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Synthesis of Hex*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$ probes for exploration of the substrate specificity of glycosyltransferases: Part II, Hex = 3-*O*-methyl-β-D-Gal, 3-deoxy-β-D-Gal, 3-deoxy-3-fluoro-β-D-Gal, 3-amino-3-deoxy-β-D-Gal, β-D-Gul, α-L-Alt, or β-L-Gal [1]

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Abstract

Seven analogues of the trisaccharide β-D-Gal*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$ have been synthesized as potential substrates for glycosyltransferases involved in the chain-termination of *N*-acetyllactosamine-type N-glycans. These compounds include: 3-*O*-methyl-β-D-Gal*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$, 3-deoxy-β-D-Gal*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$, 3-deoxy-3-fluoro-β-D-Gal*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$, 3-amino-3-deoxy-β-D-Gal*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$, β-D-Gul*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$, β-L-Gal*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$, and α-L-Alt*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$. All trisaccharides were obtained by condensation of suitably modified glycosyl donors based on imidates or thioglycosides with the same disaccharide acceptor, octyl 3,4,6-tri-*O*-benzyl-2-*O*-(3,6-di-*O*-benzyl-2-

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[1] Dedicated to Professor Dr. Hans Paulsen on the occasion of his 75th birthday.

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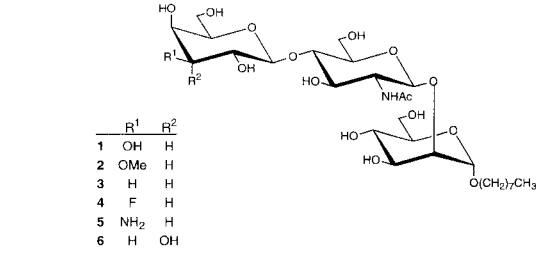
deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-mannopyranoside, followed by deprotection.

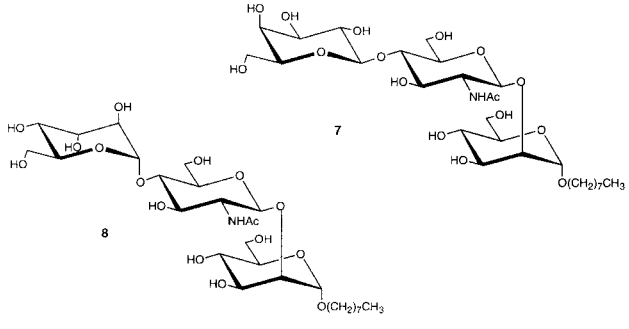
Keywords: Glycoproteins; Glycosyltransferases; *N*-Acetyllactosamine; Substrate analogues

1. Introduction

Glycosyltransferases are known to be highly specific in vivo for the acceptor substrate, as well as for the type of linkage and configuration of the newly formed glycosidic bond [1]. However, a number of studies have shown that these enzymes accept modifications in the acceptor structure in vitro (see, for example ref. [2]), indicating that some parts of the constituent monosaccharides are less important for effective glycosylation. Information concerning the recognition characteristics can be obtained by using modified oligosaccharides, probing the contribution of individual hydroxyl and/or acetamido groups to carbohydrate–protein interactions. Considering the glycosyltransferase-mediated expression of cell-surface carbohydrate ligands that are involved in biological recognition phenomena, the elucidation of the substrate specificity of the chain-terminating enzymes is particularly interesting [3,4].



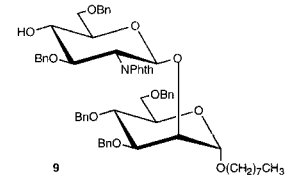
	R^1	R^2
1	OH	H
2	OMe	H
3	H	H
4	F	H
5	NH_2	H
6	H	OH

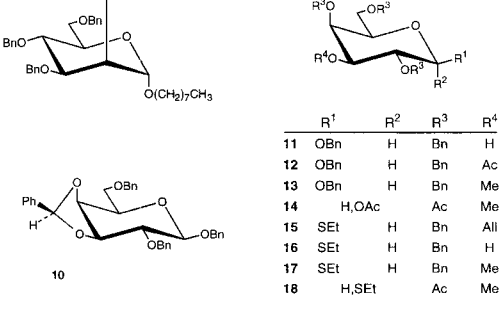


In the framework of a project aimed at the exploration of the substrate specificity of glycosyltransferases involved in the termination of *N*-acetyllactosamine type N-glycans, we have reported recently on the synthesis of β-D-Gal*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$ (**1**), and analogues modified at C-4 of the D-galactosyl group (4-deoxy-β-D-Gal, 4-*O*-methyl-β-D-Gal, 4-deoxy-4-fluoro-β-D-Gal, or β-D-Glc) [5]. In this paper, the syntheses of an additional series of trisaccharides with modifications in the D-galactosyl group are described. On the one hand, HO-3 was replaced by *O*-methoxy (**2**), hydrogen (**3**), fluorine (**4**), or amino functions (**5**), or epimerized (**6**). On the other hand, trisaccharides were synthesized that contained either β-L-galactose (**7**) or α-L-altrose (**8**) at the non-reducing terminus, being the enantiomer and the C-5 epimer of β-D-galactose, respectively.

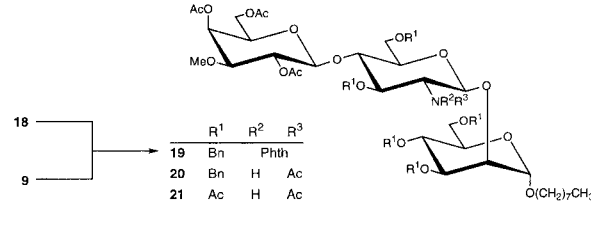
2. Results and discussion

The recently reported synthesis of a series of trisaccharides modified at C-4 of the terminal galactosyl group (see above) was based on the condensation of the general disaccharide acceptor octyl 3,4,6-tri-*O*-benzyl-2-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-mannopyranoside (**9**) with suitably modified glycosyl donors [5]. Making use of our observations [5] that thioglycosides were appropriate for activated synthons (carrying deoxy and *O*-methyl functionalities), and trichloroacetimidates for deactivated (e.g., fluorine-containing) synthons, the synthesis of the target trisaccharides **2**–**8** was straightforward, and no difficulties concerning stereoselective glycosylation were encountered.





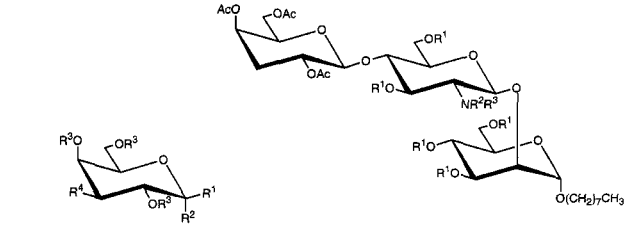
	R^1	R^2	R^3	R^4
11	OBn	H	Bn	H
12	OBn	H	Bn	Ac
13	OBn	H	Bn	Me
14	H,OAc		Ac	Me
15	SEt	H	Bn	All
16	SEt	H	Bn	H
17	SEt	H	Bn	Me
18	H,SEt		Ac	Me



	R^1	R^2	R^3
19	Bn	Phth	
20	Bn	H	Ac
21	Ac	H	Ac

For the synthesis of **2** the 3-*O*-methylgalactosyl donor **18** was prepared, and two routes to synthesize this thioglycoside were followed. Regioselective reductive ring-opening of the *endo*-benzylidene acetal in benzyl 2,6-di-*O*-benzyl-3,4-*O*-*endo*-benzylidene-β-D-galactopyranoside [6] (**10**), using lithium aluminium hydride and aluminium chloride in dichloromethane–diethyl ether [7], gave **11** (89%), characterized as its acetate **12**. It should be noted that **11** has been previously synthesized by a different reaction sequence [8], but in lower yield. Methylation of **11** (→ **13**), followed by catalytic hydrogenation and acetylation (→ **14**, 89% from **11**), and final treatment with ethanethiol in the presence of boron trifluoride etherate afforded **18** (62%, $\alpha:\beta = 1:5$). In the alternative route, ethyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside [9] (**15**) was deallylated applying Wilkinson's catalyst followed by acid-catalyzed hydrolysis (→ **16**, 71%), then methylated to give **17** (78%). Hydrogenolytic cleavage of the benzyl groups in **17**, however, gave rise to difficulties, and gave the β anomer of **18** in only 42% yield after acetylation. Reaction of **18** (β) with **9** in dichloromethane at 0 °C, using *N*-iodosuccinimide–triflic acid (NIS–TfOH) as a promoter, afforded trisaccharide derivative **19** in a yield of 55%. Dephthaloylation of **19** with hydrazine monohydrate and *N*,*O*-acetylation (→ **20**, 87%), followed by catalytic hydrogenolysis over 10% Pd–C and subsequent *O*-acetylation yielded **21** (92%). Finally, *O*-deacetylation of **21** gave **2** (96%). The *O*-acetylation step after debenzylation was carried out to allow a good chromatographic purification, ensuring a high purity of the deprotected structure. The ^{1}H NMR structural-reporter-group data of **2** are presented in Table 1.

In the synthesis of the 3″-deoxygenated trisaccharide **3**, both **11** and **16** were used as precursors for a 3-deoxy-D-galactosyl (i.e., 3-deoxy-D-*xylo*-hexosyl) donor. Treatment of **16** with phenyl thionochloroformate [10] (→ **22**) and subsequent reduction with tributyltin hydride afforded **23** (73% from **16**). Debenzylation of **23** was sluggish, and had to be repeated several times with intermediate filtration and addition of new catalyst. This procedure gave, after acetylation, the β anomer of **27** in a yield of only 25% (experimental data not shown). Alternatively, reductive deoxygenation of **11**, via thiocarbonyl ester **24**, gave **25** (76% from **11**), which was converted into **26** (63%) by hydrogenation and acetylation. Reaction of **26** with ethanethiol, catalyzed by boron trifluoride etherate, gave the glycosyl donor **27** in moderate yield (46%, $\alpha:\beta = 1:4$). Condensation of **9** with thioglycoside **27**, using NIS–TfOH in dichloromethane at 0 °C, afforded **30** in 81% yield. Dephthaloylation of **30** with ethylenediamine in 1-butanol [11], followed by *N*,*O*-acetylation (→ **31**, 92%), debenzylation, and *O*-acetylation gave **32** (89%). *O*-Deacetylation of **32** yielded target compound **3** (99%). For the ^{1}H NMR data of **3**, see Table 1.

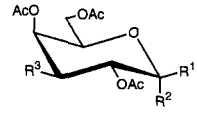


	R^1	R^2	R^3	R^4
22	SEt	H	Bn	PhOC[=S]O
23	SEt	H	Bn	H
24	OBn	H	Bn	PhOC[=S]O
25	OBn	H	Bn	H
26	H,OAc		Ac	H
27	H,SEt		Ac	H
28	H,OH		Ac	H
29	H	OC[=NH]CCl_3	Ac	H

27 or 29 → 9

	R^1	R^2	R^3
30	Bn	Phth	
31	Bn	H	Ac
32	Ac	H	Ac

In view of the low yield obtained in the synthesis of the 3-deoxy-galactosyl donor **27**, the corresponding glycosyl imidate **29** was chosen as an alternative. Removal of the acetyl group at O-1 from **26** with either hydrazine acetate in dimethylformamide (DMF) [12] or 2-aminoethanol in tetrahydrofuran (THF) [13] was not selective, and a complex mixture of partially deacetylated products was obtained. However, treatment of **26** with hydrogen bromide in acetic acid and hydrolysis of the resulting glycosyl bromide with mercuric bromide gave in good yield **28**, which was converted into imidate **29** using trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (51% from **26**). Coupling of **9** with **29** in dichloromethane at −30 °C, using trimethylsilyl triflate as the catalyst, gave stereoselectively the trisaccharide derivative **30** (39%), together with recovered acceptor **9** (50%). Therefore, thioglycoside **27** is the preferred donor for glycosylation of **9**, in spite of its laborious preparation.

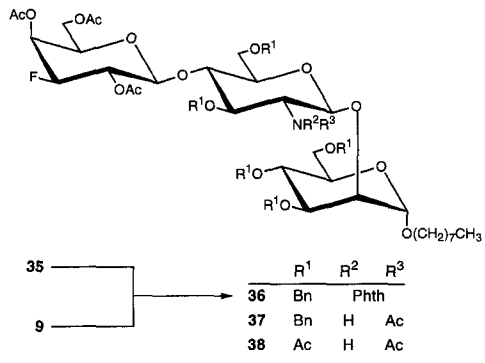


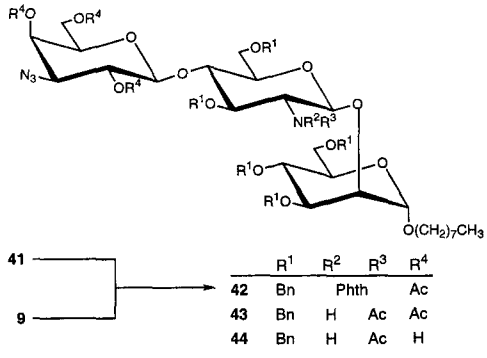
	R^1	R^2	R^3
33	H,OAc		F
34	H,OH		F
35	H	OC[=NH]CCl_3	F
39	H,OAc		N_3
40	H,OH		N_3
41	H	OC[=NH]CCl_3	N_3

Table 1
500 MHz ^{1}H NMR data of trisaccharides **1–8** with the general formula Hex*p*-(1 → 4)-β-D-Glc*p*NAc-(1 → 2)-α-D-Man*p*-(1 → O)$(CH_2)_7CH_3$

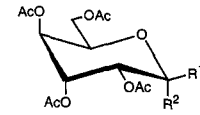
Residue	Reporter group (*J*)	δ (ppm)/ *J* (Hz)							
		1 Hex = β-D-Gal	**2** Hex = 3-OMe-β-D-Gal	**3** Hex = 3-deoxy-β-D-Gal	**4** Hex = Hex = 3-deoxy-3-fluoro-β-D-Gal	**5** Hex = 3-amino-3-deoxy-β-D-Gal	**6** Hex = β-D-Gul	**7** Hex = β-L-Gal	**8** α-L-Alt
α-D-Man*p*	H-1 ($J_{1,2}$)	4.861 (1.5)	4.861 (1.5)	4.864 (1.6)	4.862 (1.6)	4.863 (1.5)	4.863 (1.6)	4.858 (1.6)	4.860 (1.3)
	H-2 ($J_{2,3}$)	4.043 (3.5)	4.042 (3.5)	4.045 (3.5)	4.043 (3.5)	4.045 (3.4)	4.045 (3.4)	4.038 (3.5)	4.039 (3.5)
β-D-Glc*p*NAc	H-1 ($J_{1,2}$)	4.583 (7.6)	4.581 (7.9)	4.587 (7.6)	4.583 (6.7)	4.585 (7.5)	4.585 (7.6)	4.571 (8.2)	4.573 (8.2)
	NAc	2.050	2.050	2.051	2.051	2.051	2.051	2.053	2.051
Hex*p*	H-1 ($J_{1,2}$)	4.468 (7.9)	4.480 (7.9)	4.567 (7.9)	4.520 (7.9)	4.478 (7.9)	4.740 (8.3)	4.684 (7.9)	4.818 (3.2)
	H-3eq	–	–	2.218	–	–	4.076	–	n.d. [a]
	($J_{2,3eq}$)			(5.2)			(3.6)		
	($J_{3eq,4}$)			(3.1)			(3.6)		
	H-3ax	n.d.	3.365	1.747	4.598	2.870	–	n.d.	–
	($J_{2,3ax}$)		(10.0)	(12.0)	(9.7)	(9.6)			
	($J_{3eq,3ax}$)			(14.0)					
	($J_{3ax,F}$)				(48.0)				
	H-4 ($J_{3,4}$)	3.927 (3.4)	4.214 (3.2)	n.d.	4.219 (3.5)	n.d.	n.d.	n.d.	n.d.
	CH_3O	–	3.443	–	–	–	–	–	–
Octyl	CH_3	0.860	0.860	0.860	0.860	0.861	0.860	0.860	0.861

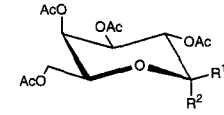
[a] n.d. = not determined.

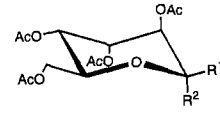


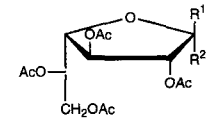


For the synthesis of the trisaccharides **4** and **5**, containing a 3-deoxy-3-fluoro- or a 3-amino-3-deoxy-D-galactosyl group, respectively, the glycosyl imidates **35** and **41** were prepared via a similar reaction sequence. Selective removal of the acetyl group at O-1 from 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-fluoro-α,β-D-galactopyranose [14] (**33**) with hydrazine acetate in DMF, and reaction of the resulting hemiacetal **34** with trichloroacetonitrile–DBU gave **35** (61% from **33**). Similarly, **41** was obtained from 1,2,4,6-tetra-*O*-acetyl-3-azido-3-deoxy-α,β-D-galactopyranose [15] (**39**) (75%). Trimethylsilyl-triflate-catalyzed coupling of **9** with **35** or **41** in dichloromethane at 0 °C afforded the 3″-deoxy-3″-fluoro- and 3″-azido-3″-deoxy-trisaccharide derivatives **36** (93%) and **42** (92%), respectively. Deblocking of **36** as described for **30** gave the target trisaccharide **4** in an overall yield of 77%. Deprotection of the azide **42** was somewhat complicated. Dephthaloylation of **42** with ethylenediamine in 1-butanol and subsequent *N,O*-acetylation yielded **43** (73%). In order to avoid acetyl group migration to the amino group after reduction of the azide function, **43** was first *O*-deacetylated (→ **44**, 95%). The subsequent hydrogenolysis of **44** over a 10% Pd–C catalyst in 6:4:1 *i*-PrOH–H_2O–HOAc was sluggish, and required repetitive intermediate filtration and replacement of the catalyst, to give the 3″-amino-3″-deoxy-trisaccharide **5** in a yield of only 21%. The ^1H NMR data of **4** and **5** are presented in Table 1.



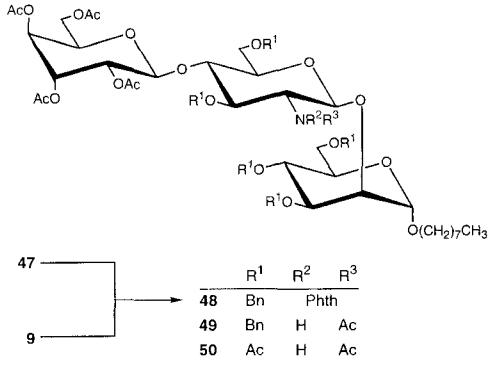




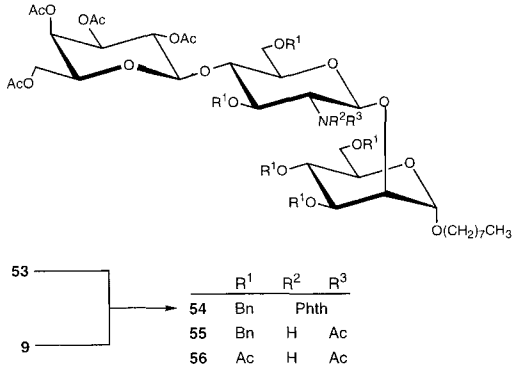


The syntheses of the trisaccharides with a D-gulosyl (**6**), L-galactosyl (**7**), or L-altrosyl (**8**) group at the non-reducing terminus, respectively, were performed by the condensation of **9** with the glycosyl imidates **47**, **53**, or **59**. Treatment of 1,2,3,4,6-penta-*O*-acetyl-α,β-D-gulopyranose (**45**) with hydrazine acetate in DMF (→ **46**), and imidation, as described for **35**, gave **47** (53% from **45**). The anomeric *O*-deacetylation was not completely selective, and a series of partially deacetylated compounds were observed. The imidate was obtained predominantly in the β configuration ($\alpha:\beta$ = 1:4), reflecting a strong diaxial repulsion of the AcO-3 and trichloroacetimidate groups. By analogy with the preparation of **47**, the synthesis of **53** was realized by selective deacetylation at O-1, starting from 1,2,3,4,6-penta-*O*-acetyl-α,β-L-galactopyranose (**51**), and subsequent imidation of the resulting hemiacetal **52** (→ **53**, 63% from **51**). For the preparation of the L-altropyranosyl imidate (**59**) a direct approach starting from L-altrose, and accepting that both pyranose and furanose forms would be present, was followed. Acetylation of L-altrose with pyridine–acetic anhydride gave a mixture of 1,2,3,4,6-penta-*O*-acetyl-α,β-L-altropyranose (**57**) and 1,2,3,5,6-penta-*O*-acetyl-α,β-L-altrofuranose (**58**)

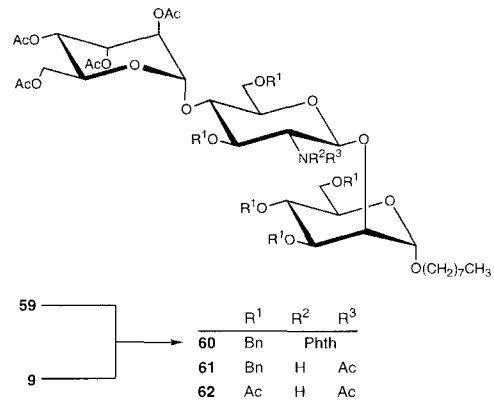
as the major and the minor products, respectively, as deduced from ^{1}H-coupled ^{13}C NMR spectroscopy [16,17]. Since a separation of the pyranose and furanose forms could not be realized, the mixture was used for the imidation. Selective removal of the acetyl group at O-1 from the peracetylated compounds (**57**/**58**) with hydrazine acetate was unsuccessful, producing an array of partially deacetylated products. However, treatment with hydrogen bromide in acetic acid, subsequent hydrolysis of the resulting glycosyl bromides in situ, and reaction with trichloroacetonitrile–DBU afforded **59** (75% from **57**/**58**). The NMR data indicated that the preparation contained mainly the α-pyranose form of the imidate, whereas furanose forms were only present as minor contaminants (< 5% with respect to **59**). The coupling of **9** with the imidates **47**, **53**, or **59** in dichloromethane at 0 °C, in the presence of trimethylsilyl triflate as a catalyst, gave the fully protected trisaccharide derivatives **48** (63%), **54** (80%), and **60** (82%), respectively. No indications were found for the presence of L-altrofuranose-containing products in **60**. Deblocking of these trisaccharides, using a sequence of reactions as described for **30**, yielded **6** (56% from **48**), **7** (78% from **54**), and **8** (79% from **60**). For ^{1}H NMR data of **6**, **7**, and **8**, see Table 1.



	R^1	R^2	R^3
48	Bn	Phth	
49	Bn	H	Ac
50	Ac	H	Ac



	R^1	R^2	R^3
54	Bn	Phth	
55	Bn	H	Ac
56	Ac	H	Ac



	R^1	R^2	R^3
60	Bn	Phth	
61	Bn	H	Ac
62	Ac	H	Ac

3. Experimental

General methods.—All solvents were distilled from appropriate drying agents. D-Gulose was obtained from Janssen Chimica (Belgium), L-galactose was obtained from ICN Biochemicals (USA), and L-altrose was purchased from Chemapol Slovakia (Slovak Republic). Reactions were monitored by TLC on Kieselgel 60 F_{254} (Merck) using solvent mixtures of appropriately adjusted polarity; solvent *A* = 4:2:2:1 1-butanol–EtOH–HOAc–H_2O. Compounds were visualized by charring with aq 50% H_2SO_4, after examination under UV light. In the workup procedures of reaction mixtures, organic solutions were washed with appropriate amounts of aqueous solutions as indicated, or with 8 mM phosphate buffer (pH 7.5), then dried ($MgSO_4$), and concentrated under reduced pressure at 20–40 °C. Column chromatography was performed on Kieselgel 60 F_{254} (70–230 mesh, Merck), unless otherwise stated. Optical rotations were determined for solutions in $CHCl_3$ unless otherwise stated, at 20 °C with a Perkin–Elmer 241 polarimeter, using a 10-cm 1-mL cell. ^{1}H NMR spectra were recorded with a Bruker AC 300 or AM 500 spectrometer; the values of δ_H are expressed in ppm relative to the signal for internal Me_4Si for solutions in $CDCl_3$, or by reference to acetone (δ 2.225) for solutions in D_2O. ^{13}C NMR spectra were recorded with a Bruker WP 200 (50 MHz) or a Varian Gemini-300 instrument (75 MHz); indicated values for δ_C are relative to the signal of $CDCl_3$ (δ 76.9). Microanalyses were carried out by the Mikroanalytisches Laboratorium of H. Kolbe (Mülheim an der Ruhr, Germany). Fast-atom-bombardment mass spectrometry (FABMS) was performed on a JEOL JMS SX/SX 102A four-sector mass spectrometer,

operated at 10 kV accelerating voltage, equipped with a JEOL MS-FAB 10 D FAB gun operated at 10 mA emission current, producing a beam of 6 keV xenon atoms.

Benzyl 2,4,6-tri-O-benzyl-β-D-galactopyranoside (**11**).—To a cooled (0 °C) solution of benzyl 2,6-di-*O*-benzyl-3,4-*O*-*endo*-benzylidene-β-D-galactopyranoside [6] (**10**; 0.21 g, 0.38 mmol) in 1:1 CH_2Cl_2–diethyl ether (6 mL) were added $LiAlH_4$ (21.9 mg, 0.58 mmol) and $AlCl_3$ (74.4 mg, 0.56 mmol) under N_2. After 20 min, when TLC (4:1 hexane–EtOAc) showed the conversion of **10** into **11** (R_f 0.51), water (1 mL) was carefully added, and the mixture was diluted with EtOAc, washed with water, and concentrated. Column chromatography (4:1 hexane–EtOAc) of the residue afforded **11**, isolated as a syrup (0.18 g, 89%); $[\alpha]_D$ −20° (*c* 1); ^{13}C NMR ($CDCl_3$): δ 102.3 (C-1), 79.2, 75.3, 73.8, and 73.4 (C-2,3,4,5), 74.7, 74.4, 73.2, 70.6, and 68.5 (C-6 and 4 PhCH_2O). Acetylation of an analytical sample (1:1 Ac_2O–pyridine) gave **12**; ^1H NMR ($CDCl_3$): δ 7.35–7.25 (m, 20 H, 4 Ph), 4.953, 4.873, 4.642, 4.641, 4.609, 4.520, 4.513, and 4.454 (8 d, each 1 H, 4 PhCH_2O), 4.889 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 3.2 Hz, H-3), 4.527 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.956 (dd, 1 H, $J_{4,5}$ < 1 Hz, H-4), 3.836 (dd, 1 H, H-2), 1.891 (s, 3 H, Ac). Anal. Calcd for **11**, $C_{34}H_{36}O_6$ (540.66): C, 75.53; H, 6.71. Found: C, 75.60; H, 6.82.

1,2,4,6-Tetra-O-acetyl-3-O-methyl-α,β-D-galactopyranose (**14**).—A solution of **11** (0.13 g, 0.24 mmol) in DMF (5 mL) was added under N_2 to NaH (12 mg, 0.5 mmol), and the mixture was stirred for 15 min. Then, MeI (45 μL, 0.78 mmol) was added, and the stirring was continued for 1.5 h, when TLC (3:1 hexane–EtOAc) showed a complete conversion of **11** into **13** (R_f 0.47). After destroying the excess of NaH with MeOH (1 mL), the solution was diluted with CH_2Cl_2, washed with phosphate buffer (2 ×) and water, and concentrated. A solution of the residue (**13**) in 1:1 EtOH–EtOAc (10 mL), containing 10% Pd–C (50 mg) and HOAc (0.3 mL), was hydrogenolyzed at atmospheric pressure for 2 h. TLC (solvent *A*) then showed the disappearance of **13** and the formation of a new compound (**14**, R_f 0.38), and the mixture was diluted with MeOH, filtered through Celite, and concentrated. The crude residue was acetylated overnight in 1:1 Ac_2O–pyridine (10 mL). After concentration, and co-concentration with toluene, column chromatography (4:1 toluene–EtOAc) of the residue gave **14**, isolated as a glass (77.3 mg, 89% from **11**); $[\alpha]_D$ −32° (*c* 0.33, α anomer), +8° (*c* 0.5, β anomer); R_f 0.26 (4:1 toluene–EtOAc); ^1H NMR ($CDCl_3$): (α), δ 6.338 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.583 (dd, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$ 1.3 Hz, H-4), 5.204 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 4.260 (ddd, 1 H, H-5), 4.141 (dd, 1 H, $J_{5,6a}$ 6.2, $J_{6a,6b}$ 11.3 Hz, H-6a), 4.058 (dd, 1 H, $J_{5,6b}$ 6.9 Hz, H-6b), 3.678 (dd, 1 H, H-3), 3.404 (s, 3 H, OCH_3), 2.152, 2.067, and 2.052 (3 s, 6,3,3 H, 4 Ac); (β), δ 5.644 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 5.514 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.2 Hz, H-4), 5.199 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.188 (dd, 1 H, $J_{5,6a}$ 6.3, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.097 (dd, 1 H, $J_{5,6b}$ 6.6 Hz, H-6b), 3.956 (ddd, 1 H, H-5), 3.409 (dd, 1 H, H-3), 3.381 (s, 3 H, OCH_3), 2.157, 2.113, 2.076, and 2.066 (4 s, each 3 H, 4 Ac). Anal. Calcd for $C_{15}H_{22}O_{10}$ (362.34): C, 49.72; H, 6.12. Found: C, 49.80; H, 6.06.

Ethyl 2,4,6-tri-O-benzyl-1-thio-β-D-galactopyranoside (**16**).—A solution of ethyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside [9] (**15**; 90.0 mg, 0.17 mmol), tris(triphenylphosphine)rhodium(I) chloride (25.0 mg, 27.0 μmol), and 1,4-diazabicyclo[2.2.2]octane (10.1 mg, 90.0 μmol) in 7:3:1 EtOH–toluene–H_2O (11 mL) was boiled under reflux for 90 min under Ar, then cooled, washed with M HCl and phosphate buffer, and concentrated. A solution of the residue in 9:1 acetone–M HCl (10 mL) was heated for 15 min at 60 °C, when TLC (11:1 toluene–EtOAc) indicated a complete conversion of the 1-propenyl analogue of **15** into **16** (R_f 0.25). The solution was neutralized with aq 10% $NaHCO_3$, filtered through Celite, and concentrated. Column chromatography (11:1 toluene–EtOAc) of the residue afforded **16**, isolated as a pale-yellow syrup (59.2 mg, 71%); $[\alpha]_D$ +1° (*c* 0.5); ^1H NMR ($CDCl_3$): δ 7.42–7.18 (m, 15 H, 3 Ph), 4.928, 4.721, 4.681, 4.641, 4.508, and 4.442 (6 d, each 1 H, 3 PhCH_2O), 4.398 (d, 1 H, $J_{1,2}$ 9.3 Hz, H-1), 3.886 (dd, 1 H, $J_{3,4}$ 3.2, $J_{4,5}$ < 1 Hz, H-4), 3.555 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2), 2.84–2.75 (m, 2 H, SCH_2CH$_3$), 2.240 (d, 1 H, $J_{3,OH}$ 6.1 Hz, OH), 1.302 (t, 3 H, SCH_2CH_3); ^{13}C: δ 85.0 (C-1), 79.4, 77.2, 76.1, and 75.5 (C-2,3,4,5), 75.2, 74.9, 73.4, and 68.6 (C-6 and 3 PhCH_2O), 24.6 (SCH_2CH$_3$), 14.9 (SCH_2CH_3). Anal. Calcd for $C_{29}H_{34}O_5S$ (494.66): C, 70.42; H, 6.93. Found: C, 70.31; H, 7.04.

Ethyl 2,4,6-tri-O-benzyl-3-O-methyl-1-thio-β-D-galactopyranoside (**17**).—A solution of **16** (0.18 g, 0.36 mmol) in DMF (5 mL) was added to NaH (19.9 mg, 0.83 mmol), and after stirring for 15 min under N_2, MeI (40 μL, 0.64 mmol) was added. TLC (11:1 toluene–EtOAc) showed the formation of **17** (R_f 0.46) to be completed in 2 h. After destroying the excess of NaH with MeOH, the mixture was diluted

with CH_2Cl_2, washed with phosphate buffer (2 ×) and water, then concentrated. Column chromatography (11:1 toluene–EtOAc) of the residue yielded **17**, isolated as a glass (0.15 g, 78%); $[\alpha]_D$ −22° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 7.45–7.22 (m, 15 H, 3 Ph), 4.910, 4.844, 4.771, 4.596, 4.459, and 4.404 (6 d, each 1 H, 3 PhCH_2O), 4.400 (d, 1 H, $J_{1,2}$ 9.6 Hz, H-1), 3.965 (dd, 1 H, $J_{3,4}$ 2.9, $J_{4,5}$ < 1 Hz, H-4), 3.718 (dd, 1 H, $J_{2,3}$ 9.4 Hz, H-2), 3.498 (s, 3 H, OCH_3), 3.288 (dd, 1 H, H-3), 2.82–2.62 (m, 2 H, SCH_2CH$_3$), 1.285 (t, 3 H, SCH$_2$CH_3); ^{13}C: δ 86.4, 85.2, 78.3, 77.2, and 72.8 (C-1,2,3,4,5), 75.5, 74.3, 73.5, and 68.8 (C-6 and 3 PhCH_2O), 58.3 (OCH_3), 24.6 (SCH_2CH$_3$), 15.0 (SCH$_2$$CH_3$). Anal. Calcd for $C_{30}H_{36}O_5S$ (508.69): C, 70.84; H, 7.13. Found: C, 71.20; H, 7.10.

Ethyl 2,4,6-tri-O-*acetyl-3*-O-*methyl-1-thio-(α)β*-D-*galactopyranoside* (**18**).—(*a*) *From* **14**. A solution of **14** (69.8 mg, 0.19 mmol) in CH_2Cl_2 (5 mL), containing 3 Å molecular sieves (0.5 g), was stirred for 30 min under N_2. Then, EtSH (0.36 mL, 4.9 mmol) and $BF_3 \cdot Et_2O$ (0.14 mL, 1.1 mmol) were added, and the stirring was continued for 2 h, when TLC (2:1 toluene–EtOAc) showed the conversion of **14** into a major (R_f 0.58) and a minor (R_f 0.63) compound. The mixture was neutralized (Et_3N), filtered, and concentrated. Column chromatography (4:1 toluene–EtOAc) of the residue afforded **18**, isolated as a colorless syrup (43.5 mg, 62%, α:β = 1:5).

(*b*) *From* **17**. A solution of **17** (0.12 g, 0.24 mmol) and HOAc (0.2 mL) in 1:1 EtOH–EtOAc (10 mL), containing 10% Pd–C (50 mg), was hydrogenolyzed at atmospheric pressure for 5 h. Because of incomplete debenzylation, the hydrogenolysis was repeated with intermediate filtration and addition of new catalyst, essentially without improvement of the reaction after 5 h. The mixture was filtered through Celite and hydrogenolyzed in the presence of a fresh amount of 10% Pd–C (50 mg) for 48 h at 4 kg cm^{-2}. TLC (solvent *A*) then showed the formation of a major product (R_f 0.56). After filtration through Celite, the mixture was concentrated, and co-concentrated with toluene. The residue was treated overnight with 1:1 Ac_2O–pyridine (8 mL), then concentrated, and co-concentrated with toluene. Column chromatography (5:1 toluene–EtOAc) of the residue afforded **18** (β anomer), isolated as a colorless syrup (36.1 mg, 42%); $[\alpha]_D$ +25° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 5.520 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.2 Hz, H-4), 5.104 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2), 4.423 (d, 1 H, $J_{1,2}$ 10.0 Hz, H-1), 4.135 (d, 2 H, H-6a,b), 3.842 (dt, 1 H, H-5), 3.370 (s, 3 H, OCH_3), 3.366 (dd, 1 H, H-3), 2.82–2.63 (m, 2 H, SCH_2CH$_3$), 2.143, 2.102, and 2.064 (3 s, each 3 H, 3 Ac), 1.276 (t, 3 H, SCH$_2$CH_3); ^{13}C: δ 170.1, 170.0, and 169.4 (3 $COCH_3$), 83.8, 80.7, 74.6, 68.8, and 65.7 (C-1,2,3,4,5), 62.0 (C-6), 57.8 (OCH_3), 23.6 (SCH_2CH$_3$), 14.6 (SCH$_2$$CH_3$). Anal. Calcd for $C_{15}H_{24}O_8S$ (364.42): C, 49.44; H, 6.64. Found: C, 49.60; H, 6.41.

Octyl (2,4,6-tri-O-*acetyl-3*-O-*methyl*-β-D-*galacto-pyranosyl)-(1 → 4)-(3,6-di*-O-*benzyl-2-deoxy-2-phthal-imido*-β-D-*glucopyranosyl)-(1 → 2)-3,4,6-tri*-O-*benzyl*-α-D-*mannopyranoside* (**19**).—A solution of **18** (β anomer; 35.2 mg, 96.6 μmol) and **9** [5] (71.4 mg, 69.0 μmol) in CH_2Cl_2 (5 mL), containing 3 Å molecular sieves (0.3 g), was stirred for 1 h under N_2. Then, a solution of NIS (31.5 mg, 0.14 mmol) and TfOH (1.5 μL, 17 μmol) in CH_2Cl_2 (2 mL) was added dropwise in 10 min at 0 °C. TLC (3:1 toluene–EtOAc) showed the disappearance of **18** and the presence of both **9** (R_f 0.61) and a new compound (R_f 0.43). The mixture was neutralized with Et_3N, diluted with CH_2Cl_2, filtered, washed with aq 5% $NaHSO_3$, aq 10% $NaHCO_3$, and water, and concentrated. Column chromatography (2:1 hexane–EtOAc) of the residue afforded **19**, isolated as a colorless syrup (50.5 mg, 55%); $[\alpha]_D$ +16° (*c* 2); ^{1}H NMR ($CDCl_3$): δ 7.62–6.80 (m, 29 H, 5 Ph and Phth), 5.366 (dd, 1 H, $J_{3'',4''}$ 3.2, $J_{4'',5''}$ < 1 Hz, H-4″), 5.242 (d, 1 H, $J_{1',2'}$ 8.3 Hz, H-1′), 5.044 (dd, 1 H, $J_{2'',3''}$ 10.0 Hz, H-2″), 4.797, 4.759, 4.721, 4.469, 4.417, 4.344, 4.070, and 3.986 (8 d, 2,1,1,2,1,1,1,1 H, 5 PhCH_2O), 4.593 (d, 1 H, $J_{1'',2''}$ 8.1 Hz, H-1″), 4.476 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 3.327 (s, 3 H, OCH_3), 3.169 (dt, 1 H, octyl OC*H*H), 2.058 and 2.053 (2 s, 3,6 H, 3 Ac), 0.868 (t, 3 H, octyl CH_3); ^{13}C: δ 170.2, 170.0, and 169.0 (3 $COCH_3$), 133.3, 131.7, and 122.9 (Phth), 100.5 and 96.8 (2 C) (C-1,1′,1″), 79.8, 78.1, 77.8, 76.2, 75.0, 74.7, 73.5, 71.6, 71.1, 70.8, and 65.2 (C-2,3,4,5,3′,4′,5′,2″,3″,4″,5″), 74.6, 74.1, 73.6, 72.7, 70.5, 69.9, 68.4, 67.6, and 61.4 (C-6,6′,6″, 5 PhCH_2O, and octyl OCH_2), 57.6 (OCH_3), 55.5 (C-2′), 31.6, 29.2 (2 C), 29.0, 25.9, and 22.4 (6 octyl CH_2), 13.9 (octyl CH_3). Anal. Calcd for $C_{76}H_{89}NO_{20}$ (1336.56): C, 68.30; H, 6.71. Found: C, 68.36; H, 6.62.

Octyl (2,4,6-tri-O-*acetyl-3*-O-*methyl*-β-D-*galacto-pyranosyl)-(1 → 4)-(2-acetamido-3,6-di*-O-*acetyl-2-deoxy*-β-D-*glucopyranosyl)-(1 → 2)-3,4,6-tri*-O-*acetyl*-α-D-*mannopyranoside* (**21**).—A solution of **19** (43.2 mg, 32.3 μmol) and hydrazine monohydrate (0.5 mL) in 9:1 EtOH–H_2O (5 mL) was heated overnight

at 90 °C, when TLC (9:1 CH_2Cl_2–MeOH) showed the formation of an intermediate amino compound (R_f 0.42). The mixture was cooled, concentrated, and co-concentrated with toluene, and the residue was dissolved in 1:1 pyridine–Ac_2O (6 mL), stirred overnight at room temperature, and concentrated. Column chromatography (3:2 hexane–EtOAc) of the residue gave **20**, isolated as a colorless syrup (35.3 mg, 87%); $[\alpha]_D$ +11° (*c* 2); R_f 0.24 (2:1 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 3.327 (s, 3 H, OCH_3), 2.091, 2.030, 2.021, and 1.779 (4 s, each 3 H, 4 Ac); ^{13}C: δ 57.7 (OCH_3), 22.7 ($NHCOCH_3$). A mixture of **20** (33.6 mg, 26.9 μmol) and HOAc (0.3 mL) in 1:1 EtOH–EtOAc (6 mL), containing 10% Pd–C (20 mg), was hydrogenolyzed at atmospheric pressure for 30 min. Then TLC (solvent *A*) indicated a single new spot (R_f 0.58), and the mixture was filtered through Celite, concentrated, and co-concentrated with toluene. A solution of the residue in pyridine (3 mL) was treated overnight with Ac_2O (3 mL), then concentrated, and co-concentrated with toluene. Column chromatography (1:3 toluene–EtOAc) of the residue afforded **21**, isolated as a colorless glass (24.9 mg, 92%); $[\alpha]_D$ −6° (*c* 2); R_f 0.21 (1:3 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.443 (dd, 1 H, $J_{3'',4''}$ 3.3, $J_{4'',5''}$ 0.8 Hz, H-4″), 5.204 (dd, 1 H, $J_{3,4} = J_{4,5}$ = 10.0 Hz, H-4), 5.122 (dd, 1 H, $J_{2',3'}$ 8.5, $J_{3',4'}$ 10.3 Hz, H-3′), 5.063 (dd, 1 H, $J_{2,3}$ 3.5 Hz, H-3), 4.937 (dd, 1 H, $J_{2'',3''}$ 10.0 Hz, H-2″), 4.731 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.562 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1′), 4.405 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1″), 3.428 (dt, 1 H, octyl OC*H*H), 3.340 (s, 3 H, OCH_3), 3.315 (dd, 1 H, H-3″), 2.138, 2.128, 2.096, 2.080, 2.062, 2.036, 1.990, and 1.922 (8 s, 3,3,6,3,3,3,3,3 H, 9 Ac), 0.889 (t, 3 H, octyl CH_3); ^{13}C: δ 100.7, 99.2, and 97.1 (C-1,1′,1″), 79.3, 76.0, 74.1, 72.3, 72.2, 70.5, 70.4, 70.0, 68.1, 65.7, and 64.8 (C-2,3,4,5,3′,4′,5′,2″,3″,4″,5″), 68.0, 62.4, 62.3, and 61.1 (C-6,6′,6″ and octyl OCH_2), 57.6 (OCH_3), 53.4 (C-2′), 31.4, 29.3, 29.0, 28.9, 25.8, and 22.9 (6 octyl CH_2), 22.9 ($NHCOCH_3$), 13.6 (octyl CH_3). Anal. Calcd for $C_{45}H_{69}NO_{24}$ (1008.05): C, 53.62; H, 6.90. Found: C, 53.72; H, 7.01.

Octyl (3-O-methyl-β-D-galactopyranosyl)-(1 → 4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1 → 2)-α-D-mannopyranoside (**2**).—A mixture of **21** (23.0 mg, 22.8 μmol) and NaOMe (pH 8) in 4:1 MeOH–CH_2Cl_2 (5 mL) was stirred for 2 h, neutralized with Dowex-50 (H^+) resin, filtered, and concentrated. Gel filtration of the residue on Bio-Gel P-2 (water) and subsequent lyophilization yielded **2** as a white powder (14.7 mg, 96%); $[\alpha]_D$ 0° (*c* 0.4, MeOH); R_f 0.44 (solvent *A*); ^{1}H NMR (D_2O): see Table 1. FABMS: *m/z* 672 $[M + H]^+$, 694 $[M + Na]^+$.

Ethyl 2,4,6-tri-O-benzyl-3-deoxy-1-thio-β-D-xylo-hexopyranoside (**23**).—A mixture of **16** (30.0 mg, 60.6 μmol), 4-dimethylaminopyridine (0.11 g, 0.9 mmol), and phenyl thionochloroformate (25 μL, 0.19 mmol) in CH_2Cl_2 (3 mL) was stirred overnight at 0 °C under Ar, when TLC (11:1 toluene–EtOAc) indicated a complete conversion of **16** into **22**. The mixture was diluted with CH_2Cl_2, washed with 0.1 M HCl, aq 10% $NaHCO_3$, phosphate buffer, and water, and then concentrated. To a solution of the crude residue (**22**) and tributyltin hydride (0.16 mL, 0.59 mmol) in toluene (5 mL), heated at 80 °C under Ar, was added a catalytic amount of 2,2-azobisisobutyronitrile. After 15 min, when TLC (10:1 toluene–EtOAc) showed the disappearance of **22** and the formation of a new compound (R_f 0.49), the mixture was concentrated. A solution of the residue in MeCN was washed with hexane, then concentrated. Column chromatography (7:1 hexane–EtOAc) of the residue yielded **23**, isolated as a colorless syrup (21.2 mg, 73% from **16**); $[\alpha]_D$ −38° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 7.40–7.18 (m, 15 H, 3 Ph), 4.702, 4.536, 4.528, 4.455, 4.486, and 4.350 (6 d, each 1 H, 3 $PhCH_2O$), 4.496 (d, 1 H, $J_{1,2}$ 9.1 Hz, H-1), 3.691 (ddd, 1 H, $J_{4,5} < 1$ Hz, H-4), 2.83–2.63 (m, 2 H, SCH_2CH_3), 2.412 (ddd, 1 H, $J_{2,3eq}$ 4.6, $J_{3eq,3ax}$ 13.7, $J_{3eq,4}$ 3.3 Hz, H-3eq), 1.450 (ddd, 1 H, $J_{2,3ax}$ 11.2, $J_{3ax,4}$ 2.7 Hz, H-3ax), 1.300 (t, 3 H, SCH_2CH_3). Anal. Calcd for $C_{29}H_{34}O_4S$ (478.66): C, 72.77; H, 7.16. Found: C, 72.93; H, 7.23.

Benzyl 2,4,6-tri-O-benzyl-3-deoxy-β-D-xylo-hexopyranoside (**25**).—A solution of **11** (0.15 g, 0.3 mmol), 4-dimethylaminopyridine (0.34 g, 2.8 mmol), and phenyl thionochloroformate (0.11 mL, 0.80 mmol) was stirred overnight under Ar, when TLC (3:1 hexane–EtOAc) showed a complete reaction (**24**, R_f 0.59). The mixture was processed as described for **22**, to give crude **24**. A mixture of **24**, tributyltin hydride (0.75 mL, 2.8 mmol), and a catalytic amount of 2,2-azobisisobutyronitrile in toluene (10 mL) was heated for 30 min at 80 °C under Ar, when TLC (3:1 hexane–EtOAc) showed the conversion of **24** into **25** (R_f 0.52). Workup as described for **23** and column chromatography (6:1 hexane–EtOAc) yielded **25**, isolated as a white foam (0.11 g, 76% from **11**); $[\alpha]_D$ −45° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 7.42–7.20 (m, 20 H, 4 Ph), 4.969, 4.852, 4.659, 4.607, 4.559, 4.541, 4.488, and 4.379 (8 d, each 1 H, 4 $PhCH_2O$), 4.501 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 2.337 (ddd, 1 H, $J_{2,3eq}$ 5.1, $J_{3eq,3ax}$ 13.9, $J_{3eq,4}$ 3.3 Hz,

H-3eq), 1.465 (ddd, 1 H, $J_{2,3ax}$ 11.6, $J_{3ax,4}$ 2.7 Hz, H-3ax). Anal. Calcd for $C_{34}H_{36}O_5$ (524.66): C, 77.84; H, 6.92. Found: C, 77.75; H, 6.95.

1,2,4,6-Tetra-O-*acetyl-3-deoxy-α,β*-D-xylo-*hexopyranose* (**26**).—A solution of **25** (83.7 mg, 0.16 mmol) in 1:1 EtOH–EtOAc (6 mL), containing 10% Pd–C (40 mg) and HOAc (0.2 mL), was hydrogenolyzed at atmospheric pressure for 60 min. Because of incomplete debenzylation, the hydrogenolysis was repeated three times with intermediate filtration and addition of new catalyst. TLC (solvent *A*) then showed the formation of a single product (R_f 0.41), and the mixture was filtered through Celite, and concentrated. The residue was acetylated overnight in 1:1 pyridine–Ac_2O (6 mL). After concentration, and co-concentration with toluene, column chromatography (3:1 toluene–EtOAc) of the residue gave **26**, isolated as a colorless syrup (33.3 mg, 63%); R_f 0.22 (3:1 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): (*β*), δ 5.713 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 5.120 (ddd, 1 H, $J_{4,5}$ 1.6 Hz, H-4), 5.060 (ddd, 1 H, H-2), 4.183 (dd, 1 H, $J_{5,6a}$ 6.1, $J_{6a,6b}$ 11.2 Hz, H-6a), 4.106 (dd, 1 H, $J_{5,6b}$ 6.6 Hz, H-6b), 4.032 (ddd, 1 H, H-5), 2.451 (ddd, 1 H, $J_{2,3eq}$ 5.3, $J_{3eq,3ax}$ 14.2, $J_{3eq,4}$ 3.4 Hz, H-3eq), 2.131, 2.053, and 2.046 (3 s, 6,3,3 H, 4 Ac), 1.800 (ddd, 1 H, $J_{2,3ax}$ 11.5, $J_{3ax,4}$ 3.3 Hz, H-3ax). Anal. Calcd for $C_{14}H_{20}O_9$ (332.31): C, 50.60; H, 6.07. Found: C, 50.56; H, 6.31.

Ethyl 2,4,6-tri-O-*acetyl-3-deoxy-1-thio-α,β*-D-xylo-*hexopyranoside* (**27**).—A solution of **26** (33.0 mg, 0.1 mmol) in CH_2Cl_2 (3 mL), containing 4 Å molecular sieves (0.2 g), was stirred for 30 min under Ar at 0 °C. Ethanethiol (0.2 mL, 2.8 mmol) and $BF_3 \cdot Et_2O$ (80 μL, 0.64 mmol) were added, and the stirring was continued for 2 h, when TLC (10:1 toluene–EtOAc) showed the presence of **26** as well as two new products with R_f 0.21 (**27***β*) and 0.26 (**27***α*). Additional amounts of EtSH (0.1 mL, 1.4 mmol) and $BF_3 \cdot Et_2O$ (40 μL, 0.32 mmol) gave no further conversion of **26** after 2 h, and the mixture was neutralized with Et_3N, diluted with CH_2Cl_2, filtered, and concentrated. Column chromatography (4:1 toluene–EtOAc) of the residue afforded **27**, isolated as a syrup (15.4 mg, 46%, $\alpha:\beta = 1:4$), and then **26** (7.3 mg, 22%); ^{1}H NMR ($CDCl_3$): (*α*), δ 5.651 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 5.224 (ddd, 1 H, $J_{2,3eq}$ 5.5, $J_{2,3ax}$ 11.3 Hz, H-2), 5.137 (m, 1 H, H-4), 4.477 (ddd, 1 H, $J_{4,5}$ 1.7 Hz, H-5), 4.156 (dd, 1 H, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.091 (dd, 1 H, $J_{5,6b}$ 7.3 Hz, H-6b), 2.118, 2.067, and 2.049 (3 s, each 3 H, 3 Ac), 1.292 (t, 3 H, SCH_2CH_3); (*β*), δ 5.128 (ddd, 1 H, $J_{4,5}$ 1.3 Hz, H-4), 5.027 (ddd, 1 H, H-2), 4.502 (d, 1 H, $J_{1,2}$ 9.9 Hz, H-1), 4.143 (d, 2 H, $J_{5,6}$ 6.0 Hz, H-6a and H-6b), 3.855 (dt, 1 H, H-5), 2.82–2.63 (m, 2 H, SCH_2CH_3), 2.414 (ddd, 1 H, $J_{2,3eq}$ 5.5, $J_{3eq,3ax}$ 14.0, $J_{3eq,4}$ 3.2 Hz, H-3eq), 2.121, 2.068, and 2.049 (3 s, each 3 H, 3 Ac), 1.770 (ddd, 1 H, $J_{2,3ax}$ 11.3, $J_{3ax,4}$ 3.2 Hz, H-3ax), 1.296 (t, 3 H, SCH_2CH_3). Anal. Calcd for $C_{14}H_{22}O_7S$ (334.40): C, 50.29; H, 6.63. Found: C, 50.22; H, 6.76.

2,4,6-Tri-O-*acetyl-3-deoxy-α*-D-xylo-*hexopyranosyl trichloroacetimidate* (**29**).—To a cooled (0 °C) solution of **26** (71.3 mg, 0.21 mmol) in CH_2Cl_2 (3 mL) was added 33% (w/w) HBr in HOAc (0.5 mL), and after 30 min, when TLC (2:1 toluene–EtOAc) indicated the conversion of **26** into a new compound (R_f 0.56), the mixture was diluted with CH_2Cl_2, washed with phosphate buffer and water, and concentrated. To a solution of the residue in 6:2:1 CH_2Cl_2–acetone–H_2O (4.5 mL) was added $HgBr_2$ (75.6 mg, 0.21 mmol), and the mixture was stirred for 20 min. TLC (1:1 toluene–EtOAc) then showed the hydrolysis to be complete (**28**, R_f 0.32), and the mixture was diluted with CH_2Cl_2, washed with aq 10% KI and water, and concentrated, yielding crude **28**. To a solution of **28** and trichloroacetonitrile (0.21 mL, 2.1 mmol) in CH_2Cl_2 (2 mL) was added DBU in CH_2Cl_2 (0.2 M, 0.5 mL) at 0 °C, and the mixture was stirred overnight. TLC (2:1 toluene–EtOAc) then showed the conversion of **28** into **29** (R_f 0.52). Column chromatography (3:1 toluene–EtOAc) of the solution afforded **29**, isolated as a pale-yellow syrup (47.6 mg, 51% from **26**); $[\alpha]_D$ +49° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 8.638 (s, 1 H, NH), 6.496 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 5.255 (ddd, 1 H, $J_{2,3eq}$ 6.7, $J_{2,3ax}$ 10.1 Hz, H-2), 5.242 (m, 1 H, H-4), 4.310 (ddd, 1 H, $J_{4,5}$ 1.6 Hz, H-5), 4.195 (dd, 1 H, $J_{5,6a}$ 5.8, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.054 (dd, 1 H, $J_{5,6b}$ 7.0 Hz, H-6b), 2.140, 2.026, and 2.020 (3 s, each 3 H, 3 Ac).

Octyl (2,4,6-tri-O-*acetyl-3-deoxy-β*-D-xylo-*hexopyranosyl)-(1 → 4)-(3,6-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-(1 → 2)-3,4,6-tri*-O-*benzyl-α*-D-*mannopyranoside* (**30**).—(*a*) *Via trichloroacetimidate* **29**. A solution of **9** [5] (36.2 mg, 35.0 μmol) and trimethylsilyl triflate (10 μmol) in CH_2Cl_2 (3 mL), containing 4 Å molecular sieves (0.25 g), was stirred for 30 min at −30 °C under N_2. Then, a solution of **29** (19.8 mg, 45.6 μmol) in CH_2Cl_2 (2 mL) was added dropwise in 45 min, and TLC (3:1 toluene–EtOAc) showed the disappearance of **29** and the presence of both **9** (R_f 0.56) and **30** (R_f 0.47). The mixture was neutralized with Et_3N, diluted with CH_2Cl_2, filtered, washed with phosphate buffer and

water, and concentrated. Column chromatography (2:1 hexane–EtOAc) of the residue first gave **9** (18.2 mg, 50%); further elution of the column afforded **30**, isolated as a colorless syrup (17.7 mg, 39%).

(*b*) *Via thioglycoside* **27**. A solution of **9** [5] (27.9 mg, 27.0 μmol) and **27** (13.5 mg, 40.3 μmol) in CH_2Cl_2 (2 mL), containing 4 Å molecular sieves (0.25 g), was stirred for 30 min at 0 °C under N_2. Then, a solution of NIS (18.2 mg, 80.9 μmol) and TfOH (1 μL, 11.3 μmol) in CH_2Cl_2 (1 mL) was added dropwise in 30 min. TLC (3:1 toluene–EtOAc) showed the disappearance of **9** and the formation of **30** (R_f 0.47), and the mixture was neutralized (Et_3N), and processed as described above, yielding, after column chromatography (2:1 hexane–EtOAc), **30**, isolated as a colorless syrup (28.7 mg, 81%); $[\alpha]_D$ −4° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 7.62–6.80 (m, 29 H, 5 Ph and Phth), 5.253 (d, 1 H, $J_{1',2'}$ 8.3 Hz, H-1'), 4.966 (m, 1 H, H-4''), 4.883 (ddd, 1 H, H-2''), 4.802, 4.800, 4.764, 4.707, 4.475, 4.466, 4.435, 4.344, 4.073, and 3.990 (10 d, each 1 H, 5 PhCH_2O), 4.683 (d, 1 H, $J_{1'',2''}$ 8.1 Hz, H-1''), 4.474 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 3.166 (dt, 1 H, octyl OC*H*H), 2.327 (ddd, 1 H, $J_{2'',3''eq}$ 5.3, $J_{3''eq,3''ax}$ 14.0, $J_{3''eq,4''}$ 2.9 Hz, H-3''eq), 2.053, 2.030, and 2.010 (3 s, each 3 H, 3 Ac), 1.533 (ddd, 1 H, $J_{2'',3''ax}$ 11.7, $J_{3''ax,4}$ 2.9 Hz, H-3''ax), 0.868 (t, 3 H, octyl CH_3); ^{13}C: δ 170.4, 170.1, and 169.2 (3 *C*OCH$_3$), 133.3, 131.6, and 122.9 (Phth), 101.7 and 96.8 (2 C) (C-1,1',1''), 77.9, 77.7, 76.7, 74.9, 74.6, 73.8, 73.4, 71.5, 68.2, and 66.7 (C-2,3,4,5,3',4',5',2'',4'',5''), 74.7, 74.0, 73.5, 72.7, 70.5, 69.8, 68.4, 67.5, and 61.7 (C-6,6',6'', 5 PhCH_2O, and octyl OCH_2), 55.4 (C-2'), 32.8 (C-3''), 31.6, 29.2 (2 C), 29.0, 25.9, and 22.5 (6 octyl CH_2), 20.9, 20.8, and 20.6 (3 CO*C*H$_3$), 13.9 (octyl CH_3). Anal. Calcd for $C_{75}H_{87}NO_{19}$ (1306.53): C, 68.95; H, 6.71. Found: C, 68.79; H, 6.88.

*Octyl (2,4,6-tri-*O*-acetyl-3-deoxy-β-*D*-xylo-hexopyranosyl)-(1 → 4)-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-mannopyranoside* (**32**).—A solution of **30** (55.0 mg, 42.1 μmol) in 1-butanol (8 mL), containing 3 Å molecular sieves (0.25 g), was stirred for 30 min under Ar. Then, ethylenediamine (0.8 mL, 12.0 mmol) was added, and the mixture was heated overnight at 90 °C, when TLC (8:1 CH_2Cl_2–MeOH) showed the dephthaloylation to be complete. The mixture was filtered, concentrated, and co-concentrated with toluene. The residue was dissolved in pyridine (3 mL) and acetylated overnight with Ac_2O (2 mL). After concentration, column chromatography (2:1 toluene–EtOAc) of the residue yielded **31**, isolated as a colorless syrup (47.2 mg, 92%); $[\alpha]_D$ −3° (*c* 1); R_f 0.20 (2:1 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.626 (d, 1 H, $J_{2',NH}$ 7.1 Hz, NH), 2.066, 1.998, 1.976, and 1.696 (4 s, each 3 H, 4 Ac). To a solution of **31** (45.6 mg, 37.4 μmol) in 1:1 EtOH–EtOAc (5 mL) were added HOAc (0.1 mL) and 10% Pd–C (30 mg), and the mixture was hydrogenolyzed at atmospheric pressure for 40 min. Then, TLC (solvent *A*) showed the presence of a single compound (R_f 0.51), and the mixture was filtered through Celite, and concentrated. A solution of the residue in 1:1 pyridine–Ac_2O (5 mL) was stirred overnight, then concentrated. Column chromatography (1:5 toluene–EtOAc) of the residue gave **32**, isolated as a colorless glass (32.6 mg, 89%); $[\alpha]_D$ −23° (*c* 1); R_f 0.28 (1:5 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.605 (d, 1 H, $J_{2',NH}$ 8.6 Hz, NH), 5.268 (dd, 1 H, $J_{2',3'}$ 8.2, $J_{3',4'}$ 9.7 Hz, H-3'), 5.230 (dd, 1 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.086 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-3), 5.035 (m, 1 H, H-4''), 4.785 (ddd, 1 H, H-2''), 4.705 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.685 (d, 1 H, $J_{1',2'}$ 7.9 Hz, H-1'), 4.445 (d, 1 H, $J_{1'',2''}$ 7.9 Hz, H-1''), 3.418 (dt, 1 H, octyl OC*H*H), 2.402 (ddd, 1 H, $J_{2'',3''eq}$ 5.2, $J_{3''eq,3''ax}$ 14.2, $J_{3''eq,4''}$ 3.1 Hz, H-3''eq), 2.120, 2.113, 2.095, 2.090, 2.079, 2.039, 2.032, 1.994, and 1.944 (9 s, each 3 H, 9 Ac), 1.641 (ddd, 1 H, $J_{2'',3''ax}$ 11.7, $J_{3''ax,4''}$ 3.2 Hz, H-3''ax), 0.888 (t, 3 H, octyl CH_3); ^{13}C: δ 102.2, 99.3, and 97.4 (C-1,1',1''), 75.8, 74.4, 73.9, 72.7, 71.5, 70.1, 68.4, 67.7, 66.3, and 66.0 (C-2,3,4,5,3',4',5',2'',4'',5''), 68.2, 62.7, 62.6, and 61.7 (C-6,6',6'' and octyl OCH_2), 54.1 (C-2'), 32.5 (C-3''), 31.6, 29.2, 29.1, 29.0, 25.9, and 22.5 (6 octyl CH_2), 23.1 (NHCO*C*H$_3$), 13.9 (octyl CH_3). FABMS: *m/z* 978 $[M + H]^+$, 1000 $[M + Na]^+$.

*Octyl (3-deoxy-β-*D*-xylo-hexopyranosyl)-(1 → 4)-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-α-*D*-mannopyranoside* (**3**).—A mixture of **32** (28.6 mg, 29.2 μmol) and NaOMe (pH 8) in 4:1 MeOH–CH_2Cl_2 (5 mL) was stirred for 5 h at room temperature, neutralized with Dowex-50 (H^+), filtered, and concentrated. Gel filtration of the resulting syrup on a Bio-Gel P-2 column, eluted with water, followed by lyophilization, gave **3** as a white powder (18.6 mg, 99%); $[\alpha]_D$ −17° (*c* 1, MeOH); R_f 0.38 (solvent *A*); ^{1}H NMR (D_2O): see Table 1. FABMS: *m/z* 642 $[M + H]^+$, 664 $[M + Na]^+$.

*2,4,6-Tri-*O*-acetyl-3-deoxy-3-fluoro-α-*D*-galactopyranosyl trichloroacetimidate* (**35**).—A solution of 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-fluoro-α,β-D-galactopyranose [14] (**33**; 0.14 g, 0.41 mmol) and hydra-

zine acetate (42 mg, 0.45 mmol) in DMF (4 mL) was heated for 60 min at 50 °C, when TLC (1:1 hexane–EtOAc) showed the conversion of **33** into a new compound (**34**, R_f 0.32). The mixture was diluted with EtOAc, washed with aq 5% NaCl (3 ×), and concentrated. To a solution of the crude residue (**34**) in CH_2Cl_2 (2 mL) were added trichloroacetonitrile (0.41 mL, 4.1 mmol) and DBU (31 μL, 0.21 mmol) at 0 °C, and the mixture was stirred for 30 min, when TLC (2:1 hexane–EtOAc) showed a complete formation of **35** (R_f 0.32). Column chromatography (2:1 hexane–EtOAc) of the solution gave **35**, isolated as a colorless syrup (0.11 g, 61% from **33**); $[\alpha]_D$ +121° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 8.685 (s, 1 H, NH), 6.605 (dd, 1 H, $J_{1,2}$ 3.8, $J_{1,F}$ 4.1 Hz, H-1), 5.709 (ddd, 1 H, $J_{3,4}$ 3.7, $J_{4,F}$ 6.2, $J_{4,5}$ 1.3 Hz, H-4), 5.415 (ddd, 1 H, $J_{2,3}$ 10.1, $J_{2,F}$ 11.1 Hz, H-2), 5.064 (ddd, 1 H, $J_{3,F}$ 48.1 Hz, H-3), 4.375 (m, 1 H, H-5), 4.206 (dd, 1 H, $J_{5,6a}$ 6.2, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.058 (ddd, 1 H, $J_{6b,F}$ 1.1, $J_{5,6b}$ 6.8 Hz, H-6b), 2.174, 2.072, and 2.024 (3 s, each 3 H, 3 Ac); ^{13}C: δ 170.2, 170.1, and 169.7 (3 *C*OCH$_3$), 160.5 (O*C*[NH]CCl$_3$), 93.6 (d, $J_{C-1,F}$ 9.2 Hz, C-1), 90.6 (OC[NH]*C*Cl$_3$), 85.4 (d, $J_{C-3,F}$ 193.6 Hz, C-3), 68.9 (d, $J_{C-5,F}$ 4.5 Hz, C-5), 67.9 (d, $J_{C-2,F}$ 19.5 Hz, C-2), 67.2 (d, $J_{C-4,F}$ 17.2 Hz, C-4), 61.2 (d, $J_{C-6,F}$ 2.3 Hz, C-6), 20.4 (CO*C*H$_3$). Anal. Calcd for $C_{14}H_{17}Cl_3FNO_8$ (452.65): C, 38.34; H, 3.91. Found: C, 38.34; H, 4.21. FABMS: *m/z* 474:476:478 (9:9:3) $[M + Na]^+$.

*Octyl (2,4,6-tri-*O*-acetyl-3-deoxy-3-fluoro-β-*D*-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranoside* (**36**).—A solution of **9** [5] (81.6 mg, 78.9 μmol) and **35** (53.6 mg, 0.12 mmol) in CH_2Cl_2 (5 mL), containing 4 Å molecular sieves (0.3 g), was stirred for 30 min under N_2 at 0 °C. Trimethylsilyl triflate in CH_2Cl_2 (0.1 M, 0.23 mL) was added, and TLC (3:2 hexane–EtOAc) showed that **36** (R_f 0.46) was formed within 50 min. The mixture was neutralized with Et_3N, diluted with CH_2Cl_2, and filtered. The filtrate was washed with 0.1 M HCl, aq 5% $NaHCO_3$, phosphate buffer, and water, and concentrated. Column chromatography (3:1 hexane–EtOAc) of the residue afforded **36**, isolated as a colorless syrup (97.2 mg, 93%); $[\alpha]_D$ +7° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 7.63–6.85 (m, 29 H, 5 Ph and Phth), 5.422 (ddd, 1 H, $J_{4'',5''} < 1$ Hz, H-4''), 5.240 (d, 1 H, $J_{1',2'}$ 8.2 Hz, H-1'), 5.230 (ddd, 1 H, $J_{2'',3''}$ 9.8, $J_{2'',F}$ 11.8 Hz, H-2''), 4.792, 4.777, 4.757, 4.738, 4.481, 4.447, 4.387, 4.305, 4.075, and 3.992 (10 d, each 1 H, 5 PhC*H*$_2$O), 4.550 (d, 1 H, $J_{1'',2''}$ 8.1 Hz, H-1''), 4.470 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.327 (ddd, 1 H, $J_{3'',4''}$ 3.8, $J_{3'',F}$ 47.4 Hz, H-3''), 3.165 (dt, 1 H, octyl OC*H*H), 2.088, 2.076, and 2.055 (3 s, each 3 H, 3 Ac), 0.870 (t, 3 H, octyl CH_3); ^{13}C: δ 170.3, 169.8, and 168.9 (3 *C*OCH$_3$), 133.4, 131.5, and 123.0 (Phth), 99.7 (d, $J_{C-1'',F}$ 11.4 Hz, C-1''), 96.8 (2 C) (C-1,1'), 88.8 (d, $J_{C-3'',F}$ 194.7 Hz, C-3''), 78.2, 78.0, 76.4, 74.7, 74.6, 73.5, and 71.5 (C-2,3,4,5,3', 4',5'), 70.3 (d, $J_{C-2'',F}$ 19.5 Hz, C-2''), 69.7 (d, $J_{C-5'',F}$ 4.6 Hz, C-5''), 66.6 (d, $J_{C-4'',F}$ 16.1 Hz, C-4''), 74.7, 74.2, 73.5, 72.7, 70.6, 69.8, 68.1, 67.6, and 60.7 (C-6,6',6'', 5 PhCH_2O, and octyl OCH_2), 55.4 (C-2'), 31.6, 29.2 (2 C), 29.0, 25.9, and 22.5 (6 octyl CH_2), 14.0 (octyl CH_3). Anal. Calcd for $C_{75}H_{86}FNO_{19}$ (1324.52): C, 68.01; H, 6.54. Found: C, 68.21; H, 6.49.

*Octyl (2,4,6-tri-*O*-acetyl-3-deoxy-3-fluoro-β-*D*-galactopyranosyl)-(1 → 4)-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-mannopyranoside* (**38**).—A solution of **36** (92.4 mg, 69.8 μmol) and ethylenediamine (1.0 mL) in 1-butanol (10 mL), containing 3 Å molecular sieves (0.25 g), was boiled under reflux overnight, when TLC (8:1 CH_2Cl_2–MeOH) indicated the disappearance of **36** and the formation of a new compound (R_f 0.80). The mixture was filtered, concentrated, and co-concentrated with toluene. To a solution of the residue in pyridine (5 mL) was added Ac_2O (4 mL), and the mixture was stirred overnight, then concentrated. Column chromatography (2:1 toluene–EtOAc) of the residue afforded **37**, isolated as a syrup (76.2 mg, 88%); $[\alpha]_D$ +7° (*c* 1); R_f 0.31 (2:1 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.625 (d, 1 H, $J_{2',NH}$ 7.0 Hz, NH); ^{13}C: δ 88.7 (d, $J_{C-3'',F}$ 194.7 Hz, C-3''), 23.2 (NHCO*C*H$_3$). A solution of **37** (74.2 mg, 60.0 μmol) in 1:1 EtOH–EtOAc (5 mL), containing HOAc (0.1 mL) and 10% Pd–C (35 mg), was hydrogenolyzed under atmospheric pressure for 45 min, when TLC (solvent *A*) showed a single new compound (R_f 0.62). The mixture was filtered through Celite, the filtrate was concentrated, and the residue was acetylated overnight in 2:1 pyridine–Ac_2O (7.5 mL). After concentration, column chromatography (1:4 toluene–EtOAc) of the residue gave **38**, isolated as a colorless glass (54.9 mg, 92%); $[\alpha]_D$ −3° (*c* 1); R_f 0.22 (1:3 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.680 (d, 1 H, $J_{2',NH}$ 8.6 Hz, NH), 5.533 (m, 1 H, H-4''), 5.245 (dd, 1 H, $J_{2',3'}$ 8.0, $J_{3',4'}$ 9.7 Hz, H-3'), 5.221 (dd, 1 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.179 (ddd, $J_{2'',3''}$ 9.8, $J_{2'',F}$ 11.7 Hz, H-2''), 5.093 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-3), 4.716 (d, 1 H, $J_{1,2}$

1.6 Hz, H-1), 4.675 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1'), 4.572 (ddd, 1 H, $J_{3'',F}$ 47.3, $J_{3'',4''}$ 3.8 Hz, H-3''), 4.416 (d, 1 H, $J_{1'',2''}$ 7.9 Hz, H-1''), 3.419 (dt, 1 H, octyl OC*H*H), 2.166, 2.116, 2.103, 2.090, 2.084, 2.029, 1.992, and 1.947 (8 s, 3,3,3,3,6,3,3,3 H, 9 Ac), 0.889 (t, 3 H, octyl CH_3); ^{13}C: δ 100.1 (d, $J_{C\text{-}1'',F}$ 11.5 Hz, C-1''), 99.2 and 97.3 (C-1,1'), 88.6 (d, $J_{C\text{-}3'',F}$ 194.7 Hz, C-3''), 76.0, 74.5, 72.5, 71.3, 70.1, 68.4, and 66.0 (C-2,3,4,5,3',4',5'), 69.9 (d, $J_{C\text{-}2'',F}$ 20.6 Hz, C-2''), 69.8 (d, $J_{C\text{-}5'',F}$ 6.8 Hz, C-5''), 66.4 (d, $J_{C\text{-}4'',F}$ 16.0 Hz, C-4''), 68.4, 62.6, 62.4, and 60.8 (C-6,6',6'' and octyl OCH_2), 53.9 (C-2'), 31.6, 29.2, 29.1, 29.0, 25.9, and 22.4 (6 octyl CH_2), 23.0 ($NHCOCH_3$), 13.9 (octyl CH_3). Anal. Calcd for $C_{44}H_{66}FNO_{23}$ (996.02): C, 53.06; H, 6.68. Found: C, 53.18; H, 6.61.

*Octyl (3-deoxy-3-fluoro-β-*D*-galactopyranosyl)-(1 → 4)-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-α-*D*-mannopyranoside* (**4**).—A solution of **38** (49.2 mg, 49.4 μmol) in 4:1 MeOH–CH_2Cl_2 (5 mL) was treated with NaOMe (pH 8) for 90 min, then neutralized [Dowex-50 (H^+)], and filtered. After concentration, purification of the residue by Bio-Gel P-2 gel-permeation chromatography (water) and subsequent lyophilization yielded **4** as a white powder (30.8 mg, 95%); $[\alpha]_D$ −7° (*c* 1.4, MeOH); R_f 0.38 (solvent *A*); ^1H NMR (D_2O): see Table 1. FABMS: *m/z* 660 $[M + H]^+$, 682 $[M + Na]^+$.

*2,4,6-Tri-*O*-acetyl-3-azido-3-deoxy-α-*D*-galactopyranosyl trichloroacetimidate* (**41**).—A solution of 1,2,4,6-tetra-*O*-acetyl-3-azido-3-deoxy-α,β-D-galactopyranose [15] (**39**; 0.19 g, 0.51 mmol) and hydrazine acetate (51.7 mg, 0.56 mmol) in DMF (4 mL) was heated for 40 min at 50 °C, when TLC (1:1 hexane–EtOAc) showed the formation of **40** (R_f 0.38). The mixture was diluted with EtOAc, washed with aq 5% NaCl (2 ×) and water, then concentrated, and co-concentrated with toluene. To a solution of the residue (**40**) in CH_2Cl_2 (2 mL) was added trichloroacetonitrile (0.40 mL, 4.0 mmol), and the mixture was cooled to 0 °C. Then, DBU (30 μL, 0.2 mmol) was added, and the mixture was stirred for 60 min, when TLC (2:1 hexane–EtOAc) showed the appearance of **41** (R_f 0.51). Column chromatography (2:1 hexane–EtOAc) of the solution gave **41**, isolated as a white solid (0.18 g, 75% from **39**); $[\alpha]_D$ +95° (*c* 1); IR (KBr): ν 2114 cm^{-1} (N_3); ^1H NMR ($CDCl_3$): δ 8.698 (s, 1 H, NH), 6.583 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.545 (dd, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$ 1.4 Hz, H-4), 5.286 (dd, 1 H, $J_{2,3}$ 10.9 Hz, H-2), 4.385 (ddd, 1 H, H-5), 4.176 (dd, 1 H, $J_{5,6a}$ 6.3, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.125 (dd, 1 H, H-3), 4.018 (dd, 1 H, $J_{5,6b}$ 6.8 Hz, H-6b), 2.180, 2.092, and 2.029 (3 s, each 3 H, 3 Ac). FABMS: *m/z* 497:499:501 (9:9:3) $[M + Na]^+$.

*Octyl (2,4,6-tri-*O*-acetyl-3-azido-3-deoxy-β-*D*-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranoside* (**42**).—A solution of **9** [5] (82.0 mg, 79.3 μmol) and **41** (76.7 mg, 0.16 mmol) in CH_2Cl_2 (5 mL), containing 4 Å molecular sieves (0.3 g), was stirred for 30 min at 0 °C under N_2, then trimethylsilyl triflate (24.0 μmol) was added. After 60 min, when TLC (2:1 toluene–EtOAc) showed the disappearance of **9** and the appearance of a new spot (R_f 0.37), the mixture was neutralized with Et_3N, diluted with CH_2Cl_2, filtered, washed with phosphate buffer, and concentrated. Column chromatography (5:1 toluene–EtOAc) of the residue gave **42**, isolated as a colorless syrup (98.2 mg, 92%); $[\alpha]_D$ 0° (*c* 1); IR (NaCl): ν 2110 cm^{-1} (N_3); ^1H NMR ($CDCl_3$): δ 7.63–6.83 (m, 29 H, 5 Ph and Phth), 5.287 (dd, 1 H, $J_{3'',4''}$ 3.5, $J_{4'',5''}$ 0.9 Hz, H-4''), 5.238 (d, 1 H, $J_{1',2'}$ 8.4 Hz, H-1'), 5.088 (dd, 1 H, $J_{2'',3''}$ 10.6 Hz, H-2''), 4.791, 4.773, 4.762, 4.759, 4.497, 4.434, 4.375, 4.351, 4.075, and 3.994 (10 d, each 1 H, 5 PhCH_2O), 4.544 (d, 1 H, $J_{1'',2''}$ 7.9 Hz, H-1''), 4.466 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 3.228 (dd, 1 H, H-3''), 3.165 (dt, 1 H, octyl OC*H*H), 2.096, 2.075, and 2.061 (3 s, each 3 H, 3 Ac), 0.871 (t, 3 H, octyl CH_3); ^{13}C: δ 170.3, 169.8, and 168.9 (3 $COCH_3$), 133.4, 131.5, and 123.0 (Phth), 100.4 and 96.7 (2 C) (C-1,1',1''), 78.1, 78.0, 76.2, 74.6 (2 C), 73.5, 71.5 (2 C), 70.0, and 67.5 (C-2,3,4,5,3',4',5',2'',4'',5''), 74.7, 74.1, 73.6, 72.7, 70.7, 69.7, 67.9, 67.6, and 60.9 (C-6,6',6'', 5 PhCH_2O, and octyl OCH_2), 61.5 (C-3''), 55.3 (C-2'), 31.6, 29.2 (2 C), 29.0, 25.9, and 22.5 (6 octyl CH_2), 13.9 (octyl CH_3). Anal. Calcd for $C_{75}H_{86}N_4O_{19}$ (1347.54): C, 66.85; H, 6.43. Found: C, 66.68; H, 6.62.

*Octyl (2,4,6-tri-*O*-acetyl-3-azido-3-deoxy-β-*D*-galactopyranosyl)-(1 → 4)-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranoside* (**43**).—A mixture of **42** (93.1 mg, 69.1 μmol) and ethylenediamine (1 mL) in 1-butanol (10 mL), containing 3 Å molecular sieves (0.25 g), was heated overnight at 90 °C under Ar. TLC (8:1 CH_2Cl_2–MeOH) then showed the presence of a single new compound (R_f 0.70), and the mixture was filtered, concentrated, and co-concentrated with toluene. The residue was acetylated overnight with 1:1 pyridine–Ac_2O (8 mL), then concentrated, and purified by column chromatography

(2:1 toluene–EtOAc) to afford **43**, isolated as a syrup (63.7 mg, 73%); $[\alpha]_D$ +3° (*c* 1); R_f 0.32 (2:1 toluene–EtOAc); IR (NaCl): ν 2110 cm^{-1} (N_3); ^1H NMR ($CDCl_3$): δ 7.42–7.19 (m, 25 H, 5 Ph), 5.628 (d, 1 H, $J_{2',NH}$ 7.1 Hz, NH), 5.285 (dd, 1 H, $J_{3'',4''}$ 3.3, $J_{4'',5''} < 1$ Hz, H-4''), 5.119 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1'), 5.059 (dd, 1 H, $J_{2'',3''}$ 10.6 Hz, H-2''), 4.872, 4.830, 4.810, 4.686, 4.559, 4.476, and 4.355 (7 d, 1,1,1,1,3,2,1 H, 5 PhCH_2O), 4.744 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.553 (d, 1 H, $J_{1'',2''}$ 7.9 Hz, H-1''), 3.331 (dt, 1 H, octyl OC*H*H), 3.256 (dd, 1 H, H-3''), 2.089, 2.056, 2.024, and 1.701 (4 s, each 3 H, 4 Ac), 0.878 (t, 3 H, octyl CH_3); ^{13}C: δ 171.1, 170.1, 169.8, and 168.9 (4 *C*OCH_3), 99.9, 97.5, and 97.4 (C-1,1',1''), 78.3, 76.8, 74.4 (2 C), 73.4, 71.5, 71.4 (2 C), 70.0, and 67.4 (C-2,3,4,5,3',4',5',2'',4'',5''), 75.0, 73.8, 73.5, 73.1, 71.0, 69.1, 68.6, 67.8, and 60.9 (C-6,6',6'', 5 PhCH_2O, and octyl OCH_2), 61.5 (C-3''), 57.1 (C-2'), 31.7, 29.4, 29.2, 29.1, 26.0, and 22.5 (6 octyl CH_2), 23.2 (NHCO*C*H_3), 20.6, 20.5, and 20.4 (3 OCO*C*H_3), 13.9 (octyl CH_3). Anal. Calcd for $C_{69}H_{86}N_4O_{18}$ (1259.48): C, 65.80; H, 6.88. Found: C, 65.96; H, 6.74.

*Octyl (3-amino-3-deoxy-β-*D*-galactopyranosyl)-(1 → 4)-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-α-*D*-mannopyranoside* (**5**).—A solution of **43** (60.6 mg, 48.1 μmol) in 1:1 CH_2Cl_2–MeOH (5 mL) containing NaOMe (pH 8) was stirred for 45 min, when TLC (1:2 toluene–EtOAc) showed the *O*-deacetylation to be complete (**44**, R_f 0.30). The mixture was neutralized [Dowex-50 (H^+)], diluted with MeOH, filtered, and concentrated. Column chromatography (1:2 toluene–EtOAc) of the residue gave **44**, isolated as a colorless syrup (51.7 mg, 95%); $[\alpha]_D$ +17° (*c* 1). A mixture of **44** (26.0 mg, 22.9 μmol) and 10% Pd–C (100 mg) in 6:4:1 *i*-PrOH–H_2O–HOAc (5.5 mL) was hydrogenolyzed at atmospheric pressure for 6 h. Since TLC (60:35:6 $CHCl_3$–MeOH–H_2O) showed that the debenzylation was incomplete, the hydrogenolysis was repeated twice with intermediate filtration through Celite and addition of new catalyst. TLC (10:4:1 CH_2Cl_2–MeOH–NH_4OH) then showed the presence of a major (**5**, R_f 0.11) and a minor (R_f 0.23) compound, and the mixture was filtered through Celite, and concentrated. Column chromatography (10:4:1 CH_2Cl_2–MeOH–NH_4OH) of the residue afforded **5** that was further purified on a preconditioned Sep-Pak C_{18} column (Waters Associates, Millipore Corporation). After washing with H_2O (30 mL), the column was eluted with MeOH (20 mL), and the eluate was concentrated. Redissolution of the residue in H_2O and lyophilization gave **5** as a white powder (3.2 mg, 21%); $[\alpha]_D$ 0° (*c* 0.25, MeOH); ^1H NMR (D_2O): see Table 1. FABMS: *m/z* 657 $[M + H]^+$, 679 $[M + Na]^+$.

*2, 3, 4, 6-Tetra-*O*-acetyl-α, β-*D*-gulopyranosyl trichloroacetimidate* (**47**).—A solution of 1,2,3,4,6-penta-*O*-acetyl-α,β-D-gulopyranose (**45**; 69.5 mg, 0.18 mmol) and hydrazine acetate (19.8 mg, 0.22 mmol) in DMF (3 mL) was heated for 30 min at 50 °C. TLC (1:1 toluene–EtOAc) then showed the formation of a major spot (**46**β, R_f 0.31), a minor spot (**46**α, R_f 0.23), as well as a number of slower moving side-products. The mixture was diluted with EtOAc, washed with aq 5% NaCl (2 ×) and water, concentrated, and repeatedly co-concentrated with toluene. Column chromatography (3:2 toluene–EtOAc) of the residue gave **46**, isolated as a colorless syrup (36.6 mg, 59%, α:β = 1:6); ^1H NMR ($CDCl_3$): (β), δ 2.162, 2.151, 2.073, and 2.060 (4 s, each 3 H, 4 Ac); ^{13}C: (β), δ 170.4, 170.3, 169.3, and 168.7 (4 *C*OCH_3). To a solution of **46** (35.0 mg, 0.1 mmol) and trichloroacetonitrile (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL) was added DBU in CH_2Cl_2 (0.2 M, 0.25 mL) at 0 °C, and the mixture was stirred overnight. TLC (2:1 toluene–EtOAc) then showed two products with R_f 0.47 (**47**α) and 0.37 (**47**β), respectively. Column chromatography (2:1 toluene–EtOAc) of the solution gave **47**, isolated as a syrup (44.8 mg, 90%, α:β = 1:4); $[\alpha]_D$ +88° (*c* 1, α anomer); +1° (*c* 1, β anomer); ^1H NMR ($CDCl_3$): (α), δ 8.681 (s, 1 H, NH), 6.431 (d, 1 H, $J_{1,2}$ 4.1 Hz, H-1), 5.391 (dd, 1 H, H-3), 5.322 (dd, 1 H, $J_{2,3}$ 3.9 Hz, H-2), 5.092 (dd, 1 H, $J_{3,4}$ 3.9, $J_{4,5}$ 1.4 Hz, H-4), 4.618 (ddd, 1 H, H-5), 4.217 (dd, 1 H, $J_{5,6a}$ 5.7, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.066 (dd, 1 H, $J_{5,6b}$ 7.2 Hz, H-6b), 2.172, 2.165, 2.030, and 2.013 (4 s, each 3 H, 4 Ac); (β), δ 8.696 (s, 1 H, NH), 6.126 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 5.470 (dd, 1 H, H-3), 5.308 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-2), 5.057 (dd, 1 H, $J_{3,4}$ 4.3, $J_{4,5}$ 2.0 Hz, H-4), 4.430 (ddd, 1 H, H-5), 4.235 (dd, 1 H, $J_{5,6a}$ 6.3, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.177 (dd, 1 H, $J_{5,6b}$ 6.9 Hz, H-6b), 2.177, 2.163, 2.058, and 2.000 (4 s, each 3 H, 4 Ac).

*Octyl (2,3,4,6-tetra-*O*-acetyl-β-*D*-gulopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranoside* (**48**).—A solution of **9** [5] (66.0 mg, 63.8 μmol) and **47** (44.0 mg, 89.3 μmol) in CH_2Cl_2 (4 mL), containing 3 Å molecular sieves (0.15 g), was stirred for 30 min under N_2. Then, trimethylsilyl triflate in CH_2Cl_2 (0.1 M, 0.1 mL) was

added at 0 °C, and the mixture was stirred for 30 min, when TLC (3:1 toluene–EtOAc) indicated the disappearance of **47** and the formation of a new product (**48**, R_f 0.50). The mixture was neutralized with Et_3N, diluted with CH_2Cl_2, filtered, washed with phosphate buffer and water, and concentrated. Column chromatography (5:1 toluene–EtOAc) of the residue yielded **48**, isolated as a colorless syrup (54.5 mg, 63%); $[\alpha]_D$ +9° (*c* 3); ^{1}H NMR ($CDCl_3$): δ 7.62–6.80 (m, 29 H, 5 Ph and Phth), 5.373 (dd, 1 H, H-3″), 5.245 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1′), 5.160 (d, 1 H, $J_{1'',2''}$ 8.5 Hz, H-1″), 5.002 (dd, 1 H, $J_{2'',3''}$ 3.3 Hz, H-2″), 4.893 (dd, 1 H, $J_{3'',4''}$ 3.6, $J_{4'',5''}$ 1.4 Hz, H-4″), 4.820, 4.787, 4.757, 4.622, 4.566, 4.484, 4.473, 4.335, 4.062, and 3.973 (10 d, each 1 H, 5 PhCH_2O), 4.456 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 3.160 (dt, 1 H, octyl OC*H*H), 2.106, 2.023, 2.018, and 1.971 (4 s, each 3 H, 4 Ac), 0.865 (t, 3 H, octyl CH_3); ^{13}C: δ 170.3, 169.3, 169.1, and 168.7 (4 *C*OCH_3), 167.5 (*C*O Phth), 133.3, 131.6, and 122.9 (Phth), 98.2 and 96.7 (2 C) (C-1,1′,1″), 78.6, 77.7, 77.0, 74.9, 74.8, 73.4, 71.5, 70.4, 69.1, 67.8, and 67.7 (C-2,3,4,5,3′,4′,5′,2″, 3″,4″,5″), 74.8, 74.2, 73.3, 72.7, 70.5, 69.9, 68.5, 67.6, and 61.3 (C-6,6′,6″, 5 PhCH_2O, and octyl OCH_2), 55.5 (C-2′), 31.6, 29.5, 29.1, 29.0, 25.9, and 22.4 (6 octyl CH_2), 13.9 (octyl CH_3). Anal. Calcd for $C_{77}H_{89}NO_{21}$ (1364.57): C, 67.78; H, 6.57. Found: C, 67.88; H, 6.61.

*Octyl (2,3,4,6-tetra-*O*-acetyl-β-*D*-gulopyranosyl)-(1 → 4)-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-mannopyranoside* (**50**).—A solution of **48** (54.5 mg, 39.9 μmol) and hydrazine monohydrate (0.5 mL) in 9:1 EtOH–H_2O (10 mL) was boiled under reflux overnight, when TLC (9:1 CH_2Cl_2–MeOH) showed the formation of an intermediate amino compound (R_f 0.50). The mixture was concentrated, and co-concentrated with toluene, and the residue was acetylated with 1:1 Ac_2O–pyridine (6 mL) overnight. The solution was concentrated, and co-concentrated with toluene, and the residue was purified by column chromatography (3:1 toluene–EtOAc) to afford **49**, isolated as a colorless syrup (32.6 mg, 64%); $[\alpha]_D$ +6° (*c* 1); R_f 0.31 (2:1 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.666 (d, 1 H, $J_{2',NH}$ 7.0 Hz, NH), 2.104, 1.999, 1.974, 1.965, and 1.684 (5 s, each 3 H, 5 Ac); ^{13}C: δ 23.2 (NHCO*C*H_3). A solution of **49** (32.0 mg, 25.1 μmol) and HOAc (0.1 mL) in 1:1 EtOH–EtOAc (6 mL), containing 10% Pd–C (20 mg), was hydrogenolyzed at atmospheric pressure for 2 h, when TLC (solvent *A*) showed the presence of a single compound (R_f 0.56). The mixture was filtered through Celite, concentrated, and co-concentrated with toluene. A solution of the residue in 1:1 Ac_2O–pyridine (6 mL) was stirred for 16 h, concentrated, and co-concentrated with toluene. Column chromatography (1:3 toluene–EtOAc) of the residue yielded **50**, isolated as a colorless glass (23.1 mg, 89%); $[\alpha]_D$ −12° (*c* 1); R_f 0.29 (1:3 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.951 (d, 1 H, $J_{2',NH}$ 8.6 Hz, NH), 5.372 (dd, 1 H, H-3″), 5.259 (dd, 1 H, $J_{2',3'}$ 8.7, $J_{3',4'}$ 10.4 Hz, H-3′), 5.222 (dd, 1 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.071 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-3), 4.909 (dd, 1 H, $J_{3'',4''}$ 3.8, $J_{4'',5''}$ 1.4 Hz, H-4″), 4.839 (dd, 1 H, $J_{2'',3''}$ 3.3 Hz, H-2″), 4.713 (d, 1 H, $J_{1'',2''}$ 8.3 Hz, H-1″), 4.694 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.666 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1′), 3.417 (dt, 1 H, octyl OC*H*H), 2.146, 2.141, 2.119, 2.094, 2.085, 2.082, 2.034, 1.996, 1.990, and 1.934 (10 s, each 3 H, 10 Ac), 0.888 (t, 3 H, octyl CH_3); ^{13}C: δ 99.3, 98.3, and 97.2 (C-1,1′,1″), 74.2, 72.3, 72.2, 70.2 (3 C), 68.6, 68.2, 67.3, 66.9, and 65.9 (C-2,3,4,5,3′,4′,5′,2″,3″,4″,5″), 68.0, 62.5, 62.2, and 61.1 (C-6,6′,6″ and octyl OCH_2), 53.8 (C-2′), 31.4, 28.9 (2 C), 28.8, 25.7, and 22.2 (6 octyl CH_2), 22.2 (NHCO*C*H_3), 13.9 (octyl CH_3). Anal. Calcd for $C_{46}H_{69}NO_{25}$ (1036.06): C, 53.33; H, 6.71. Found: C, 53.40; H, 6.82.

*Octyl β-*D*-gulopyranosyl-(1 → 4)-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-α-*D*-mannopyranoside* (**6**).—To a solution of **50** (16.0 mg, 15.4 μmol) in 4:1 MeOH–CH_2Cl_2 (5 mL) was added NaOMe to pH 8. The mixture was stirred for 2 h, neutralized with Dowex-50 (H^+) resin, filtered, and concentrated. Gel filtration of the residue on a Bio-Gel P-2 column, eluted with water, and subsequent lyophilization gave **6** as a white powder (10.1 mg, 99%); $[\alpha]_D$ −8° (*c* 0.5, MeOH); R_f 0.38 (solvent *A*); ^{1}H NMR (D_2O): see Table 1. FABMS: *m/z* 658 $[M + H]^+$, 680 $[M + Na]^+$.

*2,3,4,6-Tetra-*O*-acetyl-α-*L*-galactopyranosyl trichloroacetimidate* (**53**).—To a solution of 1,2,3,4,6-penta-*O*-acetyl-α,β-L-galactopyranose (**51**; 0.14 g, 0.37 mmol) in DMF (1 mL) was added hydrazine acetate (40.4 mg, 0.44 mmol) at 50 °C under Ar. After 30 min, when TLC (1:1 hexane–EtOAc) showed the formation of **52** (R_f 0.25), the mixture was diluted with EtOAc, washed with aq 5% NaCl (2×) and water, concentrated, and co-concentrated with toluene. A solution of the crude product (**52**), trichloroacetonitrile (0.40 mL, 4.0 mmol), and DBU (30 μL, 0.2 mmol) in CH_2Cl_2 (2 mL) was

stirred for 60 min at 0 °C, when TLC (2:1 hexane–EtOAc) showed the conversion of **52** into **53** (R_f 0.33) to be complete. Column chromatography (3:2 hexane–EtOAc) of the solution gave **53**, isolated as a white solid (0.11 g, 63% from **51**); $[\alpha]_D$ −105° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 8.666 (s, 1 H, NH), 6.606 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 5.564 (dd, 1 H, $J_{3,4}$ 3.0, $J_{4,5}$ 1.4 Hz, H-4), 5.433 (dd, 1 H, $J_{2,3}$ 10.8 Hz, H-3), 5.364 (dd, 1 H, H-2), 4.443 (ddd, 1 H, H-5), 4.171 (dd, 1 H, $J_{5,6a}$ 6.6, $J_{6a,6b}$ 11.3 Hz, H-6a), 4.083 (dd, 1 H, $J_{5,6b}$ 6.7 Hz, H-6b), 2.167, 2.028, 2.019, and 2.014 (4 s, each 3 H, 4 Ac); ^{13}C: δ 160.8 (O*C*[NH]CCl_3), 93.4 (C-1), 68.8, 67.3 (2 C), and 66.4 (C-2,3,4,5), 61.1 (C-6). FABMS: *m/z* 514:516:518 (9:9:3) $[M + Na]^+$.

*Octyl (2,3,4,6-tetra-*O*-acetyl-β-*L*-galactopyranosyl)-(1 → 4)-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranoside* (**54**).—A solution of **9** (54.6 mg, 52.8 μmol) and **53** (39.1 mg, 79.4 μmol) in CH_2Cl_2 (4 mL), containing 3 Å molecular sieves (0.25 g), was stirred for 30 min at 0 °C under N_2. Then, trimethylsilyl triflate in CH_2Cl_2 (0.1 M, 0.16 mL) was added, and TLC (3:1 toluene–EtOAc) showed the formation of **54** (R_f 0.44) to be complete in 30 min. The mixture was neutralized with Et_3N, diluted with CH_2Cl_2, filtered, washed with phosphate buffer and water, and concentrated. Column chromatography (2:1 hexane–EtOAc) of the residue afforded **54**, isolated as a colorless syrup (57.6 mg, 80%); $[\alpha]_D$ +16° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 7.62–6.82 (m, 29 H, 5 Ph and Phth), 5.341 (dd, 1 H, $J_{3'',4''}$ 3.4, $J_{4'',5''}$ 1.0 Hz, H-4″), 5.253 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 5.226 (dd, 1 H, $J_{2'',3''}$ 10.4 Hz, H-2″), 4.953 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1″), 4.939 (dd, 1 H, H-3″), 4.807, 4.798, 4.789, 4.585, 4.535, 4.462, 4.333, 4.294, 4.048, and 3.964 (10 d, each 1 H, 5 PhCH_2O), 4.457 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 4.365 (dd, 1 H, $J_{5'',6''a}$ 7.7, $J_{6''a,6''b}$ 10.9 Hz, H-6″a), 4.293 (dd, 1 H, $J_{5'',6''b}$ 7.9 Hz, H-6″b), 3.178 (dt, 1 H, octyl OC*H*H), 2.141, 2.059, 2.055, and 1.973 (4 s, each 3 H, 4 Ac), 0.869 (t, 3 H, octyl CH_3); ^{13}C: δ 170.3, 170.0, 169.9, and 168.9 (4 *C*OCH_3), 133.4, 131.5, and 122.9 (Phth), 100.1 and 96.4 (2 C) (C-1,1′,1″), 79.7, 77.6, 76.6, 74.4, 74.2, 73.2, 71.5, 70.8, 70.7, 69.2, and 67.2 (C-2,3,4,5,3′,4′,5′,2″,3″,4″,5″), 75.2, 74.8, 73.5, 72.6 (2 C), 70.3, 69.6, 67.6, and 61.4 (C-6,6′,6″, 5 Ph*C*H_2O, and octyl OCH_2), 55.5 (C-2′), 31.7, 29.2 (2 C), 29.0, 25.9, and 22.5 (6 octyl CH_2), 13.9 (octyl CH_3). Anal. Calcd for $C_{77}H_{89}NO_{21}$ (1364.57): C, 67.78; H, 6.57. Found: C, 67.64; H, 6.63.

*Octyl (2,3,4,6-tetra-*O*-acetyl-β-*L*-galactopyranosyl)-(1 → 4)-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-mannopyranoside* (**56**).—A solution of **54** (55.7 mg, 40.8 μmol) in 1-butanol (8 mL), containing 3 Å molecular sieves (0.25 g), was stirred for 30 min under Ar. Then, ethylenediamine (0.8 mL) was added, and the mixture was boiled under reflux overnight, when TLC (8:1 CH_2Cl_2–MeOH) indicated the conversion of **54** into a single compound (R_f 0.45). The mixture was filtered, concentrated, and co-concentrated with toluene, and the residue, dissolved in pyridine (3 mL), was acetylated with Ac_2O (2 mL) for 16 h. After concentration, column chromatography (2:1 toluene–EtOAc) of the residue gave **55**, isolated as a colorless syrup (45.5 mg, 87%); $[\alpha]_D$ +20° (*c* 1); R_f 0.23 (2:1 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.569 (d, 1 H, $J_{2',NH}$ 6.7 Hz, NH), 2.130, 2.048, 2.013, 1.978, and 1.692 (5 s, each 3 H, 5 Ac). A solution of **55** (44.5 mg, 34.9 μmol) in 1:1 EtOH–EtOAc (5 mL), containing HOAc (0.1 mL) and 10% Pd–C (25 mg), was hydrogenolyzed at atmospheric pressure for 2 h, when TLC (solvent *A*) showed complete debenzylation. The mixture was filtered through Celite, concentrated, and co-concentrated with toluene. To a solution of the residue in pyridine (3 mL) was added Ac_2O (3 mL), and after overnight stirring, the mixture was concentrated. Column chromatography (1:4 toluene–EtOAc) of the residue yielded **56**, isolated as a colorless glass (34.2 mg, 95%); $[\alpha]_D$ +6° (*c* 1); R_f 0.17 (1:3 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.467 (d, 1 H, $J_{2',NH}$ 8.3 Hz, NH), 5.356 (dd, 1 H, $J_{4'',5''} < 1$ Hz, H-4″), 5.266 (dd, 1 H, $J_{2',3'}$ 9.6, $J_{3',4'}$ 11.4 Hz, H-3′), 5.219 (dd, 1 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.108 (dd, 1 H, $J_{2'',3''}$ 10.5 Hz, H-2″), 5.075 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-3), 4.924 (dd, 1 H, $J_{3'',4''}$ 3.4 Hz, H-3″), 4.692 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.683 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.603 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1″), 3.420 (dt, 1 H, octyl OC*H*H), 2.149, 2.125, 2.098, 2.088, 2.068, 2.029, 2.002, 1.986, 1.965, and 1.925 (10 s, each 3 H, 10 Ac), 0.888 (t, 3 H, octyl CH_3); ^{13}C: δ 100.9, 98.9, and 97.3 (C-1,1′,1″), 74.6, 74.1, 73.8, 71.9, 70.7, 70.6, 70.0, 68.4, 66.7, 65.9, and 65.5 (C-2,3,4,5,3′,4′,5′,2″,3″,4″,5″), 68.3, 62.9, 62.7, and 61.0 (C-6,6′,6″ and octyl OCH_2), 54.7 (C-2′), 31.6, 29.2 (2 C), 29.0, 25.9, and 22.4 (6 octyl CH_2), 23.0 (NHCOCH_3), 13.9 (octyl CH_3). FABMS: *m/z* 1036 $[M + H]^+$, 1058 $[M + Na]^+$.

*Octyl β-*L*-galactopyranosyl-(1 → 4)-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-α-*D*-mannopyra-*

noside (**7**).—To a solution of **56** (26.0 mg, 25.1 μmol) in 4:1 MeOH–CH_2Cl_2 (5 mL) was added NaOMe to pH 8, and the mixture was stirred for 2 h, then neutralized [Dowex-50 (H^+)], filtered, and concentrated. Gel filtration of the residue on a Bio-Gel P-2 column, using water as the eluent, and subsequent lyophilization afforded **7** as a white powder (15.5 mg, 94%); $[\alpha]_D$ −1° (*c* 0.8, MeOH); R_f 0.29 (solvent *A*); ^{1}H NMR (D_2O): see Table 1. FABMS: *m/z* 658 $[M + H]^+$, 680 $[M + Na]^+$.

2,3,4,6-Tetra-O-acetyl-α,β-L-altropyranosyl trichloroacetimidate (**59**).—L-Altrose (0.1 g, 0.56 mmol) was acetylated in 1:1 pyridine–Ac_2O (8 mL) for 16 h. TLC (1:1 hexane–EtOAc) then showed the presence of a single spot (R_f 0.42), and the solution was concentrated and co-concentrated with toluene. Column chromatography (1:1 hexane–EtOAc) of the residue afforded a colorless syrup (0.39 g) consisting of 1,2,3,4,6-penta-*O*-acetyl-α-L-altropyranose (**57**α), 1,2,3,4,6-penta-*O*-acetyl-β-L-altropyranose (**57**β), 1,2,3,5,6-penta-*O*-acetyl-α-L-altrofuranose (**58**α), and 1,2,3,5,6-penta-*O*-acetyl-β-L-altrofuranose (**58**β). ^{13}C (^{1}H-coupled) NMR ($CDCl_3$): δ 99.1 (d, $J_{C\text{-}1,H\text{-}1}$ 182 Hz, C-1 α-furanose), 93.7 (d, $J_{C\text{-}1,H\text{-}1}$ 187 Hz, C-1 β-furanose), 90.3 (d, $J_{C\text{-}1,H\text{-}1}$ 175 Hz, C-1 α-pyranose), 89.9 (d, $J_{C\text{-}1,H\text{-}1}$ 168 Hz, C-1 β-pyranose). The ratios between the anomers, as determined by integration of the C-1 resonances, were α-*f*:β-*f*:α-*p*:β-*p* = 15:6:34:45.

To a cooled (0 °C) solution of **57/58** (0.12 g, 0.3 mmol) in CH_2Cl_2 (1 mL) was added 33% (w/w) HBr in HOAc (0.25 mL). After 30 min, TLC (1:1 hexane–EtOAc) showed a complete disappearance of **57/58**, and the mixture was diluted with CH_2Cl_2, washed with water, aq 10% $NaHCO_3$, and water, concentrated, and purified by column chromatography (1:1 hexane–EtOAc). To a solution of the resulting syrup (65.4 mg) in CH_2Cl_2 (2 mL) were added trichloroacetonitrile (0.19 mL, 1.9 mmol) and DBU (14 μL, 0.1 mmol) at 0 °C under Ar, and the mixture was stirred for 60 min. Column chromatography (1:1 hexane–EtOAc) of the solution gave **59**, isolated as a colorless syrup (0.11 g, 75% from **57/58**); ^{1}H NMR ($CDCl_3$): (α), δ 8.739 (s, 1 H, NH), 6.201 (bs, 1 H, H-1), 5.359 (dd, 1 H, H-3), 5.232 (dd, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$ 10.2 Hz, H-4), 5.130 (dd, 1 H, $J_{1,2}$ 1.1, $J_{2,3}$ 3.4 Hz, H-2), 4.513 (ddd, 1 H, H-5), 4.292 (dd, 1 H, $J_{5,6b}$ 4.8, $J_{6a,6b}$ 12.3 Hz, H-6b), 4.201 (dd, 1 H, $J_{5,6a}$ 2.4 Hz, H-6a), 2.184, 2.152, 2.066, and 2.028 (4 s, each 3 H, 4 Ac); (β), δ 8.639 (s, 1 H, NH), 6.471 (d, 1 H, $J_{1,2}$ 2.9 Hz, H-1), 5.532 (dd, 1 H, $J_{3,4}$ 3.1, $J_{4,5}$ 8.1 Hz, H-4), 5.423 (dd, 1 H, $J_{2,3}$ 5.5 Hz, H-2), 5.405 (dd, 1 H, H-3), 4.347 (d, 2 H, $J_{5,6}$ 6.1 Hz, H-6a and H-6b), 4.254 (m, 1 H, H-5), 2.170, 2.110, 2.092, and 2.085 (4 s, each 3 H, 4 Ac); ^{13}C (^{1}H-coupled): δ 94.4 (d, $J_{C\text{-}1,H\text{-}1}$ 175 Hz, C-1β), 93.6 (d, $J_{C\text{-}1,H\text{-}1}$ 179 Hz, C-1α). FABMS: *m/z* 514:516:518 (9:9:3) $[M + Na]^+$.

Octyl (2,3,4,6-tetra-O-acetyl-α-L-altropyranosyl)-(1 → 4)-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**60**).—To a solution of **9** [5] (54.9 mg, 53.1 μmol) and **59** (49.6 mg, 0.1 mmol) in CH_2Cl_2 (4 mL), containing 3 Å molecular sieves (0.25 g), was added, at 0 °C, trimethylsilyl triflate in CH_2Cl_2 (0.1 M, 0.16 mL). After 15 min, TLC (1:1 hexane–EtOAc) showed the formation of **60** (R_f 0.57), and the mixture was neutralized with Et_3N. After dilution with CH_2Cl_2, the solution was filtered, washed with phosphate buffer and water, then concentrated. Column chromatography of the residue (2:1 hexane–EtOAc) yielded **60**, isolated as a colorless syrup (59.6 mg, 82%); $[\alpha]_D$ −23° (*c* 1); ^{1}H NMR ($CDCl_3$): δ 7.64–6.88 (m, 29 H, 5 Ph and Phth), 5.293 (dd, 1 H, H-3″), 5.277 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1′), 5.100 (dd, 1 H, $J_{3'',4''}$ 3.5, $J_{4'',5''}$ 10.1 Hz, H-4″), 5.057 (s, 1 H, $J_{1'',2''} < 1$ Hz, H-1″), 4.950 (dd, 1 H, $J_{2'',3''}$ 3.5 Hz, H-2″), 4.829, 4.769, 4.751, 4.557, 4.492, 4.450, 4.327, 4.095, and 4.012 (9 d, 1,1,1,1,1,2,1,1,1 H, 5 PhCH_2O), 4.468 (s, 1 H, H-1), 3.876 (dd, 1 H, $J_{5'',6''a}$ 2.5, $J_{6''a,6''b}$ 11.3 Hz, H-6″a), 3.791 (dd, 1 H, $J_{5'',6''b}$ 3.1 Hz, H-6″b), 3.163 (dt, 1 H, octyl OC*H*H), 2.160, 2.077, 2.068, and 1.977 (4 s, each 3 H, 4 Ac), 0.870 (t, 3 H, octyl CH_3); ^{13}C: δ 133.5, 131.5, and 123.0 (Phth), 96.6 (3 C) (C-1,1′,1″), 78.5, 77.5, 75.3, 75.1, 74.5, 73.3, 71.4, 69.5, 67.5, 64.6, and 64.5 (C-2,3,4,5,3′,4′,5′,2″,3″,4″,5″), 75.0, 74.7, 73.1, 72.6, 70.5, 69.9, 68.5, 67.5, and 61.8 (C-6,6′,6″, 5 Ph*C*H_2O, and octyl O*C*H_2), 55.8 (C-2′), 31.6, 29.2 (2 C), 29.0, 25.9, and 22.5 (6 octyl CH_2), 13.9 (octyl CH_3). Anal. Calcd for $C_{77}H_{89}NO_{21}$ (1364.57): C, 67.78; H, 6.57. Found: C, 67.66; H, 6.54.

Octyl (2,3,4,6-tetra-O-acetyl-α-L-altropyranosyl)-(1 → 4)-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 2)-3,4,6-tri-O-acetyl-α-D-mannopyranoside (**62**).—To a solution of **60** (57.0 mg, 41.8 μmol) in 1-butanol (8 mL), containing 3 Å molecular sieves (0.25 g) and stirred for 30 min under Ar, was added ethylenediamine (0.8 mL), and the mixture was heated overnight at 90 °C. TLC (8:1 CH_2Cl_2–MeOH) then showed the disappearance of

60 and the appearance of a new compound (R_f 0.35), and the mixture was filtered, concentrated, and co-concentrated with toluene. The residue was dissolved in pyridine (3 mL) and acetylated with Ac_2O (2 mL) for 16 h. After concentration, the residue was purified by column chromatography (2:1 toluene–EtOAc), affording **61**, isolated as a syrup (48.3 mg, 91%); $[\alpha]_D$ −8° (*c* 1); R_f 0.25 (2:1 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.692 (d, 1 H, $J_{2',NH}$ 6.7 Hz, NH), 2.169, 2.057, 1.990, 1.987, and 1.662 (5 s, each 3 H, 5 Ac). A solution of **61** (46.8 mg, 36.7 μmol) and HOAc (0.1 mL) in 1:1 EtOH–EtOAc (5 mL), containing 10% Pd–C (30 mg), was hydrogenolyzed at atmospheric pressure for 40 min, then filtered through Celite, concentrated, and co-concentrated with toluene. A solution of the residue in 1:1 pyridine–Ac_2O (6 mL) was stirred for 16 h, and concentrated. Column chromatography (1:5 toluene–EtOAc) of the residue afforded **62**, isolated as a colorless glass (35.1 mg, 92%); $[\alpha]_D$ −34° (*c* 1); R_f 0.29 (1:4 toluene–EtOAc); ^{1}H NMR ($CDCl_3$): δ 5.514 (d, 1 H, $J_{2',NH}$ 8.2 Hz, NH), 5.434 (dd, 1 H, $J_{2',3'}$ 8.8, $J_{3',4'}$ 10.5 Hz, H-3′), 5.232 (dd, 1 H, H-3″), 5.217 (dd, 1 H, $J_{4,5}$ 10.1 Hz, H-4), 5.132 (dd, 1 H, $J_{3'',4''}$ 3.4, $J_{4'',5''}$ 9.2 Hz, H-4″), 5.069 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.1 Hz, H-3), 4.853 (d, 1 H, $J_{1',2'}$ 8.2 Hz, H-1′), 4.803 (s, 1 H, H-1″), 4.743 (dd, 1 H, $J_{1'',2''}$ 1.2, $J_{2'',3''}$ 3.9 Hz, H-2″), 4.670 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 3.408 (dt, 1 H, octyl OC*H*H), 2.137, 2.109, 2.106, 2.086, 2.084, 2.079, 2.035, 2.006, 2.002, and 1.927 (10 s, each 3 H, 10 Ac), 0.869 (t, 3 H, octyl CH_3); ^{13}C: δ 99.0, 98.5, and 97.4 (C-1,1′,1″), 75.9, 74.4, 72.6, 72.5, 70.0, 69.7, 68.4, 66.8, 66.0, 65.8, and 64.4 (C-2,3,4,5,3′,4′,5′,2″,3″,4″,5″), 68.2, 62.7, 62.1, and 61.8 (C-6,6′,6″ and octyl OCH_2), 55.5 (C-2′), 31.6, 29.1 (2 C), 29.0, 25.9, and 22.4 (6 octyl CH_2), 23.1 ($NHCOCH_3$), 13.9 (octyl CH_3). FABMS: *m/z* 1036 $[M + H]^+$, 1058 $[M + Na]^+$.

*Octyl α-*L*-altropyranosyl-(1 → 4)-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1 → 2)-α-*D*-mannopyranoside* (**8**).—A solution of **62** (29.6 mg, 28.6 μmol) in 4:1 MeOH–CH_2Cl_2 (5 mL) was *O*-deacetylated with NaOMe (pH 8) for 2 h. Then, the mixture was neutralized with Dowex-50 (H^+), filtered, and concentrated. Gel permeation chromatography of the syrup on a Bio-Gel P-2 column (water) and subsequent lyophilization gave **8** as a white powder (17.7 mg, 94%); $[\alpha]_D$ −31° (*c* 0.7, MeOH); R_f 0.36 (solvent *A*); ^{1}H NMR (D_2O): see Table 1; ^{13}C (^{1}H-coupled): δ 101.5 (d, $J_{C-1'',H-1''}$ 168 Hz, C-1″), 99.9 (d, $J_{C-1',H-1'}$ 161 Hz, C-1′), 97.2 (d, $J_{C-1,H-1}$ 170 Hz, C-1). FABMS: *m/z* 658 $[M + H]^+$, 680 $[M + Na]^+$.

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