Synthesis of β-D-Gal*p*-(1→4)-β-D-Glc*p*NAc-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_7CH_3$ Mimics to Explore the Substrate Specificity of Sialyltransferases and *trans*-Sialidases

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Eleven trisaccharide octyl glycosides related to the N-glycan sequence β-D-Gal*p*-(1→4)-β-D-Glc*p*NAc-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_7CH_3$ (**1**) designed for detailed exploration of the acceptor specificity of α-2,3- and α-2,6-sialyltransferases as well as *trans*-sialidases, have been synthesised: β-D-Gal*p*-(1→4)-β-D-Glc*p*NPr-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_7CH_3$ (**2**), β-D-Fuc*p*-(1→4)-β-D-Glc*p*NR-(1→2)-α-D-Man*p*-(1→O)-$(CH_2)_7CH_3$ (**3**, R = Ac; **4**, R = Pr), 6-amino-6-deoxy-β-D-Gal*p*-(1→4)-β-D-Glc*p*NR-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_7CH_3$ (**5**, R = Ac; **6**, R = Pr), 2-deoxy-β-D-Gal*p*-(1→4)-β-D-Glc*p*NR-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_7CH_3$ (**7**, R = Ac; **8**, R = Pr), β-D-Gal*p*NR^1-(1→4)-β-D-Glc*p*NR-(1→2)-α-D-Man*p*-(1→O)-$(CH_2)_7CH_3$ (**9**, R = R^1 = Ac; **10**, R = R^1 = Pr; **11**, R = Ac, R^1 = Pr; **12**, R = Pr, R^1 = Ac). All trisaccharides were obtained by condensation of suitably modified glycosyl donors based on imidates or thioglycosides with the single disaccharide acceptor octyl (3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside, followed by deprotection. For the trisaccharides containing an *N*-acylated glucosamine as well as an *N*-acylated galactosamine unit, use was made of a combination of *N*-phthaloyl and *N*-dimethylmaleoyl protection.

Introduction

Sialic acids occur at the non-reducing termini of many glycoconjugates, and are considered to be key determinants in the regulation of a variety of biological processes.[1−3] In the biosynthesis of human and animal sialylated glycans at least 18 sialyltransferases are active with different substrate specificities.[2,4] Furthermore, several protozoal and bacterial sialidases have shown to act as *trans*-sialidases, transferring sialyl residues in α-2,3- or α-2,6-linkage from one glycan to the terminal galactose unit of another non-sialylated oligosaccharide or glycoconjugate.[2,5] One of the most abundant elements that is sialylated is the β-D-Gal*p*-(1→4)-β-D-Glc*p*NAc-(1→2)-α-D-Man*p*-(1→ sequence in glycoprotein N-glycans. A thorough analysis of the substrate specificity of sialyltransferases and *trans*-sialidases can be attained by using modified oligosaccharides, probing the contribution of individual hydroxy groups and the *N*-acetylated amino function in recognition and binding.

Initially, focusing on identifying key polar groups required for transfer of sialic acid from CPM-Neu5Ac by rat liver sialyltransferases, the acceptors β-D-Gal*p*-(1→3)-β-D-Glc*p*NAc and β-D-Gal*p*-(1→4)-β-D-Glc*p*NAc, using mimics, mainly deoxygenated forms of the pyranose rings, were studied.[6−8] It turned out that both the HO-6 group of the galactose residue and the *N*-acetyl group of the *N*-acetylglucosamine unit are required for the activity of α-2,6-sialyltransferase I (ST6Gal I). α-2,3-Sialyltransferase III (ST3Gal III) required the HO-3, HO-4, and HO-6 groups of the terminal galactose residue, and some influence from the subterminal *N*-acetylglucosamine was noticed.

Currently, we have studied sialyltransferases involved in the α-2,3- and α-2,6-sialylation of terminal galactose units in N-glycoprotein glycans. At first instance it was shown that rat liver ST6Gal I recognises, in addition to β-D-Gal*p*-(1→4)-β-D-Glc*p*NAc-(1→OMe) and β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*NAc-(1→OMe), also β-D-Man*p*-(1→4)-β-D-Glc*p*NAc-(1→OMe).[9] Then, the trisaccharide β-D-Gal*p*-(1→4)-β-D-Glc*p*NAc-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_7CH_3$ and eleven analogues containing structural variants of D-galactose were synthesised and employed as substrates for rat liver ST6Gal I, recombinant full length human liver ST6Gal I, and recombinant N-terminal truncated rat liver ST3Gal III.[10,11,12] Hydroxy groups at either C-3 or C-4 of the D-galactose residue were substituted by hydrogen (3- and 4-deoxy-β-D-Gal*p*-R) or fluorine (3- and 4-fluoro-β-D-Gal*p*-R), by amino (3-amino-β-D-Gal*p*-R) or *O*-methyl groups (3- and 4-*O*-methyl-β-D-Gal*p*-R), or were inverted (β-D-Gul*p*-R and β-D-Glc*p*-R), to determine their involvement in binding to and catalytic activity of the enzyme. In addition, trisaccharides containing α-L-Alt*p* (inverted

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hydroxymethyl group at C-5) or β-L-Gal*p* (enantiomer) at the non-reducing terminus were constructed as probes. The ST6Gal I tolerated most of the modifications at the D-galactose residue to some extent. The best substrates were the 4-deoxy and 4-fluoro analogues, followed by the 3-deoxy and 3-fluoro analogues. The ST3Gal III displayed a narrower specificity; only the 4-*O*-methyl analogue showed to be a relatively good substrate, and the 4-deoxy and 4-fluoro analogues show a minor activity.[13] Recently, it was demonstrated that also conformationally constrained oligosaccharides can act as acceptors for rat liver ST6Gal I.[14]

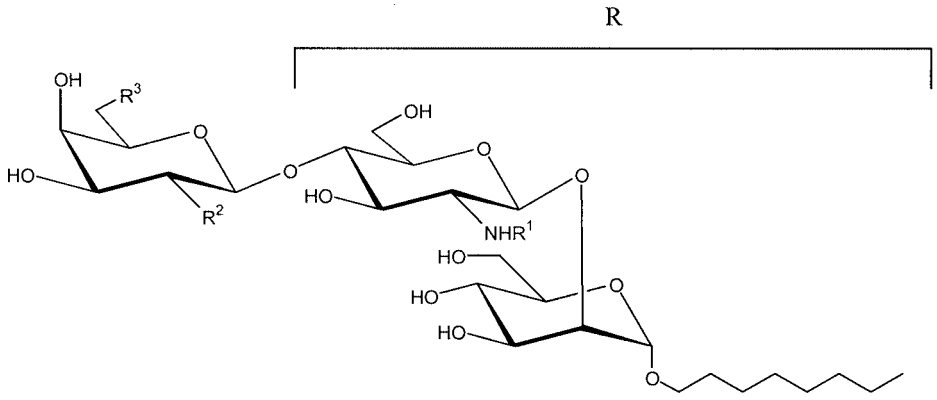
In the framework of ongoing studies focused on the understanding of the substrate specificity of sialyltransferases and *trans*-sialidases, we have synthesised an additional series of 11 trisaccharide octyl glycosides. The trisaccharides are of the type β-D-Sug*p*-(1→4)-β-D-Glc*p*NR-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_7CH_3$, with modifications at C-6 (Sug = 6-deoxy-Gal or 6-amino-6-deoxy-Gal) or at C-2 (Sug = 2-deoxy-Gal, GalNAc or GalNPr) of the D-galactose residue, in combination with *N*-acetylated or *N*-propionylated D-glucosamine [R = Ac or Pr (note that Pr = propionyl and not propyl throughout the paper)].

Results and Discussion

In the synthesis of the trisaccharide variants **1**−**12** (Scheme 1), all containing the element →4)-β-D-Glc*p*NR-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_7CH_3$ with R = Ac (*N*-acetyl) for **1**, **3**, **5**, **7**, **9**, and **11**, and R = Pr (*N*-propionyl) for **2**, **4**, **6**, **8**, **10**, and **12**, the key disaccharide acceptor was the earlier synthesised octyl (3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (**13**),[10] having a free HO-4′ function for elongation with suitably modified glycosyl residues. The final glycosyl residues incorporated were mimics of the native β-D-galactopyranosyl residue, i.e. a 6-deoxy-β-D-galactopyranosyl (β-D-fucopyranosyl; **3** and **4**), a 6-amino-6-deoxy-β-D-galactopyranosyl (**5** and **6**), a 2-deoxy-β-D-*lyxo*-hexopyranosyl (2-deoxy-β-D-galactopyranosyl; **7** and **8**), a 2-acetamido-2-deoxy-β-D-galactopyranosyl (**9** and **12**), and a 2-deoxy-2-propionamido-β-D-galactopyranosyl (**10** and **11**) residue.

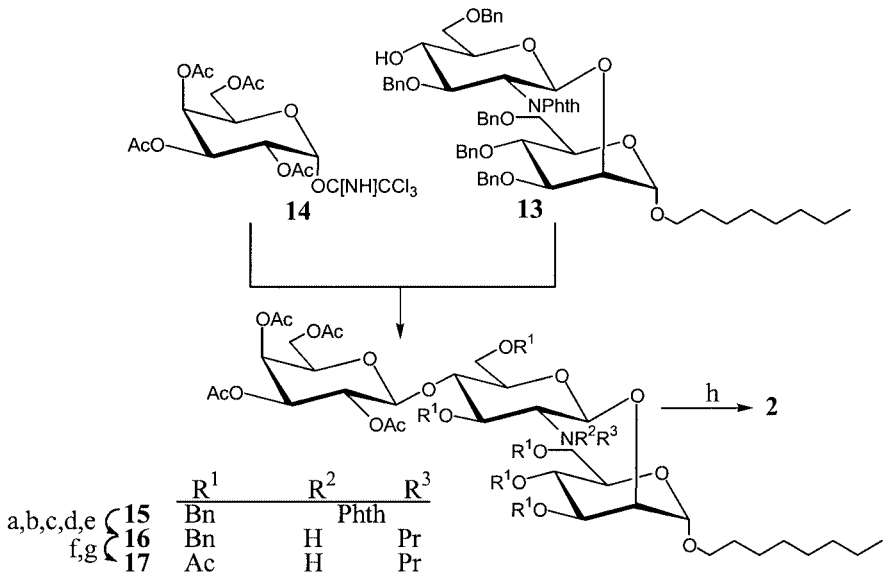
Compounds 1 and 2

Trisaccharide **1**, octyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (Scheme 1), was synthesised as described earlier, starting by coupling 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate (**14**)[15] with acceptor **13**, using trimethylsilyl trifluoromethanesulfonate as a catalyst, to yield trisaccharide derivative **15**[10] (Scheme 2). Along a similar route octyl β-D-galactopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**2**) (Scheme 1), the *N*-propionylated analogue of **1**, was prepared. To this end **15** was de-*O*-acetylated, then de-*N*-phthaloylated using 1,2-diaminoethane in 1-butanol at 90 °C[16] (Scheme 2), and *N*,*O*-propionylated using propi-



Code	Structure	R^1	R^2	R^3
1	β-D-Gal-R	Ac	OH	OH
2	β-D-Gal-R	Pr	OH	OH
3	6-deoxy-β-D-Gal-R	Ac	OH	H
4	6-deoxy-β-D-Gal-R	Pr	OH	H
5	6-amino-6-deoxy-β-D-Gal-R	Ac	OH	NH_2
6	6-amino-6-deoxy-β-D-Gal-R	Pr	OH	NH_2
7	2-deoxy-β-D-Gal-R	Ac	H	OH
8	2-deoxy-β-D-Gal-R	Pr	H	OH
9	2-acetamido-2-deoxy-β-D-Gal-R	Ac	NHAc	OH
10	2-deoxy-2-propionamido-β-D-Gal-R	Pr	NHPr	OH
11	2-deoxy-2-propionamido-β-D-Gal-R	Ac	NHPr	OH
12	2-acetamido-2-deoxy-β-D-Gal-R	Pr	NHAc	OH

Scheme 1. List of structures of synthesized trisaccharide octyl glycosides



Scheme 2. Synthesis of trisaccharide **2**: a) NaOMe (pH = 9), CH_2Cl_2, MeOH; b) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH, molecular sieves (3 Å); c) Pr_2O, pyridine; d) NaOMe (pH = 9), MeOH; e) Ac_2O, pyridine, 72% over five steps; f) 10% Pd/C, H_2C, HOAc, EtOH, EtOAc; g) Ac_2O, pyridine, 65% over two steps; h) NaOMe (pH = 9), CH_2Cl_2, MeOH, 94%

onic anhydride in pyridine. Subsequent de-*O*-propionylation and *O*-acetylation (acetic anhydride in pyridine) yielded **16** in an overall yield of 72%. Then, de-*O*-benzylation of **16** by hydrogenation using 10% Pd/C as a catalyst, followed by *O*-acetylation (→ **17**, 65%) and finally de-*O*-acetylation yielded **2** (94%). The last *O*-acetylation step was carried out to facilitate chromatographic purification. The ^1H and ^{13}C NMR spectroscopic data of **1** and **2** are presented in Tables 1 and 2, respectively.

Compounds 3 and 4

For the syntheses of the 6′′-deoxy mimics of **1** and **2**, octyl β-D-fucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**3**) and octyl β-D-fucopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**4**) (Scheme 1), respectively, ethyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-fucopyranoside (**19**) was used as a donor (Scheme 3). To this end D-fucose **18** was *O*-acetylated, after which the thioethyl function was introduced by reaction with ethanethiol in the presence of boron trifluoride−diethyl ether. Separation of the anomeric mixture by column chromatography yielded the β-anomer **19** in a yield of 61%, whereas the α-anomer was isolated in a yield of 36%. Donor **19** was coupled with **13** by in situ activation of the donor with bromine/silver trifluoromethanesulfonate, yielding trisaccharide derivative **20** (74%) (Scheme 3). It should be noted that fucosylation using 2,3,4-tri-*O*-acetyl-D-fucopyranosyl trichloroacetimidate was not successful (data not shown). De-*N*-phthaloylation/de-*O*-acetylation of **20**, followed by *N*,*O*-acetylation (→ **21**, 85%), de-*O*-benzylation, and *O*-acetylation yielded **22** (72%). Finally, de-*O*-acetylation of **22** afforded **3** (61%). In a similar way, de-*N*-phthaloylation/de-*O*-acetylation of **20**, followed by *N*,*O*-propionylation (→ **23**, 87%), de-*O*-benzylation, de-*O*-propionylation, and *O*-acetylation (→ **24**, 55%), and de-*O*-acetylation yielded **4** (93%) (Scheme 4). The last *O*-acetylation step was carried out to facilitate chromatographic purification. The ^1H and ^{13}C NMR spectroscopic data of **3** and **4** are presented in Tables 1 and 2, respectively.

Compounds 5 and 6

For the syntheses of the 6′′-amino-6′′-deoxy mimics of **1** and **2**, octyl 6-amino-6-deoxy-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**5**) and octyl 6-amino-6-deoxy-β-D-galactopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**6**) (Scheme 1), respectively, the galactosyl imidate donor **30** with an azide function at C-6 was applied (Scheme 5). This donor was synthesised starting from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**25**). Treatment of **25** with *p*-toluenesulfonyl chloride in pyridine (→ **26**, 92%) and subsequent displacement of the tosyl group by an azide group using sodium azide in dimethyl sulfoxide yielded **27** (99%). The introduction of the azide group in **27** was verified by IR spectroscopy [$\tilde{\nu}$ = 2110 cm^{-1}]. Then, **27** was de-*O*-isopropylidenated using aqueous trifluoroacetic acid and *O*-acetylated (→ **28**, 50%), followed by selective de-*O*-acetylation at C-1 using hydrazinium acetate in dimethylformamide (→ **29**, 89%), and imidation with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene, to yield **30** (63%). Donor **30** was coupled with **13**, using trimethylsilyl trifluoromethanesulfonate as a catalyst, affording trisaccharide derivative **31** (61%) (Scheme 6). De-*N*-phthaloylation/de-*O*-acetylation and *N*,*O*-acetylation of **31** (→ **32**, 99%), followed by de-*O*-acetylation (→ **33**, 70%) and reduction with hydrogen in the presence of 10% Pd/C of the

Table 1. 500 MHz ^{1}H NMR chemical shifts of the carbohydrate residues in the compounds **1**−**12**

Residue[a]	Reporter group	**1**	**2**	**3**	**4**
Man	H-1	4.858 (1.4)	4.849 (1.5)	4.860 (1.6)	4.808
	H-2	4.038 (3.2)	4.048 (3.5)	4.041 (3.3)	4.006
	H-3	3.80	3.79	3.79	3.79
	H-4	3.53	3.50	3.51	3.51
	H-5	3.60	3.59	3.58	3.51
	H-6a[b]	3.63	3.62	3.63	3.68
	H-6b[b]	3.89	3.88	3.88	3.79
GlcNHR[c]	H-1	4.583 (7.0)	4.597 (7.6)	4.583 (7.6)	4.609 (7.6)
	H-2	3.75	3.75	3.75	3.79
	H-3	3.73	3.74	3.72	3.75
	H-4	3.76	3.76	3.71	3.68
	H-5	3.56	3.57	3.58	3.58
	H-6a	3.98	3.98	3.97	3.96
	H-6b	3.84	3.84	3.82	3.84
	CH_2	–	2.323	–	2.324
	CH_3	2.052	1.138	2.052	1.142
Gal	H-1	4.470 (7.7)	4.470 (7.7)	4.423 (7.9)	4.429 (7.8)
	H-2	3.55	3.55	3.51	3.51
	H-3	3.67	3.66	3.66	3.67
	H-4	3.93 (3.2[d])	3.92 (3.3[d])	3.75	3.76
	H-5	3.74	3.74	3.84	3.84
	H-6a	3.75	3.75	1.252 (6.4[e])	1.257 (6.5[e])
	H-6b	3.75	3.75	–	–
Spacer	OC*H*H	3.53	3.52	3.53	3.48
	OCH*H*	3.74	3.79	3.72	3.69
	CH_3	0.872	0.861	0.861	0.868
Residue	Reporter group	**5**	**6**	**7**	**8**
Man	H-1	4.855	4.845	4.854 (1.5)	4.820
	H-2	4.032	4.043	4.033 (3.3)	4.018
	H-3	3.80	3.81	3.78	3.78
	H-4	3.55	3.51	3.51	3.57
	H-5	3.56	3.59	3.58	3.54
	H-6a[b]	3.65	3.62	3.63	3.65
	H-6b[b]	3.86	3.87	3.87	3.82
GlcNHR[c]	H-1	4.585 (7.8)	4.596 (8.1)	4.569 (8.1)	4.589 (7.8)
	H-2	3.75	3.77	3.75	3.75
	H-3	3.74	3.73	3.72	3.72
	H-4	3.78	3.78	3.76	3.75
	H-5	3.55	3.55	3.51	3.51
	H-6a	3.99	3.99	3.77[b]	3.77[b]
	H-6b	3.86	3.85	3.89[b]	3.88[b]
	CH_2	–	2.327	–	2.325
	CH_3	2.057	1.139	2.051	1.140
Gal	H-1	4.501 (7.6)	4.497 (7.7)	4.715	4.719
	$H\text{-}2_{ax}$	3.55	3.53	1.69	1.70
	$H\text{-}2_{eq}$	–	–	2.08	2.08
	H-3	3.68	3.69	3.89	3.90
	H-4	3.93	3.93	3.77	3.77
	H-5	3.84	3.81	3.61	3.61
	H-6a	3.23	3.22	3.77	3.77
	H-6b	3.15	3.15	3.77	3.77
Spacer	OC*H*H	3.51	3.51	3.51	3.50
	OCH*H*	3.75	3.71	3.73	3.71
	CH_3	0.865	0.861	0.865	0.867
Residue	Reporter group	**9**	**10**	**11**	**12**
Man	H-1	4.852	4.840	4.846	4.837
	H-2	4.026	4.027	4.008	4.027
	H-3	3.79	3.78	3.79	3.79
	H-4	3.50	3.51	3.55	3.50
	H-5	3.58	3.59	3.56	3.57
	H-6a[b]	3.62	3.61	3.64	3.60
	H-6b[b]	3.88	3.87	3.85	3.86
GlcNHR^1 [f]	H-1	4.558 (7.9)	4.565 (7.9)	4.551 (8.0)	4.571 (7.5)
	H-2	3.73	3.73	3.71	3.73
	H-3	3.72	3.74	3.75	3.74
	H-4	3.63	3.64	3.68	3.64
	H-5	3.47	3.48	3.46	3.48
	H-6a[b]	3.66	3.67	3.68	3.66
	H-6b[b]	3.84	3.85	3.84	3.84
	CH_2	–	2.32	–	2.32
	CH_3	2.045	1.133	2.047	1.133
GalNHR^2[f]	H-1	4.516 (8.4)	4.517 (8.4)	4.523 (8.4)	4.519 (8.3)
	H-2	3.94	3.94	3.95	3.92
	H-3	3.78	3.75	3.75	3.76
	H-4	3.93	3.93	3.94	3.94
	H-5	3.72	3.73	3.75	3.73
	H-6a	3.78	3.78	3.78	3.81
	H-6b	3.78	3.78	3.78	3.81
	CH_2	–	2.32	2.33	–
	CH_3	2.067	1.133	1.133	2.068
Spacer	OC*H*H	3.53	3.55	3.50	3.51
	OCH*H*	3.73	3.75	3.71	3.73
	CH_3	0.861	0.860	0.866	0.861

[a] Data were measured in D_2O at 300 K. Chemical shifts are relative to internal acetone (δ = 2.225 ppm). Coupling constants are given in Hertz between parentheses. [b] The assignment of H-6a and H-6b may have to be interchanged within one residue. [c] R = acetyl for odd numbers and propionyl for even numbers. [d] $J_{3'',4''}$ in **1** and **2**. [e] H-6,6,6 signal and $J_{5'',6''}$ for D-fucose in **3** and **4**. [f] R^1 = acetyl for **9** and **11**, and propionyl for **10** and **12**. R^2 = acetyl for **9** and **12**, and propionyl for **10** and **11**.

Table 2. 125 MHz ^{13}C NMR chemical shifts of the carbohydrate residues in the compounds **1**−**12**

Residue[a]	Reporter group	**1**	**2**	**3**	**4**
Man	C-1	97.5	97.5	97.4	98.0
	C-2	77.3	77.4	77.3	78.3
	C-3	70.4	70.4	70.4	70.6
	C-4	67.8	68.0	67.9	67.5
	C-5	73.4	73.5	73.5	73.5
	C-6	62.0	62.1	62.1	61.8
GlcNHR[b]	C-1	100.1	100.2	100.1	100.8
	C-2	55.6	55.5	55.5	55.6
	C-3	72.5	72.7	72.6	72.5
	C-4	79.2	79.3	79.8	79.8
	C-5	75.3	75.4	75.3	75.2
	C-6	60.6	60.7	60.6	60.7
	CO	175.2	179.0	175.2	178.5
	CH_2	−	30.0	−	29.9
	CH_3	22.9	9.9	22.9	9.9
Gal	C-1	103.5	103.6	103.6	103.6
	C-2	71.5	71.6	71.3	71.3
	C-3	73.1	73.2	73.3	73.4
	C-4	69.1	69.2	71.8	71.8
	C-5	75.9	76.0	71.7	71.7
	C-6	61.6	61.6	15.9	16.0
Spacer	OCH_2	68.7	68.7	68.7	68.5
	CH_2	31.7	31.7	31.7	32.1
	CH_2	29.2	29.1	29.1	29.6
	CH_2	29.1	29.0	29.0	29.5
	CH_2	29.0	28.9	28.9	29.4
	CH_2	26.0	26.0	26.0	26.3
	CH_2	22.6	22.6	22.6	22.9
	CH_3	14.0	14.0	14.0	14.2
Residue	Reporter group	**5**	**6**	**7**	**8**
Man	C-1	97.5	97.6	97.5	97.8
	C-2	77.5	77.7	77.3	77.9
	C-3	70.4	70.4	70.4	70.5
	C-4	67.8	67.9	67.8	67.6
	C-5	73.5	73.5	73.5	73.5
	C-6	62.0	62.0	62.1	62.0
GlcNHR[b]	C-1	100.2	100.4	100.2	100.6
	C-2	55.8	55.7	55.6	55.7
	C-3	72.5	72.5	72.6	72.6
	C-4	77.5	77.6	79.1	79.1
	C-5	75.5	75.5	75.3	75.3
	C-6	60.4	60.4	60.7	60.8
	CO	175.3	179.0	175.2	178.7
	CH_2	−	29.9	−	29.9
	CH_3	23.0	9.9	23.0	9.9
Gal	C-1	103.1	103.1	101.1	101.1
	C-2	71.5	71.5	34.1	34.2
	C-3	73.0	73.0	68.3	68.3
	C-4	69.7	69.8	67.3	67.3
	C-5	72.7	72.9	76.2	76.2
	C-6	41.1	41.1	62.0	61.9
Spacer	OCH_2	68.7	68.7	68.7	68.5
	CH_2	31.8	31.7	31.8	31.9
	CH_2	29.3	29.1	29.2	29.4
	CH_2	29.2	29.1	29.2	29.4
	CH_2	29.0	29.0	29.0	29.2
	CH_2	26.1	26.0	26.1	26.2
	CH_2	22.6	22.6	22.6	22.8
	CH_3	14.0	14.0	14.0	14.1

Table 2. *(Continued)*

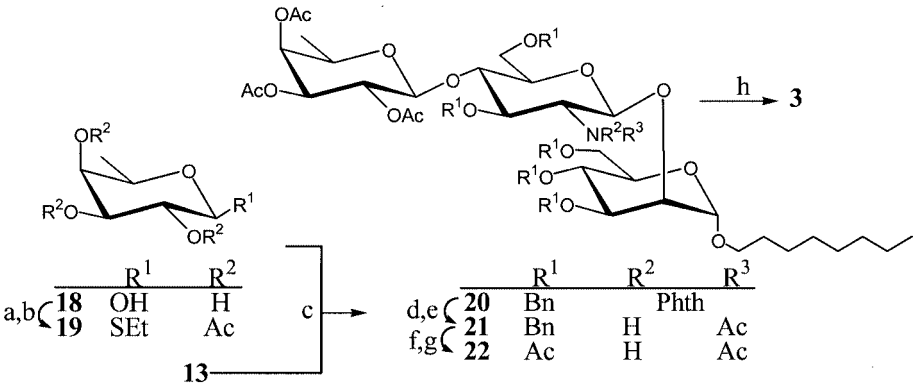
Residue	Reporter group	**9**	**10**	**11**	**12**
Man	C-1	97.4	97.4	97.4	97.5
	C-2	77.3	77.3	77.3	77.4
	C-3	70.4	70.4	70.4	70.4
	C-4	67.9	67.9	67.7	67.9
	C-5	73.5	73.5	73.5	73.5
	C-6	62.1	62.1	62.0	62.0
GlcNHR1 [c]	C-1	100.1	100.1	100.1	100.2
	C-2	55.4	55.2	55.4	55.3
	C-3	72.7	72.8	72.6	72.8
	C-4	79.9	79.6	79.5	79.9
	C-5	75.1	75.2	75.2	75.1
	C-6	60.7	60.8	60.7	60.7
	CO	175.2	179.0	175.2	179.0
	CH_2	−	30.0	−	29.9
	CH_3	23.0	9.9	23.0	9.9
GalNHR2[c]	C-1	102.4	102.2	102.3	102.4
	C-2	53.2	53.0	53.0	53.2
	C-3	71.3	71.3	71.3	71.3
	C-4	68.2	68.3	68.3	68.2
	C-5	75.9	75.9	75.9	75.9
	C-6	61.5	61.6	61.6	61.5
	CO	175.2	179.1	178.9	175.3
	CH_2	−	30.0	29.9	−
	CH_3	22.8	9.9	9.9	22.8
Spacer	OCH_2	68.7	68.7	68.6	68.7
	CH_2	31.7	31.7	31.9	31.7
	CH_2	29.1	29.1	29.4	29.1
	CH_2	29.1	29.0	29.3	29.1
	CH_2	29.0	28.9	29.2	29.0
	CH_2	26.0	26.0	26.2	26.0
	CH_2	22.6	22.6	22.7	22.6
	CH_3	14.0	14.0	14.1	14.0

[a] Data measured in D_2O at 300 K. Chemical shifts are relative to internal acetone (δ_{CH3} = 30.89 ppm). [b] R = acetyl for odd numbers and propionyl for even numbers. [c] R^1 = acetyl for **9** and **11**, and propionyl for **10** and **12**. R^2 = acetyl for **9** and **12**, and propionyl for **10** and **11**.

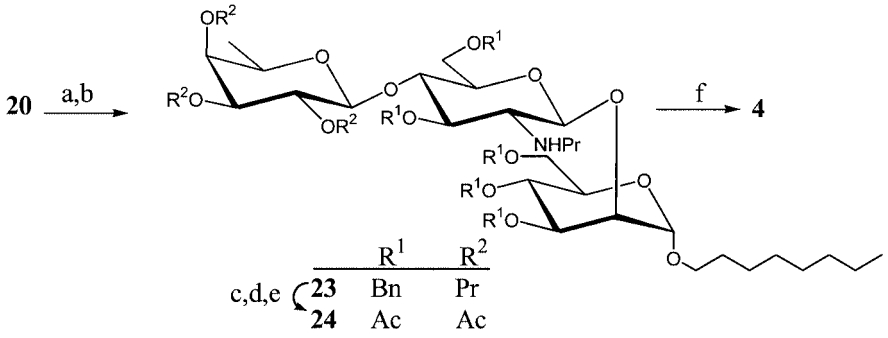
azido function (pH = 10, ammonia; conversion into amino) and of the *O*-benzyl groups (pH ≈ 5, acetic acid; conversion into hydroxy), yielded **5** (99%). In a similar way, de-*N*-phthaloylation/de-*O*-acetylation and *N*,*O*-propionylation of **31** (→ **34**, 94%), followed by de-*O*-propionylation (→ **35**, 79%), and conversion of the azido function into an amino group combined with the removal of the *O*-benzyl groups, yielded **6** (48%) (Scheme 7). The ^1H and ^{13}C NMR spectroscopic data of **5** and **6** are presented in Tables 1 and 2, respectively.

Compounds 7 and 8

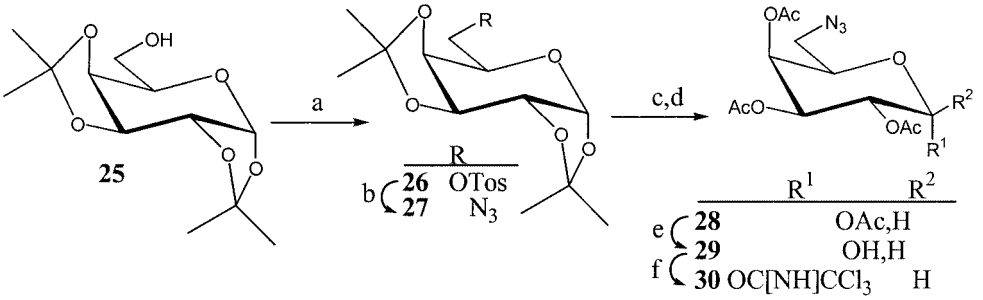
For the syntheses of the 2′′-deoxy mimics of **1** and **2**, octyl 2-deoxy-β-D-*lyxo*-hexopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**7**) and octyl 2-deoxy-β-D-*lyxo*-hexopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**8**) (Scheme 1), respectively, use was made of



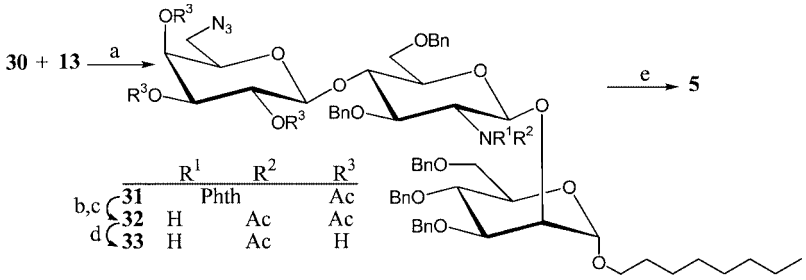
Scheme 3. Synthesis of trisaccharide **3**: a) Ac_2O, pyridine; b) 4 equiv. $BF_3{\cdot}Et_2O$, 1.2 equiv. EtSH, 0 °C, CH_2Cl_2, molecular sieves (4 Å), 61% over two steps; c) 3.5 equiv. AgOTf, 1.1 equiv. Br_2, CH_2Cl_2, toluene, molecular sieves (4 Å), 74%; d) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH, molecular sieves (3 Å); e) Ac_2O, pyridine, 85% over two steps; f) 10% Pd/C, H_2, HOAc, EtOH, EtOAc; g) Ac_2O, pyridine, 72% over two steps; h) NaOMe (pH = 9), CH_2Cl_2, MeOH, 61%



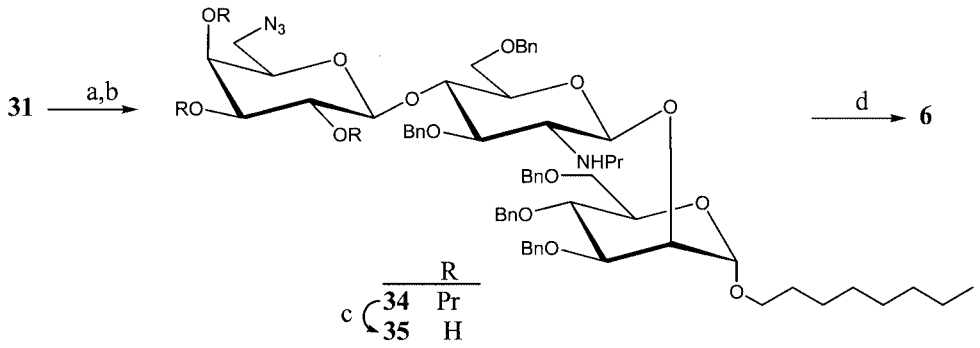
Scheme 4. Synthesis of trisaccharide **4**: a) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH, molecular sieves (3 Å); b) Pr_2O, pyridine, 87% over two steps; c) 10% Pd/C, H_2, HOAc, EtOH, EtOAc; d) NaOMe (pH = 9), MeOH; e) Ac_2O, pyridine, 55% over three steps; f) NaOMe (pH = 9), MeOH, 93%



Scheme 5. Synthesis of 6-azido galactose donor **30**: a) *p*-TosCl, CH_2Cl_2, pyridine, 92%; b) NaN_3, Me_2SO, 160 °C, 99%; c) TFA, H_2O, CH_2Cl_2; d) Ac_2O, pyridine, 50% over two steps; e) hydrazinium acetate, DMF, 50 °C, 89%; f) Cl_3CCN, DBU, 0 °C, CH_2Cl_2, 63%

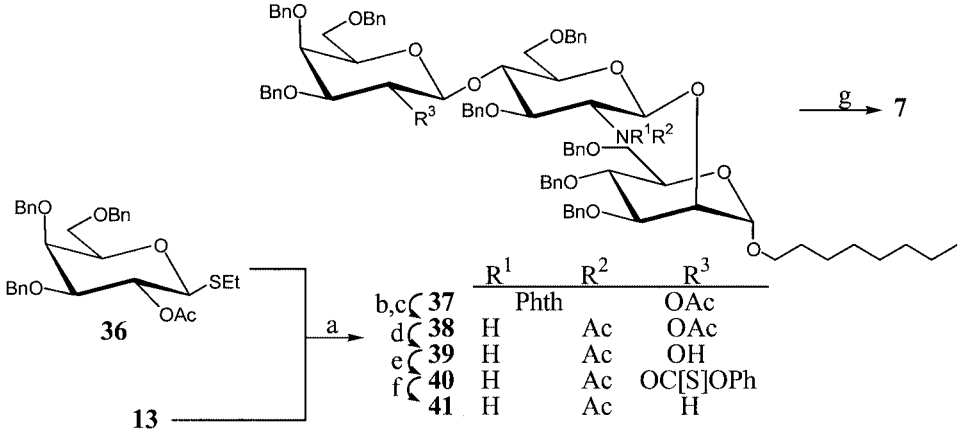


Scheme 6. Synthesis of trisaccharide **5**: a) 17% TMSOTf, CH_2Cl_2, 0 °C, molecular sieves (4 Å), 61%; b) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH, molecular sieves (3 Å); c) Ac_2O, pyridine, 99% over two steps; d) NaOMe (pH = 9), MeOH, 70%; e) 10% Pd/C, H_2, NH_3, 2-PrOH, H_2O, HOAc, 99%

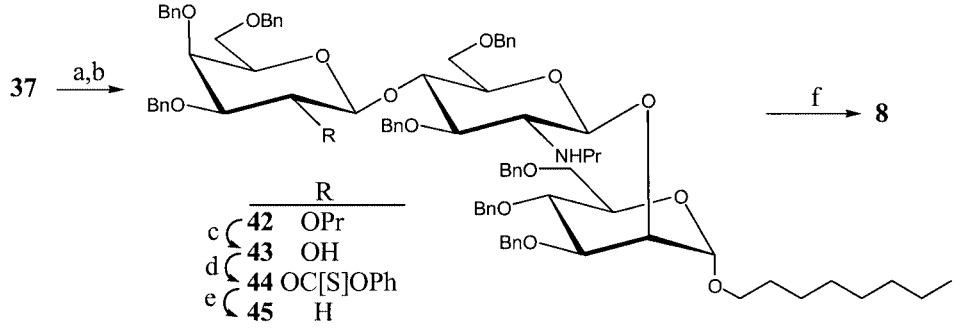


Scheme 7. Synthesis of trisaccharide **6**: a) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH, molecular sieves (3 Å); b) Pr_2O, pyridine, 94% over two steps; c) NaOMe (pH = 9), MeOH, 79%; d) 10% Pd/C, H_2, NH_3, 2-PrOH, H_2O, HOAc, 48%

ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (**36**).[17] Coupling of **36** with **13**, using *N*-iodosuccinimide/trifluoromethanesulfonic acid as the catalytic system, yielded trisaccharide derivative **37** (70%) (Scheme 8). De-*N*-phthaloylation/de-*O*-acetylation and *N*,*O*-acetylation of **37** (→ **38**, 94%), followed by de-*O*-acetylation (→ **39**) and treatment with phenyl chlorothionocarbonate in 4-dimethylaminopyridine/acetonitrile,[18] yielded **40** (61%). 2′′-Deoxygenation of **40** with tributylstannane in the presence of catalytic amounts of α,α′-azoisobutyronitrile (AIBN) at 100 °C[18] afforded **41** (70%), which was catalytically de-*O*-benzylated to give **7** (75%). In a similar way, de-*N*-phthaloylation/de-*O*-acetylation and *N*,*O*-propionylation of **37** (→ **42**, 94%), followed by de-*O*-propionylation (→ **43**), *O*-phenoxythiocarbonylation at C-2′′ (→ **44**, 43%), 2′′-deoxygenation (→ **45**, 62%), and de-*O*-benzylation yielded **8** (57%) (Scheme 9). The ^1H and ^{13}C NMR spectroscopic data of **7** and **8** are presented in Tables 1 and 2, respectively.



Scheme 8. Synthesis of trisaccharide **7**: a) 1.4 equiv. NIS, 20% TfOH, CH_2Cl_2, 0 °C, molecular sieves (4 Å), 70%; b) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH, molecular sieves (3 Å); c) Ac_2O, pyridine, 94% over two steps; d) NaOMe (pH = 10), CH_2Cl_2, MeOH, 40 °C; e) $C_6H_5OC[S]Cl$, DMAP, CH_3CN, 100 °C, 61% over two steps; f) Bu_3SnH, AIBN, 100 °C, toluene, 70%; g) 10% Pd/C, H_2, HOAc, EtOH, EtOAc, 75%



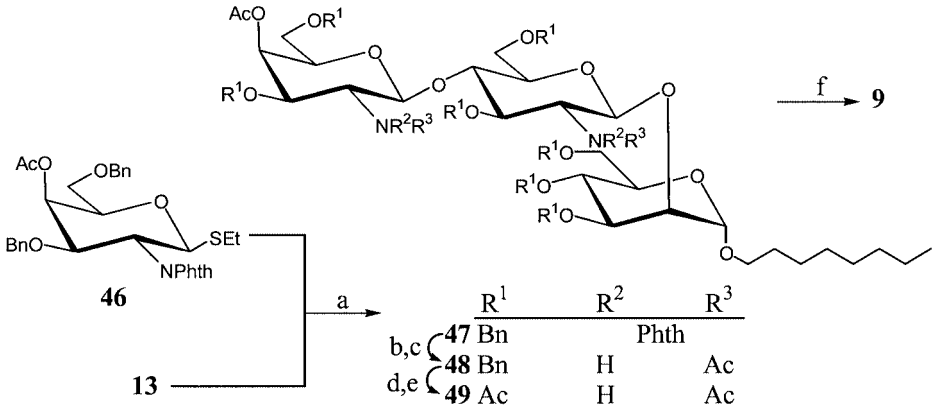
Scheme 9. Synthesis of trisaccharide **8**: a) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH, molecular sieves (3 Å); b) Pr_2O, pyridine, 94% over two steps; c) NaOMe (pH = 10), CH_2Cl_2, MeOH, 40 °C; d) $C_6H_5OC[S]Cl$, DMAP, CH_3CN, 100 °C, 43% over two steps; e) Bu_3SnH, AIBN, 100 °C, toluene, 62%; f) 10% Pd/C, H_2, HOAc, EtOH, EtOAc, 57%

Compounds 9 and 10

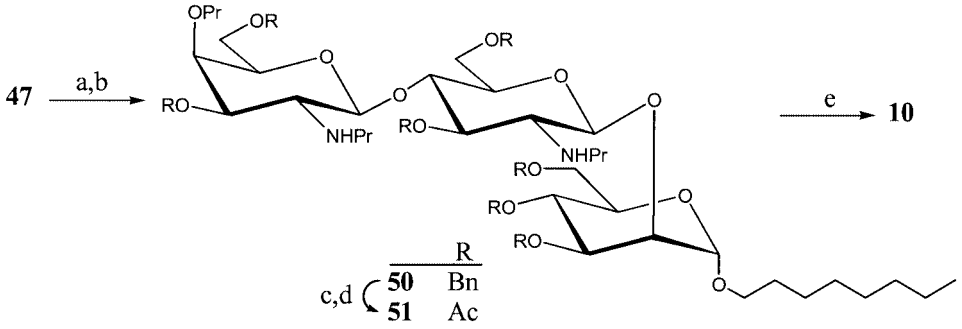
For the syntheses of the 2′′-acylamido-2′′-deoxy mimics of **1** and **2**, octyl 2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**9**) and octyl 2-deoxy-2-propionamido-β-D-galactopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**10**) (Scheme 1), respectively, the earlier reported donor ethyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (**46**)[19] was used. This fragment was synthesised from a known glucosamine building block,[20] which was applied in the synthesis of disaccharide **13**.[10,11] Compound **46** was coupled to acceptor **13**, using bromine/silver trifluoromethanesulfonate as the catalytic system, to yield trisaccharide derivative **47** (51%) (Scheme 10). De-*N*-phthaloylation/de-*O*-acetylation and *N*,*O*-acetylation of **47** (→ **48**, 61%), followed by de-*O*-benzylation and *O*-acetylation (→ **49**, 86%), and final de-*O*-acetylation yielded **9** (56%). In a similar way, de-*N*-phthaloylation/de-*O*-acetylation and *N*,*O*-propionylation of **47** (→ **50**, 80%), followed by de-*O*-benzylation and *O*-acetylation (→ **51**, 92%), and final de-*O*-acylation yielded **10** (91%) (Scheme 11). It should been noted that two analogues of **9**, β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*NAc-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_8COOCH_3$[21] and β-D-Gal*p*NAc-(1→4)-β-D-Glc*p*NAc-(1→2)-α-D-Man*p*-(1→O)$(CH_2)_2$-CH_3,[22] have been synthesised earlier along similar routes. The ^1H and ^{13}C NMR spectroscopic data of **9** and **10** are presented in Tables 1 and 2, respectively.

Compounds 11 and 12

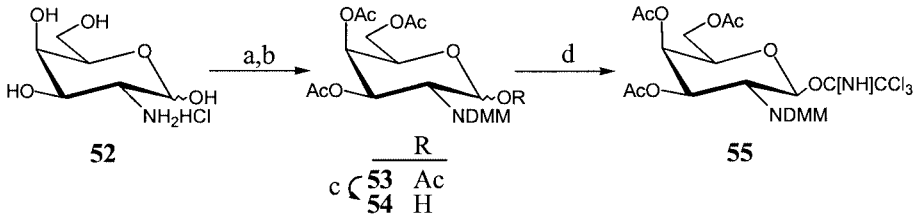
The syntheses of the 2′′-acylamido-2′′-deoxy mimics of **1** and **2**, octyl 2-deoxy-2-propionamido-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**11**) and octyl 2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (**12**) (Scheme 1), respectively, required in addition to the phthalimido function for the glucosamine unit in acceptor **13**, the selection of another *N*-protective group for the galactosamine donor. Introductory experiments with donors containing an *N*-acetyl or an *N*-(tetrachlorophthalimido)[23,24] protective group gave rise to irreproducible results only. Testing of the promising *N*-(2,2,2-trichloroethoxycarbonyl) protective group[25–27] in terms of yields, showed problems in the deprotection using activated zinc;[28] here also primary *O*-benzyl groups were removed, leading to mixtures that could not be fractionated. The *N*-(dimethylmaleoyl) protective group[29,30] turned out to be the best choice. According to the earlier reported route for D-glucosamine hydrochloride,[29,30] D-galactosamine hydrochloride (**52**) was neutralised with sodium methoxide in methanol, then *N*-acylated



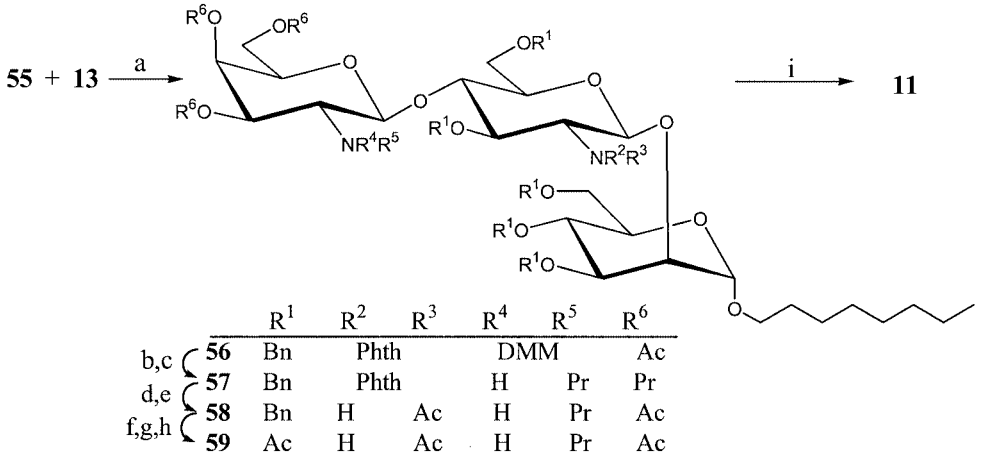
Scheme 10. Synthesis of trisaccharide **9**: a) 0.5 equiv. Br_2, 1.2 equiv. AgOTf, CH_2Cl_2, toluene, molecular sieves (4 Å), 51%; b) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH, molecular sieves (3 Å); c) Ac_2O, pyridine, 61% over two steps; d) 10% Pd/C, H_2, HOAc, EtOH, EtOAc; e) Ac_2O, pyridine, 86% over two steps; f) NaOMe (pH = 10), MeOH, 56%



Scheme 11. Synthesis of trisaccharide **10**: a) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH, molecular sieves (3 Å); b) Pr_2O, pyridine, 80% over two steps; c) 10% Pd/C, H_2, HOAc, EtOH, EtOAc; d) Ac_2O, pyridine, 92% over two steps; e) NaOMe (pH = 10), MeOH, 91%

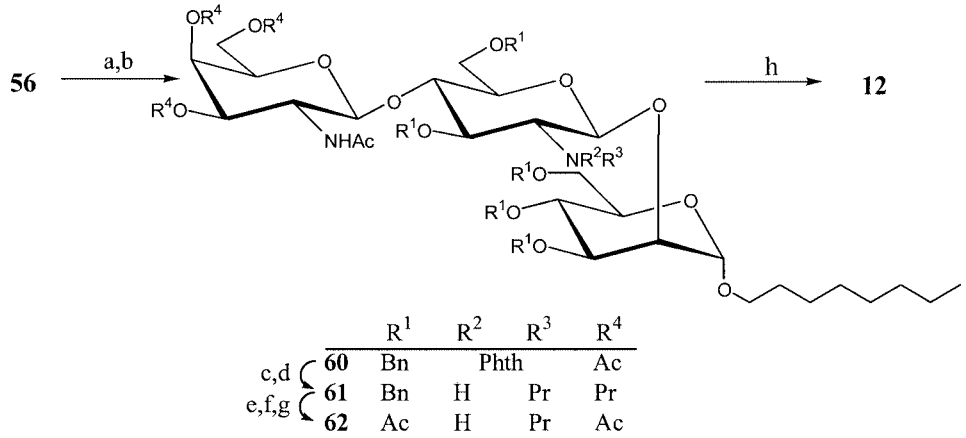


Scheme 12. Synthesis of galactose donor **55**: a) 1 equiv. NaOMe, DMMA, NEt_3, 60 °C, MeOH; b) Ac_2O, pyridine, 31% over two steps; c) hydrazinium acetate, DMF, 61%; d) CCl_3CN, DBU, CH_2Cl_2, 59%



Scheme 13. Synthesis of trisaccharide **11**: a) 10% TMSOTf, 0 °C, CH_2Cl_2, molecular sieves (4 Å), 84%; b) NaOH, HCl, dioxane, H_2O; c) Pr_2O, pyridine, 33% over two steps; d) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH; e) Ac_2O, pyridine, 74% over two steps; f) NaOMe (pH = 9), CH_2Cl_2, MeOH; g) 10% Pd/C, H_2, HOAc, EtOH, EtOAc; h) Ac_2O, pyridine, 72% over three steps; i) NaOMe (pH = 10), CH_2Cl_2, MeOH, 77%

with dimethylmaleic anhydride in the presence of triethylamine at 60 °C, and *O*-acetylated to give **53** (31%) (Scheme 12). Subsequent de-*O*-acetylation at C-1 using hydrazinium acetate in dimethylformamide (→ **54**, 61%) and imidation with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene, yielded donor **55** (59%). Coupling of **55** [*N*-(dimethylmaleoyl) function] with **13** (*N*-phthaloyl group), using trimethylsilyl trifluoromethanesulfonate as a catalyst, afforded trisaccharide derivative **56** (84%) (Scheme 13). De-*N*-(dimethylmaleoyl)ation and de-*O*-acetylation of **56** by sequential incubation with sodium hydroxide in aqueous dioxane (alkaline pH), and, after acidification with HCl at pH = 3,[29,30] followed by *N*,*O*-propionylation yielded **57** (33%). De-*N*-phthaloylation/de-*O*-propionylation and *N*,*O*-acetylation of **57** (→ **58**, 74%), followed by de-*O*-acetylation, de-*O*-benzylation, and *O*-acetylation (→ **59**, 72%), and final de-*O*-acetylation yielded **11** (77%). The last *O*-acetylation step was carried out to facilitate chromatographic purification. In a similar way, de-*N*-(dimethylmaleoyl)ation/de-*O*-acetylation and *N*,*O*-acety-



Scheme 14. Synthesis of trisaccharide **12**: a) NaOH, HCl, AcCl, dioxane, H_2O; b) Ac_2O, pyridine, 48% over two steps; c) $NH_2CH_2CH_2NH_2$, 90 °C, 1-BuOH; d) Pr_2O, pyridine, 80% over two steps; e) NaOMe (pH = 9), CH_2Cl_2, MeOH; f) 10% Pd/C, H_2, HOAc, EtOH, EtOAc; g) Ac_2O, pyridine, 67% over three steps; h) NaOMe (pH = 9), CH_2Cl_2, MeOH, 84%

lation of **56** (→ **60**, 48%) (Scheme 14), followed by de-*N*-phthaloylation/de-*O*-acetylation and *N*,*O*-propionylation (→ **61**, 80%), and de-*O*-propionylation, de-*O*-benzylation, and *O*-acetylation (→ **62**, 67%), and final de-*O*-acetylation yielded **12** (84%). The ^{1}H and ^{13}C NMR spectroscopic data of **11** and **12** are presented in Tables 1 and 2, respectively. The NMR spectra of **11** and **12** are almost identical, except for the *N*-acetyl methyl signal in the ^{1}H NMR spectra. The NAc signal in **11** resonates at δ = 2.047 ppm, and in **12** at δ = 2.068 ppm. Note that in **9** the two NAc signals resonate at δ = 2.045 and 2.067 ppm.

Conclusion

Summarising, to prepare a series of relevant trisaccharide mimics for enzymatic sialyl-transfer studies, the strategy of condensing a series of galactosyl-modified monosaccharide donors with a general glucosaminyl-mannosyl acceptor has proven to be successful. In earlier work, we have shown that such an approach leads to better results than preparing disaccharide donors by introducing modifications at the galactosyl-glucosaminyl level, followed by coupling to a fixed mannosyl acceptor.[12] In the present approach, monosaccharide thioglycosides were used for coupling of synthons containing besides acyl groups also benzyl groups or a deoxy function (**19**, **36**, **46**), and trichloroacetimidates for coupling of acylated deactivated synthons (**14**, **30**, **55**). For the activation of the thioglycosides, bromine/silver trifluoromethanesulfonate gave the best results for **19** and **46**, whereby **19** needed more activation than **46**, and *N*-iodosuccinimide/trifluoromethanesulfonic acid for **36**. TMSOTf gave always the best results in trichloroacetimidate couplings.

The trisaccharides **1**−**12** will be used in α-2,3- and α-2,6-sialyltransferase as well as in *trans*-sialidase kinetic studies in order to investigate the relevance in the substrate/enzyme interaction of the replaced hydroxy functions in the terminal galactose unit of **1** in combination with the effect of replacing the *N*-acetyl function of the middle glucosamine unit by an *N*-propionyl function.

Experimental Section

General: All solvents used were distilled from appropriate drying agents. In the workup procedures of reaction mixtures, organic solutions were washed with appropriate amounts of aqueous solutions as indicated. Solutions were concentrated under reduced pressure at 40 °C (water bath). Reactions were monitored by TLC on Silica Gel 60 F_{254} (Merck), compounds were visualized under UV light, and by charring with either 10% ethanolic H_2SO_4 or 0.2% orcinol in 20% methanolic H_2SO_4. Column chromatography was performed on Kieselgel 60 F_{254} (Merck, 0.063−0.200 mm). Size-exclusion chromatography was carried out on Sephadex LH-20 or Bio-Gel P-2. ^{1}H (300 MHz) and ^{13}C NMR spectra (75.5 MHz) of protected compounds were recorded at 300 K using a Bruker AC 300 spectrometer; only relevant NMR spectroscopic data are included in the experimental procedures. Two-dimensional ^{1}H-^{1}H correlated spectra (TOCSY, ROESY) and ^{1}H-^{13}C correlated spectra (HSQC) of compounds **1**−**12**, **59** and **62** were recorded at 300 K using a Bruker AMX 500 spectrometer. ^{1}H NMR chemical shifts (δ_H) are given in ppm relative to the signal for internal Me_4Si (δ_H = 0 ppm) for solutions in $CDCl_3$ or by reference to acetone (δ_H = 2.225 ppm) for solutions in D_2O. ^{13}C NMR chemical shifts (δ_C) are relative to the signal for $CDCl_3$ (δ_C = 76.9 ppm) for solutions in $CDCl_3$ or by reference to acetone (δ_C = 30.89 ppm) for solutions in D_2O. *J* values are given in Hz. Optical rotations were determined for solutions in $CHCl_3$ or H_2O at 20 °C with a Perkin−Elmer 241 polarimeter, using a 10-cm 1-mL cell. Fast-atom-bombardment mass spectrometry (FABMS) was performed with 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. MALDI-TOF mass spectra were recorded with a Voyager-DE (PerSeptive Biosystems) instrument using dihydroxybenzoic acid (DHB) as a matrix. The matrix was dissolved in a 1:1 (v/v) mixture of acetonitrile/H_2O (10 mg DHB/mL), and the sample was dissolved in acetone (5 mg/mL). Subsequently, 0.5 μL of matrix solution and 0.5 μL of sample solution were brought on the sample plate of the mass spectrometer. Spectra were generated by summing positive-ion signals of 256 laser shots with constant intensity. Exact masses were measured by nano electrospray time-of-flight mass spectrometry using a Micromass LCToF mass spectrometer at a resolution of 5000 FWHM. Gold-coated capillaries were loaded with 1 μL of sample (conc. 20 μM), dissolved in a 1:1 (v/v) mixture of acetonitrile/H_2O and 0.1% formic acid. Pentafluorophenylalanine was added as internal standard. The capillary voltage was set at 1500 V and the cone voltage was set at 30 V.

Octyl (2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (16): To a solution of octyl (2,3,4,6-tetra-*O*-acetyl-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 (**15**; 246 mg, 0.18 mmol)[10] in CH_2Cl_2/MeOH (20 mL, 3:1) was added NaOMe (pH = 9), and the mixture was stirred for 4 h. After neutralisation with Dowex 50 × 8 (H^+), and filtration, the solution was concentrated. A solution of the residue in 1-BuOH (20 mL), containing molecular sieves 3 Å (0.75 g), was stirred for 30 min under Ar, then 1,2-diaminoethane (2.2 mL, 33 mmol) was added. The mixture was stirred at 90 °C overnight, filtered through Celite, and co-concentrated with toluene. The residue was dissolved in pyridine/propionic anhydride (10 mL, 1:1) and stirred overnight, then co-concentrated with toluene. A solution of the residue in MeOH (20 mL) was treated with NaOMe (pH = 9) for 4 h, then neutralised with Dowex 50 × 8 (H^+), filtered, and concentrated. The residue was dissolved in pyridine/acetic anhydride (10 mL, 1:1) and stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 3:1) of the residue yielded **16**, isolated as a syrup (172 mg, 72%). TLC (toluene/EtOAc, 1:1): R_f = 0.69. $[\alpha]_D^{20}$ = +3 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.00 (t, 3 H, $COCH_2CH_3$), 1.26 (m, 10 H, 5 octyl CH_2), 1.50 (m, 2 H, octyl CH_2), 1.97, 1.98, 2.01, and 2.08 (4 s, each 3 H, 4 $COCH_3$), 2.15 (q, 2 H, $COCH_2CH_3$), 3.13 and 3.42 (2 m, each 1 H, octyl OCH_2), 4.11 (d, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.12 (dd, 1 H, 2′′-H), 5.17 (d, $J_{1',2'}$ = 7.7 Hz, 1 H, 1′-H), 5.18 (d, $J_{2',NH}$ = 7.7 Hz, 1 H, NH), 5.28 (d, $J_{3'',4''}$ = 2.9, $J_{4'',5''}$ < 1 Hz, 1 H, 4′′-H), 7.45−7.10 (m, 25 H, 5 $OCH_2C_6H_5$) ppm. MS (FAB$^+$) of $C_{72}H_{91}NO_{20}$ (1289): found *m*/*z* = 1290 [M + H]$^+$, 1312 [M + Na]$^+$.

Octyl (2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (17): To a solution of **16** (172 mg,

1.13 mmol) in EtOH/EtOAc (20 mL, 1:1) were added 10% Pd/C (140 mg) and HOAc (0.25 mL), and the mixture was stirred for 2.5 h under H_2, then filtered through Celite, and concentrated. A solution of the residue in pyridine/acetic anhydride (22 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 1:3) of the residue yielded **17**, isolated as a syrup (88 mg, 65%). TLC (toluene/EtOAc, 1:3): R_f = 0.14. $[\alpha]_D^{20}$ = −7 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.08 (t, 3 H, $COCH_2CH_3$), 1.28 (m, 10 H, 5 octyl CH_2), 1.59 (m, 2 H, octyl CH_2), 1.96, 1.99, 2.02, 2.04, 2.06, 2.07, 2.11, and 2.14 (8 s, 3, 3, 3, 3, 3, 3, 6, 3, 3 H, 9 $COCH_3$), 2.15 (m, 2 H, $COCH_2CH_3$), 3.40 (m, 1 H, octyl OC*H*H), 4.39 (dd, $J_{5',6'a}$ = 2.5, $J_{6'a,6'b}$ = 11.8 Hz, 1 H, 6′a-H), 4.48 (d, $J_{1'',2''}$ = 7.7 Hz, 1 H, 1′′-H), 4.69 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H), 4.73 (d, $J_{1',2'}$ = 7.7 Hz, 1 H, 1′-H), 4.96 (dd, $J_{2'',3''}$ = 10.4, $J_{3'',4''}$ = 3.3 Hz, 1 H, 3′′-H), 5.15 (dd, 1 H, 4-H), 5.29 (dd, 1 H, 3′-H), 5.34 (d, $J_{4'',5''}$ < 1 Hz, 1 H, 4′′-H), 5.69 (d, $J_{2',NH}$ = 8.5 Hz, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 9.4 ($COCH_2CH_3$), 13.8 (octyl CH_3), 20.3−20.6 ($COCH_3$), 22.4, 25.9, 28.9, 29.0, 29.1, 29.4, and 31.6 (6 octyl CH_2, $COCH_2CH_3$), 54.0 (C-2′), 60.7, 62.6, 62.7, and 68.1 (C-6, C-6′, C-6′′, octyl OCH_2), 66.0, 66.5, 68.3, 68.9, 70.0, 70.5, 70.6, 71.4, 72.5, 74.6, and 75.9 (C-2, C-3, C-4, C-5, C-3′, C-4′, C-5′, C-2′′, C-3′′, C-4′′, C-5′′), 97.2, 99.2, and 100.7 (C-1, C-1′, C-1′′), 168.9, 169.3, 169.8, 169.9, 170.0 (2 C), 170.1, 170.2, and 170.5 (9 *C*OCH$_3$), 173.8 (*C*OCH_2CH_3) ppm. MS (FAB$^+$) of $C_{47}H_{71}NO_{25}$ (1049): found *m*/*z* = 1050 [M + H]$^+$, 1072 [M + Na]$^+$.

Octyl β-D-Galactopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (2): To a solution of **17** (88 mg, 84 μmol) in MeOH/CH_2Cl_2 (10 mL, 4:1) was added NaOMe (pH = 9), and the mixture was stirred for 2.5 h. After neutralisation with Dowex 50 × 8 (H$^+$) and filtration, the solution was concentrated. Gel-filtration of the residue on a Bio-Gel P-2 column, eluted with H_2O, and subsequent lyophilization yielded **2**, isolated as a white powder (53 mg, 94%). TLC (CH_2Cl_2/MeOH/H_2O, 5:10:3): R_f = 0.88. $[\alpha]_D^{20}$ = −2 (*c* = 1, H_2O). High-resolution MS of $C_{29}H_{53}NO_{16}$ (671.3364): calcd. 694.3262, found 694.3265 [M + Na]. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Ethyl 2,3,4-Tri-*O*-acetyl-1-thio-β-D-fucopyranoside (19): A solution of D-fucose (**18**; 936 mg, 5.7 mmol) in pyridine/acetic anhydride (20 mL, 1:1) was stirred for 7 h, then co-concentrated with toluene. The residue was dissolved in dry CH_2Cl_2 (10 mL), containing molecular sieves 4 Å (200 mg), and ethanethiol (507 μL, 6.84 mmol) was added. The mixture was stirred under Ar for 60 min, then cooled to 0 °C, and BF_3·Et_2O (2.86 mL, 22.8 mmol) was added. After 100 min, during which period the temperature was allowed to reach room temperature, the mixture was neutralised with NEt_3, and filtered. The filtrate was diluted with CH_2Cl_2, washed with water and aq. saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated. Column chromatography (toluene/EtOAc, 4:1) of the residue yielded **19**, isolated as a white foam (1.16 g, 61%), and the α-product (700 mg, 36%). TLC (toluene/EtOAc, 4:1): R_f = 0.42. $[\alpha]_D^{20}$ = −28 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, $J_{5,6}$ = 6.3 Hz, 3 H, 6-H), 1.02 (t, 3 H, SCH_2CH_3), 1.70, 1.79, and 1.89 (3 s, each 3 H, 3 $COCH_3$), 2.37−2.57 (m, 2 H, SCH_2CH_3), 3.63 (m, 1 H, 5-H), 4.26 (d, $J_{1,2}$ = 9.7 Hz, 1 H, 1-H), 4.83 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.2 Hz, 1 H, 3-H), 4.95 (t, 1 H, 2-H), 5.01 (dd, $J_{4,5}$ < 1 Hz, 1 H, 4-H) ppm. MS (FAB$^+$) of $C_{14}H_{22}O_7S$ (334): found *m*/*z* = 335 [M + H]$^+$, 357 [M + Na]$^+$.

Octyl (2,3,4-Tri-*O*-acetyl-β-D-fucopyranosyl)-(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 (20): A solution of **19** (109 mg, 325 μmol) and **13** (250 mg, 242 μmol) in dry CH_2Cl_2 (10 mL), containing powdered molecular sieves 4 Å (0.3 g), was stirred for 3.5 h under Ar, then a solution of AgOTf (296 mg, 1.15 mmol) in dry toluene (4.3 mL) was added, followed after 20 min by a solution of Br_2 (371 μmol) in dry CH_2Cl_2 (0.69 mL). After additional stirring for 60 min, the mixture was neutralised with NEt_3 and filtered through Celite. The filtrate was diluted with CH_2Cl_2, washed with aq. 10% NaS_2O_3, aq. saturated $NaHCO_3$, and water, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (toluene/EtOAc, 3:1) of the residue afforded **20**, isolated as a syrup (233 mg, 74%). TLC (toluene/EtOAc, 3:1): R_f = 0.56. $[\alpha]_D^{20}$ = −6 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, octyl CH_3), 1.06 (d, $J_{5'',6''}$ = 6.0 Hz, 3 H, 6′′-H), 1.23 (br. s, 10 H, 5 octyl CH_2), 1.42 (m, 2 H, octyl CH_2), 1.96, 2.01, and 2.07 (3 s, each 3 H, 3 $COCH_3$), 2.97 and 3.19 (2 m, each 1 H, octyl OCH_2), 5.26 (d, $J_{1',2'}$ = 7.4 Hz, 1 H, 1′-H), 6.80−7.42 (m, 25 H, 5 $OCH_2C_6H_5$), 7.45−7.70 (m, 4 H, Phth) ppm. MS (FAB$^+$) of $C_{75}H_{87}NO_{19}$ (1305): found *m*/*z* = 1306 [M + H]$^+$, 1328 [M + Na]$^+$.

Octyl (2,3,4-Tri-*O*-acetyl-β-D-fucopyranosyl)-(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 (21): A solution of **20** (72 mg, 55 μmol) in 1-BuOH (8 mL), containing molecular sieves 3 Å (0.25 g), was stirred under Ar for 30 min, then 1,2-diaminoethane (0.74 mL, 11 mmol) was added. The mixture was stirred overnight at 90 °C, filtered through Celite, and co-concentrated with toluene and EtOH. A solution of the residue in pyridine/acetic anhydride (6 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 3:1 → 1:1) of the residue yielded **21**, isolated as a syrup (58 mg, 85%). TLC (toluene/EtOAc, 3:1): R_f = 0.29. $[\alpha]_D^{20}$ = −3 (*c* = 0.8, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.07 (d, $J_{5'',6''}$ = 6.0 Hz, 3 H, 6′′-H), 1.26 (m, 10 H, 5 octyl CH_2), 1.50 (m, 2 H, octyl CH_2), 1.74 (s, 3 H, $NHCOCH_3$), 1.96, 1.97, and 2.11 (3 s, each 3 H, 3 $COCH_3$), 4.13 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.73 (d, $J_{2',NH}$ = 8.7 Hz, 1 H, NH), 7.10−7.58 (m, 25 H, 5 $OCH_2C_6H_5$) ppm. MS (FAB$^+$) of $C_{69}H_{87}NO_{18}$ (1217): found *m*/*z* = 1218 [M + H]$^+$, 1240 [M + Na]$^+$.

Octyl (2,3,4-Tri-*O*-acetyl-β-D-fucopyranosyl)-(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 (22): To a solution of **21** (106 mg, 86 μmol) in EtOH/EtOAc (15 mL, 1:1) were added 10% Pd/C (48 mg) and HOAc (165 μL), and the mixture was stirred overnight under H_2, then filtered through Celite, and concentrated. A solution of the residue in pyridine/acetic anhydride (43 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 1:3) of the residue yielded **22**, isolated as a syrup (61 mg, 72%). TLC (toluene/EtOAc, 1:3): R_f = 0.17. $[\alpha]_D^{20}$ = −21 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.19 (d, $J_{5'',6''}$ = 6.4 Hz, 3 H, 6′′-H), 1.30 (m, 10 H, 5 octyl CH_2), 1.58 (m, 2 H, octyl CH_2), 1.95, 1.98, 2.01, 2.03, 2.08, 2.10, and 2.15 (7 s, 3, 3, 3, 6, 6, 3, 3 H, 9 $COCH_3$), 3.41 (m, 1 H, octyl OC*H*H), 4.44 (d, $J_{1'',2''}$ = 7.8 Hz, 1 H, 1′′-H), 4.63 (d, $J_{1',2'}$ = 7.4 Hz, 1 H, 1′-H), 4.71 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.68 (d, $J_{2',NH}$ = 8.7 Hz, 1 H, NH) ppm. MS (FAB$^+$) of $C_{44}H_{67}NO_{23}$ (977): found *m*/*z* = 978 [M + H]$^+$, 1000 [M + Na]$^+$.

Octyl β-D-Fucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (3): To a solution of **22** (61 mg, 62 μmol) in MeOH/CH_2Cl_2 (8 mL, 3:1) was added NaOMe (pH = 9), and the mixture was stirred for 5 h. After neutralisation with Dowex 50 × 8 (H$^+$) and filtration, the solution was concentrated. Gel-filtration of the residue on a Bio-Gel P-2 column, eluted with water, and subsequent lyophilization yielded **3**, isolated as a white powder (24 mg, 61%). TLC (1-BuOH/EtOH/HOAc/H_2O, 4:2:2:1):

R_f = 0.32. $[\alpha]_D^{20}$ = −7 (*c* = 1, H_2O). High-resolution MS of $C_{28}H_{51}NO_{15}$ (641.3259): calcd. 664.3156, found 664.3170 [M + Na]. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Octyl (2,3,4-Tri-*O*-acetyl-β-D-fucopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (24): A solution of **20** (161 mg, 123 μmol) in 1-BuOH (17 mL), containing molecular sieves 3 Å (0.55 g), was stirred for 30 min under Ar, then 1,2-diaminoethane (1.66 mL, 25 mmol) was added. The mixture was stirred at 90 °C overnight, filtered through Celite, and co-concentrated with toluene and EtOH. A solution of the residue in pyridine/propionic anhydride (12 mL, 1:1) was stirred overnight, then co-concentrated with toluene and EtOH. Column chromatography (toluene/EtOAc, 3:1) of the residue yielded **23**, isolated as a syrup (138 mg, 87%). To a solution of **23** in EtOH/EtOAc (16 mL, 1:1) were added 10% Pd/C (60 mg) and HOAc (0.2 mL), and the mixture was stirred overnight under H_2, then filtered through Celite, and concentrated. To a solution of the residue in MeOH (15 mL) was added NaOMe (pH = 9), and the mixture was stirred for 6 h, then neutralised with Dowex 50 × 8 (H^+), and concentrated. The residue was dissolved in pyridine/acetic anhydride (16 mL, 1:1) and stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 1:2) of the residue yielded **24**, isolated as a syrup (58 mg, 55%). TLC (toluene/EtOAc, 1:2): R_f = 0.25. $[\alpha]_D^{20}$ = −18 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 3 H, octyl CH_3), 1.11 (t, 3 H, $COCH_2CH_3$), 1.21 (d, $J_{5'',6''}$ = 5.8 Hz, 3 H, 6″-H), 1.33 (m, 10 H, 5 octyl CH_2), 1.59 (m, 2 H, octyl CH_2), 1.89−2.16 (m, 26 H, 8 $COCH_3$, $COCH_2CH_3$), 3.39 (m, 1 H, octyl OC*H*H), 4.42 (d, $J_{1'',2''}$ = 7.8 Hz, 1 H, 1″-H), 4.62 (d, $J_{1',2'}$ = 7.3 Hz, 1 H, 1′-H), 4.67 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.60 (d, $J_{2',NH}$ = 7.4 Hz, 1 H, NH) ppm. MS (FAB^+) of $C_{45}H_{69}NO_{23}$ (991): found *m*/*z* = 992 $[M + H]^+$, 1014 $[M + Na]^+$.

Octyl β-D-Fucopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (4): To a solution of **24** (58 mg, 58 μmol) in MeOH (10 mL) was added NaOMe (pH = 9), and the mixture was stirred for 24 h. After neutralisation with Dowex 50 × 8 (H^+) and filtration, the solution was concentrated. Gel-filtration of the residue on a Bio-Gel P-2 column, eluted with water, and subsequent lyophilization yielded **4**, isolated as a white powder (36 mg, 93%). TLC (1-BuOH/EtOH/HOAc/H_2O, 4:2:2:1): R_f = 0.38. $[\alpha]_D^{20}$ = −1 (*c* = 1, H_2O). High-resolution MS of $C_{29}H_{53}NO_{15}$ (655.3415): calcd. 678.3313, found 678.3331 [M + Na]. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

6-Azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (27): To a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**25**; 1.08 g, 4.15 mmol) in pyridine (10 mL) was added dropwise a solution of *p*-toluenesulfonyl chloride (1.3 g, 6.3 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 5 h. After the addition of water (1 mL), the mixture was stirred for 10 min, then co-concentrated with toluene. A solution of the residue in CH_2Cl_2 was washed with water and aq. $NaHCO_3$, dried ($MgSO_4$), and concentrated. Column chromatography (toluene/EtOAc, 5:1) of the residue yielded **26**, isolated as a syrup (1.59 g, 92%). To a solution of **26** (1.31 g, 3.17 mmol) in Me_2SO (30 mL) was added NaN_3 (1 g, 15.7 mmol), and the mixture was stirred for 2 h at 160 °C, then cooled to room temperature, poured into iced water, extracted with EtOAc, and the organic phase was dried ($MgSO_4$), and concentrated to yield **27**, isolated as a syrup (900 mg, 99%). TLC (toluene/EtOAc, 3:1): R_f = 0.62. IR (KBr): $\tilde{\nu}$ = 2110 cm^{-1} (N_3). $[\alpha]_D^{20}$ = +43 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $[D_6]Me_2SO$): δ = 1.31, 1.32, 1.43, and 1.52 (4 s, each 3 H, 4 $COCH_3$), 3.33 (dd, $J_{5,6a}$ = 5.4, $J_{6a,6b}$ = 12.7 Hz, 1 H, 6a-H), 3.47 (dd, $J_{5,6b}$ = 7.8 Hz, 1 H, 6b-H), 3.89 (ddd, 1 H, 5-H), 4.17 (dd, $J_{3,4}$ = 7.9, $J_{4,5}$ = 2.0 Hz, 1 H, 4-H), 4.30 (dd, $J_{1,2}$ = 5.0, $J_{2,3}$ = 2.5 Hz, 1 H, 2-H), 4.60 (dd, 1 H, 3-H), 5.52 (d, 1 H, 1-H) ppm. MS (FAB^+) of $C_{12}H_{19}N_3O_5$ (285): found *m*/*z* = 286 $[M + H]^+$, 308 $[M + Na]^+$.

2,3,4-Tri-*O*-acetyl-6-azido-6-deoxy-α-D-galactopyranosyl Trichloroacetimidate (30): To a solution of **27** (900 mg, 3.15 mmol) in CH_2Cl_2 (30 mL) were added trifluoroacetic acid (5.6 mL, 73 mmol) and water (0.7 mL), and the mixture was stirred for 2 h, then co-concentrated with toluene. A solution of the residue in pyridine/acetic anhydride (20 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 3:1) of the residue yielded **28**, isolated as a syrup (583 mg, 50%). To a solution of **28** in DMF (3 mL) was added hydrazinium acetate (158 mg, 1.72 mmol), and the solution was stirred for 70 min at 50 °C, then diluted with EtOAc, washed with water and aq. saturated NaCl, dried ($MgSO_4$), and concentrated to give **29**, isolated as a foam (461 mg, 89%). To a solution of **29** (461 mg, 1.4 mmol) in CH_2Cl_2 (8 mL) was added, at 0 °C, trichloroacetonitrile (1.4 mL, 14 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (104 μL, 0.7 mmol), and the mixture was stirred for 1 h, then concentrated. Column chromatography (toluene/EtOAc, 4:1) of the residue yielded **30**, isolated as a syrup (380 mg, 63%). TLC (toluene/EtOAc, 4:1): R_f = 0.33. $[\alpha]_D^{20}$ = +68 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.94, 1.97, and 2.12 (3 s, each 3 H, 3 $COCH_3$), 3.16 (dd, $J_{5,6a}$ = 4.9, $J_{6a,6b}$ = 12.9 Hz, 1 H, 6a-H), 3.39 (dd, $J_{5,6b}$ = 7.7 Hz, 1 H, 6b-H), 4.30 (m, 1 H, 5-H), 5.28 (dd, $J_{1,2}$ = 3.3, $J_{2,3}$ = 10.8 Hz, 1 H, 2-H), 5.35 (dd, $J_{3,4}$ = 2.9 Hz, 1 H, 3-H), 5.47 (dd, $J_{4,5}$ = 1.1 Hz, 1 H, 4-H), 6.55 (d, 1 H, 1-H), 8.60 (s, 1 H, NH) ppm. MS (FAB^+) of $C_{14}H_{17}Cl_3N_4O_8$ (474): found *m*/*z* = 475 $[M + H]^+$, 497 $[M + Na]^+$.

Octyl (2,3,4-Tri-*O*-acetyl-6-azido-6-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 (31): A solution of **13** (260 mg, 251 μmol) and **30** (195 mg, 450 μmol) in CH_2Cl_2 (12.5 mL), containing molecular sieves 4 Å (50 mg), was stirred under Ar at 0 °C for 2.5 h, then TMSOTf (17 μL, 80 μmol) was added. After stirring for 35 min, the mixture was neutralised with NEt_3, filtered, diluted with CH_2Cl_2, washed with water, dried ($MgSO_4$), and concentrated. Column chromatography (toluene/EtOAc, 3:1) of the residue yielded **31**, isolated as a syrup (206 mg, 61%). TLC (toluene/EtOAc, 3:1): R_f = 0.59. $[\alpha]_D^{20}$ = +1 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 3 H, octyl CH_3), 1.25 (m, 10 H, 5 octyl CH_2), 1.46 (m, 2 H, octyl CH_2), 2.00, 2.05, and 2.10 (3 s, each 3 H, 3 $COCH_3$), 4.67 (d, $J_{1'',2''}$ = 8.0 Hz, 1 H, 1″-H), 5.17 (dd, $J_{2'',3''}$ = 10.4 Hz, 1 H, 2″-H), 5.28 (d, $J_{1',2'}$ = 7.6 Hz, 1 H, 1′-H), 5.28 (d, $J_{3'',4''}$ = 3.0, $J_{4'',5''}$ < 1 Hz, 1 H, 4″-H), 6.90−7.48 (m, 25 H, 5 $OCH_2C_6H_5$), 7.51−7.68 (2 m, each 2 H, Phth) ppm. MS (FAB^+) of $C_{75}H_{86}N_4O_{19}$ (1346): found *m*/*z* = 1347 $[M + H]^+$, 1369 $[M + Na]^+$.

Octyl (2,3,4-Tri-*O*-acetyl-6-azido-6-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 (32): A solution of **31** (103 mg, 76 μmol) in 1-BuOH (10 mL), containing molecular sieves 3 Å (0.3 g), was stirred under Ar for 30 min, then 1,2-diaminoethane (1.05 mL, 15.7 mmol) was added. The mixture was stirred overnight at 90 °C, filtered through Celite, and co-concentrated with toluene and EtOH. A solution of the residue in pyridine/acetic anhydride (30 mL, 1:1) was stirred overnight, then co-concentrated with toluene and EtOH. Column chromatography (toluene/EtOAc, 2:1) of the residue yielded **32**, isolated as a syrup (96 mg, 99%). TLC (toluene/EtOAc, 2:1): R_f = 0.50. $[\alpha]_D^{20}$ = +5 (*c* = 1, $CHCl_3$). ^1H NMR

(300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.27 (m, 10 H, 5 octyl CH_2), 1.51 (m, 2 H, octyl CH_2), 1.72 (s, 3 H, NHCOCH_3), 1.96, 2.01, and 2.10 (3 s, each 3 H, 3 $COCH_3$), 4.11 (d, $J_{1,2} < 1$ Hz, 1 H, 1-H), 5.23 (d, $J_{3'',4''} = 3.3$, $J_{4'',5''} < 1$ Hz, 1 H, 4''-H), 5.69 (d, $J_{2',NH} = 7.1$ Hz, 1 H, NH), 7.15−7.45 (m, 25 H, 5 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{69}H_{86}N_4O_{18}$ (1258): found *m*/*z* = 1259 $[M + H]^+$, 1281 $[M + Na]^+$.

Octyl (6-Azido-6-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 (33): To a solution of **32** (96 mg, 76 μmol) in MeOH (15 mL) was added NaOMe (pH = 9), and the mixture was stirred for 2 h. After neutralisation with Dowex 50 × 8 (H^+), and filtration, the solution was concentrated. Column chromatography (CH_2Cl_2/MeOH, 95:5) of the residue yielded **33**, isolated as a syrup (61 mg, 70%). TLC (CH_2Cl_2/MeOH, 95:5): $R_f = 0.77$. $[\alpha]_D^{20} = -8$ (*c* = 1, MeOH). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 3 H, octyl CH_3), 1.27 (m, 10 H, 5 octyl CH_2), 1.52 (m, 2 H, octyl CH_2), 1.66 (s, 3 H, NHCOCH_3), 3.04 (m, 1 H, octyl OC*H*H), 4.13 (d, $J_{1,2} < 1$ Hz, 1 H, 1-H), 5.13 (d, $J_{1',2'} = 7.3$ Hz, 1 H, 1'-H), 5.87 (d, $J_{2',NH} = 7.1$ Hz, 1 H, NH), 7.25−7.40 (m, 25 H, 5 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{63}H_{80}N_4O_{15}$ (1132): found *m*/*z* = 1133 $[M + H]^+$, 1155 $[M + Na]^+$.

Octyl 6-Amino-6-deoxy-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (5): To a solution of **33** (61 mg, 53 μmol) in 2-propanol (6 mL) and water (4 mL) were added 10% Pd/C (160 mg) and aq. 25% NH_3 (pH = 10), and the mixture was stirred under H_2 for 3 h. After the removal of NH_3 by bubbling N_2 through the mixture, the solution was acidified with HOAc, stirred under H_2 for 23 h, filtered through Celite, and concentrated. Gel-filtration of the residue on a Bio-Gel P-2 column, eluted with water, yielded crude **5**. The residue was dissolved in water (1 mL), and applied on a SepPak C_{18} cartridge that was eluted first with water, then with MeOH. The MeOH fraction was concentrated and lyophilized to yield **5**, isolated as a white powder (34.5 mg, 99%). TLC (1-BuOH/EtOH/HOAc/H_2O, 4:2:2:1): $R_f = 0.16$. $[\alpha]_D^{20} = -15$ (*c* = 1, H_2O). High-resolution MS of $C_{28}H_{52}N_2O_{15}$ (656.3368): calcd. 657.3446, found 657.3441 [M + H]. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Octyl (6-Azido-6-deoxy-2,3,4-tri-*O*-propionyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (34): A solution of **31** (103 mg, 76 μmol) in 1-BuOH (10 mL), containing molecular sieves 3 Å (0.3 g), was stirred under Ar for 30 min, then 1,2-diaminoethane (1.05 mL, 15.7 mmol) was added. The mixture was stirred at 90 °C overnight, filtered through Celite, and co-concentrated with toluene and EtOH. A solution of the residue in pyridine/propionic anhydride (30 mL, 1:1) was stirred overnight, then co-concentrated with toluene and EtOH. Column chromatography (toluene/EtOAc, 4:1) of the residue yielded **34**, isolated as a syrup (91 mg, 94%). TLC (toluene/EtOAc, 3:1): $R_f = 0.56$. $[\alpha]_D^{20} = +7$ (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 0.94−1.23 (m, 12 H, 3 $COCH_2CH_3$, $NHCOCH_2CH_3$), 1.29 (m, 10 H, 5 octyl CH_2), 1.51 (m, 2 H, octyl CH_2), 1.95 (m, 2 H, $NHCOCH_2CH_3$), 2.18−2.53 (m, 6 H, 3 $COCH_2CH_3$), 4.12 (d, $J_{1,2} < 1$ Hz, 1 H, 1-H), 4.87 (dd, $J_{2'',3''} = 10.3$, $J_{3'',4''} = 3.1$ Hz, 1 H, 3''-H), 5.14 (dd, $J_{1'',2''} = 8.0$ Hz, 1 H, 2''-H), 5.18 (d, $J_{1',2'} = 7.7$ Hz, 1 H, 1'-H), 5.24 (d, $J_{4'',5''} < 1$ Hz, 1 H, 4''-H), 5.74 (d, $J_{2',NH} = 6.8$ Hz, 1 H, NH), 7.13−7.42 (m, 25 H, 5 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{73}H_{94}N_4O_{18}$ (1314): found *m*/*z* = 1315 $[M + H]^+$, 1337 $[M + Na]^+$.

Octyl 6-Amino-6-deoxy-β-D-galactopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (6): To a solution of **34** (91 mg, 71 μmol) in MeOH (15 mL) was added NaOMe (pH = 9), and the mixture was stirred for 2.5 h. After neutralisation with Dowex 50 × 8 (H^+) and filtration, the solution was concentrated. Column chromatography (CH_2Cl_2/MeOH, 9:1) of the residue yielded **35**, isolated as a syrup (65 mg, 79%). To a solution of **35** (65 mg, 53 μmol) in 2-propanol/water (10 mL, 3:2) were added 10% Pd/C (160 mg) and aq. 25% NH_3 (pH = 9), and the mixture was stirred under H_2 for 3.5 h. After the removal of NH_3 by bubbling N_2 through the mixture, the solution was acidified with HOAc, stirred under H_2 for 23 h, filtered through Celite, and concentrated. Gel-filtration of the residue on a Bio-Gel P-2 column, eluted with water, yielded crude **6**. The residue was dissolved in water (1 mL), and applied on a SepPak C_{18} cartridge that was eluted first with water, then with MeOH. The MeOH fraction was concentrated and lyophilized to yield **6**, isolated as a white powder (18 mg, 48%). TLC (1-BuOH/EtOH/HOAc/H_2O, 4:2:2:1): $R_f = 0.15$. $[\alpha]_D^{20} = -1$ (*c* = 1, H_2O). High-resolution MS of $C_{29}H_{54}N_2O_{15}$ (670.3524): calcd. 671.3602, found 671.3597 [M + H]. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

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-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (37): A solution of ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside **36**[17] (486 mg, 906 μmol) and **13** (541 mg, 522 μmol) in CH_2Cl_2 (25 mL), containing powdered molecular sieves 4 Å (0.5 g), was stirred under Ar for 3 h. The mixture was cooled to 0 °C, then *N*-iodosuccinimide (289 mg, 1.28 mmol) and triflic acid (16 μL, 181 μmol) were added. After 40 min, the solution was neutralised with NEt_3, filtered, diluted with CH_2Cl_2, washed with aq. 10% $NaHSO_3$, aq. saturated $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. Column chromatography (toluene/EtOAc, 8:1) of the residue yielded **37**, isolated as a syrup (548 mg, 70%). TLC (toluene/EtOAc, 6:1): $R_f = 0.61$. $[\alpha]_D^{20} = +4$ (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.22 (m, 10 H, 5 octyl CH_2), 1.41 (m, 2 H, octyl CH_2), 1.98 (s, 3 H, $COCH_3$), 2.75 and 3.19 (2 m, each 1 H, octyl OCH_2), 5.23 (d, $J_{1',2'} = 8.0$ Hz, 1 H, 1'-H), 5.38 (dd, $J_{1'',2''} = 7.7$, $J_{2'',3''} = 9.9$ Hz, 1 H, 2''-H), 6.75−7.38 (m, 40 H, 8 $OCH_2C_6H_5$), 7.45−7.70 (m, 4 H, Phth) ppm. MS (FAB^+) of $C_{92}H_{101}NO_{18}$ (1507): found *m*/*z* = 1508 $[M + H]^+$, 1530 $[M + Na]^+$.

Octyl (2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-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 (38): A solution of **37** (238 mg, 158 μmol) in 1-BuOH (22 mL), containing molecular sieves 3 Å (0.2 g), was stirred under Ar for 1 h, then 1,2-diaminoethane (2.0 mL, 30 mmol) was added. The mixture was stirred overnight at 90 °C, filtered through Celite, and co-concentrated with toluene. A solution of the residue in pyridine/acetic anhydride (60 mL, 1:1) was stirred overnight, then co-concentrated with toluene to give **38**, isolated as a syrup (211 mg, 94%). TLC (toluene/EtOAc, 3:1): $R_f = 0.29$. $[\alpha]_D^{20} = -1$ (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, octyl CH_3), 1.25 (m, 10 H, 5 octyl CH_2), 1.52 (m, 2 H, octyl CH_2), 1.76 (s, 3 H, NHCOCH_3), 1.96 (s, 3 H, $COCH_3$), 4.11 (s, $J_{1,2} < 1$ Hz, 1 H, 1-H), 5.33 (dd, $J_{1'',2''} = 8.1$, $J_{2'',3''} = 10.1$ Hz, 1 H, 2''-H), 5.82 (d, $J_{2',NH} = 7.8$ Hz, 1 H, NH), 7.10−7.45 (m, 40 H, 8 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{86}H_{101}NO_{17}$ (1419): found *m*/*z* = 1420 $[M + H]^+$, 1442 $[M + Na]^+$.

Octyl (3,4,6-Tri-*O*-benzyl-2-*O*-phenoxythiocarbonyl-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 (40): To a solution of **38** (211 mg, 148 μmol) in MeOH/CH_2Cl_2 (100 mL, 3:1) was added NaOMe (pH = 10), and the mixture was stirred at 40

°C for 17 h, then neutralised with Dowex 50 × 8 (H^+), filtered, and concentrated to give **39**. To a solution of the residue in acetonitrile (25 mL) were added 4-(dimethylamino)pyridine (825 mg, 6.75 mmol) and phenyl chlorothionocarbonate (540 μL, 3.90 mmol), and the mixture was stirred at 100 °C for 4.5 h, then at room temperature overnight. After dilution with CH_2Cl_2, the solution was washed with aq. 0.5 M HCl, aq. saturated $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. Column chromatography (toluene/EtOAc, 4:1) of the residue yielded **40**, isolated as a syrup (139 mg, 61%). TLC (toluene/EtOAc, 4:1): R_f = 0.50. $[\alpha]_D^{20}$ = −7 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, 3 H, octyl CH_3), 1.31 (m, 10 H, 5 octyl CH_2), 1.58 (m, 2 H, octyl CH_2), 1.73 (s, 3 H, NHCOC*H*$_3$), 3.22 (m, 1 H, octyl OC*H*H), 4.13 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.18 (d, $J_{1',2'}$ = 7.1 Hz, 1 H, 1′-H), 5.66 (d, $J_{2',NH}$ = 7.1 Hz, 1 H, NH), 5.95 (dd, $J_{1'',2''}$ = 7.8, $J_{2'',3''}$ = 10.0 Hz, 1 H, 2′′-H), 7.00−7.50 (m, 45 H, 9 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{91}H_{103}NO_{17}S$ (1513): found *m*/*z* = 1514 $[M + H]^+$, 1536 $[M + Na]^+$.

Octyl (2-Deoxy-3,4,6-tri-*O*-benzyl-β-D-*lyxo*-hexopyranosyl)-(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 (41): To a solution of **40** (139 mg, 91 μmol) in dry toluene (3 mL) was added tributylstannane (295 μL, 1.1 mmol), and the mixture was stirred at 100 °C. A catalytic amount of α,α′-azoisobutyronitrile was added, and the mixture was stirred at 100 °C for 2 h, then concentrated. A solution of the residue in acetonitrile was extracted with hexane (3 ×), and concentrated. Column chromatography (toluene/EtOAc, 3:1) of the residue yielded **41**, isolated as a syrup (87 mg, 70%). TLC (toluene/EtOAc, 3:1): R_f = 0.53. $[\alpha]_D^{20}$ = −5 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.26 (m, 10 H, 5 octyl CH_2), 1.50 (m, 2 H, octyl CH_2), 1.67 (s, 3 H, NHCOC*H*$_3$), 1.90−2.11 (m, 2 H, 2_{ax}′′-H, 2_{eq}′′-H), 3.12 (m, 1 H, octyl OC*H*H), 4.13 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.11 (d, $J_{1',2'}$ = 7.7 Hz, 1 H, 1′-H), 5.61 (d, $J_{2',NH}$ = 6.8 Hz, 1 H, NH), 7.10−7.45 (m, 40 H, 8 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{84}H_{99}NO_{15}$ (1361): found *m*/*z* = 1362 $[M + H]^+$, 1384 $[M + Na]^+$.

Octyl 2-Deoxy-β-D-*lyxo*-hexopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (7): To a solution of **41** (107 mg, 79 μmol) in EtOH/EtOAc (14 mL, 1:1) were added 10% Pd/C (45 mg) and 6 drops of HOAc, and the mixture was stirred under H_2 for 21 h, then filtered through Celite, and concentrated. Gel-filtration of the residue on a Bio-Gel P-2 column, eluted with water, and subsequent lyophilization yielded **7**, isolated as a white powder (38 mg, 75%). TLC (1-BuOH/EtOH/HOAc/H_2O, 4:2:2:1): R_f = 0.29. $[\alpha]_D^{20}$ = −9 (*c* = 1, H_2O). High-resolution MS of $C_{28}H_{51}NO_{15}$ (643.3259): calcd. 664.3156, found 664.3175 [M + H]. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Octyl (3,4,6-Tri-*O*-benzyl-2-*O*-phenoxythiocarbonyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (44): A solution of **37** (310 mg, 205 μmol) in 1-BuOH (28 mL), containing molecular sieves 3 Å (1 g), was stirred under Ar for 1 h, then 1,2-diaminoethane (2.6 mL, 39 mmol) was added. The mixture was stirred at 90 °C overnight, filtered through Celite, and co-concentrated with toluene. A solution of the residue in pyridine/propionic anhydride (60 mL, 1:1) was stirred overnight, then co-concentrated with toluene and EtOH. Column chromatography (toluene/EtOAc, 2:1) of the residue yielded **42** (280 mg, 94%), which was immediately employed in the next reaction. To a solution of **42** (280 mg, 193 μmol) in MeOH/CH_2Cl_2 (75 mL, 2:1) was added NaOMe (pH = 10), and the solution was stirred at 40 °C overnight, then neutralised with Dowex 50 × 8 (H^+), filtered, and concentrated. To a solution of the residue (**43**) in dry acetonitrile (22 mL) were added 4-(dimethylamino)pyridine (825 mg, 6.75 mmol) and phenyl chlorothionocarbonate (534 μL, 3.86 mmol), and the mixture was stirred at 100 °C for 2 h, then overnight at room temperature. After dilution with CH_2Cl_2, the solution was washed with aq. 0.5 M HCl, aq. saturated $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. Column chromatography (toluene/EtOAc, 5:1) of the residue yielded **44**, isolated as a syrup (128 mg, 43%). TLC (toluene/EtOAc, 5:1): R_f = 0.61. $[\alpha]_D^{20}$ = −2 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 0.97 (t, 3 H, NHCOCH$_2$C*H*$_3$), 1.26 (m, 10 H, 5 octyl CH_2), 1.52 (m, 2 H, octyl CH_2), 1.82−2.05 (m, 2 H, NHCOC*H*$_2$CH$_3$), 3.17 (m, 1 H, octyl OC*H*H), 4.13 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.18 (d, $J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 5.62 (d, $J_{2',NH}$ = 6.8 Hz, 1 H, NH), 5.90 (dd, $J_{1'',2''}$ = 7.8, $J_{2'',3''}$ = 9.9 Hz, 1 H, 2′′-H), 6.92−7.47 (m, 45 H, 9 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{92}H_{105}NO_{17}S$ (1527): found *m*/*z* = 1528 $[M + H]^+$, 1550 $[M + Na]^+$.

Octyl (2-Deoxy-3,4,6-tri-*O*-benzyl-β-D-*lyxo*-hexopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (45): To a solution of **44** (127 mg, 83 μmol) in dry toluene (3 mL) was added tributylstannane (270 μL, 1.0 mmol), and the mixture was stirred at 100 °C. A catalytic amount of α,α′-azoisobutyronitrile was added and the mixture was stirred at 100 °C for 2 h, then concentrated. A solution of the residue in acetonitrile was extracted with hexane (3 ×), and concentrated. Column chromatography (toluene/EtOAc, 4:1) of the residue yielded **45**, isolated as a syrup (71 mg, 62%). TLC (toluene/EtOAc, 4:1): R_f = 0.45. $[\alpha]_D^{20}$ = −1 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 0.98 (t, 3 H, NHCOCH$_2$C*H*$_3$), 1.25 (m, 10 H, 5 octyl CH_2), 1.50 (m, 2 H, octyl CH_2), 1.82−2.12 (m, 4 H, NHCOC*H*$_2$CH$_3$, 2_{ax}′′-H, 2_{eq}′′-H), 3.10 (m, 1 H, octyl OC*H*H), 4.12 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.15 (d, $J_{1',2'}$ = 7.6 Hz, 1 H, 1′-H), 5.63 (d, $J_{2',NH}$ = 6.8 Hz, 1 H, NH), 7.10−7.43 (m, 40 H, 8 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{85}H_{101}NO_{15}$ (1375): found *m*/*z* = 1376 $[M + H]^+$, 1398 $[M + Na]^+$.

Octyl 2-Deoxy-β-D-*lyxo*-hexopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (8): To a solution of **45** (70 mg, 51 μmol) in EtOH/EtOAc (9 mL, 1:1) were added 10% Pd/C (30 mg) and 6 drops of HOAc, and the mixture was stirred under H_2 overnight, then filtered through Celite, and concentrated. Gel-filtration of the residue on a Bio-Gel P-2 column, eluted with water, and subsequent lyophilization yielded **8**, isolated as a white powder (19 mg, 57%). TLC (1-BuOH/EtOH/HOAc/H_2O, 4:2:2:1): R_f = 0.44. $[\alpha]_D^{20}$ = −14 (*c* = 1, H_2O). High-resolution MS of $C_{29}H_{53}NO_{15}$ (655.3415): calcd. 678.3313, found 678.3326 [M + Na]. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Octyl (4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-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 (47): A solution of ethyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside[19] (**46**; 228 mg, 0.40 mmol) and **13** (169 mg, 0.16 mmol) in dry CH_2Cl_2 (5 mL), containing powdered molecular sieves 4 Å (0.46 g), was stirred under Ar for 4 h. Then a solution of AgOTf (83 mg, 0.32 mmol) in dry toluene (1 mL) was added and the stirring was continued for 20 min. After the addition of a solution of Br_2 (0.21 mmol) in dry CH_2Cl_2 (0.5 mL) and stirring for 1 h, a second solution of AgOTf (43 mg, 0.17 mmol) in dry toluene (0.5 mL) was added. When TLC (toluene/EtOAc, 5:1) showed the reaction to be complete, the mix-

ture was neutralised with NEt_3, filtered through Celite, diluted with CH_2Cl_2, washed with aq. 10% $NaHSO_3$, aq. saturated $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. Column chromatography (toluene/EtOAc, 5:1) of the residue yielded **47**, isolated as a white foam (135 mg, 51%). TLC (toluene/EtOAc, 5:1): R_f = 0.58. $[\alpha]_D^{20}$ = −3 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.27 (m, 10 H, 5 octyl CH_2), 1.60 (m, 2 H, octyl CH_2), 2.05 (s, 3 H, $COCH_3$), 2.98 and 3.10 (2 m, each 1 H, octyl OCH_2), 3.97 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.13 (d, $J_{1',2'}$ = 7.5 Hz, 1 H, 1′-H), 5.37 (d, $J_{1'',2''}$ = 8.2 Hz, 1 H, 1′′-H), 5.64 (d, $J_{3'',4''}$ = 2.9, $J_{4'',5''}$ < 1 Hz, 1 H, 4′′-H), 6.85−7.91 (m, 43 H, 2 Phth, 7 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{93}H_{98}N_2O_{19}$ (1546): found *m*/*z* = 1547 $[M + H]^+$, 1569 $[M + Na]^+$.

Octyl (2-Acetamido-4-*O*-acetyl-3,6-di-*O*-benzyl-2-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 (48): A solution of **47** (186 mg, 120 μmol) in 1-BuOH (17 mL), containing molecular sieves 3 Å (0.5 g), was stirred under Ar for 30 min, then 1,2-diaminoethane (1.7 mL, 25.3 mmol) was added. The mixture was stirred overnight at 90 °C, filtered through Celite, and co-concentrated with toluene, EtOH and CH_2Cl_2. A solution of the residue in pyridine/acetic anhydride (10 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 2:3) of the residue yielded **48**, isolated as a white foam (102 mg, 61%). TLC (toluene/EtOAc, 2:3): R_f = 0.59. $[\alpha]_D^{20}$ = −2 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, 3 H, octyl CH_3), 1.29 (m, 10 H, 5 octyl CH_2), 1.53 (m, 2 H, octyl CH_2), 1.77 and 1.82 (2 s, each 3 H, 2 $NHCOCH_3$), 2.02 (s, 3 H, $COCH_3$), 4.13 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.06 (d, $J_{1',2'}$ = 7.5 Hz, 1 H, 1′-H), 5.12 (d, $J_{1'',2''}$ = 8.0 Hz, 1 H, 1′′-H), 5.59 (dd, $J_{3'',4''}$ = 2.9, $J_{4'',5''}$ < 1 Hz, 1 H, 4′′-H), 5.87 (d, 2 H, 2 NH), 7.18−7.39 (m, 35 H, 7 $OCH_2C_6H_5$) ppm. MS (FAB^+) of $C_{81}H_{98}N_2O_{17}$ (1370): found *m*/*z* = 1371 $[M + H]^+$, 1393 $[M + Na]^+$.

Octyl (2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-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 (49): To a solution of **48** (102 mg, 74 μmol) in EtOH/EtOAc (7 mL, 1:1) were added 10% Pd/C (62 mg) and 3 drops of HOAc. The mixture was stirred under H_2 overnight, then filtered through Celite, and concentrated. A solution of the residue in pyridine/acetic anhydride (10 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (CH_2Cl_2/MeOH, 9:1) of the residue yielded **49**, isolated as a syrup (67 mg, 86%). TLC (CH_2Cl_2/MeOH, 9:1): R_f = 0.59. $[\alpha]_D^{20}$ = −2 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, 3 H, octyl CH_3), 1.25 (m, 10 H, 5 octyl CH_2), 1.54 (m, 2 H, octyl CH_2), 1.90, 1.91, 1.94, 1.96, 1.99, 2.02, 2.05, 2.06, 2.07, and 2.11 (10 s, each 3 H, 8 $COCH_3$, 2 $NHCOCH_3$), 3.37 (m, 1 H, octyl OC*H*H), 5.05 (dd, $J_{2'',3''}$ = 9.9, $J_{3'',4''}$ = 3.3 Hz, 1 H, 3′′-H), 6.10 and 6.27 (2 d, each 1 H, 2 NH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.9 (octyl CH_3), 20.5−20.8 ($COCH_3$), 23.0 and 23.1 ($NHCOCH_3$), 22.5, 26.0, 29.0, 29.2, 29.3, and 31.6 (6 octyl CH_2), 51.6 and 54.1 (C-2′, C-2′′), 61.0, 62.6, 62.7, and 68.2 (C-6, C-6′, C-6′′, octyl OCH_2), 97.4, 99.0, and 100.5 (C-1, C-1′, C-1′′), 169.3, 170.0, 170.1, 170.2 (3 C), 170.3, 170.5 (2 C), and 170.7 ($COCH_3$, $NHCOCH_3$) ppm. MS (FAB^+) of $C_{46}H_{70}N_2O_{24}$ (1034): found *m*/*z* = 1035 $[M + H]^+$, 1057 $[M + Na]^+$.

Octyl 2-Acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (9): To a solution of **49** (65 mg, 63 μmol) in MeOH (4 mL) was added NaOMe (pH = 10), and the mixture was stirred overnight. After neutralisation with Dowex 50 × 8 (H^+) and filtration, the solution was concentrated. Gel-filtration through a Bio-Gel P-2 column, eluted with water, and subsequent lyophilization yielded **9**, isolated as a white foam (24.9 mg, 56%). TLC (1-BuOH/EtOH/HOAc/H_2O, 4:2:2:1): R_f = 0.39. $[\alpha]_D^{20}$ = −6 (*c* = 0.5, H_2O). High-resolution MS of $C_{30}H_{54}N_2O_{16}$ (698.3473): calcd. 721.3371, found 721.3351 [M + Na]. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Octyl (3,6-Di-*O*-acetyl-2-deoxy-2-propionamido-4-*O*-propionyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (51): A solution of **47** (138 mg, 89 μmol) in 1-BuOH (13 mL), containing molecular sieves 3 Å (0.4 g), was stirred under Ar for 30 min, then 1,2-diaminoethane (1.3 mL, 18.6 mmol) was added. The mixture was stirred at 90 °C overnight, filtered through Celite, and co-concentrated with toluene and EtOH. A solution of the residue in pyridine/propionic anhydride (10 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 5:1) of the residue yielded **50**, isolated as a white foam (100 mg, 80%). TLC (CH_2Cl_2/MeOH, 9:1): R_f = 0.90. To a solution of **50** (100 mg, 71 μmol) in EtOH/EtOAc (7 mL, 1:1) were added 10% Pd/C (102 mg) and 5 drops of HOAc, and the mixture was stirred under H_2 overnight, then filtered through Celite and concentrated. A solution of the residue in pyridine/acetic anhydride (10 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (CH_2Cl_2/MeOH, 9:1) of the residue yielded **51**, isolated as a syrup (71 mg, 92%). TLC (CH_2Cl_2/MeOH, 9:1): R_f = 0.70. $[\alpha]_D^{20}$ = −7 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, 3 H, octyl CH_3), 1.02−1.16 (m, 9 H, $COCH_2CH_3$, 2 $NHCOCH_2CH_3$), 1.26 (m, 10 H, 5 octyl CH_2), 1.55 (m, 2 H, octyl CH_2), 1.92−2.12 (m, 27 H, 7 $COCH_3$, $COCH_2CH_3$, 2 $NHCOCH_2CH_3$), 3.39 (m, 1 H, octyl OC*H*H), 5.07 (dd, $J_{2'',3''}$ = 9.9, $J_{3'',4''}$ = 3.3 Hz, 1 H, 3′′-H), 5.93−6.05 (m, 2 H, 2 NH) ppm. MS (FAB^+) of $C_{49}H_{76}N_2O_{24}$ (1076): found *m*/*z* = 1077 $[M + H]^+$, 1099 $[M + Na]^+$.

Octyl 2-Deoxy-2-propionamido-β-D-galactopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (10): To a solution of **51** (71 mg, 66 μmol) in MeOH (5 mL) was added NaOMe (pH = 10), and the mixture was stirred overnight. After neutralisation with Dowex 50 × 8 (H^+) and filtration, the solution was concentrated. Gel-filtration of the residue on a Bio-Gel P-2 column, eluted with water, and subsequent lyophilization yielded **10**, isolated as a white foam (44 mg, 91%). TLC (1-BuOH/EtOH/HOAc/H_2O, 4:2:2:1): R_f = 0.32. $[\alpha]_D^{20}$ = −12 (*c* = 1, H_2O). High-resolution MS of $C_{32}H_{58}N_2O_{16}$ (726.3786): calcd. 749.3684, found 749.3681 [M + Na]. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(dimethylmaleimido)-β-D-galactopyranose (53): To a solution of D-galactosamine·HCl (**52**; 2.0 g, 9.3 mmol) in MeOH (69 mL) was added NaOMe (0.5 g, 9.3 mmol) and dimethylmaleic anhydride (0.6 g, 4.8 mmol), and the mixture was stirred at 60 °C for 30 min. Then, NEt_3 (0.93 mL) and dimethylmaleic anhydride (0.6 g, 4.8 mmol) were added, and the stirring was continued at 60 °C for 1.5 h. After concentration of the mixture, a solution of the residue in pyridine/acetic anhydride (28.5 mL, 2:1) was stirred overnight, then co-concentrated with toluene. A solution of the residue in CH_2Cl_2 (50 mL) was washed with aq. 3% HCl, aq. saturated $NaHCO_3$, and water, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (hexane/EtOAc, 1:1) of the residue yielded **53**, isolated as a white foam (1.3 g, 31%). TLC (hexane/EtOAc, 1:1): R_f = 0.30. $[\alpha]_D^{20}$ = +48 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.91, 1.98, 2.04, and 2.17 (4 s, 3, 6, 6, 3 H, 2 CH_3, 4 $COCH_3$), 4.41 (dd, $J_{1,2}$ = 8.9, $J_{2,3}$ = 11.4 Hz, 1 H, 2-H), 5.47 (d, $J_{3,4}$ = 3.4, $J_{4,5}$ < 1 Hz, 1

H, 4-H), 5.77 (dd, 1 H, 3-H), 6.28 (d, 1 H, 1-H) ppm. MS (MALDI-TOF) of $C_{20}H_{25}NO_{11}$ (455): found *m/z* = 478 [M + Na]$^+$, 494 [M + K]$^+$.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-(dimethylmaleimido)-D-galactopyranose (54): To a solution of **53** (0.78 g, 1.7 mmol) in DMF (6 mL) was added hydrazinium acetate (0.19 g, 2.1 mmol). The mixture was stirred at room temperature for 1 h, diluted with EtOAc, washed with cold aq. saturated $NaHCO_3$ and water, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (toluene/EtOAc, 1:1) of the residue yielded **54**, isolated as a white foam (0.43 g, 61%). TLC (toluene/EtOAc, 1:1): R_f = 0.37. ^{1}H NMR β-anomer (300 MHz, $CDCl_3$): δ = 1.89, 1.96, 2.05, and 2.17 (4 s, 3, 6, 3, 3 H, 2 CH_3, 3 $COCH_3$), 4.83 (dd, $J_{1,2}$ = 7.0, $J_{2,3}$ = 11.5 Hz, 1 H, 2-H), 5.33 (d, 1 H, 1-H), 5.43 (d, $J_{3,4}$ = 3.3, $J_{4,5}$ < 1 Hz, 1 H, 4-H), 5.65 (dd, 1 H, 3-H) ppm. MS (MALDI-TOF) of $C_{18}H_{23}NO_{10}$ (413): found *m/z* = 436 [M + Na]$^+$, 452 [M + K]$^+$.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-(dimethylmaleimido)-β-D-galactopyranosyl trichloroacetimidate (55): To a solution of **54** (0.30 g, 0.73 mmol) in CH_2Cl_2 (6 mL) were added trichloroacetonitrile (1.05 g, 7.3 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (29 mg, 0.19 mmol), and the mixture was stirred for 30 min at room temperature, then concentrated. Column chromatography (toluene/EtOAc, 1:1) of the residue yielded **55**, isolated as a white foam (0.24 g, 59%). TLC (toluene/EtOAc, 1:1): R_f = 0.56. $[\alpha]_D^{20}$ = +36 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93, 2.05, and 2.20 (3 s, 9, 3, 3 H, 2 CH_3, 3 $COCH_3$), 4.58 (dd, $J_{1,2}$ = 8.6, $J_{2,3}$ = 11.5 Hz, 1 H, 2-H), 5.50 (d, $J_{3,4}$ = 3.4, $J_{4,5}$ < 1 Hz, 1 H, 4-H), 5.78 (dd, 1 H, 3-H), 6.40 (d, 1 H, 1-H), 8.67 (s, 1 H, NH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 8.6 (CH_3), 20.3−20.5 ($CO\mathit{C}H_3$), 49.9 (C-2), 60.8 (C-6), 66.2, 67.6, and 71.6 (C-3, C-4, C-5), 93.9 (C-1), 137.3 (C=C NDMM), 160.4 ($\mathit{C}ONHCCl_3$), 169.5−170.2 ($\mathit{C}OCH_3$, CO NDMM).

Octyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-dimethylmaleimido-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 (56): A solution of **55** (147 mg, 264 μmol) and **13** (182 mg, 176 μmol) in dry CH_2Cl_2 (2.2 mL), containing molecular sieves 4 Å (30 mg), was stirred under Ar at room temperature for 45 min. After cooling to 0 °C, a solution of TMSOTf (2.64 μmol) in dry CH_2Cl_2 (26.4 μL) was added. When TLC (hexane/EtOAc, 1:1) showed the reaction to be complete, the mixture was neutralised with NEt_3 and concentrated. Column chromatography (hexane/EtOAc, 1:1) of the residue yielded **56**, isolated as a colourless syrup (212 mg, 84%). TLC (hexane/EtOAc, 1:1): R_f = 0.59. $[\alpha]_D^{20}$ = +6 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, 3 H, octyl CH_3), 1.23 (m, 10 H, 5 octyl CH_2), 1.36 (m, 2 H, octyl CH_2), 1.88, 1.93, 2.02, and 2.04 (4 s, 3, 3, 6, 3 H, 2 CH_3, 3 $COCH_3$), 2.91 and 3.13 (2 m, each 1 H, octyl OCH_2), 5.32 (d, $J_{3'',4''}$ = 3.4, $J_{4'',5''}$ < 1 Hz, 1 H, 4''-H), 5.32 (d, $J_{1',2'}$ = 8.2 Hz, 1 H, 1'-H), 5.61 (dd, $J_{2'',3''}$ = 11.5 Hz, 1 H, 3''-H), 6.90−7.34 (m, 25 H, 5 $OCH_2C_6H_5$), 7.55 and 7.68 (2 m, each 2 H, Phth) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 8.9 (CH_3), 14.0 (octyl CH_3), 20.4−20.5 ($CO\mathit{C}H_3$), 22.5, 25.9, 29.1, 29.2, 29.6, and 31.7 (octyl CH_2), 51.8 and 55.3 (C-2', C-2''), 60.9, 67.6, 68.7, 69.8, 70.5, 72.7, 73.1, 73.7, and 74.7 (C-6, C-6', C-6'', 5 $OCH_2C_6H_5$, octyl OCH_2), 66.6, 67.8, 70.5, 72.5, 73.3, 74.6, 74.7, 75.9, 76.3, and 77.6 (C-2, C-3, C-4, C-5, C-3', C-4', C-5', C-3'', C-4'', C-5''), 96.6 (2 C) and 97.1 (C-1, C-1', C-1''), 169.6−170.2 ($\mathit{C}OCH_3$, CO NDMM) ppm. MS (MALDI-TOF) of $C_{81}H_{92}N_2O_{21}$ (1429): found *m/z* = 1452 [M + Na]$^+$, 1468 [M + K]$^+$.

Octyl (2-Deoxy-2-propionamido-3,4,6-tri-*O*-propionyl-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 (57): To a solution of **56** (364 mg, 255 μmol) in dioxane/water (14.4 mL, 4:1) was added NaOH (287 mg, 7.18 mmol), and the mixture was stirred at room temperature overnight. Then, the pH was adjusted to 3 using aq. 4 M HCl, and the stirring was continued overnight. The mixture was neutralised with solid K_2CO_3, and co-concentrated with toluene. A solution of the residue in pyridine/propionic anhydride (20 mL, 1:1) was stirred overnight, then co-concentrated with toluene. The residue was dissolved in CH_2Cl_2, and the solution was washed with aq. 1 M HCl, aq. saturated $NaHCO_3$, and water, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (hexane/EtOAc, 1:2) of the residue yielded **57**, isolated as a colourless syrup (116 mg, 33%). TLC (hexane/EtOAc, 1:1): R_f = 0.45. $[\alpha]_D^{20}$ = +9 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, octyl CH_3), 1.02−1.14 (m, 12 H, 3 $COCH_2C\mathit{H}_3$, $NHCOCH_2C\mathit{H}_3$), 1.24 (m, 10 H, 5 octyl CH_2), 1.44 (m, 2 H, octyl CH_2), 1.90 (m, 2 H, $NHCOC\mathit{H}_2CH_3$), 2.20−2.36 (m, 6 H, 3 $COC\mathit{H}_2CH_3$), 3.20 (m, 1 H, octyl OC*H*H), 5.29 (d, $J_{4'',5''}$ < 1 Hz, 1 H, 4''-H), 6.99−7.41 (m, 29 H, Phth, 5 $OCH_2C_6\mathit{H}_5$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 8.7, 8.8, 9.0, and 9.6 (3 $COCH_2\mathit{C}H_3$, $NHCOCH_2\mathit{C}H_3$), 13.9 (octyl CH_3), 22.5, 25.9, 27.2 (2 C), 29.0, 29.2 (2 C), 29.5 (2 C), and 31.6 (6 octyl CH_2, 3 $CO\mathit{C}H_2CH_3$, $NHCO\mathit{C}H_2CH_3$), 50.8 (2 C) (C-2', C-2''), 60.8, 67.4, 69.0, 69.6, 70.5, 72.7 (2 C), 73.8, and 74.0 (C-6, C-6', C-6'', 5 $O\mathit{C}H_2C_6H_5$, octyl OCH_2), 63.9, 66.1, 70.5 (2 C), 71.4, 74.7, 74.8, 77.0, 78.1, and 82.1 (C-2, C-3, C-4, C-5, C-3', C-4', C-5', C-3'', C-4'', C-5''), 97.5, 100.8, and 101.7 (C-1, C-1', C-1''), 173.4 and 173.5 ($\mathit{C}OCH_2CH_3$, $NH\mathit{C}OCH_2CH_3$) ppm. MS (MALDI-TOF) of $C_{81}H_{98}N_2O_{20}$ (1419): found *m/z* = 1442 [M + Na]$^+$, 1458 [M + K]$^+$.

Octyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-propionamido-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 (58): A solution of **57** (116 mg, 84.2 μmol) in 1-BuOH (22 mL) was stirred at room temperature for 30 min, then 1,2-diaminoethane (1.2 mL, 18 mmol) was added. The solution was stirred at 90 °C overnight, then co-concentrated with toluene. A solution of the residue in pyridine/acetic anhydride (9.6 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 2:3) of the residue yielded **58**, isolated as a colourless syrup (78 mg, 74%). TLC (toluene/EtOAc, 2:3): R_f = 0.41. $[\alpha]_D^{20}$ = +3 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.06 (t, 3 H, $NHCOCH_2C\mathit{H}_3$), 1.26 (m, 10 H, 5 octyl CH_2), 1.57 (m, 2 H, octyl CH_2), 1.78 (s, 3 H, $NHCOC\mathit{H}_3$), 1.96, 2.01, and 2.07 (3 s, each 3 H, 3 $COCH_3$), 2.05 (m, 2 H, $NHCOC\mathit{H}_2CH_3$), 3.34 (m, 1 H, octyl OC*H*H), 4.09 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 4.91 (dd, $J_{2'',3''}$ = 11.3, $J_{3'',4''}$ = 3.2 Hz, 1 H, 3''-H), 5.25 (d, $J_{4'',5''}$ < 1 Hz, 1 H, 4''-H), 5.91 (d, 1 H, NH), 7.20−7.39 (m, 25 H, 5 $OCH_2C_6H_5$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 9.6 ($NHCOCH_2\mathit{C}H_3$), 13.9 (octyl CH_3), 20.4−20.5 ($CO\mathit{C}H_3$), 23.1 ($NHCO\mathit{C}H_3$), 22.5, 26.0, 29.0−29.8, and 31.6 (octyl CH_2, $NHCO\mathit{C}H_2CH_3$), 50.9 and 55.7 (C-2', C-2''), 61.0, 67.7, 69.2, 71.1, 73.1 (2 C), 73.3, 73.5, and 74.9 (C-6, C-6', C-6'', 5 $O\mathit{C}H_2C_6H_5$, octyl OCH_2), 66.3, 70.1, 70.4, 71.5, 73.6, 74.1, 74.5, 76.2, 77.0, and 78.4 (C-2, C-3, C-4, C-5, C-3', C-4', C-5', C-3'', C-4'', C-5''), 97.5, 97.9, and 100.2 (C-1, C-1', C-1''), 170.1−171.0 ($\mathit{C}OCH_3$, $NH\mathit{C}OCH_3$), 173.8 ($NH\mathit{C}OCH_2CH_3$) ppm.

Octyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-propionamido-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 (59): To a

solution of **58** (78 mg, 63 μmol) in MeOH/CH_2Cl_2 (4.0 mL, 1:1) was added NaOMe (pH = 9), and the mixture was stirred overnight. After neutralisation with Dowex 50 × 8 (H^+) and filtration, the solution was concentrated. To a solution of the residue in EtOH/EtOAc (6.0 mL, 1:1) were added 10% Pd/C (52 mg) and 3 drops of HOAc, and the mixture was stirred under H_2 overnight, then filtered, and concentrated. A solution of the residue in pyridine/acetic anhydride (9.0 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (CH_2Cl_2/acetone, 2:1) of the residue yielded **59**, isolated as a white solid (48 mg, 72%). TLC (CH_2Cl_2/acetone, 2:1): R_f = 0.32. $[\alpha]_D^{20}$ = −18 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$; 2D TOCSY, ROESY, HSQC): δ = 0.89 (t, 3 H, octyl CH_3), 1.09 (t, 3 H, $NHCOCH_2CH_3$), 1.29 (m, 10 H, 5 octyl CH_2), 1.59 (m, 2 H, octyl CH_2), 1.96, 1.97, 2.00, 2.03, 2.06, 2.09, 2.11, and 2.15 (8 s, 3, 3, 3, 3, 3, 6, 3, 3 H, 8 $COCH_3$, $NHCOCH_3$), 2.16 (m, 2 H, $NHCOCH_2CH_3$), 3.41 and 3.63 (2 ddd, each 1 H, octyl OCH_2), 3.63−3.79 (m, 3 H, 2′-H, 4′-H, 5′-H), 3.84−3.90 (m, 2 H, 5-H, 5′′-H), 3.92 (dd, $J_{1'',2''}$ = 8.3, $J_{2'',3''}$ = 11.2 Hz, 1 H, 2′′-H), 4.05−4.14 (m, 4 H, 2-H, 6a-H, 6′′a-H, 6′′b-H), 4.18 (dd, $J_{5,6b}$ = 5.8, $J_{6a,6b}$ = 12.1 Hz, 1 H, 6b-H), 4.29 (dd, $J_{5',6'b}$ = 5.0, $J_{6'a,6'b}$ = 11.8 Hz, 1 H, 6′b-H), 4.34 (dd, $J_{5',6'a}$ = 3.0 Hz, 1 H, 6′a-H), 4.66 (d, 1 H, 1′′-H), 4.72 (d, $J_{1,2}$ < 1 Hz, 2 H, 1-H, 1′-H), 5.10 (dd, $J_{2,3}$ = 3.4, $J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 5.20 (dd, $J_{3'',4''}$ = 3.4 Hz, 1 H, 3′′-H), 5.22 (t, 1 H, 4-H), 5.30 (t, 1 H, 3′-H), 5.32 (d, $J_{4'',5''}$ < 1 Hz, 1 H, 4′′-H), 5.87 (d, $J_{2'',NH''}$ = 8.7 Hz, 1 H, NH′′), 5.94 (d, $J_{2',NH'}$ = 8.6 Hz, 1 H, NH′) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 9.5 ($NHCOCH_2CH_3$), 13.9 (octyl CH_3), 20.4−20.8 ($COCH_3$), 23.0 ($NHCOCH_3$), 22.5, 26.0, 29.1−29.6, and 31.7 (octyl CH_2, $NHCOCH_2CH_3$), 51.5 (C-2′′), 53.9 (C-2′), 61.0, 62.7 (2 C), and 68.3 (C-6, C-6′, C-6′′, octyl OCH_2), 66.1, 66.3, 68.4, 69.6, 70.2, 70.5, 71.2, 72.7, 74.5, and 75.2 (C-2, C-3, C-4, C-5, C-3′, C-4′, C-5′, C-3′′, C-4′′, C-5′′), 97.4 and 99.1 (C-1, C-1′), 100.5 (C-1′′), 169.3−170.7 ($COCH_3$, $NHCOCH_3$), 174.2 ($NHCOCH_2CH_3$) ppm. MS (MALDI-TOF) of $C_{47}H_{72}N_2O_{24}$ (1048): found *m*/*z* = 1049 [M + H]$^+$, 1071 [M + Na]$^+$, 1087 [M + K]$^+$.

Octyl 2-Deoxy-2-propionamido-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (11): To a solution of **59** (33 mg, 31 μmol) in MeOH/CH_2Cl_2 (2.0 mL, 1:1) was added NaOMe (pH = 10), and the mixture was stirred overnight. After neutralisation with Dowex 50 × 8 (H^+) and filtration, the solution was concentrated. The residue was applied on a C18-Bakerbond spe^{tm} column (500 mg), eluted with water and MeOH, and the MeOH fractions were concentrated. Gel-filtration of the residue on a HW-40S Toyopearl column, eluted with aq. 5 mM NH_4OAc, and subsequent lyophilization yielded **11**, isolated as a white foam (17 mg, 77%). TLC (MeOH/CH_2Cl_2, 3:1): R_f = 0.65. $[\alpha]_D^{20}$ = −9 (*c* = 1, H_2O). High-resolution MS of $C_{31}H_{56}N_2O_{16}$ (712.3630): calcd. 735.3528, found 735.3507 [M + Na]. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Octyl (2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (60): To a solution of **56** (50 mg, 35 μmol) in dioxane/water (1.75 mL, 4:1) was added NaOH (35 mg, 0.88 mmol), and the mixture was stirred at room temperature overnight. Then the pH was adjusted to 3 using aq. 4 M HCl, and the stirring was continued overnight. Subsequently, the solution was made alkaline with aq. 1 M NaOH followed by the addition of AcCl (43.8 μL). After stirring at pH = 10 for 45 min, the pH was lowered to 3 using aq. 4 M HCl, and the mixture was stirred overnight, neutralised with solid K_2CO_3, and co-concentrated with toluene. A solution of the residue in pyridine/acetic anhydride (5.3 mL, 2:1) was stirred overnight, then co-concentrated with toluene. The residue was dissolved in CH_2Cl_2, and the solution was washed with aq. 1 M HCl, aq. saturated $NaHCO_3$, and water, dried ($MgSO_4$), filtered, and concentrated. Column chromatography (hexane/EtOAc, 1:2) of the residue yielded **60**, isolated as a colourless syrup (23 mg, 48%). TLC (hexane/EtOAc, 1:2): R_f = 0.36. $[\alpha]_D^{20}$ = +4 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, octyl CH_3), 1.22 (m, 10 H, 5 octyl CH_2), 1.43 (m, 2 H, octyl CH_2), 1.76 (s, 3 H, $NHCOCH_3$), 1.97 and 2.05 (2 s, 3, 6 H, 3 $COCH_3$), 2.99 and 3.17 (2 m, each 1 H, octyl OCH_2), 5.24 (d, $J_{4'',5''}$ < 1 Hz, 1 H, 4′′-H), 6.85−7.62 (m, 29 H, Phth, 5 $OCH_2C_6H_5$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.0 (octyl CH_3), 20.5−20.6 ($COCH_3$), 23.1 ($NHCOCH_3$), 22.5, 25.9, 29.0, 29.2, 29.5, and 31.7 (octyl CH_2), 50.7 (C-2′′), 55.5 (C-2′), 96.9 (2 C) and 100.8 (C-1, C-1′, C-1′′), 169.6−170.2 ($COCH_3$, $NHCOCH_3$) ppm.

Octyl (2-Acetamido-2-deoxy-3,4,6-tri-*O*-propionyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (61): A solution of **60** (54 mg, 40 μmol) in 1-BuOH (5.6 mL) was stirred for 30 min at room temperature, then 1,2-diaminoethane (0.56 mL, 8.4 mmol) was added. The mixture was stirred overnight at 90 °C, then co-concentrated with toluene. A solution of the residue in pyridine/propionic anhydride (4.4 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (toluene/EtOAc, 2:3) of the residue yielded **61**, isolated as a colourless syrup (42 mg, 80%). TLC (toluene/EtOAc, 2:3): R_f = 0.39. $[\alpha]_D^{20}$ = +1 (*c* = 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3 H, octyl CH_3), 1.01 (m, 3 H, $NHCOCH_2CH_3$), 1.04−1.16 (m, 9 H, 3 $COCH_2CH_3$), 1.26 (m, 10 H, 5 octyl CH_2), 1.51 (m, 2 H, octyl CH_2), 1.75 (s, 3 H, $NHCOCH_3$), 1.96 (m, 2 H, $NHCOCH_2CH_3$), 2.25 (m, 6 H, 3 $COCH_2CH_3$), 3.33 (m, 1 H, octyl OCHH), 4.09 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 5.24 (d, $J_{4'',5''}$ < 1 Hz, 1 H, 4′′-H), 7.18−7.41 (m, 25 H, 5 $OCH_2C_6H_5$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 8.7, 8.8, 9.0, and 9.4 ($COCH_2CH_3$, $NHCOCH_2CH_3$), 14.0 (octyl CH_3), 23.1 ($NHCOCH_3$), 22.5, 26.0, 27.2, 29.1−29.5, and 31.7 (octyl CH_2, $COCH_2CH_3$, $NHCOCH_2CH_3$), 51.2 (C-2′′), 56.5 (C-2′), 97.6, 98.0, and 100.2 (C-1, C-1′, C-1′′), 169.8 ($NHCOCH_3$), 173.5−174.5 ($COCH_2CH_3$, $NHCOCH_2CH_3$) ppm.

Octyl (2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-acetyl-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside (62): To a solution of **61** (42 mg, 32 μmol) in MeOH/CH_2Cl_2 (2.0 mL, 1:1) was added NaOMe (pH = 9), and the mixture was stirred overnight. After neutralisation with Dowex 50 × 8 (H^+) and filtration, the solution was concentrated. To a solution of the residue in EtOH/EtOAc (3.0 mL, 1:1) were added 10% Pd/C (27 mg) and 2 drops of HOAc, and the mixture was stirred under H_2 overnight, then filtered through Celite, and concentrated. A solution of the residue in pyridine/acetic anhydride (5.0 mL, 1:1) was stirred overnight, then co-concentrated with toluene. Column chromatography (CH_2Cl_2/acetone, 1:1) of the residue yielded **62**, isolated as a white solid (22 mg, 67%). TLC (CH_2Cl_2/acetone, 1:1): R_f = 0.53. $[\alpha]_D^{20}$ = −21 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$; 2D TOCSY, ROESY, HSQC): δ = 0.89 (t, 3 H, octyl CH_3), 1.11 (t, 3 H, $NHCOCH_2CH_3$), 1.28 (m, 10 H, 5 octyl CH_2), 1.59 (m, 2 H, octyl CH_2), 1.94, 1.98, 2.01, 2.03, 2.06, 2.08, 2.12, and 2.14 (8 s, 3, 3, 3, 3, 3, 6, 3, 3 H, 8 $COCH_3$, $NHCOCH_3$), 2.17 (m, 2 H, $NHCOCH_2CH_3$), 3.40 and 3.63 (2 ddd, each 1 H, octyl OCH_2), 3.65−3.73 (m, 3 H, 2′-H, 4′-H, 5′-H), 3.83−3.91 (m, 3 H, 5-H,

2′′-H, 5′′-H), 4.05 (dd, $J_{5,6a}$ = 2.8, $J_{6a,6b}$ = 11.9 Hz, 1 H, 6a-H), 4.07−4.13 (m, 3 H, 2-H, 6′′a-H, 6′′b-H), 4.17 (dd, $J_{5,6b}$ = 5.7 Hz, 1 H, 6b-H), 4.27 (dd, $J_{5',6'b}$ = 5.2, $J_{6'a,6'b}$ = 12.0 Hz, 1 H, 6′b-H), 4.33 (dd, $J_{5',6'a}$ = 2.6 Hz, 1 H, 6′a-H), 4.66 (d, $J_{1'',2''}$ = 8.1 Hz, 1 H, 1′′-H), 4.67 (s, $J_{1,2}$ < 1 Hz, 1 H, 1-H), 4.77 (d, $J_{1',2'}$ = 7.6 Hz, 1 H, 1′-H), 5.08 (dd, $J_{2,3}$ = 3.5, $J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 5.19 (dd, $J_{2'',3''}$ = 10.8, $J_{3'',4''}$ = 3.3 Hz, 1 H, 3′′-H), 5.21 (t, 1 H, 4-H), 5.32 (d, $J_{4'',5''}$ < 1 Hz, 1 H, 4′′-H), 5.38 (dd, $J_{2',3'}$ = 8.2, $J_{3',4'}$ = 9.4 Hz, 1 H, 3′-H), 5.68 (d, $J_{2',NH'}$ = 8.3 Hz, 1 H, NH′), 5.76 (d, $J_{2'',NH''}$ = 8.8 Hz, 1 H, NH′′) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 9.5 ($NHCOCH_2CH_3$), 13.9 (octyl CH_3), 20.4−20.7 ($COCH_3$), 23.1 ($NHCOCH_3$), 22.5, 25.9, 29.1 (2 C), 29.3, 29.5, and 31.6 (octyl CH_2, $NHCOCH_2CH_3$), 51.6 (C-2′′), 54.4 (C-2′), 61.0, 62.6, 62.7, and 68.2 (C-6, C-6′, C-6′′, octyl OCH_2), 66.1, 66.3, 68.5, 69.6, 70.2, 70.5, 71.3, 72.6, 74.5, and 75.2 (C-2, C-3, C-4, C-5, C-3′, C-4′, C-5′, C-3′′, C-4′′, C-5′′), 97.3 and 99.1 (C-1, C-1′), 100.3 (C-1′′), 169.3−170.8 ($COCH_3$, $NHCOCH_3$), 173.9 ($NHCOCH_2CH_3$) ppm.

Octyl 2-Acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-2-deoxy-2-propionamido-β-D-glucopyranosyl)-(1→2)-α-D-mannopyranoside (12): To a solution of **62** (22 mg, 21 μmol) in $MeOH/CH_2Cl_2$ (2.0 mL, 1:1) was added NaOMe (pH = 9), and the mixture was stirred overnight. After neutralisation with Dowex 50 × 8 (H^+) and filtration, the solution was concentrated. The residue was applied on a C18-Bakerbond spe^{tm} column (500 mg), eluted with water and MeOH, and the MeOH fractions were concentrated. Gel-filtration of the residue on a HW-40S Toyopearl column, eluted with aq. 5 mM NH_4OAc, and subsequent lyophilization yielded **12**, isolated as a white foam (13 mg, 84%). TLC ($MeOH/CH_2Cl_2$, 3:1): R_f = 0.65. $[\alpha]_D^{20}$ = −8 (*c* = 0.5; H_2O). High-resolution MS of $C_{31}H_{56}N_2O_{16}$ (712.3630): calcd. 735.3528, found 735.3515 [M + Na]. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

[1] T. W. Rademacher, R. B. Parekh, R. A. Dwek, *Annu. Rev. Biochem.* **1988**, *57*, 785−838.
[2] R. Schauer, J. P. Kamerling, "Chemistry, biochemistry and biology of sialic acids", in *Glycoproteins II* (Eds.: J. Montreuil, J. F. G. Vliegenthart, H. Schachter), Elsevier, Amsterdam, **1997**, p. 243−402.
[3] P. Sears, C.-H. Wong, *Cell. Mol. Life Sci.* **1998**, *54*, 223−252.
[4] A. Harduin-Lepers, V. Vallejo-Ruiz, M.-A. Krzewinski-Recchi, B. Samyn-Petit, S. Julien, P. Delannoy, *Biochimie* **2001**, *83*, 727−737.
[5] F. Vandekerckhove, S. Schenkman, L. Pontes de Carvalho, S. Tomlinson, M. Kiso, M. Yoshida, A. Hasegawa, V. Nussenzweig, *Glycobiology* **1992**, *2*, 541−548.
[6] K. B. Wlasichuk, M. A. Kashem, P. V. Nikrad, P. Bird, C. Jiang, A. P. Venot, *J. Biol. Chem.* **1993**, *268*, 13971−13977.
[7] G. Baisch, R. Öhrlein, M. Streiff, B. Ernst, *Bioorg. Med. Chem. Lett.* **1996**, *6*, 755−758.
[8] A. Lubineau, K. Basset-Carpentier, C. Augé, *Carbohydr. Res.* **1997**, *300*, 161−167.
[9] C. H. Hokke, J. G. M. van der Ven, J. P. Kamerling, J. F. G. Vliegenthart, *Glycoconjugate J.* **1993**, *10*, 82−90.
[10] J. A. L. M. van Dorst, C. J. van Heusden, A. F. Voskamp, J. P. Kamerling, J. F. G. Vliegenthart, *Carbohydr. Res.* **1996**, *291*, 63−83.
[11] J. A. L. M. van Dorst, C. J. van Heusden, J. M. Tikkanen, J. P. Kamerling, J. F. G. Vliegenthart, *Carbohydr. Res.* **1997**, *297*, 209−227.
[12] J. A. L. M. van Dorst, A. F. Voskamp, J. P. Kamerling, J. F. G. Vliegenthart, *Liebigs Ann./Recueil* **1997**, 1227−1233.
[13] J. A. L. M. van Dorst, J. M. Tikkanen, C. H. Krezdorn, M. B. Streiff, E. G. Berger, J. A. van Kuik, J. P. Kamerling, J. F. G. Vliegenthart, *Eur. J. Biochem.* **1996**, *242*, 674−681.
[14] M. C. Galan, A. P. Venot, J. Glushka, A. Imberty, G. J. Boons, *J. Am. Chem. Soc.* **2002**, *124*, 5964−5973.
[15] R. R. Schmidt, M. Stumpp, *Liebigs Ann. Chem.* **1983**, 1249−1256.
[16] O. Kanie, S. C. Crawley, M. M. Palcic, O. Hindsgaul, *Carbohydr. Res.* **1993**, *243*, 139−164.
[17] S. Nilsson, H. Lönn, T. Norberg, *Glycoconjugate J.* **1989**, *6*, 21−34.
[18] D. P. Khare, O. Hindsgaul, R. U. Lemieux, *Carbohydr. Res.* **1985**, *136*, 285−308.
[19] P. B. van Seeventer, M. A. Corsten, M. P. Sanders, J. P. Kamerling, J. F. G. Vliegenthart, *Carbohydr. Res.* **1997**, *299*, 171−179.
[20] J. Kerékgyártó, J. G. M. van der Ven, A. Lipták, J. P. Kamerling, J. F. G. Vliegenthart, *Carbohydr. Res.* **1993**, *238*, 135−145.
[21] V. Srivastava, O. Hindsgaul, J. U. Baenziger, *Can. J. Chem.* **1987**, *65*, 1645−1652.
[22] P. B. van Seeventer, J. Kerékgyártó, J. A. L. M. van Dorst, K. M. Halkes, J. P. Kamerling, J. F. G. Vliegenthart, *Carbohydr. Res.* **1997**, *300*, 127−138.
[23] J. C. Castro-Palomino, R. R. Schmidt, *Tetrahedron Lett.* **1995**, *36*, 5343−5346.
[24] J. Debenham, R. Rodebaugh, B. Fraser-Reid, *Liebigs Ann./Recueil* **1997**, 791−802.
[25] T. Ziegler, *Carbohydr. Res.* **1994**, *262*, 195−212.
[26] U. Ellervik, G. Magnusson, *Carbohydr. Res.* **1996**, *280*, 251−260.
[27] W. Dullenkopf, J. C. Castro-Palomino, L. Manzoni, R. R. Schmidt, *Carbohydr. Res.* **1996**, *296*, 135−147.
[28] M. S. Newman, F. J. Evans Jr., *J. Am. Chem. Soc.* **1955**, *77*, 946−947.
[29] M. R. E. Aly, J. C. Castro-Palomino, E-S. I. Ibrahim, E-S. H. El-Ashry, R. R. Schmidt, *Eur. J. Org. Chem.* **1998**, *11*, 2305−2316.
[30] M. R. E. Aly, E-S. I. Ibrahim, E-S. H. El-Ashry, R. R. Schmidt, *Carbohydr. Res.* **1999**, *316*, 121−132.

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