Efficient Synthesis of 3,6-Dideoxy-β-D-*arabino*-hexopyranosyl-Terminated LacdiNac Glycan Chains of the *Trichinella spiralis* Parasite

Mark Nitz and David R. Bundle*

Department of Chemistry, The University of Alberta, Edmonton, Alberta T6G 2G2, Canada

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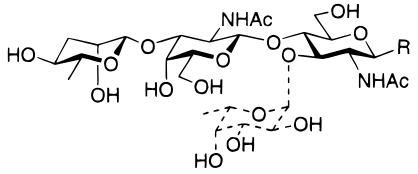
The synthesis of a linear trisaccharide epitope of the *Trichinella spiralis* N-linked glycan, in a form amenable to glycoconjugate formation, is reported. The trisaccharide contains the synthetically challenging LacdiNac [β-Gal*p*NAc(1→4)-β-Glc*p*NAc] element, as well as a terminal 3,6-dideoxy-β-D-*arabino*-hexopyranose (tyvelose) residue. An orthogonal protection strategy is described, which permits the protection and manipulation of three amino groups present in the disaccharide β-GalNAc(1→4)-β-GlcNAc and the tether used to prepare neoglycoconjugates. The β-linked dideoxyhexose was generated in excellent yield by the introduction of the dideoxyhexose unit as a β-D-*ribo*-hexopyranoside (paratose) followed by an oxidation−reduction sequence to generate the β-D-*arabino* configuration in high diastereomeric excess. The required dideoxyhexose donor was synthesized in a series of high-yielding steps from glucose utilizing the *p*-methoxyphenyl glycoside.

Introduction

Trichinella spiralis is a parasitic nematode that can establish itself in the intestinal epithelia of carnivorous animals. During invasion, *T. spiralis* secretes an array of glycoproteins,[1] the glycan chains of which have been identified as large tri- and tetra-antennary structures, terminating in a rare 3,6-dideoxy-β-D-*arabino*-hexopyranosyl (β-tyvelose or β-Tyv) linkage to a Lewis-x-like trisaccharide.[2,3] Immunochemical evidence using monoclonal antibodies established that not all of the glycan chains are capped by the tetrasaccharide β-D-Tyv*p*(1→3)-β-D-Gal*p*NAc(1→4)[α-L-Fuc*p*(1→3)]-β-D-Glc*p*NAc; a nonfucosylated glycan tyvelose capped structure may also be present (Figure 1).[4−6] These highly unique glycan chains are thought to play an important role in pathogenesis. One line of evidence that points toward such a conclusion is the *in vivo* protection afforded by certain monoclonal antibodies that recognize the dideoxyhexose capped glycans.[7,8] Recognition of the glycan epitope by C-type lectins may also play a role in mediating parasite adherence as an initial step in pathogenesis. To investigate potential roles for the surface glycans of this parasite in the pathogenesis of *T. spiralis*, chemically defined neoglycoconjugates that can be used to locate glycan receptors in tissue or cells are required. For this purpose, epitopes labeled with fluorescent reporter groups are required.



1 R = $OC_6H_{12}NHCSFluor$
2 R = OMe
33 R = $OC_6H_{12}NH_2$

Figure 1. *T. spiralis* capping tetrasaccharide. Dashed line indicates absence of fucose residue in linear trisaccharide.

We report here the synthesis of a linear nonfucosylated epitope with an ω-amino tether (**33**) to facilitate synthesis of the corresponding fluorescein conjugate (**1**), as well as the corresponding simple methyl glycoside (**2**) (Figure 1). The latter molecule was also required to define the fine specificity of one set of protective monoclonal antibodies that appear to recognize the linear as opposed to the fucose-branched epitope.[4] The approach employs an orthogonal protection strategy that permits the protection and manipulation of three amino groups, present in the tether, and the two amino sugars. It also accommodates the introduction, manipulation, and deprotection of the acid-labile 3,6-dideoxy-β-D-*arabino*-hexopyranosyl residue, which, if not hydrolyzed, is readily anomerized.

Results and Discussion

Synthetic Strategy and Preparation of Monosaccharide Building Blocks (Figure 2). The target oligosaccharides to be synthesized were 6-aminohexyl glycoside (**33**) and methyl glycoside (**2**). The strategy chosen relies on the stepwise addition of monosaccharides from the reducing terminus of the molecule, with the glycosidic linkage to the most valuable sugar, tyvelose, being established last. Elaboration of the oligosaccharides as the 6-aminohexyl glycoside facilitates later attachment to fluorescent reporter groups that will be used to study

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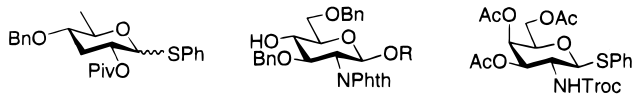

13 **17** R = $C_6H_{14}Cl$ **19**
18 R = Me

Figure 2. Monosaccharide building blocks.

the trisaccharide's biological significance.[9] The methyl glycoside functions as the most convenient form for crystallography and epitope mapping.[10] The glucosamine synthons **17** and **18**[11] employed the persistent phthalimido derivative of the amine, ensuring solubility of the compound and stability of this group to all subsequent reaction conditions. The 6-chlorohexyl agylcone could easily be transformed to the azide after all steps employing reducing conditions had been performed. The galactosamine derivative **19** was chosen as an efficient glycosyl donor for the formation of LacdiNac glycoside. It could be synthesized in high yield from the comparatively expensive galactosamine starting material. Furthermore, this choice of protecting groups provides three levels of orthogonal amine protection (as in **26**), which is required to minimize solubility and chromatographic difficulties often encountered in small compounds with multiple acetamido groups. This also provides a free amine after the final deprotection steps to allow for facile neoglycoconjugate formation.

The paratose glycosyl donor **13** was available through a series of high-yielding steps from the easily synthesized *p*-methoxyphenyl 2,3,4,6-tetraacetyl-β-D-glucopyranoside.[12] The *p*-methoxyphenyl protecting group was an ideal persistent protecting group for this synthesis, being readily available, stable to many conditions, and easily converted to the thiophenyl glycoside necessary for glycosylation.

Synthesis of the 1,2-cis β linkage remains one of the most challenging tasks in oligosaccharide chemistry. New methodologies have been developed based on specialized glycosyl donors,[13,14] heterogeneous catalysis,[15] and elegant intramolecular aglycone delivery.[16−18] However, many of these methods either are not applicable to highly reactive 3,6-dideoxyhexose sugars or give anomeric mixtures.[5,6] Preliminary and quite extensive attempts to synthesize the target compounds employing intramolecular aglycon delivery with tethers derived from *p*-methoxybenzyl and silyl ethers and activated donors in the form of tethered glycosyl fluorides, thioglycosides, or sulfoxides failed to give acceptable yields. Nontethered 3-deoxyhexose donors locked in the $^4C_1$ conformation and bearing nonparticipating groups at C2 were also tried without success. The most general and robust method remains the oxidation and reduction of the C2 alcohol to convert the 1,2-trans (2-D-glycero) to the 1,2-cis (2-L-glycero) configuration.[19,20] This approach was applied here to introduce the terminal tyveloside via its 3,6-dideoxy-D-*ribo*-hexopyranose (paratose) epimer.

Early synthetic investigations showed a facile elimination reaction upon oxidation of the paratose C2 position in the presence of a benzoyl group at the 4 position. Therefore, the thioglycoside donor was synthesized with benzyl protection at C4 and a participating pivaloyl ester at position C2 to ensure β selectivity and to avoid complications of ortho ester formation previously encountered for other paratose donors.[21]

Synthesis of Monosaccharide Synthons. Beginning with the easily accessible *p*-methoxyphenyl tetra-*O*-2,3,4,6-acetyl-β-D-glucopyranoside,[12] deacetylation and conversion to the benzylidene acetal by treatment with benzyaldhyde dimethyl acetal gave the highly crystalline compound **3**. According to a series of high-yielding steps introduced by Bundle,[22] the 3-deoxy-*ribo*-hexopyranoside (**7**) was synthesized. The crystalline bis-chlorosulfate ester (**4**) was cleanly prepared by treatment of the diol (**3**) with sulfuryl chloride. Reaction of the dichlorosulfate ester (**4**) with tetrabutylammonium bromide followed by hydrolysis with an aqueous solution of potassium carbonate and potassium iodide gave the 3-bromo-3-deoxy-*allo*-pyranoside (**5**) in high yield. The stereochemistry at C3 was confirmed by proton NMR analysis of the coupling constants $^3J_{2,3} \approx {}^3J_{3,4} \approx 3.4$ Hz, indicative of an axial orientation of the bromide. This compound was protected as the TDBMS ether (**6**) and hydrogenated over palladium to give the desired 3-deoxy-*ribo*-hexopyranoside (**7**). The 6-deoxy function was introduced in two steps via treatment of the benzylidene acetal with NBS, to the give the 6-bromo derivative (**8**), and reduction over palladium on carbon. The hydrogenolysis was accomplished in the presence of potassium carbonate in a solution of ethanol, resulting in concurrent debenzoylation to give the paratose derivative (**9**) in high yield. A benzyl ether was then introduced at C4 under standard conditions (**10**); removal of the silyl ether with tetrabutylammonium fluoride (**11**) and protection as the pivolyl ester gave compound **12**. Finally, the *p*-methoxyphenyl glycoside could be readily converted to the thioglycoside[12] by treatment with thiophenol and boron trifluoride diethyl etherate to give an anomeric mixture of the desired glycosyl donor (**13**) in 90% yield (Figure 3).

The methyl glycoside (**18**) was prepared according to literature procedures,[11] and the 6-chlorohexyl glycoside (**17**) was prepared analogously (Figure 4). The terminal chloride proved to be stable to the reductive opening of the benzylidiene acetal and the basic Zemplen deacetylation conditions, providing a simple way to introduce a terminal azide later in the synthesis.

Assembly of Oligosaccharides (Figure 5). Galactosaminyl donor **19** was synthesized from the literature derivative 1,3,4,6-*O*-tetraacetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranose by treat-

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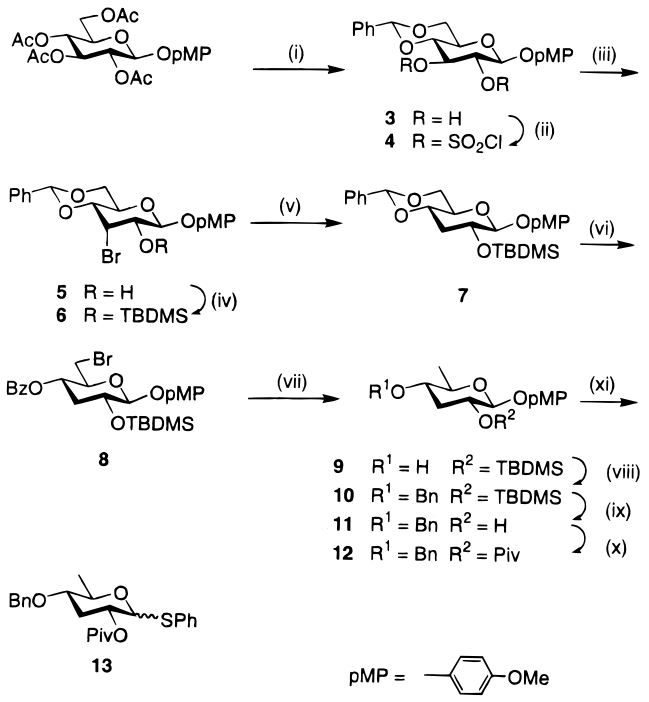

Figure 3. (i) (a) MeONa/MeOH, (b) $PhCH(OMe)_2$, *p*TSA, CH_3CN, 86%; (ii) SO_2Cl_2, pyridine, CH_2Cl_2, 91%; (iii) (a) Et_4NBr, CH_2Cl_2, (b) KI, $KHCO_3$, $MeOH/H_2O$, 96%; (iv) TBDMSCl, imidazole, DMF, 91%; (v) H_2, Pd/C, EtOAc/EtOH, 87%; (vi) NBS, $BaCO_3$, CCl_4, reflux, 93%; (vii) H_2, Pd/C, $KHCO_3$, EtOH, 93%; (viii) BnBr, NaH, DMF, 88%; (ix) Bu_4NF, THF, 92%; (x) PivCl, pyr, 91%; (xi) PhSH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 2:1 α:*β*, 90%.

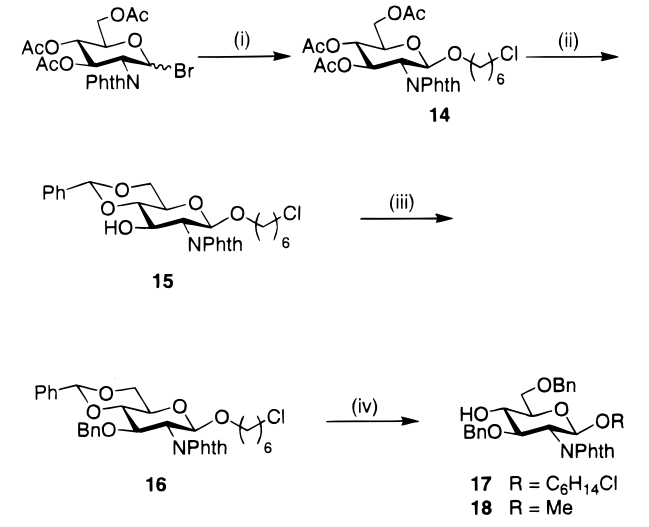

Figure 4. (i) $Cl(CH_2)_6OH$, lutidine, AgOTf, CH_2Cl_2, 90%; (ii) (a) NaOMe/MeOH, (b) $PhCH(OMe)_2$, CH_3CN, *p*TSA, 86%; (iii) BnBr, NaH, DMF, 89%; (iv) $NaCNBH_3$, HCl, THF, 92%.

ment with thiophenol and $BF_3{\cdot}OEt_2$.[23] This proved to be an excellent glycosyl donor for the formation of glycosides **20** and **21** in greater than 87% yield using *N*-iodosuccinimide[24,25] and a catalytic portion of silver triflate.[26] This combination of donor and acceptor proved to give higher yields than other combinations used to synthesize LacdiNAc.[23,27] Cleavage of the trichloroethylcarbamate was most efficient and reproducible using cadmium metal in a 1:1 solution of DMF and acetic acid.[28] The free amine was acetylated in methanol to give compounds **22** and **23**. The benzylidene acetal was installed with benzaldehyde dimethyl acetal and toluenesulfonic acid after Zemplen deacetylation to give the target acceptors **24** and **25** in good yield. The terminal chloride was then easily displaced with sodium azide to give the orthogonally protected amine-terminated linker **26**.

Activation of paratose donor **13** with *N*-iodosuccinimide[24,25] and a catalytic amount of silver triflate[26] in the presence of the alcohol **24** or **26** gave the desired trisaccharide **27** or **28** in greater than 75% yield. Unfortunately, a 20:1 *β*:α ratio that could not be separated by standard silica gel chromatography was obtained in the reaction. This mixture was separated in subsequent steps of the synthesis.

The pivaloyl and phthalimido protecting groups were removed in the next steps via treatment with ethylenediamine[29] at 110 °C for 16 h, but these conditions failed to completely remove the pivaloyl ester. The free amine was acetylated using acetic anhydride in methanol, and the remaining pivaloyl ester was removed with a solution of sodium methoxide in methanol to give the glycosides **29** and **30**.

The oxidation and reduction[19,20] of the paratose glycosides **29** and **30** was accomplished in two steps, performed sequentially in a one-pot reaction. Treatment for 18 h with a 2:1 mixture of dimethyl sulfoxide and acetic anhydride, followed by removal of the volatile components under high vacuum, gave the corresponding ulosides as yellow solids. Reduction with excess L-selectride gave the tyvelose-terminated trisaccharides **31** and **32**. Quenching the reaction of the 6-azidohexyl glycoside (**30)** with ethylenediamine avoided reduction of the azide and gave **32** in 75% yield. Previous model studies on the oxidation and reduction of methyl 4-*O*-benzoyl-3,6-dideoxy-*β*-D-*ribo*-hexopyranoside indicated that the sterically bulky L-selectride gave superior selectivity upon reduction than did sodium borohydride.

The inversion of stereochemistry was confirmed by NMR. The $^3J_{1,2}$ value of <1 Hz was indicative of a 1,2-*cis*-mannosyl linkage,[30] while the heteronuclear $^1J_{C1,H1}$ constant of 158 Hz unambiguously established the *β* configuration.[31] No products with the *ribo* configuration were observed in the NMR spectrum of the crude product, indicating that the selectivity of the reduction was better than 95%.

Final deprotection of **31** and **32** gave the desired trisaccharides **2** and **33**. The methyl glycoside was hydrogenated over palladium hydroxide and could be crystallized from methanol/ethanol mixtures as fine needles in 93% yield. The 6-azidohexyl trisaccharide was

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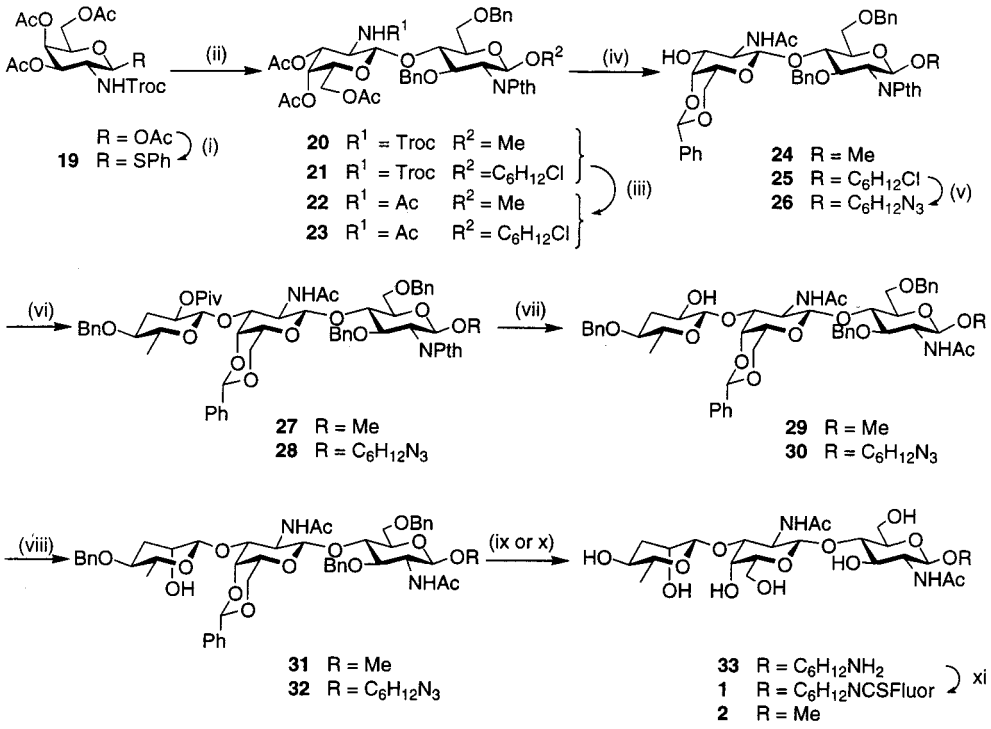

Figure 5. (i) PhSH, BF_3·OEt_2, 74%; (ii) **17**, NIS, AgOTf, CH_2Cl_2, 87−93%; (iii) (a) Cd, 1:1 AcOH/DMF, (b) MeOH, Ac_2O, 79−88%; (iv) (a) MeONa/MeOH, (b) $PhCH(OMe)_2$, *p*TSA, CH_3CN, 79−85%; (v) NaN_3, DMSO, 96%; (vi) **13**, NIS, AgOTf, CH_2Cl_2, 81−85%; (vii) (a) $NH_2CH_2CH_2NH_2$, BuOH, (b) Ac_2O, MeOH, (c) MeONa/MeOH, 85−88%; (viii) (a) DMSO, Ac_2O, (b) L-selectride, THF, 81%; (ix) $Pd(OH)_2$/C, EtOH, 88%; (x) $NH_2CH_2CH_2NH_2$, Li, 82%; (xi) 1:1 DMF/H_2O, $NaHCO_3$, FluorNCS, 75%.

deprotected under dissolving metal conditions[32] using ethylenediamine as the solvent because of the low solubility of the LacdiNAc structure in THF/ammonia mixtures. Final purification by HPLC and lyophization gave **33** as a white powder in 82% yield. The 6-aminohexyl tether was then simply derivatized as its fluoresceine conjugate by stirring with fluoresceine isothiocynate in a DMF/water solution; final purification gave **1** in 75% yield.

Summary

Through the use of an oxidation−reduction protocol at C2 of 3,6-dideoxy-β-D-*ribo*-hexopyranose, the difficult to synthesize 3,6-dideoxy-β-D-*arabino*-hexopyranose linkage has been introduced at O3 of the disaccharide β-D-Gal*p*NAc(1→4)-β-D-Glc*p*NAc. This approach provides the methyl glycoside (**2**) and linker-derivatized trisaccharide (**33**) for the preparation of the fluorescein glycoconjugate (**1**).

Experimental Section

Melting points were determined on glass plates using a Fisher-Johns melting point apparatus and are uncorrected. Optical rotations were measured using a polarimeter at 22 ± 2 °C. The ^{1}H NMR spectra were recorded at 300 and 600 MHz on a Varian Inova spectrometer and at 500 MHz on a Varian Unity spectrometer. All data were obtained with temperature control to 25 °C. Chemical shifts are referenced to residual $CHCl_3$ at 7.24 ppm for $CDCl_3$ solutions, to residual CHD_2OD at 3.30 ppm for CD_3OD solutions, and to 0.1% external acetone at 2.225 ppm for D_2O solutions. NMR assignments were made by two-dimensional homonuclear and heteronuclear shift-correlation experiments. Thin-layer chromatography was performed on Silica Gel F254 (Merck) precoated glass plates and visualized with 5% H_2SO_4 in ethanol. Flash chromatography was performed on Silica Gel 60 (40−63 μm, Merck no. 9385). AG 50W H^+ resin was purchased from Bio-Rad Laboratories.

***p*-Methoxybenzyl 4,6-*O*-benzylidene-β-D-glucopyranoside (3).** *p*-Methoxyphenyl 2,3,4,6-*O*-β-D-tetraacetylglucopyranoside[12] (8.0 g, 17 mmol) was dissolved in dry methanol (50 mL), and a catalytic amount of sodium metal (~10 mg) was added to the reaction mixture. After the solution was stirred for 2 h, TLC in 1:1 EtOAc/hexane showed complete conversion to baseline material. The solution was then neutralized with AG 50W H^+ resin and filtered. Concentration to dryness gave a white solid to which dry acetonitrile (100 mL) was added, followed by benzaldehyde dimethyl acetal (4.0 mL, 26 mmol). The mixture was then heated to reflux, and *p*-toluenesulfonic acid (200 mg) was added. Once a homogeneous solution was obtained, heating was terminated, and the solution was neutralized with triethylamine. The reaction mixture was then concentrated to dryness to give a white solid. Recrystallization from methanol gave white needles (5.46 g, 86%). Mp: 213−214 °C. $[\alpha]_D$: −35.0 (*c* 1.0, DMF). ^{1}H NMR (300 MHz, CD_3OD): δ 7.48−7.51 (m, 2H, Ar), 7.32−7.35 (m, 3H, Ar), 6.99−7.04 (m, 2H, Ar), 6.82−6.86 (m, 2H, Ar), 5.59 (s, 1H, PhC*H*O_2), 4.91 (d, 1H, $J_{1,2}$ = 7.7 Hz, H1), 4.20 (dd, 1H, J_{gem} = 10.1 Hz, $J_{5,6eq}$ = 3.8 Hz, $H6_{eq}$), 3.78 (dd, 1H, $J_{5,6ax}$ = 8.25 Hz, $H6_{ax}$), 3.74 (s, 3H, OCH_3), 3.72 (dd, 1H, $J_{2,3} \approx J_{3,4}$ = 9.0 Hz, H3), 3.49−3.57 (m, 3H, H2, H5, H4). Anal. Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.14; H, 5.79.

***p*-Methoxybenzyl 4,6-*O*-benzylidene-2,3-di-*O*-chlorosulfate-β-D-glucopyranoside (4).** A solution of **3** (4.7 g, 12.7 mmol) in dry dichloromethane (50 mL) and dry pyridine (25 mL) was cooled to −78 °C. Sulfuryl chloride (2.25 mL, 28.0 mmol) was then added dropwise with stirring over 15 min, and the solution was then allowed to warm to room temperature over 2 h. The reaction mixture was diluted with dichloromethane, washed with 10% H_2SO_4 and then water, dried over Na_2SO_4, and concentrated, and compound **4** was crystallized from EtOAc/hexane (6.56 g, 91%). Mp: 148 °C, dec. $[\alpha]_D$: −63.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.47−7.50 (m, 3H, Ar), 7.36−7.40 (m, 2H, Ar), 7.02−7.05 (m,

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2H, Ar), 6.85−6.88 (m, 2H, Ar), 5.66 (s, 1H, PhC*H*O_2), 5.14−5.29 (m, 3H, H1, H2, H3), 4.48 (dd, 1H, J_{gem} = 10.6 Hz, $J_{5,6eq}$ = 4.9 Hz, H6$_{eq}$), 4.04 (dd, 1H, $J_{3,4} \approx J_{4,5}$ = 9.4 Hz, H4), 3.90 (dd, 1H, $J_{5,6ax}$ = 10.0 Hz, H6$_{ax}$), 3.77 (s, 3H, OCH_3), 3.68 (ddd, 1H, H5). Anal. Calcd for $C_{20}H_{26}Cl_2O_{11}S_2$: C, 42.04; H, 3.53; Cl, 12.41. Found: C, 41.88; H, 3.28; Cl, 12.69.

***p*-Methoxybenzyl 4,6-*O*-benzylidene-3-bromo-3-deoxy-*β*-D-*allo*-pyranoside (5).** To a solution of **4** (10.9 g, 19.1 mmol) in dry dichloromethane (75 mL) was added tetrabutylammonium bromide (10.9 g, 42.4 mmol), and the reaction mixture was stirred for 1 h at room temperature. The solution was diluted with dichloromethane and washed with saturated sodium bicarbonate; the organic solution was dried over sodium sulfate and concentrated to yellow syrup. The syrup was dissolved in methanol (200 mL); water (5 mL), $KHCO_3$ (20 g), and KI (100 mg) were added; and stirring was continued for 15 min. The solution was filtered and concentrated to a syrup. Chromatography in 2:1 hexane/EtOAc gave a colorless oil (8.01 g, 96%). $[\alpha]_D$: −18.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.49−7.52 (m, 3H, Ar), 7.38−7.41 (m, 2H, Ar), 7.38−6.99 (m, 2H, Ar), 6.88−6.83 (m, 2H, Ar), 5.65 (s, 1H, PhC*H*O_2), 5.22 (d, 1H, $J_{1,2}$ = 7.6 Hz, H1), 4.89 (dd, 1H, $J_{2,3} \approx J_{3,4}$ = 3.4 Hz, H3), 4.39 (dd, 1H, J_{gem} = 10.4 Hz, $J_{5,6eq}$ = 5.1 Hz, H6$_{eq}$), 4.15 (ddd, 1H, $J_{4,5} \approx J_{5,6ax}$ = 9.7 Hz, H5), 3.76−3.88 (m, 3H, H2, H4, H6$_{ax}$), 3.71 (s, 3H, OCH_3). Anal. Calcd for $C_{20}H_{21}O_6Br$: C, 54.93; H, 4.84. Found: C, 54.39; H, 4.83. HR electrospray *m*/*z*: calcd for $C_{20}H_{21}O_6BrNa$, 459.041919 (M + Na)$^+$; found, 459.041886.

***p*-Methoxybenzyl 4,6-*O*-benzylidene-3-bromo-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-*β*-D- *allo*-pyranoside (6).** To a solution of **5** (2.6 g, 5.6 mmol) in dry DMF (20 mL) were added imidazole (600 mg, 8.81 mmol) and *tert*-butylchlorodimethylsilane (1.2 g, 8.0 mmol). The solution was heated to 60 °C and stirred for 3 h. After cooling, the reaction mixture was diluted with dichloromethane (150 mL) and washed with water, and the organic phase was dried over sodium sulfate and concentrated to a syrup. Column chromatography in 10:1 hexane/Et_2O gave a colorless syrup (3.2 g, 91%). $[\alpha]_D$: −41.8 (*c* 1.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.50 (m, 2H, Ar), 7.36−7.34 (m, 3H, Ar), 6.94−6.98 (m, 2H, Ar), 6.80−6.83 (m, 2H, Ar), 5.59 (s, 1H, PhC*H*O_2), 5.23 (d, 1H, $J_{1,2}$ = 7.2 Hz, H1), 4.67 (dd, 1H, $J_{2,3} \approx J_{3,4}$ = 3.0 Hz, H3), 4.38 (dd, 1H, $J_{5,6ax}$ = 9.6 Hz, J_{gem} = 10.3 Hz, H6$_{ax}$), 4.20 (ddd, 1H, $J_{4,5}$ = 9.0 Hz, $J_{5,6eq}$ = 5.2 Hz, H5), 3.85 (dd, 1H, H2), 3.81 (dd, 1H, H6$_{eq}$), 3.71 (dd, 1H, H4), 3.70 (s, 3H, OMe), 0.90 (9H, s, $(CH_3)_3$CSi), 0.16 (s, 3H, C*H*$_3$Si), 0.13 (s, 3H, C*H*$_3$Si). Anal. Calcd for $C_{26}H_{35}BrO_6Si$: C, 56.62; H, 6.40. Found: C, 56.93; H, 6.50.

***p*-Methoxybenzyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-deoxy-*β*-D-*ribo*-hexopyranoside (7).** The *allo*-pyranoside **6** (5.00 g, 10.5 mmol) was dissolved in a 1:1 mixture of EtOAc and EtOH, and $KHCO_3$ (3 g) and 10% Pd/carbon (500 mg) were added. The mixture was then stirred under 1 atm of hydrogen for 4 days, filtered through Celite, and concentrated to dryness. The resulting white solid was taken up in dichloromethane (200 mL) and washed with water, and the organics were dried and concentrated. The resulting white solid was recrystallized from EtOAc/hexane (4.32 g, 87%). Mp: 143 °C. $[\alpha]_D$: −63.6 (*c* 0.55, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46−7.48 (m, 2H, Ph), 7.32−7.37 (m, 3H, Ph), 6.93−6.98 (m, 2H, Ar), 6.81−6.83 (m, 2H, Ar), 5.60 (s, 1H, PhCHO_2), 4.83 (d, 1H, $J_{1,2}$ = 7.3 Hz, H1), 4.31 (dd, 1H, J_{gem} = 10.6 Hz, $J_{5,6eq}$ = 4.3 Hz, H6$_{eq}$), 3.84 (ddd, 1H, $J_{2,3eq}$ = 5.2 Hz, $J_{2,3ax}$ = 11.5 Hz, H2), 3.75 (dd, 1H, $J_{5,6ax}$ = 10.6 Hz, H6$_{ax}$), 3.75 (s, 3H, CH_3O), 3.62 (ddd, 1H, $J_{3ax,4}$ = 11.7 Hz, $J_{3eq,4}$ = 2.3 Hz, $J_{4,5}$ = 9.0 Hz, H4), 3.50 (ddd, 1H, H5), 2.43 (ddd, 1H, J_{gem} = 12.2 Hz, H3$_{eq}$), 1.84 (ddd, 1H, H3$_{ax}$), 0.87 (s, 9H, $(CH_3)_3$CSi), 0.12 (s, 3H, SiC*H*$_3$), 0.09 (s, 3H, SiC*H*$_3$). Anal. Calcd for $C_{26}H_{36}O_6Si$: C, 66.07; H, 7.68. Found: C, 65.73; H, 7.72. HR electrospray *m*/*z*: calcd for $C_{26}H_{36}O_6SiNa$, 495.217887; found, 495.217680.

***p*-Methoxybenzyl 4-*O*-benzoyl-6-bromo-2-*tert*-butyldimethylsilyl-3,6-dideoxy-*β*-D-*ribo*-hexopyranoside (8).** The 3-deoxy-*ribo*-hexopyranoside (**7**) (2.5 g, 5.29 mmol) was refluxed with *N*-bromosuccinimide (1.04 g, 5.84 mmol) and barium carbonate (0.63 g, 3.1 mmol) in carbon tetrachloride (50 mL) for 30 min. During this time, the solution changed from colorless to deep orange and then to pale yellow. The reaction mixture was filtered, diluted with dichloromethane, washed with 5% sodium thiosulfate and then water, and dried over sodium sulfate. The solution was then concentrated to a syrup and chromatographed in 4:1 EtOAc/hexane to give the 6-bromo derivative (**8**), which crystallized upon standing (2.72 g, 93%). Mp: 108−110 °C. $[\alpha]_D$: −40.7 (*c* 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99−8.02 (m, 2H, Ph), 7.55−7.61 (m, 1H, Ar), 7.42−7.47 (m, 2H, Ar), 7.04−7.08 (m, 2H, *Ph*OMe), 6.81−6.85 (m, 2H, *Ph*OMe), 4.98 (ddd, 1H, $J_{3ax,4}$ = 11.1 Hz, $J_{3eq,4}$ = 4.8 Hz, $J_{4,5}$ = 9.4 Hz, H4), 4.80 (d, 1H, $J_{1,2}$ = 7.3 Hz, H1), 3.86−3.95 (m, 2H, H2, H5), 3.57 (dd, 1H, $J_{5,6}$ = 2.5 Hz, J_{gem} = 11.1 Hz, H6a), 3.76 (s, 3H, OCH_3), 3.41 (dd, 1H, $J_{5,6}$ = 8.2 Hz, H6b), 2.56 (ddd, 1H, J_{gem} = 12.5 Hz, $J_{2,3eq}$ = 5.1 Hz, H3$_{eq}$), 1.79 (ddd, 1H, $J_{2,3}$ = 12.5 Hz, H3$_{ax}$), 0.86 (s, 9H, $(CH_3)_3$CSi), 0.13 (s, 3H, SiC*H*$_3$), 0.12 (s, 3H, SiC*H*$_3$). Anal. Calcd for $C_{26}H_{35}BrO_6Si$: C, 56.62; H, 6.40. Found: C, 56.40; H, 6.30.

***p*-Methoxybenzyl 2-*O*-*tert*-butyldimethylsilyl-3,6-dideoxy-*ribo*-hexopyranoside (9).** To a solution of 6-bromo derivative **8** (1.0 g, 1.81 mmol) in ethanol were added $KHCO_3$ (500 mg) and then 10% Pd/carbon (100 mg). The mixture was hydrogenated with stirring for 48 h at 1 atm. The mixture was filtered through Celite, concentrated to a syrup, taken up in EtOAc, and washed twice with water. The organic phase was dried over sodium sulfate and concentrated to a colorless syrup, which was chromatographed in 2:1 EtOAc/hexane to give a colorless oil (0.62 g, 93%). $[\alpha]_D$: −51.9 (*c* 1.6, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92−6.96 (m, 2H, Ar), 6.78−6.82 (m, 2H, Ar), 4.77 (d, 1H, $J_{1,2}$ = 6.7 Hz, H1), 3.78 (ddd, 1H, $J_{2,3ax}$ = 10.3 Hz, $J_{2,3eq}$ = 5.0 Hz, H2), 3.75 (s, 3H, CH_3O), 3.40−3.48 (m, 2H, H4, H5), 2.32 (ddd, 1H, J_{gem} = 12.6 Hz, $J_{3,4}$ = 4.6 Hz, H3$_{eq}$), 1.63 (ddd, 1H, $J_{3ax,4}$ = 10.3 Hz, H3$_{ax}$), 1.30 (d, 3H, $J_{5,6}$ = 5.9 Hz, H6), 0.88 (s, 9H, $(CH_3)_3$CSi), 0.12 (s, 3H, SiC*H*$_3$), 0.09 (s, 3H, SiC*H*$_3$). Anal. Calcd for $C_{19}H_{32}O_5Si$: C, 61.92; H, 8.75. Found: C, 61.61; H, 8.69. HR electrospray *m*/*z*: calcd for $C_{19}H_{32}O_5SiNa$, 391.191673; found, 391.191592.

***p*-Methoxybenzyl 4-*O*-benzyl-2-*O*-*tert*-butyldimethylsilyl-3,6-dideoxy-*β*-D-*ribo*-hexopyranoside (10).** To a solution of **9** (600 mg, 1.63 mmol) in dry DMF (10 mL) at room temperature were added benzyl bromide (420 μL, 3.53 mmol) and then sodium hydride (65 mg, 2.7 mmol). After 5 h, TLC indicated the absence of starting material. The solution was diluted with dichloromethane and washed with water, and the organic layer was dried over sodium sulfate and concentrated. The resulting syrup was chromatographed in 9:1 hexane/Et_2O to give a white solid (658 mg, 88%), which was recrystallized from EtOAc/hexane. Mp: 59−60 °C. $[\alpha]_D$: −25.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29−7.34 (m, 5H, Ph), 6.93−6.96 (m, 2H, Ar), 6.78−6.81 (m, 2H, Ar), 4.70 (d, 1H, $J_{1,2}$ = 7.4 Hz, H1), 4.64 (d, 1H, J_{gem} = 11.5 Hz, PhC*H*$_2$), 4.48 (d, 1H, PhC*H*$_2$), 3.75 (s, 3H, CH_3O), 3.69 (ddd, 1H, $J_{2,3eq}$ = 5.2 Hz, $J_{2,3ax}$ = 11.4 Hz, H2), 3.50 (dq, 1H, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.1 Hz, H5), 3.17 (ddd, 1H, $J_{3eq,4}$ = 4.5 Hz, $J_{3ax,4}$ = 11.2 Hz, H4), 2.40 (ddd, 1H, J_{gem} = 12.6 Hz, H3$_{eq}$), 1.56 (ddd, 1H, H3$_{ax}$), 1.31 (d, 3H, H6), 0.87 (s, 9H,$(CH_3)_3$CSi), 0.12 (s, 3H, SiC*H*$_3$), 0.08 (s, 3H, SiC*H*$_3$). Anal. Calcd for $C_{26}H_{38}O_5Si$: C, 68.08; H, 8.35. Found: C, 68.00; H, 8.58.

***p*-Methoxybenzyl 4-*O*-benzyl-3,6-dideoxy-*ribo*-hexopyranoside (11).** The paratose derivative (**10**) (532 mg, 1.21 mmol) was dissolved in 1 M tetrabutylammonium fluoride in THF (4 mL), and the resulting solution was stirred at room temperature for 1 h. The solution was then concentrated and subjected to chromatography in 1:1 EtOAc/hexane to give a white solid (385 mg, 92%), which was recrystallized from EtOAc/hexane. Mp: 132 °C. $[\alpha]_D$: −25.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29−7.34 (m, 5H, Ar), 6.93−6.96 (m, 2H, Ar), 6.78−6.81 (m, 2H, Ar), 4.78 (d, 1H, $J_{1,2}$ = 7.1 Hz, H1), 4.64 (d, 1H, J_{gem} = 11.5 Hz, PhC*H*$_2$), 4.50 (d, 1H, PhC*H*$_2$), 3.76 (s, 3H, C*H*$_3$O), 3.68 (m, 1H, H2), 3.61 (dq, 1H, $J_{4,5}$ = 8.2 Hz, $J_{5,6}$ = 6.2 Hz, H5), 3.25 (ddd, 1H, $J_{3ax,4}$ = 10.6 Hz, $J_{3eq,4}$ = 4.3 Hz, H4), 2.56 (ddd, 1H, J_{gem} = 12.5 Hz, $J_{2,3eq}$ = Hz, H3$_{eq}$), 1.60 (ddd, 1H, $J_{2,3ax}$ = 12.5 Hz, H3$_{ax}$), 1.32 (d, 3H, H6). Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.55; H, 7.20.

***p*-Methoxybenzyl 4-*O*-benzyl-3,6-dideoxy-2-*O*-pivaloyl-*ribo*-hexopyranoside (12).** Compound **11** (300 mg, 0.87 mmol) was dissolved in pyridine, 4-(dimethylamino)pyridine (25 mg) and pivaloyl chloride (214 μL, 1.7 mmol) were added, and the solution was stirred at room temperature overnight. The reaction mixture was then concentrated, and the residue was dissolved in dichloromethane, washed with water, dried over sodium sulfate, concentrated, and chromatographed in 7:1 hexane/diethyl ether. The colorless syrup crystallized on standing (338 mg, 91%) and was recrystallized from EtOAc/hexane. Mp: 82−83 °C. $[\alpha]_D$: −16.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25−7.36 (m, 5H, Ar), 6.91−6.96 (m, 2H, Ar), 6.76−6.82 (m, 2H, Ar), 4.82−4.91 (ABX, 2H, H1, H2), 4.62 (d, 1H, J_{gem} = 11.4 Hz, PhCH_2), 4.45 (d, 1H, PhCH_2), 3.74 (s, 3H, CH_3O), 3.56 (dq, 1H, $J_{4,5}$ = 8.9 Hz, $J_{5,6}$ = 6.1 Hz, H5), 3.28 (ddd, 1H, $J_{3ax,4}$ = 11.0 Hz, $J_{3eq,4}$ = 4.6 Hz, H4), 2.56 (ddd, 1H, J_{gem} = 12.5 Hz, $J_{2,3eq}$ = 4.6 Hz, $H3_{eq}$), 1.51 (ddd, 1H, $J_{2,3ax}$ = 11.0 Hz, $H3_{ax}$), 1.34 (d, 3H, H6), 1.19 (s, 9H, C(CH_3)$_3$). Anal. Calcd for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53. Found: C, 69.86; H, 7.66.

Phenyl 4-*O*-benzyl-3,6-dideoxy-2-*O*-pivaloyl-*ribo*-1-thio-hexopyranoside (13). To an ice cold solution of **12** (510 mg, 1.19 mmol) dissolved in dry dichloromethane were added dropwise thiophenol (196 μL, 1.8 mmol) and then BF_3·OEt_2 (200 μL, 1.43 mmol). The reaction mixture was stirred for 2 h on an ice bath, and then the reaction was quenched with triethylamine. The resulting solution was diluted with dichloromethane and washed with saturated sodium bicarbonate solution. The organic phase was dried over sodium sulfate and concentrated to an oil, which was subjected to chromatography in 7:1 hexane/EtOAc to give a colorless syrup (445 mg, 90%). NMR revealed a 2:1 mixture of α and β anomers. Crystallization from hexane/EtOAc gave the pure α isomer. The following data are for the α anomer only. Mp: 131 °C. $[\alpha]_D$: +272.2 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.43 (m, 10H, Ar), 5.64 (d, 1H, $J_{1,2}$ = 5.1 Hz, H1), 4.97 (ddd, 1H, $J_{2,3eq}$ = 4.8 Hz, $J_{2,3ax}$ = 12.5 Hz, H2), 4.66 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2), 4.48 (d, 1H, PhCH_2), 4.21 (dq, 1H, $J_{4,5}$ = 9.3 Hz, $J_{5,6}$ = 6.2 Hz, H5), 3.22 (ddd, 1H, $J_{3ax,4}$ = 11.9 Hz, $J_{3eq,4}$ = 4.5 Hz, H4), 2.36 (ddd, 1H, J_{gem} = 11.9 Hz, $H3_{eq}$), 1.83 (ddd, 1H, $H3_{ax}$), 1.25 (d, 3H, H6), 1.22 (s, 9H, C(CH_3)$_3$). Anal. Calcd for $C_{24}H_{30}O_4S$: C, 69.53; H, 7.29. Found: C, 69.33; H, 7.33.

6-Chlorohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (14). 3,4,6-Triacetyl-2-deoxy-2-phthalimido-D-glucopyranosyl bromide (1 g, 2.0 mmol) was dissolved in dry dichloromethane (20 mL), and lutidine (200 μL, 1.7 mmol), 6-chloro-1-hexanol (420 μL, 3.1 mmol), and freshly dried 4-Å molecular sieves were added. The mixture was stirred for 2 h under argon and then cooled in an ice bath. Silver triflate (565 mg, 2.2 mmol) was added, and the reaction mixture was stirred in the dark for 3 h. The mixture was neutralized with triethylamine (2 mL) and filtered through Celite. The solution was then concentrated and chromatographed in 2:1 EtOAc/pentane to yield a colorless oil (997 mg, 90%). $[\alpha]_D$: +19.0 (*c* 1.7, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79−7.84 (m, 2H, Ar), 7.70−7.74 (m, 2H, Ar), 5.75 (dd, 1H, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 9.0 Hz, H3), 5.31 (d, 1H, $J_{1,2}$ = 8.5 Hz, H1), 5.13 (dd, 1H, $J_{4,5}$ = 9.0 Hz, H4), 4.29 (dd, 1H, $J_{5,6}$ = 4.6 Hz, J_{gem} = 12.2 Hz, H6a), 4.27 (dd, 1H, H2), 4.13 (dd, 1H, $J_{5,6}$ = 2.4 Hz, H6b), 3.82 (m, 2H, CH_2O, H5), 3.39 (ddd, 1H, J_{gem} = 9.9 Hz, J_{vic} = 7.2 Hz, J_{vic} = 5.6 Hz, CH_2O), 3.27 (t, 2H, *J* = 6.9 Hz, CH_2Cl), 2.07 (s, 3H, CH_3CO), 1.99 (s, 3H, CH_3CO), 1.82 (s, 3H, CH_3CO), 1.39 (m, 4H, OCH_2CH_2, CH_2CH_2Cl), 1.11 (m, 4H, $OCH_2CH_2CH_2CH_2$). Anal. Calcd for $C_{26}H_{32}NO_{10}$: C, 56.37; H, 5.82; N, 2.53. Found: C, 56.08; H, 5.81; N, 2.47.

6-Chlorohexyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (15). The triacetate **14** (1.0 g, 1.8 mmol) was dissolved in dry methanol (25 mL), and a catalytic amount of sodium metal (~10 mg) was added. The reaction mixture was stirred for 3 h, and AG 50W H^+ resin was added until the solution was neutral on pH paper. The reaction mixture was then filtered and concentrated. The resulting white solid was then dissolved in dry acetonitrile (20 mL), and benzaldehyde dimethyl acetal (325 μL, 2.2 mmol) was added, followed by *p*-toluenesulfonic acid (50 mg). The mixture was stirred for 20 min, and then the reaction was quenched by the addition of triethylamine. The reaction mixture was concentrated and subjected to column chromatography in 2:1 hexane/EtOAc to give an amorphous solid (798 mg, 86%). $[\alpha]_D$: +35.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79−7.84 (m, 2H, Ar), 7.70−7.74 (m, 2H, Ar), 7.44−7.46 (m, 2H, Ar), 7.32−7.38 (m, 3H, Ar), 5.55 (s, 1H, PhCHO_2), 5.24 (d, 1H, $J_{1,2}$ = 8.4 Hz, H1), 4.61 (dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 8.5 Hz, H3), 4.37 (dd, 1H, J_{gem} = 10.5 Hz, $J_{5,6}$ = 4.5 Hz, $H6_{eq}$), 4.22 (dd, 1H, H2), 3.78−3.85 (m, 2H, CH_2O, H5), 3.67−3.53 (m, 2H, H4, $H6_{ax}$), 3.41 (ddd, 1H, J_{gem} = 9.7 Hz, J_{vic} = 7.2 Hz, J_{vic} = 5.9 Hz, CH_2O), 3.29 (t, 2H, t, *J* = 6.9 Hz, CH_2Cl), 1.33−1.48 (m, 4H, OCH_2CH_2, CH_2CH_2Cl), 1.04−1.25 (m, 4H, $OCH_2CH_2CH_2CH_2$); Anal. Calcd for $C_{23}H_{22}ClNO_7$: C, 60.07; H, 4.82; N, 3.05. Found: C, 59.72; H, 4.67; N, 2.93. HR electrospray *m/z*: calcd for $C_{27}H_{30}NO_7NaCl$, 538.16085; found, 538.161042.

6-Chlorohexyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (16). To a solution of **15** (2.5 g, 4.8 mmol) in dry dimethylformamide (20 mL) were added benzyl bromide (700 μL, 5.8 mmol) and then sodium hydride (150 mg, 6.2 mmol). The reaction mixture was stirred overnight and then diluted with dichloromethane and washed with water. The organic phase was dried over sodium sulfate, concentrated, and subjected to column chromatography in 3:1 hexane/EtOAc to yield a white solid, which was recrystallized from EtOAc/hexane (2.6 g, 89%). Mp: 111 °C. $[\alpha]_D$: +47.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6−7.9 (br m, 4H, Ar), 7.49−7.52 (m, 2H, Ar), 7.35−7.40 (m, 3H, Ar), 6.84−7.00 (m, 5H, Ar), 5.60 (s, 1H, PhCHO_2), 5.17 (d, 1H, $J_{1,2}$ = 8.4 Hz, H1), 4.78 (d, 1H, J_{gem} = 12.3 Hz, CH_2Ph), 4.49 (d, 1H, CH_2-Ph), 4.40 (dd, 1H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 8.6 Hz, H3), 4.38 (dd, 1H, J_{gem} = 10.4 Hz, $J_{5,6eq}$ = 3.9 Hz, $H6_{eq}$), 4.16 (dd, 1H, H2), 3.73−3.88 (m, 3H, H4, $H6_{ax}$, CH_2CH_2O), 3.62 (ddd, 1H, $J_{4,5} \approx J_{5,6ax}$ = 9.7 Hz, H5), 3.36 (dt, 1H, J_{gem} = 8.7 Hz, J_{vic} = 6.0 Hz, CH_2CH_2O), 3.27 (t, 2H, *J* = 6.9 Hz, CH_2Cl), 1.29−1.47 (m, 4H, OCH_2CH_2, CH_2CH_2Cl), 0.98−1.20 (m, 4H, $OCH_2CH_2CH_2CH_2$). Anal. Calcd for $C_{34}H_{38}NO_7$: C, 67.38; H, 5.99; N, 2.31. Found: C, 67.20; H, 6.04; N, 2.28.

6-Chlorohexyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (17). The benzylidene acetal **16** (700 mg, 1.15 mmol) was added to a round-bottom flask containing 3-Å molecular sieves, methyl orange (2 mg), and sodium cyanoborohydride (360 mg, 5.73 mmol). The flask was purged with argon, and dry THF (15 mL) was added. The mixture was allowed to stir for 2 h, and then the flask was fitted with a dropping funnel containing a saturated solution of HCl in diethyl ether. This solution was added dropwise to the reaction mixture until the pink color remained and no further gas evolution was evident. The reaction mixture was stirred for 30 min, the reaction was quenched with triethylamine, and the reaction mixture was filtered through Celite and concentrated. The resulting syrup was subjected to column chromatography, yielding a colorless oil (645 mg, 92%). $[\alpha]_D$: +18.3 (*c* 0.7, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60−7.85 (br, 4H, Ar), 7.27−7.38 (m, 5H, Ar), 6.92−7.06 (m, 5H, Ar), 5.11 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1), 4.73 (d, 1H, J_{gem} = 12.2 Hz, CH_2-Ph), 4.60 (AB, 2H, OCH_2Ph), 4.52 (d, 1H, OCH_2Ph), 4.09−4.24 (m, 2H, H2, H3), 3.72−3.84 (m, 4H, H4, H5, H6a, CH_2CH_2O), 3.62 (dd, 1H, $J_{5,6b}$ = 5.0 Hz, J_{gem} = 9.8 Hz, H6b), 3.36 (ddd, 1H, J_{gem} = 9.7 Hz, J_{vic} = 7.1 Hz, J_{vic} = 5.9 Hz, CH_2CH_2O), 3.26 (t, 2H, *J* = 6.9 Hz, CH_2Cl), 2.85 (s, 1H, $J_{OH,4}$ = 2.5 Hz, OH), 1.30−1.45 (m, 4H, OCH_2CH_2, CH_2CH_2Cl), 0.99−1.20 (m, 4H, CH_2CH_2). Anal. Calcd for $C_{34}H_{38}NO_7$: C, 67.15; H, 6.30; N, 2.30. Found: C, 66.91; H, 6.46; N, 2.27.

Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-2-(2′,2′,2′-trichloroethoxycarbonylamino)-β-D-galactopyranoside (19). 1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(2′,2′,2′-trichloroethoxycarbonylamino)-β-D-galactopyranoside[23] (1.23 g, 2.35 mmol) was dissolved in dichloromethane (20 mL). Thiophenol (480 μL, 4.62 mmol) and BF_3·OEt_2 (390 μL, 3.0 mmol) were then added in succession under argon. After being stirred for 3 h at room temperature, the reaction mixture was diluted with dichloromethane and washed with saturated sodium bicarbonate solution. The organic phase was dried over sodium sulfate and

concentrated to a yellow oil that was subjected to column chromatography in 2:1 hexane/EtOAc to give a colorless oil (1.0 g, 74%) that crystallized on standing. Mp: 117 °C. $[\alpha]_D$: −5.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53−7.48 (m, 2H, Ar), 7.32−7.27 (m, 3H, Ar), 5.38 (d, 1H, $J_{3,4}$ = 3.3 Hz, H4), 5.18 (dd, 1H, $J_{2,3}$ = 10.7 Hz, H3), 5.01 (d, 1H, $J_{1,2}$ = 8.8 Hz, H1), 4.89 (d, 1H, $J_{NH,2}$ = 10.4 Hz, N*H*), 4.73 (AB, 2H, CH_2-CCl_3), 4.17 (dd, 1H, J_{gem} = 11.4 Hz, $J_{5,6a}$ = 7.1 Hz, H6a), 4.11 (dd, 1H, $J_{5,6}$ = 6.1 Hz, H6b), 3.91 (ddd, 1H, H5), 3.89 (ddd, 1H, H2), 2.10 (s, 3H, CH_3CO), 2.02 (s, 3H, CH_3CO), 1.97 (s, 3H, CH_3CO). Anal. Calcd for $C_{21}H_{24}Cl_3NO_9S$: C, 44.03; H, 4.22; N, 2.45. Found: C, 44.12; H, 3.95; N, 2.45.

Methyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-(2′,2′,2′-trichloroethoxycarbonylamino)-*β*-D-galactopyranosyl)(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (20). Methyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside[11] (664 mg, 1.16 mmol) and glycosyl donor **19** (530 mg 1.15 mmol) were added to a round-bottom flask containing 4-Å molecular sieves, the flask was purged with argon, and dichloromethane (5 mL) was added. The mixture was then stirred for 1 h at room temperature, *N*-iodosuccinimide (103 mg, 0.46 mmol) and then silver triflate (20 mg, 0.078 mmol) were added to the reaction flask, and stirring was continued for 20 min. The reaction mixture was then diluted with dichloromethane and filtered through Celite. The organic phase was washed with solutions of sodium bicarbonate and sodium thiosulfate and concentrated to a yellow oil. Column chromatography in 2:1 toluene/EtOAc gave a white solid that was recrystallized (EtOAc/hexane) to give white needles (967 mg, 87%). Mp: 83−85 °C. $[\alpha]_D$: +2.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32−7.76 (m, 9H, Ar), 6.97 (m, 2H, Ar), 6.78−6.86 (m, 3H, Ar), 5.19 (d, 1H, $J_{3,4}$ = 3.3 Hz, H4′), 4.97 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1), 4.92 (d, 1H, J_{gem} = 12.2 Hz, PhCH_2), 4.79 (d, 1H, J_{gem} = 12.4 Hz, CH_2CCl$_3$), 4.76 (d, 1H, J_{gem} = 12.2 Hz, PhCH_2), 4.66 (d, 1H, CH_2CCl$_3$), 4.51 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H3′), 4.35 (d, 2H, PhCH_2O, PHCH_2O), 4.22 (d, 1H, $J_{1,2}$ = 7.9 Hz, H1′), 4.19 (dd, 1H, $J_{3,4}$ = 8.4 Hz, $J_{2,3}$ = 10.7 Hz, H3), 4.10 (dd, 1H, H2), 3.99 (dd, 1H, $J_{4,5}$ = 9.5 Hz, H4), 3.96 (dd, 1H, J_{gem} = 11.1 Hz, $J_{5,6}$ = 6.6 Hz, H6a′), 3.85 (dd, 1H, $J_{5,6}$ = 7.3 Hz, H6b′), 3.80 (dd, 1H, J_{gem} = 10.6 Hz, $J_{5,6}$ = 2.4 Hz, H6a), 3.76 (m, 2H, NH, H2′), 3.64 (ddd, 1H, H5′), 3.59 (dd, 1H, $J_{5,6}$ = 1.4 Hz, H6b), 3.46 (ddd, 1H, H5), 3.36 (s, 3H, OMe), 2.02 (s, 3H, CH_3CO), 2.00 (s, 3H, CH_3CO), 1.95 (s, 3H, CH_3CO). Anal. Calcd for $C_{44}H_{47}Cl_3N_2O_{16}$: C, 54.70; H, 4.90; N, 2.90. Found: C, 54.66; H, 4.84; N, 2.81.

6-Chlorohexyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-*β*-D-galactopyranosyl)(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (21). The phenyl thioglycoside **19** (240 mg, 0.39 mmol) and **17** (230 mg, 0.38 mmol) were added to a round-bottom flask containing 4-Å molecular sieves, and the flask was purged with argon. Dichloromethane (10 mL) was added, and the mixture was stirred for 1 h at room temperature. *N*-Iodosuccinimide (103 mg, 0.46 mmol) and silver triflate (20 mg, 0.078 mmol) were added to the reaction flask, and stirring was continued for 20 min. The reaction mixture was then diluted with dichloromethane and filtered through Celite, and the organic phase was washed with sodium bicarbonate and sodium thiosulfate solutions, dried over sodium sulfate, and concentrated to a yellow oil. Column chromatography (2:1, toluene/EtOAc) gave a white solid that was recrystallized (EtOAc/hexane) to give needles (396 mg, 93%). Mp: 153 °C. $[\alpha]_D$: −12.5 (*c* 0.52, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53−7.78 (br, 4H, Ar), 7.37−7.51 (m, 5H, Ar), 6.95−6.97 (m, 2H, Ar), 6.78−6.86 (m, 3H, Ar), 5.20 (dd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 0.9 Hz, H4′), 5.03 (d, 1H, $J_{1,2}$ = 8.4 Hz, H1), 4.90 (d, 1H, J_{gem} = 12.1 Hz, CH_2Ph), 4.78 (d, 1H, J_{gem} = 12.1 Hz, CH_2CCl$_3$), 4.76 (d, 1H, CH_2Ph), 4.66 (d, 1H, CH_2CCl$_3$), 4.53 (dd, 1H, $J_{2,3}$ = 10.7 Hz, H3′), 4.36 (d, 1H, J_{gem} = 12.4 Hz, CH_2Ph), 4.34 (d, 1H, CH_2Ph), 4.24 (d, 1H, $J_{1,2}$ = 7.9 Hz, H1′), 4.18 (dd, 1H, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 8.2 Hz, H3), 4.10 (dd, 1H, H2), 3.98 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H4), 3.94 (d, 1H, J_{gem} = 11.2 Hz, H6a), 3.87 (dd, $J_{5,6b}$ = 7.3 Hz, H6b), 3.75−3.83 (m, 3H, H2′, H6a′, CH_2CH_2O), 3.64 (ddd, 1H, $J_{5,6}$ = 6.9 Hz, H5′), 3.58 (d, 1H, J_{gem} = 10.2 Hz, H6b′), 3.45 (d, 1H, H5), 3.32 (ddd, 1H, J_{gem} = 9.8 Hz, J_{vic} = 5.8 Hz, J_{vic} = 7.32 Hz, CH_2CH_2O), 3.35 (t, 2H, CH_2Cl), 2.02 (s, 3H, CH_3CO), 2.01 (s, 3H, CH_3CO), 1.94 (s, 3H, CH_3CO), 1.29−1.42 (m, 4H, OCH_2CH_2, CH_2CH_2Cl), 0.98−1.1.18 (m, 4H, $OCH_2CH_2CH_2CH_2$). Anal. Calcd for $C_{49}H_{56}Cl_4N_2O_{16}$: C, 54.96; H, 5.23; N, 2.62. Found: C, 54.94; H, 5.16; N, 2.56.

Methyl (2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-*β*-D-galactopyranosyl)(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (22). To a solution of the disaccharide **20** (746 mg, 0.77 mmol) in 1:1 DMF/AcOH (20 mL) was added cadmium metal powder (490 mg, 11.5 mmol), and the reaction mixture was stirred under argon overnight. The solution was then filtered and concentrated to a yellow oil. The oil was taken up in methanol (20 mL) and treated with acetic anhydride (0.5 mL). The solution was stirred for 1 h and then concentrated to dryness; column chromatography (10:4:1, EtOAc/hexane/methanol) yielded a white amorphous solid (474 mg, 74%). $[\alpha]_D$: +9.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, CD_3OD): δ 7.66−7.80 (m, 4H, Ar), 7.27−7.45 (m, 5H, Ar), 6.97−7.00 (m, 2H, Ar), 6.58−6.87 (m, 3H, Ar), 5.28 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 1.7 Hz, H4′), 5.08 (dd, 1H, $J_{2,3}$ = 11.3 Hz, H3′), 5.03 (d, 1H, $J_{1,2}$ = 8.5 Hz, H1), 4.85 (d, 1H, J_{gem} = 12.2 Hz, PhCH_2O), 4.77 (d, 1H, $J_{1,2}$ = 8.4 Hz, H1′), 4.72 (d, 1H, J_{gem} = 11.6 Hz, PhCH_2O), 4.64 (d, 1H, PhCH_2O), 4.44 (d, 1H, PhCH_2O), 4.25 (dd, 1H, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 8.6 Hz, H3), 4.03−4.10 (m, 4H, H2′, H4, H6a′, H6b′), 3.97 (dd, 1H, H2), 3.86 (dd, 1H, J_{gem} = 11.3 Hz, $J_{5,6}$ = 1.8 Hz, H6a), 3.81 (dd, 1H, $J_{5,6}$ = 3.8 Hz, H6b), 3.78 (ddd, 1H, $J_{5,6a} \approx J_{5,6b}$ = 6.7 Hz, H5′), 3.60 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, H5), 3.36 (s, 3H, OMe), 2.30 (s, 3H, CH_3CO), 1.99 (s, 3H, CH_3CO), 1.96 (s, 3H, CH_3CO), 1.94 (s, 3H, CH_3NHCO). Anal. Calcd for $C_{43}H_{48}N_2O_{15}$: C, 62.01; H, 5.81; N, 3.36. Found: C, 61.93; H, 5.65; N, 3.20.

6-Chlorohexyl (2-acetamido-3,4,6- tri-*O*-acetyl-2-deoxy-*β*-D-galactopyranosyl)(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (23). To a solution of **21** (2.2 g, 2.1 mmol) in 1:1 DMF/AcOH (30 mL) was added cadmium metal powder (1.3 g, 11.5 mmol), and the reaction mixture was stirred under argon overnight. The solution was then filtered and concentrated to a yellow oil. The oil was taken up in methanol (20 mL), and acetic anhydride (1 mL) was added. The solution was stirred for 1 h and concentrated to a yellow syrup. Column chromatography (10:4:1, EtOAc/hexane/methanol) yielded 1.7 g (86%) of a white solid, which was recrystallized from EtOAc/hexane. Mp: 150 °C. $[\alpha]_D$: +2.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56−7.76 (br, 4H, Ar), 7.40−7.50 (m, 5H, Ar), 6.99−7.00 (m, 2H, Ar), 6.78−6.87 (m, 3H, Ar), 5.21 (d, 1H, $J_{3,4}$ = 3.5 Hz, H4′), 5.04 (d, 1H, d, $J_{1,2}$ = 8.4 Hz, H1), 4.91 (d, 1H, J_{gem} = 12.1 Hz, CH_2Ph), 4.77 (d, 1H, J_{gem} = 12.5 Hz, CH_2Ph), 4.58 (dd, 1H, $J_{2,3}$ = 11.3 Hz, $J_{3,4}$ = 3.5 Hz, H3′), 4.43 (d, 1H, $J_{1,2}$ = 9.6 Hz, H1′), 4.39 (d, 1H, $J_{NH,2}$ = 8.4 Hz, N*H*), 4.38 (d, 1H, J_{gem} = 12.5 Hz, CH_2Ph), 4.38 (d, 1H, J_{gem} = 12.0 Hz, CH_2Ph), 4.21 (dd, 1H, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 8.4 Hz, H3), 4.10 (ddd, 1H, H2′), 4.10 (dd, 1H, H2), 3.98 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H4), 3.97 (dd, 1H, $J_{5,6}$ = 6.4 Hz, J_{gem} = 11.5 Hz, H6a′), 3.89 (dd, 1H, $J_{5,6}$ = 6.4 Hz, H6b′), 3.77 (dt, 1H, J_{gem} = 9.7 Hz, J_{vic} = 6.1 Hz, CH_2CH_2O), 3.68 (m, 2H, H5′, H6a), 3.62 (dd, 1H, J_{gem} = 10.8 Hz, $J_{5,6}$ = 2.1 Hz, H6b), 3.51 (ddd, 1H, $J_{5,6a}$ = 2.4 Hz, H5), 3.31 (ddd, 1H, J_{vic} = 7.2 Hz, J_{vic} = 6.0 Hz, CH_2CH_2O), 3.25 (t, 2H, J = 6.9 Hz, CH_2Cl), 2.02 (s, 3H, CH_3CO), 1.95 (s, 3H, CH_3CO), 1.74 (s, 3H, CH_3CO), 1.29−1.43 (m, 4H, OCH_2CH_2, CH_2CH_2Cl), 0.86−1.16 (m, 4H, $OCH_2CH_2CH_2CH_2$). Anal. Calcd for $C_{48}H_{57}ClN_2O_{15}$: C, 61.50; H, 6.13; N, 2.99. Found: C, 61.25; H, 6.16; N, 2.93.

Methyl (2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-galactopyranosyl)(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (24). To a solution of **22** (300 mg, 0.36 mmol) in dry methanol (15 mL) was added a catalytic amount of sodium metal (5 mg). The reaction mixture was stirred at room temperature for 3 h and then the reaction was quenched with AG 50W 50 H^+ resin; the reaction mixture was filtered and concentrated to dryness. The white solid was taken up in dry acetonitrile (15 mL), and benzaldehyde dimethyl acetal (108 μL, 0.71 mmol) and then *p*-toluenesulfonic acid (20 mg) were added. The reaction mixture was stirred for 20 min, neutralized with triethylamine, concentrated, and subjected to column chromatography (10:4:1, EtOAc/hexane/methanol)

to yield a white solid (245 mg, 88%). Recrystallization from EtOAc/hexane gave the title compound. Mp: 123−125 °C. $[\alpha]_D$: +3.3 (*c* 1.2, $CHCl_3$). ^{1}H NMR (500 MHz, CD_3OD): δ 7.54−7.78 (br, 4H, Ar), 7.32−7.44 (m, 6H, Ar), 7.02−7.24 (m, 5H, Ar), 6.94−6.98 (m, 2H, Ar), 6.72−6.76 (m, 2H, Ar), 5.84 (d, 1H, $J_{NH,2}$ = 6.8 Hz, N*H*), 5.47 (s, 1H, C*H*O_2Ph), 4.89 (d, 1H, J_{gem} = 12.8 Hz, PhCH_2O), 4.99 (d, 1H, $J_{1,2}$ = 7.9 Hz, H1), 4.79 (d, 1H, J_{gem} = 11.7 Hz, PhCH_2O), 4.57 (d, 1H, $J_{1,2}$ = 8.6 Hz, H1′), 4.55 (d, 1H, J_{gem} = 12.1 Hz, PhCH_2O), 4.51 (d, 1H, J_{gem} = 12.7 Hz, PhCH_2O), 4.29 (dd, 1H, $J_{2,3}$ = 8.2 Hz, $J_{3,4}$ = 10.7 Hz, H3), 4.24 (d, 1H, J_{gem} = 12.4 Hz, H6a′), 4.11 (dd, 1H, H2), 4.09 (dd, 1H, $J_{3,4}$ = 3.5 Hz, H4′), 4.01 (dd, 1H, $J_{4,5}$ = 9.3 Hz, H4), 3.91 (dd, 1H, H6b′), 3.86 (dd, 1H, J_{gem} = 10.8 Hz, $J_{5,6}$ = 3.6 Hz, H6a), 3.75 (dd, 1H, $J_{5,6}$ = 3.6 Hz, H6b), 3.64 (ddd, 1H, H5), 3.92 (ddd, 1H, H2′), 3.59 (dd, 1H, $J_{2,3}$ = 10.6 Hz, H3′), 3.37 (s, 3H, OMe), 3.25 (s, 1H, H5′), 1.89 (s, 3H, CH_3CONH). Anal. Calcd for $C_{44}H_{46}N_2O_{12}$ + 0.5 H_2O: C, 65.74; H, 5.89; N, 3.48. Found: C, 65.75; H, 5.76; N, 3.44. HR electrospray *m*/*z*: calcd, 817.29484; found, 817.29467.

6-Chlorohexyl (2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-galactopyranosyl)(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (25). To a solution of **23** (1.31 g, 1.4 mmol) in dry methanol (25 mL) was added a small piece of sodium metal (5 mg). The reaction mixture was stirred at room temperature for 3 h and then the reaction was quenched with Ag 50W 50 H^+ resin; the reaction mixture was filtered and concentrated to dryness. The white solid was then taken up in dry acetonitrile, and benzaldhyde dimethyl acetal (320 μL, 2.1 mmol) and then *p*-toluenesulfonic acid (10 mg) were added. The reaction mixture was stirred for 20 min, neutralized with triethylamine, concentrated, and subjected to column chromatography (10:4:1, EtOAc/hexane/methanol) to give a white solid (993 mg, 79%), which could be recrystallized from EtOAc/hexane. Mp: 102−103 °C. $[\alpha]_D$: −4.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56−7.76 (br, 4H, Ar), 7.34−7.43 (m, 5H, Ar), 7.16−7.21 (m, 5H, Ar), 6.96−6.98 (m, 2H, Ar), 6.72−6.86 (m, 3H, Ar), 5.85 (d, 1H, $J_{NH,2}$ = 6.9 Hz, N*H*Ac), 5.48 (s, 1H, PhC*H*O_2), 5.06 (d, 1H, $J_{1,2}$ = 8.6 Hz, H1), 4.91 (d, 1H, J_{gem} = 12.7 Hz, OCH_2Ph), 4.79 (d, 1H, J_{gem} = 11.8 Hz, OCH_2Ph), 4.56 (d, 1H, $J_{1,2}$ = 8.7 Hz, H1′), 4.54 (d, 1H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.52 (d, 1H, d, J = 12.8 Hz, OCH_2-Ph), 4.28 (dd, 1H, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 8.7 Hz, H3), 4.24 (d, 1H, J_{gem} = 12.4 Hz, H6a′), 4.11 (dd, 1H, H2), 4.08 (d, 1H, $J_{3,4}$ = 3.3 Hz, H4′), 3.97 (dd, 1H, $J_{4,5}$ = 8.4 Hz, H4), 3.90−3.94 (m, 2H, H2′, H6b′), 3.84 (dd, 1H, $J_{5,6}$ = 3.1 Hz, J_{gem} = 10.8 Hz, H6a), 3.76 (dt, 1H, J_{gem} = 9.8 Hz, J_{vic} = 5.8 Hz, CH_2CH_2O), 3.74 (dd, 1H, $J_{5,6}$ = 3.4 Hz, H6b), 3.58 (dd, 1H, H5), 3.58 (dd, 1H, $J_{2,3}$ = 10.7 Hz, H3′), 3.32 (dt, 1H, J = 6.1 Hz, CH_2CH_2O), 3.25 (d, 1H, $J_{5,6b}$ = 4.6 Hz, H5′), 3.25 (t, 2H, J = 6.9 Hz, CH_2-Cl), 1.88 (s, 3H, CH_3CO), 1.29−1.43 (m, 4H, OCH_2CH_2, CH_2CH_2Cl), 0.97−1.16 (m, 4H, CH_2CH_2), Anal. Calcd for $C_{49}H_{55}ClN_2O_{12}$: C, 65.43; H, 6.16; N, 3.11. Found: C, 65.16; H, 6.1; N, 3.07.

6-Azidohexyl (2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-galactopyranosyl)(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (26). To a solution of **25** (993 mg, 1.10 mmol) in DMSO (10 mL) was added sodium azide (400 mg, 6.2 mmol). The mixture was heated to 60 °C overnight. The solution was then diluted with dichloromethane and washed three times with water. After drying, the solution was concentrated and crystallized from EtOAc/hexane to give **26** (946 mg, 96%). Mp: 108−111 °C. $[\alpha]_D$: −5.4 (*c* 0.52, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56−7.76 (br, 4H, Ar), 7.34−7.43 (m, 5H, Ar), 7.16−7.21 (m, 5H, Ar), 6.96−6.98 (m, 2H, Ar), 6.72−6.86 (m, 3H, Ar), 5.85 (d, 1H, $J_{NH,2}$ = 6.9 Hz, N*H*Ac), 5.48 (s, 1H, PhC*H*O_2), 5.06 (d, 1H, $J_{1,2}$ = 8.6 Hz, H1), 4.91 (d, 1H, J_{gem} = 12.7 Hz, CH_2Ph), 4.79 (d, 1H, J_{gem} = 11.8 Hz, CH_2-Ph), 4.56 (d, 1H, $J_{1,2}$ = 8.7 Hz, H1′), 4.54 (d, 1H, J_{gem} = 12.1 Hz, CH_2Ph), 4.52 (d, 1H, J_{gem} = 12.8 Hz, CH_2Ph), 4.28 (dd, 1H, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 10.4 Hz, H3), 4.24 (d, 1H, J_{gem} = 11.3 Hz, H6a′), 4.11 (dd, 1H, H2), 4.04 (d, 1H, $J_{3,4}$ = 3.2 Hz, H4′), 3.97 (dd, 1H, H4), 3.90−3.94 (m, 2H, H2′, H6b′), 3.84 (dd, 1H, J_{gem} = 10.8 Hz, $J_{5,6}$ = 3.1 Hz, H6a), 3.76 (dt, 1H, J_{gem} = 9.8 Hz, J_{vic} = 5.8 Hz, CH_2CH_2O), 3.74 (dd, 1H, $J_{5,6}$ = 3.4 Hz, H6b), 3.62 (ddd, 1H, $J_{4,5}$ = 9.6 Hz, H5), 3.58 (dd, 1H, $J_{2,3}$ = 10.7 Hz, H3′), 3.32 (dt, 1H, J_{vic} = 5.6 Hz, CH_2CH_2O), 2.97 (t, 2H, J = 7.0 Hz, CH_2N_3), 3.25 (s, 1H, H5′), 1.88 (s, 3H, CH_3CO), 1.28−1.42 (m, 2H, OCH_2CH_2), 1.14−1.23 (m, 2H, $CH_2CH_2N_3$), 0.97−1.10 (m, 4H, $OCH_2CH_2CH_2CH_2$). IR (cast): N_3 stretch, 2094 cm^{-1}. Anal. Calcd for $C_{49}H_{55}N_3O_{12}$: C, 64.96; H, 6.12; N, 7.73. Found: C, 64.73; H, 6.13; N, 7.65.

Methyl (4-*O*-benzyl-3,6-dideoxy-2-*O*-pivaloyl-*ribo*-hexopyranosyl)(1→3)(2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-galactopyranosyl)(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (27). A solution of **24** (85 mg, 0.11 mmol), **13** (49 mg, 0.119 mmol), and freshly activated 4-Å sieves in dichloromethane (3 mL) was stirred for 1 h. The reaction mixture was cooled in an ice bath, and *N*-iodosuccinimide (29 mg, 129 mmol) and then silver triflate (10 mg) were added. The ice bath was removed, and the reaction mixture was allowed to warm to room temperature. After 30 min, the reaction mixture was filtered through Celite, and the solids were washed with dichloromethane. The combined filtrate was washed with thiosulfate and bicarbonate solutions, dried over sodium sulfate, and concentrated. Chromatography in 5:2 toluene/EtOAc yielded a clear amorphous solid (95 mg, 85%). $[\alpha]_D$: +4.2 (*c* 1.0, $CHCl_3$). ^{1}H (500 MHz, $CDCl_3$): δ 7.56−7.76 (m, 4H, Ar), 7.12−7.44 (m, 15H, Ar), 6.91−6.93 (m, 2H, Ar), 6.79−6.82 (m, 1H, Ar), 6.71 (m, 2H, Ar), 5.59 (d, 1H, $J_{NH,2}$ = 7.0 Hz, NH), 5.47 (s, 1H, PhC*H*O_2), 5.17 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1′), 5.00 (d, 1H, J_{gem} = 12.5 Hz, PhCH_2O), 4.99 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1), 4.69 (d, 1H, J_{gem} = 11.8 Hz, PhCH_2O), 4.65 (d, 1H, $J_{1,2}$ = 8.6 Hz, H1″), 4.64 (d, 1H, J_{gem} = 11.9 Hz, PhCH_2O), 4.60 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2O), 4.58 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 3.8 Hz, H3′), 4.57 (d, 1H, J_{gem} = 12.8 Hz, PhCH_2O), 4.54 (ddd, 1H, $J_{2,3ax}$ = 11.1 Hz, $J_{2,3eq}$ = 5.2 Hz, H2″), 4.42 (d, 1H, J_{gem} = 11.4 Hz, PhCH_2O), 4.28 (dd, 1H, J_{gem} = 12.8 Hz, $J_{5,6a}$ = 1.4 Hz, H6a′), 4.26 (d, 1H, H4′), 4.20−4.24 (m, 2H, H3, H4), 4.01 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H2), 3.96 (dd, 1H, $J_{5,6b}$ = 1.5 Hz, H6b′), 3.81 (dd, 1H, J_{gem} = 10.8 Hz, $J_{5,6a}$ = 1.5 Hz, H6a), 3.76 (dd, 1H, $J_{5,6b}$ = 3.7 Hz, H6b), 3.59 (ddd, 1H, $J_{4,5}$ = 9.5 Hz, H5), 3.49 (dt, 1H, $J_{4,5}$ = 8.9 Hz, $J_{5,6}$ = 6.3 Hz, H5″), 3.48 (dd, 1H, H2′), 3.36 (s, 3H, OMe), 3.29 (dd, 1H, H5′), 3.23 (ddd, 1H, $J_{3ax,4}$ = 10.7 Hz, $J_{3eq,4}$ = 4.6 Hz, H4″), 2.62 (ddd, 1H, J_{gem} = 12.1 Hz, $H3_{eq}$″), 1.97 (s, 3H, CH_3CONH), 1.37 (ddd, 1H, $H3_{ax}$″), 1.33 (d, 3H, H6″), 1.20 (s, 9H, $(CH_3)_3$CO). Anal. Calcd for $C_{62}H_{70}N_2O_{16}$: C, 67.74; H, 6.42; N, 2.55. Found: C, 66.98; H, 6.15; N, 2.65. HR electrospray *m*/*z*: calcd, 1099.48036; found, 1099.48045.

6-Azidohexyl (4-*O*-benzyl-3,6-dideoxy-2-*O*-pivaloyl-*ribo*-hexopyranosyl)(1→3)(2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-galactopyranosyl)(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (28). A solution of **26** (200 mg, 0.22 mmol), **13** (100 mg, 0.24 mmol), and freshly activated 4-Å sieves in dichloromethane (4 mL) was stirred for 1 h. The reaction mixture was then cooled in an ice bath, and *N*-iodosuccinimde (65 mg) and then silver triflate (10 mg) were added. The ice bath was removed, and the reaction mixture was allowed to warm to room temperature. After 30 min, the reaction mixture was filtered through Celite, and the solids were washed with dichloromethane. The combined filtrate was washed with thiosulfate and bicarbonate solutions, dried over sodium sulfate, and concentrated to a yellow oil. Chromatography in 5:2 toluene/EtOAc yielded 216 mg (81%) of a colorless amorphous solid. $[\alpha]_D$: −5.4 (*c* 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80−7.54 (br, 4H, Ar), 7.40−7.10 (m, 15H, Ar), 6.94−6.93 (m, 2H, Ar), 6.74−6.70 (m, 3H, Ar), 5.56 (d, 1H, $J_{NH,2}$ = 7.0 Hz, N*H*Ac), 5.43 (s, 1H, O_2C*H*Ph), 5.14 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1′), 5.05 (d, 1H, $J_{1,2}$ = 8.6 Hz, H1), 4.99 (d, 1H, J_{gem} = 12.8 Hz, OCH_2Ph), 4.68 (d, 1H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.66 (d, 1H, $J_{1,2}$ = 7.7 Hz, H1″), 4.62 (d, 1H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.60−4.52 (m, 2H, H2″, H3′), 4.58 (d, 1H, J_{gem} = 11.5 Hz, OCH_2Ph), 4.53 (d, 1H, J_{gem} = 12.8 Hz, OCH_2-Ph), 4.39 (d, 1H, J_{gem} = 11.5 Hz, OCH_2Ph), 4.28 (dd, 1H, $J_{2,3}$ = 8.2 Hz, $J_{3,4}$ = 10.6 Hz, H3), 4.26 (d, 1H, J_{gem} = 10.6 Hz, H6a′), 4.20 (d, 1H, $J_{3,4}$ = 3.5 Hz, H4′), 4.15−4.12 (m, 2H, H4, H2), 3.87 (d, 1H, H6b′), 3.80 (d, 1H, J_{gem} = 9.9 Hz, H6a), 3.76 (dt, 1H, J_{gem} = 9.9 Hz, J_{vic} = 6.0 Hz, OCH_2CH_2), 3.72 (dd, 1H, $J_{5,6}$ = 4.2 Hz, H6b), 3.59 (dd, 1H, $J_{4,5}$ = 10.6 Hz, H5), 3.48 (dd, 1H, $J_{2,3}$ = 6.4 Hz, H2′), 3.46 (dq, 1H, $J_{5,6}$ = 5.8 Hz, H5″), 3.33

(dt, 1H, J_{vic} = 7.1 Hz, OCH_2CH$_2$), 3.22 (s, 1H, H5′), 3.21 (1H, ddd, $J_{3eq,4}$ = 4.7 Hz, $J_{3ax,4}$ = 12.1 Hz, H4″), 2.97 (t, 3H, J_{vic} = 7.1 Hz, CH_2N$_3$), 2.61 (1H, ddd, J_{gem} = 12.1 Hz, $J_{2,3}$ = 4.9 Hz, H3$_{eq}$″), 1.95 (s, 3H, NHCOCH_3), 1.41−1.28 (m, 2H, OCH$_2$CH_2), 1.33 (ddd, 1H, $J_{2,3}$ = 12.0 Hz, H3$_{ax}$″), 1.31 (d, 3H, H6″), 1.25−1.17 (m, 2H, CH_2CH$_2$N$_3$), 1.17 (s, 9H, COC(CH_3)$_3$), 1.11−1.00 (m, 4H, OCH$_2$CH$_2$CH_2CH_2). Anal. Calcd for $C_{67}H_{79}N_5O_{16}$ + H$_2$O: C, 65.51; H, 6.65; N, 5.70. Found: C, 65.51; H, 6.66; N, 5.68. HR electrospray *m*/*z*: calcd for $C_{67}H_{80}N_5O_{16}$, 1210.5600; found, 1210.5596.

Methyl (4-*O*-benzyl-3,6-dideoxy-*ribo*-hexopyranosyl)-(1→3)(2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-galactopyranosyl)(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (29). The protected trisaccharide **27** (95 mg, 0.086 mmol) was dissolved in butanol (4 mL) and ethylenediamine (1 mL). The solution was heated to 110 °C for 16 h and then concentrated to a yellow oil. The oil was taken up in methanol, 500 μL of acetic anhydride was added, and the mixture was stirred for 1 h and then concentrated to dryness. The oil was dissolved in dry methanol (10 mL), and sodium metal (10 mg) was added. The solution was refluxed for an additional 12 h, neutralized with Ag 50W 50 H$^+$ resin, filtered, and concentrated to dryness. The resulting oil was chromatographed in 10:4:1 EtOAc/hexane/methanol, yielding a white amorphous solid **29** (68 mg, 85%). [α]$_D$: +6.6 (*c* 0.45, CH$_3$OH). ^{1}H (600 MHz, CD$_3$OD): δ 7.18−7.44 (m, 20H, Ar), 5.33 (s, 1H, PhCHO$_2$), 5.16 (d, 1H, J_{gem} = 12.1 Hz, PhCH_2O), 4.74 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1′), 4.67 (d, 1H, J_{gem} = 11.7 Hz, PhCH_2O), 4.62 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2O), 4.61 (d, 1H, J_{gem} = 11.9 Hz, PhCH_2O), 4.47 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2O), 4.47 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2O), 4.32 (d, 1H, $J_{1,2}$ = 8.1 Hz, H1), 4.31 (d, 1H, $J_{1,2}$ = 7.5 Hz, H1″), 4.26 (d, 1H, $J_{3,4}$ = 3.5 Hz, H4′), 4.14 (dd, 1H, J_{gem} = 12.1 Hz, $J_{5,6}$ = 1.7 Hz, H6a′), 4.10 (dd, 1H, $J_{2,3}$ = 10.6 Hz, H2′), 3.96 (dd, 1H, $J_{5,6}$ = 2.2 Hz, H6b′), 3.95 (dd, 1H, $J_{4,5} \approx J_{3,4}$ = 8.5 Hz, H4), 3.91 (dd, 1H, dd, $J_{2,3}$ = 11.0 Hz, $J_{3,4}$ = 3.1 Hz, H3′), 3.83 (dd, 1H, J_{gem} = 11.2 Hz, $J_{5,6}$ = 2.4 Hz, H6b), 3.81 (dd, 1H, $J_{2,3}$ = 9.1 Hz, H2), 3.79 (dd, 1H, $J_{5,6}$ = 4.4 Hz, H6a), 3.65 (dd, 1H, H3), 3.51 (1H, ddd, H5), 3.40 (dq, 1H, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H5″), 3.34 (ddd, 1H, $J_{2,3ax}$ = 12.5 Hz, $J_{2,3eq}$ = 7.7 Hz, H2″), 3.43 (s, 3H, OMe), 3.23 (s, 1H, H5′), 3.13 (ddd, 1H, $J_{3ax,4}$ = 11.0 Hz, $J_{3eq,4}$ = 4.6 Hz, H4″), 2.42 (1H, ddd, J_{gem} = 12.0 Hz, H3$_{eq}$″), 1.94 (s, 3H, CH_3NHCO), 1.82 (s, 3H, CH_3NHCO), 1.33 (ddd, 1H, H3$_{ax}$″), 1.27 (d, 3H, H6″). Anal. Calcd for $C_{51}H_{62}N_2O_{14}$ + H$_2$O: C, 64.82; H, 6.83; N, 2.96. Found: C, 64.83; H, 6.64; N, 2.92. HR electrospray *m*/*z*: calcd for $C_{51}H_{62}N_2O_{14}$Na, 949.4098; found, 949.4088.

6-Azidohexyl (4-*O*-benzyl-3,6-dideoxy-*ribo*-hexopyranosyl)(1→3)(2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-galactopyranosyl)(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (30). The protected trisaccharide **28** (176 mg, 0.145 mmol) was dissolved in butanol (4 mL) and ethenediamine (1 mL). The solution was heated to 110 °C for 12 h and then concentrated to a yellow oil. The oil was taken up in methanol, and acetic anhydride (500 μL) was added; the mixture was then stirred for 1 h. After concentration of the reaction mixture, the resulting oil was dissolved in dry methanol (10 mL), and sodium metal (10 mg) was added. The solution was refluxed for an additional 12 h, neutralized with Ag 50W 50 H$^+$ resin, filtered, and concentrated. The remaining oil was chromatographed in 10:4:1 EtOAc/hexane/methanol, yielding a white amorphous solid (132 mg, 88%). [α]$_D$: −5.4 (*c* 0.52, CHCl$_3$). ^{1}H NMR (500 MHz, CD$_3$OD): δ 7.43−7.17 (m, 20H, Ar), 5.52 (s, 1H, O$_2$CHPh), 5.15 (d, 1H, J_{gem} = 11.9 Hz, OCH_2Ph), 4.73 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1′), 4.68 (d, 1H, J_{gem} = 11.9 Hz, OCH_2Ph), 4.67 (d, 1H, J_{gem} = 11.8 Hz, OCH_2Ph), 4.62 (d, 1H, J_{gem} = 11.4 Hz, OCH_2Ph), 4.60 (d, 1H, J_{gem} = 11.8 Hz, OCH_2Ph), 4.47 (d, 1H, J_{gem} = 11.6 Hz, OCH_2Ph), 4.40 (d, 1H, $J_{1,2}$ = 8.1 Hz, H1), 4.30 (d, 1H, $J_{1,2}$ = 7.6 Hz, H1″), 4.25 (d, 1H, $J_{3,4}$ = 3.3 Hz, H4′), 4.14 (dd, 1H, J_{gem} = 12.2 Hz, $J_{5,6}$ = 1.4 Hz, H6a′), 4.09 (dd, $J_{2,3}$ = 11.0 Hz, H2′), 3.95 (dd, 1H, $J_{5,6}$ = 1.4 Hz, H6′b′), 3.94 (dd, 1H, $J_{3,4} \approx J_{4,5}$ = 8.5 Hz, H4), 3.90 (dd, 1H, $J_{2,3}$ = 11.1 Hz, $J_{3,4}$ = 3.4 Hz, H3′), 3.84−3.76 (m, 4H, H6a, H6b, H2, CH$_2$CH_2O), 3.67 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H3), 3.50 (ddd, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 4.6 Hz, H5), 3.45 (ddd, 1H, J_{gem} = 9.8 Hz, J_{vic} = 6.4 Hz, CH$_2$CH_2O), 3.40 (dq, 1H, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 2.9 Hz, H5″), 3.35 (ddd, 1H, $J_{2,3eq}$ = 5.0 Hz, $J_{2,3ax}$ = 12.2 Hz, H2″), 3.23 (s, 1H, H5′), 3.23 (t, 2H, J_{vic} = 7.0 Hz, CH_2N$_3$), 3.14 (ddd, 1H, $J_{3,4}$ = 4.6 Hz, $J_{3,4}$ = 11.0 Hz, H4″), 2.42 (ddd, 1H, J_{gem} = 12.1 Hz, H3$_{eq}$″), 1.94 (s, 3H, NHCOCH_3), 1.82 (s, 3H, NHCOCH_3), 1.58−1.52 (m, 4H, OCH$_2$CH_2, CH_2CH$_2$N$_3$), 1.39−1.36 (m, 4H, OCH$_2$CH$_2$CH_2CH_2), 1.35 (ddd, 1H, H3$_{ax}$″), 1.27 (d, 3H, H6″). Anal. Calcd for $C_{56}H_{71}N_5O_{14}$ + H$_2$O: C, 63.68; H, 6.97; N, 6.63. Found: C, 63.82; H, 6.94; N, 6.63.

Methyl (4-*O*-benzyl-3,6-dideoxy-*arabino*-hexopyranosyl)(1→3)(2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-galactopyranosyl)(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (31). Compound **29** (75 mg) was dissolved in dry DMSO (2 mL) and acetic anhydride (0.5 mL). The reaction mixture was stirred overnight and concentrated to dryness. The yellow solid was dissolved in DMF (0.5 mL) and then diluted with dry THF (10 mL). The reaction mixture was cooled to −78 °C, and 1 M L-selectride (500 μL) in THF was added dropwise. The reaction mixture was allowed to warm to room temperature, and the reaction was quenched with acetone. Silica gel was then added to the solution, and the volatiles were removed under vacuum. The silica gel was then slurried onto the top of a silica column, and the product was eluted with 4% methanol in dichloromethane to give **31** (62 mg, 82%). [α]$_D$: +4.3 (*c* 0.67 CH$_3$OH). ^{1}H NMR (500 MHz, CD$_3$OD): δ 7.18−7.46 (m, 20H, Ar), 5.17 (d, 1H, J_{gem} = 11.9 Hz, PhCH_2O), 5.55 (s, 1H, PhCHO$_2$), 4.74 (d, 1H, $J_{1,2}$ = 8.4 Hz, H1′), 4.71 (d, 1H, J_{gem} = 11.9 Hz, PhCH_2O), 4.68 (d, 1H, J_{gem} = 11.9 Hz, PhCH_2O), 4.61 (d, 1H, J_{gem} = 11.9 Hz, PhCH_2O), 4.58 (d, 1H, $J_{1,2}$ < 1 Hz, H1″), 4.57 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2O), 4.43 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2O), 4.32 (d, 1H, $J_{1,2}$ = 8.2 Hz, H1), 4.30 (dd, 1H, $J_{3,4}$ = 3.5 Hz, H4′), 4.14 (dd, 1H, J_{gem} = 12.4 Hz, $J_{5,6}$ = 1.4 Hz, H6a′), 4.09 (dd, 1H, $J_{2,3}$ = 8.7 Hz, H2′), 3.97 (dd, 1H, $J_{5,6}$ = 2.0 Hz, H6b′), 3.95 (dd, 1H, $J_{4,5}$ = 6.9 Hz, $J_{3,4}$ = 8.2 Hz, H4), 3.93 (dd, 1H, H3′), 3.84 (dd, 1H, J_{gem} = 11.6 Hz, $J_{5,6a}$ = 2.4 Hz, H6a), 3.80 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H2), 3.79 (dd, 1H, $J_{5,6b}$ = 4.2 Hz, H6b), 3.76 (ddd, 1H, $J_{2,3a} \approx J_{2,3b}$ = 3.4 Hz, H2″), 3.66 (dd, 1H, H3), 3.51 (ddd, 1H, H5), 3.43 (s, 3H, OMe), 3.38−3.48 (m, 2H, H5″, H4″), 3.23 (s, 1H, H5′), 2.31 (ddd, 1H, J_{gem} = 13.5 Hz, H3$_{eq}$″), 1.94 (s, 3H, CH_3NHCO), 1.82 (s, 3H, CH_3NHCO), 1.48 (ddd, 1H, H3$_{ax}$″), 1.30 (d, 3H, $J_{5,6}$ = 6.1 Hz, H6″). ^{13}C NMR (500 MHz, CD$_3$OD): δ 101.72 (J_{C1-H1} = 162 Hz, C1′, β), 103.20 (J_{C1-H1} = 161 Hz, C1, β), 140.10 (J_{C1-H1} = 158 Hz, C1″, β). Anal. Calcd for $C_{51}H_{62}N_2O_{14}$ + H$_2$O: C, 64.82; H, 6.83; N, 2.96. Found: C, 64.77; H, 6.80; N, 2.95. HR electrospray *m*/*z*: calcd for $C_{51}H_{63}N_2O_{14}$, 927.4279; found, 927.4294.

6-Azidohexyl (4-*O*-benzyl-3,6-dideoxy-*arabino*-hexopyranosyl)(1→3)(2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-galactopyranosyl)(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (32). The alcohol **30** (75 mg, 0.072 mmol) was dissolved in 2:1 dimethyl sulfoxide/acetic anhydride (6 mL), and the mixture was stirred overnight under argon. The resulting yellow solution was concentrated to dryness, and the yellow solid was taken up in DMF (0.5 mL) and diluted with tetrahydrofuran (10 mL). The solution was then cooled to −78 °C and treated dropwise with 20 equiv of a 1 M L-selectride solution in THF (150 μL). The reaction mixture was allowed to warm to −20 °C over 20 min, the reaction was quenched with ethylenediamine (1 mL), and the reaction mixture was allowed to warm to room temperature. Silica gel was added to the reaction mixture, and the volatiles were removed under vaccum. The silica was slurried onto the top of a column, and the product was eluted with 4% methanol in dichloromethane to give **32** (61 mg, 81%) as an amorphous solid. [α]$_D$: +8.9 (*c* 0.45, CH$_3$OH). ^{1}H NMR (500 MHz, CD$_3$OD): δ 7.46−7.18 (m, 20H, Ar), 5.55 (s, 1H, O$_2$CHPh), 5.17 (d, 1H, J_{gem} = 12.1 Hz, OCH_2Ph), 4.74 (d, 1H, $J_{1,2}$ = 8.4 Hz, H1′), 4.71 (d, 1H, J_{gem} = 11.7 Hz, OCH_2Ph), 4.68 (d, 1H, J_{gem} = 11.7 Hz, OCH_2Ph), 4.61 (d, 1H, J_{gem} = 11.7 Hz, OCH_2Ph), 4.59 (s, 1H, H1″), 4.58 (d, 1H, J_{gem} = 11.6 Hz, OCH_2Ph), 4.43 (d, 1H, J_{gem} = 11.6 Hz, OCH_2Ph), 4.41 (d, 1H, $J_{1,2}$ = 8.1 Hz, H1), 4.30 (d, 1H, $J_{3,4}$ = 3.4 Hz, H4′), 4.14 (dd, 1H, J_{gem} = 12.4 Hz, $J_{5,6}$ = 1.4 Hz, H6a′), 4.10 (dd, 1H, $J_{2,3}$ = 8.6 Hz, H2′), 3.96 (dd, 1H, $J_{5,6}$ = 1.7 Hz, H6b′), 3.94 (dd, 1H, $J_{4,5} \approx J_{3,4}$ = 8.6 Hz, H4), 3.93 (dd, 1H, H3′), 3.86−3.78 (m, 3H, H6a, H6b, OCH_2-

CH_2), 3.81 (m, 1H, H2), 3.76 (dd, 1H, $J_{2,3a} \approx J_{2,3b} = 4.0$ Hz, H2″), 3.68 (dd, 1H, $J_{2,3} = 9.7$ Hz, H3), 3.51 (ddd, 1H, $J_{5,6} = 2.3$ Hz, $J_{5,6} = 4.6$ Hz, H5), 3.48−3.38 (m, 3H, OCH_2CH$_2$, H4″, H5″), 3.23 (t, 2H, $J_{vic} = 6.9$ Hz, CH_2N$_3$), 3.23 (s, 1H, H5′), 2.31 (ddd, 1H, $J_{gem} = 13.6$ Hz, $J_{3,4} = 3.8$ Hz, H3$_{eq}$″), 1.94 (s, 3H, CH_3CONH), 1.83 (s, 3H, CH_3CONH), 1.58−1.52 (m, 4H, OCH$_2$CH_2CH$_2$CH$_2$CH_2), 1.48 (ddd, 1H, $J_{3,4} = 10.4$ Hz, H3$_{ax}$″), 1.40 (m, 4H, OCH$_2$CH$_2$CH_2CH_2), 1.30 (d, 3H, $J_{5,6} = 5.8$ Hz, H6″). Anal. Calcd for $C_{56}H_{71}N_5O_{14} + 0.5$ H$_2$O: C, 64.23; H, 6.93; N, 6.69. Found: C, 64.15; H, 6.58; N, 6.42. HR electrospray *m*/*z*: calcd for $C_{56}H_{72}N_5O_{14}$, 1038.5075; found, 1038.5083.

Methyl (3,6-dideoxy-*arabino*-hexopyranosyl)(1→3)(2-acetamido-2-deoxy-*β*-D-galactopyranosyl)(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranoside (2). The trisaccharide **31** (55 mg) was hydrogenated for 16 h over 20% paladium hydroxide on carbon (10 mg) in methanol. After filtration, the product was dissolved in a minimal amount of methanol and allowed to crystallize in an atmosphere of ethanol. The fine crystals were collected, dissolved in water, and lyophilized to give **2** as a white solid (30 mg, 88%). $[\alpha]_D$: −26.9 (*c* 0.36, H$_2$O). ^{1}H NMR (600 MHz, D$_2$O): δ 4.70 (d, 1H, $J_{1,2} < 1$ Hz, H1″), 4.58 (d, 1H, $J_{1,2} = 8.4$ Hz, H1′), 4.44 (d, 1H, $J_{1,2} = 8.1$ Hz, H1), 4.13 (d, 1H, $J_{3,4} = 3.1$ Hz, H4′), 4.04 (dd, 1H, $J_{2,3} = 10.6$ Hz, H2′), 3.91 (dd, 1H, $J_{2,3ax} \approx J_{2,3eq} = 3.3$ Hz, H2″), 3.89 (dd, 1H, $J_{3,4} = 2.9$ Hz, H3′), 3.86 (dd, 1H, $J_{gem} = 12.1$ Hz, $J_{5,6} = 2.0$ Hz, H6b), 3.80 (dd, 1H, $J_{gem} = 11.7$ Hz, $J_{5,6} = 8.2$ Hz, H6b′), 3.77 (dd, 1H, $J_{5,6} = 7.3$ Hz, H6a′), 3.74 (dd, 1H, H5′), 3.71 (m, 2H, H2, H3), 3.67 (dd, 1H, $J_{5,6} = 5.5$ Hz, H6a), 3.63 (dd, 1H, $J_{3,4} \approx J_{4,5} = 8.0$ Hz, H4), 3.55 (ddd, 1H, $J_{3ax,4} = 11.5$ Hz, $J_{3eq,4} = 4.7$ Hz, $J_{4,5} = 9.3$ Hz, H4″), 3.53 (ddd, 1H, H5), 3.50 (s, 3H, OMe), 3.44 (dq, 1H, $J_{5,6} = 6.2$ Hz, H5″), 2.17 (ddd, 1H, $J_{gem} = 13.9$ Hz, H3b″), 2.06 (s, 3H, CH_3NHCO), 2.02 (s, 3H, CH_3NHCO), 1.66 (ddd, 1H, H3a″), 1.27 (d, 3H, H6″). ^{13}C NMR (600 MHz, D$_2$O): δ 18.2 (C6″), 23.1 (CH$_3$NHCO), 23.2 (CH$_3$NHCO), 37.5 (C3″), 52.4 (C2′), 55.9 (C2), 61.1 (C6′), 61.8 (C6′), 67.8 (C4″), 68. 5 (C2″), 68.8 (C4′), 73.7 (C3), 75.6 (C5), 76.0 (C5′), 76.5 (C5″), 79.9 (C3′), 80.3 (C4), 102.8 ($J_{C1-H1} = 161.81$ Hz, C1, *β*), 102.2 ($J_{C1-H1} = 163.18$ Hz, C1′, *β*), 103.5 ($J_{C1-H1} = 159.76$ Hz, C1″, *β*). HR electrospray *m*/*z*: calcd for $C_{23}H_{40}N_2O_{14}Na$, 591.2377; found, 591.2379.

6-Aminohexyl (3,6-dideoxy-*arabino*-hexopyranosyl)-(1→3)(2-acetamido-2-deoxy-*β*-D-galactopyranosyl)(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranoside (33). The protected trisaccharide **32** (30 mg) was dissolved in 3 mL of ethylenediamine under argon. Lithium ribbon (10 mg) was added, and the solution slowly turned deep blue. When the solution returned to a yellow color, the reaction was quenched with methanol, and the volatiles were removed under vacuum. The white solid obtained was dissolved in water, and the solution was brought to neutral pH by the addition of 5 M acetic acid, as monitored on pH paper (1−12). The solution was then applied to a Sep Pak C18 reverse-phase cartridge (Waters), washed with water, and the crude product was eluted with 50% methanol. Further purification by HPLC on C18 silica (water + 0.1% TFA/methanol) gave pure **33** (14 mg, 75% yield) as the trifluoroacetate salt. $[\alpha]_D$: −17.0 (*c* 0.27, H$_2$O). ^{1}H (600 MHz, D$_2$O): δ 4.70 (d, 1H, $J_{1,2} < 1$ Hz, H1″), 4.58 (d, 1H, $J_{1,2} = 8.4$ Hz, H1′), 4.49 (ABX, 1H, $J_{1,2} = 8.4$ Hz, H1), 4.13 (d, 1H, $J_{3,4} = 3.3$ Hz, H4′), 4.04 (dd, 1H, $J_{2,3} = 10.8$ Hz, H2′), 3.91−3.87 (m, 3H, H2″, H3′, OCH_2CH$_2$), 3.84 (dd, 1H, $J_{gem} = 12.1$ Hz, $J_{5,6} = 2.0$ Hz, H6a), 3.80 (dd, 1H, $J_{gem} = 11.7$ Hz, $J_{5,6} = 8.2$ Hz, H6a′), 3.76 (dd, 1H, $J_{5,6} = 3.9$ Hz, H6b′), 3.74 (dd, 1H, H5′), 3.71 (ABX, 2H, H2, H3), 3.65 (dd, 1H, $J_{5,6} = 5.7$ Hz, H6b), 3.63 (ABX, 1H, H4), 3.57 (dt, 1H, $J_{gem} = 10.1$ Hz, $J_{vic} = 6.4$ Hz, OCH_2CH$_2$), 3.55 (ddd, 1H, $J_{3ax,4} = 11.5$ Hz, $J_{3eq,4} = 4.8$ Hz, $J_{4,5} = 9.3$ Hz, H4″), 3.51 (ddd, 1H, $J_{4,5} = 7.7$ Hz, H5), 3.43 (dq, 1H, $J_{5,6} = 6.2$ Hz, H5″), 2.98 (t, 2H, $J_{vic} = 7.7$ Hz, CH$_2$N$_3$), 2.17 (ddd, 1H, $J_{gem} = 13.9$ Hz, H3$_{eq}$″), 2.06 (s, 3H, CH_3CONH), 2.20 (s, 3H, CH_3CONH), 1.65 (ddd, 1H, H3$_{ax}$″), 1.65 (m, 2H, CH$_2$CH_2CH$_2$NH$_3^+$), 1.55 (m, 2H, $J = 6.4$ Hz, CH$_2$CH_2CH$_2$O), 1.40−1.30 (m, 4H, CH$_2$CH_2CH_2CH$_2$), 1.27 (d, 3H, H6″). ^{13}C NMR (600 MHz, D$_2$O): δ 17.9 (C6″), 22.9 (*C*H$_3$NHCO), 23.0 (*C*H$_3$NHCO), 25.3, 25.97 (OCH$_2$CH$_2$*C*H$_2$, OCH$_2$CH$_2$CH$_2$*C*H$_2$), 27.41 (*C*H$_2$CH$_2$NH$_3$), 29.09 (OCH$_2$*C*H$_2$), 37.3 (C3″), 52.6 (C2′), 55.8 (C2), 61.9 (C6′), 67.7 (C4″), 68.5 (C2″), 68.8 (C4′), 73.5 (C3), 75.38 (C5), 75.9 (C5′), 76.9 (H5″), 79.8 (C3′), 80.2 (C4), 102.0 ($J_{C1-H1} = 162.6$ Hz, C1, *β*), 102.2 ($J_{C1-H1} = 162.3$ Hz, C1′, *β*), 103.4 ($J_{C1-H1} = 159.4$ Hz, C1″, *β*). HR electrospray *m*/*z*: calcd for $C_{28}H_{51}N_3O_{14}Na$, 676.3268; found, 676.3269.

6-(Fluoresceinylthioureido)hexyl (3,6-dideoxy-*arabino*-hexopyranosyl)(1→3)(2-acetamido-2-deoxy-*β*-D-galactopyranosyl)(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranoside (1). The trisaccharide **33** (10 mg) was dissolved in 1 mL of DMF/H$_2$O (1:1) containing sodium bicarbonate (20 mg). Fluorescein isothiocyanate (10 mg) was added, the reaction mixture was stirred for 1 h, the reaction was quenched with ethylenediamine (20 *μ*L), and the reaction mixture was concentrated to a yellow film. This film was taken up in water and purified by HPLC on C18 reverse-phase silica using a 10−50% acetonitrile gradient. The fractions were collected and lyophilized to give **1** (11 mg, 75%). $[\alpha]_D$: −12.7 (*c* 0.11, H$_2$O). ^{1}H NMR (600 MHz, CD$_3$OD): 8.12 (s, 1H, H4fl), 7.76 (br d, 1H, H6fl), 7.41 (d, 1H, $J = 8.2$ Hz, H7fl), 6.67−6.52 (m, 4H, H2′fl, H5′fl, H7′fl), 4.56 (d, 1H, $J_{1,2} = 0.8$ Hz, H1″), 4.51 (d, 1H, $J_{1,2} = 8.6$ Hz, H1′), 4.35 (d, 1H, $J_{1,2} = 8.4$ Hz, H1), 4.07 (dd, 1H, $J_{2,3} = 10.6$ Hz, H2′), 4.02 (d, 1H, $J_{3,4} = 3.1$ Hz, H4′), 3.88 (dd, $J_{vic} = 6.0$ Hz, $J_{gem} = 9.7$ Hz, OCH_2CH$_2$), 3.80 (dd, 1H, $J_{5,6a} = 2.0$ Hz, $J_{gem} = 12.0$ Hz, H6a), 3.78 (br t, 2H, $J_{2,3ax} \approx J_{2,3eq} = 3.4$ Hz, H2″), 3.76 (d, 1H, $J_{gem} = 11.4$ Hz, H6a′), 3.75 (dd, $J_{2,3} = 9.7$ Hz, H3′), 3.72 (dd, 1H, $J_{2,3} = 10.3$ Hz, H2), 3.67 (dd, 1H, $J_{5,6} = 4.4$ Hz, H6b′), 3.62 (dd, $J_{5,6} = 4.8$ Hz, H6b), 3.61−3.57 (m, 4H, H3, H5′, CH_2NHCS), 3.52 (dd, $J_{3,4} \approx J_{4,5} = 9.5$ Hz, H4), 3.48 (dd, 1H, $J_{vic} = 2.2$ Hz, CH$_2$CH_2O), 3.46 (ddd, $J_{3eq,4} = 4.4$ Hz, $J_{3ax,4} \approx J_{4,5} = 10.9$ Hz, H4″), 3.31 (ddd, 1H, H5), 3.27 (dq, 1H, $J_{5,6} = 6.2$ Hz, H5″), 2.11 (ddd, 1H, $J_{gem} = 13.5$ Hz, H3$_{eq}$″), 1.97 (s, 3H, CH_3CONH), 1.96 (s, 3H, CH_3-CONH), 1.69−1.63 (m, 2H, CH_2CH$_2$NHCS), 1.62−1.55 (m, 2H, CH$_2$CH_2CH$_2$O), 1.52 (ddd, 1H, H3$_{ax}$″), 1.48−1.37 (m, 4H, CH$_2$CH_2CH_2CH$_2$), 1.25 (d, 3H, H6″). HR electrospray *m*/*z*: calcd for $C_{49}H_{62}N_4O_{19}SNa$, 1065.3626; found, 1065.3627.

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