C NMR data (D_2O): δ 175.7, 175.4, 104.1, 103.6, 102.2, 101.2, 94.4, 79.7, 79.5, 78.1, 76.2, 75.7, 75.6, 75.5, 73.8, 73.0, 72.1, 71.7, 71.2, 69.7, 69.3, 69.1, 68.5, 68.4, 64.5, 61.9, 61.7, 61.23, 61.21, 61.16, 60.9, 51.8, 50.2, 23.1, 22.8, 18.4, −1.7.

4-O-(4-O-{3-O-[2-Acetamido-3-O-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-2-deoxy-β-D-galactopyranosyl]-α-D-galactopyranosyl}-β-D-galactopyranosyl)-α,β-D-glucopyranose (**6**).—Compound **5** (7.3 mg, 7.2 μmol) was dissolved in dry CH_2Cl_2 (23.6 mL) and CF_3CO_2H (47.2 mL) under N_2[6a]. After 19 min, propyl acetate (0.3 mL) and toluene (1.5 mL) were added and the solution was concentrated. Column chromatography (5:5:1 CH_2Cl_2–MeOH–H_2O) of the residue gave **6** (5.8 mg, 88%), $[\alpha]_D^{25}$ +161° (*c* 0.46, H_2O); lit.[7] $[\alpha]_D^{20}$ +134° (*c* 0.25, H_2O). ^1H NMR data (D_2O): δ 5.18 (d, 1 H, *J* 3.7 Hz, H-1α), 5.02 (d, 1 H, *J* 3.7 Hz, H-1‴), 4.88 (d, 1 H, *J* 3.9 Hz, H-1″), 4.67 (d, 1 H, *J* 8.5 Hz, H-1‴), 4.62 (d, 1 H, *J* 7.8 Hz, H-1β), 4.47 (d, 1 H, *J* 7.8 Hz, H-1′), 4.35 (br t, 1 H, *J* 6.4 Hz, H-5″), 4.22 (br d, 1 H, *J* 2.2 Hz, H-4″), 4.17 (dd, 1 H, *J* 3.7, 10.2 Hz, H-2‴), 3.23 (br t, 1 H, *J* 8.2 Hz, H-2β), 2.02, 1.99 (2 s, 3 H each, Ac).

Methyl 2,4,6-tri-O-benzyl-3-O-(4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-galactopyranosyl)-α-D-galactopyranoside (**8**).—A mixture of methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2-deoxy-2-phthalimido-β-D-galactopyranosyl)-α-D-galactopyranoside[1] (**7**; 3.27 g, 4.33 mmol), α,α-dimethoxytoluene (1.5 mL, 10 mmol), *p*-toluenesulfonic acid (100 mg), and MeCN (80 mL) was stirred overnight, Et_3N (2 mL) was added, and the solution was concentrated. Column chromatography (3:1 → 1:1 gradient heptane–EtOAc) gave **8** (2.96 g, 81%), $[\alpha]_D^{25}$ −47° (*c* 0.7, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.62 (s, 1 H, PhC*H*), 5.57 (d, 1 H, *J* 8.1 Hz, H-1′), 4.55 (dd, 1 H, *J* 8.1, 11.0 Hz, H-2′), 4.28 (d, 1 H, *J* 3.7 Hz, H-1), 3.86 (br t, 1 H, *J* 6.0 Hz, H-5), 3.48 (dd, 1 H, *J* 6.3, 9.6 Hz, H-6), 3.39 (dd, 1 H, *J* 6.2, 9.6 Hz, H-6), 3.22 (s, 3 H, OMe), 1.62 (s, 3 H, Ac). Mass spectrum: calcd for $C_{49}H_{53}N_2O_{12}$ ($M + NH_4$): *m/z* 861.3598; found: *m/z* 861.3606.

Methyl-3-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-galactopyranosyl)-2,4,6-tri-O-benzyl-α-D-galactopyranoside (**9**).—Compound **8** (506 mg, 0.60 mmol) and hydrazine hydrate (0.6 mL) in EtOH (15 mL) were heated to 80°C for 1 h 10 min, and then concentrated. The residue was co-concentrated several times with EtOH to remove excess of hydrazine hydrate, then acetylated in Ac_2O (10 mL) and

pyridine (10 mL), and *O*-deacetylated in methanolic NaOMe (15.5 mL, 0.06 M). Column chromatography (10:1 toluene–EtOH) of the residue gave **9** (397 mg, 88%). Recrystallisation from MeOH gave an analytical sample; $[\alpha]_D^{25}$ +5.2° (*c* 1, $CDCl_3$), mp 177–178°C. ^1H NMR data ($CDCl_3$): δ 5.88 (d, 1 H, *J* 4.5 Hz, NH), 5.59 (s, 1 H, PhC*H*), 4.72 (d, 1 H, *J* 2.5 Hz, H-1), 4.67 (d, 1 H, *J* 8.3 Hz, H-1′), 4.32 (dd, 1 H, *J* 1.3, 12.3 Hz, H-6), 4.19 (d, 1 H, *J* 3.4 Hz, H-4′), 3.90 (br t, 1 H, *J* 6.3 Hz, H-5), 3.52 (dd, 1 H, *J* 6.3, 9.7 Hz, H-6), 3.38 (dd, 1 H, *J* 6.0, 9.7 Hz, H-6), 3.34 (s, 3 H, OMe), 1.69 (s, 3 H, Ac). Mass spectrum: calcd for $C_{43}H_{50}NO_{11}$ (M + 1): *m/z* 756.3383; found: *m/z* 756.3391.

*2-(Trimethylsilyl)ethyl 4-O-[3-O-(2-acetamido-2-deoxy-β-*D*-galactopyranosyl)-2,4,6-tri-O-benzyl-α-*D*-galactopyranosyl]-2,3,6-tri-O-benzyl-β-*D*-galactopyranoside* (**11**).—A mixture of 2-(trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-α,β-D-galactopyranosyl)-α-D-galactopyranosyl]-β-D-galactopyranoside[1] (**10**; 4.5 g, 3.21 mmol; α/β 8:92), hydrazine hydrate (6 mL), and EtOH (150 mL) was heated to 85°C for 50 min and then concentrated. The residue was co-concentrated several times with EtOH to remove excess of hydrazine hydrate. *N*-Acetylation with Ac_2O (5 mL) in MeOH (100 mL) for 20 min at room temperature, followed by column chromatography (40:1 CH_2Cl_2–MeOH), gave **11** (2.96 g, 78%), $[\alpha]_D^{25}$ +18° (*c* 0.7, MeOH). ^1H NMR data ($CDCl_3$): δ 5.05 (d, 1 H, *J* 3.4 Hz, H-1′), 4.64 (d, 1 H, *J* 8.3 Hz, H-1″), 4.38 (d, 1 H, *J* 7.4 Hz, H-1), 1.60 (s, 3 H, Ac), 1.08–1.00 (m, 2 H, CH_2CH_2Si), 0.03 (s, 9 H, $SiMe_3$). Mass spectrum: calcd for $C_{67}H_{84}NO_{16}Si$ (M + 1): *m/z* 1186.5559; found: *m/z* 1186.5520.

*2-(Trimethylsilyl)ethyl 4-O-[3-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-*D*-galactopyranosyl)-2,4,6-tri-O-benzyl-α-*D*-galactopyranosyl]-2,3,6-tri-O-benzyl-β-*D*-galactopyranoside* (**12**).—A mixture of **11** (2.9 g, 2.44 mmol), α,α-dimethoxytoluene (0.76 g, 5 mmol), *p*-toluenesulfonic acid (50 mg), and dry MeCN (50 mL) was stirred overnight, then neutralised with Et_3N and concentrated. Column chromatography (1:1 → 1:2 gradient heptane–EtOAc) of the residue gave **12** (2.38 g, 77%), $[\alpha]_D^{25}$ +23° (*c* 0.8, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.58 (s, 1 H, PhC*H*), 5.02 (d, 1 H, *J* 3.4 Hz, H-1′), 4.77 (d, 1 H, *J* 8.1 Hz, H-1″), 4.38 (d, 1 H, *J* 7.5 Hz, H-1), 1.59 (s, 3 H, Ac), 1.08–1.00 (m, 2 H, CH_2CH_2Si), 0.04 (s, 9 H, $SiMe_3$). Mass spectrum: calcd for $C_{74}H_{88}NO_{16}Si$ (M + 1): *m/z* 1274.5872; found: *m/z* 1274.5850.

*2-(Trimethylsilyl)ethyl 4-O-{4-O-[3-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-*D*-galactopyranosyl)-2,4,6-tri-O-benzyl-α-*D*-galactopyranosyl]-2,3,6-tri-O-benzyl-β-*D*-galactopyranosyl}-2,3,6-tri-O-benzyl-β-*D*-glucopyranoside* (**14**).—2-(Trimethylsilyl)-ethyl 2,3,6-tri-*O*-benzyl-4-*O*-{2,3,6-tri-*O*-benzyl-4-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl)-α-D-galactopyranosyl]-β-D-galactopyranosyl}-β-D-glucopyranoside[1] (**13**; 251.5 mg, 0.137 mmol) was treated with methanolic NaOMe (3.1 mL, 0.07 M) for 2 h, and the mixture was neutralised with Duolite (H^+) resin, filtered, and concentrated. The residue was treated with α,α-dimethoxytoluene (43 mL, 0.28 mmol) and *p*-toluenesulfonic acid (3 mg) in MeCN (4.9 mL) for 14 h, and the mixture was neutralised with Et_3N and

concentrated. The residue was passed through a silica gel column (2:1 heptane–EtOAc) to remove excess of reagents. Removal of the solvent left a residue which was treated with hydrazine hydrate (30 μL) in EtOH (6.4 mL) at 85°C. After 1.5 h, more hydrazine hydrate (30 μL) was added and, after 1 h, the mixture was concentrated and co-concentrated with EtOH three times. The residue was acetylated in Ac_2O (4 mL) and pyridine (4 mL) for 1 h, concentrated, then *O*-deacetylated in methanolic NaOMe (3.1 mL, 0.07 M) for 2 h, neutralised with Duolite (H^+) resin, filtered, and concentrated. Column chromatography (20:1 toluene–EtOH) of the residue gave pure **14** (187.3 mg, 80%), $[\alpha]_D^{25}$ +13.7° (*c* 1, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.74 (br d, 1 H, *J* 6.3 Hz, NH), 5.49 (s, 1 H, PhC*H*), 5.05 (br s, 1 H, H-1″), 4.65 (d, 1 H, *J* 8.1 Hz, H-1‴), 4.37, 4.34 (2 d, 1 H each, *J* 7.2, 7.8 Hz, H-1,1′), 1.03 (m, 2 H, CH_2CH_2Si), 0.03 (s, 9 H, $SiMe_3$). ^{13}C NMR data ($CDCl_3$): δ 103.1, 103.0, 100.4, 99.8. Mass spectrum: calcd for $C_{101}H_{116}NO_{21}Si$ (M + 1): *m/z* 1706.7809; found: *m/z* 1706.7780.

*Methyl 2-azido-2-deoxy-3-*O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-*D*-galactopyranosyl)-β-*D*-galactopyranoside* (**17**).—A mixture of **16** (ref 10) (45.5 mg, 0.148 mmol), silver trifluoromethanesulfonate (0.10 g, 0.37 mmol), and 4A molecular sieves (0.2 g) in dry toluene (4 mL) was stirred under N_2 for 35 min at room temperature, then cooled to −10°C and 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl bromide[9] (**15**; 116.7 mg, 0.296 mmol) in dry CH_2Cl_2 (0.2 mL) was added. After 65 min, the mixture was filtered through Celite and concentrated. Column chromatography (1:2 heptane–EtOAc) gave an inseparable α/β mixture (64.8 mg, 71%; α/β 9:2). The residue was dissolved in AcOH (24 mL) and water (6 mL), and heated to 80°C for 1 h. Concentration and column chromatography (40:1 CH_2Cl_2–MeOH) gave **17** (34.5 mg, 44%) and **17β** (4.1 mg, 5.2%). Recrystallisation of **17** from heptane–Et_2O gave an analytical sample; $[\alpha]_D^{25}$ +96° (*c* 1, $CHCl_3$), mp 156–157°C. ^1H NMR data ($CDCl_3$): δ 5.50 (dd, 1 H, *J* 1.2, 3.2 Hz, H-4′), 5.36 (dd, 1 H, *J* 3.2, 10.8 Hz, H-3′), 5.04 (d, 1 H, *J* 3.8 Hz, H-1′), 4.56 (br t, 1 H, *J* 6.6 Hz, H-5′), 4.22 (d, 1 H, *J* 7.9 Hz, H-1), 3.97 (dd, 1 H, *J* 3.8, 10.8 Hz, H-2′), 3.63 (dd, 1 H, *J* 7.9, 10.3 Hz, H-2), 3.60 (s, 3 H, OMe), 3.49 (br t, 1 H, *J* 5.4 Hz, H-5), 3.46 (dd, 1 H, *J* 3.2, 10.3 Hz, H-3), 2.16, 2.06 (2 s, 9 H, Ac). Mass spectrum: calcd for $C_{19}H_{29}N_6O_{12}$ (M + 1): *m/z* 533.1843; found: *m/z* 533.1841. Compound **17β** had: ^1H NMR data ($CDCl_3$): δ 5.33 (dd, 1 H, *J* 0.8, 3.3 Hz, H-4′), 4.79 (dd, 1 H, *J* 3.3, 10.9 Hz, H-3′), 4.56 (d, 1 H, *J* 8.0 Hz, H-1′), 4.22 (d, 1 H, *J* 8.0 Hz, H-1), 3.80 (dd, 1 H, *J* 8.0, 10.9 Hz, H-2′), 3.71 (dd, 1 H, *J* 8.0, 10.2 Hz, H-2), 3.60 (s, 3 H, OMe), 3.46 (dd, 1 H, *J* 3.4, 10.2 Hz, H-3), 2.17, 2.06, 2.05 (3 s, 3 H each, Ac).

*Methyl 2-acetamido-3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-galactopyranosyl)-4,6-di-*O*-acetyl-2-deoxy-β-*D*-galactopyranoside* (**18**).—Compound **17** (97.7 mg, 0.183 mmol) was acetylated in Ac_2O (2.5 mL) and pyridine (2.5 mL) at 50°C for 5 h 25 min and the mixture was concentrated. A solution of the residue in thioacetic acid[11] (3 mL) was stirred for 5 days and the mixture concentrated. Column chromatography (15:1 toluene–EtOH) gave **18** (73.3 mg, 62%), $[\alpha]_D^{25}$

+45° (*c* 0.9, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 6.55 (d, 1 H, *J* 9.8 Hz, NH′), 6.37 (d, 1 H, *J* 7.5 Hz, NH), 5.35 (br d, 1 H, *J* 3.9 Hz, H-4), 5.34 (br d, 1 H, *J* 3.2 Hz, H-4′), 4.98 (d, 1 H, *J* 8.2 Hz, H-1), 4.94 (d, 1 H, *J* 3.4 Hz, H-1′), 4.92 (dd, 1 H, *J* 3.3, 11.5 Hz, H-3′), 4.70 (dd, 1 H, *J* 3.3, 10.3 Hz, H-3), 4.58 (ddd, 1 H, *J* 3.4, 10.0, 11.5 Hz, H-2′), 3.52 (s, 3 H, OMe), 3.20 (br dt, 1 H, *J* 8.0, 10.3 Hz, H-2), 2.21, 2.16, 2.10, 2.03, 2.00, 1.99, 1.97 (7 s, 3 H each, Ac). Mass spectrum: calcd for $C_{27}H_{41}N_2O_{16}$ (M + 1): *m/z* 649.2456; found: *m/z* 649.2447.

Methyl 3-O-[2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-β-D-galactopyranosyl]-2,4,6-tri-O-benzyl-α-D-galactopyranoside (**19**).—To a mixture of **9** (383 mg, 0.609 mmol), silver trifluoromethanesulfonate (299 mg, 1.18 mmol), tetramethylurea (143 μL, 1.18 mmol), and 4A molecular sieves (0.3 g) in dry toluene (7.5 mL) was added bromide[9] **15** (240 mg, 0.609 mmol), dissolved in dry toluene (1.5 mL), under N_2 at −10°C. After 5 h at −10°C, additional bromide **15** (247 mg, 0.627 mmol), dissolved in dry toluene (1.5 mL), was added. The temperature was allowed to rise to room temperature overnight and the mixture was filtered through Celite and concentrated. Column chromatography (60:1 → 30:1 gradient toluene–EtOH) of the residue gave **19** (217 mg, 41%), $[\alpha]_D^{25}$ +53° (*c* 1, $CHCl_3$), and methyl 3-*O*-[2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-galactopyranosyl)-β-D-galactopyranosyl]-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (**19β**; 72 mg, 15%). Compound **19** had: ^1H NMR data ($CDCl_3$): δ 5.76 (d, 1 H, *J* 7.3 Hz, NH), 5.61 (s, 1 H, PhC*H*), 5.42 (br d, 1 H, *J* 3.0 Hz, H-4″), 5.35 (dd, 1 H, *J* 3.2, 11.2 Hz, H-3″), 5.34 (d, 1 H, *J* 8.0 Hz, H-1′), 5.22 (d, 1 H, *J* 3.4 Hz, H-1″), 4.54 (d, 1 H, *J* 3.9 Hz, H-1), 3.31 (s, 3 H, OMe), 2.13, 2.04, 2.03, 1.76 (4 s, 12 H, Ac). Anal. Calcd for $C_{55}H_{64}N_4O_{18}$: C, 61.8; H, 6.0. Found: C, 61.0; H, 6.0.

Compound **19β** had: ^1H NMR data ($CDCl_3$): δ 5.68 (d, 1 H, *J* 6.9 Hz, NH), 5.58 (s, 1 H, PhC*H*), 5.34 (d, 1 H, *J* 8.1 Hz, H-1′), 5.30 (br d, 1 H, *J* 3.7 Hz, H-4″), 4.95 (dd, 1 H, *J* 3.2, 11.0 Hz, H-3″), 4.56 (d, 1 H, *J* 3.9 Hz, H-1), 4.49 (d, 1 H, *J* 8.1 Hz, H-1″), 3.75 (dd, 1 H, *J* 8.1, 11.0 Hz, H-2″), 3.32 (s, 3 H, OMe), 2.13, 2.06, 2.03, 1.74 (4 s, 12 H, Ac).

Methyl 3-O-[2-acetamido-3-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-galactopyranosyl)-4,6-di-O-acetyl-2-deoxy-β-D-galactopyranosyl]-2,4,6-tri-O-acetyl-α-D-galactopyranoside (**20**).—To a solution of **19** (190.3 mg, 0.178 mmol), nickel(II) chloride hexahydrate (791 mg, 3.33 mmol), and boric acid (396 mg, 6.40 mmol) in EtOH (20 mL) was added dropwise a mixture of sodium borohydride (178 mg, 4.70 mmol) in EtOH (18 mL) at 0°C. After 40 min, Ac_2O (12 mL) was added and, after 10 min, the mixture was concentrated. The residue was dissolved in CH_2Cl_2, and the mixture washed with water and satd aq $NaHCO_3$, dried, and concentrated. The residue was hydrogenated (1 atm) in AcOH (6 mL) over Pd–C (200 mg, 5%) overnight, then the mixture was filtered through Celite and concentrated. Acetylation of the residue in Ac_2O (5 mL) and pyridine (5 mL) overnight, concentration, and column chromatography (15:1 toluene–EtOH) of the residue gave **20** (127.1 mg, 76%), $[\alpha]_D^{25}$ +90° (*c* 1, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 6.57 (d, 1 H, *J* 10.0

Hz, NH), 6.49 (d, 1 H, *J* 6.9 Hz, NH), 5.41 (d, 1 H, *J* 3.4 Hz, H-1″), 5.24 (d, 1 H, *J* 8.2 Hz, H-1′), 5.15 (dd, 1 H, *J* 3.7, 10.4 Hz, H-2), 4.91 (d, 1 H, *J* 3.7 Hz, H-1), 3.36 (s, 3 H, OMe), 2.20, 2.148, 2.145, 2.13, 2.08, 2.06, 2.02, 1.97, 1.96, 1.93 (10 s, 3 H each, Ac). ^{13}C NMR data ($CDCl_3$): δ 101.1, 98.6, 97.0, 76.8, 71.8, 70.2, 70.1, 68.0, 67.5, 67.1, 67.0, 66.9, 62.7, 61.8, 61.0, 56.2, 55.3, 47.5. Mass spectrum: calcd for $C_{39}H_{57}N_2O_{24}$ (M + 1): *m/z* 937.3301; found: *m/z* 937.3311.

2-(Trimethylsilyl)ethyl 4-O-{3-O-[2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-β-D-galactopyranosyl]-2,4,6-tri-O-benzyl-α-D-galactopyranosyl}-2,3,6-tri-O-benzyl-β-D-galactopyranoside (**21**).—A mixture of **12** (1.066 g, 0.836 mmol), silver trifluoromethanesulfonate (0.7 g, 2.5 mmol), tetramethylurea (310 μL, 2.6 mmol), and activated 4A molecular sieves (2 g) in dry toluene (50 mL) was stirred under N_2 for 30 min at room temperature, then cooled to −25°C, and bromide[9] **15** (821 mg, 2.09 mmol) in dry CH_2Cl_2 (1.25 mL) was added. The mixture was stirred for 20 min and allowed to reach room temperature. After 19 h, the mixture was filtered through Celite and concentrated. Column chromatography (4 : 1 → 2 : 1 gradient heptane–EtOAc) gave **21** (1.115 mg, 84%), $[\alpha]_D^{25}$ +68° (*c* 0.9, $CHCl_3$). ^{1}H NMR data ($CDCl_3$): δ 5.63 (s, 1 H, PhC*H*), 5.41 (br d, 1 H, *J* 3.0 Hz, H-4‴), 5.33 (d, 1 H, *J* 8.3 Hz, H-1″), 5.22 (d, 1 H, *J* 3.6 Hz, H-1‴), 4.99 (d, 1 H, *J* 3.4 Hz, H-1′), 4.31 (d, 1 H, *J* 7.6 Hz, H-1), 2.13, 2.04, 2.03 (3 s, 3 H each, Ac), 1.56 (s, 3 H, NAc), 1.09–1.02 (m, 2 H, CH_2CH_2Si), 0.02 (s, 9 H, $SiMe_3$). Anal. Calcd for $C_{86}H_{102}N_4O_{23}Si$: C, 65.0; H, 6.5; N, 3.5. Found: C, 64.1; H, 6.5; N, 3.7.

2-(Trimethylsilyl)ethyl 4-O-{3-O-[2-acetamido-3-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-galactopyranosyl)-4,6-di-O-acetyl-2-deoxy-β-D-galactopyranosyl]-2,4,6-tri-O-acetyl-α-D-galactopyranosyl}-2,3,6-tri-O-acetyl-β-D-galactopyranoside (**22**).—To a solution of **21** (106.6 mg, 0.067 mmol), nickel(II) chloride hexahydrate (312 mg, 1.31 mmol), and boric acid (156 mg, 2.52 mmol) in EtOH (7.8 mL) was added dropwise a solution of sodium borohydride (70.1 mg, 1.85 mmol) in EtOH (7 mL) at 0°C. After 35 min, Ac_2O (5 mL) was added and, after 25 min, the mixture was concentrated, the residue was dissolved in CH_2Cl_2, and the solution was washed with water and satd aq $NaHCO_3$, dried, and concentrated. The residue was hydrogenated (1 atm) in AcOH (3 mL) over Pd–C (100 mg, 5%) overnight, then the solution was filtered through Celite and concentrated. Acetylation in Ac_2O (3 mL) and pyridine (3 mL) overnight, concentration, and column chromatography (15 : 1 → 10 : 1 gradient toluene–EtOH) of the residue gave **22** (58.9 mg, 67%), $[\alpha]_D^{25}$ +74° (*c* 1, $CHCl_3$). ^{1}H NMR data ($CDCl_3$): δ 5.54 (br d, 1 H, *J* 3.1 Hz, H-4′), 5.31 (br d, 2 H, *J* 2.7 Hz, H-4″,4‴), 5.18 (d, 1 H, *J* 8.5 Hz, H-1″), 5.17 (dd, 1 H, *J* 3.6, 10.6 Hz, H-2′), 5.14 (dd, 1 H, *J* 7.6, 10.8 Hz, H-2), 4.93 (d, 1 H, *J* 3.6 Hz, H-1′), 4.91 (d, 1 H, *J* 2.9 Hz, H-1‴), 4.89 (dd, 1 H, *J* 2.9, 9.8 Hz, H-3‴), 4.81 (dd, 1 H, *J* 2.5, 10.8 Hz, H-3), 4.44 (d, 1 H, *J* 7.6 Hz, H-1), 4.27 (dd, 1 H, *J* 3.4, 10.5 Hz, H-3′), 2.20, 2.15, 2.11, 2.08, 2.04, 2.02, 1.98, 1.96, 1.95 (9 s, 39 H, Ac), 0.00 (s, 9 H, $SiMe_3$). ^{13}C NMR data ($CDCl_3$): δ 100.8, 100.5, 99.0, 98.7, 76.6, 76.5, 72.7, 71.93, 71.86, 70.3, 69.8, 68.8, 67.7, 67.6, 67.1, 66.9, 62.1, 61.8, 61.4, 61.1,

55.7, 47.4, 17.9, −1.4. Mass spectrum: calcd for $C_{55}H_{83}N_2O_{32}Si$ (M + 1): *m/z* 1311.4698; found: *m/z* 1311.4700.

2-(Trimethylsilyl)ethyl 4-O-(4-O-{3-O-[2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-β-D-galactopyranosyl]-2,4,6-tri-O-benzyl-α-D-galactopyranosyl}-2,3,6-tri-O-benzyl-β-D-galactopyranosyl)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**23**).—A mixture of **14** (187.3 mg, 0.110 mmol), silver trifluoromethanesulfonate (0.09 g, 0.33 mmol), tetramethylurea (41 μL, 0.34 mmol), and activated 4A molecular sieves (0.3 g) in dry toluene (7 mL) was stirred under N_2 for 30 min at room temperature, then cooled to −25°C, and bromide[9] **15** (108 mg, 0.275 mmol) in dry CH_2Cl_2 (0.5 mL) was added. After 30 min, the mixture was allowed to reach room temperature overnight, then filtered through Celite, and concentrated. Column chromatography (60:1 toluene–EtOH) gave **23** (165.3 mg, 74%), $[\alpha]_D^{25}$ +57° (*c* 0.7, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.54 (s, 1 H, PhC*H*), 5.42 (br d, 1 H, *J* 3.1 Hz, H-4''''), 5.32 (dd, 1 H, *J* 3.3, 11.0 Hz, H-3''''), 5.14 (d, 1 H, *J* 3.2 Hz, H-1''''), 2.14, 2.03, 2.02, 1.60 (4 s, 3 H each, Ac), 1.03 (m, 2 H, CH_2CH_2Si), 0.03 (s, 9 H, $SiMe_3$). Mass spectrum: calcd for $C_{113}H_{131}N_4O_{28}Si$ (M + 1): *m/z* 2019.8720; found: *m/z* 2019.8720.

2-(Trimethylsilyl)ethyl 4-O-(4-O-{3-O-[2-acetamido-3-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-galactopyranosyl)-4,6-di-O-acetyl-2-deoxy-β-D-galactopyranosyl]-2,4,6-tri-O-acetyl-α-D-galactopyranosyl}-2,3,6-tri-O-acetyl-β-D-galacto-pyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**24**).—To a solution of **23** (229.2 mg, 0.113 mmol), nickel(II) chloride hexahydrate (504 mg, 2.12 mmol), and boric acid (252 mg, 4.07 mmol) in EtOH (12.8 mL) was added dropwise a mixture of sodium borohydride (113 mg, 2.98 mmol) in EtOH (11.5 mL) at 0°C. After 15 min, Ac_2O (8 mL) was added and, after 90 min, the mixture was concentrated, the residue was dissolved in CH_2Cl_2, and the solution was washed with water and satd aq $NaHCO_3$, dried, and concentrated. The residue was hydrogenated (1 atm) in AcOH (4 mL) over Pd–C (130 mg, 10%) overnight and the mixture was filtered through Celite and concentrated. Acetylation in Ac_2O (4 mL) and pyridine (4 mL) overnight, concentration, and column chromatography (15:1 → 10:1 gradient toluene–EtOH) of the residue gave **24** (91.9 mg, 51%), $[\alpha]_D^{25}$ +36° (*c* 0.54, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.59 (br d, 1 H, *J* 2.9 Hz, H-4''), 5.33 (br s, 2 H, H-4''',4''''), 5.20 (dd, 1 H, *J* 3.2, 10.7 Hz, H-2''), 5.19 (d, 1 H, *J* 2.5 Hz, H-1''''), 5.16 (t, 1 H, *J* 9.2 Hz, H-3), 5.11, (dd, 1 H, *J* 7.8, 10.9 Hz, H-2'), 4.94 (d, 1 H, *J* 3.7 Hz, H-1''), 4.93 (d, 1 H, *J* 8.5 Hz, H-1'''), 4.90 (dd, 1 H, *J* 2.2, 11.2 Hz, H-3''''), 4.85 (dd, 1 H, *J* 8.0, 9.2 Hz, H-2), 4.74 (dd, 1 H, *J* 2.4, 10.9 Hz, H-3'), 4.51 (d, 1 H, *J* 7.8 Hz, H-1'), 4.48 (d, 1 H, *J* 8.0 Hz, H-1), 4.24 (dd, 1 H, *J* 3.6, 10.8 Hz, H-3''), 2.21, 2.16, 2.12, 2.094, 2.087, 2.07, 2.05, 2.03, 2.02, 1.99, 1.97, 1.95 (12 s, 48 H, Ac), 0.90 (m, 2 H, CH_2CH_2Si), −0.01 (s, 9 H, $SiMe_3$). Mass spectrum: calcd for $C_{67}H_{99}N_2O_{40}Si$ (M + 1): *m/z* 1599.5540; found: *m/z* 1599.5540.

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