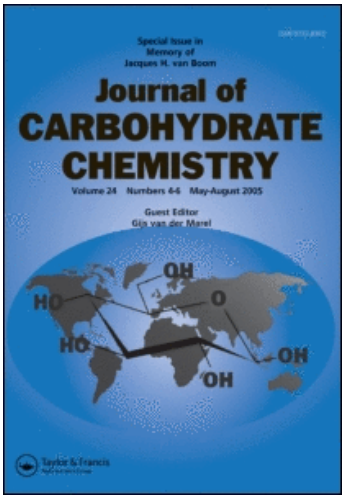

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HIGHLY REGIOSELECTIVE GLYCOSYLATION OF A SECONDARY POSITION IN SUGAR PRIMARY-SECONDARY DITRITYL ETHERS[1]

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ABSTRACT

The glycosylation of sugar primary-secondary ditrityl ethers with glycosylating agents of different kinds occurs regioselectively at the secondary trityloxy group to give good yields of 6-*O*-trityl ethers of 1-2-, 1-3-, and 1-4-linked disaccharides.

INTRODUCTION

It is well known that the primary hydroxyl group in carbohydrates exhibits higher reactivity in the glycosylation reactions than the secondary one.[2] This makes it possible to synthesise oligosaccharides with 1-6-glycosidic linkages by the regioselective glycosylation of the corresponding primary-

secondary diols. Recently, in the framework of a study of the mechanism of the trityl-cyanoethylidene condensation,[3] we have observed an opposite picture, viz., that secondary trityl ethers are considerably more reactive glycosyl acceptors than the primary ones.[4] This implies that the glycosylation of primary-secondary dityrityl ethers should regioselectively occur at the secondary position. Here we describe the regioselective glycosylation of 2,6-, 3,6-, and 4,6-dityrityl ethers of monosaccharides with glycosylating agents of different kinds, and the use of this approach for the synthesis of branched oligosaccharides.

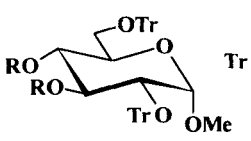
RESULTS AND DISCUSSION

The derivatives of D-glucose (**1-4**), D-mannose (**5**), D-galactose (**6**), and D-glucosamine (**7**) have been used as model dityrityl ethers. Compounds **1-3** and **5** were prepared by conventional acetylation or benzylation of the known[5] dityrityl ethers **8-10**. Compounds **4**, **6**, and **7** were prepared by bis-tritylation of the corresponding 4,6-diols **11-13** using triphenylmethylium perchlorate in the presence of 2,4,6-collidine.[6]

The structure of the dityrityl ethers was confirmed from ^{1}H NMR spectral data. It is noteworthy that the presence of two bulky trityl groups in the molecules of dityrityl ethers does not introduce any pecularities into the pattern of their ^{1}H NMR spectra. The coupling constant values correspond to the ordinary $^4C_1$ conformation of the pyranoid cycle. D-Galactose derivative **6** was an exception: a resolved ^{1}H NMR spectrum could not be obtained at room temperature. This is likely associated with a hindered rotation of trityl groups due to their spatial closeness. A well-resolved spectrum of **6** was obtained at 80 °C in pyridine-d_5, the observed coupling constant values also corresponding to the $^4C_1$ conformation.

The set of glycosylating agents used comprised 1,2-*O*-(1-cyano)ethylidene derivatives (CED) of D-mannose (**14**) and D-galactose (**15**), tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**16**) as well as tetra-*O*-acetyl- and tetra-*O*-benzyl-1-thio-β-D-galactopyranosides (**17**, **18**).

The glycosylation of dityrityl ethers **1-7** with equimolar amounts of CEDs **14** and **15** was conducted in dichloromethane in the presence of 0.1 equiv of triphenylmethylium perchlorate. This resulted in good yields of the



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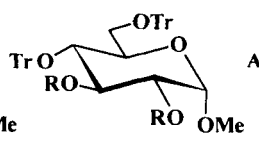

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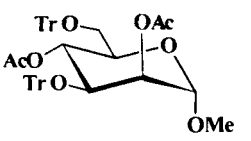

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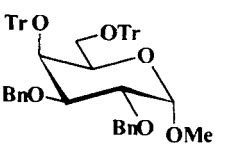

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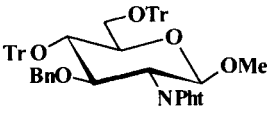

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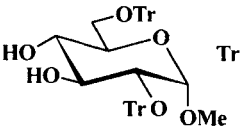

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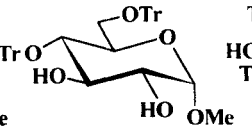

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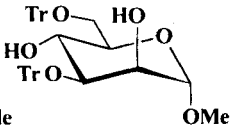

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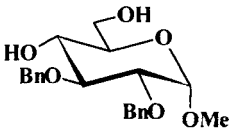

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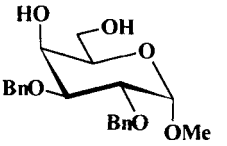

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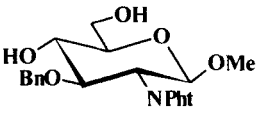

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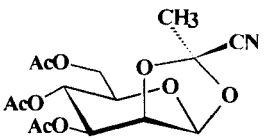

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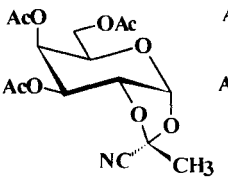

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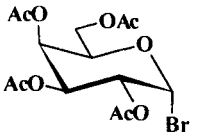

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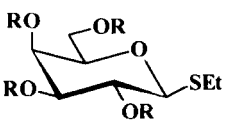

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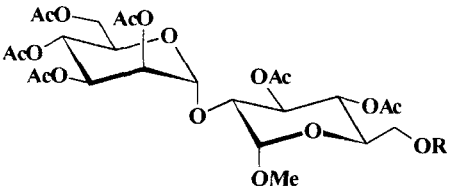
18 R = Bn

products of glycosylation at the secondary position, viz., disaccharide 6-*O*-trityl ethers **19**, **21**, **23**, **24**, **26**, **28**, and **30** (see Table 1).

The position of the glycosidic linkage in the disaccharide derivatives **19**, **21**, **24**, **26**, and **28** has been confirmed by the comparison of their ^{1}H NMR spectral data with those of disaccharides **20**, **22**, **25**, **27**, and **29** derived therefrom upon detritylation and acetylation. This transformation resulted in a

displacement of the signals for H-6 of the "reducing" monosaccharide unit from the region of 3.1-3.8 ppm (—CH_2OTr group) to the region of 4.1-4.6 ppm (—CH_2OAc group). In some cases, the position of a glycosidic linkage



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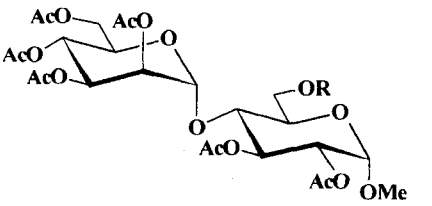
20 R = Ac



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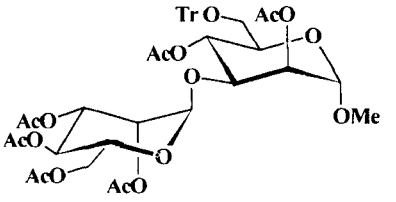
22 R = Ac



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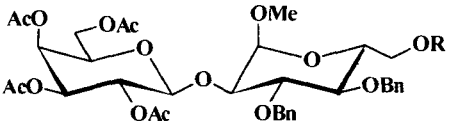

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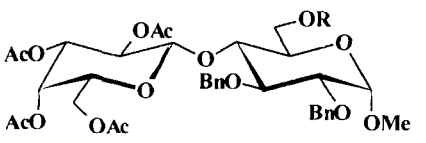
25 R = Ac



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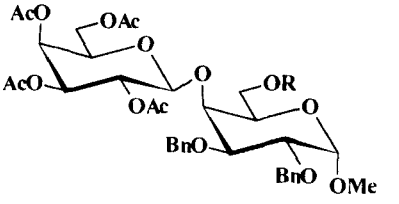
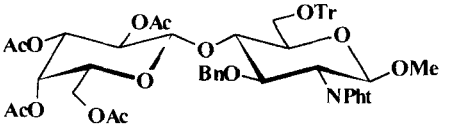
27 R = Ac



28 R = Tr

29 R = Ac



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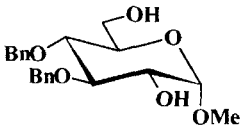
was confirmed from ^{13}C NMR data: the region of 61-62 ppm contained two signals for C-6's of the —CH_2OAc and —CH_2OTr groups.

Table 1. Regioselective glycosylation of sugar dityrityl ethers

Entry	Donor	Acceptor	Product	Yield (%)
1	**14**	**1**	**19**	75
2	**14**	**3**	**21**	53
3	**14**	**5**	**23**	68
4	**15**	**2**	**24**	69
5	**17**	**2**	**24**	72
6	**15**	**4**	**26**	66
7	**16**	**4**	**26**	58
8	**17**	**4**	**26**	69
9	**15**	**6**	**28**	54
10	**15**	**7**	**30**	84
11	**17**	**7**	**30**	89
12	**18**	**2**	**38+39** (2.8:1)	69
13	**18**	**4**	**40+41** (4.8:1)	83

For the purpose of comparison we have carried out the glycosylation of diols **31** and **11**, which correspond to dityrityl ethers **2** and **4**, with glycosyl bromide **16** under the conditions of the Helferich reaction. As expected, 1-6-linked disaccharides **32** and **33** were obtained in both cases. The position of a free hydroxyl group and, respectively, the position of a glycosidic bond in these disaccharide derivatives has been established by ^1H NMR using trichloroacetylisocyanate as a "shift reagent". ^{13}C NMR spectra of the disaccharides **32** and **33** contained only one signal in the region of 61-62 ppm (—CH_2OAc group), while the signal for C-6 involved in the glycosidic bond is displaced to ~68 ppm.

In none of the glycosylations of dityrityl ethers **1-7** was the formation of isomeric 1-6-linked disaccharides observed. Presumably, the latter are not accumulated in the reaction mixture due to subsequent fast glycosylation at the secondary trityloxy group resulting in trisaccharides. In fact, a detailed examination of the reaction mixture (Entry 1, Table 1) revealed that a product of bis-glycosylation, trisaccharide **34**, has been formed.



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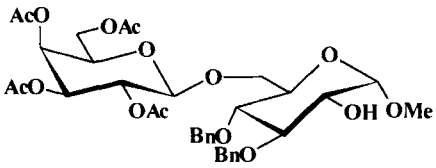

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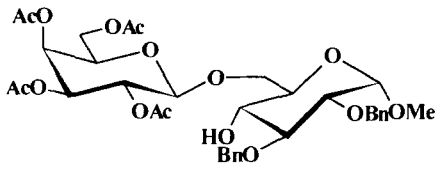

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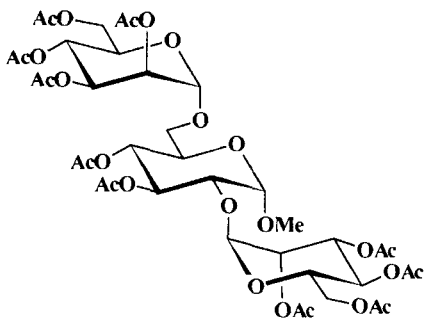

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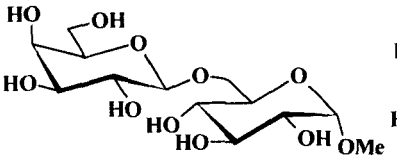
The degree of regioselectivity of the glycosylation of a secondary trityloxy group depends essentially on the nature of the monosaccharide used as the glycosyl donor and on the type of the protective groups adjacent to the trityloxy group in the glycosyl acceptor. The high regioselectivity was achieved in the glycosylation of the acetylated substrates **1**, **3**, and **5** with the D-mannose CED (Entries 1-3). However, the interaction of dityrityl ether **1** with the D-galactose CED **15** afforded a chromatographically homogeneous mixture of three tritylated disaccharides. Following deprotection, the mixture was analyzed by ^{1}H NMR using COSY and COSY RCT techniques that allowed us to identify 1-6-linked disaccharide **35** and anomeric 1-2-linked disaccharides **36** and **37** in a *ca.* 1:1.5:1 ratio. Thus, the reaction of the galactose derivative **15** with the acetylated acceptor **1** exhibits low regioselectivity (~2.5:1) and, additionally, is complicated by low stereoselectivity in the glycosylation at the secondary position.



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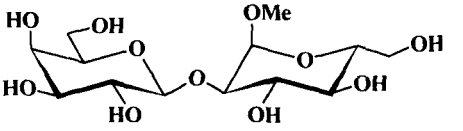

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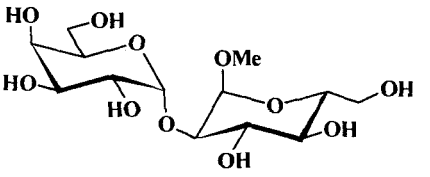

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This result is in accord with our data[4] that it is with D-mannose CED **14** that the maximum difference in the reactivity of the acetylated primary and secondary trityl ethers is observed, whereas it is not so pronounced with the D-galactose derivative **15**.

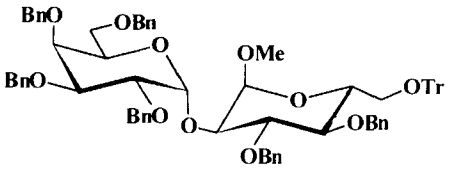
Previously, it was shown that the replacement of an acyl protective group by a benzyl group in a glycosyl acceptor considerably enhanced the reactivity of the adjacent secondary trityloxy function,[7] and the stereoselectivity of the glycosylation also increased.[7,8]

In fact, the glycosylation of a benzyl analogue of **1**, dityrityl ether **2**, with the galactose CED **15** occurs regio- and stereoselectively to give a 69% yield of disaccharide **24** (Entry 4). The use of benzylated glycosyl acceptors makes it possible to selectively glycosylate such low reactive positions as O-4 in *gluco*-series (Entries 6,10) and even O-4 of galactose (Entry 9).

The selective glycosylation of the secondary position in dityrityl ethers is of general character; this can successfully be accomplished not only with cyanoethylidene derivatives, but also with some other types of glycosyl donors, e.g., with galactosyl bromide **16** under the conditions of the Bredereck reactions[9] (Entry 7) or with thiogalactoside **17** using methyl triflate as a promotor (Entries 5,8,11).

α-Glycosylation of dityrityl ethers also proceeds regioselectively at the secondary position. The interaction of the benzylated thiogalactoside **18** with the acceptors **2** and **4** in the presence of methyl triflate resulted in good yields

of α-1-2- and α-1-4-linked disaccharides **38** and **40** together with the corresponding β-anomers, **39** and **41** (Entries 12 and 13).



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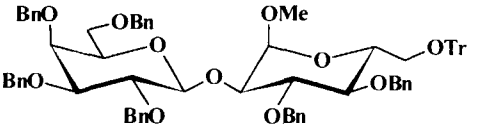

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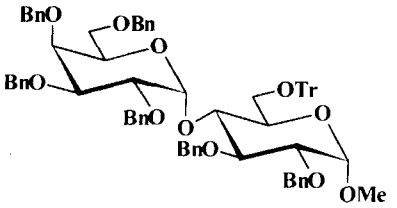

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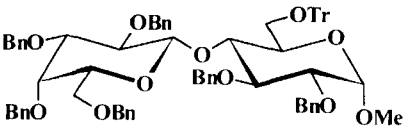

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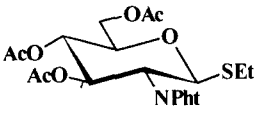
6-*O*-Tritylated disaccharide derivatives obtained in the regioselective glycosylation of the primary-secondary dityrityl ethers are valuable intermediates in the synthesis of branched oligosaccharides, since they may undergo further glycosylation at O-6 either directly or following prior transformation into the corresponding 6-OH-derivatives. The use of this approach for the synthesis of branched oligosaccharides offers certain advantages over conventional ways since it omits selective, temporary protection of O-6 and its subsequent deprotection. An illustration of the realization of this approach is given by the two-step synthesis of the branched trisaccharide **45**, which represents a protected core fragment of N-linked glycan chains of glycoproteins. The first step, the reaction of thioglycoside **42** with ditrityl ether **7** in the presence of methyl triflate, yielded 68% of chitobiose derivative **43**. Its subsequent O-6-glycosylation with thiofucoside **44** gave the target trisacchride **45** in 76% yield together with 21% of the β-anomer **46**.

The regioselective glycosylation of a secondary position in primary-secondary ditrityl ethers is of interest by itself as an unusual example of the reversal of the reactivity of hydroxyl groups. The reaction described allows for considerable expansion of the existing set of approaches to the synthesis of branched oligosaccharides.



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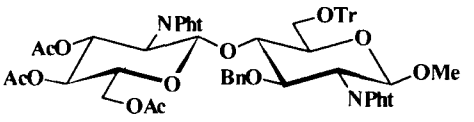

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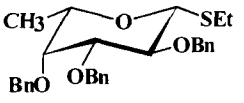

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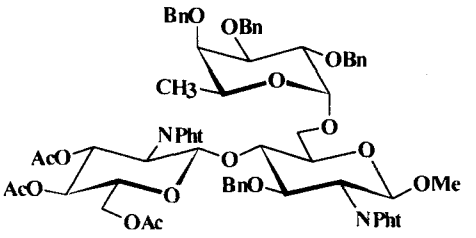

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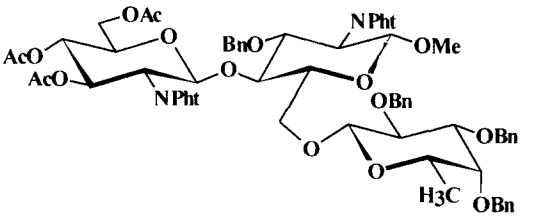

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EXPERIMENTAL

Melting points were determined with a Kofler apparatus and are uncorrected. Optical rotations for solutions in chloroform were measured with a JASCO DIP-360 polarimeter at 20±2 °C. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WM-250 (250 MHz) and Bruker AM-300 (300 MHz) instruments for solutions in deuteriochloroform (unless otherwise stated). Chemical shifts are given in ppm relative to internal tetramethylsilane. TLC was performed on Merck precoated aluminium foil plates F_{254} with UV detection or by charring with 20% sulfuric acid. Column chromatography was performed on silica gel Silpearl (Kavalier, Czechoslovakia) in a medium pressure mode. Preparative HPLC was performed on a Knauer prepacked column (250×16 mm) with LiChrosorb Si 60 (5 μm) using a differential refractometer type 88.00 Knauer. Dichloromethane and acetonitrile were

distilled from P_2O_5 and CaH_2 and stored over molecular sieves 3A (Merck). Ether was distilled from $LiAlH_4$. Solutions were concentrated *in vacuo*.

Methyl 3,4-Di-*O*-acetyl-2,6-di-*O*-trityl-α-D-glucopyranoside (1). Compound **1** was obtained by conventional acetylation of **8**[5] with Ac_2O in pyridine in a nearly quantitative yield as a foam: $[\alpha]_D$ +62.8° (*c* 2); ^1H NMR δ 1.74, 1.82 (2s, 6H, 2 AcO), 3.03 (d, 2H, $J_{6,5}$ = 3.3 Hz, 2 H-6), 3.35 (s, 3H, MeO), 3.51 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 3.85 (dt, 1H, H-5), 3.96 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 4.63 (dd, 1H, $J_{4,3}$ = 9.2 Hz, $J_{4,5}$ =10.2 Hz, H-4), 5.61 (t, 1H, H-3), 7.17-7.53 (m, 30H, aromatics).

Anal. Calcd for $C_{49}H_{46}O_8$ (762.9): C, 77.14; H, 6.08. Found: C, 77.09; H, 6.23.

Methyl 3,4-Di-*O*-benzyl-2,6-di-*O*-trityl-α-D-glucopyranoside (2). To a solution of **8** (1.03 g, 1.52 mmol) in dry DMF (10 mL) was added an 80% suspension of NaH in mineral oil (182 mg, 6.1 mmol), the mixture was stirred for 20 min at room temperature then cooled to 5-7 °C. Benzyl bromide (0.63 mL, 5.3 mmol) was added and the resulting mixture was stirred for 4 h at room temperature. The excess of NaH was destroyed with MeOH, the mixture was diluted with EtOAc, washed with water, dried with $MgSO_4$, and concentrated. Column chromatography of the residue in benzene gave **2** (1.24 g, 95%) as a foam: $[\alpha]_D$ +2.0° (*c* 0.7); ^1H NMR δ 3.07 (dd, 1H, $J_{6a,5}$ = 5.5 Hz, $J_{6a,6b}$ = 10.1 Hz, H-6a), 3.17 (s, 3H, MeO), 3.38 (dd, 1H, $J_{4,5}$ = 9.9 Hz, H-4), 3.39 (dd, 1H, $J_{6b,5}$ = 2.0 Hz, H-6b), 3.46 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 3.70 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 3.76 (ddd, 1H, H-5), 4.13 (t, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 4.22 (d, 1H, J_{gem} = 10.6 Hz, PhCH_2), 4.68 (d, 1H, J_{gem} = 10.6 Hz, PhCH_2), 4.93 (d, 1H, J_{gem} = 10.8 Hz, PhCH_2), 5.16 (d, 1H, J_{gem} = 10.8 Hz, PhCH_2), 6.80-7.70 (m, 40H, aromatics).

Anal. Calcd for $C_{59}H_{54}O_6$ (859.1): C, 82.49; H, 6.34. Found: C, 82.46; H, 6.19.

Methyl 2,3-Di-*O*-acetyl-4,6-di-*O*-trityl-α-D-glucopyranoside (3). Compound **3** was obtained by acetylation of **9**[5] with Ac_2O in pyridine in the presence of 4-dimethylaminopyridine: mp 300-303 °C (benzene-hexane), $[\alpha]_D$ +31.6° (*c* 1.3); ^1H NMR δ 1.18, 2.03 (2s, 6H, 2 AcO), 2.42 (t, 1H, $J_{6a,6b}$ = $J_{6a,5}$ = 10.0 Hz, H-6a), 2.83 (t, 1H, $J_{4,5}$ =10.0 Hz, H-4), 3.28 (dd, 1H, $J_{6b,5}$ = 1.9 Hz, H-6b), 3.70 (s, 3H, MeO), 4.41 (dt, 1H, H-5), 4.46 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 4.85 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.61 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 7.03-7.43 (m, 30H, aromatics).

Anal. Calcd for $C_{49}H_{46}O_8$ (762.9): C, 77.14; H, 6.08. Found: C, 77.28; H, 6.14.

Methyl 2,3-Di-*O*-benzyl-4,6-di-*O*-trityl-α-D-glucopyranoside (4). To a solution of **11**[10] (168 mg, 0.45 mmol) in CH_2Cl_2 (5 mL) were added 2,4,6-collidine (160 μL, 1.22 mmol) and triphenylmethylium perchlorate[11] (385 mg, 1.13 mmol). The mixture was stirred for 3 h at room temperature. A few drops of pyridine were added to destroy excess $TrClO_4$, the solution was diluted with $CHCl_3$, washed with water, and concentrated. The residue was subjected to column chromatography (benzene-hexane-ether 50:50:3) to give **4** (375 mg, 97%) as a foam: $[\alpha]_D$ +52.2° (*c* 0.6); ^{1}H NMR δ 2.43 (t, 1H, $J_{6a,5} = J_{6a,6b}$ = 9.6 Hz, H-6a), 2.63 (dd, 1H, $J_{4,5}$ = 10.2 Hz, $J_{4,3}$ = 8.5 Hz, H-4), 3.23 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 3.30 (dd, 1H, $J_{6b,5}$ = 2.0 Hz, H-6b), 3.67 (s, 3H, MeO), 4.00 (d, 1H, J_{gem} = 11.3 Hz, PhCH_2), 4.05 (t, 1H, H-3), 4.37 (ddd, 1H, H-5), 4.40 (d, 1H, J_{gem} = 12.3 Hz, PhCH_2), 4.53 (d, 1H, J_{gem} = 12.3 Hz, PhCH_2), 4.60 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.75 (d, 1H, J_{gem} = 11.3 Hz, PhCH_2), 6.67-7.37 (m, 40H, aromatics).

Anal. Calcd for $C_{59}H_{54}O_6$ (859.1): C, 82.49; H, 6.34. Found: C, 82.31; H, 6.37.

Methyl 2,4-Di-*O*-acetyl-3,6-di-*O*-trityl-α-D-mannopyranoside (5). Compound **5** was obtained by conventional acetylation of **10**:[5] mp 238-240 °C (EtOAc-hexane); $[\alpha]_D$ +5.6° (*c* 2.1); ^{1}H NMR δ 1.59, 2.23 (2s, 6H, 2 AcO), 3.02 (dd, 1H, $J_{6a,5}$ = 2.2 Hz, $J_{6a,6b}$ = 10.1 Hz, H-6a), 3.17 (dd, 1H, $J_{6b,5}$ = 6.3 Hz, H-6b), 3.29 (s, 3H, MeO), 3.59 (ddd, 1H, H-5), 3.93 (dd, 1H, $J_{3,2}$ = 3.1 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 4.21 (dd, 1H, H-2), 4.61 (d, 1H, $J_{1,2}$ = 2.2 Hz, H-1), 5.38 (t, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 7.17-7.50 (m, 30H, aromatics).

Anal. Calcd for $C_{49}H_{46}O_8$ (762.9): C, 77.14; H, 6.08. Found: C, 77.16; H, 5.92.

Methyl 2,3-Di-*O*-benzyl-4,6-di-*O*-trityl-α-D-galactopyranoside (6). To a solution of **12**[12] (450 mg, 1.2 mmol) in CH_2Cl_2 (10 mL) were added 2,4,6-collidine (0.5 mL, 4.1 mmol) and triphenylmethylium perchlorate (1.23 g, 3.6 mmol). The mixture was stirred for 1.5 h at room temperature, and then worked-up as described for **4**. Column chromatography in hexane-EtOAc (4:1) gave **6** (750 mg, 73%) as a foam: $[\alpha]_D$ +20.8° (*c* 1.5); ^{1}H NMR (Pyr-d_5, 80°C): δ 2.65 (br. d, 1H, $J_{5,6}$ = 6.6Hz, H-5), 3.49 (br. s, 1H, H-4), 3.56 (s, 3H, MeO), 3.67 (dd, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 3.81 (m, 2H, H-6a,6b),

4.33 (d, 1H, J_{gem} = 12.5 Hz, PhCH_2), 4.48 (dd, 1H, $J_{2,3}$ = 8.9 Hz, H-2), 4.57 (d, 1H, J_{gem} = 12.5 Hz, PhCH_2), 4.81 (s, 2H, PhCH_2), 5.23 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1).

Anal. Calcd for $C_{59}H_{54}O_6$ (859.1): C, 82.49; H, 6.34. Found: C, 82.72; H, 6.54.

Methyl 3-*O*-Benzyl-2-deoxy-2-phthalimido-4,6-di-*O*-trityl-β-D-glucopyranoside (7). To a solution of **13**[13] (413 mg, 1 mmol) in CH_2Cl_2 (10 mL) were added 2,4,6-collidine (0.45 mL, 3.4 mmol) and triphenylmethylium perchlorate (1.03 g, 3 mmol). The mixture was stirred for 9 h at room temperature and then worked-up as described for **4**. Column chromatography in hexane-EtOAc (4:1) gave **7** (817 mg, 91%); mp 175-177 °C (EtOAc-hexane); $[\alpha]_D$ +75° (*c* 1.5); ^{1}H NMR δ 2.62 (dd, 1H, $J_{6a,5}$ = 8.6 Hz, $J_{6a,6b}$ = 10.0 Hz, H-6a), 2.85 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 3.34 (dd, 1H, $J_{6b,5}$ = 1.8 Hz, H-6b), 3.55 (s, 3H, MeO), 3.85 (d, 1H, J_{gem} = 12.0 Hz, PhCH_2), 3.93 (d, 1H, PhCH_2), 3.94 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2), 4.26 (ddd, 1H, H-5), 4.63 (dd, 1H, $J_{3,4}$ = 8.0 Hz, H-3), 5.15 (d, 1H, $J_{1,2}$ = 8.7 Hz, H-1), 6.53-7.42 (m, 39H, aromatics).

Anal. Calcd for $C_{60}H_{51}NO_7$ (898.1): C, 80.25; H, 5.72; N, 1.56. Found: C, 80.31; H, 5.67; N, 1.64.

General procedure for glycosylation of the dityrityl ethers with cyanoethylidene derivatives (Procedure A). In one limb of a tuning-fork-shaped tube were placed a solution of equimolar amounts of a dityrityl ether and a cyanoethylidene derivative in benzene, and in the other, a solution of triphenylmethylium perchlorate (0.1 equiv) in nitromethane. The tube was attached to a high-vacuum system and the solutions were lyophilised. CH_2Cl_2 was distilled into the reaction tube and the solutions of the reactants were mixed. After time specified (see below), a drop of pyridine was added, the mixture was diluted with $CHCl_3$, washed with water, and concentrated. The target disaccharides were isolated from the residue by column chromatography.

General procedure for glycosylation of the dityrityl ethers with the thiogalactoside 17 (Procedure B). A mixture of a dityrityl ether, **17** (1.1-1.2 equiv), and molecular sieves 3A in CH_2Cl_2 was stirred under argon for 1 h at room temperature. Methyl triflate (3 equiv relative to **17**) was added and the stirring was continued for 2-3 h. The reaction was quenched by addition of a few drops of pyridine. The solids were filtered off and washed with $CHCl_3$,

the filtrate was washed with water and concentrated. Column chromatography of the residue gave the target disaccharides.

The following 6-*O*-tritylated disaccharides were obtained:

Methyl 3,4-Di-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-6-*O*-trityl-α-D-glucopyranoside (19). Compounds **1** (433 mg, 0.57 mmol) and **14**[14] (198 mg, 0.54 mmol) were allowed to react according to the procedure A for 17 h. Column chromatography of the reaction mixture in benzene-EtOAc (4:1) gave first **19** (346 mg, 75%). Further elution with benzene-acetone (4:1) gave methyl 3,4-di-*O*-acetyl-2,6-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-glucopyranoside (**34**) (67 mg, 12.5%).

Compound **19** was obtained as a foam: $[\alpha]_D$ +106° (*c* 0.6); ^{1}H NMR δ 1.74, 2.00, 2.04, 2.06, 2.16, 2.19 (6s, 18H, 6 AcO), 3.09 (dd, 1H, $J_{6a,5}$ = 5.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H-6a), 3.23 (dd, 1H, $J_{6b,5}$ = 2.2 Hz, H-6b), 3.50 (s, 3H, MeO), 3.90 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-2), 3.91 (ddd, 1H, H-5), 4.05 (ddd, 1H, H-5'), 4.22 (m, 2H, H-6'a,6'b), 4.97 (d, 1H, $J_{1',2'}$ = 1.5 Hz, H-1'), 4.98 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.05 (dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 5.25 (m, 3H, H-2',3',4'), 5.41 (t, 1H, $J_{3,4}$ = 10.1 Hz, H-3), 7.20-7.48 (m, 15H, aromatics).

Anal. Calcd for $C_{44}H_{50}O_{17}$ (850.9): C, 62.11; H, 5.92. Found: C, 62.23; H, 6.05.

Compound **34** was obtained as a foam: $[\alpha]_D$ +97.9° (*c* 2.3); ^{1}H NMR δ 1.98×2, 2.03, 2.05×2, 2.07, 2.10, 2.13, 2.16, 2.17 (8s, 30H, 10 AcO), 3.47 (s, 3H, MeO), 3.55 (dd, 1H, $J_{6a,5}$ = 2.5 Hz, $J_{6a,6b}$ = 10.8 Hz, H-6a Glc), 3.73 (dd, 1H, $J_{6b,5}$ = 5.4 Hz, H-6b Glc), 3.83 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2 Glc), 3.98 (m, 3H, H-5 Glc, Man, Man'), 4.05-4.30 (m, 4H, H-6 Man, Man'), 4.84 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-1 Man), 4.89 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1 Glc), 4.93 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1 Man'), 4.97 (dd, 1H, $J_{4,5}$ = 10.1 Hz, H-4 Glc), 5.16-5.31 (m, 6H, H-2,3,4 Man, Man'), 5.46 (t, 1H, $J_{3,4}$ = 9.2 Hz, H-3 Glc).

Anal. Calcd for $C_{39}H_{54}O_{26}$ (938.8): C, 49.89; H, 5.80. Found: C, 49.94; H, 5.68.

Methyl 2,3-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-6-*O*-trityl-α-D-glucopyranoside (21). Glycosylation of **3** (168 mg, 0.22 mmol) with **14** (78.5 mg, 0.22 mmol) according to the procedure A for 17 h followed by column chromatography in benzene-EtOAc (4:1) afforded **21** (99 mg, 53%) as a foam: $[\alpha]_D$ +57.1° (*c* 0.8); ^{1}H NMR δ 1.98, 1.99, 2.02, 2.06, 2.07, 2.08 (6s, 18H, 6 AcO), 3.32 (dd, 1H, $J_{6a,5}$ = 6.7 Hz, $J_{6a,6b}$ = 10.1 Hz,

H-6a), 3.50 (dd, 1H, $J_{6b,5}$ = 2.1 Hz, H-6b), 3.52 (s, 3H, MeO), 3.55 (m, 2H, H-5',6'a), 3.74 (t, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 3.84 (dd, 1H, $J_{6'b,5}$ = 5.0 Hz, $J_{6'b,6'a}$ = 12.9 Hz, H-6'b), 3.94 (ddd, 1H, H-5), 4.82 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2), 4.95 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.96 (d, 1H, $J_{1',2'}$ = 2.0 Hz, H-1'), 4.99 (t, 1H, $J_{2',3'}$ = 2.0 Hz, H-2'), 5.10 (dd, 1H, $J_{3',4'}$ = 9.7 Hz, H-3'), 5.16 (t, 1H, $J_{4',5'}$ = 9.7 Hz, H-4'), 5.53 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 7.20-7.50 (m, 15H, aromatics).

Anal. Calcd for $C_{44}H_{50}O_{17}$ (850.9): C, 62.11; H, 5.92. Found: C, 62.02; H, 5.98.

Methyl 2,4-Di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-6-*O*-trityl-α-D-mannopyranoside (23). Glycosylation of **5** (450 mg, 0.59 mmol) with **14** (201 mg, 0.56 mmol) according to the procedure A for 17 h and subsequent column chromatography in hexane-EtOAc (1:1) gave **23** (322 mg, 68%) as a foam: $[\alpha]_D$ +25.6° (*c* 2.3); ^{1}H NMR δ 1.74, 1.90, 1.98, 2.04, 2.05, 2.13 (6s, 18H, 6 AcO), 3.04 (dd, 1H, $J_{6a,5}$ = 2.5 Hz, $J_{6a,6b}$ = 10.6 Hz, H-6a), 3.17 (dd, 1H, $J_{6b,5}$ = 6.4 Hz, H-6b), 3.40 (s, 3H, MeO), 3.71 (ddd, 1H, H-5), 4.00 (m, 2H, H-5',6'a), 4.05 (dd, 1H, $J_{2,3}$ = 3.6 Hz, H-3), 4.20 (dd, 1H, $J_{6'b,5'}$ = 6.0 Hz, $J_{6'b,6'a}$ = 11.8 Hz, H-6'b), 4.67 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.85 (d, 1H, $J_{1',2'}$ = 1.6 Hz, H-1'), 4.89 (dd, 1H, $J_{2',3'}$ = 2.8 Hz, H-2'), 5.10 (t, 1H, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, H-4), 5.14 (m, 3H, H-2,3',4'), 7.10-7.42 (m, 15H, aromatics). ^{13}C NMR δ 54.9 (MeO), 62.5, 63.0 (C-6,6'), 66.2 (C-4'), 68.4×2, 69.4, 70.2, 70.6, 71.1 (C-2,2',3',4,5,5'), 74.7 (C-3), 86.9 (Ph_3C), 98.4, 98.8 (C-1,1').

Anal. Calcd for $C_{44}H_{50}O_{17}$ (850.9): C, 62.11; H, 5.92. Found: C, 62.10; H, 5.99.

Methyl 3,4-Di-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-trityl-α-D-glucopyranoside (24). (a) Glycosylation of **2** (313 mg, 0.365 mmol) with **15**[14] (130 mg, 0.365 mmol) according to the procedure A for 3 h followed by column chromatography in benzene-EtOAc (85:15) gave **24** (238 mg, 69%) as a foam: $[\alpha]_D$ +25.6° (*c* 0.8); ^{1}H NMR δ 1.71, 2.00, 2.10, 2.19 (4s, 12H, 4 AcO), 3.22 (dd, 1H, $J_{6a,5}$ = 4.2 Hz, $J_{6a,6b}$ = 10.4 Hz, H-6a), 3.44 (s, 3H, MeO), 3.54 (dd, 1H, $J_{6b,5}$ = 1.8 Hz, H-6b), 3.72 (dd, 1H, $J_{4,5}$ = 10.2 Hz, H-4), 3.79 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 3.81 (m, 1H, H-5), 3.97 (dd, 1H, $J_{3,4}$ = 8.5 Hz, H-3), 3.98 (m, 1H, H-5'), 4.18 (dd, 1H, $J_{6'a,5'}$ = 5.9 Hz, $J_{6'a,6'b}$ = 11.4 Hz, H-6'a), 4.25 (dd, 1H, $J_{6'b,5'}$ = 7.3 Hz, H-6'b), 4.28 (d, 1H, J_{gem} = 10.5 Hz, PhCH_2), 4.64 (d, 1H, J_{gem} =

10.5 Hz, PhCH_2), 4.74 (d, 1H, J_{gem} = 11.3 Hz, PhCH_2), 4.83 (d, 1H, J_{gem} = 11.3 Hz, PhCH_2), 4.83 (d, 1H, $J_{1',2'}$ = 8.1 Hz, H-1'), 4.97 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.03 (dd, 1H, $J_{3',4'}$ = 3.5 Hz, H-3'), 5.40 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 5.42 (dd, 1H, $J_{4',5'}$ = 1.1 Hz, H-4'), 6.75-7.53 (m, 25H, aromatics). ^{13}C NMR δ 55.0 (MeO), 62.1, 62.5 (C-6,6'), 67.2 (C-4'), 69.1 (C-2'), 70.2, 71.0, 71.5 (C-3',5,5'), 75.1, 75.4 (2 PhCH_2), 78.4 (C-4), 80.9 (C-2), 81.9 (C-3), 86.3 (Ph$_3$C), 99.2 (C-1), 102.5 (C-1').

Anal. Calcd for $C_{54}H_{58}O_{15}$ (947.1): C, 68.49; H, 6.17. Found: C, 68.55; H, 6.14.

(b) Reaction of **2** (366 mg, 0.43 mmol) with **17** (209 mg, 0.53 mmol) according to the procedure B for 2 h gave **24** (292 mg, 72%), identical with that obtained in run (a).

Methyl 2,3-Di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-trityl-α-D-glucopyranoside (26). (a) Reaction of **4** (385 mg, 0.45 mmol) with **15** (160 mg, 0.45 mmol) according to the procedure A for 4 h followed by column chromatography in benzene-EtOAc (9:1) afforded **26** (281 mg, 66%) as a foam: $[\alpha]_D$ -26.2° (*c* 0.9); ^{1}H NMR δ 1.67, 1.97, 2.04, 2.10 (4s, 12H, 4 AcO), 3.11 (dd, 1H, $J_{6a,5}$ = 2.6 Hz, $J_{6a,6b}$ = 10.2 Hz, H-6a), 3.57 (m, 3H, H-5,5',6b), 3.64 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.84 (t, 1H, $J_{4,5}$ = 9.1 Hz, H-4), 4.06 (dd, 1H, $J_{6'a,5'}$ = 5.6 Hz, $J_{6'a,6'b}$ = 10.9 Hz, H-6'a), 4.19 (dd, 1H, $J_{6'b,5'}$ = 8.6 Hz, H-6'b), 4.28 (dd, 1H, $J_{3,4}$ = 8.8 Hz, H-3), 4.46 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.67 (dd, 1H, $J_{3',4'}$ = 3.6 Hz, H-3'), 4.74 (d, 1H, J_{gem} = 10.3 Hz, PhCH_2), 4.75 (d, 1H, J_{gem} = 12.4 Hz, PhCH_2), 4.77 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.90 (d, 1H, J_{gem} = 12.4 Hz, PhCH_2), 4.97 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 4.99 (d, 1H, J_{gem} = 10.3 Hz, PhCH_2), 5.25 (dd 1H, $J_{4',5'}$ = 0.9 Hz, H-4'), 7.22-7.60 (m, 25H, aromatics). ^{13}C NMR δ 55.3 (MeO), 60.5, 61.4 (C-6,6'), 66.8 (C-4'), 69.3, 69.7, 70.4, 71.0 (C-2',3',5,5'), 73.6 (PhCH_2), 75.5 C-4), 75.8 (PhCH_2), 79.5, 79.8 (C-2,3), 86.3 (Ph$_3$C), 98.5 (C-1), 99.2 (C-1').

Anal. Calcd for $C_{54}H_{58}O_{15}$ (947.1): C, 68.49; H, 6.17. Found: C, 68.54; H, 6.15.

(b) Glycosylation of **4** (359 mg, 0.42 mmol) with **17** (206 mg, 0.525 mmol) according to the procedure B for 2 h afforded **26** (273 mg, 69%) identical with that obtained in run (a).

(c) A mixture of **4** (461 mg, 0.54 mmol), AgOTf (139 mg, 0.54 mmol), and 2,4,6-collidine (7 μL, 0.054 mmol) was lyophilised from benzene. A solution of **16** (221 mg, 0.54 mmol) (that has been previously lyophilised from

benzene) in CH_2Cl_2 (5 mL) was added dropwise to a solution of the above mixture in CH_2Cl_2 (3 mL) at room temperature. After 5 min, a few drops of pyridine were added, the mixture was filtered, the filtrate was diluted with $CHCl_3$, washed with M $Na_2S_2O_3$, and water, and concentrated. Column chromatography of the residue gave **26** (294 mg, 58%).

Methyl 2,3-Di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-trityl-α-D-galactopyranoside (28). Glycosylation of **6** (352 mg, 0.41 mmol) with **15** (146 mg, 0.41 mmol) according to the procedure A for 3 h and subsequent column chromatography in benzene-EtOAc (9:1) afforded **28** (206 mg, 54%) as a foam: $[\alpha]_D$ +12.6° (*c* 2.1); ^{1}H NMR δ 1.82, 1.96, 2.00, 2.13 (4s, 12H, 4 AcO), 3.25 (dd, 1H, $J_{6a,5}$ = 4.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H-6a), 3.43 (s, 3H, MeO), 3.48 (dd, 1H, $J_{6b,5}$ = 7.4 Hz, H-6b), 3.62 (ddd, 1H, H-5), 3.68, 3.76 (2m, 4H, H-2,3,5',6'a), 3.85 (br. s, 1H, H-4), 3.94 (dd, 1H, $J_{6'a,5'}$ = 9.7 Hz, $J_{6'b,6'a}$ = 12.6 Hz, H-6'b), 4.60 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2), 4.64 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2), 4.64 (d, 1H, $J_{1',2'}$ = 7.4 Hz, H-1'), 4.68 (d, 1H, $J_{1,2}$ = 2.5 Hz, H-1), 4.76 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2), 4.84 (d, 1H, J_{gem} = 11.5 Hz, PhCH_2), 4.94 (dd, 1H, $J_{3',4'}$ = 3.3 Hz, H-3'), 5.07 (dd, 1H, $J_{2',3'}$ = 10.2 Hz, H-2'), 5.29 (dd, 1H, $J_{4',5'}$ = 0.9 Hz, H-4'), 7.20-7.48 (m, 25H, aromatics).

Anal. Calcd for $C_{54}H_{58}O_{15}$ (947.1): C, 68.49; H, 6.17. Found: C, 68.44; H, 6.25.

Methyl 3-*O*-Benzyl-2-deoxy-2-phthalimido-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-trityl-β-D-glucopyranoside (30). (a) Glycosylation of **7** (714 mg, 0.79 mmol) with **15** (284 mg, 0.79 mmol) according to the procedure A for 3 h followed by column chromatography in benzene-EtOAc (85:15) gave **30** (654 mg, 84%) as a foam: $[\alpha]_D$ +1.6° (*c* 2.7); ^{1}H NMR δ 1.67, 1.96, 2.06, 2.11 (4s, 12H, 4 AcO), 3.11 (dd, 1H, $J_{6a,5}$ = 2.2 Hz, $J_{6a,6b}$ = 10.2 Hz, H-6a), 3.46 (s, 3H, MeO), 3.47 (ddd, 1H, $J_{5,4}$ = 10.4 Hz, H-5), 3.64 (ddd, 1H, H-5'), 3.76 (dd, 1H, $J_{6b,5}$ = 1.5 Hz, H-6b), 4.04 (dd, 1H, $J_{6'a,5'}$ = 7.4 Hz, $J_{6'a,6'b}$ = 10.9 Hz, H-6'a), 4.19 (dd, 1H, $J_{6'b,5'}$ = 6.4 Hz, H-6'b), 4.27 (m, 2H, H-3,4), 4.47 (d, 1H, J_{gem} = 12.0 Hz, PhCH_2), 4.51 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 4.63 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.71 (dd, 1H, $J_{3',4'}$ = 3.5 Hz, H-3'), 4.84 (d, 1H, PhCH_2), 5.00 (dd, 1H, $J_{2',3'}$ = 10.3 Hz, H-2'), 5.05 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 5.25 (dd, 1H, $J_{4',5'}$ = 1.0 Hz, H-4'), 6.88-7.89 (m, 24H, aromatics). ^{13}C NMR δ 55.7, 56.0 (MeO, C-2), 60.6, 61.1 (C-6,6'), 66.8 (C-4'), 69.0 (C-2'), 70.4 (C-3'), 70.7

(C-5'), 73.9 (C-5), 74.2 (PhCH$_2$), 75.9 (C-4), 76.8 (C-3), 88.3 (Ph$_3$C), 98.8, 99.2 (C-1,1').

Anal. Calcd for $C_{55}H_{55}NO_{16}$ (986.0): C, 67.00; H, 5.62; N, 1.42. Found: C, 67.27; H, 5.71; N, 1.43.

(b) Glycosylation of **7** (232 mg, 0.26 mmol), with **17** (114 mg, 0.29 mmol) according to the procedure B for 3 h gave **30** (228 mg, 89%) identical with that obtained in run (a).

General procedure for detritylation and acetylation of the disaccharide derivatives. To a solution of a tritylated disaccharide (0.1-0.2 mmol) in CH_2Cl_2 (4 mL) was added 90% aq CF_3CO_2H (0.5 mL), the mixture was kept for 2 h at room temperature, then diluted with $CHCl_3$, washed with sat. $NaHCO_3$, and water, and concentrated. The residue was treated with Ac_2O (1 mL) in pyridine (2 mL) overnight. After addition of MeOH (1 mL), the mixture was taken to dryness, and toluene was distilled several times from the residue. Acetylated disaccharides were isolated by column chromatography.

Methyl 3,4,6-Tri-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-manno-pyranosyl)-α-D-glucopyranoside (20). Compound **20** was obtained from **19** in 81.5% yield as a foam: $[\alpha]_D$ +101.9° (*c* 1.4); ^{1}H NMR δ 1.98, 2.03×2, 2.06, 2.08, 2.13, 2.17 (6s, 21H, 7 AcO), 3.46 (s, 3H, MeO), 3.84 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-2), 4.00 (m, 2H, H-5,5'), 4.08 (dd, 1H, $J_{6a,5}$ = 2.3 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6a), 4.16 (dd, 1H, $J_{6'a,5'}$ = 2.6 Hz, $J_{6'a,6'b}$ = 12.5 Hz, H-6'a), 4.24 (dd, 1H, $J_{6'b,5'}$ = 4.9 Hz, H-6'b), 4.29 (dd, 1H, $J_{6b,5}$ = 4.6 Hz, H-6b), 4.90 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 4.92 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1'), 5.00 (t, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 5.19 (dd, 1H, $J_{2',3'}$ = 3.4 Hz, H-2'), 5.26 (m, 2H, H-3',4'), 5.46 (t, 1H, $J_{3,4}$ = 9.8 Hz, H-3).

Anal. Calcd for $C_{27}H_{38}O_{18}$ (650.6): C, 49.85; H, 5.89. Found: C, 49.91; H, 5.91.

Methyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-manno-pyranosyl)-α-D-glucopyranoside (22). Compound **22** was obtained from **21** in 78% yield as a foam: $[\alpha]_D$ +67.8° (*c* 1.2); ^{1}H NMR δ 1.98, 2.03, 2.07, 2.09×2, 2.11, 2.13 (6s, 21H, 7 AcO), 3.40 (s, 3H, MeO), 3.78 (t, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 3.92 (ddd, 1H, H-5), 4.06 (m, 2H, H-5',6'a), 4.20 (dd, 1H, $J_{6a,5}$ = 4.7 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.26 (dd, 1H, $J_{6'b,5'}$ = 5.1 Hz, $J_{6'a,6'b}$ = 12.5 Hz, H-6'b), 4.45 (dd, 1H, $J_{6b,5}$ = 2.1 Hz, H-6b), 4.78 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 4.85 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.00 (m, 2H, H-1',2'), 5.26 (m, 2H, H-3',4'), 5.53 (dd, 1H, $J_{3,4}$ = 9.1 Hz, H-3).

Anal. Calcd for $C_{27}H_{38}O_{18}$ (650.6): C, 49.85; H, 5.89. Found: C, 50.06; H, 5.92.

Methyl 6-*O*-Acetyl-3,4-di-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside (25). Compound **25** was obtained from **24** in 90% yield as a foam: $[\alpha]_D$ +36.7° (*c* 0.5); ^{1}H NMR δ 1.67, 1.96, 2.05, 2.06, 2.17 (5s, 15H, 5 AcO), 3.40 (s, 3H, MeO), 3.51 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 3.69 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 3.84 (dt, 1H, H-5), 3.91 (m, 1H, H-5'), 4.01 (dd, 1H, $J_{3,4}$ = 8.6 Hz, H-3), 4.12 (dd, 1H, $J_{6a,5}$ = 6.4 Hz, $J_{6a,6b}$ = 11.1 Hz, H-6a), 4.17 (dd, 1H, $J_{6b,5}$ = 6.5 Hz, H-6b), 4.27 (m, 2H, H-6'a,6'b), 4.53 (d, 1H, J_{gem} = 10.7 Hz, PhCH_2), 4.74 (d, 1H, J_{gem} = 11.4 Hz, PhCH_2), 4.76 (d, 1H, $J_{1',2'}$ = 8.1 Hz, H-1'), 4.80 (d, 1H, J_{gem} = 10.7 Hz, PhCH_2), 4.86 (d, 1H, J_{gem} = 11.4 Hz, PhCH_2), 4.89 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.00 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, H-3'), 5.36 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 5.37 (dd, 1H, $J_{4',5'}$ = 1.0 Hz, H-4'), 7.17-7.40 (m, 10H, aromatics).

Anal. Calcd for $C_{37}H_{46}O_{16}$ (746.8): C, 59.51; H, 6.21. Found: C, 59.54; H, 6.25.

Methyl 6-*O*-Acetyl-2,3-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside (27). Compound **27** was obtained from **26** in 85% yield as a foam: $[\alpha]_D$ +15.6° (*c* 0.55); ^{1}H NMR δ 1.95, 1.97, 2.07, 2.09, 2.12 (5s, 15H, 5 AcO), 3.37 (s, 3H, MeO), 3.49 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 3.64 (ddd, 1H, H-5'), 3.68 (dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.80 (ddd, 1H, H-5), 3.82 (dd, 1H, $J_{6'a,5'}$ = 6.0 Hz, $J_{6'a,6'b}$ = 10.8 Hz, H-6'a), 3.94 (dd, 1H, $J_{6'b,5'}$ = 8.2 Hz, H-6'b), 3.95 (dd, 1H, $J_{3,4}$ = 8.2 Hz, H-3), 4.12 (dd, 1H, $J_{6a,5}$ = 5.1 Hz, $J_{6a,6b}$ = 11.7 Hz, H-6a), 4.38 (dd, 1H, $J_{6b,5}$ = 2.1 Hz, H-6b), 4.56 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.61 (d, 1H, J_{gem} = 12.0 Hz, PhCH_2), 4.70 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.75 (d, 1H, J_{gem} = 12.0 Hz, PhCH_2), 4.92 (d, 1H, J_{gem} = 11.2 Hz, PhCH_2), 4.93 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, H-3'), 4.98 (d, 1H, J_{gem} = 11.2 Hz, PhCH_2), 5.19 (dd, 1H, $J_{2',3'}$ = 10.3 Hz, H-2'), 5.29 (dd, 1H, $J_{4',5'}$ = 1.0 Hz, H-4'), 7.25-7.40 (m, 10H, aromatics).

Anal. Calcd for $C_{37}H_{46}O_{16}$ (746.8): C, 59.51; H, 6.21. Found: C, 59.55; H, 6.27

Methyl 6-*O*-Acetyl-2,3-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-galactopyranoside (29) Compound **29** was obtained from **28** in 87% yield as a foam: $[\alpha]_D$ +29.7° (*c* 1.5); ^{1}H NMR δ 1.79, 1.99, 2.04, 2.06, 2.15 (5s, 15H, 5 AcO), 3.35 (s, 3H, MeO), 3.77 (dd, 1H, $J_{2,3}$ =

10.1 Hz, H-2), 3.82 (ddd, 1H, H-5'), 3.86 (dd, 1H, $J_{3,4}$ = 2.6 Hz, H-3), 3.87 (ddd, 1H, H-5), 3.96 (dd, 1H, $J_{4,5}$ = 1.0 Hz, H-4), 4.06 (dd, 1H, $J_{6'a,5'}$ = 6.6 Hz, $J_{6'a,6'b}$ = 11.3 Hz, H-6'a), 4.13 (dd, 1H, $J_{6'b,5'}$ = 6.9 Hz, H-6'b), 4.14 (dd, 1H, $J_{6a,5}$ = 7.9 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.31 (dd, 1H, $J_{6b,5}$ = 4.2 Hz, H-6b), 4.57 (d, 1H, J_{gem} = 11.9 Hz, PhCH_2), 4.59 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 4.62 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1'), 4.66 (d, 1H, J_{gem} = 11.7 Hz, PhCH_2), 4.78 (d, 1H, J_{gem} = 11.9 Hz, PhCH_2), 4.81 (d, 1H, J_{gem} = 11.7 Hz, PhCH_2), 4.99 (dd, 1H, $J_{3',4'}$ = 3.3 Hz, H-3'), 5.18 (dd, 1H, $J_{2',3'}$ = 10.4 Hz, H-2'), 5.36 (dd, 1H, $J_{4',5'}$ = 1.0 Hz, H-4'), 7.29-7.40 (m, 10H, aromatics).

Anal. Calcd for $C_{37}H_{46}O_{16}$ (746.8): C, 59.51; H, 6.21. Found: C, 59.63; H, 6.16.

Methyl 3,4-Di-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside (32). To a solution of **31**[5] (190 mg, 0.51 mmol), $Hg(CN)_2$ (141 mg, 0.56 mmol), and $HgBr_2$ (20 mg, 0.056 mmol) in MeCN (3 mL) was added dropwise a solution of **16** (230 mg, 0.56 mmol) in MeCN (2 mL). The mixture was stirred for 2 h at room temperature, then diluted with $CHCl_3$, washed with M KBr, and water, and concentrated. Column chromatography of the residue in benzene-EtOAc (3:2) gave **32** (244 mg, 68%) as an amorphous mass: $[\alpha]_D$ +56.7° (*c* 1.1); ^{1}H NMR δ 1.98, 2.00, 2.03, 2.13 (4s, 12H, 4 AcO), 3.41 (s, 3H, MeO), 3.78 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 4.50 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.75 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.01 (dd, 1H, $J_{3',4'}$ = 3.5 Hz, H-3'), 5.28 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 5.38 (dd, 1H, $J_{4',5'}$ = 1.2 Hz, H-4'), 7.25-7.40 (m, 10H, aromatics). ^{13}C NMR δ 55.1 (MeO), 61.2 (C-6'), 67.0 (C-4'), 68.4 (C-6), 68.8 (C-2'), 70.0, 70.7, 71.0 (C-3',5,5'), 72.9 (C-2), 74.8, 75.3 (2 Ph*C*H_2), 77.5 (C-4), 83.1 (C-3), 99.2 (C-1), 101.3 (C-1'). ^{1}H NMR after addition of a drop of $Cl_3CCONCO$ into the NMR-tube: δ 4.85 (dd, 1H, $J_{2,1}$ = 3.7 Hz, $J_{2,3}$ = 10.1 Hz, H-2).

Anal. Calcd for $C_{35}H_{44}O_{15}$ (704.7): C, 59.65; H, 6.29. Found: C, 59.56; H, 6.42.

Methyl 2,3-Di-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside (33). Glycosylation of **11** (196 mg, 0.52 mmol) with **16** (237 mg, 0.58 mmol) as described for **32** afforded **33** (250 mg, 68%) as an amorphous mass, $[\alpha]_D$ +2.6° (*c* 0.8); ^{1}H NMR δ 1.98, 2.02, 2.03, 2.13 (4s, 12H, 4 AcO), 3.38 (s, 3H, MeO), 3.43 (t, 1H, $J_{4,5}$ = $J_{4,3}$ = 9.3 Hz, H-4), 4.54 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.59 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1),

5.00 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, H-3'), 5.23 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 5.37 (dd, 1H, $J_{4',5'}$ = 1.1 Hz, H-4'), 7.28-7.38 (m, 10H, aromatics). ^{13}C NMR δ 55.2 (MeO), 61.3 (C-6'), 67.1 (C-4'), 68.8×2 (C-2',6), 70.0×2, 70.7, 70.9 (C-3',4,5,5'), 73.1, 75.3 (2 Ph*C*H_2), 77.6 (C-2), 81.3 (C-3), 98.1 (C-1), 101.5 (C-1'). ^1H NMR after addition of a drop of $Cl_3CCONCO$ into the NMR-tube: δ 4.85 (dd, 1H, $J_{4,3}$ = 9.3 Hz, $J_{4,5}$ = 10.3 Hz, H-4).

Anal. Calcd for $C_{35}H_{44}O_{15}$ (704.7): C, 59.65; H, 6.29. Found: C, 59.49; H, 6.33.

Glycosylation of dityrityl ether 1 with cyanoethylidene derivative 15. Reaction of **1** (385 mg, 0.505 mmol) with **15** (180 mg, 0.505 mmol) according to the procedure A for 16 h and subsequent column chromatography in benzene-EtOAc (4:1) afforded a homogeneous mixture of tritylated disaccharides (176 mg, 41%). A solution of this mixture in CH_2Cl_2 (3 mL) was treated with 90% aq CF_3CO_2H (0.2 mL) for 30 min, then diluted with $CHCl_3$, washed with sat. $NaHCO_3$, and water, and concentrated. To a solution of the residue in MeOH (2 mL) was added M MeONa (0.3 mL), the mixture was kept for 16 h, neutralised with KU-2 (H^+) resin, and filtered. The filtrate was diluted with water (10 mL), washed with $CHCl_3$, and the aqueous phase was taken to dryness to give a mixture of **35**, **36**, and **37**. ^1H NMR (D_2O) of the anomeric region: δ 4.45 (d, $J_{1,2}$ = 7.5 Hz, H-1' of **35**), 4.57 (d, $J_{1,2}$ = 7.4 Hz, H-1' of **36**), 4.83 (d, $J_{1,2}$ = 3.6 Hz, H-1 of **35**), 5.05 (d, $J_{1,2}$ = 3.5 Hz, H-1 of **36** and H-1 of **37**), 5.12 (d, $J_{1,2}$ = 3.8 Hz, H-1' of **37**). ^{13}C NMR of the anomeric region: δ 97.6 (C-1 of **37**), 97.7 (C-1' of **37**), 100.2 (C-1 of **35**), 100.6 (C-1 of **36**), 104.8 (C-1' of **35**), 105.9 (C-1' of **36**).

Methyl 3,4-Di-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-6-*O*-trityl-α-D-glucopyranoside (38) and β-Anomer (39). A mixture of **2** (321 mg, 0.37 mmol), **18**[15] (270 mg, 0.46 mmol), and molecular sieves 3A (800 mg) in ether (5 mL) was stirred under argon for 1 h at room temperature. Methyl triflate (130 μL, 1.15 mmol) was added and stirring was continued for 30 min. The reaction was quenched by addition of a few drops of pyridine-MeOH (3:1) mixture, the solids were filtered off and washed with $CHCl_3$. The filtrate was washed with water and concentrated. Column chromatography of the residue gave a homogeneous mixture (292 mg, 69%) of **38** and **39** in a ratio (^{13}C NMR) of ~2.8:1. Individual anomers were isolated by HPLC in hexane-EtOAc (4:1).

α-Anomer **38**: foam; $[\alpha]_D$ +51.7° (*c* 1.3); ^1H NMR δ 3.28 (dd, 1H, $J_{6a,5}$ = 5.0 Hz, $J_{6a,6b}$ = 10.2 Hz, H-6a), 3.41 (dd, 1H, $J_{6'a,5'}$ = 6.8 Hz,

$J_{6'a,6'b}$ = 9.5 Hz, H-6'a), 3.55 (s, 3H, MeO), 3.57 (dd, 1H, H-6b), 3.61 (dd, 1H, $J_{6'b,5'}$ = 6.3 Hz, H-6'b), 3.63 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 3.83 (br. d, 1H, H-4'), 3.92 (ddd, 1H, H-5), 4.00 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 4.02 (dd, 1H, $J_{3',4'}$ = 2.8 Hz, H-3'), 4.10 (dd, 1H, $J_{3,4}$ = 8.7 Hz, H-3), 4.14 (dd, 1H, $J_{2',3'}$ = 10.0 Hz, H-3'), 4.28 (br. t, 1H, H-5'), 4.31-5.00 (cluster of doublets, 12H, 6 PhCH_2), 5.07 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 5.17 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1'), 6.87-7.60 (m, 45H, aromatics). ^{13}C NMR δ 54.7 (MeO), 62.9 (C-6), 68.9 (C-6'), 69.3 (C-5'), 70.3 (C-5), 86.4 (Ph$_3C$), 95.0 (C-1), 96.4 (C-1').

Anal. Calcd for $C_{74}H_{74}O_{11}$ (1139.4): C, 78.01; H, 6.55. Found: C, 78.02; H, 6.46.

β-Anomer **39**: foam; $[\alpha]_D$ +29.5° (*c* 1.8); ^{1}H NMR δ 3.28 (dd, 1H, $J_{6a,5}$ = 4.8 Hz, $J_{6a,6b}$ = 9.9 Hz, H-6a), 3.50 (s 3H, MeO), 3.54 (dd, 1H, $J_{3',4'}$ = 3.2 Hz, $J_{3',2'}$ = 9.9 Hz, H-3'), 3.58 (dd, 1H, $J_{6b,5}$ = 2.1 Hz, H-6b), 3.59 (m, 1H, H-5'), 3.67 (m, 2H, H-6'a,6'b), 3.69 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 3.94 (m, 4H, H-2,2',4',5), 4.07 (t, 1H, $J_{3,4}$ = $J_{3,2}$ = 9.1 Hz, H-3), 4.32-5.10 (cluster of doublets, 12H, 6 PhCH_2), 4.82 (d, 1H, $J_{1',2'}$ = 7.3 Hz, H-1'), 5.00 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 6.83-7.60 (m, 45H, aromatics). ^{13}C NMR δ 55.0 (MeO), 62.8 (C-6), 68.9 (C-6'), 70.2 (C-5), 86.4 (Ph$_3C$), 99.6 (C-1), 104.2 (C-1').

Anal. Calcd for $C_{74}H_{74}O_{11}$ (1139.4): C, 78.01; H, 6.55. Found: C, 78.04; H, 6.59.

Methyl 2,3-Di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-6-*O*-trityl-α-D-glucopyranoside (40) and β-Anomer (41). Glycosylation of **4** (321 mg, 0.37 mmol) with **18** (270 mg, 0.46 mmol) was performed as described for **38**. Column chromatography of the reaction mixture in hexane-EtOAc (5:1) gave first **41** (61 mg, 14%). Eluted second was **40** (290 mg, 69%).

α-anomer **40**: foam; $[\alpha]_D$ +16.2° (*c* 2.1); ^{1}H NMR δ 3.30 (m, 6H, H-3',5',6a,6b,6'a,6'b), 3.63 (s, 3H, MeO), 3.64 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 3.70 (br. d, 1H, $J_{4',5'}$ = <1 Hz, H-4'), 3.75 (dd, 1H, $J_{4,5}$ = 10.1 Hz, H-4), 3.92 (dd, 1H, $J_{2',3'}$ = 10.4 Hz, H-2'), 4.13 (t, 1H, $J_{3,4}$ = 8.8 Hz, H-3), 4.14 (m, 1H, H-5), 4.21-5.10 (cluster of doublets, 12H, 6 PhCH_2), 4.77 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.78 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1'), 7.00-7.55 (m, 45H, aromatics). ^{13}C NMR δ 54.8 (MeO), 64.2 (C-6), 69.0 (C-6'), 69.5 (C-5'), 69.8 (C-5), 86.3 (Ph$_3C$), 96.3 (C-1), 97.3 (C-1').

Anal. Calcd for $C_{74}H_{74}O_{11}$ (1139.4): C, 78.01; H, 6.55. Found: C, 77.98; H, 6.53.

β-Anomer **41**: foam; $[\alpha]_D$ +0.7° (*c* 1.4); ^1H NMR δ 3.17 (dd, 1H, $J_{3',2'}$ = 9.8 Hz, $J_{3',4'}$ = 3.2 Hz, H-3'), 3.23 (dd, 1H, $J_{6a,5}$ = 2.8 Hz, $J_{6a,6b}$ = 10.3 Hz, H-6a), 3.32 (m, 1H, H-5'), 3.39 (s, 3H, MeO), 3.45 (dd, 1H, $J_{6b,5}$ = 1.8 Hz, H-6b), 3.53 (ddd, 1H, H-5), 3.63 (m, 2H, H-2',6'a), 3.65 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 3.75 (t, 1H, $J_{6'b,5'} = J_{6'b,6'a}$ = 9.0 Hz, H-6'b), 3.85 (t, 1H, $J_{3,4}$ = 8.9 Hz, H-3), 3.94 (br. d, 1H, $J_{4',5'}$ < 1Hz, H-4'), 4.30 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1'), 4.32 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 4.39-5.10 (cluster of doublets, 12H, 6 PhC*H*$_2$), 4.77 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 7.03-7.50 (m, 45H, aromatics). ^{13}C NMR δ 55.1 (MeO), 61.9 (C-6), 68.3 (C-6'), 69.8 (C-5), 86.1 (Ph$_3$*C*), 98.3 (C-1), 101.5 (C-1').

Anal. Calcd for $C_{74}H_{74}O_{11}$ (1139.4): C, 78.01; H, 6.55. Found: C, 78.23; H, 6.53.

Methyl 3-*O*-Benzyl-2-deoxy-2-phthalimido-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-6-*O*-trityl-β-D-glucopyranoside (43). A mixture of **7** (449 mg, 0.5 mmol), **42**[16] (265 mg, 0.55 mmol), and molecular sieves 3A (700 mg) in CH_2Cl_2 (8 mL) was stirred under argon for 1 h, then methyl triflate (310 μL, 2.74 mmol) was added. Stirring was continued for 26 h at room temperature. A few drops of pyridine were added, solids were filtered off and washed with $CHCl_3$. The filtrate was washed with water and concentrated. Column chromatography of the residue in benzene-EtOAc (85:15) gave **43** (362 mg, 68%): mp 213-215 °C ($CHCl_3$-hexane); $[\alpha]_D$ -7° (*c* 2.1); ^1H NMR δ 1.80, 2.02×2 (2s, 9H, 3 AcO), 3.32 (m, 2H, H-6a,6b), 3.34 (s, 3H, MeO), 3.55 (ddd, 1H, H-5'), 3.66 (m, 1H, H-5), 4.13 (dd, 1H, $J_{6'a,5'}$ = 2.4 Hz, $J_{6'a,6'b}$ = 12.5 Hz, H-6'a), 4.23 (m, 3H, H-2,2',3), 4.30 (dd, 1H, $J_{6'b,5'}$ = 3.8 Hz, H-6'b), 4.49 (d, 1H, J_{gem} = 12.3 Hz, PhC*H*$_2$), 4.63 (m, 1H, H-4), 4.86 (d, 1H, PhC*H*$_2$), 4.92 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 5.12 (dd, 1H, $J_{4',5'}$ = 10.0 Hz, H-4'), 5.21 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 5.52 (dd, 1H, $J_{3',2'}$ = 11.2 Hz, $J_{3',4'}$ = 8.9 Hz, H-3'), 6.78-7.85 (m, 28H, aromatics). ^{13}C NMR δ 55.1, 55.6, 56.0 (MeO, C-2,2'), 61.6, 62.8 (C-6,6'), 69.1 (C-4'), 70.5 (C-3'), 71.7 (C-5'), 73.9, 74.3, 74.5 (Ph*C*H$_2$, C-4,5), 76.6 (C-3), 86.9 (Ph$_3$*C*), 95.6 (C-1), 98.6 (C-1').

Anal. Calcd for $C_{61}H_{56}N_2O_{16}$·0.5$CHCl_3$ (1132.8): C, 65.20; H, 5.03; Cl, 5.27; N, 2.47. Found: C, 64.95; H, 5.22; Cl 5.03; N, 2.56.

Methyl 3-*O*-Benzyl-2-deoxy-2-phthalimido-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-6-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-glucopyranoside (45) and β-Anomer (46). A mixture of **43**

(152 mg, 0.14 mmol), **44**[16] (134 mg, 0.28 mmol) and molecular sieves 3A (600 mg) in CH_2Cl_2 (4 mL) was stirred under argon for 1 h. Methyl triflate (120μL, 1.06 mmol) was added and stirring was continued for 2.5 h. The reaction was processed as described for **43**. Column chromatography in benzene-EtOAc (85:15) gave first **45** (132 mg, 76%). Eluted second was **46** (37 mg, 21%).

α-Anomer **45**: foam; $[\alpha]_D$ -45.3° (*c* 3.1); ^{1}H NMR δ 1.08 (d, 3H, $J_{6",5"}$ = 6.7 Hz, H-6"), 1.85, 1.88, 1.93 (3s, 9H, 3 AcO), 3.23 (s, 3H, MeO), 3.29 (ddd, 1H, H-5), 3.35 (dd, 1H, $J_{6a,5}$ = 2.7 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6a), 3.50 (ddd, 1H, H-5'), 3.75 (br. d, 1H, $J_{4",3"}$ = 3.0 Hz, $J_{4",5"}$ < 1 Hz, H-4"), 3.80 (dd, 1H, $J_{6b,5}$ = 1.3 Hz, H-6b), 3.93 (dd, 1H, $J_{6'a,5'}$ = 2.3 Hz, $J_{6'a,6'b}$ = 12.2 Hz, H-6'a), 3.99-4.20 (m, 6H, H-2,2",3,3",5",6'b), 4.29 (dd, Hz, H-1), 5.08 (dd, 1H, $J_{4',5'}$ = 10.3 Hz, H-4'), 5.11 (d, 1H, $J_{1",2"}$ = 3.4 Hz, H-1"), 5.66 (d, 1H, $J_{1',2'}$ = 8.2 Hz, H-1'), 5.75 (dd, 1H, $J_{3',4'}$ = 9.1 Hz, H-3'), 6.80-7.95 (m, 28H, aromatics).

Anal. Calcd for $C_{69}H_{70}N_2O_{20}$ (1247.3): C, 66.44; H, 5.66; N, 2.25. Found: C, 66.34; H, 5.69; N, 2.35.

β-Anomer **46**: foam; $[\alpha]_D$ +4.4° (*c* 3); ^{1}H NMR δ 1.46 (d, 3H, $J_{6",5"}$ = 6.4 Hz, H-6"), 1.86, 1.93, 2.03 (3s, 9H, 3 AcO), 3.30 (s, 3H, MeO), 3.36 (ddd, 1H, H-5), 3.58 (dd, 1H, $J_{3",4"}$ = 3.0 Hz, H-3"), 3.62 (br. d, 1H, $J_{4",5"}$ < 1 Hz, H-4"), 3.65 (br. q, 1H, H-5"), 3.80 (dd, 1H, $J_{6a,5}$ = 1.4 Hz, $J_{6a,6b}$ = 10.6 Hz, H-6a), 3.83 (dd, 1H, $J_{2",3"}$ = 9.5 Hz, H-2"), 4.05 (dd, 1H, $J_{6'a,5'}$ = 2.2 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6'a), 4.16 (m, 3H, H-2,3,6b), 4.23 (dd, 1H, $J_{6'b,5'}$ = 4.2 Hz, H-6'b), 4.36 (dd, 1H, $J_{2',3'}$ = 11.0 Hz, H-2'), 4.39 (ddd, 1H, H-5'), 4.48 (d, 1H, $J_{1",2"}$ = 7.7 Hz, H-1"), 4.51-5.10 (cluster of doublets, 8H, 4 PhC*H*$_2$), 4.62 (dd, 1H, $J_{4,3}$ = 8.1 Hz, $J_{4,5}$ = 9.9 Hz, H-4), 5.08 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 5.19 (dd, 1H, $J_{4',5'}$ = 10.4 Hz, H-4'), 5.86 (dd, 1H, $J_{3',4'}$ = 9.0 Hz, H-3'), 5.88 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 6.70-7.85 (m, 28H, aromatics).

Anal. Calcd for $C_{69}H_{70}N_2O_{20}$ (1247.3): C, 66.44; H, 5.66; N, 2.25. Found: C, 67.09; H, 5.96; N, 2.32.

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REFERENCES AND NOTES

1. For a preliminary communication see Yu. E. Tsvetkov, P. I. Kitov, L. V. Backinowsky, and N. K. Kochetkov, *Tetrahedron Lett.*, **34**, 7977 (1993).
2. H. Paulsen, *Angew. Chem. Int. Ed. Engl.*, **21**, 155 (1983).
3. N. K. Kochetkov, *Tetrahedron*, **43**, 2398 (1987).
4. P. I. Kitov, Yu. E. Tsvetkov, L. V. Backinowsky, and N. K. Kochetkov, *Russ. Chem. Bull.*, **42**, 1909 (1993).
5. S. Koto, N. Morishima, T. Yoshida, M. Uchino, and S. Zen, *Bull. Chem. Soc. Jpn.*, **56**, 1171 (1983).
6. V. I. Betaneli, M. V. Ovchinnikov, L. V. Backinowsky, and N. K. Kochetkov, *Carbohydr. Res.*, **76**, 252 (1979).
7. N. E. Nifant'ev, L. V. Backinowsky, and N. K. Kochetkov, *Carbohydr. Res.*, **191**, 13 (1989).
8. P. I. Kitov, Yu. E. Tsvetkov, L. V. Backinowsky, and N. K. Kochetkov, *Mendeleev Commun.*, 176 (1995).
9. H. Bredereck, A. Wagner, D. Geissel, P. Gross, U. Hutten, and H. Ott, *Chem. Ber.*, **95**, 3056 (1962).
10. K Yoshimoto, Y. Itatani, K. Shibata, and Y. Tsuda, *Chem. Pharm. Bull.*, **28**, 208 (1980).
11. H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).
12. J. Schneider, Y. C. Lee, and H. M. Flowers, *Carbohydr. Res.*, **36**, 159 (1974).
13. D. A. Schwartz, H.-H. Lee, J. P. Carver, and J. J. Krepinsky, *Can. J. Chem.*, **63**, 1073 (1985).
14. V. I. Betaneli, M. V. Ovchinnikov, L. V. Backinowsky, and N. K. Kochetkov, *Carbohydr. Res.*, **68**, C11 (1979).
15. J. O. Kihlberg, D. A. Leigh, and D. R. Bundle, *J. Org. Chem.*, **55**, 2860 (1990).
16. H. Lönn, *Carbohydr. Res.*, **139**, 105 (1985).