Selective Formation of β-D-Glucosides of Hindered Alcohols[1])

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Alternative conditions for the classical glycosidation method of *Koenigs-Knorr* allowed us to prepare selectively β-D-glucosides of several hindered alcohols in good yields in a weakly acidic to almost neutral medium. To illustrate the versatility of our conditions, we prepared the β-D-glucoside of an acid-sensitive aglycone, a key-intermediate for the total synthesis of a natural cyanoglucoside, bauhinin.

Introduction. – As reported recently during the syntheses of complex natural molecules, the formation of β-D-glucosides of secondary alcohols with acceptable yields remains a challenge. Numerous methods for the formation of the glycosidic bond can be found in the literature, but they have been mostly devised for oligosaccharide synthesis and are often not well-suited for the glycosidation of aglycones. Therefore, the efficient formation of the glycosidic bond is the key reaction in the synthesis of many biologically active substances [2–6]. For example, the difficulties encountered for the glycosidation of a tertiary alcohol in the total synthesis of (−)-paeniflorin reveal a deficiency that still exists in the methodology [7].

Classical methods for the glycosidation of alcohols have already been proposed during the early days of organic chemistry by *Fischer* or *Koenigs* and *Knorr* [8], but the need of alternative methodologies, or of improvements of existing methodologies, has stimulated research in this field, and several new procedures have appeared during the last few years [9][10]. However, the reported yields of glycosidation were often low, even in the presence of an excess of the glycosyl donor [11]. The *Koenigs-Knorr* method, which has been steadily improved, remains one of the most-often used; to avoid the formation of α-D-glucosides, an ester participating group should be present in position 2′ of the glycosyl donor (*e.g.*, **1**), but the formation of the orthoester [12] becomes then a sizeable side reaction (see *Scheme 1*) (for a similar observation in *Schmidt*'s glycosidation procedure, see [13]). Therefore, *Kunz* and *Harreus* [14] have proposed the replacement of the traditionally used tetraacetate **1** by the sterically hindered tetrapivalate **1′**. The orthoester formation is then limited, but at the expense of the reactivity of this glycosyl donor (for a similar observation in *Kahne*'s sulfoxide glycosidation method, see [15]).

Another method to synthesize the desired β-D-glucoside is the *Helferich* [13b][16] rearrangement of the formed orthoester. Unfortunately, this reaction has to be performed in the presence of the corresponding alcohol ROH **2** and, furthermore, gives good results only in simple cases.

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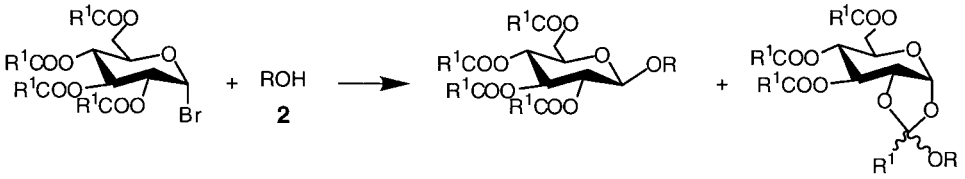
[1]) For a preliminary communication, see [1].

Scheme 1



1 R^1 = Me; **1'** R^1 = ^{t}Bu; **1''** R^1 = i-Pr

4 R^1 = Me; **4'** R^1 = ^{t}Bu; **4''** R^1 = i-Pr

5 R^1 = Me; **5'** R^1 = ^{t}Bu; **5''** R^1 = i-Pr

ROH	β-D-Glucoside **4″**	Orthoester **5″**
(−)-Borneol (**2a**)[a])	**4″a**	**5″a**
(+)-Fenchol (**2b**)[b])	**4″b**	**5″b**
(−)-Citronellol (**2c**)[c])	**4″c**	**5″c**
(−)-Isopinocampheol (**2d**)[d])	**4″d**	**5″d**
(−)-Isopulegol (**2e**)[e])	**4″e**	**5″e**
(−)-*cis*-Verbenol (**2f**)[f])	**4″f**	**5″f**

[a]) (−)-Borneol = (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol.
[b]) (+)-Fenchol = (1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol.
[c]) (−)-Citronellol = (3*S*)-3,7-dimethyloct-6-en-1-ol.
[d]) (−)-Isopinocampheol = (1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-ol.
[e]) (−)-Isopulegol = (1*R*,2*S*,5*R*)-2-isopropenyl-5-methylcyclohexanol.
[f]) (−)-*cis*-Verbenol = (1*S*,2*S*,5*S*)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-ol.

Results and Discussion. – The formation of the glycosidic bond during the synthesis of a naturally occurring cyanoglucoside [17], (−)-bauhinin, could not be achieved in acceptable yields by any of the usual methods, despite our numerous attempts[2]). Thus, we decided to improve one of the existing procedures, and we chose the *Koenigs-Knorr* method, which was found to be the most promising in preliminary experiments. The reaction of, *e.g.*, the aglycone **2g**, used in the synthesis of bauhinin (see below, *Scheme 2*), with tetra-*O*-acetylglucosyl bromide **1** afforded almost exclusively the orthoester, the formation of which was avoided with tetra-*O*-pivaloylglucosyl bromide **1′**, but unfortunately the reactivity was very weak in this latter case. We chose, therefore, a glycosyl donor bearing ester groups of intermediate steric hindrance, *i.e.*, tetra-*O*-isobutyrylglucosyl bromide **1″**[3]). In the following, we describe the optimization of the glycosidation of (−)-borneol (**2a**) and other optically pure terpenoid alcohols **2b**–**f** by means of this alternative reagent **1″**.

Many silver salts have been used in the *Koenigs-Knorr* reaction but, in our case, good results could be obtained only with silver trifluoromethanesulfonate (=silver triflate; AgOTf) [19], which required the presence of a very hindered base, 2,6-di(*tert*-butyl)-4-methylpyridine (**3**), as TfOH scavenger. We found that the acidity of the

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2) This result was not unexpected since a similar cyanoglucoside, simmondsin, was synthesized in 1992, and a yield of only 27% was reported for the glycosidation step performed by *Schmidt*'s method [3].

3) Tetra-*O*-isobutyrylglucosyl bromide **1″** has been used before in two cases for the glycosidation of phenols [18].

reaction medium was a key factor for the glycosidation of **2a–e**: when equimolar amounts of AgOTf, glucosyl bromide **1″**, and base **3** were present at the outset of the reaction (*General Procedure* (*G.P.*) *A*, *Table 1*), orthoester **5″a** was obtained as the major compound, whereas, under more acidic conditions (*G.P. B*), orthoester formation was only a very limited side reaction. However, in the latter case, the acidity of the medium during the first 15 min was found to be incompatible with acid-sensitive aglycones for which *G.P. C* and *G.P. E* (*Table 1*) were the methods of choice, the former involving slightly more acidic conditions at the outset of the reaction than the latter[4]).

These methods, representing two different compromises between limitation of orthoester formation and limitation of the acidity of the reaction mixture, were selected for the glycosidation of several other terpenoid alcohols. Except for (−)-*cis*-verbenol (**2f**), the reported glycosidation yields [11b][20] were greatly improved (see *Table 2*).

Table 1. *Comparison of Different Addition Procedures for the Glycosidation of (−)-Borneol* (**2a**): *General Procedures* (*G.P.*) *A–E*

	Isolated yields [%]				
	G.P. A[a])	*G.P. B*[b])	*G.P. C*[c])	*G.P. D*[d])	*G.P. E*[e])
β-D-Glucoside **4″a**[f])	33	45	45	48	35
Orthoester **5″a**	47	< 5	18	20	45

[a]) *G.P. A:* AgOTf (2 equiv.), glucosyl bromide **1″** (2 equiv.), 2,6-di(*tert*-butyl)-4-methylpyridine (**3**; 2 equiv.), and alcohol **2** were mixed in $C_2H_4Cl_2$ at −20°. The mixture was then stirred at −20° for 45 min, warmed up slowly within 1 h to 20°, and left at 20° for 12 h.
[b]) *G.P. B:* same conditions as in *G.P. A*, except that the base **3** was only added, at −20°, 15 min after the beginning of the reaction.
[c]) *G.P. C:* same conditions as in *G.P. A*, except that a small amount of base **3** (0.3 equiv.) was added at the outset of the reaction, followed by the slow addition of a further amount of **3** (1.7 equiv.) within 45 min, at −20° and at a constant rate.
[d]) *G.P. D:* same conditions as in *G.P. A*, except that the base **3** (2 equiv.) was slowly added within 45 min, at −20° and at a decreasing rate.
[e]) *G.P. E:* AgOTf (2 equiv.) glucosyl bromide **1″** (2 equiv.), alcohol **2**, and base **3** (1.36 equiv.) were mixed in $C_2H_4Cl_2$ at 20°. Then, additional base **3** (0.64 equiv.) was slowly added within 30 min at a constant rate and at 20°, thereafter the mixture was stirred for 12 h.
[f]) The closely related β-D-glucoside **4a** has been prepared from **2a** with a yield of only 9% [20].

Table 2. *Glycosidation of Terpenoid Alcohols* **2b–f**: *Isolated Yields of the β-Glucosides* **4″b–f** *and the Orthoesters* **5″b–f**

	G.P. C		*G.P. E*		Reported yield of β-D-glucoside **4** [%]
ROH	β-D-glucoside **4″** [%]	orthoester **5″** [%]	β-D-glucoside **4″** [%]	orthoester **5″** [%]	
2b	46	27	42	28	–
2c	40	25	52	11	43 [20]
2d	50	15	35	38	–
2e	67	26	45	40	18 [20]
2f	< 3	< 3	< 3	4	6 [11b]

[4]) *G.P. D* was not retained since it was technically much more difficult to carry out, while bringing only a marginal improvement over *G.P. C*.

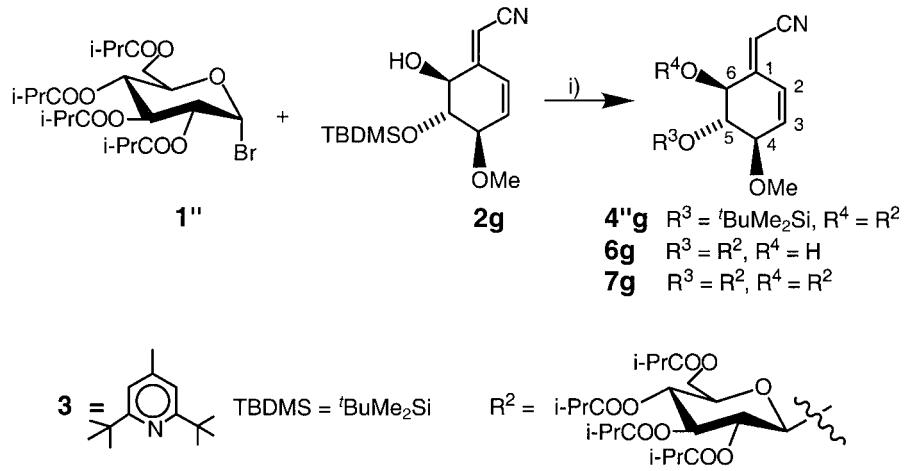
Then, the optically pure aglycone **2g**, the key intermediate for the total synthesis of bauhinin (see following paper [21]), was glycosidated following all the *G.P.*s of *Table 1* (see *Table 3*). According to the results reported above, it seemed that the difficulty would be to avoid orthoester formation while keeping the acidity of the medium as low as possible to limit the cleavage of the silyl-ether moiety. However, whereas on glycosidation according to *G.P. A*, (−)-borneol (**2a**) yielded orthoester **5″a** as the major product (see *Table 1*), orthoester **5″g** could not be isolated on glycosidation of **2g**. It was also not obtained with the other glycosidation procedures (*G.P. B*–*E*). In *G.P. B*–*D*, the acidity of the medium during the early stages of the reaction was sufficient to cause the cleavage of the silyl ether, which was responsible for the formation of glucosides **6g** and **7g** (*Scheme 2*). The formation of compound **6g** showed that OH–C(5) is more reactive towards glycosidation than OH–C(6). Finally, *G.P. E* was found to be a good compromise for the glycosidation of this particular aglycone, for which, surprisingly, orthoester formation was never observed when the glycosidation was carried out with **1″** and **3**.

Table 3. *Glycosidation of Aglycone* **2g**

	Isolated yields [%]			
	4″g	**6g**	**7g**	**2g**
G.P. A	39	–[a])	–[a])	20
G.P. B	–[a])	–[a])	70	–[a])
G.P. C	30	32	13	–[a])
G.P. D	28	28	27	–[a])
G.P. E	58	–[a])	–[a])	–[a])

[a]) No effort was made to isolate products that were formed in insignificant yields (< 5%).

Scheme 2



i) Glucosyl bromide **1″** (2 equiv.), alcohol **2g** (1 equiv.), AgOTf (2 equiv.), base **3** (2 equiv.), 4-Å molecular sieves, $C_2H_4Cl_2$.

In principle, two isomers could be formed for the orthoesters **5″** (see *Scheme 1*); however, one isomer only was isolated in the cases of **5″a**, **5″b**, **5″d**, and **5″e**. Two isomers were formed for **5″c** in a 7:1 ratio (see *Exper. Part*). The '*endo*' or '*exo*' configuration at the orthoester C-atom was not established.

It should be noted that the yields of β-D-glucosides depend considerably on the quality of AgOTf. Therefore, a reproducible preparation method for AgOTf is described in the *Exper. Part*. Moreover, we attempted to replace the very hindered, but expensive, base **3** with 2,6-lutidine (=2,6-dimethylpyridine), but these efforts were unsuccessful: *e.g.*, glycosidation of (−)-borneol (**2a**) according to *G.P. A* in the presence of 2,6-lutidine instead of **3** afforded 77% of orthoester **5″a** and only 9% of β-D-glucoside **4″a**. Under the same conditions, glycosidation of aglycone **2g** afforded no β-D-glucoside, but only orthoester **5″g** in very low yield. During the early stages of this study, we tested several solvents for the glycosidation of **2a**. Thus, 1,2-dichloroethane ($C_2H_4Cl_2$) afforded better results than CH_2Cl_2 or $CHCl_3$, whereas MeCN or CH_2Cl_2/Et_2O gave poor yields. In Et_2O, only orthoester **5″a** was obtained, albeit in almost quantitative yield.

Conclusion. – We hope that the hitherto seldomly used reagent **1**″ for the *Koenigs-Knorr* glycosidation will represent a useful alternative, especially for the glycosidation of hindered secondary aglycones. As shown above, the addition procedure of the base is the critical point and should be determined for each aglycone; as a general rule, *G.P. E* should be prefered for acid-sensitive alcohols and *G.P. C* in other cases.

We are grateful to Prof. *P. Vogel*, Lausanne, Dr. *E. Vieira*, Basle, and Prof. *J. Eustache*, Mulhouse, for helpful discussions, and to the undergraduate students who worked with enthusiasm and dedication at various stages of this project: *D. Christian*, *G. Doledec*, *F. Marlin*, *V. Peretti*, *C. Sigwalt*, *S. Wojeik*, and especially, *D. Reingpach*. We are grateful also to the *Centre National de la Recherche Scientifique* (UPRES-A Q7015), for financial support, and to Dr. *D. Le Nouen* and Dr. *S. Bourg* for the recording of many NMR spectra.

Experimental Part

General. All reactions were run under N_2 or Ar. CH_2Cl_2, $CHCl_3$, and 1,2-dichloroethane were freshly distilled over P_2O_5 and kept under Ar on 4 Å molecular sieves. For the glycosidation reactions, on one hand, powdered 4 Å molecular sieves were activated at *ca*. 400°/0.1 Torr for 1 h in a quartz flask heated by a *Bunsen* burner; on the other hand, the solid reagents were added quickly, as powders, under a steady stream of Ar. Column chromatography = CC. Microanalyses were performed by the 'Service Central d'Analyse du CNRS', Vernaison, France.

1,2,3,4,6-Penta-O-*isobutyryl*-α-D-*glucopyranose and 1,2,3,4,6-Penta*-O-*isobutyryl*-β-D-*glucopyranose.* Isobutyryl chloride (75 ml, 767 mmol) was added under stirring to a soln. of (+)-D-glucose (20 g, 113 mmol) and pyridine (80 ml, 986 mmol) in $CHCl_3$ (120 ml) cooled to 4°. The mixture was stirred for 2 days at 20° and then evaporated. After addition of 2N H_2SO_4 (100 ml) to the residue, the mixture was extracted twice with Et_2O (500 ml) and the org. phase washed successively with 2N H_2SO_4 (50 ml), sat. $NaHCO_3$ soln. (100 ml), and H_2O (100 ml), dried ($MgSO_4$) and evaporated. A soln. of the resulting oil in MeOH/H_2O was left at −15° to afford a *ca*. 1:1 mixture of α/β-D epimers as colorless crystals. (55.1 g, 92%). ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.06–1.25 (*m*, 5 *Me*$_2$CH); 2.42–2.7 (*m*, 5 Me$_2$C*H*); 3.85 (*ddd*, ^3J = 9.6, 4.8, 2.1, H–C(5)(β)); 4.17 (*m*, H–C(6)(β), H–C(5)(α), CH_2(6)(α)); 4.22 (*dd*, ^2J = 12.4, ^3J = 4.8, H–C(6)(β)); 5.11 (*dd*, ^3J = 9.9, 3.7, H–C(2)(α)); 5.16 (*t*, ^3J = 9.6, H–C(4)(β)); 5.17 (*dd*, ^3J = 9.6, 8.2, H–C(2)(β)); 5.18 (*t*, ^3J = 9.9, H–C(4)(α)); 5.32 (*t*, ^3J = 9.6, H–C(3)(β)); 5.53 (*t*, ^3J = 9.9, H–C(3)(α)); 5.73 (*d*, ^3J = 8.2, H–C(1)(β)); 6.34 (*d*, ^3J = 3.7, H–C(1)(α)). Anal. calc. for $C_{26}H_{41}O_{11}$ (529.60): C 58.96, H 7.80; found: C 58.95, H 8.00.

(+)-2,3,4,6-Tetra-O-*isobutyryl*-α-D-*glucopyranosyl Bromide* (**1″**). At 0°, 5.7M HBr/AcOH (14 ml, 80 mmol) was added under stirring to a soln. of penta-*O*-isobutyryl-D-glucopyranose (mixture of α-D- and β-D-epimers; 10 g, 19 mmol) in CH_2Cl_2 at 0°. After 14 h at 0°, toluene (160 ml) was added, and the mixture was evaporated. A soln. of the oily residue in Et_2O (200 ml) was successively washed with sat. aq. $NaHCO_3$ soln. (50 ml) and H_2O (50 ml), dried ($MgSO_4$), and evaporated. A soln. of the resulting oil in MeOH/H_2O was left at −15° to afford colorless crystals (7.5 g) of m.p. 69–70° ([18b]: 67–69°). Concentration of the mother liquor gave 700 mg of white crystals, m.p. 68–69°. Total yield of **1″**, 82%. $[\alpha]_D^{25} = +161$ ($c = 1.05$, $CHCl_3$) ([18b]: $[\alpha]_D^{25} = +189$ ($c = 1.7$, $CHCl_3$)). IR (KBr): 2976, 2937, 2878, 1742, 1470, 1389, 1348, 1192, 1149, 1116, 1048, 987, 922, 850, 828, 754. ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.06–1.25 (*m*, 4 Me_2CH); 2.42–2.64 (*m*, 4 Me_2CH); 4.14 (*dd*, $^2J = 14.8$, $^3J = 1.9$, H–C(6)); 4.20 (*dd*, $^2J = 14.8$, $^3J = 4.2$, H–C(6)); 4.30 (*ddd*, $^3J = 9.9$, 4.2, 1.9, H–C(5)); 4.83 (*dd*, $^3J = 9.9$, 4, H–C(2)); 5.20 (*t*, $^3J = 9.9$, H–C(4)); 5.61 (*t*, $^3J = 9.9$, H–C(3)); 6.61 (*d*, $^3J = 4$, H–C(1)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 18.70, 18.63, 18.56, 18.48 (4 Me_2CH); 33.66, 33.62, 33.58 (4 Me_2CH); 60.56 (C(6)); 66.37 (C(4)); 69.51 (C(3)); 70.37 (C(2)); 72.37 (C(5)); 86.76 (C(1)); 176.21, 175.40, 175.34, 175 (4 CO). Anal. calc. for $C_{22}H_{35}BrO_9$ (523.41): C 50.48, H 6.73, Br 15.26; found: C 50.30, H 6.69, Br 15.09.

General Glycosidation Procedures of Alcohols **2a**–**g**: *Example of (−)-Borneol* (**2a**). *General Procedure A* (*G.P. A*): To a stirred suspension of AgOTf (164 mg, 0.64 mmol) in 1,2-dichloroethane (3.5 ml) protected from light, activated 4 Å molecular sieves (500 mg) and the base **3** (132 mg, 0.64 mmol) were added at 20°. After cooling to −20°, (−)-borneol (**2a**; 50 mg, 0.32 mmol) and glucosyl bromide **1″** (336 mg, 0.64 mmol) were successively added. After 20 min at −20°, the cooling bath was removed, and the mixture was left for 14 h at 20° under stirring. After filtration over *Celite*® and washing of the *Celite*® with CH_2Cl_2 (10 ml), the combined filtrates were evaporated. The resulting oil was purified by CC (silica gel, AcOEt/petroleum ether 1:9) to yield first the oily orthoester **5″a** (90 mg, 47%) and then solid β-D-glucoside **4″a** which was recrystallized in MeOH/H_2O: 63 mg (33%) of white needles.

General Procedure B (*G.P. B*): To a stirred suspension of AgOTf (164 mg, 0.64 mmol) in 1,2-dichloroethane (3.5 ml) protected from light, activated 4 Å molecular sieves (500 mg) were added at 20°. After cooling to −20°, **2a** (50 mg, 0.32 mmol) and **1″** (336 mg, 0.64 mmol) were successively added. After 15 min at −20°, **3** (132 mg, 0.64 mmol) was added, the cooling bath removed, and the mixture left for 14 h at 20° under stirring. Workup as described in *G.P. A* gave solid **4″a**, which was recrystallized in MeOH/H_2O: 86 mg (45%) of white needles.

General Procedure C (*G.P. C*): To a stirred suspension of AgOTf (164 mg, 0.64 mmol) in 1,2-dichloroethane (3.5 ml) protected from light, activated 4 Å molecular sieves (500 mg) and **3** (22 mg, 0.10 mmol) were added at 20°. After cooling to −20°, **2a** (50 mg, 0.32 mmol) and **1″** (336 mg, 0.64 mmol) were successively added, followed by a soln. of additional **3** (110 mg, 0.54 mmol) in 1,2-dichloroethane (2 ml), under stirring at −20° and at a rate of 45 µl/min. Thereafter, the cooling bath was removed and the mixture left for 14 h at 20° under stirring. Workup as described in *G.P. A* gave oily **5″a** (35 mg, 18%) and solid **4″a**, which was recrystallized in MeOH/H_2O: 86 mg (45%) of white needles.

General Procedure D (*G.P. D*): To a stirred suspension of AgOTf (164 mg, 0.64 mmol) in 1,2-dichloroethane (3.5 ml) protected from light, activated 4 Å molecular sieves (500 mg) were added at 20°. After cooling to −20°, **2a** (50 mg, 0.32 mmol) and **1″** (336 mg, 0.64 mmol) were successively added. Then, while the mixture was stirred at −20°, a soln. of **3** (132 mg, 0.64 mmol) in 1,2-dichloroethane (3.5 ml) was added at the following decreasing addition rate: 0–1 min, 0.40 ml/min; 1–2 min, 0.33 ml/min; 2–3 min, 0.26 ml/min; 3–4 min, 0.21 ml/min; 4–5 min, 0.15 ml/min; 5–6 min; 0.12 ml/min; 7–14 min, 0.1 ml/min; 15–24 min, 0.05 ml/min; 25–55 min, 0.03 ml/min. Thereafter, the cooling bath was removed and the mixture left for 14 h at 20° under stirring. Workup as described in *G.P. A* gave oily **5″a** (38 mg, 20%) and solid **4″a**, which was recrystallized in MeOH/H_2O: 92 mg (48%) of white needles.

General Procedure E (G.P. E). To a stirred suspension of AgOTf (164 mg, 0.64 mmol) in 1,2-dichloroethane (2 ml) protected from light, activated 4-Å molecular sieves (500 mg, powder), **3** (90 mg, 0.44 mmol), **2a** (50 mg, 0.32 mmol), and **1″** (336 mg, 0.64 mmol) were successively added at 20°, followed by a soln. of additional **3** (42 mg, 0.20 mmol) in 1,2-dichloroethane (2.4 ml) at a rate of 80 µl/min, within 30 min at 20°. The mixture was left for 14 h under stirring. Workup as described in *G.P. A* gave oily **5″a** (86 mg, 45%) and solid **4″a**, which was recrystallized in MeOH/H_2O: 66 mg (35%) of white needles.

*(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2*-endo-*yl 2,3,4,6-Tetra*-O-*isobutyryl*-β-D-*glucopyranoside* (**4″a**). M.p. 115–116°. $[\alpha]_D^{25} = -24$ ($c = 2.3$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.81, 0.83 (2*s*, 2 Me–C(7), Me–C(1)); 1.05–1.2 (*m*, 4 Me_2CH); 0.9–2.0 (3*m*, CH_2(3), CH_2(5), CH_2(6)); 2.09 (*m*, H–C(4)); 2.4–2.7 (*m*, 4 Me_2CH); 3.65 (*ddd*, $^3J = 9.5$, 4.75, 3, H–C(5′)); 4.0 (br. *d*, $^3J = 8$, H–C(2)); 4.1 (*dd*, $^2J = 12.1$, $^3J = 5.3$, H–C(6′)); 4.18 (*dd*, $^2J = 12.1$, $^3J = 2.6$, H–C(6′)); 4.46 (*d*, $^3J = 8$, H–C(1′)); 5.00 (*dd*, $^3J = 9.5$, 8, H–C(2′)); 5.07 (*t*, $^3J = 9.5$, H–C(4′)); 5.23 (*t*, $^3J = 9.5$, H–C(3′)). ^{13}C-NMR ($CDCl_3$, 100.577 MHz): 13.24 (*Me*–C(1)); 18.79, 18.85, 18.90,

18.98, 19.73 (2 *Me*–C(7), 4 *Me*$_2$CH); 26.33 (C(5)); 28.21 (C(6)); 33.87, 33.97 (4 Me$_2$*C*H); 35.86 (C(3)); 44.89 (C(4)); 47.95 (C(7)); 49.0 (C(1)); 62.12 (C(6′)); 68.41 (C(4′)); 71.25 (C(5′)); 71.92 (C(2′)); 72.48 (C(3′)); 83.37 (C(2)); 99.48 (C(1′)); 175.10, 175.34, 176.10,179.69 (4 CO). Anal. calc. for $C_{32}H_{52}O_{10}$ (596.76): C 64.40, H 8.78, O 26.8; found: C 64.43, H 8.98, O 26.57.

3,4,6-Tri-O-*isobutyryl-1,2*-O-*{1-{[(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2*-endo-*yl]oxy}-2-methylpropylidene}-α*-D-*glucopyranose* (**5″a**). $[\alpha]_D^{25} = +14.2$ ($c = 3.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.81, 0.83 (2*s*, 2 Me–C(7), Me–C(1)); 1.05–1.23 (*m*, 4 *Me*$_2$CH); 1.2–2.0 (3*m*, CH_2(3), CH_2(5), CH_2(6)); 1.94 (*m*, H–C(4)); 2.2 (*m*, Me$_2$*C*H–C(O)$_3$); 2.45–2.65 (*m*, 3 Me$_2$*C*H); 3.81 (br. *d*, $^3J = 8.7$, H–C(2)); 4.12 (*m*, H–C(5′)); 4.20 (*m*, CH_2(6′)); 4.30 (*dd*, $^3J = 5.2$, 4, H–C(2′)); 4.94 (*dd*, $^3J = 8.9$, 5.5, H–C(4′)); 5.22 (*dd*, $^3J = 5.5$, 4, H–C(3′)); 5.70 (*d*, $^3J = 5.2$, H–C(1′)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 13.7 (*Me*–C(1)); 17.33, 17.41 (2*s*, *Me*$_2$CH–C(O)$_3$); 18.72, 18.75, 18.82, 18.89, 19.69 (3 *Me*$_2$CH, 2 *Me*–C(7)); 26.66 (C(5)); 28.22 (C(6)); 33.82, 33.85 (3 Me$_2$*C*H); 35.03 (Me$_2$*C*H–C(O)$_3$)); 37.23 (C(3)); 45.07 (C(4)); 47.12 (C(7)); 49.39 (C(1)); 62.5 (C(6′)); 67.09 (C(5′)); 68.18 (C(4′)); 71.62 (C(2′)); 74.81 (C(3′)); 77.20 (C(2)); 96.91 (C(1′)); 124.5 (Me$_2$CH–*C*(O)$_3$); 175.37, 175.5, 176.67 (3 CO). Anal. calc. for $C_{32}H_{52}O_{10}$ (596.76): C 64.40, H 8.78; found: C 64.58, H 8.83.

*(1*R*,2*R*,4*S*)-1,3,3-Trimethylbicyclo[2.2.1]hept-2*-endo-*yl 2,3,4,6-Tetra*-O-*isobutyryl-β*-D-*glucopyranoside* (**4″b**). M.p. 134–135°. $[\alpha]_D^{25} = +38.7$ ($c = 1.55$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.75, 0.96 (2*s*, 2 Me); 1.05–1.21 (*m*, Me, 4 *Me*$_2$CH); 1.25–1.7 (*m*, H–C(4), CH_2(5), CH_2(6), CH_2(7)); 2.4–2.65 (*m*, 4 Me$_2$*C*H); 3.0 (br. *s*, H–C(2)); 3.65 (*ddd*, $^3J = 9.5$, 5.3, 2.2, H–C(5′)); 4.10 (*dd*, $^2J = 12.2$, $^3J = 5.3$, H–C(6′)); 4.20 (*dd*, $^2J = 12.2$, $^3J = 2.2$, H–C(6′)); 4.40 (*d*, $^3J = 8$, H–C(1′)); 5.04–5.1 (*m*, H–C(2′), H–C(3′)); 5.26 (*t*, $^3J = 9.5$, H–C(4′)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 18.71, 18.78, 18.94, 19.14 (4 *Me*$_2$CH); 19.54 (*Me*–C(1)); 21.42, 25.64 (2 *Me*–C(3)); 26.09 (C(5)); 29.64 (C(6)); 33.87, 33.95 (4 Me$_2$*C*H); 39.21 (C(3)); 41.11 (C(7)); 47.94 (C(4)); 49.04 (C(1)); 62.11 (C(6′)); 68.30 (C(5′)); 71.44 (C(4′)); 71.82 (C(2′)); 72.44 (C(3′)); 93.68 (C(2)); 102.10 (C(1′)); 175.22, 175.34, 176.06, 179.74 (4 CO). Anal. calc. for $C_{32}H_{52}O_{10}$ (596.76): C 64.40, H 8.73; found: C 64.25, H 9.07.

3,4,6-Tri-O-*isobutyryl-1,2*-O-*{1-{[(1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]hept-2*-endo-*yl]oxy}-2-methylpropylidene}-α*-D-*glucopyranose* (**5″b**). M.p. 59–60°. $[\alpha]_D^{25} = +42.2$ ($c = 6.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.81, 0.95 (2*s*, 2 Me); 1.05–1.23 (*m*, Me, 4 *Me*$_2$CH); 1.2–1.7 (*m*, H–C(4), CH_2(5), CH_2(6), CH_2(7)); 2.1–2.17 (Me$_2$*C*H–C(O)$_3$); 2.45–2.65 (*m*, 3 Me$_2$*C*H); 2.9 (br. *s*, H–C(2)); 4.05 (*ddd*, $^3J = 8.2$, 4.2, 3, H–C(5′)); 4.15 (*m*, CH_2(6′)); 4.35 (*t*, $^3J = 5.1$, H–C(2′)); 5.00 (*dd*, $^3J = 8.2$, 7.5, H–C(4′)); 5.24 (*dd*, $^3J = 7.5$, 5.1, H–C(3′)); 5.80 (*d*, $^3J = 5.1$, H–C(1′)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 17.59, 17.79 (*Me*$_2$CH–C(O)$_3$); 18.75, 18.88, 18.92, 19.53 (3 *Me*$_2$CH, *Me*–C(1)); 21.32, 22.65, 26.09 (2 *Me*–C(3), C(5)); 29.88 (C(6)); 33.88 (3 Me$_2$*C*H)); 38.60 (Me$_2$CH–C(O)$_3$); 39.68 (C(3)); 41.31 (C(7)); 48.46 (C(4)); 49.06 (C(1)); 62.36 (C(6′)); 66.58 (C(2′)); 69.41 (C(5′)); 72.67 (C(4′)); 76.71 (C(3′)); 84.67 (C(2)); 97.34 (C(1′)); 125.85 (Me$_2$CH–*C*(O)$_3$); 174.5, 175.55, 176.65 (3 CO). Anal. calc. for $C_{32}H_{52}O_{10}$ (596.76): C 64.40, H 8.78; found: C 64.15, H 8.64.

*(3*S*)-3,7-Dimethyloct-6-en-1-yl 2,3,4,6-Tetra*-O-*isobutyryl-β*-D-*glucopyranoside* (**4″c**). Moderately unstable oil, could not be obtained anal. pure. ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.85 (*d*, $^3J = 6.5$, Me–C(3)); 1.05–1.11 (*m*, 4 *Me*$_2$CH); 1.18–1.4 (*m*, CH_2(2), H–C(3), CH_2(4)); 1.58, 1.67 (2*s*, 2 Me–C(7)); 1.85–2.05 (*m*, CH_2(5)); 2.40–2.65 (*m*, 4 Me$_2$*C*H); 3.45–3.49 (*m*, H–C(1)); 3.70 (*ddd*, $^3J = 9.7$, 4.2, 2.7, H–C(5′)); 3.86–3.93 (*m*, H–C(1)); 4.10–4.18 (*m*, CH_2(6′)); 4.47 (*d*, $^3J = 8.0$, H–C(1′)); 5.01 (‘*dd*’, $^3J = 9.7$, 8.0, H–C(2′)); 5.06–5.09 (*m*, H–C(6)); 5.11 (*t*, $^3J = 9.7$, H–C(4′)); 5.28 (*t*, $^3J = 9.7$, H–C(3′)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 17.62 (*Me*–C(7)); 18.75, 18.79, 18.84, 18.88 (4 *Me*$_2$CH); 19.16 (*Me*–C(3)); 25.39 (*Me*–C(7)); 25.7 (C(5)); 29.1 (C(3)); 33.82, 33.87, 34.1 (4 Me$_2$*C*H); 36.31 (C(4)); 37.2 (C(2)); 61.87 (C(1)); 67.98 (C(6′)); 68.31 (C(4′)); 70.95 (C(2′)); 72.05 (C(5′)); 73.30 (C(3′)); 101.10 (C(1′)); 124.61 (C(6)); 131.24 (C(7)); 175.21, 175.29, 176.13, 176.78 (4 CO).

1,2-O-*{1-{[(3*S*)-3,7-Dimethyloct-6-en-1-yl]oxy}-2-methylpropylidene}-3,4,6-tri*-O-*isobutyryl-α*-D-*glucopyranose* (**5″c**). Isomer mixture 7:1. TLC: not separated. ^{1}H-NMR ($CDCl_3$, 250 MHz; major isomer, except otherwise noted): 0.85 (*d*, $^3J = 6.5$, Me–C(3)); 1.05–1.18 (*m*, 4 *Me*$_2$CH); 1.18–1.4 (*m*, CH_2(2), H–C(3), CH_2(4)); 1.57–1.66 (2*s*, 2 Me–C(7)); 1.85–2.05 (*m*, CH_2(5)); 2.25 (*m*, Me$_2$*C*H–C(O)$_3$); 2.40–2.70 (*m*, 3 Me$_2$*C*H); 3.39–3.47 (*m*, CH_2(1)); 4.06 (*m*, H–C(5′)); 4.15 (*m*, CH_2(6′)); 4.25 (*dd*, $^3J = 5.4$, 3.3, H–C(2′)); 4.88 (*dd*, $^3J = 9.5$, 4.7, H–C(4′)); 5.08 (*m*, H–C(6)); 5.18 (*dd*, $^3J = 4.7$, 3.3, H–C(3′)); 5.44 (*dd*, $^3J = 9.5$, 4.8, minor isomer); 5.61 (*d*, $^3J = 5.8$, H–C(1′) of the minor isomer); 5.70 (*d*, $^3J = 5.4$, H–C(1′)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 16.98, 17.03 (*Me*–C(3), *Me*–C(7)); 17.58, 18.70, 18.77, 18.86, 19.31 (4 *Me*$_2$CH)); 25.37 (*Me*–C(7)); 25.68 (C(5)); 29.20 (C(3)); 32.74, 33.78 (4 Me$_2$*C*H); 36.53 (C(4)); 37.01 (C(2)); 60.6 (C(1)); 62.53 (C(6′)); 67.17 (C(4′)); 67.68 (C(2′)); 71.06 (C(5′)); 74.03 (C(3′)); 96.95 (C(1′)); 123.62 (Me$_2$CH–*C*(O)$_3$); 124.7 (C(6)); 131.17 (C(7)); 175.26, 175.51, 176.63 (3 CO).

*(1*R*,2*R*,3*R*,5*S*)-2,6,6-Trimethylbicyclo[3.1.1]hept-3-yl 2,3,4,6-Tetra*-O-*isobutyryl-β*-D-*glucopyranoside* (**4″d**). M.p. 99–100°. $[\alpha]_D^{25} = -30.6$ ($c = 1.6$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.9–1.21 (*m*, Me–C(2),

2 Me–C(6), 4 *Me*$_2$CH); 1.7–2.4 (*m*, H–C(1), H–C(2), CH$_2$(4), H–C(5), CH$_2$(7)); 2.4–2.60 (*m*, 4 Me$_2$C*H*); 3.72 (*ddd*, ^3J = 9.7, 5.2, 2.7, H–C(5′)); 3.95 (*dt*, ^3J = 4.7, 9.2, H–C(3)); 4.16 (*m*, CH$_2$(6′)); 4.55 (*d*, ^3J = 8.0, H–C(1′)); 5.0 (*dd*, ^3J = 8, 9.7, H–C(2′)); 5.1 (*t*, ^3J = 9.7, H–C(4′)); 5.26 (*t*, ^3J = 9.7, H–C(3′)). ^{13}C-NMR (CDCl$_3$, 62.9 MHz): 18.79, 18.81, 18.90, 19.05, 20.30 (*Me*–C(2), 4 *Me*$_2$CH); 23.73, 27.43, 29.67 (C(7), 2 *Me*–C(6)); 33.35, 33.88, 33.99 (4 Me$_2$*C*H); 35.44 (C(4)); 38.34 (C(6)); 41.25 (C(5)); 44.25 (C(2)); 47.39 (C(1)); 62.25 (C(6′)); 68.39 (C(5′)); 71.29 (C(4′)); 72.08 (C(3′)); 72.51 (C(2′)); 78.82 (C(3)); 99.50 (C(1′)); 175.16, 175.35, 176.15, 176.75 (4 CO). Anal. calc. for C$_{32}$H$_{52}$O$_{10}$ (596.76): C 64.40, H 8.78; found: C 64.43, H 8.86.

3,4,6-Tri-O-*isobutyryl-1,2*-O-*{1-[[(1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]oxy}-2-methyl propylidene}-α*-D-*glucopyranose* (**5″d**). $[\alpha]_D^{25}$ = +26.6 (*c* = 1.1, CHCl$_3$). ^{1}H-NMR (CDCl$_3$, 250 MHz): 0.9–1.30 (*m*, Me–C(2), 2 Me–C(6), 4 *Me*$_2$CH); 1.7–2.4 (*m*, H–C(1), H–C(2), CH$_2$(4), H–C(5), CH$_2$(7)); 2.17–2.26 (*m*, Me$_2$C*H*–C(O)$_3$); 2.4–2.60 (*m*, 3 Me$_2$C*H*); 3.90 (*dt*, ^3J = 9.2, 4.5, H–C(5′)); 4.10 (*dt*, ^3J = 8.1, 4.7, H–C(3)); 4.16 (*m*, CH$_2$(6′)); 4.35 (*dd*, ^3J = 5.4, 4, H–C(2′)); 4.95 (*dd*, ^3J = 9.2, 6, H–C(4′)); 5.22 (*dd*, ^3J = 6, 4, H–C(3′)); 5.75 (*d*, ^3J = 5.4, H–C(1′)). ^{13}C-NMR (CDCl$_3$, 62.9 MHz): 17.29 (*Me*–C(2)); 17.35, 18.70, 18.72, 18.77, 18.86 (4 *Me*$_2$CH); 20.31, 23.82 (2 *Me*–C(6)); 27.40 (C(7)); 33.49 (C(4)); 33.76, 33.79, 34.08 (3 Me$_2$*C*H); 37.53 (Me$_2$*C*H–C(O)$_3$); 38.09 (C(6)); 41.35 (C(2)); 44.95 (C(5)); 47.61 (C(1)); 62.3 (C(6′)); 66.89 (C(2′)); 68.24 (C(5′)); 71.81 (C(3′)); 72.35 (C(4′)); 74.76 (C(3)); 97.03 (C(1′)); 124.11 (Me$_2$CH–*C*(O)$_3$); 175.39, 175.50, 176.67 (3 CO).

*(1*R*,2*S*,5*R*)-2-Isopropenyl-5-methylcyclohexyl 2,3,4,6-Tetra*-O-*isobutyryl-β*-D-*glucopyranoside* (**4″e**). M.p. 104–105°. $[\alpha]_D^{25}$ = −25.2 (*c* = 2.7, CHCl$_3$). ^{1}H-NMR (CDCl$_3$, 250 MHz): 0.92 (*d*, ^3J = 6.5, Me–C(5)); 1.05–1.5 (4 *Me*$_2$CH, CH$_2$(3), CH$_2$(4), H–C(5), CH$_2$(6)); 1.6 (br. *s*, Me–C(7)); 1.89 (*m*, H–C(2)); 2.4–2.60 (*m*, 4 Me$_2$C*H*); 3.45 (*dt*, ^3J = 10, 4, H–C(1)); 3.55 (*ddd*, ^3J = 9.7, 5.2, 2.2, H–C(5′)); 4.01 (*dd*, ^2J = 12, ^3J = 5.2, H–C(6′)); 4.09 (*dd*, ^2J = 12, ^3J = 2.2, H–C(6′)); 4.54 (*d*, ^3J = 8.0, H–C(1′)); 4.65 (br. *s*, CH$_2$(8)); 4.88 (*dd*, ^3J = 8, 9.7, H–C(2′)); 5.00 (*t*, ^3J = 9.7, H–C(4′)); 5.21 (*t*, ^3J = 9.7, H–C(3′)). ^{13}C-NMR (CDCl$_3$, 62.9 MHz): 18.76, 18.83, 18.86, 18.94, 19.19, 22.20 (4 *Me*$_2$CH, *Me*–C(5), *Me*–C(7)); 31.05 (C(3)); 31.35 (C(5)); 33.83, 33.85, 33.94 (4 Me$_2$*C*H); 34.13, 40.23 (C(4), C(6)); 51.13 (C(2)); 62.10 (C(6′)); 68.20 (C(5′)); 71.24 C(4′); 71.78 C(3′); 72.62 C(2′)); 78.76 (C(1)); 97.69 (C(1′)); 111.41 (C(8)); 146.84 (C(7)); 175.01, 175.34, 176.15, 176.75 (4 CO). Anal. calc. for C$_{32}$H$_{52}$O$_{10}$ (596.76): C 64.40, H 8.78; found: C 64.49, H 9.19.

3,4,6-Tri-O-*isobutyryl-1,2*-O-*{1-[[(1*R*,2*S*,5*R*)-2-isopropenyl-5-methylcyclohexyl]oxy}-2-methylpropylidene}-α*-D-*glucopyranose* (**5″e**). $[\alpha]_D^{25}$ = +20.5 (*c* = 3, CHCl$_3$). ^{1}H-NMR (CDCl$_3$, 250 MHz): 0.92 (*d*, ^3J = 6.5, Me–C(5)); 1.05–1.9 (*m*, 4 *Me*$_2$CH, CH$_2$(3), CH$_2$(4), H–C(5), CH$_2$(6)); 1.7 (br. *s*, Me–C(7)); 2.03 (*m*, H–C(2)); 2.05–2.2 (*m*, Me$_2$C*H*–C(O)$_3$); 2.4–2.60 (*m*, 3 Me$_2$C*H*); 3.45 (*dt*, ^3J = 10.5, 4.2, H–C(1)); 4.05 (*m*, H–C(5′)); 4.10 (*m*, CH$_2$(6′)); 4.35 (*dd*, ^3J = 5.5, 3.5, H–C(2′)); 4.70–4.75 (*m*, CH$_2$(8)); 4.92 (*dd*, ^3J = 9.2, 4.7, H–C(4′)); 5.15 (*dd*, ^3J = 4.7, 3.5, H–C(3′)); 5.65 (*d*, ^3J = 5.2, H–C(1′)). ^{13}C-NMR (CDCl$_3$, 62.9 MHz): 17.42, 17.54, 18.67, 18.69, 18.74, 18.86, 18.90, 18.92, 19.52, 22.27 (*Me*–C(5), *Me*–C(7), 4 *Me*$_2$CH); 30.67 (C(3)); 31.76 (C(5)); 33.77, 33.78, 33.81, 33.96 (3 Me$_2$*C*H, Me$_2$*C*H–C(O)$_3$); 34.58 (C(4)); 42.93 (C(6)); 52.11 (C(2)); 62.64 (C(6′)); 67.27 (C(5′)); 67.90 (C(4′)); 71.05 (C(3′)); 72.48 (C(2′)); 74.57 (C(1)); 96.82 (C(1′)); 112.06 (C(8)); 124.20 (Me$_2$CH–*C*(O)$_3$); 147.45 (C(7)); 175.17, 175.58, 176.71 (3 CO).

*(−)-(1*E*)-{(4*R*,5*S*,6*S*)-5-[[*(tert-*Butyl)dimethylsilyl]oxy}-4-methoxy-6-[(2,3,4,6-tetra*-O-*isobutyryl-β*-D-*glucopyranosyl)oxy]cyclohex-2-en-1-yliden}acetonitrile* (**4″g**). M.p. 94–95°. $[\alpha]_D^{25}$ = −11.1 (*c* = 1.1, CHCl$_3$). ^{1}H-NMR (CDCl$_3$, 400 MHz): 0.12, 0.13 (2*s*, Me$_2$Si); 0.9 (*s*, ^{t}BuSi); 1.04–1.22 (*m*, 4 *Me*$_2$CH); 2.38–2.6 (*m*, 4 Me$_2$C*H*); 3.38 (*s*, MeO); 3.66 (*ddd*, ^3J = 10, 4.8, 2.4, H–C(5′)); 3.75 (*m*, H–C(5), H–C(6)); 4.10 (*dd*, ^3J = 12.4, 4.8, H–C(6′)); 4.20 (*dd*, ^3J = 12.4, 2.4, H–C(6′)); 4.53 (*dd*, ^3J = 8.4, 1.6, H–C(4)); 5.10 (‘*dd*’, ^3J = 9, 7.6, H–C(2′)); 5.13 (‘*dd*’, ^3J = 10, 9.6, H–C(4′)); 5.15 (*d*, ^3J = 7.6, H–C(1′)); 5.24 (‘*dd*’, ^3J = 9.6, 9, H–C(3′)); 5.58 (br. *s*, H–C(7)); 6.17 (br. *d*, ^3J = 10, H–C(2)); 6.66 (*dd*, ^3J = 10, 1.6, H–C(3)). ^{13}C-NMR (CDCl$_3$, 100.577 MHz): −4.15 (Me$_2$Si); 18.30, 18.47, 18.71, 18.75, 18.80, 18.98, 19.25 (4 *Me*$_2$CH, Me$_3$CSi); 26.14 (*Me*$_3$CSi); 33.76, 33.80, 33.86 (4 Me$_2$*C*H); 56.56 (MeO); 61.33 (C(6′)); 68.16 (C(3′)); 71.47 (C(2′)); 72.11 (C(4′)); 72.37 (C(5′)); 74.65 (C(4)); 76.51 (C(5)); 82.28 (C(6)); 95.3 (C(7)); 99.15 (C(1′)); 116.69 (CN); 124.77 (C(3)); 133 (C(2)); 155.56 (C(1)); 175.29, 175.49, 175.88, 176.54 (4 CO). Anal. calc. for C$_{37}$H$_{59}$NO$_{12}$Si (737.95): C 60.21, H 8.05, N 1.89; found: C 60.41, H 8.04, N 1.69.

*(+)-(1*E*)-{(4*R*,5*R*,6*S*)-6-Hydroxy-4-methoxy-5-[(2,3,4,6-tetra*-O-*isobutyryl-β*-D-*glucopyranosyl)oxy]cyclohex-2-en-1-yliden}acetonitrile* (**6g**). M.p. 129–130°. $[\alpha]_D^{25}$ = +20.6 (*c* = 0.7, CHCl$_3$). ^{1}H-NMR (CDCl$_3$, 400 MHz): 1.04–1.22 (*m*, 4 *Me*$_2$CH); 2.42–2.60 (*m*, 4 Me$_2$C*H*); 3.11 (*d*, ^3J = 2.3, OH–C(6)); 3.48 (*s*, MeO); 3.55 (*dd*, ^3J = 10.2, 7.5, H–C(5)); 3.76 (*m*, H–C(5′)); 4.05 (br. *d*, ^3J = 7.5, H–C(4)); 4.20 (*m*, CH$_2$(6′)); 4.28 (br. *d*, ^3J = 10.2, H–C(6)); 4.91 (*d*, ^3J = 8, H–C(1′)); 5.05 (‘*dd*’, ^3J = 9.5, 8, H–C(2′)); 5.13 (*t*, ^3J = 9.5, H–C(4′)); 5.31 (*t*, ^3J = 9.5, H–C(3′)); 5.61 (br. *s*, H–C(7)); 6.12 (*dt*, ^3J = 10, ^4J = 1.8, H–C(2)); 6.64 (*dd*, ^3J = 10, 2, H–C(3)). ^{13}C-NMR (CDCl$_3$, 100.577 MHz): 18.48, 18.61, 18.64, 18.70, 18.72, 18.75 (4 *Me*$_2$CH); 33.65,

33.95 (4 Me_2*C*H); 57.05 (MeO); 61.40 (C(6′)); 67.4 (C(4′)); 69.99 (C(6)); 71.69 (C(3′)); 71.85 (C(2′)); 72.17 (C(5′)); 79.84 (C(4)); 83.2 (C(5)); 93.86 (C(7)); 101.83 (C(1′)); 116.27 (CN); 124.19 (C(3)); 133.76 (C(2)); 154.88 (C(1)); 175.05, 175.75, 176.5, 176.60 (4 CO). Anal. calc. for $C_{31}H_{45}NO_{12}$ (623.7): C 59.69, H 7.27, N 2.24; found: C 60.04, H 7.4, N 2.23.

*(+)-(1*E*)-{(4*R*,5*S*,6*S*)-4-Methoxy-5,6-bis[(2,3,4,6-tetra-*O*-isobutyryl-β-*D*-glucopyranosyl)oxy]cyclohex-2-en-1-yliden}acetonitrile* (**7g**). $[\alpha]_D^{25} = +8.6$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 250 MHz): 1.04 – 1.22 (*m*, 8 *Me*$_2$CH); 2.42 – 2.60 (*m*, 8 Me$_2$C*H*); 3.42 (*s*, MeO); 3.67 (*m*, H–C(5′), H–C(5″)); 4.00 (*dd*, $^3J = 10.25$, 8.1, H–C(5)); 4.06 – 4.16 (*m*, H–C(6′), CH_2(6″), H–C(4)); 4.26 (*dd*, $^2J = 12.5$, $^3J = 5.6$, H–C(6′)); 4.5 (*dd*, $^3J = 10.5$, $^4J = 2$, H–C(6)); 4.88, 4.89 (2*d*, $^3J = 7.5$, H–C(1′), H–C(1″)); 5.06 – 5.24 (*m*, 5 H (glc)); 5.29 (*t*, $^3J = 9.5$, 1 H (glc)); 5.63 (br. *s*, H–C(7)); 6.10 (br. *d*, $^3J = 10$, H–C(2)); 6.64 (br. *d*, $^3J = 10$, H–C(3)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 18.40, 18.49, 18.60, 18.64, 16.70, 18.75, 18.80, 19.04, 19.26 (8 *Me*$_2$CH); 33.66, 33.72, 33.83 (8 Me$_2$*C*H); 56.21 (MeO); 61.01, 61.73, 67.76, 67.81, 71.18, 71.57, 72.02, 72.07, 72.18, 72.41 (C (glc)); 76.33, 76.52, 78.57 (C(6), C(5), C(4)); 96.20 (C(7)); 98.70, 99.98 (C(1′), C(1″)); 116.19 (CN); 124.78 (C(3)); 135.47 (C(2)); 154.63 (C(1)); 175.00, 175.04, 175.09, 175.50, 175.66, 175.79, 176.35 (8 CO). Anal. calc. for $C_{53}H_{79}NO_{21}$ (1066.07): C 59.71, H 7.47, N 1.31; found: C 59.41, H 7.76, N 1.24.

Influence of the Method of Preparation of AgOTf on the Glycosidation of Aglycone **2g** *by* G.P. E *to Yield Glycoside* **4″g**. The following isolated yields were obtained using AgOTf prepared according to: *Method 1*, 58% of **4″g** and 4% of **2g**; *Method 2*, 20% of **4″g** and 52% of **2g**; *Method 2′*, 41% of **4″g** and 37% of **2g**; *Method 3*, 30% of **4″g** and 60% of **2g**; *Method 3′*, 52% of **4″g** and 20% of **2g**.

Preparation of AgOTf. Method 1. Procedure adapted from [22]. Finely powdered Ag_2O (2.00 g, 8.6 mmol) was slowly added within 1 h, under vigorous stirring and with exclusion of light, to a soln. of distilled TfOH (2.59 g, 17.2 mmol) in distilled H_2O (15 ml) at 4°. After the addition, the mixture was warmed slowly to 20°, and stirring was continued until total dissolution of Ag_2O. The H_2O was then evaporated and the residue recrystallized twice from Et_2O (10 – 15 ml). The long white needles obtained were dried under 0.1 Torr, the temp. being raised within 6 h from 20° to 100°: 1.9 g (43%) of AgOTf. Additional recrystallizations were unnecessary since they did not increase the glycosidation yields.

Method 2. Identical to *Method 1*, except that a two-fold excess of TfOH (5.33 g, 35.5 mmol, 2.06 equiv.) was used: 2.29 g (52%) of AgOTf.

Method 2′. The crystals of AgOTf obtained by *Method 2* were recrystallized twice more from Et_2O and then dried at 20 – 100°/0.1 Torr (*vide supra*): 1.96 g (85.5%) of AgOTf.

Method 3. Finely powdered Ag_2O (2.00 g, 8.6 mmol) was slowly added within 1 h, under vigorous stirring and with exclusion of light, to a soln. of distilled TfOH (0.86 g, 5.73 mmol, 0.33 equiv.) in distilled H_2O (15 ml) at 4°. After the addition, the mixture was warmed to 20° and stirring was continued for 2 h. The resulting suspension was filtered over *Celite*®. The clear soln. was evaporated and the residue recrystallized twice from Et_2O (10 – 15 ml). The long white needles were dried at 20 – 100°/0.1 Torr (*vide supra*): 780 mg (53%) of AgOTf.

Method 3′. The crystals of AgOTf obtained by *Method 3* were recrystallized twice more from Et_2O and then dried at 20 – 100°/0.1 Torr (*vide supra*): 587 mg (75%) of AgOTf.

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