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Ganglioside GQ1b: Efficient Total Synthesis and the Expansion to Synthetic Derivatives To Elucidate Its Biological Roles†

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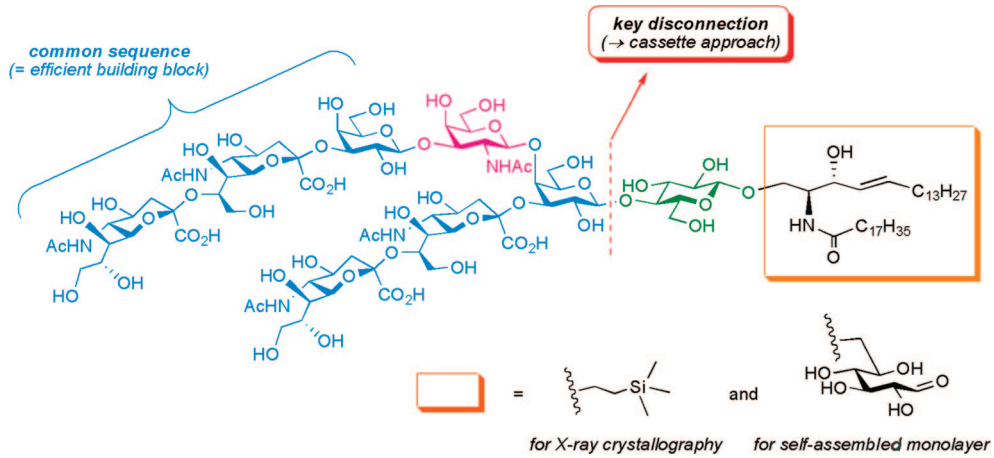

The convergent total synthesis of ganglioside GQ1b based on the "cassette approach" between the nonreducing end GQ1b-core heptasaccharide and glucosylceramide building blocks was accomplished in high overall yield. The use of a sialylα(2→8)sialylα(2→3)galactose sequence as the key building block enhanced the efficiency of the glycan assembly and led to preparative-scale synthesis readily applicable for large-scale preparation. In addition, a judicious choice of *p*-methoxybenzyl protecting groups on glucosylceramide provided a solution to the previous synthetic problems, including a decrease in the yield of the deprotection steps, and led to elevation of the total yield. Furthermore, unnatural-type GQ1b derivatives were synthesized systematically in good yields by capitalizing on a similar approach in order to elucidate their biological roles.

Introduction

Gangliosides, sialylated glycosphingolipids, are the components of the membranes in the cells of all living organisms and are particularly abundant in the nervous system on the vertebrate cell plasma membrane.[2] For the past two decades, gangliosides have attracted wide attention in various scientific fields, because they play various important roles in vital processes. Ganglioside GQ1b, which is classified as one of the b-series gangliosides, exists abundantly in the mammalian central nervous system and participates in many physiological events, such as neurite extension,[3] toxin binding,[4] modulation of protein phosphorylation,[5] cell adhesion and growth,[6,7] and apoptosis.[8] Despite its biological importance, advancement in the biological study of b-series gangliosides, including GQ1b, has been restricted due

† Synthetic studies on sialoglycoconjugates, part 147. For part 146, see ref 1.

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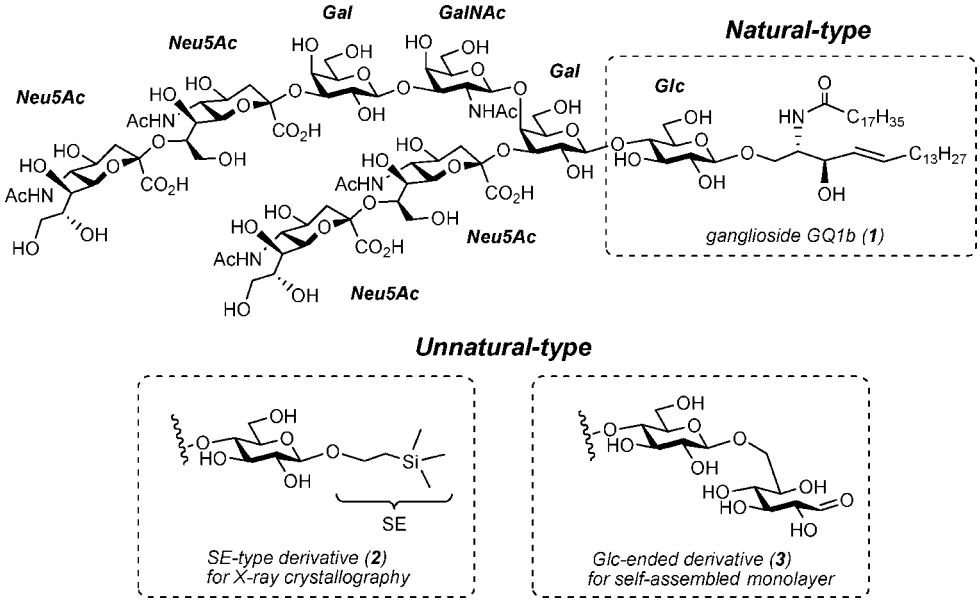

FIGURE 1. Structure of target compounds.

to a deficiency in the supply of pure gangliosides. In 1994, our group first achieved the total synthesis of ganglioside GQ1b, which led to the elucidation of the biological functions of GQ1b at the molecular level.[9] However, there were problems yet to be solved with regard to the overall yields and stereoselectivity of the coupling reactions, which prevented large quantity synthesis. Recently, it has become essential to develop large-scale synthesis of gangliosides, because of multifaceted research needs, e.g., microarray, molecular imaging, and X-ray crystallographic studies. Therefore, we envisioned renewal of the total synthetic method for natural ganglioside GQ1b (**1**) (Figure 1). Furthermore, we decided to develop access to versatile unnatural GQ1b derivatives to elucidate their biological roles. The following were designed as unnatural GQ1b derivatives (Figure 1): (i) *SE [2-(trimethylsilyl)ethyl]-type derivative* (**2**) demonstrated that SE-type GT1b derivatives serve as good tools for X-ray crystallographic analysis with lectins such as Siglec-7,[10] botulinum neurotoxin,[11] and tetanus toxin,[12] because replacement of ceramide with an SE group may render it more amenable to crystallization (being more water-soluble, less flexible, and less likely to form micelles) and (ii) *Glc-ended derivative* (**3**) allowed accomplishment of the synthesis of GM1, GM2, and GM3 bearing D-glucose at the reducing terminal and succeeded in the assembly of the sugar microarray.[13] The D-glucose residue in this derivative provided a reactive aldehyde functionality at the reducing end and served as a spacer between the targeted sugar chain and the scaffold for immobilization because of its appropriate hydrophilicity and flexibility.

Herein, we report the renewed efficient synthesis of natural ganglioside GQ1b and its unnatural derivatives.

Results and Discussion

To achieve the efficient and systematic synthesis of the targeted compounds bearing different reducing terminals, sialylα(2→8)sialylα(2→3)galactose sequences were focused on as the common trisaccharide building blocks. Using this common sequence, a synthetic scheme for the targets was devised, as shown in Figure 2. This included four important glycosylation steps: (1) sialylation to produce the common trisaccharide; (2) galactosaminidation; (3) coupling of the trisaccharide donor and the tetrasaccharide acceptor, derived from the common trisaccharide; and (4) final glycosylation of the reducing terminal acceptors.

According to the above-mentioned scheme, disialylgalactose unit **6** was selected as the key compound and was prepared by glycosylation of the known galactose acceptor **5**[14] with sialylα(2→8)sialyl phenylthioglycoside donor **4**.[9] We were eager to find out how stereo- and regioselectivity in sialylation increases, and therefore a series of sialylations under various conditions were conducted. The results are summarized in Table 1. First, the sialylation of **5** in the presence of dimethyl(methylthio)sulfonium triflate (DMTST)[15] as a promoter in acetonitrile at −35 °C hardly gave **6** (entry 1). In entry 2, by using

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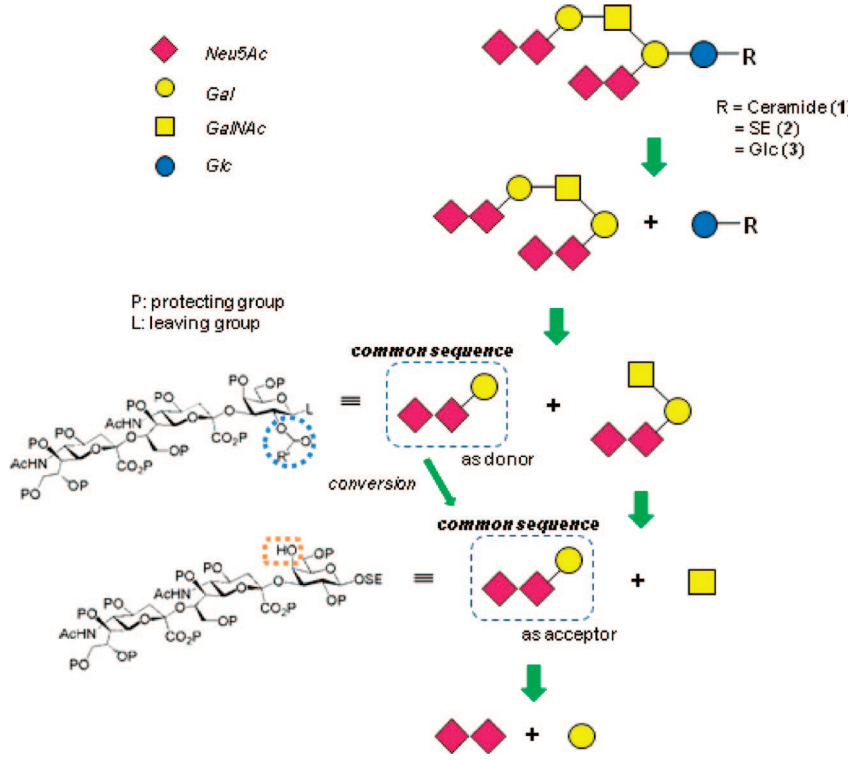
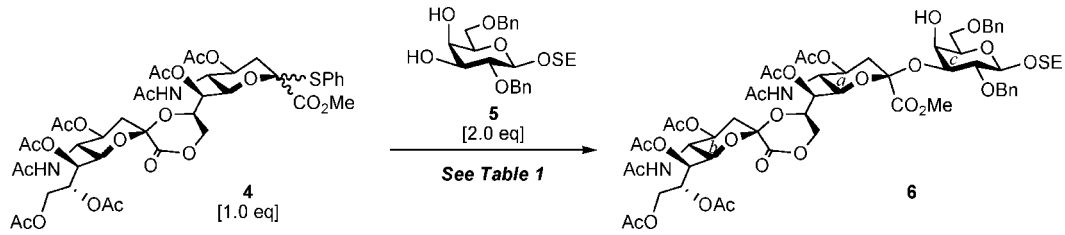


FIGURE 2. Outline of renewed synthetic approach for ganglioside GQ1b and its analogs.

TABLE 1. Preparation of the Key Building Block 6, Sialylα(2→8)sialylα(2→3)galactose Unit



				% yield of products[a]			
				(2→3) glycoside			
entry	promoter	solvent	T (°C)	α	β	(2→4) glycoside	2,3-ene of donor
1	DMTST[b]	MeCN	−35	trace	trace	trace	trace
2	NIS−TfOH	MeCN	−35	33	17	10	22
3	NIS−BF_3·OEt_2	MeCN	−35	21	19	11	23
4	NIS−TMSOTf	MeCN	−35	31	15	9	20
5	NIS−TfOH	EtCN	−50	44	14	8	16

[a] Isolated yield. [b] DMTST: dimethyl(methylthio)sulfonium triflate.

NIS−TfOH[16] as a promoter system with the assistance of the solvent effect of acetonitrile,[17] the desired α-sialoside **6** was obtained in 33% yield with a scarcely better α/β-ratio (2/1). However, adverse side reactions also occurred and resulted in a 2,3-ene derivative of the donor as a byproduct. In entry 3, the use of BF_3·OEt_2 instead of TfOH led to a reduction in both the yield of **6** and its stereoselectivity. On the other hand, the use of NIS−TMSOTf (entry 4) as a promoter system gave results similar to NIS−TfOH. In entry 5, when the reaction was conducted in the presence of NIS−TfOH in propionitrile at −50 °C, the desired **6** was obtained in a rewarding 44% yield, and stereoselectivity was improved with a slight reduction of the byproduct. The α-configuration of the glycoside of **6** was assigned according to empirical rules[18] and was further confirmed by observation of a strong cross peak between H^a-3ax and C^a-1 in the HMBC spectrum[19] of **6**, because the α-sialosides has a larger heteronuclear coupling constant ($^3J_{C\text{-}1,H\text{-}3ax}$) than β-sialoside (see the Supporting Information).

The difficulty of introducing a β-galactosaminyl glycoside at the C-4 position of galactose has been revealed in the literature[20] in relation to the assembly of a ganglio-series

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SCHEME 1. Preparation of Novel GalNAc Glycosyl Donors

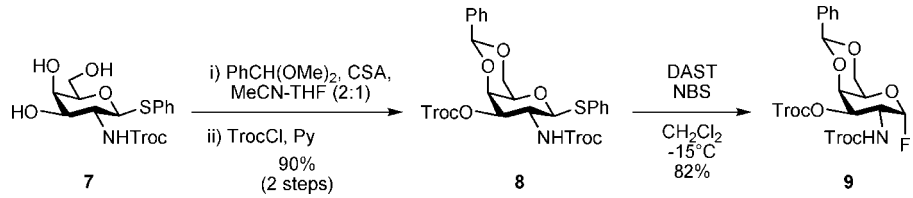
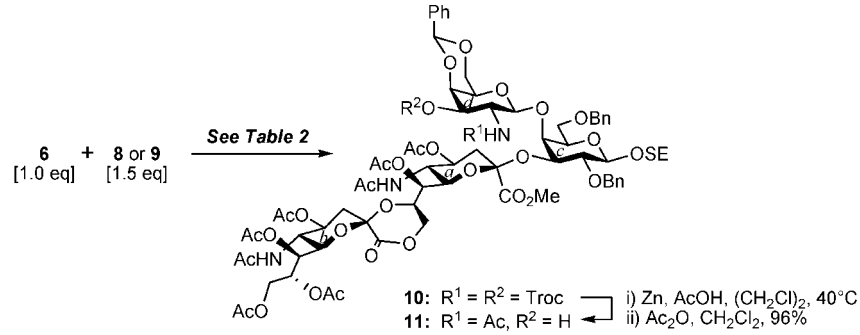


TABLE 2. Galactosaminidations of 6 and Subsequent Conversion into Tetrasaccharide Acceptor 11



entry	donor	promoter	solvent	T (°C)	% yield[a]
1	**8**	NIS−TfOH	CH_2Cl_2	0	58
2	**8**	NIS−TfOH	CH_2Cl_2	−35	50
3	**9**	$SnCl_2$−$AgClO_4$	CH_2Cl_2	rt	52
4	**9**	$HNTf_2$	BTF−^{t}BuCN[b]	rt	trace
5	**9**	Cp_2ZrCl_2−AgOTf	CH_2Cl_2	−20	85

[a] Isolated yield. [b] BTF: benzotrifluoride.

ganglioside skeleton, and the choice of the neighboring group of the anomeric center and the mode of protection for GalNAc has been examined in several ways.[21] In this study, two kinds of GalNAc donors **8** and **9**, which commonly carry a 2,2,2-trichloroethoxycarbonyl (Troc) group at C-2, were designed, as shown in Scheme 1. It is known that the Troc group should ensure β-selective glycosylation as well as increased reactivity as a glycosyl donor compared with the *N*-phthaloyl group.[22] Additionally, the advantage of the Troc group lies in the high degree of efficiency in installment and chemoselective deprotection.

Acetalization of the previously described phenylthio-galactosaminide **7**[23] with $PhCH(OMe)_2$ and (±)-10-camphorsulfonic acid (CSA) and subsequent protection of the remaining C-3-hydroxyl group by the Troc group afforded novel GalNAc thioglycoside donor **8** in 90% yield over two steps. Thioglycoside **8** was then efficiently converted into fluoride **9** as another GalNAc donor.[24] In the design of GalNAc donors, the Troc group was also exploited for the protection of the C-3 hydroxyl group to facilitate access to the tetrasaccharide acceptor for the next coupling reaction. The obtained GalNAc donors **8** and **9** were subjected to galactosaminidation with **6**. The results are summarized in Table 2.

In entries 1 and 2, the glycosidations of thioglycoside **8** with **6** were carried out in the presence of NIS−TfOH in CH_2Cl_2, affording the tetrasaccharide **10** in moderate yield along with several byproducts. Although the byproducts were inseparable, the mass spectrum of the mixture of byproducts indicated the presence of a molecule with the same molecular weight of **10**, probably α-glycoside. This result is in accordance with the report[25] that the *galacto*-type donor bearing the benzylidene group at the C-4,6 positions gave α-glycoside, which is unusual even in the presence of the neighboring participating acyl group at C-2. Next, in entries 3−5, the glycosidation of fluoride donor **9** in the presence of various promoters was attempted. When $SnCl_2$−$AgClO_4$[26] was used (entry 3), the yield of **10** was not improved, and the stereoselectivity did not change appreciably. The use of $HNTf_2$[27] in the mixture solvent (BTF/^{t}BuCN) hardly gave **10** (entry 4). On the other hand, when the reaction was conducted in the presence of Cp_2ZrCl_2−AgOTf[28] at −20 °C (entry 5), both yield and stereoselectivity were dramatically improved to afford **10** in 85% yield. Furthermore, it was found

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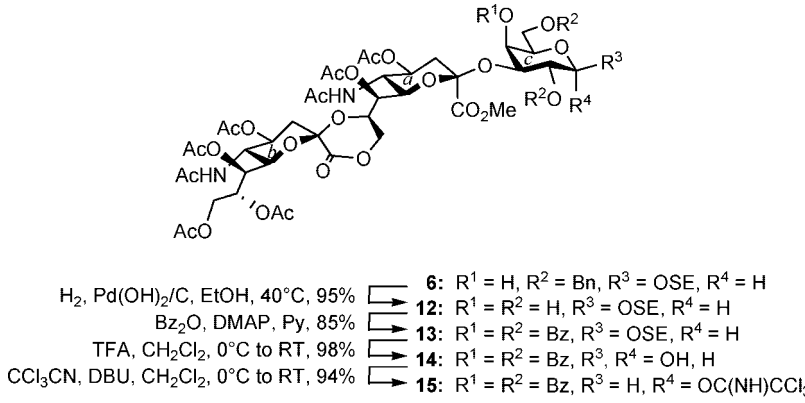
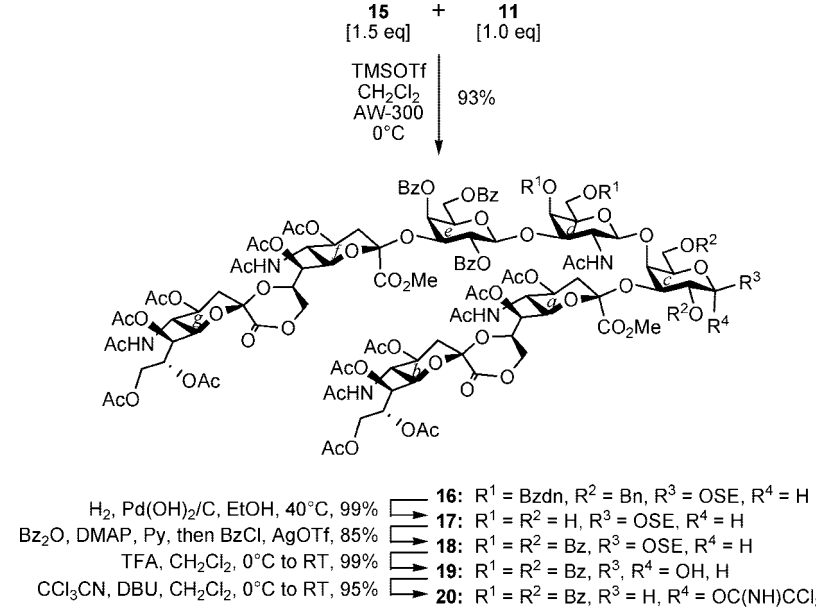
SCHEME 2. Conversion of 6 into Donor Form 15



SCHEME 3. Glycosylation of 11 with 15 and Conversion into GQ1b Epitope Donor 20



that these conditions were applicable in a large-scale synthesis. As expected, the obtained tetrasaccharide **10** could be efficiently converted into tetrasaccharide acceptor **11** through the removal of the Troc groups by treatment with preactivated zinc, followed by the selective acetylation of the liberated amine of the GalNAc residue at C-2.

Scheme 2 shows the facile conversion of the key common unit **6** into donor form **15**. Thus, hydrogenolysis of the benzyl groups afforded the triol **12** in excellent yield, and subsequent benzoylation of the exposed three hydroxyl groups successfully proceeded to give **13** in 85% yield. In order to introduce a leaving group at the reducing end of **13**, the SE group was removed by exposure to trifluoroacetic acid.[29] The obtained hemiacetal **14** was then converted into α-trichloroacetimidate **15** by treatment with CCl_3CN and DBU.[30]

Next, as shown in Scheme 3, the coupling reaction of **15** and **11** was conducted. The reaction was performed in the presence of TMSOTf in CH_2Cl_2 at 0 °C. This block coupling surprisingly afforded the desired GQ1b-core heptasaccharide **16** in excellent yield (93%). The reaction was also successful in large scale (∼10 g). Undoubtedly, the branched tetrasaccharide acceptor **11** performed excellent couplings with other glycosyl donors. As shown in Scheme 4, the glycosylation of **11** with the known sialylα(2→3)galactose donor **21**[31] and galactose donor **22**[32] resulted in the delivery of other glycan structures of b-series gangliosides, **23** (GT1b-core hexasaccharide) and **24** (GD1b-core saccharide) in excellent 95% and 90% yields, respectively. These results demonstrated that **11** was the expedient common unit for the synthesis of the entire b-series gangliosides.

Referring back to Scheme 3, the cleavage of benzyl groups and the benzylidene group of **16** was executed by hydrogenolysis on $Pd(OH)_2$, and the following benzoylation of the resulting hydroxyl groups gave **18**. In this benzoylation, the combination of Bz_2O and DMAP in pyridine could not completely protect

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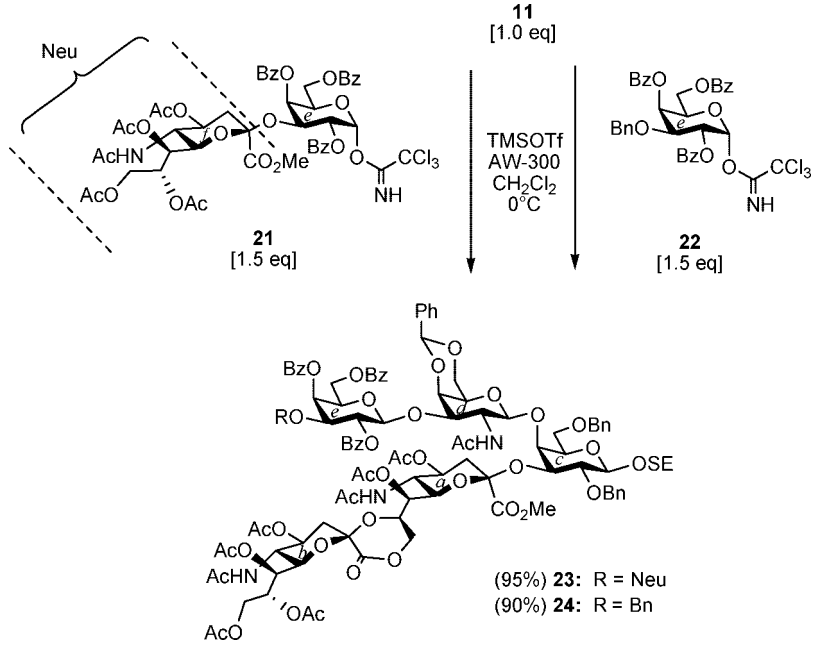
SCHEME 4. Potential as an Acceptor of 11 for the Systematical Synthesis of B-Series Gangliosides



the hydroxyl groups. Therefore, to complete the reaction, BzCl and AgOTf were added, which generated more reactive BzOTf in situ, whereas the addition of BzCl and DMAP could not complete the reaction. The use of BzOTf from the beginning of the reaction gave a crude mixture of *O*- and *N*-benzoylated products. The reason underlying this phenomenon is yet unclear. Liberation of the anomeric hydroxyl group of **18** was achieved by treatment with TFA, and the resulting hemiacetal **19** was then converted into the α-trichloroacetimidate **20**, which was ready for the final glycosylation.

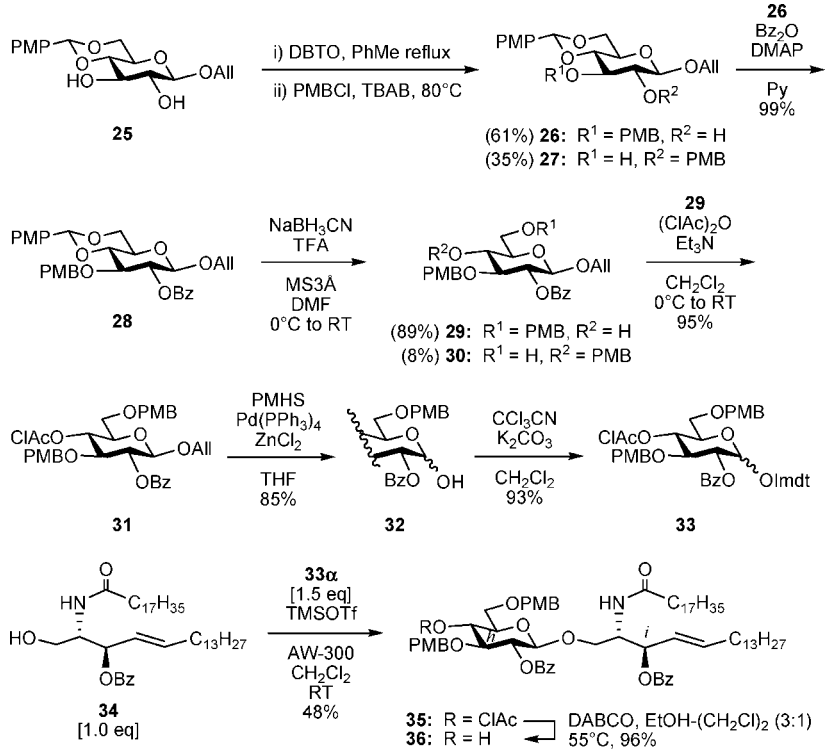
Hashimoto et al. reported the useful convergent synthesis of ganglioside GM3 using a glucosylceramide (GlcCer) building block equipped with benzyl groups at the C-3 and C-6 positions of the Glc residue.[33] However, the use of benzyl groups impaired the efficiency of the deprotection steps, since conventional hydrogenolysis of benzyl groups cannot be utilized due to the presence of the olefin functionality at the ceramide moiety. As a result, it has caused great loss of the samples at the final stage. Therefore, in this study, we envisioned the use of the *p*-methoxybenzyl (PMB) group as a surrogate of the benzyl group, since it can be removed by nonreductive conditions without affecting olefin functionality.

Starting from the known glucose derivative **25**,[34] the GlcCer acceptor with PMB groups at the C-3 and C-6 positions (**36**) was prepared via eight steps (Scheme 5). Derivative **25** was subjected to selective *p*-methoxybenzylation by way of stannylidenation[35] with DBTO in toluene, followed by treatment of PMBCl with TBAB to afford the 3-PMB and 2-PMB derivatives in 61% and 35% yields, respectively. Benzoylation of **26** was achieved under standard conditions to give **28** in almost a quantitative yield. Reductive opening of the anisylidene ring of **28** by treatment with $NaBH_3CN$ and TFA in DMF[36] afforded the 6-*O*-PMB derivative **29** (89%), along with a small amount (8%) of the 4-*O*-PMB derivative **30**. Monochloroacetylation of **29** proceeded smoothly to provide **31** in 95% yield. Selective exposure of the anomeric hydroxyl group of **31** was executed by treatment of polymethylhydrosiloxane (PMHS), $Pd(PPh_3)_4$, and $ZnCl_2$ in THF,[37] which afforded the hemiacetal **32** in 85% yield. The obtained hemiacetal **32** was converted into the corresponding trichloroacetimidate **33** in 93% (α/β = 40/53) yield upon reaction with CCl_3CN and DBU. The α-imidate **33α** was then subjected to glycosidation with the known ceramide acceptor **34**[38] in the presence of TMSOTf in CH_2Cl_2 to afford **35** in 48% yield. The selective deprotection of the monochloroacetyl group was accomplished by treatment of DABCO in the mixed solvent of EtOH/1,2-dichloroethane[39] to furnish the novel GlcCer acceptor **36** in 96% yield.

The final couplings of GQ1b-core heptasaccharide donor **20** (1.0 equiv) with glucosyl acceptors **36**, **37**, **38**, and **39** (1.5 equiv each) were conducted in the presence of TMSOTf (0.1 equiv) in CH_2Cl_2 at 0 °C, and the results are summarized in Table 3. In entry 1, the glycosylation of the novel GlcCer acceptor **36** with **20** afforded the desired fully protected ganglioside GQ1b **40** in an excellent 91% yield. On the other hand, a Hashimoto-type GlcCer acceptor **37** bearing the corresponding benzyl groups at the C-3 and C-6 positions afforded **41** in 73% yield (entry 2). These results indicated that the PMB groups at the C-3 and C-6 positions of the Glc residue enhanced the reactivity of the 4-hydroxyl group owing to its electron-donating property and elevated the coupling yield. Next, the previously described glucose derivative **38**[40] was used as a coupling partner of **20** for the preparation of the SE-type GQ1b derivative (entry 3). As a result, the desired compound **42** was obtained in 63% yield.

(33) Sakamoto, H.; Nakamura, S.; Tsuda, T.; Hashimoto, S. *Tetrahedron Lett.* **2000**, *41*, 7691–7695.
(34) Aspinall, G. O.; Gammon, D. W.; Sood, R. K.; Chatterjee, D.; Rivoire, B.; Brennan, P. J. *Carbohydr. Res.* **1992**, *237*, 57–77.
(35) Qin, H.; Grindley, B. *J. Carbohydr. Chem.* **1996**, *15*, 95–108.
(36) Johansson, R.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2371–2374.
(37) Chandrasekhar, S.; Reddy, Ch. R.; Rao, R. J. *Tetrahedron* **2001**, *57*, 3435–3438.
(38) (a) Kiso, M.; Nakamura, A.; Tomita, Y.; Hasegawa, A. *Carbohydr. Res.* **1986**, *158*, 101–111. (b) Kiso, M.; Nakamura, A.; Nakamura, J.; Tomita, Y.; Hasegawa, A. *J. Carbohydr. Chem.* **1986**, *5*, 335–340.
(39) Lefeber, D. J.; Kamerling, J. P.; Vliegenthart, J. F. G. *Org. Lett.* **2000**, *2*, 701–703.
(40) Fuse, T.; Ando, H.; Imamura, A.; Sawada, N.; Ishida, H.; Kiso, M.; Ando, T.; Li, S.-C.; Li, Y.-T. *Glycoconjugate J.* **2006**, *23*, 329–343.

SCHEME 5. Preparation of a Novel Glucosyl Ceramide Acceptor 36



In entry 4, glycosylation of the previously described gentiobiose acceptor **39**[13] with **20** provided the nonasaccharide **43** in 80% yield. These results strongly suggested that our synthetic strategy is applicable to the assembly of both natural gangliosides and unnatural ganglioside derivatives.

Scheme 6 incorporated global deprotection steps toward target compounds. Selective removal of the PMB groups of **40** was performed in the presence of TFA in CH_2Cl_2 at 0 °C, and the reaction was completed within 1 h. After a facile workup and purification by silica gel column chromatography, the target compound **44** was obtained in almost a quantitative yield (97%). The outcome demonstrated that the use of the PMB group was effective for the synthesis of natural gangliosides. Importantly, this strategy can be applied to the syntheses of compounds with hydrogenolysis-sensitive functionalities, such as allyls, alkynes, azides, and so on. Furthermore, the sustainability of azide and alkyne groups enables their application to 1,3-dipolar cycloadditions. Finally, the conventional deacylation[41] and subsequent saponification gave natural ganglioside GQ1b **1** in 97% yield. It is noteworthy that the synthesis of the complex ganglioside GQ1b was first accomplished in the scale of ca. 80 mg per batch. Global deprotections of **42** and **43** were also executed by conventional methods to provide the targeted unnatural GQ1b derivatives **2** and **3** in good yields, respectively.

Conclusion

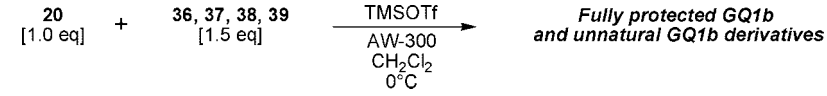
In conclusion, we have accomplished the highly efficient and practical synthesis of complex ganglioside GQ1b and its unnatural derivatives by convergent synthetic routes, based on the key coupling reactions of a GQ1b-core heptasaccharide and derivatized-Glc building blocks. In particular, a judicious choice of a PMB group as a protecting group at the C-3 and C-6 positions of the GlcCer led to not only the elevation of coupling yields but also to facilitate global deprotection with almost quantitative yields. Furthermore, our approach can efficiently reach various unnatural ganglioside derivatives with azide or alkyne groups for 1,3-dipolar cycloaddition. We are currently undertaking the syntheses of various gangliosides using this approach, and the extension of synthesized ganglioside derivatives to the chemical biology field is in progress.

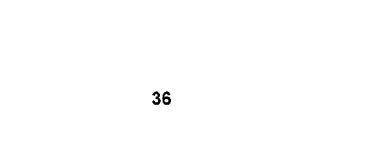
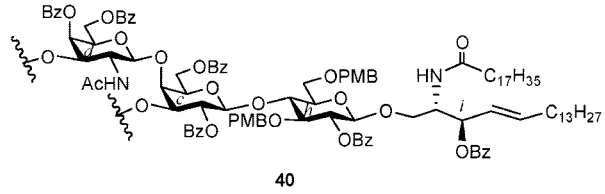
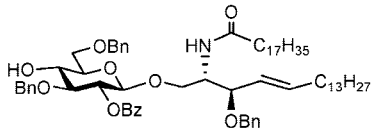
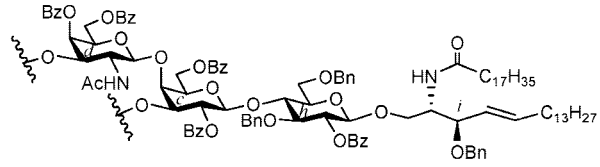
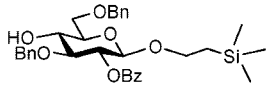
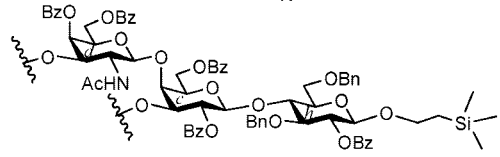
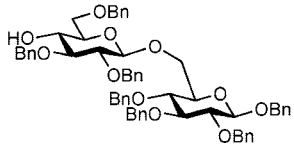
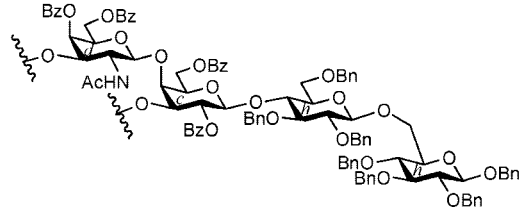
Experimental Section

Ganglioside GQ1b (1). To a mixture of **44** (122 mg, 0.0316 mmol) in MeOH (6.2 mL) was added catalytic amounts of sodium methoxide (28% solution in MeOH). After stirring for 24 h at room temperature as the reaction was monitored by TLC (1-BuOH/MeOH/5% $CaCl_2$ (aq) = 2:1:1), the mixure was heated at 50 °C, and stirring was continued for 2 days at 50 °C. Then, H_2O (0.3 mL) was added to the mixture. After stirring for 5 h at room temperature as the reaction was monitored by TLC (1-BuOH/MeOH/5% $CaCl_2$ (aq) = 2:1:1), the reaction was neutralized with IR-120 (H^+) resin and filtered through cotton, and the resin was washed with mixed solvent ($CHCl_3$/MeOH/H_2O = 5:5:1). The combined filtrate and washings were concentrated. The resulting residue was purified by gel filtration column chromatography on Sephadex LH-20 using $CHCl_3$/MeOH/H_2O (5:5:1) as the eluent to give **1** (77 mg, 97%): $[\alpha]_D = -6.3°$ (*c* 0.3, $CHCl_3$/MeOH/H_2O = 5:5:1); ^{1}H NMR (600 MHz, $CDCl_3$/CD_3OD/D_2O = 5:5:1) δ 5.70 (m, 1 H, $J_{4,5}$ = 15.1 Hz, $J_{5,6}$ = 8.2 Hz, $J_{5,6'}$ = 6.8 Hz, H-5^{Cer}), 5.43 (dd, 1 H, $J_{4,5}$ = 15.1 Hz, $J_{3,4}$ = 7.5 Hz, H-4^{Cer}), 4.88 (d, 1 H, $J_{1,2}$ = 8.2 Hz, anomer H), 4.61 (d, 1 H, anomer H), 4.46 (d, 1 H, $J_{1,2}$ = 7.5 Hz, anomer H), 4.34 (d, 1 H, $J_{1,2}$ = 7.5 Hz, anomer H), 3.02, 2.80, 2.74, and 2.63 (4 br dd, 4 H, 4 H-3eq), 2.17 (t, 1 H, NHCOCH_2), 2.06, 2.03, 2.03, and 2.02 (4 s, 17 H, 5 NAc, H-6^{Cer}, and 6$'^{Cer}$), 1.84 (br t, 1 H, H-3ax), 1.69 (m, 3 H, 3 H-3ax), 1.57 (m, 1 H, NHCOCH_2), 1.36 (m, 1 H, H-7^{Cer}), 1.27 (m, 51 H, H-7$'^{Cer}$, 25 CH_2), 0.89 (t, 6 H, 2 Me); ^{13}C NMR (150 MHz, $CDCl_3$/CD_3OD/D_2O = 5:5:1) δ 174.8, 174.0, 173.8, 173.7, 173.4, 173.3, 172.8, 172.6, 172.4, 172.3, 133.6, 128.8, 103.7, 102.7, 102.2, 101.9, 100.7, 100.1, 100.1, 99.0, 80.5, 78.5,

(41) Zemplén, G. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 1555–1564.

TABLE 3. Final Glycosylations



Entry	Acceptor	Product	% Yield[a]
1	 **36**	 **40**	91
2	 **37**	 **41**	73
3	 **38**	 **42**	63
4	 **39**	 **43**	80

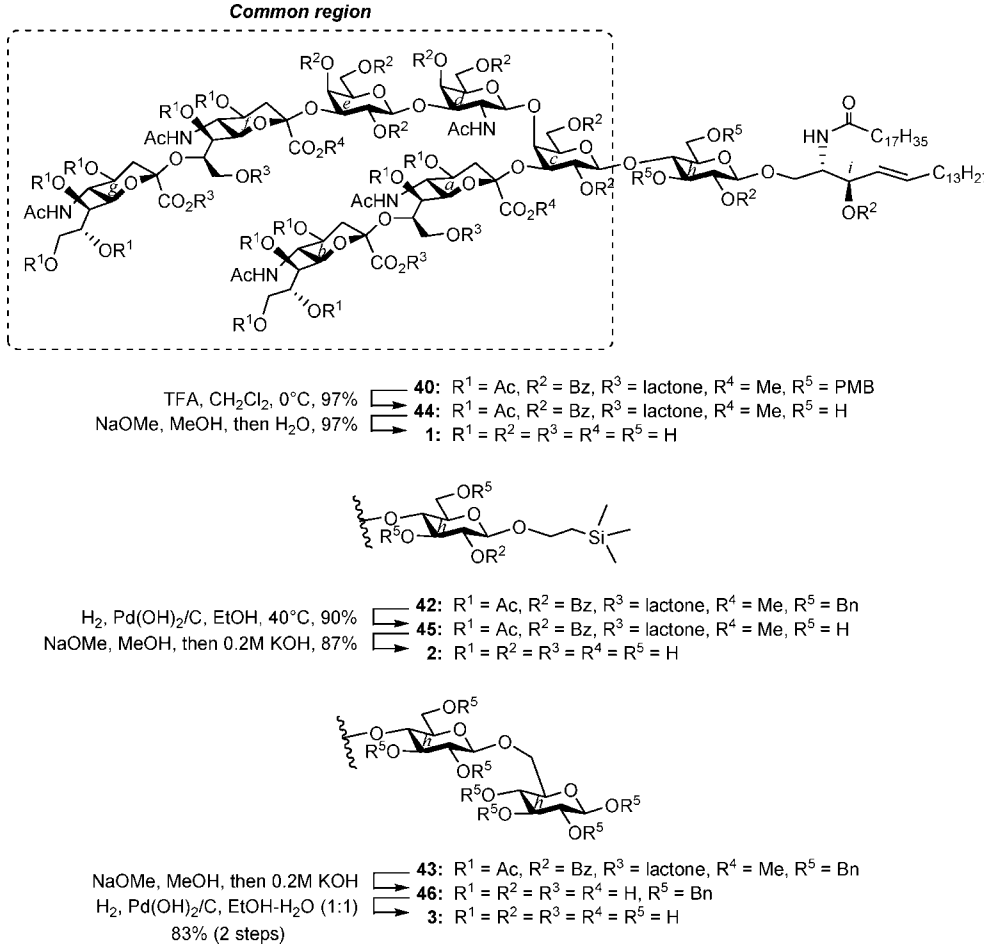
[a] Isolated yield.

74.3, 73.9, 73.8, 73.8, 73.5, 73.4, 73.3, 73.2, 73.0, 72.8, 72.5, 72.4, 70.9, 70.8, 69.1, 69.0, 68.9, 68.9, 68.3, 68.1, 68.0, 68.0, 67.9, 67.3, 67.3, 67.0, 66.6, 66.2, 66.1, 65.5, 65.5, 64.9, 62.6, 62.5, 61.2, 61.1, 61.0, 60.9, 60.7, 60.6, 60.5, 59.7, 59.6, 59.3, 59.3, 52.7, 52.4, 52.1, 51.9, 51.7, 50.9, 40.3, 37.9, 35.5, 31.5, 31.0, 31.0, 28.8, 28.8, 28.7, 28.7, 28.6, 28.6, 28.4, 28.4, 25.2, 22.2, 21.7, 21.4, 21.3, 21.2, 21.0, 12.7; HRMS (ESI) *m/z* found $[M - 2H^+]^{2-}$ 1208.5783, $C_{106}H_{182}N_6O_{55}$ calcd for $[M - 2H^+]^{2-}$ 1208.5736.

2-(Trimethylsilyl)ethyl (5-Acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→8)-(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)-*β*-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-*β*-D-galactopyranosyl-(1→4)-[(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→8)-(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)]-*β*-D-galactopyranosyl-(1→4)-*β*-D-glucopyranoside (2). To a mixture of **45** (40 mg, 0.0121 mmol) in MeOH (1.0 mL) was added catalytic amounts of sodium methoxide (28% solution in MeOH). After stirring for 17 h at room temperature as the reaction was monitored by TLC (1-BuOH/MeOH/5% $CaCl_2$ (aq) = 2:1:1), the mixure was heated at 50 °C, and the stirring was continued for 17 h at 50 °C. Then, 0.2 M KOH (0.5 mL) was added to the mixture. After stirring for 30 h at 75 °C as the reaction was monitored by TLC (1-BuOH/MeOH/5% $CaCl_2$ (aq) = 2:1:1), the reaction was neutralized with IR-120 (H^+) resin and filtered through cotton, and the resin was washed with MeOH and H_2O. The combined filtrate and washings were concentrated. The resulting residue was purified by gel filtration column chromatography on Sephadex LH-20 using H_2O as the eluent to give **2** (20 mg, 87%): $[\alpha]_D = -5.0°$ (*c* 0.7, H_2O); ^1H NMR (500 MHz, $D_2O/(CD_3)_2CO$ = 10:1) δ 4.73 (d, 1 H, H-1h), 4.59 (d, 1 H, $J_{1,2}$ = 7.4 Hz, H-1e), 4.49 (d, 1 H, $J_{1,2}$ = 8.6 Hz, H-1c), 4.47 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1d), 3.41 (t, 1 H, $J_{1,2} = J_{2,3}$ = 8.6 Hz, H-2c), 3.25 (near t, 1 H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.1 Hz, H-2d), 2.77−2.63 (m, 4 H, H-3eq-a, 3eq-b, 3eq-f, and 3eq-g), 2.05, 2.04, and 2.01 (3 s, 15 H, 5 NAc), 1.76−1.69 (m, 4 H, H-3ax-a, 3ax-b, 3ax-f, and 3ax-g), 1.07−0.91 (m, 2 H, $OCH_2CH_2SiMe_3$), 0.00 (s, 9 H, $OCH_2CH_2SiMe_3$); ^{13}C NMR (125 MHz, $D_2O/(CD_3)_2CO$ = 10:1) δ 175.2, 175.1, 175.0, 173.9, 173.6, 173.6, 173.5, 104.5, 103.1, 102.8, 101.7, 100.8, 100.6, 100.5, 100.5, 80.2, 78.8, 78.6, 75.6, 75.5, 75.1, 74.9, 74.7, 74.6, 74.5, 74.3, 74.0, 73.1, 72.9, 72.0, 69.8, 69.8, 69.7, 69.5, 68.8, 68.7, 68.5, 68.3, 68.3, 67.9, 67.6, 62.9, 61.9, 61.8, 61.3, 61.2, 60.9, 60.3, 52.6, 52.5, 52.1, 51.4, 40.9, 40.8, 39.9, 39.8, 22.9, 22.6, 22.6, 22.3, 17.8, −2.1; HRMS (ESI) *m/z* found $[M - 4H^+]^{4-}$ 491.9194, $C_{75}H_{125}N_5O_{53}Si$ calcd for $[M - 4H^+]^{4-}$ 491.9192.

(5-Acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→8)-(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)-*β*-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-*β*-D-galactopyranosyl-(1→4)-[(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→8)-(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)]-*β*-D-galacto-

SCHEME 6. Global Deprotections



pyranosyl-(1→4)-*β*-D-glucopyranosyl-(1→6)-D-glucopyranose (3). To a mixture of **43** (46 mg, 0.0118 mmol) in MeOH (0.8 mL) was added catalytic amounts of sodium methoxide (28% solution in MeOH). After stirring for 12 h at room temperature as the reaction was monitored by TLC (1-BuOH/MeOH/5% $CaCl_2$ (aq) = 2:1:1), the mixure was heated at 50 °C, and the stirring was continued for 24 h at 50 °C. Then 0.2 M KOH (0.2 mL) was added to the mixture. After stirring for 3 h at room temperature as the reaction was monitored by TLC (1-BuOH/MeOH/5% $CaCl_2$ (aq) = 2:1:1), the reaction was neutralized with IR-120 (H^+) resin and filtered through cotton, and the resin was washed with H_2O. The combined filtrate and washings were concentrated. The resulting residue was purified by gel filtration column chromatography on Sephadex LH-20 using H_2O as the eluent. Then, to a solution of the obtained white solid **46** in EtOH/H_2O (1.0 mL/1.0 mL) was added palladium hydroxide [20 wt % Pd (dry basis) on carbon, wet] (90 mg) at room temperature. After stirring for 14 h at room temperature under a H_2 atmosphere as the reaction was monitored by TLC (1-BuOH/MeOH/5% $CaCl_2$ (aq) = 1:1:1), the mixture was filtered through a membrane filter and washed with H_2O. The combined filtrate and washings were concentrated. The resulting residue was purified by gel filtration column chromatography on Sephadex LH-20 using H_2O as the eluent to give **3** (20 mg, 83%): $[\alpha]_D = -3.7°$ (*c* 0.4, H_2O); ^{1}H NMR (600 MHz, D_2O) δ 5.20 (d, 1 H, $J_{1,2} = 3.4$ Hz, H-1 of Glc unit), 4.71 (m, anomer H), 4.63 (d, 1 H, $J_{1,2} = 8.2$ Hz, H-1 of Glc unit), 4.58 (m, anomer H), 4.52 (d, 1 H, $J_{1,2} = 8.2$ Hz, anomer H), 4.50 (d, 1 H, $J_{1,2} = 7.5$ Hz, anomer H), 4.47 (d, 1 H, $J_{1,2} = 8.2$ Hz, anomer H), 3.51 (dd, 1 H, $J_{1,2} = 3.4$ Hz, $J_{2,3} = 10.3$ Hz, H-2 of Glc unit), 3.44 (t, 1 H, $J_{2,3} = J_{3,4} = 8.9$ Hz, H-3 of Glc unit), 3.40−3.30 (m, 3 H, 3 H-2), 3.22 (near t, 1 H, $J_{1,2} = 8.2$ Hz, $J_{2,3} = 8.9$ Hz, H-2), 2.76−2.62 (m, 4 H, H-3eq-a, 3eq-b, 3eq-f, and 3eq-g), 2.04, 2.03, 2.02, and 2.00 (4 s, 15 H, 5 NAc), 1.78−1.69 (m, 4 H, H-3ax-a, 3ax-b, 3ax-f, and 3ax-g); ^{13}C NMR (150 MHz, D_2O/$(CD_3)_2CO$ = 10:1) δ 165.9, 164.8−163.9, 95.3, 93.8, 93.6, 93.5, 92.0−90.9, 87.0, 83.1, 71.0, 69.2, 69.1, 66.7, 66.4, 65.9, 65.8, 65.8, 65.6, 65.3, 65.2, 65.1, 65.1, 64.8, 63.7, 62.7, 62.4, 61.4, 60.6, 60.5, 60.4, 60.2, 59.8, 59.8, 59.6, 59.4, 59.3, 59.2, 59.0, 58.6, 58.6, 53.6, 52.5, 52.4, 52.0, 52.0, 51.6, 51.0, 43.3, 43.2, 42.8, 42.1, 31.6, 31.5, 30.7, 30.2, 13.6, 13.4, 13.3, 13.1; HRMS (ESI) *m*/*z* found $[M - 4H^+]^{4-}$ 507.4145, $C_{76}H_{123}N_5O_{58}$ calcd for $[M - 4H^+]^{4-}$ 507.4143.

2-(Trimethylsilyl)ethyl [Methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,6-di-*O*-benzyl-*β*-D-galactopyranoside (6). To a mixture of **4** (200 mg, 210 μmol) and **5** (196 mg, 420 μmol) in propionitrile (4.0 mL) were added 3 Å molecular sieves (400 mg) at room temperature. After stirring for 1 h, NIS (96 mg, 420 μmol) was added to the mixture. After cooling to −50 °C, TfOH (11 μL, 130 μmol) was added to the mixture. After stirring for 96 h at −50 °C as the reaction was monitored by TLC (EtOAc/MeOH = 10:1), reagents (NIS, 2 × 96 mg, 192 mg in total; TfOH, 2 × 11 μL, 22 μL in total) were added to the mixture after 120 and 144 h. The mixture was stirred for a total of 168 h at the same temperature. Then, the reaction was quenched by triethylamine and filtered through a Celite pad, and the pad was washed with $CHCl_3$. The combined filtrate and washings were evaporated. The residue was extracted with $CHCl_3$ and washed with saturated Na_2CO_3 (aq), saturated $Na_2S_2O_3$ (aq), and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography twice (first with $CHCl_3$/MeOH = 50:1 and second with EtOAc) to give **6** (120

mg, 44%) and its β-isomer **6β** (39 mg, 14%). **6α**: $[\alpha]_D = -28.1°$ (*c* 3.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35−7.24 (m, 10 H, 2 Ph), 5.69 (d, 1 H, NH-a), 5.67 (d, 1 H, NH-b), 5.38 (dt, 1 H, H-4b), 5.35 (dd, 1 H, H-7b), 5.15 (dt, 1 H, H-8b), 5.09 (dd, 1 H, H-7a), 5.07 (dt, 1 H, H-4a), 4.90 and 4.62 (2 d, 2 H, J_{gem} = 11.2 Hz, PhCH_2), 4.56 (2 d, 2 H, J_{gem} = 11.6 Hz, PhCH_2), 4.40 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1c), 4.37 (dd, 1 H, H-9′a), 4.29−4.19 (m, 3 H, H-9a, 9′b, and 8a), 4.18 (q, 1 H, H-5b), 4.07−3.95 (m, 6 H, H-9b, 5a, 3c, 6a, 6b, and OCH_2CH$_2$SiMe$_3$), 3.87 (br s, 1 H, H-4c), 3.82 (s, 3 H, CO_2Me), 3.81 (dd, 1 H, H-6′c), 3.73 (dd, 1 H, H-6c), 3.61 (m, 2 H, H-5c and OCH_2CH$_2$SiMe$_3$), 3.54 (t, 1 H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.1 Hz, H-2c), 2.80 (s, 1 H, OH), 2.46 (dt, 2 H, H-3eq-a and H-3eq-b), 2.14−1.88 (8 s and 2 t, 26 H, H-3ax-a, H-3ax-b, and 8 Ac), 1.03 (t, 2 H, OCH$_2$CH_2SiMe$_3$), 0.02 (s, 9 H, OCH$_2$CH$_2$Si*Me*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.7, 170.6, 170.5, 170.2, 169.8, 169.7, 168.1, 165.4, 138.6, 138.1, 128.4, 128.1, 128.0, 127.7, 127.6, 127.5, 103.3, 99.4, 96.1, 75.8, 74.9, 73.6, 73.0, 72.8, 72.1, 70.7, 69.4, 69.2, 69.1, 68.9, 67.8, 67.4, 67.1, 67.1, 66.6, 61.8, 53.1, 49.3, 49.0, 38.3, 35.8, 23.1, 20.9, 20.8, 20.7, 20.6, 18.5; HRMS (ESI) *m/z* found $[M + Na]^+$ 1313.4779, $C_{60}H_{82}N_2O_{27}Si$ calcd for $[M + Na]^+$ 1313.4771. **6β**: $[\alpha]_D = -31.9°$ (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.50−7.27 (m, 10 H, 2 Ph), 5.46 (dt, 1 H, $J_{3eq,4}$ = 5.4 Hz, $J_{4,5}$ = 10.2 Hz, H-4b), 5.38 (d, 1 H, NH-b), 5.35 (dd, 1 H, H-7b), 5.17−5.09 (m, 3 H, H-4a, 7a, and 8b), 5.06 and 4.62 (2 d, 2 H, J_{gem} = 10.9 Hz, PhCH_2), 4.58−4.52 (m, 4 H, H-9′a, PhCH_2, and H-9a), 4.45 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1c), 4.34−4.28 (m, 3 H, H-6a, 8a, and 9b), 4.17 (q, 1 H, $J_{4,5}$ = 10.2 Hz, H-5b), 4.05−3.99 (m, 3 H, H-5a, 9b, and OCH_2CH$_2$SiMe$_3$), 3.83 (br s, 1 H, H-4c), 3.81−3.75 (m, 3 H, H-6b, 3c, and 6′c), 3.73 (s, 3 H, CO_2Me), 3.71 (dd, 1 H, $J_{5,6}$ = 9.6 Hz, H-6c), 3.61 (m, 2 H, $J_{5,6}$ = 9.6 Hz, H-5c, and OCH_2CH$_2$SiMe$_3$), 3.64 (t, 1 H, $J_{1,2}$ = 7.5 Hz, H-2c), 3.62−3.58 (m, 2 H, H-5c and OCH_2CH$_2$SiMe$_3$), 3.30 (s, 1 H, OH), 2.56 (dd, 1 H, J_{gem} = 13.7 Hz, $J_{3eq,4}$ = 4.3 Hz, H-3eq-a), 2.46 (dd, 1 H, J_{gem} = 13.5 Hz, $J_{3eq,4}$ = 5.4 Hz, H-3eq-b), 2.12, 2.08, 2.04, 2.03, 2.02, and 2.00 (6 s, 18 H, 6 Ac), 2.02 (m, 1 H, J_{gem} = 13.7 Hz, H-3ax-a), 1.91 (t, 1 H, J_{gem} = 13.5 Hz, H-3ax-b), 1.89 and 1.73 (2 s, 6 H, 2 NAc), 1.02 (t, 2 H, OCH$_2$CH_2SiMe$_3$), 0.01 (s, 9 H, OCH$_2$CH$_2$Si*Me*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.9, 170.6, 170.5, 170.3, 169.9, 169.8, 169.6, 168.2, 164.7, 138.9, 137.8, 128.5, 128.4, 128.3, 128.1, 128.1, 127.8, 127.7, 103.3, 99.3, 96.6, 77.9, 77.7, 74.9, 73.6, 72.7, 72.3, 72.2, 70.8, 69.8, 69.0, 68.7, 68.6, 68.2, 67.6, 67.5, 66.6, 61.6, 53.2, 49.0, 48.4, 37.9, 34.7, 30.3, 23.2, 23.1, 21.0, 20.9, 20.8, 20.7, 20.6, 18.5; HRMS (ESI) *m/z* found $[M + Na]^+$ 1313.4773, $C_{60}H_{82}N_2O_{27}Si$ calcd for $[M + Na]^+$ 1313.4771.

2-(Trimethylsilyl)ethyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranosyl-(1→4)-{[methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)}-2,6-di-*O*-benzyl-β-D-galactopyranoside (11). To a solution of **10** (6.30 g, 3.33 mmol) in $(CH_2Cl)_2$ (30 mL) were added activated Zn powder (25.2 g) and acetic acid (60 mL) at room temperature. After stirring for 1 h at 40 °C as the reaction was monitored by TLC ($CHCl_3$/MeOH = 10:1), the mixture was filtered through a Celite pad and washed with $CHCl_3$. The combined filtrate and washings were diluted with $CHCl_3$ and washed with saturated $NaHCO_3$ (aq), H_2O, and brine. After drying over Na_2SO_4 and being concentrated, the resulting residue was dissolved in CH_2Cl_2 (50 mL). Acetic anhydride (471 μL, 5.00 mmol) was then added to the mixture at room temperature. After stirring for 30 min as the reaction was monitored by TLC ($CHCl_3$/MeOH = 10:1), the reaction mixture was concentrated. The residue was purified by flash column chromatography using $CHCl_3$/MeOH (28:1 to 20:1) as the eluent to give **11** (5.04 g, 96%): $[\alpha]_D = -23.6°$ (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.53−7.23 (m, 15 H, 3 Ph), 6.86 (d, 1 H, NH-d), 5.59 (s, 1 H, PhC*H*<), 5.56 (d, 1 H, NH-b), 5.46 (near d, 1 H, NH-a), 5.40 (dt, 1 H, $J_{4,5}$ = 10.4 Hz, H-4b), 5.33 (dd, 1 H, $J_{6,7}$ = 2.1 Hz, H-7b), 5.12 (m, 2 H, H-8b and 4a), 4.98 and 4.51 (2 d, 2 H, J_{gem} = 11.2 Hz, PhCH_2), 4.96 (d, 1 H, H-4d), 4.92 (dd, 1 H, H-7a), 4.77 (d, 1 H, $J_{1,2}$ = 8.3 Hz, H-1d), 4.60 and 4.52 (2 d, 2 H, J_{gem} = 11.7 Hz, PhCH_2), 4.44 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1c), 4.43 (dd, 1 H, J_{gem} = 12.4 Hz, H-9a), 4.26 (dd, 1 H, H-9′b), 4.19 (q, 1 H, $J_{4,5} = J_{5,6} = J_{5,NH}$ =10.4 Hz, H-5b), 4.17 (m, 2 H, H-2d and 4c), 4.15−3.98 (m, 14 H, H-6a, 5a, 6d, 6′d, 5d, 3c, 9b, 6′c, 8a, and OCH_2CH$_2$SiMe$_3$), 3.89 (s, 3 H, COOMe), 3.82 (dd, 1 H, J_{gem} = 12.4 Hz, H-9′a), 3.74 (dd, 1 H, $J_{5,6}$ = 10.4 Hz, $J_{6,7}$ = 2.1 Hz, H-6b), 3.70 (s, 3 H, COOMe), 3.66 (dd, 1 H, H-6c), 3.62−3.54 (m, 3 H, OCH_2CH$_2$SiMe$_3$, H-3d, and 5c), 3.51 (near t, 1 H, $J_{1,2}$ = 7.5 Hz, H-2c), 3.02 (s, 1 H, OH), 2.32 (m, 3 H, H-3eq-b, 3eq-a, and 3ax-a,), 2.12−1.89 (8 s, 24 H, 8 Ac), 1.81 (near t, 1 H, H-3ax-b), 1.04 (m, 2 H, OCH$_2$CH_2SiMe$_3$), 0.02 (s, 9 H, OCH$_2$CH$_2$Si*Me*$_3$); HRMS (ESI) *m/z* found $[M + Na]^+$ 1604.5873, $C_{75}H_{99}N_3O_{32}Si$ calcd for $[M + Na]^+$ 1604.5878.

[Methyl 5-Acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,4,6-tri-*O*-benzoyl-α-D-galactopyranosyl Trichloroacetimidate (15). To a solution of **13** (2.50 g, 1.75 mmol) in CH_2Cl_2 (12 mL) was added trifluoroacetic acid (4.0 mL) at 0 °C. After stirring for 5 h at room temperature as the reaction was monitored by TLC ($CHCl_3$/MeOH = 10:1), the reaction mixture was coevaporated with toluene. The residue was purified by flash column chromatography using $CHCl_3$/MeOH (30:1) as the eluent to give the hemiacetal **14** (2.29 g, 98%): HRMS (ESI) *m/z* found $[M + Na]^+$ 1345.3912, $C_{62}H_{70}N_2O_{30}$ calcd for $[M + Na]^+$ 1345.3911.

To a solution of **14** (827 mg, 624 μmol) in CH_2Cl_2 (6.2 mL) were added trichloroacetonitrile (1.25 mL, 12.5 mmol) and DBU (112 μL, 750 μmol) at 0 °C. After stirring for 2 h at room temperature as the reaction was monitored by TLC ($CHCl_3$/MeOH = 10:1), the reaction mixture was concentrated. The resulting residue was purified by flash column chromatography using $CHCl_3$/MeOH (30:1) as the eluent to give **15** (862 mg, 94%): $[\alpha]_D$ = +21.4° (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 1 H, C=NH), 8.10−7.40 (m, 15 H, 3 Ph), 6.83 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1c), 5.94 (d, 1 H, $J_{3,4}$ = 3.6 Hz, $J_{4,5}$ = 1.2 Hz, H-4c), 5.68 (dd, 1 H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.4 Hz, H-2c), 5.56 (dt, 1 H, $J_{3eq,4}$ = 5.3 Hz, $J_{3ax,4}$ = 11.4 Hz, $J_{4,5}$ = 10.4 Hz, H-4b), 5.44 (d, 1 H, NH-a), 5.35 (dd, 1 H, $J_{6,7}$ = 2.1 Hz, H-7b), 5.27 (d, 1 H, $J_{5,NH}$ = 10.4 Hz, NH-b), 5.19 (m, 2 H, H-4a and 8b), 4.98 (dd, 1 H, $J_{6,7}$ = 1.7 Hz, $J_{7,8}$ = 9.2 Hz, H-7a), 4.93 (dd, 1 H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.6 Hz, H-3c), 4.74 (near dt, 1 H, $J_{4,5}$ = 1.2 Hz, H-5c), 4.65 (dt, 1 H, $J_{7,8}$ = 9.2 Hz, $J_{8,9'}$ = 2.6 Hz, H-8a), 4.48−4.40 (m, 3 H, H-6′c, 9a, and 6c), 4.28 (dd, 1 H, J_{gem} = 12.6 Hz, H-9′b), 4.17 (q, 1 H, $J_{4,5} = J_{5,NH}$ = 10.4 Hz, H-5b), 4.15 (q, 1 H, H-5a), 4.04 (dd, 1 H, $J_{8,9'}$ = 2.6 Hz, H-9′a), 4.02 (dd, 1 H, J_{gem} = 12.6 Hz, H-9b), 3.96 (dd, 1 H, $J_{6,7}$ = 1.7 Hz, H-6a), 3.91 (dd, 1 H, $J_{6,7}$ = 2.1 Hz, H-6b), 3.36 (s, 3 H, COOMe), 2.56 (dd, 1 H, J_{gem} = 13.1 Hz, $J_{3eq,4}$ = 5.3 Hz, H-3eq-b), 2.24 (dd, 1 H, H-3eq-a), 2.12−1.89 (8 s and t, 25 H, 8 Ac and H-3ax-a), 1.70 (t, 1 H, J_{gem} = 13.1 Hz, $J_{3ax,4}$ = 11.4 Hz, H-3*ax*-b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 170.4, 170.4, 170.0, 169.8, 169.8, 167.4, 166.0, 165.6, 165.2, 164.4, 160.2, 133.5, 133.3, 133.2, 129.9, 129.7, 129.5, 129.3, 129.3, 128.9, 128.5, 128.4, 98.9, 97.0, 93.9, 90.8, 77.1, 72.5, 71.9, 70.6, 69.8, 69.5, 69.5, 69.2, 68.8, 68.4, 68.3, 67.9, 67.7, 66.7, 62.9, 62.0, 52.5. 49.1, 38.2, 36.1, 23.1, 23.0, 20.7, 20.7, 20.7, 20.7, 20.6, 20.4; HRMS (ESI) *m/z* found $[M + Na]^+$ 1488.3004, $C_{64}H_{70}Cl_3N_3O_{30}$ calcd for $[M + Na]^+$ 1488.3007.

2-(Trimethylsilyl)ethyl [Methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranosyl-(1→4)-{[methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-non-

ulopyranosylonate]-(2→3)}-2,6-di-*O*-benzyl-*β*-D-galactopyranoside (16). To a mixture of **15** (2.71 g, 1.84 mmol) and **11** (1.93 g, 1.22 mmol) in CH_2Cl_2 (30 mL) was added 4 Å molecular sieves (AW-300) (4.6 g) at room temperature. After stirring for 1 h and then cooling to 0 °C, TMSOTf (6.7 μL, 36.8 μmol) was added to the mixture. After stirring for 22 h at 0 °C as the reaction was monitored by TLC ($CHCl_3$/MeOH/EtOAc = 15:1:1), the reaction was quenched by saturated $NaHCO_3$ (aq) and filtered through a Celite pad, and the pad was washed with $CHCl_3$. The combined filtrate and washings were washed with brine, dried over Na_2SO_4, and concentrated. The resulting residue was purified by flash column chromatography using $CHCl_3$/MeOH/EtOAc (20:1:1) to $CHCl_3$/MeOH (9:1) as the eluent to give **16** (3.29 g, 93%): $[\alpha]_D = -11.5°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09−7.18 (m, 30 H, 6 Ph), 5.74 (d, 1 H, H-4e), 5.54 (dt, 1 H, $J_{3eq,4} = 5.2$ Hz, $J_{4,5} = 10.5$ Hz, H-4g), 5.48 (t, 1 H $J_{1,2} = 7.7$ Hz, H-2e), 5.43 (m, 3 H, H-4b, NH-f, and PhC*H*), 5.34 (m, 6 H, H-7b, 7g, and 4 NH), 5.17 (m, 3 H, H-4f, 8b, and 8g), 5.14 (d, 1 H, $J_{1,2} = 8.0$ Hz, H-1d), 5.03 (dd, 1 H, H-7a), 4.97 (br d, 1 H, $J_{1,2} = 7.7$ Hz, H-1e), 4.95 (dd, 1 H, $J_{7,8} = 9.6$ Hz, H-7f), 4.88 (m, 2 H, H-4a and 3d), 4.80 and 4.52 (2 d, 2 H, $J_{gem} = 11.4$ Hz, PhCH_2), 4.65 (dt, 1 H, $J_{7,8} = 9.6$ Hz, H-8f), 4.57 (dd, 1 H, H-6e), 4.52 and 4.46 (2 d, 2 H, $J_{gem} = 11.6$ Hz, PhCH_2), 4.42 (m, 3 H, H-9′a, 6′e, and 3e), 4.38−4.19 (m, 8 H, H-8a, 9′f, 1c, 4d, 9′g, 9′b, 5b, and 5e), 4.11 (2 q, 2 H, H-5g, and 5f), 4.08−3.80 (m, 18 H, OCH_2CH$_2$SiMe$_3$, H-5a, 9a, 9b, 9g, 6a, 6′d, 4c, 9f, 3c, 6g, 6f, 6b, 6′c, 5d, and COOMe-a), 3.71 (d, 1 H, H-6d), 3.55 (m, 2 H, H-6c and OCH_2CH$_2$SiMe$_3$), 3.44 (t, 1 H, H-5c), 3.34 (near q, 1 H, $J_{1,2} = 8.0$ Hz, H-2d), 3.33 (near t, 1 H, H-2c), 3.17 (s, 3 H, COOMe-f), 2.54 (dt, 2 H, H-3eq-a and 3eq-b), 2.44 (dd, 1 H, $J_{3eq,4} = 5.2$ Hz, $J_{gem} = 13.5$ Hz, H-3eq-g), 2.13−1.88 (m, 55 H, 17 Ac, H-3ax-a, 3ax-b, 3ax-f, and 3eq-f), 1.59 (t, 1 H, $J_{gem} = 13.5$ Hz, H-3ax-g), 1.01 (near t, 2 H, OCH$_2$CH_2SiMe$_3$), 0.00 (s, 9 H, OCH$_2$CH$_2$Si*Me*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.8, 170.7, 170.6, 170.5, 170.5, 170.5, 170.4, 170.4, 170.3, 170.3, 169.9, 169.8, 169.8, 169.8, 169.7, 169.6, 167.7, 167.3, 166.0, 164.7, 164.4, 164.2, 138.7, 138.5, 138.4, 133.4, 133.2, 133.0, 130.2, 129.9, 129.6, 129.5, 128.7, 128.6, 128.4, 128.4, 128.1, 128.0, 128.0, 127.9, 127.6, 127.5, 127.3, 126.4, 126.2, 103.4, 102.3, 100.7, 99.4, 99.1, 98.1, 97.1, 96.7, 77.8, 77.2, 75.9, 75.5, 74.6, 73.3, 72.9, 72.6, 72.5, 72.4, 72.1, 71.8, 71.5, 71.0, 70.6, 70.1, 69.6, 69.5, 69.3, 68.9, 68.7, 68.6, 68.5, 67.8, 67.7, 67.4, 66.7, 66.6, 66.0, 62.7, 62.0, 61.8, 54.3, 52.3, 49.1, 49.0, 48.9, 38.2, 35.9, 35.7, 30.0, 29.6, 23.1, 22.8, 20.9, 20.7, 20.7, 20.6, 20.6, 20.6, 20.5, 20.5, 18.5, 14.1, −1.5; HRMS (ESI) *m*/*z* found $[M + 2Na]^{2+}$ 1465.9833, $C_{137}H_{167}N_5O_{61}Si$ calcd for $[M + 2Na]^{2+}$ 1465.9838.

[Methyl 5-Acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,4,6-tri-*O*-benzoyl-*β*-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-benzoyl-2-deoxy-*β*-D-galactopyranosyl-(1→4)-{[methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)}-2,6-di-*O*-benzoyl-α-D-galactopyranosyl Trichloroacetimidate (20). To a solution of **18** (795 mg, 261 μmol) in CH_2Cl_2 (3.9 mL) was added trifluoroacetic acid (1.3 mL) at 0 °C. After stirring for 3 h at room temperature as the reaction was monitored by TLC (PhMe/MeOH = 5:1), the reaction mixture was coevaporated with toluene. The resulting residue was purified by flash column chromatography using $CHCl_3$/MeOH (17.5:1 → 15:1 → 10:1) as the eluent to give **19** (765 mg, 99%): HRMS (ESI) *m*/*z* found $[M + 2Na]^+$ 1489.9383, $C_{139}H_{155}N_5O_{65}$ calcd for $[M + 2Na]^+$ 1489.9380.

To a solution of **19** (200 mg, 68.1 μmol) in CH_2Cl_2 (0.68 mL) were added trichloroacetonitrile (136 μL, 1.36 mmol) and DBU (12 μL, 81.7 μmol) at 0 °C. After stirring for 2 h at room temperature as the reaction was monitored by TLC (PhMe/MeOH = 5:1), the reaction mixture was evaporated. The resulting residue was purified by flash column chromatography using $CHCl_3$/MeOH (20:1 to 13:1) as the eluent to give **20** (199 mg, 95%): $[\alpha]_D = +4.8°$ (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1 H, C═NH), 8.12−7.25 (m, 35 H, 7 Ph), 6.55 (d, 1 H, $J_{1,2} = 3.4$ Hz, H-1c), 5.95 (br d, 1 H, H-4d), 5.89 (br d, 2 H, 2 NH), 5.70 (d, 1 H, H-4e), 5.63 (dd, 1 H, $J_{1,2} = 3.4$ Hz, $J_{2,3} = 10.4$ Hz, H-2c), 5.58 (d, 1 H, NH-b), 5.55 (dt, 1 H, H-4g), 5.46 (2 d, 2 H, 2 NH), 5.36−5.31 (m, 4 H, H-4b, 2e, 7g, and 7b), 5.29 (d, 1 H, $J_{1,2} = 8.5$ Hz, H-1d), 5.24 (m, 1 H, H-8b), 5.16 (m, 1 H, H-8g), 5.10 (near q, 1 H, H-4f), 5.04 (br d, 1 H, H-1e), 5.20 (m, 2 H, H-4a and 7a), 4.93 (br dd, 1 H, H-3d), 4.86 (dd, 1 H, H-7f), 4.80 (dd, 1 H, $J_{2,3} = 10.4$ Hz, H-3c), 4.63−4.58 (m, 3 H, H-8f, 6′e, and 6′d), 4.45−4.33 (m, 5 H, H-5d, 6′c, 3e, 6c, and 6d), 4.30−4.16 (m, 10 H, H-8a, 9g, 9b, 9f, 4c, 6b, 5b, 9′a, 9a, and 5e), 4.11 (q, 1 H, H-5g), 4.06−3.98 (m, 6 H, H-5f, 9b, 9g, 6b, 5c, and 5a), 3.91 (2 dd, 2 H, H-6a and 6g), 3.86 (dd, 1 H, H-6f), 3.82 (s, 3 H, COOMe-a), 3.75 (m, 2 H, H-2d and 9′f), 3.24 (s, 3 H, COOMe-f), 2.57−2.49 (m, 3 H, H-3eq-a, 3eq-b, and 3eq-g), 2.10−1.81 (m, 53 H, 17 Ac, H-3eq-f, and 3ax-f), 1.63 (t, 1 H, H-3ax-g); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 171.2, 170.6, 170.6, 170.4, 170.2, 170.2, 169.8, 169.7, 169.6, 167.7, 167.1, 166.5, 166.0, 165.9, 165.5, 165.3, 164.8, 164.2, 160.0, 133.4, 133.2, 133.1, 133.0, 132.8, 132.8, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.4, 129.3, 129.0, 128.4, 128.3, 128.2, 101.3, 99.8, 99.0, 98.9, 96.8, 95.4, 95.1, 94.1, 90.8, 76.2, 75.0, 73.3, 72.5, 71.9, 71.5, 71.3, 71.1, 71.0, 70.6, 70.1, 69.8, 69.6, 69.3, 69.2, 69.1, 68.8, 68.6, 68.1, 67.5, 67.1, 66.8, 66.7, 66.4, 64.2, 62.3, 62.1, 62.1, 61.9, 54.3, 53.0, 52.3, 49.0, 48.9, 48.7, 38.8, 38.2, 36.9, 36.1, 35.4, 29.5, 22.9, 22.8, 22.8, 22.6, 22.5, 20.7, 20.6, 20.6, 20.5, 20.4, 20.3, 20.2, 13.9; HRMS (ESI) *m*/*z* found $[M + 2Na]^{2+}$ 1561.3934, $C_{141}H_{155}Cl_3N_6O_{65}$ calcd for $[M + 2Na]^{2+}$ 1561.3934.

2-*O*-Benzoyl-4-*O*-chloroacetyl-3,6-di-*O*-*p*-methoxylbenzyl-D-glucopyranosyl Trichloroacetimidate (33). To a solution of **31** (500 mg, 0.779 mmol) in degassed THF (7.8 mL) were added polymethylhydrosiloxane (PMHS) (140 μL, 2.33 mmol), tetrakis(triphenylphosphine)palladium (179 mg, 0.155 mmol), and $ZnCl_2$ (106 mg, 0.779 mmol) at room temperature. After stirring for 32 h at room temperature, the completion of the reaction was confirmed by TLC (EtOAc/PhMe = 1:4). Then, H_2O was added to the mixture and filtered through a Celite pad, and the pad was washed with EtOAc. The combined filtrate and washings were washed with saturated $NaHCO_3$ (aq), and brine. After drying over Na_2SO_4 and being concentrated, the resulting residue was purified by flash column chromatography using EtOAc/PhMe (1:5) as the eluent to give the hemiacetal **32** (400 mg, 85%, α/*β* = 7/1): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05−7.42 (m, 5 H, Ph), 7.21−6.75 (4 d, 8 H, Ar), 5.55 (br t, 1 H, $J_{1,2} = J_{1,OH} = 3.4$ Hz, H-1α), 5.19 (t, 1 H, $J_{3,4} = 8.9$ Hz, H-4*β*), 5.15 (t, 1 H, $J_{1,2} = J_{2,3} = 8.9$ Hz, H-2*β*), 5.09 (t, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4α), 5.08 (dd, 1 H, $J_{1,2} = 3.4$ Hz, $J_{2,3} = 9.6$ Hz, H-2α), 4.73 (t, 1 H, $J_{1,2} = J_{1,OH} = 8.9$ Hz, H-1*β*), 4.67 and 4.52 (2 d, 2 H, $J_{gem} = 11.6$ Hz, ArCH_2O), 4.44 and 4.39 (2 d, 2 H, $J_{gem} = 11.7$ Hz, ArCH_2O), 4.18 (m, 2 H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3α and 5α), 3.92 (d, 1 H, $J_{1,OH} = 8.9$ Hz, OH-*β*), 3.87 (t, 1 H, $J_{2,3} = J_{3,4} = 8.9$ Hz, H-3*β*), 3.78 and 3.74 (2 s, 6 H, 2 MeO), 3.69 and 3.61 (2 d, 2 H, $J_{gem} = 14.4$ Hz, ClCH$_2$), 3.58 (d, 1 H, $J_{1,OH} = 3.4$ Hz, OH-α), 3.47 (dd, 1 H, $J_{gem} = 10.3$ Hz, $J_{5,6} = 5.5$ Hz, H-6α), 3.43 (dd, 1 H, $J_{gem} = 10.3$ Hz, $J_{5,6'} = 3.4$ Hz, H-6′α); HRMS (ESI) *m*/*z* found $[M + Na]^+$ 623.1658, $C_{31}H_{33}ClO_{10}$ calcd for $[M + Na]^+$ 623.1659.

To a solution of **32** (352 mg, 0.585 mmol) in CH_2Cl_2 (5.8 mL) were added trichloroacetonitrile (1.2 mL, 11.7 mmol) and K_2CO_3 (243 mg, 1.76 mmol) at room temperature. After stirring for 3 h at room temperature as the reaction was monitored by TLC (EtOAc/hexane = 1:2), the reaction mixture was filtered through cotton, washed with CH_2Cl_2, and then evaporated. The resulting residue was purified by flash column chromatography using EtOAc/hexane (1:5 to 1:4) as the eluent to give **33**: [α-isomer, 176 mg (40%) and *β*-isomer, 230 mg (53%)]. **33α**: $[\alpha]_D = +77.1°$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1 H, C═NH), 7.98−7.41 (m, 5 H, Ph), 7.23−6.75 (4 d, 8 H, Ar), 6.63 (d, 1 H, $J_{1,2} = 3.5$ Hz, H-1), 5.38 (dd, 1 H, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 9.5$ Hz, H-2), 5.35 (t, 1

H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 4.65 and 4.54 (2 d, 2 H, $J_{gem} = 11.5$ Hz, ArCH_2O), 4.46 and 4.37 (2 d, 2 H, $J_{gem} = 11.5$ Hz, ArCH_2O), 4.23 (near t, 1 H, $J_{2,3} = 9.5$ Hz, $J_{3,4} = 10.0$ Hz, H-3), 4.11 (m, 1 H, $J_{4,5} = 10.0$ Hz, $J_{5,6} = J_{5,6'} = 4.0$ Hz, H-5), 3.80 and 3.75 (2 s, 6 H, 2 MeO), 3.71 and 3.66 (2 d, 2 H, $J_{gem} = 15.0$ Hz, ClCH_2), 3.57 (dd, 1 H, $J_{gem} = 11.0$ Hz, $J_{5,6} = 4.0$ Hz, H-6), 3.52 (dd, 1 H, $J_{gem} = 11.0$ Hz, $J_{5,6'} = 4.0$ Hz, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 165.1, 160.3, 159.3, 133.4, 129.7, 129.7, 129.7, 129.4, 129.0, 128.4, 113.7, 93.5, 75.8, 74.3, 73.2, 72.3, 71.7, 71.1, 68.2, 55.2, 55.2, 40.5; HRMS (ESI) *m/z* found $[M + Na]^+$ 766.0750, $C_{33}H_{33}Cl_4NO_{10}$ calcd for $[M + Na]^+$ 766.0756. **33β**: $[\alpha]_D = +43.5°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1 H, C═NH), 7.98−7.40 (m, 5 H, Ph), 7.24−6.69 (4 d, 8 H, Ar), 5.96 (d, 1 H, $J_{1,2} = 7.8$ Hz, H-1), 5.58 (near t, 1 H, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 8.6$ Hz, H-2), 5.33 (t, 1 H, $J_{3,4} = J_{4,5} = 9.1$ Hz, H-4), 4.58 and 4.50 (2 d, 2 H, $J_{gem} = 11.4$ Hz, ArCH_2O), 4.45 and 4.40 (2 d, 2 H, $J_{gem} = 11.2$ Hz, ArCH_2O), 3.93 (near t, 1 H, $J_{2,3} = 8.6$ Hz, $J_{3,4} = 9.1$ Hz, H-3), 3.85 (m, 1 H, $J_{4,5} = 9.1$ Hz, H-5), 3.79 and 3.71 (2 s, 6 H, 2 MeO), 3.74−3.59 (m, 4 H, ClCH_2, H-6, and 6′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 164.5, 161.2, 159.3, 159.2, 133.3, 129.7, 129.6, 129.5, 129.4, 129.3, 128.4, 113.7, 113.6, 95.8, 90.2, 78.5, 73.7, 73.4, 73.2, 72.2, 71.8, 68.8, 55.2, 55.1, 40.5; HRMS (ESI) *m/z* found $[M + Na]^+$ 766.0750, $C_{33}H_{33}Cl_4NO_{10}$ calcd for $[M + Na]^+$ 766.0756.

2-*O*-Benzoyl-4-*O*-chloroacetyl-3,6-di-*O*-*p*-methoxybenzyl-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (35). To a mixture of **33α** (176 mg, 0.236 mmol) and **34** (105 mg, 0.157 mmol) in CH_2Cl_2 (3.9 mL) was added 4 Å molecular sieves (AW-300) (300 mg) at room temperature. After stirring for 2 h, TMSOTf (2.1 μL, 11.8 μmol) was added to the mixture. After stirring for 3 h at room temperature as the reaction was monitored by TLC (EtOAc/PhMe = 1:5), the reaction was quenched by saturated $NaHCO_3$ (aq) and filtered through a Celite pad, and the pad was washed with $CHCl_3$. The combined filtrate and washings were washed with brine, dried over Na_2SO_4, and concentrated. The resulting residue was purified by flash column chromatography using EtOAc/PhMe (1:10) as the eluent to give **35** (95 mg, 48%): $[\alpha]_D = +10.7°$ (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.39 (m, 10 H, 2 Ph), 7.16−6.68 (4 d, 8 H, Ar), 5.83 (m, 1 H, $J_{4,5} = 15.1$ Hz, $J_{5,6} = 7.3$ Hz, $J_{5,6'} = 6.8$ Hz, H-5i), 5.71 (d, 1 H, $J_{2,NH} = 9.1$ Hz, NH), 5.51 (t, 1 H, $J_{2,3} = J_{3,4} = 6.8$ Hz, H-3i), 5.44 (dd, 1 H, $J_{3,4} = 6.8$ Hz, $J_{4,5} = 15.1$ Hz, H-4i), 5.25 (near t, 1 H, $J_{1,2} = 8.2$ Hz, $J_{2,3} = 9.6$ Hz, H-2h), 5.15 (t, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4h), 4.53 and 4.46 (2 d, 2 H, $J_{gem} = 11.4$ Hz, ArCH_2O), 4.50 (d, 1 H, $J_{1,2} = 8.2$ Hz, H-1h), 4.40 (m, 1 H, $J_{1,2} = 2.7$ Hz, $J_{2,3} = 6.8$ Hz, H-2i), 4.28 and 4.22 (2 d, 2 H, $J_{gem} = 11.0$ Hz, ArCH_2O), 4.10 (dd, 1 H, $J_{gem} = 9.6$ Hz, $J_{1,2} = 2.7$ Hz, H-1i), 3.82 (t, 1 H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3h), 3.78 and 3.70 (2 s, 6 H, 2 MeO), 3.65 (m, 2 H, ClCH_2), 3.58 (m, 2 H, H-5h and H-1′i), 3.45 (dd, 1 H, $J_{gem} = 10.0$ Hz, $J_{5,6} = 5.0$ Hz, H-6h), 3.38 (dd, 1 H, $J_{gem} = 10.0$ Hz, $J_{5,6'} = 4.6$ Hz, H-6′h), 1.98 (br dd, 2 H, $J_{gem} = 14.1$ Hz, $J_{5,6} = 7.3$ Hz, $J_{5,6'} = 6.8$ Hz, H-6i and 6′i), 1.74 and 1.37 (2 m, 2 H, NHCOCH_2), 1.26 (m, 52 H, 26 CH_2), 0.87 (t, 6 H, 2 Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 165.9, 165.0, 164.9, 159.2, 159.1, 137.2, 133.3, 132.8, 130.2, 129.6, 129.5, 129.5, 129.3, 128.4, 128.2, 124.7, 113.7, 113.6, 100.6, 78.8, 74.3, 73.6, 73.5, 73.2, 72.9, 72.6, 69.3, 67.1, 55.1, 55.0, 50.3, 40.5, 36.3, 32.2, 31.8, 29.6, 29.4, 29.4, 29.3, 29.2, 29.1, 28.8, 25.4, 22.6, 14.0; HRMS (ESI) *m/z* found $[M + Na]^+$ 1274.7255, $C_{74}H_{106}ClNO_{13}$ calcd for $[M + Na]^+$ 1274.7250.

2-*O*-Benzoyl-3,6-di-*O*-*p*-methoxybenzyl-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (36). To a solution of **35** (95 mg, 0.0758 mmol) in EtOH/$(CH_2Cl)_2$ (3.6 mL/1.2 mL) was added DABCO (127 mg, 1.13 mmol) at room temperature. After stirring for 5 h at 55 °C as the reaction was monitored by TLC (EtOAc/PhMe = 1:3), the mixture was diluted with EtOAc. The organic layer was washed with 2 M HCl, saturated $NaHCO_3$ (aq), and brine. After drying over Na_2SO_4 and being concentrated, the resulting residue was purified by flash column chromatography using EtOAc/PhMe (1:5) as the eluent to give **36** (85 mg, 96%): $[\alpha]_D = +5.4°$ (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.37 (m, 10 H, 2 Ph), 7.18−6.66 (4 d, 8 H, Ar), 5.81 (m, 1 H, $J_{4,5} = 15.1$ Hz, $J_{5,6} = 7.8$ Hz, $J_{5,6'} = 6.8$ Hz, H-5i), 5.70 (d, 1 H, $J_{2,NH} = 9.1$ Hz, NH), 5.48 (t, 1 H, $J_{2,3} = J_{3,4} = 7.3$ Hz, H-3i), 5.42 (dd, 1 H, $J_{3,4} = 7.3$ Hz, $J_{4,5} = 15.1$ Hz, H-4i), 5.16 (near t, 1 H, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.2$ Hz, H-2h), 4.64 (t, 2 H, $J_{gem} = 11.4$ Hz, 2 ArCH_2O), 4.45 (d, 1 H, $J_{1,2} = 7.8$ Hz, H-1h), 4.40 and 4.33 (2 d, 2 H, $J_{gem} = 11.4$ Hz, 2 ArCH_2O), 4.38 (m, 1 H, H-2i), 4.08 (dd, 1 H, $J_{gem} = 9.6$ Hz, $J_{1,2} = 2.3$ Hz, H-1i), 3.78 and 3.74 (2 s, 6 H, 2 MeO), 3.74 (dt, 1 H, $J_{3,4} = J_{4,5} = 9.2$ Hz, $J_{4,OH} = 1.8$ Hz, H-4h), 3.63 (t, 1 H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3h), 3.57 (m, 3 H, H-6h, 6′h, and H-1′i), 3.45 (m, 1 H, $J_{4,5} = 9.2$ Hz, H-5h), 2.93 (d, 1 H, $J_{4,OH} = 1.8$ Hz, OH), 1.97 (near dd, 2 H, $J_{gem} = 13.2$ Hz, $J_{5,6} = 7.8$ Hz, $J_{5,6'} = 6.8$ Hz, H-6i and 6′i), 1.72 (t, 1 H, NHCOCH_2), 1.37 (m, 1 H, NHCOCH_2), 1.26 (m, 52 H, 26 CH_2), 0.87 (t, 6 H, 2 Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 165.2, 165.0, 159.2, 159.1, 137.1, 133.2, 132.7, 130.3, 130.0, 129.6, 129.5, 129.3, 128.4, 128.2, 124.7, 113.7, 113.6, 100.8, 81.1, 74.3, 73.9, 73.8, 73.5, 73.3, 72.6, 70.1, 67.0, 55.1, 55.0, 50.3, 36.3, 32.2, 31.8, 29.6, 29.6, 29.4, 29.4, 29.3, 29.2, 29.1, 28.8, 25.4, 22.6, 14.0; HRMS (ESI) *m/z* found $[M + Na]^+$ 1198.7533, $C_{72}H_{105}NO_{12}$ calcd for $[M + Na]^+$ 1198.7534.

[Methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-benzoyl-2-deoxy-β-D-galactopyranosyl-(1→4)-{[methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)}-2,6-di-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-*p*-methoxybenzyl-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (40). To a mixture of **20** (146 mg, 0.0474 mmol) and **36** (85 mg, 0.0722 mmol) in CH_2Cl_2 (1.2 mL) was added 4 Å molecular sieves (AW-300) (200 mg) at room temperature. After stirring for 2 h and then cooling to 0 °C, TMSOTf (1.0 μL, 5.52 μmol) was added to the mixture. After stirring for 1 h at 0 °C as the reaction was monitored by TLC (PhMe/MeOH = 4:1), the reaction was quenched by saturated $NaHCO_3$ (aq) and filtered through a Celite pad, and the pad was washed with $CHCl_3$. The combined filtrate and washings were washed with brine, dried over Na_2SO_4, and concentrated. The resulting residue was purified by flash column chromatography using PhMe/MeOH (8:1 to 7:1) as the eluent to give **40** (177 mg, 91%): $[\alpha]_D = +3.2°$ (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08−7.28 (m, 45 H, 9 Ph), 7.07−6.56 (4 d, 8 H, Ar), 5.97 (near s, 1 H, H-4d), 5.76 (m, 1 H, $J_{4,5} = 14.4$ Hz, $J_{5,6} = 7.5$ Hz, $J_{5,6'} = 6.9$ Hz, H-5i), 5.69 (d, 1 H, $J_{3,4} = 4.1$ Hz, H-4e), 5.66 (d, 1 H, $J_{2,NH} = 8.9$ Hz, NH-i), 5.55 (dt, 2 H, $J_{3eq,4} = 4.0$ Hz, $J_{4,5} = 10.9$ Hz, H-4g and NH-d), 5.49 (br d, 1 H, NH-b), 5.45 (t, 1 H, H-3i), 5.39 (dd, 2 H, H-4i and NH-f), 5.35−5.26 (m, 5 H, H-7g, 7b, 4b, 2c, and 2e), 5.22 (d, 1 H, $J_{1,2} = 8.9$ Hz, H-1d), 5.15 (m, 4 H, H-8b, 8g, 2h, and NH-a), 5.08 (m, 1 H, H-4f), 4.98 (br dd, 1 H, H-7a), 4.95 (m, 1 H, H-4a), 4.84 (br dd, 1 H, H-7f), 4.82 (d, 1 H, $J_{1,2} = 9.6$ Hz, H-1c), 4.80 (m, 2 H, H-3d and ArCH_2O), 4.63 (m, 3 H, H-6c, 8f, and ArCH_2O), 4.55 (d, 1 H, $J_{gem} = 10.9$ Hz, ArCH_2O), 4.40 (br d, 2 H, $J_{1,2} = 7.5$ Hz, H-1e and 3e), 4.34 (d, 1 H, $J_{1,2} = 8.2$ Hz, H-1h), 4.32 (m, 1 H, H-2i), 4.28−3.96 (m, 24 H, H-9′b, 9′g, 9′f, 9′a, 4c, 5b, 3c, 6′c, 5g, 6b, 8a, 9a, 9b, 9g, 5a, 4h, 5e, 6e, 6′e, 5d, 6′d, 6d, 1i, and ArCH_2O), 3.89 (dd, 1 H, H-6g), 3.84 (dd, 2 H, H-6a and 6f), 3.80 (t, 1 H, $J_{2,3} = J_{3,4} = 8.9$ Hz, H-3h), 3.77 (s, 3 H, COOMe-a), 3.71 (s, 3 H, MeO), 3.70 (m, 2 H, H-2d and 9f), 3.62 (near t, 1 H, H-5c), 3.43 (m, 6 H, H-6′h, 6h, 1′i, and MeO), 3.33 (m, 1 H, H-5h), 3.23 (s, 3 H, COOMe-f), 2.57 (dd, 1 H, $J_{gem} = 13.0$ Hz, $J_{3eq,4} = 4.1$ Hz, H-3eq-b), 2.50 (dd, 1 H, $J_{gem} = 12.2$ Hz, $J_{3eq,4} = 4.0$ Hz, H-3eq-g), 2.33 (br dd, 1 H, H-3eq-a), 2.10−1.76 (m, 57 H, 17 Ac, H-3eq-f, 3ax-f, 3ax-a, 3ax-b, 6i, and

6′i), 1.67 (t, 1 H, NHCOCH_2), 1.63 (t, 1 H, $J_{gem} = J_{3ax,4} = 12.2$ Hz, H-3ax-g), 1.34 (m, 1 H, NHCOCH_2), 1.26 (m, 52 H, 26 CH_2), 0.87 (2 t, 6 H, 2 Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 170.8, 170.6, 170.5, 170.4, 170.4, 170.3, 170.3, 170.1, 170.1, 169.7, 169.6, 169.5, 167.3, 167.1, 166.3, 165.9, 165.8, 165.6, 165.4, 165.2, 165.0, 164.9, 164.7, 164.1, 164.0, 158.9, 158.7, 136.9, 133.1, 133.0, 132.9, 132.6, 130.1, 130.1, 130.0, 129.8, 129.6, 129.5, 129.4, 129.4, 129.3, 128.9, 128.8, 128.4, 128.3, 128.1, 124.6, 113.4, 113.3, 101.3, 100.8, 100.3, 99.6, 99.4, 98.9, 96.8, 95.7, 80.1, 77.2, 76.4, 75.1, 74.3, 73.9, 73.8, 73.4, 73.1, 72.8, 72.5, 72.1, 71.8, 71.5, 71.3, 71.2, 71.1, 70.8, 70.7, 70.3, 69.8, 69.4, 69.3, 69.2, 68.7, 68.5, 68.2, 67.8, 67.1, 66.8, 66.6, 63.3, 62.0, 61.7, 55.0, 54.6, 53.0, 52.2, 50.2, 48.9, 48.7, 38.8, 38.2, 36.9, 36.2, 35.4, 32.5, 32.1, 31.7, 29.8, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 25.3, 22.9, 22.8, 22.6, 22.5, 20.6, 20.6, 20.5, 20.4, 20.2, 20.1, 14.0; HRMS (ESI) *m*/*z* found $[M + 2Na]^{2+}$ 2068.8101, $C_{211}H_{258}N_6O_{76}$ calcd for $[M + 2Na]^{2+}$ 2068.8146.

[Methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,4,6-tri-*O*-benzoyl-*β*-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-benzoyl-2-deoxy-*β*-D-galactopyranosyl-(1→4)-{[methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)}-2,6-di-*O*-benzoyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzyl-2-octadecanamido-4-octadecene-1,3-diol (41). To a mixture of **20** (148 mg, 0.0480 mmol) and **37** (79 mg, 0.0720 mmol) in CH_2Cl_2 (1.0 mL) was added 4 Å molecular sieves (AW-300) (180 mg) at room temperature. After stirring for 2 h and then cooling to 0 °C, TMSOTf (1.0 μL, 5.52 μmol) was added to the mixture. After stirring for 2 h at 0 °C as the reaction was monitored by TLC (PhMe/MeOH = 4:1), additional TMSOTf (1.0 μL, 5.52 μmol) was added to the mixture. After the stirring was continued for 24 h, the reaction was quenched by saturated $NaHCO_3$ (aq) and filtered through a Celite pad, and the pad was washed with $CHCl_3$. The combined filtrate and washings were washed with brine, dried over Na_2SO_4 and concentrated. The resulting residue was purified by flash column chromatography (PhMe/MeOH = 9:1 to 8:1) to give **41** (140 mg, 73%): $[\alpha]_D = -2.5°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01−6.89 (m, 55 H, 11 Ph), 5.97 (near s, 1 H, H-4d), 5.69 (d, 1 H, $J_{3,4} = 2.7$ Hz, H-4e), 5.54 (m, 4 H, H-4g, 5i, and 2 NH), 5.36 (m, 5 H, H-4b, 7b, and 3 NH), 5.32 (dd, 1 H, $J_{6,7} = 2.0$ Hz, $J_{7,8} = 8.2$ Hz, H-7g), 5.19 (m, 7 H, H-8b, 2e, 2c, 1d, 2h, 8g, and 4i), 5.08 (m, 1 H, H-4f), 5.01 (near d, 1 H, $J_{7,8} = 8.9$ Hz, H-7a), 4.98 (m, 1 H, H-4a), 4.89 (d, 1 H, $J_{gem} = 10.9$ Hz, PhCH_2), 4.83 (near dd, 1 H, $J_{7,8} = 9.6$ Hz, H-7f), 4.62 (m, 5 H, H-3d, 8f, 6c, 6′c, and PhCH_2), 4.60 (d, 1 H, $J_{1,2} = 7.5$ Hz, H-1c), 4.49 and 4.28 (2 d, 2 H, $J_{gem} = 11.6$ Hz, PhCH_2), 4.49 and 4.17 (2 d, 2 H, $J_{gem} = 11.6$ Hz, PhCH_2), 4.44 (m, 2 H, H-1e and 3e), 4.35 (d, 1 H, $J_{1,2} = 7.5$ Hz, H-1h), 4.31−4.20 (m, 8 H, H-9′g, 9′b, 9′f, 9f, 5b, 9′a, 1′i, and 8a), 4.13−3.97 (m, 10 H, H-6b, 5a, 5g, 4h, 4c, 3c, 5f, 2i, 9b, and 9g), 3.89 (dd, 1 H, $J_{5,6} = 10.3$ Hz, $J_{6,7} = 2.0$ Hz, H-6g), 3.84 (m, 2 H, H-6a and 6f), 3.78 (m, 5 H, H-3h, 2d, and COOMe-a), 3.71 (m, 2 H, H-3i and 9a), 3.61 (br t, 1 H, H-5c), 3.53 (br dd, 1 H, $J_{gem} = 10.9$ Hz, H-6′h), 3.46 (br d, 1 H, $J_{gem} = 10.9$ Hz, H-6h), 3.35 (br dd, 1 H, H-1i), 3.26 (m, 1 H, H-5h), 3.23 (s, 3 H, COOMe-f), 2.57 (br dd, 1 H, H-3eq-b), 2.48 (dd, 1 H, H-3eq-g), 2.22 (m, 1 H, H-3eq-a), 2.11−1.82 (13 s and m, 57 H, 17 Ac, H-3eq-f, 3ax-f, 3ax-a, 3ax-b, 6i, and 6′i), 1.61 (m, 3 H, H-3ax-g, NHCOCH_2), 1.26 (m, 52 H, 26 CH_2), 0.87 (t, 6 H, 2 Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 170.8, 170.7, 170.6, 170.6, 170.5, 170.4, 170.4, 170.2, 169.8, 169.8, 169.7, 167.5, 167.3, 166.2, 166.0, 165.8, 165.4, 165.2, 164.6, 164.2, 164.1, 138.5, 138.2, 138.0, 137.0, 133.4, 133.3, 133.1, 133.1, 133.0, 132.8, 130.3, 130.0, 129.9, 129.8, 129.8, 129.7, 129.6, 129.6, 129.5, 129.5, 129.3, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 127.2, 101.3, 100.2, 100.2, 99.9, 99.6, 99.0, 97.1, 96.1, 80.3, 79.0, 75.6, 74.8, 74.2, 74.0, 73.6, 73.3, 73.1, 72.5, 72.1, 72.0, 71.6, 71.4, 71.0, 70.9, 70.4, 70.1, 69.9, 69.5, 69.4, 69.4, 69.0, 68.7, 68.6, 68.5, 67.9, 67.7, 67.2, 67.0, 66.7, 63.7, 62.1, 62.0, 61.8, 54.0, 53.2, 52.4, 51.2, 49.1, 48.9, 48.8, 38.8, 38.3, 36.4, 35.4, 32.2, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.2, 25.4, 23.1, 23.1, 23.0, 22.6, 20.8, 20.7, 20.6, 20.3, 14.1; HRMS (ESI) *m*/*z* found $[M + 2Na]^{2+}$ 2031.8146, $C_{209}H_{256}N_6O_{73}$ calcd for $[M + 2Na]^{2+}$ 2031.8149.

2-(Trimethylsilyl)ethyl [Methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,4,6-tri-*O*-benzoyl-*β*-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-benzoyl-2-deoxy-*β*-D-galactopyranosyl-(1→4)-{[methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)}-2,6-di-*O*-benzoyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranoside (42). To a mixture of **20** (189 mg, 0.0613 mmol) and **38** (52 mg, 0.0919 mmol) in CH_2Cl_2 (1.5 mL) was added 4 Å molecular sieves (AW-300) (250 mg) at room temperature. After stirring for 2 h and then cooling to 0 °C, TMSOTf (1.1 μL, 6.13 μmol) was added to the mixture. After stirring for 2 h at 0 °C as the reaction was monitored by TLC (PhMe/MeOH = 4:1), the reaction was quenched by saturated $NaHCO_3$ (aq) and filtered through a Celite pad, and the pad was washed with $CHCl_3$. The combined filtrate and washings were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography using PhMe/MeOH (6:1) as the eluent to give **42** (135 mg, 63%): $[\alpha]_D = -0.6°$ (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13−6.89 (m, 50 H, 10 Ph), 5.95 (br s, 1 H, H-4d), 5.85 (br d, 1 H, NH-d), 5.70 (d, 1 H, $J_{3,4} = 3.4$ Hz, H-4e), 5.63 (d, 1 H, $J_{5,NH} = 9.0$ Hz, NH-b), 5.54 (dt, 1 H, $J_{3eq,4} = 5.3$ Hz, $J_{3ax,4} = 12.2$ Hz, $J_{4,5} = 10.2$ Hz, H-4g), 5.45 (d, 1 H, $J_{5,NH} = 8.7$ Hz, NH-g), 5.43 (d, 1 H, $J_{5,NH} = 8.5$ Hz, NH-a), 5.34 (m, 1 H, H-4b), 5.32 (dd, 3 H, $J_{6,7} = 2.1$ Hz, $J_{7,8} = 9.0$ Hz, $J_{1,2} = 7.8$ Hz, H-7b, 7g, and 2e), 5.27 (d, 1 H, NH-f), 5.24 (t, 1 H, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.5$ Hz, H-2c), 5.21 (d, 1 H, $J_{1,2} = 8.5$ Hz, H-1d), 5.17 (m, 3 H, $J_{1,2} = 7.8$ Hz, $J_{7,8} = 9.0$ Hz, H-2h, 8b, and 8g), 5.08 (m, 1 H, H-4f), 5.01 (dd, 1 H, $J_{6,7} = 1.7$ Hz, $J_{7,8} = 11.2$ Hz, H-7a), 4.96 (br dt, 1 H, H-4a), 4.86 and 4.62 (2 d, 2 H, $J_{gem} = 10.9$ Hz, PhCH_2), 4.84 (dd, 1 H, $J_{6,7} = 2.9$ Hz, $J_{7,8} = 9.2$ Hz, H-7f), 4.75 (br dd, 1 H, H-3d), 4.67 (d, 1 H, $J_{1,2} = 7.8$ Hz, H-1c), 4.63 (m, 1 H, $J_{7,8} = 9.2$ Hz, H-8f), 4.55 (br d, 1 H, H-6c), 4.50 and 4.28 (2 d, 2 H, $J_{gem} = 12.2$ Hz, PhCH_2), 4.42 (d, 3 H, $J_{1,2} = 7.8$ Hz, H-1e, 3e, and 1h), 4.33−4.19 (m, 10 H, H-9′b, 9′g, 9′a, 9′f, 8a, 6e, 6′e, 6′d, 6d, and 5b), 4.11 (q, 1 H, $J_{4,5} = 10.2$ Hz, $J_{5,6} = 10.4$ Hz, $J_{5,NH} = 8.7$ Hz, H-5g), 4.06−3.97 (m, 12 H, H-5f, 6b, 5a, 3c, 9a, 9b, 4c, 4h, 6′c, 9b, 5e, and 5d), 3.92 (dd, 1 H, $J_{5,6} = 10.4$ Hz, $J_{6,7} = 2.1$ Hz, H-6g), 3.87 (m, 1 H, OCH_2CH$_2$SiMe$_3$), 3.85−3.72 (m, 8 H, H-6a, 6f, 3h, 9f, 2d, and COOMe-a), 3.56 (m, 2 H, $J_{gem} = 10.7$ Hz, H-6′h and 5c), 3.50 (dd, 1 H, $J_{gem} = 10.7$ Hz, H-6h), 3.41 (m, 1 H, OCH_2CH$_2$SiMe$_3$), 3.35 (m, 1 H, H-5h), 3.22 (s, 3 H, COOMe-f), 2.58 (br dd, 1 H, H-3eq-b), 2.50 (dd, 1 H, $J_{3eq,4} = 5.3$ Hz, $J_{gem} = 12.2$ Hz, H-3eq-g), 2.27 (br dd, 1 H, H-3eq-a), 2.11−1.80 (m, 55 H, 17 Ac, H-3ax-b, 3ax-a, 3eq-f, and 3ax-f), 1.63 (t, 1 H, $J_{3ax,4} = J_{gem} = 12.2$ Hz, H-3ax-g), 0.81 (m, 2 H, OCH$_2$CH_2SiMe$_3$), −0.12 (s, 9 H, OCH$_2$CH$_2$SiMe_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.6, 170.5, 170.5, 170.5, 170.4, 170.3, 170.2, 170.2, 169.8, 169.7, 169.7, 169.6, 167.4, 167.2, 166.1, 165.9, 165.9, 165.7, 165.4, 164.9, 164.6, 164.1, 138.2, 138.2, 133.2, 133.1, 133.1, 132.9, 132.8, 132.7, 130.2, 130.1, 129.9, 129.9, 129.7, 129.6, 129.6, 129.5, 129.5, 129.4, 128.9, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.4, 127.1, 101.2, 100.4, 100.1, 99.8, 99.5, 99.0, 97.1, 96.0, 80.8, 77.2, 76.4, 76.2, 74.7, 74.0, 73.8, 73.2, 73.1, 72.5, 72.1, 72.0, 71.6, 71.3, 70.9, 70.4, 69.8, 69.5, 69.3, 69.2, 69.0, 68.7, 68.5, 68.4, 68.0, 67.2, 67.1, 67.0, 66.9, 66.7, 63.5, 62.1, 62.0, 61.8, 54.3, 53.1, 52.3, 49.1, 48.9, 38.7, 38.2, 35.5, 35.4, 29.6, 23.0, 23.0, 22.9, 22.7, 20.7, 20.7, 20.6, 20.6, 20.6, 20.5, 20.3, 20.2, 17.8, −1.5; HRMS (ESI) *m*/*z* found $[M + 2Na]^{2+}$ 1763.0599, $C_{171}H_{193}N_5O_{71}Si$ calcd for $[M + 2Na]^{2+}$ 1763.0599.

Benzyl [Methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-benzoyl-2-deoxy-β-D-galactopyranosyl-(1→4)-{[methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)}-2,6-di-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (43). To a mixture of **20** (140 mg, 0.0454 mmol) and **39** (66 mg, 0.0681 mmol) in CH_2Cl_2 (1.1 mL) was added 4 Å molecular sieves (AW-300) (210 mg) at room temperature. After stirring for 2 h and then cooling to 0 °C, TMSOTf (1.0 μL, 5.53 μmol) was added to the mixture. After stirring for 5 h at 0 °C as the reaction was monitored by TLC (PhMe/MeOH = 4:1), the reaction was quenched by saturated $NaHCO_3$ (aq) and filtered through a Celite pad, and the pad was washed with $CHCl_3$. The combined filtrate and washings were washed with brine, dried over Na_2SO_4, and concentrated. The resulting residue was purified by flash column chromatography using PhMe/MeOH (8:1) as the eluent to give **43** (140 mg, 80%): $[\alpha]_D = -5.0$ (*c* 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13−6.94 (m, 70 H, 14 Ph), 5.97 (br s, 1 H, H-4d), 5.78 (br d, 1 H, NH-d), 5.70 (d, 1 H, $J_{3,4}$ = 3.4 Hz, H-4e), 5.55 (dt, 1 H, $J_{3eq,4}$ = 4.8 Hz, $J_{3ax,4}$ = 13.0 Hz, $J_{4,5}$ = 10.3 Hz, H-4g), 5.52 (d, 1 H, $J_{5,NH}$ = 9.6 Hz, NH-b), 5.39−5.31 (m, 6 H, H-4b, 7b, 7g, and 3 NH), 5.28 (m, 1 H, H-2e), 5.24 (d, 1 H, $J_{1,2}$ = 8.9 Hz, H-1d), 5.20 (near t, 1 H, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 8.2 Hz, H-2c), 5.16 (m, 2 H, H-8b and 8g), 5.08 (m, 1 H, H-4f), 5.01 (dd, 1 H, $J_{6,7}$ = 1.7 Hz, $J_{7,8}$ = 10.3 Hz, H-7a), 4.95 (dt, 1 H, $J_{3eq,4}$ = 4.1 Hz, H-4a), 4.92−4.20 (14 d, 14 H, PhCH_2), 4.84 (dd, 1 H, H-7f), 4.67 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1c), 4.63 (dt, 1 H, H-8f), 4.41 (d, 3 H, $J_{1,2}$ = 7.5 Hz, H-1e, 3e, and H-1h), 4.36 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1h), 4.28−4.18 (m, 7 H, H-9′b, 9′g, 9f, 9a, 8a, 6b, and 5b), 4.13−3.98 (m, 8 H, H-5g, 5a, 3c, 4c, 5f, 9′a, 9b, and 9g), 3.91−3.35 (m, 11 H, Glc unit), 3.89 (br dd, 1 H, H-6g), 3.85 (br dd, 1 H, H-6f), 3.83 (br dd, 1 H, $J_{6,7}$ = 1.7 Hz, H-6a), 3.78 (s, 3 H, COOMe-a), 3.70 (br d, 1 H, H-9′f), 3.60 (m, 1 H, H-2d), 3.24 (s, 3 H, COOMe-f), 3.15 (m, 1 H, H-5h), 2.57 (dd, 1 H, J_{gem} = 13.0 Hz, $J_{3eq,4}$ = 4.8 Hz, H-3eq-b), 2.50 (dd, 1 H, J_{gem} = 13.0 Hz, $J_{3eq,4}$ = 4.8 Hz, H-3eq-g), 2.29 (br dd, 1 H, H-3eq-a), 2.11−1.78 (m, 55 H, 17 Ac, H-3ax-b, 3ax-a, 3ax-f, and 3eq-f), 1.63 (t, 1 H, J_{gem} = $J_{3ax,4}$ = 13.0 Hz, H-3ax-g); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 170.7, 170.6, 170.6, 170.5, 170.5, 170.4, 170.3, 170.2, 169.8, 169.8, 169.7, 167.4, 167.3, 166.1, 166.0, 165.7, 165.7, 165.4, 164.7, 164.2, 138.8, 138.5, 138.5, 138.3, 138.2, 138.0, 137.5, 133.3, 133.2, 133.1, 133.0, 132.8, 132.8, 130.3, 129.9, 129.9, 129.7, 129.7, 129.6, 129.6, 129.5, 129.4, 129.3, 128.5, 128.3, 128.3, 128.2, 128.2, 128.2, 128.0, 128.0, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 103. 7, 102.6, 101.4, 100.0, 99.5, 99.0, 97.1, 96.0, 84.6, 82.8, 82.2, 81.5, 78.2, 76.2, 76.0, 75.6, 75.1, 75.0, 74.8, 74.8, 74.7, 74.3, 74.0, 73.3, 73.1, 72.5, 72.2, 72.0, 71.6, 71.4, 71.1, 70.8, 70.4, 69.9, 69.8, 69.5, 69.4, 69.4, 69.2, 69.0, 68.8, 68.6, 68.4, 68.4, 68.1, 67.3, 67.0, 66.7, 66.7, 63.4, 62.1, 62.0, 61.9, 54.6, 53.2, 52.4, 49.1, 48.9, 48.9, 38.7, 38.3, 35.7, 35.4, 29.6, 23.1, 23.0, 22.8, 20.8, 20.7, 20.7, 20.7, 20.6, 20.6, 20.3, 20.3; HRMS (ESI) *m/z* found $[M + 2Na]^{2+}$ 1967.1553, $C_{200}H_{217}N_5O_{75}$ calcd for $[M + 2Na]^{2+}$ 1967.1557.

[Methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-benzoyl-2-deoxy-β-D-galactopyranosyl-(1→4)-{[methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)}-2,6-di-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (44). To a solution of **40** (144 mg, 0.0351 mmol) in CH_2Cl_2 (4.0 mL) was added trifluoroacetic acid (2.0 mL) at 0 °C. After stirring for 1 h at 0 °C as the reaction was monitored by TLC (PhMe/MeOH = 4:1), the reaction mixture was diluted with $CHCl_3$. The organic layer was washed with ice-cooled saturated Na_2CO_3 (aq) (twice) and brine. After drying over Na_2SO_4 and being concentrated, the resulting residue was purified by flash column chromatography using $CHCl_3$/MeOH (25:1 to 10:1) to give **44** (131 mg, 97%): $[\alpha]_D = +4.7$ (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 Hz, $CDCl_3$) δ 8.08−7.28 (m, 45 H, 9 Ph), 5.94 (br s, 1 H, H-4d), 5.86 (m, 1 H, $J_{4,5}$ = 15.1 Hz, $J_{5,6}$ = 7.5 Hz, $J_{5,6'}$ = 6.9 Hz, H-5i), 5.74 (d, 1 H, $J_{2,NH}$ = 9.6 Hz, NH-i), 5.70 (d, 1 H, $J_{3,4}$ = 3.4 Hz, H-4e), 5.57 (m, 1 H, H-4g), 5.54 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 8.2 Hz, H-3i), 5.42 (dd, 1 H, $J_{3,4}$ = 8.2 Hz, $J_{4,5}$ = 15.1 Hz, H-4i), 5.38 (d, 1 H, $J_{5,NH}$ = 10.9 Hz, NH-f), 5.34 (m, 3 H, H-7b, 7g, and 2c), 5.28 (m, 1 H, H-2e), 5.20 (m, 2 H, H-8b and 8g), 5.16 (d, 1 H, $J_{1,2}$ = 8.2 Hz, H-1d), 5.10 (m, 2 H, H-4f and 2h), 5.00 (br dd, 1 H, H-7a), 4.92 (m, 1 H, H-4a), 4.86 (d, 2 H, H-7f and 3d), 4.77 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1c), 4.72 (m, 1 H, H-6′c), 4.65 (br dt, 1 H, H-8f), 4.61 (m, 1 H, H-6′e), 4.45−4.39 (m, 7 H, H-1e, 3e, 1h, 4c, 5d, 5e, and 2i), 4.28−4.21 (m, 9 H, H-3c, 8a, 9′b, 9′g, 9′a, 9f, 5c, 6c, and 6e), 4.12 (q, 2 H, $J_{4,5}$ = 10.3 Hz, H-5g and 5b), 4.07−3.94 (m, 6 H, H-5f, 9b, 9g, 9a, 6d, and 6′d), 3.92−3.83 (m, 7 H, H-3h, 6g, 6b, 6f, 6a, 5a, and 1i), 3.77 (t, 1 H, $J_{4,5}$ = 9.6 Hz, H-4h), 3.76 (m, 4 H, COOMe-a and H-9′f), 3.64 (m, 1 H, H-2d), 3.50 (dd, 1 H, J_{gem} = 9.6 Hz, $J_{1',2}$ = 3.4 Hz, H-1′i), 3.24 (s, 3 H, COOMe-f), 3.16 (t, 1 H, J_{gem} = 10.9 Hz, H-6h), 3.05 (d, 1 H, $J_{4,5}$ = 9.6 Hz, H-5h), 2.91 (br dd, 1 H, J_{gem} = 10.9 Hz, H-6′h), 2.66 (dd, 1 H, 6h-OH), 2.59 (br dd, 1 H, H-3eq-b), 2.50 (dd, 1 H, $J_{3eq,4}$ = 5.4 Hz, J_{gem} = 12.3 Hz, H-3eq-g), 2.41 (br dd, 1 H, H-3eq-a), 2.11−1.81 (m, 58 H, 17 Ac, H-3eq-f, 3ax-f, 3ax-a, 3ax-b, 6i, 6′i, and NHCOCH_2), 1.63 (t, 1 H, J_{gem} = $J_{3ax,4}$ = 12.3 Hz, H-3ax-g), 1.43 (m, 1 H, NHCOCH_2), 1.26 (m, 52 H, 26 CH_2), 0.88 (t, 6 H, 2 Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 171.1, 170.6, 170.5, 170.3, 170.1, 169.7, 169.6, 167.4, 167.2, 166.1, 166.0, 165.9, 165.7, 165.5, 165.4, 165.3, 164.7, 164.3, 164.1, 138.3, 133.2, 133.1, 133.0, 132.9, 132.7, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.4, 129.2, 129.1, 128.4, 128.3, 128.2, 124.6, 101.5, 101.3, 99.6, 99.4, 99.2, 98.9, 96.8, 95.8, 80.4, 75.8, 73.8, 73.6, 73.0, 72.7, 72.5, 72.3, 71.9, 71.5, 71.3, 71.7, 71.0, 70.5, 69.8, 69.7, 69.3, 69.3, 68.9, 68.7, 68.5, 68.2, 67.1, 66.9, 66.6, 66.6, 66.1, 64.0, 63.9, 62.3, 62.3, 62.2, 62.1, 62.0, 61.9, 61.9, 59.4, 54.7, 54.6, 54.6, 54.5, 54.5, 53.1, 52.2, 50.2, 49.1, 49.1, 48.9, 48.8, 48.7, 38.6, 38.2, 36.5, 35.4, 32.1, 31.7, 29.5, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 28.7, 25.4, 22.9, 22.9, 22.7, 22.5, 20.7, 20.6, 20.6, 20.5, 20.5, 20.3, 20.2, 14.0; HRMS (ESI) *m/z* found $[M + 2Na]^{2+}$ 1948.7547, $C_{195}H_{242}N_6O_{74}$ calcd for $[M + 2Na]^{2+}$ 1948.7571.

2-(Trimethylsilyl)ethyl [Methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-benzoyl-2-deoxy-β-D-galactopyranosyl-(1→4)-{[methyl 5-acetamido-8-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylono-1′,9-lactone)-4,7-di-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)}-2,6-di-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-β-D-glucopyranoside (45). To a solution of **42** (75 mg, 0.0215 mmol) in EtOH (2.1 mL) was added palladium hydroxide [20 wt % Pd (dry basis) on carbon, wet] (75 mg) at room temperature. After stirring for 33 h at 40 °C under a H_2 atmosphere as the reaction was monitored by TLC (PhMe/MeOH = 4:1), the mixture was filtered through a Celite pad and washed with $CHCl_3$. The combined filtrate and washings were concentrated. The resulting residue was purified by flash column chromatography using $CHCl_3$/MeOH (20:1 to 15:1) as the eluent to give **45** (63 mg, 90%): $[\alpha]_D = -2.3°$ (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10−7.26 (m, 40 H, 8 Ph), 5.93 (br s, 1 H, H-4d), 5.74 (br d, 1 H, NH-b), 5.70 (d, 1 H, $J_{3,4}$ = 3.6 Hz, H-4e), 5.55 (dt, 1 H, $J_{4,5}$ = 10.4 Hz, $J_{3eq,4}$ = 5.1 Hz, $J_{3ax,4}$ = 12.2 Hz, H-4g), 5.45 (d, 1 H, $J_{5,NH}$ = 10.0 Hz, NH-b), 5.34 (m, 7 H, H-4b, 2c, 2e, 7g, 7b, NH-g, and NH-f), 5.18 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1d), 5.17 (m, 2 H, H-8b and 8g), 5.11 (t, 1 H, $J_{1,2}$

= 8.0 Hz, H-2h), 5.10 (m, 2 H, H-4f and NH-a), 5.01 (dd, 1 H, $J_{6,7}$ = 1.7 Hz, $J_{7,8}$ = 8.5 Hz, H-7a), 4.92 (m, 2 H, H-3d and 4a), 4.87 (dd, 1 H, $J_{6,7}$ = 1.7 Hz, $J_{7,8}$ = 9.5 Hz, H-7f), 4.77 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1c), 4.71 (br dd, 1 H, H-6c), 4.63 (dt, 1 H, $J_{7,8}$ = 9.5 Hz, H-8f), 4.59 (m, 1 H, H-6e), 4.50 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1h), 4.42 (m, 4 H, H-1e, 3e, 4c, and 6d), 4.29−4.19 (m, 11 H, H-5b, 8a, 3c, 6′e, 6b, 5e, 6′c, 9b, 9g, 9′f, and 9a), 4.12 (q, 1 H, $J_{4,5}$ = 10.4 Hz, $J_{5,6}$ = 10.2 Hz, H-5g), 4.06−3.98 (m, 5 H, H-5f, 9′a, 9′b, 9′g, and 6′d), 3.94−3.85 (m, 7 H, H-3h, 6g, 6f, 5a, 5c, 5d, and $OCH_2CH_2SiMe_3$), 3.81 (dd, 1 H, $J_{6,7}$ = 1.7 Hz, H-6a), 3.75 (m, 4 H, H-9f and COOMe-a), 3.69 (t, 1 H, $J_{3,4} = J_{4,5}$ = 8.7 Hz, H-4h), 3.63 (br q, 1 H, $J_{1,2}$ = 8.0 Hz, H-2d), 3.46 (m, 2 H, H-6h and $OCH_2CH_2SiMe_3$), 3.43 (m, 1 H, H-6′h), 3.30 (m, 1 H, H-5h), 3.24 (s, 3 H, COOMe-f), 2.57 (br dd, 1 H, H-3eq-b), 2.51 (dd, 1 H, J_{gem} = 12.2 Hz, $J_{3eq,4}$ = 5.1 Hz, H-3eq-g), 2.45 (m, 1 H, H-3eq-a), 2.11−1.70 (m, 55 H, 17 Ac, H-3ax-b, 3ax-a, 3eq-f, and 3ax-f), 1.64 (t, 1 H, $J_{gem} = J_{3ax,4}$ = 12.2 Hz, H-3ax-g), 0.82 (m, 2 H, $OCH_2CH_2SiMe_3$), 0.00 and −0.12 (2 s, 9 H, $OCH_2CH_2SiMe_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 170.7, 170.7, 170.6, 170.5, 170.4, 170.4, 170.4, 170.3, 169.9, 169.8, 169.8, 169.8, 169.7, 167.6, 167.3, 166.2, 166.1, 166.0, 165.6, 165.4, 165.1, 164.6, 164.5, 164.2, 133.5, 133.3, 133.3, 133.1, 133.0, 132.8, 130.3, 130.2, 129.9, 128.8, 129.7, 129.6, 129.6, 129.2, 128.6, 128.5, 128.4, 128.4, 128.2, 101.6, 100.5, 99.4, 99.2, 99.0, 97.1, 96.2, 81.2, 77.2, 75.8, 74.0, 73.8, 73.4, 73.2, 73.0, 72.8, 72.5, 72.1, 71.7, 71.4, 71.2, 70.6, 70.1, 69.9, 69.6, 69.4, 68.9, 68.8, 68.6, 68.5, 67.4, 67.3, 66.7, 64.0, 62.1, 62.0, 61.8, 60.6, 54.8, 53.2, 52.4, 49.3, 49.1, 49.1, 48.9, 38.6, 38.5, 38.3, 36.1, 35.6, 29.6, 23.1, 23.1, 23.0, 22.9, 20.8, 20.7, 20.7, 20.7, 20.6, 20.4, 20.3, 17.9, −1.1; HRMS (ESI) *m*/*z* found $[M + 2Na]^{2+}$ 1673.0130, $C_{157}H_{181}N_5O_{71}Si$ calcd for $[M + 2Na]^{2+}$ 1673.0130.

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Supporting Information Available: Experimental data for compounds **8**−**10**, **12**, **13**, **17**−**19**, **23**, **24**, and **26**−**31**, and copies of ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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