205. Glycosylidene Carbenes

Part 13

Synthesis and Thermolysis of Representative 1-Azi-glycoses

by **Andrea Vasella***[1]), **Christian Witzig, Christian Waldraff, Peter Uhlmann, Karin Briner, Bruno Bernet, Luigi Panza**, and **René Husi**

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

Dedicated to *Duilio Arigoni* on the occasion of his 65th birthday

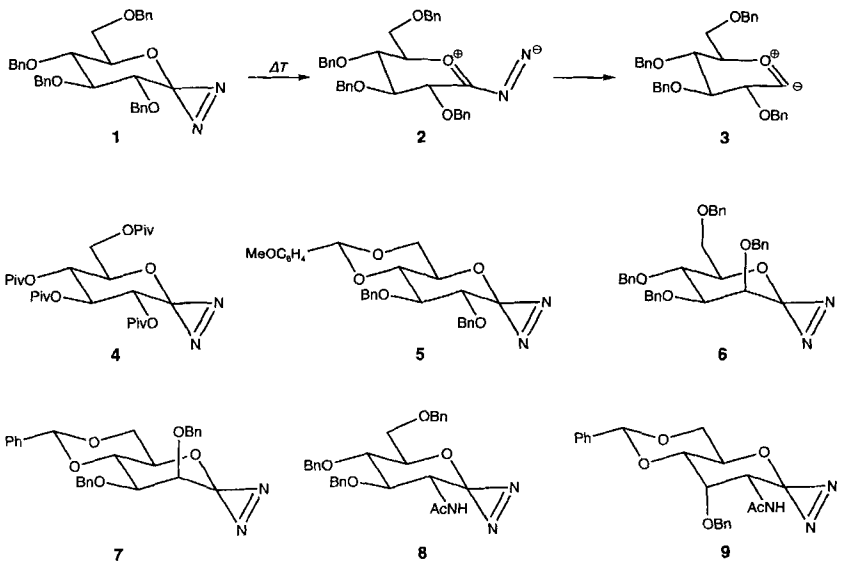
(1.X.93)

In the context of the hypothesis postulating a heterolytic cleavage of a C–N bond during thermolysis of alkoxydiazirines (*Scheme 1*), we report the preparation of the diazirines **4**, **5**, **7**, and **8**, the kinetic parameters for the thermolysis in MeOH of the diazirines **1** and **4–9**, and the products of their thermolysis in an aprotic environment. The diazirines **4**, **5**, **7**, and **8** (*Schemes 2–5*) were prepared from the known hemiacetals **10**, **19**, **34** (prepared from **31** in an improved way), and **42** according to an established method. The oximes **11**, **20**, **35**, and **43** were obtained from the corresponding hemiacetals as (*E*/*Z*)-mixtures; **43** was formed together with the cyclic hydroxylamine **44**. Oxidation of **11**, **35**, and **43** (*N*-chlorosuccinimide/1,8-diazabicyclo[5.4.0]undec-7-ene (NCS/DBU) or $NaIO_4$) gave good yields of the (*Z*)-hydroximolactones **12**, **36**, and **45**, while the oxime **20** led to a mixture of the (*E*)- and (*Z*)-hydroximolactones **21** and **22**, which adopt different conformations. Their configuration was assigned, *inter alia*, by a comparison with the enol ethers **28** and **29**, which were obtained, together with **30**, from the reaction of the diazirine **5** with benzaldehyde and PBu_3. Treatment of the hydroximolactone *O*-sulfonates **13**, **23**, **37**, and **46** with NH_3/MeOH afforded the diaziridines **15**, **25**, **38**, and **47** in good yields, while the (*E*)-sulfonate **24** decomposed readily. Oxidation of the diaziridines gave **4**, **5**, **7**, and **8**, respectively. Thermolysis of the diazirines **1** and **4–9** in MeOH yielded the anomeric methyl glycosides **50**/**51**, **16**/**17**, **26**/**27**, **52**/**53**, **39**/**40**, **48**/**49**, and **54**/**55**, respectively. A comparison of the kinetic data of the thermolysis at four different temperatures shows the importance of conformational and electronic factors and is compatible with the hypothesis of a heterolytic cleavage of a C–N bond. An early transition state is evidenced by the absence of torsional strain by an annulated 1,3-dioxane ring. Thermolysis of **1** in MeCN at 23° led mostly to the diastereoisomeric (*Z*,*Z*)-, (*E*,*E*)-, and (*E*,*Z*)-lactone azines **56**, **57**, and **58** (*Scheme 6*), which convert to **56** under mild conditions, and to **59** (3%). The benzyloxyglucal **59** was obtained in higher yields (18%), together with 44% of **56–58**, by thermolysis of solid **1**. Similarly, thermolysis at higher temperatures of **4** in toluene, THF, or dioxane and of **9** in CH_2Cl_2 or THF yielded the (*Z*,*Z*)-lactone azines **60** and **61**, respectively, the latter being accompanied by the dihydro-oxazole **62**.

Introduction. – Diazirines [1] are important precursors of carbenes, and the mechanism of their thermolysis attracted considerable attention, which focused on the concertedness of the cleavage of the two C–N bonds and the homo- or heterolytic nature of the bond breaking [2–7]. The mechanism and the kinetics of the thermolysis of (alkoxy)alkyldiazirines (see [8] and earlier papers of the series [9–13]) have not been studied, but we hypothesized that thermolysis of 1-azisugars, such as **1**, *i.e.* cyclic (alkoxy)alkyldiazirines, is initiated by heterolysis of one of the C(1)–N bonds, accord-

[1]) New address: Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich.

Scheme 1



Piv = Pivaloyl (= 2,2-dimethylpropanoyl), $MeOC_6H_4$ = 4-Methoxyphenyl

ing to *Scheme 1* [14]. This heterolysis leads to a zwitterion – **2** in *Scheme 1* – and, hence, by loss of N_2 to a carbene such as **3**. Although the structure of 1-azisugars does not provide supporting evidence for such a heterolytic process – X-ray analysis of **9** established that the length of the two C(1)–N bonds is almost equal (the pseudoaxial bond is slightly longer) [15] –, one may evidence the intermediacy of a species possessing a cationic character at C(1) by considering its analogy to a glycosyl cation. Similarly as a glycosyl cation, such an intermediate should be destabilized by electron-withdrawing substituents. Such substituents (σ-acceptors) are expected to stabilize both 1-azisugars and glycosyl derivatives with a potential leaving group at the anomeric center [16–20]. A mechanistic proposal in keeping with such a ionic transition state, relating log k with the substituent parameters $\sigma^+-\sigma$, has been derived from the study of the effect of *para*-substituents on the thermolysis of 3-aryl-3-chlorodiazirines [21][2]).

To demonstrate such a dependency, we determined the kinetic parameters for the thermolysis in MeOH of the 1-azisugars **1** and **4**–**9** (*Scheme 1*). We expected that **4**, possessing more highly electronegative *O*-acyl instead of *O*-alkyl groups, would be more stable than **1** [16] [18–20] [24]. The zwitterion, derived from the 4,6-*O*-benzylidene-pro-

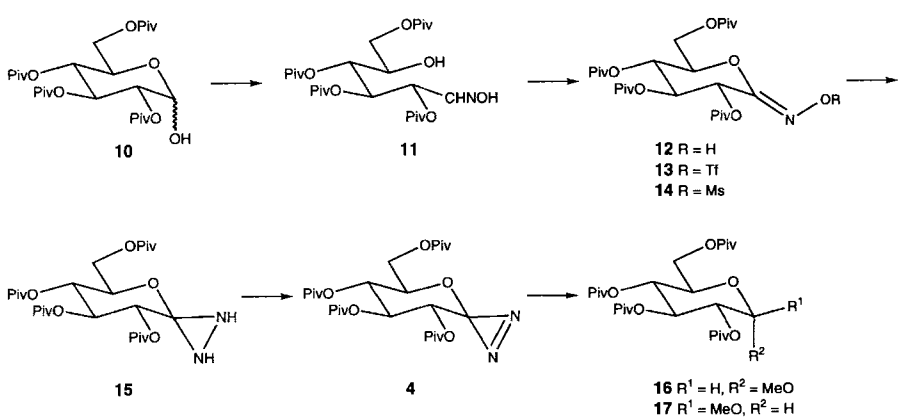
[2]) *Moss et al.* [11] have shown that push-pull carbenes like methoxy(trifluoromethyl)carbene are not stabilized, and that the precursor 3-(trifluoromethyl)-3-methoxydiazirine is unstable at room temperature. To the best of our knowledge, however, kinetic parameters have not been determined for this diazirine. We expect the activation energy for the thermolysis of this diazirine to be higher than for 3-methoxy-3-methyldiazirine [13]. The low stability of 3-methoxydiazirine-3-carbonitrile [22] may be related with the ability of a CN group to stabilize cationic centers (see [23] and ref. cit. therein; compare, however, [23b]. Alternatively, the diazirine could be destabilized by the geminal-group interaction of the CN and MeO groups [23c].

tected *trans*-trioxadecalins **5**, **7**, and **9** should be destabilized by torsional strain, similarly to analogous glycosyl cations, as it was demonstrated by *Fraser-Reid* and coworkers [25] [26]. The influence of the annulated dioxane ring may be evaluated by comparing the thermolysis of **1** and **5**, on the one hand, and the one of **6** and **7**, on the other hand. The *N*-acetylglucosamine derivative **8** differs from **1** only by the substitution of BnO at C(2) by an acetamido substituent, which is not expected to lead to large differences in activation energy [27] [28]. The *N*-acetylallosamine derivative **9** [29] possesses a 2-acetamido substituent, a 4,6-*O*-benzylidene group, and a different configuration. A comparison of the thermolysis of **9** with the one of **1** and **4–8** should allow to distinguish between the contribution of these structural parameters. Depending upon the influence of the annulation and of the configuration (*cf.* [16] [18] [30–33]), **9** may be more or less stable than **8**. We were also interested in the nature of the products of thermolysis in an aprotic environment, as they are invariably formed when 1-azisugars are exposed to a relatively unreactive partner [8] [34–36], and of which only a relatively minor component, the alkoxyglycal **59** [37] (*ca.* 5%) had been characterized [38].

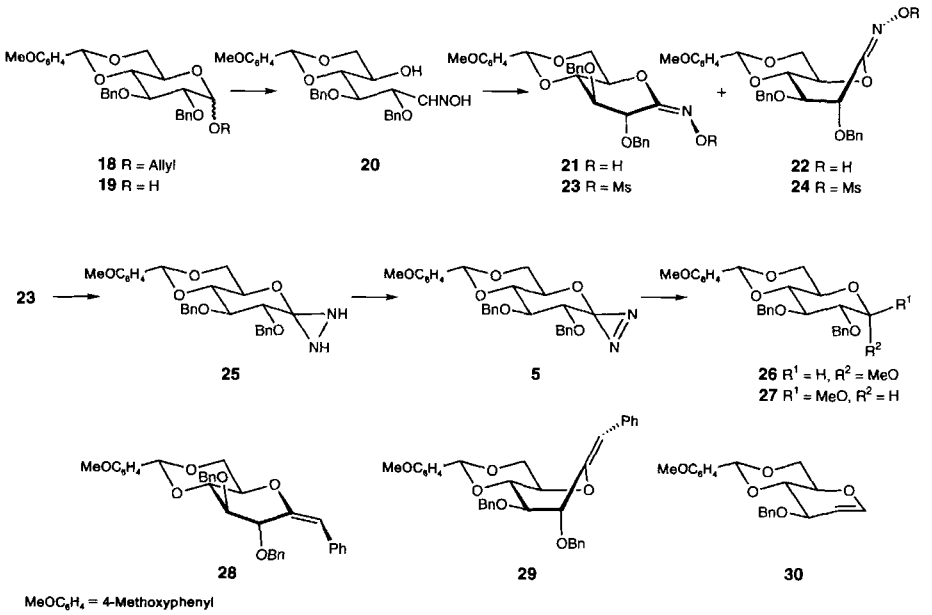
Results and Discussion. – 1. *Preparation of the Diazirines.* The preparation of the diazirines **1** [39], **6** [39], and **9** [29] has been described. The pivaloylated 1-aziglucose **4**, the (4-methoxybenzylidene)-protected 1-aziglucose **5**, the benzylidene-protected 1-azimannose **7**, and the tribenzylated *N*-acetyl-1-aziglucosamine derivative **8** were prepared according to the same method with some variations, where appropriate, as depicted in the *Schemes 2–5*.

Aziglucose **4**. The oximes **11** (*Scheme 2*) were obtained from the known tetrapivaloate **10** [40] as an (*E*/*Z*)-mixture (3:1; 87%). Oxidation of **11** was best effected with *N*-chlorosuccinimide (NCS) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and led to 79% of a single hydroximo-1,5-lactone **12**. Other reagents, such as $NaIO_4$, MnO_2, or PhIO, led to complex mixtures or to by-products which were difficult to remove. The crystalline triflate **13**, obtained in 92% yield from **12**, was treated at low temperature with NH_3 in MeOH, using CH_2Cl_2 as cosolvent, to yield 72% of the diaziridine **15**, while the mesylate **14** led to a mixture. Oxidation of **15** with I_2 in CH_2Cl_2 under basic conditions, followed by aqueous workup at 0° and flash chromatography, afforded the diazirine **4**

Scheme 2



Scheme 3



which was stored in the freezer for several days without noticeable decomposition (TLC). Methanolysis yielded the methyl glucosides **16** [66] and **17** in 69% and in a ratio of 85:15.

Aziglucose **5**. A mixture of the fully protected allyl glucosides **18** (*Scheme 3*) were prepared similarly to the pure α-D-anomer [41a] and to the analogous methyl α-D-glucosides [41b, c] (*cf.* also [42]). Removal of the allyl group according to the procedure of *Nashed* and *Anderson* [43], using first KO(*t*-Bu) and then I_2 in aqueous THF, afforded the crystalline hemiacetals **19** (77%). Oximation led almost quantitatively to the oximes **20** ((*E*)/(*Z*) ≈ 4:1), which were oxidized with NCS in the presence of DBU at low temperatures to yield 96% of a mixture of the (*E*)- and (*Z*)-hydroximolactones **21** and **22** in a ratio which appeared to depend upon batch size and conditions and varied from *ca.* 9:1 for a 11-g batch to *ca.* 1:1 on a 2-g scale. The major, crystalline product **21** was obtained pure in 82% yield. Oxidation with buffered periodate was not complete and yielded **21**/**22** in a ratio of *ca.* 5:1. This is the first time that we have obtained a mixture of diastereoisomeric, fully substituted glyconhydroximo-1,5-lactones.

The disappearance of the H–C(1) signal, the IR bands at 1670 and 1660 cm^{-1}, and the C(1) signals at 150.73 and 151.14 ppm for **21** and **22**, respectively, confirm that both products are hydroximolactones. Their ^{1}H-NMR spectra ($CDCl_3/C_6D_6$)[3]) show striking differences of the chemical shift for H–C(3), H–C(4), and H–C(5), and significant differences in the values of the corresponding coupling constants, as may be seen from *Table 2* (see *Exper. Part*). The large $\Delta\delta$ value of 1.01 ppm for H–C(5) suggests a conformation, where the BnO–C(2) group of **21** is close to H–C(5). This is best realized in a $B_{2,5}$ to $^1S_5$ conformer, which is in keeping with a very small J(1,2) and a large J(4,5), and with a $\Delta\delta$ value of 0.41 ppm for H–C(3), due to the small dihedral angle with O–C(2) and

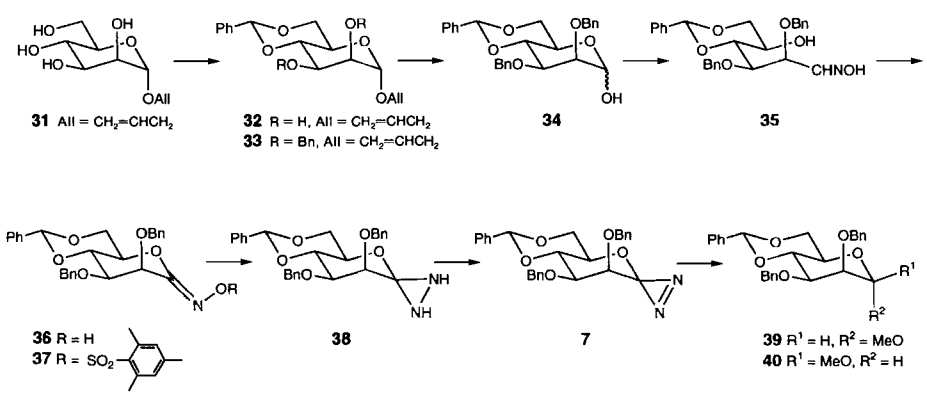
[3]) A comparison with the spectrum of **21** in $CDCl_3$ shows that the influence of the solvent on the chemical shift does not lead to a $\Delta\delta > 0.25$ ppm.

O–C(4). The minor isomer **22** is characterized by an upfield shift of H–C(4) by 0.68 ppm, and by larger coupling constants, both being consistent with a $^{1,4}B$, where H–C(4) is in a flagpole position and deshielded by the hydroximo function. The isomers did not equilibrate upon standing in $CDCl_3$ at ambient temperature for 14 days, unlike the behavior of the known (*E*)-hydroximo-1,4-lactones [44]. Isomerization of an (*E*)-2-deoxy-hydroximo-1,5-lactone, however, also required stronger acid catalysis [45]. It is difficult to assign the (*E*/*Z*)-configuration. Unfortunately, a small $\Delta\delta$ value for C(1) (0.4 ppm; *Table 3*, see *Exper. Part*) does not allow any assignment (*cf.* [45] [46] and ref. cit. therein). However, upfield shifts for C(5) of **21** ($\Delta\delta$ = 8 ppm) and for C(2) of **22** ($\Delta\delta$ > 3.8 ppm, γ-effect)) suggest an (*E*)-configuration for the main isomer **21**. A weak NOE between NOH and H–C(2) (2% upon irradiation of NOH and 1% upon irradiation of H–C(2)) is in keeping with this assignment. There is also evidence for the (*E*)-configuration of the major isomer **21** based on a comparison with the diastereoisomeric enol ethers **28** and **29**, which were obtained (together with **30**) in preliminary experiments, exploring the reaction of the diazirine **5** with benzaldehyde in the presence of phosphines [47–50]. These diastereoisomers adopt conformations which are similar to those of **21** and **22**, respectively. The signal for the olefinic H of the isomer adopting a $B_{2,5}$ to $^1S_5$ conformation resonates at 6.43 ppm, evidencing the *cis*-arrangement of this H and O–C(1), while the other diastereoisomer shows the corresponding signal at 5.60 ppm (cf. [51] [52]). In agreement with this, the two H_{ortho} of the olefinically bound Ph group of the latter isomer (**29**) are deshielded by the *cis*-alkoxy substituent, and resonate at 7.57–7.61 ppm, while the corresponding signal of the former isomer is found below 7.41 ppm.

Both hydroximolactones **21** and **22** were mesylated to yield **23** and **24**, respectively. The mesylate **23**, derived from the major (*E*)-hydroximolactone, formed a single, crystalline diaziridine **25** in high yields, while the presumed (*Z*)-isomer **24** decomposed readily and gave only small amounts of **25**. The diazirine **5** was obtained in the usual way in 79% from **25**.

Azimannose **7**. This diazirine was prepared similarly to the *gluco*-diazirine **5**. The synthesis of the known 2,3-di-*O*-benzylated benzylidene-mannopyranose **34** [53] (*Scheme 4*) was simplified. Benzylidenation with benzaldehyde dimethyl acetal [54] of allyl mannopyranoside **31**, which was prepared from mannose according to *Lee* and *Lee* [55] yielded the known mannopyranoside **32** [56] in 59% yield from mannose. Benzylation of **32**, and removal of the allyl group, again according to the procedure by *Nashed* and *Anderson* [43] gave **34**, which was treated with NH_2OH. The crystalline oximes **35** ((*E*)/(*Z*) ≈ 4:1) were obtained in 74% yield from **32**. Oxidation of **35** was again best effected with NCS in the presence of DBU and gave the hydroximolactone **36** as a single isomer which was directly transformed in the crystalline mesitylenesulfonate **37** (90%). Treatment of **37** with a solution of NH_3 in $MeOH/CH_2Cl_2$ 1:2 yielded the diaziridines **38**

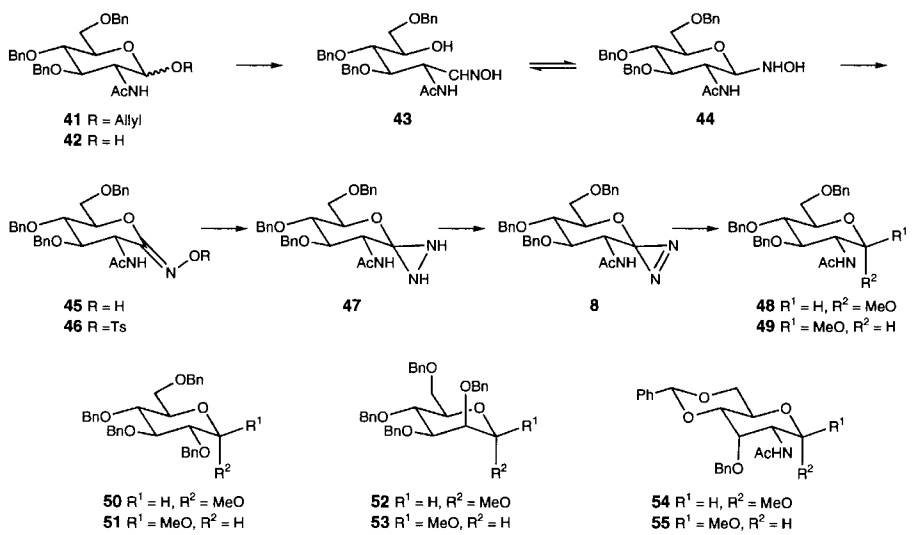
Scheme 4



(70%). The mesitylenesulfonate **37** proved more suitable than the corresponding mesylate, which gave **38** in only 12% yield. Oxidation of **38** with I_2 in CH_2Cl_2 in the presence of Me_3N gave the poorly stable diazirine **7** (80%).

N-*Acetylaziglucosamine* **8**. The known *N*-acetyl-tri-*O*-benzyl-D-glucosamine **42** [57] (*Scheme 5*) was prepared by partial deprotection [43] of the allyl glycoside **41** [58] [59]. Treating **42** with a solution of NH_2OH in MeOH at neutral pH gave a mixture of the oximes **43** and the *N*-(alkoxyalkyl)hydroxylamine **44**. Oxidation of this mixture with a buffered solution of $NaIO_4$ in aqueous EtOH afforded the crystalline lactone oxime **45** in 70% yield from **42**. The tosylate **46** was obtained in almost quantitative yield and proved the best of several sulfonates for the preparation of the relatively sensitive diaziridines **47** which were immediately oxidized with I_2 in the presence of Et_3N to give the crystalline diazirine **8** in 63% yield from **46**. The diazirine **8** was stored without significant decomposition for several days at −20°.

Scheme 5



The oximes **11**, **20**, **35**, and **43** were obtained as mixtures of the (*E*)- and (*Z*)-isomers, with an (*E*)/(*Z*) ratio between 2.5:1 for **43** and 4:1 for **20** and **35**. The relative configurations were assigned on the basis of the chemical-shift differences for H–C(1) ($\Delta\delta$ = 0.77, 0.56, 0.53, and 0.72 ppm, resp.). This signal is consistently found at higher fields for the minor (*Z*)-isomer, particularly for **11** and **43**, carrying at C(2) an acyloxy or acetamido substituent. These assignments are corroborated by the γ-effect, shifting the C(2) signal of the (*Z*)-isomers to higher fields (*Table 3*), and by the relative position of the H–C(2) signal, which appears at higher fields for the (*E*)-isomer (*Table 2*). Only the mixture obtained by treating **42** with NH_2OH consisted of three species (TLC, ^{1}H- and ^{13}C-NMR spectroscopy). Chromatographic separation of the components and immediate measurement of the NMR spectra confirmed the presence, in addition of the (*E*)- and (*Z*)-oximes **43**, of the β-D-configurated *N*-(glycosyl)hydroxylamine **44**. Signals of three exchangeable H at 6.62 (NHO*H*), 5.37 (N*H*OH), and 4.85 ppm (AcN*H*), the chemical shift for the *d* of H–C(1) at 3.79 ppm, and the vicinal coupling constants $J(1,2) = 9.4$, $J(2,3) = 10.4$, $J(3,4) = 8.5$, and $J(4,5) = 9.6$ Hz, which are typical for a $^4C_1$ conformation, evidence the cyclic nature and the β-D-configuration of **44**. The structure of **44** is corroborated by the chemical shift of C(1) at 91.7 ppm.

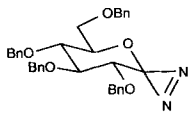
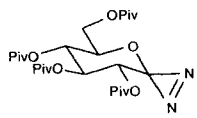
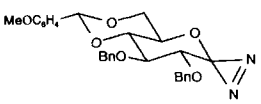
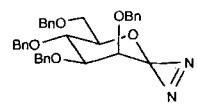
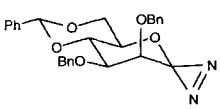
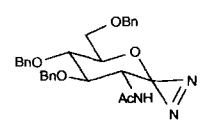
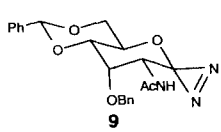
Oxidation of **11**, **35**, and **43**/**44** led diastereoselectively to the homogeneous hydroximolactones **12**, **36**, and **45**, to which the (*Z*)-configuration was assigned by analogy with earlier results [44] [60]. Formation of both the (*Z*)- and (*E*)-hydroximolactones had so far only been observed for 2-deoxyaldose oximes [45] [61] and for the oxime of 2,3:5,6-di-*O*-isopropylidene-D-mannose under mild conditions. The formation of two diastereoisomers from **20** may be due, at least in part, to the improved, mild oxidation method. Sulfonation of the hydroximolactones resulted in a downfield shift of C(1), characterized by $\Delta\delta$ values between 1.1 ppm for the triflate **13** and 4.2 ppm for the mesitylenesulfonate **37** (*Table 3*). The sulfonates adopt the same conformations as the parent hydroximolactones (*Table 2*).

Depending upon the *gluco*- or *manno*-configuration of the parent aldose, the known 1-hydrazisugars are either predominantly a single diastereoisomer or a nearly 1:1 mixture of two *trans*-configurated diastereoisomers [39]. In keeping with this, we found only traces of a second isomer for the *gluco*-configurated **15** and one diastereoisomer only of **25**. The *N*-acetylglucosamine derivative **47** is a 5.2:1 mixture of two diastereoisomers. The *manno*-diaziridine **38**, however, although migrating as a single spot on TLC, is a 2:3 mixture of two diastereoisomers as evidenced by two sets of signals in the ^{1}H- and ^{13}C-NMR spectra. All these diaziridines show the characteristic IR absorption for N–H at 3270–3280 cm^{-1} and a large J_{trans} (NH,N'H) of 9.2–9.4 Hz. The chemical-shift values for the hydrazi group of the isomers of **38** are remarkably different from each other, with $\Delta\delta$ (NH) = 1.17 ppm for the major **38a** and 0.05 ppm for the minor isomer **38b**. A tentative assignment of the NHNH configuration of the two isomers of **38** is based on the following reasoning: The chemical shift of 1.18 ppm for one of the NH groups of **38a** is at very high fields, by comparison to all the other glycosylidene-diaziridines; the only value close to it (1.45 ppm) belongs to one of the structurally related 1,5-anhydro-2,3,4,6-tetra-*O*-benzyl-1-hydrazi-D-mannitols [39]. The extreme value of the chemical shift suggests that it is due to a NH located on the same side (as defined by a plane through C(1) and the two N) as BnO–C(2), and the shielding suggests that it is not in the vicinity of the O–C(2), hence located below the plane of the pyranose ring (pseudoaxial). The relative chemical shift of H–C(3) and H–C(5) is in agreement with this assignment, in that H–C(3) and H–C(5) of the major isomer **38a** resonate at 3.56 and 3.81 ppm, respectively, while the corresponding signals for **38b** are found at 3.91 and 3.25 ppm, in keeping with the deshielding effect of the nearby N-atom lone pair [62]. The significant low-field shift of AcN*H* ($\Delta\delta$ = 0.88 ppm) in the minor isomer **47b** may result from an interaction with the lone-pair of a N-atom of the diaziridine ring [62]. The conformation of the pyranose ring of the diaziridines is hardly influenced by the spiro-annulation and is close to a $^4C_1$. As evidenced by a two-dimensional TLC experiment, the isomers of **47** equilibrate under slightly acidic conditions.

The diazirines **4**, **5**, **7**, and **8** show the characteristic IR bands, UV maxima, and NMR data of glycosylidene-diazirines, as exemplified by the *s* of C(1) of **4** at 56.41 ppm, and its UV maxima at 252 and 340 nm. In the ^{1}H-NMR spectrum of **7**, H–C(2) is under the influence of the diazirine ring and resonates at 2.94 ppm (3.24 and 3.40 in the diaziridines **38**). The high-field shift of Me (1.64 ppm) of the acetamido group of **8** is presumably also due to the shielding properties of the N=N bond [39] [63].

2. *Determination of the Activation Energy.* We determined the activation energy for the thermolysis of the diazirines **1** and **4**–**9** in MeOH. The reaction of the intermediate carbenes with MeOH led to mixtures of the anomeric methyl glycosides **50**/**51** [35] [64] [65], **16**/**17** [66], **26**/**27** [41], **52**/**53** [65] [67], **39**/**40** [68] [69], **48**/**49** [70], and **54**/**55** (*Schemes 2–5*) and was faster than bimolecular reactions of carbenes and diazirines (see below). First-order rate constants were thus obtained for the decrease [64] of diazirine concentration. The methyl glycosides do not interfere with the n,π^* transition of the diazirines at 350 nm [29] [34] [39], and the disappearance of the diazirines was followed by measuring the decrease of the intensity of this absorption as a function of time. The rate constants were determined at three or four different temperatures, and the activation energy E_a was calculated using the *Arrhenius* equation [71]. The activation enthalpy ($\Delta H^{\neq}$) and the activation entropy ($\Delta S^{\neq}$) were derived from the same set of data using the *Eyring* equation [71].

Table 1. *Kinetic Parameters for the Thermolysis of 1-Aziglycoses in MeOH*

Diazirine	E_a [kcal/mol]	log A	τ (298 K) [min]	$\Delta H^{\neq}$ (298 K) [kcal/mol]	$\Delta S^{\neq}$ (298 K) [cal/mol·K]
 **1**	23.0	13.4	33	22.4	1.7
 **4**	25.0	14.1	202	24.0	4.8
 **5**	22.2	12.4	110	21.7	−3.2
 **6**	23.2	14.2	7	22.6	5.5
 **7**	20.0	11.4	23	19.5	−8.2
 **8**	22.6	12.6	112	22.0	−3.1
 **9**	28.1	15.1	4159	27.2	8.1

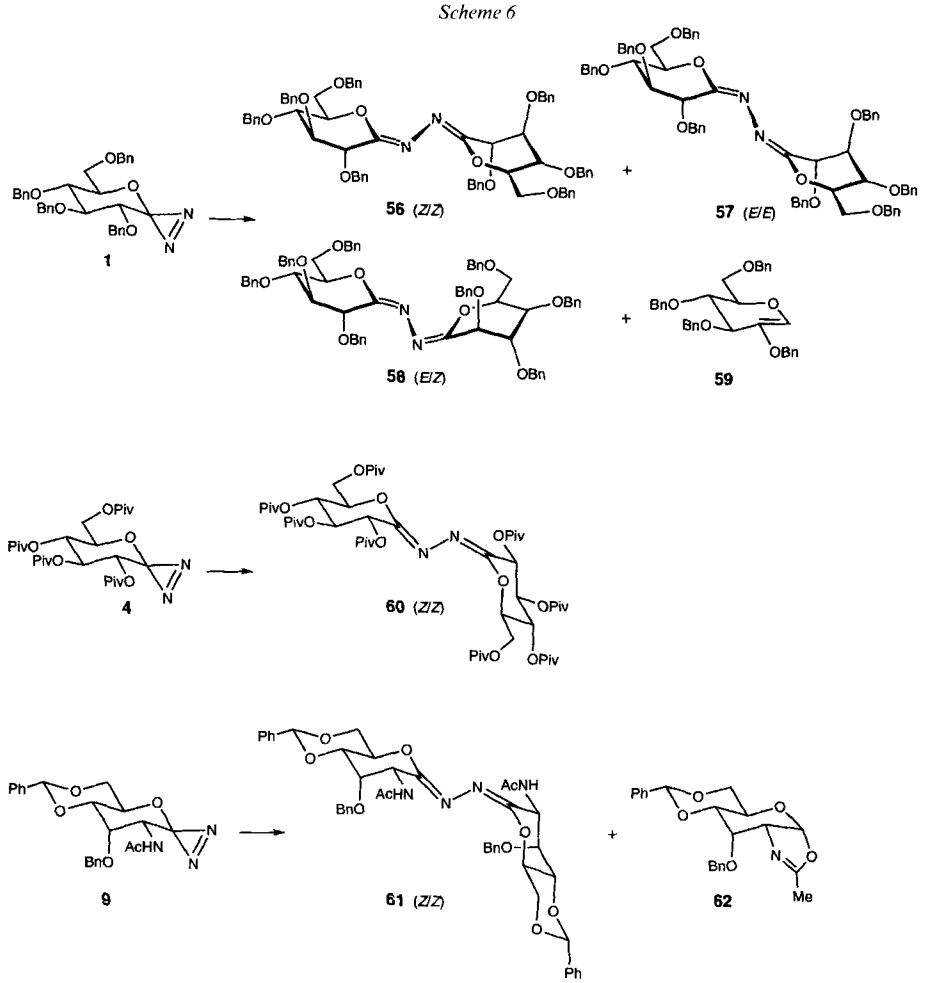
The activation energies E_a (*Table 1*) span a range between 20.0 and 28.1 kcal/mol ($\Delta H^{\neq}$ between 19.5 kcal/mol for **7** and 27.2 kcal/mol for **9**), and the half-lives τ at 25° are between 7 and 4159 min. The activation energy for the tetra-O-benzylaziglucose **1** (23 kcal/mol, log A = 13.4) is similar to E_a for (alkoxy)- and (aryloxy)chlorodiazirines [72] [73], but higher than E_a for dimethoxydiazirine (18.9 kcal/mol, pentane) [4] and (methoxy)phenoxydiazirine (*ca.* 20 kcal/mol, pentane) [3]. log A is close to the theoretical value of 13.55 for unimolecular reactions; concordingly, the activation entropy is small. An influence of the electronegativity of the diazirine substituents on kinetic stability has been found for 3-halo-3-phenoxydiazirines, where the F-atom led to the highest kinetic

stability (E_a = 26.4 kcal/mol for 3-fluoro-3-phenoxydiazirine, *i.e.* 3 kcal/mol higher than for the corresponding chloro derivative (log A = 13, hexane) [6]). Similarly, replacement of the alkoxy substituents in **1** by acyloxy substituents in **4** raises E_a by 2 kcal/mol ($\Delta\Delta H^{\neq}$ = 2.6 kcal/mol). $\Delta S^{\neq}$ is higher by 3 e.u. and positive.

A comparison of the kinetic data for **1** and **5** shows that annulation of a 1,3-dioxane ring has a slight influence only on E_a, lowering it by 0.8 kcal/mol. $\Delta S^{\neq}$ for **5** is still small, but negative ($\Delta\Delta S^{\neq}$ = 4.9 e.u.). A lowering of $\Delta H^{\neq}$ by 3.1 kcal/mol and $\Delta S^{\neq}$ by 13.7 e.u. upon annulation of a 1,3-dioxane ring is also observed in the *manno*-series, as seen by comparing the azimannoses **6** and **7**. The negative and quite important $\Delta S^{\neq}$ values for the benzylidenated diazirines are surprising, as annulation of the 1,3-dioxane ring leads to a *trans*-trioxadecalin system, and hence to a restriction of conformational flexibility of the starting material. The influence of annulation may, however, be rationalized by assuming that heterolysis of the C–N bond requires a change of the ring conformation to allow a donor-acceptor interaction between the π-type lone pair of O–C(5) with the LUMO associated with the bond breaking, *i.e.* a lowering of the C(5)–O–C(1)–C(2) dihedral angle. The number of possible ways to effect this conformational change is restricted by annulation of a dioxane ring, as in **5** and **7**, and this leads to a negative entropy of activation. During this conformational change – presumably from $^4C_1$ in the direction of $B_{2,5}$ – the axial substituent at C(2) of **7** moves towards a more favorable pseudoequatorial orientation, hence the lowered activation enthalpy for the thermolysis of **7** as compared to **6**. No such difference for E_a is found in the thermolysis of the tetra-*O*-benzylated *gluco*- and *manno*-diazirines **1** and **6**, and one has to conclude that the conformational change associated with thermolysis of **6** is different from the one of **7**. Some credibility is lent to the above rationalization by comparing the kinetic data for **1**, **8**, and **9**. The activation enthalpies for the thermolysis of **1** and **8** differ by only 0.4 kcal/mol, and the activation entropy by 4.8 e.u. The 1,3-dioxane ring in **9** is expected to lower E_a, as the conformational change from a $^4C_1$ in the direction of a $B_{2,5}$ implies that the axial BnO–C(3) group moves towards a pseudoequatorial position. Also, one expects $\Delta S^{\neq}$ to be negative. The opposite is found. Both the increased $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are, however, consistent with the breaking of the H-bond between the acetamido and the BnO–C(3) groups in the transition state. This is similar to the direct influence of the ease of rotation around the C(2)–C(3) bond on the rate of glycoside hydrolysis found by *Feather* and *Harris* [32] and consistent with a change of the pyranose-ring conformation during thermolysis. That the torsional strain of the annulated dioxane ring on the hydrolytic stability of glycosides, which has been described by *Fraser-Reid* and coworkers [25] is not observed in the thermolysis of the benzylidenated diazirines **5**, **7**, and **9** may be explained by the strongly exergonic nature of the thermolysis (release of ring strain and formation of N_2) and, thus, an early transition state, while a late transition state close to the oxycarbenium intermediate is characteristic for glycoside hydrolysis. A comparison of the steric and electronic factors on the thermal stability of glycosylidene-diazirines, on the one hand, and on the hydrolytic stability of glycosides, on the other hand, may thus contribute to distinguish early and late events on these reaction paths. The thermal stability of the glycosylidene-diazirines does not contradict the hypothesis illustrated in *Scheme 1* and suggests that the ease of conformational changes associated with thermolysis modulates the thermal stability of spirocyclic alkoxydiazirines at least as efficiently as changes of the electronic properties of the substituents.

3. *Products of Thermolysis in Aprotic Solvents.* Thermolysis of **1** in MeCN at 23° for 16 h transformed the starting material completely into a mixture of products (*Scheme 6*). The major products were diastereoisomeric lactone azines. The (*Z,Z*)-azine **56** (46%) and the (*E,E*)-isomer **57** (5%) were isolated as pure compounds, whereas the (*E,Z*)-azine **58** was only observed in the ^{1}H-NMR spectrum of a mixture with **56**. This mixture was completely transformed to the (*Z,Z*)-isomer **56** after standing for one week in $CDCl_3$ at 4°. The ready isomerization of **58** prevented its purification and the determination of the yield in which it was initially formed. Besides the azines, we isolated 3% of the benzyloxyglucal **59** [37] [74][4]). Remarkably, thermolysis of crystalline **1** at room temperature yielded **59** in a higher yield (18%), besides 44% of the azine mixture.

Scheme 6



[4]) Traces of H_2O led to 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose and a mixture of anomeric octa-*O*-benzyl-trehaloses.

Thermolysis of the diazirine **4** in toluene, THF, or dioxane gave good yields of the (*Z*,*Z*)-lactone azine **60**; no other products were isolated in significant amounts. Thermolysis of the diazirine **9** in boiling CH_2Cl_2 yielded mainly the (*Z*,*Z*)-azine **61** and the dihydro-1,3-oxazole **62** [29][5]). The same products were obtained by thermolysis of **9** in THF at 50°, as judged from TLC and the ^{1}H-NMR spectra of the crude mixture.

Formation of (diastereoisomeric) azines and of hetero-substituted azines from diazirines and from diazo compounds is well known [2] [75–83]. Azines result from the reaction of carbenes with the parent diazirine or diazo compound [79] [84–88] or by (stereoselective) dimerization of diazo compounds with loss of N_2 [89] [90]. Diazo compounds may be formed even from donor-substituted diazirines [91] [92]. We found no evidence for the formation of an intermediate diazo compound, but cannot exclude the rearrangement of some **1** to the corresponding diazo compound. Complete rearrangement of **1** in MeOH can be excluded, as the disappearance of the UV absorption at 350 nm during thermolysis is of first order (*cf.* [93]).

The ready isomerization of the (*E*,*Z*)-lactone azine **58** to the (*Z*/*Z*)-isomer **56** and the exclusive formation, at higher temperatures, of the (*Z*,*Z*)-isomers from the diazirines **4** and **9** demonstrate the relative stability of these isomers, which is in keeping with the preferred (*Z*)-configuration of lactone hydrazones [46] [94], lactone semicarbazones [95], lactone oximes [44] [60] [96], and lactam oximes [97], but differs from the preferred conformation of ester azines [98]. The conformation of acyclic alkoxyazines is presumably similar to the one of acyclic imino ethers [99] and characterized by a N=C–O–C angle of 0°, which leads to a stabilizing n(O)-donor→σ*(C–N)-acceptor interaction ('generalized anomeric effect'). Such a conformation is inaccessible to cyclic alkoxyazines (= lactone azines), but favored in ester azines [98], where it will lead, in the (*Z*)-isomers, to a destabilizing 1,5-interaction. The (*Z*)-configuration of lactone azines, however, may be stabilized by a n(N)-donor→σ*(C–O)-acceptor interaction, while the (*E*)-isomers are destabilized by a 1,5-interaction with the equatorial substituent at C(2) [45] [60].

The benzyloxy glucal **59** is formed by a [1,2-H] shift in the intermediate carbene. Intramolecular [1,2-H] shifts are rapid for singlet alkyl carbenes [100], but considerably slowed down for donor-substituted carbenes with reduced electrophilic character. This is also valid for the alkoxy-carbenes derived from 1-aziglycoses, in spite of the axial orientation of H–C(2) [101] and the expected stabilization by the BnO–C(2) group of the positive charge which is developed at C(2) in the transition state of the [1,2-H] shift [102–105], factors which should both facilitate such a shift. A similar behavior is found for other resonance-stabilized carbenes [102] [106] [107].

The C=N bonds of **56** and **57** absorb at 1645 and 1635 cm^{-1}, respectively. In the ^{1}H-NMR spectra, the small values of J(2,3) (1.7 (**56**), 1.6 (**57**), and 1.6 and 2.2 Hz (**58**)) and of J(3,4) (4.7 (**56**), 3.8 (**57**), and 4.1 and 4.6 Hz (**58**)) are similar to the values for tetra-*O*-benzyl-D-gluconhydroximolactone [44] [60] and for the lactone oxime **21** which adopt a $B_{2,5}$ to $^1S_5$ conformation and indicate the presence of an sp^2-configurated C(1). The signal of H–C(5) appears at a relatively low field (4.67 (**56**), 4.70 (**57**), and 4.7–4.6 ppm (**58**)) as for the corresponding hydroximolactone derivatives. Since **56** and **57** have a C_2 axis, the two pyranosylidene moieties give rise to only one set of signals in the NMR spectra, whereas **58** shows two sets (*Table 2*). The CI-MS spectra of **56** and **57** are characterized by

[5]) This dihydro-oxazole is the main product of the thermolysis of **4** in the presence of i-PrOH at 50°. The rationalization of the formation of **62** by an intermolecular protonation of the carbene, followed by attack of the lone-pair of the carbonyl O-atom on the intermediate oxocarbenium ion is in keeping with the increased yield of **62** in the presence of a proton source [29].

$[M + 1]^+$ at m/z 1073.6. Acidic hydrolysis of **56** gave 2,3,4,6-tetra-*O*-benzyl-D-gluconolactone. The constitution of the pivaloylated lactone azine **60** is evidenced by elemental analysis, the MS, showing $[M + 1]^+$ at m/z 1025, and the absence of a signal for an anomeric H in the ^{1}H-NMR spectrum. The azine function is characterized by an IR band at 1660 cm^{-1}. The ^{1}H-NMR spectrum shows the typical coupling constants (*Table 2*) of a flattened $^4C_1$. The IR bands of **61** at 3440, 1660, and 1495 cm^{-1} evidence the presence of an acetamido group. The band at 1660 cm^{-1} is very broad due to the absorption of the C=N bond. The signals at m/z 791 ($[M + 1]^+$) and 683 ($[M - OBn]^+$) in the CI-MS are in agreement with a molecular formula of $C_{44}H_{46}N_4O_{10}$. The ^{1}H- and ^{13}C-NMR spectra (*Tables 2* and *3*) show only one set of signals, in agreement with a symmetric structure of **61**. The chemical shift of H–C(2) (4.79 ppm) is typical for a lactone derivative; H–C(2) of the corresponding hydroximolactone resonates at 4.89 ppm [29]. The coupling constants evidence a flattened $^4C_1$ conformation.

The ^{13}C-NMR chemical shift values for C(1) (149.2 (**56**), 163.7 (**57**), 148.2 (**60**) and 149.1 ppm (**61**)) confirm the sp^2-hybridization. By analogy to the δ values for C(1) of a (*Z*)- and (*E*)-hydroximolactone phosphate (157.3 and 169.3 ppm, resp.) [29], of (*Z*)- and (*E*)-hydroximolactones (150.2 and 158.6 ppm, resp.) [45], and (*Z*)- and (*E*)-lactone tosylimines (171.4 and 176.5 ppm, resp.) [94], the (*Z,Z*)-configuration is assigned to **56**, **60**, and **61** and the (*E,E*)-configuration to **57**. This assignment is also in agreement with the C(1) chemical shift of a gluconolactone semicarbazone (147.9 ppm), of which the (*Z*)-configuration was determined by X-ray analysis [95]. In addition, the signal for C(2) of the (*E,E*)-azine **57** is shifted upfield by 6.6 ppm (γ-effect), whereas C(2) of **60** and **61** exhibits similar chemical shifts as for the corresponding lactone oximes. H–C(2) of **57** resonates at lower field than H–C(2) of **56** ($\Delta\delta$ = 1.34 ppm). This is again similar to what is found for hydroximolactones [44] [96] and related lactone hydrazones **13** [94] [108]. In the (*E,Z*)-azine **58**, H–C(2) of the (*E*)-configurated moiety resonates at 5.42 ppm and H–C(2) of the (*Z*)-configurated moiety at 4.19 ppm, in agreement with the values for the (*E,E*)-isomer on the one hand and the (*Z,Z*)-isomer on the other hand.

We thank the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basle, for generous support.

Experimental Part

General. See [29]. UV Spectra (determination of the kinetic parameters): MeOH solns., *Photal-MCPD-1100* spectrometer, immersion cell. ^{1}H-NMR: in ambiguous cases, signal assignment by homonuclear decoupling experiments. Mass spectra: CI (chemical ionization; NH_3), in special cases (indicated) by ESI (electrospray ionization).

*(E/Z)-2,3,4,6-Tetra-*O*-pivaloyl-*D*-glucose Oxime* (= *(E/Z)-2,3,4,6-Tetrakis-*O*-(2,2-dimethylpropanoyl)-*D*-glucose Oxime*; **11**). A soln. of $NH_2OH \cdot HCl$ (8 g, 115.12 mmol) in pyridine (31 ml) and H_2O (31 ml) was added dropwise to a soln. of **10** (15.7 g, 30.39 mmol) [40] in THF (170 ml) and MeOH (55 ml). The mixture was stirred for 3 d at 50°, concentrated to a small volume, and diluted with Et_2O. The org. phase was washed with 5% aq. HCl soln., sat. aq. $NaHCO_3$ soln., and H_2O, dried ($MgSO_4$), and evaporated. FC (hexane/Et_2O 1:2) afforded **11** (14.1 g, 87%; (*E*)/(*Z*) 3:1). Colorless foam. R_f (hexane/Et_2O 1:2) 0.39. $[\alpha]_D^{25}$ = +54.3 (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3580*w*, 3560*w* (sh), 3380*w* (br.), 2980*s*, 2940*m*, 2910*m*, 2880*m*, 1735*s*, 1720*s* (sh), 1690*w*, 1480*s*, 1460*m*, 1400*m*, 1360*m*, 1280*s*, 1150*s*, 1070*w*, 1035*m*, 990*w*, 995*w* (sh), 940*m*, 885*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.01 (br. *s*, exchangeable with D_2O, 0.25 H), 7.70 (br. *s*, exchangeable with D_2O, 0.75 H, NOH); 7.35 (*d*, *J* = 5.0, 0.75 H), 6.58 (*d*, *J* = 6.1, 0.25 H, H–C(1)); 6.06 (*t*, *J* = 6.2, 0.25 H), 5.48 (*dd*, *J* = 5.9, 8.4, 0.75 H, H–C(2)); 5.67 (*dd*, *J* = 3.9, 6.3, 0.25 H), 5.64 (*dd*, *J* = 1.9, 8.4, 0.75 H, H–C(3)); 5.14 (*dd*, *J* = 1.9, 8.8, 0.75 H), 5.11 (*dd*, *J* = 3.8, 8.0, 0.25 H, H–C(4)); 4.17 (*dd*, *J* = 2.6, 11.9, 0.25 H), 4.14 (*dd*, *J* = 2.4, 12.0, 0.75 H, H–C(6)); 3.99 (*dd*, *J* = 5.5, 12.0, H'–C(6)); 3.77 (*m*, 0.25 H), 3.66 (*m*, 0.75 H, H–C(5)); 3.13 (*d*, *J* = 5.4, exchange with D_2O, 0.75 H), 2.99 (*d*, *J* = 5.5, exchange with D_2O, 0.25 H, OH–C(5)); 1.23–1.17 (several *s*, 4 *t*-Bu). ^{13}C-NMR (150 MHz, $CDCl_3$): (*E*)-isomer: 178.59 (*s*); 178.29 (*s*); 176.92 (*s*); 176.79 (*s*); 145.68 (*s*); 70.21 (*d*); 69.58 (*d*); 68.89 (*d*); 68.36 (*d*); 64.39 (*t*); 39.19–38.90 (several *s*); 27.13–26.98 (several *q*); (*Z*)-isomer: 178.70 (*s*); 177.82 (*s*); 177.01 (*s*); 176.87 (*s*); 146.21 (*s*); 69.97 (*d*); 69.88 (*d*); 68.85 (*d*); 65.19 (*d*); 64.65 (*t*). CI-MS: 533 (14), 532 (44, $[M + 1]^+$), 515 (23), 514 (84), 499 (32), 431 (26), 430 (100), 412 (13), 385 (14), 328 (17), 103 (10). Anal. calc. for $C_{26}H_{45}NO_{10}$ (531.65): C 58.74, H 8.53, N 2.63; found: C 58.88, H 8.65, N 2.88.

*2,3,4,6-Tetra-*O*-pivaloyl-*D*-gluconhydroximo-1,5-lactone* (**12**). A soln. of **11** (10.1 g, 18.81 mmol) in abs. CH_2Cl_2 (100 ml) at −20° was treated under N_2 with DBU (3.07 ml, 20.61 mmol). NCS (2.77 g, 20.7 mmol) was added in small portions over 5 min. The mixture was stirred for 10 min at −20°, warmed to r.t., diluted with CH_2Cl_2 (200 ml), and washed with H_2O (200 ml). The org. layer was dried ($MgSO_4$) and evaporated. FC (hexane/Et_2O 1:1)

yielded **12** (7.9 g, 79%). Colorless hygroscopic foam. R_f (hexane/Et_2O 1:2) 0.54. $[\alpha]_D^{25} = +63.1$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 3580*m*, 3450*w* (br.), 3340*w* (br.), 3030*w* (sh), 2970*s*, 2930*m*, 2910*m*, 2870*m*, 1755*s* (sh), 1740*s*, 1720*s* (sh), 1700*m* (sh), 1680*m*, 1480*m*, 1460*m*, 1395*m*, 1365*m*, 1340*w*, 1265*s*, 1150*s* (sh), 1130*s*, 1095*s* (sh), 1030*m*, 1000*m*, 985*m*, 950*m* (sh), 940*m*, 900*w*, 880*w*. ^{1}H-NMR (400 MHz, C_6D_6): 6.69 (br. *s*, exchange with D_2O, NOH); 5.73 (*d*, $J = 7.3$, H–C(2)); 5.45 (*t*, $J = 7.6$, H–(3)); 5.33 (*dd*, $J = 7.7$, 10.2, H–(4)); 4.15 (*dd*, $J = 1.9$, 12.8, H–C(6)); 4.08 (*dd*, $J = 4.1$, 12.8, H′–C(6)); 3.64 (*ddd*, $J = 1.9$, 4.1, 10.2, H–C(5)); 1.20 (*s*), 1.16 (*s*), 1.11 (*s*), 1.07 (*s*, 4 *t*-Bu). ^{1}H-NMR (300 MHz, $CDCl_3$): 6.77 (br. *s*, exchange with D_2O, NOH); 5.45 (*m*, H–C(2)); 5.25 (*m*, H–C(3), H–C(4)); 4.42 (*m*, H–C(5), H–C(6)); 4.23 (*dd*, $J = 4.5$, 13.1, H′–C(6)); 1.23 (*s*), 1.22 (*s*), 1.18 (*s*), 1.17 (*s*, 4 *t*-Bu). ^{13}C-NMR (50 MHz, C_6D_6): 177.63 (*s*); 176.58 (*s*); 176.07 (*s*); 148.47 (*s*); 75.33 (*d*); 72.22 (*d*); 68.00 (*d*); 67.38 (*d*); 61.20 (*t*); 38.98 (*s*); 38.84 (*s*); 38.74 (*s*); 27.14 (*q*); 27.09 (*q*); 26.98 (*q*). ^{13}C-NMR (50 MHz, $CDCl_3$): 177.90 (*s*); 176.49 (*s*); 176.16 (*s*); 175.96 (*s*); 148.58 (*s*); 74.93 (*d*); 71.48 (*d*); 67.40 (*d*); 67.27 (*d*); 61.06 (*t*); 38.91 (*s*); 38.79 (*s*); 38.68 (*s*); 27.04 (*q*); 26.96 (*q*); 26.93 (*q*). CI-MS: 531 (29), 530 (100, $[M + 1]^+$), 107 (57), 92 (29), 91 (16). Anal. calc. for $C_{26}H_{43}NO_{10} \cdot 0.75\ H_2O$ (543.14): C 57.50, H 8.26, N 2.58; found: C 57.34, H 8.34, N 2.39.

*(2,3,4,6-Tetra-*O*-pivaloyl-*D*-glucopyranosylidene)amino Trifluoromethanesulfonate* (**13**). Et_3N (5.97 ml, 42.83 mmol) and Tf_2O (5.34 ml, 32.54 mmol) were added through a syringe to a cooled (0°) soln. of **12** (10.0 g, 18.88 mmol) in benzene (700 ml). The mixture was warmed to r.t., stirred for 30 min, and filtered through SiO_2 (360 g, toluene) to give pure (TLC) **13** (11.54 g, 92%), which was recrystallized in MeOH. Colorless fine needles. R_f (hexane/Et_2O 1:2) 0.72 M.p. 166° (dec.). $[\alpha]_D^{25} = +48.8$ ($c = 1.08$, $CHCl_3$). IR ($CHCl_3$): 2970*m*, 2940*m*, 2910*m*, 2870*w*, 1745*s*, 1720*m* (sh), 1650*w* (br)., 1480*m*, 1460*m*, 1425*s*, 1400*m*, 1365*m*, 1275*m*, 1150*s* (sh), 1135*s*, 1115*s* (sh), 1030*m* (sh), 1010*m* (sh), 990*w* (sh), 940*w*, 885*w* (sh), 850*s*, 830*m* (sh). ^{1}H-NMR (400 MHz, C_6D_6): 5.45 (*d*, $J = 7.7$, H–C(2)); 5.41 (*t*, $J = 7.8$, H–C(3)); 5.10 (*dd*, $J = 7.8$, 10.0, H–C(4)); 4.00 (*dd*, $J = 5.2$, 12.9, H–C(6)); 3.92 (*dd*, $J = 2.0$, 12.9, H′–C(6)); 3.64 (*ddd*, $J = 2.0$, 5.2, 10.1, H–C(5)); 1.16 (*s*), 1.06 (*s*), 1.03 (*s*, 4 *t*-Bu). ^{1}H-NMR (300 MHz, $CDCl_3$): 5.52 (*d*, $J = 5.9$, H–C(2)); 5.34 (*t*, $J = 6.0$, H–C(3)); 5.26 (*dd*, $J = 6.0$, 9.7, H–C(4)); 4.64 (*ddd*, $J = 2.0$, 4.2, 9.7, H–C(5)); 4.39 (*dd*, $J = 2.0$, 13.0, H–C(6)); 4.27 (*dd*, $J = 4.3$, 13.0, H′–C(6)); 1.24 (*s*), 1.19 (*s*), 1.17 (*s*, 4 *t*-Bu). ^{13}C-NMR (50 MHz, C_6D_6): 177.54 (*s*); 176.39 (*s*); 175.92 (*s*); 159.11 (*s*); 77.99 (*d*); 70.37 (*d*); 66.90 (*d*); 66.04 (*d*); 60.75 (*t*); 38.82 (*s*); 38.74 (*s*); 27.02 (*q*); 26.96 (*q*); 26.85 (*q*). ^{13}C-NMR (50 MHz, $CDCl_3$): 177.65 (*s*); 176.28 (*s*); 176.06 (*s*); 175.61 (*s*); 158.33 (*s*); 118.64 (*q*, $J = 322.0$, CF_3); 77.20 (*d*); 70.27 (*d*); 66.71 (*d*); 66.50 (*d*); 60.30 (*t*); 38.94 (*s*); 38.88 (*s*); 38.78 (*s*); 38.74 (*s*); 26.98 (*q*); 26.90 (*q*); 26.87 (*q*); 26.84 (*q*). CI-MS: 664 (11), 663 (30), 662 (100, $[M + 1]^+$), 514 (14), 412 (13), 310 (48), 210 (20), 208 (21), 107 (70), 103 (57), 92 (20), 91 (22), 85 (11). Anal. calc. for $C_{27}H_{42}F_3NO_{12}S$ (661.69): C 49.01, H 6.40, N 2.12, S 4.85; found: C 49.13, H 6.28, N 2.36, S 5.09.

*1,5-Anhydro-1-hydrazi-2,3,4,6-tetra-*O*-pivaloyl-*D*-glucitol* (**15**). At −25°, a sat. soln. of NH_3 in MeOH (95 ml) was added dropwise under N_2 to a soln. of **13** (9.38 g, 14.18 mmol) in abs. CH_2Cl_2 (190 ml). The mixture was stirred at −25° for 2 h, kept at the same temp. for 12 h, diluted with CH_2Cl_2 (100 ml), and washed with brine. The aq. layer was extracted with CH_2Cl_2 and the combined org. phase dried ($MgSO_4$) and evaporated. FC (hexane/Et_2O 1:1) afforded **15** (5.36 g, 72%). Colorless foam. R_f (hexane/Et_2O 1:2) 0.50. $[\alpha]_D^{25} = +18.2$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3280*w*, 2960*m*, 2940*m* (sh), 2910*w* (sh), 2880*w*, 1740*s*, 1720*s* (sh), 1700*w* (sh), 1480*m*, 1460*m*, 1400*w*, 1365*m*, 1325*w*, 1270*m*, 1155*s* (sh), 1135*s*, 1085*m*, 1035*m*, 1005*w*, 995*w*, 970*w*, 940*w*, 910*w*, 890*w*. ^{1}H-NMR (400 MHz, C_6D_6): 5.87 (*d*, $J = 9.6$, H–C(2)); 5.47 (*m*, H–C(3), H–C(4)); 4.18 (*dd*, $J = 1.8$, 12.6, H–C(6)); 4.07 (*dd*, $J = 4.6$, 12.6, H′–C(6)); 3.88 (*ddd*, $J = 1.8$, 4.5, 9.9, H–C(5)); 2.13 (*d*, $J = 9.4$, exchangeable with D_2O, NH); 2.10 (*d*, $J = 9.6$, exchangeable with D_2O, NH); 1.18 (*s*), 1.15 (*s*), 1.14 (*s*), 1.03 (*s*, 4 *t*-Bu). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.66 (*m*, H–C(2)); 5.37 (*m*, H–C(3), H–C(4)); 4.17 (*dd*, $J = 2.0$, 12.5, H–C(6)); 4.12 (*dd*, $J = 3.7$, 12.5, H′–C(6)); 4.08 (*ddd*, $J = 2.0$, 3.7, 9.6, H–C(5)); 2.40 (*d*, $J = 9.4$, NH); 2.29 (*d*, $J = 9.4$, NH); 1.23 (*s*), 1.15 (*s*), 1.14 (*s*), 1.12 (*s*, 4 *t*-Bu). ^{13}C-NMR (50 MHz, C_6D_6): 177.39 (*s*); 176.87 (*s*); 176.11 (*s*); 175.67 (*s*); 82.11 (*s*); 75.06 (*d*); 72.58 (*d*); 67.78 (*d*); 66.26 (*d*); 61.19 (*t*); 38.90 (*s*); 38.80 (*s*); 38.61 (*s*); 27.23 (*q*); 27.15 (*q*); 26.94 (*q*). ^{13}C-NMR (50 MHz, $CDCl_3$): 177.86 (*s*); 177.05 (*s*); 176.11 (*s*); 81.70 (*s*); 74.56 (*d*); 71.80 (*d*); 67.17 (*d*); 65.79 (*d*); 60.93 (*t*); 38.85 (*s*); 38.71 (*s*); 38.64 (*s*); 27.05 (*q*); 26.98 (*q*); 26.86 (*q*). CI-MS: 530 (28), 529 (100, $[M + 1]^+$), 456 (6), 427 (7), 385 (6), 325 (6), 133 (6), 117 (13), 103 (13). Anal. calc. for $C_{26}H_{44}N_2O_9$ (528.65): C 59.07, H 8.39, N 5.30; found: C 59.18, H 8.60, N 5.12.

*1,5-Anhydro-1-azi-2,3,4,6-tetra-*O*-pivaloyl-*D*-glucitol* (**4**). A precooled (0°) soln. of I_2 (0.65 g, 2.56 mmol) in CH_2Cl_2 (20 ml) was added dropwise under N_2 over 10 min through a syringe to a cooled (0°) soln. of **15** (1.0 g, 1.89 mmol) and Et_3N (3 ml, 21.6 mmol) in abs. CH_2Cl_2 (30 ml). The soln. was stirred for 30 min at 0° and washed with cold 5% aq. $Na_2S_2O_3$ soln. and cold H_2O. The org. layer was dried ($MgSO_4$) and evaporated. The residue was dried at $0°/10^{-2}$ mbar for 30 min. FC (10 g, AcOEt/hexane 1:7) afforded **4** (919 mg, 92%) as a glassy oil after drying at $0°/10^{-2}$ mbar for 2 h. R_f (hexane/Et_2O 1:2) 0.76. $[\alpha]_D^{25} = +87.2$ ($c = 1.01$, $CHCl_3$). UV ($CHCl_3$): 252 (176), 340 (82), 351 (sh, 53). CD ($c = 6.76$ mM, $CHCl_3$): 353 (1.82), 341 (1.65), 308 (0), 296 (−0.15), 270 (0), 249 (0.22). FT-IR ($c = 3.46$, $CHCl_3$): 3030*w*, 2976*s*, 2937*m*, 2909*m*, 2874*m*, 1741*s*, 1568*w*, 1480*s*, 1462*m*, 1399*m*, 1371*m*, 1331*w*,

1280*s*, 1132*s*, 1090*m*, 1036*m*, 994*w*, 960*w*, 942*w*, 892*w*. ^{1}H-NMR (400 MHz, C_6D_6): 5.68 (*m*, H–C(2), H–C(3)); 5.39 (*m*, irrad. at 3.45→*d*, *J* = 8.2, H–C(4)); 3.94 (*dd*, *J* = 4.7, 12.8, H–C(6)); 3.84 (*dd*, *J* = 1.8, 12.7, H′–C(6)); 3.45 (*ddd*, *J* = 1.8, 4.7, 10.3, H–C(5)); 1.12 (*s*), 1.11 (*s*), 1.10 (*s*), 0.92 (*s*, 4 *t*-Bu). ^{1}H-NMR (300 MHz, $CDCl_3$): 5.62 (*t*, *J* = 9.0, H–C(3)); 5.56 (*d*, *J* = 8.7, H–C(2)); 5.35 (br. *t*, *J* = 8.9, H–C(4)); 4.10–4.00 (*m*, 2 H–C(6), H–C(5)); 1.18 (*s*), 1.17 (*s*), 1.12 (*s*), 1.00 (*s*, 4 *t*-Bu). ^{13}C-NMR (50 MHz, C_6D_6): 177.05 (*s*); 176.51 (*s*); 175.92 (*s*); 175.21 (*s*); 74.70 (*d*); 72.64 (*d*); 67.45 (*d*); 65.59 (*d*); 60.83 (*t*); 56.41 (*s*); 38.80 (*s*); 38.74 (*s*); 38.49 (*s*); 27.17 (*q*); 27.07 (*q*); 26.73 (*q*). ^{13}C-NMR (75 MHz, $CDCl_3$): 177.84 (*s*); 176.78 (*s*); 176.11 (*s*); 175.74 (*s*); 74.03 (*d*); 71.53 (*d*); 66.64 (*d*); 64.78 (*d*); 60.44 (*t*); 55.92 (*s*); 38.67 (*s*); 38.62 (*s*); 38.57 (*s*); 38.31 (*s*); 26.89 (*q*); 26.82 (*q*); 26.45 (*q*). CI-MS: 517 (13), 516 (45, $[M - N_2 + NH_4]^+$), 415 (22), 414 (100, $[M - N_2 - OPiv + NH_4]^+$), 296 (10), 295 (63), 102 (20). Anal. calc. for $C_{26}H_{42}N_2O_9$ (526.63): C 59.30, H 8.04, N 5.32; found: C 59.42, H 7.91, N 5.06.

Methanolysis of **4**. A soln. of **4** (699 mg) in MeOH (10 ml) was stored for 6 h at r.t. Evaporation and FC (hexane/Et_2O 4:1) gave **16** (519 mg, 59%) and **17** (88 mg, 10%; α-D/β-D 85:15).

*Methyl 2,3,4,6-Tetra-*O*-pivaloyl-*α*-D-glucopyranoside* [66] (**16**): R_f (hexane/Et_2O 1:2) 0.76. IR ($CHCl_3$): 3080*w*, 3050*w*, 3020*w* (sh), 2960*s*, 2930*s* (sh), 2900*m* (sh), 2870*m*, 1735*s*, 1555*w*, 1540*w*, 1520*w*, 1480*s*, 1460*s*, 1395*s*, 1370*s*, 1325*m* (sh), 1280*s*, 1225*m* (sh), 1190*s* (sh), 1165*s* (sh), 1135*s* (br.), 1080*s*, 1055*s*, 1035*s*, 1000*w*, 980*m*, 940*w*, 920*m*, 890*m*, 850*w*, 805*w*, 790*w*, 760*m*, 690*w*. ^{1}H-NMR (400 MHz, C_6D_6): 5.90 (*t*, *J* = 9.8, irrad. at 5.00→*d*, *J* = 9.4, H–C(3)); 5.33 (*dd*, *J* = 9.6, 10.2, H–C(4)); 5.00 (*dd*, *J* = 3.8, 10.2, H–C(2)); 4.91 (*d*, *J* = 3.8, irrad. at 5.00→*s*, H–C(1)); 4.22 (*dd*, *J* = 1.9, 12.3, H–C(6)); 4.13 (*dd*, *J* = 5.1, 12.2, H′–C(6)); 3.91 (*ddd*, *J* = 1.8, 5.0, 10.3, H–C(5)); 2.95 (*s*, MeO); 1.19 (*s*), 1.16 (*s*), 1.14 (*s*, 4 *t*-Bu). ^{13}C-NMR (50 MHz, C_6D_6): 177.24 (*s*); 177.04 (*s*); 176.57 (*s*); 176.26 (*s*); 96.95 (*d*); 71.57 (*d*); 70.06 (*d*); 68.26 (*d*); 68.13 (*d*); 62.02 (*t*); 55.13 (*q*); 38.87 (*s*); 38.76 (*s*); 27.34 (*q*); 27.24 (*q*); 27.16 (*q*); 27.11 (*q*). CI-MS: 550 (6), 549 (32), 548 (100, $[M + NH_4]^+$), 499 (7, $[M - MeO]^+$).

*Methyl 2,3,4,6-Tetra-*O*-pivaloyl-*β*-D-glucopyranoside* (**17**): R_f (hexane/Et_2O 1:2) 0.71. IR ($CHCl_3$): 3000*w* (sh), 2960*m*, 2930*m*, 2920*m* (sh), 2900*m* (sh), 2870*w*, 1740*s*, 1555*w*, 1540*w*, 1520*w*, 1480*s*, 1460*s*, 1395*m*, 1365*m*, 1280*s*, 1260*m* (sh), 1230*m*, 1205*m* (sh), 1180*s* (sh), 1160*s* (sh), 1140*s* (sh), 1100*s* (sh), 1065*s*, 1045*s*, 1035*s* (sh), 1005*m*, 940*w*, 910*w*, 890*m*, 800*m* (br.), 760*m*, 660*w*, 645*w*, 610*w*. ^{1}H-NMR (400 MHz, C_6D_6): 5.37 (*t*, *J* = 9.5, H–C(3)); 5.27 (*dd*, *J* = 8.0, 9.6, irrad. at. 3.89→*d*, *J* = 9.6, H–C(2)); 5.20 (*t*, *J* ≈ 9.7, H–C(4)); 4.21 (*dd*, *J* = 1.8, 12.2, H–C(6)); 4.02 (*dd*, *J* = 5.5, 12.2, H′–C(6)); 3.89 (*d*, *J* = 7.9, H–C(1)); 3.17 (*ddd*, *J* = 1.8, 5.4, 10.2, H–C(5));

Table 2. *Selected ^{1}H-NMR* ($CDCl_3$) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of* **4–9**, **11–40**, **43–49**, **54–58**, **60**, *and* **61**

	(*E*)-**11**	(*Z*)-**11**	**12**[a])	**13**[a])	**15**[a])	**4**[a])	**4**	**16**[a])	**17**[a])	**60**[a])
H–C(1)	7.35	6.58	–	–	–	–	–	4.91	3.89	–
H–C(2)	5.48	6.06	5.73	5.45	5.87	5.68	5.56	5.00	5.27	5.72
H–C(3)	5.64	5.67	5.45	5.41	5.47	5.68	5.62	5.90	5.37	5.57
H–C(4)	5.14	5.11	5.33	5.10	5.47	5.39	5.35	5.33	5.20	5.39
H–C(5)	3.66	3.77	3.64	3.64	3.88	3.45	4.10–4.00	3.91	3.17	3.76
H–C(6)	4.14	4.17	4.15	4.00	4.18	3.94	4.10–4.00	4.22	4.21	4.25–4.20
H′–C(6)	3.99	3.99	4.08	3.92	4.07	3.84	4.10–4.00	4.13	4.02	4.25–4.20
MeO	–	–	–	–	–	–	–	2.95	3.16	–
OH or	7.70	8.01	–	–	2.13[b])	–	–	–	–	–
NH	3.13	2.99			2.10[b])					
J(1,2)	5.9	6.1	–	–	–	–	–	3.8	8.0	–
J(2,3)	8.4	6.3	7.3	7.7	9.6	[c])	8.7	10.2	9.6	8.1
J(3,4)	1.9	3.9	7.7	7.8	[c])	8.2	9.0	9.6	9.5	8.5
J(4,5)	8.8	8.0	10.2	10.0	9.9	10.3	9.0	10.2	10.2	10.1
J(5,6)	2.4	2.6	1.9	5.2	1.8	4.7	[c])	1.9	1.8	2.2
J(5,6′)	5.5	5.5	4.1	2.0	4.6	1.8	[c])	5.1	5.5	3.3
J(6,6′)	12.0	11.9	12.8	12.9	12.6	12.8	[c])	12.3	12.2	[c])

	α-D-**18**	β-D-**18**	α-D-**19**	β-D-**19**	(*E*)-**20**	(*Z*)-**20**	**21**	**21**[d])	**22**[d])
H–C(1)	4.79	4.56	5.19[e])	[c])	7.49	6.93	–	–	–
H–C(2)	3.56	3.49	3.59	3.41	4.45	4.45	4.06	4.10	4.16
H–C(3)	4.06	3.74	4.00	3.69	3.98–3.85	3.98–3.85	4.00	3.99	3.58

Table 2 (cont.)

	α-D-**18**	β-D-**18**	α-D-**19**	β-D-**19**	(*E*)-**20**	(*Z*)-**20**	**21**	**21**[d])	**22**[d])
H–C(4)	3.59	3.67	3.775	3.77	3.68	3.72	3.865	3.73	4.41
H–C(5)	3.88	3.39	4.07	3.45	3.98–3.85	3.98–3.85	4.60–4.51	4.51	3.50
H_{eq}–C(6)	4.24	4.33	4.33	4.28	4.20	4.21	4.60–4.51	4.37	4.25
H_{ax}–C(6)	3.68	3.78	3.65	3.68	3.48	3.50	3.85	3.62	3.66
ArC*H*	5.51	5.53	5.52	5.53	5.33	5.37	5.52	5.27	5.37
MeO	3.82	3.81	3.82	3.82	3.79	3.79	3.82	3.48	3.49
OH or	–	–	3.10[e])	3.23[f])	7.59–7.55,	7.80–7.75,	7.07	6.51	6.66
NH					2.00	2.14			
MsO	–	–	–	–	–	–	–	–	–
J(1,2)	3.7	7.7	3.7	7.7	7.8	7.1	–	–	–
J(2,3)	9.3	8.6	8.9	8.4	6.7	[c])	0.7	0.7	3.7
J(3,4)	9.3	9.0	9.2	9.5	3.4	3.5	6.6	6.6	10.0
J(4,5)	9.7	9.9	9.6	9.1	9.3	9.3	9.5	10.1	9.4
J(5,6eq)	4.8	5.0	5.0	4.9	5.2	5.2	[c])	5.3	4.6
J(5,6ax)	10.1	10.3	10.2	9.8	10.3	10.3	10.1	10.1	10.2
J(6eq,6ax)	10.2	10.5	10.4	10.2	10.7	10.6	10.5	10.5	10.1

	23[d])	**24**[d])	**25**	**5**	α-D-**26**	β-D-**27**	**28**[g])	**29**[g])	**30**[d])
H–C(1)	–	–	–	–	4.59	4.35	–		6.18[h])
H–C(2)	4.12	4.15	4.11	4.13	3.55	3.44	4.62	4.02	4.71
H–C(3)	3.98	3.54	3.88–3.80	4.07	4.04	3.67	3.96	3.98	4.26[h])
H–C(4)	3.66	4.33	3.88–3.80	3.85–3.82	3.585	3.74	3.92	3.88	3.93
H–C(5)	4.49	3.46	3.88–3.80	3.85–3.82	3.87–3.78	3.44–3.38	4.50–4.41	4.37	3.77
H_{eq}–C(6)	4.23	4.135	4.33	4.21–4.18	4.25	4.35	4.50–4.41	4.56	4.21
H_{ax}–C(6)	3.48	3.53	3.73	3.65	3.69	3.78	3.76	3.86	3.62
ArC*H*	5.21	5.27	5.57	5.56	5.56	5.56	5.53	5.53	5.38
MeO	3.47	3.48	3.83	3.83	3.82, 3.40	3.82, 3.59	3.82	3.82	3.49
OH or	–	–	2.84[b]),	–	–	–	–	–	–
NH			2.34[b])						
MsO	2.72	2.71	–	–	–	–	–	–	–
J(1,2)	–	–	–	–	3.7	7.6	–	–	6.0
J(2,3)	0.7	3.8	8.1	8.5	9.4	8.9	0	2.2	2.0
J(3,4)	6.6	9.8	[c])	8.4	9.3	9.3	6.6	7.1	7.4
J(4,5)	10.2	9.4	[c])	[c])	9.3	9.8	9.1	9.9	10.1
J(5,6eq)	5.4	3.7	4.0	[c])	4.6	5.0	[c])	5.2	5.0
J(5,6ax)	10.2	10.0	9.7	9.9	10.2	9.9	11.8	10.0	10.1
J(6eq,6ax)	10.6	10.0	10.6	9.9	10.0	10.4	11.8	10.3	10.3

	(*E*)-**35**	(*Z*)-**35**	**36**[a])	**37**[a])	**38a**[a])	**38b**[a])	**7**[a])	**40**[a])
H–C(1)	7.58	7.05	–	–	–	–	–	3.86
H–C(2)	4.46	5.27	4.27	3.99	3.24	3.40	2.94	3.79
H–C(3)	4.08	4.13	3.48	3.23	3.56	3.91	4.10	3.48
H–C(4)	3.84	3.85–3.82	4.45	4.27	4.45	4.42	4.40–4.36	4.38
H–C(5)	3.94–3.91	4.06–4.03	3.32	3.15	3.81	3.25	3.83–3.75	3.15
H_{eq}–C(6)	4.25	4.27	4.04	3.93	4.11	4.04	4.19–4.12	4.25
H_{ax}–C(6)	3.52	3.53	3.41	3.25	3.52	3.52	3.83–3.75	3.69
PhC*H*	5.36	5.39	5.14	5.03	5.27	5.26	5.65	5.31
OH or	8.23,	8.60,	6.68	–	2.35[b]),	1.82[b]),	–	–
NH	2.06	2.46			1.18[b])	1.77[b])		
J(1,2)	7.8	7.1	–	–	–	–	–	0
J(2,3)	6.2	4.8	3.7	3.7	3.2	3.2	3.6	3.0
J(3,4)	2.9	3.8	10.0	10.0	9.8	9.8	9.9	9.9

Table 2 (cont.)

	(*E*)-**35**	(*Z*)-**35**	**36**[a])	**37**[a])	**38a**[a])	**38b**[a])	**7**[i])	**40**[a])
J(4,5)	9.5	[c])	9.6	9.5	9.4	9.4	[c])	9.5
J(5,6eq)	5.2	5.3	4.5	4.6	4.9	4.9	[c])	9.2
J(5,6ax)	10.2	10.4	10.0	10.0	10.2	10.0	[c])	10.2
J(6eq,6ax)	10.6	10.6	10.0	10.2	10.2	10.3	[c])	10.3

	(*E*)-**43**	(*Z*)-**43**	**44**	**45**	**46**	**47a/47b**	**8**	**48/49**
H–C(1)	7.41	6.69	3.79	–	–	–	–	4.68, 4.71
H–C(2)	5.00	5.26	4.05	4.86	4.68	4.65, 4.25	4.35	4.26, 3.45
H–C(3)	4.06	4.25	3.51	3.78	3.80	3.61	3.77	3.79–3.59, 4.06
H–C(4)	3.71–3.59	3.71–3.59	3.62	3.89	3.89	3.94	3.94	3.79–3.59
H–C(5)	3.97–3.90	3.97–3.90	3.50	4.33	4.31	3.60	3.86	3.79–3.59
H–C(6)	3.71–3.59	3.71–3.59	3.74	3.78	3.76	3.75	3.76	3.79–3.59
H′–C(6)	3.71–3.59	3.71–3.59	3.67	3.74	3.71	3.68	3.64	3.79–3.59
MeO	–	–	–	–	–	–	–	3.33, 3.48
AcN	1.90	1.85	1.77	1.88	1.80	1.79, 1.82	1.64	1.84, 1.86
OH or NH	7.63, 2.95	8.22, 2.87	6.62, 5.37	7.33	–	2.33, 2.50[b]), 1.95, 2.26[b])	–	–
AcN*H*	6.33	6.49	4.85	6.19	5.90	5.19, 6.07	4.88	5.29, 5.51
J(1,2)	4.0	5.4	9.4	–	–	–	–	3.7, 7.7
J(2,3)	2.9	1.7	10.4	6.5	7.0	10.2, 6.6	8.5	10.1, 9.5
J(3,4)	5.2	4.7	8.5	6.3	6.6	8.8	7.0	[c]), 7.9
J(4,5)	[c])	[c])	9.6	6.2	7.3	9.9	7.5	[c])
J(5,6)	[c])	[c])	2.1	4.7	3.6	4.1	4.3	[c])
J(5,6′)	[c])	[c])	5.3	4.1	4.0	2.1	3.2	[c])
J(6,6′)	[c])	[c])	10.6	11.0	11.1	11.0	10.9	[c])
J(2,NH)	7.9	6.9	8.0	8.5	8.2	9.5, 8.3	8.1	9.3, 8.1

	54	**55**	**61**	**56**	**57**	**58**
H–C(1)	4.61	4.55	–	–	–	–
H–C(2)	4.27	4.18–4.09	4.79	4.28	5.64	4.19, 5.72
H–C(3)	4.05	4.18–4.09	4.41	3.93	3.94	3.94, 3.97
H–C(4)	3.72	3.74	3.97	3.82	3.80–3.76	3.92–3.77
H–C(5)	4.39–4.28	4.10	4.43	4.62	4.70	4.70–4.30
H–C(6)	4.39–4.28	4.41	4.25	3.72	3.86	3.92–3.77
H′–C(6)	3.80–3.72	3.81	3.75	3.72	3.80–3.76	3.92–3.77
PhC*H*	5.56	5.55	5.54	–	–	–
MeO	3.41	3.47	–	–	–	–
AcN	1.83	1.86	1.94	–	–	–
AcN*H*	5.99	5.70	6.27	–	–	–
J(1,2)	4.5	8.1	–	–	–	–
J(2,3)	3.7	[c])	3.0	1.7	1.7	2.2, 1.5
J(3,4)	2.6	2.1	1.5	4.7	3.8	4.7, 4.1
J(4,5)	9.4	9.5	9.8	10.3	10.1	[c])
J(5,6)	[c])	5.1	5.1	3.2	1.9	[c])
J(5,6′)	[c])	10.3	10.4	3.2	4.5	[c])
J(6,6′)	[c])	10.4	10.4	[c])	11.2	[c])
J(2,NH)	9.3	8.8	7.2	–	–	–

[a]) In C_6D_6. [b]) *J*(NH,N′H) = 9.2 (**38a**, **38b**, **47a**) or 9.4 Hz (**15**, **25**, **47b**). [c]) Not determined. [d]) In $CDCl_3/C_6D_6$ 1:1. [e]) *J*(1,OH) = 2.1 Hz. [f]) *J*(1,OH) = 5.5 Hz. [g]) Same numbering as for **5**. [i]) In CD_2Cl_2 at −40°. [h]) $^4J(1,3)$ = 1.5 Hz.

3.16 (*s*, MeO); 1.19 (*s*), 1.16 (*s*), 1.15 (*s*), 1.15 (*s*, 4 *t*-Bu). ^{13}C-NMR (50 MHz, C_6D_6): 177.45 (*s*); 177.03 (*s*); 176.16 (2*s*); 102.14 (*d*); 72.77 (*d*); 72.54 (*d*); 71.44 (*d*); 68.35 (*d*); 61.99 (*t*); 56.25 (*q*); 38.87 (*s*); 38.80 (*s*); 27.31 (*q*); 27.16 (*q*). CI-MS: 550 (5), 549 (29), 548 (100, $[M + NH_4]^+$), 499 (13, $[M - MeO]^+$).

*Allyl 2,3-Di-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-*α*/*β*-*D*-glucopyranoside* (**18**). A 4:1 mixture of allyl α/β-D-glucopyranoside was transformed into a 4:1 mixture of α/β-D-**18** by methoxybenzylidenation and benzylation [41]. FC (60 g, AcOEt/hexane 1:8) of a sample (841 mg) gave crystalline β-D-**18** (66 mg), impure α-D-**18** (44 mg, oil), and crystalline α-D-**18** (522 mg).

Data of α/β-D-**18** 4:1: M.p. 85–95° (AcOEt/hexane). IR ($CHCl_3$): 3090*w*, 3070*w*, 3000*w*, 2930*m*, 2870*m*, *2850m (sh)*, *1615m*, *1590w* (sh), *1515w*, *1500w*, *1455m*, *1370m*, *1305m*, *1170s*, *1085s*, *1030s*, *995s*, *935m*, *830m*. ^{13}C-NMR (50 MHz, $CDCl_3$): α-D-anomer: 159.90 (*s*); 138.77 (*s*); 138.15 (*s*); 133.57 (*d*); 129.86 (*s*); 128.29–127.23 (several *d*); 118.16 (*t*); 113.47 (2*d*); 101.13 (*d*); 96.71 (*d*); 82.09 (*d*); 79.21 (*d*); 78.53 (*d*); 75.19 (*t*); 73.46 (*t*); 68.87 (*t*); 68.39 (*t*); 62.49 (*d*); 55.16 (*q*); β-D-anomer: 133.8 (*d*); 117.4 (*t*); 103.0 (*d*); 100.9 (*d*); 81.4 (*d*); 80.8 (*d*); 78.7 (*d*); 75.3 (*t*); 75.0 (*t*); 70.6 (*t*); 68.6 (*t*); 66.0 (*d*). CI-MS (NH_3): 520 (38), 519 (100, $[M + 1]^+$).

Data of α-D-**18**. R_f (AcOEt/hexane 1:6) 0.20. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44–7.24 (*m*, 12 arom. H); 6.92–6.88 (*m*, 2 arom. H); 5.94 (*dddd*, *J* = 5.5, 6.6, 10.3, 17.2, 1 olef. H); 5.51 (*s*, ArC*H*); 5.33 (*qd*, *J* = 1.5, 17.2, 1 olef. H); 5.24 (*qd*, *J* = 1.2, 10.3, 1 olef. H); 4.91 (*d*, *J* = 11.3, PhC*H*); 4.83 (*d*, *J* ≈ 11.4, 2 PhC*H*); 4.79 (*d*, *J* = 3.7, H–C(1)); 4.68 (*d*, *J* = 12.1, PhC*H*); 4.24 (*dd*, *J* = 4.8, 10.1, H_{eq}–C(6)); 4.19 (*tdd*, *J* = 1.4, 5.2, 12.9, 1 allyl. H); 4.06 (*t*, *J* = 9.3, H–C(3)); 4.03 (*tdd*, *J* = 1.2, 6.7, 12.9, 1 allyl. H); 3.88 (*dt*, *J* = 4.7, 9.9, H–C(5)); 3.82 (*s*, MeO); 3.68 (*t*, *J* = 10.2, H_{ax}–C(6)); 3.59 (*t*, *J* = 9.4, H–C(4)); 3.56 (*dd*, *J* = 3.8, 9.3, H–C(2)).

Data of β-D-**18** [41a]. R_f (AcOEt/hexane 1:6) 0.22. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44–7.26 (*m*, 12 arom. H); 6.92–6.88 (*m*, 2 arom. H); 5.97 (*dddd*, *J* = 5.3, 5.9, 10.5, 17.2, 1 olef. H); 5.53 (*s*, ArC*H*); 5.35 (*qd*, *J* = 1.6, 17.2, 1 olef. H); 5.22 (*qd*, *J* = 1.4, 10.5, 1 olef. H); 4.91 (*d*, *J* = 10.8, PhC*H*); 4.90 (*d*, *J* = 11.4, PhC*H*); 4.79 (*d*, *J* = 11.4, PhC*H*); 4.77 (*d*, *J* = 10.8, PhC*H*); 4.56 (*d*, *J* = 7.7, H–C(1)); 4.41 (*tdd*, *J* = 1.5, 5.3, 12.8, 1 allyl. H); 4.33 (*dd*, *J* = 5.0, 10.4, H_{eq}–C(6)); 4.16 (*tdd*, *J* = 1.4, 6.0, 12.8, 1 allyl. H); 3.81 (*s*, MeO); 3.78 (*t*, *J* = 10.3, H_{ax}–C(6)); 3.74 (*t*, *J* = 8.8, H–C(3)); 3.67 (*t*, *J* = 9.0, H–C(4)); 3.49 (*t*, *J* ≈ 8.2, H–C(2)); 3.39 (*ddd*, *J* = 5.0, 9.0, 9.9, H–C(5)).

*2,3-Di-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-*D*-glucopyranose* (**19**). KO(*t*-Bu) (7.46 g, 2.25 equiv.) was added at r.t. to crude **18** (15.66 g, 29.56 mmol; α-D/β-D 4:1 in DMSO (250 ml)). The mixture was warmed under N_2 to 50° for 1 h (red→dark brown), poured onto ice/H_2O (400 ml), distributed between AcOEt and H_2O, and processed as usual to yield the yellow, crystalline isomerization product (15.7 g, 98.3%).

I_2 (21.64 g, 2 equiv.) was added in 1 portion at r.t. to a soln. of the above material in THF (540 ml), H_2O (135 ml), and pyridine (13.75 ml, 4 equiv.). After 10 min, the starting material had disappeared (TLC, AcOEt/toluene 1:5). The mixture was treated at 0° with 10% aq. Na_2SO_3 soln. (100 ml), stirred for 10 min, and extracted with AcOEt. The org. layer was washed with 1M Na_2SO_3, sat. $NaHCO_3$ soln., H_2O, and brine, dried (Na_2SO_4), treated with Et_3N, concentrated to *ca.* 100 ml, and poured into stirred hexane (1000 ml). The precipitate was filtered off, suspended twice in hexane, and filtered to yield light brown crystals (17.11 g) and mother liquor (7.42 g). FC (300 g, CH_2Cl_2/MeOH 99:1→98:2) and recrystallization in toluene gave **19** (13.63 g). FC of the mother liquors afforded further **19** (2.13 g). Total yield 15.76 g (77.3%). M.p. 165–166° (AcOEt/hexane). R_f (toluene/AcOEt 4:1) 0.25. $[\alpha]_D^{25} = -36.1$ (*c* = 0.98, $CHCl_3$; after equilibration for 1 h). IR ($CHCl_3$): 3595*w*, 3350*w* (br.), 3090*w*, 3070*w*, 3040*w*, 3000*w*, 2940*m*, 2910*m*, 2875*m*, 2840*m*, 1615*m*, 1590*w*, 1515*w*, 1500*w*, 1465*w* (sh), 1455*m*, 1370*m*, 1305*m*, 1170*m*, *1090s*, *1030s*, *995s*, *910w*, *815m*. ^{1}H-NMR (300 MHz, $CDCl_3$; α-D/β-D 55:45): 7.45–7.24 (*m*, 2 arom. H); 6.93–6.88 (*m*, 2 arom. H); 5.53 (*s*, 0.45 H), 5.52 (*s*, 0.55 H, ArC*H*); 5.19 (*dd*, *J* = 2.2, 3.7, addn. of CD_3OD→*d*, *J* = 3.7, 0.55 H, H–C(1)); 4.96–4.70 (*m*, addn. of CD_3OD→change of signals, 4 PhC*H*, 0.45 H, H–C(1)); 4.33 (*dd*, *J* = 5.0, 10.4, 0.45 H), 4.28 (*dd*, *J* = 4.9, 10.2, 0.55 H, H_{eq}–C(6)); 4.07 (*dt*, *J* = 4.9, 9.9, 0.55 H), 3.45 (*dt*, *J* = 5.0, 10.0, 0.45 H, H–C(5)); 4.00 (*t*, *J* = 9.2, 0.55 H), 3.69 (*t*, *J* = 9.0, 0.45 H, H–C(3)); 3.82 (*s*, MeO); 3.775 (*t*, *J* = 9.3, 0.45 H), 3.77 (*t*, *J* = 9.5, 0.55 H, H–C(4)); 3.68 (*t*, *J* = 10.0, 0.45 H), 3.65 (*t*, *J* = 10.3, 0.55 H, H_{ax}–C(6)); 3.59 (*dd*, *J* = 3.8, 8.9, 0.55 H), 3.41 (*dd*, *J* = 7.7, 8.4, 0.45 H, H–C(2)); 3.23 (*d*, *J* = 5.5, exchange with D_2O, 0.45 H), 3.10 (*d*, *J* = 2.1, exchange with D_2O, 0.55 H, OH–C(1)). ^{13}C-NMR (50 MHz, (D_6)DMSO; α-D/β-D 40:60): α-D-anomer: 159.44 (*s*); 138.95 (*s*); 138.56 (*s*); 131.10 (*s*); 128.48–126.95 (several *d*); 113.38 (2*d*); 100.30 (*d*); 90.87 (*d*); 81.42 (*d*); 79.61 (*d*); 77.47 (*d*); 73.60 (*t*); 71.61 (*t*); 68.27 (*t*); 61.77 (*d*); 55.06 (*q*); β-D-anomer: 159.44 (*s*); 138.78 (2*s*); 130.06 (*s*); 128.48–126.95 (several *d*); 113.38 (2*d*); 100.13 (*d*); 97.24 (*d*); 83.19 (*d*); 80.91 (*d*); 80.44 (*d*); 73.98 (*t*); 73.60 (*t*); 67.92 (*t*); 65.19 (*d*); 55.06 (*q*). CI-MS (NH_3): 480 (30), 479 (100, $[M + 1]^+$), 371 (9), 360 (23). Anal. calc. for $C_{28}H_{30}O_7$ (478.54): C 70.28, H 6.32; found: C 70.25, H 6.51.

*2,3-Di-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-*D*-glucose Oximes* (**20**). $NH_2OH \cdot HCl$ (19.95 g, 287.1 mmol) was added under N_2 to a soln. of Na (5.89 g, 256.2 mmol) in MeOH (311 ml). The mixture was stirred for 15 min at r.t. and 30 min at 0° and filtered. The residue was washed with MeOH (186 ml). The combined filtrate and washings were added to **19** (11.55 g, 14.14 mmol), and the mixture was stirred at 55–60° for 3 h. After evaporation, the

Table 3. *Selected* ^{13}C*-NMR* (50.6 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of* **4**, **5**, **7**, **8**, **11–23**, **25**, **30**, **35–38**, **40**, **43–49**, **54–57**, **60**, *and* **61**

	(*E*)-**11**[a])	(*Z*)-**11**[a])	**12**	**13**[b])	**15**	**4**	**16**[c])	**17**[c])	**60**[c])		
C(1)	145.68	146.21	148.58	158.33	81.70	55.92	96.95	102.14	148.24		
C(2)	68.89	65.19	67.40[d])	66.71[d])	65.79[d])	64.64[d])	68.26[d])	71.44[d])	66.93		
C(3)	70.21	69.97	74.93[e])	77.20[e])	74.56[e])	74.03[e])	71.57[d])	72.54[d])	71.96		
C(4)	69.58	69.88	71.48[e])	70.27[e])	71.80[e])	71.53[e])	68.13[d])	68.35[d])	68.97		
C(5)	68.36	68.85	67.27[d])	66.50[d])	67.17[d])	64.78[d])	70.06[d])	72.77[d])	75.59		
C(6)	64.39	64.65	61.06	60.30	60.93	60.44	62.02	61.99	61.30		
MeO	–	–	–	–	–	–	55.13	56.25	–		
	α-D-**18**	β-D-**18**	α-D-**19**[f])	β-D-**19**[f])	(*E*)-**20**[f])	**21**	**22**	**23**	**25**[a])	**5**[a])	**30**
C(1)	96.71	103.0	90.87	97.24	147.23	150.73	151.14	156.77	[g])	[g])	144.36
C(2)	79.21[d])	78.7	79.61[d])	80.44[d])	77.16[d])	80.27[d])	76.42	79.72	76.4	74.8	102.28
C(3)	78.53[d])	81.4[d])	77.61[d])	83.19	76.74[d])	75.42	72.64	74.48	81.1	81.1	73.11
C(4)	82.09	80.8[d])	81.42	80.91[d])	80.65	81.28[d])	77.05	80.83	81.1	81.1	79.89
C(5)	62.49	66.0	61.77	65.19	60.05	63.53	71.51	66.64	68.3	67.9	68.63
C(6)	68.39[e])	68.6	68.27	67.92	70.23	68.56	68.05	68.03	68.3	67.9	68.31
Ar*C*H	101.13	100.9	100.30	100.13	99.99	101.40	101.71	101.50	101.2	101.4	101.17
MeO	55.16	55.16	55.06	55.06	55.06	56.23	55.26	55.21	55.3	55.4	55.25
AllO or MsO	68.87[e]), 133.57, 118.16	70.6, 133.8, 117.4	–	–	–	–	–	36.06	–	–	–
	(*E*)-**35**[a])	(*Z*)-**35**[a])	**36**	**37**	**38a**/**38b**		**7**[h])	**40**			
C(1)	149.93	150.43	151.12	155.39	82.53, 82.24		56.14	103.12			
C(2)	75.33	70.14	72.60	71.86[d])	78.09, 77.33[d])		76.29[d])	75.63[d])			
C(3)	77.18	77.75	76.27[d])	75.16[e])	78.62, 78.14[d])		77.62[d])	77.57[d])			
C(4)	80.53	80.75	77.00[d])	76.03[e])	78.19[d])		77.88[d])	78.41[d])			
C(5)	61.73	62.25	71.42	71.31[d])	69.83, 69.00		69.61	67.34			
C(6)	70.93	70.93	68.03	67.34	68.33		67.94	68.37			
Ph*C*H	101.09	101.15	101.65	101.39	101.70		101.82	101.14			
	(*E*)-**43**	(*Z*)-**43**	**44**	**45**	**46**	**47**[a])	**8**[a])				
C(1)	148.21	149.84	91.70	151.51	158.54	81.75	56.48				
C(2)	49.97	46.38	51.72	49.24	49.24	49.24	48.87				
C(3)	79.26[d])	78.84[d])	83.30	79.13	79.95[d])	82.04	79.34				
C(4)	79.84[d])	81.67[d])	78.34	78.62	78.26[d])	77.74	77.00				
C(5)	69.70	70.01	75.45	73.64	75.37	76.47	76.73				
C(6)	71.78	71.66	69.24	68.25	68.71	67.96	67.56				
AcNH	169.15, 22.87	169.51, 22.73	170.24, 23.10	170.49, 22.95	169.71, 22.72	170.85, 23.23	169.58, 22.80				
	54	**55**	**61**	**56**[a])	**57**[a])						
C(1)	98.30	101.11	149.07	149.2	163.7						
C(2)	48.93	51.82	50.89	74.2	67.6						
C(3)	73.82	75.85	74.64	81.8	80.4						
C(4)	79.70	80.13	78.56	77.6	77.8						
C(5)	57.62	63.72	67.73	75.6	75.4						
C(6)	69.22	69.14	68.34	68.9	69.0						
Ph*C*H	101.95	101.95	102.22	–	–						
MeO	55.91	56.52	–	–	–						
AcNH	169.22, 22.97	169.31, 23.17	169.56, 23.07	–	–						

[a]) Assignment based upon $^1H,^{13}C$-COSY or a $^1H,^{13}C$-HMQC spectrum. [b]) CF_3 at 118.64 ppm ($J(C,F) = 322.0$ Hz). [c]) In C_6D_6. [d])[e]) Assignment may be reversed. [f]) In (D_6)DMSO. [g]) Not determined. [h]) In CD_2Cl_2 at −40°.

residue was distributed between CH_2Cl_2 and H_2O and the org. phase processed as usual: crude **20** (11.81 g, 99%), showing two spots on TLC. This material was used for the next step. M.p. 143–144°. R_f (toluene/AcOEt 4:1) 0.07, 0.13. $[\alpha]_D^{25} = -16.5$ ($c = 1.14$, $CHCl_3$). IR ($CHCl_3$): 3580*m*, 3340*m* (br.), 3100*w*, 3070*w*, 3000*w*, 2910*w*, 2860*m*, 1615*m*, 1590*w*, 1515*w*, 1500*w*, 1455*m*, 1385*m*, 1355*m* (sh), 1305*m*, 1175*m*, 1130*m* (sh), 1085*s*, 1035*s*, 930*m*, 880*w*, 830*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; (*E*)/(*Z*) 4:1): 7.80–7.75 (br. *s*, exchange with D_2O, 0.2 H), 7.59–7.55 (br. *s*, exchange with D_2O, 0.8 H, NOH); 7.49 (*d*, $J = 7.8$, 0.8 H), 6.93 (*d*, $J = 7.1$, 0.2 H, H–C(1)); 7.39–7.29 (*m*, 12 arom. H); 6.88–6.84 (*m*, 2 arom. H); 5.37 (*s*, 0.2 H), 5.33 (*s*, 0.8 H, ArC*H*); 4.82 (*d*, $J = 11.8$, 0.8 H), 4.79 (*d*, $J = 11.7$, 0.2 H, PhC*H*); 4.70 (*d*, $J = 11.8$, 0.8 H), 4.64 (*d*, $J = 11.8$, 0.2 H, PhC*H*); 4.68 (*d*, $J = 11.4$, PhC*H*); 4.55 (*d*, $J = 11.6$, 0.2 H), 4.51 (*d*, $J = 11.5$, 0.8 H, PhC*H*); 4.45 (*dd*, $J = 6.7$, 7.7, H–C(2)); 4.21 (*dd*, $J = 5.2$, 10.6, 0.2 H), 4.20 (*dd*, $J = 5.2$, 10.7, 0.8 H, H_{eq}–C(6)); 3.98–3.85 (*m*, H–C(3), H–C(5)); 3.79 (*s*, MeO); 3.72 (*dd*, $J = 3.5$, 9.3, 0.2 H), 3.68 (*dd*, $J = 3.4$, 9.3, 0.8 H, H–C(4)); 3.50 (*t*, $J = 10.5$, 0.2 H), 3.48 (*t*, $J = 10.5$, 0.8 H, H_{ax}–C(6)); 2.14 (*d*, $J = 3.8$, exchange with D_2O, 0.2 H), 2.00 (*d*, $J = 4.1$, exchange with D_2O, 0.8 H, OH–C(5). ^{13}C-NMR (50 MHz, (D_6)DMSO; (*E*)-isomer): 159.31 (*s*); 147.23 (*d*); 138.63 (*s*); 138.18 (*s*); 130.39 (*s*); 128.19–127.25 (several *d*); 113.24 (2*d*); 99.99 (*d*); 80.65 (*d*); 77.16 (*d*); 76.74 (*d*); 74.02 (*t*); 71.08 (*t*); 70.23 (*t*); 60.05 (*t*); 55.06 (*d*). CI-MS (NH_3): 512 (12), 511 (26, $[M + NH_4]^+$), 495 (39), 494 (100, $[M + 1]^+$), 476 (21), 358 (20), 307 (12). Anal. calc. for $C_{28}H_{31}NO_7$ (493.56): C 68.14, H 6.33, N 2.84; found: C 68.39, H 6.57, N 2.76.

Oxidation of **20**. a) DBU (97%; 3.835 ml, 1.15 equiv.) was added within 5 min to a soln. of crude **20** (11.0 g, 22.48 mmol) in cold (–40°) CH_2Cl_2 (210 ml). The mixture was stirred for 5 min. Freshly recrystallized NCS (5 portions of 687 mg, 1.15 equiv.) was added within 15 min. The mixture was stirred for 30 min at –40°, allowed to warm to r.t., diluted with CH_2Cl_2 (50 ml), and worked up as described above, to yield **21**/**22** 9:1 (11.57 g) which crystallized during FC (250 g, CH_2Cl_2→CH_2Cl_2/MeOH 99:1→CH_2Cl_2/MeOH 9:2). The crystalline material (10.61 g, 96%) was recrystallized in CH_2Cl_2/hexane to afford **21** (9.10 g, 92%).

b) Similarly, oxidation of **20** (2 g) with NCS (595 mg, 1.1 equiv.) and DBU (664 µl, 1.1 equiv.) at –40° for 1 h yielded 2.084 g of crude material. FC (40 g, AcOEt/hexane 1:1) yielded **21** (738 mg, almost pure) and **22** (799 mg, containing 7% of **21** (^{1}H-NMR)).

c) At 60°, **20** (200 mg) and NaOAc (55.4 mg, 1.66 equiv.) were dissolved in EtOH (9.5 ml) and treated with a soln. of $NaIO_4$ (174 mg, 2 equiv.) in H_2O (3.3 ml). The same amounts of NaOAc and $NaIO_4$ were added after 30 h. After 48 h, the temp. was raised to 80° and the mixture stirred for further 24 h. Not all **20** had disappeared, but the mixture was filtered and worked up as above to yield **21**/**22** (193.7 mg, yellow oil).

Data of (E)*-2,3-Di-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-*D*-gluconhydroximo-1,5-lactone* (**21**). M.p. 157–158° (CH_2Cl_2/hexane). R_f (toluene/AcOEt 4:1) 0.33. $[\alpha]_D^{25} = +2.4$ ($c = 1.11$, $CHCl_3$). IR ($CHCl_3$): 3580*w*, 3300*w*, 3000*w*, 2940*w*, 2870*w*, 2840*w*, 1725*m*, 1670*m*, 1615*m*, 1590*w*, 1515*w*, 1500*w*, 1465*m* (sh), 1455*m*, 1370*m*, 1305*m*, 1290*m*, 1175*m*, 1125*s* (sh), 1100*s* (sh), 1085*s*, 1035*s* (sh), 1005*m*, 970*m*, 935*m*, 890*w*, 870*w*, 815*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.43–7.26 (*m*, 12 arom. H); 7.07 (*s*; exchange with D_2O, NOH); 6.93–6.88 (*m*, 2 arom. H); 5.52 (*s*, ArC*H*); 4.67 (*d*, $J = 11.8$, PhC*H*); 4.60–4.51 (*m*, H–C(5), H_{eq}–C(6)); 4.56 (*s*, PhCH_2); 4.43 (*d*, $J = 11.8$, PhC*H*); 4.06 (*d*, $J = 0.7$, H–C(2)); 4.00 (*dd*, $J = 0.7$, 6.6, H–C(3)); 3.865 (*dd*, $J = 6.6$, 9.5, H–C(4)); 3.85 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.82 (*s*, MeO). ^{1}H-NMR (300 MHz, $CDCl_3/C_6D_6$ 1:1): 7.39–7.33 (*m*, 2 arom. H); 7.25–7.11 (*m*, 10 arom. H); 6.81–6.77 (*m*, 2 arom. H); 6.51 (*s*, exchange with D_2O, irrad. at 4.10→NOE of 1%, NOH); 5.27 (*s*, irrad. at 3.62→NOE of 11%, ArC*H*); 4.58 (*d*, $J = 11.9$, irrad. at 4.10→NOE of 2%, PhC*H*); 4.51 (*dt*, $J = 5.3$, 10.1, irrad. at 3.62→NOE of 4%, H–C(5)); 4.44 (*s*, irrad. at 4.10→NOE of 4.5%, PhCH_2); 4.37 (*dd*, $J = 5.4$, 10.5, irrad. at 3.62→NOE of 26%, H_{eq}–C(6)); 4.35 (*d*, $J = 11.9$, irrad. at 4.10→NOE of 4%, PhC*H*); 4.10 (*d*, $J = 0.7$, irrad. at 6.51→NOE of 2%, H–C(2)); 3.99 (*dd*, $J = 0.8$, 6.6, irrad. at 4.10→NOE of 5%, H–C(3)); 3.73 (*dd*, $J = 6.6$, 10.1, irrad. at 3.62→NOE of 3.5%, H–C(4)); 3.62 (*t*, $J = 10.3$, H_{ax}–C(6)); 3.48 (*s*, MeO). ^{13}C-NMR (50 MHz, $CDCl_3$): 160.12 (*s*); 150.73 (*s*); 137.23 (*s*); 136.83 (*s*); 129.27 (*s*); 128.42–127.25 (several *d*); 113.56 (2*d*); 101.40 (*d*); 81.28 (*d*); 80.27 (*d*); 75.24 (*d*); 71.78 (*t*); 70.40 (*t*); 68.56 (*t*); 63.53 (*d*); 56.23 (*q*). CI-MS (NH_3): 493 (33), 492 (100, $[M + 1]^+$), 391 (29). Anal. calc. for $C_{28}H_{29}NO_7$ (491.54): C 68.42, H 5.95, N 2.85; found: C 68.59, H 6.14, N 2.98.

Data of (Z)*-2,3-Di-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-*D*-gluconhydroximo-1,5-lactone* (**22**). Containing *ca.* 7% of (*E*)-isomer **21**. R_f (toluene/AcOEt 4:1) 0.27. IR ($CHCl_3$): 3580*m*, 3300*w*, 3000*w*, 2940*m*, 2915*m*, 2875*m*, 2840*m*, 1725*w*, 1660*m*, 1615*m*, 1590*w*, 1515*w*, 1495*w*, 1455*m*, 1370*m*, 1305*m* (sh), 1280*m* (sh), 1250*s*, 1170*m*, 1095*s*, 1080*s* (sh), 1060*s*, 1000*m* (sh), 965*m*, 935*m*, 830*m*. ^{1}H-NMR (300 MHz, $CDCl_3/C_6D_6$ 1:1): 7.41–7.34 (*m*, 2 arom. H); 7.27–7.11 (*m*, 10 arom. H); 6.82–6.78 (*m*, 2 arom. H); 6.66 (*s*, exchange with D_2O, NOH); 5.37 (*s*, ArC*H*); 4.70 (*d*, $J = 12.3$, irrad. at 4.16→NOE of 2%, PhC*H*); 4.54 (*d*, $J = 12.3$, irrad. at 4.16→NOE of 2%, PhC*H*), 4.45 (*d*, $J \approx 12.6$, irrad. at 4.16→NOE of 6%, 2 PhC*H*); 4.41 (*t*, $J = 9.7$, irrad. at 4.16→NOE of 1%, H–C(4)); 4.25 (*dd*, $J = 4.6$, 10.1, H_{eq}–C(6)); 4.16 (*d*, $J = 3.7$, H–C(2)); 3.66 (*t*, $J = 10.2$, H_{ax}–C(6)); 3.58 (*dd*, $J = 3.7$, 10.0, irrad. at 4.16→NOE of 10%, H–C(3)); 3.50 (*ddd*, $J = 4.7$, 9.4, 10.1, H–C(5)); 3.49 (*s*, MeO).

^{13}C-NMR (50 MHz, $CDCl_3$): 160.07 (*s*); 151.14 (*s*); 137.71 (*s*); 137.09 (*s*); 129.45 (*s*); 128.61–126.94 (several *d*); 113.59 (2*d*, 101.71 (*d*); 77.05 (*d*); 76.42 (*d*); 72.64 (*d*); 72.32 (*t*); 71.51 (*d*); 70.58 (*t*); 68.05 (*t*); 55.26 (*q*).

(E)-[2,3-Di-O-benzyl-4,6-O-(4-methoxybenzylidene)-D-glucopyranosylidene]amino Methanesulfonate (**23**). A stirred soln. of Et_3N (228 µl, 2.7 equiv.) and **21** (3.00 g, 6.10 mmol) in CH_2Cl_2 (125 ml) at 0° was treated with MsCl (710 µl, 1.5 equiv.). After 30 min at 0°, the mixture was worked up as described above, yielding crude **23** (3.589 g, 103%). FC (225 g, AcOEt/hexane 1:1) and drying of the product at 0° yielded pure, spontaneously crystallizing **23** (3.12 g, 90%). M.p. 140–141° (dec.). R_f (toluene/AcOEt 9:1) 0.41. $[\alpha]_D^{25} = -20.2$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 3020*w* (br.), 2940*w*, 2875*w*, 2840*w*, 1650*m*, 1615*m*, 1590*w*, 1515*w*, 1500*w*, 1455*w*, 1370*s*, 1320*m* (sh), 1300*m*, 1250*m*, 1175*m* (sh), 1125*m* (sh), 1100*s* (sh), 1085*s*, 1035*m* (sh), 1000*m*, 970*s*, 910*m*, 885*w*, 865*m*, 830*s*. ^{1}H-NMR (300 MHz, $CDCl_3/C_6D_6$ 1:1): 7.36–7.31 (*m*, 2 arom. H); 7.25–7.11 (*m*, 10 arom. H); 6.82–6.77 (*m*, 2 arom. H); 5.21 (*s*, ArC*H*); 4.56 (*d*, $J = 12.0$, PhC*H*); 4.49 (*dt*, $J = 5.4$, 10.2, H–C(5)); 4.41 (*d*, $J = 12.1$, PhC*H*); 4.36 (*d*, $J = 11.8$, PhC*H*); 4.35 (*d*, $J = 12.0$, PhC*H*); 4.23 (*dd*, $J = 5.4$, 10.6, H_{eq}–C(6)); 4.12 (*d*, $J = 0.7$, H–C(2)); 3.98 (*dd*, $J = 0.8$, 6.6, H–C(3)); 3.66 (*dd*, $J = 6.6$, 10.2, H–C(4)); 3.48 (*t*, $J = 10.4$, H_{ax}–C(6)); 3.47 (*s*, MeO); 2.72 (*s*, MsO). ^{13}C-NMR (50 MHz, $CDCl_3$): 160.19 (*s*); 156.77 (*s*); 136.86 (*s*); 136.05 (*s*); 131.90 (*s*); 128.89–127.38 (several *d*); 113.56 (2*d*); 101.50 (*d*); 80.83 (*d*); 79.72 (*d*); 74.48 (*d*); 71.92 (*t*); 70.88 (*t*); 68.03 (*t*); 66.64 (*d*); 55.21 (*q*); 36.06 (*q*). ESI-MS (Na): 592 (100, $[M + Na]^+$). Anal. calc. for $C_{29}H_{31}NO_9S$ (569.63): C 61.15, H 5.49, N 2.46; found: C 61.23, H 5.34, N 2.42.

(Z)-[2,3-Di-O-benzyl-4,6-O-(4-methoxybenzylidene)-D-glucopyranosylidene]amino Methanesulfonate (**24**). Similarly as above, **22** (300 mg, 0.61 mmol), Et_3N (228 µl, 2.7 equiv.), and MsCl (71 µl, 1.5 equiv.) yielded **24** (303 mg, 87%) as a colorless foam which turned yellow upon standing and decomposed slowly at r.t. R_f (toluene/AcOEt 9:1) 0.30. ^{1}H-NMR (300 MHz, $CDCl_3/C_6D_6$ 1:1): 7.40–7.32 (*m*, 2 arom. H); 7.28–7.05 (*m*, 10 arom. H); 6.83–6.78 (*m*, 2 arom. H); 5.27 (*s*, ArC*H*), 4.72 (*d*, $J = 12.2$, PhC*H*); 4.56 (*d*, $J = 12.4$, PhC*H*); 4.49 (*d*, $J = 12.2$, PhC*H*); 4.46 (*d*, $J = 12.4$, PhC*H*); 4.33 (*t*, $J = 9.7$, H–C(4)); 4.15 (*d*, $J = 3.8$, H–C(2)); 4.135 (*dd*, $J \approx 3.6$, 10.0, H_{eq}–C(6)); 3.54 (*dd*, $J = 3.9$, 9.8, H–C(3)); 3.53 (*t*, $J = 10.2$, H_{ax}–C(6)); 3.48 (*s*, MeO); 3.46 (*dt*, $J = 3.8$, 10.0, H–C(5)); 2.71 (*s*, MsO).

1,5-Anhydro-2,3-di-O-benzyl-1-hydrazi-4,6-O-(4-methoxybenzylidene)-D-glucitol (**25**). A soln. of NH_3 in MeOH (64 ml) saturated at 0° was added at −20° to a slurry of **23** (615 mg, 1.08 mmol) in MeOH (13 ml). The suspension was stirred for 30 min at 0° and treated with CH_2Cl_2 (24 ml). The resulting colorless soln. was kept for 113 h at 0°, concentrated at r.t. to 25 ml, and kept at 0° for 3 h. The crystals were filtered off, washed with cold MeOH, and dried over night at 0°/10^{-6} mbar to yield **25** (349 mg). A second crop (67 mg, total yield 78.5%) was obtained by concentrating the mother liquor. M.p. 130–132° (MeOH). R_f (CH_2Cl_2/MeOH 98:2) 0.24. $[\alpha]_D^{25} = -20.4$ ($c = 1.04$, $CHCl_3$). IR (CH_2Cl_2): 3275*w*, 3000*w*, 2940*w*, 2910*m*, 2870*m*, 2870*m*, 2845*w*, 1615*m*, 1590*w*, 1515*w*, 1500*w*, 1465*w* (sh), 1455*w*, 1395*w* (sh), 1370*m*, 1330*m*, 1305*m*, 1270*m*, 1250*s*, 1170*m*, 1130*s*, 1090*s*, 1030*s*, 995*m*, 970*m*, 930*w* (sh), 915*w*, 865*w*, 830*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.43 (*d*, $J = 8.6$, 2 arom. H); 7.40–7.30 (*m*, 10 arom. H); 6.92 (*d*, $J = 8.7$, 2 arom. H); 5.57 (*s*, ArC*H*); 4.94 (*d*, $J = 11.2$, PhC*H*); 4.84 (*d*, $J = 10.6$, PhC*H*); 4.80 (*d*, $J = 11.3$, PhC*H*); 4.75 (*d*, $J = 10.6$, PhC*H*); 4.33 (*dd*, $J = 4.0$, 10.6, H_{eq}–C(6)); 4.11 (*d*, $J = 8.1$, H–C(2)); 3.88–3.80 (*m*, 3 H); 3.83 (*s*, MeO); 3.73 (*t*, $J = 10.0$, H_{ax}–C(6)); 2.84 (*d*, $J = 9.4$, exchange with D_2O, NH); 2.34 (*d*, $J = 9.4$, exchange with D_2O, NH). ^{13}C-NMR (150 MHz, $CDCl_3$; from ^{1}H,^{13}C-COSY): 128.3 (several *d*); 127.4 (2*d*); 113.6 (2*d*); 101.2 (*d*, ArCH); 81.1 (2*d*, C(3), C(4)); 76.4 (*d* and *t*, C(2), PhCH_2); 75.3 (*t*, PhCH_2); 68.3 (*d* and *t*, C(5), C(6)); 55.3 (*q*, MeO). CI-MS (NH_3): 492 (31), 491 (100, $[M + 1]^+$). Anal. calc. for $C_{28}H_{30}N_2O_6$ (490.56): C 68.56, H 6.16, N 5.71; found: C 68.48, H 6.37, N 5.64.

1,5-Anhydro-1-azi-2,3-di-O-benzyl-4,6-O-(4-methoxybenzylidene)-D-glucitol (**5**). A soln. of NH_3 in MeOH (52 ml) saturated at 0° was added at −20° to a slurry of **25** (501 mg, 0.88 mmol) in MeOH (11 ml). The suspension was stirred for 30 min 0° and treated with CH_2Cl_2 (20 ml). The resulting colorless soln. was kept for 65 h at 0°. The crystals obtained by evaporation of the solvents at 25° *in vacuo* were taken up in CH_2Cl_2 at 0° and washed at this temp. with H_2O. The dried ($MgSO_4$) org. phases were concentrated at 25° *in vacuo* to 10 ml. This soln. was diluted at 0° with cold CH_2Cl_2 (10 ml) and MeOH (42 ml), treated with Et_3N (486 µl, 4 equiv.), stirred for 5 min at 0°, treated dropwise within 30 min with a soln. of I_2 (246 mg, 1.1 equiv.) in CH_2Cl_2 (16 ml), and concentrated *in vacuo* to 20 ml, whereupon **5** crystallized. Storage at −20° for 2 h, filtration, washing of the crystals with cold MeOH (until colorless filtrate), and drying for 45 min over P_2O_5 at r.t. yielded **5** (305 mg, 71%). A further crop of **5** (33 mg, 7.7%) was obtained from the mother liquors. M.p. 77° (dec. with evolution of N_2). R_f (CH_2Cl_2) 0.53. $[\alpha]_D^{25} = +66.8$ ($c = 1.07$, $CHCl_3$). UV (CH_2Cl_2): 344 (95). CD (CH_2Cl_2, 275 K): 359 (+2.7 mdeg), 347 (+2.5 mdeg). IR ($CHCl_3$): 3095*w*, 3070*w*, 3000*w*, 2940*w*, 2910*w*, 2870*m*, 2845*w*, 1615*m*, 1590*w*, 1565*w*, 1515*w*, 1500*w*, 1455*w*, 1370*m*, 1305*m*, 1270*w*, 1170*s*, 1145*m* (sh), 1120*s* (sh), 1100*s*, 1085*s*, 1065*s* (sh), 1035*s*, 1000*m*, 975*m* (sh), 940*w*, 910*w*, 830*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.43 (*d*, $J = 8.0$, 2 arom. H); 7.34–7.18 (*m*, 10 arom. H); 6.93 (*d*, $J = 8.0$, 2 arom. H); 5.56 (*s*, ArC*H*); 4.93 (*d*, $J = 11.1$, PhC*H*); 4.81 (*d*, $J = 11.1$, PhC*H*); 4.30 (*d*, $J = 11.2$, PhC*H*); 4.21–4.18

(*m*, PhC*H*, H_{eq}–C(6)); 4.13 (*d*, *J* = 8.5, H–C(2)); 4.07 (*t*, *J* = 8.4, H–C(3)); 3.85–3.82 (*m*, H–C(4), H–C(5)); 3.83 (*s*, MeO); 3.65 (*t*, *J* = 9.9, H_{ax}–C(6)). ^{13}C-NMR (150 MHz, $CDCl_3$; from ^{1}H,^{13}C-COSY): 128.3 (several *d*); 127.4 (2*d*); 113.6 (2*d*); 101.4 (*d*, ArCH); 81.1 (2*d*, C(3), C(4)); 75.2 (*t*, PhCH_2); 74.8 (*d*, C(2)); 73.4 (*t*, PhCH_2); 67.9 (*d*, and *t*, C(5), C(6)); 55.4 (*q*, MeO). CI-MS (NH_3): 493 (14), 478 (13, $[M - N_2 + NH_4]^+$), 462 (29), 461 (100, $[M - N_2 + 1]^+$). Anal. calc. for $C_{28}H_{28}N_2O_6$ (488.54): C 68.84, H 5.78, N 5.73; found: C 68.71, H 6.00, N 5.80.

*Methyl 2,3-Di-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-α-*D*- and -β-*D*-glucoypyranoside* (**26** [41b, c] and **27**). A suspension of **5** (21.0 mg) in MeOH (5 ml) was shaken for 2 min at r.t. and filtered. The filtrate was used for the determination of the activation energy (see below). The solns. were then pooled, kept for 26 h at r.t., and evaporated to give a spontaneously crystallizing mixture **26**/**27** (45:55). M.p. 126–127° ([41b]: 143–144° for **26**). R_f (hexane/AcOEt 2:1) 0.60, 0.53. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.43–7.26 (*m*, 12 arom. H); 6.91 (*d*, *J* = 8.7, 2 arom. H); 5.53 (*s*, 0.55 H), 5.51 (*s*, 0.45 H, ArC*H*); 4.92–4.68 (*m*, 4 PhC*H*); 4.59 (*d*, *J* = 3.7, 0.45 H), 4.42 (*d*, *J* = 7.6, 0.55 H, H–C(1)); 4.35 (*dd*, *J* = 5.0, 10.4, 0.55 H), 4.25 (*dd*, *J* = 4.6, 9.9, 0.45 H, H_{eq}–C(6)); 4.04 (*t*, *J* = 9.3, 0.45 H), 3.67 (*t*, *J* = 9.1, 0.55 H, H–C(3)); 3.87–3.78 (*m*, 0.45 H), 3.44–3.38 (*m*, 0.55 H, H–C(5)); 3.82 (*s*, $MeOC_6H_4$); 3.78 (*t*, *J* = 10.1, 0.55 H), 3.69 (*t*, *J* = 10.2, 0.45 H, H_{ax}–C(6)); 3.74 (*t*, *J* = 9.5, 0.55 H), 3.585 (*t*, *J* = 9.3, 0.45 H, H–C(4)); 3.59 (*s*, 1.65 H), 3.40 (*s*, 1.35 H, MeO–C(1)); 3.55 (*dd*, *J* = 3.7, 9.4, 0.45 H), 3.44 (*t*, *J* ≈ 8.3, 0.55 H, H–C(2)).

Condensation of **5** *with Benzaldehyde*. CH_2Cl_2 (10 ml) was cooled to 0°, treated with **5** (54.5 mg, 0.11 mmol) and 4-Å molecular sieves (103 mg), and stirred for 30 min at 0°. After addition of Bu_3P (41 µl, 0.17 mmol) and benzaldehyde (13.5 µl, 0.12 mmol), the mixture was cooled to −70°, irradiated (quartz filter) for 3 h, then warmed up to r.t., and filtered. After evaporation, drying of the residue at r.t. *in vacuo* and FC (9 g, CH_2Cl_2/hexane 2:1) gave **29** (3.8 mg, 6%), **28** (4.9 mg, 8%), and **30** (3.1 mg, 8%).

*Data of (*E*)-2,6-Anhydro-3,4-di-*O*-benzyl-1-deoxy-5,7-*O*-(4-methoxybenzylidene)-1-phenyl-*D*-gluco-hept-1-enitol* (**28**). R_f (CH_2Cl/hexane 3:1) 0.20. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.45–7.41 (*m*, 2 arom. H); 7.35–7.16 (*m*, 13 arom. H); 7.03–6.99 (*m*, 2 arom. H); 6.93–6.89 (*m*, 2 arom. H); 6.43 (*s*, H–C(1)); 5.53 (*s*, ArC*H*); 4.62 (*s*, H–C(3)); 4.57 (*d*, *J* = 11.8, PhC*H*); 4.52 (*d*, *J* = 10.7, PhC*H*); 4.48 (*d*, *J* = 10.7, PhC*H*); 4.50–4.41 (*m*, H–C(6), H_{eq}–C(7)); 4.08 (*d*, *J* = 11.8, PhC*H*); 3.96 (*d*, *J* = 6.6, H–C(4)); 3.92 (*dd*, *J* = 6.7, 9.1, H–C(5)); 3.82 (*s*, MeO); 3.76 (*t*, *J* = 11.8, H_{ax}–C(7)).

*Data of (*Z*)-2,6-Anhydro-3,4-di-*O*-benzyl-1-deoxy-5,7-*O*-(4-methoxybenzylidene)-1-phenyl-*D*-gluco-hept-1-enitol* (**29**). R_f (CH_2Cl_2/hexane 3:1) 0.30. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.61–7.57 (*m*, 2 arom. H); 7.45–7.18 (*m*, 15 arom. H); 6.93–6.88 (*m*, 2 arom. H); 5.60 (*s*, H–C(1)); 5.53 (*s*, ArC*H*); 4.735 (*d*, *J* = 12.0, PhC*H*); 4.73 (*d*, *J* = 11.8, PhC*H*); 4.66 (*d*, *J* = 12.0, PhC*H*); 4.56 (*dd*, *J* = 5.2, 10.3, H_{eq}–C(7)); 4.52 (*d*, *J* = 11.8, PhC*H*); 4.37 (*dt*, *J* = 5.2, 10.0, H–C(6)); 4.02 (*d*, *J* = 2.2, H–C(3)); 3.98 (*dd*, *J* = 2.3, 7.1, H–C(4)); 3.88 (*dd*, *J* = 7.1, 9.9, H–C(5)); 3.86 (*t*, *J* = 10.3, H_{ax}–C(7)); 3.82 (*s*, MeO).

*Data of 1,5-Anhydro-3-*O*-benzyl-2-deoxy-4,6-*O*-(4-methoxybenzylidene)-*D*-arabino-hex-1-enitol* (**30**). R_f (CH_2Cl_2/hexane 3:1) 0.16. IR ($CHCl_3$): 3010*w*, 2940*w*, 2900*m*, 2880*m*, 2845*w*, 1645*m*, 1615*m*, 1590*w*, 1515*w*, 1465*w* (sh), 1455*m*, 1375*m*, 1305*m*, 1285*w*, 1170*m*, 1130*s*, 1100*s*, 1070*s*, 1035*s*, 1010*m*, 980*m*, 910*w*, 880*w*, 830*m*. ^{1}H-NMR (300 MHz, $CDCl_3/C_6D_6$ 1:1): 7.43–7.39 (*m*, 2 arom. H); 7.33–7.30 (*m*, 2 arom. H); 7.24–7.12 (*m*, 2 arom. H); 6.83–6.79 (*m*, 2 arom. H); 6.18 (*dd*, *J* = 1.5, 6.0, H–C(1)); 5.38 (*s*, ArC*H*); 4.73 (*d*, *J* ≈ 12.0, PhC*H*); 4.71 (*dd*, *J* = 2.0, 6.1, H–C(2)); 4.61 (*d*, *J* = 11.0, PhC*H*); 4.26 (*td*, *J* = 1.8, 7.4, H–C(3)); 4.21 (*dd*, *J* = 5.0, 10.3, H_{eq}–C(6)); 3.93 (*dd*, *J* = 7.4, 10.1, H–C(4)); 3.77 (*dt*, *J* = 4.9, 10.1, H–C(5)); 3.62 (*t*, *J* = 10.2, H_{ax}–C(6)); 3.49 (*s*, MeO). CI-MS (NH_3): 356 (23), 355 (100, $[M + 1]^+$). ^{13}C-NMR (50 MHz, $CDCl_3$): α-*D*-anomer: 160.04 (*s*); 144.36 (*d*); 138.47 (*s*); 129.79 (*s*); 128.41–127.34 (several *d*); 113.57 (2*d*); 102.28 (*d*); 101.17 (*d*); 79.89 (*d*); 73.11 (*d*); 71.92 (*t*); 68.63 (*d*); 68.31 (*t*); 55.25 (*q*).

Allyl α-*D*-*Mannopyranoside* (**31**). $BF_3 \cdot OEt_2$ (8.0 ml, 64 mmol) was added to a suspension of *D*-mannose (100 g, 556 mmol) in prop-2-enol. The mixture was kept at reflux for 4 h, and H_2O was removed by 4-Å molecular sieves, placed in a *Soxhlet* apparatus. After removal of the prop-2-enol, the crude was dissolved in H_2O, stirred for 12 h with charcoal (3 g), filtered through *Celite*, and lyophilized to give crude **31** (122 g).

*Allyl 4,6-*O*-Benzylidene-*α*-*D*-mannopyranoside* (**32**). Benzaldehyde dimethyl acetal (83 ml, 554 mmol) was added to a suspension of crude **31** (122 g, 554 mmol) in 1,4-dioxane (964 ml). The mixture was stirred at *ca.* 40 mbar for 45 min. After addition of $NaHCO_3$ (9.4 g), the solvent was evaporated, the residue treated with ice-water (470 ml) and extracted with AcOEt (3 × 400 ml), and the org. phase washed with H_2O, dried ($MgSO_4$), and evaporated. Crystallization from AcOEt/hexane gave **32** (101 g, 59% from mannose). M.p. 119–122° (56]: 148–149°).

*(*E*)- and (*Z*)-2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-*D*-mannose Oxime* (**35**). A mixture of **32** (1 g, 3.24 mmol), DMF (10 ml), and 4-Å molecular sieves was treated with NaH (234 mg, 9.75 mmol) at 0° and stirred for 30 min. BnBr (1.07 ml, 9.00 mmol) was slowly added at 0°. The mixture was stirred for 4 h, treated dropwise with MeOH (0.1 ml), poured onto ice-water (5 ml), and extracted with Et_2O (3 × 10 ml). The org. phase was washed with brine (2 × 5 ml), dried ($MgSo_4$), and evaporated: crude **33** (1.62 g).

A soln. of crude **33** (1.62 g, ca. 3.2 mmol) and KO(*t*-Bu) (1 g, 8.9 mmol) in DMSO (20 ml) was heated to 55° for 20 min, poured onto ice-water (40 ml), and extracted with Et_2O (3 × 40 ml). The org. phase was washed with brine (2 × 40 ml). Normal workup and drying of the residue under high vacuum yielded 1.55 g of crude material, which was dissolved in THF/H_2O 4:1 (35 ml) and treated with I_2 (1.65 g, 6.5 mmol) under vigorous stirring. Pyridine (1.05 ml, 13 mmol) was added immediately after I_2. The mixture was diluted with H_2O (35 ml) and extracted with $CHCl_3$ (2 × 90 ml). The org. phase was washed successively with freshly prepared 5% aq. $Na_2S_2O_5$ soln. (2 × 90 ml), sat. aq. Na_2CO_3 soln. (90 ml), and brine (2 × 90 ml), dried (Na_2SO_4), and evaporated: 1.48 g of crude **34** (1.48 g, α-D/β-D ≈ 3:1) [53].

A soln. of crude **34** (1.48 g, *ca.* 3.2 mmol) in EtOH (15 ml) was added to a suspension of Na (291 mg, 12.7 mmol) and $NH_2OH \cdot HCl$ (1.75 g, 25.2 mmol) in boiling EtOH (40 ml). The solvent was evaporated after 2 h. The residue was taken up in CH_2Cl_2 (70 ml) and H_2O (35 ml). Normal workup and crystallization from Et_2O/hexane at 35° yielded **35** (786 mg, 52% from **32**). FC (AcOEt/hexane 1:1) of the mother liquor gave additional pure **35** (333 mg, 22%). M.p. 137°. R_f (AcOEt/hexane 1:1) 0.32. $[\alpha]_D^{20} = -49.5$ (*c* = 1.09, $CHCl_3$). IR ($CHCl_3$): 3580*w*, 3347*w*, 3067*w*, 2932*w*, 2863*w*, 1496*w*, 1455*m*, 1398*m*, 1357*w*, 1310*w*, 1092*s*, 1028*s*, 983*m*, 918*m*. ^{1}H-NMR (400 MHz, $CDCl_3$, (*E*)/(*Z*) ≈ 4:1): (*E*)-isomer: 8.23 (br. *s*, NOH); 7.58 (*d*, *J* = 7.8, H–C(1)); 7.45–7.24 (*m*, 15 arom. H); 5.36 (*s*, PhC*H*); 4.81 (*d*, *J* = 11.6, PhC*H*); 4.69 (*d*, *J* = 11.8, PhC*H*); 4.65 (*d*, *J* = 11.6, PhC*H*); 4.46 (*dd*, *J* = 6.2, 7.8, H–C(2)); 4.44 (*d*, *J* = 11.7, PhC*H*); 4.25 (*dd*, *J* = 5.2, 10.6, H_{eq}–C(6)); 4.08 (*dd*, *J* = 2.9, 6.2, H–C(3)); 3.94–3.91 (*m*, H–C(5)); 3.84 (*dd*, *J* = 2.9, 9.5, H–C(4)); 3.52 (*t*, *J* ≈ 10.4, H_{ax}–C(6)); 2.06 (br. *s*, OH); (*Z*)-isomer: 8.60 (br. *s*, NOH); 7.45–7.24 (*m*, 15 arom. H); 7.05 (*d*, *J* = 7.1, H–C(1)); 5.39 (*s*, PhC*H*); 5.27 (*dd*, *J* = 4.8, 7.1, H–C(2)); 4.82–4.46 (*m*, 4 PhC*H*); 4.27 (*dd*, *J* = 5.3, 10.6, H_{eq}–C(6)); 4.13 (*dd*, *J* = 3.8, 4.6, H–C(3)); 4.06–4.03 (*m*, H–C(5)); 3.85–3.82 (*m*, H–C(4)); 3.53 (*t*, *J* ≈ 10.4, H_{ax}–C(6)); 2.46 (br. *s*, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): (*E*)-isomer: 149.93 (*d*); 137.50 (*s*); 137.39 (2*s*); 128.79–126.12 (several *d*); 101.09 (*d*); 80.53 (*d*); 77.18 (*d*); 75.33 (*d*); 73.64 (*t*); 71.13 (*t*); 70.93 (*t*); 61.73 (*d*); (*Z*)-isomer: 150.43 (*d*); 137.53 (*s*); 137.50–137.39 (2*s*); 128.79–126.12 (several *d*); 101.15 (*d*); 80.75 (*d*); 77.75 (*d*); 73.42 (*t*); 72.20 (*t*); 70.93 (*t*); 70.14 (*d*); 62.25 (*d*). CI-MS: 481 (85, $[M + NH_4]^+$), 464 (100, $[M + 1]^+$), 446 (16), 358 (26). Anal. calc. for $C_{27}H_{29}NO_6$ (463.53): C 69.96, H 6.31; found: C 70.02, H 6.53.

*2,3-Di-O-benzyl-4,6-O-benzylidene-*D*-mannonhydroximo-1,5-lactone* (**36**). A soln. of **35** (2.00 g, 4.31 mmol) and DBU (0.7 ml, 4.70 mmol) in CH_2Cl_2 (40 ml) at −20° was treated with NCS (633 mg, 4.74 mmol). The mixture was stirred for 10 min at −20°, allowed to warm up to 0°, diluted with CH_2Cl_2 (40 ml), and washed with H_2O (2 × 80 ml). The org. phase was dried ($MgSO_4$) and evaporated: **36** (2.03 g) as a yellow foam. A sample was crystallized from Et_2O/hexane. M.p. 118°. R_f (toluene/MeOH 9:1) 0.30. $[\alpha]_D^{20} = 0$ (*c* = 1.02, $CHCl_3$). IR ($CHCl_3$): 3576*m*, 3312*w*, 3090*w*, 3067*w*, 2912*w*, 2872*m*, 1662*m*, 1630*w*, 1497*m*, 1454*m*, 1372*m*, 1332*w*, 1313*w*, 1281*m*, 1255*m*, 1173*m*, 1094*s*, 1059*s*, 1028*s*, 967*m*, 937*m*, 915*m*, 890*w*, 870*w*, 644*w*, 599*w*, 512*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.52–7.06 (*m*, 15 arom. H); 6.68 (br. *s*, NOH, exchange with D_2O); 5.14 (*s*, PhC*H*); 4.74 (*d*, *J* = 12.0, PhC*H*); 4.50 (*d*, *J* ≈ 11.4, 2 PhC*H*); 4.45 (*t*, *J* ≈ 9.7, H–C(4)); 4.40 (*d*, *J* = 12.2, PhC*H*); 4.27 (*d*, *J* = 3.7, H–C(2)); 4.04 (*dd*, *J* = 4.5, 10.0, H_{eq}–C(6)); 3.48 (*dd*, *J* = 3.6, 10.0, H–C(3)); 3.41 (*t*, *J* ≈ 10.1, H_{ax}–C(6)); 3.32 (*dt*, *J* ≈ 4.5, 9.5, H–C(5)). ^{13}C-NMR (50 MHz, $CDCl_3$): 151.12 (*s*); 137.61 (*s*); 136.99 (*s*); 136.87 (*s*); 128.99–125.98 (several *d*); 101.65 (*d*); 77.00 (*d*); 76.27 (*d*); 72.60 (*d*); 72.28 (*t*); 71.42 (*d*); 70.57 (*t*); 68.03 (*t*). CI-MS: 462 (100, $[M + 1]^+$). Anal. calc. for $C_{27}H_{27}NO_6$ (461.51): C 70.27, H 5.90; found: C 70.49, H 6.18.

*(2,3-Di-O-benzyl-4,6-O-benzylidene-*D*-mannopyranosylidene)amino 2,4,6-Trimethylbenzene-1-sulfonate* (**37**). A soln. of crude **36** (2.03 g, *ca.* 4.3 mmol) in CH_2Cl_2 (40 ml) at 0° was treated with Et_3N (1.2 ml, 8.66 mmol) and 2,4,6-trimethylbenzene-1-sulfonyl chloride (1.2 g, 5.49 mmol). The mixture was stirred for 30 min, diluted with CH_2Cl_2 (40 ml), and washed with sat. aq. $NaHCO_3$ soln. (40 ml) and brine (40 ml). The org. phase was dried ($MgSO_4$) and evaporated and the residue crystallized from AcOEt/hexane: **37** (2.49 g, 90% from **35**). M.p. 152°. R_f (AcOEt/hexane 1:2) 0.42. $[\alpha]_D^{20} = +17.6$ (*c* = 1.03, $CHCl_3$). IR ($CHCl_3$): 3067*w*, 2941*m*, 2874*m*, 1647*m*, 1604*m*, 1568*w*, 1496*m*, 1469*m*, 1455*m*, 1369*s*, 1314*m*, 1296*m*, 1148*m*, 1094*s*, 1058*s*, 1027*m*, 966*m*, 913*m*, 855*m*, 581*s*, 539*m*, 530*m*, 514*w*, 504*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.45–7.05 (*m*, 15 arom. H); 6.58 (*s*, 2 arom. H); 5.03 (*s*, PhC*H*); 4.35 (*d*, *J* ≈ 12.1, 2 PhC*H*); 4.27 (*t*, *J* ≈ 9.7, H–C(4)); 4.25 (*d*, *J* ≈ 12.3, PhC*H*); 4.08 (*d*, *J* = 12.1, PhC*H*); 3.99 (*d*, *J* = 3.7, H–C(2)); 3.93 (*dd*, *J* = 4.6, 10.1, H_{eq}–C(6)); 3.25 (*t*, *J* ≈ 10.2, H_{ax}–C(6)); 3.23 (*dd*, *J* = 3.8, 10.0, H–C(3)); 3.15 (*dt*, *J* ≈ 4.5, 9.8, H–C(5)); 2.84 (*s*, 2 Me); 1.81 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 155.39 (*s*); 143.57 (*s*); 140.46 (2*s*); 137.17 (*s*); 136.47 (*s*); 135.93 (*s*); 131.39 (2*d*); 129.92–125.76 (several *d*); 101.39 (*d*); 76.03 (*d*); 75.16 (*d*); 72.10 (*t*); 71.86 (*d*); 71.31 (*d*); 69.92 (*t*); 67.34 (*t*); 22.44 (2*q*); 20.71 (*q*). FAB-MS: 644 (46, $[M + 1]^+$), 181 (14), 107 (29), 91 (100). Anal. calc. for $C_{36}H_{37}NO_8S$ (643.77): C 67.17, H 5.79, N 2.18; found: C 67.24, H 6.00, N 2.13.

*1,5-Anhydro-2,3-di-O-benzyl-4,6-O-benzylidene-1-hydrazi-*D*-mannitols* (**38**). A soln. of **37** (500 mg, 0.78 mmol) in CH_2Cl_2 (40 ml) was treated with a sat. soln. of NH_3 in MeOH (20 ml) and stirred in a closed flask for 48 h. The solvents were evaporated at 25°. FC (Et_2O) of the residue gave **38** (250 mg, 70%). White foam. R_f (Et_2O)

0.36. $[\alpha]_D^{20} = +22.9$ ($c = 1.12$, $CHCl_3$). IR ($CHCl_3$): 3271*w*, 3090*w*, 3067*w*, 2937*w*, 2874*w*, 1497*w*, 1454*m*, 1374*m*, 1347*m*, 1314*w*, 1281*w*, 1100*s*, 1065*s*, 1028*s*, 1003*m*, 915*w*, 871*w*, 611*w*, 594*w*, 539*w*, 532*w*. ^{1}H-NMR (400 MHz, C_6D_6): major diastereoisomer **38a** (*ca.* 60%): 7.60–7.03 (*m*, 15 arom. H); 5.27 (*s*, PhC*H*); 4.94–4.48 (*m*, 4 PhC*H*); 4.45 (*t*, $J \approx 9.4$, H–C(4)); 4.11 (*dd*, $J = 4.9$, 10.2, H_{eq}–C(6)); 3.81 (*dt*, $J \approx 4.8$, 9.8, H–C(5)); 3.56 (*dd*, $J = 3.3$, 9.8, H–C(3)); 3.52 (*t*, $J \approx 10.2$, H_{ax}–C(6)); 3.24 (*d*, $J \approx 3.2$, H–C(2)); 2.35 (*d*, $J = 9.2$, NH); 1.18 (*d*, $J = 9.1$, NH); minor diastereoisomer **38b** (*ca.* 40%): 7.60–7.03 (*m*, 15 arom. H); 5.26 (*s*, PhC*H*); 4.94–4.48 (*m*, 4 PhC*H*); 4.42 (*t*, $J \approx 9.6$, H–C(4)); 4.04 (*dd*, $J = 4.9$, 10.3, H_{eq}–C(6)); 3.91 (*dd*, $J = 3.2$, 9.8, H–C(3)); 3.52 (*t*, $J \approx 10.2$, H_{ax}–C(6)); 3.40 (*d*, $J = 3.2$, H–C(2)); 3.25 (*dt*, $J \approx 4.8$, 9.7, H–C(5)); 1.82 (*d*, $J = 9.3$, NH); 1.77 (*d*, $J = 9.2$, NH). ^{13}C-NMR (75 MHz, $CDCl_3$): mixture of 2 diastereoisomers: 138.25 (*s*); 138.17 (*s*); 137.88 (*s*); 137.70 (*s*); 137.42 (*s*); 137.37 (*s*); 129.08–126.17 (several *d*); 101.70 (2*d*); 82.53 (*s*); 82.24 (*s*); 78.62 (*d*); 78.19 (2*d*); 78.14 (*d*); 78.09 (*d*); 77.33 (*d*); 73.80 (*t*); 73.45 (*t*); 72.80 (2*t*); 69.83 (*d*); 69.00 (*d*); 68.33 (2*t*). FAB-MS: 461 (46, $[M + 1]^+$), 307 (12), 154 (48), 136 (37), 91 (100). Anal. calc. for $C_{27}H_{28}N_2O_5$ (460.54): C 70.42, H 6.13, N 6.08; found: C 70.48, H 6.09, N 5.92.

*1,5-Anhydro-1-azi-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-*D*-mannitol* (**7**). A soln. of **38** (100 mg, 0.22 mmol), Me_3N (0.4 ml, 4.3 mmol), and 4-Å molecular sieves (500 mg) in CH_2Cl_2 (12.5 ml) under Ar at −50° was treated dropwise with a soln. of I_2 (52 mg, 0.21 mmol) in CH_2Cl_2 (2 ml). The mixture was concentrated at 0°. The residue was taken up in Et_2O (20 ml). Precipitated (Me_3NH)I and molecular sieves were filtered off, and the filtrate was evaporated at −20° to give **7** (80 mg, 80%) which was immediately used for the next step. R_f (CH_2Cl_2/hexane 9:1) 0.45. UV: 348. IR ($CHCl_3$): 3034*w*, 2977*w*, 2935*w*, 2872*w*, 1637*w*, 1605*w*, 1577*w*, 1497*w*, 1454*w*, 1383*w*, 1372*w*, 1214*w*, 1176*w*, 1156*w*, 1107*s*, 1059*m*, 1028*m*, 966*w*, 917*w*. ^{1}H-NMR (400 MHz, CD_2Cl_2, −40°): 7.51–7.25 (*m*, 15 arom. H); 5.65 (*s*, PhC*H*); 4.99 (*d*, $J = 11.7$, PhC*H*); 4.70 (*d*, $J \approx 11.8$, 2 PhC*H*); 4.60 (*d*, $J = 11.9$, PhC*H*); 4.40–4.36 (*m*, H–C(4)); 4.19–4.12 (*m*, H_{eq}–C(6)); 4.10 (*dd*, $J = 3.6$, 9.9, H–C(3)); 3.83–3.75 (*m*, H–C(5), H_{ax}–C(6)); 2.94 (*d*, $J = 3.6$, H–C(2)). ^{13}C-NMR (100 MHz, CD_2Cl_2, −40°): 138.12 (*s*); 137.48 (*s*); 137.47 (*s*); 129.25–1126.30 (several *d*); 101.82 (*d*); 77.88 (*d*); 77.62 (*d*); 76.29 (*d*); 72.62 (*t*); 72.48 (*t*); 69.61 (*d*); 67.94 (*t*); 56.14 (*s*).

*Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α- and -β-*D*-mannopyranoside* (**39** and **40**). A soln. of **7** (64 mg, 0.138 mol) in MeOH (5 ml) and CH_2Cl_2 (4 ml) was kept for 16 h at r.t. Evaporation of the solvent and FC (5 g, AcOEt/hexane 1:3) of the crude (77 mg) gave **39** (47.1 mg, 73%) [69] [68] and **40** (17.2 mg, 27%).

Data of **40**: R_f (AcOEt/hexane 1:3) 0.23 (**39**: 0.31). ^{1}H-NMR (400 MHz, C_6D_6): 7.71–7.17 (*m*, 15 arom. H); 5.31 (*s*, PhC*H*); 5.15 (*d*, $J = 11.7$, PhC*H*); 4.96 (*d*, $J = 11.7$, PhC*H*); 4.83 (*d*, $J = 12.6$, PhC*H*); 4.70 (*d*, $J = 12.6$, PhC*H*); 4.38 (*t*, $J \approx 9.5$, H–C(4)); 4.25 (*dd*, $J = 4.9$, 10.3, H_{eq}–C(6)); 3.86 (*s*, H–C(1)); 3.79 (*d*, $J = 3.0$, H–C(2)); 3.69 (*t*, $J = 10.2$, H_{ax}–C(6)); 3.48 (*dd*, $J = 3.1$, 9.9, H–C(3)); 3.30 (*s*, MeO); 3.15 (*dt*, $J \approx 4.9$, 9.7, H–C(5)). CI-MS: 481 (31), 480 (100, $[M + NH_4]^+$), 463 (18, $[M + 1]^+$). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.21 (*s*); 138.06 (*s*); 137.32 (*s*); 128.24–125.78 (several *d*); 103.12 (*d*); 101.14 (*d*); 78.41 (*d*); 77.57 (*d*); 75.63 (*d*); 74.54 (*t*); 72.09 (*t*); 68.37 (*t*); 67.34 (*d*); 57.13 (*q*).

*2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*D*-glucopyranose* (**42**) [57]. KO(*t*-Bu) (22.1 g, 197 mmol) was added at 50° to a soln. of crude **41** [58] (46.6 g, 87.6 mmol) in DMSO (400 ml; dried over 4-Å molecular sieves). The dark brown mixture was stirred for 15 min at 50° and then poured onto ice (500 g). Extraction with AcOEt/Et_2O 4:1 (1 × 600 ml, 2 × 300 ml) and normal workup yielded a crude, crystalline residue (43.6 g; isomerization product) which was dissolved in THF/H_2O 4:1 (310 ml). The soln. was treated with I_2 (40.7 g, 160.4 mmol), stirred for 15 min at 26°, poured onto ice (250 g), and treated with 10% aq. $NaHSO_3$ soln. until the mixture turned form dark brown to bright yellow. The mixture was distributed between AcOEt (2 l) and H_2O and the org. phase dried ($MgSO_4$), concentrated *in vacuo* to 1.5 l, and cooled to 4° to yield a first crop of pure **42** (19.6 g). FC (1 kg, CH_2Cl_2/MeOH 95:5) of the mother liquor and crystallisation yielded more pure **42** (2.40 g). Total yield 22.0 g (50%).

*(E)- and (Z)-2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*D*-glucose Oximes* (**43**) *and* N*-(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-glucopyranosyl)hydroxylamine* (**44**). $NH_2OH \cdot HCl$ (14.2 g, 204 mmol) was added to a soln. of Na (4.19 g, 182 mmol) in MeOH (221 ml). The mixture was stirred for 15 min, cooled to 0°, and filtered. The residue was washed with MeOH (132 ml). The pH of the colorless filtrate was 7. MeOH (92 ml) and EtOH (68 ml) were added to a slurry of **42** (20.8 g, 42.3 mmol) in the NH_2OH soln. (293 ml). Heating to 60° led to a clear soln. which was stirred at this temp. for 33 h. The slightly turbid soln. was filtered, the solvent evaporated, the residue taken up in $CHCl_3$ (300 ml) and H_2O (250 ml), and the aq. layer further extracted with $CHCl_3$ (2 × 100 ml). Normal workup yielded crude **43**/**44** (21.7 g). White foam.

Data of **43**/**44**: $[\alpha]_D^{25} = 16.5$ ($c = 1.12$, $CHCl_3$); constant after 20 min). IR ($CHCl_3$): 3580*w*, 3435*m*, 3325*m*, 3000*m*, 2870*m*, 1670*s*, 1495*m*, 1455*m*, 1365*m*, 1095*s*, 1065*s*, 1030*s*, 915*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): (*E*)-**43**/(*Z*)-**43** *ca.* 2:1, 10% of **44**. ^{13}C-NMR (50 MHz, (D_6)DMSO; **44**/(*E*)-**43**/(*Z*)-**43** 42:38:20): data of (*E*)-**43**: 169.15 (*s*); 148.21 (*d*); 139.03–138.37 (several *s*); 128.57–127.22 (several *d*); 79.84 (*d*); 79.26 (*d*); 74.06 (*t*); 73.34 (*t*); 72.62 (*t*); 71.78 (*t*); 69.70 (*d*); 49.97 (*d*); 22.87 (*q*); data of (*Z*)-**43**: 169.51 (*s*); 149.84 (*d*); 139.03–138.37 (several *s*);

128.57–127.22 (several *d*); 81.67 (*d*); 78.84 (*d*); 74.59 (*t*); 74.06 (*t*); 72.62 (*t*); 71.66 (*t*); 70.01 (*d*); 46.38 (*d*); 22.73 (*q*); data of **44**: 170.24 (*s*); 139.03–138.37 (several *s*); 128.57–127.22 (several *d*); 91.70 (*d*); 83.30 (*d*); 78.34 (*d*); 75.45 (*d*); 74.06 (*t*); 72.62 (2*t*); 69.24 (*t*); 51.72 (*d*); 23.10 (*q*). Anal. calc. for $C_{29}H_{34}N_2O_6$ (506.60): C 68.76, H 6.77, N 5.53; found: C 68.56, H 6.56, N 5.31.

FC (CH_2Cl_2/MeOH 96:4) of a sample of **43**/**44** (220 mg) gave **43** (130 mg, containing some **44**), **43**/**44** (28 mg), and pure **44** (30 mg). Upon standing in $CDCl_3$ soln., **44** was completey transformed into **43**.

Data of **43**: R_f (AcOEt) 0.50. ^{1}H-NMR (300 MHz, $CDCl_3$, (*E*)/(*Z*) 7:3): 8.22 (br. *s*, exchange with D_2O, 0.3 H), 7.63 (br. *s*, exchange with D_2O, 0.7 H, NOH); 7.41 (*d*, *J* = 4.0, 0.7 H); 6.69 (*d*, *J* = 5.3, 0.3 H, H–C(1)); 7.39–7.21 (*m*, 15 arom. H); 6.49 (*d*, *J* = 6.8, 0.3 H), 6.33 (*d*, *J* = 8.0, 0.7 H, AcN*H*); 5.26 (*ddd*, *J* = 1.7, 5.5, 7.0, 0.3 H), 5.00 (*ddd*, *J* = 2.9, 3.9, 7.8, 0.7 H, H–C(2)); 4.74–4.47 (*m*, 6 PhC*H*); 4.25 (*dd*, *J* = 1.7, 4.7, 0.3 H), 4.06 (*d*, *J* = 2.9, 5.2, 0.7 H, H–C(3)); 3.97–3.90 (*m*, addn. of D_2O→change of signal, H–C(5)); 3.71–3.59 (*m*, H–C(4), 2 H–C(6)); 2.95 (*d*, *J* = 6.6, exchange with D_2O, 0.7 H), 2.87 (*d*, *J* = 6.5, exchange with D_2O, 0.3 H, OH–C(5)); 1.90 (*s*, 2.1 H); 1.85 (*s*, 0.9 H, AcN). CI-MS: 507 (12, $[M + 1]^+$), 506 (17), 491 (39), 489 (30), 462 (15), 420 (10), 383 (30), 382 (15), 381 (100), 374 (12).

Data of **44**: R_f (AcOEt) 0.06. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.43–7.28 (*m*, 13 arom. H); 7.24–7.19 (*m*, 2 arom. H); 6.62 (br. *s*, exchange with D_2O, OH); 5.37 (br. *s*, exchange with D_2O, NH); 4.88 (*d*, *J* = 12.1, PhC*H*); 4.85 (*d*, *J* = 7.9, exchange with D_2O, AcN*H*); 4.83 (*d*, *J* = 10.8, PhC*H*); 4.64 (*d*, *J* = 12.1, PhC*H*); 4.58 (*d*, *J* = 10.7, PhC*H*); 4.58 (*s*, PhCH_2); 4.05 (*ddd*, *J* = 8.1, 9.5, 10.3, addn. of D_2O→*dd*, *J* = 9.5, 10.3, H–C(2)); 3.79 (*d*, *J* = 9.3, H–C(1)); 3.74 (*dd*, *J* = 2.1, 10.6, H–C(6)); 3.67 (*dd*, *J* = 5.3, 10.6, H′–C(6)); 3.62 (*dd*, *J* = 8.5, 9.6, H–C(4)); 3.51 (*dd*, *J* = 8.4, 10.5, H–C(3)); 3.50 (*ddd*, *J* = 2.1, 5.3, 9.5, H–C(5)); 1.77 (*s*, AcN). CI-MS: 507 (11, $[M + 1]^+$), 491 (8), 489 (9), 420 (9), 383 (12), 382 (21), 381 (100).

*2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*D*-gluconhydroximo-1,5-lactone* (**45**). A soln. of $NaIO_4$ (17.4 g, 81.4 mmol) in H_2O (330 ml) was added within 105 min at 50° to a soln. of crude **43**/**44** (20.9 g, 40.7 mmol) and NaOAc (5.54 g, 67.5 mmol) in abs. EtOH (955 ml). A white precipitate formed immediately. After stirring for 17.75 h under N_2, the suspension was filtered and the filtrate evaporated. The remaining slurry was taken up in H_2O (100 ml) and AcOEt (400 ml). The aq. layer was extracted with AcOEt (2 × 100 ml), which was washed with 5% aq. $Na_2S_2O_3$ soln. (250 ml), H_2O (2 × 150 ml), and brine (150 ml). Normal workup yielded crude **45** (20.0 g) as a yellow foam, which was crystallized from Et_2O and recrystallized in AcOEt/hexane: pure **45** (11.9 g). FC (450 g, AcOEt→AcOEt/MeOH 95:5) of the mother liquor and crystallization (AcOEt/hexane) gave further **45** (2.49 g, 70% from **42**). R_f (AcOEt) 0.32. $[\alpha]_D^{25} = 24.5$ (*c* = 1.08, $CHCl_3$). M.p. 119–120°. IR ($CHCl_3$): 3580*w*, 3435*m*, 3000*m*, 2870*m*, 1670*s*, 1495*m*, 1453*m*, 1365*m*, 1295*m*, 1080*s*, 1027*m*, 995*m*, 935*m*, 910*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.29 (*m*, 13 arom. H, NOH); 7.21–7.19 (*m*, 2 arom. H); 6.19 (*d*, *J* = 8.5, NH); 4.86 (*dd*, *J* = 6.5, 8.5, H–C(2)); 4.73 (*d*, *J* = 11.8, PhC*H*); 4.68 (*d*, *J* = 11.8, PhC*H*); 4.64 (*d*, *J* = 11.2, PhC*H*); 4.56 (*d*, *J* = 11.1, PhC*H*); 4.55 (*s*, PhCH_2); 4.33 (*td*, *J* = 4.6, 6.2, H–C(5)); 3.89 (*t*, *J* = 6.2, H–C(4)); 3.78 (*t*, *J* = 6.4, H–C(3)); 3.78 (*dd*, *J* = 4.7, 11.2, H–C(6)); 3.74 (*dd*, *J* = 4.1, 10.9, H′–C(6)); 1.88 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.49 (*s*); 151.51 (*s*); 137.59 (*s*); 137.49 (*s*); 137.17 (*s*); 128.28–127.62 (*m*); 79.13 (*d*); 78.63 (*d*); 73.64 (*d*); 73.42 (*t*); 73.30 (2*t*); 68.25 (*t*); 49.24 (*d*); 22.95 (*q*). CI-MS: 506 (17), 505 (22, $[M + 1]^+$), 489 (20), 382 (22), 381 (100), 379 (12). Anal. calc. for $C_{29}H_{32}N_2O_6$ (504.58): C 69.03, H 6.39, N 5.55; found: C 69.25, H 6.53, N 5.49.

*(2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*D*-glucopyranosylidene)amino 4-Methylbenzene-1-sulfonate* (**46**). At 0°, a soln. of **45** (5.00 g, 9.91 mmol) in CH_2Cl_2 (100 ml) was treated with Et_3N (3.7 ml, 26.5 mmol) and, after 5 min, with TsCl (2.84 g, 14.9 mmol), stirred for 3 h under N_2, and then poured onto ice-water (150 ml). Extraction with CH_2Cl_2 (2 × 50 ml) and normal workup yielded crude **46** (7.82 g). FC (300 g, CH_2Cl_2/MeOH 99:1→CH_2Cl_2/MeOH 98:2) gave colorless, spontaneously crystallizing **46** (6.45 g, 100%). R_f (AcOEt) 0.81. $[\alpha]_D^{25} = 16.3$ (*c* = 1.10, $CHCl_3$). M.p. 99–100°, IR ($CHCl_3$): 3435*w*, 3000*m*, 2925*m*, 2870*m*, 1685*s*, 1645*m*, 1600*m*, 1495*m*, 1453*m*, 1370*s*, 1295*m*, 1175*s*, 1093*s*, 1075*s*, 1028*m*, 830*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.82–7.78 (*m*, 2 arom. H); 7.37–7.16 (*m*, 17 arom. H); 5.90 (*d*, *J* = 8.2, NH); 4.68 (*dd*, *J* = 7.0, 8.1, H–C(2)); 4.67 (*d*, *J* = 11.7, PhC*H*); 4.63 (*d*, *J* = 11.0, PhC*H*); 4.62 (*d*, *J* = 11.7, PhC*H*); 4.56 (*d*, *J* = 12.0, PhC*H*); 4.53 (*d*, *J* = 11.0, PhC*H*); 4.50 (*d*, *J* = 12.0, PhC*H*); 4.31 (*dt*, *J* = 3.7, 7.3, H–C(5)); 3.89 (*t*, *J* ≈ 6.9, H–C(4)); 3.80 (*t*, *J* = 6.8, H–C(3)); 3.76 (*dd*, *J* = 3.6, 11.1, H–C(6)); 3.71 (*dd*, *J* = 4.0, 11.1, H′–C(6)); 2.40 (*s*, Me); 1.80 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.71 (*s*); 158.54 (*s*); 144.77 (*s*); 137.48 (*s*); 137.37 (*s*); 137.06 (*s*); 132.10 (*s*); 129.32–127.63 (several *d*); 79.95 (*d*); 78.26 (*d*); 75.37 (*d*); 73.55 (*t*); 73.30 (*t*); 73.19 (*t*); 67.81 (*t*); 49.24 (*d*); 22.72 (*q*); 21.48 (*q*). Anal. calc. for $C_{36}H_{38}N_2O_8S$ (658.77): C 65.64, H 5.81, N 4.25; found: C 65.61, H 5.95, N 4.41.

*2-Acetamido-1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-1-hydrazi-*D*-glucitols* (**47**). MeOH (30 ml) was cooled to 0°, saturated with NH_3, diluted with MeOH (30 ml), cooled to −20°, and treated with a cold (−20°) soln. of **46** (500 mg, 0.759 mmol) in MeOH (13 ml). The soln. was kept for 168 h at −20° (TLC: traces of **46**), concentrated to 10 ml at 30°/100 mbar, and cooled to −20° yielding a first crop of **47** (116 mg). The mother liquor was cooled to 0° and

treated with Et_2O (50 ml). The precipitate (79 mg of NH_4OTs) was filtered off. After evaporation of the filtrate, the residue was dried for 15 min *in vacuo* and suspended in CH_2Cl_2 (20 ml). After filtration, the filtrate was treated with pentane (100 ml) and left overnight at −20° affording a second crop of **47** (193 mg, sticky, yellowish crystals containing *ca.* 20% of several by-products). Total yield of **47** *ca.* 70%. R_f (CH_2Cl_2/MeOH/Et_3N 95:5:0.5): 0.23, 0.19. IR ($CHCl_3$): 3425*w*, 3280*w*, 3000*w*, 2870*w*, 1685*s*, 1500*m*, 1455*m*, 1370*m*, 1320*m*, 1100*s*, 1000*m*, 915*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; **47a**/**47b** 85:15): major isomer **47a**: 7.38–7.20 (*m*, 15 arom. H); 5.19 (*d*, *J* = 9.5, exchange with D_2O, AcN*H*); 4.88 (*d*, *J* = 11.5, PhC*H*); 4.84 (*d*, *J* = 10.8, PhC*H*); 4.66 (*d*, *J* = 11.5, PhC*H*); 4.65 (*t*, *J* ≈ 9.8, addn. of D_2O→*d*, *J* = 10.2, H–C(2)); 4.64 (*d*, *J* = 10.8, PhC*H*); 4.60 (*d*, *J* = 12.1, PhC*H*); 4.50 (*d*, *J* = 12.1, PhC*H*); 3.94 (*t*, *J* = 9.3, H–C(4)); 3.75 (*dd*, *J* = 4.1, 10.9, H–C(6)); 3.68 (*d*, *J* = 2.1, 11.0, H′–C(6)); 3.61 (*dd*, *J* = 8.8, 10.2, H–C(2)); 3.60 (*ddd*, *J* = 2.1, 4.1, 10.2, H–C(5)); 2.33 (*d*, *J* = 9.3, exchange with D_2O, NH); 1.95 (*d*, *J* = 9.2, exchange with D_2O, NH); 1.79 (*s*, AcN); minor isomer **47b**: 6.07 (*d*, *J* = 8.6, exchange with D_2O, AcN*H*); 4.56 (*d*, *J* = 12.1, PhC*H*); 4.45 (*d*, *J* = 12.1, PhC*H*); 4.25 (*dd*, *J* = 6.6, 8.1, addn. of D_2O→*d*, *J* = 6.6, H–C(2)); 4.20 (br. *q*, *J* ≈ 5.2, 1 H); 3.88–3.80 (*m*, 2 H); 2.50 (*d*, *J* = 9.5, exchange with D_2O, NH); 2.26 (*d*, *J* = 9.4, exchange with D_2O, NH); 1.82 (*s*, AcN). ^{13}C-NMR (150 MHz, $CDCl_3$, 10°): 170.85 (*s*); 137.74 (*s*); 137.50 (*s*); 137.39 (*s*); 128.52–127.67 (several *d*); 82.04 (*d*); 81.75 (*s*); 77.74 (*d*); 76.47 (*d*); 74.99 (*t*); 74.68 (*t*); 73.42 (*t*); 67.96 (*t*); 49.79 (*d*); 23.23 (*q*). CI-MS: 504 (27, $[M + 1]^+$), 489 (10), 462 (11), 397 (19), 396 (75), 382 (12), 381 (52), 288 (99), 273 (26), 272 (25), 270 (100), 180 (27), 108 (35).

*2-Acetamido-1,5-anhydro-1-azi-3,4,6-tri-*O*-benzyl-2-deoxy-*D*-glucitol* (**8**). MeOH (60 ml) was cooled to 0°, saturated with NH_3, cooled to −20°, and treated with a cold (−20°) soln. of **46** (500 mg, 0.759 mmol) in MeOH (13 ml). The soln. was kept for 64 h at −20° to complete formation of **47**, concentrated to 10 ml at 23° *in vacuo* (partial crystallization of **47**), cooled to 0°, diluted with CH_2Cl_2 (25 ml; →clear soln.) and MeOH (25 ml), and treated with Et_3N (420 µl, 3.04 mmol), and then dropwise within 30 min with a soln. of I_2 (385 mg, 1.518 mmol) in MeOH (14 ml). The mixture was stirred for 3 h at 0° (orange soln.), concentrated at 23° to 20 ml, and cooled to −20° to complete crystallization. Filtration and drying *in vacuo* gave **8** (257 mg, 68% from **46**). R_f (AcOEt/hexane/Et_3N 2:1:0.015) 0.69. M.p. 107–114° (dec.; AcOEt/hexane). UV (CH_2Cl_2): 352 (72), 246 (375). CD (CH_2Cl_2): 359 (0.53), 315 (0), 295 (−0.9), 278 (0). IR ($CHCl_3$): 3430*m*, 3000*m*, 2920*m*, 2870*m*, 1675*s*, 1600*m*, 1495*m*, 1450*m*, 1360*m*, 1070*s*, 1025*s*, 908*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44–7.24 (*m*, 15 arom. H); 4.88 (*d*, *J* = 8.1, NH); 4.79 (*d*, *J* = 12.0, PhC*H*); 4.77 (*d*, *J* = 10.9, PhC*H*); 4.66 (*d*, *J* = 10.9, PhC*H*); 4.65 (*d*, *J* = 12.1, PhC*H*); 4.54 (*d*, *J* = 12.0, PhC*H*); 4.47 (*d*, *J* = 12.0, PhC*H*); 4.35 (*t*, *J* = 8.3, H–C(2)); 3.94 (*t*, *J* = 7.4, H–C(4)); 3.86 (*ddd*, *J* = 3.3, 4.2, 7.5, H–C(5)); 3.77 (*dd*, *J* = 7.0, 8.5, H–C(3)); 3.76 (*dd*, *J* = 4.4, 10.9, H–C(6)); 3.64 (*dd*, *J* = 3.2, 10.9, H′–C(6)); 1.64 (*s*, AcN). ^{13}C-NMR (150 MHz, $CDCl_3$, 10°): 169.58 (*s*); 137.46 (*s*); 137.44 (*s*); 137.21 (*s*); 128.73–127.72 (several *d*); 79.34 (*d*); 77.00 (*d*); 76.73 (*d*); 74.56 (*t*); 73.97 (*t*); 73.43 (*t*); 67.57 (*t*); 56.48 (*s*); 48.87 (*d*); 22.80 (*q*). CI-MS: 475 (33), 474 (100, $[M - N_2 + 1]^+$), 383 (30), 366 (43), 260 (16), 259 (13), 258 (81), 150 (15), 108 (26), 106 (40). Anal. calc. for $C_{29}H_{31}N_3O_5$ (501.58): C 69.44, H 6.23, N 8.38; found: C 69.35, H 6.48, N 8.16.

*Methyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-*D*- and -β-*D*-glucopyranoside* (**48** and **49** [70]). The pooled soln. of the kinetic experiments (see below) was evaporated and the crystalline residue dried under high vacuum. ^{1}H-NMR (300 MHz, $CDCl_3$, α-D/β-D 2:1): 7.36–7.17 (*m*, 15 arom. H); 5.51 (*d*, *J* = 8.1, 0.33 H), 5.29 (*d*, *J* = 9.3, 0.67 H, NH); 4.84 (*d*, *J* = 11.6, 0.67 H), 4.82 (*d*, *J* = 11.7, 0.33 H), 4.81 (*d*, *J* = 10.7, 0.67 H), 4.78 (*d*, *J* = 11.7, 0.33 H, 2 PhC*H*); 4.71 (*d*, *J* = 7.7, 0.33 H), 4.68 (*d*, *J* = 3.7, 0.67 H, H–C(1)); 4.64 (*d*, *J* = 12.1, 0.67 H), 4.635 (*d*, *J* = 10.9, 0.67 H), 4.62 (*d*, *J* = 10.2, 0.33 H), 4.59 (*d*, *J* = 12.2, 0.33 H), 4.55 (*d*, *J* = 12.2, 0.33 H), 4.545 (*d*, *J* = 10.6, 0.33 H), 4.535 (*d*, *J* = 10.9, 0.67 H), 4.53 (*d*, *J* = 12.2, 0.67 H, 4 PhC*H*); 4.26 (*dt*, *J* = 3.7, 9.7, 0.67 H), 3.45 (*td*, *J* = 7.8, 9.5, 0.33 H, H–C(2)); 4.06 (*dd*, *J* = 7.9, 9.6, 0.33 H, H–C(3)); 3.79–3.59 (*m*, 4.67 H); 3.48 (*s*, 1 H), 3.33 (*s*, 2 H, MeO); 1.86 (*s*, 1 H), 1.84 (*s*, 2 H, AcN). CI-MS: 507 (16), 506 (100, $[M + 1]^+$), 475 (32), 474 (100, $[M - MeO]^+$), 234 (27), 168 (20), 108 (11).

*Methyl 2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-*D*- and -β-*D*-allopyranoside* (**54** and **55**). The pooled soln. of the kinetic experiments (see below; 100.5 mg (0.245 mmol) of **9**) was evaporated and the crystalline residue (^{1}H-NMR: α-D/β-D 58:42) dried under high vacuum. HPLC (Et_2O/MeOH 98:2, 6.3 ml/min) yielded **54** (40.8 mg, 40%) and **55** (33.6 mg, 33%).

Data of **54**: R_f (AcOEt/hexane 2:1) 0.42. HPLC (see above): t_R 23.8 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.51–7.47 (*m*, 2 arom. H); 7.42–7.28 (*m*, 8 arom. H); 5.99 (*d*, *J* = 9.3, AcN*H*); 5.56 (*s*, PhC*H*); 5.02 (*d*, *J* = 12.3, PhC*H*); 4.61 (*d*, *J* = 4.5, H–C(1)); 4.57 (*d*, *J* = 12.4, PhC*H*); 4.39–4.28 (*m*, H–C(5), H_{eq}–C(6)); 4.27 (*td*, *J* ≈ 4.1, 9.4, H–C(2)); 4.05 (*t*, *J* ≈ 3.1, H–C(3)); 3.80–3.72 (*m*, H_{ax}–C(6)); 3.72 (*dd*, *J* = 2.6, 9.4, H–C(4)); 3.41 (*s*, MeO); 1.83 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.22 (*s*); 138.53 (*s*); 137.51 (*s*); 128.99–126.12 (several *d*); 101.95 (*d*); 98.30 (*d*); 79.70 (*d*); 74.40 (*t*); 73.82 (*d*); 69.22 (*t*); 57.62 (*d*); 55.91 (*q*); 48.93 (*d*); 22.97 (*q*). CI-MS: 415 (25), 414 (100, $[M + 1]^+$), 383 (15), 382 (67, $[M - MeO]^+$), 309 (45).

Data of **55**: R_f (AcOEt/hexane 2:1) 0.42. HPLC (see above): 25.3 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.56–7.48 (*m*, 2 arom. H); 7.43–7.31 (*m*, 8 arom. H); 5.70 (*d*, *J* = 8.8, AcN*H*); 5.55 (*s*, PhC*H*); 5.03 (*d*, *J* = 11.6, PhC*H*); 4.55 (*d*, *J* = 8.1, H–C(1)); 4.54 (*d*, *J* = 11.6, PhC*H*); 4.41 (*dd*, *J* = 5.1, 10.4, H_{eq}–C(6)); 4.18–4.09 (*m*, H–C(2), H–C(3)); 4.10 (*dt*, *J* = 5.4, 9.9, H–C(5)); 3.81 (*t*, *J* = 10.3, H_{ax}–C(6)); 3.74 (*dd*, *J* = 2.1, 9.5, H–C(4)); 3.47 (*s*, MeO); 1.86 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.31 (*s*); 138.19 (*s*); 137.38 (*s*); 129.02–126.05 (several *d*); 101.95 (*d*); 101.11 (*d*); 80.13 (*d*); 75.85 (*d*); 74.68 (*t*); 69.14 (*t*); 63.72 (*d*); 56.52 (*q*); 51.82 (*d*); 23.17 (*q*). CI-MS: 415 (24), 414 (100, $[M + 1]^+$), 382 (37, $[M - MeO]^+$), 274 (25).

Determination of the Activation Energy of the Diazirines **1** *and* **4–9**. In a *Schlenk* tube equipped with a magnetic stirring bar, a immersion-cell, and a thermo element, the diazirine (*ca.* 30 mg each) was dissolved in abs. MeOH (5 ml), with the exception of **1** and **8** which were poorly soluble and of which a sat. soln. (< 20 mg) was used. The temp. was controlled by an external water bath. When the mixture had reached a constant temp., 12 readings of absorption were taken during at least one half-life period. k_1 was calculated using a least-square-fit linear regression. The clear, colorless solns. of each experiment were pooled, the solvent was evaporated, and a ^{1}H-NMR spectrum of the crude mixture was measured. In all cases, only signals of the corresponding methyl glycopyranosides were observed. Their structures were confirmed by NMR and CI-MS (see above).

1: $T(1) = 292.7$ K, $k_1(1) = 1.725 \cdot 10^{-4}$; $T(2) = 297.5$ K, $k_1(2) = 3.412 \cdot 10^{-4}$; $T(3) = 303.0$ K, $k_1(3) = 6.626 \cdot 10^{-4}$. $E_A = 23.0$ kcal/mol, log $A = 13.4$, τ (298 K) = 33 min; $\Delta S^{\neq} = 1.7$ cal/mol·K; $\Delta H^{\neq} = 22.4$ kcal/mol.

4: $T(1) = 297.6$ K, $k_1(1) = 5.918 \cdot 10^{-5}$; $T(2) = 302.1$ K, $k_1(2) = 1.158 \cdot 10^{-4}$; $T(3) = 307.4$ K, $k_1(3) = 2.296 \cdot 10^{-4}$; $T(4) = 312.4$ K, $k_1(4) = 4.425 \cdot 10^{-4}$. $E_A = 25.0$ kcal/mol, log $A = 14.1$, τ (298 K) = 202 min; $\Delta S^{\neq} = 4.8$ cal/mol·K; $\Delta H^{\neq} = 24.0$ kcal/mol.

5: $T(1) = 291.2$ K, $k_1(1) = 4.369 \cdot 10^{-5}$; $T(2) = 303.1$ K, $k_1(2) = 1.996 \cdot 10^{-4}$; $T(3) = 307.9$ K, $k_1(3) = 3.508 \cdot 10^{-4}$. $E_A = 22.2$ kcal/mol, log $A = 12.4$, τ (298 K) = 110 min; $\Delta S^{\neq} = -3.2$ cal/mol·K; $\Delta H^{\neq} = 21.7$ kcal/mol.

6: $T(1) = 273.3$ K, $k_1(1) = 4.949 \cdot 10^{-5}$; $T(2) = 285.4$ K, $k_1(2) = 3.345 \cdot 10^{-4}$; $T(3) = 289.4$ K, $k_1(3) = 5.374 \cdot 10^{-4}$, $T(4) = 293.6$ K, $k_1(4) = 9.354 \cdot 10^{-4}$. $E_A = 23.2$ kcal/mol, log $A = 14.2$, τ (298 K) = 6.7 min; $\Delta S^{\neq} = 5.5$ cal/mol·K; $\Delta H^{\neq} = 22.6$ kcal/mol.

7: $T(1) = 273.3$ K, $k_1(1) = 2.4084 \cdot 10^{-5}$; $T(2) = 283.4$ K, $k_1(2) = 1.6017 \cdot 10^{-5}$; $T(3) = 289.0$ K, $k_1(3) = 1.8046 \cdot 10^{-4}$. $E_A = 20.0$ kcal/mol, log $A = 11.4$, τ (298 K) = 23 min, $\Delta S^{\neq} = -8.2$ cal/mol·K; $\Delta H^{\neq} = 19.5$ kcal/mol.

8: $T(1) = 297.0$ K, $k_1(1) = 8.894 \cdot 10^{-5}$; $T(2) = 307.5$ K, $k_1(2) = 3.228 \cdot 10^{-4}$; $T(3) = 314.0$ K, $k_1(3) = 7.087 \cdot 10^{-4}$. $E_A = 22.6$ kcal/mol, log $A = 12.6$, τ (298 K) = 112 min; $\Delta S^{\neq} = -3.1$ cal/mol·K; $\Delta H^{\neq} = 22.0$ kcal/mol.

9: $T(1) = 308.2$ K, $k_1(1) = 1.429 \cdot 10^{-5}$; $T(2) = 316.7$ K, $k_1(2) = 4.823 \cdot 10^{-5}$; $T(3) = 322.9$ K, $k_1(3) = 1.249 \cdot 10^{-4}$; $T(4) = 330.4$ K, $k_1(4) = 3.009 \cdot 10^{-4}$. $E_A = 28.1$ kcal/mol, log $A = 15.1$, τ (298 K) = 4159 min; $\Delta S^{\neq} = 8.1$ cal/mol·K; $\Delta H^{\neq} = 27.2$ kcal/mol.

Thermolysis of **1**. a) *In MeCN*. A soln. of **1** (220 mg, 0.40 mmol) in MeCN (4.5 ml) was stirred under N_2 at 23° for 16 h. Evaporation and FC (hexane→hexane/AcOEt 6:1) of the residue gave **56** (99.4 mg, 46%), **57** (11 mg, 5%), **56**/**58** (9 mg, 4%), and **59** (6 mg, 3%). A soln. of **56**/**58** in $CDCl_3$ was completely transformed into **56** after storage for 1 week at 4°.

b) *Neat*. Crystalline **1** (40 mg, 0.073 mmol) was kept in a closed flask at r.t. for 2 h. FC (hexane/AcOEt 4:1) of the resulting yellow oil afforded **59** (7 mg, 18%) and a mixture **56**–**58** (17 mg, 44%). A soln. of **56**–**58** in C_6D_6 was kept at r.t. for 3 d, whereupon the ^{1}H-NMR spectra (integration of H–C(2) signals) showed signals only of **56** and **57** in a *ca.* 3:1 ratio.

*Data of (*Z,Z*)-2,3,4,6-Tetra-*O*-benzyl-*D*-glucono-1,5-lactone Azine* (**56**). R_f (hexane/AcOEt 4:1) 0.12. M.p. 116–7°. IR ($CHCl_3$): 3080*w*, 3060*w*, 3030*w*, 2990*w*, 2900*m*, 2860*m*, 1950*w*, 1875*w*, 1810*w*, 1645*m*, 1490*w*, 1450*w*, 1350*m*, 1065*s*, 1025*s*, 990*m* (sh), 905*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.43–7.41 (*m*, 2 arom. H); 7.35–7.17 (*m*, 16 arom. H); 7.14–7.11 (*m*, 2 arom. H); 4.85 (*d*, *J* = 12.0, PhC*H*); 4.66 (*d*, *J* = 12.1, PhC*H*); 4.62 (*dt*, *J* = 3.2, 10.3, H–C(5)); 4.60–4.51 (*m*, 2 PhC*H*); 4.47–4.41 (*m*, 2 PhC*H*); 4.35 (*d*, *J* = 11.6, PhC*H*); 4.33 (*d*, *J* = 12.0, PhC*H*); 4.28 (*d*, *J* = 1.7, H–C(2)); 3.93 (*dd*, *J* = 1.7, 4.7, H–C(3)); 3.82 (*dd*, *J* = 4.7, 10.3, H–C(4)); 3.72 (*d*, *J* = 3.2, 2 H–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 149.2 (*s*); 138.0 (*s*); 137.8 (*s*); 137.4 (*s*); 137.3 (*s*); 128.6–127.4 (several *d*); 81.8 (*d*); 77.6 (*d*); 75.6 (*d*); 74.2 (*d*); 73.4 (*t*); 72.8 (*t*); 71.2 (*t*); 70.2 (*t*); 68.9 (*t*). CI-MS: 1073 ($[M + 1]^+$). Anal. calc. for $C_{68}H_{68}N_2O_{10}$ (1073.29): C 76.10, H 6.39, N 2.61; found: C 76.39, H 6.11, N 2.43.

*Data of (*E,E*)-2,3,4,6-Tetra-*O*-benzyl-*D*-glucono-1,5-lactone Azine* (**57**). R_f (hexane/AcOEt 4:1) 0.22. IR ($CHCl_3$): 3090*w*, 3060*w*, 3000*w*, 2960*m*, 2930*m*, 2860*m*, 1950*w*, 1875*w*, 1810*w*, 1635*m*, 1495*w*, 1455*w*, 1360*w*, 1340*w*, 1260*s*, 1090*s*, 1015*s*, 910*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42–7.39 (*m*, 2 arom. H); 7.35–7.20 (*m*, 16 arom.

H); 7.17–7.13 (*m*, 2 arom. H); 5.64 (*d*, *J* = 1.6, H–C(2)); 4.70 (*ddd*, *J* = 1.9, 4.5, 10.1, H–C(5)); 4.66 (*d*, *J* = 12.1, PhC*H*); 4.66 (*s*, PhCH_2); 4.58 (*d*, *J* = 12.1, PhC*H*); 4.56 (*d*, *J* = 11.8, PhC*H*); 4.52 (*d*, *J* = 11.5, PhC*H*); 4.41 (*d*, *J* = 11.5, PhC*H*); 4.31 (*d*, *J* = 11.8, PhC*H*); 3.94 (*dd*, *J* = 1.8, 3.8, H–C(3)); 3.86 (*dd*, *J* = 1.9, 11.2, H–C(6)); 3.80–3.76 (*m*, H–C(4), H′–C(6)). ^{13}C-NMR (100 MHz, $CDCl_3$): 163.7 (*s*); 138.3 (*s*); 137.9 (*s*); 137.8 (*s*); 137.4 (*s*); 128.4–127.5 (several *d*); 80.4 (*d*); 77.8 (*d*); 75.4 (*d*); 73.5 (*t*); 72.5 (*t*); 71.5 (*t*); 71.2 (*t*); 69.0 (*t*); 67.6 (*d*). CI-MS: 1073 ([*M* + 1]$^+$.

*^{1}H-NMR Data of (*E,Z*)-2,3,4,6-Tetra-*O*-benzyl-*D*-glucono-1,5-lactone Azine* (**58**). Difference spectrum between **56**/**58** and **56**: 7.4–7.1 (*m*, 40 arom. H); 5.42 (*d*, *J* = 1.4, H–C(2′)); 4.7–4.3 (*m*, H–C(5), H–C(5′), 8 PhCH_2); 4.19 (*d*, *J* = 2.2, H–C(2)); 3.97 (*dd*, *J* = 1.6, 4.1, H–C(3′)); 3.94 (*dd*, *J* = 2.2, 4.7, H–C(3)); 3.92–3.77 (*m*, H–C(4), H–C(4′), 2 H–C(6), 2 H–C(6′)).

Thermolysis of **4**. An ice-cold soln. of **4** (620 mg, 1.18 mmol) in toluene (5 ml) was added dropwise *via* a syringe to toluene (5 ml) and stirred for 2 h at 45° under N_2. Evaporation and FC (hexane/Et_2O 2:1) gave **60** (463 mg, 77%). Similarly, thermolysis of **4** (650 mg, 1.23 mmol) in THF (5 ml) *or* **4** (610 mg, 1.16 mmol) in dioxane (5 ml) yielded **60** (400 mg (63%) and 326 mg (55%), resp.). Prep. HPLC (hexane/Et_2O 3:1, 14 ml/min) and crystallization from Et_2O/hexane gave pure *(Z,Z)-2,3,4,6-tetra-O-pivaloyl-D-glucono-1,5-lactone Azine* (**60**). R_f (hexane/Et_2O 1:2) 0.71. M.p. 120° (dec.). $[\alpha]_D^{25}$ = 61.2 (*c* = 1.05, $CHCl_3$). IR ($CHCl_3$): 3020*w* (sh), 2970*m*, 2930*m*, 2910*m* (sh), 2870*w*, 1745*s*, 1660*m*, 1480*m*, 1460*m*, 1400*w*, 1370*w*, 1280*m*, 1240*m*, 1170*m* (sh), 1140*s*, 1100*m* (sh), 1070*w* (sh), 1060*w*, 1040*m*, 1000*w*, 890*w*, 760*w*. ^{1}H-NMR (400 MHz, C_6D_6): 5.72 (*d*, *J* = 8.1, H–C(2)); 5.57 (*t*, *J* = 8.3, H–C(3)); 5.39 (*dd*, *J* = 8.5, 10.1, H–C(4)); 4.25–4.15 (*m*, 2 H–C(6)); 3.76 (*ddd*, *J* = 2.2, 3.3, 10.2, H–C(5)); 1.27 (*s*), 1.23 (*s*), 1.12 (*s*), 1.08 (*s*, 4 *t*-Bu). ^{13}C-NMR (50 MHz, C_6D_6): 177.31 (*s*); 176.46 (*s*); 176.02 (*s*); 175.88 (*s*); 148.24 (*s*); 75.59 (*d*); 71.96 (*d*); 68.97 (*d*); 66.93 (*d*); 61.30 (*t*); 38.96 (*s*); 38.82 (*s*); 38.71 (*s*); 27.21 (*q*); 27.11 (*q*); 26.98 (*q*); 26.74 (*q*). CI-MS: 1027 (20), 1026 (58), 1025 (100, [*M* + 1]$^+$), 924 (25), 923 (47), 823 (12), 822 (25), 821 (49), 532 (24), 120 (12). Anal. calc. for $C_{52}H_{84}N_2O_{18}$ (1025.25): C 60.92, H 8.26, N 2.73; found: C 60.95, H 8.30, N 2.85.

Thermolysis of **9**. A soln. of **9** (200 mg, 0.488 mmol) in CH_2Cl_2 (4 ml) was heated under reflux for 24 h. The solvent was evaporated. Prep. HPLC (CH_2Cl_2/MeOH 97:3) of the white foamy residue gave **61** (93.1 mg, 48%) and **62** (14.6 mg, 8%) [29].

Data of (Z,Z)-2-Acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-D-allono-1,5-lactone Azine (**61**). R_f (Et_2O/MeOH 97:3) 0.03. $[\alpha]_D^{21}$ = 108.0 (*c* = 0.87, $CHCl_3$). IR ($CHCl_3$): 3440*w*, 3000*w*, 2940*w*, 2870*w*, 1660*s*, 1495*s*, 1455*w*, 1370*m*, 1345*w*, 1305*w*, 1150*m*, 1120*s*, 1100*s*, 1060*s*, 1030*s*, 960*w*, 910*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.51–7.47 (*m*, 2 arom. H); 7.42–7.28 (*m*, 8 arom. H); 6.27 (*d*, *J* = 7.2, AcN*H*); 5.54 (*s*, PhC*H*); 4.93 (*d*, *J* = 11.6, PhC*H*), 4.79 (*dd*, *J* = 3.0, 7.2, H–C(2)); 4.57 (*d*, *J* = 11.6, PhC*H*); 4.43 (*dt*, *J* = 5.1, 10.1, H–C(5)); 4.41 (*dd*, *J* ≈ 1.8, 2.8, H–C(3)); 4.25 (*dd*, *J* = 5.0, 10.4, H_{eq}–C(6)); 3.97 (*dd*, *J* = 1.5, 9.8, H–C(4)); 3.75 (*t*, *J* = 10.5, H_{ax}–C(6)); 1.94 (*s*, AcN). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.56 (*s*); 149.07 (*s*); 137.81 (*s*); 136.78 (*s*); 129.27–126.10 (several *d*); 102.22 (*d*); 78.56 (*d*); 74.64 (*d*); 74.44 (*t*); 68.34 (*t*); 67.73 (*d*); 50.89 (*d*); 23.07 (*q*). CI-MS: 791 (3, [*M* + 1]$^+$), 683 (43, [*M* – BnOH + 1]$^+$), 576 (36), 575 (100, [*M* – 2 BnOH + 1]$^+$), 303 (46), 289 (38). Anal. calc. for $C_{44}H_{46}N_4O_{10}$ (790.89): C 66.82, H 5.86, N 7.08; found: C 66.97, H 5.82, N 6.92.

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