TCP- and Phthalimide-Protected *n*-Pentenyl Glucosaminide Precursors for the Synthesis of Nodulation Factors As Illustrated by the Total Synthesis of NodRf-III (C18:1, MeFuc)

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TCP- and phthalimide-protected *n*-pentenyl glucosaminide (NPG) precursors have been utilized in a convergent stereocontrolled synthesis of the nodulation factor NodRf-III (C18:1, MeFuc) produced by *Rhizobium fredii* USDA257, **2**. Nodulation factors are lipooligosaccharides that are secreted by bacteria which trigger the early steps in the formation of root nodules in leguminous plants. This symbiotic relationship between plant and bacteria plays a major role in the global nitrogen cycle. Key to our synthetic approach was the use of the TCP (tetrachlorophthaloyl) group to provide for *N*-differentiation of the linear glucosamine backbone and the use of $FeCl_3$ for the removal of benzyl protecting groups from the tetrasaccharide. The saccharide skeleton was assembled *via* the NPG-based coupling of a linear $\beta(1\rightarrow4)$ glucosamine disaccharide to a 6-*O*-fucosylated glucosamine acceptor. Significant yield enhancements for NPG couplings were observed at lower temperatures. Subsequent exchange of benzyl to *tert*-butyldimethylsilyl protecting groups *via* $FeCl_3$ mediation and installation of the fatty chain on the nonreducing terminus via selective removal of TCP led to a late intermediate which was deprotected in high yield to afford the natural product.

Introduction

A symbiotic relationship exists between bacteria of the genera *Rhizobium*, *Bradyrhizobium*, and *Azorhizobium* and leguminous plants which fix atmospheric nitrogen into a metabolizable form. So important is this relationship that it is estimated that leguminous root nodules account for the production of as much metabolizable nitrogen per year as do industrial sources. Root nodules can therefore be considered the largest source of organic nitrogen in the global nitrogen cycle.[1] In order for this process to occur, the soil bacteria secrete a lipochitooligosaccharide, called a nodulation factor, which initiates the early steps in formation of a root nodule that eventually provides a home for the nitrogen-fixing bacteria.

Nodulation factors, **1**, are composed primarily of a linear glucosamine (2-amino-2-deoxy-D-glucose) backbone which is *N*-acylated with acetic and fatty acid residues (Figure 1), the latter residing at the nonreducing terminus.[2] Their agricultural and ecological value have made them important targets of laboratory synthesis.[3] Key requirements are (a) the need to differentiate between the constituent glucosamines and (b) ready oligosaccharide assembly. Both of these themes resonate with current interests in our laboratory on amine protection[4,5] and glycosyl donors.[6] Requirements a and b must be met while ensuring that the assembly occurs with 1,2-*trans*-glycosidic linkages, and both can be accomplished by the use of a tetrachlorophthaloyl (TCP)[4,7] protected glucosamine in the presence of other phthalimide-protected amino sugars.

n-Pentenyl glycosides (NPGs)[6] are glycosyl donors that are able to survive many protecting group and other chemical manipulations, yet be ready for immediate activation with *N*-iodosuccinimide/triethylsilyl trifluoromethanesulfonate (NIS/TESOTf) (Figure 2). An additional advantage for larger nod factors, e.g., **1**, $n = 2$, 3, etc., is that the repeating glucosamine unit can be prepared in bulk as **8b** and divided into portions which can be utilized directly as glycosyl donors or be "sidetracked" by bromination,[8] as in **5**, to serve as glycosyl acceptors. These unique properties of NPGs have facilitated the preparation of a diverse array of naturally occurring oligosaccharides.[9] Herein we give full details[10] of our strategy for the construction of the *N*-differentiated nodulation factor backbone through the synthesis of NodRf-III (C18:1, MeFuc),[11] **2**, produced by *Rhizobium fredii* USDA257, which requires 11 synthetic operations,

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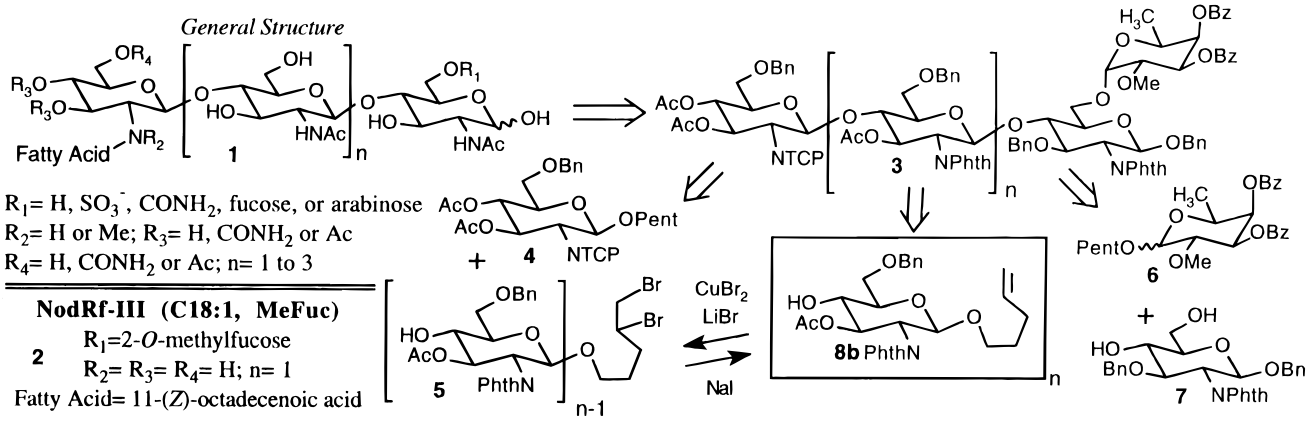


Figure 1.

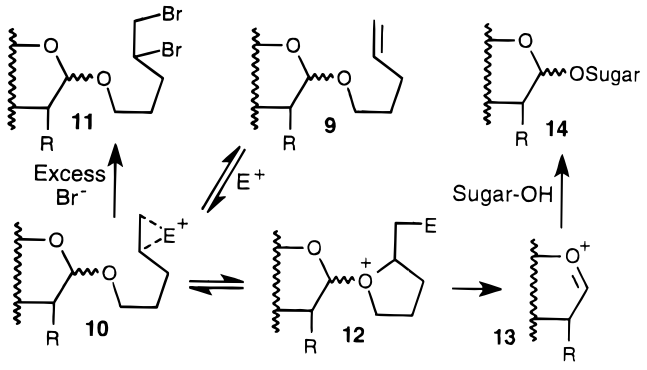


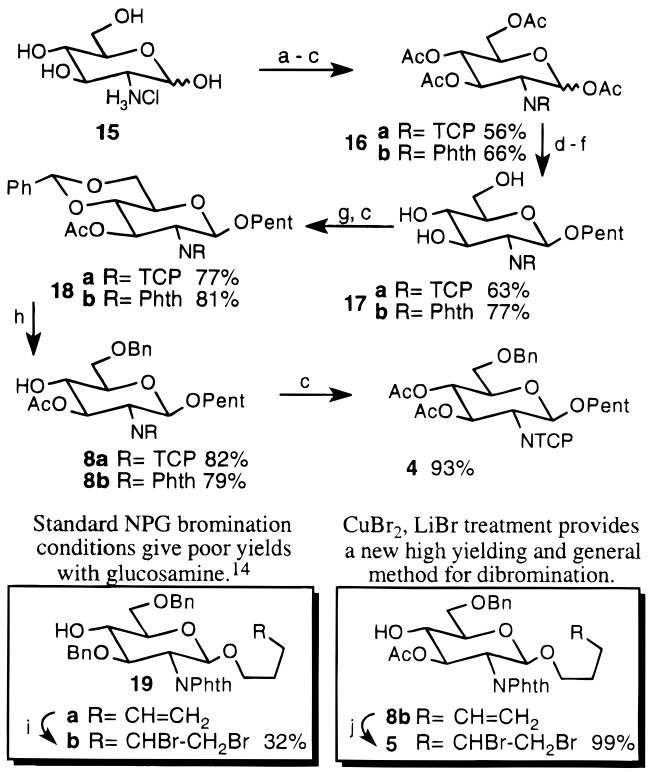
Figure 2.

most of them being chemoselective, for obtaining the fully deprotected nod factor from the constituent monosaccharides.

Discussion

The logical disconnection of **3** (n = 1) into two disaccharides facilitated a strategy involving convergent coupling to give a late stage key tetrasaccharide intermediate, installing the fatty acid residue thereon, and then deprotecting to generate **2**. With this aim the nonreducing end disaccharide was made of monosaccharides prepared from D-glucosamine hydrochloride (Scheme 1), while the reducing end disaccharide was prepared from L-fucose and D-glucosamine hydrochloride (Scheme 2). In the construction of the former, the procedure of Lemieux and co-workers[12] was adapted for preparing the phthalimides **16a** and **16b**, and a Koenigs–Knorr reaction was used for converting them into the corresponding *n*-pentenyl glycosides **17a** and **17b**. Benzylidination followed by chemoselective Garegg[13] reductive cleavage lead to alcohols **8a** and **8b**. The TCP-containing donor was generated through acetylation to afford **4**. In the case of

Scheme 1



[a] Reagents and Conditions: (a) NaOMe / MeOH, 25 °C; (b) TCP or Phth anhydride, NEt_3, CH_2Cl_2, 25 °C; (c) Ac_2O, pyr, 25 °C; (d) HBr/AcOH, Ac_2O, 25 °C; (e) pent-4-enyl alcohol, Ag zeolite, CH_2Cl_2, 40 °C; (f) H_2O, HCl, Acetone, reflux; (g) $PhCH(OMe)_2$, *p*-TsOH, MeCN, reflux; (h) $NaCNBH_3$, HCl, Et_2O, THF, 0 °C; (i) Br_2, Et_4NBr, CH_2Cl_2 25 °C; (j) $CuBr_2$, LiBr, MeCN, THF, 25 °C

the acceptor residue, standard bromination with Br_2 and Et_4NBr would be undesirable, since our previous experience has shown that NPG glucosamine species dibrominated poorly.[14] Substantial hydrolysis of the pentenyl glycosidic group turned out to be the major reaction course, and efforts to counteract this trend were not availing. That glucosamine derivatives should be so reactive to hydrolysis during dibromination was unfortunate, since the analogous glucose and mannose derivatives could be consistently dibrominated in 80–90%

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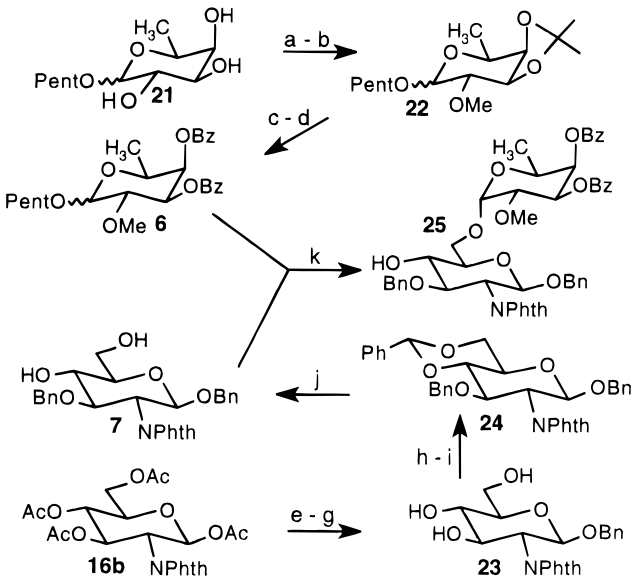
Scheme 2



Reagents and Conditions: (a) $(Me)_2C(OMe)_2$, *p*-TsOH, 25 °C, 81%; (b) MeI, NaH, DMF, 0-25 °C, 93%; (c) 80% aq AcOH, 60 °C, 96%; (d) BzCl, pyr, 0-25 °C, 84%; (e) HBr/AcOH, Ac_2O, 25 °C; (f) benzyl alcohol, Ag zeolite, CH_2Cl_2, 40 °C, 74% (e-f); (g) H_2O, HCl, Acetone, reflux; (h) $PhCH(OMe)_2$, *p*-TsOH, MeCN, reflux, 93% (g-h); (i) NaH, BnBr, DMF, 25 °C; (j) p-TsOH, CH_2Cl_2:MeOH (2:1), 50 °C, 90%; (k) NIS, TESOTf, Et_2O:CH_2Cl_2 (5:1), 0 °C, 85%

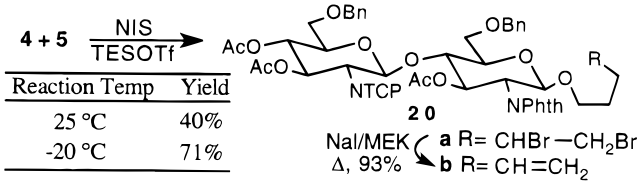
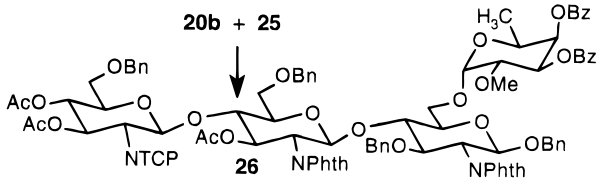


Figure 3.

yields.[6a,8] Clearly a more efficient method of dibromination would be required if glucosamine NPGs were going to be sidetracked in a synthetically useful manner. As a result of exhaustive model studies it was shown that the use of 5 equiv of $CuBr_2$ and 10 equiv LiBr in 3:1 MeCN:THF could afford virtually quantitative recovery of the dibromide **5**.[15]

Typically NPG couplings promoted with NIS/TESOTf, carried out at room temperature, are complete within 15 min. Under these conditions coupling of **4** and **5** afforded a disappointing 40% yield of disaccharide **20a** (Figure 3). However, when the temperature was lowered to −20 °C, **20a** was formed just as rapidly, but in a much improved 71% yield.[16] As anticipated, the TCP group, as with phthalimide, directed the glycosidation to give only the β-linked disaccharide as was evident by the ^{1}H NMR doublet at δ 5.51 ppm (J_{H1-2} = 8.3 Hz) for the newly formed anomeric center. Debromination with NaI afforded the donor **20b** in near quantitative yield. Notably other methods of debromination such as Zn or SmI_2 proved less reliable in the presence of the TCP group.[17]

Table 1. Key Tetrasachharide Coupling



reagents/conditions	temp, °C	yield, %
1.3 equiv of donor	25	45
1.3 equiv of NIS 0.35 equiv of TESOTf	10	56
CH_2Cl_2	0	65

The reducing end disaccharide was then prepared. Installation of isopropylidene on **21** allowed for subsequent 2-*O*-methylation affording **22**. Hydrolysis followed by benzoylation gave the fucosyl donor **6.** The glucosamine acceptor **7**[18] was prepared from **16b**, *via* the glycosyl bromide, and Koenigs−Knorr coupling to benzyl alcohol. Hydrolysis then produced the benzyl glycoside **23**. Benzylidination followed by benzylation at the 3-position then gave **24** which could be hydrolyzed to afford the diol **7**.

The acceptor disaccharide **25** was prepared by coupling the *n*-pentenyl fucoside **6**, used as an anomeric mixture, to diol **7** using a 1:1 stoichiometric ratio of donor to acceptor. Regioselectivity was readily achieved by relying upon the increased reactivity of the primary hydroxyl group[19] of **7**, while the α-anomeric stereoselectivity, attributable to solvent control[20] and the presence of the benzoate esters of **6**, was anticipated from literature precedents.[21] This afforded **25** in 85% yield based on recovered acceptor (or 62% isolated) with only the α-anomer being formed as was evident by the ^{1}H NMR doublet at δ 5.22 ppm (J_{H1-2} = 3.7 Hz). Use of more than 1 equiv of the pentenyl donor resulted in difucosylation even at lower temperatures.

Convergent coupling of disaccharides **20b** and **25** then afforded the tetrasaccharide intermediate **26** in 65% yield, and it was again noted that the yield increased as the temperature was lowered from room temperature to 0 °C (Table 1).

With the oligosaccharide scaffolding in place, the objective was to replace the TCP group with the fatty acid chain to complete the carbon skeleton of the nod factor. Successive deprotection events would then lead to the desired product **2**. Accordingly the TCP moiety of **26** was cleaved with 2 equiv of ethylenediamine affording the free base; but the latter proved to be a modest nucleophile in the condensation with the activated 11-(*Z*)-octadecenoic acid. For example, activation with 2-chloro-1-methylpyridinium iodide[22] did afford the lipidated material, and the unpurified reaction mixture was acetylated to facilitate isolation of product **27** in 19% yield over three steps. Recovery of an additional 26% of the *N*-acetylated **28** illustrates the poor nucleophilicity of the amino sugar toward the fatty acid. Experience in other laboratories has shown that many higher amino sugars

(15) A complete description of the use of the $CuBr_2$/LiBr brominating reagent including mechanistic analysis will be published shortly.

(16) Further reductions in temperture did not improve the yield of **20a**.

(17) Merritt, J. R.; Debenham, J. S.; Fraser-Reid, B. *J. Carbohydr. Chem.* **1996**, *15*, 1, 65−72.

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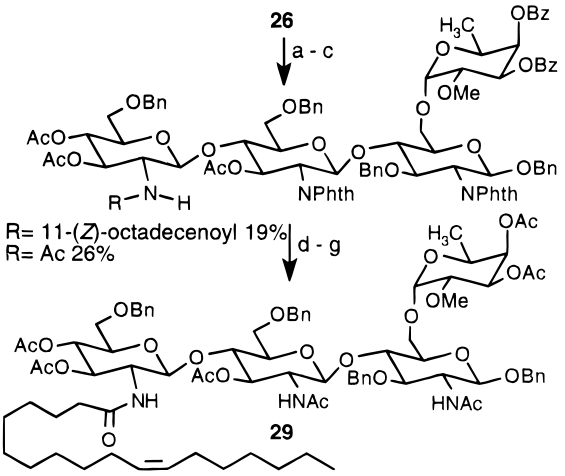
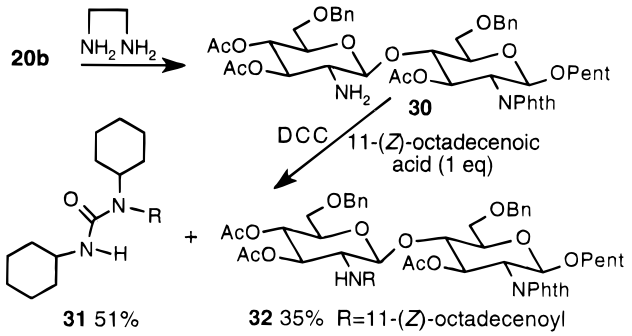
(22) Sutherland, J. K.; Widdowson, P. A. *J. Chem. Soc.* **1964**, 4650. See also, ref 3a.

Scheme 3



[a] Reagents and Conditions: (a) 2 eq. ethylenediamine, MeCN:THF (3:1), 60 °C; (b) 2.5 eq 2-chloro-N-methylpyridinium iodide, MeCN, NEt_3, 2.5 eq 11-(*Z*)-octadecenoic acid, 40 °C; (c) Ac_2O, NEt_3, DMAP, CH_2Cl_2, 25 °C; (d) 150 eq ethylenediamine, EtOH, 60 °C; (e) Ac_2O, NEt_3, CH_2Cl_2, 25 °C; (f) NaOMe/MeOH; (g) Ac_2O, NEt_3, DMAP, CH_2Cl_2, 25°C, 64% (d-g)

Scheme 4

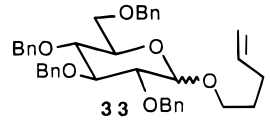


are poor nucleophiles toward fatty acids activated by 2-chloro-1-methylpyridinium iodide,[3a] *O*-acyl-*N*-hydroxysuccinimide,[3d–e] 3-acylthiazolidine-2-thione,[3b] and acyl chlorides[3c] even when treated with excess activated acid (3−10 equiv) over prolonged reaction times (up to 3 days). Indeed in the DCC-mediated coupling of **30** to 11-(*Z*)-octadecenoic acid (Scheme 4), only 35% of amide **32** was formed while half of the activated acid was consumed through the undesired formation of the *N*-acylurea **31** even in the presence of excess HOBt (1-hydroxybenzotriazole).

Treatment of **27** with 150 equiv of ethylenediamine at 60 °C for 10 h effected the removal of the phthalimides and most of the esters. *N*-Acetylation followed by methoxide treatment and then peracetylation[23] gave **29** in 64% yield over four steps.

The presence of the unsaturation in the fatty chain precluded debenzylation by hydrogenolysis, while metal/ammonia reduction might have caused amide cleavage.[24] We were therefore attracted to anhydrous Lewis acid catalyzed debenzylation using $FeCl_3$, a procedure that to our knowledge had not previously been used on structures larger than monosaccharides.[25] Our support studies on model systems,[26] Table 2, were most encouraging. Note that in the debenzylation of the NPG **33** in 83% yield, the terminal double bond is left untouched. Of particular interest is the survival of the glycosidic linkages, including the very acid labile (1→6) fucosyl linkages[27] of the tetrasaccharides **26** and **28**. Amides and esters were also unreactive to this process. Unfortunately, when this debenzylation procedure was employed for **29** containing the 11-(*Z*)-octadecenoyl chain, a complex product resulted. It was evident that this outcome was associated with the fatty acid moiety.

Table 2. Debenzylation with $FeCl_3$[a]

Conditions	Substrate	Yield
$FeCl_3$ 2-5 eq. per benzyl group CH_2Cl_2, 0 °C under strict anhydrous conditions 2-5 hours	 **33**	83%
	26	81%
	28	70%
	29	complex mixture

[a] Products were completely debenzylated. The pent-4-enyl side chain was left unharmed as a result of debenzylation.

Thus it was necessary to revise our approach so that the benzyl groups could be cleaved before installation of the fatty chain. However, it would still be necessary to protect the anomeric center during the amine-promoted dephthaloylation step in order to avoid decomposition of the tetrasaccharide. Their replacement would have to be installed under nonbasic conditions, be stable to high temperatures, excess amine, and NaOMe/MeOH, and yet be cleaved without affecting unsaturation, amides, or glycosidic linkages. Thus, *tert*-butyldimethylsilyl protection seemed the logical choice. To this end, tetrasaccharide **26** was treated with $FeCl_3$ at 0 °C, and the resultant tetrol, **34a**, was exposed to excess *tert*-butyldimethylsilyl chloride affording the trisilylated material **34b** (Scheme 5). This intermediate also allowed for ^{1}H NMR resolution of all of the anomeric protons, which had been partially obscured on the benzylated intermediate. All of the glucosamine β-glycosidic linkages were verified by the ^{1}H NMR doublets at δ 5.41 ppm (J_{H1-2} = 8.5 Hz), 5.37 ppm (J_{H1-2} = 8.5 Hz), and 5.35 ppm (J_{H1-2} = 8.2 Hz) along with the α-fucosyl linkage at 4.91 ppm (J_{H1-2} = 3.4 Hz).

At this point the tetrasaccharide was ready for fatty acid installation. Treatment with ethylenediamine as before yielded the amino sugar which was now subjected to 5 equiv of 11-(*Z*)-octadecenoic acid activated with 2-chloro-1-methylpyridinium iodide (twice as much as the previous time). Acetylation of the unpurified reaction mixture afforded the desired lipooligosaccharide **34c** in 25% yield over three steps. Treatment of **34c** with ethylenediamine (500 equiv) at 90 °C for 34 h removed all of the phthalimides as expected, but surprisingly one of the acetates was only cleaved partially. As a result

(23) Peracetylation of the tetrasachharide was required for solubility purposes since debenzylation with $FeCl_3$ required the use of CH_2Cl_2. These reactions end prematurely if the substrate precipitates as a result of its increased polarity due to deprotection.

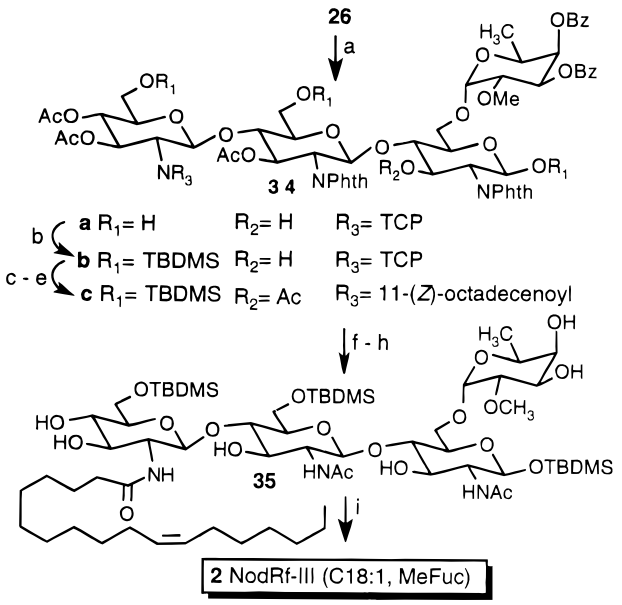
(24) Pearson, A. J.; Rees, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 1118−1119

(25) For application of $FeCl_3$ to debenzylation, see: (a) Park, M. H.; Takeda, R.; Nakanishi, K. *Tetrahedron Lett.* **1987**, *28*, 3823−3824. (b) Kartha, K. P. R.; Dasgupta, F.; Singh, P. P.; Srivastava, H. C. *J. Carbohydr. Chem.* **1986**, *5*, 437. For application of $FeCl_3$ to anomerization, see: (c) Ikemoto, N.; Kim, O. K.; Lo, L. C.; Satyanarayana, V.; Chang, M.; Nakanishi, K. *Tetrahedron Lett.* **1992**, *33*, 4295−4298.

(26) Rodebaugh, R.; Debenham, J. S.; Fraser-Reid, B. *Tetrahedron Lett.* **1996**, *37*, 5477−5478.

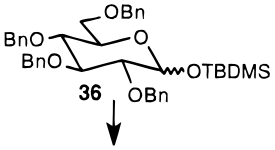
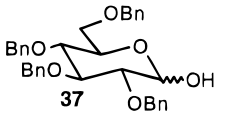
(27) Kunz, H.; Unverzagt, C. *Agnew. Chem., Int. Ed. Engl.* **1988**, *27*, 1697−1699.

Scheme 5



[a] Reagents and Conditions: (a) $FeCl_3$, CH_2Cl_2, 0 °C, 81%; (b) TBDMSCl, imidazole, DMF, 0-25 °C, 80%; (c-e) 25% as per a-c Scheme 3 except using 5 eq of activated fatty acid step b; (f-h) 80% as per d-f Scheme 3 except using 500 eq ethylenediamine, EtOH, MeOH at 90 °C step d; (i) TBAF, AcOH, MeOH, THF, 25 °C, 83%.

Table 3. Desilylation Conditions

Substrate	Conditions	Time	Product/Yield
 **36**	TBAF (8 eq) AcOH,THF, 25 °C	2 h	**37** 75%
	HF/Pyr, 25 °C	5 h	**37** 70%
	AcOH:THF:H_2O 3:1:1, 60 °C	13 h	**37** 10% **36** 85%
 **37**	PPTS (3 eq) MeOH, THF 55 °C	15 h	**36** 100%

the product mixture was *N*-acetylated and then treated with NaOMe/MeOH to afford **35** in 80% yield over three steps.

In order to obtain the natural product **2** desilylation was necessary. While this is normally a trivial process, the operation can be problematic for desilylation at the anomeric position. In order to avoid Lobry de Bruyn-Alberda van Ekenstein rearrangement and other base-promoted degradations,[28] we examined the desilylation of **36** to afford the reducing sugar **37**[29] under a variety of conditions to ensure that the final deprotection step would be uneventful (Table 3). The mildly acidic methods for TBDMS removal were fruitless even after extended reaction times. However buffering the tetrabutylammonium fluoride reaction with AcOH provided good conversion to **37**, as did treatment with HF in pyridine. In view of these encouraging results, compound **35** was treated with tetrabutylammonium fluoride and AcOH which afforded NodRf-III (C18:1, MeFuc), **2**, in 83% yield.[30]

Further studies to extend the methodologies reported herein are underway and will be reported in due course.

Experimental Section

General Procedures. General methods have been followed as previously reported.[31] Experimental procedures and analytical data for monosaccharides not described herein can be found elsewhere.[12,31]

Pent-4-enyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranoside (18a). To pent-4-enyl 4,6-*O*-benzylidene-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranoside[31] (21.81 g, 34.88 mmol) in pyridine (75 mL) was added acetic anhydride (9.87 mL, 104.6 mmol). The reaction was stirred for 2 h before the pyridine was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (300 mL) and washed with 5% aqueous HCl (1 × 100 mL). The aqueous portion was back extracted with CH_2Cl_2 (1 × 70 mL). The solution was then washed with a saturated aqueous $NaHCO_3$ solution (1 × 100 mL) and back extracted with CH_2Cl_2 (1 × 70 mL). The product was purified *via* flash chromatography eluting with 12:88 EtOAc/petroleum ether to afford **18a** as a foam (21.85 g, 97%): R_f 0.40 (15:85 EtOAc/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.47 (m, 5H), 5.78 (app t, J = 9.3 Hz, 1H), 5.62−5.71 (m, 1H), 5.54 (s, 1H), 5.42 (d, J = 8.4 Hz, 1H), 4.44−4.87 (m, 2H), 4.41 (dd, J = 4.6, 6.3 Hz, 1H), 4.28 (dd, J = 4.6, 6.3 Hz, 1H), 3.69−3.89 (m, 4H), 3.45−3.53 (m, 1H), 1.93 (s, 3H), 1.87−1.98 (m, 2H), 1.54−1.63 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.56, 163.29, 162.56, 140.42, 140.17, 137.38, 136.65, 129.79, 129.67, 129.03, 128.06, 126.91, 126.71, 126.05, 114.76, 101.48, 98.07, 78.72, 69.84, 69.23, 68.41, 65.99, 55.99, 29.62, 28.28, 20.47; $[\alpha]^{20}_D$ −5.8° (*c* 1.04, CH_2Cl_2). Anal. Calcd for $C_{28}H_{25}NO_8Cl_4$: C, 51.12; H, 3.90. Found: C, 52.10; H, 3.86.

Pent-4-enyl 3-*O*-Acetyl-6-*O*-benzyl-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranoside (8a). To **18a** (20.70 g, 32.09 mmol) in THF (175 mL) and ether (175 mL) were added 4 Å molecular sieves (9.7 g) and $NaCNBH_3$ (22.90 g, 364.6 mmol). $HCl_{(g)}$ was bubbled through the solution until the foaming had stopped at which point it was diluted with $CHCl_3$ (350 mL) and washed vigorously with saturated aqueous $NaHCO_3$ (1 × 150 mL) solution, back extracting with $CHCl_3$ (1 × 70 mL), and with 5% aqueous HCl (1 × 300 mL), back extracting with $CHCl_3$ (1 × 70 mL). The concentrated solution was purified *via* flash chromatography, eluting with 5:95 EtOAc/CH_2Cl_2 to afford **8a** as a white foam (16.98 g, 82%): R_f 0.33 (5:95 EtOAc/CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.36 (m, 5H), 5.58−5.70 (m, 1H), 5.55 (dd, J = 8.8, 10.6 Hz, 1H), 5.35 (d, 1H), 4.81−4.87 (m, 2H), 4.62 (dd, J = 12, 19.4 Hz, 2H), 4.21 (dd, J = 8.5, 10.7 Hz, 1H), 3.78−3.87 (m, 4H), 3.67−3.72 (m, 1H), 3.45−3.51 (m, 1H), 3.10 (d, J = 4.0 Hz, 1H), 1.96 (s, 3H), 1.80−1.96 (m, 2H), 1.53−1.59 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.39, 163.36, 162.79, 140.40, 137.64, 137.50, 129.82, 128.45, 127.87, 127.71, 126.96, 114.77, 97.59, 73.94, 73.73, 73.58, 71.15, 69.97, 69.02, 55.39, 29.81, 28.42, 20.70; MS (FAB) m/e 647.04 M^-; $[\alpha]^{20}_D$ −4.5° (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{28}H_{27}NO_8Cl_4$: C, 51.95; H, 4.20. Found: C, 51.86; H, 4.24.

Pent-4-enyl 3,4-Di-*O*-Acetyl-6-*O*-benzyl-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranoside (4). Acetylation procedure as per **18a.** The title compound was purified *via* flash chromatography, eluting with 18:82 EtOAc/petroleum ether to afford a white foam (0.495 g, 93%): R_f 0.24 (15:85 EtOAc/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.33 (m, 5H), 5.65−5.71 (m, 2H), 5.34 (d, J = 8.4 Hz, 1H), 5.18 (t, J = 9.1 Hz, 1H), 4.82−4.88 (m, 2H), 4.56 (dd, J = 12, 13.6 Hz, 2H), 4.30 (dd, J = 8.4 Hz, 10.6H), 3.78−3.86 (m, 2H), 3.58−3.62 (m, 2H), 3.47−3.50 (m, 1H), 1.92 (s, 3H), 1.89 (s, 3H), 1.89−1.95 (m, 2H), 1.55−1.66 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.64, 169.45 (bs), 14.49, 137.63, 129.95, 129.90, 128.35, 127.83, 127.72, 126.93, 114.81, 97.60, 73.58, 73.26,

(28) Collins, P.; Ferrier, R. In *Monosaccharides Their Chemistry and Their Roles in Natural Products*; Wiley: Chichester, 1995; pp 139−143.

(29) Glaudemans, C. O. J.; Fletcer, H. G. In *Methods in Carbohydrate Chemistry*, Vol. 2.; Whistler, R., BeMiller, T. N., Eds.; Academic Press: New York; pp 373−375.

(30) ^{1}H NMR, ^{13}C NMR, and HRMS data were consistent with the proposed structure for **2**.

(31) Debenham, J. S.; Debenham, S. D.; Fraser-Reid, B. *Bioorg. Med. Chem.* **1996**, *4*, 1909−1918.

71.12, 69.62, 69.12, 68.80, 55.49, 29.81, 28.41, 20.59, 20.50; MS (FAB) *m/e* 689.06 M^-; $[\alpha]^{20}_D$ 41.2° (*c* 1.02, $CHCl_3$). Anal. Calcd for $C_{30}H_{29}NO_9Cl_4$: C, 52.27; H, 4.24. Found: C, 52.24; H, 4.29.

Pent-4-enyl 3-*O*-Acetyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (18b). Acetylation procedure as per **18a.** The title compound was purified *via* flash chromatography, eluting with 25:75 EtOAc/petroleum ether to afford a white foam (16.64 g, 97%): R_f 0.34 (30:70 EtOAc/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73−7.88 (m, 4H), 7.34−7.48 (m, 5H), 5.89 (dd, J = 8.9, 10.4 Hz, 1H), 5.55 (s, 1H), 5.53−5.66 (m, 1H), 5.43 (d, J = 8.4 Hz, 1H), 4.69−4.79 (m, 2H), 4.42 (dd, J = 4.2, 10.2 Hz, 1H), 4.30 (dd, J = 8.5, 10.4 Hz, 1H), 3.73−3.89 (m, 4H), 3.43−3.50 (m, 1H), 1.90 (s, 3H), 1.83−1.90 (m, 2H), 1.50−1.59 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.11, 168.01 (bs), 137.49, 136.87, 134.20, 131.4 (bs), 129.09, 128.18, 126.17, 123.49, 114.74, 101.56, 98.61, 79.29, 69.72, 69.34, 68.64, 66.15, 55.35, 29.68, 28.40, 20.54; MS (CI) *m/e* 508 MH^+, 525 $(M+NH_4)^+$; $[\alpha]^{20}_D$ −20.7° (*c* 1.07, $CHCl_3$). Anal. Calcd for $C_{28}H_{29}NO_8$: C, 66.26; H, 5.76. Found: C, 66.36; H, 5.79.

Pent-4-enyl 3-*O*-Acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (8b). Reductive benzylidene cleavage as per **8a**. The title compound was purified *via* flash chromatography, eluting with a gradient of 30 → 45% EtOAc/petroleum ether to afford **8** as a white foam (12.75 g, 79%): R_f 0.28 (40:60 EtOAc/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70−7.86 (m, 4H), 7.30−7.37 (m, 5H), 5.58−5.69 (m, 2H), 5.35 (d, J = 8.4 Hz, 1H), 4.58−4.78 (m, 4H), 4.23 (dd, J = 8.5, 10.8 Hz, 1H), 3.74−3.86 (m, 5H), 3.40−3.47 (m, 1H), 3.07 (d, J = 3.7 Hz, 1H), 1.93 (s, 3H), 1.86−1.89 (m, 2H), 1.51−1.56 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.05, 167.60 (bs), 137.77, 137.48, 134.04, 131.19, 128.20, 127.49, 127.43, 123.27, 114.49, 97.68, 74.59, 73.41, 70.63, 69.77, 68.74, 54.60, 29.60, 28.27, 20.44; MS (CI) *m/e* 527 $(M + NH_4)^+$; $[\alpha]^{20}_D$ −19.7° (*c* 1.12, CH_2Cl_2). Anal. Calcd for $C_{28}H_{31}NO_8$: C, 66.00; H, 6.13. Found: C, 66.02; H, 6.15.

4,5-Dibromopentanyl 3-*O*-Acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (5). To $CuBr_2$ (3.134 g, 14.0 mmol) and LiBr (2.432 g, 28.0 mmol) in CH_3CN (37.0 mL) and THF (16 mL) was cannulated **8b** (1.430 g, 2.806 mmol) in CH_3CN (16.0 mL) and THF (7 mL). The reaction was stirred for 12 h in darkness at which point the solution was concentrated to 20% of its original volume. The solution was then diluted with EtOAc (140 mL) and washed with H_2O (1 × 70 mL) and brine (1 × 70 mL) before the aqueous portions were combined and back extracted with EtOAc (1 × 70 mL). The concentrated solution was purified *via* flash chromatography, eluting with 40:60 EtOAc/petroleum ether affording a white foam (1.852 g, 99%): R_f 0.36 (45:55 EtOAc/petroleum ether); $[\alpha]^{20}_D$ 13.0° (*c* 1.36, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71−7.87 (m, 4H), 7.31−7.37 (m, 5H), 5.64 (dd, J = 8.6, 10.4 Hz, 1H), 5.37 (d, J = 8.4 Hz, 1H), 4.63 (dd, J = 12.1, 18.1 Hz, 2H), 4.23 (dd, J = 8.5, 10.8 Hz, 1H), 3.72−4.00 (m, 6H), 3.59−3.65 (m, 1H), 3.45−3.58 (m, 1H), 3.29−3.38 (m, 1H), 3.01 (d, J = 2.9 Hz, 1H), 1.93 (s, 3H), 1.92−1.22 (m, 1H), 1.56−1.66 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.16, 168.88 (bs), 137.67, 134.18, 131.31, 128.37, 127.71, 127.60, 123.51, 97.91, 97.83, 74.38, 73.60, 73.43, 71.05, 69.94, 68.56, 68.51, 54.54, 52.36, 52.27, 36.10, 36.06, 32.71, 32.63, 26.94, 26.82, 20.60; MS (FAB) *m/e* 670.09 MH^+.

4,5-Dibromopentanyl (3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranosyl)-(1→4)-3-*O*-acetyl-6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (20a). To **5** (0.673 g, 0.924 mmol) and **4** (0.476 g, 0.711 mmol) (both dried by azeotroping together with toluene) in CH_2Cl_2 (6.6 mL) were added *N*-iodosuccinimide (0.291 g, 1.294 mmol) and triethylsilyl triflate (83.6 μL, 0.370 mmol). After the solution was stirred for 16 min at −20 °C, the glycosyl donor had been consumed and the reaction was quenched with 10% aqueous $Na_2S_2O_3$ (4 mL) and a saturated aqueous $NaHCO_3$ (4 mL) solution. The mixture was stirred for an additional 5 min before the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The concentrated CH_2Cl_2 solution was purified *via* flash chromatography, eluting with 25:75 EtOAc/petroleum ether to afford **20a** as a white foam (0.643 g, 71%): R_f = 0.16 (25:75 EtOAc/petroleum ether); $[\alpha]^{20}_D$ 43.2° (*c* 1.14, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71−7.85 (m, 4H), 7.09−7.36 (m, 10H), 5.76 (t, J = 9.6 Hz, 1H), 5.61 (dd, J = 9.3, 10.2 Hz, 1H), 5.51 (d, J = 8.3 Hz, 1H), 5.19−5.29 (m, 2H), 4.34−4.53 (m, 4H), 4.09−4.23 (m, 3H), 3.88−3.90 (m, 1H), 3.72−3.85 (m, 1H), 3.28−3.64 (m, 9H), 1.89 (s, 3H), 1.85 (s, 3H), 1.81 (s, 3H), 1.51−2.05 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.33, 169.62, 168.98, 167.74, 167.32, 163.51, 162.21, 140.01, 137.56, 137.22, 134.01, 131.31, 131.14, 129.35, 128.09, 127.95, 127.67, 127.47, 127.22, 126.71, 126.31, 123.30, 97.82, 97.75, 96.81, 74.56, 74.27, 73.16, 72.99, 72.57, 71.54, 70.63, 68.91, 68.27, 68.02, 67.73, 55.69, 54.81, 52.11, 35.92, 32.51, 32.46, 26.71, 26.65, 20.40, 20.35, 20.23; MS (FAB) *m/z* 1272.0 M^-. Anal. Calcd for $C_{53}H_{50}N_2O_{16}Br_2Cl_4$: C, 50.02; H, 3.96; N, 2.20. Found: C, 49.91; H, 3.92; N, 2.16.

Pent-4-enyl (3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranosyl)-(1→4)-3-*O*-acetyl-6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (20b). To **20a** (0.506 g, 0.398 mmol) in methyl ethyl ketone (18 mL) was added NaI (0.894g, 5.964 mmol). The reaction stirred 13 h at 80 °C and was then concentrated *in vacuo*. The syrup was dissolved in EtOAc (20 mL) and washed with 10% aqueous $Na_2S_2O_3$ (15 mL), back extracting the aqueous phase with EtOAc (2 × 15 mL). The concentrated EtOAc solution was purified *via* flash chromatography, eluting with 40:60 EtOAc/petroleum ether to afford **20b** as a white foam (0.442 g, 93%): R_f 0.16 (25:75 EtOAc/petroleum ether); $[\alpha]^{20}_D$ 53.0° (*c* 1.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.85 (m, 4H), 7.10−7.34 (m, 10H), 5.78 (dd, J = 8.9, 10.6 Hz, 1H), 5.50−5.66 (m, 3H), 5.18−5.30 (m, 2H), 4.66−4.76 (m, 2H), 4.36−4.56 (m, 4H), 4.08−4.24 (m, 3H), 3.37−3.78 (m, 8H), 1.90 (s, 3H), 1.85 (s, 6H), 1.81−1.92 (m, 2H), 1.40−1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.45, 169.74, 169.09, 167.79, 167.65, 163.64, 162.32, 140.11, 137.72, 137.47, 137.32, 134.08, 131.33 (bd), 129.46, 128.18, 128.01, 127.77, 127.55, 127.27, 126.83, 126.44, 123.28, 114.55, 97.85, 96.94, 74.74, 74.35, 73.27, 73.04, 72.65, 71.71, 70.77, 69.06, 68.71, 68.16, 67.78, 55.79, 54.98, 29.62, 28.28, 20.49, 20.41, 20.30; MS (FAB) *m/z* 1112.1 M^-. Anal. Calcd for $C_{53}H_{50}N_2O_{16}Cl_4 \cdot H_2O$: C, 56.29; H, 4.64; N, 2.48. Found: C, 56.48; H, 4.65; N, 2.42.

Pent-4-enyl L-Fucopyranoside (21). To a mixture of L-fucose (21.4 g, 130.4 mmol) and pentenyl alcohol (115 mL) was added a catalytic amount of camphorsulfonic acid (300 mg) and the mixture was heated at 90 °C for 48 h. The reaction mixture was cooled, neutralized with triethylamine, and then the excess pentenyl alcohol was removed under high vacuum. The residue was purified by flash chromatography eluting with 96:4 → 90:10 CH_2Cl_2/MeOH to afford **21** as a clear syrup (26.05 g, 86%): R_f 0.35 (90:10 CH_2Cl_2/MeOH); ^{1}H NMR (300 MHz) δ 5.74−5.89 (m, 1H), 4.81−5.05 (m, 3H), 4.21 (d, 1H), 3.89−4.00 (m, 1H), 3.65−3.79 (m, 3H), 3.41−3.63 (m, 3H), 3.21−3.41 (bs, 3H), 2.08−2.18 (m, 2H), 1.69−1.78 (m, 2H), 1.21−1.39 (m, 3H); ^{13}C NMR (75 MHz) 138.02, 114.96, 103.14, 98.67, 74.05, 72.11, 71.73, 71.19, 70.99, 70.59, 69.48, 68.91, 67.56, 66.04, 30.31, 30.02, 28.66, 16.35, 16.25; MS (FAB) *m/e* 233.14 MH^+. Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56,62; H, 8.55.

Pent-4-enyl 3,4-*O*-Isopropylidene-2-*O*-methyl-L-fucopyranoside (22). To a solution of pent-4-enyl L-fucopyranoside **21** (21.20 g, 91.3 mmol) in acetone previously dried over 3 Å molecular sieves (250 mL) was added *p*-toluenesulfonic acid (1.042 g, 0.06 equiv). After 30 min, 2,2-dimethoxypropane (21.3 mL, 173.5 mmol, 1.9 equiv) was added, and the mixture was stirred for an additional 30 min before being quenched with saturated aqueous $NaHCO_3$ (10 mL). The concentrated material was taken up in $CHCl_3$ (300 mL) and washed consecutively with H_2O (2 × 125 mL) and brine (2 × 100 mL) before concentration. The residue was purified *via* flash chromatography eluting with 75:25 → 70:30 petroleum ether/EtOAc to afford pent-4-enyl 3,4-*O*-isopropylidene-L-fucopyranoside as a yellow oil (20.14 g, 81%): R_f 0.60 (3:1 petroleum ether/EtOAc); ^{1}H NMR (300 MHz) δ 5.74−5.89 (m, 1H), 4.96−5.05 (m, 2H), 4.80 (d, J = 3.5 Hz, 1H), 4.21 (t, 1H), 4.01−4.16 (m, 2H), 3.71−3.79 (m, 2H), 3.48−3.55 (m, 2H), 2.42 (d, 1H), 2.08−2.18 (m, 2H), 1.69−1.78 (m, 2H), 1.52 (d, 3H), 1.31−1.46

(m, 6H); ^{13}C NMR (75 MHz) 138.12, 137.90, 114.91, 114.78, 102.61, 96.41, 79.37, 76.07, 75.72, 74.11, 69.56, 67.52, 63.02, 30.22, 28.84, 28.38, 27.91, 26.38, 26.28, 16.53, 16.31; MS (FAB) *m/e* 273.18 MH^+. Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.64; H, 8.82.

A solution of pent-4-enyl 3,4-*O*-isopropylidene-L-fucopyranoside (16.7 g, 61.3 mmol) in THF was cooled to 0 °C, and NaH (3.433 g of a 60% dispersion in mineral oil, 1.4 equiv) was added. After the evolution of H_2 subsided, MeI (5.7 mL, 1.5 equiv) was added dropwise. The solution was allowed to slowly come to room temperature after 3 h at 0 °C, and it was stirred overnight before being quenched with glacial acetic acid. The mixture was diluted with ether (600 mL) and consecutively washed with H_2O (1 × 200 mL), saturated aqueous $NaHCO_3$ (2 × 250 mL), and brine (1 × 250 mL). The concentrated solution was purified *via* flash chromatography (90:10 → 85:15 petroleum ether/EtOAc) to give **22** as a yellow oil (16.27 g, 93%). R_f 0.45 (90:10 petroleum ether/EtOAc); ^{1}H NMR (300 MHz) 5.74−5.86 (m, 1H), 4.94−5.06 (m, 2H), 4.88 (d, J = 3.5 Hz, 1H), 4.15−4.25 (m, 1H), 3.91−4.11 (m, 2H), 3.61−3.69 (m, 1H), 3.54−3.59 (m, 1H), 3.51 (s, 3H), 3.33−3.37 (dd, J = 3.5, 7.9 Hz, 1H), 2.08−2.15 (m, 2H), 1.68−1.78 (m, 2H), 1.61 (s, 1H), 1.31−1.42 (m, 5H); ^{13}C NMR (75 MHz) 138.12, 137.99, 114.89, 114.79, 102.68, 96.47, 82.32, 79.27, 79.07, 76.39, 76.10, 75.72, 67.48, 63.00, 58.52, 30.23, 28.49, 28.38, 26.36, 26.28, 16.54, 16.31; MS (FAB) *m/e* 287.2 MH^+. Anal. Calcd for $C_{15}H_{26}O_5$: C, 62.91; H, 9.15. Found: C, 62.97; H, 9.09.

Pent-4-enyl 3,4-Di-*O*-benzoyl-2-*O*-methyl-L-fucopyranoside (6). A solution of **22** (16.06 g, 56.08 mmol) in 80% glacial acetic acid (200 mL) was heated at 60 °C for 5 h. The acetic acid was then azeotroped with toluene to give pent-4-enyl 2-*O*-methyl-L-fucopyranoside as a clear oil (13.27 g, 96%): ^{1}H NMR (300 MHz) 5.76−5.85 (m, 1H), 4.95 −5.05 (m, 3H), 4.21 (d, J = 7.7 Hz, 1H), 3.82−3.99 (m, 2H), 3.67−3.73 (m, 1H), 3.61 (s, 1H), 3.41−3.53 (m, 5H), 2.11−2.20 (m, 2H), 1.68−1.79 (m, 2H), 1.26−1.37 (m, 3H); MS (FAB) *m/e* 247.2 MH^+.

Pent-4-enyl 2-*O*-methyl-L-fucopyranoside (13.27 g, 53.9 mmol) was dissolved in pyridine (50 mL) at 0 °C, and benzoyl chloride (19.8 mL, 3 equiv) was slowly added via a syringe. The mixture was allowed to slowly warm to room temperature and was stirred overnight before being quenched with saturated aqueous $NaHCO_3$ (50 mL). The reaction mixture was diluted with ether (400 mL) and washed consecutively with saturated aqueous $NaHCO_3$ (2 × 150 mL), H_2O (1 × 200 mL), 5% HCl (2 × 100 mL), and saturated aqueous $NaHCO_3$ (2 × 150 mL). The concentrated solution was purified *via* flash chromatography (95:5 → 87:13 petroleum ether/EtOAc) to afford **6** as a yellow syrup (20.58 g, 84%): R_f 0.47 (87:13 petroleum ether/EtOAc); ^{1}H NMR (300 MHz) 7.84−8.12 (m, 4H), 7.47−7.63 (m, 4 H), 7.31−7.39 (m, 2H), 5.76−5.85 (m, 1H), 5.62−5.71 (m, 2 H), 4.95−5.19 (m, 3H), 4.30−4.42 (m, 1H), 3.90−3.99 (m, 1H), 3.52-3.65 (m, 2H), 3.49 (s, 3H), 2.15−2.29 (m, 2H), 1.75−1.88 (m, 2H), 1.21−1.33 (m, 3H); ^{13}C NMR (75 MHz) 165.95, 165.87, 165.65, 165.61, 138.02, 133.35, 133.23, 133.01, 132.87, 129.94, 129.77, 129.60, 128.50, 128.21, 115.00, 103.70, 97.17, 78.72, 76.07, 73.53, 72.27, 71.42, 70.93, 69.67, 69.22, 67.75, 64.73, 60.98, 59.03, 30.29, 30.14, 28.88, 28.61, 16.34, 16.12; MS (FAB) *m/e* 455.19 MH^+. Anal. Calcd for $C_{26}H_{30}O_7$: C, 68.71; H, 6.65. Found: C, 68.61; H, 6.65.

Benzyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (24). To **16b**[12] (43.00 g, 90.0 mmol) was added HBr (577 mmol, 78 mL, 30 wt % in acetic acid) in acetic anhydride (20 mL). After being stirred in darkness for 24 h, the reaction mixture was diluted with $CHCl_3$ (500 mL) and poured onto ice-cold H_2O (500 mL). The layers were separated, and the organic portion was washed with H_2O (2 × 400 mL) and saturated aqueous $NaHCO_3$ (2 × 300 mL), dried, and concentrated to a syrup. To the crude glycosyl bromide were added benzyl alcohol (18.6 mL, 180 mmol, 2 equiv) and Ag zeolite powder (72.1 g) in CH_2Cl_2 (300 mL). The reaction was stirred in darkness at 50 °C for 36 h and was then filtered through Celite. After concentration of the CH_2Cl_2 solution, the residue was flash chromatographed, eluting with 70:30 petroleum ether/EtOAc → 60:40 petroleum ether/EtOAc to give benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside as a white solid (34.95 g, 74%): R_f 0.42 (70:30 petroleum ether/EtOAc); mp 106 °C; $[\alpha]^{21}_D$ −11.2° (*c* 1.32, $CHCl_3$); ^{1}H NMR (300 MHz) 7.71−7.86 (m, 4H), 7.07−7.12 (m, 5H), 5.79 (dd, J = 9.2, 10.5 Hz, 1H), 5.37 (d, J = 8.4 Hz, 1H), 5.19 (t, J = 9.8 Hz, 1H), 4.85 (d, J = 12.3 Hz, 1H), 4.53 (d, J = 12.2 Hz, 1H), 4.32−4.41 (m, 2H), 4.18−4.22 (m, 1H), 3.84−3.90 (m, 1H), 2.14 (s, 3H), 2.03 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (75 MHz) 170.76, 170.13, 169.51, 167.50, 136.61, 134.19, 131.37, 128.25, 127.84, 127.75, 127.61, 127.58, 123.55, 97.18, 71.32, 70.64, 68.97, 62.02, 54.62, 20.81, 20.65, 20.47; MS (FAB) *m/e* 526.19 MH^+. Anal. Calcd for $C_{27}H_{27}NO_{20}$: C, 61.70; H, 5.18; N, 2.67. Found: C, 61.54; H, 5.20; N, 2.68.

To benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (34.52 g, 65.69 mmol) in acetone (710 mL) were added H_2O (325 mL) and concentrated HCl (75 mL). The mixture was heated at 80 °C for 16 h before the mixture was concentrated and the residue was diluted in EtOAc (600 mL). The EtOAc layer was washed with H_2O (2 × 300 mL) and saturated aqueous $NaHCO_3$ (2 × 300 mL) before concentration to give the triol **23** as a white solid (24.40 g, 93%). **23** was then dissolved in acetonitrile (250 mL) before addition of benzaldehyde dimethyl acetal (17.3 mL, 115.4 mmol, 2 equiv) and *p*-toluenesulfonic acid (439 mg, 2.31 mmol). After the solution was refluxed for 15 h, the reaction was quenched with Et_3N (2 mL) and concentrated to $^1/_4$ of its original volume before being diluted with EtOAc (500 mL). The organic solution was then washed with saturated aqueous $NaHCO_3$ (1 × 250 mL) and H_2O (1 × 250 mL), back extracting the combined aqueous portions with EtOAc (3 × 150 mL). The concentrated residue was recrystallized from EtOAc/petroleum ether (2:1) to give benzyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside as a white solid (26.013 g, 93%): R_f 0.44 (70:30 petroleum ether/EtOAc); mp 189 °C; $[\alpha]^{21}_D$ −81.8° (*c* 1.67, $CHCl_3$); ^{1}H NMR (300 MHz) 7.71−7.86 (m, 4H), 7.36−7.51 (m, 5H), 7.03−7.10 (m, 5H), 5.58 (s, 1H), 5.26 (d, J = 8.4 Hz, 1H), 4.84 (d, J = 12.3 Hz, 1H), 4.61−4.68 (m, 1H), 4.52 (d, J = 12.4 Hz, 1H), 4.45 (m, 1H), 4.29 (dt, J = 8.5, 10.5 Hz, 1H), 3.81−3.90 (m, 1H), 3.62−3.71 (m, 1H), 2.55 (bs, 1H); ^{13}C NMR (75 MHz) 167.66, 136.71, 136.53, 133.70, 131.28, 129.05, 128.09, 127.94, 127.43, 127.35, 126.04, 123.10, 101.61, 97.59, 81.82, 70.94, 68.38, 68.11, 65.79, 56.32; MS (FAB) *m/e* 488.2 MH^+. Anal. Calcd for $C_{28}H_{25}NO_7$: C, 68.99; H, 5.17; N, 2.87. Found: C, 68.76; H, 5.25; N, 2.83.

To benzyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (11.80 g, 24.2 mmol) in dimethylformamide (47 mL) were added NaH (1.452 g of a 60% dispersion in mineral oil, 36.3 mmol, 1.5 equiv) and benzyl bromide (5.76 mL, 48.4 mmol, 2 equiv) at 0 °C. The reaction was allowed to come to room temperature after 10 min and was quenched after an additional 1 h of stirring with AcOH (3 mL). The DMF was evaporated under high vacuum, and the residue was taken up in CH_2Cl_2 (250 mL). The organic solution was washed with H_2O (1 × 150 mL) and saturated aqueous $NaHCO_3$ (1 × 150 mL). The combined aqueous layers were back extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were concentrated and purified *via* flash chromatography, eluting with 12:88 → 20:80 EtOAc/petroleum ether to afford **24** as an oil (13.36 g, 96%): R_f 0.76 (70:30 petroleum ether/EtOAc); $[\alpha]^{21}_D$ −95.6° (*c* 1.55, $CHCl_3$); ^{1}H NMR (300 MHz) 7.71−7.86 (m, 4H), 7.36−7.51 (m, 5H), 6.84−7.10 (m, 10H), 5.64 (s, 1H), 5.20 (d, J = 8.4 Hz, 1H), 4.76−4.83 (m, 2H), 4.38−4.46 (m, 4H), 4.23−4.29 (m, 1H), 3.80−3.92 (m, 2H), 3.62−3.68 (m, 1H); ^{13}C NMR (75 MHz) 167.56, 137.94, 137.37, 136.87, 133.73, 131.57, 129.06, 128.34, 128.21, 128.09, 128.04, 127.67, 127.39, 126.10, 123.28, 101.35, 97.91, 83.04, 74.42, 74.08, 71.19, 68.82, 66.06, 55.84; MS (FAB) *m/e* 578.2 MH^+. Anal. Calcd for $C_{35}H_{31}NO_7$: C, 72.78; H, 5.41; N, 2.42. Found: C, 72.78; H, 5.42; N, 2.37.

Benzyl 3-*O*-Benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (7). To **24** (14.13 g, 24.45 mmol) in CH_2Cl_2/MeOH (2:1, 280 mL) was added *p*-toluenesulfonic acid (930 mg, 4.89 mmol, 0.2 equiv), and the reaction mixture was refluxed at 50 °C for 15 h. The reaction was then quenched with Et_3N (0.5 mL) and concentrated, and the residue was purified via flash

chromatography (53:47 → 62:38 EtOAc/CH_2Cl_2) to afford **7** as an oil (10.75 g, 90%): R_f 0.31 (1:1 EtOAc/CH_2Cl_2); $[\alpha]^{21}_D$ −2.65° (*c* 1.77, $CHCl_3$); ^{1}H NMR (300 MHz) δ 7.55−7.84 (m, 4H), 6.96−7.26 (m, 10H) 5.18 (d, J = 8.0 Hz, 1H), 4.76 (d, J = 12.3 Hz, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.51 (d, J = 12.3 Hz, 2H), 4.17−4.31 (m, 2H), 3.75−3.98 (m, 3H), 3.51 (m, 1H), 2.53 (bs, 1H); ^{13}C NMR (75 MHz) δ 167.95 (bs), 138.08, 137.09, 133.76 (bs), 131.56 (bs), 128.34, 128.22, 127.88, 127.69, 127.51, 123.32, 97.61, 78.97, 75.25, 74.46, 72.07, 71.24, 62.32, 55.62. Anal. Calcd for $C_{28}H_{26}NO_7$: C, 68.70; H, 5.56; N, 2.86. Found: C, 68.41; H, 5.67; N, 2.80.

Benzyl (3,4-Di-*O*-benzoyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (25). To **6** (887.0 mg, 1.95 mmol) and **7** (958.1, 1.95 mmol) (both dried by azeotroping together with toluene) in Et_2O:CH_2Cl_2 (5:1, 17 mL) were added *N*-iodosuccinimide (677 mg, 3.01 mmol) and triethylsilyl triflate (146 μL, 0.645 mmol). After the solution was stirred for 25 min at room temperature, the glycosyl donor had been consumed and the reaction was quenched with 10% aqueous $Na_2S_2O_3$ (5 mL) and saturated aqueous $NaHCO_3$ (5 mL). The mixture was diluted with $CHCl_3$ (150 mL) and washed with brine (2 × 50 mL). The aqueous layers were back extracted with $CHCl_3$ (3 × 50 mL). The concentrated $CHCl_3$ solution was purified *via* flash chromatography, eluting with 65:35 → 45:55 petroleum ether/EtOAc to afford **25** as a white foam (1.0373 g, 1.21 mmol) and recovered **7** (259.5 mg, 0.53 mmol). The total yield of **25** was 85% on the basis of on recovered alcohol **7**: R_f 0.39 (45:55 EtOAc/petroleum ether); $[\alpha]^{20}_D$ −128.0° (*c* 1.30, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 7.1 Hz, 2H), 7.89 (d, J = 7.1 Hz, 2H), 7.49−7.86 (m, 8H), 7.30−7.35 (m, 3H), 6.92−7.11 (m, 9H), 5.66−5.71 (m, 2H), 5.22 (d, J = 3.7 Hz, 1H), 5.16−5.19 (m, 1H), 4.78 (dt, J = 2.4 Hz, 12.5 Hz, 2H), 4.52 (t, J = 13.3 Hz, 2H), 4.43−4.46 (m, 1 H), 4.25 (dd, J = 3.5, 4.5 Hz, 2H), 3.89−4.14 (m, 4H), 3.70−3.75 (m, 1H), 3.51 (s, 3H), 2.75 (m, 1H), 1.23 (d, J = 6.57 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.92, 165.87, 165.50, 138.34, 137.11, 133.70, 133.32, 133.00, 131.67, 130.01, 129.81, 129.75, 129.65, 128.58, 128.29, 128.20, 128.10, 127.93, 127.59, 127.34, 123.27, 97.92, 97.28, 78.41, 76.34, 74.25, 73.69, 73.41, 72.19. 71.07, 70.64, 68.73, 65.25, 59.55, 55.55, 16.13; MS (FAB) m/z 857.2 M^-. Anal. Calcd for $C_{49}H_{47}NO_{13}\cdot H_2O$: C, 66.98; H, 5.48; N, 1.58. Found: C, 67.19; H, 5.64; N, 1.60.

Benzyl (3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-benzoyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→6)]-3-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (26). To **20b** (0.413 g, 0.37 mmol) and **25** (0.245 g, 0.29 mmol) (both dried by azeotroping together with toluene) in CH_2Cl_2 (2.9 mL) at 0 °C were added *N*-iodosuccinimide (0.110 g, 0.48 mmol) and triethylsilyl triflate (30 μL, 0.13 mmol). After the solution was stirred for 22 min at 0 °C, the reaction was quenched with 10% aqueous $Na_2S_2O_3$ (2 mL) and saturated aqueous $NaHCO_3$ (2 mL). The mixture was diluted with CH_2Cl_2 (15 mL) before the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The concentrated residue was purified via flash chromatography, eluting with 2:3 EtOAc/petroleum ether to give **26** as a white amorphous powder (0.349 g, 65%): R_f 0.39 (45:55 EtOAc/petroleum ether); $[\alpha]^{20}_D$ −30.0° (*c* 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.3 Hz, 2H), 7.90−7.92 (bs, 2H), 7.88 (d, J = 7.3 Hz, 2H), 7.71−7.81 (m, 3H), 7.58−7.66 (m, 2H), 7.46−7.54 (m, 3H), 7.37 (t, J = 7.8 Hz, 2H), 7.20−7.32 (m, 6H), 7.12−7.19 (m, 3H), 6.96−7.04 (m, 5H), 6.93 (d, J = 6.7 Hz, 2H), 6.77 (d, J = 6.7 Hz, 2H), 6.61−6.70 (m, 4H), 5.80 (dt, J = 1.6 Hz, 8.6 Hz, 1H), 5.58−5.66 (m, 4H), 5.49 (d, J = 8.3 Hz, 1H), 5.27 (d, J = 3.5 Hz, 1H), 5.17 (t, 9.4 Hz, 1H), 4.94 (d, J = 8.6 Hz, 1H), 4.67 (d, J = 12.4 Hz, 1H), 4.59 (d, J = 12.9 Hz, 1H), 4.32−4.47 (m, 7H), 4.11−4.24 (m, 5H), 4.03−4.08 (m, 1H), 3.91 (dd, J = 6.5 Hz, 3.5 Hz, 2H), 3.85 (d, J = 11.0 Hz, 1H), 3.78 (d, J = 12.1 Hz, 1H), 3.72 (d, J = 9.6 Hz, 1H), 3.41−3.60 (m, 8H), 3.32 (bd, J = 7.8 Hz, 1H), 1.89 (s, 3H), 1.80 (s, 6H), 1.14 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.55, 169.77, 169.27, 168.26, 167.63, 165.87, 165.31, 140.06, 138.27, 137.92, 137.46, 137.02, 134.49, 134.25, 133.17, 132.81, 131.59, 131.41, 129.98, 129.87, 129.77, 129.65, 129.42, 128.49, 128.26, 128.08, 128.04, 127.91, 127.65, 127.63, 127.55, 127.45, 127.34, 127.21, 126.94, 126.76, 126.71, 126.63, 126.33, 123.74, 123.41, 97.76, 96.79, 96.54, 96.28, 76.48, 76.12, 75.52, 75.28, 74.28, 74.18, 73.52, 73.40, 73.25, 72.65, 72.59, 72.37, 70.77, 70.64, 69.95, 69.33, 68.49, 67.50, 64.74, 64.58, 59.44, 55.94, 55.84, 55.63, 20.63, 20.53, 20.41, 15.98; MS (FAB) m/z 1883.34 M^-. Anal. Calcd for $C_{97}H_{87}N_3O_{28}Cl_4\cdot 2H_2O$: C, 60.66; H, 4.78; N, 2.19. Found: C, 60.71; H, 4.60; N, 2.10.

Benzyl (3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-{11(*Z*)-octadecenamido}-*β*-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-benzoyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→6)]-3-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (27). To **26** (132.0 mg, 70.04 μmol) in 1.0 mL of 3:1 acetonitrile/ tetrahydrofuran was added ethylenediamine (10.6 μL, 0.1582 mmol) before the solution was heated to 60 °C. The reaction mixture was stirred for 10.5 h, allowed to cool to room temperature, concentrated and then filtered through a short column of silica gel with 5:95 MeOH/CH_2Cl_2. The amine in CH_3CN (1.5 mL) was then added to *cis*-11-octadecenoic acid (50.3 mg, 0.178 mmol) pretreated with both triethylamine (37.2 μL, 0.267 mmol) for 15 min and then 2-chloro-N-methylpyridinium iodide (45.5 mg, 0.178 mmol) in CH_3CN (0.5 mL) for 15 min at 40 °C. The reaction was stirred 2 h at 45 °C and was then concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (30 mL) and washed with saturated aqueous $NaHCO_3$ (10 mL), back extracting the aqueous portion with CH_2Cl_2 (2 × 5 mL). The solution was dried (Na_2SO_4) and concentrated. To the residue were added acetic anhydride (0.280 mL, 2.965 mmol), triethylamine (49.6 μL, 0.3558 mmol), and DMAP (29.0 mg, 0.237 mmol) in pyridine (1 mL) for 10 h. The reaction mixture was concentrated *in vacuo* before being diluted with CH_2Cl_2 (25 mL) and washed with both 5% aqueous HCl (1 × 8 mL), back extracting with CH_2Cl_2 (2 × 10 mL), and saturated aqueous $NaHCO_3$ (8 mL), back extracting the aqueous portion with CH_2Cl_2 (2 × 10 mL). The reaction mixture was concentrated, and the residue was purified by flash chromatography, eluting with a gradient of 3.5 → 5% MeOH/CH_2Cl_2. Compound **27** was recovered as a film (24.2 mg, 19%): R_f 0.71 (5:95 MeOH/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78−8.12 (m, 38H), 5.62−5.74 (m, 4H), 5.31−5.38 (m, 3H), 4.67−5.20 (m, 6H), 4.22−4.61 (m, 10H), 4.12 (t, J = 8.5 Hz, 1H), 4.04 (t, J = 8.9 Hz, 1H), 3.51 (s, 3H), 3.40−3.96 (m, 12H), 3.33 (bd, J = 9.9 Hz, 1H), 1.98−2.08 (m, 6H), 1.88 (s, 3H), 1.85 (s, 3H), 1.79 (s, 3H), 1.16 (d, J = 6.5 Hz, 3H), 1.04−1.38 (m, 20H), 0.82−0.92 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.17, 170.51, 170.22, 169.48, 168.20, 167.58, 165.92, 165.03, 163.83, 138.57, 137.83, 137.34, 136.95, 134.37, 134.18, 133.54, 133.47, 133.44, 133.41, 133.21, 132.86, 131.65, 131.54, 131.45, 129.93, 129.89, 129.78, 129.67, 129.60, 129.22, 128.80, 128.73, 128.67, 128.51, 128.34, 128.27, 128.10, 127.87, 127.77, 127.51, 127.39, 126.87, 123.66, 123.44, 100.40, 96.78, 96.14, 95.91, 77.54, 77.25, 77.16, 76.78, 75.57, 75.34, 74.81, 73.85, 73.71, 73.57, 73.45, 73.31, 72.82, 72.42, 72.30, 71.06, 70.26, 70.01, 69.63, 68.91, 64.54, 58.99, 55.68, 55.57, 53.39, 36.09, 31.76, 29.79, 29.71, 29.57, 29.49, 29.41, 29.35, 29.31, 28.97, 28.81, 27.20, 25.52, 25.28, 22.64, 20.65, 20.60, 20.38, 15.95, 14.12; MS (FAB) m/e 1880.8 MH^+.

Benzyl (2-Acetamido-3,4-di-*O*-acetyl-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-benzoyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→6)]-3-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (28). This compound was isolated as a reaction byproduct of the above reaction (30 mg, 26%): R_f 0.32 (5:95 MeOH/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78−8.10 (m, 38H), 5.71−5.78 (m, 2H), 5.62−5.68 (m, 2H), 5.35 (d, J = 3.4 Hz, 1H), 4.99 (d, J = 8.5 Hz, 1H), 4.67−4.98 (m, 5H), 4.53−4.62 (m, 2H), 4.20−4.48 (m, 6H), 4.12 (dd, J = 8.5, 10.2 Hz, 1H), 3.54 (s, 3H), 3.38−4.44 (m, 14H), 3.33 (bd, J = 9.6 Hz, 1H), 1.89 (s, 3H), 1.85 (s, 3H), 1.80 (bs, 3H), 1.77 (s, 3H), 1.16 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.66, 170.17, 169.41, 169.20, 168.19, 167.58, 165.94, 165.02, 138.56, 137.72, 137.34, 136.96, 134.32, 134.13, 133.42, 133.19, 132.91, 131.68, 131.59, 131.51, 129.91, 129.83, 129.76, 129.63, 129.34, 128.82, 128.63, 128.51, 128.43,

128.32, 128.24, 128.10, 127.84, 127.78, 127.74, 127.52, 127.39, 126.89, 123.64, 123.42, 100.42, 96.84, 95.95, 95.71, 76.52, 75.63, 75.41, 74.44, 73.73, 73.67, 73.61, 73.37, 73.33, 72.96, 72.49, 72.32, 71.13, 70.11, 69.99, 69.61, 68.98, 64.61, 64.53, 58.83, 55.71, 55.54, 53.49, 22.22, 20.62, 20.58, 20.33, 15.94; MS (FAB) *m/e* 1658.4 MH^+.

Benzyl (3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-{11(*Z*)-octadecenamido}-β-D-glucopyranosyl)-(1→4)-(2-acetamido-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→6)]-2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (29). To **27** (23.0 mg, 12.22 μmol) in EtOH (1 mL) was added ethylenediamine (0.122 mL, 1.833 mmol). The reaction was stirred for 10 h at 60 °C and then concentrated *in vacuo*. The reaction mixture was filtered through a short column of silica gel with 10:90 MeOH/CH_2Cl_2. The residue was then treated with acetic anhydride (11.5 μL, 0.122 mmol) and NEt_3 (17 μL, 0.122 mmol) in CH_2Cl_2 (1 mL) for 25 min before the reaction mixture was concentrated *in vacuo*. To the residue were added a NaOMe solution (0.125 mmol in 0.25 mL MeOH) in MeOH (0.5 mL) and THF (0.5 mL). After being stirred for 4 h, the reaction mixture was quenched with AcOH (7.0 μL, .125 mmol), concentrated, and then treated with acetic anhydride (68.0 μL, 0.726 mmol), NEt_3 (14.2 μL, 0.103 mmol) and DMAP (7.3 mg, 0.060 mmol) in pyridine (0.75 mL) and CH_2Cl_2 (0.5 mL) for 12 h. The reaction mixture was concentrated *in vacuo* before being diluted with CH_2Cl_2 (25 mL) and washed with both 5% aqueous HCl (1 × 8 mL), back extracting with CH_2Cl_2 (2 × 10 mL), and saturated aqueous $NaHCO_3$ (8 mL), back extracting the aqueous portion with CH_2Cl_2 (2 × 10 mL). The reaction mixture was concentrated, and the residue was purified by flash chromatography, eluting with 5:95 MeOH/CH_2Cl_2. Compound **29** was recovered as a film (12.3 mg, 64%): R_f 0.20 (5:95 MeOH/CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.22−7.44 (m, 20H), 6.50 (d, *J* = 9.6 Hz, 1H), 5.90 (bs, 1H), 5.18−5.38 (m, 4H), 4.32−5.20 (m, 15H), 3.53 (s, 3H), 3.42−4.20 (m, 18H), 2.16 (s, 3H), 2.04 (s, 3H), 1.94 (s, 3H), 1.93 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.83 (s, 3H), 1.82−2.06 (m, 8H), 1.18−1.42 (m, 20H), 0.93 (d, *J* = 6.2 Hz, 3H), 0.86−0.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.80, 170.99, 170.59, 170.39, 170.31, 170.23, 169.45, 139.17, 137.59, 137.46, 129.93, 129.80, 129.08, 128.90, 128.72, 128.39, 128.33, 128.26, 127.89, 127.77, 127.65, 127.57, 127.53, 127.24, 102.02, 99.90, 99.67, 97.29, 78.33, 77.20, 76.26, 73.92, 73.48, 73.43, 72.95, 72.49, 71.55, 70.26, 69.61, 68.88, 67.58, 67.48, 65.02, 60.29, 53.87, 53.65, 36.44, 31.76, 29.78, 29.71, 29.58, 29.39, 29.34, 28.96, 27.21, 25.52, 23.20, 22.63, 20.90, 20.69, 15.55, 14.10; HRMS (FAB) calcd for MH^+ $C_{85}H_{118}N_3O_{25}$ 1580.8054, found 1580.8022.

Pent-4-enyl (3,4-Di-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-{11-(*Z*)-octadecenamido}-β-D-glucopyranosyl)-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (32). To **20b** (136.0 mg, 0.1222 mmol) in 0.9 mL of 2:1:1 acetonitrile/tetrahydrofuran/ethanol was added ethylenediamine (15.5 μL, 0.2322 mmol) before the solution was heated to 60 °C. The reaction mixture was stirred for 16 h, allowed to cool to room temperature, concentrated, and then filtered through a short column of silica gel with 5:95 MeOH/CH_2Cl_2. The amine residue was dissolved in CH_2Cl_2 (1 mL) along with 11(*Z*)-octadecenoic acid (28.4 mg, 0.1005 mmol). To this was added DCC (20.8 mg, 0.1008 mmol) in CH_2Cl_2 (1 mL). The reaction was stirred for 2.5 h and then filtered through Celite before being concentrated *in vacuo*. To the residue were added acetic anhydride (0.280 mL, 2.965 mmol), triethylamine (0.125 mL, 0.93 mmol), and DMAP (49.0 mg, 0.401 mmol) in CH_2Cl_2 (3 mL) for 12 h. The reaction mixture was concentrated *in vacuo* before being diluted with CH_2Cl_2 (30 mL) and washed with saturated aqueous $NaHCO_3$ (8 mL), back extracting the aqueous portion with CH_2Cl_2 (2 × 10 mL). The reaction mixture was concentrated, and the residue was purified by flash chromatography eluting with a gradient of 5 → 15% EtOAc/CH_2Cl_2. Compound **32** was recovered as a film (47 mg, 35%): R_f 0.64 (5:95 EtOAc/CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69−7.85 (m, 4H), 7.26−7.48 (m, 10H), 5.68 (app t, *J* = 9.4 Hz, 1H), 5.54−5.64 (m, 1H), 5.32−5.38 (m, 2H), 5.29 (d, *J* = 8.8 Hz, 1H), 5.09 (t, *J* = 10 Hz, 1H), 5.00 (t, *J* = 8.8 Hz, 1H), 4.70−4.88 (m, 4H), 4.58 (d, *J* = 8.2 Hz, 1H), 4.48 (d, *J* = 12.3 Hz, 2H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.24 (dd, *J* = 8.8, 11.1 Hz, 1H), 4.44 (t, *J* = 9.4 Hz, 1H), 3.80−3.86 (m, 1H), 3.40−3.66 (m, 8H), 1.97 (s, 3H), 1.89 (s, 3H), 1.82 (s, 3H), 1.82−2.40 (m, 8H), 1.48−1.72 (m, 4H), 1.06−1.38 (m, 20H), 0.84−0.92 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.75, 170.53, 170.30, 169.51, 167.86, 167.54, 137.83, 137.70, 137.43, 134.05, 131.41, 131.38, 129.91, 129.78, 128.76, 128.71, 128.46, 128.37, 127.85, 127.74, 123.43, 114.66, 99.72, 98.13, 77.21, 75.01, 74.26, 73.54, 73.31, 72.47, 70.80, 69.57, 69.02, 68.74, 67.32, 54.90, 54.75, 49.07, 36.62, 33.91, 31.74, 29.79, 29.76, 29.69, 29.54, 29.50, 29.36, 29.29, 28.95, 28.43, 27.18, 25.57, 25.50, 24.92, 22.62, 20.65, 20.48, 14.09; MS (FAB) *m/e* 1109.57 MH^+; $[\alpha]^{20}_D$ 5.8° (*c* 1.00, $CHCl_3$). Reaction byproduct **31** (24 mg, 51%). MS (FAB) *m/e* 489.4 MH^+.

***tert*-Butyldimethylsilyl (3,4-Di-*O*-acetyl-2-deoxy-6-*O*-(*tert*-butyldimethylsilyl)-2-tetrachlorophthalimido-β-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-2-deoxy-2-phthalimido-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranosyl)-(1→4)-[(3,4-di-*O*-benzoyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→6)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (34b).** To **26** (73.2 mg, 0.0388 mmol) in CH_2Cl_2 (2.6 mL) at 0 °C under strict anhydrous conditions was added $FeCl_3$ (100.6 mg, 0.62 mmol). The reaction was stirred at 0 °C for 2 h 20 min before being quenched with H_2O (1 mL). The mixture was diluted with $CHCl_3$ (25 mL) and extracted with brine (10 mL). The aqueous phase was extracted with $CHCl_3$ (2 × 10 mL), and the organic layers were combined, filtered, and concentrated. The residue was flash chromatographed, eluting with 45:55 CH_2Cl_2/EtOAc to give the tetrol (48 mg, 81%) as a white solid (MS (FAB) *m/z* 1523 M^-). To the tetrol **34a** (196.4 mg, 0.129 mmol) in dimethylformamide (6 mL) at 0 °C was added imidazole (98.3 mg, 1.44 mmol). After 10 min, TBDMSCl (282.2 mg, 1.87 mmol) was added at 0 °C. The reaction was allowed to slowly come to room temperature and stirred for 12 h before being quenched by addition of saturated aqueous $NaHCO_3$. The excess dimethylformamide was concentrated *in vacuo*, and the residue was taken up in $CHCl_3$ (100 mL) and washed successively with saturated aqueous $NaHCO_3$ (25 mL) and brine (25 mL). The aqueous layers were extracted with $CHCl_3$ (4 × 25 mL). The organic layers were combined, filtered, and concentrated. The residue was flash chromatographed eluting with 30:70 → 35:65 EtOAc/petroleum ether to afford **34b** (192.3 mg, 80%) as a white amorphous powder: R_f = 0.51 (35:65 EtOAc/petroleum ether); $[\alpha]^{20}_D$ −35.7° (*c* 1.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.9 Hz, 2H), 7.91−7.96 (m, 2H), 7.78−7.87 (m, 5H), 7.68−7.73 (m, 2H), 7.59−7.65 (m, 1 H), 7.46−7.53 (m, 3H), 7.28−7.35 (m, 3H), 5.74 (dd, *J* = 8.9, 10.6 Hz, 1H), 5.64 (dd, *J* = 9.2, 10.6 Hz, 1H), 5.55 (d, *J* = 3.4 Hz, 1H), 5.40−5.42 (m, 1H), 5.41 (d, *J* = 8.5 Hz, 1H), 5.37 (d, *J* = 8.5 Hz, 1H), 5.35 (d, *J* = 8.2 Hz, 1H), 5.11 (t, *J* = 9.4 Hz, 1H), 4.91 (d, 3.4 Hz, 1H), 4.32 (bdd, *J* = 7.5, 10.9 Hz, 1H), 4.18 (dd, *J* = 8.2, 10.6 Hz, 1H), 4.12 (dd, *J* = 8.2, 10.3 Hz, 1H), 3.96−4.05 (m, 4H), 3.69−3.81 (m, 4H), 3.49−3.62 (m, 6H), 3.41 (s, 3H), 3.38 (m, 1H), 3.26 (bdd, *J* =4.5, 10.6 Hz, 1H), 1.99 (s, 3H), 1.94 (s, 3H), 1.84 (s, 3H), 1.12 (d, *J* = 6.5 Hz, 3H), 0.92 (s, 9H), 0.77 (m, 9H), 0.66 (m, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.03 (s, 3H), −0.04 (s, 3H), −0.08 (s, 3H), −0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.57, 169.87, 169.16, 168.35, 167.80, 167.48, 167.09, 165.75, 165.31, 163.24, 162.44, 162.06, 140.62, 134.63, 134.42, 134.36, 134.13, 133.73, 133.14, 132.79, 131.81, 131.31, 131.17, 129.88, 129.72, 129.67, 129.49, 128.42, 128.17, 126.64, 123.91, 123.78, 123.45, 123.29, 122.75, 98.00, 97.00, 96.08, 93.17, 80.91, 75.99, 75.21, 74.42, 73.59, 73.57, 71.91, 71.04, 70.94, 70.15, 69.33, 69.20, 65.38, 64.27, 62.23, 61.48, 59.46, 57.95, 55.77, 54.86, 25.84, 25.69, 25.23, 20.75, 20.68, 20.40, 18.25, 18.01, 17.44, 16.03, −4.36, −5.54, −5.59, −5.62; MS (FAB) *m/e* 1865.1 M^-.

***tert*-Butyldimethylsilyl (3,4-Di-*O*-acetyl-2-deoxy-2-{11-(*Z*)-octadecenamido}-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranosyl)-(1→4)-(3-*O*-acetyl-2-deoxy-2-phthalimido-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranosyl)-(1→4)-3-O-acetyl-[(3,4-Di-*O*-benzoyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→6)]-2-deoxy-2-phthalimido-β-D-glucopyranoside (34c).** To **34b** (194.6 mg, 0.108 mmol) in 1.3 mL of 3:1 acetonitrile/ tetrahydrofuran was added ethylenediamine (15.2 μL, 0.227 mmol) before the solution was heated to 60

°C. The reaction mixture was stirred for 10 h, allowed to cool to room temperature, concentrated, and then filtered through a short column of silica gel with 10:90 MeOH/CH_2Cl_2. The amine in CH_3CN (1.5 mL) was then added to 11(*Z*)-octadecenoic acid (0.146 g, 0.517 mmol) pretreated with both triethylamine (0.144 mL, 1.03 mmol) for 15 min and then 2-chloro-*N*-methylpyridinium iodide (0.132 g, 0.517 mmol) in CH_3CN (0.5 mL) for 15 min at 40 °C. The reaction was stirred for 2.5 h at 40 °C and was then concentrated *in vacuo*. To the residue were added acetic anhydride (0.256 mL, 2.71 mmol), triethylamine (45 μL, 0.325 mmol), and DMAP (40.0 mg, 0.325 mmol) in CH_2Cl_2 (1 mL) for 12 h. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and washed with saturated aqueous $NaHCO_3$ (8 mL), back extracting the aqueous portion with CH_2Cl_2 (4 × 15 mL). The reaction mixture was concentrated, and the residue was purified by flash chromatography eluting with 40:60 EtOAc/petroleum ether. Compound **34b** was recovered as a film (49 mg, 25%): R_f 0.43 (40:60 EtOAc/petroleum ether); $[\alpha]^{20}_D$ −39.3° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 6.8 Hz, 2H), 7.78−7.87 (m, 5H), 7.62−7.75 (m, 5H), 7.44−7.54 (m, 3H), 7.26−7.32 (m, 3H), 5.54−5.76 (m, 5H), 5.46 (d, J = 7.9 Hz, 1H), 5.32−5.37 (m, 2H), 5.29 (d, J = 3.4 Hz, 1H), 5.14 (d, J = 8.9 Hz, 1H), 5.07 (t, J = 10.3 Hz, 1H), 4.98 (t, J = 9.2 Hz, 1H), 4.69 (d, J = 8.5 Hz, 1H), 4.48 (m, 1H), 4.18−4.27 (m, 2H), 4.02−4.10 (m, 2H), 3.85−3.96 (m, 3H), 3.63−3.75 (m, 5H), 3.57 (d, J = 9.6 Hz, 2H), 3.47 (s, 3H), 3.36−3.42 (m, 1H), 1.97−2.05 (m, 6H,), 1.96 (s, 3H), 1.94 (s, 3H), 1.92 (s, 3H), 1.87 (s, 3H), 1.20−1.37 (m, 22H), 1.17 (d, J = 6.8 Hz, 3H), 0.97 (s, 9H), 0.83−0.09 (m, 12H), 0.66 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H), −0.01 (s, 3H), −0.02 (s, 3H), −0.03 (s, 3H), −0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.27, 170.93, 170.29, 169.28, 168.11 (bs), 167.39, 167.27, 165.92, 165.18, 134.23, 134.08, 133.93, 133.23, 132.85, 131.69, 131.48, 131.37, 129.93, 129.79, 129.75, 128.53, 128.24, 123.67, 123.26 (bs), 100.23, 96.19, 95.68, 93.24, 77.20, 76.47, 75.09, 74.88, 74.38, 73.64, 72.96, 72.37, 72.31, 71.23, 70.28, 70.21, 69.19, 64.98, 64.51, 62.33, 61.41, 59.02, 57.22, 55.29, 54.54, 36.44, 31.77, 29.78, 29.72, 29.55, 29.39, 29.34, 29.29, 28.98, 28.88, 27.21, 26.09, 25.82, 25.24, 22.65, 21.05, 20.78, 20.67, 18.20, 17.48, 16.20, 14.12, −0.02, −4.35, −4.94, −5.27, −5.59, −5.62, −5.66; HRMS (FAB) calcd for MH^+ $C_{99}H_{142}N_3O_{28}Si_3$ 1904.9088, found 1904.9178.

***tert*-Butyldimethylsilyl (2-Deoxy-2-{11(*Z*)-octadecenamido}-6-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranosyl)-(1→4)-(2-acetamido-2-deoxy-6-*O*-(*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-(1→4)-[(2-*O*-methyl-α-L-fucopyranosyl)-(1→6)]-2-acetamido-2-deoxy-β-D-glucopyranoside (35).** To **34c** (14.0 mg, 7.347 μmol) in EtOH (0.67 mL) and MeOH (0.33 mL) was added ethylenediamine (0.45 mL, 6.74 mmol). The reaction was stirred for 34 h at 90 °C and then concentrated *in vacuo*. The reaction mixture was filtered through a short column of silica gel with 12:88 MeOH/CH_2Cl_2. The residue was then treated with acetic anhydride (17 μL, 0.184 mmol) and NEt_3 (25 μL, 0.184 mmol) in CH_2Cl_2 for 45 min before the reaction mixture was concentrated *in vacuo*. To the residue was added NaOMe solution (0.25 mmol in 0.5 mL MeOH) in MeOH (1 mL). The reaction mixture was concentrated after 2 h and then purified by flash chromatography eluting with 12:88 MeOH/CH_2Cl_2. Compound **35** was recovered as a film (8.0 mg, 80%): R_f 0.32 (10:90 MeOH/CH_2Cl_2); ^{1}H NMR (400 MHz, 20% MeOD-d_4/80% $CDCl_3$) δ 5.19−5.27 (m, 2H), 4.73 (d, J = 3.1 Hz, 1H), 4.44−4.50 (m, 1H), 4.33−4.41 (m, 1H), 4.3 (d, J = 8.6 Hz, 1H), 3.92−4.0 (m, 1H), 3.15−3.90 (m, 33H), 2.05−2.12 (m, 1H), 1.86−1.92 (m, 4H), 1.85 (s, 3H), 1.84 (s, 3H), 1.12−1.25 (m, 22H), 1.10 (d, J = 6.5 Hz, 3H), 0.78−0.82 (m, 12H), 0.77 (s, 9H), 0.73 (s, 9H), −0.08 to −0.02 (m, 15H), −0.13 (s, 3H); ^{13}C NMR (100 MHz, 20% MeOD-d_4/80% $CDCl_3$) δ 175.67, 171.74 (bs), 129.71, 129.61, 101.49, 101.34, 95.54, 96.15, 79.67, 79.25, 78.62, 77.20, 76.29, 74.62, 72.96, 72.72, 72.36, 71.78, 70.53, 69.99, 65.96, 65.36, 63.26, 61.13, 59.86, 59.61, 57.32, 55.40, 54.65, 36.23, 31.55, 29.58, 29.47, 29.39, 29.25, 29.14, 28.75, 26.98, 25.64, 25.49, 25.34, 25.13, 22.63, 22.57, 22.42, 18.18, 17.76, 17.57, 15.75, 13.80, −0.34, −4.11, −4.61, −5.82, −6.10; HRMS (FAB) calcd for MH^+ $C_{65}H_{126}N_3O_{20}Si_3$ 1352.8243, found 1352.8263.

***O*-(2-Deoxy-2-{11(*Z*)-octadecenamido}-β-D-glucopyranosyl)-(1→4)-(2-acetamido-2-deoxy-2-β-D-glucopyranosyl)-(1→4)-[(2-*O*-methyl-α-L-fucopyranosyl)-(1→6)]-2-acetamido-2-deoxy-D-glucopyranose (2).** To **35** (2.5 mg, 1.8 μmol) in 300 μL of THF:MeOH (3:1) was added glacial acetic acid (40 μL), and the mixture was cooled to 0 °C before dropwise addition of a 1 M solution of TBAF (200 μL). The reaction was allowed to slowly come to room temperature and was stirred for 6 h before addition of an additional 100 μL of acetic acid. The mixture was concentrated and purified by C_{18} chromatography, eluting with H_2O → 3:1 H_2O/MeOH → 1:1 H_2O/MeOH → 1:3 H_2O/MeOH → MeOH. Lyophilization of the fractions containing the desired product gave compound **2** (1.5 mg, 83%) as a white powder and a monsilylated derivative of **35** (0.3 mg, 15%): **2**: R_f 0.62 (2:1:1 *n*-BuOH/EtOH/H_2O); ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.57 (bs, 1H), 5.32 (m, 2H), 5.10 (bs, 1H), 4.90−4.98 (m, 2H), 4.85 (bs, 1H), 4.78 (d, J = 5.81 Hz, 1H), 4.67−4.76 (m, 2H), 4.42−4.53 (m, 1H), 4.34 (d, J = 8.2 Hz, 2H), 3.57−3.8 (m, 6H), 3.26−3.49 (m, 10H), 2.97−3.19 (m, 6H), 1.95−2.07 (m, 4H), 1.82 (s, 3H), 1.80 (s, 3H), 1.40−1.54 (m, 4H), 1.21−1.3 (m, 24H), 1.52 (d, J = 6.5 Hz, 3H), 0.95 (s, 3H), 0.92 (t, J = 7.5 Hz, 2H), 0.81−0.87 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.11, 172.00, 168.99, 129.66, 129.60, 101.96, 101.53, 96.47, 90.53, 81.09, 80.62, 78.04, 76.93, 74.71, 73.99, 72.14, 71.80, 70.72, 66.37, 65.63, 65.03, 61.04, 60.09, 58.38, 57.49, 55.24, 53.65,37.59, 35.75, 31.11, 29.15, 29.06, 29.02, 28.96, 28.66, 28.24, 27.57, 25.71, 25.65, 24.97, 23.04, 22.95, 22.06, 19.19, 16.33, 13.93; HRMS (FAB) calcd for MH^+ $C_{47}H_{84}N_3O_{20}$ 1010.5648, found 1010.5676.

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Supporting Information Available: Listings of experimental procedures for the desilylation and debenzylation studies with selected analytical data (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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