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Synthetic studies toward pyruvate acetal-containing saccharides: en route to the efficient synthesis of *Rhizobium*-related exopolysaccharide fragments ☆

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Abstract

The disaccharide building block benzyl *O*-{2,3-di-*O*-benzoyl-4,6-*O*-[(*R*)-1-(methoxycarbonyl)ethylidene]-β-D-galactopyranosyl}-(1→3)-2-*O*-benzoyl-4,6-*O*-[(*S*)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside (**13**), related to a *Rhizobium* exopolysaccharide, was prepared by coupling various 4,6-*O*-[(*R*)-1-(methoxycarbonyl)ethylidene]-D-galactosyl donors (benzoyl-protected chloride **1**, pivaloyl-protected chloride **2**, and benzoyl-protected fluorides **3** and **4**, and trichloroacetimidate **5**) with benzyl 2-*O*-benzoyl-4,6-*O*-[(*S*)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside (**10**) and the corresponding 2,3-*O*-tetraisopropyldisiloxane-protected glucoside **12**. The best results, with respect to β-selectivity and yield of the coupling, were obtained with **5** and **10** in dichloromethane. The β-linked (**13**) and α-linked (**14**) disaccharides were efficiently converted via the 1-OH derivatives **17** and **21** into the corresponding trichloroacetimidates **18** and **22**. The latter were used for the synthesis of the disaccharide ligands 4,6-(*R*)-pyruvate-β-D-Gal*p*-(1→3)-4,6-(*S*)-pyruvate-β-D-Glc*p*-$O(CH_2)_5NH_2$ (**20**), and 4,6-(*R*)-pyruvate-α-D-Gal*p*-(1→3)-4,6-(*S*)-pyruvate-β-D-Glc*p*-$O(CH_2)_5NH_2$ (**24**). The corresponding tri- and tetra-saccharide derivatives 4,6-(*R*)-pyruvate-β-D-Gal*p*-(1→3)-4,6-(*S*)-pyruvate-β-D-Glc*p*-(1→4)-β-D-Glc*p*-$O(CH_2)_5NH_2$ (**28**) and 4,6-(*R*)-pyruvate-β-D-Gal*p*-(1→3)-4,6-(*S*)-pyruvate-β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→4)-β-D-Glc*p*-$O(CH_2)_5NH_2$ (**36**) were obtained similarly.

Keywords: Pyruvate acetal; *Rhizobium* bacteria; Exopolysaccharide

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1. Introduction

Exopolysaccharides and lipooligosaccharides secreted by symbiotic bacteria of the genus *Rhizobium* display a unique structural diversity and are thought to be essential determinants

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☆ Rhizobial Saccharides, Part 1.

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Table 1
Condensation of donors **1**–**5** with acceptors **10** and **12**, respectively

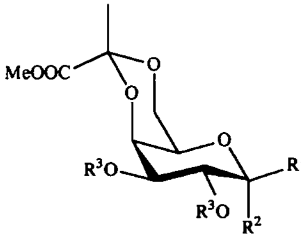
Entry	Donor	Acceptor	Conditions [a]	Products (yield)		
1	**1**	**10**	AgOTf, *sym*-collidine, CH_2Cl_2, r.t. [b]	**13** (trace)	**14** (68%)	
2	**2**	**10**	AgOTf, *sym*-collidine, CH_2Cl_2, r.t.		**15** (82%)	
3	**1**	**10**	Ag-silicate, CH_2Cl_2, r.t.	**13** (28%)	**16** (12%)	
4	**3**	**12**	1 equiv BF_3OEt_2, CH_2Cl_2, r.t. [c]	**13** (trace)	**14** (15%)	**11** (45%)
5	**4**	**12**	1 equiv BF_3OEt_2, CH_2Cl_2, r.t.		**7** (33%)	**8** (47%)
6	**5**	**10**	catal. TMSOTf, CH_3CN, −20°C	**13** (68%)	**14** (12%)	**6** (20%)
7	**5**	**10**	catal. TMSOTf, CH_2Cl_2, 0°C	**13** (80%)	**14** (20%)	

[a] All reactions were performed until the educt was consumed completely.
[b] r.t., Room temperature.
[c] Work-up with Bu_4NF in THF, followed by BzCl–pyridine.

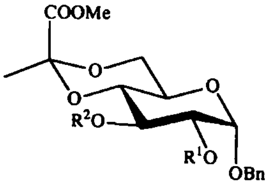
and signal factors for the highly specific interaction of these organisms with their host leguminous plants [1–4]. Synthetic saccharide fragments related to the distinct *Rhizobium* species should therefore be useful probes to obtain deeper insight into the mechanisms of this carbohydrate-mediated cell–cell interaction. Recently, the first chemical syntheses of the NodRm-IV factors (i.e., unique sulfated lipooligosaccharides, responsible for the root hair nodulation of the host plants [4]) have been performed [5] in order to provide sufficient pure material for further biological studies. A significant feature of the rhizobial exopolysaccharides is the presence of acidic pyruvate acetals in many of these carbohydrate structures. For example, the double-pyruvated disaccharide fragment 4,6-(*R*)-pyruvate-β-D-Gal*p*-(1→3)-4,6-(*S*)-pyruvate-β-D-Glc*p* is relatively widespread among various *Rhizobium* species [6–15]. Therefore, this structure appears to be an attractive target for chemical syntheses. We now report on our recent approach to 5-aminopentyl di-, tri-, and tetra-saccharide glycosides derived from this double-pyruvated disaccharide key structure.

2. Results and discussion

Previously, the double-pyruvated laminaribiose derivative 4,6-(*S*)-pyruvate-β-D-Glc*p*-(1→3)-4,6-(*S*)-pyruvate-β-D-Glc*p* — a carbohydrate fragment related to a glycolipid of *Mycobacterium smegmatis* — was prepared by efficient coupling of a 4,6-pyruvated glucosyl donor (halide or trichloroacetimidate) to benzyl 2-*O*-benzoyl-4,6-*O*-[(*S*)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside (**10**) [16]. Furthermore, it was found that, in general, 4,6-pyruvated glucosyl donors were significantly less reactive than their galactosyl counterparts [16,17]. However, undesired side reactions occurred when the more reactive 4,6-pyruvated galactosyl donors were condensed with unreactive nucleophiles [18]. Therefore, a series of 4,6-*O*-[(*R*)-1-(methoxycarbonyl)ethylidene]-D-galactopyranosyl donors (i.e., chlorides **1** [17,18] and **2**, fluorides **3** [18] and **4** [18], and trichloroacetimidate **5** [18]) were condensed with the pyruvated glucosyl acceptor **10** in order to find suitable conditions for the preparation of the β-(1→3)-linked disaccharide **13**. Table 1 summarizes the results of these couplings. Rather unexpectedly, we found almost exclusively the α-(1→3)-linked disaccharide **14** in the silver trifluoromethanesulfonate-promoted condensation of **1** and **10** (entry 1). Although it is known that benzoyl-protected galactosyl halides can give significant amounts of α-linked glycosylation products under similar coupling conditions [19], steric effects may be operative in this case since only traces of the β-product **13** could be detected on TLC of the crude mixture. Spijker and van Boeckel [20] ascribed that selectivity in comparable galactosylations to the formation of a "mismatched" ion pair between donor and acceptor during β-couplings. In contrast, a sterically favoured "matched" ion pair should be possible for the α-case. That such an influence of a "matched–mismatched" ion-pair mechanism may also be effective here was supported by the fact that the more hindered pivaloylated chloride **2** gave *exclusively* the α-linked disaccharide **15** (entry 2). No trace of the corresponding β-product could be detected on TLC. Furthermore, Nakahara and Ogawa [21] recently reported an unusually high α-selectivity when 4,6-*O*-isopropylidene-protected galactosyl donors were used. This was interpreted by the authors in terms of a preferred attack of the nucleophile from the convex side of the donor, leading to the α-linked glycosylation product. Since the 4,6-pyruvated galactosyl donors used here were structurally related to the donors of Nakahara and Ogawa, a similar discrimination between the convex and concave side of the chlorides **1** and **2** seems reasonable in our case. In order to avoid the undesired formation of α-(1→3)-linked products, silver silicate [22,23] was next used as an insoluble promoter that was expected to give higher amounts of β-products. Indeed, when silver silicate was applied to the condensation of **1** and **10** (entry 3), the β-linked product **13** could be isolated besides the ortho ester **16**. Although no α-linked product was found, yields of **13** were unsatisfactory for preparative purposes.

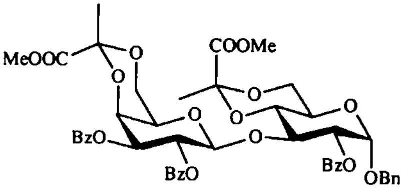


	R¹	R²	R³
1	H	Cl	Bz
2	H	Cl	Piv
3	F	H	Bz
4	H	F	Bz
5	H	OC(NH)CCl$_3$	Bz
6	NHCOCCl$_3$	H	Bz
7	OEt	H	Bz
8	- OH, H -		Bz

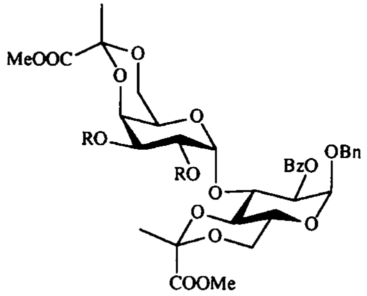


	R^1	R^2
9	H	H
10	Bz	H
11	Bz	Bz
12	- TIPS -	

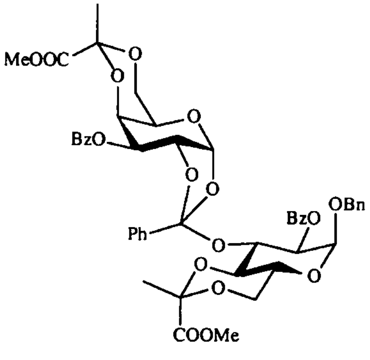
TIPS = $-Si(i\text{-}Pr)_2OSi(i\text{-}Pr)_2-$



13



14 R = Bz
15 R = Piv

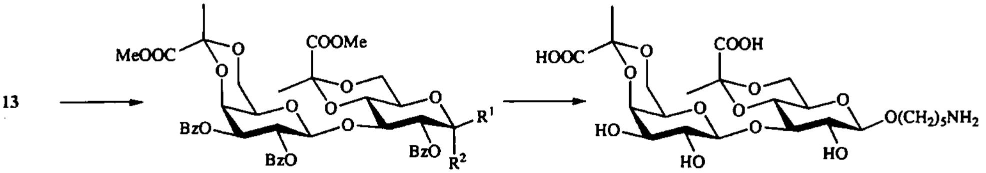


16

We then applied the fluorides **3** and **4** as pyruvated galactosyl donors and the 2,3-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-protected glucosyl acceptor **12**. The latter was recently obtained from diol **9**, and was used for the Lewis acid-catalyzed addition of pyruvated glucosyl fluorides via an efficient glycodesilylation protocol [24], to give double-pyruvated laminaribiosides related to Mycobacteria [25]. Originally, as outlined above, we expected the galactosyl fluorides **3** and **4** to be more reactive than the corresponding pyruvated glucosyl fluorides [16,17]. However, the BF_3-etherate-catalyzed coupling of **3** and **4** with **12** (entries 4 and 5) followed by subsequent desilylation and rebenzoylation of the mixture for entry 4 gave only a small amount of disaccharide **13** in one case. The byproducts **7**, **8**, and **11**, formed either by hydrolysis of the fluorides and the acceptor **12**, respectively, followed by benzoylation during the work-up or by attack of the diethyl ether component of the catalyst, were similar to those previously obtained from Z-protected aminopentanol [18]. Obviously, the otherwise useful glycodesilylation protocol was not applicable for 4,6-pyruvated galactosyl fluorides.

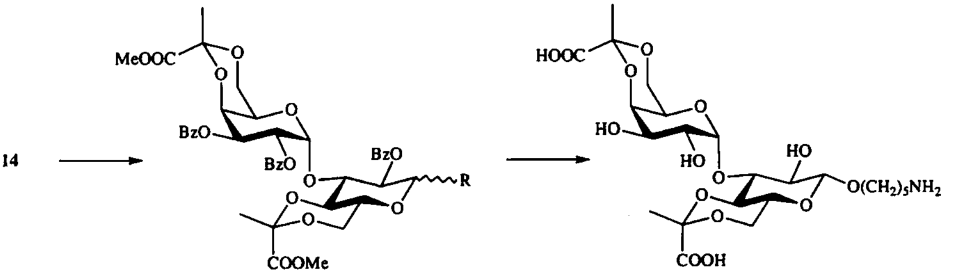
Best results were obtained with the trichloroacetimidate **5** (entries 6 and 7). In acetonitrile as solvent, the disaccharides **13** and **14** were accompanied by the rearrangment product **6** as was previously observed [18] for glycosylations with donor **5**. In dichloromethane, however, 80% of the desired β-(1→3)-linked product **13** could be isolated. Thus, using the imidate **5** in dichloromethane was by far the most effective glycosylation system for the construction of saccharides containing 4,6-pyruvated galactosyl residues and should be used preferentially over other donor-solvent systems.

Further conversion of **13** into 5-aminopentyl di- and tri-saccharide glycosides as well as higher oligosaccharides was performed as previously described for the *Mycobacterium*-related laminaribiose derivatives [16]. Hydrogenolysis of **13** gave first the 1-OH compound **17** (88%), treatment of which with trichloroacetonitrile afforded the imidate **18** (90%). Coupling of the latter with 5-[(benzyloxycarbonyl)amino]pentanol [26] was, however, sluggish and gave compound **19** in poor (40%) yield. This was due to the previously observed reduced reactivity of the amino alcohol derivative in combination with trichloroacetimidates [16,18]. Final sequential deblocking [16] afforded the free ligand **20** (93%).



17 $R^1, R^2 = H, OH$
18 $R^1, R^2 = H, OC(NH)CCl_3$
19 $R^1 = O(CH_2)_5NHZ, R^2 = H$

20

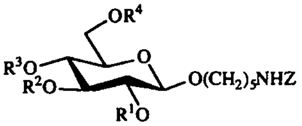


21 R = OH
22 $R = OC(NH)CCl_3$
23 $R = O(CH_2)_5NHZ$

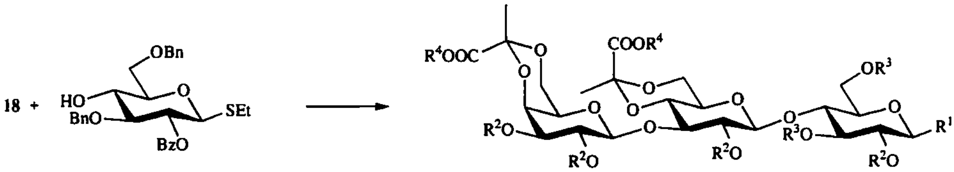
24

Similarly, the α-linked disaccharide **14** was converted via **21** into the imidate **22**, condensation of which with 5-[(benzyloxycarbonyl)amino]pentanol afforded compound **23** (69%) as an inseparable 1:3 α,β-anomeric mixture at the glucose residue. The minor byproduct, having an α-glucose residue, could be removed after debenzoylation of **23**. The final deblocking then gave the disaccharide ligand **24** (76%) which represented an "unnatural" anomeric isomer of the pyruvated rhizobial disaccharide fragment.

In order to demonstrate further the usefulness of the disaccharide donor **18** for the preparation of *Rhizobium*-related oligosaccharide structures the following tri- and tetrasaccharides were synthesized as well. Condensation of the imidate **18** with ethyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-1-thio-β-D-glucopyranoside [16] (**25**) afforded the trisaccharide **26** (73%) that was coupled with 5-[(benzyloxycarbonyl)amino]pentanol to give the blocked aminopentyl glycoside **27** in 68% yield. Deblocking of the latter gave 4,6-(*R*)-pyruvate-β-D-Gal*p*-(1→3)-4,6-(*S*)-pyruvate-β-D-Glc*p*-(1→4)-β-D-Glc*p*-O$(CH_2)_5NH_2$ (**28**) in 75% yield.

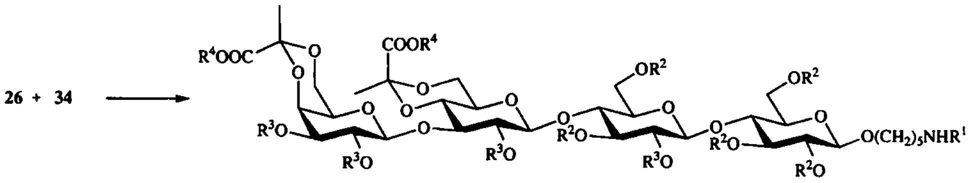


	R^1	R^2	R^3	R^4
29	Ac	Ac	Ac	Ac
30	H	H	H	H
31	H	H	- PhCH -	
32	Bn	Bn	- PhCH -	
33	H	Bn	- PhCH -	
34	Bn	Bn	H	Bn



25

26 R^1 = SEt, R^2 = Bz, R^3 = Bn, R^4 = Me
27 R^1 = $O(CH_2)_5NHZ$, R^2 = Bz, R^3 = Bn, R^4 = Me
28 R^1 = $O(CH_2)_5NH_2$, R^2 = R^3 = R^4 = H



35 R^1 = Z, R^2 = Bn, R^3 = Bz, R^4 = Me
36 R^1 = R^2 = R^3 = R^4 = H

For the construction of the double-pyruvated tetrasaccharide aminopentyl glycoside **36**, the acceptor **34** was needed and prepared as follows. 5-[(Benzyloxycarbonyl)amino]pentanol was glucosylated with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide, to give first **29** (30%), debocking of which (Zemplén) afforded **30** in practically quantitative yield. Next, **30** was treated with benzaldehyde and zinc chloride, and the intermediate **31** (88%) was benzylated at positions 2 and 3, to give **32** (77%). As a byproduct of that benzylation, the 3-*O*-monobenzylated derivative **33** (21%) was obtained as well. Regioselective reduction of the benzylidene moiety of glucoside **32** with sodium cyanoborohydride [27] then afforded **34** in 70% yield. Finally, the tetrasaccharide **35** was obtained in 45% yield via *N*-iodosuccinimide-promoted condensation of donor **26** and acceptor **34**. Deblocking of **35** then gave 4,6-(*R*)-pyruvate-β-D-Gal*p*-(1→3)-4,6-(*S*)-pyruvate-β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→4)-β-D-Glc*p*-O$(CH_2)_5NH_2$ (**36**) in 85% yield.

3. Experimental

General methods.—The NMR data in the Experimental section and in Table 2 were extracted from spectra measured in $CDCl_3$ solutions for blocked compounds (with Me_4Si as internal standard) and in D_2O for deblocked and partially deblocked compounds (with MeOH set to δ 49.3 as internal standard) at 25°C with a Bruker AC 250F spectrometer. ^1H NMR signal assignments of significant peaks were made by first-order analysis of the spectra. Of the two magnetically non-equivalent geminal protons at C-6, the one resonating at lower field was allocated H-6a and the one resonating at higher field H-6b. ^{13}C NMR assignments were made by mutual comparison of the spectra, by DEPT spectra, and by comparison with spectra of related compounds. Optical rotations were measured at 25°C with a Perkin–Elmer automatic polarimeter, Model 241. Melting points were measured with a Büchi apparatus, Model SMP-20. Thin-layer chromatography (TLC) was performed on precoated plastic sheets, Polygram SIL UV_{254}, 40 × 80 mm (Macherey–Nagel) using appropriately adjusted mixtures of CCl_4–acetone for development. Detection was effected with UV light, where applicable, by I_2, and by charring with 5% H_2SO_4 in EtOH. Preparative chromatography was performed by elution from columns of Silica Gel 60 (Merck) using CCl_4–acetone. Solutions in organic solvents were dried with anhyd Na_2SO_4, and concentrated at 2 kPa, ≤40°C.

4,6-O-[(R)-1-(Methoxycarbonyl)ethylidene]-2,3-di-O-pivaloyl-α-D-galactopyranosyl chloride (**2**).—Freshly molten $ZnCl_2$ (15 mg) was added to a solution of methyl 4,6-*O*-[(*R*)-1-(methoxycarbonyl)ethylidene]-2,3-di-*O*-pivaloyl-α-D-galactopyranoside [28] (0.89 g, 2.0 mmol) and dichloromethyl methyl ether (5 mL) in $CHCl_3$ (20 mL), and the mixture was stirred for 10 h at 65°C. Concentration of the mixture and chromatography of the residue gave compound **2** (0.51 g, 57%); $[\alpha]_D$ +188.3° (*c* 1.2, $CHCl_3$); ^1H NMR data: δ 6.44 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.42 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 5.25 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 4.42 (bd, 1 H, $J_{4,5}$ <1 Hz, H-4), 4.03 (bs, 1 H, H-5), 4.04 (s, 2 H, H-6a,6b). Anal. Calcd for $C_{20}H_{31}ClO_9$: C, 53.27; H, 6.93; Cl, 7.86. Found: C, 53.21; H, 7.03; Cl, 8.06.

Benzyl 2,3-di-O-benzoyl-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside (**11**).—BF_3-etherate (1.42 g, 10.0 mmol) was added at room temperature to a

Table 2
^{13}C NMR data [a]

Compound	Chemical shifts (δ)						
	C-1	C-2	C-3	C-4	C-5	C-6	Others
2	92.3	67.2 [b]	67.4 [b]	68.3	64.1	64.7	98.7 C_{acetal}; 52.6, 38.8, 27.0, 25.7 C_{Piv}
13	96.2	69.5	74.8 [b]	74.7 [b]	62.5	64.8 [d]	99.1, 98.4 C_{acetal}
	98.8	72.9 [c]	68.8	73.2 [c]	65.5	65.3 [d]	52.8, 52.3 COO*Me*; 25.3, 25.1 Me
14	95.6	68.6 [c]	76.9	72.0 [b]	61.9 [e]	65.0 [d]	98.8, 98.4 C_{acetal}; 69.7 Bn
	97.2	68.6 [c]	69.5 [c]	73.0 [b]	61.1 [e]	64.8 [d]	52.1, 51.9 COO*Me*; 25.6, 24.8 Me
15	95.4	68.5 [b]	76.3	72.2	61.6 [d]	65.0 [c]	98.7, 98.2 C_{acetal}; 69.6 Bn
	95.8	67.9 [b]	67.0 [b]	71.4	60.8 [d]	64.8 [c]	52.4, 51.9 COO*Me*; 25.5, 25.1 Me
16	96.0	73.8	66.9	77.2	62.2 [d]	65.2 [c]	99.2, 98.4 C_{acetal}; 120.1 $C_{\text{ortho ester}}$
	98.7	70.5 [b]	70.1 [b]	72.1	63.6 [d]	65.4 [c]	52.9, 52.5 COO*Me*; 25.4, 24.3 Me
17 [f]	91.1	69.5	74.5 [b]	74.1 [b]	62.2	64.8	99.1, 98.4 C_{acetal}
	98.6	73.3 [c]	68.8	73.2 [c]	65.5	65.4	52.8, 52.3 COO*Me*, 25.2 2 Me
18 [f]	93.9	69.5	74.6	74.0	65.56 [b]	64.7 [c]	99.3, 98.5 C_{acetal}; 90.7 CCl_3
	98.5	71.3	68.8	73.3	65.8 [b]	65.0 [c]	52.9, 52.3 COO*Me*, 25.2, 25.0 Me
18 [g]	95.6	68.9 [b]	77.4	74.3	65.8 [c]	64.7 [d]	99.3, 98.5 C_{acetal}; 90.7 CCl_3
	98.5	72.1	68.8 [b]	73.1	66.2 [c]	65.0 [d]	52.3 2 COO*Me*, 25.3, 25.1 Me
19	101.6	69.5 [b]	78.0	77.2	64.7	65.8 [c]	99.1, 98.5 C_{acetal}; 66.5 OCH_2; 40.7 NCH_2
	99.1	73.2	68.8 [b]	74.9	65.9 [c]	65.0 [c]	52.7, 52.3 COO*Me*, 25.4, 25.3 Me
20 [h]	104.0	72.1 [c]	80.8	75.4 [b]	67.6 [d]	66.2 [e]	103.2, 102.0 C_{acetal}; 71.6 OCH_2; 40.7 NCH_2
	103.6	71.4 [c]	75.3 [b]	72.9	67.1 [d]	65.6 [e]	26.4, 25.7 Me; 29.5, 27.7, 23.4 CH_2
21 [f]	90.9	69.6 [b]	77.2	72.6 [c]	61.7 [d]	64.9	98.9, 98.5 C_{acetal}
	97.2	68.6 [b]	69.6 [b]	72.3 [c]	61.2 [d]	64.9	52.3, 52.0 COO*Me*; 25.6, 25.0 Me
22 [f]	93.6	68.6	76.3	72.9	61.5	64.9	99.0, 98.5 C_{acetal}; 90.7 CCl_3
	97.5	69.5	68.6	70.9	64.7	64.6	52.3, 52.1 COO*Me*; 25.6, 24.7 Me
22 [g]	96.0	68.5 [b]	75.9	75.9	61.5	64.5	99.0, 98.4 C_{acetal}; 90.1 CCl_3
	97.4	69.3	68.5 [b]	71.6	66.2	64.6	52.1, 52.0 COO*Me*; 25.5, 24.7 Me
23 [g]	101.8	68.6 [b]	77.2	75.9	61.4	64.7	98.9, 98.5 C_{acetal}; 66.5 OCH_2; 40.8 NCH_2
	97.4	69.4	68.5 [b]	72.8	65.7	64.7	52.3, 52.1 COO*Me*; 25.6, 24.8 Me
24 [h]	104.2	69.8 [b]	80.0	73.6 [c]	63.9	66.3 [d]	102.8, 102.0 C_{acetal}; 71.7 OCH_2; 40.7 NCH_2
	100.8	69.3 [b]	78.1	72.7 [c]	66.6	65.8 [d]	26.5, 25.9 Me, 29.4, 27.7, 23.4 CH_2
26	83.4	71.8	81.7 [b]	78.5 [b]	77.2	67.6	23.7 SCH_2; 14.8 SCH_2CH_3
	100.8	69.7 [c]	79.0 [b]	77.2	65.8 [d]	64.8	98.8, 98.5 C_{acetal}; 74.9, 73.4 CH_2Ph
	99.3	72.3	68.8 [c]	75.1	65.7 [d]	64.8	52.7, 52.3 COO*Me*, 25.5 2 Me
27	101.1	73.2	80.3 [b]	76.6 [b]	73.4 [c]	67.5	69.3 Z; 66.5 OCH_2; 40.8 NCH_2
	100.9	69.7 [d]	78.5 [b]	77.2	65.8 [e]	64.8	98.8, 98.5 C_{acetal}; 74.7 2 CH_2Ph
	99.2	73.2	68.9 [d]	75.1 [c]	65.7 [e]	64.8	52.7, 52.3 COO*Me*, 25.5 2 Me
28 [h]	105.7 [b]	77.0	77.0	81.3 [d]	77.7	62.8	72.9 OCH_2; 42.2 NCH_2
	105.3 [b]	68.5	82.2 [d]	77.0	75.9	67.3 [e]	104.2, 103.1 C_{acetal}; 31.0, 29.3, 25.0 CH_2
	104.9 [b]	73.9 [c]	73.1 [c]	74.4 [c]	69.1	67.8 [e]	27.9, 27.3 Me
29	100.4	71.0 [b]	72.5	68.2	71.4 [b]	61.6	69.5 Z; 66.2 OCH_2; 40.6 NCH_2
30 [h]	104.4	75.1 [b]	77.9 [b]	71.7	78.1 [b]	62.8	70.7 Z; 67.3 OCH_2; 41.7 NCH_2
31	103.2	74.5	73.2	80.4	66.3	68.6	101.7 C_{acetal}; 66.6 OCH_2; 40.8 NCH_2
32	103.8	81.9 [b]	81.2 [b]	80.6 [b]	65.7	66.3	100.8 C_{acetal}; 68.5 OCH_2; 40.6 NCH_2
33	103.8	73.1	80.4 [b]	81.8 [b]	66.1	66.6	103.7 C_{acetal}; 68.7 OCH_2; 40.9 NCH_2
34	103.6	81.7 [b]	84.0 [b]	71.5	74.1	66.5	70.3 Z, 69.7 OCH_2; 40.9 NCH_2
	103.1	74.1 [c]	82.8 [b]	78.4 [b]	76.0 [b]	67.7 [e]	69.5 Z, 66.5 OCH_2; 40.8 NCH_2
	100.4	73.5 [c]	81.4 [b]	76.9 [b]	75.2 [b]	67.3 [e]	74.9, 74.6, 73.4, 73.1 CH_2Ph
	100.2	69.6 [d]	80.1 [b]	76.7 [b]	65.6	64.8	98.8, 98.5 C_{acetal}
	99.3	73.3 [c]	68.8 [d]	76.1 [b]	65.6	64.8	52.6, 52.2 COO*Me*; 25.4, 25.3 Me

Table 2 (continued)

Compound	Chemical shifts (δ)						
	C-1	C-2	C-3	C-4	C-5	C-6	Others
36 [h]	105.8 [b]	77.0	77.0	81.5 [d]	77.7	63.0	73.2 OCH_2; 42.2 NCH_2
	105.2 [b]	77.1	77.7	81.1 [d]	77.7	63.0	31.5, 29.3, 25.0 CH_2
	105.2 [b]	68.6	82.0 [d]	75.9 [c]	75.9 [c]	68.6 [e]	104.2, 103.2 COO*Me*
	105.0 [b]	74.3 [c]	75.9 [c]	73.8 [c]	69.1	68.1 [e]	28.0, 27.3 Me

[a] For solutions in $CDCl_3$ unless otherwise indicated. Data in the 1st row of each entry refer to sugar residue 1; data in the 2nd, 3rd, and 4th row, if present, refer to sugar residue 2, 3, and 4, respectively.

[b–e] Assignments may be reversed.

[f] Signals of the α anomer.

[g] Signals of the β anomer.

[h] For solutions in D_2O.

solution of benzyl 2,3-di-*O*-benzoyl-α-D-glucopyranoside [29] (2.36 g, 4.93 mmol) and methyl pyruvate (1.01 g, 10.0 mmol) in MeCN (5 mL), and the mixture was stirred for 2 h, diluted with CH_2Cl_2, and washed with aq $NaHCO_3$. Concentration of the solution and chromatography of the residue gave compound **11** (1.96 g, 76%), identical in all respects to the previously described compound [17,30].

Benzyl 4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-2,3-O-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranoside (**12**).—Compound **11** (1.14 g, 2.0 mmol) was debenzoylated (Zemplén) as previousely described [16], to give crude compound **9**. 1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane [31,32] (0.64 mL, 2.0 mmol) was added at room temperature to a solution of crude compound **9** and imidazole (0.55 g, 8.13 mmol) in DMF (20 mL), and the mixture was stirred for 1.5 h, poured onto water, and extracted with CH_2Cl_2. The organic layers were washed with aq $NaHCO_3$ and concentrated. Chromatography of the residue gave compound **12** (0.94 g, 77%); $[\alpha]_D$ +70.1° (*c* 4.3, $CHCl_3$). For NMR data see Ref [25]. Anal. Calcd for $C_{29}H_{48}O_9Si_2$: C, 58.36; H, 8.11. Found: C, 58.39; H, 8.17.

Benzyl O-{2,3-di-O-benzoyl-4,6-O-[(R)-1-(methoxycarbonyl)ethylidene]-β-(**13**), *and α-D-galactopyranosyl}-(1→3)-2-O-benzoyl-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside* (**14**).—(*a*) A solution of compound **1** [17,18] (1.0 g, 2.0 mmol) and *sym*-collidine (146 mg, 1.21 mmol) in CH_2Cl_2 (5 mL) was added at room temperature to a suspension of compound **10** [16] (0.69 g, 1.5 mmol), silver trifluoromethanesulfonate (0.65 g, 2.51 mmol), and 3A molecular sieves (0.5 g) in CH_2Cl_2 (5 mL), and the mixture was stirred for 0.5 h. Pyridine (2 mL) and BzCl (0.5 mL) were added, and stirring was continued for 0.5 h. The mixture was diluted with CH_2Cl_2, filtered, washed with aq $Na_2S_2O_3$, HCl and aq $NaHCO_3$, and concentrated. Chromatography of the residue gave compound **14** (0.94 g, 68%); $[\alpha]_D$ +223.0° (*c* 1.1, $CHCl_3$); ^1H NMR data: δ 5.93 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1^2), 5.62 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3^2), 5.49 (dd, 1 H, $J_{2,3}$ 10.9 Hz, H-2^2), 5.18–5.14 (m, 2 H, H-1^1, H-2^1), 4.70, 4.47 (2 d, 2 H, *J* −12.2 Hz, CH_2Ph), 4.44 (t, 1 H, $J_{4,5}$ 9.1 Hz, H-4^1), 3.56, 3.15 (2 s, 6 H, 2 COOMe), 1.52, 1.41 (s, 6 H, 2 Me). Anal. Calcd for $C_{48}H_{48}O_{18}$: C, 63.15; H, 5.30. Found: C, 63.04; H, 5.35.

(*b*) A solution of compound **1** (0.86 g, 1.75 mmol) in CH_2Cl_2 (5 mL) was added at −15°C to a suspension of compound **10** (0.60 g, 1.3 mmol), silver silicate [22,23] (1.2

g), and 3A molecular sieves (1.2 g) in CH_2Cl_2 (7 mL), and the mixture was stirred at room temperature for 10 h. The suspension was filtered through a layer of Celite, washed with aq $NaHCO_3$, and concentrated. Chromatography of the residue gave first compound **16** (0.14 g, 12%); $[\alpha]_D$ +132.3° (*c* 1.1, $CHCl_3$); ^1H NMR data: δ 6.26 (d, 1 H, $J_{1,2}$ 4.6 Hz, H-1^2), 5.21 (dd, 1 H, $J_{3,4}$ 4.4 Hz, H-3^2), 5.05 (dd, 1 H, $J_{2,3}$ 9.4 Hz, H-2^1), 4.97 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1^1), 4.95 (dd, 1 H, $J_{2,3}$ 5.5 Hz, H-2^2), 4.65, 4.42 (2 d, 2 H, J −12.4 Hz, CH_2Ph), 4.55 (t, 1 H, $J_{4,5}$ 9.3 Hz, H-4^1), 4.37 (dd, 1 H, $J_{5,6a}$ 2.5 Hz, H-5^2), 4.04 (dd, 1 H, $J_{6a,6b}$ −12.8 Hz, H-$6a^2$), 4.00 (dd, 1 H, $J_{5,6a}$ 4.8, $J_{6a,6b}$ −9.8 Hz, H-$6a^1$), 3.90 (dd, 1 H, $J_{5,6b}$ 2.7 Hz, H-$6b^2$), 3.87 (dd, 1 H, $J_{5,6b}$ 4.8 Hz, H-$6b^1$), 3.82, 3.64 (2 s, 6 H, 2 COOMe), 3.78–3.65 (m, 2 H, H-4^2, H-5^1), 3.46 (t, 1 H, $J_{2,3}$ 9.3 Hz, H-3^1), 1.49, 1.44 (s, 6 H, 2 Me). FABMS: *m/z* 853 $(M-COOMe)^+$; 936 $(M-Na)^+$. Anal. Calcd for $C_{48}H_{48}O_{18}$: C, 63.15; H, 5.30. Found: C, 62.63; H, 5.19.

Eluted next was compound **13** (0.34 g, 28%); $[\alpha]_D$ +107.7° (*c* 1.0, $CHCl_3$); ^1H NMR data: δ 5.72 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2^2), 5.15 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1^2), 5.14–5.10 (m, 1 H, H-2^1), 5.10 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1^1), 5.10 (dd, 1 H, $J_{3,4}$ 3.6 Hz, H-3^2), 4.67, 4.43 (2 d, 2 H, J −12.2 Hz, CH_2Ph), 4.52–4.44 (m, 2 H, H-3^1, H-4^2), 4.18 (dd, 1 H, $J_{5,6a}$ 1.4, $J_{6a,6b}$ −12.7 Hz, H-6a), 3.67 (dd, 1 H, $J_{5,6b}$ 2.5 Hz, H-6b), 3.54 (s, 1 H, H-5), 3.88, 3.62 (2 s, 6 H, 2 COOMe), 1.45, 1.37 (2 s, 6 H, 2 Me). Anal. Calcd for $C_{48}H_{48}O_{18}$: C, 63.15; H, 5.30. Found: C, 62.88; H, 5.25.

(*c*) BF_3-etherate (65 μL, 0.52 mmol) was added at room temperature to a solution of compounds **3** [18] (0.49 g, 1.03 mmol) and **12** (0.61 g, 1.03 mmol) in CH_2Cl_2, and the mixture was stirred for 24 h. The solution was diluted with CH_2Cl_2, washed with aq $NaHCO_3$, and concentrated. The residue was dissolved in THF (10 mL) and treated with a catalytic amount of $Bu_4NF \cdot 3H_2O$ for 3 h at room temperature. The solution was concentrated and the residue was dissolved in a mixture of pyridine (5 mL) and BzCl (2 mL). TLC revealed the formation of traces of compound **13**. After standing for 24 h at room temperature, the mixture was worked up as described under (*a*). Chromatography of the residue gave first compound **14** (0.14 g, 15%).

Eluted next was compound **11** (0.26 g, 45%).

(*d*) Compounds **4** [18] (87 mg, 0.19 mmol) and **12** (113 mg, 0.19 mmol) were treated in CH_2Cl_2 (8 mL) with BF_3-etherate (8 μL, 76 μmol) for 42 h at room temperature as described under (*c*), however, without treatment with Bu_4NF and BzCl. Chromatography gave first compound **7** (32 mg, 33%), identical in all respects to the previously described compound [18].

Eluted next was compound **8** (42.7 mg, 47%), identical in all respects to the previousely described compound [18].

(*e*) TMSOTf (20 μL, 0.11 mmol) was added at −20°C to a solution of compound **10** (0.91 g, 1.0 mmol) in MeCN (7 mL), followed by a solution of compound **5** [18] (0.68 g, 1.1 mmol) in MeCN (2 mL). The mixture was stirred at −20°C for 0.5 h and neutralized by addition of pyridine (1 mL). Benzoyl chloride (0.5 mL) was added, and the mixture was stirred at room temperature for 2 h. Work-up and chromatography as described under (*a*) gave first compound **14** (0.11 g, 12%).

Eluted next was compound **6** (0.14 g, 20%), identical in all respects to the previously described compound [18].

Eluted next was compound **13** (0.62 g, 68%).

(*f*) Compounds **5** (0.5 g, 0.81 mmol) and **10** (0.23 g, 0.5 mmol) were treated in CH_2Cl_2 (2 mL) with TMSOTf (10 μL, 0.05 mmol) at 0°C for 15 min, as described under (*e*). Chromatography gave first compound **14** (90 mg, 20%).

Eluted next was compound **13** (0.36 g, 78%).

*Benzyl O-{4,6-O-[(R)-1-(methoxycarbonyl)ethylidene]-2,3-di-O-pivaloyl-α-*D*-galactopyranosyl}-(1 → 3)-2-O-benzoyl-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-*D*-glucopyranoside* (**15**).—A solution of compound **2** (0.31 g, 0.69 mmol) and *sym*-collidine (56 mg, 0.47 mmol) in CH_2Cl_2 (6 mL) was added at room temperature to a suspension of compound **10** (0.23 g, 0.5 mmol), silver trifluoromethanesulfonate (0.22 g, 0.86 mmol), and 3A molecular sieves (0.5 g) in CH_2Cl_2 (3 mL), and the mixture was stirred for 0.5 h. Workup as described for compound **13** under (*a*) gave compound **15** (0.36 g, 82%); $[\alpha]_D$ +182.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR data: δ 5.70 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1^2), 5.27 (dd, 1 H, $J_{2,3}$ 10.8 Hz, H-2^2), 5.13–5.05 (m, 2 H, H-1^1, H-2^1), 4.96 (dd, 1 H, $J_{3,4}$ 3.7 Hz, H-3^2), 4.70, 4.49 (2 d, 2 H, J −12.3 Hz, CH_2Ph), 3.80, 3.66 (2 s, 6 H, 2 COOMe), 1.51, 1.47 (2 s, 6 H, 2 Me), 1.23, 1.16 (2 s, 18 H, 2 Piv). Anal. Calcd for $C_{44}H_{56}O_{18}$: C, 60.54; H, 6.47. Found: C, 60.40; H, 6.54.

*O-{2,3-Di-O-benzoyl-4,6-O-[(R)-1-(methoxycarbonyl)ethylidene]-β-*D*-galactopyranosyl}-(1 → 3)-2-O-benzoyl-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-*D*-glucopyranose* (**17**).—A suspension of compound **13** (0.6 g, 0.65 mmol) and a catalytic amount of Pd (10% on charcoal) in EtOAc (75 mL) was treated with H_2 (2000–2500 hPa) at room temperature for 20 h. The mixture was filtered and concentrated. Chromatography of the residue gave compound **17** (0.47 g, 88%); ^{1}H NMR data (α anomer): δ 5.73 (dd, 1 H, $J_{2,3}$ 10.2 Hz, H-2^2), 5.46 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^1), 5.17 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1^2), 5.12 (dd, 1 H, $J_{2,3}$ 9.9 Hz, H-2^2), 5.10 (dd, 1 H, $J_{3,4}$ 3.7 Hz, H-3^2), 4.71 (d, 1 H, $J_{1,2}$ 8.0 Hz, β-H-1^1), 4.47 (t, 1 H, $J_{3,4}$ 9.8 Hz, H-3^1), 4.46 (bs, 1 H, $J_{4,5}$ <1 Hz, H-4^2), 4.18 (dd, 1 H, $J_{6a,6b}$ −12.7 Hz, H-6a), 3.96 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 3.82 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4^1), 3.67 (bs, 1 H, $J_{5,6a}$ 1.4 Hz, H-5), 3.54 (bs, 1 H, H-5), 3.87, 3.61 (s, 2 α-COOMe), 3.86, 3.60 (2 s, 2 β-COOMe), 1.42, 1.33 (2 s, 2 Me). Anal. Calcd for $C_{41}H_{42}O_{18}$: C, 59.85; H, 5.15. Found: C, 59.84; H, 5.03.

*O-{2,3-Di-O-benzoyl-4,6-O-[(R)-1-(methoxycarbonyl)ethylidene]-β-*D*-galactopyranosyl}-(1 → 3)-2-O-benzoyl-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-*D*-glucopyranosyl trichloroacetimidate* (**18**).—A mixture of compound **17** (0.32 g, 0.39 mmol), Cl_3CCN (0.12 mL, 1.12 mmol), and K_2CO_3 (91 mg, 0.66 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 2 h. The mixture was centrifuged and decanted, and the solution was concentrated. Chromatography of the residue gave compound **18** (0.34 g, 90%); ^{1}H NMR data (α anomer): δ 8.51 (s, 1 H, NH), 6.50 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1^1), 5.73 (dd, 1 H, $J_{2,3}$ 10.9 Hz, H-2^2), 5.45 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-2^1), 5.23 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1^2), 5.11 (t, 1 H, $J_{4,5}$ 10.5 Hz, H-4^1), 4.54 (t, 1 H, $J_{3,4}$ 9.9 Hz, H-3^1), 4.47 (d, 1 H, $J_{4,5}$ <1 Hz, H-4^2), 3.75 (dd, 1 H, $J_{3,4}$ 3.7 Hz, H-3^2), 3.89, 3.62 (2 s, 2 COOMe), 1.42, 1.34 (2 s, 2 Me); ^{1}H NMR data (β anomer): δ 8.53 (s, 1 H, NH), 6.02 (d, 1 H, $J_{1,2}$ 6.2 Hz, H-1^2), 5.77 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2^1), 5.57 (t, 1 H, $J_{2,3}$ 6.3 Hz, H-2^2), 5.12 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1^1), 5.09 (dd, 1 H, $J_{3,4}$ 3.6 Hz, H-3^2), 4.47 (d, 1 H, $J_{4,5}$ <1 Hz, H-4^2), 3.76, 3.62 (2 s, 2 COOMe), 1.49, 1.43 (2 s, 2 Me). Anal. Calcd for $C_{43}H_{42}Cl_3NO_{18}$: C, 53.40; H, 4.39; Cl, 11.00; N, 1.45. Found: C, 53.29; H, 4.50; Cl, 11.02; N, 1.44.

5-[(Benzyloxycarbonyl)amino]pentyl O-*{2,3-di*-O-*benzoyl-4,6*-O-*[*(R)*-1-(methoxycarbonyl)ethylidene]-β-*D*-galactopyranosyl}-(1→3)-2*-O-*benzoyl-4,6*-O-*[*(S)*-1-(methoxycarbonyl)ethylidene]-α-*D*-glucopyranoside* (**19**).—A solution of compound **18** (0.24 g, 0.25 mmol) in CH_2Cl_2 (3 mL) was added at −20°C during 20 min to a solution of 5-[(benzyloxycarbonyl)amino]pentanol [26] (0.12 g, 0.5 mmol) and TMSOTf (10 μL, 0.05 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred for 1 h. Pyridine (1 mL) and BzCl (0.25 mL) were added, and stirring was continued for 2 h at room temperature. Workup as described for compound **13** under (*a*) and chromatography gave compound **19** (0.10 g, 40%); $[\alpha]_D$ +51.8° (*c* 1.0, $CHCl_3$); ^1H NMR data: δ 5.70 (dd, 1 H, $J_{2,3}$ 10.2 Hz, H-2^2), 5.27 (dd, 1 H, $J_{2,3}$ 8.6 Hz, H-2^1), 5.09–4.59 (m, 4 H, CH_2Ph, H-1^2, H-3^2), 4.50 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1^1), 4.44 (d, 1 H, $J_{4,5}$ < 1 Hz, H-4^2), 4.23 (bd, 1 H, $J_{6a,6b}$ −11.5 Hz, H-$6a^2$), 4.12 (t, 1 H, $J_{3,4}$ 9.1 Hz, H-3^1), 4.09 (dd, 1 H, $J_{6a,6b}$ −10.9, $J_{5,6a}$ 5.7 Hz, H-$6a^1$), 3.94 (dd, 1 H, $J_{5,6b}$ 1.7 Hz, H-$6b^2$), 3.84 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4^1), 3.81, 3.62 (2 s, 6 H, 2 COOMe), 1.47, 1.46 (2 s, 6 H, 2 Me). Anal. Calcd for $C_{59}H_{59}NO_{20}$: C, 62.24; H, 5.71; N, 1.34. Found: C, 62.48; H, 5.85; N, 1.28.

5-Aminopentyl O-*{4,6*-O-*[*(R)*-1-carboxyethylidene]-β-*D*-galactopyranosyl}-(1→3)-4,6*-O-*[*(S)*-1-carboxyethylidene]-β-*D*-glucopyranoside* (**20**).—A solution of compound **19** (60 mg, 57 mmol) in 2:1 toluene–MeOH (5 mL) was treated with a catalytic amount of NaOMe at room temperature for 24 h, neutralized by addition of ion-exchange resign (H^+ form), filtered, and concentrated. The residue was chromatographed on silica gel (10:1 CH_2Cl_2–MeOH); carbohydrate-containing fractions were pooled and concentrated. The residue was dissolved in MeOH (10 mL) and treated with aq NaOH (0.1 M, 1 mL) at 40°C for 3 h. The mixture was neutralized as described above and filtered. A catalytic amount of Pd (10% on charcoal) was added to the filtrate, and the mixture was treated with H_2 (100 hPa) for 12 h. Filtration of the mixture, concentration of the filtrate, and chromatography of the residue on Bio-Gel P2 (water) gave compound **20** (30.4 mg, 93%); $[\alpha]_D$ −12.0° (*c* 0.1, H_2O). FABMS: *m/z* 566 ($M-H^+$).

O-*{2,3-Di*-O-*benzoyl-4,6*-O-*[*(R)*-1-(methoxycarbonyl)ethylidene]-α-*D*-galactopyranosyl}*-(1→3)-2-O-*benzoyl*-4,6-O-[(S)-1-(*methoxycarbonyl*)*ethylidene*]-D-*glucopyranose* (**21**).—A suspension of compound **14** (0.8 g, 0.88 mmol) and a catalytic amount of Pd (10% on charcoal) in EtOAc (50 mL) was treated with H_2 (2000–2500 hPa) at room temperature for 10 h. The mixture was filtered and concentrated. Chromatography of the residue gave compound **21** (0.7 g, 97%); ^1H NMR data (significant signals of the α anomer): δ 5.94 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1^2), 5.66 (dd, 1 H, $J_{2,3}$ 10.9 Hz, H-2^2), 5.49 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1^1), 5.47 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3^2), 4.43 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3^1), 3.56, 3.13 (2 s, 2 COOMe), 1.51, 1.41 (2 s, 2 Me); (significant signals of the β anomer): δ 5.88 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1^2), 5.19 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1^1), 4.84 (t, 1 H, $J_{2,3}$ 8.5 Hz, H-2^1), 3.56, 3.17 (2 s, 2 COOMe), 1.48, 1.37 (2 s, 2 Me). Anal. Calcd for $C_{41}H_{42}O_{18}$: C, 59.85; H, 5.15. Found: C, 59.62; H, 5.16.

O-*{2,3-Di*-O-*benzoyl-4,6*-O-*[*(R)*-1-(methoxycarbonyl)ethylidene]-α-*D*-galactopyranosyl}*-(1→3)-2-O-*benzoyl*-4,6-O-[(S)-1-(*methoxycarbonyl*)*ethylidene*]-D-*glucopyranosyl trichloroacetimidate* (**22**).—A mixture of compound **21** (0.51 g, 0.61 mmol), Cl_3CCN (0.18 mL, 1.76 mmol), and K_2CO_3 (142 mg, 1.03 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 2 h. The mixture was centrifuged and decanted, and the solution was concentrated. Chromatography of the residue gave first the α anomer of compound **22**

(0.11 g, 18%); $[\alpha]_D$ +219.7° (*c* 0.6, $CHCl_3$); ^{1}H NMR data: δ 8.53 (s, 1 H, NH), 6.57 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1^1), 5.95 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1^2), 5.61 (dd, 1 H, $J_{2,3}$ 11.0 Hz, H-2^2), 5.49 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3^2), 5.41 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2^1), 4.52 (t, 1 H, $J_{3,4}$ 9.3 Hz, H-3^1), 4.16 (d, 1 H, $J_{4,5}$ <1 Hz, H-4^2), 3.72 (bs, 1 H, $J_{5,6a}$ 1.2 Hz, H-5^2), 3.85 (bd, 1 H, $J_{6a,6b}$ −12.9 Hz, H-6a^2), 3.56, 3.17 (2 s, 2 COOMe), 1.52, 1.42 (2 s, 2 Me). Anal. Calcd for $C_{43}H_{42}Cl_3NO_{18}$: C, 53.40; H, 4.39; Cl, 11.00; N, 1.45. Found: C, 53.64; H, 4.44; Cl, 10.82; N, 1.34.

Eluted next was the β anomer of compound **22** (0.42 g, 73%); $[\alpha]_D$ +158.8° (*c* 1.3, $CHCl_3$); ^{1}H NMR data: δ 8.72 (s, 1 H, NH), 6.08 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1^1), 5.89 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1^2), 5.66 (dd, 1 H, $J_{2,3}$ 10.9 Hz, H-2^2), 5.60 (t, 1 H, $J_{2,3}$ 8.0 Hz, H-2^1), 5.51 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3^2), 4.22 (t, 1 H, $J_{3,4}$ 9.3 Hz, H-3^1), 4.19 (d, 1 H, $J_{4,5}$ <1 Hz, H-4^2), 4.12 (bd, 1 H, $J_{5,6a}$ 3.8 Hz, H-5^1), 3.99 (t, 1 H, $J_{4,5}$ 9.1 Hz, H-4^1), 3.77 (bd, 1 H, $J_{6a,6b}$ −12.3 Hz, H-6a^2), 3.69 (dd, 1 H, $J_{6a,6b}$ −10.2 Hz, H-6a^1), 3.63 (bs, 1 H, $J_{5,6a}$ 1.0 Hz, H-5^2), 3.37 (bd, 1 H, $J_{5,6b}$ 1.0 Hz, H-6b^2), 3.58, 3.23 (2 s, 2 COOMe), 1.50, 1.37 (2 s, 2 Me). Anal. Calcd for $C_{43}H_{42}Cl_3NO_{18}$: C, 53.40; H, 4.39; Cl, 11.00; N, 1.45. Found: C, 53.34; H, 4.35; Cl, 10.85; N, 1.31.

5-[(Benzyloxycarbonyl)amino]pentyl O-*{2,3-di-*O-*benzoyl-4,6-*O-*[(*R*)-1-(methoxycarbonyl)ethylidene]-α-*D-*galactopyranosyl}-(1→3)-2-*O-*benzoyl-4,6-*O-*[(*S*)-1-(methoxycarbonyl)ethylidene]-*D-*glucopyranoside* (**23**).—A solution of an anomeric mixture of compound **22** (0.44 g, 0.45 mmol) in CH_2Cl_2 (5 mL) was added at −20°C to a solution of 5-[(benzyloxycarbonyl)amino]pentanol (0.24 g, 1 mmol) and BF_3-etherate (40 μL, 0.32 mmol) in CH_2Cl_2 (3 mL), and the mixture was stirred for 30 min. Work-up as described for compound **13** under (*c*) and chromatography gave compound **23** (0.32 g, 69%), as a 1:3 α,β-mixture of anomers at the glucose residue; ^{1}H NMR data (significant signals of the α anomer): δ 6.42 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1^1), 5.93 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1^2), 5.77 (dd, 1 H, $J_{2,3}$ 10.9 Hz, H-2^2), 5.69 (dd, 1 H, $J_{3,4}$ 3.3 Hz, H-3^2), 4.29 (bs, 1 H, $J_{4,5}$<1 Hz, H-4^2), 3.56, 3.16 (2 s, 2 COOMe), 1.48, 1.36 (2 s, 2 Me); (significant signals of the β anomer): δ 5.86 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1^2), 5.59 (dd, 1 H, $J_{2,3}$ 10.9 Hz, H-2^2), 5.47 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3^2), 5.26 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2^1), 4.60 (bd, 1 H, $J_{4,5}$<1 Hz, H-4^2), 4.59 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1^1), 3.56, 3.16 (2 s, 2 COOMe), 1.48, 1.36 (2 s, 2 Me). Anal. Calcd for $C_{59}H_{59}NO_{20}$: C, 62.24; H, 5.71; N, 1.34. Found: C, 62.19; H, 5.95; N, 1.13.

5-Aminopentyl O-*{4,6-*O-*[(*R*)-1-carboxyethylidene]-α-*D-*galactopyranosyl}-(1→3)-4,6-*O-*[(*S*)-1-carboxyethylidene]-β-*D-*glucopyranoside* (**24**).—A solution of compound **23** (360 mg, 0.34 mmol) in 2:1 toluene–MeOH (20 mL) was treated with a catalytic amount of NaOMe at room temperature for 12 h, neutralized by addition of ion-exchange resign (H^+ form), filtered, and concentrated. The residue was chromatographed on silica gel (30:1 CH_2Cl_2–MeOH), and carbohydrate-containing fractions were pooled and concentrated. First eluted was the α anomer at the glucose residue which was discharged. Eluted next was the β anomer at the glucose residue (0.19 g) which was dissolved in MeOH (20 mL) and treated with aq NaOH (0.1 M, 7.8 mL) at room temperature for 48 h and then at 50°C for 48 h. The mixture was neutralized as described above and filtered. A catalytic amount of Pd (10% on charcoal) was added to the filtrate, and the mixture was treated with H_2 (100 hPa) for 12 h. Filtration of the mixture, concentration of the filtrate, and chromatography of the residue on Bio-Gel P2 (water) gave compound **24** (147.3 mg, 76%); $[\alpha]_D$ +250° (*c* 0.1 Hz, H_2O). FABMS: *m*/*z* 566 $(M-H^+)$.

Ethyl O-{2,3-di-O-benzoyl-4,6-O-[(R)-1-(methoxycarbonyl)ethylidene]-β-D-galactopyranosyl}-(1→3)-O-{2-O-benzoyl-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-β-D-glucopyranosyl}-(1→4)-2-O-benzoyl-3,6-di-O-benzyl-1-thio-β-D-glucopyranoside (**26**).—TMSOTf (11 μL, 0.06 mmol) was added at −20°C to a solution of compound **25** [16] (0.26 g, 0.51 mmol) in CH_2Cl_2 (5 mL). A solution of compound **18** (0.58 g, 0.6 mmol) in CH_2Cl_2 (5 mL) was added during 20 min to this mixture, and stirring was continued at −20°C for 2 h. The mixture was neutralized with pyridine, diluted with CH_2Cl_2, washed with aq $NaHCO_3$, and concentrated. Chromatography of the residue gave compound **26** (0.48 g, 73%); $[\alpha]_D$ +34.0° (*c* 1.1, $CHCl_3$); ^{1}H NMR data: δ 5.65 (dd, 1 H, $J_{2,3}$ 10.6 Hz, H-2^3), 5.29 (t, 1 H, $J_{2,3}$ 8.5 Hz, H-2^2), 5.19 (t, 1 H, $J_{2,3}$ 9.3 Hz, H-2^1), 5.06 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3^3), 5.00 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^3), 4.76, 4.54 (2 d, 2 H, *J* −11.2 Hz, C*H*$_2$Ph), 4.65 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^2), 4.58, 4.39 (2 d, 2 H, *J* −12.1 Hz, C*H*$_2$Ph), 4.44 (d, 1 H, $J_{4,5}$ <1 Hz, H-4^3), 4.32 (d, 1 H, $J_{1,2}$ 9.9 Hz, H-1^1), 4.28 (dd, 1 H, $J_{6a,6b}$ −12.6, $J_{5,6a}$ 2.5 Hz, H-6a), 4.05 (t, 1 H, $J_{3,4}$ 9.3 Hz, H-3^1), 3.83, 3.62 (2 s, 6 H, 2 COOMe), 3.39 (dd, 1 H, $J_{6a,6b}$ −10.5, $J_{5,6b}$ 5.5 Hz, H-6b), 2.61 (m, 2 H, SCH_2), 1.50, 1.48 (2 s, 6 H, 2 Me), 1.14 (t, 3 H, *J* 7.5 Hz, SCH_2C*H*$_3$). Anal. Calcd for $C_{70}H_{72}O_{23}S$: C, 64.01; H, 5.53; S, 2.44. Found: C, 63.63; H, 5.50; S, 2.27.

5-[(Benzyloxycarbonyl)amino]pentyl O-{2,3-di-O-benzoyl-4,6-O-[(R)-1-(methoxycarbonyl)ethylidene]-β-D-galactopyranosyl}-(1→3)-O-{2-O-benzoyl-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-β-D-glucopyranosyl}-(1→4)-2-O-benzoyl-3,6-di-O-benzyl-β-D-glucopyranoside (**27**).—A solution of *N*-iodosuccinimide (56 mg, 0.25 mmol) and trifluoromethanesulfonic acid (3 mL, 27 mmol) in 1:1 CH_2Cl_2–diethyl ether (3 mL) was added at −40°C to a suspension of compound **26** (0.29 g, 0.22 mmol), 5-[(benzyloxycarbonyl)amino]pentanol (60 mg, 0.25 mmol), and 4A molecular sieves (0.29 g) in CH_2Cl_2 (5 mL), and the mixture was stirred at −25°C for 2 h. The suspension was diluted with CH_2Cl_2, filtered, and the filtrate was washed with aq $NaHCO_3$ and aq $Na_2S_2O_3$. Concentration of the solution and chromatography of the residue gave compound **27** (0.22 g, 68%); $[\alpha]_D$ +28.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR data: δ 5.66 (dd, 1 H, $J_{2,3}$ 10.2 Hz, H-2^3), 5.29 (t, 1 H, $J_{2,3}$ 8.9 Hz, H-2^2), 5.12 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2^1), 5.06 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3^3), 5.04 (s, 2 H, Z-C*H*$_2$Ph), 5.00 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^3), 4.74, 4.54 (2 d, 2 H, *J* −11.3 Hz, C*H*$_2$Ph), 4.62 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^2), 4.58, 4.27 (2 d, 2 H, *J* −12.1 Hz, C*H*$_2$Ph), 4.44 (d, 1 H, $J_{4,5}$ <1 Hz, H-4^3), 4.28 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^1), 3.83, 3.61 (2 s, 6 H, 2 COOMe), 1.50, 1.47 (2 s, 6 H, 2 Me). FABMS: *m/z* 1489 $(M+H)^+$. Anal. Calcd for $C_{81}H_{85}NO_{26}$: C, 65.36; H, 5.76; N, 0.94. Found: C, 64.80; H, 5.76; N, 0.87.

5-Aminopentyl O-{4,6-O-[(R)-1-carboxyethylidene]-β-D-galactopyranosyl}-(1→3)-O-{4,6-O-[(S)-1-carboxyethylidene]-β-D-glucopyranosyl}-(1→4)-β-D-glucopyranoside (**28**).—A solution of compound **27** (104.2 mg, 70 mmol) in MeOH (15 mL) was treated with a catalytic amount of NaOMe at 40°C for 24 h, neutralized by addition of ion-exchange resign (H^+ form), filtered, and concentrated. The residue was chromatographed on silica gel (20:1 CH_2Cl_2–MeOH), and carbohydrate-containing fractions were pooled and concentrated. The residue was dissolved in MeOH (10 mL), and the solution diluted with water (1 mL) and treated with aq KOH (1 M, 0.1 mL) at 40°C for 24 h. The mixture was neutralized as described above and filtered. Pd (10% on charcoal, 300 mg) was added to the filtrate, and the mixture was treated with H_2 (100 hPa) for 4 days. The mixture was filtered and the catalyst which still contained the saccharide bound to the charcoal was washed with water. Carbohydrates were eluted from the charcoal by washing with aq AcOH (80%) and the combined filtrates were concentrated. Chromatography of the residue on Bio-Gel P2 (water) gave compound **28** (35.9 mg, 70%); $[\alpha]_D$ −22.0° (*c* 1.0 Hz, H_2O). FABMS: *m/z* 730 ($M+H^+$).

5-[(Benzyloxycarbonyl)amino]pentyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**29**). —2,3,4,6-Tetra-*O*-acetyl-*α*-D-glucopyranosyl bromide (7.87 g, 19.14 mmol) was added at room temperature to a suspension of 5-[(benzyloxycarbonyl)amino]pentanol (4.51 g, 19.0 mmol), Ag_2CO_3 (7.6 g, 27.6 mmol), and $CaSO_4$ (20 g) in $CHCl_3$ (90 mL), and the mixture was stirred for 20 h and filtered through a layer of Celite. The filtrate was washed with aq $NaHCO_3$ and aq $Na_2S_2O_3$ and concentrated. The residue was chromatographed and carbohydrate-containing fractions were concentrated. Crystallization of the residue from EtOH gave compound **29** (3.36 g, 30%); mp 74–76°C; $[\alpha]_D$ −15.8° (*c* 1.3, $CHCl_3$); ^{1}H NMR data: δ 4.49 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.97 (dd, 1 H, $J_{2,3}$ 9.4 Hz, H-2), 5.21 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.07 (t, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 3.68 (ddd, 1 H, $J_{5,6a}$ 4.6, $J_{5,6b}$ 2.4 Hz, H-5), 4.26 (dd, 1 H, $J_{6a,6b}$ −12.3 Hz, H-6a), 4.12 (dd, 1 H, H-6b). Anal. Calcd for $C_{27}H_{27}NO_{12}$: C, 57.14; H, 6.57; N, 2.47. Found: C, 57.21; H, 6.56; N, 2.43.

5-[(Benzyloxycarbonyl)amino]pentyl β-D-glucopyranoside (**30**).—A solution of compound **29** (3.7 g, 6.4 mmol) and a catalytic amount of NaOMe in MeOH (75 mL) was stirred at room temperature for 24 h, neutralized with ion-exchange resign (H^+ form), filtered, and concentrated. Crystallization of the residue from EtOAc gave compound **30** (1.6 g, 63%); mp 115–116°C; $[\alpha]_D$ −13.3° (*c* 1.0, MeOH). Anal. Calcd for $C_{19}H_{29}NO_8$: C, 57.13; H, 7.32; N, 3.51. Found: C, 57.11; H, 7.31; N, 3.41.

5-[(Benzyloxycarbonyl)amino]pentyl 4,6-O-benzylidene-β-D-glucopyranoside (**31**).— Freshly molten $ZnCl_2$ (0.2 g) was added to a suspension of compound **30** (1.21 g, 3.03 mmol) in benzaldehyde (3 mL), and the mixture was stirred at room temperature for 48 h. A second catalytic amount of $ZnCl_2$ was added, and stirring was continued for 6 days. The mixture was poured into water and extracted with CH_2Cl_2. The combined organic layers were washed with aq $NaHCO_3$, and concentrated. Chromatography of the residue, concentration of carbohydrate-containing fractions, and crystallization of the residue from EtOH gave compound **31** (1.3 g, 88%); mp 113–116°C; $[\alpha]_D$ −33.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR data: δ 4.39 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.78 (t, 1 H, $J_{2,3}$ 8.8 Hz, H-2), 3.56 (t, 1 H, $J_{3,4}$ 9.1 Hz, H-3), 3.89 (t, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 4.33 (dd, 1 H, $J_{6a,6b}$ −10.4 Hz, H-6a), 3.87–3.96, 3.40–3.49 (2 m, 4 H, H-5,6b, OCH_2). Anal. Calcd for $C_{26}H_{33}NO_8$: C, 64.05; H, 6.82; N, 2.87. Found: C, 63.81; H, 6.87; N, 2.78.

5-[(Benzyloxycarbonyl)amino]pentyl 2,3-di-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (**32**) *and 5-[(benzyloxycarbonyl)amino]pentyl 3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside* (**33**).—A suspension of compound **31** (1.7 g, 3.48 mmol), benzyl bromide (2.5 mL, 20.9 mmol), and powdered KOH (1.21 g, 21.6 mmol) in DMF (10 mL) was stirred at 0°C for 1 h. Methanol was added in order to destroy the excess of benzyl bromide, and stirring was continued for 30 min. The mixture was poured into water, and the precipitate was collected by filtration. The filtrate was extracted with EtOAc and the extracts were combined with a solution of the solid material from the filtration in EtOAc (300 mL). The solution was washed with water and concentrated. Chromatography of the residue gave first compound **32** (1.78 g, 77%); mp 113–117°C (EtOH); $[\alpha]_D$ −30.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR data: δ 4.46 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.32–3.39 (m, 4 H, H-2,3,

OCH_2), 3.41–3.48 (m, 3 H, H-4,5,6b), 4.31 (dd, 1 H, $J_{6a,6b}$ −10.4 Hz, H-6a), 5.05 (s, 2 H, CH_2Ph), 4.90, 4.78 (2 d, 2 H, J −11.5 Hz, CH_2Ph), 4.87, 4.76 (2 d, 2 H, J −11.1 Hz, CH_2Ph). Anal. Calcd for $C_{40}H_{45}NO_8$: C, 71.94; H, 6.79; N, 2.10. Found: C, 71.81; H, 6.75; N, 2.02.

Eluted next was compound **33** (0.42 g, 21%); mp 113–114°C (EtOH); $[\alpha]_D$ −19.5° (c 1.1, $CHCl_3$); ^1H NMR data: δ 4.47 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.32 (dd, 1 H, $J_{2,3}$ 8.8 Hz, H-2), 3.81 (t, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 3.51 (t, 1 H, $J_{4,5}$ 9.1 Hz, H-4), 3.40 (dd, 1 H, $J_{5,6a}$ 4.9, $J_{5,6b}$ 9.8 Hz, H-5), 3.31 (dd, 1 H, $J_{6a,6b}$ −10.4 Hz, H-6a), 3.74 (dd, 1 H, H-6b). Anal. Calcd for $C_{33}H_{39}NO_8$: C, 68.61; H, 6.80; N, 2.42. Found: C, 68.80; H, 6.89; N, 2.34.

5-[(Benzyloxycarbonyl)amino]pentyl 2,3,6-tri-O-benzyl-β-D-glucopyranoside (**34**).—A solution of HCl in diethyl ether was added in small portions at room temperature to a solution of compound **32** (0.84 g, 1.26 mmol), sodium cyanoborohydride (0.99 g, 15.8 mmol), and 3A molecular sieves (1 g) in THF (20 mL) until no more evolution of H_2 could be observed. The solution was diluted with CH_2Cl_2, washed with aq $NaHCO_3$, and concentrated. Chromatography of the residue gave compound **34** (0.59 g, 70%); mp 65–67°C (acetone–n-hexane); $[\alpha]_D$ −10.8° (c 1.2, $CHCl_3$); ^1H NMR data: δ 4.38 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1), 3.36–3.61 (m, 6 H, H-2,3,4,5, OCH_2). Anal. Calcd for $C_{40}H_{47}NO_8$: C, 71.73; H, 7.07; N, 2.09. Found: C, 71.58; H, 7.20; N, 2.00.

5-[(Benzyloxycarbonyl)amino]pentyl O-{2,3-di-O-benzoyl-4,6-O-[(R)-1-(methoxycarbonyl)ethylidene]-β-D-galactopyranosyl}-(1 → 3)-O-{2-O-benzoyl-4,6-O-[(S)-1-(methoxycarbonyl)ethylidene]-β-D-glucopyranosyl}-(1 → 4)-O-(2-O-benzoyl-3,6-di-O-benzyl-β-D-glucopyranosyl)-(1 → 4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**35**).—A solution of N-iodosuccinimide (95 mg, 0.42 mmol) and trifluoromethanesulfonic acid (4 μL, 45 μmol) in 1:1 CH_2Cl_2–diethyl ether (5 mL) was added at −40°C to a suspension of compounds **26** (0.55 g, 0.42 mmol) and **34** (0.28 g, 0.42 mmol) and 4A molecular sieves (0.49 g) in CH_2Cl_2 (5 mL), and the mixture was stirred at −40°C for 3 h. Work-up as described for compound **27** gave compound **35** (0.37 g, 45%); $[\alpha]_D$ +23.0° (c 1.0, $CHCl_3$); ^1H NMR data: δ 5.67 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.2 Hz, H-2^3), 5.29 (t, 1 H, $J_{2,3}$ 8.6 Hz, H-2^2), 5.04 (s, 2 H, CH_2Ph), 4.97 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^3), 4.32 (d, 1 H, $J_{3,4}$ 3.7, $J_{4,5}$ < 1 Hz, H-4^3), 3.82, 3.62 (2 s, 6 H, 2 COOMe), 1.51, 1.47 (2 s, 6 H, 2 Me). FABMS: m/z 1921 $(M)^+$. Anal. Calcd for $C_{108}H_{113}NO_{31}$: C, 67.52; H, 5.93; N, 0.73. Found: C, 67.08; H, 5.96; N, 0.64.

5-Aminopentyl O-{4,6-O-[(R)-1-carboxyethylidene]-β-D-galactopyranosyl}-(1 → 3)-O-{4,6-O-[(S)-1-carboxyethylidene]-β-D-glucopyranosyl}-(1 → 4)-O-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranoside (**36**).—A solution of compound **35** (105.7 mg, 55 μmol) in MeOH (20 mL) was treated exactly as described for compound **28**. Chromatography on Bio-Gel P2 (water) gave compound **36** (42 mg, 85%); $[\alpha]_D$ −26.5° (c 0.6, H_2O). FABMS: m/z 892 $(M+H^+)$.

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