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A Diversity-Oriented Strategy for Chemical Synthesis of Glycosphingolipids: Synthesis of Glycosphingolipid LcGg4 and Its Analogues and Derivatives

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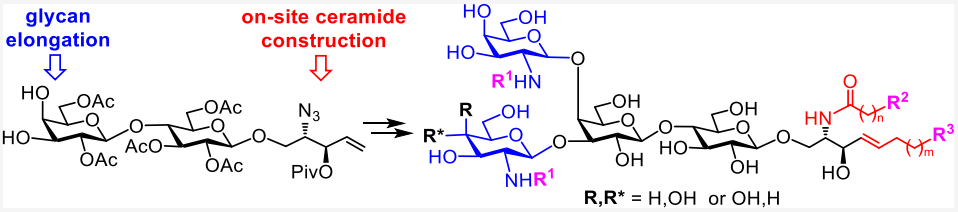

ABSTRACT: A diversity-oriented strategy was developed for the synthesis of glycosphingolipids (GSLs). This strategy was highlighted by using a simple lactoside containing the core structures of GSL glycan and lipid as the universal starting material to obtain different synthetic targets upon stepwise elongation of the glycan via chemical glycosylations and on-site remodeling of the lipid via chemoselective cross-metathesis and *N*-acylation. The strategy was verified with the synthesis of a lacto-ganglio GSL, LcGg4, which is a biomarker of undifferentiated malignant myeloid cells, and a series of its analogues or derivatives carrying different sugar chains and unique functionalities or molecular labels. This synthetic strategy should be widely applicable and, therefore, be utilized to rapidly access various GSLs and related derivatives by using different donors for glycosylations and different substrates for lipid remodeling following each glycosylation.

INTRODUCTION

Glycosphingolipids (GSLs) are major and essential constituents of the cell membrane and play a pivotal role in various biological and pathological processes.[1−7] For example, GSLs are involved in the modulation of signal transduction, cell recognition, proliferation and differentiation,[8] cell−cell interaction,[9,10] and other cellular functions,[11] as well as in the pathogenesis of many diseases such as cancer,[12−14] diabetes,[15] Alzheimer's disease,[16,17] Gaucher and related disorders,[18] bacterial and viral infections,[19−21] etc. Structurally, GSLs are composed of a hydrophilic carbohydrate headgroup and a hydrophobic sphingolipid, known as ceramide, which are stitched together through a β-glycosidic bond (Figure 1). GSLs are attached to cells via insertion of their lipid tails into the cell membrane while exposing their glycans onto the cell surface. Both the glycans and the lipids of GSLs can serve as recognition motifs to interact with other molecules and implement important functions. As a result, GSLs are structurally diverse in both the glycan and the lipid.

To study GSLs and gain in-depth understanding of their functions, it is necessary to have access to these molecules in homogeneous and structurally defined forms. However, the amphiphilic property and the relatively low abundance of individual GSLs in nature make their isolation and purification from biological tissues a daunting task. Consequently, their total synthesis has become the most attractive and probably the only practical means to access not only pure natural GSLs but also their functionalized derivatives. In the past several decades, a number of GSLs have been successfully synthesized by various strategies,[22−25] but overall, GSL synthesis remains a significant challenge.[26] For their chemical synthesis, in addition to conventional problems associated with oligosaccharide assembly, the ceramide moiety of GSL has brought about a series of other issues. For instance, the hydrogen bonding between the amido and the primary hydroxyl groups in ceramide and the high steric hindrance caused by its sheer size have substantially reduced the nucleophilicity of ceramide (Figure 1A), rendering its direct coupling with glycans exceptionally difficult, although this is still the most common strategy used for GSL synthesis.[22,23] On the other hand, if the ceramide moiety is introduced at the very beginning of the synthesis, although the efficiency to install ceramide can be improved, subsequent glycosylation reactions for glycan elongation can be affected. To address this problem, partial ceramide structures, such as azido sphingosine or its short

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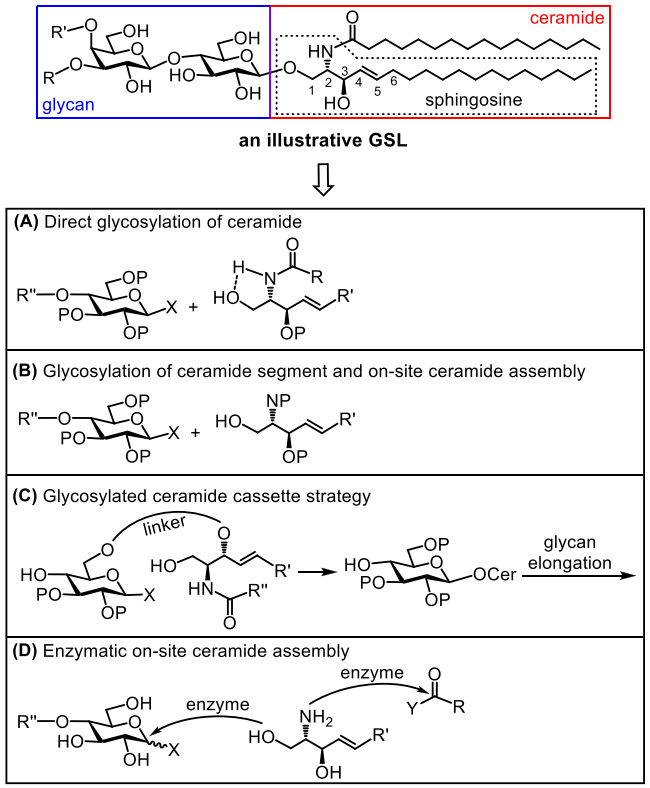
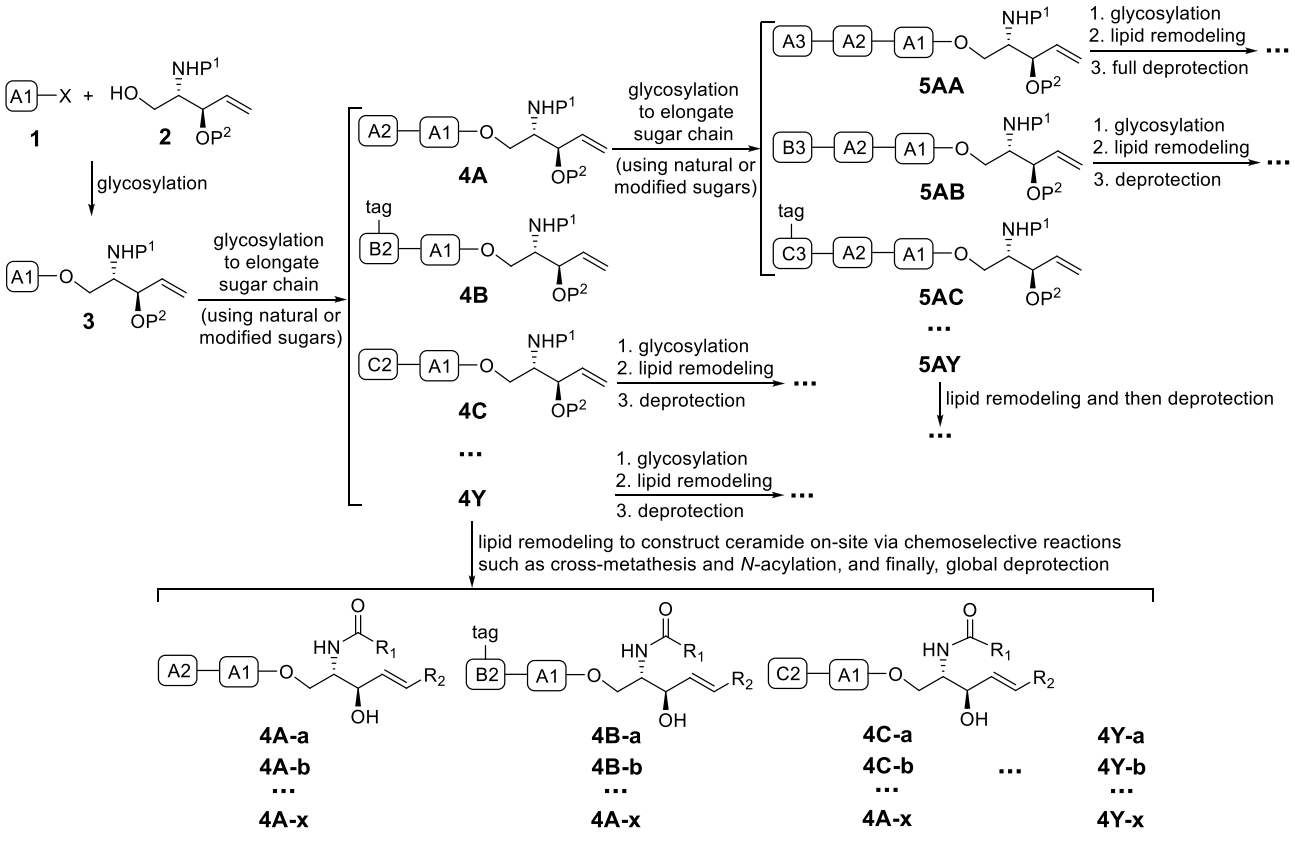


Figure 1. Representative structure of GSL and strategies developed for GSL synthesis.

fragments (Figure 1B), were employed to couple with glycans and then converted into ceramide on-site, upon lipid remodeling via, e.g., selective *N*-acylation, olefin metathesis,[27] or Wittig reaction.[24] Kiso and co-workers[28,29] also developed a glyco-ceramide cassette strategy (Figure 1C), in which ceramide was linked to a simple glycan first, which enabled intramolecular glycosylation, and the resultant glycoside was subsequently subjected to glycan elongation. Although the strategy could improve the efficiency and stereoselectivity of ceramide glycosylation, a major issue was that subsequent glycosylations suffered from a significant decrease in reaction yields. For enzymatic GSL synthesis, Chen[30−33] and others[34−41] have demonstrated that elongating glycans through glycosyltransferase-catalyzed glycosylations was efficient, while a major problem was related to the ceramide moiety as well. Its presence can have an impact on substrate solubility in aqueous solution, whereas late-stage installation and/or on-site construction of the ceramide moiety using complex free glycans can be challenging. To address this problem, the Withers group[42−45] developed an elegant enzymatic methodology for on-site ceramide assembly using engineered endoglycoceramidase and ceramide *N*-deacylase to catalyze sphingosine attachment to glycans and then acyl group attachment to the sphingosine amino group, respectively (Figure 1D). Unfortunately, due to some limitations of the enzymes and other issues, the methodology has not been widely adopted by other groups to prepare GSLs yet.

Despite the great advancements in GSL total synthesis[22−25] and in carbohydrate chemistry at large, currently, access to homogeneous GSLs and related derivatives remains difficult. In addition to problems associated with each individual synthetic

Scheme 1. A Diversity-Oriented Strategy for Chemical Synthesis of Natural GSLs and GSL Derivatives



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strategy as mentioned above, a common and important issue about the reported strategies is that they are target-oriented; i.e., they are designed for synthesizing a specific GSL at a time. Therefore, although the strategies may give satisfactory results for certain GSLs, it is rather difficult to adopt them for the synthesis of a variety of GSLs and GSL derivatives at once. Hence, each synthetic target needs to be addressed as an independent challenge. Given the vast structural diversity of natural GSLs and their derivatives in demand, a general and facile method for the synthesis of these important molecules is highly desirable.

RESULTS AND DISCUSSION

Our work aimed at establishing a robust, versatile, and scalable method to prepare GSLs and GSL derivatives. To this end, we have envisioned a novel diversity-oriented synthetic strategy, as outlined in Scheme 1, employing a simple glycoside **3** as the common starting material, which can be readily and efficiently prepared by glycosylation of a small headgroup of sphingosine **2** using a mono- or disaccharide core of GSL. Thereafter, the sugar and lipid moieties in **3** can be modified independently or in parallel to accomplish a diversity of GSLs and their functionalized derivatives rapidly. For example, glycosylation of **3** using either natural or unnatural sugar donors will provide **4A**, **4B**, and so on to have the glycan elongated. Then, the lipid moiety in each of these products will be remodeled to construct the ceramide moiety on-site via chemoselective reactions including cross-metathesis and *N*-acylation employing straight and/or functionalized olefins and *N*-acylating reagents, respectively, to provide different species of natural GSLs and their derivatives **4A-a** to **4A-x**, **4B-a** to **4B-x**, and so on. As the reactions involved in lipid remodeling are chemoselective and their conditions are very mild, labile molecular probes including fluorescent, radioactive, and chemical labels can be incorporated at this stage to obtain functionalized GSL derivatives that are useful for biological studies. On the other hand, the glycan in each of the products **4A**, **4B**, ..., and **4Y** can be further elongated through glycosylation to yield more complex glycosides, such as **5AA**−**5AY**, **5BA**−**5BY**, and so on. They can be subjected to lipid remodeling by the same method as mentioned to provide other GSLs and GSL derivatives.

To verify the above strategy, we applied it to the chemical synthesis of a unique lacto-ganglio series GSL, LcGg4 (**6**, Figure 2), having a GlcNAc and a GalNAc residue β-linked to the 3- and 4-*O*-positions of the Gal residue within the core lactose structure of GSLs, respectively.[46] LcGg4 was discovered in undifferentiated leukemia cells, but its expression declined with differentiation and became virtually absent in differentiated $M1^+$ cell.[47] Thus, it has been identified as a biomarker of undifferentiated, malignant myeloid cells useful for the development of novel diagnostics and therapeutics for cancer. LcGg4 is a minor GSL in nature; hence, scientists had to rely on chemical synthesis to obtain sufficient quantities of homogeneous LcGg4 for biological studies.[48] However, LcGg4 represents a synthetic challenge, and to the best of our knowledge, currently, there has been only one reported total synthesis of LcGg4 by Ito et al.[48] On the other hand, there are many reports about the synthesis of other related, more complex lacto-ganglio GSLs, such as gangliosides X1 and X2.[49,50] To further demonstrate the application scopes of the new synthetic strategy, we have also applied it to the preparation of an artificial analogue of LcGg4, namely, **6a**

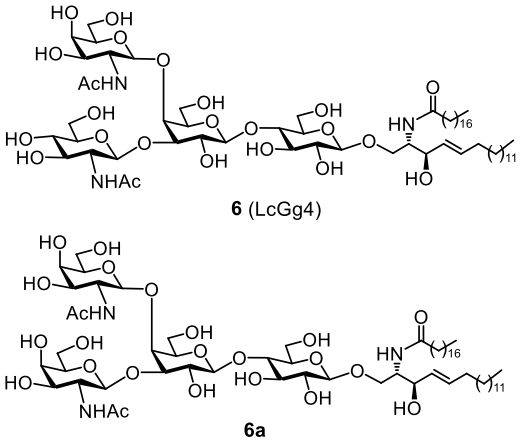
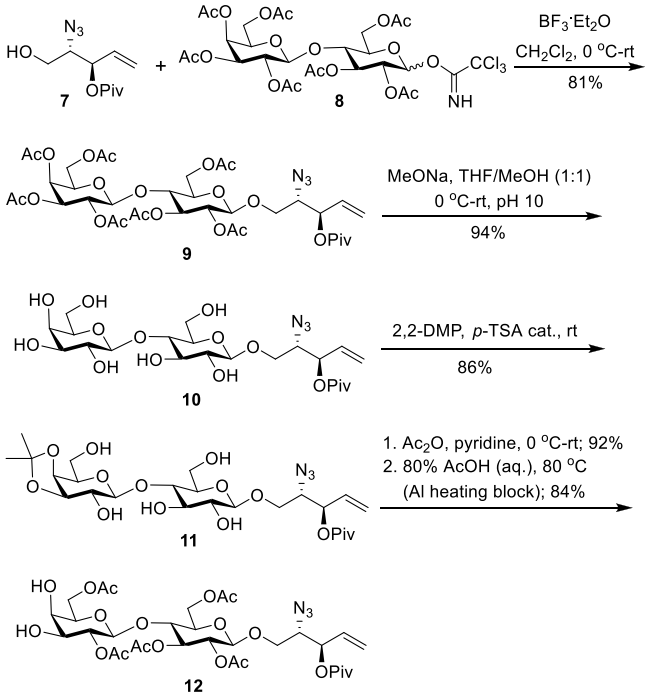


Figure 2. Structures of LcGg4 **6** and its analogue **6a**.

(Figure 2), which had two GalNAc residues β-linked to the 3- and 4-*O*-positions of the Gal residue of the lactose moiety, as well as a series of its derivatives containing different lipids and unique molecular labels.

Our synthesis commenced with a large-scale preparation of the key building block lactoside **12** (Scheme 2), which has the

Scheme 2. Synthesis of the Key Building Block 12



functional headgroup of sphingosine β-linked to the downstream terminal (reducing end) anomeric position of lactose. Compound **12** can serve as the starting point for many GSLs, as most GSLs share this core structure. Multigram scale glycosylation of the headgroup of sphingosine **7**[27] with peracetylated lactosyl trichloroacetimidate **8**[51] using BF_3·Et_2O as the promoter was straightforward and stereoselective to afford **9** in an 81% yield. The newly generated β-glycosidic bond in **9** was confirmed by the large coupling constant (J = 8.3 Hz) of its anomeric ^{1}H signal (δ 4.47 ppm) in the ^{1}H NMR spectrum. Selective deacetylation of the glycosylation product with NaOMe in methanol and THF (pH 10) provided

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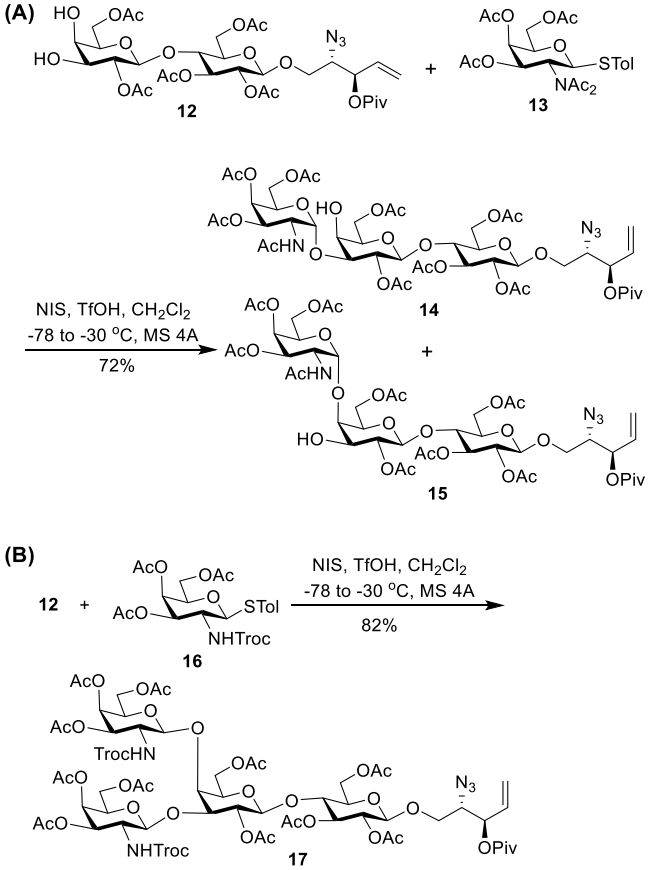
10 in a 94% yield. Finally, 10 was converted into 11 in an excellent overall yield in three established steps including regioselective protection of the 3′,4′-*O*-positions with isopropylidene, acetylation of the remaining hydroxyl groups, and then removal of the 3′,4′-*O*-isopropylidene group with aqueous acetic acid. The structure of 12 was verified by NMR and MS data.

Having the key building block 12 in hand, we proceeded to modify its glycan first (Scheme 3). We tried to prepare the

Scheme 3. Synthesis of Branched Tetrasaccharide 17



LcGg4 analogue **6a** first, as it had two identical residues linked to the lactose 3- and 4-*O*-positions and was thus believed to be easier to synthesize. Initially, we attempted to introduce both *β*-GalNAc residues to **12** at once, using *N*,*N*-diacetylgalactosamine thioglycoside[52] **13** as the glycosyl donor and *N*-iodosuccinimide (NIS) and triflic acid (TfOH) as the promoters (Scheme 3A). We chose **13** because the first acetyl group of its *N*,*N*-diacetylamino group was supposed to be readily and selectively removed under mild conditions to afford the desired -NHAc group in one step, which might simplify global deprotection later. However, this reaction afforded only monoglycosylated products **14** and **15** (2:1), even after prolonged reaction time using an excess of **13**, with partial *N*-deacetylation. The stereo- and regiochemistry of **14** and **15** were verified by their ^{1}H NMR data and by their ^{1}H−^{13}C HMBC correlation NMR data, as correlations were observed between C-1 of GalNAc and H-3 of Gal (δ 6.20 ppm) for **14** and between C-1 of GalNAc and H-4 of Gal (δ 6.24 ppm) for **15**. More interestingly, in both **14** and **15**, the GalNAc residue had an α-configuration ($J_{1'',2''}$ = 3.7 and 3.6 Hz, respectively), although the −NAc_2 group is deemed to be a participating group to usually favor 1,2-*trans* glycosylation. Clearly, **13** behaved strangely as a glycosyl donor, which is worth further investigation.

To alleviate the above problem, we replaced **13** with *N*-(2,2,2-trichloroethoxy)carbonyl (Troc)-protected thioglycoside **16**[53] for the glycosylation of **12** (Scheme 3B). Under similar conditions, i.e., using NIS and TfOH as the promotors at −78 to −30 °C, **12** was smoothly glycosylated with **16** to provide **17** in excellent stereoselectivity and yield (82%). The structure of **17** was verified with NMR and MS data, and the *β*-stereochemistry of its newly formed glycosidic bonds was confirmed by the relatively large coupling constants ($J_{1'',2''}$ = 7.9 and 8.8 Hz) between the H-1 (δ 4.51 and 5.21 ppm) and H-2 signals of its two GalNTroc residues linked to the Gal 3-*O*- and 4-*O*-positions, respectively. The exclusive *β*-selectivity of this glycosylation reaction was most likely directed by the neighboring group participation effect of the Troc group.

Subsequently, we assessed the reactions and conditions needed for remodeling the lipid in **17** and for on-site ceramide construction. In this regard, there are two potential strategies. One strategy is to attach the side chain *N*-acyl group first, followed by elongation of the sphingosine headgroup. The other strategy is to construct sphingosine first and introduce the *N*-acyl group thereafter. Each of the two strategies can have its own advantages. For example, the former strategy can help reduce self-dimerization of the involved glycolipids during cross-metathesis because of increased steric hindrance around the olefin group; the latter strategy is more favorable for lipid functionalization involving various sensitive labels because *N*-acylation will be the last synthetic step before global deprotection and its reaction condition is mild. To examine the first strategy, as outlined in Scheme 4, the azido group in **17** was selectively reduced with triphenylphosphine to give the corresponding primary amine, which was then coupled with stearic acid under the influence of 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide (EDC) and 4-dimethylaminopyridine (DMAP) to afford **18** in an excellent overall yield (86%).[54] The construction of the sphingosine moiety was achieved by cross-metathesis.[55,56] The reaction of **18** and 1-pentadecene **19** in the presence of the second-generation Hoveyda−Grubbs catalyst (**20**, 3 mol %) in refluxing dichloromethane was slow (5 days to finish) but clean to afford the desired *Z*-olefin **21** selectively in an excellent yield (88%), along with dimerization of **19**, whereas dimerization of **18** was not observed. The *Z*-configuration of the C═C double bond in **21** was confirmed by the coupling constant (J = 15 Hz) of its vinyl protons. The *N*-Troc groups in **21** were then replaced with acetyl groups upon their removal with Zn/AcOH and acetylation of the exposed free amino groups with Ac_2O in pyridine to provide **22**.[57] Finally, all of the *O*-acyl groups in **22** were removed with NaOMe in methanol (4.5 M) to produce the synthetic target, LcGg4 analogue **6a**, in a good overall yield (54% for the last three steps).

To further test the above reaction conditions and demonstrate that the synthetic strategy can be employed to rapidly access different lipid forms of any GSL, we applied it subsequently to the preparation of different lipid form of **6a**, namely, **6a*** (Scheme 4). Cross-metathesis of **18** and **19***, instead of **19**, gave **21***, which upon *N*-acyl group switching and global deprotection as described above afforded **6a*** containing a lipid moiety different from that of **6a**. Evidently, this procedure can be utilized to readily and rapidly access GSLs carrying other sphingosines; in the meantime, different

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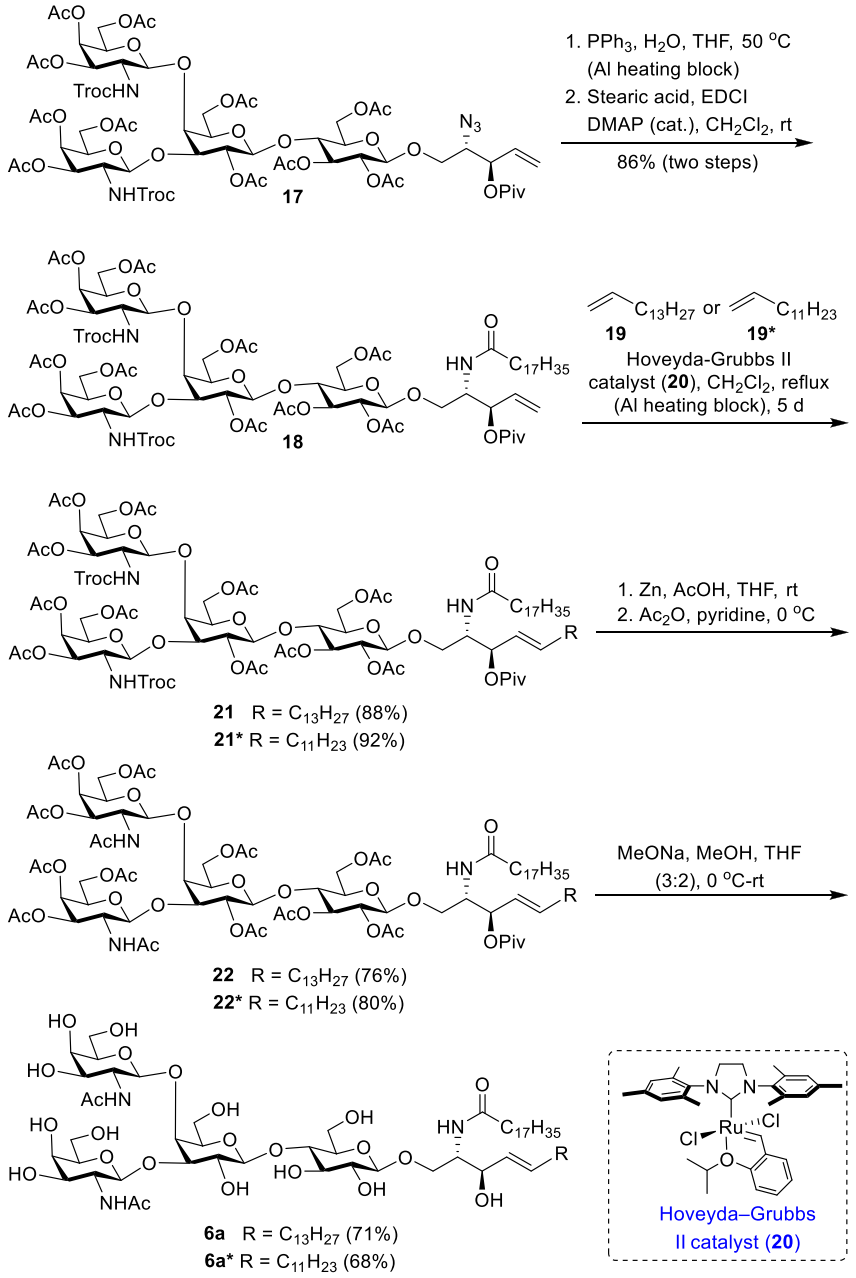
Scheme 4. Synthesis of LcGg4 Analogue 6a and Its Different Lipid Form 6a*



fatty acids can be used to couple with the azide reduction product of **17** to prepare GSLs containing other *N*-acyl groups as well.

After the reactions and conditions for lipid remodeling were optimized and verified with **6a** and **6a***, we moved on to the synthesis of LcGg4 **6** by a similar procedure. The glycosylation of diol **12** with *N*-Troc-protected glucosamine donor **23** (1.8 equiv) under the promotion of NIS (1.8 equiv) and TfOH (0.1 equiv) was smooth and fast. To our surprise, however, this reaction afforded a mixture of mono- and diglycosylated products **24** (12%) and **25** (72%) (Supporting Information, Table S1). The β-configuration of the GlcNTroc residue in **24** was confirmed by the relatively large coupling constant of its H-1 signal (δ 5.20 ppm, $J_{1,2}$ = 7.2 Hz), and its regiochemistry was confirmed by the correlation between GlcNTroc C-1 and Gal H-3 (δ 5.34 ppm) signals in its $^{1}H-^{13}C$ HMBC NMR spectrum. For **25**, the β-configuration of its two GlcNTroc residues was also confirmed by the relatively large coupling constants ($J_{1,2}$ = 8.1 and 8.4 Hz) of their H-1 signals. To improve the yield of monoglycosylation, different reaction conditions including various donor/acceptor ratios and concentrations were tried. We found that reduced substrate concentration and donor equivalent were helpful. Finally, **24** was obtained in a 41% yield when only 1.1 equiv of **23** was used, but under this condition, diglycosylated product **25** was still formed in substantial quantity (32%) (Scheme 5). The results indicated clearly that, after 3′-*O*-glycosylation, the 4′-*O*-position in **24** was still very reactive.

Glycosylation of **24** with **16** under the above conditions went smoothly to provide **26** in a 75% yield. Its β-linked GalNTroc residue was verified with NMR data ($J_{1,2}$ = 8.7 Hz). Subsequent lipid remodeling of **26** followed the same procedure as that described for **6a** and **6a*** (Scheme 4), including reduction of the azide with triphenylphosphine to

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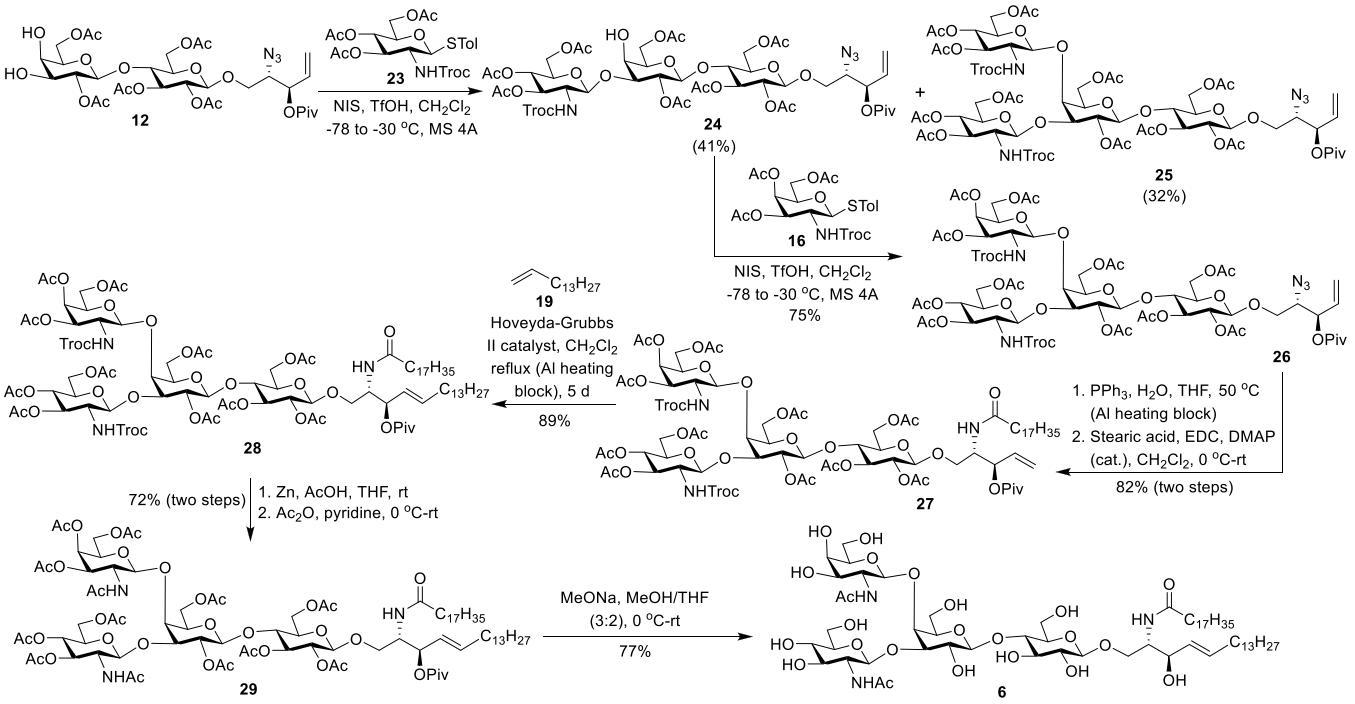
Scheme 5. Total Synthesis of LcGg4 6



form the corresponding amine and acylation of the resultant amine with stearic acid, EDC, and DMAP to afford **27** (82%), cross-metathesis of **27** and 1-pentadecene to give **28** (89%), substitution of the *N*-Troc groups in **28** with *N*-acetyl groups upon reduction with Zn/AcOH and *N*-acetylation with Ac_2O, and then global de-*O*-acylation with NaOMe, to finally produce **6** (Scheme 5). The *Z*-configuration of the C=C double bond in **28** was confirmed by the coupling constant (J = 14.3 Hz) of its vinyl protons.

We also assessed the other strategy for on-site ceramide construction starting from **17**, i.e., to assemble sphingosine first and introduce the *N*-acyl group next, as depicted in Scheme 6. Attempts for direct cross-metathesis of **17** and olefin were unsuccessful, probably due to the influence of the azido group. Then, the azido group in **17** was reduced, and the resultant amine was protected with a *tert*-butyloxycarbonyl (Boc) group to obtain **30**. Cross-metathesis of **30** and **19** under the above conditions afforded **31** in an excellent yield (82%). At this stage, we chose to replace the *N*-Troc groups with *N*-acetyl groups by the aforementioned method to convert **31** into **32** for subsequent lipid remodeling.[57] For subsequent *N*-acylation reaction, we chose fatty acid **33** that carried a fluorescent label, and our argument is that, if it works, other simple fatty acids should work too. Accordingly, the *N*-Boc group in **32** was selectively removed with trifluoroacetic acid (TFA), and the resultant free amine was acylated with **33** using EDC and DMAP as the coupling reagents to provide **34** in an 83% yield. Finally, all of the *O*-acyl groups in **34** were removed with NaOMe to provide LcGg4 analogue **35** having a fluorescent label attached to the lipid moiety.

As discussed previously, another important and useful property of this new synthetic strategy is the convenience to achieve GSL diversity with the glycan. There are also two potential strategies for this. The first one is to introduce diversity in the glycan assembly stage by employing various natural and modified glycosyl donors for glycosylations, which has already been demonstrated by the synthesis of **6** and **6a** containing different glycans. Clearly, various series of natural GSLs and their derivatives can be easily achieved in this way. Another strategy is to introduce an orthogonal protecting group in the glycan during its assembly and then selectively remove this group at a later step for glycan modification. To demonstrate this, we selectively removed the *N*-Troc groups in **21** with Zn/AcOH and acylated the resultant amine with 2-azidoacetic acid in the presence of EDC and DMAP to obtain **36** in a good yield (79%). Finally, global deprotection to remove all of the *O*-acyl groups in **36** with NaOMe produced another LcGg4 analogue **37**, which contained two azido sugar residues (Scheme 7). The azido groups can be used as molecular handles to introduce labels via click reaction to facilitate various biological studies and applications.

CONCLUSION

In this study, we proposed a new strategy for diversity-oriented synthesis of GSLs and had verified the strategy with the synthesis of a lacto-ganglio GSL LcGg4 **6** and its analogue **6a** that contained a different glycan, as well as a series of derivatives carrying a fluorophore or azido groups in the lipid or sugar moieties. An important feature of the new strategy is to start the synthesis of various target molecules from the same simple building block **12** following the same protocols. Compound **12** consisting of the core of GSL glycans and the core of ceramides was readily and efficiently prepared from **7** and **8** on large scales. Another important feature of this strategy is that it allows stepwise elongation of the glycan in **12** using different glycosyl donors and remodeling of the lipid for on-site ceramide construction with different lipids after each glycosylation step, which could lead to a huge number of natural GSLs and functionalized GSL derivatives rapidly. The application scope of this synthetic strategy to various GSLs, as well as biological studies using the synthesized GSLs and their derivatives, is currently pursued in our laboratory.

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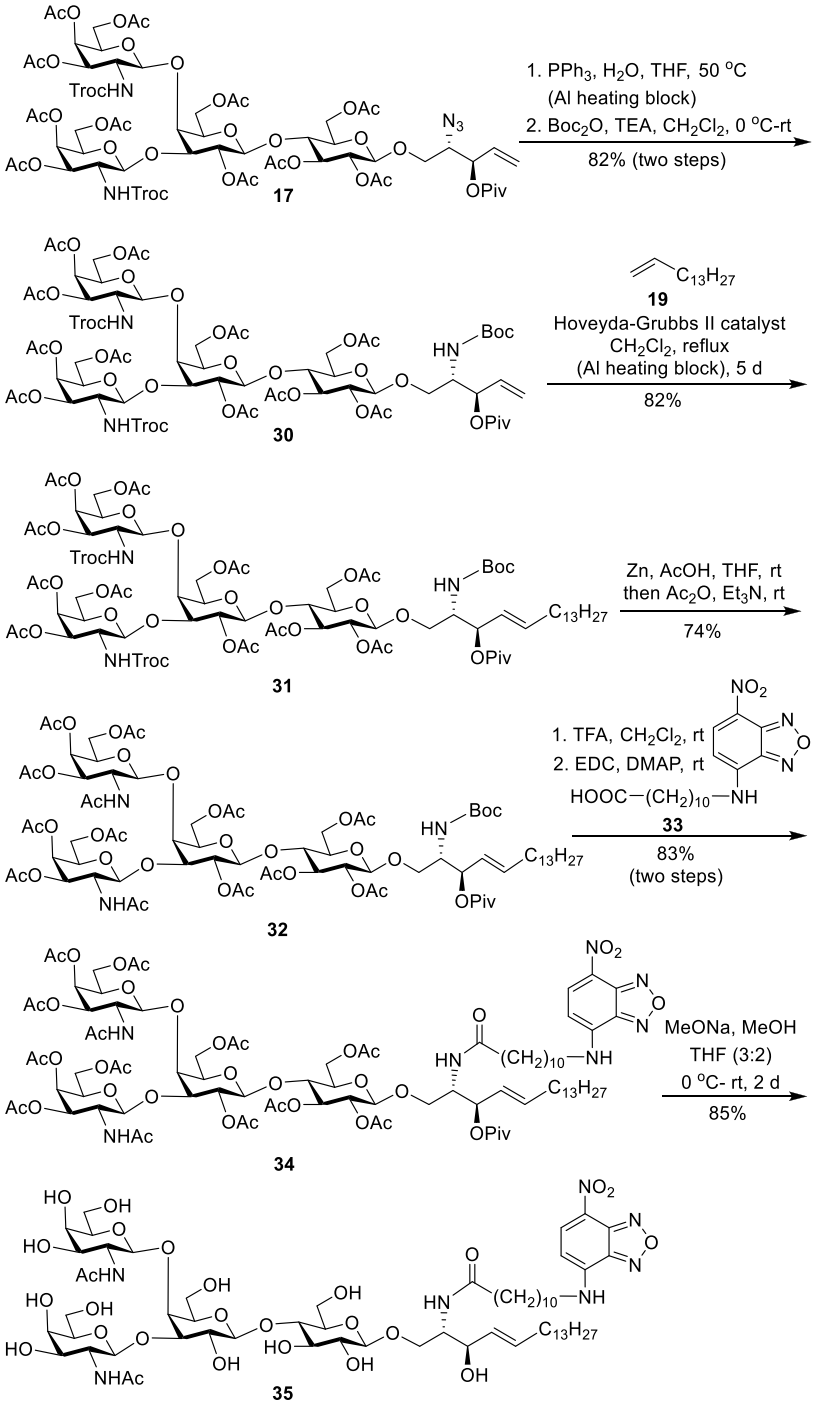
Scheme 6. Synthesis of Fluorophore-Tagged LcGg4 Analogue 35



EXPERIMENTAL SECTION

General Procedures. Chemicals and materials were purchased from commercial sources and were used as received without further purification unless otherwise noted. Molecular sieves 4 Å (MS 4 Å) were flame-dried under high vacuum and used immediately after being cooled to rt under a N_2 atmosphere. Analytical TLC was carried out on silica gel 60 Å F_{254} plates with detection by a UV detector and/or by charring with 10% (v/v) H_2SO_4 in ethanol. Flash column chromatography was performed on silica gel 60 (230−400 mesh). NMR spectra were acquired on a 600 MHz NMR spectrometer with chemical shifts reported in ppm (δ) referenced to $CDCl_3$ (^{1}H NMR, δ 7.26 ppm; ^{13}C NMR, δ 77.16 ppm) or CD_3OD (^{1}H NMR, δ 3.31 ppm; ^{13}C NMR, δ 49.0 ppm). Peak and coupling constant assignments are made based on ^{1}H NMR, ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC experiments. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. Aluminum heating blocks were used as the heating source for the reactions.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**9**).* After a mixture of (3*R*,4*S*)-4-azido-5-hydroxypent-1-en-3-yl pivalate **7** (1.5 g, 6.6 mmol), 2,3,6,2′,3′,4′,6′-septa-*O*-acteyl-β-lactosyl trichloroimidate **8** (7.2 g, 9.24 mmol), $BF_3{\cdot}Et_2O$ (0.174 mL, 1.32 mmol), and flame-dried MS 4 Å (12 g) in dry CH_2Cl_2 (50 mL) was stirred at 0 °C for 60 min, it was allowed to warm to rt and stirred overnight. TLC showed complete consumption of the starting material, and then, water was added in the reaction mixture. The

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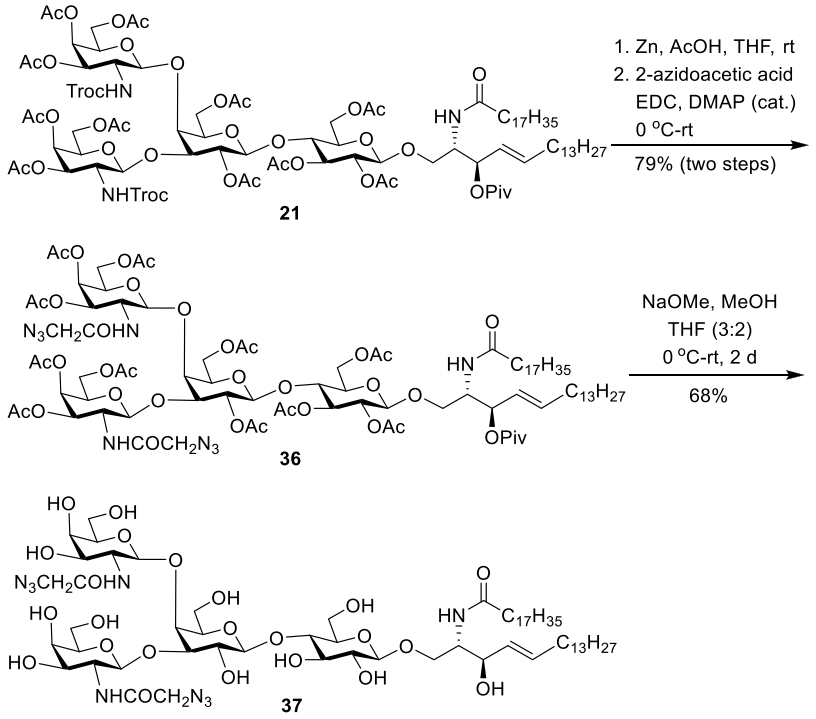
Scheme 7. Synthesis of Azide-Labeled LcGg4 Analogue 37



organic layer was separated and washed with saturated aqueous $NaHCO_3$ solution, water, and brine and dried over Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel to afford **9** (4.6 g, 81%) as a white solid. TLC: R_f = 0.6 (hexane/EtOAc 7:3). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.78 (ddd, J = 17.5, 10.6, 6.7 Hz, 1H), 5.39−5.29 (m, 4H), 5.17 (t, J = 9.2 Hz, 1H), 5.09 (dd, J = 10.4, 7.9 Hz, 1H), 4.94 (dd, J = 10.4, 3.5 Hz, 1H), 4.89 (dd, J = 9.4, 7.8 Hz, 1H), 4.49 (d, J = 8.4 Hz, 1H anomeric), 4.48 (m, 1H), 4.47 (d, J = 8.3 Hz, 1H anomeric), 4.14−4.04 (m, 3H), 3.88−3.80 (m, 3H), 3.80−3.76 (m, 1H), 3.60 (ddd, J = 9.9, 5.0, 2.1 Hz, 1H), 3.51 (dd, J = 10.3, 5.8 Hz, 1H), 2.13 (s, 3H), 2.10 (s, 3H), 2.05 (s, 2 × 3H), 2.03 (s, 2 × 3H), 1.95 (s, 3H), 1.21 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.9, 170.5, 170.4, 170.2, 170.2, 169.9, 169.7, 169.2, 131.6, 120.4, 101.2, 100.4, 76.2, 73.7, 72.9, 72.8, 71.5, 71.1, 70.8, 69.2, 68.0, 66.7, 63.1, 61.9, 60.9, 39.0, 27.1, 20.9, 20.8, 20.7, 20.7, 20.7, 20.6. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{36}H_{51}N_3O_{20}Na$ 868.2958; Found 868.2984.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl β-D-Galactopyranosyl-(1→4)-β-D-glucopyranoside (**10**).* To a solution of **9** (4.6 g, 5.44 mmol) dissolved in THF/MeOH (1:1, v/v, 50 mL) was added a solution of MeONa in MeOH (0.4 M) at 0 °C until the pH reached 10. The solution was stirred at rt (~23 °C) for 6 h. When TLC showed the completion of reaction indicated by one single spot, the reaction was neutralized to pH 6−7 with Amberlyst (H$^+$) resin. The resin was removed by filtration, and the filtrate was concentrated under vacuo to give the crude product, which was purified by flash column chromatography (MeOH/CH_2Cl_2) to give **10** (2.8 g, 94%) as a white solid. TLC: R_f = 0.4 (CH_2Cl_2/MeOH 4:1). ^{1}H NMR (600 MHz, CD_3OD): δ 5.95−5.80 (m, 1H), 5.48 (m, 1H), 5.38 (dt, J = 17.2, 1.3 Hz, 1H), 5.34 (dt, J = 10.6, 1.3 Hz, 1H), 4.36 (d, J = 7.7 Hz, 1H anomeric), 4.32 (d, J = 7.8 Hz, 1H anomeric), 4.01 (ddd, J = 7.5, 5.5, 3.9 Hz, 1H), 3.93−3.88 (m, 2H), 3.87−3.83 (m, 1H), 3.81 (dd, J = 3.3, 1.0 Hz, 1H), 3.78 (dd, J = 11.4, 7.5 Hz, 1H), 3.70 (dd, J = 11.4, 4.6 Hz, 1H), 3.64 (dd, J = 10.6, 5.5 Hz, 1H), 3.61−3.55 (m, 2H), 3.55−3.50 (m, 2H), 3.48 (dd, J = 9.7, 3.3 Hz, 1H), 3.43−3.41 (m, 1H), 3.27 (dd, J = 9.1, 7.8 Hz, 1H), 1.24 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD): δ 178.5, 133.0, 120.2, 105.0, 104.4, 80.5, 75.5, 74.8, 74.6, 72.5, 70.3, 69.3, 64.9, 62.4, 61.9, 49.4, 49.2, 49.1, 49.0, 48.8, 48.7, 48.5, 39.9 27.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{22}H_{38}N_3O_{13}$ 552.2399; Found 552.2374.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 3,4-O-Isopropylidene-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside (**11**).* After a suspension of **10** (2.8 g, 5.08 mmol) and anhydrous *p*-toluene sulfonic acid (0.241 g, 1.27 mmol) in 2,2-dimethoxypropane (30 mL) was stirred at rt for 20 h, it was diluted with methanol. Water (5 mL) was added, and the solution was neutralized with triethylamine (5 mL) and then concentrated in a vacuum. The residue was purified by column chromatography to give **11** as a white solid (2.6 g, 86%). TLC: R_f = 0.7 (CH_2Cl_2/MeOH 4:1). ^{1}H NMR (600 MHz, CD_3OD): δ 5.90 (ddd, J = 17.2, 10.6, 6.6 Hz, 1H), 5.50 (dd, J = 6.2, 4.4 Hz, 1H), 5.42−5.37 (m, 1H), 5.36−5.34 (m, 1H), 4.38 (d, J = 7.7 Hz, 1H anomeric), 4.34 (d, J = 7.8 Hz, 1H anomeric), 4.21 (dd, J = 5.6, 2.0 Hz, 1H), 4.07 (dd, J = 7.4, 5.5 Hz, 1H), 4.05−4.00 (m, 1H), 3.97−3.94 (m, 1H), 3.93−3.87 (m, 2H), 3.87−3.73 (m, 3H), 3.66 (dd, J = 10.7, 5.4 Hz, 1H), 3.60−3.52 (m, 2H), 3.50−3.41 (m, 2H), 3.29 (dd, J = 9.2, 7.7 Hz, 1H), 1.49 (s, 3H), 1.34 (s, 3H), 1.25 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD): δ 178.5, 133.0, 120.2, 111.1, 104.3, 104.1, 80.8, 80.8, 76.4, 76.2, 75.5, 75.3, 75.0, 74.7, 74.4, 69.3, 64.9, 62.4, 61.8, 39.9, 28.4, 27.5, 26.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{25}H_{41}N_3O_{13}Na$ 614.2531; Found 614.2532.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 2,6-Di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**12**).* To a solution of **11** (2.6 g, 4.39 mmol) in pyridine (30 mL) was added acetic anhydride (5.6 mL, 65.9 mmol) dropwise over 10 min at 0 °C, and the solution was stirred overnight and then diluted with EtOAc (50 mL). The mixture was washed with 45 mL of 2 N HCl and 50 mL of sat. $NaHCO_3$ solution and brine and then dried (Na_2SO_4), filtered, and concentrated in vacuo to yield (2*S*,3*R*)-2-azido-3-(pivaloyloxy)pent-4-en-1-yl 2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**11a**, 3.25 g, 92%) as a pale yellow foamy solid. TLC: R_f = 0.8 (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.78 (ddd, J = 17.3, 10.5, 6.8 Hz, 1H), 5.44−5.24 (m, 3H), 5.15 (t, J = 9.3 Hz, 1H), 4.90 (dd, J = 9.5, 7.8 Hz, 1H), 4.86−4.81 (m, 1H), 4.47 (d, J = 7.9 Hz, 1H anomeric), 4.43 (dd, J = 12.0, 2.1 Hz, 1H), 4.36 (d, J = 7.4 Hz, 1H anomeric), 4.32−4.20 (m, 2H), 4.15−4.08 (m, 3H), 3.91 (ddd, J = 6.9, 4.8, 1.6 Hz, 1H), 3.83 (dd, J = 10.3, 6.6 Hz, 1H), 3.80−3.72 (m, 2H), 3.60 (ddd, J = 9.8, 5.2, 2.1 Hz, 1H), 3.51 (dd, J = 10.4, 5.8 Hz,

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1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.51 (s, 3H), 1.29 (s, 3H), 1.20 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.9, 170.8, 170.4, 170.0, 169.6, 169.2, 131.5, 120.3, 110.96, 100.6, 100.4, 76.9, 76.0, 73.7, 73.1, 73.0, 72.8, 72.5, 71.5, 71.0, 67.9, 63.2, 63.1, 62.1, 39.0, 27.4, 27.1, 26.2, 20.9, 20.9, 20.9, 20.8, 20.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{51}N_3O_{18}Na$ 824.3060; Found 824.3059. After **11a** (3.2 g, 3.99 mmol) was dissolved in 80% aqueous AcOH (25 mL), the solution was kept at 80 °C for 1 h when TLC indicated the complete disappearance of starting material. Acetic acid was removed in a vacuum, and the residue was coevaporated with toluene (3 × 20 mL) and then purified by column chromatography on a silica gel column to provide **12** (2.6 g, 84%). TLC: R_f = 0.45 (EtOAc/MeOH, 40:1). ^1H NMR (600 MHz, $CDCl_3$): δ 5.79 (ddd, J = 17.3, 10.5, 6.8 Hz, 1H), 5.41−5.30 (m, 3H), 5.16 (t, J = 9.3 Hz, 1H), 4.93 (dd, J = 9.6, 7.9 Hz, 1H), 4.88 (dd, J = 9.8, 7.8 Hz, 1H), 4.51−4.48 (m, 2H), 4.38−4.30 (m, 2H), 4.22 (dd, J = 11.4, 6.5 Hz, 1H), 4.14 (dd, J = 12.0, 5.3 Hz, 1H), 3.94−3.81 (m, 2H), 3.81−3.71 (m, 2H), 3.66−3.56 (m, 3H), 3.53 (dd, J = 10.4, 5.8 Hz, 1H), 3.36 (d, J = 7.4 Hz, 1H), 3.14 (d, J = 5.5 Hz, 1H), 2.15−2.08 (3s, 9H), 2.06 (s, 3H), 2.04 (s, 3H), 1.22 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.9, 171.5, 171.1, 170.5, 170.5, 169.6, 131.6, 120.4, 101.0, 100.5, 76.2, 73.7, 73.6, 73.0, 72.8, 72.7, 72.3, 71.3, 68.5, 68.0, 63.2, 62.4, 62.2, 39.0, 27.1, 21.0, 20.9, 20.9, 20.9, 20.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{47}N_3O_{18}Na$ 784.2746; Found 784.2750.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-galactopyranosyl-(1→3)-2,6-di-O-acetyl-β-O-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**14**) and (2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**15**).* After a mixture of **12** (40 mg, 0.52 mmol), **13** (78 mg, 0.157 mmol), and flame-dried MS 4 Å in dry CH_2Cl_2 (4 mL) was stirred at rt for 30 min, it was cooled to −78 °C and NIS (41 mg, 0.184 mmol) was added, which was followed by TfOH (0.5 μL, 0.005 mmol). The mixture was warmed to −40 to −30 °C and stirred at this temperature for 2 h, and the reaction was quenched with triethyl amine (1 mL). The mixture was diluted with CH_2Cl_2 and filtered through a Celite pad. The CH_2Cl_2 layer was washed with saturated $Na_2S_2O_3$ solution, saturated aqueous $NaHCO_3$ solution, water, and brine and then dried with Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatography to afford **14** (28 mg, 48%) and **15** (14 mg, 24%) as off-white solids. Compound **14**: TLC: R_f = 0.3 (EtOAc/toluene 3:2). ^1H NMR (600 MHz, $CDCl_3$): δ 6.20 (d, J = 3.6 Hz, 1H), 5.79 (ddd, J = 17.3, 10.5, 6.8 Hz, 1H), 5.47 (d, J = 9.2 Hz, 1H), 5.41 (d, J = 2.3 Hz, 1H), 5.38−5.31 (m, 3H), 5.21 (dd, J = 11.5, 3.2 Hz, 1H), 5.15 (t, J = 9.3 Hz, 1H), 4.92 (dd, J = 9.5, 8.0 Hz, 1H), 4.87 (dd, J = 9.6, 8.0 Hz, 1H), 4.72 (ddd, J = 11.7, 9.3, 3.7 Hz, 1H), 4.54−4.44 (m, 2H), 4.35−4.32 (m, 2H), 4.27−4.19 (m, 2H), 4.17−4.11 (m, 1H), 4.11−4.03 (m, 2H), 3.88−3.80 (m, 2H), 3.81−3.73 (m, 2H), 3.65−3.61 (m, 3H), 3.59 (dd, J = 9.7, 3.5 Hz, 1H), 3.52 (dd, J = 10.4, 5.8 Hz, 1H), 2.16 (s, 3H), 2.11 (brs, 3 × 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (brs, 2 × 3H), 1.94 (s, 3H), 1.21 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.9, 171.5, 171.3, 171.1, 170.5, 170.4, 170.3, 170.2, 169.6, 168.9, 131.6, 120.3, 100.9, 100.4, 91.4, 76.2, 73.7, 73.7, 73.0, 72.8, 72.7, 72.3, 71.3, 68.6, 68.4, 68.0, 68.0, 66.8, 63.2, 62.4, 62.2, 61.4, 47.1, 39.0, 27.1, 23.3, 21.0, 21.0, 20.9, 20.9, 20.8, 20.8, 20.8, 20.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{46}H_{66}N_4O_{26}Na$ 1113.3857; Found 1113.3874. Compound **15**: TLC: R_f = 0.5 (EtOAc/toluene, 3:2). ^1H NMR (600 MHz, $CDCl_3$): δ 6.24 (d, J = 3.6 Hz, 1H, anomeric), 5.79 (ddd, J = 17.3, 10.5, 6.8 Hz, 1H), 5.59 (d, J = 9.1 Hz, 1H), 5.45 (d, J = 2.2 Hz, 1H), 5.39−5.30 (m, 3H), 5.24 (dd, J = 11.6, 3.2 Hz, 1H), 5.15 (t, J = 9.3 Hz, 1H), 4.92 (dd, J = 9.5, 7.9 Hz, 1H), 4.86 (dd, J = 9.6, 8.0 Hz, 1H), 4.77 (ddd, J = 11.7, 9.2, 3.6 Hz, 1H), 4.58−4.45 (m, 2H), 4.35−4.32 (m, 3H), 4.22 (dd, J = 11.4, 6.5 Hz, 1H), 4.18−4.09 (m, 2H), 4.06 (dd, J = 11.4, 6.7 Hz, 1H), 3.90−3.71 (m, 5H), 3.62 (q, J = 6.1, 5.6 Hz, 2H), 3.59 (dd, J = 9.7, 3.3 Hz, 1H), 3.53 (dd, J = 10.4, 5.8 Hz, 1H), 2.17 (s, 3H), 2.10 (brs, 3 × 3H), 2.05 (s, 3H), 2.03 (brs, 3 × 3H), 1.96 (s, 3H), 1.21 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 176.9, 171.5, 171.3, 171.1, 170.5, 170.5, 170.4, 170.3, 170.3, 169.6, 167.1, 131.6, 120.3, 100.9, 100.4, 92.6, 76.2, 73.7, 73.7, 73.0, 72.8, 72.7, 72.3, 71.3, 69.2, 68.4, 68.0, 67.8, 66.8, 63.2, 62.4, 62.2, 61.4, 47.4, 39.0, 27.1, 23.2, 21.0, 20.9 (2C), 20.9, 20.8, 20.8, 20.8 (3C). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{46}H_{66}N_4O_{26}Na$ 1113.3863; Found 1113.3854.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**17**).* After a mixture of **12** (1.2 g, 1.58 mmol), **16** (3.7 g, 6.30 mmol), and flame-dried MS 4 Å in dry CH_2Cl_2 (12 mL) was stirred at rt for 30 min, it was cooled to −78 °C and NIS (1.95 g, 8.66 mmol) was added, which was followed by TfOH (28 μL, 0.315 mmol). The mixture was stirred at −40 to −30 °C for 2 h, and the reaction was quenched with triethyl amine (1 mL). The mixture was diluted with CH_2Cl_2 and filtered through a Celite pad. The CH_2Cl_2 layer was washed with saturated $Na_2S_2O_3$ solution, saturated $NaHCO_3$ solution, water, and brine and then dried with Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatography to afford **17** (2 g, 82%) as an off-white solid. TLC: R_f = 0.52 (toluene/EtOAc 3:2). ^1H NMR (600 MHz, $CDCl_3$): δ 6.12 (d, J = 10.0 Hz, 1H, —N*H*), 5.78 (ddd, J = 17.4, 10.5, 6.8 Hz, 1H, =C*H*—), 5.40 (d, J = 3.0 Hz, 1H), 5.38−5.30 (m, 4H), 5.26 (d, J = 12.6 Hz, 1H, —OCH_2CCl$_3$), 5.22 (d, J = 8.6 Hz, 1H, anomeric), 5.19−5.07 (m, 3H), 5.05−5.00 (m, 1H), 4.96−4.92 (m, 3H), 4.62 (d, J = 12.1 Hz, 1H, —OCH_2CCl$_3$), 4.55 (d, J = 12.6 Hz, 1H, —OCH_2CCl$_3$), 4.52 (d, J = 8.2 Hz, 1H, anomeric), 4.46 (d, J = 7.8 Hz, 1H, anomeric), 4.42 (d, J = 11.3 Hz, 1H, —OCH_2CCl$_3$), 4.32−4.17 (m, 4H), 4.15−4.02 (m, 6H), 3.92−3.88 (m, 2H), 3.85−3.75 (m, 3H), 3.73−3.69 (m, 1H), 3.68−3.65 (m, 1H), 3.63−3.58 (m, 1H), 3.58−3.56 (m, 1H), 3.51 (dd, J = 10.2, 5.7 Hz, 1H, —OCH_2—CHN$_3$—), 2.19 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.05 (s, 6H, 2 × CH$_3$), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.21 (s, 9H, —O*P*iv). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.8, 170.9, 170.8, 170.6, 170.5, 170.4, 170.3, 170.2, 170.1, 169.8, 169.5, 168.31, 155.3, 154.4, 131.4, 120.2, 102.9, 100.7, 100.6, 100.3, 96.5, 95.3, 79.7, 74.9, 74.2, 73.6, 73.0, 72.5, 71.9, 71.5, 71.2, 70.9, 70.8, 70.0, 68.3, 67.9, 66.5, 66.4, 63.2, 63.1, 62.0, 61.4, 61.0, 52.9, 52.0, 38.9, 27.0, 20.8, 20.8, 20.7, 20.7, 20.6, 20.6, 20.6, 20.5, 20.5, 20.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{62}H_{83}Cl_6N_5O_{36}Na$ 1708.2825; Found 1708.2851.

*(2S,3R)-2-Octadecanamido-3-(pivaloyloxy)pent-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**18**).* After PPh_3 (161.6 mg, 0.616 mmol) and water (55.5 μL, 3.08 mmol) were added to a stirred solution of **17** (520 mg, 0.308 mmol) in THF (6 mL), the mixture was heated with stirring at 50 °C using an aluminum heating block until TLC indicated the disappearance of **17**. The solvents were removed under a vacuum, and the residue was dissolved in dry CH_2Cl_2 (6 mL). Then, EDC (118 mg, 0.616 mmol), DMAP (0.7 mg, 0.006 mmol), and stearic acid (175.4 mg, 0.616 mmol) were added under argon, and the mixture was stirred at rt for 12 h. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography to afford **18** (515 mg, 86%) as a white powder. TLC: R_f = 0.8 (EtOAc). ^1H NMR (600 MHz, $CDCl_3$): δ 6.11 (d, J = 10.1 Hz, 1H, —N*H*), 5.78 (ddd, J = 17.0, 10.6, 6.1 Hz, 1H), 5.67 (d, J = 9.2 Hz, 1H, —N*H*), 5.41 (d, J = 3.3 Hz, 1H), 5.35 (d, J = 3.4 Hz, 1H), 5.33−5.27 (m, 3H), 5.25 (dt, J = 10.5, 1.2 Hz, 1H), 5.22 (d, J = 8.8 Hz, 1H, anomeric), 5.18−5.08 (m, 3H), 5.02 (dd, J = 11.3, 3.4 Hz, 1H), 4.96 (d, J = 12.3 Hz, 1H, —OCH_2CCl$_3$), 4.94−4.92 (m, 1H), 4.88 (dd, J = 9.9, 7.8 Hz, 1H, —OCH_2CCl$_3$), 4.62 (d, J = 12.1 Hz, 1H, —OCH_2CCl$_3$), 4.54 (d, J = 12.7 Hz, 1H, —OCH_2CCl$_3$), 4.50 (d, J = 8.2 Hz, 1H, anomeric), 4.42−4.35 (m, 3H, 1 anomeric H), 4.30−4.18 (m, 5H, 1 anomeric H), 4.17−4.13 (m, 2H), 4.09−4.02 (m, 4H), 3.94 (dd, J = 9.9, 3.6 Hz, 1H), 3.97−3.88 (m, 2H), 3.86−3.79 (m, 1H), 3.67 (dd, J = 11.3, 8.1 Hz, 2H), 3.62 (t, J = 5.9 Hz, 1H), 3.60−3.54

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(m, 1H), 3.51 (dd, J = 9.9, 4.6 Hz, 1H), 2.20 (s, 3H), 2.18 (s, 3H), 2.12 (s, 3H (CH_3), 2H (—CH_2CH_2CO)), 2.11 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.04 (s, 2 × 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.62−1.52 (m, 2H), 1.30−1.24 (m, 30H), 1.19 (s, 9H), 0.87 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 177.0, 172.8, 170.9, 170.9, 170.6, 170.6, 170.4, 170.2, 169.8, 168.4, 155.4, 154.5, 133.3, 118.9, 103.2, 100.9, 100.4, 96.6, 95.4, 79.8, 75.1, 74.9, 74.4, 74.3, 73.1, 73.1, 72.6, 72.1, 71.5, 71.4, 71.1, 70.9, 70.0, 68.4, 67.7, 66.6, 66.5, 63.3, 62.2, 61.5, 61.0, 53.1, 52.2, 50.2, 38.9, 36.9, 32.0, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.4, 27.5, 27.1, 25.8, 22.8, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7, 20.7, 20.6, 14.2, 9.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{80}H_{119}Cl_6N_3O_{37}Na$ 1950.5525; Found 1950.5602.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**21**).* To a solution of **18** (510 mg, 0.264 mmol) and pentadecene-1 **19** (0.359 mL, 1.32 mmol) in dry CH_2Cl_2 (25 mL) was added Hoveyda−Grubbs second-generation catalyst (**20**, 50 mg, 0.079 mmol). The mixture was heated to reflux using an aluminum heating block for 5 days. After every 24 h, another batch of **19** (0.35 mL, 1.32 mmol) and Hoveyda−Grubbs second-generation catalyst (10 mol %) was added. After the reaction was completed, 2 drops of DMSO was added in the mixture at rt followed by stirring for an additional 2 h. The mixture was concentrated, and the product was purified by silica gel column chromatography to give **21** (492 mg, 88%) as a white glassy solid. TLC: R_f = 0.4 (Hex/EtOAc 2:3). ^1H NMR (600 MHz, $CDCl_3$): δ 6.10 (d, J = 10.1 Hz, 1H, —N*H*), 5.75 (ddd, J = 14.4, 6.8 Hz, 1H, =C*H*—), 5.61 (d, J = 9.3 Hz, 1H, —N*H*), 5.41 (d, J = 3.3 Hz, 1H), 5.38−5.30 (m, 3H), 5.25−5.19 (m, 2H), 5.15−5.07 (m, 3H), 5.03 (dd, J = 11.3, 3.4 Hz, 1H), 5.00−4.92 (m, 2H), 4.89 (dd, J = 9.9, 7.8 Hz, 1H), 4.63 (d, J = 12.1 Hz, 1H, —OCH_2CCl_3), 4.55 (d, J = 12.6 Hz, 1H, —OCH_2CCl_3), 4.50 (d, J = 8.2 Hz, 1H, anomeric), 4.42−4.38 (m, 2H, 1 anomeric H), 4.35−4.31 (m, 1H), 4.30−4.18 (m, 5H), 4.17−4.12 (m, 2H), 4.11−3.99 (m, 3H), 3.95−3.88 (m, 3H), 3.85−3.80 (m, 1H), 3.70−3.64 (m, 2H), 3.63−3.60 (m, 1H), 3.56 (dt, J = 9.2, 3.9 Hz, 1H), 3.48 (dd, J = 9.8, 4.4 Hz, 1H), 2.20 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H (CH_3), 2H (−CH_2CH_2CO), 2.11 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.58−1.55 (m, 3H), 1.34−1.21 (m, 52H), 1.16 (s, 9H), 0.88 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 177.0, 172.6, 170.9, 170.6, 170.6, 170.4, 170.4, 170.2, 169.9, 169.8, 168.4, 155.4, 154.5, 137.2, 124.9, 103.2, 100.9, 100.8, 100.4, 96.6, 95.4, 79.9, 75.1, 74.9, 74.4, 73.0, 72.6, 72.1, 71.5, 71.4, 71.1, 70.9, 70.0, 68.4, 67.7, 66.6, 66.5, 63.3, 62.2, 61.5, 61.0, 53.1, 52.1, 50.4, 38.9, 37.0, 32.4, 32.0, 29.8, 29.8, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 27.5, 27.1, 25.8, 22.8, 21.0, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7, 20.6, 14.2. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{93}H_{149}Cl_6N_4O_{37}$ 2124.8013; Found 2124.8021.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 2-Actamino-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→3)-[2-actamino-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**22**).* To a solution of **21** (21 mg, 0.009 mmol) in AcOH/THF (2:3, 2 mL) was added activated Zn (33 mg). After the mixture was stirred at rt for 12 h, it was filtered through a Celite pad and the solution was concentrated under reduced pressure. The crude product was dissolved in pyridine (1 mL) and Ac_2O (0.7 mL) at 0 °C, and the solution was stirred at rt overnight. After completion of the reaction, the solution was concentrated under a vacuum and the product was purified by silica gel column chromatography to afford **22** (14 mg, 76%); TLC: R_f = 0.25 (EtOAc). ^1H NMR (600 MHz, $CDCl_3$): δ 6.72 (d, J = 8.6 Hz, 1H, —N*H*), 6.02 (d, J = 7.9 Hz, 1H, —N*H*), 5.75 (dt, J = 14.3, 6.7 Hz, 1H, =C*H*—), 5.61 (d, J = 9.3 Hz, 1H, —N*H*), 5.54 (bd, J = 11.3 Hz, 1H), 5.44−5.30 (m, 5H), 5.22 (t, J = 7.4 Hz, 1H), 5.15 (t, J = 9.4 Hz, 1H), 4.95 (dd, J = 10.0, 7.9 Hz, 1H), 4.89 (dd, J = 9.7, 7.8 Hz, 1H), 4.76 (d, J = 8.2 Hz, 1H, anomeric), 4.40 (t, J = 9.4 Hz, 2H), 4.36−4.30 (m, 1H), 4.29−4.22 (m, 2H), 4.21−4.10 (m, 5H), 4.08−4.03 (m, 3H), 3.95−3.86 (m, 3H), 3.77 (t, J = 8.9 Hz, 1H), 3.72 (t, J = 9.6 Hz, 1H), 3.66 (dd, J = 9.9, 3.3 Hz, 1H), 3.61 (t, J = 6.0 Hz, 1H), 3.60−3.55 (m, 1H), 3.49 (dd, J = 9.9, 4.4 Hz, 1H), 2.19 (2s, 6H), 2.12 (brs, 5H, —CH_3, —CHCH_2CO—), 2.11 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (2s, 6H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.92 (s, 3H), 1.59−1.52 (m, 2H), 1.34−1.20 (m, 52H), 1.17 (s, 9H), 0.88 (t, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 177.0, 172.6, 171.9, 171.0, 170.8, 170.7, 170.6, 170.6, 170.4, 170.4, 170.3, 170.0, 169.8, 168.9, 137.2, 124.9, 101.5, 100.8, 100.2, 99.8, 78.4, 74.9, 73.1, 73.0, 72.4, 72.2, 72.1, 71.7, 71.2, 71.0, 70.7, 70.0, 68.3, 67.7, 66.9, 66.8, 63.3, 62.3, 61.6, 61.1, 52.4, 50.5, 38.9, 37.0, 32.4, 32.0, 31.0, 29.8, 29.8, 29.8, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 27.1, 25.8, 23.5, 23.4, 22.8, 21.0, 21.0, 20.9, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7, 14.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{91}H_{147}N_3O_{35}Na$ 1865.9707; Found 1865.9742.

*(2S,3R,E)-2-Octadecanamido-3-hydroxyoctadec-4-en-1-yl 2-Actamino-2-deoxy-β-D-galactopyranosyl-(1→3)-[2-actamino-2-deoxy-β-D-galactopyranosyl-(1→4)]-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside (**6a**).* To a solution of **22** (12 mg, 0.0065 mmol) in dry MeOH/THF (3:2, 2 mL) was added NaOMe in MeOH (4 M, 48 μL) at 0 °C. After the solution was stirred at rt for 2 days, the reaction mixture was neutralized with Dowex 50W (H^+) resin, filtered, and concentrated under reduced pressure. The product was purified by silica gel column chromatography to give **6a** as a gummy solid (6 mg, 71%). TLC: R_f = 0.2 ($CHCl_3$/MeOH 1:1). ^1H NMR (600 MHz, CD_3OD:$CDCl_3$ 3:2): δ 5.66 (ddd, J = 14.2, 6.7 Hz, 1H, =C*H*—), 5.42 (ddt, J = 15.3, 7.8, 1.5 Hz, 1H, —C*H*=), 4.84 (d, J = 8.5 Hz, 1H, anomeric), 4.48 (d, J = 8.4 Hz, 1H, anomeric), 4.30 (d, J = 5.7 Hz, 1H, anomeric), 4.26 (d, J = 7.8 Hz, 1H, anomeric), 4.25 (d, J = 2.1 Hz, 1H), 4.20 (dd, J = 9.9, 3.9 Hz, 1H), 4.06 (t, J = 8.0 Hz, 1H), 3.99 (dd, J = 10.6, 8.4 Hz, 1H), 3.97−3.91 (m, 2H), 3.90−3.77 (m, 6H), 3.75 (dd, J = 7.5, 3.9 Hz, 1H), 3.73−3.67 (m, 2H), 3.64−3.59 (m, 2H), 3.57−3.46 (m, 8H), 3.38−3.34 (m, 1H), 3.31−3.27 (m, 1H), 2.14 (t, J = 7.7 Hz, 2H), 2.01 (s, 3H), 1.99 (s, 3H), 1.64−1.48 (m, 3H), 1.38−1.20 (m, 53H), 0.86 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, CD_3OD:$CDCl_3$ 3:2): δ 175.3, 174.4, 134.9, 130.3, 104.7, 104.4, 103.7, 102.9, 84.1, 80.2, 78.6, 78.3, 78.1, 76.1, 76.0, 75.7, 75.4, 74.9, 74.1, 73.3, 73.0, 72.5, 70.5, 69.3, 69.0, 62.4, 61.3, 60.5, 55.0, 52.6, 37.0, 33.0, 32.6, 32.5, 30.3, 30.3, 30.3, 30.3, 30.3, 30.2, 30.2, 30.1, 30.0, 30.0, 30.0, 29.9, 29.9, 27.6, 26.6, 23.3, 23.1, 23.0, 14.3. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{64}H_{121}N_4O_{23}$ 1313.8416; Found 1313.8451.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)hexadec-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**21***).* Compound **21*** (63 mg, 92%, a white solid) was synthesized from **18** (63 mg, 0.032 mmol) and **19** by the same procedure and conditions employed for the synthesis of **21**. TLC: R_f = 0.4 (hexane/EtOAc 2:3). ^1H NMR (600 MHz, $CDCl_3$): δ 6.12 (d, J = 9.9 Hz, 1H, —N*H*), 5.75 (dt, J = 14.4, 6.8 Hz, 1H, =C*H*—), 5.62 (d, J = 9.3 Hz, 1H, —N*H*), 5.40 (d, J = 2.5 Hz, 1H), 5.37−5.28 (m, 3H), 5.26−5.18 (m, 2H), 5.14−5.09 (m, 3H), 5.02 (d, J = 11.5 Hz, 1H), 4.98−4.91 (m, 2H), 4.91−4.84 (m, 2H), 4.62 (d, J = 12.1 Hz, 1H, —OCH_2CCl_3), 4.54 (d, J = 12.6 Hz, 1H, —OCH_2CCl_3), 4.50 (d, J = 8.1 Hz, 1H, anomeric), 4.41−4.38 (m, 2H), 4.35−4.29 (m, 1H), 4.29−4.16 (m, 5H), 4.18−4.10 (m, 2H), 4.09−4.02 (m, 3H), 3.96−3.86 (m, 3H), 3.86−3.78 (m, 1H), 3.69−3.65 (m, 2H), 3.71−3.59 (m, 1H), 3.58−3.52 (m, 1H), 3.48 (dd, J = 9.7, 4.4 Hz, 1H), 2.20 (s, 3H), 2.18 (s, 3H), 2.12 (bs, 5H, —CH_3 and —CHCH_2CO—), 2.10 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.60−1.53 (m, 2H), 1.34−1.22 (m, 50H), 1.16 (s, 9H), 0.87 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.8, 172.5, 170.9, 170.8, 170.5, 170.5, 170.2, 170.2, 170.1, 170.1, 170.0, 169.7, 168.2, 155.3, 154.4, 137.1, 124.8, 103.0, 100.7, 100.7, 100.3, 96.5, 95.3, 79.7, 74.9, 74.2, 72.9, 72.9, 72.4, 72.0, 71.4, 71.3, 70.9, 70.8, 69.9, 68.3, 67.6, 67.6, 67.5, 66.5, 66.3, 63.2, 62.1, 61.4, 60.9, 55.9, 52.9, 52.1, 52.0, 50.3, 38.7, 36.8, 36.8, 32.2, 31.9, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3,

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29.1, 29.0, 27.0, 25.7, 22.6, 20.8, 20.8, 20.8, 20.7, 20.6, 20.6, 20.5, 20.4, 14.1. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{91}H_{145}Cl_6N_4O_{37}$ 2099.7699; Found 2099.7773.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)hexadec-4-en-1-yl 2-Actamino-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→3)-[2-actamino-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**22***).* Compound **22*** (12.5 mg, 80%, a white solid) was synthesized from **21*** (18 mg, 0.0065) by the same procedure and conditions employed for the synthesis of **22**. TLC: R_f = 0.25 (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.74 (d, J = 8.4 Hz, 1H, —*N*H), 6.06 (d, J = 7.7 Hz, 1H, —*N*H), 5.75 (ddt, J = 14.2, 6.8 Hz, 1H, =C*H*—), 5.61 (d, J = 9.3 Hz, 1H, —*N*H), 5.54−5.48 (m, 1H). 5.43−5.30 (m, 6H), 5.21 (t, J = 7.3 Hz, 1H), 5.18−5.09 (m, 2H), 4.94 (dd, J = 9.9, 8.0 Hz, 1H), 4.88 (dd, J = 9.6, 7.9 Hz, 1H), 4.75 (d, J = 8.1 Hz, 1H), 4.43−4.37 (m, 2H), 4.36−4.29 (m, 1H), 4.28−4.21 (m, 2H), 4.20 (m, 4H), 4.10−4.01 (m, 2H), 3.93−3.86 (m, 3H), 3.81−3.76 (m, 2H), 3.71 (td, J = 9.7, 3.9 Hz, 1H), 3.66 (dd, J = 10.0, 3.0 Hz, 1H), 3.61 (bt, J = 5.7 Hz, 1H), 3.57 (dq, J = 7.7, 3.1 Hz, 1H), 3.49 (dd, J = 9.8, 4.3 Hz, 1H), 2.18 (s, 3H), 2.18 (s, 3H), 2.12 (bs, 5H, —CH_3 and —CHCH_2CO—), 2.10 (s, 3H), 2.08 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.03 (brs, 3 × 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.91 (s, 3H), 1.61−1.52 (m, 2H), 1.34−1.21 (m, 50H), 1.16 (s, 9H), 0.87 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.6, 171.9, 171.0, 170.8, 170.7, 170.6, 170.5, 170.4, 170.4, 170.3, 170.0, 169.8, 168.9, 137.2, 124.9, 101.5, 100.7, 100.2, 99.8, 78.4, 74.9, 73.11, 72.4, 72.2, 72.1, 71.7, 71.2, 71.0, 70.7, 70.0, 68.3, 67.7, 67.7, 66.9, 66.8, 63.3, 62.3, 61.6, 61.1, 52.3, 51.6, 50.5, 38.9, 36.9, 32.4, 32.0, 29.8, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 27.1, 25.8, 23.5, 23.4, 22.8, 21.0, 21.0, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7, 14.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{89}H_{143}N_3O_{35}Na$ 1836.9394; Found 1836.9383.

*(2S,3R,E)-2-Octadecanamido-3-hydroxyhexadec-4-en-1-yl 2-Actamino-2-deoxy-β-D-galactopyranosyl-(1→3)-[2-actamino-2-deoxy-β-D-galactopyranosyl-(1→4)]-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside (**6a***).* Compound **6a*** (5.7 mg, 68%, a glassy solid) was synthesized from compound **22*** (12 mg, 0.0066 mmol) by the same procedure and conditions employed for the synthesis of **6a**. TLC: R_f = 0.2 ($CHCl_3$/MeOH 1:1). ^{1}H NMR (600 MHz, CD_3OD:$CDCl_3$, 3:2): δ 5.72−5.61 (m, 1H, =C*H*—), 5.42 (dd, J = 15.3, 7.7 Hz, 1H, —C*H*=), 4.84 (d, J = 8.5 Hz, 1H, anomeric), 4.48 (d, J = 8.4 Hz, 1H, anomeric), 4.37−4.29 (m, 1H), 4.26 (d, J = 7.8 Hz, 1H, anomeric), 4.25 (bs, 1H), 4.19 (dd, J = 10.0, 3.8 Hz, 1H), 4.06 (t, J = 8.1 Hz, 1H), 4.01−3.91 (m, 3H), 3.90−3.78 (m, 6H), 3.76−3.66 (m, 4H), 3.66−3.58 (m, 3H), 3.56−3.46 (m, 7H), 3.38−3.35 (m, 1H), 3.30−3.28 (m, 1H), 2.14 (t, J = 7.6 Hz, 2H), 2.01 (s, 3H), 1.99 (s, 3H), 1.66−1.52 (m, 2H), 1.38−1.19 (m, 48H), 0.86 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD:$CDCl_3$, 3:2): δ 175.3, 174.4, 134.9, 130.3, 104.6, 104.4, 103.6, 102.9, 84.1, 80.1, 76.1, 75.9, 75.7, 75.3, 74.8, 74.1, 73.3, 73.0, 72.5, 70.4, 69.2, 69.0, 62.3, 61.2, 60.5, 54.3, 53.9, 53.9, 53.8, 37.0, 33.0, 32.5, 32.5, 30.3, 30.3, 30.2, 30.2, 30.2, 30.1, 30.1, 30.1, 30.0, 30.0, 29.9, 29.9, 29.9, 29.9, 26.6, 23.2, 23.2, 14.3, 14.3. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{62}H_{117}N_4O_{23}H$ 1285.8103; Found 1285.8127.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**24**).* After a mixture of **12** (0.362 g, 0.475 mmol), **23** (0.306 g, 0.522 mmol), and flame activated MS 4 Å in dry CH_2Cl_2 (40 mL) was stirred at rt for 30 min, NIS (0.160 g, 0.712 mmol) was added at −78 °C, followed by TfOH (4.2 μL, 0.047 mmol). The mixture was stirred at −40 to −30 °C for 2 h, after the disappearance of **12**. The reaction was quenched with triethyl amine (1 mL). The mixture was diluted with CH_2Cl_2 and filtered through a Celite bed. The CH_2Cl_2 layer was washed with saturated $Na_2S_2O_3$ solution, saturated $NaHCO_3$ solution, water, and brine sequentially and then dried with Na_2SO_4. Solvent was evaporated in vacuo, and the residue was purified by silica gel chromatography to afford **24** (0.219 g, 41%) as an off-white solid, as well as **25** (0.238 g, 32%, an off-white solid) and recovered **12** (31 mg). **24**: TLC: R_f = 0.3 (toluene/EtOAc 3:7); ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.80 (ddd, J = 17.3, 10.5, 6.8 Hz, 1H), 5.55 (d, J = 6.7 Hz, 1H), 5.40−5.27 (m, 4H), 5.20 (d, J = 7.2 Hz, 1H, anomeric), 5.14 (t, J = 9.4 Hz, 1H), 5.04 (t, J = 9.6 Hz, 1H), 4.99−4.89 (m, 1H), 4.81 (brs, 2H), 4.73 (t, J = 8.8 Hz, 1H), 4.58−4.45 (m, 2H, anomeric), 4.33 (d, J = 7.7 Hz, 1H, amoneric), 4.28 (dd, J = 11.8, 4.9 Hz, 1H), 4.22−4.10 (m, 4H), 4.06 (brs, 1H, −*OH*), 3.84 (dd, J = 10.3, 6.7 Hz, 1H), 3.80−3.73 (m, 2H), 3.71−3.67 (m, 1H), 3.64−3.60 (m, 3H), 3.53 (dd, J = 10.3, 5.8 Hz, 1H), 3.50−3.46 (m, 1H), 2.10 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.9, 171.4, 170.9, 170.7, 170.6, 170.5, 170.3, 169.6, 169.6, 154.6, 131.6, 120.4, 100.7, 100.6, 100.5, 95.8, 75.9, 74.8, 73.7, 73.6, 73.1, 72.4, 72.1, 72.0, 71.3, 68.9, 68.0, 63.3, 63.2, 62.28, 62.1, 56.9, 39.0, 27.1, 21.0, 20.9, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{47}H_{65}Cl_3N_4O_{27}Na$ 1247.2780; Found 1247.2794.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**25**).* TLC: R_f = 0.52 (toluene/EtOAc 3:7); ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.04 (d, J = 9.9 Hz, 1H, −N*H*), 5.85−5.70 (m, 1H), 5.46−5.28 (m, 3H), 5.25−5.21 (m, 3H), 5.15−5.09 (m, 4H (anomeric *H*)), 5.07−5.02 (m, 2H), 4.99 (d, J = 11.9 Hz, 1H), 4.97−4.86 (m, 3H), 4.59 (d, J = 12.1 Hz, 1H), 4.55 (d, J = 12.2 Hz, 1H), 4.48−4.41 (m, 3H (anomeric 2*H*)), 4.38 (dd, J = 12.1, 4.6 Hz, 1H), 4.24−4.16 (m, 3H (anomeric *H*)), 4.17−4.09 (m, 2H), 4.08−4.04 (m, 2H), 3.85−3.82 (m, 2H), 3.81−3.75 (m, 1H), 3.72−3.65 (m, 2H), 3.67−3.59 (m, 3H), 3.57 (dd, J = 9.9, 5.4 Hz, 1H), 3.51 (dd, J = 8.5, 5.8 Hz, 1H), 2.10 (s, 3H), 2.08 (brs, 9H (3 × 3H)), 2.06 (brs, 9H (3 × 3H)), 2.02 (brs, 9H (3 × 3H)), 1.99 (s, 3H), 1.21 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.9, 171.5, 170.9, 170.8, 170.7, 170.6, 170.4, 170.3, 169.6, 169.6, 169.5, 168.3, 155.1, 154.6, 131.6, 120.4, 102.8, 100.7, 100.4, 100.0, 96.5, 95.4, 79.3, 75.0, 74.8, 74.5, 73.8, 73.2, 72.6, 72.1, 72.0, 71.6, 71.1, 70.8, 70.3, 69.2, 68.5, 68.1, 63.3, 63.1, 63.0, 62.3, 62.1, 62.0, 56.7, 55.9, 39.0, 27.2, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7, 20.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{62}H_{83}Cl_6N_5O_{36}Na$ 1708.2824; Found 1708.2825.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**26**).* After a mixture of **24** (0.196 g, 0.160 mmol), **16** (0.272 g, 0.464 mmol), and flame activated MS 4 Å in dry CH_2Cl_2 (3 mL) was stirred at rt for 30 min, it was cooled to −78 °C and then NIS (0.140 g, 0.624 mmol) was added, followed by 2.8 μL of TfOH (0.032 mmol). The mixture was stirred at −40 to −30 °C for 2 h until the **16** disapeared. The reaction was quenched with Et_3N (1 mL), and the mixture was diluted with CH_2Cl_2 and filtered through a Celite bed. The CH_2Cl_2 layer was washed with saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, water, and brine and dried with Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified by silica gel chromatography to afford **26** (0.098 g, 75%), with recovered **24** (0.102 g). **26**: TLC: R_f = 0.52; (toluene/EtOAc 3:7); ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.17 (d, J = 9.8 Hz, 1H), 5.79 (ddd, J = 17.3, 10.5, 6.8 Hz, 1H), 5.41 (d, J = 2.7 Hz, 1H), 5.38−5.29 (m, 3H), 5.24 (t, J = 10.6 Hz, 2H), 5.17 (d, J = 8.7 Hz, 1H), 5.16−5.10 (m, 2H), 5.06 (t, J = 9.5 Hz, 1H), 5.00−4.84 (m, 3H), 4.67 (d, J = 12.1 Hz, 1H), 4.57 (d, J = 12.5 Hz, 1H), 4.53 (d, J = 8.1 Hz, 1H, anomeric), 4.46 (d, J = 7.9 Hz, 1 H, anomeric), 4.43 (d, J = 11.3 Hz, 1H), 4.32−4.11 (m, 8H), 4.06 (dd, J = 11.3, 6.2 Hz, 2H), 3.91 (t, J = 6.5 Hz, 1H), 3.89−3.81 (m, 3H), 3.81−3.76 (m, 1H), 3.73−3.65 (m, 3H), 3.64−3.60 (m, 1H), 3.58 (dd, J = 8.7, 4.7 Hz, 1H), 3.55−3.51 (m, 1H), 2.19 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.08 (brs, 6H (2 × 3H)), 2.07 (brs, 6H (2 × 3H)), 2.06 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.9, 170.9, 170.9, 170.8, 170.7, 170.6, 170.4, 170.3, 169.9, 169.6, 169.4, 168.4, 155.3, 154.5, 131.5, 120.4, 103.0, 100.7, 100.4, 100.1, 96.5, 95.4, 79.7, 75.1, 75.0, 74.4, 73.8, 73.1, 72.8, 72.6, 72.3, 71.9, 71.7, 71.4, 71.10, 70.1, 69.5, 68.4, 68.0, 66.6, 63.2, 63.0, 62.4, 62.2, 61.0, 55.7, 53.1, 39.0, 29.8,

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27.2, 20.9, 20.8, 20.8, 20.7, 20.7, 20.7, 20.7, 20.6, 20.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{62}H_{83}Cl_6N_5O_{36}Na$ 1708.2824; Found 1708.2834.

*(2S,3R)-2-Octadecanamido-3-(pivaloyloxy)pent-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**27**).* After PPh_3 (28.7 mg, 0.109 mmol) and water (29.6 μL, 1.65 mmol) were added to a stirred solution of **26** (92.6 mg, 0.054 mmol) in THF (3 mL), the mixture was heated with stirring at 50 °C using an aluminum heating block until TLC indicated the disappearance of **26**. The solvent was removed under a vacuum, and the residue was dissolved in dry dichloromethane (3 mL). Then, EDC (24.1 mg, 0.126 mmol), DMAP (1.3 mg, 0.010 mmol), and stearic acid (35.8 mg, 0.126 mmol) were added at 0 °C under argon, and the mixture was stirred at rt for 12 h. The reaction was quenched with water, and the product was extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography to afford **27** (92.7 mg, 82%) as a glassy solid. TLC: R_f = 0.8 (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.19 (d, J = 9.8 Hz, 1H), 5.78 (ddd, J = 17.0, 10.6, 6.2 Hz, 1H), 5.67 (d, J = 9.2 Hz, 1H), 5.41−5.41 (m, 1H), 5.32−5.20 (m, 5H), 5.17 (d, J = 7.9 Hz, 1H), 5.14−5.11 (m, 2H), 5.06 (t, J = 9.6 Hz, 1H), 4.96−4.91 (m, 2H), 4.90−4.85 (m, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 12.6 Hz, 1H), 4.51 (d, J = 8.0 Hz, 1H), 4.43−4.34 (m, 3H), 4.27−4.14 (m, 7H), 4.08−4.01 (m, 2H), 3.96−3.83 (m, 4H), 3.75−3.64 (m, 3H), 3.64−3.60 (m, 1H), 3.56 (dd, J = 9.1, 5.1 Hz, 1H), 3.51 (dd, J = 9.9, 4.5 Hz, 1H), 2.19 (s, 3H), 2.10 (brs, 8H (2 × 3H and 2H −COCH_2−CH$_2$)), 2.08 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.63−1.53 (m, 2H), 1.31−1.22 (m, 28H), 1.19 (s, 9H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 177.0, 172.8, 170.9, 170.8, 170.6, 170.6, 170.3, 170.2, 169.8, 169.3, 168.3, 155.3, 154.5, 133.3, 118.9, 103.1, 100.9, 100.4, 100.1, 96.5, 95.4, 79.6, 75.1, 74.8, 74.4, 73.1, 73.1, 72.8, 72.6, 72.3, 72.0, 71.5, 71.4, 70.1, 69.5, 68.4, 67.7, 66.6, 63.0, 62.4, 62.2, 61.0, 55.7, 53.1, 50.2, 38.9, 36.9, 32.0, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 27.1, 25.8, 22.8, 20.9, 20.9, 20.9, 20.8, 20.7, 20.7, 20.7, 20.6, 20.6, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{80}H_{120}Cl_6N_3O_{37}$ 1928.5705; Found 1928.5688.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**28**).* To a solution of **27** (64 mg, 0.033 mmol) and pentadecene-1 **19** (72 μL, 0.265 mmol) in dry CH_2Cl_2 (16 mL) was added catalyst **20** (6.2 mg, 0.009 mmol). The mixture was heated to reflux in an aluminum heating block for 5 days. After every 24 h, another batch of **19** (0.36 μL , 0.132 mmol) and the catalyst (10 mol %) was added. After the reaction was completed, 2 drops of DMSO was added at rt, followed by stirring for an additional 2 h. The mixture was concentrated, and the product was purified by silica gel column chromatography to give **28** (62.7 mg, 89%) as a white glassy solid. TLC: R_f = 0.4 (Hex/EtOAc 2:3). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.18 (d, J = 9.8 Hz, 1H), 5.75 (dt, J = 14.3, 6.8 Hz, 1H), 5.61 (d, J = 9.3 Hz, 1H), 5.41 (brs, 1H), 5.33 (dd, J = 15.4, 7.5 Hz, 1H), 5.30−5.17 (m, 4H), 5.12 (dd, J = 11.9, 7.1 Hz, 3H), 5.08−5.02 (m, 1H), 4.95−4.92 (m, 2H), 4.91−4.86 (m, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 12.6 Hz, 1H), 4.52 (d, J = 7.9 Hz, 1H), 4.42−4.38 (m, 2H), 4.34−4.30 (m, 1H), 4.27−4.14 (m, 7H), 4.06 (dd, J = 11.2, 6.3 Hz, 1H), 4.02 (dd, J = 11.7, 5.1 Hz, 1H), 3.93−3.84 (m, 4H), 3.70−3.65 (m, 3H), 3.64−3.61 (m, 1H), 3.55 (dd, J = 8.7, 4.8 Hz, 1H), 3.48 (dd, J = 9.8, 4.4 Hz, 1H), 2.20 (s, 3H), 2.10 (brd, 8H, 2 × 3H and 2H −COCH_2−), 2.08 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.59−1.55 (m, 2H), 1.34−1.22 (m, 52H), 1.16 (s, 9H), 0.88 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 177.0, 172.6, 170.9, 170.8, 170.6, 170.6, 170.3, 170.2, 169.8, 169.3, 168.3, 155.3, 154.5, 137.2, 124.9, 103.2, 100.9, 100.4, 100.2, 96.5, 95.4, 79.7, 75.1, 74.8, 74.5, 73.0, 73.0, 72.8, 72.6, 72.3, 72.0, 71.6, 71.4, 70.0, 69.5, 68.5, 67.7, 66.6, 63.0, 62.4, 62.2, 60.9, 55.7, 53.1, 50.4, 38.9, 37.0, 32.4, 32.0, 29.8, 29.8, 29.8, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 27.1, 25.8, 22.8, 20.9, 20.9, 20.8, 20.7, 20.7, 20.7, 20.7, 20.6, 14.2. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{93}H_{145}Cl_6N_3O_{37}NH_4$ 2125.8020; Found 2125.7974.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 2-Actamino-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-[2-actamino-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**29**).* To a solution of **28** (27 mg, 0.012 mmol) in AcOH and THF (2:3, 2 mL) was added activated Zn (83.6 mg, 1.28 mmol). After the mixture was stirred at rt for 12 h, it was filtered through a Celite pad and the solution was concentrated under reduced pressure. The crude product was dissolved in pyridine (1 mL) and Ac_2O (0.7 mL) at 0 °C, and the solution was stirred at rt overnight. After completion of the reaction, the solution was concentrated under a vacuum and the product was purified by silica gel column chromatography to give **29** (16 mg, 72%) as yellow syrup. TLC: R_f = 0.25 (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.89 (d, J = 8.2 Hz, 1H), 5.99 (d, J = 7.6 Hz, 1H), 5.75 (dt, J = 14.3, 6.8 Hz, 1H), 5.62 (d, J = 9.3 Hz, 1H), 5.57 (t, J = 9.8 Hz, 1H), 5.46−5.38 (m, 2H), 5.41−5.30 (m, 2H), 5.21 (t, J = 7.4 Hz, 1H), 5.13 (t, J = 9.5 Hz, 1H), 5.04 (t, J = 9.6 Hz, 1H), 4.93 (dd, J = 9.9, 8.0 Hz, 1H), 4.88 (dd, J = 9.7, 7.9 Hz, 1H), 4.71 (d, J = 8.1 Hz, 1H), 4.44−4.37 (m, 2H), 4.36−4.27 (m, 1H), 4.27−4.21 (m, 3H), 4.19 (t, J = 3.9 Hz, 2H), 4.14 (d, J = 2.6 Hz, 1H), 4.10 (dd, J = 11.7, 6.8 Hz, 1H), 4.07−4.00 (m, 2H), 3.94−3.87 (m, 3H), 3.74−3.63 (m, 5H), 3.61 (t, J = 5.9 Hz, 1H), 3.55 (ddd, J = 9.6, 5.3, 1.8 Hz, 1H), 3.49 (dd, J = 9.8, 4.3 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (brs, 5H (1 × 3H and 2H −COCH_2−CH$_2$)), 2.08 (s, 3H), 2.06 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (s, 6H (2 × 3H)), 2.02 (s, 3H), 1.97 (s, 3H), 1.93 (s, 3H), 1.62−1.50 (m, 1H), 1.34−1.22 (m, 52H), 1.16 (s, 9H), 0.87 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 177.0, 172.6, 171.8, 171.1, 170.8, 170.8, 170.7, 170.6, 170.5, 170.5, 170.3, 169.9, 169.8, 169.5, 168.8, 137.2, 124.9, 101.8, 100.8, 100.2, 99.2, 78.4, 74.7, 73.1, 73.0, 72.5, 72.4, 72.1, 72.0, 71.6, 71.2, 70.7, 69.7, 68.4, 67.7, 66.9, 63.1, 62.4, 62.2, 61.0, 54.9, 52.1, 50.5, 38.9, 37.0, 32.4, 32.0, 29.8, 29.8, 29.8, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 27.1, 25.8, 23.5, 23.2, 22.8, 20.9, 20.9, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7, 20.7, 20.6, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{91}H_{148}N_3O_{35}$ 1842.9888; Found 1865.9870.

*(2S,3R,E)-2-Octadecanamido-3-hydroxyoctadec-4-en-1-yl 2-Actamino-2-deoxy-β-D-glucopyranosyl-(1→3)-[2-actamino-2-deoxy-β-D-galactopyranosyl-(1→4)]-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside (**6**, LcGg4).* To a solution of **29** (15 mg, 0.008 mmol) in dry MeOH and THF (2 mL) was added NaOMe in MeOH (4 M, 48 μL) at 0 °C. After the solution was stirred at rt for 2 d, the reaction was neutralized with Dowex 50W (H^+) resin, and the solution was filtered and concentrated under reduced pressure. The product was purified by silica gel column chromatography to give **6** as a gummy solid (8.2 mg, 77%). TLC: R_f = 0.2 ($CHCl_3$/MeOH 1:1). ^{1}H NMR (600 MHz, CD_3OD:$CDCl_3$, 1:1): δ 5.66 (dt, J = 14.0, 6.7 Hz, 1H), 5.42 (dd, J = 15.3, 7.7 Hz, 1H), 4.84 (d, J = 8.5 Hz, 1H, anomeric), 4.47 (d, J = 8.4 Hz, 1H, anomeric), 4.31−4.27 (m, 1H), 4.25 (d, J = 7.8 Hz, 1H, anomeric), 4.22 (brs, 1H), 4.19 (dd, J = 10.0, 3.8 Hz, 1H), 4.05 (t, J = 7.9 Hz, 1H), 4.00−3.92 (m, 2H), 3.92−3.89 (m, 2H), 3.87−3.77 (m, 5H), 3.76−3.68 (m, 2H), 3.61−3.54 (m, 3H), 3.54−3.44 (m, 7H), 3.36−3.33 (m, 2H), 3.30−3.26 (m, 1H), 3.25−3.17 (m, 2H), 2.17−2.11 (m, 2H), 1.99 (s, 3H), 1.98 (s, 3H), 1.64−1.50 (m, 3H), 1.36−1.18 (m, 51H), 0.85 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD:$CDCl_3$, 1:1): δ 175.2, 174.3, 173.8, 134.9, 130.0, 104.4, 104.3, 103.5, 102.5, 83.9, 80.0, 76.6, 76.0, 75.9, 75.9, 75.5, 75.2, 74.6, 73.9, 73.0, 72.4, 72.2, 70.3, 69.1, 68.8, 62.8, 62.2, 61.2, 60.2, 59.5, 56.6, 54.3, 53.8, 49.5, 36.9, 32.9, 32.4, 32.4, 30.2, 30.2, 30.1, 30.1, 30.1, 30.1, 30.0, 29.9, 29.8, 29.8, 29.8, 26.5, 23.1, 23.01, 23.0, 14.3. HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{64}H_{117}N_3O_{23}NH_4$ 1313.8416; Found 1313.8421.

(2S,3R)-2-(tert-Butoxycarbonyl)amino-3-(pivaloyloxy)pent-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-

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*(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**30**).* A mixture of PPh_3 (62.5 mg, 0.238 mmol), water (22 μL, 1.19 mmol), and **17** (201 mg, 0.119 mmol) in THF (4 mL) was stirred at 50 °C using an aluminum heating block until TLC indicated the complete consumption of **17**. The solvents were removed under reduced pressure, and the residue was dissolved in dry CH_2Cl_2 (6 mL). After the solution was cooled to 0 °C, Boc_2O (38.8 mg, 0.178 mmol), DMAP (0.7 mg, 0.006 mmol), and DIPEA (75.4 μL, 0.355 mmol) were added under argon. After stirring at rt for 12 h, the solvent was removed in vacuo and the residue was purified by silica gel column chromatography to afford **30** (172 mg, 82%) as a white solid. TLC: R_f = 0.4 (EtOAc/Hex 3:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.10 (d, *J* = 9.9 Hz, 1H, —*NH*), 5.78 (ddd, *J* = 16.9, 10.6, 6.1 Hz, 1H, ═*CH*—), 5.41 (d, *J* = 3.0 Hz, 1H), 5.37−5.33 (m, 1H), 5.31−5.21 (m, 4H), 5.19−5.06 (m, 3H), 5.05−4.99 (m, 1H), 4.98−4.86 (m, 3H), 4.70 (d, *J* = 9.4 Hz, 1H, —OCH_2CCl_3), 4.63 (d, *J* = 12.1 Hz, 1H, —OCH_2CCl_3), 4.55 (d, *J* = 12.6 Hz, 1H, —OCH_2CCl_3), 4.50 (d, *J* = 8.2 Hz, 1H, anomeric), 4.40 (bd, *J* = 8.3 Hz, 2H, anomeric 1H), 4.31−4.17 (m, 4H), 4.17−4.11 (m, 2H), 4.10−3.98 (m, 5H), 3.94 (dd, *J* = 10.0, 3.2 Hz, 1H), 3.92−3.89 (m, 2H), 3.87−3.76 (m, 1H), 3.70−3.64 (m, 2H), 3.63−3.60 (m, 1H), 3.58−3.54 (m, 1H), 3.49 (dd, *J* = 10.0, 4.8 Hz, 1H), 2.20 (s, 3H), 2.18 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.06 (brs, 2 × 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.41 (s, 9H), 1.19 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 177.0, 170.9, 170.7, 170.6, 170.6, 170.4, 170.4, 170.2, 169.9, 169.8, 169.8, 168.3, 155.3, 154.5, 133.1, 118.7, 103.2, 101.2, 100.8, 100.4, 96.6, 95.4, 79.9, 79.8, 75.1, 75.0, 74.4, 73.2, 73.0, 72.6, 72.1, 71.5, 71.4, 71.3, 71.0, 70.9, 70.1, 68.6, 68.4, 66.6, 66.5, 63.3, 62.2, 61.5, 61.0, 53.1, 52.1, 52.1, 38.9, 28.4, 27.1, 21.0, 20.9, 20.9, 20.8, 20.7, 20.7, 20.7, 20.7, 20.7, 20.6. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{67}H_{93}Cl_6N_3O_{38}Na$ 1782.3554; Found 1782.3531.

*(2S,3R,E)-2-(tert-Butoxycarbonyl)amino-3-(pivaloyloxy)octadec-4-en-1-yl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**31**).* Compound **31** (155 mg, 82%, a brownish solid) was synthesized from **30** (170 mg, 0.096 mmol) by the same procedure and conditions employed for the synthesis of **21**. TLC: R_f = 0.5 (EtOAc/hexane, 3/2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.12 (d, *J* = 10.0 Hz, 1H, —*NH*), 5.78 (dt, *J* = 14.1, 6.6 Hz, 1H, ═*CH*—), 5.43 (d, *J* = 3.0 Hz, 1H), 5.41−5.29 (m, 3H), 5.25 (d, *J* = 8.6 Hz, 1H), 5.22−5.19 (m, 1H), 5.18−5.10 (m, 3H), 5.05 (dd, *J* = 11.4, 3.0 Hz, 1H), 5.01−4.90 (m, 3H), 4.69 (d, *J* = 9.4 Hz, 1H, —OCH_2CCl_3), 4.65 (d, *J* = 12.1 Hz, 1H, —OCH_2CCl_3), 4.57 (d, *J* = 12.6 Hz, 1H, —OCH_2CCl_3), 4.53 (d, *J* = 8.1 Hz, 1H, anomeric), 4.42 (broad d, *J* = 7.7 Hz, 2H, anomeric 1H), 4.31−4.20 (m, 5H), 4.20−4.14 (m, 2H), 4.13−4.03 (m, 3H), 4.01−3.90 (m, 4H), 3.89−3.79 (m, 1H), 3.74−3.67 (m, 2H), 3.66−3.62 (m, 1H), 3.61−3.56 (m, 1H), 3.49 (dd, *J* = 9.7, 4.4 Hz, 1H), 2.23 (s, 3H), 2.21 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.43 (s, 9H), 1.39−1.24 (m, 24H), 1.18 (s, 9H), 0.90 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.9, 170.9, 170.7, 170.6, 170.6, 170.4, 170.4, 170.2, 169.9, 169.8, 168.4, 155.4, 154.5, 137.1, 124.6, 103.2, 101.2, 100.8, 100.5, 96.6, 95.4, 79.9, 79.6, 75.1, 75.0, 74.4, 73.2, 73.0, 72.6, 72.1, 71.5, 71.4, 71.3, 71.1, 70.9, 70.1, 68.6, 68.4, 66.6, 66.5, 63.3, 62.3, 61.5, 61.0, 53.1, 52.2, 52.2, 42.8, 38.8, 32.4, 32.0, 29.8, 29.7, 29.7, 29.7, 29.6, 29.4, 29.3, 29.0, 28.4, 27.1, 22.8, 21.0, 20.9, 20.9, 20.8, 20.7, 20.7, 20.7, 20.6, 14.2. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{80}H_{119}Cl_6N_3O_{38}Na$ 1966.5484; Found 1966.5475.

*(2S,3R,E)-2-(tert-Butoxycarbonyl)amino-3-(pivaloyloxy)octadec-4-en-1-yl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→3)-[2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**32**).* Freshly activated Zn dust (474 mg, 7.25 mmol) was added to a solution of **31** (141 mg, 0.0723 mmol) in AcOH and THF (2:3, 5 mL), and the mixture was stirred at rt for 12 h until TLC indicated the disappearance of **31**. The mixture was filtered through a Celite pad, and the solution was concentrated under reduced pressure. The residue was dissolved in Ac_2O (3 mL) and Et_3N (50 μL, 0.362 mmol), and the solution was stirred at rt for 8 h. The solution was concentrated, and the product was purified by silica gel column chromatography to give **32** (91 mg, 74%) as a white solid. TLC: R_f = 0.2 (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.74 (d, *J* = 8.3 Hz, 1H, —*NH*), 6.08 (d, *J* = 7.5 Hz, 1H, —*NH*), 5.76 (dt, *J* = 14.0, 6.7 Hz, 1H, ═*CH*—), 5.55 (d, *J* = 9.7 Hz, 1H, —*NH*), 5.41−5.32 (m, 6H), 5.18 (t, *J* = 7.1 Hz, 1H), 5.16−5.10 (m, 1H), 5.00−4.87 (m, 2H), 4.77 (d, *J* = 8.0 Hz, 1H, anomeric), 4.66 (d, *J* = 9.5 Hz, 1H, anomeric), 4.40 (broad d, *J* = 8.4 Hz, 2H, anomeric), 4.27−4.22 (m, 3H), 4.19−4.03 (m, 7H), 4.00−3.94 (m, 1H), 3.92−3.88 (m, 3H), 3.80−3.69 (m, 3H), 3.66 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.63−3.60 (m, 1H), 3.60−3.54 (m, 1H), 3.47 (dd, *J* = 9.9, 4.5 Hz, 1H), 2.27−2.16 (2s, 6H), 2.12 (s, 3H), 2.10 (s, 3H), 2.08 (broad s, 2 × 3H), 2.05 (broad s, 2 × 3H), 2.03 (2s, 2 × 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.91 (s, 3H), 1.41 (s, 9H), 1.34−1.21 (m, 24H), 1.16 (s, 9H), 0.87 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.9, 171.9, 171.0, 170.8, 170.7, 170.7, 170.6, 170.4, 170.4, 170.3, 170.0, 169.7, 168.9, 137.1, 124.6, 101.5, 101.1, 100.3, 99.7, 79.6, 78.4, 75.0, 73.2, 73.0, 72.4, 72.3, 72.2, 71.5, 71.2, 71.0, 70.7, 70.0, 68.5, 68.5, 68.2, 66.9, 66.8, 63.3, 62.3, 61.6, 61.1, 52.4, 52.2, 51.7, 38.9, 32.4, 32.0, 29.8, 29.7, 29.7, 29.7, 29.6, 29.4, 29.3, 29.0, 28.4, 27.1, 23.5, 23.4, 22.8, 21.0, 21.0, 20.9, 20.9, 20.8, 20.8, 20.8, 20.7, 20.7. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{78}H_{121}N_3O_{36}Na$ 1698.7622; Found 1698.7604.

*(2S,3R,E)-2-{11-[(7-Nitrobenzo[c][1,2,5]oxadiazol-4-yl)amino]-undecanamido}-3-(pivaloyloxy)octadec-4-en-1-yl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→3)-[2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**34**).* TFA (68 μL, 0.894 mmol) was added to a stirred solution of **32** (30 mg, 0.017 mmol) in CH_2Cl_2 (4 mL) at rt, and the mixture was stirred until TLC indicated the disappearance of **32**. The solvent was removed under reduced pressure, and the residue was dissolved in dry CH_2Cl_2 (3 mL). Then, EDC (15.5 mg, 0.081 mmol), DMAP (2 mg, 0.017 mmol), and 11-{(7-nitrobenzo[c]-[1,2,5]oxadiazol-4-yl)amino}undecanoic acid **33** (29.5 mg, 0.081 mmol) were added at 0 °C, which was followed by DIPEA (52 μL, 0.243). The mixture was stirred under argon at rt for 12 h. After completion of the reaction, water was added in the reaction mixture. The organic layer was separated and washed with saturated $NaHCO_3$ solution, water, and brine and then dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography to afford **34** (29 mg, 83%) as a yellowish brown solid. TLC: R_f = 0.7 (EtOAc/MeOH, 6:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.6 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H, —N*H*), 6.60 (bs, 1H, —N*H*), 6.21 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.12 (d, *J* = 7.9 Hz, 1H, —N*H*), 5.76 (dt, *J* = 14.5, 7.0 Hz, 1H, ═*CH*—), 5.68 (d, *J* = 9.2 Hz, 1H, —N*H*), 5.42 (d, *J* = 3.1 Hz, 1H), 5.40−5.30 (m, 4H), 5.24 (t, *J* = 7.2 Hz, 1H), 5.15 (t, *J* = 9.4 Hz, 1H), 4.96 (dd, *J* = 9.9, 8.0 Hz, 1H), 4.89 (dd, *J* = 9.7, 7.9 Hz, 1H), 4.75 (d, *J* = 8.1 Hz, 1H), 4.44−4.41 (m, 2H), 4.36−4.32 (m,1H), 4.30−4.24 (m, 3H), 4.24−4.12 (m, 4H), 4.11−4.03 (m, 2H), 4.00−3.83 (m, 4H), 3.74 (t, *J* = 9.5 Hz, 1H), 3.70 (dd, *J* = 10.1, 3.0 Hz, 1H), 3.67−3.62 (m, 1H), 3.62−3.56 (m, 2H), 3.54−3.52 (m, 3H), 2.36 (t, *J* = 7.4 Hz, 1H), 2.21 (s, 3H), 2.20 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06−2.04 (s, 3 × 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.95 (s, 3H), 1.85−1.80 (m, 2H), 1.68−1.61 (m, 2H), 1.49−1.46 (m, 2H), 1.42−1.23 (m, 37H), 1.18 (s, 9H), 0.89 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 176.9, 172.5, 171.8, 171.0, 170.7, 170.5, 170.4, 170.3, 170.3, 170.1, 169.9, 169.7, 168.7, 144.3, 143.9, 136.9, 136.6, 136.6, 124.8, 100.6, 100.1, 99.9, 98.5, 78.4, 74.7, 72.9, 72.3, 72.0, 72.0, 71.6, 71.0, 70.9, 70.5, 68.3, 67.5, 66.7, 66.6, 63.1, 61.5, 60.9, 51.8, 51.0, 50.5, 44.0, 43.9, 38.7, 36.7, 33.5, 32.2, 31.9, 29.7, 29.6, 29.5, 29.3, 29.1, 29.1, 29.1, 29.1, 29.0, 29.0, 29.0, 29.0, 28.8, 28.4, 27.0, 26.8, 25.5, 24.6, 23.3, 23.1, 22.6, 20.8, 20.8, 20.8, 20.7, 20.6, 20.5, 14.1. HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{90}H_{135}N_7O_{38}Na$ 1944.8739; Found 1944.8776.

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*(2S,3R,E)-2-{11-[(7-Nitrobenzo[c][1,2,5]oxadiazol-4-yl)amino]-undecanamido}-3-hydroxyoctadec-4-en-1-yl 2-Acetamido-2-deoxy-β-D-galactopyranosyl-(1→3)-[2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)]-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside (**35**).* Compound **35** (8.1 mg, 85%, a yellowish brown solid) was synthesized from **34** (14 mg, 0.007 mmol) by the same procedure and reaction conditions employed for the synthesis of **6a**. TLC: R_f = 0.3 ($CHCl_3$/MeOH 1:1). ^{1}H NMR (600 MHz, CD_3OD:$CDCl_3$, 3:2): δ 8.50 (d, *J* = 8.0 Hz, 1H), 6.23 (d, *J* = 7.6 Hz, 1H), 5.66 (dt, *J* = 14.3, 6.7 Hz, 1H, ═C*H*—), 5.42 (dd, *J* = 15.3, 7.7 Hz, 1H, —C*H*═), 4.83 (d, *J* = 8.5 Hz, 1H, anomeric), 4.48 (d, *J* = 8.3 Hz, 1H, anomeric), 4.30 (d, *J* = 6.9 Hz, 1H, anomeric), 4.26−4.22 (m, 4H), 4.18 (dd, *J* = 9.8, 3.8 Hz, 1H), 4.06 (t, *J* = 7.8 Hz, 1H), 4.01−3.90 (m, 3H), 3.89−3.76 (m, 6H), 3.74 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.70 (td, *J* = 12.2, 11.3, 4.0 Hz, 2H), 3.62 (ddd, *J* = 13.8, 10.5, 3.9 Hz, 2H), 3.57−3.46 (m, 9H), 3.39−3.33 (m, 1H), 3.30−3.27 (m, 1H), 2.14 (t, *J* = 7.6 Hz, 2H), 2.01 (s, 3H), 1.98 (s, 3H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.66−1.50 (m, 3H), 1.46−1.42 (m, 2H), 1.38−1.19 (m, 34H), 0.84 (t, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD:$CDCl_3$, 1:1): δ 175.2, 174.3, 174.3, 146.0, 145.1, 138.1, 134.8, 130.1, 105.6, 104.5, 104.3, 103.6, 102.8, 98.9, 84.0, 80.0, 76.0, 76.0, 75.8, 75.6, 75.2, 74.7, 74.0, 73.2, 72.9, 72.5, 70.3, 69.2, 69.1, 68.9, 62.3, 62.3, 61.1, 60.4, 54.2, 53.8, 53.7, 53.2, 36.9, 32.9, 32.4, 30.2, 30.2, 30.2, 30.1, 30.0, 30.0, 29.9, 29.9, 29.9, 29.8, 29.8, 29.8, 29.8, 27.5, 27.3, 26.4, 23.1, 23.0, 23.0, 14.3. HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ Calcd for $C_{63}H_{105}N_7O_{26}Na$ 1398.7001; Found 1398.7015.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 3,4,6-Tri-O-acetyl-2-azidoactamino-2-deoxy-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-azidoactamino-2-deoxy-β-D-galactopyranosyl-(1→4)]-2,6-di-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**36**).* To a solution of **21** (21 mg, 0.010 mmol) in AcOH/THF (2/3, 2 mL) was added activated Zn (65 mg, 0.99 mmol). After the mixture was stirred at rt for 12 h, it was filtered through a Celite pad and the filtrate was concentrated under reduced pressure. The crude product was stripped with dry toluene (3 × 3 mL) and then dissolved in 1 mL of dry CH_2Cl_2. To this solution were added azidoacetic acid (9.2 mg, 0.091 mmol), EDC (17.4 mg, 0.091 mmol), DMAP (1.1 mg, 0.009 mmol), and DIPEA (19.3 μL, 0.091 mmol) in 2 mL of dry CH_2Cl_2 at 0 °C. The mixture was stirred at rt overnight and diluted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ solution, water, and brine and then dried over Na_2SO_4. The solution was concentrated under a vacuum, and the residue was purified by silica gel column chromatography to offer **36** (14 mg, 79%) as a white solid. TLC: R_f = 0.3 (EtOAc/hexane 3:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13 (d, *J* = 9.2 Hz, 1H, —N*H*), 6.58 (d, *J* = 8.6 Hz, 1H, —N*H*), 5.75 (dt, *J* = 14.1, 6.8 Hz, 1H, ═C*H*—), 5.62 (d, *J* = 9.3 Hz, 1H, —N*H*), 5.42 (t, *J* = 3.0 Hz, 1H), 5.38−5.30 (m, 3H), 5.25−5.19 (m, 2H), 5.15−5.09 (m, 2H), 4.89 (dd, *J* = 9.8, 7.8 Hz, 1H), 4.83 (ddd, *J* = 10.0, 8.0, 4.1 Hz, 1H), 4.58 (dd, *J* = 12.8, 8.4 Hz, 1H), 4.42−4.36 (m, 2H), 4.35−4.30 (m, 1H), 4.28−4.23 (m, 4H), 4.21−4.12 (m, 7H), 4.09−3.95 (m, 4H), 3.94−3.87 (m, 3H), 3.81 (dd, *J* = 15.9, 9.3 Hz, 1H), 3.73−3.67 (m, 1H), 3.63−3.59 (m, 2H), 3.56 (ddd, *J* = 9.8, 5.2, 2.0 Hz, 1H), 3.48 (dd, *J* = 9.8, 4.4 Hz, 1H), 2.20 (s, 3H), 2.19 (s, 3H), 2.12 (bs, 5H, —C*H*$_3$ and —C*H*$_2$CO—), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (bs, 2 × 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.59−1.53 (m, 2H), 1.32−1.22 (m, 52H), 1.16 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 177.0, 172.6, 170.9, 170.9, 170.7, 170.6, 170.4, 170.2, 169.9, 169.8, 169.3, 168.5, 168.2, 137.2, 124.9, 102.3, 100.9, 100.0, 99.8, 79.2, 74.5, 73.1, 73.0, 72.1, 71.8, 71.5, 71.2, 70.7, 68.4, 68.3, 67.7, 66.7, 66.5, 63.2, 62.2, 61.6, 60.9, 56.1, 52.8, 51.9, 50.4, 38.9, 37.0, 32.4, 32.0, 29.8, 29.8, 29.8, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 27.1, 25.8, 22.8, 20.9, 20.9, 20.9, 20.8, 20.8, 20.8, 20.8, 20.7, 20.7, 20.7, 20.6, 14.2. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{91}H_{148}N_9O_{35}$ 1925.9948; Found 1925.9997.

*(2S,3R,E)-2-Octadecanamido-3-hydroxyoctadec-4-en-1-yl 2-Azidoactamino-2-deoxy-β-D-galactopyranosyl-(1→3)-[2-azidoactamino-2-deoxy-β-D-galactopyranosyl-(1→4)]-β-D-galactopyranosyl-(1→4)-β-D-glucopyranoside (**37**).* Compound **36** (6.8 mg, 68%, a white glassy solid) was prepared from **37** (14 mg, 0.007 mmol) by the same procedure and reaction conditions employed for the synthesis of **6a**. TLC: R_f = 0.3 ($CHCl_3$/MeOH 1:1). ^{1}H NMR (600 MHz, CD_3OD:$CDCl_3$, 3:2): δ 5.70−5.62 (m, 1H), 5.42 (dd, *J* = 15.2, 7.9 Hz, 1H), 4.90 (d, *J* = 8.6 Hz, 1H, anomeric), 4.56 (d, *J* = 8.2 Hz, 1H, anomeric), 4.33−4.22 (m, 4H), 4.19 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.09−4.00 (m, 2H), 4.00−3.89 (m, 4H), 3.90−3.75 (m, 7H), 3.75−3.60 (m, 7H), 3.57−3.47 (m, 7H), 3.37−3.33 (m, 1H), 2.14 (t, *J* = 7.6 Hz, 2H), 2.06−1.95 (m, 2H), 1.65−1.49 (m, 3H), 1.37−1.20 (m, 49H), 0.86 (t, *J* = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, CD_3OD): δ 174.8, 174.6, 134.2, 129.3, 103.6, 103.5, 102.9, 101.8, 83.3, 79.0, 75.2, 74.98, 74.5, 73.9, 73.3, 71.7, 71.5, 71.3, 69.6, 68.5, 61.5, 60.4, 59.9, 58.8, 53.1, 51.8, 36.2, 32.2, 31.7, 29.5, 29.3, 29.2, 26.9, 25.8, 22.4, 13.5. HRMS (ESI-TOF) *m*/*z*: [M − H]$^-$ Calcd for $C_{64}H_{114}N_9O_{23}$ 1376.8022; Found 1376.8009.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02490.

1D and 2D NMR spectra of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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