

191. Glycosylidene Carbenes

Part 10

Regioselective Glycosidation of 4,6-*O*-Benzylidene-*D*-altropyranosides

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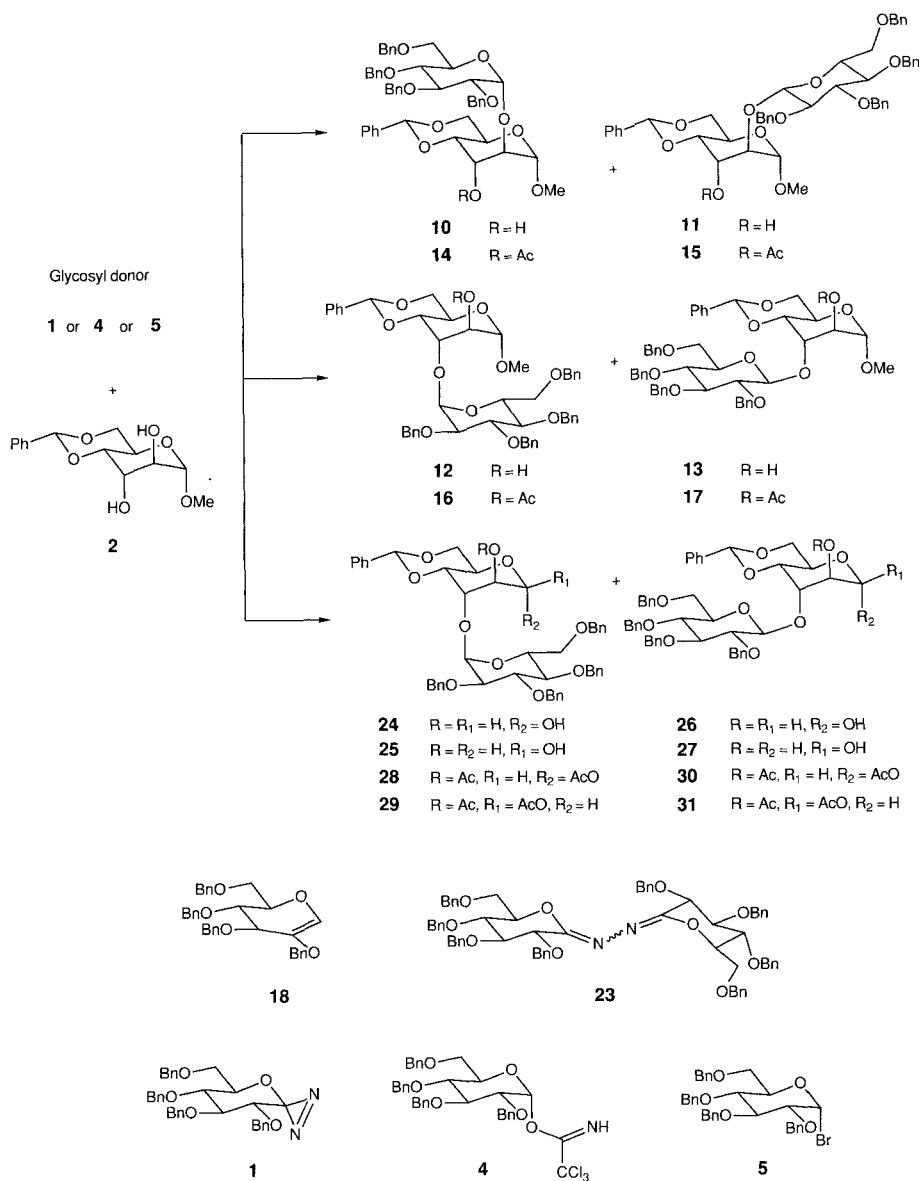
(31. VII. 92)

Glycosidation by the diazirine **1**, the trichloroacetimidate **4**, and the bromide **5** of the *altro*-diol **2**, possessing an intramolecular H-bond (HO–C(3) to O–C(1)) in solution, but not in the solid state, proceeds with high and complementary regioselectivity. From **2** and **1**, one obtains mostly the 1,2-linked disaccharides **10** and **11** (β -D > α -D), together with the 1,3-linked isomers **12** and **13** (α -D > β -D; 1,2-/1,3-linked products *ca.* 9:1), the demethylated 1,3-linked disaccharides **24–27**, the trisaccharides **19–22**, the lactone azines **23**, and the hydroxyglucal **18**, while **2** reacted with **4** or **5** to yield mostly the 1,3-linked disaccharides (1,2-/1,3-linked products *ca.* 1:9). The disaccharides were additionally characterized as acetates ($\rightarrow$ **14–17**, **28–31**). Yields and stereoselectivity depended upon the donor, stoichiometry, solvent, temperature, and concentration. Glycosidation of the 1,3-linked disaccharides with **1** yielded the trisaccharides **19–22**. Reaction of the β -D-*altro*-diol **3** with **1** gave the 1,2- and 1,3-linked disaccharides **32/33** and **34/35** in a 1:1 ratio, characterized as the acetates **36–39**, while glycosidation with **5** according to Lemieux proceeded regioselectively (1,2-/1,3-linked products 91:9). The monotosylates **6** and **7** reacted with **1** to yield the anomeric pairs **40/41**, and **42/43** of the tosylated disaccharides; the oxiranes **44** and **45** were not observed.

Introduction. – In the context of our studies on glycosidation of diols and triols by 1-azisugars, we wish to explore the extent to which differences in the kinetic acidity of OH groups lead to regioselective glycosidation. Regioselective glycosidation is feasible for phenols [1], when one of two OH groups acts as a donor in an intramolecular H-bond, and for a diol or triol [2], when one of the OH groups acts as an acceptor in a relatively strong intramolecular H-bond. In the first case, the kinetic acidity of the H-bond forming OH group is reduced, and so is its reactivity towards a glycosylidene carbene. In the second case, involving alcoholic, much less acidic OH groups, the kinetic acidity of a H-bond-accepting OH group is enhanced. The resulting higher degree of kinetic acidity led to higher yields of glycosides and to a much better stereoselectivity than what was observed for intermolecularly H-bonded alcohols.

We now describe the glycosidation of the *altro*-diols **2** and **3** by the diazirine **1**, the trichloroacetimidate **4**, and the bromide **5** (*Scheme 1*). In the α -D-anomer **2**, one expects that HO–C(3) acts as a H-bond donor to O–C(1) or, less likely, O–C(4) [3]. The kinetic acidity of HO–C(3) should thereby be lowered, and its nucleophilicity should be enhanced. The kinetic acidity of HO–C(2) will presumably be affected to a minor extent only. This should lead to a predominant glycosidation of HO–C(2) by **1**, and to a complementary regioselectivity for glycosidations by the trichloroacetimidate **4** and the bromide **5**, as the nucleophilic properties of OH groups are essential for glycosidations of the *Koenigs-Knorr* type. This was not expected for the β -D-anomer. We also hoped to

Scheme 1



learn more about the extent to which intermolecular H-bonding is required for a successful, carbene-mediated glycosidation of an alcoholic OH group, as it is for 1,6-anhydroglucose [2]. Finally, we wished to see if the oxy anion resulting from deprotonation by a glycosylidene carbene of HO-C(2) and HO-C(3) of the methyl 3-*O*- and 2-*O*-tosyl- α -D-altropyranosides **6**, and **7**, respectively, can be intercepted.

Results and Discussion. – 1. *Glycosidation of the Methyl α -D-Altropyranoside 2.*
 1.1. *Hydrogen Bonds.* The crystal structure of **2** shows no intramolecular H-bonds (see Fig. 1, 2 and Tables 1, 2, and 3). In keeping with this, the O–C(3), O–C(1) distance is

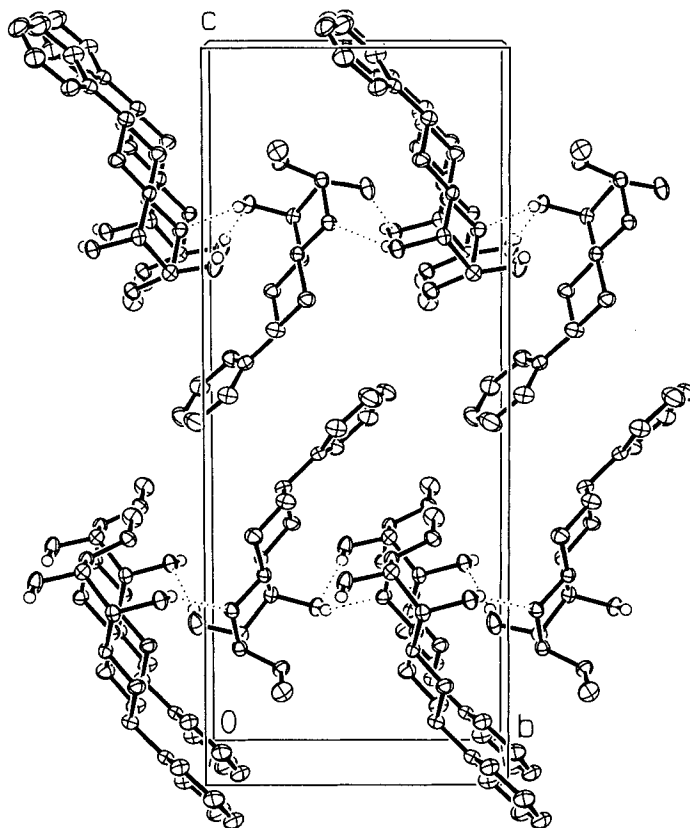


Fig. 1. Packing diagram for **2** viewed down the *a*-axis, showing the intermolecular H-bonds. Uninvolved H-atoms have been omitted for clarity.

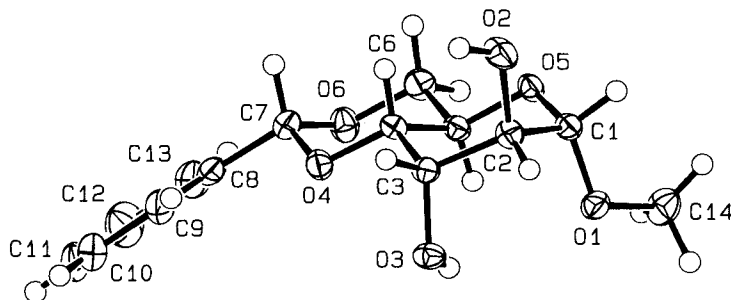


Fig. 2. ORTEP Plot of **2** showing the atom numbering

sensibly longer (2.98 Å) than the O–O distance of the two axial OH groups in the X-ray spectrum of a previously described, intramolecularly H-bonded *myo*-inositol-derived triol (2.767 Å) [2]. There are two intermolecular H-bonds, one from HO–C(2) to O–C(3) of an adjacent molecule, with an O–O distance of 2.777(2) Å and an O–H–O angle of 154°(3), and a weaker one from HO–C(3) to O–C(5) of a different adjacent molecule (O–O: 2.895(2) Å; O–H–O: 146°(3)).

The IR spectra (CCl₄, 0.005M) of the α -D-altroside **2** and of the corresponding 3- and 2-*O*-methyl ethers **8** and **9** (*cf. Scheme 5*) have been measured and discussed by *Spedding* [4]. We have measured the IR spectra (CH₂Cl₂) of **2**, the 3-*O*-tosyl derivative **6**, and the 2-*O*-tosyl derivative **7** at concentrations of 0.25, 0.05, and 0.03M. Each spectrum shows two bands. For the 3-*O*-tosylate **6**, these are found at 3596 (*s*) and 3515 cm^{−1} (*sh*), for the 2-*O*-tosylate **7** at 3595 (*sh*) and 3525 cm^{−1} (*s*) and for the diol **2** at 3598 and 3520 cm^{−1} (similar intensity). The absorption at 3515 cm^{−1} for **6** decreased, when the concentration was reduced from 0.25 to 0.05M, and is presumably due to intermolecular H-bonding, while the IR spectrum of **7** does not depend upon concentration. The diol **2** is insufficiently soluble in CH₂Cl₂, and its IR spectra were measured only at concentrations of 0.05 and 0.03M. This dilution did not affect the spectrum. The relative intensity of the OH

Table 1. *Crystal Data and Experimental Conditions for the X-Ray Analysis of 2*

Molecular formula	C ₁₄ H ₁₈ O ₆	Temp. of data collection [°C]	−60
Formula weight	282.29	Radiation	MoK α
Crystal system	orthorhombic	λ [Å]	0.71069
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	Diffractionmeter	Nicolet-R3
<i>a</i> [Å]	6.642(1)	2 $\theta_{\text{(max)}}$ [°]	60
<i>b</i> [Å]	9.016(2)	No. of reflections measured	3004
<i>c</i> [Å]	22.044(4)	Observed reflections [<i>I</i> > 3 σ (<i>I</i>)]	2021
<i>V</i> [Å ³]	1320.0(4)	No. of refined parameters	254
<i>Z</i>	4	Final <i>R</i> factor	0.0364
Calc. density [g/cm ³]	1.420	<i>R</i> _w	0.0374
μ (MoK α) [cm ^{−1}]	1.041		

Table 2. *Selected Bond Angles [°] with e.s.d.'s in Parentheses for 2*

C(1)–O(1)–C(14)	113.3(2)	O(5)–C(5)–C(4)	109.6(2)
C(4)–O(4)–C(7)	111.2(2)	O(5)–C(5)–C(6)	109.8(2)
C(1)–O(5)–C(5)	112.3(1)	C(4)–C(5)–C(6)	108.4(2)
C(6)–O(6)–C(7)	112.5(2)	O(6)–C(6)–C(5)	107.6(2)
O(1)–C(1)–O(5)	111.9(2)	O(4)–C(7)–O(6)	111.7(2)
O(1)–C(1)–C(2)	107.1(2)	O(4)–C(7)–C(8)	107.1(2)
O(5)–C(1)–C(2)	112.3(2)	O(6)–C(7)–C(8)	108.7(2)
O(2)–C(2)–C(1)	104.9(2)	C(7)–C(8)–C(9)	120.3(2)
O(2)–C(2)–C(3)	110.7(2)	C(7)–C(8)–C(13)	120.1(2)
C(1)–C(2)–C(3)	112.7(2)	C(9)–C(8)–C(13)	119.6(2)
O(3)–C(3)–C(2)	112.2(2)	C(8)–C(9)–C(10)	119.9(2)
O(3)–C(3)–C(4)	113.2(2)	C(9)–C(10)–C(11)	120.4(3)
C(2)–C(3)–C(4)	108.8(2)	C(10)–C(11)–C(12)	119.9(3)
O(4)–C(4)–C(3)	109.6(2)	C(11)–C(12)–C(13)	120.9(3)
O(4)–C(4)–C(5)	108.9(2)	C(8)–C(13)–C(12)	119.3(3)
C(3)–C(4)–C(5)	111.5(2)		

Table 3. Selected Torsion Angles [°] with e.s.d.'s in Parentheses of **2**

C(14)–O(1)–C(1)–O(5)	68.8(2)	O(3)–C(3)–C(4)–C(5)	–71.8(2)
C(14)–O(1)–C(1)–C(2)	–167.7(2)	C(2)–C(3)–C(4)–O(4)	174.3(1)
C(4)–O(4)–C(7)–O(6)	58.7(2)	C(2)–C(3)–C(4)–C(5)	53.6(2)
C(4)–O(4)–C(7)–C(8)	177.6(2)	O(4)–C(4)–C(5)–O(5)	178.0(1)
C(7)–O(4)–C(4)–C(3)	179.4(2)	O(4)–C(4)–C(5)–C(6)	58.2(2)
C(7)–O(4)–C(4)–C(5)	–58.3(2)	C(3)–C(4)–C(5)–O(5)	–60.9(2)
C(1)–O(5)–C(5)–C(4)	61.8(2)	C(3)–C(4)–C(5)–C(6)	179.3(2)
C(1)–O(5)–C(5)–C(6)	–179.3(2)	O(5)–C(5)–C(6)–O(6)	–177.2(1)
C(5)–O(5)–C(1)–O(1)	63.6(2)	C(4)–C(5)–C(6)–O(6)	–57.6(2)
C(5)–O(5)–C(1)–C(2)	–56.9(2)	O(4)–C(7)–C(8)–C(9)	35.0(3)
C(6)–O(6)–C(7)–O(4)	–59.7(2)	O(4)–C(7)–C(8)–C(13)	–144.2(2)
C(6)–O(6)–C(7)–C(8)	–177.7(2)	O(6)–C(7)–C(8)–C(9)	155.9(2)
C(7)–O(6)–C(6)–C(5)	58.9(2)	O(6)–C(7)–C(8)–C(13)	–23.4(3)
O(1)–C(1)–C(2)–O(2)	166.4(1)	C(7)–C(8)–C(9)–C(10)	–177.7(2)
O(1)–C(1)–C(2)–C(3)	–73.2(2)	C(7)–C(8)–C(13)–C(12)	177.8(2)
O(5)–C(1)–C(2)–O(2)	–70.4(2)	C(9)–C(8)–C(13)–C(12)	–1.5(3)
O(5)–C(1)–C(2)–C(3)	50.1(2)	C(13)–C(8)–C(9)–C(10)	1.6(3)
O(2)–C(2)–C(3)–O(3)	–165.0(1)	C(8)–C(9)–C(10)–C(11)	–0.3(3)
O(2)–C(2)–C(3)–C(4)	69.1(2)	C(9)–C(10)–C(11)–C(12)	–1.2(4)
C(1)–C(2)–C(3)–O(3)	77.9(2)	C(10)–C(11)–C(12)–C(13)	1.3(4)
C(1)–C(2)–C(3)–C(4)	–48.1(2)	C(11)–C(12)–C(13)–C(8)	0.0(4)
O(3)–C(3)–C(4)–O(4)	48.9(2)		

bands in the spectra of the tosyl derivatives and their dependence upon concentration show that HO–C(3) is mostly – but not completely – intramolecularly H-bonded. This is consistent with the small frequency shift (78 cm^{–1}) between the monomeric and the associated OH band. The IR spectra also show that HO–C(2) forms intermolecular H-bonds at higher concentrations (above 0.05M), but at best a weak intramolecular H-bond, in agreement with *Spedding's* results. The IR spectra of the β -D-anomer **3** show one band at 3600 cm^{–1} (CCl₄, 0.005M), which may be due to weak H-bonds of HO–C(2) to O–C(1) and/or O–C(5) and of HO–C(3) to O–C(4). In keeping with these results, the osmometrically determined molecular weight of **2** (282.29) in dioxane at concentrations of $\sim$ 0.015M (281) and $\sim$ 0.07M (356) shows the tendency of **2** to form aggregates at higher concentrations. This difference of apparent molecular weight does not find a parallel in the IR spectra in dioxane; at concentrations of 0.20, 0.10, 0.05, 0.025, and 0.005M only one broad band at 3440 cm^{–1} is observed.

The ¹H-NMR spectrum of **2** in (D₆)DMSO (0.05M) shows the HO–C(2) and HO–C(3) signals as *doublets* at 5.32 ($J = 4.2$ Hz) and 4.64 ppm ($J = 4.8$ Hz) ($\Delta\delta = 0.88$ ppm), respectively. In CDCl₃, HO–C(2) resonates at 2.12 ($J = 5.8$ Hz) and HO–C(3) at 2.89 ppm ($J = 6.6$ Hz) ($\Delta\delta = -0.77$ ppm). The relative chemical shift for HO–C(2) and HO–C(3) evidences that HO–C(2) has the higher tendency to form intermolecular H-bonds, and that HO–C(3) forms an intramolecular H-bond. The ¹H-NMR spectrum of **3** in CDCl₃ shows no significant shift differences for the OH signals. They resonate at relatively high fields (HO–C(2) as a *doublet* at 2.44 ($J = 1.8$ Hz) and HO–C(3) as a broad *singlet* at 2.24 ppm), indicating that the two OH groups of **3** do not form strong H-bonds.

1.2. *Glycosidation with the Diazirine 1* (see *Scheme 1* and *Table 4*). The diazirine **1** reacted with **2** to yield mostly 1,2-linked disaccharides. Regio- and stereoselectivity

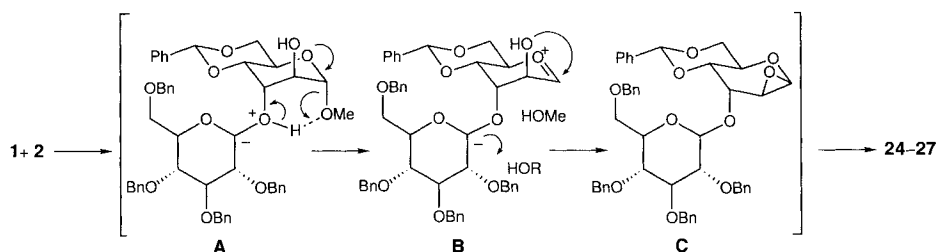
Table 4. Glycosidation of **2** with the Diazirine **1**

Conc. of 2 [M]	Conditions	Relative amount of 1 [equiv.]	Yield ^{a)} [%]	Regioselectivity (10 + 11)/(12 + 13)	Stereoselectivity	
					10/11	12/13
0.20	dioxane, 24°	1.1	54	87:13	20:80	21:79
0.10	dioxane, 24°	1.1	68	88:12	18:82	18:82
0.05	dioxane, 24°	1.1	57	87:13	18:82	18:82
0.025	dioxane, 24°	1.1	43	89:11	22:78	16:84
0.005	dioxane, 24°	1.1	22	87:13	13:87	28:72
0.05	dioxane, 24°	0.5	52	83:17	20:80	23:77
0.05	DME, 24°	1.1	53	79:21	23:77	27:73
0.05	toluene, 70°	1.1	44	71:29	19:81	80:20
0.025	ClCH ₂ CH ₂ Cl, 24°	1.1	62	92:8	34:66	70:30
0.05	ClCH ₂ CH ₂ Cl, 24°	1.1	66	94:6	35:65	55:45
0.25	ClCH ₂ CH ₂ Cl, 24°	1.1	71	93:7	35:65	51:49
0.065	ClCH ₂ CH ₂ Cl, 24°	0.5	62	95:5	37:63	40:60
0.13	ClCH ₂ CH ₂ Cl, 24°	0.5	67	89:11	37:63	69:31
0.066	ClCH ₂ CH ₂ Cl, –15°, <i>hν</i>	1.1	49	91:9	36:64	81:19
0.05	ClCH ₂ CH ₂ Cl, –30°, <i>hν</i>	1.1	65	91:9	34:66	83:17
0.05	ClCH ₂ CH ₂ Cl, 24°	2.2	80	88:12	35:65	80:20
0.05	THF, –80°, <i>hν</i>	1.1	50	71:29	5:95	17:83
0.065	THF, 24°	1.1	51	86:14	14:86	19:81
0.05	CH ₂ Cl ₂ , –80°, <i>hν</i>	1.1	47	86:14	37:63	83:17
0.05	CH ₂ Cl ₂ , 24°	1.1	52	82:18	41:59	73:27

^{a)} Total yield of disaccharides after FC.

depend upon solvent and temperature (cf. Table 4). The best regioselectivity was obtained in ClCH₂CH₂Cl, with a ratio 1,2-/1,3-linked disaccharides ranging from 88:12 to 95:5. This solvent also led to the highest yields (62–80%), but to poor stereoselectivities. The β -D-anomer **11** of the major regioisomer is always preferred, particularly when the reaction is run in THF at low temperatures (α -D/ β -D = 5:95 at –80°), or in dioxane (α -D/ β -D = 18:82), as we had to expect in the light of earlier results [5]. Yields with these solvents were, however, somewhat lower. Addition of SnCl₂, B(OEt)₃, BF₃·OEt₂ or of Bu₄NBr did not change the regio- and diastereoselectivity. While the β -D-anomer of the 1,2-linked disaccharides was predominantly formed under all conditions, this was not so for the 1,3-linked products. With ethers as solvents, the β -D-anomer **13** is formed preferentially (β -D/ α -D = up to 83:17); with ClCH₂CH₂Cl, the ratio depends upon concentration, relative amount of **2**, and temperature. Lower concentrations (24°, 1.1 equiv. of **2**) lead mostly to the α -D-anomer **12**, as it is observed at a lower temperature (1.1 equiv. of **2**, 0.05M) and with excess **2**. This was not expected, and the reason for it is not clear. Conceivably, glycosidation at HO–C(3) starts by protonation of the carbene by an isomer of **2** possessing a non-intramolecularly H-bonded HO–C(3) (cf. [6]), or by electrophilic attack of the carbene on the isomer in which HO–C(3) forms an intramolecular H-bond. Indirect evidence for the electrophilic attack, for which there is precedence (see e.g. [7]), stems from the by-products of the glycosidation. Besides the 2-hydroxyglucal **18** [8] and the trisaccharides **19**–**22** (see below and Scheme 3), one observes formation of the azines **23** [9] and, at low temperatures, of the methyl 2,3,4,6-tetra-O-benzyl- α - and - β -D-glucopyranosides [10] [11] (ca. 10%) and of a mixture of the 1,3-linked, demethyl-

Scheme 2



ated disaccharides **24–27** (ca. 10%). As the glycosidation is performed under neutral conditions, formation of the demethylated products presumably reflects intramolecular protonation of the MeO group, triggered by an electrophilic attack of the carbene onto the H-bonded HO–C(3) (Scheme 2). The intermediate **A** could lose MeOH, and the resulting glycosyl cation **B** may be intercepted by HO–C(2) to lead to a 1,2-anhydro derivative **C** which is rapidly hydrolyzed in contact with SiO₂. Reaction of the carbene with the liberated MeOH leads to the methyl 2,3,4,6-tetra-*O*-benzyl- α - and - β -D-glucopyranosides, which are formed in about the same yield as the demethylated products.

The ratio of the products was determined by analytical HPLC (*LiChrosorb Si 60*, 1.5 ml/min, hexane/AcOEt 2:1). The 1,2- and 1,3-linked glycosides were separated by chromatography, while the anomeric mixtures of **10/11** and **12/13** could only be separated after acetylation. The products were characterized as acetates. Selected ¹H- and ¹³C-NMR data of **14–17** are given in Tables 5 and 6. The constitution of the products was deduced from the chemical shifts of the acetylation products, and their configuration from the *J*(1', 2') values.

Table 5. Selected ¹H-NMR (400 MHz, CDCl₃) Chemical Shifts [ppm] and Coupling Constants [Hz] for **2**, **14–17**, and **40–43**

Compound	2	14	15	16	17	40	41	42	43
H–C(1)	4.68	4.72	4.66	4.60	4.59	4.78	4.69	4.60	4.41
H–C(2)	4.03	3.95	4.06	5.07	5.26	4.16	4.21	4.59	4.97
H–C(3)	4.12	5.25	5.51	4.14	4.30	4.74	5.06	4.05–4.02	4.34
H–C(4)	3.98	4.08	4.13	3.91	3.96	3.90	3.96	3.87	3.96
H–C(5)	4.22	4.32–4.22	4.28	4.43	4.38	4.19	4.27–4.21	4.32–4.27	4.31–4.23
H _A –C(6)	4.34	4.32–4.22	4.35	4.33	4.27	4.25	4.31	4.32–4.27	4.31–4.23
H _B –C(6)	3.84	3.80	3.79	3.75	3.76	3.71	3.71	3.72	3.74
H–C(1')		5.07	4.51	5.20	4.79	5.02	4.50	4.81	4.63
H–C(2')		3.60	3.50	3.63	3.52	3.57	3.49–3.45	3.53	3.50
H–C(3')		3.98	3.64	4.09	3.63–3.57	3.92	3.65	4.00	3.59
H–C(4')		3.64	3.73	3.62	3.63–3.57	3.64	3.76	3.63	3.72
H–C(5')		3.88	3.46	4.19	3.43–3.39	3.88	3.49–3.45	4.05–4.02	3.38
H _A –C(6')		3.73	3.78	3.41	3.72	3.74	3.84–3.83	3.32	3.82–3.81
H _B –C(6')		3.65	3.78	3.27	3.70	3.65	3.84–3.83	3.04	3.82–3.81
<i>J</i> (1', 2')		3.7	7.7	3.5	7.7	3.7	7.5	2.7	7.5

Table 6. Selected ^{13}C -NMR (50 MHz, CDCl_3) Chemical Shifts [ppm] for **2** and **14–17**

Compound	2 ^{a)}	14	15	16	17
C(1)	101.6	100.04	99.93	99.18	99.30
C(2)	69.6	75.57	76.07	69.19	71.65
C(3)	68.8	67.88	68.65	69.69	71.58
C(4)	76.0	74.03	74.29	75.16	76.71
C(5)	57.8	58.62	58.82	57.97	58.48
C(6)	68.8	69.18	69.39	69.19	69.24
PhCH	101.8	101.82	102.00	102.19	102.51
C(1')		98.43	104.31	94.77	103.61
C(2')		79.74	81.95	79.83	81.88
C(3')		81.61	84.58	81.60	84.41
C(4')		77.63	77.41	77.46	77.73
C(5')		70.95	75.19	69.69	75.10
C(6')		68.45	68.42	68.10	69.08

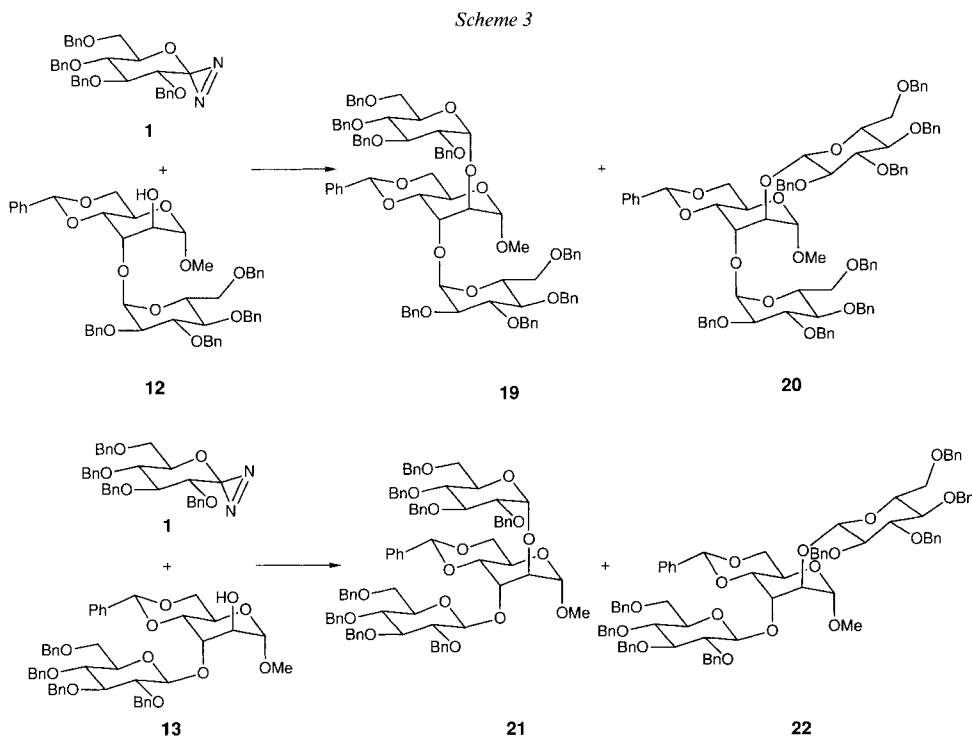
^{a)} From [12].

In the ^1H -NMR spectra of **14** and **15**, the *doublets* of H–C(2) appear at 3.95 and 4.06 ppm, while the *triplets* of H–C(3) appear at 5.25 and 5.51 ppm, respectively. In the ^1H -NMR spectra of **16** and **17**, the *doublets* of H–C(2) are at 5.07 and 5.26 ppm, while the *triplets* of H–C(3) are at 4.14 and 4.30 ppm, respectively. The signal of H–C(1') appears at 5.07 ($J = 3.7$ Hz) and 5.20 ppm ($J = 3.5$ Hz) in the spectra of the α -D-configured disaccharides **14** and **16**, while the *doublets* of H–C(1') in the spectra of the β -D-configured disaccharides **15** and **17** are at 4.51 ($J = 7.7$ Hz) and 4.79 ppm ($J = 7.7$ Hz).

The influence of the concentration of **2** and **1**, and thus of intermolecular H-bonds was studied for 0.20, 0.10, 0.05, 0.025, and 0.005M solutions in dioxane, at 24°, by monitoring the formation of products (analytical HPLC). The overall yield depended upon concentration, attaining 54% at 0.20M, 68% at 0.10M, 57% at 0.05M, 43% at 0.025M, and 22% at 0.005M, whereas the regio- and stereoselectivity remained constant. The main by-products (24–39%) were the azines **23**, and their amount was highest at the lowest concentration. These results are in keeping with the observation that intermolecular H-bonds, *i.e.* a sufficiently high degree of acidity, are required for glycosidation.

1.3. *Glycosidation with the Donors 4 and 5* (see Scheme 1). In the Koenigs-Knorr-type glycosidations of **2** with **4** or **5**, where nucleophilic properties are essential, HO–C(3) was predominantly glycosylated, as expected. The trichloroacetimidate **4** reacted with **2** in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at -30° in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ [13] [14] to yield 67% of the disaccharides **10–13**. The regioselectivity (1,2-/1,3-linked disaccharides 9:91) is, indeed, complementary to the one observed for the diazirine **1**. The stereoselectivity was very low (α -D/ β -D C(2)O = 46:54, and α -D/ β -D C(3)O = 52:48). Substantial amounts (22%) of the trisaccharides **19–22** and a trace of the 2-hydroxyglucal **18** [8] were also formed. Glycosidation of **2** with the bromide **5**, in CH_2Cl_2 at 24° in the presence of Et_4NBr [15], gave very similar results with respect to regioselectivity (1,2-/1,3-linked disaccharides 7:93 in the presence of Hünig's base, or 12:88 in the presence of 4-Å molecular sieves), but higher yields (72–78%) and a much higher stereoselectivity for the major product (α -D/ β -D = 98.5:1.5, or exclusively α -D, respectively). The main by-products (*ca.* 8%) were the trisaccharides **19–22**.

2. *Glycosidation of the Disaccharides 12 and 13 with the Diazirine 1* (see Scheme 3). The disaccharides **12** and **13**, obtained from the *Koenigs-Knorr*-type glycosidations, were glycosylated with the diazirine **1** to obtain larger amounts of the trisaccharides **19–22**, and to examine the dependence of the glycosidation at O–C(2) from the substituents at C(3). The α -D-isomer **12** gave 69% of the trisaccharides **19** and **20**, and the β -D-anomer **13** yielded 71% of the trisaccharides **21** and **22**. In $\text{ClCH}_2\text{CH}_2\text{Cl}$, the stereoselectivity of the



glycosidation of the α -D-isomer **12** was lower than the one for the diol **2** (**19/20** 48:52), while the one for the β -D-anomer **13** remained unchanged (**21/22** 36:64). The stereoselectivity for the glycosidation of **12** was significantly improved by changing the solvent to dioxane (**19/20** 27:73), but the one of **13** was not influenced, while yields were only 49 and 46%, respectively. The trisaccharides **19** and **20** were separated by chromatography, whereas **21** and **22** could only be partially separated. Selected ^1H - and ^{13}C -NMR data of **19–22** are given in Tables 7 and 8.

Table 7. Selected ^1H -NMR (400 MHz, CDCl_3) Chemical Shifts [ppm] and Coupling Constants [Hz] for **19–22**

Compound	19	20	21	22
H–C(1)	4.73	4.71	4.69	4.67
H–C(2)	3.89	4.00	4.01	4.22
H–C(3)	4.22	4.41–4.36	4.33	4.63

Table 7 (cont.)

Compound	19	20	21	22
H–C(4)	4.02	4.00	4.01	4.10
H–C(5)	4.39	4.41–4.36	4.28	4.35
H _A –C(6)	4.28	4.34	4.19	4.28
H _B –C(6)	3.76	3.74	3.76	3.77
H–C(1')	4.89	4.40	4.90	4.44
H–C(2')	3.54	3.46	3.41	3.74–3.44
H–C(3')	3.99	3.74–3.58	3.96	3.74–3.44
H–C(4')	3.71–3.61	3.74–3.58	3.68–3.54	3.74–3.44
H–C(5')	3.87	3.37–3.33	3.86	3.17
H _A –C(6')	3.75	3.74–3.58	3.75	3.74–3.44
H _B –C(6')	3.71–3.61	3.74–3.58	3.68–3.54	3.74–3.44
H–C(1'')	5.11	5.11	4.76	4.50
H–C(2'')	3.71–3.61	3.53	3.51	3.74–3.44
H–C(3'')	4.12	4.10	3.68–3.54	3.74–3.44
H–C(4'')	3.71–3.61	3.74–3.58	3.68–3.54	3.74–3.44
H–C(5'')	4.20–4.17	4.20–4.17	3.39–3.35	3.35
H _A –C(6'')	3.41	3.42	3.68–3.54	3.74–3.44
H _B –C(6'')	3.23–3.20	3.22	3.68–3.54	3.74–3.44
<i>J</i> (1',2')	3.4	7.6	3.7	7.7
<i>J</i> (1'',2'')	3.7	3.4	7.7	5.4

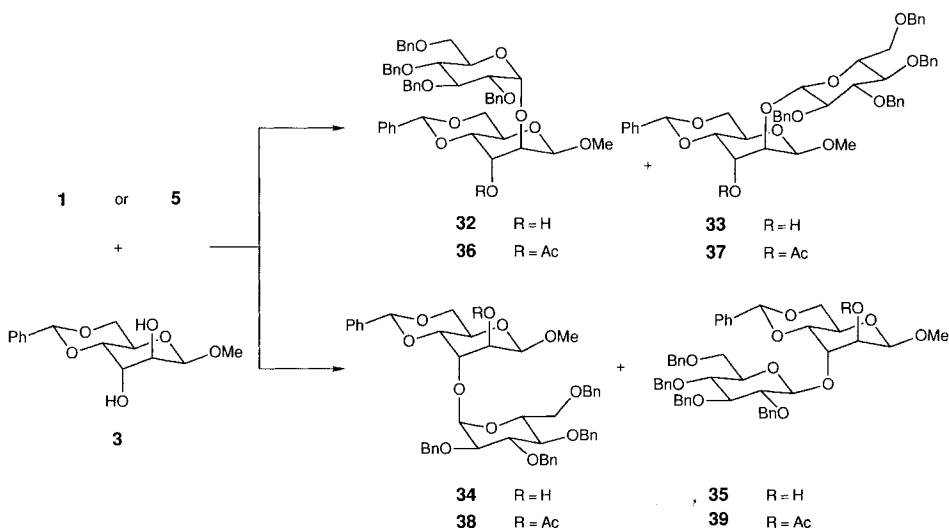
Table 8. Selected ¹³C-NMR (50 MHz, CDCl₃) Chemical Shifts [ppm] for 19–22

Compound	19	20	21	22
C(1)	100.34	100.01	100.50	100.55
C(2)	74.44	75.77 ^{a)}	77.17 ^{a)}	74.57 ^{a)}
C(3)	69.75	69.87	71.61	73.84
C(4)	75.02	75.36 ^{a)}	77.22 ^{a)}	77.56 ^{b)}
C(5)	58.24	58.31	58.56	58.71
C(6)	69.25	69.49	69.22	69.49
PhCH	102.00	102.21	102.25	102.50
C(1')	97.77	103.73	98.12	104.72
C(2')	79.80 ^{a)}	81.96 ^{b)}	80.17	82.09
C(3')	81.77 ^{b)}	84.51	81.59 ^{b)}	84.58 ^{c)}
C(4')	77.64	77.51	77.74 ^{a)}	77.63 ^{b)}
C(5')	70.99	75.01 ^{a)}	70.83	74.91 ^{a)}
C(6')	68.39	68.71	68.57	68.70
C(1'')	94.58	95.62	103.73	104.30
C(2'')	79.95 ^{a)}	80.23	81.69 ^{b)}	81.71
C(3'')	81.63 ^{b)}	81.78 ^{b)}	84.42	84.34 ^{c)}
C(4'')	77.44	77.51	77.86 ^{a)}	79.62
C(5'')	69.85	72.11	74.64	74.91 ^{a)}
C(6'')	68.08	68.15	69.22	68.96

^{a)} ^{b)} ^{c)} Assignments may be interchanged.

3. *Glycosidation of the Methyl β-D-Altopyranoside* 3. Glycosidation of **3** in ClCH₂CH₂Cl with **1** (see *Scheme 4*) gave 56% of a 1:1 mixture of the 1,2- and 1,3-linked disaccharides **32**, **33**, and **34**, **35**, respectively. The stereoselectivity was similar to the one

Scheme 4



observed for **2** (α -D/ β -D = 33.67 and 28:72, respectively). Glycosidation in dioxane led to the same regioselectivity and to higher stereoselectivity, corresponding to an α -D/ β -D ratio of 25:75 for the 1,2- and of 17:83 for the 1,3-linked disaccharides. Glycosidation with the bromide **5** in CH_2Cl_2 according to the *Lemieux* procedure was regioselective, yielding the 1,2- and 1,3-linked pairs of anomers in a ratio of 91:9 and in a yield of 78%. The stereoselectivity was rather low with α -D/ β -D ratios of 67:33 and 52:48 for the 1,2- and 1,3-linked products. Both the regioselectivity and the influence of the anomeric configuration on it are much higher than what has been observed in the glycosidation of the *gluco*-isomer corresponding to **3** [16]. This may be taken as evidence that HO–C(2) in **3** forms stronger intramolecular H-bonds than HO–C(3), and it may mean that axial HO–C(2) groups in 1,2-*cis*-glycosides (β -D-*manno*-type) form stronger H-bonds (*exo*-anomeric effect?) than equatorial HO–C(2) groups in 1,2-*cis*-glycosides (α -D-*gluco*-type).

The ratio of the products **32**–**35** was determined by analytical HPLC, and the products were separated by chromatography. They were characterized as the acetates **36**–**39**. Selected ^1H - and ^{13}C -NMR data of **36**–**39**, establishing the regioselectivity of the glycosidation, are given in *Tables 9* and *10*. The anomeric configuration of the products was deduced from the $J(1',2')$ values.

In the ^1H -NMR spectra of **36** and **37**, the *triplets* of H–C(3) are at 5.39 and 5.71 ppm, while the *doublets* of H–C(2) appear at 3.89 and 4.00 ppm. In the ^1H -NMR spectra of **38** and **39**, the *doublets* of H–C(2) are at 5.08 and 5.55 ppm, whereas the *triplets* of H–C(3) appear at 4.14 and 4.26 ppm. H–C(1') appears at 5.08 ($J = 3.7$ Hz) and 5.06 ppm ($J = 3.6$ Hz) in the spectra of the α -D-configured disaccharides **36** and **38**, while in the spectra of the β -D-configured disaccharides **37** and **39** the *doublets* of H–C(1') are at 4.67 ($J = 7.8$ Hz) and 4.68 ppm ($J = 7.5$ Hz), respectively.

Table 9. Selected ^1H -NMR (400 MHz, CDCl_3) Chemical Shifts [ppm] and Coupling Constants [Hz] for **3** and **36–39**

Compound	3	36	37	38	39
H–C(1)	4.81	4.68	4.74	4.92	4.93
H–C(2)	3.95	3.89	4.00	5.08	5.65
H–C(3)	4.29	5.39	5.71	4.14	4.26
H–C(4)	4.00–3.98	4.11	4.12	3.86	3.94
H–C(5)	4.00–3.98	3.88	3.94	4.04	4.08
H _A –C(6)	4.38	4.33	4.38	4.35	4.37
H _B –C(6)	3.84	3.82	3.82	3.81	3.85
H–C(1')		5.08	4.67	5.06	4.68
H–C(2')		3.62	3.52–3.46	3.61	3.52
H–C(3')		4.08	3.67–3.63	3.98	3.63
H–C(4')		3.68	3.67–3.63	3.68	3.71
H–C(5')		4.26	3.52–3.46	4.19	3.46
H _A –C(6')		3.77	3.76	3.39	3.77
H _B –C(6')		3.61	3.76	3.18	3.77
$J(1',2')$		3.7	7.8	3.6	7.5

Table 10. Selected ^{13}C -NMR (50 MHz, CDCl_3) Chemical Shifts [ppm] for **3** and **36–39**

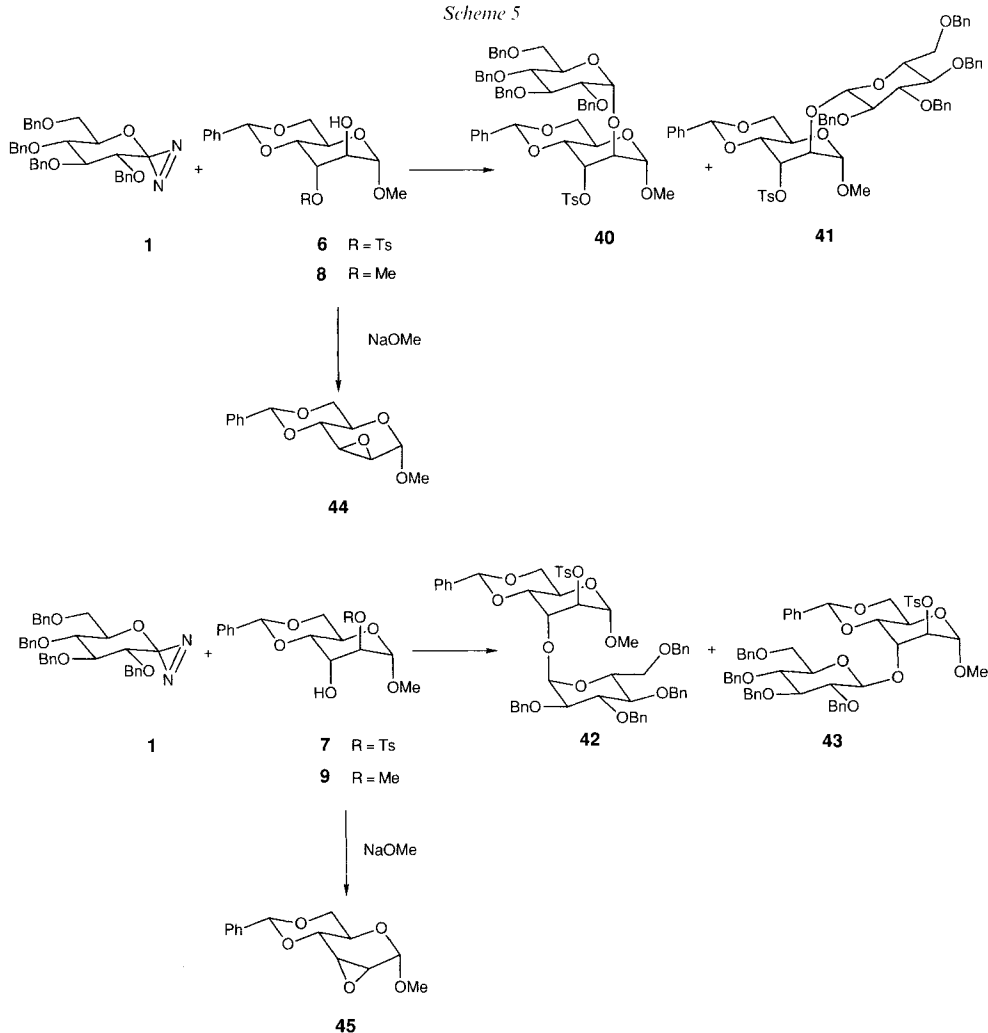
Compound	3^{a)}	36	37	38	39
C(1)	99.4	99.75	100.02	98.53	98.68
C(2)	70.8 ^{b)}	73.79 ^{b)}	74.88	70.07	70.41
C(3)	68.6 ^{b)}	68.28	69.96	71.85	74.89
C(4)	76.5	74.43 ^{b)}	76.06	75.65	76.37
C(5)	62.8	64.47	64.51	63.71	63.78
C(6)	68.6	68.99	69.27	69.03	69.14
PhC'H	101.8	101.62	101.84	102.40	102.46
C(1')		96.75	105.09	96.23	104.49
C(2')		79.82	81.90	79.77	82.29
C(3')		81.76	84.51	82.08	84.50
C(4')		77.71	77.52	77.63	77.42
C(5')		70.38	75.02	69.03	75.20
C(6')		68.41	68.88	67.85	68.75

^{a)} From [12].^{b)} Assignments may be interchanged.

4. *Glycosidation of the Monotosylates 6 and 7 with 1* (see Scheme 5). Glycosidation of these monotosylates by **1** will lead to an ion pair, where the oxy anion is initially located in the σ -plane of the glycosyl cation and cannot immediately add to it. Depending upon the character of the ion pair, and the nucleophilicity of the H-bonded oxy anion (presuming that dimeric alcohol reacts), one might observe competing formation of glycosides and/or epoxides.

The reaction of **6** and **7** with the diazirine **1** in dioxane, $\text{ClCH}_2\text{CH}_2\text{Cl}$ and in THF gave only the disaccharides **40**, **41**, and **42**, **43**, respectively. We observed no trace (*i.e.* < *ca.* 0.5%) of the epoxides **44** and **45**, which we had prepared in a separate experiment under mildly basic conditions [17]. With 1.1 equiv. of **1**, the yields in the glycosidation of the C(2)-tosylate **7** were only *ca.* 30%, while the C(3)-tosylate **6** yielded 60–73% of **40** and

Scheme 5



41. Ca. 65% of **7** and 22–38% of **6** were recovered. Selected $^1\text{H-NMR}$ data of **40–43** are given in Table 5.

These results are in agreement with the mechanistic hypotheses about the carbene-mediated glycosidation which we formulated in earlier papers. They show that a complementary regioselectivity is possible for the *Koenigs-Knorr* type *vs.* the carbene-mediated glycosidation. It is also apparent that *Lemieux's* halide-exchange method may lead to regioselective glycosidation, even when the different degrees of nucleophilicity of OH groups are due to relatively small differences between weak H-bonds.

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Experimental Part

1. *General.* After workup, processing of the org. layer as usual implies drying (MgSO_4) and evaporation of the solvent at or below 40° . Solvents were distilled before use: CH_2Cl_2 and 1,2-dimethoxyethane (DME) over CaH_2 , 1,4-dioxane and THF over Na and benzophenone, toluene over NaH, and $\text{ClCH}_2\text{CH}_2\text{Cl}$ over P_2O_5 . TLC: *Merck* precoated silica gel 60 F_{254} plates, with the solvent systems indicated; detection by spraying the plates with a 0.02M soln. of I_2 and a 0.30M soln. of KI in 10% aq. H_2SO_4 soln. followed by heating at ca. 200° . Flash chromatography (FC): silica gel *Merck* 60 (0.040–0.063 mm). High-performance liquid chromatography (HPLC): anal. 250×4.6 mm column with *Spherisorb* silica (5 μm) for **40/41** (CH_2Cl_2 /hexane 9:1, 1.5 ml/min) and 250×4.0 mm cartridge with *Merck LiChrosorb Si60* for **10–13**, **32–35** (hexane/AcOEt 2:1, 1.5 ml/min), and for **42/43** (CH_2Cl_2 /hexane 9:1, 1.5 ml/min). M.p. uncorrected. Optical rotations: 1-dm cell at 25° and 365, 436, 546, 578, and 589 nm; values at 589 nm were determined from a regression curve. IR spectra: 3% CHCl_3 soln. NMR spectra: 400 MHz for ^1H , at 50 MHz for ^{13}C ; unless stated otherwise, CDCl_3 as solvent, chemical shifts in ppm relative to TMS; in ambiguous cases, ^1H -NMR assignments by selective homonuclear-decoupling experiments; ^{13}C -NMR assignments based upon ^1H , ^{13}C -HMQC (^1H , 400 MHz) of **14–17**.

2. *General Glycosidation Procedures.* 2.1. *Glycosidations by 1 under Thermal Conditions.* Under N_2 , solid diazirine **1** was added to a soln. of the glycosyl acceptor in the indicated solvent. The mixture was stirred at the indicated temp., until all **1** had disappeared. Evaporation of the solvent gave the crude product.

2.2. *Glycosidations by 1 and Photolytic Conditions.* Under N_2 , the soln. of the glycosyl acceptor in the indicated solvent was added to solid diazirine **1**. The mixture was stirred and irradiated (*HPK-125-Philips* high-pressure Hg lamp, *Solidex* glass filter) at the temp. indicated. After disappearance of all **1**, the solvent was evaporated to give the crude product.

2.3. *Glycosidations by 4.* The soln. of the catalyst in $\text{ClCH}_2\text{CH}_2\text{Cl}$ was added under N_2 to a suspension of the glycosyl acceptor, 4-Å molecular sieves, and **4** in $\text{ClCH}_2\text{CH}_2\text{Cl}$. The mixture was maintained at the temp. indicated, until all **4** had disappeared. After addition of excess Et_3N , the mixture was filtered through *Celite*, and the filtrate was concentrated.

2.4. *Glycosidation by 5.* After the addition of **5** to a suspension of the glycosyl acceptor, Et_4NBr , and 4-Å molecular sieves or *Hünig's* base in CH_2Cl_2 , the mixture was stirred under N_2 at the temp. indicated. After all **5** had disappeared, the mixture was filtered through *Celite* and the filtrate was concentrated.

3. *Glycosidation of 2 with 1.* 3.1. *Thermal Conditions.* Reaction of **1** [**18**] (303 mg, 0.55 mmol) and **2** [**19**] (141 mg, 0.50 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (10 ml) for 5 h at 24° and FC (hexane/AcOEt 2:1) gave 265 mg (66%) of a 33:61:3:3 mixture (HPLC) **10/11/12/13**, 23 mg (8%) of **18** [**8**], and 46.4 mg (7%) of a mixture of the trisaccharides **19–22**. Partial separation by another FC (hexane/AcOEt 2:1) gave pure mixtures **10/11** (235 mg) and **12/13** (13.2 mg), which were acetylated in pyridine/ Ac_2O 2:1 for 12 h at r.t. Dilution with CH_2Cl_2 washing the 1M aq. Na_2CO_3 and with H_2O , processing of the org. layer as usual, and FC (hexane/AcOEt 5:1, and CH_2Cl_2 /AcOt 98:2, resp.) afforded **14** (84.8 mg, 34%), **15** (157.5 mg, 64%), **16** (7.5 mg, 54%), and **17** (6.2 mg, 45%), respectively. The separation and characterization of trisaccharides **19–22** are described below.

Reaction of **1** (121.2 mg, 0.22 mmol) and **2** (56.4 mg, 0.2 mmol) in dioxane (4 ml) for 5 h at 24° and FC (hexane/AcOEt 2:1) gave 91.7 mg (57%) of a 16:71:2:11 mixture (HPLC) **10/11/12/13**, 7.3 mg (7%) of **18**, 13.3 mg (5%) of a mixture of the trisaccharides **19–22**, and 28.3 mg (24%) of the (*Z,Z*)-isomer of **23** (its ^1H -NMR spectra were identical to the literature data [9]). Formation of the (*Z,E*)- and (*E,E*)-isomers of **23** was detected on TLC.

3.2. *Photolytic Conditions.* Irradiation of a soln. of **1** (60.6 mg, 0.11 mmol) and **2** (28.2 mg, 0.1 mmol) in CH_2Cl_2 (2 ml) for 1 h at -78° under N_2 and FC (hexane/AcOEt 2:1) gave 37.5 mg (47%) of a 32:54:12:2 mixture (HPLC) **10/11/12/13**, 4.2 mg (8%) of **18**, 9.3 mg (7%) of the trisaccharides **19–22**, 7.2 mg (13%) of methyl 2,3,4,6-tetra-*O*-benzyl- α -D- and - β -D-glucopyranoside [10][11], and 9.8 mg (12%) of **24–27**. This mixture was acetylated in pyridine/ Ac_2O 2:1 for 12 h at r.t. Dilution with CH_2Cl_2 , washing with 1M aq. Na_2CO_3 soln. and with H_2O , processing of the org. layer as usual, and FC (hexane/AcOEt 2:1) afforded **28** (4.0 mg, 36%), **29** (6.3 mg, 57%), and **30/31** (0.6 mg, 6%). FC of combined fractions of different reactions gave pure **31**, while **30** was detected only in the ^1H -NMR spectrum of **30/31**.

For details of analogous reactions of **2** with **1** in various solvents and at different temperatures see Table 4.

Methyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl)- α -D-altropyranoside (**14**). R_f (hexane/AcOEt 2:1) 0.49. $[\alpha]_D^{25} = +54.8$ ($c = 1.01$, CHCl_3). IR: 3060w, 3005m, 2930m, 2870m, 1735s, 1495w, 1455m, 1375m, 1310w, 1245s, 1140s, 1090s, 1070s (sh), 1040s, 1030s (sh), 915w, 820w, 715m (sh), 700s, 670w. ^1H -NMR: 7.48–7.15 (m, 25 arom. H); 5.54 (s, PhCH); 5.25 (t, $J \approx 2.8$, H-C(3)); 5.07 (d, $J = 3.7$, H-C(1'')); 5.00 (d, $J = 10.9$, PhCH_2); 4.86 (d, $J = 9.4$, PhCH_2); 4.86 (d, $J = 10.9$, PhCH_2); 4.76 (d, $J = 11.4$, PhCH_2); 4.72 (s,

H–C(1)); 4.70 (*d*, *J* = 11.4, PhCH₂); 4.62 (*d*, *J* = 12.1, PhCH₂); 4.51 (*d*, *J* = 10.6, PhCH₂); 4.49 (*d*, *J* = 12.1, PhCH₂); 4.32–4.22 (*m*, H_A–C(6), H–C(5)); 4.08 (*dd*, *J* = 3.2, 9.4, H–C(4)); 3.98 (*t*, *J* ≈ 9.3, H–C(3)); 3.95 (*d*, *J* = 2.6, H–C(2)); 3.88 (*ddd*, *J* = 1.8, 3.9, 10.1, H–C(5')); 3.80 (*t*, *J* = 10.0, H_B–C(6)); 3.73 (*dd*, *J* = 4.1, 10.7, H_A–C(6')); 3.65, (*br. d*, *J* ≈ 9.4, H_B–C(6')); 3.64 (*t*, *J* ≈ 9.4, H–C(4')); 3.60 (*dd*, *J* = 3.9, 9.8, H–C(2')); 3.30 (*s*, MeO); 2.12 (*s*, Ac). ¹³C-NMR: 170.60 (*s*, CO); 138.74 (*s*, arom. C); 137.97 (*s*, arom. C); 137.87 (*s*, arom. C); 137.80 (*s*, arom. C); 137.38 (*s*, arom. C); 129.00–126.16 (*m*, arom. C); 101.82 (*d*, PhCH); 100.04 (*d*, C(1)); 98.43 (*d*, C(1')); 81.61 (*d*, C(3')); 79.74 (*d*, C(2')); 77.63 (*d*, C(4')), 75.57 (*d*, C(2)); 75.25 (2*t*, 2 PhCH₂); 74.03 (*d*, C(4)); 73.41 (*t*, PhCH₂); 73.25 (*t*, PhCH₂); 70.95 (*d*, C(5')); 69.18 (*t*, C(6)); 68.45 (*t*, C(6')); 67.88 (*d*, C(3)); 58.62 (*d*, C(5)); 55.28 (*q*, MeO); 21.11 (*q*, Ac). Anal. calc. for C₅₀H₅₄O₁₂ (846.96): C 70.91, H 6.43; found: C 70.65, H 6.25.

Methyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-altropyranoside (15). *R*_f (hexane/AcOEt 2:1) 0.43. M.p. 106–107°. [α]_D²⁵ = +15.8 (*c* = 2.63, CHCl₃). IR: 3090w, 3070w, 3000m, 2920m, 2870m, 1738s, 1605w, 1495w, 1455m, 1375m, 1365m, 1305w, 1220s (br.), 1140s, 1115s (sh), 1070s (br.), 1030s, 915w, 880w, 865w, 820w, 695m, 660w (sh). ¹H-NMR: 7.46–7.16 (*m*, 25 arom. H); 5.59 (*s*, PhCH); 5.51 (*t*, *J* = 2.9, H–C(3)); 4.92 (*d*, *J* = 10.8, PhCH₂); 4.92 (*d*, *J* = 11.0, PhCH₂); 4.81 (*d*, *J* = 10.9, PhCH₂); 4.81 (*d*, *J* = 10.9, PhCH₂); 4.75 (*d*, *J* = 10.9, PhCH₂); 4.67 (*d*, *J* = 12.2, PhCH₂); 4.66 (*s*, H–C(1)); 4.59 (*d*, *J* = 10.8, PhCH₂); 4.54 (*d*, *J* = 12.1, PhCH₂); 4.51 (*d*, *J* = 7.7, H–C(1')); 4.35 (*dd*, *J* = 5.2, 9.9, H_A–C(6)); 4.28 (*dt*, *J* = 5.2, 9.5, H–C(5)); 4.13 (*dd*, *J* = 3.1, 9.5, H–C(4)); 4.06 (*d*, *J* = 2.8, H–C(2)); 3.79 (*t*, *J* = 9.9, H_B–C(6)); 3.78 (*d*, *J* = 2.8, 2 H–C(6')); 3.73 (*t*, *J* = 9.2, H–C(4')); 3.64 (*t*, *J* = 9.0, H–C(3')); 3.50 (*dd*, *J* = 7.8, 8.8, H–C(2')); 3.46 (*dt*, *J* = 2.8, 9.9, H–C(5')), 3.36 (*s*, MeO); 2.09 (*s*, Ac). ¹³C-NMR: 170.34 (*s*, CO); 138.52 (*s*, arom. C); 138.20 (2*s*, 2 arom. C); 138.08 (*s*, arom. C); 137.36 (*s*, arom. C); 128.99–126.14 (*m*, arom. C); 104.31 (*d*, C(1')); 102.00 (*d*, PhCH); 99.93 (*d*, C(1)); 84.58 (*d*, C(3')); 81.95 (*d*, C(2')); 77.41 (*d*, C(4')), 76.07 (*d*, C(2)); 75.19 (*d*, C(5')), 74.97 (2*t*, 2 PhCH₂); 74.29 (*d*, C(4)); 73.64 (2*t*, PhCH₂); 69.39 (*t*, C(6)); 68.65 (*d*, C(3)); 68.42 (*t*, C(6')); 58.82 (*d*, C(5)); 55.34 (*q*, MeO); 21.07 (*q*, Ac). Anal. calc. for C₅₀H₅₄O₁₂ (846.96): C 70.91, H 6.43; found: C 70.63, H 6.61.

Methyl 2-O-Acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-altropyranoside (16). *R*_f (CH₂Cl₂/AcOEt 98:2) 0.51. [α]_D²⁵ = +95.1 (*c* = 1.215, CHCl₃). IR: 3060w, 3005m, 2930m, 2870m, 1740s, 1495w, 1453m, 1385m (sh), 1370m, 1330w, 1310w, 1265m (sh), 1235s, 1160s (sh), 1140s, 1100s, 1070s, 1050s, 1035s, 915m, 890w, 700s, 660w. ¹H-NMR: 7.44–7.05 (*m*, 25 arom. H); 5.57 (*s*, PhCH); 5.20 (*d*, *J* = 3.5, H–C(1')); 5.07 (*d*, *J* = 2.5, H–C(2)); 5.00 (*d*, *J* = 10.9, PhCH₂); 4.83 (3*d*, *J* = 11.7, 3 PhCH₂); 4.67 (*d*, *J* = 11.8, PhCH₂); 4.60 (*s*, H–C(1)); 4.46 (*d*, *J* = 12.5, PhCH₂); 4.43 (*d*, *J* = 11.1, PhCH₂); 4.43 (*dt*, *J* = 5.0, 10.0, H–C(5)); 4.33 (*dd*, *J* = 5.3, 10.3, H_A–C(6)); 4.23 (*d*, *J* = 12.2, PhCH₂); 4.19 (*ddd*, *J* = 2.0, 3.2, 10.2, H–C(5')); 4.14 (*t*, *J* ≈ 2.8, H–C(3)); 4.09 (*t*, *J* = 9.3, H–C(3')); 3.91 (*dd*, *J* = 3.4, 9.7, H–C(4)); 3.75 (*t*, *J* = 10.4, H_B–C(6)); 3.62 (*t*, *J* ≈ 10.0, H–C(4')); 3.63 (*dd*, *J* ≈ 3.4, 9.8, H–C(2')); 3.41 (*dd*, *J* = 3.6, 11.0, H_A–C(6')); 3.27 (*dd*, *J* = 1.9, 10.8, H_B–C(6')); 3.28 (*s*, MeO); 2.13 (*s*, Ac). ¹³C-NMR: 169.24 (*s*, CO); 138.93 (*s*, arom. C); 138.72 (2*s*, 2 arom. C); 138.02 (*s*, arom. C); 137.28 (*s*, arom. C); 128.79–126.21 (*m*, arom. C); 102.19 (*d*, PhCH); 99.18 (*d*, C(1)); 94.77 (*d*, C(1')); 81.60 (*d*, C(3')); 79.83 (*d*, C(2')); 77.46 (*d*, C(4')); 75.37 (*t*, PhCH₂); 75.16 (*d*, C(4)); 74.54 (*t*, PhCH₂); 72.90 (*t*, PhCH₂); 71.69 (*t*, PhCH₂); 69.69 (2*d*, C(3), C(5')); 69.19 (*d* and *t*, C(2), C(6)); 68.10 (*t*, C(6')); 57.97 (*d*, C(5)); 55.34 (*q*, MeO); 20.81 (*q*, Ac). Anal. calc. for C₅₀H₅₄O₁₂ (846.96): C 70.91, H 6.43; found: C 70.65, H 6.16.

Methyl 2-O-Acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-altropyranoside (17). *R*_f (CH₂Cl₂/AcOEt 98:2) 0.36. [α]_D²⁵ = +33.7 (*c* = 2.05, CHCl₃). IR: 3060w, 3030w (sh), 3005m, 2940w, 2870m, 1742s, 1498w, 1455m, 1380m (sh), 1370m, 1360m (sh), 1310w, 1240s, 1200w, 1140s, 1118s, 1095s, 1070s, 1030s, 1010s, 920w, 895w, 722s, 700s, 665m. ¹H-NMR: 7.51–7.16 (*m*, 25 arom. H); 5.59 (*s*, PhCH); 5.26 (*d*, *J* = 2.6, H–C(2)); 5.14 (*d*, *J* = 11.5, PhCH₂); 4.91 (*d*, *J* = 11.0, PhCH₂); 4.80 (*d*, *J* = 11.0, PhCH₂); 4.79 (*d*, *J* = 7.7, H–C(1')); 4.79 (*d*, *J* = 10.9, PhCH₂); 4.73 (*d*, *J* = 11.0, PhCH₂); 4.64 (*d*, *J* = 12.2, PhCH₂); 4.59 (*s*, H–C(1)); 4.56 (*d*, *J* = 12.2, PhCH₂); 4.55 (*d*, *J* = 10.8, PhCH₂); 4.38 (*dt*, *J* = 5.3, 10.1, H–C(5)); 4.30 (*t*, *J* = 2.8, H–C(3)); 4.27 (*dd*, *J* = 5.4, 10.4, H_A–C(6)); 3.96 (*dd*, *J* = 3.0, 9.7, H–C(4)); 3.76 (*t*, *J* = 10.4, H_B–C(6)); 3.72 (*dd*, *J* = 1.6, 11.6, H_A–C(6')); 3.70 (*dd*, *J* = 4.6, 11.1, H_B–C(6')); 3.63–3.57 (*m*, H–C(3'), H–C(4')); 3.52 ('*td*', *J* = 7.5, 2.5 (virtual coupling), H–C(2')); 3.43–3.39 (*m*, *J* = 2.1, 4.4, 6.8, H–C(5')); 3.34 (*s*, MeO); 2.09 (*s*, Ac). ¹³C-NMR: 169.08 (*s*, CO); 138.80 (*s*, arom. C); 138.76 (*s*, arom. C); 138.55 (*s*, arom. C); 138.20 (*s*, arom. C); 137.47 (*s*, arom. C); 129.02–126.16 (*m*, arom. C); 103.61 (*d*, C(1')); 102.51 (*d*, PhCH); 99.30 (*d*, C(1)); 84.41 (*d*, C(3')); 81.88 (*d*, C(2')); 77.73 (*d*, C(4')); 76.71 (*d*, C(4)); 75.42 (*t*, PhCH₂); 75.10 (*d*, C(5')); 74.91 (*t*, PhCH₂); 74.09 (*t*, PhCH₂); 73.55 (*t*, PhCH₂); 71.65 (*d*, C(2)); 71.58 (*d*, C(3)); 69.24 (*t*, C(6)); 69.08 (*t*, C(6')); 58.48 (*d*, C(5)); 55.45 (*q*, MeO); 20.90 (*q*, Ac). Anal. calc. for C₅₀H₅₄O₁₂ (846.96): C 70.91, H 6.43; found: C 70.68, H 6.57.

1,2-Di-O-acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-altropyranose (28). *R*_f (hexane/AcOEt 2:1) 0.46. [α]_D²⁵ = +68.1 (*c* = 1.10, CHCl₃). IR: 3060w, 3040w, 3000w, 2920w, 2870w, 1745s, 1498w, 1470w (sh), 1455m, 1410w (sh), 1370m, 1330w, 1310w, 1260w, 1242m, 1160s (sh), 1150s, 1105s, 1072s, 1045s, 1030s (sh), 1015s, 1005s (sh), 985m (sh), 910w, 870w, 700s. ¹H-NMR: 7.46–7.11 (*m*, 25 arom. H); 5.95 (*br. s*,

H–C(1)); 5.57 (s, PhCH); 5.06 (dd, $J = 0.9, 2.8$, H–C(2)); 5.01 (d, $J = 3.4$, H–C(1')); 4.94 (d, $J = 10.9$, PhCH₂); 4.85 (d, $J = 10.9$, PhCH₂); 4.78 (d, $J = 10.9$, PhCH₂); 4.71 (d, $J = 11.4$, PhCH₂); 4.67 (d, $J = 11.6$, PhCH₂); 4.42 (d, $J = 12.2$, PhCH₂); 4.42 (dt, $J \approx 5.0, 9.9$, H–C(5)); 4.40 (d, $J = 10.7$, PhCH₂); 4.35 (dd, $J = 5.3, 10.3$, H_A–C(6)); 4.15 (td, $J \approx 2, 10.3$, H–C(5')); 4.12 (d, $J = 12.2$, PhCH₂); 4.08 (t, $J = 2.7$, H–C(3)); 3.99 (t, $J \approx 9.5$, H–C(3')); 3.91 (dd, $J = 3.3, 9.7$, H–C(4)); 3.73 (t, $J = 10.3$, H_B–C(6)); 3.67 (dd, $J = 9.2, 10.0$, H–C(4')); 3.56 (dd, $J = 3.4, 9.8$, H–C(2')); 3.20 (dd, $J = 2.5, 11.1$, H_A–C(6')); 2.89 (dd, $J = 1.9, 11.0$, H_B–C(6')); 2.18 (s, Ac); 1.85 (s, Ac). ¹³C-NMR: 169.36 (s); 169.15 (s); 138.82 (s); 138.65 (s); 137.93 (s); 137.90 (s); 137.19 (s); 129.13–126.24 (m); 102.47 (d); 97.81 (d); 91.23 (d); 81.99 (d); 79.71 (d); 77.57 (d); 75.58 (t); 74.93 (d); 74.75 (t); 73.42 (t); 73.24 (t); 72.33 (d); 70.16 (d); 69.55 (d); 68.90 (t); 67.53 (t); 60.46 (d); 20.88 (q); 20.53 (q). Anal. calc. for C₁₅H₅₄O₁₃ (890.97): C 68.75, H 6.11; found: C 68.76, H 6.12.

1,2-Di-O-acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl)- β -D-altropyranose (29). R_f (hexane/AcOEt 2:1) 0.31. $[\alpha]_D^{25} = +39.0$ ($c = 1.75$, CHCl₃). IR: 3060w, 3030w (sh), 3000m, 2930m, 2870m, 1755s (br.), 1500m, 1455s, 1395m (sh), 1370s, 1330m, 1315m, 1245s, 1200m, 1160s (sh), 1140s, 1100s, 1070s (br.), 1030s (sh), 1010s (sh), 960m, 915m, 870w, 700s, 660w. ¹H-NMR: 7.41–7.09 (m, 25 arom. H); 6.26 (d, $J = 1.5$, H–C(1)); 5.54 (s, PhCH); 5.12 (dd, $J = 1.5, 3.7$, H–C(2)); 4.97 (d, $J = 10.9$, PhCH₂); 4.95 (d, $J = 3.6$, H–C(1')); 4.86 (d, $J = 10.9$, PhCH₂); 4.82 (d, $J = 10.7$, PhCH₂); 4.79 (d, $J = 11.4$, PhCH₂); 4.68 (d, $J = 11.9$, PhCH₂); 4.44 (d, $J = 9.9$, PhCH₂); 4.44 (d, $J = 12.4$, PhCH₂); 4.37 (dd, $J = 5.2, 10.4$, H_A–C(6)); 4.23 (dt, $J = 5.1, 9.9$, H–C(5)); 4.19 (d, $J = 12.2$, PhCH₂); 4.18–4.15 (m, H–C(3), H–C(5')); 4.00 (t, $J = 9.4$, H–C(3')); 3.91 (dd, $J = 3.0, 9.8$, H–C(4)); 3.79 (t, $J = 10.3$, H_B–C(6)); 3.64 (t, $J = 10.0$, H–C(4')); 3.58 (dd, $J = 3.6, 9.6$, H–C(2')); 3.36 (dd, $J = 3.1, 10.9$, H_A–C(6')); 3.17 (dd, $J = 1.9, 10.9$, H_B–C(6')); 2.19 (s, Ac); 2.09 (s, Ac). ¹³C-NMR: 169.41 (s); 168.01 (s); 138.78 (s); 138.62 (s); 137.25 (s); 137.93 (s); 137.09 (s); 129.03–126.26 (m); 102.45 (d); 96.54 (d); 90.08 (d); 81.93 (d); 79.55 (d); 77.48 (d); 75.60 (t); 75.14 (d); 74.71 (t); 73.41 (t); 73.14 (t); 71.75 (d); 70.14 (d); 68.72 (t); 68.24 (d); 67.90 (t); 64.52 (d); 20.81 (q); 20.70 (q). Anal. calc. for C₅₁H₅₄O₁₃ (890.97): C 68.75, H 6.11; found: C 68.99, H 6.12.

1,2-Di-O-acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl- β -D-glucopyranosyl)- β -D-altropyranoside (31). R_f (hexane/AcOEt 2:1) 0.37. $[\alpha]_D^{25} = +3.6$ ($c = 0.41$, CHCl₃). IR: 3030w (sh), 3000w, 2950w (sh), 2920m, 2860w, 1755m (br.), 1498w, 1465w (sh), 1455w, 1395w (sh), 1375m, 1310w, 1260m, 1240m, 1200w, 1135m (sh), 1095s (sh), 1070s (br.), 1030m (sh), 1010m (br.), 950w (sh), 910w, 815w, 700m, 665w. ¹H-NMR: 7.44–7.11 (m, 25 arom. H); 6.23 (d, $J = 1.4$, H–C(1)); 5.58 (s, PhCH); 5.58 (dd, $J = 1.4, 4.0$, H–C(2)); 5.05 (d, $J = 11.1$, PhCH₂); 4.89 (d, $J = 10.9$, PhCH₂); 4.81 (d, $J = 10.8$, PhCH₂); 4.75 (d, $J = 11.0$, PhCH₂); 4.69 (d, $J = 7.6$, H–C(1)); 4.68 (d, $J = 11.2$, PhCH₂); 4.62 (d, $J = 12.2$, PhCH₂); 4.57 (d, $J = 10.9$, PhCH₂); 4.53 (d, $J = 12.2$, PhCH₂); 4.36 (dd, $J = 5.2, 10.4$, H_A–C(6)); 4.30 (br. t, $J \approx 3.3$, H–C(3)); 4.21 (dt, $J = 5.0, 9.9$, H–C(5)); 3.98 (dd, $J = 2.8, 9.7$, H–C(4)); 3.80 (t, $J = 10.3$, H_B–C(6)); 3.74–3.71 (m, 2 H–C(6')); 3.64–3.62 (m, H–C(3'), H–C(4')); 3.53 (dd, $J = 7.7, 8.3$, H–C(2')); 3.48–3.44 (m, H–C(5')), 2.18 (s, Ac); 2.03 (s, Ac). Anal. calc. for C₅₁H₅₄O₁₃ (890.97): C 68.75, H 6.11; found: C 68.54, H 6.35.

4. Glycosidation of 2 with 4. A 0.1M soln. of BF₃·OEt₂ in ClCH₂CH₂Cl (3.3 ml, 0.33 mmol) was added to a cooled (–30°) mixture of **4** [20] [21] (226 mg, 0.33 mmol), **2** (84.6 mg, 0.3 mmol), and 4-Å molecular sieves (230 mg) in ClCH₂CH₂Cl (6 ml). The mixture was stirred for 1 h at –30°, treated with Et₃N (0.15 ml, 1.08 mmol), and filtered through Celite. Evaporation of the filtrate and FC (hexane/AcOEt 2:1) of the residue gave 161.6 mg (67%) of a 4:5:47:44 mixture (HPLC) **10/11/12/13**, 3 mg (2%) of **18**, and 87.6 mg (22%) of the trisaccharides **19–22**.

5. Glycosidation of 2 with 5. A soln. of **5** [22] (795 mg, 1.32 mmol), **2** (409 mg, 1.45 mmol), Et₄NBr (304.5 mg, 1.45 mmol), and Hünig's base (0.25 ml, 1.43 mmol) in CH₂Cl₂ (15 ml) was stirred for 2 d at 24°. FC (hexane/AcOEt 2:1) gave 765.8 mg (72%) of a 5:2:92:1 mixture (HPLC) **10/11/12/13**, 13.4 mg (2%) of **18**, and 70 mg (8%) of the trisaccharides **19–22**.

An analogous reaction of **5** (820 mg, 1.34 mmol), **2** (409 mg, 1.45 mmol), Et₄NBr (304.5 mg, 1.45 mmol), and 4-Å molecular sieves (600 mg) in CH₂Cl₂ (15 ml) gave 841.3 mg (78%) of a 3:9:88 mixture **10/11/12**, 20.1 mg (3%) of **18**, and 75.3 mg (8.5%) of the trisaccharide **19**.

6. Glycosidation of 12 with 1. Reaction of **1** (65.1 mg, 0.118 mmol) and **12** (86.5 mg, 0.107 mmol) in dioxane (2 ml) for 5 h at 24° and FC (hexane/AcOEt 4:1) gave 18.7 mg (13%) **19** and 50.7 mg (36%) **20**.

An analogous reaction of **1** (32.3 mg, 0.058 mmol) and **12** (43.0 mg, 0.05 mmol) in ClCH₂CH₂Cl (1 ml) gave 23.6 mg (33%) of **19** and 25.2 mg (36%) of **20**.

Methyl 2,3-Bis-O-(2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl)-4,6-O-benzylidene- α -D-altropyranoside (19). R_f (hexane/AcOEt 4:1) 0.17. $[\alpha]_D^{25} = +78.4$ ($c = 1.67$, CHCl₃). IR: 3060w, 3030w (sh), 3000m, 2920m (br.), 2870m,

1500m, 1455s, 1382m, 1365s, 1330w, 1310w (sh), 1260m, 1200w, 1160s (sh), 1142s, 1100s (br.), 1070s (sh), 1030s, 960w (sh), 910s, 860w, 820w, 700s, 650w. ¹H-NMR: 7.45–7.07 (m, 45 arom. H); 5.52 (s, PhCH); 5.11 (d, *J* = 3.4, H–C(1'')); 4.98 (d, *J* = 10.9, PhCH₂); 4.97 (d, *J* = 10.9, PhCH₂); 4.89 (d, *J* = 3.7, H–C(1'')); 4.85 (d, *J* = 10.3, PhCH₂); 4.84 (d, *J* = 11.0, PhCH₂); 4.83 (d, *J* = 11.0, PhCH₂); 4.82 (d, *J* = 10.6, PhCH₂); 4.76 (d, *J* = 11.9, PhCH₂); 4.73 (s, H–C(1)); 4.67 (d, *J* = 11.8, PhCH₂); 4.64 (d, *J* = 12.8, PhCH₂); 4.61 (d, *J* = 12.3, PhCH₂); 4.55 (d, *J* = 11.6, PhCH₂); 4.50 (d, *J* = 9.6, PhCH₂); 4.48 (d, *J* = 11.6, PhCH₂); 4.45 (d, *J* = 10.7, PhCH₂); 4.43 (d, *J* = 12.2, PhCH₂); 4.39 (dt, *J* = 5.2, 10.0, H–C(5)); 4.28 (dd, *J* = 5.3, 10.3, H_A–C(6)); 4.22 (d, *J* = 12.2, PhCH₂); 4.22 (t, *J* ≈ 2.9, H–C(3)); 4.20–4.17 (m, H–C(5'')); 4.12 (t, *J* = 9.2, H–C(3'')); 4.02 (dd, *J* = 3.2, 9.7, H–C(4)); 3.99 (t, *J* = 9.3, H–C(3'')); 3.89 (d, *J* = 2.7, H–C(2)); 3.87 (ddd, *J* = 1.7, 3.8, 10.0, H–C(5'')); 3.76 (t, *J* = 10.3, H_B–C(6)); 3.75 (dd, *J* = 3.8, 9.7, H_A–C(6'')); 3.71–3.61 (m, H–C(4'), H_B–C(6'), H–C(2''), H–C(4'')); 3.54 (dd, *J* = 3.7, 9.7, H–C(2'')); 3.41 (dd, *J* = 2.9, 10.8, H_A–C(6'')); 3.23–3.20 (m, H_B–C(6'')); 3.21 (s, MeO). ¹³C-NMR: 138.99 (s); 138.92 (s); 138.85 (s); 138.72 (s); 138.01 (3s); 137.80 (s); 137.62 (s); 128.79–126.34 (m); 102.00 (d); 100.34 (d); 97.77 (d); 94.58 (d); 81.77 (d); 81.63 (d); 79.95 (d); 79.80 (d); 77.64 (d); 77.44 (d); 75.56 (t); 75.53 (t); 75.21 (t); 75.02 (d); 74.61 (t); 74.44 (t); 73.40 (t); 73.25 (t); 73.13 (t); 71.62 (t); 70.99 (d); 69.85 (d); 69.75 (d); 69.25 (t); 68.39 (t); 68.08 (t); 58.24 (d); 55.22 (q). Anal. calc. for C₈₂H₈₆O₁₆ (1327.57): C 74.19, H 6.53; found: C 73.96, H 6.76.

Methyl 4,6-O-Benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-altropyranoside (20). *R*_f (hexane/AcOEt 4:1) 0.38. [α]_D²⁵ = +53.1 (*c* = 1.75, CHCl₃). IR: 3060w, 3030w (sh), 3000m, 2920m, 2870m, 1498m, 1455s, 1400w (sh), 1380w, 1360m, 1330w, 1310w, 1265w, 1195w (sh), 1145s, 1100s (br.), 1070s, 1030s, 910s, 825w, 700s, 650w. ¹H-NMR: 7.44–7.07 (m, 45 arom. H); 5.55 (s, PhCH); 5.11 (d, *J* = 3.4, H–C(1'')); 4.96 (d, *J* = 11.3, PhCH₂); 4.96 (d, *J* = 10.4, PhCH₂); 4.93 (d, *J* = 12.5, PhCH₂); 4.83 (d, *J* = 9.6, 2 PhCH₂); 4.81 (d, *J* = 10.8, 2 PhCH₂); 4.72 (d, *J* = 10.6, PhCH₂); 4.71 (s, H–C(1)); 4.69 (d, *J* = 13.3, PhCH₂); 4.59 (d, *J* = 12.0, PhCH₂); 4.55 (d, *J* = 10.8, PhCH₂); 4.54 (d, *J* = 12.1, PhCH₂); 4.48 (d, *J* = 12.0, PhCH₂); 4.46 (d, *J* = 10.9, PhCH₂); 4.44 (d, *J* = 12.1, PhCH₂); 4.41–4.36 (m, H–C(3), H–C(5)); 4.40 (d, *J* ≈ 7.6, H–C(1'')); 4.34 (dd, *J* = 5.4, 10.0, H_A–C(6)); 4.19 (d, *J* = 12.1, PhCH₂); 4.20–4.17 (m, H–C(5'')); 4.10 (t, *J* = 9.3, H–C(3'')); 4.00 (dd, *J* = 3.3, 9.3, H–C(4)); 4.00 (d, *J* = 2.9, H–C(2)); 3.74 (t, *J* = 10.0, H_B–C(6)); 3.74–3.58 (m, H–C(3''), H–C(4'), 2 H–C(6''), H–C(4'')); 3.53 (dd, *J* = 3.4, 9.6, H–C(2'')); 3.46 (t, *J* ≈ 8.6, H–C(2'')); 3.42 (dd, *J* = 2.6, 10.9, H_A–C(6'')); 3.37–3.33 (m, H–C(5'')); 3.27 (s, MeO); 3.22 (dd, *J* = 1.7, 10.8, H_B–C(6'')). ¹³C-NMR: 139.07 (s); 139.03 (s); 138.90 (s); 138.53 (s); 138.17 (s); 138.13 (s); 138.02 (2s); 137.63 (s); 128.81–126.34 (m); 103.73 (d); 102.21 (d); 100.01 (d); 95.62 (d); 84.51 (d); 81.96 (d); 81.78 (d); 80.23 (d); 77.51 (2d); 75.77 (d); 75.71 (t); 75.51 (t); 75.36 (d); 75.09 (t); 75.01 (t and d); 74.79 (t); 73.55 (t); 73.13 (t); 72.11 (d); 71.68 (t); 69.87 (d); 69.49 (t); 68.71 (t); 68.15 (t); 58.31 (d); 55.27 (q). Anal. calc. for C₈₂H₈₆O₁₆ (1327.57): C 74.19, H 6.53; found: C 74.01, H 6.67.

7. Glycosidation of 13 with 1. Reaction of **1** (123.4 mg, 0.224 mmol) and **13** (164 mg, 0.204 mmol) in dioxane (4 ml) for 5 h at 24° and FC (hexane/AcOEt 4:1) gave a 3:7 mixture (¹H-NMR: signals of PhCH and MeO) **21/22** (125.3 mg, 46%), which were partially separated by another FC (CH₂Cl₂/AcOEt 98:2).

An analogous reaction of **1** (65.0 mg, 0.118 mmol) and **13** (86.5 mg, 0.107 mmol) in ClCH₂CH₂Cl (2 ml) gave a 36:64 mixture **21/22** (101.4 mg, 71%).

Methyl 4,6-O-Benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-3-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-altropyranoside (21). *R*_f (CH₂Cl₂/AcOEt 98:2) 0.22. [α]_D²⁵ = +35.6 (*c* = 0.75, CHCl₃). IR: 3060w, 3030w (sh), 3000m, 2930m, 2870m, 1500m, 1455s, 1405w, 1380m, 1360m, 1310w, 1265m, 1140s, 1090s (sh), 1070s (br.), 1030s, 915w, 820w, 700s. ¹H-NMR: 7.52–7.13 (m, 45 arom. H); 5.50 (s, PhCH); 5.15 (d, *J* = 11.5, PhCH₂); 4.97 (d, *J* = 11.0, PhCH₂); 4.93 (d, *J* = 11.1, PhCH₂); 4.90 (d, *J* = 3.7, H–C(1'')); 4.85 (d, *J* = 10.0, PhCH₂); 4.83 (d, *J* = 10.6, PhCH₂); 4.81 (d, *J* = 11.5, PhCH₂); 4.79 (d, *J* = 10.9, PhCH₂); 4.76 (d, *J* = 7.7, H–C(1'')); 4.73 (d, *J* = 11.1, PhCH₂); 4.69 (s, H–C(1)); 4.60 (d, *J* = 12.0, PhCH₂); 4.59 (d, *J* = 11.6, PhCH₂); 4.52 (d, *J* = 10.6, PhCH₂); 4.50 (d, *J* = 10.8, PhCH₂); 4.47 (d, *J* = 11.7, PhCH₂); 4.46 (d, *J* = 12.1, PhCH₂); 4.46 (d, *J* = 12.2, PhCH₂); 4.42 (d, *J* = 12.0, PhCH₂); 4.33 (t, *J* = 2.8, H–C(3)); 4.28 (dt, *J* = 5.2, 10.3, H–C(5)); 4.19 (dd, *J* = 5.3, 10.3, H_A–C(6)); 4.01 (d, *J* = 2.7, H–C(2)); 4.01 (dd, *J* = 2.9, 9.6, H–C(4)); 3.96 (t, *J* = 9.3, H–C(3'')); 3.86 (ddd, *J* = 1.7, 4.2, 9.8, H–C(5'')); 3.76 (t, *J* = 10.3, H_B–C(6)); 3.75 (dd, *J* = 4.2, 10.8, H_A–C(6'')); 3.68–3.54 (m, H–C(4'), H_B–C(6'), H–C(3''), H–C(4''), 2 H–C(6'')); 3.51 (dd, *J* = 8.0, 8.6, H–C(2'')); 3.41 (dd, *J* = 3.7, 9.5, H–C(2'')); 3.39–3.35 (m, H–C(5'')); 3.26 (s, MeO). ¹³C-NMR: 138.85 (s); 138.81 (s); 138.75 (2s); 138.18 (s); 138.13 (2s); 137.94 (s); 137.80 (s); 128.97–126.46 (m); 103.73 (d); 102.25 (d); 100.50 (d); 98.12 (d); 84.42 (d); 81.69 (d); 81.59 (d); 80.17 (d); 77.86 (d); 77.74 (d); 77.22 (d); 77.17 (d); 75.54 (t); 75.49 (t); 75.22 (t); 74.99 (t); 74.64 (d); 73.41 (t); 73.35 (t); 73.24 (t); 71.61 (d); 70.83 (d); 69.22 (2t); 68.57 (t); 58.56 (d); 55.20 (q). Anal. calc. for C₈₂H₈₆O₁₆·H₂O (1345.58): C 73.19, H 6.59; found: C 73.25, H 6.78.

Methyl 2,3-Bis-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-4,6-O-benzylidene-α-D-altropyranoside (22). R_f ($\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 98:2) 0.16. $[\alpha]_D^{25} = +26.0$ ($c = 1.84$, CHCl_3). IR: 3070w, 3040w (sh), 3010w, 2910m, 2865m, 1500m, 1458m, 1400w, 1382m, 1360m, 1310w, 1260w, 1195w, 1145s (sh), 1115s (sh), 1090s (sh), 1070s (br.), 1030s, 1010s (sh), 915w, 865w, 820w, 700s. $^1\text{H-NMR}$: 7.51–7.12 (m, 45 arom. H); 5.60 (s, PhCH); 5.15 (d, $J = 11.6$, PhCH_2); 4.95 (d, $J = 10.9$, PhCH_2); 4.90 (d, $J = 11.0$, PhCH_2); 4.90 (d, $J = 11.0$, PhCH_2); 4.81 (d, $J = 11.0$, PhCH_2); 4.78 (d, $J = 11.4$, PhCH_2); 4.78 (d, $J \approx 9.5$, PhCH_2); 4.77 (d, $J = 11.0$, PhCH_2); 4.75 (d, $J = 10.7$, PhCH_2); 4.70 (d, $J = 11.0$, PhCH_2); 4.67 (s, $\text{H-C}(1)$); 4.64 (d, $J = 11.2$, PhCH_2); 4.63 (t, $J \approx 3.5$, $\text{H-C}(3)$); 4.55 (d, $J = 10.9$, PhCH_2); 4.50 (d, $J \approx 5.4$, $\text{H-C}(1')$); 4.50 (s, 2 PhCH_2); 4.49 (d, $J = 11.0$, PhCH_2); 4.48 (d, $J = 12.1$, PhCH_2); 4.44 (d, $J = 7.7$, $\text{H-C}(1')$); 4.35 (dt, $J = 5.2$, 9.9, $\text{H-C}(5)$); 4.28 (dd, $J = 5.3$, 10.2, $\text{H}_A\text{-C}(6)$); 4.22 (d, $J = 2.9$, $\text{H-C}(2)$); 4.10 (dd, $J = 2.9$, 9.6, $\text{H-C}(4)$); 3.77 (t, $J = 10.3$, $\text{H}_B\text{-C}(6)$); 3.74–3.44 (m, $\text{H-C}(2')$, $\text{H-C}(3')$, $\text{H-C}(4')$, 2 $\text{H-C}(6')$, $\text{H-C}(2'')$, $\text{H-C}(3'')$, $\text{H-C}(4'')$, 2 $\text{H-C}(6'')$); 3.35 (td, $J = 3.4$, 9.5, $\text{H-C}(5'')$); 3.31 (s, MeO); 3.17 (ddd, $J = 1.7$, 4.3, 9.3, $\text{H-C}(5')$). $^{13}\text{C-NMR}$: 138.97 (s); 138.83 (s); 138.56 (s); 138.42 (2s); 138.23 (2s); 137.96 (s); 137.76 (s); 128.89–126.46 (m); 104.72 (d); 104.30 (d); 102.50 (d); 100.55 (d); 84.58 (d); 84.34 (d); 82.09 (d); 81.71 (d); 79.62 (d); 77.63 (d); 77.56 (d); 75.59 (t); 75.35 (t); 74.91 (2d); 74.84 (2t); 74.71 (t); 74.57 (d); 74.04 (t); 73.84 (d); 73.48 (t); 73.28 (t); 69.49 (t); 68.96 (t); 68.70 (t); 58.71 (d); 55.27 (q). Anal. calc. for $\text{C}_{82}\text{H}_{86}\text{O}_{16} \cdot \text{H}_2\text{O}$ (1345.58): C 73.19, H 6.59; found: C 73.05, H 6.57.

8. *Glycosidation of 3 with 1.* Reaction of **1** (185.2 mg, 0.336 mmol) and **3** [23] (86.3 mg, 0.306 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (6 ml) for 5 h at 24° gave, after FC (hexane/AcOEt 2:1), 137.5 mg (56%) of a 17:34:14:35 mixture (HPLC) **32/33/34/35**. The disaccharides were separated by another FC (hexane/AcOEt 4:1) and acetylated in pyridine/Ac₂O 2:1 for 12 h at r.t. Dilution with CH_2Cl_2 , washing with 1M aq. Na_2CO_3 soln. and with H_2O , and processing of the org. layer as usual afforded **36–39**.

An analogous reaction of **1** (185.2 mg, 0.336 mmol) and **3** (86.3 mg, 0.306 mmol) in dioxane (6 ml) gave 121 mg (48%) of a 13:39:8:40 mixture **32/33/34/35**.

Methyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-altropyranoside (36). R_f (hexane/AcOEt 2:1) 0.41. $[\alpha]_D^{25} = +9.0$ ($c = 0.98$, CHCl_3). IR: 3060w, 3030w, 3000w, 2930m, 2870m, 1750s, 1498w, 1470w (sh), 1455m, 1365m (br.), 1310w, 1260w (sh), 1240s, 1195w, 1165s, 1140s, 1110s, 1085s, 1070s (sh), 1030s, 1005s, 915w, 890w, 700s, 640w. $^1\text{H-NMR}$: 7.42–7.15 (m, 25 arom. H); 5.41 (s, PhCH); 5.39 (t, $J \approx 3.3$, $\text{H-C}(3)$); 5.08 (d, $J = 3.7$, $\text{H-C}(1')$); 4.96 (d, $J = 10.9$, PhCH_2); 4.85 (d, $J = 10.9$, 2 PhCH_2); 4.78 (d, $J = 11.3$, PhCH_2); 4.68 (d, $J = 11.2$, PhCH_2); 4.68 (d, $J = 1.4$, $\text{H-C}(1)$); 4.64 (d, $J = 12.2$, PhCH_2); 4.53 (d, $J = 10.9$, PhCH_2); 4.48 (d, $J = 12.2$, PhCH_2); 4.33 (d, $J = 4.4$, 9.8, $\text{H}_A\text{-C}(6)$); 4.26 (br. td, $J = 2.6$, 9.8, $\text{H-C}(5')$); 4.11 (dd, $J = 3.1$, 9.4, $\text{H-C}(4)$); 4.08 (t, $J = 9.3$, $\text{H-C}(3')$); 3.89 (dd, $J = 1.4$, 3.6, $\text{H-C}(2)$); 3.88 (dt, $J = 4.2$, 9.0, $\text{H-C}(5)$); 3.82 (t, $J = 9.9$, $\text{H}_B\text{-C}(6)$); 3.77 (dd, $J = 3.3$, 10.7, $\text{H}_A\text{-C}(6')$); 3.68 (t, $J = 9.3$, $\text{H-C}(4')$); 3.62 (dd, $J = 3.8$, 9.6, $\text{H-C}(2'')$); 3.61 (dd, $J = 2.3$, 10.7, $\text{H}_B\text{-C}(6'')$); 3.49 (s, MeO); 2.13 (s, Ac). $^{13}\text{C-NMR}$: 169.53 (s); 138.91 (s); 138.52 (s); 138.14 (2s); 137.30 (s); 128.79–126.09 (m); 101.62 (d); 99.75 (d); 96.75 (d); 81.76 (d); 79.82 (d); 77.71 (d); 75.50 (t); 74.87 (t); 74.43 (d); 73.79 (d); 73.34 (t); 73.29 (t); 70.38 (d); 68.99 (t); 68.41 (t); 68.28 (d); 64.47 (d); 57.34 (q, MeO); 21.00 (q, Ac). Anal. calc. for $\text{C}_{50}\text{H}_{54}\text{O}_{12}$ (846.96): C 70.91, H 6.43; found: C 70.89, H 6.32.

Methyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-β-D-altropyranoside (37). R_f (hexane/AcOEt 2:1) 0.40. $[\alpha]_D^{25} = +30.1$ ($c = 2.44$, CHCl_3). IR: 3080w (sh), 3050w, 3020m, 2920m, 2880s, 1755s, 1500m, 1470m (sh), 1455s, 1390s (sh), 1370s (br.), 1310m, 1240s, 1165s (sh), 1150s (sh), 1110s, 1075s (br.), 1030s, 1005s, 915m, 885w, 700s, 665w. $^1\text{H-NMR}$: 7.44–7.18 (m, 25 arom. H); 5.71 (t, $J \approx 3.3$, $\text{H-C}(3)$); 5.55 (s, PhCH); 5.17 (d, $J = 10.6$, PhCH_2); 4.97 (d, $J = 11.0$, PhCH_2); 4.83 (d, $J = 10.9$, PhCH_2); 4.79 (d, $J = 11.0$, PhCH_2); 4.74 (s, $\text{H-C}(1)$); 4.71 (d, $J = 10.6$, PhCH_2); 4.67 (d, $J = 7.8$, $\text{H-C}(1')$); 4.66 (d, $J = 12.1$, PhCH_2); 4.59 (d, $J = 11.9$, PhCH_2); 4.56 (d, $J = 12.5$, PhCH_2); 4.38 (d, $J = 4.8$, 10.2, $\text{H}_A\text{-C}(6)$); 4.12 (dd, $J = 3.0$, 9.7, $\text{H-C}(4)$); 4.00 (d, $J = 3.7$, $\text{H-C}(2)$); 3.94 (dt, $J = 4.9$, 10.0, $\text{H-C}(5)$); 3.82 (t, $J = 10.2$, $\text{H}_B\text{-C}(6)$); 3.76 (d', $J \approx 2.8$, 2 $\text{H-C}(6')$); 3.67–3.63 (m, $\text{H-C}(3')$, $\text{H-C}(4')$); 3.53 (s, MeO); 3.52–3.46 (m, $\text{H-C}(2')$, $\text{H-C}(5')$); 2.12 (s, Ac). $^{13}\text{C-NMR}$: 169.23 (s); 138.78 (s); 138.40 (s); 138.23 (2s); 137.31 (s); 128.91–126.06 (m); 105.09 (d); 101.84 (d); 100.02 (d); 84.51 (d); 81.90 (d); 77.52 (d); 76.06 (d); 75.64 (t); 75.02 (d); 74.93 (t); 74.88 (d); 74.26 (t); 73.75 (t); 69.96 (d); 69.27 (t); 68.88 (t); 64.51 (d); 57.15 (q, MeO); 20.97 (q, Ac). Anal. calc. for $\text{C}_{50}\text{H}_{54}\text{O}_{12}$ (846.96): C 70.91, H 6.43; found: C 70.88, H 6.25.

Methyl 2-O-Acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-altropyranoside (38). R_f (hexane/AcOEt 2:1) 0.36. $[\alpha]_D^{25} = +44.9$ ($c = 1.11$, CHCl_3). IR: 3060w, 3030w (sh), 3000m, 2930m, 2870m, 1750s, 1495w, 1465w (sh), 1455m, 1390m, 1370m, 1330w, 1315w, 1240s, 1195w, 1160s, 1140s, 1100s (br), 1055s, 1030s, 1015s, 940w, 915w, 885w, 700s, 660w. $^1\text{H-NMR}$: 7.45–7.11 (m, 25 arom. H); 5.53 (s, PhCH); 5.08 (dd, $J = 1.4$, 3.6, $\text{H-C}(2)$); 5.06 (d, $J = 3.6$, $\text{H-C}(1')$); 4.97 (d, $J = 10.9$, PhCH_2); 4.92 (d, $J = 1.3$, $\text{H-C}(1)$); 4.87 (d, $J = 10.9$, PhCH_2); 4.81 (d, $J = 11.0$, PhCH_2); 4.80 (d, $J = 11.3$, PhCH_2); 4.66 (d, $J = 11.4$, PhCH_2); 4.46 (d,

$J = 12.1$, PhCH_2); 4.46 (d , $J = 10.9$, PhCH_2); 4.35 (dd , $J = 5.0$, 10.3 , $\text{H}_A\text{--C}(6)$); 4.20 (d , $J = 12.1$, PhCH_2); 4.19 (br. td , $J \approx 2.3$, 10.1 , $\text{H--C}(5')$); 4.14 (t , $J \approx 3.3$, $\text{H--C}(3)$); 4.04 (dt , $J = 5.0$, 9.9 , $\text{H--C}(5)$); 3.98 (t , $J \approx 9.3$, $\text{H--C}(3')$); 3.86 (dd , $J = 2.9$, 9.6 , $\text{H--C}(4)$); 3.81 (t , $J = 10.4$, $\text{H}_B\text{--C}(6)$); 3.68 (t , $J \approx 9.3$, $\text{H--C}(4')$); 3.61 (dd , $J = 3.6$, 9.6 , $\text{H--C}(2')$); 3.43 (s , MeO); 3.39 (dd , $J = 2.8$, 11.0 , $\text{H}_A\text{--C}(6')$); 3.18 (dd , $J = 1.9$, 11.0 , $\text{H}_B\text{--C}(6')$); 2.17 (s , Ac). ^{13}C -NMR: 169.73 (s); 138.83 (s); 138.63 (s); 138.12 (s); 137.94 (s); 137.28 (s); 129.02–126.29 (m); 102.40 (d); 98.53 (d); 96.23 (d); 82.08 (d); 79.77 (d); 77.63 (d); 75.65 (d); 75.57 (t); 74.72 (t); 73.54 (t); 73.22 (t); 71.85 (d); 70.07 (d); 69.03 (t and d); 67.85 (t); 63.71 (d); 57.47 (q , MeO); 20.98 (q , Ac). Anal. calc. for $\text{C}_{50}\text{H}_{54}\text{O}_{12}$ (846.96): C 70.91, H 6.43; found: C 70.68, H 6.47.

Methyl 2-O-Acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl- β -D-glucopyranosyl)- β -D-altropyranoside (39). R_f (hexane/AcOEt 2:1) 0.45. $[\alpha]_D^{25} = -6.8$ ($c = 1.71$, CHCl_3). IR: 3060w, 3030w (sh), 3000m, 2930m (sh), 2900m (sh), 2870s, 1745s, 1498m, 1465m (sh), 1455s, 1390s, 1375s, 1360s (sh), 1310m, 1280m, 1245s, 1198w, 1135s (sh), 1090s (br.), 1070s (sh), 1030s, 1010s, 940w, 915m, 885w, 870w, 700s, 660w. ^1H -NMR: 7.45–7.12 (m , 25 arom. H); 5.59 (s , PhCH); 5.55 (dd , $J = 1.3$, 3.7 , $\text{H--C}(2)$); 5.05 (d , $J = 11.3$, PhCH_2); 4.93 (d , $J = 1.2$, $\text{H--C}(1)$); 4.88 (d , $J = 11.0$, PhCH_2); 4.82 (d , $J = 10.9$, PhCH_2); 4.76 (d , $J = 10.9$, PhCH_2); 4.68 (d , $J = 7.5$, $\text{H--C}(1')$); 4.67 (d , $J = 11.3$, PhCH_2); 4.66 (d , $J = 11.2$, PhCH_2); 4.59 (d , $J = 10.9$, PhCH_2); 4.56 (d , $J = 12.1$, PhCH_2); 4.37 (dd , $J = 5.1$, 10.4 , $\text{H}_A\text{--C}(6)$); 4.26 (t , $J \approx 3.3$, $\text{H--C}(3)$); 4.08 (dt , $J = 5.0$, 9.8 , $\text{H--C}(5)$); 3.94 (dd , $J = 2.8$, 9.6 , $\text{H--C}(4)$); 3.85 (t , $J = 10.3$, $\text{H}_B\text{--C}(6)$); 3.77 (d' , $J \approx 2.5$, $2\text{H--C}(6')$); 3.71 (t , $J = 9.3$, $\text{H--C}(4')$); 3.63 (t , $J = 8.9$, $\text{H--C}(3')$); 3.52 (dd , $J = 7.8$, 8.9 , $\text{H--C}(2')$); 3.51 (s , MeO); 3.46 (td , $J = 2.6$, 9.7 , $\text{H--C}(5')$); 2.16 (s , Ac). ^{13}C -NMR: 169.48 (s), 138.60 (s); 138.41 (s); 138.31 (s); 138.17 (s); 137.20 (s); 128.91–126.21 (m); 104.49 (d); 102.46 (d); 98.68 (d); 84.50 (d); 82.29 (d); 77.42 (d); 76.37 (d); 75.58 (t); 75.20 (d); 74.89 (t and d); 74.64 (t); 73.69 (t); 70.41 (d); 69.14 (t); 68.75 (t); 63.78 (d); 57.44 (q , MeO); 20.93 (q , Ac). Anal. calc. for $\text{C}_{50}\text{H}_{54}\text{O}_{12}$ (846.96): C 70.91, H 6.43; found: C 70.78, H 6.66.

9. *Glycosidation of 3 with 5.* A mixture of **5** (144.8 mg, 0.24 mmol), **3** (56.5 mg, 0.2 mmol), Et_4NBr (42.0 mg, 0.2 mmol), and 4-Å molecular sieves (100 mg) in CH_2Cl_2 (6 ml) was stirred for 2 d at 24° . FC (hexane/AcOEt 2:1) gave 125.6 mg (78%) of a 61:30:5:4 mixture (HPLC) **32/33/34/35**.

10. *Glycosidation of 6 with 1.* Reaction of **1** (110.5 mg, 0.2 mmol) and **6** [24] (79.6 mg, 0.18 mmol) in THF (2 ml) for 5 h at 24° and FC (hexane/AcOEt 4:1) gave a 28:72 mixture (HPLC) **40/41** (105.7 mg, 60%) and 30.2 mg (38%) of recovered **6**. An additional FC (CH_2Cl_2 /hexane 9:1) afforded pure **40** and **41**.

An analogous reaction of **1** (60.6 mg, 0.11 mmol) and **6** (43.6 mg, 0.1 mmol) in dioxane (3 ml) gave a 29:71 mixture **40/41** (60.0 mg, 62.5%) and 15.2 mg (35%) of recovered **6**.

An analogous reaction of **1** (79.4 mg, 0.14 mmol) and **6** (57.3 mg, 0.13 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (2 ml) gave a 48:52 mixture **40/41** (92 mg, 73%) and 12.6 mg (22%) of recovered **6**.

Methyl 4,6-O-Benzylidene-2-O-(2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl)-3-O-tosyl- α -D-altropyranoside (40). R_f (CH_2Cl_2 /hexane 9:1) 0.25. $[\alpha]_D^{25} = +37.6$ ($c = 2.03$, CHCl_3). IR: 3060w, 3030w (sh), 3005w, 2930m, 2870m, 1600w, 1498w, 1455s, 1400w (sh), 1360s (br.), 1310w, 1295w, 1260w, 1190s, 1178s, 1140s, 1115s (sh), 1100s (sh), 1070s, 1040s, 965s, 920w, 890m, 855w, 815w, 700s, 660w. ^1H -NMR: 7.69 (d , $J = 8.3$, 2 arom. H); 7.39–7.14 (m , 25 arom. H); 6.95 (d , $J = 8.1$, 2 arom. H); 5.40 (s , PhCH); 5.02 (d , $J = 3.7$, $\text{H--C}(1')$); 4.96 (d , $J = 10.9$, PhCH_2); 4.83 (d , $J = 10.8$, 2 PhCH_2); 4.78 (s , $\text{H--C}(1)$); 4.74 (d , $J = 11.4$, PhCH_2); 4.74 (t , $J \approx 2.8$, $\text{H--C}(3)$); 4.65 (d , $J = 11.4$, PhCH_2); 4.62 (d , $J = 12.0$, PhCH_2); 4.50 (d , $J = 9.4$, PhCH_2); 4.49 (d , $J = 12.2$, PhCH_2); 4.25 (dd , $J = 5.3$, 9.9 , $\text{H}_A\text{--C}(6)$); 4.19 (dt , $J = 5.3$, 9.9 , $\text{H--C}(5)$); 4.16 (d , $J = 2.4$, $\text{H--C}(2)$); 3.92 (t , $J = 9.4$, $\text{H--C}(3')$); 3.90 (dd , $J = 3.3$, 9.5 , $\text{H--C}(4)$); 3.88 (ddd , $J = 1.9$, 3.9 , 9.9 , $\text{H--C}(5')$); 3.74 (dd , $J = 4.0$, 10.6 , $\text{H}_A\text{--C}(6')$); 3.71 (t , $J = 9.5$, $\text{H}_B\text{--C}(6)$); 3.65 (dd , $J = 2.1$, 10.6 , $\text{H}_B\text{--C}(6')$); 3.64 (t , $J = 9.8$, $\text{H--C}(4')$); 3.57 (dd , $J = 3.7$, 9.7 , $\text{H--C}(2')$); 3.32 (s , MeO); 2.27 (s , Me). ^{13}C -NMR: 144.23 (s), 138.62 (s); 137.86 (s); 137.76 (2s); 137.16 (s); 132.98 (s); 129.27–126.08 (m); 101.64 (d); 99.88 (d); 99.35 (d); 81.57 (d); 79.66 (d); 77.67 (d); 77.56 (d); 75.55 (t); 75.29 (t); 74.31 (d); 73.43 (t and d); 73.30 (t); 71.02 (d); 68.95 (t); 68.36 (t); 58.00 (d); 55.52 (q , MeO); 21.53 (q , Me). Anal. calc. for $\text{C}_{55}\text{H}_{58}\text{O}_{13}\text{S}$ (959.11): C 68.88, H 6.09, S 3.34; found: C 69.10, H 6.12, S 3.32.

Methyl 4,6-O-Benzylidene-2-O-(2,3,4,6-tetra-O-benzyl- β -D-glucopyranosyl)-3-O-tosyl- α -D-altropyranoside (41). R_f (CH_2Cl_2 /hexane 9:1) 0.14. $[\alpha]_D^{25} = +21.2$ ($c = 2.08$, CHCl_3). IR: 3060w, 3030w (sh), 3005w, 2930w, 2910w, 2870m, 1600w, 1498w, 1455m, 1410w (sh), 1360s, 1310w, 1260m, 1238w (sh), 1190w, 1178s, 1140s (sh), 1115s, 1105s (sh), 1075s, 1055s (sh), 1030s, 1005s, 970s, 915w, 890m, 855w, 815m, 700s, 662w. ^1H -NMR: 7.72 (d , $J = 8.3$, 2 arom. H), 7.37–7.16 (m , 25 arom. H); 6.92 (d , $J = 8.2$, 2 arom. H), 5.43 (s , PhCH); 5.06 (t , $J = 2.9$, $\text{H--C}(3)$); 4.93 (d , $J = 10.9$, PhCH_2); 4.88 (d , $J = 10.9$, PhCH_2); 4.83 (d , $J = 10.3$, 2 PhCH_2); 4.74 (d , $J = 10.9$, PhCH_2); 4.69 (s , $\text{H--C}(1)$); 4.68 (d , $J = 12.0$, PhCH_2); 4.58 (d , $J = 10.7$, PhCH_2); 4.50 (d , $J = 7.5$, $\text{H--C}(1')$); 4.48 (d , $J = 12.0$, PhCH_2); 4.31 (dd , $J = 5.3$, 10.1 , $\text{H}_A\text{--C}(6)$); 4.27–4.21 (m , $\text{H--C}(5)$); 4.21 (d , $J = 2.9$, $\text{H--C}(2)$); 3.96 (dd , $J = 3.1$, 9.6 , $\text{H--C}(4)$); 3.84–3.83 (m , 2 $\text{H--C}(6')$); 3.76 (t , $J = 9.3$, $\text{H--C}(4')$); 3.71 (t , $J = 10.1$, $\text{H}_B\text{--C}(6)$); 3.65 (t , $J = 9.1$,

H–C(3''); 3.49–3.45 (*m*, H–C(2'), H–C(5')); 3.39 (*s*, MeO); 2.24 (*s*, Me). ^{13}C -NMR: 144.08 (*s*); 138.44 (*s*); 138.06 (*2s*); 137.14 (*2s*); 133.16 (*s*); 129.19–126.21 (*m*); 104.65 (*d*); 101.77 (*d*); 100.03 (*d*); 84.48 (*d*); 81.77 (*d*); 77.38 (*d*); 77.24 (*d*); 75.66 (*t*); 75.10 (*d*); 74.93 (*t*); 74.88 (*t*); 74.75 (*d*); 73.61 (*t*); 73.56 (*d*); 69.13 (*t*); 68.34 (*t*); 58.23 (*d*); 55.48 (*q*, MeO); 21.47 (*q*, Me). Anal. calc. for $\text{C}_{55}\text{H}_{58}\text{O}_{13}\text{S}$ (959.11): C 68.88, H 6.09, S 3.34; found: C 68.77; H 6.23, S 3.33.

11. *Glycosidation of 7 with 1*. Reaction of **1** (242.3 mg, 0.44 mmol) and **7** [24] (174.6 mg, 0.4 mmol) in THF (5 ml) for 5 h at 24° and FC (hexane/AcOEt 4:1) gave a 12:88 mixture (HPLC) **42/43** (119.7 mg, 31%) and 118.7 mg (68%) of recovered **7**. An additional FC (CH_2Cl_2 /hexane 9:1) afforded pure **42** and **43**.

An analogous reaction of **1** (60.6 mg, 0.11 mmol) and **7** (43.6 mg, 0.1 mmol) in dioxane (3 ml) gave a 14:86 mixture **42/43** (29.6 mg, 31%) and 29.2 mg (67%) of recovered **7**.

An analogous reaction of **1** (42.6 mg, 0.08 mmol) and **7** (30.6 mg, 0.07 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1 ml) gave a 35:65 mixture of **42/43** (22.5 mg, 33%) and 19.9 mg (65%) of recovered **7**.

Methyl 4,6-O-Benzylidene-3-O-(2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl)-2-O-tosyl- α -D-altropyranoside (42). R_f (CH_2Cl_2 /hexane 9:1) 0.34. $[\alpha]_D^{25} = +69.2$ ($c = 2.40$, CHCl_3). IR: 3060*m*, 3030*m* (sh), 3000*m*, 2925*s*, 2870*s*, 1600*m*, 1500*m*, 1470*m* (sh), 1455*s*, 1365*s* (br.), 1310*m*, 1295*m*, 1260*m*, 1240*m* (sh), 1190*s*, 1178*s*, 1140*s*, 1100*s* (br.), 1070*s* (sh), 1045*s*, 1030*s*, 1005*s*, 965*s*, 915*m*, 882*m*, 835*s*, 815*s*, 700*s*, 660*m*. ^1H -NMR: 7.69 (*d*, $J = 8.3$, 2 arom. H); 7.42–7.09 (*m*, 27 arom. H); 5.53 (*s*, PhCH); 4.92 (*d*, $J = 10.9$, PhCH₂); 4.81 (*d*, $J \approx 2.7$, H–C(1')); 4.80 (*d*, $J = 10.7$, PhCH₂); 4.79 (*d*, $J = 11.0$, PhCH₂); 4.68 (*s*, 2 PhCH₂); 4.60 (*s*, H–C(1)); 4.59 (*d*, $J = 4.6$, H–C(2)); 4.44 (*d*, $J = 12.2$, PhCH₂); 4.41 (*d*, $J = 10.9$, PhCH₂); 4.32–4.27 (*m*, H–C(5), H_A–C(6)); 4.18 (*d*, $J = 12.1$, PhCH₂); 4.05–4.02 (*m*, H–C(3), H–C(5')); 4.00 (*t*, $J \approx 9.3$, H–C(3')); 3.87 (*dd*, $J = 3.3$, 9.1, H–C(4)); 3.72 (*t*, $J = 12.2$, H_B–C(6)); 3.63 (*t*, $J \approx 9.6$, H–C(4')); 3.53 (*dd*, $J = 3.4$, 9.6, H–C(2')); 3.32 (*dd*, $J = 2.7$, 10.9, H_A–C(6')); 3.25 (*s*, MeO); 3.04 (*dd*, $J = 1.8$, 10.9, H_B–C(6')); 2.42 (*s*, Me). ^{13}C -NMR: 145.37 (*s*); 138.88 (*s*); 138.78 (*s*); 138.70 (*s*); 138.02 (*s*); 137.28 (*s*); 132.78 (*s*); 130.04–126.19 (*m*); 102.19 (*d*); 99.18 (*d*); 96.55 (*d*); 81.67 (*d*); 79.82 (*d*); 77.38 (*d*); 75.42 (*t*); 75.34 (*d*); 74.67 (*t*); 74.50 (*d*); 73.14 (*t*); 72.13 (*t*); 71.94 (*d*); 70.12 (*d*); 69.04 (*t*); 67.82 (*t*); 57.97 (*d*); 55.46 (*q*, MeO); 21.63 (*q*, Me). Anal. calc. for $\text{C}_{55}\text{H}_{58}\text{O}_{13}\text{S}$ (959.11): C 68.88, H 6.09, S 3.34; found: C 69.10, H 6.36, S 3.07.

Methyl 4,6-O-Benzylidene-3-O-(2,3,4,6-tetra-O-benzyl- β -D-glucopyranosyl)-2-O-tosyl- α -D-altropyranoside (43). R_f (CH_2Cl_2 /hexane 9:1) 0.29. $[\alpha]_D^{25} = +45.7$ ($c = 1.855$, CHCl_3). IR: 3060*w*, 3030*w* (sh), 3000*m*, 2930*m*, 2870*m*, 1600*w*, 1498*m*, 1465*m* (sh), 1455*s*, 1365*s* (br.), 1310*m*, 1258*w*, 1192*s*, 1180*s*, 1140*s*, 1115*s* (sh), 1095*s*, 1070*s*, 1050*s* (sh), 1030*s*, 1008*s*, 968*s*, 913*m*, 880*w*, 865*w*, 835*s*, 815*m*, 700*s*, 660*w*, 615*w*. ^1H -NMR: 7.81 (*m*, 2 arom. H), 7.46–7.13 (*m*, 27 arom. H); 5.58 (*s*, PhCH); 5.05 (*d*, $J = 11.4$, PhCH₂); 4.97 (*d*, $J = 2.6$, H–C(2)); 4.89 (*d*, $J = 11.0$, PhCH₂); 4.81 (*d*, $J = 10.8$, PhCH₂); 4.73 (*d*, $J = 10.5$, PhCH₂); 4.72 (*d*, $J = 12.2$, PhCH₂); 4.70 (*d*, $J = 11$, PhCH₂); 4.63 (*d*, $J = 7.5$, H–C(1')); 4.58 (*d*, $J = 10.7$, PhCH₂); 4.57 (*d*, $J = 12.2$, PhCH₂); 4.41 (*s*, H–C(1)); 4.34 (*t*, $J = 2.9$, H–C(3)); 4.31–4.23 (*m*, H–C(5), H_A–C(6)); 3.96 (*dd*, $J = 2.9$, 9.3, H–C(4)); 3.82–3.81 (*m*, 2 H–C(6')); 3.74 (*t*, $J = 9.8$, H_B–C(6)); 3.72 (*t*, $J = 9.1$, H–C(4')); 3.59 (*t*, $J = 9.0$, H–C(3')); 3.50 (*dd*, $J = 7.6$, 8.9, H–C(2')); 3.38 (*td*, $J = 2.3$, 9.8, H–C(5')); 3.24 (*s*, MeO); 2.41 (*s*, Me). ^{13}C -NMR: 145.23 (*s*); 138.74 (*s*); 138.62 (*s*); 138.55 (*s*); 138.27 (*s*); 137.28 (*s*); 133.18 (*s*); 130.01–126.30 (*m*), 104.28 (*d*); 102.45 (*d*); 99.21 (*d*); 84.32 (*d*); 81.89 (*d*); 77.42 (*d*); 76.74 (*d*); 75.51 (*d*); 75.45 (*t*); 74.95 (*d* and *t*); 74.23 (*t*); 73.60 (*t*); 72.85 (*d*); 69.11 (*t*); 68.82 (*t*); 58.47 (*d*); 55.47 (*q*, MeO); 21.62 (*q*, Me). Anal. calc. for $\text{C}_{55}\text{H}_{58}\text{O}_{13}\text{S}$ (959.11): C 68.88, H 6.09, S 3.34; found: C 68.67, H 5.96, S 3.52.

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