Synthesis and Oxidation of *N*-Aminoglyconolactams: A Synthesis of Mannostatin A

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The *N*-amino-ribono-1,5-lactam **4** was prepared in two high-yielding steps from the known methanesulfonate **2**. Oxidation of **4** with *t*-BuOCl in the presence of 2,6-lutidine afforded the tetrazene **6** (63%). Oxidation with MnO_2 gave the deaminated lactam **7** (40%), which was also obtained, together with the lactone **8**, upon oxidation of **4** with $PhSeO_2H$. Oxidation with $Mn(OAc)_3/Cu(OAc)_2$ provided the lactam **7** as the major and the dimer **9** as the minor product. Oxidation of **4** with 3 equiv. of $Pb(OAc)_4$ in toluene at room temperature gave two cyclopentanes, *viz*. the acetoxy epoxide **10** and the diazo ketone **11** in a combined yield of 78%. Oxidation with $Pb(OBz)_4$ provided **11** and the crystalline benzoyloxy epoxide **12**. The crystal structure of **12** was established by X-ray analysis. The *N*-amino-glyconolactams **41**, **46**, and **51** were prepared similarly to **4**. Their oxidation with $Pb(OAc)_4$ provided the diazo ketones **56**, **57**, and **58** as the only isolable products. Oxidation of the *N*-amino-mannono-1,5-lactam **55** with $Pb(OAc)_4$ in the presence of DMSO gave the sulfoximine **59**. Mannostatin A, a strong α-mannosidase inhibitor, was synthesized from the acetoxy epoxide **10** (obtained in 48% from **4**) in seven steps and in an overall yield of 45%.

Introduction. – Several naturally occurring cyclopentane derivatives[1]) are notable glycosidase inhibitors[2]), such as trehazoline [3], allosamidine [4], and the mannostatins [5–7]. Further cyclopentane-derived glycosidase inhibitors were prepared by *Farr et al.* [8], *Jäger* and co-workers [9][10], *Lundt* and co-workers [11], *Ganem* and co-workers [12], *Mehta* and *Mohal* [13], and *Reymond* and co-workers [14–16]. We synthesized and tested two bicyclo[3.1.0]hexanes ('cyclopropanated cyclopentanes') in the context of a comparison of the mechanism of action of snail β-mannosidase with the one of the β-glucosidases from *C. saccharolyticum* and from sweet almonds [17]. This synthesis renewed our interest in the transformation of carbohydrates into cyclopentanes. Carbohydrates indeed appear to be ideal starting materials for the synthesis of highly functionalized, enantiomerically pure cyclopentanes. The first general method for the transformation of monosaccharides to cyclopentanes is based on a fragmentation and intramolecular 1,3-dipolar cycloaddition [18]. Intramolecular 1,3-dipolar cycloadditions of oximes [19], nitrile oxides [9][20], and azomethine imines [21] have also been widely exploited for the synthesis of functionalized cyclopentanes [8]. Other methods for the transformation of carbohydrates into cyclopentanes[3]) are based on free radical cyclizations[4]) of alkenes [11][25], aldehydes [26], hydrazones [27], and oxime ethers [16][28], on carbanion cyclizations [14][29][30], tandem aldol-*Wittig*-

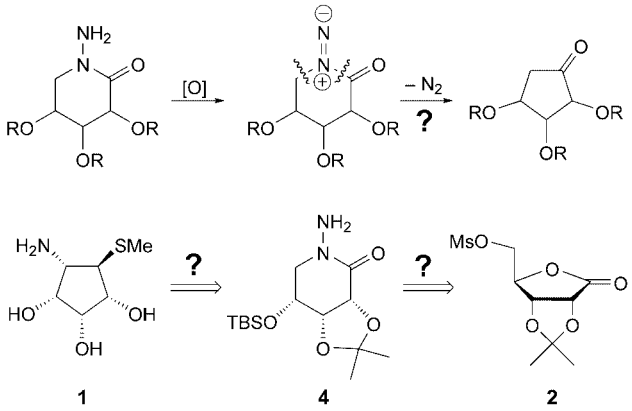
[1]) For reviews of carbapentoses and carbocyclic nucleosides, see [1].
[2]) For a review of aminocyclopentanes as glycosidase inhibitors, see [2].
[3]) For reviews, see [22][23].
[4]) For reviews, see [24].

type reactions [31], *Diels–Alder* cycloadditions [32], [2 + 2] photocycloaddition [33], ring closing metathesis [34], rearrangements [23][35] including a ring contraction [36], on the *Pauson–Khand* reaction [37], and the *Ramberg–Bäcklund* rearrangement [38].

We desired to combine the invention of a new method for the transformation of monosaccharides into cyclopentanes with a synthesis of mannostatin A (**1**), a strong competitive inhibitor of α-mannosidase from rat epididymis ($K_i = 4.8 \times 10^{-8}$ M) [5]. Mannostatin A was isolated in 1989 by *Aoyagi et al.* [5–7], together with mannostatin B (the corresponding (*R*)-sulfoxide), from the culture broth of *Streptoverticillium verticillus* var. *quantum*. Mannostatin A has been synthesized a number of times [30][39–45], but only once from carbohydrates [30][44], and once from *myo*-inositol [41][42].

In devising a new method for the transformation of carbohydrates into cyclopentanes, we noticed that the chemistry of *N*-aminoglyconolactams remained unexplored; such *N*-amino lactams were mentioned once only [46], whilst the chemistry of non-carbohydrate-derived *N*-amino lactams has been studied[5]). Although not precedented by these studies, oxidation of *N*-aminoglyconoloactams may lead to *N*-acyldiazenes [50][51][53] and hence, by homo- or heterolytic bond cleavage and extrusion of dinitrogen [51][54] to cyclopentane derivatives [55] (*Scheme 1*). A related transformation is illustrated by the oxidation with MnO_2 of *cis*-2-aminodihydro-1,3-diphenylisoindole (a *N,N*-disubstituted hydrazine) to yield 27% of *cis*-1,2-diphenylbenzocyclobutene [56]. A protected *N*-amino lactam **4**, ideally derived from the known ribonolactone derivative **2**, appeared a suitable intermediate for the synthesis of mannostatin A (**1**). We have recently communicated the successful implementation of this oxidation[6]), resulting in a new synthesis of **1** [58], and now we wish to provide experimental details and a full account on the oxidation of different *N*-aminoglyconolactams leading to cyclopentanes.

Scheme 1

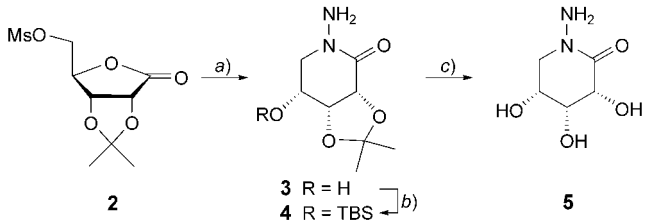


[5]) For leading references, see [47–52].

[6]) Based on the diploma work of *M. Zimmermann* [57], supervised by Dr. *C. V. Ramana*.

Results and Discussion. – 1. *Synthesis and Oxidation of the* N-*Amino-ribonolactam* **4**. Treatment of the known methanesulfonate **2** [59] with neat $NH_2NH_2 \cdot H_2O$ at room temperature led to the *N*-amino-ribonolactam **3** as the only product (*Scheme 2*); it was isolated by removing excess $NH_2NH_2 \cdot H_2O$ and hydrazinium methanesulfonate, and silylated to yield 85% of the (*tert*-butyl)dimethylsilyl (TBS) ether **4**. Deprotection of **3** provided **5** in a yield of 89%.

Scheme 2



a) $NH_2NH_2 \cdot H_2O$, 23°. *b*) TBSOTf, pyridine, CH_2Cl_2, 0°; 85% from **2**. *c*) THF/2N HCl 3 :1, 80°, 6 h; 89%.

The concept of the intended cyclopentane synthesis was tested by oxidizing the *N*-amino-ribonolactam **4** (*Scheme 3*). *t*-BuOCl provided the tetrazene **6** (63%) instead of the expected 1,2-diacyl-diazene [50] or of a cyclopentane derivative. It is known that tetrazenes are formed upon oxidation of hydrazines[7]) with $PhSeO_2H$ [61], $KBrO_3 \cdot HCl$ [62], $KMnO_4$ [63], Br_2 [64], MnO_2 [60], and other oxidants [55][65]. Tetrazenes are considered to result from the dimerization of diazenes (*N*-amino-nitrenes); **6** may, however, result from dimerization of an intermediate *N*-chlorohydrazide (X-philic substitution followed by elimination). When **4** was oxidized by *t*-BuOCl in the presence of DMSO to trap the expected diazene, the yield of **6** dropped to 12% and the lactam **7** resulting from deamination of **4** was isolated in a yield of 47%; no sulfoximine or cyclopentane was observed. The formation of deamination products upon oxidation of 1,2-disubstitued hydrazines is well precedented [63–65].

Oxidation of **4** with MnO_2 gave the lactam **7** (40%) as the sole product (*Scheme 3*), and oxidation with $PhSeO_2H$ in MeOH also afforded **7** (33%), together with the lactone **8** (22%; *Scheme 3*).

We next investigated the oxidation of **4** by $Mn(OAc)_3$ and $Cu(OAc)_2$ in MeOH at room temperature (*Scheme 3*). This oxidation gave **7** and the 1,2-diacylhydrazine **9** in 55 and 22% yield, respectively. The tetrazene **6** was not affected by these reaction conditions, and can be excluded as intermediate. The product **7** could, however, be formed *via* a tetrazane by elimination of a lactam anion. The simultaneously formed *N*-acyltriazenium cation may be deprotonated and oxidized; substitution at the N-atom of the ensuing *N*-acylated azide may lead to the diacylhydrazine **9**.

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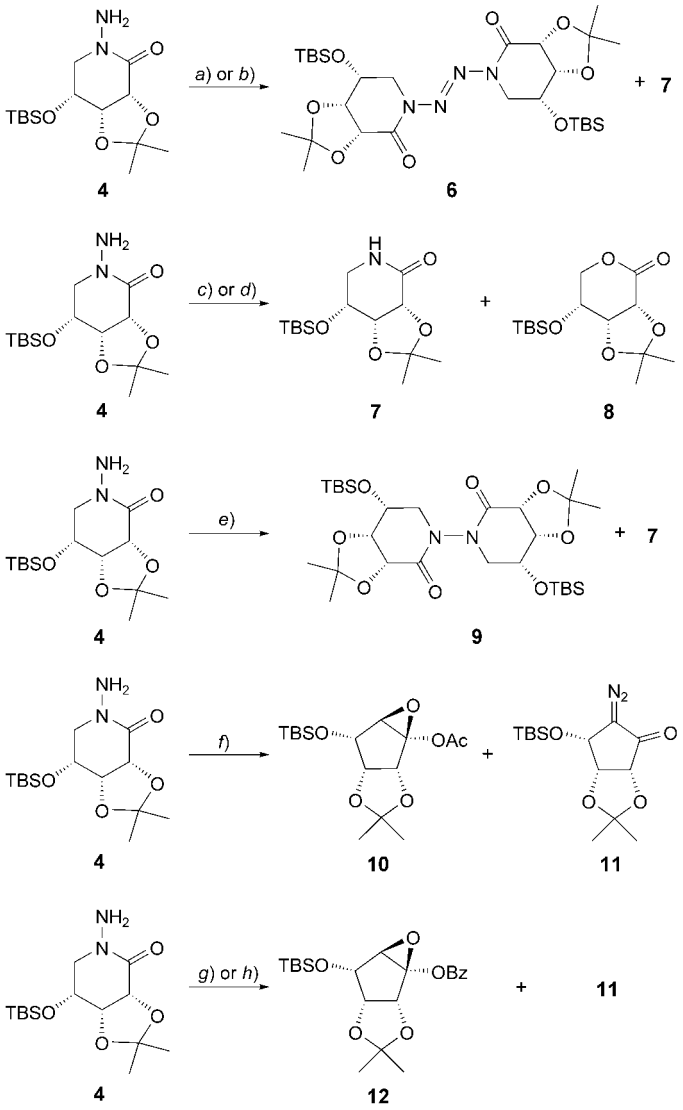
[7]) For leading references to the oxidation of N-containing compounds by metal compounds, see [49][60].

Scheme 3



a) *t*-BuOCl, 2,6-lutidine, THF, −78°, 1 h, then 23°, 12 h; 63% of **6**. *b*) *t*-BuOCl, 2,6-lutidine, DMSO, THF, −78°, 0.5 h, then 23°, 2 h; 47% of **7**, 12% of **6**. *c*) MnO_2, CH_2Cl_2, 23°, 24 h; 40% of **7**, 11% of **4**. *d*) $PhSeO_2H$, MeOH, 23°, 48 h; 33% of **7**, 22% of **8**. *e*) $Mn(OAc)_3 \cdot 2\,H_2O$, $Cu(OAc)_2 \cdot H_2O$, MeOH, 23°, 24 h; 55% of **7**, 22% of **9**. *f*) $Pb(OAc)_4$, for conditions and yields, see *Table 1*. *g*) $Pb(OBz)_4$, CH_2Cl_2, 23°, 1 h; 23% of **12**, 15% of **11**. *h*) $Pb(OBz)_4$, toluene, 23°, 2 h; 33% of **12**, 44% of **11**.

However, treatment of **4** with $Pb(OAc)_4$[8]) in CH_2Cl_2 gave a mixture of two cyclopentanes, the acetoxy epoxide **10** and the diazo ketone **11**, in a combined yield of 55% (*Scheme 3*). We cursorily examined[9]) the influence of the amount and the quality of $Pb(OAc)_4$ on the oxidation of **4**. The relative amount of $Pb(OAc)_4$ had no effect on the ratio **10**/**11** (1.8:1). Two equiv. of unpurified, commercial $Pb(OAc)_4$ were required to effect complete consumption of **4** within 1 h at 23 to 25°. As shown in *Table 1* (*Entries 1* and *5*), the quality of $Pb(OAc)_4$ influenced the result to a limited extent only. Three equivalents of commercial $Pb(OAc)_4$ were used to investigate the influence of the nature of the solvent and of the temperature. As shown in *Table 1*, the result of the oxidation depends upon the nature of the solvent, with benzene and toluene giving the best yields, reaching 47–49% of **10** and 26–30% of **11**. Increasing the temperature did not have a major influence on the yield of the acetoxy epoxide **10**, but lowered the yield the diazo ketone **11** (17% when the oxidation was performed at 110°; *Entry 11*) evidencing that the diazo ketone **11** and/or a crucial intermediate are not stable at higher temperatures. Oxidation on a gram scale (*Entry 12*) led to slightly improved yields. An attempt to intercept a diazene by performing the oxidation in the presence of DMSO yielded 25% of **10** and 28% of **11** besides 5% of the lactone **8**; no other products were observed.

Table 1. *Oxidation of the* N-*Aminolactam* **4** *with* $Pb(OAc)_4$

	4	$Pb(OAc)_4$	Solvent	Temp.	Time	Yield [%][a])	
Entry	[mg] ([mmol])	[g] ([mmol])	([ml])	[°]	[h]	**10**	**11**
1	105 (0.33)	0.443 (1.0)[b])	CH_2Cl_2 (4)	23	1.5	32.5	21
2	316 (1.0)	1.33 (3.0)[b])	CH_2Cl_2 (40)	23	1	33	21
3	316 (1.0)	1.33 (3.0)	CH_2Cl_2 (30)	−78	2	23	21.5
4	316 (1.0)	1.33 (3.0)	CH_2Cl_2 (30)	0	2	30	22
5	316 (1.0)	1.33 (3.0)	CH_2Cl_2 (30)	23	2	28	23
6	316 (1.0)	1.33 (3.0)	hexane (30)	23	12	32	13.5
7	316 (1.0)	1.33 (3.0)	cyclohexane (30)	23	2	38	18
8	316 (1.0)	1.33 (3.0)	benzene (30)	23	2	48	26
9	316 (1.0)	1.33 (3.0)	toluene (30)	23	2	47.5	26
10	316 (1.0)	1.33 (3.0)	toluene (30)	70	2	48	27
11	316 (1.0)	1.33 (3.0)	toluene (30)	110	2	45	17
12	3160 (10)	11.1 (25)	toluene (250)	23	2	48.5	29.5

[a]) Isolated yield. [b]) Purified by washing with Et_2O and drying *in vacuo*.

As expected, oxidation of **4** with $Pb(OBz)_4$ in CH_2Cl_2 provided the (crystalline) benzoyloxy epoxide **12** and the diazo ketone **11**, albeit in lower yields (**12**: 23%; **11**: 15%; *Scheme 3*). The yield of **12** and **11** was increased to 33 and 42%, respectively, by replacing CH_2Cl_2 with toluene.

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[8]) For leading references to the oxidation of N-containing compounds by $Pb(OAc)_4$ see [66–68].

[9]) A soln. of $Pb(OAc)_4$ (1, 1.5, 2, 2.5, and 3 equiv.) in CH_2Cl_2 (4 ml) was treated with a soln. of **4** (100 mg, 0.32 mmol, 1 equiv.) in CH_2Cl_2 (2 ml) at r.t. After 60 min, the mixture was worked up and analysed by ^{1}H-NMR to assess the ratio of starting material and products by integrating the H–C(5) signal of **4** and of the acetoxy phenoxide **10**, and the H–C(4) signal of the diazo ketone **11**.

The *N*-amino-ribonolactam **4** is characterized by a broad, D_2O-exchangeable *s* of two H at 4.46 ppm (exocyclic NH_2). The *N*-acyl moiety is evidenced by a ^{13}C *s* at 166.38 ppm, and six-membered *N*-aminolactam by a strong IR band at 1654 cm^{-1}. The structure of **3** and **4** was confirmed by X-ray analysis of the triol **5**[10]) (*Fig. 1*). The deprotected *N*-aminolactam **5** adopts a $^4H_3$ conformation in the solid state, which agrees well with the NMR data (D_2O solution). The NH_2 group is located in the mean plane of the lactam ring with one N*H* forming a H-bond to the carbonyl O-atom.

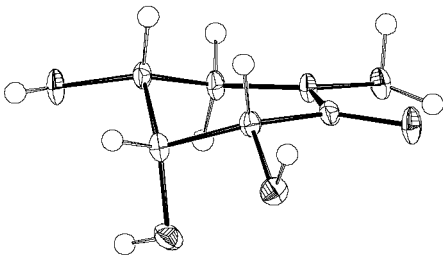

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Fig. 1. *Crystal structure of the* N-*amino-ribonolactam* **5**

The ^1H- and ^{13}C-NMR data of the lactam **7** could not be distinguished from those reported for its enantiomer [69]; the specific rotation of **7** is very similar, and of opposite sign. There is a single C=O band in the IR spectra of the *N*-amino lactam **4** (1654), the lactam **7** (1681), the tetrazene **6** (1693), and the lactone **8** (1757); two bands (1675 and 1701 cm^{-1}) are found in *N*,*N*′-diacylhydrazine **9**. There are no NH bands in the IR spectra of **6**, **8**, and **9**. The NMR spectra of **6** and **9** show *J*(2,3), *J*(3,4), *J*(4,5), and *J*(4,5′) values similar to those of **4** and **7** (see *Table 2* in *Exper. Part*), and the NMR data of **4**, **6**, **7**, and **9** reveal a 2,3-*O*-isopropylidene-4-*O*-silyl-1,5-ribonolactam substructure. The MALDI mass spectra show $[M+Na]^+$ and $[M+H]^+$ peaks of **7** at *m*/*z* 324 and 302, respectively, corresponding peaks of **6** at *m*/*z* 651 and 623, and of **9** at *m*/*z* 623 and 601, suggesting that **6** and **9** are *N*-aminoribonolactam-derived dimers. The tetrazene and bislactamyl structure was confirmed by elemental analysis. The crystal structure of **6**[10]), co-crystallizing with two molecules of cyclohexane, was established by a low-temperature X-ray analysis (*Scheme 3* and *Fig. 2*). The conformation of both ribonolactam rings of **6** is $B_{1,4}$, in agreement with a *J*(2,3) value of 7.2 Hz that is also observed for **3**, **4**, and **7**–**9**. The two C=O groups and the four N-atoms are in the same plane. Compared to the parent tetrazene N_4H_4, the bond lengths for N=N and N–N in **6** change from 1.205 and 1.429 Å in N_4H_4 [70] to 1.258 and 1.381/1.375 Å, respectively, in agreement with values of other tetrazenes [71]. The N–N bonds are also shorter than those in the *N*-aminoribonolactam **5** (1.429 Å). The C=O bond lengths of **6** (1.190/1.199 Å) are in the normal range, and the N–C(sp^2) bond (1.392/1.389 Å) is shorter than the N–C(sp^3) bond (1.473/1.477 Å).

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[10]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-235432 (**5**), CCDC-235433 (**6**), CCDC-235434 (**8**), CCDC-235435 (**12**), CCDC-202048 (**29**), CCDC-235436 (**56**), and CCDC-235437 (**59**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

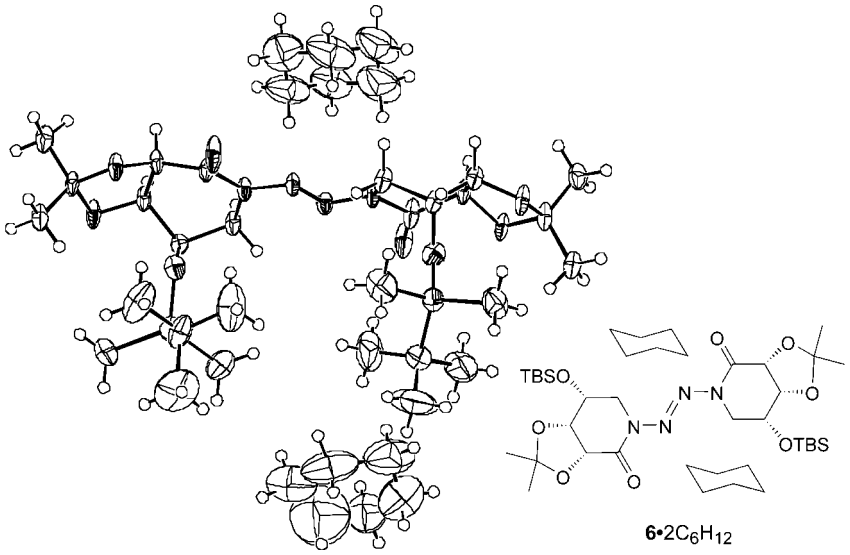


Fig. 2. *Crystal structure of the ribono-tetrazene* **6** · *2* C_6H_{12}

The structure of the ribono-1,5-lactone **8** was originally reported for a compound prepared by *Saburi et al.* [72], but the ^{1}H- and ^{13}C-NMR spectra of **8** differ from those reported by these authors. Analysis of the original data suggested that the reported compound, showing a typical 1,4-lactone IR band at 1776 cm^{-1}, is the corresponding ribono-1,4-lactone [73], evidenced by $J(2,3) = 5.6$ Hz, and the absence of coupling between H–C(3) and H–C(4). The NMR data of this 1,4-lactone agree indeed with those reported by *Saburi et al.* [72]. The ribono-1,5-lactone structure of **8** is evidenced by a strong IR band at 1757 cm^{-1}, and its crystal structure was subsequently established by X-ray analysis[10]) (*Fig. 3*).

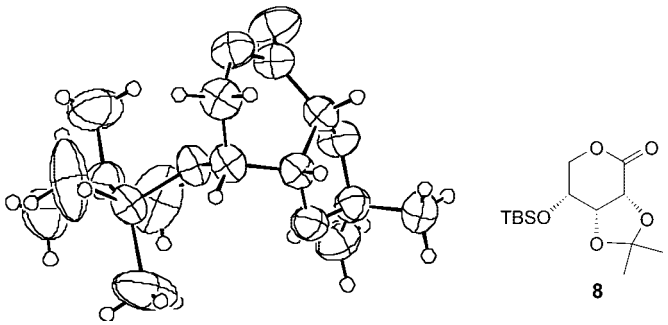


Fig. 3. *Crystal structure of the ribono-1,5-lactone* **8**

The $[M + Na]^+$ peak at *m*/*z* 429.1703 and the combustion analysis evidence the elemental composition $C_{21}H_{30}O_6Si$ of the acetoxy epoxide **10.** The two *s* at 1.49 and 1.36, the *s* at 0.92, and the *s* at 0.12 ppm evidence that the **10** possesses the dimethyl-1,3-dioxolanyl and the silyloxy moieties. A strong IR band at 1779 cm^{-1}, a *s* at 2.15 ppm,

and a ^{13}C *s* at 169.43 ppm evidence an activated AcO group, suggesting the structure of an acetoxy epoxide. A *dd* at 5.01 ppm ($J = 5.3$, 1.0 Hz) and the *td* at 4.41 ppm ($J \approx 5.4$, 1.0 Hz) were assigned to H–C(2) and H–C(3), respectively; a *d* ($J = 5.6$ Hz) resonating at 3.94 ppm was assigned to H–C(4), geminal to the silyloxy group, and a *t* at 3.74 ppm ($J = 1.0$ Hz) to H–C(5). A NOE (6.6%) between the *dd* at 5.01 and the *td* at 4.41 ppm and a NOE (5.7%) between the *td* at 4.41 and the *d* at 3.94 ppm evidence that H–C(2), H–C(3), and H–C(4) are *cis* to each other, while a small NOE of 2.8% between the *d* at 3.94 and the *t* at 3.74 ppm is agreement with the *trans*-orientation of H–C(4) and H–C(5). The analogous benzoyloxy epoxide **12** shows similar NMR spectra (see *Table 3* in *Exper. Part*) except for the signals of the BzO group replacing those of the AcO group. X-Ray analysis established the crystal structure of **12**[10]) (*Fig. 4*), and indirectly the one of **10**. It shows the *endo*-orientation of the BzO group relative to the dioxabicyclo[3.3.0]octane system, the *exo*-orientation of the epoxide O-atom, and the proximity of the oxirane and the carbonyl O-atoms. The diazo ketone substructure of **11** is evidenced by strong IR bands at 2102 and 1679 cm^{-1}, and by a ^{13}C *s* at 191.06 ppm, and confirmed by a comparison of its NMR data with those of the *lyxo*-configured diazo ketone **53** (see *Table 3* in *Exper. Part*).

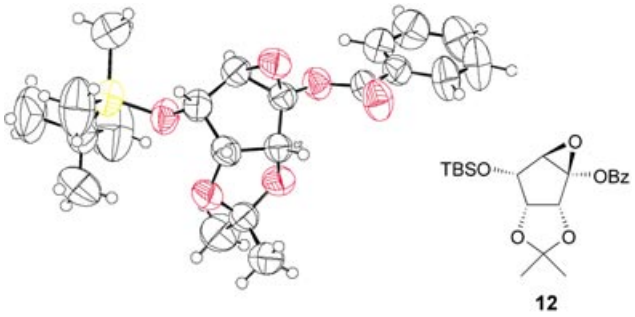


Fig. 4. *Crystal structure of the benzoyloxy epoxide* **12**

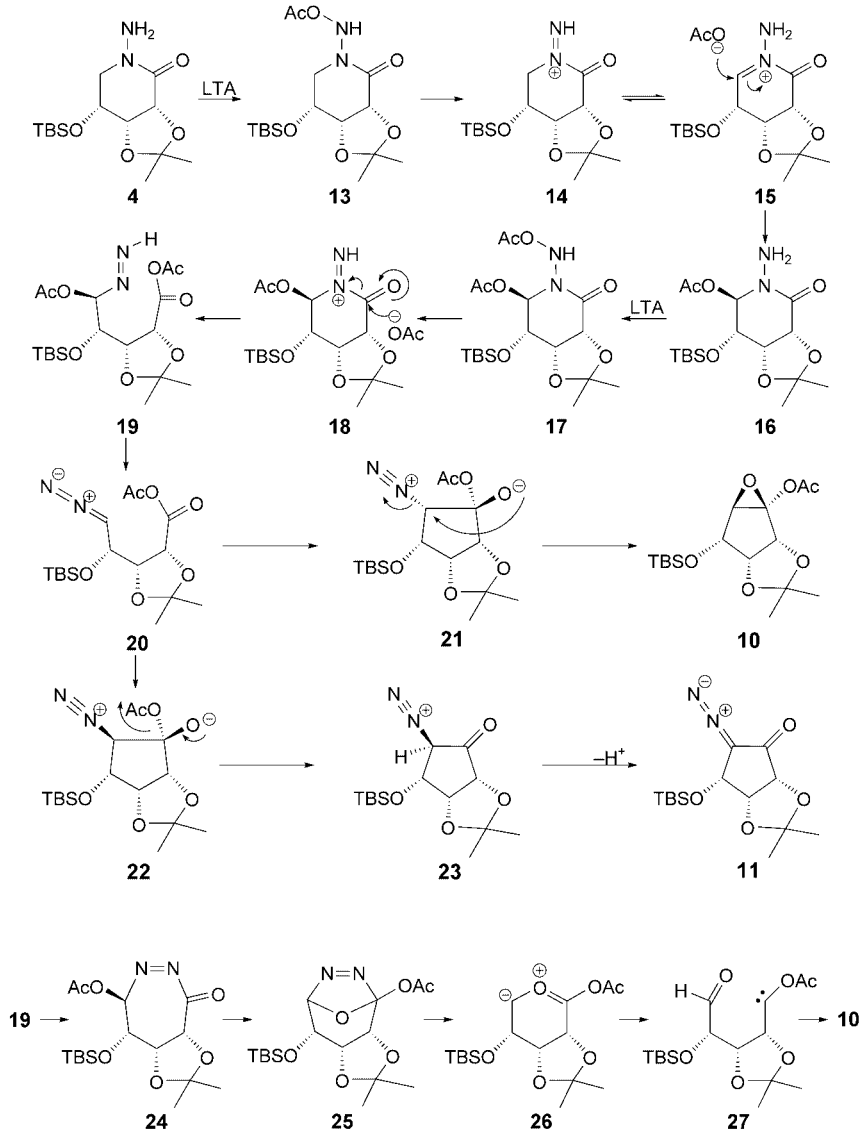
A hypothetical reaction mechanism for the transformation of **4** into **10** and **11** is formulated in *Scheme 4*. According to it, the *N*-aminolactam **4** is first acetoxylated to the *N'*-acetoxy-*N*-amino lactam **13**. Such acetoxylations are well precedented [52][74]. Elimination of the AcO group generates the diazenium cation **14** [75]. Alternatively, substitution of an AcO ligand of $Pb(OAc)_4$ by **4**, followed by elimination of $Pb(OAc)_2$ and AcOH, would also generate **14**. Isomerization of **14** leads to the *N*-acyl-*N*-amino immonium cation **15**. This sequence is in keeping with the fruitless attempt to intercept a nitrene (diazene) with DMSO and also with the results of AM1 calculations according to which the cation **15** is more stable (in the gas phase) by 11.8 kcal/mol than the isomer **14**[11]). (Formal) addition of acetate to **15** leads to the acetoxylated *N*-amino lactam **16**. A second *N*-acetoxylation/elimination (or substitution of AcO^- of $Pb(OAc)_4$, as above) transforms **16** to **17**, and further to **18** that reacts with AcOH (or acetate) to form the anhydride **19**. Most probably, heterolysis of the C–OAc bond then generates

[11]) We thank Dr. *Bruno Bernet* for these calculations.

the diazoanhydride **20** [67]. Intramolecular nucleophilic addition to the activated C=O group is hypothesized to lead to the two diastereoisomeric diazonium salts **21** and **22**. The configuration of the acetoxylated stereogenic C-atom results from the constraints of the *Bürgi–Dunitz* trajectory and of the reactive conformation of the α-alkoxy carbonyl moiety (RO in π-plane of the C=O group [76]). The conformation of the second stereogenic C-atom results from the reacting conformers resulting from rotation about the C(4)–C(5) bond of **20**. The diastereoisomer **21**, characterized by the *trans*-orientation of the nucleophilic oxy and the leaving groups, will form the acetoxy epoxide **10**. The analogous *cis*-configurated **22** cannot undergo substitution; elimination of acetate and deprotonation will lead to the diazo ketone **11** [77]. Two alternative pathways were considered. The azo compound **19** might be *N*-acylated to generate **24** and, hence, the dihydro-oxadiazole **25** [78][79]. Such transformations were well-studied for open-chain analogues [79][80], and the oxidation of acyclic *N*-acylhydrazones with $Pb(OAc)_4$ to Δ^3-1,3,4-oxadiazolines has been reviewed several times [67][68]. Loss of dinitrogen from **25** leads to the acetoxylated carbonyl ylide **26** [81]. A thermally allowed conrotatory electrocyclization of **26** can, however, be excluded, as it would lead to a *trans*-oxirane [82]. Fragmentation of the carbonyl ylide [83] to form a nucleophilic carbene **27** [84], followed by intramolecular nucleophilic addition of the acetoxy carbene center to the C=O group in **27**, would also lead to the acetoxy epoxide **10** [85]. This mechanism cannot be rigorously excluded. It should be noted the *endo*-acetoxy epoxide **10** is more stable (in the gas phase) by 2.38 kcal/mol than its diastereoisomer possessing an *exo*-oriented AcO group (AM1 calculations).

2. *Synthesis of Mannostatin A.* The synthesis started with the $LiAlH_4$ reduction of the acetoxy epoxide **10** to the *trans*-diol **28** (81%; *Scheme 5*). A H-bond between the *endo*-oriented HO–C(1) and O–C(2), evidenced by a *J*(H,OH) value of 9.7 Hz, should enhance the nucleophilicity of HO–C(1) and favour a regioselective acylation. Indeed, benzoylation of **28** by BzCl and TMEDA at $-40°$ gave a mixture of a monobenzoate **30** (67%) and a dibenzoate **29** (26%). Crystal structure analysis (*Fig. 5*) of the dibenzoate **29**[10]**)** established the configuration of **29** and **28**, and provided further evidence for the structure of **10**. Triflation of **28** at $-60°$ proceeded selectively to provide the monotriflate **31** (91%) which was mesylated to yield 99% of **32**. Treating **32** with excess NaSMe in THF gave the mesyloxy thioether **33** (95%). Substitution of the MsO group by azide did not proceed at room temperature, and increasing the temperature led to elimination. Desilylation of **33** at room temperature provided both the alcohol **35** and the epoxide **34**, while desilylation at $-30°$ yielded only the alcohol **35** (99%). Treating **35** with Cl_3CCN in the presence of DBU led in high yields to the trichloroacetimidate **36**. Cyclization of isolated **36** in the presence of $EtN(i\text{-}Pr)_2$ provided the dihydrooxazole **37** in a rather low yield, while treating the alcohol **35** sequentially with Cl_3CCN, DBU, and $EtN(i\text{-}Pr)_2$ yielded 80% of the desired dihydrooxazole **37** besides 13% of the trichloroacetamide **36**. The dihydrooxazole **37** was hydrolysed with HCl in MeOH to afford the hydrochloride of mannostatin A (**1**·HCl) [6]. Its ^{1}H- and ^{13}C-NMR spectra, and its specific rotation are in agreement with published data [39][42][44][45]. Acetylation of **1**·HCl provided the known tetraacetate **38** [6]. Its melting point and its ^{1}H- and ^{13}C-NMR data are in agreement with the literature [6][39][42][43], and its specific rotation corresponds to the highest published value [42]. The free base **1** was obtained by ion-exchange chromatography

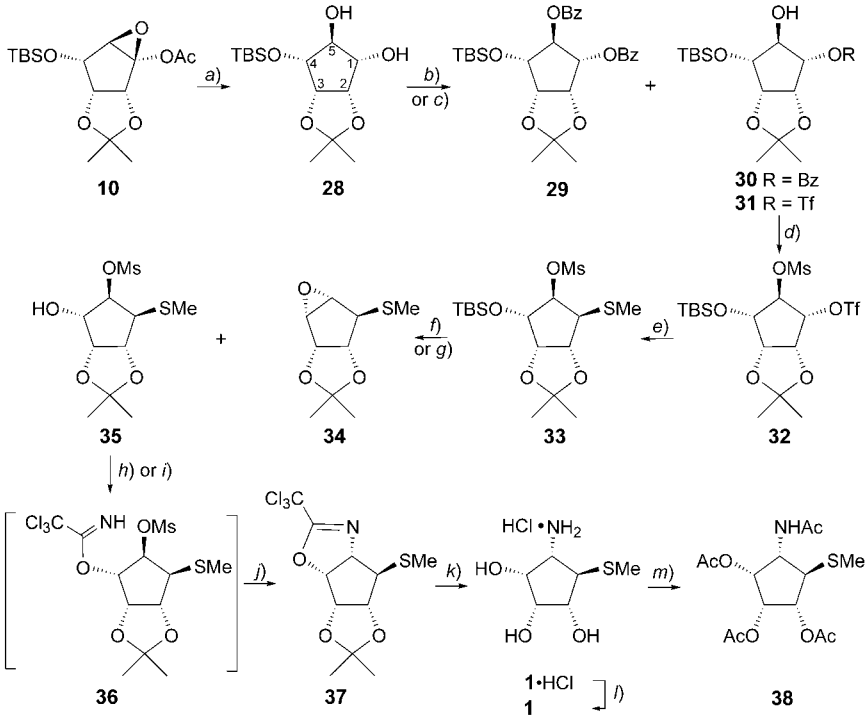
Scheme 4. *Hypothetical Reaction Mechanisms for the Transformation of* **4** *into the Acetoxy Epoxide* **10** *and the Diazo Ketone* **11**



of **1** · HCl on *Amberlite IR-120* (H^+) resin with 0.5N aqueous NH_3 as eluent; it inhibited jack bean α-mannosidase with an IC_{50} of 48 nM ([7]: $IC_{50} = 70$ nM).

For **28**, two D_2O exchangeable H (2.63 and 2.46 ppm) and the broad IR band at 3540 cm^{-1} reveal two OH groups Their *trans*-configuration is evidenced by the H–C(5) *td* at 3.88 ppm ($J \approx 9.0$, 2.2 Hz) and the D_2O exchangeable HO–C(1) *d* at 2.63 ppm

Scheme 5



a) $LiAlH_4$, THF, 0°, 0.5–1 h; 81%. *b*) BzCl, TMEDA, CH_2Cl_2, −40°, 30 h; 26% of **29**, 67% of **30**. *c*) Tf_2O, pyridine, CH_2Cl_2, −60°, 3 h; 91% of **31**. *d*) Ms_2O, pyridine, CH_2Cl_2, 0°, 3 h; 99%. *e*) NaSMe, 15-crown-5, THF, 23°, 2 h; 95%. *f*) TBAF, THF, 0°, 5 min; 30% of **34**, 66% of **35**. *g*) TBAF, THF, −30°, 2 h; 99% of **35**. *h*) Cl_3CCN, DBU, CH_2Cl_2, 23°, 1 h; 100% of **36**. *i*) Cl_3CCN, DBU, xylene, 23°, 2 h, then $EtN(i\text{-}Pr)_2$, 110°, 12 h; 13% of **36**, 80% of **37**. *j*) $EtN(i\text{-}Pr)_2$, xylene, 110°, 24 h; 33%. *k*) 7N HCl/MeOH 1:1, 23°; 94–98%. *l*) *Amberlite IR-120* (H^+); 80%. *m*) Ac_2O, pyridine; 93% from **37**.

($J = 9.7$ Hz). The structure of the monobenzoate **30** is evidenced by the downfield shift of the H–C(1) *dd* (4.72 ppm), the downfield shift for the C(1) *d* (75.96 ppm), the upfield shift for the C(2) *d* (74.23 ppm) and the C(5) *d* (76.75 ppm). The monotrifluoroacetylation at *O*-C(1) of **28** leads to a downfield shift for H–C(1) and C(1) of **31**, resonating at δ 4.61 and 86.58 ppm, respectively. Mesylation to **32** is evidenced by a downfield shift for H–C(5) (5.14 ppm) and for C(5) at 83.53 ppm. The formation of the thioether **33** is evidenced by a *s* at 3.08 ppm for the MsO group, a *s* at 2.23 ppm (MeS), a *dd* at 3.34 ppm for H–C(1), and a *d* at 50.39 ppm for C(5). A *d* each at 3.58 and 3.62 ppm for **34** and two ^{13}C *d* at 58.37 and at 61.59 ppm evidence the formation of an oxirane ring. Formation of the imidate **36** is denoted by a strong IR absorption at 1669 cm^{-1}, a broad *s* at 8.52 ppm, and a ^{13}C *s* at 161.08 ppm. The dihydrooxazole **37** is characterized by a strong IR band at 1653 cm^{-1} and by the absence of NH and MsO signals; the assignment of ^1H-NMR signals is based on homonuclear irradiation experiments (see *Exper. Part*).

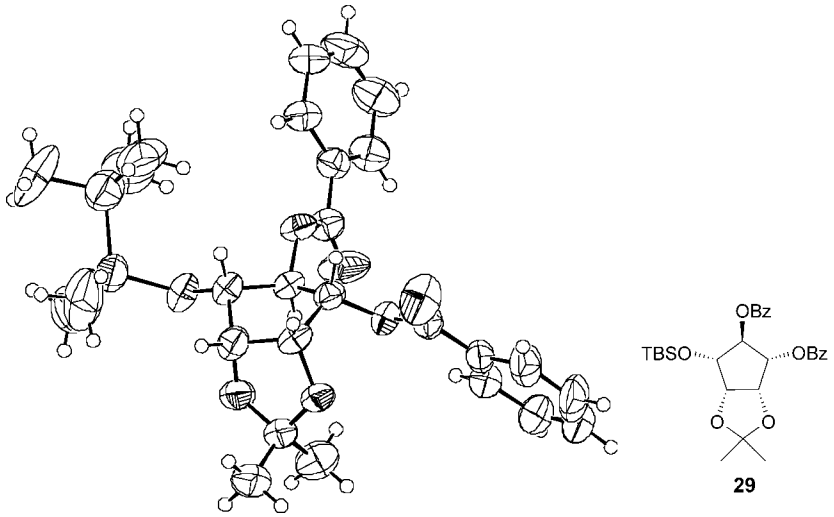
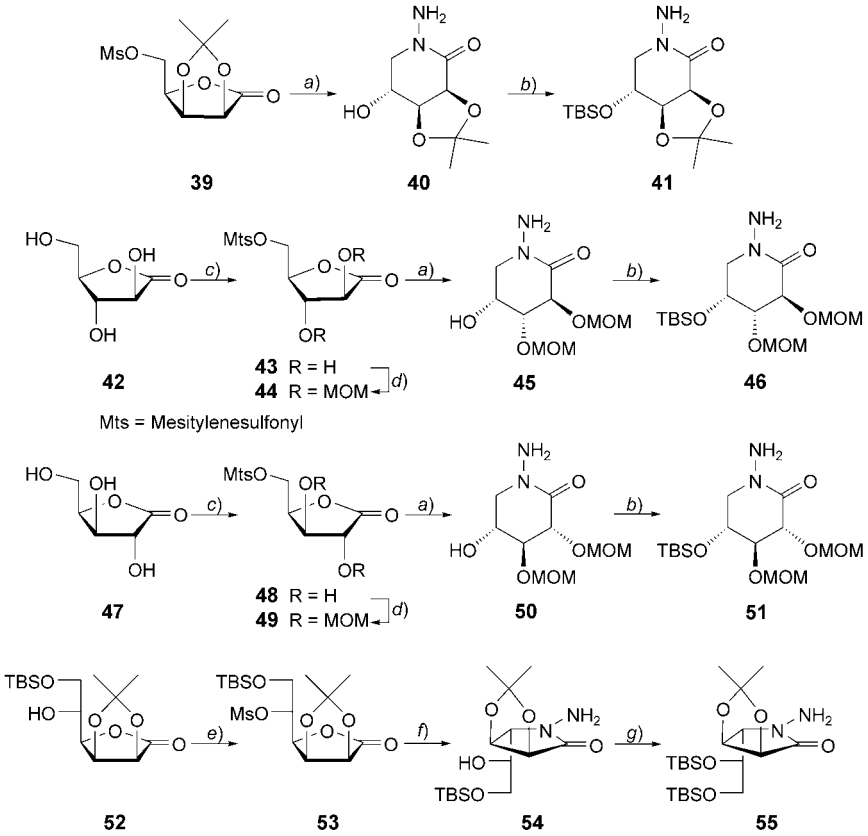


Fig. 5. *Crystal structure of the dibenzoate* **29**

3. *Synthesis and Oxidation of the* N-*Amino*-D-*lyxono*-, -D-*arabino*-, -D-*xylono*-, *and* -D-*mannonolactams* **41**, **46**, **51**, *and* **55**. We briefly tested the scope of the transformation of *N*-amino lactams into cyclopentane derivatives by oxidizing the *N*-amino lactams **41**, **46**, **51**, and **55** with $Pb(OAc)_4$. These amino lactams were obtained from the lactones **39**, **44**, **49**, and **53**, respectively, by a similar route as described for the synthesis of **4**. The D-lyxonolactone **39** was prepared according to *Pedersen* and co-workers [59]. The arabino- and xylonolactones **44** and **49** were synthesized from the known lactones **42** and **47** [86]. Regioselective mesitylenesulfonylation of **42** yielded 69% of the D-arabinolactone **43**; similarly, mesitylenesulfonylation of **47** resulted in 62% of the D-xylonolactone **48** (*Scheme 6*). Methoxymethylation of **43** and **48** provided the desired protected lactones **44** (86%) and **49** (78%). The D-mannonolactone **53** was prepared by mesylating **52** [87].

Exposure of the lyxonolactone **39** to hydrazine hydrate gave the *N*-amino-lyxono-1,5-lactam **40**, which was protected as the TBS ether **41** (64% from **39**). Similarly, **44** gave the *N*-aminopiperidinone **45** and the corresponding silyl ether **46** (81%). In the same way, **49** was transformed into **50** and further into **51** (85%). However, treatment of **53** with $NH_2NH_2 \cdot H_2O$ at 23° and then at 60°, followed by silylation, gave the crystalline *N*-aminopyrrolidinone **55** (92% from **53**). The L-*allo* configuration of **54** and **55** evidences that hydrazinolysis of the lactones is accompanied by formation and then regioselective opening of an epoxide. These transformations find a precedent in the hydrazinolysis of ethyl 5-bromopentanoate that provided exclusively *N*-amino-pentane-1,5-lactam [47] and in the ammonolysis of lactones possessing a suitably located leaving group leading to lactams [88]. These results are consistent with the hypothesis that excess ammonia or hydrazine promotes an intramolecular nucleophilic attack by the N-center of the amide moiety, presumably by progressive deprotonation of the acylamino group, while neutral, or acidic conditions promote a nucleophilic attack by the O-center of the amide moiety [89]. In addition, the position of the amide/

Scheme 6



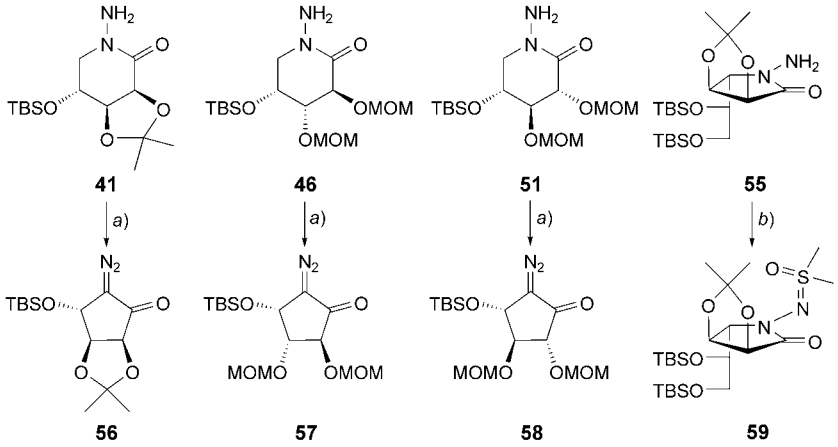
a) $NH_2NH_2 \cdot H_2O$, 23°. *b*) TBSOTf, pyridine, CH_2Cl_2, 0°; 64% of **41** from **39**, 81% of **46** from **44**, 85% of **51** from **49**. *c*) MtsCl, pyridine, 0–23°; 69% of **43**, 62% of **48**. *d*) $CH_2(OMe)_2$, P_2O_5, 23°; 86% of **44**, 78% of **49**. *e*) MsCl, pyridine, CH_2Cl_2, 0–23°, 13 h; 80%. *f*) $NH_2NH_2 \cdot H_2O$, 23°, 14 h, 60°, 3 h; 97%. *g*) TBSOTf, pyridine, CH_2Cl_2, 0°, 1 h, 23°, 24 h; 95%.

hydroxy imine equilibrium of *N*-acylhydrazines may be more strongly shifted towards the imine form than the one of amides, considering that the pK_{HA} of *N*-acylhydrazines (dissociation of C(O)NH) is lower by *ca.* 2 pK units than the one of amides [90]; this also would favour nucleophilic attack by N rather than by O.

Treatment of the amino lactam **41** in toluene with excess $Pb(OAc)_4$ under the conditions optimized for the oxidation of **4** provided the diazo ketone **56** (37%) as the only conveniently isolated product (*Scheme 7*). Similarly, **46** and **51** provided only the diazo ketones **57** (22%) and **58** (25%). Oxidation of the *N*-aminoallono-1,4-lactam **55**, however, led to generation of a purple colour that disappeared within a few minutes. The ^{1}H-NMR spectrum of the crude was in keeping with a mixture of two major products that could not, however, be isolated by column chromatography. These observations suggested the intermediate formation of a diazene. In keeping with this, oxidation of **55** with $Pb(OAc)_4$ in the presence of DMSO led to the crystalline

sulfoximine **59** (54%). These results show the strong influence of the structure of the *N*-amino lactams and of the reaction conditions on the course of the reaction. Further studies are ongoing.

Scheme 7



a) $Pb(OAc)_4$, toluene, 23°, 1 h; 37% of **56**, 22% of **57**, 25% of **58**. *b*) $Pb(OAc)_4$, toluene, DMSO, 0°, 2 h; 54%.

The *N*-amino lactams **41**, **46**, and **51** show a strong C=O band at 1650–1660 cm^{-1}, a broad D_2O exchangeable *s* (2 H) around 4.4 ppm, and a ^{13}C *s* at *ca.* 166–168 ppm. A strong IR band at 1718 cm^{-1}, a broad D_2O exchangeable *s* (2 H) at 3.94 ppm, and a ^{13}C *s* at 169.45 ppm suggest that **55** is a five-membered *N*-amino 1,4-lactam.

The L-*allo* configuration of **54** and **55** was deduced from a comparison of the small $J(3,4) = 0$ and $J(4,5) = 1.2$ Hz with the corresponding *J* values of the D-*manno*-configured **52** ($J(3,4) = 2.5$, $J(4,5) = 8.1$ Hz) and confirmed by transforming **55** into **59** whose crystal structure was established by X-ray analysis (see *Fig. 7*). The diazo ketone moiety of **56**–**58** is evidenced by IR bands around 2100 cm^{-1} and three ^{13}C *s* at 192.94, 192.00, and 190.93 ppm, respectively. The structure of the diazo ketone **56** was established by X-ray analysis[10]) (*Fig. 6*). The atoms of the diazo ketone subunit lie in the same plane and the bond lengths (O=C–C=N=N: 1.224/1.425/1.316/1.130 Å) agree well with those of [(benzyloxy)carbonyl]-3-diazopyrrolidin-2-one (1.222/1.437/1.301/1.130 Å) [91], possessing a longer C=O bond than that of a trimethyltin diazoacetate ester (1.196/1.446/1.317/1.119 Å) [92]. The small coupling of 0.6 Hz between a *d* at 5.23 ppm and a *dd* at 4.43 ppm in the ^1H-NMR spectrum of **56** is in agreement with the H(4)–C(4)–C(3)–H(3) torsion angle ($\theta \approx 85°$) of the crystal structure. Similarly, a H–C(4) *d* was observed at 5.33 ppm for **11**, at 5.28 ppm for **57**, and at 5.09 ppm for **58** (see *Table 3* in *Exper. Part*). The constitution of the sulfoximine **59** is evidenced by the elemental analysis and by two *s* at 3.20 and 3.14 ppm and two ^{13}C *q* at 40.83 and 40.14 ppm, and the L-*allo* configuration is evidenced by a large $J(2,3)$ value of 6.2 Hz and by the H–C(4) *s* at 3.98 ppm. The crystal structure of **59** was established by X-ray analysis[10]) (*Fig. 7*), which also allows to assign the L-allono-configuration to **55**.

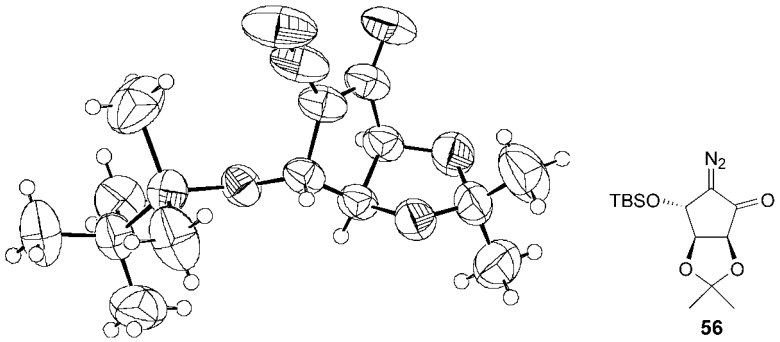


Fig. 6. *Crystal structure of the diazo ketone* **56**

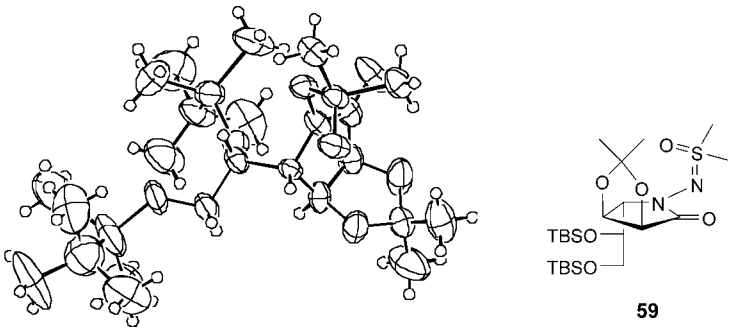


Fig. 7. *Crystal structure of the sulfoximine* **59**

We thank Dr. *B. Schweizer* for the crystal-structure determination, Dr. *B. Bernet* for checking the *Exper. Part*, and the *Swiss National Science Foundation* and *F. Hoffman-La Roche AG*, Basel, for generous support.

Experimental Part

General. Unless specified otherwise, reactions were carried out under a N_2 atmosphere. Solvents were removed under reduced pressure (rotatory evaporator). CH_2Cl_2 was distilled over CaH_2 and THF was distilled over Na/benzophenone immediately before use. DMF was dried over 4-Å molecular sieves. Et_3N was distilled over CaH_2 and stored over 4-Å molecular sieves. Organic phases were dried with $MgSO_4$. TLC: *Merck* silica gel *60F-254* plates; detection with UV and/or by heating with 'mostain' (400 ml of 10% H_2SO_4 soln., 20 g of $(NH_4)_6Mo_7O_{24}\cdot 6\,H_2O$, 0.4 g of $Ce(SO_4)_2$). Melting points are uncorrected. Optical rotations $[\alpha]_D^{25}$ were determined at 589 nm. UV spectra were taken in a 1-cm cell at 25° in the range of 200 to 800 nm (log ε values in parenthesis). IR Spectra were recorded on a *Perkin-Elmer 298* FT-IR spectrometer. NMR spectra were recorded at 200 or 300 MHz apparatus using $CDCl_3$ as the solvent. Crystal structures were analysed by the direct method (*SIR 97*), and non-H-atoms were refined anisotropically with SHELX-97.

5-Deoxy-5-hydrazino-2,3-O-*isopropylidene*-D-*ribono-1,5-lactam* (**3**). A suspension of *2,3*-O-*isopropylidene-5*-O-*(methylsulfonyl)-ribono-1,4-lactone* (**2**) [59] (2.66 g, 10 mmol) in $NH_2NH_2\cdot H_2O$ (4 ml) was stirred at 23° for 6 h. The resulting clear soln. was co-evaporated with toluene (2×300 ml). A soln. of the residue in CH_2Cl_2 (150 ml, formation of some crystals) was dried and evaporated to afford **3** (2.02 g, quant.). Colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 4.48 (br. *s*, exchange with D_2O, NH_2); 2.75–2.35 (br. *s*, HO–C(4), exchange with D_2O); 1.51, 1.42 (2*s*, Me_2C). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 111.10 (*s*, Me_2C); 26.60, 24.87 (2*q*, *Me*$_2$C). ESI-MS: 241 (23, $[M+K]^+$), 225 (100, $[M+Na]^+$), 203 (4, $[M+H]^+$).

Table 2. *Selected ^1H- and ^{13}C-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *for the* N-*Amino-ribonolactams and for the Oxidation Products of* **4** *in* $CDCl_3$

	3	**4**	**5**[a])	**6**	**7**	**8**	**9**
H–C(2)	4.59	4.47	4.29	4.65	4.42–4.34	4.57	4.54
H–C(3)	4.53	4.39	4.26–4.21	4.48	4.42–4.34	4.48	4.47–4.36
H–C(4)	4.10	4.12	4.26–4.21	4.22	4.09	4.17	4.47–4.36
H–C(5)	3.73	3.76	3.65	4.09	3.52	4.35	3.75
H′–C(5)	3.59	3.41	3.54	3.89	3.13	4.09	3.43
J(2,3)	7.9	5.9	3.1	7.2	[b])	8.4	6.5
J(3,4)	3.4	1.9	[b])	2.5	1.9	3.3	[b])
J(4,5)	7.5	9.3	6.4	7.8	9.0	6.3	8.4
J(4,5′)	3.4	4.3	10.6	3.1	4.4	1.8	4.0
J(5,5′)	12.8	11.8	11.4	13.4	11.8	11.4	11.2
	3	**4**	**5**[a])	**6**	**7**	**8**	**9**
C(1)	165.80	166.38	172.07	165.50	170.18	168.53	165.46
C(2)	73.48	73.81	71.06	75.70[c])	73.69	72.39	74.02
C(3)	75.39	76.68	73.79	74.55[c])	76.17	75.00	76.37
C(4)	64.26	65.72	66.57	65.03	66.46	67.86	65.51
C(5)	51.82	52.11	54.44	46.24	42.79	64.92	50.26

[a]) In D_2O. [b]) Not assigned. [c]) Assignments may be interchanged.

4-O-*[(*tert-*Butyl)dimethylsilyl]-5-deoxy-5-hydrazino-2,3*-O-*isopropylidene*-D-*ribono-1,5-lactam* (**4**). (*tert*-Butyl)dimethylsilyl trifluromethanesulfonate (TBSOTf; 18 ml, 75 mmol) was added over 10 min to a soln. of **3** (10.1 g, 50 mmol) in CH_2Cl_2 (100 ml) and pyridine (30 ml) at 0°. The mixture was stirred for 1 h at 0° and for 10 h at 23°, treated with H_2O (100 ml), and extracted with CH_2Cl_2 (3 × 150 ml). The combined org. phases were dried and evaporated. FC (cyclohexane/AcOEt 1:1) and crystallization from hexane gave **4** (13.5 g, 85%). White crystals. M.p. 105–105.5° (hexane). R_f (cyclohexane/AcOEt 1:2) 0.33. $[\alpha]_D^{25} = -6.9$ ($c = 0.61$, $CHCl_3$). IR ($CHCl_3$): 3321*w*, 3030*w*, 2956*m*, 2933*m*, 2899*w*, 2860*m*, 1654*s*, 1616*m*, 1472*m*, 1384*m*, 1376*m*, 1260*s*, 1231*m*, 1166*m*, 1134*s*, 1096*m*, 1088*m*, 1053*w*, 988*w*, 881*s*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 4.46 (*s*, exchanged with D_2O, NH_2); 4.39 (br. *dd*, $J \approx 5.9, 1.9$, addition of D_2O and irrad. at 3.41 → sharp *dd*, $J =$ 6.2, 2.5, H–C(3)); 1.43, 1.39 (2*s*, Me_2C); 0.90 (*s*, Me_3C); 0.12, 0.11 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*, additionally, 111.22 (*s*, Me_2C); 27.17, 25.57 (2*q*, *Me*$_2$C); 26.00 (*q*, *Me*$_3$C); 18.45 (*s*, Me$_3$*C*); −4.35, −4.45 (2*q*, Me_2Si). MALDI-MS: 339 (35, $[M + Na]^+$), 317 (75, $[M + H]^+$). Anal. calc. for $C_{14}H_{28}N_2O_4Si$ (316.47): C 53.13, H 8.92, N 8.85; found: C 53.39, H 8.86, N 8.86.

5-Deoxy-5-hydrazino-D-*ribono-1,5-lactam* (**5**). A soln. of **3** (800 mg, 3.96 mmol) in THF/2N HCl 3:1 (30 ml) was boiled under reflux at 80° for 6 h, concentrated to 1/4 of its volume, and filtered through a small column packed with *Amberlite IRA-910* (HCO_3^- form, elution with H_2O). Lyophilization gave **5** (560 mg, 89%), which was recrystallized in H_2O/EtOH. Colourless crystals. M.p. 150–151° (H_2O/EtOH). $[\alpha]_D^{25} = +59.5$ ($c = 1.0$, H_2O). p$K_a = 6.91$. IR (KBr): 3469*s*, 3319*s*, 3258*s*, 2911*m*, 2862*s*, 1628*s*, 1587*s*, 1510*m*, 1469*m*, 1413*m*, 1359*m*, 1327*m*, 1290*m*, 1272*s*, 1250*m*, 1227*m*, 1207*m*, 1152*s*, 1125*m*, 1109*s*, 1055*s*, 982*m*, 944*s*, 906*w*, 835*m*. ^{1}H-NMR (300 MHz, D_2O): see *Table 2*, additionally, 4.26–4.21 (*m*, H–C(3), H–C(4)). ^{13}C-NMR (75 MHz, D_2O): see *Table 2*. EI-MS: 162 (100, M^+). Anal. calc. for $C_5H_{10}N_2O_4$ (162.14): C 37.04, H 6.22, N 17.28; found: C 37.29, H 6.25, N 17.16.

Crystal Structure of **5**. Recrystallization of **5** in H_2O/MeOH/Et_2O gave crystals suitable for X-ray analysis: $C_5H_{10}N_2O_4$ (162.14); orthorhombic $P2_12_12_1$; $a = 6.438$ (6) Å, $b = 7.916$ (4) Å, $c = 13.256$ (6) Å, $\beta = 90°$; $V = 675.6$ (8) Å^3; $D_{calc.} = 1.594$ Mg/m^3; $Z = 4$. From a crystal of size 0.30 × 0.25 × 0.20 mm, 1156 reflections were measured on an *Enraf Nonius CAD-4* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 170 (2) K. $R = 0.0371$, $R_w = 0.0957$. H-Atoms were obtained from a difference *Fourier* map and refined isotropically.

Oxidation of 4-O-*[(*tert-*Butyl)dimethylsilyl]-5-deoxy-5-hydrazino-2,3*-O-*isopropylidene*-D-*ribono-1,5-lactam* (**4**) *with* t-*BuOCl*. A soln. of **4** (270 mg, 0.85 mmol) and 2,6-lutidine (300 mg, 2.8 mmol) in THF (4 ml) was

cooled to −78°, treated dropwise with *t*-butyl hypochlorite (*t*-BuOCl; 290 µl, 2.55 mmol), stirred for 1 h, warmed to 23°, stirred for 12 h, and filtered (Et_2O). Evaporation and FC (hexane/AcOEt 1:2) gave **6** (168 mg, 63%). White crystals.

*Data of Bis[5-amino-4-*O*-[(*tert*-butyl)dimethylsilyl]-5-deoxy-2,3-*O*-isopropylidene-*D*-ribono-1,5-lactam-5a-yl]diazene* (**6**). White crystals (cyclohexane/Et_2O). M.p.: sintering at 117–119° and melting at 156–157° with slightly dec. R_f (cyclohexane/AcOEt 1:4) 0.45. $[\alpha]_D^{25} = +69.4$ ($c = 0.8$, $CHCl_3$). IR ($CHCl_3$): 2994*w*, 2931*m*, 2859*m*, 1693*s*, 1464*m*, 1377*s*, 1321*m*, 1258*s*, 1156*s*, 1127*m*, 1101*s*, 1053*w*, 989*m*, 957*m*, 883*m*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 1.48, 1.40 (2*s*, Me_2C); 0.86 (*s*, Me_3C); 0.09, 0.06 (2*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 2*; additionally, 111.66 (*s*, $Me_2\mathit{C}$); 26.46, 24.93 (2*q*, Me_2C); 25.66 (*q*, Me_3C); 18.08 (*s*, $Me_3\mathit{C}$); −4.69, −4.88 (2*q*, Me_2Si). MALDI-MS: 651 (100, $[M+Na]^+$), 623 (77, $[M-N_2+Na]^+$). Anal. calc. for $C_{28}H_{52}N_4O_8Si_2$ (628.91): C 53.47, H 8.33, N 8.91; found: C 53.58, H 8.16, N 8.88.

Crystal Structure of **6**·2 (C_6H_{12}). Recrystallization of **6** in cyclohexane/benzene gave crystals suitable for X-ray analysis: $C_{28}H_{52}N_4O_8Si_2 \cdot 2\ (C_6H_{12})$ (797.24); monoclinic $P2_1$; $a = 12.5480$ (6) Å, $b = 14.8854$ (8) Å, $c = 13.16631$ (10) Å, $\beta = 99.641$ (3)°; $V = 2424.5$ (3) Å^3; $D_{calc.} = 1.092$ Mg/m^3; $Z = 2$. From a crystal of size 0.56 × 0.2 × 0.1 mm, 7450 reflections were measured on an *KappyCCD* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 143 K. $R = 0.1103$, $R_w = 0.2613$.

Oxidation of **4** *with* t-*BuOCl in the Presence of DMSO*. A soln. of **4** (64 mg, 0.2 mmol), 2,6-lutidine (82 mg, 0.7 mmol), and DMSO (0.2 ml) in THF (2 ml) was cooled to −78°, treated with *t*-BuOCl (68 µl, 0.6 mmol) for 0.5 h, warmed to 23°, stirred for 2 h, and filtered (Et_2O). Evaporation and FC (Et_2O/MeOH 29:1) gave **6** (7 mg, 12%) and **7** (28 mg, 47%).

*Data of 5-Amino-4-*O*-[(*tert*-butyl)dimethylsilyl]-5-deoxy-2,3-*O*-isopropylidene-*D*-ribono-1,5-lactam* (**7**). M.p. 117.5–118.5° (hexane/Et_2O). R_f (Et_2O/MeOH 20:1) 0.52. $[\alpha]_D^{24} = 17.4$ ($c = 0.7$, $CHCl_3$). IR ($CHCl_3$): 3404*w*, 3216*w*, 3002*w*, 2956*m*, 2932*m*, 2898*w*, 2859*m*, 1681*s*, 1481*w*, 1472*w*, 1463*w*, 1384*m*, 1375*m*, 1258*m*, 1167*m*, 1132*m*, 1093*m*, 1085*m*, 1057*m*, 1006*w*, 985*w*, 934*w*, 881*m*, 862*m*, 838*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 7.22 (br. *s*, NH); 1.48, 1.40 (2*s*, Me_2C); 0.89 (*s*, Me_3C); 0.11, 0.10 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 110.97 (*s*, $Me_2\mathit{C}$); 26.97, 25.46 (2*q*, Me_2C); 25.91 (*q*, Me_3C); 18.37 (*s*, $Me_3\mathit{C}$); −4.47, −4.57 (2*q*, Me_2Si). MALDI-MS: 324 (100, $[M+Na]^+$), 302 (80, $[M+H]^+$). Anal. calc. for $C_{14}H_{27}NO_4Si$ (301.46): C 55.78, H 9.03, N 4.65; found: C 55.95, H 9.08, N 4.62.

Oxidation of **4** *with* MnO_2 [93]. A soln. of **4** (158 mg, 0.5 mmol) in CH_2Cl_2 (5 ml) was added to a suspension of MnO_2 (435 mg, 0.5 mmol) in CH_2Cl_2 (5 ml). The mixture was heated to reflux for 24 h and filtered through silica gel (AcOEt). Evaporation and FC (Et_2O/MeOH 50:1) gave **7** as white crystals (62 mg, 40%) and **5** (18 mg, 11%).

Oxidation of **4** *with Phenylseleninic Acid* ($PhSeO_2H$). A cooled (0°) soln. of **4** (96 mg, 0.3 mmol) in MeOH (2 ml) was treated with $PhSeO_2H$ (60 mg, 0.3 mmol), stirred at 23° for 48 h, treated with sat. $NaHCO_3$ soln., and extracted with CH_2Cl_2. The org. layers were dried ($MgSO_4$) and evaporated. FC (cyclohexane/AcOEt 4:1 → 1:4) gave **8** (20 mg, 22%) and **7** (33 mg, 33%).

*Data of 4-*O*-[(*tert*-Butyl)dimethylsilyl]-2,3-*O*-isopropylidene-*D*-ribono-1,5-lactone* (**8**). White crystals. M.p. 119–120° (hexane/AcOEt). R_f (cyclohexane/AcOEt 2:1) 0.41. $[\alpha]_D^{25} = +6.5$ ($c = 0.23$, $CHCl_3$). IR (neat): 2962*w*, 2930*w*, 2886*w*, 2853*m*, 1757*s*, 1474*w*, 1382*m*, 1376*m*, 1364*w*, 1258*s*, 1233*m*, 1186*s*, 1159*s*, 1100*s*, 1088*s*, 1070*w*, 1054*s*, 1008*w*, 984*s*, 973*m*, 950*vs*, 923*w*, 909*m*, 865*s*, 832*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 1.53, 1.40 (2*s*, Me_2C); 0.90 (*s*, Me_3C); 0.116, 0.112 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 111.50 (*s*, $Me_2\mathit{C}$); 26.14, 24.77 (2*q*, Me_2C); 25.77 (*q*, Me_3C); 18.31 (*s*, $Me_3\mathit{C}$); −4.39, −4.86 (2*q*, Me_2Si). MALDI-MS: 325 (100, $[M+Na]^+$). HR-MALDI-MS: 325.1438 (100, $[M+Na]^+$, $C_{14}H_{26}O_5NaSi^+$; calc. 325.1442). Anal. calc. for $C_{14}H_{26}O_5Si$ (302.44): C 55.60, H 8.67; found: C 55.71, H 8.42.

Crystal Structure of **8**. Recrystallization of **8** in hexane/AcOEt gave crystals suitable for X-ray analysis: $C_{14}H_{26}O_5Si$ (302.44); orthorhombic $P2_12_12_1$; $a = 8.6484$ (3) Å, $b = 10.3483$ (3) Å, $c = 19.5168$ (7) Å, $\beta = 104.695$ (2)°; $V = 1746.68$ (10) Å^3; $D_{calc.} = 1.150$ Mg/m^3; $Z = 4$. From a crystal of size 0.24 × 0.2 × 0.1 mm, 3989 reflections were measured on an *KappyCCD* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 298 K. $R = 0.0701$, $R_w = 0.1574$.

Oxidation of **4** *with Mn(OAc)$_3$ and Cu(OAc)$_2$*. A soln. of **4** (95 mg, 0.3 mmol) in MeOH (2 ml) was added dropwise to a suspension of $Mn(OAc)_3 \cdot 2\ H_2O$ (846 mg, 3.0 mmol) and $Cu(OAc)_2 \cdot H_2O$ (60 mg, 0.3 mmol) in MeOH (2 ml). The mixture was stirred at 23° for 24 h and filtered through silica gel (AcOEt). Evaporation and FC (cyclohexane/AcOEt 1:1 → 1:2) gave **9** (20 mg, 22%) and **7** (50 mg, 55%).

*Data of 5,5′-Bi[5-amino-4-*O*-[(*tert*-butyl)dimethylsilyl]-5-deoxy-2,3-*O*-isopropylidene-*D*-ribono-1,5-lactam]* (**9**). R_f (cyclohexane/AcOEt 1:2) 0.4. $[\alpha]_D^{25} = +3.4$ ($c = 0.53$, $CHCl_3$). IR ($CHCl_3$): 2992*m*, 2955*m*, 2932*s*, 2900*m*, 2859*m*, 1701*s*, 1675*s*, 1471*m*, 1414*m*, 1384*m*, 1376*m*, 1258*s*, 1164*m*, 1128*s*, 1094*s*, 1055*m*, 992*m*, 956*w*,

936*m*, 882*s*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 1.49, 1.41 (2*s*, Me_2C); 0.90 (*s*, Me_3C); 0.14, 0.12 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 111.27 (*s*, Me_2C); 27.18, 25.21 (2*q*, *Me*$_2$C); 26.12 (*q*, *Me*$_3$C); 18.48 (*s*, Me_3C); −4.36, −4.38 (2*q*, Me_2Si). MALDI-MS: 623 (100, $[M+Na]^+$), 601 (64, $[M+H]^+$). Anal. calc. for $C_{28}H_{52}N_2O_8Si_2$ (600.94): C 55.97, H 8.72, N 4.66; found: C 55.96, H 8.59, N 4.71.

General Procedure for the Oxidation of **4** *with Pb(OAc)*$_4$. At the temp. specified in *Table 1*, a soln. of **4** in dry CH_2Cl_2, hexane, cyclohexane, benzene, or toluene was treated with a soln. of $Pb(OAc)_4$ in the same solvent, stirred for the indicated duration, treated with H_2O, extracted with Et_2O, and dried ($MgSO_4$). Evaporation and FC (cyclohexane/AcOEt 10:1 → 2.1) gave **10** and **11**.

Data of 2D-*(1,5/1,2,3,4)-1*-O-*Acetyl-1,5-anhydro-4*-O-*[(*tert-*butyl)dimethylsilyl]-2,3*-O-*isopropylidenecyclopentane-1,1,2,3,4,5-hexol* (**10**). Colourless liquid. R_f (cyclohexane/AcOEt 4:1) 0.67. $[\alpha]_D^{25} = +27.4$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 3031*w*, 2952*m*, 2932*m*, 2858*m*, 1779*s*, 1472*w*, 1464*w*, 1438*w*, 1373*m*, 1251*m*, 1167*m*, 1136*s*, 1090*s*, 1018*m*, 973*w*, 866*s*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*, additionally, 4.41 (irrad. at 5.01 → NOE of 6.6%, irrad. at 3.94 → NOE of 5.7%, H−C(3)); 3.94 (irrad. at 3.74 → NOE of 2.8%, H−C(4)); 3.74 (irrad. at 3.94 → NOE of 2.8%, H−C(5)); 2.15 (*s*, AcO); 1.49, 1.36 (2*s*, Me_2C); 0.92 (*s*, Me_3C); 0.12 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 169.43 (*s*, C=O); 113.71 (*s*, Me_2C); 26.88 (*q*, *Me*$_2$C); 26.12 (*q*, *Me*$_3$C); 21.19 (*q*, Me); 18.80 (*s*, Me_3C); −4.28, −4.95 (2*q*, Me_2Si). ESI-MS: 383 (14, $[M+K]^+$), 367 (19, $[M+Na]^+$), 362 (90, $[M+NH_4]^+$), 345 (100, $[M+H]^+$). Anal. calc. for $C_{16}H_{28}O_6Si$ (344.48): C 55.79, H 8.19; found: C 55.82, H 8.21.

Table 3. *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *for the Cyclopentyl* ^{1}*H- and* ^{13}*C-NMR Signals of the Acyloxy Epoxides* **10** *and* **12**, *and of the Diazo Ketones* **11**, **56**, **57**, *and* **58** *in* $CDCl_3$

	10	**12**	**11**	**56**[a])	**57**	**58**
H−C(2)	5.01	5.16	4.49	4.74	4.53	4.16
H−C(3)	4.41	4.49	4.62	4.43	4.07	4.07
H−C(4)	3.94	4.00	5.33	5.23	5.28	5.09
H−C(5)	3.74	3.88	–	–	–	–
J(2,3)	5.3	5.3	5.6	5.6	8.7	6.5
J(3,4)	5.6	5.6	5.3	0.6	5.0	4.0
J(4,5)	0	0	–	–	–	–
J(2,5)	1.0	0.6	–	–	–	–
J(3,5)	1.0	1.0	–	–	–	–
	10[b])	**12**	**11**[b])	**56**	**57**	**58**
C(1)	86.78	87.37	191.06	192.94	192.00	190.93
C(2)	78.05	78.28	81.31	82.54[c])	78.46[c])	85.27[c])
C(3)	81.44	81.74	76.34	80.43[c])	77.28[c])	80.74[c])
C(4)	69.65	69.92	68.87	73.94	68.69	72.47
C(5)	64.28	64.46	[d])	[d])	[d])	[d])

[a]) Coupling constants expected for the conformation in the solid state. [b]) Assignment based on a ^{1}H,^{13}C-COSY spectrum. [c]) Assignments may be interchanged. [d]) Hidden.

Data of 2D-*(2,3,4/0)-4*-O-*[(*tert-*Butyl)dimethylsilyl]-5-diazo-2,3*-O-*isopropylidene-2,3,4-trihydroxycyclopentanone* (**11**). Yellow crystals. M.p. 117–119.5° (hexane/Et_2O). R_f (hexane/AcOEt 4:1) 0.28. $[\alpha]_D^{25} = +43.3$ ($c = 0.51$, $CHCl_3$). UV (MeOH): 300 (3.23), 255 (3.89). IR ($CHCl_3$): 3019*m*, 2954*w*, 2932*w*, 2860*w*, 2102*s*, 1679*s*, 1472*w*, 1384*w*, 1375*m*, 1349*m*, 1326*m*, 1306*w*, 1255*m*, 1156*m*, 1133*m*, 1102*m*, 873*m*, 840*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 1.48, 1.39 (2*s*, Me_2C); 0.93 (*s*, Me_3C); 0.18 (*s*, Me_2Si); 0.16 (*s*, Me_2Si). ^{13}C-NMR (150 MHz, $CDCl_3$): see *Table 3*; additionally, 113.66 (*s*, Me_2C); 27.35, 26.06 (2*q*, *Me*$_2$C); 25.72 (*q*, *Me*$_3$C); 18.39 (*s*, Me_3C); −4.43, −4.71 (2*q*, Me_2Si). EI-MS: 351 ($[M+K]^+$); 335 ($[M+Na]^+$). Anal. calc. for $C_{14}H_{24}N_2O_4Si$ (312.44): C 53.82, H 7.74, N 8.97; found: C 53.91, H 7.65, N 8.89.

Oxidation of **4** *with Pb(OBz)*$_4$ [94]. *a*) A soln. of **4** (158 mg, 0.5 mmol) in CH_2Cl_2 (4 ml) was treated with a soln. of $Pb(OBz)_4$ (1.04 g, 1.5 mmol) in CH_2Cl_2 (10 ml), stirred at r.t. for 1 h, treated with H_2O, and extracted with Et_2O (3 × 30 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 20:1 → 2:1) gave **12** (46 mg, 23%) and **11** (23 mg, 15%).

b) A soln. of **4** (316 mg, 1.0 mmol) in toluene (5 ml) was treated with a soln. of $Pb(OBz)_4$ (2.08 g, 3.0 mmol) in toluene (25 ml), stirred at r.t. for 2 h, treated with H_2O, and extracted with Et_2O (3×30 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 20:1 → 2:1) gave **12** (134 mg, 33%) and **11** (130 mg, 42%).

Data of 2D-*(1,5/1,2,3,4)-1,5-Anhydro-1*-O-*benzoyl-4*-O-*[(*tert-*butyl)dimethylsilyl]-2,3*-O-*isopropylidene-cyclopentane-1,1,2,3,4,5-hexol* (**12**). White crystals. M.p. 114–115° (MeOH). R_f (cyclohexane/AcOEt 4:1) 0.74. $[\alpha]_D^{25} = +25.9$ ($c = 0.58$, $CHCl_3$). IR ($CHCl_3$): 2991*w*, 2954*m*, 2931*m*, 2897*w*, 2886*w*, 2858*m*, 1745*s*, 1601*w*, 1472*w*, 1463*w*, 1453*w*, 1383*m*, 1375*m*, 1362*w*, 1316*w*, 1271*s*, 1259*s*, 1234*s*, 1158*m*, 1137*s*, 1090*s*, 1064*s*, 1026*m*, 999*w*, 866*m*, 838*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 8.12–8.04 (*m*, 2 arom. H); 7.64–7.55 (*m*, 1 arom. H); 7.50–7.41 (*m*, 2 arom. H); 1.49, 1.36 (2*s*, Me_2C); 0.95 (*s*, Me_3C); 0.151, 0.146 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 165.08 (*s*, C=O); 133.88 (*d*); 130.28 (2*d*); 128.77 (*s*); 128.55 (2*d*); 113.59 (*s*, Me_2C); 26.93 (*q*, *Me*$_2$C); 26.15 (*q*, *Me*$_3$C); 18.82 (*s*, Me_3C); −4.27, −4.92 (2*q*, Me_2Si). HR-MALDI-MS: 429.1703 (78, $[M + Na]^+$; $C_{21}H_{30}NaO_6Si^+$; calc. 429.1704). Anal. calc. for $C_{21}H_{30}O_6Si$ (406.55): C 62.04, H 7.44; found: C 62.13, H 7.37.

Crystal Structure of **12**. Recrystallization of **12** in MeOH gave crystals suitable for X-ray analysis, $C_{21}H_{30}O_6Si$ (406.55); orthorhombic $P2_12_12_1$; $a = 6.8920$ (3) Å, $b = 18.0783$ (8) Å, $c = 18.5672$ (8) Å, $\beta = 90°$; $V = 2313.4$ (2) Å^3; $D_{calc.} = 1.167$ Mg/m^3; $Z = 4$. From a crystal of size $0.4 \times 0.24 \times 0.2$ mm, 4897 reflections were measured on an *KappyCCD* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 298 K. $R = 0.0983$, $R_w = 0.2184$. The structure was solved by direct method with SIR-97. The non-H-atoms were refined anisotropically with SHELXS-97.

*1*D-*(1,2,3,4/5)-4*-O-*[(*tert-*Butyl)dimethylsilyl]-2,3*-O-*isopropylidenecyclopentane-1,2,3,4,5-pentol* (**28**). A soln. of **10** (578 mg, 1.68 mmol) in THF (12 ml) was cooled to 0°, treated with $LiAlH_4$ (114 mg, 3.36 mmol) in portions, stirred for 2 h, and cautiously poured into ice/H_2O (20 ml). After extraction with CH_2Cl_2 (4×50 ml), the combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 2:1) gave **28** as a colourless syrup (410 mg, 80.5%), which crystallized upon standing. White crystals. M.p. 65.0–66.5°. R_f (cyclohexane/AcOEt 2:1) 0.10. $[\alpha]_D^{25} = +31.3$ ($c = 0.55$, $CHCl_3$). IR ($CHCl_3$): 3611*w*, 3540*w* (br.), 3019*s*, 2932*m*, 2859*m*, 1473*w*, 1384*m*, 1259*m*, 1162*s*, 1107*s*, 1028*m*, 981*w*, 876*s*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 3.88 (addition of $D_2O \rightarrow t$, $J = 8.7$, H–C(5)); 3.59 (irrad. at 4.44 → *t*, $J = 9.9$, addition of $D_2O \rightarrow dd$, $J = 9.7$, 5.6, H–C(1)); 2.63 (*d*, $J = 9.7$, exchanged with D_2O, HO–C(1)); 2.46 (br. *d*, $J = 2.2$,

Table 4. *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *for the Cyclopentyl ^{1}H- and ^{13}C-NMR Signals of the Cyclopentane Derivatives* **28**–**37** *in $CDCl_3$*

	28[a])	**29**[a])	**30**	**31**	**32**	**33**[a])[b])	**34**[a])[b])	**35**[b])	**36**[b])	**37**[b])
H–C(1)	3.59	4.97	4.72	4.61	4.78	3.34	3.41	3.36	3.52	3.55
H–C(2)	4.44	4.87	4.78	4.57	4.63	4.54	4.56	4.63–4.57	4.68	4.58
H–C(3)	4.41	4.57	4.48	4.44	4.50	4.47	4.74	4.63–4.57	4.97	4.82
H–C(4)	3.60	4.17	3.80	3.69	3.96	4.22	3.58	4.23	5.09	5.25
H–C(5)	3.88	6.02	4.41	4.34	5.14	4.95	3.62	4.97	5.35	4.61
J(1,2)	5.6	5.9	5.6	5.6	5.6	0.6	0	[c])	0	2.2
J(2,3)	5.8	5.6	5.0	5.6	5.6	6.2	6.5	[c])	5.6	5.6
J(3,4)	5.0	5.3	5.0	5.3	5.3	5.3	1.6	[c])	5.8	5.6
J(4,5)	9.0	9.0	8.7	9.0	9.0	8.1	2.2	8.1	9.0	8.0
J(5,1)	10.0	9.0	8.4	8.4	8.4	6.2	0	6.2	6.2	2.0
	28[a])	**29**[a])	**30**	**31**	**32**	**33**[a])[b])	**34**[a])[b])	**35**[b])	**36**[b])	**37**[b])
C(1)	73.23	74.16	75.96	86.58	84.29	50.39	48.62	50.26	49.17	53.07
C(2)	75.42	74.31	74.23	73.19	73.87	82.27	85.82	81.86	81.83	80.29[d])
C(3)	77.55	77.96	77.98	78.03	77.56	75.77	79.46	74.85	72.67	79.61[d])
C(4)	74.37	72.28	74.31	74.16	71.19	74.41	58.37	73.40	79.08	86.39[e])
C(5)	79.54	77.96	76.75	76.26	83.53	85.37	61.59	85.54	82.37	85.15[e])

[a]) Assignment based on a ^{1}H,^{13}C-COSY spectrum. [b]) Arbitrary numbering as for **28**. [c]) Not assigned. [d]) [e]) Assignments may be interchanged.

exchanged with D_2O, HO–C(5)); 1.48, 1.32 (2*s*, Me_2C); 0.92 (*s*, Me_3C); 0.12 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 111.40 (*s*, Me_2C); 25.95 (*q*, *Me*$_3$C, *Me*C); 24.28 (*q*, *Me*C); 18.41 (*s*, Me_3C); −4.50, −4.55 (2*q*, Me_2Si). ESI-MS: 327 (79, $[M+Na]^+$), 305 (100, $[M+H]^+$). HR-MALDI-MS: 327.1595 (100, $[M+Na]^+$; $C_{14}O_{28}O_5NaSi^+$; calc. 327.1598). Anal. calc. for $C_{14}O_{28}O_5Si$ (304.46): C 55.23, H 9.27; found: C 55.19, H 9.10.

*I*D-*(1,2,3,4/5)-1,5-Di*-O-*benzoyl-4*-O-*[(*tert*-butyl)dimethylsilyl]-2,3*-O-*isopropylidenecyclopentane-1,2,3,4,5-pentol* (**29**) *and I*D-*(1,2,3,4/5)-1*-O-*Benzoyl-4*-O-*[(*tert*-*butyl)dimethylsilyl]-2,3*-O-*isopropylidenecyclopentane-1,2,3,4,5-pentol* (**30**). A soln. of **28** (300 mg, 0.98 mmol) in CH_2Cl_2 (25 ml) was cooled to −40°, treated with TMEDA (300 µl, 2.0 mmol) and BzCl (100 µl, 0.86 mmol), and stirred for 30 h. In regular intervals, additional TMEDA and BzCl (a total of 450 µl, 3.0 mmol TMEDA and 200 µl, 1.7 mmol BzCl) were added until TLC showed completion of the reaction. The mixture was treated with brine (20 ml), extracted with CH_2Cl_2 (3 × 30 ml), and dried. Evaporation and FC (hexane/AcOEt 12:1) gave **29** (132 mg, 26 %) and **30** (265 mg, 67%).

Data of **29**. White crystals. M.p. 161.5–163° (benzene). R_f (hexane/AcOEt 4:1) 0.48. $[\alpha]_D^{25} = -64.6$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 2940*m*, 2858*w*, 1719*s*, 1452*w*, 1384*w*, 1372*w*, 1261*s*, 1108*s*, 873*m*, 841*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Table 4*; additionally, 8.09–8.02 (*m*, 4 arom. H); 7.56–7.52 (*m*, 2 arom. H); 7.44–7.39 (*m*, 4 arom. H); 1.54, 1.32 (2*s*, Me_2C); 0.85 (*s*, Me_3C); 0.11, 0.02 (2*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 4*; additionally, 166.27, 165.48 (2*s*, 2 C=O); 133.12, 133.00 (2*d*); 129.98 (2*d*); 129.90 (*s*); 129.68 (2*d*); 129.42 (*s*); 128.34 (2*d*); 128.31 (2*d*); 112.15 (*s*, Me_2C); 26.01, 24.95 (2*q*, *Me*$_2$C); 25.61 (*q*, *Me*$_3$C); 18.17 (*s*, Me_3C); −4.69, −4.83 (2*q*, Me_2Si). MALDI-MS: 535 (100, $[M+Na]^+$). Anal. calc. for $C_{28}H_{36}O_7Si$ (512.67): C 65.60, H 7.08; found: C 65.64, H 6.87.

Data of **30**. White crystals. M.p. 100.5–101°. R_f (hexane/AcOEt 4:1) 0.31. $[\alpha]_D^{25} = -31.7$ (*c* = 0.54, $CHCl_3$). IR ($CHCl_3$): 3609*w*, 2954*m*, 2935*m*, 2861*w*, 1717*s*, 1472*w*, 1444*w*, 1372*w*, 1265*s*, 1122*s*, 1028*w*, 877*s*, 841*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 8.15–8.05 (*m*, 2 arom. H); 7.56 (*m*, 1 arom. H); 7.48–7.40 (*m*, 2 arom. H); 2.40 (br. *s*, exchanged with D_2O, HO–C(5)); 1.45, 1.28 (2*s*, Me_2C); 0.95 (*s*, Me_3C); 0.16, 0.15 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 166.80 (*s*, C=O); 133.18 (*d*); 129.95 (2*d*); 129.79 (*s*); 128.38 (2*d*); 111.65 (*s*, Me_2C), 25.83, 24.60 (2*q*, *Me*$_2$C); 25.73 (*q*, *Me*$_3$C); 18.21 (*s*, Me_3C); −4.73 (*q*, Me_2Si). HR-MALDI-MS: 431.1859 (100, $[M+Na]^+$, $C_{21}H_{32}NaO_6Si^+$; calc. 431.1860). Anal. calc. for $C_{21}H_{32}O_6Si$ (408.57): C 61.74, H 7.89; found: C 61.78, H 7.65.

Crystal Structure of **30**. Recrystallization of **30** in benzene gave crystals suitable for X-ray analysis, $C_{28}H_{36}O_7Si$ (512.67); monoclinic $P2_1$; $a = 6.3780$ (10) Å, $b = 19.449$ (5) Å, $c = 11.752$ (3) Å, $\beta = 103.00$ (2)°; $V = 1420.4$ (4) Å^3; $D_{calc.} = 1.199$ Mg/m^3; $Z = 2$. From a crystal of size 0.35 × 0.08 × 0.08 mm, 2283 reflections were measured on an *Enraf Nonius CAD-4* diffractometer with CuK_α radiation (graphite monochromator, $\lambda = 1.54184$ Å) at 293 K. $R = 0.0863$, $R_w = 0.1632$. The H-atoms were calculated at idealized positions and included in the structure-factor calculation with fixed isotropic displacement parameters.

*I*D-*(1,2,3,4/5)-4*-O-*[(*tert*-*Butyl)dimethylsilyl]-2,3*-O-*isopropylidene-1*-O-*[(trifluromethyl)sulfonyl]cyclopentane-1,2,3,4,5-pentol* (**31**). A soln. of **28** (410 mg, 1.35 mmol) in CH_2Cl_2 (40 ml) was cooled to −60°, treated with pyridine (2.5 ml) and Tf_2O (245 µl, 1.48 mmol), stirred for 1 h, treated slowly with more Tf_2O (200 µl, 1.2 mmol), and stirred for 5 h when TLC showed completion of the reaction. The mixture was treated with H_2O (20 ml), warmed to r.t., and extracted with CH_2Cl_2 (3 × 30 ml). The combined org. layers were dried and evaporated. FC (hexane/AcOEt 8:1) gave **31** (550 mg, 91%). Colourless syrup R_f (hexane/AcOEt 4:1) 0.60. $[\alpha]_D^{25} = -20.5$ (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): 3620*w*, 3580*w* (br.), 3033*w*, 2931*m*, 2859*m*, 1472*w*, 1463*w*, 1416*s*, 1385*m*, 1375*m*, 1246*s*, 1226*s*, 1202*s*, 1163*s*, 1144*s*, 1098*m*, 994*s*, 876*s*, 837*s*, 615*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 4.44 (addition of D_2O and irrad. at 3.69 → *d*, *J* = 4.8, H–C(3)); 4.34 (addition of D_2O → *t*, *J* = 8.4, addition of D_2O and irrad. at 3.69 → *d*, *J* = 8.4, H–C(5)); 2.52 (*d*, *J* = 4.4, exchanged with D_2O, HO–C(5)); 1.49, 1.33 (2*s*, Me_2C); 0.92 (*s*, Me_3C); 0.123, 0.120 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 118.63 (*q*, *J* = 317.5, CF_3); 112.70 (*s*, Me_2C), 26.03 (*q*, *Me*$_3$C, *Me*C); 24.81 (*q*, *Me*C); 18.58 (*s*, Me_3C); −4.31 (*q*, Me_2Si). ESI-MS: 475 (10.5, $[M+K]^+$), 459 (100, $[M+Na]^+$), 437 (2, $[M+H]^+$). Anal. calc. for $C_{15}H_{27}F_3O_7SSi$ (436.52): C 41.27, H 6.23, F 13.06, S 7.35; found: C 41.47, H 6.04, F 12.95, S 7.40.

*I*D-*(1,2,3,4/5)-4*-O-*[(*tert*-*Butyl)dimethylsilyl]-2,3*-O-*isopropylidene-5*-O-*(methylsulfonyl)-1*-O-*[(trifluoromethyl)sulfonyl]cyclopentane-1,2,3,4,5-pentol* (**32**). A soln. of **31** (534 mg, 1.23 mmol) in CH_2Cl_2 (15 ml) was cooled to 0°, treated with pyridine (2.0 ml) and Ms_2O (426 mg, 2.44 mmol), stirred for 3 h at 0° and for 2 h at 23°, treated with H_2O (15 ml), and extracted with CH_2Cl_2 (3 × 30 ml). The combined org. layers were dried and evaporated. FC (hexane/AcOEt 4:1) gave **32** (625 mg, 99%). Colourless syrup. R_f (hexane/AcOEt 4:1) 0.44. $[\alpha]_D^{25} = -9.7$ (*c* = 1.2, $CHCl_3$). IR ($CHCl_3$): 3035*w*, 2933*m*, 2860*w*, 1473*w*, 1464*w*, 1421*s*, 1376*s*, 1334*w*, 1247*s*, 1182*s*, 1163*m*, 1143*s*, 1101*m*, 1034*s*, 1000*s*, 966*s*, 882*s*, 837*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*;

additionally, 5.14 (irrad. at 3.96 → *d*, *J* = 8.4, H–C(5)); 4.78 (irrad. at 5.14 → *d*, *J* = 6.0, H–C(1)); 4.50 (irrad. at 3.96 → *d*, *J* = 5.4, H–C(3)); 3.96 (irrad. at 5.14 → *d*, *J* = 4.8, H–C(4)); 3.07 (*s*, MsO); 1.55, 1.35 (2*s*, Me_2C); 0.92 (*s*, Me_3C); 0.14, 0.13 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 118.51 (*q*, *J* = 319.2, CF_3); 113.34 (*s*, Me_2C), 39.11 (*q*, MsO); 26.03, 24.89 (2*q*, Me_2C); 25.91 (*q*, Me_3C); 18.44 (*s*, Me_3C); −4.38, −4.43 (2*q*, Me_2Si). MALDI-MS: 537 (100, $[M+Na]^+$). Anal. calc. for $C_{16}H_{29}F_3O_9S_2Si$ (514.61): C 37.34, H 5.68, F 11.08, S 12.46; found: C 37.63, H 5.81, F 11.29, S 12.58.

D-(1,2,3/4,5)-3-O-*[(*tert-*Butyl)dimethylsilyl]-1,2*-O-*isopropylidene-5-(methylsulfanyl)-4*-O-*(methylsulfonyl)cyclopentane-1,2,3,4-tetrol* (**33**). A soln. of **32** (598 mg, 1.16 mmol) and 15-crown-5 (510 mg, 2.32 mmol) in THF (40 ml) was treated with NaSMe (812 mg, 11.6 mmol), stirred at 23° for 2 h, treated with H_2O (20 ml), and extracted with CH_2Cl_2 (3 × 30 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 8:1) gave **33** (450 mg, 94%). White crystals. M.p. 92.5–93° (hexane). R_f (cyclohexane/AcOEt 4:1) 0.41. $[\alpha]_D^{25} = +91.8$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3018*w*, 2932*m*, 2859*w*, 1473*w*, 1364*s*, 1254*m*, 1178*s*, 1094*m*, 1022*m*, 965*m*, 893*m*, 862*s*, 840*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 4.95 (irrad. at 3.34 → *d*, *J* = 8.1, irrad. at 4.22 → *d*, *J* = 6.2, H–C(4)); 4.54 (br. *d*, *J* ≈ 6.2, irrad. at 3.34 → sharp *d*, *J* = 5.9, H–C(1)); 4.47 (irrad. at 4.22 → *d*, *J* = 5.9, H–C(2)); 4.22 (irrad. at 4.95 → *d*, *J* = 5.3, H–C(3)); 3.34 (irrad. at 4.95 → *d*, *J* = 0.9, H–C(5)); 3.08 (*s*, MsO); 2.23 (*s*, MeS); 1.47, 1.30 (2*s*, Me_2C); 0.92 (*s*, Me_3C); 0.13, 0.12 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 111.93 (*s*, Me_2C), 38.49 (*q*, MsO); 26.41, 24.71 (2*q*, Me_2C); 26.04 (*q*, Me_3C); 18.51 (*s*, Me_3C); 16.09 (*q*, MeS); −4.29, −4.42 (2*q*, Me_2Si). ESI-MS: 451 (14, $[M+K]^+$), 435 (12, $[M+Na]^+$), 413 (18, $[M+H]^+$), 355 (100). Anal. calc. for $C_{16}H_{32}O_6S_2Si$ (412.64): C 46.57, H 7.82, S 15.54; found: C 46.74, H 7.79, S 15.58.

D-(1,2,3,4/5)-3,4-Anhydro-1,2-O-*isopropylidene-5-(methylsulfanyl)cyclopentane-1,2,3,4-tetrol* (**34**) and *D-(1,2,3/4,5)-1,2*-O-*Isopropylidene-5-(methylsulfanyl)-4*-O-*(methylsulfonyl)cyclopentane-1,2,3,4-tetrol* (**35**). *a*) A soln. of **33** (289 mg, 0.7 mmol) in THF (30 ml) was cooled to 0°, treated with 1M TBAF in THF (735 µl, 0.735 mmol), stirred at 0° for 5 min, treated with sat. aq. NH_4Cl (10 ml), and extracted with CH_2Cl_2 (3 × 30 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 4:1 → 1:1) gave **34** (42 mg, 30%) and **35** (137 mg, 66%).

b) A soln. of **33** (358 mg, 0.87 mmol) in THF (16 ml) was cooled to −30°, treated with 1 M TBAF in THF (960 µl, 0.96 mmol), stirred for 2.5 h, treated with sat. aq. NH_4Cl soln. (10 ml) at −30°, warmed to r.t., and extracted with CH_2Cl_2 (3 × 30 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 4:1 → 1:1) gave **35** (257 mg, 99%).

Data of **34**. R_f (hexane/AcOEt 4:1) 0.49. $[\alpha]_D^{25} = -14.0$ (*c* = 0.5, $CHCl_3$). IR (neat): 2990*w*, 2978*w*, 2953*w*, 2930*w*, 2915*w*, 2856*w*, 1453*w*, 1429*w*, 1381*m*, 1370*m*, 1267*m*, 1253*m*, 1223*m*, 1203*s*, 1159*m*, 1114*w*, 1071*s*, 1056*s*, 1031*m*, 994*m*, 958*m*, 939*w*, 892*m*, 853*s*, 846*s*, 830*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 4.74 (irrad. at 4.56 → *d*, *J* = 1.5, H–C(2)); 4.56 (br. *d*, *J* ≈ 6.5, irrad. at 4.74 → br. *s*, H–C(1)); 3.62 (irrad. at 4.56 → *d*, *J* = 2.7, H–C(4)); 3.58 (irrad. at 4.74 → *d*, *J* = 2.4, H–C(3)); 2.18 (*s*, MeS); 1.52, 1.28 (2*s*, Me_2C). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 112.90 (*s*, Me_2C); 26.33, 25.46 (2*q*, Me_2C); 14.64 (*q*, MeS). ESI-MS: 203 (100, $[M+H]^+$).

Data of **35**. R_f (cyclohexane/AcOEt 2:1) 0.16. $[\alpha]_D^{25} = +89.0$ (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): 3547*w* (br.), 3032*w*, 2994*w*, 2940*w*, 1456*w*, 1361*s*, 1264*w*, 1230*m*, 1176v*s*, 1112*m*, 1067*s*, 1022*s*, 966*s*, 921*w*, 886*m*, 864*m*, 840*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 4.97 (irrad. at 4.23 → *d*, *J* = 5.9, irrad. at 3.36 → *d*, *J* = 8.1, H–C(4)); 4.23 (br. *s*, addition of D_2O → *m*, H–C(3)); 3.17 (*s*, MsO); 2.76 (br. *d*, *J* = 7.6, exchanged with D_2O, HO–C(3)); 2.23 (*s*, MeS); 1.50, 1.34 (2*s*, Me_2C). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 112.19 (*s*, Me_2C), 38.97 (*q*, MsO); 26.18, 24.28 (2*q*, Me_2C); 16.12 (*q*, MeS). ESI-MS: 337 (16, $[M+K]^+$), 321 (100, $[M+Na]^+$). Anal. calc. for $C_{10}H_{18}O_6S_2$ (298.38): C 40.25, H 6.08, S 21.49; found: C 40.25, H 6.13, S 21.50.

D-(1,2,3/4,5)-1,2-O-*Isopropylidene-5-(methylsulfanyl)-4*-O-*(methylsulfonyl)-3*-O-*(2,2,2-trichloro-1-iminoethyl)cyclopentane-1,2,3,4-tetrol* (**36**). A soln. of **35** (27 mg, 0.09 mmol) in CH_2Cl_2 (5 ml) was treated with Cl_3CCN (130 mg, 0.9 mmol) and DBU (15 mg, 0.1 mmol), and stirred at 23° for 1 h. Evaporation and FC (cyclohexane/CH_2Cl_2 2:1 → cyclohexane/AcOEt 4:1) gave **36** (40 mg, 100%). White crystals. M.p. 96.5–98.5° (hexane/Et_2O). R_f (cyclohexane/AcOEt 4:1) 0.33. $[\alpha]_D^{25} = +96.7$ (*c* = 0.31, $CHCl_3$). IR ($CHCl_3$): 3346*w*, 3030*w*, 2995*w*, 2939*w*, 2926*w*, 1669*s*, 1602*w*, 1368v*s*, 1315*m*, 1289*m*, 1255*m*, 1178*s*, 1088*s*, 1054*s*, 1024*m*, 968*s*, 868*m*, 833*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 8.52 (br. *s*, C=NH); 5.35 (irrad. at 3.52 → *d*, *J* = 9.0, H–C(4)); 4.97 (irrad. at 4.68 → *d*, *J* = 5.6, H–C(2)); 3.13 (*s*, MsO); 2.30 (*s*, MeS); 1.47, 1.31 (2*s*, Me_2C). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 161.06 (*s*, C=N); 112.07 (*s*, Me_2C); 90.57 (*s*, Cl_3C); 38.45 (*q*, MsO); 26.21, 24.67 (2*q*, Me_2C); 16.28 (*q*, MeS). ESI-MS: 486 (5), 484 (21), 482 (51), 480 (41, $[M+K]^+$), 470 (9), 468 (37), 466 (100), 464 (94, $[M+Na]^+$). Anal. calc. for $C_{12}H_{18}Cl_3NO_6S_2$ (442.77): C 32.55, H 4.10, Cl 24.02, N 3.16, S 14.48; found: C 32.75, H 4.11, Cl 23.93, N 3.04, S 14.31.

*ID-(1,2,3,4/5)-4-Amino-1,2-*O*-isopropylidene-5-(methylsulfanyl)-3-*O*,4-*N*-(2,2,2-trichloroethylidyne)cyclopentane-1,2,3-triol* (**37**). *a*) A soln. of **36** (93 mg, 0.21 mmol) in xylene (10 ml) was treated with $EtN(i\text{-}Pr)_2$ (0.2 ml), stirred at 110° for 24 h, cooled to r.t., treated with H_2O (10 ml), and extracted with Et_2O (3×10 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 8:1 → 1:1) gave **37** (26 mg, 33%).

b) A soln. of **35** (210 mg, 0.7 mmol) in xylene (30 ml) was treated with Cl_3CCN (0.7 ml, 7.0 mmol) and DBU (120 mg, 0.77 mmol), stirred at 23° for 2 h, treated with $EtN(i\text{-}Pr)_2$ (1.18 ml), heated to 110°, stirred for 12 h, cooled to r.t., treated with H_2O (20 ml), and extracted with Et_2O (2×30 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 12:1) gave **37** (193 mg, 80%) and **36** (41 mg, 13%).

Data of **37**. White crystals from hexane/Et_2O. M.p. 88–88.5°. R_f (cyclohexane/AcOEt 4:1) 0.44. $[\alpha]_D^{25} = +22.0$ ($c = 0.52$, $CHCl_3$). IR ($CHCl_3$): 3029*w*, 2996*m*, 2941*w*, 2923*w*, 1653*s*, 1456*w*, 1434*w*, 1385*m*, 1377*m*, 1311*m*, 1266*m*, 1240*m*, 1200*m*, 1157*m*, 1105*m*, 1059v*s*, 1005*m*, 966*w*, 878*m*, 836v*s*, 814*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 4*; additionally, 5.25 (irrad. at 3.55 → *dd*, $J = 8.4, 5.9$, H–C(3)); 4.61 (irrad. at 3.55 → *d*, $J = 8.3$, H–C(4)); 4.58 (irrad. at 3.55 → *d*, $J = 5.6$, H–C(1)); 2.25 (*s*, MeS); 1.49, 1.33 (2*s*, Me_2C). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 162.10 (*s*, C=N); 112.93 (*s*, Me_2C); 26.53, 24.41 (2*q*, Me_2C); 15.58 (*q*, MeS); *s* for CCl_3 hidden by the noise. ESI-MS: 352 (4), 350 (35), 348 (100), 346 (96, $[M+H]^+$). Anal. calc. for $C_{11}H_{14}Cl_3NO_3S$ (346.66): C 38.11, H 4.07, Cl 30.68, N 4.04, S 9.25; found: C 38.32, H 4.30, Cl 30.61, N 4.04, S 9.20.

IL-(1,2,3,4/5)-2,3,4-Trihydroxy-5-(methylsulfanyl)cyclopentane-1-ammonium Chloride (**1**·HCl; *(+)-Mannostatin A hydrochloride*) [57]. A suspension of **37** (33 mg, 0.095 mmol) in 7N HCl/MeOH 1:1 (5 ml) was stirred at 23° for 3 h. The mixture was coevaporated with toluene. A soln. of the residue in H_2O was washed with CH_2Cl_2 and Et_2O. Evaporation of the aq. layer gave **1**·HCl (19 mg, 93%). $[\alpha]_D^{25} = +7.5$ ($c = 0.95$, MeOH) ([39]: $[\alpha]_D = 5.9$ ($c = 1.08$, MeOH); [42]: $[\alpha]_D^{21} = 6$ ($c = 0.46$, MeOH)). ^{1}H-NMR (300 MHz, D_2O): 4.15 (*dd*, $J = 6.2, 4.0$, H–C(4)); 3.96 (*t*, $J \approx 4.3$, H–C(3)); 3.87 (*dd*, $J = 7.5, 4.7$, H–C(2)); 3.41 (*t*, $J \approx 6.8$, H–C(5)); 2.98 (*t*, $J \approx 7.3$, H–C(1)); 2.01 (*s*, MeS). ^{13}C-NMR (75 MHz, D_2O): 73.71, 72.06, 68.25 (3*d*, C(2), C(3), C(4)); 55.00 (*d*, C(1)); 51.73 (*d*, C(5)); 12.10 (*q*, MeS).

ID-(1,2,3,4/5)-4-Amino-5-(methylsulfanyl)cyclopentane-1,2,3-triol (**1**; *(+)-Mannostatin A*) [57]. *a*) A suspension of **37** (45 mg, 0.13 mmol) in 7N HCl/MeOH 1:1 (7 ml) was stirred at 23° for 3 h. The mixture was co-evaporated with toluene. Filtration of the residue through a small column packed with *Amberlite IR-120* (H^+ form, 0.5N NH_3) gave **1** (19 mg, 81.5% from **37**).

b) Filtration of **1**·HCl (18 mg, 0.084 mmol) in H_2O (5 ml) through a small column packed with *Amberlite IR-120* (H^+ form, 0.5N NH_3) gave **1** (12 mg, 80%).

Biological activity: synthetic **1** inhibited jack bean α-D-mannosidase with $IC_{50} = 48$ nM; (*p*-nitrophenyl α-D-mannopyranoside, acetate buffer, pH 4.5)

*ID-(1,2,3,4/5)-4-Acetamido-1,2,3-tri-*O*-acetyl-5-(methylsulfanyl)cyclopentane-1,2,3-triol* (**38**; *(+)-Tetraacetylmannostatin A*) [6]. A suspension of **37** (28 mg, 0.081 mmol) in 7N HCl/MeOH 1:1 (5 ml) was stirred at 23° for 1 h. The mixture was co-evaporated with toluene. A soln. of the residue in pyridine (1 ml) was cooled to 0°, treated with Ac_2O (153 µl, 1.62 mmol) for 3 h, diluted with H_2O, and extracted with CH_2Cl_2 (3×10 ml). The combined org. layers were dried ($MgSO_4$) and evaporated. FC (cyclohexane/AcOEt 1:2) gave **38** (26 mg, 93% from **37**). White crystals from hexane/AcOEt. M.p. 121.5–122.5° ([6]: m.p. 121°; [30]: m.p. 119–120°; [42]: 122–123°). R_f (cyclohexane/AcOEt 4:1) 0.41. $[\alpha]_D^{25} = +18.3$ ($c = 1.02$, $CHCl_3$); [30]: $[\alpha]_D = +8.5$ ($c = 0.9$, $CHCl_3$); [95]: $[\alpha]_D^{28} = +7.4$ ($c = 0.45$, $CHCl_3$); [42]: $[\alpha]_D^{27} = +16$ ($c = 0.88$, $CHCl_3$)). IR (neat): 3304*w*, 3061*w*, 2985*w*, 2954*w*, 2924*w*, 1735v*s*, 1647*m*, 1535*m*, 1435*w*, 1374*m*, 1360*m*, 1283*w*, 1250*s*, 1230*s*, 1219*s*, 1084*s*, 1014*m*, 929*m*, 912*m*, 873*w*, 822*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.70 (*d*, $J = 9.3$, NH); 5.39 (*dd*, $J = 6.0, 4.0$, H–C(2)); 5.33 (*d*, $J = 5.6, 4.0$, H–C(3)); 5.16 (*td*, $J = 6.5, 0.6$, H–C(1)); 4.53 (br. *td*, $J \approx 9.0, 5.6$, H–C(4)); 3.10 (*dd*, $J = 8.1, 6.2$, H–C(5)); 2.16, 2.11, 2.07, 2.05, 2.04 (5*s*, 4 Ac, MeS). ^{13}C-NMR (75 MHz, $CDCl_3$): 169.53, 169.47, 169.23, 168.84 (4*s*, 4 C=O); 73.85, 71.14, 70.46 (3*d*, C(1), C(2), C(3)); 53.29, 51.74 (2*d*, C(4), C(5)); 23.53, 20.86, 20.83, 20.70 (4*q*, 4 Me); 13.71 (*q*, MeS). HR-MALDI-MS: 370.0935 (100, $[M+Na]^+$, $C_{14}H_{21}NNaO_7S^+$; calc. 370.0931); 348.1111 (43, $[M+H]^+$, $C_{14}H_{22}NO_7S^+$; calc. 348.1112); 288.0897 (86, $[M-AcO]^+$, $C_{12}H_{18}NO_5S^+$; calc. 288.0900).

*5-Deoxy-5-hydrazino-2,3-*O*-isopropylidene-*D*-lyxono-1,5-lactam* (**40**). A suspension of **39** [59] (266 mg, 1.0 mmol) in $NH_2NH_2 \cdot H_2O$ (0.4 ml) was stirred at 23° for 3 h. The resulting clear soln. was co-evaporated with toluene (2×30 ml). A soln. of the residue in CH_2Cl_2 (15 ml; formation of some crystals) was dried, and evaporated to afford crude **40** (240 mg). Colourless oil. The crude was used for the next step. ^{1}H-NMR (200 MHz, $CDCl_3$): see *Table 5*; additionally, 1.43, 1.38 (2*s*, Me_2C). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 5*; additionally, 110.82 (*s*, Me_2C); 27.08, 24.98 (2*q*, Me_2C).

Table 5. *Selected ^{1}H- and ^{13}C-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the* N*-Amino-glyconolactams in $CDCl_3$*

	40	**41**	**45**	**46**	**50**	**51**
H–C(2)	4.63	4.55	4.33	4.80–4.72[a])	4.16	4.07
H–C(3)	4.39	4.22	3.90	3.89	3.69	3.76
H–C(4)	4.14	4.06	4.30	4.30	3.93	3.94
H–C(5)	3.89	3.82	3.63	3.52	3.74	3.61
H′–C(5)	3.53	3.36	3.54	3.52	3.39	3.34
J(2,3)	6.2	6.2	6.8	6.5	7.5	7.1
J(3,4)	4.2[b])	4.0[b])	2.2	1.9	7.5	7.1
J(4,5)	2.5	2.5	4.6	5.3	5.4	4.7
J(4,5′)	4.2	3.7	5.3	5.3	7.6	7.1
J(5,5′)	13.3	13.1	12.4	[c])	12.0	12.5
	40	**41**	**45**	**46**		**51**
C(1)	166.22	166.35	166.63	166.64		168.20
C(2)	73.93	74.25	73.05	73.40		74.53
C(3)	76.85	77.07	78.87	76.01		79.60
C(4)	66.69	67.26	64.87	66.09		68.79
C(5)	53.14	53.66	53.11	54.28		54.88

[a]) Signal overlapping with MOM signals. [b]) $J(3,5') = 1.2$ Hz. [c]) Not assigned.

4-O-*[(*tert*-Butyl)dimethylsilyl]-5-deoxy-5-hydrazino-2,3*-O-*isopropylidene*-D-*lyxono-1,5-lactam* (**41**). TBSOTf (0.56 ml, 2.4 mmol) was added dropwise to a cooled (0°) soln. of crude **40** (240 mg) in CH_2Cl_2 (2 ml) and pyridine (0.6 ml). The mixture was stirred at 0° for 1 h and at r.t. for 3 h, treated with H_2O (10 ml), extracted with CH_2Cl_2 (3 × 50 ml), and dried. Evaporation and FC (hexane/AcOEt 3:2) gave **41** (202 mg, 64% from **39**). White crystals M.p. 52–53°. R_f (cyclohexane/AcOEt 1:2) 0.50. $[\alpha]_D^{26} = +11.4$ ($c = 0.45$, $CHCl_3$). IR ($CHCl_3$): 3449*w* (br.), 3320*w*, 3024*w*, 3016*m*, 2955*m*, 2931*m*, 2858*m*, 1655*s*, 1616*w*, 1471*w*, 1463*w*, 1385*m*, 1376*m*, 1257*m*, 1235*m*, 1162*w*, 1123*s*, 1095*m*, 1042*w*, 1006*w*, 937*m*, 866*w*, 839*s*, 825*m*, 810*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 4.44 (*s*, exchanged with D_2O, NH_2); 1.38, 1.34 (2*s*, Me_2C); 0.83 (*s*, Me_3C); 0.066, 0.063 (2*s*, 2 Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 110.72 (*s*, Me_2C); 27.05, 25.09 (2*q*, *Me*$_2$C); 25.67 (*q*, *Me*$_3$C); 17.98 (*s*, Me_3C); −4.81 (2*q*, Me_2Si). MALDI-MS: 339 (25, $[M+Na]^+$), 317 (53, $[M+H]^+$). HR-MALDI-MS: 317.1885, (53, $[M+H]^+$, $C_{14}H_{29}N_2O_4Si^+$; calc. 317.1891). Anal. calc. for $C_{14}H_{28}N_2O_4Si$ (316.47): C 53.13, H 8.92, N 8.85; found: C 53.26, H 8.95, N 8.55.

5-O-*[(2,4,6-Trimethylphenyl)sulfonyl]*-D-*arabino-1,4-lactone* (**43**). A soln. of **42** (3.85 g, 26 mmol) and 'mesitylene-2-sulfonyl chloride' (MtsCl; 6.82 g, 31.2 mmol) in pyridine (20 ml) was stirred at 0° for 1 h and at 23° for 4 h. The mixture was treated with H_2O (10 ml) and extracted with CH_2Cl_2 (3 × 30 ml). Removal of the solvent by co-evaporation with toluene and FC (cyclohexane/AcOEt 1:1) gave **43** (5.95 g, 69%). Colourless syrup. R_f (hexane/AcOEt 1:2) 0.46. $[\alpha]_D^{25} = +59.4$ ($c = 1.42$, $CHCl_3$). IR ($CHCl_3$): 3564*w* (br.), 3368*w* (br.), 2981*w*, 2942*w*, 1798*s*, 1604*m*, 1450*w*, 1356*s*, 1167v*s*, 1139*m*, 1072*m*, 1036*m*, 920*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.99 (*s*, 2 arom. H); 4.54 (*d*, $J = 8.4$, H–C(2)); 4.42 (*t*, $J = 8.4$, H–C(3)); 4.34 (*dt*, $J = 8.4, 3.1$, H–C(4)); 4.25 (*d*, $J = 3.1, 2$ H–C(5)); 2.60 (*s*, 2 Me); 2.31 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 173.86 (*s*, C=O); 144.01 (*s*); 140.16 (2*s*); 131.97 (2*d*); 129.45 (*s*); 77.77 (*d*, C(4)); 74.38, 73.46 (2*d*, C(2), C(3)); 66.31 (*t*, C(5)); 22.77 (*q*, 2 Me); 21.31 (*q*, Me). MALDI-MS: 353 (100, $[M+Na]^+$). Anal. calc. for $C_{14}H_{18}O_7S$ (330.36): C 50.90, H 5.49, S 9.71; found: C 50.80, H 5.63, S 9.60.

2,3-Bis-O-*(methoxymethyl)-5*-O-*[(2,4,6-trimethylphenyl)sulfonyl]*-D-*arabino-1,4-lactone* (**44**). A soln. of **43** (1.83 g, 5.55 mmol) in $CH_2(OMe)_2$ (4 ml) was added at r.t. to a suspension of P_2O_5 (1.0 g) in $CH_2(OMe)_2$ (1.0 ml). The mixture was stirred overnight, treated with ice/sat. $NaHCO_3$ soln., and extracted with Et_2O. The org. layer was washed with brine, dried, and evaporated. FC (hexane/AcOEt 2:1) gave **44** (1.99 g, 86%). White needles M.p. 69–70.5°. R_f (hexane/AcOEt 2:1) 0.35. $[\alpha]_D^{25} = +41.7$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 2955*w*, 2901*w*, 2830*w*, 1802*s*, 1604*w*, 1567*w*, 1467*w*, 1452*w*, 1404*w*, 1362*m*, 1190*s*, 1175v*s*, 1153*s*, 1124*m*, 1078*m*, 1046v*s*, 976*s*, 919*m*, 814*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.96 (*s*, 2 arom. H); 4.97 (*d*, $J = 6.9$), 4.75 (*d*, $J = 6.9$), 4.72 (*d*, $J = 6.9$),

4.66 (*d*, *J* = 6.9) (2 MeOC*H*$_2$); 4.49 (*d*, *J* = 7.5, H–C(2)); 4.35 (*ddd*, *J* = 7.2, 4.6, 2.5, H–C(4)); 4.29 (*dd*, *J* = 11.5, 2.2, H–C(5)); 4.26 (*t*, *J* = 7.4, H–C(3)); 4.21 (*dd*, *J* = 11.5, 4.4, H′–C(5)); 3.41, 3.35 (2*s*, 2 MeO); 2.60 (*s*, 2 Me); 2.29 (*s*, Me). ^{13}C NMR (75 MHz, $CDCl_3$): 170.97 (*s*, C=O); 143.89 (*s*); 140.27 (2*s*); 131.93 (2*d*); 130.01 (*s*); 97.02, 96.08 (2*t*, 2 MeO*C*H$_2$), 78.10, 77.65 (2*d*, C(2) and C(3)); 75.55 (*d*, C(4)); 65.94 (*t*, C(5)); 56.11, 56.00 (2*q*, 2 MeO); 22.43 (*q*, 2 Me); 20.92 (*q*, Me). MALDI-MS: 441 (100, $[M+Na]^+$). Anal. calc. for $C_{18}H_{26}O_9S$ (418.46): C 51.66, H 6.26, S 7.66; found: C 51.70, H 6.29, S 7.76.

5-Deoxy-5-hydrazino-2,3-bis-O-*(methoxymethyl)*-D-*arabino-1,5-lactam* (**45**). A suspension of **44** (1.99 g, 4.76 mmol) in $NH_2NH_2 \cdot H_2O$ (4 ml) was stirred at r.t. for 3 h. After removal of $NH_2NH_2 \cdot H_2O$ by co-evaporation with toluene, a soln. of the residue in CH_2Cl_2 (100 ml; formation of some crystals) was dried and evaporated to give crude **45** (1.88 g). Colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 5.06 (*d*, *J* = 6.5), 4.80 (*d*, *J* = 6.9), 4.77 (*d*, *J* = 6.9), 4.76 (*d*, *J* = 6.5) (2 MeOC*H*$_2$); 3.44 (*s*, 2 MeO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 97.41, 97.19 (2*t*, 2 MeO*C*H$_2$); 56.02, 55.98 (2*q*, 2 MeO). MALDI-MS: 273 (71, $[M+Na]^+$), 187 (100). HR-MALDI-MS: 273.1056 (71, $[M+Na]^+$, $C_9H_{18}N_2NaO_6Si^+$; calc. 273.1057).

4-O-*[(*tert*-Butyl)dimethylsilyl]-5-deoxy-5-hydrazino-2,3-bis*-O-*(methoxymethyl)*-D-*arabino-1,5-lactam* (**46**). A soln. of crude **45** (1.88 g) in CH_2Cl_2 (10 ml) and pyridine (3 ml) was treated with TBSOTf (2.74 ml, 11.9 mmol). The mixture was stirred at 0° for 1 h and at r.t. for 3 h, treated with H_2O (30 ml), extracted with CH_2Cl_2 (3 × 50 ml), and dried. Evaporation and FC (hexane/AcOEt 3:2) gave **46** (1.4 g, 81% from **44**). Colourless syrup. R_f (hexane/AcOEt 1:2) 0.30. $[\alpha]_D^{25} = -95.8$ (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): 3486*w* (br.), 3319*w*, 3009*m*, 2955*s*, 2931*s*, 2897*m*, 2858*m*, 1651*s*, 1614*w*, 1472*m*, 1463*w*, 1442*w*, 1390*w*, 1362*w*, 1288*w*, 1256*m*, 1152*s*, 1140*s*, 1106*s*, 1039*vs*, 962*w*, 919*m*, 869*m*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 5.04 (*d*, *J* = 6.2, MeOC*H*); 4.80–4.72 (*m*, H–C(2), 2 MeOC*H*); 4.40 (br. *s*, exchange with D_2O, NH_2); 4.29 (*d*, *J* = 6.2, MeOC*H*); 3.45, 3.39 (2*s*, 2 MeO); 0.89 (*s*, Me_3C); 0.12, 0.10 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 5*; additionally, 97.30, 96.21 (2*t*, 2 MeO*C*H$_2$); 56.12, 55.85 (2*q*, 2 MeO); 25.86 (*q*, *Me*$_3$C); 18.24 (*s*, Me$_3$*C*); −4.54, −4.65 (2*q*, Me_2Si). MALDI-MS: 387 (100, $[M+Na]^+$), 365 (28, $[M+H]^+$), 333 (83, $[M-MeO]^+$), 301 (64). Anal. calc. for $C_{15}H_{32}N_2O_6Si$ (364.51): C 49.43, H 8.85, N 7.69; found: C 49.52, H 8.66, N 7.63.

5-O-*[(2,4,6-Trimethylphenyl)sulfonyl]*-D-*xylono-1,4-lactone* (**48**). A soln. of **47** (330 mg, 2.23 mmol) and MtsCl (537 mg, 2.45 mmol) in pyridine (1.5 ml) was stirred at 0° for 3 h and at 23° overnight, treated with H_2O (10 ml) and extracted with CH_2Cl_2 (3 × 30 ml). Removal of the solvents by co-evaporation with toluene, followed by FC (cyclohexane/AcOEt 1:1) gave **48** (458 mg, 62%). Colourless syrup. R_f (cyclohexane/AcOEt 1:1) 0.27. $[\alpha]_D^{25} = +51.3$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3520*w* (br.), 3356*w* (br.), 3032*w*, 2944*w*, 1803*m*, 1604*w*, 1456*w*, 1359*s*, 1176*s*, 1097*m*, 1065*m*, 965*m*, 854*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.96 (*s*, 2 arom. H); 4.74 (*dt*, *J* ≈ 7.5, 3.5, H–C(4)); 4.66 (*t*, *J* ≈ 7.5, H–C(3)); 4.6–3.8 (br. *s*, exchanged with D_2O, HO–C(2), HO–C(3)); 4.59 (*d*, *J* = 7.8, H–C(2)); 4.30 (*dd*, *J* = 11.2, 4.0, H–C(5)); 4.20 (*dd*, *J* = 11.2, 2.8, H'–C(5)); 2.56 (*s*, 2 Me), 2.28 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 174.81 (*s*, C=O); 143.95 (*s*); 140.17 (2*s*); 131.92 (2*d*); 129.32 (*s*); 76.62 (*d*, C(4)); 73.10, 72.68 (2*d*, C(2), C(3)); 66.11 (*t*, C(5)); 22.46 (*q*, 2 Me); 21.00 (*q*, Me). MALDI-MS: 353 (100, $[M+Na]^+$). Anal. calc. for $C_{14}H_{18}O_7S$ (330.36): C 50.90, H 5.49, S 9.71; found: C 50.98, H 5.53, S 9.66.

2,3-Bis-O-*(methoxymethyl)*-*5*-O-*[(2,4,6-trimethylphenyl)sulfonyl]*-D-*xylono-1,4-lactone* (**49**). A soln. of **48** (2.04 mg, 6.18 mmol) in $CH_2(OMe)_2$ (8 ml) was added to a suspension of P_2O_5 (3 g) in $CH_2(OMe)_2$ (6 ml) and stirred at r.t. overnight. The mixture was treated with ice/sat. $NaHCO_3$ soln. and extracted with Et_2O. The org. layer was washed with brine, dried, and evaporated. FC (hexane/AcOEt 2:1) gave **49** (2.01 g, 78%). Colourless oil. R_f (hexane/AcOEt 2:1) 0.33. $[\alpha]_D^{25} = +81.1$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3019*w*, 2956*w*, 2903*w*, 1800*s*, 1604*w*, 1452*w*, 1362*m*, 1176*s*, 1154*s*, 1115*m*, 1048*s*, 979*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.98 (*s*, 2 arom. H); 4.94 (*d*, *J* = 6.9), 4.72 (*d*, *J* = 6.9, 2 H), 4.71 (*d*, *J* = 6.9) (2 MeOC*H*$_2$); 4.80–4.76 (*m*, H–C(4)); 4.46–4.40 (*AB*, H–C(2), H–C(3)); 4.30 (*dd*, *J* = 10.9, 3.4, H–C(5)); 4.20 (*dd*, *J* = 10.9, 5.0, H′–C(5)); 3.41, 3.35 (2*s*, 2 MeO); 2.62 (*s*, 2 Me); 2.31 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 171.88 (*s*, C=O); 144.04 (*s*); 140.40 (2*s*); 132.10 (2*d*); 130.19 (*s*); 97.22, 96.21 (2*t*, 2 MeO*C*H$_2$); 77.67, 76.77 (2*d*, C(2), C(3)); 74.03 (*d*, C(4)); 66.04 (*t*, C(5)); 56.35, 56.21 (2*q*, 2 MeO); 22.59 (*q*, 2 Me); 21.07 (*q*, Me). MALDI-MS: 441 (100, $[M+Na]^+$). Anal. calc. for $C_{18}H_{26}O_9S$ (418.46): C 51.66, H 6.26, S 7.66; found: C 51.72, H 6.21, S 7.47.

5-Deoxy-5-hydrazino-2,3-bis-O-*(methoxymethyl)*-D-*xylono-1,5-lactam* (**50**). A suspension of **49** (688 mg, 1.65 mmol) in $NH_2NH_2 \cdot H_2O$ (1 ml) was stirred at r.t. for 48 h. After removal of $NH_2NH_2 \cdot H_2O$ by co-evaporation with toluene, a soln. of the residue was dried and evaporated to afford crude **50** (480 mg). Colourless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): see *Table 5*; additionally, 5.09 (*d*, *J* = 6.6, MeOC*H*); 4.84–4.74 (*m*, 3 MeOC*H*); 4.43 (br. *s*, exchanged with D_2O, NH_2); 3.45 (*s*, 2 MeO).

4-O-*[(*tert*-Butyl)dimethylsilyl]-5-deoxy-5-hydrazino-2,3-bis*-O-*(methoxymethyl)*-D-*xylono-1,5-lactam* (**51**). A soln. of crude **50** (360 mg) in CH_2Cl_2 (4 ml) and pyridine (1 ml) was treated with TBSOTf (0.66 ml,

2.88 mmol), stirred at 0° for 1 h and at r.t. for 3 h, treated with H_2O (10 ml), and extracted with CH_2Cl_2 (3 × 10 ml). The org. layer was dried and evaporated. FC (hexane/AcOEt 1:1) gave **51** as a syrup (380 mg, 85% from **49**), which crystallized at 5°. R_f (hexane/AcOEt 1:1) 0.44. $[\alpha]_D^{25} = +58.5$ ($c = 0.37$, $CHCl_3$). IR (neat): 3316*w*, 2952*w*, 2929*w*, 2891*w*, 2857*w*, 1661*m*, 1472*w*, 1463*w*, 1441*w*, 1389*w*, 1361*w*, 1254*m*, 1214*w*, 1154*m*, 1103s, 1078*m*, 1029*s*, 964*m*, 919*m*, 893*m*, 864*m*, 834v*s*, 776*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 5*; additionally, 5.04 (*d*, *J* = 6.5), 4.83 (*d*, *J* = 6.5), 4.82 (*d*, *J* = 6.5), 4.76 (*d*, *J* = 6.5) (2 MeOCH_2); 4.37 (br. *s*, exchanged with D_2O, NH_2); 3.47, 3.41 (2*s*, 2 MeO); 0.87 (*s*, Me_3C); 0.10, 0.09 (2*s*, Me_2Si). ^{13}C NMR ($CDCl_3$): see *Table 5*; additionally, 97.46, 97.30 (2*t*, 2 MeOCH_2); 56.41, 56.23 (2*q*, 2 MeO); 25.81 (*q*, *Me*$_3$C); 18.08 (*s*, Me_3C); −4.56, −4.77 (2*q*, Me_2Si). HR-MALDI-MS: 387.1927 (100, $[M+Na]^+$; $C_{15}H_{32}N_2NaO_6Si^+$; calc. 387.1922). Anal. calc. for $C_{15}H_{32}N_2O_6Si$ (364.51): C 49.43, H 8.85, N 7.69; found: C 49.65, H 8.86, N 7.60.

6-O-*[(*tert*-Butyl)dimethylsilyl]-2,3*-O-*isopropylidene-5*-O-*(methylsulfonyl)*-D-*mannono-1,4-lactone* (**53**). A cooled (0°) soln. of **52** [87] (550 mg, 1.66 mmol) in CH_2Cl_2 (2 ml) and pyridine (1 ml) was treated with MsCl (194 µl, 2.5 mmol), stirred at 0° for 1 h and at 23° for 12 h, treated with H_2O (10 ml), and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. layers were dried and evaporated. FC (CH_2Cl_2) gave **53** (545 mg, 80%). White crystals. M.p. 119–120° (CH_2Cl_2). R_f (cyclohexane/AcOEt 2:1) 0.41. $[\alpha]_D^{25} = +17.0$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3031*w*, 2992*w*, 2956*m*, 2931*m*, 2888*w*, 2858*w*, 1799*s*, 1473*w*, 1463*w*, 1376*m*, 1364*s*, 1259*m*, 1219*m*, 1176*s*, 1155*m*, 1111*s*, 1026*m*, 970*m*, 959*m*, 926*s*, 838*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.94–4.84 (*m*, H−C(2), H−C(3), H−C(5)); 4.77 (*dd*, *J* = 8.1, 2.5, H−C(4)); 4.14 (*dd*, *J* = 12.1, 2.2, H−C(6)); 3.93 (*dd*, *J* = 12.1, 3.7, H′−C(6)); 3.10 (*s*, MsO); 1.49, 1.41 (2*s*, Me_2C); 0.90 (*s*, Me_3C); 0.10, 0.09 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 172.75 (*s*, C=O); 114.65 (*s*, Me_2C); 79.05 (*d*, C(2)); 76.07, 75.64, 74.82 (3*d*, C(3), C(4), C(5)); 62.28 (*t*, C(6)); 37.92 (*q*, MsO); 27.09, 26.22 (2*q*, *Me*$_2$C); 26.07 (*q*, *Me*$_3$C); 18.60 (*s*, Me_3C); −5.14, −5.21 (2*q*, Me_2Si). HR-MALDI-MS: 433.1325 (100, $[M+Na]^+$, $C_{16}H_{30}NaO_8SSi^+$; calc. 433.1329). Anal. calc. for $C_{16}H_{30}O_8SSi$ (410.56): C 46.81, H 7.36, S 7.81; found: C 46.91, H 7.30, S 7.74.

5,6-Bis-O-*[(*tert*-butyl)dimethylsilyl]-4-deoxy-4-hydrazino-2,3*-O-*isopropylidene*-L-*allono-1,4-lactam* (**55**). *1*) A suspension of **53** (500 mg, 1.22 mmol) in $NH_2NH_2 \cdot H_2O$ (3 ml) was stirred at 23° for 14 h and at 60° for 3 h. Co-evaporation with toluene and FC (CH_2Cl_2/MeOH/Et_3N 95:5:3) gave *6*-O-*[(*tert*-butyl)dimethylsilyl]-4-deoxy-4-hydrazino-2,3*-O-*isopropylidene*-L-*allono-1,4-lactam* (**54**; 409 mg, 97%). White solid. R_f (cyclohexane/AcOEt 1:2) 0.27. $[\alpha]_D^{25} = +46.3$ ($c = 0.7$, $CHCl_3$). IR (neat): 3327*w* (br.), 2953*m*, 2929*w*, 2857*w*, 1689*s*, 1621*w*, 1472*w*, 1463*w*, 1382*w*, 1374*m*, 1252*m*, 1211*m*, 1155*m*, 1117*m*, 1094*s*, 1050*m*, 998*m*, 936*w*, 902*w*, 873*m*, 833v*s*, 812*s*, 806*s*, 775v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.67 (*d*, *J* = 6.2, H−C(2)); 4.54 (*d*, *J* = 6.2, H−C(3)); 4.24 (br. *s*, exchanged with D_2O, NH_2); 4.12 (br. *t*, *J* = 6.6, H−C(5)); 3.82–3.63 (*m*, H−C(4), 2 H−C(6)); 1.38, 1.30 (2*s*, Me_2C); 0.88 (*s*, Me_3C); 0.07 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.82 (*s*, C=O); 111.67 (*s*, Me_2C); 76.57 (*d*, C(2)); 72.57 (*d*, C(3)); 67.57, 67.50 (2*d*, C(4), C(5)); 64.00 (*t*, C(6)); 27.08, 25.44 (2*q*, *Me*$_2$C); 26.11 (*q*, *Me*$_3$C); 18.51 (*s*, Me_3C); −5.15, −5.20 (2*q*, Me_2Si).

2) A soln. of **54** (520 mg, 1.5 mmol) in CH_2Cl_2 (5 ml) and pyridine (1 ml) was treated with TBSOTf (0.69 ml, 3.0 mmol), stirred at 0° for 1 h and at 23° for 24 h, treated with H_2O (10 ml), and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 4:1) gave **55** (654 mg, 95%). White crystals. M.p. 66–68° (cyclohexane/AcOEt). R_f (cyclohexane/AcOEt 1:2) 0.80. $[\alpha]_D^{25} = +64.8$ ($c = 0.37$, $CHCl_3$). IR (neat): 3322*w*, 3280*w*, 3211*w*, 2989*w*, 2953*m*, 2929*m*, 2885*w*, 2857*w*, 1718*s*, 1629*w*, 1471*w*, 1462*w*, 1428*w*, 1376*w*, 1368*w*, 1361*w*, 1255*m*, 1230*m*, 1116*s*, 1084*s*, 1051*w*, 1001*m*, 937*w*, 916*m*, 891*m*, 831v*s*, 806*s*, 773v*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.71 (*d*, *J* = 6.2, H−C(2)); 4.54 (*d*, *J* = 6.2, H−C(3)); 4.11 (*ddd*, *J* = 7.3, 4.8, 1.3, H−C(5)); 3.94 (*s*, NH_2); 3.82 (*d*, *J* = 1.2, H−C(4)); 3.69 (*dd*, *J* = 10.5, 4.8, H−C(6)); 3.66 (*dd*, *J* = 10.5, 7.2, H′−C(6)); 1.41, 1.34 (2*s*, Me_2C); 0.90, 0.82 (2*s*, 2 Me_3C); 0.074, 0.073, 0.047, −0.039 (4*s*, 2 Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 169.45 (*s*, C=O); 111.52 (*s*, Me_2C); 76.36 (*d*, C(2)); 72.21 (*d*, C(3)); 68.98, 66.93 (2*d*, C(4), C(5)); 64.21 (*t*, C(6)); 26.97, 25.31 (2*q*, *Me*$_2$C); 25.82, 25.68 (2*q*, 2 *Me*$_3$C); 18.20, 17.69 (2*s*, 2 Me_3C); −4.75, −4.83, −5.51, −5.55 (4*q*, 2 Me_2Si). MALDI-MS: 483 (11, $[M+Na]^+$), 461 (26, $[M+H]^+$). Anal. calc. for $C_{21}H_{44}N_2O_5Si_2$ (460.76): C 54.74, H 9.62, N 6.08; found: C 54.85, H 9.49, N 5.98.

*2*L-*(2,3/4)-4*-O-*[(*tert*-Butyl)dimethylsilyl]-5-diazo-2,3*-O-*isopropylidene-2,3,4-trihydroxycyclopentanone* (**56**). A soln. of **41** (95 mg, 0.3 mmol) in toluene (2 ml) was treated with a suspension of $Pb(OAc)_4$ (400 mg, 0.9 mmol) in toluene (2 ml), stirred at r.t. for 1 h, treated with H_2O, and extracted with Et_2O (3 × 30 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 12:1 → 6:1) gave **56** (35 mg, 37%). Yellow crystals. M.p. 69–71° (hexane). R_f (hexane/AcOEt 4:1) 0.50. $[\alpha]_D^{25} = +72.7$ ($c = 0.8$, $CHCl_3$). UV (MeOH): 294 (3.38), 253 (4.01). IR ($CHCl_3$): 3026*w*, 2994*w*, 2955*m*, 2932*m*, 2859*w*, 2100*s*, 1683*s*, 1471*w*, 1463*w*, 1385*w*, 1376*m*, 1354*m*, 1334*m*, 1313*w*, 1289*m*, 1261*m*, 1154*w*, 1084*s*, 1004*w*, 926*w*, 839*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 1.42, 1.36 (2*s*, Me_2C); 0.91 (*s*, Me_3C); 0.17, 0.13 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 113.19 (*s*, Me_2C); 27.52 (*q*, *Me*C); 25.81 (*q*, *Me*$_3$C, *Me*C); 18.21 (*s*,

Me_3C); −4.45, −4.59 (2*q*, Me_2Si). ESI-MS: 647 (72, $[2M+Na]^+$); 367 (80, $[M+MeOH+Na]^+$); 351 (100, $[M+K]^+$); 335 (65, $[M+Na]^+$); 313 (25, $[M+H]^+$). Anal. calc. for $C_{14}H_{24}N_2O_4Si$ (312.44): C 53.82, H 7.74, N 8.97; found: C 53.97, H 7.55, N 8.78.

Crystal Structure of **56**. Recrystallization of **56** in hexane gave crystals suitable for X-ray analysis, $C_{14}H_{24}N_2O_4Si$ (312.44); monoclinic $P2_1$; $a=7.3727$ (3) Å, $b=9.7904$ (4) Å, $c=13.0287$ (6) Å, $\beta=104.695$ (2)°; $V=909.67$ (7) Å^3; $D_{calc.}=1.141$ Mg/m^3; $Z=2$. From a crystal of size $0.24\times0.2\times0.04$ mm, 3743 reflections were measured on an *KappyCCD* diffractometer with MoK_α radiation (graphite monochromator, $\lambda=0.71073$ Å) at 293 K. $R=0.0661$, $R_w=0.1583$.

2L-*(2/3,4)-4*-O-*[(*tert-*Butyl)dimethylsilyl]-5-diazo-2,3-bis*-O-*(methoxymethyl)-2,3,4-trihydroxycyclopentanone* (**57**). A soln. of **46** (36 mg, 0.1 mmol) in toluene (1 ml) was treated with a suspension of $Pb(OAc)_4$ (133 mg, 0.3 mmol) in toluene (2.5 ml), stirred at r.t. for 1 h, treated with H_2O, and extracted with Et_2O (3 × 5 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 16:1 → 4:1) gave **57** (8 mg, 22%). Pale yellow syrup. R_f (cyclohexane/AcOEt 2:1) 0.50. $[\alpha]_D^{25}=-140.7$ ($c=0.5$, $CHCl_3$). UV (MeOH): 294 (3.15), 254 (3.87). IR ($CHCl_3$): 2956*m*, 2932*m*, 2897*m*, 2859*m*, 2827*w*, 2097*s*, 1692*s*, 1472*w*, 1456*m*, 1317*s*, 1255*m*, 1210*m*, 1153*s*, 1124*s*, 1090*m*, 1043*s*, 1015*s*, 833*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 5.01, 4.81 (2*d*, $J=6.5$, MeOCH_2); 4.75 (*s*, MeOCH_2); 3.46, 3.42 (2*s*, 2 MeO); 0.91 (*s*, Me_3C); 0.12, 0.10 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 96.38, 94.90 (2*t*, 2 MeO*C*H$_2$); 55.96, 55.83 (2*q*, 2 MeO); 25.72 (*q*, *Me*$_3$C); 18.21 (*s*, Me_3C); −4.08, −4.61 (2*q*, Me_2Si). ESI-MS: 399 (34, $[M+K]^+$), 383 (100, $[M+Na]^+$), 355 (80, $[M+Na-N_2]^+$). Anal. calc. for $C_{15}H_{28}N_2O_6Si$ (360.48): C 49.98, H 7.83, N 7.77; found: C 50.10, H 7.95, N 7.60.

2D-*(2,4/3)-4*-O-*[(*tert-*Butyl)dimethylsilyl]-5-diazo-2,3-bis*-O-*(methoxymethyl)-2,3,4-trihydroxycyclopentanone* (**58**). A soln. of **51** (36 mg, 0.1 mmol) in toluene (1 ml) was treated with a suspension of $Pb(OAc)_4$ (400 mg, 0.9 mmol) in toluene (3 ml), stirred at r.t. for 1 h, treated with H_2O, and extracted with Et_2O (3 × 5 ml). The combined org. layers were dried and evaporated. FC (cyclohexane/AcOEt 16:1 → 8:1) gave **58** (9 mg, 25%). Yellow syrup. R_f (cyclohexane/AcOEt 2:1) 0.58. $[\alpha]_D^{25}=+103.3$ ($c=0.5$, $CHCl_3$). UV (MeOH): 294 (3.22), 258 (3.85). IR ($CHCl_3$): 3012*w*, 2956m, 2932*m*, 2898*w*, 2859*w*, 2827*w*, 2098*s*, 1686*s*, 1472*w*, 1464*w*, 1318*s*, 1261*m*, 1153*s*, 1110*s*, 1078*m*, 1034*s*, 1004*m*, 919w, 844*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 5.06, 4.83, 4.78, 4.77 (4*d*, $J=6.5$, 2 MeOCH_2); 3.45, 3.43 (2*s*, 2 MeO); 0.91 (*s*, Me_3C); 0.17, 0.12 (2*s*, Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 96.70, 96.47 (2*t*, MeO*C*H$_2$); 56.31 (*q*, 2 MeO); 25.74 (*q*, *Me*$_3$C); 18.10 (*s*, Me_3C); −4.16, −4.43 (2*q*, Me_2Si). ESI-MS: 743 (9, $[2M+K]^+$), 399 (42, $[M+K]^+$), 383 (100, $[M+Na]^+$), 355 (93, $[M-N_2+Na]^+$).

4-Amino-5,6-bis-O-*[(*tert*-butyl)dimethylsilyl]-4-deoxy-4a-[(dimethylsulfinylidene)amino]-2,3*-O-*isopropylidene*-L-*allono-1,4-lactam* (**59**). A soln. of **55** (230 mg, 0.5 mmol) in toluene (10 ml) was added dropwise to a cooled (0°) suspension of $Pb(OAc)_4$ (665 mg, 1.5 mmol) in toluene (10 ml) and DMSO (2 ml). The mixture was stirred for 2 h at 0°, treated with H_2O (10 ml), and extracted with Et_2O (3 × 30 ml). The combined org. layers were dried ($MgSO_4$) and evaporated. FC (cyclohexane/AcOEt 1:2) gave **59** (144 mg, 54%). White crystals. M.p. 152–154° (hexane/Et_2O). R_f (cyclohexane/AcOEt 1:2) 0.10. $[\alpha]_D^{24}=-4.5$ ($c=0.5$, $CHCl_3$). IR ($CHCl_3$): 3018*s*, 2956*m*, 2931*m*, 2858*m*, 1694*s*, 1471*w*, 1462*w*, 1410*w*, 1383*w*, 1374*m*, 1256*m*, 1154*w*, 1118*m*, 1088*s*, 1045*m*, 1021*m*, 937*w*, 839*s*, 814*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.77 (*d*, $J=6.2$, H−C(2)); 4.53 (*d*, $J=6.2$, H−C(3)); 4.29 (*t*, $J\approx5.3$, H−C(5)); 3.98 (*s*, H−C(4)); 3.75–3.62 (*m*, 2 H−C(6)); 3.20, 3.14 (2*s*, Me_2S=O); 1.47, 1.35 (2*s*, Me_2C); 0.90, 0.84 (2*s*, 2 Me_3C); 0.07, 0.02 (2*s*, 2 Me_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 169.42 (*s*, C=O); 111.00 (*s*, Me_2C); 76.33 (*d*, C(2)); 72.68 (*d*, C(3)); 69.33, 68.40 (2*d*, C(4), C(5)); 64.69 (*t*, C(6)); 40.83, 40.14 (2*q*, Me_2S=O); 27.45, 25.38 (2*q*, *Me*$_2$C); 25.91 (*q*, 2 *Me*$_3$C); 18.28, 17.89 (2*s*, 2 Me_3C); −4.40, −4.82, −5.31, −5.39 (4*q*, 2 Me_2Si). MALDI-MS: 559 (8.5, $[M+Na]^+$), 353 (100). Anal. calc. for $C_{23}H_{48}N_2O_6SSi_2$ (536.88): C 51.46, H 9.01, N 5.22, S 5.97; found: C 51.56, H 8.84, N 5.06, S 6.09.

Crystal Structure of **59**. Recrystallization of **59** in hexane/Et_2O gave crystals suitable for X-ray analysis: $C_{23}H_{48}N_2O_6SSi_2$ (536.88): orthorhombic $P2_12_12_1$; $a=8.10130$ (10) Å, $b=9.00780$ (10) Å, $c=42.9596$ (6) Å, $\beta=90°$; $V=3134.97$ (8) Å^3; $D_{calc.}=1.138$ Mg/m^3; $Z=4$. From a crystal of size $0.24\times0.2\times0.1$ mm, 6850 reflections were measured on an *KappyCCD* diffractometer with MoK_α radiation (graphite monochromator, $\lambda=0.71073$ Å) at 298 K. $R=0.1766$, $R_w=0.2822$.

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