Glycosylidene Carbenes

Part 31[1])

Glycosylidene Diaziridines: Stereoselective Addition of Ammonia and Methylamine to Lactone Oxime Sulfonates

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Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

The diastereoselectivity of the addition of NH_3 and $MeNH_2$ to glyconolactone oxime sulfonates and the structures of the resulting *N*-unsubstituted and *N*-methylated glycosylidene diaziridines were

The ^{15}N-labelled glucono- and galactono-1,5-lactone oxime mesylates **1*** and **9*** add NH_3 mostly axially (> 3:1; *Scheme 4*), while the ^{15}N-labelled mannono-1,5-lactone oxime sulfonate **19*** adds NH_3 mostly equatorially (9:1; *Scheme 7*). The ^{15}N-labelled mannono-1,4-lactone oxime sulfonate **30*** adds NH_3 mostly from the *exo* side (>4:1; *Scheme 9*). The configuration of the *N*-methylated pyranosylidene diaziridines **17**, **18**, **28**, and **29** suggests that $MeNH_2$ adds to **1**, **9**, **19**, and **23** mostly to exclusively from the equatorial direction (>7:3; *Schemes 5* and *8*). The mannono-1,4-lactone oxime sulfonate **30** adds $MeNH_2$ mostly from the *exo* side (85:15; *Scheme 10*), while the *ribo* analogue **37** adds $MeNH_2$ mostly from the *endo* side (4:1; *Scheme 10*). Analysis of the preferred and of the reactive conformers of the tetrahedral intermediates suggests that the addition of the amine to lactone oxime sulfonates is kinetically controlled. The diastereoselectivity of the diaziridine formation is rationalized as the result of the competing influences of intramolecular H-bonding during addition of the amines, steric interactions (addition of $MeNH_2$), and the kinetic anomeric effect.

The diaziridines obtained from 2,3,5-tri-*O*-benzyl-D-ribono- and -D-arabinono-1,4-lactone oxime methanesulfonate (**42** and **48**; *Scheme 11*) decomposed readily to mixtures of 1,4-dihydro-1,2,4,5-tetrazines, pentono-1,4-lactones, and pentonamides.

The *N*-unsubstituted gluco- and galactopyranosylidene diaziridines **2**, **4**, **6**, **8**, and **10** are mixtures of two *trans*-substituted isomers (**S**/**R** *ca.* 19:1, *Scheme 2*). The main, (*S*,*S*)-configured isomers **S** are stabilised by a weak intramolecular H-bond from the pseudoaxial NH to RO–C(2). The diaziridines **12**, derived from GlcNAc, cannot form such a H-bond; the (*R*,*R*)-isomer dominates (**R**/**S** 85:15; *Scheme 3*). The 2,3-di-*O*-benzyl-D-mannopyranosylidene diaziridines **20** and **22** adopt a $^4C_1$ conformation, which does not allow an intramolecular H-bond; they are nearly 1:1 mixtures of **R** and **S** diastereoisomers, whereas the $^OH_5$ conformation of the 2,3:5,6-di-*O*-isopropylidene-D-mannopyranosylidene diaziridines **24** is compatible with a weak H-bond from the equatorial NH to O–C(2); the (*R*,*R*)-isomer is favoured (**R**/**S** ≥ 7:3; *Scheme 6*). The mannofuranosylidene diaziridine **31** completely prefers the (*R*,*R*)-configuration (*Scheme 9*).

Introduction. – Glycosylidene carbenes (**VI** in *Scheme 1*) are glycosylating agents. They are particularly useful for the glycosylation of tertiary, sterically hindered, and poorly nucleophilic hydroxy compounds and for the detection of intramolecular H-bonds in partially protected monosaccharides (see [2–6] and refs. cit. therein). These carbenes are generated by thermolysis or photolysis of glycosylidene diazirines **V**. The diazirines were prepared from partially protected aldose oximes **I** by oxidation (→ **II**),

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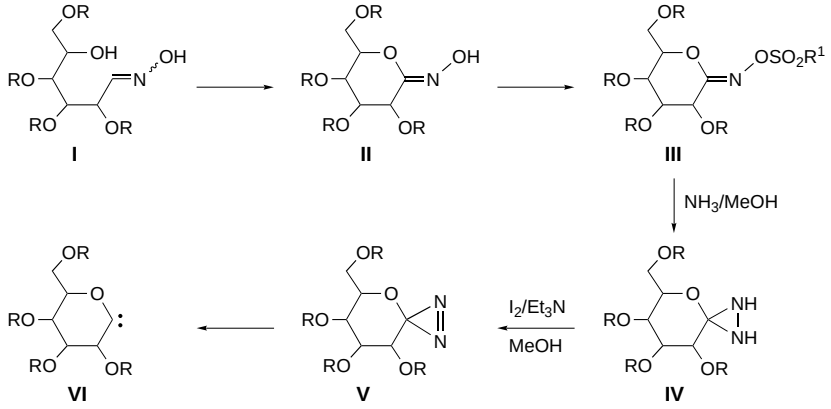
sulfonylation (→ **III**), treatment with NH_3 in MeOH, and oxidation of the diaziridines **IV** with I_2 (*Scheme 1*). These diaziridines are, as a rule, mixtures of *trans*-configured diastereoisomers.

Scheme 1



The transformation of glyconolactone oxime sulfonates to spirodiaziridines is initiated by the addition of NH_3 to the C=N bond, but the structure of the resulting diastereoisomeric *trans* diaziridines does not betray the equatorial or axial direction of this attack. We report on the configuration of the diaziridines and on the direction of the addition of NH_3 and of $MeNH_2$.

Results and Discussion. – 1. D-*Gluco- and* D-*Galactopyranosylidene Diaziridines.* The transformation of the *gluco*- and the *galacto*-configured sulfonates **1** [7], **3** [5], **5** [8], **7** [5], and **9** [7] (*Scheme 2*) into the corresponding diaziridines has already been described. According to the ^{1}H-NMR spectra of $CDCl_3$ solutions, the diaziridines are *ca.* 19:1 mixtures of two *trans*-configured diastereoisomers **2S**/**2R**[2]), **4S**/**4R**, **6S**/**6R**, **8S**/**8R**, and **10S**/**10R** as evidenced by the vicinal $J(NH_e,NH_a)$ values of 9.4 Hz.

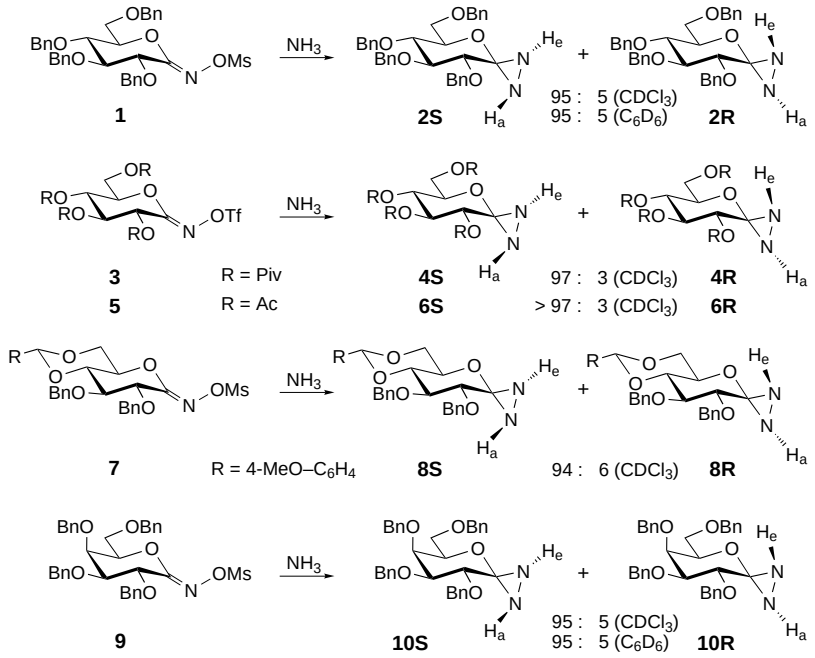
We started our investigation by repeating the addition of NH_3 to the benzylated **1** and **9**, and found that benzene solutions of the diaziridines **2S**/**2R** and **10S**/**10R** are more-stable than the previously described $CHCl_3$ solutions, so that solutions in C_6D_6 were used for the more-recent NMR investigations. In either solvent, **2** and **10** were 19:1 mixtures of the **S** and **R** diastereoisomers.

^{1}H-NMR Analysis showed that the (*S*,*S*)-diastereoisomers of the *C*(2)-alkoxy- and *C*(2)-acyloxy-diaziridines **2**, **4**, **6**, **8**, and **10** dominate in solution. In contradistinction, the major diastereoisomers of the *C*(2)-acetamido-diaziridines **12** and **14** possess the (*R*,*R*)-configuration. This difference appears to be mostly due to an intramolecular $N-H_a\cdots OC(2)$ H-bond that is possible only for the C(2)-OR diaziridines.

The vicinal coupling constants $J(2,3)$, $J(3,4)$, and $J(4,5)$ evidence a $^4C_1$ conformation for **2S**, **4S**, **4R**, **8S**, **8R**, and **10S**. The configuration of the N-atoms of the tetra-*O*-benzylated diaziridines **2S** and **10S** was analysed on the basis of nuclear *Overhauser* effects (NOEs; *Fig. 1*). NOEs of 2.2–3.3% were observed between the NH of **2S**

[2]) Throughout the paper, **S** denotes the (*S*,*S*)- and **R** the (*R*,*R*)-configuration at the N-atoms.

Scheme 2



resonating at lower field (H_a; 2.68 ppm in C_6D_6) and H–C(3). A weaker NOE (1.3%) was detected between NH_a and H–C(5), but there was no NOE between NH_a and H–C(2). No NOE's were detected for the NH of **2S** resonating at higher field (NH_e). These observations evidence the (*S*,*S*) configuration of the major diastereoisomer of **2** in solution; the same configuration was established for **2** in the solid state [1]. Similarly, we observed a NOE of *ca.* 2% between the low field NH_a of **10S** and H–C(3). A remarkable chemical-shift difference ($\Delta\delta$) between H_a and H_e of **2S** was observed for solutions in C_6D_6 ($\Delta\delta = 0.42$ ppm) and $CDCl_3$ ($\Delta\delta = 0.30$ ppm; *Table 2* in *Exper. Part*). The corresponding $\Delta\delta$ values for **10S** are even larger by 0.1 ppm. A similar, large $\Delta\delta$ value of 0.52 ppm for the 4,6-*O*-benzylidenated analogue **8S** allows us to unambiguously assign the NH groups and the configuration. However, only small $\Delta\delta$ values were observed for the major isomers **S** of the pivaloate **4** ($\Delta\delta = 0.03$ ppm) and of the acetate **6** ($\Delta\delta = 0.07$ ppm), probably mainly due to the anisotropy effect of the C(2)OC=O (and C(6)OC=O?) groups. We tentatively assume that H_a is still more deshielded. The assignment of the NH of the minor isomers **4R** and **8R** is based on a comparison with the data of the *N*-Me analogues (see below). For the minor isomers (**R** series), the proximity of the lone pair of the pseudoaxial *N*-atom and H-C(3) leads to a downfield shift for H–C(3) ($\Delta\delta = 0.2$–0.3 ppm for **4S**/**4R** and **8S**/**8R**). For the major isomers (**S** series), the corresponding lone pair is close to H–C(5), which is deshielded ($\Delta\delta = 0.74$ ppm for **4S**/**4R** and *ca.* 0.1 ppm for **8S**/**8R**). The large shift difference for H–C(5) of the pivaloate **4S**/**4R** correlates with a different orientation of the (pivaloyloxy)methyl side chain of **4S** in C_6D_6 as indicated by an inversion of the ratio of the *J*(5,6) and *J*(5,6′) values.

The plausibility of the assumed $N-H_a\cdots OC(2)$ H-bond was checked by AMPAC calculations (AM1, gas phase [9]) of 6-deoxy-2,3,4-tri-*O*-methyl-D-glucopyranosylidene diaziridines. According to these calculations, the **S** isomer is by 3.5 kcal/mol more stable than the **R** isomer, and H_a of the **S** isomer may form a stronger intramolecular H-bond to MeO–C(2) ($d(H_a\cdots O) = 2.49$ Å, $\measuredangle(N-H_a\cdots O) = 103°$) than H_e of the **R** isomer ($d(H_e\cdots O) = 2.56$ Å, $\measuredangle(N-H_e\cdots O) = 100°$). This result is in

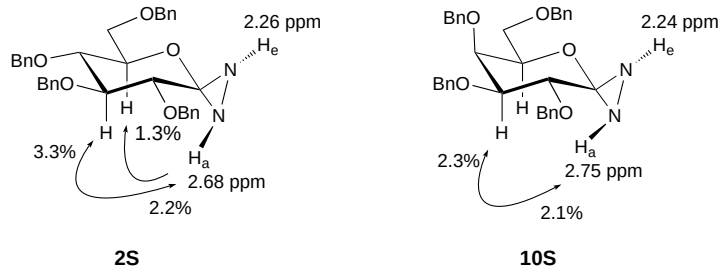


Fig. 1. *NOEs between NH and glycosylidene H-atoms of the diaziridines* **2S** *and* **10S** *in* C_6D_6 *solution*

accordance with the fact that intramolecular H-bonds between axial and equatorial OH groups are stronger than intramolecular H-bonds between two equatorial OH groups [10–12].

Analogues of the above diaziridines possessing an equatorial C(2)–NHAc instead of a C(2)–OR group cannot form a H-bond equivalent to the one postulated for the C(2)–OR diaziridines of the **S** series. AM1 Calculations, indeed, predict the absence of an intramolecular H-bond in 2-acetamido-2,6-dideoxy-3,4-di-*O*-methyl-D-glucopyranosylidene diaziridines both in the **S** isomer ($d(H_a \cdots N) = 2.81$ Å) and in the **R** isomer ($d(H_e \cdots N) = 2.68$ Å). The **R** isomer is favoured by only 0.2 kcal/mol.

The preparation of the GlcNAc- and AllNAc-derived diaziridines **12S**/**12R** [5] and **14S**/**14R** [13] (*Scheme 3*) has already been described. In both cases, a 85 : 15 mixture of diastereoisomers was obtained. A closer analysis of the ^{1}H-NMR data of these diaziridines (*cf. Table 2* in *Exper. Part*) allowed determination of the configuration in the absence of NOE data. The determination is based on the relative chemical shifts of H–C(5) of the **S**/**R** diastereoisomers. The major isomers possess the (*R*,*R*) configuration, as indicated by the downfield shift for H–C(5) of the minor isomer ($\Delta\delta = 0.49$ (**12S**/**12R**) and 0.14 ppm (**14S**/**14R**)), evidencing the proximity to the lone pair of the pseudoaxial NH group. However, despite the proximity to the N lone pair, H–C(3) of **12R** (3.62 ppm) is more-shielded than H–C(3) of **12S** (3.87 ppm), probably due to a different orientation of the AcNH group, as evidenced by the *J*(2,HN) values of 9.4 Hz for **12R** and of 8.2 Hz for **12S** (steric repulsion between H_a–N and H–NAc?), and by the $\Delta\delta$ values for H–C(2), as compared to those of **4S**/**4R** and **8S**/**8R** (opposite relative shifts). The signals for H_a and H_e of **12S** and **12R** were assigned by comparing the δ(NH) values with those for **2S**/**2R** ($\Delta\delta \leq 0.04$ ppm, except for $\Delta\delta = 0.19$ ppm for NH_a of the **R** isomer). The small shift difference between NH_a and NH_e of **14S** and **14R** ($\Delta\delta \leq 0.11$ ppm) prevents an assignment. The isomers **12R**, **14S**, and **14R** adopt a $^4C_1$ conformation, whereas **12S** exists as mixture of the $^4C_1$ chair and (presumably) a boat conformer ($J(2,3) = 7.6$, $J(3,4) = 5.5$ Hz, $J(4,5)$ not assigned). The preference for the (*R*,*R*)-configuration of the 2-acetamido diaziridines **12** and **14** evidences the effect of the intramolecular H-bond between H_a and RO–C(2) of the (*S*,*S*)-configured *gluco* and *galacto* diaziridines; the origin for the preference of **12R** and **14R** is not clear (interaction between H_a–N and H–NAc?).

To assess the diasteroselectivity in the transformation of **1** to **2**, one needs to selectively label one N-atom of **2**. It appeared convenient to introduce a ^{15}N label in the

Scheme 3

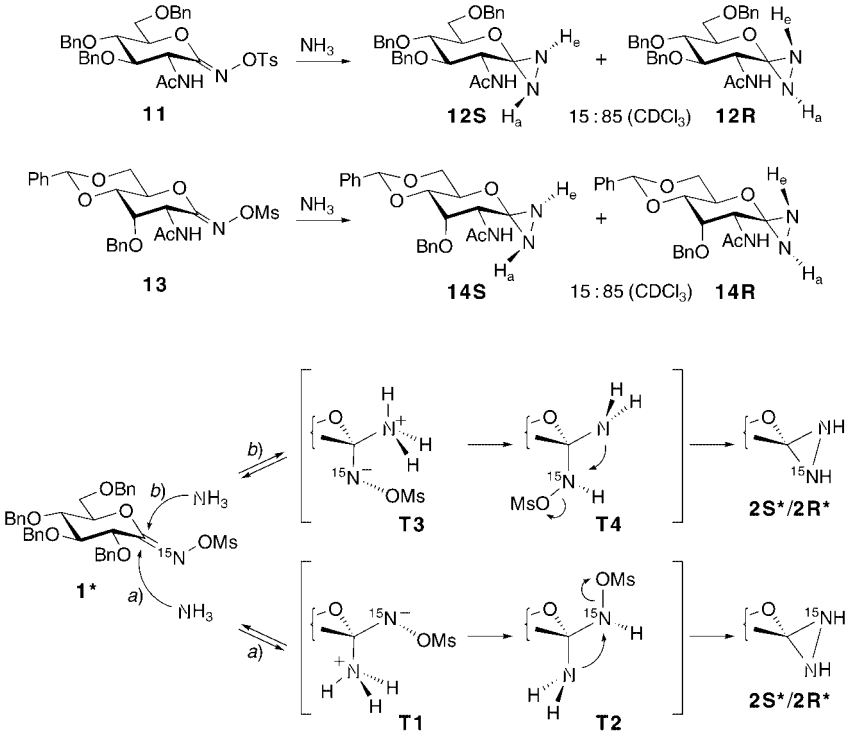


Fig. 2. *Mechanism of the diaziridine formation: pseudoaxial* vs. *pseudoequatorial attack of NH_3 at the anomeric centre of* **1***

oximes **I** (*Scheme 1*) using solid $^{15}NH_2OH \cdot HCl$. A preferred labelling of the pseudoequatorial N-atom of the resulting diaziridines upon addition of NH_3 (*Fig. 2*) may evidence an axial attack on the C=^{15}N bond of **1***[3])[4]), as postulated by the rules of *Deslongchamps* [14][15]. To yield the diaziridine with pseudoequatorial ^{15}N, this attack must lead, irreversibly or reversibly, to the equatorial mesyloxy amine **T2**. If **T2** is formed reversibly, ring closure from **T2** must be faster than from the axial diastereoisomer **T4**. Conversely, labelling of the axial N-atom of **2** upon addition of NH_3 would evidence cyclisation of the axial mesyloxy amine **T4**. Assuming the validity of *Deslongchamps*'s rules, this would mean that **T2** is formed reversibly, and that **T4** cyclises more rapidly than **T2**.

The reaction of the unlabelled oximes **1** and **9** with NH_3 proceeded in good yields, speaking against fast equilibrium between **T2** and **T4** *via* **1***, and a slow ring closure of **T2** and **T4**. The initially formed zwitterions **T1** and **T3** must be transformed into **T2** and **T4** before cyclising to the diaziridines. Breakdown of **T2** and **T4** by elimination of the

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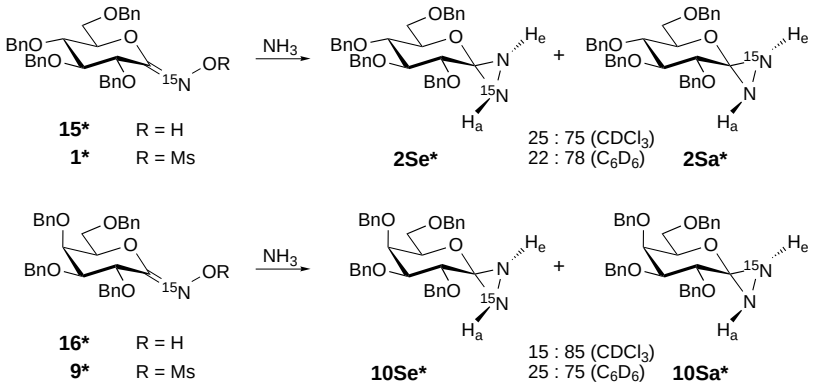
[3]) The asterisk denotes ^{15}N-labelled compounds.

[4]) Under the basic conditions, protonation of the ring O-atom, followed by the intermediate opening of the pyranosylidene ring and (partial) epimerisation at C(1), appears improbable.

better leaving group ($MsONH_2$) is expected to lead to glycosylidene imines, well-known intermediates of the *Fischer-Kiliani* cyanhydrin synthesis that are rapidly hydrolysed or transformed into amides [16].

Oxime formation was optimised for the reaction of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose with $^{15}NH_2OH \cdot HCl$. Reducing the amount of $NH_2OH \cdot HCl$ from 8 [17] to 1.3 equiv. still afforded a nearly quantitative yield of the corresponding crude (*E*/*Z*)-oximes. Oxidation of the crude ^{15}N-labelled hydroxy oximes derived from 2,3,4,6-tetra-*O*-benzyl-D-gluco- and -galactopyranose with MnO_2 gave a 61–62% yield of the lactone oximes **15*** and **16*** (*Scheme 4*). Mesylation of **15*** and **16*** (MsCl, Et_3N) and crystallisation from Et_2O gave **1*** and **9*** in 56 and 87% yield, respectively. Treatment of **1*** with a saturated solution of NH_3 in MeOH, followed by crystallisation at $-15°$, gave the isotopomers **2Se*** and **2Sa***[5]) in a 25:75 ratio. Repetition of the reaction led to **2Se***/**2Sa*** 22:78. Similar transformations of **9*** gave the isotopomers **10Se*** and **10Sa*** in ratios of 15:85 and 25:75. These results are compatible with either an irreversible pseudoaxial attack of NH_3 to **1*** and **9***, or with a preferred ring closure of the equatorial mesyloxy amine.

Scheme 4



In the ^{15}N-NMR spectra of the gluconolactone oximes **15*** and **1***, a br. *d* ($J = 1.7–2.2$ Hz) is found at -65.80 and -60.67 ppm, and, in those of the galactonolactone oximes **16*** and **9***, one finds a *dd* ($J = 1.2–1.3$ and 0.2 Hz) at -77.91 and -80.36 ppm, respectively. The incorporation of ^{15}N into **15***, **1***, **16***, and **9*** leads to an additional splitting of the signals for H–C(2) ($^3J(^{15}N,H) = 1.2–1.6$ Hz), H–C(3) (only of **15*** and **1***: $^4J(^{15}N,H) = 1.0–1.6$ Hz), OH (of **15*** and **16***: $^2J(^{15}N,H) \leq 0.8$ Hz), C(1) (only of **16*** and **9***: $^1J(^{15}N,C) = 0.8–1.2$ Hz), C(2) ($^2J(^{15}N,C) = 9.5–11.4$ Hz), and C(3) ($^3J(^{15}N,C) = 1.7–2.6$ Hz).

In the ^1H-NMR spectra, the ^{15}N label of the *N*-unsubstituted diaziridines **2Se***/**2Sa*** and **10Se***/**10Sa*** is evidenced by additional splitting of only the NH signals, characterized by $^1J(^{15}N,H)$ of 56.8–57.3 Hz[6]) and $^2J(^{15}N,H)$ of 2.8–3.7 Hz (*cf. Table 2* in *Exper. Part*). The *dd* for the NH groups of the (*R*,*R*)-configured diastereoisomers (*ca.* 5% expected) are probably hidden by noise. The ^{13}C-NMR spectra of **2Se***/**2Sa*** and **10Se***/**10Sa*** show a single set of signals; the chemical-shift values are identical to those of the unlabelled **2S** and **10S** (*cf. Table 3* in *Expert. Part*). C(1) and C(2) of **2Se***/**2Sa*** and **10Se***/**10Sa*** show couplings of 5.1–6.1 and

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[5]) The letters **a** and **e** denote the pseudo**a**xial and the pseudo**e**quatorial position of the NR group stemming from the amine.

[6]) Compare with 56.3–60.7 Hz for ^{15}N-labelled bis(trifluoromethyl)-diaziridines [18].

$\leq$ 3.9 Hz with ^{15}N, respectively. The ^{15}N-NMR spectra of **2Se***/**2Sa*** and **10Se***/**10Sa*** in $CDCl_3$ and C_6D_6 reflect the same product ratios as in the ^{1}H-NMR spectra (*cf. Table 4* in *Exper. Part*). The ^{15}N signals appear as *dd*'s showing a large $^1J(^{15}N,H)$ of 56.5–58.0 ppm and a small $^2J(^{15}N,H)$ of 2.7–3.6 Hz. The weaker signal for the pseudoaxial ^{15}N-atom resonates at higher field ($\Delta\delta = 8.4–10.4$ ppm).

To evaluate the scope of the diaziridine formation, we cursorily examined the addition of $MeNH_2$, Me_2CHNH_2, Me_3CNH_2, and aniline in MeOH to **9**; of these amines, only $MeNH_2$ reacted to a discernible extent. Treatment of **1** with a 7M solution of $MeNH_2$ in dry MeOH for 2.5 h at room temperature and purification of the product by filtration through *LiChroPrep*-NH_2 gave 97% of a 72:28 mixture of **17Se** and **17Ra** containing traces (*ca.* 5%) of an unassigned epimer. Similarly, treatment of **9** led to a 85:15 mixture of the *galacto*-configured **18Se** and **18Ra**. $MeNH_2$ was also added to the ^{15}N-labelled sulfonates **1*** and **9*** to facilitate the measurement of ^{15}N-NMR spectra. The mixture **18Se**/**18Ra** solidified upon standing. Crystallisation from MeOH afforded pure **18Se**, and recrystallisation in AcOEt/hexane gave crystals suitable for X-ray analysis.

The solid-state structure of **18Se** reveals a pseudoequatorial MeN group, the (*S*,*S*)-configuration of the N-atoms, a $^4C_1$ conformation of the pyranosylidene ring, and a *tg* conformation for the $BnOCH_2$ side chain (*Fig. 3*)[7]). The structure closely resembles that of the *N*-unsubstituted **2S** [1] (*Table 1*). Even a (weak) intramolecular H-bond from N_a–H to BnO–(2) is found in both structures, in keeping with the results of the AM1 calculations. This H-bond is slightly weaker in **18Se** than in **2S** as evidenced by larger $N_a \cdots O(2)$ ($\Delta d = 0.05–0.07$ Å) and $H_a \cdots O(2)$ distances.

Table 1. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for the Diaziridines* **18Se** *and* **2S**

	18Se	**2S** [1]		**18Se**	**2S** [1]
C(5)–O(5)	1.448(3)	1.451(3)	O(5)–C(1)–N_a	115.8(2)	115.5(2)
O(5)–C(1)	1.388(3)	1.385(4)	O(5)–C(1)–N_e	117.8(2)	117.7(3)
C(1)–N_a	1.445(3)	1.436(4)	C(1)–N_a–N_e	56.6(1)	57.17(19)
C(1)–N_e	1.422(3)	1.426(4)	C(1)–N_e–N_a	58.1(1)	57.8(2)
N_a–N_e	1.547(3)	1.539(4)	N_a–C(1)–N_e	65.3(1)	65.0(2)
N_a–H_a	0.94(2)	0.90(3)	C(1)–N_a–H	109(2)	109(2)
$N_a \cdots O(2)$	2.906(3)	2.840(3)	N_e–N_a–H	103(2)	106.2(19)
$H_a \cdots O(2)$	2.43(3)	2.38(3)	N_a–H$\cdots$O(2)	111(2)	112(2)
N_e–H_e	–	0.92(4)	N_a–N_e–H	–	104(2)
N_e–CH_3	1.448(3)	–	N_a–N_e–CH_3	109.4(2)	–

The configurations of the N-atoms of **17Se**, **17Ra**, **18Se**, and **18Ra** in solution were revealed by NOE experiments (*Fig. 4*). NOEs of 2.8–2.9% were observed for H–C(3) of the major isomers **17Se** and **18Se** upon irradiating the NH signal at 3.02 and 3.08 ppm, respectively. This evidences a pseudoaxial NH group and the (*S*,*S*)-configuration of the major isomers. Irradiation of the NMe group of the minor isomers **17Ra** and **18Ra** leads to a NOE for H–C(5) of 2.0–3.3%. In addition, a NOE (3.1%) between NH and H–C(2) of **17Ra** was observed. Thus, the minor isomers possess a pseudoaxial NMe group and the (*R*,*R*) configuration. The

7) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-197608. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

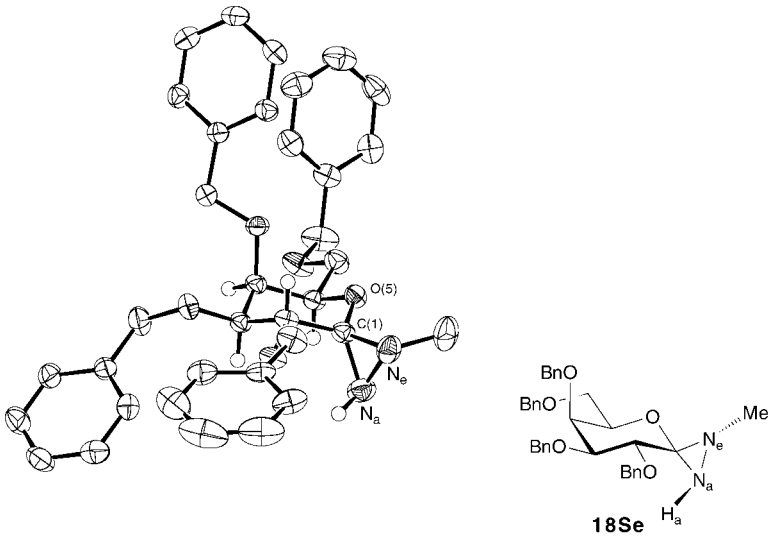

Fig. 3. *X-Ray structure of* **18Se**. The H-atoms of the Me and the Bn groups are omitted for clarity.

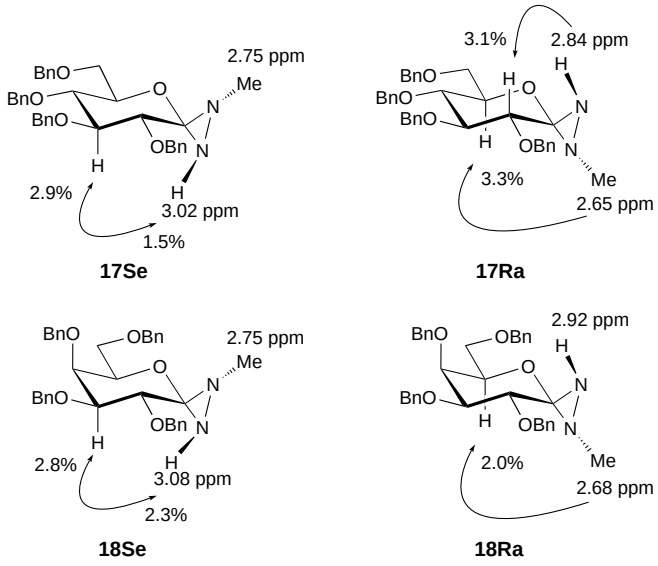

Fig. 4. *NOEs between NH or NMe, and glycosylidene H-atoms of the diaziridines* **17Se**, **17Ra**, **18Se**, *and* **18Ra** *in* C_6D_6 *solution*

configuration of the diaziridine ring has no influence on the pyranose ring conformation. The same $J(2,3)$, $J(3,4)$, and $J(4,5)$ (*cf. Table 2* in *Exper. Part*) were observed for the major and the minor isomers, and they evidence a $^4C_1$ conformation of **17Se**, **17Ra**, **18Se**, and **18Ra**. As expected, the (*S*,*S*)-configuration of the major isomers correlates with a downfield shift for H–C(5) of the **S** isomers ($\Delta\delta \approx 0.3$ ppm), and the (*R*,*R*)-configuration of the minor isomers correlates with a downfield shift for H–C(3) of the **R** isomers ($\Delta\delta = 0.4$ ppm).

The incorporation of ^{15}N in **17Se*/17Ra*** and **18Se*/18Ra*** leads to additional splitting of the signals for NH ($^1J(^{15}N,H) = 57.4-58.3$ Hz) and NMe ($^3J(^{15}N,H) = 2.7-2.9$ Hz). The same couplings are also visible in the ^{15}N-NMR spectra of **17Se*/17Ra*** 72:28 and **18Se*/18Ra*** 85:15 where *dq*s appear at -297.3 to -299.6 ppm (*cf. Table 4* in *Exper. Part*). In the ^{13}C-NMR spectra, the signal for the NMe group of **17Se**, **17Ra**, **18Se**, and **18Ra** is split by coupling with ^{15}N ($^2J(^{15}N,C) = 3.6-4.1$ Hz). Only the pseudoaxial ^{15}N-atom of the major isomers **17Se*** and **18Se*** couples with C(1) ($^1J(^{15}N,C) = 4.1-4.3$ Hz; *Table 3* in *Exper. Part*).

Out of the four possible *N*-Me-diaziridines only the two were detected that can form an intramolecular H-bond from N–H to BnO–C(2). The other isomers are also disfavoured by a 1,5-interaction between the NMe and BnO–C(2) groups.

The ratios of the isotopomeric *gluco*- and *galacto*-configured diaziridines (**2Se*/2Sa*** and **10Se*/10Sa*** 22:78 and 25:75, resp.) and the ratios of the corresponding *N*-Me-diaziridines (**17Se/17Ra** and **18Se/18Ra** 72:28 and 85:15, resp.) characterize a preferred ring closure from a tetrahedral intermediate with an axial NH_2 group (derived from added NH_3) and an equatorial MeNH group, respectively. This difference may be due to steric and/or electronic interactions operating either during the addition of NH_3 and $MeNH_2$ to the imino group or during ring closure of the intermediate mesyloxy amines (see *Fig. 2*)[8]). As mentioned above, the axial attack of the nucleophiles on the lactone oxime sulfonates is stereoelectronically favoured. The axial attack may also be favoured by an (initially intermolecular) H-bond between the attacking amine and C(2)–OR. The strength of such a H-bond should increase parallel to the C(1)–N bond-formation during which the amine is transformed into an ammonium substituent. That a *cis*-axial ammonium group may form a stronger H-bond to C(2)–OR than a *trans*-equatorial one is suggested by the stronger H-bond between the pseudoaxial NH and C(2)–OBn of the C(2)-alkoxylated *N*-unsubstituted diaziridines[9]).

To get better insight into the stereoselectivity of the ring-closing step, we modelled the reactive conformers of the diasteroisomeric 2-amino- and 2-(methylamino)-2-(mesyloxyamino)-tetrahydropyrans **M1/M2** and **M3/M4** (AM1 calculation; *Fig. 5*). In the reactive conformations, the lone pair of the amino group at C(1) is directed towards the (mesyloxy)amino substituent. This implies synperiplanar orientation of the H–N bonds of **M1** and **M2** and of the H–N and Me–N bonds of **M3** and **M4** with C(2)–C(3) and C(2)–O. The MsO group is oriented away from the amino group, and the N-lone pair of the MsONH group is antiperiplanar to the C(1)–O bond (*exo*-anomeric effect). Thus, the reactive conformers **M11** and **M21** of the epimeric intermediates **M1** and **M2** have to be compared, and, similarly, the two pairs **M31/M32** and **M41/M42** of the epimeric intermediates **M3** and **M4**, respectively. The significantly greater stability of **M11** over **M21** shows that the orientation of the MsO group is the main energetic factor. Among the MeNH isomers, **M31** is by far the most favoured (reactive) conformer. A comparison to **M41** and **M42** shows that this is due to the equatorial orientation of the MsONH substituent and to a coplanar arrangement of Me–N and O–C(2), avoiding the interaction with MeO–C(3) that destabilises **M32**. The

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[8]) The formation of an intermediate nitrene appears improbable, since hydroxylamine *O*-sulfonic acid does not form the corresponding nitrene under basic conditions [19].

[9]) The relative strength of these H-bonds derives from the ratio of the equilibrating *trans*-diaziridines. For the nonequilibrating *N*-Me-diaziridines, one finds the same relative N···O distances as for the unsubstituted analogues, suggesting the same relative strength of their N–H···O–C(2) H-bonds.

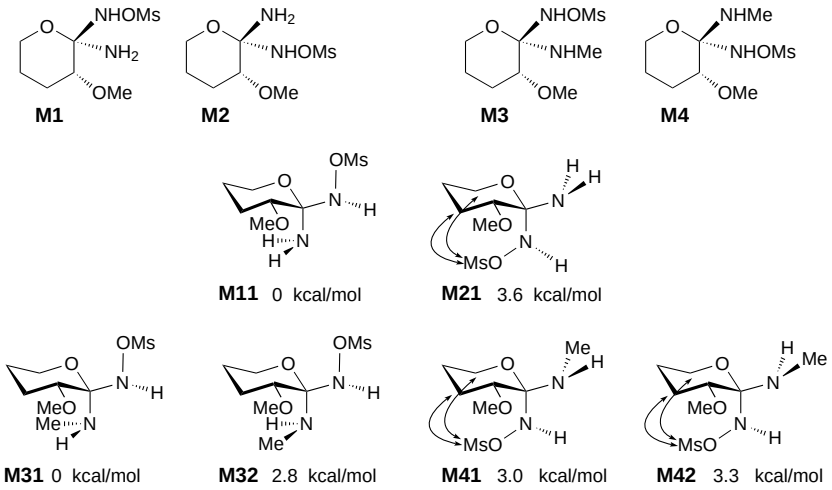


Fig. 5. *Calculated (AM1) relative energies of the reactive intermediates* **M11**, **M12**, **M31**, **M32**, **M41**, *and* **M42** *of the epimeric 2-aminotetrahydropyrans* **M1** *and* **M2**, *and of the epimeric 2-(methylamino)tetrahydropyrans* **M3** *and* **M4**. Destabilizing 1,5-interaction indicated by double-headed arrows.

difference between the coplanar arrangements of Me–N and C(3)–C(2) *vs.* Me–N and O–C(2) amounts to only 0.3 kcal/mol (compare **M41** and **M42**).

The relative stabilities of these reactive conformers imply a more-facile formation of the diaziridines derived from the tetrahedral intermediate resulting from an axial attack of NH_3 or $MeNH_2$. This is not in agreement with the configuration of the *N*-Me-diaziridines **17** and **18**, although the axial attack is favoured by the kinetic anomeric effect and by H-bonding of the attacking amine to the *cis*-oriented RO–C(2). Steric interactions in the addition step must then be responsible for the preferred addition of $MeNH_2$ from the equatorial side. To evaluate the steric interactions during the addition, we analysed the conformations **A1**–**A6** of the primary addition products resulting from an equatorial and an axial attack of $MeNH_2$ on **1** (*Fig. 6*). The conformers **A1** and **A4** cannot form an intramolecular H-bond and are disfavoured by a 1,5-interaction between the MeN and the BnO–C(2) groups. The conformers **A2**, **A3**, **A5**, and **A6** can form an intramolecular H-bond, but conformers **A2** and **A5** are disfavoured by a 1,5-interaction between the MeN and the MsO group, and **A6** is disfavoured by 1,5-interactions between MeN and both C(3) and C(5). Only **A3** is not disfavoured by steric interactions. It results from an equatorial addition of $MeNH_2$ to **1**. This means that the kinetic anomeric effect is overruled by the combined influence of H-bonding and steric interactions that favour the equatorial addition of $MeNH_2$, a conclusion that could not be drawn from the addition of NH_3, since, here, both the kinetic anomeric effect and H-bonding of the *cis*-axial ammonium group to BnO–C(2) favour the axial addition[10]).

[10]) For another case, where the interaction of the attacking nucleophile with C(2)–OR dominates over the stereoelectronic control, see [20].

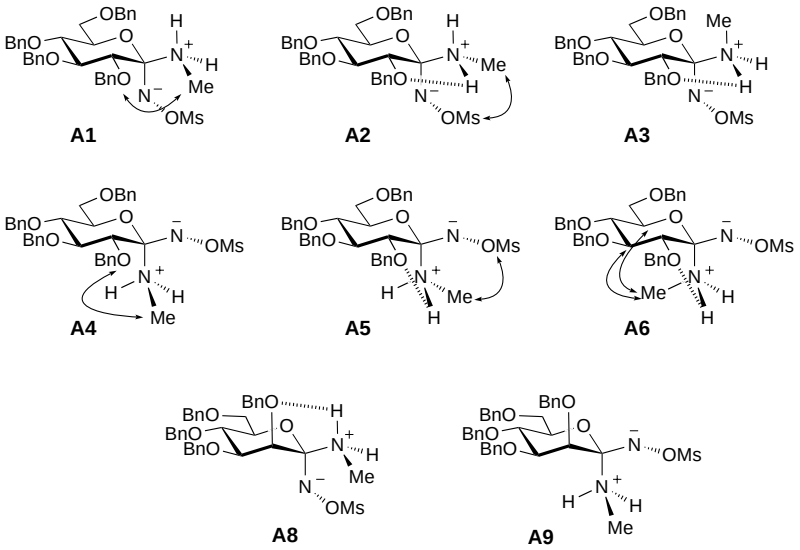


Fig. 6. *Intramolecular H-bonds* (hashed lines) *and destabilizing 1,5-interactions* (double-headed arrows) *in the intermediate zwitterionic addition products of* $MeNH_2$ *to* **1** (**A1**–**A6**) *and to* **19** (**A8** and **A9**).

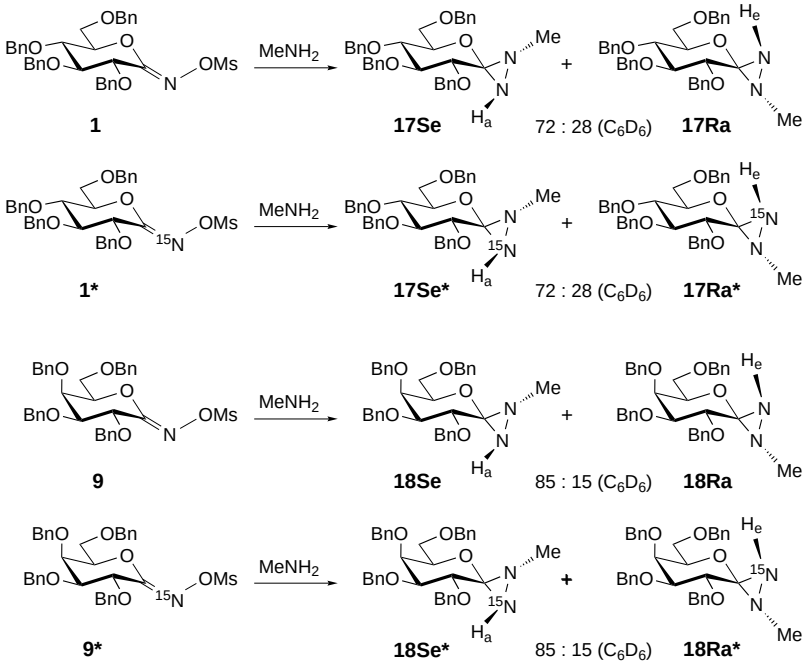
The analysis of the tetrahedral intermediates formed upon equatorial and axial addition of $MeNH_2$ to the *manno*-configured analogue **19** of **1** showed that the epimeric **A8** and **A9** (*Fig. 6*) are the preferred conformers, differing essentially by the intramolecular H-bond of **A8**. The hypothesis of this dominant influence of the H-bond predicts a preferred equatorial addition of both NH_3 and $MeNH_2$ to **19**.

A thermodynamic control of the diastereoselective formation of the diaziridines was evaluated by calculating the relative energies of the ground-state of **M1**–**M4** (*Fig. 5*) and of the corresponding diastereoisomers with an axial MeO group. The gas-phase calculations speak against thermodynamic control; they show higher stability of the equatorial amines **M2** and **M4** over **M1** and **M3** ($\Delta E = 1.0$ and 0.6 kcal/mol, resp.), and higher stability of the axial amine and methylamine of the diastereoisomers possessing an axial MeO group ($\Delta E = 2.8$ and 0.8 kcal/mol, resp.), corresponding to *manno*-configured derivatives.

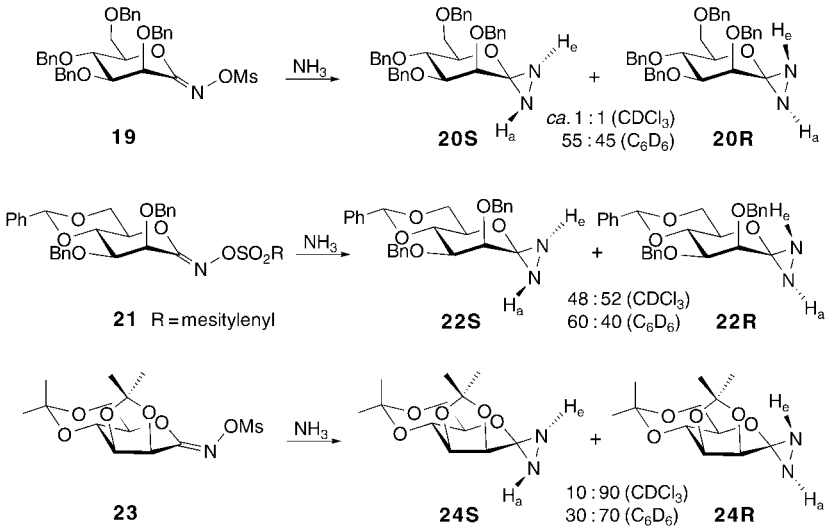
2. D-*Mannopyranosylidene-diaziridines.* The preparation of lactone oxime sulfonates **19** [7], **21** [5], and **23** [21] has been described (*Scheme 6*). Reaction of these sulfonates with NH_3 in MeOH gave **20S**/**20R**, **22S**/**22R**, and **24S**/**24R** in ratios of *ca.* 1:1 [7], 48:52 [5], and 1:9 [21] ($CDCl_3$), respectively. Repetition of the reactions with NH_3 and analysis in C_6D_6 led to only slightly different ratios; *i.e.*, **20S**/**20R** 55:45, **22S**/**22R** 60:40, and **24S**/**24R** 3:7, indicating a slightly stronger solvent dependence of the product ratio in the *manno* than in the *gluco*/*galacto* series.

The assignment of the NH groups is based on NOE experiments for **20S**, **20R**, **24S**, and **24R** (*Fig. 7*). NOEs of 3.5–5.9% evidence the *cis*-arrangement of H_a of **20S** and H_e of **20R** with H–C(2). The unambiguous assignment of **20S** and **20R** is based on a NOE of 3.8% between H_a and H–C(3) of **20S**. The assignment is corroborated by the NOESY spectrum of **20S**/**20R** 55:45 in C_6D_6 showing strong cross-peaks between H_a and H–C(2) of **20S**, and between H_e and H–C(2) of **20R**, a weaker cross-peak between H_a and H–C(3) of **20S**,

Scheme 5



Scheme 6



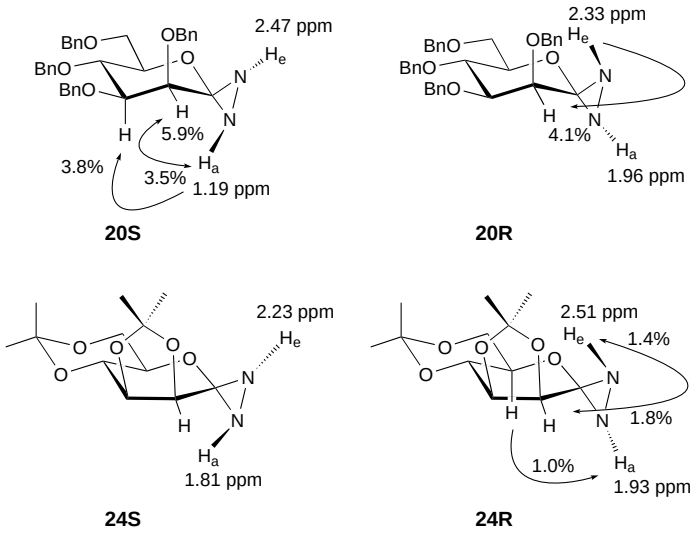


Fig. 7. *NOEs between NH and glycosylidene H-atoms of the mannopyranosylidene diaziridines* **20S**, **20R**, **24S**, *and* **24R** *in* C_6D_6 *solution*

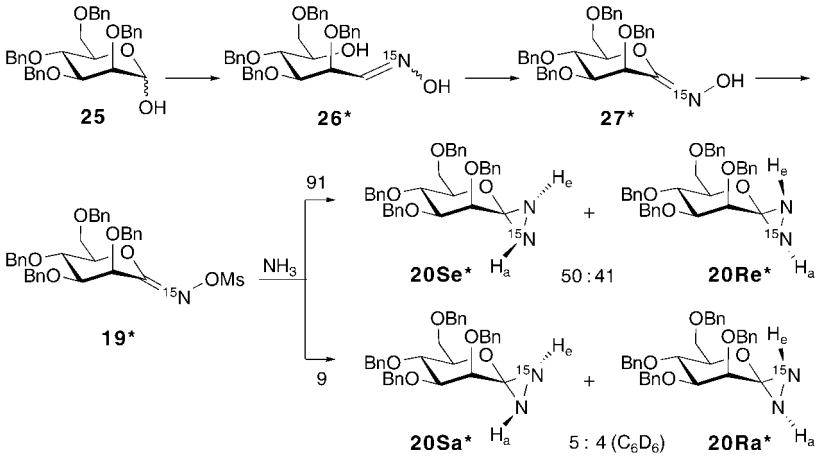
and a weak cross-peak between H_a and $CH_2(6)$ of **20R**. Additional weak cross-peaks between H_a of **20S** and H–C(2) of **20R**, between H_e and H–C(2) of **20S**, and between H_e of **20R** and H–C(2) of **20S** evidence rapid interconversion of **20S** and **20R**. Saturation transfer between the NH groups and H_2O prevents quantitative analysis of the NOESY spectrum. The (*R*,*R*)-configuration of the major isomer **24R** is established by weak NOEs (1.4–1.8%) between H_e and H–C(2), and between H_a and H–C(5).

The $^4C_1$ configuration of **22S** and **22R** in $CDCl_3$ and C_6D_6, and of **20S** in C_6D_6 (the glycosylidene H of **20S**/**20R** *ca.* 1:1 in $CDCl_3$ were not assigned) is evidenced by $J(2,3) = 3.0–3.2$ and $J(3,4) = J(4,5) = 9.3–9.8$ Hz (*cf. Table 5* in *Exper. Part*). This allows ready assignment of the isomers **22S** and **22R** according to the relative shifts of H–C(3) (downfield shift for H–C(3) of **22R** by 0.2–0.35 ppm) and H–C(5) (downfield shift for H–C(5) of **22S** by 0.2–0.55 ppm). The isomer **20R** does not completely prefer a $^4C_1$ conformation, as indicated by $J(3,4) = 7.1$ and $J(4,5) = 6.1$ Hz. Similar values for $J(3,4)$ and $J(4,5)$ suggest a *ca.* 2:1 equilibrium between the $^4C_1$ conformer lacking an intramolecular H-bond and the $^1C_4$ conformer possessing an intramolecular N–H···OBn H-bond, rather than the participation of a twist-boat conformer ($J(4,5)$ of *ca.* 10 and $J(3,4)$ of *ca.* 5 Hz are expected for the most probable $^4S_2$ conformer).

The nearly 1:1 ratio of **20S**/**20R** and **22S**/**22R** is not surprising, since there are no intramolecular H-bonds in the $^4C_1$ conformers. AM1 Calculations for the **R** isomer of 6-deoxy-2,3,4-tri-*O*-methyl-D-mannopyranosylidene diaziridine show that H_e of the $^4C_1$ conformer does not form an intramolecular H-bond to BnO–C(2) ($d(H_e \cdots O) = 3.16$ Å, $\sphericalangle(N - H_e \cdots O) = 83°$). However, a weak corresponding H-bond is possible in the $^1C_4$ conformer ($d(H \cdots O) = 2.61$ Å, $\sphericalangle(N–H \cdots O) = 101°$). $^4C_1$ and the $^4S_2$ conformers ($\Delta E = 3.7$ and 1.8 kcal/mol, resp.). AM1 Calculations predict an $^OH_5$ conformation for **24S** and an S_5 conformation for **24R**, which agrees well with the observed $J(2,3)$, $J(3,4)$, and $J(4,5)$ values (6.7–8.0, 6.0–7.8, and 10.3–10.4 Hz, resp.; *cf. Table 5* in *Exper. Part*). The intramolecular H-bond of H_e of **24R** to the OC(2) ($d(H_e \cdots O) = 2.36$ Å, $\sphericalangle(N–H_{eb} \cdots O) = 105°$) is responsible for the strong preference of **24R**.

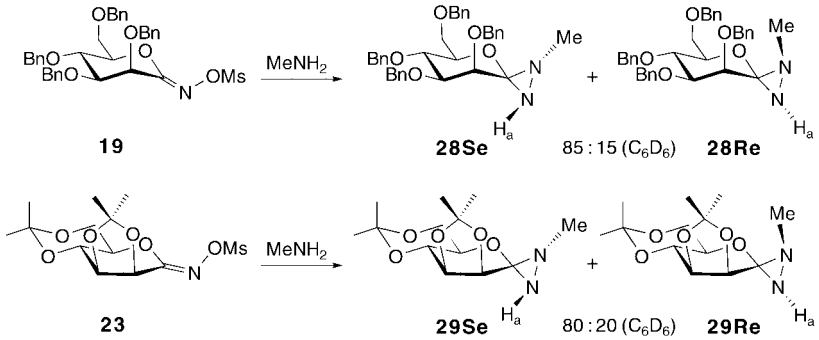
The ^{15}N-labelled methanesulfonate **19*** (*Scheme 7*) was prepared from **25**, similarly as described above for the *gluco* and *galacto* isomers **1*** and **9***, respectively, and obtained in an overall yield of 74% from **25**. Treatment of **19*** with NH_3 in MeOH gave a 50:41:5:4 mixture of **20Se***, **20Re***, **20Sa***, and **20Ra***. The product ratio in C_6D_6 was unambiguously assigned by means of the $^1J(^{15}N,H)$ and $^2J(^{15}N,H)$ couplings (*cf. Table 5* in *Exper. Part*). The ratio **20Se***/**20Sa*** to **20Re***/**20Ra*** 55:45 was exactly the same as for the unlabelled **20S** to **20R**.

Scheme 7



The reaction of **19** with $MeNH_2$ in MeOH gave 98% of a 85:15 mixture of **28Se** and **28Re** (*Scheme 8*). Similarly, **23** was transformed into a 80:20 mixture of **29Se** and **29Re**.

Scheme 8



The presence of ^{15}N in **27*** and **19*** is evidenced by odd *m/z* values for $[M + H]^+$ in the high-resolution mass spectra (**27***: 555.2522, **19***: 633.2282). The ^{15}N-label leads to additional splitting of the NMR signals for H–C(2) (^3J(H,N) = 1.3 Hz), C(2) (^2J(C,N) = 10.8 Hz), and C(3) (^3J(C,N) ≤ 2.6 Hz). The ^{15}N-NMR spectra of **27*** and **19*** display a *s* at −76.4 and −76.6 ppm, resp.

The configuration of **28Se**, **28Re**, **29Se**, and **29Re** was established by NOE experiments and by the relative chemical shifts of H–C(3) and H–C(5). The *cis*-arrangement of H_a and H–C(2) of **28Se** and **29Se** is evidenced by NOEs of 3.6–8.1% (*Fig. 8*). Similarly, NOEs of 2.3–3.6% reveal the *cis*-arrangement of MeN and H–C(2) of **28Re** and **29Re**. The unambiguous assignment of the (*S*,*S*)-configuration to **28Se** and **29Se** is based on a NOE of 3.4% between H_a and H–C(3) of **28Se**, and on NOEs of 0.8–0.9% between MeM and both CH_2(6) of **29Se**. The assignment of the (*R*,*R*) configuration of **28Re** and **29Re** is based on the downfield shift of H–C(5) of **28Re** and **29Re** ($\Delta\delta = 0.42$ for **28Se**/**28Re** and 0.49 ppm for **29Se**/**29Re**), and on the downfield shift of H–C(3) of **28Se** ($\Delta\delta = 0.40$ ppm; *cf. Table 5* in *Exper. Part*). Due to the $^{O}H_5$ conformation of **29Se** and **29Re**, H–C(3) should be influenced only weakly by the configuration of the pseudoaxial N-atom; this is indeed observed ($\Delta\delta =$ 0.05 ppm). The pseudoequatorial N-atoms of **28Se** and **28Re** are methylated, preventing any intramolecular H-bonds to BnO–C(2) also in the inverted $^1C_4$ conformers, and both diastereoisomers adopt completely the $^4C_1$ conformation.

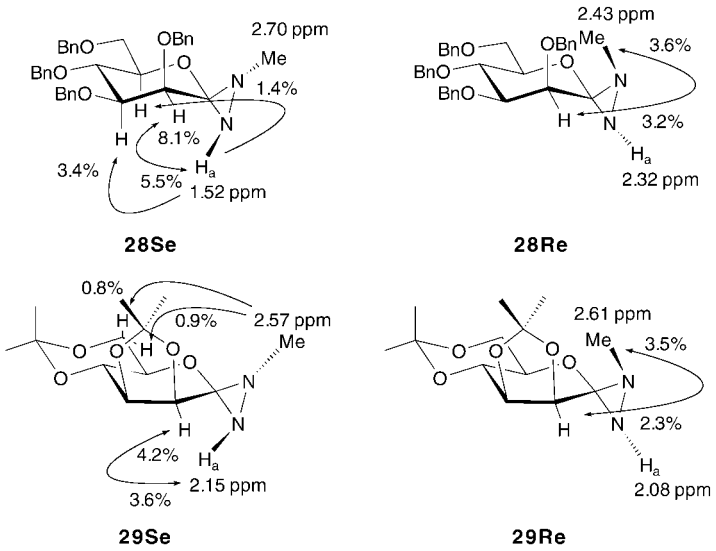
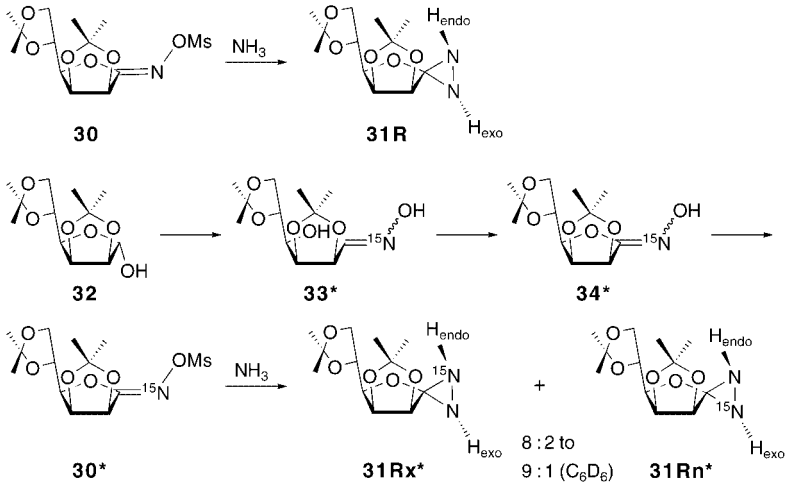


Fig. 8. *NOEs between NH or NMe, and glycosylidene H-atoms of the* N*-methylated mannopyranosylidene diaziridines* **28Se**, **28Re**, **29Se**, *and* **29Re** *in* C_6D_6 *solution*

In the mannopyranose series, a nearly exclusive ring closure of the mesyloxy amines obtained by equatorial addition of NH_3 (91%) and of $MeNH_2$ (> 95%, limit of ^{1}H-NMR analysis) was observed. This result agrees with the hypothesis that the amine adding to to the C=N bond forms a H-bond to C(2)–OR even in MeOH solution. To further test the influence of this H-bond, we subjected the 2,3-*O*-isopropylidene-protected D-mannono- and D-ribono-1,4-lactone oxime sulfonates **30** and **37** (*Schemes 9* and *10*) to the action of NH_3 and $MeNH_2$, since formation of a H-bond to C(2)–OR is only possible if the amines add from the sterically disfavoured *endo* side.

3. D-*Pentofuranosylidene-Diaziridines.* Reaction of the mannono-1,4-lactone oxime methanesulfonate **30** (*Scheme 9*) with NH_3 in MeOH at ambient temperature, followed by crystallisation of the product at 4°, gave 70% of **31R**; no isomer was detected in the ^{1}H-NMR spectrum ($CDCl_3$) [7]. The reaction was repeated, and the product was analysed in C_6D_6; exclusively **31R** was detected. The ribono-1,4-lactone oxime methanesulfonate **37** (*Scheme 10*) did not react under these conditions (14 d at ambient temperature), but was completely consumed within 24 h when the reaction

Scheme 9



was conducted in a closed vessel at a pressure of 5 atm and at ambient temperature. However, no diaziridine could be isolated; it probably decomposed prior to isolation [22]. A single diaziridine (δ(NH) = 2.68 and 2.37 ppm, J(NH,NH) = 8.0 Hz) was detected in the crude mixture obtained from the reaction of the corresponding 5-*O*-[(phenylamino)carbonyl]ribosylidene methanesulfonate with NH_3, but it decomposed during attempted purification [23].

The ^{15}N-labelled hydroximo lactone (*Z*)-**34*** (*Scheme 9*) was prepared from **32** according to [24], but without adapting the reaction conditions to the reduced amount of $^{15}NH_2OH \cdot HCl$. The hemiacetal **32** was transformed to the (*E*/*Z*)-oximes **33*** and then oxidised by MnO_2 to (*E*)-**34*** and (*Z*)-**34***. Separation of the diastereoisomers by flash chromatography and crystallisation yielded 35% of (*Z*)-**34*** and 5% of (*E*)-**34***. The minor (*E*)-**34*** completely isomerised to (*Z*)-**34*** upon standing at room temperature for 3 d. Mesylation of (*Z*)-**34*** gave **30***. It reacted with NH_3 in MeOH to a 8 : 2 mixture of the isotopomers **31Rx*** and **31Rn***[11]) (57%); repeating the addition led to a 9 : 1 mixture of **31Rx***/**31Rn***.

The incorporation of ^{15}N in (*Z*)-**34*** is evidenced by the peak for $[M + Na]^+$ at *m*/*z* 297.108 in the high-resolution mass spectrum, the *s* at −91.1 ppm in the ^{15}N-NMR spectrum, and by the additional splittings of the signals of C(1) ($^1J(^{15}N,C) = 3.0$ Hz) and C(2) ($^2J(^{15}N,C) = 8.7$ Hz). H−C(2) of (*Z*)-**34*** does not show a $^3J(^{15}N,H)$ coupling, in contradistinction to the pyranose series.

The reaction of **30** with $MeNH_2$ in MeOH, followed by filtration of the crude through *LiChroprep*-NH_2, gave 92% of a mixture **35Rx/35Sn**, and two unknown secondary products[12]) (*Scheme 10*). Their ratio in C_6D_6 was 74 : 14 : 6 : 6. The analogous

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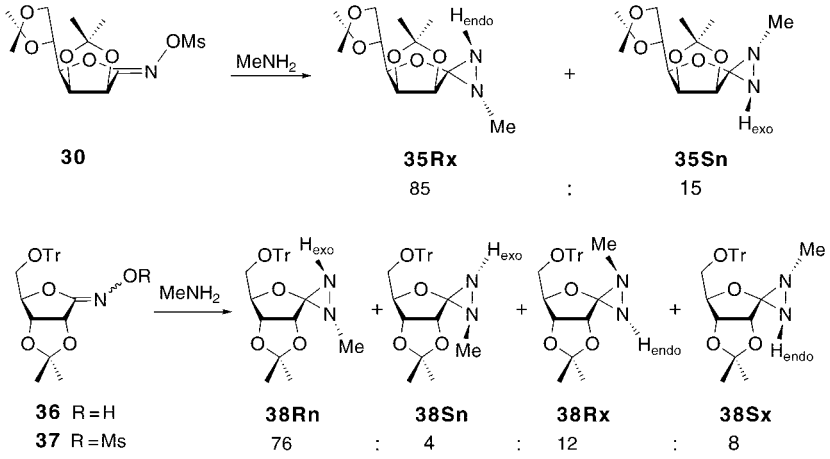
[11]) The letters **x** and **n** denote the ***ex****o* and ***en****do* positions, respectively, of the NR group stemming from the amine.

[12]) The larger values of J(2,3) (8.1 and 7.6 *vs.* 5.7–5.8 Hz) indicate that the secondary products no longer possess a furanose ring. Four NMe signals at 2.34–2.44 ppm indicate that these minor products are *N*-methyl amides (*cf.* formation of **45** and **46**; *Scheme 11*).

Scheme 10



reaction of the *ribo* methanesulfonate **37** led to the formation of the four possible isomeric *N*-Me-diaziridines **38Rn**, **38Sn**, **38Rx**, and **38Sx**; their ratio in C_6D_6 was 76:4:12:8.

Remarkably, the *exo* addition is preferred (>4:1) in the reaction of NH_3 and $MeNH_2$ with the mannono-1,4-lactone oxime methanesulfonate **30**, and the *endo* addition (4:1) in the reaction of $MeNH_2$ with the ribono-1,4-lactone oxime methanesulfonate **37**; *i.e.*, both add *trans* to the substituent at C(4). The stereoselectivity of the addition to ^{O}E conformers is as predicted by the stereoelectronic effect, favouring *exo* addition to the mannono-1,4-lactone and *endo* addition to the ribono-1,4-lactone derivative[13]). The sterically favoured *exo* addition to the ribono-1,4-lactone oxime methanesulfonate is disfavoured both by a pseudoequatorial trajectory and by an unfavourable interaction of the pseudoaxial (negatively charged) (mesyloxy)imido substituent with O–C(2). It is not clear to what extent the stereoselectivities are influenced by different H-bonding to O–C(2) in the *endo* addition to the manno- and ribofuranosylidene derivatives. However, stereoelectronic control, and not H-bonding, appears to be the decisive factor.

The strikingly different selectivities observed for the mannopyranosylidene and -furanosylidene derivatives demonstrate the difficulty of predicting the direction of the addition, and justify a detailed discussion of the configuration of the furanose-derived diaziridines.

NOE measurements allowed unambiguous assignment of the configuration of the ribose derivatives **38Rn**, **38Sn**, **38Rx**, and **38Sx**, and proved helpful for the interpretation of the weak NOEs obtained from the mannofuranose derivatives **31R** and **35Rx**. NOEs of 3.4–3.7% were observed between H–N and H–C(2) of **38Rn**, evidencing the *cis*-arrangement of H_{exo}–N and H–C(2), and the (*R*,*R*)-configuration of the N-atoms (*Fig. 9*). Irradiation of NMe of both **38Rn** and **38Rx**, resonating at 2.79 and 2.81 ppm, respectively, led to signal enhancements of 1.05 and 0.4% for H–C(2) and H–C(3) only of **38Rx**. Considering the 76:12 ratio of **38Rn**/

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[13]) For similar *endo vs. exo* selectivity in the radical transfer to 2,3-*O*-isopropylidene-D-mannofuranose and -D-ribofuranose derivatives, see [25].

38Rx and the fact that the NOE enhancement is related to the sum of the NMe integrals of **38Rn**/**38Rx**, one calculates NOEs of 7 and 2.8% for H–C(2) and H–C(3) of **38Rx**, evidencing the *cis*-arrangement of MeN, H–C(2), and H–C(3), and the (*R*,*R*)-configuration. This conclusion is corroborated by a NOE of 3.6% for NMe of **38Rx** upon irradiation of H–C(2). Irradiation of NMe of **38Sx** at 2.54 ppm led to signal enhancements of 1.0 and 0.7% for H–C(2) and H–C(3) of **38Rx**, respectively, evidencing isomerisation of **38Sx** into **38Rx**. This indicates the *cis*-arrangement of NMe, H–C(2), and H–C(3), and the (*S*,*S*)-configuration of **38Sx**. Not surprisingly, no NOE could be observed upon irradiation of NH and NMe of **38Sn**.

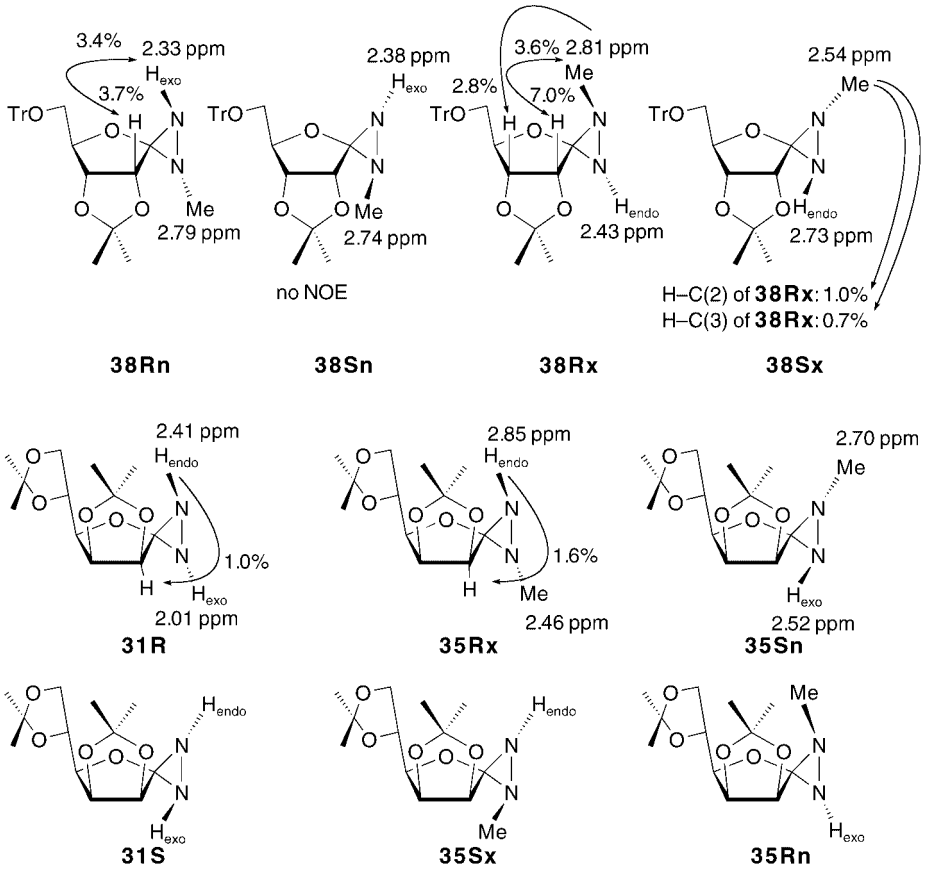

Fig. 9. *NOEs between NH or NMe, and glycosylidene H-atoms of the furanosylidene diaziridines* **38Rn**, **38Sn**, **38Rx**, **38Sx**, **31R**, **35Rx**, *and* **35Sn** *in* C_6D_6 *solution*. The structures **31S**, **35Sx**, and **35Rn**, diastereoisomers of **31R**, **35Rx**, and **35Sn**, respectively, have been calculated.

In the mannofuranose series (*Fig. 9*), weak NOEs were observed upon irradiating the low-field NH of the *N*-unsubstituted diaziridine **31** at 2.41 ppm and the NH of the major *N*-Me-diaziridine (**35Rx**) at 2.85 ppm, whereas irradiations of the high-field NH of **31** at 2.01 ppm, and of the NMe of **35Rx** at 2.46 ppm did not lead to intensity enhancements for the corresponding H–C(2) signals. These NOE measurements evidence that H–C(2) is on the same side of the diaziridine ring as the low-field NH of **31**, and as NH of **35Rx**; the assignment of the structure **31A** to **31** and of **35Rx** to the major isomer of **35** was based on the NOE intensities and on the

H–N chemical-shift values[14]). The enhancements (1–1.6%) are distinctly smaller than the one observed for H–C(2) of **38Rn** (3.7%), suggesting a *trans*-arrangement (relative to the furanose ring) of H–N and H–C(2) of **31R** and **35Rx**, and thus the (*R*,*R*)-configuration at the N-atoms. This interpretation is confirmed by the small enhancement (1.8%) observed for H–C(2) of **24R** upon irradiating a similarly *trans*-oriented H–N (see *Fig. 7*). The configurational assignment of **31R** and **35Rx** is corroborated by the H–N chemical-shift values.

The *N*-Me group of the diaziridines leads to a downfield shift for the adjacent H–N. For pyranosylidene diaziridines, a downfield shift of 0.31 to 0.36 ppm is observed upon formal *N*-methylation of **2S** to **17Se**, **2R** to **17Ra**, **10S** to **18Se**, **10R** to **18Ra**, **20S** to **28Se**, **20R** to **28Re**, and **24S** to **29Se**, with one exception, *viz*. formal *N*-methylation of the isopropylidene-protected **24R** to **29Re**, which leads only to a downfield shift of 0.15 ppm. The shift difference between H–N of **35Rx**, resonating at 2.85 ppm, and the high-field H–N of **31R**, resonating at 2.01 ppm, is 0.84 ppm, and thus too large to be due to the *N*-methylation. It evidences that H–N of **35Rx** corresponds to the low-field H–N of **31R**, resonating at 2.41 ppm. The shift difference of 0.44 ppm is slightly larger than that observed in the pyranose series, perhaps indicating a larger downfield shift upon *N*-methylation of furanosylidene diaziridines. This value was used to calculate the δ(NH) values of the *N*-unsubstituted *manno*-diaziridines **31R** and **31S** from the δ(NH) values of the *ribo*-*N*-Me-diaziridines **38**. The calculated δ values for H_{exo}–N and H_{endo}–N of **31R** are 1.94 and 2.29 ppm, respectively, and those for H_{exo}–N and H_{endo}–N of **31S** 1.89 and 1.99 ppm, respectively. The experimental δ values of **31** (2.01 and 2.41 ppm) agree distinctly better with the calculated values for **31R**, evidencing the (*R*,*R*)-configuration of the N-atoms. δ(NH) and δ(NMe) of the major *manno*-*N*-Me-diaziridine **35Rx** agree only with those of **38Sx**, confirming the configurational assignment of **35Rx**. The configuration of the minor *N*-Me-diaziridine **35Sn** cannot be determined by such a comparison, since H–N and MeN of **38Rn**, **38Sn**, and **38Rx** resonate in the narrow range of 2.33–2.43 and 2.74–2.81 ppm, respectively. The configurational assignment of **35Sn** is based on the observation that **31** completely favours the (*R*,*R*) configuration and on the strong preference of **38Rn** over **38Sn**.

The strong preference for **31R** and **35Rx** in solution agrees with AM1 gas-phase calculations. Compounds **31R** and **35Rx** are favoured by 1.5–2.1 kcal/mol over **31S** and **35Sx**, respectively, due to a weak intramolecular H-bond $N-H_{endo}\cdots OC(2)$ ($d(H_{endo}\cdots O) = 2.63$ Å; $\sphericalangle(N-H_{endo}\cdots O) = 98°$). According to the calculations, the conformation of the furanose ring is determined by the configuration of C(4) and the annulation of the 1,3-dioxolane ring; the configuration of the N-atoms is irrelevant. All the furanosylidene diaziridines mentioned above adopt a southern-type conformation close to a (flat) ^{O}E.

The isopropylidene groups enhance the stability of the furanosylidene-diaziridines **31**, **35**, and **38** relative to the corresponding benzylated analogues derived from **42** and **48** (*Scheme 11*).

The *O*-benzylated ribono-1,4-lactone oxime methanesulfonate **42** was prepared in the usual way from 2,3,5-tri-*O*-benzyl-D-ribofuranose (**39**) [26][27] by oxime formation to **40**, oxidation to **41**, and mesylation. The *arabino*-methanesulfonate **48** was obtained from the known hydroximo lactone **47** [28]. Treatment of **42** with NH_3 in MeOH gave the crystalline 1,4-dihydro-1,2,4,5-tetrazine **43** (21%), the ribonolactone **44** [29–31] (10%), and the hydroxyribonamide **45** (25%). The analogous reaction of **48** afforded the crystalline 1,4-dihydro-1,2,4,5-tetrazine **49** (21%), the arabinolactone **50** (23%), and a mixture that was not analysed (*ca*. 12%). Only the ribonolactone **44** (44%) and the *N*-Me-ribonamide **46** (17%) were isolated from the reaction of **42** with $MeNH_2$ in MeOH.

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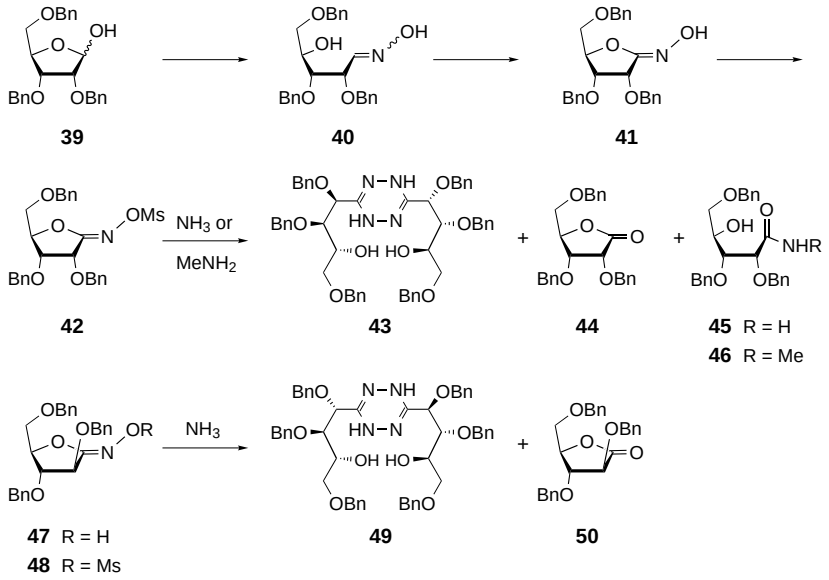
14) Signal overlap and the presence of two side products prevented NOE analysis of minor *N*-Me-diaziridine (**35Sn**).

Scheme 11



A single set of ^{1}H- and ^{13}C-NMR signals reveals the C_2 symmetry of **43** and **49**. Their 1,4-dihydrotetrazine structure[15]) was evidenced by the $[M+Na]^+$ and $[M+K]^+$ peaks at *m*/*z* 887 and 903, respectively, in the mass spectrum, and the N–H band at 3250–3260 cm^{-1} in the IR spectrum (KBr). The OH groups of **43** and **49** resonate in $CDCl_3$ as *d*s at 2.73 and 2.51 ppm, respectively (*cf. Table 8* in *Exper. Part*). The relatively large *J*(H,OH) value of 5.7 and 7.2 Hz indicate intramolecular H-bonds. The H–N and Ph groups resonate at 7.21–7.34 ppm. The *s*s for C(3) and C(6) of **43** and **49** appear at 148.3 and 149.5 ppm, respectively (*cf. Table 9* in *Exper. Part*), these are shift values typical of 1,4-dihydro-1,2,4,5-tetrazines [34–36]. The hydroxy-amide structure of **45** and **46** is revealed by the downfield shift of H–N (**45**: 5.49 and 6.65; **46**: 6.71 ppm) and C(1) (**45**: 173.9; **46**: 171.2 ppm) and by O–H, N–H, and C=O bands (**45**: 3510, 3400, and 1680; **46**: 3560, 3430, and 1660 cm^{-1}).

The 1,4-dihydro-1,2,4,5-tetrazines **43** and **49** derive from the intermediate furanosylidene diaziridines[16]). Ring opening of the diaziridines obtained by the reaction of **42** and **48** with NH_3 or $MeNH_2$ is assumed to lead to lactone hydrazones. These hydrazones, in part, dimerise (*via* azomethine imines?) to the 1,4-dihydro-1,2,4,5-tetrazines **43** and **49**, and they also react with NH_3 or $MeNH_2$ to generate, *via* imino ethers, the lactones **44** and **50**, and the hydroxy amides **45** and **46**[17]).

We thank *Matthias Böhm*, *Lukas Frunz*, and *Patricia Nickut* for the preparation of the ^{15}N-labelled mannose derivatives, Dr. *A. Linden*, University Zürich, for the X-ray analysis, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

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15) The 1,4-dihydro-1,2,4,5-tetrazines adopt a flattened $^{3,6}B$ conformation with the 3- and 6-substituents in bowsprit position [32]. A 1,2-dihydro-1,2,4,5-tetrazine structure is excluded, since 1,2-dihydro-1,2,4,5-tetrazines rearrange readily to the more-stable 1,4-dihydro-1,2,4,5-tetrazines [33].

16) For the reaction of hexono-1,5-lactone hydrazone to a 4-amino-4*H*-1,2,4-triazole and a 1,2,4,5-tetrazine *via* a 1,2-dihydro-1,2,4,5-tetrazine, see [37].

17) We cannot exclude the direct transformation of **42** and **48** into imino ethers although lactone oxime sulfonates that yield stable diaziridines did not give rise to either lactones or open-chain amides.

Experimental Part

General. See [29]. Sat. solns. of NH_3 in MeOH were prepared by bubbling NH_3 through cooled (0°) MeOH. Normal workup means concentrating below 30° in a *Büchi* rotary evaporator, dissolving the residue in Et_2O, filtering through *LiChroprep*-NH_2, concentrating, and drying under high vacuum at a pressure below 0.1 mbar at 20°. NMR Spectra: chemical shifts δ in ppm relative to TMS (^{1}H- and ^{13}C-NMR) or $MeNO_2$ (^{15}N-NMR) as an internal standard, coupling constants J in Hz.

General Procedure for the Preparation of N-*Methyldiaziridines.* A soln. of the methansulfonate in 7.04M $MeNH_2$ in anh. MeOH was stirred at r.t. for the indicated period and evaporated. The residue was dissolved in Et_2O and filtered through *LiChroprep*-NH_2. Evaporation and drying for 5 h at r.t. gave a mixture of the diaziridines.

(1′S,2′S)- and (1′R,2′R)-1,5-Anhydro-2,3,4,6-tetra-O-*benzyl-1-hydrazi*-D-*glucitol* (**2S**/**2R**). According to [7]. ^{1}H-NMR (400 MHz, C_6D_6, **2S**/**2R** 95:5): *Table 2*; additionally for **2S**, 7.30–7.06 (*m*, 20 arom. H); 4.88 (*d*, J = 11.0), 4.86 (*d*, J = 10.2), 4.77 (*d*, J = 10.8), 4.72 (*d*, J = 11.4), 4.62 (*d*, J = 11.4,), 4.46 (*d*, J = 10.9), 4.38 (*d*, J = 12.0), 4.28 (*d*, J = 12.0) (8 PhC*H*). ^{13}C-NMR (50.3 MHz, C_6D_6, only signals of **2S** present): *Table 3*; additionally, 139.39, 139.15, 138.71, 138.48 (4*s*); 128.50–127.38 (several *d*); 75.61 (*t*, 2 Ph*C*H$_2$); 75.02, 73.55 (2*t*, 2 Ph*C*H$_2$).

(1′S,2′S)- and (1′R,2′R)-1,5-Anhydro-2,3,4,6-tetra-O-*benzyl-1-hydrazi*-D-*galactitol* (**10S**/**10R**). According to [7]. ^{1}H-NMR (400 MHz, C_6D_6, **10S**/**10R** 95:5): *Table 2*; additionally for **10S**, 7.37–7.04 (*m*, 20 arom. H); 5.03 (*d*, J = 11.2), 4.74 (*d*, J = 10.8), 4.59 (*d*, J = 11.6), 4.54 (*d*, J = 11.9), 4.47 (*d*, J = 10.8), 4.40 (*d*, J = 11.9), 4.28 (*d*, J = 11.8), 4.21 (*d*, J = 11.8) (8 PhC*H*). ^{1}H-NMR (400 MHz, $CDCl_3$, **10S**/**10R** 9:1): *Table 2* and [7]. ^{13}C-NMR (50.3 MHz, C_6D_6, only signals of **10S** visible): *Table 3*; additionally, 138.84, 138.64, 138.28, 138.08 (4*s*); 128.12–127.12 (several *d*); 75.41, 74.90, 73.06, 72.82 (4*t*, 4 Ph*C*H$_2$).

2,3,4,6-Tetra-O-*benzyl*-D-*(*^{15}*N)gluconhydroximo-1,5-lactone* (**15***). A soln. of EtONa in EtOH (33.55 ml; 1.15 g of Na dissolved in 250 ml of EtOH) was treated with a soln. of $^{15}NH_2OH \cdot HCl$ (*Cambridge Isotope Laboratories*, > 98% of ^{15}N; 505 mg, 7.17 mmol) in dry MeOH (35 ml), stirred for 5 min, treated with 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (3 g, 5.56 mmol), and stirred at reflux for 35 h. The soln. was cooled to r.t., diluted with H_2O (100 ml), and extracted with CH_2Cl_2 (3 × 75 ml). Drying the combined org. layers ($MgSO_4$) and evaporation gave crude (*E*/*Z*)-2,3,4,6-tetra-*O*-benzyl-D-(^{15}N)glucose oxime (3 g, 97%), which was dissolved in dry MeOH (24 ml), treated with MnO_2 (prepared according to [38]; 1.33 g, 16.3 mmol), and stirred at reflux for 6 h. After filtration through *Celite* (washing the residue with warm MeOH), evaporation and FC (hexane/AcOEt 7:3) gave crystalline **15*** (1.83 g, 61%), which was recrystallized in AcOEt/hexane 3:4 (7 ml). R_f (hexane/AcOEt 3:2) 0.4. $[\alpha]_D^{25} = +44.1$ (c = 1.0, $CHCl_3$). M.p. 87°. IR ($CHCl_3$): 3580*m*, 3450*w*, 3360*w* (br.), 3090*w*, 3060*w*, 3030*w* (sh.), 3000*m*, 2920*m*, 2860*m*, 1970*w* (sh.), 1950*w*, 1875*w*, 1810*w*, 1780*w* (br.), 1655*m* (sh.), 1645*m*, 1635*m* (sh.), 1620*w*, 1605*w* (sh.), 1585*w*, 1575*w* (sh.), 1490*w*, 1450*m*, 1360*m*, 1280*m*, 1260*m*, 1080*s* (sh.), 1070*s*, 1025*s*, 995*m* (sh.), 910*s*, 850*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.23 (*m*, 18 arom. H); 7.18–7.15 (*m*, 2 arom. H); 7.05 (*d*, ^2J(H,N) = 0.8, exchange with D_2O, OH); 4.73 (*d*, J = 11.9, PhC*H*); 4.65 (*d*, J = 12.2, PhC*H*); 4.60–4.59 (*m*, 2 PhC*H*); 4.59 (*ddd*, J = 10.1, 4.2, 2.0, H–C(5)); 4.55 (*d*, J = 11.7), 4.49 (*d*, J = 12.1), 4.47 (*d*, J = 11.5), 4.37 (*d*, J = 11.7) (4 PhC*H*); 4.11 (*t*, $J \approx {}^3J$(H,N) ≈ 1.5, H–C(2)); 3.93 (*ddd*, J = 4.5, 2.1, ^4J(H,N) = 1.6, H–C(3)); 3.85 (*dd*, J = 11.3, 2.1, H–C(6)); 3.82 (*dd*, J = 10.1, 4.3, H – C(4)); 3.78 (*dd*, J = 11.4, 4.2, H′–C(6)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 151.21 (*s*, C(1)); 137.90, 137.62, 137.13, 137.05 (4*s*); 128.55–127.49 (several *d*); 81.28 (*dd*, ^3J(C,N) = 1.9, C(3)); 77.46 (*d*, C(4)); 75.97 (*d*, C(5)); 73.43 (*t*, Ph*C*H$_2$); 73.09 (*dd*, ^2J(C,N) = 10.7, C(2)); 72.89, 71.54, 70.48 (3*t*, 3 Ph*C*H$_2$); 68.10 (*t*, C(6)). ^{15}N-NMR (40.6 MHz, $CDCl_3$): −65.80 (br. *d*, J = 2.2). Anal. calc. for $C_{34}H_{35}{}^{15}NO_6$ (554.66): C 73.63, H 6.36, N 2.70; found: C 73.48, H 6.46, N 2.54.

[2,3,4,6-Tetra-O-*benzyl*-D-*(*^{15}*N)glucopyranosylidene]amino Methanesulfonate* (**1***). A soln. of **15*** (1 g, 1.8 mmol) in dry CH_2Cl_2 (20 ml) was treated dropwise at 0° with Et_3N (0.6 ml, 4.3 mmol) and then slowly with MsCl (0.15 ml, 1.96 mmol). The clear soln. was stirred for 30 min, washed with 1M $NaHCO_3$ soln. (2 × 15 ml) and H_2O (3 × 30 ml), dried ($MgSO_4$), and evaporated. Recrystallizion in Et_2O gave **1*** (638 mg, 56%). M.p. 63°. R_f (hexane/AcOEt 3:2) 0.55. $[\alpha]_D^{25} = +38.8$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3060*w*, 3030*w* (sh.), 3010*w*, 2920*w* (br.), 2870*w*, 1970*w*, 1950*w*, 1870*w*, 1810*w*, 1755*w*, 1635*m*, 1620*w* (sh.), 1605*w* (sh.), 1585*w* (sh.), 1555*w*, 1490*w*, 1450*m*, 1370*s*, 1325*m*, 1290*m*, 1260*m*, 1175*m*, 1095*s* (sh.), 1070*s*, 1025*m*, 1005*m* (sh.), 1000*m* (sh.), 965*s*, 955*w*, 910*w*, 835*s*, 825*s* (sh.). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.26 (*m*, 18 arom. H); 7.23–7.16 (*m*, 2 arom. H); 4.74 (*d*, J = 12.0, PhC*H*); 4.65 (*d*, J = 12.4, PhC*H*); 4.67–4.62 (*m*, H–C(5)); 4.59 (*d*, J = 12.3), 4.55 (*d*, J = 12.0), 4.53 (*d*, J = 11.8), 4.49 (*d*, J = 11.7), 4.48 (*d*, J = 11.9), 4.35 (*d*, J = 11.8) (6 PhC*H*); 4.16 (*t*, $J \approx {}^3J$(H,N) ≈ 1.6, H–C(2)); 3.95 (*ddd*, J = 4.1, 2.0, ^4J(H,N) = 1.0, H–C(3)); 3.86 (*dd*, J = 10.2, 3.9, H–C(4)); 3.83 (*dd*, J = 11.6, 2.1, H–C(6)); 3.76 (*dd*, J = 11.6, 3.9, H′–C(6)); 3.12 (*s*, MsO). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 157.32 (*s*, C(1)); 137.74, 137.33, 136.76, 136.29 (4*s*); 128.66–127.68 (several *d*); 80.41 (*dd*, ^3J(C,N) = 1.7, C(3)); 77.40 (*d*, C(4));

Table 2. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Gluco-, Galacto-, and Allopyranosylidene Diaziridines* **2**, **4**, **6**, **8**, **10**, **12**, **14**, **17**, *and* **18**

	2S/2R [7]		**2S/2R**		**2Se*/2Sa***		**2Se*/2Sa***		**4S/4R** [5]		**6S** [8]	**8S/8R**[a]) [5]	
Ratio	95 :	5	95 :	5	25 :	75	22 :	78	97 :	3	> 97%	94 :	6
Solvent	$CDCl_3$		C_6D_6		$CDCl_3$		C_6D_6		C_6D_6		$CDCl_3$	$CDCl_3$	
H–C(2)	4.11	[b])	3.93	[b])	4.11		3.93		5.87	5.61	5.68–5.63	4.11	3.92
H–C(3)	3.68	[b])	3.59	[b])	3.69		3.60		5.49	5.69	5.31–5.26	3.83–3.78	4.13
H–C(4)	3.91	[b])	3.94	[b])	3.92		3.95		5.47	5.48	5.31–5.26	3.83–3.78	3.85
H–C(5)	3.82–3.78	[b])	3.88	[b])	3.82–3.78		3.89		3.89	3.15	4.06	3.83–3.78	3.78–3.74
H–C(6)	3.78	[b])	3.66	[b])	3.78		3.67		4.18	4.075	4.28	4.33	4.30
H′–C(6)	3.68	[b])	3.56	[b])	3.68		3.57		4.07	3.97	4.11	3.74	3.73
H_aN[c])	2.66	1.95	2.68	1.79	2.67 (57.9/3.0)		2.69 (57.0/2.9)		2.13[d])	1.74	2.47[d])	2.84	2.04
H_eN[c])	2.36	2.32	2.26	2.53	2.37 (3.7/57.7)		2.26 (3.7/57.4)		2.10[d])	2.22	2.40[d])	2.32	2.34
J(2,3)	9.4	[b])	9.4	[b])	9.5		9.4		9.3	9.3	[b])	8.1	9.0
J(3,4)	9.1	[b])	9.1	[b])	9.1		9.1		9.5	9.5	[b])	[b])	9.0
J(4,5)	9.9	[b])	9.9	[b])	9.8		10.0		9.9	9.8	[b])	[b])	9.0
J(5,6)	2.8	[b])	3.4	[b])	3.0		3.4		1.8	4.6	4.1	4.0	4.4
J(5,6′)	2.8	[b])	1.7	[b])	2.8		1.7		4.6	1.8	2.2	9.8	9.8
J(6,6′)	10.7	[b])	11.0	[b])	10.6		11.0		12.6	12.5	12.8	10.6	10.6
$J(H_a,H_e)$	9.4	9.4	9.4	9.5	9.4/9.4		9.4/9.4		9.4	9.4	9.4	9.4	9.4

	10S/10R [7]		**10S/10R**		**10Se*/10Sa***		**10Se*/10Sa***		**12S/12R**[a])[f]) [5]		**14S/14R**[d]) [13]	
Ratio	95 :	5	95 :	5	15 :	85	25 :	75	15 :	85	15 :	85
Solvent	$CDCl_3$		C_6D_6		$CDCl_3$		C_6D_6		$CDCl_3$		$CDCl_3$	
H–C(2)	4.50	[b])	4.59	[b])	4.50		4.59		4.39	4.68	4.83	4.70
H–C(3)	3.64	[b])	3.39	[b])	3.64		3.39		3.87	3.62	4.19	4.22
H–C(4)	4.07	[b])	3.92	[b])	4.08		3.92		3.93	3.93	3.88	3.91
H–C(5)	3.96	[b])	4.03	[b])	3.97		4.04		4.11	3.62	4.47	4.33
H–C(6)	3.58	[b])	3.76	[b])	3.58		3.76		3.82	3.74	4.38	4.38
H′–C(6)	3.54	[b])	3.61	[b])	3.54		3.62		3.62–3.66	3.665	3.77	3.81
H_aN	2.68	1.91	2.75	1.77	2.68 (56.9/2.9)		2.76 (56.8/2.8)		2.62	2.14	2.18[d])	2.08[e])
H_eN	2.25	2.41	2.24	2.60	2.24 (3.7/57.6)		2.27 (3.6/57.3)		2.36	2.36	2.07[d])	2.15[e])
J(2,3)	9.9	[b])	9.8	[b])	9.9		9.8		7.6	9.4	2.8	3.2
J(3,4)	2.7	[b])	2.9	[b])	2.8		2.9		5.5	9.5	2.0	2.2
J(4,5)	1.1	[b])	1.2	[b])	1.2		1.2		[b])	9.8	9.3	9.3
J(5,6)	7.6	[b])	7.8	[b])	7.6		7.8		4.5	3.9	5.0	5.2
J(5,6′)	5.9	[b])	5.6	[b])	5.9		5.6		[b])	< 1.0	9.8	9.8
J(6,6′)	9.2	[b])	9.0	[b])	9.1		9.0		10.4	10.8	11.8	11.8
$J(H_a,H_e)$	9.4	9.4	9.4	9.4	9.4/9.4		9.4/9.4		9.3	9.1	8.8	9.3

	17Se/17Ra		**17Se*/17Ra***		**18Se/18Ra**[a])[g])		**18Se*/18Ra***	
Ratio	72 :	28	72 :	28	85 :	15	85 :	15
Solvent	C_6D_6		C_6D_6		C_6D_6		C_6D_6	
H–C(2)	3.85	3.73	3.85	3.73	4.49	4.41	4.51	4.41
H–C(3)	3.60	4.01	3.60	4.01	3.38	3.78	3.39	3.81
H–C(4)	3.95	3.94	3.95	3.94	3.93	3.93	3.93	3.93
H–C(5)	3.89	3.64–3.59	3.89	3.64–3.59	4.03	3.75–3.72	4.03	3.74–3.70
H–C(6)	3.69	3.66	3.69	3.66	3.79	3.75–3.72	3.80	3.74–3.70
H′–C(6)	3.62	3.64–3.59	3.62	3.64–3.59	3.65	3.75–3.72	3.65	3.74–3.70
H_aN[c])	3.02	–	3.02 (57.5)	–	3.08	–	3.09 (57.4)	–
H_eN[c])	–	2.84	–	2.84 (58.2)	–	2.92	–	2.91 (58.3)
MeN[c])	2.75	2.65	2.75 (2.7)	2.65 (2.9)	2.75	2.68	2.74 (2.7)	2.68 (2.7)
J(2,3)	9.4	9.4	9.4	9.4	9.9	9.8	9.8	9.8
J(3,4)	9.0	9.0	9.0	9.0	3.0	3.0	2.9	3.0
J(4,5)	10.0	9.9	10.0	9.9	1.0	1.0	1.0	1.0
J(5,6)	3.6	4.0	3.6	4.0	7.7	[b])	7.8	[b])
J(5,6′)	1.7	[b])	1.7	[b])	5.7	[b])	5.7	[b])
J(6,6′)	11.0	10.5	11.0	10.5	9.0	[b])	9.0	[b])

[a]) Assignment based on a ^{1}H,^{13}C-COSY spectrum. [b]) Not assigned. [c]) In parentheses, $J(H,^{15}N)$ or $J(Me,^{15}N)$. [d]) [e]) Tentative assignment, may be interchanged. [f]) Signals for AcNH: **12S**: 6.37 (*d*, *J* = 8.2), 1.83 (*s*); **12R**: 5.53 (*d*, *J* = 9.4), 1.81 (*s*); **14S**: 5.53 (*d*, *J* = 8.5), 1.78 (*s*); **14R**: 5.91 (*d*, *J* = 9.4), 1.79 (*s*). [g]) Assignment based on a ^{1}H,^{1}H-COSY spectrum.

Table 3. *Selected ^{13}C-NMR Chemical Shifts* [ppm] *of the Gluco- and Galactopyranosylidene-diaziridines* **2**, **10**, **17**, *and* **18** (J(C,^{15}N) in parentheses)

	2S [7]	**2S**	**2Se*/2Sa***	**2Se*/2Sa***	**10S**[a]) [7]	**10S**	**10Se*/10Sa***	**10Se*/10Sa***
Solvent	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
C(1)	82.97	83.46	82.97 (5.1)	83.44 (5.9)	83.28	83.46	83.30 (5.5)	83.91 (6.1)
C(2)	76.53	77.15	76.62 (br.)	77.15 (3.5)	74.14	74.44	74.18 (3.9)	74.93 (br.)
C(3)	84.29	84.68	84.32	84.70	81.55	81.63	81.60	82.10
C(4)	76.53	77.15	76.56	77.18	74.17	74.77	74.23	75.30
C(5)	77.00	77.64	77.00	77.66	75.42	75.33	75.46	75.42
C(6)	67.77	68.72	67.84	68.75	67.79	68.14	67.83	68.66
	17Se	**17Se***	**17Ra**	**17Ra***	**18Se**[a])	**18Se***	**18Ra**[a])	**18Ra***
Solvent	C_6D_6	C_6D_6	C_6D_6	C_6D_6	C_6D_6	C_6D_6	C_6D_6	C_6D_6
C(1)	85.90	85.94 (4.1)	86.08	86.14	86.37	86.36 (4.3)	86.49	86.45
C(2)	77.51[b])	77.59[b])	77.36[d])	77.52[b])	75.25	75.27	74.78	74.89
C(3)	84.71	84.79	85.47	85.55	82.20	82.25	83.07	83.06
C(4)	77.29[b])	77.37[b])	76.80[d])	76.90[b])	75.25	75.33	75.25	75.17
C(5)	77.74[b])	77.80[b])	78.28[d])	78.38[b])	75.99	76.02	75.66	75.71
C(6)	68.49	68.57	68.79	68.86	68.57	68.61	69.05	69.08
MeN	39.11	39.14 (3.7)	38.32	38.33 (3.9)	39.03	38.99 (3.6)	38.52	38.52 (4.1)

[a]) Assignment based upon a ^{1}H,^{13}C-HMQC spectrum. [b]) Assignments may be interchanged.

76.87 (*d*, C(5)); 73.33, 72.98 (2*t*, 2 Ph*C*H$_2$); 72.31 (*dd*, ^2J(C,N) = 11.4, C(2)); 71.63, 71.07 (2*t*, 2 Ph*C*H$_2$); 67.35 (*t*, C(6)); 36.07 (*q*, MsO). ^{15}N-NMR (40.6 MHz, $CDCl_3$): −60.67 (br. *d*, J = 1.7). Anal. calc. for $C_{35}H_{37}{}^{15}NO_8S$ (632.75): C 66.44, H 5.89, N 2.37, S 5.07; found: C 66.44, H 6.10, N 2.30, S 4.89.

*(1*R*,1′*S*,2′*S*)- and (1*S*,1′*S*,2′*S*)-1,5-Anhydro-2,3,4,6-tetra*-O-*benzyl-1-hydrazi*-D-*(*^{15}*N)glucitol* (**2Se*/2Sa***). After dissolution of **1*** (400 mg, 0.632 mmol) in a sat. soln. of NH_3 in MeOH (7.2 ml) and stirring for 30 h at r.t., the soln. was half-concentrated and then cooled at −15° overnight. The crystals were filtered off and dried under high vacuum to give **2Se*/2Sa*** (271 mg, 77%). Evaporation of the mother liquor, filtration through *LiChroprep*-NH_2 (Et_2O), evaporation, and crystallisation from MeOH gave an additional crop of **2Se*/2Sa*** (*ca.* 7%). R_f (hexane/AcOEt 1:1) 0.49. M.p. 50–51°. $[\alpha]_D^{25} = +44.1$ (c = 1.1, $CHCl_3$). IR ($CHCl_3$): 3270*w*, 3090*w*, 3060*w*, 3030*w* (sh.), 3000*w*, 2960*w*, 2910*m*, 2870*m*, 1955*w*, 1875*w*, 1810*w*, 1605*w*, 1495*w*, 1455*m*, 1400*w*, 1360*m*, 1320*w*, 1285*m* (sh.), 1260*m*, 1145*m*, 1125*s*, 1085*s* (br.), 1035*s*, 1025*s*, 1015*m*, 1005*m*, 950*w*, 910*w*, 885*w*, 860*w*. ^{1}H-NMR (600 MHz, C_6D_6, **2Sa*/2Se*** 78:22): *Table 2*; additionally, 7.30–7.06 (*m*, 20 arom. H); 4.89 (*d*, J = 11.3), 4.86 (*d*, J = 11.4), 4.77 (*d*, J = 10.8), 4.73 (*d*, J = 11.3), 4.63 (*d*, J = 11.3), 4.48 (*d*, J = 10.9), 4.39 (*d*, J = 12.0), 4.29 (*d*, J = 12.0) (8 Ph*CH*). ^{1}H-NMR (400 MHz, $CDCl_3$, **2Sa*/2Se*** 75:25): *Table 2*; additionally, 7.37–7.26 (*m*, 18 arom. H); 7.19–7.13 (*m*, 2 arom. H); 4.92 (*d*, J = 10.9), 4.87 (*d*, J = 10.7), 4.86 (*d*, J = 10.8), 4.81 (*d*, J = 10.9), 4.68 (*d*, J = 10.7), 4.64 (*d*, J = 12.1), 4.55 (*d*, J = 10.6), 4.48 (*d*, J = 12.1) (8 Ph*CH*). ^{13}C-NMR (150.9 MHz, C_6D_6, only one set of signals for **2Se*/2Sa***): *Table 3*; additionally, 139.39, 139.15, 138.71, 138.44 (4*s*); 128.59–127.63 (several *d*); 75.62, 75.09, 75.03, 73.57 (4*t*, 4 Ph*C*H$_2$). ^{13}C-NMR (100.6 MHz, $CDCl_3$, only one set of signals for **2Se*/2Sa***): *Table 3*; additionally, 138.39, 138.02, 137.70, 137.64 (4*s*); 128.36–127.63 (several *d*); 75.69, 75.52, 75.06, 73.52 (4*t*, 4 Ph*C*H$_2$). ^{15}N-NMR (60.8 MHz, C_6D_6, **2Sa*/2Se*** 75:25): *Table 4*. ^{15}N-NMR (40.6 MHz, $CDCl_3$, **2Sa*/2Se*** 75:25): *Table 4*.

2,3,4,6-Tetra-O-*benzyl*-D-*(*^{15}*N)galactonhydroximo-1,5-lactone* (**16***). A soln. of EtONa in EtOH (33.55 ml; 1.15 g of Na dissolved in 250 ml of EtOH) was treated with a soln. of $^{15}NH_2OH \cdot HCl$ (505 mg, 7.17 mmol) in dry MeOH (35 ml), stirred for 5 min, treated with 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose [26][39] (3 g, 5.56 mmol), and stirred at reflux for 35 h. The soln. was cooled to r.t., diluted with H_2O (100 ml), and extracted with CH_2Cl_2 (3 × 75 ml). Drying the combined org. layers ($MgSO_4$) and evaporation gave crude (*E/Z*)-2,3,4,6-tetra-*O*-benzyl-D-galactose (^{15}N)oxime (3 g, 97%), which was dissolved in dry MeOH (24 ml), treated with MnO_2 (1.33 g, 16.3 mmol), and stirred at reflux for 6 h. After filtration through *Celite* (washing the residue with warm MeOH), evaporation and FC (hexane/AcOEt 7:3) gave crude **16*** (2.5 g, 81%) as a pale yellow oil. An additional FC (hexane/AcOEt 85:15) afforded **16*** (1.85 g, 62%) as a colourless oil. IR ($CHCl_3$):

Table 4. *^{15}N-NMR (40.6 MHz) Chemical Shifts* [ppm] *of the ^{15}N-Labelled Diaziridines* **2***, **10***, **17***, *and* **18***, *and of the Unlabelled Diaziridines* **20**, **28**, **29**, *and* **38**

	2Se*/2Sa*		**2Se*/2Sa***		**10Se*/10Sa***		**10Se*/10Sa***		**17Se*/17Ra***		**18Se*/18Ra***	
Ratio	25 :	75	25 :	75	15 :	85	17 :	83	72 :	28	85 :	15
Solvent	$CDCl_3$		C_6D_6		$CDCl_3$		C_6D_6		C_6D_6		C_6D_6	
δ(N)	−317.0[a])	−306.9[a])	−312.8	−304.4	−314.4	−304.0	−313.4	−304.2	−297.3	−297.5	−298.1	−299.6
^1J(N,H)	58.0	57.8	57.1	57.5	57.7	57.7	56.5	57.2	57.5	58.4	57.2	58.2
^2J(N,H)	3.6	3.0	3.6	2.7	2.9	2.9	3.0	3.0	–	–	–	–
^3J(N,Me)	–	–	–	–	–	–	–	–	2.9	3.0	2.6	2.8

	20S/20R		**28Se/28Re**		**29Se/29Re**		**38Rn/38Rx**	
Ratio	55 :	45	85 :	15	80 :	20	85 :	15
Solvent	$CDCl_3$		C_6D_6		C_6D_6		C_6D_6	
δ(HN)	−292.0 to	−290.5	−294.2	−294.2	−291.7	−275.9	−284.7	−275.3
^1J(N,H)	[b])	[b])	57.1	57.1	59.1	58.0	54.7	59.6
δ(HN)	–	–	−293.8	−296.7	−296.2	−297.9	−300.4	−301.9
^1J(N,Me)	–	–	[c])	[c])	[c])	[c])	[c])	[c])

[a]) This spectrum was recorded at SF parameter differing by 0.001 MHz, leading to a shift difference of 24.7 ppm. The original δ values were corrected by this value. Since also a different SR parameter was used, the corrected shift values may still not be accurate. [b]) Not assigned. [c]) Only line broadening.

3580*m*, 3350*m*, 3050*m*, 2870*s*, 1960*w*, 1845*w*, 1805*w*, 1645*m*, 1605*m*, 1445*m*, 1350*s*, 1260–1200*s*, 1150–1000*s*, 950–900*s*, 850*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.66 (br. *s*, NOH); 7.36–7.25 (*m*, 20 arom. H); 4.78 (*d*, *J* = 11.6), 4.76 (*d*, *J* = 11.6), 4.67 (*d*, *J* = 12.0), 4.57 (*d*, *J* = 12.0), 4.56 (*d*, *J* = 11.6) (5 PhC*H*); 4.56–4.45 (*m*, 3 PhC*H*, H–C(5)); 4.30 (*dd*, *J* = 5.2, ^3J(H,N) = 1.2, H–C(2)); 4.19 (*t*, *J* = 3.3, H–C(4)); 3.89 (*dd*, *J* = 5.2, 3.0, H–C(3)); 3.83 (*dd*, *J* = 10.4, 7.2, H–C(6)); 3.77 (*dd*, *J* = 10.4, 5.2, H′–C(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 151.51 (*d*, ^1J(C,N) = 0.8, C(1)); 137.81, 137.68 (2 C), 137.40 (3*s*); 128.47–127.54 (several *d*); 78.33 (*d*, C(4)); 78.23 (*dd*, ^3J(C,N) = 2.1, C(3)); 74.16 (*dd*, ^2J(C,N) = 9.5, C(2)); 73.47, 73.31 (2*t*, 2 Ph*C*H$_2$); 72.49 (*d*, C(5)); 72.46, 71.72 (2*t*, 2 Ph*C*H$_2$); 68.53 (*t*, C(6)). ^{15}N-NMR (40.6 MHz, $CDCl_3$): −77.91 (*dd*, *J* = 1.2, 0.2).

[2,3,4,6-Tetra-O*-benzyl*-D*-(*^{15}*N)galactopyranosylidene]amino Methanesulfonate* (**9***). At 0°, a soln. of **16*** (1 g, 1.8 mmol) in dry CH_2Cl_2 (20 ml) was treated dropwise with Et_3N (0.6 ml, 4.3 mmol) and then with MsCl (150 µl, 1.96 mmol). The clear soln. was stirred for 30 min, washed with 1M $NaHCO_3$ soln. (2 × 15 ml) and H_2O (3 × 30 ml). Drying ($MgSO_4$), evaporation, and recrystallisation in Et_2O gave **9*** (991 mg, 87%). M.p. 76°. R_f (hexane/AcOEt 3:2) 0.55. $[\alpha]_D^{25} = +11.7$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3000*w*, 2950*m*, 2930*m*, 2870*m*, 1720*w*, 1615*m*, 1495*w*, 1450*w*, 1360*m*, 1325*m,* 1170*m*, 1100–1000*s*, 970*s*, 820*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.21 (*m*, 20 arom. H); 4.86 (*d*, *J* = 11.3), 4.85 (*d*, *J* = 11.5), 4.64 (*d*, *J* = 12.0), 4.59 (*d*, *J* = 11.4), 4.56 (*d*, *J* = 12.0), 4.54 (*d*, *J* = 11.3), 4.53 (*d*, *J* = 12.0), 4.47 (*d*, *J* = 11.9) (8 PhC*H*); 4.45–4.41 (*m*, H–C(5)); 4.38 (*dd*, *J* = 5.0, ^3J(H,N) = 1.3, H–C(2)); 4.14 (*dd*, *J* = 3.2, 1.8, H–C(4)); 3.88 (*dd*, *J* = 5.0, 3.2, H–C(3)); 3.73 (*AB*, 2 H–C(6)); 3.00 (*s*, MsO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 158.70 (*d*, ^1J(C,N) = 1.2, C(1)); 137.66, 137.43, 137.35, 136.85 (4*s*); 128.52–127.59 (several *d*); 80.15 (*dd*, ^3J(C,N) = 2.6, C(3)); 78.67 (*d*, C(4)); 74.65 (*dd*, ^2J(C,N) = 10.0, C(2)); 74.40, 73.58, 72.35, 72.16 (4*t*, 4 Ph*C*H$_2$); 71.93 (*d*, C(5)); 67.48 (*t*, C(6)); 35.93 (*q*, MsO). ^{15}N-NMR (40.6 MHz, $CDCl_3$): −80.36 (*dd*, *J* = 1.3, 0.2). Anal. calc. for $C_{35}H_{37}{}^{15}NO_8$ (632.75): C 66.44, H 5.89, N 2.37, S 5.07; found: C 66.70, H 6.15, N 2.62, S 4.89.

*(1*R*,1′*S*,2′*S*)- and (1*S*,1′*S*,2′*S*)-1,5-Anhydro-2,3,4,6-tetra*-O*-benzyl-1-hydrazi*-D*-(*^{15}*N)galactitol* (**10Se***/**10Sa***). After dissolution of **9*** (1.00 g, 1.58 mmol) in a sat. soln. of NH_3 in MeOH (40 ml) and stirring for 5 h, the soln. was half-concentrated and then cooled at −15° overnight. The crystals were filtered off and dried under high vacuum to give **10Se***/**10Sa*** (718 mg, 82%) as white long needles. Evaporation of the mother liquor, filtration through *LiChroprep*-NH_2 (Et_2O), evaporation, and crystallisation from MeOH gave an additional crop of **10Se***/**10Sa*** (*ca.* 10%). R_f (hexane/AcOEt 1:1) 0.47. M.p. 90–91°. $[\alpha]_D^{25} = +19.5$ (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): 3250*w*, 3050*w*, 3000*w*, 2905*w*, 2860*m*, 1495*w*, 1450*w*, 1350*w*, 1250–1200*w*, 1090*s*, 945*w*, 910*w*. ^{1}H-NMR (600 MHz, C_6D_6, **10Sa***/**10Se*** 3:1): *Table 2*; additionally, 7.37–7.06 (*m*, 20 arom. H); 5.03 (*d*, *J* = 11.1), 4.74 (*d*, *J* = 10.8), 4.59 (*d*, *J* = 12.3), 4.55 (*d*, *J* = 11.9), 4.47 (*d*, *J* = 10.8), 4.41 (*d*, *J* = 11.8), 4.28 (*d*, *J* = 11.8), 4.22 (*d*, *J* = 11.8) (8 PhC*H*). ^{1}H-NMR (400 MHz, $CDCl_3$, **10Sa***/**10Se*** 85:15): *Table 2*; additionally, 7.39–7.26 (*m*, 20

arom. H); 5.00 (*d*, *J* = 11.3), 4.84 (*d*, *J* = 10.8), 4.78 (*d*, *J* = 11.7), 4.77–4.74 (*m*), 4.73 (*d*, *J* = 11.7), 4.64 (*d*, *J* = 11.3), 4.46 (*d*, *J* = 11.9), 4.42 (*d*, *J* = 11.9) (8 PhC*H*). ^{13}C-NMR (150.9 MHz, C_6D_6, only one set of signals for **10Se***/**10Sa***): *Table 3*; additionally, 139.32, 139.13, 138.74, 138.56 (4*s*); 128.60–127.59 (several *d*); 75.92, 75.85, 73.58, 72.36 (4*t*, 4 PhCH_2). ^{13}C-NMR (100.6 MHz, $CDCl_3$, only one set of signals for **10Se***/**10Sa***): *Table 3*; additionally, 138.30, 138.17, 137.92, 137.64 (4*s*); 128.71–127.43 (several *d*); 75.78 (*J*(C,N) = 0.8), 74.97, 73.42, 73.18 (*J*(C,N) = 0.8) (4*t*, 4 PhCH_2). ^{15}N-NMR (60.8 MHz, C_6D_6, **10Sa***/**10Se*** 83:17): *Table 4*. ^{15}N-NMR (40.6 MHz, $CDCl_3$, **10Sa***/**10Se*** 3:1): *Table 4*. Anal. calc. for $C_{34}H_{36}{}^{14}N^{15}NO_5$ (553.68): C 66.44, H 5.89, N 2.37; found: C 66.70, H 6.15, N 2.62.

(1S,1′S,2′S)- and (1R,1′R,2′R)-1,5-Anhydro-2,3,4,6-tetra-O-*benzyl-1-(1-methylhydrazi)*-D-*glucitol* (**17Se**/**17Ra**). The reaction of powdered **1** (500 mg, 0.79 mmol) in 7.04M $MeNH_2$ in dry MeOH (20 ml; 2.5 h) gave **17Se**/**17Ra** 5:2 (436 mg, 97%). Colourless oil. R_f (hexane/AcOEt 1:1) 0.58. $[\alpha]_D^{25} = +35.3$ (*c* = 0.56, MeOH). IR ($CHCl_3$): 3250*w*, 3050*w*, 2990*w*, 2980*w*, 2920*w*, 2860*m*, 1650*w* (br.), 1495*w*, 1450*m*, 1410*w* (sh.), 1355*m*, 1305*w*, 1240*w* (br.), 1195*w* (sh.), 1175*m* (sh.), 1145*m* (sh.), 1110*s* (sh.), 1085*s*, 1060*s*, 1025*m*, 995*m*, 910*w*. ^{1}H-NMR (600 MHz, C_6D_6; **17Se**/**17Ra** 5:2, *ca*. 95% pure, assignment based on a ^{1}H,^{1}H-COSY spectrum): *Table 2*; additionally for **17Se**/**17Ra**, 7.30–7.01 (*m*, 20 arom. H); additionally for **17Se**: 4.90 (*d*, *J* = 11.3), 4.87 (*d*, *J* = 11.5), 4.86 (*d*, *J* = 10.9), 4.73 (*d*, *J* = 11.5), 4.63 (*d*, *J* = 11.3), 4.50 (*d*, *J* = 10.9), 4.39 (*d*, *J* = 12.1), 4.31 (*d*, *J* = 12.1) (8 PhC*H*); additionally for **17Ra**, 4.89 (*d*, *J* ≈ 11.2, PhC*H*); 4.79 (*s*, PhCH_2); 4.74 (*d*, *J* ≈ 11.8), 4.62 (*d*, *J* = 11.1), 4.45 (*d*, *J* = 12.1), 4.33 (*d*, *J* = 12.2), 4.21 (*d*, *J* = 11.8) (5 PhC*H*). ^{13}C-NMR (50.3 MHz, C_6D_6, **17Se**/**17Ra** 5:2): *Table 3*; additionally for **17Se**/**Ra**, 128.73–127.53 (several *d*); additionally for **17Se**, 139.38, 139.10, 138.75, 138.61 (4*s*); 75.70, 75.57, 74.95, 73.36 (4*t*, 4 PhCH_2); additionally for **17Ra**, 139.05, 138.86, 138.69, 138.29 (4*s*); 75.31, 75.19, 75.07, 73.59 (4*t*, 4 PhCH_2). CI-MS (NH_3): 568 (28), 567 (79, $[M+1]^+$), 478 (13), 477 (44), 459 (19), 448 (38), 447 (100), 445 (10), 444 (37), 436 (20), 431 (11), 430 (34). Anal. calc. for $C_{35}H_{38}N_2O_5 \cdot 0.5\ H_2O$ (575.69): C 73.02, H 6.82, N 4.89; found: C 73.21, H 6.68, N 5.11.

(1R,1′S,2′S)- and (1S,1′R,2′R)-1,5-Anhydro-2,3,4,6-tetra-O-*benzyl-1-(1-methylhydrazi)*-D-*(2′-*^{15}*N)glucitol* (**17Se***/**17Ra***). The reaction of **1*** (112 mg, 0.18 mmol) in 7.04M $MeNH_2$ in dry MeOH (8 ml; 2.5 h) gave **17Se***/**17Ra*** 5:2 (101 mg, 98%). R_f (hexane/AcOEt 1:1) 0.58. ^{1}H-NMR (600 MHz, C_6D_6, **17Se***/**17Ra*** 5:2): *Table 2*. ^{13}C-NMR (150.9 MHz, C_6D_6, **17Se***/**17Ra*** 5:2) *Table 3*; additionally for **17Se***/**17Ra***, 139.44–138.45 (several *s*), 128.80–127.60 (several *d*); additionally for **17Se***, 75.75, 75.63, 74.99, 73.44 (4*t*, 4 PhCH_2); additionally for **17Ra***, 75.35, 75.25, 75.12, 73.69 (4*t*, 4 PhCH_2). ^{15}N-NMR (60.8 MHz, C_6D_6): *Table 4*.

(1S,1′S,2′S)- and (1R,1′R,2′R)-1,5-Anhydro-2,3,4,6-tetra-O-*benzyl-1-(1-methylhydrazi)*-D-*galactitol* (**18Se**/**18Ra**). The reaction of **9** (500 mg, 0.79 mmol) in 7.04M $MeNH_2$ in dry MeOH (20 ml; 45 min) gave **18Se**/**18Ra** 85:15 (427 mg, 95%). Crystallization from dry MeOH afforded **18Se** (306 mg, 68%) as colourless crystals.

Data of **18Se**: R_f (hexane/AcOEt 1:1) 0.57. M.p. 79–81°. $[\alpha]_D^{25} = +41.8$ (*c* = 0.58, MeOH). IR (KBr): 3230*w*, 3040*w*, 3020*w*, 2950*w*, 2910*m*, 2860*m*, 1600*w*, 1490*m*, 1465*w*, 1445*m*, 1405*w*, 1395*w*, 1365*m*, 1340*m*, 1300*m*, 1270*w*, 1260*w*, 1250*w*, 1225*m*, 1210*m*, 1150*m*, 1135*m*, 1105*s*, 1070*m*, 1055*m*, 1040*m*, 1020*m*, 1005*m*, 980*m*, 955*m*, 920*w*, 905*w*. ^{1}H-NMR (400 MHz, C_6D_6): *Table 2*; additionally, 7.37–7.06 (*m*, 20 arom. H); 5.04 (*d*, *J* = 11.2), 4.84 (*d*, *J* = 10.8), 4.59 (*d*, *J* = 11.2), 4.55 (*d*, *J* = 11.9), 4.49 (*d*, *J* = 11.0), 4.41 (*d*, *J* = 11.9), 4.31 (*d*, *J* = 11.8), 4.24 (*d*, *J* = 11.8) (8 PhC*H*). CI-MS (NH_3): 567 (100, $[M+1]^+$), 108 (14), 91 (6).

Data of **18Se**/**18Ra** 85:15: R_f (hexane/AcOEt 1:1) 0.57. ^{1}H-NMR (600 MHz, C_6D_6): *Table 2*; additionally for **18Ra**, 4.99 (*d*, *J* = 11.3), 4.79 (*d*, *J* = 11.7), 4.59 (*d*, *J* = 11.2), 4.46 (*d*, *J* = 11.8), 4.42 (*d*, *J* = 11.7), 4.32 (*d*, *J* = 11.8), 4.24 (*d*, *J* = 11.8), 4.19 (*d*, *J* = 11.8) (8 PhC*H*). ^{13}C-NMR (150.9 MHz, C_6D_6, assignment based on a ^{1}H,^{13}C-COSY spectrum): *Table 3*; additionally for **18Se**/**18Ra**, 139.32–138.35 (several *s*); 128.68–127.60 (several *d*); additionally for **18Se**, 76.02, 75.47, 73.55, 73.36 (4*t*, 4 PhCH_2); additionally for **18Ra**, 75.28, 75.20, 73.69, 72.81 (4*t*, 4 PhCH_2).

(1R,1′S,2′S)- and (1S,1′R,2′R)-1,5-Anhydro-2,3,4,6-tetra-O-*benzyl-1-(1-methylhydrazi)*-D-*(2′-*^{15}*N)galactitol* (**18Se***/**18Ra***). The reaction of **9*** (100 mg, 0.16 mmol) in 7.04M $MeNH_2$ in dry MeOH (8 ml; 2 h) gave **18Se***/**18Ra*** 85:15 (85 mg, 93%). Crystallization from dry MeOH afforded **18Se*** (60 mg, 63%) as colourless crystals.

Data of **18Se***: ^{1}H-NMR (600 MHz, C_6D_6): *Table 2*; additionally, 7.42–7.02 (*m*, 20 arom. H); 5.04 (*d*, *J* = 11.2), 4.84 (*d*, *J* = 10.8), 4.60 (*d*, *J* = 11.2), 4.56 (*d*, *J* = 11.8), 4.50 (*d*, *J* = 11.1), 4.42 (*d*, *J* = 11.8), 4.32 (*d*, *J* = 11.8), 4.24 (*d*, *J* = 11.8) (8 PhC*H*). ^{13}C-NMR (150.9 MHz, C_6D_6): *Table 3*; additionally, 139.34, 139.20, 138.98, 138.65 (4*s*); 128.75–127.48 (several *d*); 76.01, 75.46, 73.57, 73.41 (4*t*, 4 PhCH_2).

Data of **18Ra***: ^{1}H-NMR (600 MHz, C_6D_6, **18Se***/**18Ra*** 85:15): *Table 2*. ^{13}C-NMR (150.9 MHz, C_6D_6, **18Se***/**18Ra*** 85:15): *Table 3*. ^{15}N-NMR (60.8 MHz, C_6D_6): *Table 4*.

X-Ray Analysis of **18Se**[7]). Recrystallization of **18Se** in AcOEt/hexane gave crystals suitable for X-ray analysis: $C_{35}H_{38}N_2O_5$ (566.70); monoclinic $P2_1$; *a* = 11.851 (3), *b* = 7.836 (1), *c* = 16.652 (3), *β* = 104.18 (1)°; $D_{calc.} = 1.255$ Mg/m^3; Z = 2. From a crystal of size 0.08 × 0.22 × 0.38 mm 5634 reflections were measured on an

Rigaku AFC5R diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) and a 12-kW rotating anode generator at 173 K. $R = 0.0358$, $R_w = 0.0350$. The unit-cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $48° < 2\theta < 52°$. The $\omega/2\theta$ scan mode was employed for data collection, where the ω scan width was $(1.30 + 0.35 \tan\theta)°$ and the ω scan speed was 8° min^{-1}. The structure was solved by direct methods with SHELXS86, which revealed the positions of all non-H-atoms, which were refined anisotropically. The amine H-atom was placed in the position indicated by a difference-electron-density map, and its position was allowed to refine together with an isotropic displacement parameter. All remaining H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å). The structure shows no unusual features. The only H-bonding interaction is a very weak intramolecular interaction between the amine H-atom and the neighbouring O-atom O–C(2).

(1′S,2′S)- and (1′R,2′R)-1,5-Anhydro-2,3,4,6-tetra-O-*benzyl-1-hydrazi*-D-*mannitol* (**20S**/**20R**). According to [7]. The crude product was dissolved in Et_2O and filtered through *LiChroprep*-NH_2. Evaporation and drying gave **20S**/**20R** as a clear oil. ^{1}H-NMR (600 MHz, C_6D_6; **20S**/**20R** 55 : 45; assignment based on a ^{1}H,^{1}H-COSY spectrum): *Table 5*; additionally for **20S**/**20R**, 7.48 – 7.42 (*m*, 2 arom. H); 7.31 – 7.04 (*m*, 18 arom. H); 4.96 – 4.26 (*m*, 8 PhC*H*). ^{13}C-NMR (50.3 MHz, C_6D_6; **20S**/**20R** 55 : 45): *Table 6*; additionally for **20S**/**20R**, 139.34, 138.99, 138.96, 138.86, 138.71 (5*s*); 128.65 – 127.35 (several *d*), 73.55 (*t*, Ph*C*H$_2$); additionally for **20S**, 75.22, 73.39, 71.61 (3*t*, 3 Ph*C*H$_2$); additionally for **20R**, 73.99, 72.61, 71.85 (3*t*, 3 Ph*C*H$_2$). ^{15}N-NMR (60.8 MHz, C_6D_6): *Table 4*.

(1′S,2′S)- and (1′R,2′R)-1,5-Anhydro-2,3:4,6-di-O-*isopropylidene-1-hydrazi*-D-*mannitol* (**24S**/**24R**). According to [21]. Filtration of the crude product through *LiChroprep*-NH_2 gave **24S**/**24R** (95%) as a colourless foam. Solutions of **24S**/**24R** slowly isomerized and partially decomposed. R_f (hexane/AcOEt 1 : 1) 0.18. $[\alpha]_D^{25} = +22.1$ ($c = 0.43$, MeOH). ^{1}H-NMR (600 MHz, C_6D_6; **24S**/**24R** 3 : 7): *Table 5*; additionally for **24S**, 1.50, 1.28, 1.14, 0.95 (4*s*, 4 Me); additionally for **24R**, 1.40, 1.35, 1.20, 1.08 (4*s*, 4 Me). ^{13}C-NMR (50.3 MHz, C_6D_6; **24S**/**24R** 2 : 3): *Table 6*; additionally for **24S**, 112.25, 99.23 (2*s*, 2 Me$_2$*C*); 28.23, 26.77, 26.42, 18.02 (4*q*, 2 *Me*$_2$C); additionally for **24R**, 110.10, 99.44 (2*s*, 2 Me$_2$*C*); 28.68, 27.08, 25.13, 18.19 (4*q*, 2 *Me*$_2$C). ^{13}C-NMR (50.3 MHz, $CDCl_3$; **24S**/**24R** 2 : 3): *Table 6*; additionally for **24S**, 111.20, 99.82 (2*s*, 2 Me$_2$*C*); 28.82, 27.06, 25.01, 18.82 (4*q*, 2 *Me*$_2$C); additionally for **24R**, 110.98, 99.87 (2*s*, 2 Me$_2$*C*); 28.69, 27.51, 25.49, 18.75 (4*q*, 2 *Me*$_2$C).

(E/Z)-2,3,4,6-Tetra-O-benzyl-D-*mannose (*^{15}*N)Oxime* (**26***). A soln. of 0.52N MeONa in MeOH (0.46 ml, 0.24 mmol) was diluted with MeOH (1.5 ml), treated with $^{15}NH_2OH \cdot HCl$ (32.4 mg, 0.45 mmol), warmed to 55°, treated dropwise with a soln. of **25** (111 mg, 0.21 mmol) in MeOH (1.5 ml), and stirred at 55° for 20 h. After evaporation, a soln. of the residue in AcOEt was washed with H_2O (2 ×) and brine, dried ($MgSO_4$), evaporated, and dried *i.v.* to affording crude **26*** (112 mg, 98%). Yellowish oil. R_f (hexane/1,2-Dimethoxyethane 1 : 1) 0.21.

(Z)-2,3,4,6-Tetra-O-benzyl-D-*(*^{15}*N)mannonhydroximolactone* (**27***). A soln. of **26*** (112 mg, 0.2 mmol) and AcONa (63 mg, 0.76 mmol) in EtOH (7 ml) was warmed to 75°, treated dropwise within 1 h with a soln of $NaIO_4$ (198 mg, 0.95 mmol) in 3 ml H_2O (3 ml), and stirred for 2 h. After evaporation, a soln. of the residue in AcOEt was washed with H_2O, sat. $NaHCO_3$ soln., H_2O, and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 2.1) gave **27*** (85 mg, 76%). Slightly yellowish oil. R_f (hexane/AcOEt 1 : 1) 0.42. IR ($CHCl_3$): 3380*w*, 3324*w* (br.), 3066*w*, 2910*m*, 2870*m*, 1641*m*, 1612*w*, 1497*m*, 1454*s*, 1364*m*, 1285*m*, 1105*s*, 1071*s*, 1027*s*, 945*w*, 913*m*, 877*w*, 846*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42 – 7.17 (*m*, 20 arom. H, OH); 4.88 (*d*, $J = 10.8$), 4.72 (*d*, $J = 12.4$), 4.62 (*d*, $J = 12.1$) (3 PhC*H*); 4.53 (*d*, $J \approx 11.8$, 2 PhC*H*); 4.51 (*d*, $J \approx 12.5$), 4.46 (*d*, $J = 12.1$), 4.45 (*d*, $J = 12.1$) (3 PhC*H*); 4.30 (*t*, $J = 9.0$, H–C(4)); 4.19 (*dd*, $J = 3.1$, ^3J(H,^{15}N) = 1.3, H–C(2)); 4.00 (*dt*, $J = 9.0$, 3.6, H–C(5)); 3.79 (*d*, $J = 3.7$, 2 H–C(6)); 3.71 (*dd*, $J = 9.0$, 3.0, H–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 151.80 (*s*, C(1)); 137.79, 137.88, 137.64, 137.26 (4*s*); 128.42 – 127.72 (several *d*); 80.80 (*d*, C(4)); 79.65 (*dd*, ^3J(C,N) = 2.6, C(3)); 74.95 (*t*, Ph*C*H$_2$); 73.48 (*d*, C(5)); 73.44, 71.60 (2*t*, 2 Ph*C*H$_2$); 70.84 (*dd*, ^2J(C,N) = 10.8, C(2)); 70.35 (*t*, Ph*C*H$_2$); 68.85 (*t*, C(6)). ^{15}N-NMR (40.6 MHz, $CDCl_3$): –76.41 (*s*). HR-MALDI-MS: 593.2068 (5, $[M+K]^+$), 577.2340 (100, $[M+Na]^+$; $C_{34}H_{35}{}^{15}NNaO_6^+$; calc. 577.2332), 555.2522 (39, $[M+H]^+$; $C_{34}H_{36}{}^{15}NO_6^+$; calc. 555.2513), 539.2581 (9).

(Z)-[2,3,4,6-Tetra-O-benzyl-D-*(*^{15}*N)mannopyranosylidene]amino Methanesulfonate* (**19***). A suspension of **27*** (40 mg, 0.072 mmol) and 4-Å molecular sieves (10 mg) in CH_2Cl_2 (0.7 ml) was cooled to 0°, treated with Et_3N (13 µl, 0.093 mmol), stirred for 5 min, treated with a soln. of MsCl (5.6 µl, 0.072 mmol) in CH_2Cl_2 (0.3 ml), and stirred for 10 min. The mixture was diluted with cold AcOEt (10 ml), washed with cold sat. Na_2CO_3 soln., ice/H_2O, and cold brine, and dried (Na_2SO_4). Evaporation at 25° gave **19*** (45 mg, 99%). Colourless oil. R_f (hexane/AcOEt 3 : 2) 0.57. IR ($CHCl_3$): 3089*w*, 3066*w*, 2928*w*, 2870*m*, 1627*m*, 1497*m*, 1451*m*, 1371*s*, 1326*m*, 1295*m*, 1103*s*, 1065*s*, 1027*s*, 968*s*, 911*w*. ^{1}H-NMR (300 MHz, C_6D_6): 7.37 (br. *d*, $J = 6.5$, 2 arom. H); 7.24 – 7.04 (*m*, 18 arom. H); 4.70 (*d*, $J = 12.1$), 4.69 (*d*, $J = 11.5$) (2 PhC*H*); 4.46 (*t*, $J = 8.5$, H–C(4)); 4.41 (*d*, $J = 12.7$), 4.36 (*d*, $J = 11.5$), 4.34 (*d*, $J = 12.1$), 4.26 (*d*, $J = 11.8$) (4 PhC*H*); 4.205 (*dd*, $J = 3.1$, ^3J(H,N) = 1.3, H–C(2)); 4.17

Table 5. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Mannopyranosylidene and -furanosylidene-diaziridines* **20**, **22**, **24**, **28**, **29**, **31**, *and* **35**

	20S/20R[a])		**22S/22R**		**22S/22R** [5]		**24S/24R** [21]		**24S/24R**[a])	
Ratio	55 :	45	48 :	52	60 :	40	10 :	90	30 :	70
Solvent	C_6D_6		$CDCl_3$		C_6D_6		$CDCl_3$		C_6D_6	
H–C(2)	3.28	3.81	3.54	3.53	3.24	3.40	[b])	4.35	4.24	3.99
H–C(3)	3.53	3.94	3.81	4.02	3.56	3.91	[b])	4.33	4.03	4.16
H–C(4)	4.46	4.19	4.40	4.42	4.45	4.42	[b])	3.96	3.72	4.05
H–C(5)	3.97	3.90	3.81	3.60	3.81	3.25	[b])	3.55	3.19	3.27
H–C(6)	3.76	3.87	4.31	4.30	4.11	4.04	[b])	3.86	3.67	3.77
H′–C(6)	3.64	3.87	3.88	3.93	3.52	3.52	[b])	3.73	3.39	3.64
H_aN	1.19	1.96	1.68	1.67	1.18	1.77	2.12	2.10	1.81	1.93
H_eN	2.47	2.33	2.53	2.09	2.35	1.82	2.28	2.55	2.23	2.51
J(2,3)	3.0	3.0	3.2	3.2	3.2	3.2	[b])	8.0	7.4	6.7
J(3,4)	9.3	7.1	9.8	9.9	9.8	9.8	[b])	6.0	6.5	7.8
J(4,5)	9.8	6.1	9.4	9.4	9.4	9.4	[b])	10.4	10.4	10.3
J(5,6)	4.6	[b])	5.0	5.0	4.9	4.9	[b])	5.6	5.7	5.6
J(5,6′)	1.5	[b])	10.1	10.2	10.2	10.0	[b])	10.5	10.1	10.5
J(6,6′)	11.2	[b])	10.4	10.4	10.2	10.3	[b])	11.0	11.0	10.9
J(H_a,H_e)	9.1	9.4	9.1	9.2	9.2	9.2	9.3	9.3	9.4	9.5

	20S/20R [7]		**20Se*/20Re*/20Sa*/20Ra***			
Ratio	*ca.* 1 : 1		50 :	41:	5 :	4
Solvent	$CDCl_3$		C_6D_6			
H_aN[c])	1.45	1.90	1.16 (56.9)	1.94 (57.4)	1.16 (2.8)	1.94 (3.5)
H_eN[c])	2.49	2.04	2.46 (3.8)	2.36 (3.2)	2.46 (58.2)	2.36 (57.2)
J(H_a,H_e)	8.7	8.7	9.2	9.4	9.1	9.4

	28Se/28Re		**29Se/29Re**[a])		**31R** [7]	**31R**	**31Rx*/31Rn***		**35Rx/35Sn**[a])	
Ratio	85 :	15	80 :	20	100%	100%	4 :	1	85 :	15
Solvent	C_6D_6		C_6D_6		$CDCl_3$	C_6D_6	C_6D_6		C_6D_6	
H–C(2)	3.24	3.915	3.65	4.08	4.76	4.34	4.34		4.34	[b])
H–C(3)	3.53	3.925	4.14	4.19	4.96	4.37	4.37		4.39	[b])
H–C(4)	4.44	4.44	3.99	3.93	4.08	3.65	3.64		3.58	[b])
H–C(5)	3.97	3.45	3.55	3.06	4.45	4.46	4.46		4.51	[b])
H–C(6)	3.79	3.73	3.85	3.69	4.10	4.01	4.01		4.06	[b])
H′–C(6)	3.69	3.61	3.59	3.61	4.01	3.97	3.97		4.00	[b])
H_aN or H_{exo}–N[c])	1.52	2.32	2.15	2.08	2.21	2.01	2.02 (*ca.* 3.0/57.2)		–	2.52
H_eN or H_{endo}–N[c])	–	–	–	–	2.51	2.41	2.43 (57.8/*ca.* 3.0)		2.85	–
MeN	2.70	2.43	2.57	2.61	–	–	–		2.46	2.70
J(2,3)	2.9	< 1	6.3	5.5	5.8	5.7	5.7		5.7	[b])
J(3,4)	9.3	[c])	7.2	7.9	3.3	3.1	3.1		3.1	[b])
J(4,5)	9.9	10.0	10.4	10.1	8.0	7.2	7.3		7.4	[b])
J(5,6)	4.6	4.8	5.2	5.7	5.9	5.5	5.3		5.2	[b])
J(5,6′)	1.6	1.6	10.4	10.1	4.3	6.4	6.5		6.4	[b])
J(6,6′)	11.2	11.3	10.4	10.3	9.0	8.8	8.7		8.7	[b])
J(H_a,H_e)	–	–	–	–	9.5	9.0	9.3/9.3		–	–

[a]) Assignment based on a ^{1}H,^{1}H-COSY spectrum. [b]) Not assigned. [c]) In parentheses, J(^{15}N,H).

Table 6. *Selected ^{13}C-NMR Chemical Shifts* [ppm] *of the Mannopyranosylidene and -furanosylidene-diaziridines* **20**, **22**, **24**, **28**, **29**, **31**, *and* **35**

	20S/20R		**22S/22R** [5]	**24S/24R**		**24S/24R**	
Ratio	55 :	45	*ca.* 1 : 1	1 :	9	55 :	45
Solvent	C_6D_6		$CDCl_3$	$CDCl_3$		C_6D_6	
C(1)	82.18	81.47	82.53, 82.24	[a])	[a])	80.96	81.22
C(2)	78.20	77.66	78.62, 77.32	76.06[b])	76.15[b])	76.51[b])	76.41[b])
C(3)	81.72	81.13	78.14, 78.09	73.67[b])	72.24[b])	71.71[b])	75.31[b])
C(4)	74.53	74.53	78.19	71.66	72.03	70.10	71.86
C(5)	76.40	76.01	69.83, 69.00	66.81	67.66	67.96	66.65
C(6)	69.35	69.78	68.33	62.28	61.58	60.79	61.88

	28Se/28Re		**29Se/29Re**		**31R**	**31R**	**35Rx/35Sn**	
Ratio	85 :	15	80 :	20			4 :	1
Solvent	C_6D_6		C_6D_6		$CDCl_3$	C_6D_6	C_6D_6	
C(1)	84.08	[a])	84.06	83.96	90.83	91.40	93.69	92.74
C(2)	78.50	78.59	77.11[b])	77.27[b])	80.25[b])	80.60[b])	80.24[b])	80.40[b])
C(3)	82.04	84.08	76.16[b])	75.33[b])	79.36[b])	79.61[b])	79.66[b])	79.95[b])
C(4)	74.87	74.30	67.70	66.94	80.95	81.42	82.58	80.74
C(5)	77.88	77.2	72.87	72.87	72.97	73.51	73.45	[a])
C(6)	69.22	69.44	62.38	61.95	66.67	66.93	67.05	66.86
MeN	38.88	38.80	38.63	41.37	–	–	39.13	40.14

[a]) Not assigned. [b]) Assignments may be interchanged.

(*d, J* = 12.1, 2 PhC*H*); 3.77 (*dt, J* = 8.4, 3.1, H–C(5)); 3.49 (*d, J* = 3.1, 2 H–C(6)); 3.43 (*dd, J* = 8.4, 2.8, H–C(3)); 2.51 (*s*, MsO). ^{13}C-NMR (75.6 MHz, $CDCl_3$): 157.74 (*s*, C(1)); 138.52, 138.40, 138.29, 137.49 (4*s*); 128.7–127.6 (several *d*); 82.17 (*d*, C(4)); 79.25 (br. *d*, C(3)); 74.84 (*t*, Ph*C*H$_2$); 73.43 (*d*, C(5)); 73.31, 72.03, 71.52 (3*t,* 3 Ph*C*H$_2$); 68.31 (*t*, C(6)); 35.73 (*q*, MsO), *dd* for C(2) hidden by the noise or other signals. ^{15}N-NMR (40.6 MHz, C_6D_6): –76.6 (*s*). HR-MALDI: 671.1820 (25, $[M+K]^+$, $C_{35}H_{37}K^{15}NO_8S^+$; calc. 671.1842), 655.2107 (100, $[M+Na]^+$; calc. for $C_{35}H_{37}{}^{15}NNaO_8S^+$ 655.2102), 633.2282 (19, $[M+H]^+$; calc. for $C_{35}H_{38}{}^{15}NO_8S^+$ 633.2283), 561 (32), 559 (30), 539 (49), 470 (25), 469 (82), 425 (25), 181 (27).

*(1*R*,1′*S*,2′*S*)-, (1*R*,1′*R*,2′*R*)-, (1*S*,1′*S*,2′*S*)-, and (1*S*,1′*R*,2′*R*)-1,5-Anhydro-2,3,4,6-tetra*-O-*benzyl-1-hydrazi*-D-*(*^{15}*N)mannitol* (**20Se*/20Re*/20Sa*/20Ra***). A sat. soln. of NH_3 in MeOH (NH_3 was dumped into MeOH at 0°, 2 ml) was cooled to 0°, treated with **19*** (10 mg, 15.8 μmol), and stirred for 23 h at 23°. After evaporation at 0°, the residue was dissolved in Et_2O and filtered through *Lichroprep*-NH_2 (2 ml). Evaporation of the filtrate at 25° gave a 50 : 41 : 5 : 4 mixture **20Se*/20Re*/20Sa*/20Ra*** (7.5 mg, 86%). Colourless oil. R_f (hexane/AcOEt 1 : 1) 0.28. ^{1}H-NMR (300 MHz, C_6D_6; **20Se*/20Re*/20Sa*/20Ra*** 50 : 41 : 5 : 4): *Table 5*; additionally, 7.49 (br. *d*, *J* = 6.8, 2 arom. H); 7.44–7.01 (*m*, 18 arom. H); additionally for **20Se*/20Sa***, 4.62 (*d*, *J* = 11.8, PhC*H*); 4.52–4.23 (*m*, 7 PhC*H*, H–C(4)); 3.98 (*ddd, J* = 10.0, 4.4,1.6, H–C(5)); 3.76 (*dd, J* = 11.2, 4.3, H–C(6)); 3.63 (*dd, J* = 11.2, 1.6, H′–C(6)); 3.50 (*d, J* = 9.3, 2.9, H–C(3)); 3.25 (*d, J* = 3.1, H–C(2)); additionally for **20Re*/20Ra***, 4.95 (*d, J* = 11.3, PhC*H*); 4.92 (*d, J* = 10.6, PhC*H*); 4.56 (*d, J* = 11.5, PhC*H*); 4.52–4.23 (*m*, 5 PhC*H*); 4.19 (*t*, *J* ≈ 6.4, H–C(4)); 3.94 (*dd, J* = 6.8, 2.8, H–C(3)); 3.91–3.84 (*m*, H–C(5), 2 H–C(6)); 3.80 (*d, J* = 3.1, H–C(2)).

*(1*S*,1′*S*,2′*S*)- and (1*S*,1′*R*,2′*R*)-1,5-Anhydro-2,3,4,6-tetra*-O-*benzyl-1-(1-methylhydrazi)*-D-*mannitol* (**28Se/28Re**). The reaction of **19** (515 mg, 0.81 mmol) in 7.04M $MeNH_2$ in dry MeOH (20 ml; 2 h) and drying for 3 h at 0° gave **28Se/28Re** 85 : 15 (461 mg, 98%). R_f (hexane/AcOEt 1 : 1) 0.27. $[\alpha]_D^{25} = -10.2$ (*c* = 0.61, MeOH). IR ($CHCl_3$): 3250*w*, 3050*w*, 3020*w* (sh.), 2990*m*, 2930*m*, 2860*m*, 1665*w*, 1495*m*, 1450*m*, 1410*w*, 1380*w*, 1360*m*, 1325*w*, 1285*m*, 1110*s* (br.), 1085*s* (sh.), 1050*s*, 1025*m*, 910*w*, 840*w* (br.). ^{1}H-NMR (400 MHz, C_6D_6; **28Se/28Re** 85 : 15): *Table 5*; additionally for **28Se/28Re**, 7.49 (*d, J* = 7.2, 2 arom. H); 7.36–7.05 (*m*, 18 arom. H); additionally for **28Se**, 4.96 (*d*, *J* = 11.3), 4.89 (*d*, *J* = 12.5), 4.73 (*d*, *J* = 12.4), 4.56 (*d*, *J* = 11.4), 4.49 (*d*, *J* = 12.1), 4.36 (*d, J* =

12.1), 4.35 (*d*, *J* = 11.8), 4.28 (*d*, *J* = 11.7) (8 PhC*H*); additionally for **28Re**, 5.00 (*d*, *J* = 11.4), 4.55 (*d*, *J* = 12.0), 4.53 (*d*, *J* = 12.6), 4.38 (*d*, *J* = 12.7) (4 PhC*H*). ^{13}C-NMR (50.3 MHz, C_6D_6, **28Se**/**28Re** 85:15): *Table 6*; additionally for **28Se**/**28Re**, 139.41–138.94 (several *s*); 128.62–127.59 (several *d*); additionally for **28Se**, 75.22, 73.43, 71.60, 71.55 (4*t*, 4 PhCH_2); additionally for **28Re**, 73.92, 73.73, 72.92, 71.55 (4*t*, 4 PhCH_2). ^{15}N-NMR (60.8 MHz, C_6D_6): *Table 4*. ESI-MS : 589 (100, $[M+Na]^+$).

(1S,1′S,2′S)- and (1R,1′S,2′S)-1,5-Anhydro-2,3:4,6-di-O-*isopropylidene-1-(1-methylhydrazi)*-D-*mannitol* (**29Se**/**29Re**). The reaction of **23** (507 mg, 1.44 mmol) in 7.04M $MeNH_2$ in dry MeOH (20 ml; 1 h) gave **29Se**/**29Re** 4:1 (368 mg, 83%) as a colourless foam. R_f (hexane/AcOEt 1:1) 0.26. IR ($CHCl_3$): 3260*w*, 2990*m*, 2930*m*, 1455*w*, 1440*w*, 1380*s*, 1370*m*, 1345*w*, 1295*m*, 1265*m*, 1240*m*, 1195*m*, 1160*m*, 1105*s*, 1090*s*, 1080*s*, 1030*m*, 995*m*, 970*m*, 940*m*, 850*m*. ^{1}H-NMR (600 MHz, C_6D_6; **29Se**/**29Re** 4:1, assignment based on a ^{1}H,^{1}H-COSY spectrum): *Table 5*; additionally for **29Se**, 1.54, 1.43, 1.21, 1.19 (4*s*, 2 Me_2C); additionally for **29Re**, 1.50, 1.42, 1.24, 1.11 (4*s*, 2 Me_2C). ^{13}C-NMR (50.3 MHz, C_6D_6, **29Se**/**29Re** 4:1): *Table 6*; additionally for **29Se**, 111.18, 99.63 (2*s*, 2 Me_2C); 29.15, 27.55, 26.41, 18.68 (4*q*, 2 Me_2C); additionally for **29Re**, 110.45, 99.75 (2*s*, 2 Me_2C); 29.21, 28.38, 26.41, 18.68 (4*q*, 2 Me_2C). ^{15}N-NMR (60.8 MHz, C_6D_6): *Table 4*. ESI-MS: 325 (92, $[M+K]^+$), 309 (45, $[M+Na]^+$), 287 (100, $[M+1]^+$). Anal. calc. for $C_{13}H_{22}N_2O_5$ (286.45): C 54.51, H 7.74, N 9.77; found: C 54.27, H 8.00, N 9.85.

(1′S,2′S)-1,4-Anhydro-2,3:5,6-di-O-*isopropylidene-1-hydrazi*-D-*mannitol* (**31R**). According to [7]. ^{1}H-NMR (400 MHz, C_6D_6): *Table 5*; additionally, 1.41, 1.32, 1.26, 1.08 (4*s*, 4 Me). ^{13}C-NMR (50.3 MHz, C_6D_6): *Table 6*; additionally, 113.45, 109.16 (2*s*, 2 Me_2C); 27.02, 26.27, 25.59, 25.42 (4*q*, 2 Me_2C).

(E/Z)-2,3:5,6-Di-O-*isopropylidene*-D-*mannofuranose (15N)Oxime* ((*E*/*Z*)-**33***). A soln. of MeONa in MeOH (92 mg of Na, 4 mmol; 30 ml of MeOH) was diluted with. MeOH (20 ml), treated with $^{15}NH_2OH\cdot HCl$ (308 mg, 4.4 mmol), warmed to 50°, treated portionwise with **32** (0.75 g, 2.9 mmol), stirred for 9 h at 50°, 3 d at r.t., and 8 h at 50°, and evaporated. A soln. of the residue in AcOEt, was washed with H_2O (2×) and brine, dried ($MgSO_4$), and evaporated. FC (AcOEt/hexane 1:1) gave (*E*/*Z*)-**33*** (0.4 g, 50%). R_f (AcOEt/hexane 1:1) 0.47.

(E)- and (Z)-2,3:5,6-Di-O-*isopropylidene*-D-*(15N)mannonhydroximo-1,4-lactone* ((*E*)- *and* (*Z*)-**34***). A soln. of (*E*/*Z*)-**33*** (0.4 g, 1.45 mmol) in MeOH (12 ml) was treated with MnO_2 (prepared according to [38]; 0.3 g, 3.42 mmol), stirred for 3 h, and filtered through *Celite*. Evaporation of the filtrate, FC (AcOEt/hexane 1:1) and crystallisation from CH_2Cl_2/hexane gave (*Z*)-**34*** (140 mg, 35%) und (*E*)-**34*** (20 mg, 5%).

*Data of (*Z*)-***34***: R_f (AcOEt/hexane 3:2) 0.48. M.p. 175°. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.35 (br. *s*, OH); 5.15 (*d*, *J* = 5.6, H–C(2)); 4.88 (*dd*, *J* = 5.6, 3.7, H–C(3)); 4.50 (*dt*, *J* = 8.1, 5.0, H–C(5)); 4.30 (*dd*, *J* = 8.4, 3.7, H–C(4)); 4.15 (*d*, *J* = 4.7, 2 H–C(6)); 1.51, 1.47, 1.42, 1.40 (4*s*, 2 Me_2C). ^{1}H-NMR (500 MHz, C_6D_6): 6.75 (br. *s*, OH); 4.62 (*d*, *J* = 5.6, H–C(2)); 4.39 (*ddd*, *J* = 7.7, 6.3, 4.9, H–C(5)); 4.11 (*dd*, *J* = 5.6, 3.5, H–C(3)); 4.05 (*dd*, *J* = 8.9, 4.9, H–C(6)); 3.92 (*dd*, *J* = 8.9, 6.3, H′–C(6)); 3.65 (*dd*, *J* = 7.7, 3.5, H–C(4)); 1.38, 1.33, 1.22, 1.09 (4*s*, 2 Me_2C). ^{13}C-NMR (125.8 MHz, C_6D_6): 156.58 (*d*, ^1J(C,N) = 3.0, C(1)); 113.66, 109.43 (2*s*, 2 Me_2C); 82.33 (*d*, C(4)); 77.89 (*dd*, ^2J(C,N) = 8.7, C(2)); 77.71 (br. *d*, C(3)); 73.14 (*d*, C(5)); 66.76 (*t*, C(6)); 26.97, 26.90, 25.81, 25.36 (4*q*, 2 Me_2C). ^{15}N-NMR (50.7 MHz, C_6D_6): −91.1 (*s*). HR-MALDI-MS: 298.111 (12), 297.108 (100, $[M+Na]^+$; $C_{12}H_{18}{}^{15}NNaO_6^+$; calc. 297.108).

*Data of (*E*)-***34***: R_f (AcOEt/hexane 3:2) 0.75. M.p. 122°. (*E*)-**34*** isomerized to (*Z*)-**34*** upon storage at r.t.

(Z)-(2,3:5,6-Di-O-*isopropylidene*-D-*(15N)mannofuranosylidene)amino Methanesulfonate* (**30***). At r.t. and under N_2, a soln. of (*Z*)-**34*** (120 mg, 0.43 mmol) in dry CH_2Cl_2 (10 ml) was treated with Et_3N (0.14 ml, 1 mmol) and dropwise with MsCl (0.05 ml, 0.65 mmol), stirred for 1 h, diluted with CH_2Cl_2, washed with sat. $NaHCO_3$ soln. and H_2O (2×), dried ($MgSO_4$), and evaporated. FC (AcOEt/hexane 1:1) gave crude **30*** (150 mg) as yellowish oil. Crystallisation from Et_2O/hexane gave **30*** (131 mg, 87%). Colourless crystals. R_f (AcOEt/hexane 1:1) 0.45. M.p. 100–101°.

(1R,1′S,2′S)- and (1S,1′S,2′S)-1,4-Anhydro-1-hydrazi-2,3:5,6-di-O-*isopropylidene*-D-*(15N)mannitol* (**31Rx***/**31Rn***). A soln. of **30*** (63 mg, 0.22 mmol) in a saturated soln. of NH_3 in dry MeOH (4 ml) was stirred for 5 h under N_2 and at r.t. and stored for 10 h at 4°. Filtration through *LiChroprep*-NH_2, evaporation, and drying gave a colourless resin (46 mg). FC (AcOEt/hexane 1:1, column cooled with acetone/dry ice) afforded **31Rx***/**31Rn*** 4:1 (28 mg, 57%). R_f (AcOEt/hexane 1:1) 0.24. ^{1}H-NMR (300 MHz, C_6D_6): *Table 5*; additionally, 1.42, 1.32, 1.26, 1.08 (4*s*, 2 Me_2C).

(1S,1′S,2′S)- and (1R,1′R,2′R)-1,4-Anhydro-2,3:5,6-di-O-*isopropylidene-1-(1-methylhydrazi)*-D-*mannitol* (**35Rx**/**35Sn**). The reaction of **30** (142 mg, 0.4 mmol) in 7.04M $MeNH_2$ in dry MeOH (8 ml; 1.5 h) and drying at 0° for 4 h gave a 74:14:6:6 mixture of **35Rx**, **35Sn**, and two secondary products (107 mg, 92%). R_f (hexane/AcOEt 1:2) 0.32 and 0.16. IR ($CHCl_3$): 3260*w*, 2980*m*, 2950*w*, 2930*m*, 2880*w*, 1665*m*, 1530*w*, 1450*w*, 1415*w*, 1380*m*, 1370*m*, 1250*m* (br.), 1195*m*, 1155*m*, 1145*m*, 1110*m*, 1070*s*, 1045*m*, 995*w*, 970*m*, 950*w*, 935*w* (sh.), 885*w*,

840*w*. ^{1}H-NMR (400 MHz, C_6D_6; **35Rx**/**35Sn** 85:15, assignment based on a ^{1}H,^{1}H-COSY spectrum): *Table 5*; additionally for **35Rx**, 1.41, 1.33, 1.26, 1.11 (4*s*, 2 Me_2C); additionally for the secondary products, 4.65 (*d*, *J* = 8.1, H–C(2)); 4.23 (*d*, *J* = 7.6, H–C(2)); 2.44, 2.43, 2.36, 2.34 (4*s*, 2 MeN). ^{13}C-NMR (50.3 MHz, C_6D_6; **35Rx**/**35Sn** 85:15): *Table 6*; additionally for **35Rx**, 113.36, 109.19 (2*s*, 2 Me_2C); 26.90, 26.22, 25.62, 25.38 (4*q*, 2 Me_2C); additionally for **35Sn**, 113.19, 109.34 (2*s*, 2 Me_2C). CI-MS (NH_3): 288 (12), 287 (100, $[M+1]^+$).

*(Z)-[2,3-*O*-Isopropylidene-5-*O*-(triphenylmethyl)-*D*-ribofuranosylidene]amino Methanesulfonate* ((Z)-**37**). A soln. of (*Z*)-**36**[18]) [17] (4.44 g, 10 mmol) and Et_3N (3.0 ml, 21.5 mmol) in dry CH_2Cl_2 (100 ml) was treated dropwise with MsCl (0.85 ml, 10.9 mmol), and stirred for 1 h. Washing with sat. $NaHCO_3$ soln. and H_2O, drying ($MgSO_4$), evaporation, and FC (hexane/AcOEt 2:1) gave (*Z*)-**37** (4.46 mg, 85%). Colourless foam. R_f (hexane/AcOEt 1:1) 0.56. IR ($CHCl_3$): 3090*w* (sh.), 3060*w* (sh.), 3020*w*, 3000*w* (sh.), 2940*w*, 2880*w*, 1675*m*, 1600*w*, 1490*m*, 1450*m*, 1370*s*, 1325*m*, 1255*m*, 1180*s*, 1150*m*, 1095s, 1080*s* (sh.), 1000*s*, 970*s*, 960*w*, 935*w*, 900*w*, 870*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.16 (*m*, Ph_3C); 5.43 (*d*, *J* = 5.8, H–C(2)); 4.84 (*t*, *J* ≈ 1.9, H–C(4)); 4.60 (*dd*, *J* = 5.9, 1.0, H–C(3)); 3.73 (*dd*, *J* = 10.9, 2.5, H–C(5)); 3.02 (*dd*, *J* = 10.9, 1.6, H′–C(5)); 3.12 (*s*, MsO); 1.50, 1.36 (2*s*, Me_2C). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 164.73 (*s*, C(1)); 142.82 (3*s*); 128.36–127.46 (several *d*); 114.01 (*s*, Me_2C); 88.23 (*d*, C(4)); 87.94 (*s*, Ph_3C); 80.16 (*d*, C(3)); 78.52 (*d*, C(2)); 63.31 (*t*, C(5)); 36.01 (*q*, MsO); 26.75, 25.52 (2*q*, Me_2C). CI-MS: 541 (7, $[M+NH_4]^+$), 482 (3), 431 (29), 430 (100, $[M-MsO+2]^+$), 299 (27), 244 (14), 243 (82, Ph_3C^+), 188 (13). Anal. calc. for $C_{28}H_{29}NO_7S$ (523.59): C 64.23, H 5.58, N 2.67, S 6.12; found: C 63.98, H 5.67, N 2.52, S 6.30.

*(1R,1′R,2′R)-, (1R,1′S,2′S)-, (1S,1′R,2′R)-, and (1S,1′S,2′S)-1,4-Anhydro-2,3-*O*-isopropylidene-1-(1-methylhydrazi)-5-*O*-(triphenylmethyl)-*D*-ribitol* (**38Rn**/**38Sn**/**38Rx**/**38Sx**). The reaction of (*Z*)-**37** (510 mg, 0.97 mmol) in 7.04M $MeNH_2$ in dry MeOH (20 ml; 3.5 h) gave **38Rn**/**38Sn**/**38Rx**/**38Sx** 76:4:12:8 (418 mg, 94%). R_f (hexane/AcOEt 1:1) 0.25. M.p. 48–50°. $[\alpha]_D^{25} = -36.7$ (*c* = 0.53, MeOH). IR (KBr): 3240*m*, 3040*w*, 3010*w*, 2980*m*, 2920*m*, 2860*w*, 1650*w* (br.), 1595*w*, 1485*m*, 1445*s*, 1410*w*, 1370*s*, 1320*m*, 1250*m*, 1210*s*, 1175*m*, 1150*m*, 1115*s*, 1075*s*, 1040*m* (sh.), 1025*m* (sh.), 995*m*, 975*m*, 945*w*, 895*w*, 865*m*, 805*w*. ^{1}H-NMR (400 MHz, C_6D_6; **38Rn**/**38Sn**/**38Rx**/**38Sx** 76:4:12:8, assignment based on a ^{1}H,^{1}H-COSY spectrum): *Table 7*; additionally for **38Rn**/**38Sn**/**38Rx**/**38Sx**, 7.52–7.33 (*m*, 6 arom. H); 7.15–6.97 (*m*, 9 arom. H); additionally for **38Rn**, 1.54, 1.21 (2*s*, Me_2C); additionally for **38Sn**, 1.41, 1.15 (2*s*, Me_2C); additionally for **38Rx**, 1.48, 1.14 (2*s*, Me_2C); additionally for **38Sx**, 1.36, 1.06 (2*s*, Me_2C). ^{13}C-NMR (50.3 MHz, C_6D_6, **38Rn**/**38Rx** 85:15): *Table 7*; additionally for **38Rn**/**38Rx**, 144.11 (3*s*); 129.42–127.03 (several *d*), 87.69 (*s*, Ph_3C); additionally for **38Rn**, 113.06 (*s*, Me_2C); 27.04, 26.02 (2*q*, Me_2C); additionally for **38Rx**, 26.86, 25.47 (2*q*, Me_2C). ^{15}N-NMR (60.8 MHz, C_6D_6): *Table 4*. CI-MS (NH_3): 460 (25), 459 (100, $[M+1]^+$), 243 (27, Ph_3C^+).

*(E/Z)-2,3,5-Tri-*O*-benzyl-*D*-ribose Oxime* (**40**) [40]. A soln. of NaOEt (0.92 g of Na, 40.0 mmol) in abs. EtOH (150 ml) was treated at 55° with $NH_2OH \cdot HCl$ (5.56 g, 80.0 mmol) and portionwise with **39** [26][27] (4.21 g, 10.0 mmol), stirred for 2.5 h at 55°, and evaporated. The residue was dissolved in CH_2Cl_2, washed (2 × with H_2O, 1 × with brine), and dried ($MgSO_4$). Evaporation and drying gave (*E*)-**40**/(*Z*)-**40** 4:1 (4.50 g, quant.). Colourless oil. R_f (hexane/AcOEt 1:1) 0.42. $[\alpha]_D^{25} = +42.0$ (*c* = 1.06, $CHCl_3$). IR ($CHCl_3$): 3570*m*, 3340*m*, 3060*w*, 3020*w* (sh.), 2990*m*, 2910*m*, 2865*m*, 1495*m*, 1455*m*, 1390*w*, 1370*m*, 1350*m*, 1325*m* (br.), 1260*w*, 1090*s* (br.), 1070*s* (sh.), 1025*m*, 945*m*, 910*m*, 815*w*. ^{1}H-NMR (400 MHz, $CDCl_3$, (*E*)-**40**/(*Z*)-**40** 4:1): 8.89 (br. *s*, exchange with D_2O, NOH); 7.52 (*d*, *J* = 8.4, 0.8 H), 6.98 (*d*, *J* = 6.3, 0.2 H) (H–C(1)); 7.38–7.21 (*m*, 15 arom. H); 5.15 (*dd*, *J* = 2.1, 6.3, 0.2 H), 4.47 (*dd*, *J* = 1.7, 8.3, 0.8 H) (H–C(2)); 4.88 (*d*, *J* = 11.4, 0.8 H), 4.76 (*d*, *J* = 11.4, 0.2 H), 4.76 (*d*, *J* = 11.4, 0.2 H), 4.70 (*d*, *J* = 10.9, 0.2 H), 4.64 (*d*, *J* = 10.3, 0.2 H), 4.61 (*d*, *J* = 11.7, 0.8 H), 4.58 (*d*, *J* = 12.0, 0.8 H), 4.60–4.49 (*m*, 2 H), 4.45 (*d*, *J* = 11.7, 0.8 H) (6 PhC*H*); 4.63–4.58 (br. *s*, exchange with D_2O, 0.8 H), 4.42–4.37 (br. *s*, exchange with D_2O, 0.2 H) (OH); 3.93–3.88 (*m*, 0.2 H), 3.45 (br. *dd*, *J* = 7.0, 8.9, 0.8 H) (H–C(4)); 3.86 (*dd*, *J* = 2.1, 8.9, 0.2 H), 3.78 (*dd*, *J* = 2.1, 8.9, 0.8 H) (H–C(3)); 3.78–3.74 (*m*, 1.6 H), 3.67 (*dd*, *J* = 2.7, 9.6, 0.2 H), 3.62 (*dd*, *J* = 4.9, 9.7, 0.2 H) (2 H–C(5)). ^{13}C-NMR (50.3 MHz, $CDCl_3$, (*E*)-**40**/(*Z*)-**40** 4:1): (*E*)-**40**: 149.03 (*d*, C(1)); 137.91, 137.83, 136.76 (3*s*); 128.42–127.21 (several *d*); 80.64 (*d*, C(3)); 78.21 (*d*, C(2); 74.13, 73.57, 72.87 (3*t*, 3 PhCH_2); 71.14 (*t*, C(5)); 68.79 (*d*, C(4)); (*Z*)-**40**: 151.70 (*d*, C(1)); 137.83, 136.04 (2*s*); 79.65 (*d*, C(3)); 74.06, 73.12, 72.47 (3*t*, 3 PhCH_2); 71.99 (*d*, C(2)); 71.23 (*t*, C(5)); 69.22 (*d*, C(4)). CI-MS (NH_3): 453 (8, $[M+NH_4]^+$), 437 (28), 436 (100, $[M+1]^+$). Anal. calc. for $C_{26}H_{29}NO_5$ (435.52): C 71.71, H 6.71, N 3.22; found: C 71.44, H 6.46, N 3.24.

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[18]) The preparation of **36** by oxidation with MnO_2 [24] instead of $NaIO_4$ [17] gave (*Z*)-**37**/(*E*)-**36** 4:1 and, hence, by mesylation, (*Z*)-**36**/(*E*)-**37** 4:1. ^{1}H-NMR data of (*Z*)-**37** (400 MHz, $CDCl_3$, (*Z*)-**37**/(*E*)-**37** 4:1): 5.58 (*d*, *J* = 5.8, H–C(2)); 4.78 (br. *t*, *J* ≈ 1.9, H–C(4)); 4.41 (*d*, *J* = 5.8, H–C(3)); 3.76 (*dd*, *J* = 10.9, 2.5, H–C(5)); 3.13 (*s*, MsO); 3.07 (*dd*, *J* = 10.9, 1.6, H′–C(5)); 1.48, 1.33 (2*s*, 2 Me_2C).

Table 7. *Selected ^1H- and ^{13}C-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Ribofurano-sylidene-diaziridines* **38**

	38Rn/38Sn/38Rx/38Sx[a])					**38Rn/38Sx**	
Ratio	76 :	4 :	12 :	8		85 :	15
Solvent	C_6D_6					C_6D_6	
H−C(2)	4.41	4.91	4.80	5.40	C(1)	93.97	[b])
H−C(3)	4.49	4.47	4.65	4.14	C(2)	82.82[c])	82.90[c])
H−C(4)	4.34	4.40	4.34	4.25	C(3)	82.53[c])	82.48[c])
H−C(5)	3.37	3.30	3.20	3.32–3.28	C(4)	81.91[c])	81.21[c])
H′−C(5)	3.11	2.98	3.06	3.32–3.28	C(5)	64.84	64.73
H_{exo}−N	2.33	2.38	–	–	MeN	39.98	[b])
H_{endo}−N	–	–	2.43	2.73			
MeN	2.79	2.74	2.81	2.54			
J(2,3)	5.9	5.9	6.1	5.7			
J(3,4)	1.0	< 0.8	1.3	< 0.8			
J(4,5)	4.3	[b])	4.5	[b])			
J(4,5′)	3.7	3.2	4.6	[b])			
J(5,5′)	10.1	10.3	10.3	[b])			

[a]) Assignment based on a $^1H,^1H$-COSY spectrum. [b]) Not assigned. [c]) Assignments may be interchanged.

(Z)-2,3,5-Tri-O-*benzyl*-D-*ribonhydroximo-1,4-lactone* (**41**). A soln. of **40** (0.50 g, 1.2 mmol) in dry MeOH (10 ml) was treated with activated MnO_2 [38] (0.19 g, 2.2 mmol) and kept for 14 h at reflux. Filtration through *Celite*, evaporation, and FC (hexane/AcOEt 7:4 → 2:1) gave **41** (0.46 g, 92%). Colourless oil. R_f (hexane/AcOEt 1:1) 0.56. $[\alpha]_D^{25} = +112.6$ ($c = 0.48$, $CHCl_3$). IR (KBr): 3580*m*, 3320*w* (br.), 3060*w*, 3020*w* (sh.), 3000*m*, 2930*m*, 2880*m*, 1730*w*, 1675*m*, 1495*m*, 1455*m*, 1365*m*, 1325*w*, 1280*w*, 1250*m*, 1195*w*, 1120*s* (br.), 1080*s* (sh.), 1025*m*, 960*m*, 930*m*, 860*w*. ^1H-NMR (300 MHz, $CDCl_3$): 7.39–7.19 (*m*, 15 arom. H); 7.02 (*s*, exchange with D_2O, OH); 4.81 (*d*, *J* = 12.1, PhC*H*); 4.68 (*ddd*, *J* = 2.4, 3.5, 7.7, H−C(4)); 4.56 (*d*, *J* = 12.0), 4.55 (*d*, *J* = 12.0, 2 H), 4.46 (*d*, *J* = 12.0), 4.39 (*d*, *J* = 11.8) (5 PhC*H*); 4.19 (*d*, *J* = 5.0, H−C(2)); 4.08 (*dd*, *J* = 5.0, 7.7, H−C(3)); 3.83 (*dd*, *J* = 2.3, 11.6, H−C(5)); 3.63 (*dd*, *J* = 3.6, 11.6, H′−C(5)). ^1H-NMR (400 MHz, C_6D_6): *Table 8*; additionally, 7.36 (*d*, *J* = 7.1, 2 arom. H); 7.25 (br. *s*, exchange with D_2O, OH); 7.20–7.05 (*m*, 13 arom. H); 4.86 (*d*, *J* = 12.0), 4.56 (*d*, *J* = 12.0), 4.32 (*d*, *J* = 11.5, 2 H), 4.20 (*d*, *J* = 12.1), 4.05 (*d*, *J* = 11.6) (6 PhC*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 9*; additionally, 137.38, 136.81, 136.73 (3*s*); 128.41–127.37 (several *d*); 73.05, 71.76, 70.29 (3*t*, 3 Ph*C*H$_2$). CI-MS (NH_3): 436 (10), 435 (30), 434 (100, $[M+1]^+$). Anal. calc. for $C_{26}H_{27}NO_5$ (433.50): C 72.04, H 6.28, N 3.23; found: C 71.85, H 6.44, N 3.16.

(Z)-(2,3,5-Tri-O-*benzyl*-D-*ribofuranosylidene)amino Methanesulfonate* (**42**). At 30° under N_2, a soln. of **41** (2.29 g, 5.3 mmol) in dry CH_2Cl_2 (60 ml) was treated with Et_3N (2.2 ml, 15.9 mmol) and dropwise with MsCl (0.62 ml, 7.9 mmol)), stirred for 1 h at 30°, and poured in ice/H_2O. The org. layer was washed (2 × with sat. $NaHCO_3$ soln., 1 × with brine), and dried (Na_2SO_4). FC (hexane/AcOEt 3:1) gave **42** (2.43 g, 90%). Yellowish oil. R_f (hexane/AcOEt 2:1) 0.55. $[\alpha]_D^{25} = +82.9$ ($c = 0.97$, $CHCl_3$). IR ($CHCl_3$): 3050*w*, 3020*w* (br.), 2930*w* (br.), 2860*w*, 1675*m*, 1495*w*, 1450*m*, 1365*s*, 1320*m*, 1295*w*, 1250*m*, 1175*s*, 1115*m* (br.), 1020*m*, 990*m*, 965*m*, 910*w*, 825*s*. ^1H-NMR (300 MHz, $CDCl_3$): 7.32–7.16 (*m*, 15 arom. H); 4.80 (*d*, *J* = 12.0, PhC*H*); 4.69 (*td*, *J* ≈ 2.7, 6.4, H−C(4)); 4.52 (*d*, *J* ≈ 12.0, 2 H), 4.48 (*d*, *J* = 11.5), 4.465 (*d*, *J* = 12.2), 4.460 (*d*, *J* = 12.2) (5 PhC*H*); 4.31 (*d*, *J* = 5.1, H−C(2)); 4.09 (*dd*, *J* = 5.2, 6.7, H−C(3)); 3.74 (*dd*, *J* = 2.3, 11.8, H−C(5)); 3.55 (*dd*, *J* = 3.1, 11.8, H′−C(5)); 3.07 (*s*, MsO). ^1H-NMR (400 MHz, C_6D_6): *Table 8*; additionally, 7.31–7.29 (*m*, 2 arom. H); 7.20–7.05 (*m*, 13 arom. H); 4.76 (*d*, *J* = 11.9), 4.42 (*d*, *J* = 11.8), 4.29 (*d*, *J* = 11.7), 4.18 (*d*, *J* = 12.1), 4.10 (*d*, *J* = 11.7), 4.08 (*d*, *J* = 12.1) (6 PhC*H*); 2.50 (*s*, MsO). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 9*; additionally, 137.11, 136.56, 136.33 (3*s*); 128.38–127.21 (several *d*); 73.16, 72.34, 71.48 (3*t*, 3 Ph*C*H$_2$); 35.74 (*q*, MsO). CI-MS (NH_3): 347 (16), 346 (84), 237 (38), 216 (19), 205 (10), 204 (100). Anal. calc. for $C_{27}H_{29}NO_7S$ (511.59): C 68.39, H 5.71, N 2.74, S 6.27; found: C 68.22, H 5.98, N 2.91, S 6.51.

Treatment of **42** *with* NH_3. Compound **42** (500 mg, 0.98 mmol) was dissolved in a sat. soln. of NH_3 in MeOH (20 ml) and stirred for 24 h at r.t. Evaporation and FC (hexane/AcOEt 2:1) gave **43** (90 mg, 21%), **45** (95 mg, 25%), and **44** [29–31] (43 mg, 10%).

Table 8. *^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Ribose Derivatives* **41**–**43**, **45**, *and* **46**, *and of the Arabinose Derivatives* **48** *and* **49**

Solvent	**41** C_6D_6	**42** C_6D_6	**43**[a]) $CDCl_3$	**45** $CDCl_3$	**46** $CDCl_3$	**47** C_6D_6	**48** C_6D_6	**49**[a]) $CDCl_3$
H–C(2)	4.15	4.15	4.51	4.35	4.34	4.40	4.32	4.47
H–C(3)	3.89	3.84	3.90	4.07	4.07	4.12	4.16	3.70
H–C(4)	4.70	4.51	3.78	4.01	3.99	4.56	4.36	3.99
H–C(5)	3.50	3.28	3.53	3.62	3.61	3.50	3.35	3.58
H–C(5′)	3.34	3.13	3.50	3.62	3.61	3.46	3.27	3.58
HN	–	–	[b])	6.65/5.49	6.71	–	–	[b])
HO–C(4)	–	–	2.73	3.21	3.61–3.50	–	–	2.51
MeN	–	–	–	–	2.82	–	–	–
J(2,3)	4.9	5.0	3.0	1.9	1.9	2.5	3.3	2.7
J(3,4)	8.2	6.8	8.7	8.3	8.0	2.8	3.5	7.6
J(4,5)	2.2	2.3	3.3	3.9	4.2	6.4	6.1	4.1
J(4,5′)	3.8	3.1	4.6	3.9	4.2	5.8	5.1	4.1
J(5,5′)	11.7	11.8	9.7	[c])	[c])	10.2	10.6	[c])
J(4,OH)	–	–	5.7	6.3	[c])	–	–	7.2

[a]) Arbitrary numbering, as for **41** and **47**. [b]) Hidden by the signal of the Ph groups at 7.34–7.21 ppm, exchanging with D_2O. [c]) Not assigned.

Table 9. *^{13}C-NMR Chemical Shifts* [ppm] *of the Ribose Derivatives* **41**–**43**, **45**, *and* **46**, *and of the Arabinose Derivatives* **47**–**49**

	41 $CDCl_3$	**42** $CDCl_3$	**43**[a]) $CDCl_3$	**45** $CDCl_3$	**46** $CDCl_3$	**47** $CDCl_3$	**48** $CDCl_3$	**49**[a]) $CDCl_3$
C(1)	156.03	162.31	148.28	173.90	171.23	156.72	162.71	149.46
C(2)	72.15	73.68	77.27	79.59	79.90	78.42	79.19	75.43
C(3)	75.10	75.12	80.40	80.00	80.03	80.71	80.10	80.92
C(4)	82.87	85.79	69.96	69.57	69.79	84.65	86.59	69.56
C(5)	67.22	66.95	70.51	70.88	70.83	68.31	67.56	70.33
MeN	–	–	–	–	25.73	–	–	–

[a]) Arbitrary numbering, as for **41** and **47**.

Treatment of **42** *with MeNH$_2$*. Compound **42** (500 mg, 0.98 mmol) was dissolved in a 7.04M soln. of $MeNH_2$ in MeOH (20 ml) and stirred for 1 h at r.t. Evaporation and FC (hexane/AcOEt/Et_3N 5:10:0.1) gave **46** (76 mg, 17%) and **44** (181 mg, 44%).

1,4-Dihydro-3,6-bis[(1S)-1,2,4-tri-O-*benzyl*-D-*erytritol-1-yl]-1,2,4,5-tetrazine* (**43**). Colourless crystals. R_f (hexane/AcOEt 1:1) 0.27. M.p. 108–109°. $[\alpha]_D^{25} = +73.5$ ($c = 0.34$, $CHCl_3$). IR (KBr): 3400*m*, 3260*m*, 3050*w*, 3020*w*, 2910*w*, 2900*w* (br.), 2860*w*, 1640*w* (br.), 1490*w*, 1450*m*, 1425*m*, 1390*m* (sh.), 1340*w*, 1300*w*, 1205*w*, 1120*s* (sh.), 1095*s*, 1070*s*, 1020*m*, 965*w*, 930*m* (br.), 800*w* (br.). ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 8*; additionally, 7.34–7.21 (*m*, 15 arom. H); 4.80 (*d*, $J = 11.1$), 4.71 (*d*, $J = 11.5$), 4.50 (*d*, $J = 10.5$), 4.48 (*d*, $J = 11.5$), 4.46 (*d*, $J = 12.0$), 4.39 (*d*, $J = 11.9$) (6 PhC*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 9*; additionally, 137.77 (*s*, 2 C); 137.20 (*s*); 128.84–127.79 (several *d*); 75.01, 73.25, 71.83 (3*t*, 3 PhCH_2). ESI-MS: 903 (18, $[M+K]^+$), 887 (100, $[M+Na]^+$). Anal. calc. for $C_{52}H_{56}N_4O_8$ (865.02): C 72.20, H 6.53, N 6.48; found: C 72.50, H 6.45, N 6.48.

2,3,5-Tri-O-*benzyl*-D-*ribonamide* (**45**). R_f (hexane/AcOEt 1:1) 0.07. $[\alpha]_D^{25} = +36.3$ ($c = 0.59$, $CHCl_3$). IR ($CHCl_3$): 3510*m*, 3400*m*, 3060*w*, 3020*w* (sh.), 2995*m*, 2910*w*, 2870*m*, 1680*s*, 1565*m*, 1495*w*, 1455*m*, 1380*w* (br.),

1360*w* (br.), 1240*w* (br.), 1080*s* (br.), 1070*s*, 1025*s*, 910*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 8*; additionally, 7.36–7.16 (*m*, 15 arom. H); 6.65 (br. *s*, NH); 5.49 (br. *s*, NH); 4.72 (*d*, *J* = 11.4,), 4.71 (*d*, *J* = 11.6), 4.64 (*d*, *J* = 11.6), 4.55 (*d*, *J* = 12.0), 4.51 (*d*, *J* = 11.5), 4.48 (*d*, *J* = 12.0) (6 PhC*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 9*; additionally, 137.81 (*s*, 2 C); 137.00 (*s*); 128.33–127.46 (several *d*); 73.23, 73.09, 73.05 (3*t*, 3 Ph*C*H$_2$). CI-MS (NH_3): 437 (20), 436 (100, $[M+1]^+$).

2,3,5-Tri-O-*benzyl*-N-*methyl*-D-*ribonamide* (**46**). R_f (hexane/AcOEt 1:2) 0.18. $[\alpha]_D^{25} = +33.0$ ($c = 0.56$, $CHCl_3$). IR ($CHCl_3$): 3560*w*, 3430*m*, 3060*w*, 3020*w* (sh.), 2995*m*, 2920*m*, 2860*m*, 1660*s*, 1545*m*, 1535*m*, 1495*w*, 1455*m*, 1415*w*, 1355*w* (br.), 1240*w*, 1090*s* (br.), 1070*s*, 1025*s*, 910*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 8*; additionally, 7.38–7.22 (*m*, 15 arom. H); 6.71 (br. *q*, *J* = 4.5, irrad. at 2.82 → *s*, slow exchange with D_2O, NH); 4.71 (*d*, *J* = 11.7), 4.68 (*d*, *J* = 11.7), 4.58 (*d*, *J* = 11.6), 4.54 (*d*, *J* = 12.0), 4.52 (*d*, *J* = 11.5), 4.48 (*d*, *J* = 12.0) (6 PhC*H*); 2.82 (*d*, *J* = 5.0, irrad. at 6.71 → *s*, MeN). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 9*; additionally, 138.00, 137.93, 137.03 (3*s*); 128.46–127.53 (several *d*); 73.24 (*t*, 3 Ph*C*H$_2$). CI-MS (NH_3): 451 (30), 450 (100, $[M+1]^+$).

(Z)-2,3,5-Tri-O-*benzyl*-D-*arabinonhydroximo-1,4-lactone* (**47**). At 50°, a soln. of (*E*/*Z*)-2,3,5-tri-*O*-benzyl-D-arabinose oximes [28] (4.00 g, 9.2 mmol) and Et_3N (1.6 ml, 11.5 mmol) in DMF (80 ml) was treated portionwise with dibromantine (2.63 g, 9.2 mmol), stirred for 20 min, and poured on ice/H_2O. After extraction with Et_2O (3×), the org. layer was washed 2× with a soln. of $Na_2S_2O_5$ (0.37 g, 2.0 mmol) and $Na_2CO_3 \cdot 10\ H_2O$ (1.00 g, 4.0 mmol) in H_2O (200 ml) and 1× with brine, and dried (Na_2SO_4). Evaporation and FC (hexane/AcOEt 4:1) gave **47** (2.98 g, 75%). Colourless oil. R_f (hexane/AcOEt 1:1) 0.56. $[\alpha]_D^{25} = 25.7$ ($c = 1.11$, $CHCl_3$). IR ($CHCl_3$): 3580*m*, 3060*w*, 3020*w* (sh.), 3000*w*, 2910*m*, 2860*m*, 1690*m*, 1495*m*, 1455*s*, 1365*m*, 1320*m*, 1240*m*, 1195*w*, 1090*s*, 1070*s* (sh.), 1025*s*, 940*m*, 910*m*, 855*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.34–7.18 (*m*, 15 arom. H); 6.86 (*s*, exchange with D_2O, OH); 4.77 (*d*, *J* = 11.8, PhC*H*); 4.59 (*dt*, *J* ≈ 3.1, 5.9, H–C(4)); 4.53–4.43 (*m*, 3 PhC*H*); 4.50 (*s*, PhCH_2); 4.36 (*d*, *J* = 2.6, H–C(2)); 4.13 (*t*, *J* = 2.6, H–C(3)); 3.68 (*dd*, *J* = 5.6, 10.2, H–C(5)); 3.63 (*dd*, *J* = 6.4, 10.4, H′–C(5)). ^{1}H-NMR (400 MHz, C_6D_6): *Table 8*; additionally, 7.33 (br. *s*, exchange with D_2O, OH); 7.25–7.23 (*m*, 2 arom. H); 7.14–7.05 (*m*, 13 arom. H); 4.83 (*d*, *J* = 11.8), 4.48 (*d*, *J* = 11.7), 4.26 (*d*, *J* = 12.1), 4.23 (*d*, *J* = 11.8), 4.21 (*d*, *J* = 11.9), 4.20 (*d*, *J* = 11.9) (6 PhC*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 9*; additionally, 137.23, 136.77, 136.63 (3*s*); 127.95–127.31 (several *d*); 72.88, 71.18, 71.01 (3*t*, 3 Ph*C*H$_2$). CI-MS (NH_3): 436 (17), 435 (28), 434 (100, $[M+1]^+$), 418 (10).

(Z)-(2,3,5-Tri-O-*benzyl*-D-*arabinofuranosylidene)amino Methanesulfonate* (**48**). At −20° under N_2, a soln. of **47** (3.00 g, 6.9 mmol) in abs. CH_2Cl_2 (60 ml) was treated with Et_3N (2.9 ml, 20.8 mmol) and dropwise with MsCl (0.80 ml, 10.4 mmol)), stirred for 1 h at 20°, and poured onto ice/H_2O. The org. layer was washed 2× with sat. $NaHCO_3$ soln. and 1× with brine, and dried (Na_2SO_4). Evaporation and FC (hexane/AcOEt 3:1) gave **48** (3.04 g, 86%), Yellowish oil. R_f (hexane/AcOEt 1:1) 0.68. $[\alpha]_D^{25} = 23.8$ ($c = 0.96$, $CHCl_3$). IR ($CHCl_3$): 3050*w* (sh.), 3020*m* (br.), 2930*w*, 2860*m*, 1670*m*, 1490*m*, 1450*m*, 1410*w*, 1365*s*, 1325*m*, 1245*m*, 1175*s*, 1090*s* (br.), 1075*m* (sh.), 1040*m*, 1025*m*, 965*m*, 905*w*, 825*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.16 (*m*, 15 arom. H); 4.83 (*d*, *J* = 11.7, PhC*H*); 4.69 (*dt*, *J* = 3.4, 5.6, H–C(4)); 4.54 (*d*, *J* = 11.7, PhC*H*); 4.51 (*d*, *J* = 11.2, PhC*H*); 4.50 (*s*, PhCH_2); 4.48 (*d*, *J* = 3.0, H–C(2)); 4.46 (*d*, *J* = 11.2, PhC*H*); 4.20 (*t*, *J* = 3.3, H–C(3)); 3.64 (*d*, *J* = 5.6, 2 H–C(5)); 3.10 (*s*, MsO). ^{1}H-NMR (400 MHz, C_6D_6): *Table 8*; additionally, 7.25–7.21 (*m*, 2 arom. H); 7.15–7.03 (*m*, 13 arom. H); 4.77 (*d*, *J* = 11.7), 4.41 (*d*, *J* = 11.7), 4.20 (*d*, *J* = 12.0), 4.15 (*d*, *J* = 12.0) (4 PhC*H*); 4.13 (*s*, PhCH_2); 2.47 (*s*, MsO). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 9*; additionally, 137.07, 136.35, 136.13 (3*s*); 128.09–127.26 (several *d*); 72.79, 71.69, 71.54 (3*t*, 3 PhCH_2); 35.44 (*q*, Ms). CI-MS (NH_3): 347 (22), 346 (87), 237 (28), 216 (18), 206 (10), 205 (19), 204 (100). Anal. calc. for $C_{27}H_{29}NO_7S \cdot 0.5\ H_2O$ (520.60): C 62.29, H 5.81, N 2.69, S 6.16; found: C 62.42, H 6.11, N 3.10, S 6.03.

Treatment of **48** *with* NH_3. Compound **48** (500 mg, 0.98 mmol) was dissolved in a sat. soln. of NH_3 in MeOH (20 ml) and stirred for 24 h at r.t. Evaporation and FC (hexane/AcOEt 2:1) gave an unassigned fraction (51 mg, *ca.* 12%), **49** (94 mg, 21%), and **50** [29][41][42] (93 mg, 23%).

1,4-Dihydro-3,6-bis[(1R)-1,2,4-tri-O-*benzyl*-D-*erytritol-1-yl]-1,2,4,5-tetrazine* (**49**). R_f (hexane/AcOEt 1:1) 0.07. M.p. 144–145°. $[\alpha]_D^{25} = -10.8$ ($c = 0.17$, $CHCl_3$). IR (KBr): 3470*m*, 3250*m*, 3050*w*, 3020*m*, 2920*m*, 2850*m*, 1650*w*, 1490*w*, 1450*m*, 1405*m*, 1365*m*, 1345*m*, 1305*m*, 1250*w*, 1205*m*, 1130*m* (sh.), 1120*m* (sh.), 1085*s*, 1070*s*, 1020*m*, 1000*m*, 960*w*, 940*w*, 905*w*, 870*w*, 815*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 8*; additionally, 7.34–7.24 (*m*, 15 arom. H); 4.70 (*d*, *J* = 10.7, PhC*H*); 4.68 (*d*, *J* = 11.4, PhC*H*); 4.46 (*s*, PhCH_2); 4.44 (*d*, *J* ≈ 11.0, 2 PhC*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 9*; additionally, 137.62, 137.35, 136.70 (3*s*); 128.49–127.84 (several *d*); 74.27, 73.38, 72.29 (3*t*, 3 Ph*C*H$_2$). ESI-MS: 903 (60, $[M+K]^+$), 887 (100, $[M+Na]^+$). Anal. calc. for $C_{52}H_{56}N_4O_8$ (865.02): C 72.20, H 6.53, N 6.48; found: C 72.33, H 6.36, N 6.76.

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