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Synthesis of Spin-Labeled α-/β-Galactosylceramides and Glucosylceramides as Electron Paramagnetic Probes

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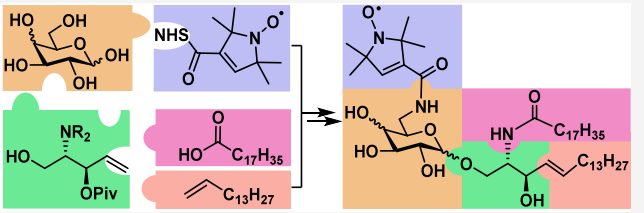
ABSTRACT: α-/β-Galactosylceramide (GalCer) and glucosylceramide (GlcCer) derivatives having a radical label at the 6-*C*-position suitable for electron paramagnetic resonance spectroscopic studies were synthesized by a diversity-oriented strategy that is highlighted by the efficient glycosylation of a lipid precursor and late-stage ceramide assembly to enable lipid diversification. The strategy was also utilized to synthesize natural α-/β-GalCers and GlcCers. Furthermore, the involved azido-intermediates are flexible platforms to access various other GalCer and GlcCer derivatives.



The outer surface of cells is coated with a dense layer of carbohydrates, called the cell glycocalyx.[1] Carbohydrates on cells typically exist as glycoconjugates, such as glycolipids and glycoproteins, and are directly involved in many biological processes.[2] Glycosphingolipids (GSLs) are the major glycolipids in vertebrates and a crucial constituent of the cell membrane and thus have a decisive impact on the structure, organization, and other properties of the cell membrane, to play a key role in human physiology and pathology.[3−5] For instance, GSLs comprise >20% of the total membrane lipids of myelin[6] and >80% of all glycans in the glycocalyx of brain cells.[7] Thus, they participate in a variety of brain activities, including cell recognition, signal transduction and nervous system development,[8−14] and in human diseases like cancer and neurodegeneration.[15−17]

Galactosylceramide (GalCer) and glucosylceramide (GlcCer) belong to a subset of GSLs known as cerebrosides, which are the simplest GSLs with a monosaccharide attached to a ceramide (Cer). In nature, GalCer and GlcCer are predominantly present in the β-linkage form. β-GalCer (**1**, Figure 1) is abundant in the central nervous system and is found to regulate oligodendrocyte differentiation and myelin structure and stability.[18] β-GlcCer (**2**, Figure 1) is widely present in various cells but usually in lower concentrations than β-GalCer. It is most abundant in the human skin and essential for the proper functioning of epidermis.[18] Moreover, β-GalCer and β-GlcCer are the biosynthetic precursors for most other GSLs.[19−21] In mammalians, α-GalCer and α-GlcCer (**3** and **4**, Figure 1) are much less common than the β-counterparts but have been discovered in natural killer T cells.[22] Interestingly, α-linked GalCer/GlcCer and β-GalCer/GlcCer are functionally distinctive. While β-GalCer and β-GlcCer are essential for many physiological functions, α-GalCer and α-GlcCer show unique properties. For example, α-GalCer is proven to provoke immune responses in humans.[23−25] However, the mechanisms by which the glycosidic configuration of cerebrosides influences their biological activities remain unknown.

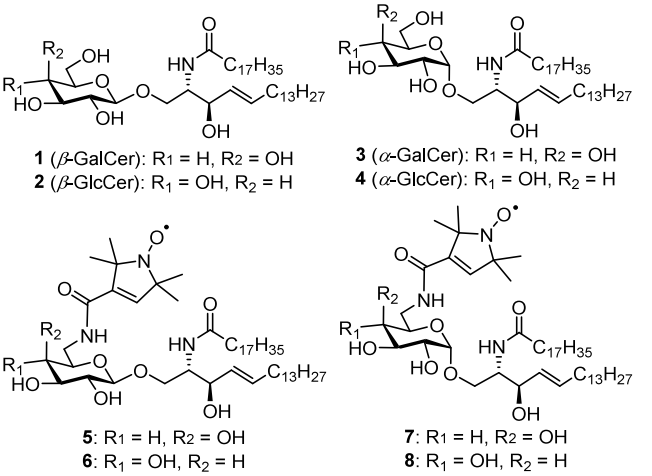


Figure 1. Structures of β-GalCer (**1**), β-GlcCer (**2**), α-GalCer (**3**), and α-GlcCer (**4**) and their spin-labeled derivatives **5**−**8** with a nitroxide radical attached to the sugar residue 6-*C*-position.

For the investigation of GSL organization in the plasma membrane and their influences on the cell membrane properties, electron paramagnetic resonance (EPR) spectroscopy can be a powerful tool since it can provide crucial

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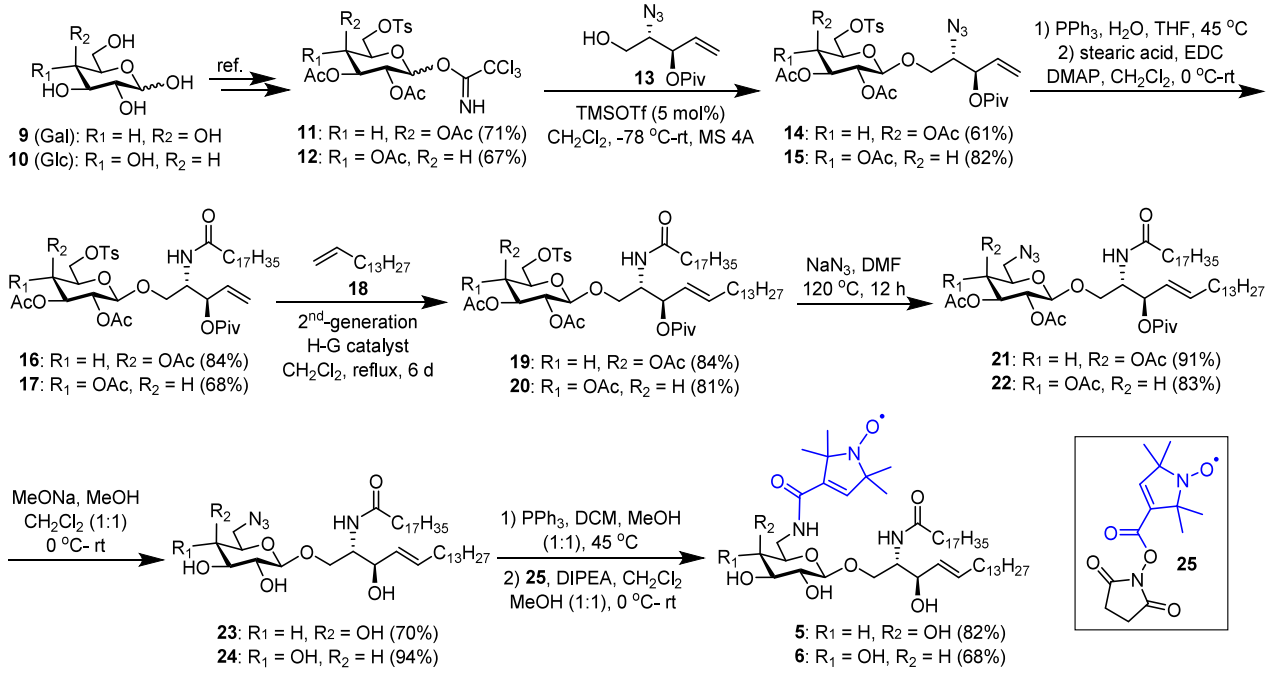
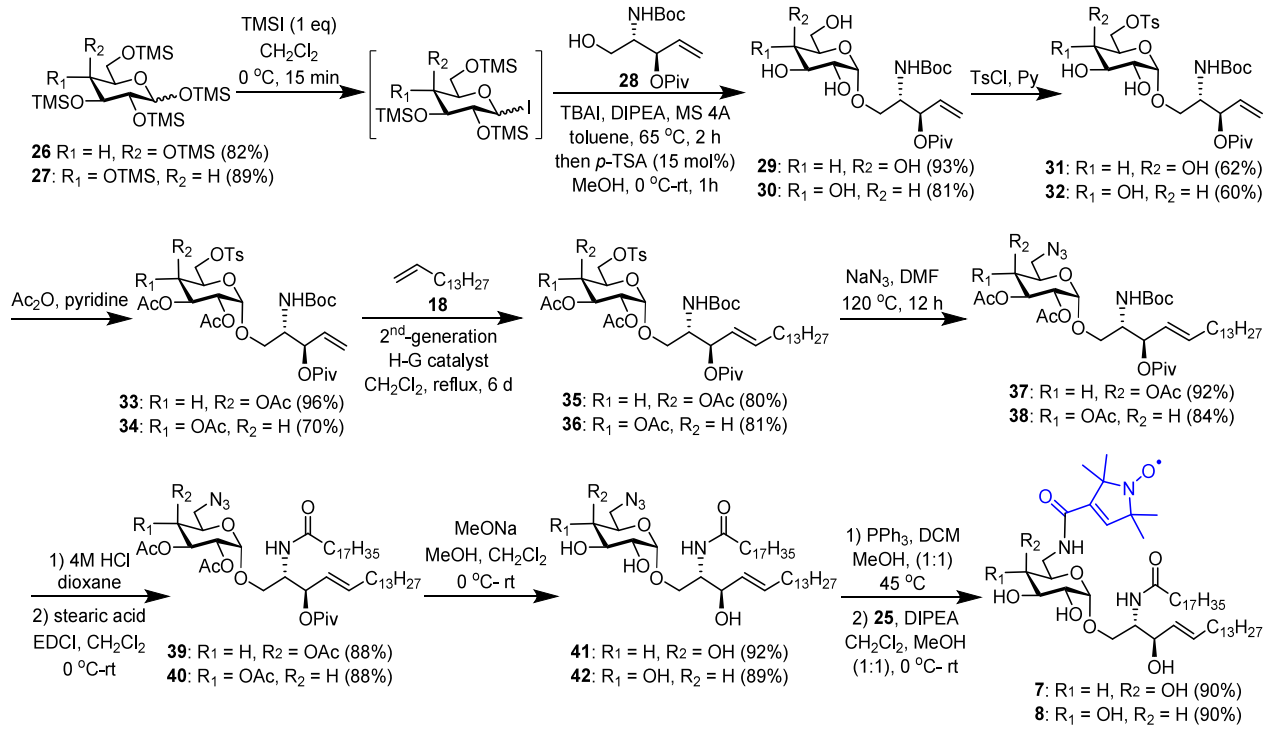
Scheme 1. Synthesis of β-GalCer Probe 5 and β-GlcCer Probe 6



Scheme 2. Synthesis of α-GalCer Probe 7 and α-GlcCer Probe 8



information concerning the orientation, mobility, and dynamics of spin-labeled molecules and their environments through spectral simulation and line shape analysis.[26−28] Therefore, EPR has been widely utilized to explore biological problems.[29−31] For example, we have recently developed methods for spin labeling of glycans on the cell surface through metabolic and enzymatic glycoengineering to facilitate the investigation of glycans on cells by EPR, which have resulted in interesting discoveries, such as targeting of different glycans on the same cell surface by sialyltransferases Pd2,6ST and CSTII.[32−34] To study the functions of β-GalCer and β-GlcCer, we designed and synthesized here spin-labeled GalCer and GlcCer derivatives as paramagnetic probes to facilitate EPR spectroscopic studies. The designed probes, including both β- and α-linked GalCer and GlcCer derivatives **5**−**8** (Figure 1), have a nitroxide radical linked to the sugar unit 6-*C*-position. Comparative EPR studies on these molecules will reveal the influences of the glycan and glycosidic linkage on the biophysical and biochemical properties of GSLs.

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As shown in Scheme 1, our synthesis of spin-labeled β-GalCer **5** and β-GlcCer **6** commenced with the conversion of D-galactose (Gal, **9**) and D-glucose (Glc, **10**) into 6-*O*-tosylated glycosyl donors **11** and **12**,[35−37] respectively, by literature procedures. Glycosylation of the Cer precursor **13**[38] with imidate **11** as a glycosyl donor and trimethylsilyl triflate (TMSOTf) as a promotor was β-selective, probably due to the participation of the 2-*O*-acetyl group, to afford **14** in a good yield (61%). The newly formed β-glycosidic bond in **14** was confirmed by the large coupling constant (J = 7.9 Hz) of its anomeric ^{1}H signal at δ 4.53 ppm. Next, the azido group in **14** was reduced with PPh_3, which was followed by attaching a stearoyl group to the resultant free amine via reacting with steric acid employing 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDC) and 4-dimethylaminopyridine (DMAP) as the condensation reagents to give **16** in an excellent overall yield (84%). Subsequently, the sphingosine moiety was constructed via elongating the olefin in **16** by cross-metathesis using 1-pentadecene **18** in the presence of second generation Hoveyda−Grubbs catalyst (5 mol %) in refluxing dichloromethane (DCM). This reaction was slow (taking 6 days to complete) but clean to yield the desired *E*-olefin **19** selectively without forming the dimer of **17**. The *E*-configuration of the C═C double bond in **19** was verified by the coupling constant (J = 15.4 Hz). For the transformation of **14** into **19**, we also tested an alternative method which was to conduct cross-metathesis first, but it was unsuccessful. We believe that the azido group in **14** may have a negative impact on the catalyst and thus the metathesis. Therefore, the protocol to elongate the olefin chain after reducing the azide and installing the *N*-acyl group proved to be optimal.

To introduce the radical label to **19**, its 6-*C*-(*p*-toluene)-sulfonate group was substituted for an azido group via reacting with NaN_3, which was followed by removing all *O*-acyl groups in **21** to give **23** (70%, two steps). After the azido group in **23** was reduced with PPh_3, the radical label was readily introduced to the resultant free amine with activated ester **25**[39] to afford synthetic target **5** smoothly (82%, two steps). Compound **6** was synthesized from Glc by the same procedure. The final products **5** and **6**, and all synthetic intermediates, were characterized with NMR and HRMS data. Notably, the paramagnetic radicals in **5** and **6** were expected to significantly broaden the NMR signals, making it difficult to determine the coupling constants in the ^{1}H NMR spectra. Indeed, broad NMR signals were observed for **5** and **6**, suggesting the presence of a radical label in their structure. Nonetheless, their NMR spectra have provided critical structural information, including the chemical shifts of proton and carbon signals and the integrals of proton signals.

The synthesis of spin-labeled α-GalCer **7** and α-GlcCer **8** (Scheme 2) started with the preparation of trimethylsilyl (TMS)-protected Gal **26**[40−42] and Glc **27**[43] according to a reported protocol. Here, the nonparticipating TMS group was utilized to protect their 2-*O*-position to promote α-selective glycosylation. The reaction between Cer precursor **28**[44] and **26** or **27** and then deprotection of TMS ethers were achieved in one pot, including converting **26** and **27** into corresponding glycosyl iodides using TMS iodide (TMSI), the reaction of the resultant iodides with **28**, and removal of all TMS groups using *p*-toluenesulfonic acid (*p*-TSA), to give **29** and **30** in excellent overall yields (81−93%). The α-selectivity of this glycosylation was a result of the S_N2 rection between β-glycosyl iodide and **28**. The less reactive α-glycosyl iodide could only react with **28** after being converted into the β-iodide via an S_N2 reaction with tetrabutylammonium iodide (TBAI), thereby realizing a double-reversion transformation.[45] The α-configuration of **29** and **30** was substantiated by a small coupling constant (J = 3.4 Hz) of their anomeric ^{1}H NMR signals.

To functionalize the 6-*C*-position of **29**, first, its 6-OH group was regioselectively tosylated using toluenesulfonic chloride (TsCl) in pyridine, which was followed by protecting the remaining OH groups with acetyl groups using acetic anhydride (Ac_2O). Subsequently, the olefin chain in **33** was elongated via cross-metathesis using **18** and then substitution of the 6-*C*-(*p*-toluene)sulfonate group with an azido group as mentioned previously. Removal of the *N*-*tert*-butyloxycarbonyl (Boc) group in **37** was achieved under acidic conditions to expose the free amine for coupling with stearic acid, which was followed by acetyl group deletion using NaOMe to produce **41**. Finally, the azido group in **41** was reduced with PPh_3, and the radical label was attached to the resultant amine by reacting with activated ester **25** to provide **7**. Compound **8** was prepared by the same procedure. The targets **7** and **8** and all synthetic intermediates were characterized with NMR and HRMS data.

Next, we studied the application of this synthetic strategy for **5**−**8** to prepare natural β-/α-GalCer and GlcCer **1**−**4**. Compared to the syntheses of **1**−**4** by others in literature,[40−42,46−51] this new synthetic strategy has several advantages. First, it constructs the Cer moiety at the final stage, which not only enables large-scale synthesis but also offers high efficiency, as the glycosylation engages a simple Cer precursor. Second, this strategy facilitates Cer diversification, as different lipid chains can be formed at the lipid remodeling stage.

In the synthesis of β-isomers **1** and **2** (Scheme 3A), Gal and Glc were converted into galactosyl and glucosyl donors **43**[35] and **44**[35] by conventional procedures[40−42,48] and then efficiently coupled with **13** under above-mentioned conditions. Again, this glycosylation was β-selective due to neighboring group participation. Then, **45** and **46** were subjected to lipid remodeling by the two-stage protocol, i.e., reducing the azide and coupling the resultant amine with stearic acid to install the *N*-fatty acyl group followed by olefin elongation, to produce **49** and **50**. The *E*-configuration of the C═C double bond in **49** and **50** was verified by the coupling constant of their vinyl protons (J = 15.4 Hz). Finally, all *O*-acetyl groups in **49** and **50** were removed with NaOMe in MeOH to give the synthetic targets **1**[42,47] and **2**[48,49] in excellent overall yields (41−44%) starting from **43** and **44**, respectively. In the synthesis of α-GalCer **3** and α-GlcCer **4** (Scheme 3B), the free OH groups in **29** and **30** were protected with acetyl groups, and the products **51** and **52** were subjected to the two-stage lipid remodeling protocol conducted in the reversed order, i.e., elongating the olefin via cross-metathesis first and then introducing the *N*-fatty acyl group after deprotection of the amino group, to produce **55** and **56**. Subsequent global deprotection of **55** and **56** afforded **3**[40,50,51] and **4**,[41] respectively, in overall yields of 53−62% starting from **29** and **30**.

In conclusion, we have developed an efficient method for the synthesis of both α- and β-GalCer and GlcCer and their spin-labeled derivatives. This method is highlighted by utilizing a simple Cer precursor to build the glycosidic linkage between glycan and lipid, which can be realized in a large scale and high efficiency, and assemble the Cer moiety at the final stage, which enables diversity-oriented synthesis to access various

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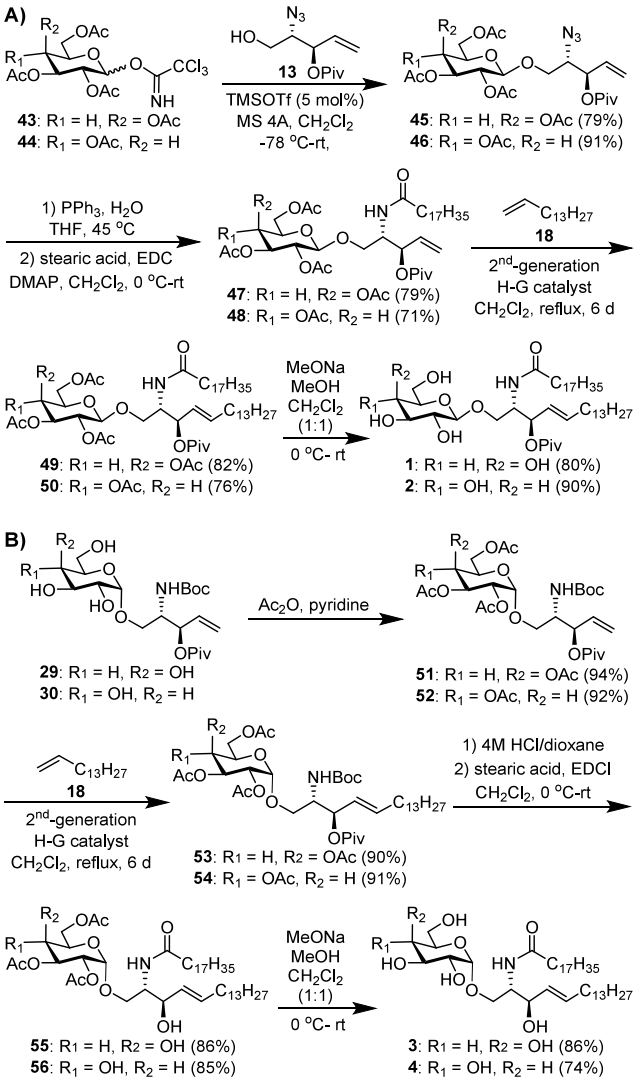
Scheme 3. Synthesis of (A) β-GalCer 1 and β-GlcCer 2, and (B) α-GalCer 3 and α-GlcCer 4



lipid forms of target cerebrosides. This method can be applied to other natural cerebrosides and their derivatives. Spin-labeled GalCer and GlcCer probes **5**–**8** are useful tools for biochemical and biophysical studies by EPR spectroscopy, currently pursued in our lab. Moreover, the involved azido intermediates **23**, **24**, **41**, and **42** are also flexible platforms to access other functionalized GalCer and GlcCer probes. For example, molecular labels such as fluorescent and affinity tags can be easily linked to **23**, **24**, **41**, and **42** either by click chemistry or via selective azide reduction and *N*-acylation. The resulting probes should be widely useful.

EXPERIMENTAL SECTION

General Procedures. Chemicals and materials were purchased from commercial sources and used as received without further purification unless otherwise noted. Molecular sieves 4 Å (MS 4 Å) were flame-dried under a high vacuum and used immediately after being cooled to rt under an N_2 atmosphere. Analytical TLC was carried out on silica gel 60 Å F254 plates with detection by a UV detector and/or by charring with 10% (v/v) H_2SO_4 in ethanol and anisaldehyde stain. Flash column chromatography was performed on silica gel 60 (230–400 mesh). NMR spectra were acquired on a 400 or 600 MHz NMR spectrometer with chemical shifts (δ) reported in ppm referenced to $CDCl_3$ (^{1}H NMR: δ 7.26 ppm; $^{13}C\{^1H\}$ NMR: δ 77.16 ppm) or CD_3OD (^{1}H NMR: δ 3.31 ppm; $^{13}C\{^1H\}$ NMR: δ 49.0 ppm). Peak and coupling constant assignments are based on ^{1}H NMR, ^{1}H–^{1}H COSY, ^{1}H–$^{13}C\{^1H\}$ HSQC, and ^{1}H–$^{13}C\{^1H\}$ HMBC experiments. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. High-resolution mass spectra (HRMS) were recorded with a Bruker Daltonics, Impact II QTOF (ESI) instrument. An aluminum heating block was used as the heating source for reactions.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-β-D-galactopyranoside (**14**).* After a mixture of (3*R*,4*S*)-4-azido-5-hydroxypent-1-en-3-yl pivalate **13**[38] (210 mg, 0.92 mmol), 2,3,4-tri-*O*-acteyl-6-*O*-(*p*-toluenesulfonyl)-galactosyl trichloroimidate **11** (894 mg, 1.48 mmol), TMSOTf (9.33 μL, 0.046 mmol), and flame-dried MS 4 Å (1.00 g) in dry CH_2Cl_2 (10 mL) was stirred at −50 °C for 60 min, it was allowed to warm to room temperature (rt) and stirred for 3 h, when TLC showed the complete consumption of **13**. Thereafter, the reaction was quenched with triethylamine. MS 4 Å was removed by filtration through a Celite pad. The organic layer was extracted with saturated aq. $NaHCO_3$ solution and brine and dried over Na_2SO_4. The solvent was evaporated in vacuo, and the product was purified by silica gel column chromatography to afford **14** (380 mg, 61%) as syrup. TLC: R_f = 0.3 (EtOAc/Hex, 2/3). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 5.81 (ddd, J = 17.3, 10.3, 7.1 Hz, 1H), 5.39–5.32 (m, 4H), 5.17 (dd, J = 10.5, 7.9 Hz, 1H), 4.97 (dd, J = 10.5, 3.4 Hz, 1H), 4.45 (d, J = 8.0 Hz, 1H, anomeric), 4.11 (dd, J = 10.2, 6.6 Hz, 1H), 4.00 (dd, J = 10.2, 6.1 Hz, 1H), 3.94 (td, J = 6.4, 1.2 Hz, 1H), 3.86 (dd, J = 10.4, 6.6 Hz, 1H), 3.78 (td, J = 6.3, 4.0 Hz, 1H), 3.51 (dd, J = 10.4, 6.0 Hz, 1H), 2.46 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.96 (s, 3H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.0, 170.13, 170.1, 169.5, 145.5, 132.4, 131.6, 130.2, 128.2, 120.5, 101.0, 73.9, 71.0, 70.8, 68.5, 68.0, 67.0, 66.3, 63.2, 39.1, 27.2, 21.8, 20.8, 20.1. HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{29}H_{39}N_3O_{13}S$ 687.2542; Found 687.2558.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-β-D-glucopyranoside (**15**).* Compound **15** (228 mg, 82%) as syrup was synthesized from **12** (250 mg, 0.41 mmol) and **13** (75.2 mg, 0.33 mmol) by the same procedure and conditions employed to synthesize **14**. TLC: R_f = 0.6 (EtOAc/Toluene, 2/3). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 5.84–5.77 (m, 1H), 5.39–5.35 (m, 1H), 5.35–5.30 (m, 2H), 5.17 (t, J = 9.5 Hz, 1H), 4.96–4.90 (m, 2H), 4.48 (d, J = 7.9 Hz, 1H), 4.11 (dd, J = 11.1, 2.9 Hz, 1H), 4.07 (dd, J = 11.1, 5.9 Hz, 1H), 3.82 (dd, J = 10.1, 6.7 Hz, 1H), 3.79–3.73 (m, 2H), 3.50 (dd, J = 10.1, 5.5 Hz, 1H), 2.46 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.22 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.0, 170.3, 169.6, 169.4, 145.4, 132.9, 131.6, 130.1, 128.2, 120.5, 100.4, 73.8, 72.6, 72.0, 71.0, 68.7, 68.0, 67.7, 63.2, 39.1, 27.2, 21.8, 20.8, 20.7, 20.6. HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{29}H_{39}N_3O_{13}S$ 687.2542; Found 687.2561.

*(2S,3R)-2-Octadecanamido-3-(pivaloyloxy)pent-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-β-D-galactopyranoside (**16**).* PPh_3 (286 mg, 1.09 mmol) and water (98 μL, 5.45 mmol) were added to a stirred solution of **14** (365 mg, 0.55 mmol) in THF (6 mL), and the mixture was heated at 45 °C with stirring until TLC indicated the disappearance of **14**. After the solvent was removed under vacuum and stripped with toluene three times, the residue was dissolved in dry DCM (4 mL). Then, EDC (208 mg, 1.09 mmol), DMAP (13.3 mg, 0.11 mmol), and stearic acid (309 mg, 1.1 mmol) in DCM (4 mL) 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 in vacuo. The residue was purified by silica gel column chromatography to afford **16** (419 mg, 84%) as a colorless syrup. TLC: R_f = 0.76 (EtOAc/Hex, 3/2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 5.79 (ddd, J = 17.0, 10.6, 6.2 Hz, 1H), 5.71 (d, J = 9.2 Hz, 1H, −N*H*CO−), 5.37–5.24 (m, 4H), 5.10 (dd, J = 10.5, 7.8 Hz, 1H), 4.97 (dd, J = 10.5, 3.4 Hz, 1H), 4.41 (d, J

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= 7.9 Hz, 1H, anomeric), 4.40−4.35 (m, 1H), 4.08 (dd, J = 10.2, 6.5 Hz, 1H), 4.01−3.95 (m, 2H), 3.92 (dd, J = 6.3, 1.8 Hz, 1H), 3.56 (dd, J = 9.9, 4.5 Hz, 1H), 2.46 (s, 3H), 2.18−2.10 (m, 2H), 2.06 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.64−1.53 (m, 2H), 1.33−1.23 (m, 28H), 1.21 (s, 9H), 0.88 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.2, 172.9, 170.1, 169.8, 145.5, 133.3, 132.4, 130.2, 128.2, 118.9, 101.1, 73.5, 70.9, 70.6, 68.9, 67.6, 66.9, 66.2, 50.3, 39.0, 36.9, 32.1, 29.9, 29.8, 29.8, 29.7, 29.5, 29.5, 29.5, 27.2, 25.8, 22.8, 21.8, 21.0, 20.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{47}H_{75}NO_{14}S$ 910.4981; Found 910.5006.

(2S,3R)-2-Octadecanamido-3-(pivaloyloxy)pent-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-β-D-glucopyranoside (17). Compound **17** (210 mg, 68%) was synthesized from **15** (230 mg, 0.34 mmol) by the same procedure and conditions employed to synthesize **16**. TLC: R_f = 0.9 (EtOAc/Hex, 4/2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 5.85−5.73 (m, 1H), 5.71 (d, J = 9.1 Hz, 1H, −N*H*CO−), 5.34−5.22 (m, 3H), 5.17 (t, J = 9.4 Hz, 1H), 4.98−4.85 (m, 2H), 4.44 (d, J = 7.8 Hz, 1H, anomeric), 4.37 (dt, J = 9.8, 4.5 Hz, 1H), 4.15−4.03 (m, 2H), 3.92 (dd, J = 10.0, 4.4 Hz, 1H), 3.79−3.71 (m, 1H), 3.57 (dd, J = 10.0, 4.5 Hz, 1H), 2.46 (s, 3H), 2.13 (td, J = 7.7, 3.2 Hz, 2H), 2.03 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.64−1.58 (s, 2H), 1.35−1.21 (s, 28H), 1.19 (s, 9H), 0.88 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 177.2, 173.0, 170.3, 169.6, 169.5, 145.4, 133.2, 132.6, 130.1, 128.2, 118.8, 100.6, 73.5, 72.4, 71.8, 71.4, 68.6, 67.7, 67.5, 50.4, 39.0, 36.9, 32.1, 29.9, 29.8, 29.7, 29.5, 29.5, 29.4, 27.2, 25.9, 22.8, 21.8, 20.9, 20.7, 20.6, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{47}H_{75}NO_{14}S$ 910.4981; Found 910.5007.

(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-β-D-galactopyranoside (19). To a solution of **16** (249 mg, 0.27 mmol) and pentadec-1-ene **18** (0.45 mL, 1.64 mmol) in dry CH_2Cl_2 (28 mL) was added the Hoveyda−Grubbs second-generation catalyst (8.59 mg, 0.014 mmol). The mixture was heated to reflux for 6 days. During the process, a batch of **18** (0.074 mL, 0.27 mmol) and Hoveyda−Grubbs second-generation catalyst (2 mol %) were added every 24 h. Thereafter, 2 drops of DMSO were added to the mixture at rt, followed by stirring for 2 h. The mixture was concentrated, and the product was purified by silica gel column chromatography to give **19** (252 mg, 84%) as a colorless syrup. TLC: R_f = 0.41 (EtOAc/Hex, 2/3).^1H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 5.76 (dt, J = 14.0, 6.8 Hz, 1H), 5.66 (d, J = 9.3 Hz, 1H. −N*H*CO−), 5.38−5.30 (m, 2H), 5.20 (t, J = 7.0 Hz, 1H), 5.10 (dd, J = 10.5, 7.8 Hz, 1H), 4.97 (dd, J = 10.5, 3.4 Hz, 1H), 4.40 (d, J = 7.8 Hz, 1H, anomeric), 4.36−4.30 (m, 1H), 4.07 (dd, J = 10.2, 6.4 Hz, 1H), 4.01−3.87 (m, 3H), 3.53 (dd, J = 9.9, 4.4 Hz, 1H), 2.46 (s, 2H), 2.19−2.09 (m, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03−1.99 (m, 2H), 1.97 (s, 3H), 1.61−1.52 (m, 2H), 1.36−1.22 (m, 50H), 1.18 (s, 9H), 0.88 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.2, 172.8, 170.1, 169.7, 145.5, 137.2, 132.4, 130.2, 128.2, 124.9, 101.1, 73.5, 70.8, 70.6, 68.9, 67.8, 66.8, 66.1, 50.6, 39.0, 37.0, 32.4, 32.1, 29.9, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 27.2, 25.9, 22.8, 21.8, 21.0, 20.7, 20.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{60}H_{101}NO_{14}S$ 1092.7016; Found 1092.7048.

(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-β-D-glucopyranoside (20). Compound **20** (131 mg, 81%) was synthesized from **17** (135 mg, 0.15 mmol) by the same procedure and conditions employed to synthesize **19**. TLC: R_f = 0.5 (EtOAc/Hex, 2/3). ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 5.80−5.69 (m, 1H), 5.65 (d, J = 9.2 Hz, 1H, −N*H*CO−), 5.34 (dd, J = 15.4, 7.3 Hz, 1H), 5.24−5.12 (m, 2H), 4.98−4.84 (m, 2H), 4.43 (d, J = 7.8 Hz, 1H, anomeric), 4.33 (dq, J = 6.5, 4.4 Hz, 1H), 4.09 (qd, J = 11.1, 4.2 Hz, 2H), 3.89 (dd, J = 9.9, 4.4 Hz, 1H), 3.74 (ddd, J = 10.0, 5.2, 3.1 Hz, 1H), 3.54 (dd, J = 9.9, 4.4 Hz, 1H), 2.45 (s, 3H), 2.17−2.07 (m, 2H), 2.02 (s, 3H), 2.02−1.99 (m, 2H), 1.99 (s, 3H), 1.98 (s, 3H), 1.60−1.51 (m, 2H), 1.33−1.22 (m, 50H), 1.16 (s, 9H), 0.87 (t, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 177.2, 172.8, 170.3, 169.6, 169.5, 145.4, 137.1, 132.6, 130.1, 128.2, 124.8, 100.6, 73.4, 72.5, 71.8, 71.3, 68.6, 67.8, 67.5, 50.6, 39.0, 37.0, 32.4, 32.1, 29.9, 29.8, 29.7, 29.6, 29.6, 29.5, 29.3, 29.1, 27.2, 25.9, 22.8, 21.8, 20.8, 20.7, 20.6, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{60}H_{101}NO_{14}S$ 1092.7016; Found 1092.7051.

(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-β-D-galactopyranoside (21). After compound **19** (233 mg, 0.21 mmol) was dissolved in dry DMF (6 mL), NaN_3 (69.4 mg, 1.07 mmol) was added, and the mixture was heated at 120 °C for 12 h. After the reaction was complete, as indicated by TLC, it was cooled to rt and then diluted with ethyl acetate. The organic layer was separated, washed with cold brine and water, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography to afford **21** (187.5 mg, 91%) as colorless syrup. TLC: R_f = 0.56 (EtOAc/Hex, 2/3). ^1H NMR (600 MHz, $CDCl_3$): δ 5.80−5.73 (m, 1H), 5.66 (d, J = 9.3 Hz, 1H, −N*H*CO−), 5.39−5.32 (m, 2H), 5.24 (t, J = 6.9 Hz, 1H), 5.16 (dd, J = 10.5, 7.8 Hz, 1H), 5.00 (dd, J = 10.5, 3.4 Hz, 1H), 4.46 (d, J = 7.9 Hz, 1H, anomeric), 4.40−4.33 (m, 1H), 3.98 (dd, J = 10.0, 4.4 Hz, 1H), 3.81 (ddd, J = 8.0, 4.6, 1.3 Hz, 1H), 3.60 (dd, J = 10.1, 4.4 Hz, 1H), 3.49 (dd, J = 12.9, 8.1 Hz, 1H), 3.16 (dd, J = 12.9, 4.6 Hz, 1H), 2.18 (s, 3H), 2.16−2.10 (m, 2H), 2.05 (s, 3H), 2.05−2.00 (m, 2H), 1.99 (s, 3H), 1.62−1.55 (m, 2H), 1.37−1.21 (m, 50H), 1.19 (s, 9H), 0.88 (t, J = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.3, 172.7, 170.3, 170.1, 169.7, 137.0, 124.8, 101.2, 73.7, 72.9, 70.8, 69.0, 67.9, 67.6, 50.7, 50.6, 39.0, 37.0, 32.4, 32.1, 29.9, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.3, 29.1, 27.3, 27.2, 25.9, 22.8, 21.0, 20.8, 20.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{53}H_{94}N_4O_{11}$ 963.6992; Found 963.7012.

(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-β-D-glucopyranoside (22). Compound **22** (110 mg, 83%) as the colorless syrup was prepared from **20** (150 mg, 0.14 mmol) by the same procedure and conditions employed to synthesize **21**. TLC: R_f = 0.65 (EtOAc/Hex, 2/3). ^1H NMR (400 MHz, $CDCl_3$): δ 5.81−5.70 (m, 1H), 5.62 (d, J = 9.2 Hz, 1H, −N*H*CO−), 5.35 (dd, J = 15.3, 7.2 Hz, 1H), 5.29−5.16 (m, 2H), 5.03−4.92 (m, 2H), 4.51 (d, J = 7.9 Hz, 1H, anomeric), 4.36 (dt, J = 10.4, 4.5 Hz, 1H), 3.93 (dd, J = 10.1, 4.6 Hz, 1H), 3.69 (ddd, J = 9.7, 6.7, 2.7 Hz, 1H), 3.63 (dd, J = 10.1, 4.3 Hz, 1H), 3.36 (dd, J = 13.4, 6.7 Hz, 1H), 3.28 (dd, J = 13.4, 2.8 Hz, 1H), 2.16−2.07 (m, 2H), 2.04 (s, 3H), 2.04 (s, 3H), 2.03−1.97 (m, 5H, COC*H*$_3$ and −CH═CH−C*H*$_2$−), 1.60−1.55 (m, 2H), 1.35−1.21 (m, 50 H), 1.19 (s, 9H), 0.88 (t, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 177.2, 172.7, 170.3, 169.6, 169.5, 136.9, 124.7, 100.7, 73.7, 72.5, 71.4, 69.6, 67.8, 51.1, 50.6, 39.0, 37.0, 32.4, 32.0, 29.8, 29.8, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 27.2, 25.8, 22.8, 20.8, 20.7, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{53}H_{94}N_4O_{11}$ 963.6992; Found 963.7020.

(2S,3R,E)-2-Octadecanamido-3-(hydroxy)octadec-4-en-1-yl 6-azido-6-deoxy-β-D-galactopyranoside (23). To a solution of **21** (70 mg, 0.072 mmol) in dry MeOH/DCM (1:1, 3 mL) was added NaOMe in MeOH (4 M, 150 μL, 0.44 mmol) at 0 °C. After stirring the reaction mixture at rt for 2 days, it was neutralized with Dowex 50W (H^+) resin, filtered, and concentrated under reduced pressure. The product was purified by silica gel column chromatography to give **23** (38.2 mg, 70%) as a glassy solid. TLC: R_f = 0.2 (DCM/MeOH, 4/1). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 5.67 (dt, J = 15.6, 6.8 Hz, 1H), 5.50−5.36 (m, 1H), 4.18 (d, J = 7.3 Hz, 1H, anomeric), 4.13−3.96 (m, 3H), 3.78−3.73 (m, 1H), 3.68−3.53 (m, 4H), 3.53−3.45 (m, 2H), 3.25 (dd, J = 12.1, 3.5 Hz, 1H), 2.15 (dd, J = 8.6, 6.8 Hz, 2H), 1.98 (q, J = 7.2 Hz, 2H), 1.56 (p, J = 7.5 Hz, 2H), 1.22 (s, 50H), 0.84 (t, J = 6.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$:CD_3OD 4:1): δ 174.6, 134.2, 128.7, 103.6, 74.3, 73.1, 72.6, 71.0, 68.9, 53.2, 51.0, 36.5, 32.3, 31.8, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 25.8, 22.6, 14.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{80}N_4O_7$ 753.6100; Found 753.6121.

(2S,3R,E)-2-Octadecanamido-3-(hydroxy)octadec-4-en-1-yl 6-azido-6-deoxy-β-D-glucopyranoside (24). Compound **24** (55 mg, 94%) as colorless syrup was prepared from **22** (75 mg, 0.077 mmol) by the same procedure and conditions utilized to synthesize **23**. TLC: R_f = 0.45 (DCM/MeOH, 9/1). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 5.66−5.57 (m, 1H), 5.36 (dd, J = 15.4, 6.8 Hz, 1H), 4.17 (d, J = 7.7 Hz, 1H), 4.07−3.92 (m, 3H), 3.55−3.53 (m, 1H), 3.47−3.41 (s,

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1H), 3.39−3.34 (m, 2H), 3.30 (dd, J = 16.5, 7.7 Hz, 2H), 3.23 (d, J = 30.2 Hz, 1H), 3.20−3.15 (m, 1H), 2.10−2.08 (m, 2H), 1.96−1.88 (m, 2H), 1.54−1.46 (m, 2H), 1.30−1.10 (m, 50H), 0.78 (t, J = 6.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$:CD_3OD 4:1): δ 174.1, 134.0, 128.1, 102.8, 75.8, 75.0, 72.9, 72.7, 70.3, 68.7, 52.7, 51.0, 36.3, 31.9, 31.5, 29.3, 29.2, 29.1, 29.1, 29.0, 28.9, 28.8, 28.7, 25.4, 22.3, 13.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{80}N_4O_7$ 753.6100; Found 753.6126.

*(2S,3R,E)-2-Octadecanamido-octadec-4-en-1-yl 6-deoxy-6-[(1-oxyl-2,2,5,5-tetramethyl-2,5-dihydro-1H-pyrrole)-3-carboxamido]-6-deoxy-β-D-galactopyranoside (**5**).* After compound **23** (11.0 mg, 0.015 mmol) was dissolved in DCM/MeOH (1:1, 1.0 mL), triphenylphosphine (4.6 mg, 0.020 mmol) was added, and the reaction mixture was stirred at rt overnight. After the reaction was complete, as determined by TLC, the mixture was filtrated through a short silica gel column. The solution was condensed under vacuum, and the crude product was dissolved in DCM/MeOH (1:1, 2 mL). Then, DIPEA (19.2 μL, 0.11 mmol) and activated ester **25** (31.2 mg, 0.11 mmol) were added. After the reaction was complete, as determined by TLC, the mixture was condensed under vacuum, and the product was purified by silica gel column chromatography to give **5** (10 mg, 82%) as a pale-yellow glassy solid. TLC: R_f = 0.46 (DCM/MeOH, 4.5/0.5). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD 3:2): δ 5.70 (brs, 1H), 5.47 (brs, 1H), 4.26−4.15 (brm, 3H), 4.13 (brs, 1H), 4.00 (brs, 2H), 3.81−3.46 (brm, 6H), 2.18 (brs, 2H), 2.03 (brs, 2H), 1.59 (brs, 2H), 1.27 (brs, 50H), 0.89 (t, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$: CD_3OD 3:2): δ 175.8, 136.9, 134.6, 129.0, 103.9, 74.1, 73.5, 72.3, 71.5, 69.3, 69.2, 54.1, 36.8, 32.7, 32.2, 32.1, 30.0, 29.9, 29.9, 29.9, 29.9, 29.9, 29.8, 29.7, 29.7, 29.6, 29.6, 29.6, 26.3, 22.9, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{51}H_{94}N_3O_9$ 893.7063; Found 893.7082.

*(2S,3R,E)-2-Octadecanamido-octadec-4-en-1-yl 6-deoxy-6-[(1-oxyl-2,2,5,5-tetramethyl-2,5-dihydro-1H-pyrrole)-3-carboxamido]-6-deoxy-β-D-glucopyranoside (**6**).* Compound **6** (6.50 mg, 68%) as a pale-yellow glassy solid was prepared from **24** (8.00 mg, 0.011 mmol) by the same procedure and conditions utilized to synthesize **5**. TLC: R_f = 0.55 (DCM/MeOH, 4.5/0.5). ^1H NMR (600 MHz, $CDCl_3$: CD_3OD 3:2): δ 5.72 (brs, 1H), 5.48 (brs, 1H), 4.33 (brs, 1H), 4.15 (brs, 3H), 4.04 (brs, 1H), 3.66 (brs, 2H), 3.54 (brs, 2H), 3.30−3.10 (brm, 3H), 2.16 (brs, 2H), 2.02 (brs, 2H), 1.59 (brs, 2H), 1.46−1.15 (m, 50H), 0.86 (t, J = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$: CD_3OD 3:2): δ 173.5, 134.2, 128.1, 103.1, 74.6, 72.8, 72.2, 69.5, 68.7, 52.6, 36.1, 31.8, 31.3, 31.3, 29.1, 29.1, 29.1, 29.0, 28.9, 28.8, 28.7, 28.7, 28.6, 25.2, 22.1, 22.1, 13.5, 13.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{51}H_{94}N_3O_9$ 893.7063; Found 893.7084.

*(2S,3R)-2-[(tert-Butoxycarbonyl)amino]-3-(pivaloyloxy)-pent-4-en-1-yl α-D-galactopyranoside (**29**).* TMSI (528 μL, 3.70 mmol) was added to a solution of **26**[40−42] (2.00 g, 3.70 mmol) in CH_2Cl_2 (30.0 mL) at 0 °C. The reaction mixture was stirred under an argon atmosphere for 15 min. The reaction was diluted with 15 mL of toluene and azeotrope thrice with toluene. The slightly yellow glycosyl iodide intermediate obtained was dissolved in toluene (10.0 mL) and kept under an argon atmosphere. In a separate flask, a mixture of activated molecular sieves 4 Å (MS 4 Å) (800 mg), n-Bu_4NI (3.86 g, 10.5 mmol), i-Pr_2NEt (1.37 mL, 7.84 mmol), and **28**[44] (0.53 g, 1.74 mmol) in toluene (15 mL) was stirred under an argon atmosphere at 65 °C for 40 min. The solution of glycosyl iodide was then added dropwise over 10 min to this mixture, and the resulting mixture was stirred at 65 °C for 5 h. The reaction was stopped by adding EtOAc (20.0 mL) and cooling to 0 °C, and the white precipitates and MS 4 Å were filtered through a Celite pad. The filtrate was washed with saturated $Na_2S_3O_3$ aq. solution and brine, dried with anhydrous Na_2SO_4, and concentrated in vacuo, and the resulting residue was dissolved in MeOH (30 mL) and cooled to 0 °C. This was followed by adding *para*-toluene sulfonic acid (29.9 mg, 0.174 mmol), and the reaction was stirred at rt for 45 min. After completion of the reaction as indicated by TLC, it was quenched with saturated $NaHCO_3$ aq. solution. The product was extracted, and the solvent was removed in vacuo. The residue was purified by silica gel to afford **29** (0.75 g, 94%) as a colorless syrup. TLC: R_f = 0.29 (DCM/MeOH, 7/1). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 5.83 (ddd, J = 17.1, 10.6, 6.4 Hz, 1H), 5.38−5.25 (m, 3H), 4.81 (d, J = 3.7 Hz, 1H, anomeric), 4.04−3.98 (m, 2H), 3.82−3.72 (m, 6H), 3.51 (dd, J = 10.8, 5.7 Hz, 1H), 1.44 (s, 9H), 1.22 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$: CD_3OD 4:1): δ 177.9, 156.3, 132.6, 118.9, 99.8, 79.8, 73.1, 70.5, 70.2, 69.7, 69.1, 67.2, 61.8, 52.8, 38.9, 28.2, 26.9. HRMS (ESI) m/z: $[M + CO_2H]^-$ Calcd for $C_{21}H_{37}NO_{10}$ 508.2389; Found 508.2405.

*(2S,3R)-2-[(tert-Butoxycarbonyl)amino]-3-(pivaloyloxy)-pent-4-en-1-yl α-D-glucopyranoside (**30**).* Compound **30** (0.650 g, 81%) as a colorless syrup was prepared from **27**[43] (2.14 g, 3.70 mmol) and **28**[44] (0.53 g, 1.74 mmol) by the same procedure and conditions employed to synthesize **29**. TLC: R_f = 0.27 (DCM/MeOH, 9/1). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 5.79 (ddd, J = 17.0, 10.4, 6.4 Hz, 1H), 5.41 (d, J = 9.5 Hz, 1H), 5.35 (t, J = 6.5 Hz, 1H), 5.32−5.25 (m, 2H), 4.72 (d, J = 3.2 Hz, 1H, anomeric), 4.05−3.95 (m, 1H), 3.81−3.72 (m, 3H), 3.68 (t, J = 9.2 Hz, 1H), 3.56−3.54 (m, 1H), 3.46−3.41 (m, 3H), 1.40 (s, 9H), 1.18 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$:CD_3OD 4:1): δ 177.5, 155.5, 132.3, 118.7, 98.9, 79.5, 73.5, 72.3, 71.7, 71.4, 69.6, 66.9, 61.3, 52.1, 38.5, 27.8, 26.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{37}NO_{10}$ 464.2490; Found 464.2498.

*(2S,3R)-2-[(tert-Butoxycarbonyl)amino]-3-(pivaloyloxy)-pent-4-en-1-yl 6-O-(p-toluenesulfonyl)-α-D-galactopyranoside (**31**).* To a solution of **29** (330 mg, 0.71 mmol) in pyridine (1.0 mL) was added *para*-toluene sulfonyl chloride (136 mg, 0.71 mmol) in portions at 0 °C, and the solution was stirred at rt overnight. After completion of the reaction, it was quenched with MeOH. The solvents were removed under vacuum. The residue was stripped with toluene three times. The resultant residue was purified with silica gel column chromatography to offer **31** (273 mg, 62%) as syrup. TLC: R_f = 0.73 (DCM/MeOH, 7/1). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 7.74 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.79 (ddd, J = 16.8, 10.5, 6.1 Hz, 1H), 5.40−5.21 (m, 3H), 4.71 (d, J = 3.0 Hz, 1H, anomeric), 4.31−4.04 (m, 2H), 4.04−3.92 (m, 2H), 3.86 (brs, 1H), 3.80−3.65 (m, 3H), 3.51−3.30 (m, 1H), 2.41 (s, 3H), 1.40 (s, 9H), 1.18 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$:CD_3OD 4:1): δ 156.0, 145.2, 132.6, 132.4, 132.38, 120.0, 128.0, 119.3, 99.5, 80.1, 72.9, 70.0, 69.2, 69.2, 69.0, 68.7, 67.5, 67.5, 52.5, 39.1, 28.3, 27.1, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{43}NO_{12}S$ 618.2579; Found 618.2594.

*(2S,3R)-2-[(tert-Butoxycarbonyl)amino]-3-(pivaloyloxy)-pent-4-en-1-yl 6-O-(p-toluenesulfonyl)-α-D-glucopyranoside (**32**).* Compound **32** (160 mg, 60%) as colorless syrup was prepared from **30** (200 mg, 0.43 mmol) by the same procedure and conditions employed to synthesize **31**. TLC: R_f = 0.6 (DCM/MeOH, 9/1). ^1H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 5.82 (ddd, J = 17.2, 10.4, 6.7 Hz, 1H), 5.41 (t, J = 9.7 Hz, 1H), 5.33 (dd, J = 24.3, 13.9 Hz, 1H), 5.27 (t, J = 6.9 Hz, 1H), 4.95 (t, J = 9.8 Hz, 1H), 4.91 (d, J = 3.2 Hz, 1H), 4.77 (dt, J = 16.3, 8.0 Hz, 1H), 4.16−4.07 (m, 2H), 4.07−3.97 (m, 2H), 3.70 (dd, J = 10.3, 3.3 Hz, 1H), 3.47 (dd, J = 10.3, 3.5 Hz, 1H), 2.47 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.47 (s, 9H), 1.20 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.0, 176.8, 170.2, 170.2, 169.4, 155.3, 145.1, 133.0, 129.9, 128.1, 119.3, 96.5, 80.0, 72.8, 70.3, 69.9, 68.6, 67.7, 67.3, 67.2, 52.2, 38.8, 28.3, 27.1, 21.7, 20.7, 20.6, 20.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{43}NO_{12}S$ 618.2579; Found 618.2595.

*(2S,3R)-2-[(tert-Butoxycarbonyl)amino)-3-(pivaloyloxy)-pent-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-α-D-galactopyranoside (**33**).* To a solution of **31** (260 mg, 0.42 mmol) in pyridine (6 mL) was added acetic anhydride (0.48 mL, 5.06 mmol) dropwise over 2 min at 0 °C, and the solution was stirred overnight. The solvents were removed under vacuum. The residue was diluted with EtOAc (20 mL). The mixture was washed with 25 mL of 2 N HCl and 30 mL of saturated $NaHCO_3$ aq. solution and then brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified with FCC using ethyl acetate and hexane to offer **33** (301 mg, 96%) as a colorless syrup. TLC: R_f = 0.36 (EtOAc/Hex, 1.5/3.5). ^1H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.1 Hz,

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2H), 5.80 (ddd, J = 17.1, 10.5, 6.7 Hz, 1H), 5.41 (brs, 1H), 5.38−5.21 (m, 4H), 5.06 (dd, J = 10.9, 3.6 Hz, 1H), 4.96 (d, J = 3.2 Hz, 1H, anomeric), 4.72 (d, J = 9.8 Hz, 1H, −N*H*CO−), 4.18 (t, J = 6.3 Hz, 1H), 4.08−4.01 (m, 2H), 3.98 (dd, J = 10.0, 6.0 Hz, 1H), 3.67 (dd, J = 10.4, 3.6 Hz, 1H), 3.45 (dd, J = 10.3, 3.1 Hz, 1H), 2.45 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.44 (s, 9H), 1.18 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 176.9, 170.7, 170.13, 170.1, 155.4, 145.3, 133.2, 132.6, 130.1, 128.2, 119.4, 97.1, 80.2, 72.8, 67.83, 67.8, 67.7, 67.4, 66.7, 66.6, 52.2, 39.0, 28.5, 27.3, 27.2, 21.8, 20.8, 20.7, 20.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{49}NO_{15}S$ 744.2896; Found 744.2907.

*(2S,3R)-2-[(tert-Butoxycarbonyl)amino]-3-(pivaloyloxy)-pent-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-α-D-glucopyranoside (**34**).* Compound **34** (127 mg, 70%) as colorless syrup was prepared from **32** (150 mg, 0.24 mmol) by the same procedure and conditions employed to synthesize **33**. TLC: R_f = 0.40 (EtOAc/Hex, 2/3). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 5.79 (ddd, J = 17.2, 10.5, 6.6 Hz, 1H), 5.44−5.21 (m, 4H), 4.96−4.85 (m, 2H), 4.79−4.67 (m, 2H), 4.08 (d, J = 3.5 Hz, 2H), 4.04−3.94 (m, 2H), 3.68 (dd, J = 10.5, 3.6 Hz, 1H), 3.44 (dd, J = 10.5, 3.8 Hz, 1H), 2.45 (s, 3H), 2.07 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.44 (s, 9H), 1.18 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 176.9, 170.4, 170.3, 169.5, 155.4, 145.2, 133.1, 132.6, 130.0, 128.2, 119.5, 96.6, 80.1, 76.8, 72.9, 70.4, 70.0, 68.7, 67.8, 67.4, 67.3, 52.3, 39.0, 28.5, 27.3, 27.2, 21.8, 20.8, 20.7, 20.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{49}NO_{15}S$ 744.2896; Found 744.2911.

*(2S,3R,E)-2-[(tert-Butoxycarbonyl)amino]-3-(pivaloyloxy)-octadec-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-α-D-galactopyranoside (**35**).* Compound **35** (291 mg, 80%) as colorless syrup was prepared from **33** (290 mg, 0.39 mmol) by the same procedure and conditions used to synthesize **19**. TLC: R_f = 0.48 (EtOAc/Hex, 2/3). ^1H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 5.80 (dt, J = 14.0, 6.7 Hz, 1H), 5.41 (brs, 1H), 5.37 (dd, J = 15.3, 7.9 Hz, 1H), 5.26 (dd, J = 10.9, 3.1 Hz, 1H), 5.19 (t, J = 8.1 Hz, 1H), 5.06 (dd, J = 10.9, 3.6 Hz, 1H), 4.93 (d, J = 3.1 Hz, 1H, anomeric), 4.67 (d, J = 9.9 Hz, 1H, −N*H*CO−), 4.18 (t, J = 6.4 Hz, 1H), 4.05 (dd, J = 10.0, 6.7 Hz, 1H), 4.01−3.94 (m, 2H), 3.65 (dd, J = 9.8, 2.8 Hz, 1H), 3.41 (dd, J = 10.5, 2.2 Hz, 1H), 2.45 (s, 3H), 2.10 (s, 3H), 2.05−1.98 (m, 5H, 3H−COC*H*$_3$ and 2H−C═CH$_2$−C*H*$_2$−), 1.97 (s, 3H), 1.44 (s, 9H), 1.38−1.32 (m, 2H), 1.24 (s, 21H), 1.15 (s, 9H), 0.87 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 176.9, 170.7, 170.1, 170.0, 155.4, 145.3, 138.0, 132.6, 130.1, 128.2, 124.7, 97.2, 80.0, 72.8, 67.9, 67.8, 67.7, 67.5, 66.6, 66.4, 52.3, 38.9, 32.4, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 29.0, 28.5, 27.3, 27.2, 22.8, 21.8, 20.9, 20.8, 20.6, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{47}H_{75}NO_{15}S$ 926.4930; Found 926.4949.

*(2S,3R,E)-2-[(tert-Butoxycarbonyl)amino]-3-(pivaloyloxy)-octadec-4-en-1-yl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-α-D-glucopyranoside (**36**).* Compound **36** (121 mg, 81%) as colorless syrup was prepared from **34** (120 mg, 0.16 mmol) by the same procedure and conditions used to synthesize **19**. TLC: R_f = 0.58 (EtOAc/Hex, 2/3). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.86−5.74 (m, 1H), 5.44−5.30 (m, 2H), 5.18 (t, J = 7.9 Hz, 1H), 4.93 (t, J = 9.7 Hz, 1H), 4.86 (d, J = 3.5 Hz, 1H, anomeric), 4.75 (dd, J = 10.2, 3.7 Hz, 1H), 4.70 (d, J = 9.9 Hz, 1H), 4.10−4.05 (d, J = 14.9 Hz, 2H), 4.02−3.92 (m, 2H), 3.66 (dd, J = 10.4, 3.2 Hz, 1H), 3.41 (dd, J = 10.5, 3.5 Hz, 1H), 2.45 (s, 3H), 2.08 (s, 3H), 2.05−1.94 (m, 8H, 2 x −COC*H*$_3$ and −CH = CH−C*H*$_2$−), 1.44 (s, 9H), 1.36−1.31 (m, 2H), 1.24 (s, 20H), 1.15 (s, 9H), 0.87 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 176.9, 170.4, 169.5, 155.4, 145.2, 137.9, 132.7, 129.9, 128.2, 124.6, 96.6, 79.9, 72.8, 70.3, 70.1, 68.7, 67.9, 67.3, 67.2, 52.4, 38.9, 32.4, 32.1, 29.8, 29.6, 29.5, 29.3, 29.0, 28.5, 27.2, 22.8, 21.8, 20.8, 20.7, 20.6, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{47}H_{75}NO_{15}S$ 926.4930; Found 926.4958.

*(2S,3R,E)-2-[(tert-Butoxycarbonyl)amino]-3-(pivaloyloxy)-octadec-4-en-1-yl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-α-D-galactopyranoside (**37**).* Compound **37** (221 mg, 92%) as colorless syrup was prepared from **35** (278 mg, 0.30 mmol) by the same procedure and conditions used to synthesize **21**. TLC: R_f = 0.6 (EtOAc/Hex, 2/4). ^1H NMR (600 MHz, $CDCl_3$): δ 5.81 (dt, J = 14.0, 6.7 Hz, 1H), 5.43−5.35 (m, 2H), 5.30 (dd, J = 10.9, 3.3 Hz, 1H), 5.22 (t, J = 8.0 Hz, 1H), 5.11 (dd, J = 10.9, 3.7 Hz, 1H), 5.02 (d, J = 3.3 Hz, 1H, anomeric), 4.71 (d, J = 9.9 Hz, 1H, −N*H*CO−), 4.10 (dd, J = 7.7, 4.4 Hz, 1H), 4.01 (t, J = 8.8 Hz, 1H), 3.78 (dd, J = 10.4, 3.3 Hz, 1H), 3.55−3.49 (m, 1H), 3.44 (dd, J = 12.8, 8.3 Hz, 1H), 3.15 (dd, J = 12.8, 4.4 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 2.05−1.97 (m, 5H, 3H−COC*H*$_3$ and 2H−C═CH$_2$−C*H*$_2$−), 1.44 (s, 9H), 1.38−1.32 (m, 2H), 1.31−1.21 (m, 21H), 1.16 (s, 9H), 0.87 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 176.9, 170.7, 170.3, 170.2, 155.4, 137.9, 124.8, 97.2, 80.0, 72.8, 68.9, 68.2, 68.0, 67.8, 67.7, 52.5, 50.9, 38.9, 32.4, 32.1, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.3, 29.0, 28.5, 27.2, 22.8, 20.9, 20.8, 20.8, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{40}H_{68}N_4O_{12}$ 797.4907; Found 797.4927.

*(2S,3R,E)-2-[(tert-Butoxycarbonyl)amino]-3-(pivaloyloxy)-octadec-4-en-1-yl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-α-D-glucopyranoside (**38**).* Compound **38** (66.0 mg, 84%) as colorless syrup was prepared from **36** (91.0 mg, 0.098 mmol) by the same procedure and conditions employed to synthesize **21**. TLC: R_f = 0.75 (EtOAc/Hex, 2/4). ^1H NMR (400 MHz, $CDCl_3$): δ 5.88−5.76 (m, 1H), 5.48−5.32 (m, 2H), 5.22 (t, J = 8.0 Hz, 1H), 5.06−4.92 (m, 2H), 4.85 (dd, J = 10.2, 3.7 Hz, 1H), 4.75 (d, J = 9.8 Hz, 1H), 4.06−3.99 (m, 1H), 3.98−3.89 (m, 1H), 3.79 (dd, J = 10.5, 3.5 Hz, 1H), 3.52 (dd, J = 10.3, 3.5 Hz, 1H), 3.31 (d, J = 4.4 Hz, 2H), 2.10 (s, 3H), 2.07−2.00 (m, 8H, 2 × −COC*H*$_3$ and −CH═CH−C*H*$_2$−), 1.45 (s, 9H), 1.39−1.31 (m, 2H), 1.25 (s, 20H), 1.17 (s, 9H), 0.88 (t, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 177.0, 170.5, 170.4, 169.8, 155.5, 138.0, 124.8, 103.3, 96.7, 79.9, 77.4, 72.9, 70.6, 70.1, 69.9, 68.9, 68.0, 52.6, 51.1, 38.9, 32.5, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 29.0, 28.5, 27.2, 22.8, 20.9, 20.8, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{40}H_{68}N_4O_{12}$ 797.4907; Found 797.4923.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-α-D-galactopyranoside (**39**).* 4 M HCl dioxane (1.3 mL, 5.14 mmol) was added to a stirred solution of **37** (205 mg, 0.26 mmol) in CH_2Cl_2 (12.0 mL) at 0 °C. The mixture was stirred at rt until the reaction was completed, as indicated by TLC. The solvent was removed under reduced pressure, and the residue was stripped with toluene three times and dried in a high vacuum. In the meantime, steric acid (138 mg, 0.48 mmol) dissolved in dry DCM (5.0 mL) was mixed with EDC (92.8 mg, 0.48 mmol) and DMAP (5.91 mg, 0.048 mmol) at 0 °C. After 10 min of stirring, the solution was added to the crude amine dissolved in dry CH_2Cl_2 (8.0 mL). The mixture was stirred under argon at rt for 12 h. After the reaction was completed, water was added. The organic layer was separated and washed with saturated $NaHCO_3$ aq. solution, water, and brine and then dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography to afford **39** (197 mg, 88%) as a syrup. TLC: R_f = 0.81 (EtOAc/Hex, 1/1). ^1H NMR (600 MHz, $CDCl_3$): δ 5.80 (dt, J = 14.2, 6.7 Hz, 1H), 5.64 (d, J = 9.5 Hz, 1H, −N*H*CO−), 5.41 (d, J = 2.9 Hz, 1H), 5.40−5.34 (m, 1H), 5.31 (dd, J = 10.9, 3.3 Hz, 1H), 5.24 (t, J = 7.9 Hz, 1H), 5.12 (dd, J = 10.9, 3.7 Hz, 1H), 5.03 (d, J = 3.7 Hz, 1H, anomeric), 4.40 (t, J = 8.6 Hz, 2H), 4.06 (dd, J = 8.1, 4.3 Hz, 1H), 3.75 (dd, J = 10.9, 2.0 Hz, 1H), 3.59 (dd, J = 11.7, 1.7 Hz, 2H), 3.44 (dd, J = 12.8, 8.3 Hz, 1H), 3.17 (dd, J = 12.8, 4.3 Hz, 1H), 2.29−2.13 (m, 5H, 2H−COC*H*$_2$− and −COC*H*$_3$), 2.12 (s, 3H), 2.07−1.93 (m, 5H, 3H−COC*H*$_3$ and 2H−C═CH$_2$−C*H*$_2$−), 1.64−1.58 (m, 2H), 1.39−1.20 (m, 50H), 1.17 (s, 9H), 0.88 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.0, 170.7, 170.3, 170.2, 138.1, 125.1, 97.4, 72.5, 68.8, 68.3, 68.2, 67.8, 67.6, 50.9, 50.8, 38.9, 32.4, 32.1, 29.9, 29.8, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 29.1, 27.2, 27.18, 25.9, 22.8, 20.9, 20.8, 20.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{53}H_{94}N_4O_{11}$ 963.6992; Found 963.7011.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl-2,3,4-tri-O-acetyl-6-azido-6-deoxy-α-D-glucopyranoside (**40**).* Compound **40** (76.6 mg, 88%) as a colorless syrup was prepared from **38** (90.0 mg, 0.11 mmol) by the same procedure and conditions utilized to synthesize **39**. TLC: R_f = 0.81 (EtOAc/Hex, 1/1). ^1H NMR (600 MHz, $CDCl_3$): δ 5.80 (dt, J = 14.2, 6.8 Hz, 1H), 5.69 (d, J = 9.6 Hz, 1H), 5.47 (t, J = 9.8 Hz, 1H), 5.36 (dd, J = 15.3, 7.9 Hz, 1H), 5.24 (t,

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J = 8.2 Hz, 1H), 4.98 (d, J = 3.8 Hz, 1H, anomeric-H), 4.92 (t, J = 9.8 Hz, 1H), 4.84 (dd, J = 10.3, 3.8 Hz, 1H), 4.40 (tt, J = 9.2, 3.1 Hz, 1H), 3.92 (dt, J = 9.5, 4.5 Hz, 1H), 3.76 (dd, J = 10.5, 3.3 Hz, 1H), 3.56 (dd, J = 10.6, 3.2 Hz, 1H), 3.43−3.22 (m, 2H), 2.24−2.14 (m, 2H), 2.10 (s, 3H), 2.03 (s, 2H), 2.02 (s, 5H, $-CH_3$ and $-CH_2-$), 1.64−1.58 (m, 2H), 1.42−1.21 (m, 53H), 1.16 (s, 9H), 0.87 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.0, 172.8, 170.4, 170.3, 169.7, 138.1, 125.1, 96.7, 72.4, 70.7, 70.1, 69.9, 68.8, 67.8, 51.1, 50.7, 38.9, 37.1, 32.4, 32.1, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 27.3, 27., 27.2, 27.2, 26.0, 22.8, 20.8, 20.8, 20.7, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{53}H_{94}N_4O_{11}$ 963.6992; Found 963.6998.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 6-azido-6-deoxy-α-D-galactopyranoside (**41**).* Compound **41** (89.4 mg, 92%) as a colorless syrup was prepared from **39** (124 mg, 0.128 mmol) by the same procedure and conditions used to synthesize **23**. TLC: R_f = 0.2 (DCM/MeOH, 4/1). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 7.14 (d, J = 8.7 Hz, 1H, $-NHCO-$), 5.75 (dt, J = 14.2, 6.8 Hz, 1H), 5.46 (dd, J = 15.4, 6.7 Hz, 1H), 4.87 (d, J = 3.6 Hz, 1H, anomeric), 4.13 (t, J = 6.3 Hz, 1H), 4.02 (dq, J = 9.1, 4.6 Hz, 1H), 3.92−3.86 (m, 1H), 3.84 (d, J = 7.5 Hz, 2H), 3.81−3.73 (m, 2H), 3.72 (dd, J = 10.6, 4.6 Hz, 1H), 3.60 (dd, J = 12.8, 8.3 Hz, 1H), 3.32 (dd, J = 12.8, 4.6 Hz, 1H), 2.32−2.14 (m, 2H), 2.04 (h, J = 7.0 Hz, 2H), 1.61 (p, J = 7.2 Hz, 2H), 1.43−1.21 (m, 50H), 0.88 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$:CD_3OD 4:1): δ 174.7, 134.3, 129.0, 100.0, 72.6, 72.59, 70.2, 70.1, 69.8, 68.9, 68.1, 68.0, 53.7, 53.6, 51.5, 36.8, 36.7, 32.6, 32.1, 29.9, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 29.5, 29.4, 26.1, 22.9, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{80}N_4O_7$ 753.6100; Found 753.6118.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 6-azido-6-deoxy-α-D-glucopyranoside (**42**).* Compound **42** (49.1 mg, 89%) as colorless syrup was synthesized from **40** (70.0 mg, 0.073 mmol) by the same procedure and conditions used to synthesize **23**. TLC: R_f = 0.2 (DCM/MeOH, 4/1). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD, 4:1): δ 5.75 (dt, J = 14.3, 6.7 Hz, 1H), 5.46 (dd, J = 15.4, 6.9 Hz, 1H), 4.83 (d, J = 3.8 Hz, 1H, anomeric-H), 4.13 (t, J = 6.6 Hz, 1H), 4.00 (dq, J = 7.0, 3.6 Hz, 1H), 3.83 (dd, J = 10.4, 3.2 Hz, 1H), 3.79−3.68 (m, 2H), 3.64 (t, J = 9.3 Hz, 1H), 3.53 (dd, J = 13.1, 2.3 Hz, 1H), 3.47 (dd, J = 9.6, 3.8 Hz, 1H), 3.43 (dd, J = 13.1, 6.2 Hz, 1H), 3.32 (t, J = 9.4 Hz, 1H), 2.25−2.17 (m, 2H), 2.09−2.00 (m, 2H), 1.65−1.56 (m, 2H), 1.41−1.21 (m, 50H), 0.88 (t, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$:CD_3OD, 4:1): δ 174.8, 134.4, 129.2, 99.6, 74.0, 72.4, 72.1, 71.6, 71.1, 68.0, 67.9, 53.7, 53.6, 51.7, 36.8, 36.7, 32.6, 32.1, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.56, 29.5, 29.5, 26.1, 22.9, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{80}N_4O_7$ 753.6100; Found 753.6118.

*(2S,3R,E)-2-Octadecanamido-octadec-4-en-1-yl 6-deoxy-6-[(1-oxyl-2,2,5,5-tetramethyl-2,5-dihydro-1H-pyrrole)-3-carboxamido]-6-deoxy-β-D-galactopyranoside (**7**).* Compound **7** (10.0 mg, 90%) was synthesized from **41** (9.00 mg, 0.012 mmol) by the same procedure and conditions employed to synthesize **5**. TLC: R_f = 0.46 (DCM/MeOH, 4.5/0.5). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 5.74 (brs, 1H), 5.50−5.35 (m, 2H), 4.87 (s, 1H, anomeric), 4.08 (brs, 2H), 3.91−3.45 (m, 9H), 2.21 (brs, 2H), 2.08−1.94 (m, 2H), 1.60 (brs, 2H), 1.26 (brs, 50H), 0.88 (t, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$:CD_3OD, 4:1): δ 174.7, 134.2, 129.0, 100.1, 72.4, 71.1, 69.4, 69.2, 69.0, 67.9, 67.8, 67.7, 53.8, 53.3, 36.6, 32.5, 31.9, 31.8, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.5, 29.4, 29.3, 29.3, 26.0, 22.6, 13.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{51}H_{94}N_3O_9$ 893.7063; Found 893.7084.

*(2S,3R,E)-2-Octadecanamido-octadec-4-en-1-yl 6-deoxy-6-[(1-oxyl-2,2,5,5-tetramethyl-2,5-dihydro-1H-pyrrole)-3-carboxamido]-6-deoxy-α-D-glucopyranoside (**8**).* Compound **8** (10.1 mg, 90%) was prepared from **42** (9.00 mg, 0.012 mmol) by the same procedure and conditions used to synthesize **5**. TLC: R_f = 0.46 (DCM/MeOH, 4.5/0.5). ^1H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 5.75 (brs, 1H), 5.46 (bs, 1H), 4.82 (brs, 1H), 4.11 (brs, 1H), 3.95 (brs, 1H), 3.91−3.65 (m, 3H), 3.58 (brs, 1H), 3.46 (brs, 1H), 3.16 (brs, 1H), 2.19 (brs, 2H), 2.04 (brs, 2H), 1.61 (brs, 2H), 1.61−1.11 (m, 26H), 0.88 (t, J = 6.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (151 MHz $CDCl_3$:CD_3OD 4:1): δ 174.7, 174.6, 134.4, 129.2, 99.6, 73.1, 72.3, 72.2, 71.5, 71.2, 67.6, 53.7, 36.8, 36.7, 32.6, 32.1, 30.0, 29.9, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.47, 26.1, 22.8, 14.2, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{51}H_{94}N_3O_9$ 893.7063; Found 893.7084.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (**45**).* Compound **45** (0.58 g, 79%) as a syrup was synthesized from **13** (0.30 g, 1.32 mmol) and **43**[35] (1.04 g, 2.11 mmol) by the same procedure and conditions employed to synthesize **14**. TLC: R_f = 0.4 (EtOAc/Hex, 2/3). ^1H NMR (600 MHz, $CDCl_3$): δ 5.82 (ddd, J = 17.5, 10.5, 6.9 Hz, 1H), 5.46−5.34 (m, 4H), 5.22 (dd, J = 10.5, 8.0 Hz, 1H), 5.01 (dd, J = 10.4, 3.5 Hz, 1H,), 4.49 (d, J = 7.9 Hz, 1H, anomeric), 4.32−4.00 (m, 2H), 4.00−3.85 (m, 2H), 3.80 (td, J = 6.3, 4.2 Hz, 1H), 3.55 (dd, J = 10.4, 5.9 Hz, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.0, 170.5, 170.4, 170.3, 169.5, 131.7, 120.4, 101.1, 73.9, 71.0, 71.0, 68.6, 67.7, 67.1, 63.3, 61.4, 39.1, 27.3, 27.2, 20.9, 20.8, 20.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{35}N_3O_{12}$ 575.2559; Found 575.2570.

*(2S,3R)-2-Azido-3-(pivaloyloxy)pent-4-en-1-yl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**46**).* Compound **46** (0.20 g, 91%) as a syrup was synthesized from **13** (0.09 g, 0.40 mmol) and **44**[35] (0.29 g, 0.59 mmol) by the same procedure and conditions employed to synthesize **14**. TLC: R_f = 0.45 (EtOAc/Hex, 2/3). ^1H NMR (400 MHz, $CDCl_3$): δ 5.80 (ddd, J = 17.4, 10.4, 7.0 Hz, 1H), 5.38−5.32 (m, 3H), 5.19 (t, J = 9.4 Hz, 1H), 5.08 (t, J = 9.6 Hz, 1H), 5.0 (t, J = 8.7 Hz, 1H), 4.53 (d, J = 7.9 Hz, 1H, anomeric), 4.23 (dd, J = 12.3, 4.7 Hz, 1H), 4.13 (dd, J = 12.3, 2.0 Hz, 1H), 3.87 (dd, J = 10.2, 6.6 Hz, 1H), 3.78 (dd, J = 10.5, 5.8 Hz, 1H), 3.69 (ddd, J = 9.8, 4.5, 2.2 Hz, 1H), 3.54 (dd, J = 10.2, 5.8 Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.21 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 176.9, 170.7, 170.4, 169.5, 169.4, 131.6, 120.4, 100.6, 76.8, 73.8, 73.0, 72.8, 72.1, 71.1, 68.4, 67.9, 63.2, 63.0, 61.9, 39.0, 27.2, 20.8, 20.8, 20.7, 20.7. HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{24}H_{35}N_3O_{12}$ 575.2559; Found 575.2561.

*(2S,3R)-2-Octadecanamido-3-(pivaloyloxy)pent-4-en-1-yl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (**47**).* Compound **47** (340 mg, 79%) as a syrup was synthesized from **45** (300 mg, 0.54 mmol) by the same procedure and conditions employed to synthesize **16**. TLC: R_f = 0.1 (EtOAc/Hex, 4/1). ^1H NMR (600 MHz, $CDCl_3$): δ 5.80 (ddd, J = 17.1, 10.6, 6.1 Hz, 1H), 5.72 (d, J = 8.9 Hz, 1H,-CONH-), 5.38 (d, J = 3.2 Hz, 1H), 5.34−5.29 (m, 2H), 5.26 (d, J = 10.6 Hz, 1H), 5.15 (dd, J = 10.4, 7.9 Hz, 1H), 5.01 (dd, J = 10.4, 3.4 Hz, 1H), 4.43 (d, J = 7.9 Hz, 1H, anomeric), 4.40−4.34 (m, 1H), 4.12 (d, J = 6.6 Hz, 2H), 4.00 (dd, J = 9.7, 3.3 Hz, 1H), 3.90 (t, J = 6.6 Hz, 1H), 3.58 (dd, J = 9.4, 3.6 Hz, 1H), 2.16 (s, 3H), 2.16−2.11 (m, 2H, $-COCH_2-$), 2.05 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.66−1.54 (m, 2H), 1.32−1.23 (m, 28H), 1.22 (s, 9H), 0.88 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 177.2, 172.9, 170.5, 170.4, 170.2, 169.8, 133.4, 118.8, 101.2, 73.5, 70.9, 70.8, 69.1, 67.0, 61.4, 50.4, 39.0, 37.0, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 29.4, 27.2, 25.8, 22.8, 20.8, 20.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{71}NO_{13}$ 798.4998; Found 798.5019.

*(2S,3R)-2-Octadecanamido-3-(pivaloyloxy)pent-4-en-1-yl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**48**).* Compound **47** (160 mg, 71%) as a syrup was prepared from **46** (200 mg, 0.36 mmol) by the same procedure and reaction conditions used to synthesize **16**. TLC: R_f = 0.9 (EtOAc/Hex, 4/1). ^1H NMR (400 MHz, $CDCl_3$): δ 5.85−5.73 (m, 1H), 5.69 (d, J = 9.1 Hz, 1H), 5.35−5.23 (m, 3H), 5.20 (t, J = 9.5 Hz, 1H), 5.06 (t, J = 9.7 Hz, 1H), 4.96 (dd, J = 9.6, 8.0 Hz, 1H), 4.46 (d, J = 7.9 Hz, 1H, anomeric), 4.38 (td, J = 10.1, 4.2 Hz, 1H), 4.22 (dd, J = 12.3, 4.7 Hz, 1H), 4.12 (dd, J = 12.3, 2.2 Hz, 1H), 3.96 (dd, J = 10.0, 3.9 Hz, 1H), 3.69 (ddd, J = 10.0, 4.6, 2.3 Hz, 1H), 3.58 (dd, J = 10.0, 4.4 Hz, 1H), 2.13 (td, J = 7.7, 3.1 Hz, 2H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.61−1.55 (m, 2H), 1.32−1.23 (m, 28H), 1.20 (s, 9H), 0.87 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 177.1, 172.9, 170.8, 170.3, 169.6, 169.5, 133.3, 118.8, 100.8, 77.4, 77.36, 77.16, 76.8, 73.3, 72.6, 72.1, 71.5, 68.3, 67.6, 61.9, 50.3, 39.0, 36.9, 32.1, 29.8, 29.8, 29.6, 29.5, 29.5, 29.4, 27.2, 25.8, 22.8, 21.0, 20.9, 20.7, 20.7, 14.3. HRMS

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(ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{71}NO_{13}$798.4998; Found 798.5015.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (**49**).* Compound **49** (205 mg, 82%) as a colorless syrup was synthesized from **47** (202 mg, 0.25 mmol) by the same procedure and conditions employed to synthesize **19**. TLC: R_f = 0.56 (EtOAc/Hex, 3/2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.76 (dt, J = 14.9, 7.7 Hz, 1H), 5.66 (d, J = 9.3 Hz, 1H), 5.40−5.32 (m, 2H) 5.22 (t, J = 7.1 Hz, 1H), 5.14 (dd, J = 10.5, 7.8 Hz, 1H), 5.00 (dd, J = 10.5, 3.5 Hz, 1H), 4.42 (d, J = 7.9 Hz, 1H, anomeric), 4.38−4.30 (m, 1H), 4.11 (dd, J = 6.7, 1.8 Hz, 2H), 3.96 (dd, J = 9.9, 3.9 Hz, 1H), 3.89 (td, J = 6.6, 1.3 Hz, 1H), 3.56 (dd, J = 9.9, 4.4 Hz, 1H), 2.16 (s, 3H), 2.15−2.09 (m, 2H), 2.04 (s, 3H), 2.03 (s, 3H), 2.06−1.97 (m, 2H). 1.98 (s, 3H), 1.64−1.54 (m, 2H), 1.37−1.20 (m, 50H), 1.19 (s, 9H), 0.87 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 177.1, 172.7, 170.5, 170.4, 170.2, 169.8, 137.1, 125.0, 101.1, 73.4, 70.9, 70.8, 69.1, 67.5, 67.0, 61.4, 50.6, 39.0, 37.0, 32.4, 32.1, 29.8, 29.8, 29.6, 29.6, 29.5, 29.5, 29.5, 29.3, 29.1, 27.2, 25.9, 22.8, 21.0, 20.8, 20.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{55}H_{97}NO_{13}$ 980.7033; Found 980.7061.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)octadec-4-en-1-yl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**50**).* Compound **50** (140 mg, 76%) as a colorless syrup was synthesized from **48** (150 mg, 0.19 mmol) by the same procedure and conditions employed to synthesize **19**. TLC: R_f = 0.65 (EtOAc/Hex, 2/3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79−5.69 (m, 1H), 5.65 (d, J = 9.2 Hz, 1H), 5.33 (dd, J = 15.4, 7.3 Hz, 1H), 5.24−5.15 (m, 2H), 5.05 (t, J = 9.7 Hz, 1H), 4.94 (dd, J = 9.6, 8.0 Hz, 1H), 4.44 (d, J = 7.9 Hz, 1H, anomeric), 4.32 (td, J = 11.0, 4.0 Hz, 1H), 4.21 (dd, J = 12.3, 4.7 Hz, 1H), 4.10 (dd, J = 12.3, 2.1 Hz, 1H), 3.91 (dd, J = 9.9, 4.0 Hz, 1H), 3.67 (ddd, J = 9.9, 4.4, 2.3 Hz, 1H), 3.61 (t, J = 6.7 Hz, 1H), 3.55 (dd, J = 9.9, 4.2 Hz, 1H), 2.17−2.06 (m, 2H, −CO−CH_2), 2.06 (s, 3H), 2.02 (s, 3H), 2.00−1.97 (m, 8H, 2 × −COCH_3 and −CH═CH−CH_2−), 1.56−1.50 (m, 2H), 1.27−1.20 (m, 50H), 1.16 (s, 9H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 177.0, 172.7, 170.7, 170.3, 169.53, 169.5, 137.0, 124.9, 100.7, 77.5, 77.2, 76.8, 73.2, 72.7, 72.0, 71.5, 68.3, 67.7, 63.1, 61.9, 50.5, 38.9, 36.9, 32.9, 32.4, 32.0, 29.8, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 27.2, 27.1, 25.9, 25.8, 25.7, 22.8, 20.8, 20.8, 20.7, 20.6, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{55}H_{91}NO_{13}$ 980.7033; Found 980.7060.

*(2S,3R,E)-2-Octadecanamido-3-hydroxyloctadec-4-en-1-yl β-D-galactopyranoside (**1**).*[42,47] Compound **1** as a glassy solid (29.8 mg, 80%) was synthesized from **49** (50.0 mg, 0.051 mmol) by the same procedure and conditions employed to synthesize **23**. TLC: R_f = 0.2 (DCM/MeOH, 4/1). ^{1}H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 5.84−5.60 (m, 1H), 5.46 (ddt, J = 15.3, 7.4, 1.6 Hz, 1H), 4.22 (d, J = 7.5 Hz, 1H, anomeric), 4.18 (dd, J = 10.2, 4.5 Hz, 1H), 4.11 (t, J = 7.2 Hz, 1H), 4.00 (ddd, J = 7.6, 4.4, 3.3 Hz, 1H), 3.88 (dd, J = 3.3, 1.2 Hz, 1H), 3.82 (dd, J = 11.6, 6.6 Hz, 1H), 3.74 (dd, J = 11.6, 5.0 Hz, 1H), 3.59 (dd, J = 10.2, 3.3 Hz, 1H), 3.58−3.46 (m, 3H), 2.38−2.10 (m, 2H), 2.12−1.96 (m, 2H), 1.64−1.56 (m, 2H), 1.45−1.19 (m, 50H), 0.89 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$:CD_3OD 4:1): δ 174.9, 134.6, 129.5, 104.0, 75.4, 73.7, 72.4, 71.7, 69.3, 69.0, 61.8, 53.7, 36.8, 32.7, 32.2, 30.0, 29.9, 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 26.2, 22.9, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{81}NO_8$ $[M + H]^+$ 728.6035; Found 728.6055.

*(2S,3R,E)-2-Octadecanamido-3-hydroxyloctadec-4-en-1-yl β-D-glucopyranoside (**β-GlcCer, 2**).*[48,49] Compound **2** as a glassy solid (67.0 mg, 90%) was synthesized from **50** (100 mg, 0.10 mmol) by the same procedure and conditions employed to synthesize **23**. TLC: R_f = 0.25 (DCM/MeOH, 4/1). ^{1}H NMR (600 MHz, $CDCl_3$:CD_3OD 4:1): δ 5.69−5.62 (m, 1H), 5.41 (dd, J = 15.3, 7.6 Hz, 1H), 4.22 (d, J = 7.8 Hz, 1H, anomeric), 4.12 (dd, J = 10.1, 4.5 Hz, 1H), 4.05 (t, J = 7.6 Hz, 1H), 3.98−3.92 (m, 1H), 3.82 (dd, J = 12.0, 2.6 Hz, 1H), 3.68 (dd, J = 12.0, 5.3 Hz, 1H), 3.54 (dd, J = 10.1, 3.2 Hz, 1H), 3.35 (ddd, J = 13.2, 11.4, 7.2 Hz, 2H), 3.28−3.23 (m, 1H), 3.23−3.18 (m, 1H), 2.17−2.10 (m, 2H), 1.98 (dd, J = 14.7, 7.0 Hz, 2H), 1.58−1.51 (m, 2H), 1.36−1.16 (m, 50H), 0.84 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$:CD_3OD 4:1): δ 175.1, 134.8, 129.6, 103.5, 76.8, 76.6, 74.0, 72.5, 70.5, 69.0, 61.8, 53.7, 36.8, 32.7, 32.3, 30.1, 30.01, 30.0, 29.9, 29.8, 29.7, 29.7, 29.6, 26.3, 23.0, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{81}NO_8$ 728.6035; Found 728.6052.

*(2S,3R)-2-[(tert-butoxycarbonyl)amino]-3-(pivaloyloxy)-pent-4-en-1-yl 2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside (**51**).* Compound **51** (288 mg, 94%) was synthesized from **29** (259 mg, 0.56 mmol) by the same procedure and conditions employed to synthesize **33**. TLC: R_f = 0.88 (EtOAc/MeOH, 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (ddd, J = 17.2, 10.5, 6.7 Hz, 1H), 5.48 (d, J = 3.6 Hz, 1H, anomeric), 5.41−5.25 (m, 4H), 5.13 (dd, J = 10.9, 3.7 Hz, 1H), 5.03 (d, J = 3.9 Hz, 1H), 4.79 (d, J = 9.7 Hz, 1H), 4.19 (t, J = 6.6 Hz, 1H), 4.09 (pd, J = 10.6, 9.9, 6.2 Hz, 3H), 3.77 (dd, J = 10.5, 3.7 Hz, 1H), 3.55 (dd, J = 10.5, 3.8 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.46 (s, 9H), 1.21 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.8, 170.6, 170.4, 170.2, 170.1, 155.3, 133.2, 119.3, 97.1, 80.0, 72.6, 67.9, 67.8, 67.7, 67.5, 66.6, 61.7, 52.2, 38.8, 28.3, 27.1, 20.7, 20.7, 20.7, 20.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{45}NO_{14}$ 632.2913; Found 632.2926.

*(2S,3R)-2-[(tert-butoxycarbonyl)amino]-3-(pivaloyloxy)-pent-4-en-1-yl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside (**52**).* Compound **51** (125 mg, 92%) was synthesized from **30** (100 mg, 0.22 mmol) by the same procedure and conditions employed to synthesize **33**. TLC: R_f = 0.9 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (ddd, J = 17.2, 10.4, 6.8 Hz, 1H), 5.45 (t, J = 9.8 Hz, 1H), 5.39−5.24 (m, 3H), 5.04 (t, J = 9.8 Hz, 1H), 4.99 (d, J = 3.7 Hz, 1H, anomeric), 4.87 (dd, J = 10.2, 3.7 Hz, 1H), 4.78 (d, J = 9.8 Hz, 1H), 4.26 (dd, J = 12.4, 4.6 Hz, 1H), 4.08 (dd, J = 12.4, 2.2 Hz, 2H), 3.97 (ddd, J = 10.2, 4.4, 2.1 Hz, 1H), 3.77 (dd, J = 10.5, 3.7 Hz, 1H), 3.52 (dd, J = 10.4, 3.6 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.45 (s, 9H), 1.19 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.9, 170.8, 170.5, 170.4, 169.7, 155.4, 133.3, 119.5, 96.8, 80.2, 72.8, 70.6, 70.3, 68.6, 67.8, 67.6, 61.9, 52.4, 39.0, 28.5, 27.2, 20.9, 20.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{45}NO_{14}$ 632.2913; Found 632.2934.

*(2S,3R,E)-2-[(tert-butoxycarbonyl)amino]-3-(pivaloyloxy)-octadec-4-en-1-yl 2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside (**53**).* Compound **53** (322 mg, 90%) was synthesized from **51** (276 mg, 0.44 mmol) by the same procedure and conditions employed to synthesize **16**. TLC: R_f = 0.3 (EtOAc/Hex, 3.5/1.5). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.88−5.77 (m, 1H), 5.46 (d, J = 4.4 Hz, 1H), 5.37 (dd, J = 15.4, 8.1 Hz, 1H), 5.33−5.29 (m, 1H), 5.21 (t, J = 8.2 Hz, 1H), 5.11 (dd, J = 10.9, 3.8 Hz, 1H), 4.99 (d, J = 3.9 Hz, 1H, anomeric), 4.73 (d, J = 10.0 Hz, 1H, −NHCO−), 4.17 (t, J = 6.8 Hz, 1H), 4.13−4.03 (m, 2H), 3.98 (t, J = 9.3 Hz, 1H), 3.73 (dd, J = 10.5, 3.4 Hz, 1H), 3.49 (dd, J = 10.4, 3.4 Hz, 1H), 2.13 (s, 3H), 2.11 (s, 3H), 2.03−1.97 (m, 5H, −COCH_3 and −C═CH_2CH_2−), 1.44 (s, 9H), 1.38−1.21 (m, 25H), 1.16 (s, 9H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 176.9, 170.7, 170.5, 170.4, 170.3, 155.4, 137.9, 124.9, 97.2, 80.0, 72.7, 68.1, 68.06, 67.9, 67.7, 66.6, 61.8, 52.5, 38.9, 32.4, 32.0, 29.8, 29.78, 29.76, 29.74, 29.6, 29.5, 29.3, 29.0, 28.5, 28.4, 27.3, 27.2, 22.8, 20.9, 20.8, 20.7, 20.7, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{71}NO_{14}$ 814.4947; Found 814.4969.

*(2S,3R,E)-2-[(tert-butoxycarbonyl)amino]-3-(pivaloyloxy)-octadec-4-en-1-yl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside (**54**).* Compound **54** (96.1 mg, 91%) was synthesized from **52** (82.0 mg, 0.072 mmol) by the same procedure and conditions employed to synthesize **16**. TLC: R_f = 0.58 (EtOAc/Hex, 2/3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88−5.78 (m, 1H), 5.46 (t, J = 9.8 Hz, 1H), 5.39 (dd, J = 15.3, 7.9 Hz, 1H), 5.23 (t, J = 8.0 Hz, 1H), 5.06 (t, J = 9.8 Hz, 1H), 4.99 (d, J = 3.7 Hz, 1H, anomeric), 4.88 (dd, J = 10.2, 3.7 Hz, 1H), 4.76 (d, J = 9.8 Hz, 1H), 4.28 (dd, J = 12.4, 4.5 Hz, 1H), 4.09 (dd, J = 12.4, 2.1 Hz, 1H), 3.99 (ddd, J = 10.2, 4.4, 2.1 Hz, 2H), 3.77 (dd, J = 10.5, 3.3 Hz, 1H), 3.51 (dd, J = 10.4, 3.3 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.09−2.00 (m, 8H, 2 × −COCH_3 and −CH═CH−CH_2CH_2−), 1.47 (s, 9H), 1.37−1.31 (m, 2H, −CH═CH−CH$_2$CH_2−), 1.34−1.21 (m, 20H), 1.18 (s, 9H), 0.89 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 176.9, 170.8, 170.5, 170.4, 169.7, 155.5, 138.0, 124.8, 96.8, 80.0, 72.8, 70.6, 70.3, 68.6, 67.9, 67.5, 61.9, 52.6, 38.9, 32.5, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 29.0,

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28.5, 27.2, 22.8, 20.9, 20.8, 20.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{71}NO_{14}$ 814.4947; Found 814.4966.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)-octadec-4-en-1-yl 2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside (**55**).* Compound **55** (88.0 mg, 86%) as the syrup was prepared from **53** (85.0 mg, 0.10 mmol) by the same procedure and conditions utilized to synthesize **39**. TLC: R_f = 0.8 (EtOAc/Hex, 3/2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74 (dt, J = 15.4, 6.8 Hz, 1H), 5.57 (d, J = 9.5 Hz, 1H, −N*H*CO−), 5.38 (dd, J = 3.5, 0.9 Hz, 1H), 5.35−5.22 (m, 2H), 5.17 (t, J = 8.3 Hz, 1H), 5.05 (dd, J = 10.8, 3.7 Hz, 1H), 4.93 (d, J = 3.7 Hz, 1H, anomeric), 4.32 (tt, J = 9.0, 3.1 Hz, 1H), 4.18−4.01 (m, 2H), 4.01−3.91 (m, 1H), 3.65 (dd, J = 10.5, 3.1 Hz, 1H), 3.46 (dd, J = 10.5, 3.1 Hz, 1H), 2.22−2.08 (m, 2H, −COC*H*$_2$−), 2.07 (s, 3H), 2.06 (s, 3H), 1.97 (s, 3H), 1.96−1.90 (m, 5H, −COC*H*$_3$ and −C═CH$_2$C*H*$_2$−), 1.62−1.47 (m, 2H), 1.30−1.12 (m, 50H), 1.09 (s, 9H), 0.80 (t, J = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 181.5, 176.8, 172.8, 170.6, 170.4, 170.23, 170.2, 138.1, 125.0, 97.0, 77.2, 72.1, 67.9, 67.8, 67.5, 66.5, 61.8, 50.5, 38.8, 36.9, 32.3, 31.9, 29.7, 29.6, 29.6, 29.5, 29.46, 29.4, 29.2, 29.0, 27.0, 25.8, 22.7, 20.8, 20.7 (2C), 20.6, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{55}H_{97}NO_{13}$ 980.7033; Found 980.7062.

*(2S,3R,E)-2-Octadecanamido-3-(pivaloyloxy)-octadec-4-en-1-yl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside (**56**).* Compound **56** (85.0 mg, 85%) as syrup was prepared from **54** (84.0 mg, 0.10 mmol) by the same procedure and conditions employed to synthesize **39**. TLC: R_f = 0.75 (EtOAc/Hex, 2/3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86−5.74 (m, 1H), 5.69 (d, J = 9.5 Hz, 1H), 5.52−5.44 (m, 1H), 5.35 (dd, J = 15.3, 8.0 Hz, 1H), 5.23 (t, J = 8.3 Hz, 1H), 5.00−4.93 (m, 2H), 4.85 (dd, J = 10.2, 3.8 Hz, 1H, anomeric), 4.38 (tt, J = 9.3, 2.9 Hz, 1H), 4.21 (dd, J = 12.4, 4.9 Hz, 1H), 4.08 (dd, J = 12.3, 2.2 Hz, 1H), 3.94 (ddd, J = 10.3, 4.8, 2.2 Hz, 1H), 3.72 (dd, J = 10.5, 3.1 Hz, 1H), 3.50 (dd, J = 10.5, 2.9 Hz, 1H), 2.25−2.14 (m, 2H, −COC*H*$_2$−), 2.11 (s, 3H), 2.08 (s, 3H), 2.04−1.97 (m, 8H, 2 × −COC*H*$_3$ and −CH═CH−C*H*$_2$−), 1.66−1.54 (m, 2H), 1.32−1.20 (m, 50H), 1.15 (s, 9H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.9, 172.9, 170.7, 170.5, 170.4, 169.7, 138.3, 125.1, 96.6, 72.2, 70.6, 70.2, 68.9, 67.5, 61.9, 50.6, 38.9, 37.0, 32.4, 32.1, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.3, 29.1, 27.2, 26.0, 22.8, 20.9, 20.8, 20.7, 20.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{55}H_{97}NO_{13}$ 980.7033; Found 980.7064.

*(2S,3R,E)-2-Octadecanamido-3-hydroxyloctadec-4-en-1-yl α-D-galactopyranoside (α-GalCer, **3**).* [40,50,51] Compound **3** (47.9 mg, 86%) was prepared from **55** (73.0 mg, 0.070 mmol) by the same procedure and conditions used to synthesize **23**. TLC: R_f = 0.54 (DCM/MeOH, 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD 3:2): δ 5.73 (t, J = 6.6 Hz, 1H), 5.50−5.40 (m, 1H), 4.88 (d, J = 3.6 Hz, 1H, anomeric), 4.09 (t, J = 7.0 Hz, 1H), 4.01−3.92 (m, 2H), 3.84−3.68 (m, 8H), 2.20 (t, J = 7.6 Hz, 2H), 2.12−1.98 (m, 2H), 1.66−1.55 (m, 2H), 1.42−1.19 (m, 50H), 0.89 (t, J = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$:CD_3OD 3:2): δ 174.8, 134.1, 129.1, 99.9, 77.6, 72.0, 70.7, 70.2, 69.7, 69.0, 67.4, 61.6, 53.7, 36.3, 32.3, 31.8, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 29.2, 25.9, 22.6, 13.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{81}NO_8$ 728.6035; Found 728.6052.

*(2S,3R,E)-2-Octadecanamido-3-hydroxyloctadec-4-en-1-yl α-D-glucopyranoside (α-GlcCer, **4**).* [41] Compound **4** (27.0 mg, 74%) was synthesized from **56** (49.0 mg, 0.049 mmol) by the same procedure and conditions employed to synthesize **23**. TLC: R_f = 0.3 (DCM/MeOH, 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD 3:2): δ 5.81−5.65 (m, 1H), 5.42 (dd, J = 15.4, 6.3 Hz, 1H), 4.77 (d, J = 3.7 Hz, 1H, anomeric), 4.11 (t, J = 5.7 Hz, 1H), 4.03−3.92 (m, 1H), 3.88−3.69 (m, 3H), 3.69−3.58 (m, 2H), 3.53−3.49 (m, 1H), 3.46−3.36 (m, 2H), 2.19−2.13 (m, 2H), 2.02−1.97 (m, 2H), 1.62−1.52 (m, 2H), 1.43−1.14 (m, 50H), 0.84 (t, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$:CD_3OD 3:2): δ 174.4, 134.2, 128.8, 99.5, 77.4, 74.0, 74.0, 73.0, 72.9, 71.92, 71.9, 70.3, 68.0, 61.9, 53.2, 36.7, 32.5, 32.0, 29.8, 29.7, 29.7, 29.6, 29.5, 29.44, 29.4, 29.3, 25.9, 22.8, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{81}NO_8$ 728.6035; Found 728.6057.

■ ASSOCIATED CONTENT

Data Availability Statement

All the data underlying this research are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.4c02423.

NMR and MS spectra of new compounds. (PDF)

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Notes

The authors declare no competing financial interest.

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