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Synthesis of Kdo-α-glycosides of lipid A derivatives *

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ABSTRACT

The synthesis of the lipopolysaccharide fragment *O*-(4,5,7,8-tetra-*O*-acetyl-3-deoxy-*N*-methyl-α-D-*manno*-2-octulopyranosylonamide)-(2 → 6)-*O*-{2-deoxy-2-[(3*R*)-3-dodecanoyloxytetradecanamido]-4-*O*-phosphono-3-*O*-tetradecanoyl-β-D-glucopyranosyl}-(1 → 6)-1-*O*-acetyl-2-deoxy-2-[(3*R*)-3-dodecanoyloxytetradecanamido]-3-*O*-tetradecanoyl-α-D-glucopyranose (**35α**) is performed via anomeric *O*-alkylation. With this objective, the 2-azido-3-*O*-benzyl-2-deoxy-6-*O*-trifluoromethanesulfonyl-β-D-glucopyranosides **5**, **7**, and **19α**, **β** were synthesized from D-glucal and employed as alkylating agents. Reaction of **5** with the *O*-cyclohexylidene-protected Kdo-derivative **10** afforded the desired α-linked disaccharide, *tert*-butyldimethylsilyl 4-*O*-allyl-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-(4,5:7,8-di-*O*-cyclohexylidene-3-deoxy-N-methyl-α-D-*manno*-2-octulopyranosylonamide)-β-D-glucopyranoside (**11**); even better yields of the structurally related disaccharide **12** were obtained with the 4-*O*-unprotected **7** as alkylating agent. 1-*O*-Desilylation of **12** furnished the lactol **20**, which could be alkylated at the anomeric position with 1-*O*-allyl protected alkylating agents **19α** and **19β**, both of which furnished exclusively the desired β-(1 → 6)-linked trisaccharides allyl *O*-(4,5:7,8-di-*O*-cyclohexylidene-3-deoxy-*N*-methyl-α-D-*manno*-2-octulopyranosylonamide)-(2 → 6)-*O*-(2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 6)-2-azido-3,4-di-*O*-benzyl-2-deoxy-α- (**21α**) and -β-D-glucopyranoside (**21β**), respectively. Phosphorylation with diphenyl phosphorochloridate, replacement of the *O*-cyclohexylidene protective group by *O*-triethylsilyl (TES) protective groups, removal of the 1-*O*-allyl group, azido group reduction, subsequent *N*-acylation, and then *O*-acetylation provided the key 1-*O*-acetyl protected intermediate **30α**. Removal of the *O*-TES groups, subsequent *O*-acetylation, and hydrogenolytic *O*-debenzylation furnished *O*-[4,5:7,8-tetra-*O*-acetyl-3-deoxy-*N*-methyl-α-D-*manno*-2-octulopyranosylonamide]-(2 → 6)-*O*-{2-deoxy-4-*O*-diphenoxyphosphoryl-2-[(3*R*)-3-dodecanoyloxytetradecanamido]-β-D-glucopyranosyl}-(1 → 6)-1-*O*-acetyl-2-deoxy-2[(3*R*)-dodecanoyloxytetradecanamido]-α-D-glucopyranose (**33α**), which underwent the required selective *O*-tetradecanoylation at the 3-O- and 3′-O-position, thus furnishing, after hydrogenolytic *O*-dephenylation of the diphenoxyphosphoryl group, the target molecule **35α**.

INTRODUCTION

Lipopolysaccharides (LPS) are important constituents of the outer membrane of Gram-negative bacteria[2,3]. The lipophilic portion of LPS, lipid A, possesses the lipid anchor required for membrane binding; it determines the toxic and immunos-

* Anomeric *O*-Alkylation, Part 10. For Part 9, see ref. 1.

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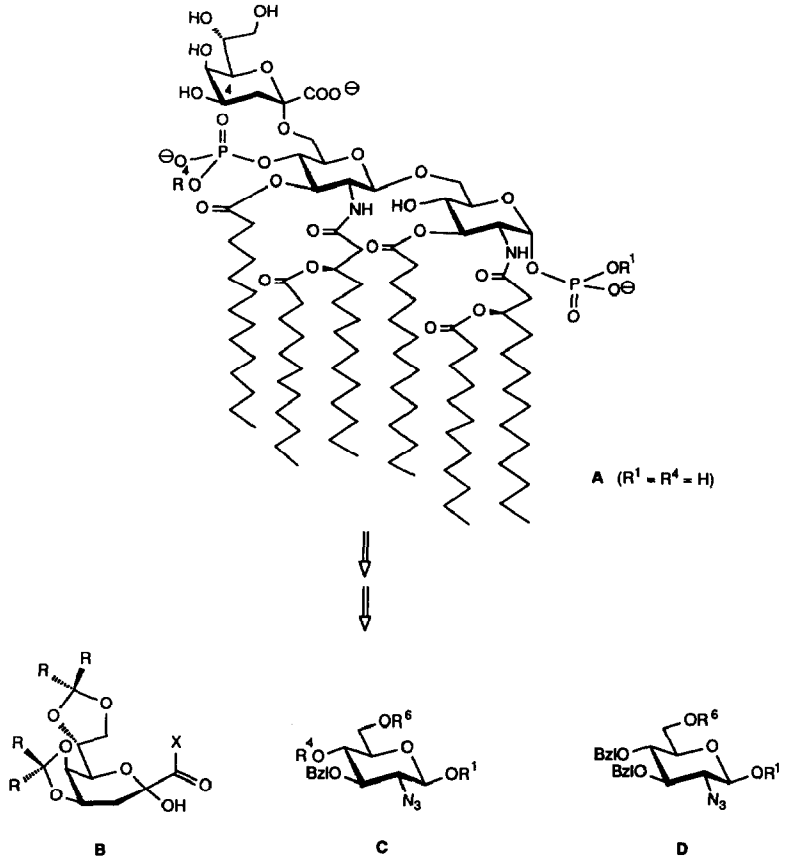


Scheme 1

timulatory properties of LPS[2]. Lipid A consists essentially of a β-(1 → 6)-linked D-glucosamine disaccharide that carries phosphate groups at positions 1 and 4′ as well as long-chain fatty acid moieties on the nitrogen and on some of the other hydroxyl groups (Scheme 1). The hydrophilic portion of LPS consists of a complex oligosaccharide chain in which Kdo (3-deoxy-D-*manno*-2-octulosonic acid) is α-(2 → 6)-linked to the glucosamine disaccharide[2,4] (Scheme 1, compound **A**). This structural unit seems to be a prerequisite for the growth and survival of the bacterial cell[2,5].

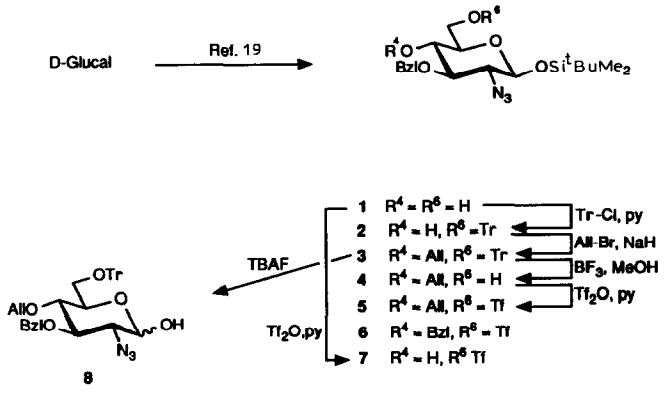
Investigations towards the synthesis of lipid A resulted finally in a total synthesis by Shiba et al.[6], thus providing material for biological testing which confirmed the high endotoxic activity of this part of LPS. Also, several lipid A analogues with structural variations in the fatty acid, the phosphate, and the oligosaccharide moiety, respectively, have been prepared[7,9]; all of them exhibited lower activity than natural lipid A[10].

The attachment of Kdo to the glucosamine disaccharide residue has also been investigated[11–14]; generally, the Koenigs–Knorr method was employed for the

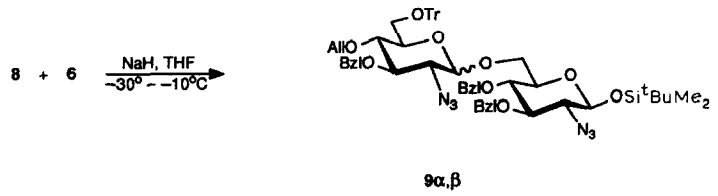
generation of the required α-glycosidic linkages. However, anomeric *O*-alkylation offers a convenient alternative for glycoside bond formation[15,16]. The successful application of this method to the highly stereoselective generation of Kdo α-glycosides was recently reported by us[17,18]. We demonstrate in this paper that the method also permits the synthesis of more complex Kdo-containing trisaccharides related to compound **A**. Selectively protected building blocks **B–D**, required for the site-specific attachment of function determining groups to the trisaccharide unit, are shown in Scheme 1. Building blocks **C** and **D** are closely related and they should allow selective access to all positions; therefore, a common strategy for their synthesis encompassing the protective group pattern was envisaged.

RESULTS AND DISCUSSION

Starting from D-glucal (Scheme 2), a transformation into the 4,6-*O*-unprotected 2-azido-2-deoxyglucoside **1** was carried out following a known, efficient, five-step procedure[19]. Treatment of **1** with trityl chloride in pyridine afforded the 6-*O*-trityl derivative **2** which gave, with allyl bromide in the presence of NaH, the fully protected compound **3** possessing the desired selective accessibility to all positions. Detritylation of **3** with Et_2O–BF_3 methanol[20] furnished the 6-hydroxy derivative **4**, which was transformed with trifluoromethanesulfonic anhydride (Tf_2O) in pyridine into the trifluoromethanesulfonate (triflate) **5**, a useful alkylating agent for the glucosamine disaccharide synthesis via anomeric *O*-alkylation. Similarly from **1**, via a known reaction sequence, triflate **6** was obtained[18]. However, direct trifluoromethanesulfonylation of **1** was achieved with Tf_2O in pyridine, to furnish the 4-*O*-unprotected triflate **7**. Thus, compounds **5–7** were available as **C** and/or **D** building blocks. 1-*O*-Deprotection of the 1-*O*-silylated compound **3** with tetrabutylammonium fluoride (TBAF) afforded the 1-*O*-unprotected compound **8**, useful as a **C** building block.



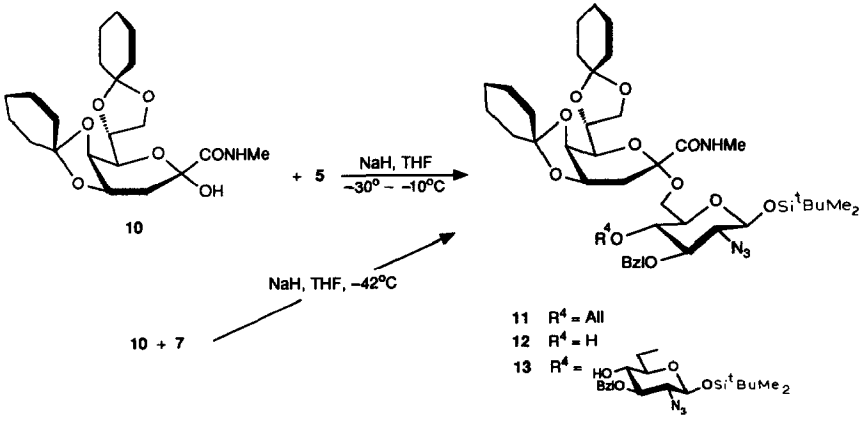
Scheme 2



Scheme 3

Reaction of **8** with triflate **6** (Scheme 3) in tetrahydrofuran (THF) in the presence of NaH as base at −30 to −10°C afforded mainly the α-linked disaccharide **9α** (**9α** : **9β** ≈ 3 : 1, 66% yield) as indicated by the ^{1}H NMR data. Reactions at higher temperatures, which generally favor formation of the equatorial product[16], led, for instance at room temperature, to a 1 : 1 ratio of **9α,β**, but in only 40% yield due to partial decomposition of **6**. Therefore, as building block **B**, the known Kdo-derivative **10**[17,18,21], which prefers α-product formation in anomeric *O*-alkylation, was reacted with triflate **5** in THF in the presence of NaH as base at −30 to −10°C, thus providing exclusively the desired α-(2 → 6)-linked disaccharide **11** in 56% yield (Scheme 4). Reaction of Kdo-derivative **10** with the 4-*O*-unprotected triflate **7** at −42°C afforded directly the α-linked disaccharide **12**, thus exhibiting that anomeric *O*-alkylation is not only successful with partially *O*-protected alkylating agent acceptors[15,16] but also with partially *O*-protected alkylating agents. When this reaction was carried out at −30°C, some *O*-alkylation of the unprotected 4-O-atom in **12** was observed, thus furnishing compound **13** as a byproduct. The anomeric configuration of disaccharides **11**–**13** could be assigned by comparison of their ^{1}H NMR data with those of related compounds[17,18] and by the subsequent transformations of **12**.

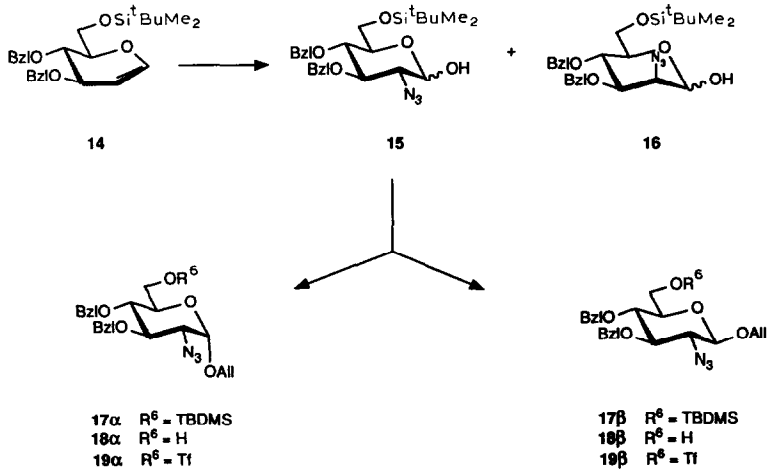
The direct access to the 4-*O*-unprotected disaccharide **12** allowed the valuable *O*-allyl protecting group, employed in the synthesis of disaccharide **11**, to be used



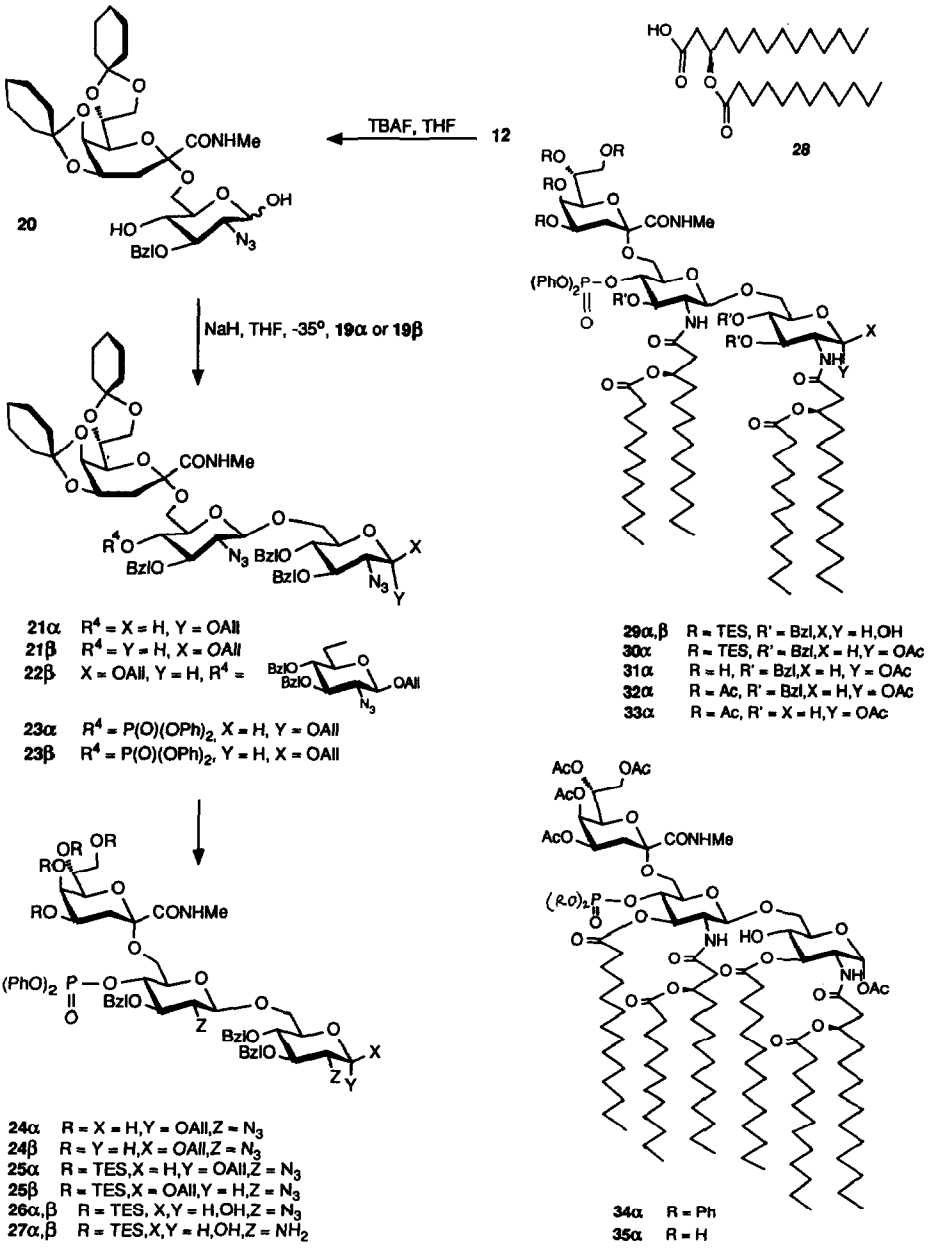
Scheme 4

at other positions. Therefore, for the anomeric oxygen of the terminal carbohydrate moiety of the desired trisaccharide, *O*-allyl protection was chosen because removal of *O*-silyl groups at this position proved to be less satisfactory in the presence of *O*-linked fatty acyl residues[22]. Accordingly, the readily available D-glucal derivative **14**[23] was employed in the azidonitration reaction[24], to furnish, after nitrate cleavage, the 2-azidoglucose derivative **15** and the 2-azidomannose derivative **16**, respectively, in a 5:1 ratio (60% yield) (Scheme 5). Anomeric *O*-allyl protection in **15** was performed via anomeric *O*-alkylation with allyl bromide–NaH, affording a 1:1 mixture of allyl glycosides **17α,β** (74%) which was separated by chromatography. Each of the two compounds was treated with tetrabutylammonium fluoride (TBAF) in THF for 6-*O*-desilylation, furnishing the 6-*O*-unprotected derivatives **18α** and **18β**. Their reaction with $(CF_3SO_2)_2O$ in pyridine afforded the 6-triflates **19α** and **19β**, respectively, as alkylating agents (building block **D**) in the anomeric *O*-alkylation. Thus, disaccharide **12** was treated with TBAF in THF, yielding the 1-*O*-unprotected derivative **20** (Scheme 6). Reaction of **20** with **19α** or **19β** in THF in the presence of NaH at −35°C afforded exclusively trisaccharides **21α** and **21β**, respectively, in high yields (**21α**, 78%, **21β**, 77%), which had the required β-(1 → 6)-connection in the glucosamine disaccharide moiety as indicated by their ^{1}H NMR data. At higher reaction temperatures, alkylation of the 4′-OH group was again observed, leading, for example with **19β** as alkylating agent, to **22β** as a byproduct.

Direct phosphorylation of trisaccharides **21α** and **21β** at the 4′-OH group was readily accomplished with diphenyl phosphorochloridate in the presence of triethylamine, furnishing the phosphate derivatives **23α** and **23β**, respectively. In the next step, the acid-sensitive cyclohexylidene groups were removed with *p*-toluenesulfonic acid as catalyst, yielding **24α** and **24β**, and triethylsilyl (TES) groups were then introduced with TES-Cl–imidazole, providing compounds **25α** and **25β**,



Scheme 5



Scheme 6

respectively. *O*-Allyl deprotection in the presence of the azido group was achieved with the iridium complex proposed by Baudry et al.[25,26] followed by HgO–$HgCl_2$ treatment in acetone–water[26,27]; thus, from **25α** and **25β**, severally, a 1-*O*-unprotected anomeric mixture of trisaccharide **26α,β** was obtained. Reduction of the

azido groups in **26α,β** was performed with hydrogen sulfide in pyridine–water, yielding amino derivatives **27α, β**, which were immediately treated with (*R*)-3-dodecanoyloxytetradecanoic acid[7] (**28**) in the presence of dicyclohexylcarbodiimide (DCC). The resulting *N*-acylated product **29α, β** gave, upon *O*-acetylation with acetic anhydride in pyridine, exclusively the α anomer **30α**.

For the introduction of the 3-*O*- and 3′-*O*-tetradecanoyl groups in the next step, hydrogenolytic *O*-debenzylation of **30α** was investigated. However, under various hydrogenolysis conditions, the TES protecting groups were removed selectively, thus providing **31α** in high yield; subsequent *O*-acetylation with acetic anhydride in pyridine led to **32α**. The *O*-benzyl groups could then be readily removed under hydrogenolytic conditions, with palladium on charcoal as catalyst, furnishing **33α** in high yield. Because of the low reactivity of glucose 4-hydroxyl groups, selective transformation of **33α**, with two equivalents of tetradecanoyl chloride in the presence of pyridine, into the 3,3′-di-*O*-tetradecanoyl derivative **34α** was expected. This was proved by a detailed ^{1}H NMR analysis (COSY) of **34α**, providing the range of hydrogen shifts and H–H-coupling constants, which reveal that the 3-O and 3′-O positions are acylated (δ, H-3: 4.99–5.21; H-3′: 5.26–5.34), but not 4-O (δ, H-4: 3.44–4.01). The removal of the *O*-phenyl protecting groups from the phosphate moiety was accomplished by hydrogenolysis in the presence of Adams' catalyst, affording compound **35α** *, which was purified by chromatography and characterized by FAB mass spectrometry †. Selective *O*-deacetylation of this product with sodium methoxide in methanol should be possible; however, the highly amphiphilic character of the material obtained precluded full characterization.

EXPERIMENTAL

General methods.—Solvents were purified in the usual way; light petroleum: boiling range 35–70°C. Melting points (uncorrected): metal block. ^{1}H NMR spectra: Jeol JNM-GX 400, Bruker AC 250; internal standard, tetramethylsilane. ^{31}P NMR spectra: Jeol JNM-GX 400; external standard, H_3PO_4. Column chromatography: Merck Silica Gel 60, 0.063–0.200 mm. Flash chromatography: Merck Silica Gel 60 (0.040–0.063 mm). Medium-pressure liquid chromatography (MPLC): Merck Silica Gel, LiChroprep Si 60, 15–25 μm. TLC: Merck plates, Silica Gel 60 F_{254}, layer thickness 0.2 mm; detection by treatment with a solution of 15% H_2SO_4 or a solution of ammonium molybdate (20 g) and cerium(IV) sulfate (0.4 mL) in 10% H_2SO_4 (400 mL) followed by heating at 120°C. Optical rotations: Perkin–Elmer polarimeter 241/MS; 1-dm cell. Mass spectra: Finnigan MAT 312/AMD-5000.

tert-*Butyldimethylsilyl 2-azido-3-*O*-benzyl-2-deoxy-6-*O*-trityl-β-*D*-glucopyranoside*

* For a structural analog also obtained by chemical synthesis, see ref. 14.

† We are grateful to Professor M. Przybylski for performing an FABMS analysis of **35α**.

(**2**).—To a solution of **1**[19] (10.4 g, 24.5 mmol) in dry pyridine (100 mL) was added chlorotriphenylmethane (8.9 g, 31.8 mmol). After stirring for 4 days at room temperature, the solvent was evaporated in vacuo. The residue was dissolved in 9:1 light petroleum–EtOAc and filtered. The filtrate was evaporated to dryness and then twice coevaporated with toluene. Purification on a short column of silica gel (9:1 light petroleum–EtOAc) yielded **2** (16.0 g, 98%) as a colorless oil; $[\alpha]_{589}^{22}$ −23° (*c* 1, $CHCl_3$); R_f 0.36 (9:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (400 MHz), δ 0.19, 0.20 [2 s, 6 H, $Si(CH_3)_2$], 0.96 [s, 9 H, $SiC(CH_3)$], 2.24 (d, 1 H, *J* 2.7 Hz, OH), 3.17 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.0$ Hz, H-3), 3.25–3.41 (m, 4 H, H-2, 5,6a,6b), 3.5 (ddd, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 4.53 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.73, 4.90 (2 d, 2 H, J_{gem} 11.2 Hz, $CH_2C_6H_5$), 7.21–7.46 [m, 20 H, $C(C_6H_5)_3$, C_6H_5]. Anal. Calcd for $C_{38}H_{45}N_3O_5Si$: C, 70.02; H, 6.96; N, 6.40. Found: C, 69.97; H, 6.97; N, 6.56.

tert-*Butyldimethylsilyl 4-O-allyl-2-azido-3-O-benzyl-2-deoxy-6-O-trityl-β-*D*-glucopyranoside* (**3**).—To a solution of **2** (960 mg, 1.47 mmol) and allyl bromide (220 mg, 1.80 mmol) in dry DMF (15 mL) was added at −25°C NaH (60 mg, 2.50 mmol). After stirring for 30 min, the mixture was filtered through Celite. The filtrate was poured into ice–water and extracted with diethyl ether. The combined organic layers were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography (9:1 light petroleum–EtOAc) yielded **3** (580 mg, 57%) as a colourless oil; $[\alpha]_{589}^{22}$ −14° (*c* 1, $CHCl_3$); R_f 0.53 (9:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 0.23, 0.27 [2 s, 6 H, $Si(CH_3)_2$], 1.00 [s, 9 H, $SiC(CH_3)$], 3.14 (dd, 1 H, $J_{5,6a}$ 4.4, J_{gem} 9.9 Hz, H-6a), 3.27 (dd, 1 H, $J_{3,4} = J_{4,5}$ −9.0 Hz, H-4), 3.32–3.46 (m, 3 H, H-2,5,6b), 3.55 (dd, 1 H, $J_{2,3}$ 9.0 Hz, H-3), 3.73 (dd, *J* 1 H, *J* 5.7, 12.0 Hz, $CH_2CH{=}CH_2$), 4.07 (dd, 1 H, *J* 5.9, 12.0 Hz, $CH_2CH{=}CH_2$), 4.53 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.82, 4.74 (2 d, 2 H, J_{gem} 10.7 Hz, 2 $CH_2C_6H_5$), 4.91–4.98 (m, 2 H, 2 $CH_2CH{=}CH_2$), 5.42–5.57 (m, 1 H, $CH_2CH{=}CH_2$), 7.18–7.52 [m, 20 H, $C(C_6H_5)_3$, C_6H_5]. Anal. Calcd for $C_{41}H_{49}N_3O_5Si$ (691.94): C, 71.17; H, 7.14; N, 6.07. Found: C, 71.04; H, 7.16; N, 6.27.

tert-*Butyldimethylsilyl 4-O-allyl-2-azido-3-O-benzyl-2-deoxy-β-*D*-glucopyranoside* (**4**).—To a solution of **3** (770 mg, 1.09 mmol) in CH_2Cl_2 (10 mL) were added MeOH (1 mL) and 0.2 M Et_2O–BF_3 in CH_2Cl_2 (0.5 mL). After stirring for 30 min at room temperature, the mixture was poured into aq $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated. Flash chromatography (17:3 light petroleum–EtOAc) yielded **4** (350 mg, 70%) as a colourless oil, $[\alpha]_{589}^{22}$ −11° (*c* 1, $CHCl_3$); R_f 0.27 (17:3 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 0.15, 0.16 [2 s, 6 H, $Si(CH_3)_2$], 0.94 [s, 9 H, $SiC(CH_3)_3$], 1.89 (dd, 1 H, *J* 5.8, 7.6 Hz, OH), 3.23–3.47 (m, 4 H, H-2,3,4,5), 3.71 (ddd, 1 H, $J_{5,6a}$ 4.4, $J_{6a,OH}$ 7.6, J_{gem} 12.1 Hz, H-6a), 3.85 (ddd, 1 H, $J_{5,6b}$ 3.0, $J_{6b,OH}$ 5.8 Hz, H-6b), 4.11 (dd, 1 H, *J* 5.8, 12.4 Hz, $CH_2CH{=}CH_2$), 4.31 (dd, 1 H, *J* 5.5, 12.4 Hz, $CH_2CH{=}CH_2$), 4.53 (d, 1 H, $J_{1,2}$ 7.1 Hz, H-1), 4.77, 4.85 (2 d, 2 H, J_{gem} 10.7 Hz, 2 $CH_2C_6H_5$), 5.18 (dd, 1 H, *J* 1.5, 10.4 Hz, $CH_2CH{=}CH_2$), 5.28 (dd, 1 H, *J* 1.5, 17.1 Hz, $CH_2CH{=}CH_2$), 5.81–5.96 (m, 1 H, $CH_2CH{=}CH_2$), 7.25–7.57 (m, 5

H, C_6H_5). Anal. Calcd for $C_{22}H_{35}N_3O_5Si$: C, 58.77; H, 7.85; N, 9.35. Found: C, 58.86; H, 7.86; N, 9.36.

tert-*Butyldimethylsilyl 4-O-allyl-2-azido-3-O-benzyl-2-deoxy-6-O-trifluoromethanesulfonyl-β-*D-*galactopyranoside* (**5**).—To a solution of **4** (370 mg, 0.82 mmol) and dry pyridine (100 mg, 1.20 mmol) in dry CH_2Cl_2 (5 mL) at −20°C under N_2 was added dropwise a solution of $(CF_3SO_2)_2O$ (255 mg, 0.90 mmol) in CH_2Cl_2 (2 mL). After stirring for 20 min at −20°C, the solvents were evaporated. Purification on a short column of silica gel (9:1 light petroleum–EtOAc) yielded **5** (440 mg, 92%) as a colourless oil; R_f 0.44 (9:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^{1}H (250 MHz), δ 0.15, 0.16 [2 s, 6 H, $Si(CH_3)_2$], 0.93 [s, 9 H, $SiC(CH_3)_3$], 3.27–3.37 (m, 3 H, H-2,3,4), 3.51–3.68 (m, 1 H, H-5), 4.06 (ddd, 1 H, *J* 1.3, 6.3, 12.4 Hz, $CH_2CH{=}CH_2$), 4.34 (ddd, 1 H, *J* 1.4, 5.4, 12.4 Hz, $CH_2CH{=}CH_2$), 4.53 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 4.55 (dd, 1 H, J_{gem} 10.6, $J_{5,6}$ 5.7 Hz, H-6a), 4.67 (dd, 1 H, $J_{5,6b}$ 2.1 Hz, H-6b), 4.74, 4.88 (2 d, 2 H, J_{gem} 10.8 Hz, 2 $CH_2C_6H_5$), 5.19 (1 d, 1 H, *J* 1.6, 10.4 Hz, $CH_2CH{=}CH_2$), 5.24 (dd, *J* 1.6, 12.3 Hz, 1 H, $CH_2CH{=}CH_2$), 5.77–5.92 (m, 1 H, $CH_2CH{=}CH_2$), 7.28–7.38 (m, 5 H, C_6H_5). A correct elemental analysis could not be obtained.

tert-*Butyldimethylsilyl 2-azido-3-O-benzyl-2-deoxy-6-O-trifluoromethanesulfonyl-β-*D-*glucopyranoside* (**7**).—To a solution of **1** (2.0 g, 4.88 mmol) and dry pyridine (580 mg, 7.3 mmol) in dry CH_2Cl_2 (25 mL) at −20°C under N_2 was added dropwise a solution of trifluoromethanesulfonic anhydride (1.37 g, 4.8 mmol) in dry CH_2Cl_2 (5 mL). Immediately after the end of the addition, the mixture was concentrated. Purification on a short column of silica gel (8:2 light petroleum–EtOAc) yielded **7** (2.4 g, 90%) as a colourless oil; R_f 0.43 (8:2 light petroleum–EtOAc). NMR data ($CDCl_3$): ^{1}H (250 MHz), δ 0.16, 0.17 [2 s, 6 H, $Si(CH_3)_2$], 0.94 [s, 9 H, $SiC(CH_3)_3$], 3.18 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 8.3 Hz, H-3), 3.34 (dd, 1 H, $J_{1,2}$ 7.6, $J_{2,3}$ 9.9 Hz, H-2), 3.43 (dd, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.53 (ddd, 1 H, $J_{5,6a}$ 6.0, $J_{5,6b}$ 1.8 Hz, H-5), 4.54 (dd, 1 H, J_{gem} 10.6 Hz, H-6a), 4.57 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.63 (d, 1 H, J_{gem} 11.6 Hz, $CH_2C_6H_5$), 4.71 (dd, 1 H, H-6b), 5.00 (d, 1 H, J_{gem} 11.6 Hz, $CH_2C_6H_5$), 7.31–7.43 (m, 5 H, C_6H_5). A correct elemental analysis could not be obtained.

*4-O-Allyl-2-azido-3-O-benzyl-2-deoxy-6-O-trityl-*D-*glucopyranose* (**8**).—To a solution of **3** (400 mg, 0.56 mmol) in dry THF (5 mL) at 0°C was added dropwise 1 M tetrabutylammonium fluoride in THF (0.7 mL). The reaction was completed at the end of TBAF addition. The mixture was poured into ice-cold aq $NaHCO_3$ and then extracted three times with ether. The organic layers were combined, dried (Na_2SO_4), and concentrated. Purification by flash chromatography yielded **8** (260 mg, 80%) as a colourless oil, $[\alpha]_{589}^{22}$ +32° (*c* 1, $CHCl_3$); R_f 0.32 (8:2 light petroleum–EtOAc). NMR data ($CDCl_3$): ^{1}H (250 MHz), δ 2.92–3.98 (m, 8 H), 4.08–4.13 (m, 1 H, $CH_2CH{=}CH_2$), 4.54 (d, 0.4 H, $J_{1,2}$ 7.6 Hz, H-1β), 4.76–5.02 (m, 4 H, 2 $CH_2C_6H_5$, 2 $CH_2CH{=}CH_2$), 5.37 (bs, 0.6 H, H-1α), 5.50–5.61 (m, 1 H, $CH_2CH{=}CH_2$), 7.20–7.48 (m, 20 H, $C(C_6H_5)_3$, C_6H_5). Anal. Calcd for $C_{35}H_{35}N_3O_5$: C, 72.77; H, 6.11; N, 7.27. Found: C, 72.43; H, 6.30; N, 7.18.

tert-*Butyldimethylsilyl 6-O-(4-O-allyl-2-azido-3-O-benzyl-6-O-trityl-α-D-glucopyranosyl)-2-azido-3,4-di-O-benzyl-2-deoxy-β-D-glucopyranoside* (**9α**) *and* tert-*butyldimethylsilyl 6-O-(4-O-allyl-2-azido-3-O-benzyl-6-O-trityl-β-D-glucopyranosyl)-2-azido-3,4-di-O-benzyl-2-deoxy-β-D-glucopyranoside* (**9β**).—To a solution of **8** (700 mg, 1.20 mmol) in dry THF (80 mL) was added NaH (40 mg, 1.50 mmol) at −30°C under N_2. After 10 min, a solution of *tert*-butyldimethylsilyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-6-*O*-trifluoromethanesulfonyl-β-D-glucopyranoside[18] (**6**; 700 mg, 1.10 mmol) was added. The mixture was stirred for 12 h, then the temperature was raised to −10°C. After an additional 30 h, MeOH (0.5 mL) was added and the mixture poured into ice–water. After extraction with ether, the organic layer was dried ($MgSO_4$) and the solvent evaporated. Flash chromatography (9:1 light petroleum–EtOAc) yielded **9α** (610 mg, 52%) as a colourless oil, $[\alpha]_{589}^{22}$ +56° (*c* 1, $CHCl_3$); R_f 0.36 (9:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 0.15, 0.17 [2 s, 6 H, $Si(CH_3)_2$], 0.91 [s, 9 H, $SiC(CH_3)_3$], 3.03 (dd, 1 H, J_{gem} 10.1, $J_{5,6a}$ 3.5 Hz, H-6a), 3.30–3.79 (m, 11 H), 3.88 (dd, 1 H, $J_{2',3'} = J_{3',4'} = 9.3$ Hz, H-3′), 4.09 (dd, 1 H, *J* 5.7, 12.3 Hz, $CH_2CH{=}CH_2$), 4.52 (1 H, $J_{1,2}$ 6.8 Hz, H-1), 4.57–4.97 (m, 8 H, $CH_2C_6H_5$, 2 $CH_2CH{=}CH_2$), 5.01 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1′), 5.46–5.61 (m, 1 H, $CH_2CH{=}CH_2$), 7.19–7.46 (m, 30 H, 6 C_6H_5). Anal. Calcd for $C_{61}H_{70}N_6O_9Si$: C, 69.16; H, 6.65; N, 7.93. Found: C, 68.86; H, 6.74; N, 8.00.

Further elution yielded **9β** (140 mg, 14%) as a colourless oil; $[\alpha]_{589}^{22}$ −4° (*c* 1, $CHCl_3$); R_f 0.34 (9:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 0.20 (s, 6 H, $Si(CH_3)_2$), 0.95, 0.96 [2 s, 9H, $SiC(CH_3)_3$], 3.10 (dd, 1 H, $J_{5,6a}$ 2.8, J_{gem} 9.9 Hz, H-6a), 3.25–3.75 (m, 10 H), 3.85 (dd, 1 H, *J* 5.8, 11.3 Hz, $CH_2CH{=}CH_2$), 4.12 (dd, 1 H, *J* 6.8, 12.8 Hz, $CH_2CH{=}CH_2$), 4.21 (dd, 1 H, J_{gem} 11.1, $J_{5',6'a} < 1$ Hz, H-6′), 4.25 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1′), 4.58 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.68–5.04 (m, 8 H, 6 $CH_2C_6H_5$, 2 $CH_2CH{=}CH_2$), 5.51–5.67 (m, 1 H, $CH_2CH{=}CH_2$), 7.03–7.51 (m, 30 H, 6 C_6H_5). Anal. Calcd for $C_{61}H_{70}N_6O_9Si$: C, 69.16; H, 6.65; N, 7.93. Found: C, 69.13; H, 6.81; N, 8.08.

tert-*Butyldimethylsilyl 4-O-allyl-2-azido-3-O-benzyl-2-deoxy-6-O-(4,5 : 7,8-di-O-cyclohexylidene-3-deoxy-*N*-methyl-α-D-manno-2-octulopyranosylonamide)-β-D-glucopyranoside* (**11**).—To a solution of **10** (225 mg, 0.54 mmol) in dry THF (50 mL) was added NaH (32 mg, 1.33 mmol) at −30°C under N_2. After 10 min, a solution of **5** (350 mg, 0.60 mmol) in THF (3 mL) was added and then the temperature was raised to −10°C. Stirring was continued for 14 h; after addition of MeOH (0.5 mL), the mixture was poured into ice–water and extracted with diethyl ether (4 × 10 mL). The organic layers were combined and dried ($MgSO_4$), and then solvents evaporated. Purification by flash chromatography (7:3 light petroleum–EtOAc) yielded **11** (260 mg, 56%) as a colourless oil; $[\alpha]_{589}^{22}$ +29° (*c* 1, $CHCl_3$); R_f 0.28 (7:3 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 0.16 [s, 6 H, $Si(CH_3)_2$], 0.93 [s, 9 H, $SiC(CH_3)_3$], 1.26–1.65 (m, 20 H, 2 C_6H_5), 1.94 (dd, 1 H, J_{gem} 15.1, $J_{3'ax,4'}$ 4.0 Hz, H-3′*ax*), 2.48 (dd, 1 H, $J_{3'eq,4'}$ 5.1 Hz, H-3′*eq*), 2.81 (d, 3 H, *J* 4.9 Hz, NCH_3), 3.03–3.12 (m, 1 H, H-4a), 3.34–3.22 (m, 2 H, H-2,3),

3.55–3.46 (m, 3 H, H-5,6a,6b), 3.78 (dd, 1 H, $J_{5',6'}$ 2.0, $J_{6',7'}$ 6.0 Hz, H-6'), 3.98 (dd, 1 H, J 5.8, 12.3 Hz, $CH_2CH{=}CH_2$), 4.00 (dd, 1 H, J_{gem} 8.5, $J_{7',8'a}$ 6.0 Hz, H-8'a), 4.11 (dd, 1 H, $J_{7',8'b}$ 6.0 Hz, H-8'b), 4.18 (dd, 1 H, $J_{4',5'}$, 7.0 Hz, H-5'), 4.24 (dd, 1 H, J 5.3, 12.6 Hz, $CH_2CH{=}CH_2$), 4.35 (ddd, 1 H, H-7b), 4.42–4.49 (m, 1 H, H-4'), 4.48 (d, $J_{1,2}$ 7.3 Hz, 1 H, H-1), 4.73, 4.83 (2 d, 2 H, J_{gem} 10.8 Hz, 2 $CH_2C_6H_5$), 5.12 (dd, 1 H, J 1.5, 10.4 Hz, $CH_2CH{=}CH_2$), 5.21 (dd, 1 H, J 1.6, 17.2 Hz, $CH_2CH{=}CH_2$), 5.73–5.86 (m, 1 H, $CH_2CH{=}CH_2$), 6.73 (q, 1 H, J 4.9 Hz, NH), 7.26–7.39 (m, 5 H, C_6H_5). Anal. Calcd for $C_{43}H_{66}N_4O_{11}Si$: C, 61.25; H, 7.90; N, 6.64. Found: C, 61.29; H, 7.98; N, 6.68.

tert-*Butyldimethylsilyl 2-azido-3-*O*-benzyl-2-deoxy-6-*O*-(4,5 : 7,8-di-*O*-cyclohexylidene-3-deoxy-*N*-methyl-α-*D*-manno-2-octulopyranosylonamide)-β-*D*-glucopyranoside* (**12**).—Under an N_2 atmosphere, **10** (1.50 g, 3.60 mmol) was dissolved in dry THF (30 mL). At −42°C, NaH (200 mg, 8.20 mmol) and, 10 min later, a solution of **7** (2.0 g, 3.67 mmol) in dry THF (5 mL) were added. The mixture was stirred for 8 h, then MeOH (0.5 mL) was added and the mixture poured into ice–water. After extraction with diethyl ether (4 × 30 mL), the combined organic layers were dried ($MgSO_4$) and concentrated. Flash chromatography (6:4 light petroleum–EtOAc) yielded **12** (1.81 g, 62%) as a colourless oil; $[\alpha]_{589}^{22}$ +21°C (*c* 1, $CHCl_3$); R_f 0.33 (6:4 light petroleum–EtOAc). NMR data ($CDCl_3$): ^{1}H (250 MHz), δ 0.13, 0.14 [2 s, 6 H, $Si(CH_3)_2$], 0.92 [s, 9 H, $SiC(CH_3)_3$], 1.17–1.59 (m, 20 H, 2 C_6H_{10}), 1.88 (dd, 1 H, J_{gem} 15.8, $J_{3'ax,4'}$ 3.5 Hz, H-3'*ax*), 2.57 (dd, 1 H, $J_{3'eq,4'}$ 3.9 Hz, H-3'*eq*), 2.84 (d, 3 H, J 5.0 Hz, NCH_3), 3.20–3.44 (m, 4 H, H-2,4,6a,6b), 3.60 (dd, $J_{2,3} = J_{3,4} = 8.8$ Hz, 1 H, H-3), 3.71 (m, 1 H, H-5), 3.82 (dd, 1 H, $J_{5',6'}$ 1.9, $J_{6',7'}$, 5.3 Hz, H-6'), 3.99 (dd, 1 H, $J_{7',8'a}$ 5.8, J_{gem} 8.6 Hz, H-8'a), 4.11 (dd, 1 H, $J_{7',8'b}$ 5.8 Hz, H-8'b), 4.21 (dd, 1 H, $J_{4',5'}$ 7.5 Hz, H-5'), 4.35 (ddd, 1 H, H-7'), 4.48 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.47 (ddd, 1 H, H-4'), 4.80 (d, 1 H, J_{gem} 11.1 Hz, $CH_2C_6H_5$), 5.00 (d, 1 H, J_{gem} 11.1 Hz, $CH_2C_6H_5$), 6.83 (q, 1 H, J 5.0 Hz, NH), 7.26–7.45 (m, 5 H, C_6H_5). Anal. Calcd for $C_{40}H_{62}N_4O_{11}Si$ (803.04): C, 59.83; H, 7.78; N, 6.98. Found: C, 59.55; H, 7.95; N, 6.82.

tert-*Butyldimethylsilyl 2-azido-3-*O*-benzyl-4-*O*-(*tert-*butyldimethylsilyl 2-azido-3-*O*-benzyl-2,6-dideoxy-β-*D*-glucopyranosid-6-yl)-2-deoxy-6-*O*-(4,5 : 7,8-di-*O*-cyclohexylidene-3-deoxy-*N*-methyl-α-*D*-manno-2-octulopyranosylonamide)-β-*D*-glucopyranoside* (**13**).—To a solution of **10** (325 mg, 0.78 mmol) in dry THF (8 mL) under N_2 was added NaH (45 mg, 1.09 mmol) at −30 °C. After 30 min, a solution of **7** (470 mg, 0.86 mmol) was added. Stirring was continued for 5 h, then MeOH (0.5 ml) was added dropwise, and the mixture was poured into ice–water and extracted three times with ether. The combined organic layers were dried ($MgSO_4$) and then concentrated under reduced pressure. Flash chromatography (6 : 4 light petroleum–EtOAc) yielded **12** (198 mg, 31%) and **13** (100 mg, 10%) as colourless oils. NMR data ($CDCl_3$): ^{1}H (250 MHz), δ 0.09, 0.13, 0.16 [3 s, 12 H, $Si(CH_3)_2$], 0.89, 0.93 [2 s, 18 H, 2 $SiC(CH_3)_3$], 1.20–1.60 (m, 20 H, 2 C_6H_{10}), 1.90 (dd, 1 H, J_{gem} 1.53, $J_{3'ax,4'}$ 3.8 Hz, H-3'*ax*), 2.52 (d, 1 H, $J_{3'eq,4'}$ 4.7 Hz, H-3'*eq*), 2.72 (d, 3 H, J 5.0 Hz, NCH_3), 3.14–3.76 (m, 13 H), 3.93 (dd, 1 H, J_{gem} 10.7, $J_{5,6a}$ 4.9 Hz, H-6a),

3.97 (dd, 1 H, J_{gem} 8.7, $J_{7',8'a}$ 5.3 Hz, H-8'a), 4.09 (dd, 1 H, $J_{7',8'b}$ 6.3 Hz, H-8'b), 4.16 (dd, 1 H, $J_{5',6'}$ 1.8, $J_{4',5'}$ 7.1 Hz, H-5'), 4.29 (ddd, 1 H, $J_{6',7'}$ 5.9 Hz, H-7'), 4.40 (ddd, 1 H, H-4b), 4.46 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1), 4.48 (d, 1 H, $J_{1'',2''}$ 7.3 Hz, H-1''), 4.74–4.84 (m, 2 H, $CH_2C_6H_5$), 4.87 (s, 2 H, $CH_2C_6H_5$), 6.79 (q, 1 H, J 5.0 Hz, NH), 7.26–7.44 (m, 10 H, 2 C_6H_5).

2-Azido-3,4-di-O-benzyl-6-O-tert-butyldimethylsilyl-2-deoxy-D-glucopyranose (**15**) *and 2-azido-3,4-di-O-benzyl-6-O-tert-butyldimethylsilyl-2-deoxy-D-mannopyranose* (**16**).—A solution of **14** (35.0 g, 79.0 mmol) in dry MeCN (1000 mL) was cooled to −40°C under an inert gas atmosphere. Then a mixture of carefully dried and powdered ceric ammonium nitrate (130 g, 237 mmol) and sodium azide (7.7 g, 118 mmol) was added. The suspension was stirred vigorously for 24 h and then poured into 2:1 ice–water–diethyl ether (300 mL). The aqueous phase was separated and extracted with ether (2 × 200 mL). The combined organic layers were neutralized with aq $NaHCO_3$ and concentrated. The residue was dissolved in dioxane (200 mL) and then a solution of $NaNO_2$ (27 g, 391 mmol) in water (50 mL) was added. The mixture was heated to 75°C for 8 h, then poured onto ice, and extracted four times with diethyl ether. The combined organic layers were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography (17:3 light petroleum–EtOAc) yielded **15** (18.3 g, 51%) as a colourless oil; $[\alpha]_{589}^{22}$ +6°C (*c* 1, $CHCl_3$); R_f 0.35 (17:3 light petroleum–EtOAc). NMR data ($CDCl_3$): ^{1}H (250 MHz), δ 0.05, 0.06, 0.07, 0.08 [4 s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $SiC(CH_3)_3$], 3.08–4.05 (m, 6 H), 3.57 (d, 0.4 H, $J_{1,2}$ 7.8 Hz, H-1β), 4.65–4.93 (m, 4 H, 4 $CH_2C_6H_5$), 5.28 (d, 0.6 H, $J_{1,2}$ 3.4 Hz, H-1α), 7.25–7.39 (m, 10 H, 2 C_6H_5). Anal. Calcd for $C_{26}H_{37}N_3O_5Si$: C, 62.50; H, 7.46; N, 8.41. Found, C, 62.38; H, 7.51; N, 8.50.

Further elution yielded **16** (3.5 g, 9%) as a colourless oil; $[\alpha]_{589}^{22}$ +29° (*c* 1, $CHCl_3$); R_f 0.18 (17:3 light petroleum–EtOAc). Anal. Calcd for $C_{26}H_{37}N_3O_5Si$: C, 62.50; H, 7.46; N, 8.41. Found: C, 62.47; H, 7.52; N, 8.50.

Allyl 2-azido-3,4-di-O-benzyl-6-O-tert-butyldimethylsilyl-2-deoxy-α-D-glucopyranoside (**17α**) *and allyl 2-azido-3,4-di-O-benzyl-6-O-tert-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside* (**17β**).—To a solution of **15** (16.3 g, 32.6 mmol) in dry DMF (175 mL) was added allyl bromide (4.2 mL, 49.6 mmol) at −30°C. After addition of NaH (1.6 g, 66.6 mmol), the mixture was stirred for 6 h, then filtered through Celite, and poured into ice–water. After extraction with diethyl ether (3 × 100 mL), the combined organic phases were washed with water (200 mL), dried ($MgSO_4$), and concentrated. Separation by flash chromatography (95:5 light petroleum–EtOAc) yielded **17α** (6.4 g, 36%) as a colourless oil; $[\alpha]_{589}^{22}$ +71° (*c* 1, $CHCl_3$); R_f 0.33 (95:5 light petroleum–EtOAc). NMR data ($CDCl_3$): ^{1}H (250 MHz), δ 0.06 [s, 6 H, $Si(CH_3)_2$], 0.90 [s, 9 H, $SiC(CH_3)_3$], 3.25 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 10.2 Hz, H-2), 3.60–3.88 (m, 4 H, H-4,5,6a,6b), 3.98–4.06 (m, 2 H, H-3, $CH_2CH{=}CH_2$), 4.18 (dd, 1 H, J 5.2, 12.9 Hz, $CH_2CH{=}CH_2$), 4.07 (d, 1 H, J_{gem} 10.3 Hz, $CH_2C_6H_5$), 4.86 (d, 1 H, J_{gem} 10.3 Hz, $CH_2C_6H_5$), 4.87 (m, 2 H, 2 $CH_2C_6H_5$), 4.93 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.22 (dd, 1 H, J 1.6, 10.4 Hz,

$CH_2CH{=}CH_2$), 5.32 (dd, 1 H, J 1.6, 17.3 Hz, $CH_2CH{=}CH_2$), 5.84–6.00 (m, 1 H, $CH_2CH{=}CH_2$), 7.24–7.40 (m, 10 H, 2 C_6H_5). Anal. Calcd for $C_{29}H_{41}N_3O_5Si$: C, 64.53; H, 7.66; N, 7.78. Found: C, 64.42; H, 7.74; N, 7.50.

Further elution yielded **17β** (6.8 g, 39%) as a colourless oil; $[\alpha]_{589}^{22}$ −28° (*c* 1, $CHCl_3$); R_f 0.33 (95:5 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 0.06, 0.07 [2 s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $SiC(CH_3)_3$], 3.24 (ddd, 1 H, $J_{4,5} = J_{5,6a} = 3.0$ Hz, H-5), 3.36–3.47 (m, 2 H, H-2,3), 3.59–3.66 (m, 1 H, H-4), 3.83–3.84 (m, 2 H, H-6a,6b), 4.14 (dd, 1 H, J 6.1, 12.9 Hz, $CH_2CH{=}CH_2$), 4.30 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.35 (dd, 1 H, J 5.1, 12.9 Hz, $CH_2CH{=}CH_2$), 4.68 (d, 1 H, J_{gem} 10.6 Hz, $CH_2C_6H_5$), 4.80 (d, 1 H, J_{gem} 7.1 Hz, $CH_2C_6H_5$), 4.82 (d, 1 H, J_{gem} 7.1 Hz, $CH_2C_6H_5$), 4.86 (d, 1 H, J_{gem} 10.6 Hz, $CH_2C_6H_5$), 5.22 (dd, 1 H, J 1.6, 10.4 Hz, $CH_2CH{=}CH_2$), 5.33 (dd, 1 H, J 1.6, 17.2 Hz, $CH_2CH{=}CH_2$), 5.86–6.03 (m, 1 H, $CH_2CH{=}CH_2$), 7.25–7.39 (m, 10 H, 2 C_6H_5). Anal. Calcd for $C_{29}H_{41}N_3O_5Si$: C, 64.53; H, 7.66; N, 7.78. Found: C, 64.54; H, 7.75; N, 8.00.

*Allyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (**18α**).—A solution of **17α** (400 mg, 0.74 mmol) in dry THF (3 mL) was cooled to −10°C in an N_2 atmosphere. Then a mixture of 1 M acetic acid (1 mL) and 1 M TBAF (1.5 mL) in THF was added dropwise. The mixture was warmed to ambient temperature within 1 h and then poured into ice–water (10 mL). After extraction with diethyl ether (4 × 5 mL), the organic layers were combined, dried ($MGSO_4$), and concentrated in vacuo. Purification by flash chromatography (7:3 light petroleum–EtOAc) yielded **18α** (280 mg, 93%) as a colourless oil; $[\alpha]_{589}^{22}$ +84°C (*c* 1, $CHCl_3$); R_f 0.24 (7:3 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 3.36 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 10.2 Hz, H-2), 3.58–3.67 (m, 1 H, H-4), 3.69–3.84 (m, 3 H, H-5,6a,6b), 3.99–4.09 (m, 2 H, H-3, $CH_2CH{=}CH_2$), 4.19 (ddd, 1 H, J 1.4, 5.3, 13.0 Hz, $CH_2CH{=}CH_2$), 4.67 (d, 1 H, J_{gem} 11.0 Hz, $CH_2C_6H_5$), 4.85–4.89 (m, 3 H, 3 $CH_2C_6H_5$), 4.95 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.23 (dd, 1 H, J 1.6, 10.4 Hz, $CH_2CH{=}CH_2$), 5.34 (dd, 1 H, J 1.6, 17.3 Hz, $CH_2CH{=}CH_2$), 5.84–5.99 (m, 1 H, $CH_2CH{=}CH_2$), 7.25–7.41 (m, 10 H, 2 C_6H_5). Anal. calcd for $C_{23}H_{27}N_3O_5$: C, 64.93; H, 6.40; N, 9.88. Found: C, 64.95; H, 6.42; N, 9.50.

*Allyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-β-*D*-glucopyranoside* (**18β**).—Compound **18β** was prepared as described for **18α**: **16** (380 mg, 0.70 mmol) was dissolved in dry THF (3 mL) and treated with 1 M TBAF (1.5 mL) and 1 M acetic acid in THF (1 mL), to yield **18β** (280 mg, 89%) as colourless crystals; mp 71.5–71.8°C (from light petroleum–EtOAc); $[\alpha]_{589}^{22}$ −38° (*c* 1, $CHCl_3$); R_f 0.33 (7:3 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 3.33 (ddd, 1 H, $J_{4,5}$ 8.3, $J_{5,6a}$ 2.7, $J_{5,6b}$ 4.4 Hz, H-5), 3.38–3.49 (m, 2 H, H-2,3), 3.55–3.63 (m, 1 H, H-4), 3.71 (dd, 1 H, J_{gem} 12.1 Hz, H-6a), 3.85 (dd, 1 H, H-6b), 4.15 (dd, 1 H, J 6.0, 12.8 Hz, $CH_2CH{=}CH_2$), 4.38 (dd, 1 H, J 5.3, 12.8 Hz, $CH_2CH{=}CH_2$), 4.36 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.65, 4.81, 4.90 (4 d, 4 H, J_{gem} 10.9 Hz, 4 $CH_2C_6H_5$), 5.24 (ddd, 1 H, J 1.3, 2.7, 10.4 Hz, $CH_2CH{=}CH_2$), 5.35 (ddd, 1 H, J 1.6, 3.1, 17.3 Hz, $CH_2CH{=}CH_2$), 5.87–6.02 (m, 1 H, $CH_2CH{=}CH_2$), 7.25–7.39 (m, 10 H, 2 C_6H_5). Anal. Calcd for $C_{23}H_{27}N_3O_5$: C, 64.93; H, 6.40; N, 9.88. Found: C, 64.81; H, 6.41; N, 9.80.

Allyl 2-azido-3,4-di-O-benzyl-2-deoxy-6-O-trifluoromethansulfonyl-α-D-glucopyranoside (**19α**).—Under an N_2 atmosphere, **18α** (780 mg, 1.80 mmol) was dissolved in dry CH_2Cl_2 (8 mL). After addition of pyridine (215 mg, 2.70 mmol), the mixture was cooled to −20°C. Then a solution of $(CF_3SO_2)_2O$ (570 mg, 2.00 mmol) in CH_2Cl_2 (2 mL) was added dropwise. Immediately at the end of the addition, the mixture was concentrated in vacuo and filtered through a short column of silica gel (9:1 light petroleum–EtOAc). Evaporation of the solvent yielded **19α** (1.0 g, 86%) as colourless crystals; mp 55.6–55.9°C (from light petroleum–EtOAc); R_f 0.29 (9:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 3.38 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 10.0 Hz, H-2), 3.50 (dd, 1 H, $J_{3,4}$ 8.7, $J_{4,5}$ 10.0 Hz, H-4), 3.95 (ddd, 1 H, $J_{5,6a}$ 2.1, $J_{5,6b}$ 4.9 Hz, H-5), 4.01–4.10 (m, 2 H, H-3, $CH_2CH{=}CH_2$), 4.19 (dd, 1 H, J 5.8, 12.8 Hz, $CH_2CH{=}CH_2$), 4.45 (dd, 1 H, J_{gem} 10.8 Hz, H-6a), 4.55 (dd, 1 H, H-6b), 4.57 (d, 1 H, J_{gem} 10.6 Hz, $CH_2C_6H_5$), 4.85, 4.92, 4.94 (3 d, 1 H, J_{gem} 10.6 Hz, 3 $CH_2C_6H_5$), 4.97 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.25 (dd, 1 H, J 1.5, 10.4 Hz, $CH_2CH{=}CH_2$), 5.35 (dd, 1 H, J 1.5, 17.2 Hz, $CH_2CH{=}CH_2$), 5.83–5.99 (m, 1 H, $CH_2CH{=}CH_2$), 7.24–7.40 (m, 10 H, 2 C_6H_5). Anal. Calcd for $C_{24}F_3H_{26}N_3O_7S$: C, 51.70; H, 4.70; N, 7.54. Found: C, 51.87; H, 4.73; N, 7.49.

Allyl 2-azido-3,4-di-O-benzyl-2-deoxy-6-O-trifluoromethanesulfonyl-β-D-glucopyranoside (**19β**).—Compound **19β** was synthesized as described for **19α**: **18β** was treated with pyridine (0.58 g, 7.4 mmol) and $(CF_3SO_2)O$ (1.53 g, 5.4 mmol) in CH_2Cl_2 (10 mL) and yielded **19β** (2.57 g, 82%) as colourless crystals; mp 48.7–49°C (from light petroleum–EtOAc); $[\alpha]_{589}^{22}$ + 28° (*c* 1, $CHCl_3$); R_f 0.27 (9:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 3.37–3.57 (m, 4 H, H-2,3,4,5), 4.14 (dd, 1 H, J 6.2, 12.8 Hz, $CH_2CH{=}CH_2$), 4.31–4.41 (m, 3 H, H-1, 6a, $CH_2CH{=}CH_2$), 4.54 (dd, 1 H, J_{gem} 10.8, $J_{5,6b}$ 1.8 Hz, H-6b), 4.55 (d, 1 H, J_{gem} 10.8 Hz, $CH_2C_6H_5$), 4.79, 4.90, 4.94 (3 d, 3 H, J_{gem} 10.3 Hz, 3 $CH_2C_6H_5$), 5.24 (ddd, 1 H, J 1.5, 2.7, 10.4 Hz, $CH_2CH{=}CH_2$), 5.34 (ddd, 1 H, J 1.5, 3.0, 17.2 Hz, $CH_2CH{=}CH_2$), 5.85–6.01 (m, 1 H, $CH_2CH{=}CH_2$), 7.22–7.39 (m, 10 H, 2 C_6H_5). Anal. Calcd for $C_{24}F_3H_{26}N_3O_7S$: C, 51.70; H, 4.70; N, 7.54. Found: C, 51.67; H, 4.74; N, 7.50.

2-Azido-3-O-benzyl-2-deoxy-6-O-(4,5 : 7,8-di-O-cyclohexylidene-3-deoxy-N-methyl-α-D-manno-2-octulopyranosylamide)-D-glucopyranose (**20**).—A solution of **7** (760 mg, 0.95 mmol) in dry THF (4 mL) was cooled to 0°C in an ice-bath. Then a mixture of 1 M TBAF (2 mL) and 1 M acetic acid (2 mL) in dry THF was added dropwise. The mixture was stirred for 1 h, then poured into ice–water and extracted with diethyl ether (4 × 10 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated. Flash chromatography (1:3 light petroleum–EtOAc) yielded **20** (580 mg, 89%) as a colourless oil; $[\alpha]_{589}^{22}$ +22° (*c* 1, $CHCl_3$); R_f 0.37 (1:3 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 1.21–1.63 (m, 20 H, 2 C_6H_{10}), 1.81–1.89 (m, 1 H, H-3′*ax*), 2.66–2.77 (m, 1 H, H-3′*eq*), 2.82–2.84 (m, 3 H, NCH_3), 4.55 (m, 0.5 H, H-1β), 4.83–5.02 (m, 2 H, 2 $CH_2C_6H_5$), 5.32 (d, 0.5 H, $J_{1,2}$ 3.4 Hz, H-1α), 6.73–6.78 (m, 1 H, NH). Anal. Calcd for $C_{34}H_{48}N_4O_{11} \cdot H_2O$: C, 57.77; H, 7.13; N, 7.92. Found: C, 58.19; H, 7.05; N, 7.52.

Allyl O-*(4,5 : 7,8-di*-O-*cyclohexylidene-3-deoxy*-N-*methyl-α*-D-manno-*2-octulopyranosylonamide)-(2 → 6)*-O-*(2-azido-3*-O-*benzyl-2-deoxy-β*-D-*glucopyranosyl)-(1 → 6)-2-azido-3,4-di*-O-*benzyl-2-deoxy-α*-D-*glucopyranoside* (**21α**).—A solution of **20** (2.29 g, 3.32 mmol) in dry THF (100 mL) was cooled to −30°C. Then NaH (200 mg, 8.32 mmol) was added. After stirring for 20 min, a solution of **19α** (1.91 g, 3.02 mmol) in dry THF (5 mL) was added dropwise and the mixture stirred at −35°C for 20 h. For workup, MeOH (0.5 mL) was added and then the mixture poured into ice–water. Extraction by diethyl ether (4 × 30 mL), drying of the combined organic layers ($MgSO_4$), and removal of the solvent in vacuo yielded, after flash chromatography (1:1 light petroleum–EtOAc), **21α** (2.84 g, 78%) as a colourless oil; $[\alpha]_{589}^{22}$ +52° (*c* 1, $CHCl_3$); R_f 0.33 (1:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^{1}H (250 MHz), δ 1.25–1.62 (m, 20 H, 2 C_6H_{10}), 1.87 (dd, 1 H, J_{gem} 15.8, $J_{3''ax,4''}$ 3.4 Hz, H-3″*ax*), 2.63 (dd, 1 H, $J_{3''eq,4''}$ 3.7 Hz, H-3″*eq*), 2.85 (d, 3 H, *J* 5.1 Hz, NCH_3), 3.26–3.44 (m, 5 H, H-2, 4,2′,6′a,6′b), 3.63–3.87 (m, 6 H, H-4,5,6a,3′, 6″), 3.98–4.25 (m, 6 H, 2 $CH_2CH{=}CH_2$, H-6b, 3,8″a,8″b), 4.15 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.21 (dd, 1 H, $J_{4'',5''}$ 7.8, $J_{5'',6''}$ 1.7 Hz, H-5″), 4.36 (ddd, 1 H, $J_{6'',7''} = J_{7'',8''a} = J_{7'',8''b} = 5.7$ Hz, H-7″), 4.46 (ddd, 1 H, H-4″), 4.71, 4.80, 4.93 (3 d, 3 H, J_{gem} 11.0 Hz, 3 $CH_2C_6H_5$), 4.88 (m, 2 H, 2 $CH_2C_6H_5$), 4.97 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.02 (d, 1 H, J_{gem} 11.0 Hz, $CH_2C_6H_5$), 5.22 (dd, 1 H, *J* 1.5, 10.4 Hz, $CH_2CH{=}CH_2$), 5.34 1 H (dd, *J* 1.5, 17.2 Hz, $CH_2CH{=}CH_2$), 5.83–5.99 (m, 1 H, $CH_2CH{=}CH_2$), 6.81 (q, 1 H, *J* 5.1 Hz, NH), 7.26–7.45 (m, 15 H, 3 C_6H_5). Anal. Calcd for $C_{57}H_{73}N_7O_{15}$: C, 62.45; H, 6.71; N, 8.94. Found: C, 62.00; H, 6.67; N, 8.43.

Allyl O-*(4,5 : 7,8-di*-O-*cyclohexylidene-3-deoxy*-N-*methyl-α*-D-manno-*2-octulopyranosylonamide)-(2 → 6)*-O-*(2-azido-3*-O-*benzyl-2-deoxy-β*-D-*glucopyranosyl)-(1 → 6)-2-azido-3,4-di*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**21β**).—Compound **21β** was synthesized as described for **21α**. Reaction of **20** (3.10 g, 4.39 mmol) with NaH (270 mg, 11.25 mmol) and **19β** (2.57 g, 4.07 mmol) yielded **21β** (3.80 g, 77%) as a colourless oil; $[\alpha]_{589}^{22}$ +5° (*c* 1, $CHCl_3$); R_f 0.32 (1:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^{1}H (250 MHz), δ 1.23–1.62 (m, 20 H, 2 C_6H_{10}), 1.87 (dd, 1 H, J_{gem} 15.8, $J_{3''ax,4''}$ 3.3 Hz, H-3″*ax*), 2.65 (dd, 1 H, $J_3''eq$, 4″ 3.6 Hz, H-3″*eq*), 2.85 (d, 3 H, *J* 5.0 Hz, NCH_3), 3.22–3.81 (m, 13 H), 4.02 (dd, 1 H, J_{gem} 8.7, $J_{7'',8''a}$ 5.6 Hz, H-8″a), 4.11 (dd, 1 H, $J_{1',2'}$ 9.8 Hz, H-1′), 4.07–4.19 (m, 2 H, H-8″b, $CH_2CH{=}CH_2$), 4.24 (dd, 1 H, $J_{5'',6''}$ 1.8, $J_{4'',5''}$ 7.8 Hz, H-5″), 4.32 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.35–4.48 (m, 5 H, H-4″, 7″, $CH_2CH{=}CH_2$, OH), 4.61, 4.78, 4.80, 4.87, 4.89, 4.98 (6 d, 6 H, J_{gem} 11.0 Hz, 6 $CH_2C_6H_5$), 5.23 (dd, 1 H, *J* 1.6, 10.4 Hz, $CH_2CH{=}CH_2$), 5.35 (dd, 1 H, *J* 1.6, 17.2 Hz, $CH_2CH{=}CH_2$), 5.87–6.02 (m, 1 H, $CH_2CH{=}CH_2$), 6.80 (q, 1 H, *J* 4.7 Hz, NH), 7.25–7.45 (m, 15 H, 3 C_6H_5). Anal. Calcd for $C_{57}H_{73}N_7O_{15}$: C, 62.45; H, 6.71; N, 8.94. Found: C, 61.96; H, 6.69; N, 8.90.

Allyl O-*(4,5 : 7,8-di*-O-*cyclohexylidene-3-deoxy*-N-*methyl-α*-D-manno-*2-octulopyranosylonamide)-(2 → 6)*-O-*[4*-O-*(allyl 2-azido-3,4-di*-O-*benzyl-2,6-dideoxy-β*-D-*glucopyranosid-6-yl)-2-azido-3*-O-*benzyl-2-deoxy-β*-D-*glucopyranosyl]-(1 → 6)-2-azido-3,4-di*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**22β**).—NMR data ($CDCl_3$): ^{1}H

(250 MHz), δ 1.20–1.65 (m, 20 H, 2 C_6H_{10}), 1.75 (dd, 1 H, J_{gem} 15.4, $J_{3''ax,4''}$ 3.5 Hz, H-3″*ax*), 2.48 (dd, 1 H, $J_{3''eq,4''}$ 5.5 Hz, H-3″*eq*), 2.69 (d, 3 H, *J* 4.9 Hz, NCH_3), 3.16–4.90 (m, 43 H), 5.17–5.39 (m, 8 H, 4 $CH_2CH{=}CH_2$), 5.84–6.03 (m, 2 H, 2 $CH_2CH{=}CH_2$), 6.58 (q, 1 H, *J* 5.0 Hz, NH), 7.20–7.38 (m, 25 H, 5 C_6H_5).

*Allyl-O-(4,5:7,8-di-O-cyclohexylidene-3-deoxy-*N*-methyl-α-*D*-manno-2-octulopyranosylonamide)-(2 → 6)-O-(2-azido-3-O-benzyl-2-deoxy-4-O-diphenoxyphosphoryl-β-D-glucopyranosyl)-(1 → 6)-2-azido-3,4-di-O-benzyl-2-deoxy-α-D-glucopyranoside* (**23α**).—Compound **21α** (2.58 g, 2.60 mmol) was dissolved in dry CH_2Cl_2 (10 mL); then were added triethylamine (526 mg, 5.20 mmol), DMAP (350 mg, 2.86 mmol), and diphenyl phosphorochloridate (908 mg, 3.38 mmol). The mixture was stirred at ambient temperature for 12 h, then poured into ice–water, and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification by flash chromatography (6 : 4 light petroleum–EtOAc) yielded **23α** (3.36 g, 97%) as a colourless oil; $[\alpha]_{589}^{22}$ +43° (*c* 1, $CHCl_3$); R_f 0.40 (7:3 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz), δ 1.23–1.74 (m, 20 H, 2 C_6H_{10}), 1.85 (dd, 1 H, J_{gem} 15.3, $J_{3''ax,4''}$ 3.5 Hz, H-3″*ax*), 2.56 (dd, 1 H, $J_{3''eq,4''}$ 4.4 Hz, H-3″*eq*), 2.60 (d, 3 H, *J* 4.9 Hz, NCH_3), 3.40–4.33 (m, 19 H), 4.63–4.94 (m, 6 H, 6 $CH_2C_6H_5$), 4.98 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.23 (dd, 1 H, *J* 1.5, 10.4 Hz, $CH_2CH{=}CH_2$), 5.35 (dd, 1 H, *J* 1.5, 17.1 Hz, $CH_2CH{=}CH_2$), 5.84–6.00 (m, 1 H, $CH_2CH{=}CH_2$), 6.71 (q, 1 H, *J* 5.0 Hz, NH), 7.01–7.40 (m, 25 H, 5 C_6H_5). Anal. Calcd for $C_{69}H_{82}N_7O_{18}P$: C, 62.39; H, 6.62; N, 7.38. Found: C, 62.54; H, 6.29; N, 7.23.

Allyl O-*(4,5:7,8-di-O-cyclohexylidene-3-deoxy-*N*-methyl-α-*D*-manno-2-octulopyranosylonamide)-(2 → 6)-O-(2-azido-3-O-*benzyl-2-deoxy-4-O-diphenoxyphosphoryl-β-D-glucopyranosyl)-(1 → 6)-2-azido-3,4-di-O-benzyl-2-deoxy-β-D-glucopyranoside* (**23β**).—Compound **23β** was synthesized as described for **23α**; **21β** (3.98 g, 3.63 mmol) was treated with triethylamine (735 mg, 7.26 mmol), DMAP (490 mg, 4.01 mmol), and diphenyl phosphorochloridate (1.26 g, 4.69 mmol) in dry CH_2Cl_2 (20 mL), to yield **23β** (4.52 g, 94%) as a colourless oil, $[\alpha]_{589}^{22}$ +6° (c 1, $CHCl_3$); R_f 0.25 (7:3 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz): δ 1.26–1.64 (m, 20 H, 2 C_6H_{10}), 1.82 (dd, 1 H, J_{gem} 15.4, $J_{3''ax,4''}$ 3.5 Hz, H-3″*ax*), 2.53 (dd, 1 H, $J_{3''eq,4''}$ 4.5 Hz, H-3″*eq*), 2.60 (d, 3 H, *J* 5.0 Hz, NCH_3), 3.37–3.75 (m, 10 H, H-2,3,4,6a,6b,2′,3′,5′,6′a,6′b), 3.90–4.16 (m, 6 H, $CH_2CH{=}CH_2$, H-5a,6′,5″,8″a, 8″b), 4.18 (d, 1 H, $J_{1',2'}$ 9.0 Hz, H-1′), 4.22–4.38 (m, 3 H, H-4′,4″,7″), 4.38 (d, 1 H, $J_{1,1}$ 7.6 Hz, H-1), 4.45 (ddd, 1 H, *J* 1.5, 6.2, 12.8 Hz, $CH_2CH{=}CH_2$), 4.62 (d, 1 H, J_{gem} 11.0 Hz, $CH_2C_6H_5$), 4.63 (d, 1 H, J_{gem} 10.6 Hz, $CH_2C_6H_5$), 4.70 (d, 1 H, J_{gem} 10.6 Hz, $CH_2C_6H_5$), 4.76 (d, 1 H, J_{gem} 10.7 Hz, $CH_2C_6H_5$), 4.86 (d, 1 H, J_{gem} 11.0 Hz, $CH_2C_6H_5$), 4.88 (d, 1 H, J_{gem} 10.7 Hz, $CH_2C_6H_5$), 5.23 (dd, 1 H, *J* 1.6, 10.4 Hz, $CH_2CH{=}CH_2$), 5.36 (dd, 1 H, *J* 1.6, 17.3 Hz, $CH_2CH{=}CH_2$), 5.88–6.01 (m, 1 H, $CH_2CH{=}CH_2$), 6.68 (q, 1 H, *J* 5.0 Hz, NH), 7.01–7.40 (m, 25 H, 5 C_6H_5). Anal. Calcd for $C_{69}H_{82}N_7O_{18}P$: C, 62.39; H, 6.62; N, 7.38. Found: C, 61.96; H, 6.31; N, 7.19.

Allyl O-*(3-deoxy-*N*-methyl-α-*D*-manno-2-octulopyranosylonamide)-(2 → 6)-O-(2-*

azido-3-O-benzyl-2-deoxy-4-O-diphenoxyphosphoryl-β-D-glucopyranosyl)-(1 → 6)-2-azido-3,4-di-O-benzyl-2-deoxy-α-D-glucopyranoside (**24α**).—Compound **23α** (2.0 g, 1.50 mmol) was dissolved in dry MeOH (200 mL), then *p*-toluenesulfonic acid (200 mg, 1.05 mmol) was added. After stirring at room temperature for 5 h, $NaHCO_3$ was added and the mixture stirred for another 5 h. After filtration, the solvent was removed under reduced pressure and the residue filtered through a short column of silica gel (9:1 $CHCl_3$–MeOH). Purification by flash chromatography (9:1 $CHCl_3$–MeOH) yielded **23α** (1.50 g, 85%) as a colourless oil; $[\alpha]_{589}^{22}$ +7° (*c* 1, $CHCl_3$); R_f 0.22 (9:1 $CHCl_3$–MeOH). NMR data ($CDCl_3$): ^1H (250 MHz), δ 1.75 (dd, 1 H, $J_{gem} = J_{3''ax,4''} = 12.7$ Hz, H-3″*ax*), 2.02 (dd, 1 H, $J_{3''eq,4''}$ 4.0 Hz, H-3″*eq*), 2.62 (d, 3 H, *J* 4.8 Hz, NCH_3), 3.09–4.92 (m, 32 H), 5.23 (dd, 1 H, *J* 1.3, 10.5 Hz, $CH_2CH{=}CH_2$), 5.34 (dd, 1 H, *J* 1.5, 17.3 Hz, $CH_2CH{=}CH_2$), 5.86–6.01 (m, 1 H, $CH_2CH{=}CH_2$), 6.92–7.38 (m, 25 H, 5 C_6H_5). Anal. Calcd for $C_{57}H_{66}N_7O_{18}P$: C, 58.16; H, 5.69; N, 8.39. Found: C, 58.04; H, 5.68; N, 7.94.

Allyl O-*(3-deoxy-*N*-methyl-α-D-*manno*-2-octulopyranosylonamide)-(2 → 6)-*O-*(2-azido-3-O-benzyl-2-deoxy-4-O-diphenoxyphosphoryl-β-D-glucopyranosyl)-(1 → 6)-2-azido-3,4-di-O-benzyl-2-deoxy-2-deoxy-β-D-glucopyranoside* (**24β**).—Compound **24β** was synthesized as described for **24α**. Reaction of **23β** (3.0 g, 2.26 mmol) with *p*-toluenesulfonic acid (300 mg, 1.53 mmol) in dry MeOH (150 mL) yielded **24β** (2.1 g, 80%) as a colourless oil; $[\alpha]_{589}^{22}$ +8° (*c* 1, $CHCl_3$); R_f 0.29 (9:1 $CHCl_3$–MeOH). NMR data ($CDCl_3$): ^1H (250 MHz), δ 1.76 (dd, 1 H, $J_{gem} = J_{3''ax,4''} = 12.2$ Hz, H-3″*ax*), 1.97–2.01 (m, 1 H, H-3″*eq*), 2.59 (d, 3 H, *J* 4.6 Hz, NCH_3), 3.11–4.91 (m, 32 H), 5.21 (d, 1 H, *J* 10.6 Hz, $CH_2CH{=}CH_2$), 5.34 (d, 1 H, *J* 10.4 Hz, $CH_2CH{=}CH_2$), 5.85–6.00 (m, 1 H, $CH_2CH{=}CH_2$), 6.96–7.33 (m, 25 H, 5 C_6H_5). Anal. Calcd for $C_{57}H_{66}N_7O_{18}P$: C, 58.16; H, 5.69; N, 8.39. Found: C, 57.98; H, 5.76; N, 7.94.

Allyl O-*(3-deoxy-*N*-methyl-4,5,7,8-tetra-O-triethylsilyl-α-D-*manno*-2-octulopyranosylonamide)-(2 → 6)-*O-*(2-azido-3-O-benzyl-2-deoxy-4-O-diphenoxyphosphoryl-β-D-glucopyranosyl)-(1 → 6)-2-azido-3,4-di-O-benzyl-2-deoxy-α-D-glucopyranoside* (**25α**). —To a solution of **24α** (1.50 g, 1.28 mmol) in dry CH_2Cl_2 (15 mL) was added imidazole (700 mg, 10.20 mmol) and triethylsilyl chloride (1.16 g, 7.70 mmol). After stirring with exclusion of moisture for 12 h at ambient temperature, the mixture was poured into an ice-cold solution of $NaHCO_3$. After extraction with CH_2Cl_2 (3 × 200 mL), the organic layers were combined, washed with water, and dried ($MgSO_4$). After removal of the solvent, flash chromatography (17:3 light petroleum EtOAc) yielded **25α** (2.03 g, 97%) as a colourless oil; $[\alpha]_{589}^{22}$ +32° (*c* 1, $CHCl_3$); R_f 0.24 (17:3 light petroleum EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz): δ 0.53–0.77 (m, 24 H, 12 CH_2), 0.88–1.63 (m, 36 H, 12 CH_3), 1.88 (dd, 1 H, $J_{gem} = J_{3''ax,4''} = 12.7$ Hz, H-3″*ax*), 1.96 (dd, 1 H, $J_{3''eq,4''}$ 5.2 Hz, H-3″*eq*), 2.57 (d, 3 H, *J* 4.9 Hz, NCH_3) 3.37–3.51 (m, 7 H), 3.70–4.22 (m, 13 H), 4.30 (ddd, 1 H, $J_{3',4'} = J_{4',5'} = J_{4',P} = 8.8$ Hz, H-4′), 4.67–4.93 (m, 6 H, $CH_2C_6H_5$), 4.99 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.23 (dd, 1 H, *J* 1.5, 10.2 Hz, $CH_2CH{=}CH_2$), 5.33 (dd, 1 H, *J* 1.5 17.2 Hz, $CH_2CH{=}CH_2$), 5.83–5.98 (m, 1 H, $CH_2CH{=}CH_2$), 6.58 (q, 1 H, *J* 4.9 Hz,

NH), 7.00–7.41 (m, 25 H, 5 C_6H_5). Anal. Calcd for $C_{81}H_{122}N_7O_{18}Si_4P$: C, 59.86; H, 7.75; N, 6.03. Found: C, 59.30; H, 7.51; N. 6.00.

Allyl O-*(3-deoxy-*N-*methyl-4,5,7,8-tetra-*O-*triethylsilyl-α-*D-manno-*2-octulopyranosylonamide)-(2 → 6)-*O-*(2-azido-3-*O-*benzyl-2-deoxy-4-*O-*diphenoxyphosphoryl-β-*D-*glucopyranosyl)-(1 → 6)-2-azido-3,4-di-*O-*benzyl-2-deoxy-β-*D-*glucopyranoside* (**25β**). —Compound **25β** was synthesized as described for **25α**. Reaction of **24β** (2.10 g, 1.79 mmol), imidazole (980 mg, 14.40 mmol), and triethylsilyl chloride (1.63 g, 10.80 mmol) yielded **25β** (2.88 g, 98%) as a colourless oil; $[\alpha]_{589}^{22}$ +13° (*c* 1, $CHCl_3$); R_f 0.50 (8:2 light petroleum–EtOAc) NMR data ($CDCl_3$): ^{1}H (250 MHz): δ 0.53–0.70 (m, 24 H, 12 CH_2), 0.89–0.96 (m, 36 H, 12 CH_3), 1.85 (dd, 1 H, $J_{gem} = J_{3''ax,4''} = 12.8$ Hz, H-3″*ax*), 1.97 (dd, 1 H, $J_{3''eq,4''}$ 4.8 Hz, H-3″*eq*), 2.58 (d, 3 H, *J* 5.0 Hz, NCH_3), 3.35–4.22 (m, 19 H), 4.33 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.32 (ddd, 1 H, $J_{3',4'} = J_{4',5'} = J_{4',P} = 8.8$ Hz, H-4′), 4.45 (dd, 1 H, *J* 4.9, 12.9 Hz, $CH_2CH{=}CH_2$), 4.64 (d, 1 H, J_{gem} 11.2 Hz, $CH_2C_6H_5$), 4.67 (s, 2 H, 2 $CH_2C_6H_5$), 4.77 (d, 1 H, J_{gem} 10.8 Hz, $CH_2C_6H_5$), 4.90 (d, 1 H, J_{gem} 10.8 Hz, $CH_2C_6H_5$), 4.92 (d, 1 H, J_{gem} 11.2 Hz, $CH_2C_6H_5$), 5.24 (dd, 1 H, *J* 1.1, 10.4 Hz, $CH_2CH{=}CH_2$), 5.35 (dd, 1 H, *J* 1.4, 17.2 Hz, $CH_2CH{=}CH_2$), 5.88–6.03 (m, 1 H, $CH_2CH{=}CH_2$), 6.58 (q, 1 H, *J* 5.0 Hz, NH), 7.11–7.39 (m, 25 H, 5 C_6H_5). Anal. Calcd for $C_{81}H_{122}N_7O_{18}Si_4P$: C, 59.86; H, 7.57; N, 6.03. Found: C, 59.55; H, 7.57; N, 6.00.

*O-(3-Deoxy-*N-*methyl-4,5,7,8-tetra-*O-*triethylsilyl-α-*D-*manno-2-octulopyranosylonamide)-2(2 → 6)-*O-*(2-azido-3-*O-*benzyl-2-deoxy-4-*O-*diphenoxyphosphoryl-β-*D-*glucopyranosyl)-(1 → 6)-2-azido-3,4-di-*O-*benzyl-2-deoxy-*D-*glucopyranose* (**26α,β**). —*From* **25α**: **25α** (1.20 g, 0.74 mmol) was dissolved in dry THF (20 mL). Traces of oxygen were removed by repeated evacuation and degassing with Ar. After addition of (1,5-cyclooctadiene)bis(methyldiphenylphosphine)iridium hexafluorophosphate, the reaction flask was evacuated and degassed with Ar once more. The catalyst was activated by bubbling H_2 through the solution. After 1 min, residual H_2 was removed. The mixture was stirred for 4 h at room temperature, then the solvent was removed and the residue filtered through a short column of silica gel (8:2 light petroleum–EtOAc). The filtrate was concentrated and then dissolved in 9:1 acetone–water (20 mL). After addition of yellow mercury(II) oxide (230 mg, 1.0 mmol) and mercury(II) chloride (220 mg, 0.81 mmol), the mixture was stirred for 18 h at ambient temperature. After filtration through Celite, the filtrate was concentrated and the residue dissolved in diethyl ether. After washing with aq. NaI, the organic layer was dried ($MgSO_4$) and the solvent removed in vacuo. Purification by flash chromatography (8:2 light petroleum–EtOAc) yielded **26α,β** (890 mg, 77%).

From **25β**: the reaction procedure was as described for **25α**: **25β** (2.50 g, 1.54 mmol) was dissolved in dry THF (40 mL) and isomerized with (1,5-cyclooctadiene)bis(methyldiphenylphosphine)iridium hexafluorophosphate. The enol ether was treated in 9:1 acetone–water (30 mL) with yellow mercury(II) oside (470 mg, 2.17 mmol) and mercury(II) chloride (460 mg, 1.69 mmol).

The material synthesized from **25α** and **25β**, respectively, had the same physical

properties, $[\alpha]_{589}^{22}$ +30° (*c* 1, $CHCl_3$); R_f 0.21 (8:2 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz): δ 0.47–0.74 (m, 24 H, 12 CH_2), 0.86–0.96 (m, 36 H, 12 CH_3), 1.82–2.04 (m, 3 H, H-3″*ax*, H-3″*eq*, OH), 2.66–2.69 (m, 3 H, NCH_3), 3.34–4.96 (m, 25 H), 5.28–5.41 (m, 1 H, H-1α,β), 6.68–6.73 (m, 1 H, NH), 6.97–7.40 (m, 25 H, 5 C_6H_5). Anal. Calcd for $C_{78}H_{118}N_7O_{18}PSi$: C, 59.10; H, 7.50; N, 6.18. Found: C, 58.58; H, 7.51; N, 5.96.

O-(*3-Deoxy*-N-*methyl-4,5,7,8-tetra*-O-*triethylsilyl*-α-D-manno-*2-octulopyranosyl-onamide*)-(2 → 6)-O-(*2-amino-3*-O-*benzyl-2-deoxy-4*-O-*diphenoxyphosphoryl*-β-D-*glucopyranosyl*)-(1 → 6)-*2-amino-3*-O-*benzyl-2-deoxy*-D-*glucopyranose* (**27α,β**) *and* O-(*3-deoxy*-N-*methyl-4,5,7,8-tetra*-O-*triethylsilyl*-α-D-manno-*2-octulopyra-nosylonamide*)-(2 → 6)-O-{*3*-O-*benzyl-2-deoxy-4*-O-*diphenoxyphosphoryl-2-[(3*R*)-3-dodecanoyloxytetradecanamido]*β-D-*glucopyranosyl*}-(1 → 6)-*3,4-di*-O-*benzyl-2-deoxy-2-[(3*R*)-3-dodecanoyloxytetradecanamido]*-D-*glucopyranose* (**29α,β**).—Compound **26α,β** (760 mg, 0.48 mmol) was dissolved in 3:1 pyridine–water (20 mL) and then H_2S was bubbled through the solution for 5 min. The mixture was stirred at room temperature for 3 days, then the solvent was removed in vacuo. By gradient elution (9:3 → 1:1 → 1:3 light petroleum–EtOAc → 9:1 $CHCl_3$–MeOH), part of the sulfur was removed. Fractions with a positive ninhydrin reaction were combined and concentrated to yield **27α,β** (640 mg) as a yellow oil which was used in the next step without further characterization. Compound **27α,β** (100 mg, 0.07 mmol) was dissolved in dry CH_2Cl_2 (1 mL) and then **28** (85 mg, 0.20 mmol) and DCC (55 mg, 0.27 mmol) were added. After 24 h, additional **28** (85 mg, 0.20 mmol) and DCC (55 mg, 0.27 mmol) were added. For workup, the mixture was filtered and concentrated. Purification by MPLC (9:1 toluene–acetone) yielded **29α,β** (80 mg, 50%) as a colourless oil; $[\alpha]_{589}^{22}$ +35° (*c* 1, $CHCl_3$); R_f 0.30 (9:1 toluene–acetone). NMR data ($CDCl_3$): ^1H (250 MHz): δ 0.53–0.74 (m, 24 H, 12 CH_3), 0.85–0.96 (m, 36 H, 12 CH_3), 1.05–1.35 (bs, 68 H, 34 CH_2), 1.38–1.70 (m, 8 H, 4 CH_2CH_2CO), 1.85–2.38 (m, 10 H, H-3″*ax*,3″*eq*, CH_2CO), 2.57–2.61 (m, 3 H, NCH_3), 3.09–5.29 (m, 29 H), 5.53 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.77 (d, 1 H, *J* 9.0 Hz, NH), 6.13 (d, 1 H, *J* 6.8 Hz, CH), 6.57–6.62 (m, 1 H, NH), 7.03–7.31 (m, 15 H, 5 C_6H_6). Anal. Calcd for $C_{130}H_{128}N_3O_{23}PSi_4$: C, 66.88; H, 9.41; N, 1.80. Found: C, 66.47; *H*, 9.20; N, 1.38.

O-(*3-Deoxy*-N-*methyl-4,5,7,8-tetra*-O-*triethylsilyl*-α-D-manno-*2-octulopyra nosyl-onamide*)-(2 → 6)-O-{*3*-O-*benzyl-2-deoxy-4*-O-*diphenoxyphosphoryl-2[(3*R*)-3-dode-canoyloxytetradecanamido]*-β-D-*glucopyranosyl*}-(1 → 6)-*1*-O-*acetyl-3,4-di*-O-*benzyl-2-deoxy-2-[(3*R*)-3-dodecanoyloxytetradecanamido]*-α-D-*glucopyranose* (**30α**).—Compound **29α,β** (114 mg, 0.05 mmol) was dissolved in dry pyridine (1 mL) and Ac_2O (1 mL). After stirring for 12 h at room temperature, the solvent was removed under reduced pressure. Purification by MPLC (3:1 light petroleum–EtOAc) yielded **30α** (83 mg, 70%) as a colourless oil; $[\alpha]_{589}^{22}$ +34° (*c* 1, $CHCl_3$); R_f 0.30 (9:1 toluene–acetone). NMR data ($CDCl_3$): ^1H (250 MHz): δ 0.51–0.75 (m, 24 H, 12 CH_2), 0.85–0.96 (m, 36 H, 12 CH_3), 1.00–1.32 (bs, 68 H, 34 CH_2), 1.38–1.62 (m, 8 H, 4 CH_2CH_2CO), 2.10 (s, 3 H, CH_3CO), 1.93–2.35 (m, 10 H,

H-3″*ax*, H-3″*eq*, 4 CH_2CO), 2.58 (d, 3 H, *J* 4.9 Hz, NCH_3), 3.39–4.14 (m, 15 H), 4.29–4.89 (m, 15 H), 5.04–5.30 (m, 2 H), 6.08 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 6.60 (q, 1 H, *J* 4.9 Hz, NH), 6.98–7.38 (m, 25 H, 5 C_6H_5). Anal. Calcd for $C_{132}H_{212}N_3O_{24}P$-Si · $2H_2O$: C, 65.71; H, 9.35; N, 1.74. Found: C, 65.83; H, 9.25; N, 1.41.

*O-(3-Deoxy-*N*-methyl-α-*D*-*manno*-2-octulopyranosylamide)-(2 → 6)-O-{3-O-benzyl-2-deoxy-4-diphenoxyphosphoryl-2-[(3*R*)-3-dodecanoyloxytetradecanamido]-β-*D*-glucopyranosyl}-(1 → 6)-1-O-acetyl-3,4-di-O-benzyl-3-deoxy-2-[(3*R*)-3-dodecanoyloxytetradecanamido]-α-*D*-glucopyranose* (**31α**).—Compound **30α** (165 mg, 0.06 mmol) was dissolved in EtOAc (5 mL), then 10% Pd–C was added and the mixture was stirred under an H_2 atmosphere for 15 h. After filtration, the solvent was removed under reduced pressure. Purification by flash chromatography (9:1 $CHCl_3$–MeOH) yielded **31α** (119 mg, 88%) as a colourless oil; $[\alpha]_{589}^{22}$ +37° (*c* 1, $CHCl_2$); R_f 0.36 (9:1 $CHCl_3$–MeOH). NMR data ($CDCl_3$): ^1H (250 MHz): δ 0.87 (t, 12 H, *J* 5.2 Hz, 4 CH_3), 1.23 (sb, 68 H, 34 CH_2), 1.40–1.60 (m, 8 H, 4 C*H*$_2$$CH_2CO$), 1.79 (dd, 1 H, $J_{gem} = J_{3''ax,4''} = 12.0$ Hz, H-3″*ax*), 2.10 (s, 3 H, CH_3CO), 2.04–2.31 (m, 9 H, H-3″*eq*, 8 CH_2CO), 2.61 (d, 3 H, *J* 4.8 Hz, NCH_3), 2.89 (bs, 1 H, OH), 3.22 (bs, 1 H, OH), 3.47–4.01 (m, 18 H), 4.22–4.29 (m, 2 H), 4.52–5.08 (m, 10 H), 5.89 (d, 1 H, *J* 8.2 Hz, NH), 6.06 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 6.31 (d, 1 H, *J* 7.6 Hz, NH), 6.84–7.68 (m, 26 H, 5 C_6H_5, NH). Anal. Calcd for $C_{108}H_{164}N_3O_{25}P \cdot 2H_2O$: C, 65.79; H, 8.59; N, 2.13. Found: C, 65.84; H, 8.45; N, 1.98.

*O-(4,5,7,8-Tetra-O-acetyl-3-deoxy-*N*-methyl-α-*D*-*manno*-2-octulopyranosylamide)-(2 → 6)-O-{3-O-benzyl-2-deoxy-4-O-diphenoxyphosphoryl-2-[(3*R*)-3-dodecanoyloxytetradecanamido]-β-*D*-glucopyranosyl}-(1 → 6)-1-O-acetyl-3,4-di-O-benzyl-2-deoxy-2-[(3*R*)-3-dodecanoyloxytetradecanamido]-α-*D*-glucopyranose* (**32α**).—Compound **31α** (418 mg, 0.22 mmol) was dissolved in dry pyridine (1 mL) and dry Ac_2O (1 mL), and stirred at room temperature for 12 h. After removal of the solvents under reduced pressure, purification by flash chromatography (1:1 light petroleum–EtOAc) yielded **32α** as colourless crystals; mp 48.5–49.3°C (light petroleum–EtOAc); $[\alpha]_{589}^{22}$ +44° (*c* 1, $CHCl_3$); R_f 0.38 (1:1 light petroleum–EtOAc). NMR data ($CDCl_3$): ^1H (250 MHz): δ 0.88 (t, 12 H, *J* 5.2 Hz, 4 CH_3), 1.00–1.30 (bs, 68 H, 34 CH_2), 1.40–1.60 (m, 8 H, 4 C*H*$_2$$CH_2CO$), 1.87, 1.90, 2.04, 2.06, 2.12 (5 s, 15 H, 5 CH_3CO), 1.94–2.37 (m, 9 H, H-3″*eq*, 4 CH_2CO), 2.67 (d, 3 H, *J* 4.9 Hz, NCH_3), 3.55–4.26 (m, 12 H), 4.28–4.33 (m, 1 H, H-2), 4.52–4.93 (m, 8 H, H-4′, 8″a, 6 C*H*$_2$$C_6H_5$), 5.05 (d, 1 H, $J_{1',2'}$, 7.8 Hz, 1 H, H-1′), 5.09–5.19 (m, 3 H, H-7″, 2 CH_2CHO), 5.29–5.36 (m, 2 H, H-4″, 5″), 5.83 (d, 1 H, *J* 8.7 Hz, NH), 6.00 (d, 1 H, *J* 8.0 Hz, NH′), 6.04 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 6.80 (q, 1 H, *J* 4.7 Hz, NH″), 7.00–7.23 (m, 25 H, 5 C_6H_5). Anal. Calcd for $C_{116}H_{172}N_3O_{29}P$: C, 66.23; H, 8.24; N, 1.99. Found: C, 66.11; H, 8.26; N, 1.69.

*O-(4,5,7,8-Tetra-O-acetyl-3-deoxy-*N*-methyl-α-*D*-*manno*-2-octulopyranosylonamide)-(2 → 6)-O-{2-deoxy-4-O-diphenoxyphosphoryl-2-[(3*R*)-3-dodecanoyloxytetradecanamido]-β-*D*-glucopyranosyl}-(1 → 6)-1-O-acetyl-2-deoxy-2[(3*R*)-3-dodecanoyloxytetradecanamido]-α-*D*-glucopyranose* (**33α**).—Compound **32α** (150 mg, 0.07

mmol) was dissolved in EtOAc (2 mL) and MeOH (2 mL); then 10% Pd–C (10 mg) was added. After stirring for 10 h under H_2, the mixture was filtered and the solvent removed under reduced pressure. Purification of the residue by flash chromatography (95:5 $CHCl_3$–MeOH) yielded **33α** (115 mg, 91%) as colourless crystals; mp 135.2–137.1°C (from $CHCl_3$–MeOH); $[\alpha]_{589}^{22}$ +31° (*c* 1, $CHCl_3$); R_f 0.29 (95:5 $CHCl_3$–MeOH). NMR data ($CDCl_3$): ^{1}H (250 MHz): δ 0.88 (t, 12 H, *J* 5.2 Hz, 4 CH_3), 1.25 (bs, 68 H, 34 CH_2), 1.50–1.73 (m, 8 H, 4 CH_2CH_2CO), 1.93 (dd, 1 H, $J_{gem} = J_{3''ax,4''} = 13.0$ Hz, H-3″*ax*), 1.96, 1.97, 2.06, 2.07, 2.16 (5 s, 15 H, 5 CH_3CO), 2.23–2.33 (m, 5 H, H-3″*eq*, 4 CH_2CO), 2.49–2.56 (m, 4 H, 2 OCHCH_2CO), 2.76 (d, 3 H, *J* 4.9 Hz, NCH_3), 2.90–3.57 (m, 3 H), 3.60–3.81 (m, 5 H), 3.90–4.02 (m, 2 H, H-3′,8″a), 4.10–4.34 (m, 5 H), 4.65 (dd, 1 H, J_{gem} 10.1, $J_{7'',8''b} < 1$ Hz, H-8″b), 4.74 (d, 1 H, $J_{1',2'}$ 8.6 Hz, H-1′), 4.90 (d, 1 H, *J* 3.0 Hz, OH), 5.02–5.20 (m, 3 H, H-7″, 2 CH_2C*H*O), 5.22–5.32 (m, 2 H, H-5″,4″), 6.06 (d, $J_{1,2}$ 3.7 Hz, 1 H, H-1), 6.10 (d, 1 H, *J* 10.9 Hz, NH), 6.16 (d, 1 H, *J* 6.2 Hz, NH), 6.73 (q, 1 H, *J* 4.9 Hz, NH), 7.13–7.39 (m, 10 H, 2 C_6H_5). Anal. Calcd for $C_{95}H_{154}N_3O_{29}P$: C, 62.24; H, 8.47; N, 2.29. Found: C, 62.18; H, 8.39; N, 2.13.

O-(4,5,7,8-tetra-O-acetyl-3-deoxy-N-methyl-α-D-manno-2-octulopyranosylonamide)-(2 → 6)-O-{2-deoxy-4-O-diphenoxyphosphoryl-2-[(3R)-3-dodecanoyloxytetradecanamido]-3-O-tetradecanoyl-β-D-glucopyranosyl}-(1 → 6)-1-O-acetyl-2-deoxy-2-[(3R)-3-dodecanoyloxytetradecanamido]-3-O-tetradecanoyl-α-D-glucopyranose (**34α**).—Compound **33α** (140 mg, 0.08 mmol) was dissolved in dry pyridine (0.5 mL) and dry CH_2Cl_2 (0.5 mL), then tetradecanoyl chloride (38 mg, 0.15 mmol) was added. The mixture was stirred with exclusion of moisture for 12 h. After removal of the solvents under reduced pressure, the residue was purified by flash chromatography (95:5 $CHCl_3$–MeOH). Lyophilization from dioxane yielded **34α** (78 mg, 45%) as a white powder; $[\alpha]_{589}^{22}$ +35° (*c* 1, $CHCl_3$); R_f 0.41 (95:5 $CHCl_3$–MeOH). NMR data ($CDCl_3$): ^{1}H (250 MHz): δ 0.88 (t, 12 H, *J* 6.3 Hz, 6 CH_3), 1.00–1.40 (bs, 116 H, 58 CH_2), 1.52–1.71 (m, 12 H, 4 CH_2CH_2CO), 1.93 (dd, 1 H, $J_{gem} = J_{3''ax,4''}$ 12.6 Hz, H-3″*ax*), 1.95, 1.97, 2.08, 2.16 (5 s, 15 H, 5 CH_3CO), 2.21–2.55 (m, 13 H, H-3″*eq*, 12 OCHCH_2CO), 2.71 (d, 3 H, *J* 4.9 Hz, NCH_3), 3.44–4.01 (m, 8 H, H-4,5,6,2′,5′,6′a,6′b,8″a), 4.06 (d, 1 H, *J* 5.7 Hz, OH), 4.12–4.16 (m, 1 H, H-6′a), 4.21–4.34 (m, 2 H, H-2, 6″), 4.49 (ddd, 1 H, $J_{3',4'} = J_{4',5'} = J_{4',P} = 9.2$ Hz, H-4′), 4.63 (dd, 1 H, J_{gem} 10.1, $J_{7'',8''b} < 1$ Hz, H-8″b), 4.73 (d, 1 H, $J_{1',2'}$ 8.5 Hz, H-1′), 4.99–5.21 (m, 4 H, H-3, 7″, 2 CH_2C*H*O), 5.26–5.34 (m, 3 H, H-3′,4″,5″), 5.86 (d, 1 H, *J* 8.8 Hz, NH′), 6.02 (d, 1 H, *J* 10.0 Hz, NH), 6.05 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 6.75 (q, 1 H, *J* 4.7 Hz, NH″), 7.07–7.36 (m, 10 H, 2 C_6H_5). ^{31}P (161.7 MHz): δ −12.2. Anal. Calcd for $C_{123}H_{206}N_3O_3P$: C, 65.54; H, 9.21; N, 1.86. Found: C, 65.66; H, 9.47; N, 1.50.

O-(4,5,7,8-Tetra-O-acetyl-3-deoxy-N-methyl-α D-manno-2-octulopyranosylonamide)-(2 → 6)-O-{2-deoxy-2-[(3R)-3-dodecanoyloxytetradecanamido]-4-O-phosphono-3-O-tetradecanoyl-β-D-glucopyranosyl}-(1 → 6)-1-O-acetyl-2-deoxy-2-[(3R)-3-dodecanoyloxytetradecanamido]-3-O-tetradecanoyl-α-D-glucopyranose (**35α**).—Compound **34α** (58.0 mg, 0.025 mmol) was dissolved in MeOH (2 mL) and then

newly activated Adams' catalyst (5 mg) was added. After stirring under H_2 for 24 h, further catalyst (85 mg) was added and stirring was continued for 4 days. After filtration, the solvent was removed in vacuo and the residue purified by flash chromatography (8:2 $CHCl_3$–MeOH). Lyophilization from dioxane yielded **35α** (47 mg, 84%) as a colourless powder, $[\alpha]_{589}^{22}$ +22° (*c* 1, $CHCl_3$); R_f 0.53 (8:2 $CHCl_3$–MeOH). $M^+ + K = 2141$ (glycerol–*m*-nitrobenzyl alcohol).

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