147. Glycosylidene Carbenes

Part 22

α-D-Selectivity in the Glycosidation by Carbenes Derived from 2-Acetamido-hexoses

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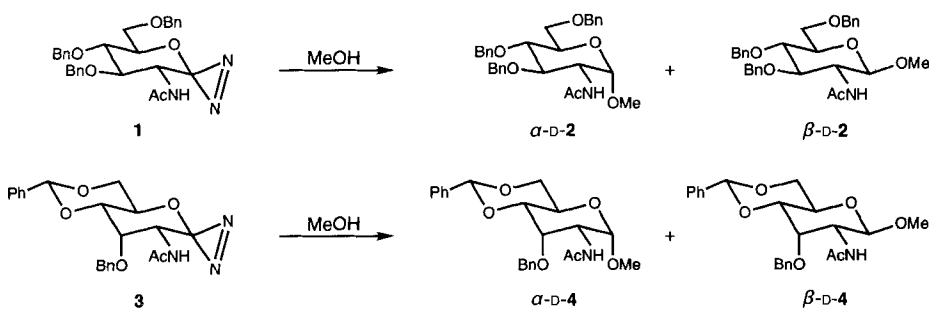
Glycosylidene carbenes derived from the GlcNAc and AllNAc diazirines **1** and **3** were generated by thermolysis or photolysis of the diazirines. The reaction of **1** with i-PrOH gave exclusively the isopropyl α-D-glycoside of **5** besides some dihydrooxazole **9** (*Scheme 2*). A similar reaction with $(CF_3)_2CHOH$ yielded predominantly the α-D-anomer of **6**, while glycosidation of 4-nitrophenol (→**7**) proceeded with markedly lower diastereoselectivity. Similarly, the *allo*-diazirine **3** gave the corresponding glycosides **12**–**14**, but with a lower preference for the α-D-anomers (*Scheme 3*). The reactions of the carbene derived from **1** with Ph_3COH (→**8**) and diisopropylideneglucose **10** (→**11**) gave selectively the α-D-anomers (*Scheme 2*). The α-D-selectivity increases with increasing basicity (decreasing acidity) of the alcohols. It is rationalized by an intermolecular H-bond between the acetamido group and the glycosyl acceptor. This H-bond increases the probability for the formation of a 1,2-*cis*-glycosidic C–O bond. The *gluco*-intermediates are more prone to forming a N–H···(H)OR bond than the *allo*-isomers, since the acetamido group in the *N*-acetylallosamine derivatives forms an intramolecular H-bond to the *cis*-oriented benzyloxy group at C(3), as evidenced by δ/T and δ/c experiments.

Introduction. – Kinetically controlled glycosidation by glycosyl donors derived from 2-(acylamino)-2-deoxyhexoses and -pentoses leads to 1,2-*trans*-configurated glycosides (see [1] for a review, *cf.* also [2] [3]). The stereoselectivity may be different for glycosidations by glycosylidene carbenes. We had observed evidence for a different selectivity

Scheme 1



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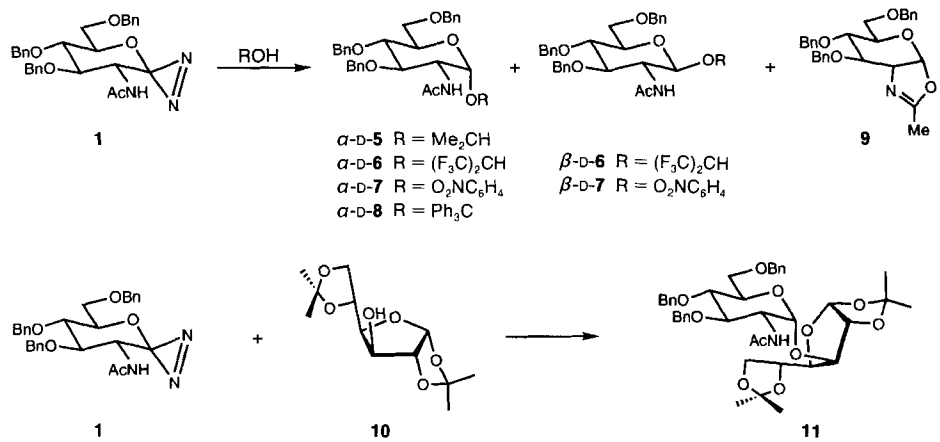
while studying the stability of 1-azi-aldoses. Thermolysis in MeOH of the *N*-acetyl-glucosamine-derived diazirine **1** and of the *N*-acetylallosamine-derived diazirine **3** led predominantly to the methyl α-D-pyranosides α-D-**2** and α-D-**4**, respectively (*Scheme 1*) [4].

We wondered about the generality and the origin of this selectivity, and now describe[2]) the glycosidation by **1** and **3**, under photolytic or thermolytic conditions, of alcohols differing in their degree of acidity (pK_A (i-PrOH) = 16.5, pK_A ($(CF_3)_2CHOH$) = 9.3, pK_A (4-nitrophenol) = 7.2) and their steric demand. By analogy to the *Königs-Knorr*-type glycosidation, we used 2 equiv. or less of the alcohols.

Scheme 2



Results and Discussion. – *Glycosidation by the Diazirines* **1** *and* **3**. Photolysis of **1** at low temperature in CH_2Cl_2 in the presence of 2 equiv. of i-PrOH gave 70% of the α-D-anomer of **5** and 13% of the known dihydrooxazole **9** [6–8]; β-D-**5** was not detected (*Scheme 2*, *Table*). Under thermal conditions (24°), only traces of α-D-**5** were formed; the dihydrooxazole **9** was the main product.

Photolysis of **1** in the presence of 0.5, 1.0, 2.0, and 10 equiv. of $(CF_3)_2CHOH$ in CH_2Cl_2 gave **6** in 28, 58, 59, and 91% yield and in α-D/β-D ratios of 79:21, 77:23, 72:28, and 80:20, respectively. Thermolysis of **1** and 2 equiv. of $(CF_3)_2CHOH$ gave **6** in a slightly better α-D/β-D ratio of 88:12. The anomers α-D-**6** (63%) and β-D-**6** (9%) were separated by prep. HPLC.

Photolysis of **1** in the presence of 4-nitrophenol was progressively inhibited by the formation of colored by-products, strongly absorbing at 350 nm. The glycosides **7** were isolated in only 36% yield. The α-D/β-D ratio was 37:63. Thermolysis of **1** and 4-nitrophenol yielded 48% of α-D-**7** and 39% of β-D-**7** (α-D/β-D ratio 58:42).

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[2]) Part of the results have been reported in [5].

Table. *Glycosidation of the Diazirines* **1** *and* **3** *with Some Model Hydroxy Compounds*

Diazirine	ROH (equiv.)	Conditions	Glycosides (yield)[a]	Ratio α-D/β-D	Side products (yield)
1	i-PrOH (2)	CH_2Cl_2, −84°, *hv*	**5** (70%)	only α-D	**9** (13%)
1	i-PrOH (2)	CH_2Cl_2, 26°	**5** (traces)	only α-D	
1	$(CF_3)_2CHOH$ (0.5)	CH_2Cl_2, −84°, *hv*	**6** (28%)	79:21[b]	
1	$(CF_3)_2CHOH$ (1)	CH_2Cl_2, −84°, *hv*	**6** (58%)	77:23[b]	
1	$(CF_3)_2CHOH$ (2)	CH_2Cl_2, −84°, *hv*	**6** (59%)	72:28[b]	
1	$(CF_3)_2CHOH$ (10)	CH_2Cl_2, −84°, *hv*	**6** (91%)	80:20[b]	
1	$(CF_3)_2CHOH$ (2)	CH_2Cl_2, 26°	**6** (72%)	88:12[b]	
1	4-nitrophenol (1.6)	CH_2Cl_2, −84, *hv*	**7** (36%)	37:63[c]	
1	4-nitrophenol (1.6)	CH_2Cl_2, 26°	**7** (87%)	58:42[c]	
1	Ph_3COH (2)	CH_2Cl_2, −84°, *hv*	**8** (39%)	only α-D	
1	Ph_3COH (2)	CH_2Cl_2, 26°	**8** (29%)	only α-D	**9** (> 32%)
1	**10** (2)	CH_2Cl_2, −84°, *hv*	**11** (30%)	only α-D	**9** (7%)
3	i-PrOH (2)	CH_2Cl_2, −84°, *hv*	**12** (64%)	78:22[d]	**16** (7%)
3	i-PrOH (2)	THF, −84°, *hv*	**12** (43%)	81:19[d]	
3	i-PrOH (2)	CH_2Cl_2, 41°	**12** (12%)	only α-D	**15**[e]
3	$(CF_3)_2CHOH$ (2)	CH_2Cl_2, −84°, *hv*	**13** (88%)	48:52[d]	
3	$(CF_3)_2CHOH$ (2)	THF, −84°, *hv*	**13** (12%)	67:33[d]	**17** (39%)
3	$(CF_3)_2CHOH$ (2)	CH_2Cl_2, 41°	**13** (63%)	76:24[d]	
3	$(CF_3)_2CHOH$ (2)	1,4-dioxane, 50°	**13** (63%)	65:35[d]	
3	$(CF_3)_2CHOH$ (2)	MeCN, 50°	**13** (68%)	65:35[d]	**18** (18%)
3	4-nitrophenol (1.6)	CH_2Cl_2, 41°	**14** (77%)	51:49[d]	

[a]) Combined yields of both anomers after chromatographic separation. [b]) Determined by a ^{1}H-NMR spectrum of the crude product. [c]) Determined by HPLC of the crude product. [d]) Ratio of isolated anomers. [e]) Not isolated.

To check the dependence of the diastereoselectivity of the glycosidation on steric hindrance, we examined the glycosidation of trityl alcohol and of the diisopropylideneglucofuranose **10**, both weakly acidic, bulky alcohols. Photolysis of **1** in the presence of 2 equiv. of Ph_3OH gave selectively the α-D-anomer of **8** (39%). Thermolysis led to α-D-**8** (29%) and to the dihydrooxazole **9** (> 32%). Photolysis of **1** and 1.2 equiv. of **10** gave only 30% of the (1→3)-α-D-configurated disaccharide **11** (30%) besides traces of **9** and 65% of recovered **10**.

Photolysis of **1** in the presence of 1 equiv. of i-PrOH and 1 equiv. of $(CF_3)_2CHOH$ yielded α-D-**5** (30%) and α-D/β-D-**6** 77:23 (44%). Although $(CF_3)_2CHOH$ is more highly acidic than i-PrOH by 7.2 pK_a units, its glycosides were only formed in a slight excess. The anomeric selectivity was hardly affected, and this remained so when **1** was photolysed in the presence of 9 equiv. of i-PrOH and 1 equiv. of $(CF_3)_2CHOH$ under the same conditions, yielding 66% of α-D-**5** and 14% of α-D/β-D-**6** in a ratio of 74:26.

The significantly higher thermal stability of the *N*-acetylallosamine-derived diazirine **3** has been correlated with the presence of an intramolecular H-bond between the acetamido substituent and the axial benzyloxy group at C(3) [4]. This H-bond and the 1,3-diaxial interaction between the 3-benzyloxy group and the substituent at C(1) in α-D-glycosides prompted us to examine the glycosidation of the diazirine **3**.

Photolysis of **3** in CH_2Cl_2 containing 2 equiv. of i-PrOH (*Scheme 3*, *Table*) yielded a mixture of the isopropyl glycosides **12** (72%) and the acetamidoallal **16** [9] (7%). HPLC of **12** gave 50% of α-D-**12** and 14% of β-D-**12**. A similar photolysis in THF yielded 35%

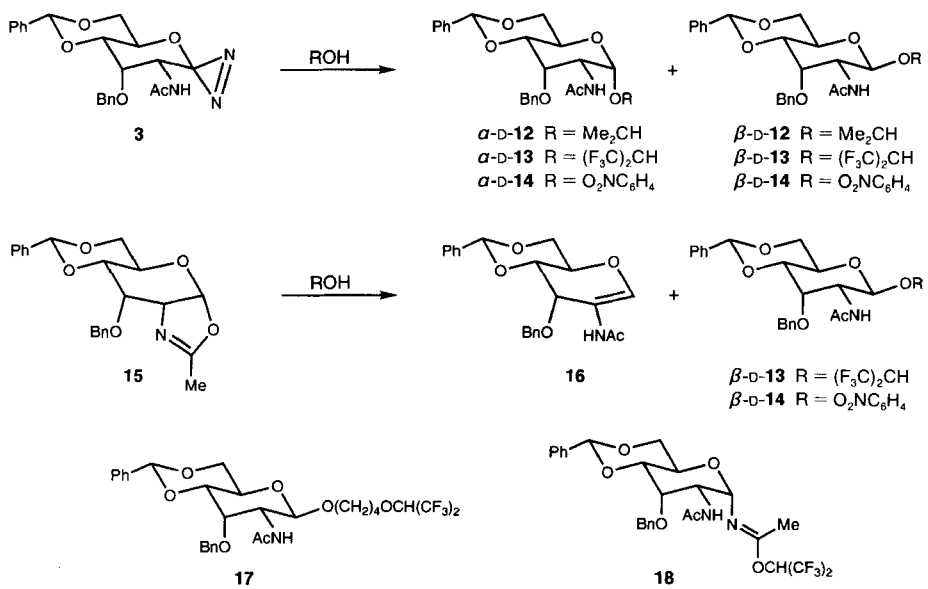
of α-D-**12** and 8% of β-D-**12**. Thermolysis of **3** and i-PrOH in boiling CH_2Cl_2 yielded only 12% of α-D-**12**, besides the dihydrooxazole **15** [9][3]).

Photolysis of **3** in the presence of $(CF_3)_2CHOH$ in CH_2Cl_2 yielded the anomeric glycosides α-D- and β-D-**13** in 42 and 46%, respectively. In THF, the yields of α-D- and β-D-**13** dropped to 8 and 4%, respectively. The main product was the β-D-glycoside **17** (39%), resulting from nucleophilic attack of THF on the intermediate oxycarbenium ion, followed by ring-opening nucleophilic attack of the alcohol (*cf.* [10]). The thermolysis of **3** and $(CF_3)_2CHOH$ was performed at 41° in CH_2Cl_2, and at 50° in 1,4-dioxane and MeCN. It led to α-D- and β-D-**13** (CH_2Cl_2: 48 and 15%; 1,4-dioxane: 41 and 22%; MeCN: 44 and 24%, resp.). The presence of 4-Å molecular sieves in CH_2Cl_2 had only a weak influence on the yield. Interception by $(CF_3)_2CHOH$ of the nitrilium ion resulting from the nucleophilic attack of MeCN on the intermediate oxycarbenium ion led to the iminoether **18** (18%) as by-product, a reaction that is precedented [10].

Photolysis of **3** in the presence of 4-nitrophenol did not go to completion due to the formation of the above mentioned UV-active by-products. Thermolysis in CH_2Cl_2, however, gave the glycosides α-D- and β-D-**14** in 39 and 38% yield, respectively.

To demonstrate that the 2-acetamido-2-deoxyallopyranosides are not derived from the dihydrooxazole **15**, we treated **15** with $(CF_3)_2CHOH$ in 1,2-dichloroethane at reflux. In the presence of 1,6 equiv. of this alcohol, we obtained 81% of the acetamidoallal **16**, but no glycosides, while the analogous reaction with 16 equiv. of $(CF_3)_2CHOH$ yielded 61% of β-D-**13** and 25% of **16**. The analogous reaction of **15** with 16 equiv. of 4-nitrophenol led to 81% of β-D-**14**.

Scheme 3



[3]) An exploratory glycosidation in 1,4-dioxane at 50° showed an increased ratio of dihydrooxazole to glycosides; 16% of **15** were isolated.

The anomeric configuration of the pyranosides **5**–**8**, **11**–**14**, **17**, and **18** is easily deduced from the $J(1,2)$ values (α-D-glucosides: 3.4–3.7 Hz; α-D-allosides: 4.3–5.0 Hz; β-D-glucosides: 6.5, 7.9 Hz; β-D-allosides: 8.3–8.5 Hz). The assignments are consistent with *Hudson*'s rule of isorotation. In keeping with the expected γ-effect, C(3) and C(5) of the α-D-pyranosides resonate by *ca.* 3–5 ppm at higher field than the corresponding C-atoms of the β-D-pyranosides. Characteristic heteronuclear couplings are observed for the fluorides **6**, **13**, and **18** (^3J(H,F) = 5.1–6.5 Hz, ^1J(C,F) = 278–288 Hz, ^2J(C,F) = 33–35 Hz, *cf.* [10]). Both H–C(6) and AcN of α-D-**8** are shielded ($\Delta\delta$ related to α-D-**5**/**6**/**7** *ca.* 0.3, 0.85, and 0.12 ppm, resp.) due to the anisotropy effect of the trityl group[4]). The (*E*)-configuration of the C=N bond of **18** is suggested by the absence of a visible long-range coupling between the Me group of the aglycon and H–C(1) [12]. The chemical-shift values for the imidate moiety (3 H–C(2′) at 1.99, C(1′) at 160.78, and C(2′) at 14.48 ppm) agree well with literature values for (*E*)-imidates [13–15]. In the ^{13}C-NMR spectrum of **17**, 4 *t* at 74.70, 69.19, 26.17, and 25.66 ppm evidence the presence of the 1,4-dialkoxybutyl moiety.

Discussion and NMR Experiments. As shown in the *Table*, the more strongly acidic alcohols were glycosylated in higher yields, and the yields of the isopropyl glycosides were higher at lower temperatures. This is in keeping with earlier results [10]. It reflects the more efficient protonation of the intermediate carbene by stronger acids and is not specific for HexNAc derivatives. The dihydrooxazoles **9** and **15** were only observed in the glycosidation of the weakly acidic i-PrOH. They were probably formed *via* a competing (intermolecular) protonation of the carbene by the acetamido group.

The *Table* also shows that most glycosidations of **1** and **3** at a higher, and to a minor extent, also at a lower temperature led exclusively or predominantly to 1,2-*cis*-glycosides. The anomeric selectivity depended on the pK_{HA} of the glycosyl acceptor. It was higher for the more weakly acidic OH compounds, and lower for the more highly acidic acceptors; it increased with temperature. The diastereoselectivity was generally lower for glycosidations by **3**. Glycosidation of i-PrOH at 41° gave only the α-D-allopyranoside (albeit in very low yields); at −84°, however, (where **1** led exclusively to the α-D-glycoside) it yielded a 78:22 mixture of the α-D- and β-D-anomers. Similarly, the diastereoselectivity of the glycosidation of $(CF_3)_2CHOH$ by **3** dropped from 76:24 at 41° to 1:1 at −84°. The 4-nitrophenol, the most acidic among the OH compounds we glycosylated, gave a 1:1 mixture of allopyranosides already at 41°.

However, the preferred α-D-selectivity in the glycosidation reactions of **1** and **3** contrasts with the β-D-selectivity observed in the glycosidation by 1,5-anhydro-1-azi-2,3,4,6-tetra-*O*-benzyl-D-glucitol of acidic alcohols and phenols, and the absence of stereoselectivity in the glycosidation of i-PrOH [10] [16]. Neighboring-group participation, as it is the rule in *Königs-Knorr*-type glycosidations of GlcNAc derivatives, would lead to β-D-glucosides and is, therefore, not operating in the glycosidation with **1** and **3**.

This unexpected diastereoselectivity is rationalized by postulating an intermolecular H-bond of the acetamido H–N to the glycosyl acceptor[5]). This H-bond should parallel the basicity of the OH compounds, which is inversely proportional to their acidity. The relevance of this H-bond becomes clear in the light of the mechanism of glycosidation by carbenes (see *e.g.* [17] [18]). It proceeds by protonation of the carbene in the σ-plane (defined by O(5), C(1), and C(2)) and interception of the ensuing oxycarbenium ion by an alcohol or alkoxide in the π-plane. A RO(H)···H–N H-bond increases the probability of

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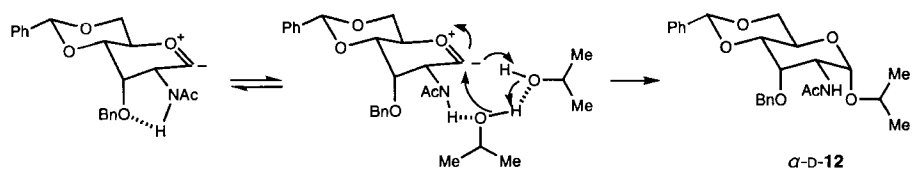
[4]) A similar upfield shift for both H–C(6) has been observed for trityl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside, but not for the corresponding β-D-anomer [11].

[5]) This H-bond may only be formed (or be strengthened) upon protonation of the carbene, as the H–N bond of the oxycarbenium cation is expected to be more acidic than the one of the carbene.

an attack of ROH from the side of the acetamido group, *i.e.*, from below the plane of the pyranose ring (a H-bond to ROH of the rotamer where N–H is more or less coplanar with H–C(2) leads to an orientation of ROH which is less favorable for attack in the π-plane of the oxycarbenium cation[6]). For an orientation of H-bonded glycosyl acceptor required for C–O bond formation, the acetamido group may have to deviate from the most favorable orientation; hence the temperature dependence in the glycosidation by the *gluco*-diazirine **1**. The H–N group of the intermediates derived from *N*-acetylallosamine is less available for intermolecular H-bonding than the one of the *N*-acetylglucosamine analogues, as the *allo*-configurated intermediates exist as a mixture of intramolecularly H-bonded and free tautomers [4] (*Scheme 4*); the proportion of the latter (and the rate of equilibration) should increase with temperature.

Scheme 4. Hydrogen Bonding and Glycosidation by the Carbene Derived from **3**. Protonation of the carbene by associated rather than by monomolecular i-PrOH (0.03M in CH_2Cl_2) is expected, as the concentration-dependent glycosidation of the presumably more highly acidic 1,6-anhydroglucose still proceeds at an acceptor concentration of 0.025M in 1,4-dioxane [19].



Evidence for intra- and/or intermolecular H-bonds of *N*-acetylglucosamine and -allosamine derivative was obtained from the dependence of the chemical shift on temperature and concentration (δ/T and δ/c ^{1}H-NMR experiments [20–22]). ^{1}H-NMR Spectra of 0.03M solutions of **1**, α-D-**6**, β-D-**6**, **3**, and α-D-**13** in CD_2Cl_2 were measured at four different temperatures in the range of 180–300 K. The chemical shift of H–N of the *N*-acetylallosamine derivatives α-D-**6**, **3**, and α-D-**13** shows a linear, negative δ/T dependence; J(2,NH) does not change (*Fig. a*). The $\Delta\delta/\Delta T$ values (–3.9, –2.6, and –3.1 ppb/K, resp.) suggest the presence on an intramolecular H-bond. In the three compounds, at least one *cis*-alkoxy substituent vicinal to the acetamido group could act as a H-bond acceptor. That J(2,NH) remains constant, and that the $|\Delta\delta/\Delta T|$ values for H–C(1), H–C(2), H–C(3), and the Me groups are small (< 0.9 ppb/K) indicates the absence of a temperature-dependent equilibrium of rotamers relative to the C(2)–N bond. For **1** and β-D-**6**, a nonlinear δ/T dependence for H–N is observed, but again, J(2,NH) is unchanged. However, enhanced δ/T dependencies are observed for H–C(1) and H–C(3) of β-D-**6** ($\Delta\delta/\Delta T$ = +2.9 and –2.9 ppb/K) and H–C(2) of **1** ($\Delta\delta/\Delta T$ = –1.7 ppb/K), indicating a change in the population of the rotamers. The slope for H–N of β-D-**6** does not deviate strongly from linearity. Linear regression leads to a $\Delta\delta/\Delta T$ value of *ca.* –6 ppb/K which is typical for intermolecular H-bonds.

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[6]) One expects that at the least the more highly acidic OH compounds form a H-bond to the acetamido carbonyl O-atom; this may play a role in the formation of the β-D-anomers. Note, however, that – apart from the question of the appropriate orientation of ROH in these associates – this type of H-bonding reduces the kinetic acidity of the alcohol and disfavours protonation of the carbene.

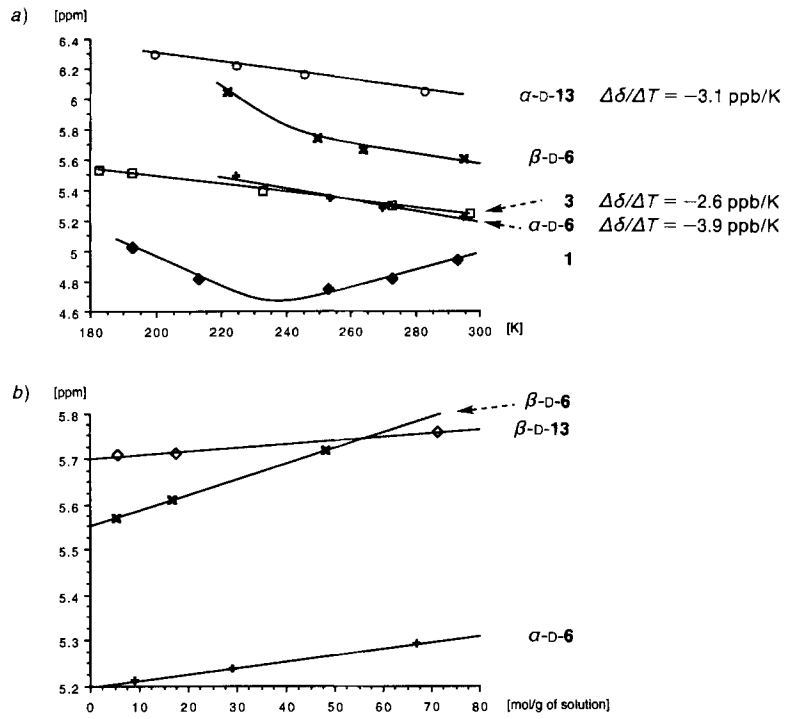

Figure. *Temperature and concentration dependence of the H–N chemical shift of selected acetamides. a*) Temperature dependence of the H–N chemical shifts of **1**, **3**, α-D-**6**, β-D-**6**, and α-D-**13**. *b*) Concentration dependence of the H–N chemical shifts of α-D-**6**, β-D-**6**, and β-D-**13**.

^{1}H-NMR Spectra of α-D-**6**, β-D-**6**, and β-D-**13** were measured at 3 concentrations between 0.005 and 0.07M at room temperature. β-D-**6** shows a clear δ/c dependence (*Fig. b*) in keeping with intermolecular H-bonds. α-D-**6** and β-D-**13**, however, show only a weak dependency, indicating a predominant intramolecular H-bond.

We thank Dr. *B. Bernet* for his help in the preparation of the manuscript and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. See [9]. For photolysis, a *Philips-HPK-125* Hg high-pressure lamp equipped with a quartz filter and a rod made of sintered natural quartz as a light guide was used. ^{1}H-NMR Assignments were ascertained by homonuclear decoupling experiments. MS: chemical ionization (CI; NH_3), or, where indicated, electron-spray ionization (ESI).

Reaction of **1** *with i-PrOH. a*) Photolysis: A soln. of **1** (50.6 mg, 0.1 mmol) in CH_2Cl_2 (4.4 ml) was treated with i-PrOH (15.6 µl, 0.2 mmol) and 4-Å molecular sieves (80 mg), stirred at −84° for 15 min, and irradiated for 75 min. Filtration through *Celite*, evaporation, and FC (5.5 g of SiO_2, AcOEt/hexane 1:1) gave α-D-**5**/**9** (42.9 mg). Separation by prep. HPLC (Et_2O/hexane 7:3) yielded α-D-**5** (37.8 mg, 70%) and **9** [6–8] (6.1 mg, 13%).

b) Thermolysis: A soln. of **1** (9.7 mg, 0.02 mmol) and i-PrOH (3 µl, 0.06 mmol) was kept at 24° for 69 h and evaporated. ^{1}H-NMR of the crude product: mainly **9** and only traces of **5**.

*Isopropyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (α-D-**5**): R_f (AcOEt/hexane 1:1) 0.22. $[\alpha]_D^{25} = +88.0$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3450*w*, 2980, 2920*w*, 2870*w*, 1675*s*, 1500*m*, 1455*w*, 1365*m*, 1320*w*, 1150*s*, 1125*s*, 1100*s*, 1055*s*, 1000*s*, 915*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.17 (*m*, 15 arom. H); 5.27 (*d*, *J* = 9.4, NH); 4.89 (*d*, *J* = 3.6, H–C(1)); 4.85 (*d*, *J* = 11.6, PhC*H*); 4.80 (*d*, *J* = 10.7, PhC*H*); 4.66 (*d*, *J* = 11,6, PhC*H*); 4.65 (*d*, *J* = 12.2, PhC*H*); 4.53 (*d*, *J* = 10.6, PhC*H*); 4.52 (*d*, *J* = 12.2, PhC*H*); 4.25 (*dt*, *J* = 3.8, 9.8, H–C(2)); 3.88 (*sept.*, *J* = 6.1, H–C(2′)); 3.86 (*ddd*, *J* = 2.0, 3.7, 9.7, H–C(5)); 3.77 (*dd*, *J* = 4.0, 10.7, H–C(6)); 3.745 (*t*, *J* = 9.5, H–C(4)); 3.68 (*t*, *J* = 9.5 H–C(3)); 3.67 (*dd*, *J* = 1.8, 10.7, H–C(6)); 1.86 (*s*, AcN); 1.19 (*d*, *J* = 6.2, Me); 1.10 (*d*, *J* = 6.1, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.50 (*s*); 138.50 (*s*); 138.04 (*s*); 138.01 (*s*); 128.50–127.50 (several *d*); 95.89 (*d*, C(1)); 80.61 (*d*, C(3)); 78.42 (*d*, C(4)); 74.98 (*t*); 74.71 (*t*); 73.36 (*t*); 70.91 (*d*, C(5)); 69.72 (*d*, C(2′)); 68.59 (*t*, C(6)); 52.48 (*d*, C(2)); 23.33 (*q*, Me); 23.17 (*q*, Me); 21.44 (*q*, AcN). CI-MS: 551 (12, $[M + NH_4]^+$), 535 (33), 534 (100, $[M + 1]^+$), 475 (13), 474 (37), 444 (12). Anal. calc. for $C_{32}H_{39}NO_6$ (533.66): C 72.02, H 7.37, N 2.63; found: C 72.13, H 7.21, N 2.78.

*2-Amino-3,4,6-tri-*O*-benzyl-2-deoxy-1-*O*,2-*N*-(ethan-1-yl-1-ylidene)-α-*D*-glucopyranose* (**9**): R_f (AcOEt/hexane) 0.24. $[\alpha]_D^{25} = +38.1$ (*c* = 1.11, $CHCl_3$; [6]: $[\alpha]_D^{25} = 29.7$; [8]: $[\alpha]_D = 33.5$). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.26 (*m*, 13 arom. H); 7.21–7.16 (*m*, 2 arom. H); 6.02 (*d*, *J* = 7.4, H–C(1)); 4.70 (*d*, *J* = 12.0, PhC*H*); 4.60 (*d*, *J* = 12.0, PhC*H*); 4.55 (*d*, *J* = 11.7, PhC*H*); 4.55 (*d*, *J* = 12.4, PhC*H*); 4.50 (*d*, *J* = 12.2, PhC*H*); 4.30 (*d*, *J* = 11.6, PhC*H*); 4.22–4.20 (*m*, H–C(2)); 4.00 (*t*, *J* = 2.8, H–C(3)); 3.67 (*ddd*, *J* = 0.9, 2.8, 8.9, H–C(4)); 3.60 (*dd*, *J* = 2.2, 10.6, H–C(6)); 3.54 (*dd*, *J* = 4.7, 10.6, H–C(6)); 3.50 (*ddd*, *J* = 2.2, 4.7, 8.9, H–C(5)); 2.04 (*d*, *J* = 1.7, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 165.77 (*s*); 137.99 (*s*); 137.78 (*s*); 137.67 (*s*); 128.41–127.53 (several *d*); 100.40 (*d*, C(1)); 77.00 (*d*, C(4)); 74.98 (*d*, C(3)); 73.29 (*t*); 71.93 (*t*); 71.39 (*t*); 70.35 (*d*, C(5)); 69.49 (*t*, C(6)); 65.73 (*d*, C(2)); 14.04 (*q*, Me).

Reaction of **1** *with* $(CF_3)_2CHOH$. *a*) Photolysis: A soln. of **1** (125 mg, 0.25 mmol) in CH_2Cl_2 (10 ml) was treated with $(CF_3)_2CHOH$ (51 µl, 0.49 mmol), cooled to −84°, and irradiated for 165 min. Evaporation gave crude **6** (167 mg) in a ratio of 72:28 (^{1}H-NMR). Separation by prep. HPLC yielded α-D-**6** (66.6 mg, 42%) and β-D-**6** (26.6 mg, 17%).

b) Thermolysis: At 0° and under N_2, a suspension of **1** (46.1 mg, 0.09 mmol) in CH_2Cl_2 (1.0 ml) was treated with $(CF_3)_2CHOH$ (19 µl, 0.18 mmol), stirred for 30 min at 0° and for 24 h at r.t. Evaporation gave crude **6** (58.7 mg) in α-D/β-D ratio of 88:12 (^{1}H-NMR). FC (6 g of SiO_2, AcOEt/hexane 2:5) and prep. HPLC (AcOEt/hexane 5:9) yielded α-D-**6** (37.2, 63%) and β-D-**6** (5.3 mg, 9%).

*2,2,2-Trifluoro-1-(trifluoromethyl)ethyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (α-D-**6**): R_f (AcOEt/hexane 1:2) 0.25. $[\alpha]_D^{25} = +89.1$ (*c* = 1.14, $CHCl_3$). M.p. 135.5° (CH_2Cl_2/pentane). IR ($CHCl_3$): 3450*w*, 3000*w*, 2930*w*, 2870*w*, 1680*s*, 1605*w*, 1500*m*, 1455*m*, 1365*s*, 1290*s*, 1260*s*, 1195*s*, 1140*s*, 1105*s*, 1030*s*, 940*m*, 895*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.28 (*m*, 13 arom. H); 7.22–7.18 (*m*, 2 arom. H); 5.14 (*d*, *J* = 3.7, H–C(1)); 5.06 (*d*, *J* = 8.7, NH); 4.89 (*d*, *J* = 11.7, PhC*H*); 4.82 (*d*, *J* = 10.7, PhC*H*); 4.65 (*d*, *J* = 11.8, PhC*H*); 4.64 (*d*, *J* = 12.1, PhC*H*); 4.57 (*d*, *J* = 10.7, PhC*H*); 4.50 (*d*, *J* = 12.1, PhC*H*); 4.37 (*sept.*, *J*(H,F) = 5.9, H–C(1′)); 4.28 (*ddd*, *J* = 3.8, 8.7, 10.8, H–C(2)); 3.88–3.79 (*m*, H–C(4), H–C(5), H–C(6)); 3.69 (*dd*, *J* = 8.4, 10.8, H–C(3)); 3.63 (*dd*, *J* = 1.6, 11.0, H–C(6)); 1.80 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.98 (*s*); 138.02 (*s*); 137.68 (*s*); 137.59 (*s*); 128.49–127.67 (several *d*); 123.02 (*q*, *J*(C,F) = 288.0, CF_3); 122.54 (*q*, *J*(C,F) = 284.0, CF_3); 100.71 (*d*, C(1)); 78.47 (*d*, C(3)); 77.64 (*d*, C(4)); 75.21 (*t*); 74.80 (*t*); 73.38 (*t*); 72.93 (*dsept.*, *J*(C,F) ≈ 35, C(1′)); 72.48 (*d*, C(5)); 67.69 (*t*, C(6)); 52.29 (*d*, C(2)); 22.72 (*q*, AcN). CI-MS: 643 (12), 642 (37, $[M + 1]^+$), 475 (32), 474 (100). Anal. calc. for $C_{32}H_{33}F_6NO_6$ (641.61): C 59.91, H 5.18, N 2.18; found: C 59.88, H 5.32, N 2.26.

*2,2,2-Trifluoro-1-(trifluoromethyl)ethyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-glucopyranoside* (β-D-**6**): R_f (AcOEt/hexane 1:2) 0.36. $[\alpha]_D^{25} = +18.7$ (*c* = 0.76, $CHCl_3$). M.p. 193.5° (CH_2Cl_2/pentane). IR ($CHCl_3$): 3465*w*, 3000*w*, 2875*w*, 1680*s*, 1500*m*, 1455*m*, 1365*s*, 1290*s*, 1265*s*, 1190*s*, 1105*s*, 1080*s*, 1030*m*, 900*m*, 870*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.28 (*m*, 13 arom. H); 7.26–7.22 (*m*, 2 arom. H), 5.60 (*d*, *J* = 7.3, exchange with D_2O, NH); 5.21 (*d*, *J* = 7.9, H–C(1)); 4.84 (*d*, *J* = 11.6, PhC*H*); 4.80 (*d*, *J* = 11.1, PhC*H*); 4.66 (*d*, *J* = 11.4, PhC*H*); 4.63 (*d*, *J* = 10.9, PhC*H*); 4.61 (*d*, *J* = 12.4, PhC*H*); 4.55 (*d*, *J* = 12.4, PhC*H*); 4.47 (*sept.*, *J*(H,F) = 6.0, H–C(1′)); 4.33 (*dd*, *J* = 8.1, 9.8, H–C(3)); 3.76–3.59 (*m*, H–C(4), H–C(5), 2 H–C(6)); 3.26 (*td*, *J* = 7.7, 9.9, addn. of D_2O→*dd*, *J* = 7.9, 9.9, H–C(2)); 1.84 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.70 (*s*); 138.41 (*s*); 138.18 (*s*); 137.94 (*s*); 128.75–127.48 (several *d*); 121.49 (*q*, *J*(C,F) = 282.3, CF_3); 120.74 (*q*, *J*(C,F) = 281.6, CF_3); 100.19 (*d*, C(1)); 79.69 (*d*, C(3)); 78.37 (*d*, C(4)); 75.41 (*d*, C(5)); 74.85 (*t*); 74.71 (*t*); 73.45 (*t*); 73.45 (*dsept.*, *J*(C,F) = 33.0, C(1′)); 68.60 (*t*, C(6)); 57.68 (*d*, C(2)); 23.17 (*q*, AcN). CI-MS: 642 (2, $[M + 1]^+$), 475 (32), 474 (100). Anal. calc. for $C_{32}H_{33}F_6NO_6$ (641.61): C 59.91, H 5.18, N 2.18; found: C 60.00, H 5.21, N 2.21.

Reaction of **1** *with 4-Nitrophenol. a*) Photolysis: At −84°, a soln. of **1** (50 mg, 0.10 mmol) and 4-nitrophenol (22.2 mg, 0.16 mmol) in CH_2Cl_2 (4 ml) was irradiated for 9.5 h. The colour of the soln. turned progressively darker, slowing the reaction. Anal. HPLC of the crude indicated **7** in a α-D/β-D ratio of 37:63. Separation by cyclic prep. HPLC gave α-D-**7** (7.2 mg, 12%) and β-D-**7** (14.6 mg, 24%) after 3 cycles.

b) Thermolysis: At 0°, a suspension of **1** (99.5 mg, 0.2 mmol) and 3-Å molecular sieves (90 mg) in CH_2Cl_2 (2 ml) was treated with 4-nitrophenol (44.2 mg, 0.32 mmol) and stirred for 30 min at 0° and for 48 h at 26°. Filtration through *Celite* and evaporation gave crude **7** in a α-D/β-D ratio of 58:42 (HPLC). Separation by cyclic prep. HPLC (AcOEt/$CHCl_3$/hexane 5:1:7) gave α-D-**7** (58.1 mg, 48%) and β-D-**7** (47.5 mg, 39%) after two cycles.

*4-Nitrophenyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-*D*-glucopyranoside* (α-D-**7**): R_f (AcOEt/hexane 1:1) 0.27. M.p. 194–197° (AcOEt/hexane). $[\alpha]_D^{25} = +222.4$ ($c = 0.99$, $CHCl_3$). IR ($CHCl_3$): 3445*w*, 3000*w*, 2920*w*, 2860*w*, 1680*s*, 1615*m*, 1595*s*, 1515*s*, 1495*s*, 1455*m*, 1345*s*, 1220*m*, 1115*s*, 1030*s*, 950*m*, 870*m*, 850*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.18–8.15 (*m*, 2 arom. H); 7.42–7.09 (*m*, 17 arom. H); 5.70 (*d*, $J = 3.4$, H–C(1)); 5.15 (*d*, $J = 8.3$, NH); 4.93 (*d*, $J = 11.8$, PhC*H*); 4.84 (*d*, $J = 10.7$, PhC*H*); 4.70 (*d*, $J = 11.8$, PhC*H*); 4.60 (*d*, $J = 12.0$, PhC*H*); 4.58 (*d*, $J = 10.7$, PhC*H*); 4.46 (*d*, $J = 12.0$, PhC*H*); 4.37 (*ddd*, $J = 3.5$, 8.4, 10.6, H–C(2)); 3.91–3.87 (*m*, H–C(3), H–C(4)); 3.75 (*ddd*, $J = 2.0$, 3.8, 10.0, H–C(5)); 3.74 (*dd*, $J = 3.8$, 10.8, H–C(6)); 3.58 (*dd*, $J = 1.9$, 10.8, H–C(6)); 1.80 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.99 (*s*); 160.83 (*s*); 142.66 (*s*); 138.09 (*s*); 137.63 (*s*); 137.60 (*s*); 128.66–127.71 (several *d*); 125.75 (2*d*); 116.37 (2*d*); 96.20 (*d*, C(1)); 78.97 (*d*, C(3)); 77.91 (*d*, C(4)); 75.16 (*t*); 74.80 (*t*); 73.39 (*t*); 72.12 (*d*, C(5)); 67.97 (*t*, C(6)); 52.35 (*d*, C(2)); 23.20 (*q*, AcN). CI-MS: 630 (21, $[M + NH_4]^+$), 475 (32), 474 (100, $[M - C_6H_4NO_3]^+$), 384 (24), 174 (44), 157 (50). Anal. calc. for $C_{35}H_{36}N_2O_8$ (612.68): C 68.61, H 5.92, N 4.57; found: C 68.52, H 6.10, N 4.81.

*4-Nitrophenyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside* (β-D-**7**): R_f (AcOEt/hexane 1:1) 0.32. M.p. 212–213° (AcOEt). $[\alpha]_D^{25} = -136.6$ ($c = 0.87$, $CHCl_3$). IR ($CHCl_3$): 3465*w*, 3000*w*, 2920*w*, 2870*w*, 1680*s*, 1615*m*, 1595*s*, 1515*s*, 1495*s*, 1455*w*, 1345*s*, 1225*m*, 1115*s*, 1070*s*, 1030*m*, 990*m*, 915*w*, 865*m*, 850*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.15–8.11 (*m*, 2 arom. H); 7.38–7.22 (*m*, 15 arom. H); 7.07–7.04 (*m*, 2 arom. H); 5.84 (*d*, $J = 7.9$, NH); 5.58 (*dd*, $J = 1.9$, 6.5, H–C(1)); 4.81 (*d*, $J = 11.6$, PhC*H*); 4.77 (*d*, $J = 11.1$, PhC*H*); 4.71 (*d*, $J = 11.1$, PhC*H*); 4.64 (*d*, $J = 11.1$, PhC*H*); 4.50 (*d*, $J = 11.9$, PhC*H*); 4.43 (*d*, $J = 11.9$, PhC*H*); 4.13 (*dt*, $J = 2.2$, 7.8, H–C(3)); 3.91–3.85 (*m*, H–C(2), H–C(5)); 3.80 (*dd*, $J = 3.5$, 10.5, H–C(6)); 3.75 (*t*, $J = 7.5$, H–C(4)); 3.66 (*dd*, $J = 5.5$, 10.4, H–C(6)); 1.84 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.42 (*s*); 161.79 (*s*); 142.50 (*s*); 137.99 (*s*); 137.72 (*s*); 137.54 (*s*); 128.51–127.48 (several *d*); 125.66 (2*d*); 116.45 (2*d*); 97.16 (*d*, C(1)); 78.81 (*d*, C(3)); 77.36 (*d*, C(4)); 75.00 (*d*, C(5)); 74.26 (2*t*); 73.39 (*t*); 68.91 (*t*, C(6)); 54.67 (*d*, C(2)); 23.40 (*q*, AcN). CI-MS: 475 (32), 474 (100, $[M - C_6H_4NO_3]^+$). Anal. calc. for $C_{35}H_{36}N_2O_8$ (612.68): C 68.61, H 5.92, N 4.57; found: C 68.51, H 5.70, N 4.56.

Reaction of **1** *with* Ph_3COH. *a*) Photolysis: At 0°, a suspension of **1** (44.6 mg, 0.9 mmol) and 3-Å molecular sieves (90 mg) in CH_2Cl_2 (3.9 ml) was treated with Ph_3COH (46.3 mg, 0.18 mmol), stirred for 10 min at 0°, cooled to −84°, and irradiated for 6.75 h. Filtration through *Celite*, evaporation, and FC (5 g of SiO_2, AcOEt/hexane 4:7) gave α-D-**8** (25.7 mg, 39%) and a mixture of by-products (20 mg).

b) Thermolysis: At 0°, a suspension of **1** (49.5 mg, 0.1 mmol) and 3-Å molecular sieves (105 mg) in CH_2Cl_2 (1 ml) was treated with Ph_3COH (51.4 mg, 0.2 mmol) and stirred for 10 min at 0° and for 70 h at 26°. Filtration through *Celite*, evaporation, and FC (10 g of SiO_2, AcOEt/hexane 4:7→1:0) gave α-D-**8** (21 mg, 29%), **9** (13.7 mg, 32%), and a mixture of **9** and an unknown compound (13.6 mg).

*Triphenylmethyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-*D*-glucopyranoside* (α-D-**8**): R_f (AcOEt/hexane 4:7) 0.22. $[\alpha]_D^{21} = +115.4$ ($c = 0.52$, $CHCl_3$). IR ($CHCl_3$): 3435*w*, 3090*w*, 3070*w*, 3005*w*, 2920*w*, 2870*w*, 1675*s*, 1495*m*, 1365*m*, 1145*m*, 1105*s*, 1055*s*, 995*s*, 945*m*, 900*w*, 695*m*, 665*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42–7.19 (*m*, 30 arom. H); 5.32 (*d*, $J = 3.5$, H–C(1)); 4.91 (*d*, $J = 11.8$, PhC*H*); 4.90 (*d*, $J = 8.6$, NH); 4.81 (*d*, $J = 10.5$, PhC*H*); 4.70 (*d*, $J = 11.8$, PhC*H*); 4.56 (*d*, $J = 10.6$, PhC*H*); 4.46 (*d*, $J = 12.3$, PhC*H*); 4.31 (*d*, $J = 12.3$, PhC*H*); 4.11 (*ddd*, $J = 3.5$, 8.8, 10.8, H–C(2)); 3.98 (*dd*, $J = 8.8$, 10.7, H–C(3)); 3.80 (*t*, $J \approx 9.3$, H–C(4)); 3.61 (*td*, $J \approx 2.4$, 9.8, H–C(5)); 3.47 (*dd*, $J = 2.9$, 10.9, H–C(6)); 2.75 (*dd*, $J = 2.0$, 10.9, H–C(6)); 1.68 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.40 (*s*); 143.69 (3*s*); 138.39 (*s*); 138.17 (*s*); 138.06 (*s*); 129.23–127.34 (several *d*); 93.51 (*d*, C(1)); 87.95 (*s*, Ph_3C); 78.75 (*d*, C(3)); 78.60 (*d*, C(4)); 75.06 (*t*); 74.21 (*t*); 73.62 (*t*); 71.40 (*d*, C(5)); 67.64 (*t*, C(6)); 53.25 (*d*, C(2)); 23.28 (*q*, AcN). ESI-MS: 756 ($[M + Na]^+$). Anal. calc. for $C_{48}H_{47}NO_6$ (733.90): C 78.56, H 6.45, N 1.91; found: C 78.42, H 6.72, N 1.83.

*3-*O*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-*D*-glucopyranosyl)-1,2:5,6-di-*O*-isopropylidene-*α*-*D*-glucofuranose* (**11**). A soln. of **1** (50 mg, 0.1 mmol) and **10** (31.2 mg, 0.12 mmol) in CH_2Cl_2 (4 ml) was cooled to −84° and irradiated for 75 min. Evaporation and FC (8.5 g of SiO_2, AcOEt/hexane 2:3→1:1→2:1) gave **10** (20.2 mg, 65%) and a mixture containing **9** and **11** (30.2 mg). Prep. HPLC (AcOEt/hexane 1:1) yielded **11** (21.9 mg, 30%) and **9** (3.2 mg, 7%). **11**: R_f (AcOEt/hexane 1:1) 0.47. $[\alpha]_D^{25} = +39.9$ ($c = 1.40$, $CHCl_3$). IR ($CHCl_3$): 3480*w*, 2995*m*,

2940*m*, 1675*s*, 1515*m*, 1500*m*, 1455*m*, 1375*s*, 1300*m*, 1225*m*, 1135*s*, 1070*s*, 1050*s*, 1025*s*, 965*m*, 840*m*. ^{1}H-NMR (400 MHz, $CDCl_3$; assignment corroborated by COSY): 7.35–7.18 (*m*, 15 arom. H); 5.84 (*d*, *J* = 9.7, NH); 5.81 (*d*, *J* = 3.5, H–C(1)); 4.91 (*d*, *J* = 3.4, H–C(1′)); 4.90 (*d*, *J* = 3.5, H–C(2)); 4.84 (*d*, *J* = 11.6, PhC*H*); 4.83 (*d*, *J* = 10.7, PhC*H*); 4.64 (*d*, *J* = 11.5, PhC*H*); 4.58 (*d*, *J* = 12.2, PhC*H*); 4.515 (*d*, *J* ≈ 12.5, PhC*H*); 4.51 (*d*, *J* = 10.6, PhC*H*); 4.31 (*dt*, *J* = 3.9, 9.7, H–C(2′)); 4.11–4.04 (*m*, H–C(3), H–C(4), H–C(5), 2 H–C(6)); 3.88–3.85 (*m*, H–C(5′)); 3.70 (*dd*, *J* = 2.0, 10.4, H–C(6′)); 3.67–3.60 (*m*, H–C(3′), H–C(4′), H–C(6′)); 1.84 (*s*, AcN); 1.46 (*s*, Me); 1.40 (*s*, Me); 1.30 (*s*, Me); 1.16 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.79 (*s*); 138.14 (*s*); 137.78 (*s*); 137.63 (*s*); 128.46–127.69 (several *d*); 111.95 (*s*, Me_2C); 109.46 (*s*, Me_2C); 105.34 (*d*, C(1)); 100.04 (*d*, C(1′)); 83.67 (*d*, C(3)); 82.42 (*d*, C(2)); 80.73 (*d*, C(4)); 79.87 (*d*, C(3′)); 78.39 (*d*, C(4′)); 75.22 (*t*); 74.73 (*t*); 73.46 (*t*); 72.91 (*d*, C(5)); 72.04 (*d*, C(5′)); 68.87 (*t*, C(6′)); 67.62 (*t*, C(6)); 52.51 (*d*, C(2′)); 27.28 (*q*, Me); 26.72 (*q*, Me); 25.90 (*q*, Me); 25.85 (*q*, Me); 23.29 (*q*, AcN). ESI-MS: 734 (100, $[M + 1]^+$), 733 (50, M^+). Anal. calc. for $C_{41}H_{51}NO_{11}$ (733.85): C 67.10, H 7.00, N 1.91; found: C 67.18, H 7.10, N 1.96.

Reaction of **3** *with i-PrOH. a*) Photolysis: Under Ar, a soln. of **3** (50 mg, 0.12 mmol) and i-PrOH (18 µl, 0.24 mmol) in CH_2Cl_2 (1 ml) was cooled to −84°, irradiated for 90 min, warmed to 40°, and evaporated. FC (4.5 g of SiO_2, Et_2O) gave **12** (39 mg, 72%) and **16** [9] (3.3 mg, 7%). Prep. HPLC (Et_2O) yielded α-D-**12** (27.2 mg, 50%) and β-D-**12** (7.7 mg, 14%).

b) Thermolysis: The reaction of **3** (50 mg, 0.12 mmol) and i-PrOH (19 µl, 0.25 mmol) in CH_2Cl_2 (1 ml) at 41° yielded α-D-**12** (6.2 mg, 12%) and **15** (not isolated).

*Isopropyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*α*-*D*-allopyranoside* (α-D-**12**). R_f (Et_2O/MeOH 98:2) 0.38. $[\alpha]_D^{25} = -2.4$ (*c* = 1.21, $CHCl_3$). IR ($CHCl_3$): 3440*m*, 2970*m*, 2930*m*, 2860*m*, 1660*s*, 1490*m*, 1450*w*, 1370*m*, 1310*w*, 1120*s*, 1100*s*, 1060*s*, 1020*s*, 960*w*, 910*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.50–7.29 (*m*, 10 arom. H); 6.02 (*d*, *J* = 9.3, NH); 5.54 (*s*, PhC*H*); 5.05 (*d*, *J* = 12.4, PhC*H*); 4.83 (*d*, *J* = 4.5, H–C(1)); 4.52 (*d*, *J* = 12.4, PhC*H*); 4.43 (*dt*, *J* = 5.3, 10.0, H–C(5)); 4.43 (*dd*, *J* = 5.3, 10.3, H_{eq}–C(6)); 4.26 (*td*, *J* ≈ 4.1, 9.6, H–C(2)); 4.05 (*t*, *J* ≈ 3.0, H–C(3)); 3.86 (*sept.*, *J* = 6.2, H–C(2′)); 3.73 (*t*, *J* = 10.4, H_{ax}–C(6)); 3.72 (*dd*, *J* = 2.2, 10.0, H–C(4)); 1.86 (*s*, AcN); 1.29 (*d*, *J* = 6.2, Me); 1.14 (*d*, *J* = 6.1, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.30 (*s*); 139.00 (*s*); 137.54 (*s*); 129.03 (*d*); 128.23 (4*d*); 127.23 (*d*); 127.11 (2*d*); 126.15 (2*d*); 101.98 (*d*, PhC*H*); 95.49 (*d*, C(1)); 79.97 (*d*, C(4)); 74.72 (*d*, C(3)); 74.18 (*t*); 70.40 (*d*, C(2′)); 69.30 (*t*, C(6)); 57.77 (*d*, C(5)); 49.05 (*d*, C(2)); 23.46 (*q*, Me); 23.05 (*q*, Me); 21.55 (*q*, AcN). CI-MS: 443 (26), 442 (100, $[M + 1]^+$), 383 (17), 382 (72), 274 (13). Anal. calc. for $C_{25}H_{31}NO_6$ (441.53): C 68.01, H 7.08, N 3.17; found: C 67.88, H 7.08, N 3.26.

*Isopropyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-allopyranoside* (β-D-**12**). R_f (Et_2O/MeOH 98:2) 0.30. IR ($CHCl_3$): 3440*m*, 2980*m*, 2930*w*, 2870*m*, 1670*s*, 1495*m*, 1450*w*, 1370*m*, 1315*w*, 1120*s*, 1085*s*, 1000*s*, 935*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52–7.32 (*m*, 10 arom. H); 5.62 (*d*, 9.2, NH); 5.54 (*s*, PhC*H*); 5.02 (*d*, *J* = 11.6, PhC*H*); 4.64 (*d*, *J* = 8.3, H–C(1)); 4.55 (*d*, *J* = 11.6, PhC*H*); 4.37 (*dd*, *J* = 5.1, 10.4, H_{eq}–C(6)); 4.14–4.04 (*m*, H–C(2), H–C(3), H–C(5)); 3.88 (*sept.*, *J* = 6.1, H–C(1′)); 3.80 (*t*, *J* = 10.5 H_{ax}–C(6)); 3.75 (*dd*, *J* = 2.0, 9.4, H–C(4)); 1.85 (*s*, AcN); 1.23 (*d*, *J* = 6.1, Me); 1.11 (*d*, *J* = 6.1, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.09 (*s*); 138.28 (*s*); 137.47 (*s*); 129.05–128.03 (several *d*); 126.10 (2*d*); 102.00 (*d*, PhC*H*); 99.28 (*d*, C(1)); 80.18 (*d*, C(4)); 75.88 (*d*, C(3)); 74.70 (*t*); 72.23 (*d*, C(2′)); 69.29 (*t*, C(6)); 63.69 (*d*, C(5)); 52.16 (*d*, C(2)); 23.41 (*q*, Me); 23.18 (*q*, Me); 22.03 (*q*, AcN). CI-MS: 443 (20), 442 (75, $[M + 1]^+$), 382 (24), 382 (100).

Reaction of **3** *with* $(CF_3)_2CHOH$. *a*) Photolysis in CH_2Cl_2: Under Ar, a soln. of **3** (50 mg, 0.12 mmol) and $(CF_3)_2CHOH$ (25 µl, 0.24 mmol) in CH_2Cl_2 (1 ml) was cooled to −84° and irradiated for 90 min. Evaporation and FC (SiO_2, AcOEt/hexane 4:7) gave α-D-**13** (28.3 mg, 42%) and β-D-**13** (31 mg, 46%).

b) Photolysis in THF: Similarly, photolysis (90 min at −84°) of **3** (50 mg, 0.12 mmol) and $(CF_3)_2CHOH$ (25 µl, 0.24 mmol) in THF (1 ml) gave α-D-**13** (5.4 mg, 8%), β-D-**13** (2.6 mg, 4%), and **17** (29.2 mg, 39%).

c) Thermolysis in CH_2Cl_2: Thermolysis (27 h at 41°) of **3** (50 mg, 0.12 mmol) and $(CF_3)_2CHOH$ (25 µl, 0.24 mmol) in CH_2Cl_2 (1 ml) gave α-D-**13** (32.4 mg, 48%) and β-D-**13** (9.8 mg, 15%).

d) Thermolysis in MeCN: Similarly, thermolysis (5.25 h at 50°) of **3** (50 mg, 0.12 mmol), $(CF_3)_2CHOH$ (25 µl, 0.24 mmol), and 4-Å molecular sieves (10 mg) in MeCN (1 ml) gave α-D-**13** (29.8 mg, 44%), β-D-**13** (16.3 mg, 24%), and **18** (13.3 mg, 18%).

*2,2,2-Trifluoro-1-(trifluoromethyl)ethyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside* (α-D-**13**): R_f (AcOEt/hexane 1:1) 0.25. M.p. 85–87° ($CHCl_3$/hexane). $[\alpha]_D^{25} = +13.8$ (*c* = 0.98, $CHCl_3$). IR ($CHCl_3$): 3440*m*, 2990*w*, 2950*w*, 2860*w*, 1665*s*, 1490*m*, 1365*s*, 1285*s*, 1100*s*, 1070*s*, 1020*s*, 950*m*, 890*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52–7.42 (*m*, 2 arom. H); 7.42–7.29 (*m*, 8 arom. H); 6.03 (*d*, *J* = 9.3, NH); 5.55 (*s*, PhC*H*); 5.15 (*d*, *J* = 12.4, PhC*H*); 5.03 (*d*, *J* = 4.5, H–C(1)); 4.53 (*d*, *J* = 12.4, PhC*H*); 4.48 (*dt*, *J* ≈ 5.3, 10.1, H–C(5)); 4.42–4.35 (*m*, H–C(2)); 4.37 (*sept.*, *J*(H,F) = 5.9, H–C(1′)); 4.32 (*dd*, *J* = 5.3, 10.4, H_{eq}–C(6)); 4.06 (*t*, *J* ≈ 2.8, H–C(3)); 3.78 (*dd*, *J* = 2.3, 9.5, H–C(4)); 3.75 (*t*, *J* = 10.5, H_{ax}–C(6)); 1.86 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.54 (*s*); 138.57 (*s*); 137.07 (*s*); 129.07 (*d*); 128.29 (2*d*); 128.20 (2*d*); 127.34 (*d*); 126.79 (2*d*); 126.06 (2*d*);

121.24 (*q*, J(C,F) = 287.2, CF_3); 120.89 (*q*, J(C,F) = 285.8, CF_3); 101.96 (*s*, PhCH); 99.47 (*d*, C(1)); 79.18 (*d*, C(4)); 74.11 (*d*, C(3)); 74.11 (*t*); 73.52 (*dsept.*, J(C,F) = 33, C(1')); 68.47 (*t*, C(6)); 58.96 (*d*, C(5)); 48.66 (*d*, C(2)); 22.49 (*q*, AcN). CI-MS: 551 (28), 550 (11, $[M+1]^+$), 382 (22), 208 (16). Anal. calc. for $C_{25}H_{25}F_6NO_6$ (549.48): C 54.65, H 4.59, N 2.55; found: C 54.67, H 4.53, N 2.48.

*2,2,2-Trifluoro-1-(trifluoromethyl)ethyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranoside* (β-D-**13**): R_f (AcOEt/hexane 1:1) 0.42. M.p. 184–185° ($CHCl_3$/hexane). $[\alpha]_D^{25} = +105.8$ ($c = 0.98$, $CHCl_3$). IR ($CHCl_3$): 3440*w*, 2990*w*, 2870*w*, 1680*s*, 1490*m*, 1360*m*, 1290*s*, 1100*s*, 1080*s*, 1035*s*, 1025*s*, 960*m*, 900*m*, 865*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52–7.42 (*m*, 2 arom. H); 7.42–7.34 (*m*, 8 arom. H); 5.63 (*d*, $J = 9.7$, NH); 5.55 (*s*, PhCH); 5.01 (*d*, $J = 11.7$, PhCH); 4.80 (*d*, $J = 8.5$, H–C(1)); 4.56 (*d*, $J = 11.7$, PhCH); 4.48–4.37 (*m*, H–C(5), H_{eq}–C(6)); 4.27 (*ddd*, $J = 3.2$, 8.5, 9.5, H–C(2)); 4.12 (*sept.*, J(H,F) = 5.1, H–C(1')); 4.11 (*t*, $J \approx 2.5$, H–C(3)); 3.82 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.79 (*dd*, $J = 2.1$, 9.5, H–C(4)); 1.84 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.26 (*s*); 137.76 (*s*); 137.06 (*s*); 129.15 (*d*); 128.62 (2*d*); 128.36 (2*d*); 128.28 (2*d*); 128.18 (*d*); 126.02 (2*d*); 121.42 (*q*, J(C,F) = 287, CF_3); 120.40 (*q*, J(C,F) = 285, CF_3); 101.70, 101.51 (2*d*, PhCH, C(1)); 79.53 (*d*, C(4)); 75.28 (*d*, C(3)); 74.66 (*t*); 73.40 (*dsept.*, J(C,F) = 33, C(1')); 68.64 (*t*, C(6)); 64.09 (*d*, C(5)); 51.47 (*d*, C(2)); 22.77 (*q*, AcN). CI-MS: 551 (28), 550 (100, $[M+1]^+$), 382 (16). Anal. calc. for $C_{25}H_{25}F_6NO_6$ (549.48): C 54.65, H 4.59, N 2.55; found: C 54.56, H 4.70, N 2.48.

*4-[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]butyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranoside* (**17**): R_f (AcOEt/hexane 6:4) 0.42. IR ($CHCl_3$): 3440*w*, 3000*w*, 2930*w*, 2870*w*, 1675*s*, 1500*m*, 1455*w*, 1370*s*, 1290*s*, 1100*s*, 1045*s*, 1025*s*, 1010*s*, 910*m*, 900*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52–7.37 (*m*, 10 arom. H); 5.69 (*d*, $J = 9.2$, NH); 5.564 (*s*, PhCH); 5.03 (*d*, $J = 11.6$, PhCH); 4.58 (*d*, $J = 8.4$, H–C(1)); 4.54 (*d*, $J = 11.7$, PhCH); 4.39 (*dd*, $J = 5.1$, 10.4, H_{eq}–C(6)); 4.16–4.03 (*m*, 4 H); 3.92–3.85 (*m*, 3 H); 3.79 (*t*, $J = 10.4$, H_{ax}–C(6)); 3.74 (*dd*, $J = 2.1$, 9.4, H–C(4)); 3.45 (*td*, $J = 5.9$, 9.7, 1 H); 1.82 (*s*, AcN); 1.73–1.66 (*m*, 4 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.20 (*s*); 138.16 (*s*); 137.40 (*s*); 129.01 (*d*); 128.63 (2*d*); 128.39 (2*d*); 128.30 (2*d*); 128.11 (*d*); 126.11 (2*d*); 102.05 (*d*, PhCH); 100.46 (*d*, C(1)); 80.21 (*d*, C(4)); 75.88 (*d*, C(3)); 75.23 (*t*); 74.70 (*t*); 69.19 (*t*); 68.90 (*t*, C(6)); 63.75 (*d*, C(5)); 51.76 (*d*, C(2)); 26.17 (*t*); 25.66 (*t*); 23.07 (*q*, AcN); signals of $(CF_3)_2CH$ hidden by the noise. CI-MS: 623 (30), 622 (100, $[M+1]^+$), 447 (10), 383 (13), 382 (59).

2,2,2-Trifluoro-1-(trifluoromethyl)ethyl N-*(2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-*D*-allopyranosyl)*-O-*ethanimidate* (**18**): R_f (AcOEt/hexane 1:1) 0.16. IR ($CHCl_3$): 3430*w*, 2940*w*, 2860*w*, 1700*m*, 1665*s*, 1490*m*, 1375*m*, 1340*m*, 1280*m*, 1110*s*, 905*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.55–7.44 (*m*, 2 arom. H); 7.42–7.30 (*m*, 8 arom. H); 6.33 (*sept.*, J(H,F) = 6.5, H–C(1'')); 5.62 (*d*, $J \approx 8.8$, NH); 5.60 (*s*, PhCH); 5.14 (*d*, $J = 5.0$, H–C(1)); 4.98 (*d*, $J = 11.6$, PhCH); 4.50 (*d*, $J = 11.6$, PhCH); 4.40 (*dt*, $J \approx 5.2$, 9.8, H–C(5)); 4.32 (*dd*, $J = 5.5$, 10.3 H_{eq}–C(6)); 4.28 (*ddd*, $J = 3.9$, 5.0, 8.8, H–C(2)); 4.07 (*t*, $J \approx 3.1$, H–C(3)); 3.78 (*dd*, $J = 2.5$, 9.3, H–C(4)); 3.73 (*t*, $J = 10.5$, H_{ax}–C(6)); 1.99 (*s*, Me); 1.73 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.33 (*s*); 160.76 (*s*, C(1')); 139.06 (*s*); 137.38 (*s*); 129.15 (*d*); 128.75 (2*d*); 128.51 (2*d*); 128.36 (2*d*); 128.20 (*d*); 126.11 (2*d*); 121.01 (*q*, J(C,F) = 282.2, CF_3); 120.77 (*q*, J(C,F) = 278.8, CF_3); 102.03 (*d*, PhCH); 81.80 (*d*, C(1)); 80.05 (*d*, C(4)); 75.19 (*t*); 74.03 (*d*, C(3)); 69.39 (*t*, C(6)); 66.22 (*sept.*, J(C,F) = 34.2, C(1'')); 58.95 (*d*, C(5)); 49.26 (*d*, C(2)); 22.72 (*q*, AcN); 14.48 (*q*, Me). CI-MS: 592 (308), 591 (100, $[M+1]^+$), 154 (34).

Reaction of **3** *with 4-Nitrophenol.* Thermolysis: A soln. of **3** (50 mg, 0.12 mmol) and 4-nitrophenol (26.8 mg, 0.19 mmol) in CH_2Cl_2 (1 ml) was kept at reflux for 21 h. Dilution with AcOEt (30 ml), washing with 10% aq. Na_2CO_3 soln. (2 × 10 ml), H_2O (1 × 10 ml), and brine (1 × 10 ml), and normal workup yielded crude **14** (62.1 mg). Prep. HPLC (Et_2O/hexane/CH_2Cl_2 1:1:2) gave α-D-**14** (25 mg, 39%) and β-D-**14** (24.4 mg, 38%).

*4-Nitrophenyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-*D*-allopyranoside* (α-D-**14**): R_f (AcOEt/hexane 6:4) 0.36. M.p. 185–186° (AcOEt/hexane). $[\alpha]_D^{25} = +50.7$ ($c = 1.19$, $CHCl_3$). IR ($CHCl_3$): 3440*m*, 2990*w*, 2940*w*, 2860*w*, 1665*s*, 1590*s*, 1485*s*, 1370*m*, 1340*s*, 1110*s*, 1065*s*, 1015*s*, 995*s*, 955*s*, 860*m*, 845*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.25–8.21 (*m*, 2 arom. H); 7.47–7.36 (*m*, 10 arom. H); 7.14–7.11 (*m*, 2 arom. H); 6.07 (*d*, $J = 9.3$, NH); 5.59 (*d*, $J = 4.3$, H–C(1)); 5.57 (*s*, PhCH); 5.14 (*d*, $J = 12.1$, PhCH); 4.57 (*d*, $J = 12.1$, PhCH); 4.50 (*td*, $J \approx 4.0$, 9.4, H–C(2)); 4.39 (*dt*, $J \approx 5.1$, 10.0, H–C(5)); 4.24 (*dd*, $J = 5.3$, 10.4, H_{eq}–C(6)); 4.16 (*t*, $J \approx 2.5$, H–C(3)); 3.83 (*dd*, $J = 2.4$, 9.6, H–C(4)); 3.75 (*t*, $J = 10.4$, H_{ax}–C(6)); 1.85 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.55 (*s*); 161.46 (*s*); 142.64 (*s*); 138.62 (*s*); 137.17 (*s*); 129.22 (*d*); 128.61 (2*d*); 128.33 (2*d*); 127.87 (*d*); 127.68 (2*d*); 126.15 (2*d*); 125.77 (2*d*); 116.45 (2*d*); 102.20 (*d*, PhCH); 95.12 (*d*, C(1)); 79.44 (*d*, C(4)); 74.63 (*t*); 74.28 (*d*, C(3)); 68.83 (*t*, C(6)); 59.14 (*d*, C(5)); 48.74 (*d*, C(2)); 23.01 (*q*, AcN). CI-MS: 521 (10, $[M+1]^+$), 491 (15), 383 (27), 382 (100), 292 (11), 274 (48). Anal. calc. for $C_{28}H_{28}N_2O_8$ (520.54): C 64.61, H 5.42, N 5.38; found: C 64.71, H 5.24, N 5.42.

*4-Nitrophenyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranoside* (β-D-**14**): R_f (AcOEt/hexane 6:4) 0.49. M.p. 231° (dec., AcOEt). $[\alpha]_D^{25} = -47.8$ ($c = 1.19$, $CHCl_3$). IR ($CHCl_3$): 3440*m*, 2990*w*, 2870*w*, 1730*w*, 1675*s*, 1590*s*, 1490*s*, 1370*m*, 1340*s*, 1080*s*, 1035*s*, 1005*s*, 865*m*, 845*m*. ^{1}H-NMR (300 MHz, $CDCl_3$):

8.21–8.16 (*m*, 2 arom. H); 7.54–7.50 (*m*, 2 arom. H); 7.43–7.35 (*m*, 8 arom. H); 7.07–7.03 (2 arom. H); 5.75 (*d*, $J = 9.6$, NH); 5.59 (*s*, PhC*H*); 5.29 (*d*, $J = 8.5$, H–C(1)); 5.07 (*d*, $J = 11.6$,, PhC*H*); 4.58 (*d*, $J = 11.6$, PhC*H*); 4.49 (*dt*, $J = 3.2$, 9.6, H–C(2)); 4.45 (*dd*, $J = 5.3$, 10.5, H_{eq}–C(6)); 4.30 (*dt*, $J \approx 5.1$, 9.8, H–C(5)); 4.18 (*t*, $J \approx 2.4$, H–C(3)); 3.86 (*dd*, $J = 2.4$, 9.8, H–C(4)); 3.84 (*t*, $J = 10.2$, H_{ax}–C(6)); 1.83 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.36 (*s*); 161.75 (*s*); 142.59 (*s*); 137.69 (*s*); 137.01 (*s*); 129.14 (*d*); 128.64 (2*d*); 128.41 (2*d*); 128.26 (2*d*); 128.21 (*d*); 126.00 (2*d*); 125.53 (2*d*); 116.28 (2*d*); 102.08 (*d*, PhCH); 98.11 (*d*, C(1)); 79.60 (*d*, C(4)); 75.53 (*d*, C(3)); 74.78 (*t*); 68.78 (*t*, C(6)); 64.07 (*d*, C(5)); 51.42 (*d*, C(2)); 23.05 (*q*, AcN). CI-MS: 521 (17, $[M + 1]^+$), 383 (16), 382 (100), 274 (21). Anal. calc. for $C_{28}H_{28}N_2O_8$ (520.54): C 64.61, H 5.42, N 5.38; found: C 64.35, H 5.23, N 5.16.

Reaction of **15** *with* $(CF_3)_2CHOH$. *a*) Under Ar, a soln. of **15** (93 mg, 0.24 mmol) and $(CF_3)_2CHOH$ (40 µl, 0.38 mmol) in $(CH_2Cl)_2$ (2 ml) was kept at reflux for 17 h. Evaporation left a brownish residue (94 mg). Crystallization from AcOEt gave **16** (75.2 mg, 81%).

b) As *a*), but with 400 µl (3.8 mmol) of $(CF_3)_2CHOH$. Evaporation and FC (SiO_2, $Et_2O \rightarrow Et_2O$/MeOH 98:2 $\rightarrow Et_2O$/MeOH 97:3) gave β-D-**13** (82.4 mg, 61%) and **16** (23.5 mg, 25%).

Reaction of **15** *with 4-Nitrophenol.* Under Ar, a soln. of **15** (93 mg, 0.24 mmol) and 4-nitrophenol (543 mg, 3.9 mmol) in $(CH_2Cl)_2$ (2 ml) was kept at reflux for 17 h, diluted with $(CH_2Cl)_2$ (6 ml), washed with $NaHCO_3$ soln. (4 × 2 ml) and H_2O (2 ml), dried ($MgSO_4$), and evaporated. Crystallization from AcOEt gave β-D-**15** (104.4 mg, 81%).

δ/T ^{1}*H-NMR Experiments of* **1**, α-D-**6**, β-D-**6**, **3**, *and* α-D-**13**. ^{1}H-NMR Spectra of *ca* 0.03M **1** (10.5 mg), **6** (13.3 mg), **3** (8.5 mg), or α-D-**13** (11.5 mg) in CD_2Cl_2 (0.7 ml) were measured at 4 temp. in the range of 180–300 K.

δ/c ^{1}*H-NMR Experiments of* α-D-**6**, β-D-**6**, *and* β-D-**13**. ^{1}H-NMR Spectra of *ca* 0.005, 0.02, and 0.06M α-D-**6**, β-D-**6**, and β-D-**13** in CD_2Cl_2 (0.7 ml) were measured 293 K.

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