132. Glycosylidene Carbenes

Part 4

Synthesis of Spirocyclopropanes from Acetamidoglycosylidene-Derived Diazirines

by **Andrea Vasella***, **Christian Witzig**, and **René Husi**

Organisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH–8057 Zürich

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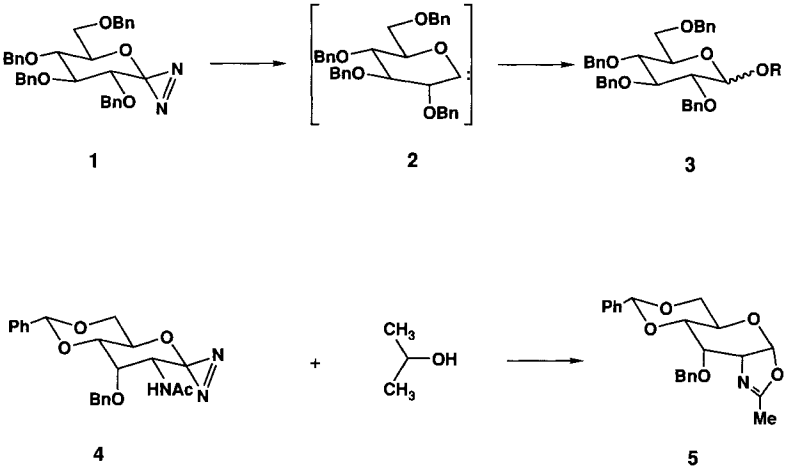
The synthesis of the first glycosylidene-derived 2-acetamido-2-deoxydiazirine **4** from *N*-acetylglucosamine **6** is described. Thus, **6** was transformed into the 3-*O*-mesylglucopyranoside **9** by glycosidation with allyl alcohol, benzylidenation, and mesylation (*Scheme 2*). Solvolysis of **9** gave the allopyranoside **10** which, upon benzylation and glycoside cleavage, yielded the hemiacetals **12**. Using our established method (*via* the lactone oxime **14** and the diaziridines **16**), **12** gave the diazirine **4**. Thermolysis of this diazirine in the presence of i-PrOH gave the dihydro-1,3-oxazole **5** (*Scheme 1*); in the presence of acrylonitrile, the four diastereoisomeric spirocyclopropanes **17–20** and the acetamidoallal **21** were obtained and separated by prep. HPLC (*Scheme 3*). Assignment of the configuration of **17–20** is based on NOE measurements and on the effect of diamagnetic anisotropy of the CN group. The ratio of the four cyclopropanes, which is in keeping with earlier results, is rationalized.

Introduction. – The glycosylidene-derived diazirine **1** [1a] is a precursor of the glycosylidene carbene **2**, which formally inserts into the O–H bond of phenols [1b][2] and alcohols [1a] to give glycosides **3** (*Scheme 1*). The available evidence shows that the formal insertion into *acidic* O–H bonds is initiated by a proton transfer to the intermediate carbene **2**, leading to a tight ion pair, whilst the insertion into the O–H bond of less acidic alcohols, such as i-PrOH, occurs either by a concerted process or *via* an ylide. Preliminary experiments have shown that the 2-acetamido-2-deoxyallose-derived diazirine **4**, prepared in the context of the synthesis of allosamidin [3], reacts with i-PrOH to form the dihydro-1,3-oxazole **5** as the main product (*Scheme 1*). Such dihydrooxazoles are typically formed by the neighboring group participation of the acetamido group during S_N1 type substitutions at the anomeric center. As the glycosidation of i-PrOH by **1** appears not to proceed by an initial protonation of **2**, one has to consider a direct or indirect participation of the acetamido group of **4** in the protonation of the corresponding carbene. The diazirine **1** also reacts thermally or under photolytic conditions with acceptor-substituted alkenes to yield cyclopropanes [4][1]). To investigate, if the presence of an acetamido group is compatible with the formation of cyclopropanes, we have examined the reaction of **4** with acrylonitrile. In the following, we report the synthesis of the aziallose **4**, the experimental details of its reaction with i-PrOH, and the results of its cyclopropane formation using acrylonitrile under thermal conditions.

[1]) Acetyl-protected, glucopyranosylidene-derived 1,1-diazides also react with acrylonitrile under photolytic conditions to form cyclopropanes [5].

Scheme 1



Results and Discussion. – *Preparation of the Aziallose* **4**. The synthesis of **4** follows the established method for the synthesis of 1-azisugars [1a] (see *Scheme 2*). The allyl allopyranosides **10** are available from *N*-acetylglucosamine in four steps (**6** → **7** [6] → **8** [7] → **9** [8] → **10** [9]; 33% overall yield of the α-D-**10**) by following the strategy which was worked out by *Jeanloz* [9] for the synthesis of the corresponding methyl glycoside. Benzylation (BnBr, BaO, $Ba(OH)_2 \cdot 8H_2O$, DMF) converted **10** in high yields into **11**. The usual two-step procedure for the removal of the allyl group ($KOBu^t$; $HgCl_2$, HgO) gave the crystalline hemiacetals **12** (89%). The oximes **13** were obtained in high yields ((*E*)/(*Z*) 4:1). Oxidation of **13** with periodate gave the hydroximolactone **14**, again in high yields. It was directly transformed into the triflate **15**. Treatment of **15** with a soln. of H_3N in MeOH yielded the diaziridines **16**[2]) (64%) which, upon oxidation with I_2 in CH_2Cl_2 in the presence of Et_3N, gave the crystalline diazirine **4** (87%). This product was stored at –20° for several weeks without significant decomposition. The triflate **15** is a more suitable starting material than the corresponding mesylate, which gave **16** in only 20% yield. The structures of **4** and **11**–**16** were confirmed by their spectroscopic data (see *Tables 1* and *2* and *Exper. Part*).

The ratio of β-D- to α-D-anomers of **12** was 2:1 after 10 min of equilibration in $CDCl_3$. The large J(OH, H–C(1)) value of 11.5 Hz for the α-D-anomer evidences a H-bond between the BnO–C(3) and the OH group. The (*E*)/(*Z*) configuration of **13** was mainly deduced from the chemical shift of the C(2) signals, found at 49.58 ppm for the major, and at 44.81 ppm for the minor isomer (γ effect), and from the chemical shift of H–C(1), resonating between 7.44 and 7.25 ppm (major isomer) and at 6.72 ppm (minor isomer). No NMR signals of the tautomeric hydroxylamines were observed. The hydroximolactone **14** is presumably (*Z*)-configurated (*cf.* [10]). The diaziridines **16** appeared as a single spot on TLC. The presence of two diastereoisomers in a ratio of 1 : 5 is evidenced by the appearence of two sets of signals for H–C(2), H–C(3), and AcN in the ^{1}H-NMR spectrum. The NH band of the diaziridines **16** is found at 3280 cm^{-1}. The hydrazi groups resonate at 2.15 and 2.08 ppm (broad signals, J = 9.3

[2]) *trans* Configuration of the hydrazi group appears probable (see below). For similar observations and for a discussion, *cf.* [1a] and ref. cit. therein.

Hz), and C(1) appears at 90.67 ppm (see *Table 2*). The UV spectrum of **4** shows a maximum at 345 nm with a small extinction coefficient of 105, as expected for the n-π^* transition of diazirines [11]. The N=N stretching vibration appears at 1560 cm^{-1}. C(1) resonates at 56.46 ppm [1a]. The small variation of the coupling constants $J(2,3)$, $J(3,4)$, and $J(4,5)$ (see *Table 1*) for **11**, and for **14–16** reflects the small influence of the hybridization of the anomeric center on the ring conformation.

Scheme 2

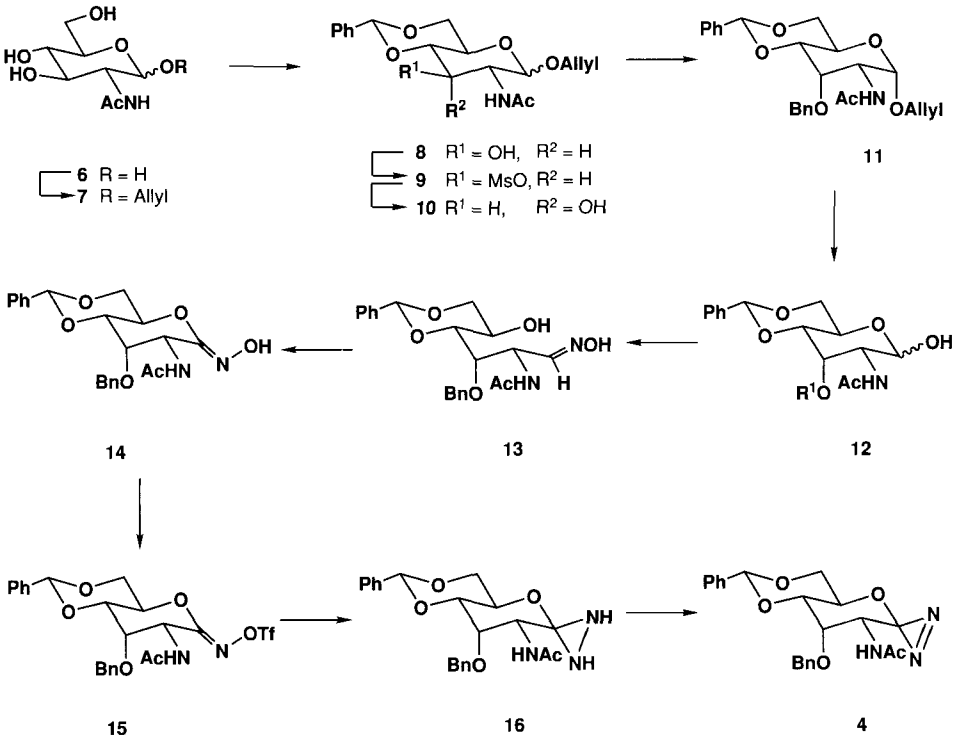


Table 1. *Selected* ^{1}*H-NMR* (300 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *and Vicinal Coupling Constants* [Hz] *of Compounds* **4**, **11–16**, *and* **21**

	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H_{ax}–C(6)	H_{eq}–C(6)	AcNH	$J(2,3)$	$J(3,4)$	$J(4,5)$
4	–	4.85	4.16	3.92	4.46	3.69	4.26	5.21, 1.62	3.3	2.0	9.5
11	4.78	4.33	4.06	3.73	4.33	3.74	4.40	6.04, 1.85	3.1	2.1	9.0
12	4.85	3.90	4.05	3.74	4.11	3.81	4.43	5.89, 1.84	3.0	2.3	9.5
13[a])	7.35	4.86	3.88	3.84	3.76	3.50	4.08	8.13, 1.83	5.9	1.9	9.5
14	–	4.89	4.32	4.00	4.56	3.92	4.56	6.23, 1.89	3.2	1.4	9.8
15	–	5.12	4.26	4.04	4.69	3.93	4.61	5.90, 1.91	3.2	1.6	10.1
16	–	4.70	4.22	3.91	4.36	3.81	4.36	5.91, 1.79	3.2	2.6	9.4
21	6.91	–	4.17	4.08	4.18	3.85	4.50	5.96, 1.82	–	3.5	10.6

[a]) In (D_6) DMSO.

Table 2. *Selected* ^{13}*C-NMR* (50 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of Compounds* **4** *and* **11–21**

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	AcNH	CH_2–C(2)
4	56.46	46.10	74.62	79.68	64.50	68.15	–	–	168.86, 22.30	–
11	95.97	48.78	74.03	79.55	57.70	68.31	–	–	169.90, 22.81	–
12[a])	93.75	54.57	75.44	79.50	63.73	68.63	–	–	169.16, 22.76	–
13[a])	148.46	49.58	80.09	81.13	61.50	71.29	–	–	169.01, 22.98	–
14	149.35	48.94	74.96	77.92	66.91	68.01	–	–	169.42, 22.63	–
15	161.29	48.94	74.24	77.72	69.13	67.70	–	–	169.70, 22.40	–
16	90.67	47.61	74.70	75.63	64.55	68.68	–	–	170.39, 22.92	–
17	118.48	6.02	61.78	47.22	74.26	79.87	65.31	68.54	169.85, 22.68	14.68
18	117.85	5.71	61.33	47.27	74.90	80.19	66.05	68.73	169.87, 22.82	16.37
19	119.69	7.56	62.84	47.92	73.45	79.85	65.88	68.31	169.58, 22.62	15.46
20	117.05	6.37	62.53	45.82	75.90	80.24	65.63	68.74	170.22, 23.16	16.28
21	141.87	113.31	69.47	78.27	64.32	68.62	–	–	169.28, 23.32	–

[a]) In (D_6) DMSO.

Reaction of **4** *with i-PrOH.* A large number of products was observed when the diazirine **4** was treated with 1.2 equiv. of i-PrOH at 50° either in THF or in MeCN solution. Dihydro-1,3-oxazole **5** was isolated in 31% yield from the thermolysis in MeCN.

The ^{1}H-NMR spectrum of **5** shows a typical *d* for the Me group at 1.98 ppm with a ^5J coupling constant of 0.8 Hz with H–C(2). H–C(1) resonates at 5.83 ppm with a J(1,2) value of 6.5 Hz, in agreement with the chemical shifts and J(1,2) values found for other dihydro-1,3-oxazoles [12]. The IR spectrum of **5** is characterized by the presence of the C=N stretching vibration at 1665 cm^{-1} and the absence of bands at 1500 or above 3440 cm^{-1}.

Cyclopropanes from **4** *and Acrylonitrile.* The aziallose **4** reacted with acrylonitrile at 50° to yield 76% of the four cyclopropanes **17–20** and 5% of the acetamidoallal **21** (*Scheme 3*). All products were separated by prep. HPLC and their structures established by spectroscopic data (see *Tables 3* and *4* and *Exper. Part*).

Scheme 3

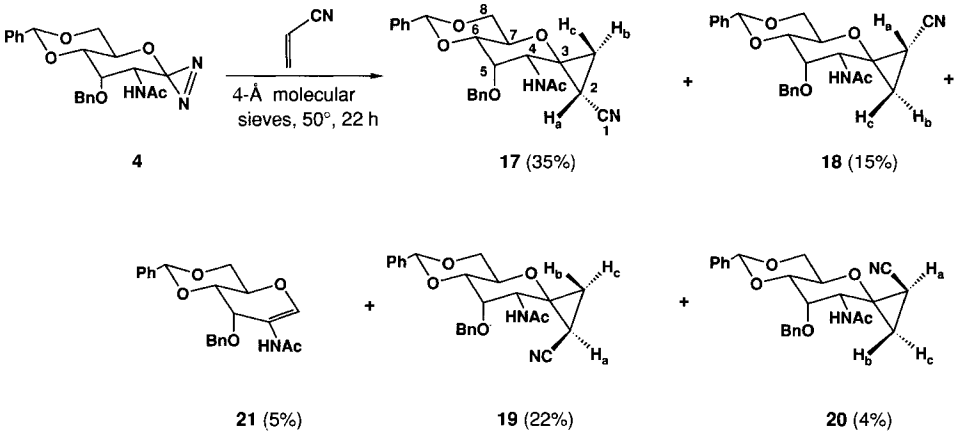


Table 3. *Selected ^{1}H-NMR* (300 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of the Cyclopropanes* **17–20**

	H–C(4)	H–C(5)	H–C(6)	H–C(7)	H_{ax}–C(8)	H_{eq}–C(8)	AcNH	H_a[a])	H_b[a])	H_c[a])
17	4.61	4.03	3.83	4.45	3.74	4.45	5.43, 1.68	1.54	1.33	1.10
18	4.63	4.04	3.85	4.15	3.80	4.39	5.40, 1.67	1.48	1.30	1.30
19	4.71	4.04	3.80	4.20	3.68	4.25	5.89, 1.69	1.54	1.23	1.39
20	4.97	4.06	3.82	4.06	3.69	4.25	5.45, 1.74	1.63	1.32	1.40
20[b])	5.18	3.75	3.16	3.90	3.41	4.07	5.18, 1.74	1.16	0.83	0.68

[a]) H_a, H_b, and H_c = H geminal, *cis*, and *trans*, resp., to the CN group. [b]) In C_6D_6.

Table 4. *Selected ^{1}H-NMR* (300 MHz, $CDCl_3$) *Coupling Constants of the Cyclopropanes* **17–20**

	^3J(a,b)[a])	^3J(a,c)[a])	^2J(b,c)[a])	^3J(4,5)	^3J(5,6)	^3J(6,7)
17	6.6	9.9	6.9	2.9	2.2	9.3
18	6.9	9.7	[b])	3.0	2.3	9.4
19	7.4	10.6	6.8	2.7	2.3	9.3
20	7.3	10.6	6.7	2.8	2.3	9.5

[a]) H_a, H_b, and H_c = H geminal, *cis*, and *trans*, resp., to the CN group. [b]) Not assigned.

The determination of the configuration of the cyclopropyl moiety of **17–20** is based upon the ^{1}H-NMR spectra and performed in two steps. In the first one, the relative position of the cyclopropyl protons (H geminal, *cis*, and *trans* to the CN group = H_a, H_b, and H_c, resp.) was deduced from the values of the chemical shifts and the coupling constants. H_a is easily assigned; it resonates in all cases at lower field between 1.48 and 1.63 ppm, while the H_b and H_c signals are found between 1.10 and 1.40 ppm (see *Table 3*). According to [13], J(1,2) between *cis*-H-atoms of cyclopropanes is always larger then J(1,2) between *trans*-H-atoms. Hence, the signals showing a ^3J value of 7.0 ± 0.4 Hz and occurring as *t*, are assigned to H_b, and those with $^3J = 10.0 \pm 0.4$ Hz to H_c (see *Table 4*). Chemical shift differences for the H_b and the H_c signals are not easily interpreted at this stage, as they depend upon the orientation not only relative to the CN substituent, but also relative to the substituents of the tetrahydropyran ring. In the second step, we deduced the orientation of the cyclopropyl substituents relative to the substituents of the tetrahydropyran ring from NOE experiments, which were interpreted on the basis of interatomic distances, calculated (ALCHEMY II) for the four diastereoisomers **17–20**. These calculations and a comparison of the coupling constants of the protons of the tetrahydropyran ring (see *Table 4*) show that the conformational changes of the four diastereoisomers are negligible. The distances between H–C(4) and the protons on the four positions of the cyclopropyl ring are 3.1, 3.7, 3.9, and 4.3 Å. For **17**, H_c is closest to H–C(4) followed by H_b, H_a, and the hypothetical H_d, formally replacing the CN group, as calculated for **17** to **20**. Irradiation of H–C(4) of **17** gave a NOE with H_c; similarly, NOE's were observed between H–C(4) and H_a of **18**, and between H–C(4) and H_b of **19**. According to these observations, the configuration of **17–19** were assigned as indicated in *Scheme 3*. NOE experiments with **20** were performed for solutions in C_6D_6, where the signals of H_b and H_c are separated. Irradiation of H_c gave a NOE only with H–C(7). This is not unexpected, considering the distance between H_c and H–C(7), H_{ax}–C(8), and H_{eq}–C(8), which amount to 3.0, 5.1 and 4.4 Å, respectively. Irradiation of H_b of **20** gave NOE's with H–C(4) and with AcN*H*.

The relative shifts of H–C(4), H–C(7), H_{ax}–C(8), H_{eq}–C(8) and AcN*H* are affected by the anisotropic CN group, and may be used as independent evidence for the proposed assignment (see *Table 3*). The shift to lower field of H–C(4) in **20** (4.97 ppm; **17–19**: 4.61–4.71 ppm), AcN*H* in **19** (5.89 ppm; **17**, **18**, **20**: 5.40–5.45 ppm), and H–C(7) in **17** (4.45 ppm; **18–20**: 4.06–4.20 ppm) indicate the proximity of these protons and the CN group, in agreement with the result of the NOE measurements. For **17**, H_{ax}–C(8) and H_{eq}–C(8) are also deshielded, although to a much lower extent than H–C(7). For **18**, H_{ax}–C(8) and H_{eq}–C(8) are deshielded, whereas H–C(7) is not.

The NMR spectra of **21** are characterized by the lowfield shift of C(1) (*d* at 141.87 ppm), C(2) (*s* at 113.31 ppm), H–C(1) (*s* at 6.91 ppm), and the absence of H–C(2) (see *Tables 1* and *2*). The coupling constants $J(3,4) = 3.5$ and $J(4,5) = 10.6$ Hz are in agreement with a $^4H_5$ conformation. The signal at *m/z* 382 for $[M + 1]^+$ in the MS is in agreement with the postulated structure.

Obviously, protonation of the intermediate carbene or diazo ether by the acetamido group does not interfere with the formation of cyclopropanes. The acetamidoallal **21** is assumed to be the product of a 1,2-H shift in the intermediate singlet carbene [14]. Although it evidences the generation of a carbene, we can not rule out the intermediate formation of a diazo compound and its 1,3-dipolar cycloaddition to acrylonitrile to form a dihydropyrazole, which quickly collapses to the cyclopropanes [15]. The preferred formation of **17** and **19**, carrying the CN group below the plane formed by O–C(7), C(3), and C(4) is in keeping with earlier results of *Vasella* and *Waldraff* [4] and *Descotes* and coworkers [5]. It may be rationalized by a two-step process, where attack by the nucleophilic carbene leads to a dipole, and where the second step occurs with stereoelectronic control by a preferred pseudoaxial attack on C(1) of the oxonium ion. The same dipolar intermediate may also be generated by ring opening of an initially formed 4,5-dihydro-3*H*-pyrazole-3-carbonitrile [16], followed by the loss of N_2. The somewhat surprising absence of 4,5-dihydro-1*H*-pyrazole-3-carbonitriles [17] could then reflect the leaving group properties of the R–N=N$^-$ in this azo ether.

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Experimental Part

General. Solvents were distilled before use. Normal workup means drying the org. phase (Na_2SO_4), filtration through a cotton plug, and evaporation. Solns. were evaporated at or below 40° in a *Büchi* rotary evaporator. Samples were dried under high vacuum (h.v.) at a pressure below 0.1 mbar. Qual. TLC: *Merck* precoated silica gel *60 F-254* plates; detection by spraying the plates with a soln. of 0.02M I_2 and 0.30M KI in 10% aq. H_2SO_4 soln., followed by heating at *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (40-63 μm). M.p. uncorrected. Optical rotations: 1-dm cell at 25°; at 365, 436, 546, 578, and 589 nm; values at 589 nm were obtained from a regression curve. IR spectra: 3% $CHCl_3$ soln. ^{1}H- and ^{13}C-NMR spectra: at 300 (^{1}H) and 50 MHz (^{13}C); chemical shifts δ in ppm rel. to tetramethylsilane (= 0 ppm) and coupling constants *J* in Hz. MS: EI at 70 eV and CI with isobutane. For calculations, the program ALCHEMY II for PC (*Tripos Associates*) was used.

*Allyl 2-Acetamido-2-deoxy-*D*-glucopyranoside* (**7**). $BF_3 \cdot OEt_2$ (92 ml, dist. under Ar) was added in one portion to a suspension of **6** (1.00 kg, 4.52 mol) in allyl alcohol (10.4 l, 152 mol). The mixture was stirred for 4.5 h at 95° under N_2. Evaporation at 60°, grinding the solid residue in a ball mill and drying under h.v. gave 1.189 kg (100%) of crude **7** [6], which was used for the next step without further purification.

*Allyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-*D*-glucopyranoside* (**8**). Anh. $ZnCl_2$ (0.900 kg, 6.60 mol, powdered) was added to a suspension of **7** (1.175 kg, 4.50 mol) in benzaldehyde (4.00 l, 39.6 mol). The suspension was stirred at r.t. under N_2. After 19 h, toluene (7 l) and H_2O (7 l) were simultaneously added under vigorous stirring. The immediately formed precipitate was filtered off (glass frit *G3*), washed with hexane (4 l), H_2O (5 × 10 l), sat. aq. $NaHCO_3$ soln. and again with H_2O. Drying of the residue (60°/16 mbar) gave 775 g (49%) of **8** [7] (α-D/β-D *ca.* 9:1).

*Allyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(methanesulfonyl)-*D*-glucopyranoside* (**9**). A soln. of methanesulfonyl chloride (0.252 l, 3.24 mol) in CH_2Cl_2 (2 l) was added within 2 min to a soln. of **8** (755 g, 2.16 mol) and Et_3N (0.502 l, 3.60 mol) in CH_2Cl_2 (14 l). The soln. was stirred for 50 min at 24°, washed with H_2O (3 × 4 l), 2M aq. NaOH (2 l) and again with H_2O (4 l). Normal workup (drying over $MgSO_4$) and crystallization in CH_2Cl_2/hexane gave 887 g (96%) of **9** (α-D/β-D *ca.* 9:1). R_f (AcOEt) 0.50. $[\alpha]_D^{25} = +61.5$ (*c* = 1.0, $CHCl_3$). M.p. 183–184°. IR: 3450*w*, 3000*w*, 2940*w*, 2880*w*, 1685*s*, 1510*m*, 1365*s*, 1175*s*, 1130*s*, 1095*s*, 1055*m*, 1040*m*, 1000*s*, 980*s*, 970*s*,

945*m*, 850*m*. ^{1}H-NMR (α-D-anomer; 200 MHz, CD_3OD): 7.55–7.40 (*m*, 2 arom. H); 7.40–7.30 (*m*, 3 arom. H); 7.99 (*dddd*, *J* = 5.4, 6.5, 10.3, 17.0, 1 olef. H); 5.67 (*s*, PhC*H*); 5.35 (*qd*, *J* = 1.6, 17.0, 1 olef. H); 5.25 (*qd*, *J* = 1.3, 10.3, 1 olef. H); 4.90 (*d*, *J* = 3.7, H–C(1)); 4.90-4.75 (HDO, H–C(3)); 4.40 (*dd*, *J* = 3.8, 10.4, H–C(2)); 4.32-4.18 (*m*, 2 H, 1 allyl. H); 4.08 (*tdd*, *J* = 1.2, 6.5, 12.9, 1 allyl. H); 3.97–3.80 (*m*, 3 H); 2.96 (*s*, MsO); 2.00 (*s*, AcN). ^{13}C-NMR (CD_3OD): 173.62 (*s*); 138.62 (*s*); 134.98 (*d*); 130.13 (*d*); 129.22 (*d*); 127.34 (*d*); 118.64 (*t*); 102.87 (*d*); 98.76 (*d*); 80.63 (*d*); 80.08 (*d*); 69.64 (*d*); 69.60 (*t*); 64.40 (*d*); 53.28 (*d*); 38.96 (*q*); 22.58 (*q*). Anal. calc. for $C_{19}H_{25}NO_8S$ (427.48): C 53.38, H 5.89, N 3.28; found: C 53.62, H 5.90, N 3.55.

Allyl 2-Acetamido-4,6-O-benzylidene-2-deoxy-α*-*D*-allopyranoside* (α-D-**10**). A mixture of **9** (895 g, 2.09 mol), 2-methoxyethanol (10 l), NaOAc (875 g), and H_2O (500 ml) was stirred at 118° under N_2. After 70 h, the soln. was concentrated *i.v.* to 3 l and CH_2Cl_2 (10 l) was addcd. Washing with H_2O (2 × 5 l), drying ($MgSO_4$) in the presence of charcoal (15 g), and filtration gave a colourless soln. During evaporation *i.v.*, CH_2Cl_2 was replaced by hexane (9 l). The slowly formed precipitate was filtered off (glass frit *G3*) and dried *i.v.*: 609 g (83%) of crude **10**. Recrystallization in AcOEt gave 562 g (72%) of pure α-D-**10**. Crystallization of the mother liquor yielded 60 g (8%) of **10** as a 96.5:3.5 α-D/β-D mixture. R_f (AcOEt) 0.39. $[\alpha]_D^{25} = +84.5$ (*c* = 1.2, $CHCl_3$). M.p. 197–198°. IR: 3680*w*, 3600*w*, 3450*m*, 3080*w*, 3040*w*, 3010*m*, 2940*m*, 2880*m*, 1675*s*, 1605*w*, 1505*s*, 1470*m*, 1455*m*, 1380*s*, 1315*m*, 1125*s*, 1105*s*, 1090*s*, 1075*s*, 1030*s*, 1000*s*, 970*m*, 940*m*, 920*m*, 885*w*. ^{1}H-NMR (200 MHz, CD_3OD): 7.55–7.45 (*m*, 2 arom. H); 7.40–7.25 (*m*, 3 arom. H); 5.96 (*dddd*, *J* = 5.1, 6.4, 10.4, 17.1, 1 olef. H); 5.65 (*s*, PhC*H*); 5.32 (*qd*, *J* = 1.6, 17.2, 1 olef. H); 5.20 (*qd*, *J* = 1.4, 10.4, 1 olef. H); 4.83 (*d*, *J* = 4.0, H–C(1)); 4.35–3.95 (*m*, 6 H); 3.76 (*t*, *J* = 9.7, H_{ax}–C(6)); 3.69 (*dd*, *J* = 2.7, 9.7, H_{eq}–C(6)); 2.01 (*s*, AcN). ^{13}C-NMR (CD_3OD): 172.86 (*s*); 139.24 (*s*); 135.47 (*d*); 129.93 (*d*); 129.04 (*d*); 127.58 (*d*); 118.03 (*t*); 103.05 (*d*); 98.06 (*d*); 79.99 (*d*); 70.12 (2*t*); 68.72 (*d*); 58.94 (*d*); 51.48 (*d*); 22.57 (*q*). CI-MS: 351 (23), 350 (83, $[M+1]^+$), 293 (14), 292 (100). Anal. calc. for $C_{18}H_{23}NO_6$ (349.39): C 61.88, H 6.63, N 4.01; found: C 61.93, H 6.55, N 4.25.

*Allyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*α*-*D*-allopyranoside* (**11**). A vigourously stirred soln. of **10** (10.0 g, 29.0 mmol) in DMF (100 ml, dist. *i.v.* over CaH_2) was treated with BaO (10 g, 65 mmol), $Ba(OH)_2 \cdot 8\,H_2O$ (2.4 g, 7.6 mmol), and BnBr (4.47 ml, 38 mmol). Stirring was continued under N_2 at 23° for 3 h 45 min. Filtration through *Celite* and evaporation under h.v. yielded white, crystalline crude **11**, which was recrystallized in AcOEt: 11.54 g (92%). R_f (Et_2O/MeOH 98:2) 0.53. For analysis, a sample was recrystallized from AcOEt/hexane 2:1. $[\alpha]_D^{25} = -1.7$ (*c* = 0.87, $CHCl_3$). M.p. 145–146° (AcOEt/hexane 2:1). IR (2%, $CHCl_3$): 3440*m*, 3070*w*, 3000*m*, 2940*m*, 2860*m*, 1670*s*, 1500*m*, 1455*m*, 1375*m*, 1310*m*, 1120*s*, 1100*s*, 1070*s*, 1025*s*, 995*s*, 950*m*. ^{1}H-NMR: 7.51–7.45 (*m*, 2 arom. H); 7.39 (*m*, 8 arom. H); 6.04 (*d*, *J* = 7.0, NH); 5.91 (*dddd*, *J* = 4.7, 6.0, 10.5, 17.2, 1 olef. H); 5.55 (*s*, PhC*H*); 5.32 (*ddd*, *J* = 1.8, 3.4, 17.2, 1 olef. H); 5.19 (*ddd*, *J* = 1.5, 3.1, 10.5, 1 olef. H); 5.05 (*d*, *J* = 12.2, 1 H, PhCH_2); 4.78 (*d*, *J* = 4.5, H–C(1)); 4.54 (*d*, *J* = 12.3, 1 H, PhCH_2); 4.40 (*dd*, *J* = 5.4, 9.7, H_{eq}–C(6)); 4.36–4.29 (*m*, H–C(2), H–C(5)); 4.25 (*tdd J* = 1.6, 4.7, 13.4, 1 allyl. H); 4.06 (*t*, *J* = 3.1, H–C(3)); 4.00 (*tdd*, *J* = 1.4, 6.0, 13.4, 1 allyl. H); 3.74 (*t*, *J* = 10.0, H_{ax}–C(6)); 3.73 (*dd*, *J* = 2.1, 9.0, H–C(4)); 1.85 (*s*, AcN). ^{13}C-NMR: 169.9 (*s*); 138.57 (*s*); 137.35 (*s*); 133.71 (*d*); 128.82 (*d*); 128.13 (*d*); 128.04 (*d*); 127.61 (*d*); 127.32 (*d*); 125.96 (*d*); 116.81 (*t*); 101.71 (*d*); 95.97 (*d*); 79.55 (*d*); 74.22 (*t*); 74.03 (*d*); 68.67 (*t*); 68.31 (*t*); 57.70 (*d*); 48.78 (*d*); 22.81 (*q*). CI-MS: 441 (29), 440 (100, $[M+1]^+$), 383 (19), 382 (77), 274 (12). Anal. calc. for $C_{25}H_{29}NO_6$ (439.52): C 68.32, H 6.65, N 3.19; found: C 68.27, H 6.63, N 3.30.

*2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*D*-allopyranose* (**12**). A soln. of **11** (20.0 g, 45.5 mmol) in DMSO (250 ml) was added to a vigorously stirred suspension of KOBu^t (11.46 g, 101.2 mmol) in DMSO (250 ml, dried over 4-Å molecular sieves for 1 h). The slightly turbid, brown mixture was heated to 50° under N_2 for 2 h, poured onto 500 ml of ice-water, and extracted with Et_2O (4 × 350 ml). The org. phase was washed with H_2O (250 ml) and brine (250 ml). Normal workup and drying of the residue at 23°/h.v. yielded 19.8 g (99%) of crude material, which was dissolved in acetone/H_2O 9:1 (1680 ml), treatcd with $HgCl_2$ (20.09 g, 74.0 mmol) and HgO (18.02 g, 83.2 mmol), and vigorously stirred under N_2 at 23°. After 1 h 35 min, the mixture was filtered through *Celite*, and most of the solvent was evaporated. The residue was poured onto ice-water (250 ml) and extracted with CH_2Cl_2 (400 ml, 2 × 200 ml). The org. layer was washed with sat. KI soln. (150 ml) and H_2O (2 × 200 ml). Normal workup and crystallization of the residue (22.1 g) from AcOEt/hexane gave 15.64 g (89%) of pure **12**. R_f (CH_2Cl_2/MeOH 98:2) 0.25. $[\alpha]_D^{25} = -90.3$ (0.60, $CHCl_3$, after 10 min). M.p. 189–192°. IR: 3440*m*, 3000*w*, 2860*w*, 1660*s*, 1490*s*, 1450*m*, 1370*m*, 1310*m*, 1115*s*, 1095*s*, 1000*s*, 960*m*, 910*w*. ^{1}H-NMR (α-D/β-D 1:2): β-D-anomer: 7.56–7.47 (*m*, 2 arom. H); 7.46–7.32 (*m*, 8 arom. H); 5.89 (*d*, *J* = 8.0, NH); 5.56 (*s*, PhC*H*); 5.07 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.89-4.81 (*m*, 2 H, H–C(1), OH–C(1); after addn. of D_2O: *d*, *J* = 7.9, 1 H); 4.55 (*d*, *J* = 12.0, 1 H, PhCH_2); 4.43 (*dd*, *J* = 5.1, 10.3, H_{eq}–C(6)); 4.11 (*dt*, *J* = 5.1, 9.9, H–C(5)); 4.05 (*t*, *J* = 2.7, H–C(3)); 3.90 (*dt*, *J* = 3.0, 7.9, H–C(2)); 3.81 (*t*, *J* = 10.4, H_{ax}–C(6)); 3.74 (*dd*, *J* = 2.3, 9.5, H–C(4)); 1.84 (*s*, AcN); α-D-anomer: 5.58 (*s*, PhC*H*); 5.06 (*d*, *J* = 11.6, 1 H, PhCH_2); 5.00 (*dd*, *J* = 3.3, 11.5, H–C(1); after addn. of D_2O: *d*, *J* = 3.3); 4.56 (*d*, *J* = 11.6, 1 H, PhCH_2); 4.33 (*dt*, *J* = 5.1, 9.5, H–C(5)); 4.27 (br. *s*, H–C(3)); 4.21 (*td*, *J* = 3.2, 8.8, H–C(2)); 1.88 (*s*, AcN). ^{13}C-NMR

((D$_6$)DMSO): β-D-anomer: 169.33 (*s*); 138.89 (*s*); 138.09 (*s*); 129.02 (*d*); 128.30 (*d*); 128.26 (*d*); 128.02 (*d*); 127.95 (*d*); 127.54 (*d*); 126.35 (*d*); 101.10 (*d*); 93.75 (*d*); 79.50 (*d*); 75.44 (*d*); 73.93 (*t*); 68.63 (*t*); 63.73 (*d*); 54.57 (*d*); 22.76 (*q*). Signals of α-D-anomer: 169.33 (*s*); 138.97 (*s*); 91.29 (*d*); 79.35 (*d*); 74.93 (*d*); 57.67 (*d*); 49.75 (*d*); 22.70 (*q*). CI-MS: 401 (12); 400 (50, $[M+1]^+$); 383 (24), 382 (100), 294 (14), 274 (17), 186 (12), 149 (10), 107 (16), 91 (25). Anal. calc. for $C_{22}H_{25}NO_6$ (399.46): C 66.15, H 6.31, N 3.51; found: C 66.14, H 6.24, N 3.78.

*(E)- and(Z)-2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*D*-allose Oximes* (**13**). A mixture of NaOMe (953 mg of Na, 41.5 mmol) in MeOH (50 ml, dist. over Mg(OMe)$_2$) and $NH_2OH \cdot HCl$ (3.20 g, 46.1 mmol) was stirred for 15 min under N_2 at 23°, cooled to 0°, and filtered through a glass frit *G3*. The combined filtrate and washing were treated with **12** (4.60 g, 11.5 mmol), heated to 50°, stirred for 4 h under N_2, and evaporated. The residue was dissolved in CH_2Cl_2/H_2O 2:1 (700 ml). The aq. phase was further extracted with CH_2Cl_2 (3 × 200 ml). Normal workup afforded 4.76 g (100%) of **13**. White foam. R_f (CH_2Cl_2/MeOH 98:2) 0.10. $[\alpha]_D^{25} = -40.0$ (*c* = 1.0, MeOH, after 10 min). M.p. 196–198° (dec.; AcOEt). IR (KBr): 3510*m*, 3400*s*, 3270*s*, 3090*w*, 3030*w*, 2910*w*, 2860*w*, 1645*s*, 1630*s*, 1550*m*, 1530*m*, 1450*w*, 1375*m*, 1330*w*, 1220*w*, 1080*s*, 1030*s*, 965*m*. ^{1}H-NMR (400 MHz, (D$_6$)DMSO, 5 h, *(E)*/*(Z)* 4:1): *(E)*-isomer: 10.66 (*s*, NOH, exchanged with D_2O); 8.13 (*d*, *J* = 8.4, NH, exchanged with D_2O); 7.44–7.25 (*m*, 10 arom. H, H–C(1)); 5.47 (*s*, PhC*H*); 5.26 (*d*, *J* = 6.0, OH, exchanged with D_2O); 4.86 (*dt*, *J* = 6.1, 8.3, H–C(2)); 4.69 (*d*, *J* = 11.7, 1 H, PhCH_2); 4.57 (*d*, *J* = 11.7, 1 H, PhCH_2); 4.08 (*dd*, *J* = 5.0, 10.5, H_{eq}–C(6)); 3.88 (*dd*, *J* = 1.6, 5.9, H–C(3)); 3.83 (*dd*, *J* = 1.9, 9.5, H–C(4)); 3.76 (*tt*, *J* = 5.9, 9.6, H–C(5)); 3.50 (*t*, *J* = 10.2, H_{ax}–C(6)); 1.83 (*s*, AcN); *(Z)*-isomer: 10.99 (*s*, NOH, exchanged with D_2O); 6.72 (*d*, *J* = 6.2, H–C(1)); 1.82 (*s*, AcN). ^{13}C-NMR ((D$_6$)DMSO, 5 h): *(E)*-isomer: 169.36 (*s*); 169.01 (*s*); 148.46 (*d*); 148.35 (*d*); 138.53 (*s*); 138.34 (*s*); 128.99 (*d*); 128.40 (*d*); 128.28 (*d*); 128.01 (*d*); 127.74 (*d*); 126.56 (*d*); 100.76 (*d*); 100.61 (*d*); 81.13 (*d*); 81.00 (*d*); 80.09 (*d*); 79.14 (*d*); 72.33 (*t*); 72.21 (*t*); 71.98 (*t*); 71.29 (*t*); 61.64 (*d*); 61.50 (*d*); 49.58 (*d*); 22.98 (*q*). *(Z)*-isomer: 169.36 (*s*); 148.46 (*s*); 138.24 (*d*); 100.61 (*d*); 81.00 (*d*); 79.14 (*d*); 75.74 (*d*); 72.21 (*t*); 71.98 (*t*); 61.64 (*d*); 44.81 (*d*). CI-MS: 416 (27), 415 (100, $[M+1]^+$), 397 (21), 382 (30), 379 (13), 309 (12), 291 (11), 289 (19). Anal. calc. for $C_{22}H_{26}N_2O_6$ (414.47): C 63.76, H 6.32, N 6.76; found: C 63.53, H 6.42, N 6.58.

*2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*D*-allonhydroximo-1,5-lactone* (**14**). Within 1 h, a soln. of $NaIO_4$ (515 mg, 2.41 mmol) in H_2O (10 ml) was added by syringe to a soln. of **13** (500 mg, 1.21 mmol) and NaOAc (165 mg, 2.00 mmol) in EtOH (28 ml, 99.9%) at 50°. A white precipitate formed immediately. After stirring under N_2 for 18 h at 50°, EtOH was evaporated at 30°. Extraction with AcOEt, washing with H_2O, 5% aq. $Na_2S_2O_3$ soln. and brine, normal workup and drying (h.v.) yielded 471 mg (95%) of **14**, which was directly used for the next step. R_f (CH_2Cl_2/MeOH 95:5) 0.17. For analysis, a sample was crystallized from abs. EtOH. $[\alpha]_D^{25} = -14.6$ (*c* = 1.1 $CHCl_3$). M.p. 228° (dec.). IR (KBr): 3430*s*, 3310*s*, 3070*w*, 2940*w*, 2890*m*, 1680*s*, 1650*s*, 1540*s*, 1455*m*, 1380*s*, 1355*s*, 1310*m*, 1215*s*, 1150*s*, 1120*s*, 1050*s*, 1010*s*, 960*s*, 755*s*, 740*s*, 700*s*, 670*m*. ^{1}H-NMR: 7.52–7.48 (*m*, 2 arom. H); 7.43–7.31 (*m*, 8 arom. H); 7.11 (br. *s*, NOH, exchanged with D_2O); 6.23 (*d*, *J* = 8.1, NH); 5.60 (*s*, PhC*H*); 4.98 (*d*, *J* = 11.7, 1 H, PhCH_2); 4.89 (*dd*, *J* = 3.2, 8.1, H–C(2)); 4.60 (*d*, *J* = 11.8, 1 H, PhCH_2); 4.60–4.51 (*m*, H–C(5), H_{eq}–C(6)); 4.32 (*dd*, *J* = 1.8, 2.9, H–C(3)); 4.00 (*dd*, *J* = 1.4, 9.8, H–C(4)); 3.92 (*m*, H_{ax}–C(6)); 1.89 (*s*, AcN). ^{13}C-NMR: 169.42 (*s*); 149.35 (*s*); 138.41 (*s*); 137.65 (*s*); 129.33 (*d*); 128.47 (*d*); 128.42 (*d*); 128.34 (*d*); 127.87 (*d*); 126.45 (*d*); 101.38 (*d*); 77.92 (*d*); 74.96 (*d*); 73.65 (*t*); 68.01 (*t*); 66.91 (*d*); 48.94 (*d*); 22.63 (*q*). CI-MS: 413 (3, $[M+1]^+$), 305 (4), 147 (9), 123 (5), 108 (4), 107 (100). Anal. calc. for $C_{22}H_{24}N_2O_6$ (412.45): C 64.07, H 5.87, N 6.79; found: C 64.13, H 5.81, N 6.82.

*(2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*D*-allopyranosylidene)amino Trifluoromethanesulfonate* (**15**). A soln. of **14** (227 mg, 0.551 mmol) and CH_2Cl_2 (11 ml, dist. from $CaCl_2$) at 0° was treated with Et_3N (230 µl, 1.65 mmol). Triflic anhydride (200 µl, 1.22 mmol) was added by syringe. The soln. was stirred for 20 min, poured onto ice-water, and extracted with CH_2Cl_2. The org. phase was washed with H_2O. Normal workup and FC (25 g of SiO_2, CH_2Cl_2) gave 243 mg (81%) of **15**. R_f (AcOEt/0.1% Et_3N) 0.78. $[\alpha]_D^{25} = +73.7$ (*c* = 1.3 $CHCl_3$). M.p. 100–104° (dec.; Et_2O/hexane). IR: 3440*m*, 3000*w*, 2870*w*, 1685*s*, 1640*m*, 1495*s*, 1420*s*, 1370*m*, 1345*w*, 1160*m* 1135*s*, 1105*s*, 1070*s*, 910*s*. ^{1}H-NMR: 7.52–7.48 (*m*, 2 arom. H); 7.44–7.31 (*m*, 8 arom. H); 5.90 (*d*, *J* = 8.8, NH); 5.60 (*s*, PhC*H*); 5.12 (*dd*, *J* = 3.2, 8.8, H–C(2)); 5.01 (*d*, *J* = 11.7, 1 H, PhCH_2); 4.69 (*dt*, *J* = 5.0, 10.1, H–C(5)); 4.62 (*d*, *J* = 11.8, 1 H, PhCH_2); 4.61 (*dd*, *J* = 5.1, 10.2, H_{eq}–C(6)); 4.26 (*dd*, *J* = 1.6, 3.8, H–C(3)); 4.04 (*dd*, *J* = 1.5, 9.7, H–C(4)); 3.93 (*t*, *J* = 10.2, H_{ax}–C(6)); 1.91 (*s*, AcN). ^{13}C-NMR: 169.70 (*s*); 161.29 (*s*); 136.91 (*s*); 136.26 (*s*); 129.42 (*d*); 128.59 (*d*); 128.31 (*d*); 126.01 (*d*); 124.91 (*q*, *J*(C,F) = 319); 102.36 (*d*); 77.72 (*d*); 74.24 (*d*); 73.48 (*t*); 69.13 (*d*); 67.70 (*t*); 48.94 (*d*); 22.40 (*q*). Anal. calc. for $C_{23}H_{23}F_3N_2O_8S$ (544.51): C 50.73, H 4.26, N 5.14; found: C 50.47, H 4.47, N 4.96.

*2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-1,2-dideoxy-1-hydrazi-*D*-allopyranose* (= *2-Acetamido-1,5-anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-hydrazi-*D*-allitol*; **16**). MeOH (150 ml, dist. over Mg(OMe)$_2$) was saturated with NH_3 at 0°, cooled to –42° (MeCN/liquid N_2), and treated dropwise within 20 min with a soln. of **15** (4.25 g, 7.80 mmol) in MeOH (98 ml, dist. over Mg(OMe)$_2$). After stirring for 3 h 45 min under N_2, the soln.

was concentrated at 30° *i.v.* to 1/3 of its original volume. CH_2Cl_2 (360 ml, 0°) was added, and the mixture was extracted with ice-water (2 × 100 ml). Normal workup and FC (150 g of SiO_2, CH_2Cl_2/MeOH 97:3) gave 2.04 g (64%) of **16**. R_f (AcOEt/0.1% Et_3N) 0.12. $[\alpha]_D^{25} = -80.3$ (c = 1.07, $CHCl_3$). M.p. 192–193° (CH_2Cl_2/pentane). IR: 3670*w*, 3430*m*, 3280*w*, 2990*m*, 2940*w*, 2860*m*, 1730*s*, 1670*s*, 1490*s*, 1370*s*, 1100*s*, 1040*s*, 990*s*, 910*m*. ^{1}H-NMR: 7.52–7.45 (*m*, 2 arom. H); 7.41–7.31 (*m*, 8 arom. H); 5.91 (*d*, J = 9.3, NHAc); 5.59 (*s*, PhC*H*); 5.04 (*d*, J = 12.1, 1 H, PhCH_2); 4.70 (*dd*, J = 3.2, 9.5, H–C(2)); 4.61 (*d*, J = 12.1, 1 H, PhCH_2); 4.41–4.30 (*m*, H–C(5), H_{eq}–C(6)); 4.22 (*t*, J = 2.6, H–C(3)); 3.91 (*dd*, J = 2.2, 9.4, H–C(4)); 3.81 (*m*, H_{ax}–C(6)); 2.15 (*d*, J = 9.3, exchanged with D_2O, NH); 2.08 (*d*, J = 9.3, exchanged with D_2O, NH); 1.79 (*s*, AcN); signals of the minor diastereoisomer: 4.83 (*dd*, J = 2.8, 8.4, H–C(2)); 4.19 (*m*, H–C(3)); 1.78 (*s*, AcN). ^{13}C-NMR: 170.39 (*s*); 137.92 (*s*); 137.06 (*s*); 129.19 (*d*); 128.58 (*d*); 128.30 (*d*); 128.20 (*d*); 128.01 (*d*); 126.07 (*d*); 102.10 (*d*); 90.67 (*s*); 75.63 (*d*); 74.70 (*d*); 74.61 (*t*); 68.68 (*t*); 64.55 (*d*); 47.61 (*d*); 22.92 (*q*). Anal. calc. for: $C_{22}H_{25}N_3O_5$ (411.47): C 64.22, H 6.12, N 10.21; found: C 63.98, H 5.91, N 9.99.

*2-Acetamido-1-azi-3-*O*-benzyl-4,6-*O*-benzylidene-1,2-dideoxy-*D*-allopyranose* (= *2-Acetamido-1,5-anhydro-1-azi-3-*O*-benzyl-4,6-*O*-benzylidene-1,2-deoxy-*D*-allitol*; **4**). Et_3N (2.14 ml, 15.4 mmol) was added at 0° to a soln. of **16** (2.43 g, 5.94 mmol) in CH_2Cl_2 (428 ml, dist. from $CaCl_2$). After 3 min, a soln. of I_2 (1.65 g, 6.50 mmol) in CH_2Cl_2 (65 ml) was added within 25 min by syringe. The slightly orange soln. was immediately poured onto 5% aq. $Na_2S_2O_3$ soln. (30 ml) and stirred vigorously. The colorless organic layer was separated and washed with H_2O (2 × 150 ml). Normal workup and FC (150 g of SiO_2, AcOEt/hexane 1:1) gave 1.77 g (73%) of pure, white **4**. For analysis, a sample was crystallized from CH_2Cl_2/pentane. R_f (AcOEt/0.1% Et_3N) 0.78. $[\alpha]_D^{25} = 13.9$ (c = 1.06, $CHCl_3$). M.p. 85–87° (dec.; CH_2Cl_2/pentane). IR: 3430*m*, 3000*w*, 2930*w*, 2870*w*, 1680*s*, 1560*w*, 1490*m*, 1370*m*, 1150*m*, 1125*m*, 1100*s*, 1055*s*, 970*m*, 915*w*.^{1}H-NMR: 7.59–7.54 (*m*, 2 arom. H); 7.52–7.33 (*m*, 8 arom. H); 5.58 (*s*, PhC*H*); 5.21 (*d*, J = 9.2, NH); 5.15 (*d*, J = 12.0, 1 H, PhCH_2); 4.85 (*dd*, J = 3.3, 9.2, H–C(2)); 4.63 (*d*, J = 12.0, 1 H, PhCH_2); 4.46 (*dt*, J = 5.2, 9.9, H–C(5)); 4.26 (*dd*, J = 5.3, 10.5, H_{eq}–C(6)); 4.16 (*t*, J = 2.5, H–C(3)); 3.92 (*dd*, J = 2.0, 9.5, H–C(4)); 3.69 (*t*, J = 10.5, H_{ax}–C(6)); 1.62 (*s*, AcN). ^{13}C-NMR: 168.86 (*s*); 137.62 (*s*); 136.88 (*s*); 129.11 (*d*); 128.58 (*d*); 128.20 (*d*); 128.11 (*d*); 128.05 (*d*); 125.98 (*d*); 102.02 (*d*); 79.68 (*d*); 74.62 (*d*); 74.16 (*t*); 65.15 (*t*); 64.50 (*d*); 56.46 (*s*); 46.10 (*d*); 22.30 (*q*). Anal. calc. for $C_{22}H_{23}N_3O_5$ (409.45): C 64.54, H 5.66, N 10.26; found: C 64.35, H 5.66, N 10.11.

*2-Amino-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-*O*,2-*N*-(ethan-1-yl-1-ylidene)-α-*D*-allopyranose* (**5**). i-PrOH (4.5 ml, 0.058 mmol; dist. from CaH_2) was added to a soln. of **4** (20 mg, 0.049 mmol) in MeCN (1 ml, dist. from CaH_2). The soln. was stirred at 50° under N_2. After 18 h, the solvent was evaporated, and the residue was purified by FC (1 g of SiO_2, AcOEt/hexane 7:3): 5.7 mg (31%) of **5**. R_f (AcOEt) 0.12. $[\alpha]_D^{25} = +153.8$ (c = 0.80, $CHCl_3$). IR: 2950*m*, 2860*m*, 1655*s*, 1455*w*, 1380*m*, 1340*w*, 1310*w*, 1155*s*, 1105s, 1060*s*, 985*s*, 910*m*, 880*m*. ^{1}H-NMR: 7.51–7.37 (*m*, 10 arom. H); 5.83 (*d*, J = 6.5, H–C(1)); 5.58 (*s*, PhC*H*); 4.76 (*d*, J = 11.8, 1 H, PhCH_2); 4.70 (*d*, J = 11.8, 1 H, PhCH_2); 4.53 (*dd*, J = 5.3, 9.8, H_{eq}–C(6)); 4.40 (*dt*, J = 5.6, 10.7, H–C(5)); 4.03 (*dd*, J = 2.0, 5.0, H–C(3)); 3.95 (*dt*, J = 1.0, 6.2, H–C(2)); 3.71 (*t*, J = 10.2, H_{ax}–C(6)); 3.65 (*dd*, J = 2.1, 9.3, H–C(4)); 1.98 (*s*, CH_3). ^{13}C-NMR: 166.68 (*s*); 138.76 (*s*); 137.32 (*s*); 129.16 (*d*); 128.28 (*d*); 128.03 (*d*); 127.42 (*d*); 127.23 (*d*); 126.24 (*d*); 103.35 (*d*); 102.01 (*d*); 77.63 (*d*); 74.77 (*t*); 72.19 (*d*); 69.26 (*t*); 63.51 (*d*); 59.67 (*d*); 14.90 (*q*). CI-MS: 383 (24); 382 (100, $[M + 1]^+$); 274 (11).

*4-Acetamido-3,7-anhydro-5-*O*-benzyl-6,8-*O*-benzylidene-2,4-dideoxy-2,3-*C*-methylene-*D*-erythro-*D*-manno-octononitrile* (**17**), *4-Acetamido-3,7-anhydro-5-*O*-benzyl-6,8-*O*-benzylidene-2,4-dideoxy-2,3-*C*-methylene-*D*-erythro-*D*-allo-octononitrile* (**18**) *4-Acetamido-3,7-anhydro-5-*O*-benzyl-6,8-*O*-benzylidene-2,4-dideoxy-2,3-*C*-methylene-*D*-erythro-*D*-gluco-octononitrile* (**19**), *4-Acetamido-3,7-anhydro-5-*O*-benzyl-6,8-*O*-benzylidene-2,4-dideoxy-2,3-*C*-methylene-*D*-erythro-*D*-altro-octononitrile* (**20**), and *2-Acetamido-1,5-anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-*D*-ribo-hex-1-enitol* (**21**). Acrylonitrile (3.5 ml, dist. under N_2) was stirred at 23° for 1 h under N_2 in the presence of 4-Å molecular sieves (500 mg). Then, **4** (150 mg, 0.366 mmol) was added at once and the mixture heated to 50° for 22 h. The mixture was filtered through *Celite*, the residue was washed with CH_2Cl_2, and the filtrate was evaporated. FC (13 g of SiO_2, AcOEt/Et_2O/hexane 3:3:4) and prep. HPLC (*Spherisorb Si* 5 μm, dioxane/hexane 2:5) gave 35 mg (22%) of **19**, 6 mg (4%) of **20**, 8 mg (5%) of **21**, 56 mg (35%) of **17**, and 24 mg (15 %) of **18**.

17: R_f (AcOEt) 0.63. t_R 7.00 min. $[\alpha]_D^{25} = +88.4$ (c = 1.13 $CHCl_3$). IR: 3430*w*, 3000*w*, 2940*w*, 2870*w*, 2240*m*, 1680*s*, 1490*s*, 1455*m*, 1370*m*, 1345*m*, 1160*m*, 1130*s*, 1100*s*, 1080*s*, 910*s*. ^{1}H-NMR: 7.52–7.49 (*m*, 2 arom. H); 7.48–7.33 (*m*, 8 arom. H); 5.57 (*s*, PhC*H*); 5.43 (*d*, J = 8.5, NH); 5.11 (*d*, J = 12.1, 1 H, PhCH_2); 4.61 (*dd*, J = 2.9, 8.6, H–C(4)); 4.55 (*d*, J = 12.1, 1 H, PhCH_2); 4.47–4.34 (*m*, H–C(7), H_{eq}–C(8)); 4.03 (*t*, J = 2.5, H–C(5)); 3.83 (*dd*, J = 2.2, 9.3, H–C(6)); 3.74 (*t*, J = 9.9, H_{ax}–C(8)); 1.68 (*s*, AcN); 1.54 (*dd*, J = 6.6, 9.9, H–C(2)); 1.33 (*t*, J = 6.8, $H_{pro\text{-}R}$ of CH_2–C(2)); 1.10 (*dd*, J = 6.9, 9.9, $H_{pro\text{-}S}$ of CH_2–C(2)). ^{13}C-NMR: 169.85 (*s*);137.90 (*s*); 137.08 (*s*); 129.05 (*d*); 128.74 (*d*); 128.33 (*d*); 128.17 (*d*); 126.04 (*d*); 118.48 (*s*); 102.01 (*d*); 79.87 (*d*); 74.26 (*d*); 74.03 (*t*); 68.54 (*t*);

65.31 (*d*); 61.78 (*s*); 47.22 (*d*); 22.68 (*q*); 14.68 (*t*); 6.02 (*d*). CI-MS: 436 (26), 435 (100, $[M+1]O^{(+)}$), 382 (10), 345 (14), 327 (30), 107 (11). Anal. calc. for $C_{25}H_{26}N_2O_5$ (434.51): C 69.11, H 6.03, N 6.45; found: C 68.87, H 6.25, N 6.45.

18: R_f (AcOEt) 0.70. t_R 7.54 min. $[\alpha]_D^{25} = -77.8$ ($c = 1.47$ $CHCl_3$). IR: 3430*m*, 3000*m*, 2930*m*, 2870*m*, 2250*m*, 1680*s*, 1490*s*, 1450*s*, 1370*s*, 1125*s*, 1100*s*, 1080*s*. ^{1}H-NMR: 7.52–7.48 (*m*, 2 arom. H); 7.44–7.30 (*m*, 8 arom. H); 5.58 (*s*, PhC*H*); 5.40 (*d*, $J = 8.9$, NH); 5.06 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.63 (*dd*, $J = 3.0, 8.9$, H–C(4)); 4.55 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.39 (*dd*, $J = 5.2, 10.5$, H_{eq}–C(8)); 4.15 (*dt*, $J = 5.0, 9.9$, H–C(7)); 4.04 (*t*, $J = 2.6$, H–C(5)); 3.85 (*dd*, $J = 2.3, 9.4$, H–C(4)); 3.80 (*t*, $J = 10.4$, H_{ax}–C(8)); 1.67 (*s*, AcN); 1.48 (*dd*, $J = 6.9, 9.7$, H–C(2)); 1.35-1.24 (*m*, CH_2–C(2)). ^{13}C-NMR: 169.87 (*s*); 137.92 (*s*); 137.09 (*s*); 129.13 (*d*); 128.82 (*d*); 128.26 (*d*); 128.22 (*d*); 126.03 (*d*); 117.85 (*s*); 102.04 (*d*); 80.19 (*d*); 74.90 (*d*); 74.20 (*t*); 68.73 (*t*); 66.05 (*d*); 61.33 (*d*); 47.27 (*d*); 22.82 (*q*); 16.37 (*t*); 5.71 (*d*). CI-MS: 436 (27), 435 (100, $[M+1]^+$), 345 (18), 327 (38), 91 (12). Anal. calc. for $C_{25}H_{26}N_2O_5$ (434.51): C 69.11, H 6.03, N 6.45; found: C 69.31, H 5.93, N 6.72.

19: R_f (AcOEt) 0.72. t_R 3.36 min. $[\alpha]_D^{25} = -102.0$ ($c = 1.69$, $CHCl_3$). IR: 3420*m*, 3000*w*, 2940*w*, 2870*w*, 2240*w*, 1675*s*, 1500*s*, 1450*m*, 1370*m*, 1310*m*, 1260*m*, 1100*s*, 10.25*s*, 900*m*. ^{1}H-NMR: 7.54–7.46 (*m*, 2 arom. H); 7.44–7.31 (*m*, 8 arom. H); 5.89 (*d*, $J = 9.1$, NH); 5.87 (*s*, PhC*H*); 5.12 (*d*, $J = 12.3$, 1 H, PhCH_2); 4.71 (*dd*, $J = 2.7, 9.2$, H–C(4)); 4.63 (*d*, $J = 12.3$, 1 H, PhCH_2); 4.25, (*dd*, $J = 5.2, 10.0$, H_{eq}–C(8)); 4.16 (*dt*, $J = 5.1, 9.7$, H–C(7)); 4.04 (*t*, $J = 2.5$, H–C(5)); 3.80 (*dd*, $J = 2.3, 9.3$, H–C(6)); 3.68 (*t*, $J = 10.2$, H_{ax}–C(8)); 1.69 (*s*, AcN); 1.54 (*dd*, $J = 7.4, 10.6$, H–C(2)); 1.38 (*dd*, $J = 6.8, 10.5$, $H_{pro\text{-}R}$ of CH_2–C(2)); 1.23 (*t*, $J = 7.1$, $H_{pro\text{-}S}$ of CH_2–C(2)). ^{13}C-NMR: 169.58 (*s*); 137.57 (*s*); 137.02 (*s*); 129.00 (*d*); 128.87 (*d*); 128.11 (*d*); 128.05 (*d*); 127.95 (*d*); 125.95 (*d*); 119.69 (*s*); 101.76 (*d*); 80.41 (*d*); 79.85 (*d*); 73.88 (*t*); 73.45 (*d*); 68.31 (*t*); 65.88 (*d*); 62.84 (*s*); 47.92 (*d*); 22.62 (*q*); 15.46 (*t*); 7.56 (*d*). CI-MS: 436 (28), 435(100, $[M+1]^+$), 327 (20), 165 (10), 73 (29). Anal. calc. for $C_{25}H_{26}N_2O_5$ (434.51): C 69.11, H 6.03, N 6.45; found: C 68.91, H 6.31 , N 6.27.

20: R_f (AcOEt) 0.72. t_R 5.08 min. $[\alpha]_D^{25} = -89.5°$ ($c = 0.58$ $CHCl_3$). IR: 3440*w*, 3000*w*, 2930*m*, 2860*m*, 2250*m*, 1685*s*, 1490*s*, 1455*m*, 1440*m*, 1370*s*, 1155*m*, 1125*s*, 1100*s*, 1085*s*, 1040*s*, 1025*s*, 915*m*. ^{1}H-NMR: 7.51–7.47 (*m*, 2 arom. H); 7.44–7.33 (*m*, 8 arom. H); 5.56 (*s*, PhC*H*); 5.45 (*d*, $J = 10.1$, NH); 5.06 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.98 (*dd*, $J = 2.8, 10.0$, H–C(4)); 4.56 (*d*, $J = 12.1$, 1 H, PhCH_2); 4.25 (*dd*, $J = 5.2, 10.3$, H_{eq}–C(8)); 4.06 (*t*, $J = 2.6$, H–C(5)); 4.06 (*dt*, $J = 5.1, 9.8$, H–C(7)); 3.82 (*dd*, $J = 2.3, 9.5$, H–C(6)); 3.69 (*t*, $J = 10.3$, H_{ax}–C(8)); 1.74 (*s*, AcN); 1.63 (*dd*, $J = 7.4, 10.4$, H–C(2)); 1.40 (*dd*, $J = 6.7, 10.6$, $H_{pro\text{-}S}$ of CH_2–C(2)); 1.32 (*t*, $J = 7.0$, $H_{pro\text{-}R}$ of CH_2–C(2)). ^{1}H-NMR (C_6D_6): 7.73–7.70 (*m*, 2 arom. H); 7.35–7.12 (*m*, 8 arom. H); 5.30 (*s*, PhC*H*); 5.18 (*m*, NH and H–C(4)); 4.92 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.37 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.07 (*dd*, $J = 5.1, 10.2$, H_{eq}–C(8)); 3.90 (*dt*; $J = 5.1, 9.9$, H–C(7)); 3.75 (br. *s*, H–C(5)); 3.41 (*t*, $J = 10.3$, H_{ax}–C(8)); 3.16 (*dd*, $J = 2.3, 9.5$, H–C(6)); 1.74 (*s*, AcN); 1.16 (*dd*, $J = 7.2, 10.6$, H–C(2)); 0.83 (*t*, $J = 6.8$, $H_{pro\text{-}R}$ of CH_2–C(2)); 0.68 (*dd*, $J = 6.6, 10.6$, $H_{pro\text{-}S}$ of CH_2–C(2)). ^{13}C-NMR: 170.22 (*s*); 138.11 (*s*); 137.12 (*s*); 129.24 (*s*); 129.05 (*d*); 128.87 (*d*); 128.36 (*d*); 128.25 (*d*); 126.09 (*d*); 117.05 (*s*); 102.11 (*d*); 94.11 (*d*); 80.24 (*d*); 75.90 (*d*); 74.43 (*t*); 68.74 (*t*); 65.63 (*d*); 62.53 (*s*); 45.82 (*d*); 23.16 (*q*); 16.28 (*t*); 6.37 (*d*). CI-MS: 436 (28), 435 (100, $[M+1]^+$), 327 (24). Anal. calc. for $C_{25}H_{26}N_2O_5$ (434.51): C 69.11, H 6.03; found: C 69.11, H 5.96.

21: R_f (AcOEt) 0.57. t_R 6.32 min. IR: 3430*w*, 3000*m*, 2960*m*, 2930*m*, 2860*m*, 1735*w*, 1680*s*, 1455*m*, 1370*m*, 1180*m*, 1125*s*, 1025*s*, 875*m*. ^{1}H-NMR: 7.55–7.51 (*m*, 2 arom. H); 7.43–7.29 (*m*, 8 arom. H); 6.91 (*s*, H–C(1)); 5.96 (br. *s*, NH); 5.60, (*s*, PhC*H*); 4.97 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.57 (*d*, $J = 12.0$, 1 H, PhCH_2); 4.50 (*dd*, $J = 5.2, 10.5$, H_{eq}–C(6)); 4.18 (*dt*, $J = 5.6, 10.3$, H–C(5)); 4.17 (*d*, $J = 3.7$, H–C(3)); 4.08 (*dd*, $J = 3.5, 10.6$, H–C(4)); 3.85 (*t*, $J = 10.2$, H_{ax}–C(6)); 1.82 (*s*, AcN). ^{13}C-NMR: 169.28 (*s*); 141.87 (*d*); 138.66 (*s*); 137.29 (*s*); 129.16 (*d*); 128.63 (*d*); 128.33 (*d*); 128.21 (*d*); 128.08 (*d*); 126.15 (*d*); 113.31 (*s*); 101.74 (*d*); 78.21 (*d*); 74.24 (*t*); 69.47 (*d*); 68.62 (*t*); 64.32 (*d*); 23.32 (*q*). CI-MS: 382 (31, $[M+1]^+$), 275 (20), 274 (100).

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