# 191. Glycosylidene Carbenes

Part 10

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

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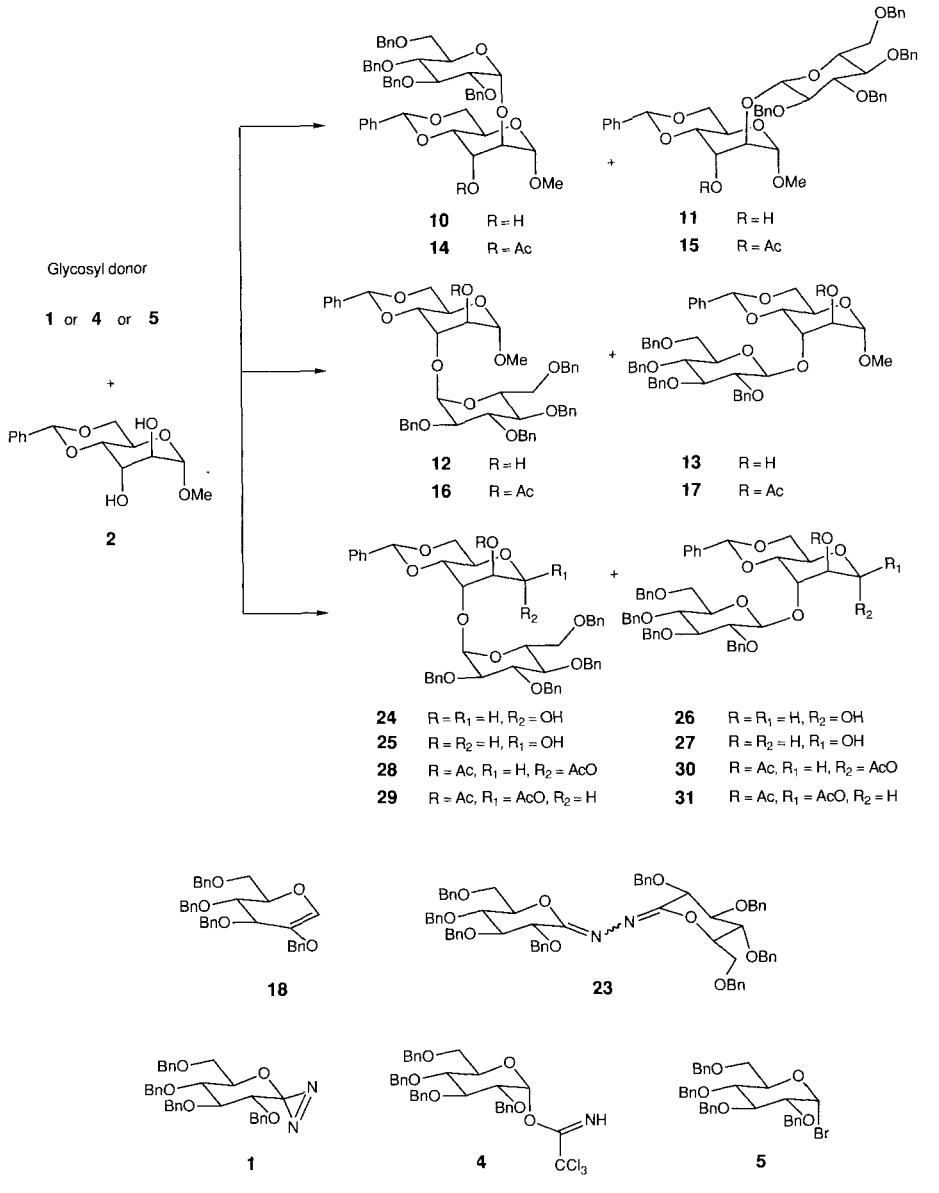
Glycosidation by the diazirine **1**, the trichloroacetimidate **4**, and the bromide **5** of the *altro*-diol **2**, possessing an intramolecular H-bond (HO–C(3) to O–C(1)) in solution, but not in the solid state, proceeds with high and complementary regioselectivity. From **2** and **1**, one obtains 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 (→**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

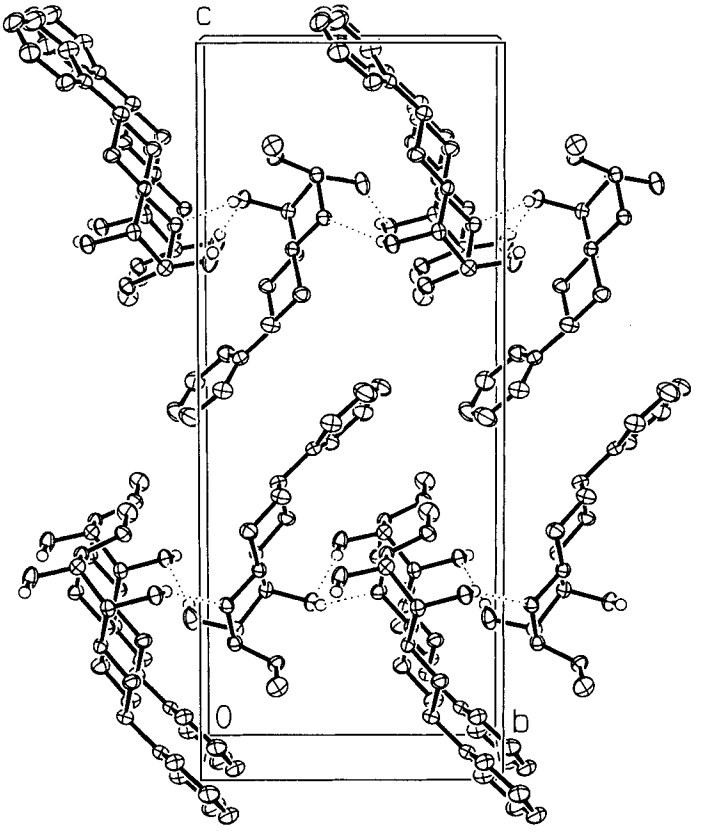



Fig. 1. *Packing diagram for* **2** *viewed down the* a-*axis, showing the intermolecular H-bonds.* Uninvolved H-atoms have been omitted for clarity.

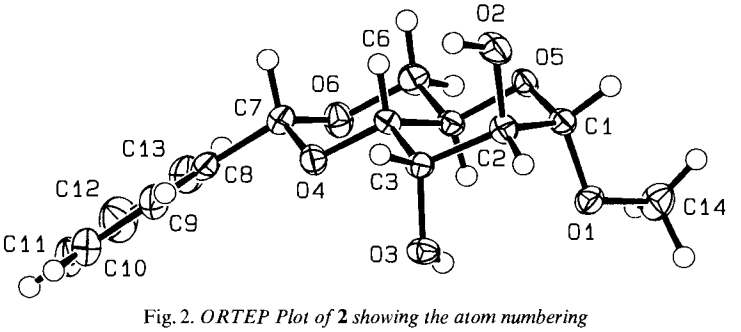



Fig. 2. *ORTEP Plot of* **2** *showing the atom numbering*

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 ($CCl_4$, 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 ($CH_2Cl_2$) 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 $CH_2Cl_2$, 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 | Mo$K_\alpha$ |
| Crystal system | orthorhombic | $\lambda$ [Å] | 0.71069 |
| Space group | $P2_12_12_1$ | Diffractometer | *Nicolet-R3* |
| $a$ [Å] | 6.642(1) | $2\theta_{(max)}$ [°] | 60 |
| $b$ [Å] | 9.016(2) | No. of reflections measured | 3004 |
| $c$ [Å] | 22.044(4) | Observed reflections [$I > 3\sigma(I)$] | 2021 |
| $V$ [Å$^3$] | 1320.0(4) | No. of refined parameters | 254 |
| $Z$ | 4 | Final $R$ factor | 0.0364 |
| Calc. density [g/cm$^3$] | 1.420 | $R_w$ | 0.0374 |
| $\mu$(Mo$K_\alpha$) [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 $cm^{-1}$ ($CCl_4$, 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 ~ 0.015M (281) and ~ 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 $^1$H-NMR spectrum of **2** in ($D_6$)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 $CDCl_3$, 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 $^1$H-NMR spectrum of **3** in $CDCl_3$ 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

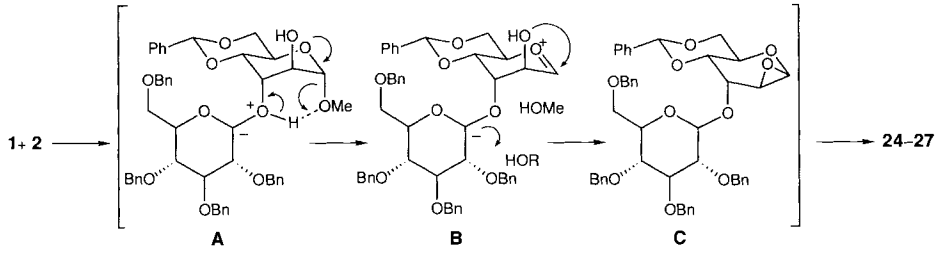
Table 4. *Glycosidation of* **2** *with the Diazirine* **1**

| 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 | $ClCH_2CH_2Cl$, 24° | 1.1 | 62 | 92:8 | 34:66 | 70:30 |
| 0.05 | $ClCH_2CH_2Cl$, 24° | 1.1 | 66 | 94:6 | 35:65 | 55:45 |
| 0.25 | $ClCH_2CH_2Cl$, 24° | 1.1 | 71 | 93:7 | 35:65 | 51:49 |
| 0.065 | $ClCH_2CH_2Cl$, 24° | 0.5 | 62 | 95:5 | 37:63 | 40:60 |
| 0.13 | $ClCH_2CH_2Cl$, 24° | 0.5 | 67 | 89:11 | 37:63 | 69:31 |
| 0.066 | $ClCH_2CH_2Cl$, −15°, *hv* | 1.1 | 49 | 91:9 | 36:64 | 81:19 |
| 0.05 | $ClCH_2CH_2Cl$, −30°, *hv* | 1.1 | 65 | 91:9 | 34:66 | 83:17 |
| 0.05 | $ClCH_2CH_2Cl$, 24° | 2.2 | 80 | 88:12 | 35:65 | 80:20 |
| 0.05 | THF, −80°, *hv* | 1.1 | 50 | 71:29 | 5:95 | 17:83 |
| 0.065 | THF, 24° | 1.1 | 51 | 86:14 | 14:86 | 19:81 |
| 0.05 | $CH_2Cl_2$, −80°, *hv* | 1.1 | 47 | 86:14 | 37:63 | 83:17 |
| 0.05 | $CH_2Cl_2$, 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 $ClCH_2CH_2Cl$, 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 $SnCl_2$, $B(OEt)_3$, $BF_3 \cdot OEt_2$ or of $Bu_4NBr$ 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 $ClCH_2CH_2Cl$, 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 $SiO_2$. 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 $^1$H- and $^{13}$C-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 $^1$H-NMR* (400 MHz, $CDCl_3$) *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 |
| $J(1',2')$ | | 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].

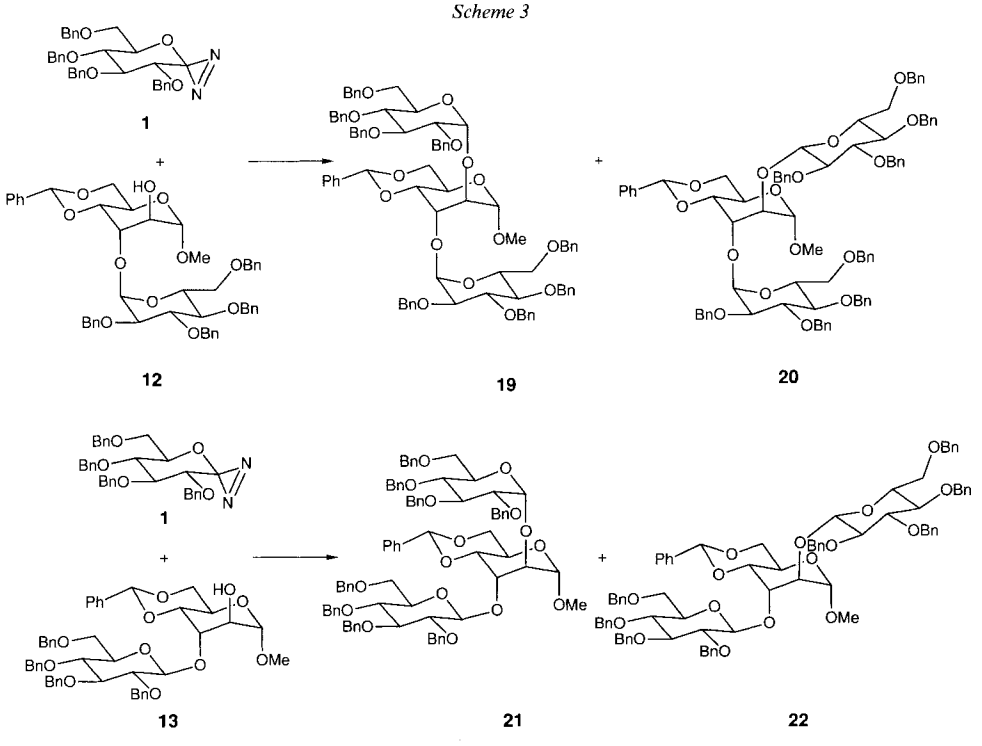
In the $^1$H-NMR spectra of **14** and **15**, the *doublets* of H–C(2) appear at 3.95 and 4.06 ppm, while the *triplets* of H–C(3) appear at 5.25 and 5.51 ppm, respectively. In the $^1$H-NMR spectra of **16** and **17**, the *doublets* of H–C(2) are at 5.07 and 5.26 ppm, while the *triplets* of H–C(3) 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-configurated disaccharides **14** and **16**, while the *doublets* of H–C(1′) in the spectra of the β-D-configurated 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 $ClCH_2CH_2Cl$ at −30° in the presence of $BF_3 \cdot OEt_2$ [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 $ClCH_2CH_2Cl$, the stereoselectivity of the

*Scheme 3*




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 $^1$H- and $^{13}$C-NMR data of **19–22** are given in *Tables 7* and *8*.

Table 7. *Selected* $^1$*H-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 |
| *J*(1′,2′) | 3.4 | 7.6 | 3.7 | 7.7 |
| *J*(1″,2″) | 3.7 | 3.4 | 7.7 | 5.4 |

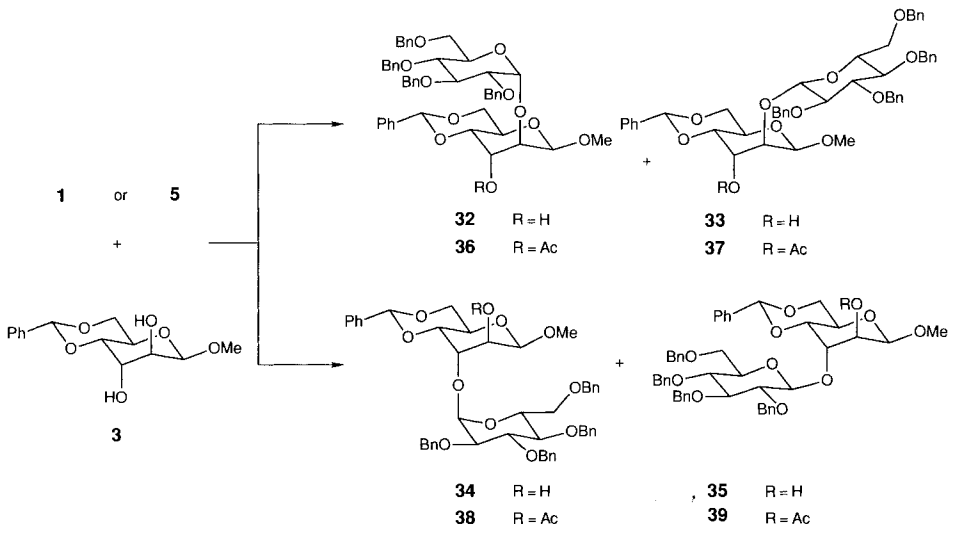
Table 8. *Selected* $^{13}$*C-NMR* (50 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *for* **19**–**22**

| 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 |
| Ph*C*H | 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*-Altropyranoside* **3**. Glycosidation of **3** in $ClCH_2CH_2Cl$ 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 $^1$H- 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 $^1$H-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 $^1$H-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-configurated disaccharides **36** and **38**, while in the spectra of the β-D-configurated 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 $^1$H-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**

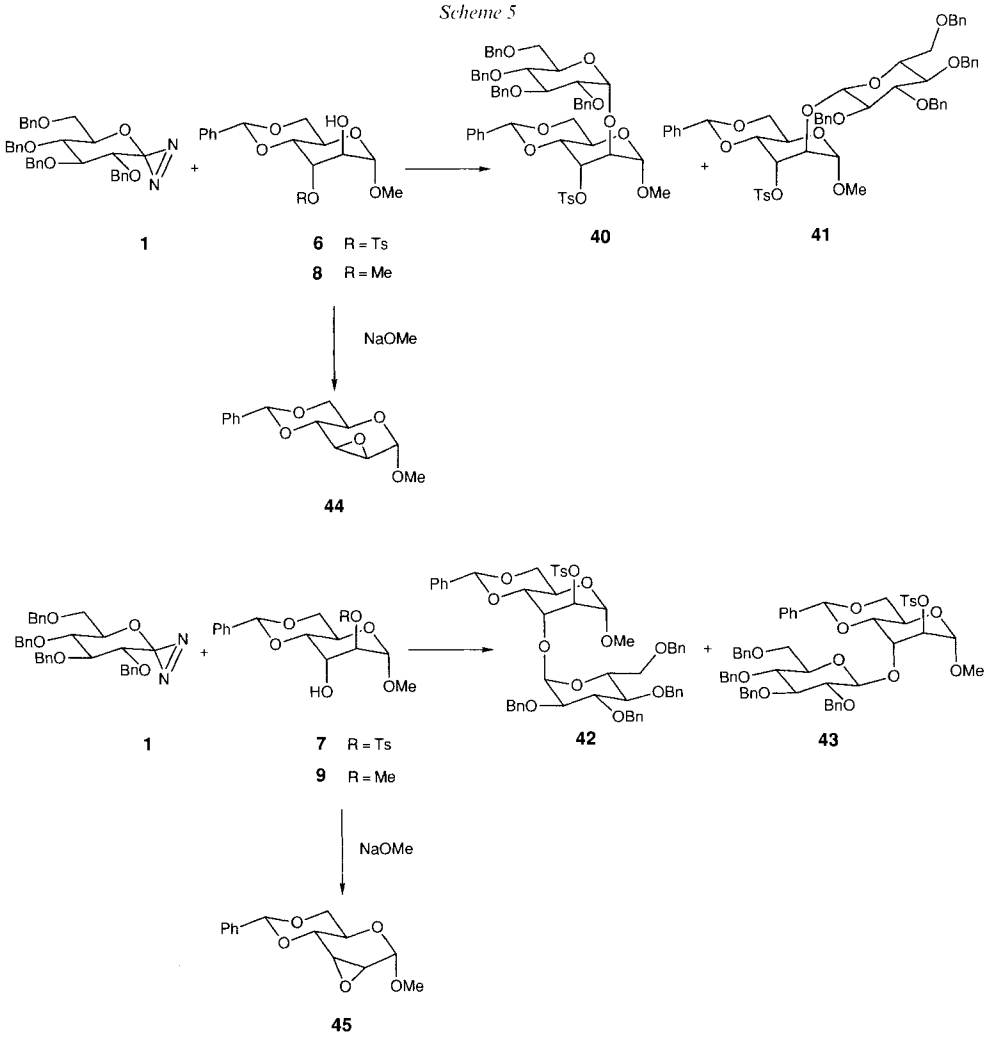
| Compound | **3**[a]) | **36** | **37** | **38** | **39** |
|---|---|---|---|---|---|
| C(1) | 99.4 | 99.75 | 100.02 | 98.53 | 98.68 |
| C(2) | 70.8[b]) | 73.79[b]) | 74.88 | 70.07 | 70.41 |
| C(3) | 68.6[b]) | 68.28 | 69.96 | 71.85 | 74.89 |
| C(4) | 76.5 | 74.43[b]) | 76.06 | 75.65 | 76.37 |
| C(5) | 62.8 | 64.47 | 64.51 | 63.71 | 63.78 |
| C(6) | 68.6 | 68.99 | 69.27 | 69.03 | 69.14 |
| Ph*C*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 $\sigma$-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, $ClCH_2CH_2Cl$ 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 $^1$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.

We thank Dr. *A. Linden* for determining the X-ray structure, Mr. *D. Nanz*, Mr. *T. Plüss*, and Mr. *M. Vöhler* for performing NMR experiments, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

## 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 $ClCH_2CH_2Cl$ 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** *und 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 disappearence of all **1**, the solvent was evaporated to give the crude product.

2.3. *Glycosidations by* **4**. The soln. of the catalyst in $ClCH_2CH_2Cl$ was added under $N_2$ to a suspension of the glycosyl acceptor, 4-Å molecular sieves, and **4** in $ClCH_2CH_2Cl$. 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 $ClCH_2CH_2Cl$ (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: 3060*w*, 3005*m*, 2930*m*, 2870*m*, 1735*s*, 1495*w*, 1455*m*, 1375*m*, 1310*w*, 1245*s*, 1140*s*, 1090*s*, 1070*s* (sh), 1040*s*, 1030*s* (sh), 915*w*, 820*w*, 715*m* (sh), 700*s*, 670*w*. $^1H$-NMR: 7.48–7.15 (*m*, 25 arom. H); 5.54 (*s*, PhC*H*); 5.25 (*t*, $J \approx 2.8$, H–C(3)); 5.07 (*d*, $J = 3.7$, H–C(1′)); 5.00 (*d*, $J = 10.9$, PhC$H_2$); 4.86 (*d*, $J = 9.4$, PhC$H_2$); 4.86 (*d*, $J = 10.9$, PhC$H_2$); 4.76 (*d*, $J = 11.4$, PhC$H_2$); 4.72 (*s*,

H–C(1)); 4.70 (*d*, $J$ = 11.4, PhC$H_2$); 4.62 (*d*, $J$ = 12.1, PhC$H_2$); 4.51 (*d*, $J$ = 10.6, PhC$H_2$); 4.49 (*d*, $J$ = 12.1, PhC$H_2$); 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*, $J \approx 9.3$, 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*, $J \approx 9.4$, $H_B$–C(6′)); 3.64 (*t*, $J \approx 9.4$, H–C(4′)); 3.60 (*dd*, $J$ = 3.9, 9.8, H–C(2′)); 3.30 (*s*, MeO); 2.12 (*s*, Ac). $^{13}$C-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 PhC$H_2$); 74.03 (*d*, C(4)); 73.41 (*t*, PhC$H_2$); 73.25 (*t*, PhC$H_2$); 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 $C_{50}H_{54}O_{12}$ (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°. $[\alpha]_D^{25}$ = +15.8 ($c$ = 2.63, $CHCl_3$). IR: 3090*w*, 3070*w*, 3000*m*, 2920*m*, 2870*m*, 1738*s*, 1605*w*, 1495*w*, 1455*m*, 1375*m*, 1365*m*, 1305*w*, 1220*s* (br.), 1140*s*, 1115*s* (sh), 1070*s* (br.), 1030*s*, 915*w*, 880*w*, 865*w*, 820*w*, 695*m*, 660*w* (sh). $^1$H-NMR: 7.46–7.16 (*m*, 25 arom. H); 5.59 (*s*, PhC*H*); 5.51 (*t*, $J$ = 2.9, H–C(3)); 4.92 (*d*, $J$ = 10.8, PhC$H_2$); 4.92 (*d*, $J$ = 11.0, PhC$H_2$); 4.81 (*d*, $J$ = 10.9, PhC$H_2$); 4.81 (*d*, $J$ = 10.9, PhC$H_2$); 4.75 (*d*, $J$ = 10.9, PhC$H_2$); 4.67 (*d*, $J$ = 12.2, PhC$H_2$); 4.66 (*s*, H–C(1)); 4.59 (*d*, $J$ = 10.8, PhC$H_2$); 4.54 (*d*, $J$ = 12.1, PhC$H_2$); 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). $^{13}$C-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 PhC$H_2$); 74.29 (*d*, C(4)); 73.64 (2*t*, PhC$H_2$); 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 $C_{50}H_{54}O_{12}$ (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**). $R_f$ ($CH_2Cl_2$/AcOEt 98:2) 0.51. $[\alpha]_D^{25}$ = +95.1 ($c$ = 1.215, $CHCl_3$). IR: 3060*w*, 3005*m*, 2930*m*, 2870*m*, 1740*s*, 1495*w*, 1453*m*, 1385*m* (sh), 1370*m*, 1330*w*, 1310*w*, 1265*m* (sh), 1235*s*, 1160*s* (sh), 1140*s*, 1100*s*, 1070*s*, 1050*s*, 1035*s*, 915*m*, 890*w*, 700*s*, 660*w*. $^1$H-NMR: 7.44–7.05 (*m*, 25 arom. H); 5.57 (*s*, PhC*H*); 5.20 (*d*, $J$ = 3.5, H–C(1′)); 5.07 (*d*, $J$ = 2.5, H–C(2)); 5.00 (*d*, $J$ = 10.9, PhC$H_2$); 4.83 (3*d*, $J$ = 11.7, 3 PhC$H_2$); 4.67 (*d*, $J$ = 11.8, PhC$H_2$); 4.60 (*s*, H–C(1)); 4.46 (*d*, $J$ = 12.5, PhC$H_2$); 4.43 (*d*, $J$ = 11.1, PhC$H_2$); 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, PhC$H_2$); 4.19 (*ddd*, $J$ = 2.0, 3.2, 10.2, H–C(5′)); 4.14 (*t*, $J \approx 2.8$, 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*, $J \approx 10.0$, H–C(4′)); 3.63 (*dd*, $J \approx 3.4$, 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). $^{13}$C-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*, PhC$H_2$); 75.16 (*d*, C(4)); 74.54 (*t*, PhC$H_2$); 72.90 (*t*, PhC$H_2$); 71.69 (*t*, PhC$H_2$); 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 $C_{50}H_{54}O_{12}$ (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**). $R_f$ ($CH_2Cl_2$/AcOEt 98:2) 0.36. $[\alpha]_D^{25}$ = +33.7 ($c$ = 2.05, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3005*m*, 2940*w*, 2870*m*, 1742*s*, 1498*w*, 1455*m*, 1380*m* (sh), 1370*m*, 1360*m* (sh), 1310*w*, 1240*s*, 1200*w*, 1140*s*, 1118*s*, 1095*s*, 1070*s*, 1030*s*, 1010*s*, 920*w*, 895*w*, 722*s*, 700*s*, 665*m*. $^1$H-NMR: 7.51–7.16 (*m*, 25 arom. H); 5.59 (*s*, PhC*H*); 5.26 (*d*, $J$ = 2.6, H–C(2)); 5.14 (*d*, $J$ = 11.5, PhC$H_2$); 4.91 (*d*, $J$ = 11.0, PhC$H_2$); 4.80 (*d*, $J$ = 11.0, PhC$H_2$); 4.79 (*d*, $J$ = 7.7, H–C(1′)); 4.79 (*d*, $J$ = 10.9, PhC$H_2$); 4.73 (*d*, $J$ = 11.0, PhC$H_2$); 4.64 (*d*, $J$ = 12.2, PhC$H_2$); 4.59 (*s*, H–C(1)); 4.56 (*d*, $J$ = 12.2, PhC$H_2$); 4.55 (*d*, $J$ = 10.8, PhC$H_2$); 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). $^{13}$C-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*, PhC$H_2$); 75.10 (*d*, C(5′)); 74.91 (*t*, PhC$H_2$); 74.09 (*t*, PhC$H_2$); 73.55 (*t*, PhC$H_2$); 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 $C_{50}H_{54}O_{12}$ (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. $[\alpha]_D^{25}$ = +68.1 ($c$ = 1.10, $CHCl_3$). IR: 3060*w*, 3040*w*, 3000*w*, 2920*w*, 2870*w*, 1745*s*, 1498*w*, 1470*w* (sh), 1455*m*, 1410*w* (sh), 1370*m*, 1330*w*, 1310*w*, 1260*w*, 1242*m*, 1160*s* (sh), 1150*s*, 1105*s*, 1072*s*, 1045*s*, 1030*s* (sh), 1015*s*, 1005*s* (sh), 985*m* (sh), 910*w*, 870*w*, 700*s*. $^1$H-NMR: 7.46–7.11 (*m*, 25 arom. H); 5.95 (br. *s*,

H–C(1)); 5.57 (*s*, PhC*H*); 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, PhC$H_2$); 4.85 (*d*, *J* = 10.9, PhC$H_2$); 4.78 (*d*, *J* = 10.9, PhC$H_2$); 4.71 (*d*, *J* = 11.4, PhC$H_2$); 4.67 (*d*, *J* = 11.6, PhC$H_2$); 4.42 (*d*, *J* = 12.2, PhC$H_2$); 4.42 (*dt*, *J* ≈ 5.0, 9.9, H–C(5)); 4.40 (*d*, *J* = 10.7, PhC$H_2$); 4.35 (*dd*, *J* = 5.3, 10.3, $H_A$–C(6)); 4.15 (*td*, *J* ≈ 2, 10.3, H–C(5′)); 4.12 (*d*, *J* = 12.2, PhC$H_2$); 4.08 (*t*, *J* = 2.7, H–C(3)); 3.99 (*t*, *J* ≈ 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). $^{13}$C-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 $C_{15}H_{54}O_{13}$ (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, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3000*m*, 2930*m*, 2870*m*, 1755*s* (br.), 1500*m*, 1455*s*, 1395*m* (sh), 1370*s*, 1330*m*, 1315*m*, 1245*s*, 1200*m*, 1160*s* (sh), 1140*s*, 1100*s*, 1070*s* (br.), 1030*s* (sh), 1010*s* (sh), 960*m*, 915*m*, 870*w*, 700*s*, 660*w*. $^1$H-NMR: 7.41–7.09 (*m*, 25 arom. H); 6.26 (*d*, *J* = 1.5, H–C(1)); 5.54 (s, PhC*H*); 5.12 (*dd*, *J* = 1.5, 3.7, H–C(2)); 4.97 (*d*, *J* = 10.9, PhC$H_2$); 4.95 (*d*, *J* = 3.6, H–C(1′)); 4.86 (*d*, *J* = 10.9, PhC$H_2$); 4.82 (*d*, *J* = 10.7, PhC$H_2$); 4.79 (*d*, *J* = 11.4, PhC$H_2$); 4.68 (*d*, *J* = 11.9, PhC$H_2$); 4.44 (*d*, *J* = 9.9, PhC$H_2$); 4.44 (*d*, *J* = 12.4, PhC$H_2$); 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, PhC$H_2$); 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). $^{13}$C-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 $C_{51}H_{54}O_{13}$ (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, $CHCl_3$). IR: 3030*w* (sh), 3000*w*, 2950*w* (sh), 2920*m*, 2860*w*, 1755*m* (br.), 1498*w*, 1465*w* (sh), 1455*w*, 1395*w* (sh), 1375*m*, 1310*w*, 1260*m*, 1240*m*, 1200*w*, 1135*m* (sh), 1095*s* (sh), 1070*s* (br.), 1030*m* (sh), 1010*m* (br.), 950*w* (sh), 910*w*, 815*w*, 700*m*, 665*w*. $^1$H-NMR: 7.44–7.11 (*m*, 25 arom. H); 6.23 (*d*, *J* = 1.4, H–C(1)); 5.58 (*s*, PhC*H*); 5.58 (*dd*, *J* = 1.4, 4.0, H–C(2)); 5.05 (*d*, *J* = 11.1, PhC$H_2$); 4.89 (*d*, *J* = 10.9, PhC$H_2$); 4.81 (*d*, *J* = 10.8, PhC$H_2$); 4.75 (*d*, *J* = 11.0, PhC$H_2$); 4.69 (*d*, *J* = 7.6, H–C(1)); 4.68 (*d*, *J* = 11.2, PhC$H_2$); 4.62 (*d*, *J* = 12.2, PhC$H_2$); 4.57 (*d*, *J* = 10.9, PhC$H_2$); 4.53 (*d*, *J* = 12.2, PhC$H_2$); 4.36 (*dd*, *J* = 5.2, 10.4, $H_A$–C(6)); 4.30 (br. *t*, *J* ≈ 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 $C_{51}H_{54}O_{13}$ (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 $BF_3 \cdot OEt_2$ in $ClCH_2CH_2Cl$ (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 $ClCH_2CH_2Cl$ (6 ml). The mixture was stirred for 1 h at –30°, treated with $Et_3N$ (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), $Et_4NBr$ (304.5 mg, 1.45 mmol), and *Hünig*'s base (0.25 ml, 1.43 mmol) in $CH_2Cl_2$ (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), $Et_4NBr$ (304.5 mg, 1.45 mmol), and 4-Å molecular sieves (600 mg) in $CH_2Cl_2$ (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 $ClCH_2CH_2Cl$ (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, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3000*m*, 2920*m* (br.), 2870*m*,

1500*m*, 1455*s*, 1382*m*, 1365*s*, 1330*w*, 1310*w* (sh), 1260*m*, 1200*w*, 1160*s* (sh), 1142*s*, 1100*s* (br.), 1070*s* (sh), 1030*s*, 960*w* (sh), 910*s*, 860*w*, 820*w*, 700*s*, 650*w*. $^1$H-NMR: 7.45–7.07 (*m*, 45 arom. H); 5.52 (*s*, PhC*H*); 5.11 (*d*, *J* = 3.4, H–C(1″)); 4.98 (*d*, *J* = 10.9, PhC$H_2$); 4.97 (*d*, *J* = 10.9, PhC$H_2$); 4.89 (d, *J* = 3.7, H–C(1′)); 4.85 (*d*, *J* = 10.3, PhC$H_2$); 4.84 (*d*, *J* = 11.0, PhC$H_2$); 4.83 (*d*, *J* = 11.0, PhC$H_2$); 4.82 (*d*, *J* = 10.6, PhC$H_2$); 4.76 (*d*, *J* = 11.9, PhC$H_2$); 4.73 (*s*, H–C(1)); 4.67 (*d*, *J* = 11.8, PhC$H_2$); 4.64 (*d*, *J* = 12.8, PhC$H_2$); 4.61 (*d*, *J* = 12.3, PhC$H_2$); 4.55 (*d*, *J* = 11.6, PhC$H_2$); 4.50 (*d*, *J* = 9.6, PhC$H_2$); 4.48 (*d*, *J* = 11.6, PhC$H_2$); 4.45 (*d*, *J* = 10.7, PhC$H_2$); 4.43 (*d*, *J* = 12.2, PhC$H_2$); 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, PhC$H_2$); 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). $^{13}$C-NMR: 138.99 (*s*); 138.92 (*s*); 138.85 (*s*); 138.72 (*s*); 138.01 (3*s*); 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 (*d*); 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 $C_{82}H_{86}O_{16}$ (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. $[\alpha]_D^{25}$ = +53.1 (*c* = 1.75, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3000*m*, 2920*m*, 2870*m*, 1498*m*, 1455*s*, 1400*w* (sh), 1380*w*, 1360*m*, 1330*w*, 1310*w*, 1265*w*, 1195*w* (sh), 1145*s*, 1100*s* (br.), 1070*s*, 1030*s*, 910*s*, 825*w*, 700*s*, 650*w*. $^1$H-NMR: 7.44–7.07 (*m*, 45 arom. H); 5.55 (*s*, PhC*H*); 5.11 (*d*, *J* = 3.4, H–C(1″)); 4.96 (*d*, *J* = 11.3, PhC$H_2$); 4.96 (*d*, *J* = 10.4, PhC$H_2$); 4.93 (*d*, *J* = 12.5, PhC$H_2$); 4.83 (*d*, *J* = 9.6, 2 PhC$H_2$); 4.81 (*d*, *J* = 10.8, 2 PhC$H_2$);4.72 (*d*, *J* = 10.6, PhC$H_2$); 4.71 (*s*, H–C(1)); 4.69 (*d*, *J* = 13.3, PhC$H_2$); 4.59 (*d*, *J* = 12.0, PhC$H_2$); 4.55 (*d*, *J* = 10.8, PhC$H_2$); 4.54 (*d*, *J* = 12.1, PhC$H_2$); 4.48 (*d*, *J* = 12.0, PhC$H_2$); 4.46 (*d*, *J* = 10.9, PhC$H_2$); 4.44 (*d*, *J* = 12.1, PhC$H_2$); 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, PhC$H_2$); 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″)). $^{13}$C-NMR: 139.07 (*s*); 139.03 (*s*); 138.90 (*s*); 138.53 (*s*); 138.17 (*s*); 138.13 (*s*); 138.02 (2*s*); 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 (2*d*); 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 $C_{82}H_{86}O_{16}$ (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 ($^1$H-NMR: signals of PhC*H* and MeO) **21**/**22** (125.3 mg, 46%), which were partially separated by another FC ($CH_2Cl_2$/AcOEt 98:2).

An analogous reaction of **1** (65.0 mg, 0.118 mmol) and **13** (86.5 mg, 0.107 mmol) in $ClCH_2CH_2Cl$ (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**). $R_f$ ($CH_2Cl_2$/AcOEt 98:2) 0.22. $[\alpha]_D^{25}$ = +35.6 (*c* = 0.75, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3000*m*, 2930*m*, 2870*m*, 1500*m*, 1455*s*, 1405*w*, 1380*m*, 1360*m*, 1310*w*, 1265*m*, 1140*s*, 1090*s* (sh), 1070*s* (br.), 1030*s*, 915*w*, 820*w*, 700*s*. $^1$H-NMR: 7.52–7.13 (*m*, 45 arom. H); 5.50 (*s*, PhC*H*); 5.15 (*d*, *J* = 11.5, PhC$H_2$); 4.97 (*d*, *J* = 11.0, PhC$H_2$); 4.93 (*d*, *J* = 11.1, PhC$H_2$); 4.90 (*d*, *J* = 3.7, H–C(1′)); 4.85 (*d*, *J* = 10.0, PhC$H_2$); 4.83 (*d*, *J* = 10.6, PhC$H_2$); 4.81 (*d*, *J* = 11.5, PhC$H_2$); 4.79 (*d*, *J* = 10.9, PhC$H_2$); 4.76 (*d*, *J* = 7.7, H–C(1″)); 4.73 (*d*, *J* = 11.1, PhC$H_2$); 4.69 (*s*, H–C(1)); 4.60 (*d*, *J* = 12.0, PhC$H_2$); 4.59 (*d*, *J* = 11.6, PhC$H_2$); 4.52 (*d*, *J* = 10.6, PhC$H_2$); 4.50 (*d*, *J* = 10.8, PhC$H_2$); 4.47 (*d*, *J* = 11.7, PhC$H_2$); 4.46 (*d*, *J* = 12.1, PhC$H_2$); 4.46 (*d*, *J* = 12.2, PhC$H_2$); 4.42 (*d*, *J* = 12.0, PhC$H_2$); 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). $^{13}$C-NMR: 138.85 (*s*); 138.81 (*s*); 138.75 (2*s*); 138.18 (*s*); 138.13 (2*s*); 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 (2*t*); 68.57 (*t*); 58.56 (*d*); 55.20 (*q*). Anal. calc. for $C_{82}H_{86}O_{16} \cdot H_2O$ (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**). $R_f$ ($CH_2Cl_2$/AcOEt 98:2) 0.16. $[\alpha]_D^{25} = +26.0$ ($c = 1.84$, $CHCl_3$). IR: 3070*w*, 3040*w* (sh), 3010*w*, 2910*m*, 2865*m*, 1500*m*, 1458*m*, 1400*w*, 1382*m*, 1360*m*, 1310*w*, 1260*w*, 1195*w*, 1145*s* (sh), 1115*s* (sh), 1090*s* (sh), 1070*s* (br.), 1030*s*, 1010*s* (sh), 915*w*, 865*w*, 820*w*, 700*s*. $^1$H-NMR: 7.51–7.12 (*m*, 45 arom. H); 5.60 (*s*, PhC*H*); 5.15 (*d*, $J = 11.6$, PhC$H_2$); 4.95 (*d*, $J = 10.9$, PhC$H_2$); 4.90 (*d*, $J = 11.0$, PhC$H_2$); 4.90 (*d*, $J = 11.0$, PhC$H_2$); 4.81 (*d*, $J = 11.0$, PhC$H_2$); 4.78 (*d*, $J = 11.4$, PhC$H_2$); 4.78 (*d*, $J \approx 9.5$, PhC$H_2$); 4.77 (*d*, $J = 11.0$, PhC$H_2$); 4.75 (*d*, $J = 10.7$, PhC$H_2$); 4.70 (*d*, $J = 11.0$, PhC$H_2$); 4.67 (*s*, H–C(1)); 4.64 (*d*, $J = 11.2$, PhC$H_2$); 4.63 (*t*, $J \approx 3.5$, H–C(3)); 4.55 (*d*, $J = 10.9$, PhC$H_2$); 4.50 (*d*, $J \approx 5.4$, H–C(1″)); 4.50 (*s*, 2 PhC$H_2$); 4.49 (*d*, $J = 11.0$, PhC$H_2$); 4.48 (*d*, $J = 12.1$, PhC$H_2$); 4.44 (*d*, $J = 7.7$, H–C(1′)); 4.35 (*dt*, $J = 5.2$, 9.9, H–C(5)); 4.28 (*dd*, $J = 5.3$, 10.2, $H_A$–C(6)); 4.22 (*d*, $J = 2.9$, H–C(2)); 4.10 (*dd*, $J = 2.9$, 9.6, H–C(4)); 3.77 (*t*, $J = 10.3$, $H_B$–C(6)); 3.74–3.44 (*m*, H–C(2′), H–C(3′), H–C(4′), 2 H–C(6′), H–C(2″), H–C(3″), H–C(4″), 2 H–C(6″)); 3.35 (*td*, $J = 3.4$, 9.5, H–C(5″)); 3.31 (*s*, MeO); 3.17 (*ddd*, $J = 1.7$, 4.3, 9.3, H–C(5′)). $^{13}$C-NMR: 138.97 (*s*); 138.83 (*s*); 138.56 (*s*); 138.42 (2*s*); 138.23 (2*s*); 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 (2*d*); 74.84 (2*t*); 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 $C_{82}H_{86}O_{16} \cdot H_2O$ (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 $ClCH_2CH_2Cl$ (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/$Ac_2O$ 2:1 for 12 h at r.t. Dilution with $CH_2Cl_2$, washing with 1M aq. $Na_2CO_3$ soln. and with $H_2O$, 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: 3060*w*, 3030*w*, 3000*w*, 2930*m*, 2870*m*, 1750*s*, 1498*w*, 1470*w* (sh), 1455*m*, 1365*m* (br.), 1310*w*, 1260*w* (sh), 1240*s*, 1195*w*, 1165*s*, 1140*s*, 1110*s*, 1085*s*, 1070*s* (sh), 1030*s*, 1005*s*, 915*w*, 890*w*, 700*s*, 640*w*. $^1$H-NMR: 7.42–7.15 (*m*, 25 arom. H); 5.41 (*s*, PhC*H*); 5.39 (*t*, $J \approx 3.3$, H–C(3); 5.08 (*d*, $J = 3.7$, H–C(1′)); 4.96 (*d*, $J = 10.9$, PhC$H_2$); 4.85 (*d*, $J = 10.9$, 2 PhC$H_2$); 4.78 (*d*, $J = 11.3$, PhC$H_2$); 4.68 (*d*, $J = 11.2$, PhC$H_2$); 4.68 (*d*, $J = 1.4$, H–C(1)); 4.64 (*d*, $J = 12.2$, PhC$H_2$); 4.53 (*d*, $J = 10.9$, PhC$H_2$); 4.48 (*d*, $J = 12.2$, PhC$H_2$); 4.33 (*d*, $J = 4.4$, 9.8, $H_A$–C(6)); 4.26 (br. *td*, $J = 2.6$, 9.8, H–C(5′)); 4.11 (*dd*, $J = 3.1$, 9.4, H–C(4)); 4.08 (*t*, $J = 9.3$, H–C(3′)); 3.89 (*dd*, $J = 1.4$, 3.6, H–C(2)); 3.88 (*dt*, $J = 4.2$, 9.0, H–C(5)); 3.82 (*t*, $J = 9.9$, $H_B$–C(6)); 3.77 (*dd*, $J = 3.3$, 10.7, $H_A$–C(6′)); 3.68 (*t*, $J = 9.3$, H–C(4′)); 3.62 (*dd*, $J = 3.8$, 9.6, H–C(2′)); 3.61 (*dd*, $J = 2.3$, 10.7, $H_B$–C(6′)); 3.49 (*s*, MeO); 2.13 (*s*, Ac). $^{13}$C-NMR: 169.53 (*s*); 138.91 (*s*); 138.52 (*s*); 138.14 (2*s*); 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 $C_{50}H_{54}O_{12}$ (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: 3080*w* (sh), 3050*w*, 3020*m*, 2920*m*, 2880*s*, 1755*s*, 1500*m*, 1470*m* (sh), 1455*s*, 1390*s* (sh), 1370*s* (br.), 1310*m*, 1240*s*, 1165*s* (sh), 1150*s* (sh), 1110*s*, 1075*s* (br.), 1030*s*, 1005*s*, 915*m*, 885*w*, 700*s*, 665*w*. $^1$H-NMR: 7.44–7.18 (*m*, 25 arom. H); 5.71 (*t*, $J \approx 3.3$, H–C(3)); 5.55 (*s*, PhC*H*); 5.17 (*d*, $J = 10.6$, PhC$H_2$); 4.97 (*d*, $J = 11.0$, PhC$H_2$); 4.83 (*d*, $J = 10.9$, PhC$H_2$); 4.79 (*d*, $J = 11.0$, PhC$H_2$); 4.74 (*s*, H–C(1)); 4.71 (*d*, $J = 10.6$, PhC$H_2$); 4.67 (*d*, $J = 7.8$, H–C(1′)); 4.66 (*d*, $J = 12.1$, PhC$H_2$); 4.59 (*d*, $J = 11.9$, PhC$H_2$); 4.56 (*d*, $J = 12.5$, PhC$H_2$); 4.38 (*d*, $J = 4.8$, 10.2, $H_A$–C(6)); 4.12 (*dd*, $J = 3.0$, 9.7, H–C(4)); 4.00 (*d*, $J = 3.7$, H–C(2)); 3.94 (*dt*, $J = 4.9$, 10.0, H–C(5)); 3.82 (*t*, $J = 10.2$, $H_B$–C(6)); 3.76 ('*d*', $J \approx 2.8$, 2 H–C(6′)); 3.67–3.63 (*m*, H–C(3′), H–C(4′)); 3.53 (*s*, MeO); 3.52–3.46 (*m*, H–C(2′), H–C(5′)); 2.12 (*s*, Ac). $^{13}$C-NMR: 169.23 (*s*); 138.78 (*s*); 138.40 (*s*); 138.23 (2*s*); 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 $C_{50}H_{54}O_{12}$ (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: 3060*w*, 3030*w* (sh), 3000*m*, 2930*m*, 2870*m*, 1750*s*, 1495*w*, 1465*w* (sh), 1455*m*, 1390*m*, 1370*m*, 1330*w*, 1315*w*, 1240*s*, 1195*w*, 1160*s*, 1140*s*, 1100*s* (br), 1055*s*, 1030*s*, 1015*s*, 940*w*, 915*w*, 885*w*, 700*s*, 660*w*. $^1$H-NMR: 7.45–7.11 (*m*, 25 arom. H); 5.53 (*s*, PhC*H*); 5.08 (*dd*, $J = 1.4$, 3.6, H–C(2)); 5.06 (*d*, $J = 3.6$, H–C(1′)); 4.97 (*d*, $J = 10.9$, PhC$H_2$); 4.92 (*d*, $J = 1.3$, H–C(1)); 4.87 (*d*, $J = 10.9$, PhC$H_2$); 4.81 (*d*, $J = 11.0$, PhC$H_2$); 4.80 (*d*, $J = 11.3$, PhC$H_2$); 4.66 (*d*, $J = 11.4$, PhC$H_2$); 4.46 (*d*,

$J$ = 12.1, PhC$H_2$); 4.46 (*d*, $J$ = 10.9, PhC$H_2$); 4.35 (*dd*, $J$ = 5.0, 10.3, $H_A$–C(6)); 4.20 (*d*, $J$ = 12.1, PhC$H_2$); 4.19 (br. *td*, $J \approx 2.3$, 10.1, H–C(5′)); 4.14 (*t*, $J \approx 3.3$, H–C(3)); 4.04 (*dt*, $J$ = 5.0, 9.9, H–C(5)); 3.98 (*t*, $J \approx 9.3$, H–C(3′)); 3.86 (*dd*, $J$ = 2.9, 9.6, H–C(4)); 3.81 (*t*, $J$ = 10.4, $H_B$–C(6)); 3.68 (*t*, $J \approx 9.3$, H–C(4′)); 3.61 (*dd*, $J$ = 3.6, 9.6, H–C(2′)); 3.43 (*s*, MeO); 3.39 (*dd*, $J$ = 2.8, 11.0, $H_A$–C(6′)); 3.18 (*dd*, $J$ = 1.9, 11.0, $H_B$–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 $C_{50}H_{54}O_{12}$ (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: 3060*w*, 3030*w* (sh), 3000*m*, 2930*m* (sh), 2900*m* (sh), 2870*s*, 1745*s*, 1498*m*, 1465*m* (sh), 1455*s*, 1390*s*, 1375*s*, 1360*s* (sh), 1310*m*, 1280*m*, 1245*s*, 1198*w*, 1135*s* (sh), 1090*s* (br.), 1070*s* (sh), 1030*s*, 1010*s*, 940*w*, 915*m*, 885*w*, 870*w*, 700*s*, 660*w*. $^1$H-NMR: 7.45–7.12 (*m*, 25 arom. H); 5.59 (*s*, PhC$H$); 5.55 (*dd*, $J$ = 1.3, 3.7, H–C(2)); 5.05 (*d*, $J$ = 11.3, PhC$H_2$); 4.93 (*d*, $J$ = 1.2, H–C(1)); 4.88 (*d*, $J$ = 11.0, PhC$H_2$); 4.82 (*d*, $J$ = 10.9, PhC$H_2$); 4.76 (*d*, $J$ = 10.9, PhC$H_2$); 4.68 (*d*, $J$ = 7.5, H–C(1′)); 4.67 (*d*, $J$ = 11.3, PhC$H_2$); 4.66 (*d*, $J$ = 11.2, PhC$H_2$); 4.59 (*d*, $J$ = 10.9, PhC$H_2$); 4.56 (*d*, $J$ = 12.1, PhC$H_2$); 4.37 (*dd*, $J$ = 5.1, 10.4, $H_A$–C(6)); 4.26 (*t*, $J \approx 3.3$, H–C(3)); 4.08 (*dt*, $J$ = 5.0, 9.8, H–C(5)); 3.94 (*dd*, $J$ = 2.8, 9.6, H–C(4)); 3.85 (*t*, $J$ = 10.3, $H_B$–C(6)); 3.77 (*d'*, $J \approx 2.5$, 2 H–C(6′)); 3.71 (*t*, $J$ = 9.3, H–C(4′)); 3.63 (*t*, $J$ = 8.9, H–C(3′)); 3.52 (*dd*, $J$ = 7.8, 8.9, H–C(2′)); 3.51 (*s*, MeO); 3.46 (*td*, $J$ = 2.6, 9.7, 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 $C_{50}H_{54}O_{12}$ (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 $ClCH_2CH_2Cl$ (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: 3060*w*, 3030*w* (sh), 3005*w*, 2930*m*, 2870*m*, 1600*w*, 1498*w*, 1455*s*, 1400*w* (sh), 1360*s* (br.), 1310*w*, 1295*w*, 1260*w*, 1190*s*, 1178*s*, 1140*s*, 1115*s* (sh), 1100*s* (sh), 1070*s*, 1040*s*, 965*s*, 920*w*, 890*m*, 855*w*, 815*w*, 700*s*, 660*w*. $^1$H-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*, PhC$H$); 5.02 (*d*, $J$ = 3.7, H–C(1′)); 4.96 (*d*, $J$ = 10.9, PhC$H_2$); 4.83 (*d*, $J$ = 10.8, 2 PhC$H_2$); 4.78 (*s*, H–C(1)); 4.74 (*d*, $J$ = 11.4, PhC$H_2$); 4.74 (*t*, $J \approx 2.8$, H–C(3)); 4.65 (*d*, $J$ = 11.4, PhC$H_2$); 4.62 (*d*, $J$ = 12.0, PhC$H_2$); 4.50 (*d*, $J$ = 9.4, PhC$H_2$); 4.49 (*d*, $J$ = 12.2, PhC$H_2$); 4.25 (*dd*, $J$ = 5.3, 9.9, $H_A$–C(6)); 4.19 (*dt*, $J$ = 5.3, 9.9, H–C(5)); 4.16 (*d*, $J$ = 2.4, H–C(2)); 3.92 (*t*, $J$ = 9.4, H–C(3′)); 3.90 (*dd*, $J$ = 3.3, 9.5, H–C(4)); 3.88 (*ddd*, $J$ = 1.9, 3.9, 9.9, H–C(5′)); 3.74 (*dd*, $J$ = 4.0, 10.6, $H_A$–C(6′)); 3.71 (*t*, $J$ = 9.5, $H_B$–C(6)); 3.65 (*dd*, $J$ = 2.1, 10.6, $H_B$–C(6′)); 3.64 (*t*, $J$ = 9.8, H–C(4′)); 3.57 (*dd*, $J$ = 3.7, 9.7, 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 (2*s*); 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 $C_{55}H_{58}O_{13}S$ (959.11): C 68.88, H 6.09, S 3.34; found: C 69.10, H 6.12, H 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: 3060*w*, 3030*w* (sh), 3005*w*, 2930*w*, 2910*w*, 2870*m*, 1600*w*, 1498*w*, 1455*m*, 1410*w* (sh), 1360*s*, 1310*w*, 1260*m*, 1238*w* (sh), 1190*w*, 1178*s*, 1140*s* (sh), 1115*s*, 1105*s* (sh), 1075*s*, 1055*s* (sh), 1030*s*, 1005*s*, 970*s*, 915*w*, 890*m*, 855*w*, 815*m*, 700*s*, 662*w*. $^1$H-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*, PhC$H$); 5.06 (*t*, $J$ = 2.9, H–C(3)); 4.93 (*d*, $J$ = 10.9, PhC$H_2$); 4.88 (*d*, $J$ = 10.9, PhC$H_2$); 4.83 (*d*, $J$ = 10.3, 2 PhC$H_2$); 4.74 (*d*, $J$ = 10.9, PhC$H_2$); 4.69 (*s*, H–C(1)); 4.68 (*d*, $J$ = 12.0, PhC$H_2$); 4.58 (*d*, $J$ = 10.7, PhC$H_2$); 4.50 (*d*, $J$ = 7.5, H–C(1′)); 4.48 (*d*, $J$ = 12.0, PhC$H_2$); 4.31 (*dd*, $J$ = 5.3, 10.1, $H_A$–C(6)); 4.27–4.21 (*m*, H–C(5)); 4.21 (*d*, $J$ = 2.9, H–C(2)); 3.96 (*dd*, $J$ = 3.1, 9.6, H–C(4)); 3.84–3.83 (*m*, 2 H–C(6′)); 3.76 (*t*, $J$ = 9.3, H–C(4′)); 3.71 (*t*, $J$ = 10.1, $H_B$–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 (2*s*); 137.14 (2*s*); 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 $C_{55}H_{58}O_{13}S$ (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 $ClCH_2CH_2Cl$ (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*. $^1$H-NMR: 7.69 (*d*, *J* = 8.3, 2 arom. H); 7.42–7.09 (*m*, 27 arom. H); 5.53 (*s*, PhC*H*); 4.92 (*d*, *J* = 10.9, PhC$H_2$); 4.81 (*d*, *J* ≈ 2.7, H–C(1')); 4.80 (*d*, *J* = 10.7, PhC$H_2$); 4.79 (*d*, *J* = 11.0, PhC$H_2$); 4.68 (*s*, 2 PhC$H_2$); 4.60 (*s*, H–C(1)); 4.59 (*d*, *J* = 4.6, H–C(2)); 4.44 (*d*, *J* = 12.2, PhC$H_2$); 4.41 (*d*, *J* = 10.9, PhC$H_2$); 4.32–4.27 (*m*, H–C(5), $H_A$–C(6)); 4.18 (*d*, *J* = 12.1, PhC$H_2$); 4.05–4.02 (*m*, H–C(3), H–C(5')); 4.00 (*t*, *J* ≈ 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* ≈ 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 $C_{55}H_{58}O_{13}S$ (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*. $^1$H-NMR: 7.81 (*m*, 2 arom. H), 7.46–7.13 (*m*, 27 arom. H); 5.58 (*s*, PhC*H*); 5.05 (*d*, *J* = 11.4, PhC$H_2$), 4.97 (*d*, *J* = 2.6, H–C(2)); 4.89 (*d*, *J* = 11.0, PhC$H_2$); 4.81 (*d*, *J* = 10.8, PhC$H_2$); 4.73 (*d*, *J* = 10.5, PhC$H_2$); 4.72 (*d*, *J* = 12.2, PhC$H_2$); 4.70 (*d*, *J* = 11, PhC$H_2$); 4.63 (*d*, *J* = 7.5, H–C(1')); 4.58 (*d*, *J* = 10.7, PhC$H_2$); 4.57 (*d*, *J* = 12.2, PhC$H_2$); 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 $C_{55}H_{58}O_{13}S$ (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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