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Synthesis and NMR characterization of the six regioisomeric monophosphates of octyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside

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

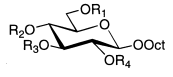
Abstract

All six regioisomeric monophosphates of octyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside have been chemically synthesized and characterized by high-resolution ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Phosphorylation causes characteristic downfield shifts of the nucleus at the substituted site in the ^{1}H and ^{13}C NMR signals and resulted in a unique ^{31}P signal for each compound. © 2002 Elsevier Science Ltd. All rights reserved.

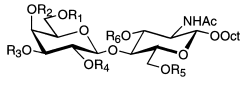
Keywords: Disaccharide-phosphate; Monophosphates; *N*-acetyllactosamine; NMR spectroscopy; Phosphorylation

1. Introduction

Phosphorylation is ubiquitous in nature and often used transiently in signaling,[1] but very rarely are phosphorylated oligosaccharides encountered. Preliminary characterization of complex oligosaccharides usually relies on ^{1}H NMR spectroscopy, where any phosphates (or sulfates) would be "invisible".[2] The availability of well-characterized standards of phosphorylated oligosaccharides and especially those of the ubiquitous terminal *N*-acetyllactosamine (LacNAc) units should therefore facilitate the detection of species should they occur, or at least eliminate their possible presence in unidentified anionic oligosaccharrides.



	R_1	R_2	R_3	R_4
1	PO_3Na_2	H	H	H
2	H	PO_3Na_2	H	H
3	H	H	PO_3Na_2	H
4	H	H	H	PO_3Na_2



	R_1	R_2	R_3	R_4	R_5	R_6
5	PO_3Na_2	H	H	H	H	H
6	H	PO_3Na_2	H	H	H	H
7	H	H	PO_3Na_2	H	H	H
8	H	H	H	PO_3Na_2	H	H
9	H	H	H	H	PO_3Na_2	H
10	H	H	H	H	H	PO_3Na_2

Fig. 1. Synthetic targets.

Herein we report the synthesis and ^{1}H, ^{13}C and ^{31}P NMR characterization of the four monophosphates of octyl β-D-Glc, model compounds for methodology development, and the six regioisomeric monophosphates of octyl β-LacNAc (Fig. 1).

2. Results and discussion

Chemical synthesis.—The four isomeric monophosphates of octyl β-D-Glc and the six isomeric monophosphates of octyl β-LacNAc were prepared using reported synthetic methods. The simpler monosaccharide phosphates were prepared first to establish the reaction conditions for selective protection, phosphorylation and

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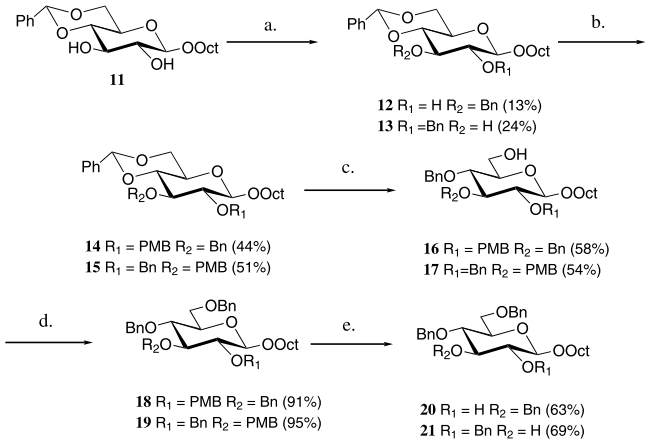
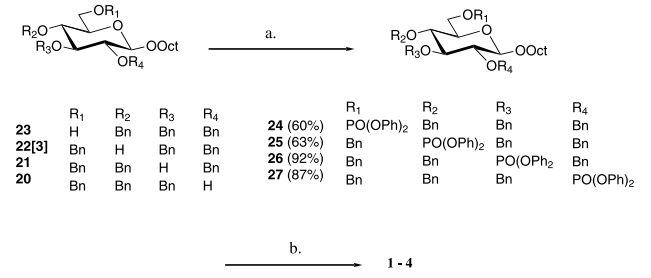
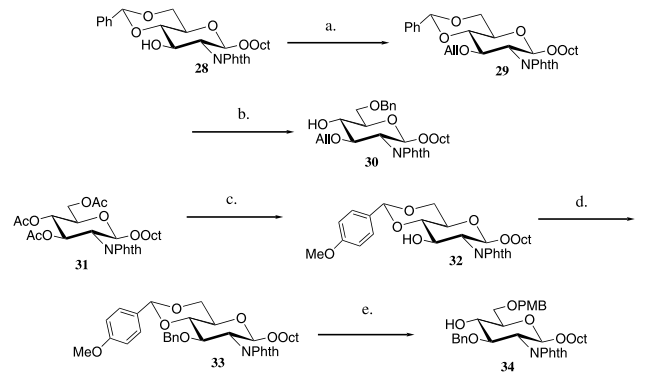


Scheme 1. Reagents: (a) Bu_4Br, 15% NaOH, BnBr, DCM. (b) PMB–Cl, NaH, DMF. (c) $LiAlH_4$, $AlCl_3$, Et_2O. (d) BnBr, NaH, DMF. (e) DDQ. DCM.



Scheme 2. Reagents: (a) $(PhO)_2POCl$, DMAP, pyr. (b) (i) 5% Pd–C, 95% EtOH, H_2. (ii) PtO_2, 95% EtOH, H_2.



Scheme 3. Reagents: (a) AllCl, DMF, NaH (56%). (b) $NaCNBH_3$, HCl Et_2O, THF (96%). (c) (i) NaOMe–MeOH. (ii) *p*TsOH, DMF, anisaldehyde dimethyl acetal (90% over two steps). (d) BnBr, NaH, DMF (81%). (e) $NaCNBH_3$, CF_3COOH, DMF, 0 °C, (82%).

deprotection that would later be applied to the more complex LacNAc targets.

Synthesis of the selectively blocked monosaccharides began from known octyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**11**),[3] which was subjected to selective benzylation using phase-transfer conditions to afford the 3-*O*-benzyl **12** (13%) and 2-*O*-benzyl **13** (24%) derivatives. In order to determine the stereochemistry of the two regioisomers, small amounts of **12** and **13** were acetylated to afford **12′** and **13′**, which could then be characterized. Further reaction with *p*-methoxybenzyl chloride (PMB-Cl) gave **14** (44%) and **15** (51%). Regioselective opening of the benzylidene acetals **14** and **15** gave **16** (58%) and **17** (54%), respectively. O-Benzylation gave the fully protected **18** (91%) and **19** (95%). Selective removal of the PMB ether provided **20** (63%) and **21** (69%) (Scheme 1). Phosphoryation of octyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**22**),[4] octyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**23**),[5] **20** and **21** using diphenyl phosphorochloridate and DMAP in pyridine[6] gave the phosphoric triesters **24** (60%), **25** (63%), **26** (92%) and **27** (87%). Deprotection of the benzyl ethers and phenyl phosphoesters then provided the phosphates **1** (90%), **2** (84%), **3** (90%) and **4** (78%) (Scheme 2).

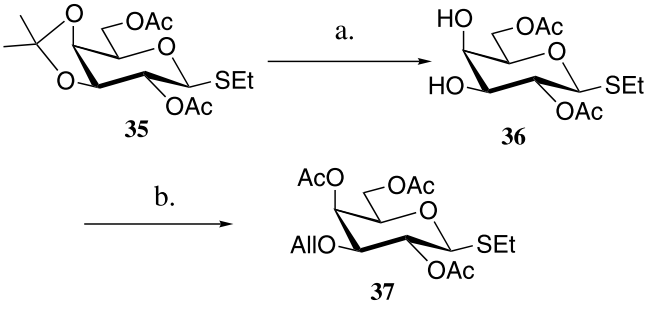
The synthesis of the selectively blocked disaccharides required three unique acceptors and three unique donors. Octyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (**28**)[7] was treated with allyl chloride and sodium hydride in DMF to afford **29** (56%), followed by regioselective opening of the benzylidene acetal to give **30** (96%) (Scheme 3). Octyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**31**)[6] was deacetylated and reacted with anisaldehyde dimethyl acetal and *p*-toluenesulfonic acid monohydrate in acetonitrile to afford **32** (38%). The free OH group in **32** was converted to the benzyl ether, and the *p*-methoxybenzylidene acetal was then regioselectively opened to give **34** (62%) (Scheme 3). Treatment of ethyl 2,6-di-*O*-acetyl-3,4-di-*O*-isopropylidene-1-thio-β-D-galactopyranoside (**35**)[8] with 70% acetic acid gave **36** (95%). The stannylidene intermediate was prepared, and regioselective alkylation with allyl bromide afforded three compounds that were isolated from the mixture. ^1H NMR analysis revealed that, although the regioselective alkylation was successful, the acetate protecting groups had migrated during the course of the reaction. All three compounds were pooled and then O-acetylated resulting in the formation of the single compound **37** (77%) (Scheme 4).

Glycosylation of octyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**38**)[7] with ethyl 4,6-*O*-benzylidene-thio-1-β-D-galactopyranoside (**39**)[9] afforded **40** (62%). Deacetylation gave **41**, which was reprotected by benzylation at OH-3 and OH-4 to afford **42** (66%). The benzylidene acetal was removed using 80% acetic acid to give **43** (92%). The 6-OH group was selectively protected as the trityl ether affording **44** (quant). The 4-OH group was protected as the benzyl ether to give **45** (84%). The trityl group was selectively removed using a solution of 5% trifluoroacetic acid and 5% triisopropylsilane to afford **46** (97%). Removal of the phthalimido group, followed by N-acetylation, gave

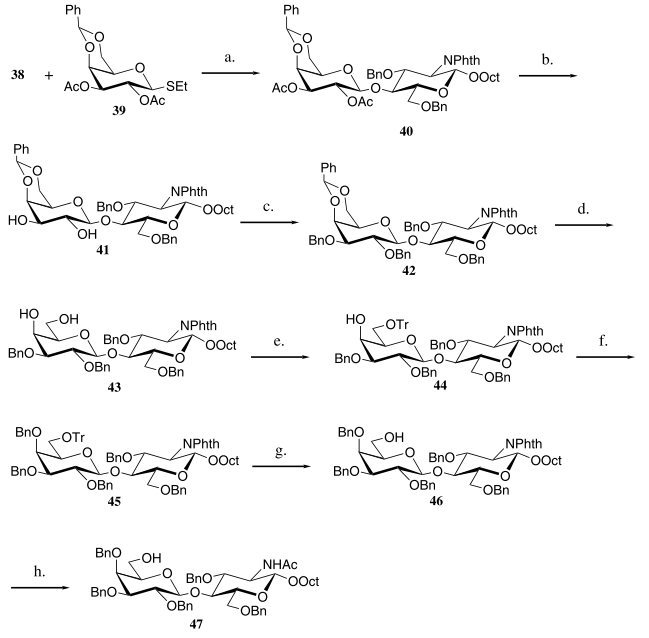
47 (86%) (Scheme 5). The regioselective opening of the acetal ring in **42** afforded **48** (57%). The removal of the phthalimido group and N-acetylation then gave **49** (90%) (Scheme 6).

Glycosylation of octyl 3,6,-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**38**)[7] with **37** afforded **50** (81%). Deactylation, followed by benzylation, afforded **51** (27%). The allyl protecting group was selectively removed with palladium chloride to give **52** (88%), followed by the removal of the phthalimido group and N-acetylation to give **53** (94%) (Scheme 6).

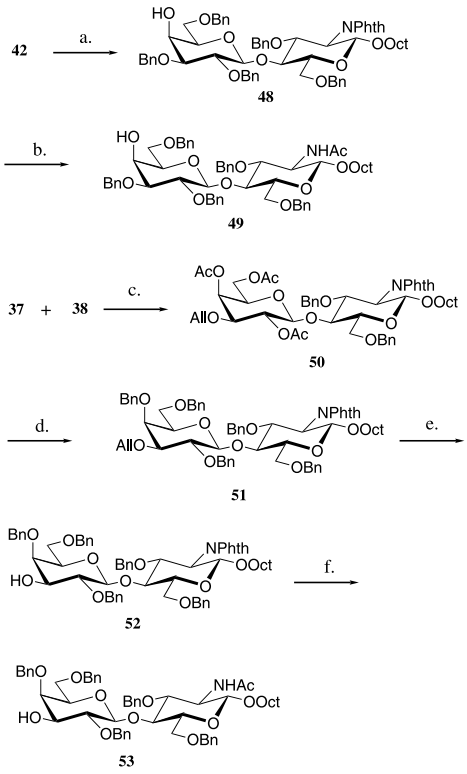
Glycosylation of octyl 3,6,-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**38**)[7] with ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-galactoside (**54**)[10]



Scheme 4. Reagents: (a) 70% AcOH, CH_3CN, 60 °C (95%). (b) (i) Bu_2SnO, tol. (ii) AllBr, Bu_4NBr. (iii) Ac_2O, pyr (77% over three steps).



Scheme 5. Reagents: (a) NIS, AgOTf, sieves 4 Å, DCM (62%). (b) NaOMe, MeOH (70%). (c) BnBr, NaH, Bu_4NI (66%). (d) 80% AcOH, 80 °C (92%). (e) TrCl, *i*-Pr_2NEt, DCM (quant.). (f) BnBr, NaH, Bu_4NI (84%). (g) 5% TFA, 5% TIS, DCM (97%). (h) (i) $NH_2CH_2CH_2NH_2$, *t*-BuOH. (ii) Ac_2O, MeOH, Et_3N (86% over two steps).



Scheme 6. Reagents: (a) $NaCNBH_3$, HCl Et_2O, sieves 4 Å, THF (57%). (b) (i) $NH_2CH_2CH_2NH_2$, *t*-BuOH. (ii) Ac_2O, MeOH, Et_3N (90% over two steps). (c) NIS, AgOTf, sieves 4 Å, DCM (81%). (d) (i) NaOMe, MeOH. (ii) BnBr, NaH, Bu_4NI (27% over two steps). (e) $PdCl_2$, DCM, (88%). (f) (i) $NH_2CH_2CH_2NH_2$, *t*-BuOH. (ii) Ac_2O, MeOH, Et_3N (94% over two steps).

afforded **55** (81%). The phthalimido and acetate groups were then removed concurrently, followed by N-acetylation to provide **56** (92%) (Scheme 7).

Glycosylation of **34** with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (**54**)[10] gave **57** (88%) which was O-deacetylated to afford **58** (77%). O-Benzylation then yielded **59** (35%). Selective deprotection with DDQ afforded **60** (59%), and removal of the phthalimido group, followed by N-acetylation gave **61** (82%) (Scheme 7).

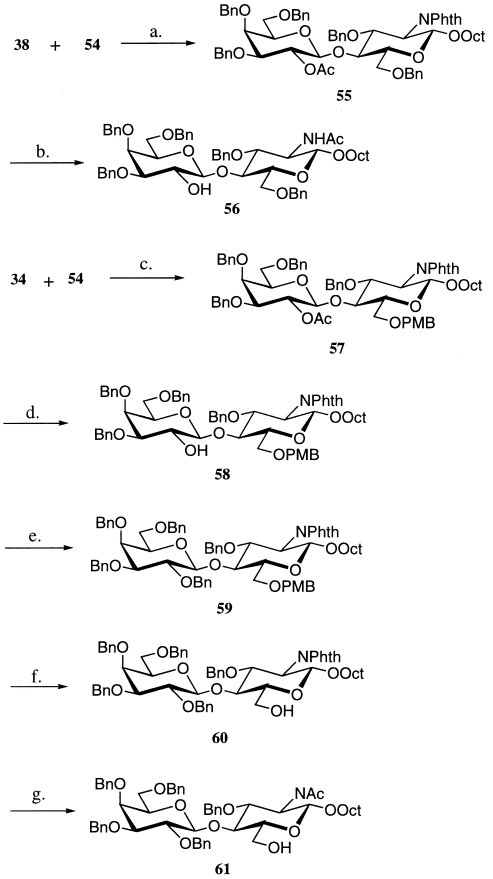
Glycosylation of **30** with **54**[10] gave **62** (80%). Removal of the acetate afforded **63** (78%), which was benzylated to give **64** (45%). Selective removal of the allyl protecting group with palladium chloride gave **65** (95%). Removal of the phthalimido group and N-acetylation afforded **66** (96%) (Scheme 8).

The six monohydroxy octyl β-LacNAc compounds **5**–**10** were functionalized and deprotected to give their respective phosphates. Compounds **47** and **53** were phosphorylated using the conditions established for the octyl β-Glc compounds to afford **67** (72%) and **68** (80%), respectively. Deprotection gave the final target compounds **5** (65%) and **7** (56%) (Scheme 9). Attempts to phosphorylate **66** under the same conditions were

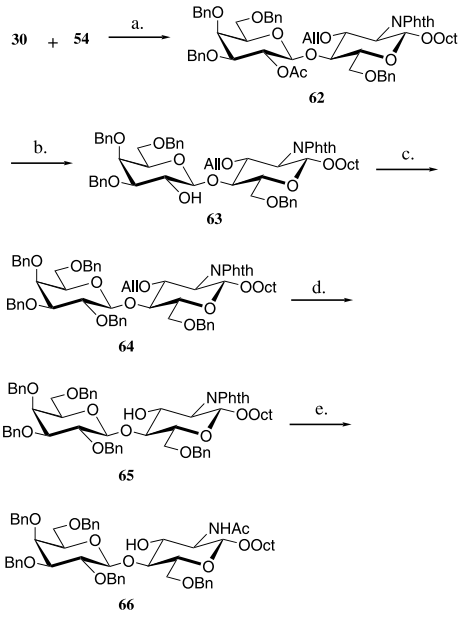
unsuccessful, and a different approach[11] had to be used. Compounds **49**, **56**, **61** and **66** were reacted with *N*,*N*-diethylphosphoramidite and 1,2,4-triazole in DCM to afford the phosphitylated compounds **69** (59%), **70** (89%), **71** (98%) and **72** (45%), which were oxidized to the phosphates **73** (79%), **74** (87%), **75** (85%) and **76** (66%). Hydrogenolysis gave the final target compounds **6** (73%), **8** (67%), **9** (73%) and **10** (71%) (Scheme 10).

NMR characterization.—The proton chemical shift and coupling constants for the monosaccharides **1**–**4** and the disaccharides **5**–**10** are presented in Tables 1–4. The chemical changes induced by the presence of a phosphate are presented in Figs. 2 and 3. All samples were run in a basic buffer of sodium deuteroxide (0.045 M) and sodium bicarbonate-d_1 (0.05 M) in D_2O to ensure complete ionization of the phosphate.

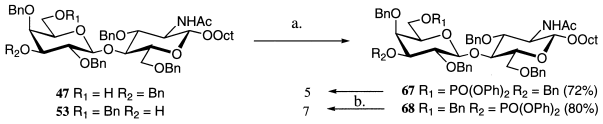
The changes in proton chemical shift due to phosphoryation are strongest at the site of substitution, with changes in the chemical shift typically 0.3–0.6 ppm downfield for the secondary alcohols and 0.2 ppm for the primary alcohols. The deshielding effects dramatically drop off with distance from the site of substitution with immediate neighboring sites exhibiting changes in the 0.1–0.2 ppm range or demonstrating no change



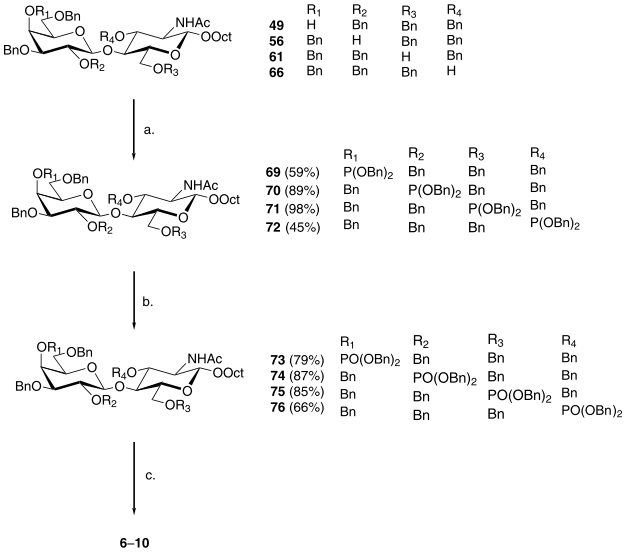
Scheme 7. Reagents: (a) NIS, AgOTf, 4 Å MS, DCM (81%). (b) (i) $NH_2CH_2CH_2NH_2$, *t*-BuOH. (ii) Ac_2O, MeOH, Et_3N (92%, two steps). (c) NIS, AgOTf, 4 Å MS, DCM (88%). (d) NaOMe, MeOH (77%). (e) BnBr, NaH, Bu_4NI, DMF (35%). (f) DDQ, DCM (59%). (g) (i) $NH_2CH_2CH_2NH_2$, *t*-BuOH. (ii) Ac_2O, MeOH, Et_3N (82%, two steps).



Scheme 8. Reagents: (a) NIS, AgOTf, sieves 4 Å, DCM (80%). (b) NaOMe, MeOH (78%). (c) BnBr, NaH, Bu_4NI (45%). (d) $PdCl_2$, DCM (95%). (e) (i) $NH_2CH_2CH_2NH_2$, *t*-BuOH. (ii) Ac_2O, MeOH, Et_3N (96%).



Scheme 9. Reagents: (a) $(PhO)_2POCl$, DMAP, pyr. (b) (i) Pd–C, H_2, 95% EtOH. (ii) PtO_2, H_2, 95% EtOH.



Scheme 10. Reagents: (a) $(BnO)_2PN(Et)_2$, 1,2,4-triazole. DCM. (b) 30% H_2O_2, THF. (c) Pd–C, H_2, 95% EtOH.

Table 1
^{1}H chemical shifts [a] of phosphorylated octyl β-Glc monosaccharides [b,c]

	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b
Octyl β-Glc	4.37	3.27	3.47	3.43	3.38	3.86	3.77
6-Phosphate **1**	4.43	3.27	3.48	3.59	4.02	3.96	3.44
4-Phosphate **2**	4.44	3.30	3.65	3.81	3.46	3.83	3.79
3-Phosphate **3**	4.50	3.34	3.94	3.47	3.47	3.89	3.69
2-Phosphate **4**	4.49	3.70	3.67	3.41	3.46	3.91	3.69

[a] Chemical shifts are referenced to external 0.1% acetone at 2.225 ppm.
[b] All data were recorded on a 600 MHz Varian Inova spectrometer in D_2O buffered with 0.05 M $NaDCO_3$/0.045 M NaOD. The temperature was 30.0 ± 0.1 °C.
[c] Geminal protons are not assigned stereospecifically. The higher chemical shift was arbitrarily assigned to H-6a.

with the exception of phosphorylation at a primary alcohol. The ^{1}H NMR spectra of the 6-phosphate of octyl-Glc (**9**) showed a relatively large downfield shift of H-4, as did the H-4′ of octyl β-LacNAc 6′-phosphate (**5**). The deshielding may be due to the spacial proximity of the phosphate at the 6-position and the proton at the 4-position. A downfield shift can also be observed for H-1′ in the ^{1}H spectra of octyl β-LacNAc 6-phosphate (**9**), again possibly due to the spacial proximity of the negatively charged phosphate and H-1′.

The analysis of the coupling constants for the phosphorylated octyl β-LacNAc compounds **5**–**10** is severely hampered by spectral overlap and higher order effects. The chemical shifts of H-2, H-3, and H-4 are almost identical for many of the compounds, leading to higher order coupling in the H-1 signal. Trends in coupling constants are difficult to discern with respect to the position of substitution.

The ^{13}C chemical shifts for compounds **1**–**4** are summarized in Table 5. The changes due to the substitution are approximately 3–4 ppm, with the effects being very site specific. Very little change was observed in the ^{13}C chemical shifts for any of the unsubstituted positions. The ^{13}C chemical shifts of the phosphorylated octyl β-LacNAc compounds **5**–**10** and the unsubstituted octyl β-LacNAc are presented in Table 6. The effect of phosphorylation is very complex, suggesting that conformational changes may accompany phosphorylation since no clear pattern of change on phosphorylation is apparent.

The ^{31}P chemical shifts and coupling constants for compounds **1**–**4** are shown in Table 7. The 6-phosphate had the expected ''doublet of doublet'' coupling pattern, while the other phosphates were doublets due to three-bond coupling with vicinal protons. The ^{31}P chemical shifts and coupling constants of the phosphorylated octyl β-LacNAc compounds **5**–**10** are presented in Table 8. The proton–phosphorous coupling of the 6-phosphate was too small to be observed resulting in a broad singlet. All the other coupling patterns were as expected, with all signals being doublets with the exception of the 6′-phosphate, which was a doublet of doublets. The 4′-phosphate showed the most dramatic downfield shift.

In conclusion, the six monophosphate esters of octyl β-LacNAc were chemically synthesized. Their ^{1}H, ^{13}C and ^{31}P NMR spectra reveal characteristic chemical shifts and/or coupling constants that should prove useful in detecting (or excluding) the presence of these structures in complex oligosaccharides isolated from natural sources.

3. Experimental

General methods.—Analytical TLC was performed on Silica Gel 60-F_{254} (E. Merck, Darmstadt) with detection by charring with 5% H_2SO_4 in EtOH or ninhydrin. All commercial reagents were used as supplied, unless otherwise stated. Column chromatography was performed on Silica Gel 60 (E. Merck, 40–63 μm, Darmstadt). Millex-GV (0.22 μm) filter units were from Millipore (Missisauga, ON). C_{18} Sep-Pak sample preparation cartridges were from Waters Associates (Missisauga, ON). ^{1}H NMR spectra were recorded at 300 MHz (Varian Inova 300), 500 MHz (Varian Unity 500) or 600 MHz (Varian Inova 600). ^{13}C NMR spectra

Table 2
^{1}H coupling constants [a] of phosphorylated octyl β-Glc monosaccharides [b,c,d]

	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
Octyl β-Glc	8.0	8.4	8.8	8.9	2.4	4.8	12.2
6-Phosphate **1**	8.0	9.1	9.3	9.5	3.5	2.6	11.3
4-Phosphate **2**	8.1	9.3	9.0	9.7	2.4	4.9	12.8
3-Phosphate **3**	8.2	8.4	8.8	[d]	2.6	[d]	11.0
2-Phosphate **4**	7.5	[d]	9.8	9.8	2.2	6.1	12.3

[a,b,c] See footnotes a,b,c, for Table 1. *J*-values are in Hz.
[d] Due to spectral overlap, the coupling constants could not be accurately determined.

Table 3
^{1}H chemical shifts [a] of phosphorylated octyl β-LacNAc disaccharides [b,c]

	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	H-1′	H-2′	H-3′	H-4′	H-5′	H-6a′	H-6b′
Octyl β-LacNAc	4.64	3.91	3.75	3.71	3.56	3.97	3.82	4.45	3.53	3.64	3.91	3.67	3.69	3.69
6′-Phosphate **5**	4.50	3.68	3.70	3.69	3.56	3.97	3.81	4.47	3.52	3.67	4.03	3.81	3.88	3.86
4′-Phosphate **6**	4.50	3.69	3.68	3.66	3.56	3.96	3.82	4.47	3.61	3.78	4.38	3.61	3.75	3.75
3′-Phosphate **7**	4.50	3.71	3.73	3.74	3.56	3.97	3.83	4.54	3.66	4.23	4.03	3.69	3.76	3.76
2′-Phosphate **8**	4.50	3.71	3.73	3.70	3.62	4.05	3.88	4.53	3.95	3.78	3.90	3.61	3.74	3.74
6-Phosphate **9**	4.52	3.71	3.79	3.81	3.65	4.04	4.04	4.66	3.44	3.70	3.91	3.66	3.74	3.74
3-Phosphate **10**	4.48	3.68	4.19	3.91	3.62	3.98	3.81	4.47	3.52	3.67	4.03	3.81	3.88	3.86

[a,b,c] See footnotes a,b,c, for Table 1.

Table 4
^{1}H coupling constants [a] of phosphorylated octyl β-LacNAc disaccharides [b,c]

	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6a'}$	$J_{5',6b'}$	$J_{6a',6b'}$
Octyl β-LacNAc	7.9	[d]	[d]	[d]	2.4	5.1	12.5	7.8	10.0	3.3	[d]	[d]	[d]	[d]
6′-Phosphate **5**	7.7	[d]	[d]	9.2	2.3	6.5	12.2	7.9	10.0	3.6	[d]	[d]	[d]	[d]
4′-Phosphate **6**	7.1	[d]	[d]	[d]	2.2	5.1	12.2	7.7	[d]	1.1	[d]	[d]	[d]	[d]
3′-Phosphate **7**	8.1	[d]	[d]	[d]	2.0	[d]	12.1	7.9	8.4	3.3	[d]	[d]	[d]	[d]
2′-Phosphate **8**	8.0	[d]	[d]	[d]	1.5	[d]	12.7	7.7	9.2	3.5	[d]	[d]	[d]	[d]
6-Phosphate **9**	8.4	8.8	9.2	9.2	[d]	[d]	[d]	8.0	10.2	3.5	[d]	[d]	[d]	[d]
3-Phosphate **10**	8.3	9.4	9.4	9.2	2.6	[d]	12.3	7.5	9.9	3.5	[d]	[d]	[d]	[d]

[a,b,c] See footnotes a,b,c, for Table 1. J-values are in Hz.
[d] Due to spectral overlap, the coupling constants could not be determined with accuracy.

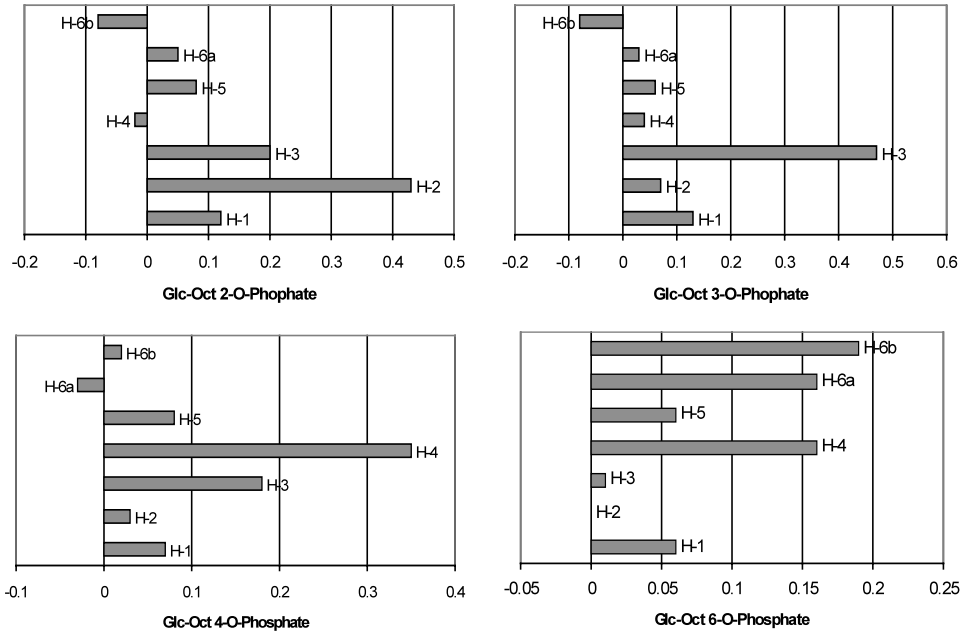


Fig. 2. ^{1}H NMR chemical shift changes (in ppm) induced by phosphate substitution at different positions of octyl β-Glc. Chemical shift changes are quoted in ppm relative to the unsubstituted octyl β-Glc. Only changes larger than ± 0.01 are shown.

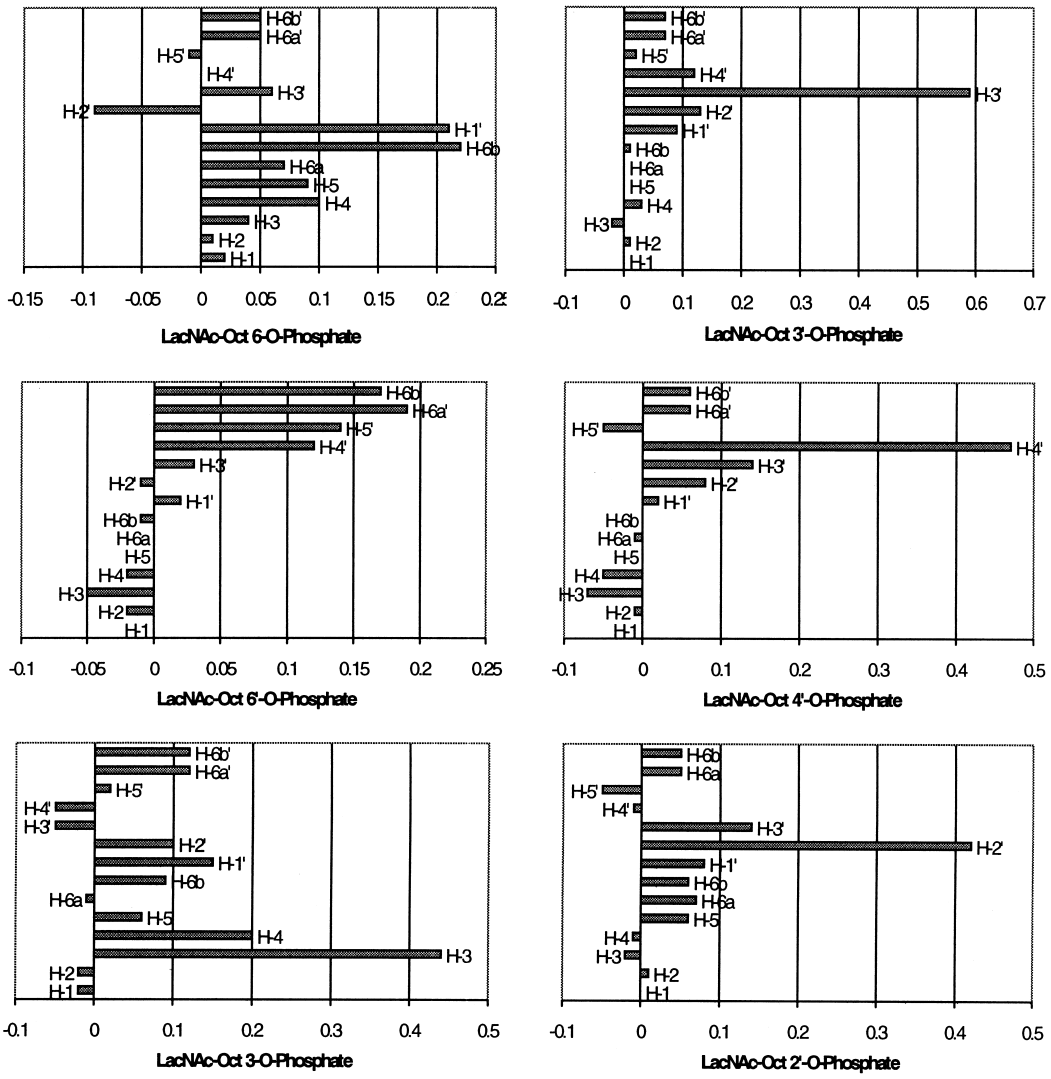


Fig. 3. ^{1}H NMR chemical shift changes (in ppm) induced by phosphate substitution at different positions of octyl β-LacNAc. Chemical shift changes are quoted in ppm relative to the unsubstituted octyl β-LacNAc. Only changes larger than ± 0.01 are shown.

were recorded either at 75 MHz (Bruker AM-300) or 125 MHz (Varian Unity 500). ^{31}P NMR spectra were recorded at 202 MHz (Varian Unity 500). The proton chemical shifts were referenced to solvent residual peaks for solutions in $CDCl_3$ ($CHCl_3$, δ 7.26), CD_3OD (CHD_2OD δ 5.32) or external 1% acetone (δ 2.225). The carbon chemical shifts were referenced to solvent signals for solutions in $CDCl_3$ (δ 77.06), CD_3OD (δ 53.80) or external 1% acetone (δ 31.07). The phosphorous chemical shifts were referenced to external 5% phosphoric acid (δ 0.00). High-resolution electrospray-ionization (HRESIMS) mass spectra were recorded on a Micro-Mass ZabSpec Hydroid Sector-TOF. Microanalyses were carried out by the analytical services at the department of Chemistry at the University of Alberta. Melting points are uncorrected. Dichloromethane (DCM) distilled from CaH_2 was used as the solvent for glycosidation.

Table 5
^{13}C chemical shifts [a] of phosphorylated octyl β-Glc monosaccharides [b]

	C-1	C-2	C-3	C-4	C-5	C-6
Octyl β-Glc	102.8	73.8	76.9	70.1	76.5	61.7
6-Phosphate **1**	103.6	73.8	76.3	69.3	75.3	64.5
4-Phosphate **2**	103.0	74.2	76.9	73.4	75.9	61.4
3-Phosphate **3**	103.0	73.8	81.7	70.3	76.5	61.7
2-Phosphate **4**	102.1	76.9	77.7	70.3	76.4	61.6

[a] Chemical shifts are referenced to external 0.1% acetone at 31.07 ppm.

[b] All data were recorded on a 500 MHz Varian Unity spectrometer in D_2O buffered with 0.05 M $NaDCO_3$/0.045 M NaOD. The temperature was 30.0 ± 0.1 °C.

Table 6
^{13}C chemical shifts [a] of phosphorylated octyl β-LacNAc disaccharides [b]

	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
Octyl β-LacNAc	103.5	57.6	75.0	81.9	77.3	62.8	105.9	73.4	75.6	71.0	77.9	62.8
6′-Phosphate **5**	101.9	55.8	73.2	73.2	75.7	61.1	104.1	72.8	80.0	68.0	74.9	65.7
4′-Phosphate **6**	101.6	56.2	73.1	79.7	75.5	61.1	104.0	72.4	75.6	71.7	73.8	61.4
3′-Phosphate **7**	102.1	56.5	73.2	78.2	75.7	60.8	103.8	71.8	77.6	69.1	79.3	62.9
2′-Phosphate **8**	102.1	55.6	73.3	75.3	75.7	60.6	103.5	74.5	74.4	68.8	80.6	61.7
6-Phosphate **9**	102.0	55.9	76.2	79.0	75.3	62.9	103.5	71.8	74.4	69.5	74.3	61.9
3-Phosphate **10**	102.7	56.3	73.5	74.7	76.6	61.7	102.0	71.7	73.6	69.7	76.0	61.7

[a,b] See footnotes for Table 5.

Octyl 3-O-*benzyl-4,6*-O-*benzylidene-β*-D-*glucopyranoside* (**12**) *and octyl 2*-O-*benzyl-4,6*-O-*benzylidene-β*-D-*glucopyranoside* (**13**).—Octyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**11**)[3] (4.71 g, 12.4 mmol) was dissolved in DCM (200 mL), and tetrabutylammonium bromide (2.00 g, 6.2 mmol) was added, followed by 15% NaOH (15 mL) and benzyl bromide (2.2 mL, 18 mmol). The solution was stirred at rt for 48 h, washed successively with water and brine, dried over sodium sulfate and concentrated under reduced pressure. Column chromatography of the resulting clear oil (25:1 toluene–EtOAc) gave compound **12** (730 mg, 12.5%), compound **13** (1.42 g, 24.0%) and a mixture of **12** and **13** (500 mg, 8.5%) as white solids. Compounds **12** and **13** (10 mg) were dissolved in pyridine (1 mL) and Ac_2O (0.5 mL) and stirred at rt for 1 h. Water (1 mL) was added to the mixture, followed by extraction with DCM. The solution was dried over sodium sulfate and concentrated under reduced pressure to afford a white solid. Column chromatography (10:1 hexane–EtOAc) resulted in the separation of the acetylated products, **12′** and **13′**. **12′**: ^1H NMR ($CDCl_3$): δ 7.43–7.25 (10 H, Ph), 5.44 (s, 1 H, PhC*H*O_2), 5.28 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.3 Hz, H-3), 4.86, 4.63 (d, 1 H, *J* 11.9 Hz, PhCH_2), 4.57 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.33 (dd, 1 H, $J_{5,6b}$ 4.8, $J_{5,6a}$ 10.5 Hz, H-5), 3.93 (dt, 1 H, *J* 6.4, 9.4 Hz, OC$H_2$$CH_2$), 3.77 (dd, 1 H, $J_{6a,6b}$ 10.0 Hz, H-6a), 3.62–3.38 (4 H, H-2, H-4, H-6b, OC$H_2$$CH_2$), 1.95 (s, 3 H, CH_3, acetyl), 1.72 (2 H, OCH_2CH_2), 1.34–1.20 (10 H, CH_2, octyl), 0.85 (t, 3 H, *J* 7.0 Hz, CH_3, octyl). **13′**: ^1H NMR ($CDCl_3$): δ 7.43–7.21 (10 H, Ph), 5.58 (s, 1 H, PhC*H*O_2), 4.99 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 8.7 Hz, H-2) 4.96, 4.65 (d, 1 H, *J* 11.7 Hz, PhCH_2), 4.43 (d, 1 H, H-1), 4.34 (dd, 1 H, *J* 5.0, 10.4 Hz, H-5), 3.87–3.67 (4 H, H-3, H-6a, H-6b, OC$H_2$$CH_2$), 3.58–3.51 (2 H, H-4, OC$H_2$$CH_2$), 1.95 (s, 3 H, CH_3, acetyl), 1.55 (2 H, OCH_2CH_2), 1.35–1.18 (10 H, CH_2, octyl), 0.88 (t, 3 H, *J* 7.0 Hz, CH_3, octyl).

Octyl 3-O-*benzyl-4,6*-O-*benzylidene-2*-O-p-*methoxybenzyl-β*-D-*glucopyranoside* (**14**).—Compound **12** (720 mg 1.5 mmol) was dissolved in DMF (5 mL), and NaH (118 mg, 60% dispersion in oil, 3.0 mmol) was added. The suspension was stirred at rt for 30 min, followed by addition of *p*-methoxybenzyl chloride (450 μL, 3.0 mmol). The solution was stirred for an additional 2 h, and ice-water was added to decompose the excess NaH. The reaction mixture was diluted with DCM, washed with water, dried over sodium sulfate and concentrated under reduced pressure. The resulting solid was recrystallized in isopropyl alcohol to give **14** (390 mg, 44%) as a white solid: $[\alpha]_D$ +29.5° (*c* 1.2, $CHCl_3$); mp 83–84 °C: ^1H NMR ($CDCl_3$): δ 7.47 (2 H, Ph), 7.40–7.22 (10 H, Ph), 6.85 (d, 2 H, *J* 7.5 Hz, Ph), 5.55 (s, 1 H, PhC*H*O_2), 4.93, 4,82, 4.78, 4.69 (d, 1 H, *J* 11.5 Hz, PhCH_2), 4.48 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.35 (dd, 1 H, $J_{5,6b}$ 4.9, $J_{5,6a}$ 10.5 Hz, H-5), 3.91 (dt, 1 H, *J* 6.4, 9.4 Hz, OC$H_2$$CH_2$), 3.79 (5 H, H-3, H-4, OCH_3), 3.68 (dd, 1 H, $J_{6a,6b}$ 8.1 Hz, H-6a), 3.55 (dt, 1 H, *J* 9.4, 6.4 Hz,

Table 7
^{31}P chemical shifts [a] and coupling constants of octyl β-Glc monosaccharides [b]

Octyl β-Glc 6-Phosphate **1**	4.98	dd, 7.1 Hz
Octyl β-Glc 4-Phosphate **2**	4.63	d, 8.4 Hz
Octyl β-Glc 3-Phosphate **3**	4.58	d, 7.0 Hz
Octyl β-Glc 2-Phosphate **4**	3.92	d, 6.8 Hz

[a] Chemical shifts are referenced to external 5% phosphoric acid at 0.0 ppm.

[b] All data were recorded on a 500 MHz Varian Unity spectrometer in D_2O buffered with 0.05 M $NaDCO_3$/0.045 M NaOD. The temperature was 30.0 ± 0.1 °C

Table 8
^{31}P chemical shifts [a] and coupling constants of octyl β-LacNAc disaccharides [b]

Octyl β-LacNAc 6′-phosphate **5**	4.64	dd, 6.5
Octyl β-LacNAc 4′-phosphate **6**	5.43	d, 9.7
Octyl β-LacNAc 3′-phosphate **7**	4.44	d, 8.4
Octyl β-LacNAc 2′-phosphate **8**	4.13	d, 7.9
Octyl β-LacNAc 6-phosphate **9**	4.10	s
Octyl β-LacNAc 3-phosphate **10**	4.18	d, 9.4

[a,b] See footnotes a,b for Table 7.

OCH_2CH$_2$), 3.46–3.33 (2 H, H-2, H-6b), 1.72 (2 H, OCH$_2$CH_2), 1.34–1.20 (10 H, CH$_2$, octyl), 0.85 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 159.3, 138.7, 137.4, 130.6 (aromatic quat), 129.8, 128.9, 128.3, 128.0, 127.6, 126.1, 113.8 (aromatic CH), 104.3 (C-1), 101.2 (Ph*C*HO$_2$), 81.7, 81.6, 81.0, 75.1, 75.0, 70.7, 68.9, 66.1 (C-2, C-3, C-4, C-5, C-6, O*C*H$_2$CH$_2$, Ph*C*H$_2$ × 2), 55.3 (OCH$_3$), 31.9, 29.9, 29.5, 29.3, 26.2, 22.7 (CH$_2$ octyl), 14.1 (CH$_3$ octyl). Anal. Calcd for $C_{38}H_{52}O_6$ (604.90): C, 72.44; H, 8.16. Found: C, 72.68; H, 7.91.

Octyl 2-O-*benzyl-4,6*-O-*benzylidene-3*-O-p-*methoxybenzyl-β*-D-*glucopyranoside* (**15**).—Compound **13** (1.42 g, 3.0 mmol) was dissolved in DMF (10 mL), and NaH (240 mg, 60% dispersion in oil, 6.0 mmol) was added. The solution was stirred at rt for 30 min, followed by the addition of *p*-methoxybenzyl chloride (850 μL, 6.0 mmol). The reaction mixture was stirred for 1 h, and ice-water was added to decompose the excess NaH. The solution was diluted with DCM, washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The resulting solid was recrystallized from isopropyl alcohol to give **15** (900 mg, 51%) as a white solid: mp 69–70 °C; $[\alpha]_D$ +30.2° (*c* 1.2, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.54 (2 H, Ph), 7.40–7.22 (10 H, Ph), 6.80 (d, 2 H, *J* 7.5 Hz, Ph), 5.55 (s, 1 H, PhC*H*O$_2$), 4.89, 4.83, 4.75, 4.71 (d, 1 H, *J* 11.0 Hz, PhCH_2), 4.47 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.35 (dd, 1 H, *J* 5.0, 10.4 Hz, H-5), 3.90 (dt, 1 H, *J* 6.4, 9.4 Hz, OCH_2CH$_2$), 3.81–3.62 (6 H, H-3, H-4, H-6a, OCH$_3$), 3.54 (dt, 1 H, *J* 9.4, 6.4 Hz, OCH_2CH$_2$), 3.45–3.34 (2 H, H-2, H-6b), 1.63 (2 H, OCH$_2$CH_2), 1.36 (10 H, CH$_2$, octyl), 0.87 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 159.3, 138.5, 137.4, 130.7 (aromatic quat), 129.7, 128.9, 128.3, 128.2, 127.7, 126.1, 113.7 (aromatic CH), 104.2 (C-1), 101.1 (Ph*C*HO$_2$), 82.2, 81.5, 75.3, 74.8, 70.7, 68.9, 66.1 (C-2, C-3, C-4, C-5, C-6, O*C*H$_2$CH$_2$, Ph*C*H$_2$ × 2), 55.3 (OCH$_3$), 31.9, 29.9, 29.5, 29.3, 26.2, 22.7 (CH$_2$, octyl), 14.1 (CH$_3$, octyl).

Octyl 3,4-di-O-*benzyl-2*-O-p-*methoxybenzyl-β*-D-*glucopyranoside* (**16**).—Compound **14** (290 mg, 0.52 mmol) was dissolved in Et$_2$O, and lithium aluminum hydride (200 mg, 5.2 mmol) was added. The solution was cooled to 0 °C, and aluminum trichloride (611 mg, 5.3 mmol) in Et$_2$O (5 mL) was added dropwise over 30 min. The solution was warmed to rt and stirring continued for 1 h. The reaction was quenched with water (1 mL), filtered through Celite, diluted with Et$_2$O and washed successively with water and brine. Column chromatography (10:1 toluene–EtOAc) gave **16** (170 mg 58%) as a white solid: mp 59–60 °C; $[\alpha]_D$ +8.6° (*c* 0.7, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.38–7.21 (12 H, Ph), 6.82 (d, 2 H, *J* 7.4 Hz, Ph), 4.92, 4.85, 4.83, 4.77, 4.64, 4.61 (d, 1 H, *J* 11.1 Hz, PhCH_2), 4.40 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 3.90 (dt, 1 H, *J* 6.3, 9.5 Hz, OCH_2CH$_2$), 3.84–3.68 (5 H, H-4, H-5, OCH$_3$), 3.63 (dd, 1 H $J_{2,3} = J_{3,4}$ 9.0 Hz, H-3), 3.58–3.49 (2 H, H-6a, OCH_2CH$_2$), 3.41–3.30 (2 H, H-2, H-6b), 1.87 (bs, 1 H, OH), 1.64 (2 H, OCH$_2$CH_2), 1.50–1.22 (10 H, CH$_2$, octyl), 0.94 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 153.1, 130.6, 129.8 (aromatic quat), 128.5, 128.4, 128.1, 127.9, 127.6, 113.8 (aromatic CH), 103.8 (C-1), 84.6, 82.0, 77.7, 75.6, 75.1, 75.0, 74.6, 70.0, 62.2 (C-2, C-3, C-4, C-5, C-6, O*C*H$_2$CH$_2$, Ph*C*H$_2$ × 3), 55.3 (OCH$_3$), 31.9, 29.9, 29.5, 29.3, 26.2, 22.7 (CH$_2$, octyl), 14.1 (CH$_3$, octyl). Anal. Calcd for $C_{38}H_{54}O_6$ (606.83): C, 72.94; H, 8.16. Found: C, 72.43; H, 8.47.

Octyl 2,4-di-O-*benzyl-3*-O-p-*methoxybenzyl-β*-D-*glucopyranoside* (**17**).—Compound **17** (430 mg, 54%) was synthesized from **15** (800 mg, 14.0 mmol), lithium aluminum hydride (532 mg, 140 mmol), and aluminum trichloride (1.82 g, 140 mmol) as described for **16**: mp 70–71 °C; $[\alpha]_D$ +2.9° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.38–7.19 (12 H, Ph), 6.81 (d, 2 H, *J* 7.6 Hz, Ph), 4.93, 4.85, 4.83, 4.72, 4.71, 4.61 (d, 1 H, *J* 11.0 Hz, PhCH_2), 4.41 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.90 (dt, 1 H, *J* 6.4, 9.4 Hz, OCH_2CH$_2$), 3.86–3.68 (5 H, H-4, H-5, OCH$_3$), 3.64 (dd, 1 H $J_{2,3} = J_{3,4}$ 9.0 Hz, H-3), 3.57–3.48 (2 H, H-6a, OCH_2CH$_2$), 3.40–3.31 (2 H, H-2, H-6b), 1.86 (bs, 1 H, OH), 1.63 (2 H, OCH$_2$CH_2), 1.41–1.22 (10 H, CH$_2$, octyl), 0.88 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 159.3, 138.5, 138.1, 130.8 (aromatic quat.), 129.6, 128.5, 128.4, 128.0, 127.9, 127.7, 113.8 (aromatic CH), 103.8 (C-1), 84.2, 82.5, 77.6, 75.0 (C-2, C-3, C-4, C-5), 75.4, 75.1, 74.9, 70.5, 62.2 (C-6, O*C*H$_2$CH$_2$, Ph*C*H$_2$ × 3), 55.3 (OCH$_3$), 31.8, 29.8, 29.5, 29.3, 26.2, 22.7 (CH$_2$, octyl), 14.1 (CH$_3$, octyl).

Octyl 3,4,6-tri-O-*benzyl-2*-O-p-*methoxybenzyl-β*-D-*glucopyranoside* (**18**).—Compound **16** (130 mg, 0.20 mmol) was dissolved in dry DMF (1 mL), NaH (11 mg, 60% dispersion in oil, 0.28 mmol) was added, and the solution was stirred at rt for 20 min. Benzyl bromide (30 μL, 0.28 mmol) was added, and the reaction was stirred for 3 h. Ice-water was added to decompose the excess NaH, and the reaction was diluted with DCM and washed with water. The organic layer was dried with sodium sulfate and concentrated. Column chromatography (4:1 hexane–EtOAc) gave **18** (315 mg, 91%) as a colorless oil: ^{1}H NMR (CDCl$_3$): δ 7.35–7.21 (15 H, Ph), 7.17–7.12 (2 H, Ph), 6.91 (d, 2 H, *J* 7.0 Hz, Ph), 4.91, 4.86, 4.82, 4.75, 4.64, 4.59, 4,54, 4.50 (d, 1 H, *J* 11.0 Hz, PhCH_2), 4.36 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.94 (dt, 1 H, *J* 6.2, 9.5 Hz, OCH_2CH$_2$), 3.77 (s, 3 H, OCH$_3$), 3.73 (dd, 1 H $J_{3,4}$ 2.0, $J_{2,3}$ 9.0 Hz, H-3), 3.65 (dd, 1 H, $J_{4,5}$ 10.8 Hz, H-4), 3.60 (dd, 1 H, $J_{5,6a} = J_{6a,6b}$ 8.4 Hz, H-6a), 3.46–3.38 (2 H, H-5, OCH_2CH$_2$), 3.46–3.38 (2 H, H-2, H-6b), 1.67 (2 H, OCH$_2$CH_2), 1.50–1.22 (10 H, CH$_2$, octyl), 0.86 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl). Anal. Calcd for $C_{45}H_{60}O_6$ (682.88): C, 75.63; H, 7.97. Found: C, 75.44; H, 8.16.

Octyl 2,4,6-tri-O-*benzyl-3*-O-p-*methoxybenzyl-β*-D-*glucopyranoside* (**19**).—Compound **19** (430 mg, 95%) was synthesized from **17** (400 mg, 0.60 mmol) in dry

DMF (4 mL) containing NaH (50 mg, 60% dispersion in oil, 1.3 mmol) and benzyl bromide (120 μL, 1.1 mmol) as described for **18**: mp 62–63 °C; $[\alpha]_D$ +3.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.37–7.23 (17 H, Ph), 6.80 (d, 2 H, *J* 8.7 Hz, Ph), 4.95, 4.83, 4.81, 4.71, 4.69, 4.59, 4,53, 4.51 (d, 1 H, *J* 11.0 Hz, PhC*H*$_2$), 4.36 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.92 (dt, 1 H, *J* 6.4, 9.5 Hz, OC*H*$_2$CH$_2$), 3.77 (s, 3 H, OCH_3), 3.73 (dd, 1 H, H-3), 3.64 (dd, 1 H, H-4), 3.61 (dd, 1 H, $J_{5,6a} = J_{6a,6b}$ 8.9 Hz, H-6a), 3.56–3.49 (2 H, H-5, OC*H*$_2$CH$_2$), 3.47–3.41 (2 H, H-2, H-6b), 1.64 (2 H, OCH$_2$C*H*$_2$), 1.42–1.20 (10 H, CH_2, octyl), 0.86 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 159.2, 138.6, 138.4, 138.3, 130.9 (aromatic quat), 129.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 113.8 (aromatic CH), 103.7 (C-1), 84.5, 82.4, 78.1, 74.9 (C-2, C-3, C-4, C-5), 75.4, 75.0, 74.8, 73.5, 70.2, 69.1 (C-6, OCH$_2$CH$_2$, PhCH$_2$ × 4), 55.3 (OCH_3), 31.9, 29.9, 29.5, 29.3, 26.3, 22.7 (CH_2, octyl), 14.1 (CH_3, octyl). Anal. Calcd for $C_{43}H_{54}O_7$ (682.88): C, 75.63; H, 7.97. Found: C, 75.75; H, 8.27.

Octyl 3,4,6-tri-O-*benzyl*-β-D-*glucopyranoside* (**20**).—Compound **18** (135 mg, 0.18 mmol) was dissolved in DCM (2 mL), and DDQ (60 mg, 0.27 mmol) was added. The mixture was stirred for 2 h at rt and additional DDQ (28 mg, 0.13 mmol) was added before stirring for an additional 2 h. The solution was diluted with DCM and washed with water. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. Column chromatography (4:1 hexane–EtOAc) gave **20** (75 mg, 63%) as a white solid: mp 34–37 °C; $[\alpha]_D$ −5.6° (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.45–7.18 (15 H, Ph), 4.95, 4.84, 4.62, 4.58, 4,55, 4.51 (d, 6 H, *J* 11.0 Hz, PhC*H*$_2$), 4.24 (d, 1 H, $J_{1,2}$ 7.1 Hz, H-1), 3.91 (dt, 1 H, *J* 6.4, 9.5 Hz, OC*H*$_2$CH$_2$), 3.75 (dd, 1 H, H-3), 3.62–3.44 (5 H, H-2, H-5, H-6a, H-6b, OC*H*$_2$CH$_2$), 2.17 (bs, 1 H, OH), 1.84 (2 H, OCH$_2$C*H*$_2$), 1.42–1.22 (10 H, CH_2, octyl), 0.86 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 139.4, 138.9, 138.8 (aromatic quat.), 129.2, 129.1, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3 (aromatic CH), 103.4 (C-1), 85.2, 78.3, 75.4, 74.2 (C-2, C-3, C-4, C-5), 75.9, 75.3, 73.7, 70.8, 69.6 (C-6, OCH$_2$CH$_2$, PhCH$_2$ × 3), 32.5, 30.3, 30.1, 29.9, 26.7, 23.4 (CH_2, octyl), 14.8 (CH_3, octyl).

Octyl 2,4,6-tri-O-*benzyl*-β-D-*glucopyranoside* (**21**).—Compound **21** (225 mg, 69%) was prepared, as a white solid, from **19** (380 mg, 0.50 mmol) by reaction in DCM (5 mL) with DDQ (171 mg, 0.75 mmol) as described for the preparation of **20**: mp 47–49 °C; $[\alpha]_D$ +14.0° (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.41–7.22 (15 H, Ph), 4.88, 4.82, 4.65, 4.60, 4,58, 4.53 (d, 6 H, *J* 11.3 Hz, PhC*H*$_2$), 4.36 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.92 (dt, 1 H, *J* 6.4, 9.5 Hz, OC*H*$_2$CH$_2$), 3.78–3.63 (3 H, H-3, H-4, H-6a), 3.55–3.40 (3 H, H-2, H-5, OC*H*$_2$CH$_2$), 3.25 d, 1 H, *J* 7.8, 9.2 Hz, H-6b), 2.40 (bs, 1 H, OH), 1.65 (2 H, OCH$_2$C*H*$_2$), 1.42–1.20 (10 H, CH_2, octyl), 0.86 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 138.4, 138.2, 138.1 (aromatic quat.), 129.2, 129.1, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3 (aromatic CH), 103.3 (C-1), 81.3, 77.4, 76.6, 74.3 (C-2, C-3, C-4, C-5), 74.6, 74.4, 73.5, 70.1, 69.2 (C-6, OCH$_2$CH$_2$, PhCH$_2$ × 3), 31.9, 30.0, 29.8, 29.5, 26.2, 22.7 (CH_2, octyl), 14.1 (CH_3, octyl).

Octyl 2,3,4-tri-O-*benzyl-6*-O-*diphenoxyphosphono*-β-D-*glucopyranoside* (**24**).—*Octyl 2,3,4-tri*-O-*benzyl*-β-D-*glucopyranoside* (**22**)[5] (50 mg, 0.09 mmol) was dissolved in pyridine (1 mL), and the solution was cooled to 0 °C. To the cooled solution, DMAP (27 mg, 0.22 mmol) and diphenylphosphorochloridate (30 μL, 0.14 mmol) were added, and the solution was allowed to warm to rt. After 15 h the solution was diluted with DCM, and washed sequentially with water, sodium bicarbonate and water, followed by concentration under reduced pressure. Column chromatography (3:1 hexane–EtOAc) resulted in **24** (43 mg, 60%) as an oil: $[\alpha]_D$ −3.6° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.34–7.12 (25 H, Ph), 4.93, 4.91, 4.77, 4.76, 4,69 (d, 6 H, *J* 11.3 Hz, PhC*H*$_2$), 4.51 (ddd, 1 H, *J* 1.7, 6.4, 11.0 Hz, H-6a), 4.45 (d, 6 H, *J* 10.8 Hz, PhC*H*$_2$), 4.38 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.32 (ddd, 1 H, *J* 3.6, 7.2, 12.6 Hz, H-6b), 3.87 (dt, 1 H, *J* 6.4, 9.5 Hz, OC*H*$_2$CH$_2$), 3.63 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.9 Hz, H-3), 3.52–3.43 (3 H, H-4, H-5, OC*H*$_2$CH$_2$), 3.39 (dd, 1 H, H-2), 1.60 (2 H, OCH$_2$C*H*$_2$), 1.39–1.20 (10 H CH_2, octyl), 0.86 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 150.6, 150.5 (d, *J* 5.5 Hz, aromatic quat), 138.5, 138.4, 137.8 (aromatic quat), 129.8, 129.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7 (aromatic CH), 125.4, 125.3 (d, $J_{C,P}$ 1.5 Hz, aromatic CH), 120.3, 120.1 (d, $J_{C,P}$ 4.5 Hz, aromatic CH), 103.5 (C-1), 85.5 (C-3), 82.2 (C-2), 77.1 (C-4), 76.5, 75.9, 71.5 (PhCH$_2$ × 3), 73.5 (d, $J_{5,P}$ 7.6 Hz, C-5), 71.4 (OCH$_2$CH$_2$), 67.7 (d, $J_{6,P}$ 5.9 Hz, C-6), 31.9, 29.8, 29.4, 29.3, 26.2, 22.7 (CH_2, octyl), 14.1 (CH_3, octyl). HRES-IMS Calcd for $C_{47}H_{55}NO_9Na$ 817.3481. Found 817.3482. Anal. Calcd for $C_{47}H_{55}O_9$ (794.91): C, 71.01; H, 6.97. Found: C, 71.04; H, 6.96.

Octyl 2,3,6-tri-O-*benzyl-4*-O-*diphenoxyphosphono*-β-D-*glucopyranoside* (**25**).—Compound **25** (83 mg, 63%) was synthesized from octyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**23**)[4] (90 mg, 0.16 mmol), diphenylphosphorochloridate (80 μL, 0.35 mmol), DMAP (32 mg 0.26 mmol), and pyridine (2 mL) as described for the preparation of **24**: $[\alpha]_D$ +3.6° (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.30–7.02 (25 H, Ph), 4.92, 4.86, 4.72, 4.64, (d, 4 H, *J* 10.8 Hz, PhC*H*$_2$), 4.62 (ddd, 1 H, $J_{3,4} = J_{4,5}$ 9.3, $J_{4,P}$ 9.5 Hz), 4.57 (d, 1 H, *J* 12.0 Hz, PhC*H*$_2$), 4.43 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.41 (d, 1 H, *J* 11.8 Hz, PhC*H*$_2$), 3.93 (dt, 1 H, *J* 6.4, 9.5 Hz, OC*H*$_2$CH$_2$), 3.75–3.71 (2 H, H-3, H-6a), 3.66–3.60 (2H, H-5, H-6b), 3.52 (dt, 1 H, *J* 6.7, 9.5 Hz, OC*H*$_2$CH$_2$), 3.50 (dd, 1 H, $J_{2,3}$ 9.1 Hz, H-2), 1.63 (2 H, OCH$_2$C*H*$_2$), 1.41–1.22 (10 H, CH_2, octyl), 0.88 (t, 3 H,

J 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 150.6, 150.5 (d, $J_{C,P}$ 5.5 Hz, aromatic quat), 138.3, 138.2 (aromatic quat), 129.7, 129.6, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 127.3 (aromatic CH), 125.4, 125.3 (d, $J_{C,P}$ 1.2 Hz, aromatic CH), 120.3, 120.1 (d, $J_{C,P}$ 4.8 Hz, aromatic CH), 103.5 (C-1), 82.2 (d, $J_{3,P}$ 2.8 Hz, C-3), 82.0 (C-2), 77.2 (C-4), 75.0, 74.8, 73.4 (Ph*C*$H_2 \times 3$), 74.2 (d, $J_{5,P}$ 5.6 Hz, C-5), 70.3 (O*C*H_2CH_2), 69.1 (C-6), 31.9, 29.8, 29.5, 29.3, 26.2, 22.7 (CH_2, octyl), 14.1 (CH_3, octyl). HRESIMS Calcd for $C_{47}H_{55}NO_9Na$ 817.3481. Found 817.3488. Anal. Calcd for $C_{47}H_{55}O_9$ (794.91): C, 71.01; H, 6.97. Found: C, 70.84; H, 7.06.

Octyl 2,4,6-tri-O-*benzyl-3*-O-*diphenoxyphosphono-β*-D-*glucopyranoside* (**26**).—Compound **26** (57 mg, 92%) was synthesized from compound **20** (44 mg, 0.051 mmol), diphenylphosphorochloridate (40 μL, 0.17 mmol), DMAP (32 mg, 0.26 mmol) and pyridine (2 mL) as described for **24**: $[\alpha]_D$ + 3.2° (*c* 0.3, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.18–7.00 (25 H, Ph), 4.89 (d, 1 H, *J* 10.8 Hz, PhCH_2), 4.81 (ddd, 1 H, $J_{2,3} = J_{3,4}$ 8.9, $J_{3,P}$ 17.8 Hz, H-3), 4.77, 4.65, 4.59, 4.53, 4.45 (d, 1 H, *J* 10.8 Hz, PhCH_2), 4.20 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 3.92 (dt, 1 H, *J* 6.6, 9.5 Hz, OCH_2CH$_2$), 3.77 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.72–3.67 (2 H, H-6a, H-6b), 3.53 (dd, 1 H, H-2), 3.51–3.44 (2 H, H-5, OCH_2CH$_2$), 1.50–1.42 (2 H, OCH$_2$CH_2), 1.30–1.14 (10 H, CH_2, octyl), 0.88 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 150.6, 150.5 (d, $J_{C,P}$ 3.2 Hz, aromatic quat), 138.2, 138.0, 137.8 (aromatic quat), 129.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.3 (aromatic CH), 125.0 (d, $J_{C,P}$ 1.2 Hz, aromatic CH), 120.1 (d, $J_{C,P}$ 5.0 Hz, aromatic CH), 103.4 (C-1), 83.9 (d, $J_{3,P}$ 8.0 Hz, C-3), 82.0 (d, $J_{2,P}$ 2.4 Hz, C-2), 76.8 (d, $J_{4,P}$ 4.2 Hz, C-4), 74.5, 74.1, 73.6 (Ph*C*$H_2 \times 3$), 74.3 (C-5), 70.3 (O*C*H_2CH_2), 68.6 (C-6), 31.8, 29.8, 29.3, 29.2, 26.1, 22.7 (CH_2, octyl), 14.1 (CH_3, octyl). Anal. Calcd for $C_{47}H_{55}O_9$ (794.91): C, 71.01; H, 6.97. Found: C, 71.08; H, 6.97.

Octyl 3,4,6-tri-O-*benzyl-2*-O-*diphenoxyphosphono-β*-D-*glucopyranoside* (**27**).—Compound **27** (42 mg, 87%) was synthesized from compound **21** (34 mg, 0.060 mmol), diphenylphosphorochloridate (30 μL, 0.13 mmol), DMAP (22 mg, 0.18 mmol) and pyridine (2 mL) as described for **24**: $[\alpha]_D$ − 7.0° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.35–7.10 (25 H, Ph), 4.84 (d, 1 H, *J* 10.8 Hz, PhCH_2), 4.75 (d, 2 H, *J* 10.8 Hz, PhCH_2), 4.61 (d, 1 H, *J* 10.8 Hz, PhCH_2), 4.58–4.49 (4 H, H-1, H-2, PhCH_2), 3.82–3.61 (5 H, H-3, H-4, H-6a, H-6b, OCH_2CH$_2$), 3.51 (ddd, 1 H, *J* 2.0, 4.6, 9.8 Hz, H-5), 3.44 (dt, 1 H, *J* 7.3, 9.2 Hz, OCH_2CH$_2$), 1.48 (2 H, OCH$_2$CH_2), 1.30–1.14 (10 H, CH_2, octyl), 0.88 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 150.9, 150.8 (d, $J_{C,P}$ 6.8 Hz, aromatic quat), 138.2, 138.1, 137.9 (aromatic quat.), 129.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 125.0 (aromatic CH), 120.2 (d, $J_{C,P}$ 5.7 Hz, aromatic CH), 101.1 (d, $J_{1,P}$ 3.2 Hz, C-1), 83.5 (d, $J_{3,P}$ 4.1 Hz, C-3), 82.0 (d, $J_{2,P}$ 7.1 Hz, C-2), 78.0 (C-4), 75.2, 75.0, 73.5 (Ph*C*$H_2 \times 3$), 75.1 (C-5), 70.2 (O*C*H_2CH_2), 68.7 (C-6), 31.9, 29.5, 29.4, 29.2, 25.9, 22.7 (CH_2 octyl), 14.1 (CH_3 octyl). Anal. Calcd for $C_{47}H_{55}O_9$ (794.91): C, 71.01; H, 6.97. Found: C, 70.83; H, 6.96.

Octyl 6-O-*phosphono-β*-D-*glucopyranoside disodium salt* (**1**).—Compound **24** (43 mg, 0.05 mmol) was dissolved in 95% EtOH (2 mL) containing 5% Pd–C (8 mg), and the mixture was stirred under hydrogen at ambient pressure for 15 h. TLC (5:2:1 EtOAc–hexane–MeOH) indicated complete disappearance of starting material. The catalyst was removed by filtration, the solvent concentrated, and the residue was redissolved in 95% EtOH (4 mL). Adams' catalyst (PtO_2, 7 mg) was added, and the mixture was stirred under hydrogen for 3 h. The solution was filtered and concentrated. The resulting residue was dissolved in water and purified on a C_{18} Sep-Pak cartridge using water and MeOH. The carbohydrate-containing fractions were pooled, concentrated and converted to the sodium salt by passage through Dowex 50-X8 (Na^+) cation-exchange resin. Lyophilization of the eluent provided **1** (19 mg, 90%): ^1H NMR (600 MHz, D_2O (0.05 M $NaDCO_3$/0.045 M NaOD)): δ 4.43 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.02 (ddd, 1 H, $J_{5,6a}$ 4.0, $J_{6a,P}$ 7.5, $J_{6a,6b}$ 12.2 Hz), 3.89 (dt. 1 H. *J* 7.0, 9.9 Hz, OCH_2CH$_2$), 3.64 (dt, 1 H, *J* 7.0, 9.9 Hz, OCH_2CH$_2$), 3.59 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), 3.48 (dd, 1 H, $J_{2,3}$ 9.3 Hz, H-3), 3.44 (ddd, 1 H, $J_{5,6b}$ 2.6, H-5), 3.27 (dd, 1 H, H-2), 1.61 (2 H, OCH$_2$CH_2), 1.56–1.22 (10 H, CH_2, octyl), 0.88 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR (D_2O): δ 103.5 (C-1), 76.3 (C-3), 75.3 (d, *J* 10.2 Hz, C-5), 73.8 (C-2), 71.4 (O*C*H_2CH_2), 69.7 (C-4), 64.5 (d, *J* 5.9 Hz, C-6), 31.8, 29.4, 29.2, 29.1, 25.7, 22.6 (CH_2, octyl), 14.1 (CH_3, octyl); HRESIMS Calcd for $C_{14}H_{28}O_9Na_2P$ 417.1266. Found 417.1262.

Octyl 4-O-*phosphono-β*-D-*glucopyranoside disodium salt* (**2**).—Compound **2** (14 mg, 84%) was deprotected as described in the preparation of compound **1** from compound **25** (31 mg, 0.039 mmol): ^1H NMR (D_2O (0.05 M $NaDCO_3$ 0.045 M NaOD)): δ 4.44 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 3.89 (dt, 1 H, *J* 6.4, 9.5 Hz, OCH_2CH$_2$), 3.85–3.78 (3 H, H-4, H-6a, H-6b), 3.68–3.64 (2 H, H-3, OCH_2CH$_2$), 3.46 (dddd, 1 H, *J* 2.4, 4.8, 7.1, 9.7 Hz, H-5), 3.30 (dd, 1 H, $J_{2,3}$ 9.3 Hz, H-2), 1.64–1.58 (2 H, OCH$_2$CH_2), 1.38–1.24 (10 H, CH_2, octyl), 0.85 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR (D_2O): δ 103.1 (C-1), 75.9 (d, $J_{3,P}$ 2.0 Hz, C-3), 75.9 (d, $J_{5,P}$ 6.0 Hz, C-5), 74.7 (d, *J* 6.0 Hz, C-2), 73.8 (C-4), 71.6 (O*C*H_2CH_2), 61.4 (C-6), 31.9, 29.6, 29.3, 29.2, 25.9, 22.9 (CH_2 octyl), 14.3 (CH_3 octyl); HRESIMS Calcd for $C_{14}H_{28}O_9Na_2P$ 417.1266. Found 417.1267.

Octyl 3-O-*phosphono-β*-D-*glucopyranoside disodium salt* (**3**).—Compound **3** (7 mg, 90%) was deprotected as described in the preparation of compound **1** from compound **26** (15 mg, 0.020 mmol): ^1H NMR (D_2O (0.05 M $NaDCO_3$/0.045 M NaOD)): δ 4.50 (d, 1 H, $J_{1,2}$ 8.2 Hz,

H-1), 3.97–3.88 (3 H, H-3, H-6a, OCH_2CH$_2$), 3.73–3.63 (2 H, H-5, OCH_2CH$_2$), 3.58–3.47 (2 H, H-4, H-6b), 3.34 (dd, 1 H, $J_{2,3}$ 8.4 Hz, H-2), 1.64–1.60 (2 H, OCH$_2$CH_2), 1.37–1.22 (10 H, CH$_2$, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (D$_2$O): δ 103.0 (C-1), 81.7 (d, $J_{3,P}$ 6.1 Hz, C-3), 76.5 (C-5), 73.8 (d, $J_{2,P}$ 3.7 Hz, C-2), 71.9 (OCH$_2$CH$_2$), 70.3 (d, $J_{4,P}$ 3.7 Hz, C-4), 61.7 (C-6), 31.9, 29.6, 29.3, 29.2, 25.9, 22.8 (CH$_2$, octyl), 14.3 (CH$_3$, octyl); HRESIMS Calcd for $C_{14}H_{27}O_9Na_3P$ 439.1086. Found 439.1082.

*Octyl 2-*O*-phosphono-β-*D*-glucopyranoside disodium salt* (**4**).—Compound **4** (4 mg, 78%) was deprotected as described in the preparation of compound **1** from compound **27** (10 mg, 0.012 mmol): ^{1}H NMR (D$_2$O (0.05 M NaDCO$_3$/0.045 M NaOD)): δ 4.49 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.92–3.86 (2 H, H-6a, OCH_2CH$_2$), 3.73–3.66 (4 H, H-2, H-3, H-6b, OCH_2CH$_2$), 3.49–3.41 (2 H, H-4, H-5), 1.65–1.60 (2 H, OCH$_2$CH_2), 1.36–1.24 (10 H CH$_2$ octyl), 0.86 (t, 3 H, J 7.0 Hz, CH$_3$ octyl); ^{13}C NMR (D$_2$O): δ 103.0 (d, $J_{1,P}$ 7.3 Hz, C-1), 81.7 (d, J 6.1 Hz, C-3), 76.5 (C-5), 73.8 (d, $J_{2,P}$ 3.7 Hz, C-2), 71.9 (OCH$_2$CH$_2$), 70.3 (d, $J_{4,P}$ 3.7 Hz, C-4), 61.7 (C-6), 31.9, 29.6, 29.3, 29.2, 25.9, 22.8 (CH$_2$ octyl), 14.3 (CH$_3$ octyl); HRESIMS Calcd for $C_{14}H_{27}O_9Na_3P$ 439.1086. Found 439.1089.

*Octyl 3-*O*-allyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**29**).—Octyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (**28**)[6] (2.11 g, 4.17 mmol) was dissolved in DMF (20 mL) and cooled to 0 °C. Sodium hydride (180 mg, 60% dispersion in oil, 4.59 mmol) was added, and the mixture was allowed to stir for 30 min. Allyl chloride (550 μL, 6.23 mmol) was added, and the mixture was warmed to rt and stirred for an additional 3 h. Methanol was added to decompose the excess NaH, and the mixture was diluted with toluene, extracted with water and concentrated under reduced pressure. Column chromatography (10:1 hexane–EtOAc) gave unreacted starting material (520 mg 24%) and **29** (1.28 g 56%): $[\alpha]_D$ + 21.3° (*c* 0.9, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.92–7.72 (4 H, Phth), 7.28–7.15 (5 H, Ph), 5.58 (s, 1 H, PhCHO$_2$), 5.56 (1 H, OCH$_2$CHCH$_2$), 5.23 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 5.02 (1 H, J_{cis} 10.5 Hz, OCH$_2$CH=CHH), 4.85 (1 H, J_{trans} 17.0 Hz, OCH$_2$CH=CHH), 4.44–4.35 (2-H, H-3, H-6a), 4.30–4.19 (2 H, H-2, OCH-HCH=CH$_2$), 3.96 (1 H, OCHHCH = CH$_2$), 3.88–3.70 (3 H, H-4, H-6b, OCH_2CH$_2$), 3.61 (ddd, 1 H, J 4.8, 9.7, 9.7 Hz, H-5), 3.40 (dt, 1 H, J 6.6, 9.8 Hz, OCH_2CH$_2$), 1.52–1.30 (2 H, OCH$_2$CH_2), 1.20–0.92 (10 H, CH$_2$, octyl), 0.80 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 160.1 (CO, Phth), 137.3, 131.7 (aromatic quat.), 134.5 (CH$_2$=CHCH$_2$O), 134.1, 129.0, 128.2, 126.0 (aromatic CH), 116.8 (CH$_2$=CHCH$_2$O), 101.3, 99.1, 82.8, 75.2, 66.2 (C-1, C-3, C-4, C-5, PhCHO$_2$), 73.1, 70.1, 68.8 (C-6, OCH$_2$CH$_2$, CH$_2$=CHCH$_2$O), 55.0 (C-2), 31.6, 29.3, 29.1, 29.0, 25.7, 22.6 (CH$_2$ octyl), 14.0 (CH$_3$ octyl). Anal. Calcd for $C_{32}H_{39}NO_7$ (553.29): C, 69.51; H, 6.96. Found: C, 69.71; H, 7.26.

*Octyl 3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**30**).—Compound **29** (1.28 g, 2.39 mmol), sodium cyanoborohydride (753 mg, 11.95 mmol) and methyl orange indicator were dissolved in dry tetrahydrofuran (THF) containing crushed 4 Å molecular sieves. The solution was cooled to 0 °C and ethereal hydrogen chloride was added dropwise until the red color of the solution persisted. The mixture was warmed to rt and stirred for an additional hour, filtered through Celite, washed with water and brine and concentrated under reduced pressure. Column chromatography of the resulting pink oil (5:1 hexane–EtOAc) afforded **30** (1.24 g 96%) as a colorless oil: $[\alpha]_D$ + 23.2° (*c* 0.4, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.91–7.68 (4 H, Phth), 7.38–7.22 (5 H, Ph), 5.60 (1 H, OCH$_2$CH=CH$_2$), 5.14 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 5.05 (1 H, J_{cis} 10.5 Hz, OCH$_2$CH=CHH), 4.87 (1 H, J_{trans} 17.0 Hz, OCH$_2$CH=CHH), 4.63, 4.57 (d, 1 H, J 12.0 Hz, PhCH$_2$), 4.22–4.13 (3 H, H-2, H-3, OCHHCH=CH$_2$), 3.97 (1 H, OCHHCH=CH$_2$), 3.84–3.71 (4 H, H-4, H-6a, H-6b, OCH_2CH$_2$), 3.63 (ddd, 1 H, H-5), 3.38 (dt, 1 H, J 6.4, 9.2 Hz, OCH_2CH$_2$), 2.92 (bs, 1 H, OH), 1.45–1.35 (2 H, OCH$_2$CH_2), 1.20–0.90 (10 H, CH$_2$, octyl), 0.89 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 137.8, 131.8 (aromatic quat.), 134.7 (CH$_2$=CHCH$_2$O), 134.1, 128.6, 127. (aromatic CH), 117.1 (CH$_2$=CHCH$_2$O), 98.5 (C-1), 79.0, 74.0, 73.7 (C-3, C-4, C-5), 73.9, 73.1 (PhCH$_2$, CH$_2$=CHCH$_2$O), 70.8 (OCH$_2$CH$_2$,), 60.8 (C-6), 55.6 (C-2), 31.7, 29.4, 29.2, 25.9, 22.6 (CH$_2$, octyl), 14.1 (CH$_3$, octyl). Anal. Calcd for $C_{32}H_{41}NO_7$ (553.29): C, 69.67; H, 7.49. Found: C, 69.37; H, 7.19.

*Octyl 2-deoxy-4,6-*O*-p-methoxybenzylidene-2-phthalimido-β-*D*-glucopyranoside* (**32**).—Octyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside-(**31**)[6] (1.25 g, 2.3 mmol) was dissolved in dry MeOH (40 mL), and sodium (8 mg) was added. The reaction was stirred at rt for 2 h, neutralized by adding amberlite IR-120 (H$^+$) resin, filtered and concentrated. The resulting yellow syrup was dissolved in MeCN, and *p*-toluenesulfonic acid monohydrate (30 mg, 17.0 mmol) and anisaldehyde dimethyl acetal (800 μL, 4.6 mmol) were added. The solution was heated to 60 °C and stirred for 15 h. The mixture was cooled to rt, neutralized with triethylamine and concentrated. Column chromatography (4:1 hexane–EtOAc) afforded **32** (1.03 g, 83%): ^{1}H NMR (CDCl$_3$): δ 7.92–7.70 (4 H, Phth), 7.43 (d, 2 H, J 8.2 Hz, Ph), 6.92 (d, 2 H, J 8.2 Hz, Ph), 5.51 (s, 1 H, PhCHO$_2$), 5.25 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.61 (dd, 1 H, $J_{3,4}$ 8.4, $J_{2,3}$ 10.4 Hz, H-3), 4.37 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 10.4 Hz, H-6a), 4.23 (dd, 1 H, H-2), 3.86–3.77 (5 H, H-4, OCH_2CH$_2$, OCH$_3$), 3.66–3.54 (2 H, H-5, H-6b), 3.41 (dt, 1 H, J 6.5, 9.7 Hz, OCH_2CH$_2$), 1.48–1.30 (2 H, OCH$_2$CH_2), 1.23–0.92 (10 H, CH$_2$, octyl), 0.82 (t, 3 H, J 7.0 Hz, CH$_3$, octyl).

Octyl 3-O-benzyl-2-deoxy-4,6-O-p-methoxybenzylidene-2-phthalimido-β-D-glucopyranoside (**33**).—Compound **33** (778 mg, 65%) was synthesized from **32** (1.03 g, 1.91 mmol) as described for compound **18**: $[\alpha]_D$ + 34.4° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.90–7.60 (4 H, Phth), 7.43–6.85 (9 H, Ph), 5.57 (s, 1 H, PhC*H*O_2), 5.18 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.78, 4.48 (d, 1 H, *J* 12.4 Hz, PhCH_2), 4.43–4.33 (2 H, H-3, H-6a), 4.19 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2), 3.88–3.72 (6 H, H-4, H-6b, OCH_2CH_2, OCH_3), 3.61 (ddd, 1 H, *J* 2.3, 4.9, 9.8 Hz, H-5), 3.36 (dt, 1 H, *J* 6.5, 9.8 Hz, OCH_2CH_2), 1.22–1.12 (2 H, OCH_2CH_2), 1.18–0.85 (10 H, CH_2, octyl), 0.80 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 160.1 (CO, Phth), 138.0, 131.7, 130.0 (aromatic quat), 133.8, 128.0, 127.4, 123.3 (aromatic CH), 113.6 (Ph*C*HO_2), 101.3, 98.0, 83.1, 74.4 (C-1, C-3, C-4, C-5), 74.0 (Ph*C*H_2), 70.0 (O*C*H_2CH_2), 68.8 (C-6), 66.1 (OCH_3), 55.9 (C-2), 31.6, 29.3, 29.1, 29.0, 25.7, 22.6 (CH_2, octyl), 14.0 (CH_3, octyl). Anal. Calcd for $C_{37}H_{43}NO_8$ (629.74): C, 70.57; H, 6.88. Found: C, 70.48; H, 6.83.

Octyl 3-O-benzyl-2-deoxy-6-O-p-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (**34**).—Compound **33** (778 mg, 1.24 mmol) and sodium cyanoborohydride (603 mg, 9.92 mmol) were dissolved in DMF (5 mL) containing crushed molecular 4 Å sieves. The solution was cooled to 0 °C and trifluoracetic acid (1 mL) in DMF (4 mL) was added dropwise. The solution was allowed to warm to rt and stirred for 12 h. The reaction was quenched by the addition of triethylamine, filtered through Celite, diluted with DCM, washed with water and brine and concentrated under reduced pressure. Column chromatography (5:1 hexane–EtOAc) gave **34** (636 mg, 82%): ^1H NMR ($CDCl_3$): δ 7.82–7.61 (4 H, Phth), 7.24–6.82 (9 H, Ph), 5.11 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.74 (d, 1 H, *J* 12.2 Hz, PhCH_2), 4.60–4.48 (3 H, H-2, PhCH_2), 4.25–4.08 (3 H, H-3, H-4, PhCH_2), 3.90–3.70 (6 H, H-5, H-6a, H-6b, OCH_3), 3.63 (dt, 1 H, *J* 4.8, 9.4 Hz, OCH_2CH_2), 3.34 (dt, 1 H, *J* 4.8, 9.7 Hz, OCH_2CH_2), 2.96 (bs, 1 H, OH), 1.40–1.25 (2 H, OCH_2CH_2), 1.20–0.85 (10 H, CH_2, octyl), 0.80 (t, 3 H, *J* 7.0 Hz, CH_3, octyl).

Ethyl 2,6-di-O-acetyl-1-thio-β-D-galactopyranoside (**36**).—Ethyl 2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside (**35**)[7] (790 mg, 1.7 mmol) was dissolved in MeCN (2 mL) and was added to 70% AcOH (20 mL). The solution was heated to 60 °C and stirred for 13 h. The mixture was cooled to rt and co-concentrated with toluene. Column chromatography (5:1 toluene–EtOAc) yielded **39** (624 mg, 95%): $[\alpha]_D$ + 15.4° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 4.99 (dd, 1 H, $J_{1,2} = J_{2,3}$ 9.7 Hz, H-2), 4.35 (d, 1 H, H-1), 4.32 (dd, 1 H, $J_{5,6a}$ 5.9, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.23 (dd, 1 H, $J_{5,6b}$ 6.7, H-6b), 3.94 (bs, 1 H, OH), 3.70–3.62 (2 H, H-3, H-5), 3.70 (2 H, H-4, OH), 2.65 (m, 2 H, S$CH_2$$CH_3$), 2.10, 2.07 (s, 3 H, CH_3, acetate), 1.22 (t, 3 H, *J* 7.5 Hz, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 170.7, 169.5 (CO, acetate), 137.6 (aromatic quat), 129.1, 128.2, 126.4 (aromatic CH), 101.2 (Ph*C*HO_2), 82.8 (C-1), 73.6, 73.0, 69.8, 66.1 (C-2, C-3, C-4, C-5), 66.6 (C-6), 21.0 (S*C*$H_2$$CH_3$), 14.8 ($SCH_2CH_3$). Anal. Calcd for $C_{12}H_{20}O_7S$ (308.09): C, 46.74; H, 6.54. Found: C, 46.85; H, 6.46.

Ethyl 2,4,6-tri-O-acetyl-3-O-allyl-1-thio-β-D-galactopyranoside (**37**).—Compound **39** (589 mg, 1.5 mmol) was dissolved in toluene (50 mL) and was added to a flask equipped with a Dean-Stark separator containing dibutyl tin oxide (470 mg, 1.90 mmol). The solution was refluxed for 20 h and cooled to rt. Allyl bromide (2 mL, 23.0 mmol) and tetrabutylammonium bromide (214 mg, 0.66 mmol) were added, and the solution was heated to 60 °C. After stirring for 2 h, the mixture was cooled to rt and concentrated. Column chromatography resulted in the recovery of three compounds, which were pooled and acetylated, as described for the preparation of **37**, affording **40** (447 mg 77%): mp 31–33 °C; $[\alpha]_D$ + 18.1° (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.74 (1 H, $OCH_2CH{=}CH_2$), 5.42 (d, 1 H, $J_{3,4}$ 3.3 Hz, H-4), 5.20 (1 H, J_{cis} 10.5 Hz, $OCH_2CH{=}CHH$), 5.12 (1 H, J_{trans} 17.0 Hz, $OCH_2CH{=}CHH$), 5.08 (dd, 1 H, $J_{1,2} = J_{2,3}$ 9.8 Hz, H-2), 4.39 (d, 1 H, H-1), 4.12–4.04 (3 H, H-6a, H-6b, $OCHCH{=}CH_2$), 3.89 (1 H, OC*H*-$HCH{=}CH_2$), 3.79 (dd, 1 H, $J_{5,6a} = J_{5,6b}$ 6.5 Hz, H-5), 3.49 (dd, 1 H, H-3), 2.67 (m, 2 H, S$CH_2$$CH_3$), 2.10, 2.07, 2.03 (s, 3 H, CH_3 acetate), 1.24 (t, 3 H, *J* 7.5 Hz, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 170.5, 170.3, 169.5 (CO, acetate), 134.1 ($CH_2{=}CHCH_2O$), 117.3 ($CH_2{=}CHCH_2O$), 84.0 (C-1), 77.7, 74.7, 68.9, 66.4 (C-2, C-3, C-4, C-5), 70.3 ($CH_2{=}CHCH_2O$), 62.2 (C-6), 24.1 (S*C*$H_2$$CH_3$), 20.9, 20.8, 20.7 ($CH_3$, acetate), 14.9 ($SCH_2CH_3$). Anal. Calcd for $C_{17}H_{26}O_8S$ (390.45): C, 52.29; H, 6.71. Found: C, 52.25; H, 6.78.

Octyl 2,3-di-O-acetyl-4,6-O-benzylidine-β-D-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**40**).—Compound **40** (610 mg, 61%) was synthesized from octyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**38**)[6] (612 mg, 1.14 mmol), ethyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (**39**, 1.066 g, 1.26 mmol), *N*-iodosuccinimide (513 mg, 1.28 mmol), a catalytic amount of silver triflate, dry DCM (40 mL) and 4 Å sieves as described for the preparation of **57**: ^1H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.40–6.82 (25 H, Ph), 5.40 (s, 1 H, PhC*H*O_2), 5.34 (dd, 1 H, $J_{1',2'}$ 7.9, $J_{2',3'}$ 10.2 Hz, H-2′), 5.06 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 4.97, 4.79, 4.52, 4.50 (d, 1 H, *J* 11.5 Hz, PhCH_2), 4.77 (dd, 1 H, $J_{3',4'}$ 3.6 Hz, H-3′), 4.62 (d, 1 H, H-1′), 4.28–4.22 (2 H, H-4′, H-6a′), 4.12–4.06 (3 H, H-2, H-6a, H-6b), 3.90 (dd, 1 H, $J_{5',6b'}$ 1.6, $J_{6a',6b'}$ 12.3 Hz, H-6b′), 3.84–3.72 (3 H, H-3, H-4, OCH_2CH_2), 3.52 (1 H, H-5), 3.33 (dt, 1 H, *J* 7.0, 9.4 Hz, OCH_2CH_2), 3.21 (d, 1 H, H-5′), 2.03 (s, 6 H, CH_3, acetate), 1.42–1.30 (2 H, OCH_2CH_2),

1.28–0.92 (10 H, CH_2, octyl), 0.88 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 139.7, 139.5, 139.4, 133.8 (aromatic quat), 129.1, 128.4, 128.3, 128.2, 128.0, 124.3 (aromatic CH), 101.8 (Ph*C*HO$_2$), 100.3 (C-1′), 98.1 (C-1), 78.2 (C-2′), 77.0 (C-3), 75.1, 73.1 (Ph*C*H$_2$), 73.8 (C-5), 72.6 (C-4′), 71.3 (C-3′), 69.8 (O*C*H$_2$CH$_2$), 69.2 (C-2′), 68.8 (C-6′), 68.0 (C-6), 66.1 (C-5′), 55.6 (C-2) 31.5, 29.3, 29.2, 29.1, 25.8, 22.6 (CH_2, octyl), 14.1 (CH_3, octyl). HRESIMS Calcd for $C_{53}H_{61}NO_{14}Na$ 958.3990. Found 958.3997.

*Octyl 4,6-*O*-benzylidene-β-*D*-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**41**).—Compound **41** (43 mg, 70%) was synthesized from compound **40** (67 mg, 0.072 mmol), and a catalytic amount of sodium and in MeOH (2 mL) as described for the preparation of **58**: ^{1}H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.32–7.20 (15 H, Ph), 5.44 (s, 1 H, PhC*H*O$_2$), 5.01, 4.69, 4.67, 4.53 (d, 1 H, *J* 11.6 Hz, PhC*H*$_2$), 4.83 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.49 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.18 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.0 Hz, H-3), 4.10 (dd, 1 H, $J_{6a',5'}$ 1.1, $J_{6a',6b'}$ 9.3 Hz, H-6a′), 4.04–3.96 (3 H, H-2, H-6a, H-6b), 3.65 (dd, 1 H, $J_{2',3'}$ 9.6 Hz, H-2′), 3.55 (ddd, 1 H, $J_{5,6a} = J_{5,6b}$ 3.0, $J_{4,5}$ 11.1 Hz, H-5), 3.32 (1 H, OC*H*$_2$CH$_2$), 3.47–3.40 (2 H, H-3′, H-6b′), 3.33 (dt, 1 H, *J* 7.0, 9.4 Hz, OC*H*$_2$CH$_2$), 2.99 (bs, 1 H, H-5′), 1.66–1.45 (2 H, OCH$_2$C*H*$_2$), 1.36–1.20 (10 H, CH_2, octyl), 0.82 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 139.0, 138.0, 137.7, 134.2 (aromatic quat.), 129.2, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.5, 126.5,123.5 (aromatic CH), 103.4 (C-1′), 101.4 (Ph*C*HO$_2$), 99.9 (C-1), 79.2, 78.1, 75.3, 75.1, 72.8, 72.3, (C-2′, C-3, C-3′, C-4, C-4′, C-5), 74.7, 73.9 (Ph*C*H$_2$), 69.7 (O*C*H$_2$CH$_2$), 69.0, 68.8 (C-6, C-6′), 66.9 (C-5′), 57.2 (C-2) 31.8, 29.6, 29.4, 26.0, 23.6, 22.7 (CH_2, octyl), 14.1 (CH_3, octyl).

*Octyl 2,3,-di-*O*-benzyl-4,6-*O*-benzylidene-β-*D*-galactopyranosyl-(1→4)-3,6,-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**42**).—Compound **42** (255 mg, 66%) was synthesized from compound **41** (320 mg, 0.38 mmol), NaH (44 mg, 60% dispersion in oil, 1.1 mmol), tetrabutyl ammonium iodide (191 mg, 0.52 mmol), benzyl bromide (100 μL, 0.92 mmol) and DMF (2 mL) as described for the preparation of **59**: ^{1}H NMR ($CDCl_3$): δ 7.82–7.58 (4 H, Phth), 7.20–6.75 (25 H, Ph), 5.40 (s, 1 H, PhC*H*O$_2$), 5.09 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 5.03, 4.86, 4.83, 4.72, 4.62, 4.59, 4.34 (d, 1 H, *J* 12.7 Hz, PhC*H*$_2$), 4.47 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.28 (dd, 1 H, $J_{3,4}$ 8.4, $J_{2,3}$ 10.7 Hz, H-3), 4.26 (dd, 1 H, $J_{6a',5'}$ 1.2, $J_{6a',6b'}$ 12.2 Hz, H-6a′), 4.17 (dd, 1 H, H-2), 4.08 (dd, 1 H, $J_{4,5}$ 8.5 Hz, H-4), 4.01 (d, 1 H, $J_{3',4'}$ 3.7 Hz, H-4′), 3.91 (dd, 1 H, $J_{5,6a}$ 3.8, $J_{6a,6b}$ 12.0 Hz, H-6a), 3.85 (dd, 1 H, $J_{5,6b}$ 1.7 Hz, H-6b), 3.80–3.69 (3 H, H-2′, H-6b′, OC*H*$_2$CH$_2$), 3.53 (1 H, H-5), 3.40 (dd, 1 H, $J_{2',3'}$ 9.6 Hz, H-3′), 3.32 (dt, 1 H, *J* 6.1, 9.3 Hz, OC*H*$_2$CH$_2$), 3.14 (bs, 1 H, H-5′), 1.40–1.25 (2 H, OCH$_2$C*H*$_2$), 1.15–0.90 (10 H, CH_2, octyl), 0.78 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 138.7, 138.3, 138.1, 137.9, 134.2 (aromatic quat.), 128.9, 128.7, 128.5, 128.4, 128.3, 127.9, 127.6, 127.4, 125.3, 123.4 (aromatic CH), 102.3 (C-1′), 101.1 (Ph*C*HO$_2$), 97.0 (C-1), 79.4 (C-3′), 78.8 (C-2′), 78.4 (C-4), 76.9 (C-3), 74.3 (C-5), 75.1, 74.7, 72.5 71.6 (PhCH$_2$), 71.2 (C-4′), 69.2 (O*C*H$_2$CH$_2$), 68.1 (C-6′), 67.5 (C-6), 64.7 (C-5′), 55.0 (C-2) 31.2, 29.9, 29.4, 29.0, 23.6, 22.7 (CH_2, octyl), 14.7 (CH_3, octyl). Anal. Calcd for $C_{63}H_{69}NO_{12}$ (1031.48): C, 73.31; H, 6.74. Found: C, 73.23; H, 6.61.

*Octyl 2,3-di-*O*-benzyl-β-*D*-galactopyranosyl (1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**43**).—Compound **42** (549 mg, 0.52 mmol) was dissolved in 80% AcOH (50 mL). The solution was heated to 80 °C, stirred for 4 h, cooled to rt and co-concentrated with toluene. Column chromatography (5:1 toluene–EtOAc) of the crude resulted in **43** (449 mg, 92%) as a colorless oil: ^{1}H NMR ($CDCl_3$): δ 7.82–7.60 (4 H, Phth), 7.38–6.82 (20 H, Ph), 5.09 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 4.87, 4.84, 4.79, 4.69, 4.46, 4.39 (d, 1 H, *J* 12.0 Hz, PhC*H*$_2$), 4.41 (d, 1 H, $J_{1',2'}$ 8.4 Hz, H-1′), 4.28 (dd, 1 H, $J_{3,4}$ 8.6, $J_{2,3}$ 10.8 Hz, H-3), 4.15 (dd, 1 H, H-2), 4.03 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 3.88 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-4′), 3.85 (dd, 1 H, $J_{5,6a}$ 4.0, $J_{6a,6b}$ 10.8 Hz, H-6a), 3.76 (dt, 1 H, *J* 6.4, 9.4 Hz, OC*H*$_2$CH$_2$), 3.74–3.68 (2 H, H-6a′, H-6b), 3.62–3.54 (3 H, H-2′, H-5, H-6b′), 3.38–3.34 (2 H, H-3′,OC*H*$_2$CH$_2$), 3.20 (dd, 1 H, *J* 4.1, 5.7 Hz, H-5′), 2.60 (bs, 1 H, OH), 2.05 (bs, 1 H, OH), 1.42–1.30 (2 H, OCH$_2$C*H*$_2$), 1.20–0.90 (10 H, CH_2, octyl), 0.78 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 139.3, 139.2, 139.1, 138.6, 134.3 (aromatic quat), 129.2, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 127.8, 124.0 (aromatic CH), 103.5 (C-1′), 99.0 (C-1), 81.6 (C-3′), 80.0 (C-2′), 79.2 (C-4), 77.9 (C-3), 76.1, 75.9, 75.4, 74.6, 73.9, 72.9 (C-5, C-5′, Ph*C*H$_2$ × 4), 70.2 (O*C*H$_2$CH$_2$), 68.7 (C-6, C-4′), 68.0 (C-6′), 63.2 (C-2) 32.3, 30.0, 29.8, 29.7, 26.5, 23.3 (CH_2, octyl), 14.7 (CH_3, octyl). Anal. Calcd for $C_{56}H_{65}NO_{12}$ (943.45): C, 71.24; H, 6.94. Found: C, 71.02; H, 6.94.

*Octyl 2,3-di-*O*-benzyl-6-*O*-trityl-β-*D*-galactopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**44**).—Compound **43** (428 mg, 0.45 mmol) was dissolved in dry DCM (15 mL), and trityl chloride (184 mg, 0.65 mmol) and diisopropylethylamine (115 μL, 0.64 mmol) were added. The solution was stirred at rt for 8 h, diluted with toluene and concentrated under reduced pressure. Column chromatography (10:1 toluene–EtOAc) of the crude material afforded **44** (556 mg, quant): ^{1}H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.40–6.85 (35 H, Ph), 5.07 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.82, 4.79, 4.74, 4,71, 4.68, 4.60, 4.46, 4.40 (d, 1 H, *J* 12.2 Hz, PhC*H*$_2$), 4.38 (d, 1 H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.21 (dd, 1 H, $J_{3,4}$ 8.3, $J_{2,3}$ 10.7 Hz, H-3), 4.16 (dd, 1 H, H-2), 4.09 (dd, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 3.97 (d, 1 H, $J_{3',4'}$ 2.9 Hz, H-4′), 3.86 (dd, 1 H, $J_{5,6a}$ 4.0, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.75 (dt, 1 H,

J 6.4, 9.2 Hz, OCH_2CH$_2$), 3.71 (dd, 1 H, $J_{5,6b}$ 1.5, H-6b), 3.64 (dd, 1 H, $J_{2',3'}$ 9.3 Hz, H-2′), 3.51 (ddd, 1 H, $J_{5,4}$ 9.9 Hz, H-5), 3.42 (dd, 1 H, $J_{5'6a'}$ 6.4, $J_{6a',6b'}$ 9.6 Hz, H-6a′), 3.33 (dt, 1 H, *J* 6.2, 9.0 Hz, OCH_2CH$_2$), 3.31 (dd, 1 H, $J_{2',3'}$ 9.3 Hz, H-3′), 3.21 (dd, 1 H, $J_{5',6b'}$ 4.6, H-6b′), 3.09 (dd, 1 H, H-5′), 2.60 (bs, 1 H, OH), 1.40–1.30 (2 H, OCH$_2$CH_2), 1.25–0.90 (10 H, CH$_2$, octyl), 0.80 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 144.7, 139.4, 139.3, 139.1, 138.9, 134.3 (aromatic quat), 129.7, 129.4, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.5, 123.8 (aromatic CH), 103.4 (C-1′), 99.1 (C-1), 87.6 (Ph$_3$*C*), 81.7 (C-3′), 80.3 (C-2′), 78.4 (C-4), 77.7 (C-3), 76.0 (C-5), 73.3 (C-5′), 76.1, 74.9, 73.9, 72.7 (Ph*C*H$_2$), 70.2 (O*C*H$_2$CH$_2$), 68.7 (C-6), 67.9 (C-4′), 63.5 (C-6′), 56.2 (C-2) 32.3, 30.0, 29.9, 29.8, 26.5, 23.3 (CH$_2$, octyl), 14.7 (CH$_3$, octyl).

Octyl 2,3,4-tri-O-*benzyl-6*-O-*trityl-β*-D-*galactopyranosyl-(1→4)-3,6-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranoside* (**45**).—Compound **45** (477 mg, 84%) was synthesized from **44** (521 mg, 0.45 mmol), NaH (31mg, 60% dispersion in oil, 0.68 mmol), benzyl bromide (150 μL, 1.35 mmol), tetrabutylammonium iodide (550 mg, 1.35 mmol) and DMF (5 ml) as described for the preparation of **60**: ^{1}H NMR (CDCl$_3$): δ 7.80–7.60 (4 H, Phth), 7.38–6.70 (40 H, Ph), 5.02 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 4.84, 4.78, 4.75, 4,70, 4.69, 4.58, 4.43, 4.41, 4.37 (d, 1 H, *J* 11.5 Hz, PhCH_2), 4.36 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.20 (dd, 1 H, $J_{3,4}$ 8.3, $J_{2,3}$ 10.8 Hz, H-3), 4.11 (dd, 1 H, H-2), 3.98 (dd, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 3.96 (d, 1 H, $J_{3',4'}$ 2.9 Hz, H-4′), 3.84 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 10.8 Hz, H-6a), 3.75–3.68 (3 H, H-2′, H-6b, OCH_2CH$_2$), 3.49 (ddd, 1 H, $J_{5,6b}$ 1.9 Hz, H-5), 3.37–3.30 (3 H, H-3′, H-6a′, OCH_2CH$_2$), 3.21 (dd, 1 H, $J_{5',6b'} = J_{6a',6b'}$ 9.1 Hz, H-6b′), 3.11 (dd, 1 H, $J_{5',6a'}$ 5.9 Hz, H-5′), 1.40–1.25 (2 H, OCH$_2$CH_2), 1.08–0.92 (10 H, CH$_2$, octyl), 0.80 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 144.9, 139.9, 139.6, 139.4, 139.3, 139.2, 134.2 (aromatic quat.), 129.3, 129.1, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 123.4 (aromatic CH), 103.6 (C-1′), 99.0 (C-1), 87.5 (Ph$_3$*C*), 83.0 (C-3′), 80.9 (C-2′), 78.6 (C-4), 78.6 (C-3), 77.9 (C-5), 76.1, 74.9, 74.7, 74.5 (Ph*C*H$_2$), 74.8 (C-4′), 73.9 (C-5′), 73.8, 70.1 (O*C*H$_2$CH$_2$), 68.8 (C-6), 62.4 (C-6′), 56.4 (C-2) 32.3, 30.0, 29.9, 29.8, 26.5, 23.3 (CH$_2$, octyl), 14.7 (CH$_3$, octyl). Anal. Calcd for $C_{82}H_{85}NO_{12}$ (1276.55): C, 77.15; H, 6.71. Found: C, 76.92; H, 6.84.

Octyl 2,3,4-tri-O-*benzyl-β*-D-*galactopyranosyl-(1→4)-3,6-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranoside* (**46**).—Compound **45** (456 mg, 0.36 mmol) was dissolved in a solution of 5% trifluoroacetic acid and 5% triisopropylsilane in DCM (20 mL). The reaction mixture was stirred at rt for 2 h and concentrated with toluene as a co-solvent. Column chromatography (7:1 toluene–EtOAc) resulted in **46** (330 mg, 97%) as a colorless oil: ^{1}H NMR (CDCl$_3$): δ 7.80–7.60 (4H, Phth), 7.38–6.85 (25 H, Ph), 5.08 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.89, 4.88, 4.84, 4,82, 4.56, 4.52, 4.45, 4.38 (d, 1 H, *J* 11.9 Hz, PhCH_2), 4.41 (d, 1 H, $J_{1',2'}$ 8.5 Hz, H-1′), 4.28 (dd, 1 H, $J_{3,4}$ 9.3, $J_{2,3}$ 10.8 Hz, H-3), 4.14 (dd, 1 H, H-2), 3.98 (dd, 1 H, $J_{4,5}$ 8.9 Hz, H-4), 3.84 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 10.8 Hz, H-6a), 3.78–3.72 (3 H, H-2′, H-6b, OCH_2CH$_2$), 3.66 (d, 1 H, $J_{3',4'}$ 3.9 Hz, H-4′), 3.58–3.52 (2 H, H-5, H-6a′), 3.39 (dd, 1 H, $J_{2',3'}$ 9.3 Hz, H-3′), 3.34 (dt, 1 H, *J* 6.1, 9.5 Hz, OCH_2CH$_2$), 3.29 (dd, 1 H, $J_{5',6b'}$ 4.5, $J_{6a',6b'}$ 12.0 Hz, H-6b′), 3.20 (dd, 1 H, $J_{5',6a'}$ 7.7 Hz, H-5′), 2.34 (bs, 1 H, OH), 1.40–1.20 (2 H, OCH$_2$CH_2), 1.15–0.92 (10 H, CH$_2$, octyl), 0.80 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 138.8, 138.7, 138.6, 138.5, 133.7 (aromatic quat), 131.8, 128.5, 128.3, 127.9, 127.6, 127.5, 127.0, 123.2 (aromatic CH), 103.1 (C-1′), 98.4 (C-1), 82.6 (C-3′), 80.0 (C-2′), 78.6 (C-4), 77.3 (C-3), 75.4 (C-5), 75.3, 74.9, 74.7, 74.3, 73.8, 73.2, 73.1 (C-4′, C-5′, Ph*C*H$_2$ × 5), 69.5 (O*C*H$_2$CH$_2$), 68.1 (C-6), 62.0 (C-6′), 55.9 (C-2) 31.7, 29.3, 29.2, 29.1, 25.9, 22.6 (CH$_2$, octyl), 14.7 (CH$_3$, octyl). Anal. Calcd for $C_{63}H_{71}NO_{12}$ (1034.24): C, 73.16; H, 6.92. Found: C, 72.90; H, 6.85.

Octyl 2,3,4-tri-O-*benzyl-β*-D-*galactopyranosyl-(1→4)-2-acetamido-3,6-di*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**47**).—Compound **47** (255 mg, 86%) was synthesized from compound **46** (311 mg, 0.30 mmol), *tert*-butanol (15 mL) and ethylenediamine (5 mL), followed by Ac$_2$O (4 mL), MeOH (10 mL) and triethylamine (0.1 mL) as described for the preparation of **61**: ^{1}H NMR (CDCl$_3$): δ 7.38–7.20 (25 H, Ph), 5.65 (d, 1 H, *J* 7.7 Hz, N*H*Ac), 4.98, 4.92, 4.82, 4.79, 4.74, 4.72, 4.58, 4.56, 4.53, 4.41 (d, 1 H, *J* 11.2 Hz, PhCH_2), 4.90 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.39 (d, 1 H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.17 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.8 Hz, H-3), 3.89 (dd, 1 H, $J_{4,5}$ 8.2 Hz, H-4), 3.83–3.74 (4 H, H-2′, H-6a, H-6b, OCH_2CH$_2$), 3.70 (d, 1 H, $J_{3',4'}$ 2.7 Hz, H-4′), 3.62 (ddd, 1 H, *J* 3.3, 7.9 Hz, H-5), 3.58 (dd, 1 H, *J* 3.5, 7.7, H-6a′), 3.44 (dt, 1 H, *J* 6.2, 9.0 Hz, OCH_2CH$_2$), 3.39 (dd, 1 H, $J_{2',3'}$ 10.7 Hz, H-3′), 3.35 (m, 1 H, H-6b′), 3.29 (ddd, 1 H, H-2), 3.19 (dd, 1 H, *J* 5.1, 8.5 Hz, H-5′), 2.40 (bs, 1 H, OH), 1.84 (s, 3 H, CH$_3$ NHAc), 1.62–1.45 (2 H, OCH$_2$CH_2), 1.35–1.20 (10 H, CH$_2$, octyl), 0.84 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 171.0 (CO, acetate), 139.6, 139.3, 139.2, 139.1, 139.0 (aromatic quat), 129.1, 129.0, 128.9, 128.8, 128.6, 128.4, 128.2, 128.1 (aromatic CH), 103.9 (C-1′), 100.2 (C-1), 83.2 (C-3′), 80.6 (C-2′), 78.2 (C-4), 78.1 (C-3), 76.0, 75.7, 75.5, 75.1, 74.4, 73.9, 73.8, (C-4′, C-5, C-5′, Ph*C*H$_2$ × 5), 70.3 (O*C*H$_2$CH$_2$), 69.4 (C-6), 62.5 (C-6′), 57.1 (C-2) 32.5, 30.3, 30.1, 30.0, 26.7, 24.3 (CH$_2$, octyl), 23.3 (CH$_3$, acetate), 14.7 (CH$_3$, octyl). Anal. Calcd for $C_{57}H_{71}NO_{11}$ (945.17): C, 72.36; H, 7.56. Found: C, 72.16; H, 7.71.

Octyl 2,3,6-tri-O-*benzyl-β*-D-*galactopyranosyl-(1→4)-3,6-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*gluco*-

pyranoside (**48**).—Compound **42** (214 mg, 0.21 mmol), sodium cyanoborohydride (64 mg, 1.01 mmol), and methyl orange indicator were dissolved in dry THF (5 mL) containing crushed 4 Å molecular sieves. The solution was cooled to 0 °C, followed by the addition of ethereal hydrogen chloride until the red color of the solution persisted. After 3 h the reaction was quenched with sodium bicarbonate, filtered through Celite, diluted with DCM, washed with water and concentrated under reduced pressure. Column chromatography (7:1 toluene–EtOAc) of the residue gave **48** (124 mg, 57%) as a colorless oil: ^{1}H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.38–6.80 (25 H, Ph), 5.07 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.83, 4.82, 4.78, 4,70, 4.66, 4.57, 4.46, 4.42, 4.37 (d, 1 H, J 12.1 Hz, PhCH_2), 4.41 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.26 (dd, 1 H, $J_{3,4}$ 8.6, $J_{2,3}$ 10.9 Hz, H-3), 4.15 (dd, 1 H, H-2), 4.04 (dd, 1 H, $J_{4,5}$ 8.7 Hz, H-4), 3.99 (s, 1 H, H-4′), 3.85 (dd, 1 H, $J_{5,6a}$ 4.1, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.75 (dt, 1 H, J 6.0, 9.5 Hz, OCH_2CH$_2$), 3.71 (dd, 1 H, $J_{5,6b}$ 1.2 Hz, H-6b), 3.65 (dd, 1 H, $J_{5',6a'}$ 6.8, $J_{6a',6b'}$ 10.0 Hz, H-6a′), 3.60 (dd, 1 H, $J_{2',3'}$ 7.9 Hz, H-2′), 3.56–3.50 (2 H, H-5, H-6b′), 3.37–3.30 (3 H, H-3′, H-5′, OCH_2CH$_2$), 1.40–1.30 (2 H, OCH$_2$CH_2), 1.18–0.88 (10 H, CH$_2$, octyl), 0.78 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR ($CDCl_3$): δ 139.6, 139.3, 139.1, 138.8, 138.7, 134.3 (aromatic quat.), 132.4, 129.2, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6 (aromatic CH), 103.9 (C-1′), 99.0 (C-1), 81.7 (C-3′), 80.1 (C-2′), 78.9 (C-4), 77.8 (C-3), 76.1, 75.1, 74.3, 73.8, 73.5 (PhCH$_2$), 75.0 (C-5), 72.8 (C-5′), 70.2 (OCH$_2$CH$_2$), 69.5 (C-6′), 68.7 (C-6), 67.2 (C-4′), 56.5 (C-2) 32.3, 30.0, 29.9, 29.8, 26.5, 23.3 (CH$_2$, octyl), 14.7 (CH$_3$, octyl). Anal. Calcd for $C_{63}H_{71}NO_{12}$ (1034.24): C, 73.16; H, 6.92. Found: C, 73.32; H, 6.87.

Octyl 2,3,6-tri-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*2-acetamido*-*3,6-di*-O-*benzyl*-*2-deoxy*-β-D-*glucopyranoside* (**49**).—Compound **49** (91 mg, 90%) was synthesized from compound **48** (110 mg, 0.11 mmol), *tert*-butanol (5 mL) and ethylenediamine (2 mL), followed by Ac_2O (2 mL), MeOH (5 mL) and triethylamine (0.1 mL) as described for the preparation of **61**: ^{1}H NMR ($CDCl_3$): δ 7.35–7.20 (25 H, Ph), 5.68 (s, 1 H NHAc), 4.89 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 4.88, 4.81, 4.74, 4,70, 4.66, 4.58, 4.54, 4.47, 4.43, 4.37 (d, 1 H, J 11.3 Hz, PhCH_2), 4.41 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.12 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.4 Hz, H-3), 4.00 (d, 1 H, $J_{3',4'}$ 3.5 Hz, H-4′), 3.96 (dd, 1 H, $J_{4,5}$ 7.8 Hz, H-4), 3.83–3.78 (2 H, H-6a, OCH_2CH$_2$), 3.73 (dd, 1 H, $J_{5',6a'}$ 3.0, $J_{6a',6b'}$ 10.6 Hz, H-6a′), 3.68 (dd, 1 H, $J_{5,6b}$ 6.8, $J_{6a,6b}$ 9.7 Hz, H-6b), 3.61–3.56 (2 H, H-2′, H-5), 3.53 (dd, 1 H, $J_{5',6b'}$ 5.3 Hz, H-6b′), 3.43 (dt, 1 H, J 6.4, 9.1 Hz, OCH_2CH$_2$), 3.38–3.30 (3 H, H-2, H-3′, H-5′), 2.42 (bs, 1 H, OH), 1.84 (s, 3 H, CH$_3$, acetate), 1.60–1.48 (2 H, OCH$_2$CH_2), 1.35–1.20 (10 H, CH$_2$, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR ($CDCl_3$): δ 139.2, 139.1, 138.3, 138.2, 138.0 (aromatic quat), 128.9, 128.7, 128.6, 128.4, 128.3, 127.4, 127.1, 125.3 (aromatic CH), 102.5 (C-1′), 99.1 (C-1), 81.3 (C-3′), 78.7 (C-2′), 77.3 (C-3), 76.4 (C-4), 74.9, 73.8, 73.1, 72.2, 71.8 (PhCH$_2$), 74.0 (C-5), 72.1 (C-5′), 69.0 (OCH$_2$CH$_2$), 62.9, 62.8 (C-6, C-6′), 65.2 (C-4′), 54.7 (C-2) 34.8, 32.8, 32.7, 28.9, 22.3 (CH$_2$, octyl), 23.3 (CH$_3$, acetate), 14.7 (CH$_3$, octyl). Anal. Calcd for $C_{57}H_{71}NO_{11}$ (945.17): C, 72.36; H, 7.56. Found: C, 71.87; H, 7.58.

Octyl 2,4,6-tri-O-*acetyl*-*3*-O-*allyl*-β-D-*galactopyranosyl*-(1→4)-*3,6-di*-O-*benzyl*-*2-deoxy*-*2-phthalimido*-β-D-*glucopyranoside* (**50**).—Compound **50** (447 mg, 81%) was synthesized from octyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**38**)[6] (343 mg, 0.64 mmol), donor **37** (381 mg, 0.98 mmol), *N*-iodosuccinimide (247 mg, 0.99 mmol), a catalytic amount of silver triflate, and dry DCM (20 mL) as described for compound **57**: ^{1}H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.38–6.80 (10 H, Ph), 5.76 (1 H, OCH$_2$CH=CH$_2$), 5.28 (dd, 1 H, $J_{4',5'}$ 1.1, $J_{3',4'}$ 3.3 Hz, H-4′), 5.22 (1 H, J_{cis} 10.5 Hz, OCH$_2$CH=CHH), 5.15 (1 H, J_{trans} 17.0 Hz, OCH$_2$CH=CHH), 5.05 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 5.03 (dd, 1 H, $J_{1',2'}$ 8.1, $J_{2',3'}$ 10.0 Hz, H-2′), 4.79, 4.77, 4.50, 4.42 (d, 1 H, J 12.3 Hz, PhCH_2), 4.54 (d, 1 H, H-1′), 4.22 (dd, 1 H, $J_{3,4}$ 8.6, $J_{2,3}$ 10.9 Hz, H-3), 4.10 (dd, 1 H, H-2), 4.08 (1 H, OCHHCH=CH$_2$), 4.00 (dd, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 3.94 (dd, 1 H, $J_{5',6a'}$ 1.7, $J_{6a',6b'}$ 6.7 Hz, H-6a′), 3.84 (1 H, OCHHCH=CH$_2$), 3.79–3.76 (3 H, H-6a, H-6b, H-6b′), 3.73 (dt, 1 H, J 6.4, 9.5 Hz, OCH_2CH$_2$), 3.56 (ddd, 1 H, $J_{4',5'}$ 1.2, $J_{5',6b'}$ 5.5 Hz, H-5′), 3.52 (1 H, H-5), 3.32 (dt, 1 H, J 6.2, 9.4 Hz, OCH_2CH$_2$), 3.27 (dd, 1 H, H-3′), 2.02 (s, 9 H, CH$_3$, acetate), 1.42–1.34 (2 H, OCH$_2$CH_2), 1.18–0.90 (10 H, CH$_2$, octyl), 0.78 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR ($CDCl_3$): δ 170.5, 170.3, 169.3 (CO, acetate), 138.8, 138.3 (aromatic quat.), 134.2 (CH$_2$=CHCH$_2$O), 128.5, 128.0, 127.9, 127.8, 127.0, 123.2 (aromatic CH), 117.1 (CH$_2$=CHCH$_2$O), 100.6 (C-1′), 98.4 (C-1), 78.3 (C-4), 77.0 76.9 (C-3, C-3′), 75.0 (C-5), 74.4, 73.6 (PhCH$_2$), 71.1 (C-2′), 70.7 (C-5′), 70.5 (CH$_2$=CHCH$_2$O), 69.6 (OCH$_2$CH$_2$), 67.9 (C-6), 65.9 (C-4′), 61.4 (C-6′), 55.8 (C-2) 31.7, 29.2, 29.1, 25.8, 22.6 (CH$_2$, octyl), 21.0, 20.8 (CH$_3$, acetate), 14.7 (CH$_3$, octyl). HRESIMS Calcd for $C_{51}H_{63}NO_{15}Na$ 952.4095. Found 952.4094.

Octyl 3-O-*allyl*-*2,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*3,6-di*-O-*benzyl*-*2-deoxy*-*2-phthalimido*-β-D-*glucopyranoside* (**51**).—Compound **51** (142 mg, 27%) was synthesized through an initial deacetylation of **50** (446 mg, 0.52 mmol) with sodium and MeOH as described for compound **58**. The crude was redissolved in DMF (5 mL) with NaH (32 mg, 60% dispersion in oil, 0.80 mmol), tetrabutylammonium iodide (87 mg, 2.4 mmol) and benzyl bromide (250 μL, 2.3 mmol) as described for the preparation of **59**: ^{1}H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.38–6.80 (25 H, Ph), 5.91 (1 H, OCH$_2$CH=CH$_2$), 5.31 (1 H, J_{cis} 10.5 Hz,

$OCH_2CH{=}CH\mathit{H}$), 5.15 (1 H, J_{trans} 17.0 Hz, $OCH_2CH{=}C\mathit{H}H$), 5.08 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.91, 4.86, 4.80, 4.76, 4.55, 4.50, 4.34 (d, 1 H, J 11.7 Hz, $PhC\mathit{H}_2$), 4.45–4.38 (4 H, H-1′, $PhC\mathit{H}_2 \times 3$), 4.27–4.22 (3 H, H-3, H-6a, $PhC\mathit{H}_2$), 4.27–4.13 (2 H, H-2, $OCH\text{-}\mathit{H}CH{=}CH_2$), 4.00 (dd, 1 H, $J_{3,4}$ 8.6, $J_{4,5}$ 10.0 Hz, H-4), 3.82–3.66 (6 H, H-2′, H-4′, H-6a′, H-6b, $OC\mathit{H}_2CH_2$, $OC\mathit{H}HCH{=}CH_2$), 3.54 (ddd, 1 H, J 1.6, 2.2, 11.5 Hz, H-5), 3.44–3.38 (2 H, H-5′, H-6b′), 3.36 (dt, 1 H, J 6.5, 9.5 Hz, $OC\mathit{H}_2CH_2$), 3.28 (dd, 1 H, $J_{3',4'}$ 3.1, $J_{2',3'}$ 9.7 Hz, H-3′), 1.40–1.30 (2 H, $OCH_2C\mathit{H}_2$), 1.24–0.90 (10 H, CH_2, octyl), 0.78 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 139.2, 139.1, 138.9, 138.5, 138.1, 133.3 (aromatic quat.), 135.0 ($CH_2{=}\mathit{C}HCH_2O$), 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.8 (aromatic CH), 116.5 ($\mathit{C}H_2{=}CHCH_2O$), 103.0 (C-1′), 98.4 (C-1), 82.2 (C-3′), 80.0 (C-5′),78.2 (C-2′), 77.5 (C-4), 77.3 (C-3), 75.4 (C-5), 74.5, 74.4, 73.5, 73.3, 73.1 ($Ph\mathit{C}H_2 \times 5$, $CH_2{=}CH\mathit{C}H_2O$), 69.5 ($O\mathit{C}H_2CH_2$), 68.3, 68.2 (C-4′, C-6, C-6′), 55.8 (C-2) 31.7, 29.3, 29.2, 29.1, 25.9, 22.6 (CH_2, octyl), 14.1 (CH_3, octyl). Anal. Calcd for $C_{66}H_{75}NO_{12}$ (1074.30): C, 73.79; H, 7.04. Found: C, 73.43; H, 6.74.

Octyl 2,4,6-tri-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*3,6-di*-O-*benzyl*-*2-deoxy*-*2-phthalimido*-β-D-*glucopyranoside* (**52**).—Compound **52** (204 mg, 88%) was synthesized from compound **51** (241 mg, 0.25 mmol), palladium chloride (6 mg, 0.026 mmol), and MeOH (5 mL) as described for the preparation of **65**: ^1H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.38–6.80 (25 H, Ph), 5.09 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.86, 4.72, 4.68, 4.59, 4.56 (d, 1 H, J 11.8 Hz, $PhC\mathit{H}_2$), 4.48–4.36 (4 H, H-1′, $PhC\mathit{H}_2 \times 3$), 4.30–4.24 (2 H, H-3, $PhC\mathit{H}_2$), 4.17 (dd, 1 H, $J_{2,3}$ 10.9 Hz, H-2), 3.84 (dd, 1 H, $J_{3,4} = J_{4,5}$ 8.7 Hz, H-4), 3.84 (dd, 1 H, $J_{5,6a}$ 4.1, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.81 (d, 1 H, $J_{3',4'}$ 2.2 Hz, H-4′), 3.78–3.73 (2 H, H-6b, $OC\mathit{H}_2CH_2$), 3.56 (m, 1 H, H-5), 3.51–3.42 (5 H, H-2′, H-3′, H-5′, H-6a′, H-6b′), 3.35 (dt, 1 H, J 6.2, 9.0 Hz, $OC\mathit{H}_2CH_2$), 2.16 (bs, 1 H, OH), 1.50–1.40 (2 H, $OCH_2C\mathit{H}_2$), 1.34–0.90 (10 H, CH_2, octyl), 0.80 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 139.7, 139.4, 139.1, 139.0, 138.7, 134.4 (aromatic quat.), 132.4, 129.2, 129.1, 129.0, 128.7, 128.5, 128.4, 128.3, 128.2, 127.5 (aromatic CH), 103.7 (C-1′), 99.1 (C-1), 81.4 (C-3′), 78.9 (C-4),77.2 (C-3), 76.6 (C-4′), 77.3 (C-3), 76.0 (C-5), 75.8, 75.6, 75.0, 74.7, 74.1, 74.0, 73.9 (C-2′, C-5′, $Ph\mathit{C}H_2 \times 5$), 70.2 ($O\mathit{C}H_2CH_2$), 68.8 (C-6, C-6′), 56.5 (C-2) 32.4, 32.0, 29.9, 29.8, 25.5, 23.3 (CH_2, octyl), 14.7 (CH_3, octyl). HRESIMS Calcd for $C_{63}H_{71}NO_{12}Na$ 1056.4874. Found 1056.4868.

Octyl 2,4,6-tri-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*2-acetamido*-*3,6-di*-O-*benzyl*-*2-deoxy*-β-D-*glucopyranoside* (**53**).—Compound **53** (162 mg, 94%) was synthesized from compound **52** (191 mg, 0.18 mmol), *tert*-butanol (10 mL) and ethylenediamine (4 mL) followed by Ac_2O (4 mL), MeOH (10 mL) and triethylamine (0.2 mL) as described for the preparation of **61**: ^1H NMR ($CDCl_3$): δ 7.35–7.20 (25 H, Ph), 5.70 (d, 1 H, J 7.5 Hz, $N\mathit{H}Ac$), 4.91 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1), 4.85, 4.83, 4.76, 4.57, 4.56, 4.54, 4.42, 4.38, 4.30 (d, 1 H, J 11.6 Hz, $PhC\mathit{H}_2$), 4.14 (d, 1 H, $J_{1',2'}$ 7.3 Hz, H-1′), 4.14 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.8 Hz, H-3), 3.94 (dd, 1 H, $J_{4,5}$ 8.0 Hz, H-4), 3.83 (d, 1 H, $J_{3',4'}$ 2.8 Hz, H-4′), 3.81–3.74 (3 H, H-6a, H-6b, $OC\mathit{H}_2CH_2$), 3.60 (ddd, 1 H, $J_{5,6a} = J_{5,6b}$ 3.3 Hz, H-5), 3.54 (dd, 1 H, $J_{5',6a'} = J_{5',6b'}$ 6.4 Hz, H-5′), 3.52–3.40 (5 H, H-2′, H-3′, H-6a′, H-6b′, $OC\mathit{H}_2CH_2$), 3.31 (ddd, 1 H, H-2), 2.18 (bs, 1 H, OH), 1.92 (s, 3 H, CH_3, acetate), 1.60–1.50 (2 H, $OCH_2C\mathit{H}_2$), 1.34–1.20 (10 H, CH_2, octyl), 0.84 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 170.9 (CO, acetate), 139.7, 139.7, 139.1, 139.0, 138.6 (aromatic quat.), 129.2, 129.1, 129.0, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1 (aromatic CH), 103.7 (C-1′), 100.1 (C-1), 81.4 (C-3′), 78.1 (C-3), 77.8 (C-4), 76.5 (C-4′), 75.9 (C-5), 75.8, 75.7, 75.6, 74.7, 74.1, 74.0, 73.9 (C-2′, C-5′, $Ph\mathit{C}H_2 \times 5$), 70.4 ($O\mathit{C}H_2CH_2$), 69.3, 68.8 (C-6, C-6′), 57.0 (C-2) 32.4, 32.0, 30.1, 30.0, 26.7, 24.3 (CH_2, octyl), 23.4 (CH_3, acetate), 14.8 (CH_3, octyl). Anal. Calcd for $C_{57}H_{71}NO_{11}$ (945.17): C, 72.36; H, 7.56. Found: C, 72.37; H, 7.69.

Octyl 2-O-*acetyl*-*3,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*3,6-di*-O-*benzyl*-*2-deoxy*-*2-phthalimido*-β-D-*glucopyranoside* (**55**).—Compound **55** (1.38 g, 81% based on the acceptor) was synthesized from octyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**38**)[6] (965 mg, 1.6 mmol), ethyl 2-*O*-acetyl-2,4,6-tri-*O*-benzyl-thio-β-D-galactopyranoside[9] (**54**, 1.65 g, 3.1 mmol), *N*-iodosuccinimide (765 mg, 3.1 mmol), a catalytic amount of silver triflate and dry DCM (30 mL) containing crushed 4 Å molecular sieves as described for the preparation of **57**: ^1H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.38–6.78 (25 H, Ph), 5.34 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 10.1 Hz, H-2′), 5.06 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 5.06, 4.90, 4.84, 4.73, 4.63, 4.49, 4.45, 4.41, 4.33, 4.25 (d, 1 H, J 12.1 Hz, $PhC\mathit{H}_2$), 4.47 (d, 1 H, H-1′), 4.24 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.7 Hz, H-3), 4.13 (dd, 1 H, H-2), 3.97 (d, 1 H, $J_{3',4'}$ 3.9 Hz, H-4′), 3.78–3.73 (3 H, H-6a, H-6b, $OC\mathit{H}_2CH_2$), 3.52 (ddd, 1 H, $J_{5,6a} = J_{5,6b}$ 3.1, $J_{4,5}$ 9.9 Hz, H-5), 3.48–3.37 (4 H, H-5′, H-6a′,H-6b′, $OC\mathit{H}_2CH_2$), 3.34 (dd, 1 H, H-3′), 1.98 (s, 3 H, CH_3, acetate), 1.42–1.36 (2 H, $OCH_2C\mathit{H}_2$), 1.10–0.90 (10 H, CH_2, octyl), 0.78 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 170.0 (CO, acetate), 139.6, 139.5, 138.9, 138.8, 138.7 (aromatic quat.), 134.3, 129.1, 128.8, 128.6, 128.5, 128.0, 127.4 (aromatic CH), 101.5 (C-1′), 99.1 (C-1), 80.4 (C-3′), 78.0 (C-4), 77.1 (C-3), 75.1 (C-5), 74.6, 74.4, 73.5, 73.4 ($Ph\mathit{C}H_2$), 73.3 (C-5′), 72.7 (C-4′), 71.7 (C-2′), 69.6 ($O\mathit{C}H_2CH_2$), 68.1, 68.0 (C-6, C-6′), 55.8 (C-2) 31.6, 29.3, 29.1, 25.8, 22.6 (CH_2, octyl), 21.1 (CH_3, acetate), 14.1 (CH_3, octyl). Anal. Calcd for $C_{65}H_{73}NO_{13}$ (1076.27): C, 72.54; H, 6.84. Found: C, 72.91; H, 6.86.

Octyl 3,4,6-tri-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*2-acetamido-3,6-di*-O-*benzyl-2-deoxy*-β-D-*glucopyranoside* (**56**).—Compound **56** (1.10 g, 92%) was synthesized from compound **55** (1.37 g, 1.23 mmol), *tert*-butanol (50 mL), ethylenediamine (20 mL) followed by Ac_2O (10 mL), MeOH (40 mL) and triethylamine (0.5 mL) as described for the preparation of **61**: ^{1}H NMR ($CDCl_3$): δ 7.18–7.10 (25 H, Ph), 5.69 (d, 1 H, *J* 7.7 Hz, N*H*Ac), 4.87, 4.69, 4.64, 4.62, 4.59, 4.53, 4.51, 4.33, 4.26 (d, 1 H, *J* 12.1 Hz, PhCH_2), 4.77 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.48 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.09 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.7 Hz, H-3), 3.98 (dd, 1 H, $J_{4,5}$ 8.3 Hz, H-4), 3.95–3.87 (2 H, H-2′, H-6a), 3.86 (d, 1 H, $J_{3',4'}$ 2.5 Hz, H-4′), 3.83–3.76 (2 H, H-6b, OCH_2CH_2), 3.59 (ddd, 1 H, $J_{5,6a} = J_{5,6b}$ 3.1, H-5), 3.53 (d, 1 H, $J_{5',6a'} = J_{6a',6b'}$ 7.5 Hz, H-6a′), 3.44–3.32 (4 H, H-2, H-5′, H-6b′, OCH_2CH_2), 3.34 (dd, $J_{2',3'}$ 9.8 Hz, H-3′), 1.82 (s, 3 H, CH_3, acetate), 1.56–1.49 (2 H, OCH$_2$CH_2), 1.32–1.12 (10 H, CH_2, octyl), 0.87 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 169.4 (CO, acetate), 139.0, 138.8, 138.2, 138.0, 137.9 (aromatic quat.), 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3 (aromatic CH), 103.3 (C-1′), 100.0 (C-1), 81.9 (C-3′), 78.8 (C-3), 77.4 (C-4), 74.6, 73.8, 73.4, 72.3 (Ph*C*H_2), 74.5 (C-5), 73.5 (C-4′), 72.9 (C-5′), 72.1 (C-2′), 69.6 (O*C*H_2CH_2), 68.9 (C-6), 68.2 (C-6′), 55.0 (C-2) 31.9, 29.5, 26.3, 26.0, 24.7, 21.6 (CH_2, octyl), 20.8 (CH_3, acetate), 14.1 (CH_3, octyl). Anal. Calcd for $C_{57}H_{71}NO_{11}$ (945.17): C, 72.36; H, 7.56. Found: C, 72.36; H, 7.71.

Octyl 2-O-*acetyl-3,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*3*-O-*benzyl-2-deoxy-6*-O-p-*methoxybenzyl-2-phthalimido*-β-D-*glucopyranoside* (**57**).—The acceptor compound **34** (636 mg, 1.0 mmol) and the donor compound **54** (1.00 g, 2.0 mmol) were dissolved in dry DCM (20 mL) containing crushed 4 Å molecular sieves. The mixture was cooled to 0 °C, followed by the addition of *N*-iodosuccinimide (450 mg 2.0 mmol) and stirring for 45 min. A catalytic amount of silver triflate was added, the mixture was stirred for an additional 2 h, filtered through Celite, washed successively with sodium bicarbonate, sodium thiosulfate, and water, dried over magnesium sulfate and concentrated under reduced pressure. Column chromatography (10:1 toluene–EtOAc) resulted in **57** (977 mg 88% based on the acceptor) as a colorless oil: ^{1}H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.38–6.78 (24 H, Ph), 5.35 (dd, 1 H, $J_{1',2'}$ 7.9, $J_{2'3'}$ 10.0 Hz, H-2′), 5.07 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.91, 4.84, 4.68, 4.67, 4.49, 4.47, 4.46, 4.43, 4.40, 4.25 (d, 1 H, *J* 11.6 Hz, PhCH_2), 4.42 (d, 1 H, H-1′), 4.23 (dd, 1 H, $J_{3,4}$ 8.4, $J_{2,3}$ 10.8 Hz, H-3), 4.14 (dd, 1 H, H-2), 3.97 (dd, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 3.91 (d, 1 H, $J_{3',4'}$ 2.9 Hz, H-4′), 3.79–3.73 (6 H, H-6a, H-6b, OCH_2CH_2, CH_3), 3.52 (ddd, 1 H, $J_{5,6a} = J_{5,6b}$ 2.3 Hz, H-5), 3.46 (dd, 1 H, $J_{6a',5'} = J_{6a',6b'}$ 10.1 Hz, H-6a′), 3.42–3.32 (4 H, H-3′, H-5′, H-6b′, OCH_2CH_2), 2.00 (s, 3 H, CH_3, acetate), 1.42–1.30 (2 H, OCH$_2$CH_2), 1.20–0.85 (10 H, CH_2, octyl), 0.80 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 169.3 (CO, acetate), 159.2 (CO, Phth), 139.0, 138.8, 138.2, 138.0, 130.4 (aromatic quat), 133.7, 129.5, 128.4, 128.1, 127.8, 127.7, 127.6, 127.3, 127.2, 126.7, 123.2, 113.8 (aromatic CH), 100.9 (C-1′), 98.4 (C-1), 80.6 (C-3′), 78.0 (C-4), 77.1 (C-3), 75.2 (C-5), 74.5, 74.4, 73.4, 73.3, 71.8 (Ph*C*H_2), 73.3 (C-5′), 72.8 (C-4′), 72.0 (C-2′), 69.6 (O*C*H_2CH_2), 68.1 (C-6′), 67.6 (C-6′), 55.9 (C-2), 55.3 (OCH_3), 31.7, 29.3, 29.2, 29.1, 25.9, 22.6 (CH_2, octyl), 21.1 (CH_3, acetate), 14.1 (CH_3, octyl). Anal. Calcd for $C_{66}H_{75}NO_{14}$ (1106.30): C, 71.65; H, 6.83. Found: C, 71.42; H, 6.84.

Octyl 3,4,6-tri-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*3*-O-*benzyl-2-deoxy-6*-O-p-*methoxybenzyl-2-phthalimido*-β-D-*glucopyranoside* (**58**).—Compound **57** (30 mg, 0.026 mmol) was dissolved in dry MeOH (1 mL), and sodium (0.5 mg) added. The solution was stirred at rt for 48 h, neutralized with Amberlite IR-120 (H^+) resin, filtered and concentrated. Column chromatography (5:1 hexane–EtOAc) resulted in **58** (22 mg, 77%) as a colorless oil: ^{1}H NMR ($CDCl_3$): δ 7.80–7.60 (4 H, Phth), 7.38–6.80 (24 H, Ph), 5.04 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 4.86, 4.84, 4.69, 4.66, 4.52, 4.51, 4.42, 4.31, 4.24 (d, 1 H, *J* 11.6 Hz, PhCH_2), 4.54 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.36 (dd, 1 H, $J_{3,4}$ 7.5, $J_{2,3}$ 10.7 Hz, H-3), 4.14 (dd, 1 H, H-2), 4.07 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4) 3.99 (dd, 1 H, $J_{5,6a}$ 3.5, $J_{6a,6b}$ 11.4 Hz, H-6a), 3.90 (dd, 1 H, $J_{2',3'}$ 9.8 Hz, H-2′), 3.85 (d, 1 H, $J_{3',4'}$ 2.9 Hz, H-4′), 3.78–3.72 (5 H, H-6a′, H-6b, OCH_3), 3.61 (ddd, 1 H, $J_{5,6b}$ 5.5 Hz, H-5), 3.48 (dt, 1 H, *J* 6.4, 9.2 Hz, OCH_2CH_2), 3.41–3.32 (3 H, H-5′, H-6a′, OCH_2CH_2), 3.31 (dd, 1 H, $J_{3',4'}$ 2.9, $J_{2',3'}$ 9.9 Hz, H-3′), 3.22 (bs, 1 H, OH), 1.40–1.32 (2 H, OCH$_2$CH_2), 1.08–0.95 (10 H, CH_2, octyl), 0.88 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 159.3 (CO, Phth), 138.9, 138.8, 138.3, 137.9, 131.7 (aromatic quat), 133.6, 130.0, 129.7, 129.5, 127.8, 127.7, 127.6, 127.3, 127.2, 126.7, 123.2, 113.7 (aromatic CH), 103.6 (C-1′), 98.5 (C-1), 82.0 (C-3′), 78.6 (C-4), 78.5 (C-3, C-2′), 74.8 (C-5), 74.6, 74.4, 73.4, 73.2, 72.4 (Ph*C*H_2), 73.5 (C-5′), 73.1 (C-4′), 72.4 (C-2′), 69.6 (O*C*H_2CH_2), 68.4, 68.1 (C-6, C-6′), 56.0 (C-2), 55.2 (OCH_3), 31.6, 29.3, 29.1, 29.0, 25.8, 22.5 (CH_2, octyl), 14.1 (CH_3, octyl). Anal. Calcd for $C_{64}H_{73}NO_{13}$ (1064.26): C, 72.23; H, 6.91. Found: C, 71.62; H, 6.82.

Octyl 2,3,4,6-tetra-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*3*-O-*benzyl-2-deoxy-6*-O-p-*methoxybenzyl-2-phthalimido*-β-D-*glucopyranoside* (**59**).—Compound **58** (245 mg, 0.023 mmol) was dissolved in DMF (3 mL), and tetrabutyl ammonium iodide (170 mg, 0.046 mmol) was added. The solution was cooled to 0 °C, followed by the addition of NaH (13 mg, 60% dispersion in oil, 0.033 mmol). The mixture was stirred for 15 min and benzyl bromide (13 μL, 0.12 mmol) was added. Stirring at 0 °C was continued for 30 min and the reaction was quenched with MeOH, diluted with toluene, washed successively with brine and water, dried over sodium

sulfate and concentrated under reduced pressure. Column chromatography (5:1 hexane–EtOAc) gave **59** (94 mg, 35%): ^{1}H NMR ($CDCl_3$): δ 7.85–7.60 (4 H, Phth), 7.40–6.80 (29 H, Ph), 5.08 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.92, 4.87, 4.81, 4.70, 4.51, 4.45, 4.35, 4.32, 4.22 (d, 1 H, J 11.6 Hz, PhCH_2), 4.41 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.26 (dd, 1 H, $J_{3,4}$ 8.5, $J_{2,3}$ 10.0 Hz, H-3), 4.16 (dd, 1 H, H-2), 4.02 (dd, 1 H, $J_{4,5}$ 8.4 Hz, H-4) 3.88 (d, 1 H, $J_{3',4'}$ 2.9 Hz, H-4′), 3.83 (dd, 1 H, $J_{5,6a}$ 4.1, $J_{6a,6b}$ 10.8 Hz, H-6a), 3.79–3.72 (5 H, H-2′, OCH_2CH$_2$, OCH$_3$), 3.68 (dd, 1 H, $J_{5,6b}$ 1.7 Hz, H-6b), 3.54 (ddd, 1 H, H-5), 3.47–3.37 (4 H, H-3′, H-5′, H-6a′, H-6b′), 3.34 (dt, 1 H, J 6.2, 9.0 Hz, OCH_2CH$_2$), 1.44–1.30 (2 H, OCH$_2$CH_2), 1.10–0.90 (10 H, CH$_2$, octyl), 0.88 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR ($CDCl_3$): δ 159.7 (CO, Phth), 139.8, 139.7, 139.5, 139.3, 138.8, 130.0 (aromatic quat.), 131.2, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.4, 113.7 (aromatic CH), 103.7 (C-1′), 99.0 (C-1), 83.1 (C-3′), 80.8 (C-2′), 78.7 (C-4), 77.9 (C-3), 76.0, 75.2, 75.0, 74.5, 74.1, 73.7, 73.5, 73.4 (C-4′, C-5, C-5′, PhCH$_2$ × 5), 70.2 (OCH$_2$CH$_2$), 69.0 (C-6′), 68.5 (C-6), 56.5 (C-2), 55.9 (OCH$_3$), 32.3, 30.0, 29.9, 29.8, 26.5, 23.3 (CH$_2$, octyl), 14.7 (CH$_3$, octyl). HRESIMS Calcd for $C_{71}H_{79}NO_{13}Na$ 1176.5449. Found 1176.5445.

Octyl 2,3,4,6-tetra-O-*benzyl-β*-D-*galactopyranosyl-(1→4)-3*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranoside* (**60**).—Compound **59** (95 mg, 0.082 mmol) was dissolved in DCM (10 mL), and DDQ (29 mg, 0.13 mmol) was added. The solution was stirred at rt for 2 h, and the reaction was quenched with 1,4-cyclohexadiene, followed by successive washes of sodium bicarbonate and water. The solution was dried over sodium sulfate and concentrated under reduced pressure. Column chromatography (8:1 toluene–acetone) resulted in **60** (49 mg, 59%): ^{1}H NMR ($CDCl_3$): δ 7.88–7.64 (4 H, Phth), 7.38–6.80 (25 H, Ph), 5.13 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.93, 4.88, 4.85, 4.82, 4.70, 4.52, 4.46, 4.34, 4,24 (d, 1 H, J 11.6 Hz, PhCH_2), 4.51 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.27 (dd, 1 H, $J_{3,4}$ 8.5, $J_{2,3}$ 10.8 Hz, H-3), 4.11 (dd, 1 H, H-2), 3.91 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 3.90–3.83 (3 H, H-4′, H-6a′, H-6b′), 3.81 (dd, 1 H, $J_{2',3'}$ 9.7 Hz, H-2′), 3.73 (dt, 1 H, J 6.1, 9.8 Hz, OCH_2CH$_2$), 3.56–6.52 (2 H, H-3′, H-5), 3.48–3.38 (3 H, H-5′, H-6a, H-6b), 3.34 (dt, 1 H, J 6.4, 9.8 Hz, OCH_2CH$_2$), 1.40–1.28 (2 H, OCH$_2$CH_2), 1.18–0.88 (10 H, CH$_2$, octyl), 0.79 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR ($CDCl_3$): δ 139.1, 139.0, 138.6, 138.5, 138.1, 133.7 (aromatic quat), 131.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.3, 126.8, 123.2 (aromatic CH), 103.4 (C-1′), 98.4 (C-1), 82.5 (C-3′), 80.1 (C-2′), 78.2 (C-4) 77.3 (C-3), 75.6, 74.5, 74.4, 73.8, 73.3 (PhCH$_2$), 75.5 (C-5′), 73.9 (C-4′), 72.8 (C-5), 69.9 (OCH$_2$CH$_2$), 68.7, 68.4 (C-6, C-6′), 56.3 (C-2) 31.6, 29.3, 29.2, 29.1, 25.8, 22.6 (CH$_2$, octyl), 14.1 (CH$_3$, octyl). HRESIMS Calcd for $C_{63}H_{71}NO_{12}Na$ 1056.4874. Found 1056.4877.

Octyl 2,3,4,6-tetra-O-*benzyl-β*-D-*galactopyranosyl-(1→4)-2-acetamido-3*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**61**).—Compound **60** (98 mg, 0.095 mmol) was dissolved in *tert*-butanol (5 mL) and ethylenediamine (2 mL), heated to 90 °C, and stirred for 30 h. The solution was cooled to rt and co-concentrated with toluene. The resulting oil was dissolved in MeOH (5 mL) and Ac_2O (2 mL), and triethylamine (0.1 mL) was added. The solution was stirred at rt for 2 h, followed by the addition of EtOH (10 mL) and water (2 mL). The solution was stirred for 15 min, washed successively with sodium bicarbonate and water, dried over magnesium sulfate and concentrated under reduced pressure. Column chromatography (6:1 toluene–EtOAc) gave **61** (70 mg, 82%) as a colorless oil: ^{1}H NMR ($CDCl_3$): δ 7.35–7.18 (25 H, Ph), 5.59 (d, 1 H, J 7.6 Hz, NHAc), 4.95, 4.94, 4.81, 4.79, 4.70, 4.54, 4.52, 4.35, 4.25 (d, 1 H, J 11.6 Hz, PhCH_2), 4.91 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.47 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.10 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.0 Hz, H-3), 3.92 (d, 1 H, $J_{3',4'}$ 2.5 Hz, H-4′), 3.86–3.74 (5 H, H-2′, H-4, H-6a′, H-6b′, OCH_2CH$_2$), 3.54–3.48 (3 H, H-3′, H-6a, H-5), 3.46–3.38 (3 H, H-5′, H-6b, OCH_2CH$_2$), 3.25 (ddd, 1 H, H-2) 1.84 (s, 3 H, CH$_3$ NHAc), 1.56–1.48 (2 H, OCH$_2$CH_2), 1.32–1.18 (10 H, CH$_2$, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR ($CDCl_3$): δ 170.9 (CO, acetate), 139.7, 139.6, 139.2, 139.1, 138.3 (aromatic quat.), 129.1, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1 (aromatic CH), 104.0 (C-1′), 100.5 (C-1), 83.1 (C-3′), 80.7 (C-4), 78.4 (C-3), 76.4 (C-2′), 76.1, 75.4, 75.0, 74.5, 74.2, 73.9, 73.5 (C-4′, C-5, C-5′, PhCH$_2$ × 5), 70.7 (OCH$_2$CH$_2$), 68.9 (C-6), 62.1 (C-6′), 57.8 (C-2) 32.5, 30.3, 30.0, 29.9, 26.7, 24.5 (CH$_2$, octyl), 23.4 (CH$_3$, acetate), 14.8 (CH$_3$, octyl). HRESIMS Calcd for $C_{57}H_{71}NO_{11}Na$ 968.4925. Found 968.4925.

Octyl 2-O-*acetyl-3,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl-(1→4)-3*-O-*allyl-6*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranoside* (**62**).—Compound **62** (1.85 g, 80% based on the acceptor) was synthesized from acceptor **30** (2.14 g, 2.3 mmol), donor **54** (2.33 g, 4.3 mmol), *N*-iodosuccinimide (990 mg, 4.0 mmol), a catalytic amount of silver triflate and dry DCM (40 mL) containing crushed 4 Å molecular sieves as described for the preparation of **57**: ^{1}H NMR ($CDCl_3$): δ 7.80–7.70 (4 H, Phth), 7.38–7.18 (20 H, Ph), 5.44 (1 H, OCH$_2$CH=CH$_2$), 5.26 (dd, 1 H, $J_{1',2'}$ 7.9, $J_{2',3'}$ 10.2 Hz, H-2′), 5.08 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.91–4.86 (2 H, PhCH_2, OCH$_2$CH=CHH), 4.72 (d, 1 H, J 12.2 Hz, PhCH_2), 4.68 (2 H, PhCH_2, OCH$_2$CH=CHH), 4.55–4.37 (6 H, H-1′, PhCH_2 × 5), 4.31 (1 H, OCH-HCH=CH$_2$), 4.14 (2 H, H-2, H-3), 3.91 (d, 1 H, $J_{3',4'}$ 2.3 Hz, H-4′), 3.87 (dd, 1 H, $J_{3,4}$ 8.1, $J_{4,5}$ 9.9 Hz, H-4), 3.83–3.72 (4 H, H-6a, H-6b, OCH_2CH$_2$, OCH-HCH=CH$_2$), 3.61 (dd, 1 H, $J_{5',6a'} = J_{6a',6b'}$ 9.0 Hz, H-6a′), 3.55 (dd, 1 H, $J_{5',6b'}$ 5.2 Hz, H-6b′), 3.51 (ddd, 1 H, J 2.9, 5.0, 9.9 Hz, H-5), 3.42 (dd, 1 H, H-5′), 3.36 (dt,

1 H, *J* 6.4, 9.0 Hz, OCH_2CH$_2$), 3.33 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-3′), 1.96 (s, 3 H, CH_3, acetate), 1.42–1.32 (2 H, OCH$_2$CH_2), 1.18–0.90 (10 H, CH_2, octyl), 0.88 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 169.3 (CO, acetate), 138.8, 138.2, 138.1, 138.0 (aromatic quat.), 135.1 (CH$_2$=*C*HCH$_2$O), 133.9, 131.8, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3 (aromatic CH), 116.2 (*C*H$_2$=CHCH$_2$O), 100.8 (C-1′), 98.4 (C-1), 80.4, 77.8, 77.6, 75.1, 74.3 (C-2′, C-3, C-3′, C-4, C-4′), 73.7, 73.6, 73.5, 72.6, 71.7 (C-5, C-5′, Ph*C*H$_2$, CH$_2$=CH*C*H$_2$O), 69.6 (O*C*H$_2$CH$_2$), 68.2, 68.1 (C-6, C-6′), 56.0 (C-2) 31.6, 29.3, 29.2, 29.1, 25.9, 22.6 (CH_2, octyl), 21.1 (CH_3, acetate), 14.1 (CH_3, octyl). Anal. Calcd for $C_{61}H_{71}NO_{13}$ (1026.22): C, 71.39; H, 6.97. Found: C, 71.13; H, 7.00.

Octyl 3,4,6-tri-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*3*-O-*allyl*-*6*-O-*benzyl*-*2*-*deoxy*-*2*-*phthalimido*-β-D-*glucopyranoside* (**63**).—Compound **63** (1.31 g 78% mg, 77%) was synthesized from **62** (1.76 g, 1.74 mmol), MeOH (50 mL), and sodium (12 mg) as described for the preparation of **58**: ^{1}H NMR ($CDCl_3$): δ 7.88–7.70 (4 H, Phth), 7.38–7.20 (20 H, Ph), 5.44 (1 H, OCH$_2$C*H*=CH$_2$), 5.07 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 4.90–4.84 (2 H, PhCH_2, OCH$_2$CH=CH*H*), 4.72–4.52 (7 H, H-1′, PhCH_2 × 5, OCH$_2$CH=C*H*H), 4.39, 4.35 (d, 1 H, *J* 11.9 Hz, PhCH_2), 4.28 (1 H, OCH*H*CH=CH$_2$), 4.24 (dd, 1 H, $J_{3,4}$ 8.5, $J_{2,3}$ 10.7 Hz, H-3), 4.13 (dd, 1 H, H-2), 4.02–3.97 (2 H, H-4, H-6a), 3.87–3.74 (4 H, H-2′, H-6b, OCH_2CH$_2$, OC*H*HCH=CH$_2$), 3.62–3.56 (2 H, H-5, H-6a′), 3.52–3.44 (2 H, H-5′, H-6b′), 3.35 (dt, 1 H, *J* 6.4, 9.2 Hz, OCH_2CH$_2$), 3.31 (dd, 1 H, $J_{3',4'}$ 2.9, $J_{2',3'}$ 9.7 Hz, H-3′), 3.27 (d, 1 H, H-4′), 1.44–1.30 (2 H, OCH$_2$CH_2), 1.18–0.90 (10 H, CH_2, octyl), 0.78 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 139.5, 139.0, 138.6, 138.5 (aromatic quat.), 135.6 (CH$_2$=*C*HCH$_2$O), 134.7, 132.5, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 128.0 (aromatic CH), 116.7 (*C*H$_2$=CHCH$_2$O), 104.5 (C-1′), 99.2 (C-1), 82.5 (C-3′, C-4′), 79.3 (C-3), 78.9 (C-4), 75.4 (C-5), 75.0, 74.2, 74.1, 73.7, 73.1 (C-5′, Ph*C*H$_2$ × 4, CH$_2$=CH*C*H$_2$O), 70.3 (O*C*H$_2$CH$_2$), 69.2, 69.1 (C-6, C-6′), 56.8 (C-2) 32.4, 30.0, 29.9, 29.8, 26.5, 23.3 (CH_2, octyl), 14.7 (CH_3, octyl). Anal. Calcd for $C_{59}H_{69}NO_{12}$ (983.48): C, 72.00; H, 7.07. Found: C, 71.69; H, 7.14.

Octyl 2,3,4,6-tetra-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*3*-O-*allyl*-*6*-O-*benzyl*-*2*-*deoxy*-*2*-*phthalimido*-β-D-*glucopyranoside* (**64**).—Compound **64** (94 mg, 35%, 30% unreacted starting material **63**) was synthesized from compound **63** (115 mg, 0.12 mmol), DMF (2 mL), tetrabutylammonium iodide (90 mg, 0.24 mmol), benzyl bromide (26 μL, 0.24 mmol) and NaH (10 mg, 60% dispersion in oil, 0.25 mmol) as described for the preparation of **59**: ^{1}H NMR ($CDCl_3$): δ 7.88–7.70 (4 H, Phth), 7.40–7.18 (25 H, Ph), 5.47 (1 H, OCH$_2$C*H*=CH$_2$), 5.10 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.89 (1 H, J_{cis} 10.5 Hz, OCH$_2$CH=CH*H*), 4.91, 4.78, 4.76, 4.53, 4.52, 4.44 (d, 1 H, *J* 11.2 Hz, PhCH_2), 4.70–4.65 (4 H, H-1′, PhCH_2 × 2, OCH$_2$CH=C*H*H), 4.40–4.32 (PhCH_2 × 2, OCH*H*CH=CH$_2$), 4.20–4.12 (2 H, H-2, H-3), 3.93 (dd, 1 H, $J_{3,4}$ 8.2, $J_{4,5}$ 9.9 Hz, H-4), 3.88–3.84 (2 H, H-4′, OC*H*HCH=CH$_2$), 3.81 (dd, 1 H, $J_{5,6a}$ 4.4, $J_{6a,6b}$ 10.8 Hz, H-6a), 3.77 (dt, 1 H, *J* 6.7, 9.9 Hz, OCH_2CH$_2$), 3.71 (dd, 1 H, $J_{5,6b}$ 1.7 Hz, H-6b), 3.68 (dd, 1 H, $J_{1',2'}$ 7.7, $J_{2',3'}$ 9.7 Hz, H-2′), 3.59 (dd, 1 H, $J_{6a',5'} = J_{6a',6b'}$ 8.2 Hz, H-6a′), 3.56–3.50 (2 H, H-5′, H-6b′), 3.40–3.32 (3 H, H-3′, H-5, OCH_2CH$_2$), 1.42–1.34 (2 H, OCH$_2$CH_2), 1.18–0.90 (10 H, CH_2, octyl), 0.78 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 139.8, 139.5, 139.3, 139.2, 138.8 (aromatic quat.), 136.1 (CH$_2$=*C*HCH$_2$O), 134.6, 132.5, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 127.9 (aromatic CH), 116.7 (*C*H$_2$=CHCH$_2$O), 103.6 (C-1′), 99.1 (C-1), 83.1 (C-3′), 80.7 (C-2′), 78.4 (C-4), 78.2 (C-2, C-3), 76.1, 76.0, 75.1, 74.4, 74.3, 73.8, 73.3 (C-4′, C-5, C-5′, Ph*C*H$_2$ × 5, CH$_2$=CH*C*H$_2$O), 70.2 (O*C*H$_2$CH$_2$), 69.1, 69.0 (C-6, C-6′), 56.8 (C-2) 32.4, 30.0, 29.9, 29.8, 26.5, 23.3 (CH_2, octyl), 14.7 (CH_3, octyl). Anal. Calcd for $C_{66}H_{75}NO_{12}$ (1074.30): C, 73.79; H, 7.04. Found: C, 73.79; H, 7.20.

Octyl 2,3,4,6-tetra-O-*benzyl*-β-D-*galactopyanosyl*-(1→4)-*6*-O-*benzyl*-*2*-*deoxy*-*2*-*phthalimido*-β-D-*glucopyranoside* (**65**).—Compound **64** (1.03 g, 0.91 mmol) was dissolved in dry MeOH (50 mL), and palladium chloride (25 mg, 0.14 mmol) was added. The solution was stirred at rt for 3 h. The solvent was concentrated, and the crude product was purified without further workup. Column chromatography (10:1 toluene–EtOAc) resulted in **65** (781 mg, 95%) as a colorless oil: ^{1}H NMR ($CDCl_3$): δ 7.88–7.70 (4 H, Phth), 7.38–7.20 (25 H, Ph), 5.16 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.88, 4.84, 4.76, 4.69, 4.51(d, 1 H, *J* 11.6 Hz, PhCH_2), 4.43 (dd, 1 H, $J_{3,4}$ 8.2, $J_{2,3}$ 10.8 Hz, H-3), 4.39–4.25 (6 H, H-1′, PhCH_2 × 5), 4.16 (dd, 1 H, H-2), 3.82–3.74 (4 H, H-2′, H-4′, H-6a, OCH_2CH$_2$), 3.71–3.64 (2 H, H-5, H-6), 3.59 (dd, 1 H, $J_{4,5}$ 8.3 Hz, H-4), 3.55–3.51 (2 H, H-5′, H-6a′), 3.48–3.42 (2 H, H-3′, H-6b′), 3.39 (dt, 1 H, *J* 6.4, 9.8 Hz, OCH_2CH$_2$), 1.45–1.18 (2 H, OCH$_2$CH_2), 1.15–0.82 (10 H, CH_2, octyl), 0.80 (t, 3 H, *J* 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 138.6, 138.5, 138.4, 138.2, 137.5, 133.8 (aromatic quat.), 132.0, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.4 (aromatic CH), 82.4 (C-1′), 82.2 (C-1), 79.0 (C-3′, C-4), 77.4 (C-2′), 75.5, 74.8, 74.7, 73.6, 73.3, 73.1, 73.0 (C-4′, C-5, C-5′, Ph*C*H$_2$ × 5), 69.8 (C-3), 69.7 (O*C*H$_2$CH$_2$), 68.7, 68.4 (C-6, C-6′), 56.3 (C-2) 31.7, 29.3, 29.2, 25.9, 22.6 (CH_2, octyl), 14.1 (CH_3, octyl).

Octyl 2,3,4,6-tetra-O-*benzyl*-β-D-*galactopyranosyl*-(1→4)-*6*-O-*benzyl*-*2*-*deoxy*-*2*-*acetamido*-β-D-*glucopyranoside* (**66**).—Compound **66** (615 mg, 96%) was synthesized from compound **65** (700 mg, 0.68 mmol), *tert*-butanol (35 mL) and ethylenediamine (10 mL), followed by Ac_2O (15 mL), MeOH (35 mL) and triethy-

lamine (0.5 mL) as described for the preparation of **61**: ^{1}H NMR ($CDCl_3$): δ 7.38–7.20 (25 H, Ph), 5.53 (d, 1 H, J 7.5 Hz, N*H*Ac), 4.90, 4.82, 4.73, 4.70, 4.54, 4.42, 4.35, 4.28 (d, 1 H, J 11.5 Hz, PhCH_2), 4.85 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.29 (d, 1 H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.27 (dd, 1 H, $J_{2,3} = J_{3,4}$ 9.0 Hz, H-3), 3.85 (d, 1 H, $J_{3',4'}$ 2.5 Hz, H-4′), 3.83 (dt, 1 H, J 6.4, 9.0 Hz, OCH_2CH$_2$), 3.76 (dd, 1 H, $J_{2',3'}$ 9.7 Hz, H-2′), 3.69 (d, 1 H, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 10.7 Hz, H-6a), 3.61 (d, 1 H, $J_{5,6b}$ 5.0 Hz, H-6b), 3.58–3.45 (6 H, H-4, H-5, H-5′, H-6a′, H-6b′, OCH_2CH$_2$), 3.44 (dd, 1 H, H-3′), 3.25 (ddd, 1 H, H-2) 1.98 (s, 3 H, CH_3 NHAc), 1.60–1.50 (2 H, OCH$_2$CH_2), 1.35–1.20 (10 H, CH_2, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 170.9 (CO, acetate), 139.2, 139.1, 138.9, 138.3 (aromatic quant), 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0 (aromatic CH), 104.4 (C-1′), 100.5 (C-1), 83.0 (C-3′), 82.4 (C-4), 79.7 (C-2′), 76.1, 75.3, 75.1, 74.3, 74.2, 74.0, 73.9, 73.6 (C-4′, C-5, C-5′, PhCH$_2$ × 5), 72.0 (C-3), 70.4 (OCH$_2$CH$_2$), 69.4, 68.9 (C-6, C-6′), 58.5 (C-2) 32.5, 30.3, 30.0, 26.7, 24.5 (CH_2, octyl), 23.4 (CH_3, acetate), 14.8 (CH_3, octyl). Anal. Calcd for $C_{57}H_{71}NO_{11}$ (945.17): C, 72.36; H, 7.56. Found: C, 75.59; H, 7.65.

Octyl 2,3,4-tri-O-*benzyl-6*-O-*diphenoxyphosphono-β*-D-*galactopyranosyl-(1→4)-2-acetamido-3,6-di*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**67**).—Compound **47** (30 mg, 0.32 mmol) was dissolved in pyridine (1 mL), and the solution was cooled to 0 °C. To the cooled solution, a catalytic amount of 4-dimethylaminopyridine, and diphenyl phosphorochloridate (30 μL, 0.14 mmol) were added, and the mixture was allowed to warm to rt. The solution was stirred for 24 h, diluted with DCM, washed sequentially with water, sodium bicarbonate, and water and concentrated under reduced pressure. Column chromatography (5:1 toluene–acetone) gave unreacted starting material (5 mg, 16%) and **67** (27 mg, 72%): ^{1}H NMR ($CDCl_3$): δ 7.38–7.10 (35 H, Ph), 5.67 (d, 1 H, J 7.5 Hz, N*H*Ac), 4.94, 4.85, 4.80, 4.77, 4.68, 4.55, 4.53, 4.46, 4.36 (d, 1 H, J 11.2 Hz, PhCH_2), 4.89 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.39 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.19–4.09 (3 H, H-3, H-6a′, H6b′), (dd, 1 H, $J_{3,4} = J_{4,5}$ 8.2 Hz, H-4), 3.83–3.78 (3 H, H-4′, H-6a, OCH_2CH$_2$), 3.74–3.70 (2 H, H-2′, H-6b), 3.56 (ddd, 1 H, $J_{5,6a} = J_{5,6b}$ 4.0 Hz, H-5), 3.43 (dt, 1 H, J 6.8, 9.7 Hz, OCH_2CH$_2$), 3.38 (dd, 1 H, $J_{5',6a'} = J_{5',6b'}$ 7.1 Hz, H-5′), 3.33–3.28 (2 H, H-2, H-3′), 1.84 (s, 3 H, CH_3, acetate), 1.60–1.50 (2 H, OCH$_2$CH_2), 1.34–1.20 (10 H, CH_2, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 138.9, 138.6, 138.5, 138.4, 138.3 (aromatic quat.), 130.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.4, 125.5, 120.1 (aromatic CH), 102.9 (C-1′), 99.7 (C-1), 82.0 (C-3′), 79.6 (C-2′), 77.5 (C-3), 77.3 (C-4), 75.3, 74.7, 74.0, 73.1, 72.9 (PhCH$_2$), 75.1 (C-5), 73.0 (C-4′), 72.2 (d, $J_{5',P}$ 8.4 Hz, C-5′), 69.7 (OCH$_2$CH$_2$), 68.5 (C-6), 66.0 (d, $J_{6',P}$ 5.4 Hz, C-6′), 56.4 (C-2) 31.8, 29.6, 29.4, 29.3, 26.0, 23.6 (CH_2, octyl), 22.7 (CH_3, acetate), 14.1 (CH_3, octyl). HRESIMS Calcd for $C_{69}H_{80}NO_{14}NaP$ 1200.5214. Found 1200.5230.

Octyl 6-O-*phosphono-β*-D-*galactopyanosyl-(1→4)-2-acetamido-2-deoxy-β*-D-*glucopyranoside*, *disodium salt* (**5**).—Compound **67** (25 mg, 0.021 mmol) was dissolved in 95% EtOH (2 mL) containing 5% palladium-on-activated-charcoal (12 mg), and the mixture was stirred under hydrogen at ambient pressure for 15 h. The catalyst was removed by filtration, the solvent was evaporated, and the residue was redissolved in 95% EtOH (2 mL). Adams' catalyst (PtO_2) was added, and the mixture was again stirred under hydrogen at ambient pressure for 15 h. The catalyst was removed by filtration, and the solvent was concentrated. The resulting residue was redissolved in water and purified using a C_{18} Sep-Pak cartridge. The carbohydrate-containing fractions were pooled, concentrated and converted to the sodium salt by passage through Dowex 50-X8 (Na^+) cation-exchange resin. Lyophilization of the eluent provided **5** (8 mg, 65%): ^{1}H NMR (D_2O (0.05 M $NaDCO_3$/0.045 M NaOD)): δ 4.50 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.47 (d, 1 H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.03 (d, 1 H, $J_{3',4'}$ 3.6 Hz, H-4′), 3.97 (dd, 1 H, $J_{5,6a}$ 2.3, $J_{6a,6b}$ 12.2 Hz, H-6a), 3.88 (1 H, H-6a′), 3.87 (1 H, OCH_2CH$_2$), 3.86 (1 H, H-6b′), 3.81 (2 H, H-5, H-6b), 3.70 (1 H, H-3), 3.69 (1 H, H-4), 3.68 (1 H, H-2), 3.67 (1 H, H-3′), 3.57 (1 H, OCH_2CH$_2$), 3.56 (1 H, H-5′), 3.52 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′), 2.05 (s, 3 H, CH_3, acetate), 1.56–1.50 (2 H, OCH$_2$CH_2), 1.62–1.46 (10 H, CH_2, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR (D_2O (0.05 M $NaDCO_3$/0.045 M NaOD)): δ 102.6 (C-1′), 101.9 (C-1), 76.2 (C-5), 76.0 (C-5′), 74.8 (C-4), 73.8 (C-3′), 73.3 (C-3), 71.2 (OCH_2CH$_2$), 70.9 (C-2′), 69.4 (C-4′), 61.6, 61.7 (C-6, C-6′), 56.8 (C-2), 32.1, 29.4, 29.3, 29.1, 25.5, 22.3 (CH_2, octyl), 29.2 (CH_3, acetate). HRESIMS Calcd for $C_{22}H_{41}NO_{14}Na_2P$ 620.2060. Found 620.2057.

Octyl 2,4,6-tri-O-*benzyl-3*-O-*diphenoxyphosphono-β*-D-*galactopyranosyl-(1→4)-2-acetamido-3,6-di*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**68**).—Compound **68** (22 mg, 80%) was synthesized from **53** (23 mg, 0.024 mmol), a catalytic amount of 4-dimethylamino pyridine, diphenyl phosphorochloridate (30 μL, 0.14 mmol) and pyridine (1 mL) as described for the preparation of **67**: ^{1}H NMR ($CDCl_3$): δ 7.38–7.10 (35 H, Ph), 5.67 (d, 1 H, J 7.3 Hz, N*H*Ac), 4.89 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.88, 4.76, 4.68, 4.64, 4.53, 4.37, 4.34, 4.24 (d, 1 H, J 11.2 Hz, PhCH_2), 4.56 (ddd, 1 H, $J_{3',4'}$ 3.3, $J_{2',3'}$ $J_{3',P}$ 8.6, H-3′), 4.43 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.12 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.0 Hz, H-3), 4.06 (d, 1 H, H-4′), 3.93 (dd, 1 H, $J_{4,5}$ 8.2 Hz, H-4), 3.81–3.72 (3 H, H-2′, H-6a, OCH_2CH$_2$), 3.63 (dd, 1 H, $J_{5,6b}$ 2.8, $J_{6a,6b}$ 10.6 Hz, H-6b), 3.49–3.36 (5 H, H-5, H-5′, H-6a′, H-6b′, OCH_2CH$_2$), 3.24 (ddd, 1 H, H-2), 1.82 (s, 3 H, CH_3, acetate), 1.56–1.50 (2 H, OCH$_2$CH_2), 1.30–1.20 (10 H, CH_2, octyl), 0.88 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C

NMR ($CDCl_3$): δ 171.8 (CO, acetate), 152.1, 140.4, 140.0, 139.7, 139.6, 139.4 (aromatic quat), 131.2, 129.8, 129.7, 129.4, 129.3, 129.1, 129.0, 128.8, 126.8, 121.1 (aromatic CH), 103.9 (C-1′), 100.8 (C-1), 82.4 (d, $J_{3',P}$ 6.7 Hz, C-3′), 79.2 (d, $J_{2',P}$ 5.5 Hz, C-2′), 77.3 (C-3), 76.8 (C-4), 76.5 (C-4′), 76.2, 76.1, 75.3, 74.4, 74.2 (PhCH_2), 76.0 (C-5), 73.5 (C-5′), 70.7 (OCH_2CH_2), 69.4 (C-6), 68.7 (C-6′), 57.7 (C-2) 32.7, 30.4, 30.3, 30.2, 26.8, 23.5 (CH_2, octyl), 24.9 (CH_3, acetate), 14.9 (CH_3, octyl). HRESIMS Calcd for $C_{69}H_{80}NO_{14}NaP$ 1200.5214. Found 1200.5235.

*Octyl 3-*O*-phosphono-β-*D*-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-*D*-glucopyranoside disodium salt* (**7**).—Compound **7** (6 mg, 56%) was synthesized from **68** (20 mg, 0.017 mmol) as described for the preparation of **5**: ^{1}H NMR (D_2O (0.05 M $NaDCO_3$/0.045 M NaOD)): δ 4.54 (d, 1 H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.50 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.03 (d, 1 H, $J_{3',4'}$ 3.3 Hz, H-4′), 4.23 (ddd, 1 H, $J_{2',3'} = J_{3',P}$ 8.4 Hz, H-3′), 3.97 (dd, 1 H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 12.1 Hz, H-6a), 3.87 (dt, 1 H, J 6.0, 10.5 Hz, OCH_2CH_2), 3.76 (2 H, H-6a′, H-6b′), 3.73 (1 H, H-3), 3.74 (1 H, H-4), 3.71 (1 H, H-2), 3.69 (1 H, H-5′), 3.66 (dd, 1 H, H-2′), 3.67 (1 H, H-3), 3.57 (1 H, OCH_2CH_2), 3.56 (1 H, H-5), 2.05 (s, 3 H, CH_3, acetate), 1.56–1.50 (2 H, OCH_2CH_2), 1.32–1.26 (10 H, CH_2, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR (D_2O (0.05 M $NaDCO_3$/0.045 M NaOD)): δ 103.8 (C-1′), 102.1 (C-1), 79.3 (C-5′), 78.2 (C-4), 77.6 (C-3′), 76.5 (C-2′), 75.7 (C-5), 73.2 (C-3), 71.8 (C-2′), 71.2 (OCH_2CH_2), 69.1 (C-4′), 62.9 (C-6′), 60.8 (C-6), 56.5 (C-2), 31.7, 29.3, 29.1, 29.0, 25.6, 22.4 (CH_2, octyl), 23.3 (CH_3, acetate), 14.8 (CH_3, octyl). HRESIMS Calcd for $C_{22}H_{41}NO_{14}Na_2P$ 620.2060. Found 620.2067.

*Octyl 2,3,6-tri-*O*-benzyl-4-*O*-dibenzylphosphityl-β-*D*-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-*D*-glucopyranoside* (**69**).—Compound **69** (11 mg, 58%) was synthesized from compound **49** (15 mg, 0.016 mmol), 1,2,4-triazole (8 mg), dibenzyl *N*,*N*-diethylphosphoramidite, (10 μL, 0.031 mmol) and DCM as described for the preparation of **70**: ^{1}H NMR ($CDCl_3$): δ 7.38–7.10 (35 H, Ph), 5.64 (d, 1 H, J 7.3 Hz, N*H*Ac), 5.10–5.05, 4.94–4.84 (5 H, PhCH_2), 4.79–4.75 (4 H, H-1, PhCH_2 × 3), 4.68–4.52 (7 H, PhCH_2), 4.43 (d, 1 H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.36, 4.34, 4.28 (d, 1 H, J 11.2 Hz, PhCH_2), 4.10 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.2 Hz, H-3), 3.92 (dd, 1 H, $J_{4,5}$ 8.3 Hz, H-4), 3.82–3.77 (2 H, H-6a, OCH_2CH_2), 3.71 (dd, 1 H, $J_{5,6b}$ 2.7, $J_{6a,6b}$ 10.6 Hz, H-6b), 3.59–3.54 (3 H, H-4′, H-5, H-6a′), 3.48–3.40 (3 H, H-5′, H-6b′, OCH_2CH_2), 3.35 (dd, 1 H, $J_{3',4'}$ 3.1, $J_{2',3'}$ 9.7 Hz, H-3′), 3.27 (ddd, 1 H, H-2), 1.83 (s, 3 H, CH_3, acetate), 1.56–1.48 (2 H, OCH_2CH_2), 1.30–1.20 (10 H, CH_2, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 170.8 (CO, acetate), 139.7, 139.3, 139.2, 139.1, 139.0, 138.7, 138.6 (aromatic quat), 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9 (aromatic CH), 103.7 (C-1′), 100.2 (C-1), 81.4 (C-3′), 79.8 (C-4′, C-2′), 78.3 (C-3), 77.9 (C-4), 75.9 (C-5), 75.8, 74.8, 74.1, 73.8, 73.3, 72.9 (C-5′, PhCH_2 × 5), 70.4 (OCH_2CH_2), 69.4 (PhCH_2), 69.2 (C-6), 68.7 (C-6′), 64.6, 64.1 (PhCH_2), 57.2 (C-2) 32.3, 30.2, 30.1, 30.0, 26.7, 23.5 (CH_2, octyl), 24.3 (CH_3, acetate), 14.8 (CH_3, octyl). HRESIMS Calcd for $C_{71}H_{84}NO_{13}NaP$ 1212.5578. Found 1212.5587.

*Octyl 2,3,6-tri-*O*-benzyl-4-*O*-dibenzylphosphono-β-*D*-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-*D*-glucopyranoside* (**73**).—Compound **73** (8 mg, 79%) was synthesized from compound **69** (10 mg, 8.4×10^{-3} mmol), 30% hydrogen peroxide (0.5 mL) and tetrahyrofuran (2 mL), as described for the preparation of **74**: ^{1}H NMR ($CDCl_3$): δ 7.41–7.05 (35 H, Ph), 5.63 (d, 1 H, J 7.6 Hz, N*H*Ac), 5.07 (dd, 1 H, $J_{3',4'}$ 2.9 Hz, H-4′), 4.98–4.84 (7 H, H-1, PhCH_2 × 6), 4.66, 4.62, 4.35, 4.24 (d, 1 H, J 11.7 Hz, PhCH_2), 4.56–4.50 (3 H, PhCH_2), 4.40 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.14 (dd, 1 H, $J_{2,3} = J_{3,4}$ 8.2 Hz, H-3), 3.92 (dd, 1 H, $J_{4,5}$ 8.4 Hz, H-4), 3.82–3.78 (2 H, H-6a, OCH_2CH_2), 3.69 (dd, 1 H, $J_{5,6b}$ 2.6, $J_{6a,6b}$ 10.7 Hz, H-6b), 3.59 (dd, 1 H, $J_{6a',5'} = J_{6a',6b'}$ 8.4 Hz, H-6a′), 3.53 (ddd, 1 H, $J_{5,6a}$ 4.7 Hz, H-5), 3.46–3.34 (5 H, H-2′, H-3′, H-5′, H-6b′, OCH_2CH_2), 3.21 (ddd, 1 H, H-2), 1.85 (s, 3 H, CH_3, acetate), 1.60–1.50 (2 H, OCH_2CH_2), 1.30–1.20 (10 H, CH_2, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR ($CDCl_3$): δ 170.9 (CO, acetate), 139.5, 139.1, 139.0, 138.7, 138.6 (aromatic quat.), 137.0, 136.7 (d, J 7.9 Hz, aromatic quat), 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0 (aromatic CH), 103.4 (C-1′), 100.2 (C-1), 80.6 (d, $J_{3',P}$ 1.3 Hz, C-3′), 79.3 (C-2′), 78.3 (C-3), 77.8 (C-4), 76.0 (C-5), 75.3, 75.0, 74.1, 74.0, 73.0 (C-5′, PhCH_2 × 5), 73.5 (d, $J_{4',P}$ 5.5 Hz, C-4′), 72.8 (d, $J_{5',P}$ 4.7 Hz, C-5′), 70.4 (OCH_2CH_2), 69.8, 69.7 (d, J 2.4 Hz, PhCH_2), 69.1 (C-6), 68.4 (C-6′), 57.6 (C-2) 32.3, 30.2, 30.1, 30.0, 26.7, 23.4 (CH_2, octyl), 24.3 (CH_3, acetate), 14.8 (CH_3, octyl). HRESIMS Calcd for $C_{71}H_{84}NO_{14}NaP$ 1228.5527. Found 1228.5535.

*Octyl 4-*O*-phosphono-β-*D*-galactopyanosyl-(1→4)-2-acetamido-2-deoxy-β-*D*-glucopyranoside disodium salt* (**6**).—Compound **6** (3 mg, 73%) was synthesized from compound **73** (8 mg, 6.6×10^{-3} mmol), 5% palladium-on-charcoal (9 mg) and 95% EtOH (1 mL) as described for the preparation of **8**: ^{1}H NMR (D_2O (0.05 M $NaDCO_3$/0.045 M NaOD)): δ 4.50 (d, 1 H, $J_{1,2}$ 7.1 Hz, H-1), 4.47 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.38 (dd, 1 H, $J_{3',4'}$ 1.1, $J_{4',P}$ 9.0 Hz, H-4′), 3.96 (dd, 1 H, $J_{5,6a}$ 2.2, $J_{6a,6b}$ 12.2 Hz, H-6a), 3.87 (dt, 1 H, J 5.9, 10.2 Hz, OCH_2CH_2), 3.82 (dd, 1 H, $J_{5,6b}$ 5.1 Hz, H-6b), 3.79 (1 H, H-5′), 3.75 (2 H, H-6a′, H-6b′), 3.69 (1 H, H-2), 3.68 (1 H, H-3), 3.66 (1 H, H-4), 3.63 (2 H, H-2′, H-3′), 3.58 (1 H, OCH_2CH_2), 3.56 (1 H, H-5), 2.05 (s, 3 H, CH_3, acetate), 1.62–1.50 (2 H, OCH_2CH_2), 1.32–1.20 (10 H, CH_2, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH_3, octyl); ^{13}C NMR (D_2O (0.05 M $NaDCO_3$/0.045 M NaOD)): δ 104.0 (C-1′), 101.6 (C-1), 79.7 (C-4), 75.6 (C-5′), 75.5

(C-5), 73.8 (C-3′), 73.1 (C-3), 72.4 (C-2′), 71.7 (C-4′), 71.4 (O*C*H_2CH$_2$), 61.4 (C-6′), 61.1 (C-6), 56.2 (C-2), 33.1, 29.2, 29.0, 28.9, 25.8, 22.4 (CH$_2$, octyl), 23.4 (CH$_3$, acetate), 14.8 (CH$_3$, octyl). HRESIMS Calcd for $C_{22}H_{41}NO_{14}Na_2P$ 620.2060. Found 620.2061.

Octyl 3,4,6-tri-O-*benzyl-2*-O-*dibenzylphosphityl-β*-D-*galactopyranosyl-(1→4)-2-acetamido-3,6-di*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**70**).—Compound **56** (34 mg, 0.036 mmol) was dissolved in dry DCM (500 μL) and 1,2,4-triazole (8 mg) and dibenzyl *N*,*N*-diethylphosphoramidite (30 μL, 0.093 mmol) were added. The mixture was stirred for 15 h, diluted with DCM, washed successively with sodium bicarbonate, brine, and water, dried over sodium sulfate and concentrated under reduced pressure. Column chromatography (10:1 toluene–acetone) resulted in **70** (38 mg, 89%): ^{1}H NMR (CDCl$_3$): δ 7.38–7.10 (35 H, Ph), 5.77 (d, 1 H, *J* 8.1 Hz, N*H*Ac), 5.60–4.79 (9 H, PhCH_2), 4.70–4.58 (5 H, H-1, PhCH_2 × 4), 4.50, 4.42 (d, 1 H, *J* 11.3 Hz, PhCH_2), 4.45 (d, 1 H, $J_{1',2'}$ 8.7 Hz, H-1′), 4.42–4.35 (2 H, H-2′, PhCH_2), 4.01 (dd, 1 H, $J_{3,4} = J_{4,5}$ 7.3 Hz, H-4), 3.94 (d, 1 H, $J_{3',4'}$ 2.8 Hz, H-4′), 3.91 (dd, 1 H, $J_{2,3}$ Hz, H-3), 3.85 (dd, 1 H, $J_{5,6a}$ 3.9, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.74 (dt, 1 H, *J* 6.7, 9.6 Hz, OCH_2CH$_2$), 3.66 (dd, 1 H, $J_{5,6b}$ 3.9 Hz, H-6b), 3.58–3.52 (2 H, H-2, H-6a′), 3.44–3.38 (4 H, H-3′, H-5, H-5′, H-6b′), 3.36 (dt, 1 H, *J* 6.8, 9.7 Hz, OCH_2CH$_2$), 1.84 (s, 3 H, CH$_3$, acetate), 1.60–1.50 (2 H, OCH$_2$CH_2), 1.30–1.20 (10 H, CH$_2$, octyl), 0.84 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 170.6 (CO, acetate), 139.6, 139.4, 139.2, 138.7, 138.6 (aromatic quat.), 139.1, 139.0 (d, *J* 4.8 Hz, aromatic quat.), 129.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0 (aromatic CH), 101.9 (C-1′), 100.5 (C-1), 82.5 (C-3′), 78.1 (C-3), 76.2 (C-4), 76.1, 75.4, 75.2, 74.9, 74.8, 74.2, 73.9, 73.7, 73.0 (C-2′, C-5, C-5′, Ph*C*H$_2$ × 5), 70.1 (O*C*H$_2$CH$_2$), 69.7 (C-6), 68.8 (C-6′), 64.6, 64.1 (d, *J* 8.5 Hz, Ph*C*H$_2$), 55.1 (C-2) 32.6, 30.3, 30.1, 30.0, 26.7, 23.4 (CH$_2$, octyl), 24.2 (CH$_3$, acetate), 14.8 (CH$_3$, octyl). HRESIMS Calcd for $C_{71}H_{84}NO_{13}NaP$ 1212.5578. Found 1212.5578.

Octyl 3,4,6-tri-O-*benzyl-2*-O-*dibenzylphosphono-β*-D-*galactopyranosyl-(1→4)-2-acetamido-3,6-di*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**74**).—Compound **70** (34 mg, 0.029 mmol) was dissolved in THF (2 mL) and cooled to −78 °C. To the cooled solution, 30% hydrogen peroxide (0.5 mL) was added dropwise. The mixture was warmed to rt, stirred for 2 h, diluted with DCM, washed successively with sodium thiosulfate, sodium bicarbonate, and water, dried over sodium sulfate and concentrated under reduced pressure. Column chromatography (10:1 toluene–acetone) resulted in **74** (30 mg, 87%): ^{1}H NMR (CDCl$_3$): δ 7.38–7.20 (35 H, Ph), 6.60 (bs, 1 H, N*H*Ac), 5.02–4.86 (6 H, PhCH_2), 4.70–4.52 (7 H, H-1, H-2′, PhCH_2 × 5), 4.44–4.32 (4 H, H-1′, PhCH_2 × 3), 4.03 (dd, 1 H, $J_{3,4} = J_{4,5}$ 5.9 Hz, H-4), 3.94 (d, 1 H, $J_{3',4'}$ 2.8 Hz, H-4′), 3.81 (1 H, H-3), 3.77 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 10.1 Hz, H-6a), 3.74 (dt, 1 H, *J* 6.6, 9.2 Hz, OCH_2CH$_2$), 3.66 (dd, 1 H, $J_{5,6b}$ 5.5 Hz, H-6b), 3.56–3.52 (2 H, H-5, H-6a′), 3.45–3.42 (2 H, H-3′, H-6b′), 3.38 (dd, 1 H, *J* 5.5, 7.9 Hz, H-5′), 3.31 (dt, 1 H, *J* 6.8, 9.5 Hz, OCH_2CH$_2$), 1.92 (s, 3 H, CH$_3$, acetate), 1.54–1.46 (2 H, OCH$_2$CH_2), 1.30–1.20 (10 H, CH$_2$, octyl), 0.87 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 170.9 (CO, acetate), 139.6, 139.2, 139.1, 138.5, 138.4 (aromatic quat.), 136.8, 136.7 (d, *J* 7.9 Hz, aromatic quat), 129.2, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9 (aromatic CH), 100.8 (C-1), 100.3 (d, $J_{1',P}$ 3.7 Hz, C-1′), 81.6 (d, $J_{3',P}$ 3.6 Hz, C-3′), 78.5 (C-3), 78.1 (d, $J_{2',P}$ 6.0 Hz, C-2′), 75.5, 74.2, 74.0, 73.4, 73.0 (Ph*C*H$_2$), 75.4 (C-5), 74.4 (C-4), 73.9 (C-5′), 73.7 (C-4′), 70.2 (C-6), 70.1 (O*C*H$_2$CH$_2$), 70.0, 69.9 (d, *J* 5.4 Hz, Ph*C*H$_2$), 68.6 (C-6′), 52.1 (C-2) 32.6, 30.3, 30.1, 30.0, 26.7, 23.4 (CH$_2$, octyl), 24.0 (CH$_3$, acetate), 14.8 (CH$_3$, octyl). HRESIMS Calcd for $C_{71}H_{84}NO_{14}NaP$ 1228.5527. Found 1228.5528.

Octyl 2-O-*phosphono-β*-D-*galactopyanosyl-(1→4)-2-acetamido-2-deoxy-β*-D-*glucopyranoside disodium salt* (**8**).—Compound **74** (30 mg, 0.025 mmol) was dissolved in 95% EtOH (2 mL) and 5% palladium-on-charcoal (12 mg) was added. The mixture was stirred under hydrogen for 24 h under ambient pressure, filtered, concentrated, dissolved in water and lyophylized to give **8** (10 mg 67%): ^{1}H NMR (D$_2$O (0.05 M NaDCO$_3$/0.045 M NaOD)): δ 4.53 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.50 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.05 (dd, 1 H, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 12.7 Hz, H-6a), 3.95 (ddd, 1 H, $J_{1',2'}$ 7.9, $J_{2',3'} = J_{2',P}$ 9.2 Hz, H-2′), 3.90 (d, 1 H, $J_{3',4'}$ 3.5 Hz, H-4′), 3.88 (1 H, H-6b), 3.87 (dt, 1 H, *J* 6.1, 10.2 Hz, OCH_2CH$_2$), 3.78 (dd, 1 H, H-3′), 3.74 (2 H, H-6a′, H-6b′), 3.73 (1 H, H-3), 3.71 (1 H, H-2), 3.70 (1 H, H-4), 3.62 (1 H, H-5), 3.61 (1 H, H-5), 3.58 (dt, 1 H, *J* 6.5, 10.3 Hz, OCH_2CH$_2$), 2.05 (s, 3 H, CH$_3$, acetate), 1.55–1.50 (2 H, OCH$_2$CH_2), 1.32–1.20 (10 H, CH$_2$, octyl), 0.85 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (D$_2$O (0.05 M NaDCO$_3$/0.045 M NaOD)): δ 103.5 (C-1′), 102.1 (C-1), 80.6 (C-5′), 75.9 (C-3), 75.7 (C-5), 74.5 (C-2′), 74.4 (C-3′), 73.3 (C-4), 71.2 (O*C*H$_2$CH$_2$), 68.8 (C-4′), 61.7 (C-6′), 60.6 (C-6), 55.2 (C-2), 31.9, 29.6, 29.4, 29.3, 26.0, 22.7 (CH$_2$, octyl), 23.3 (CH$_3$, acetate), 14.8 (CH$_3$, octyl). HRESIMS Calcd for $C_{22}H_{41}NO_{14}Na_2P$ 620.2060. Found 620.2057.

Octyl 2,3,4,6-tetra-O-*benzyl-β*-D-*galactopyranosyl-(1→4)-2-acetamido-3*-O-*benzyl-2-deoxy-6*-O-*dibenzylphosphityl-β*-D-*glucopyranoside* (**71**).—Compound **71** (16 mg, 98%) was synthesized from compound **61** (12 mg, 0.013 mmol), 1,2,4-triazole (10 mg), dibenzyl *N*,*N*-diethylphosphoramidite, (30 μL, 0.093 mmol) and DCM (2 mL), as described for the preparation of **70**: ^{1}H NMR (CDCl$_3$): δ 7.38–7.20 (35 H, Ph), 5.77 (d, 1 H, *J* 7.7 Hz, N*H*Ac), 5.02–4.59 (9 H, PhCH_2), 4.88 (1 H, $J_{1,2}$ 6.8 Hz, H-1), 4.65 (s, 2 H, PhCH_2), 4.58, 4.51, 4.35 (d, 1 H, *J* 11.2 Hz, PhCH_2), 4.50 (d, 1 H, $J_{1',2'}$ 7.7

Hz, H-1′), 4.38–4.34 (2 H, H-6a, PhCH_2), 4.13 (m, 1 H, H-6b), 4.08 (dd, 1 H, $J_{2,3} = J_{3,4}$ 7.8 Hz, H-3), 3.90–3.88 (2 H, H-4, H-4′), 3.78–3.74 (2 H, H-2′, OCH_2CH$_2$), 3.64 (ddd, 1 H, $J_{5,6b} = J_{5,6a}$ 4.2, $J_{4,5}$ 7.4 Hz, H-5), 3.52 (dd, 1 H, $J_{6a',5'} = J_{6a',6b'}$ 8.2 Hz, H-6a′), 3.44–3.36 (5 H, H-2, H-3′, H-5′, H-6b′, OCH_2CH$_2$), 1.82 (s, 3 H, CH$_3$, acetate), 1.55–1.45 (2 H, OCH$_2$CH_2), 1.30–1.20 (10 H, CH$_2$, octyl), 0.85 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 170.8 (CO, acetate), 139.6, 139.5, 139.3, 139.2, 138.6 (aromatic quat), 139.0, 136.3 (d, *J* 6.7 Hz, aromatic quat), 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1 (aromatic CH), 104.0 (C-1′), 100.2 (C-1), 83.1 (C-3′), 80.7 (C-2′), 77.8 (C-3), 77.4 (C-4), 76.2, 75.4, 74.4, 74.2, 73.9, 73.5 (C-4′, C-5′, PhCH_2 × 5), 75.7 (d, $J_{5,P}$ 4.9 Hz, C-5), 70.2 (OCH_2CH$_2$), 68.9 (C-6′), 64.8, 64.7 (d, *J* 11.0 Hz, PhCH_2), 62.4 (d, $J_{6,P}$ 10.9 Hz, C-6), 55.9 (C-2) 32.5, 30.2, 30.1, 30.0, 26.7, 23.4 (CH$_2$, octyl), 24.2 (CH$_3$, acetate), 14.8 (CH$_3$, octyl).

Octyl 2,3,4,6-tetra-O-*benzyl*-β-D-*galactopyranosyl-(1→4)-2-acetamido-3*-O-*benzyl-2-deoxy-6*-O-*dibenzylphosphono*-β-D-*glucopyranoside* (**75**).—Compound **75** (13 mg, 85%) was synthesized from compound **71** (16 mg, 0.013 mmol), 30% hydrogen peroxide (0.5 mL) and tetrahyrofuran (2 mL) as described for the preparation of **74**: ^{1}H NMR (CDCl$_3$): δ 7.38–7.20 (35 H, Ph), 5.80 (d, 1 H, *J* 7.9 Hz, NHAc), 5.02–5.00 (5 H, PhCH_2), 4.84 (1 H, $J_{1,2}$ 6.5 Hz, H-1), 4.78, 4.77, 4.67, 4.64, 4.55, 4.51, 4.27 (d, 1 H, *J* 11.4 Hz, PhCH_2), 4.43–4.40 (2 H, H-1′, H-6a), 4.36–4.33 (2 H, H-6b, PhCH_2), 4.05 (dd, 1 H, $J_{2,3} = J_{3,4}$ 7.4 Hz, H-3), 3.88 (d, 1 H, $J_{3',4'}$ 2.9 Hz, H-4′), 3.83 (dd, 1 H, $J_{4,5}$ 7.2 Hz, H-4), 3.78–3.72 (2 H, H-2′, OCH_2CH$_2$), 3.66 (1 H, H-5), 3.52–3.34 (6 H, H-2, H-3′, H-5′, H-6a′, H-6b′, OCH_2CH$_2$), 1.81 (s, 3 H, CH$_3$, acetate), 1.55–1.42 (2 H, OCH$_2$CH_2), 1.28–1.18 (10 H, CH$_2$, octyl), 0.86 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 170.8 (CO, acetate), 139.6, 139.5, 139.3, 139.2, 138.6 (aromatic quat), 136.6, 136.3 (d, $J_{C,P}$ 6.1 Hz, aromatic quat.), 129.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1 (aromatic CH), 104.0 (C-1′), 100.2 (C-1), 83.1 (C-3′), 80.5 (C-2′), 77.3 (C-3), 77.0 (C-4), 76.1, 75.4, 74.3, 74.2, 74.1, 73.8, 73.5 (C-4′, C-5′, PhCH_2 × 5), 74.7 (d, $J_{5,P}$ 8.5 Hz, C-5), 70.3 (OCH_2CH$_2$), 69.9, 69.7 (d, *J* 5.4 Hz, PhCH_2), 68.8 (C-6′), 67.1 (d, $J_{6,P}$ 4.9 Hz, C-6), 55.1 (C-2) 32.5, 30.2, 30.1, 30.0, 26.7, 23.4 (CH$_2$, octyl), 24.2 (CH$_3$, acetate), 14.8 (CH$_3$, octyl). HRESIMS Calcd for $C_{71}H_{84}NO_{14}NaP$ 1228.5527. Found 1228.5516.

Octyl β-D-*galactopyranosyl-(1→4)-2-acetamido-2-deoxy-6*-O-*phosphono*-β-D-*glucopyranoside disodium salt* (**9**).—Compound **9** (3 mg, 73%) was synthesized from compound **75** (8 mg, 6.6×10^{-3} mmol), 5% palladium-on-charcoal (9 mg), and 95% EtOH as described for **8**: ^{1}H NMR (D$_2$O (0.05 M NaDCO$_3$/0.045 M NaOD)): δ 4.66 (d, 1 H, $J_{1'2'}$ 8.0 Hz, H-1′), 4.52 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.04 (2 H, H-6a, H-6b), 3.91 (d, 1 H, $J_{3',4'}$ 3.5 Hz, H-4′), 3.88 (dt, 1 H, *J* 5.8, 10.3 Hz, OCH_2CH$_2$), 3.81 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4), 3.79 (1 H, H-3), 3.74 (2 H, H-6a′, H-6b′), 3.71 (1 H, H-2), 3.70 (1 H, H-3′), 3.66 (1 H, H-5′), 3.65 (1 H, H-5), 3.57 (dt, 1 H, *J* 6.2, 10.2 Hz, OCH_2CH$_2$), 3.44 (dd, $J_{2',3'}$ 10.2 Hz, H-2′), 2.05 (s, 3 H, CH$_3$, acetate), 1.55–1.50 (2 H, OCH$_2$CH_2), 1.32–1.20 (10 H, CH$_2$, octyl), 0.85 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (D$_2$O (0.05 M NaDCO$_3$/0.045 M NaOD)): δ 103.5 (C-1′), 102.0 (C-1), 79.0, C-4), 76.2 (C-3), 75.3 (C-5), 74.4 (C-3′), 74.3 (C-5′), 71.8 (C-2′), 71.2 (OCH_2CH$_2$), 69.5 (C-4′), 62.9 (C-6), 61.9 (C-6′), 55.9 (C-2), 32.5, 30.2, 30.1, 30.0, 26.7, 23.4 (CH$_2$, octyl), 24.2 (CH$_3$, acetate), 14.8 (CH$_3$, octyl). HRESIMS Calcd for $C_{22}H_{41}NO_{14}Na_2P$ 620.2060. Found 620.2059.

Octyl 2,3,4,6-tetra-O-*benzyl*-β-D-*galactosyl-(1→4)-2-acetamido-6*-O-*benzyl-2-deoxy-3*-O-*dibenzylphosphityl*-β-D-*glucopyranoside* (**72**).—Compound **72** (15 mg, 45%) was synthesized from compound **66** (27 mg, 0.029 mmol), 1,2,4-triazole (8 mg), dibenzyl *N*,*N*-diethylphosphoramidite, (27 μL, 0.083 mmol) and DCM (2 mL) as described for the preparation of **70**: ^{1}H NMR (CDCl$_3$): δ 7.38–7.15 (35 H, Ph), 5.60 (bs, 1 H, NHAc), 4.88–4.62 (10 H, H-1, PhCH_2 × 9), 4.58–4.44 (3 H, H-3, PhCH_2 × 2), 4.40–4.25 (4 H, H-1′, PhCH_2 × 3), 3.92 (dd, 1 H, $J_{3,4} = J_{4,5}$ 8.3 Hz, H-4), 3.83 (dd, 1 H, $J_{5,6a}$ 4.3, $J_{6a,6b}$ 10.9 Hz, H-6a), 3.81 (d, 1 H, $J_{3',4'}$ 3.3 Hz, H-4′), 3.78 (dt, 1 H, *J* 6.6, 9.5 Hz, OCH_2CH$_2$), 3.72 (dd, 1 H, $J_{5,6b}$ 2.7 Hz, H-6b), 3.67 (dd, 1 H, $J_{1',2'}$ 7.7, $J_{2',3'}$ 9.5 Hz, H-2′), 3.55–3.51 (2 H, H-5, H-6a′), 3.49 (dd, 1 H, $J_{5',6b'}$ 5.3, $J_{6a',6b'}$ 9.0 Hz, H-6b′), 3.46–3.38 (2 H, H-2, OCH_2CH$_2$), 3.35 (dd, 1 H, $J_{5',6a'}$ 7.9 Hz, H-5′), 3.32 (dd, 1 H, H-3′), 1.84 (s, 3 H, CH$_3$, acetate), 1.60–1.50 (2 H, OCH$_2$CH_2), 1.30–1.20 (10 H, CH$_2$, octyl), 0.84 (t, 3 H, *J* 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 171.0 (CO, acetate), 139.5, 139.4, 139.2, 139.1, 138.8 (aromatic quat.), 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1 (aromatic CH), 103.7 (C-1′), 100.7 (C-1), 83.1 (C-3′), 80.3 (C-2′), 77.8 (C-4), 76.8 (C-5), 75.9, 75.8, 75.3, 74.1, 74.0, 73.8 (C-4′, C-5, PhCH_2 × 5), 73.4 (C-3), 70.1 (OCH_2CH$_2$), 69.3 (C-6), 69.1 (C-6′), 65.1, 65.0 (PhCH_2), 57.3 (C-2) 32.5, 30.2, 30.1, 30.0, 26.7, 23.4 (CH$_2$, octyl), 24.1 (CH$_3$, acetate), 14.8 (CH$_3$, octyl). HRESIMS Calcd for $C_{71}H_{84}NO_{13}NaP$ 1212.5578. Found 1212.5552.

Octyl 2,3,4,6-tetra-O-*benzyl*-β-D-*galactopyranosyl-(1→4)-2-acetamido-6*-O-*benzyl-2-deoxy-3*-O-*dibenzylphosphono*-β-D-*glucopyranoside* (**76**).—Compound **76** (4 mg, 66%) was synthesized from compound **72** (6 mg, 5.0×10^{-3} mmol), 30% hydrogen peroxide (0.5 mL) and tetrahyrofuran (2 mL) as described for the preparation of **74**: ^{1}H NMR (CDCl$_3$): δ 7.38–7.05 (35 H, Ph), 5.99 (d, 1 H, *J* 8.4 Hz, NHAc), 5.10–5.02 (2 H, PhCH_2), 4.96–4.84 (2 H, PhCH_2), 4.68–4.53 (7 H, H-1,

PhCH_2), 4.96–4.84 (2 H, PhCH_2), 4.68–4.53 (7 H, H-1, H-3, PhC$H_2 \times 5$), 4.48–4.30 (6 H, H-1′, PhC$H_2 \times 5$), 4.03 (dd, 1 H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4), 3.91 (ddd, 1 H, $J_{1,2} = J_{2,NHAc}$ 8.2, $J_{2,3}$ 10.3 Hz, H-2), 3.88 (dd, 1 H, $J_{5,6a}$ 3.6, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.83–3.79 (2 H, H-4′, OCH_2CH$_2$), 3.66 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 3.62 (dd, 1 H, $J_{1',2'}$ 7.9, $J_{2',3'}$ 9.4 Hz, H-2′), 3.50–3.48 (2 H, H-6a′, H-6b′), 3.42 (dt, 1 H, J 6.7, 9.3 Hz, OCH_2CH$_2$), 3.39 (ddd, 1 H, H-5), 3.35–3.30 (2 H, H-3′. H-5′), 1.80 (s, 3 H, CH$_3$, acetate), 1.60–1.50 (2 H, OCH$_2$CH_2), 1.35–1.20 (10 H, CH$_2$, octyl), 0.84 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (CDCl$_3$): δ 171.4 (CO, acetate), 139.3, 139.2, 139.1, 139.0, 138.7 (aromatic quat), 137.2, 136.5 (d, J 6.1 Hz, aromatic quat.), 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1 (aromatic CH), 103.5 (C-1′), 101.8 (C-1), 83.1 (C-3′), 80.1 (C-2′), 78.5 (d, $J_{3,P}$ 6.1 Hz, C-3), 75.9 (C-5), 75.5 (d, $J_{4,P}$ 5.5 Hz, C-4), 75.3, 74.2, 74.1, 74.0, 73.9, 73.5 (C-4′, C-5, PhC$H_2 \times 5$), 70.3, 70.2 (d, J 4.3 Hz, PhCH_2), 70.1 (OCH_2CH$_2$), 69.0 (C-6′), 68.6 (C-6), 56.0 (C-2) 32.5, 30.2, 30.1, 30.0, 26.6, 23.3 (CH$_2$, octyl), 24.1 (CH$_3$, acetate), 14.8 (CH$_3$, octyl).

*Octyl β-*D*-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-3-*O*-phosphono-β-*D*-glucopyranoside disodium salt* (**10**).—Compound **10** (1.4 mg, 71%) was synthesized from compound **76** (4 mg, 3.3×10^{-3} mmol), 5% palladium-on-charcoal (11 mg) and 95% EtOH as described for the preparation of **8**: ^{1}H NMR (D$_2$O (0.05 M NaDCO$_3$/0.045 M NaOD)): δ 4.60 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1′),4.48 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1), 4.19 (ddd, 1 H, $J_{2,3} = J_{3,4} = J_{3,P}$ 9.4 Hz, H-3), 3.98 (dd, 1 H, $J_{5,6a}$ 2.6, $J_{6a,6b}$ 12.3 Hz, H-6a), 3.91 (dd, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 3.86 (d, 1 H, $J_{3',4'}$ 3.5 Hz, H-4′), 3.85 (1 H, OCH_2CH$_2$), 3.81 (2 H, H-6a′, H-6b′), 3.71 (1 H, H-6b), 3.69 (1 H, H-5′), 3.68 (1 H, H-2), 3.63 (1 H, H-2′), 3.62 (1 H, H-5), 3.59 (dd, 1 H, $J_{3',2'}$ 9.9 Hz, H-3′), 3.55 (dt, 1 H, J 6.6, 10.3 Hz, OCH_2CH$_2$), 2.05 (s, 3 H, CH$_3$, acetate), 1.55–1.50 (2 H, OCH$_2$CH_2), 1.32–1.20 (10 H, CH$_2$, octyl), 0.85 (t, 3 H, J 7.0 Hz, CH$_3$, octyl); ^{13}C NMR (D$_2$O (0.05 M NaDCO$_3$/0.045 M NaOD)): δ 102.7 (C-1), 102.0 (C-1′), 76.6 (C-5), 76.0 (C-5′), 74.7 (C-4), 73.6 (C-3′), 73.5 (C-3), 71.3 (OCH_2CH$_2$), 69.7 (C-4′), 61.8 61.7 (C-6, C-6′), 56.3 (C-2), 31.9, 29.6, 29.4, 29.3, 26.0, 22.7 (CH$_2$, octyl), 23.3 (CH$_3$, acetate), 14.8 (CH$_3$, octyl). HRESIMS Calcd for $C_{22}H_{41}NO_{14}Na_2P$ 620.2060. Found 620.2064.

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