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Total Synthesis of Sulfated Glycosphingolipid SM1a, a Kind of Human Epithelial Carcinoma Antigen

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A highly efficient and practical total synthesis of the sulfated ganglioside SM1a, a kind of human epithelial carcinoma antigen identified in mammalian kidney, has been accomplished for the first time. The characteristic sequence of SM1a, β-D-Gal*p*-(1→3)-β-D-NHAcGal*p*-(1→4)-β-D-(3-*O*-sulfate)-Gal*p*-(1→4)-β-D-Glc*p*-ceramide was assembled by a [3+2] convergent approach. A key trisaccharide building block was formed from a new galactose acceptor **7** containing a potential sulfated site, GalNHTroc donor **6**, and galactose donor **4**. The cyclic glucosyl ceramide was glycosylated with trisaccharide trichloroacetimidate **2** to give the protected ganglioside backbone in good yield. Selective sulfonation at the 3-OH of the Gal residue followed by global deprotection gave the target molecule SM1a.

Introduction

Gangliosides, sialic acid-containing glycosphingolipids, have been of great interest for more than 20 years in the search for target molecules relevant to tumor growth and metastasis, and also as potential targets for immunotherapy. They are expressed on the cell surface, so they are accessible for antibodies or other ganglioside-binding molecules that may induce cell death, inhibit cell growth, and/or inhibit tumor metastasis.[1] Meanwhile, a variety of sulfated gangliosides have been isolated from mammalian kidney cell lines and characterized;[2,3] the sugar chains of these gangliosides are modified with sulfate residues instead of with sialic acid. The attraction of ganglioside-series sulfated glycolipids is that their accumulation is related to different carcinomas.[4–7] However, to date, their structure–activity relationships have not been investigated using structurally homogeneous gangliosides.

Ganglioside-series sulfatide SM1a (Figure 1) was isolated from the rat kidney and African green monkey kidney cell lines (Verots S3).[2,3] SM1a was postulated to be a precursor of the disulfated glycolipid SB1a,[3] which has been shown to behave as a tumor-associated antigen.[6] Modern carbohydrate microarray technology found that SM1a may be a tumor-associated carbohydrate antigen since it can be recognized by the monoclonal antibody AE_3, which is the most specific antibody for the detection of human epithelial carcinoma antigens.[8] In order to better understand the biological functions of SM1a, a sufficient quantity of structurally homogeneous ganglioside is needed.

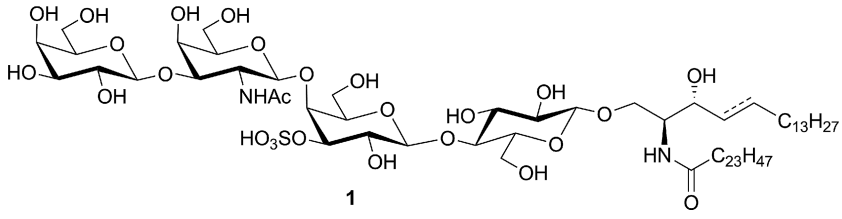

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Figure 1. The structure of SM1a.

SM1a is the sulfoglycolipid analog of sialoglycolipid GM1. Although the synthesis of gangliosides GM1, GQ1b, GD1a, and their derivatives has previously been accomplished by several laboratories,[9–15] the synthesis of a ganglioside bearing a sulfate instead of a sialic acid has never been reported. In this paper, we report the first total synthesis of SM1a.

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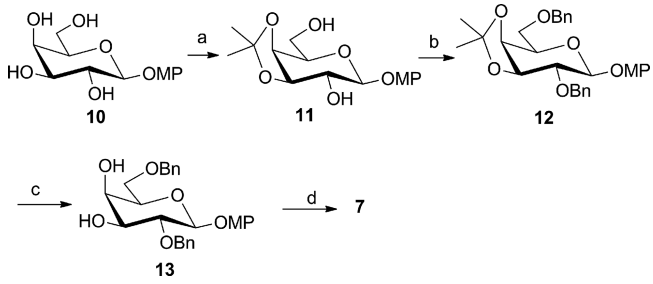
Results and Discussion

The retrosynthetic analysis of the target compound SM1a is shown in Scheme 1. The target molecule was disconnected into trisaccharide donor **2** and glucosyl-ceramide (GlcCer) acceptor **3** at the β-(1–4) linkage between galactose (Gal) and glucose (Glc). A cyclic glucosyl ceramide (GlcCer) acceptor was developed by Kiso's group as a versatile building block, and the use of such a molecule could avoid any loss of the valuable oligosaccharide unit in a coupling reaction with the lipophilic, self-aggregating, bulky, and unreactive ceramide moiety.[16] It was shown that the cyclic GlcCer acceptor could react with a variety of oligosaccharide donors.[10,15] Thus, a [3+2] convergent approach to the target molecule was devised. Trisaccharide **2** could be assembled from monosaccharide building blocks **4**, **6**, and **7**. GlcCer unit **3** could be installed by coupling glucosyl donor **8** with ceramide acceptor **9** through an intramolecular glycosylation.

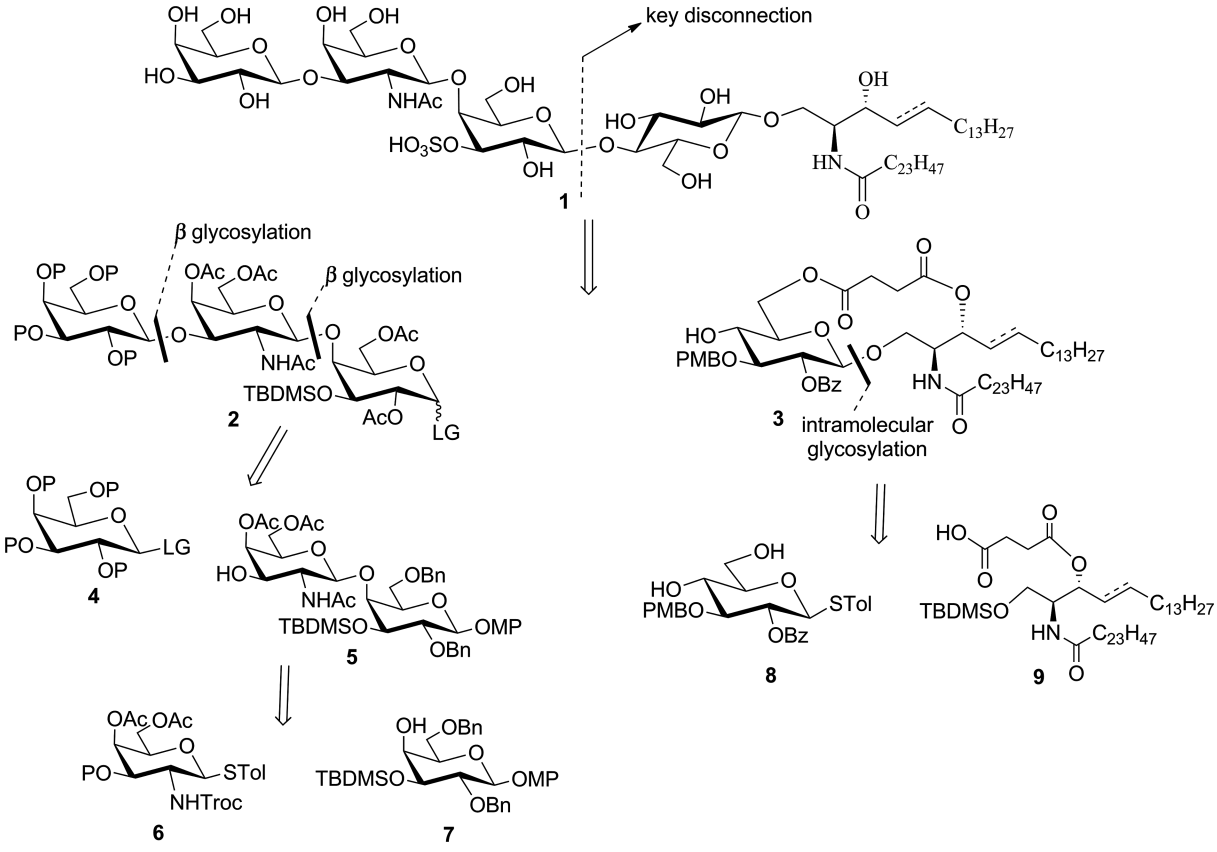
According to the above-mentioned strategy, key disaccharide **5** was prepared by the reaction of a newly designed galactosyl acceptor **7** and a galactosaminyl donor **6** having a participating 2,2,2-trichloroethoxycarbonyl (Troc) protecting group at the C-2 amine to control the β anomeric selectivity, as shown in Scheme 1.

p-Methoxyphenyl alcohol **7** was obtained from *p*-methoxyphenyl-β-D-galactopyranoside (**10**) by a four-step route (Scheme 2). Treatment of **10**[17] with acetone, a catalytic amount of iodine, and *p*-toluenesulfonic acid (*p*TsOH) gave 3,4-*O*-isopropylidene derivative **11**.[18] Compound **11** was converted into **12** by benzylation. Hydrolysis of the isopropylidene group in **12** gave compound **13**. Then a *tert*-butyldimethylsilyl (TBDMS) group was selectively introduced at the C-3 position, taking advantage of the reactivity difference between the 4-OH and the 3-OH groups of **13**. The TBDMS group was stable under both basic and acidic conditions, and furthermore, it could be selectively and effectively removed before sulfonation.



Scheme 2. Synthesis of acceptor **7**. Reagents and conditions: a) I_2/*p*TsOH, acetone, 40 °C, 70%; b) BnBr, NaH, DMF, 0 °C→room temp.; c) AcOH/H_2O (9:1), 80 °C, 87% over two steps; d) TBDMSCl, imidazole, CH_2Cl_2, 0 °C→room temp., 96%; MP = *p*-methoxyphenyl.

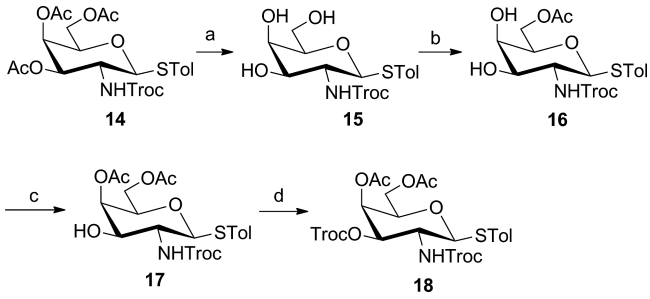
Next, we designed thioglycosides **14** and **18** as candidates for the *N*-Troc-GalN donor (i.e., **6**), which would be cou-



Scheme 1. Retrosynthetic analysis of the target compound **1**; P = protecting group, LG = leaving group.

pled with acceptor **7** to give disaccharide unit **5**. It is known that a Troc group can ensure β-selective glycosylation as well as increase the reactivity of a glycosyl donor compared with an *N*-phthaloyl group.[19] Other advantages include the high efficiency of the installation, and the possibility for chemoselective deprotection of the Troc group.

The synthesis of **18** starting from known 1-thio-β-D-galactopyranoside **14** is shown in Scheme 3. Thiogalactoside **14**[12] was deacetylated under Zemplen conditions, and this was followed by selective acetylation of 6-OH with catalytic sulfuric acid in ethyl acetate[20] to give **16**. Next, 4-OH was selectively acetylated through orthoacetate formation and regioselective hydrolysis to give galactosaminyl precursor **17**, which has previously been used as a galactosaminyl acceptor in the one-pot synthesis of fucosyl GM1.[12] We shortened the synthetic route and increased the yield of **17** from 28 to 70%. The new galactosaminyl thioglycoside donor (i.e., **18**) was obtained by further protection of the remaining C-3 hydroxy group with a Troc group in a yield of 89%.

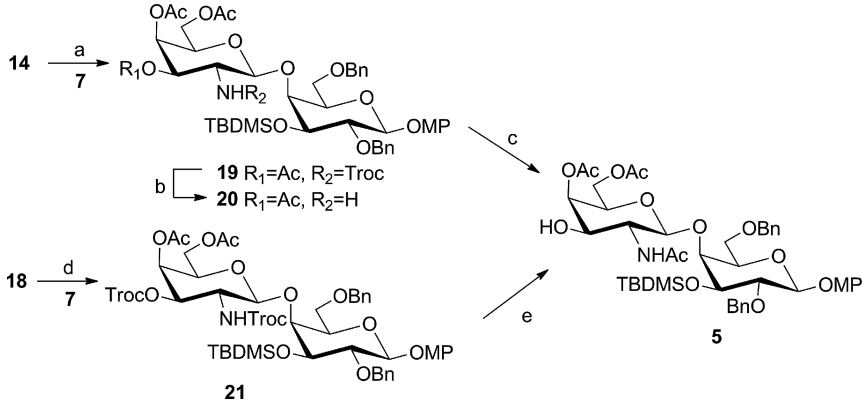


Scheme 3. Synthesis of donor **18**. Reagents and conditions: a) CH_3OH/CH_3ONa, pH 8–9, 0 °C, 99%; b) H_2SO_4, EtOAc, 45 °C; c) $(EtO)_3CCH_3$, *p*TsOH, MeCN, then $AcOH/H_2O$ (9:1), room temp., 70% over three steps; d) TrocCl, Py, 89%.

Two different strategies were explored to access disaccharide acceptor **5** (Scheme 4). Firstly, thiogalactoside **14** was chosen to couple with **7**. Using *N*-iodosuccinimide (NIS)/trifluoromethanesulfonic acid (TfOH) in CH_2Cl_2 at –45 °C, disaccharide **19** was formed in 75% yield. Disaccharide **19** could be converted into **5** through a 3-*O* to 2-*N* migration of the acetyl group upon deprotection of the C-2 amine group.[15] However, this reaction did not proceed smoothly under one-pot conditions by treatment with zinc AcOH/DMF (1:9) at 60 °C. Only a moderate yield (40%) of **5** was obtained, and side-products were generated when the reaction time was extended. Therefore, we completed this migration in two steps. Removal of the Troc group with zinc in acetic acid / 1,2-dichloroethane (1:1) gave **20** in 80% yield. Then, under acidic conditions of AcOH/DMF (1:9), the migration of the acetyl group at the C-3 position was implemented successfully to give disaccharide **5**. Although **5** was obtained in a yield of 72% over two steps, this route could not be used for large-scale synthesis as a result of the difficulties in determining the reaction endpoint, and in separating the product from by-products.

Next, we selected another donor **18** bearing a Troc group at C-3 to couple with compound **7**. Using NIS/TfOH in CH_2Cl_2 at –20 °C, disaccharide **21** was formed in 70% yield. As expected, the resulting disasaccharide (i.e., **21**) could be efficiently converted into disaccharide acceptor **5** through removal of the Troc groups by treatment with pre-activated zinc/AcOH, followed by selective acetylation of the C-2 amine group of the GalN residue in 99% yield (Scheme 4). Compared to the first method, this strategy was a much more efficient way to reveal the free OH group of C-3 for the next glycosylation.

To assemble the trisaccharide sequence Gal-GalNAc-Gal (**2**), four galactosyl donors were evaluated to couple with acceptor **5**, and the results are summarized in Table 1. In entry 1, the glycosylation of thioglycoside **22**[21] with **5** was carried out in the presence of NIS/TfOH in CH_2Cl_2. However, the reaction did not work well, and hardly any of the desired coupling product (i.e., **26**) was formed. Table 1, entries 2 and 3 showed that trichloroacetimidate donor **23**[22] could give trisaccharide **26** in moderate yield. For these two reactions, we found that part of the major product decom-

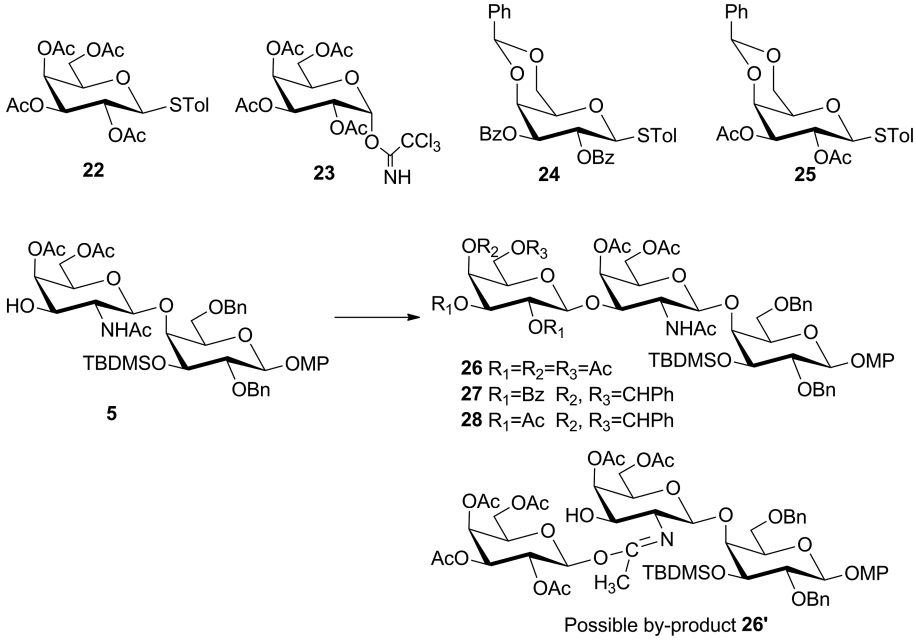


Scheme 4. Synthesis of disaccharide unit **5**. Reagents and conditions: a) NIS/TfOH, molecular sieves (4 Å), CH_2Cl_2, –45 °C, 75%; b) Zn, $ClCH_2CH_2Cl/AcOH$ (1:1), 50 °C, 80%; c) DMF/AcOH (9:1), 60 °C, 90%; d) NIS/TfOH, molecular sieves (4 Å), CH_2Cl_2, –20 °C, 70%; e) i) Zn, $ClCH_2CH_2Cl/AcOH$ (1:1), 50 °C; ii) Ac_2O, CH_2Cl_2, 0 °C→room temp., 99% over two steps.

posed into disaccharide acceptor **5** again during the purification, and it was difficult to obtain the pure product. Liao found that imidate formation could be the predominant reaction under glycosylation conditions when *N*-acetylglucosamine derivatives were used as glycosyl acceptors.[23] We suspected the major product was a mixture of imidate (**26′**) and **26** because of a competitive reaction of *N*-acetylgalactosamine.

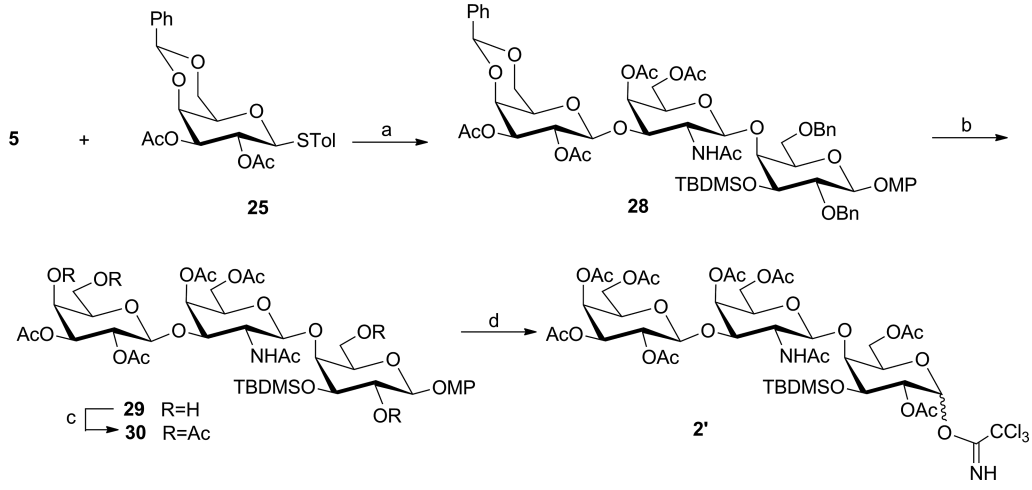
Two thioglycoside donors **24**[21] and **25**[24] bearing a 4,6-benzylidene group were evaluated as shown in Table 1, en-

Table 1. Glycosylation of **5** with different galactosyl donors.



Entry[a]	Donor	Promoter (equiv.)	Solvent	Time [h]	Yield [%]
1	**22**	NIS (2.5) / TfOH (0.2)	CH_2Cl_2	48	–[b]
2	**23**	TMSOTf (0.2)	CH_2Cl_2	1.5	40[c]
3	**23**	TMSOTf (0.2)	CH_2Cl_2/CH_3CN	2	44[c]
4	**24**	NIS (2.0) / TfOH (0.1)	CH_2Cl_2	1.5	49
5	**25**	NIS (2.5) / TfOH (0.1)	CH_2Cl_2	1	>63[d]

[a] All reactions were carried out with 2.0 equiv. of donor except for entry 4 (1.5 equiv. of donor **24** was used for entry 4), indicated promoters, solvents, and molecular sieves (4 Å) at 0 °C. [b] None of the desired product was obtained after 48 h. [c] Yield of the mixture of **26** and a by-product, which were inseparable. [d] Hard to separate, crude compound was used for the next reaction, 63% over two steps.

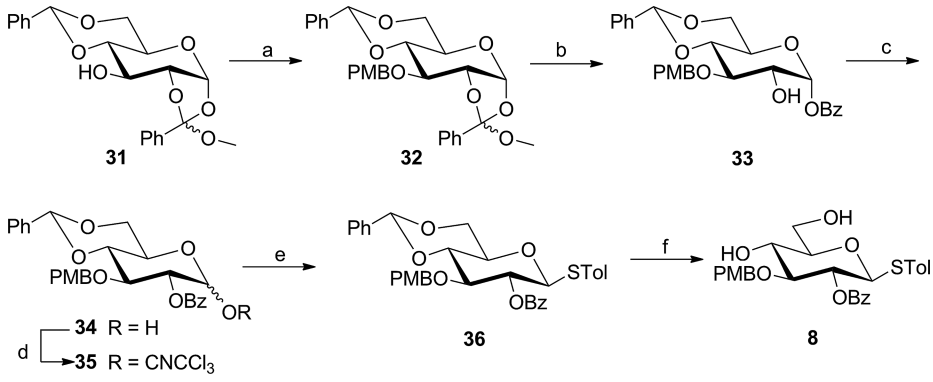


Scheme 5. Synthesis of trisaccharide donor **2′**. Reagents and conditons: a) NIS, TfOH, molecular sieves (4 Å), CH_2Cl_2, 0 °C; b) Pd/C, H_2, methanol/THF (1:2), 63% over two steps; c) Py, Ac_2O, 95%; d) i) CAN [Cerium(IV) ammonium nitrate], CH_3CN/H_2O (5:1), ii) DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), CCl_3CN, CH_2Cl_2, 0 °C, 74% over two steps.

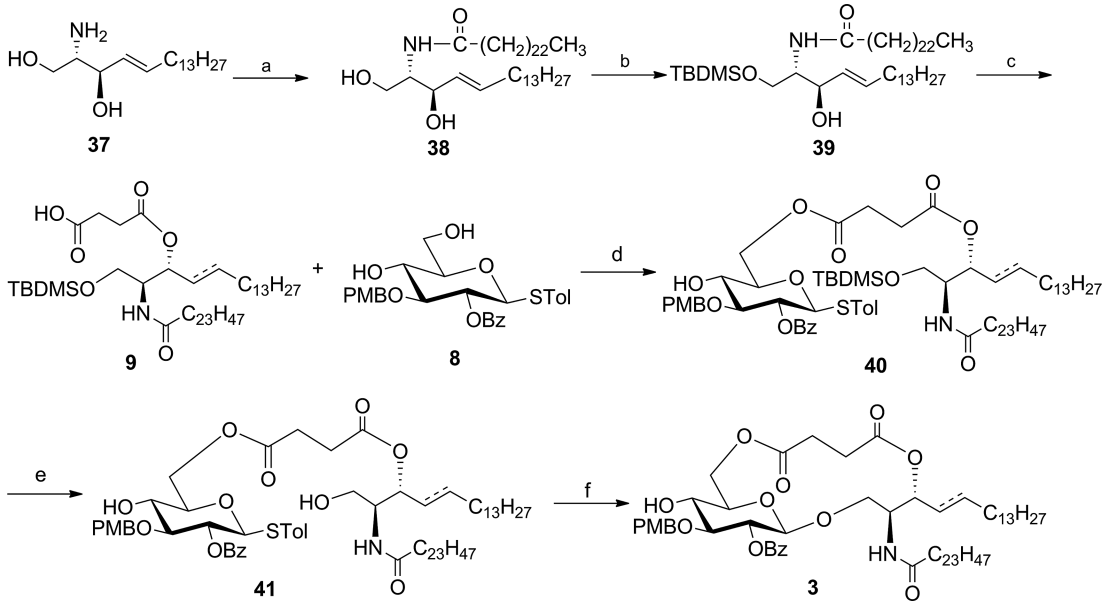
tries 4 and 5. These two donors were more reactive than peracetate donor **22**.[21] Donor **25** performed much better, and gave >63% yield, though it was difficult to obtain pure glycosylation product. This result suggested that glycosylation with the C-3 OH of acceptor **5** was favored by the presence of a bulky group rather than an electron-withdrawing group at the C-4 position of the donor. So compound **25** was selected as the donor (i.e., **4**) for the construction of trisaccharide **2**.

Thioglycoside donor **25** coupled with acceptor **5** to give trisaccharide **28**, which was then converted into imidate donor **2′** in three steps (Scheme 5). Replacement of the benzyl groups with acetyl groups, removal of the *p*-methoxyphenyl group, and conversion of the resulting hydroxy group into a trichloroacetimidate group gave compound **2′** as the trisaccharide donor (i.e., **2**) in a satisfactory yield, ready for the final glycosylation.

Kiso et al. reported the useful convergent synthesis of a series of gangliosides using a cyclic glucosyl ceramide (GlcCer) acceptor as a versatile building block.[10,15,16,25] This approach based on use of a GlcCer building block is useful in that it avoids loss of the valuable oligosaccharide unit in a coupling reaction with the lipophilic, self-aggregating, bulky, and unreactive ceramide moiety. In this study, we attempted to use cyclic GlcCer acceptor **3** from the perspective of overall efficiency. Previous research has shown that the presence of an electron-donating group for protection of the C-3 hydroxy group, even if it is bulky, could



Scheme 6. Synthesis of glucose moiety **8**. Reactions and conditions: a) NaH, PMBCl, TBAI (tetrabutylammonium iodide), DMF, 0 °C→room temp.; b) HCl (1 M), CH_2Cl_2, 85% over two steps; c) Et_3N, CH_2Cl_2; d) DBU, $CNCCl_3$, CH_2Cl_2, 0 °C, 80% over two steps; e) TolSH, $BF_3{\cdot}Et_2O$, molecular sieves (4 Å), CH_2Cl_2, 0 °C, 60%; f) AcOH/H_2O (4:1), 80 °C, 95%.

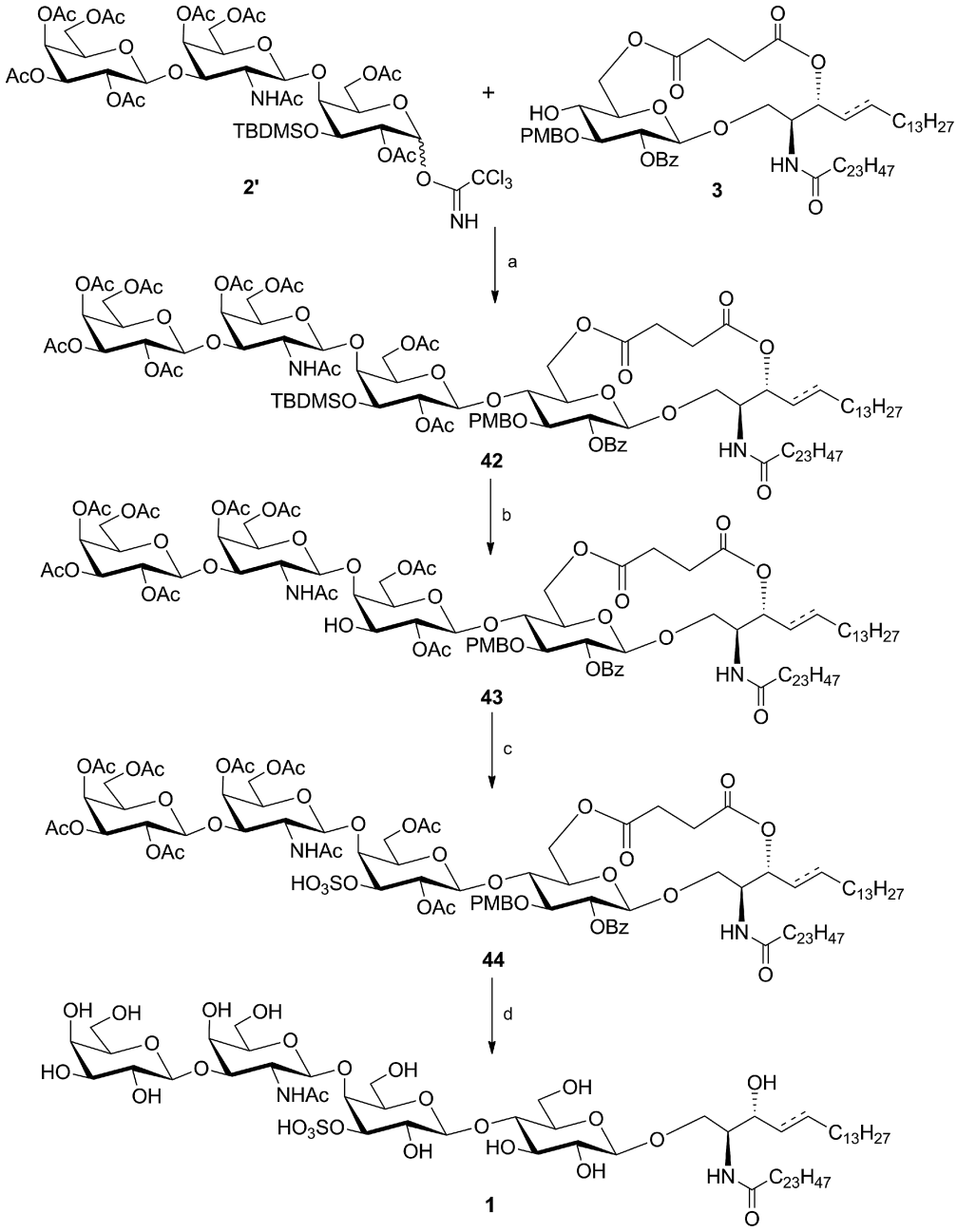


Scheme 7. Synthesis of GlcCer acceptor **3**. Reagents and conditions: a) $C_{23}H_{47}COOH$, EDC, HOBt (hydroxybenzotriazole), DIPEA (diisopropylethylamine), THF, 71%; b) TBDMSCl, Et_3N, DMAP, $CHCl_3$, 0 °C→40 °C, 80%; c) succinic anhydride, DMAP, Py, 0 °C→40 °C, 88%; d) EDC, DMAP, CH_3CN/CH_2Cl_2 (1:2), 0 °C→room temp., 68%; e) TBAF, AcOH, THF, 82%; f) DMTST, molecular sieves (4 Å), CH_2Cl_2, 0 °C, 60%.

increase the reactivity of 4-OH of the acceptor during the glycosylation.[15,16] Thus, a *p*-methoxybenzyl (PMB) group was introduced to protect the C-3 OH of acceptor **3**.

In the design of the glucose moiety (Scheme 6), a benzoyl group was introduced at the C-2 hydroxy group to impart β selectivity during the intramolecular glycosylation, and the C-3 hydroxy group was protected with an electron-donating *p*-methoxybenzyl (PMB) group to increase the reactivity. Differentiation between the C-2 and C-3 hydroxy groups of D-glucopyranosides is a big challenge because they are both secondary equatorial alcohols. Li reported that the C-2 and C-3 hydroxy groups of glucopyranoside 2,3-diols could be differentiated by using a strategy based on 4,6-*O*-benzylidene-protected 1,2-D-glucopyranosyl orthoesters.[26] According to this strategy, the PMB group was installed directly at the C-3 position of known 1,2-D-glucopyranosyl orthoester **31**[26] to give **32**. Hydrolysis of the orthoester of **32** followed by 1,2-acyl migration gave **34**, which was converted into thioglycoside **36** via trichloroacetimidate **35**. Removal of the benzylidene acetal from **36** gave the desired glucose derivative (i.e., **8**).

Cyclic GlcCer acceptor **3** was synthesized as the coupling partner for the trisaccharide **2′**. This synthesis began with the tethering of Glc donor **8** and ceramide derivative **9** with



Scheme 8. Final glycosylation, sulfonation and deprotection. Reagents and conditions: a) TMSOTf, $CHCl_3$, AW300 molecular sieves, 0 °C, 70%; b) TBAF, AcOH, THF, 0 °C→room temp., 80%; c) SO_3·Py, DMF, 90 °C, 76%; d) i) TFA (trifluoroacetic acid), CH_2Cl_2, 0 °C; ii) CH_3OH, CH_3ONa, pH 10, 79% over two steps.

a succinyl bridge (Scheme 7). Ceramide derivative **9** was synthesized from Sphingosine **37**.[27] *n*-Tetracosanoic acid was coupled with sphingosine **37** to give ceramide **38**, which was regioselectively protected at the primary hydroxy group with a *tert*-butyldimethylsilyl (TBDMS) group to give **39**. Then, **39** was treated with succinic anhydride in the presence of catalytic 4-(dimethylamino)pyridine (DMAP) to give **9**. The succinoylated Cer derivative (i.e., **9**) and the 4,6-diol thioglucoside (i.e., **8**) could thus be condensed with the aid of a carbodiimide coupling reagent [EDC; 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide] and a catalytic amount of DMAP to give tethered compound **40**. The hydroxy group at the C-1 position of the Cer moiety was deprotected by exposure to TBAF (tetrabutylammonium fluoride). Then, intramolecular coupling of **41** promoted by DMTST [dimethyl(methylthio)sulfonium tetrafluoroborate] successfully produced cyclic GlcCer acceptor **3** in very high yield without affecting the C-4,5 olefin moiety.

Cyclic GlcCer acceptor **3** and trisaccharide donor **2′** were allowed to react in the presence of TMSOTf (0.1 equiv.) in $CHCl_3$ at 0 °C, and the desired compound (i.e., **42**) was obtained in 70% yield (Scheme 8). Selective removal of the TBDMS group of **42** was carried out in the presence of TBAF/AcOH in THF at room temperature, and we found that an acetyl migration between the C-2 and C-3 hydroxy groups took place without the addition of AcOH. After a facile work-up, and purification by silica gel column chromatography, the resulting compound (i.e., **43**) was sulfonated using sulfur-trioxide–pyridine complex to give the desired sulfated ganglioside. Selective removal of the PMB group of compound **44** (TFA, 0 °C), followed by deacetylation by the Zemplen method gave the target compound **1**, SM1a, in good yield.

Conclusions

We have achieved a highly efficient and practical synthesis of the complex sulfated ganglioside SM1a by a convergent synthetic route. This convergent approach using a trisaccharide building block with a potential sulfation position and a cyclic glucosyl ceramide (GlcCer) acceptor gave access to homogeneous SM1a in sufficient quantity for biological studies. Furthermore, the approach described above can guide the chemical synthesis of other unnatural ganglioside derivatives, such as a series of differently sulfated gangliosides, which we aim to prepare. This feature makes it possible to rapidly prepare a library of structurally related compounds for structure–activity relationship research.

Experimental Section

General Methods: All chemicals were reagent grade, and were obtained from commercial sources. Dichloromethane was freshly distilled using standard procedures. Molecular sieves were flame dried under high vacuum before use. Thin-layer chromatography (TLC) was carried out on silica gel GF254 with detection by UV absorption (254 nm), or by spraying with a solution of vanillin (25 g/L) in sulfuric acid (10% in ethanol) followed by charring at ca. 150 °C. Column chromatography was conducted by elution of a column of silica gel (200–300 mesh). ^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-ECP-600 (600/150 MHz) or an Agilent DD2–500 (500/125 MHz) instrument. Chemical shifts are reported on the δ scale. $CHCl_3$ (δ = 7.26 ppm) or tetramethylsilane (δ = 0.00 ppm) was used as an internal reference. COSY and HMQC experiments were routinely used to definitively assign the signals of ^1H and ^{13}C NMR spectra.

***p*-Methoxyphenyl 3,4-*O*-Isopropylidene-β-D-galactopyranoside (11):**[18] A catalytic amount of I_2 (2 mg) and *p*TsOH (2 mg) were added to a solution of **10** (350 mg, 1.23 mmol) in dry acetone (20 mL). The mixture was stirred at 40 °C for 2 h, then TLC (petroleum ether/EtOAc, 1:1) showed that the reaction was complete. The reaction was quenched by the addition of saturated $Na_2S_2O_3$ until the mixture became colorless. Et_3N (1.0 mL) was added, and then the mixture was evaporated to dryness. The residue was diluted with water (50 mL), and the mixture was extracted with CH_2Cl_2 (3× 50 mL). The combined organic extracts were dried with Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 1:2) to give **11** (250 mg, 70%) as a white powder. ^1H NMR (600 MHz, $CDCl_3$): δ = 6.99–6.96 (m, 2 H, Ar-H), 6.84–6.81 (m, 2 H, Ar-H), 4.71 (d, *J* = 8.3 Hz, 1 H, 1-H), 4.21 (dd, *J* = 5.5, 2.1 Hz, 1 H, 4-H), 4.18 (d, *J* = 5.6 Hz, 1 H), 4.00 (dd, *J* = 11.3, 2.9 Hz, 1 H), 3.97–3.94 (m, 1 H), 3.86 (dd, *J* = 9.2, 3.4 Hz, 1 H), 3.83–3.80 (m, 1 H), 3.77 (s, 3 H, -OC*H*$_3$), 2.6 (d, *J* = 2.5 Hz, 1 H, -O*H*), 2.13 (dd, *J* = 9.4, 3.2 Hz, 1 H, -O*H*), 1.56 (s, 3 H, -C*H*$_3$), 1.37 (s, 3 H, -C*H*$_3$) ppm. MS (ESI): calcd. for $C_{16}H_{22}O_7Na$ $[M + Na]^+$ 349.1; found 349.3.

***p*-Methoxyphenyl 2,6-Di-*O*-benzyl-1-*O*-β-D-galactopyranoside (13):** Compound **11** (245 mg, 0.75 mmol) was dissolved in dry DMF (7 mL), and the solution was cooled in an ice bath. NaH (102 mg, 2.55 mmol) was added over 0.5 h. BnBr (0.3 mL, 2.55 mmol) was added, and the reaction mixture was stirred under argon for 5 h. The solvent was evaporated, the residue was diluted with ethyl acetate, and this mixture was washed with water, and with a saturated aqueous NaCl solution. The organic phase was dried with Na_2SO_4, and the solvent was evaporated.

The residue was dissolved in AcOH (90% aq.; 20 mL). The solution was stirred at 80 °C for 2 h. TLC (petroleum ether/EtOAc, 1:1) showed that the reaction was complete, and then the solution was concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 2:1) to give compound **13** (303 mg, 87% over two steps) as a white powder. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 10 H, Ar-H), 7.07–7.03 (m, 2 H, Ar-H), 6.83–6.79 (m, 2 H, Ar-H), 5.07 (d, *J* = 11.4 Hz, 1 H, PhC*H*$_2$-1), 4.86 (d, *J* = 7.7 Hz, 1 H, 1-H), 4.78 (d, *J* = 11.4 Hz, 1 H, PhC*H*$_2$-2), 4.58 (s, 2 H, PhC*H*$_2$), 4.05 (t, *J* = 2.9 Hz, 1 H, 4-H), 3.83 (dd, *J* = 10.2, 5.2 Hz, 1 H, 6a-H), 3.80–3.75 (m, 5 H, 6b-H, ArOC*H*$_3$, 2-H), 3.72 (t, *J* = 5.5 Hz, 1 H, 5-H), 3.69–3.65 (m, 1 H, 3-H), 2.64 (d, *J* = 3.0 Hz, 1 H, O*H*), 2.54 (d, *J* = 4.3 Hz, 1 H, O*H*) ppm. MS (ESI): calcd. for $C_{27}H_{30}O_7Na$ $[M + Na]^+$ 489.2; found 489.1.

***p*-Methoxyphenyl 2,6-Di-*O*-benzyl-3-*O*-*tert*-butyldimethysilyl-β-D-galactopyranoside (7):** Compound **13** (100 mg, 0.214 mmol) was dissolved in CH_2Cl_2 (0.6 mL). Imidazole (58 mg, 0.857 mmol) and TBDMSCl (96 mg, 0.642 mmol) were added at 0 °C. The reaction mixture was stirred at room temperature for 2 h. TLC (petroleum ether/EtOAc, 5:1) showed that the reaction was complete, and then CH_3OH (1 mL) was added. The mixture was diluted with CH_2Cl_2,

and washed with water, and with a saturated aqueous NaCl solution. The organic phase was dried with Na_2SO_4, and the solvent was evaporated. The residue was purified by chromatography (petroleum ether/EtOAc, 8:1) to give compound **7** (120 mg, 96%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36–6.76 (m, 14 H, Ar-*H*), 5.03 (d, *J* = 10.8 Hz, 1 H, PhC*H*$_2$), 4.84 (d, *J* = 7.5 Hz, 1 H, 1-H), 4.72 (d, *J* = 10.8 Hz, 1 H, PhC*H*$_2$), 4.60 (d, *J* = 11.8 Hz, 1 H, PhC*H*$_2$), 4.57 (d, *J* = 11.8 Hz, 1 H, PhC*H*$_2$), 3.85 (dd, *J* = 10.2, 5.3 Hz, 1 H, 6a-H), 3.83 (d, *J* = 2.7 Hz, 1 H, 4-H), 3.80 (dd, *J* = 10.1, 6.7 Hz, 1 H, 6b-H), 3.76 (s, 3 H, OC*H*$_3$), 3.75–3.71 (m, 2 H, 3-H, 2-H), 3.74 (dd, *J* = 5.3, 6.6 Hz, 1 H, 5-H), 0.92 (s, 9 H, *t*Bu), 0.10 (s, 3 H, SiC*H*$_3$), 0.08 (s, 3 H, SiC*H*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.31, 151.65, 138.51, 138.30, 128.50, 128.36, 128.19, 127.85, 127.79, 127.67, 118.60, 114.58, 103.03, 79.45, 75.36, 74.51, 73.87, 73.70, 69.85, 69.54, 55.75, 25.93, 18.15, –4.33, –4.70 ppm. HRMS (ESI): calcd. for $C_{33}H_{44}O_7Na$ [M + Na]$^+$ 603.2749; found 603.2759.

***p*-Methylphenyl 4,6-Di-*O*-acetyl-2-deoxy-2-(2′,2′,2′-trichloroethoxycarbonylamino)-1-thio-β-D-galactopyranoside (17):** Compound **14**[12] (1.30 g, 2.2 mmol) was dissolved in dry MeOH (50 mL), and a solution of NaOMe (0.5 M in MeOH) was added at 0 °C to obtain a basic pH (8–9, pH paper). The mixture was stirred for 30 min, then it was neutralized with ion-exchange resin (H^+). The resin was removed by filtration, and the solvent was concentrated to give **15** (1.02 g, 99%) as a white solid.

Compound **15** (850 mg, 1.8 mmol) was dissolved in EtOAc (50 mL), and a catalytic amount of concentrated H_2SO_4 (96% aq.) was added at room temperature. The reaction mixture was stirred at 45 °C for 18 h. TLC (CH_2Cl_2/CH_3OH, 9:1) showed that the acetylation was complete, and the mixture was neutralized with saturated $NaHCO_3$ solution (20 mL). The organic layer was separated, and the aqueous layer was washed with EtOAc (2× 20 mL). The combined organic layers were dried with $NaSO_4$, filtered, and then concentrated to dryness.

The crude product (**16** and by-products) was then dissolved in dry MeCN (20 mL). Triethyl orthoacetate (1.6 mL, 11 mmol) and *p*TsOH (20 mg, 0.11 mmol) were added at room temperature, and the mixture was stirred for 1.5 h. Et_3N was added to quench the reaction, and the mixture was concentrated. The residue was purified by chromatography (petroleum ether/EtOAc, 1:2.5) to give the orthoacetate intermediate product.

The intermediate product was dissolved in AcOH (90% aq.; 20 mL), and the solution was stirred at room temperature for 1 h. TLC (petroleum ether/EtOAc, 1:1) showed that the reaction was complete. The reaction mixture was concentrated, and the residue was coevaporated once with toluene (5 mL). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1) to give compound **17** (703 mg, 70% over three steps) as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.11 (d, *J* = 8.0 Hz, 2 H, Ar-H), 5.33 (d, *J* = 3.1 Hz, 1 H, 4-H), 5.22 (d, *J* = 7.2 Hz, 1 H, N*H*), 4.80–4.73 (m, 3 H, 1-H, C*H*$_2$CCl$_3$), 4.16 (d, *J* = 6.44 Hz, 2 H, 6-H), 4.04 (m, 1 H, 3-H), 3.86 (t, *J* = 6.4 Hz, 1 H, 5-H), 3.62–3.59 (m, 1 H, 2-H), 2.84 (d, *J* = 4.5 Hz, 1 H, 3-OH), 2.34 (s, 3 H, ArC*H*$_3$), 2.13, 2.06 (s, 6 H, 2 C*H*$_3$CO) ppm. MS (ESI): calcd. for $C_{20}H_{24}O_8NSCl_3Na$ [M + Na]$^+$ 557.0; found 557.2.

***p*-Methylphenyl 4,6-Di-*O*-acetyl-3-*O*-(2′,2′,2′-trichloroethoxycarbonyl)-2-(2′,2′,2′-trichloroethoxycarbonylamino)-2-deoxy-thio-β-D-galactopyranoside (18):** Compound **17** (410 mg, 0.75 mmol) was dissolved in pyridine (5 mL), and trichloroethoxycarbonyl chloride (124 μL, 0.90 mmol) was added. The reaction mixture was stirred for 2 h at room temperature. The mixture was concentrated, and the residue was purified by silica gel chromatography (petroleum ether/EtOAc, 4:1) to give compound **18** (483 mg, 89%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.13 (d, *J* = 7.9 Hz, 2 H, Ar-H), 5.53 (d, *J* = 2.8 Hz, 1 H, 4-H), 5.32 (d, *J* = 9.7 Hz, 1 H, N*H*), 5.22 (d, *J* = 7.3 Hz, 1 H, 1-H), 5.11 (d, *J* = 10.0 Hz, 1 H, 3-H), 4.80 (d, *J* = 11.8 Hz, 1 H, C*H*$_2$CCl$_3$), 4.78–4.68 (m, 2 H, C*H*$_2$CCl$_3$), 4.66 (d, *J* = 11.8 Hz, 1 H, C*H*$_2$CCl$_3$), 4.19 (dd, *J* = 11.3, 6.9 Hz, 1 H, 6a-H), 4.14 (dd, *J* = 11.3, 6.3 Hz, 1 H, 6b-H), 3.96 (t, *J* = 6.4 Hz, 1 H, 5-H), 3.73–3.63 (m, 1 H, 2-H), 2.35 (s, 3 H, ArC*H*$_3$), 2.11, 2.05 (s, 6 H, 2 C*H*$_3$CO) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.57, 170.23, 153.74, 153.15, 138.91, 133.64, 129.90, 127.94, 110.13, 94.04, 85.94, 77.21, 74.95, 74.54, 74.35, 66.52, 61.75, 51.45, 21.33, 20.86, 20.73 ppm. HRMS (ESI): calcd. for $C_{23}H_{25}O_{10}NSCl_6Na$ [M + Na]$^+$ 741.9199; found 741.9203.

***p*-Methoxyphenyl (2-Acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-2,6-di-*O*-benzyl-3-*O*-*tert*-butyldimethysilyl-β-D-galactopyranoside (5)**

Method A: A suspension of compound **7** (198 mg, 0.34 mmol), compound **14** (300 mg, 0.51 mmol), and molecular sieves (4 Å; 400 mg) in CH_2Cl_2 (25.0 mL) was stirred for 1 h, and then cooled to –45 °C. *N*-Iodosuccinimide (NIS; 230 mg, 0.68 mmol) and trifluoromethanesulfonic acid (TfOH; 6 μL, 0.06 mmol) were added, and the mixture was stirred for a further 0.5 h. TLC (petroleum ether/EtOAc, 2:1) showed that the reaction was complete. Et_3N was added to quench the reaction. The mixture was filtered through Celite. The combined filtrate was washed sequentially with saturated $Na_2S_2O_3$ solution (2× 30 mL), and brine (2× 30 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to give **19** (264 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 10 H, Ar-H), 6.98 (d, *J* = 8.9 Hz, 2 H, Ar-H), 6.78–6.74 (m, 2 H, Ar-H), 5.81 (d, *J* = 6.8 Hz, 1 H, N*H*), 5.36 (d, *J* = 2.4 Hz, 1 H, 4′-H), 5.09 (d, *J* = 11.6 Hz, 1 H, PhC*H*$_2$), 5.04 (d, *J* = 10.7 Hz, 1 H, C*H*$_2$CCl$_3$), 5.02–4.97 (m, 2 H, 3′-H, 1′-H), 4.83 (d, *J* = 7.2 Hz, 1 H, 1-H), 4.73 (d, *J* = 10.9 Hz, 1 H, C*H*$_2$CCl$_3$), 4.59 (d, *J* = 11.8 Hz, 1 H, PhC*H*$_2$), 4.54 (d, *J* = 11.8 Hz, 1 H, PhC*H*$_2$), 4.48 (d, *J* = 12.3 Hz, 1 H, PhC*H*$_2$), 4.16 (dd, *J* = 11.1, 7.5 Hz, 1 H, 6a′-H), 4.12–4.08 (m, 1 H, 2′-H), 4.06 (dd, *J* = 11.1, 6.0 Hz, 1 H, 6b′-H), 4.00 (d, *J* = 2.1 Hz, 1 H, 4-H), 3.84 (t, *J* = 6.8 Hz, 1 H, 5′-H), 3.81–3.76 (m, 3 H, 2-H, 3-H, 5-H), 3.75 (s, 3 H, ArOC*H*$_3$), 3.74–3.69 (m, 2 H, 6-H), 2.18, 2.00, 1.26 (3 s, 9 H, 3 C*H*$_3$CO), 0.97 (s, 9 H, *t*Bu), 0.13, 0.12 (s, 6 H, 2 SiC*H*$_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.47, 155.37, 151.48, 138.30, 129.92, 128.65, 128.59, 128.57, 128.39, 127.84, 127.77, 127.68, 118.61, 114.57, 103.30, 101.89, 95.82, 79.56, 75.80, 75.35, 74.59, 73.80, 73.51, 72.12, 71.33, 71.32, 70.67, 69.36, 66.80, 61.24, 55.74, 53.14, 27.04, 26.30, 20.78, 18.45, –4.20, –4.45 ppm. HRMS (ESI): calcd. for $C_{48}H_{62}O_{16}NCl_3SiNa$ [M + Na]$^+$ 1064.2796; found 1064.2815.

Zinc powder (2.0 g) was added to a solution of **19** (1.0 g, 0.97 mmol) in AcOH (10 mL) and 1,2-dichloroethane (10 mL). The mixture was stirred for 4 h at 50 °C. TLC (petroleum ether/EtOAc, 1:1) showed that the reaction was complete. The reaction mixture was filtered through Celite, and the removed zinc powder was washed with EtOAc. The solution was concentrated and diluted with EtOAc. The organic layer was washed sequentially with saturated aqueous $NaHCO_3$ (2× 30 mL), and brine (2× 30 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 3:2) to give **20** (667 mg, 80%).

The product was dissolved in DMF (9.0 mL) and AcOH (1.0 mL). The mixture was stirred for 24 h at 60 °C. Then the solution was

concentrated, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1) to give **5** (600 mg, 90%) as a white foam. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 10 H, Ar-H), 7.01–6.97 (m, 2 H, Ar-H), 6.79–6.75 (m, 2 H, Ar-H), 5.88 (s, 1 H, N*H*), 5.32 (d, *J* = 3.1 Hz, 1 H, 4′-H), 5.17 (d, *J* = 10.7 Hz, 1 H, PhCH_2), 4.87 (d, *J* = 7.6 Hz, 1 H, 1-H), 4.72 (d, *J* = 8.6 Hz, 1 H, 1′-H), 4.64 (d, *J* = 10.8 Hz, 1 H, PhCH_2), 4.59 (d, *J* = 11.8 Hz, 1 H, PhCH_2), 4.54 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.18 (dd, *J* = 11.2, 6.9 Hz, 1 H, 6a′-H), 4.05 (dd, *J* = 11.2, 6.3 Hz, 1 H, 6b′-H), 4.00–3.96 (m, 1 H, 2′-H), 3.92 (d, *J* = 2.9 Hz, 1 H, 4-H), 3.86 (dd, *J* = 9.4, 2.9 Hz, 1 H, 5-H), 3.81 (dd, *J* = 9.0, 4.1 Hz, 1 H, 6a-H), 3.78–3.71 (m, 7 H, 6b-H, 2-H, 5′-H, 3-H, ArOCH_3), 3.68 (d, *J* = 9.9 Hz, 1 H, 3′-H), 2.17, 2.12, 2.01 (3 s, 9 H, 3 COCH_3), 0.94 (s, 9 H, *t*Bu), 0.16, 0.11 (2 s, 6 H, 2 SiCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.98, 170.59, 170.45, 155.45, 151.20, 138.22, 137.87, 128.53, 128.52, 128.45, 128.43, 127.96, 127.94, 127.93, 127.91, 127.81, 127.71, 127.69, 118.50, 114.58, 103.17, 102.19, 79.89, 78.23, 75.71, 75.34, 74.25, 73.74, 73.59, 71.52, 69.47, 61.83, 56.06, 55.68, 26.18, 26.16, 23.32, 18.56, 18.55, –4.04, –4.59 ppm. MS (ESI): calcd. for $C_{45}H_{61}O_{14}NSiNa$ [M + Na]$^+$890.4; found 890.5.

Method B: A suspension of compound **18** (3.3 g, 4.58 mmol), **7** (2.3 g, 3.96 mmol), and molecular sieves (4 Å; 500 mg) in CH_2Cl_2 (100 mL) was stirred for 1 h, and then cooled to –20 °C. *N*-Iodosuccinimide (NIS; 1.54 g, 6.87 mmol) and trifluoromethanesulfonic acid (TfOH; 69 μL, 0.77 mmol) were added, and the mixture was stirred for a further 0.5 h. TLC (petroleum ether/EtOAc, 2:1) showed that the reaction was complete. Et_3N was added to quench the reaction. The mixture was filtered through Celite. The combined filtrate was washed sequentially with saturated $Na_2S_2O_3$ solution (2× 50 mL), and brine (2× 50 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to give **21** (3.26 g, 70%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38–6.75 (m, 14 H, Ar-H), 5.74 (d, *J* = 6.0 Hz, 1 H, N*H*), 5.51 (d, *J* = 2.7 Hz, 1 H, 4′-H), 5.16–5.00 (m, 3 H, 1′-H, 3′-H, PhCH_2), 4.91 (d, *J* = 11.7 Hz, 1 H, CH_2CCl$_3$), 4.83 (d, *J* = 7.0 Hz, 1 H, 1-H), 4.78 (d, *J* = 11.8 Hz, 1 H, CH_2CCl$_3$), 4.75–4.68 (m, 2 H, CH_2CCl$_3$, PhCH_2), 4.67–4.61 (m, 1 H, CH_2CCl$_3$), 4.59 (d, *J* = 11.8 Hz, 1 H, PhCH_2), 4.55 (d, *J* = 11.8 Hz, 1 H, PhCH_2), 4.18 (dd, *J* = 11.2, 7.2 Hz, 1 H, 6a′-H), 4.07 (dd, *J* = 11.2, 6.2 Hz, 1 H, 6b′-H), 4.04–3.97 (m, 1 H, 2′′-H), 3.86 (t, *J* = 6.8 Hz, 1 H, 5′-H), 3.83–3.77 (m, 3 H, 2-H, 3-H, 5-H), 3.77–3.70 (m, 5 H, ArOCH_3, 6-H), 2.18, 2.02 (s, 6 H, 2 COCH_3), 0.95 (s, 9 H, *t*Bu), 0.12, 0.11 (s, 6 H, 2 SiCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.46, 155.33, 151.44, 138.24, 128.57, 128.38, 127.86, 127.75, 118.51, 114.55, 103.26, 94.16, 77.22, 75.35, 73.80, 71.03, 68.70, 66.19, 61.27, 55.72, 53.24, 26.28, 20.80, 18.47, –4.21, –4.52 ppm. HRMS (ESI): calcd. for $C_{49}H_{61}O_{17}NCl_6SiNa$ [M + Na]$^+$ 1196.1732; found 1196.1760.

Zinc powder (2.0 g) was added to a solution of **21** (1.0 g, 0.84 mmol) in AcOH (10 mL) and 1,2-dichloroethane (10 mL). The mixture was stirred for 4 h at 50 °C. TLC (petroleum ether/EtOAc, 1:1) showed that the reaction was complete. The reaction mixture was filtered through Celite, and the filter residue was washed with EtOAc. The filtrate was concentrated, and EtOAc was added. The organic phase was washed sequentially with saturated aqueous $NaHCO_3$ solution (2× 30 mL), and brine (2× 30 mL), dried with Na_2SO_4, and concentrated.

The residue was dissolved in CH_2Cl_2 (10.0 mL), and Ac_2O (84 μL, 0.89 mmol) was added at 0 °C. The mixture was stirred for 2 h at room temperature. Then the solution was concentrated, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1) to give **5** (740 mg, 99% over two steps) as a white solid. This compound gave data consistent with that of the compound prepared by Method A.

***p*-Methoxyphenyl (4,6-*O*-Benzylidene-2,3-di-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-2,6-di-*O*-benzyl-3-*O*-*tert*-butyldimethysilyl-β-D-galactopyranoside (27):** A suspension of **5** (624 mg, 0.73 mmol), **24**[21] (640 mg, 1.1 mmol), and molecular sieves (4 Å; 400 mg) in CH_2Cl_2 (30.0 mL) was stirred for 1 h, and then cooled to 0 °C. *N*-Iodosuccinimide (NIS; 412 mg, 1.83 mmol) and trifluoromethanesulfonic acid (TfOH; 7 μL, 0.07 mmol) were added, and the mixture was stirred for a further 1.5 h. TLC (petroleum ether/EtOAc, 1:1) showed that the reaction was complete. Et_3N was added to quench the reaction. The mixture was filtered through Celite. The combined filtrate was washed sequentially with saturated $Na_2S_2O_3$ (2× 30 mL), and brine (2× 30 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 3:1) to give **27** (460 mg, 49%) as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02–7.26 (m, 25 H, Ar-H), 6.99–6.96 (m, 2 H, Ar-H), 6.76–6.74 (m, 2 H, Ar-H), 5.79 (dd, *J* = 10.5, 7.8 Hz, 1 H, 2′′-H), 5.55 (d, *J* = 5.7 Hz, 1 H, N*H*), 5.49 (d, *J* = 7.8 Hz, 1 H, 1′-H), 5.49 (s, 1 H, PhC*H*), 5.44 (d, *J* = 3.6 Hz, 1 H, 4′-H), 5.29 (dd, *J* = 10.5, 3.5 Hz, 1 H, 3′′-H), 4.99 (dd, *J* = 10.7, 4.0 Hz, 1 H, 3′-H), 4.93 (d, *J* = 10.7 Hz, 1 H, PhCH_2), 4.84 (d, *J* = 7.8 Hz, 1 H, 1′′-H), 4.79 (d, *J* = 7.6 Hz, 1 H, 1-H), 4.59–4.53 (m, 3 H, PhCH_2), 4.51 (d, *J* = 3.8 Hz, 1 H, 4′′-H), 4.39 (d, *J* = 12.2, 1.3 Hz, 1 H, 6a′′-H), 4.28 (dd, *J* = 11.9, 3.8 Hz, 1 H, 6a′-H), 4.12 (d, *J* = 2.7 Hz, 1 H, 4-H), 4.01 (d, *J* = 12.2, 1.5 Hz, 1 H, 6b′′-H), 3.93 (dd, *J* = 11.8, 8.0 Hz, 1 H, 6b′-H), 3.79 (dd, *J* = 8.4, 3.4 Hz, 1 H, 5′-H), 3.75 (s, 3 H, OCH_3), 3.74–3.64 (m, 4 H, 3-H, 6a-H, 6b-H, 5-H), 3.61 (d, *J* = 0.7 Hz, 1 H, 5′′-H), 3.59 (dd, *J* = 9.5, 7.7 Hz, 1 H, 2′′-H), 3.19–3.14 (m, 1 H, 2′′-H), 2.11, 2.00, 1.98 (s, 9 H, 3 CH_3CO), 0.88 (s, 9 H, *t*Bu), 0.03, 0.01 (s, 6 H, 2 SiCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.81, 170.49, 170.34, 166.12, 164.81, 155.11, 151.50, 138.31, 138.16, 137.86, 133.30, 133.24, 129.99, 129.89, 129.81, 129.74, 129.55, 129.20, 129.10, 128.86, 128.53, 128.44, 128.35, 128.33, 128.26, 128.19, 128.03, 127.89, 127.61, 126.92, 126.39, 118.19, 114.39, 103.01, 101.74, 101.55, 100.81, 97.60, 79.72, 75.23, 75.12, 74.20, 73.68, 73.31, 72.62, 72.42, 71.46, 69.97, 69.34, 69.14, 68.49, 68.43, 66.28, 63.61, 55.85, 55.59, 29.69, 26.08, 22.91, 20.91, 20.80, 18.35, –4.52, –4.95 ppm. HRMS (ESI): calcd. for $C_{72}H_{83}O_{21}NSiNa$ [M + Na]$^+$ 1348.5119; found 1348.5159.

***p*-Methoxyphenyl (4,6-*O*-Benzylidene-2,3-di-*O*-acetyl-β-D-galactopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-2,6-di-*O*-benzyl-3-*O*-*tert*-butyldimethysilyl-β-D-galactopyranoside (28):** A suspension of **5** (170 mg, 0.19 mmol), **25**[24] (179 mg, 0.39 mmol), and molecular sieves (4 Å; 400 mg) in CH_2Cl_2 (10.0 mL) was stirred for 1 h, and then cooled to 0 °C. *N*-Iodosuccinimide (NIS; 112 mg, 0.47 mmol) and trifluoromethanesulfonic acid (TfOH, 4 μL, 0.04 mmol) were added, and the mixture was stirred for a further 0.5 h. TLC (petroleum ether/EtOAc, 3:4) showed that the reaction was complete. Et_3N was added to quench the reaction. The mixture was filtered through Celite. The filtrate was washed sequentially with saturated $Na_2S_2O_3$ solution (2× 20 mL), and brine (2× 20 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:3) to give **28** (232 mg, crude product). Since it was difficult to separate, only a limited amount of pure **28** was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52–7.26 (m, 15 H, Ar-H), 7.05–7.01 (m, 2 H, Ar-H), 6.78–6.74 (m, 2 H, Ar-H), 5.88 (d, *J* = 6.7 Hz, 1 H, N*H*), 5.46 (d, *J* = 7.9 Hz, 1 H, 1′-H), 5.45 (s, 1 H, PhC*H*), 5.39 (dd, *J* = 9.8, 3.5 Hz, 1 H, 4′-H),

5.29 (dd, J = 10.3, 7.8 Hz, 1 H, 2′′-H), 5.03 (d, J = 10.6 Hz, 1 H, PhCH_2), 4.92–4.85 (m, 2 H, 3′′-H, 3′′-H), 4.85 (d, J = 7.1 Hz, 1 H, 1-H), 4.68 (d, J = 10.7 Hz, 1 H, PhCH_2), 4.62 (d, J = 7.9 Hz, 1 H, 1′′-H), 4.59–4.54 (m, 2 H, PhCH_2), 4.35–4.28 (m, 2 H, 4′′-H, 6a′-H), 4.23 (dd, J = 11.6, 4.2 Hz, 1 H, 6a′′-H), 4.13 (d, J = 2.2 Hz, 1 H, 4-H), 3.99–3.88 (m, 2 H, 3-H, 5′′-H), 3.79 (dd, J = 7.5, 4.6 Hz, 1 H, 6b′-H), 3.76 (s, 3 H, OCH_3), 3.75–3.64 (m, 5 H, 2-H, 5-H, 6a-H, 6b-H, 6b′′-H), 3.51–3.44 (m, 1 H, 5′-H), 3.33 (dt, J = 10.4, 7.9 Hz, 2′-H), 2.10, 2.07, 2.05, 2.01, 2.00 (s, 15 H, 5 CH_3CO), 0.91 (s, 9 H, tBu), 0.07 (s, 6 H, 2 SiCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.69, 170.63, 170.46, 170.11, 169.16, 155.16, 151.49, 138.29, 138.21, 137.70, 129.01, 128.33, 128.22, 128.11, 128.01, 128.01, 127.87, 127.59, 126.49, 126.35, 118.21, 118.13, 114.43, 103.06, 101.01, 100.59, 98.15, 98.09, 79.73, 75.23, 74.51, 74.17, 73.66, 73.14, 72.01, 71.37, 69.95, 68.85, 68.77, 68.54, 66.27, 55.60, 55.55, 31.91, 29.68, 29.34, 26.10, 23.92, 22.67, 20.92, 20.88, 20.86, 20.76, 18.37, 14.10, –4.47, –4.89 ppm. HRMS (ESI): calcd. for $C_{62}H_{79}O_{21}NSiNa$ $[M + Na]^+$ 1224.4806; found 1224.4834.

_p_-Methoxyphenyl (2,3,4,6-Tetra-_O_-acetyl-β-D-galactopyranosyl)-(1→3)-(4,6-di-_O_-acetyl-2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-2,6-Di-_O_-acetyl-3-_O_-_tert_-butyldimethysilyl-β-D-galactopyranoside (30): Pd/C (10%, 84 mg) was added to a solution of crude compound **28** (232 mg) in methanol (5.0 mL) and THF (10.0 mL). The mixture was stirred at room temperature under a hydrogen atmosphere (balloon) for 24 h. The mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 15:1) to give **29** (125 mg, 63% over two steps) as a white solid. HRMS (ESI): calcd. for $C_{41}H_{63}O_{21}NSiNa$ $[M + Na]^+$ 956.3554; found 956.3573.

Compound **29** (357 mg, 382 μmol) was dissolved in pyridine (5.0 mL), and acetic anhydride (200 μL, 1.97 mmol) was added. The mixture was stirred for 16 h at room temperature, and the reaction was monitored by TLC (petroleum ether/EtOAc, 2:1). The reaction mixture was coevaporated with toluene, and then CH_2Cl_2 was added to the residue. The organic layer was washed with HCl (10% aq.; 20 mL), $NaHCO_3$ (satd.; 2× 20 mL), and NaCl (satd.; 2× 20 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1) to give **30** (400 mg, 95%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.92 (dd, J = 9.0, 1.9 Hz, 2 H, Ar-H), 6.81–6.77 (m, 2 H, Ar-H), 5.99 (s, 1 H, NH), 5.39–5.36 (m, 1 H, 2-H), 5.36 (d, J = 8.3 Hz, 1 H, 1′-H), 5.34 (d, J = 3.6 Hz, 1 H, 4′-H), 5.33 (d, J = 3.5 Hz, 1 H, 4′′-H), 5.09 (dd, J = 10.1, 7.9 Hz, 1 H, 2′′-H), 4.96 (dd, J = 10.9, 3.6 Hz, 1 H, 3′-H), 4.92 (dd, J = 10.5, 3.5 Hz, 1 H, 3′′-H), 4.73 (d, J = 7.8 Hz, 1 H, 1-H), 4.59 (d, J = 7.9 Hz, 1 H, 1′′-H), 4.31 (dd, J = 11.9, 4.4 Hz, 1 H, 6a′-H), 4.27–4.22 (m, 1 H, 6b′-H), 4.16 (dd, J = 11.7, 4.5 Hz, 1 H, 6a-H), 4.12–4.06 (m, 2 H, 6′′-H), 3.94 (dd, J = 11.5, 7.6 Hz, 1 H, 6b-H), 3.84 (t, J = 6.7 Hz, 1 H, 5′′-H), 3.81–3.74 (m, 7 H, 5′-H, 5-H, 4-H, 3-H, ArOCH_3), 3.23 (m, 1 H, 2′-H), 2.13, 2.11, 2.10, 2.06, 2.06, 2.04, 2.04, 2.02, 1.95 (s, 27 H, 9 CH_3CO), 0.90 (s, 9 H, tBu), 0.11 (s, 3 H, SiCH_3), 0.08 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.61, 170.82, 170.60, 170.52, 170.28, 170.23, 169.68, 155.65, 151.50, 118.64, 114.54, 101.09 (C-1, C-1′′), 98.03 (C-1′), 74.08, 74.06, 73.77, 72.57, 72.43, 71.57, 71.42, 70.96, 70.65, 69.24, 69.01, 67.00, 63.66, 63.04, 61.12, 55.76, 25.97, 23.83, 21.28, 20.98, 20.94, 20.90, 20.88, 20.81, 20.69, 18.35, –4.61, –4.65 ppm. HRMS (ESI): calcd. for $C_{49}H_{71}O_{25}NSiNa$ $[M + Na]^+$ 1124.3977; found 1124.3993.

(2,3,4,6-Tetra-_O_-acetyl-β-D-galactopyranosyl)-(1→3)-(4,6-di-_O_-acetyl-2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-2,6-di-_O_-acetyl-3-_O_-_tert_-butyldimethysilyl-β-D-galactopyranosyl Trichloroacetimidate (2′): Compound **30** (100 mg, 91 μmol) was dissolved in a mixture of MeCN and H_2O (5:1; 6.0 mL), and diammonium cerium(IV) nitrate (CAN; 280 mg, 510 μmol) was added. The mixture was stirred for 2 h at room temperature, and the reaction was monitored by TLC (petroleum ether/EtOAc, 1:2). The reaction mixture was extracted with $CHCl_3$, and the organic layer was washed with $NaHCO_3$ (satd.; 2× 20 mL) and NaCl (satd.; 2× 20 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1) to give the intermediate product (81 mg) as a white solid.

The intermediate product was dissolved in CH_2Cl_2 (5.0 mL), and trichloroacetonitrile (85 μL, 820 μmol) and DBU (12 μL, 82 μmol) were added. The mixture was stirred for 2 h at 0 °C, and the reaction was monitored by TLC (petroleum ether/EtOAc, 1:2). The reaction mixture was concentrated, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1.5) to give **2′** (75 mg, 73% over two steps) as a white solid. HRMS (ESI): calcd. for $C_{44}H_{65}O_{24}N_2Cl_3SiNa$ $[M + Na]^+$ 1161.2654; found 1161.2676. Since glycosyl trichloroacetimidates are not stable, this compound was used for further reaction without detailed characterization.

Benzoyl 3-_O_-(_p_-Methoxybenzyl)-4,6-_O_-benzylidene-α-D-glucopyranoside (33): Compound **31**[26] (386 mg, 1.0 mmol) was dissolved in DMF (5 mL), and the solution was cooled to 0 °C. NaH (60% in oil; 60 mg, 1.5 mmol) was added. The solution was warmed to room temperature, and stirred for 30 min. Then the solution was cooled to 0 °C. TBAI (37 mg, 0.1 mmol) was added, and then PMBCl (203 μL, 1.5 mmol) was added dropwise. The solution was warmed to room temperature gradually, and stirred for 30 min at room temperature. CH_3OH (1.5 mmol) was added, and the reaction mixture was stirred for 30 min. The solution was diluted with CH_2Cl_2 (50 mL). Subsequently, HCl (1 M aqueous; 30 mL) was added. The reaction mixture was stirred until TLC (petroleum ether/EtOAc, 4:1) indicated that the 1,2-orthoesters had been completely hydrolyzed. The organic phase was washed with saturated aqueous $NaHCO_3$ solution and brine, dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 3:1) to give **33** (418 mg, 85% over two steps). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06–6.88 (m, 14 H, Ar-H), 6.48 (d, J = 3.8 Hz, 1 H, 1-H), 5.63 (s, 1 H, Ph-CH), 5.01 (d, J = 11.0 Hz, 1 H, Ph-CH_2), 4.74 (d, J = 11.0 Hz, 1 H, Ph-CH_2), 4.32 (dd, J = 4.9, 10.5 Hz, 1 H, 4-H), 4.01–4.05 (m, 2 H, 3-H, 6a-H), 3.96 (dd, J = 3.8, 9.3 Hz, 1 H, 2-H), 3.80 (s, 3 H, -OCH_3), 3.72–3.79 (m, 2 H, 5-H, 6b-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.05, 159.61, 137.19, 133.78, 130.24, 130.06, 130.04, 130.02, 129.41, 129.17, 128.67, 128.43, 128.41, 126.06, 114.06, 101.42, 92.30, 81.86, 78.00, 74.76, 71.23, 68.85, 65.42, 55.38 ppm. HRMS (ESI): calcd. for $C_{28}H_{28}O_8Na$ $[M + Na]^+$ 515.1683; found 515.1676.

4,6-_O_-Benzylidene-2-_O_-benzoyl-3-_O_-(_p_-methoxybenzyl)-1-thio-β-D-glucopyranosyl Trichloroacetimidate (35): Compound **33** (900 mg, 1.99 mmol) was dissolved in CH_2Cl_2 (20.0 mL). Et_3N (5.0 mL) was added, and the mixture was stirred for 12 h. After this time, **33** had been converted into **34**. The reaction mixture was concentrated to dryness.

The crude product was dissolved in CH_2Cl_2 (20.0 mL), and trichloroacetonitrile (997 μL, 9.95 mmol) and DBU (151 μL, 1.0 mmol) were added. The mixture was stirred for 2 h at 0 °C, and the reaction was monitored by TLC (petroleum ether/EtOAc, 2.5:1). The reaction mixture was concentrated, and the residue was

purified by column chromatography on silica gel (petroleum ether/EtOAc, 6:1) to give **35** (1.014 g, 80% over two steps). Since glycosyl trichloroacetimidates are not stable, this compound was used for further reaction without characterization.

***p*-Methylphenyl 4,6-*O*-Benzylidene-2-*O*-benzoyl-3-*O*-(*p*-methoxybenzyl)-1-thio-β-D-glucopyranoside (36):** A suspension of compound **35** (1420 mg, 2.23 mmol), TolSH (277 mg, 2.23 mmol), and molecular sieves (4 Å; 300 mg) in CH_2Cl_2 (20.0 mL) was stirred for 0.5 h, and then it was cooled to 0 °C. $BF_3{\cdot}Et_2O$ (19 μL, 35 μmol) was added, the mixture was stirred for a further 1 h. TLC (petroleum ether/EtOAc, 2:3) showed that the reaction was complete. Et_3N was added to quench the reaction. The mixture was filtered through Celite. The filtrate was washed with saturated $NaHCO_3$ (2× 20 mL), and brine (2× 20 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 6:1) to give **36** (801 mg, 60%) as a white powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02–6.55 (m, 14 H, Ar-H), 5.60 (s, 1 H, PhC*H*), 5.22 (dd, *J* = 10.0, 8.7 Hz, 1 H, 2-H), 4.76 (d, *J* = 10.0 Hz, 1 H, 1-H), 4.72 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.58 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.41 (dd, *J* = 10.6, 5.0 Hz, 1 H, 4-H), 3.87–3.81 (m, 2 H, 6-H), 3.78 (t, *J* = 9.3 Hz, 1 H, 3-H), 3.68 (s, 3 H, PhOCH_3), 3.54 (td, *J* = 9.9, 5.0 Hz, 1 H, 5-H), 2.32 (s, 3 H, PhCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.94, 159.05, 138.51, 137.18, 133.64, 133.13, 129.90, 129.84, 129.76, 129.63, 129.02, 128.32, 128.27, 128.14, 125.99, 113.51, 101.23, 87.16, 81.43, 78.75, 73.83, 72.00, 70.58, 68.60, 55.08, 21.15 ppm. HRMS: calcd. for $C_{35}H_{34}NO_7SNa$ [M + Na]$^+$ 621.1917; found 621.1917.

***p*-Methylphenyl 2-*O*-Benzoyl-3-*O*-(*p*-methoxybenzyl)-1-thio-β-D-glucopyranoside (8):** Compound **36** (210 mg, 0.35 mmol) was added to a mixture of AcOH and H_2O (4:1; 15 mL). The resulting solution was stirred at 80 °C for 3 h. TLC (petroleum ether/CH_2Cl_2, 1:2) showed that the reaction was complete, and the solution was concentrated coevaporated once with toluene (5 mL). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1) to give **8** (173 mg, 95%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08–6.74 (m, 13 H, Ar-H), 5.20 (t, *J* = 9.5 Hz, 1 H, 2-H), 4.77 (d, *J* = 10.0 Hz, 1 H, 1-H), 4.65 (d, *J* = 11.2 Hz, 1 H,PhCH_2), 4.50 (d, *J* = 11.2 Hz, 1 H, PhCH_2), 3.92 (d, *J* = 11.0 Hz, 1 H, 6a-H), 3.79 (d, *J* = 11.2 Hz, 1 H, 6b-H), 3.73 (s, 3 H, PhOCH_3), 3.70–3.63 (m, 2 H, 3-H, 4-H), 3.45 (s, 1 H, 5-H), 2.32 (s, 3 H, PhCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.32, 159.48, 138.49, 133.46, 133.24, 130.00, 129.90, 129.86, 129.84, 128.77, 128.62, 114.02, 86.75, 83.58, 79.53, 74.54, 72.53, 70.42, 62.72, 55.29, 21.27 ppm. HRMS: calcd. for $C_{28}H_{30}O_7SNa$ [M + Na]$^+$ 533.1604; found 533.1604.

(2*S*,3*R*,4*E*)-2-Tetracosanamido-4-ene-1,3-diol (38): DIPEA (327 μL, 1.87 mmol) was added dropwise to a stirred mixture of **37**[27] (487 mg, 1.63 mmol), carnaubic acid (777 mg, 2.10 mmol), HOBt (220 mg, 1.63 mmol), and EDC (311 mg, 1.63 mmol) in anhydrous THF (15 mL) under nitrogen. The reaction mixture was stirred for about 5 h. TLC (CH_2Cl_2/CH_3OH, 20:1) showed that the reaction was complete. The reaction mixture was evaporated, and the residue was dissolved in $CHCl_3$ (50 mL). The organic phase was washed successively with water (20 mL) and brine (20 mL), then it was dried with Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (CH_2Cl_2/CH_3OH, 30:1) to give **38** (762 mg, 71%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.32 (d, *J* = 7.5 Hz, 1 H, N*H*), 5.85–5.76 (m, 1 H, 5-H), 5.55 (dd, *J* = 15.5, 6.4 Hz, 1 H, 4-H), 4.37–4.32 (m, 1 H, 3-H), 3.99 (dd, *J* = 11.3, 3.7 Hz, 1 H, 1a-H), 3.93 (dd, *J* = 7.3, 3.6 Hz, 1 H, 1b-H), 3.73 (dd, *J* = 11.3, 3.2 Hz, 1 H, 2-H), 2.37 (t, *J* = 7.5 Hz, 2 H, NHCOCH_2), 2.28–2.23 (m, 2 H, CH_2-6^{cer}), 2.08 (dd, *J* = 14.1, 7.1 Hz, 2 H, NHCOCH$_2$CH_2), 1.70–1.58 (m, 4 H, 2 CH_2), 1.27 (br. s, 58 H, 29 CH_2), 0.90 (t, *J* = 6.8 Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.16, 134.52, 128.86, 74.88, 62.67, 54.56, 36.98, 33.81, 32.44, 32.08, 29.86, 29.83, 29.82, 29.80, 29.78, 29.76, 29.67, 29.60, 29.52, 29.44, 29.38, 29.26, 29.23, 25.92, 24.88, 22.85, 14.29 ppm. HRMS (ESI): calcd. for $C_{42}H_{83}NO_3Na$ [M + Na]$^+$ 672.6277; found 672.6265.

(2*S*,3*R*,4*E*)-1-*O*-*tert*-Butyldimethylsilyl-2-tetracosanamido-4-octadec-ene-1,3-diol (39): Triethylamine (128 μL, 921 μmol), TBDMSCl (51 mg, 338 μmol), and DMAP (112.5 mg, 921 μmol) were added to a solution of **38** (200 mg, 307 μmol) in $CHCl_3$ (5 mL) at 0 °C. The mixture was stirred for 6 h at 40 °C. TLC (Et_2O/hexane, 1:1) showed that the reaction was complete. The reaction mixture was concentrated, and the residue was purified by column chromatography on silica gel (Et_2O/hexane, 1:3) to give **39** (188 mg, 80%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.20 (d, *J* = 7.7 Hz, 1 H, N*H*), 5.82–5.70 (m, 1 H, 5-H), 5.50 (dd, *J* = 15.4, 5.7 Hz, 1 H, 4-H), 4.16 (br. s, 1 H, 3-H), 3.98–3.89 (m, 2 H, 1a-H, 2-H), 3.74 (dd, *J* = 9.9, 2.4 Hz, 1 H, 1b-H), 3.62 (d, *J* = 8.8 Hz, 1 H, -O*H*), 2.21 (t, *J* = 7.6 Hz, 2 H, NHCOCH_2), 2.05 (dd, *J* = 14.2, 7.1 Hz, 2 H, CH_2-6^{cer}), 1.69–1.56 (m, 2 H, NHCOCH$_2$CH_2), 1.44–1.09 (m, 62 H, 31 CH_2), 0.97–0.81 (m, 15 H, 5 CH_3), 0.06, 0.06 (s, 6 H, 2 SiCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.31, 133.26, 129.30, 74.76, 63.61, 53.35, 37.05, 32.46, 32.08, 29.86, 29.83, 29.82, 29.80, 29.68, 29.65, 29.55, 29.52, 29.45, 29.38, 29.37, 25.97, 25.94, 22.85, 18.23, 14.29, –5.48 ppm. HRMS (ESI): calcd. for $C_{48}H_{97}NO_3SiNa$ [M + Na]$^+$ 786.712; found 786.7130.

(2*S*,3*R*,4*E*)-1-*O*-*tert*-Butyldimethylsilyl-3-*O*-succinoyl-2-tetracosanamido-4-octadecene-1,3-diol (9): Succinic anhydride (120 mg, 1.2 mmol) and DMAP (5 mg, 41 μmol) were added to a solution of **39** (200 mg, 261 μmol) in pyridine (7.5 mL) at 0 °C. The mixture was stirred for 23 h at 40 °C. TLC (petroleum ether/EtOAc, 1:2) showed that the reaction was complete. The reaction mixture was coevaporated with toluene. The residue was dissolved in $CHCl_3$, and the solution was washed with H_2O, dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (Et_2O/hexane, 1:2) to give **9** (200 mg, 88%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.80–5.69 (m, 2 H, N*H*, 5-H), 5.42 (dd, *J* = 15.3, 7.5 Hz, 1 H, 4-H), 5.34 (t, *J* = 7.0 Hz, 1 H, 3-H), 4.23 (td, *J* = 9.7, 3.9 Hz, 1 H, 2-H), 3.71 (dd, *J* = 10.3, 3.2 Hz, 1 H, 1a-H), 3.58 (dd, *J* = 10.3, 4.4 Hz, 1 H, 1b-H), 2.71–2.55 (m, 4 H, OCOCH_2CH_2OCO), 2.17 (m, 2 H, NHCOCH_2), 2.00 (m, 2 H, CH_2-6^{cer}), 1.57 (m, 2 H, NHCOCH$_2$CH_2), 1.44–1.09 (m, 62 H, 31 CH_2), 0.93–0.82 (m, 15 H, 5 CH_3), 0.04, 0.04 (s, 6 H, 2 SiCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.75, 173.13, 171.05, 137.04, 124.70, 74.20, 61.64, 52.01, 37.07, 32.50, 32.08, 29.87, 29.81, 29.69, 29.67, 29.58, 29.52, 29.43, 29.41, 29.14, 29.02, 25.97, 25.91, 22.85, 18.34, 14.29, –5.41, –5.49 ppm. HRMS (ESI): calcd. for $C_{52}H_{101}NO_6SiNa$ [M + Na]$^+$ 886.730; found 886.7290.

***p*-Methylphenyl 6-*O*-{[(2*S*,3*R*,4*E*)-1-*O*-*tert*-Butyldimethylsilyl-2-tetracosanamido-octadecene-4-yloxy]carbonylpropanoyl}-2-*O*-benzoyl-3-*O*-(*p*-methoxybenzyl)-1-thio-β-D-glucopyranoside (40):** Compound **8** (41 mg, 80 μmol) and compound **9** (70 mg, 80 μmol) were dissolved in CH_2Cl_2 (2 mL) and CH_3CN (1 mL), and the solution was cooled to 0 °C. DMAP (3.0 mg, 18 μmol) and EDC·HCl (18.0 mg, 94 mmol) were added. The mixture was stirred for 5 h at room temperature. TLC (toluene/EtOAc 2:1) showed that the reaction was complete. The reaction mixture was diluted with $CHCl_3$ (50 mL), and the solution was washed with H_2O (20 mL) and brine (20 mL), dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (toluene/EtOAc, 4:1) to give **40**

(75 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04–6.64 (m, 13 H, Ar-H), 5.75 (m, 2 H, N*H*, 5^{cer}-H), 5.47–5.35 (m, 2 H, 4^{cer}-H, 3^{cer}-H), 5.17 (t, *J* = 9.5 Hz, 1 H, 2-H), 4.71 (d, *J* = 10.0 Hz, 1 H, 1-H), 4.68–4.61 (m, 2 H, PhCH_2), 4.45 (dd, *J* = 12.0, 3.8 Hz, 1 H, 6a-H), 4.39 (d, *J* = 11.9 Hz, 1 H, 6b-H), 4.24 (m, 1 H, 2^{cer}-H), 4.01 (s, 1 H, O*H*), 3.77–3.62 (m, 6 H, 4-H, 3-H, PhOCH_3, 1a^{cer}-H), 3.58 (dd, *J* = 10.3, 4.6 Hz, 1 H, 1b^{cer}-H), 3.53 (d, *J* = 9.6 Hz, 1 H, 5-H), 2.65 (m, 4 H, OCOCH_2CH_2OCO), 2.31 (s, 3 H, PhCH_3), 2.15 (t, *J* = 7.4 Hz, 2 H, NHCOCH_2), 2.01 (dd, *J* = 14.0, 6.8 Hz, 2 H, CH_2-6^{cer}), 1.59 (m, 2 H, NHCOCH$_2$CH_2), 1.44–1.10 (m, 62 H, 31 CH_2), 0.94–0.79 (m, 15 H, 5 CH_3), 0.06, 0.06 (s, 6 H, 2 SiCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.22, 172.71, 170.85, 165.23, 159.25, 138.27, 136.82, 133.34, 133.27, 130.18, 130.04, 129.99, 129.83, 129.64, 129.03, 128.50, 124.50, 113.76, 86.89, 83.02, 77.98, 74.56, 74.17, 72.17, 69.80, 63.31, 61.89, 55.22, 51.93, 37.10, 32.54, 32.07, 29.86, 29.80, 29.71, 29.67, 29.63, 29.58, 29.51, 29.45, 29.40, 29.18, 25.97, 22.84, 21.28, 18.33, 14.28, –5.35, –5.47 ppm. HRMS (ESI): calcd. for $C_{80}H_{129}NO_{12}SSiNa$ [M + Na]$^+$ 1378.8887; found 1378.8897.

***p*-Methylphenyl 6-*O*-{[(2*S*,3*R*,4*E*)-2-Tetracosanamido-octadecene-4-yloxy]carbonylpropanoyl}-2-*O*-benzoyl-3-*O*-(*p*-methoxybenzyl)-1-thio-β-D-glucopyranoside (41):** AcOH (500 μL) and TBAF (1.0 M solution in THF; 500 μL, 500 μmol) were added to a solution of **40** (140 mg, 0.103 mmol) in THF (1.5 mL) at 0 °C. The mixture was stirred for 3 h at room temperature. TLC (EtOAc/toluene, 1:1) showed that the reaction was complete. The reaction mixture was diluted with $CHCl_3$ (30 mL), and the solution was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/toluene, 1:2) to give **41** (105 mg, 82%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05–6.65 (m, 13 H, Ar-H), 6.03 (d, *J* = 8.9 Hz, 1 H, N*H*), 5.80–5.73 (m, 1 H, 5^{cer}-H), 5.46–5.34 (m, 2 H, 4^{cer}-H, 3^{cer}-H), 5.19–5.14 (m, 1 H, 2-H), 4.72 (d, *J* = 10.0 Hz, 1 H, 1-H), 4.66–4.58 (m, 2 H, PhCH_2), 4.55 (dd, *J* = 12.0, 3.9 Hz, 1 H, 6a-H), 4.32 (dd, *J* = 12.0, 2.0 Hz, 1 H, 6b-H), 4.18–4.13 (m, 1 H, 2^{cer}-H), 3.70 (s, 3 H, ArOCH_3), 3.69–3.64 (m, 3 H, 4-H, 3-H, 5-H), 3.61 (dd, *J* = 11.7, 3.4 Hz, 1 H, 1a^{cer}-H), 3.57–3.51 (m, 1 H, 1b^{cer}-H), 2.75–2.63 (m, 4 H, OCOCH_2CH_2OCO), 2.32 (s, 3 H, ArCH_3), 2.19–2.15 (m, 2 H, NHCOCH_2), 2.06–1.97 (m, 2 H, 6^{cer}-H), 1.62–1.56 (m, 2 H, NHCOCH$_2$CH_2), 1.41–1.17 (m, 62 H, 31 CH_2), 0.88 (t, *J* = 7.0 Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.82, 172.95, 171.65, 165.27, 159.42, 138.38, 137.53, 133.41, 133.38, 130.00, 129.92, 129.68, 128.94, 128.57, 124.59, 113.89, 86.91, 83.32, 77.80, 74.74, 74.73, 72.26, 69.65, 63.43, 61.90, 55.26, 53.05, 36.90, 32.44, 32.08, 29.88, 29.85, 29.82, 29.81, 29.79, 29.72, 29.65, 29.59, 29.51, 29.48, 29.42, 29.30, 29.07, 25.85, 22.84, 21.29, 14.27 ppm. HRMS (ESI): calcd. for $C_{74}H_{115}NO_{12}SNa$ [M + Na]$^+$ 1264.8036; found 1264.8032.

2-*O*-Benzoyl-3-*O*-(*p*-methoxybenzyl)-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-2-tetracosanamido-octadecene-4,6-succinate (3): Molecular sieves (4 Å; 85 mg) were added to a solution of **41** (100 mg, 80.4 μmol) in CH_2Cl_2 (2.0 mL). The suspension was stirred for 1 h at room temperature. DMTST (63 mg, 241 μmol) was added at 0 °C, and the mixture was stirred for a further 2 h at 0 °C. TLC (toluene/EtOAc, 1:1) showed that the reaction was complete. The reaction mixture was filtered through Celite, and the filter residue was washed with $CHCl_3$. The filtrate was washed with saturated aqueous $NaHCO_3$ and H_2O, dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/toluene, 1:2.5) to give **3** (54 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03–6.78 (m, 9 H, Ar-H), 5.82–5.76 (m, 1 H, 5^{cer}-H), 5.71 (d, *J* = 9.6 Hz, 1 H, NH), 5.31–5.23 (m, 2 H, 3^{cer}-H, 4^{cer}-H), 5.18 (t, *J* = 7.4 Hz, 1 H, 2-H), 4.71 (d, *J* = 11.3 Hz, 1 H, PhCH_2), 4.56 (d, *J* = 11.5 Hz, 1 H, PhCH_2), 4.55 (d, *J* = 7.0 Hz, 1 H, 1-H), 4.43 (dd, *J* = 11.7, 8.2 Hz, 1 H, 6a-H), 4.26 (m, 2 H, 6b-H, 2^{cer}-H), 3.89 (dd, *J* = 9.7, 3.5 Hz, 1 H, 1a^{cer}-H), 3.75 (s, 3 H, ArOCH_3), 3.68–3.60 (m, 4 H, 3-H, 4-H, 5-H, 1b^{cer}-H), 2.79–2.51 (m, 4 H, OCOCH_2CH_2OCO), 2.47 (d, *J* = 2.8 Hz, 1 H, OH), 2.03 (t, *J* = 7.7 Hz, 2 H, NHCOCH_2), 1.95 (dq, *J* = 14.5, 7.3 Hz, 2 H, 6^{cer}-H), 1.49 (d, *J* = 3.6 Hz, 2 H, NHCOCH$_2$CH_2), 1.36–1.17 (m, 62 H, 31 CH_2), 0.88 (t, *J* = 6.9 Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.85, 172.02, 170.75, 165.31, 159.61, 138.45, 133.57, 130.01, 129.81, 129.74, 128.70, 124.97, 114.14, 100.12, 82.17, 74.07, 73.88, 73.52, 73.07, 71.03, 66.83, 64.26, 55.34, 50.15, 48.83, 36.87, 32.43, 32.08, 29.90, 29.86, 29.83, 29.81, 29.79, 29.72, 29.65, 29.56, 29.52, 29.51, 29.46, 29.40, 29.05, 25.72, 22.84, 14.27 ppm. HRMS (ESI): calcd. for $C_{67}H_{107}NO_{12}Na$ [M + Na]$^+$ 1140.7692; found 1264.8032.

(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(2,6-di-*O*-acetyl-3-*O*-*tert*-butyldimethysilyl-β-D-galactopyranoside)-(1→4)-2-*O*-benzo-yl-3-*O*-(*p*-methoxybenzyl)-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-2-tetracosanamido-octadecene-4,6-succinate (42): A suspension of compound **2′** (60 mg, 52 μmol), compound **3** (28 mg, 25 μmol), and molecular sieves (AW-300; 80 mg) in $CHCl_3$ (3.0 mL) was stirred for 0.5 h, and then cooled to 0 °C. TMSOTf (2 μL, 11 μmol) was added, and the mixture was stirred for a further 1 h. TLC (petroleum ether/EtOAc, 1:2) showed that the reaction was complete. Et_3N was added to quench the reaction. The mixture was filtered through Celite. The filtrate was washed with saturated $NaHCO_3$ solution (2× 20 mL), and brine (2× 20 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1.2) to give **42** (36 mg, 70%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97–6.75 (m, 9 H, ArH), 5.82–5.76 (m, 1 H, 5^{cer}-H), 5.63 (d, *J* = 6.98 Hz, 1 H, NHCOCH$_3$), 5.60 (d, *J* = 9.68 Hz, 1 H, N*H*CO), 5.38–5.30 (m, 2 H, 4′′-H, 4′′′-H), 5.30–5.23 (dd, 2 H, 1′′-H, 3^{cer}-H), 5.23–5.13 (m, 3 H, 2-H, 2′-H, 4^{cer}-H), 5.07 (dd, *J* = 10.4, 7.9 Hz, 1 H, 2′′′-H), 4.91 (dd, *J* = 10.4, 3.5 Hz, 1 H, 3′′′-H), 4.80–4.74 (m, 2 H, PhCH_2, 3′′-H), 4.71 (d, *J* = 11.2 Hz, 1 H, PhCH_2), 4.66 (d, *J* = 8.0 Hz, 1 H, 1-H), 4.59–4.55 (m, 2 H, 1′-H, 1′′′-H), 4.30 (m, 3 H, 6a′′-H, 6a-H, 2^{cer}-H), 4.21–4.14 (m, 2 H, 6b-H, 4′-H), 4.10–4.07 (m, 2 H, 6′′′-H), 3.97–3.68 (m, 13 H, 6b′′-H, 1^{cer}-H, 3-H, 4-H, 5-H, 5′-H, 5′′′-H, 6a′-H, 6b′-H, ArOCH_3), 3.66 (t, *J* = 5.7 Hz, 1 H, 5′′-H), 3.48 (d, *J* = 6.5 Hz, 1 H, 3′-H), 3.34–3.27 (m, 1 H, 2′′-H), 2.78–2.47 (m, 4 H, OCCH_2CH_2CO), 2.15–2.10 (m, 11 H, NHCOCH_2, 3 COCH_3), 2.07–2.02 (m, 7 H, 6a^{cer}-H, 2 COCH_3), 1.99, 1.98 (s, 6 H, 2 COCH_3), 1.97–1.93 (m, 4 H, 6b^{cer}-H, COCH_3), 1.91 (s, 3 H, COCH_3), 1.45 (br. s, 2 H, NHCOCH$_2$CH_2), 1.35–1.17 (m, 62 H, 31 CH_2), 0.90 (s, 9 H, *t*Bu), 0.88 (t, *J* = 6.9 Hz, 6 H, 2 CH_3), 0.12, 0.08 (s, 6 H, 2 SiCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.78, 172.71, 171.44, 171.42, 171.25, 170.56, 170.49, 170.44, 170.18, 169.73, 169.38, 165.54, 165.30, 159.19, 139.10, 133.63, 130.57, 129.80, 129.59, 128.91, 128.65, 125.17, 113.92, 101.93, 101.04, 99.25, 98.37, 80.90, 78.79, 74.63, 74.06, 73.87, 73.80, 73.46, 73.08, 72.90, 72.69, 72.58, 72.39, 72.18, 71.62, 71.40, 71.01, 70.76, 69.05, 66.99, 63.78, 63.31, 63.11, 62.97, 61.15, 55.26, 50.08, 36.90, 32.44, 32.07, 29.85, 29.80, 29.72, 29.66, 29.55, 29.50, 29.45, 29.05, 26.65, 26.25, 26.06, 26.00, 25.75, 25.66, 23.77, 22.83, 21.41 20.98, 20.90, 20.86, 20.82, 20.75, 20.69, 18.30, 14.26, –4.48, –4.67 ppm. HRMS (ESI): calcd. for $C_{109}H_{170}O_{35}N_2SiNa$ [M + Na]$^+$ 2118.1216; found 2118.1246.

(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-(2,6-di-*O*-acetyl-β-D-galactopyranoside)-(1→4)-2-*O*-benzoyl-3-*O*-(*p*-methoxy-

benzyl)-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-2-tetracosanamido-octadecene-4,6-succinate (43): AcOH (450 μL) and TBAF (1.0 M solution in THF; 450 μL, 450 μmol) were added to a solution of **42** (26 mg, 12.4 μmol) in THF (1.5 mL) at 0 °C. The mixture was stirred for 3 h at room temperature. TLC (CH_2Cl_2/CH_3OH, 20:1) showed that the reaction was complete. The reaction mixture was diluted with $CHCl_3$ (30 mL), and the solution was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (CH_2Cl_2/CH_3OH, 30:1) to give **43** (20 mg, 80%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96–6.74 (m, 9 H, ArH), 5.94 (d, J = 6.4 Hz, 1 H, N*H*COCH$_3$), 5.79 (m, 1 H, 5^{cer}-H), 5.63 (d, J = 9.8 Hz, 1 H, N*H*CO), 5.54 (d, J = 8.0 Hz, 1 H, 1′′-H), 5.41 (d, J = 3.0 Hz, 1 H, 4′′-H), 5.34 (d, J = 3.2 Hz, 1 H, 4′′′-H), 5.29–5.12 (m, 4 H, 4^{cer}-H, 3^{cer}-H, 2′′′-H, 2-H), 4.96 (dd, J = 10.4, 3.4 Hz, 1 H, 3′′′-H), 4.90 (dd, J = 9.9, 8.3 Hz, 1 H, 2′-H), 4.79–4.69 (m, 3 H, PhC*H*$_2$, 1′-H), 4.59–4.57 (m, 2 H, 1-H, 1′′′-H), 4.38–4.24 (m, 4 H, 6a-H, 6a′-H, 2^{cer}-H, 3′′-H), 4.20 (dd, J = 11.5, 6.6 Hz, 1 H, 6b-H), 4.17–4.09 (m, 2 H, 6′′′-H), 4.08 (br. s, 1 H, 4′-H), 4.07–4.00 (m, 3 H, 6b′-H, 6a′′-H, 4-H), 3.97–3.76 (m, 6 H, 6b′′-H, 3-H, 5′′′-H, 5′′-H, 5-H, 1a^{cer}-H), 3.73 (s, 3 H, ArOC*H*$_3$), 3.66 (t, J = 5.8 Hz, 1 H, 5′-H), 3.61 (d, J = 9.2 Hz, 1 H, 3′-H), 3.49–3.45 (m, 1 H, 1b^{cer}-H), 3.33–3.25 (m, 1 H, 2′′-H), 2.77–2.49 (m, 4 H, OCC*H*$_2$C*H*$_2$CO), 2.15, 2.13, 2.11, 2.06, 2.05, 2.05, 2.04 (s, 21 H, 7 COC*H*$_3$), 1.98–1.93 (m, 7 H, 6^{cer}-H, COC*H*$_3$, NHCOC*H*$_2$), 1.91 (s, 3 H, COC*H*$_3$), 1.49–1.15 (m, 64 H, 32 C*H*$_2$), 0.88 (t, J = 6.8 Hz, 6 H, 2 C*H*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.05, 172.69, 171.44, 171.09, 170.67, 170.57, 170.48, 170.46, 170.30, 170.13, 170.02, 169.50, 165.27, 159.14, 138.86, 133.63, 130.55, 129.79, 129.50, 128.94, 128.65, 128.62, 125.17, 113.77, 101.30, 99.97, 99.49, 99.18, 81.10, 78.75, 75.49, 75.30, 74.18, 73.43, 73.36, 73.11, 73.06, 73.03, 72.89, 72.54, 71.79, 71.65, 71.15, 71.05, 70.75, 69.53, 67.97, 66.90, 63.46, 62.45, 61.04, 55.83, 55.25, 50.03, 36.80, 32.44, 32.07, 29.86, 29.85, 29.82, 29.80, 29.72, 29.65, 29.55, 29.51, 29.50, 29.45, 29.43, 29.04, 26.65, 25.75, 25.66, 23.69, 22.83, 21.17, 20.97, 20.88, 20.86, 20.83, 20.79, 20.77, 20.65, 14.26 ppm. HRMS (ESI): calcd. for $C_{103}H_{156}O_{35}N_2Na$ [M + Na]$^+$ 2004.0381; found 2004.0383.

β-D-Galactopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-(3-*O*-sulfonate-β-D-galactopyranoside)-(1→4)-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-2-tetracosanamido-octadecene-4,6-succinate (1): SO_3·Py (20 mg, 125 μmol) was added to a solution of **43** (20 mg, 10.1 μmol) in DMF (1.5 mL). The mixture was stirred for 36 h at 90 °C. TLC ($CHCl_3$/MeOH, 10:1) showed that the reaction was complete. The reaction mixture was concentrated, and the residue was diluted with $CHCl_3$ (30 mL). The solution was washed with brine (10 mL), dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH, 15:1) to give **44** (16 mg, 76%) as a white solid. HRMS (ESI): calcd. for $C_{103}H_{155}O_{38}N_2S$ [M – H]$^-$ 2059.9973; found 2059.9960.

Trifluoroacetic acid (180 μL) was added to a solution of **44** (13.0 mg, 6.3 μmol) in CH_2Cl_2 (540 μL) at 0 °C. The mixture was stirred for 3 h at 0 °C. TLC (CH_2Cl_2/MeOH, 5:1) showed that the reaction was complete. The reaction mixture was diluted with CH_3OH (2 mL). A catalytic amount of sodium methoxide (25% in MeOH) was added to adjust the pH to 10. The mixture was stirred for 3 h at room temperature. TLC ($CHCl_3$/MeOH/H_2O, 5:4:0.5) showed that the reaction was complete. Then the reaction mixture was neutralized with Dowex-50 (H^+). The mixture was filtered through cotton wool, which was then washed with a mixture of $CHCl_3$ and MeOH (1:1). The combined filtrate was concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH/H_2O, 5:4:0.5), then column chromatography (CH_3OH) on Sephadex LH-20 (2 g) to give **1** (7 mg, 79%). ^{1}H NMR (600 MHz, CD_3OD/$CDCl_3$, 1:1): δ = 5.69 (m, 1 H, 5^{cer}-H), 5.45 (dd, J = 15.3, 7.7 Hz, 1 H, 4^{cer}-H), 4.68 (s, 1 H, 1′′′-H), 4.44 (d, J = 7.3 Hz, 1 H, 1′-H), 4.36 (d, J = 7.1 Hz, 1 H), 4.32–4.28 (m, 2 H, 3′-H, 1′′-H), 4.22–4.16 (m, 2 H, 2′-H, 1^{cer}-H), 4.11–4.04 (m, 2 H, 3^{cer}-H, 4′′′-H), 3.99 (s, 1 H, 2^{cer}-H), 3.39 (m, 1 H, 2′′-H), 2.18 (t, J = 7.6 Hz, 2 H, NHCOC*H*$_2$), 2.06 (s, 3 H, COC*H*$_3$), 2.02 (dt, J = 15.2, 7.8 Hz, 2 H, 6^{cer}-H), 1.61 (m, 2 H, NHCOCH$_2$C*H*$_2$), 1.49–1.15 (m, 64 H, 32 C*H*$_2$), 0.89 (t, J = 6.8 Hz, 6 H, 2 C*H*$_3$) ppm. ^{13}C NMR (150 MHz, CD_3OD/$CDCl_3$, 1:1): δ = 174.65, 168.12, 134.07, 129.61, 105.25, 103.48, 103.10, 102.97, 79.58, 75.25, 75.11, 74.97, 74.77, 74.55, 74.10, 73.41, 73.10, 71.70, 71.13, 69.49, 68.85, 68.60, 68.08, 65.54, 61.26, 60.24, 59.85, 53.23, 36.23, 32.23, 31.79, 31.76, 31.24, 30.88, 30.39, 29.58, 29.53, 29.46, 29.43, 29.37, 29.24, 29.21, 29.18, 29.14, 25.89, 25.04, 22.48, 22.46, 13.50, 13.49 ppm. HRMS (ESI): calcd. for $C_{68}H_{125}O_{26}N_2S$ [M – H]$^-$ 1417.8236; found 1417.8199.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for key intermediates and final products.

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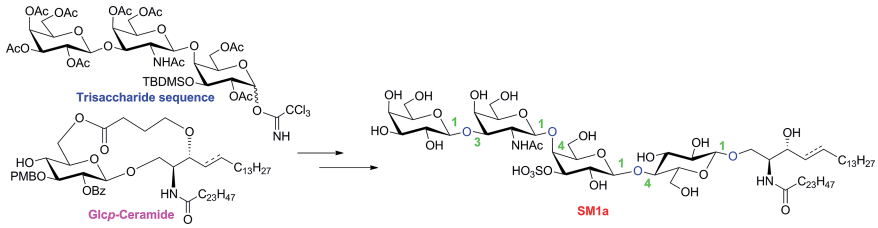

An endogenous sulfoglycolipid from mammalian kidney, SM1a, has been synthesized. A [3+2] convergent approach to the target molecule was used. Coupling of the trisaccharide containing a potential sulfation site with a cyclic glucosyl ceramide (GlcCer) unit gave the backbone structure of SM1a, which was converted into ganglioside SM1a after selective sulfonation and global deprotection.

Keywords: Total synthesis / Glycosylation / Carbohydrates / Oligosaccharides / Glycolipids / Gangliosides

