26. Glycosylidene Carbenes

Part 14

Glycosidation of Partially Protected Galactopyranose-, Glucopyranose-, and Mannopyranose-Derived Vicinal Diols

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The relation between H-bonding in diequatorial *trans*-1,2 and axial,equatorial *cis*-1,2-diols and the regioselectivity of glycosidation by the diazirine **1** was examined. H-Bonds were assigned on the basis of FT-IR and ^{1}H-NMR spectra (*Fig. 1*). Glycosidation by **1** of the *gluco*-configurated diequatorial *trans*-2,3-diols **4**–**7** yielded the mono-glucosylated products **16**/**17**/**20**/**21** (69–89%); 1,2-/1,3-linked products 37–46:63–54), **24**/**25**/**28**/**29** (60–63%; 1,2-/1,3-linked products 46–51:54–49), **32**–**35** (69–94%; 1,2-/1,3-linked products 45–52:55–48), and **36**/**37**/**40**/**41** (59–63%; 1,2-/1,3-linked products 52–59:48–41), respectively (*Scheme 1*, *Table 3*). The disaccharides derived from **4**, **5**, and **7** were characterized as their acetates **18**/**19**/**22**/**23**, **26**/**27**/**30**/**31**, and **38**/**39**/**42**/**43**, respectively. Glycosidation of the *galacto*-configurated diequatorial 2,3-diols **8** and **9** and the *manno*-configurated diequatorial 3,4-diol **10** by **1** (*Scheme 2*, *Table 3*) also proceeded in fair yields to give the disaccharides **44**–**47** (69–80%; 1,2-/1,3-linked products *ca.* 1:1), **48**–**51** (51–61%; 1,2/-1,3-linked products 54–56:56–54), and **56**/**57**/**60**/**61** (71–80%; 1,3-/1,4-linked products 49–54:51–46), respectively. The 1,3-linked disaccharides **56**/**57** derived from the diol **10** were characterized as the acetates **58**/**59**. The regio- and stereoselectivities of the glycosidation by **1** were much better for the α-D-*manno*-configurated axial,equatorial *cis*-2,3-diol **11** and the *galacto*-configurated axial,equatorial *cis*-3,4-diol **13** (1,2-/1,3-linked disaccharides *ca.* 3:7 for **11** and 1,3-/1,4-linked disaccharides *ca.* 4:1 for **13**; *Scheme 3*, *Table 4*). The regio- and stereoselectivity for the β-D-*manno*-configurated *cis*-2,3-diol **12** were, however, rather poor (1,2-/1,3-linked products 48:52). The 1,2-linked disaccharides **66**/**67** derived from **12** were characterized as the acetates **70**/**71**. *Koenigs-Knorr*-type glycosidation of the *cis*-diols **11**–**13** by **2** or **3** proceeded with a similar regio- and a higher stereoselectivity (α-D > β-D with the donor **2** and α-D < β-D with the donor **3**) than with **1**, with the exception of **12** which did not react with **2**. The regioselectivity of the glycosidations by **1** agrees fully with the H-bonding scheme of the diols and with the hypothesis that the intermediate carbene is preferentially protonated by the most weakly H-bonded OH group. The regioselectivity of the glycosidation by **2** and by **3** is determined by a higher reactivity of the equatorial OH groups and by H-bonding. Several H-bonded and equilibrating isomers of a given diol may intervene in the glycosidation by **1**, or by **2** and **3**, resulting in the same regioselectivity. The low nucleophilicity of **12** and the low degree of regioselectivity in its reaction with **3** show that stereoelectronic effects may also profoundly influence the nucleophilicity of OH groups.

Introduction. – Glycosylidene carbenes derived from 1-azisugars are protonated by OH groups [1] to form ion pairs which react further to glycosides (see [2] [3] and earlier papers of the series). Yields and regio- and stereoselectivities of such glycosidations depend strongly upon the kinetic acidity of the hydroxy compound [4–7]. Glycosidation proceeded in high yields, regioselectively, and with good stereoselectivity for those diols and triols, where one of the OH groups is a H-bond acceptor, and thus relatively more acidic [8]. Glycosidation with 1-azisugars is also regioselective when only one of the OH

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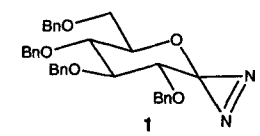
groups of a diol is a H-bond donor, and thus kinetically less acidic [5] [9]. In the absence of intramolecular H-bonds to OH groups, intermolecular H-bonds determine the reactivity of OH groups towards glycosylidene carbenes [10] [8], without, however, leading to regioselectivity.

While the type of regioselectivity should be determined by the direction of the H-bond, as conditioned by the relative acceptor and donor properties of the OH groups, its extent should depend upon the relative strength of the H-bonds [11]. The strength of intramolecular H-bonds in diols and hydroxy-ethers depends critically upon the O–H distance and the O–H···O angle [8] [11] [12]. Diaxial 1,3-diols form strong H-bonds. Weaker H-bonds are characteristic for axial,equatorial *cis*-1,2-diols. Diequatorial *trans*-1,2-diols are expected to form at best weak intramolecular H-bonds [13].

The qualitative correlation between intramolecular H-bonds, kinetic acidity, and carbene-mediated glycosidation implies that the reaction of 1-azisugars with axial,equatorial *cis*-1,2-diols should proceed with a lower degree of regioselectivity than with diaxial



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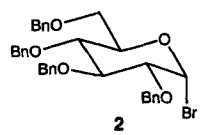

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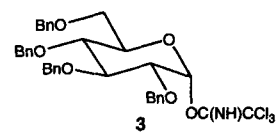

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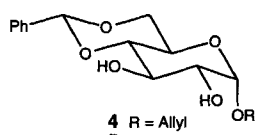

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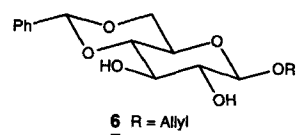

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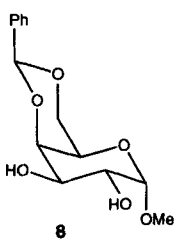

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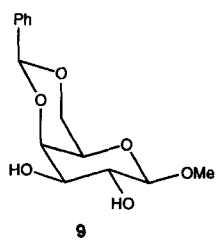

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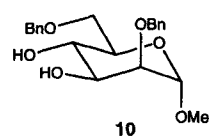

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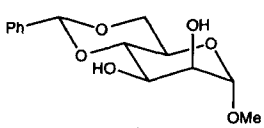

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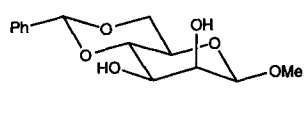

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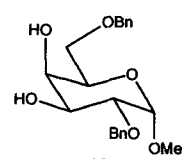

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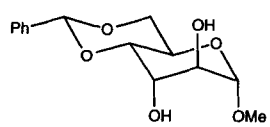

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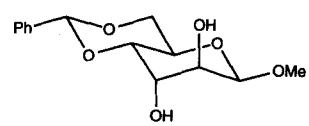

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1,3-diols, and that diequatorial *trans*-1,2-diols should react with a vanishing degree of regioselectivity, unless, evidently, one of the OH groups is involved in a strong intramolecular H-bond with a third functional group. In axial,equatorial *cis*-1,2-diols, regioselectivity should indicate the direction of the H-bond. If this correlation holds true, it should prove useful for predicting the outcome of glycosidations by 1-azisugars and conceivably other precursors of glycosylidene carbenes [14] [15] and constitute a valuable tool for the evaluation of H-bonds of di- and polyols in solution.

To study this correlation and the extent to which regioselectivity is influenced by the distance of an OH group from the anomeric center[2]) and by the relative configuration of a neighboring alkoxy group in diequatorial *trans*-1,2-diols, we explored the glycosidation of the anomeric *gluco*-diols **4**–**7** (influence of the configuration at C(1)), of the anomeric *galacto*-diols **8** and **9** (influence of the configuration at C(1) and C(4)), and of the *manno*-diol **10** (neighbourhood of the anomeric center) by the 1-aziglucose **1**. Similarly, for *cis*-1,2-diols, we studied the behaviour of the anomeric *manno*-diols **11** and **12** and of the *galacto*-diol **13**.

Finally, we studied the regioselectivity of *Lemieux*'s halide-exchange glycosidation by treating the diols **11**–**13** with the halide **2** [17] and of *Schmidt*'s trichloroacetimidate method [18] by treating the diols **11**–**13** with the imidate **3** [19]. It was demonstrated that glycosidation of the α-D-*altro*-diol **14** either by **1** or by **2** or **3** proceeds with a high and complementary regioselectivity, reflecting the relative kinetic acidity and the relative nucleophilicity of the two *trans*-1,2-diaxial OH groups [9]. Glycosidation of the β-D-anomer **15** by **1** did not proceed regioselectively, whereas the *Lemieux* procedure again led to a high degree of regioselectivity [9]. A comparison of the regioselectivity of the glycosidation of **11**–**13** by these methods should provide further information about the influence of the proximity of the anomeric center, the configuration of the diol, and the relative strength of intra- and intermolecular H-bonds.

Results and Discussion. – 1. *Hydrogen Bonds in the Diols* **4**–**15**. H-Bonding of methyl 4,6-*O*-benzylidene-aldohexopyranosides in diluted CCl_4 solution were well investigated for **5** [20–22], **7** [20] [21], **8** [21], **9** [21], **11** [20] [21], and **14** [20] [21] (*cf.* [23] for a review). Since such diols are poorly soluble in CCl_4 ($c \leqslant 0.005$M), we chose CH_2Cl_2 and $ClCH_2CH_2Cl$ as solvents. *Allerhand* and *von R. Schleyer* [24] observed a shift of *ca.* 20–30 cm^{-1} to lower wave numbers for the free and the associated IR bands of alcohols by changing the solvent from CCl_4 to CH_2Cl_2 or $ClCH_2CH_2Cl$[3]). The IR spectra of 0.1, 0.05, 0.01 and 0.005M solutions of **4**, **6**, **8**, and **11**–**13** in CH_2Cl_2 exhibit no bands for unassociated OH groups above 3595 cm^{-1} (weak absorptions at 3685–3670 cm^{-1} are due to traces of H_2O). The main bands between 3590 and 3558 cm^{-1} (*Table 1*) do not depend upon the concentration and are assigned to intramolecularly bonded OH. They agree well with the corresponding bands in CCl_4 solution [20] [21] (solvent shift *ca.* 24 cm^{-1}). A smaller

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[2]) An enhanced acidity is expected for OH–C(2) [16].

[3]) The IR spectrum of *trans*-cyclohexane-1,2-diol, a commonly used reference for 1,2-diols [20] [23], shows the unassociated OH band at 3629 cm^{-1} in CCl_4 and at 3610 cm^{-1} in CH_2Cl_2. Absorptions (CCl_4) at 3595 and 3602 (shoulder; [20]: 3600 cm^{-1}) and at 3586 cm^{-1} (CH_2Cl_2) do not depend upon the concentration and are assigned to intramolecularly bonded OH groups. For solutions in $ClCH_2CH_2Cl$, there is only one broad band at 3586 cm^{-1}. This confirms the larger solvent-shift value for the unassociated OH band in this solvent [24]. Broad bands for intermolecular H-bonds at 3500–3300 cm^{-1} (CH_2Cl_2 and $ClCH_2CH_2Cl$) are present at concentrations $\geqslant 0.04$M and disappear at concentrations $\leqslant 0.01$M.

Table 1. *FT-IR OH-Bands* [cm^{-1}] *of the Diols* **4**–**15**

Diol	Solvent	Intramolecularly bonded OH[a])	Intermolecularly bonded OH[b])
4	CH_2Cl_2	*ca.* 3585 (sh), 3568	3470
4	$ClCH_2CH_2Cl$	*ca.* 3585, 3570 (weakly separated bands)	3500
5 [20]	CCl_4	3609, 3582	
6	CH_2Cl_2	3590 (sharp)	3475
6	$ClCH_2CH_2Cl$	3583 (sharp)	3500
7 [20]	CCl_4	3615	
8	CH_2Cl_2	3568 (sharp)	3480
8	$ClCH_2CH_2Cl$	3564 (sharp)	3500
9 [21]	CCl_4	3615, 3602	
10	CH_2Cl_2	3585, 3558, *ca.* 3500 (sh)	3490
11	CH_2Cl_2	3587, *ca.* 3575 (sh)	3490
12	CH_2Cl_2	3574 (sharp)	*ca.* 3490
13	CH_2Cl_2	3577 (sharp), 3490[c])	3490[c])
14 [9]	CH_2Cl_2	3598, 3520	
14 [21]	CCl_4	3630, 3601, 3556	
15 [21]	CCl_4	3600	

[a]) No dependence upon concentration (0.1M – 0.005M) of solutions in CH_2Cl_2 or $ClCH_2CH_2Cl$.
[b]) Broad band, with tailing to *ca.* 3300 cm^{-1}; present at 0.1M and 0.05M, absent at 0.01M and 0.005M.
[c]) Band of reduced intensity also present at 0.01M and 0.005M.

solvent shift of 12 cm^{-1} for the band at 3568 cm^{-1} of the allyl glycoside **4** (as compared to the corresponding methyl glycoside **5**) may reflect the weaker acceptor properties of the allyloxy group. Absorptions at 3585–3590 cm^{-1} (as for **6**) are characteristic for H-bonded diequatorial 1,2-diols ('*trans* five-membered ring') and the ones at 3560–3570 cm^{-1} (as for **8**) for a H-bonded equatorial OH group in a 1,2-*cis*-diol ('*cis* five-membered ring'; see *Fig. 1*). The sharp bands for **6** and **12** and the small difference between the main bands for **8** and **12** suggest that the nature of the acceptor (OH *vs.* OR, glycosidic OR *vs.* non-glycosidic OR) has a negligible influence upon the position of the intramolecularly bonded OH band. It is not possible to decide if R*O*–C(1) or R*O*–C(4) of **6** acts as acceptor for the H-bond, or if there is an equilibrium between the two possibilities depicted in *Fig. 1*. As expected, **4** and **10** show bands for equatorial OH groups involved in a *trans* and in a *cis* five-membered ring. The concentration-independent shoulder at 3500 cm^{-1} of **10** indicates the presence of an isomer (**10b**) possessing a H-bond in a six-membered ring, *i.e.* between O*H*–C(4) and Bn*O*–C(6). The sharp band of **12** (3574 cm^{-1}) favours structure **12a** (two OH groups forming *cis* five-membered rings) although a contribution of **12b** (band at 3590 cm^{-1} hidden by the main band) cannot be excluded. The spectrum of **11** is indicative of structure **11a** rather than **11b** which should show an additional band at 3595–3600 cm^{-1} (cf. **14** [9]). The intensity of the absorption at 3500–3300 cm^{-1} of **4**, **6**, **8**, and **11**–**13** decreases when the concentration of the solutions is lowered from 0.1M (separated broad bands) to 0.05M (shoulders), and the bands disappear for 0.01 or 0.005M solutions of the 2,3-diols **4**, **6**, **8**, **11**, and **12** and of the *trans*-3,4-diol **10** (but not of the *cis*-3,4-diol **13**), demonstrating the presence of intermolecular H-bonds.

The interpretation of the IR spectra of **13** is more difficult. The band at 3577 cm^{-1} is due to a H-bond in a *cis* five-membered ring. Its position at 3577 cm^{-1}, as compared to

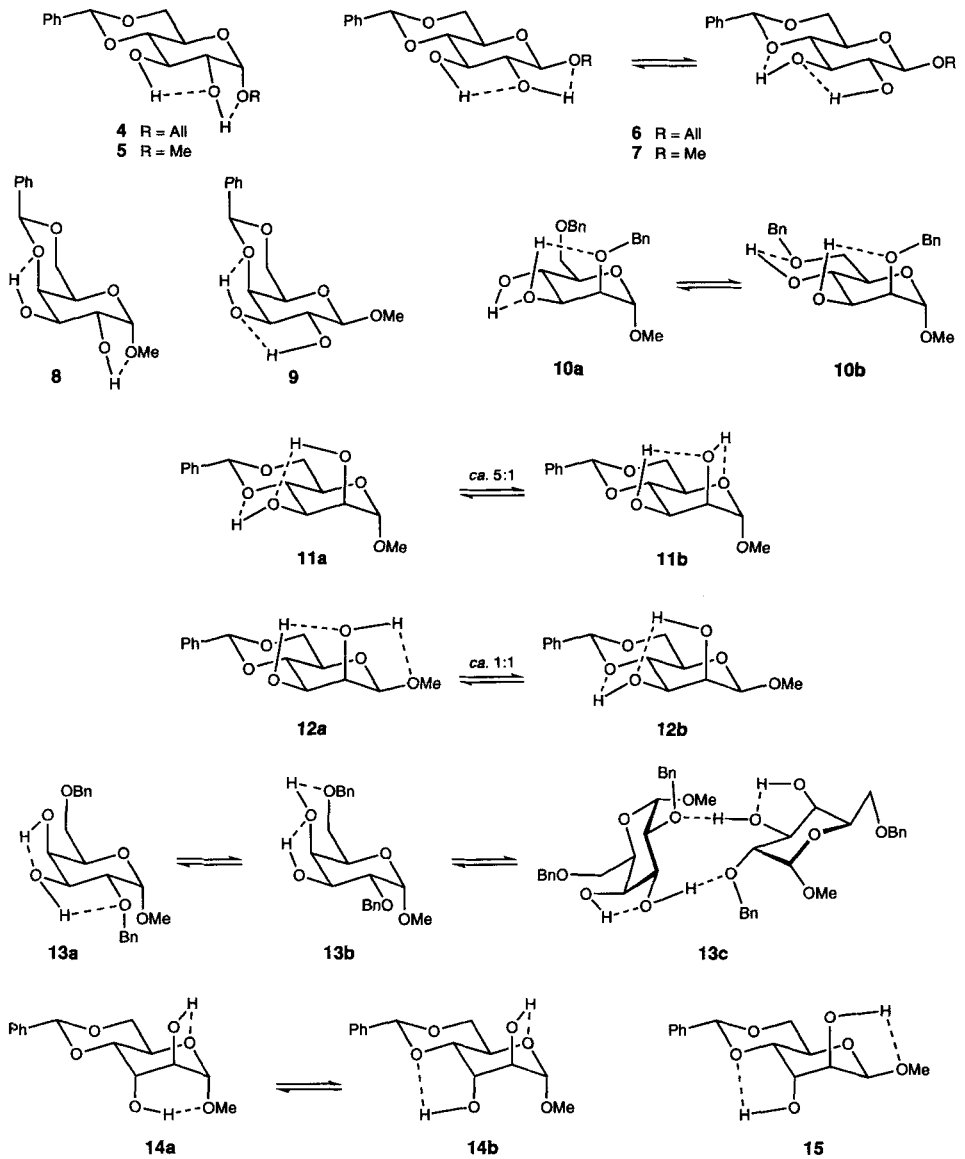


Fig. 1. *Intramolecular hydrogen bonds of the diols* **1–15** *deduced from IR* (OH bands of CH_2Cl_2 or CCl_4 solutions) *and* ^{1}*H-NMR spectroscopy* (vicinal J(OH,H) of $CDCl_3$ solutions)

3568 cm^{-1} for **8**, suggests that the axial O*H*–C(4) and not the equatorial OH–C(3) acts preferentially as H-donor [25]. There is no band around 3590 cm^{-1} of an equatorial OH in a *trans* five-membered ring as in **13a** (*Fig. 1*). The intensity of the broad (extending to *ca.* 3350 cm^{-1}) band at 3490 cm^{-1} decreases from 0.1M to 0.05M, but is insensitive to further dilution. This behaviour, the shape, and the position of this band are taken as evidence for a H-bond from O*H*–C(4) to *O*–C(3) (corroborated by ^{1}H-NMR data, see below) and

a strong intermolecular H-bond from O*H*–C(3) such as it would be realized in the dimer **13c**. We cannot, however, exclude that O*H*–C(3) acts as a donor in a weak H-bond to Bn*O*–C(2) (**13a**), nor can we exclude an equilibrium between **13a** and **13c** or only **13a** with a species where O*H*–C(3) is a H-donor to *O*–C(4), and O*H*–C(4) to Bn*O*–C(6) (**13b**).

The IR spectra of **4**, **6**, and **8** in $ClCH_2CH_2Cl$ and in CH_2Cl_2 (*Table 1*) differ hardly from each other. The spectra of **10** and **13** in 1,4-dioxane show one broad band at 3415 and 3450 cm^{-1}, respectively, which is insensitive to a change of concentration.

The ^{1}H-NMR spectra of the diols **4**–**13**, and, for reasons of comparison of **14** and **15** in $CDCl_3$ solution show well resolved OH signals (*Table 2*). The assignment is based upon the multiplicity of the vicinal H–C signals (see *Table 6* in *Exper. Part*) and may be reversed for **8** and **15**, which possess similar *J*(OH,H) values. Large *J*(OH,H) values (9–10 Hz) indicate dihedral angles of 150–170° and small ones (1.5–2.5 Hz) angles of *ca.*

Table 2. *Selected ^{1}H-NMR* (400 MHz) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Diols* **4**–**15** *in $CDCl_3$ Solution at Room Temperature*

	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**11**[a])
OH–C(2)	2.29	2.32	2.61	2.64	2.29[b])	2.63	–	2.75	5.10[b])
OH–C(3)	2.73	2.79	2.76	2.79	2.04[b])	2.60	2.27	2.78	4.97[b])
OH–C(4)	–	–	–	–	–	–	2.58	–	–
J(2,OH)	10.1	≈8.0	2.5	2.2	9.1[c])	1.6	–	2.5	4.2[b])
J(3,OH)	< 2	< 1	2.4	2.0	8.0[c])	8.9	9.6	3.6	5.9[b])
J(4,OH)	–	–	–	–	–	–	1.7	–	–

	12	**12**[a])	**13**	**13**[a])	**14**	**14**[a])	**15**
OH–C(2)	2.55	4.76	–	–	2.12	5.32	2.44[b])
OH–C(3)	2.64	4.86	2.46	4.60[b])	2.89	4.64	2.24[b])
OH–C(4)	–	–	2.78[d])	4.81[b])	–	–	–
J(2,OH)	1.7	4.6	–	–	6.7	4.2	1.5[c])
J(3,OH)	6.2	6.7	4.1	5.6[c])	5.7	4.8	1.8[c])
J(4,OH)	–	–	1.3	5.8[c])	–	–	–

[a]) In (D_6)DMSO.
[b])[c]) Assignments may be reversed.
[d]) $^4J(5,OH) = 0.5$ Hz.

90° (*cf.* [26]). The large *J*(OH,H) for the diequatorial diols possessing a neighboring axial RO substituent (OH–C(2) of **4** and **5**, OH–C(2) and OH–C(3) of **8**, OH–C(3) of **9** and **10**) indicate a H-bond to the vicinal axial RO group. The OH groups of **4**, **6**, **7**, **9**, and **10** which possess no vicinal axial RO group show only small coupling constants which are compatible with H-bonds between *trans*-diequatorial OH groups. According to the *J*(OH,H) values, all diequatorial diols with the exception of **6**, **7**, and **10** are present as single H-bonded conformers (*Fig. 1*). In contrast to this, the *J*(OH,H) values of 3.6–6.2 Hz for the axial,equatorial diols **11**–**13** are best rationalized by a conformational equilibrium between two H-bonded isomers (*Fig. 1*), as it appears to be the case for **6** and **7**. In the preferred isomer of the α-D-mannoside **11** and the α-D-galactoside **13**, the axial OH group acts as H-donor to the equatorial OH group (**11a** and **13a**), as deduced from the IR

spectra. The diaxial diols **14** and **15**, finally, prefer each one single conformation. As expected, both OH groups of **15** act as H-donors to the vicinal equatorial RO groups. For **14**, J(OH,3) = 6.6 Hz is compatible with Me*O*–C(1) or with R*O*–C(4) as H-acceptor; the IR bands (CH_2Cl_2, *Table 1*) show the presence of the isomer **14a** with a H-bond between O*H*–C(3) and *O*–C(1), but do not exclude the presence of a small percentage of the isomer **14b** with a O*H*–C(3), *O*–C(4) bond, as the corresponding absorption (expected at *ca.* 3575 cm^{-1} [9] and which is present in CCl_4 solution) could be hidden by the band at 3598 cm^{-1}. This is in agreement with the enhanced stability of a H-bond in a six-membered rather than in a five-membered ring and with the poorer acceptor properties of an anomeric RO group [11].

The ^{1}H-NMR spectra of the diols **11**–**13** in (D_6)DMSO solution show J(OH,H) in the range of 4.2–6.7 Hz (*Table 2*). These values are close to the one observed for a freely rotating OH group (*ca.* 5.3 Hz [27]), in keeping with intermolecular H-bonds to the solvent [28c].

Intramolecular H-bonds may be detected by a weak dependence of the chemical shift of OH groups upon the temperature [8] [28]. For solutions in DMSO (from 298 to 348 K), values of < -3 ppb/K indicate linear H-bonds, while values between -3 and -6 ppb/K characterize bent intramolecular H-bonds [29]. $\Delta\delta$ Values for the OH groups between -7.3 and -8.9 ppb/K confirm that **11**–**13** in (D_6)DMSO solution possess no or only weak intramolecular H-bonds.

Even relatively weak intramolecular H-bonds should be visible in an apolar solvent (*cf.* [28g]). The chemical shift of both OH groups of the *trans*- and the *cis-manno*-diols **10** and **12** depend strongly and nonlinearly upon the temperature (*Fig. 2*). The dependence does not distinguish between the two OH groups and gives no hints for intramolecular H-bonds. The curves describing the temperature dependance for O*H*–C(3) and

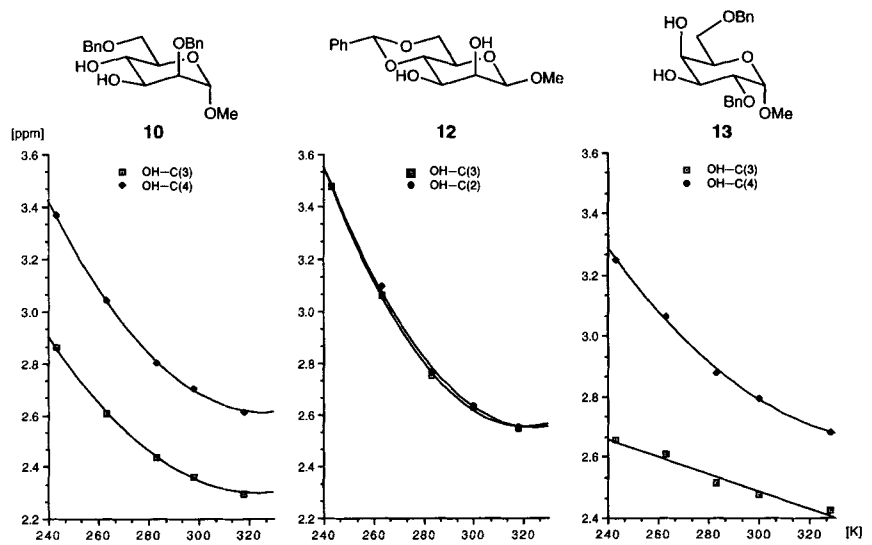


Fig. 2. *Dependence upon the temperature of the chemical shifts of the OH signals of* **10**, **12**, *and* **13** *in* $CDCl_3$ *solution*

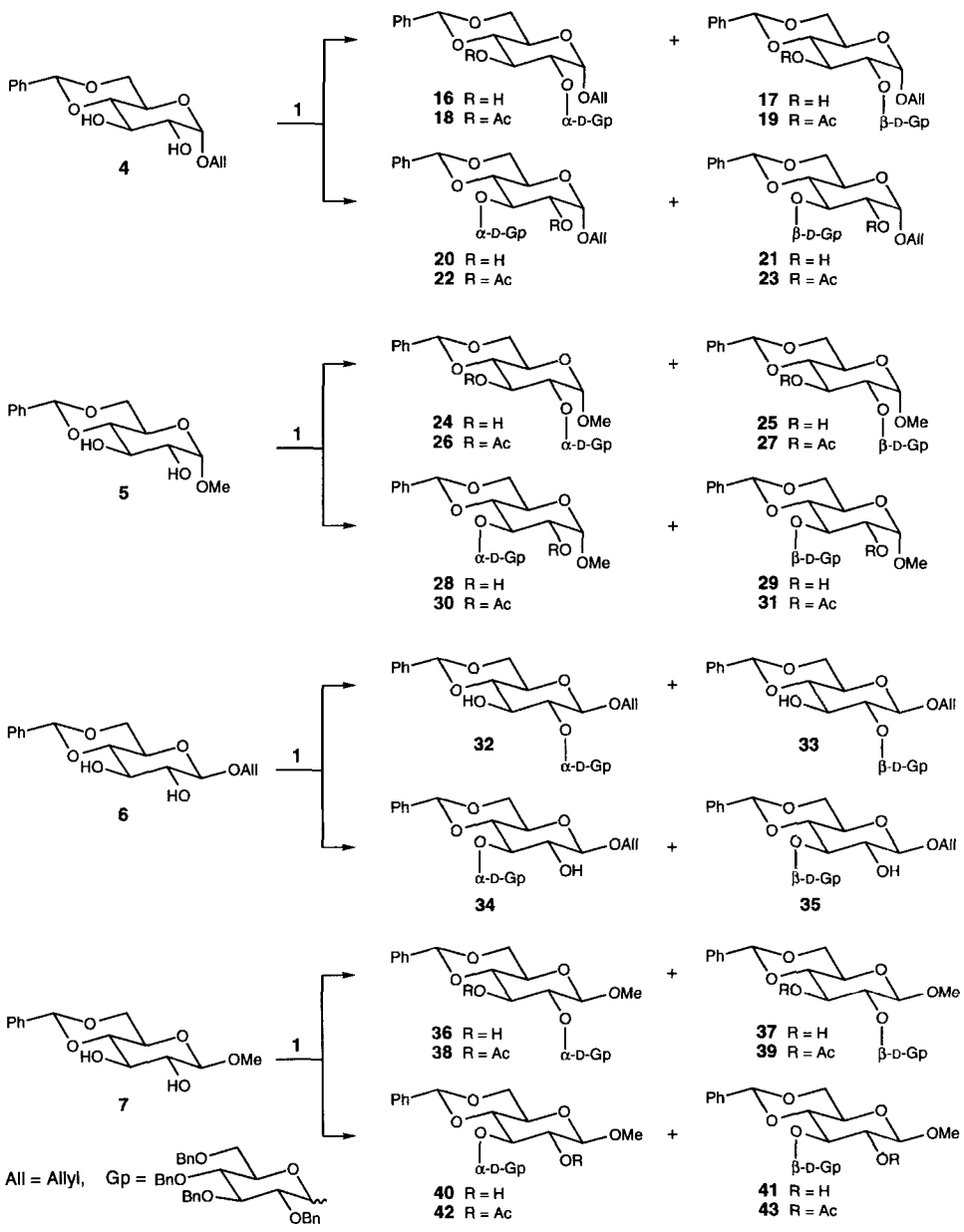
O*H*–C(4) of **13**, however, differ from those for **10** and **12** and from each other; the one for O*H*–C(4) being slightly (mean $\Delta\delta = -6.7$ ppb/K) and the one for O*H*–C(3) strongly flattened ($\Delta\delta = -2.9$ ppb/K). This indicates that O*H*–C(4) of **13** is a stronger – but still weak – H-donor than the OH groups of **10** and **12** and that O*H*–C(3) should form a relatively strong H-bond. The assignment of these OH groups is unambiguously deduced from the signal pattern in the ^{1}H-NMR spectrum (see *Table 6* in the *Exper. Part*). Apparently, the H-bonding in **13** differs from the one of the other *cis*-diols. J(3,OH) of 4.1 Hz means that only minor amounts of **13b** can be present (less than 30–40%). The upper limit for this percentage is further reduced by considering the rotamer distribution of the benzyloxymethyl group in **13**. The relatively large $J(5,6) = 5.0$ and $J(5,6') = 5.6$ Hz are in keeping with a *gt*/*tg*/*gg* rotamer equilibrium of *ca.* 4:4:2. Therefore, not more than 20% of **13b** are present. The strongest evidence against **13b** as a major isomer is the long-range coupling constant of 0.5 Hz between OH–C(4) and H–C(5) (*W* coupling). This restricts the dihedral angles for H–C(5)–C(4)–O–H to values which are only compatible with the axial OH–C(4) acting as H-donor as in **13a** or in a dimeric species where OH–C(3) acts as a H-donor, such as **13c** (*Fig. 1*). The isomer **13a** cannot be a major species. O*H*–C(3) can only form a weak intramolecular H-bond with Bn*O*–C(2). There is no corresponding band in the IR spectrum (see above), and the weak temperature dependence of the chemical shift of OH–C(3) is also incompatible with **13a**. Since **13b** is present at best to a small extent, the IR band of **13** at 3490 cm^{-1} may well be due to a relatively strong intermolecular H-bond (see above). An osmometric molecular-weight determination (*cf.* [8]) of **13** and, for reasons of comparison, of **10** (both M_r 374), however, did not corroborate the presence of a sufficiently stable dimeric structure of **13** in CH_2Cl_2 solution. Average molecular weights of 379–384 (**13**, 0.004, 0.007, and 0.06M in CH_2Cl_2) and 407 (**10**, 0.018M in CH_2Cl_2) show the presence of the monomers only. This discrepancy between the apparent molecular weight on the one hand, and the IR and ^{1}H-NMR spectra (including the weak temperature dependence of OH–C(3)) on the other hand, indicates the presence of short-lived associates or of a temperature dependence for the **13a**/**13b**/**13c** equilibrium, where higher temperatures favour **13b**. Small changes in the $J(5,6)$, $J(5,6')$, and ^3J(OH,H) values between 243 and 318 K favour the first rationalization, irrespective of the observation that the signals for H- and H′–C(6) change with increasing temperature from a *d* to an *AB* system.

Thus, in apolar solvents, all OH groups of the diols **6**–**15** are involved in intramolecular H-bonds; moreover, **13** forms a strong intermolecular H-bond. Preferential protonation of **1** by the OH group forming the less stable H-bond – or by the free OH when this H-bond is broken [10] – is expected, as it was observed for the glycosidation of a phenol [5] and of **14** and **15** [9]. In the series of the *trans*-1,2-diols, one, therefore, expects preferential glycosidation of OH–C(3) for **4** and **5**, of OH–C(2) for **9**, and of OH–C(4) for **10**. In the case of **6**–**8**, one expects *ca.* 1:1 mixtures of regioisomers. H-Bonding in the *cis*-1,2-diols **11**–**13** leads to the prediction that protonation and glycosidation should preferentially involve OH–C(3) of **11** and **13**. The prediction for **12** is more difficult; one expects a nearly 1:1 mixture of regioisomers or a weak preference of the glycosidation of OH–C(3).

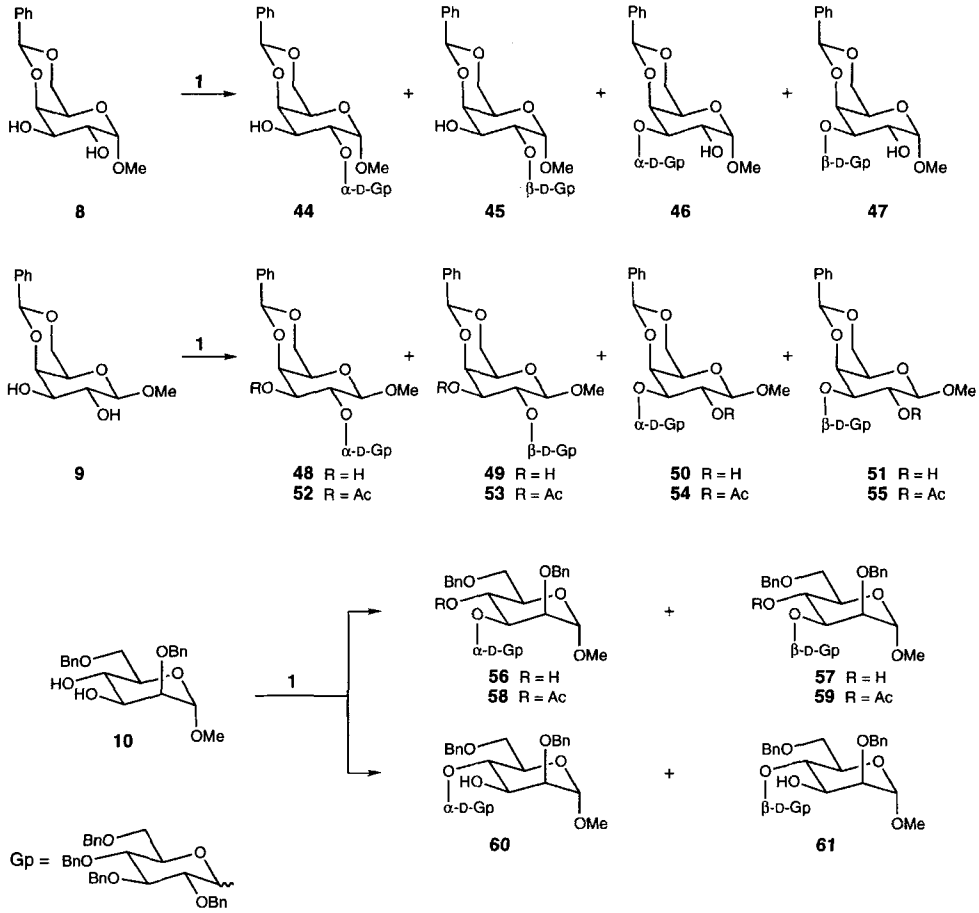
2. *Glycosidation of the Diequatorial* trans-*Diols* **4**–**10** *by the Diazirine* **1**. The glycosidation of the diols **4**–**10** by **1** was studied in $ClCH_2CH_2Cl$, 1,4-dioxane, dimethoxyethane (DME), toluene, and C_6H_5Cl at different temperatures and donor/acceptor ratios

(*Schemes 1* and *2*, *Table 3*). Each diol reacted with **1** to yield a mixture of four disaccharides, **16/17/20/21**, **24/25/28/29**, **32–35**, **36/37/40/41**, **44–47**, **48–51**, and **56/57/60/61**, respectively. No trisaccharides could be isolated. The ratio of the products was determined by anal. HPLC. The mixtures obtained from **4**, **5**, **7**, and **9** were acetylated before

Scheme 1



Scheme 2



chromatographic separation (→ **18**/**19**/**22**/**23**, **26**/**27**/**30**/**31**, **38**/**39**/**42**/**43**, and **52**–**55**, resp.). The products resulting from **10** were first separated by FC into mixtures of the regioisomers **56**/**57** and **60**/**61**. HPLC of **60**/**61** gave **60** and **61** and HPLC of the acetylation product of **56**/**57** gave the acetates **58** and **59**.

Glycosidation yields are highest with $ClCH_2CH_2Cl$ as solvent (*Table 3*). The regioselectivity, however, depends only little upon the solvent and reaches at best a ratio of 11:9. Stereoselectivity is low. The α-D/β-D ratio ranges from 1:1 to 3:7 for the 1,2-linked disaccharides, from 4:6 to 3:7 for the 1,3-linked disaccharides derived from the *gluco*-diols **4**–**7**, and from 4:6 to 6:4 for the 1,3-linked disaccharides derived from the *galacto*-diols **8** and **9**. The only exception are the glycosidation of **4** in toluene (regioselectivity of 37:63 in favour of the 1,3-linked disaccharides) and of **7** in dioxane (regioselectivity of 6:4 and α-D/β-D ratio of 3:7 for the 1,2-linked disaccharides). The aglycon (Me *vs.* allyl) in the *gluco*-series has hardly any influence upon glycosidation.

Table 3. *Glycosidation of the* trans-*Diols* **4–10** *with the Diazirine* **1**

Conc. of **1** [M]	Diol (mol-equiv.)	Conditions	Total yield [%]	Regioselectivity RO–C(2)/ RO–C(3)[a])	Stereoselectivity (α-D/β-D of R)	
					RO–C(2)[b])	RO–C(3)
0.09	**4** (1.3)	1,4-dioxane, 22°, 5 h	72	44:56	39:61	36:64
0.09	**4** (1.3)	$ClCH_2CH_2Cl$, 22°, 5 h	75	46:54	47:53	39:61
0.09	**4** (0.75)	$ClCH_2CH_2Cl$, 22°, 5 h	89	46:54	46:54	38:62
0.09	**4** (1.3)	C_6H_5Cl, 22°, 5 h	74	46:54	51:49	36:64
0.02	**4** (1.3)	toluene, 50°, 1.5 h	69	37:63	37:63	34:66
0.09	**4** (1.3)	DME, *hv*, −45°, 2 h	72	46:54	52:48	38:62
0.05	**5** (0.9)	1,4-dioxane, 24°, 5 h	60	46:54	35:65	26:74
0.10	**5** (1.5)	$ClCH_2CH_2Cl$, 24°, 5 h	77	51:49	50:50	37:63
0.05	**5** (0.9)	$ClCH_2CH_2Cl$, 24°, 5 h	73	51:49	46:54	35:65
0.06	**6** (1.3)	1,4-dioxane, 22°, 5 h	69	46:54	32:68	38:62
0.05	**6** (1.3)	DME, 22°, 5 h	71	46:54	43:57	41:59
0.06	**6** (1.3)	$ClCH_2CH_2Cl$, 22°, 5 h	80	49:51	45:55	41:59
0.06	**6** (0.75)	$ClCH_2CH_2Cl$, 22°, 5 h	94	52:48	47:53	35:65
0.02	**6** (1.3)	C_6H_5Cl, 22°, 5 h	70	45:55	39:61	41:59
0.02	**6** (1.3)	toluene, 70°, 1.5 h	70	47:53	40:60	44:56
0.05	**7** (0.9)	1,4-dioxane, 24°, 5 h	63	59:41	31:69	42:58
0.05	**7** (1.5)	$ClCH_2CH_2Cl$, 24°, 5 h	63	52:48	42:58	39:61
0.03	**7** (0.9)	$ClCH_2CH_2Cl$, 24°, 5 h	59	54:46	42:58	35:65
0.09	**8** (1.3)	1,4-dioxane, 23°, 5 h	76	50:50	39:61	59:41
0.04	**8** (1.3)	$ClCH_2CH_2Cl$, 23°, 5 h	69	51:49	44:56	52:48
0.04	**8** (0.75)	$ClCH_2CH_2Cl$, 23°, 5 h	80	50:50	44:56	52:48
0.02	**8** (1.0)	toluene, 70°, 2 h	70	50:50	35:65	46:54
0.05	**9** (0.9)	1,4-dioxane, 24°, 5 h	51	54:46	32:68	48:52
0.10	**9** (1.5)	$ClCH_2CH_2Cl$, 24°, 5 h	61	54:46	40:60	42:58
0.03	**9** (0.9)	$ClCH_2CH_2Cl$, 24°, 5 h	56	56:44	38:62	42:58
0.11	**10** (1.3)	1,4-dioxane, 24°, 5 h	71	51:49	47:53	59:41
0.11	**10** (0.75)	1,4-dioxane, 24°, 5 h	80	51:49	49:51	61:39
0.03	**10** (1.3)	toluene, 70°, 2 h	75	46:54	48:52	64:36

[a]) RO–C(4)/RO–C(3) for **10**.
[b]) RO–C(4) for **10**.

A comparison of the glycosidations of **4–10** shows that the anomeric configuration, the configuration of the glycosyl acceptor, and the distance to the anomeric center have at best a small influence on yields and selectivities (*Table 3*). The regioselectivities are, however, in keeping with the prediction based on the H-bonding in these diols (*Fig. 1*) and the preferred attack on the OH group involved in the weaker H-bond.

The nucleophilic properties of the two OH groups differ only little, as evidenced by the low degree of regioselectivity in the *Koenigs-Knorr*-type glycosidation of **5** and **7** with the bromide **2** (**24**/**28** 1:1.6; **36**/**40** 1:1.1 [30]). Similar low regioselectivities were observed in the *Koenigs-Knorr*-type glycosidation of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide with benzylidene-α-D-glucopyranosides [31], benzylidene-β-D-glucopyranosides [31], and benzylidene-β-D-galactopyranosides [32] [33] which led to ratios of 1,2- to 1,3-linked disaccharides of 3:1, 1:1, and 1:1.5, respectively.

The structure of the disaccharides is evidenced by the OH or AcO signals in the IR and NMR spectra of the glycosidation products and their acetates, respectively. Selected ^{1}H- and ^{13}C-NMR data of the disaccharides are

compiled in *Tables 7–9* (see *Exper. Part*). The constitution of the disaccharides is deduced from the signal pattern of the H–C(OH) or H–C(OAc) group in the ^{1}H-NMR spectra. The configuration of the new anomeric center is easily deduced from the $J(1',2')$ values and the chemical shifts of H–C(1′) and C(1′). The downfield shift of H–C(3′) and H–C(5′) (stronger for the alcohols than for the acetates) and the upfield shift of C(3′) and C(5′) (γ-effect) are characteristic for the α-D-configuration. The ^{13}C-NMR chemical shifts for the anomeric C's of **30** and **31** are in agreement with reported ones [34].

3. *Glycosidation of the* cis-*Diols* **11–13** *by the Donors* **1–3**. Glycosidation of the *cis*-diols **11–13** by **1** was performed similarly as described for the *trans*-2,3-diols and led again, in each case, to mixtures of the anomers of the 1,2- and 1,3-linked disaccharides **62–65**, **66–69**, and **72–75**, respectively (*Scheme 3*). The ratio of the crude products was determined by anal. HPLC (*Table 4*), and the products were separated by FC and HPLC (**66** and **67** as their acetates **70** and **71**).

Scheme 3

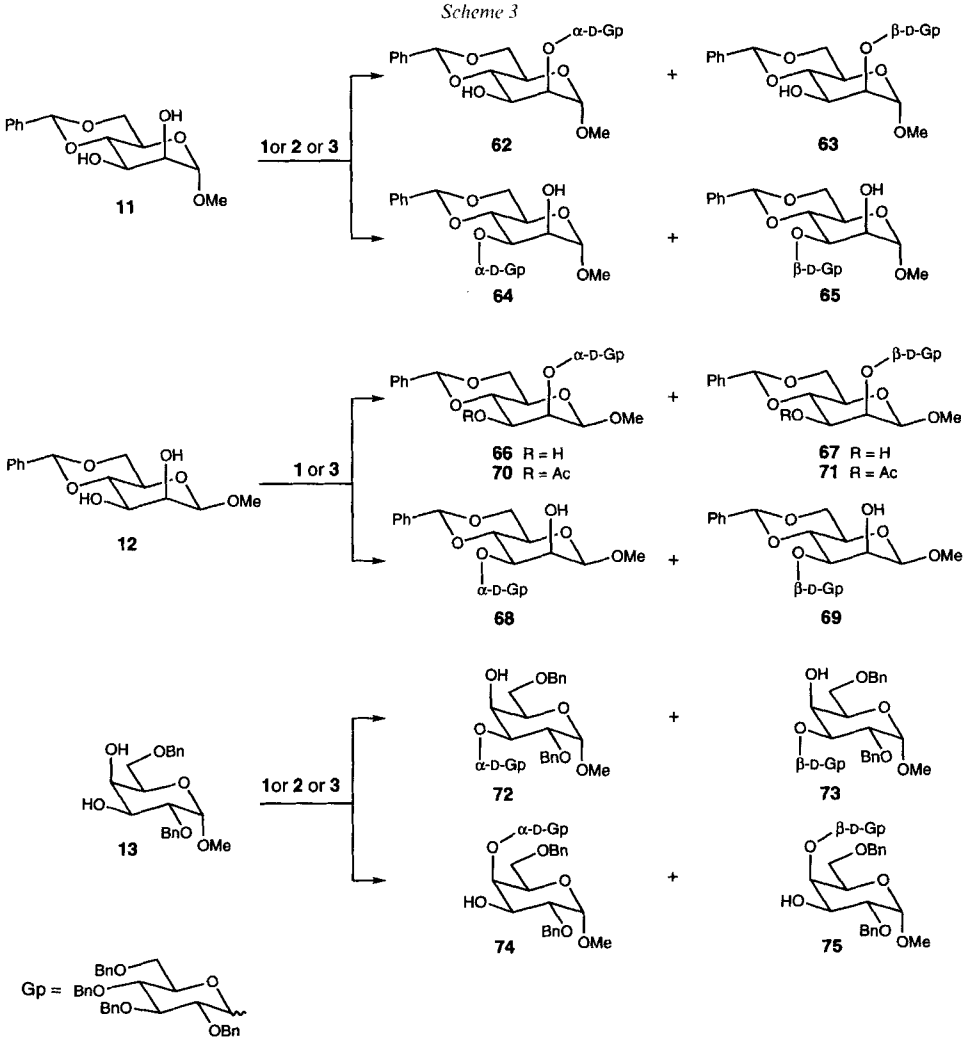


Table 4. *Glycosidation of the* cis-*Diols* **11–13** *with the Diazirine* **1**

Conc. of **1** [M]	Diol (mol-equiv.)	Conditions	Total yield [%]	Regioselectivity RO–C(2)/ RO–C(3)[a])	Stereoselectivity (α-D/β-D of R)	
					RO–C(2)[b])	RO–C(3)
0.09	**11** (1.3)	1,4-dioxane, 23°, 5 h	83	29:71	29:71	39:61
0.04	**11** (1.3)	$ClCH_2CH_2Cl$, 22°, 5 h	78	40:60	43:57	41:59
0.04	**11** (0.75)	$ClCH_2CH_2Cl$, 23°, 5 h	96	39:61	48:52	38:62
0.02	**11** (1.3)	toluene, 22°, 5 h	86	27:73	54:46	39:61
0.02	**11** (1.3)	toluene, 70°, 2 h	89	24:76	38:62	40:60
0.06	**11** (1.3)	THF, *hv*, −85°, 6 h	73	30:70	20:80	16:84
0.10	**11** (1.3)	DME, 0.1 equiv. of $SnCl_2$, 17°, 5 h	52	34:66	53:47	56:44
0.04	**12** (0.75)	$ClCH_2CH_2Cl$, 24°, 5 h	85	48:52	53:47	56:44
0.11	**13** (1.3)	1,4-dioxane, 24°, 5 h	67	26:74	39:61	51:49
0.11	**13** (0.75)	1,4-dioxane, 24°, 5 h	74	25:75	39:61	47:53
0.03	**13** (1.3)	toluene, 70°, 2 h	68	14:86	40:60	54:46
0.05	**13** (1.3)	toluene, 23°, 5 h	73	19:81	53:47	54:46

[a]) RO–C(4)/RO–C(3) for **13**. [b]) RO–C(4) for **13**.

Yields of the glycosidation of **11** with a slight excess of **1** reach 96%; they are somewhat lower but still good for **12** and **13**. Glycosidation of the equatorial OH group of **11** and **13** is preferred, and the regioselectivity ranges between 24:76 and 40:60 for **11** and between 14:86 and 26:74 for **13**; the regioselectivity is significantly lower in the glycosidation of the β-D-mannoside **12**. Stereoselectivity is poor, except for the glycosidation of **11** under photolytic conditions in THF at −85° (quartz filter) which did not affect regioselectivity (3:7), but led mainly to the β-D-configurated disaccharides (α-D/β-D ≦ 1:4). Exclusive alkylation at OH–C(3) of **11** by diphenyldiazomethane in the presence of a catalytic amount of $SnCl_2$ [35] was reported. We did not observe a similar influence of $SnCl_2$ on the glycosidation of **11** by **1**; selectivities were not affected and the total yield dropped to 52%.

For comparative reasons, we also studied the glycosidation of **11–13** according to *Lemieux* and *Schmidt*. Glycosidation of the α-D-*manno*-diol **11** with **2** according to *Lemieux* proceeded regio- and stereoselectively to yield 80% of a mixture of the anomeric 1,2- and 1,3-linked disaccharides **62**/**63** (93:7) and **64**/**65** (9:1) in a ratio of 3:7, while the anomeric diol **12** did hardly react and was largely recovered (*Table 5*). Under similar

Table 5. *Glycosidation of the Diols* **11–13** *with the Bromide* **2** *and the Trichloroacetimidate* **3**

Donor	Diol	Total yield [%]	Regioselectivity RO–C(2)/RO–C(3) or RO–C(4)/RO–C(3)	Stereoselectivity (α-D/β-D of R)	
				RO–C(2) or RO–C(4)	RO–C(3)
2	**11**	80	30:70	93:7	90:10
2	**12**	trace	–	–	–
2	**13**	75	10:90	90:10	60:40
3	**11**	93	12:88	40:60	7:93
3	**12**	91	46:54	12:88	8:92
3	**13**	86	20:80	22:78	40:60

conditions, the *galacto*-diol **13** gave 75% of the anomers of the 1,3- and 1,4-linked disaccharides **72**/**73** (3:2) and **74**/**75** (9:1) in a ratio of 9:1. The known glucosylation of **13** with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide yielded 55% of the corresponding 1,3-linked β-D-anomer [36].

The disaccharides **62**–**69** and **72**–**75** were also obtained by the glycosidation of **11**–**13** with the trichloroacetimidate **3** (CH_2Cl_2, −30°, $BF_3 \cdot Et_2O$) (*Table 5*). The α-D-*manno*-diol **11** yielded 93% of the anomeric 1,2- and 1,3-linked disaccharides **62**/**63** (2:3) and **64**/**65** (7:93) in a ratio of 12:88, and the β-D-mannoside **12** yielded 91% of **70**/**71** (11:88; after acetylation) and **68**/**69** (8:92) in a ratio of 46:54. The *galacto*-diol **13**, finally, gave 86% of the anomeric 1,3- and 1,4-linked disaccharides **72**/**73** (2:3) and **74**/**75** (22:78) in a ratio of 4:1.

The high α-D-selectivity of the *Lemieux* glycosidation is expected [17]. Also expected is the higher reactivity of the equatorial OH–C(3) of **11** and **13** which is observed both in the glycosidation according to *Lemieux* and to *Schmidt*. Very similar regioselectivities are observed in the glycosidation of **11**–**13** by the diazirine **1**, the bromide **2**, and the trichloroacetimidate **3**. The regioselectivity observed for the glycosidation of **11** by **1** is in keeping with the preferred H-bonding as depicted in *Fig. 1*, but the H-bonds are not differentiated enough to result in a high degree of regioselectivity [8] [9]. The preference for glycosidation of OH–C(3) of **13** is higher than the one for **11** and correlates with the presence of a weak H-bond involving OH–C(3) in **13a** (see above), perhaps reflecting the difference between the rotational freedom of the BnO–C(2) group in **13** and the conformational bias for the O–C(4) group in **11**. The β-D-*manno*-diol **12** is insufficiently nucleophilic to react with **2**, but leads to high yields of disaccharides when treated with either **1** or the trichloroacetimidate **3**[4]). The low regioselectivity in the glycosidation of **12** by **1** and by **3** and the low reactivity of **12** with **2** show the remarkably low nucleophilicity of the equatorial OH–C(3). This is expected for **12b** (*Fig. 1*) which should not react with **2**, due to the generally lower reactivity of the axial OH–C(2), and because the H-bond of O*H*–C(2) to *O*–C(3) is stronger than the one of O*H*–C(3) to *O*–C(4), leading to a reduced nucleophilicity of OH–C(3). Evidently, there must be a factor which lowers the nucleophilicity of OH–C(3) in **12a** (H-bonding should increase its nucleophilic properties), most probably the σ-conjugation of a doubly occupied, non-bonding orbital at O–C(3) through the C(3)–C(2) bond with the σ*(C,O) orbital of the anomeric MeO group [39], as H-bonding in **12a** leads to an antiperiplanar arrangement of a lone pair at O–C(3), the C(2)–C(3), and the C(1)–O bond.

Although in a specific H-bonded isomer of a given diol there is complementarity between the relative acidity and nucleophilicity of each OH group, the presence of two or more intra- and intermolecularly H-bonded and rapidly equilibrating species may lead to the same regioselectivity for the glycosidation by 1-azisugars and by electrophilic glycosyl donors. The glycosidation of **12** demonstrates that stereoelectronic effects may also intervene and influence the nucleophilicity of individual OH groups, and these effects must also be considered when reliable predictions of regioselectivities are at stake.

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[4]) The nucleophilicity of OH–C(3) in β-D-mannopyranosides can vary considerably. A 4-*O*-acetyl-β-D-mannopyranoside, glycosylated in position 2, did not react with acetobromomannose, but with the corresponding trichloroacetimidate [37]. Octyl β-D-mannopyranoside, however, was mannosylated by acetobromomannose in position 3 and 6 [38].

The constitution and configuration of the disaccharides **62**–**75** was determined by IR and NMR spectroscopy. Selected ^{1}H- and ^{13}C-NMR data are given in *Tables 9* and *10* (see *Exper. Part*). The *J* values of **64** agree well with published ones [40], but the chemical shifts are rather different. The δ values for C(1) and C(1′) of **74** and **75** are as reported [36].

We thank M. *D. Nanz*, M. *Th. Plüss*, and M. *M. Vöhler* for their help with NMR experiments, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. See [9]. Anal. high-performance liquid chromatography (HPLC): anal. *Spherisorb* silica gel (5 μm) 250 × 4.6 mm column for **18**–**23** (hexane/AcOEt 85:15, 1.5 ml/min), for **44**–**47** (hexane/AcOEt 65:35, 1.5 ml/min), for **58** and **59** (CH_2Cl_2/AcOEt 98.5:1.5, 1.5 ml/min), for **72** and **73** (CH_2Cl_2/AcOEt 19:1, 1.5 ml/min), for **74** and **75** (hexane/AcOEt 65:35, 1.5 ml/min), and for **62**–**65** (hexane/AcOEt 3:1, 1.5 ml/min); *Merck LiChrosorb Si60* 250 × 4.0 mm cartridge for **26**–**31** and **32**–**35** (hexane/AcOEt 4:1, 1.5 ml/min), for **38**–**43** (hexane/AcOEt 2:1, 1.5 ml/min), for **48**–**51** (hexane/AcOEt 1:1, 1.5 ml/min), for **54** and **55** (CH_2Cl_2/AcOEt 98:2, 1.5 ml/min), and for **60** and **61** (CH_2Cl_2/AcOEt 96:4, 1.5 ml/min); *Zorbax sil* 4.6 mm × 25 cm column for **68**–**71** (CH_2Cl_2/MeOH 99:1, 1.5 ml); retention times (t_R) for anal. HPLC in min. IR Spectra: 3% $CHCl_3$ soln. ^{1}H- and ^{13}C-NMR Spectra: at 400 (^{1}H) and 50 (^{13}C) MHz in $CDCl_3$ soln. CI-MS: with NH_3.

The diols **4** [41], **6** [42], **8** [43], **9** [43], **10** [44], **11** [45], and **12** [46], and the donors **1** [5], **2** [17], and **3** [19] were prepared according to the literature. Benzylation of methyl 3,4-*O*-isopropylidene-α-D-galactopyranoside [47] and subsequent hydrolysis of the isopropylidene acetal [48] led to **13** [48] [49]. ^{1}H-NMR spectra of the diols (10 mg, 0.035 mmol) in $CDCl_3$ soln. were recorded at 243, 263, 283, 298, and 318 K and in (D_6)DMSO soln. at 298, 308, 328, and 348 K. ^{1}H-NMR data of **4**–**13**: *Tables 2* and *6*.

Table 6. *Selected ^{1}H-NMR* (400 MHz) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Diols* **4**–**15** *in $CDCl_3$ Solution at Room Temperature*

	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**11**[a])
H–C(1)	4.97	4.80	4.47	4.34	4.88	4.22	4.82	4.74	4.57
H–C(2)	3.65	3.62	3.55	3.50	3.93[b])	3.74	[c])	4.01	3.70–3.62
H–C(3)	3.97	3.93	3.84	3.83	3.88[b])	3.71	[c])	4.05	3.70–3.62
H–C(4)	3.52	3.75	3.58	3.56	4.21	4.21	[c])	3.91	3.81
H–C(5)	3.86	3.81	3.47	3.48	3.65	3.49	[c])	3.81	3.53
H–C(6)	4.29	4.30	4.36	4.37	4.23	4.36	[c])	4.28[d])	4.13
H′–C(6)	3.74	3.50	3.80	3.80	4.03	4.09	[c])	3.84	3.71
MeO	–	3.46	–	3.59	3.40	3.59	3.37	3.40	3.30
PhC*H*	5.54	5.54	5.55	5.55	5.50	5.56	–	5.56	5.58
J(1,2)	4.0	3.9	7.7	7.8	3.0	7.4	1.5	0.9	0
J(2,3)	9.2	9.2	9.1	9.1	9.8	9.7	[e])	3.5	3.2[f])
J(3,4)	9.2	9.2	9.1	9.1	3.0	3.6	[e])	9.3	9.4
J(4,5)	9.7	9.7	9.4	9.2	1.6	0.9	[e])	9.2	10.0
J(5,6)	4.8	4.4	5.0	4.9	1.4	1.4	[e])	[e])	4.8
J(5,6′)	10.4	10.4	10.5	10.5	1.7	1.9	[e])	[e])	10.0
J(6,6′)	10.2	9.7	10.2	10.2	12.5	12.5	[e])	[e])	10.0

	12	**12**[a])	**13**	**13**[a])	**14**	**14**[a])	**15**
H–C(1)	4.51	4.45	4.73	4.70	4.68	4.46	4.81
H–C(2)	4.13	3.74	3.75	3.54	4.03	3.66	3.95
H–C(3)	3.84	3.57	3.97	3.72–3.67	4.12	3.84	4.29
H–C(4)	3.91	3.71	4.08	3.72–3.67	3.98	3.87	4.40–4.35
H–C(5)	3.38	3.27[g])	3.92	3.76	4.22	4.04	4.40–4.35
H–C(6)	4.36	4.17	3.76	3.56	4.34	4.19	4.38
H′–C(6)	3.87	3.72	3.72	3.49	3.84	3.68	3.84

Table 6 (cont.)

	12	**12**[a])	**13**	**13**[a])	**14**	**14**[a])	**15**
MeO	3.59	3.39	3.26	3.30	3.46	3.25	3.59
PhC*H*	5.58	5.55	–	–	5.64	5.65	5.64
J(1,2)	1.2	0	3.5	3.5	0.5	0	1.2
J(2,3)	[e])	3.2	9.7	9.0	3.0	4.2	3.4
J(3,4)	9.5	9.8	3.2	[e])	3.0	2.9	1.7
J(4,5)	9.5	9.5	≈ 1.2	< 1.5	9.8	9.6	[e])
J(5,6)	4.9	4.9	5.0	4.6	5.1	5.2	4.1
J(5,6′)	10.2	10.1	5.6	7.1	10.2	10.0	10.2
J(6,6′)	10.4	10.1	10.2	10.2	10.2	10.0	10.3

[a]) In (D_6)DMSO.
[b]) Assignments may be reversed.
[c]) Overlapping signals at 3.82–3.69 ppm.
[d]) Complex signal due to virtual coupling.
[e]) Not determined.
[f]) From a spectrum recorded at 308 K.
[g]) $^4J(5, OH) = 0.5$ Hz.

General Procedure for the Glycosidation with **1**. a) *Under Thermal Conditions*. Under Ar, solid **1** was added to a soln. of the diol in the indicated dry solvent, and the mixture was stirred at the indicated temp. for the given period of time. For glycosidations in toluene, the diols were dissolved at higher temp. and **1** added at that temp. After **1** had disappeared, the mixture was diluted with CH_2Cl_2, evaporated at or below 40° under vacuum, and purified as described below.

b) *Under Photolytic Conditions*. Under Ar, a soln. of the diol in the indicated solvent was added to solid **1** at the indicated temp. The mixture was stirred and irradiated (*HPK-125-Philips* high-pressure Hg lamp, *Solidex* glass filter) at the indicated temp. After disappearance of **1**, evaporation of the solvent gave the crude product.

Glycosidation of **4** *with* **1**. A mixture of **4** (73 mg, 0.24 mmol) and **1** (100 mg, 0.18 mmol) in $ClCH_2CH_2Cl$ (2 ml) was kept for 5 h at 22°. Evaporation and FC (hexane/AcOEt 85:15) gave **16**/**17**/**20**/**21** (113 mg, 75%). A soln. of this mixture in Ac_2O (2 ml) and pyridine (2 ml) was kept overnight at r.t., diluted with MeOH, and evaporated. FC (hexane/AcOEt 9:1) afforded **18**/**19**/**22**/**23** (112 mg, 99%). Prep. HPLC (hexane/AcOEt 85:15, 16 ml/min) gave **18** (35.3 mg, 30%), **19** (22.5 mg, 19%), **22** (25.7 mg, 22%), and **23** (23.5 mg, 20%).

For analogous reactions of **4** with **1** in various solvents at different temp., see *Table 3*.

*Allyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranoside* (**18**). R_f (hexane/AcOEt 7:3) 0.35. Anal. HPLC: t_R 10.17. $[\alpha]_D^{25} = +72.4$ ($c = 0.5$, $CHCl_3$). IR: 3090*w* (sh), 3070*w*, 3040*m* (sh), 3010*m*, 2930*m* (br.), 2870*m*, 2820*w* (sh), 1950*w* (br.), 1875*w* (br.), 1810*w* (sh), 1755*s*, 1650*w* (br.), 1610*w*, 1590*w*, 1540*w*, 1500*m*, 1465*m* (sh), 1455*s*, 1415*w* (sh), 1370*s*, 1330*w* (sh), 1315*w*, 1285*w* (sh), 1240*s*, 1200*w* (sh), 1185*s* (sh), 1150*s* (sh), 1100*s* (sh), 1075*s* (sh), 1055*s* (sh), 1030*s* (sh), 1000*m* (sh), 980*m* (sh), 940*m*, 920*m* (sh), 890*w* (sh), 860*w* (sh), 700*s*, 660*w*, 610*w*. ^{1}H-NMR: 7.46–7.43 (*m*, 2 arom. H); 7.38–7.23 (*m*, 21 arom. H); 7.14–7.11 (*m*, 2 arom. H); 5.90 (*dddd*, $J = 5.5$, 6.3, 10.3, 17.2, C*H*=CH$_2$); 5.62 (*t*, $J = 9.7$, H–C(3)); 5.45 (*s*, PhC*H*); 5.32 (*qd*, $J = 1.5$, 17.2, CH=C*H*$_2$); 5.14 (*qd*, $J = 1.5$, 10.3, CH=C*H*$_2$); 5.09 (*d*, $J = 3.6$, H–C(1)); 4.93 (*d*, $J = 11.0$, PhC*H*); 4.92 (*d*, $J \approx 3$, H–C(1′)); 4.83 (*d*, $J = 12.2$, PhC*H*); 4.80 (*d*, $J = 11.1$, PhC*H*); 4.75 (*d*, $J = 11.9$, PhC*H*); 4.68 (*d*, $J = 12.0$, PhC*H*); 4.58 (*d*, $J = 12.1$, PhC*H*); 4.47 (*d*, $J = 10.6$, PhC*H*); 4.465 (*d*, $J = 12.3$, PhC*H*); 4.28 (*dd*, $J = 4.9$, 10.2, H$_{eq}$–C(6)); 4.19 (*tdd*, $J = 1.4$, 5.3, 12.9, 1 allyl. H); 4.04 (*tdd*, $J = 1.1$, 6.4, 12.9, 1 allyl. H); 3.97 (*dt*, $J = 4.9$, 9.9, H–C(5)); 3.96 (*d*, $J = 9.3$, H–C(3′)); 3.88 (*dt*, $J = 2.4$, 9.8, H–C(5′)); 3.78 (*dd*, $J = 3.7$, 9.7, H–C(2)); 3.72 (*t*, $J = 10.3$, H$_{ax}$–C(6)); 3.71 (*dd*, $J = 2.4$, 10.7, H′–C(6)); 3.65 (*dd*, $J = 9.2$, 9.8, H–C(4′)); 3.61 (*dd*, $J = 1.9$, 10.7, H′–C(6′)); 3.55 (*dd*, $J = 3.4$, 9.7, H–C(2′)); 3.53 (*t*, $J = 9.6$, H–C(4)); 2.02 (*s*, Ac). ^{13}C-NMR: 169.55 (*s*); 138.60 (*s*); 138.41 (*s*); 138.19 (*s*); 137.80 (*s*); 136.98 (*s*); 133.48 (*d*); 128.89–126.08 (*m*); 118.12 (*t*); 101.37 (*d*); 96.62 (*d*); 95.79 (*d*); 81.55 (*d*); 79.55 (*d*); 79.29 (*d*); 77.27 (*d*); 75.57 (*d*); 75.47 (*t*); 74.68 (*t*); 73.33 (*t*); 72.82 (*t*); 70.86 (*d*); 70.05 (*d*); 68.86 (*t*); 68.71 (*t*); 68.11 (*t*); 62.44 (*d*); 20.98 (*q*). CI-MS: 892 (21), 891 (60), 890 (100, $[M + NH_4]^+$), 108 (9), 91 (20). Anal. calc. for $C_{52}H_{56}O_{12}$ (873.02): C 71.54, H 6.47; found: C 71.42, H 6.44.

Allyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**19**). R_f (hexane/AcOEt 7:3) 0.37. M.p. 113.5–114° (hexane/AcOEt). Anal. HPLC: t_R 8.54. $[\alpha]_D^{25} = +49.8$ ($c = 0.5$, $CHCl_3$). IR: 3090*w* (sh), 3060*w* (sh), 3030*w* (sh), 3000*w*, 2980*w* (sh), 2930*w* (br.), 2910*w* (br.), 2870*w*, 1750*m*, 1500*m*, 1470*w* (sh), 1455*w*, 1385*w* (sh), 1370*m*, 1310*w*, 1240*m*, 1220*w*, 1200*w* (sh), 1180*w* (sh), 1150*m* (sh), 1100*s* (sh), 1085*s* (sh), 1070*s*, 1045*s* (sh), 1040*s* (sh), 1030*s* (sh), 1000*m* (sh), 935*w* (br.), 915*w* (br.), 700*s*, 670*w* (br.). ^{1}H-NMR: 7.46–7.43 (*m*, 2 arom. H); 7.37–7.25 (*m*, 21 arom. H); 7.18–7.16 (*m*, 2 arom. H); 5.94 (*tdd*, $J = 5.4$, 10.6, 17.2, C*H*=CH$_2$); 5.69 (*t*, $J = 9.8$, H–C(3)); 5.48 (*s*, PhC*H*); 5.35 (*qd*, $J = 1.7$, 17.2, CH=C*H*$_2$); 5.18 (*d*, $J = 3.7$, H–C(1)); 5.15 (*qd*, $J = 1.4$, 10.5, CH=C*H*$_2$); 4.94 (*d*, $J = 10.9$, PhC*H*); 4.90 (*d*, $J = 11.6$, PhC*H*); 4.81 (*d*, $J = 11.3$, PhC*H*); 4.78 (*d*, $J = 11.3$, PhC*H*); 4.69 (*d*, $J = 11.6$, PhC*H*); 4.57 (*d*, $J = 12.1$, PhC*H*); 4.54 (*d*, $J = 11.1$, PhC*H*); 4.52 (*d*, $J = 7.6$, H–C(1′)); 4.51 (*d*, $J = 12.2$, PhC*H*); 4.30 (*dd*, $J = 4.9$, 10.2, H_{eq}–C(6)); 4.22 (*tdd*, $J = 1.5$, 5.3, 13.2, 1 allyl. H); 4.11 (*tdd*, $J = 1.5$, 5.6, 13.2, 1 allyl. H); 4.02 (*dt*, $J = 4.9$, 10.0, H–C(5)); 3.84 (*dd*, $J = 3.7$, 9.9, H–C(2)); 3.74 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.71 (*dd*, $J = 2.0$, 10.7, H–C(6′)); 3.65 (*dd*, $J = 4.7$, 10.7, H′–C(6)); 3.63 (*t*, $J \approx 8.8$, H–C(3′)); 3.56 (*t*, $J = 9.2$, H–C(4′)); 3.555 (*t*, $J = 9.7$, H–C(4)); 3.475 (*ddd*, $J \approx 2.0$, 4.5, 9.7, H–C(5′)); 3.47 (*dd*, $J = 7.9$, 8.8, H–C(2′)); 1.84 (*s*, Ac). ^{13}C-NMR: 169.79 (*s*); 138.41 (*s*); 138.34 (*s*); 137.93 (2*s*); 137.02 (*s*); 133.83 (*d*); 128.83–126.03 (*m*); 116.99 (*t*); 104.85 (*d*); 101.28 (*d*); 98.92 (*d*); 84.54 (*d*); 81.42 (*d*); 79.90 (*d*); 77.87 (*d*); 77.66 (*d*); 75.57 (*t*); 74.91 (*t*); 74.66 (*d*); 74.35 (*t*); 73.35 (*t*); 70.31 (*d*); 68.98 (2*t*); 62.39 (*d*); 20.67 (*q*). CI-MS: 892 (19), 891 (59), 890 (100, $[M + NH_4]^+$), 420 (8), 108 (6). Anal. calc. for $C_{52}H_{56}O_{12}$ (873.02): C 71.54, H 6.47; found: C 71.39, H 6.51.

Allyl 2-O-Acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside (**22**). R_f (hexane/AcOEt 7:3) 0.37. Anal. HPLC: t_R 7.00. $[\alpha]_D^{25} = +87.2$ ($c = 0.5$, $CHCl_3$). IR: 3060*w* (sh), 3030*w* (sh), 3000*w*, 2930*w* (br.), 2865*w*, 1745*m*, 1500*w*, 1465*w* (sh), 1455*m*, 1380*m* (sh), 1370*m*, 1330*w*, 1245*m*, 1160*m* (sh), 1145*m* (sh), 1100*s*, 1055*s*, 1030*s*, 1005*s* (sh) 970*w* (sh), 935*w*, 915*w*, 700*s*, 670*w*. ^{1}H-NMR: 7.43–7.21 (*m*, 19 arom. H); 7.20–7.00 (*m*, 4 arom. H); 6.98–6.96 (*m*, 2 arom. H); 5.87 (*dddd*, $J = 5.2$, 6.0, 10.5, 17.2, C*H*=CH$_2$); 5.59 (*d*, $J = 3.5$, H–C(1′)); 5.46 (*s*, PhC*H*); 5.31 (*qd*, $J = 1.5$, 17.2, CH=C*H*$_2$); 5.22 (*qd*, $J = 1.3$, 10.4, CH=C*H*$_2$); 5.15 (*d*, $J = 3.8$, H–C(1)); 4.96 (*d*, $J = 10.8$, PhC*H*); 4.92 (*dd*, $J = 3.8$, 9.9, H–C(2)); 4.82 (*d*, $J = 11.2$, PhC*H*); 4.74 (*d*, $J = 10.8$, PhC*H*); 4.63 (*d*, $J = 12.1$, PhC*H*); 4.56 (*d*, $J = 12.4$, PhC*H*); 4.50 (*t*, $J = 9.5$, H–C(3)); 4.48 (*d*, $J = 12.1$, PhC*H*); 4.45 (*d*, $J = 11.2$, PhC*H*); 4.36 (*d*, $J = 12.3$, PhC*H*); 4.26 (*dd*, $J = 4.8$, 10.9, H_{eq}–C(6)); 4.20 (*tdd*, $J = 1.5$, 5.1, 13.2, 1 allyl. H); 4.05 (*td*, $J = 2.4$, 10.2, H–C(5′)); 4.02 (*tdd*, $J = 1.3$, 6.1, 13.2, 1 allyl. H); 3.97 (*dt*, $J = 4.8$, 10.0, H–C(5)); 3.90 (*t*, $J = 9.3$, H–C(3′)); 3.86 (*t*, $J = 9.4$, H–C(4)); 3.75 (*t*, $J = 10.2$, H_{ax}–C(6)); 3.74 (*d*, $J = 2.3$, 2 H–C(6′)); 3.62 (*dd*, $J = 9.1$, 9.9, H–C(4′)); 3.47 (*dd*, $J = 3.5$, 9.7, H–C(2′)); 2.01 (*s*, Ac). ^{13}C-NMR: 169.83 (*s*); 138.52 (*s*); 138.33 (*s*); 137.69 (*s*); 137.52 (*s*); 136.66 (*s*); 133.14 (*d*); 129.06–126.04 (*m*); 117.47 (*t*); 101.77 (*d*); 95.76 (*d*); 95.26 (*d*); 82.37 (*d*); 81.11 (*d*); 78.41 (*d*); 76.79 (*d*); 75.30 (*t*); 74.44 (*t*); 73.18 (*t*); 71.87 (*d*); 70.90 (*t*); 70.28 (*d*); 70.04 (*d*); 68.69 (*t*); 68.27 (*t*); 68.11 (*t*); 61.83 (*d*); 20.55 (*q*). CI-MS: 892 (20), 891 (59), 890 (100, $[M + NH_4]^+$), 108 (6), 91 (15). Anal. calc. for $C_{52}H_{56}O_{12}$ (873.02): C 71.54, H 6.47; found: C 71.67, H 6.67.

Allyl 2-O-Acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**23**). R_f (hexane/AcOEt 7:3) 0.38. Anal. HPLC: t_R 6.24. M.p. 111–111.3° (hexane/AcOEt). $[\alpha]_D^{25} = +60$ ($c = 0.5$, $CHCl_3$). IR: 3065*w*, 3030*w* (sh), 3005*w*, 2920*w* (br.); 2870*w*, 1740*m*, 1500*w*, 1465*w* (sh), 1455*m*, 1400*w* (sh), 1380*m* (sh), 1370*m*, 1330*w*, 1310*w*, 1245*m*, 1170*m* (sh), 1150*m* (*sh*), 1115*m* (sh), 1100*s* (sh), 1070*s*, 1050*s* (sh), 1030*s* (sh), 1005*m* (sh), 965*w* (sh), 935*w*, 915*w*, 830*w* (br.), 720*w* (sh), 700*s*, 660*w* (br.). ^{1}H-NMR: 7.46–7.43 (*m*, 2 arom. H); 7.34–7.25 (*m*, 21 arom. H); 7.15–7.11 (*m*, 2 arom. H); 5.89 (*dddd*, $J = 5.3$, 6.1, 10.4, 17.2, C*H*=CH$_2$); 5.50 (*s*, PhC*H*); 5.32 (*qd*, $J = 1.5$, 17.2, CH=C*H*$_2$); 5.23 (*qd*, $J = 1.3$, 10.4, CH=C*H*$_2$); 5.14 (*d*, $J = 3.8$, H–C(1)); 4.93 (*dd*, $J = 3.8$, 9.7, H–C(2)); 4.88 (*d*, $J = 11.0$, PhC*H*); 4.86 (*d*, $J = 11.0$, PhC*H*); 4.75 (*d*, $J = 11.8$, 2 PhC*H*); 4.69 (*d*, $J = 7.8$, H–C(1′)); 4.66 (*d*, $J = 11.1$, PhC*H*); 4.51 (*d*, $J = 10.8$, PhC*H*); 4.46 (*d*, $J = 12.0$, PhC*H*); 4.43 (*d*, $J = 12.1$, PhC*H*); 4.425 (*t*, $J = 9.5$, H–C(3)); 4.25 (*dd*, $J = 4.7$, 10.2, H_{eq}–C(6)); 4.20 (*tdd*, $J = 1.4$, 5.2, 13.1, 1 allyl. H); 4.02 (*tdd*, $J = 1.2$, 6.2, 13.1, 1 allyl. H); 3.94 (*dt*, $J = 4.7$, 10.0, H–C(5)); 3.77 (*t*, $J = 9.3$, H–C(3)); 3.75 (*t*, $J = 10.2$, H_{ax}–C(6)); 3.62–3.53 (*m*, 2 H–C(6′)); 3.60 (*t*, $J = 8.9$, H–C(4′)); 3.55 (*t*, $J = 8.9$, H–C(3′)); 3.45 (*t*, $J \approx 8.3$, H–C(2′)); 3.27 (*ddd*, $J = 2.4$, 3.8, 9.3, H–C(5′)); 1.93 (*s*, Ac). ^{13}C-NMR: 170.13 (*s*); 138.49 (*s*); 138.25 (2*s*); 137.99 (*s*); 137.18 (*s*); 133.21 (*d*); 128.79–127.32 (*m*); 126.08 (*d*); 117.81 (*t*); 102.93 (*d*); 101.36 (*d*); 95.35 (*d*); 84.69 (*d*); 82.23 (*d*); 79.99 (*d*); 77.70 (*d*); 75.33 (*t*); 74.86 (*d*); 74.74 (*d* and 2*t*); 73.57 (*d*); 73.36 (*t*); 68.69 (*t*); 68.47 (*t*); 62.49 (*d*); 20.56 (*q*). CI-MS: 893 (11), 892 (13), 891 (37), 890 (100, $[M + NH_4]^+$). Anal. calc. for $C_{52}H_{56}O_{12}$ (873.02): C 71.54, H 6.47; found: C 71.62, H 6.27.

Glycosidation of **5** *with* **1**. Reaction of **1** (121.2 mg, 0.22 mmol) and **5** (56.4 mg, 0.2 mmol) in $ClCH_2CH_2Cl$ (4 ml) for 5 h at 24° and FC (hexane/AcOEt 2:1) gave 117.5 mg (73%) of **24/25/28/29** 23:28:17:32 (HPLC). Partial separation by another FC (hexane/AcOEt 4:1) afforded **24/25** (52.2 mg) and **28/29** (50.2 mg). These mixtures were 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 and H_2O, and

Table 7. *Selected ^{1}H-NMR* (400 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Disaccharides Derived from the Diols* **4–9**

	18[a])	**19**[a])	**22**[a])	**23**[a])	**26**	**27**[a])	**30**[a])	**31**
H–C(1)	5.09	5.18	5.15	5.14	4.91	5.05	5.00	4.99
H–C(2)	3.78	3.84	4.92	4.93	3.80	3.81	4.93	4.94
H–C(3)	5.62	5.69	4.50	4.25	5.62	5.65	4.47	4.39
H–C(4)	3.53	3.555	3.86	3.77	3.63	3.55	3.85	3.76
H–C(5)	3.97	4.02	3.97	3.94	3.92	3.95	3.91	3.88
H_{eq}–C(6)	4.28	4.30	4.26	4.25	4.30	4.31	4.28	4.26
H_{ax}–C(6)	3.72	3.74	3.75	3.75	3.73	3.74	3.77	3.755
MeO	–	–	–	–	3.44	3.44	3.40	3.41
PhC*H*	5.45	5.48	5.46	5.50	5.47	5.48	5.46	5.51
AcO	2.02	1.84	2.01	1.93	2.01	1.78	2.03	1.96
H–C(1′)	4.92	4.52	5.59	4.69	4.87	4.49	5.58	4.68
H–C(2′)	3.55	3.47	3.47	3.45	3.53	3.51	3.47	3.45
H–C(3′)	3.96	3.63	3.90	3.55	3.96	3.63	3.90	3.55
H–C(4′)	3.65	3.56	3.62	3.60	3.53	3.545	3.63	3.60
H–C(5′)	3.88	3.75	4.05	3.27	3.87	3.48	4.05	3.28
H–C(6′)	3.71	3.71	3.74	3.62–3.53	3.69	3.70	3.77–3.70	3.65–3.57
H′–C(6′)	3.61	3.65	3.74	3.62–3.53	3.62	3.63	3.77–3.70	3.65–3.57
J(1,2)	3.6	3.7	3.8	3.8	3.5	3.6	3.7	3.8
J(2,3)	9.7	9.8	9.9	9.7	9.8	9.8	9.8	9.6
J(3,4)	9.7	9.8	9.5	9.3	9.7	9.7	9.4	9.4
J(4,5)	9.9	10.0	10.0	10.0	9.5	9.9	9.7	9.8
J(1′,2′)	3.4	7.7	3.5	7.8	3.5	7.6	3.5	7.4
J(2′,3′)	9.7	8.8	9.7	8.8	9.6	8.9	9.7	8.6
J(3′,4′)	9.5	9.0	9.1	8.9	9.6	8.8	9.0	9.1
J(4′,5′)	9.8	9.2	9.9	9.3	9.7	9.8	9.8	9.2

	32[a])	**33**[a])	**34**[a])	**35**[a])	**38**	**39**	**42**[a])	**43**
H–C(1)	4.65	4.565	4.43	4.46	4.58	4.62	4.43	4.43
H–C(2)	3.68–3.61	3.65	3.67–3.58	3.64–3.51	3.82	3.90	5.14	5.14
H–C(3)	3.88	3.83	4.01[c])	3.90	5.43	5.39	4.18	4.13
H–C(4)	3.51	3.55	3.81	3.68	3.58	3.64–3.60	3.87	3.86
H–C(5)	3.42	3.41	3.49	3.42	3.55	3.49–3.44	3.51	3.55–3.40
H_{eq}–C(6)	4.34	4.33	4.33	4.31	4.37	4.38	4.35	4.31
H_{ax}–C(6)	3.77	3.77	3.79	3.78	3.77	3.79–3.70	3.80	3.74
MeO	–	–	–	–	3.50	3.50	3.51	3.49
PhC*H*	5.52	5.52	5.47	5.49	5.47	5.49	5.43	5.44
OH or AcO	3.14	3.32	2.58	3.31	2.01	1.94	2.03	1.93
H–C(1′)	5.41	4.76	5.45	4.72	5.55	4.73	5.58	4.64
H–C(2′)	3.62	3.52	3.51	3.64–3.51	3.57	3.64–3.60	3.45	3.55–3.40
H–C(3′)	3.99	3.72–3.65	3.99[c])	3.64–3.51	3.92	3.79–3.70	3.89	3.55–3.40
H–C(4′)	3.68–3.61	3.72–3.65	3.67–3.58	3.64–3.51	3.64	3.64–3.60	3.57	3.55–3.40
H–C(5′)	4.27	3.45	4.34–4.29	3.36–3.32	3.88	3.49–3.44	3.85–3.82	3.22
H–C(6′)	3.70	3.72–3.65	3.72	3.64–3.51	3.72–3.64	3.79–3.70	3.68	3.55–3.40
H′–C(6′)	3.68–3.61	3.72–3.65	3.67–3.58	3.64–3.51	3.72–3.64	3.79–3.70	3.68	3.55–3.40
J(1,2)	7.8	7.7	7.7	7.8	7.6	6.7	8.2	7.8
J(2,3)	9.0	8.7	8.6	9.1	9.4	7.8	9.4	8.5
J(3,4)	9.0	8.9	9.2	9.1	9.4	9.3	9.4	9.3
J(4,5)	9.7	9.8	9.9	9.4	9.4	[b])	9.3	9.3
J(OH,H)	3.3	2.6	3.4	2.8	–	–	–	–
J(1′,2′)	3.8	7.8	3.7	7.7	3.5	7.9	3.4	7.8
J(2′,3′)	9.4	9.1	9.6	[b])	8.9	[b])	9.8	[b])
J(3′,4′)	9.4	[b])	9.8	[b])	9.4	[b])	9.3	[b])
J(4′,5′)	10.1	9.8	[b])	[b])	9.8	[b])	9.8	9.2

Table 7 (cont.)

	44	**45**[a])	**46**[a])	**47**[a])	**52**	**53**	**54**	**55**
H–C(1)	4.94	5.15	4.95	4.90	4.54	4.50	4.37	4.38
H–C(2)	4.02	3.98	4.25	4.17	4.23	4.24	5.43	5.45
H–C(3)	4.12	4.17	3.99	4.04	4.95	4.95	3.85	3.88
H–C(4)	4.29	4.31	4.36	4.38	4.44	4.41	4.32	4.38
H–C(5)	3.73	3.74	3.69–3.60	3.63	3.51	3.52	3.37	3.37
H_{eq}–C(6)	4.29	4.30	4.29	4.24	4.34	4.35	4.35	4.28
H_{ax}–C(6)	4.10	4.10	4.09–4.05	3.97	4.07	4.06	4.05	3.90
MeO	3.43	3.43	3.43	3.45	3.54	3.54	3.52	3.50
PhC*H*	5.56	5.57	5.53	5.50	5.50	5.50	5.51	5.51
OH or AcO	3.02	2.60	2.75	2.80	2.00	1.91	2.05	1.90
H–C(1′)	4.91	4.59	5.18	4.85	5.62	4.73	5.10	4.57
H–C(2′)	3.61–3.50	3.65–3.56	3.63	3.58–3.48	3.59	3.45	3.57	3.46
H–C(3′)	4.06	3.65–3.56	4.07	3.58–3.48	3.91	3.59	3.92	3.61
H–C(4′)	3.52	3.65–3.56	3.57	3.66	3.66	3.65	3.58	3.47
H–C(5′)	4.25	3.44	4.14	3.58–3.48	4.05	3.48–3.43	3.88–3.83	3.52–3.50
H–C(6′)	3.61–3.50	3.72–3.64	3.69–3.60	3.72	3.75–3.67	3.78–3.70	3.69–3.60	3.74
H′–C(6′)	3.61–3.50	3.72–3.64	3.69–3.60	3.65	3.75–3.67	3.78–3.70	3.69–3.60	3.61
J(1,2)	3.3	3.4	3.8	3.6	7.8	7.7	8.0	8.1
J(2,3)	10.1	10.2	10.2	10.1	10.3	10.1	10.1	10.3
J(3,4)	3.7	3.8	3.2	3.1	3.7	3.5	3.5	3.5
J(4,5)	0.7	0.7	0	0	< 1	< 1	< 1	< 1
J(OH,H)	8.3	8.0	6.9	6.1	–	–	–	–
J(1′,2′)	3.8	7.3	3.7	7.8	3.6	7.8	3.4	7.8
J(2′,3′)	8.8	[b])	9.6	[b])	9.7	9.1	9.6	9.0
J(3′,4′)	8.8	[b])	9.3	9.0	9.0	9.1	9.2	9
J(4′,5′)	9.8	9.8	9.9	9.0	10.0	9.4	9.4	9

[a]) Assignments corroborated by selective irradiations. [b]) Not determined. [c]) Assignments may be interchanged.

Table 8. *Selected* ^{13}*C-NMR* (50.6 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of the Disaccharides Derived from the Diols* **4–9**

	4	**18**	**19**	**22**	**23**	**6**	**32**	**33**	**34**	**35**
C(1)	97.89	96.62	98.92	95.76	95.35	102.09	102.02	101.00	102.71	101.24
C(2)	72.71	75.57	77.66[a])	70.04[a])	73.57	74.35	80.69	81.86	72.91	74.30[a])
C(3)	71.51	70.86	70.31	71.87	74.86[a])	73.06	72.24	73.49	77.00	81.65
C(4)	80.90	79.29[a])	79.90	81.11	79.99	80.44	80.34	79.86	81.27[a])	78.63
C(5)	62.54	62.44	62.39	61.83	62.49	66.27	65.77	65.94	66.17	66.58
C(6)	68.77[a])	68.71[b])	68.98	68.69[b])	68.69[b])	68.58	68.59[a])	68.59	68.71[b])	68.52[b])
AllO	68.81[a]),	68.86[b]),	68.98,	68.27[b]),	68.47[b]),	70.52,	70.30,	70.11,	70.48,	70.26,
	133.33,	133.48,	133.83,	133.14,	133.21,	133.48,	133.64,	133.82,	133.47,	133.49,
	118.18	118.12	116.99	117.47	117.81	118.21	117.24	116.82	117.89	117.72
PhC*H*	101.81	101.37	101.28	101.77	101.36	101.78	101.66	101.57	101.92	101.88
AcO	–	169.55,	169.79,	169.83,	170.13,	–	–	–	–	–
		20.98	20.67	20.55	20.56					
C(1′)	–	95.79	104.85	95.26	102.93	–	96.99	103.31	96.36	102.99
C(2′)	–	79.55[a])	81.42	78.41	82.23	–	79.44	83.16	78.71	82.13
C(3′)	–	81.55	84.54	82.37	84.69	–	81.62	84.98	81.51[a])	84.95
C(4′)	–	77.27	77.87[a])	76.79	77.70	–	77.63	77.78	77.44	77.75
C(5′)	–	70.05	74.66	70.28[a])	74.74[a])	–	70.48	74.83	69.96	74.78[a])
C(6′)	–	68.11[b])	68.98	68.11[b])	68.69[b])	–	68.47[a])	68.59	68.41[b])	68.60[b])

Table 8 (cont.)

	5 [50]	**26**	**27**	**30**	**31**	**7** [50]	**38**	**39**	**42**	**43**
C(1)	99.9	97.66	100.41	97.44	97.31	104.2	104.94	102.80	102.55	102.52[a])
C(2)	72.4	74.73	77.62[a])	72.15	74.78	74.2	74.32	77.64[a])	71.63	73.13
C(3)	70.5	69.89	70.10	70.46[a])	73.78	72.9	71.79	73.33	73.27	77.84[b])
C(4)	80.8	79.27[a])	79.87	81.35	79.95	80.3	79.36[a])	78.61	81.21	79.67
C(5)	62.0	62.33	62.12	61.85	62.37	65.9	66.12	65.51	66.00	66.52
C(6)	68.5	68.94[b])	69.08[b])	69.00[b])	68.81	68.3	68.64[b])	68.88[b])	68.75[a])	68.86[c])
MeO	54.9	55.26	55.40	55.23	55.22	56.8	57.05	56.68	56.98	56.83
PhCH	101.5	101.46	101.31	102.04	101.45	101.5	101.34	101.29	101.92	101.35
AcO	–	169.55, 20.98	169.82, 20.61	170.17, 20.87	170.27, 20.69	–	169.52, 20.92	169.69, 20.85	169.22, 20.90	169.20, 20.83
C(1′)	–	95.94	105.09	95.99	102.98	–	95.65	102.80	95.94	102.17[a])
C(2′)	–	79.51[a])	81.50	78.64	82.28	–	79.11[a])	82.01	78.60	82.25
C(3′)	–	81.52	84.61	82.63	84.78	–	81.43	84.81	82.09	84.71
C(4′)	–	77.30	78.58[a])	77.23	77.83	–	77.44	78.15[a])	77.14	77.90[b])
C(5′)	–	70.01	74.66	70.30[a])	74.78	–	70.76	75.00	70.47	74.66
C(6′)	–	68.20[b])	68.99[b])	68.39[b])	68.81	–	68.49[b])	68.79[b])	68.35[a])	68.69[c])

	8[d])	**44**	**45**	**46**	**47**	**9** [50]	**52**	**53**	**54**	**55**
C(1)	100.21	98.66	100.24	100.23	100.24	104.2	104.43	102.37	101.74	101.72
C(2)	69.58[a])	76.37	77.61	67.09	67.99	72.8[a])	73.38[a])	74.64[a])	69.27	69.91
C(3)	69.51[a])	67.38	67.62	73.11	77.46	71.2[a])	70.49	73.46[a])	71.53	77.81
C(4)	75.89	75.96	76.15	73.96	76.45	76.0	73.13[a])	73.92[a])	73.37	76.04
C(5)	62.65	62.54	62.19	62.52	62.96	66.8	66.12	66.00	66.43	66.68
C(6)	69.23	69.25	69.28	69.36	69.18	69.3	68.91[b])	68.98[b])	69.15	69.52
MeO	55.58	55.54	55.60	55.50	55.43	57.2	56.61	55.84	55.98	55.82
PhCH	101.15	101.16	101.03	100.86	100.51	101.5	101.05	101.08	101.18	100.86
AcO	–	–	–	–	–	–	170.58, 20.99	170.70, 20.85	169.36, 20.96	169.51, 20.86
C(1′)	–	96.38	105.27	93.65	103.95	–	95.76	103.14	93.17	104.93
C(2′)	–	79.67	81.91	79.47	81.97	–	79.48	82.27	79.25	80.66
C(3′)	–	81.91	84.64	81.68	84.77	–	81.67	84.93	81.41	84.60
C(4′)	–	77.93	79.57	77.63	77.91	–	77.62	77.76	77.17	77.81
C(5′)	–	70.28	74.59	70.33	74.61	–	70.58	74.97[a])	70.52	74.61
C(6′)	–	68.45	68.93	68.66	69.13	–	68.44[b])	68.79[b])	68.50	68.86

[a])[b])[c]) Assignments may be reversed.
[d]) Assignments based upon a $^1H,^{13}C$ inverse-correlated spectrum.

processing of the org. layer as usual afforded **26**/**27** (54.1 mg, 98%) and **30**/**31** (52.3 mg, 99%), resp. FC (CH_2Cl_2/AcOEt 98:2) gave **26** (22.5 mg), **27** (29.7 mg) and FC (hexane/AcOEt 5:1) **30** (18.2 mg) and **31** (33.8 mg).

For analogous reactions under different conditions, see *Table 3*.

Methyl-3-O-Acetyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside (**26**). R_f (hexane/AcOEt 2:1) 0.46. $[\alpha]_D^{25} = +56.3$ ($c = 1.00$, $CHCl_3$). IR: 3060*w*, 3005*w*, 2930*w*, 2870*w*, 1755*m*, 1495*w*, 1455*m*, 1368*m*, 1310*w*, 1240*m*, 1145*s*, 1100*s*, 1085*s*, 1075*s*, 1055*s*, 1030*s*, 1000*s*, 915*w*, 875*w*, 700*s*, 660*w*. ^1H-NMR: 7.46–7.11 (*m*, 25 arom. H); 5.62 (*t*, $J = 9.7$, H–C(3)); 5.47 (*s*, PhC*H*); 4.96 (*d*, $J = 10.9$, PhC*H*); 4.91 (*d*, $J = 3.5$, H–C(1)); 4.87 (*d*, $J = 3.4$, H–C(1′)); 4.83 (*d*, $J = 10.9$, PhC*H*); 4.80 (*d*, $J = 10.8$, PhC*H*); 4.79 (*d*, $J = 12.1$, PhC*H*); 4.66 (*d*, $J = 12.0$, PhC*H*); 4.58 (*d*, $J = 12.1$, PhC*H*); 4.47 (*d*, $J = 10.5$, PhC*H*); 4.465 (*d*, $J = 12.2$, PhC*H*); 4.30 (*dd*, $J = 4.9$, 10.2, H_{eq}–C(6)); 3.96 (*t*, $J = 9.3$, H–C(3′)); 3.92 (*dt*, $J = 4.7$, 10.0, H–C(5)); 3.87 (*td*, $J \approx 3.0$, 9.8, H–C(5′)); 3.80 (*dd*, $J = 3.6$, 9.8, H–C(2)); 3.73 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.69 (*dd*, $J = 3.4$, 10.6, H–C(6′)); 3.63 (*t*, $J = 9.6$, H–C(4)); 3.62 (*dd*, $J = 2.0$, 10.6, H′–C(6′)); 3.53 (*t*, $J = 9.6$, H–C(4′)); 3.53 (*dd*, $J = 3.5$, 9.6, H–C(2′)); 3.44 (*s*, MeO); 2.01 (*s*, Ac). ^{13}C-NMR: 169.55 (*s*); 138.66 (*s*); 138.44 (*s*); 138.32 (*s*); 137.85 (*s*); 137.00 (*s*); 128.96–126.13 (*m*); 101.46 (*d*); 97.66 (*d*); 95.94 (*d*); 81.52 (*d*); 79.51 (*d*); 79.27 (*d*); 77.30 (*d*); 75.55

(*t*); 74.73 (*d* and *t*); 73.36 (*t*); 73.01 (*t*); 70.01 (*d*); 69.89 (*d*); 68.94 (*t*); 68.20 (*t*); 62.33 (*d*); 55.26 (*q*); 20.98 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 70.64, H 6.69.

Methyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**27**). R_f (hexane/AcOEt 2:1) 0.53. M.p. 168–169°. $[\alpha]_D^{25} = +41.4$ ($c = 2.12$, $CHCl_3$). IR: 3060*w*, 3005*m*, 2930*m*, 2870*m*, 1752*s*, 1495*m*, 1455*s*, 1368*s*, 1305*w*, 1238*s*, 1180*m*, 1148*s*, 1100*s* (sh), 1070*s*, 1030*s*, 995*s*, 915*w*, 700*s*. ^{1}H-NMR: 7.45–7.16 (*m*, 25 arom. H); 5.65 (*t*, $J = 9.8$, H–C(3)); 5.48 (*s*, PhC*H*); 5.05 (*d*, $J = 3.6$, H–C(1)); 4.91 (*d*, $J = 11.0$, PhC*H*); 4.89 (*d*, $J = 11.6$, PhC*H*); 4.80 (*d*, $J = 11.4$, PhC*H*); 4.78 (*d*, $J = 11.3$, PhC*H*); 4.68 (*d*, $J = 11.7$, PhC*H*); 4.57 (*d*, $J = 12.1$, PhC*H*); 4.53 (*d*, $J = 10.9$, PhC*H*); 4.52 (*d*, $J = 11.3$, PhC*H*); 4.49 (*d*, $J = 7.6$, H–C(1′)); 4.31 (*dd*, $J = 4.9$, 10.2, H_{eq}–C(6)); 3.95 (*dt*, $J = 4.8$, 10.0, H–C(5)); 3.81 (*dd*, $J = 3.6$, 9.9, H–C(2)); 3.74 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.70 (*dd*, $J = 1.7$, 10.3, H–C(6′)); 3.63 (*t*, $J = 8.8$, H–C(3′)); 3.63 (*dd*, $J = 5.3$, 10.3, H′–C(6′)); 3.55 (*t*, $J = 9.6$, H–C(4)); 3.545 (*t*, $J \approx 9.4$, H–C(4′)); 3.51 (*dd*, $J = 7.8$, 8.9, H–C(2′)); 3.48 (*ddd*, $J = 1.9$, 5.2, 9.8, H–C(5′)); 3.44 (*s*, MeO); 1.78 (*s*, Ac). ^{13}C-NMR: 169.82 (*s*); 138.45 (*s*); 138.39 (*s*); 137.89 (2*s*); 137.01 (*s*); 128.85–126.04 (*m*); 105.09 (*d*); 101.31 (*d*); 100.41 (*d*); 84.61 (*d*); 81.50 (*d*); 79.87 (*d*); 78.58 (*d*); 77.62 (*d*); 75.56 (*t*); 74.91 (*t*); 74.66 (*d*); 74.42 (*t*); 73.36 (*t*); 70.10 (*d*); 69.08 (*t*); 68.99 (*t*); 62.12 (*d*); 55.40 (*q*); 20.61 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 70.67, H 6.32.

Methyl 2-O-Acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside (**30**) [34]. R_f (CH_2Cl_2/AcOEt 98:2) 0.44. $[\alpha]_D^{25} = +76.5$ ($c = 1.15$, $CHCl_3$). IR: 3070*w*, 3030*w* (sh), 3005*m*, 2935*m*, 2870*m*, 1745*s*, 1498*m*, 1465*w* (sh), 1455*m*, 1370*m*, 1330*w*, 1315*w*, 1280*w* (sh), 1245*s*, 1195*w*, 1160*s* (sh), 1145*s* (sh), 1128*s* (sh), 1098*s*, 1060*s*, 1030*s*, 995*s*, 965*w* (sh), 935*w*, 915*w*, 700*s*, 663*w*. ^{1}H-NMR: 7.40–6.97 (*m*, 25 arom. H); 5.58 (*d*, $J = 3.5$, H–C(1′)); 5.46 (*s*, PhC*H*); 5.00 (*d*, $J = 3.7$, H–C(1)); 4.96 (*d*, $J = 10.7$, PhC*H*); 4.93 (*dd*, $J = 3.6$, 9.8, H–C(2)); 4.82 (*d*, $J = 11.2$, PhC*H*); 4.74 (*d*, $J = 10.9$, PhC*H*); 4.63 (*d*, $J = 12.1$, PhC*H*); 4.56 (*d*, $J = 12.3$, PhC*H*); 4.48 (*d*, $J = 12.1$, PhC*H*); 4.47 (*t*, $J \approx 9.4$, H–C(3)); 4.45 (*d*, $J = 11.6$, PhC*H*); 4.36 (*d*, $J = 12.3$, PhC*H*); 4.28 (*dd*, $J = 4.4$, 10.1, H_{eq}–C(6)); 4.05 (*td*, $J = 2.5$, 10.0, H–C(5′)); 3.91 (*dt*, $J = 4.8$, 9.7, H–C(5)); 3.90 (*t*, $J \approx 9.2$, H–C(3′)); 3.85 (*t*, $J \approx 9.4$, H–C(4)); 3.77 (*t*, $J = 10.0$, H_{ax}–C(6)); 3.77–3.70 (*m*, 2 H–C(6′)); 3.63 (*dd*, $J = 9.0$, 9.9, H–C(4′)); 3.47 (*dd*, $J = 3.5$, 9.7, H–C(2′)); 3.40 (*s*, MeO); 2.03 (*s*, Ac). ^{13}C-NMR: 170.17 (*s*); 138.76 (*s*); 138.59 (*s*); 137.93 (*s*); 137.76 (*s*); 136.90 (*s*); 129.33–126.30 (*m*); 102.04 (*d*); 97.44 (*d*); 95.99 (*d*); 82.63 (*d*); 81.35 (*d*); 78.64 (*d*); 77.23 (*d*); 75.56 (*t*); 74.69 (*t*); 73.46 (*t*); 72.15 (*d*); 71.17 (*t*); 70.46 (*d*); 70.30 (*d*); 69.00 (*t*); 68.39 (*t*); 61.85 (*d*); 55.23 (*q*); 20.87 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 70.62, H 6.19.

Methyl 2-O-Acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**31**) [34]. R_f (CH_2Cl_2/AcOEt 98:2) 0.36. M.p. 127–128°. $[\alpha]_D^{25} = +49.5$ ($c = 2.03$, $CHCl_3$). IR: 3060*w*, 3010*m*, 2935*m*, 2920*m* (sh), 2870*m*, 1740*s*, 1495*w*, 1455*m*, 1370*s*,1330*w*, 1310*w*, 1280*w*, 1240*s*, 1150*s* (sh), 1120*s* (sh), 1095*s*, 1070*s*, 1060*s* (sh), 1030*s*, 1000*s*, 965*w* (sh), 935*w*, 915*w*, 700*s*, 660*w*. ^{1}H-NMR: 7.46–7.12 (*m*, 25 arom. H); 5.51 (*s*, PhC*H*); 4.99 (*d*, $J = 3.8$, H–C(1)); 4.94 (*dd*, $J = 3.8$, 9.6, H–C(2)); 4.87 (*d*, $J = 11.0$, PhC*H*); 4.86 (*d*, $J = 11.0$, PhC*H*); 4.75 (*d*, $J = 10.9$, 2 PhC*H*); 4.68 (*d*, $J \approx 7.4$, H–C(1′)); 4.66 (*d*, $J = 10.6$, PhC*H*); 4.51 (*d*, $J = 10.9$, PhC*H*); 4.45 (*s*, $PhCH_2$); 4.39 (*t*, $J = 9.4$, H–C(3)); 4.26 (*dd*, $J = 4.5$, 10.1, H_{eq}–C(6)); 3.88 (*dt*, $J = 4,5$, 10.1, H–C(5)); 3.76 (*t*, $J = 9.5$, H–C(4)); 3.755 (*t*, $J = 10.2$, H_{ax}–C(6)); 3.65–3.57 (*m*, 2 H–C(6′)); 3.60 (*t*, $J = 9.2$, H–C(4′)); 3.55 (*t*, $J = 9.1$, H–C(3′)); 3.45 (*t*, $J \approx 8.0$, H–C(2′)); 3.41 (*s*, MeO); 3.28 (*ddd*, $J = 2.1$, 4.0, 9.1, H–C(5′)); 1.96 (*s*, Ac). ^{13}C-NMR: 170.27 (*s*); 138.57 (*s*); 138.34 (2*s*); 138.09 (*s*); 137.26 (*s*); 128.84–126.16 (*m*); 102.98 (*d*); 101.45 (*d*); 97.31 (*d*); 84.78 (*d*); 82.28 (*d*); 79.95 (*d*); 77.83 (*d*); 75.39 (*t*); 74.78 (2*d* and 2*t*); 73.78 (*d*); 73.45 (*t*); 68.81 (2*t*); 62.37 (*d*); 55.22 (*q*); 20.69 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 70.67, H 6.22.

Glycosidation of **6** *with* **1**. A soln. of **6** (73 mg, 0.24 mmol) and **1** (100 mg, 0.18 mmol) in $ClCH_2CH_2Cl$ (3 ml) was kept for 5 h at 22°. Evaporation and FC (hexane/AcOEt 4:1) gave **32**–**35** (121 mg, 80%). Prep. HPLC (hexane/AcOEt 4:1, 16 ml/min) of the mixture afforded **32** (26 mg, 17%), **33** (31.9 mg, 21%), **34** (24.8 mg, 16%), and **35** (35.4 mg, 23%).

For analogous reactions of **6** with **1** in various solvents at different temp., see *Table 3*.

Allyl 4,6-O-Benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-glucopyranoside (**32**). R_f (hexane/AcOEt 7:3) 0.41. Anal. HPLC: t_R 6.44. M.p. 172.5–173° (hexane/AcOEt). $[\alpha]_D^{25} = +44$ ($c = 0.5$, $CHCl_3$). IR: 3600*w*, 3540–3360*w* (br.), 3080*w* (sh), 3060*w* (sh), 3030*w* (sh), 3000*w*, 2980*w* (sh), 2950*w* (sh), 2870*w*, 1600*w*, 1495*w*, 1460*w* (sh), 1455*m*, 1405*w*, 1380*w* (sh), 1360*w*, 1310*w* (br.), 1200*w* (sh), 1165*m*, 1145*m* (sh), 1100*s*, 1085*s* (sh), 1070*s* (sh), 1045*s* (sh), 1030*s* (sh), 1015*s* (sh), 995*m* (sh), 930*w*, 915*w* (sh), 715*w* (sh), 700*s*, 670*w* (br.). ^{1}H-NMR: 7.50–7.47 (*m*, 2 arom. H); 7.40–7.22 (*m*, 21 arom. H); 7.14–7.12 (*m*, 2 arom. H); 5.88 (*dddd*, $J = 5.0$, 6.1, 10.6, 17.3, $CH{=}CH_2$); 5.52 (*s*, PhC*H*); 5.41 (*d*, $J = 3.8$, H–C(1′)); 5.29 (*qd*, $J = 1.6$, 17.3, $CH{=}CH_2$); 5.15 (*qd*, $J = 1.4$, 10.5, $CH{=}CH_2$); 4.98 (*d*, $J = 10.9$, PhC*H*); 4.81 (*d*, $J = 10.8$, 2 PhC*H*); 4.77 (*d*, $J = 12.0$, PhC*H*); 4.66 (*d*, $J = 1.1$, PhC*H*); 4.65 (*d*, $J = 7.8$, H–C(1)); 4.61 (*d*, $J = 12.1$, PhC*H*); 4.49 (*d*, $J = 10.0$, PhC*H*); 4.46 (*d*, $J = 11.8$, PhC*H*);

4.37 (*tdd*, J = 1.6, 4.9, 12.8, 1 allyl. H); 4.34 (*dd*, J = 5.0, 10.2, H_{eq}–C(6)); 4.27 (*ddd*, J = 2.2, 3.5, 10.1, H–C(5′)); 4.10 (*tdd*, J = 1.3, 6.1, 12.8, 1 allyl. H); 3.99 (*t*, $J \approx 9.4$, H–C(3′)); 3.88 (*dt*, J = 3.2, 9.0, addn. of $D_2O \rightarrow t$, J = 9.0, H–C(3)); 3.77 (*t*, J = 10.2, H_{ax}–C(6)); 3.70 (*dd*, J = 3.8, 10.6, H–C(6′)); 3.68–3.61 (*m*, H–C(2), H–C(4′), H′–C(6′)); 3.62 (*dd*, J = 3.9, 9.4, H–C(2′)); 3.51 (*t*, J = 9.3, H–C(4)); 3.42 (*dt*, J = 4.9, 9.7, H–C(5)); 3.14 (*d*, J = 3.3, exchange with D_2O, OH–C(3)). ^{13}C-NMR: 138.74 (*s*); 138.21 (*s*); 138.04 (*s*); 137.80 (*s*); 137.03 (*s*); 133.64 (*d*); 129.05 (*d*); 128.43–127.42 (*m*); 126.20 (*d*); 117.24 (*t*); 102.02 (*d*); 101.66 (*d*); 96.99 (*d*); 81.62 (*s*); 80.69 (*d*); 80.34 (*d*); 79.44 (*d*); 77.63 (*d*); 75.50 (*t*); 74.89 (*t*); 73.42 (*t*); 72.45 (*t*); 72.24 (*d*); 70.48 (*d*); 70.30 (*t*); 68.59 (*t*); 68.47 (*t*); 65.77 (*d*). CI-MS: 850 (17), 849 (55), 848 (100, $[M + NH_4]^+$), 431 (10), 420 (11), 415 (12), 325 (15), 324 (24), 309 (11), 307 (12), 253 (20); 217 (13), 216 (14), 187 (14), 181 (14), 108 (26), 91 (77). Anal. calc. for $C_{50}H_{54}O_{11}$ (830.98): C 72.27, H 6.55; found: C 72.28, H 6.47.

*Allyl 4,6-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**33**). R_f (hexane/AcOEt 7:3) 0.31. Anal. HPLC: t_R 10.25. M.p. 110–111° (hexane/AcOEt). $[\alpha]_D^{25} = -17.1$ (c = 0.7, $CHCl_3$). IR: 3660*w* (br.), 3600*w* (br.), 3560–3300*w* (br.), 3090*w* (sh), 3060*w* (sh), 3030*w* (sh), 3000*w*, 2980*w* (sh), 2940*w* (sh), 2910*w* (sh), 2870*w*, 1605*w*, 1500*w*, 1465*w* (sh), 1455*w* (sh), 1400*w* (sh), 1360*m*, 1330*w*, 1315*w* (sh), 1280*w*, 1235*w* (br.), 1200*w* (sh), 1170*m* (sh), 1150*m* (sh), 1095*s*, 1070*s*, 1030*m* (sh), 995*m* (br.), 930*w* (br.), 915*w*, 710*w* (sh), 700*s*, 680*w* (br.). ^{1}H-NMR: 7.50–7.48 (*m*, 2 arom. H); 7.39–7.25 (*m*, 21 arom. H); 7.18–7.10 (*m*, 2 arom. H); 5.99 (*tdd*, J = 5.3, 10.5, 17.2, C*H*=CH_2); 5.52 (*s*, PhC*H*); 5.32 (*qd*, J = 1.7, 17.2, CH=C*H*$_2$); 5.12 (*qd*, J = 1.5, 10.5, CH=C*H*$_2$); 4.93 (*d*, J = 11.2, PhC*H*); 4.87 (*d*, J = 11.0, PhC*H*); 4.84 (*d*, J = 11.0, PhC*H*); 4.83 (*d*, J = 11.0, PhC*H*); 4.81 (*d*, J = 11.6, PhC*H*); 4.76 (*d*, J = 7.8, H–C(1′)); 4.62 (*d*, J = 12.1, PhC*H*); 4.57 (*d*, J = 10.5, PhC*H*); 4.565 (*d*, J = 7.7, H–C(1)); 4.53 (*d*, J = 12.0, PhC*H*); 4.33 (*dd*, J = 5.0, 10.3, H_{eq}–C(6)); 4.33 (*tdd*, J = 1.6, 5.3, 12.8, 1 allyl. H); 4.14 (*tdd*, J = 1.5, 5.5, 12.9, 1 allyl. H); 3.83 (*dt*, J = 2.5, 8.9, addn. of $D_2O \rightarrow t$, J = 8.9, H–C(3)); 3.77 (*t*, J = 10.3, H_{ax}–C(6)); 3.72–3.65 (*m*, H–C(3′), H–C(4′), 2 H–C(6′)); 3.65 (*dd*, J = 7.7, 8.6, H–C(2)); 3.55 (*t*, J = 9.4, H–C(4)); 3.52 (*dd*, J = 7.8, 9.1, H–C(2′)); 3.45 (*td*, $J \approx 3.2, 9.6$, H–C(5′)); 3.41 (*dt*, J = 5.0, 9.8, H–C(5)); 3.32 (*d*, J = 2.6, exchange with D_2O, OH–C(3)). ^{13}C-NMR: 138.27 (*s*); 138.05 (*s*); 137.97 (*s*); 137.78 (*s*); 137.00 (*s*); 133.82 (*d*); 129.03 (*d*); 128.34–127.50 (*m*); 126.23 (*d*); 116.82 (*t*); 103.31 (*d*); 101.57 (*d*); 101.00 (*d*); 84.98 (*d*); 83.16 (*d*); 81.86 (*d*); 79.86 (*d*); 77.78 (*d*); 75.43 (*t*); 74.95 (*t*); 74.83 (*d* and *t*); 73.49 (*d* and *t*); 70.11 (*t*); 68.59 (2*t*); 65.94 (*d*). CI-MS: 850 (20), 849 (56), 848 (100, $[M + NH_4]^+$), 324 (12), 309 (11), 253 (19), 108 (18), 91 (37). Anal. calc. for $C_{50}H_{54}O_{11}$ (830.98): C 72.27, H 6.55; found: C 72.49, H 6.61.

*Allyl 4,6-*O*-Benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**34**). R_f (hexane/AcOEt 7:3) 0.34. Anal. HPLC: t_R 8.51. M.p. 135.5–136° (hexane/AcOEt). $[\alpha]_D^{25} = +28.3$ (c = 0.6, $CHCl_3$). IR: 3670*w* (br.), 3600*w*, 3540–3400*w* (br.), 3090*w* (sh), 3065*w* (sh), 3030*w* (sh), 3000*w*, 2930*w* (sh), 2910*w* (sh), 2870*w*, 2800*w* (sh), 1605*w*, 1495*w*, 1465*w* (sh), 1455*m*, 1400*w*, 1385*w* (sh), 1360*m*, 1315*w*, 1265*w*, 1240*w* (sh), 1165*m*, 1140*m* (sh), 1100*s*, 1085*s* (sh), 1070*s* (sh), 1030*s*, 1005*m* (sh), 970*m* (sh), 935*w* (br.), 915*w*, 715*w* (sh), 700*s*, 670*w* (br.). ^{1}H-NMR: 7.41–7.23 (*m*, 19 arom. H); 7.19–7.08 (*m*, 4 arom. H); 6.95–6.93 (*m*, 2 arom. H); 5.94 (*dddd*, J = 5.1, 6.2, 10.4, 17.2, C*H*=CH_2); 5.47 (*s*, PhC*H*); 5.45 (*d*, J = 3.7, H–C(1′)); 5.33 (*qd*, J = 1.5, 17.2, CH=C*H*$_2$); 5.24 (*qd*, J = 1.2, 10.4, CH=C*H*$_2$); 4.99 (*d*, J = 10.9, PhC*H*); 4.80 (*d*, J = 10.8, PhC*H*); 4.79 (*d*, J = 10.9, PhC*H*); 4.63 (*d*, J = 12.1, PhC*H*); 4.56 (*d*, J = 12.4, PhC*H*); 4.45 (*d*, J = 10.7, PhC*H*); 4.44 (*d*, J = 12.2, PhC*H*); 4.43 (*d*, J = 7.7, H–C(1)); 4.38 (*tdd*, J = 1.4, 5.2, 12.7, 1 allyl. H); 4.35 (*d*, J = 12.5, PhC*H*); 4.34–4.29 (*m*, H–C(5′)); 4.33 (*dd*, J = 5.1, 10.4, H_{eq}–C(6′)); 4.15 (*tdd*, J = 1.2, 6.3, 12.7, 1 allyl. H); 4.01 (*t*, $J \approx 9.2$, H–C(3)); 3.99 (*t*, $J \approx 9.8$, H–C(3′)); 3.81 (*t*, J = 9.4, H–C(4)); 3.79 (*t*, J = 10.3, H_{ax}–C(6)); 3.72 (*dd*, J = 3.4, 10.6, H–C(6′)); 3.67–3.58 (*m*, H–C(2), H–C(4′), H′–C(6′)); 3.51 (*dd*, J = 3.8, 9.6, H–C(2′)); 3.49 (*dt*, J = 5.0, 9.9, H–C(5)); 2.58 (*d*, J = 3.4, exchange with D_2O, OH–C(2)). ^{13}C-NMR: 138.86 (*s*); 138.28 (*s*); 137.88 (*s*); 137.73 (*s*); 136.96 (*s*); 133.47 (*d*); 129.21 (*d*); 128.24–127.29 (*m*); 126.25 (*d*); 117.89 (*t*); 102.71 (*d*); 101.92 (*d*); 96.36 (*d*); 81.51 (*d*); 81.27 (*d*); 78.71 (*d*); 77.44 (*d*); 77.00 (*d*); 75.44 (*t*); 74.84 (*t*); 73.36 (*t*); 72.91 (*d*); 71.10 (*t*); 70.48 (*t*); 69.96 (*d*); 68.71 (*t*); 68.41 (*t*); 66.17 (*d*). CI-MS: 850 (19), 849 (59), 848 (100, $[M + NH_4]^+$), 420 (10), 108 (12), 91 (22). Anal. calc. for $C_{50}H_{54}O_{11}$ (830.98): C 72.27, H 6.55; found: C 72.43, H 6.70.

*Allyl 4,6-*O*-Benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**35**). R_f (hexane/AcOEt 7:3) 0.30. Anal. HPLC: t_R 11.52. M.p. 102.5–104° (hexane/AcOEt). $[\alpha]_D^{25} = -18.1$ (c = 0.6, $CHCl_3$). IR: 3660*w* (br.), 3600*w*, 3560–3300*w* (br.), 3090*w* (sh), 3060*w* (sh), 3015*w* (sh), 3000*w*, 2930*w* (sh), 2910*w* (sh), 2870*m*, 1950*w* (br.), 1810*w* (br.), 1600*w* (br.), 1500*w*, 1465*w* (sh), 1450*m*, 1400*w* (sh), 1360*m* (br.), 1310*w*, 1275*w* (br.), 1235*w* (br.), 1200*w* (sh), 1170*m* (sh), 1145*m* (sh), 1100*s*, 1070*s*, 1030*s*, 1000*m* (br.), 970*m* (sh), 935*w*, 915*w*, 825*w* (br.), 710*w* (sh), 700*s*, 680*w* (br.), ^{1}H-NMR: 7.46–7.44 (*m*, 2 arom. H); 7.31–7.25 (*m*, 21 arom. H); 7.14–7.11 (*m*, 2 arom. H); 5.93 (*dddd*, J = 5.2, 6.1, 10.4, 17.2, C*H*=CH_2); 5.49 (*s*, PhC*H*); 5.34 (*qd*, J = 1.6, 17.2, CH=C*H*$_2$); 5.23 (*qd*, J = 1.4, 10.4, CH=C*H*$_2$); 4.93 (*d*, J = 11.2, PhC*H*); 4.86 (*d*, J = 11.0, PhC*H*); 4.81 (*d*, J = 10.9, PhC*H*); 4.79 (*d*, J = 10.2, PhC*H*); 4.75 (*d*, J = 10.8, PhC*H*); 4.72 (*d*, J = 7.7, H–C(1′)); 4.51 (*d*, J = 10.8, PhC*H*); 4.50 (*d*, J = 12.1, PhC*H*); 4.46 (*d*, J = 7.8, H–C(1)); 4.40 (*d*, J = 12.1, PhC*H*); 4.37 (*tdd*, J = 1.5, 5.2, 12.8, 1 allyl. H); 4.31

(*dd*, J = 4.9, 10.4, H_{eq}–C(6)); 4.16 (*tdd*, J = 1.3, 6.1, 12.8, 1 allyl. H); 3.90 (*t*, J = 9.1, H–C(3)); 3.78 (*t*, J = 10.3, H_{ax}–C(6)); 3.68 (*t*, J = 9.3, H–C(4)); 3.64–3.51 (*m*, H–C(2), H–C(2′), H–C(3′), H–C(4′), 2 H–C(6′)); 3.42 (*dt*, J = 4.9, 9.9, H–C(5)); 3.36–3.32 (*m*, H–C(5′)); 3.31 (*d*, J = 2.8, exchange with D_2O, OH–C(2)). ^{13}C-NMR: 138.30 (*s*); 138.07 (*s*); 137.90 (*s*); 137.74 (*s*); 137.14 (*s*); 133.49 (*d*); 128.79 (*d*); 128.30–127.42 (*m*); 126.11 (*d*); 117.72 (*t*); 102.99 (*d*); 101.88 (*d*); 101.24 (*d*); 84.95 (*d*); 82.13 (*d*); 81.65 (*d*); 78.63 (*d*); 77.75 (*d*); 75.39 (*t*); 74.87 (*t*); 74.78 (*d* and *t*); 74.30 (*d*); 73.39 (*t*); 70.26 (*t*); 68.60 (*t*); 68.52 (*t*); 66.58 (*d*). CI-MS: 850 (18), 849 (55), 848 (100, $[M + NH_4]^+$), 309 (42), 253 (16), 251 (31), 108 (13), 91 (39). Anal. calc. for $C_{50}H_{54}O_{11}$ (830.98): C 72.27, H 6.55; found: C 72.00, H 6.76.

Glycosidation of **7** *with* **1**. Reaction of **1** (60.6 mg, 0.11 mmol) and **7** (28.2 mg, 0.1 mmol) in $ClCH_2CH_2Cl$ (4 ml) for 5 h at 24° and FC (hexane/AcOEt 2:1) gave 47.5 mg (59%) of **36**/**37**/**40**/**41** 23:31:16:30 (HPLC). Partial separation by another FC (hexane/AcOEt 3:1) afforded **36** (10.6 mg), **37** (14.5 mg), and **40**/**41** (21.0 mg). The mixture **40**/**41** 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 H_2O, and processing of the org. layer as usual afforded **42**/**43** (21.6 mg, 98%). FC (CH_2Cl_2/AcOEt 98:2) gave **42** (7.3 mg) and **43** (13.9 mg). Analogous acetylation of **36** and **37** gave **38** and **39**, resp.

For analogous reactions under different conditions, see *Table 3*.

*Methyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**38**). R_f (hexane/AcOEt 3:1) 0.38. $[\alpha]_D^{25}$ = +18.5 (c = 1.10, $CHCl_3$). IR: 3060*w*, 3000*w*, 2960*w*, 2920*m*, 2860*w*, 1750*m*, 1495*w*, 1455*m*, 1390*w* (sh), 1370*m*, 1260*s*, 1240*m*, 1195*w*, 1160*m* (sh), 1100*s* (br.), 1070*s*, 1040*s*, 1030*s*, 915*w*, 865*w* (br.), 810*m*, 700*s*, 660*w*. ^{1}H-NMR: 7.45–7.12 (*m*, 25 arom. H); 5.55 (*d*, J = 3.5, H–C(1′)); 5.47 (*s*, PhC*H*); 5.43 (*t*, J = 9.4, H–C(3)); 4.95 (*d*, J = 10.9, PhC*H*); 4.84 (*d*, J = 11.2, PhC*H*); 4.79 (*d*, J = 10.9, PhC*H*); 4.77 (*d*, J = 12.1, PhC*H*); 4.72 (*d*, J = 12.1, PhC*H*); 4.59 (*d*, J = 12.1, PhC*H*); 4.58 (*d*, J = 7.6, H–C(1)); 4.49 (*d*, J = 11.9, 2 PhC*H*); 4.37 (*dd*, J = 4.8, 10.6, H_{eq}–C(6)); 3.92 (*t*, J = 9.3, H–C(3′)); 3.88 (*td*, J = 2.3, 10.0, H–C(5′)); 3.82 (*dd*, J = 7.7, 9.4, H–C(2)); 3.77 (*t*, J = 10.2, H_{ax}–C(6)); 3.72–3.64 (*m*, 2 H–C(6′)); 3.64 (*t*, J = 9.4, H–C(4′)); 3.58 (*t*, J = 9.4, H–C(4)); 3.57 (*dd*, J = 3.4, 8.9, H–C(2′)); 3.55 (*dt*, J = 4.7, 10.2, H–C(5)); 3.50 (*s*, MeO); 2.01 (*s*, Ac). ^{13}C-NMR: 169.52 (*s*); 138.77 (*s*); 138.63 (*s*); 138.27 (*s*); 138.07 (*s*); 136.95 (*s*); 128.97–126.08 (*m*); 104.94 (*d*); 101.34 (*d*); 95.65 (*d*); 81.43 (*d*); 79.36 (*d*); 79.11 (*d*); 77.44 (*d*); 75.59 (*t*); 74.69 (*t*); 74.32 (*d*); 73.47 (*t*); 72.50 (*t*); 71.79 (*d*); 70.76 (*d*); 68.64 (*t*); 68.49 (*t*); 66.12 (*d*); 57.07 (*q*); 20.92 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 71.16, H 6.65.

*Methyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**39**). R_f (hexane/AcOEt 3:1) 0.38. M.p. 143–145°. $[\alpha]_D^{25}$ = –4.3 (c = 1.05, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3000*m*, 2920*m*, 2870*m*, 1748*s*, 1498*m*, 1455*s*, 1390*m* (sh), 1370*s*, 1330*w* (sh), 1315*m*, 1280*m*, 1240*s*, 1195*m*, 1148*s*, 1100*s* (br.), 1070*s* (br.), 1030*s*, 1005*s*, 915*m*, 875*w*, 820*w*, 700*s*, 660*w*. ^{1}H-NMR: 7.46–7.15 (*m*, 25 arom. H); 5.49 (*s*, PhC*H*); 5.39 (*dd*, J = 7.9, 9.3, H–C(3)); 4.91 (*d*, J = 11.3, PhC*H*); 4.86 (*d*, J = 11.0, PhC*H*); 4.82 (*d*, J = 10.9, PhC*H*); 4.76 (*d*, J = 11.1, PhC*H*); 4.73 (*d*, J = 7.9, H–C(1′)), 4.65 (*d*, J = 11.2, PhC*H*); 4.65 (*d*, J = 12.5, PhC*H*); 4.62 (*d*, J = 6.7, H–C(1)); 4.57 (*d*, J = 12.1, PhC*H*); 4.56 (*d*, J = 11.0, PhC*H*); 4.38 (*dd*, J = 4.9, 10.4, H_{eq}–C(6)); 3.90 (*dd*, J = 6.7, 7.7, H–C(2)); 3.79–3.70 (*m*, H_{ax}–C(6), H–C(3′), 2 H–C(6′)); 3.64–3.60 (*m*, H–C(4), H–C(2′), H–C(4′)); 3.50 (*s*, MeO); 3.49–3.44 (*m*, H–C(5), H–C(5′)); 1.94 (*s*, Ac). ^{13}C-NMR: 169.69 (*s*); 138.51 (*s*); 138.40 (*s*); 138.24 (*s*); 138.10 (*s*); 136.94 (*s*); 128.96–126.07 (*m*); 102.80 (2*d*); 101.29 (*d*); 84.81 (*d*); 82.01 (*d*); 78.61 (*d*); 78.15 (*d*); 77.64 (*d*); 75.53 (*t*); 75.00 (*d*); 74.87 (*t*); 74.82 (*t*); 73.52 (*t*); 73.33 (*d*); 68.88 (*t*); 68.79 (*t*); 65.51 (*d*); 56.68 (*q*); 20.85 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 70.66, H 6.26.

*Methyl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**42**). R_f (CH_2Cl_2/AcOEt 98:2) 0.39. $[\alpha]_D^{25}$ = +8.1 (c = 1.17, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3000*w*, 2960*m*, 2930*m*, 2870*m*, 1752*s*, 1498*w*, 1455*m*, 1370*m*, 1315*w*, 1262*s*, 1240*m*, 1198*w*, 1165*m*, 1100*s* (br.), 1065*s*, 1045*s*, 1030*s*, 1005*s*, 915*w*, 860*w*, 810*m*, 700*s*. ^{1}H-NMR: 7.40–7.00 (*m*, 25 arom. H); 5.58 (*d*, J = 3.4, H–C(1′)); 5.43 (*s*, PhC*H*); 5.14 (*dd*, J = 8.1, 9.4, H–C(2)); 4.95 (*d*, J = 10.9, PhC*H*); 4.82 (*d*, J = 11.3, PhC*H*); 4.73 (*d*, J = 10.9, PhC*H*); 4.59 (*d*, J = 12.1, PhC*H*); 4.57 (*d*, J = 12.3, PhC*H*); 4.48 (*d*, J = 12.1, PhC*H*); 4.43 (*d*, J = 11.1, PhC*H*); 4.43 (*d*, J = 8.2, H–C(1)); 4.40 (*d*, J = 14.2, PhC*H*); 4.35 (*dd*, J = 5.0, 10.6, H_{eq}–C(6)); 4.18 (*t*, J = 9.4, H–C(3)); 3.89 (*t*, $J \approx$ 9.3, H–C(3′)); 3.87 (*t*, J = 9.3, H–C(4)); 3.85–3.82 (*m*, H–C(5′)); 3.80 (*t*, J = 10.2, H_{ax}–C(6)); 3.68 (*d*, J = 2.6, 2 H–C(6′)); 3.57 (*t*, $J \approx$ 9.3, H–C(4′)); 3.51 (*dt*, J = 5.1, 10.2, H–C(5)); 3.51 (*s*, MeO); 3.45 (*dd*, J = 3.5, 9.8, H–C(2′)); 2.03 (*s*, Ac). ^{13}C-NMR: 169.22 (*s*); 138.77 (*s*); 138.60 (*s*); 137.88 (2*s*); 136.78 (*s*); 129.38–126.07 (*m*); 102.55 (*d*); 101.92 (*d*); 95.94 (*d*); 82.09 (*d*); 81.21 (*d*); 78.60 (*d*); 77.14 (*d*); 75.63 (*t*); 74.63 (*t*); 73.48 (*t*); 73.27 (*d*); 71.63 (*d*); 71.29 (*t*); 70.47 (*d*); 68.75 (*t*); 68.35 (*t*); 66.00 (*d*); 56.98 (*q*); 20.90 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 70.93, H 6.23.

*Methyl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**43**). R_f (CH_2Cl_2/AcOEt 98:2) 0.34. $[\alpha]_D^{25}$ = –14.3 (c = 1.02, $CHCl_3$). IR: 3060*w*, 3000*w*, 2960*w* (sh), 2920*w*, 2870*w*, 1752*m* 1498*w*, 1455*m*, 1395*w* (sh), 1370*m*, 1315*w*, 1260*m*, 1238*m*, 1195*w* (sh), 1145*m* (sh), 1100*s* (br.), 1070*s*, 1030*s*,

1010*s*, 915*w*, 865*w*, 810*w*, 700*m*. ^{1}H-NMR: 7.43–7.10 (*m*, 25 arom. H); 5.44 (*s*, PhC*H*); 5.14 (*dd*, *J* = 7.9, 8.5, H–C(2)); 4.86 (*d*, *J* = 11.1, PhC*H*); 4.82 (*d*, *J* = 11.0, PhC*H*); 4.74 (*d*, *J* = 11.3, PhC*H*); 4.71 (*d*, *J* = 11.5, PhC*H*); 4.64 (*d*, *J* = 7.8, H–C(1′)); 4.61 (*d*, *J* = 11.2, PhC*H*); 4.48 (*d*, *J* = 13.9, PhC*H*); 4.46 (*d*, *J* = 10.9, PhC*H*); 4.43 (*d*, *J* = 7.8, H–C(1)); 4.43 (*d*, *J* = 11.8, PhC*H*); 4.31 (*dd*, *J* ≈ 4.8, 10.4, H_{eq}–C(6)); 4.13 (*t*, *J* ≈ 8.8, H–C(3)); 3.86 (*t*, *J* = 9.3, H–C(4)); 3.74 (*t*, *J* = 10.3, H_{ax}–C(6)); 3.55–3.40 (*m*, H–C(5), H–C(2′), H–C(3′), H–C(4′), 2 H–C(6′)); 3.49 (*s*, MeO); 3.22 (*ddd*, *J* = 2.3, 4.9, 9.2, H–C(5′)); 1.93 (*s*, Ac). ^{13}C-NMR: 169.20 (*s*); 138.59 (*s*); 138.46 (*s*); 138.27 (*s*); 138.04 (*s*); 137.18 (*s*); 129.01–126.08 (*m*); 102.52 (*d*); 102.17 (*d*); 101.35 (*d*); 84.71 (*d*); 82.25 (*d*); 79.67 (*d*); 77.90 (*d*); 77.84 (*d*); 75.44 (*t*); 74.88 (*t*); 74.72 (*t*); 74.66 (*d*); 73.40 (*t*); 73.13 (*d*); 68.86 (*t*); 68.69 (*t*); 66.52 (*d*); 56.83 (*q*); 20.83 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 70.71, H 6.31.

Glycosidation of **8** *with* **1**. Under Ar, solid **1** (100 mg, 0.18 mmol) was added to a soln. of **8** (67 mg, 0.24 mmol) in $ClCH_2CH_2Cl$ (5 ml) at r.t. After stirring for 5 h, removal of solvent and FC (hexane/AcOEt 7:3) of the residue gave **44**–**47** (100 mg, 68.5%). HPLC (hexane/AcOEt 65:35, 16 ml/min) afforded **44** (21.8 mg, 15%), **45** (27.7 mg, 19%), **46** (25.2 mg, 17%), and **47** (23.2 mg, 16%).

For analogous reactions of **8** with **1** in various solvents at different temp., see *Table 3*.

*Methyl 4,6-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**44**). R_f (hexane/AcOEt 1:1) 0.31. Anal. HPLC: t_R 7.50. M.p. 161.6° (hexane/AcOEt). $[\alpha]_D^{25}$ = +101 (*c* = 0.5, $CHCl_3$). IR: 3660*w* (br.), 3560*w* (br.), 3470*w* (br.), 3060*w* (sh), 3030*w* (sh), 3000*m*, 2910*m*, 2870*m* (br.), 1950*w* (br.), 1810*w* (br.), 1610*w*, 1585*w*, 1500*w*, 1450*m*, 1400*m*, 1360*m*, 1345*w* (sh), 1310*w*, 1240*m* (br.), 1190*m* (sh), 1150*s* (br.), 1090*s*, 1070*s* (br.), 1040*s*, 1030*s* (sh), 1000*m* (sh), 950*w*, 920*w* (br.), 835*w*, 710*w* (sh), 700*s*, 670*w*, 660*w*. ^{1}H-NMR: 7.51–7.49 (*m*, 2 arom. H); 7.37–7.24 (*m*, 21 arom. H); 7.14–7.11 (*m*, 2 arom. H); 5.56 (*s*, PhC*H*); 4.97 (*d*, *J* = 10.9, PhC*H*); 4.94 (*d*, *J* = 3.3, H–C(1)); 4.91 (*d*, *J* = 3.8, H–C(1′)); 4.82 (*d*, *J* = 10.9, PhC*H*); 4.80 (*d*, *J* = 10.8, PhC*H*); 4.78 (*d*, *J* = 10.6, PhC*H*), 4.66 (*d*, *J* = 12.0, PhC*H*); 4.50 (*d*, *J* = 12.5, PhC*H*); 4.46 (*d*, *J* = 11.0, PhC*H*); 4.39 (*d*, *J* = 12.4, PhC*H*); 4.29 (*dd*, *J* = 0.7, 3.7, H–C(4)); 4.29 (*dd*, *J* = 1.4, 12.5, H_{eq}–C(6)); 4.25 (*ddd*, *J* = 2.1, 4.3, 9.8, H–C(5′)); 4.12 (*ddd*, *J* = 3.7, 8.4, 10.1, H–C(3)); 4.10 (br. *d*, *J* = 12.4, H_{ax}–C(6)); 4.06 (*t*, *J* ≈ 8.8, H–C(3′)); 4.02 (*dd*, *J* = 3.3, 10.1, H–C(2)); 3.73 (br. *s*, H–C(5)); 3.62–3.52 (*m*, H–C(2′), 2 H–C(6′)); 3.52 (*dd*, *J* = 9.1, 10.0, H–C(4′)); 3.43 (*s*, MeO); 3.02 (*d*, *J* = 8.3, exchange with D_2O, OH–C(3)). ^{13}C-NMR: 138.83 (*s*); 138.26 (*s*); 138.19 (*s*); 137.80 (*s*); 137.66 (*s*); 128.93–126.24 (*m*); 101.16 (*d*); 98.66 (*d*); 96.38 (*d*); 81.91 (*d*); 79.67 (*d*); 77.93 (*d*); 76.37 (*d*); 75.96 (*d*); 75.52 (*t*); 74.83 (*t*); 73.26 (*t*); 72.99 (*t*); 70.28 (*d*); 69.25 (*t*); 68.45 (*t*); 67.38 (*d*); 62.54 (*d*); 55.54 (*q*). CI-MS: 825 (9), 824 (34), 822 (100, $[M + NH_4]^+$). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.93): C 71.62, H 6.51; found: C 71.35, H 6.38.

*Methyl 4,6-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**45**). R_f (hexane/AcOEt 1:1) 0.43. Anal. HPLC: t_R 5.68. $[\alpha]_D^{25}$ = +70.4 (*c* = 0.5, $CHCl_3$). IR: 3670*w* (br.), 3610–3300*w* (br.), 3060*w* (sh), 3030*w* (sh), 3000*m*, 2940*w* (sh), 2910*m*, 2870*m*, 1950*w* (br.), 1810*w* (br.), 1600*w* (br.), 1500*w*, 1450*m*, 1400*w*, 1360*m*, 1310*w*, 1280*w*, 1255*w* (sh), 1240*w* (br.), 1190*w* (sh), 1150*m* (sh), 1090*s*, 1070*s*, 1030*s* (sh), 1000*m* (sh), 950*w* (sh), 915*w* (br.), 890*w* (br.), 830*w*, 710*m* (sh). 700*s*, 670*w*, 660*w*. ^{1}H-NMR: 7.53–7.50 (*m*, 2 arom. H); 7.38–7.25 (*m*, 21 arom. H); 7.18–7.16 (*m*, 2 arom. H); 5.57 (*s*, PhC*H*); 5.15 (*d*, *J* = 3.4, H–C(1)); 5.09 (*d*, *J* = 10.8, PhC*H*); 4.92 (*d*, *J* = 11.0, PhC*H*); 4.81 (*d*, *J* = 10.9, PhC*H*); 4.80 (*d*, *J* = 11.0, PhC*H*); 4.76 (*d*, *J* = 10.9, PhC*H*); 4.59 (*d*, *J* = 7.3, H–C(1′)); 4.58 (*d*, *J* = 12.2, PhC*H*); 4.55 (*d*, *J* = 10.8, PhC*H*); 4.51 (*d*, *J* = 12.1, PhC*H*); 4.31 (br. *d*, *J* = 3.5, H–C(4)); 4.30 (*dd*, *J* = 0.7, 12.3, H_{eq}–C(6)); 4.17 (*ddd*, *J* = 3.8, 8.0, 10.2, addn. of D_2O → *dd*, *J* = 3.8, 10.2, H–C(3)); 4.10 (*dd*, *J* = 1.5, 12.5, H_{ax}–C(6)); 3.98 (*dd*, *J* = 3.4, 10.1, H–C(2)); 3.74 (br. *s*, H–C(5)); 3.72–3.64 (*m*, 2 H–C(6′)); 3.65–3.56 (*m*, H–C(2′), H–C(3′), H–C(4′)); 3.44 (br. *td*, *J* ≈ 3.0, 9.8, H–C(5′)); 3.43 (*s*, MeO); 2.60 (*d*, *J* = 8.0, exchange with D_2O, OH–C(3)). ^{13}C-NMR: 138.45 (*s*); 138.29 (*s*); 137.98 (2 *s*); 137.45 (*s*); 129.00–126.17 (*m*); 105.27 (*d*); 101.03 (*d*); 100.24 (*d*); 84.64 (*d*); 81.91 (*d*); 79.57 (*d*); 77.61 (*d*); 76.15 (*d*); 75.54 (*t*); 74.88 (2 *t*); 74.59 (*d*); 73.36 (*t*); 69.28 (*t*); 68.93 (*t*); 67.62 (*d*); 62.19 (*d*); 55.60 (*q*). CI-MS: 825 (6), 824 (20), 822 (100, $[M + NH_4]^+$), 733 (6), 732 (6). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.93): C 71.62, H 6.51; found: C 71.66, H 6.47.

*Methyl 4,6-*O*-Benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**46**). R_f (hexane/AcOEt 1:1) 0.21. Anal. HPLC: t_R 9.73. M.p. 169.8–170° (hexane/AcOEt). $[\alpha]_D^{25}$ = +127 (*c* = 0.5, $CHCl_3$). IR: 3680–3620*w* (br.), 3620–3240*w* (br.), 3080*w* (sh), 3060*w* (sh), 3015*w* (sh), 3000*w*, 2930*w* (sh), 2910*w*, 2885*w*, 1950*w*, 1650*w* (br.), 1495*w*, 1465*w* (sh), 1455*m*, 1400*w* (br.), 1360*m* (br.), 1345*w* (sh), 1330*w* (sh), 1310*w* (sh), 1245*w* (br.), 1190*w* (sh), 1150*m*, 1090*s*, 1070*s*, 1050*s*, 1030*s* (sh), 995*m* (br.), 955*w*, 920*w* (br.), 835*w* (br.), 700*s*, 670*w* (sh), 660*w* (sh). ^{1}H-NMR: 7.54–7.52 (*m*, 2 arom. H); 7.31–7.13 (*m*, 23 arom. H); 5.53 (*s*, PhC*H*); 5.18 (*d*, *J* = 3.7, H–C(1′)); 4.95 (*d*, *J* = 3.8, H–C(1)); 4.94 (*d*, *J* = 10.8, PhC*H*); 4.83 (*d*, *J* = 10.1, PhC*H*); 4.79 (*d*, *J* = 10.9, PhC*H*); 4.60 (*s*, $PhCH_2$); 4.58 (*d*, *J* = 12.1, PhC*H*); 4.48 (*d*, *J* = 10.4, PhC*H*); 4.46 (*d*, *J* = 11.9, PhC*H*); 4.36 (*d*, *J* = 3.1, H–C(4)); 4.29 (*dd*, *J* = 1.2, 12.4, H_{eq}–C(6)); 4.25 (*ddd*, *J* = 3.8, 6.9, 10.4, addn. of D_2O → *dd*, *J* = 3.8, 10.4, H–C(2)); 4.14 (*ddd*, *J* = 2.6, 4.0, 10.1, H–C(5′)); 4.07 (*dd*, *J* = 1.5, 12.5, H_{ax}–C(6)); 4.07 (*t*, *J* = 9.2, H–C(3′)); 3.99 (*dd*, *J* = 3.4, 10.1, H–C(3)); 3.69–3.60 (*m*, H–C(5), 2 H–C(6′)); 3.63 (*dd*, *J* = 3.7, 9.6, H–C(2′));

3.57 (*dd*, J = 9.3, 9.8, H–C(4')); 3.43 (*s*, MeO); 2.75 (*d*, J = 6.9, exchange with D_2O, OH–C(2)). ^{13}C-NMR: 138.68 (*s*); 138.18 (*s*); 137.92 (*s*); 137.74 (*s*); 137.63 (*s*); 128.78–126.14 (*m*); 100.86 (*d*); 100.23 (*d*); 93.65 (*d*); 81.68 (*d*); 79.47 (*d*); 77.63 (*d*), 75.50 (*t*); 74.71 (*t*); 73.96 (*d*); 73.33 (*t*); 73.11 (*d*); 72.19 (*t*); 70.33 (*d*); 69.36 (*t*); 68.66 (*t*); 67.09 (*d*); 62.52 (*d*); 55.50 (*q*). CI-MS: 825 (10), 824 (26), 822 (100, $[M + NH_4]^+$), 733 (6), 732 (8). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.85, H 6.52.

*Methyl 4,6-*O*-Benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**47**). R_f (hexane/AcOEt 1:1) 0.27. Anal. HPLC: t_R 8.56. $[\alpha]_D^{25}$ = +82.4 (c = 0.5, $CHCl_3$). IR: 3660*w* (br.), 3560*w* (br.), 3540–3300*w* (br.), 3060*w* (sh), 3030*w* (sh), 3000*m*, 2910*m* (br.), 2860*m* (br.), 1950*w* (br.), 1810*w* (br.), 1610*w* (br.), 1585*w* (br.), 1500*w*, 1450*m*, 1400*m*, 1360*m*, 1340*m* (sh), 1330*w* (sh), 1310*w*, 1280*w* (sh), 1265*w* (sh), 1250*w*, 1210*w*, 1190*w* (sh), 1170*m* (sh), 1150*m* (sh), 1070*s* (br.), 1030*s* (sh), 980*m* (sh), 950*w* (sh), 910*w* (br.), 840*w* (br.), 710*m* (sh), 700*s*, 670*w*, 660*w*. ^{1}H-NMR: 7.56–7.54 (*m*, 2 arom. H); 7.38–7.23 (*m*, 21 arom. H); 7.19–7.16 (*m*, 2 arom. H); 5.50 (*s*, PhC*H*); 4.96 (*d*, J = 11.2, PhC*H*); 4.95 (*d*, J = 11.0, PhC*H*); 4.90 (*d*, J = 3.6, H–C(1)); 4.85 (*d*, J = 7.8, H–C(1')); 4.83 (*d*, J = 11.4, PhC*H*); 4.83 (*d*, J = 10.9, PhC*H*); 4.82 (*d*, J = 10.9, PhC*H*); 4.59 (*d*, J = 12.1, PhC*H*); 4.53 (*d*, J = 10.9, PhC*H*); 4.52 (*d*, J = 12.0, PhC*H*); 4.38 (*d*, J = 3.0, H–C(4)); 4.24 (*dd*, J = 1.4, 12.4, H_{eq}–C(6)); 4.17 (*ddd*, J = 3.7, 6.0, 9.9, addn. of $D_2O \rightarrow$ *dd*, J = 3.7, 9.9, H–C(2)); 4.04 (*dd*, J = 3.3, 10.2, H–C(3)); 3.97 (*dd*, J = 1.5, 12.5, H_{ax}–C(6)); 3.72 (*dd*, J = 1.8, 10.6, H–C(6')); 3.66 (*t*, J = 9.0, H–C(4')); 3.65 (*dd*, J = 5.0, 10.6, H'–C(6')); 3.63 (br. *s*, H–C(5)); 3.58–3.48 (*m*, H–C(2'), H–C(3'), H–C(5')); 3.45 (*s*, MeO); 2.80 (*d*, J = 6.1, exchange with D_2O, OH–C(2)). ^{13}C-NMR: 138.41 (*s*); 138.01 (*s*); 137.96 (2 *s*); 137.92 (*s*); 128.63–126.13 (*m*); 103.95 (*d*); 100.51 (*d*); 100.24 (*d*); 84.77 (*d*); 81.97 (*d*); 77.91 (*d*); 77.46 (*d*); 75.46 (*t*); 74.89 (2 *t*); 74.61 (*d*); 73.36 (*t*); 69.18 (*t*); 69.13 (*t*); 67.99 (*d*); 62.96 (*d*); 55.43 (*q*). CI-MS: 825 (6), 824 (32), 822 (100, $[M + NH_4]^+$). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.53, H 6.80.

Glycosidation of **9** *with* **1**. Reaction of **1** (60.6 mg, 0.11 mmol) and **9** (28.2 mg, 0.1 mmol) in $ClCH_2CH_2Cl$ (4 ml) for 5 h at 24° and FC (hexane/AcOEt 1:1) gave 45.1 mg (56%) of (**48** and **49**)/**50**/**51** 56:18:26 (HPLC). Partial separation by another FC (CH_2Cl_2/AcOEt 9:1) afforded **48**/**49** (25.1 mg) and **50**/**51** (19.6 mg). FC (CH_2Cl_2/AcOEt 9:1) of **50**/**51** gave **50** (8.2 mg) and **51** (11.4 mg). Acetylation in pyridine/Ac_2O 2:1 for 12 h at r.t., dilution with CH_2Cl_2, washing with 1M aq. Na_2CO_3 and H_2O, processing of the org. layer as usual, and FC (hexane/AcOEt 2:1) afforded **54** (8.4 mg, 98%) and **55** (11.8 mg, 99%). Analogous acetylation of **48**/**49** gave 25.9 mg (98%) of **52**/**53** 38:62 (HPLC) which, upon FC (CH_2Cl_2/AcOEt 98:2), gave pure samples of **52** and **53**.

For analogous reactions under different conditions, see *Table 3*.

*Methyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-galactopyranoside* (**52**). R_f (CH_2Cl_2/AcOEt 98:2) 0.26. $[\alpha]_D^{25}$ = +96.6 (c = 1.58, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3000*m*, 2960*m*, 2930*m*, 2870*m*, 1735*s*, 1498*m*, 1455*s*, 1400*m*, 1370*s*, 1310*m*, 1270*m* (sh), 1250*s*, 1185*m*, 1160*s*, 1100*s* (br.), 1070*s* (sh), 1050*s*, 1030*s*, 1005*s*, 910*m*, 875*w*, 860*w*, 820*m*, 700*s*, 660*w*, 635*w*, 610*w*. ^{1}H-NMR: 7.52–7.10 (*m*, 25 arom. H); 5.62 (*d*, J = 3.6, H–C(1')); 5.50 (*s*, PhC*H*); 4.96 (*d*, J = 10.8, PhC*H*); 4.95 (*dd*, J = 3.7, 10.3, H–C(3)); 4.83 (*d*, J = 11.1, PhC*H*); 4.82 (*d*, J = 12.1, PhC*H*); 4.77 (*d*, J = 10.8, PhC*H*); 4.71 (*d*, J = 12.0, PhC*H*); 4.61 (*d*, J = 12.2, PhC*H*); 4.54 (*d*, J = 7.8, H–C(1)); 4.49 (*d*, J = 11.3, PhC*H*); 4.46 (*d*, J = 12.2, PhC*H*); 4.44 (br. *d*, J = 3.6, H–C(4)); 4.34 (*dd*, J = 1.4, 12.4, H_{eq}–C(6)); 4.23 (*dd*, J = 7.8, 10.3, H–C(2)); 4.07 (*dd*, J = 1.6, 12.4, H_{ax}–C(6)); 4.05 (*td*, J = 2.4, 10.0, H–C(5')); 3.91 (*t*, $J \approx$ 9.2, H–C(3')); 3.75–3.67 (*m*, 2 H–C(6')); 3.66 (*dd*, J = 9.0, 9.9, H–C(4')); 3.59 (*dd*, J = 3.6, 9.7, H–C(2')); 3.54 (*s*, MeO); 3.51 (br. *s*, H–C(5)); 2.00 (*s*, Ac). ^{13}C-NMR: 170.58 (*s*); 138.83 (*s*); 138.61 (*s*); 138.16 (*s*); 138.09 (*s*); 137.70 (*s*); 128.95–126.36 (*m*); 104.43 (*d*); 101.05 (*d*); 95.76 (*d*); 81.67 (*d*); 79.48 (*d*); 77.62 (*d*); 75.55 (*t*); 74.76 (*t*); 73.38 (*d* and *t*); 73.13 (*d*); 72.36 (*t*); 70.58 (*d*); 70.49 (*d*); 68.91 (*t*); 68.44 (*t*); 66.12 (*d*); 56.61 (*q*); 20.99 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 71.15, H 6.36.

*Methyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-β-*D*-galactopyranoside* (**53**). R_f (CH_2Cl_2/AcOEt 98:2) 0.15. M.p. 137–138°. $[\alpha]_D^{25}$ = +57.1 (c = 2.20, $CHCl_3$). IR: 3060*w*, 3000*m*, 2960*w*, 2910*m*, 2870*m*, 1745*s*, 1498*w*, 1455*s*, 1405*m*, 1370*s*, 1310*w*, 1295*w*, 1260*s* (sh), 1248*s*, 1182*m*, 1150*s*, 1100*s*, 1070*s*, 1050*s*, 1030*s*, 1005*s*, 910*w*, 820*m*, 700*s*, 660*w*, 610*w*. ^{1}H-NMR: 7.53–7.17 (*m*, 25 arom. H); 5.50 (*s*, PhC*H*); 4.95 (*dd*, J = 3.6, 10.1, H–C(3)); 4.87 (*d*, J = 11.0, PhC*H*); 4.86 (*d*, J = 11.0, PhC*H*); 4.80 (*d*, J = 12.2, PhC*H*); 4.77 (*d*, J = 11.2, PhC*H*); 4.73 (*d*, J = 7.8, H–C(1')); 4.66 (*d*, J = 10.9, PhC*H*); 4.66 (*d*, J = 13.0, PhC*H*); 4.57 (*d*, J = 12.5, PhC*H*); 4.57 (*d*, J = 10.5, PhC*H*); 4.50 (*d*, J = 7.7, H–C(1)); 4.41 (br. *d*, J = 3.4, H–C(4)); 4.35 (*dd*, J = 1.4, 12.4, H_{eq}–C(6)); 4.24 (*dd*, J = 7.7, 10.1, H–C(2)); 4.06 (*dd*, J = 1.6, 12.4, H_{ax}–C(6)); 3.78–3.70 (*m*, 2 H–C(6')); 3.65 (*t*, J = 9.1, H–C(4')); 3.59 (*t*, J = 8.8, H–C(3')); 3.54 (*s*, MeO); 3.52 (br. *s*, H–C(5)); 3.48–3.43 (*m*, H–C(5')); 3.45 (*t*, $J \approx$ 8.6, H–C(2')); 1.91 (*s*, Ac). ^{13}C-NMR: 170.70 (*s*); 138.60 (*s*); 138.36 (2 *s*); 138.18 (*s*); 137.69 (*s*); 129.01–126.38 (*m*); 103.14 (*d*); 102.37 (*d*); 101.08 (*d*); 84.93 (*d*); 82.27 (*d*); 77.76 (*d*); 75.47 (*t*); 74.97 (*d*); 74.86 (2 *t*); 74.64 (*d*); 73.92 (*d*); 73.57 (*t*); 73.46 (*d*); 68.98 (*t*); 68.79 (*t*); 66.00 (*d*); 55.84 (*q*); 20.85 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 70.70, 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-galactopyranoside (**54**). R_f (hexane(AcOEt 1:1) 0.49. M.p. 119–120°. $[\alpha]_D^{25} = +47.0$ ($c = 1.80$, $CHCl_3$). IR: 3060*w*, 3000*m*, 2930*m*, 2870*m*, 1755*s*, 1498*w*, 1455*s*, 1400*m*, 1370*s*, 1315*w*, 1260*s*, 1248*s*, 1185*s*, 1155*s* (sh), 1148*s* (sh), 1105*s* (sh), 1095*s*, 1070*s* (sh), 1055*s*, 1030*s*, 1010*s*, 910*w*, 860*w*, 820*m*, 700*s*, 660*w*. ^{1}H-NMR: 7.56–7.08 (*m*, 25 arom. H); 5.51 (*s*, PhC*H*); 5.43 (*dd*, $J = 8.0, 10.1$, H–C(2)); 5.10 (*d*, $J = 3.4$, H–C(1′)); 4.91 (*d*, $J = 10.9$, PhC*H*); 4.84 (*d*, $J = 11.3$, PhC*H*); 4.73 (*d*, $J = 10.9$, PhC*H*); 4.58 (*d*, $J = 12.1$, PhC*H*); 4.53 (*s*, PhCH_2); 4.48 (*d*, $J = 12.1$, PhC*H*); 4.46 (*d*, $J = 11.3$, PhC*H*); 4.37 (*d*, $J = 8.0$, H–C(1)); 4.35 (*dd*, $J \approx 1.4, 12.5$, H_{eq}–C(6)); 4.32 (br. *d*, $J = 3.4$, H–C(4)); 4.05 (*dd*, $J = 1.6, 12.4$, H_{ax}–C(6)); 3.92 (*t*, $J = 9.2$, H–C(3′)); 3.88–3.83 (*m*, H–C(5′)); 3.85 (*dd*, $J = 3.6, 10.2$, H–C(3)); 3.66–3.63 (*m*, 2 H–C(6′)); 3.58 (*t*, $J = 9.4$, H–C(4′)); 3.57 (*dd*, $J = 3.4, 9.6$, H–C(2′)); 3.52 (*s*, MeO); 3.37 (br. *s*, H–C(5)); 2.05 (*s*, Ac). ^{13}C-NMR: 169.36 (*s*); 138.63 (*s*); 138.46 (*s*); 138.10 (*s*); 137.88 (*s*); 137.36 (*s*); 129.70–126.25 (*m*); 101.74 (*d*); 101.18 (*d*); 93.17 (*d*); 81.41 (*d*); 79.25 (*d*); 77.17 (*d*); 75.50 (*t*); 74.62 (*t*); 73.37 (*d*); 73.26 (*t*); 71.99 (*t*); 71.53 (*d*); 70.52 (*d*); 69.27 (*d*); 69.15 (*t*); 68.50 (*t*); 66.43 (*d*); 55.98 (*q*); 20.96 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 71.03, H 6.50.

Methyl 2-O-Acetyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-β-D-galactopyranoside (**55**). R_f (hexane/AcOEt 1:1) 0.58. $[\alpha]_D^{25} = +41.2$ ($c = 1.02$, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3000*m*, 2910*s*, 2860*s*, 1755*s*, 1498*m*, 1455*s*, 1400*s*, 1368*s*, 1310*m*, 1280*m* (sh), 1260*s* (sh), 1248*s*, 1180*s*, 1150*s* (sh), 1070*s* (br.), 1030*s*, 1010*s*, 910*m*, 860*w*, 820*m*, 700*s*, 660*w*, 650*w*. ^{1}H-NMR: 7.57–7.13 (*m*, 25 arom. H); 5.51 (*s*, PhC*H*); 5.45 (*dd*, $J = 8.0, 10.3$, H–C(2)); 4.92 (*d*, $J = 11.0$, PhC*H*); 4.84 (*d*, $J = 11.8$, PhC*H*); 4.80 (*d*, $J = 10.9$, PhC*H*); 4.75 (*d*, $J = 11.0$, PhC*H*); 4.67 (*d*, $J = 11.8$, PhC*H*); 4.57 (*d*, $J = 11.8$, PhC*H*); 4.57 (*d*, $J = 7.8$, H–C(1′)); 4.50 (*d*, $J = 12.1$, 2 PhC*H*); 4.38 (*d*, $J = 8.1$, H–C(1)); 4.38 (br. *d*, $J \approx 3$, H–C(4)); 4.28 (*dd*, $J = 1.4, 12.3$, H_{eq}–C(6)); 3.90 (*dd*, $J = 1.6, 12.3$, H_{ax}–C(6)); 3.88 (*dd*, $J = 3.5, 10.2$, H–C(3)); 3.74 (*dd*, $J = 1.6, 10.4$, H–C(6′)); 3.61 (*dd*, $J \approx 5.7, 11.2$, H′–C(6′)); 3.61 (*t*, $J \approx 9$, H–C(3′)); 3.52–3.50 (*m*, H–C(5′)); 3.50 (*s*, MeO); 3.47 (*t*, $J \approx 9$, H–C(4′)); 3.46 (*dd*, $J = 7.9, 9.0$, H–C(2′)); 3.37 (br. *s*, H–C(5)); 1.90 (*s*, Ac). ^{13}C-NMR: 169.51 (*s*); 138.46 (*s*); 138.21 (*s*); 137.99 (*s*); 137.89 (2 *s*); 128.78–126.36 (*m*); 104.93 (*d*); 101.72 (*d*); 100.86 (*d*); 84.60 (*d*); 80.66 (*d*); 77.81 (2 *d*); 76.04 (*d*); 75.50 (*t*); 74.96 (*t*); 74.61 (*d*); 74.09 (*t*); 73.43 (*t*); 69.91 (*d*); 69.52 (*t*); 68.86 (*t*); 66.68 (*d*); 55.82 (*q*); 20.86 (*q*). Anal. calc. for $C_{50}H_{54}O_{12}$ (846.96): C 70.91, H 6.43; found: C 70.63, H 6.46.

Glycosidation of **10** *with* **1**. A mixture of **10** (88.0 mg, 0.24 mmol) and **1** (100 mg, 0.18 mmol) in 1,4-dioxane (2 ml) was stirred for 5 h at r.t. Evaporation and FC (hexane/AcOEt 4:1) gave **56**/**57** (57 mg, 35%) and **60**/**61** (58.5 mg, 36%). The soln. of **56**/**57** in Ac_2O (1 ml) and pyridine (1 ml) was kept overnight at r.t. and then diluted with MeOH. Evaporation of the soln., FC (hexane/AcOEt 4:1), and HPLC (hexane/AcOEt 4:1, 16 ml/min) gave **58** (32.5 mg, 55%) and **59** (22.6 mg, 18%). Prep. HPLC (CH_2Cl_2/AcOEt 98:2, 16 ml/min) of **60**/**61** afforded **60** (26.3 mg, 16%) and **61** (29.7 mg, 18%).

Methyl 4-O-Acetyl-2,6-di-O-benzyl-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-mannopyranoside (**58**). R_f (CH_2Cl_2/AcOEt 97:3) 0.24. Anal. HPLC: t_R 3.59. $[\alpha]_D^{25} = +34.8$ ($c = 0.5$, $CHCl_3$). IR: 3080*w* (sh), 3060*w*, 3030*w* (sh), 2960*w* (sh), 2920*m*, 2860*m*, 1950*w*, 1870*w*, 1810*w*, 1740*m*, 1500*w*, 1460*w* (sh), 1450*m*, 1400*w*, 1360*m*, 1320*w* (br.), 1260*m* (sh), 1240*m*, 1200*w* (sh), 1160*m* (sh), 1135*s* (sh), 1100*s*, 1070*s*, 1050*s*, 1030*s* (sh), 1010*m* (sh), 975*m* (sh), 940*w* (sh), 910*w*, 860*w*, 810*w*, 700*s*, 660*w*. ^{1}H-NMR: 7.36–7.20 (*m*, 28 arom. H); 7.13–7.11 (*m*, 2 arom. H); 5.37 (*t*, $J \approx 9.4$, H–C(4)); 5.04 (*d*, $J = 3.4$, H–C(1′)); 4.88 (*d*, $J = 10.9$, PhC*H*); 4.81 (*d*, $J = 11.2$, PhC*H*); 4.78 (*d*, $J = 11.0$, PhC*H*); 4.76 (*d*, $J = 2.2$, H–C(1)); 4.71 (*d*, $J = 11.9$, PhC*H*); 4.67 (*d*, $J = 11.8$, PhC*H*); 4.66 (*s*, PhCH_2); 4.57 (*d*, $J = 11.9$, PhC*H*); 4.53 (*d*, $J = 12.0$, PhC*H*); 4.50 (*d*, $J = 12.1$, PhC*H*); 4.44 (*d*, $J = 11.1$, PhC*H*); 4.40 (*d*, $J = 12.1$, PhC*H*); 4.04 (*dd*, $J = 3.1, 9.2$, H–C(3)); 4.00 (*t*, $J = 9.4$, H–C(3′)); 4.00 (*ddd*, $J = 2.2, 3.6, 10.1$, H–C(5′)); 3.87 (*ddd*, $J = 3.0, 6.0, 9.9$, H–C(5)); 3.86 (*t*, $J \approx 3.0$, H–C(2)); 3.63 (*dd*, $J = 6.2, 10.7$, H–C(6)); 3.58 (*dd*, $J = 9.2, 10.0$, H–C(4′)); 3.56 (*dd*, $J = 3.2, 10.8$, H′–C(6)); 3.52 (*dd*, $J = 3.3, 9.8$, H–C(2′)); 3.51 (*dd*, $J = 3.6, 10.7$, H–C(6′)); 3.47 (*dd*, $J = 2.1, 10.7$, H′–C(6′)); 3.38 (*s*, MeO); 1.77 (*s*, Ac). CI-MS: 959 (6), 958 (23), 957 (64), 956 (100, $[M + NH_4]^+$), 108 (9). Anal. calc. for $C_{57}H_{62}O_{12}$ (939.07): C 72.90, H 6.66; found: C 72.85, H 6.65.

Methyl 4-O-Acetyl-2,6-di-O-benzyl-3-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-mannopyranoside (**59**). R_f (CH_2Cl_2/AcOEt 97:3) 0.18. Anal. HPLC: t_R 4.54. M.p. 67° (hexane/AcOEt). $[\alpha]_D^{25} = +16.3$ ($c = 0.46$, $CHCl_3$). IR: 3060*w*, 3030*w* (sh), 3000*w*, 2910*m*, 2860*m*, 1950*w*, 1875*w*, 1810*w*, 1740*m*, 1500*w*, 1470*w* (sh), 1450*m*, 1400*w* (sh), 1365*m*, 1330*w* (sh), 1310*w*, 1280*w* (sh), 1240*m*, 1200*w* (sh), 1165*m* (sh), 1135*s* (sh), 1100*s*, 1070*s*, 1030*s* (sh), 1010*m* (sh), 970*w* (sh), 910*w*, 890*w* (sh), 835*w* (sh), 820*w*, 810*w* (sh), 700*s*, 675*w* (sh), 660*w*. ^{1}H-NMR: 7.37–7.17 (*m*, 30 arom. H); 5.41 (*t*, $J = 9.8$, H–C(4)); 4.96 (*d*, $J = 11.5$, PhC*H*); 4.93 (*d*, $J = 10.6$, PhC*H*); 4.82 (*d*, $J = 9.4$, PhC*H*); 4.79 (*d*, $J = 9.5$, PhC*H*); 4.77 (*d*, $J = 2.1$, H–C(1)); 4.73 (*d*, $J = 11.8$, PhC*H*); 4.62–4.53 (*m*, 7 PhC*H*); 4.45 (*d*, $J = 7.7$, H–C(1′)); 4.23 (*dd*, $J = 3.1, 9.5$, H–C(3)); 3.90 (*ddd*, $J = 2.8, 6.2, 10.0$, H–C(5)); 3.80 (*dd*, $J = 2.1, 3.0$, H–C(2)); 3.78 (*dd*, $J = 1.9, 10.9$, H–C(6′)); 3.70 (*dd*, $J = 4.4, 10.9$, H′–C(6′)); 3.67 (*dd*, $J = 6.2, 10.7$, H–C(6)); 3.69–3.60 (*m*, H–C(3′), H–C(4′)); 3.60 (*dd*, $J = 2.8, 10.7$, H′–C(6)); 3.40 (*ddd*, $J = 1.9, 4.4, 9.7$,

H–C(5′)); 3.39 (*dd*, J = 7.8, 9.0, H–C(2′)); 3.36 (*s*, MeO); 1.95 (*s*, Ac). CI-MS: 959 (6), 958 (23), 957 (63), 956 (100, $[M + NH_4]^+$), 108 (9), 91 (13). Anal. calc. for $C_{57}H_{62}O_{12}$ (939.07): C 72.90, H 6.66; found: C 72.85, H 6.65.

*Methyl 2,6-Di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-mannopyranoside* (**60**). R_f (CH_2Cl_2/AcOEt 97:3) 0.35. Anal. HPLC: t_R 2.66. $[\alpha]_D^{25}$ = +53.4 (c = 0.5, $CHCl_3$). IR: 3560*w* (sh), 3430*w* (br.), 3080*w* (sh), 3060*w*, 3030*w* (sh), 3000*m*, 2930*m*, 2910*m*, 2860*m* (sh), 1950*w*, 1870*w*, 1810*w*, 1580*w* (br.), 1500*w*, 1470*w* (sh), 1450*m*, 1400*w* (sh), 1360*m*, 1320*w* (br.), 1290*w*, 1260*w*, 1200*w* (sh), 1140*s* (sh), 1100*s* (sh), 1070*s*, 1050*s* (sh), 1030*s* (sh), 1000*m* (sh), 970*m* (sh), 910*w*, 860*w*, 820*w*, 700*s*, 660*w*, 630*w* (sh), 610*w*. ^{1}H-NMR: 7.42–7.22 (*m*, 28 arom. H); 7.15–7.13 (*m*, 2 arom. H); 5.03 (*d*, J = 3.6, H–C(1′)); 4.92 (*d*, J = 11.0, PhC*H*); 4.85 (*d*, J = 11.1, 2 PhC*H*); 4.82 (*d*, J = 11.9, PhC*H*); 4.81 (*d*, J = 10.9, PhC*H*); 4.76 (*d*, J = 1.7, H–C(1)); 4.75 (*d*, J = 12.2, PhC*H*); 4.71 (*d*, J = 11.8, PhC*H*); 4.58 (*d*, J = 12.2, PhC*H*); 4.53 (*d*, J = 12.2, PhC*H*); 4.51 (*d*, J = 12.2, PhC*H*); 4.46 (*d*, J = 10.9, PhC*H*); 4.455 (*d*, J = 3.2, exchange with D_2O, OH–C(3)); 4.37 (*d*, J = 12.1, PhC*H*); 4.08 (*td*, J = 3.2, 9.4, addn. of $D_2O \rightarrow$ *dd*, J = 3.2, 9.4, H–C(3)); 3.97 (*t*, $J \approx$ 9.4, H–C(3′)); 3.94 (*t*, J = 9.4, H–C(4)); 3.80–3.74 (*m*, 2 H–C(6)); 3.79 (*ddd*, J = 2.0, 3.3, 10.0, H–C(5′)); 3.78 (*dd*, J = 1.7, 3.2, H–C(2)); 3.73 (*td*, J = 3.3, 9.3, H–C(5)); 3.61 (*dd*, J = 9.1, 10.0, H–C(4′)); 3.55 (*dd*, J = 3.4, 10.7, H–C(6′)); 3.54 (*dd*, J = 3.6, 9.8, H–C(2′)); 3.37 (*dd*, J = 2.0, 10.6, H′–C(6′)); 3.35 (*s*, MeO): CI-MS: 916 (20), 915 (61), 914 (100, $[M + NH_4]^+$), 324 (6), 307 (18), 216 (6), 108 (19), 91 (5). Anal. calc. for $C_{55}H_{60}O_{11}$ (897.03): C 73.64, H 6.74; found: C 73.85, H 6.52.

*Methyl 2,6-Di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-α-*D*-mannopyranoside* (**61**). R_f (CH_2Cl_2/AcOEt 97:3) 0.25. Anal. HPLC: t_R 3.62. $[\alpha]_D^{25}$ = +48.6 (c = 0.5, $CHCl_3$). IR: 3470*w* (br.), 3080*w* (sh), 3060*w*, 3030*w* (sh), 3000*m*, 2910*m*, 2870*m*, 1950*w*, 1870*w*, 1810*w*, 1610*w*, 1580*w*, 1500*m*, 1470*w* (sh), 1450*m*, 1400*w* (sh), 1360*m*, 1330*w* (sh), 1290*w*, 1240*w* (sh), 1200*w* (sh), 1140*s* (sh), 1100*s*, 1070*s*, 1040*s* (sh), 1030*s* (sh), 1010*m* (sh), 970*m* (sh), 910*w* (sh), 880*w* (sh), 870*w* (br.), 700*s*, 670*w* (sh), 660*w*. ^{1}H-NMR: 7.38–7.22 (*m*, 28 arom. H); 7.18–7.15 (*m*, 2 arom. H); 4.89 (*d*, J = 11.0, PhC*H*); 4.88 (*d*, J = 12.4, PhC*H*); 4.83 (*d*, J = 11.3, PhC*H*); 4.80 (*d*, J = 11.1, 2 PhC*H*); 4.77 (*d*, J = 11.7, PhC*H*); 4.72 (*d*, J = 1.8, H–C(1)); 4.71 (*d*, J = 12.6, PhC*H*); 4.56 (*d*, J = 12.0, PhC*H*); 4.53 (*d*, J = 10.9, PhC*H*); 4.50 (*d*, J = 12.1, PhC*H*); 4.49 (*d*, J = 12.0, PhC*H*); 4.36 (*d*, J = 11.8, PhC*H*); 4.35 (*d*, J = 7.8, H–C(1′)); 4.00–3.94 (*m*, 2 H–C(6)); 3.98 (br. *s*, exchange with D_2O, OH–C(3)); 3.80 (*dd*, J = 1.8, 3.0, H–C(2)); 3.77–3.69 (*m*, H–C(5), H–C(3′), H–C(4′)); 3.67 (*dd*, J = 2.5, 10.8, H–C(6′)); 3.63 (*dd*, J = 4.4, 10.8, H′–C(6′)); 3.62–3.55 (*m*, changes after addn. of D_2O, H–C(3), H–C(4)); 3.45 (*ddd*, J = 2.5, 4.5, 10.0, H–C(5′)); 3.43 (*dd*, J = 7.8, 9.1, H–C(2′)); 3.43 (*s*, MeO). CI-MS: 916 (21), 915 (63), 914 (100, $[M + NH_4]^+$), 450 (11), 392 (13), 324 (12), 307 (36), 198 (10), 108 (37), 91 (31). Anal. calc. for $C_{55}H_{60}O_{11}$ (897.03): C 73.64, H 6.74; found: C 73.86, H 6.54.

Glycosidation of **11** *with* **1**. A soln. of **11** (67 mg, 0.24 mmol) in toluene (7 ml) was heated to 70°, treated with one crop of solid **1** (100 mg, 0.18 mmol), stirred for 2 h, and cooled to r.t. Evaporation and FC (hexane/AcOEt 4:1 → 7:3) gave **62**–**65** (130 mg, 89%). Prep. HPLC (hexane/AcOEt 3:1, 16 ml/min) afforded **62** (13.0 mg, 9%), **63** (18.7 mg, 13%), **64** (36.5 mg, 25%), and **65** (56.8 mg, 39%).

Glycosidation of **11** *with* **2**. Similarly as described for **13**+**1**, **11** (56.5 mg, 0.2 mmol) was glycosylated with **2** (168 mg, 0.28 mmol) in the presence of Et_4NBr (42 mg, 0.2 mmol) and powdered 4-Å molecular sieves (50 mg), to afford, after FC, **62**–**65** (129 mg, 80%). Prep. HPLC of this mixture gave **62** (34.8 mg, 22%), **63** (2.6 mg, 2%), **64** (82 mg, 51%), and **65** (9.2 mg, 6%).

Glycosidation of **11** *with* **3**. Under Ar, a mixture of **11** (30 mg, 0.11 mmol) and powdered 4-Å molecular sieves (50 mg) in CH_2Cl_2 (2 ml) was stirred for 30 min at r.t., cooled to − 30°, and treated with a soln of **3** (80.1 mg, 0.12 mmol) in CH_2Cl_2 (2 ml) and then with a soln. of $BF_3 \cdot Et_2O$ (14 µl, 0.12 mmol) in CH_2Cl_2 (1 ml). After stirring for 30 min and addition of Et_3N (0.1 ml), filtration through *Celite*, evaporation, FC, and HPLC (as described above) gave **62** (3.6 mg, 4%), **63** (6.0 mg, 7%), **64** (4.9 mg, 6%), and **65** (65 mg, 76%).

*Methyl 4,6-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-mannopyranoside* (**62**). R_f (hexane/AcOEt 3:2) 0.42. Anal. HPLC: t_R 4.81. $[\alpha]_D^{25}$ = +10.9 (c = 0.46, $CHCl_3$). IR: 3660*w*, 3460*w* (br.), 3060*w* (sh), 3030*w* (sh), 3000*m*, 2930*m*, 2870*m*, 1950*w* (br.), 1880*w* (br.), 1810*w* (br.), 1610*w*, 1590*w*, 1500*m*, 1470*m* (sh), 1450*s*, 1410*m* (sh), 1390*m* (sh), 1360*m*, 1315*m*, 1280*m*, 1250*w* (br.), 1200*w* (sh), 1160*s* (sh), 1130*s*, 1100*s*, 1070*s*, 1050*s*, 1000*s* (sh), 980*m* (sh), 965*m* (sh), 940*w* (sh), 910*m*, 890*w* (sh), 870*w*, 800*w*, 700*s*, 660*w*, 650*w*, 620*w* (br.). ^{1}H-NMR: 7.54–7.51 (*m*, 2 arom. H); 7.41–7.26 (*m*, 21 arom. H); 7.18–7.15 (*m*, 2 arom. H); 5.60 (*s*, PhC*H*); 4.99 (*d*, J = 11.0, PhC*H*); 4.91 (*d*, J = 11.0, PhC*H*); 4.85 (*d*, J = 10.5, PhC*H*); 4.82 (*d*, J = 3.9, H–C(1′)); 4.81 (*d*, J = 11.4, PhC*H*); 4.79 (br. *s*, H–C(1)); 4.69 (*d*, J = 11.8, PhC*H*); 4.61 (*d*, J = 12.0, PhC*H*); 4.51 (*d*, J = 11.6, PhC*H*); 4.48 (*d*, J = 12.1, PhC*H*); 4.23 (*dd*, J = 3.8, 10.0, H_{eq}–C(6)); 4.06 (*ddd*, J = 3.5, 9.5, 11.0, addn. of $D_2O \rightarrow$ *dd*, J = 3.5, 9.5, H–C(3)); 4.00 (*t*, J = 9.4, H–C(3′)); 3.99 (*ddd*, J = 2.0, 4.1, 10.1, H–C(5′)); 3.84 (*t*, J = 10.1, H_{ax}–C(6)); 3.82 (*dd*, J = 1.4, 3.9, H–C(2)); 3.80–3.74 (*m*, H–C(4), H–C(5)); 3.74 (*dd*, J = 4.2, 10.7, H–C(6′)); 3.65 (*dd*, J = 2.0, 10.6, H′–C(6′)); 3.615 (*dd*, J = 9.2, 10.0, H–C(4′)); 3.61 (*d*, J = 11.1, exchange with D_2O, OH–C(3)); 3.58 (*dd*, J = 3.8, 9.7, H–C(2′)); 3.28 (*s*, MeO). ^{13}C-NMR: 138.48 (*s*); 137.75 (*s*); 137.67 (*s*);

137.34 (*s*); 137.27 (*s*); 128.93–126.37 (*m*); 102.02 (*d*); 101.57 (*d*); 100.56 (*d*); 82.33 (*d*); 82.00 (*d*); 80.01 (*d*); 79.43 (*d*); 77.69 (*d*); 75.59 (*t*); 75.36 (*t*); 74.02 (*t*); 73.43 (*t*); 70.87 (*d*); 68.68 (*t*); 68.55 (*d*); 68.44 (*t*); 62.94 (*d*); 54.76 (*q*). CI-MS: 824 (17), 823 (53), 822 (100, $[M + NH_4]^+$), 540 (29), 432 (11), 431 (14), 416 (10), 415 (34), 325 (27), 324 (61), 307 (25), 283 (28), 253 (23), 217 (20), 216 (33), 198 (13), 187 (23), 181 (11), 108 (33), 91 (47). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.67, H 6.52.

*Methyl 4,6-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-α-*D*-mannopyranoside* (**63**). R_f (hexane/AcOEt 3:2) 0.36. Anal. HPLC: t_R 6.59. $[\alpha]_D^{25} = +1.6$ ($c = 0.5$, $CHCl_3$). IR: 3620*w* (br.), 3580–3300*w* (br.), 3060*w*, 3015*w* (sh), 3000*w*, 2985*w*, 2940*w* (sh), 2905*w*, 2885*w*, 1495*w*, 1465*w* (sh), 1450*w*, 1400*w* (sh), 1385*w* (sh), 1360*w*, 1305*w* (br.), 1280*w* (br.), 1245*w* (br.), 1200*w*, 1165*w* (sh), 1125*m* (sh), 1095*s* (sh), 1070*s*, 1030*m* (sh), 1010*w* (sh), 975*w* (sh), 915*w* (br.), 880*w* (br.), 710*w* (sh), 700*s*, 680*w* (br.). ^{1}H-NMR: 7.54–7.51 (*m*, 2 arom. H); 7.39–7.24 (*m*, 21 arom. H); 7.18–7.14 (*m*, 2 arom. H); 5.62 (*s*, PhC*H*); 4.96 (*d*, $J = 10.8$, 2 PhC*H*); 4.83 (*d*, $J = 11.0$, PhC*H*); 4.82 (*d*, $J = 10.8$, PhC*H*); 4.79 (*d*, $J = 1.4$, H–C(1)); 4.78 (*d*, $J = 10.6$, PhC*H*); 4.73 (*d*, $J = 12.1$, PhC*H*); 4.54 (*d*, $J = 11.7$, PhC*H*); 4.51 (*d*, $J = 12.3$, PhC*H*); 4.43 (*d*, $J = 7.8$, H–C(1′)); 4.33–4.27 (*m*, H_{eq}–C(6)); 4.08 (*dt*, $J = 3.4$, 9.5, addn. of $D_2O \rightarrow$*dd*, $J = 3.4$, 9.5, H–C(3)); 4.04 (*dd*, $J = 1.5$, 3.4, H–C(2)); 3.93–3.80 (*m*, H–C(4), H–C(5), H_{ax}–C(6)); 3.71 (*dd*, $J = 2.2$, 10.6, H–C(6′)); 3.70–3.61 (*m*, H–C(3′), H–C(4′), H′–C(6′)); 3.54–3.50 (*m*, H–C(5′)); 3.52 (*dd*, $J = 7.8$, 9.3, H–C(2′)); 3.48 (*d*, $J = 9.6$, exchange with D_2O, OH–C(3)); 3.36 (*s*, MeO). ^{13}C-NMR: 138.38 (*s*); 137.95 (*s*); 137.81 (*s*); 137.78 (*s*); 137.40 (*s*); 128.89–126.35 (*m*); 104.07 (*d*); 102.15 (*d*); 100.37 (*d*); 84.39 (*d*); 81.74 (*d*); 81.53 (*d*); 80.02 (*d*); 77.37 (*d*); 75.66 (*t*); 75.01 (*d* and 2*t*); 73.55 (*t*); 68.86 (*t*); 68.42 (*t*); 67.35 (*d*); 63.84 (*d*); 54.82 (*q*). CI-MS: 825 (6), 824 (23), 822 (100, $[M + NH_4]^+$), 732 (8). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.44, H 6.72.

*Methyl 4,6-*O*-Benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-mannopyranoside* (**64**) [40]. R_f (hexane/AcOEt 3:2) 0.24. Anal. HPLC: t_R 8.63. M.p. 125.5–126° (hexane/AcOEt). $[\alpha]_D^{25} = +68.8$ ($c = 0.5$, $CHCl_3$; [40]: +64 ($c = 0.1$)). IR: 3640–3540*w* (br.), 3540–3200*w* (br.), 3060*w*, 3020*w* (sh), 3000*m*, 2970*w* (sh), 2910*m*, 2860*w* (sh), 2840*w* (sh), 1950*w*, 1495*w*, 1455*w* (sh), 1450*m*, 1415*w* (sh), 1370*w* (sh), 1360*w*, 1320*w* (br.), 1240*w* (br.), 1200*w* (sh), 1160*m* (sh), 1130*s* (sh), 1100*s*, 1070*s*, 1050*s* (sh), 1030*s*, 1010*m* (sh), 980*m* (sh), 910*w*, 875*w*, 810*w*, 710*w* (sh), 700*s*, 680*w* (br.). ^{1}H-NMR: 7.42–7.40 (*m*, 2 arom. H); 7.36–7.27 (*m*, 16 arom. H); 7.22–7.12 (*m*, 5 arom. H); 7.01–6.99 (*m*, 2 arom. H); 5.52 (*s*, PhC*H*); 5.43 (*d*, $J = 3.8$, H–C(1′)); 4.98 (*d*, $J = 10.9$, PhC*H*); 4.83 (*d*, $J = 10.8$, PhC*H*); 4.78 (*d*, $J = 10.9$, PhC*H*); 4.69 (*d*, $J = 1.4$, H–C(1)); 4.61 (*d*, $J = 12.0$, PhC*H*); 4.57 (*d*, $J = 12.1$, PhC*H*); 4.49 (*d*, $J = 11.8$, PhC*H*); 4.46 (*d*, $J = 10.6$, PhC*H*); 4.38 (*d*, $J = 12.1$, PhC*H*); 4.30–4.17 (*m*, H–C(3), H–C(4), H_{eq}–C(6)); 4.06 (*q*, $J \approx 1.6$, addn. of $D_2O \rightarrow$*t*, $J \approx 1.4$, H–C(2)); 3.96 (*t*, $J = 9.3$, H–C(3′)); 3.93–3.83 (*m*, H–C(5), H_{ax}–C(6), H–C(5′)); 3.72 (*dd*, $J = 2.1$, 10.5, H–C(6′)); 3.67 (*dd*, $J = 4.6$, 10.5, H′–C(6′)); 3.55 (*t*, $J \approx 9.4$, H–C(4′)); 3.53 (*dd*, $J = 3.8$, 9.7, H–C(2′)); 3.38 (*s*, MeO); 2.89 (*d*, $J = 2.5$, exchange with D_2O, OH–C(2)). ^{13}C-NMR: 138.76 (*s*); 138.08 (*s*); 137.81 (2*s*); 137.45 (*s*); 129.15–126.26 (*m*); 102.24 (*d*); 101.40 (*d*); 97.14 (*d*); 81.41 (*d*); 79.06 (*d*); 78.70 (*d*); 77.56 (*d*); 75.53 (*t*); 75.15 (*t*); 73.58 (*d* and *t*); 71.21 (*t*); 71.04 (*d*); 70.77 (*d*); 68.98 (*t*); 68.79 (*t*); 63.44 (*d*); 54.93 (*q*). CI-MS: 825 (7), 822 (100, $[M + NH_4]^+$), 732 (6). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.60, H 6.65.

*Methyl 4,6-*O*-Benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-α-*D*-mannopyranoside* (**65**). R_f (hexane/AcOEt 3:2) 0.26. Anal. HPLC: t_R 7.62. M.p. 120–121° (hexane/AcOEt). $[\alpha]_D^{25} = +19.6$ ($c = 0.5$, $CHCl_3$). IR: 3610–3300*w* (br.), 3060*w*, 3015*w* (sh), 3000*w*, 2930*w* (sh), 2920*w*, 2865*w*, 1495*w*, 1465*w* (sh), 1450*w*, 1410–1340*w* (br.), 1310*w* (br.), 1280*w* (br.), 1250–1230*w* (br.), 1210*w*, 1200*w* (sh), 1135*m* (sh), 1120*s* (sh), 1095*s*, 1070*s*, 1030*m*, 980*w* (sh), 915*w* (br.), 860*w*, 700*s*, 680*w* (br.). ^{1}H-NMR: 7.47–7.44 (*m*, 2 arom. H); 7.35–7.25 (*m*, 21 arom. H); 7.17–7.15 (*m*, 2 arom. H); 5.55 (*s*, PhC*H*); 4.88 (*d*, $J = 11.0$, PhC*H*); 4.86 (*d*, $J = 11.2$, PhC*H*); 4.83 (*d*, $J = 10.5$, PhC*H*); 4.78 (*d*, $J = 10.8$, PhC*H*); 4.77 (*d*, $J = 10.4$, PhC*H*); 4.76 (*d*, $J = 1.4$, H–C(1)); 4.63 (*d*, $J = 7.8$, H–C(1′)); 4.56 (*d*, $J = 12.1$, PhC*H*); 4.55 (*d*, $J = 10.8$, PhC*H*); 4.50 (*d*, $J = 12.1$, PhC*H*); 4.29 (*dd*, $J = 3.2$, 9.9,

Table 9. *Selected ^{1}H-NMR* (400 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Disaccharides Derived from the Diols* **10–13**

	62	**63**[a])	**64**[a])	**65**[a])	**68**[a])	**69**[a])	**70**[a])	**71**[a])
H–C(1)	4.79	4.79	4.69	4.76	4.54	4.58	4.42	4.42
H–C(2)	3.82	4.04	4.06	4.09	4.34	4.51	4.15	4.17
H–C(3)	4.06	4.08	4.30–4.17	4.29	5.20	4.89	3.96	4.05
H–C(4)	3.80–3.74	3.93–3.80	4.30–4.17	4.30–4.23	4.27	4.12	4.21	4.13
H–C(5)	3.80–3.74	3.93–3.80	3.93–3.83	4.13	3.44	3.50	3.41	3.38
H_{eq}–C(6)	4.23	4.33–4.27	4.30–4.17	3.90–3.83	4.31	4.40	4.33	4.33

Table 9 (cont.)

	62	**63**[a])	**64**[a])	**65**[a])	**68**[a])	**69**[a])	**70**[a])	**71**[a])
H_{ax}–C(6)	3.84	3.93–3.80	3.93–3.83	3.90–3.83	3.87	3.82	3.89	3.87
MeO	3.28	3.36	3.38	3.40	3.49	3.51	3.55	3.57
PhC*H*	5.60	5.62	5.52	5.55	5.40	5.57	5.52	5.52
OH or AcO	3.66–3.56	3.48	2.89	3.08	2.05	2.08	3.52	3.63–3.55
H–C(1′)	4.82	4.43	5.43	4.63	5.36	4.66	5.38	4.66
H–C(2′)	3.58	3.52	3.53	3.54–3.49	3.68	3.55	3.52	3.52
H–C(3′)	4.00	3.70–3.61	3.96	3.67–3.57	4.10	3.66	4.02	3.64
H–C(4′)	3.615	3.70–3.61	3.55	3.67–3.57	3.73	3.72	3.52	3.63–3.55
H–C(5′)	3.99	3.54–3.50	3.93–3.83	3.36–3.33	4.35	3.38	4.00–3.95	3.39–3.32
H–C(6′)	3.66–3.56	3.71	3.72	3.67–3.57	3.81	3.74–3.68	3.70–3.62	3.63–3.55
H′–C(6′)	3.66–3.56	3.70–3.61	3.67	3.67–3.57	3.64	3.74–3.68	3.70–3.62	3.63–3.55
J(1,2)	1.4	1.4	1.4	1.4	0.9	0.7	< 1	1.0
J(2,3)	3.7	3.4	[b])	3.1	2.5	3.4	3.1	3.1
J(3,4)	9.5	9.5	[b])	9.8	10.4	10.5	9.8	9.5
J(4,5)	[b])	[b])	[b])	9.8	9.6	9.3	9.4	9.4
J(OH,H)	11.1	9.6	2.5	2.0	–	–	< 0.5	< 0.5
J(1′,2′)	3.9	7.8	3.8	7.8	3.8	7.7	3.8	7.7
J(2′,3′)	9.7	9.3	9.7	[b])	9.6	8.8	9.6	8.8
J(3′,4′)	9.2	[b])	9.4	[b])	9.2	8.8	9.3	8.8
J(4′,5′)	10.1	[b])	9.4	[b])	10.2	9.5	9.8	[b])

	58[a])	**59**[a])	**60**[a])	**61**	**72**	**73**[a])	**74**[a])	**75**[a])
H–C(1)	4.76	4.77	4.76	4.72	4.75[c])	4.61	4.71	4.67
H–C(2)	3.86	3.80	3.78	3.80	3.83	3.92	3.60	3.57
H–C(3)	4.04	4.23	4.08	3.62–3.55	4.00	4.11	4.02–3.93	4.03
H–C(4)	5.37	5.41	3.94	3.62–3.55	3.94–3.90	4.13	3.94	4.13
H–C(5)	3.87	3.90	3.73	3.77–3.69	3.94–3.90	3.97	4.02–3.93	4.03–3.99
H–C(6)	3.63	3.67	3.80–3.74	4.00–3.94	3.76	3.72–3.65	3.81	3.84
H′–C(6)	3.56	3.60	3.80–3.74	4.00–3.94	3.71	3.72–3.65	3.64	3.71
MeO	3.38	3.36	3.35	3.43	3.40	3.36	3.35	3.34
OH or AcO	1.77	1.95	4.445	3.98–3.97	3.45	2.89[d])	3.26	2.99
H–C(1′)	5.04	4.45	5.03	4.35	4.77[c])	4.735	4.90	4.76
H–C(2′)	3.52	3.39	3.54	3.43	3.58	3.53	3.54	3.50
H–C(3′)	4.00	3.69–3.60	3.97	3.77–3.69	4.01	3.66	3.96	3.71
H–C(4′)	3.58	3.69–3.60	3.61	3.77–3.69	3.75	3.61	3.56	3.66
H–C(5′)	4.00	3.40	3.79	3.45	4.05	3.47	4.01	3.42
H–C(6′)	3.51	3.78	3.55	3.67	3.59	3.65–3.57	3.60–3.53	3.69
H′–C(6′)	3.47	3.70	3.37	3.63	3.48	3.65–3.57	3.60–3.53	3.61
J(1,2)	2.2	2.1	1.7	1.8	3.6	3.7	3.7	3.6
J(2,3)	3.1	3.1	3.2	3.0	9.8	9.5	10.3	9.9
J(3,4)	9.2	9.5	9.4	[b])	3.1	3.4	2.6	3.3
J(4,5)	9.9	10.0	9.4	[b])	[b])	1.4	1.2	1.2
J(OH,H)	–	–	3.2	[b])	< 2	2.4	8.9	8.1
J(1′,2′)	3.4	7.7	3.6	7.8	3.7	7.7	3.7	8.0
J(2′,3′)	9.8	9.0	9.8	9.1	9.5	8.7	9.9	8.9
J(3′,4′)	9.2	[b])	9.1	[b])	9.1	9.0	9.1	9.1
J(4′,5′)	10.0	9.7	10.0	10.0	10.0	9.4	9.9	9.4

[a]) Assignments corroborated by selective irradiations.
[b]) Not determined.
[c]) Assignments may be interchanged.
[d]) $^4J(5,OH) = 1.4$ Hz.

Table 10. *Selected ^{13}C-NMR* (50.6 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of the Disaccharides Derived from the Diols* **11**–**13**

	11[a])	**62**	**63**	**64**	**65**	**12**	**68**	**69**	**70**	**71**
C(1)	101.31	101.57	100.37	101.40	101.26	101.26	101.48	101.88	101.45	101.35
C(2)	70.83	82.33[b])	77.37	71.21	69.37	70.70[b])	73.52[b])	73.94[b])	71.08	68.76
C(3)	68.54	68.55	81.53	73.58	75.39	70.82[b])	73.01[b])	71.41	77.97[b])	76.87[b])
C(4)	78.84	80.01	80.02	78.70[b])	77.86[b])	78.56	75.63	75.89	75.62	76.41[b])
C(5)	62.96	62.94	63.84	63.44	63.53	66.60	67.82	67.36	66.94	67.01
C(6)	68.78	68.68[c])	68.86[b])	68.98[c])	68.91[c])	68.45	68.42[c])	68.89[c])	68.72[c])	68.66[c])
MeO	55.00	54.76	54.82	54.93	54.96	57.19	57.39	57.32	57.29	57.23
Ph*C*H	102.23	102.02	102.15	102.24	101.86	102.01	101.84	102.16	102.22	101.69
AcO	–	–	–	–	–	–	169.79, 20.93	170.96, 20.89	–	–
C(1′)	–	100.56	104.07	97.14	100.18	–	96.78	104.15	97.50	100.26
C(2′)	–	79.43	81.74	79.06[b])	81.77	–	80.50	82.24	78.76	81.72
C(3′)	–	82.00[b])	84.39	81.41	85.09	–	81.52	84.64	81.36	84.78
C(4′)	–	77.69	77.37	77.56	77.01[b])	–	77.54	77.37	77.48[b])	77.66
C(5′)	–	70.87	67.37	70.77	75.08	–	70.12	74.13[b])	70.68	75.05
C(6′)	–	68.44[c])	68.42[b])	68.79[c])	68.53[c])	–	68.27[c])	68.84[c])	68.64[c])	68.58[c])

	13[a])	**72**	**73**	**74**	**75**
C(1)	97.92	97.23	98.24	98.31	98.10
C(2)	76.63	74.74[b])	77.62	77.08[b])	77.92[b])
C(3)	69.32	74.62[b])	75.85	69.41	69.05
C(4)	69.75	65.75	69.10	81.58[c])	78.09[b])
C(5)	68.31	68.01	68.37	69.68	70.38
C(6)	69.86	69.44	69.80	69.41	70.38
MeO	55.27	55.13	55.16	55.24	55.23
C(1′)	–	94.33	103.37	100.11	103.80
C(2′)	–	79.04	81.82	79.91	82.09
C(3′)	–	82.27	84.27	81.98[c])	84.78
C(4′)	–	77.58	78.01	77.87[b])	77.92[b])
C(5′)	–	70.53	74.35	71.55	74.89
C(6′)	–	67.86	68.71	68.50	68.85

[a]) Assignments based upon a $^1H,^{13}C$ inverse-correlated spectrum.
[b][c]) Assignments may be reversed.

H–C(3)); 4.30–4.23 (*m*, H–C(4)); 4.13 (*dt*, $J \approx 4.6, 9.8$, H–C(5)); 4.09 (*td*, $J = 1.7, 3.2$, addn. of $D_2O \rightarrow$ *dd*, $J = 1.5, 3.2$, H–C(2)); 3.90–3.83 (*AB* of *ABX*, 2 H–C(6)); 3.67 (*m*, 4 H); 3.54–3.49 (*m*, H–C(2′)); 3.40 (*s*, MeO); 3.36–3.33 (*m*, H–C(5′)); 3.08 (*d*, $J = 2.0$, exchange with D_2O, OH–C(2)). ^{13}C-NMR: 138.46 (*s*); 138.12 (*s*); 138.04 (2*s*); 137.52 (*s*); 128.90–126.24 (*m*); 101.86 (*d*); 101.26 (*d*); 100.18 (*d*); 85.09 (*d*); 81.77 (*d*); 77.86 (*d*); 77.01 (*d*); 75.52 (*t*); 75.39 (*d*); 75.08 (*d* and *t*); 74.92 (*t*); 73.55 (*t*); 69.37 (*d*); 68.91 (*t*); 68.53 (*t*); 63.53 (*d*); 54.96 (*q*). CI-MS: 825 (8), 824 (24), 822 (100, $[M + NH_4]^+$). Anal. calc. for $C_{48}H_{52}O_{11}$ (804.94): C 71.62, H 6.51; found: C 71.54, H 6.64.

Glycosidation of **12** *with* **1**. A mixture **12** (47.3 mg, 0.168 mmol) and **1** (120 mg, 0.218 mmol) in $ClCH_2CH_2Cl$ (4 ml) was kept for 5 h at 22°. Evaporation and FC (hexane/AcOEt 4:1 and then 7:3) gave **66**/**67** (55 mg, 41%) and **68**/**69** (60.2 mg, 44%). The mixture **66**/**67** was acetylated in Ac_2O/pyridine 1:1 (1 ml) to give, after evaporation and FC (hexane/Et_2O 1:1), **70** (30.7 mg, 53%) and **71** (27 mg, 47%). FC of **68**/**69** (CH_2Cl_2/MeOH 99.5:0.5) gave **68** (33.6 mg, 29%) and **69** (26 mg, 23%).

Glycosidation of **12** *with* **3**. Under Ar, a mixture of **12** (30 mg, 0.11 mmol) and powdered 4-Å molecular sieves (50 mg) in CH_2Cl_2 (2 ml) was stirred for 30 min at r.t., cooled to −30°, treated with a soln. of **3** (80.1 mg, 0.12 mmol) in CH_2Cl_2 (2 ml) and then with a soln. of $BF_3 \cdot Et_2O$ (14 µl, 0.12 mmol) in CH_2Cl_2 (1 ml). After stirring for 30 min and addition of Et_3N (0.1 ml), filtration through *Celite*, evaporation, and separation, as described above, gave **70** (3.9 mg, 5%; after acetylation), **71** (32 mg, 37%; after acetylation), **68** (3.4 mg, 4%), and **69** (38.7 mg, 45%).

Methyl 4,6-O-Benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-mannopyranoside (**68**). R_f (CH_2Cl_2/MeOH 99:1) 0.20. Anal. HPLC: t_R 6.71. M.p. 155° (hexane/AcOEt). $[\alpha]_D^{25} = +11.0$ ($c = 0.5$, $CHCl_3$). IR: 3570*w*, 3480*w* (br.), 3060*w* (sh), 3030*w* (sh), 3000*m*, 2900*m*, 2860*m*, 1495*m*, 1465*m* (sh), 1450*s*, 1380*m*, 1355*m*, 1325*w*, 1310*m*, 1260*w*, 1235*m*, 1200*m*, 1160*s*, 1140*s* (sh), 1090*s*, 1065*s*, 1025*s*, 1000*s* (sh), 965*m* (sh), 910*m*, 870*w*, 750*s* (br.), 700*s*, 660*m*. ^{1}H-NMR: 7.42–7.40 (*m*, 2 arom. H); 7.35–7.24 (*m*, 16 arom. H); 7.20–7.10 (*m*, 5 arom. H); 6.98–6.96 (*m*, 2 arom. H); 5.52 (*s*, PhC*H*); 5.38 (*d*, $J = 3.8$, H–C(1′)); 4.99 (*d*, $J = 10.9$, PhC*H*); 4.83 (*d*, $J = 10.9$, PhC*H*); 4.78 (*d*, $J = 10.9$, PhC*H*); 4.58 (*d*, $J = 12.3$, PhC*H*); 4.57 (*d*, $J = 12.0$, PhC*H*); 4.48 (*d*, $J = 11.8$, PhC*H*); 4.46 (*d*, $J = 10.6$, PhC*H*); 4.42 (br. *s*, H–C(1)); 4.38 (*d*, $J = 12.3$, PhC*H*); 4.33 (*dd*, $J = 3.9$, 10.4, H_{eq}–C(6)); 4.21 (*t*, $J \approx 9.4$, H–C(4)); 4.15 (br. *d*, $J = 2.9$, H–C(2)); 4.02 (*t*, $J = 9.3$, H–C(3′)); 4.00–3.95 (*m*, H–C(5′)); 3.96 (*dd*, $J = 3.2$, 9.8, H–C(3)); 3.89 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.70–3.62 (*m*, 2 H–C(6′)); 3.55 (*s*, MeO); 3.52 (*t*, $J = 9.6$, H–C(4′)); 3.52 (*dd*, $J = 3.8$, 9.6, H–C(2′)); 3.52 (br. *s*, exchange with D_2O, OH–C(2)); 3.41 (*dt*, $J = 5.1$, 9.7, H–C(5)). ^{13}C-NMR: 138.76 (*s*); 138.08 (*s*); 137.80 (2*s*); 137.22 (*s*); 129.20–126.29 (*m*); 102.22 (*d*); 101.45 (*d*); 97.50 (*d*); 81.36 (*d*); 78.76 (*d*); 77.97 (*d*); 77.48 (*d*); 75.62 (*d* and *t*); 75.03 (*t*); 73.47 (*t*); 71.08 (*d*); 71.01 (*t*); 70.68 (*d*); 68.72 (*t*); 68.64 (*t*); 66.94 (*d*); 57.29 (*q*). CI-MS: 824 (16), 823 (52), 822 (100, $[M + NH_4]^+$), 733 (9), 732 (23), 716 (7), 558 (10), 556 (6), 300 (20), 283 (8), 108 (16), 106 (17).

Methyl 4,6-O-Benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-β-D-mannopyranoside (**69**). R_f (CH_2Cl_2/MeOH 99:1) 0.27. Anal. HPLC: t_R 5.62. M.p. 124–125° (hexane/AcOEt). $[\alpha]_D^{25} = -29.2$ ($c = 0.5$, $CHCl_3$). IR: 3600–3400*w* (br.), 3080*w* (sh), 3060*w* (sh), 3000*w*, 2940*w* (sh), 2900*w*, 2860*w*, 1495*w*, 1450*w*, 1385*w* (br.), 1355*w* (br.), 1305*w*, 1295*s* (sh), 1270*w* (sh), 1240*m* (sh), 1215*m* (sh), 1190*s*, 1165*s* (sh), 1025*m*, 1010*m* (sh), 990*m* (sh), 960*w* (sh), 910*w*, 865*w*, 700*s*, 660*w*. ^{1}H-NMR: 7.46–7.44 (*m*, 2 arom. H); 7.33–7.25 (*m*, 21 arom. H); 7.17–7.14 (*m*, 2 arom. H); 5.52 (*s*, PhC*H*); 4.95 (*d*, $J = 11.1$, PhC*H*); 4.89 (*d*, $J = 11.0$, PhC*H*); 4.80 (*d*, $J = 10.5$, PhC*H*); 4.77 (*d*, $J = 10.8$, 2 PhC*H*); 4.66 (*d*, $J = 7.7$, H–C(1′)); 4.54 (*d*, $J = 12.1$, PhC*H*); 4.53 (*d*, $J = 10.8$, PhC*H*); 4.49 (*d*, $J = 12.1$, PhC*H*); 4.42 (*d*, $J = 1.0$, H–C(1)); 4.33 (*dd*, $J = 4.9$, 10.5, H_{eq}–C(6)); 4.17 (br. *dd*, $J = 1.0$, 3.2, H–C(2)); 4.13 (*t*, $J = 9.4$, H–C(4)); 4.05 (*dd*, $J = 3.1$, 9.6, H–C(3)); 3.87 (*t*, $J = 10.4$, H_{ax}–C(6)); 3.64 (*t*, $J = 8.8$, H–C(3′)); 3.63–3.55 (*m*, 4 H, 1 H exchange with D_2O); 3.57 (*s*, MeO); 3.52 (*dd*, $J = 7.7$, 8.8, H–C(2′)); 3.38 (*dt*, $J = 4.8$, 9.6, H–C(5)); 3.39–3.32 (*m*, H–C(5′)). ^{13}C-NMR: 138.44 (*s*); 138.18 (*s*); 138.11 (*s*); 137.93 (*s*); 137.30 (*s*); 128.85–126.12 (*m*); 101.69 (*d*); 101.35 (*d*); 100.26 (*d*); 84.78 (*d*); 81.72 (*d*); 77.66 (*d*); 76.87 (*d*); 76.41 (*d*); 75.41 (*t*); 75.05 (*d*); 74.86 (*t*); 74.74 (*t*); 73.37 (*t*); 68.76 (*d*); 68.66 (*t*); 68.58 (*t*); 67.01 (*d*); 57.23 (*q*). CI-MS: 824 (16), 823 (52), 822 (100, $[M + NH_4]^+$), 732 (13), 556 (6), 300 (15), 108 (11), 106 (13).

Methyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-mannopyranoside (**70**). R_f (hexane/AcOEt 7:3) 0.23. Anal. HPLC: t_R 8.63. $[\alpha]_D^{25} = +5.0$ ($c = 0.5$, $CHCl_3$). IR: 3080*w* (sh), 3060*w* (sh), 3030*w* (sh), 3000*m*, 2930*m*, 2860*m*, 1735*m*, 1495*w*, 1465*w* (sh), 1400*m*, 1390*m* (sh), 1365*m*, 1330*w*, 1310*w*, 1240*m*, 1195*w* (sh), 1180*m* (sh), 1160*m* (sh), 1135*m* (sh), 1090*s*, 1065*s*, 1045*s*, 1025*s*, 1005*s* (sh), 910*m*, 700*s*, 640*w*. ^{1}H-NMR: 7.47–7.17 (*m*, 25 arom. H); 5.40 (*s*, PhC*H*); 5.36 (*d*, $J = 3.8$, H–C(1′)); 5.20 (*dd*, $J = 2.5$, 10.4, H–C(3)); 4.98 (*d*, $J = 10.9$, PhC*H*); 4.89 (*d*, $J = 10.8$, PhC*H*); 4.87 (*d*, $J = 11.1$, PhC*H*); 4.84 (*d*, $J = 11.0$, PhC*H*); 4.69 (*d*, $J = 10.7$, PhC*H*); 4.67 (*d*, $J = 12.1$, PhC*H*); 4.54 (*d*, $J = 10.8$, PhC*H*); 4.54 (*d*, $J = 0.9$, H–C(1)); 4.49 (*d*, $J = 12.1$, PhC*H*); 4.35 (*td*, $J = 2.5$, 10.3, H–C(5′)); 4.34 (br. *d*, $J = 2.8$, H–C(2)); 4.31 (*dd*, $J = 4.8$, 10.4, H_{eq}–C(6)); 4.27 (*dd*, $J = 9.4$, 10.3, H–C(4)); 4.10 (*t*, $J = 9.4$, H–C(3′)); 3.87 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.81 (*dd*, $J = 2.9$, 10.7, H–C(6′)); 3.73 (*dd*, $J = 9.2$, 10.1, H–C(4′)); 3.68 (*dd*, $J = 3.9$, 9.6, H–C(2′)); 3.64 (*dd*, $J = 2.1$, 10.6, H′–C(6′)); 3.49 (*s*, MeO); 3.44 (*dt*, $J = 4.8$, 10.2, H–C(5)); 2.05 (*s*, Ac). ^{13}C-NMR: 169.79 (*s*); 138.96 (*s*); 138.51 (*s*); 138.42 (*s*); 138.07 (*s*); 137.25 (*s*); 129.00–126.11 (*m*); 101.84 (*d*); 101.48 (*d*); 96.78 (*d*); 81.52 (*d*); 80.50 (*d*); 77.54 (*d*); 75.63 (*d*); 75.54 (*t*); 74.89 (*t*); 73.52 (*d*); 73.36 (*t*); 73.01 (*d*); 72.41 (*t*); 70.12 (*d*); 68.42 (*t*); 68.27 (*t*); 67.82 (*d*); 57.39 (*q*); 20.93 (*q*). CI-MS: 869 (100, $[M + Na]^+$).

Methyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-β-D-mannopyranoside (**71**). R_f (hexane/AcOEt 7:3) 0.28. Anal. HPLC: t_R 8.63. $[\alpha]_D^{25} = -59.2$ ($c = 0.5$, $CHCl_3$). IR: 3060*m* (sh), 3000*m* (sh), 2930*m* (sh), 2900*s* (sh), 2860*s*, 1730*s*, 1500*m*, 1450*s*, 1370*s* (sh), 1360*s* (sh), 1330*m* (sh), 1300*m*, 1260*s* (br.), 1180*m* (sh), 1090*s*, 1060*s*, 1025*s* (sh), 1000*s* (sh), 960*s* (sh), 910*m*, 890*m*, 830*w*, 810*w*, 700*s*, 660*w*. ^{1}H-NMR: 7.50–7.45 (*m*, 3 arom. H); 7.40–7.25 (*m*, 20 arom. H); 7.17–7.14 (*m*, 2 arom. H); 5.57 (*s*, PhC*H*); 5.21 (*d*, $J = 10.6$, PhC*H*); 5.00 (*d*, $J = 11.0$, PhC*H*); 4.89 (*dd*, $J = 3.4$, 10.5, H–C(3)); 4.83 (*d*, $J = 10.9$, PhC*H*); 4.78 (*d*, $J = 11.0$, PhC*H*); 4.70 (*d*, $J = 10.5$, PhC*H*); 4.66 (*d*, $J = 7.7$, H–C(1′)); 4.58 (*d*, $J = 0.7$, H–C(1)); 4.53 (*d*, $J = 11.9$, PhC*H*); 4.53 (*d*, $J = 10.5$, PhC*H*); 4.51 (*d*, $J = 3.4$, H–C(2)); 4.45 (*d*, $J = 11.8$, PhC*H*); 4.40 (*dd*, $J = 4.8$, 10.4, H_{eq}–C(6)); 4.12 (*dd*, $J = 9.3$, 10.5, H–C(4)); 3.82 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.74–3.68 (*m*, 2 H–C(6′)); 3.72 (*t*, $J = 9.4$, H–C(4′)); 3.66 (*t*, $J \approx 8.8$, H–C(3′)); 3.55 (*dd*, $J = 7.8$, 8.9, H–C(2′)); 3.51 (*s*, MeO); 3.50 (*dt*, $J = 4.8$, 9.8, H–C(5)); 3.38 (*ddd*, $J = 2.1$, 3.4, 9.5, H–C(5′)); 2.08 (*s*, Ac). ^{13}C-NMR: 170.96 (*s*); 138.89 (2*s*); 138.26 (*s*); 137.76 (*s*); 137.10 (*s*); 129.23–126.16 (*m*); 104.15 (*d*); 102.16 (*d*); 101.88 (*d*); 84.64 (*d*); 82.24 (*d*); 77.37 (*d*); 75.89 (*d*);

75.62 (*t*); 74.88 (*t*); 74.27 (*t*); 74.13 (*d*); 73.94 (*d*); 73.14 (*t*); 71.41 (*d*); 68.89 (*t*); 68.84 (*t*); 67.36 (*d*); 57.32 (*q*); 20.89 (*q*). CI-MS: 869 (100, $[M + Na]^+$).

Glycosidation of **13** *with* **1**. A soln. of **13** (88 mg, 0.24 mmol) and **1** (100 mg, 0.18 mmol) in 1,4-dioxane (2 ml) was stirred for 5 h at r.t. Evaporation and FC (hexane/AcOEt 4:1 and 3:2) gave **72**/**73** (80.3 mg, 49%) and **74**/**75** (28.4 mg, 18%). Prep. HPLC (CH_2Cl_2/AcOEt 97:3, 16 ml/min) of **72**/**73** afforded **72** (40.8 mg, 25%) and **73** (39.2 mg, 24%). Similarly, prep. HPLC (hexane/AcOEt 65:35, 16 ml/min) of **74**/**75** afforded **74** (11.1 mg, 7%) and **75** (17.3 mg, 11%).

Glycosidation of **13** *with* **2**. A suspension of **13** (74.8 mg, 0.2 mmol), Et_4NBr (42 mg, 0.2 mmol), and powdered 4-Å molecular sieves (100 mg) in CH_2Cl_2 (4 ml) was stirred under Ar for 30 min and treated with a soln. of **2** (168 mg, 0.28 mmol) in CH_2Cl_2 (2 ml). After stirring for 2 days at r.t., filtration through *Celite*, FC, and prep. HPLC (as described above) gave **72** (73.8 mg, 41%), **73** (47.2 mg, 26%), **74** (12.6 mg, 7%), and **75** (1.4 mg, *ca.* 1%).

Glycosidation of **13** *with* **3**. A mixture of **13** (30 mg, 0.11 mmol) and powdered 4-Å molecular sieves (50 mg) in CH_2Cl_2 (2 ml) was stirred for 30 min at r.t. under Ar, cooled to −30°, and treated with a soln. of **3** (80.1 mg, 0.12 mmol) in CH_2Cl_2 (2 ml) and then with a soln. of $BF_3 \cdot Et_2O$ (14 µl, 0.12 mmol) in CH_2Cl_2 (1 ml). After stirring for 30 min and addition of Et_3N (0.1 ml), filtration through *Celite*, evaporation, FC, and HPLC (as described above) gave **72** (25 mg, 28%), **73** (36 mg, 40%), **74** (3.1 mg, 4%), and **75** (12.6 mg, 14%).

*Methyl 2,6-Di-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**72**) [36]. R_f (hexane/AcOEt 7:3) 0.19. Anal. HPLC: t_R 3.56. $[\alpha]_D^{25} = +69.2$ ($c = 0.5$, $CHCl_3$). IR: 3650*w* (br.), 3480*w* (br.), 3080*w* (sh), 3060*w*, 3030*w* (sh), 3000*w*, 2920*m*, 2860*w*, 1500*w*, 1450*m*, 1360*m*, 1330*w* (br.), 1250*w* (br.), 1200*w* (br.), 1150*m* (sh), 1090*s*, 1070*s* (sh), 1045*s* (sh), 1040*s* (sh), 1000*m* (sh), 970*w* (sh), 910*w* (br.), 860*w* (br.), 835*w* (br.), 700*s*, 665*w* (br.). ^{1}H-NMR: 7.39–7.15 (*m*, 30 arom. H); 4.93 (*d*, $J = 11.0$, PhC*H*); 4.90 (*d*, $J = 11.0$, PhC*H*); 4.84 (*d*, $J = 11.0$, PhC*H*); 4.82 (*d*, $J = 11.8$, PhC*H*); 4.77 (*d*, $J = 3.7$, H–C(1′)); 4.75 (*d*, $J = 3.6$, H–C(1)); 4.67 (*d*, $J = 12.0$, PhC*H*); 4.66 (*d*, $J = 11.6$, PhC*H*); 4.64 (*d*, $J = 12.6$, PhC*H*); 4.59 (*d*, $J = 11.9$, 2 PhC*H*); 4.57 (*d*, $J = 11.9$, PhC*H*); 4.52 (*d*, $J = 11.1$, PhC*H*); 4.35 (*d*, $J = 12.0$, PhC*H*); 4.05 (*td*, $J = 2.2$, 10.0, H–C(5′)); 4.01 (*t*, $J = 9.3$, H–C(3′)); 4.00 (*dd*, $J = 3.1$, 9.8, H–C(3)); 3.94–3.90 (*m*, H–C(4), H–C(5)); 3.83 (*dd*, $J = 3.6$, 9.8, H–C(2)); 3.76 (*dd*, $J = 4.6$, 10.0, H–C(6)); 3.75 (*dd*, $J = 9.1$, 10.0, H–C(4′)); 3.71 (*dd*, $J = 6.7$, 10.0, H′–C(6)); 3.59 (*dd*, $J = 2.6$, 10.9, H–C(6′)); 3.58 (*dd*, $J = 3.7$, 9.5, H–C(2′)); 3.48 (*dd*, $J = 2.0$, 10.9, H′–C(6′)); 3.45 (br. *s*, exchange with D_2O, OH–C(4)); 3.40 (*s*, MeO). ^{13}C-NMR: 138.55 (*s*); 138.48 (*s*); 138.12 (*s*); 137.88 (*s*); 137.80 (*s*); 137.46 (*s*); 128.46–127.37 (*m*); 97.93 (*d*); 94.33 (*d*); 82.27 (*d*); 79.04 (*d*); 77.58 (*d*); 75.46 (*t*); 74.74 (*d*); 74.71 (*t*); 74.62 (*d*); 74.25 (*t*); 73.45 (*t*); 73.30 (*t*); 73.11 (*t*); 70.53 (*d*); 69.44 (*t*); 68.01 (*d*); 67.86 (*t*); 65.75 (*d*); 55.13 (*q*). CI-MS: 916 (19), 915 (61), 914 (100, $[M + NH_4]^+$), 324 (10), 307 (12), 108 (22), 91 (16). Anal. calc. for $C_{55}H_{60}O_{11}$ (897.03): C 73.64, H 6.74; found: C 73.64, H 6.52.

*Methyl 2,6-Di-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**73**). R_f (hexane/AcOEt 7:3) 0.17. Anal. HPLC: t_R 4.43. M.p. 136° (hexane/AcOEt). $[\alpha]_D^{25} = +26.0$ ($c = 0.5$, $CHCl_3$). IR: 3660*w*, 3540*w* (br.), 3060*w*, 3030*w* (sh), 3000*w*, 2910*m*, 2870*w* (sh), 1500*w*, 1450*m*, 1400*w* (sh), 1360*m*, 1300*w*, 1240*w*, 1195*w*, 1150*m* (sh), 1095*s*, 1070*s* (sh), 1050*s* (sh), 1040*m* (sh), 970*w* (sh), 910*w* (sh), 830*w* (br.), 700*s*, 670*w* (sh), 660*w*. ^{1}H-NMR: 7.34–7.22 (*m*, 28 arom. H); 7.20–7.16 (*m*, 2 arom. H); 5.05 (*d*, $J = 11.4$, PhC*H*); 4.92 (*d*, $J = 11.0$, PhC*H*); 4.82 (*d*, $J = 10.9$, PhC*H*); 4.78 (*d*, $J = 11.3$, PhC*H*); 4.75 (*d*, $J = 11.5$, PhC*H*); 4.735 (*d*, $J = 7.6$, H–C(1′)); 4.73 (*d*, $J = 12.6$, PhC*H*); 4.61 (*d*, $J = 3.7$, H–C(1)); 4.57 (*d*, $J = 12.0$, PhC*H*); 4.54 (*d*, $J = 11.9$, PhC*H*); 4.53 (*d*, $J = 12.1$, PhC*H*); 4.50 (*d*, $J = 11.8$, PhC*H*); 4.50 (*d*, $J = 12.7$, PhC*H*); 4.46 (*d*, $J = 12.1$, PhC*H*); 4.13 (*dt*, $J = 1.4$, 3.0, addn. of D_2O→*dd*, $J = 1.4$, 3.0, H–C(4)); 4.11 (*dd*, $J = 3.4$, 9.5, H–C(3)); 3.97 (br. *tt*, $J = 1.4$, 5.9, addn. of D_2O→br. *dt*, $J = 1.4$, 5.9, H–C(5)); 3.92 (*dd*, $J = 3.7$, 9.5, H–C(2)); 3.72–3.65 (*m*, 2 H–C(6)); 3.66 (*t*, $J \approx 9.0$, H–C(3′)); 3.61 (*t*, $J \approx 9.0$, H–C(4′)); 3.65–3.57 (*m*, 2 H–C(6′)); 3.53 (*dd*, $J = 7.7$, 8.7, H–C(2′)); 3.47 (*ddd*, $J = 2.6$, 4.4, 9.4, H–C(5′)); 3.36 (*s*, MeO); 2.89 (*dd*, $J = 1.4$, 2.4, exchange with D_2O, OH–C(4)). ^{13}C-NMR: 138.48 (*s*); 138.41 (*s*); 138.27 (*s*); 138.19 (*s*); 138.00 (*s*); 137.84 (*s*); 128.25–127.26 (*m*); 103.37 (*d*); 98.24 (*d*); 84.65 (*d*); 81.82 (*d*); 78.01 (*d*); 77.62 (*d*); 75.85 (*d*); 75.54 (*t*); 74.88 (*t*); 74.46 (*t*); 74.35 (*d*); 73.43 (*t*); 73.37 (2*t*); 69.80 (*t*); 69.10 (*d*); 68.71 (*t*); 68.37 (*d*); 55.16 (*q*). CI-MS: 916 (20), 915 (59), 914 (100, $[M + NH_4]^+$), 540 (11), 360 (14), 324 (14), 307 (15), 216 (14), 198 (11), 108 (36). Anal. calc. for $C_{55}H_{60}O_{11}$ (897.03): C 73.64, H 6.74; found: C 73.69, H 7.00.

*Methyl 2,6-Di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**74**) [36]. R_f (hexane/AcOEt 1:1) 0.29. Anal. HPLC: t_R 5.96. M.p. 127° (hexane/AcOEt). $[\alpha]_D^{25} = +47.2$ ($c = 0.5$, $CHCl_3$). IR: 3660*w*, 3580*w* (sh), 3460*w* (br.), 3060*w*, 3030*w* (sh), 3000*m*, 2920*m* (br.), 2870*m*, 2100*w*, 1940*w*, 1820*w*, 1580*w*, 1500*w*, 1470*w* (sh), 1455*m*, 1400*w* (sh), 1360*m*, 1240*w* (br.), 1190*w* (sh), 1150*m* (sh), 1135*m* (sh), 1090*s*, 1050*s* (sh), 1030*s* (sh), 1010*m* (sh), 940*w* (sh), 910*w*, 860*w*, 700*s*, 670*w* (sh), 660*w*. ^{1}H-NMR: 7.35–7.00 (*m*, 30 arom. H); 4.92 (*d*, $J = 11.0$, PhC*H*); 4.90 (*d*, $J \approx 3.9$, H–C(1′)); 4.83 (*d*, $J = 10.7$, PhC*H*); 4.82 (*d*, $J = 11.0$, PhC*H*); 4.76 (*d*, $J = 11.3$, PhC*H*); 4.72 (*d*, $J = 10.7$, PhC*H*); 4.71 (*d*, $J \approx 4.0$, H–C(1)); 4.63 (*d*, $J = 12.3$, PhC*H*); 4.62 (*d*, $J = 11.9$,

PhC*H*); 4.58 (*d*, *J* = 12.2, PhC*H*); 4.47 (*d*, *J* = 10.7, PhC*H*); 4.46 (*d*, *J* = 12.3, PhC*H*); 4.36 (*d*, *J* = 12.1, PhC*H*); 4.30 (*d*, *J* = 12.1, PhC*H*); 4.02 (*ddd*, *J* = 2.5, 4.2, 10.1, H–C(5')); 4.02–3.93 (*m*, H–C(3), H–C(5)); 3.96 (*t*, *J* ≈ 9.5, H–C(3')); 3.94 (*dd*, *J* = 1.2, 2.6, H–C(4)); 3.81 (*dd*, *J* = 5.4, 10.3, H–C(6)); 3.64 (*dd*, *J* = 6.8, 10.3, H'–C(6)); 3.60 (*dd*, *J* = 3.7, 10.3, H–C(2)); 3.60–3.53 (*m*, 2 H–C(6')); 3.56 (*dd*, *J* = 9.0, 9.8, H–C(4')); 3.54 (*dd*, *J* = 3.6, 9.9, H–C(2')); 3.35 (*s*, MeO); 3.26 (*d*, *J* = 8.9, exchange with D_2O, OH–C(3)). ^{13}C-NMR: 138.62 (*s*); 138.44 (*s*); 138.34 (*s*); 138.07 (*s*); 138.04 (*s*); 137.67 (*s*); 128.37–127.26 (*m*); 100.11 (*d*); 98.31 (*d*); 81.98 (*d*); 81.58 (*d*); 79.91 (*d*); 77.87 (*d*); 77.08 (*d*); 75.57 (*t*); 75.15 (*t*); 73.63 (*t*); 73.54 (*t*); 72.97 (2*t*); 71.55 (*d*); 69.68 (*d*); 69.41 (*d* and *t*); 68.50 (*t*); 55.24 (*q*). CI-MS: 916 (19), 915 (60), 914 (100, $[M + NH_4]^+$), 600 (21), 573 (14), 541 (16), 540 (38), 450 (17), 415 (16), 360 (16), 325 (17), 324 (42), 308 (12), 307 (59), 217 (18), 216 (38), 198 (19), 187 (15), 108 (62), 91 (21).

*Methyl 2-6-Di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-α-*D*-galactopyranoside* (**75**) [36]. R_f (hexane/AcOEt 1:1) 0.38. Anal. HPLC: t_R 4.98. M.p. 112° (hexane/AcOEt). $[\alpha]_D^{25}$ = +22.2 (*c* = 0.5, $CHCl_3$). IR: 3650*w*, 3570*w* (sh), 3450*w* (br.), 3060*w* (sh), 3030*w* (sh), 3000*w*, 2910*m*, 2870*m*, 2100*w*, 1940*w*, 1820*w*, 1500*m*, 1470*w* (sh), 1400*m*, 1395*w* (sh), 1360*m*, 1310*w*, 1280*w* (sh), 1240*w* (br.), 1190*w*, 1150*m* (sh), 1100*s* (sh), 1085*s* (sh), 1070*s*, 1045*s* (sh), 1030*s* (sh), 1000*m* (sh), 970*w* (sh), 950*w* (sh), 910*w*, 885*w*, 865*w*, 830*w* (br.), 700*s*, 670*w* (br.), 660*w*. ^{1}H-NMR: 7.38–7.13 (*m*, 30 arom. H); 4.97 (*d*, *J* = 11.8, PhC*H*); 4.92 (*d*, *J* = 11.8, PhC*H*); 4.82 (*s*, PhCH_2); 4.80 (*d*, *J* = 11.0, PhC*H*); 4.76 (*d*, *J* = 7.9, H–C(1')); 4.67 (*d*, *J* = 3.6, H–C(1)); 4.57 (*d*, *J* = 10.9, PhC*H*); 4.54 (*d*, *J* = 12.2, PhC*H*); 4.51 (*d*, *J* = 12.6, PhC*H*); 4.50 (*d*, *J* = 12.0, PhC*H*); 4.42 (*d*, *J* = 12.5, PhC*H*); 4.39 (*d*, *J* = 12.3, PhC*H*); 4.21 (*d*, *J* = 11.9, PhC*H*); 4.13 (*dd*, *J* = 1.2, 3.3, H–C(4)); 4.03 (*ddd*, *J* = 3.9, 8.1, 10.9, addn. of $D_2O \rightarrow$*dd*, *J* = 3.9, 10.0, H–C(3)); 4.03–3.99 (*m*, H–C(5)); 3.84 (*dd*, *J* = 4.6, 10.5, H–C(6)); 3.71 (*dd*, *J* = 7.0, 10.6, H'–C(6)); 3.71 (*t*, *J* = 9.1, H–C(3')); 3.69 (*dd*, *J* = 4.0, 10.9, H–C(6')); 3.66 (*t*, *J* = 9.1, H–C(4')); 3.61 (*dd*, *J* = 2.0, 10.9, H'–C(6')); 3.57 (*dd*, *J* = 3.7, 9.9, H–C(2)); 3.50 (*dd*, *J* = 8.1, 8.9, H–C(2')); 3.42 (*ddd*, *J* = 2.0, 4.0, 9.4, H–C(5')); 3.34 (*s*, MeO); 2.99 (*d*, *J* = 8.1, exchange with D_2O, OH–C(3)). ^{13}C-NMR: 138.57 (*s*); 138.30 (2*s*); 138.11 (*s*); 138.07 (2*s*); 128.56–126.97 (*m*); 103.80 (*d*); 98.10 (*d*); 84.98 (*d*); 82.09 (*d*); 78.09 (*d*); 77.92 (2*d*); 75.52 (*t*); 74.89 (*d* and *t*); 74.66 (*t*); 73.42 (*t*); 73.13 (*t*); 72.95 (*t*); 70.38 (*d* and *t*); 69.05 (*d*); 68.85 (*t*); 55.23 (*q*). CI-MS: 916 (21), 915 (61), 914 (100, $[M + NH_4]^+$), 600 (20), 540 (19), 451 (11), 324 (20), 307 (17), 217 (13), 216 (21), 212 (32), 198 (16), 182 (33), 168 (26), 108 (89), 91 (18).

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