Regioselective Benzoylation of 6-*O*-Protected and 4,6-*O*-Diprotected Hexopyranosides as Promoted by Chiral and Achiral Ditertiary 1,2-Diamines

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Dieter Seebach mit allen guten Wünschen herzlich zugeeignet

Monobenzoylation of triols (6-*O*-silylated glycopyranosides) or diols (4,6-*O*-benzylidenated glycopyranosides) with benzoyl chloride and triethylamine at $-60°$ to $23°$ is promoted by catalytic amounts of ditertiary 1,2-diamines. The regioselectivity depends mostly on the structure of the alcohols; it is modulated by the configuration and constitution of the diamines, as shown by comparing the effect of *Oriyama*'s catalyst ((*S*)-**1** and (*R*)-**1**), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEEDA), Et_3N, and $EtNMe_2$. The effect of the catalysts on the reactivity is impaired by their steric hindrance. In agreement with the modest enantioselectivity of the mono- and dibenzoylation of *rac*-cyclohexane-1,2-diol in the presence of *Oriyama*'s catalyst, the influence of these diamines on the regioselectivity is rather limited. While associated with procedural simplicity, these catalysts lead, in a few cases, to higher yields of a single benzoate than established methods, *viz.* in the preparation of the 3-*O*-benzoyl β-D-glucopyranoside **4**, the 2-*O*-benzoyl α-D-galactopyranoside **22**, the 3-*O*-benzoyl α-D-galactopyranoside **23**, and the benzylidenated 2-*O*-benzoyl α-D-galactopyranoside **44**. The regioselective benzoylation of the benzylidenated β-D-mannopyranoside **47**, leading to **48**, appears to be new.

Introduction. – The selective transformation of OH groups of carbohydrates is a fundamental, but often not trivial preparative problem [1][2]. Primary and secondary OH groups are usually readily differentiated. Regioselective transformations of secondary OH groups can, however, be difficult, and even the selective introduction of a protecting group may not be straightforward [3]. Regioselective *O*-acylation is one of the most important methods to protect secondary OH groups (for some leading references, see [4]). Like other regioselective transformations, it is based directly or indirectly on intrinsic reactivity differences and requires appropriate reagents [5–7], catalysts[1]), or prior OH group activation[2]). To which extent can this regioselectivity be influenced by enantiomerically pure catalysts and promoters?

Enantioselective *O*-acylation of alcohols[3]) has been realized by nonenzymatic kinetic resolution [19] of secondary alcohols and by nonenzymatic desymmetrisation [20] of *meso*-diols. Nucleophilic catalysis of enantioselective *O*-acyl transfer [17] has been developed intensively since *Vedejs et al.* reported the use of phosphines [21] and of 4-(dimethylamino)pyridine (DMAP) derivatives [22][23]. Enantiomerically pure derivatives of DMAP and of 4-(pyrrolidino)pyridine have also been reported by the

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[1]) For the use of enzymes, see [8][9]; for other catalysts, see [8][10], and references quoted there.

[2]) Usually by stannylation [11][12]. For reviews, see [11][13][14].

[3]) For reviews of enzymatic kinetic resolution and desymmetrisation, see [15]; for reviews of nonenzymatic kinetic resolution and desymmetrisation, see [16–18].

groups of *Fu*[4]) [24][25], *Fuji* [28], and *Spivey* [29], while *Miller et al.* used peptides as enantioselective *O*-acyl transfer catalysts [30]. *Oriyama et al.* have shown that (*S*)-proline-derived diamines are useful catalysts for the kinetic resolution of racemic secondary alcohols and for the desymmetrisation of *meso*-diols [31–34]. Most relevant to the question posed above are two papers by *Kagan* reporting the transformation of a racemate or of a single enantiomer to regioisomeric products by using an asymmetric reagent or catalyst [35].

We wondered about the use of enantiomerically pure catalysts for the regioselective *O*-acylation of carbohydrates, and specifically about the extent to which *Oriyama's* catalysts (*S*)-**1** and (*R*)-**1** decrease or increase (and perhaps overcome) reactivity differences between constitutionally different secondary OH groups. We planned to first study the regioselectivity of the benzoylation of methyl 6-*O*-(*tert*-butyldiphenylsilyl)-β-D-glucopyranoside (**2**) and then of other methyl or allyl α-D- and β-D-hexopyranosides protected by a 6-*O*-TBDPS or by a 4,6-*O*-benzylidene group.

Results and Discussion. – Methyl 6-*O*-(*tert*-butyldiphenylsilyl)-β-D-glucopyranoside (**2**) [36] was benzoylated at $-60°$ with benzoyl chloride (BzCl)/triethylamine (Et_3N) in dichloromethane (CH_2Cl_2) and in the presence, or absence, of 1 or 5 mol-% of enantiomerically pure (*S*)-**1** [31] or (*R*)-**1** (*Scheme 1* and *Table 1*). The addition of 4-Å molecular sieves increased the rate of consumption of starting material [31]. These conditions led to mixtures of the regioisomeric monobenzoates **3**, **4**, and **5**, the dibenzoates **6** and **7**, and the tribenzoate **8** [36]. The dependence of the yields of these benzoates on the presence of (*S*)-**1**, the temperature, and the duration of the reaction shows a strong effect of (*S*)-**1**, resulting in a highly regioselective formation of the 3-*O*-benzoate **4** that was isolated in yields of up to 84%. The benzoate **4** is the major product even in the absence of (*S*)-**1**. It was isolated in a yield of 62.5%, when the benzoylation was performed at 0° for 24 h; at $-60°$, the yield dropped to 19.5%. Adding 1 mol-% of (*S*)-**1** and increasing the amount of BzCl and Et_3N from 1 to 1.2 equiv. shortened the reaction time from 24 h to 1 h at $-60°$, providing 73% of **4**. Performing the benzoylation in the presence of 5 mol-% of (*S*)-**1** yielded **4** in 78.5% at 0° and in 84% at $-60°$, while the analogous benzoylation at 23° (1 equiv. each of BzCl and Et_3N) gave **4** in only 47% yield. Lowering the temperature to $-60°$ raised the yield to 82.5%[5]). In the presence of (*R*)-**1** but under otherwise identical conditions, we isolated 62% of the 3-benzoate **4** and 13.5% of 4-benzoate **5**. The isomer **5** was not observed when **2** was benzoylated with 1 equiv. BzCl/Et_3N in the presence of (*S*)-**1**, while increasing amounts were formed in the presence of excess BzCl/Et_3N and (*S*)-**1** (4%), in the absence of **1** (10.5%), or in the presence of (*R*)-**1** (13.5%). As shown in *Table 2*, increasing the amount of either (*S*)-**1** or (*R*)-**1** from 1 over 3 to 5% led to a higher conversion but resulted in the same regioselectivity, respectively.

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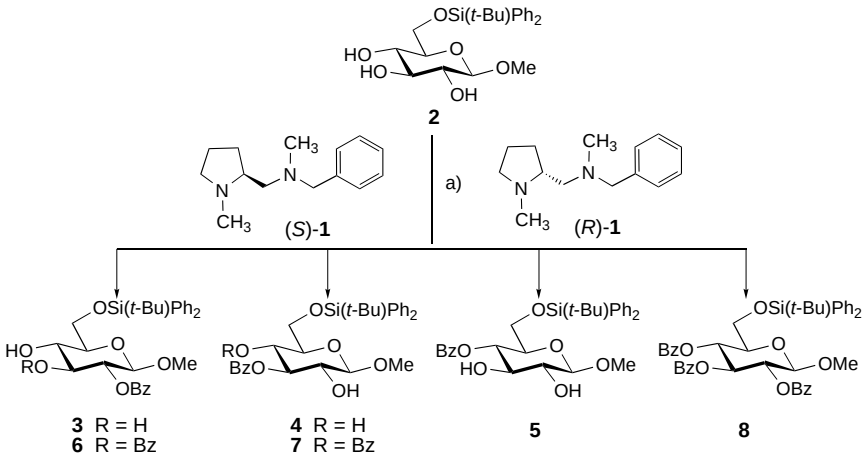
4) *Fu*'s catalysts have also been used for the enantioselective acylation of amines [26] and the construction of quaternary stereogenic centers [27].

5) Under analogous conditions, but replacing (*S*)-**1** with *Fu*'s catalyst ((–)-DMAP-Fe(C_5Ph_5) complex [25]), we obtained 41% of **4**. Acetylation of **2** under *Fu*'s conditions [25] gave 54% of the corresponding 3-acetate. We thank Prof. *G. C. Fu,* MIT, Cambridge, USA, for a generous gift of his catalyst.

Scheme 1



a) BzCl, CH_2Cl_2, molecular sieves 4 Å, catalyst, base, temperature and reaction time as specified in *Tables 1*, *2*, and *5*.

Table 1. *Influence of Reaction Conditions on the Benzoylation of* **2** (isolated yields)

Entry	Catalyst [mol-%]	Et_3N [equiv.]	BzCl [equiv.]	Temp. [°C]	Time[h]	Yield[a]) [%] of SM and products					
						2	**3**	**4**	**5**	**6**	**7**
1	0	1	1	– 60	24	26	12	19.5	10.5	[b])	4.5
2	0	1	1	0	24	9.5	2	62.5	3	5[c])	3
3	(*S*)-**1** (1)	1.2	1.2	– 60	1	6.5	7	73	4	[b])	2.5
4	(*S*)-**1** (5)	1.2	1.2	0	1	9	3.3	78.5	[d])	[b])	[b])
5	(*S*)-**1** (5)	1.2	1.2	– 60	1	trace	3.0	84	[d])	[b])	3
6	(*S*)-**1** (5)	1	1	23	1	29	1.5	47	[d])	[b])	5
7	(*S*)-**1** (5)	1	1	– 60	1	trace	4	82.5	[d])	2.5	2.5
8	(*R*)-**1** (5)	1	1	– 60	1	5.8	[d])	62	13.5	4	2

[a]) Yield of chromatographically pure product. SM: Starting material. [b]) Dibenzoates and (or) tribenzoates were detected as minor products in the ^{1}H-NMR spectra, but were not isolated. [c]) A mixture of 2,3- and 2,4-*O*-benzoate was obtained. [d]) Product not detected.

To check for *O*-acyl migration, we added the 4-benzoate **5** to the reaction mixture of **2** after consumption of BzCl at – 60° (in the presence of (*S*)-**1**), monitoring the reaction for 1 h at this temperature and at 0°, then for 12 h at 23°, and again at 40° for 2 h. The ratio of the products did not change up to 23°, and very little at 40°. In a second experiment, the 4-benzoate **5** was treated with Et_3N (10 equiv.), molecular sieves (4 Å), and (*S*)-**1** (0.5 equiv.) at – 60°, and then with additional (*S*)-**1** hydrochloride (0.5 equiv.). TLC of this mixture showed no spot for any of the other mono- or dibenzoates at temperatures of up to 23°.

The Bz groups of all products give rise to the typical IR bands around 1715 cm^{-1} and to ^{13}C signals around 168 ppm. The NMR spectra are characterized by a downfield shift of 1.0 – 2.0 ppm for the ^{1}H geminal to the BzO group, a downfield shift of *ca.* 2 ppm for the benzoyloxylated ^{13}C, and an upfield shift of *ca.* 2 ppm for the vicinal ^{13}C [11].

Table 2. *Influence of the Amount of* (S)-**1** *and* (R)-**1** *on the Benzoylation of* **2** (ratio of products)

Entry	Catalyst ([mol-%])	NEt_3 [equiv.]	BzCl [equiv.]	Temp. [°]	Time [h]	Yield[a]) [%] of SM and products					
						2	**3**	**4**	**5**	**6**	**7**
1	(*S*)-**1** (1)	1	1	−60	1	9.5	4.9	80.8	[b])	1.9	2.8
2	(*R*)-**1** (1)	1	1	−60	1	15.4	[b])	58.4	16.7	4.4	5.0
3	(*S*)-**1** (3)	1	1	−60	1	6.0	4.7	85.0	[b])	1.9	2.4
4	(*R*)-**1** (3)	1	1	−60	1	10.0	[b])	63.3	16.6	4.1	6.0
5	(*S*)-**1** (5)	1	1	−60	1	4.8	5.0	85.1	[b])	2.1	3.0
6	(*R*)-**1** (5)	1	1	−60	1	8.2	[b])	64.5	16.0	5.0	6.4

[a]) Ratio (in %) determined by integration of the ^{1}H-NMR H−C(1) signals. SM: Starting material. [b]) Product not detected.

The ^{1}H-NMR spectrum of **4** shows couplings between the signals at 5.21 (t, $J \approx 9.1$) and at 3.62 (ddd, $J = 9.5$, 7.5, 2.9, H−C(2)). The structures of **3** and **5** were also assigned on the basis of decoupling experiments. The dibenzoate **6** showed signals at 5.49 ('t', $J = 10.0$) and 5.40 (dd, $J = 10.0, 7.8$), evidencing that the BzO groups are located at C(2) and C(3). The structure of the dibenzoate **7** was evidenced by the absence of a coupling of the deshielded H-atom with H−C(1), resonating at 4.45 ppm (d, $J = 7.8$). The ^{13}C-NMR spectra of the benzoates are in agreement with these assignments.

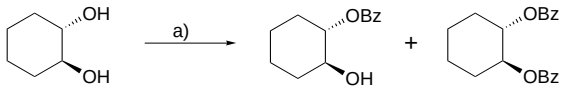
The triol **2** may be considered a combination of two 1,2-diol substructures, one comprising C(2)−OH and C(3)−OH, the other one comprising C(3)−OH and C(4)−OH. The first substructure may be compared to (*S*,*S*)-*trans*-cyclohexane-1,2-diol and the latter to its enantiomer. We, therefore, wondered about the kinetic resolution (*Scheme 2*) of racemic **9** by mono- and dibenzoylation in the presence of (*S*)-**1** or (*R*)-**1**. While the sequential kinetic resolution of the diacetate of **9** by porcine liver esterase (PLE) [37] and lipase [38] is well-known, we are not aware of reports on the enantioselective *O*-acylation of **9**.

Oriyama et al. found that OH groups at (*S*)-configured C-atoms are preferentially acylated in the presence of catalytic amounts of (*S*)-**1** [34]. Acylation of the homotopic OH groups of (*R*,*R*)-**9** or (*S*,*S*)-**9** should reflect the influence of (*S*)-**1** or (*R*)-**1** on the acylation of a pair of *trans*-1,2-diols in the absence of constitutional differences between the OH groups. The enantiomerically pure monobenzoate **10** and dibenzoate **11**, required as a reference (*Entry 1* in *Table 3*), were obtained by benzoylation of enantiomerically pure (*S*,*S*)-**9**. As expected, use of (*S*)-**1** or (*R*)-**1** for the benzoylation of racemic **9** gave parallel results (*Table 3*, *Entry 2–7*), although the diol did not dissolve completely in CH_2Cl_2 at −60°[6]). A comparison of *Entries 2* and *4* (benzoylation in the presence of 1 mol-% of (*S*)-**1**) shows that doubling the amount of Et_3N and BzCl from 0.5 and 0.6 to 1.0 and 1.2 equiv., respectively, raised the yield of the monobenzoates from 31.8 to 51.8%, while the ee, in favour of the (*S*,*S*)-enantiomer, dropped from 28.3 to 4.4%. *Entry 6* shows that a further increase of the amount of Et_3N and BzCl to 1.5 and 1.8 equiv., respectively, decreased the yield of the monobenzoate **10** to 45%, while the ee increased to 79.6%, but now in favour of the (*R*,*R*)-enantiomer. Parallel to this, the yield of the dibenzoate **11** increased from 8.6 over 22.8 to 52.2%, with a decrease in ee from 94 to 93.1 to 77.3% in favour of the (*S*,*S*)-enantiomer. A comparison of *Entries 3*, *5*, and *7* shows that (*R*)-**1** leads to parallel results. *Entry 8* shows that an increase of the concentration and a smaller amount of reagents (0.5 equiv.

6) Starting material, catalyst, and Et_3N were dissolved at 23°, cooled to −60°, and then treated with BzCl.

BzCl, 0.6 equiv. Et_3N) lowered both the yield and ee of **10** and slightly increased the yield of **11**, while lowering its ee. The enantioselective benzoylation of the racemic monobenzoate **10** in the presence of 5 mol-% of (*S*)-**1** or (*R*)-**1** yielded 41% of (*S*,*S*)-**11** or (*R*,*R*)-**11** (ee 79–80%, *Entries 9* and *10*). The advantage of sequential kinetic resolutions[7]) are well-documented, and a comparison of *Entries 3* and *10* teaches that the second benzoylation (proceeding more slowly) is more selective than the first one. That (*S*,*S*)-**9** was preferentially benzoylated in the presence of (*S*)-**1** and that (*R*,*R*)-**9** was preferentially benzoylated in the presence of (*R*)-**1** is in agreement with the observation of *Oriyama et al.* who also showed that the enantioselectivity is influenced by the nature of a vicinal substituent [33][34].

Scheme 2



9 **10** **11**

a) (*S*)-**1** or (*R*)-**1** or *N,N,N′,N′-tetramethylethylenediamine* (TMEDA), Et_3N, BzCl, molecular sieves (4 Å), CH_2Cl_2, –60°, 24 h.

Table 3. *Benzoylation of* trans-*Cyclohexane-1,2-diol* (**9**)

Entry	Substrate ([mmol])	Catalyst ([mol-%])[a])	Et_3N [mmol]	BzCl [mmol]	CH_2Cl_2 [ml]	Temp. [°]	Time [h]	Monobenzoate **10**		Dibenzoate **11**	
								Yield[b]) [%]	ee[c])	Yield[b]) [%]	ee[d])
1	(1*S*,2*S*)-**9** (0.5)	(*S*)-**1** (5.0)	0.5	0.5	8	–60	24	73.0	>99.5(*S*)	11.5	>99.5 (*S*)
2	(±)-**9** (1.0)	(*S*)-**1** (1.0)	0.5	0.6	10	–60	24	31.8	28.3 (*S*)	8.6	94.0 (*S*)
3	(±)-**9** (1.0)	(*R*)-**1** (1.0)	0.5	0.6	10	–60	24	31.8	31.9 (*R*)	8.0	94.8 (*R*)
4	(±)-**9** (1.0)	(*S*)-**1** (1.0)	1.0	1.2	10	–60	24	51.8	4.4 (*S*)	22.8	93.1 (*S*)
5	(±)-**9** (1.0)	(*R*)-**1** (1.0)	1.0	1.2	10	–60	24	52.7	4.4 (*R*)	21.6	92.9 (*R*)
6	(±)-**9** (1.0)	(*S*)-**1** (1.0)	1.5	1.8	10	–60	24	45.0	79.6 (*R*)	52.2	77.3 (*S*)
7	(±)-**9** (1.0)	(*R*)-**1** (1.0)	1.5	1.8	10	–60	24	42.3	82.9 (*S*)	52.5	81.7 (*R*)
8	(±)-**9** (5.0)	(*S*)-**1** (5.0)	3.3	2.5	10	–60	24	20.8	<0.5	12.1	88.2 (*S*)
9	(±)-**10** (0.5)	(*S*)-**1** (5.0)	0.25	0.25	6	–60	24	56.4	59.2 (*R*)	41.4	79.9 (*S*)
10	(±)-**10** (0.5)	(*R*)-**1** (5.0)	0.25	0.25	6	–60	24	54.5	60.3 (*S*)	41.4	78.9 (*R*)

[a]) Relative to Et_3N with exception of *Entry 8* where the mol-% is relative to BzCl. [b]) Yield of chromatographically pure product. [c]) Determined by HPLC (*Chiralpak AS*; hexane/i-PrOH 90 : 10; 1.0 ml/min). [d]) Determined by HPLC (*Chiralpak AS*; hexane/i-PrOH 98 : 2; 0.8 ml/min).

7) For sequential resolutions by enzymes, see [39][40], and references cited therein.

On the basis of the moderate preferential benzoylation of (*S*,*S*)-*trans*-cyclohexane-1,2-diol (**9**) under the influence of (*S*)-**1**, one expects that this catalyst will lead to a preferential benzoylation of **2** at C(2)–OH rather than C(4)–OH, while the opposite should hold for the influence of (*R*)-**1**, unless constitutional differences resulting in a larger hindrance of C(4)–OH will prevail.

Benzoylation of **2** at $-60°$ in the presence of (*S*)-**1** (*Entry 7, Table 1*) gave indeed, besides the major 3-benzoate **4**, 4% of the 2-benzoate **3**, but no 4-benzoate **5**, while (*R*)-**1** gave 13.5% of 4-benzoate **5** and no 2-benzoate **3** (*Entry 8*, *Table 1*). A second benzoylation of the 3-benzoate **4**, however, led independently of the sense of the chirality of **1** preferentially to the 2,3-dibenzoate **6** (*Table 4*). *Entries 1* and *2* also show a similar ratio of 2,3-dibenzoate to 3,4-dibenzoate (*Entry 1,* 70:30; *Entry 2,* 68:32), independently of whether the reaction is conducted for 1 or for 12 h (*Entry 3,* 71:29; *Entry 4,* 71:29). This may reflect the increased steric hindrance of C(4)–OH by C(3)–OBz rather than the requirement for a vicinal OH group, considering that (*S*)-**1** has led to a kinetic resolution of racemic monoalcohols [33].

Table 4. *Influence of Catalysts on the Benzoylation of* **4**

Entry	Catalyst ([mol-%])	Et_3N [equiv.]	BzCl [equiv.]	Temp. [°]	Time [h]	Ratio[a]) [%] of SM and products				
						4	**6**	**7**	**8**	**6/7**
1	(*R*)-**1** (5)	1.1	1	−60	1	72.5	19.0	8.3	trace	70:30
2	(*S*)-**1** (5)	1.1	1	−60	1	86.9	8.9	4.2	0	68:32
3	(*R*)-**1** (5)	1.1	1	−60	12	42.8	37.7	15.2	4.4	71:29
4	(*S*)-**1** (5)	1.1	1	−60	12	73.7	18.1	7.3	0.8	71:29

[a]) Ratio (in %) determined by integration of the H–C(1) signals in the ^{1}H-NMR spectra. SM: Starting material.

These observations suggest that constitutional differences between the three OH groups of **2** determine the regioselectivity of the benzoylation to a much larger extent than the absolute configuration of **1**. The regioselectivity correlates indeed with the expected nucleophilicity of the individual OH groups. The nucleophilicity of C(2)–OH is impaired by its proximity to the anomeric center, and that of C(4)–OH by its more-pronounced steric hindrance. It follows that the higher regioselectivity and yield of benzoylation in the presence of (*S*)-**1** is rather due to the influence of its constitution than of its configuration, and that achiral ditertiary 1,2-diamines may similarly increase the intrinsic reactivity difference of the OH groups of **2**.

A comparison of the use of (*S*)-**1** and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as catalysts for the benzoylation of **2** at $-60°$ gave the following results: the monobenzoates, the dibenzoates, and the tribenzoate are formed in a ratio of 95:5:0 (95%; 5% starting material) for (*S*)-**1** and 70:30:0 (77%; 22% starting material) for TMEDA (*Entries 3* and *17*, *Table 5*), the ratio of the monobenzoates **3**, **4** and **5** is 6:94:0 (90%) for (*S*)-**1** and 4:90:6 (53.6%) for TMEDA, and the ratio of the 2,3- to the 3,4-dibenzoates is 41:59 (5.1%) for (*S*)-**1** and 35:65 (23.4%) for TMEDA.

These results show that TMEDA is a more active catalyst than (*S*)-**1**, at least for the second benzoylation. This is seen from the increased amount of dibenzoates, correlating with a larger amount of remaining starting material, the formation of the hindered 4-benzoate **5**, and the slightly changed ratio of the 3,4- *vs.* 2,3-dibenzoates (**6**/**7**

Table 5. *Influence of Catalysts and Reaction Conditions on the Benzoylation of* **2**

Entry	Catalyst ([mol-%])	Base ([equiv.])	BzCl [equiv.]	Temp. [°]	Time [h]	Ratio[a]) of SM and products (isolated yield)					
						2	**3**	**4**	**5**	**6**	**7**
1	(*S*)-**1** (5)	Et_3N (1)	1	0	1	13.1	4.2	76.1	2.6	2.3	1.7
2	(*R*)-**1** (5)	Et_3N (1)	1	0	1	17.9	2.4	58.5	11.6	4.9	4.8
3	(*S*)-**1** (5)	Et_3N (1)	1	−60	1	4.8 (0)	5.0 (4)	85 (82)	-	2.1 (2)	3.0 (2)
4	(*R*)-**1** (5)	Et_3N (1)	1	−60	1	8.2 (6)	-	64.5 (62)	16 (14)	5.0 (4)	6.4 (2)
5	–	Pyridine (1)	1	−60	1	33.9	7.5	43.9	4.2	7.6	2.9
6	–	Pyridine (1)	1	−20	1	33.8	7.6	45.4	4.9	5.9	2.3
7	–	Pyridine (1)	1	0	1	44.4	6.7	37	5.4	4.0	1.7
8	–	Pyridine (1)	1	23	1	58.4	5.6	27.4	4.0	3.5	1.0
9	–	Pyridine (1)	1	23	48	34.0	8.6	41.1	4.8	8.8	1.4
10[b])	–	Et_3N (1)	1	−60	1	42.3	7	24.5	17	4.3	2.4
11[b])	–	Et_3N (1)	1	0	1	44.0	4.8	40.8	7.2	trace	1.3
12[b])	–	Et_3N (1)	1	23	1	49.4	2.7	40.3	5.4	trace	1.1
13[b])	–	Et_3N (1)	1	23	24	24.4 (21)	1.8 (1)	63 (58)	6.8 (4)	2.1 (1)	2.0 (2)
14	TMEDA (50)	–	1	−60	1	26.3	1.1	46.3	4.1	7.2	13.6
15	TMEDA (100)	–	1	−60	1	25.4	1.5	48.6	5.0	6.9	11.6
16	TMEDA (100)	–	1	0	1	20.9 (14)	2.2 (0)	54.5 (54)	4.5 (4)	8.6 (9)	8.5 (7)
17	TMEDA (5)	Et_3N (1)	1	−60	1	21.7 (17)	2.2 (2)	48.0 (46)	3.4 (2)	8.3 (7)	15.1 (10)
18	TMEDA (5)	Et_3N (1)	1	0	1	19.0	2.7	55	3.7	9.7	9.1
19	TMEDA (5)	Et_3N (1)	1	23	1	23.3	3.7	51	4.9	9.4	7.0
20	TMEDA (5)	Et_3N (1)	1	23	48	20.8	3.6	52.4	5.1	10.1	7.3
21	TEEDA[c]) (5)	Et_3N (1)	1	−60	1	68.4	8.0	9.3	10.9	trace	1.5
22	TEEDA (5)	Et_3N (1)	1	0	1	44	4.2	39.1	6.4	2.2	1.2
23	TEEDA (5)	Et_3N (1)	1	23	1	41	3.1	45.1	6.4	2.3	2.0
24	TEEDA (5)	Et_3N (1)	1	23	48	19.1	3.1	64.9	6.4	4.1	2.5
25	–	$EtNMe_2$ (1)	1	−60	1	35.4 (26)	19.6 (20)	10.5 (10)	12.9 (13)	12.5 (12)	7.7 (5)
26	$EtNMe_2$ (5)	Et_3N (1)	1	−60	1	24.9 (15)	21.5 (21)	11.4 (11)	16.7 (16)	16.7 (16)	8.2 (8)
27	$EtNMe_2$ (10)	Et_3N (1)	1	−60	1	25.1	21.6	11.6	17.2	16.1	8.1

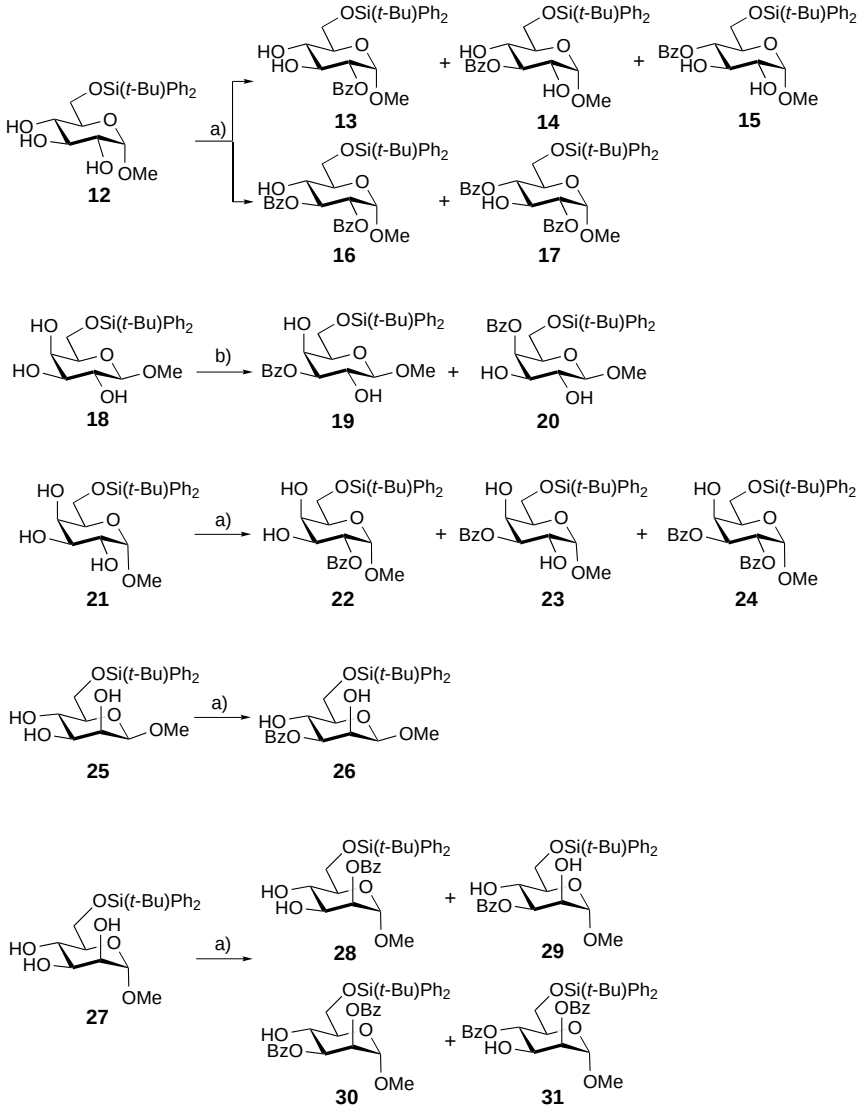
[a]) Ratio (in %) determined by integration of the ^{1}H-NMR H–C(1) signals. SM: Starting material. [b]) 1–4% of 2,4-*O*-dibenzoate were observed from the corresponding ^{1}H-NMR spectrum. [c]) TEEDA: *N,N,N′,N′*-Tetraethylethylenediamine.

6:4 *vs.* 7:3; *cf. Table 4*). The regioselectivity of the monobenzoylation of **2** at C(2)–OH and C(3)–OH, *i.e.*, the ratio **3**/**4**, is only slightly affected by replacing (*S*)-**1** with TMEDA. The higher reactivity of TMEDA *vs.* (*S*)-**1** correlates with the smaller size of its *N*-substituents. Indeed, as judged from the amount of remaining starting material, *N,N,N′,N′*-tetraethylethylenediamine (TEEDA) was not as effective as catalyst, particularly at −60° (*Table 5*, *Entries 21–24*). It leads, however, to a slightly improved regioselectivity (*Table 5*, *Entries 20* and *24*). The effect of size was further evaluated by comparing Et_3N with $EtNMe_2$. A comparison of the *Entries 10* and *25* shows that $EtNMe_2$ is more reactive than Et_3N (less starting material and higher amount of dibenzoates), but less selective. The effect of the second amino group was tested by adding catalytic amounts of either TMEDA or $EtNMe_2$ (*Entries 17* and *26*). The higher regioselectivity resulting from using ditertiary 1,2-diamines may be rationalised by postulating the intermediate formation of a reactive complex [31] that deprotonates (partially) a OH group and transfers the Bz residue to it, in a concerted and *quasi*-intramolecular way. Indeed, comparing TMEDA and $EtNMe_2$ shows that the

mere size of the reaction complex does not explain the differences of regioselectivity. The effect of factors besides the configuration (steric hindrance?) is evidenced by the observation that both (*S*)-**1** and (*R*)-**1** lead to higher yields of the 3-benzoate **4** than TMEDA (*cf. Table 6* below).

The regioselectivity of the benzoylation of the α-D-anomer **12** [41] (*Scheme 3* and *Table 6*) is more strongly affected by the catalyst. Benzoylation in the presence of (*S*)-**1**

Scheme 3



a) (*S*)-**1** or (*R*)-**1** or TMEDA, Et_3N, BzCl, molecular sieves (4 Å), CH_2Cl_2, $-60°$, 1 h. b) (*S*)-**1** or (*R*)-**1** or TMEDA, Et_3N, BzCl, molecular sieves (4 Å), CH_2Cl_2, $-5°$, 1 h.

Table 6. *Benzoylation of Methyl 6-O-TBDPS α- or β-D-Glycopyranosides Catalyzed by (S)-**1** or by (R)-**1** or by TMEDA at −60°*

Substrates (configuration)	Yield [%][a][b]			
	2-Benzoate	3-Benzoate	4-Benzoate	Others
2 (*β*-D-*gluco*)				
Cat. by (*S*)-**1**	**3** (4)	**4** (82.5)		**6** (2.5), **7** (2.5)
Cat. by (*R*)-**1**		**4** (62)	**5** (13.5)	**6** (4), **7** (2)
Cat. by TMEDA	**3** (1)	**4** (53)	**5** (2.5)	**6** (7.5), **7** (12.5)
12 (*α*-D-*gluco*)				
Cat. by (*S*)-**1**	**13** (82)	**14** (7)		**16** (3.4)
Cat. by (*R*)-**1**	**13** (11)	**14** (28)	**15** (10)	**16** (12), **17** (7)
Cat. by TMEDA	**13** (64)	**14** (3.5)		**16** (13), **17** (4)
18 (*β*-D-*galacto*)[c]				
Cat. by (*S*)-**1**		**19** (68)	trace	[b]
Cat. by (*R*)-**1**		**19** (61)	**20** (6)	[b]
Cat. by TMEDA		**19** (56)	**20** (4)	[b]
21 (α-D-*galacto*)				
Cat. by (*S*)-**1**	**22** (78)	**23** (2)		**24** (3)
Cat. by (*R*)-**1**	**22** (10)	**23** (57)		**24** (8)
Cat. by TMEDA	**22** (69)	**23** (2)		**24** (9)
25 (*β*-D-*manno*)				
Cat. by (*S*)-**1**		**26** (86)		
Cat. by (*R*)-**1**		**26** (63)		
27 (*α*-D-*manno*)				
Cat. by (*S*)-**1**	**28** (8)	**29** (86)		
Cat. by (*R*)-**1**	**28** (47)	**29** (10)		**30** (6), **31** (10)
Cat. by TMEDA	**28** (12)	**29** (34)		**30** (6), **31** (3)

[a]) Yield of chromatographically pure product. [b]) Some minor isomers and recovered starting material are not considered in this table. [c]) Benzoylation took place at −5°.

gave mostly the 2-benzoate **13** [42] (82%) besides the 3-benzoate **14** (7%) and the 2,3-dibenzoate **16** (3.4%), while benzoylation in the presence of (*R*)-**1** resulted in a poor regioselectivity, leading to the monobenzoates **13** (11%), **14** (28%), and **15** (10%), and the dibenzoates **16** (12%) and **17** (7%).

As shown in *Table 6*, TMEDA led to intermediary yields of the major 2-benzoate **13** (64 *vs.* 82% resulting from the use of (*S*)-**1**, and 11% from the use of (*R*)-**1**), but to lower yields of the 3-benzoate **14** (3.5%) than either one of the other two catalysts (similarly to the 3-*O*-benzoylation of the *β*-D-anomer **2**). The interpretation of this result is, however, not possible, considering the large amount of dibenzoates formed in the presence of TMEDA. Also in agreement with the effect of the diamines on the regioselectivity of the benzoylation of **2** is the higher yield of the 4-benzoate **15** in the presence of (*R*)-**1**. The dominant intrinsic factor determining the regioselectivity appears to be the C(2)−OH···O−C(1) H-bond, determining the relative nucleophilicity of the OH groups. Studies of this effect go back to *Foster* and co-workers [43] who showed that the regioselectivity of the acylation by acyl chlorides is determined by this intramolecular H-bond, if the rate-determining step involves attack of a non-ionised OH group on the acylating agent. Recently, *Yoshida et al.* [44] reported that an

intramolecular H-bond network plays a decisive role in the relative reactivities of OH groups of unprotected carbohydrates in the DMAP-catalyzed acylation.

Benzoylation of the anomeric galactopyranosides **18** [45] and **21** [46] also shows the well-known influence of a H-bond from an equatorial OH group to a vicinal, axial OH or OR substituent [2]. As seen from *Table 6*, the regioselectivity of the benzoylation of the β-D-anomer **18** is determined by the C(3)−OH···O−C(4) H-bond; there is little influence of the nature of the catalyst, TMEDA leading to the lowest and (*S*)-**1** to the highest yield (68%) of the 3-benzoate **19**. In contradistinction, benzoylation of the α-D-galactopyranoside **21** reflects the competing effects of the C(2)−OH···O−C(1) and the C(3)−OH···O−C(4) H-bonds and the influence of the catalyst. The highest yield of the 2-*O*-benzoate **22** (78%) was obtained in the presence of (*S*)-**1**. Benzoylation in the presence of (*R*)-**1** provided **22** in only 10% yield; the major product was the 3-benzoate **23** (57%). TMEDA yielded **22** in an intermediary yield of 69%; like (*S*)-**1**, it led to **23** in only minor amounts (2%).

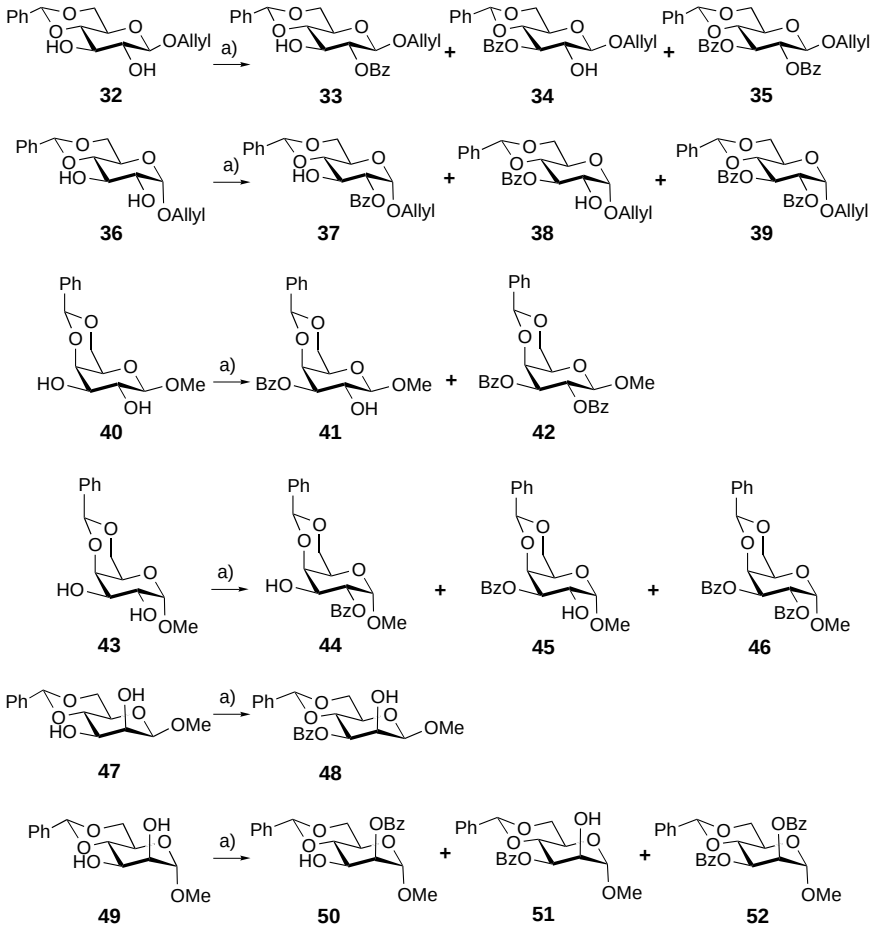
The lower reactivity of axial OH groups, the effect of the C(3)−OH···O−C(2) H-bond, and the effect of the catalyst are also evident from the benzoylation of the anomeric mannopyranosides **25** [47] and **27** [48]. Benzoylation of the β-D-mannopyranoside produced essentially the 3-benzoate **26**, and the influence of the nature of the catalyst is evidencd by the yield of 86% ((*S*)-**1**) *vs.* 63% ((*R*)-**1**). Benzoylation in the presence of (*S*)-**1** of α-D-mannopyranoside **27** provided 86% of the 3-benzoate **29** [48]; yields dropped to 10% with the enantiomeric catalyst, while TMEDA led to an intermediary result. The best yield of the 2-benzoate **28** (47%) resulted from using (*R*)-**1**; again, intermediary results were obtained in the presence of TMEDA.

The structure of the 3-benzoate **14** was evidenced by the transformation of the H−C(2) *td* at 3.74 ($J = 10.0$, 3.7) to a *d* ($J = 3.7$) upon addition of D_2O and irradiation of the *t* at 5.33 ($J = 9.3$). The structure of the 4-benzoate **15** was confirmed by comparison of its NMR spectra with those of **13** [42] and of **14**; it is evidenced by the *dd* at 5.17 ($J = 9.9$, 9.3), which shows no coupling with the *d* at 4.88 ($J = 3.7$, H−C(1)). The coupling between the *d* at 5.10 ($J = 3.7$, H−C(1)) and the *dd* at 5.21 ($J = 10.2$, 3.7) of **16**, and the coupling between the *d* at 5.13 ($J = 3.7$, H−C(1)) and the *dd* at 5.09 ($J = 9.3$, 3.7) of **17** show that C(2)−OH in these compounds is *O*-benzoylated. The *dd* at 5.77 ($J = 10.2$, 9.0, irrad. at 5.21 → br. *d*, irrad. at 3.95 → *d*, $J = 10.2$, H−C(3)) of **16** evidences 2,3-*O*-dibenzoylation. The *t* at 5.31 ($J = 9.5$, irrad. at 4.38 → *d*, $J = 9.3$, irrad. at 4.05 → *d*, $J = 9.0$, H−C(4)) of **17** evidenced 2,4-*O*-benzoylation. The br. *d* at 5.74 ($J \approx 3.0$) of **20** evidences benzoylation at C(4)−OH. The *s* at 167.0 ppm of **22** and *s* at 166.6 ppm of **23** evidence one C=O group for each compound. Benzoylation at C(2)−OH of **22** is deduced from the coupling between the *dd* at 5.23 ppm ($J = 9.7$, 3.7, H−C(2)) and the *d* at 5.01 ppm ($J = 3.7$, H−C(1)). The structure of **23** was evidenced by the absence of a coupling between the *dd* at 5.26 ppm ($J = 10.2$, 3.0, H−C(3)), showing one large coupling, and the *d* at 4.87 ppm ($J = 3.7$, H−C(1)). The ^{1}H- and ^{13}C-NMR spectra of **24** are identical to those described in [46]. The absence of a coupling between the *dd* at 5.06 ($J = 9.5$, 2.9) and the *d* at 4.51 ($J = 0.8$, H−C(1)), and the coupling between the *dd* at 5.06 and the *td* at 4.21 ($J = 2.9$, 0.8, addition of D_2O → br. *d*, $J \approx 3.3$, H−C(2)) reveal the benzoylation at C(3)−O of **26**. The structure of the 2-benzoate **28** was assigned on the basis of the coupling between the *dd* at 5.35 ($J = 2.8$, 1.5, irrad. at 4.82 → *d*, $J = 2.8$, H−C(2)) and the *d* at 4.82 ($J = 1.7$, irrad. at 5.35 → *s*, H−C(1)). The *dd* at 5.34 ($J = 9.65$, 3.2) of **29** [48] evidences benzoylation at C(3)−O. The two ^{13}C signals at 166.8 and 165.8 ppm of **30**, and the ^{13}C signals at 167.3 and 166.2 ppm of **31** evidence two C=O groups in each compound. The structure of **30** was evidenced by the absence of coupling between the *d* at 4.89 ($J = 1.2$, H−C(1)) and the br. *t* at 4.39 ($J \approx 9.3$), showing two large couplings (addition of D_2O → change to a sharp *t*, H−C(4)). The structure of **31** was evidenced by the *m* at 4.38–4.26 (addition of D_2O → *dd*, $J = 10.0$, 3.4, H−C(3)).

To further evaluate the extent to which the nature of the catalyst influences the regioselectivity of the benzoylation, we examined the anomeric pairs of the 4,6-*O*-benzylidenated glycopyranosides **32** [49] and **36** [49], **40** [50] and **43** [50], and **47** [51] and **49** [50] (*Scheme 4* and *Table 7*).

Benzoylation of the benzylidenated allyl β-D-glucopyranoside **32** was little affected by the nature of the catalyst. Regioselectivity was low, with the 3-benzoate **34** produced in higher amounts than the 2-benzoate **33**; some 2,3-dibenzoate **35** was also isolated. The regioselectivity for **32** is lower than the one for **2**, evidencing an influence of C(4)–OH on the benzoylation at C(3)–O. Benzoylation of the α-D-anomer **36** was again dominated by the intramolecular C(2)–OH···O–C(1) H-bond, yielding mostly the 2-benzoate **37** [5] (83.5% in the presence of (*S*)-**1**). The 3-benzoate **38** and the 2,3-dibenzoate **39** are by-products, particularly when (*R*)-**1** is used.

Scheme 4



a) (*S*)-**1** or (*R*)-**1** or TMEDA, Et_3N, BzCl, molecular sieves (4 Å), CH_2Cl_2, $-60°$, 1 h.

Table 7. *Benzoylation of Allyl or Methyl 4,6-O-Benzylidene α- or β-D-Glycopyranosides Catalyzed by* (*S*)-**1** *or* (*R*)-**1** *or TMEDA at* $-60°$

Substrates (configuration)	Yield [%][a])		
	2-Benzoate	3-Benzoate	2,3-Dibenzoate
32 (β-D-*gluco*)			
Cat. by (*S*)-**1**	**33** (20)	**34** (47)	**35** (5)
Cat. by (*R*)-**1**	**33** (21)	**34** (30)	**35** (9)
36 (α-D-*gluco*)			
Cat. by (*S*)-**1**	**37** (83.5)	**38** (3)	
Cat. by (*R*)-**1**	**37** (81)	**38** (9)	**39** (2)
40 (β-D-*galacto*)			
Cat. by (*S*)-**1**		**41** (83)	
Cat. by (*R*)-**1**		**41** (83)	
Cat. by TMEDA		**41** (84)	**42** (5)
43 (α-D-*galacto*)			
Cat. by (*S*)-**1**	**44** (46)	**45** (33)	**46** (7)
Cat. by (*R*)-**1**	**44** (26)	**45** (54)	**46** (10)
Cat. by TMEDA	**44** (64)	**45** (6)	**46** (15)
47 (β-D-*manno*)			
Cat. by (*S*)-**1**		**48** (90)	
Cat. by (*R*)-**1**		**48** (62.5)	
49 (α-D-*manno*)			
Cat. by (*S*)-**1**	**50** (6)	**51** (85)	
Cat. by (*R*)-**1**	**50** (19)	**51** (62)	**52** (4)
Cat. by TMEDA	**50** (8)	**51** (74)	**52** (9)

[a]) Yield of chromatographically pure product.

As expected from the C(3)–OH···O–C(4) H-bond [52] in methyl 4,6-*O*-benzylidene-β-D-galactopyranoside **40** [50], the 3-benzoate **41** [53] was the major product in the presence either of (*R*)-**1** (83%), of (*S*)-**1** (83%), or of TMEDA (84% of **41** and 5% of the 2,3-dibenzoate **42** [53] [54]). Benzoylation of the α-D-anomer **43**, however, showed again the competing effect of the C(2)–OH···O–C(1) and the C(3)–OH···O–C(4) H-bonds and the influence of the catalyst, (*S*)-**1** leading to 46% of the 2-benzoate **44** [53], 33% of the 3-benzoate **45** [53], and 7% of 2,3-dibenzoate **46** [53], (*R*)-**1** leading to 26% of **44**, 54% of **45**, and 10% of **46**, and TMEDA to 64% of **44**, 6% of **45**, and 15% of **46**.

Benzoylation of the anomeric mannopyranosides **47** and **49** reflects the same factors that dominated the benzoylation of the anomeric silylated mannopyranosides **25** and **27**. Benzoylation of the β-D-mannopyranoside **47** gave mostly the 3-benzoate **48** [65], isolated in 90% yield ((*S*)-**1**) or 62.5% ((*R*)-**1**). Benzoylation of the α-D-mannopyranoside **49** was less strongly influenced by the catalysts than that of **27**, providing 85, 62, and 74% of the 3-benzoate **51** [55] as the major product in the presence of (*S*)-**1**, (*R*)-**1**, and TMEDA, respectively.

The structure of **34** was evidenced by a single C=O *s* at 166.6 ppm and the absence of a coupling between the *t* at 5.49 ($J = 9.5$) and the *d* at 4.6 ($J = 7.8$, H–C(1)). The assignment was confirmed by decoupling experiments. Addition of D_2O simplified the *ddd* at 3.76 ($J = 9.4, 7.5, 3.1$) to a *dd* ($J = 9.4, 7.8$). Irradiation, after

the addition of D_2O, of the *t* at 5.49 further simplified the *dd* at 3.76 to a *d* ($J = 7.2$); similarly, irradiation of the *d* at 4.60 simplified the *dd* at 3.76 to a *d* ($J = 9.0$).

Benzoylation of partially protected monosaccharides with BzCl and Et_3N or $EtNMe_2$ in the presence, or absence, of catalytic amounts of either ditertiary 1,2-diamines or $EtNMe_2$ proceeded with various degrees of regioselectivity. The regioselectivity depended mostly on the constitution and configuration of the starting diols and triols.

Since acyl migration was excluded, regioselectivity reflects the relative nucleophilicity of the individual OH groups. Factors determining the nucleophilicity have been reported [2]; they comprise the equatorial or axial orientation of OH groups, intramolecular H-bonds of equatorial OH groups to germinal *cis*-OR substituents, the distance to the anomeric center, and steric hindrance. The nature of the catalysts used in this study only modulates these effects, to a larger or smaller extent, depending on how strong and how convergent the structural factors are.

A comparison with the yields resulting from benzoylation by established methods shows no general advantage of using **1** or TMEDA. Both, benzoylation following stannylation [11][14][42][56] or benzoylation with 1-benzoyl-1*H*-benzotriazole [5][6][57] resulted in higher or similar yields. Exceptions are the benzoylation of **2**, **21**, **25**, **43**, and **47**. Benzoylation of the 6-*O*-silylated β-D-glucopyranoside **2** in the presence of 5 mol-% (*S*)-**1** provided 82–84% of the 3-benzoate **4**. No alternative method was found, but benzoylation of methyl β-D-glucopyranoside with 1-benzoyloxy-1*H*-benzotriazole (3.3 equiv.) gave 60% of the 3,6-dibenzoate [6].

Regioselective benzoylation of 6-*O*-protected α-D-galactopyranosides is difficult. In the presence of 5 mol-% (*S*)-**1**, **21** yielded 78% of the 2-benzoate **22**, while (*R*)-**1** led mostly (57%) to the 3-benzoate **23**. This should be compared to the benzoylation of **21** with 2.2 equiv. BzCl and pyridine that yielded 64% of the 2,3-dibenzoate **24** [46], and to the benzoylation of methyl α-D-galactopyranoside that gave a complex mixture of monobenzoates and dibenzoates [14].

Benzoylation of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (**43**) in the presence of (*R*)-**1** provided 54% of the 3-benzoate **45** besides 26% of the regioisomer **44**, while TMEDA led to 64% of **44** besides 6% of **45**. By comparison, 1-benzoyloxy-1*H*-benzotriazole led to these isomers in a 1:1 ratio [6]. BzCl/pyridine provided **44** and **45** in 20 and 30% [53], BzCl/pyridine in $CHCl_3$ provided **44** and **45** in 10 and 46% [58], and BzCN/Et_3N in 21 and 40% yields, respectively [53].

The regioselective benzoylation of 4,6-*O*-benzylidene-β-D-mannopyranoside **47** is new, and no examples were found for the regioselective benzoylation of C(6)–*O*-protected β-D-mannopyranosides. Perhaps more important than the higher yields resulting, in these few examples, from benzoylation in the presence of ditertiary 1,2-diamines is the operational simplicity and the advantage of avoiding stannyl derivatives.

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Experimental Part

General. Solvents were removed under reduced pressure (rotatory evaporator). CH_2Cl_2 was distilled over CaH_2, and THF was distilled over Na/benzophenone before use. DMF was dried over 4-Å molecular sieves. Et_3N was distilled over CaH_2 and kept over 4-Å molecular sieves. Melting points were measured with a *Büchi 510* apparatus and are uncorrected. Optical rotations $[\alpha]$ were determined at 589 nm. IR Spectra were recorded on a *Perkin-Elmer 298 FT-IR* spectrometer. NMR Spectra were recorded on a *Gemini 200* or *300* apparatus with $CDCl_3$ as the solvent. FAB or MALDI-MS were registered on *VG ZAB SEQ* spectrometer.

Materials. The Me and allyl glycopyranosides **2** [36], **12** [41], **18** [45], **21** [46], **25** [47], **27** [48], **32** [49], **36** [49], **40** [50], **43** [50], **47** [51], and **49** [50] were prepared according to literature procedures. Commercial (±)-trans-*cyclohexane-1,2-diol* (**9**) was purified by FC before use. The enantiomeric excess of (±)-*trans*-cyclohexane-1,2-diol (ee < 0.5%) and (*S,S*)-*trans*-cyclohexane-1,2-diol (ee > 99.5%) was determined by chiral HPLC of the corresponding dibenzoates (column and conditions: see below).

*(*S*)-2-{[Benzyl(methyl)amino]methyl}-1-methylpyrrolidine* [31] ((*S*)-**1**). A soln. of *N*-Boc-L-proline (2.15 g, 10 mmol) and benzyl(methyl)amine (1.33 g, 11 mmol) in CH_2Cl_2 (45 ml) was treated dropwise with a soln. of dicyclohexylcarbodiimide (DCC, 2.27 g, 11 mmol) in CH_2Cl_2 (12 ml) at 0° and stirred at r.t. for 2 h, when a white precipitate was formed. After stirring for additional 48 h and evaporation, a suspension of the residue in Et_2O (30 ml) was filtered. Evaporation of the filterate and FC (column conditioned with hexane/Et_3N 99.5 : 0.5 and eluted with hexane/AcOEt 1 : 3) gave *tert*-butyl (*S*)-2-[(benzylmethyl)carbamoyl]pyrrolidine-1-carboxylate [59] (2.09 g, 65%). At 0°, a soln. of this amide (1.59 g, 5 mmol) in THF (35 ml) was treated dropwise with a suspension of $LiAlH_4$ (0.8 g, 21 mmol) in THF (20 ml) and stirred at 0° for 1 h, at r.t. for 1 h, at reflux overnight, cooled to 0°, and treated with sat. aq. Na_2SO_4 soln. until gas evolution ceased. After extraction with Et_2O (3 × 40 ml), the combined org. phases were dried ($MgSO_4$) and evaporated. FC (CH_2Cl_2/MeOH/Et_3N 20 : 1 : 0.5) of the colourless oily residue gave (*S*)-**1**[8]) (0.92 g, 82%). A faint yellow oil. R_f (CH_2Cl_2/MeOH/Et_3N 100 : 5 : 3) 0.45. $[\alpha]_D^{25} = -101.8$ ($c = 0.55$, $CHCl_3$). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.4–7.2 (*m*, 5 H); 3.59 (*d*, *J* = 13.0, PhC*H*); 3.44 (*d*, *J* = 13.0, PhC*H*); 3.04 (*ddd*, *J* = 9.0, 6.8, 2.2, H–C(2)); 2.62–2.50 (*m*, 1 H); 2.40 (*s*, MeN); 2.4–2.25 (*m*, 2 H); 2.22 (*s*, MeN); 2.18 (*dd*, *J* = 17.0, 9.2, 1 H); 2.1–1.9 (*m*, 1 H); 1.85–1.5 (*m*, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): 139.2 (*s*); 128.9 (2*d*); 128.1 (2*d*); 126.8 (*d*); 63.7 (*t*, Ph*C*H_2); 63.1 (*d*, C(2)); 62.6 (*t*, *C*H_2–C(2)); 57.7 (*t*, *C*(5)); 43.0 (*q*, MeN); 41.3 (*q*, MeN); 30.7 (*t*, C(3)); 22.4 (*t*, C(4)).

*(*R*)-2-{[Benzyl(methyl)amino]methyl}-1-methylpyrrolidine* ((*R*)-**1**). Similar to the preparation of (*S*)-**1**, treatment of *N*-Boc-D-proline (215 mg, 1.0 mmol) and benzyl(methyl)amine (133 mg, 1.1 mmol) in CH_2Cl_2 (5 ml) with DCC (227 mg, 1.1 mmol) in CH_2Cl_2 (1 ml) afforded *tert*-butyl (*R*)-2-[(benzylmethyl)carbamoyl]-pyrrolidine-1-carboxylate (212 mg, 67.3%), and the hydrogenation of this amide (132 mg) with $LiAlH_4$ (67 mg, 1.76 mmol) gave (*R*)-**1**[8]) (77 mg, 85%). $[\alpha]_D^{25} = +102.0$ ($c = 0.55$, $CHCl_3$). ^{1}H-NMR and ^{13}C-NMR data were identical to those of (*R*)-**1**.

General Procedure for Benzoylation. Under Ar, a suspension of the substrate (0.25 mmol) and 4-Å molecular sieves (500 mg) in CH_2Cl_2 (7 ml) was treated with (*S*)-**1**, (*R*)-**1**, TMEDA, TEEDA, or $EtNMe_2$ (2.5 to 12.5 μmol, 1 to 5 mol-%, or as indicated in the *Tables*) in CH_2Cl_2 (1 ml) at r.t., cooled to −60°, treated with Et_3N (28 mg, 0.25 mmol), $EtNMe_2$ (19 mg, 0.25 mmol), or pyridine (20 mg, 0.25 mmol), and with BzCl (36 mg, 0.25 mmol), stirred for 1 h at −60°, treated with phosphate buffer, pH 7 (5 ml), warmed to r.t., and extracted with Et_2O (15 ml). The org. phase was washed with brine (3 × 10 ml), dried ($MgSO_4$), and evaporated.

Benzoylation of **2**. According to the *General Procedure* and to *Tables 1*, *2*, and *5*. The products were isolated by FC (cyclohexane/AcOEt 8 : 1 → 1 : 2).

*Methyl 2-*O*-Benzoyl-6-*O*-[(*tert*-butyl)diphenylsilyl]-β-*D*-glucopyranoside* (**3**). White solid. R_f (hexane/AcOEt 2 : 1) 0.38. $[\alpha]_D^{25} = -31.0$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3601*w*, 3500*w*, 3072*w*, 3008*m*, 2932*m*, 2888*m*, 2859*m*, 1727*s*, 1602*w*, 1451*m*, 1428*m*, 1392*w*, 1316*m*, 1270*s*, 1114*s*, 1070*s*, 1028*m*, 980*w*, 823*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.15–8.05 (*m*, 2 arom. H); 7.80–7.65 (*m*, 4 arom. H); 7.60–7.50 (*m*, 1 arom. H); 7.50–7.35 (*m*, 8 arom. H); 5.08–4.98 (*m*, irrad. at 4.51 → change, H–C(2)); 4.51 (*d*, *J* = 7.8, irrad. at 5.04 → change, H–C(1)); 3.97 (*d*, *J* = 4.6, 2 H–C(6)); 3.86–3.70 (AB, *J* ≈ 7.8, H–C(3), H–C(4)); 3.49 (*dt*, *J* = 9.3, 4.6, H–C(5)); 3.47 (*s*, MeO); 3.16 (br. *s*, exchange with D_2O, HO–C(4)); 2.79 (br. *s*, exchange with D_2O, HO–C(3)); 1.07 (*s*, Me_3C). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.6 (*s*, C=O); 135.83 (2*d* of PhSi); 135.76 (2*d* of PhSi); 133.5 (*d* of Bz); 133.1, 132.9 (2*s* of PhSi); 130.1, 130.06 (2*d* of Bz, 2*d* of PhSi); 129.8 (*s* of Bz); 128.5 (2*d* of Bz); 128.0, 127.97 (4*d* of PhSi); 56.8 (*q*, MeO); 26.9 (*q*, *Me*$_3$C); 19.4 (*s*, Me$_3$*C*); data for C(1)–C(6), see *Table 8*.

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[8]) The enantiomer purity of (*S*)-**1** and (*R*)-**1** was determined by HPLC. (*Chiralpak* AD; hexane/Et_2NH 100 : 0.01, 0.5 ml/min). A single peak was observed for each diamine; t_R 9.6 ((*R*)-**1**) and 11.0 min ((*S*)-**1**).

Table 8. *Selected* ^{13}*C-NMR Chemical Shifts* [ppm] *of C(1) – C(6) of Some Benzoates*[a])

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
3	101.7	75.8	74.6[b])	72.8	74.8 [b])	64.7
4	103.5	72.3	78.7	70.6	75.3	64.3
5	103.5	74.3	75.1	75.1	71.7	63.0
6	102.0	71.6	76.9	71.2	75.6	64.4
7	104.0	72.9	75.9	75.2	69.0	63.0
14	99.5	71.2[b])	77.6	70.5	71.5[b])	64.4
15	99.0	71.9	73.3	73.7	70.7	64.4
16	97.1	71.8	74.1	71.0	71.3	64.3
17	97.2	74.5	70.9	72.5	70.2	64.3
20	104.1	70.0	73.2	72.3	73.9	61.6
22	97.5	72.4	68.7	69.3	70.1	63.6
23	99.8	67.4	74.2	68.9	69.6	63.7
26	100.3	69.1	76.4	67.2	75.2	64.7
28	98.7	72.3	69.4	70.4	71.4	64.1
29	100.6	69.3	75.1	67.6	71.7	64.6
30	98.8	72.3	73.1	67.7	70.7	64.2
31	98.7	73.2	70.5	71.0	69.7	64.2
33	100.2	74.8	72.4	80.9	66.2	68.6
34	101.5	73.5	74.3	78.6	66.4	68.6
39	96.1	79.6	69.1	72.5	63.0	69.0
46	98.1	69.3[b])	68.9[b])	74.3	62.3	69.2[b])
52	99.6	70.9	69.0[b])	76.8	63.8	68.9[b])

[a]) The assignment of signals are based on [11] and [60]. [b]) The assignments may be interchanged.

Methyl 3-O-*Benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-β*-D-*glucopyranoside* (**4**). White solid. R_f (hexane/AcOEt 2:1) 0.45. $[\alpha]_D^{25} = -10.0$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3603*m*, 3498*m*, 3069*w*, 2935*m*, 2889*m*, 2860*m*, 1719*s*, 1587*w*, 1451*m*, 1427*m*, 1391*m*, 1274*s*, 1114*s,* 1068*s*, 936*w*, 818*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.12 – 8.05 (*m*, 2 arom. H); 7.74 – 7.65 (*m*, 4 arom. H); 7.56 – 7.3 (*m*, 9 arom. H); 5.21 (*t*, $J = 9.1$, H–C(3)); 4.31 (*d*, $J = 7.5$, H–C(1)); 3.97 (*d*, $J = 5.0$, 2 H–C(6)); 3.87 (*td*, $J = 9.1$, 3.3, irrad. at 5.21 → change, irrad. at 3.21 → *t*, $J = 9.5$, addition of D_2O → *t*, $J = 9.1$, H–C(4)); 3.62 (*ddd*, $J = 9.5$, 7.5, 2.9, irrad. at 5.21 → change, irrad. at 4.31 → change, irrad. at 2.79 → *dd*, $J = 9.5$, 7.9, addition of D_2O → *dd*, $J = 9.5$, 7.9, H–C(2)); 3.53 (*s*, MeO); 3.50 (*dt*, $J =$ 9.1, 4.5, H–C(5)); 3.21 (*d*, $J = 3.3$, exchange with D_2O, HO–C(4)); 2.79 (*d*, $J = 2.9$, exchange with D_2O, HO–C(2)); 1.05 (*s*, Me_3C). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.6 (*s*, C=O); 135.6 (2*d* of PhSi); 135.5 (2*d* of PhSi); 133.3 (*d* of Bz); 133.0, 132.9 (2*s* of PhSi); 129.9, 129.8 (2*d* of Bz, 2*d* of PhSi); 129.5 (*s* of Bz); 128.3 (2*d* of Bz); 127.7 (4*d* of PhSi); 57.0 (*q*, MeO); 26.7 (*q*, *Me*$_3$C); 19.1 (*s*, Me$_3$*C*); for data of C(1) – C(6), see *Table 8*. FAB-MS: 1095 (5, $[2M + Na]^+$), 559 (37, $[M + Na]^+$), 537 (54, $[M + H]^+$). Anal. calc. for $C_{30}H_{36}O_7Si$ (536.70): C 67.14, H 6.76; found: C 66.94, H 6.85.

Methyl 4-O-*Benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-β*-D-*glucopyranoside* (**5**). White solid. R_f (hexane/AcOEt 2:1) 0.1. $[\alpha]_D^{25} = +5.8$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3603*w*, 3439*w* (br.), 3072*w*, 3008*m*, 2932*m*, 2880*w*, 2858*m*, 1725*s*, 1602*w*, 1472*w*, 1451*m*, 1428*m*, 1392*w*, 1316*m*, 1270*s*, 1114v*s*, 1069*s*, 1046*s*, 982*w*, 823*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.0 – 7.9 (*m*, 2 arom. H); 7.72 – 7.64 (*m*, 2 arom. H); 7.62 – 7.54 (*m*, 3 arom. H); 7.47 – 7.16 (*m*, 8 arom. H); 5.22 (*t*, $J = 9.3$, irrad. at 3.81 → *d*, $J = 8.8$, irrad. at 3.65 → *d*, $J = 10.3$, H–C(4)); 4.29 (*d*, $J = 7.5$, irrad. at 3.55 → *s*, H–C(1)); 3.83 (*d*, $J = 3.4$, irrad. at 3.65 → *s*, 2 H–C(6)); 3.81 (*t*, $J = 9.4$, irrad. at 5.22 → change, H–C(3)); 3.65 (*dt*, $J = 9.6$, 3.0, irrad. at 5.22 → br. *t*, $J = 3.1$, H–C(5)); 3.59 (*s*, MeO); 3.55 (*dd*, $J = 9.3$, 8.0, addition of D_2O → change, irrad. at 4.29 → *d*, $J = 9.5$, H–C(2)); 3.29 (br. *s*, exchange with D_2O, HO–C(3)); 3.20 (br. *s*, exchange with D_2O, HO–C(2)); 1.00 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.0 (*s*, C=O); 135.8 (2*d* of PhSi); 135.7 (2*d* of PhSi); 133.6 (*d* of Bz); 133.4 (2*s* of PhSi); 130.0, 129.8, 129.77 (2*d* of Bz, 2*d* of PhSi); 129.7 (*s* of Bz); 128.6 (2*d* of Bz); 127.8 (4*d* of PhSi); 56.9 (*q*, MeO); 26.6 (*q*, *Me*$_3$C); 19.1 (*s*, Me$_3$*C*); for data of C(1) – C(6), see *Table 8*.

Methyl 2,3-Di-O-*benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-β*-D-*glucopyranoside* (**6**). White solid. R_f (hexane/AcOEt 3:1) 0.34. $[\alpha]_D^{25} = +64.6$ ($c = 0.1$, $CHCl_3$). IR ($CHCl_3$): 3608*m*, 3443*w*, 3008*m*, 2932*w*, 2858*w*, 1729*s*,

1602*m*, 1451*w*, 1428*w*, 1279*s*, 1112*s*, 1070*m*, 931*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.05–7.90 (*m*, 4 arom. H); 7.76–7.70 (*m*, 4 arom. H); 7.54–7.34 (*m*, 12 arom. H); 5.49 (*t*, *J* = 10.0, H–C(3)); 5.40 (*dd*, *J* = 10.0, 7.8, irrad. at 4.61 → *d*, *J* = 9.6, H–C(2)); 4.61 (*d*, *J* = 7.5, H–C(1)); 4.03 (*td*, *J* = 9.2, 3.4, irrad. at 3.62 → change, irrad. at 3.23 → *t*, *J* = 9.2, addition of D_2O → *t*, *J* = 9.2, H–C(4)); 4.03 (*d*, *J* = 4.7, irrad. at 3.62 → *s*, 2 H–C(6)); 3.62 (*dt*, *J* = 9.6, 4.6, H–C(5)); 3.50 (*s*, MeO); 3.23 (*d*, *J* = 3.4, exchange with D_2O, HO–C(4)); 1.09 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.5, 165.7 (2*s*, 2 C=O); 136.0 (2*d* of PhSi); 135.9 (2*d* of PhSi); 133.6, 133.4 (2*d* of Bz); 133.3, 133.1 (2*s* of PhSi); 130.2, 130.1, 130.0 (2*d* of PhSi, 4*d* of Bz); 129.7, 129.4 (2*s* of Bz); 128.63, 128.57 (4*d* of Bz); 128.07, 128.03 (4*d* of PhSi); 56.9 (*q*, MeO); 26.9 (*q*, *Me*$_3$C); 19.3 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*. MALDI-MS: 663 ($[M+Na]^+$). Anal. calc. for $C_{37}H_{40}O_8Si$ (640.80): C 69.35, H 6.29; found: C 69.27, H 6.34.

Methyl 3,4-Di-O-*benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-β*-D-*glucopyranoside* (**7**). White solid. R_f (hexane/AcOEt 2:1) 0.49. $[\alpha]_D^{25} = -60.0$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3606*w*, 3439*w* (br.), 3008*m*, 2932*w*, 2858*w*, 1729*s*, 1602*m*, 1451*m*, 1428*w*, 1316*w*, 1277*s*, 1113*s*, 1069*m*, 1027*m*, 931*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.0–7.94 (*m*, 2 arom. H); 7.88–7.82 (*m*, 2 arom. H); 7.72–7.65 (*m*, 2 arom. H); 7.63–7.56 (*m*, 2 arom. H); 7.55–7.44 (*m*, 2 arom. H); 7.40–7.18 (*m*, 10 arom. H); 5.65–5.49 (AB, *J* ≈ 9.0, H–C(3), H–C(4)); 4.45 (*d*, *J* = 7.8, H–C(1)); 3.84–3.72 (*m*, addition of D_2O → change, irrad. at 5.53 → change, irrad. at 4.45 → change, H–C(2), H–C(5); 2 H–C(6)); 3.63 (*s*, MeO); 2.74 (*d*, *J* = 3.1, exchange with D_2O, HO–C(2)); 1.03 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.1, 165.5 (2*s*, 2 C=O); 135.9 (2*d* of PhSi); 135.8 (2*d* of PhSi); 133.5, 133.44 (2*d* of Bz); 133.38 (2*s* of PhSi); 130.2, 130.0, 129.88, 129.84 (2*d* of PhSi, 4*d* of Bz); 129.5 (2*s* of Bz); 128.6 (4*d* of Bz); 127.8 (4*d* of PhSi); 57.2 (*q*, MeO); 26.7 (*q*, *Me*$_3$C); 19.2 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*.

*Benzoylation of (1*S*,2*S*)*-**9**. According to the *General Procedure*, treatment of (1*S*,2*S*)-**9** (58 mg, 0.5 mmol) with Et_3N (56 mg), BzCl (72 mg, 0.5 mmol), and (*S*)-**1** (5.4 mg) at −60° for 24 h followed by FC (hexane/AcOEt 4:1) gave (1*S*,2*S*)-**10** (80 mg, 73%) and (1*S*,2*S*)-**11** (18 mg, 11%).

*Data of (1*S*,2*S*)-2-(benzoyloxy)cyclohexanol* (**10**): White crystals. M.p. 115.5–116.5°. $[\alpha]_D^{25} = +55.0$ (*c* = 0.5, $CHCl_3$).

*Data of (1*S*,2*S*)-cyclohexane-1,2-diyl Dibenzoate* (**11**): White solid. $[\alpha]_D^{25} = +97.4$ (*c* = 0.925, $CHCl_3$).

Benzoylation of (±)-**9**. According to the *General Procedure*, (±)-**9** with (*S*)-**1** or (*R*)-**1** at −60° for 24 h and FC (hexane/AcOEt 4:1) gave **10** and **11** (see *Table 3*). The enantiomer purity of **10** and **11** was determined by chiral HPLC (*Chiralpak AS;* solvent *A* (dibenzoate): hexane/i-PrOH 98:2, 0.8 ml/min, t_R 7.8 ((*S*,*S*)-**11**) and 8.9 min ((*R*,*R*)-**11**); solvent *B* (monobenzoate): hexane/i-PrOH 90:10, 1.0 ml/min, t_R 7.1 ((*S*,*S*)-**10**) and 14.7 min ((*R*,*R*)-**10**).

Benzoylation of **12**. According to the *General Procedure: a*) **12** (216 mg, 0.5 mmol) with (*S*)-**1** (5 mol-%) followed by FC (cyclohexane/AcOEt 6:1 → 1:2) gave **16**/**17**[9]) 89:11 (11 mg, 3.5%), **14** (19 mg, 7%), and **13** [42] (220 mg, 82%).

b) **12** (216 mg, 0.5 mmol) with (*R*)-**1** (5 mol-%) followed by FC (cyclohexane/AcOEt 6:1 → 1:2) gave **16**/**17** 63:37 (60 mg, 19%), **14** (75 mg, 28%), **13** (30 mg, 11%), **15** (27 mg, 10%), and **12** (40 mg, 18.5%).

c) **12** (216 mg, 0.5 mmol) with TMEDA (5 mol-%) followed by FC (cyclohexane/AcOEt 6:1 → 1:2) gave **16**/**17** 75:25 (55 mg, 17%), **14** (9 mg, 3.5%), **13** (172 mg, 64%).

The mixture **16**/**17** from *b* was separated by HPLC (hexane/AcOEt 5:1), yielding 35 mg of **16** and 21 mg of **17**.

Methyl 3-O-*Benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-α*-D-*glucopyranoside* (**14**). White solid. R_f (cyclohexane/AcOEt 2:1) 0.48. $[\alpha]_D^{25} = +72.8$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3568*w*, 3072*w*, 3008*m*, 2932*m*, 2859*m*, 1718*s*, 1602*m*, 1472*w*, 1452*w*, 1428*m*, 1316*m*, 1273*s*, 1113*s*, 1071*m*, 1059*m*, 998*w*, 823*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.13–8.08 (*m*, 2 arom. H); 7.75–7.65 (*m*, 4 arom. H); 7.62–7.54 (*m*, 1 arom. H); 7.50–7.35 (*m*, 8 arom. H); 5.33 (*t*, *J* = 9.3, H–C(3)); 4.81 (*d*, *J* = 3.7, H–C(1)); 3.94 (*d*, *J* = 4.4, 2 H–C(6)); 3.81 (*td*, *J* ≈ 9.3, 3.7, irrad. at 2.78 → *t*, *J* = 9.3, addition of D_2O → *t*, *J* = 9.5, addition of D_2O and irrad. at 5.33 → *d*, *J* = 9.3, H–C(4)); 3.75 (*dt*, *J* ≈ 9.5, 3.2, H–C(5)); 3.74 (*ddd*, *J* ≈ 11.0, 10.0, 3.7, irrad. at 2.20 → change, addition of D_2O → *dd*, *J* = 10.0, 3.7, addition of D_2O and irrad. at 5.33 → change, addition of D_2O and irrad. at 4.81 → *d*, *J* = 9.7, H–C(2)); 3.43 (*s*, MeO); 2.78 (*d*, *J* = 3.3, exchange with D_2O, HO–C(4)); 2.20 (*d*, *J* = 11.2, exchange with D_2O, HO–C(2)); 1.08 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.2 (*s*, C=O); 135.9 (4*d* of PhSi); 133.6 (*d* of Bz); 133.41, 133.36 (2*s* of PhSi); 130.2, 130.1 (2*d* of Bz, 2*d* of PhSi); 130.0 (*s* of Bz); 128.6 (2*d* of Bz); 128.0 (4*d* of PhSi); 55.4 (*q*, MeO); 26.9 (*q*, *Me*$_3$C); 19.3 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*.

Methyl 4-O-*Benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-α*-D-*glucopyranoside* (**15**). White solid. R_f (cyclohexane/AcOEt 2:1) 0.11. $[\alpha]_D^{25} = +94.6$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3570*w*, 3008*m*, 2932*m*, 2859*m*, 1724*s*, 1602*w*,

[9]) The ratio **16**/**17** was assigned by the integration of ^{1}H-NMR signal of MeO.

1472*w*, 1452*w*, 1428*m*, 1316*m*, 1269*s*, 1113*s*, 1075*s*, 1063*s*, 1026*m*, 977*w*, 823*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.0–7.94 (*m*, 2 arom. H); 7.68–7.52 (*m*, 5 arom. H); 7.48–7.40 (*m*, 2 arom. H); 7.38–7.25 (*m*, 4 arom. H); 7.22–7.14 (*m*, 2 arom. H); 5.17 (*dd*, *J* = 9.9, 9.3, H–C(4)); 4.88 (*d*, *J* = 3.7, H–C(1)); 3.98 (*t*, *J* = 9.3, irrad. at 5.17 → change, irrad. at 3.70 → *d*, *J* = 9.3, H–C(3)); 3.96 (*ddd*, *J* = 9.9, 4.4, 2.8, irrad. at 5.17 → change, H–C(5)); 3.81 (*dd*, *J* = 11.2, 4.4, H–C(6)); 3.77 (*dd*, *J* = 11.2, 2.8, H′–C(6)); 3.70 (*dd*, *J* = 9.3, 3.7, irrad. at 4.88 → *d*, *J* = 9.3, H–C(2)); 3.49 (*s*, MeO); 2.78 (br. *s*, exchange with D_2O, HO–C(3)); 2.30 (br. *s*, exchange with D_2O, HO–C(2)); 1.01 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.5 (*s*, C=O); 135.6, 135.5 (4*d* of PhSi); 133.4 (*d* of Bz); 133.15, 133.09 (2*s* of PhSi); 130.0 (2*d* of Bz); 129.6 (2*d* of PhSi); 129.5 (*s* of Bz); 128.5 (2*d* of Bz); 127.67, 127.63 (4*d* of PhSi); 55.6 (*q*, MeO); 26.9 (*q*, *Me*$_3$C); 19.3 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*.

Methyl 2,3-Di-O-*benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-α*-D-*glucopyranoside* (**16**). White solid. R_f (hexane/AcOEt 2:1) 0.60. $[\alpha]_D^{25} = +107.2$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3509*w*, 3071*w*, 3008*m*, 2932*m*, 2859*m*, 1723*s*, 1602*m*, 1472*m*, 1452*m*, 1428*m*, 1316*m*, 1280*s*, 1112*s*, 1070*s*, 1054*s*, 997*m*, 823*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.05–7.95 (*m*, 4 arom. H); 7.9–7.83 (*m*, 4 arom. H); 7.6–7.28 (*m*, 12 arom. H); 5.77 (*dd*, *J* = 10.2, 9.0, irrad. at 5.21 → change, irrad. at 3.95 → *d*, *J* = 10.2, H–C(3)); 5.21 (*dd*, *J* = 10.2, 3.7, irrad. at 5.77 → change, irrad. at 5.10 → change, H–C(2)); 5.10 (*d*, *J* = 3.7, irrad. at 5.21 → *s*, H–C(1)); 3.99 (*d*, *J* = 4.4, 2 H–C(6)); 3.95 (*td*, *J* = 9.0, 3.7, addition of D_2O → change, irrad. at 5.77 → change, irrad. at 2.97 → change, H–C(4)); 3.86 (*dt*, *J* = 9.3, 4.4, H–C(5)); 3.39 (*s*, MeO); 2.97 (*d*, *J* = 3.7, exchange with D_2O, HO–C(4)); 1.09 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.5, 166.4 (2*s*, 2 C=O); 135.94, 135.90 (4*d* of PhSi); 133.5 (2*d* of Bz); 133.4, 133.3 (2*s* of PhSi); 130.1 (4*d* of Bz, 2*d* of PhSi); 129.7, 129.5 (2*s* of Bz); 128.64, 128.6 (4*d* of Bz); 128.0 (4*d* of PhSi); 55.3 (*q*, MeO); 26.9 (*q*, *Me*$_3$C); 19.3 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*.

Methyl 2,4-Di-O-*benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-α*-D-*glucopyranoside* (**17**). White solid. R_f (hexane/AcOEt 2:1) 0.56. $[\alpha]_D^{25} = +93.0$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3611*w*, 3072*w*, 3008*m*, 2932*m*, 2859*w*, 1722*s*, 1602*w*, 1472*w*, 1452*m*, 1428*m*, 1316*m*, 1271*s*, 1112*s*, 1070*m*, 1043*s*, 969*w*, 823*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.14–8.08 (*m*, 2 arom. H); 8.02–7.95 (*m*, 2 arom. H); 7.69–7.53 (*m*, 6 arom. H); 7.50–7.41 (*m*, 4 arom. H); 7.40–7.28 (*m*, 4 arom. H); 7.23–7.15 (*m*, 2 arom. H); 5.31 (*t*, *J* = 9.5, irrad. at 4.38 → *d*, *J* = 9.3, irrad. at 4.05 → *d*, *J* = 9.0, H–C(4)); 5.13 (*d*, *J* = 3.7, H–C(1)); 5.09 (*dd*, *J* = 9.3, 3.7, H–C(2)); 4.38 (*td*, *J* = 9.3, 5.6, addition of D_2O → *t*, *J* = 9.3, addition of D_2O and irrad. at 5.31 → *d*, *J* = 9.7, H–C(3)); 4.05 (*ddd*, *J* = 10.0, 4.4, 2.5, H–C(5)); 3.85 (*dd*, *J* = 11.5, 4.4, H–C(6)); 3.81 (*dd*, *J* = 11.5, 2.5, H′–C(6)); 3.44 (*s*, MeO); 2.70 (*d*, *J* = 5.6, exchange with D_2O, HO–C(3)); 1.01 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.8, 166.5 (2*s*, 2 C=O); 135.8, 135.7 (4*d* of PhSi); 133.6, 133.5 (2*d* of Bz); 133.25, 133.2 (2*s* of PhSi); 130.15, 130.12, 129.8 (4*d* of Bz, 2*d* of PhSi); 129.5 (2*s* of Bz); 128.6 (4*d* of Bz); 127.8, 127.76 (4*d* of PhSi); 55.3 (*q*, MeO); 26.9 (*q*, *Me*$_3$C); 19.3 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*.

Benzoylation of **18**. According to the *General Procedure: a*) Due to the insolubility of **18** in CH_2Cl_2 at −60°, the reaction of **18** (108 mg, 0.25 mmol) with (*S*)-**1** (5 mol-%) was run at −5°. FC (cyclohexane/AcOEt 6:1 → 1:2) gave a mixture of dibenzoates (from ^{1}H-NMR) (20 mg), **19** [61] (91 mg, 68%), and **18** (8 mg, 7%).

b) **18** (108 mg, 0.25 mmol) with (*R*)-**1** (5 mol-%) at −5° followed by FC (cyclohexane/AcOEt 6:1 → 1:2) gave a mixture of dibenzoates (11 mg), **19** (82 mg, 61%), **20** (8 mg, 6%), and **18** (10 mg, 9%).

c) **18** (108 mg, 0.25 mmol) with TMEDA (5 mol-%) at −5° followed by FC (cyclohexane/AcOEt 6:1 → 1:2), gave a mixture of dibenzoates (23 mg), **19** (75 mg, 56%), **20** (5 mg, 4%), and **18** (12 mg, 11%).

Methyl 4-O-*Benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-β*-D-*galactopyranoside* (**20**). White solid. R_f (cyclohexane/AcOEt 2:1) 0.10. $[\alpha]_D^{26} = -22.6$ (*c* = 0.58, $CHCl_3$). IR ($CHCl_3$): 3598*m*, 3436*w*, 3008*m*, 2961*m*, 2932*m*, 2888*w*, 2859*m*, 1722*s*, 1602*w*, 1451*m*, 1428*m*, 1316*w*, 1275*s*, 1113*s*, 1071*s*, 825*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.1–8.02 (*m*, 2 arom. H); 7.66–7.55 (*m*, 3 arom. H); 7.5–7.22 (*m*, 8 arom. H); 7.14–7.05 (*m*, 2 arom. H); 5.74 (*d*, *J* ≈ 3.0, H–C(4)); 4.25 (*d*, *J* = 7.8, H–C(1)); 3.94 (*dt*, *J* = 9.6, 3.1, addition of D_2O → *dd*, *J* = 9.6, 3.4, H–C(3)); 3.87–3.75 (*m*, H–C(5), 2 H–C(6)); 3.72 (*ddd*, *J* = 9.9, 8.1, 1.6, addition of D_2O → *dd*, *J* = 10.0, 7.8, H–C(2)); 3.56 (*s*, MeO); 2.65, 2.49 (2 br. *s*, exchange with D_2O, HO–C(2), HO–C(3)); 0.99 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.9 (*s*, C=O); 135.6, 135.5 (4*d* of PhSi); 133.4 (*d* of Bz); 133.0, 132.7 (2*s* of PhSi); 130.1, 129.9, 129.7 (2*d* of Bz, 2*d* of PhSi); 129.6 (*s* of Bz); 128.5 (2*d* of Bz); 127.8, 127.7 (4*d* of PhSi); 57.6 (*q*, MeO); 26.9 (*q*, *Me*$_3$C); 19.3 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*. MALDI-MS: 559 ($[M + Na]^+$).

Benzoylation of **21**. According to the *General Procedure: a*) **21** (108 mg, 0.25 mmol) with (*S*)-**1** (5 mol-%) followed by FC (cyclohexane/AcOEt 6:1 → 2:1) gave **24** [46] (4 mg, 3%), **22** (104 mg, 78%), and **23** (3 mg, 2%).

b) **20** (108 mg, 0.25 mmol) with (*R*)-**1** (5 mol-%) followed by FC (cyclohexane/AcOEt 6:1 → 2:1) gave **24** (13 mg, 8%), **22** (14 mg, 10%), and **23** (76 mg, 57%).

c) **20** (108 mg, 0.25 mmol) with TMEDA (5 mol-%) followed by FC (cyclohexane/AcOEt 6:1 → 2:1) gave **24** (15 mg, 9%), **22** (93 mg, 69%), and **23** (3 mg, 2%).

Methyl 2-O-*Benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-α*-D-*galactopyranoside* (**22**). White solid. R_f (hexane/AcOEt 2:1) 0.46. $[\alpha]_D^{25} = +83.2$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3564*m*, 3470*w*, 2935*s*, 2894*m*, 2881*m*, 1718*s*, 1595*w*, 1453*m*, 1427*m*, 1332*m*, 1279*s*, 1108v*s*, 1043*s*, 822*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.1–8.05 (*m*, 2 arom. H); 7.75–7.62 (*m*, 4 arom. H); 7.6–7.3 (*m*, 9 arom. H); 5.23 (*dd*, $J = 9.7, 3.7$, H–C(2)); 5.01 (*d*, $J = 3.7$, H–C(1)); 4.20 (*t*, $J = 3.0$, irrad. at 2.98 → change, addition of D_2O → *d*, $J = 3.0$, H–C(4)); 4.11 (*ddd*, $J = 9.9, 8.3, 3.3$, irrad. at 2.63 → *dd*, $J = 10.0, 3.3$, addition of D_2O → *dd*, $J = 10.1, 3.3$, H–C(3)); 4.0–3.8 (*m*, H–C(5), 2 H–C(6)); 3.31 (*s*, MeO); 2.98 (*d*, $J = 2.9$, exchange with D_2O, HO–C(4)); 2.63 (*d*, $J = 8.3$, exchange with D_2O, HO–C(3)); 1.06 (*s*, Me_3C). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.0 (*s*, C=O); 135.9, 135.6 (4*d* of PhSi); 133.3 (*d* of Bz); 133.1, 133.0 (2*s* of PhSi); 129.9 (2*d* of Bz, 2*d* of PhSi); 129.6 (*s* of Bz); 128.4 (2*d* of Bz); 127.8 (4*d* of PhSi); 55.2 (*q*, MeO); 26.7 (*q*, *Me*$_3$C); 19.0 (*s*, Me_3C); for data of C(1)–C(6), see *Table 8*. FAB-MS: 1095 (4, $[2M + Na]^+$), 1073 (7, $[2M + H]^+$), 559 (16, $[M + Na]^+$), 537 (14, $[M + H]^+$), 505 (100). Anal. calc. for $C_{30}H_{36}O_7Si$ (536.70): C 67.14, H 6.76; found: C 66.92, H 6.86.

Methyl 3-O-*Benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-α*-D-*galactopyranoside* (**23**). White solid. R_f (hexane/AcOEt 2:1) 0.27. $[\alpha]_D^{25} = +99.6$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3567*m*, 3471*w*, 3069*w*, 2934*m*, 2861*m*, 1717*s*, 1601*w*, 1452*m*, 1427*m*, 1274*s*, 1108*s*, 1055*s*, 982*w*, 818*m*, 616*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.13–8.1 (*m*, 2 arom. H); 7.72–7.64 (*m*, 4 arom. H); 7.6–7.3 (*m*, 9 arom. H); 5.26 (*dd*, $J = 10.2$, 3.0, H–C(3)); 4.87 (*d*, $J = 3.7$, H–C(1)); 4.31 (*t*, $J = 3.0$, addition of D_2O → *d*, $J = 3.0$, H–C(4)); 4.20 (*td*, $J = 10.4, 3.7$, addition of D_2O → *dd*, $J = 10.4, 3.7$, H–C(2)); 3.95–3.84 (*m*, H–C(5), 2 H–C(6)); 3.39 (*s*, MeO); 2.70 (*d*, $J = 3.3$, exchange with D_2O, HO–C(4)); 2.00 (*d*, $J = 11.2$, exchange with D_2O, HO–C(2)); 1.04 (*s*, Me_3C). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.6 (*s*, C=O); 135.7, 135.6 (4*d* of PhSi); 133.3 (*d* of Bz); 133.0, 132.8 (2*s* of PhSi); 130.0 (2*d* of Bz, 2*d* of PhSi); 129.9 (*s* of Bz); 128.5 (2*d* of Bz); 127.8 (4*d* of PhSi); 55.3 (*q*, MeO); 26.7 (*q*, *Me*$_3$C); 19.1 (*s*, Me_3C); for data of C(1)–C(6), see *Table 8*. FAB-MS: 1073 (10, $[2M + H]^+$), 559 (15, $[M + Na]^+$), 537 (47, $[M + H]^+$), 427 (100). Anal. calc. for $C_{30}H_{36}O_7Si$ (536.70): C 67.14, H 6.76; found: C 67.03, H 6.91.

Benzoylation of **25**. According to the *General Procedure: a*) **25** (108 mg, 0.25 mmol) with (*S*)-**1** (5 mol-%) followed by FC (hexane/AcOEt 2:1) gave **26** (115 mg, 86%).

b) **25** (108 mg, 0.25 mmol) with (*R*)-**1** (5 mol-%) followed by FC (hexane/AcOEt 2:1) gave **26** (84 mg, 63%) and **25** (7 mg, 6.5%).

Methyl 3-O-*Benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-β*-D-*mannopyranoside* (**26**). White solid. R_f (hexane/AcOEt 2:1) 0.6. $[\alpha]_D^{25} = -51.2$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3577*m*, 3507*m*, 3069*w*, 3008*m*, 2935*m*, 2860*m*, 1718*s*, 1601*w*, 1452*m*, 1427*m*, 1368*m*, 1275*s*, 1111*s*, 1070*s*, 1002*m*, 936*w*, 880*w*, 818*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.2–8.0 (*m*, 2 arom. H); 7.8–7.6 (*m*, 4 arom. H); 7.6–7.3 (*m*, 9 arom. H); 5.06 (*dd*, $J = 9.5, 2.9$, H–C(3)); 4.51 (*d*, $J = 0.8$, H–C(1)); 4.27 (*td*, $J = 9.5, 2.9$, irrad. at 5.06 → change, irrad. at 3.45 → change, irrad. at 2.90 → *t*, $J = 9.5$, addition of D_2O → *t*, $J = 9.5$, H–C(4)); 4.21 (*td*, $J = 2.9, 0.8$, irrad. at 5.06 → change, irrad. at 4.51 → change, irrad. at 2.18 → change, addition of D_2O → br. *d*, $J \approx 3.3$, H–C(2)); 3.99 (*d*, $J = 5.0$, irrad. at 3.45 → *s*, 2 H–C(6)); 3.52 (*s*, MeO); 3.45 (*dt*, $J = 9.5, 5.0$, H–C(5)); 2.90 (*d*, $J = 2.9$, exchange with D_2O, HO–C(4)); 2.18 (*d*, $J = 2.9$, exchange with D_2O, HO–C(2)); 1.00 (*s*, Me_3C). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.6 (*s*, C=O); 135.3, 135.2 (4*d* of PhSi); 132.9 (*d* of Bz); 132.6, 132.5 (2*s* of PhSi); 129.6, 129.5 (2*d* of Bz, 2*d* of PhSi); 129.3 (*s* of Bz); 128.0 (2*d* of Bz); 127.4 (4*d* of PhSi); 56.8 (*q*, MeO); 26.7 (*q*, *Me*$_3$C); 19.2 (*s*, Me_3C); for data of C(1)–C(6), see *Table 8*. MALDI-MS: 559 ($[M + Na]^+$). Anal. calc. for $C_{30}H_{36}O_7Si$ (536.70): C 67.14, H 6.76; found: C 67.08, H 6.90.

Benzoylation of **27**. According to the *General Procedure: a*) **27** (108 mg, 0.25 mmol) with (*S*)-**1** (5 mol-%) followed by FC (cyclohexane/AcOEt 5:1 → 1:4) gave **29** [48] (115 mg, 86%) and **28** (11 mg, 8%).

b) **27** (108 mg, 0.25 mmol) with (*R*)-**1** (5 mol-%) followed by FC (cyclohexane/AcOEt 5:1 → 1:4) gave **30** (10 mg, 6%), **31** (16 mg, 10%), **29** (13 mg, 10%), and **28** (63 mg, 47%).

c) **27** (108 mg, 0.25 mmol) with TMEDA (5 mol-%) followed by FC (cyclohexane/AcOEt 5:1 → 1:4) gave **30** (10 mg, 6%), **31** (5 mg, 3%), **29** (45 mg, 34%), **28** (16 mg, 12%), and **27** (11 mg, 10%).

Methyl 2-O-*Benzoyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-α*-D-*mannopyranoside* (**28**). White solid. R_f (hexane/AcOEt 2:1) 0.30. $[\alpha]_D^{25} = +8.0$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3591*m*, 3514*w*, 2932*s*, 2859*m*, 1720*s*, 1602*m*, 1452*m*, 1428*m*, 1317*m*, 1271*s*, 1138*s*, 1114*s*, 1074*s*, 971*m*, 908*m*, 823*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.1–8.0 (*m*, 2 arom. H); 7.8–7.7 (*m*, 4 arom. H); 7.6–7.3 (*m*, 9 arom. H); 5.35 (*dd*, $J = 2.8, 1.5$, irrad. at 4.82 → *d*, $J = 2.8$, H–C(2)); 4.82 (*d*, $J = 1.7$, irrad. at 5.35 → *s*, H–C(1)); 4.15–4.0 (*m*, irrad. at 3.67 → change, irrad. at 2.68 → change, irrad. at 2.28 → change, addition of D_2O → change, H–C(3), H–C(4)); 4.0–3.8 (*m*, irrad. at 3.67 → change, 2 H–C(6)); 3.67 (*dt*, $J = 8.4, 4.5$, H–C(5)); 3.35 (*s*, MeO); 2.68 (*d*, $J = 2.2$, exchange with D_2O, HO–C(4)); 2.28 (*d*, $J = 4.7$, exchange with D_2O, HO–C(3)); 1.07 (*s*, Me_3C). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.3 (*s*, C=O); 135.7, 135.6 (4*d* of PhSi); 133.4 (*d* of Bz); 133.1, 133.0 (2*s* of PhSi); 129.9 (2*d* of Bz, 2*d* of PhSi); 129.5 (*s* of Bz); 128.4 (2*d* of Bz); 127.4 (4*d* of PhSi); 55.0 (*q*, MeO); 26.8 (*q*, *Me*$_3$C); 19.2 (*s*, Me_3C); for data of C(1)–C(6), see *Table 8*. FAB-MS:

559 (10, $[M+Na]^+$), 537 (6, $[M+H]^+$), 505 (100). Anal. calc. for $C_{30}H_{36}O_7Si$ (536.70): C 67.14, H 6.76; found: C 67.22, H 6.86.

*Methyl 3-*O*-Benzoyl-6-*O*-[(*tert*-butyl)diphenylsilyl]-α-*D*-mannopyranoside* (**29**) [48]. White solid. R_f (cyclohexane/AcOEt 2:1) 0.43. $[\alpha]_D^{25} = +25.5$ ($c = 0.62$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.14–8.06 (*m*, 2 arom. H); 7.76–7.66 (*m*, 4 arom. H); 7.62–7.54 (*m*, 1 arom. H); 7.50–7.35 (*m*, 8 arom. H); 5.34 (*dd*, $J = 9.7, 3.1$, H–C(3)); 4.74 (*d*, $J = 1.6$, H–C(1)); 4.18 (*td*, $J \approx 9.7, 3.4$, addition of $D_2O \rightarrow t$, $J = 9.6$, H–C(4)); 4.16–4.08 (*m*, addition of $D_2O \rightarrow$ change, H–C(2)); 4.04–3.92 (*m*, 2 H–C(6)); 3.77 (*dt*, $J \approx 9.6, 4.4$, H–C(5)); 3.38 (*s*, MeO); 2.81 (*d*, $J = 3.7$, exchange with D_2O, HO–C(4)); 2.09 (*d*, $J = 6.2$, exchange with D_2O, HO–C(2)); 1.08 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.5 (*s*, C=O); 135.6 (4*d* of PhSi); 133.3 (*d* of Bz); 132.9, 132.8 (2*s* of PhSi); 129.8 (2*d* of Bz, 2*d* of PhSi); 129.6 (*s* of Bz); 128.4 (2*d* of Bz); 127.7 (4*d* of PhSi); 55.0 (*q*, MeO); 27.0 (*q*, *Me*$_3$C); 19.4 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*.

*Methyl 2,3-Di-*O*-benzoyl-6-*O*-[(*tert*-butyl)diphenylsilyl]-α-*D*-mannopyranoside* (**30**). White solid. R_f (cyclohexane/AcOEt 2:1) 0.60. $[\alpha]_D^{26} = -33.3$ ($c = 0.85$, $CHCl_3$). IR ($CHCl_3$): 3512*w*, 3072*w*, 3008*w*, 2932*m*, 2859*w*, 1725*s*, 1602*m*, 1452*m*, 1428*m*, 1316*m*, 1277*s*, 1138*s*, 1112*s*, 1078*s*, 1026*m*, 973*w*, 823*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.12–8.04 (*m*, 2 arom. H); 7.98–7.90 (*m*, 2 arom. H); 7.82–7.70 (*m*, 4 arom. H); 7.64–7.30 (*m*, 12 arom. H); 5.62–5.54 (*m*, H–C(2), H–C(3)); 4.89 (*d*, $J \approx 1.2$, H–C(1)); 4.39 (br. *t*, $J \approx 9.3$, addition of $D_2O \rightarrow$ change, H–C(4)); 4.07 (*dd*, $J = 10.9, 4.0$, H–C(6)); 4.01 (*dd*, $J = 10.9, 4.0$, H′–C(6)); 3.82 (*dt*, $J = 9.3, 4.0$, H–C(5)); 3.42 (*s*, MeO); 2.71 (br. *s*, exchange with D_2O, HO–C(4)); 1.10 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.8, 165.8 (2*s*, 2 C=O); 135.9, 135.8 (4*d* of PhSi); 133.6, 133.4 (2*d* of Bz); 133.3, 133.2 (2*s* of PhSi); 130.1 (4*d* of Bz, 2*d* of PhSi); 129.8 (2*s* of Bz); 128.7 (2*d* of Bz); 128.5 (2*d* of Bz); 128.0, 127.9 (4*d* of PhSi); 55.2 (*q*, MeO); 27.0 (*q*, *Me*$_3$C); 19.5 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*. MALDI-MS: 663 ($[M+Na]^+$). Anal. calc. for $C_{37}H_{40}O_8Si$ (640.80): C 69.35, H 6.29; found: C 69.44, H 6.30.

*Methyl 2,4-Di-*O*-benzoyl-6-*O*-[(*tert*-butyl)diphenylsilyl]-α-*D*-mannopyranoside* (**31**). White solid. R_f (cyclohexane/AcOEt 2:1) 0.55. $[\alpha]_D^{25} = -17.0$ ($c = 0.86$, $CHCl_3$). IR ($CHCl_3$): 3570*w* (br.), 3072*w*, 3008*m*, 2932*m*, 2858*w*, 1721*s*, 1602*w*, 1452*m*, 1428*m*, 1316*m*, 1264*s*, 1113*s*, 1070*s*, 1028*m*, 983*m*, 823*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.16–8.08 (*m*, 2 arom. H); 8.02–7.94 (*m*, 2 arom. H); 7.70–7.04 (*m*, 16 arom. H); 5.73 (*t*, $J = 10.0$, H–C(4)); 5.39 (*dd*, $J = 3.4, 1.6$, H–C(2)); 4.95 (*d*, $J = 1.6$, H–C(1)); 4.38–4.26 (*m*, addition of $D_2O \rightarrow dd$, $J = 10.0, 3.4$, H–C(3)); 3.99 (*ddd*, $J = 10.0, 3.7, 1.9$, H–C(5)); 3.89 (*dd*, $J = 11.5, 4.0$, H–C(6)); 3.82 (*dd*, $J = 11.5, 1.9$, H′–C(6)); 3.43 (*s*, MeO); 2.57 (br. *d*, $J = 7.5$, exchange with D_2O, HO–C(3)); 1.00 (*s*, Me_3C). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.3, 166.2 (2*s*, 2 C=O); 135.8, 135.6 (4*d* of PhSi); 133.6 (2*d* of Bz); 133.1 (2*s* of PhSi); 130.2, 130.1, 129.8, 129.7 (4*d* of Bz, 2*d* of PhSi); 129.65, 129.6 (2*s* of Bz); 128.72 (2*d* of Bz); 128.67 (2*d* of Bz); 127.8, 127.7 (4*d* of PhSi); 55.4 (*q*, MeO); 26.8 (*q*, *Me*$_3$C); 19.4 (*s*, Me$_3$*C*); for data of C(1)–C(6), see *Table 8*. MALDI-MS: 663 ($[M+Na]^+$). Anal. calc. for $C_{37}H_{40}O_8Si$ (640.80): C 69.35, H 6.29; found: C 69.40, H 6.37.

Benzoylation of **32**. According to the *General Procedure: a*) **32** (154 mg, 0.5 mmol) with BzCl (72 mg, 0.5 mmol) and (*S*)-**1** (5.6 mg, 25 μmol) followed by FC (hexane/AcOEt 3:1) gave **35** [62] (12 mg, 5%), **33** [63] (42 mg, 20%), and **34** (97 mg, 47%).

b) **32** (154 mg, 0.5 mmol) with BzCl (72 mg, 0.5 mmol) and (*R*)-**1** (5.6 mg, 25 μmol) followed by FC (hexane/AcOEt 3:1) gave **35** (22 mg, 9%), **33** (44 mg, 21%), and **34** (62 mg, 30%).

*Allyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**33**) [63]. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.12–8.04 (*m*, 2 arom. H); 7.63–7.34 (*m*, 8 arom. H); 5.78 (*dddd*, $J = 17.1, 10.3, 6.2, 5.0$, C*H*=CH$_2$); 5.58 (*s*, PhC*H*); 5.23 (*dq*, $J = 17.1, 1.6$, CH=C*H*$_2$); 5.22 (*dd*, $J = 9.3, 8.1$, irrad. at 4.74 → *d*, $J \approx 8.4$, H–C(2)); 5.14 (*dq*, $J = 10.3, 1.2$, CH=C*H*$_2$); 4.74 (*d*, $J = 8.1$, H–C(1)); 4.40 (*dd*, $J = 10.6, 5.0$, H_{eq}–C(6)); 4.34 (*ddt*, $J = 13.4, 5.0, 1.6$); 4.12 (*ddt*, $J = 13.1, 6.2, 1.2$, OC*H*$_2$CH=CH$_2$); 4.05 (*td*, $J = 9.6, 2.8$, addition of $D_2O \rightarrow t$, $J = 9.0$, H–C(3)); 3.85 (*t*, $J \approx 10.0$, H_{ax}–C(6)); 3.69 (*t*, $J \approx 9.3$, H–C(4)); 3.53 (*td*, $J \approx 10.0, 5.0$, H–C(5)); 2.78 (br. *s*, exchange with D_2O, HO–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.7 (*s*, C=O), 136.8 (*s* of PhCH); 133.24, 133.2 (*d* of Bz, *d* of *C*H=CH$_2$); 129.8 (2*d* of Bz); 129.5 (*s* of Bz); 129.2 (*d* of PhCH); 128.3, 128.2 (2*d* of PhCH, 2*d* of Bz); 126.2 (2*d* of PhCH); 117.7 (*t*, CH=*C*H$_2$); 101.8 (*d*, Ph*C*H); 70.2 (*t*, O*C*H$_2$CH=CH$_2$); for data of C(1)–C(6), see *Table 8*.

*Allyl 3-*O*-Benzoyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**34**). White crystals. M.p. 165–166.5° (CH_2Cl_2). R_f (hexane/AcOEt 2:1) 0.40. $[\alpha]_D^{25} = -92.0$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3597*w*, 3420*w*, 3038*w*, 2879*m*, 1727*s*, 1603*w*, 1453*w*, 1374*m*, 1314*m*, 1269*s*, 1098*s*, 1028*s*, 995*s*, 933*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.12–8.04 (*m*, 2 arom. H); 7.60–7.26 (*m*, 8 arom. H); 5.96 (*dddd*, $J = 17.0, 10.5, 6.5, 5.0$, C*H*=CH$_2$); 5.53 (*s*, PhC*H*); 5.49 (*t*, $J = 9.5$, H–C(3)); 5.35 (*dq*, $J = 17.4, 1.5$), 5.23 (*dq*, $J = 10.3, 1.5$), (CH=C*H*$_2$); 4.60 (*d*, $J = 7.8$, H–C(1)); 4.42 (*ddt*, $J = 12.8, 5.6, 1.5$, OC*H*$_2$CH=CH$_2$); 4.40 (*dd*, $J = 10.6, 5.0$, irrad. at 3.60 → *d*, $J = 9.4$, H_{eq}–C(6)); 4.20 (*ddt*, $J = 12.8, 6.5, 1.5$, OC*H*$_2$CH=CH$_2$); 3.84 (*t*, $J = 10.6$, irrad. at 4.40 → *d*, $J = 10.0$, irrad. at 3.60 → change, H_{ax}–C(6)); 3.82 (*t*, $J = 9.6$, irrad. at 5.49 → *d*, $J = 10.2$, irrad. at 3.60 → change, H–C(4)); 3.76 (*ddd*, $J = 9.4, 7.5, 3.1$, addition of $D_2O \rightarrow dd$, $J = 9.4, 7.8$, addition of D_2O and irrad. at 5.49 → *d*, $J = 7.2$, addition of D_2O and irrad.

at 4.60 → *d*, *J* = 9.0, H–C(2)); 3.60 (*td*, *J* = 9.6, 5.0, irrad. at 4.40 → *t*, *J* = 10.0, H–C(5)); 2.72 (*d*, *J* = 3.1, exchange with D_2O, HO–C(2)). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.6 (*s*, C=O), 136.9 (*s* of PhCH); 133.5 (*d* of Bz); 133.3 (*d*, *C*H=CH_2); 130.0 (2*d* of Bz); 129.7 (*s* of Bz); 129.0 (*d* of PhCH); 128.4, 128.2 (2*d* of PhCH, 2*d* of Bz); 126.1 (2*d* of PhCH); 118.4 (*t*, CH=*C*H_2); 102.6 (*d*, Ph*C*H); 70.7 (*t*, O*C*H_2CH=CH_2); for data of C(1)–C(6), see *Table 8*. FAB-MS: 825 (8, $[2M + H]^+$), 413 (100, $[M + H]^+$). Anal. calc. for $C_{23}H_{24}O_7$ (412.44): C 66.98, H 5.87; found: C 66.81, H 6.09.

Benzoylation of **36**. According to the *General Procedure: a*) **36** (154 mg, 0.5 mmol) with BzCl (72 mg, 0.5 mmol) and (*S*)-**1** (5.6 mg, 25 μmol) followed by FC (hexane/AcOEt 3 :1) gave **37** [5] (172 mg, 83.5%) and **38** [49] (7 mg, 3%).

b) **36** (154 mg, 0.5 mmol) with BzCl (72 mg, 0.5 mmol) and (*R*)-**1** (5.6 mg, 25 μmol) followed by FC (hexane/AcOEt 3 :1) gave **39** [49] (5 mg, 2%), **37** (167 mg, 81%), and **38** (19 mg, 9%).

Allyl 2,3-Di-O-*benzoyl-4,6*-O-*benzylidene-α*-D-*glucopyranoside* (**39**) [49]. White crystals. R_f (hexane/AcOEt 2 :1) 0.57. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.02–7.95 (*m*, 4 arom. H); 7.56–7.28 (*m*, 11 arom. H); 6.09 (*t*, *J* = 9.8, H–C(3)); 5.84 (*dddd*, *J* = 17.4, 10.3, 6.2, 5.3, C*H*=CH_2); 5.57 (*s*, PhC*H*); 5.32 (*d, J* ≈ 4.4, H–C(1)); 5.32 (*dq*, *J* = 17.4, 1.6, CH=CH_2); 5.27 (*dd, J* = 9.8, 3.7, H–C(2)); 5.15 (*dq*, *J* = 10.3, 1.3, CH=CH_2); 4.36 (*dd, J* = 10.3, 4.7, H_{eq}–C(6)); 4.25 (*ddt, J* = 13.1, 5.3, 1.6, OCH_2CH=CH_2); 4.15 (*td*, *J* = 10.3, 5.0, H–C(5)); 4.04 (*ddt, J* = 13.1, 6.2, 1.2, OCH_2CH=CH_2); 3.91 (*t*, *J* ≈ 9.5, H–C(4)); 3.85 (*t*, *J* = 10.3, H_{ax}–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.0, 165.6 (2*s*, 2 C=O); 136.9 (*s* of PhCH); 133.4, 133.31 (2*d* of Bz); 133.06 (*d* of *C*H=CH_2); 130.0, 129.8 (4*d* of Bz, 2*s* of Bz); 129.1 (*d* of PhCH); 128.5, 128.34, 128.25 (2*d* of PhCH, 4*d* of Bz); 126.2 (2*d* of PhCH); 118.0 (*t*, CH=*C*H_2); 101.7 (*d*, Ph*C*H); 69.7 (*t*, O*C*H_2CH=CH_2); for data of C(1)–C(6), see *Table 8*.

Benzoylation of **40**. According to the *General Procedure: a*) **40** (71 mg, 0.25 mmol) with (*S*)-**1** (5 mol-%) followed by FC (cyclohexane AcOEt 2 :1) gave **41** [53] (80 mg, 83%).

b) **40** (71 mg, 0.25 mmol) with (*R*)-**1** (5 mol-%) followed by FC (cyclohexane/AcOEt 2 :1) gave **41** (81 mg, 83%).

c) **40** (71 mg, 0.25 mmol) with TMEDA (5 mol-%) followed by FC (cyclohexane AcOEt 2 :1) gave **42** [53][54] (6 mg, 5%) and **41** (82 mg, 84%).

Benzoylation of **43**. According to the *General Procedure: a*) **43** (71 mg, 0.25 mmol) with (*S*)-**1** (5 mol-%) followed by FC (CH_2Cl_2/AcOEt 9 :1) gave **46** [53][58] (9 mg, 7%), **44** [53][58] (44 mg, 46%), and **45** [53][58] (32 mg, 33%).

b) **43** (71 mg, 0.25 mmol) with (*R*)-**1** (5 mol-%) followed by FC (CH_2Cl_2/AcOEt 9 :1) gave **46** (10 mg, 10%), **44** (25 mg, 26%), and **45** (52 mg, 54%).

c) **43** (71 mg, 0.25 mmol) with TMEDA (5 mol-%) followed by FC (CH_2Cl_2/AcOEt 9 :1) gave **46** (18 mg, 15%), **44** (62 mg, 64%), and **45** (6 mg, 6%).

Methyl 2,3-Di-O-*benzoyl-4,6*-O-*benzylidene-α*-D-*galactopyranoside* (**46**) [53][58]. ^{1}H-NMR (300 MHz, $CDCl_2$): 8.05–7.98 (*m*, 4 arom. H); 7.57–7.46 (*m*, 4 arom. H); 7.42–7.32 (*m*, 7 arom. H); 5.86–5.74 (*AB*, irrad. at 4.66 → change, H–C(2), H–C(3)); 5.58 (*s*, PhC*H*); 5.29 (br. *d*, *J* ≈ 1.9 (virtual coupling), H–C(1)); 4.66 (br. *d*, *J* ≈ 1.2 (virtual compling), H–C(4)); 4.37 (*dd*, *J* = 12.5, 1.6, H–C(6)); 4.15 (*dd*, *J* = 12.5, 1.6, H′–C(6)); 3.91 (br. *s*, H–C(5)); 3.47 (*s*, MeO). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.1, 165.8 (2*s*, 2 C=O); 137.5 (*s* of PhCH); 133.16, 133.12 (2*d* of Bz); 129.78, 129.76 (4*d* of Bz); 129.46, 129.41 (2*s* of Bz); 128.8 (*d* of PhCH); 128.3, 128.1 (4*d* of Bz, 2*d* of PhCH); 126.1 (2*d* of PhCH); 100.7 (*d*, Ph*C*H); 55.0 (*q*, MeO); for data of C(1)–C(6), see *Table 8*.

Benzoylation of **47**. According to the *General Procedure: a*) **47** (71 mg, 0.25 mmol) with (*S*)-**1** (5 mol-%) followed by FC (hexane/AcOEt 2 :1) gave **48** [55][64][65] (86 mg, 90%).

b) **47** (71 mg, 0.25 mmol) with (*R*)-**1** (5 mol-%) followed by FC (hexane/AcOEt 2 :1) gave **48** (60 mg, 63%) and **47** (16 mg, 23%).

Benzoylation of **49**. According to the *General Procedure: a*) **49** (71 mg, 0.25 mmol) with (*S*)-**1** (5 mol-%) followed by FC (cyclohexane/AcOEt 9 :1 → 1 :1) gave **50** [55][66] (6 mg, 6%), **51** [55] [65–67] (82 mg, 85%), and **49** (6 mg).

b) **49** (71 mg, 0.25 mmol) with (*R*)-**1** (5 mol-%) followed by FC (cyclohexane/AcOEt 9 :1 → 1 :1) gave **52** [55][68] (5 mg, 4%), **50** (18 mg, 19%), **51** (60 mg, 62%), and **49** (8 mg).

c) **49** (71 mg, 0.25 mmol) with TMEDA (5 mol-%) followed by FC (cyclohexane/AcOEt 9 :1 → 1 :1) gave **52** (11 mg, 9%), **50** (8 mg, 8%), **51** (73 mg, 74%), and **49** (8 mg).

Methyl 2,3-Di-O-*benzoyl-4,6*-O-*benzylidene-α*-D-*mannopyranoside* (**52**) [68][69]. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.13–8.06 (*m*, 2 arom. H); 7.95–7.88 (*m*, 2 arom. H); 7.67–7.59 (*m*, 1 arom. H); 7.55–7.41 (*m*, 5 arom. H); 7.38–7.27 (*m*, 5 arom. H); 5.80 (*dd*, *J* = 10.3, 3.4, H–C(3)); 5.69 (*dd*, *J* = 3.7, 1.6, H–C(2)); 5.67 (*s*, PhC*H*); 4.90 (*d*, *J* ≈ 1.6, H–C(1)); 4.38 (*dd*, *J* = 10.3, 4.7, H–C(6)); 4.32 (*t*, *J* = 10.0, H–C(4)); 4.11 (*td*, *J* = 10.0, 4.7, H–C(5)); 3.96 (*t*, *J* = 10.0, H′–C(6)); 3.49 (*s*, MeO). ^{13}C-NMR (75 MHz, $CDCl_2$): 165.3, 165.2 (2*s*, 2 C=O);

137.0 (*s* of PhCH); 133.4, 132.9 (2*d* of Bz); 129.8, 129.7 (4*d* of Bz); 129.6, 129.4 (2*s* of Bz); 129.0 (*d* of PhCH); 128.5, 128.1 (4*d* of Bz, 2*d* of PhCH); 126.1 (2*d* of PhCH); 101.9 (*d*, PhCH); 55.4 (*q*, MeO); for data of C(1) – C(6), see *Table 8*.

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