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Toward the automated solid-phase synthesis of oligoglucosamines: systematic evaluation of glycosyl phosphate and glycosyl trichloroacetimidate building blocks

Luis G. Melean, Kerry R. Love, Peter H. Seeberger*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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Dedicated to Professor Derek Horton on the occasion of his 70th birthday

Abstract

Glucosamines are common components of many biologically important oligosaccharides. Reported is a systematic evaluation of glucosamine phosphates and trichloroacetimidates as glycosylating agents for the efficient construction of β-(1→6) glucosamine linkages. A set of differentially protected glucosamine donors incorporating a host of amine protecting groups, including 2-phthaloyl, benzyloxycarbonyl (Z), trichloroethoxycarbonyl (Troc) and trichloroacetyl (TCA) protective groups, were prepared. Donors were initially evaluated for reactivity and protecting group compatibility in a solution-phase study with a model 6-hydroxyl galactose acceptor. Based on these results, glucosamine donor **10** was selected for the solution-phase synthesis of a β-(1→6)-glucosamine pentasaccharide. Finally, building block **10** proved well suited for use in the automated solid-phase synthesis of a repeating unit trisaccharide. An assessment of glucosamine phosphate donors as potential glycosylating agents for a variety of glucosamine linkages is also discussed.

Keywords: Glucosamines; Glycosyl phosphates; Automated solid-phase synthesis

1. Introduction

Oligosaccharides serve to mediate a host of biological processes including cell–cell adhesion, immune response, and parasitic infection.[1,2] Cell-surface carbohydrates often are highly specific for a pathogen or cell type, and the induction of an immune response against a unique carbohydrate antigen may allow for the creation of carbohydrate-based vaccines. Vaccines against bacteria and cancer based on carbohydrate antigens have spurred substantial interest in recent years.[3]

In Nature, 2-amino-2-deoxy glycosides are frequently encountered in glycoproteins and glycolipids.[4] Poly-*N*-succinyl-β-(1→6)-glucosamine (PNSG, Fig. 1), for example, is an in vivo-expressed surface polysaccharide in human *Staphylococcus aureus* infection.[5] Recently, active and passive immunization with PNSG was effective in protecting mice against metastatic kidney infection by *S. aureus*, making PNSG a potential vaccine for clinical use.[6] The isolation of PNSG from natural sources is a difficult task that yields a heterogeneous mixture of oligosaccharides. Synthetic polyglucosamine oligosaccharides would be important tools to determine the minimal length required to illicit a specific immune response and to provide the necessary substrates for biochemical and biophysical studies.

The coupling efficiency and relative ease in the preparation of 2-amino-2-deoxy glycosides is significantly lower than for other glycosides. Ideally, the construc-

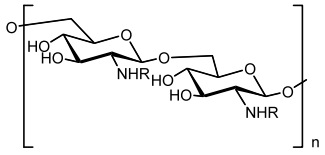

Figure 1. Structure of PNSG. R = acetyl or succinyl.

* Corresponding author. Fax: +1-617-2537929
E-mail address: seeberg@mit.edu (P.H. Seeberger).

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tion of polyglucosamine oligosaccharides, such as PSNG, could be simplified by rapid assembly in an automated fashion on solid support. Automated solid-phase oligosaccharide synthesis requires differentially protected building blocks that allow for the efficient and selective creation of each desired linkage. In this case, glucosamine building blocks would be added sequentially to a growing oligosaccharide chain, until completion of the oligomer of desired length. Stepwise synthesis of this kind can greatly reduce overall reaction times as longer oligomers can be assembled using the same donor created for shorter constructs. Although glucosamine building blocks have been utilized for solid-phase carbohydrate synthesis[7] and even automated synthesis,[8] the preparation of polyglucosamine sequences on solid support has not been reported to date. Here we report a systematic evaluation of differentially protected glycosyl phosphate and glycosyl trichloroacetimidate monosaccharide building blocks for the synthesis of oligosaccharides in solution, and by automated solid-phase synthesis.

2. Results and discussion

Glucosamine building blocks for the assembly of linear β-(1→6)-glucosamine antigens containing acetylated and succinylated amino groups must be equipped with: (a) two orthogonal, participating amine protecting groups to ensure the formation of trans β-(1→6) linkages; (b) a temporary protecting group for the 6-hydroxyl group that is stable to the glycosylation reactions but can be readily removed under mild conditions; and (c) stable, permanent protecting groups for the 3- and 4-hydroxyl groups to be removed only at the end of the synthesis.

In addition to these considerations, we were mindful that different protecting groups have a fundamental impact on the reactivity of glucosamine building blocks both as glycosylating agents and as glycosyl acceptors.[9,10] Fine-tuning the glucosamine building blocks to fulfill these requirements necessitated a systematic evaluation of glucosamine monosaccharides containing different anomeric leaving groups, as well as various combinations of hydroxyl and amine protecting groups (Fig. 2).

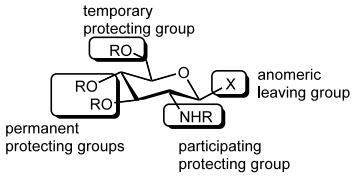


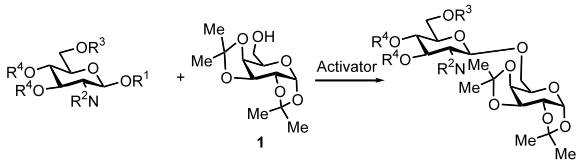
Figure 2. Glucosamine phosphate building block design considerations.

Two anomeric leaving groups were evaluated as they had successfully been used in previous solid-phase oligosaccharide syntheses: glycosyl trichloroacetimidates and glycosyl phosphates. Glycosyl trichloroacetimidates historically have served well in the formation of a host of glycosidic linkages in solution and on solid support.[11] More recently, glycosyl phosphates have proven useful building blocks in the preparation of a variety of glycosidic linkages in solution[12] and for solid-phase oligosaccharide assembly.[8,13] Several differentially protected glucosamine trichloroacetimidates and glucosamine phosphates were prepared using standard protecting group manipulations. These glucosamine building blocks were initially screened for their performance in couplings with 1,2:3,4-di-*O*-isopropylidene-D-galctose (**1**) as a model acceptor (Table 1).

The construction of 2-amino-2-deoxy β-glycosides typically relies on a 2-phthalimido group for the amino-protecting and C-2 participating group.[10] Consequently, our initial investigations focused on the synthesis and use of 2-phthalimido-containing donors. The 6-hydroxyl temporary protecting group was then chosen for orthogonality with the amino protecting group, since removal must be effected without the use of strong base. 6-*O*-Triisopropylsilyl (TIPS) protected glucosamine trichloroacetimidate 2 performed well in the solution coupling with **1** to fashion disaccharide **3** in 70% yield, but removal of the silyl ether proved too slow to be useful in automated synthesis. Installation of an acid-labile *p*-methoxybenzyl PMB ether to mask the 6-hydroxyl group (donor 4) was not useful; exposure to catalytic TMSOTf for donor activation resulted in a loss of the PMB ether. Protection using the recently developed 2-(azidomethyl)benzoate (AZMB)[14] or levulinate esters, which are both removed under neutral conditions via assisted cleavage reactions, proved successful and allowed for the use of acetate esters as permanent protecting groups on the 3- and 4-hydroxyl groups. Coupling of glucosamine imidate donors **6** and **8** with acceptor **1** procured the corresponding disaccharides **7** and **9** in similar yields.

While glycosyl phosphates have proven to be excellent glycosylating agents for the installation of a variety of glycosidic linkages,[12,15] no systematic study of differentially protected glycosyl phosphates for the formation of β-glucosamine glycosidic linkages had been undertaken. In order to address this challenge and to compare glycosyl phosphates to the corresponding glycosyl trichloracetimidate building blocks, we prepared glucosamine phosphate donors **10** and **12**. Based on previous experiments, a 6-*O*-levulinoyl group was selected for temporary protection and acetate and benzyl ether groups were employed as permanent protecting groups for evaluation the electronic effects of the protective groups on donor reactivity. Coupling of glycosyl phos-

Table 1
Summary of the glycosylation experiments involving different glucosamine building blocks



Glucosamine	R^1	R^2	R^3	R^4	Disaccharide	Coupling yield (%)
2	$C(NH)CCl_3$	Phth	TIPS	Bn	**3**	70
4	$C(NH)CCl_3$	Phth	PMB	Bn	**5**	decompos.
6	$C(NH)CCl_3$	Phth	AZMB	Ac	**7**	68
8	$C(NH)CCl_3$	Phth	Lev	Ac	**9**	65
10	$PO(OBu)_2$	Phth	Lev	Bn	**11**	85
12	$PO(OBu)_2$	Phth	Lev	Ac	**13**	83
14	$C(NH)CCl_3$	Z	Ac	Bn	**15**	88
16	$C(NH)CCl_3$	Z	Lev	Ac	**17**	90
18	$PO(OBu)_2$	Z	Lev	Bn	**19**	91
20	$PO(OBu)_2$	Z	Lev	Ac	**21**	81
22	$C(NH)CCl_3$	Troc	Ac	Bn	**23**	87
24	$C(NH)CCl_3$	TCA	Lev	Ac	**25**	88
26	$PO(OBu)_2$	TCA	Lev	Bn	**27**	50

phate donors **10** and **12** with galactose **1** furnished the desired disaccharides **11** and **13** in good yields of 85 and 83%, respectively.

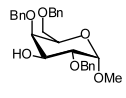
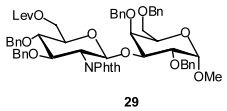
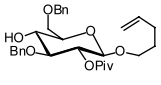
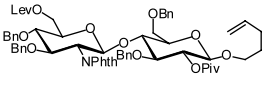
The limitations imposed by base lability of the phthalimido group for amine protection prompted us to study the use of other, more base-stable participating protecting groups. Benzyloxycarbonyl (Z) protected glucosamine trichloroacetimidates (**14**, **16**) and phosphates (**18**, **20**) resulted in acceptable coupling yields regardless of the protecting group pattern selected. Trichloroethoxycarbonyl (Troc) protected trichloroacetimidate **22** also yielded high levels of desired disaccharide **23**. Finally, *N*-trichloroacetate-protected glucosamine trichloroacetimidate **24** outperformed phosphate **26** due to electronically favorable oxazoline formation in the case of electron-rich donor **26**.[16]

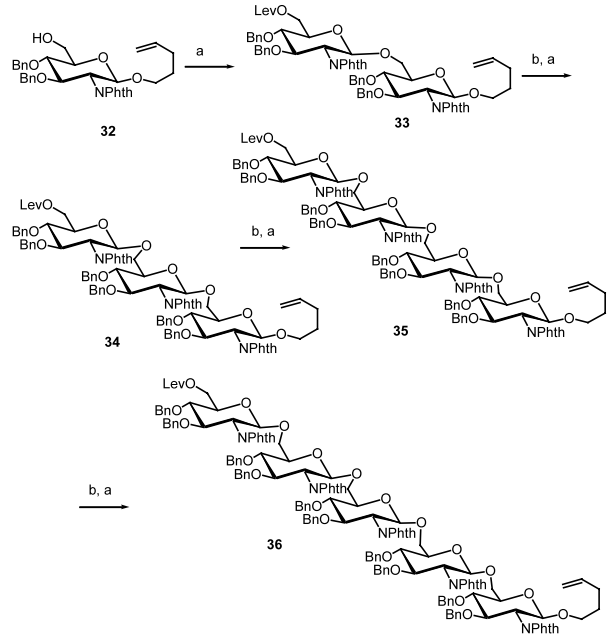
Additionally, we wanted to demonstrate the scope of glycosylations involving glucosamine phosphate building blocks. Phosphate **10** was successfully reacted with the 3-hydroxyl group of galactopyranoside **28** and the 4-hydroxyl group of glucopyranoside **30** to afford disaccharides **29** and **31** (Table 2).

Encouraged by the performance of differentially protected glucosamine phosphates in the formation of disaccharides, we conducted the solution-phase assembly of pentaglucoside **36**. Glycosyl phosphate **10** proved to be the highest yielding donor amenable to conditions for automated solid-phase synthesis. Coupling of glycosyl phosphate **10** with *n*-pentenyl glucosamine **32**, followed by removal of the 6-O levulinate group with hydrazine monohydrate[17] in a pyridine–AcOH solution furnished disaccharide **33** (Scheme 1). Glycosylation with donor **10** and subsequent deprotection of the 6-hydroxyl was repeated an additional 3 times to complete pentasaccharide **36** in a 33% overall yield. Solution phase studies indicated that coupling yields for the formation of β-(1→6) linkages are lower than those obtained for other glucosamine couplings.[8]

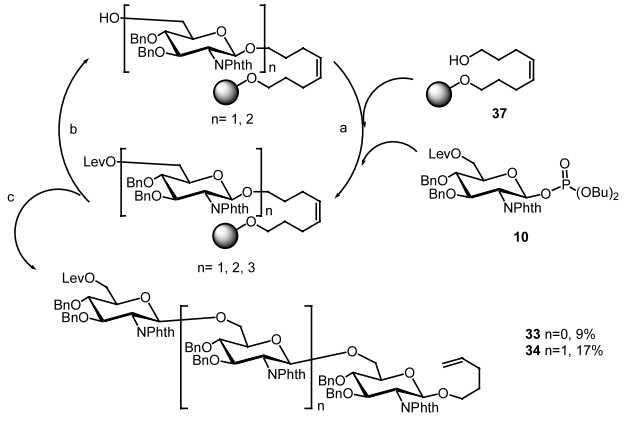
Based on our solution-phase results, the automated synthesis of polyglucosamine oligosaccharides was investigated. Octenediol-functionalized resin **37**[18] was used as the initial acceptor in the automated assembly of trisaccharide **34** (Scheme 2). Each monomer unit was incorporated via a coupling cycle employing five equivalents of donor **10** for each glycosylation step. Building block **10** was delivered to the reaction vessel and activated by stoichiometric TMSOTf at −15 °C. Each

Table 2
Scope of glycosylation reactions involving glucosamine glycosyl phosphates

Donor	Acceptor	Product	Yield
10			96%
	28	**29**	
10			71%
	30	**31**	



Scheme 1. Synthesis of pentasaccharide **36** in solution using phosphate donor **10**. (a) **10**, TMSOTf, CH_2Cl_2, -20 °C; (b) hydrazine, AcOH, Pyr.



Scheme 2. Automated synthesis of trisaccharide **34** using phosphate donor **10**. (a) TMSOTf, CH_2Cl_2, -15 °C; (b) NH_2NH_2, AcOH, pyr; (c) Grubbs' catalyst, ethylene, CH_2Cl_2.

30-minute glycosylation sequence was followed by extensive washing of the resin before removal of the levunilate esters was carried out as a double deprotection at ambient temperature with a solution of hydrazine monohydrate (0.5 M) in pyridine–AcOH (Table 3). Iteration of glycosylation and deprotection steps for incorporation of each monomer unit resulted in completion of the trisaccharide in 9 h. After completion of the synthesis, cleavage of the resin-bound products using Grubbs' catalyst under an atmosphere of ethylene afforded the fully protected trisaccharide **34** in 17% yield (74% per step over six reactions), along with disaccharide **31** (9%) resulting from incomplete glycosylation and deprotection steps (Schemes 3–14.

3. Conclusions

Glucosamine trichloroacetimidate and phosphate donors were evaluated for the construction of β-(1→6)-polyglucosamines. Glucosamine phosphates also demonstrated usefulness in glycosylation of other positions; both the 3-hydroxyl of a galactose acceptor and the 4-hydroxyl of a glucose acceptor were glycosylated in high yield. Phosphate donor **10** was selected for use in the solution-phase synthesis of a repeating unit pentasaccharide based on a good coupling yield with model acceptor **1** and possession of a protecting group scheme amenable to future automation. Protected pentasaccharide **36** was subsequently synthesized in a 33% overall yield. This solution-phase synthesis served as the basis for an automated solid-phase synthesis of a repeating unit trisaccharide. Again, phosphate **10** was used in a series of three coupling–deprotection cycles to afford trisaccharide **34** in a 17% yield in nine hours.

4. Experimental

General methods.—All chemicals were reagent grade and used as supplied unless otherwise noted. Dichloromethane (CH_2C1_2), tetrahydrofuran (THF), and toluene were purified and supplied in a J.T. Baker Cycle Tainer Solvent Delivery System. Pyridine, acetonitrile and triethylamine were refluxed over calcium hydride and distilled prior to use. Analytical thin-layer chromatography was performed on E. Merck Silica Gel 60 F_{254} plates (0.25 mm). Compounds were visualized by dipping the plates in cerium sulfate–ammonium molybdate solution, followed by heating. Liquid column chromatography was performed using forced flow of the indicated solvent on Silicycle silica 230–400 mesh (60 Å pore diameter). ^{1}H NMR spectra were obtained using a Bruker 400 spectrometer (400 MHz) or a Varian VXR-500 (500 MHz) spectrometer and are reported in parts per million (δ) relative to $CDCl_3$ (7.27 ppm) or CD_3OD (4.84 ppm). Coupling constants (J) are reported in Hertz. ^{13}C NMR spectra were obtained using a Bruker 400 NMR spectrometer (100 MHz) or a Varian VXR-500 (125 MHz) and are reported in δ relative to $CDCl_3$ (77.23 ppm) or CD_3OD (49.15 ppm). ^{31}P spectra were obtained using a Varian VXR-300 (120 MHz) or a Varian-300 (200 MHz) instrument and are reported in δ relative to H_3PO_4 (0.00 ppm) as an external reference. IR spectra were obtained on a Perkin–Elmer 1600 series FTIR spectrometer. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter using a sodium lamp (589 μm). MALDI-TOF mass spectrometry was performed on a PE Biosystems

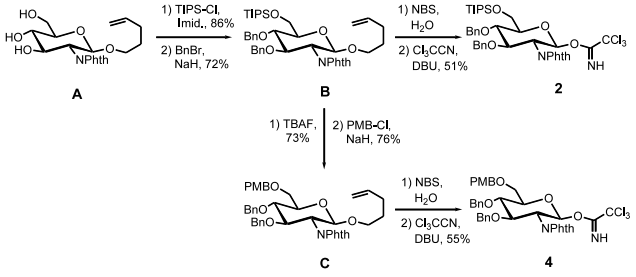
Table 3
Automated cycle for glycosylation and deprotection used with glucosamine phosphate donors

Step	Function	Reagent	Time (min)
1	Couple	5 equiv donor and 5 equiv TMSOTf	30
2	Wash	Dichloromethane	10
3	Couple	5 equiv donor and 5 equiv TMSOTf	30
4	Wash	Dichloromethane	10
5	Wash	Tetrahydrofuran	10
6	Deprotection	2×20 equiv hydrazine (3:2 pyridine–acetic acid)	80
7	Wash	0.2 M acetic acid in tetrahydrofuran	10
8	Wash	Tetrahydrofuran	10
9	Wash	Dichloromethane	10

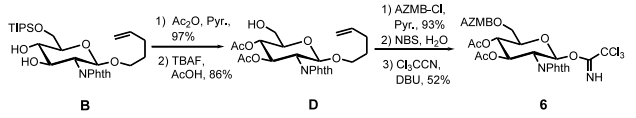
Voyager System 102 on a 2,5-dihydrobenzoic acid matrix. HPLC analysis was performed on a Waters Model 600E Multisolvent Delivery System.

n-*Pentenyl 3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-6*-O-*triisopropylsilyl-β*-D-*glucopyranoside* (**B**).—To a stirred solution of *n*-pentenyl glycoside **A** (2.84 g, 7.82 mmol) in dry DMF (80 mL) at 0 °C was added imidazole (0.55 g, 8.06 mmol) and triisoprophylchlorosilane (1.66 g, 8.06 mmol). The solution was slowly warmed to ambient temperature and stirred for 14 h. Water (100 mL) was added, the aqueous layer was extracted with ether (3×100 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (4:6 EtOAc–hexanes) to afford 3.56 g (86%) of *n*-pentenyl 2-deoxy-2-phthalimide-6-*O*-triisopropylsilane-β-D-glucopyranoside as a white solid. $[\alpha]_D$ −35.2° (*c* 1.01, CH_2Cl_2); IR (thin film): 3447, 1776, 1716, 1392, 1069 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86–7.75 (m, 2H), 7.74–7.64 (m, 2H), 5.63–5.49 (m, 1H), 5.18 (d, *J* 8.4 Hz, 1H), 4.79–4.65 (m, 2H), 4.39–4.28 (m, 1H) 4.09 (dd, *J* 4.9, 10.0 Hz, 1H), 4.00–3.92 (m, 2H), 3.77 (td, *J* 6.3, 9.7 Hz, 1H), 3.66–3.58 (m, 1H), 3.58–3.44 (m, 1H), 3.40 (td, *J* 6.8, 9.7 Hz, 1H), 3.27–3.20 (m, 1H), 1.91–1.77 (m, 2H), 1.58–1.36 (m, 2H), 1.22–0.91 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 137.9, 134.2, 131.8, 123.5, 114.8, 98.3, 75.6, 73.8, 71.7, 68.9, 65.8, 56.3, 30.0, 28.6, 17.5, 12.3; ESI FT-MS: m/z $(m + Na)^+$ calcd 556.2707, obsd 556.2693.

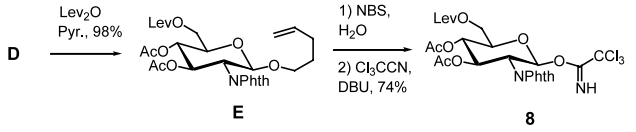
n-Pentenyl 2-deoxy-2-phthalimido-6-*O*-triisopropylsilane-β-D-glucopyranoside (4.32 g, 8.15 mmol) was azeotroped with toluene (3×10 mL), dried under vacuum for 1 h, dissolved in DMF (40 mL), and cooled to 0 °C. Benzyl bromide (3.34 g, 19.6 mmol) was passed through basic aluminum oxide and added to the reaction mixture. After 30 min, sodium hydride (782 mg, 19.6 mmol, 60% dispersion in mineral oil) was added to the reaction mixture in 4 batches over a period of 1 h. The solution was stirred for 12 h at ambient temperature, then quenched by the dropwise addition of water (100 mL). The aqueous layer was extracted with ether (3×100 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and



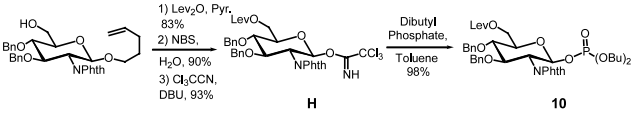
Scheme 3. Synthesis of trichloroacetimidate donors **2** and **4**.



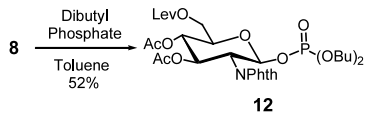
Scheme 4. Synthesis of glucosamine donors **6**.



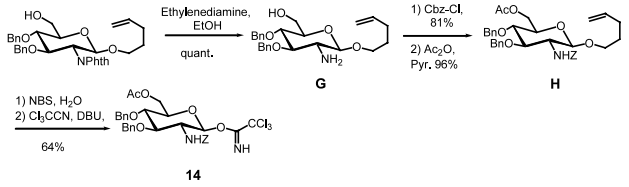
Scheme 5. Synthesis of trichloroacetimidate **8**.



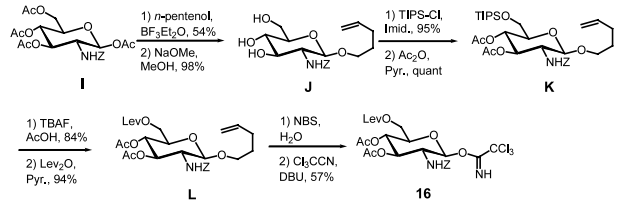
Scheme 6. Synthesis of glucosamine phosphate donor **10**.



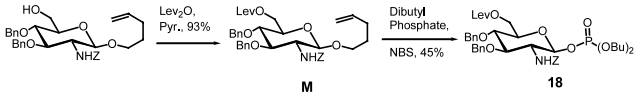
Scheme 7. Synthesis of glucosamine phosphate donor **12**.



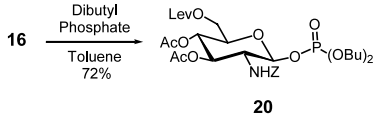
Scheme 8. Synthesis of trichloroacetimidate donor **14**.



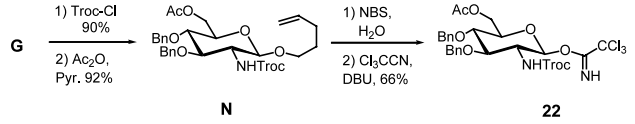
Scheme 9. Synthesis of glucosamine donor **16**.



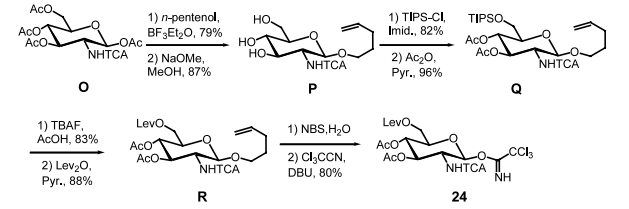
Scheme 10. Synthesis of glucosamine phosphate **18**.



Scheme 11. Synthesis of glucosamine phosphate **20**.



Scheme 12. Synthesis of glucosamine trichloroacetimidate donor **22**.



Scheme 13. Synthesis of trichloroacetimidate donor **24**.

concentrated in vacuo. Purification by flash silica gel chromatography (2:8 EtOAc–hexanes), afforded 4.17 g (72%) of **B** as a clear oil. $[\alpha]_D$ +17.5° (*c* 1.06, CH_2C1_2); IR (thin film): 1777, 1715, 1388, 1071 cm^{-1}; ^1H NMR (500 MHz, $CDC1_3$) δ 7.84–7.60 (m, 4H), 7.40–7.24 (m, 5H), 7.04–7.00 (m, 2H), 6.93–6.82 (m, 3H), 5.64–5.54 (m, 1H), 5.12 (d, *J* 8.5 Hz, 1H), 4.89 (d, *J* 11.0 Hz, 1H), 4.84–4.80 (m, 2H), 4.79–4.69 (m, 2H), 4.48 (d, *J* 12.2 Hz, 1H), 4.35 (dd, *J* 8.9, 10.7 Hz, 1H), 4.06–3.98 (m, 2H), 3.83 (dd, *J* 9.2, 9.5 Hz, 1H), 3.74 (td, *J* 6.4, 9.8 Hz, 1H), 3.52–3.46 (m, 1H), 3.38 (td, *J* 7.3, 9.7 Hz, 1H), 1.88–1.78 (m, 2H), 1.55–1.41 (m, 2H), 1.23–0.94 (m, 21H); ^{13}C NMR (125 MHz, $CDC1_3$) δ 138.5, 138.3, 138.2, 133.9, 128.7, 128.6, 128.2, 128.1, 128.9, 127.5, 123.5, 123.3, 114.7, 98.0, 79.6, 79.4, 76.2, 75.2, 75.0, 68.4, 62.5, 56.2, 30.1, 28.7, 18.2, 12.2; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 736.3645, obsd 736.3617.

*3,4-Di-*O*-benzyl-2-deoxy-2-phthalimido-6-*O*-triisopropylsilyl-β-*D*-glucopyranosyl trichloroacetimidate* (**2**).—To a stirred solution of **B** (411 mg, 0.57 mmol) in CH_3CN (5 mL) and H_2O (0.50 mL) was added NBS (307 mg, 1.73 mmol). The reaction mixture was shielded from light and stirred, diluted with ether (50 mL), and extracted with satd $Na_2S_2O_3$ (5 × 10 mL). The aqueous layer was extracted with ether (50 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2C1_2 (2.0 mL). After cooling to 0 °C, trichloroacetonitrile (0.68 g, 4.69 mmol) and DBU (14.0 mg, 94.0 μmol) were added, and the reaction mixture was stirred for 2 h. The solution was concentrated in vacuo and purified by flash silica gel chromatography (3:7 EtOAc–hexanes) to afford 233 mg (51%) of **2** as a clear oil. $[\alpha]_D$ +55.1° (*c* 0.87, CH_2Cl_2); IR (thin film): 1779, 1717, 1387, 1054, 2942 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* 4.6 Hz, 1H), 7.78–7.45 (m, 4H), 7.38–7.19 (m, 5H), 6.98–6.89 (m, 2H), 6.85–6.68 (m, 3H), 6.36 (d, *J* 8.6 Hz, 1H), 4.81 (d, *J* 4.1 Hz, 2H), 4.70 (d, *J* 12.3 Hz, 1H), 4.40 (d, *J* 11.7 Hz, 1H), 4.38 (d, *J* 10.6 Hz, 1H), 4.31 (dd, *J* 8.6, 10.7 Hz, 1H), 4.04–3.97 (m, 2H), 3.92 (dd, *J* 8.9, 9.4 Hz, 1H), 3.58 (d, *J* 9.7 Hz, 1H), 1.15–0.84 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 138.4, 138.1, 134.0, 131.6, 128.8, 128.7, 128.2, 128.1, 128.0, 127.5, 123.4, 93.8, 90.7, 78.7, 77.4, 76.7, 75.2, 75.1, 61.9, 55.2, 18.1, 12.1; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 811.2115, obsd 811.2147.

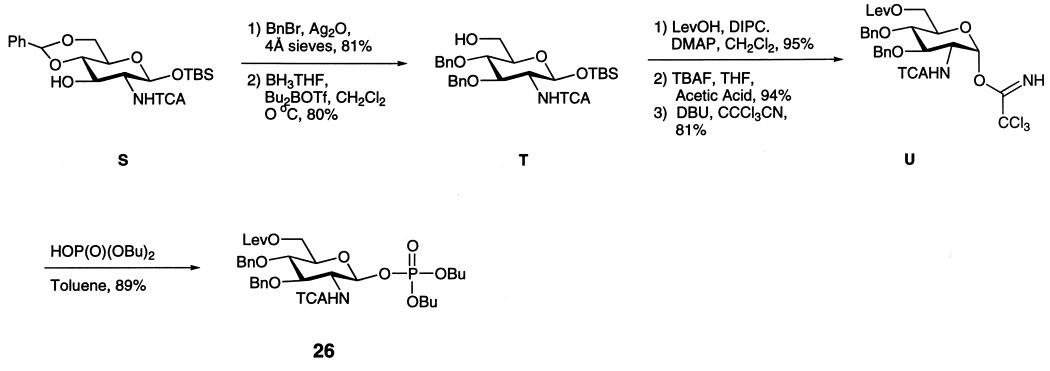
n-*Pentenyl 3,4-di-*O*-benzyl-2-deoxy-6-*O*-(4′-methoxybenzyl)-2-phthalimido-β-*D*-glucopyranoside* (**C**).—To a stirred solution of **B** (0.97 g, 1.36 mmol) in THF (20 mL) was added AcOH (61 μL, 1.02 mmol) and TBAF (2 mL, 2 mmol, 1 M in THF). After 12 h, the reaction was quenched by the addition of satd $NaHCO_3$ (50 mL), and the aqueous layer was extracted with ether (3 × 100 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (3:7 EtOAc–hexanes) afforded 570 mg (73%) of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside as a white solid. $[\alpha]_D$ +27.5° (*c* 0.56, CH_2C1_2); IR (thin film): 3475, 1775, 1713, 1390, 1076 cm^{-1}; ^1H NMR (500 MHz, $CDC1_3$) δ 7.85–7.57 (m, 4H), 7.40–7.28 (m, 5H), 7.04–6.92 (m, 2H), 6.92–6.83 (m, 3H), 5.59–5.50 (m, 1H), 5.17 (d, *J*

8.5 Hz, 1H), 4.90 (d, *J* 11.0 Hz, 1H), 4.82 (d, *J* 11.9 Hz, 1H), 4.76–4.73 (m, 2H), 4.70 (dd, *J* 8.5, 10.7 Hz, 1H), 4.13 (dd, *J* 8.2, 10.7 Hz, 1H) 3.94 (ddd, *J* 2.8, 4.5, 11.9 Hz, 1H), 3.82–3.71 (m, 3H), 3.56 (ddd, *J* 2.4, 4.3, 9.8 Hz, 1H), 3.39 (ddd, *J* 6.4, 7.0, 13.4 Hz, 1H), 1.96 (dd, *J* 5.5, 7.9 Hz, 1H), 1.89–1.75 (m, 2H), 1.56–1.39 (m, 2H); ^{13}C NMR (125 MHz, $CDC1_3$) δ 138.1, 138.0, 137.8, 133.9, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.5, 123.5, 114.8, 98.4, 79.5, 79.2, 77.43, 75.3, 75.2, 74.9, 69.1, 61.9, 56.1, 29.9, 28.6; ESI FT-MS: m/z $(M + Na)^+$ calcd 580.2311, obsd 580.2316.

n-Pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (5.32 g, 9.55 mmol) was azeotroped with toluene (3 × 10 mL), dried under vacuum for 1 h, and dissolved in DMF (30 mL). The solution was cooled to 0 °C, sodium hydride (476 mg, 12.4 mmol, 60% dispersion in mineral oil) was added, and the reaction mixture was stirred for 1 h. After addition of PMB-Cl (2.23 g, 14.3 mmol), the solution was warmed to 80 °C and stirred for 14 h. The reaction was cooled to ambient temperature and quenched by the dropwise addition of H_2O (100 mL). The aqueous layer was extracted with ether (3 × 100 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by flash silica gel chromatography (2:8 EtOA–hexanes) afforded 4.85 g (76%) of **C** as a clear oil. $[\alpha]_D$ + 83.5° (*c* 1.00, CH_2C1_2); IR (thin film): 1777, 1716, 1387, 1056 cm^{-1}; ^{1}H NMR (500 MHz, $CDC1_3$) δ 7.85–7.58 (m, 4H), 7.37–7.25 (m, 4H), 7.23–7.19 (m, 2H), 7.04–6.99 (m, 2H), 6.93–6.83 (m, 3H), 5.62–5.51 (m, 1H), 5.12 (d, *J* 8.5 Hz, 1H), 4.83 (d, *J* 11.0 Hz, 1H), 4.80 (d, *J* 13.1 Hz, 1H), 4.76–4.68 (m, 2H), 4.64 (d, *J* 11.9 Hz, 1H), 4.60 (d, *J* 11.0 Hz, 1H), 4.52 (d, *J* 11.9 Hz, 1H), 4.45 (d, *J* 11.9 Hz, 1H), 4.34 (dd, *J* 8.5, 10.7 Hz, 1H), 4.18 (dd, *J* 8.5, 10.7 Hz, 1H), 3.80 (s, 3H), 3.78–3.72 (m, 2H), 3.64 (td, *J* 3.7, 9.8 Hz, 1H), 3.39 (td, *J* 6.1, 9.8 Hz, 1H), 1.90–1.78 (m, 2H), 1.56–1.40 (m, 2H); ^{13}C NMR (125 MHz, $CDC1_3$) δ 163.8, 159.4, 138.1, 137.9, 133.9, 130.3, 129.8, 128.6, 128.2, 128.1, 128.0, 127.9, 127.5, 123.4, 114.8, 113.9, 98.4, 79.4, 79.4, 77.4, 75.1, 74.9, 73.3, 68.9, 68.3, 56.1, 55.4, 29.9, 28.6; ESI FT-MS: m/z $(M + Na)^+$ calcd 700.2886, obsd $(M - (n\text{-pentenyl}) + Na)^+$ 632.2224.

3,4-Di-O-benzyl-2-deoxy-6-O-(4′-methoxybenzyl)-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (**4**).—To a stirred solution of **C** (572 mg, 0.94 mmo1) in CH_3CN (2 mL) and H_2O (0.25 mL) was added NBS (502 mg, 2.82 mmol). After stirring for 14 h shielded from light, the solution was diluted with ether (10 mL) and extracted with satd $Na_2S_2O_3$ (5 × 10 mL). The aqueous layer was extracted with ether (100 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was azeotroped with toluene (3 × 3 mL), dried under vacuum for 2 h, and dissolved in CH_2Cl_2 (2 mL). After cooling to 0 °C, trichloroacetonitrile (0.714 g, 4.97 mmol) and DBU (43 mg, 0.28 mmol) were added, and the reaction mixture was stirred for 2 h. The solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (3:7 EtOAc–hexanes) to afford 388 mg (55%) of **4** as a clear oil. $[\alpha]_D$ + 66.0° (*c* 1.04, CH_2Cl_2); IR (thin film): 3446, 1773, 1712, 1389, 1050 cm^{-1}; ^{1}H NMR (500 MHz, $CDC1_3$) δ 8.55 (s, 1H), 7.75–7.62 (m, 4H), 7.38–7.26 (m, 5H), 7.24–7.18 (m, 2H), 7.05–6.92 (m, 2H), 6.92–6.82 (m, 5H), 6.44–6.39 (m, 1H), 4.84 (d, *J* 10.7 Hz, 1H), 4.81 (d, *J* 12.2 Hz, 1H), 4.66 (d, *J* 11.9 Hz, 1H), 4.63 (d, *J* 0.7 Hz, 1H), 4.52 (d, *J* 11.9 Hz, 1H), 4.50–4.42 (m, 2H), 3.96–3.88 (m, 1H), 3.86–3.80 (m, 1H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDC1_3$) δ 161.0, 159.4, 138.1, 134.0, 131.6, 130.2, 129.9, 128.6, 128.3, 128.1, 128.0, 127.6, 123.5, 114.0, 94.3, 90.6, 79.2, 79.1, 76.2, 75.2, 75.0, 73.3, 67.8, 55.4, 55.0; ESI FT-MS: m/z $(M + Na)^+$ calcd 775.1356, obsd 775.1348.

n-*Pentenyl 3,4-di-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside* (**D**).—To a stirred solution of **B** (2.60 g, 4.88 mmol) in CH_2Cl_2 (30 mL) and pyridine (10 mL) was added DMAP (120 mg, 0.98 mmol) and Ac_2O (1.49 g, 14.6 mmol). After 2 h, the solution was diluted with CH_2Cl_2 (70 mL) and washed with HCl (10% aq solution, 3 × 100 mL), H_2O (1 × 100 mL), brine (1 × 50 mL), dried over Na_2SO_4, filtered, and concentrated in



Scheme 14. Synthesis of phosphate donor **26**.

vacuo. Purification by flash silica gel chromatography (2:3 EtOAc–hexanes) yielded 3.04 g (97%) of *n*-pentenyl 3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-6-*O*-triisopropylsilyl-β-D-glucopyranoside as a white solid. $[\alpha]_D$ +30.6° (*c* 1.02, CH_2C1_2); IR (thin film): 1752, 1719, 1387, 1235, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.89–7.80 (m, 2H), 7.77–7.69 (m, 2H), 5.78 (dd, *J* 9.1, 10.7 Hz, 1H), 5.67–5.51 (m, 1H), 5.32 (d, *J* 8.5 Hz, 1H), 5.12 (dd, *J* 9.2, 9.9 Hz, 1H), 4.80–4.69 (m, 2H), 4.27 (dd, *J* 8.5, 10.7 Hz, 1H), 3.86–3.82 (m, 2H), 3.79 (td, *J* 6.3, 9.7 Hz, 1H), 3.70 (td, *J* 3.5, 10.1 Hz, 1H), 3.44 (td, *J* 6.7, 9.7 Hz, 1H), 2.01 (s, 3H), 1.86 (s, 3H), 1.87–1.83 (m, 2H), 1.59–1.42 (m, 2H), 1.14–1.01 (m, 21H); ^{13}C NMR (125 MHz, $CDC1_3$) δ 170.6, 169.6, 137.9, 134.6, 131.6, 123.9, 114.9, 98.0, 77.4, 75.1, 71.4, 69.8, 69.0, 62.9, 54.0, 30.1, 28.7, 20.9, 20.7, 18.1, 11.9; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 640.2918, obsd 640.2904.

To a stirred solution of *n*-pentenyl 3,4-di-*O*-acetyl-2-deoxy-2-phthalimido-6-*O*-triisopropylsilyl-β-D-glucopyranoside (3.00 g, 4.86 mmol) in THF (50 mL) was added AcOH (128 μL, 2.14 mmol) and TBAF (4.9 mL, 4.9 mmol, 1 M in THF). After 12 h, satd $NaHCO_3$ (50 mL) was added, and the aqueous layer was extracted with ether (3 × 100 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (40% EtOAc/hexanes) afforded 1.93 g (86%) of **D** as a white solid. $[\alpha]_D$ −12.8° (*c* 0.98, CH_2C1_2); IR (thin film): 3479, 1777, 1716, 1388, 1230 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.91–7.82 (m, 2H), 7.79–7.70 (m, 2H), 5.65 (dd, *J* 8.7, 10.8 Hz, 1H), 5.62–5.51 (m, 1H), 5.35 (d, *J* 8.5 Hz, 1H), 4.79–4.67 (m, 2H), 4.52 (dd, *J* 7.9, 12.1 Hz, 1H), 4.38 (dd, *J* 2.0, 12.1 Hz, 1H), 4.22 (dd, *J* 8.5, 10.8 Hz, 1H), 3.88–3.79 (m, 1H), 3.74 (ddd, *J* 2.2, 4.2, 9.9 Hz, 1H), 3.71–3.62 (m, 1H), 3.50–3.40 (m, 1H), 3.22 (d, *J* 5.2 Hz, 1H), 2.19 (s, 3H), 1.92 (s, 3H), 1.91–1.78 (m, 2H), 1.64–1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.5, 137.8, 134.5, 131.6, 114.9, 98.3, 77.4, 74.2, 73.4, 69.8, 69.4, 54.8, 29.9, 28.6, 21.1, 20.7; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd, 484.1583, obsd 484.1559.

3,4-Di-O-acetyl-6-O-(2′-(azidomethyl)benzoyl)-2-deoxy-2-phthalimido-α,β-D-glucopyranosyl trichoroacetimidate (**6**).—To a stirred solution of **D** (1.70 g, 3.68 mmol) in dry CH_2Cl_2 (40 mL) was added DMAP (494 mg, 4.05 mmol) and 2-(azidomethyl)benzoyl chloride (0.79 g, 4.05 mmol). After 5 min, the reaction mixture was diluted with CH_2Cl_2 (60 mL), washed with satd $NaHCO_3$, H_2O, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (3:7 EtOAc–hexanes) yielded 2.11 g (93%) of *n*-pentenyl 3,4-di-*O*-acetyl-6-*O*-(2′-(azidomethyl)benzoyl)-2-deoxy-2-phthalimido-(β-D-glucopyranoside as a yellow solid. $[\alpha]_D$ −5.96° (*c* 0.13, CH_2Cl_2); IR (thin film): 2103, 1777, 1746, 1717, 1388 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* 1.2, 7.9 Hz, 1H), 7.91–7.84 (m, 2H), 7.80–7.71 (m, 2H), 7.62–7.55 (m, 1H), 7.49 (d, *J* 7.0 Hz, 1H), 7.45–7.30 (m, 1H), 5.99 (dd, *J* 9.2, 10.7 Hz, 1H), 5.68–5.54 (m, 1H), 5.44 (d, *J* 8.4 Hz, 2H), 4.86–4.72 (m, 3H), 4.68 (d, *J* 14.4 Hz, 1H), 4.40 (dd, *J* 8.6, 10.5 Hz, 1H), 4.38 (dd, *J* 4.6, 7.8 Hz, 1H), 4.24 (dd, *J* 2.6, 12.2 Hz, 1H), 4.01 (ddd, *J* 2.7, 4.5, 10.1 Hz, 1H), 3.87 (td, *J* 6.2, 9.7 Hz, 1H), 3.50 (td, *J* 6.8, 9.7 Hz, 1H), 2.09 (s, 3H), 1.97–1.85 (m, 2H), 1.82 (s, 3H), 1.67–1.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.4, 165.2, 138.0, 137.8, 134.6, 133.5, 131.3, 130.2, 128.6, 128.2, 127.8, 123.8, 115.0, 98.4, 72.1, 70.8, 69.9, 69.6, 62.4, 54.9, 53.1, 30.0, 28.6, 21.0, 20.6; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 643.2110, obsd 643.2014.

To a stirred solution of *n*-pentenyl 3,4-di-*O*-acetyl-6-*O*-(2′-(azidomethyl)benzoyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (2.05 g, 3.31 mmol) in CH_3CN (30 mL) and H_2O (0.3 mL) was added NBS (1.17 g, 6.62 mmol). After 14 h shielded from light, the reaction was diluted with ether (50 mL) and washed with satd $Na_2S_2O_3$ (5 × 50 mL). The aqueous layers were combined and extracted with ether (50 mL), and the combined organic layers were washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was azeotroped with toluene (3 × 10 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (20 mL). After cooling to 0 °C, trichloroacetonitrile (5.08 g, 35.0 mmol) and DBU (107 mg, 0.71 mmol) were added, and the reaction mixture was stirred for 2 h. The solution was concentrated in vacuo and purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to yield 1.23 g (52%, α:β = 1:10) of **6** as a yellow solid. IR (thin film): 3322, 2104, 1780, 1721, 1386 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.64 (s, 0.1H), 8.09 (dd, *J* 1.1, 7.8 Hz, 0.1H), 7.94 (dd, *J* 1.1, 7.8 Hz, 1H), 7.89–7.82 (m, 2.2H), 7.78–7.66 (m, 2.2H), 7.62–7.54 (m, 1.1H), 7.53–7.46 (m, 1.1H), 7.45–7.39 (m, 1H), 7.38–7.34 (m, 0.2H), 6.71 (d, *J* 8.9 Hz, 1H), 6.50 (d, *J* 3.7 Hz, 0.1H), 6.19 (dd, *J* 9.2, 10.7 Hz, 0.1H), 6.12 (dd, *J* 9.2, 10.7 Hz, 1H), 5.56 (dd, *J* 9.6, 9.4 Hz, 1H), 5.48 (dt, *J* 3.0, 9.9 Hz, 0.1H), 4.88 (dd, *J* 3.7, 11.5 Hz, 0.1H), 4.82 (d, *J* 14.3 Hz, 1.1H), 4.74 (d, *J* 8.9 Hz, 1.1H), 4.67 (d, *J* 14.3 Hz, 1.1H), 4.48–4.37 (m, 1.1H), 4.31–4.12 (m, 2.2H), 2.14 (s, 0.3H), 2.09 (s, 3H), 1.99 (s, 0.3H), 1.84 (s, 3H); ^{13}C NMR (125 MHz, $CDC1_3$) δ 170.9, 170.3, 165.1, 160.8, 138.0, 134.7, 134.6, 133.6, 131.5, 131.4, 130.3, 128.6, 127.6, 123.9, 93.8, 73.1, 70.4, 69.2, 61.9, 54.9, 53.9, 53.1, 21.0, 20.6; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 718.0487, obsd 718.0478.

n-*Pentenyl 3,4-di*-O-*acetyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β-D-glucopyranoside* (**E**).—A solution of **D** (2.36 g, 5.12 mmol) in CH_2Cl_2 (40 mL) and pyridine (10 mL) was treated with DMAP (63 mg; 0.51 mmol) and levulinic anhydride (1.64 g, 7.68 mmol). The solution

was stirred for 2 h in the dark, then diluted with CH_2Cl_2 (60 mL) and washed with HCl (10% aq solution, 3×100 mL), H_2O (1×100 mL), brine (1×50 mL), and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (4:6 EtOAc–hexanes) to afford 2.80 g (98%) of **E** as a white solid. $[\alpha]_D$ +19.4° (*c* 1.03, CH_2Cl_2); IR (thin film): 1748, 1717, 1388, 1225 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93–7.82 (m, 2H), 7.81–7.69 (m, 2H), 5.81 (dd, *J* 9.5, 10.4 Hz, 1H), 5.66–5.51 (m, 1H), 5.37 (d, *J* 8.5 Hz, 1H), 5.20 (dd, *J* 9.6, 9.7 Hz, 1H), 4.82–4.69 (m, 2H), 4.37–4.27 (m, 2H), 4.20 (d, *J* 12.2 Hz, 1H), 3.92–3.77 (m, 2H), 3.51–3.39 (m, 1H), 2.86–2.61 (m, 2H), 2.60–2.40 (m, 2H), 2.16 (s, 3H), 2.11 (s, 3H), 1.92 (s, 3H), 1.90–1.79 (m, 2H), 1.58–1.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 171.5, 171.0, 170.7, 137.8, 134.5, 123.8, 115.0, 98.3, 72.1, 70.6, 69.5, 69.2, 62.2, 54.9, 37.9, 30.0, 29.8, 28.7, 28.6, 28.0, 21.0, 20.7; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 582.1952, obsd 582.1927.

3,4-Di-O-*acetyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranosyl trichloroacetimidate* (**8**).—A solution of **E** (2.86 g, 5.12 mmol) in CH_3CN (50 mL) and H_2O (5.0 mL) was treated with NBS (1.82 g, 10.2 mmol). After stirring for 13 h in the dark, the solution was diluted with ether (100 mL) and washed with satd $Na_2S_2O_3$ (5×100 mL). The aqueous layer was extracted with ether (100 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford 2.01 g (80%) of the crude lactol as a yellow oil. The crude product (2.00 g, 4.07 mmol) was azeotroped with toluene (3×10 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (40 mL). After cooling to 0 °C, trichloroacetonitrile (5.80 g, 40.7 mmol) and DBU (44 mg, 0.41 mmol) were added, and the reaction mixture was stirred for 2 h. The solution was concentrated in vacuo and purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to afford 1.93 g (74%, $\alpha:\beta = 3:7$) of **8** as a clear oil. IR (thin film): 1748, 1718, 1386, 1225 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.86–7.81 (m, 2H), 7.76–7.68 (m, 2H), 6.75 (d, *J* 8.9 Hz, 0.7H), 6.71 (d, *J* 8.9 Hz, 0.3H), 5.95 (dd, *J* 9.2, 10.7 Hz, 0.3H), 5.93 (dd, *J* 9.2, 10.4 Hz, 0.7H), 5.30 (dd, *J* 9.2, 10.1 Hz, 1H), 4.62 (dd, *J* 9.2, 10.7 Hz, 1H), 4.39 (dd, *J* 4.6, 12.2 Hz, 0.3H), 4.38 (dd, *J* 4.3, 12.5 Hz, 0.7H), 4.22 (dd, *J* 2.1, 12.5 Hz, 0.7H), 4.21 (dd, *J* 2.4, 12.2 Hz, 0.3H), 4.08 (ddd, *J* 2.1, 4.3, 10.4 Hz, 1H), 2.83–2.64 (m, 2H), 2.59–2.45 (m, 2H), 2.14 (s, 2.1H), 2.13 (s, 0.9H), 2.11 (s, 2.1H), 2.09 (s, 0.9H), 1.98 (s, 0.9H), 1.94 (s, 2.1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 171.5, 170.9, 160.7, 134.6, 131.4, 123.9, 93.8, 73.2, 73.0, 70.3, 68.6, 68.5, 61.7, 53.9, 53.8, 37.9, 28.0, 21.1, 20.8; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 657.0422, obsd 657.0403.

3,4-Di-O-*benzyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranosyl trichloroacetimidate* (**F**).—To a stirred solution of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (2.34 g, 4.21 mmol) in CH_2Cl_2 (30 mL) and pyridine (5 mL) was added DMAP (51 mg, 0.42 mmol) and levulinic anhydride (901 mg, 4.21 mmol). After 2 h shielded from light, the solution was diluted with CH_2Cl_2 (70 mL) and washed with HCl (10% aq solution, 3×100 mL), H_2O (1×100 mL), brine (1×50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (1:4 EtOAc–hexanes) yielded 2.29 g (83%) of the *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-6-*O*-levulinyl-2-phthalimido-β-D-glucopyranoside as a clear oil. $[\alpha]_D$ +83.5° (*c* 1.00, CH_2Cl_2); IR (thin film): 1777, 1716, 1387, 1056 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.86–7.55 (m, 4H), 7.41–7.19 (m, 5H), 7.04–6.99 (m, 2H), 6.93–6.83 (m, 3H), 5.60–5.50 (m, 1H), 5.14 (d, *J* 8.6 Hz, 1H), 4.91 (d, *J* 10.7 Hz, 1H), 4.83 (d, *J* 12.2 Hz, 1H), 4.76–4.66 (m, 3H), 4.64 (d, *J* 10.7 Hz, 1H), 4.47 (d, *J* 12.2 Hz, 1H), 4.44–4.29 (m, 3H), 4.17 (dd, *J* 8.2, 11.0 Hz, 1H), 3.76 (td, *J* 6.1, 9.8 Hz, 1H), 3.70 (d, *J* 4.9 Hz, 2H), 3.39 (td, *J* 6.1, 9.8 Hz, 1H), 2.83–2.70 (m, 2H), 2.68–2.59 (m, 2H), 2.20 (s, 3H), 1.89–1.74 (m, 2H), 1.56–1.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.5, 172.6, 137.9, 137.8, 137.7, 133.9, 128.7, 128.3, 128.2, 128.1, 128.0, 127.5, 123.4, 114.8, 98.3, 79.6, 79.5, 77.4, 75.2, 75.0, 73.0, 69.0, 63.2, 55.9, 38.0, 30.0, 29.9, 28.6, 28.1; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 678.2678, obsd 678.2675.

To a stirred solution of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-6-*O*-levulinyl-2-phthalimido-β-D-glucopyranoside (3.80 g, 5.80 mmol) in CH_3CN (40 mL) and H_2O (5 mL) was added NBS (3.09 g, 17.4 mmol). After stirring for 13 h shielded form light, the reaction was diluted with ether (100 mL) and washed with satd $Na_2S_2O_3$ (5×100 mL). The aqueous layer was extracted with ether (100 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo to afford 3.07 g (90%) of the crude lactol as a yellow oil. The crude product (2.70 g, 4.60 mmol) was azeotroped with toluene (3×10 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (40.0 mL). After cooling to 0 °C, trichloroacetonitrile (10.0 g, 69.4 mmol) and DBU (35 mg, 23 μmol) were added, and the reaction mixture was stirred for 2 h. The solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (3:7 EtOAc–hexanes) to afford 3.11 g (93%) of **F** as a yellow foam. $[\alpha]_D$ +60.9° (*c* 1.10, CH_2Cl_2); IR (thin film): 1777, 1716, 1387, 1062 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.78–7.55 (m, 4H), 7.45–7.18 (m, 5H), 7.14–6.98 (m, 2H), 6.97–6.78 (m, 3H), 6.41 (d, *J* 8.4 Hz, 1H), 4.92 (d, *J* 10.9 Hz, 1H), 4.85 (d, *J* 12.1 Hz, 1H), 4.70 (d, *J* 10.9 Hz, 1H), 4.58–4.31 (m, 5H), 3.89 (td, *J* 3.5, 10.0 Hz, 1H), 3.83–3.74 (m, 1H),

2.85–2.71 (m, 2H), 2.70–2.58 (m, 2H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.8, 172.7, 167.8, 160.8, 137.9, 137.6, 134.2, 131.5, 128.8, 128.4, 128.3, 127.7, 123.5, 94.1, 90.5, 79.2, 78.9, 77.4, 75.3, 75.2, 74.0, 62.7, 54.7, 38.0, 29.9, 28.1; ESI FT-MS: m/z $(M + Na)^+$ calcd 753.1150, obsd 753.1151.

3,4-Di-O-*benzyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-α,β*-D-*glucopyranose, 1-dibutylphosphate* (**10**).—Glucosamine trichloroacetimidate **F** (3.00 g, 4.10 mmol) was azeotroped with toluene (3 × 5 mL), and dissolved in toluene (40 mL). Dibutyl phosphate (1.12 g, 5.33 mmol) was added, and the solution was stirred for 14 h. After concentration *in vacuo*, the crude product was purified by flash silica gel chromatography (1:1 EtOAc–hexanes) to afford 4.02 g (98%, α:β = 1:4) of **10** as a yellow oil. IR (thin film): 1777, 1717, 1387, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77–7.65 (m, 4H), 7.38–7.29 (m, 5H), 7.09–6.98 (m, 2H), 6.95–6.82 (m, 3H), 5.83 (dd, *J* 8.2, 7.6 Hz, 0.8H), 5.70 (dd, *J* 3.4, 6.7 Hz, 0.2H), 5.27 (dd, *J* 8.9, 11.0 Hz, 0.2H), 4.96 (d, *J* 11.9 Hz, 0.2H), 4.89 (d, *J* 10.7 Hz, 0.8H), 4.49 (dd, *J* 8.5, 10.7 Hz, 1H), 4.46–4.39 (m, 2H), 4.32 (dd, *J* 4.6, 12.2 Hz, 1H), 4.24 (dd, *J* 8.5, 10.7 Hz, 1H), 4.00–3.86 (m, 2H), 3.81 (ddd, *J* 1.8, 4.0, 10.1 Hz, 1H), 3.78–3.73 (m, 3H), 2.84–2.69 (m, 2H), 2.67–2.54 (m, 2H), 2.20 (s, 3H), 1.57–1.48 (m, 2H), 1.35–1.23 (m, 4H), 1.09–1.00 (m, 2H), 0.90–0.81 (m, 3H), 0.74–0.66 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.5, 172.5, 137.8, 137.5, 134.0, 131.6, 128.7, 128.3, 128.2, 127.9, 127.6, 126.9, 123.5, 94.1, 78.9, 78.7, 75.3, 75.2, 73.7, 68.1, 67.9, 62.6, 56.2, 38.0, 32.0, 31.9, 30.0, 27.9, 18.6, 18.4, 13.7, 13.5; ^{31}P NMR (120 MHz, $CDCl_3$): −2.01 (s, 0.2P), −2.70 (s, 0.8P); ESI FT-MS: m/z $(M + Na)^+$ calcd 802.2969, obsd 802.2933.

3,4-Di-O-*acetyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranose-1-dibutylphosphate* (**12**).—Glucosamine trichloroacetimidate **8** (4.85 g, 7.64 mmol) was azeotroped with toluene (3 × 5 mL) and dissolved in toluene (40 mL). Dibutyl phosphate (2.08 g, 9.94 mmol) was added, and the solution was stirred for 14 h. After concentration in vacuo, the crude product was purified by flash silica gel chromatography (1:1 EtOAc–hexanes) to afford 2.72 g (52%) of **12** as a clear oil. $[\alpha]_D$ +25.9° (*c* 0.97, CH_2Cl_2); IR (thin film): 1750, 1720, 1386, 1224, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.81 (m, 2H), 7.81–7.67 (m, 2H), 6.06 (dd, *J* 7.5, 8.3 Hz, 1H), 5.90 (dd, *J* 9.2, 10.7 Hz, 1H), 5.23 (dd, *J* 9.4, 10.1 Hz, 1H), 4.40 (dd, *J* 8.5, 10.7 Hz, 1H), 4.32 (dd, *J* 4.8, 12.5 Hz, 1H), 4.21 (dd, *J* 2.0, 12.5 Hz, 1H), 4.07–3.92 (m, 3H), 3.84–3.62 (m, 2H), 2.84–2.63 (m, 2H), 2.62–2.40 (m, 2H), 2.15 (s, 3H), 2.10 (s, 3H), 1.92 (s, 3H), 1.62–1.51 (m, 2H), 1.39–1.23 (m, 4H), 1.16–1.01 (m, 2H), 0.94–0.84 (m, 3H), 0.76–0.66 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 171.5, 170.8, 170.4, 134.6, 131.6, 123.8, 93.8, 72.7, 69.9, 68.4, 68.2, 68.0, 61.7, 55.1, 37.8, 32.1, 32.0, 31.9, 29.8, 27.9, 20.9, 20.6, 18.6, 18.5, 13.7, 13.5; ^{31}P NMR (120 MHz, $CDCl_3$): −2.73 (s, 1P); ESI FT-MS: m/z $(M + Na)^+$ calcd 706.2241, obsd 706.2246.

n-*Pentenyl 2-amino-3,4-di*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**G**).—To a stirred solution of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (2.06 g, 3.71 mmol) in dry EtOH (20 mL) was added ethylenediamine (11.1 g, 0.19 mol), and the solution refluxed for 16 h. After concentration in vacuo, the crude product was dissolved in EtOAc (50 mL) and washed with HCl (10% in H_2O, 3 × 20 mL), H_2O, brine, dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by flash silica gel chromatography (3:2 EtOAc–hexanes) afforded 1.58 g (100%) of **G** as a white solid. $[\alpha]_D$ −6.54° (*c* 0.95, CH_2Cl_2); IR (thin film): 2871, 1097, 1049, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.28 (m, 10H), 5.90–5.75 (m, 1H), 5.09–4.96 (m, 3H), 4.86 (d, *J* 10.9 Hz, 1H), 4.75 (d, *J* 10.9 Hz, 1H), 4.70 (d, *J* 10.9 Hz, 1H), 4.25 (d, *J* 7.9 Hz, 1H), 3.97–3.86 (m, 2H), 3.77 (dd, *J* 4.3, 12.0 Hz, 1H), 3.65 (dd, *J* 9.2, 9.4 Hz, 1H), 3.58–3.45 (m, 2H), 3.44–3.36 (m, 1H), 2.85 (dd, *J* 8.0, 10.0 Hz, 1H), 2.21–2.07 (m, 2H), 1.80 (br s, 3H), 1.79–1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.1, 138.0, 128.7, 128.5, 128.2, 128.1, 128.0, 115.2, 104.0, 84.9, 78.4, 75.6, 75.1, 69.6, 61.9, 57.1, 30.3, 28.9; ESI FT-MS: m/z $(M + Na)^+$ calcd 450.2257, obsd 450.2253.

n-*Pentenyl 6*-O-*acetyl-3,4-di*-O-*benzyl-2-benzyloxycarbonylamino-2-deoxy-β*-D-*glucopyranoside* (**H**).—To a vigorously stirred solution of amine **G** (1.50 g, 3.51 mmol) in H_2O (20 mL) and Et_2O (20 mL) was added $NaHCO_3$ (1.17 g, 14.0 mmol) and benzyl chloroformate (0.89 g, 5.26 mmol). After 1 h, the solution was partitioned between organic and aqueous layers, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic phases were washed with H_2O, brine, and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (3:2 EtOAc–hexanes) to afford 1.59 g (81%) of *n*-pentenyl 3,4-di-*O*-benzyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside as a white solid. $[\alpha]_D$ +1.21° (*c* 0.67, CH_2Cl_2); IR (thin film): 3306, 1693, 1548, 1089 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.20 (m, 15H), 5.83–5.70 (m, 1H), 5.09 (s, 2H), 5.01 (ddd, *J* 1.5, 3.4, 17.1 Hz, 1H), 4.98–4.89 (m, 1H), 4.86 (d, *J* 11.0 Hz, 1H), 4.80 (d, *J* 11.3 Hz, 1H), 4.68 (d, *J* 11.3 Hz, 1H), 4.64 (d, *J* 11.6 Hz, 1H), 4.00 (br s, 1H), 3.90–3.81 (m, 2H), 3.73 (dd, *J* 4.0, 11.6 Hz, 1H), 3.58 (t, *J* 9.2 Hz, 1H), 3.50–3.38 (m, 2H), 3.25 (br s, 1H), 2.14–2.01 (m, 2H), 1.96 (br s, 1H), 1.72–1.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 138.2, 138.1, 136.6, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 115.2, 101.8, 78.6, 75.2, 75.1, 69.5, 66.9, 62.1, 58.3, 30.1, 28.8; ESI FT-MS: m/z $(M + Na)^+$ calcd 584.2625, obsd 584.2622.

To a stirred solution of *n*-pentenyl 3,4-di-*O*-benzyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (1.59 g, 2.83 mmol) in CH_2Cl_2 (20 mL) and pyridine (10 mL) was added DMAP (35 mg, 0.28 mmol) and Ac_2O (0.58 g, 5.67 mmol). After 2 h, the solution was diluted with CH_2Cl_2 (100 mL), washed with HCl (10% aq solution, 3 × 100 mL), H_2O (1 × 100 mL), brine (1 × 50 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by flash silica gel chromatography (1:4 EtOAc–hexanes) yielded 1.66 g (96%) of **H** as a white solid. $[\alpha]_D$ +6.16° (*c* 0.73, CH_2Cl_2); IR (thin film): 3342, 1735, 1699, 1536, 1244 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.23 (m, 15H), 5.83–5.74 (m, 1H), 5.09 (br s, 2H), 5.01 (ddd, *J* 1.8, 3.7, 17.4 Hz, 1H), 4.98 (dd, *J* 1.8, 8.6 Hz, 1H), 4.85 (d, *J* 11.0 Hz, 1H), 4.78 (d, *J* 11.0 Hz, 1H), 4.66 (d, *J* 11.0 Hz, 1H), 4.58 (d, *J* 11.0 Hz, 1H), 4.35 (d, *J* 12.2 Hz, 1H), 4.24 (dd, *J* 4.6, 11.6 Hz, 1H), 4.03 (bs, 1H), 3.85 (td, *J* 6.1, 9.8 Hz, 1H), 3.61–3.52 (m, 2H), 3.49–3.41 (m, 1H), 3.28 (br s, 1H), 2.13–2.01 (m, 2H), 2.04 (s, 3H), 1.71–1.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 155.9, 138.2, 137.8, 136.6, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 115.1, 100.8, 78.4, 75.2, 75.0, 73.0, 69.5, 67.0, 63.4, 58.1, 30.2, 28.9, 21.1; ESI FT-MS: m/z $(M+Na)^+$ calcd 626.2730, obsd 626.2703.

6-O-Acetyl-3,4-di-O-benzyl-2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranosyl trichloroacetimidate (**14**).—To a stirred solution of **H** (1.66 g, 2.75 mmol) in CH_3CN (20 mL) and H_2O (2.5 mL) was added NBS (1.47 g, 8.26 mmol). The reaction mixture was shielded from light and stirred for 12 h, diluted with ether (100 mL), and washed with satd $Na_2S_2O_3$ (5 × 50 mL). The aqueous layer was extracted with ether (100 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was azeotroped with toluene (3 × 10 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (20.0 mL). After cooling to 0 °C, trichloroacetonitrile (7.92 g, 55.0 mmol) and DBU (209 mg, 1.38 mmol) were added and the reaction mixture was stirred for 2 h. The solution was concentrated in vacuo, and purified by flash silica gel chromatography (3:7 EtOAc–hexanes) to afford 1.19 g (64%) of **14** as a white foam. $[\alpha]_D$ +50.5° (*c* 0.34, CH_2Cl_2); IR (thin film): 3311, 1724, 1515, 1240, 1025 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.41–7.25 (m, 15H), 6.27 (d, *J* 3.7 Hz, 1H), 5.15 (d, *J* 12.2 Hz, 1H), 5.03 (d, *J* 12.2 Hz, 1H), 4.89 (d, *J* 11.0 Hz, 2H), 4.75 (d, *J* 10.7 Hz, 1H), 4.72 (d, *J* 11.0 Hz, 1H), 4.62 (d, *J* 10.7 Hz, 1H), 4.43 (d, *J* 9.8 Hz, 1H), 4.31 (dd, *J* 2.1, 12.2 Hz, 1H), 4.24 (dd, *J* 3.7, 11.9 Hz, 1H), 4.19 (dt, *J* 3.4, 10.1 Hz, 1H), 4.01–3.95 (m, 1H), 3.86 (dd, *J* 6.1, 6.4 Hz, 1H), 3.84–3.78 (m, 1H), 3.71–3.78 (m, 2H), 2.96 (dd, *J* 6.1, 6.4 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 160.5, 156.1, 137.7, 137.4, 136.3, 128.8, 128.7, 128.6, 128.5, 128.3, 96.1, 91.1, 79.4, 75.6, 75.4, 72.1, 67.4, 62.5, 54.4, 21.0; ESI FT-MS: m/z $(M+Na)^+$ calcd 701.1195, obsd 701.1193.

n-*Pentenyl 2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside* (**J**).—To a stirred solution of **I** (15.7 g, 32.6 mmol) in CH_2Cl_2 (300 mL) at 0 °C was added $BF_3{\cdot}Et_2O$ (6.94 g, 48.9 mmol), flame-dried 4 Å molecular sieves (5.0 g) and 4-penten-1-ol (7.0 g, 81.5 mmol). The reaction mixture was stirred for 48 h at ambient temperature, diluted with CH_2Cl_2 (100 mL), and washed with satd $NaHCO_3$ (3 × 100 mL). The aqueous layer was extracted with CH_2Cl_2 (100 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to afford 8.88 g (54%) of *n*-pentenyl 3,4,6-tri-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside as a white solid. $[\alpha]_D$ +2.5° (*c* 1.06, CH_2Cl_2); IR (thin film): 3344, 1746, 1702, 1539, 1235 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.21 (m, 5H), 5.89–5.66 (m, 1H), 5.42–5.21 (m, 1H), 5.21–5.01 (m, 3H), 4.96 (d, *J* 11.3 Hz, 2H), 4.72–4.53 (m, 1H), 4.27 (dd, *J* 4.6, 12.2 Hz, 1H), 4.12 (d, *J* 12.2 Hz, 1H), 3.96–3.80 (m, 1H), 3.75–3.55 (m, 2H), 3.55–3.39 (m, 1H), 2.08 (s, 3H), 2.16–2.05 (m, 2H), 2.02 (s, 3H), 1.96 (s, 3H), 1.75–1.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.9, 169.7, 155.9, 138.1, 136.4, 128.7, 128.6, 128.4, 115.2, 101.2, 77.4, 72.2, 71.8, 69.6, 68.9, 67.1, 62.3, 56.3, 30.0, 28.7, 21.0, 20.8; ESI FT-MS: m/z $(M+Na)^+$ calcd 530.1997, obsd 530.1983.

A solution of *n*-pentenyl 3,4,6-tri-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (2.40 g, 4.73 mmol) in dry MeOH (50 mL) was treated with NaOMe (310 μL, 1.42 mmol, 25% w/v in MeOH). The reaction mixture was stirred for 14 h, then quenched by the addition of strongly acidic ion-exchange resin until the pH of the solution reached 5–6. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (3:2 EtOAc–hexanes) to afford 1.77 g (98%) of **J** as an orange solid. $[\alpha]_D$ −20.2° (*c* 0.60, CH_2Cl_2); IR (thin film): 3296, 1694, 1558, 1077 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 7.49–6.97 (m, 5H), 5.88–5.54 (m, 1H), 5.17–4.92 (m, 3H), 4.27 (d, *J* 7.9 Hz, 1H), 3.96–3.69 (m, 2H), 3.60 (dd, *J* 5.7, 11.9 Hz, 1H), 3.47–3.29 (m, 3H), 3.21–2.99 (m, 1H), 2.14–1.82 (m, 2H), 1.70–1.29 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 159.2, 139.6, 138.5, 129.6, 129.1, 129.0, 115.5, 103.3, 78.0, 76.1, 72.3, 70.1, 67.6, 62.9, 59.2, 31.4, 30.1; ESI FT-MS: m/z $(M+Na)^+$ calcd 404.1680, obsd 404.1670.

n-*Pentenyl 3,4-di-O-acetyl-2-benzyloxycarbonylamino-2-deoxy-6-O-triisopropylsilyl-β-D-glucopyranoside* (**K**).—To a stirred solution of **J** (1.70 g, 4.46 mmol) in dry DMF (40 mL) at 0 °C, was added imidazole (0.36 g, 5.35 mmol) and triisopropylchlorosilane (1.03 g, 5.35 mmol). After 14 h, the reaction was

quenched by the addition of water (100 mL). The aqueous layer was extracted with ether (3 × 100 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (3:2 EtOAc–hexanes) afforded 2.27 g (95%) of *n*-pentenyl 2-benzyloxycarbonylamino-2-deoxy-6-*O*-triisopropylsilyl-β-D-glucopyranoside as a white solid. $[\alpha]_D$ −26.7° (*c* 0.88, CH_2Cl_2), IR (thin film): 3328, 1699, 1540, 1254, 1062 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.26 (m, 5H), 5.82–5.70 (m, 1H), 5.18–5.06 (m, 3H), 5.00 (dd, *J* 1.5, 17.1 Hz, 1H), 4.98 (dd, *J* 1.2, 10.1 Hz, 1H), 4.42 (br s, 1H), 4.01–3.89 (m, 2H), 3.84 (td, *J* 6.4, 9.5 Hz, 1H), 3.57 (dd, *J* 8.9, 9.2 Hz, 2H), 3.48–3.38 (m, 2H), 3.31 (br s, 1H), 2.08 (dd, *J* 7.3, 14.3 Hz, 2H), 1.72–1.58 (m, 2H), 1.20–0.92 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2, 138.2, 136.3, 128.7, 128.4, 115.2, 101.3, 74.9, 74.0, 69.2, 67.4, 65.3, 58.1, 30.3, 28.8, 18.1, 12.0; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 560.3020, obsd 560.3032.

To a stirred solution of *n*-pentenyl 2-benzyloxycarbonylamino-2-deoxy-6-*O*-triisopropylsilyl-β-D-glucopyranoside (2.27 g, 4.22 mmol) in CH_2Cl_2 (30 mL) and pyridine (10 mL) was added DMAP (52 mg, 0.42 mmol) and Ac_2O (1.30 g, 12.6 mmol). After 2 h, the solution was diluted with CH_2Cl_2 (70 mL), washed with HCl (10% aq solution, 3 × 100 mL), H_2O (100 mL), brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (3:2 EtOAc–hexanes) yielded 2.62 g (100%) of **K** as a white solid. $[\alpha]_D$ +10.3° (*c* 0.95, CH_2Cl_2); IR (thin film): 3284, 1749, 1692, 1238 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.28 (m, 5H), 5.83–5.69 (m, 1H), 5.24 (br s, 1H), 5.09 (br s, 2H), 5.05–4.98 (m, 2H), 4.97–4.88 (m, 2H), 4.54 (br s, 1H), 3.85 (td, *J* 6.3, 9.5 Hz, 1H), 3.80–3.71 (m, 2H), 3.61 (d, *J* 8.0 Hz, 1H), 3.53 (d, *J* 9.2 Hz, 1H), 3.46 (dd, *J* 6.9, 15.9 Hz, 1H), 2.12–2.02 (m, 2H), 1.99 (s, 3H), 1.95 (s, 3H), 1.73–1.55 (m, 2H), 1.13–0.92 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.6, 156.0, 138.2, 136.5, 128.6, 128.2, 115.0, 101.0, 77.4, 75.0, 72.9, 69.4, 69.1, 67.0, 62.9, 56.3, 30.1, 28.8, 20.8, 18.0, 12.3; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 644.3225, obsd 644.3203.

n-*Pentenyl 3,4-di*-O-*acetyl-2-benzyloxycarbonylamino-2-deoxy-6*-O-*levuliny-β*-D-*glucopyranoside* (**L**). —To a stirred solution of **K** (2.64 g, 4.25 mmol) in THF (40 mL) was added AcOH (250 μL, 4.25 mmol) and TBAF (6.4 mL, 6.4 mmol, 1 M in THF). After 12 h, the reaction was quenched by the addition of satd $NaHCO_3$ (50 mL), and the aqueous layer was extracted with ether (3 × 100 mL). The combined organic phases were washed with brine and dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (2:3 EtOAc–hexanes) afforded 1.66 g (84%) of *n*-pentenyl 3,4-di-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside as a white solid. $[\alpha]_D$ −31.9° (*c* 0.98, CH_2Cl_2); IR (thin film): 3342, 1741, 1540, 1239 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 5H), 5.84–5.66 (m, 1H), 5.27 (d, *J* 8.0 Hz, 1H), 5.14–5.03 (m, 3H), 5.02–4.98 (m, 2H), 4.49 (d, *J* 5.9 Hz, 1H), 4.44–4.27 (m, 2H), 3.85 (td, *J* 6.2, 9.6 Hz, 1H), 3.68–3.56 (m, 1H), 3.56–3.49 (m, 2H), 3.49–3.40 (m, 2H), 2.10 (s, 3H), 2.08–2.02 (m, 2H), 2.00 (s, 3H), 1.75–1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.9, 156.3, 138.1, 136.6, 128.6, 128.1, 115.1, 101.4, 77.4, 75.1, 73.9, 69.4, 69.2, 66.9, 63.4, 61.4, 56.0, 30.0, 28.7, 20.8; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd, 488.1891, obsd 488.1882.

To a stirred solution of *n*-pentenyl 3,4-di-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (1.57 g, 3.39 mmol) in CH_2Cl_2 (30 mL) and pyridine (10 mL) was added DMAP (41 mg, 0.34 mmol) and levulinic anhydride (1.36 g, 6.38 mmol). After 2 h in the dark, the reaction was diluted with CH_2Cl_2 (60 mL), washed with HCl (10% aq solution, 3 × 100 mL), H_2O (100 mL), brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (2:3 EtOAc–hexanes) yielded 1.77 g (94%) of **L** as a white solid. $[\alpha]_D$ +3.30° (*c* 1.01, CH_2Cl_2); IR (thin film): 3335, 1748, 1540, 1365, 1231 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5H), 5.81–5.71 (m, 1H), 5.29 (br s, 1H), 5.15–5.04 (m, 4H), 5.00 (ddd, *J* 1.5, 3.4, 17.1 Hz, 1H), 4.95 (ddd, *J* 0.9, 1.8, 10.1 Hz, 1H), 4.86 (br s, 1H), 4.60 (br s, 1H), 4.25 (dd, *J* 5.2, 12.5 Hz, 1H), 4.12 (dd, *J* 1.8, 12.2 Hz, 1H), 3.88 (td, *J* 6.1, 9.8 Hz, 1H), 3.72–3.54 (m, 2H), 3.50–3.42 (m, 1H), 2.70–2.60 (m, 2H), 2.16 (s, 3H), 2.12–2.05 (m, 2H), 2.08 (s, 3H), 2.02 (s, 3H), 1.72–1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 171.6, 171.1, 170.9, 155.9, 138.1, 136.5, 128.6, 128.2, 115.2, 101.3, 71.9, 69.6, 68.9, 67.1, 62.3, 56.4, 37.8, 30.0, 29.8, 28.7, 27.9, 26.3, 21.0, 20.8; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 586.2259, obsd 586.2255.

3,4-Di-O-*acetyl-2-benzyloxycarbonylamino-2-deoxy-6*-O-*levulinyl-β*-D-*glucopyranosyl trichloroacetimidate* (**16**).—To a stirred solution of *n*-pentenyl glycoside **L** (1.77 g, 3.14 mmol) in CH_3CN (20 mL) and H_2O (2 mL) was added NBS (1.12 g, 6.29 mmol). After 13 h shielded from light, the solution was diluted with Et_2O (100 mL) and washed with satd $Na_2S_2O_3$ (5 × 100 mL). The aqueous layer was extracted with Et_2O (100 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo to afford the crude lactol as a yellow oil. The crude product was azeotroped with toluene (3 × 10 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (30 mL). After cooling to 0 °C, trichloroacetonitrile (2.91 g, 20.2 mmol) and DBU (108 mg, 1.01 mmol) were added, and the reaction mixture was stirred for 2 h. The solution was concentrated in vacuo and purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to afford 730 mg (57%) of **16** as a white foam.

$[\alpha]_D$ +57.3° (*c* 0.96, CH_2Cl_2); IR (thin film): 3320, 1744, 1521, 1226 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.40–7.24 (m, 5H), 6.37 (d, *J* 3.7 Hz, 1H), 5.32–5.07 (m, 3H), 5.01 (d, *J* 11.9 Hz, 2H), 4.32–4.18 (m, 2H), 4.17–4.05 (m, 2H), 2.83–2.64 (m, 2H), 2.63–2.51 (m, 2H), 2.16 (s, 3H), 2.01 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 177.7, 172.3, 171.1, 169.4, 160.3, 155.8, 135.8, 128.6, 128.4, 128.2, 94.9, 90.8, 77.4, 70.6, 67.6, 67.2, 61.8, 53.7, 37.9, 29.9, 27.9, 20.6; ESI FT-MS: m/z $(M+Na)^+$ calcd 661.0735, obsd 661.0734.

n-*Pentenyl 3,4-di*-O-*benzyl-2-benzyloxycarbonyl-amino-2-deoxy-6*-O-*levulinyl-β*-D-*glucopyranoside* (**M**).—To a stirred solution of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-benzyloxycarbonylamino-β-D-glucopyranoside (1.58 g, 2.82 mmol) in CH_2Cl_2 (25 mL) and pyridine (5 mL) was added DMAP (34 mg, 0.28 mmol) and levulinic anhydride (1.13 g, 5.26 mmol). After 2 h shielded from light, the reaction was diluted with CH_2Cl_2 (70 mL), washed with HCl (10% v/v in H_2O, 3 × 100 mL), H_2O (100 mL), brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (20% EtOAc/hexanes) afforded 1.73 g (93%) of **M** as a clear oil. $[\alpha]_D$ +1.79° (*c* 0.56, CH_2Cl_2); IR (thin film): 3323, 1734, 1696, 1543 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.22 (m, 15H), 5.86–5.71 (m, 1H), 5.09 (s, 2H), 5.04–4.93 (m, 3H), 4.85 (d, *J* 10.8 Hz, 1H), 4.79 (d, *J* 11.0 Hz, 1H), 4.72–4.63 (m, 2H), 4.60 (d, *J* 10.8 Hz, 1H), 4.36 (d, *J* 11.6 Hz, 1H), 4.31–4.22 (m, 1H), 4.01 (br s, 1H), 3.85 (td, *J* 6.2, 9.6 Hz, 1H), 3.59–3.51 (m, 2H), 3.51–3.39 (m, 1H), 3.29 (br s, 1H), 2.81–2.67 (m, 2H), 2.65–2.56 (m, 2H), 2.21 (s, 3H), 2.14–1.99 (m, 2H), 1.67–1.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.7, 172.7, 156.2, 138.3, 138.2, 137.9, 136.6, 128.7,128.6, 128.2, 128.1, 128.0, 115.1, 101.2, 78.4, 75.2, 75.0, 72.9, 69.4, 66.9, 63.5, 58.0, 38.0, 30.2, 28.8, 28.1; ESI FT-MS: m/z $(M+Na)^+$ calcd 682.2992, obsd 682.2964.

3,4-Di-O-*benzyl-2-benzyloxycarbonylamino-2-deoxy-6*-O-*levulinyl-α,β*-D-*glucopyranose*, *1-dibutylphosphate* (**18**).—*n*-Pentenyl glycoside **M** (27 mg, 41.5 μmol) was azeotroped with toluene (3 × 5 mL) and dried under vacuum for 1 h. CH_2Cl_2 (1.0 mL) was added followed by flame-dried 4 Å molecular sieves (50 mg), dibutyl phosphate (18 mg, 83.0 μmol) and NBS (15 mg, 41.0 μmol). The reaction mixture was shielded from light and stirred for 14 h, diluted with ether (10 mL), and washed with satd $Na_2S_2O_3$ (5 × 5 mL). The aqueous layer was extracted with ether (10 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (1:1 EtOAc–hexanes) to afford 14 mg (45%, α:β = 1:1) of **18** as a white solid. IR (thin film): 3291, 1717, 1540, 1260, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.21 (m, 15H), 5.65–5.60 (m, 1H), 5.16 (d, *J* 12.2 Hz, 1H), 5.05 (d, *J* 12.2 Hz, 1H), 4.87 (d, *J* 11.0 Hz, 1H), 4.84 (d, *J* 11.0 Hz, 1H), 4.70 (d, *J* 11.0 Hz, 1H), 4.61 (d, *J* 11.0 Hz, 1H), 4.33 (dd, *J* 3.7, 12.2 Hz, 1H), 4.27 (dd, *J* 1.8, 11.9 Hz, 1H), 4.01–3.98 (m, 6H), 3.76–3.66 (m, 2H), 2.82–2.68 (m, 2H), 2.62–2.55 (m, 2H), 2.19 (s, 3H), 1.83–1.70 (m, 2H), 1.68–1.57 (m, 4H), 1.43–1.31 (m, 4H), 0.98–0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.5, 172.5, 156.0, 137.9, 137.8, 137.7, 137.6, 136.4, 136.3, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 97.2, 96.9, 81.1, 79.7, 77.3, 75.5, 75.4, 75.1, 73.8, 71.3, 68.1, 67.3, 67.0, 62.9, 62.5, 57.3, 55.0, 38.0, 32.4, 32.3, 32.2, 30.0, 28.0, 18.8, 13.8; ^{31}P NMR (120 MHz, $CDCl_3$): −1.57 (s, 0.5P), −1.94 (s, 0.5P); ESI FT-MS: m/z $(M+Na)^+$ calcd 806.3282, obsd 806.3281.

3,4-Di-O-*acetyl-2-benzyloxycarbonylamino-2-deoxy-6*-O-*levulinyl-β*-D-*glucopyranose*, *1-dibutylphosphate* (**20**).—Glucosamine trichloroacetimidate **16** (135 mg, 211 μmol) was azeotroped with toluene (3 × 5 mL), and dissolved in toluene (2 mL). Dibutyl phosphate (48 mg, 232 μmol) was added, and the solution was stirred for 14 h. After concentration in vacuo, the crude product was purified by flash silica gel chromatography (1:1 EtOAc–hexanes) to afford 103 mg (72%) of **20** as a clear oil. $[\alpha]_D$ +23.6° (*c* 0.95, CH_2Cl_2); IR (thin film): 3355, 1716, 1539, 1236 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.28 (m, 5H), 5.30–5.22 (m, 2H), 5.20–5.07 (m, 3H), 5.01 (d, *J* 12.5 Hz, 1H), 4.24 (dd, *J* 4.9, 12.5 Hz, 1H), 4.15 (d, *J* 12.3 Hz, 1H), 4.09–4.01 (m, 2H), 3.99–3.86 (m, 3H), 3.81–3.75 (m, 1H), 2.80–2.72 (m, 1H), 2.70–2.62 (m, 1H), 2.55–2.40 (m, 2H), 2.15 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H), 1.67–1.60 (m, 2H), 1.57–1.49 (m, 2H), 1.42–1.35 (m, 2H), 1.34–1.25 (m, 2H), 0.92 (t, *J* 7.3 Hz, 3H), 0.88 (t, *J* 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 171.5, 171.2, 170.8, 136.4, 128.7, 128.4, 128.1, 97.0, 72.8, 72.0, 68.3, 68.2, 68.1, 67.0, 61.9, 56.3, 37.9, 32.2, 29.8, 27.9, 20.9, 20.7, 19.0, 18.8, 18.7, 13.9, 13.7; ^{31}P NMR (120 MHz, $CDCl_3$): −2.44 (s, 1P); ESI FT-MS: m/z $(M+Na)^+$ calcd 710.2548, obsd 710.2539.

n-*Pentenyl 6*-O-*acetyl-3,4-di*-O-*benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β*-D-*glucopyranoside* (**N**).—To a stirred solution of **G** (3.26 g, 8.09 mmol) in Et_2O (40 mL) and satd aq $NaHCO_3$ (40 mL) was added 2,2,2-trichloroethyl chloroformate (1.65 g, 9.71 mmol). After 1 h, the solution was diluted with ether (60 mL), washed with satd $NaHCO_3$ (3 × 50 mL), H_2O, brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (1:4 EtOAc–hexanes) yielded 4.38 g (90%) of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside as a white solid. $[\alpha]_D$ +0.66° (*c* 0.91, CH_2Cl_2); IR (thin film): 3319, 1709, 1548, 1071 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.27 (m, 10H), 5.87–5.69 (m,

1H), 5.11 (br s, 1H), 5.06–4.93 (m, 2H), 4.87 (d, *J* 11.0 Hz, 1H), 4.86 (d, *J* 11.2 Hz, 1H), 4.78–4.60 (m, 5H), 3.95 (br s, 1H), 3.93–3.82 (m, 2H), 3.76 (br s, 1H), 3.63 (dd, *J* 8.9, 9.4 Hz, 1H), 3.48 (td, *J* 6.8, 9.6 Hz, 1H), 3.46–3.39 (m, 1H), 3.38–3.27 (m, 1H), 2.18–2.05 (m, 2H), 1.96 (br s, 1H), 1.76–1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 138.2, 138.1, 138.0, 128.8, 128.7, 128.3, 128.1, 115.2, 100.7, 95.7, 80.6, 78.6, 77.4, 75.4, 75.2, 75.1, 74.6, 69.6, 62.1, 58.3, 30.2, 28.9; ESI FT-MS: m/z $(M + Na)^+$ calcd 624.1299, obsd 624.1289.

To a stirred solution of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (4.38 g, 7.28 mmol) in CH_2Cl_2 (60 mL) and pyridine (20 mL) was added DMAP (89 mg, 0.73 mmol) and Ac_2O (1.48 g, 14.6 mmol). After 2 h, the reaction mixture was diluted with CH_2Cl_2 (60 mL), washed with HCl (10% aq, 5 × 50 mL), H_2O, brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (1:4 EtOAc–hexanes) afforded 4.31 g (92%) of **N** as a yellow solid. $[\alpha]_D$ +7.46° (*c* 0.93, CH_2Cl_2); IR (thin film): 3362, 1730, 1715, 1533, 1249 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.27 (m, 10H), 5.83–5.73 (m, 1H), 5.20 (br s, 1H), 5.02 (ddd, *J* 1.8, 3.7, 17.1 Hz, 1H), 4.96 (ddd, *J* 1.2, 2.1, 10.4 Hz, 1H), 4.86 (d, *J* 11.0 Hz, 1H), 4.84 (d, *J* 11.3 Hz, 1H), 4.75 (d, *J* 11.3 Hz, 1H), 4.71 (bs, 1H), 4.65 (bs, 1H), 4.59 (d, *J* 11.0 Hz, 1H), 4.36 (d, *J* 11.3 Hz, 1H), 4.25 (dd, *J* 4.6, 11.9 Hz, 1H), 3.99 (bs, 1H), 3.87 (td, *J* 6.4, 9.5 Hz, 1H), 3.62–3.55 (m, 2H), 3.47 (td, *J* 7.0, 9.8 Hz, 1H), 3.42–3.31 (m, 1H), 2.15–2.07 (m, 2H), 2.06 (s, 3H), 1.73–1.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 154.1, 138.2, 138.0, 137.7, 128.8, 128.7, 128.3, 128.2, 128.1, 115.2, 100.4, 95.6, 80.8, 78.5, 75.2, 75.1, 74.6, 73.0, 69.5, 63.3, 58.1, 30.2, 28.8, 21.1; ESI FT-MS: m/z $(M + Na)^+$ calcd 666.1416, obsd 666.1391.

6-O-Acetyl-3,4-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranosyl trichoroacetimidate (**22**).—To a stirred solution of **N** (1.26 g, 1.96 mmol) in CH_3CN (10.0 mL) and H_2O (0.1 mL) was added NBS (0.69 g, 3.91 mmol). After 14 h shielded from light, the reaction was diluted with ether (20 mL), washed with satd sodium thiosulfate (5 × 20 mL), H_2O, brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was azeotroped with toluene (3 × 5 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (15 mL). After cooling to 0 °C, trichloroacetonitrile (5.08 g, 35.0 mmol) and DBU (119 mg, 0.79 mmol) were added, and the reaction mixture was stirred for 2 h. The solution was concentrated in vacuo, and purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to yield 922 mg (66%) of **22** as a white solid. $[\alpha]_D$ +63.2° (*c* 1.05, CH_2Cl_2); IR (thin film): 3340, 1740, 1675, 1516, 1239 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (s, 1H), 7.46–7.28 (m, 10H), 6.32 (d, *J* 3.4 Hz, 1H), 4.96 (d, *J* 11.5 Hz, 1H), 4.92 (d, *J* 10.9 Hz, 1H), 4.78 (d, *J* 11.5 Hz, 1H), 4.76 (d, *J* 12.0 Hz, 1H), 4.66 (d, *J* 12.0 Hz, 1H), 4.65 (d, *J* 10.9 Hz, 1H), 4.60 (d, *J* 8.9 Hz, 1H), 4.33 (dd, *J* 2.2, 12.2 Hz, 1H), 4.26 (dd, *J* 3.7, 12.2 Hz, 1H), 4.11 (ddd, *J* 3.5, 9.1, 10.6 Hz, 1H), 4.03–3.95 (m, 1H), 3.86 (dd, *J* 9.0, 10.5 Hz, 1H), 3.75 (dd, *J* 9.3, 9.7 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.7, 160.5, 154.3, 137.5, 137.3, 129.0, 128.9, 128.8, 128.6, 128.5, 128.2, 95.6, 95.4, 91.0, 79.3, 78.1, 77.4, 75.5, 75.2, 74.8, 54.6, 20.9; ESI FT-MS: m/z $(M + Na)^+$ calcd 740.9668, obsd 740.9862.

n-*Pentenyl 2-deoxy-2-trichloroacetylamino-β-D-glucopyranoside* (**P**).—To a stirred solution of **O** (5.90 g, 12.1 mmol) in CH_2Cl_2 (120 mL) at 0 °C, was added $BF_3{\cdot}Et_2O$ (4.43 g, 31.3 mmol) and 4-penten-1-ol (1.14 g, 13.3 mmol). The reaction mixture was warmed to ambient temperature, then stirred for 48 h, diluted with CH_2Cl_2 (100 mL), and washed with satd $NaHCO_3$ (3 × 100 mL). The aqueous layer was extracted with CH_2Cl_2 (100 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to afford 4.94 g (79%) of *n*-pentenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetylamino-β-D-glucopyranoside as a white solid. $[\alpha]_D$ +74.7° (*c* 0.99, CH_2Cl_2); IR (thin film): 3320, 1749, 1519, 1227, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* 9.2 Hz, 1H), 5.84–5.72 (m, 1H), 5.32 (dd, *J* 9.8, 10.4 Hz, 1H), 5.14 (dd, *J* 9.5, 10.1 Hz, 1H), 5.06–4.97 (m, 2H), 4.93 (d, *J* 3.7 Hz, 1H), 4.29–4.20 (m, 2H), 4.13–4.06 (m, 1H), 3.98 (ddd, *J* 2.4, 4.6, 10.1 Hz, 1H), 3.74 (td, *J* 6.4, 16.2 Hz, 1H), 3.48 (td, *J* 6.4, 12.8 Hz, 1H), 2.16–2.10 (m, 2H), 2.09 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.75–1.68 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 170.8, 169.5, 161.9, 137.5, 115.7, 96.5, 92.2, 71.0, 68.2, 68.1, 61.9, 54.1, 54.0, 30.3, 28.5, 21.0, 20.8; ESI FT-MS: m/z $(M + Na)^+$ calcd 540.0565, obsd 540.0540.

To a stirred solution of *n*-pentenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetylamino-β-D-glucopyranoside (3.86 g, 7.46 mmol) in MeOH (80 mL), was added NaOMe (161 μL, 0.75 mmol, 25% w/v in MeOH). After 14 h, the reaction was quenched by the addition of strongly acidic ion-exchange resin until the pH of the solution reached 5–6, and the solution was filtered and concentrated in vacuo. Purification by flash silica gel chromatography (3:2 EtOAc–hexanes) afforded 2.55 g (87%) of **P** as an orange solid. $[\alpha]_D$ +72.8° (*c* 0.94, CH_2Cl_2); IR (thin film): 3335, 1699, 1521, 1034 cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD) δ 8.21 (d, *J* 6.7 Hz, 1H), 5.83–5.75 (m, 1H), 4.98 (d, *J* 17.1 Hz, 1H), 4.92 (d, *J* 10.4 Hz, 1H), 3.84–3.77 (m, 3H), 3.76–3.69 (m, 2H), 3.68–3.66 (m, 1H), 3.61–3.56 (m, 2H), 3.42–3.33 (m, 3H), 2.16–2.11 (m, 2H), 1.69–1.63 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 164.3, 139.4, 115.3, 97.8, 93.9, 70.1, 68.8, 62.6, 57.8, 31.5, 31.4, 30.1, 29.9; ESI FT-MS: m/z $(M + Na)^+$ calcd 414.0248, obsd 414.0247.

n-*Pentenyl 3,4-di*-O-*acetyl-2-deoxy-2-trichloroacetylamino-6*-O-*triisopropylsilyl-β*-D-*glucopyranoside* (**Q**).—To a stirred solution of **P** (2.48 g, 6.34 mmol) in DMF (60 mL) at 0 °C, was added imidazole (0.86 g, 12.6 mmol) and triisopropylchlorosilane (1.46 g, 7.61 mmol). The reaction mixture was allowed to warm to ambient temperature over 16 h, then water (100 mL) was added. The aqueous layer was extracted with ether (3 × 100 mL), and the combined organic phases were washed with brine and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (1:1 EtOAc–hexanes) to afford 2.84 g (82%) of *n*-pentenyl 2-deoxy-2-trichloroacetylamino-6-*O*-triisopropylsilyl-β-D-glucopyranoside as a white solid. $[\alpha]_D$ +53.3° (*c* 0.98, CH_2Cl_2); IR (thin film): 3419, 1716, 1516, 1057 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.00 (d, *J* 8.5 Hz, 1H), 5.82–5.72 (m, 1H), 5.04–4.95 (m, 2H), 4.86 (d, *J* 3.7 Hz, 1H), 3.99 (dt, *J* 3.7, 8.6 Hz, 1H), 3.93 (d, *J* 5.2 Hz, 2H), 3.86–3.78 (m, 2H), 3.73 (td, *J* 6.4, 9.8 Hz, 1H), 3.68 (td, *J* 5.5, 9.5 Hz, 1H), 3.62–3.56 (m, 1H), 3.47–3.44 (m, 1H), 3.42 (td, *J* 7.7, 9.8 Hz, 1H), 2.16–2.08 (m, 2H), 1.73–1.64 (m, 2H), 1.21–0.98 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 137.8, 115.4, 96.5, 92.6, 73.7, 72.9, 70.9, 67.4, 65.0, 55.2, 30.4, 28.7, 18.1, 11.9; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 570.1583, obsd 570.1587.

To a stirred solution of *n*-pentenyl 2-deoxy-2-trichloroacetylamino-6-*O*-triisopropylsilyl-β-D-glucopyranoside (2.84 g, 5.19 mmol) in CH_2Cl_2 (30 mL) and pyridine (10 mL) was added DMAP (63 mg, 0.52 mmol) and Ac_2O (1.66 g, 20.8 mmol). After 3 h, the solution was diluted with CH_2Cl_2 (70 mL), washed with HCl (10% aq solution, 3 × 100 mL), H_2O (100 mL), brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography 3:7 EtOAc–hexanes) yielded 3.18 g (96%) of **Q** as a white solid. $[\alpha]_D$ +76.5° (*c* 1.09, CH_2Cl_2); IR (thin film): 3425, 1753, 1724, 1515, 1238 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, *J* 9.2 Hz, 1H), 5.83–5.73 (m, 1H), 5.31 (dd, *J* 9.9, 10.4 Hz, 1H), 5.06 (t, *J* 9.8 Hz, 1H), 5.04–4.95 (m, 2H), 4.90 (d, *J* 3.9 Hz, 1H), 4.19 (ddt, *J* 0.9, 3.7, 9.5 Hz, 1H), 3.84 (ddd, *J* 2.8, 4.9, 10.1 Hz, 1H), 3.80–3.70 (m, 3H), 3.45 (td, *J* 6.4, 9.8 Hz, 1H), 2.15–2.10 (m, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.12–0.92 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 169.5, 161.9, 137.7, 115.5, 96.2, 71.4, 71.2, 68.7, 67.6, 62.8, 54.1, 30.4, 28.6, 20.9, 20.8, 18.0, 17.9, 12.0; ES1 FT-MS: *m*/*z* $(M + Na)^+$ calcd 654.1794, obsd 654.1793.

n-*Pentenyl 3,4-di*-O-*acetyl-2-deoxy-6*-O-*levulinyl-2-trichloroacetylamino-β*-D-*glucopyranoside* (**R**).—To a stirred solution of **Q** (3.18 g, 5.03 mmol) in THF (30 mL) was added AcOH (453 μL, 7.54 mmol) and TBAF (7.5 mL, 7.5 mmol, 1 M in THF). After 12 h, $NaHCO_3$ (50 mL) was added, and the aqueous layer was extracted with ether (3 × 100 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (2:3 EtOAc–hexanes) afforded 2.00 g (83%) of *n*-pentenyl 3,4-di-*O*-acetyl-2-deoxy-2-trichloroacetylamino-β-D-glucopyranoside as a white solid. $[\alpha]_D$ −47.3° (*c* 1.00, CH_2Cl_2); IR (thin film): 2226, 1716, 1695, 1532, 1233 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* 8.9 Hz, 1H), 5.80–5.71 (m, 1H), 5.35 (dd, *J* 8.9, 10.7 Hz, 1H), 5.02–4.92 (m, 2H), 4.63 (d, *J* 8.2 Hz, 1H), 4.45 (dd, *J* 4.3, 12.2 Hz, 1H), 4.34 (dd, *J* 1.2, 11.9 Hz, 1H), 3.97–2.36 (m, 2H), 3.64–3.56 (m, 2H), 3.51–3.45 (m, 1H), 3.43 (d, *J* 5.2 Hz, 1H), 2.13 (s, 3H), 2.10 (s, 3H), 2.09–2.01 (m, 2H), 1.72–1.58 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 172.1, 162.4, 138.0, 115.2, 100.8, 92.6, 74.4, 74.1, 69.6, 63.3, 56.1, 30.1, 28.8, 21.1; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd, 498.0465, obsd 498.0456.

To a stirred solution of *n*-pentenyl 3,4-di-*O*-acetyl-2-deoxy-2-trichloroacetylamino-β-D-glucopyranoside (2.0 g, 4.2 mmol) in CH_2Cl_2 (40 mL) and pyridine (10 mL) was added DMAP (51 mg, 0.42 mmol) and levulinic anhydride (1.38 g, 6.45 mmol). After 2 h in the dark, the reaction mixture was diluted with CH_2Cl_2 (60 mL), washed with HCl (10% aq solution, 3 × 100 mL), H_2O (100 mL), brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash silica gel chromatography (2:3 EtOAc–hexanes) yielded 2.13 g (88%) of **R** as a white solid. $[\alpha]_D$ −8.37° (*c* 0.90, CH_2Cl_2); IR (thin film): 3337, 1749, 1717, 1532, 1229 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, *J* 8.5 Hz, 1H), 5.79–5.69 (m, 1H), 5.40 (dd, *J* 10.3, 10.7 Hz, 1H), 5.14 (dd, *J* 9.7, 9.8 Hz, 1H), 4.98 (dd, *J* 1.5, 17.4 Hz, 1H), 4.93 (d, *J* 10.1 Hz, 1H), 4.67 (d, *J* 8.2 Hz, 1H), 4.28 (dd, *J* 4.9, 12.5 Hz, 1H), 4.14 (dd, *J* 2.1, 12.5 Hz, 1H), 3.98 (td, *J* 8.5, 10.7 Hz, 1H), 3.88 (td, *J* 6.1, 9.8 Hz, 1H), 3.75 (ddd, *J* 2.1, 4.9, 10.1 Hz, 1H), 3.47 (td, *J* 6.7, 9.5 Hz, 1H), 2.85–2.76 (m, 1H), 2.72–2.62 (m, 1H), 2.55–2.40 (m, 2H), 2.18 (s, 3H), 2.11–2.00 (m, 2H), 2.07 (s, 6H), 1.72–1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 171.6, 171.4, 170.9, 162.2, 137.9, 115.2, 100.8, 92.5, 72.2, 71.6, 69.6, 68.5, 62.2, 56.1, 37.9, 30.0, 29.8, 27.9, 21.0, 20.8; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 596.0833, obsd 596.0821.

3,4-Di-O-*acetyl-2-deoxy-6*-O-*levulinyl-2-trichloroacetylamino-α*-D-*glucopyranosyl trichloroacetimidate* (**24**).—To a stirred solution of **R** (2.2 g, 3.8 mmol) in CH_3CN (40 mL) and H_2O (4 mL) was added NBS (1.36 g, 7.66 mmol). After 13 h shielded from light, the solution was diluted with ether (100 mL) and washed with satd $Na_2S_2O_3$ (5 × 100 mL). The aqueous layer was extracted with ether (100 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo to afford the crude lactol as a yellow oil. The crude product was azeotroped with toluene (3 × 10 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (40 mL). After

cooling to 0 °C, trichloroacetonitrile (5.51 g, 38.3 mmol) and DBU (123 mg, 1.15 mmol) were added, and the reaction mixture was stirred for 2 h. The solution was concentrated in vacuo and purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to afford 1.99 g (80 %) of **24** as a white foam. $[\alpha]_D$ +72.0° (*c* 0.98, CH_2Cl_2); IR (thin film): 3315, 1749, 1718, 1683, 1519 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.00 (d, *J* 8.6 Hz, 1H), 6.48 (d, *J* 3.7 Hz, 1H), 5.43 (dd, *J* 9.8, 11.0 Hz, 1H), 5.27 (dd, *J* 10.1, 10.2 Hz, 1H), 4.44 (ddd, *J* 3.4, 8.6, 10.7 Hz, 1H), 4.27 (dd, *J* 4.6, 12.5 Hz, 1H), 4.20–4.10 (m, 2H), 2.82–2.68 (m, 2H), 2.66–2.32 (m, 2H), 2.19 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.5, 172.5, 171.7, 169.3, 162.2, 160.1, 93.8, 91.9, 90.7, 70.7, 70.3, 67.1, 61.7, 54.0, 38.0, 29.8, 30.0, 29.8, 28.0, 20.8; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 670.9304, obsd 670.9297.

tert-*Butyldimethylsilyl 3,4-di*-O-*benzyl-2-deoxy-2-trichloroacetylamino-α*-D-*glucopyranoside* (**T**).—To a stirred solution of **S** (1.03 g, 2.01 mmol) in CH_2Cl_2 (10 mL) were added activated 4 Å molecular sieves (1 g), benzyl bromide (0.60 mL, 5.02 mmol), and Ag_2O (1.40 g, 6.03 mmol). The flask was shielded from light, and the solution was stirred for 2 h. The solution was filtered through a pad of silica gel, and the filtrate was concentrated in vacuo. The resulting residue was purified by flash silica gel chromatography (5:95→10:90 EtOAc–hexanes) to yield 1.01 g (82%) of *tert*-butyldimethylsilyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetylamino-α-D-glucopyranoside as a white solid. $[\alpha]_D$ −21.0° (*c* 0.64, CH_2Cl_2); IR (thin film): 3321, 2929, 2857, 1692, 1085 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2H), 7.43–7.38 (m, 3H), 7.31–7.28 (m, 5H), 6.87 (d, *J* 8.7 Hz, 1H), 5.60 (s, 1H), 5.18 (d, *J* 7.9 Hz, 1H), 4.91 (d, *J* 11.2 Hz, 1H), 4.70 (d, *J* 11.2, 1H), 4.33 (dd, *J* 5.0, 10.5 Hz, 1H), 4.25 (dd, *J* 9.0, 10.2 Hz, 1H), 3.83 (t, *J* 10.3 Hz, 1H), 3.77 (t, *J* 9.2 Hz, 1H), 3.58–3.47 (m, 2H), 0.89 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 138.1, 137.4, 129.3, 128.6, 128.5, 128.1, 126.2, 101.5, 995.2, 83.0, 75.8, 74.9, 68.9, 66.4, 61.2, 25.8, 18.0, −4.0, −5.0; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 638.1270, obsd 638.1250.

A solution of BH_3 (1.0 M in THF, 14.0 mL) was added *tert*-butyldimethylsilyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetylamino-α-D-glucopyranoside (0.89 g, 1.40 mmol) at 0 °C. After 5 min, a solution of Bu_2BOTf (1.0 M in CH_2Cl_2, 1.68 mL) was added. After 1 h, the reaction was quenched by addition of TEA (1.50 mL), and methanol was then slowly added until the evolution of gas had ceased. The solution was concentrated, and the resulting residue was azeotroped with methanol (3 × 10 mL). The residue was then purified by flash silica gel chromatography (10:90→25:75 EtOAc–hexanes) affording 0.68 g (80%) of **T** as a white foam. $[\alpha]_D$ −6.2° (*c* 3.19, CH_2Cl_2); IR (thin film): 3503, 3329, 2929, 1692, 1529 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 10H), 6.94 (d, *J* 7.9 Hz, 1H), 5.13 (d, *J* 7.8 Hz, 1H), 4.85 (d, *J* 11.1 Hz, 1H), 4.84 (d, *J* 10.8 Hz, 1H), 4.73 (d, *J* 10.8 Hz, 1H), 4.69 (d, *J* 11.1 Hz, 1H), 4.15 (dd, *J* 8.6, 10.2 Hz, 1H), 3.87 (dd, *J* 2.8, 11.9 Hz, 1H), 3.74 (dd, *J* 4.6, 11.9 Hz, 1H), 3.64 (app t, *J* 9.3 Hz, 1H), 3.55–3.48 (m, 2H), 1.83 (br s, 1H), 0.90 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 138.0, 137.9, 128.7, 128.7, 128.2, 128.1, 94.6, 92.7, 79.7, 78.6, 75.4, 75.2, 75.0, 62.2, 60.9, 25.8, 18.0, −3.9, −4.9; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 640.1432, obsd 640.1424.

3,4-Di-O-*benzyl-2-deoxy-6*-O-*levulinyl-2-trichloroacetylamino-α*-D-*glucopyranosyl trichloroacetimidate* (**U**).—To a stirred solution of **T** (0.687 g, 1.11 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added, levulinic acid (0.12 mL, 1.17 mmol) and DMAP (0.149 g, 1.22 mmol). After 5 min, DIPC (0.17 mL, 1.11 mmol) was added, and the solution was left to slowly warm to room temperature. After 6 h, the reaction mixture was concentrated in vacuo, and the residue was purified by flash silica gel chromatography (10:90→25:75 EtOAc–hexanes) yielding 0.756 g (95%) of *tert*-butyldimethylsilyl 3,4-di-*O*-benzyl-2-deoxy-6-*O*-levulinyl-2-trichloroacetylamino-α-D-glucopyranoside as a clear oil. $[\alpha]_D$ +0.8° (*c* 0.76, CH_2Cl_2); IR (thin film): 3333, 2928, 1739, 1718, 1695 cm^{-1}; H NMR (400 MHz, $CDCl_3$) δ 7.37–7.29 (m, 10H), 6.94 (d, *J* 7.9 Hz, 1H), 5.07 (d, *J* 7.5 Hz, 1H), 4.84 (d, *J* 11.2 Hz, 1H), 4.81 (d, *J* 11.9 Hz, 1H), 4.73 (d, *J* 11.0 Hz, 1H), 4.62 (d, *J* 11.0 Hz, 1H), 4.40 (dd, *J* 2.5, 11.7 Hz, 1H), 4.21 (dd, *J* 5.9, 11.7 Hz, 1H), 4.13 (dd, *J* 8.2, 10.0 Hz, 1H), 3.68–3.64 (m, 1H), 3.58–3.51 (m, 1H), 2.75 (app t, *J* 6.5 Hz, 1H), 2.59 (td, *J* 0.8, 6.5 Hz, 1H), 2.20 (s, 3H), 0.88, (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 172.6, 161.9, 137.9, 137.6, 128.9, 128.2, 128.2, 128.1, 128.1, 94.5, 92.7, 79.8, 78.6, 77.4, 75.1, 74.9, 73.2, 63.5, 60.4, 38.1, 30.1, 30.0, 28.0, 25.8, 18.1, −4.0, −5.0; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 738.1794, obsd 738.1768.

To a stirred solution of *tert*-butyldimethylsilyl 3,4-di-*O*-benzyl-2-deoxy-6-*O*-levulinyl-2-trichloroacetylamino-α-D-glucopyranoside (0.745 g, 1.04 mmol) in THF (10 mL) at 0 °C were added dropwise and simultaneously TBAF (1.56 mL of a 1.0 M solution in THF) and HOAc (90 μL, 1.56 mmol). After 4 h, the reaction mixture was diluted with water (50 mL) and extracted with EtOAc (2 × 100 mL). Combined organic extracts were washed with water and satd aq $NaHCO_3$ (100 mL each), dried over Na_2SO_4, filtered and concentrated in vacuo. Residue was dissolved in a solution of CH_2Cl_2 (10 mL), and CCl_3CN (2 mL) and DBU (29 μL, 0.196 mmol) added. After 90 min, the reaction mixture was concentrated in vacuo. The resulting brown residue was purified by flash silica gel chromatography (25:75→40:60 EtOAc–hexanes) to yield 0.609 g (78% over two

steps) of imidate **U** as white foam. $[\alpha]_D$ +32.6° (*c* 0.76, CH_2Cl_2); IR (thin film): 3411, 3345, 2917, 1716, 1070 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.39–7.30 (m, 10H), 6.54 (d, *J* 8.6 Hz, 1H), 6.39 (d, *J* 3.5 Hz, 1H), 4.91 (d, *J* 11.2 Hz, 1H), 4.90 (d, *J* 10.6 Hz, 1H), 4.82 (d, *J* 11.2 Hz, 1H), 4.66 (d, *J* 10.6 Hz, 1H), 4.42–4.31 (m, 3H), 4.05–4.02 (m, 1H), 3.98 (dd, *J* 8.9, 10.5 Hz, 1H), 3.81 (app t, *J* 9.6 Hz, 1H), 2.82–2.74 (m, 2H), 2.63–2.58 (m, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 206.7, 172.7, 172.6, 163.6, 163.2, 137.4, 129.0, 128.9, 128.8, 128.6, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 104.3, 95.0, 79.3, 78.3, 77.4, 75.5, 74.9, 74.8, 74.6, 71.9, 70.0, 65.9, 63.2, 38.1, 38.0, 30.1, 28.1, 28.0; ESI FT-MS: m/z $(M+Na)^+$ calcd 767.0026, obsd 767.0012.

*3,4-Di-*O*-benzyl-2-deoxy-6-*O*-levulinyl-2-trichloroacetylamino-α-*D*-glucopyranose, 1-dibutylphosphate* (**26**).—To a solution of **U** (592 mg, 0.79 mmol) in toluene (10 mL) at 0 °C was added dibutylphosphate (0.19 mL, 0.95 mmol). The solution was left to slowly warm to room temperature and after 90 min was concentrated in vacuo. The resulting residue was purified by flash silica gel chromatography (25:70 → 40:60 EtOAc–hexanes) affording **26** (561 mg, 89%) as a yellow oil. $[\alpha]_D$ −30.6° (*c* 6.56, CH_2Cl_2); IR (thin film): 3415, 3337, 3032, 2961, 1717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 10H), 6.93 (d, *J* 9.4 Hz, 1H), 5.47 (app t, *J* 7.9 Hz, 1H), 4.83 (app d, *J* 9.7 Hz, 2H), 4.77 (d, *J* 10.8 Hz, 1H), 4.58 (d, *J* 10.9 Hz, 1H), 4.40 (dd, *J* 2.2, 12.0 Hz, 1H), 4.26 (dd, *J* 5.1, 11.9 Hz, 1H), 4.18–3.96 (m, 8H), 3.73–3.68 (m, 1H), 3.63 (app t, *J* 8.3 Hz, 1H), 2.84–2.73 (m, 2H), 2.63–2.54 (m, 2H), 2.20 (s, 3H), 1.70–1.64 (m, 4H), 1.44–1.34 (m, 4H), 0.94 (t, *J* 7.4 Hz, 3H), 0.93 (t, *J* 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 206.5, 172.6 (d, *J* 4.3 Hz), 162.2, 161.9, 137.8 (d, *J* 7.3 Hz), 137.5, 128.8, 128.8, 128.7, 128.3, 128.2, 128.1, 128.1, 92.7, 92.3, 91.4, 80.1, 79.0, 78.2, 77.4, 75.6, 75.4, 75.2, 71.5, 69.3, 68.5, 63.1, 62.3, 55.2, 54.9, 38.3, 38.0, 32.4, 30.0 (d, *J* 3.7 Hz), 28.2, 27.9 (d, J = 10.0 Hz), 18.8, 13.8; ^{31}P (120 MHz, $CDCl_3$) δ −3.13; ESI FT-MS: m/z $(M+Na)^+$ calcd 816.1845, obsd 816.1833.

Synthesis of disaccharides using glycosyl trichloroacetimidates as glycosylating agents. General procedure A.—A mixture of glucosamine trichloroacetimidate (1.3 equiv) and 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (**1**) (1.0 equiv) was coevaporated with toluene, dried under vacuum for 2 h, and dissolved in CH_2Cl_2. The solution was cooled and TMSOTf or TBSOTf (0.13 equiv, 0.5 M in CH_2Cl_2) was added. Et_3N was added to quench the reaction, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to afford the desired disaccharide.

Synthesis of disaccharides using glycosyl phosphates as glycosylating agents. General procedure B.—A mixture of glucosamine phosphate (1.3 equiv) and acceptor **1** (1.0 equiv) was coevaporated with toluene, dried under vacuum for 2 h, and dissolved in CH_2Cl_2. The solution was cooled to −15 °C, and TMSOTf (1.3 equiv, 1.0 M in CH_2Cl_2) was added. Et_3N was added to quench the reaction, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (1:4 EtOAc–hexanes) to afford the desired disaccharide.

*3,4-Di-*O*-benzyl-2-deoxy-2-phthalimido-6-*O*-triisopropylsilyl-β-*D*-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**3**).—Coupling of **2** (97 mg, 0.122 mmol) and **1** (25 mg, 94 μmol) following general procedure A at −20 °C using TMSOTf (25 μL, 12.5 μmol, 0.5 M in CH_2Cl_2) for 1 h, afforded 76 mg (70%) of **3** as a white solid. $[\alpha]_D$ −8.2° (*c* 0.86, CH_2Cl_2); IR (thin film): 1777, 1716, 1387, 1071 cm^{-1}; ^1H NMR (500 MHz, $CDC1_3$) δ 7.81–7.60 (m, 4H), 7.37–7.34 (m, 4H), 7.32–7.28 (m, 1H), 7.03–6.99 (m, 2H), 6.92–6.83 (m, 3H), 5.19 (d, *J* 8.5 Hz, 1H), 5.15 (d, *J* 4.9 Hz, 1H), 4.87 (d, *J* 10.7 Hz, 1H), 4.83 (d, *J* 11.0 Hz, 1H), 4.80 (d, *J* 12.2 Hz, 1H), 4.47 (d, *J* 11.9 Hz, 1H), 4.41 (dd, *J* 8.5, 10.7 Hz, 1H), 4.08 (dd, *J* 2.4, 5.2 Hz, 1H), 4.05–4.01 (m, 2H), 3.95 (dd, *J* 1.2, 7.9 Hz, 1H), 3.88–3.80 (m, 2H), 3.64–3.58 (m, 2H), 3.49 (td, *J* 2.8, 9.8 Hz, 1H), 1.38 (s, 3H), 1.21 (s, 3H), 1.19–1.06 (m, 21H), 1.01 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 163.6, 138.5, 138.3, 133.4, 128.7, 128.2, 128.1, 128.0, 127.9, 127.5, 123.2, 109.3, 108.1, 99.1, 96.1, 79.4, 79.2, 77.4, 75.9, 75.0, 71.0, 70.7, 70.3, 68.3, 67.5, 62.4, 56.2, 26.0, 25.4, 24.8, 24.3, 18.2, 12.2; ESI FT-MS: m/z $(M+Na)^+$ calcd 910.4173, obsd 910.4145.

*3,4-Di-*O*-acetyl-6-*O*-2-(azidomethyl)benzoyl)-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**7**).—Coupling of **6** (86 mg, 0.12 mmol) and **1** (27 mg, 0.10 mmol) following general procedure A for 1 h at 0 °C using TMSOTf afforded 52 mg (65%) of **7** as a white solid. $[\alpha]_D$ −24.3° (*c* 0.44, CH_2Cl_2); IR (thin film): 2103, 1748, 1719, 1386, 1257 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* 1.2, 7.84 Hz, 1H), 7.90–7.82 (m, 2H), 7.76–7.68 (m, 2H), 7.61–7.54 (m, 1H), 7.53–7.47 (m, 1H), 7.45–7.37 (m, 1H), 6.05 (dd, *J* 9.2, 10.6 Hz, 1H), 5.53 (d, *J* 8.5 Hz, 1H), 5.45 (dd, *J* 9.4, 10.0 Hz, 1H), 5.12 (d, *J* 5.1 Hz, 1H), 4.82 (d, *J* 14.4 Hz, 1H), 4.68 (d, *J* 14.4 Hz, 1H), 4.45–4.34 (m, 3H), 4.23 (dd, *J* 2.6, 12.3 Hz, 1H), 4.11 (dd, *J* 2.4, 5.1 Hz, 1H), 4.06–3.93 (m, 3H), 3.78–3.67 (m, 2H), 2.09 (s, 3H), 1.81 (s, 3H), 1.41 (s, 3H), 1.25 (s, 3H), 1.05 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.3, 165.2, 137.9, 133.9, 133.5, 131.3, 130.2, 128.5, 127.8, 123.7, 109.5, 108.1, 99.6, 96.1, 77.4, 71.8, 71.0, 70.8, 70.6, 70.3, 70.2, 69.9, 69.6, 67.7, 62.4, 54.8, 53.0, 26.0, 25.5, 24.8, 24.4, 20.9; ESI FT-MS: m/z $(M+Na)^+$ calcd 817.2539, obsd 817.2555.

3,4-Di-O-*acetyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-1,2:3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**9**).—Coupling of **8** (241 mg, 0.38 mmol) and **1** (50 mg, 0.19 mmol following general procedure A for 3 h at 0 °C using TMSOTf yielded 94 mg (68%) of **9** as a white solid. $[\alpha]_D$ −14.5° (*c* 0.92, CH_2Cl_2); IR (thin film): 1778, 1748, 1719, 1386, 1224 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.69 (m, 4H), 5.85 (dd, *J* 9.2, 10.7 Hz, 1H), 5.46 (d, *J* 8.5 Hz, 1H), 5.18 (dd, *J* 9.5, 10.1 Hz, 1H), 5.10 (d, *J* 5.2 Hz, 1H), 4.40 (dd, *J* 2.4, 5.5 Hz, 1H), 4.32 (dd, *J* 4.9, 12.5 Hz, 1H), 4.30 (dd, *J* 8.6, 10.7 Hz, 1H), 4.18 (dd, *J* 2.1, 12.2 Hz, 1H), 4.10 (dd, *J* 2.4, 5.2 Hz, 1H), 3.99 (d, *J* 7.9 Hz, 1H), 3.88 (ddd, *J* 2.1, 4.6, 10.1 Hz, 1H), 3.76–3.65 (m, 2H), 2.80–2.63 (m, 2H), 2.58–2.44 (m, 2H), 2.15 (s, 3H), 2.11 (s, 3H), 1.90 (s, 311), 1.39 (s, 3H), 1.23 (s, 3H), 1.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 171.5, 170.9, 170.5, 133.9, 123.6, 109.4, 108.1, 99.5, 96.1, 77.4, 71.8, 71.0, 70.8, 70.5, 70.3, 69.5, 69.2, 67.6, 62.2, 54.8, 37.9, 30.0, 28.0, 26.0, 25.5, 24.8, 24.4, 21.0, 20.9, 20.7; ESI FT-MS: m/z $(M+Na)^+$ calcd 756.2480, obsd 756.2474.

3,4-Di-O-*benzyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-1,2:3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**11**).—Glucosamine phosphate **10** (101 mg, 0.128 mmol) and galactopyranoside acceptor **1** (27 mg, 0.10 mmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1.3 mL). The solution was cooled to −15 °C, and TMSOTf (103 μL, 103 μmol, 1.0 M in CH_2Cl_2) was added. After 2 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (1:4 EtOAc–hexanes) to yield 74 mg (85%) of **11** as a white solid. $[\alpha]_D$ −8.97° (*c* 1.01, CH_2Cl_2); IR (thin film): 1776, 1715, 1387, 1069 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.53 (m, 4H), 7.42–7.28 (m, 5H), 7.06–6.96 (m, 2H), 6.95–6.78 (m, 3H), 5.22 (d, *J* 8.5 Hz, 1H), 5.08 (d, *J* 5.1 Hz, 1H), 4.89 (d, *J* 10.8 Hz, 1H), 4.81 (d, *J* 11.9 Hz, 1H), 4.65 (d, *J* 10.8 Hz, 1H), 4.45 (d, *J* 11.9 Hz, 1H), 4.55–4.26 (m, 4H), 4.16 (dd, *J* 8.6, 10.7 Hz, 1H), 4.07 (dd, *J* 2.3, 5.1 Hz, 1H), 3.96 (dd, *J* 1.2, 8.0 Hz, 1H), 3.89 (dd, *J* 7.4, 15.2 Hz, 1H), 3.74–3.67 (m, 2H), 3.67–3.56 (m, 2H), 2.87–2.69 (m, 2H), 2.68–2.54 (m, 2H), 2.22 (s, 3H), 1.37 (s, 3H), 1.21 (s, 3H), 1.01 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.1, 173.2, 138.6, 138.4, 134.0, 132.8, 129.2, 128.8, 128.7, 128.6, 128.5, 128.1, 123.9, 109.9, 100.2, 96.6, 80.0, 79.9, 75.7, 75.6, 73.4, 71.5, 71.3, 70.8, 69.8, 68.0, 63.8, 56.5, 38.6, 30.6, 28.7, 26.6, 26.0, 25.4, 24.9; ESI FT-MS: m/z $(M+Na)^+$ calcd 852.3208, obsd 852.2868.

3,4-Di-O-*acetyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-1,2:3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**13**).—Glucosamine phosphate **12** (100 mg, 0.146 mmol) and galactopyranoside acceptor **1** (32 mg, 0.12 mmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1.5 mL). The solution was cooled to −20 °C, and TMSOTf (146 μL, 146 μmol, 1.0 M in CH_2Cl_2) was added. After 3 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to yield 74 mg (83%) of **13** as a white solid. $[\alpha]_D$ −14.5° (*c* 0.92, CH_2Cl_2); IR (thin film): 1778, 1748, 1719, 1386 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.69 (m, 4H), 5.85 (dd, *J* 9.2, 10.7 Hz, 1H), 5.46 (d, *J* 8.5 Hz, 1H), 5.18 (dd, *J* 9.5, 10.1 Hz, 1H), 5.10 (d, *J* 5.2 Hz, 1H), 4.40 (dd, *J* 2.4, 5.5 Hz, 1H), 4.32 (dd, *J* 4.9, 12.5 Hz, 1H), 4.30 (dd, *J* 8.6, 10.7 Hz, 1H), 4.18 (dd, *J* 2.1, 12.2 Hz, 1H), 4.10 (dd, *J* 2.4, 5.2 Hz, 1H), 3.99 (d, *J* 7.9 Hz, 1H), 3.88 (ddd, *J* 2.1, 4.6, 10.1 Hz, 1H), 3.76–3.65 (m, 2H), 2.80–2.63 (m, 2H), 2.58–2.44 (m, 2H), 2.15 (s, 3H), 2.11 (s, 3H), 1.90 (s, 3H), 1.39 (s, 3H), 1.23 (s, 3H), 1.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 171.5, 170.9, 170.5, 133.9, 123.6, 109.4, 108.1, 99.5, 96.1, 77.4, 71.8, 71.0, 70.8, 70.5, 70.3, 69.5, 69.2, 67.6, 62.2, 54.8, 37.9, 30.0, 28.0, 26.0, 25.5, 24.8, 24.4, 21.0, 20.9, 20.7; ESI FT-MS: m/z $(M+Na)^+$ calcd 756.2480, obsd 756.2474.

6-O-*Acetyl-3,4-di*-O-*benzyl-2-benzyloxycarbonylamino-2-deoxy-β*-D-*glucopyranosyl-(1→6)-1,2:3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**15**).—A mixture of glucosamine trichloroacetimidate **14** (51 mg, 75 μmol) and galactopyranoside **1** (16 mg, 63 μmol) were coevaporated with toluene (3 × 3 mL), dried under vacuum for 2 h, and dissolved in CH_2Cl_2 (1.0 mL). The solution was cooled to 0 °C, and TMSOTf (15 μL, 7.5 μmol, 0.5 M in CH_2C1_2) was added. After 1 h, Et_3N (50 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to afford 41 mg (88%) of **15** as a white solid. $[\alpha]_D$ −18.3° (*c* 1.01, CH_2Cl_2); IR (thin film): 3339, 1739, 1540, 1240 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.21 (m, 15H), 5.51 (d, *J* 5.0 Hz, 1H), 5.13 (d, *J* 12.3 Hz, 1H), 5.07 (d, *J* 12.3 Hz, 1H), 4.84 (d, *J* 11.0 Hz, 1H), 4.77 (d, *J* 11.0 Hz, 1H), 4.69 (d, *J* 11.0 Hz, 1H), 4.59–4.53 (m, 2H), 4.34 (d, *J* 11.0 Hz, 1H), 4.30 (dd, *J* 2.4, 5.0 Hz, 1H), 4.24 (dd, *J* 2.4, 11.9 Hz, 1H), 4.18 (d, *J* 8.0 Hz, 1H), 4.01–3.96 (m, 2H), 3.94 (d, *J* 4.3 Hz, 1H), 3.76 (dt, *J* 3.4, 9.3 Hz, 1H), 3.57 (d, *J* 5.3 Hz, 2H), 2.05 (s, 3H), 1.49 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 156.2, 138.3, 137.9, 136.7, 128.7, 128.6, 128.5, 128.2, 127.9, 109.5, 108.9, 101.0, 96.4, 81.8, 78.2, 77.4, 75.3, 74.9, 73.1, 71.3, 70.8, 70.6, 68.4, 68.0, 66.9, 63.4, 57.7, 29.9, 26.2, 25.1, 24.5, 21.1; ESI FT-MS: m/z $(M+Na)^+$ calcd 800.3252, obsd 800.3234.

3,4-Di-O-*acetyl-2-benzyloxycarbonylamino-2-deoxy-6*-O-*levulinyl-β*-D-*glucopyranosyl-(1→6)1,2:3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**17**).—Glucosamine trichloroacetimidate **16** (74 mg, 0.12 mmol) and

galactopyranoside acceptor **1** (25 mg, 96.0 μmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1.00 mL). The solution cooled to 0 °C, and TMSOTf (24 μL, 12 μmol, 0.5 M in CH_2Cl_2) was added. After 1 h Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to yield 63 mg (90%) of **17** as a white solid. $[\alpha]_D$ −18.5° (*c* 1.03, CH_2Cl_2); IR (thin film): 3348, 2986, 1746, 1350, 1372 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5H), 5.50 (d, *J* 5.2 Hz, 1H), 5.25–5.12 (m, 2H), 5.07 (dd, *J* 9.4, 9.5 Hz, 1H), 5.02–4.96 (m, 2H), 4.86–4.78 (m, 1H), 4.55 (dd, *J* 2.4, 7.93 Hz, 1H), 4.28 (dd, *J* 2.4, 4.9 Hz, 1H), 4.26 (dd, *J* 4.6, 12.2 Hz, 1H), 4.16 (dd, *J* 1.5, 7.9 Hz, 1H), 4.12 (dd, *J* 2.1, 12.5 Hz, 1H), 4.00–3.90 (m, 2H), 3.80 (dd, *J* 7.6, 12.2 Hz, 1H), 3.78–3.66 (m, 2H), 2.79–2.62 (m, 2H), 2.54–2.40 (m, 2H), 2.15 (s, 3H), 2.07(s, 3H), 1.95 (s, 3H), 1.44 (s, 3H), 1.43 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 171.5, 171.1, 171.0, 156.1, 136.6, 128.6, 128.3, 128.2, 109.6, 109.0, 96.4, 77.4, 72.7, 72.0, 71.3, 70.8, 70.4, 68.8, 68.6, 67.0, 62.2, 56.2, 37.9, 29.8, 27.9, 26.1, 25.1, 24.5, 21.0, 20.8; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 760.2793, obsd 760.2756.

3,4-Di-O-*benzyl-2-benzyloxycarbonylamino-2-deoxy-6*-O-*levulinyl-β*-D-*glucopyranosyl-(1→6)-1,2:3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**19**).—Glucosamine phosphate **18** (117 mg, 0.15 mmol) and galactopyranoside acceptor **1** (26 mg, 0.10 mmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1 mL). The solution was cooled to −20 °C, and TMSOTf (150 μL, 150 μmol, 1.0 M in CH_2Cl_2) was added. After 2 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (1:4 EtOAc–hexanes) to yield 75 mg (91%) of **19** as a white solid. $[\alpha]_D$ −8.9° (*c* 1.01, CH_2Cl_2); IR (thin film): 1776, 1715, 1387, 1069 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.20 (m, 15H), 5.49 (d, *J* 15.0 Hz, 1H), 5.12 (d, *J* 12.3 Hz, 1H), 5.05 (d, *J* 12.3 Hz, 2H), 4.83 (d, *J* 10.9 Hz, 1H), 4.76 (d, *J* 11.0 Hz, 1H), 4.67 (d, *J* 11.0 Hz, 1H), 4.57 (d, *J* 10.8 Hz, 1H), 4.54 (dd, *J* 2.4, 9.4 Hz, 1H), 4.34 (d, *J* 11.6 Hz, 1H), 4.30–4.22 (m, 2H), 4.18 (d, *J* 8.0 Hz, 1H), 3.99–3.88 (m, 3H), 3.78–3.69 (m, 1H), 3.59–3.52 (m, 2H), 2.76–2.69 (m, 1H), 2.62–2.53 (m, 2H), 2.14 (s, 3H), 1.47 (s, 3H), 1.42 (s, 3H), 1.30 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.5, 172.6, 156.1, 138.2, 137.9, 136.7, 128.6, 128.1, 128.0, 127.9, 109.5, 108.8, 100.9, 96.4, 81.7, 78.2, 77.4, 75.2, 74.9, 73.0, 71.2, 70.8, 70.5, 68.3, 67.8, 66.8, 63.4, 57.5, 38.0, 30.0, 28.0, 26.1, 25.1, 24.5; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 856.3521, obsd 856.3546.

3,4-Di-O-*acetyl-2-deoxy-6*-O-*levulinyl-2-benzyloxycarbonylamino-β*-D-*glucopyranosyl-(1→6)-1,2:3,4-di*-O-*isopropylidene-α*-D-*galactopyranoside* (**21**).—Glucosamine phosphate **20** (80 mg, 0.116 mmol) and galactopyranoside acceptor **1** (20 mg, 77 μmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1 mL). The solution was cooled to −20 °C, and TMSOTf (116 μL, 116 μmol, 1.0 M in CH_2Cl_2) was added. After 2 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to yield 45 mg (81%) of **21** as a white solid. $[\alpha]_D$ −18.5 (*c* 1.03, CH_2Cl_2); IR (thin film): 3348, 2986, 1746, 1350, 1372 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5H), 5.50 (d, *J* 5.2 Hz, 1H), 5.25–5.12 (m, 2H), 5.07 (dd, *J* 9.4, 9.5 Hz, 1H), 5.02–4.96 (m, 2H), 4.86–4.78 (m, 1H), 4.55 (dd, *J* 2.4, 7.9 Hz, 1H), 4.28 (dd, *J* 2.4, 4.9 Hz, 1H), 4.26 (dd, *J* 4.6, 12.2 Hz, 1H), 4.16 (dd, *J* 1.5, 7.9 Hz, 1H), 4.12 (dd, *J* 2.1, 12.5 Hz, 1H), 4.00–3.90 (m, 2H), 3.80 (dd, *J* 7.6, 12.2 Hz, 1H), 3.78–3.66 (m, 2H), 2.79–2.62 (m, 2H), 2.54–2.40 (m, 2H), 2.15 (s, 3H), 2.07 (s, 3H), 1.95 (s, 3H), 1.44 (s, 3H), 1.43 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 171.5, 171.1, 171.0, 156.1, 136.6, 128.6, 128.3, 128.2, 109.6, 109.0, 96.4, 77.4, 72.7, 72.0, 71.3, 70.8, 70.4, 68.8, 68.6, 67.0, 62.2, 56.2, 37.9, 29.8, 27.9, 26.1, 25.1, 24.5, 21.0, 20.8; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 760.2793, obsd 760.2756.

6-O-*Acetyl-3,4-di*-O-*benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β*-D-*glucopyranosyl-(1→6)-1,2;3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**23**).—Glucosamine trichloroacetimidate **22** (126 mg, 0.18 mmol) and galactopyranoside **1** (38 mg, 0.15 mmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1.7 mL). The solution was cooled to −20 °C, and TBSOTf (36 μL, 18 μmol, 0.5 M in CH_2Cl_2) was added. After 1 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to yield 103 mg (87%) of **23** as a white solid. $[\alpha]_D$ +25.0° (*c* 0.40, CH_2Cl_2); IR (thin film): 3342, 1740, 1537, 1236, 1070 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.19 (m, 10H), 5.51 (d, *J* 5.0 Hz, 2H), 5.25 (bs, 1H), 4.85 (d, *J* 10.8 Hz, 1H), 4.82 (d, *J* 11.1 Hz, 1H), 4.77 (d, *J* 11.1 Hz, 1H), 4.68–4.61 (m, 1H), 4.61–4.54 (m, 2H), 4.40–4.33 (m, 1H), 4.30 (dd, *J* 2.4, 5.0 Hz, 1H), 4.27–4.21 (m, 1H), 4.19 (dd, *J* 1.7, 7.9 Hz, 1H), 4.01–3.84 (m, 3H), 3.72 (dd, *J* 8.5, 12.5 Hz, 1H), 3.64–3.55 (m, 2H), 3.55–3.41 (m, 1H), 2.00 (s, 3H), 1.54 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 154.3, 138.1, 137.8, 128.7, 128.6, 128.2, 128.0, 109.5, 108.8, 101.0, 96.4, 95.7, 81.2, 78.3, 77.4, 75.1, 75.0, 74.7, 73.1, 70.9, 70.8, 70.7, 68.6, 67.9, 63.2, 57.7, 56.2, 56.1, 25.2, 24.5, 24.4, 21.1; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 840.1927, obsd 840.1937.

*3,4-Di-*O*-acetyl-2-deoxy-6-*O*-levulinyl-2-trichloroacetylamino-β-*D*-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**25**).—Glucosamine trichloroacetimidate **24** (78 mg, 0.12 mmol) and galactopyranoside **1** (26 mg, 0.10 mmol) were azeotroped with toluene (3 × 3 mL) and dried under vacuum for 1 h. CH_2Cl_2 (1.0 mL) was added to the mixture, the solution cooled to −20 °C, and a solution of TMSOTf (24.0 μL, 0.012 mmol, 0.5 M in CH_2Cl_2) was added. After 1 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to afford 66 mg (88%) of **25** as a white solid. $[\alpha]_D$ −28.5° (*c* 0.84, CH_2Cl_2); IR (thin film): 3320, 1749, 1717, 1373 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* 8.9 Hz, 1H), 5.43 (d, *J* 5.0 Hz, 1H), 5.37 (dd, *J* 9.5, 10.5 Hz, 1H), 5.10 (dd, *J* 9.7, 9.7 Hz, 1H), 4.77 (d, *J* 8.3 Hz, 1H), 4.53 (dd, *J* 2.3, 7.9 Hz, 1H), 4.28–4.20 (m, 2H), 4.17 (dd, *J* 1.7, 7.9 Hz, 1H), 4.11 (dd, *J* 2.0, 12.3 Hz, 1H), 4.05–3.93 (m, 2H), 3.93–3.84 (m, 1H), 3.73 (ddd, *J* 2.1, 4.8, 9.9 Hz, 1H), 3.66 (dd, *J* 6.8, 10.8 Hz, 1H), 2.83–2.71 (m, 1H), 2.71–2.59 (m, 1H), 2.53–2.34 (m, 2H), 2.13 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 171.7, 171.0, 162.2, 109.3, 108.7, 101.0, 96.3, 92.4, 77.4, 72.2, 71.6, 71.0, 70.6, 70.5, 68.5, 67.2, 62.1, 55.9, 37.8, 29.8, 29.7, 27.8, 26.3, 26.1, 25.1, 24.5, 20.9, 20.8; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 770.1362, obsd 770.1356.

*3,4-Di-*O*-benzyl-2-deoxy-6-*O*-levulinyl-2-trichloroacetylamino-β-*D*-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**27**).—Glucosamine phosphate **26** (67 mg, 86 μmol) and galactopyranoside acceptor **1** (19 mg, 71 μmol) were azeotroped with toluene (3 × 1 mL), then dried under vacuum for 3 h. Residue dissolved in CH_2Cl_2 (2 mL) and cooled to −20 °C. TMSOTf (15 μL, 85 μmol) was added, and the solution was allowed to slowly warm to −10 °C over 30 min, before quenching with TEA (20 μL). The reaction mixture was warmed to ambient temperature and concentrated in vacuo. The resulting residue was purified by flash silica gel chromatography (25:75 → 40:60 EtOAc–hexanes) to afford 33 mg (50%) of the desired disaccharide **27** as a white solid. $[\alpha]_D$ −22.4° (*c* 2.16 CH_2Cl_2); IR (thin film): 3325, 2988, 1736, 1718, 1697 cm^{-1};^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 10H), 7.14 (d, *J* 7.8 Hz, 1H), 5.49 (d, *J* 5.0 Hz, 1H), 4.92 (d, *J* 7.5 Hz, 1H), 4.82 (d, *J* 11.0 Hz, 1H), 4.89 (d, *J* 11.1 Hz, 1H), 4.74 (d, *J* 10.8 Hz, 1H), 4.61 (d, *J* 10.9 Hz, 1H), 4.57 (dd, *J* 1.8, 7.9 Hz, 1H), 4.16 (dd, *J* 7.9, 9.4 Hz, 1H), 4.01 (dd, *J* 5.5, 10.6 Hz, 1H), 3.96–3.92 (m, 1H), 3.72–3.59 (m, 4H), 2.78–2.72 (m, 2H), 2.60 (app t, *J* 6.4 Hz, 2H), 2.19 (s, 3H), 1.50 (s, 3H), 1.43 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 172.7, 162.1, 137.8, 137.6, 128.7, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 109.5, 108.8, 97.8, 96.4, 92.6,79.5, 78.0, 77.4, 75.0, 74.8, 73.1, 71.1, 70.7, 70.6, 68.7, 66.9, 63.4, 57.6, 38.3, 38.1, 30.1, 28.1, 26.3, 26.2, 25.1, 24.6; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 866.2083, obsd 866.2071.

*Methyl 3,4-di-*O*-benzyl-2-deoxy-6-*O*-levulinyl-2-phthalimido-β-*D*-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-*D*-galactopyranoside* (**29**).—Glucosamine phosphate **10** (63 mg, 81 μmol) and galactopyranoside acceptor **28** (25 mg, 54 μmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1 mL). The solution was cooled to −20 °C, and TMSOTf (81 μL, 81 μmol, 1.0 M in CH_2Cl_2) was added. After 2 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (1:4 EtOAc–hexanes) to yield 54 mg (96%) of **29** as a white solid. $[\alpha]_D$ +10.8° (*c* 1.00, CH_2Cl_2); IR (thin film): 1775, 1715, 1389, 1099 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62–7.32 (m, 4H), 7.23–7.12 (m, 10H), 7.12–7.06 (m, 4H), 7.02–6.97 (m, 3H), 6.88–6.84 (m, 2H), 6.81–6.73 (m, 3H), 6.72–6.67 (m, 1H), 5.27 (d, *J* 8.2 Hz, 1H), 4.78 (d, *J* 11.3 Hz, 1H), 4.73 (d, *J* 11.0 Hz, 1H), 4.68 (d, *J* 11.9 Hz, 1H), 4.50 (d, *J* 11.0 Hz, 1H), 4.39 (dd, *J* 8.2, 10.7 Hz, 1H), 4.34 (d, *J* 11.6 Hz, 1H), 4.30 (d, *J* 11.9 Hz, 1H), 4.27 (d, *J* 11.9 Hz, 1H), 4.21 (d, *J* 11.9 Hz, 1H), 4.17 (3d, *J* 4.6, 11.9 Hz, 1H), 4.14 (dd, *J* 8.6, 11.0 Hz, 1H), 4.01 (d, *J* 3.7 Hz, 1H), 3.95 (d, *J* 12.8 Hz, 1H), 3.86 (dd, *J* 2.8, 10.1 Hz, 1H), 3.84–3.80 (m, 1H), 3.70–3.68 (m, 1H), 3.62–3.56 (m, 2H), 3.54 (dd, *J* 8.2, 9.8 Hz, 1H), 3.44 (dd, *J* 3.7, 10.1 Hz, 1H), 3.29 (dd, *J* 2.1, 6.1 Hz, 1H), 3.00 (s, 3H), 2.47–2.40 (m, 2H), 2.34–2.28 (m, 2H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 172.6, 167.9, 167.8, 139.1, 138.6, 138.3, 138.1, 137.7, 133.9, 131.7, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.1, 123.4, 99.8, 98.8, 79.5, 79.4, 78.9, 77.7, 77.4, 75.3, 75.2, 75.1, 73.5, 72.8, 69.6, 69.2, 69.6, 69.2, 63.1, 56.6, 55.2, 37.9, 29.9, 28.0; ESI FT-MS: *m*/*z* $(M + Na)^+$ calcd 1056.4147, obsd 1056.4141.

n-*Pentenyl-3,4-di-*O*-benzyl-2-deoxy-6-*O*-levulinyl-2-phthalimido-β-*D*-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-*D*-glucopyranoside* (**31**).—Glucosamine phosphate **10** (91 mg, 117 μmol) and glucopyranoside acceptor **30** (40 mg, 78 μmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1 mL). The solution was cooled to −20 °C, and TMSOTf (234 μL, 117 μmol, 0.5 M in CH_2Cl_2) was added. After 2 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (1:4 EtOAc–hexanes) to yield 60 mg (71%) of **31** as a white solid. $[\alpha]_D$ +1.55° (*c* 0.91, CH_2Cl_2); IR (thin film): 1775, 1738, 1713, 1388, 1153 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85–7.53 (m, 4H), 7.39–7.18 (m, 17H), 7.00–6.95 (m, 2H), 6.95–6.82 (m, 3H),

(m, 3H), 5.80–5.67 (m, 1H), 5.37 (d, *J* 8.4 Hz, 1H), 4.99–4.88 (m, 4H), 4.81 (d, *J* 10.8 Hz, 1H), 4.79 (d, *J* 11.9 Hz, 1H), 4.60 (d, *J* 11.9 Hz, 1H), 4.58 (d, *J* 10.8 Hz, 1H), 4.44–4.28 (m, 4H), 4.22 (d, *J* 7.9 Hz, 1H), 4.17–4.09 (m, 2H), 4.08–3.99 (m, 2H), 3.75–3.67 (m, 1H), 3.65–3.57 (m, 2H), 3.47 (dd, *J* 1.5, 11.1 Hz, 1H), 3.40–3.28 (m, 3H), 3.27–3.20 (m, 1H), 2.70–2.51 (m, 2H), 2.49–2.39 (m, 1H), 2.36–2.25 (m, 1H), 2.14 (s, 3H), 2.06–1.95 (m, 2H), 1.62–1.51 (m, 2H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 176.8, 172.5, 139.1, 138.3, 138.1, 137.9, 137.7, 134.0, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 127.1, 126.8, 123.4, 114.9, 101.1, 97.4, 81.3, 79.5, 79.2, 75.1, 74.8, 73.4, 72.8, 72.7, 72.5, 68.9, 68.2, 62.7, 56.6, 38.8, 38.0, 30.1, 29.9, 28.8, 27.9, 27.2; ESI FT-MS: m/z $(M + Na)^+$ calcd 1104.4722, obsd 1104.4171.

n-*Pentenyl-3,4-di*-O-*benzyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranoside* (**33**).—Glucosamine phosphate (**10**) (112 mg, 143 μmol) and *n*-pentenyl glucosamine acceptor **32** (70 mg, 119 μmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2C1_2 (2 mL). The solution was cooled to −20 °C, and TMSOTf (143 μL, 143 μmol, 1.0 M in CH_2Cl_2) was added. After 2 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (1:4 EtOAc–hexanes) to yield 103 mg (77%) of **33** as a white foam. $[\alpha]_D$ +27.4° (*c* 1.04, CH_2Cl_2); IR (thin film): 1774, 1714, 1453, 1389 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.38 (m, 8H), 7.35–7.13 (m, 9H), 7.13–7.01 (m, 2H), 7.01–6.89 (m, 2H), 6.89–6.65 (m, 8H), 5.52–5.31 (m, 1H), 5.21 (d, *J* 8.4 Hz, 1H), 4.88 (d, *J* 8.5 Hz, 1H), 4.83 (d, *J* 10.8 Hz, 1H), 4.74 (d, *J* 12.2 Hz, 1H), 4.67–4.51 (m, 4H), 4.46 (d, *J* 10.7 Hz, 1H), 4.42–4.19 (m, 6H), 4.18–4.08 (m, 2H), 4.02 (d, *J* 9.6 Hz, 1H), 3.95 (dd, *J* 8.5, 10.8 Hz, 1H), 3.71–3.53 (m, 3H), 3.48–3.38 (m, 2H), 3.34 (dd, *J* 8.6, 9.8 Hz, 1H), 3.17–3.02 (m, 1H), 2.74–2.60 (m, 2H), 2.59–2.47 (m, 2H), 2.11 (s, 3H), 1.70–1.57 (m, 2H), 1.36–1.13 (m, 2H); ^{13}C NMR (100 MHz, $CDC1_3$) δ 206.5, 172.6, 168.2, 167.7, 138.0, 137.9, 137.7, 137.6, 133.8, 131.6, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 123.4, 114.6, 98.0, 79.8, 79.4, 79.2, 77.4, 75.2, 75.0, 74.7, 74.6, 73.1, 68.5, 67.7, 63.0, 55.8, 55.7, 38.0, 30.0, 29.8, 28.4,28.1; ESI FT-MS: m/z $(M + Na)^+$ calcd 1149.4361, obsd 1149.4328.

n-*Pentenyl 3,4-di*-O-*benzyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranoside* (**34**).—Disaccharide **33** (93.0 mg, 82.5 μmol) was dissolved in pyridine (0.60 mL) and AcOH (0.40 mL) at 0 °C. Hydrazine monohydrate (20 μL, 0.41 mmol) was added, and the reaction mixture was stirred for 1 h, then diluted with Et_2O (10 mL), washed with HCl (10% in H_2O, 3 × 5 mL), H_2O, brine, and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to yield 79.7 mg (94%) of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside as a white foam. $[\alpha]_D$ +31.8° (*c* 0.98, CH_2Cl_2); IR (thin film): 3062, 1774, 1713, 1388 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82–7.52 (m, 8H), 7.42–7.21 (m, 10H), 7.15–7.09 (m, 2H), 7.03–6.98 (m, 2H), 6.97–6.93 (m, 2H), 6.91–6.80 (m, 6H), 5.55–5.46 (m, 1H), 5.27 (d, *J* 8.2 Hz, 1H), 4.98 (d, *J* 8.6 Hz, 1H), 4.90 (d, *J* 11.0 Hz, 1H), 4.82 (d, *J* 12.2 Hz, 1H), 4.75 (d, *J* 10.7 Hz, 1H), 4.73–4.69 (m, 1H), 4.64 (ddd, *J* 1.8, 3.7, 17.1 Hz, 1H), 4.58 (d, *J* 10.7 Hz, 1H), 4.46 (d, *J* 12.2 Hz, 1H), 4.40 (d, *J* 11.0 Hz, 1H), 4.39 (dd, *J* 8.5, 10.7 Hz, 1H), 4.34 (d, *J* 12.2 Hz, 1H), 4.23 (dd, *J* 8.3, 10.7 Hz, 1H), 4.23–4.20 (m, 1H), 4.04 (dd, *J* 8.2, 11.0 Hz, 1H), 3.99 (d, *J* 10.4 Hz, 1H), 3.96–3.90 (m, 1H), 3.84–3.68 (m, 4H), 3.59–3.46 (m, 4H), 3.24–3.16 (m, 1H), 2.26–2.20 (m, 1H), 1.80–1.68 (m, 2H), 1.43–1.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 167.7, 138.1, 138.0, 137.7, 133.8, 131.6, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.5, 127.2, 127.0, 123.4, 114.7, 98.4, 98.2, 79.7, 79.6, 79.3, 79.2, 77.4, 75.5, 75.2, 75.0, 74.8, 74.7, 68.8, 68.4, 62.0, 55.9, 29.9, 28.5; ESI FT-MS: m/z $(M + Na)^+$ calcd 1051.3993, obsd 1051.3974.

Glucosamine phosphate (**10**) (88 mg, 112 μmol) and *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (77 mg, 75 μmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1 mL). The solution was cooled to −20 °C, and TMSOTf (112 μL, 112 μmol, 1.0 M in CH_2Cl_2) was added. After 2 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (1:4 EtOAc–hexanes) to yield 94 mg (79%) of **34** as a white foam. $[\alpha]_D$ +23.4° (*c* 1.00, CH_2Cl_2); IR (thin film): 1774, 1713, 1388, 1108 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82–7.44 (m, 12H), 7.37–7.22 (m, 13H), 7.19–7.11 (m, 5H), 7.03–6.98 (m, 3H), 6.95–6.77 (m, 13H), 5.53–5.43 (m, 1H), 5.32 (d, *J* 8.6 Hz, 1H), 5.12 (d, *J* 8.6 Hz, 1H), 4.91 (d, *J* 8.6 Hz, 1H), 4.89 (d, *J* 10.9 Hz, 1H), 4.81 (d, *J* 12.2 Hz, 1H), 4.72–4.58 (m, 5H), 4.52 (d, *J* 10.4 Hz, 1H), 4.48–4.36 (m, 6H), 4.36–4.08 (m, 1H), 4.01 (d, *J* 8.5 Hz, 1H), 3.98 (d, *J* 8.5 Hz, 1H), 3.96–3.91 (m, 1H), 3.78 (dd, *J* 4.9, 11.3 Hz, 1H), 3.75–3.66 (m, 3H), 3.56–3.43 (m, 5H), 3.39–3.31 (m, 2H), 3.19–3.11 (m, 1H), 2.80–2.66 (m, 2H), 2.64–2.56 (m, 2H), 2.20 (s, 3H), 1.75–1.64 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.6, 172.6, 168.2, 167.7, 138.1, 138.0, 137.9, 137.8, 137.7, 137.6, 133.7, 131.6, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 123.4, 114.6,

98.1, 97.9, 79.7, 79.4, 79.3, 79.2, 77.4, 75.2, 75.0, 74.9, 74.8, 74.7, 74.6, 73.2, 68.3, 67.5, 67.4, 63.0, 55.8, 55.7, 38.0, 30.0, 29.9, 28.5, 28.1; ESI FT-MS: m/z $(M+Na)^+$ calcd 1620.6043, obsd 1620.6079.

n-*Pentenyl 3,4-di*-O-*benzyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranoside* (**35**).—Trisaccharide **34** (91 mg, 57 μmol) was dissolved in pyridine (0.60 mL) and AcOH (0.40 mL) at 0 °C. Hydrazine monohydrate (15 μL, 0.29 mmol) was added, and the reaction mixture was stirred for 1 h, then diluted with Et_2O (10 mL), washed with HCl (10% in H_2O, 3 × 5 mL), H_2O, brine, and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to yield 85 mg (99%) of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside as a white foam. $[\alpha]_D$ +21.4° (*c* 0.90, CH_2Cl_2); IR (thin film): 3062, 1774, 1713, 1388, 1069 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83–7.44 (m, 12H), 7.44–7.33 (m, 6H), 7.33–7.23 (m, 4H), 7.23–7.19 (m, 3H), 7.19–7.14 (m, 2H), 7.09–7.03 (m, 2H), 7.03–6.99 (m, 2H), 6.99–6.94 (m, 2H), 6.94–6.90 (m, 2H), 6.90–6.78 (m, 9H), 5.56–5.46 (m, 1H), 5.35 (d, *J* 8.3 Hz, 1H), 5.19 (d, *J* 7.9 Hz, 1H), 4.98 (d, *J* 8.5 Hz, 1H), 4.91 (d, *J* 10.9 Hz, 1H), 4.83 (d, *J* 12.2 Hz, 1H), 4.78 (d, *J* 10.9 Hz, 1H), 4.71 (d, *J* 10.8 Hz, 1H), 4.69 (d, *J* 11.9 Hz, 1H), 4.67 (d, *J* 12.2 Hz, 1H), 4.64 (ddd, *J* 1.5, 3.4, 17.1 Hz, 1H), 4.51 (d, *J* 10.7 Hz, 1H), 4.47 (d, *J* 11.9 Hz, 1H), 4.44–4.38 (m, 2H), 4.35 (d, *J* 5.5 Hz, 1H), 4.33–4.27 (m, 3H), 4.23 (dd, *J* 8.2, 10.9 Hz, 1H), 4.21 (dd, *J* 7.9, 14.9 Hz, 1H), 4.18 (dd, *J* 7.9, 10.7 Hz, 1H), 4.09 (d, *J* 10.4 Hz, 1H), 4.05 (dd, *J* 8.5, 10.9 Hz, 1H), 4.01–3.95 (m, 2H), 3.84 (dd, *J* 4.0, 11.3 Hz, 1H), 3.80 (t, *J* 8.9 Hz, 2H), 3.67–3.55 (m, 4H), 3.51 (dd, *J* 2.8, 9.8 Hz, 1H), 3.49–3.42 (m, 2H), 3.26–3.20 (m, 1H), 1.79–1.67 (m, 2H), 1.43–1.24 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 167.7, 138.1, 138.0, 137.9, 137.7, 137.6, 133.8, 131.6, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.4, 127.1, 123.4, 114.6, 98.4, 98.3, 98.0, 79.6, 79.5, 79.3, 79.2, 79.1, 77.4, 75.7, 75.2, 74.9, 74.7, 74.6, 68.6, 68.0, 67.9, 61.7, 56.0, 55.8, 55.7, 29.9, 29.8, 28.5; ESI FT-MS: m/z $(M+Na)^+$ calcd 1522.5675, obsd 1522.5802.

Glucosamine phosphate **10** (65.0 mg, 84 μmol) and the *n*-pentenyl glucosamine acceptor, *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (83 mg, 55 μmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1 mL). The solution was cooled to −20 °C, and TMSOTf (84 μL, 84 μmol, 1.0 M in CH_2Cl_2) was added. After 2 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (1:4 EtOAc–hexanes to yield 93 mg (81%) **35** as a white foam. $[\alpha]_D$ +19.5° (*c* 0.99, CH_2Cl_2); IR (thin film): 1775, 1713, 1388, 1061 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.84–7.44 (m, 12H), 7.42–7.24 (m, 12H), 7.20–7.12 (m, 4H), 7.05–6.78 (m, 16H), 5.52–5.40 (m, 1H), 5.27 (d, *J* 8.5 Hz, 1H), 5.14 (d, *J* 8.2 Hz, 1H), 5.08 (d, *J* 8.2 Hz, 1H), 4.94 (d, *J* 8.2 Hz, 1H), 4.92 (d, *J* 10.7 Hz, 1H), 4.84 (d, *J* 12.2 Hz, 1H), 4.73–4.58 (m, 5H), 4.54 (d, *J* 10.7 Hz, 1H), 4.50–4.38 (m, 6H), 4.36–4.25 (m, 4H), 4.25–4.18 (m, 2H), 4.17–4.08 (m, 3H), 4.05 (dd, *J* 8.2, 10.7 Hz, 1H), 3.98 (d, *J* 10.4 Hz, 1H), 3.84 (d, *J* 9.8 Hz, 1H), 3.75–3.70 (m, 1H), 3.69–3.63 (m, 1H), 3.63–3.56 (m, 2H), 3.54–3.47 (m, 2H), 3.44–3.35 (m, 3H), 3.31–3.25 (m, 1H), 3.18–3.12 (m, 1H), 2.80–2.70 (m, 2H), 2.66–2.58 (m, 2H), 2.20 (s, 3H), 1.75–1.63 (m, 2H), 1.40–1.20 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.6, 172.6, 168.8, 168.3, 138.1, 138.0, 137.9, 137.8, 137.7, 137.6, 134.0, 133.8, 131.5, 128.6 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 127.3, 127.0, 126.9, 123.5, 123.3, 114.6, 98.1, 97.9, 97.8, 97.7, 79.7, 79.4, 79.3, 79.2, 79.1, 77.5, 75.2, 75.0, 74.9, 74.8, 74.7, 74.6, 73.1, 68.3, 67.7, 67.0, 66.9, 63.0, 55.9, 55.8, 55.6, 38.0, 30.0, 29.9, 28.4, 28.0, 23.6; ESI FT-MS: m/z $(M+2Na)^{2+}$ calcd 1057.3812, obsd 1057.3797.

n-*Pentenyl 3,4-di*-O-*benzyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranoside* (**36**).—Tetrasaccharide **35** (81 mg, 39 μmol) was dissolved in pyridine (0.60 mL) and AcOH (0.40 mL) at 0 °C. Hydrazine monohydrate (10 μL, 0.20 mmol) was added, and the reaction mixture was stirred for 1 h, then diluted with Et_2O (10 mL), washed with HCl (10% in H_2O, 3 × 5 mL), H_2O, brine, and dried over Na_2SO_4. After filtration and concentration in vacuo, the crude product was purified by flash silica gel chromatography (2:3 EtOAc–hexanes) to yield 64 mg (83%) of *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside as a white foam. $[\alpha]_D$ +18.7° (*c* 1.03, CH_2Cl_2); IR (thin film): 1774, 1715, 1388, 1061 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81–7.45 (m, 16H), 7.43–7.19 (m, 18H), 7.18–7.13 (m, 4H), 7.09–7.05 (m, 2H), 7.03–6.99 (m, 2H), 6.96–6.79 (m, 18H), 5.50–5.40 (m, 1H), 5.30 (d, *J* 8.5 Hz, 1H), 5.19 (d, *J* 8.2 Hz, 1H), 5.12 (d,

J 8.2 Hz, 1H), 4.92 (d, *J* 8.5 Hz, 1H), 4.89 (d, *J* 11.0 Hz, 1H), 4.83 (d, *J* 12.2 Hz, 1H), 4.75 (d, *J* 11.0 Hz, 1H), 4.70–4.63 (m, 4H), 4.62–4.56 (m, 1H), 4.52–4.38 (m, 7H), 4.34–4.26 (m, 5H), 4.24–4.11 (m, 6H), 4.08–3.94 (m, 4H), 3.89 (dd, *J* 1.5, 11.6 Hz, 1H), 3.82–3.76 (m, 3H), 3.72–3.64 (m, 2H), 3.62–3.55 (m, 3H), 3.53–3.45 (m, 4H), 3.40–3.36 (m, 3H), 3.19–3.12 (m, 1H), 2.66–2.53 (m, 1H), 1.72–1.59 (m, 2H), 1.36–1.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 167.8, 138.1, 138.0, 137.8, 137.7, 133.8, 131.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.5, 127.4, 127.1, 123.4, 114.6, 98.3, 97.9, 97.8, 79.8, 79.6, 79.5, 79.3, 79.1, 79.0, 75.6, 75.1, 75.0, 74.9, 74.7, 74.6, 68.4, 68.0, 67.7, 67.2, 61.7, 56.0, 55.9, 55.8, 55.7, 29.9, 28.5; ESI FT-MS: m/z $(M+Na)^+$ calcd 1993.7357, obsd 1993.6614.

Glucosamine phosphate **10** (38 mg, 49 μmol) and tetrasaccharide acceptor *n*-pentenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (63 mg, 32 μmol) were azeotroped with toluene (3 × 3 mL), dried under vacuum for 1 h, and dissolved in CH_2Cl_2 (1 mL). The solution was cooled to −20 °C, and TMSOTf (49 μL, 49 μmol, 1.0 M in CH_2Cl_2) was added. After 2 h, Et_3N (100 μL) was added, the solution was concentrated in vacuo, and the crude product was purified by flash silica gel chromatography (1:4 EtOAc–hexanes) to yield 70 mg (86%) of **36** as a white foam. $[\alpha]_D$ +29.4° (*c* 0.78, CH_2Cl_2); IR (thin film): 1775, 1714, 1388, 1066 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–7.44 (m, 20H), 7.44–6.98 (m, 30H), 6.97–6.75 (m, 20H), 5.45–5.35 (m, 1H), 5.22 (d, *J* 8.2 Hz, 1H), 5.08 (d, *J* 8.2 Hz, 1H), 5.05 (d, *J* 8.2 Hz, 1H), 4.93 (d, *J* 8.2 Hz, 1H), 4.90 (d, *J* 8.9 Hz, 1H), 4.84 (d, *J* 12.2 Hz, 1H), 4.74–4.60 (m, 5H), 4.60–4.49 (m, 3H), 4.46 (d, *J* 11.9 Hz, 1H), 4.44–4.35 (m, 4H), 4.34–4.16 (m, 9H), 4.15–4.06 (m, 3H), 4.04–3.94 (m, 2H), 3.88 (d, *J* 10.4 Hz, 1H), 3.76–3.61 (m, 4H), 3.59–3.31 (m, 8H), 3.20–3.08 (m, 2H), 2.82–2.69 (m, 2H), 2.68–2.54 (m, 2H), 2.18 (s, 3H), 1.71–1.57 (m, 2H), 1.34–1.17 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.9, 172.9, 168.5, 168.0, 138.4, 138.3, 138.2, 138.1, 138.0, 134.4, 134.1, 131.8, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 123.8, 114.8, 98.5, 98.3, 98.1, 98.0, 80.3, 80.0, 79.9, 79.8, 79.6, 79.4, 79.3, 77.4, 75.6, 75.5, 75.3, 75.2, 75.1, 75.0, 74.9, 74.8, 73.4, 68.6, 68.2, 67.5, 67.2, 66.8, 63.3, 56.2, 56.1, 38.3, 30.3, 30.2, 28.7, 28.4; ESI FT-MS: m/z $(M+Na)^{2+}$ calcd 1292.9653, obsd 1292.9695.

Automated solid-phase synthesis.—General Procedure A. Automated glycosylation using glucosamine phosphates. Octenediol functionalized resin (1 equiv) was washed with CH_2Cl_2 (6 × 2 mL) before beginning automation. Glucosamine phosphate (5 equiv) was added, as a solution in CH_2Cl_2 (4 mL). After cooling to −15 °C, TMSOTf (5 equiv, 0.125 M in CH_2Cl_2) was added, the reaction mixture shaken for 30 min. The reaction vessel was drained, and the resin was washed with CH_2Cl_2 (6 × 2 mL). A second quantity of glucosamine phosphate (5 equiv was again added to the reaction vessel as a solution in CH_2Cl_2, and the mixture shaken an additional 30 min. The vessel was drained, and the resin was washed again with CH_2Cl_2 (6 × 2 mL).

General Procedure B. Automated cleavage of levulinyl esters. The resin-bound saccharide (1 equiv) was washed with THF (6 × 2 mL). Hydrazine monohydrate (20 equiv, 0.5 M in 2:3 AcOH–Pyr.), was added, and the reaction mixture shaken for 30 min at 15 °C. The reaction vessel was drained, and the deprotection was repeated by a second addition of hydrazine monohydrate (20 equiv), 0.5 M in 2:3 AcOH–Pyr.), and the reaction mixture was shaken for 30 min. The reaction vessel was drained, and the resin was washed with AcOH–MeOH (0.2 M in THF, 6 × 2 mL), THF (6 × 2 mL), and CH_2Cl_2 (6 × 2 mL).

General Procedure C. Cleavage of saccharides from resin. The resin-bound saccharide (1 equiv) was placed in a round-bottom flask, and CH_2Cl_2 (2 mL) was added. Following addition of Grubbs' catalyst (0.2 equiv), the suspension was stirred under an ethylene atmosphere for 48 h. Tri(hydroxymethyl)phosphine (10 equiv) was added, and the solution was stirred until the color turned yellow, then diluted with CH_2Cl_2 (5 mL), washed with H_2O (5 × 5 mL), brine, dried over Na_2SO_4, filtered and concentrated. Purification by flash silica chromatography yielded the *n*-pentenyl saccharide.

n-*Pentenyl 3,4-di*-O-*benzyl-2-deoxy-6*-O-*levulinyl-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di*-O-*benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside* (**34**).—General Procedure A using functionalized polystyrene resin **37** (25 mg, 1 mmol/g, 25 μmol) and glucosamine phosphate 10 (97 mg, 125 μmol) was followed by general Procedure **B**. The process was repeated three times, and then followed by general Procedure **C** to afford 6 mg (17%) of **34**, and 3 mg (9%) of disaccharide **33**. Analytical and NMR spectral data matched those of the compounds made by solution-phase synthesis.

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