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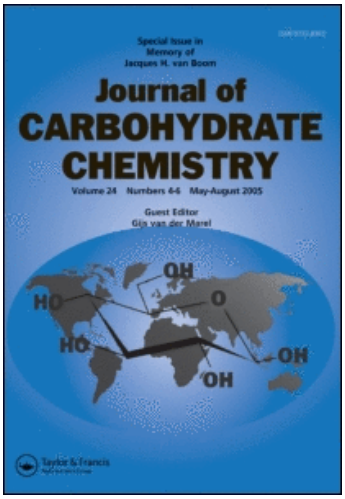

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SYNTHESIS OF SIALYL-α-(2⟶3)-NEOLACTOTETRAOSE DERIVATIVES MODIFIED AT C-2 OF THE *N*-ACETYLGLUCOSAMINE RESIDUE: PROBES FOR INVESTIGATION OF ACCEPTOR SPECIFICITY OF HUMAN α-1,3-FUCOSYLTRANSFERASES, FUC-TVII, AND FUC-TVI *

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SYNTHESIS OF SIALYL-α-(2→3)-NEOLACTOTETRAOSE DERIVATIVES MODIFIED AT C-2 OF THE *N*-ACETYLGLUCOSAMINE RESIDUE: PROBES FOR INVESTIGATION OF ACCEPTOR SPECIFICITY OF HUMAN α-1,3-FUCOSYLTRANSFERASES, FUC-TVII AND FUC-TVI*

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ABSTRACT

A variety of sialyl-α-(2→3)-neolactotetraose (IV^3NeuAcnLcOse$_4$ or IV^3NeuGcnLcOse$_4$) derivatives (**23**, **31–37**, **58–60**) modified at C-2 of the GlcNAc residue have been synthesized. The phthalimido group at C-2 of GlcNAc in 2-(trimethylsilyl)ethyl (3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**5**) was systematically converted to a series of acylamino groups, to give the per-*O*-benzylated trisaccharide acceptors (**6–11**). On the other hand, modification of the hydroxyl group at C-2 of the terminal Glc residue in 2-(trimethylsilyl)ethyl (4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**42**) gave three dif-

*Synthetic studies on sialoglycoconjugates, Part 125. For Part 124, see Otsubo, N.; Ishida, H.; Kiso, M. Chemical approach to selectin ligands: total synthesis of *O*-glycan on GlyCAM-1. Aust. J. Chem.-Int. J. Chem. Sci., **2002**, *55*, 105–112.

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ferent kinds of trisaccharide acceptors containing D-glucose (**49**), *N*-acetyl-D-mannosamine (**50**), and D-mannose (**51**) instead of the GlcNAc residue. Totally ten trisaccharide acceptors (**5–11** and **49–51**) were each coupled with sialyl-α-(2→3)-galactose donor **12** to afford the corresponding pentasaccharides (**14–21** and **52–54**) in good yields, respectively, which were then transformed into the target compounds. Acceptor specificity of the synthetic sialyl-α-(2→3)-neolactotetraose probes for the human α-(1→3)-fucosyltransferases, Fuc-TVII and Fuc-TVI, was examined.

Key Words: Selectin; Sialyl Lewis x; Sialyl paragloboside; Fucosyl transferase

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INTRODUCTION

The sialyl Lewis x (sLe^x) determinant, NeuAc-α-(2→3)-Gal-β-(1→4)-[Fuc-α-(1→3)]-GlcNAc, has been identified[1,2] as a common carbohydrate ligand for E-, P-, and L-selectin, a family of cell adhesion molecules involved in leukocyte recruitment to sites of inflammation, thrombosis, and in lymphocyte binding to high endothelial venules (HEV) of lymph nodes during lymphocyte recirculation. Recent studies have demonstrated that Fuc-TVII, a member of α-1,3-fucosyltransferase (Fuc-T) family, is implicated in the biosynthesis of selectin ligands as a key enzyme.[3–6] Sialyl-α-(2→3)-neolactotetraose is a biosynthetic precursor which undergoes enzymatic fucosylation at C-3 of the *N*-acetylglucosamine (GlcNAc) residue to give sLe^x hexasaccharide. We have recently reported the synthesis of a series of sialyl-α-(2→3)-neolactotetraose derivatives[7,8] containing modified sialic acids and the sulfated Gal/GlcNAc residues to investigate[9] the acceptor specificity of human α-1,3-fucosyltransferases, Fuc-TVII and Fuc-TVI which show activity toward both α-2,3-sialylated and nonsialylated type-2 oligosaccharides. In the continuing study to demonstrate the detailed substrate specificity of Fuc-TVII and Fuc-TVI, we describe herein the synthesis of a variety of novel sialyl-α-(2→3)-neolactotetraose derivatives modified at C-2 of the GlcNAc residue.

RESULTS AND DISCUSSION

The key synthetic intermediate 2-(trimethylsilyl)ethyl (3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**5**) was prepared from compound **1**[10] in four steps, via removal of the acetyl groups, formation of the benzylidene acetal, benzylation, and reductive opening of the benzylidene ring. After cleavage of the phthalimido group in **5** with hydrazine monohydrate, the resulting amine derivative was treated with carbobenzoxy chloride, benzoic anhydride, butanoic anhydride, octanoic anhydride, lauric acid, and palmitic acid, respectively, in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC), to give a series of *N*-acylglucosamine-containing trisaccharide acceptors **6–11** (Scheme 1). Glycosylation of **5–11** with methyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-2,4,6-tri-*O*-benzoyl-1-thio-β-D-galactopy-

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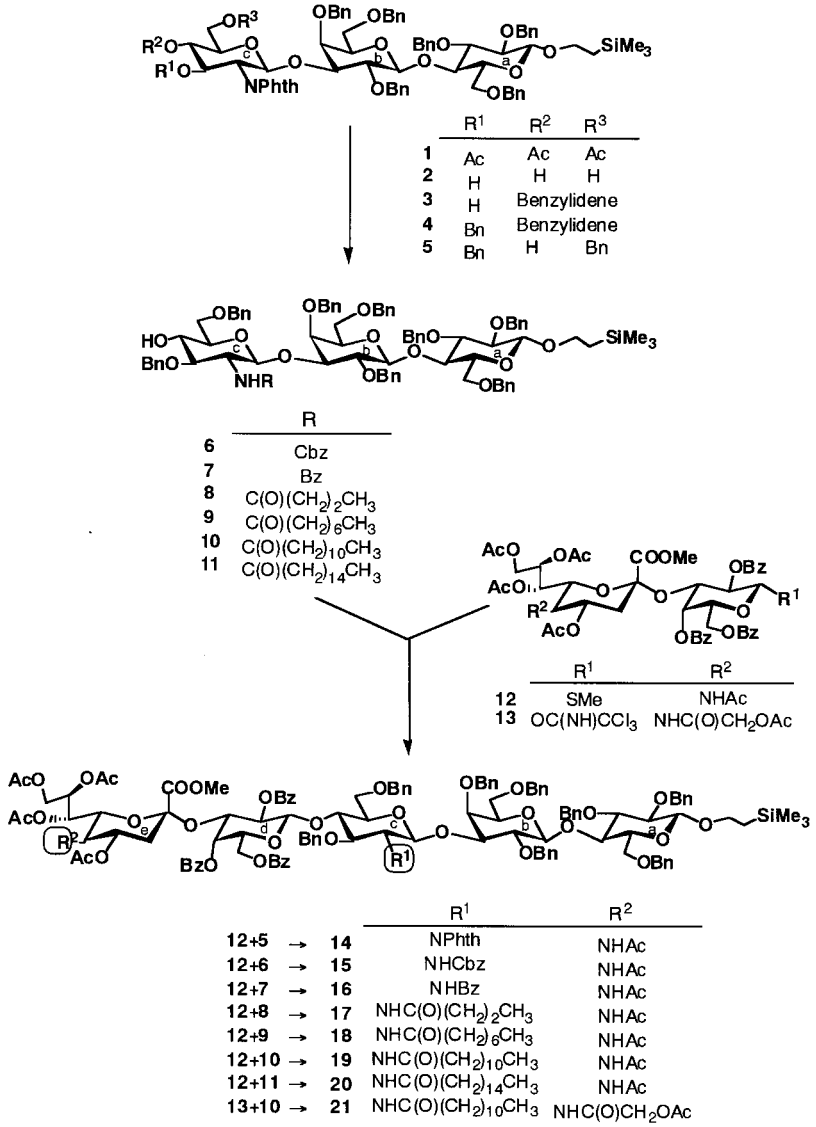

Scheme 1. Synthesis of the title compounds (1).

ranoside **12**[10] in dichloromethane in the presence of dimethyl(methylthio)sulfonium triflate (DMTST)[11,12] and powdered 4Å molecular sieves (MS4A) gave the desired pentasaccharide derivatives **14–20** in 75–85% yields, respectively (Scheme 1).

In the same way, glycosylation of **10** with *N*-glycolylneuraminyl-α-(2→3)-galactose donor **13**[7] in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) gave another pentasaccharide derivative **21** in 81% yield.

Removal of the *O*-acetyl and *O*-benzoyl groups in **15** with sodium methoxide in methanol, and subsequent saponification of the methyl ester group afforded **22**, which

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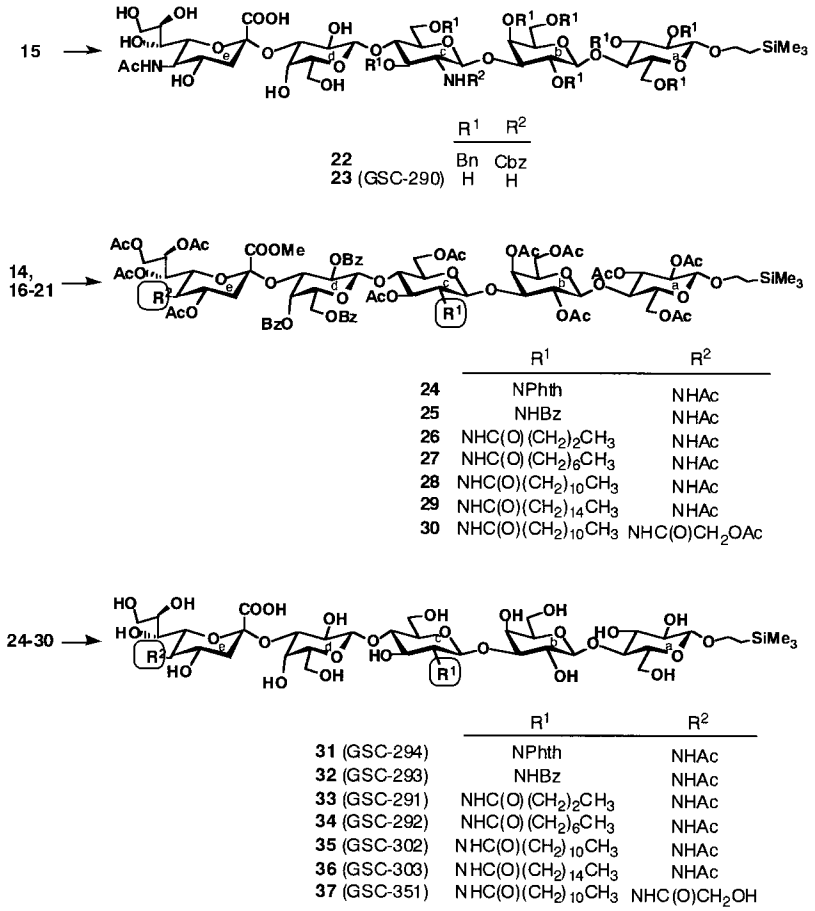
was then hydrogenolyzed over $Pd(OH)_2$ in acetic acid to give the 2-amino derivative **23** (GSC-290). On the other hand, hydrogenolytic removal of the benzyl groups in **14** and **16–21** over $Pd(OH)_2$, and subsequent treatment with acetic anhydride in pyridine gave the per-*O*-acylated pentasaccharides **24–30**, which were converted, by removal of the *O*-acyl groups and saponification of the methyl ester group, to a series of the GlcNAc-modified (*N*-acyl) sialyl-α-(2→3)-neolactotetraose derivatives **31–37** (Scheme 2).

For the synthesis of another three $IV^3NeuAcnLcOse_4$ probes (**58–60**) modified at C-2 of the GlcNAc residue, we employed 2-(trimethylsilyl)ethyl (4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside **42** as the common intermediate (Scheme 3).

Coupling of **38** and **39**[10] according to Koenigs-Knorr conditions in the presence of silver perchlorate and silver carbonate gave the expected β-glycoside **40** in 60% yield (Scheme 4). *O*-Deacetylation of **40** and the formation of benzylidene acetal in **41** gave **42**. 2,3-Di-*O*-benzylation of **42**, and reductive ring opening of the benzylidene acetal in **43** gave the desired trisaccharide acceptor **49**. In comparison, regioselective



Scheme 2. Synthesis of the title compounds (2).

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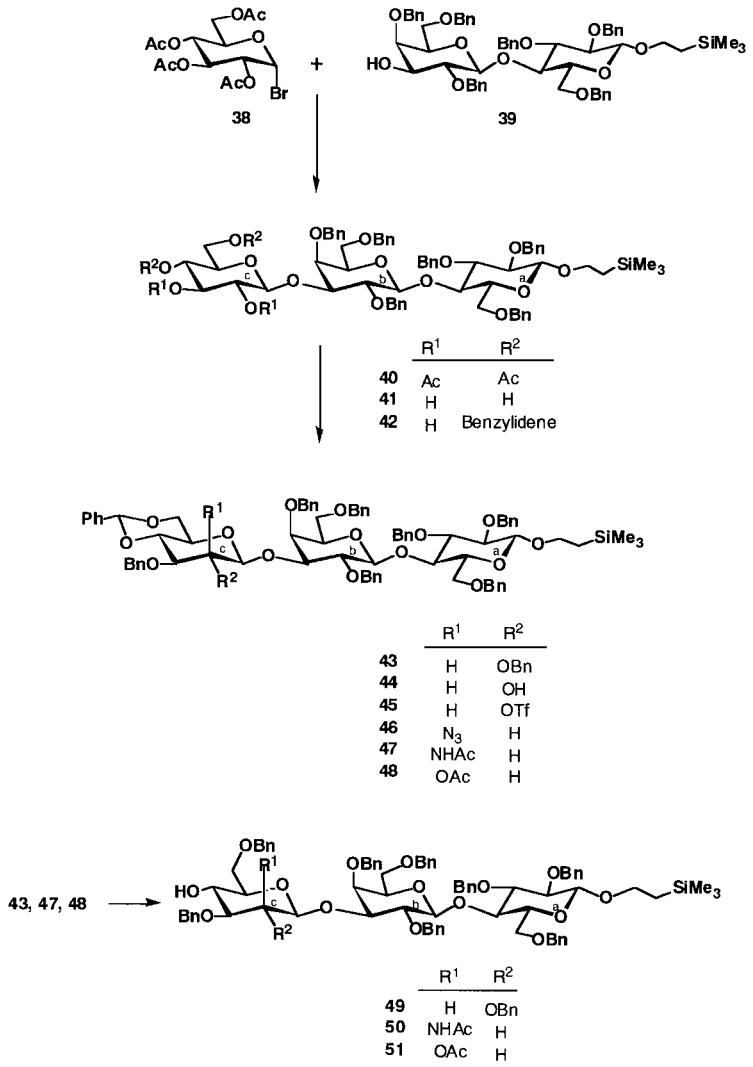

Scheme 3. Synthesis of the title compounds (3).

benzylation of **42** using phase transfer catalysis[13] afforded the 3-*O*-benzyl derivative **44** in 80% yield accompanied by the 2-*O*-benzyl derivative (11%). After introduction of the trifluoromethanesulfonyl (Tf) group of **44**, S_N2 type displacement using sodium azide or cesium acetate as a nucleophile was achieved to give the C-2 epimerized azido (**46**) and OAc (**48**) derivatives. Treatment of **46** with triphenylphosphine and water, and subsequent acetylation gave the desired trisaccharide (**47**) containing *N*-acetyl-D-mannosamine. Reductive ring opening of the benzylidene acetal in **47** and **48** gave the manno-type trisaccharide acceptors **50** and **51** (Scheme 3).

Glycosylation of **49–51** with **12** in the presence of DMTST afforded the desired pentasaccharide derivatives **52** (73%), **53** (80%), and **54** (84%), respectively, which

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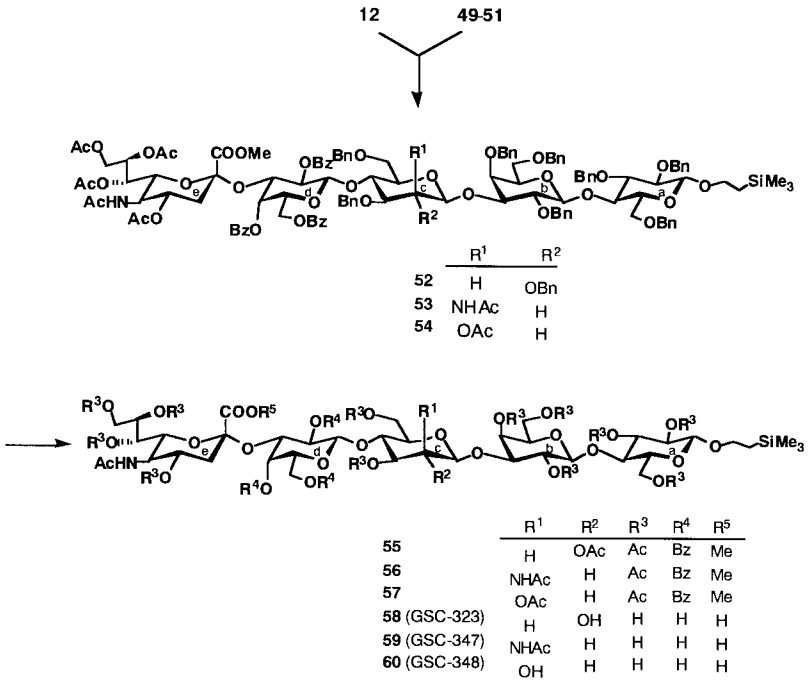

Scheme 4. Synthesis of the title compounds (4).

were converted, by catalytic hydrogenolysis over $Pd(OH)_2$ followed by *O*-acetylation to give the per–*O*-acylated pentasaccharides **55–57**. Finally, complete *O*-deacylation and saponification of the methyl ester group in **55–57** afforded the novel Glc (**58**), ManNAc (**59**) and Man (**60**) derivatives of sialyl-α-(2→3)-neolactotetraose.

The synthetic sialyl-α-(2→3)-neolactotetraose probes (**23**, **31–37**, and **58–60**) were subjected to a competitive enzyme assay[9] using human Fuc-TVII and Fuc-TVI (Scheme 5, Table 1). Substitution of the acetamido group at C-2 of GlcNAc with the lauroylamino group (**35**;GSC-302) significantly increased the relative competition (141.8%) for Fuc-TVI, while the degree for Fuc-TVII was 73.8%. It is of interest that the affinities of the compounds are dependent on the length of fatty acids introduced (**33–35**; GSC-291, 292, 302). In contrast, modifications of the acetamido group both at C-5 of *N*-acetylneuraminic acid and at C-2 of GlcNAc (**37**;GSC-351) showed almost comparable competition activity for either Fuc-TVII (102.4%) or Fuc-TVI (103.5%). In addition, modification of the acetamido group at C-2 with a bulky *N*-acyl group, such as phthalimido (**31**;GSC-294) or benzoylamino group (**32**;GSC-293) decreased the activity, significantly. Replacement of the acetamido group by the free amino (**23**;GSC-290) and hydroxyl group (**58**;GSC-323), as well as epimerization of the configuration at C-2 of GlcNAc (**59**;GSC-347, **60**;GSC-348) abolished the activity for both Fuc-TVII and Fuc-TVI. Therefore, the acylamino portion at C-2 of GlcNAc is essential for acceptor recognition and may be designated as a key functional group for both enzymes.

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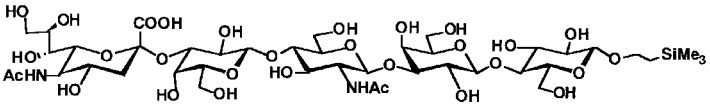
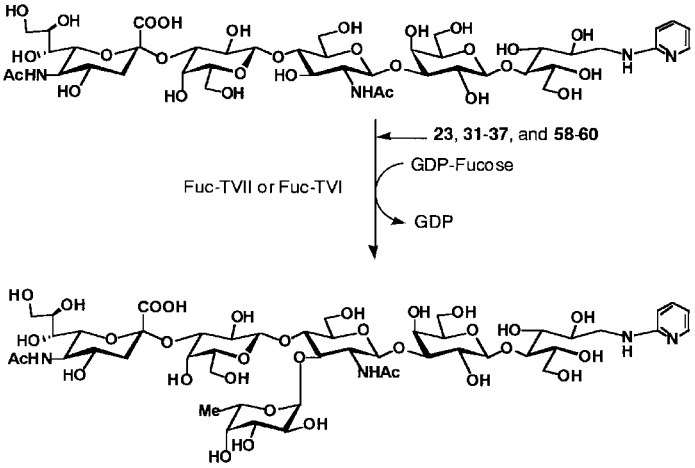


Natural-type sialyl-α-(2-3)-neolactotetraose derivative (GSC-253)



Scheme 5. Principle of competitive enzyme assay.

Table 1. Relative Competition of **23**, **31**–**37**, and **58**–**60**

	Relative Competition (%)[a]	
Compound	Fuc-TVII	Fuc-TVI
(GSC-253)	100	100
23 (GSC-290)	ND[b]	ND
31 (GSC-294)	19.5	35.3
32 (GSC-293)	20.5	40.9
33 (GSC-291)	28.4	53.1
34 (GSC-292)	44.6	104.6
35 (GSC-302)	73.8	141.8
36 (GSC-303)	9.2	25.6
37 (GSC-351)	102.4	103.5
58 (GSC-323)	ND	ND
59 (GSC-347)	ND	ND
60 (GSC-348)	ND	ND

[a]Relative competition was determined with the competition of GSC-253, in the presence of 25 mM pyridylaminated acceptor.[9]
[b]ND, Not detected (<5.0%).

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EXPERIMENTAL

General procedures. Optical rotations were determined with a Union PM-201 polarimeter at 25°C, and IR spectra were recorded with a Jasco IRA-100 spectrophotometer. ^{1}H NMR spectra were recorded at 400 or 200 MHz with a Varian Inova 400 or Varian Gemini-2000 spectrometer using deuterated solvents ($CDCl_3$, CD_3OD) with TMS as the internal standard. TLC was performed on Silica Gel 60 (E. Merck), and column chromatography on silica gel (Fuji Silysia Co., 300 mesh) was accomplished with the solvent systems (v/v) specified. Concentrations were conducted in vacuo.

2-(Trimethylsilyl)ethyl (2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (2). To a solution of **1** (6.33 g, 4.5 mmol) in MeOH (80 mL) was added a catalytic amount of NaOMe, and the mixture was stirred for 2 h at room temperature and then neutralized with Amberlite IR-120 (H^+) resin. The resin was filtered off and washed with MeOH, and the combined filtrate and washings were concentrated. Column chromatography (AcOEt:hexane = 1:1) of the residue on silica gel gave **2** (5.08 g, 88%) as a syrup; $[\alpha]_D$-19.8° (*c* 0.98, $CHCl_3$); IR (film) 3550, 2950, 1800, 1750, 860, 840, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (m, 2H, $Me_3SiCH_2CH_2$), 5.42 (d, 1H, J = 8.2 Hz, H-1c), 6.92–7.42 (m, 34H, 6Ph and NPhth).

Anal. Calcd for $C_{73}H_{83}NO_{17}Si$: C, 68.79; H, 6.56; N, 1.10. Found: C, 68.60; H, 6.33; N, 0.94.

2-(Trimethylsilyl)ethyl (4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (3). To a solution of **2** (5.0 g, 4.0 mmol) in acetonitrile (30 mL) were added Drierite (2.5 g), benzaldehyde dimethyl acetal (1.2 mL, 8.0 mmol), and catalytic amount of *p*-toluenesulfonic acid, and the reaction mixture was stirred for 2 h at room temperature. The mixture was neutralized with Na_2CO_3, and the solids were filtered off and washed with CH_2Cl_2. The combined filtrate and washings was concentrated. Column chromatography (AcOEt:hexane = 1:4) of the residue on silica gel gave **3** (4.8 g, 88%) as an amorphous mass; $[\alpha]_D$ − 21.9° (*c* 4.1, CH_2Cl_2); IR(film) 3500, 2950, 1800, 1750, 860, 840, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (m, 2H, $Me_3SiCH_2CH_2$), 5.46 (d, 1H, J = 8.4 Hz, H-1c), 5.56 (s, 1H, PhC*H*), 6.90–7.52 (m, 39H, 7Ph and NPhth).

Anal. Calcd for $C_{80}H_{87}NO_{17}Si$: C, 70.52; H, 6.44; N, 1.03. Found: C, 70.45; H, 6.42; N, 0.96.

2-(Trimethylsilyl)ethyl (3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (4). To a solution of **3** (4.8 g, 3.5 mmol) in DMF (20 mL) was added 60% NaH in oil (0.17 g, 4.2 mmol) at 0°C. After 30 min, BnBr (0.62 mL, 5.3 mmol) was added to the mixture, which was stirred for 2 h at room temperature. The mixture was extracted with AcOEt and washed with water. The organic layer was dried over Na_2SO_4 and concentrated. Column chromatography (AcOEt:hexane = 1:6) of the residue on silica gel gave **4** (4.2 g, 82%) as a syrup; $[\alpha]_D$–4.4° (*c* 0.5, CH_2Cl_2); IR (film) 2950, 1800, 1750, 860, 840, 700 cm^{-1}; ^{1}H NMR

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($CDCl_3$) δ 0.99 (m, 2H, $Me_3SiCH_2CH_2$), 5.50 (d, 1H, J = 8.3 Hz, H-1c), 5.63 (s, 1H, PhC*H*), 6.83–7.56 (m, 44H, 8Ph and NPhth).

Anal. Calcd for $C_{87}H_{93}NO_{17}Si$: C, 71.93; H, 6.45; N, 0.96. Found: C, 71.83; H, 6.31; N, 0.83.

2-(Trimethylsilyl)ethyl (3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (5). To a solution of **4** (580 mg, 0.4 mmol) in THF (5 mL) was added MS3A (300 mg), and the reaction mixture was stirred for 3 h at room temperature. Sodium cyanoborohydride (380 mg, 6.0 mmol) was added to the mixture, and then hydrogen chloride in diethyl ether was added dropwise to the stirred mixture, with stirring being continued for 30 min. The mixture was neutralized with Et_3N and diluted with CH_2Cl_2 and water. The solids were removed through celite, and the filtrate was washed with water. The organic layer was dried over Na_2SO_4 and concentrated. Column chromatography (AcOEt:hexane = 1:4) of the residue on silica gel gave **5** (510 mg, 88%) as a syrup; $[\alpha]_D - 8.1°$ (*c* 7.0, CH_2Cl_2); IR(film) 3500, 2950, 1800, 1750, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (m, 2H, $Me_3SiCH_2CH_2$), 5.43 (d, 1H, J = 7.9 Hz, H-1c), 7.00–7.74 (m, 44H, 8Ph and NPhth).

Anal. Calcd for $C_{87}H_{95}NO_{17}Si$: C, 71.83; H, 6.58; N, 0.96. Found: C, 71.72; H, 6.58; N, 0.73.

2-(Trimethylsilyl)ethyl (3,6-di-*O*-benzyl-2-carbobenzyloxyamino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (6). To a solution of **5** (260 mg, 0.18 mmol) in ethanol (10 mL) was added hydrazine monohydrate (0.4 mL, 7.2 mmol), and the reaction mixture was stirred for 36 h under reflux. After completion of the reaction, the mixture was concentrated, and the residue was treated with carbobenzoxy chloride (30 μL, 0.2 mmol) in acetone (8 mL) and sat Na_2CO_3 (1 mL) for 12 h at room temperature. The mixture was concentrated and the residue was taken up in CH_2Cl_2, and washed with water, dried (Na_2SO_4), and concentrated. Column chromatography (AcOEt:hexane = 1:3) of the residue on silica gel gave **6** (248 mg, 95%) as an amorphous mass; $[\alpha]_D - 9.0°$ (*c* 2.5, CH_2Cl_2); IR (KBr) 3400, 2900, 1720, 1606, 1587, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 4.84 (d, 1H, J = 9.2 Hz, NH), 5.08(d, 1H, J = 7.69 Hz, H-1c), 7.12–7.37(m, 45H, 9Ph).

Anal. Calcd for $C_{83}H_{97}NO_{17}Si$: C, 70.81; H, 6.70; N, 0.96. Found: C, 70.80; H, 6.60; N, 0.67.

2-(Trimethylsilyl)ethyl (2-benzoylamino-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (7). To a solution of **5** (780 mg, 0.54 mmol) in ethanol (20 mL) was added hydrazine monohydrate (0.6 mL, 13.0 mmol) and then the reaction mixture was refluxed for 48 h as described for **6**. The mixture was concentrated, and the residue was treated with benzoic anhydride (0.5 g, 1.1 mmol) in MeOH (10 mL) for 12 h at room temperature. After completion of the reaction, the mixture was concentrated, and the residue was taken up in CH_2Cl_2, washed with 2 M HCl, sat Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (CH_2Cl_2:MeOH = 100:1) of the residue on silica gel gave **7** (522 mg, 68%) as an amorphous mass;

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$[\alpha]_D - 16.1°$ (*c* 2.8, CH_2Cl_2); IR (film) 3400, 2950, 1650, 1550, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 5.79 (d, 1H, J = 8.33 Hz, NH), 7.02–7.42 (m, 45H, 9Ph).

Anal. Calcd for $C_{86}H_{97}NO_{16}Si$: C, 72.29; H, 6.84; N, 0.98. Found: C, 72.14; H, 6.56; N, 0.81.

2-(Trimethylsilyl)ethyl (3,6-di-*O*-benzyl-2-butanoylamino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (8). Compound **5** (830 mg, 0.56 mmol) was treated with hydrazine monohydrate (0.27 mL, 5.6 mmol) as described for **6**, and the resulting amine was treated with butanoic anhydride (0.36 mL, 2.24 mmol) in MeOH (8 mL) for 2 h at room temperature. Work-up and column chromatography as described for **7** gave **8** (792 mg, 98%); $[\alpha]_D - 10°$ (*c* 2.9, CH_2Cl_2); IR (film) 3400, 2950, 1670, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (t, 3H, $CH_3CH_2CH_2C(O)NH$), 1.02 (m, 2H, $Me_3SiCH_2CH_2$), 1.42 (m, 2H, $CH_3CH_2CH_2C(O)NH$), 1.60 (m, 2H, $CH_3CH_2CH_2C(O)NH$), 7.11–7.64 (m, 40H, 8Ph).

Anal. Calcd for $C_{83}H_{99}NO_{16}Si$: C, 71.47; H, 7.15; N, 1.00. Found: C, 71.44; H, 6.90; N, 0.75.

2-(Trimethylsilyl)ethyl (3,6-di-*O*-benzyl-2-deoxy-2-octanoylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (9). The phthalimido group of **5** (500 mg, 0.34 mmol) was cleaved in ethanol (6 mL) by treatment with hydrazine monohydrate (0.17 mL, 3.4 mmol) as described for **6**, and the resulting amine was reacted with octanoic anhydride (0.41 mL, 1.4 mmol) in MeOH (5 mL) for 12 h at room temperature. Work-up and column chromatography as described for **7** gave **9** (417 mg, 84%) as a syrup; $[\alpha]_D - 8.7°$ (*c* 8.3, CH_2Cl_2); IR (film) 3400, 2950, 1660, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (t, 3H, $CH_3(CH_2)_5CH_2C(O)NH$), 1.03 (m, 2H, $Me_3SiCH_2CH_2$), 1.26 (m, 10H, $CH_3(CH_2)_5CH_2C(O)NH$), 1.60 (m, 2H, $CH_3(CH_2)_5CH_2C(O)NH$), 7.15–7.68 (m, 40H, 8Ph).

Anal. Calcd for $C_{87}H_{107}NO_{16}Si$: C, 72.02; H, 7.43; N, 0.97. Found: C, 71.78; H, 7.05; N, 0.90.

2-(Trimethylsilyl)ethyl (3,6-di-*O*-benzyl-2-deoxy-2-lauroylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (10). The amine obtained from **5** (300 mg, 0.21 mmol) as described for **6**, was treated with lauric acid (210 mg, 1.05 mmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC;200 mg, 1.05 mmol) in CH_2Cl_2 (10 mL) for 12 h at room temperature. After completion of the reaction, the mixture was concentrated and the residue was taken up in CH_2Cl_2, and washed with sat Na_2CO_3, 2M HCl and water, dried (Na_2SO_4), and concentrated. Column chromatography (AcOEt:hexane = 1:3) of the residue on silica gel gave **10** (295 mg, 95%) as a syrup; $[\alpha]_D - 8.0°$ (*c* 1.0, CH_2Cl_2); IR (film) 3400, 2950, 1660, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3H, $CH_3(CH_2)_9CH_2C(O)NH$), 0.97 (m, 2H, $Me_3SiCH_2CH_2$), 1.05–1.32 (m, 18H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.63 (m, 2H, $CH_3(CH_2)_9CH_2C(O)NH$), 4.99 (d, 1H, J = 10.4 Hz, NH), 7.07–7.32 (m, 40H, 8Ph).

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Anal. Calcd for $C_{91}H_{115}NO_{16}Si$: C, 72.53; H, 7.69; N, 0.93. Found: C, 72,24; H, 7.55; N, 0.87.

2-(Trimethylsilyl)ethyl (3,6-di-*O*-benzyl-2-deoxy-2-palmitoylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (11). Compound **5** (300 mg, 0.21 mmol) in ethanol (20 mL) was treated with hydrazine monohydrate (0.56 mL, 8.4 mmol) as described for **6**. The resulting amine was reacted with palmitic acid (197 mg, 1.05 mmol) and WSC (264 mg, 1.05 mmol) in CH_2Cl_2 (20 mL) for 36 h at room temperature. Work-up and column chromatography as described for **10** gave **11** (304 mg, 94%) as a syrup; $[\alpha]_D - 8.7°$ (*c* 1.2, CH_2Cl_2); IR (film) 3400, 2950, 1660, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 1.02 (m, 2H, $Me_3SiCH_2CH_2$), 1.13–1.26 (m, 26H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 1.63 (m, 2H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 5.00 (d, 1H, J = 9.7 Hz, NH), 7.08–7.32 (m, 40H, 8Ph).

Anal. Calcd for $C_{95}H_{123}NO_{16}Si$: C, 73.00; H, 7.93; N, 0.90. Found: C, 72.73; H, 7.84; N, 0.82.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (14). To a solution of **12** (103 mg, 0.10 mmol) and **5** (100 mg, 0.069 mmol) in CH_2Cl_2 (2 mL) was added MS4A (100 mg) and the reaction mixture was stirred for 6 h at room temperature, then cooled to 0°C. A mixture of dimethyl(methylthio)sulfonium triflate (DMTST; 110 mg, 0.41 mmol) and MS4Å (90 mg) was added, and the reaction mixture was stirred for 24 h at 7°C, being monitored by TLC. The solids were collected and washed with CH_2Cl_2. The filtrate and washings were combined, and washed with sat Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (CH_2Cl_2:MeOH = 100:1) of the residue on silica gel gave **14** (113 mg, 68.9%) as an amorphous mass; $[\alpha]_D + 14.4°$ (*c* 2.1, CH_2Cl_2); IR(film) 3400, 2950, 1760, 1550, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (m, 2H, $Me_3SiCH_2CH_2$), 1.53 (s, 3H, AcN), 1.80, 1.94, 1.99, 2.17 (4s, 12H, 4AcO), 2.48 (dd, 1H, J = 12.6, 4.21 Hz, H-3e(eq)), 3.84 (s, 3H, MeO), 5.37 (~d, 1H, J = 3.2 Hz, H-4d), 5.57 (t, 1H, $J_{1,2} = J_{2,3} = 9.7$ Hz, H-2d), 5.74 (m, 1H, H-8e), 7.00–8.06 (m, 59H, 11Ph, NPhth).

Anal. Calcd for $C_{134}H_{144}N_2O_{37}Si$: C, 66.99; H, 6.04; N, 1.17. Found: C, 66.79; H, 5.91; N, 1.14.

Coupling of **12** (0.2 mmol) with **6–11** (0.15 mmol) performed as described for **14** gave **15** (86.5%), **16** (74.5%), **17** (78.4%), **18** (76%), **19** (64%), and **20** (75.4%), respectively.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-carbobenzoxyamino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (15). An amorphous mass; $[\alpha]_D + 4.3°$ (*c* 3.0, CH_2Cl_2);

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IR(KBr) 3400, 2920, 1740, 1680, 1515, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 1.48 (s, 3H, AcN), 1.75, 1.90, 1.95, 2.13 (4s, 12H, 4AcO), 2.44 (dd, 1H, J = 12.5, 4.22 Hz, H-3e(eq)), 3.80 (s, 3H, MeO), 4.80 (m, 1H, H-4e), 5.33 (d, 1H, $J_{3,4}$ = 3.4 Hz, H-4d), 5.50 (t, 1H, $J_{1,2} = J_{2,3}$ = 9.4 Hz, H-2d), 5.69 (m, 1H, H-8e), 7.01–8.25 (m, 60H, 12Ph).

Anal. Calcd for $C_{133}H_{146}N_2O_{37}Si$: C, 66.76; H, 6.15; N, 1.17. Found: C, 66.51; H, 5.91; N, 0.82.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(2-benzoylamino-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (16). An amorphous mass; $[\alpha]_D$ + 3.1° (*c* 1.8, CH_2Cl_2); IR (film) 3400, 2950, 1750, 1660, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 1.50 (s, 3H, AcN), 1.78, 1.92, 1.97, 2.15 (4s, 12H, 4AcO), 2.47 (dd, 1H, J = 12.3, 4.3 Hz, H-3e(eq)), 3.83 (s, 3H, MeO), 5.23 (dd, 1H, $J_{6,7}$ = 2.5 Hz, $J_{7,8}$ = 9.6 Hz, H-7e), 5.38 (d, 1H, $J_{3,4}$ = 2.7 Hz, H-4d), 5.53 (t, 1H, $J_{1,2} = J_{2,3}$ = 9.7 Hz, H-2d), 5.71 (m, 1H, H-8e), 6.11 (d, 1H, J = 8.6 Hz, NH), 6.95–8.02 (m, 60H, 12Ph).

Anal. Calcd for $C_{133}H_{146}N_2O_{36}Si$: C, 67.21; H, 6.19; N, 1.18. Found: C, 67.17; H, 6.18; N, 1.14.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-butanoylamino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (17). An amorphous mass; $[\alpha]_D$ + 3.4° (*c* 1.3, CH_2Cl_2); IR (film) 3350, 2950, 1750, 1660, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (t, 3H, $CH_3CH_2CH_2C(O)NH$), 1.03 (m, 2H, $Me_3SiCH_2CH_2$) 1.36 (m, 2H, $CH_3CH_2CH_2C(O)NH$), 1.51 (s, 3H, AcN), 1.64 (m, 2H, $CH_3CH_2CH_2C(O)NH$), 1.75, 1.89, 1.95, 2.15 (4s, 12H, 4AcO), 2.47 (dd, 1H, J = 12.6, 4.39 Hz, H-3e(eq)), 3.81 (s, 3H, MeO), 5.38 (d, 1H, $J_{3,4}$ = 3.2 Hz, H-4d), 5.50 (t, 1H, $J_{1,2} = J_{2,3}$ = 10.9 Hz, H-2d), 5.71 (m, 1H, H-8e), 7.08–8.04 (m, 55H, 11Ph).

Anal. Calcd for $C_{130}H_{148}N_2O_{36}Si$: C, 66.65; H, 6.37; N, 1.20. Found: C, 66.43; H, 6.26; N, 1.09.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-deoxy-2-octanoylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (18). An amorphous mass; $[\alpha]_D$ + 3.3° (*c* 5.0, $CHCl_3$); IR (film) 3350, 2950, 1740, 1660, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (t, 3H, J = 6.9 Hz, $CH_3(CH_2)_5CH_2C(O)NH$), 0.99 (m, 2H, $Me_3SiCH_2CH_2$), 1.22 (m, 10H, $CH_3(CH_2)_5CH_2C(O)NH$), 1.52 (s, 3H, AcN), 1.67 (m, 2H, $CH_3(CH_2)_5CH_2C(O)NH$), 1.78, 1.92, 1.97, 2.16 (4s, 12H, 4AcO), 2.45 (dd, 1H, J = 12.5, 4.0 Hz, H-3e(eq)), 3.83 (s, 3H, MeO), 5.38 (d, 1H, $J_{3,4}$ = 3.0 Hz, H-4d), 5.54 (t, 1H, $J_{1,2} = J_{2,3}$ = 9.9 Hz, H-2d), 5.70 (m, 1H, H-8e), 7.06–8.05 (m, 55H, 11Ph).

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Anal. Calcd for $C_{134}H_{156}N_2O_{36}Si$: C, 67.10; H, 6.56; N, 1.17. Found: C, 66.93; H, 6.48; N, 1.08.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-deoxy-2-lauroylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (19). An amorphous mass; $[\alpha]_D + 4.9°$ (*c* 0.41, CH_2Cl_2); IR (film) 3400, 2950, 1740, 1660, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 1.23 (m, 18H, $CH_3(CH_2)_9CH_2C(O)N$ H), 1.49 (s, 3H, AcN), 1.63 (m, 2H, $CH_3(CH_2)_9CH_2C(O)N$ H), 1.78, 1.92, 1.96, 2.14 (4s, 12H, 4AcO), 2.45 (dd, 1H, J = 12.1, 4.23 Hz, H-3e(eq)), 3.82 (s, 3H, MeO), 5.34 (d, 1H, $J_{3,4} = 3.2$ Hz, H-4d), 5.47 (t, 1H, $J_{1,2} = J_{2,3} = 10.2$ Hz, H-2d), 5.72 (m, 1H, H-8e), 7.03–8.07 (m, 55H, 11Ph).

Anal. Calcd for $C_{138}H_{164}N_2O_{36}Si$: C, 67.52; H, 6.73; N, 1.14. Found: C, 67.29; H, 6.62; N, 0.92.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-deoxy-2-palmitoylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (20). An amorphous mass; $[\alpha]_D + 3.3°$ (*c* 0.48, CH_2Cl_2); IR (film) 3350, 2950, 1740, 1660, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.25 (m, 26H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 1.49 (s, 3H, AcN), 1.66 (m, 2H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 1.78, 1.92, 1.96, 2.14 (4s, 12H, 4AcO), 2.45 (dd, 1H, J = 12.6, 4.0 Hz, H-3e(eq)), 3.82 (s, 3H, MeO), 5.34 (d, 1H, $J_{3,4} = 2.7$ Hz, H-4d), 5.48 (t, 1H, $J_{1,2} = J_{2,3} = 10.2$ Hz, H-2d), 5.68 (m, 1H, H-8e), 7.04–8.09 (m, 55H, 11Ph).

Anal. Calcd for $C_{142}H_{172}N_2O_{36}Si$: C, 67.92; H, 6.90; N, 1.12. Found: C, 67.72; H, 6.71; N, 0.89.

2-(Trimethylsilyl)ethyl (methyl 5-acetoxyacetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-deoxy-2-lauroylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (21). To a solution of **13** (132 mg, 0.12 mmol) and **10** (150 mg, 99 μmol) in CH_2Cl_2 (1 mL) was added MS4A (150 mg), the reaction mixture was stirred for 3 h at room temperature and then cooled to 0°C. To the mixture was added TMSOTf (3.8 μL, 19.9 μmol), and the reaction mixture was stirred for 12 h at 0°C, being monitored by TLC. The solids were collected and washed with CH_2Cl_2, and the filtrate and washings were combined and washed with sat Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (CH_2Cl_2:MeOH = 80:1) of the residue on silica gel gave **21** (200 mg, 81%) as an amorphous mass; $[\alpha]_D + 2.8°$ (*c* 1.6, $CHCl_3$); IR (film) 3400, 2950, 1750, 1660, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 1.21 (m, 18H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.47 (m, 2H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.77, 1.89,

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1.96, 2.14, 2.15 (5s, 15H, 5AcO), 2.46 (dd, 1H, J = 12.5, 4.39 Hz, H-3e(eq)), 3.83 (s, 3H, MeO), 4.20, 4.46 (2d, 2H, J_{gem} = 15.4 Hz, AcOCH_2C(O)NH), 5.17 (dd, 1H, J = 2.56, 9.52 Hz, H-7e), 5.34 (d, 1H, J = 3.29 Hz, H-4d), 5.48 (dd, 1H, J = 8.06, 9.88 Hz, H-2d), 5.68 (m, 1H, H-8e), 5.72 (d, 1H, $J_{NH,5}$ = 10.0 Hz, NH), 7.01–8.24 (m, 55H, 11Ph).

Anal. Calcd for $C_{140}H_{166}N_2O_{38}Si$: C, 66.92; H, 6.66; N, 1.11. Found: C, 66.86; H, 6.44; N, 1.08.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-(β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-carbobenzyloxyamino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (22). To a solution of **15** (136 mg, 57 μmol) in MeOH (8 mL) was added a catalytic amount of sodium methoxide, the reaction mixture was stirred for 12 h at room temperature and then water was added. After completion of the reaction, it was neutralized with Amberlite IR-120(H^+) resin. The resin was filtered off and washed with MeOH, and the combined filtrate and washings was concentrated. Column chromatography (MeOH) of the residue on Sephadex LH-20 gave **22** (108 mg, 95%) as an amorphous mass; $[\alpha]_D$ − 6.2° (*c* 0.45, MeOH); IR (KBr) 3400, 2950, 1730, 1620, 1560, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 2.00 (s, 3H, AcN), 2.89 (dd, 1H, J = 12.5, 4.2 Hz, H-3e(eq)), 7.06–7.27 (m, 45H, 9Ph).

Anal. Calcd for $C_{103}H_{124}N_2O_{30}Si$: C, 65.17; H, 6.58; N, 1.48. Found: C, 65.11; H, 6.49; N, 1.35.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-β-D-galactopyranosyl-(1 → 4)-(2-amino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (23). A solution of **22** (108 mg, 57 μmol) in acetic acid (8 mL) was treated with hydrogen over $Pd(OH)_2$ (110 mg) for 5 days at 40°C. The solid was filtered off and the filtrate was concentrated. Column chromatography (MeOH:H_2O = 1:1) of the residue on Sephadex LH-20 gave **23** (43 mg, 73%) as an amorphous mass (ninhydrin positive); $[\alpha]_D$ − 0.46° (*c* 0.87, MeOH); IR (KBr) 3400, 2900, 1670, 1590, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 2.00 (s, 3H, AcN), 2.89 (dd, 1H, J = 12.5, 4.22 Hz, H-3e(eq)).

Anal. Calcd for $C_{40}H_{72}N_2O_{28}Si$: C, 45.45; H, 6.87; N, 2.65. Found C, 45.37; H, 6.63; N, 2.43.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (24). A solution of **14** (113 mg, 47 μmol) in acetic acid (2 mL) and EtOH (12 mL) was treated with hydrogen over Pd-C (113 mg) for 5 days at 40°C. The solid was filtered off and the filtrate was concentrated. The residue was acetylated with acetic anhydride (0.15 mL) in pyridine (1.5 mL) for 12 h at room temperature. The mixture was diluted with CH_2Cl_2, and the solution was washed with 2 M HCl and water, dried (Na_2SO_4) and concentrated. Column chromatography

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(CH_2Cl_2:MeOH = 50:1) of the residue on silica gel gave **24** (74 mg, 78%) as an amorphous mass; $[\alpha]_D + 25.7°$ (*c* 1.5, $CHCl_3$); IR (film) 3450, 2950, 1740, 1520, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (m, 2H, $Me_3SiCH_2CH_2$), 1.57 (s, 3H, AcN), 1.80–2.14 (s, 36H, 12AcO), 2.46 (dd, 1H, J = 11.7, 4.02 Hz, H-3e(eq)), 3.73 (s, 3H, MeO), 5.68 (m, 1H, H-8e), 7.49–8.21 (m, 19H, 3Ph, NPhth).

Anal. Calcd for $C_{94}H_{112}N_2O_{45}Si$: C, 55.95; H, 5.59; N, 1.39. Found: C, 55.79; H, 5.55; N, 1.23.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-acetyl-2-benzoylamino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (25). A solution of **16** (246 mg, 104 μmol) in acetic acid (2 mL) and EtOH (15 mL) was treated with hydrogen over Pd-C (250 mg) for 3 days at 40°C. Work-up, acetylation of the free hydroxyls, and column chromatography as described for **24** gave **25** (138 mg, 67%) as an amorphous mass; $[\alpha]_D + 18.1°$ (*c* 0.54, $CHCl_3$); IR (film) 3400, 2950, 1750, 1650, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (m, 2H, $Me_3SiCH_2CH_2$), 1.55 (s, 3H, AcN), 1.78–2.14 (s, 36H, 12AcO), 2.50 (dd, 1H, J = 12.6, 4.39 Hz, H-3e(eq)), 3.82 (s, 3H, MeO), 5.63 (m, 1H, H-8e), 7.40–8.22 (m, 20H, 3OBz, NHBz).

Anal. Calcd for $C_{93}H_{114}N_2O_{44}Si$: C, 56.08; H, 5.77; N, 1.41. Found: C, 56.06; H, 5.74; N, 1.14.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-acetyl-2-butanoylamino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (26). Hydrogenolysis of **17** (392 mg, 168 μmol) in acetic acid (1.5 mL) and EtOH (10 mL) was performed over Pd-C (400 mg) for 3 days at 40°C. The residue was acetylated with acetic anhydride (0.21 mL) in pyridine (2 mL) for 12 h at room temperature. Work-up, acetylation, and column chromatography as described for **24** gave **26** (253 mg, 77%) as an amorphous mass; $[\alpha]_D + 18.3°$ (*c* 5.1, $CHCl_3$); IR (film) 3350, 2950, 1740, 1660, 1530, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 6.9 Hz, $CH_3CH_2CH_2C(O)NH$), 0.95 (m, 2H, $Me_3SiCH_2CH_2$), 1.54 (m, 2H, $CH_3CH_2CH_2C(O)NH$), 1.58 (s, 3H, AcN), 1.76 (m, 2H, $CH_3CH_2CH_2C(O)NH$), 1.90–2.12 (s, 36H, 12AcO), 2.46 (dd, 1H, J = 12.4, 4.02 Hz, H-3e(eq)), 3.70 (s, 3H, MeO), 5.62 (m, 1H, H-8e), 7.39–8.20 (m, 15H, 3Bz).

Anal. Calcd for $C_{90}H_{116}N_2O_{44}Si$: C, 55.21; H, 5.97; N, 1.43. Found: C, 55.15; H, 5.72; N, 1.31.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-acetyl-2-deoxy-2-octanoylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (27). Hydrogenolysis of **18** (249 mg, 104 μmol) in EtOH (15 mL) was performed over $Pd(OH)_2$ (250 mg) for 12 h at 40°C, and the product was acetylated as described for **24** to give **27** (191 mg, 92%) as an amorphous

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mass; $[\alpha]_D + 10.3°$ (*c* 0.87, $CHCl_3$); IR (KBr) 3400, 2960, 1750, 1690, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, 3H, $CH_3(CH_2)_5CH_2C(O)NH$), 0.97 (m, 2H, $Me_3SiCH_2CH_2$), 1.25 (m, 10H, $CH_3(CH_2)_5CH_2C(O)NH$), 1.53 (s, 3H, AcN), 1.77 (m, 2H, $CH_3(CH_2)_5CH_2C(O)NH$), 1.91–2.13 (s, 36H, 12AcO), 2.46 (dd, 1H, J = 12.4, 4.30 Hz, H-3e(eq)), 3.81 (s, 3H, MeO), 5.63 (m, 1H, H-8e), 7.43–8.20 (m, 15H, 3Ph).

Anal. Calcd for $C_{94}H_{124}N_2O_{44}Si$: C, 56.06; H, 6.21; N, 1.39. Found: C, 55.90; H, 5.94; N, 1.39.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-acetyl-2-deoxy-2-lauroylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (28). Hydrogenolysis of **19** (380 mg, 160 μmol) and subsequent acetylation as described for **27** gave **28** (279 mg, 87%) as an amorphous mass; $[\alpha]_D + 22.4°$ (*c* 0.41, CH_2Cl_2); IR (film) 3450, 2950, 1750, 1660, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, 3H, $CH_3(CH_2)_9CH_2C(O)NH$), 0.90 (m, 2H, $Me_3SiCH_2CH_2$), 1.23 (m, 18H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.52 (s, 3H, AcN), 1.56 (m, 2H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.73–2.14 (s, 36H, 12AcO), 2.45 (dd, 1H, J = 12.1, 4.23 Hz, H-3e(eq)), 3.87 (s, 3H, MeO), 5.78 (m, 1H, H-8e), 7.43–8.19 (m, 15H, 3Ph).

Anal. Calcd for $C_{98}H_{132}N_2O_{44}Si$: C, 56.86; H, 6.43; N, 1.35. Found: C, 56.67; H, 6.34; N, 1.31.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-acetyl-2-deoxy-2-palmitoylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (29). Hydrogenolysis of **20** (345 mg, 140 μmol) and subsequent acetylation as described for **27** gave **29** (249 mg, 86%) as an amorphous mass; $[\alpha]_D + 21.9°$ (*c* 0.42, CH_2Cl_2); IR (film) 3400, 2950, 1740, 1660, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, 3H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 0.91 (m, 2H, $Me_3SiCH_2CH_2$), 1.22 (m, 26H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 1.53 (s, 3H, AcN), 1.55 (m, 2H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 1.78–2.10 (s, 36H, 12AcO), 2.49 (dd, 1H, J = 12.6, 4.02 Hz, H-3e(eq)), 3.87 (s, 3H, MeO), 5.61 (m, 1H, H-8e), 7.42–8.23 (m, 3H, 15Ph).

Anal. Calcd for $C_{102}H_{140}N_2O_{44}Si$: C, 57.62; H, 6.64; N, 1.32. Found: C, 57.38; H, 6.38; N, 1.26.

2-(Trimethylsilyl)ethyl (methyl 5-acetoxyacetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-acetyl-2-deoxy-2-lauroylamino-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (30). Hydrogenolysis of **21** (183 mg, 74 μmol) and subsequent acetylation as described for **27** gave **30** (133 mg, 86%) as an amorphous mass; $[\alpha]_D + 9.2°$ (*c* 1.3, $CHCl_3$); IR (film) 3400, 2950, 1750, 1660, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, 3H, J = 6.9 Hz, $CH_3(CH_2)_9CH_2C(O)NH$), 0.93 (m, 2H, $Me_3SiCH_2CH_2$), 1.23 (m, 18H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.51 (m, 2H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.58 (t, 1H, J = 12.6 Hz, H-3e(ax)), 1.87–2.13 (s, 39H,

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13AcO), 2.47 (dd, 1H, J = 12.6, 4.35 Hz, H-3e(eq)), 3.82 (s, 3H, MeO), 4.19, 4.45 (2d, 2H, J_{gem} = 15.3 Hz, AcOCH_2C(O)NH), 5.20 (dd, 1H, J = 2.74, 9.61 Hz, H-7e), 5.35 (d, 1H, J = 3.20 Hz, H-4d), 5.38 (dd, 1H, J = 8.01, 10.1 Hz, H-2d), 5.62 (m, 1H, H-8e), 5.66 (d, 1H, $J_{NH,5}$ = 10.5 Hz, NH), 7.44–8.17 (m, 15H, 3Ph).

Anal. Calcd for $C_{100}H_{134}N_2O_{46}Si$: C, 56.44; H, 6.35; N, 1.32. Found: C, 56.28; H, 6.28; N, 1.08.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-β-D-galactopyranosyl-(1 → 4)-(2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (31). To a solution of **24** (82 mg, 41 μmol) in MeOH (5 mL) was added a catalytic amount of sodium methoxide, the reaction mixture was stirred for 24 h at room temperature and then water was added. After completion of the reaction, the solution was neutralized with Amberlite IR-120 (H^+) resin. The resin was filtered off and washed with MeOH. The combined filtrate and washings was concentrated to a residue, which was chromatographed ($CHCl_3$:MeOH = 3:2) on a column of silica gel to give **31** (35 mg, 73%) as an amorphous mass; $[\alpha]_D$ −4.8° (*c* 0.12, MeOH:H_2O = 1:1); IR (KBr) 3550, 300, 2930, 1630, 1560, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 1.97 (s, 3H, AcN), 2.81 (dd, 1H, J = 11.8, 2.81 Hz, H-3e(eq)), 7.40–7.87 (m, 4H, NPhth).

Anal. Calcd for $C_{48}H_{74}N_2O_{30}Si$: C, 48.56; H, 6.28; N, 2.36. Found: C, 48.50; H, 6.01; N, 2.36.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-β-D-galactopyranosyl-(1 → 4)-(2-benzoylamino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (32). To a solution of **25** (138 mg, 70 μmol) in MeOH (5 mL) was added sodium methoxide, the reaction mixture was stirred for 7 days at room temperature then water was added. Work-up and column chromatography (MeOH:H_2O = 1:1) of the residue on Sephadex LH-20 gave **32** (77 mg, 96%) as an amorphous mass; $[\alpha]_D$ −6.5° (*c* 0.77, MeOH); IR (KBr) 3550, 3350, 2930, 1620, 1560, 860, 840, 700 cm^{-1}; ^1H NMR (CD_3OD) δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 1.88 (s, 3H, AcN), 2.85 (dd, 1H, J = 12.6, 4.39 Hz, H-3e(eq)), 7.40–7.87 (m, 5H, NHBz).

Anal. Calcd for $C_{47}H_{76}N_2O_{29}Si$: C, 48.61; H, 6.60; N,2.41. Found: C, 48.38; H, 6.51; N, 2.17.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-β-D-galactopyranosyl-(1 → 4)-(2-butanoylamino-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (33). To a solution of **26** (252 mg, 130 μmol) in MeOH (2 mL) was added sodium methoxide, the reaction mixture was stirred for 6 days at 35°C and then water was added. Work-up and column chromatography as described for **32** gave **33** (98 mg, 68%) as an amorphous mass; $[\alpha]_D$ −14.6° (*c* 0.53, MeOH); IR (KBr) 3550, 3400, 2940, 1640, 1560, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 0.95 (t, 3H, $CH_3CH_2CH_2C(O)NH$), 1.04 (m, 2H, $Me_3SiCH_2CH_2$), 1.63 (m, 2H, CH_3CH_2-$CH_2C(O)NH$), 1.99 (s, 3H, AcN), 2.20 (m, 2H, $CH_3CH_2CH_2C(O)NH$), 2.81 (dd, 1H, J = 12.4, 4.02 Hz, H-3e(eq)).

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Anal. Calcd for $C_{44}H_{78}N_2O_{29}Si$: C, 46.89; H, 6.98; N,2.49. Found: C, 46.68; H, 6.73; N, 2.20.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-β-D-galactopyranosyl-(1 → 4)-(2-deoxy-2-octanoylamino-β-D-glucopyranosyl)-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (34). To a solution of **27** (191 mg, 100 μmol) in MeOH (5 mL) was added sodium methoxide, the reaction mixture was stirred for 5 days at room temperature and then water was added. Work-up as described for **32** gave **34** (67 mg, 60%) as an amorphous mass; $[\alpha]_D - 8.2°$ (*c* 0.25, MeOH); IR (KBr) 3550, 3400, 2930, 1640, 1560, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 0.87 (t, 3H, $CH_3(CH_2)_5CH_2C(O)NH$), 0.97 (m, 2H, $Me_3SiCH_2CH_2$), 1.29 (m, 10H, $CH_3(CH_2)_5CH_2C(O)NH$), 1.64 (m, 2H, $CH_3(CH_2)_5CH_2C(O)NH$), 1.99 (s, 3H, AcN), 2.84 (dd, 1H, J = 12.1, 4.03 Hz, H-3e(eq)).

Anal. Calcd for $C_{48}H_{86}N_2O_{29}Si$: C, 48.72; H, 7.33; N, 2.37. Found: C, 48.65; H, 7.24; N, 2.07.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-β-D-galactopyranosyl-(1 → 4)-(2-deoxy-2-lauroylamino-β-D-glucopyranosyl)-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (35) and 2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-β-D-galactopyranosyl-(1 → 4)-(2-deoxy-2-palmitoylamino-β-D-glucopyranosyl)-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (36). To a solution of **28** (83 mg) or **29** (70 mg) in MeOH (4 mL) was added sodium methoxide, the reaction mixture was stirred for 7 days at 35°C and then water was added. Work-up and column chromatography as described for **32** gave **35** (48 mg, 97%) or **36** (28 mg, 67%) as an amorphous mass; **35**, $[\alpha]_D - 10.9°$ (*c* 1.0, MeOH); IR (KBr) 3550, 3360, 2930, 1640, 1540, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 0.87 (t, 3H, J = 6.8 Hz, $CH_3(CH_2)_9CH_2C(O)NH$), 0.99 (m, 2H, $Me_3SiCH_2CH_2$), 1.26 (m, 18H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.60 (m, 2H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.98 (s, 3H, AcN), 2.83 (dd, 1H, J = 12.1, 4.23 Hz, H-3e(eq)).

Anal. Calcd for $C_{52}H_{94}N_2O_{29}Si$: C, 50.39; H, 7.64; N, 2.26. Found: C, 50.23; H, 7.40; N, 2.05.

36, $[\alpha]_D - 9.3°$ (*c* 0.58, MeOH); IR (KBr) 3550, 3400, 2950, 1630, 1550, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 0.87 (t, 3H, J = 7.3 Hz, $CH_3(CH_2)_{13}CH_2C(O)NH$), 0.99 (m, 2H, $Me_3SiCH_2CH_2$), 1.26 (m, 26H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 1.60 (m, 2H, $CH_3(CH_2)_{13}CH_2C(O)NH$), 1.98 (s, 3H, AcN), 2.83 (dd, 1H, J = 11.2, 4.02 Hz, H-3e(eq)).

Anal. Calcd for $C_{56}H_{102}N_2O_{29}Si$: C, 51.92; H, 7.94; N, 2.16. Found: C, 51.73; H, 7.74; N, 1.89.

2-(Trimethylsilyl)ethyl (3,5-dideoxy-5-glycolylamino-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-β-D-galactopyranosyl-(1 → 4)-(2-deoxy-2-lauroylamino-β-D-glucopyranosyl)-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (37). To a solution of **30** (133 mg, 63 μmol) in MeOH (1.5 mL) was added sodium methoxide, the reaction mixture was stirred for 2 days at room temperature and then water was added. Work-up and column chromatography as described for **32** gave **37** (69 mg, 89%) as an amorphous mass; $[\alpha]_D - 10.6°$ (*c* 1.4, MeOH); IR (KBr) 3400,

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2950, 1660, 1550, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 0.87 (t, 3H, J = 6.9 Hz, $CH_3(CH_2)_9CH_2C(O)NH$), 0.97 (m, 2H, $Me_3SiCH_2CH_2$), 1.26 (m, 18H, $CH_3(CH_2)_9CH_2C(O)NH$), 1.70 (t, 1H, J = 12.6 Hz, H-3e(ax)), 2.22 (m, 2H, $CH_3(CH_2)_9CH_2C(O)NH$), 2.84 (dd, 1H, J = 12.6, 4.16 Hz, H-3e(eq)).

Anal. Calcd for $C_{52}H_{94}N_2O_{30}Si$: C, 49.75; H, 7.55; N, 2.23. Found: C, 49.55; H, 7.51; N, 2.19.

2-(Trimethylsilyl)ethyl (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (40). To a solution of **39** (2.56 g, 6.2 mmol) in CH_2Cl_2 (30 mL) were added MS4A (1.5 g), $AgClO_4$ (0.94 g, 11 mmol), and Ag_2CO_3 (1.26 g, 11 mmol), and the reaction mixture was stirred for 5 h at room temperature. **38** (1.71 g, 6.2 mmol) was added to the mixture at 0°C and stirring was continued overnight at room temperature. The solids were removed through celite and washed with CH_2Cl_2. The combined filtrate and washings was concentrated. Column chromatography (AcOEt:hexane = 1:5) of the residue on silica gel gave **40** (2.02 g, 60%) as a syrup; $[\alpha]_D - 9.3°$ (*c* 0.6, CH_2Cl_2); IR(film) 2950, 1750, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (m, 2H, $Me_3SiCH_2CH_2$), 1.82, 1.97, 1.99, 2.13 (4s, 12H, 4AcO), 4.93 (d, 1H, J = 8.1 Hz, H-1c), 7.08–7.34 (m, 30H, 6Ph).

Anal. Calcd for $C_{73}H_{88}O_{20}Si$: C, 66.75; H, 6.75. Found: C, 66.55; H, 6.73.

2-(Trimethylsilyl)ethyl (β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (41) and 2-(Trimethylsilyl)ethyl (4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (42). To a solution of **40** (2.03 g, 1.5 mmol) in MeOH (20 mL) was added NaOMe, the reaction mixture was stirred overnight at room temperature, and then neutralized with Amberlite IR-120 (H^+) resin. The resin was filtered off and washed with MeOH. The combined filtrate and washings was concentrated to give **41** (1.72 g, 97%) as a syrup; $[\alpha]_D - 1.4°$ (*c* 0.56, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.03 (m, 2H, $Me_3SiCH_2CH_2$), 7.07–7.37 (m, 45H, 9Ph).

To a solution of **41** (2.0 g, 1.8 mmol) in acetonitrile (30 mL) were added Drierite (1.0 g), benzaldehyde dimethyl acetal (0.52 mL, 3.5 mmol), and a catalytic amount of *p*-toluenesulfonic acid, and the reaction mixture was stirred for 2 h at room temperature. The solution was neutralized with Na_2CO_3, and the solids were filtered off and washed with CH_2Cl_2. The combined filtrate and washings was concentrated. Column chromatography (AcOEt:hexane = 1:1) of the residue on silica gel gave **42** (1.72 g, 80%) as an amorphous mass; $[\alpha]_D - 3.0°$ (*c* 0.26, CH_2Cl_2); IR(film) 3500, 2950, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (m, 2H, $Me_3SiCH_2CH_2$), 5.54 (s, 1H, PhC*H)*, 7.08–7.53 (m, 35H, 7Ph).

Anal. Calcd for $C_{72}H_{84}O_{16}Si$: C, 70.11; H, 6.86. Found: C, 70.25; H, 6.81.

2-(Trimethylsilyl)ethyl (2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (43). To a solution of **42** (0.24 g, 0.18 mmol) in DMF (5 mL) was added 60% NaH in oil (0.17 g, 4.2 mmol) at 0°C. After 30 min, BnBr (0.62 mL, 5.3 mmol) was added to the mixture which was then stirred for 2 h at room temperature.

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The mixture was extracted with AcOEt and washed with water. The organic layer was dried over Na_2SO_4 and concentrated. Column chromatography (AcOEt:hexane = 1:3) of the residue on silica gel gave **43** (0.24 g, 94%) as a syrup; $[\alpha]_D - 5.9°$ (*c* 1.4, $CHCl_3$); IR(film) 2950, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 5.51 (s, 1H, PhC*H*), 7.05–7.50 (m, 45H, 9Ph).

Anal. Calcd for $C_{86}H_{96}O_{16}Si$: C, 73.06; H, 6.84. Found: C, 72.91; H, 6.84.

2-(Trimethylsilyl)ethyl (3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (44). To a solution of **42** (100 mg, 0.08 mmol) in CH_2Cl_2 (10 mL) were added tetrabutylammonium hydrogen sulfate (5.5 mg, 0.02 mmol), BnBr (14 μL, 0.12 mmol), and aq 5% NaOH (5 mL). The mixture was stirred overnight under reflux. The mixture was diluted with CH_2Cl_2, and washed with water. The organic layer was dried over Na_2SO_4 and concentrated. Column chromatography (AcOEt:hexane = 1:3) of the residue on silica gel gave **44** (85 mg, 80%) as an amorphous mass; $[\alpha]_D - 1.1°$ (*c* 1.7, $CHCl_3$); IR (film) 3500, 2950, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (m, 2H, $Me_3SiCH_2CH_2$), 5.57 (s, 1H, PhC*H*), 7.10–7.54 (m, 40H, 8Ph).

Anal. Calcd for $C_{79}H_{90}O_{16}Si$: C, 71.68; H, 6.85. Found: C, 71.46; H, 6.86.

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2-(Trimethylsilyl)ethyl (2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-mannopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (46). To a solution of **44** (80 mg, 60.4 μmol) in pyridine (1.5 mL) were added Tf_2O (42 μL, 0.24 mmol) and *N,N*-diisopropylethylamine (22 μL, 0.12 mmol), and the reaction mixture was stirred overnight at room temperature. The mixture was diluted with CH_2Cl_2, and the solution was successively washed with 2 M HCl, Na_2CO_3, and water. The organic layer was dried (Na_2SO_4), and concentrated to give **45** as a syrup, which was dissolved in DMF (1.3 mL). To this solution was added NaN_3 (40 mg, 0.64 mmol) and 18-crown-6 (80 mg, 0.32 mmol), the mixture was stirred overnight at 70°C and then extracted with AcOEt. The extract was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography ($CHCl_3$:MeOH = 400:1) of the residue on silica gel gave **46** (73 mg, 92%) as an amorphous mass; $[\alpha]_D - 37.8°$ (*c* 1.5, $CHCl_3$); IR(film) 2950, 2080, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (m, 2H, $Me_3SiCH_2CH_2$), 5.57 (s, 1H, PhC*H*), 7.03–7.49 (m, 40H, 8Ph).

Anal. Calcd for $C_{79}H_{89}N_3O_{15}Si$: C, 70.36; H, 6.65; N, 3.12. Found: C, 70.15; H, 6.64; N, 2.97.

2-(Trimethylsilyl)ethyl (2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-mannopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (47). To a solution of **46** (73 mg, 54 μmol) in benzene (1 mL) were added water (54 μL) and triphenylphosphine (30 mg, 0.11 mmol), the reaction mixture was stirred overnight at room temperature and then concentrated to dryness. The residue was dissolved in 1:1 CH_2Cl_2-pyridine (2 mL), and acetic anhydride (0.1 mL) was added. The mixture was stirred overnight at room temperature, and concentrated. Column chromatography (AcOEt:hexane = 1:3) of the residue on silica gel gave **47** (44 mg, 60%) as an amorphous mass; $[\alpha]_D - 14.4°$ (*c* 0.5, $CHCl_3$); IR(film) 3400, 2950, 1640, 1560, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (m, 2H,

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$Me_3SiCH_2CH_2$), 1.81 (s, 3H, AcN), 5.52 (s, 1H, PhC*H*), 5.57 (d, 1H, $J_{NH,2} = 8.5$ Hz, NH), 7.03–7.49 (m, 40H, 8Ph).

Anal. Calcd for $C_{81}H_{93}NO_{16}Si$: C, 71.29; H, 6.87; N, 1.03. Found: C, 71.50; H, 6.90; N, 0.78.

2-(Trimethylsilyl)ethyl (2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (48). To a solution of **44** (250 mg, 0.18 mmol) in pyridine (1 mL) were added Tf_2O (127 μL, 0.72 mmol) and *N,N*-diisopropylethylamine (66 μL, 0.36 mmol), and the reaction mixture was stirred overnight at room temperature. Work-up as described for **46** gave **45** as a syrup, which was dissolved in DMF (1.5 mL). To this solution was added cesium acetate (255 mg, 1.3 mmol) and 18-crown-6 (150 mg, 0.54 mmol), and the mixture was stirred overnight at 70°C. Work-up as described for **46** gave **48** (187 mg, 73%); $[\alpha]_D - 14.4°$ (*c* 0.5, $CHCl_3$); IR(film) 2950, 1750, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (m, 2H, $Me_3SiCH_2CH_2$), 1.98 (s, 3H, OAc), 5.46 (br s, 1H, H-2c), 5.58 (s, 1H, PhC*H*), 7.04–7.49 (m, 40H, 8Ph).

Anal. Calcd for $C_{81}H_{92}O_{17}Si$: C, 71.24; H, 6.79. Found: C, 71.38; H, 6.82.

2-(Trimethylsilyl)ethyl (2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (49). To a solution of **43** (100 mg, 0.71 mmol) in THF (5 mL) was added MS3A (100 mg), and the mixture was stirred for 2 h at room temperature. Sodium cyanoborohydride (44 mg, 7.1 mmol) was added to the solution, and then hydrogen chloride in diethyl ether was added dropwise to the stirred mixture: stirring was continued for 30 min. The mixture was neutralized with Et_3N and diluted with CH_2Cl_2 and water. The solids were removed through celite, and the filtrate was washed with water, and the organic layer was dried over Na_2SO_4 and concentrated. Column chromatography (AcOEt:hexane = 1:2) of the residue on silica gel gave **49** (89 mg, 89%) as a syrup; $[\alpha]_D - 8.5°$ (*c* 1.8, CH_2Cl_2); IR(film) 3500, 2950, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 7.03–7.49 (m, 45H, 9Ph).

Anal. Calcd for $C_{86}H_{98}O_{16}Si$: C, 72.96; H, 6.98. Found: C, 73.03; H, 6.82.

2-(Trimethylsilyl)ethyl (2-acetamido-3,6-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (50). Treatment of **47** (202 mg, 0.15 mmol) in THF (5 mL) with sodium cyanoborohydride (95 mg, 1.5 mmol) was performed as described for **49**. Work-up and column chromatography as described for **49** gave **50** (183 mg, 89%) as a syrup; $[\alpha]_D - 21.6°$ (*c* 4.0, CH_2Cl_2); IR(film) 3500, 2950, 1750, 1640, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (m, 2H, $Me_3SiCH_2CH_2$), 1.83 (s, 3H, AcN), 7.10–7.42 (m, 40H, 8Ph).

Anal. Calcd for $C_{81}H_{95}NO_{16}Si$: C, 71.18; H, 7.01; N, 1.02. Found: C, 71.15; H, 7.01; N, 1.01.

2-(Trimethylsilyl)ethyl (2-*O*-acetyl-3,6-di-*O*-benzyl-β-D-mannopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (51). Treatment of **48** (187 mg, 0.14 mmol) in THF (5 mL) with sodium cyanoborohydride (86 mg, 1.4 mmol) was performed as described for **49**.

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Work-up and column chromatography as described for **49** gave **51** (112 mg, 60%) as a syrup; $[\alpha]_D - 21.5°$ (*c* 2.2, CH_2Cl_2); IR(film) 3500, 2950, 1750, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.86 (s, 3H, OAc), 7.04–7.48 (m, 40H, 8Ph).

Anal. Calcd for $C_{81}H_{94}O_{17}Si$: C, 71.13; H, 6.93. Found: C, 70.99; H, 6.97.

DMTST catalyzed couplings of **12** with **49–51** were performed as described for **14–20** to give **52** (73%), **53** (80%), and **54** (84%), respectively.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (52). An amorphous mass; $[\alpha]_D + 14.4°$ (*c* 2.1, $CHCl_3$); IR (film) 3400, 2950, 1750, 1640, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (m, 2H, $Me_3SiCH_2CH_2$), 1.44 (s, 3H, AcN), 1.76, 1.90, 1.96, 2.14 (4s, 12H, 4AcO), 2.40 (dd, 1H, J = 12.8, 4.4 Hz, H-3e(eq)), 3.77 (s, 3H, MeO), 7.02–7.99 (m, 60H, 12Ph).

Anal. Calcd for $C_{133}H_{147}NO_{36}Si$: C, 67.58; H, 6.27; N, 0.59. Found: C, 67.44; H, 6.26; N, 0.59.

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2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-mannopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (53). An amorphous mass; $[\alpha]_D + 0.97°$ (*c* 1.0, $CHCl_3$); IR (film) 3400, 2950, 1750, 1640, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (m, 2H, $Me_3SiCH_2CH_2$), 1.47, 1.76 (2s, 6H, 2AcN), 1.66, 1.89, 1.90, 2.17 (4s, 12H, 4AcO), 2.45 (dd, 1H, J = 12.1, 4.4 Hz, H-3e(eq)), 3.80 (s, 3H, MeO), 7.01–8.26 (m, 55H, 11Ph).

Anal. Calcd for $C_{128}H_{144}N_2O_{36}Si$: C, 66.42; H, 6.27; N, 1.21. Found: C, 66.22; H, 6.29; N, 1.20.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(2-*O*-acetyl-3,6-di-*O*-benzyl-β-D-mannopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (54). An amorphous mass; $[\alpha]_D + 10.9°$ (*c* 0.31, $CHCl_3$); IR (film) 3400, 2950, 1750, 1640, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (m, 2H, $Me_3SiCH_2CH_2$), 1.49 (s, 3H, AcN), 1.66, 1.77, 1.91, 1.95, 2.19 (5s, 15H, 5AcO), 2.40 (dd, 1H, J = 12.5, 4.4 Hz, H-3e(eq)), 3.81 (s, 3H, MeO), 7.04–8.26 (m, 55H, 11Ph).

Anal. Calcd for $C_{128}H_{143}NO_{37}Si$: C, 66.39; H, 6.22; N, 0.60. Found: C, 66.59; H, 6.26; N, 0.60.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyra-

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noside (55). A solution of **52** (150 mg, 64 μmol) in EtOH (15 mL) was hydrogenolyzed over $Pd(OH)_2$ on carbon (150 mg) overnight. The catalyst was filtered off and the filtrate was concentrated. The residue was acetylated with acetic anhydride (0.1 mL) in pyridine (2 mL) overnight at room temperature. Work-up and column chromatography ($CHCl_3$:MeOH = 25:1) on silica gave **55** (85 mg, 69%) as an amorphous mass; $[\alpha]_D + 36.3°$ (*c* 1.6, $CHCl_3$); IR (film) 3400, 2950, 1750, 1640, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (m, 2H, $Me_3SiCH_2CH_2$), 1.76–2.20 (14s, 42H, AcN and 13AcO), 2.40 (dd, 1H, J = 12.8, 4.4 Hz, H-3e(eq)), 3.86 (s, 3H, MeO), 7.42–8.17 (m, 15H, 3Ph).

Anal. Calcd for $C_{88}H_{111}NO_{45}Si$: C, 54.74; H, 5.79; N, 0.73. Found: C, 54.63; H, 5.82; N, 0.73.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-mannopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (56). Hydrogenolysis of **53** (150 mg) and subsequent acetylation was performed as described for **55** to give **56** (99 mg, 79%) as an amorphous mass; $[\alpha]_D + 23.4°$ (*c* 2.0, $CHCl_3$); IR (film) 3400, 2950, 1750, 1640, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (m, 2H, $Me_3SiCH_2CH_2$), 1.56–2.11 (14s, 42H, 2AcN and 12AcO), 2.46 (dd, 1H, J = 12.5, 4.4 Hz, H-3e(eq)), 3.78 (s, 3H, MeO), 7.28–8.22 (m, 15H, 3Ph).

Anal. Calcd for $C_{88}H_{112}N_2O_{44}Si$: C, 54.77; H, 5.85; N, 1.45. Found: C, 54.88; H, 5.88; N, 1.45.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopranosylonate)-(2 → 3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-(2,3,6-tri-*O*-acetyl-β-D-mannopyranosyl)-(1 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (57). Hydrogenolysis of **54** (157 mg) and subsequent acetylation was performed as described for **55** to give **57** (135 mg, 95%) as an amorphous mass; $[\alpha]_D + 11.7°$ (*c* 1.6, $CHCl_3$); IR (film) 3400, 2950, 1750, 1640, 1540, 860, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (m, 2H, $Me_3SiCH_2CH_2$), 1.54–2.13 (14s, 42H, AcN and 13AcO), 2.40 (dd, 1H, J = 12.5, 4.4 Hz, H-3e(eq)), 3.82 (s, 3H, MeO), 7.43–8.19 (m, 15H, 3Ph).

Anal. Calcd for $C_{88}H_{111}NO_{45}Si$: C, 54.74; H, 5.79; N, 0.73. Found: C, 54.79; H, 5.81; N, 0.73.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 3)-β-D-galactopyranosyl-(1 → 4)-β-D-glucopyranoside (58). To a solution of **55** (45 mg, 23 μmol) in MeOH (4 mL) was added sodium methoxide, the reaction mixture was stirred at room temperature overnight and then water was added. Work-up and column chromatography as described for **32** gave **58** (23 mg, 96%) as an amorphous mass; $[\alpha]_D - 4.5°$ (*c* 0.44, CH_3OH); IR (film) 3500, 3400, 2950, 1640, 1560, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 0.91 (m, 2H, $Me_3SiCH_2CH_2$), 2.00 (s, 3H, AcN), 2.73 (dd, 1H, J = 12.5, 4.4 Hz, H-3e(eq)).

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Anal. Calcd for $C_{40}H_{71}NO_{29}Si$: C, 45.41; H, 6.76; N, 1.32. Found: C, 45.40; H, 6.62; N, 1.29.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)-β-D-galactopyranosyl-(1→4)-(2-acetamido-2-deoxy-β-D-mannopyranosyl)-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside (59). *O*-Deacylation of **56** (40 mg) as described for **32** gave **59** (20 mg, 89%) as an amorphous mass; $[\alpha]_D - 11.5°$ (*c* 0.40, CH_3OH); IR (film) 3500, 3400, 2950, 1640, 1560, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 0.99 (m, 2H, $Me_3SiCH_2CH_2$), 2.01 (s, 3H, AcN), 2.05 (s, 3H, AcN), 2.73 (dd, 1H, J = 12.5, 4.4 Hz, H-3e(eq)).

Anal. Calcd for $C_{42}H_{74}N_2O_{29}Si$: C, 45.90; H, 6.79; N, 2.55. Found: C, 45.98; H, 6.65; N, 2.50.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)-β-D-galactopyranosyl-(1→4)-β-D-mannopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside (60). *O*-Deacylation of **57** (45 mg) as described for **32** gave **60** (27 mg, 98%) as an amorphous mass; $[\alpha]_D - 14.3°$ (*c* 0.54, CH_3OH); IR (film) 3500, 3400, 2950, 1640, 1560, 860, 840 cm^{-1}; ^1H NMR (CD_3OD) δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 2.01 (s, 3H, AcN), 2.73 (dd, 1H, J = 12.5, 4.5 Hz, H-3e(eq)).

Anal. Calcd $C_{40}H_{71}NO_{29}Si$: C, 45.41; H, 6.76; N, 1.32. Found: C, 45.45; H, 6.79; N, 1.32.

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