Glycosylidene Carbenes

Part 32

Reaction of Glycosylidene Diaziridines with Acylating and Sulfonylating Agents

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Dedicated to the memory of *Jorge F. López-Herrera*

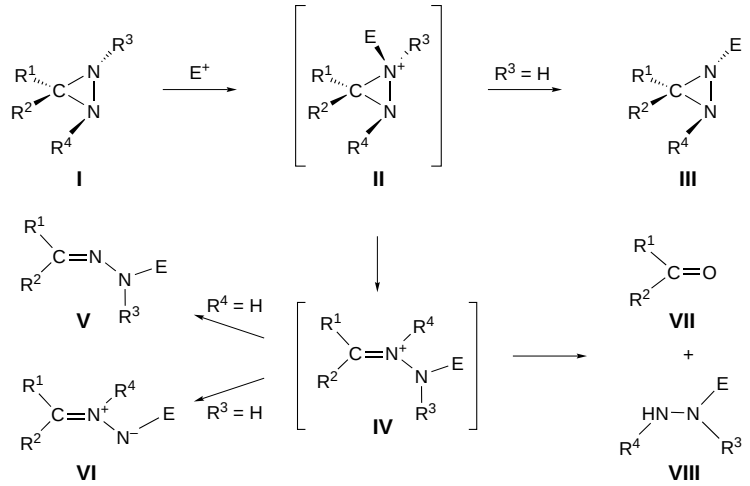
Acylation and sulfonylation of the *N,N′*-unsubstituted glucosylidenespirodiaziridines **1A/1B** 95:5 with Ac_2O, BzCl, FmocCl, TsCl, (naphthalen-2-yl)sulfonyl, and (2,4,6-triisopropylphenyl)sulfonyl chloride, and concomitant rearrangement gave the acylated and sulfonylated gluconolactone hydrazones **2B**–**2G** in 40–83% yield (*Scheme 2*). Similarly, the *galacto* and *manno* analogues **3A/3B** 95:5 and **5A/5B** 55:45 and the mannofuransoylidene-diaziridine **30** were acetylated and tosylated to give **4A**, **4B**, **6**, **31A**, and **31B** (55–73% yield; *Schemes 2* and *5*). ^{15}N-Labelling of **11A/11B** and **14A/14B** showed that the pseudoequatorial NH of the *gluco* diaziridines **1** and the pseudoaxial NH of the *galacto* diaziridines **3** were preferentially acetylated and tosylated (*Scheme 3*). Sulfonylation of the *N*-methylated diaziridines **19A/19B** 72:28, **22A/22B** 85:15, **25A/25B** 85:15, **28A/28B** 80:20, and **33A/33B/33C/33D** 76:4:12:8 yielded the *N*-methyl-*N*-tosylglyconolactone hydrazones **20**, **23**, **26**, **29**, and **34** (44–66%; *Schemes 4* and *5*). The methylated N-atom of the diaziridines proved more reactive, irrespective of the configuration at C(2) and C(4). The products were readily hydrolysed to glyconolactones.

Introduction. – The reactivity of glycosylidene diaziridines has not been well-explored. Apart from an investigation of their formation [1], with special emphasis on the stereoselectivity of the addition of NH_3 and $MeNH_2$ to the precursor glyconolactone oxime sulfonates [2], only the oxidation of these diaziridines with iodine and Et_3N or Me_3N in MeOH, Et_2O, or CH_2Cl_2 [3] to *N*-unsubstituted-glycosylidene diazirines was investigated. These diazirines have been studied as precursors of glycosylidene carbenes [3–5].

The reactivity of 3-alkyldiaziridines has been explored more extensively. Their reaction with electrophiles is strongly influenced by the nature of the electrophile and by the *N*-substituents. Attack of electrophiles on the diaziridines **I** leads to diaziridinium ions **II** (*Scheme 1*). For $R^3 = H$, deprotonation of **II** afforded substituted diaziridines **III** [6–10]. Alternatively, diaziridine ring opening of **II** led to the hydrazonium ions **IV**, which were transformed into hydrazones **V** ($R^4 = H$) [11][12] and into azomethine imines **VI** ($R^3 = H$) [13]. Hydrolysis of **IV** afforded ketones **VII** and hydrazines **VIII** [13a][14][15]. This transformation to hydrazines constitutes a valuable method for the selective preparation of otherwise hardly accessible *N*-alkyl- and *N,N′*-dialkylhydrazines [16]. The reaction of 1,3,3-trimethyldiaziridine with AcCl led to a 4:1 mixture of *N*-methyl-*N′*-isopropylidene-acethydrazide and 2-acetyl-1,3,3-trimethyldiaziridine [17].

Except for the oxidation with I_2, we found no reaction of glycosylidene diaziridines, nor of any other 3-alkoxydiaziridine with electrophiles. We have examined the

Scheme 1. *Products Obtained from Diaziridines* **I** (R^1–R^4 = alkyl or H) *upon Reaction with Electrophiles* E^+



reactions of glycosylidene-diaziridines with acylating and sulfonylating reagents, and describe the results of these experiments.

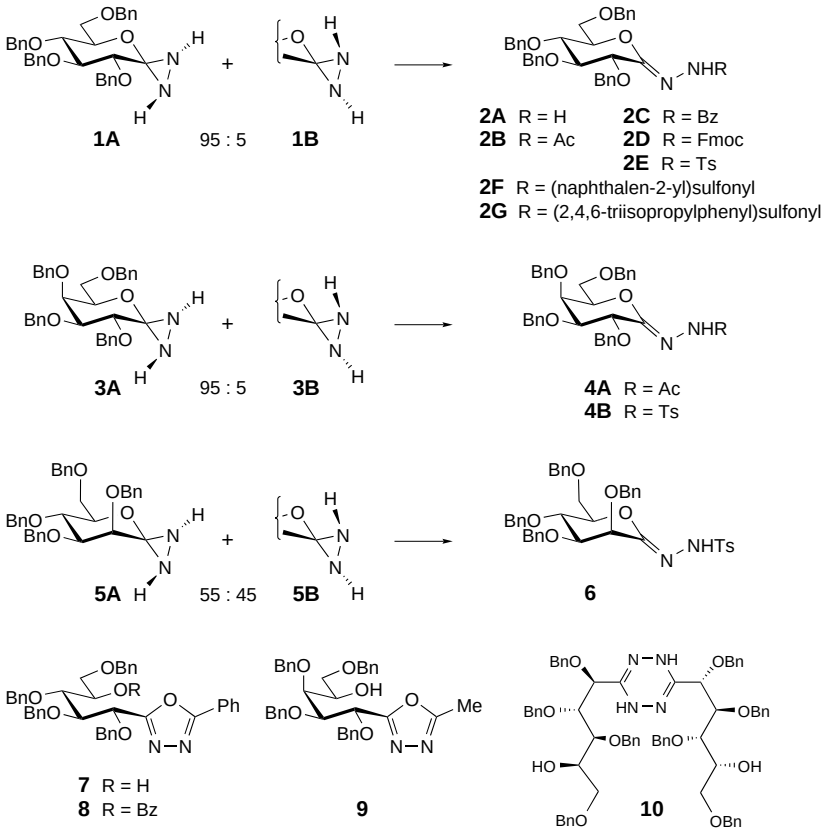
Results and Discussion. – 1. *Acylation and Sulfonylation of* N,N′-*Unsubstituted Pyranosylidene-diaziridines.* Scouting experiments showed that thermolysis of the D-*gluco* diaziridines **1A**/**1B** 95:5 [2] at 80° in toluene led to a mixture of the *N*-unsubstituted lactone hydrazone **2A**, the corresponding glyconolactone, and traces of side products (*Scheme 2*). This lactone hydrazone decomposed during an attempted isolation, and we focused our investigation on the formation and rearrangement of *N*-acyl- and *N*-sulfonyldiaziridines.

Acetylation of **1A**/**1B** 95:5 with one equiv. Ac_2O in CH_2Cl_2 at 0–25° gave the *N*-acetylhydrazone **2B** in 70–80% yield. Similar results were obtained upon acetylation either with Ac_2O and pyridine (1 equiv. each) in CH_2Cl_2, or in a 1:1 mixture of Ac_2O and pyridine. With stoichiometric amounts of Ac_2O, the reaction was typically terminated within 12 h, while the use of excess Ac_2O reduced the reaction time to 1 h.

Acetylation of the D-*galacto* diaziridines **3A**/**3B** 95:5 [2] with excess Ac_2O in CH_2Cl_2 for 90 min at room temperature proceeded similarly, yielding 83% of the *N*-acetylhydrazone **4A** and 5% of the 1,3,4-oxadiazole **9**. Prolonging the reaction time to 3 h reduced the yield of **4A** to 65% and increased that of **9** to 8%. Acetylation of **3A**/**3B** 95:5 with 1.07 equiv. of Ac_2O provided 73% of **4A** and 6% of the 1,4-dihydro-1,2,4,5-tetrazine **10**.

Benzoylation of **1A**/**1B** 95:5 with 1.1 equiv. Bz_2O in pyridine for 20.5 h gave 61% of the *N*-benzoylhydrazone **2C** and 8% of the oxadiazole **7** (*Scheme 2*), whereas benzoylation with 1 equiv. BzCl in pyridine afforded only 14% of **2C** besides 10% of the 1,3,4-oxadiazole **7** and 27% of its benzoate **8**. Similarly, treatment of **1A**/**1B** 95:5 with 1.2 equiv. FmocCl and $Na_2CO_3 \cdot 10\ H_2O$ in dioxane [18] yielded 40% of the hydrazone **2D**.

Scheme 2



Sulfonylations were performed with 1.1 – 1.2 equiv. of the sulfonylating agent in pyridine at ambient temperature. Sulfonylation of **1A**/**1B** 95 : 5 with TsCl, naphthalene-2-sulfonyl chloride, and 2,4,6-triisopropylbenzenesulfonyl chloride gave 81% of **2E** [19], 83% of **2F**, and 64% of **2G**, respectively. Similarly, the D-*galacto* diaziridines **3A**/**3B** 95 : 5 and of the D-*manno* analogues **5A**/**5B** 55 : 45 [2] yielded **4B** and **6** in 63 and 55%, respectively.

No diacylated or disulfonylated glycosylidene-diaziridines or hydrazones were obtained, even when **1A**/**1B** 95 : 5 was treated with large excesses of Ac_2O, BzCl, or TsCl[1]). This evidences a facile rearrangement of monoacetylated and monosulfonylated 3-alkoxydiaziridines. The acylated hydrazones **2B**, **2C**, **2D**, and **4A** are the major products, although the rearrangement of the acylated pyranosylidene-diaziridines is less selective than that of the corresponding sulfonylated diaziridines. The minor 1,3,4-oxadiazoles **7**, **8**, and **9** are formed by a 1,5-electrocyclic ring closure of an intermediate

[1]) For the *N*,*N*′-diacylation of 3,3-dialkyldiaziridines, see [20 – 22].

N-acyl azomethine imine (corresponding to **VI** in *Scheme 1*)[2]). The 1,4-dihydro-1,2,4,5-tetrazine **10** is the product of (AcOH-catalyzed?) rearrangement of **3A**/**3B** to **4** (R = H), followed by dimerisation (*cf.* [24]).

At 25°, the acetylated lactone hydrazones **2B** and **4A** are mixtures of diastereoisomers resulting from rotation about the NH–C(O)Me bond[3]). A single diastereoisomer was observed in the NMR spectra of the benzoylated lactone hydrazones **2C** and **4B**, and of the Fmoc analogue **2D**. The (*Z*)/(*E*) ratio was 7:3 for **2B** in $CDCl_3$, 9:1 for **2B** in C_6D_6, 11:9 for **2B** in (D_6)DMSO, 4:1 for **4A** in $CDCl_3$, and 10:1 for **4A** in C_6D_6[4]). In $CDCl_3$, the NH of the major diastereoisomer resonates at higher field (**2B**: 8.70 *vs.* 8.80 ppm; **4A**: 8.76 *vs.* 9.05 ppm); C(1) resonates at higher field (**2B**: 143.7 *vs.* 146.8 ppm; **4A**: 144.4 *vs.* 146.5 ppm), Me also at higher field (**2B**: 19.9 *vs.* 21.7 ppm; **4A**: 19.9 *vs.* 21.2 ppm), but C=O at lower field (**2B**: 171.9 *vs.* 165.6 ppm; **4A**: 171.6 *vs.* 165.5 ppm; *Tables 2* and *3*, and *Exper. Part*). As expected, a single set of signals was observed for **2B** and **4A** at 75° in $CDCl_3$ and for **2B** at 100° in (D_6)DMSO (see *Exper. Part*).

The pyranose ring of the glucosylidene hydrazides **2B**–**2G** adopts a $^1S_5$ conformation as evidenced by $J(2,3) = 1.8–2.5$, $J(3,4) = 4.2–5.0$, and $J(4,5) = 9.6–10.2$ Hz (*Table 2* in *Exper. Part*). This same conformation had been observed for protected gluconolactone oximes and hydrazones [19][26][27]. The pyranose ring of the galactosylidene hydrazides **4A**–**4B** ($J(2,3) = 3.8–6.5$, $J(3,4) = 2.7–3.7$, and $J(4,5) = 2.2–2.6$ Hz) and of the mannosylidene hydrazide **6** ($J(2,3) = 3.1$, $J(3,4) = J(4,5) = 8.9$ Hz) is a flattened $^4C_1$. The (*Z*) configuration of the C=N bond of **2B**–**2G** is revealed by the chemical-shift value of C(1) resonating at 143.7–152.9 ppm (*Table 3* in *Exper. Part*)[5]).

The OH groups of **7**, **9**, and **10** in $CDCl_3$ resonate at 2.41–2.78 ppm (*Table 4* in *Exper. Part*). The values of *J*(4,OH) of the arabinitol **7** and the lyxitols **9** and **10** (5.6 *vs.* 7.6–8.4 Hz) reveal the presence of unequal intramolecular H-bonds. Typical chemical shifts were observed for C(2) and C(4) of the 1,3,4-oxadiazole moiety of **7**–**9** (163.7–165.1 ppm; *cf.* [31][32]), and for C(3) and C(6) of the 1,4-dihydro-1,2,4,5-tetrazine nucleus of **10** (149.7 ppm; *cf.* [2][33–35]). The NH signal of **10** is hidden by the signals of the Ph groups. The IR spectrum corroborates the structure of **10** (OH band at 3550 cm^{-1} and NH band at 3370 cm^{-1}).

The nucleophilic properties of the pseudoequatorial and pseudoaxial NH groups of *N*-unsubstituted glycosylidene diazirines should differ. To explore the difference, we acetylated and sulfonylated isotopomeric mixtures of the ^{15}N labelled D-*gluco* and D-*galacto* diaziridines **11** and **14** [2] (*Scheme 3*). Treatment of **11A**/**11B** 75:25 with excess

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[2]) For the formation of 2,3-dihydro-1,3,4-oxadiazoles from *N*-acyl-3,3-dialkyl-diaziridines, see [13d][20][21][23].

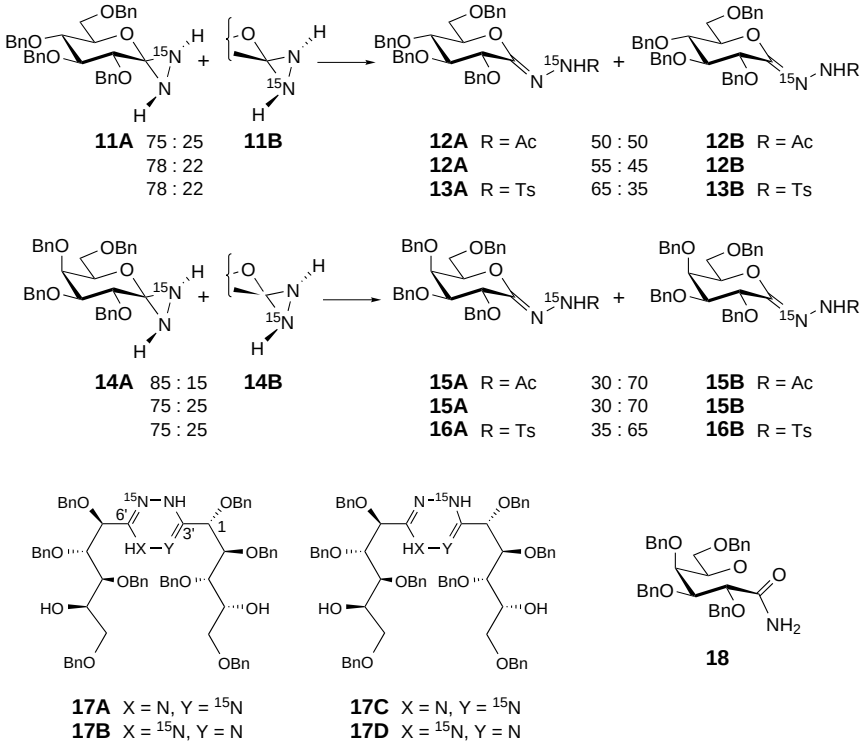
[3]) For (*E*)/(*Z*) diastereoisomers of carbohydrate-derived acetamides, see [25] and refs. cit. therein.

[4]) After one week at ambient temperature, (*Z*)-**2B**/(*E*)-**2B** 7:3 in $CDCl_3$ was completely transformed into (*Z*)-**2B**, suggesting that (*E*)-**2B** is preferred in the solid state.

[5]) The chemical shift for C(1) of glycosylidene imines is strongly influenced by the configuration of the double bond ($\delta(E) - \delta(Z) = 17$ ppm for lactone hydrazones [28] and 8–12 ppm for lactone oximes [26][29][30]), the substituents at C(2) and at N, the ring size (δ(furanosylidene) – δ(pyranosylidene) = 4–5.5 ppm for lactone hydrazones [19][28] and 3–5 ppm for lactone oximes [26]), and the conformation of the ring. C(1) of (*Z*)- and (*E*)-*N'*-(2,3,5-tri-*O*-benzyl-D-ribofuranosylidene)toluene-4-sulfonohydrazide resonates at 152.6 and 169.5 ppm, respectively [28].

Ac_2O gave a 1:1 mixture of the isotopomers **12A** and **12B** (77%), evidencing that the pseudoequatorial and the pseudoaxial NH groups were acetylated to the same extent. Repetition of the reaction with a 78:22 mixture of **11A** and **11B**, and equimolar amounts of Ac_2O afforded **12A**/**12B** 55:45, evidencing a slightly higher nucleophilicity of the pseudoequatorial NH (60%). An even higher nucleophilicity of this NH (75%) was observed upon tosylation that transformed **11A**/**11B** 78:22 into **13A**/**13B** 65:35.

Scheme 3



Acetylation of the *galacto*-configured **14A**/**14B** 85:15 with excess Ac_2O yielded 83% of a 3:7 mixture of the isotopomers **15A** and **15B**, evidencing a higher reactivity (*ca.* 80%) of the pseudoaxial NH group. Acetylation of **14A**/**14B** 75:25 with equimolar amounts of Ac_2O afforded 80% of **15A**/**15B** 3:7 and 5% of a 3:1 mixture of **17A** – **17D**, and **18**. Again, the pseudoaxial NH group proved more nucleophilic (90%). Tosylation of **14A**/**14B** 75:25 with an equimolar amount of TsCl gave **16A**/**16B** 35:65, evidencing that 80% of the pseudoaxial NH was sulfonylated.

Remarkably, the *gluco* diaziridines **11A**/**11B** are preferentially acetylated or tosylated at the pseudoequatorial NH group and the *galacto* diaziridines **14A**/**14B** at the pseudoaxial NH group. This difference shows that the diastereoselectivity is determined by the orientation of BnO–C(4), an equatorial orientation of BnO–C(4) enhancing the reactivity of the pseudoequatorial NH and an axial orientation of BnO–C(4) the reactivity of the pseudoaxial NH. The interpretation of this selectivity is

difficult. It is not clear if acylation and rearrangement are concerted, or not. If concerted, then breaking of the C(1)–N bond will be strongly influenced by the kinetic anomeric effect, *i.e.*, the donor properties of the ring O-atom. In the glucose derivatives, this may be enhanced by a conformational change towards, *e.g.*, a $^1S_3$, where O–C(4) and C(5)–O are no longer in an *app* orientation, as in the ground-state $^4C_1$ conformer, so that the ring O-atom should be a better donor and the originally pseudoequatorial NH will become pseudoaxial. In such a $^1S_3$ conformer, breaking of the C(1)–N bond to the pseudoaxial N, interacting with the acylating agent, will lead, after proton transfer, to the observed major acetylhydrazone **12A**. In the galactose derivatives, there is no *app* interaction between two C–O bonds, and the conformational change to a $^1S_3$ is disfavoured by the axial orientation of BnO–C(4)[6]). Again, the pseudoaxial C(1)–N bond is broken upon interaction with the acylating agent.

The ^{15}N-labelled tosylhydrazones **13A**/**13B** and **16A**/**16B** were each mixtures of a single pair of isotopomers, and the acetylhydrazones **12A**/**12B** and **15A**/**15B** mixtures of two diastereoisomeric pairs of isotopomers. ^{15}N in **12A**/**12B**, **13A**/**13B**, **15A**/**15B**, and **16A**/**16B** leads to a splitting of the NH signals, whereas the other ^{1}H-NMR signals are identical to those of the unlabelled **2B**, **2E**, **4A**, and **4B**, respectively. Labelling of the amino N-atom led to a large splitting of the NH signal ($^1J(^{15}N,H) = 92.9 – 94.4$ Hz for the acetylhydrazones **12A** and **15A** and $^1J(^{15}N,H) = 83.5 – 84.4$ Hz for the tosylhydrazones **13A** and **16A**; *Table 1*), whereas labelling of the imino N-atom led to a small splitting or to only line broadening ($^2J(^{15}N,H) \leq 1.7$ Hz). The same couplings were observed in the ^{15}N-NMR spectra, where the *d* of the amino-labelled isotopomer resonates at lower field (– 222 to – 224 ppm for the acetylhydrazones **12A** and **15A** and – 230 to – 232 ppm for the tosylhydrazones **13A** and **16A**) than the slightly broadened *s* of the imino-labelled isotopomer (– 119 to – 134.7 ppm). In the ^{13}C-NMR spectra, labelling of the imino N-atom leads to a splitting of the signals of C(1) ($^1J(^{15}N,C) = 5.3 – 6.2$ Hz) and C(2) ($^2J(^{15}N,C) = 9.3 – 11.3$ Hz), whereas labelling of the amino N-atom gives rise to line broadening or to a small splitting of the C(2) signals ($^2J(^{15}N,C) = 0$ and $^3J(^{15}N,C) \leq 1.6$ Hz). Only the well-resolved C=O signals of (*Z*)-**12A**, (*Z*)-**12B**, and (*Z*)-**15A**, and the Me signals of (*Z*)-**12A** and (*Z*)-**12B** allow us to assign the ^{15}N-couplings to the Ac group (*Table 1*). As expected, $^1J(^{15}N,C{=}O)$ (6.6 Hz) is larger than $^2J(^{15}N,C{=}O)$ (≤ 2.5 Hz). The antiperiplanar arrangement of the ^{15}N–N and the C(O)–Me bond of (*Z*)-**12B** is evidenced by the $^3J(^{15}N,Me)$ of (*Z*)-**12B** (7.2 Hz), which is distinctly larger than $^2J(^{15}N,Me)$ of (*Z*)-**12A** (1.4 Hz). This confirms the (*Z*)-configuration of the major diastereoisomers of the acetylhydrazones **12A**/**12B** and **15A**/**15B**.

The ^{15}N-NMR spectrum of a 3 : 1 mixture of the 1,4-dihydro-1,2,4,5-tetrazine **17** and the galactonamide **18** shows two *d*'s of equal intensity at – 252.63 ppm ($^1J(^{15}N,H) =$ 86.7 Hz) and at – 125.26 ppm ($^1J(^{15}N,H) = 5.7$ Hz). The coupling constants are typical for 1,4-dihydro-1,2,4,5-tetrazines [37]. Since **17** is formally a dimer of **14A**/**14B**, two ^{15}N-atoms must be present in **17**, either in a 1,3- (**17B** or **17C**) or in a 1,4-position (**17A** or **17D**). No long-range couplings between the ^{15}N-atoms was detected. The 1 : 1 ratio of the ^{15}N-signals indicates that the amino and imino N-atoms are labelled to the same

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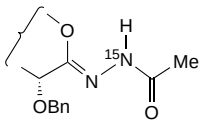
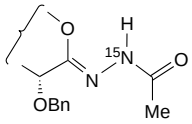
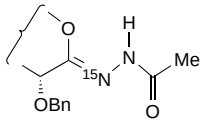
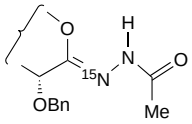
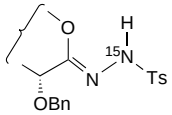
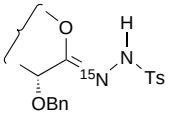
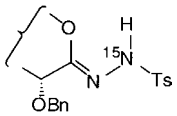
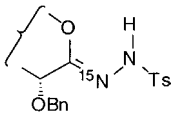
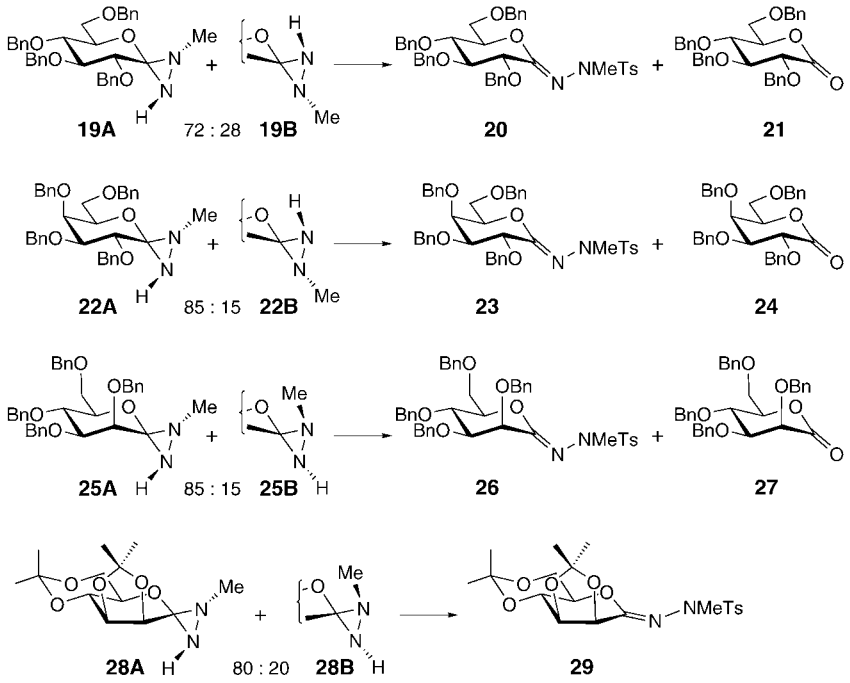
[6]) Ampac calculations (AM1, gas phase [36]) indicate that the $^1S_3$ conformer of the *galacto* diaziridine **3A** is more strongly disfavoured than the $^1S_3$ conformer of gluco analogue **1A** (8.6 *vs.* 7.75 kcal/mol).

Table 1. *Chemical Shifts* [ppm] *of H–N, C(1), C(2), C=O, Me, and* ^{15}N *of the Isotopomeric Acetylhydrazones* **12A/12B** *and* **15A/15B** *and Chemical Shifts* [ppm] *of H–N, C(1), C(2), and* ^{15}N *of the Isotopomeric Tosylhydrazones* **13A/13B** *and* **16A/16B** (in parentheses, $J(^{15}N,H)$, $J(^{15}N,C)$ [Hz], or the shape of the signal)

				
	(*Z*)-**12A**	(*E*)-**12A**	(*Z*)-**12B**	(*E*)-**12B**
$CDCl_3$				
Ratio	35	15	35	15
δ(NH)	8.74 (93.5)	8.78 (94.4)	8.74 (0)	8.78 (0)
C_6D_6				
Ratio	49.5	5.5	40.5	4.5
δ(NH)	8.98 (92.9)	8.59 (92.9)	8.98 (1.7)	8.59 (br. *s*)
δ(C(1))	143.96 (0)	not assigned	143.38 (6.2)	not assigned
δ(C(2))	75.20 (1.6)	74.2 (not assigned)	75.20 (10.8)	74.2 (not assigned)
δ(C=O)	170.96 (6.6)	164.46 (br. *s*)	171.03 (2.5)	164.46 (br. *s*)
δ(Me)	20.20 (1.4)	20.54 (br. *q*)	20.20 (7.2)	20.54 (br. *q*)
δ(^{15}N)	– 222.95 (92.4)	– 224 (*ca.* 92)	– 130.43 (br. *s*)	– 132 (br. *s*)
	(*Z*)-**15A**	(*E*)-**15A**	(*Z*)-**15B**	(*E*)-**15B**
$CDCl_3$				
Ratio	18	12	42	28
δ(^{15}N)	– 221.5 (97.3)	– 225 (*ca.* 97)	– 128.9 (br. *s*)	– 123.5 (br. *s*)
C_6D_6				
Ratio	27	3	64	6
δ(NH)	9.29 (93.2)	9.07 (93.2)	9.29 (1.7)	9.07 (br. *s*)
δ(C(1))	144.11 (0)	not assigned	144.09 (5.9)	not assigned
δ(C(2))	75.90 (0)	not assigned	75.90 (9.3)	not assigned
δ(C=O)	171.22 (6.6)	not assigned	171.22 (br. *s*)	not assigned
δ(Me)	20.39 (br. *q*)	not assigned	20.39 (br. *q*)	not assigned
δ(^{15}N)	– 222.08 (93.0)	not assigned	– 124.72 (br. *s*)	– 118.98 (br. s)
				
	13A	**13B**	**16A**	**16B**
	$CDCl_3$		C_6D_6	
Ratio	65	35	35	65
δ(NH)	7.96 (83.5)	7.96 (br. *s*)	8.76 (84.4)	8.76 (br. *s*)
δ(C(1))	147.55 (0)	147.54 (5.3)	147.81 (0)	147.81 (6.2)
δ(C(2))	74.02 (< 1.5)	74.02 (11.3)	75.48 (< 1.5)	75.48 (9.7)
δ(^{15}N)	– 232.05 (83.9)	– 134.74 (br. *s*)	– 230.00 (84.5)	– 125.02 (br. *s*)

extent, but is does not allow us to assign the ratio of the isotopomers **17A** – **17D**. There is no signal for **18** in the ^{15}N-NMR spectrum of **17A** – **17D**/**18** 3 : 1, evidencing that the amino group of **18** is introduced by substitution of the labelled hydrazino group. C(1) of **17A** – **17D** resonates as *d* at 75.00 ppm ($^2J(^{15}N,H) \approx 5$ Hz). Assuming that only

Scheme 4



$^1J(^{15}N,C)$ couplings are visible[7]), one expects six overlapping signals for C(3) and C(6) of the 1,4-dihydro-1,2,4,5-tetrazine nucleus of **17A**–**17D** (a *d* for each **17A** and **17D**, and a *dd* and an *s* for each **17B** and **17C**) at *ca.* 150 ppm. Only two sharp peaks in a ratio of 3:2 are visible at 149.67 and 149.64 ppm, which could be assigned either to two *s*'s or to an *s* at 149.67 ppm and a *d* at 149.655 ppm ($^1J(^{15}N,H) \approx 4.5$ Hz).

2. *Sulfonylation of* N-*Methylated Pyranosylidene-Diaziridines.* Sulfonylation of the *gluco N*-methyldiaziridines **19A**/**19B** 72:28 [2] with 1.1 equiv. of TsCl and purification of the products by flash chromatography gave 78% of a 3:1 mixture of the *N*-tosylated lactone hydrazone **20** and the lactone **21** [40][41] (*Scheme 4*). Similarly, the *galacto* diaziridines **22A**/**22B** 85:15 and the *manno* diaziridines **25A**/**25B** 85:15 and **28A**/**28B** 80:20 [2] were treated with TsCl. Workup with dry solvents afforded exclusively the *N*-tosylated lactone hydrazones **23**, **26**, and **29** in yields of 56, 66, and 60%, respectively. The *N*-methyl-*N*-tosylhydrazones **20**, **23**, and **26** are very moisture-sensitive. Upon standing in wet solution, they decomposed within a few hours to the lactones **21**, **24** [42], and **27** [43]. This indicates that **21** is the hydrolysis product of **20**, although it could also, in part, result from hydrolysis of the intermediate hydrazonium chloride that is formed upon sulfonylation of the NH group of **19A**/**19B**. Only the MeN group of **19A**/

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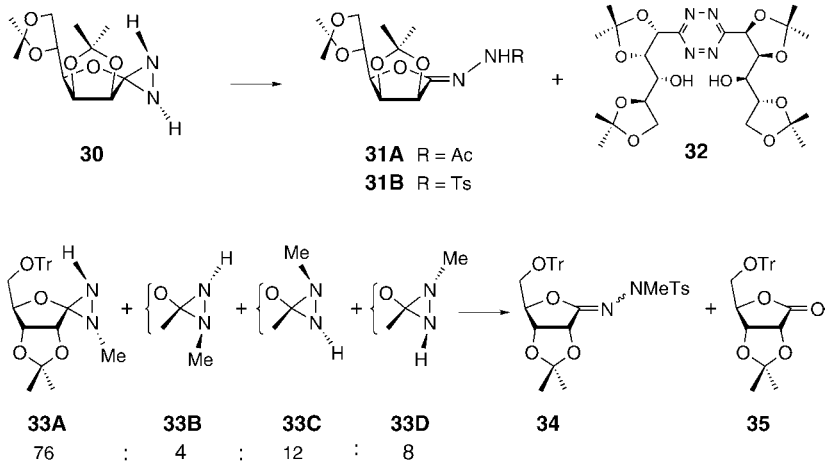
7) To the best of our knowledge, no ^{13}C-NMR data are available for ^{15}N labelled 1,4-dihydro-1,2,4,5-tetrazines. No $J(^{15}N,C)$ values of a ^{15}N-labelled pyrazole were reported [38]. $^1J(^{15}N,C)$ and $^2J(^{15}N,C)$ values of 5–19 Hz were observed in the ^{13}C-NMR spectra of ^{15}N-labelled hydrazones [39].

19B, **22A**/**22B**, **25A**/**25B**, and **28A**/**28B** is attacked by TsCl[8]), irrespective of the configuration at C(4) or at C(2).

The MeN groups of **20**, **23**, **26**, and **29** in C_6D_6 resonate at 2.50–3.04 ppm (*Table 2* in *Exper. Part*). The vicinal couplings $J(2,3)$, $J(3,4)$, and $J(4,5)$ of **20** and **26** (in C_6D_6) are similar to those of **2E** and **6** (in $CDCl_3$), respectively. They indicate a $^1S_5$ conformation of **20** and a flattened $^4C_1$ conformation of **26**. However, $J(2,3) = 1.2$, $J(3,4) = 7.1$, and $J(4,5) < 1$ Hz of **23** are distinctly different from those of **4B** (5.7, 3.6, and 2.6 Hz, resp.) and evidence a change from a flattened $^4C_1$ to a $^1S_5$ upon formal *N*-methylation. $J(2,3)$, $J(3,4)$, and $J(4,5)$ values of **29** are similar to those of the starting diaziridines **28A**/**28B** and reveal a $^OH_5$ conformation. Formal *N*-methylation of **2E** and **6** leads to a downfield shift of 8.1–8.3 ppm for C(1) of **20** and **26** (*Table 3* in *Exper. Part*). Formal *N*-methylation of **4B** leads to stronger downfield shift of 10.9 ppm for C(1) of **23**, probably due to the conformational change of the pyranose ring.

3. *Acetylation and Sulfonylation of Furanosylidene-Diaziridines.* Acetylation of the mannofuranosylidene-diaziridine **30** [2] with Ac_2O gave 63% of the *N*-acetylhydrazone **31A** and 8% of the 1,2,4,5-tetrazine **32** (*Scheme 5*). Sulfonylation of **30** led to a similar result, namely to 61% of the *N*-tosylhydrazone **31B** and 11% of **32**. The tetrazine **32** is probably formed by oxidation of the expected 1,4-dihydro-1,2,4,5-tetrazine. Tosylation of the *N*-methylated ribofuranosylidene-diaziridines **33A**/**33B**/**33C**/**33D** 76 : 4 : 12 : 8 [2] with TsCl and chromatographic separation of the products yielded 44% of a 2 : 1 (*E*)/(*Z*)-mixture of the *N*-methyl-*N*-tosylhydrazone **34** and 30% of the ribonolactone **35** [44][45].

Scheme 5



In $CDCl_3$, the (*Z*)-acetylhydrazone **31A** is a 85 : 15 (*E*)/(*Z*)-mixture of the diastereoisomers obtained by rotation about the NH–C(O)Me bond. The (*Z*)-configuration of the C=N bond of **31A** und **31B** is evidenced by the chemical-shift

[8]) For a 2-sulfonylation of a 1,3,3-trialkyldiaziridine, see [13e]. For examples of a 2-acylation of 1,3,3-trialkyldiaziridines, see [10][16][20].

value of C(1) (149.5 – 153.5 ppm; *Table 3* in *Exper. Part*). Relative to C(1) of **31**, C(1) of the *N*-methyl-*N*-tosylhydrazone (*Z*)-**34** resonates downfield (165.8 ppm) by *ca.* 10 ppm, as expected, and C(1) of the corresponding (*E*)-isomer downfield (180.7 ppm) by an additional 15 ppm.

The structure of the 1,2,4,5-tetrazine **32** is evidenced by the pink colour, the OH band at 3450 cm^{-1}, the absence of a NH band, and the typical chemical shift for C(3) and C(6) of the tetrazine nucleus at 168.5 ppm [33][35][46] (*Table 4* in *Exper. Part*).

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

Experimental Part

General Procedure for the Treatment of the Diaziridines with Acylating or Sulfonylating Agents. At 0°, a soln. of the diaziridine in dry CH_2Cl_2 or pyridine was treated with a soln. of the acylating or sulfonylating agent in pyridine and stirred for the indicated period at r.t., and evaporated. A soln. of the residue in AcOEt was washed with sat. $NaHCO_3$ soln. and brine (2×), dried ($MgSO_4$), and evaporated.

*(Z)-*N′*-(2,3,4,6-Tetra-*O*-benzyl-*D*-glucopyranosylidene)acetohydrazide* (**2B**). *a*) The reaction of **1A/1B** 95:5 (1.50 g, 2.71 mmol) in Ac_2O (5 ml; 3 h at 25°), workup (dilution with CH_2Cl_2 and washing with 5% $NaHCO_3$ soln.), and FC (hexane/AcOEt 2:1 → 1:1) gave **2B** (1.26 g, 79%).

b) The reaction of **1A/1B** 95:5 (410 mg, 0.74 mmol) in CH_2Cl_2/pyridine 5:1 (12 ml) with Ac_2O (75 µl, 0.79 mmol; 4 h) and FC (hexane/AcOEt 1:1) gave **2B** (320 mg, 73%). Colourless oil. R_f (hexane/AcOEt 1:1) 0.20. $[\alpha]_D^{25} = +33.1$ ($c = 0.49$, $CHCl_3$). IR ($CHCl_3$): 3380*w* (sh), 3350*w*, 3060*w*, 3020*w* (sh), 2995*m*, 2920*w* (br.), 2870*m*, 1690*m* (sh), 1665*s*, 1495*m*, 1450*m*, 1360*m*, 1320*m*, 1250*m*, 1190*w* (sh), 1070*s*, 1025*m*, 990*w* (sh), 910*w*, 850*w*, 815*w*. ^{1}H-NMR (600 MHz, $CDCl_3$, 298 K, 2 diastereoisomers in the ratio 7:3, assignment based on a ^{1}H,^{1}H-COSY spectrum): *Table 2*; additionally, 7.50 – 7.14 (*m*, 20 arom. H); 4.75 (*d*, $J = 12.0$, 0.7 H), 4.74 (*d*, $J = 12.0$, 0.3 H) (PhC*H*); 4.68 – 4.53 (*m*, 5 PhC*H*); 4.48 (*d*, $J = 11.8$, 0.7 H), 4.45 (*d*, $J = 11.8$, 0.7 H), 4.42 (*d*, $J = 11.9$, 0.3 H), 4.39 (*d*, $J = 12.0$, 0.3 H) (2 PhC*H*); 2.28 (*s*, 2.1 H), 2.05 (*s*, 0.9 H) (AcN). ^{1}H-NMR (400 MHz, C_6D_6, 298 K, 2 diastereoisomers in the ratio 9:1): *Table 2*, additionally for the major isomer, 7.28 – 7.04 (*m*, 20 arom. H); 4.57 (*d*, $J = 11.6$), 4.56 (*d*, $J = 12.0$) (2 PhC*H*); 4.43 (*d*, $J = 11.6$, PhC*H*); 4.33 (br. *d*, $J \approx 11.3$, 2 PhC*H*); 4.26 (*d*, $J = 12.5$), 4.23 (*d*, $J = 12.4$), 4.17 (*d*, $J = 11.6$) (3 PhC*H*); 2.23 (*s*, Ac); additionally for the minor isomer: 8.56 (*s*, NH); 4.77 (br. *d*, $J = 12.0$), 4.68 (br. *d*, $J = 11.2$), 4.08 (br. *d*, $J = 11.2$) (3 PhC*H*); 4.01 (br. *s*, H–C(2)); 3.58 (br. *s*, 2 H–C(6)). ^{1}H-NMR (300 MHz, C_6D_6, 348 K): 8.74 (br. *s*, NH); 7.28 – 7.05 (*m*, 20 arom. H); 4.595 (*d*, $J = 12.0$), 4.590 (*d*, $J = 11.7$) (2 PhC*H*); 4.51 – 4.47 (*m*, H–C(5)); 4.45 (*d*, $J = 11.8$, PhC*H*); 4.40 (*d*, $J = 11.8$, 2 PhC*H*); 4.31 (*s*, PhCH_2); 4.27 (*d*, $J = 11.8$, PhC*H*); 4.17 (br. *s*, H–C(2)); 3.97 (*dd*, $J = 2.5$, 4.9, H–C(3)); 3.86 (*dd*, $J = 4.9$, 9.9, H–C(4)); 3.56 (*d*, $J = 3.1$, 2 H–C(6)); 2.18 (br. *s*, AcN). ^{1}H-NMR (400 MHz, (D_6)DMSO, 298 K, 2 diastereoisomers in the ratio 55:45): 10.13 (*s*, 0.45 H), 9.63 (*s*, 0.55 H) (NH); 7.40 – 7.20 (*m*, 18 arom. H); 7.20 – 7.13 (*m*, 2 arom. H); 4.72 – 4.37 (*m*, 8 PhC*H*, H–C(5)); 4.27 (*d*, $J = 2.3$, 0.55 H), 4.19 (*d*, $J = 3.0$, 0.45 H) (H–C(2)); 3.95 (*t*, $J \approx 3.5$, 0.55 H), 3.93 (*t*, $J \approx 3.5$, 0.45 H) (H–C(3)); 3.83 (br. *d*, $J = 11.1$, H–C(6)); 3.78 – 3.67 (*m*, H–C(4), H′–C(6)); 2.10 (*s*, 1.35 H), 1.92 (*s*, 1.65 H) (AcN). ^{1}H-NMR (400 MHz, (D_6)DMSO, 370 K): 9.35 – 9.05 (br. *s*, NH); 7.38 – 7.20 (*m*, 20 arom. H); 4.71 (*d*, $J = 11.1$), 4.62 (*d*, $J = 11.8$), 4.61 (*d*, $J = 10.7$) (3 PhC*H*); 4.60 – 4.50 (*m*, 5 PhC*H*); 4.50 (*ddd*, $J = 2.4$, 4.5, 10.0, H–C(5)); 4.22 (*d*, $J = 3.0$, H–C(2)); 3.97 (*t*, $J = 3.3$, H–C(3)); 3.86 (*dd*, $J = 2.4$, 11.2, H–C(6)); 3.78 (*dd*, $J = 4.5$, 11.2, H′–C(6)); 3.76 (*dd*, $J = 3.5$, 9.8, H–C(4)); 2.03 (br. *s*, AcN). ^{13}C-NMR (50.3 MHz, $CDCl_3$, 298 K, 2 diastereoisomers in the ratio 7:3): *Table 3*, additionally, for the major isomer: 171.86 (*s*, C=O); 137.46, 137.37, 137.02, 136.83 (4*s*); 128.57 – 127.38 (several *d*); 73.28, 72.91, 71.70, 70.73 (4*t*, 4 PhCH_2); 19.98 (*q*, Me); additionally, for the minor isomer: 165.64 (*s*, C=O); 137.28 (*s*); 73.08, 72.38, 71.38, 70.79 (4*t*, 4 PhCH_2); 21.67 (*q*, Me). CI-MS (NH_3): 597 (8), 596 (42), 595 (100, $[M+1]^+$). Anal. calc. for $C_{36}H_{38}N_2O_6$ (594.70): C 72.71, H 6.44, N 4.71; found: C 72.65, H 6.64, N 4.84.

Benzoylation of **1A/1B** 95:5. *a*) A soln. of **1A/1B** 95:5 (2.00 g, 3.62 mmol) in pyridine (4.0 ml) was treated at r.t. with a soln. of benzoic anhydride (0.90 g, 3.98 mmol) in pyridine (1.7 ml), stirred for 6 h, diluted with CH_2Cl_2, washed with 1M aq. $NaHCO_3$ soln., dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 3:1) gave **7** (191 mg, 8%) and **2C** (1.45 g, 61%).

Table 2. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Glucosylidene Hydrazides* **2**, **12**, **13**, *and* **20**, *the Galactosylidene Hydrazides* **4**, **15**, **16**, *and* **23**, *the Galactonamide* **18**, *the Mannosylidene Hydrazides* **6**, **26**, **29**, *and* **31**, *and the Ribosylidene Hydrazides* **34** (measured at 298 K)

	2B[a][b])		**2B**[b][c])	**2C**	**2D**	**2E** [19]	**2F**	**2G**	**12A/12B**[d])	**13A/13B**
Solvent	$CDCl_3$		C_6D_6	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	C_6D_6	$CDCl_3$
Ratio	7 : 3		9 : 1						55 : 45	65 : 55
H–C(2)	4.11	4.43	4.16	4.47	4.34	4.08	4.04	3.94	4.16	4.08
H–C(3)	3.94	4.00	3.96	4.00	3.96	3.83	3.79	3.81	3.97	3.84
H–C(4)	3.81	3.77	3.91	3.84–3.77	3.78	3.61	3.56	3.69	3.91	3.61
H–C(5)	4.57	4.71	4.49	4.70–4.60	4.59–4.52	4.46	4.44	4.48	4.50	4.46
H–C(6)	3.77	3.82	3.50	3.80	3.80	3.72	3.71	3.72	3.51	3.73
H′–C(6)	3.72	3.73	3.45	3.71	3.72	3.66	3.64	3.67	3.48	3.66
HN[e]) or MeN	8.70	8.80	8.94	9.39	8.27	7.94	8.05	7.98	8.98 (92.9)/ 8.98 (1.7)	7.96 (83.5)/ 7.96 (<1.5)
J(2,3)	2.5	1.8	2.0	1.8	2.0	2.0	2.1	1.9	2.0	1.8
J(3,4)	4.7	4.3	5.0	4.5	4.2	4.7	4.7	4.4	5.0	4.7
J(4,5)	10.1	10.1	10.1	[f])	9.6	10.1	10.0	10.2	10.1	10.2
J(5,6)	2.3	2.2	3.5	2.2	1.9	2.0	2.0	2.1	3.5	1.9
J(5,6′)	4.2	4.4	2.1	4.6	4.5	4.4	4.5	4.3	2.0	4.5
J(6,6′)	11.1	11.0	11.1	11.0	11.0	11.1	11.1	11.0	11.1	11.1

	20	**4A**[b])	**4A**[a][b][c])	**4B**	**15A/15B**[d])	**16A/16B**	**18**[g])	**23**
Solvent	C_6D_6	$CDCl_3$	C_6D_6	C_6D_6	C_6D_6	C_6D_6	$CDCl_3$	C_6D_6
Ratio		8 : 2	10 : 1		3 : 7	35 : 65		
H–C(2)	4.26	4.38	4.41	4.41	4.33	4.405	4.33	4.55	4.18–4.17
H–C(3)	3.94	3.85	3.97	3.64	3.63–3.56	3.66	3.60	3.96	3.91
H–C(4)	3.91	4.13	4.30–4.26	3.96	3.87	3.97	3.89	3.90	4.35
H–C(5)	4.64	4.30	4.70–4.42	4.08	4.11–4.08	4.09	4.12	4.13	4.07
H–C(6)	3.54	3.68	3.91	3.64	3.63–3.56	3.64	3.64	3.57	3.42
H′–C(6)	3.54	3.65	3.78	3.64	3.63–3.56	3.62	3.60	3.49	3.34
HN[e]) or MeN	3.04	8.76	9.05	9.42	8.68	9.29 (93.2)/ 9.29 (1.7)	8.76 (84.4)/ 8.76 (<1.5)	5.39 (2 H)	2.50
J(2,3)	1.9	6.5	3.8	6.2	5.7	6.5	5.7	2.7	1.2
J(3,4)	4.8	2.7	3.0	3.0	3.6	2.8	3.0	8.2	7.1
J(4,5)	9.8	2.2	[f])	2.6	2.6	2.8	3.2	1.0	<1.0
J(5,6)	2.6	6.3	8.9	6.4	[f])	6.0	7.4	6.6	6.3
J(5,6′)	2.6	6.3	3.5	6.4	[f])	6.7	5.4	6.5	7.0
J(6,6′)	[f])	9.7	10.9	[f])	[f])	9.7	10.2	9.4	9.3

	6 [19]	**26**[a])	**29**	**31A**[a])		**31B**	(*E*)-**34**/(*Z*)-**34**	
Solvent	$CDCl_3$	C_6D_6	C_6D_6	$CDCl_3$		$CDCl_3$	C_6D_6	
Ratio				85 : 15			2 : 1	
H–C(2)	4.18	4.30	4.22	5.12	5.19	5.06	6.06	5.31
H–C(3)	3.67	3.55–3.52	4.11	4.91	4.89	4.79	4.33	4.13
H–C(4)	4.18	4.27	3.92	4.33	4.39	4.28	4.33	4.33
H–C(5)	3.97–3.93	3.87	3.26	4.46	4.50–4.45	4.42	3.44	3.37
H–C(6)	3.72	3.55–3.52	3.74	4.15	4.13–4.05	4.11		
H′–C(6)	3.68	3.55–3.52	3.62	4.05	4.13–4.05	3.98	2.75[h])	2.57[h])
HN	8.17	–	–	8.34	8.31	7.42	–	–
MeN	–	3.03	2.82	–	–	–	3.00	3.01
J(2,3)	3.1	2.1	8.1	5.8	5.7	5.6	6.2	5.8
J(3,4)	8.9	10.2	6.6	3.8	3.9	3.6	0	0
J(4,5)	8.9	8.4	10.3	7.5	6.8	7.5	2.6	2.6
J(5,6)	4.6	4.0	5.8	6.2	[f])	6.1		
J(5,6′)	3.0	4.0	10.0	4.1	[f])	4.1	2.0[i])	1.8[i])
J(6,6′)	11.2	[f])	11.0	9.0	[f])	9.0	11.1[j])	10.7[j])

[a]) Assignment based on the ^{1}H,^{1}H-COSY spectrum. [b]) Two diastereoisomers at 298 K; for data of a single diastereoisomer of **2B** and **4A** at 348 K in C_6D_6, see *Exper. Part.* [c]) Data for the major diastereoisomer at 298 K. For some values of the minor diastereoisomer, see *Exper. Part.* [d]) Mixture of two isotopomeric pairs of diastereoisomers (**12**: 9 : 1, **15**: 10 : 1); data for the major isotopomeric pair given. For values of the minor isotopomeric pair, see *Exper. Part.* [e]) In parentheses, $^1J(^{15}N,H)$ or $^2J(^{15}N,H)$. [f]) Not assigned. [g]) δ(HO–C(5)) = 2.48 ppm, J(5,OH) = 8.0 Hz. [h]) Values of δ(H′–C(5)). [i]) Values of J(4,5′). [j]) Values of J(5,5′).

Table 3. *Selected ^{13}C-NMR Chemical Shifts* [ppm] *of the Glucosylidene Hydrazides* **2**, **12**, **13**, *and* **20**, *the Galactosylidene Hydrazides* **4**, **15**, **16**, *and* **23**, *the Galactonamide* **18**, *the Mannosylidene Hydrazides* **6**, **26**, **29**, *and* **31**, *and the Ribosylidene Hydrazides* **34** (measured at 298 K)

	2B		**2C**	**2D**	**2E** [19]	**2F**	**2G**	**12A/12B**[a])	**13A/13B**
Solvent	$CDCl_3$		$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	C_6D_6	$CDCl_3$
Ratio	7 :	3						55 : 45	65 : 35
C(1)[b])	143.73	146.84	148.04	145.23	147.58	147.81	152.87	143.96 (0)/ 143.38 (6.2)	147.55 (0)/ 147.54 (5.3)
C(2)[b])	74.16	74.29	74.15	74.80	74.00	73.90	73.25	75.20 (1.6)/ 75.20 (10.8)	74.02 (<1.5)/ 74.02 (11.3)
C(3)	81.28	80.48	80.57	81.92	81.28	81.06	80.83	82.50	81.30
C(4)	77.00	77.17	77.00	77.84	77.00	77.00	77.03	77.78	77.05
C(5)	76.10	75.78	75.85	75.35	76.30	76.31	75.96	76.63	76.31
C(6)	67.98	68.18	67.94	67.87	68.00	67.92	67.64	67.74	68.04
MeN	–	–	–	–	–	–	–	–	–

	20	**4A**		**4B**	**15A/15B**[a])	**16A/16B**[c])	**18**	**23**
Solvent	C_6D_6	$CDCl_3$		C_6D_6	C_6D_6	C_6D_6	$CDCl_3$	C_6D_6
Ratio		8 :	2	3 : 7	35 : 65			
C(1)[b])	155.67	144.38	146.50	148.32	144.11 (0)/ 144.09 (5.9)	147.81 (0)/ 147.81 (6.2)	[d])	157.36
C(2)[b])	74.38	74.98	74.74	75.55	75.90 (0)/ 75.90 (9.3)	75.48 (<1.5)/ 75.48 (9.7)	75.13	73.22
C(3)	81.33	79.30	78.11	79.29	79.78	78.96	81.16	80.47
C(4)	77.09	72.26	72.07	72.94	73.20	72.95	77.22	77.79
C(5)	76.40	77.60	76.36	78.44	78.21	78.60	69.04	69.1
C(6)	67.41	67.78	68.83	68.64	68.41	68.73	71.28	70.9
MeN	37.74	–	–	–	–	–	–	38.26

	6 [19]	**26**[c])	**29**	**31A**[a])		**31B**[c])	(*E*)-**34**/(*Z*)-**34**	
Solvent	$CDCl_3$	C_6D_6	C_6D_6	$CDCl_3$		$CDCl_3$	C_6D_6	
Ratio				85 :	15		2 :	1
C(1)	147.02	155.31	158.20	149.47	152.59	153.49	180.72	165.78
C(2)	71.61	73.15	71.83[e])	77.00[e])	76.29[e])	77.26	77.73	79.27[e])
C(3)	79.20	79.57	77.53	77.08[e])	77.56[e])	77.37	79.35	79.85[e])
C(4)	72.96	73.95	72.59[e])	81.84	82.18	83.30	86.50	86.64
C(5)	80.56	80.78	68.05	72.25	72.40	72.60	63.94	63.60
C(6)	68.46	69.10	61.62	65.91	65.66	66.17	–	–
MeN	–	38.63	38.75	–	–	–	41.08	38.73

[a]) Mixture of two isotopomeric pairs of diastereoisomers (**12**: 9 : 1, **15**: 10 : 1); data for the major isotopomeric pair given. For values of the minor isotopomeric pair, see *Exper. Part.* [b]) In parentheses, $J(^{15}N,C)$. [c]) Assignment based on the $^1H,^{13}C$-COSY spectrum. [d]) Not assigned. [e]) Assignments may be interchanged.

b) A soln. of **1A/1B** 95 : 5 (500 mg, 0.91 mmol) in pyridine (0.5 ml) was treated at 0° with benzoyl chloride (0.156 ml, 0.9 mmol), stirred at r.t. for 5.5 h, diluted with CH_2Cl_2, washed with H_2O (3×), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4 : 1 → 3 : 1) gave **8** (186 mg, 27%), **7** (59 mg, 10%), and **2C** (83 mg, 14%).

*(Z)-*N′*-(2,3,4,6-Tetra-*O*-benzyl-*D*-glucopyranosylidene)benzohydrazide* (**2C**). R_f (hexane/AcOEt 3 : 1) 0.21. IR ($CHCl_3$): 3400*w*, 3350*w* (sh), 3110*w*, 3090*w*, 3070*m*, 3030*m* (sh), 3000*s* 2910*m*, 2870*m*, 1685*s*, 1655*s*, 1605*m*, 1585*m*, 1510*s*, 1500*s*, 1490*s*, 1455*s*, 1360*s*, 1340*m* (sh), 1290*m* (sh), 1255*s*, 1140*s*, 1090*s* (br.), 1075*s*, 1030*s*, 1000*m*, 900*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): *Table 2*; additionally, 7.78 (*d*, *J* = 7.0, 2 arom. H); 7.57–7.13 (*m*, 23 arom. H); 4.78–4.53 (*m*, 4 PhC*H*); 4.54 (*s*, PhCH_2); 4.42 (*d*, *J* = 11.4), 4.38 (*d*, *J* = 11.6) (2 PhC*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 3*; additionally, 163.18 (*s*, C=O); 137.32, 137.13, 136.88, 136.63, 133.35 (5*s*); 131.42 (*d*); 128.63–126.70 (several *d*); 73.00, 72.40, 71.31, 70.72 (4*t*, 4 PhCH_2).

*(1R)-1,2,3,5-Tetra-*O*-benzyl-1-*C*-(5-phenyl-1,3,4-oxadiazol-2-yl)-*D*-arabinitol* (**7**). R_f (hexane/AcOEt 3 : 1) 0.32. IR ($CHCl_3$): 3570*w*, 3110*w*, 3090*w*, 3070*w*, 3040*w* (sh), 3005*m*, 2920*w* (br.), 2875*m*, 1960*w* (br.), 1885*w* (br.), 1815*w*, 1610*w*, 1590*w*, 1565*w* (sh), 1555*m* (sh), 1545*w* (sh), 1495*m*, 1455*m*, 1395*w*, 1365*m*, 1220*s* (sh) 1200*s*,

1090*s*, 1070*s*, 1030*s*, 960*w*, 930*m*, 910*m* (sh). ^{1}H-NMR (200 MHz, $CDCl_3$): *Table 4*; additionally, 7.95 (*m*, 2 arom. H); 7.55–7.06 (*m*, 3 arom. H); 4.86 (*d*, $J = 11.2$), 4.75 (*d*, $J = 11.2$), 4.68 (*d*, $J = 11.5$), 4.61 (*d*, $J = 11.6$), 4.51 (*d*, $J = 11.5$), 4.45 (*d*, $J = 11.3$), 4.43 (*d*, $J = 11.7$), 4.29 (*d*, $J = 11.3$) (8 PhC*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 4*; additionally, 137.67, 137.59, 137.44, 136.63 (4*s*); 131.58 (*d*); 128.84–126.84 (several *d*); 123.45 (*s*); 75.21, 73.42, 73.17, 72.81 (4*t*, 4 PhCH_2).

Table 4. *Selected ^{1}H- and ^{13}C-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the 1-C-Aryl-pentitols* **7**–**10**, **17**, *and* **32**

	7	**8**	**9**	**10**[a])	**17A**–**17D**	**32**[a])
Solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
H–C(1)	5.22	5.15	5.00	4.43	4.43	5.90
H–C(2)	4.32	4.30	4.19	3.92	3.91	4.92
H–C(3)	3.63	4.04	3.81	3.88	3.87	3.29
H–C(4)	4.03	5.56	4.11	4.14	4.13	4.01
H–C(5)	3.62	3.97	3.56	3.55	3.54	3.95
H′–C(5)	3.55	3.82	3.49	3.45	3.44	3.70
HO–C(4)	2.78	–	2.61	2.41	2.41	2.32
J(1,2)	7.3	7.2	5.0	1.8	2.0	7.4
J(2,3)	3.7	4.2	7.6	8.4	8.3	0.9
J(3,4)	7.3	5.7	1.7	0.8	1.1	7.7
J(4,5)	3.5	3.4	6.3	6.8	6.7	6.2
J(4,5′)	4.7	5.1	6.4	6.4	6.4	5.1
J(4,OH)	5.6	–	7.6	8.2	8.2	8.8
J(5,5′)	9.7	11.1	9.4	9.3	9.4	8.5
C(1)	73.74	73.73	73.67	74.91	75.00 (*ca.* 5)	76.82[b])
C(2)	79.86[b])	79.60[b])	79.97	80.54	80.62	77.58[b])
C(3)	77.37[b])	77.79[b])	77.11	76.90	77.01	68.32
C(4)	70.27	72.98	69.23	68.81	68.88	75.66[b])
C(5)	70.67	67.91	71.01	71.26	71.33	66.57
C(2) of Ar	165.05	165.13	164.47[b])	–	–	–
C(5) of Ar	163.94	163.74	164.27[b])	–	–	–
C(3)/C(6) of Ar	–	–	–	149.68	[c])	168.51

[a]) Assignment of ^{1}H-NMR data based on a ^{1}H,^{1}H-COSY spectrum. [b]) Assignments may be interchanged. [c]) Two peaks at 149.67 and 149.64 ppm in the ratio of 3 : 2.

*(1*R*)-4-*O*-Benzoyl-1,2,3,5-tetra-*O*-benzyl-1-*C*-(5-phenyl-1,3,4-oxadiazol-2-yl)-*D*-arabinitol* (**8**). R_f (hexane/AcOEt 3 : 1) 0.46. IR ($CHCl_3$): 3090*w*, 3070*w*, 3030*w*, 3010*w*, 2960*w*, 2930*w*, 2880*w*, 1720*s*, 1610*w*, 1605*w*, 1590*w*, 1555*m*, 1500*w*, 1455*s*, 1395*w*, 1375*m*, 1365*m*, 1320*m*, 1270*s*, 1250*s*, 1180*w*, 1115*s*, 1100*s*, 1070*s*, 1030*s*, 915*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): *Table 4*; additionally, 8.03–7.93 (*m*, 4 arom. H); 7.61–7.10 (*m*, 26 arom. H); 4.79 (*d*, $J = 10.9$), 4.70 (*d*, $J = 10.7$), 4.64 (*d*, $J = 10.8$), 4.63 (*d*, $J \approx 10.5$, 2 H), 4.55 (*d*, $J = 11.0$), 4.52 (*d*, $J = 12.2$), 4.42 (*d*, $J = 12.1$) (8 PhC*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 4*; additionally, 165.39 (*s*, C=O); 137.71, 137.61, 137.53, 136.54 (4*s*); 132.96 (*d*); 131.66 (*d*); 129.88 (*s*); 129.64–126.93 (several *d*); 123.52 (*s*); 75.60, 74.42, 73.06, 72.98 (4*t*, 4 PhCH_2).

*(Z)-*N*-[(2,3,4,6-Tetra-*O*-benzyl-*D*-glucopyranosylidene)amino]* O*-[(9*H*-Fluoren-9-yl)methyl]carbamate* (**2D**). According to [18], a soln. of **1A**/**1B** 95 : 5 (1.0 g, 1.8 mmol) in dioxane (10 ml) was treated with $Na_2CO_3 \cdot 10\ H_2O$ (1.0 g, 9 mmol) and a soln. of FmocCl (570 mg, 2.2 mmol) in dioxane (10 ml) and stirred for 12 h at r.t. After filtration, the filtrate was diluted with Et_2O, washed with H_2O (2×) and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 4 : 1) and crystallisation from Et_2O/hexane gave **2D** (564 mg, 40%). Colourless crystals. R_f (hexane/AcOEt 1 : 1) 0.67. M.p. 97–100°. $[\alpha]_D^{25} = +20.6$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3380*w* (br.), 3060*w*, 3025*w*, 2950*w*, 2860*w,* 1740*s*, 1655*m*, 1510*m,* 1495*m* (sh), 1450*m*, 1405*w*, 1360*m*, 1350*m*, 1320*w*, 1290*m*, 1250*m*, 1210*s*, 1145*m*, 1125*m*, 1090*s*, 1070*s*, 1040*m*, 1030*m*, 1010*m*, 990*m*, 905*w*, 850*w*. ^{1}H-NMR

(400 MHz, $CDCl_3$): *Table 2*; additionally, 7.78 (*d*, *J* = 7.3, 2 arom. H); 7.66 (br. *s*, 2 arom. H); 7.42–7.27 (*m*, 22 arom. H); 7.18–7.14 (*m*, 2 arom. H); 4.74 (br. *d*, *J* ≈ 10.3, PhC*H*); 4.63–4.60 (*m*, CO_2CH_2); 4.62 (*d*, *J* = 11.7, PhC*H*); 4.59–4.51 (*m*, 4 PhC*H*); 4.44 (*d*, *J* = 11.4), 4.39 (*d*, *J* = 11.8) (2 PhC*H*); 4.37–4.34 (*m*, H–C(9′)). ^{13}C-NMR (50.3 MHz, C_6D_6): *Table 3*; additionally, 153.69 (br. *s*, C=O); 144.43 (2*s*); 141.71 (2*s*); 138.41 (2*s*); 137.77 (2*s*); 128.66–127.32 (several *d*); 125.63 (br. *d*, 2 C); 120.14 (2*d*); 73.11, 72.96, 71.51, 70.84 (4*t*, 4 Ph*C*H_2); 67.51 (br. *t*, $CO_2C$$H_2$); 47.55 (*d*, C(9′)). Anal. calc. for $C_{49}H_{46}N_2O_7$ (774.91): C 75.95, H 5.98, N 3.62; found: C 76.17, H 5.90, N 3.58.

N′*-(2,3,4,6-Tetra*-O*-benzyl*-D*-glucopyranosylidene)-4-toluenesulfonohydrazide* (**2E**). The reaction of **1A**/**1B** 95:5 (515 mg, 0.93 mmol) in CH_2Cl_2 (20 ml) with TsCl (214 mg, 1.12 mmol) in pyridine (5 ml; 1.5 h), FC (CH_2Cl_2), and crystallisation from MeOH gave **2E** [19] (532 mg, 81%).

N′*-(2,3,4,6-Tetra*-O*-benzyl*-D*-glucopyranosylidene)naphthalene-2-sulfonohydrazide* (**2F**). The reaction of **1A**/**1B** 95:5 (201 mg, 0.36 mmol) and naphthalene-2-sulfonyl chloride (107 mg, 0.47 mmol) in pyridine (2.5 ml; 1.5 h), FC (CH_2Cl_2), and crystallisation from AcOEt/hexane gave **2F** (225 mg, 83%). Fine needles. R_f (hexane/AcOEt 1:1) 0.65. M.p. 154°. $[\alpha]_D^{25} = -9.5$ (*c* = 0.81, $CHCl_3$). IR (KBr): 3220*m*, 3060*w,* 3025*w*, 2930*m*, 2860*m,* 1730*m*, 1660*m*, 1585*w,* 1555*w*, 1540*w*, 1495*w*, 1455*m*, 1390*m*, 1360*m*, 1340*s*, 1265*w*, 1205*w*, 1170*s*, 1090*m* (br.), 1070*s*, 1030*s*, 905*w*, 865*w*, 850*w*, 820*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 2*; additionally, 7.93–7.82 (*m*, 4 arom. H); 7.63–7.53 (*m*, 2 arom. H); 7.40–7.19 (*m*, 16 arom. H); 7.13–7.07 (*m*, 3 arom. H); 6.97–6.94 (*m*, 2 arom. H); 4.55 (*d*, *J* = 12.0), 4.51 (*d*, *J* = 12.0), 4.46 (*d*, *J* = 11.4), 4.40 (*d*, *J* = 11.8), 4.32 (*d*, *J* = 11.4), 4.22 (*d*, *J* = 11.5), 4.19 (*d*, *J* = 11.3), 4.11 (*d*, *J* = 11.9) (8 PhC*H*). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 3*; additionally, 137.52, 137.40, 136.90, 136.62, 135.12, 134.92, 132.01 (7*s*); 129.54–127.39 (several *d*); 122.83 (*d*); 73.32, 72.90, 71.40, 70.21 (4*t*, 4 Ph*C*H_2). CI-MS (C_4H_{10}): 746 (14), 745 (22), 744 (33), 743 (100, $[M+1]^+$), 553 (10).

N′*-(2,3,4,6-Tetra*-O*-benzyl*-D*-glucopyranosylidene)-2,4,6-triisopropylbenzenesulfonohydrazide* (**2G**). The reaction of **1A**/**1B** 95:5 (225 mg, 0.41 mmol) in pyridine (2.5 ml; 1.5 h) with 2,4,6-triisopropylbenzenesulfonyl chloride (152 mg, 0.47 mmol) in pyridine (2.5 ml; 3.5 h) and FC (CH_2Cl_2) gave **2G** (211 mg, 64%). Yellow oil. R_f (hexane/AcOEt 1:1) 0.74. $[\alpha]_D^{25} = -0.4$ (*c* = 1.25, $CHCl_3$). IR ($CHCl_3$): 3290*w* (br.), 3060*m* (sh), 3010*m*, 2960*s*, 2930*s*, 2870*m*, 1730*m*, 1660*m*, 1600*m*, 1560*w*, 1495*m*, 1455*s*, 1425*m*, 1385*m* (sh), 1365*s*, 1330*m*, 1285*m*, 1255*m*, 1165*s*, 1155*m* (sh), 1105*s* (sh), 1070*s*, 1030*s*, 940*w*, 885*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 2*; additionally, 7.42–7.26 (*m*, 14 arom. H); 7.14–7.09 (*m*, 8 arom. H); 4.54 (*s*, PhCH_2); 4.53 (*d*, *J* = 11.9), 4.41 (*d*, *J* = 11.5), 4.38 (*d*, *J* = 11.8) (3 PhC*H*); 4.28–4.21 (*m*, irrad. at 1.26 or 1.22 → change, 2 Me_2C*H*); 4.27 (*d*, *J* = 11.9), 4.22 (*d*, *J* = 12.1), 4.07 (*d*, *J* = 11.9) (3 PhC*H*); 2.82 (*sept.*, *J* = 6.9, irrad. at 1.16 → *s*, Me_2C*H*); 1.26 (*d*, *J* = 6.7), 1.22 (*d*, *J* = 6.8), 1.16 (*d*, *J* = 6.9) (3 *Me*$_2$CH). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 3*; additionally, 150.99 (2*s*); 146.14, 137.61, 137.40, 136.85, 136.52, 131.23 (6*s*); 128.37–127.73 (several *d*); 123.50 (2*d*); 72.99, 72.72, 71.18, 69.87 (4*t*, 4 Ph*C*H_2); 33.93 (*d*, Me_2*C*H); 29.71 (*d*, 2 Me_2*C*H); 24.75 (*q*, *Me*$_2$CH); 24.72 (*q*, *Me*$_2$CH); 23.34, 23.31 (2*q*, *Me*$_2$CH). CI-MS (C_4H_{10}): 821 (24), 820 (59), 819 (100, $[M+1]^+$), 605 (16), 604 (36), 554 (15), 91 (13).

Treatment of **3A**/**3B** *95:5 with* Ac_2O. *a*) The reaction of **3A**/**3B** 95:5 (500 mg, 0.9 mmol) in CH_2Cl_2 (15 ml) with Ac_2O (2 ml at start and 1 ml after 2 h; 3 h at r.t.), workup (concentrated to 5 ml, dilution with CH_2Cl_2, washing with 1M aq. $NaHCO_3$ soln., drying ($MgSO_4$), and evaporation), and FC (hexane/AcOEt 7:3) gave **9** (43 mg, 8%) and **4A** (358.5 mg, 65%).

b) The reaction of **3A**/**3B** 95:5 (420 mg, 0.76 mmol) in CH_2Cl_2 (10 ml) with Ac_2O (80 µl, 0.81 mmol; 1.5 h) and FC (hexane/AcOEt 2:1) gave **10** (25 mg, 6%) and **4A** (331 mg, 73%).

*(*Z*)*-N′*-(2,3,4,6-Tetra*-O*-benzyl*-D*-galactopyranosylidene)acetohydrazide* (**4A**). Colourless oil. R_f (hexane/AcOEt 1:1) 0.16. $[\alpha]_D^{25} = -13.9$ (*c* = 0.55, $CHCl_3$). IR ($CHCl_3$): 3360*w*, 3060*w*, 3020*w* (sh), 2990*m*, 2920*w*, 2860*m*, 1665*s*, 1495*m*, 1450*s*, 1360*m*, 1325*m*, 1245*m* (br.), 1195*w*, 1090*s* (br.), 1060*s* (sh), 1025*m*, 910*w*, 850*w*, 815*w*. ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K, 2 diastereoisomers in the ratio 4:1): *Table 2*; additionally, for the major isomer: 7.39–7.25 (*m*, 20 arom. H); 4.91 (*d*, *J* = 11.4), 4.86 (*d*, *J* = 11.5), 4.72 (*d*, *J* = 12.0), 4.64 (*d*, *J* = 12.1), 4.63 (*d*, *J* = 11.4), 4.58 (*d*, *J* = 11.6), 4.50 (*d*, *J* = 11.8), 4.45 (*d*, *J* = 11.8) (8 PhC*H*); 2.29 (*s*, AcN); additionally, for the minor isomer: 1.91 (*s*, AcN). ^{1}H-NMR (300 MHz, C_6D_6, 298 K, 2 diastereoisomers in the ratio 10:1): *Table 2*; additionally, for the major isomer: 7.39–7.03 (*m*, 20 arom. H); 4.81 (*d*, *J* = 11.6), 4.62 (*d*, *J* = 11.5), 4.45 (*d*, *J* = 12.1), 4.40 (*d*, *J* = 11.8), 4.36 (*d*, *J* = 11.5), 4.33 (*d*, *J* = 12.1), 4.26 (*d*, *J* = 11.9), 4.20 (*d*, *J* = 11.9) (8 PhC*H*); 2.23 (*s*, AcN); additionally for the minor isomer: 9.09 (br. *s*, NH); 4.87 (*d*, *J* = 11.0), 4.82 (*d*, *J* = 10.8) (2 PhC*H*). ^{1}H-NMR (300 MHz, C_6D_6, 348 K): 8.84 (*s*, NH); 7.30 (*d*, *J* = 8.3, 2 arom. H); 7.23–7.05 (*m*, 18 arom. H); 4.78 (*d*, *J* = 11.7), 4.59 (*d*, *J* = 11.7), 4.49 (*d*, *J* = 12.0), 4.47 (*d*, *J* = 11.7), 4.39 (*d*, *J* = 12.4), 4.37 (*d*, *J* = 11.4) (6 PhC*H*); 4.36 (*d*, *J* = 5.8, H–C(2)); 4.30 (*d*, *J* = 12.0), 4.25 (*d*, *J* = 12.0) (2 PhC*H*); 4.22–4.17 (*m*, H–C(5)); 4.01 (*t*, *J* ≈ 3.1, H–C(4)); 3.72 (*dd*, *J* = 2.9, 5.6, H–C(3)); 3.65 (br. *d*, *J* = 5.7, 2 H–C(6)); 2.13 (br. *s*, AcN). ^{13}C-NMR (50.3 MHz, $CDCl_3$, 298 K, 2 diastereoisomers in the ratio 4:1): *Table 3*; additionally, for the major isomer: 171.60 (*s*, C=O); 137.46 (2 C), 137.19, 137.11 (3*s*); 128.21–127.16 (*s*everal *d*); 73.61, 73.11,

72.39, 72.26 (4*t*, 4 Ph*C*H$_2$); 19.87 (*q*, Me); additionally for the minor isomer: 165.52 (*s*, C=O); 137.31 (*s*); 72.86, 72.39, 71.71, 71.18 (4*t*, 4 Ph*C*H$_2$); 21.22 (*q*, Me). CI-MS (NH$_3$): 596 (48), 595 (100, $[M+1]^+$). Anal. calc. for $C_{36}H_{38}N_2O_6$ (594.70): C 72.71, H 6.44, N 4.71; found: C 72.68, H 6.67, N 4.60.

*(1*R*)-1,2,3,5-Tetra*-O-*benzyl-1*-C-*(5-methyl-1,3,4-oxadiazol-2-yl)*-D-*lyxitol* (**9**). R_f (hexane/AcOEt 3:2) 0.8. IR (CHCl$_3$): 3550*w*, 3090*w*, 3060*w*, 3020*w*, 3000*w*, 2960*w*, 2930*w* (br.), 2860*m*, 1665*w*, 1590*w*, 1555*w*, 1495*w*, 1450*w*, 1390*w*, 1350*w*, 1250*m*, 1230–1200*m*, 1090*s*, 1020*s*, 950*w*. ^{1}H-NMR (300 MHz, CDCl$_3$): *Table 4*; additionally, 7.37–7.21 (*m*, 18 arom. H); 7.13–7.09 (*m*, 2 arom. H); 4.71 (*d*, *J* = 11.1), 4.63 (*d*, *J* = 11.7), 4.57 (*d*, *J* = 11.1), 4.52 (*d*, *J* = 11.9), 4.45 (*d*, *J* = 11.7), 4.43 (*d*, *J* = 11.9), 4.38 (*d*, *J* = 11.4), 4.29 (*d*, *J* = 11.4) (8 PhC*H*); 2.29 (*s*, Me). ^{13}C-NMR (50.3 MHz, CDCl$_3$): *Table 4*; additionally, 137.85 137.59 (2 C), 136.65 (3*s*); 128.49–127.38 (several *d*); 74.97, 73.37, 73.24, 72.39 (4*t*, 4 Ph*C*H$_2$); 10.73 (*s*, Me).

*1,4-Dihydrobis[(1*S*)-1,2,3,5-tetra*-O-*benzyl*-D-*lyxitol-1-yl]-1,2,4,5-tetrazine* (**10**). R_f (hexane/AcOEt 1:1) 0.40. $[\alpha]_D^{25} = -9.2$ (*c* = 0.22, CHCl$_3$). UV (*c* = 3.9 · 10^{-4}, EtOH): 229 (3.74), 252 (2.22), 258 (2.49), 263 (2.30). IR (CHCl$_3$): 3550*m*, 3370*m*, 3050*m*, 2990*m*, 2900*m*, 2860*m*, 1645*m*, 1495*m*, 1450*s*, 1395*s*, 1330*m*, 1305*m*, 1240*m*, 1090*s* (br.), 1065*s*, 1025*s*, 955*m*, 905*m*, 865*w*, 830*w*, 820*w*. ^{1}H-NMR (400 MHz, CDCl$_3$): *Table 4*; additionally, 7.41–7.26 (*m*, 18 arom. H, NH); 7.12–7.10 (*m*, 2 arom. H); 4.83 (*d*, *J* = 10.1), 4.72 (*d*, *J* ≈ 11.9, 2 H), 4.53 (*d*, *J* = 12.0), 4.45 (*d*, *J* = 11.9), 4.36 (*d*, *J* = 11.6), 4.30 (*d*, *J* = 10.5), 4.28 (*d*, *J* = 11.4) (8 PhC*H*). ^{13}C-NMR (50.3 MHz, CDCl$_3$): *Table 4*; additionally, 137.87, 137.73, 137.38, 136.56 (4*s*); 128.50–127.57 (several *d*); 75.00, 73.87, 73.14, 71.50 (4*t*, 4 Ph*C*H$_2$). ESI-MS: 1143 (15, $[M+K]^+$), 1127 (100, $[M+Na]^+$).

*(*Z*)-2′-(2,3,4,6-Tetra*-O-*benzyl*-D-*galactopyranosylidene)toluene-4-sulfonohydrazide* (**4B**). The reaction of **3A**/**3B** 95:5 (141 mg, 0.25 mmol) in pyridine (2.5 ml) with TsCl (67 mg, 0.30 mmol) in pyridine (2.5 ml; 1.5 h) and FC (CH$_2$Cl$_2$) gave **4B** [19] (111 mg, 63%). ^{1}H-NMR (400 MHz, C$_6$D$_6$): *Table 2*; additionally, 7.99 (*d*, *J* = 8.2, 2 arom. H); 7.27–7.06 (*m*, 20 arom. H); 6.68 (*d*, *J* = 8.2, 2 arom. H); 4.60 (*d*, *J* = 11.4), 4.43 (*d*, *J* = 11.6), 4.38 (*d*, *J* = 12.1), 4.26 (*d*, *J* = 11.9), 4.24 (*d*, *J* = 11.8), 4.23 (*d*, *J* = 12.4), 4.21 (*d*, *J* = 11.7), 4.14 (*d*, *J* = 11.9, 8 PhC*H*); 1.77 (*s*, Me). ^{13}C-NMR (50.3 MHz, C$_6$D$_6$): *Table 3*; additionally, 143.34, 138.45 (2 C), 138.30 (2 C), 136.81 (4*s*); 129.57 (*d*, 2 C); 128.64–127.51 (several *d*); 73.72, 73.38, 72.48, 72.36 (4*t*, 4 Ph*C*H$_2$); 21.08 (*q*, Me).

*(*Z*)-2′-(2,3,4,6-Tetra*-O-*benzyl*-D-*mannopyranosylidene)toluene-4-sulfonohydrazide* (**6** [19]). The reaction of **5A**/**5B** 55:45 (179 mg, 0.32 mmol) in pyridine (6 ml) with TsCl (68 mg, 0.36 mmol) in pyridine (4 ml; 1.5 h) and FC (hexane/AcOEt 4:1) gave **6** [22] (124 mg, 55%).

*(*Z*)-2′-(2,3,4,6-Tetra*-O-*benzyl*-D-*glucopyranosylidene)aceto(1′-*^{15}*N)- and -(2′-*^{15}*N)hydrazide* (**12A**/**12B**). *a*) The reaction of **11A**/**11B** 75:25 (45 mg, 0.08 mmol) in CH$_2$Cl$_2$ (4 ml) with Ac$_2$O (200 µl, 1.11 mmol; 1 h) and FC (hexane/AcOEt 2:1 → 1:1) gave **12A**/**12B** 1:1 (37.5 mg, 77%).

b) The reaction of **11A**/**11B** 78:22 (300 mg, 0.54 mmol) in CH$_2$Cl$_2$ (10 ml) with Ac$_2$O (55 µl, 0.58 mmol; 3 h) and FC (hexane/AcOEt 2:1) gave **12A**/**12B** 55:45 (272 mg, 85%). ^{1}H-NMR (300 MHz, CDCl$_3$, 298 K, 7:3 mixture of 2 isotopomeric pairs of diastereoisomers, **12A**/**12B** 1:1): 8.78 (*d*, *J* = 94.4, exchanged with D$_2$O, 0.15 NH); 8.78 (*s*, exchanged with D$_2$O, 0.15 NH); 8.74 (*d*, *J* = 93.5 exchanged with D$_2$O, 0.35 NH); 8.74 (*s*, exchanged with D$_2$O, 0.35 NH); 7.40–7.25 (*m*, 18 arom. H); 7.19–7.15 (*m*, 2 arom. H); 4.76–4.36 (*m*, 8 PhC*H*); 4.11 (*d*, *J* = 2.4, 0.7 H–C(2)); 3.99 (*dd*, *J* = 1.8, 3.8, 0.3 H), 3.93 (*dd*, *J* = 2.6, 4.7, 0.7 H) (H–C(3)); 3.83–3.68 (*m*, 3 H); 2.30 (*s*, 2.1 H), 2.07 (*s*, 0.9 H) (Ac). ^{1}H-NMR (600 MHz, C$_6$D$_6$, 298 K, 9:1 mixture of 2 isotopomeric pairs of diastereoisomers, **12A**/**12B** 55:45): *Table 2*; additional values for the major isotopomeric pair: 7.28–7.24 (*m*, 6 arom. H); 7.17–7.05 (*m*, 14 arom. H); 4.58 (*d*, *J* = 11.5), 4.56 (*d*, *J* = 11.9), 4.44 (*d*, *J* = 11.5), 4.345 (*d*, *J* = 11.7), 4.340 (*d*, *J* = 11.9), 4.27 (*d*, *J* = 12.3), 4.25 (*d*, *J* = 12.2), 4.18 (*d*, *J* = 11.9) (6 PhC*H*); additional values for the minor isotopomeric pair: 8.59 (*d*, $^1J(^{15}N,H) = 92.9$, 0.5 H), 8.59 (br. *s*, 0.5 H) (NH); 4.77 (*d*, *J* = 11.9), 4.69 (*d*, *J* = 12.2), 4.09 (*d*, *J* = 11.2) (3 PhC*H*); 4.02 (br. *s*, H–C(2)); 3.61–3.59 (*m*, 2 H–C(6)). ^{13}C-NMR (150.9 MHz, C$_6$D$_6$, 298 K, 9:1 mixture of 2 isotopomeric pairs of diastereoisomers, **12A**/**12B** 55:45): *Table 3*; additional values for the major isotopomeric pair: 171.03 (*d*, $^2J(^{15}N,C) = 2.5$, 0.45 C), 170.96 (*d*, $^1J(^{15}N,C) = 6.6$, 0.55 C) (C=O); 138.49, 138.42, 137.89, 137.68 (4*s*); 129.40–127.56 (several *d*); 73.34, 73.24, 71.84, 70.84 (4*t*, 4 Ph*C*H$_2$); 20.20 (*d*, $^2J(^{15}N,C) = 1.4$, 0.55 C), 20.20 (*d*, $^3J(^{15}N,C) = 7.2$, 0.45 C) (Me); additional values for the minor isotopomeric pair: 164.46 (br. *s*, C=O); 81.46 (*d*, C(3)); 77.97 (*d*, C(4)); 76.63 (*d*, C(5)); 74.2 (2 overlapping *dd*, C(2)); 73.26, 72.70, 71.47, 71.06 (4*t*, 4 Ph*C*H$_2$); 68.59 (*t*, C(6)); 20.54 (br. *q*, Me). ^{15}N-NMR (60.8 MHz, C$_6$D$_6$, 9:1 mixture of 2 isotopomeric pairs of diastereoisomers, **12A**/**12B** 55:45): −224 (*d*, *J* ≈ 92, 0.05 N), −222.95 (*d*, *J* = 92.4, 0.5 N) (^{15}N of **12A**); −132 (br. *s*, 0.04 N), −130.43 (br. *s*, 0.41 N) (^{15}N of **12B**).

*(*Z*)-2′-(2,3,4,6-Tetra*-O-*benzyl*-D-*glucopyranosylidene)toluene-4-sulfono(1′-*^{15}*N)- and -(2′-*^{15}*N)hydrazide* (**13A**/**13B**). The reaction of **11A**/**11B** 78:22 (100 mg, 0.18 mmol) in CH$_2$Cl$_2$ (8 ml) with TsCl (38 mg, 0.20 mmol) in pyridine (2 ml; 3 h), FC (hexane/AcOEt 4:1), and crystallisation from MeOH gave **13A**/**13B** 65:35 (98 mg, 77%) as fine needles. R_f (hexane/AcOEt 1:1) 0.59. M.p. 132–132.5°. ^{1}H-NMR (600 MHz, CDCl$_3$,

13A/B 65:35): *Table 2*; additionally, 7.82 (*d*, *J* = 8.3, 2 arom. H); 7.39–7.12 (*m*, 22 arom. H); 4.54 (*d*, *J* = 11.9), 4.53 (*d*, *J* = 11.5), 4.51 (*d*, *J* = 12.0), 4.48 (*d*, *J* = 11.7), 4.40 (*d*, *J* = 11.4), 4.31 (*d*, *J* = 11.7), 4.29 (*d*, *J* = 11.5), 4.22 (*d*, *J* = 11.9) (8 PhC*H*); 2.30 (*s*, Me). ^{13}C-NMR (150.9 MHz, $CDCl_3$, **13A/13B** 65:35): *Table 3*; additionally, 143.79, 137.54, 137.45, 137.02, 136.83, 135.35 (6*s*); 129.46–127.85 (several *d*); 73.39, 73.00, 71.53, 70.37 (4*t*, 4 PhCH_2); 21.49 (*q*, Me). ^{15}N-NMR (60.8 MHz, $CDCl_3$, **13A/13B** *ca.* 7:3): −232.05 (*d*, *J* = 83.9, 0.7 N, N of **13A**); −134.74 (br. *s*, 0.3 N, N′ of **13B**).

Treatment of **14A/14B** *with* Ac_2O. *a*) The reaction of **14A/14B** 85:15 (100 mg, 0.18 mmol) in CH_2Cl_2 (3 ml) with Ac_2O (0.4 ml; 90 min) and FC (hexane/AcOEt 2:1) gave **15A/15B** 3:7 (89 mg, 83%).

b) The reaction of **14A/14B** 3:1 (230 mg, 0.42 mmol) in CH_2Cl_2 (10 ml) with Ac_2O (55 µl, 0.42 mmol; 3 h) and FC (hexane/AcOEt 2:1) gave **17A–17D/18** 3:1 (10 mg, 5%) and **15A/15B** 3:7 (204 mg, 81%).

*(*Z*)-2′-(2,3,4,6-Tetra-O-benzyl-*D*-galactopyranosylidene)aceto(1′-*^{15}*N)- and -(2′-*^{15}*N)hydrazide* (**15A/15B**): R_f (hexane/AcOEt 1:1) 0.18. ^{1}H-NMR (600 MHz, C_6D_6, 298 K, 10:1 mixture of 2 isotopomeric pairs of diastereoisomers, **15A/15B** 3:7): *Table 2*; additional values for the major isotopomeric pair: 7.33 (*d*, *J* = 7.4, 2 arom. H); 7.26 (*d*, *J* = 7.4, 2 arom. H); 7.21–7.06 (*m*, 16 arom. H); 4.81 (*d*, *J* = 11.6), 4.62 (*d*, *J* = 11.5), 4.46 (*d*, *J* = 12.0), 4.41 (*d*, *J* = 12.1), 4.36 (*d*, *J* = 11.5), 4.35 (*d*, *J* = 12.0), 4.26 (*d*, *J* = 11.8), 4.22 (*d*, *J* = 11.9) (8 PhC*H*); 2.24 (*s*, AcN); additional values for the minor isotopomeric pair: 9.07 (*d*, $^1J(^{15}N,H)$ = 93.2, 0.3 H), 9.07 (br. *s*, 0.7 H) (NH); 4.86 (*d*, *J* = 11.2), 4.53 (*d*, *J* = 11.7) (2 PhC*H*); 4.49 (br. *s*, H–C(2)); 4.29 (*d*, *J* = 11.7), 4.19 (*d*, *J* = 11.5), 4.17 (*d*, *J* = 11.7) (3 PhC*H*); 4.15–4.13 (*m*, H–C(5)); 3.99–3.97 (*m*, H–C(4)); 3.88–3.84 (*m*, H–C(3)); 3.78 (*dd*, *J* = 1.2, 10.5, H–C(6)). ^{13}C-NMR (150.9 MHz, C_6D_6, 298 K, 10:1 mixture of 2 isotopomeric pairs of diastereoisomers, **15A/15B** 3:7): *Table 3*; additional values for the major isotopomeric pair: 171.22 (*s*, 0.7 C), 171.22 (*d*, ^1J(C,N) = 6.6, 0.3 C) (C=O); 138.50 (2 C), 138.41, 138.32 (3*s*); 128.59–127.76 (several *d*); 74.01, 73.57, 72.80, 72.62 (4*t*, 4 PhCH_2); 20.39 (br. *q*, Me); additional values for the minor isotopomeric pair: 78.79 (*d*, C(3)); 77.55 (*d*, C(5)); 73.27 (*t*, PhCH_2); 72.93 (*d*, C(4)); 71.89 (*t*, PhCH_2); 69.77 (*t*, C(6)). ^{15}N-NMR (40.6 MHz, $CDCl_3$, 298 K, 3:2 mixture of 2 isotopomeric pairs of diastereoisomers, **15A/15B** 3:7): −221.5 (*d*, *J* = 97.3, 0.18 N), −221.5 (*d*, *J* ≈ 115, 0.12 N) (^{15}N of **15A**); −128.9 (*s*, 0.42 N), −123.5 (*s*, 0.28 N) (^{15}N of **15B**). ^{15}N-NMR (60.8 MHz, C_6D_6, 298 K, 10:1 mixture of 2 isotopomeric pairs of diastereoisomers, **15A/15B** *ca.* 1:2): −222.08 (*d*, *J* = 93.0 0.3 N, ^{15}N of **15A**); −124.72 (*s*, 0.6 N), −118.98 (*s*, 0.07 N) (^{15}N of **15B**); *d* for minor diastereoisomer (0.03 N) hidden by the noise.

*Data of 1,4-Dihydrobis[(1*S*)-2,3,4,6-tetra-*O*-benzyl-*D*-lyxitol-1-yl](1,4- and -1,6-*^{15}*N_2)-1,2,4,5-tetrazine and 1,2,3,5-Tetra-*O*-benzyl-*D*-galactonamide* (**17A–17D** and **18**). R_f (hexane/AcOEt 1:1) 0.40. ^{1}H-NMR (600 MHz, $CDCl_3$, **17A–17D/18** 3:1): *Tables 1* and *3*; additionally for **17A–17D**: 7.42–7.10 (*m*, 20 aro*m*. H, NH); 4.83 (*d*, *J* = 10.1), 4.71 (*d*, *J* = 10.2), 4.70 (*d*, *J* = 11.4), 4.52 (*d*, *J* = 12.0), 4.44 (*d*, *J* = 12.3), 4.35 (*d*, *J* = 11.3), 4.32 (*d*, *J* = 11.3), 4.28 (*d*, *J* = 11.3) (8 PhC*H*); additionally for **18**: 4.77 (*d*, *J* = 10.7), 4.60 (*d*, *J* = 10.9), 4.59 (*d*, *J* = 11.4), 4.54 (*d*, *J* = 12.0), 4.46 (*d*, *J* ≈ 12.5), 4.41 (*d*, *J* = 11.4), 4.37 (*d*, *J* ≈ 11.5), 4.28 (*d*, *J* = 11.3) (8 PhC*H*). ^{13}C-NMR (150.9 MHz, $CDCl_3$, **17A–17D/18** 3:1): *Tables 2* and *3*, additionally for **17A–17D**: 137.91, 137.76, 137.42, 136.60 (4*s*); 128.51–127.59 (several *d*); 75.03, 73.91, 73.21, 71.56 (4*t*, 4 PhCH_2); additionally for **18**: 137.84, 137.60, 137.42, 136.45 (4*s*); 75.16, 74.06, 73.33, 71.89 (4*t*, 4 PhCH_2). ^{15}N-NMR (60.8 MHz, C_6D_6, 298 K): −252.63 (*d*, *J* = 86.7, NH); −125.26 (*d*, *J* = 5.7, C=N).

*(*Z*)-2′-(2,3,4,6-Tetra-O-benzyl-*D*-galactopyranosylidene)toluene-4-sulfono(1′-*^{15}*N)- and -(2′-*^{15}*N)hydrazide* (**16A/16B**). The reaction of **14A/14B** 4:1 (100 mg, 0.18 mmol) in CH_2Cl_2 (8 ml) with TsCl (38 mg, 0.20 mmol) in pyridine (5 ml; 3 h) and FC (hexane/AcOEt 4:1) gave **16A/16B** 35:65 (100 mg, 78%). Yellowish oil. R_f (hexane/AcOEt 2:1) 0.33. ^{1}H-NMR (600 MHz, C_6D_6, **16A/16B** 35:65): *Table 2*; additionally, 8.00 (*d*, *J* = 8.2, 2 arom. H); 7.27–7.06 (*m*, 20 arom. H); 6.69 (*d*, *J* = 8.1, 2 arom. H); 4.62 (*d*, *J* = 11.4), 4.46 (*d*, *J* = 11.6), 4.39 (*d*, *J* = 12.1), 4.28 (*d*, *J* = 10.9), 4.24 (*d*, *J* = 12.2, 2 H), 4.23 (*d*, *J* = 11.6), 4.16 (*d*, *J* = 11.8) (8 PhC*H*); 1.79 (*s*, Me). ^{13}C-NMR (150.9 MHz, C_6D_6, **16A/16B** 35:65, assignment based on a ^{1}H,^{13}C-COSY spectrum): *Table 3*; additionally, 143.24, 138.42, 138.41, 138.31, 138.23, 137.02 (6*s*); 129.52 (2*d*); 128.71–127.69 (several *d*); 73.55, 73.45, 72.59, 72.16 (4*t*, 4 PhCH_2); 21.10 (*q*, Me). ^{15}N-NMR (60.8 MHz, C_6D_6, **16A/16B** *ca.* 2:3): −230.00 (*d*, *J* = 84.5, 0.4 N, ^{15}N of **16A**); −125.02 (br. *s*, 0.6 N, ^{15}N of **16B**).

*1′-Methyl-2′-[(*Z*)-2,3,4,6-tetra-O-benzyl-*D*-glucopyranosylidene]toluene-4-sulfonohydrazide* (**20**) *and 2,3,4,6-Tetra-O-benzyl-*D*-glucono-1,5-lactone* (**21** [40][41]). The reaction of **19A/19D** 72:28 (600 mg, 1.06 mmol) in CH_2Cl_2/pyridine 5:1 (30 ml) with TsCl (222 mg, 1.17 mmol; 3.5 h) and FC (hexane/AcOEt 4:1) gave **20/21** 3:1 (600 mg, 79%). Colourless oil. R_f (hexane/AcOEt 1:1) 0.67. IR ($CHCl_3$, **20/21** 3:1): 3060*w* (sh), 3020*w* (sh), 3000*w*, 2920*m*, 2870*m*, 1750*m*, 1645*m*, 1595*w*, 1495*m*, 1455*m*, 1350*s*, 1305*m*, 1280*m*, 1260*m* (br.), 1185*m*, 1160*s*, 1090*s* (sh), 1070*s*, 1025*s*, 995*m* (sh), 910*m*, 860*w*, 810*m*. ^{1}H-NMR (400 MHz, C_6D_6, **20/21** 3:1): *Table 2*; additionally for **20**, 8.02 (*d*, *J* = 8.2, 2 arom. H); 7.45 (*d*, *J* = 7.2, 2 arom. H); 7.32–7.02 (*m*, 18 arom. H); 6.82 (*d*, *J* = 8.0, 2 arom. H); 4.71 (*d*, *J* = 12.1), 4.59 (*d*, *J* = 12.1), 4.52 (*d*, *J* = 11.6), 4.39

(*d*, *J* = 11.6), 4.34 (*d*, *J* = 12.4), 4.26 (*d*, *J* = 12.1), 4.22 (*d*, *J* = 11.7), 4.06 (*d*, *J* = 11.8) (8 PhC*H*); 1.88 (*s*, Me); characteristic signals of **21**: 4.27 (*dt*, *J* ≈ 8.5, 2.8, H–C(5)); 4.07 (*d*, *J* = 6.5, H–C(2)); 3.92 (*d*, *J* = 8.7, 6.8, H–C(4)); 3.81 (*t*, *J* = 6.6, H–C(3)); 3.46 (*dd*, *J* = 11.1, 2.4, H–C(6)); 3.42 (*dd*, *J* = 11.1, 3.2, H′–C(6)). ^{13}C-NMR (50.3 MHz, C_6D_6, **20**/**21** 3:1): *Table 3*; additionally for **20**, 142.85, 138.01, 137.89, 137.26, 137.06, 132.35 (6*s*); 129.38–127.02 (several *d*); 72.78, 72.61, 70.97, 70.26 (4*t*, 4 PhCH_2); 20.71 (*q*, Me); characteristic signals of **21**: 169.23 (*s*, C(1)); 80.91 (*d*, C(3)); 78.12 (*d*, C(4)); 77.35 (*d*, C(2)); 76.03 (*d*, C(5)); 68.23 (*t*, C(6)). CI-MS (NH_3): 723 (11), 722 (36), 721 (81, $[M+1]^+$of **20**), 614 (19), 613 (54), 506 (14), 505 (48), 351 (10), 203 (100), 174 (21), 139 (15), 108 (17).

*1′-Methyl-2′-[(*Z*)-2,3,4,6-Tetra-*O*-benzyl-*D*-galactopyranosylidene]toluene-4-sulfonohydrazide* (**23**) *and 2,3,4,6-Tetra-*O*-benzyl-*D*-galactono-1,5-lactone* (**24** [42]). The reaction of **22A**/**22B** 85:15 (427 mg, 0.75 mmol) in CH_2Cl_2/pyridine 4:1 (25 ml) with TsCl (158 mg, 0.83 mmol; 3 h) and FC (dry hexane/AcOEt 4:1) gave **23** (305 mg, 56%). Colourless oil. Upon standing for 10 h at r.t., **23** mostly decomposed to **24** [42] (→ **23**/**24** 1:3). R_f (hexane/AcOEt 1:1) 0.67. ^{1}H-NMR (600 MHz, C_6D_6, **23**/**24** 1:3): *Table 2*; additionally for **23**, 7.62 (*d*, *J* = 8.2, 2 arom. H); 7.23 (*d*, *J* = 7.0, 2 arom. H); 7.20–7.01 (*m*, 18 arom. H); 6.79 (*d*, *J* = 8.3, 2 arom. H); 4.69 (*d*, *J* = 11.6), 4.55 (*d*, *J* = 11.3), 4.54 (*d*, *J* = 11.5), 4.26 (*d*, *J* = 11.9), 4.23 (*d*, *J* = 11.2), 4.18 (*d*, *J* = 12.0) (6 PhC*H*); 1.95 (*s*, Me); characteristic signals of **24**: 4.43 (*d*, *J* = 9.6, H–C(2)); 3.95 (*ddd*, *J* = 7.6, 5.9, 1.0, H–C(5)); 3.86 (br. *d*, *J* = 1.6, H–C(4)); 3.57 (*d*, *J* = 9.5, 1.7, H–C(3)); 3.54 (*dd*, *J* = 8.8, 7.6, H–C(6)); 3.46 (*dd*, *J* = 9.2, 5.6, H′–C(6)). ^{13}C-NMR (50.3 MHz, C_6D_6, **23**/**24** 1:3): *Table 3*; additionally for **23**, 143.35, 138.50 (2 C), 138.42, 132.89 (4*s*); 74.51, 73.47 (2*t*, 2 PhCH_2); 72.73 (*t*, 2 PhCH_2); 21.20 (*q*, Me); characteristic signals of **24**: 169.73 (*s*, C(1)); 80.86 (*d*, C(3)); 78.16 (*d*, C(5)); 77.32 (*d*, C(2)); 72.96 (*d*, C(4)); 67.80 (*t*, C(6)).

*1′-Methyl-2′-[(*Z*)-2,3,4,6-Tetra-*O*-benzyl-*D*-mannopyranosylidene]toluene-4-sulfonohydrazide* (**26**) *and 2,3,4,6-Tetra-*O*-benzyl-*D*-manno-1,5-lactone* (**27** [43]). The reaction of **25A**/**25B** 85:15 (390 mg, 0.69 mmol) in CH_2Cl_2/pyridine 4:1 (25 ml) with TsCl (146 mg, 0.76 mmol; 1.5 h) and FC (dry hexane/AcOEt 4:1) gave **26** (326 mg, 66%). Colourless oil. Upon standing for 10 h at r.t., **26** partially decomposed to **27** [43] (→ **26**/**27** 1:1). R_f (hexane/AcOEt 1:1) 0.67. IR ($CHCl_3$): 3060*w*, 3020*m* (sh), 3000*m*, 2920*m*, 2870*m*, 1770*m*, 1640*m*, 1595*w*, 1495*m*, 1450*m*, 1395*w* (sh), 1350*m*, 1305*w*, 1285*m*, 1255*m*, 1185*m*, 1160*s*, 1080*s* (br.), 1025*s*, 905*m*, 880*w*, 810*w*. ^{1}H-NMR (600 MHz, C_6D_6, 300 K; **26**/**27** 1:2, assignment based on a ^{1}H,^{1}H-COSY spectrum): *Table 2*; additionally for **26**: 8.02 (*d*, *J* = 8.2, 2 arom. H); 7.25–7.01 (*m*, 20 arom. H); 6.86 (*d*, *J* = 8.0, 2 arom. H); 4.74 (*d*, *J* = 12.3), 4.70 (*d*, *J* = 11.6), 4.48 (*d*, *J* = 12.3), 4.37 (*d*, *J* = 11.6); 4.34 (*d*, *J* = 12.1) (5 PhC*H*); 4.27 (*s*, PhCH_2); 4.14 (*d*, *J* = 11.6, PhC*H*); 1.89 (*s*, Me); characteristic signals of **27**: 4.23 (*d*, *J* = 2.7, H–C(2)); 4.11 (*ddd*, *J* = 7.0, 5.5, 3.8, H–C(5)); 4.05 (*t*, *J* ≈ 2.2, H–C(3)); 3.83 (*d*, *J* = 7.1, 1.8, H–C(4)); 3.53 (*dd*, *J* = 10.7, 3.9, H–C(6)); 3.48 (*dd*, *J* = 10.9, 5.5, H′–C(6)). ^{13}C-NMR (50.3 MHz, C_6D_6, 297 K; **26**/**27** 1:1 assignment based on a ^{1}H,^{13}C-COSY spectrum): *Table 3*; additionally for **26**/**27**: 138.60–137.67 (several *s*); 129.89–127.51 (several *d*); additionally for **26**: 143.52, 132.85 (2*s*); 74.06, 73.28, 71.78, 70.88 (4*t*, 4 PhCH_2); 21.18 (*q*, Me); characteristic signals of **27**: 168.77 (*s*, C(1)); 78.66 (*d*, C(5)); 77.62 (*d*, C(3)); 76.72 (*d*, C(4)); 76.36 (*d*, C(2)); 69.67 (*t*, C(6)).

*1′-Methyl-2′-[(*Z*)-(2,3:4,6-Di-*O*-isopropylidene)-*D*-mannopyranosylidene]toluene-4-sulfonohydrazide* (**29**). The reaction of **28A**/**28B** 1:1 (368 mg, 1.28 mmol) in CH_2Cl_2/pyridine 4:1 (25 ml) with TsCl (268 mg, 1.41 mmol; 2 h) and FC (dry hexane/AcOEt 3:1) gave **29** (336 mg, 60%). Colourless foam. R_f (hexane/AcOEt 1:1) 0.37. $[\alpha]_D^{25} = +114.8$ (*c* = 0.45, $CHCl_3$). IR ($CHCl_3$): 2990*w*, 2985*w* (sh), 2930*w* 2910*w* (br.), 1640*m*, 1595*w*, 1450*w* (br.), 1385*m*, 1375*m*, 1350*m*, 1305*w*, 1240*m* (br.), 1205*w*, 1185*m*, 1160*s*, 1105*s*, 1085*s*, 1065*s*, 1025*s*, 940*w*, 920*w*, 870*w*. IR (KBr): 2980*m*, 2920*m*, 2880*m* (sh), 1640*m*, 1595*m*, 1490*w*, 1455*m*, 1380*m* (sh), 1370*s*, 1345*s*, 1305*m*, 1240*s*, 1220*s*, 1195*s*, 1185*s*, 1160*s*, 1105*s*, 1085*s*, 1065*s*, 1010*m*, 945*m*, 915*w*, 880*m*, 815*m*. ^{1}H-NMR (400 MHz, C_6D_6): *Table 2*; additionally, 8.04 (*d*, *J* = 8.3, 2 arom. H); 6.85 (*d*, *J* = 8.1, 2 arom. H); 1.87 (*s*, Me); 1.60, 1.34, 1.19, 1.08 (4*s*, 2 Me_2C). ^{13}C-NMR (50.3 MHz, C_6D_6): *Table 3*; additionally, 143.61, 132.26 (2*s*); 129.96, 129.24 (2*d*, 4 C); 112.24, 99.77 (2*s*, 2 Me_2C); 28.84, 27.41, 25.81, 18.66 (4*q*, 2 Me_2C); 21.19 (*q*, Me). CI-MS (NH_3): 442 (25), 441 (100, $[M+1]^+$). Anal. calc. for $C_{20}H_{28}N_2O_7S$ (440.51): C 54.53, H 6.41, N 6.36, S 7.28; found: C 54.69, H 6.37, N 6.35, S 7.49.

Treatment of **30** *with* Ac_2O. The reaction of crude **30** (324 mg, *ca*. 1.2 mmol) in CH_2Cl_2 (10 ml) with Ac_2O (150 µl, 1.57 mmol; 12 h) and FC (hexane/AcOEt 1:1) gave **32** (27 mg, 8%) and **31A** (237 mg, 63%).

Treatment of **30** *with TsCl*. The reaction of crude **30** (493 mg, *ca*. 1.8 mmol) in pyridine (5 ml) with TsCl (369 mg, 1.9 mmol) in pyridine (5 ml; 20 min) and FC (CH_2Cl_2) gave **32** (55 mg, 11%) and **31B** (467 mg, 61%).

*(*Z*)-2′-(2,3:5,6-Di-*O*-isopropylidene-*D*-mannofuranosylidene)acetohydrazide* (**31A**). Colourless oil. R_f (hexane/AcOEt 1:2) 0.07. $[\alpha]_D^{25} = +114.4$ (*c* = 0.66, $CHCl_3$). UV (*c* = 8.27 · 10^{-4}, EtOH): 232 (3.295). IR ($CHCl_3$): 3390*w*, 3360*w*, 2980*m*, 2930*w*, 2880*w*, 1700*m* (sh), 1670*s*, 1500*w*, 1455*m*, 1380*s*, 1370*s*, 1315*m*, 1250*m*, 1195*m*, 1155*m*, 1115*m*, 1070*s*, 1030*m*, 990*w*, 970*m*, 940*w*, 860*m*, 840*m*, 815*w*. ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K, 2 diastereoisomers in the ratio 85:15): *Table 2*; additionally, for the major isomer, 2.23 (*s*, AcN); 1.47, 1.46, 1.42,

1.39 (4*s*, 2 Me_2C); additionally, for the minor isomer, 2.05 (*s*, AcN); 1.46, 1.45, 1.41, 1.39 (4*s*, 2 Me_2C). ^{13}C-NMR (50.3 MHz, $CDCl_3$, 298 K, 2 diastereoisomers in the ratio 85:15): *Table 3*; additionally, for the major isomer, 172.22 (*s*, C=O); 113.79, 109.30 (2*s*, 2 Me_2C); 26.59, 26.30, 25.19, 24.63 (4*q*, 2 Me_2C); 19.61 (*q*, Me); additionally for the minor isomer, 113.69, 109.17 (2*s*, 2 Me_2C); 26.41, 25.70, 24.95, 24.84 (4*q*, 2 Me_2C); 20.11 (*q*, Me). CI-MS: (NH_3): 332 (41, $[M+NH_4]^+$), 316 (14), 315 (100, $[M+1]^+$). Anal. calc. for $C_{14}H_{22}N_2O_6$ (314.34): C 53.49, H 7.05, N 8.91; found: C 53.29, H 7.04, N 8.73.

*(*Z*)-2′-(2,3:5,6-Di-*O*-isopropylidene-*D*-mannofuranosylidene)toluene-4-sulfonohydrazide* (**31B**). Yellowish crystals. R_f (hexane/AcOEt 1:1) 0.31. M.p. 76–77°. $[\alpha]_D^{25} = +145.4$ ($c = 0.32$, $CHCl_3$). UV ($c = 1.88 \cdot 10^{-4}$, EtOH): 206 (2.202), 216 (2.231). IR (KBr): 3210*w*, 3070*w*, 2990*m*, 2960*m*, 2940*m*, 2870*w*, 1730*m*, 1695*m*, 1600*w*, 1540*w*, 1495*w*, 1455*m*, 1385*m*, 1375*m*, 1345*m*, 1290*m*, 1255*m*, 1220*s*, 1185*m*, 1170*s*, 1120*m*, 1090*m*, 1070*m*, 1040*m* (br.), 975*m*, 945*w*, 845*m*, 810*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 2*; additionally, 7.85 (*d*, $J = 8.2$, 2 arom. H); 7.30 (*d*, $J = 8.2$, 2 arom. H); 2.41 (*s*, Me); 1.45, 1.37, 1.35, 1.18 (4*s*, 2 Me_2C). ^{13}C-NMR (150.9 MHz, $CDCl_3$, assignment based on a ^{1}H,^{13}C-COSY spectrum): *Table 3*; additionally, 143.89, 135.25 (2*s*); 129.48, 128.00 (2*d*, 4 C); 114.16, 109.67 (2*s*, 2 Me_2C); 26.90, 26.42, 25.86, 24.94 (4*q*, 2 Me_2C); 21.53 (*q*, Me). ^{15}N-NMR (40.6 MHz, $CDCl_3$): −230.9 (*d*, $^1J(^{15}N,H) = 83.6$, NH); −144.8 (*s*, C=N). CI-MS (C_4H_{10}): 428 (22), 427 (100, $[M+1]^+$), 273 (14), 259 (31), 157 (10). Anal. calc. for $C_{19}H_{26}N_2O_7S$ (426.48): C 53.51, H 6.14, N 6.57, S 7.52; found: C 53.34, H 5.95, N 6.42, S 7.75.

*Bis[(1*R*)-1,2:4,5-di-*O*-isopropylidene-*D*-arabinitol-1-yl]-1,2,4,5-tetrazine* (**32**). Pink foam. R_f (hexane/AcOEt 1:1) 0.38. $[\alpha]_D^{25} = -16.9$ ($c = 0.34$, $CHCl_3$). UV ($c = 8.1 \cdot 10^{-5}$, EtOH): 216 (0.729), 264 (0.139), 522 (0.031). IR (KBr): 3450*m*, 2985*m*, 2935*m*, 1730*w*, 1630*w*, 1455*w*, 1380*m*, 1370*m* (sh), 1250*s*, 1215*s*, 1160*m*, 1120*m*, 1095*m*, 1070*s*, 1010*m*, 975*w*, 885*w*, 850*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 4*; additionally, 1.82, 1.59, 1.36, 1.32 (4*s*, 2 Me_2C). ^{13}C-NMR (50.3 MHz, $CDCl_3$): *Table 4*; additionally, 111.41, 109.47 (2*s*, 2 Me_2C); 26.68, 26.25, 25.35, 25.15 (4*q*, 2 Me_2C). EI-MS: 542 (2, M^+), 499 (21), 301 (25), 272 (18), 243 (16), 185 (29), 141 (44), 139 (15), 127 (16), 126 (20), 113 (15), 101 (100, $C_5H_9O_2^+$), 100 (20), 99 (29), 98 (40), 97 (28), 85 (32), 83 (15), 81 (28), 73 (21), 72 (22), 71 (24), 70 (27), 69 (31), 60 (78), 58 (19), 56 (23), 44 (74), 43 (16), 42 (35). Anal. calc. for $C_{24}H_{38}N_4O_{10}$ (542.58): C 53.13, H 7.06, N 10.33; found: C 53.14, H 7.22, N 10.07.

Treatment of **33A**–**33D** *with TsCl*. The reaction of **33A**/**33B**/**33C**/**33D** 76:4:12:8 (413 mg, 0.90 mmol) in CH_2Cl_2/pyridine 4:1 (25 ml) with TsCl (189 mg, 0.99 mmol; 1.5 h) and FC (hexane/AcOEt 4:1) gave (*E*/*Z*)-**34** 2:1 (242 mg, 44%) and **35** [44][45] (116 mg, 30%).

1′-Methyl-2′-[(E/Z)*-2,3-*O*-Isopropylidene-5-*O*-triphenylmethyl-*D*-ribofuranosylidene]toluene-4-sulfonohydrazide* ((*E*/*Z*)-**34**). Colourless foam. R_f (hexane/AcOEt 1:1) 0.61. M.p. 115–116°. $[\alpha]_D^{25} = -120.6$ ($c = 0.57$, $CHCl_3$). IR (KBr): 3040*w*, 3010*w*, 2975*m*, 2920*m*, 2860*w*, 1660*s*, 1595*m*, 1485*m*, 1445*m*, 1370*m*, 1345*s*, 1245*m*, 1225*s*, 1180*m*, 1160*s*, 1085*s*, 1020*m*, 995*s*, 930*w*, 895*w*, 870*w*, 845*w*, 810*m*. ^{1}H-NMR (400 MHz, C_6D_6, (*E*)/(*Z*) 2:1): *Table 2*; additionally for (*E*)-**34**, 7.95 (*d*, $J = 8.2$, 2 arom. H); 7.566 (*d*, $J = 8.1$, 4 arom. H); 7.409 (*d*, $J = 7.2$, 2 arom. H); 7.22–6.97 (*m*, 9 arom. H); 6.82 (*d*, $J = 7.9$, 2 arom. H); 1.88 (*s*, Me); 1.30, 1.04 (2*s*, Me_2C); additionally, for (*Z*)-**34**, 8.10 (*d*, $J = 8.2$, 2 arom. H); 7.570 (*d*, $J = 8.5$, 4 arom. H); 7.407 (*d*, $J = 7.9$, 2 arom. H); 7.22–6.97 (*m*, 9 arom. H); 6.82 (*d*, $J = 7.9$, 2 arom. H); 1.85 (*s*, Me); 1.43, 1.12 (2*s*, Me_2C). ^{13}C-NMR (50.3 MHz, C_6D_6, (*E*)/(*Z*) 2:1): *Table 3*; additionally, for (*E*)-**35**, 143.81 (3*s*); 143.39, 131.65 (2*s*); 130.11–127.51 (several *d*); 112.88 (*s*, Me_2C); 87.98 (*s*, Ph_3C); 26.74, 25.17 (2*q*, Me_2C); 21.25 (*q*, Me); additionally, for (*E*)-**35**, 143.53 (4*s*); 132.39 (*s*); 113.15 (*s*, Me_2C); 87.98 (*s*, Ph_3C); 27.16, 25.93 (2*q*, Me_2C); 21.25 (*q*, Me). CI-MS (NH_3): 613 (6, $[M+1]^+$), 460 (14), 459 (40), 430 (15), 372 (14), 371 (65), 370 (10), 243 (100, Tr^+). Anal. calc. for $C_{35}H_{36}N_2O_6S$ (612.73): C 68.61, H 5.92, N 4.57, S 5.23; found: C 68.34, H 6.07, N 4.82, S 5.50.

*2,3-*O*-Isopropylidene-5-*O*-triphenylmethyl-*D*-ribono-1,4-lactone* [45] (**35**). Colourless crystals. R_f (hexane/AcOEt 2:1) 0.44. M.p. 112–113° ([47]: 115–116°). ^{1}H-NMR ($CDCl_3$): see [45]. ^{13}C-NMR (50.3 MHz, $CDCl_3$): 174.30 (*s*, C(1)); 142.87 (3*s*); 128.42–127.17 (several *d*); 113.17 (*s*, Me_2C); 87.83 (*s*, Ph_3C); 81.33 (*d*, C(4)); 78.54 (*d*, C(3)); 75.74 (*d*, C(2)); 62.80 (*t*, C(5)); 26.74, 25.58 (2*q*, Me_2C).

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Received March 26, 2003