Properties and Reactions of Substituted 1,2-Thiazetidine 1,1-Dioxides: Functionalization and Reactions at C(4) of the β-Sultam

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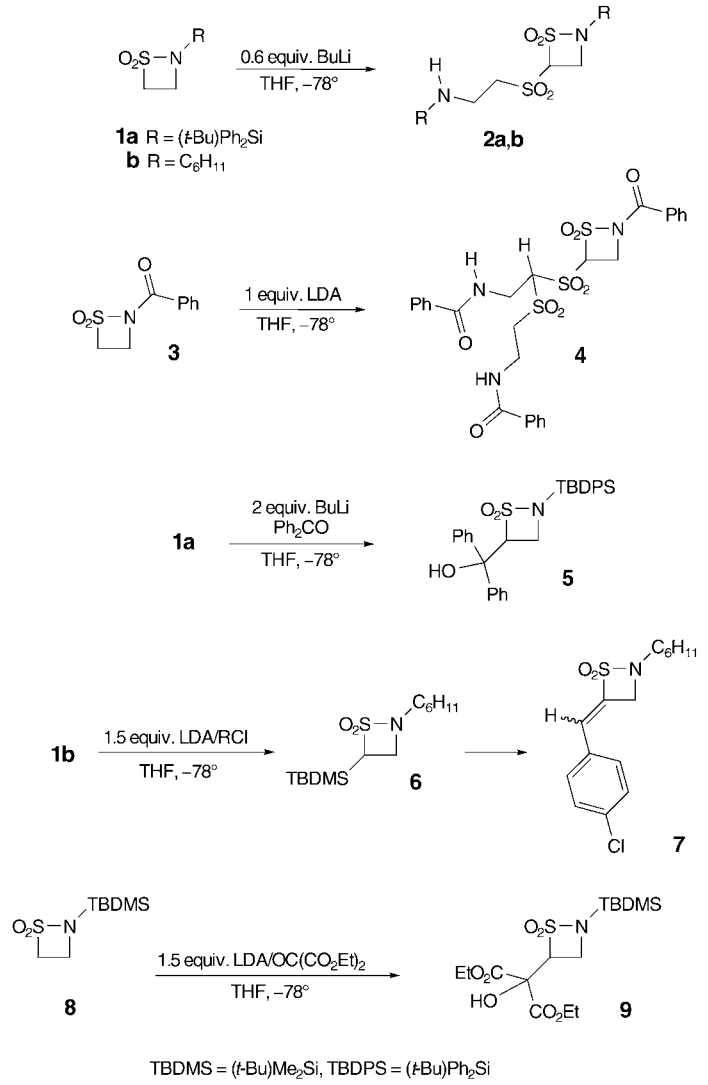
The introduction of functional groups at the 4-position of the β-sultam ring was realized by the synthesis of mono- and disubstituted derivatives by reactions of *N*-silylated β-sultams with electrophiles in the presence of BuLi or LDA. As electrophiles, ketones, chlorosilanes, a β-sultam, CO_2, chloroformiate, halogen, azodicarboxylate, phenyltriazoledione, tosyl azide, 1,3,5-triazine, propyl nitrate, and phenyl isocyanate were used. Furthermore, a number of derivatives of these substitution products were synthesized. All products were characterized by standard spectroscopic methods, and conformations were studied, supported by calculation.

Introduction. – The β-sultam ring (1,2-thiazetidine 1,1-dioxide) is a highly reactive cyclic sulfonamide that can be used as a building block in drug synthesis. But, in contrast to its less-reactive lactam analog, which can be easily functionalized, reactions at the β-sultam ring are much more difficult due to the sulfonyl group. In preceding papers, we have reported reactions at N(2) and at C(3) [1][2]. Here, we describe the introduction of functional groups at C(4). This position causes special problems, as the introduction of a heteroatom results in an unstable, aminal-like structure, which is readily hydrolyzed. Therefore, until now, no derivatives with an *N*-substituent at C(4) have been described.

After deprotonation, the C(4) atom of β-sultams can be attacked by electrophiles. Thereby, a deprotonated intermediate is formed [3] that, by reaction with C-electrophiles, yields relatively stable products, as demonstrated by silylation [4], acylation [5], reactions with aromatic nitriles yielding enamino β-sultams [6], and by the rearrangement of 2,3-disubstituted β-sultams into 2,4,1-dithiazine derivatives [7].

Results. – *Syntheses.* When a solution of 0.6–1 equiv. of BuLi or LDA (lithium diisopropylamide) was added to a solution of β-sultams **1a** or **1b** [4] at −78°, we isolated, after hydrolytic workup, the 'dimeric' (aminoethyl)sulfonyl β-sultams **2a** and **2b** in nearly quantitative yields (*Scheme 1*), probably formed by deprotonation of the β-sultam, followed by an attack of the deprotonated intermediate at the sulfonyl group of a second β-sultam molecule. A similar reaction was observed when a soln. of the *N*-benzoyl β-sultam **3** [8] was added to a soln. of 1 equiv.of LDA, but the reaction did not stop after the formation of the dimer. Rather, a second deprotonation and reaction with a third β-sultam yielded the 'trimeric' compound **4** as a mixture of two diastereoisomers. On the other hand, the reaction between **1a** and benzophenone, after deprotonation with 2 equiv. of BuLi, yielded the aldol adduct **5** [9]; and analogous reactions

Scheme 1

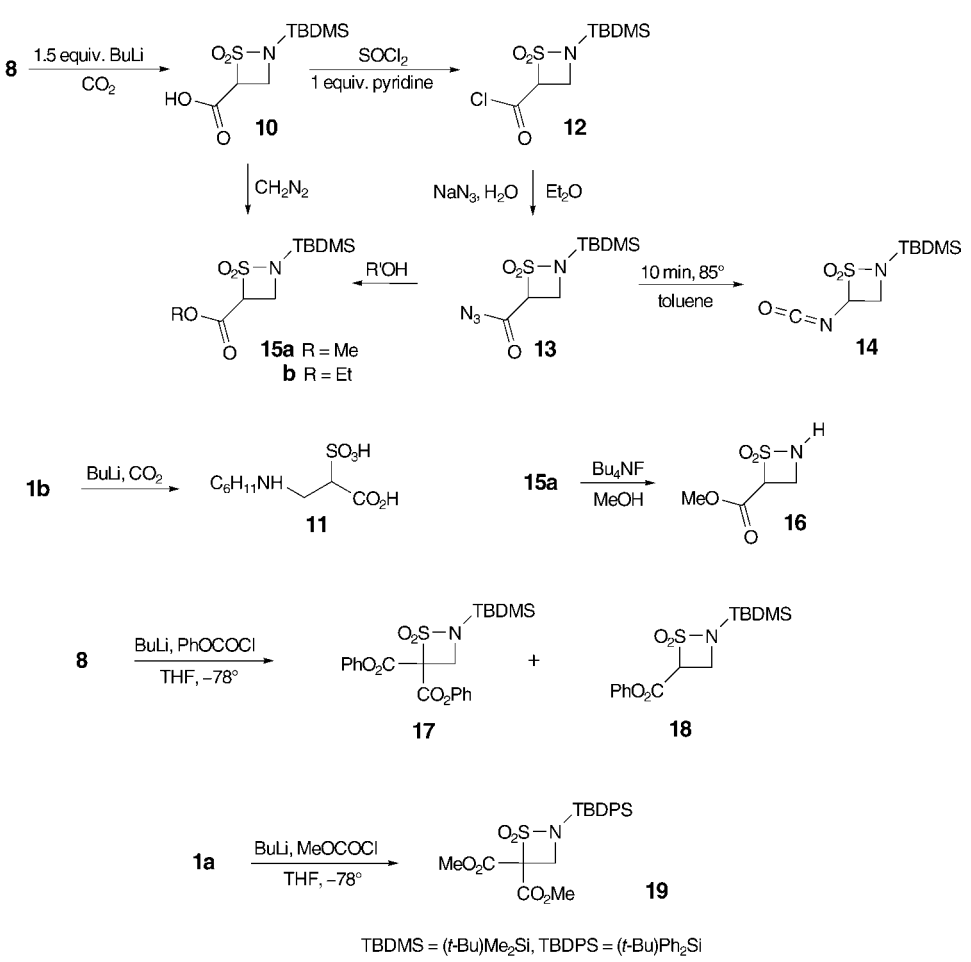


occurred, when **1b** was silylated after deprotonation with an excess of LDA, yielding **6**, which was transformed into the benzylidene derivative **7**. Analogously, **8** [4], after deprotonation with an excess of LDA, reacted with diethyl mesoxalate, yielding the aldol adduct **9**. These experiments clearly demonstrate that, for 1:1 reactions between the β-sultam ring and electrophiles, an excess of base is necessary.

Until now, no β-sultam with an N-substituent at C(4) has been described. As the *Curtius* rearrangement is known to be a mild and effective method to transform an isocyanate into an amine, we intended to prepare first an isocyanate from **8**, and then to

rearrange it into the corresponding 4-amino-β-sultam. Deprotonation of **8** with BuLi, followed by reaction with gaseous CO_2, led to the carboxylic acid **10**, which was isolated as a stable, crystalline compound in 45% yield (*Scheme 2*). An analogous reaction with **1b** did not yield the corresponding β-sultam, but the taurine derivative **11**, formerly prepared from the Cl derivative and cyclohexylamine [10]. The transformation of **10** into the acid chloride **12** was possible only when using $SOCl_2$ in the presence of 1 equiv. of pyridine. Then, **12** was obtained as a colorless viscous liquid in *ca.* 50% yield after purification by *Kugelrohr* distillation. The formation of the azide **13** was not possible by standard procedures, but when a solution of **12** in Et_2O was reacted with an aqueous solution of NaN_3 at 0°, **13** was obtained in yields of $>80\%$. Despite much effort, **13** could be rearranged only into the isocyanate **14** or the amine at exactly 85° in toluene, where the reaction is complete within 10 min, as shown by ^{1}H-NMR. Thus, we could not isolate pure compound **14**, which seems to be very unstable (probably due to the two electron-withdrawing heteroatoms at C(4)).

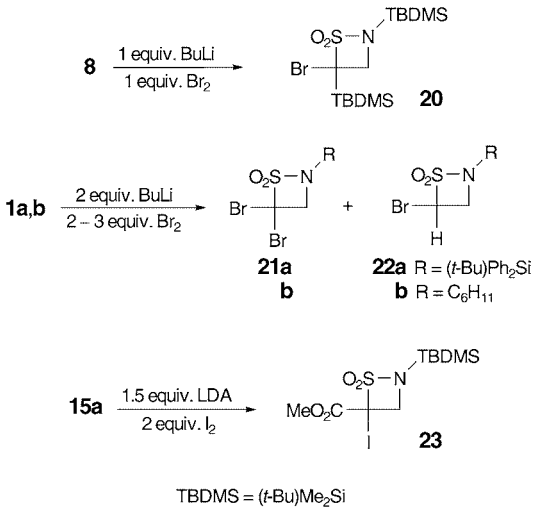
Scheme 2



When we tried the *Curtius* rearrangement of **13** in MeOH or EtOH to obtain the alkyl carbamates, we observed no rearrangement, but alcoholysis of the azide, and we isolated the esters **15a** or **15b**. These esters were obtained in higher yields from reactions of **12** and the parent alcohol. Furthermore, **15a** was synthesized by reaction of **10** with diazomethane, and was desilylated with TBAF on silica gel in MeOH at room temperature, yielding **16**. When **8**, after deprotonation with BuLi, was acylated with phenyl chloroformiate, a mixture of the diacylated product **17** and the monoacylated compound **18** was always obtained, which was separated by column chromatography (CC). Under similar conditions, the acylation of **1a** with methyl chloroformiate yielded only the diacylated compound **19**. While the monoacylated product **18** was obtained as a viscous liquid, all diacylated products were obtained as stable, crystalline compounds.

To explore the possibility of halogenation at C(4), **8** was deprotonated with equimolar amounts of BuLi and then reacted with Br_2, leading to **20**, which was isolated as a stable crystalline product in yields of *ca.* 20%, formed by a trans-silylation reaction followed by bromination of the intermediate silylated β-sultam (*Scheme 3*). Using an excess of BuLi (1.5–2 equiv.) and Br_2 (2–3 equiv.), we obtained in all experiments from **8**, **1a**, or **1b** mixtures of the mono- and dibrominated products. Separation by CC was possible, when the N-atom was protected with a (*t*-Bu)Ph_2Si group (**21a**, **22a**) or a cyclohexyl substituent (**21b**, **22b**), but separation was not possible when we used the (*t*-Bu)Me_2Si group for protection. Experiments with the aim of introducing Cl instead of Br failed. While analogous halogenations of β-lactams [11], depending on the conditions, yield stable monohalogenated compounds, our experiments demonstrate that the reactions of β-sultams with halogens yield mixtures of relatively unstable mono- and dihalogenated compounds in low yields. Furthermore, halogen exchange by *Finkelstein* reaction was not successful either. Finally, iodination of β-sultam was

Scheme 3



possible when one C-substituent was present at C(4), as demonstrated by the reaction of **15a** with LDA and I_2, yielding the crystalline compound **23** in 20% yield.

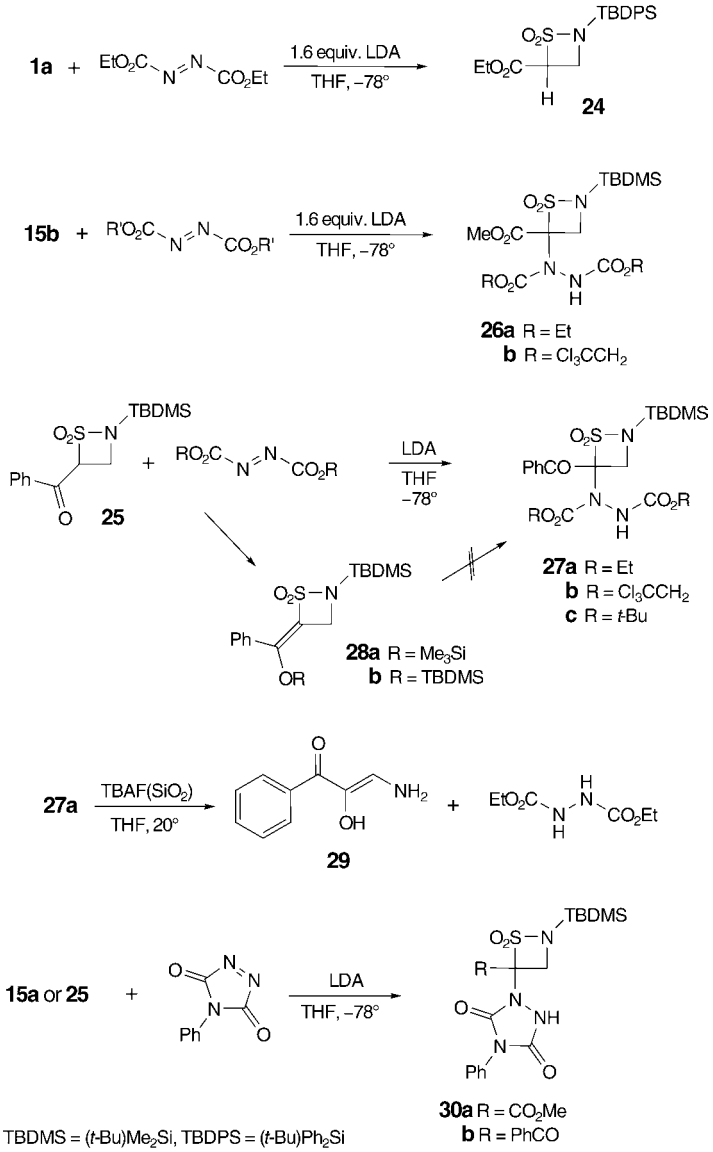
Unexpected results were obtained when we tried to introduce N-substituents at position 4. Thus, the reaction between **1a**, deprotonated with LDA at $-78°$, and an excess of diethyl azodicarboxylate (DEAD) did not give the expected addition product, but the carboxylate **24** and hydrazine-1,2-dicarboxylate. Apparently, in this reaction, the azodicarboxylate did not serve as an N-electrophile, but, like chloroformiate, as a C-electrophile, and the excess of azodicarboxylate was reduced by LDA (*Scheme 4*). However, when we performed the reaction with *C*(4)-monosubstituted *β*-sultams like **15a** or **25**, prepared from **8** and ethyl benzoate or benzonitrile, we obtained the addition products in yields of 30–80%. Thus, from reactions of **15a**, we isolated the addition products **26a** and **26b** as stable crystalline compounds. The analogous products **27a–c** were obtained from the 4-benzoyl derivative **25**. Even these products were obtained as stable crystalline compounds. In another experiment, we tried first to silylate **25**, and then to replace the silyl group by an N-substituent, but we obtained the silyl enol ethers **28a** and **28b** from the silylation reaction, and no further reaction with DEAD occurred. Upon trying to desilylate these addition products by stirring with TBAF (SiO_2) in THF at room temperature, we noticed in all experiments complete decomposition of the starting materials. In a detailed study with **27a**, we found two products, diethyl hydrazine-1,2-dicarboxylate and 3-amino-2-hydroxy-1-phenylprop-2-en-1-one (**29**). (This reaction is best explained by fluoride-catalyzed desilylation, followed by fluoride-catalyzed SO_2 extrusion and elimination of the hydrazine-1,2-dicarboxylate; the structure of **29** was established by spectroscopic methods, including high-resolution MS). On the other hand, additions readily occurred between **15a** or **25** and 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione, yielding the adducts **30a** and **30b**, respectively.

When we tried to prepare an azido *β*-sultam from **25** according to the method of *Kühlein* and *Jensen* [12] in the presence of Me_3SiCl, we did not isolate the desired azido compound, but silylated **28a**. By modifying the reaction conditions (warming the reaction mixture to 0° before addition of Me_3SiCl), we obtained **31a** in low yield. Under analogous conditions, we obtained from **15a** two fractions of the azido derivative **31b** (see below). Both azido compounds were isolated after chromatographic purification as viscous liquids. In the reaction between deprotonated **8** and 1,3,5-triazine, the latter reacted as the C-electrophile, and we obtained the dihydrotriazinyl derivative **32** as a crystalline compound (*Scheme 5*).

Finally, we prepared for the first time a 4-nitro *β*-sultam. For this purpose, **8** was silylated at $-78°$ with LDA and Et_3SiCl, yielding the *C*-monosilylated product **33** in 89% yield. The latter was deprotonated with BuLi, and then reacted with propyl nitrate at $-78°$, leading to the strongly moisture-sensitive product **34** as an unstable yellow liquid in 24% yield.

Reactions of **8** with phenyl isocyanate were similar to those with chloroformiates, and yielded mixtures of mono- and disubstituted products like **35** and **36**, which were isolated as stable crystalline compounds (*Scheme 6*). The monoamide **35** was prepared in higher yield from **12** and aniline in the presence of pyridine, and by the reaction of **12** in NH_3-saturated $CHCl_3$ at 0°, giving rise to the *β*-sultam 4-carboxamide **37**. Finally, we prepared two substituted amides, **38a** and **38b**, bearing an aminothiazolyl substituent

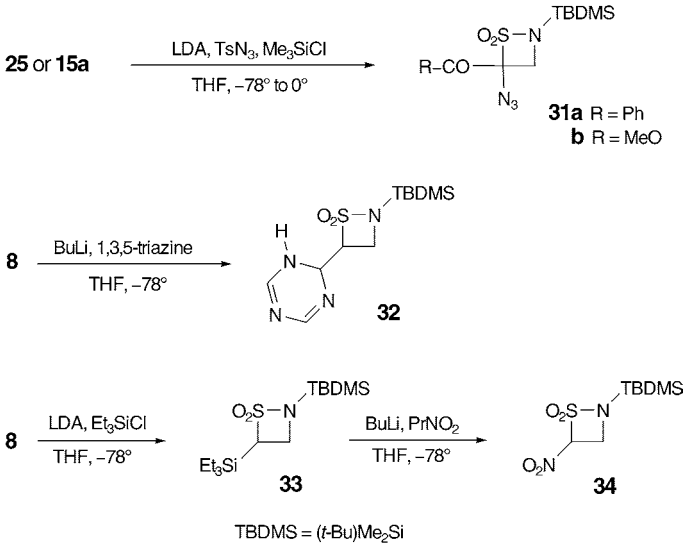
Scheme 4



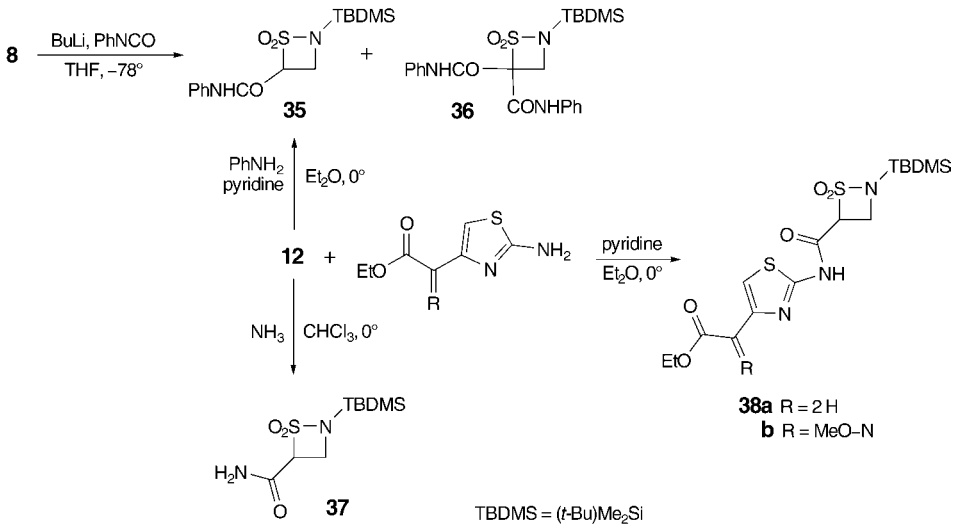
known to increase the anti-infective activity of cephalosporins. Unfortunately, both compounds exhibited no remarkable antibacterial activities in standard tests.

In conclusion, our experiments demonstrate that reactions at C(4) of β-sultam rings significantly differ from analogous reactions of β-lactams, while reactions at positions 2 or 3 are comparable with those at the β-lactam ring [11]. The most-significant difference concerns the introduction of a heteroatom at C(4). While α-halogeno and α-

Scheme 5



Scheme 6



amino β-lactams are relatively stable compounds that can be prepared mostly by standard methods [11], β-sultam derivatives are unstable, as demonstrated for halogeno and nitro compounds. This explains why the synthesis of α-amino β-sultams has not been described so far.

Spectroscopy and Stereochemistry. The IR spectra of all β-sultams are characterized by the bands of the SO_2 group at 1340–1295 (SO_2, asym.) and 1200–1140 cm^{-1} (SO_2,

sym.), depending on the substituents. When comparing the data of the *N*-silyl compound **8** with those of the *N*-benzoyl derivative **3**, both lacking substituents at C(4), a shift to higher wave numbers is observed for both bands. The data of the 4-substituted derivatives show no or only a small shift of both bands, when the substituent is silyl, an sp^3-C-atom, or when C(4) is sp^2 hybridized (**7**). When the substituent at C(4) is an electron-withdrawing group as in **10**, **15a**, **13**, **14**, **31b**, and **34**, the shift to higher wave numbers of $\nu(SO_2$, asym.) is relatively small (0–30 cm^{-1}), but the shift of $\nu(SO_2$, sym.) increases by up to 60 cm^{-1} (*Table 1*).

Table 1. *IR Data of Selected β-Sultams*

Compound	$\nu(SO_2$, asym.)	$\nu(SO_2$, sym.)	Other bands, literature
3	1340	1155	1660 (C=O) [12]
5	1310, 1295	1175, 1140	
6	1310	1155	
7	1300	1150	
8	1300	1140	[4]
10	1315	1170	1730 (C=O)
12	1335	1180	1805, 1775 (C=O)
13	1330	1200, 1170	2180 (N_3), 1720 (C=O)
14	1320	1180	2260 (N=C=O)
15a	1320	1170	1750 (C=O)
16	1340	1170	1745 (C=O)
17	1320	1180, 1160	1750, 1730 (C=O)
21a	1330	1170	
31b	1300	1180	2140 (N_3), 1760 (C=O
33	1301	1161	
34	1328	1184	1570, 1359 (NO_2)

All C(4)-monosubstituted β-sultams show in their ^{1}H-NMR spectra an *AB(M)X* system for H–C(4) and H–C(3). When the substituent at C(4) is electron withdrawing (as in **10**, **12**, **13**, **14**, **15a**, **18**, or **34**), the signal of one H-atom at C(3) shows a significant downfield shift (*Table 2*). We interprete this effect by the anisotropy effect of the substituent at C(4) on the vicinal proton in the *cis* position, while the *trans* proton is nearly unaffected. This is in agreement with the coupling constants $J_{3',4} = J_{cis} = 7-8$ Hz, and $J_{3,4} = J_{trans} = 4-5$ Hz, and with the postulate of a favored pseudo-equatorial orientation of the substituent at C(4) (*Fig. 1,a*), which is supported by an *ab initio*

Table 2. *^{1}H-NMR Data of Selected β-Sultams.* Solvent: $CDCl_3$; δ in ppm, *J* in Hz.

Compound	H′–C(3)	H–C(3)	H–C(4)	*J*(3,3′)	*J*(3′,4)	*J*(3,4)
10	3.47	3.65	5.25	6	8	5
12	3.50	3.70	5.57	6	7.6	4.5
13[a])	2.93	3.50	4.70	6	7.6	4.5
14[a])	2.72	3.16	4.86	6	7	5
15a	3.44	3.67	5.18	5.7	7.5	4.5
18	3.53	3.76	5.40	6.3	7.7	4.6
34	3.69	3.94	6.42	8	7	4

[a]) In (D_8)toluene.

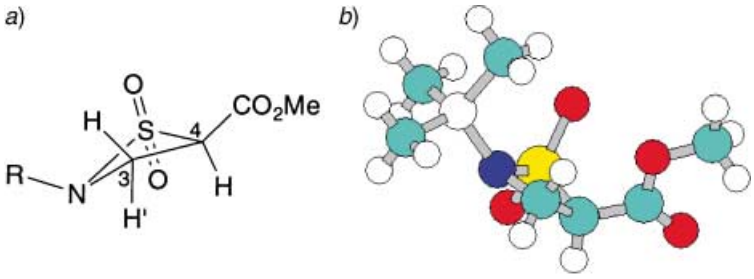
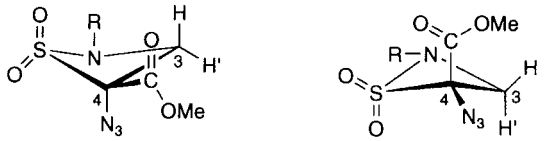


Fig. 1. *Favored conformation of* a) **15a** *according to NMR data, and of* b) *(*R*)*-**15a**, *as derived by* ab initio *calculation* (Gauss STO-3G; *Hyperchem 5.11*)

calculation of **15a**, showing a 'folding' of 18° for the β-sultam ring (*Fig. 1,b*). This folding agrees with results from former X-ray analyses [4][8].

A remarkable observation was made when we reacted **15a** with tosyl azide. The purification of the crude product by CC (SiO_2) yielded two fractions, **31ba** and **31bb**, which showed identical IR spectra, ^{13}C-NMR spectra, and elemental analyses, but exhibited significant differences in the shifts of H′−C(3) and H−C(3) in the ^{1}H-NMR spectra. While, in the spectrum of **31ba**, the signal of H′−C(3) at δ(H) 4.23 showed a downfield shift compared to that of H−C(3) at 3.93 ppm, in the spectrum of **31bb**, the effect was opposite. Here, the signal of H−C(3) at 4.37 ppm showed a downfield shift compared to that of H′−C(3) at 3.57 ppm. We suspect that we have isolated two different conformers (*Fig. 2*) that are stable at room temperature. To estimate the free energy of activation for their interconversion, we tried to record ^{1}H-NMR spectra at elevated temperature, but, unfortunately, the compound(s) completely decomposed on warming.



31ba R = (*t*-Bu)Me_2Si **31bb**

Fig. 2. *Favored conformers* **31ba** *and* **31bb** *of compound* **31b**, *as deduced from NMR data*

We wish to thank *Novartis*, Basel, for biological tests, *Degussa AG* for generous support with chemicals, *E. Merck KGaG*, Darmstadt, for extended support with chemicals, with chromatography materials, and for HPLC experiments, and we thank the '*Fonds der Chemischen Industrie*', Frankfurt a. Main, for continuous financial support.

Experimental Part

General. Abbreviations: HMPT, hexamethylphosphortriamide; LDA, lithium diisopropylamide; PE, petroleum ether; TBAF, tetrabutylammonium fluoride; THF, tetrahydrofuran. THF was stored over $CaCl_2$, refluxed over $LiAlH_4$, and distilled prior to use. Other solvents were dried and purified according to literature procedures. Compounds **1a** [4], **1b** [6], **3** [8], **8** [4], and **11** [10] were prepared according to lit. procedures. Lithium diisopropylamide (LDA) was freshly prepared by mixing equivalent amounts of $(i\text{-}Pr)_2NH$ and BuLi

(15% in hexane) in THF at −78°. Thin-layer chromatography (TLC): pre-coated silica-gel *60F*$_{254}$ plates (*Merck*). Column (CC) and flash chromatography (FC): silica gel *60* (*Merck*). M.p.: *Kofler* apparatus; uncorrected. IR Spectra (KBr): *Perkin-Elmer IR-1310*, *Beckman IR-4240*; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Varian T-60* (^{1}H, 60 MHz), *Bruker WP-80* (80/20.15 MHz for ^{1}H and ^{13}C, resp.), *WP-250*, *AM-400* (^{1}H, 250/400 MHz); δ in ppm rel. to $SiMe_4$ (=0 ppm), *J* in Hz; in $CDCl_3$, if not stated otherwise. MS: *Finnigan GC-MS 4000*, *MAT-312*, *MAT-44-S*; in *m*/*z* (rel. %); EI spectra at 200° (70 eV), CI spectra with CH_4, NH_3, ca. 300 μbar. Elemental analyses: Institute of Pharmacy, or Chemisches Laboratorium, University of Freiburg (Germany) or Greifswald (Germany), resp. All compounds[1]) gave satisfactory elemental analyses or were analyzed by MS and/or HR-MS.

*2-[(*tert*-Butyl)diphenylsilyl]-4-[(2-{[(*tert*-butyl)diphenylsilyl]amino}ethyl)sulfonyl]-1,2-thiazetidine 1,1-Dioxide* (**2a**). BuLi (3.8 ml, 6 mmol) was added to a soln. of **1a** (3.45 g, 10 mmol) in THF (100 ml) at −78°. The mixture was stirred for 30 min at this temp. and hydrolyzed with aq. sat. NaCl soln. (200 ml). The org. layer was dried (Na_2SO_4) and concentrated *in vacuo:* 1.55 g (45%) of **2a**. Colorless crystals. M.p. 150° (EtOH). IR: 3400 (NH), 3070, 3040, 2960, 2930, 2900, 2860 (CH), 1330, 1300, 1185, 1140, 1110 (SO_2), 820, 745 (Me−Si). ^{1}H-NMR (80 MHz): 1.01 (*s*, *t*-Bu); 1.18 (*s*, *t*-Bu); 1.55 (*s*, NH); 3.15–3.60 (*m*, 2 CH_2, H−C(3), H′−C(3)); 5.36 (*dd*, *J* = 7.8, 4.4, H−C(4)); 7.25–7.85 (*m*, 20 arom. H). EI-MS: 691 (0.8, M^+), 135 (100). Anal. calc. for $C_{36}H_{46}N_2O_4S_2Si_2$ (691.06): C 62.56, H 6.71, N 4.05, S 9.27; found: C 62.29, H 6.60, N 4.27, S 9.00.

2-Cyclohexyl-4-{[2-(cyclohexylamino)ethyl]sulfonyl}-1,2-thiazetidine 1,1-Dioxide (**2b**). Prepared from **1b** (950 mg, 5 mmol), as described for **2a**. Some drops of Et_2O were added to the residue, which was cooled for 24 h to 0°: 450 mg (48%) of **2b**. M.p. 86–88° (Et_2O). IR: 3290 (NH), 2920, 2850 (CH), 1330, 1295, 1170, 1120 (SO_2). ^{1}H-NMR (250 MHz): 0.98–2.04 (*m*, 10 CH_2, NH); 2.46 (*m*, cyclohexyl CH); 3.08–3.34 (*m*, CH−CH_2, cyclohexyl CH); 3.36 (*dd*, *J* = 6.3, 7.7, H′−C(3)); 3.70 (*m*, CH); 3.78 (*dd*, *J* = 4.3, 6.3, H−C(3)); 5.74 (*dd*, *J* = 7.7, 4.3, H−C(4)). Anal. calc. for $C_{16}H_{30}N_2O_4S_2$ (378.54): C 50.76, H 7.99, N 7.40, S 16.94; found C 50.71, H 7.89, N 7.28, S 16.81.

2-Benzoyl-4-[(2-(benzoylamino)-1-{[(benzoylamino)ethyl]sulfonyl}ethyl)sulfonyl]-1,2-thiazetidine 1,1-Dioxide[1]) (**4**). A soln. of **3** (2.1 g, 10 mmol) in THF (40 ml) was added to a soln. of LDA (10 mmol) in THF (30 ml) at −78° over 10 min at −78° under stirring. Then, a mixture of an aq. sat. NaCl soln. (152 ml) and conc. HCl soln. (8 ml) was added, the org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo:* 900 mg (43%) of **4**. Colorless crystals. M.p. 204–208° (EtOH; dec.). IR: 3420, 3320 (NH), 3060, 2990, 2960, 2940 (CH), 1680, 1640 (C=O), 1535 (NH), 1350, 1330, 1310, 1290, 1190, 1160, 1140 (SO_2). Anal. calc. for $C_{27}H_{27}N_3O_9S_3$ (633.72): C 51.17, H 4.29, N 6.63, S 15.17; found: C 50.94, H 4.39, N 6.50, S 15.01.

Isomer 1. ^{1}H-NMR (250 MHz, (D_6)DMSO): 3.76 (*m*, 2 CH_2); 4.00 (*dd*, *J* = 6.0, H−C(7), H′−C(7)); 4.23 (*dd*, *J* = 8.7, 5.2, H′−C(3)); 4.42 (*dd*, *J* = 8.7, 8.7, H−C(3)); 6.77 (*t*, *J* = 6.0, H−C(6)); 6.89 (*dd*, *J* = 8.7, 5.2, H−C(4)); 7.4–8.0 (*m*, 15 arom. H); 8.84 (*s*, NH); 9.14 (*t*, *J* = 6.0, NH).

Isomer 2. ^{1}H-NMR (250 MHz, (D_6)DMSO): 3.76 (*m*, 2 CH_2); 4.09 (*dd*, *J* = 6, H−C(7), H′−C(7)); 4.23 (*dd*, *J* = 8.7, 5.2, H′−C(3)); 4.42 (*dd*, *J* = 8.7, 8.7, H−C(3)); 6.55 (*t*, *J* = 6.0, H−C(6)); 6.89 (*dd*, *J* = 8.7, 5.2, H−C(4)); 7.4–8.0 (*m*, 15 arom. H); 8.84 (*s*, NH); 9.06 (*t*, *J* = 6.0, NH).

*2-[(*tert*-Butyl)diphenylsilyl]-4-[hydroxy(diphenyl)methyl]-1,2-thiazetidine 1,1-Dioxide*[1]) (**5**). BuLi (12.5 ml, 20 mmol) was added to a soln. of **1a** (3.45 g, 10 mmol) in THF (100 ml) at −78°, and after 45 s, a soln. of benzophenone (4.5 g, 25 mmol) in THF (20 ml) was added. After stirring for 10 min at −78°, a sat. aq. soln. of NaCl (200 ml) was added, the org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. Some drops of MeOH were added to the residue, which, on cooling (24 h, 0°), crystallized: 2.2 g (41%) of **5**. Colorless crystals. M.p. 66–80° (MeOH). IR: 3490 (OH), 3060, 3040, 3020, 2960, 2920, 2890, 2860 (CH), 1310, 1295, 1175, 1140 (SO_2). ^{1}H-NMR (80 MHz): 1.16 (*s*, *t*-Bu); 2.93 (*dd*, *J* = 5.6, 8.6, H′−C(3)); 3.41 (*dd*, *J* = 5.6, 5.6, H−C(3)); 4.40 (*s*, OH); 5.52 (*dd*, *J* = 8.6, 5.6, H−C(4)); 7.05–7.9 (*m*, 20 arom. H). Anal. calc. for $C_{31}H_{33}NO_3SSi$ (527.74): C 70.55, H 6.30, N 2.65, S 6.07; found: C 70.50, H 6.37, N 2.73, S 6.18.

*4-[(*tert*-Butyl)dimethylsilyl]-2-cyclohexyl-1,2-thiazetidine 1,1-Dioxide* (**6**). A soln. of **1b** (1.89 g, 15 mmol) in THF (70 ml) was added dropwise at −78° to a mixture of a soln. of LDA (20 mmol) in THF (20 ml) and a soln. of (*t*-Bu)Me_2SiCl (2.26 g, 15 mmol) in THF (20 ml). The mixture was stirred for 1 h at −78°, and then hydrolyzed with aq. sat. soln. of NaCl (100 ml). The org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. Some drops of pentane were added to the residue to induce crystallization: 1.95 g (65%) of **6**. Colorless crystals. M.p. 79° (pentane). IR: 2930, 2900, 2850 (CH), 1310, 1155 (SO_2), 1250 (Me−Si). ^{1}H-NMR (80 MHz):

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[1]) For simplicity, all compounds were named taking the thiazetidine 1,1-dioxide core as the parent structure, ignoring potentially higher-ranking side chains.

0.21, 0.27 (2*s*, Me_2Si); 0.95 (*s*, *t*-Bu); 1.10–2.13 (*m*, 5 CH_2); 2.91 (*dd*, *J* = 4.5, 6, H′–C(3)); 3.22 (*m*, CH); 3.29 (*dd*, *J* = 8.5, 4.5, H–C(3)); 3.95 (*dd*, *J* = 8.5, 6, H–C(4)). Anal. calc. for $C_{14}H_{29}NO_2SSi$ (303.54): C 55.40, H 9.63, N 4.61, S 10.56; found: C 55.15, H 9.51, N 4.72, S 10.68.

4-(4-Chlorobenzylidene)-2-cyclohexyl-1,2-thiazetidine 1,1-Dioxide (**7**). A cooled soln. of **6** (1.5 g, 5 mmol) in THF (40 ml) was added dropwise to a soln. of LDA (10 mmol) in THF (20 ml) at −78°. Then, a soln. of 4-chlorobenzaldehyde (2.1 g, 15 mmol) in THF (10 ml) was added under stirring. Stirring was continued for 1 h, the mixture was hydrolyzed with a sat. aq. soln. of NaCl (100 ml), the org. layer was separated, and stirred for 1.5 h with an aq. soln. of $NaHSO_3$ (37%). The org. layer was again separated, dried (Na_2SO_4), and evaporated *in vacuo:* 1 g (66%) of **7**. Colorless crystals. M.p. 177° (MeOH). IR: 2920, 2850 (CH), 1675 (C=C), 1590 (arom.), 1300, 1150 (SO_2). ^{1}H-NMR (80 MHz; (*Z*)-Isomer): 1.05–2.15 (*m*, 5 CH_2); 2.26 (*m*, CH); 3.75 (*d*, *J* = 1.5, H′–C(3), H–C(3)); 6.58 (*t*, *J* = 1.5, H–C(*α*)); 7.10–7.62 (*m*, 4 arom. H). ^{1}H-NMR (80 MHz; (*E*)-Isomer): 1.05–2.15 (*m*, 5 CH_2); 2.26 (*m*, CH); 3.97 (*d*, *J* = 2, H′–C(3), H–C(3)); 7.10 (*t*, *J* = 2, H–C(*α*)); 7.10–7.62 (*m*, 4 arom. H). Anal. calc. for $C_{15}H_{18}ClNO_2S$ (311.83): C 57.78, H 5.82, Cl 11.37, N 4.49, S 10.28; found: C 57.58, H 5.72, Cl 11.46, N 4.44, S 10.38.

*2-[(*tert*-Butyl)dimethylsilyl]-4-[2-ethoxy-1-(ethoxycarbonyl)-1-hydroxy-2-oxoethyl]-1,2-thiazetidine 1,1-Dioxide*[1]) (**9**). A soln. of **8** (660 mg, 3 mmol) was added to a soln. of LDA (4.5 mmol) in THF (25 ml) at −78°. Then, diethyl mesoxalate (= diethyl 2-oxopropane-1,3-dioic acid; 1.4 ml, 9 mmol) was added. After stirring for 10 min at −78°, the mixture was hydrolyzed with a sat. aq. soln. of NaCl (80 ml). The org. layer was separated, dried (Na_2SO_4), and evaporated. The residue was purified by CC ($CHCl_3$/acetone 95:5; R_f 0.4): 200 mg (17%) of **9**. Yellow liquid. IR (film): 3480 (OH), 2970, 2940, 2920, 2870 (CH), 1745 (C=O), 1310, 1175 (SO_2). ^{1}H-NMR (80 MHz): 0.23 (*s*, Me_2Si); 0.95 (*s*, *t*-Bu); 1.31 (*t*, Me); 1.36 (*t*, Me); 3.32–3.66 (*m*, H′–C(3), H–C(3)); 4.08–4.60 (*m*, 2 OCH_2); 4.37 (*s*, OH); 5.22 (*dd*, *J* = 8.0, 5.5, H–C(4)). Anal. calc. for $C_{15}H_{29}NO_7SSi$ (395.55): C 45.55, H 7.39, N 3.54; found: C 45.82, H 7.37, N 3.47.

*2-[(*tert*-Butyl)dimethylsilyl]-1,2-thiazetidine-4-carboxylic Acid 1,1-Dioxide* (**10**). BuLi (9.4 ml, 15 mmol) was added to a soln. of **8** (2.2 g, 10 mmol) in THF (150 ml) at −78°. After 45 s, CO_2 gas was bubbled through the soln. for 10–15 min, and stirring was continued for 10 min at −78°. Then, a mixture of a sat. aq. soln. of NaCl (114 ml) and conc. HCl (6 ml) was added, the org. layer was separated, dried (Na_2SO_4), and evaporated. The residue was dissolved in a few milliliters of pentane, and cooled (0°, 24 h): 1.2 g (45%) of **10**. Colorless crystals. M.p. 100° (pentane). IR: 3200–2540 (OH), 2960, 2940, 2900, 2860 (CH), 1730 (C=O), 1315, 1170 (SO_2). ^{1}H-NMR (80 MHz): 0.30 (*s*, Me_2Si); 0.99 (*s*, *t*-Bu); 3.47 (*dd*, *J* = 6, 8, H′–C(3)); 3.65 (*dd*(*t*), *J* = 5, 6, H–C(3)); 5.25 (*dd*, *J* = 8, 5, H–C(4)); 8.82 (*s*, OH). Anal. calc. for $C_9H_{19}NO_4SSi$ (265.39): C 40.73, H 7.21, N 5.28, S 12.08; found: C 40.47, H 7.10, N 5.41, S 12.18.

*2-[(*tert*-Butyl)dimethylsilyl]-1,2-thiazetidine-4-carbonyl Chloride 1,1-Dioxide* (**12**). Pyridine (0.4 ml, 5 mmol) was added at 0° to a soln. of **10** (1.32 g, 5 mmol) in Et_2O (150 ml) under N_2. Then, $SOCl_2$ (0.38 ml, 5 mmol) was added dropwise, and stirring was continued for 30 min at 0°, and then for 1 h at r.t. The precipitate was filtered off, the filtrate was concentrated *in vacuo*, and the resulting residue was purified by *Kugelrohr* distillation: 700 mg (49%) of **12**. Colorless liquid. B.p. 130°/0.01 Torr. IR (film): 2960, 2940, 2910, 2900, 2870 (CH), 1805, 1775 (C=O), 1335, 1180 (SO_2), 1260 (Me–Si). ^{1}H-NMR (80 MHz): 0.31 (*s*, Me_2Si); 1.00 (*s*, *t*-Bu); 3.50 (*dd*, *J* = 6, 7.6, H′–C(3)); 3.70 (*dd*(*t*), *J* = 4.5, 6, H–C(3)); 5.57 (d*d*, *J* = 7.6, 4.5, H–C(4)). Anal. calc. for $C_9H_{18}ClNO_3SSi$ (283.85): C 38.08, H 6.39, N 4.93; found: C 37.81, H 6.24, N 5.08.

*2-[(*tert*-Butyl)dimethylsilyl]-1,2-thiazetidine-4-carbonyl Azide 1,1-Dioxide* (**13**). A soln. of **11** (700 mg, 2.45 mmol) in Et_2O (20 ml) was added under vigorous stirring at 0° to a soln. of NaN_3 (580 mg, 9.3 mmol) in H_2O (3 ml). Stirring was continued for 1.5 h at 0°, the org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo:* 600 mg (85%) of **13**. Colorless liquid. IR (film): 2970, 2940, 2920, 2900, 2880 (CH), 2180 (N_3), 1720 (C=O), 1330, 1200–1170 (SO_2), 1265 (Me–Si), 1210–1180 (N_3). ^{1}H-NMR (80 MHz): 0.31 (*s*, Me_2Si); 1.00 (*s*, *t*-Bu); 3.45 (*dd*, *J* = 6, 7.6, H′–C(3)); 3.67 (*dd*, *J* = 4.5, 6, H–C(3)); 5.17 (*dd*, *J* = 7.6, 4.5, H–C(4)); ^{1}H-NMR (80 MHz; (D_8)toluene): 0.31 (*s*, Me_2Si); 1.05 (*s*, *t*-Bu); 2.93 (*dd*, *J* = 6, 7.6, H′–C(3)); 3.50 (*dd*, *J* = 4.5, 6, H–C(3)); 4.70 (*dd*, *J* = 7.6, 4.5, H–C(4)). EI-MS: 291 (3.4, $[M+1]^+$), 100 (100), 233 (12), 141 (30), 136 (20), 129 (17), 113 (37), 102 (16), 101 (38), 99 (23), 86 (60), 75 (42), 74 (22), 73 (88), 72 (41), 59 (76), 58 (26), 57 (82), 56 (30), 55 (91), 45 (30), 44 (12), 43 (44), 42 (11), 41 (19). CI-MS (CH_4): 291 ($[M+H]^+$). Molecular formula: $C_9H_{18}N_4O_3SSi$ (290.41 g mol^{-1}).

*2-[(*tert*-Butyl)dimethylsilyl]-1,2-thiazetidine-4-carbonyl Isocyanate 1,1-Dioxide* (**14**). In an NMR tube, a soln. of **13** (290 mg, 1 mmol) in [D_8]toluene (1.5 ml) was warmed for 10 min to 80° in an NMR spectrometer. Longer heating resulted in product decomposition. IR (film): 2960, 2940, 2910, 2900, 2860 (CH), 2260 (N=C=O), 1320, 1180 (SO_2), 1260 (Me–Si). ^{1}H-NMR (80 MHz, (D_8)toluene): 0.31 (*s*, Me_2Si); 1.00 (*s*, *t*-Bu);

2.72 (*dd*, *J* = 6, 5, H′–C(3)); 3.16 (*dd*, *J* = 7, 6, H–C(3)); 4.86 (*dd*, *J* = 7, 5, H–C(4)). Molecular formula: $C_9H_{18}N_2O_3SSi$ (262.40 g mol^{-1}).

*Methyl 2-[(*tert*-Butyl)dimethylsilyl]-1,2-thiazetidine-4-carboxylate 1,1-Dioxide* (**15a**). *Method A*. A soln. of diazomethane – prepared from *Diazald*® (3 g), dissolved in Et_2O (30 ml) and aq. KOH (2 ml, 65%), and diethyleneglycolmonomethyl ether (5 ml) – was distilled into a soln. of **10** (1.6 g, 6 mmol) in Et_2O (200 ml) under stirring at 0°. Stirring was continued for 3 h at 0°, the excess diazomethane was blown out with a stream of N_2, the solvent was evaporated *in vacuo*, and the residue was purified by *Kugelrohr* distillation: 1.2 g (72%) of **15a**. Colorless liquid. B.p. 110°/0.01 Torr. IR (film): 2960, 2940, 2900, 2890, 2860 (CH), 1750 (C=O), 1320, 1170 (SO_2). ^{1}H-NMR (250 MHz): 0.28, 0.30 (2*s*, Me_2Si); 1.00 (*s*, *t*-Bu); 3.44 (*dd*, *J* = 5.7, 7.5, H′–C(3)); 3.67 (*dd*, *J* = 4.5, 5.7, H–C(3)); 3.89 (*s*, MeO); 5.18 (*dd*, *J* = 7.5, 4.5, H–C(4)). EI-MS: 222 (26, $[M - t\text{-Bu}]^+$), 55 (100). Anal. calc. for $C_{10}H_{21}NO_4SSi$ (279.39): C 42.99, H 7.57, N 5.01, S 11.47; found: C 42.76, H 7.47, N 5.12, S 11.22.

Method B. A soln. of **12** (1.6 g, 6 mmol) in MeOH (15 ml) was stirred for 30 min at r.t. The solvent was evaporated, and the residue was purified as in *Method A* (see above): 1.1 g (65%) of **15a**.

*Ethyl 2-[(*tert*-Butyl)dimethylsilyl]-1,2-thiazetidine-4-carboxylate 1,1-Dioxide* (**15b**). *Method A*. A soln. of **13** (600 mg, 2 mmol) in EtOH (15 ml) was refluxed for 15 min, the solvent was evaporated, and the residue was purified by *Kugelrohr* distillation: 350 mg (60%) of **15b**. Colorless liquid. B.p. 165°/0.02 Torr. IR (film): 2960, 2940, 2860 (CH), 1745 (C=O), 1330, 1175 (SO_2). ^{1}H-NMR (80 MHz): 0.33 (*s*, Me_2Si); 1.00 (*s*, *t*-Bu); 1.35 (*t*, Me); 3.45 (*dd*, *J* = 5.8, 8.0, H′–C(3)); 3.70 (*dd*, *J* = 4.5, 5.8, H–C(3)); 4.36 (*q*, CH_2); 5.17 (*dd*, *J* = 8, 4.5, H–C(4)). Anal. calc. for $C_{11}H_{23}NO_4SSi$ (293.45): C 45.02, H 7.89, N 4.77; found: C 45.29, H 7.88, N 4.94.

Method B. A soln. of **12** (600 mg, 2 mmol) in EtOH (15 ml) was stirred for 30 min at r.t. Workup as described for *Method A*: 360 mg (62%) of **15b**.

Methyl 1,2-Thiezetidine-4-carboxylate 1,1-Dioxide (**16**). Under N_2, **15a** (270 mg, 1 mmol), and TBAF (55 mg, 20% on SiO_2) in MeOH (20 ml) were stirred for 14 h. The solvent was evaporated, and the residue was purified by CC (acetone; R_f 0.64): 110 mg (70%) of **16**. Colorless liquid. IR (film): 3300 (NH), 3000, 2960 (CH), 1745 (C=O), 1340, 1170 (SO_2). ^{1}H-NMR (80 MHz): 3.3–3.8 (*m*, H′–C(3), H–C(3)); 3.88 (*s*, MeO); 5.27 (*dd*, *J* = 8.0, 5.6, H–C(4)); 5.83 (*s*, NH). Anal. calc. for $C_4H_7NO_4S$ (165.16): C 29.09, H 4.27, N 8.48, S 19.41; found: C 29.30, H 4.23, N 8.45, S 19.53.

*Diphenyl 2-[(*tert*-Butyl)dimethylsilyl]-1,2-thiazetidine-4,4-dicarboxylate 1,1-Dioxide* (**17**). Prepared from **8** (2.2 g, 10 mmol) in THF (100 ml), BuLi (9.4 ml, 15 mmol), and phenyl chloroformate (1.8 ml, 15 mmol) at −78°, as described for **32**. The product was purified by CC (CH_2Cl_2; R_f 0.54): 960 mg (21%) of **17**. Colorless crystals. M.p. 80° (pentane). IR: 3060, 2960, 2930, 2900, 2880, 2860 (CH), 1750, 1730 (C=O), 1320, 1180, 1160 (SO_2). ^{1}H-NMR (80 MHz): 0.33 (*s*, Me_2Si); 1.00 (*s*, *t*-Bu); 4.00 (*s*, H′–C(3), H–C(3)); 7.12–7.60 (*m*, 10 arom. H). Anal. calc. for $C_{22}H_{27}NO_6SSi$ (461.59): C 57.25, H 5.89, N 3.03, S 6.95; found: C 57.45, H 5.93, N 3.10, S 6.85.

*Phenyl 2-[(*tert*-Butyl)dimethylsilyl]-1,2-thiazetidine-4-carboxylate 1,1-Dioxide* (**18**). This compound was obtained as a side product in the synthesis of **17** (R_f 0.40): 540 mg (16%). Colorless, viscous liquid. B.p. 175°/0.01 Torr. IR (film): 3030, 2960, 2940, 2900, 2860 (CH), 1760 (C=O), 1330, 1165 (SO_2), 1260 (Me–Si). ^{1}H-NMR (250 MHz); 0.32, 0.33 (2*s*, Me_2Si); 1.00 (*s*, *t*-Bu); 3.53 (*dd*, *J* = 6.3, 7.7, H′–C(3)); 3.76 (*dd*, *J* = 4.6, 6.3, H–C(3)); 5.40 (*dd*, *J* = 7.7, 4.6, H–C(4)); 7.14–7.47 (*m*, 5 arom. H). Anal. calc. for $C_{15}H_{23}NO_4SSi$ (341.49): C 52.76, H 6.79, N 4.10, S 9.39; found: C 52.85, H 6.72, N 4.01, S 9.25.

*Dimethyl 2-[(*tert*-Butyl)diphenylsilyl]-1,2-thiazetidine-4,4-dicarboxylate 1,1-Dioxide* (**19**). Prepared from **1a** (3.45 g, 10 mmol) in THF (100 ml), BuLi (9.4 ml, 15 mmol), and ethyl chloroformate (1.2 ml, 15 mmol) at −78°, as described for **32**. Some drops of MeOH were added to the residue to induce crystallization: 1.2 g (26%) of **19**. Colorless crystals. M.p. 95° (MeOH). IR: 3090, 3060, 2970, 2940, 2900, 2880 (CH), 1780, 1760 (C=O), 1335, 1320, 1175 (SO_2). ^{1}H-NMR (80 MHz): 1.19 (*s*, *t*-Bu); 3.63 (*s*, H′–C(3), H–C(3)); 3.88 (*s*, MeO); 7.32–7.90 (*m*, 10 arom. H). Anal. calc. for $C_{22}H_{27}NO_6SSi$ (461.59): C 57.25, H 5.89, N 3.03, S 6.95; found: C 57.10, H 5.99, N 3.03, S 6.84.

*4-Bromo-2,4-bis[(*tert*-butyl)dimethylsilyl]-1,2-thiazetidine 1,1-Dioxide* (**20**). A soln. of Br_2 (0.5 ml, 10 mmol) in THF (20 ml) was added under stirring at −78° to a soln. of **8** (2.2 g, 10 mmol) and BuLi (6.25 ml, 10 mmol) in THF (100 ml), and stirring was continued for 45 min at −78°. Then, a sat. aq. soln. of NaCl (150 ml) was added, the org. layer was separated, washed with aq. NaCl soln., dried (Na_2SO_4), and evaporated *in vacuo*. The residue was dissolved in a few ml of MeOH, and cooled (0°, 2–3 d): 370 mg (17%) of **20**. Colorless crystals. M.p. 45–48° (MeOH). IR: 2950, 2920, 2880, 2860 (CH), 1305, 1160 (SO_2). ^{1}H-NMR (250 MHz): 0.28, 0.30 (2*s*, Me_2Si); 0.34 (*s*, Me_2Si); 0.98 (*s*, *t*-Bu); 1.07 (*s*, *t*-Bu); 3.43 (*d*, *J* = 6.5, H′–C(3)); 3.77 (*d*, *J* = 6.5, H–C(3)). ^{13}C-NMR (20.15 MHz): −6.28 (Me); −5.91 (Me); 18.30 (Me_3C); 18.49 (Me_3C); 25.86 (Me_3C); 27.83 (Me_3C); 46.71 (C(3)); 75.37 (C(4)). Anal. calc. for $C_{14}H_{32}BrNO_2SSi$ (414.53): C 40.56, H 7.78, Br 19.28, N 3.38, S 7.73; found: C 40.80, H 7.88, Br 19.10, N 3.58, S 7.60.

*4,4-Dibromo-2-[(*tert*-butyl)diphenylsilyl]-1,2-thiazetidine 1,1-Dioxide* (**21a**). A cooled soln. of Br_2 (1.0 ml, 20 mmol) in THF (30 ml) was added under stirring at $-78°$ to a soln. of **1a** (3.45 g, 10 mmol) and BuLi (9.4 ml, 15 mmol) in THF (100 ml). Stirring was continued for 1 h at $-78°$, and for 30 min at r.t. Then, a mixture of a sat. aq. soln. of NaCl (70 ml) and an aq. soln. of $NaHSO_3$ (70 ml, 37%) was added, the org. layer was separated, washed twice with aq. NaCl soln., dried (Na_2SO_4), and evaporated. The residue was purified by CC ($CHCl_3$; R_f 0.65): 1.5 g (29%) of **21a**. Colorless crystals. M.p. 120–122° (MeOH). IR: 3060, 3040, 2960, 2940, 2880, 2860 (CH), 1330, 1170 (SO_2). ^{1}H-NMR (80 MHz): 1.22 (*s*, *t*-Bu); 3.88 (*s*, H′–C(3), H–C(3)); 7.30–7.87 (*m*, 10 arom. H). Anal. calc. for $C_{18}H_{21}Br_2NO_2SSi$ (503.30): C 42.95, H 4.20, Br 31.75, N 2.78, S 6.37; found: C 42.80, H 4.30, Br 31.58, N 2.72, S 6.38.

4,4-Dibromo-2-cyclohexyl-1,2-thiazetidine 1,1-Dioxide (**21b**). Prepared from **1b** (1.9 g, 10 mmol), as described for **21a** (R_f 0.61): 680 mg (20%). Colorless crystals. M.p. 95° (MeOH). IR: 2930, 2860 (CH), 1330, 1180, 1170 (SO_2). ^{1}H-NMR (80 MHz): 1.0–2.1 (*m*, 5 CH_2); 3.28 (*m*, CH); 3.96 (*s*, H′–C(3), H–C(3)). Anal. calc. for $C_8H_{13}Br_2NO_2S$ (347.06): C 27.69, H 3.77, Br 46.05, N 4.03, S 9.24; found: C 27.89, H 3.72, Br 45.85, N 4.12, S 9.14.

*4-Bromo-2-[(*tert*-butyl)diphenylsilyl]-1,2-thiazetidine 1,1-Dioxide* (**22a**). Obtained as a side product in the synthesis of **21a** (R_f 0.59): 530 mg (13%). Colorless crystals. M.p. 127–129° (MeOH). IR: 3070, 3000, 2960, 2940, 2860 (CH), 1320, 1185 (SO_2). ^{1}H-NMR (80 MHz): 1.21 (*s*, *t*-Bu); 3.17 (*dd*, $J = 7.5$, H′–C(3)); 3.63 (*dd*(*t*), $J = 7.5$, 7.5, H–C(3)); 5.77 (*dd*, $J = 7.5$, 5, H–C(4)); 7.30–7.80 (*m*, 10 arom. H). Anal. calc. for $C_{18}H_{22}BrNO_2SSi$ (424.40): C 50.94, H 5.22, Br 18.82, N 3.30, S 7.55; found: C 50.27, H 4.99, Br 18.51, N 3.51, S 7.34.

4-Bromo-2-cyclohexyl-1,2-thiazetidine 1,1-Dioxide (**22b**). Obtained as a side product in the synthesis of **21b** (R_f 0.43): 400 mg (15%). Colorless crystals. M.p. 51° (MeOH; lit. 60–61° [13]). IR: 2940, 2860 (CH), 1330, 1320, 1180, 1170 (SO_2). ^{1}H-NMR (80 MHz): 1.1–2.1 (*m*, 5 cyclohexyl CH_2); 3.22 (*m*, cyclohexyl CH); 3.21 (*dd*, $J = 7.0$, 4.5, H′–C(3)); 3.76 (*dd*, $J = 7.0$, 7.0, H–C(3)); 5.57 (*dd*, $J = 7.0$, 4.5, H–C(4)). Anal. calc. for $C_8H_{14}BrNO_2S$ (268.17): C 35.83, H 5.26, Br 29.80, N 5.22, S 11.95; found C 36.01, H 5.22, Br 29.79, N 5.25, S 11.80.

*Methyl 2-[(*tert*-butyl)dimethylsilyl-4-iodo-1,2-thiazetidine-4-carboxylate 1,1-Dioxide* (**23**). A soln. of **15a** (550 mg, 2 mmol) in THF (20 ml) was added at $-78°$ to a soln. of LDA (3 mmol) in THF (20 ml). Then, the mixture was added dropwise *via* syringe to a soln. of I_2 (1.0 g, 4 mmol) in THF (30 ml) at $-78°$. After warming to r.t., a mixture of an aq. sat. soln. of NaCl (100 ml) and an aq. soln. of $NaHSO_3$ (15 ml, 37%) was added, the org. layer was separated, washed twice with aq. NaCl soln., dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by CC ($CHCl_3$; R_f 0.59): 160 mg (20%) of **23**. Colorless crystals. M.p. 53° (pentane). IR: 2980, 2950, 2910, 2880 (CH), 1750 (C=O), 1330, 1305, 1290, 1170 (SO_2). ^{1}H-NMR (80 MHz): 0.29 (*s*, Me_2Si); 0.99 (*s*, *t*-Bu); 3.56 (*d*, $J = 7$, H′–C(3)); 3.90 (*s*, MeO); 4.35 (*d*, $J = 7$, H–C(3)). Anal. calc. for $C_{10}H_{20}INO_4SSi$ (405.28): C 29.63, H 4.97, N 3.46, S 7.91; found: C 29.53, H 4.89, N 3.37, S 8.12.

*Ethyl 2-[(*tert*-Butyl)diphenylsilyl]-1,2-thiazetidine-4-carboxylate 1,1-Dioxide* (**24**). A cooled soln. of **1a** (1.72 g, 5 mmol) in THF (30 ml) was added to a soln. of LDA (8 mmol) in THF (20 ml) at $-78°$. After 2 min, a soln. of diethyl azodicarboxylate (DEAD; 1.4 g, 8 mmol) in THF (10 ml) was added dropwise under stirring, and stirring was continued for 20 min. Then, a sat. aq. soln. of NaCl (100 ml) was added, the org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was dissolved in a few milliliters of $CHCl_3$, and cooled (24 h, 0°). The precipitate (diethyl hydrazine-1,2-dicarboxylate; m.p. 130°) was separated, and the filtrate was purified by CC ($CHCl_3$; R_f 0.52): 200 mg (10%) of **24**. Colorless crystals. M.p. 93° (pentane). IR: 3070, 3050, 3000, 2960, 2940, 2900, 2860 (CH), 1740 (C=O), 1320, 1170, 1150 (SO_2). ^{1}H-NMR (80 MHz): 1.80 (*s*, *t*-Bu); 1.32 (*t*, Me); 3.20 (*dd*, $J = 6, 8$, H′–C(3)); 3.52 (*dd*, $J = 4.4, 6$, H–C(3)); 4.31 (*q*, CH_2); 5.11 (*dd*, $J = 8, 4.4$, H–C(4)); 7.30–7.92 (*m*, 10 arom. H). Anal. calc. for $C_{21}H_{27}NO_4SSi$ (417.55): C 60.41, H 6.52, N 3.35, S 7.68; found: C 60.35, H 6.56, N 3.27, S 7.87.

*Methyl 2-[(*tert*-Butyl)dimethylsilyl]-4-[1,2-bis(ethoxycarbonyl)hydrazino]-1,2-thiazetidine-4-carboxylate 1,1-Dioxide*[1]) (**26a**). A soln. of **15a** (410 mg, 1.5 mmol) in THF (15 ml) was added to a soln. of LDA (1.6 mmol) in THF at $-78°$, and the mixture was stirred for 15 min. Then, a soln. of diethyl azodicarboxylate (290 mg, 1.6 mmol) was added, and stirring was continued for 45 min at $-78°$. The mixture was hydrolyzed with a sat. aq. soln. of $NaHCO_3$, extracted with CH_2Cl_2 (2×40 ml), and the combined org. layers were dried (Na_2SO_4) and evaporated. The residue was purified by CC ($CHCl_3$/acetone 95:5; R_f 0.22): 260 mg (38%) of **26a**. Colorless crystals. M.p. 94° (pentane). IR: 3250 (NH), 2990, 2960, 2940, 2860 (CH), 1765, 1730 (C=O), 1540 (amide), 1310, 1145 (SO_2). ^{1}H-NMR (250 MHz): 0.22, 0.29 (2*s*, Me_2Si); 0.91 (*s*, *t*-Bu); 1.27 (*t*, Me); 1.30 (*t*, Me); 3.72 (*d*, $J = 11$, H′–C(3)); 3.87 (*s*, MeO); 4.20 (*d*, $J = 11$, H–C(3)); 4.20–4.32 (*m*, 2 OCH_2); 7.19 (*s*, NH). Anal. calc. for $C_{16}H_{31}N_3O_8SSi$ (453.58): C 42.37, H 6.89, N 9.26, S 7.07; found C 42.60, H 6.92, N 9.45, S 7.00.

*Methyl 2-[(*tert*-Butyl)dimethylsilyl]-4-[1,2-bis[(2,2,2-trichloroethoxy)carbonyl]hydrazino]-1,2-thiazetidine-4-carboxylate 1,1-Dioxide*[1]) (**26b**). Prepared from **15a** (410 mg, 1.5 mmol) and bis(2,2,2-trichloroethyl)

azodicarboxylate (600 mg, 1.6 mmol), as described for **26a**, and purified by CC ($CHCl_3$/acetone 9:1; R_f 0.68): 480 mg (49%) of **26b**. Colorless crystals. M.p. 162° (Et_2O/pentane). IR: 3230 (NH), 2960, 2930, 2890, 2860 (CH), 1770, 1740 (C=O), 1540 (amide), 1325, 1290, 1180, 1140 (SO_2), 1260 (Me–Si), 810, 720 (Cl_3C). ^{1}H-NMR (80 MHz): 0.22, 0.27 (2*s*, Me_2Si); 0.90 (*s*, *t*-Bu); 3.81 (*d*, *J* = 11.5, H′–C(3)); 3.82 (*s*, MeO); 4.26 (*d*, *J* = 11.5, H–C(3)); 4.76 (*s*, 2 CH_2); 7.76 (*s*, NH). Anal. calc. for $C_{16}H_{25}Cl_6N_3O_8SSi$ (660.26): C 29.11, H 3.82, Cl 32.22, N 6.36, S 4.86; found: C 29.31, H 3.85, Cl 32.03, N 6.47, S 4.98.

*4-Benzoyl-2-[(*tert*-butyl)dimethylsilyl]-1,2-thiazetidine 1,1-Dioxide*[1] (**25**). A soln. of **8** (2.2 g, 10 mmol) in THF (60 ml) was added to a soln. of LDA (20 mmol) in THF (30 ml) at −78°. Then, ethyl benzoate (3 ml, 20 mmol) was added dropwise. After stirring for 1 h, the mixture was hydrolyzed with a sat. aq. soln. of NaCl, the org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by CC (cyclohexane/AcOEt 4:1; R_f 0.27): 1.8 g (55%) of **25**. Colorless crystals. M.p. 87° (cyclohexane; lit. 87° [6]). Molecular formula: $C_{15}H_{23}NO_3SSi$ (325.49 g mol^{-1}).

*Phenyl 2-[(*tert*-Butyl)dimethylsilyl]-4-[1,2-bis(ethoxycarbonyl)hydrazino]-1,2-thiazetidine-4-carboxylate 1,1-Dioxide*[1] (**27a**). Prepared from **25** (480 mg, 1.5 mmol) and ethyl diazodicarboxylate (290 mg, 1.6 mmol), as described for **26a** (R_f 0.5): 460 mg (63%). Colorless crystals. M.p. 85° (pentane). IR: 3250 (NH), 2990, 2940, 2870 (CH), 1750, 1720 (C=O), 1530 (amide), 1325, 1180, 1160 (SO_2). ^{1}H-NMR (250 MHz): 0.08, 0.26 (2*s*, Me_2Si); 0.86 (*s*, *t*-Bu); 1.09 (*t*, Me); 1.34 (*t*, Me); 3.65 (*d*, *J* = 11.3, H′–C(3)); 4.08 (*m*, OCH_2); 4.30 (*m*, OCH_2); 4.30 (*d*, *J* = 11.3, H–C(3)); 7.3–7.6 (*m*, 3 arom. H, NH); 8.43 (*d*, 2 arom. H). Anal. calc. for $C_{21}H_{33}N_3O_7SSi$ (499.65): C 50.48, H 6.66, N 8.41, S 6.42; found: C 50.45, H 6.64, N 8.49, S 6.50.

*Phenyl 2-[(*tert*-Butyl)dimethylsilyl]-4-{1,2-bis[(2,2,2-trichloroethoxy)carbonyl]hydrazino}-1,2-thiazetidine-4-carboxylate 1,1-Dioxide*[1] (**27b**). Prepared from **25** (480 mg, 1.5 mmol) and bis(2,2,2-trichloroethyl) azodicarboxylate (600 mg, 1.6 mmol), as described for **26a**: 800 mg (77%). Colorless crystals. M.p. 161° (Et_2O/pentane). IR: 3260 (NH), 2950, 2920, 2890, 2860 (CH), 1750, 1710 (C=O), 1525 (amide), 1320, 1170 (SO_2), 1265 (Me–Si), 820, 720 (Cl_3C). ^{1}H-NMR (80 MHz): 0.15, 0.28 (2*s*, Me_2Si); 0.90 (*s*, *t*-Bu); 3.85 (*d*, *J* = 11.5, H′–C(3)); 4.36 (*d*, *J* = 11.5, H–C(3)); 4.67 (*s*, CH_2); 4.87 (*s*, CH_2); 7.32–7.73 (*m*, 3 arom. H); 8.12 (*s*, NH); 8.22–8.47 (*m*, 2 arom. H). Anal. calc. for $C_{21}H_{27}Cl_6N_3O_7SSi$ (706.33): C 35.71, H 3.85, Cl 30.12, N 5.95, S 4.54; found: C 35.63, H 3.80, Cl 30.22, N 6.07, S 4.63.

*Phenyl 2-[(*tert*-Butyl)dimethylsilyl]-4-{1,2-bis[(*tert*-butoxy)carbonyl]hydrazino}-1,2-thiazetidine-4-carboxylate 1,1-Dioxide*[1] (**27c**). Prepared from **25** (480 mg, 1.5 mmol) and di(*tert*-butyl) azodicarboxylate (370 mg, 1.6 mmol), as described for **26a**, and purified by CC ($CHCl_3$/acetone 95:5; R_f 0.39): 240 mg (29%) of **27c**. Colorless crystals. M.p. 81° (Et_2O/pentane). IR: 3240 (NH), 2980, 2960, 2940, 2860 (CH), 1730, 1710 (C=O), 1325, 1170, 1150 (SO_2), 1260 (Me–Si). ^{1}H-NMR (80 MHz): 0.05, 0.27 (2*s*, Me_2Si); 0.88 (*s*, *t*-Bu); 1.26 (*s*, (*t*-Bu)O); 1.55 (*s*, (*t*-Bu)O); 3.70 (*d*, *J* = 11.5, H′–C(3)); 4.35 (*d*, *J* = 11.5, H–C(3)); 7.07 (*s*, NH); 7.40–7.70 (*m*, 3 arom. H); 8.40–8.60 (*m*, 2 arom. H). MS: 491 (0.89, $[M-SO_2]^+$), 105 (100). DCI-MS (NH_3): 573 ($[M+NH_4]^+$). HR-MS: 491.2831 ($M-SO_2]^+$), $C_{25}H_{41}N_3O_5Si^+$; calc. 491.2816). Anal. calc. for $C_{25}H_{41}N_3O_7SSi$ (555.77): C 54.03, H 7.44, N 7.56, S 5.77; found: C 53.96, H 7.36, N 7.30, S 5.63.

*2-(*tert*-Butyl)dimethylsilyl]-4-(α-(trimethylsilyl)oxy]benzylidene)-1,2-thiazetidine 1,1-Dioxide* (**28a**). A cooled soln. of **25** (480 mg, 1.5 mmol) in THF (15 ml) was added dropwise to a soln. of LDA (2 mmol) in THF (15 ml) at −78°. After stirring for 15 min at −78°, Me_3SiCl (0.4 ml, 3 mmol) was added, and stirring was continued for 45 min at r.t., before the solvent was evaporated: 410 mg (70%) of **28a**. Light-yellow liquid. IR (film): 3060, 3020, 2940, 2920, 2860 (CH), 1685, 1660 (C=C), 1320, 1295, 1175, 1145 (SO_2), 1250 (Me–Si). ^{1}H-NMR (60 MHz): 0.13, 0.26 (2*s*, Me_2Si, Me_3Si); 0.96 (*s*, *t*-Bu); 3.86, 3.97 (2*s*, H′–C(3), H–C(3)); 7.16–8.23 (*m*, 5 arom. H). EI-MS: 340 (29, $[M-t\text{-}Bu]^+$), 73 (100, 268 (14), 205 (21), 204 (20), 203 (15), 147 (68), 131 (20), 105 (27), 103 (26), 77 (29). CI-MS (CH_4): 398 ($[M+H]^+$). Molecular formula: $C_{18}H_{31}NO_3SSi_2$ (397.67 g mol^{-1}).

*2-[(*tert*-Butyl)dimethylsilyl]-4-(α-{[(*tert*-butyl)dimethylsilyl]oxy}benzylidene)-1,2-thiazetidine 1,1-Dioxide* (**28b**). Prepared from **25** (480 mg, 1.5 mmol), LDA (1.6 mmol) in THF (20 ml), and (*t*-Bu)Me_2SiCl (240 mg, 1.6 mmol) in THF (5 ml) at −78°, as described for **28a**, and purified by *Kugelrohr* distillation: 590 mg (90%) of **28b**. Colorless liquid. B.p. 170°/0.01 Torr. IR: 3060, 2960, 2940, 2890, 2860 (CH), 1670 (C=C), 1310, 1150 (SO_2). ^{1}H-NMR (80 MHz): 0.0 (*s*, Me_2Si); 0.27 (*s*, Me_2Si); 0.95 (*s*, *t*-Bu); 1.00 (*s*, *t*-Bu); 3.88 (*s*, H′–C(3), H–C(3)); 7.3–7.8 (*m*, 5 arom. H). Anal. calc. for $C_{21}H_{37}NO_3SSi_2$ (439.76): C 57.36, H 8.48, N 3.19, S 7.29; found: C 57.31, H 8.40, N 3.30, S 7.43.

3-Amino-2-hydroxy-1-phenylprop-2-en-1-one (**29**). A soln. of TBAF (0.5 ml, 0.5 mmol) was added under stirring to a soln. of **27a** (250 mg, 0.5 mmol) in THF (20 ml) under N_2. After 30 s, the mixture was hydrolyzed with a sat. aq. soln. of NaCl (40 ml), extracted with CH_2Cl_2 (2 × 50 ml), and the combined org. layers were dried (Na_2SO_4) and evaporated. The residue was purified by CC ($CHCl_3$/acetone 9:2; R_f 0.32): 27 mg (33%). IR:

3460, 3300, 3180 (NH_2, OH), 1660 (C=O), 1580 (C=O). ^{1}H-NMR (80 MHz; (D_6)acetone): 5.60 (*s*, NH_2); 6.65 (*s*, H–C(3)); 7.45 (*m*, 5 arom. H); 8.0 (*s*, OH). EI-MS: 163 (26, M^+), 162 (22), 105 (41), 77 (81), 58 (43), 57 (100), 51 (45), 50 (22). CI-MS (CH_4): 164 ($[M+H]^+$). HR-EI-MS: 163.0647 (M^+, $C_9H_9NO_2^+$; calc. 163.0633).

*Methyl 2-[(*tert*-Butyl)dimethylsilyl]-4-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-1,2-thiazetidine-4-carboxylate 1,1-Dioxide*[1]) (**30a**). Prepared from **15a** (410 mg, 1.5 mmol) and 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (280 mg, 1.6 mmol), as described for **26a**. Hydrolysis with a mixture of a sat. aq. soln. of NaCl (57 ml) and conc. HCl (3 ml): 400 mg (60%) of **30a**. Light-yellow crystals. M.p. 80–82° (dec.; pentane). IR: 3200–3100 (NH), 2950, 2920, 2850 (CH), 1760–1710, 1690 (C=O), 1290, 1170, 1150 (SO_2). ^{1}H-NMR (80 MHz): 0.25, 0.32 (2*s*, Me_2Si); 0.96 (*s*, *t*-Bu); 3.83 (*s*, MeO); 4.25 (*d*, *J* = 12, H′–C(3)); 4.83 (*d*, *J* = 12, H–C(3)); 6.17 (*s*, NH); 7.47 (*m*, 5 arom. H). Anal. calc. for $C_{18}H_{26}N_4O_6SSi$ (454.58): C 47.56, H 5.76, N 12.33, S 7.05; found: C 47.66, H 5.83, N 12.45, S 6.96.

*4-Benzoyl-2-[(*tert*-butyl)dimethylsilyl]-4-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)-1,2-thiazetidine 1,1-Dioxide*[1]) (**30b**). Prepared from **25** (480 mg, 1.5 mmol) and 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (280 mg, 1.6 mmol), as described for **26a**. The residue was recrystallized from pentane/Et_2O: 310 mg (41%) of **30b**. Light-yellow crystals. M.p. 110° (dec.). IR: 3200 (NH), 2960, 2940, 2890, 2860 (CH), 1730 (C=O), 1300, 1180, 1160 (SO_2). ^{1}H-NMR (80 MHz): 0.25, 0.30 (2*s*, Me_2Si); 0.97 (*s*, *t*-Bu); 4.52 (*d*, *J* = 11.5, H′–C(3)); 4.73 (*d*, *J* = 11.5, H–C(3)); 7.3–7.7 (*m*, 8 arom. H, NH); 8.14 (*d*, 2 arom. H). Anal. calc. for $C_{23}H_{28}N_4O_5SSi$ (500.64): C 55.18, H 5.64, N 11.19, S 6.40; found: C 55.46, H 5.75, N 11.01, S 6.20.

*4-Azido-4-benzoyl-2-[(*tert*-butyl)dimethylsilyl]-1,2-thiazetidine 1,1-Dioxide*[1]) (**31a**). A soln. of **25** (480 mg, 1.5 mmol) in THF (15 ml) was added dropwise to a soln. of LDA (1.6 mmol) in THF (15 ml) at −78°. After stirring for 15 min at −78°, a soln. of tosyl azide (310 mg, 1.6 mmol) in THF (5 ml) was added. After 10 min, the mixture was warmed to 0°, Me_3SiCl (0.44 ml, 3.5 mmol) was added, and stirring was continued for 30 min at r.t. The solvent was evaporated *in vacuo*, and the residue was purified by CC (1. cyclohexane/AcOEt 4 : 1 (R_f 0.45); 2. $CHCl_3$ (R_f 0.36)): 45 mg (8%) of **31a**. Colorless, viscous liquid. IR (film): 2960, 2940, 2890, 2860 (CH), 2120 (N_3), 1700 (C=O), 1300, 1175, 1150 (SO_2), 1260 (Me–Si). ^{1}H-NMR (80 MHz): 0.26 (*s*, Me_2Si); 0.95 (s, *t*-Bu); 4.03 (*d*, *J* = 11.5, H′–C(3)); 4.70 (*d*, *J* = 11.5, H–C(3)); 7.3–7.7 (*m*, 3 arom. H); 8.15 (*d*, 2 arom. H). Molecular formula: $C_{15}H_{22}N_4O_3SSi$ (366.51 g mol^{-1}).

*Methyl 4-Azido-2-[(*tert*-butyl)dimethylsilyl]-1,2-thiazetidine-4-carboxylate 1,1-Dioxide* (**31b**). A soln. of **15a** (410 mg, 1.5 mmol) in THF (15 ml) was added dropwise to a soln. of LDA (1.6 mmol) in THF (15 ml) at −78°. After stirring for 15 min at −78°, tosyl azide (310 mg, 1.6 mmol) in THF (5 ml), and after 45 min, Me_3SiCl (0.44 ml, 3.5 mmol), were added. The mixture was stirred for another 30 min, then hydrolyzed with a sat. aq. soln. of NaCl (50 ml). The org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by FC (CH_2Cl_2), probably yielding two stable conformers (**31ba** and **31bb**; see *Fig. 2*) with distinct properties (spectral data not assigned): *a*) 170 mg (35%) and *b*) 90 mg (19%).

Data of Major Conformer: Colorless liquid. R_f 0.27 (CH_2Cl_2). IR (film): 2970, 2940, 2900, 2870 (CH), 2140 (N_3), 1760 (C=O), 1300, 1180 (SO_2), 1260 (Me–Si). ^{1}H-NMR (80 MHz): 0.26, 0.30 (2*s*, Me_2Si); 0.95 (*s*, *t*-Bu); 3.89 (*s*, MeO); 3.93 (*d*, *J* = 11.5, H–C(3)); 4.23 (*d*, *J* = 11.5, H′–C(3)). ^{13}C-NMR: −5.57, −5.42 (Me_2Si); 18.80, 25.87 (*t*-Bu); 53.68 (MeO); 55.31 (C(3)); 98.36 (C(4)); 165.99 (C=O). Anal. calc. for $C_{10}H_{20}N_4O_4SSi$ (320.44): C 37.48, H 6.29, N 17.48, S 10.00; found: C 37.74, H 6.26, N 17.25, S 9.89.

Data of Minor Conformer. Colorless liquid. R_f 0.20 (CH_2Cl_2). IR (film): identical with major conformer. ^{1}H-NMR (80 MHz): 0.31, 0.32 (2*s*, Me_2Si); 0.97 (*s*, *t*-Bu); 3.57 (*d*, *J* = 11.5, H′–C(3)); 3.90 (*s*, MeO); 4.37 (*d*, *J* = 11.5, H–C(3)). ^{13}C-NMR: −5.36 (Me_2Si); 18.85, 25.84 (*t*-Bu); 53.86 (MeO); 55.03 (C(3)); 97.33 (C(4)); 165.43 (C=O). Anal. calc. for $C_{10}H_{20}N_4O_4SSi$ (320.44): C 37.48, H 6.29, N 17.48; found: C 38.47, H 6.69, N 16.06.

*2-[(*tert*-Butyl)dimethylsilyl]-4-(1,2-dihydro-1,3,5-triazin-2-yl)-1,2-thiazetidine 1,1-Dioxide*[1]) (**32**). BuLi (4.7 ml, 7.5 mmol) was added at −78° to a soln. of **8** (1.1 g, 5 mmol) in THF (80 ml). Then, a cooled soln. of 1,3,5-triazine (640 mg, 8 mmol) in THF (15 ml) was added, and the mixture was stirred for 10 min at −78°. The mixture was hydrolyzed with a sat. aq. soln. of NaCl (100 ml). The org. layer was separated, the aq. layer was washed with CH_2Cl_2 (2 × 50 ml), and the combined org. layers were dried (Na_2SO_4) and evaporated *in vacuo:* 490 mg (33%) of **32**. Colorless crystals. M.p. 133° (Et_2O). IR: 3360–3180 (NH), 2960, 2940, 2900, 2860 (CH), 1685 (C=N), 1310, 1195, 1140 (SO_2), 1260 (Me–Si). ^{1}H-NMR (250 MHz): 0.27 (*s*, Me_2Si); 0.97 (*s*, *t*-Bu); 3.38 (*dd*(*t*), *J* = 5.0, 5.0, H′–C(3)); 3.51 (*dd*, *J* = 7.5, 5.0, H–C(3)); 4.68 (*ddd*, *J* = 9.7, 7.5, 5.0, H–C(4)); 5.20 (*d*, *J* = 9.7, triazinyl H–C(2)); 7.26, 7.28 (2*s*, triazinyl H–C(4), triazinyl H–C(6)); 8.48 (*s*, NH). Anal. calc. for $C_{11}H_{22}N_4O_2SSi$ (302.47): C 43.68, H 7.33, N 18.52, S 10.60; found: C 43.42, H 7.27, N 18.73, S 10.75.

*2-[(*tert*-Butyl)dimethylsilyl]-4-(triethylsilyl)-1,2-thiazetidine 1,1-Dioxide* (**33**). A soln. of **8** (2.2 g, 10 mmol) in THF (40 ml) was added dropwise under stirring to a mixture of LDA (15 mmol) and Et_3SiCl (2.26 g, 15 mmol) in THF at −78°, and stirring was continued for 1 h at this temp. Then, a sat. aq. soln. of NH_4Cl (50 ml)

and AcOEt (50 ml) were added, the org. layer was separated, washed with a sat. aq. soln. of NH_4Cl, dried (Na_2SO_4), and evaporated. The resulting residue was purified by FC (cyclohexane/Et_2O 9:1; R_f 0.2): 3.0 g (89%) of **33**. Colorless liquid. IR (film): 2957, 2880, 2862 (CH), 1470 (Me), 1301, 1161 (SO_2). ^{1}H-NMR (300 MHz): 0.20 (*s*, Me_2Si); 0.63–0.87 (*m*, 3 $SiCH_2$); 0.92 (*s*, *t*-Bu); 0.94–1.00 (*m*, 3 Me); 3.12 (*dd*, J = 5.0, 6.0, H′–C(3)); 3.34 (*dd*, J = 5.0, 9.0, H–C(3)); 4.17 (*dd*, J = 6.0, 9.0, H–C(4)). ^{13}C-NMR: −6.13, −6.08 (2*s*, Me_2Si); 2.27 (*s*, $SiCH_2$); 7.23, 18.16 (*s*, Me); 25.88 (*s*, Me_3C); 32.08 (*s*, C(3)); 62.23 (*s*, C(4)). Anal. calc. for $C_{14}H_{33}NO_2SSi_2$ (335.65): C 50.10, H 9.91, N 4.17, S 9.55; found: C 50.22, H 9.87, N 4.12, S 9.62.

*2-[(*tert*-Butyl)dimethylsilyl]-4-nitro-1,2-thiazetidine 1,1-Dioxide* (**34**). Propyl nitrate (450 µl, 4.5 mmol) was added at −78° to a soln. of **33** (500 mg, 1.49 mmol) and BuLi (1.9 ml, 3 mmol) in THF (30 ml). The mixture was warmed to r.t., and after 1 h, AcOH (0.6 ml) was added, and the mixture was stirred for 15 min. Then, Et_2O (50 ml) was added, the mixture was washed with a sat. aq. soln. of NH_4Cl (50 ml), the org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was purified by FC (Et_2O/cyclohexane 1:1; R_f 0.38): 97 mg (24%) of **34**. Yellow liquid. IR: 2962, 2933, 2862 (CH), 1570, 1359 (NO_2), 1328, 1184 (SO_2). ^{1}H-NMR (300 MHz): 0.29, 0.31 (2*s*, Me_2Si); 0.97 (*s*, *t*-Bu); 3.69 (*dd*, J = 7.0, 8.0, H′–C(3)); 3.94 (*dd*, J = 8.0, 4.0, H–C(3)); 6.42 (*dd*, J = 7.0, 4.0, H–C(4)). Anal. calc. for $C_8H_{18}N_2O_4SSi$ (266.39): C 36.07, H 6.81, N 10.52; found: C 35.80, H 6.55, N 10.16.

*2-[(*tert*-Butyl)dimethylsilyl]*-N-*phenyl-1,2-thiazetidine-4-carboxamide 1,1-Dioxide* (**35**). A soln. of **12** (480 mg, 1.7 mmol) in Et_2O (10 ml) was added dropwise at 0° to a soln. of aniline (0.15 g, 1.7 mmol) and pyridine (0.13 ml, 1.7 mmol) in Et_2O (50 ml). After 4 h, the precipitate was separated, and the solvent was evaporated. The residue was purified by CC (acetone/AcOEt 1:1; R_f 0.73): 230 mg (14%). (Compound **35** was also obtained (in higher yield!) as a 'side product' in the synthesis of **36** from **8**: 180 mg (31%)). Colorless crystals. M.p. 113° (pentane). IR: 3340 (NH), 3080, 3060, 3020, 2950, 2920, 2900, 2880, 2860 (CH), 1700 (C=O), 1540 (amide), 1300, 1160, 1150 (SO_2), 1250 (Me–Si). ^{1}H-NMR (250 MHz): 0.32, 0.33 (2*s*, Me_2Si); 1.00 (*s*, *t*-Bu); 3.56 (*dd*, J = 5.8, 8.0, H′–C(3)); 3.75 (*dd*(*t*), J = 4.6, 5.8, H–C(3)); 5.29 (*dd*, J = 8.0, 4.6, H–C(4)); 7.11–7.64 (*m*, 5 arom. H); 8.77 (*s*, NH). Anal. calc. for $C_{15}H_{24}N_2O_2SSi$ (340.50): C 52.91, H 7.10, N 8.23, S 9.41; found: C 52.99, H 7.14, N 8.33, S 9.30.

*2-[(*tert*-Butyl)dimethylsilyl]*-N,N′-*diphenyl-1,2-thiazetidine-4,4-dicarboxamide 1,1-Dioxide* (**36**). BuLi (4.4 ml, 7 mmol) was added to a soln. of **8** (1.1 g, 5 mmol) in THF (60 ml), and the mixture was cooled to −78°. A soln. of phenylisocyanate (0.75 ml, 7 mmol) in THF (10 ml) was added. The mixture was stirred for 30 min at −78° and then hydrolyzed with a mixture of a sat. aq. soln. of NaCl (95 ml) and conc. HCl (5 ml). The org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo:* 520 mg (22%) of **36**. Colorless crystals. M.p. 172° (toluene). IR: 3340 (NH), 3060, 2960, 2940, 2900, 2860 (CH), 1700, 1670 (C=O), 1535 (amide), 1330, 1320, 1160 (SO_2), 1260 (Me–Si). ^{1}H-NMR (80 MHz): 0.22 (*s*, Me_2Si); 0.92 (*s*, *t*-Bu); 4.00 (*s*, H′–C(3), H–C(3)); 6.95–7.55 (*m*, 10 arom. H); 8.85 (*s*, 2 NH). Anal. calc. for $C_{22}H_{29}N_3O_4SSi$ (459.62): C 57.62, H 6.36, N 9.14, S 6.97; found: C 57.76, H 6.25, N 9.30, S 7.19.

*2-[(*tert*-Butyl)dimethylsilyl)-1,2-thiazetidine-4-carboxamide 1,1-Dioxide* (**37**). A sat. soln. of NH_3 in $CHCl_3$ (10 ml) was added to a soln. of **12** (280 mg, 1 mmol) in $CHCl_3$ (25 ml) at 0°. After stirring for 1 h, the mixture was hydrolyzed with an aq. sat. soln. of NaCl (40 ml). The org. layer was separated, dried (Na_2SO_4), and evaporated *in vacuo:* 65 mg (25%) of **37**. Colorless crystals. M.p. 123–125° (pentane). IR: 3460, 3230–3180 (NH), 2990, 2960, 2940, 2900, 2890, 2860 (CH), 1690 (C=O), 1300, 1170 (SO_2), 1260 (Me–Si). ^{1}H-NMR (80 MHz; (D_6)acetone): 0.26 (*s*, Me_2Si); 0.98 (*s*, *t*-Bu); 3.46 (*dd*, J = 5.8, 7.8, H′–C(3)); 3.69 (*dd*(*t*), J = 4.5, 5.8, H–C(3)); 5.25 (*dd*, J = 7.8, 4.5, H–C(4)); 6.82 (*s*, NH); 7.38 (*s*, NH). EI-MS: 207 (73, $[M - t\text{-Bu}]^+$), 128 (100%). CI-MS (CH_4): 265 ($[M + H]^+$). Anal. calc. for $C_9H_{20}N_2O_3SSi$ (264.41): C 40.88, H 7.62, N 10.59, S 12.13; found: C 40.46, H 7.24, N 10.20, S 12.33.

*2-[(*tert*-Butyl)dimethylsilyl]*-N-*[4-(2-ethoxy-2-oxoethyl)-1,3-thiazol-2-yl]-1,2-thiazetidine-4-carboxamide*[1]) (**38a**). Prepared from **12** (480 mg, 1.7 mmol) and ethyl 2-amino-1,3-thiazol-4-acetate (320 mg, 1.7 mmol) in Et_2O (40 ml), as described for **35** (reaction time: 3–4 h). The residue crystallized, when some drops of MeOH were added: 180 mg (25%) of **38a**. Colorless crystals. M.p. 186° (MeOH). IR: 3330 (NH), 2990, 2960, 2940, 2900, 2860 (CH), 1740, 1700 (C=O), 1560 (amide), 1310, 1300, 1170 (SO_2), 1260 (Me–Si). ^{1}H-NMR (80 MHz): 0.32 (*s*, Me_2Si); 1.00 (*s*, *t*-Bu); 1.27 (*t*, Me); 3.52 (*dd*, J = 6, 8, H′–C(3)); 3.71 (*s*, CH_2); 3.80 (*dd*(*t*), J = 4.4, 6, H–C(3)); 4.17 (*q*, OCH_2); 5.42 (*dd*, J = 8, 4.4, H–C(4)); 6.85 (*s*, thiazolyl H–C(5)); 7.32 (*s*, NH). Anal. calc. for $C_{16}H_{27}N_3O_5S_2Si$ (433.61): C 44.32, H 6.28, N 9.69, S 14.79; found: C 44.22, H 6.27, N 9.44, S 14.74.

*2-[(*tert*-Butyl)dimethylsilyl]*-N-*[4-[2-ethoxy-1-[(Z)-methoxyimino]-2-oxoethyl]-1,3-thiazol-2-yl)-1,2-thiazetidine-4-carboxamide*[1]) (**38b**). Prepared from **12** (480 mg, 1.7 mmol) and ethyl (*Z*)-(methoxyimino)(1,3-thiazol-4-yl)acetate (380 mg, 1.7 mmol) in Et_2O (40 ml), as described for **35** (reaction time: 3–4 h at 0°). The residue was purified by CC (acetone/AcOEt 1:1; R_f 0.73): 170 mg (21%). Colorless crystals. M.p. 86° (MeOH).

IR: 3280 (NH), 2960, 2940, 2900, 2860 (CH), 1735, 1695 (C=O), 1555 (amide), 1320, 1300, 1175 (SO_2), 1265 (Me−Si). ^{1}H-NMR (80 MHz): 0.30 (*s*, Me_2Si); 0.99 (*s*, *t*-Bu); 1.32 (*t*, Me); 3.50 (*dd*, $J = 5.8, 8$, H′−C(3)); 3.72 (*dd*(*t*), $J = 4.6, 5.8$, H−C(3)); 3.97 (*s*, MeO); 4.37 (*q*, OCH_2); 5.40 (*dd*, $J = 8, 4.6$, H−C(4)); 7.27 (*s*, thiazolyl, H−C(5)); 10.3 (*s*, NH). EI-MS: 476 (5, M^+), 421 (16), 420 (23), 419 (100), 355 (42), 340 (27), 326 (22), 251 (26), 236 (30), 99 (22), 75 (36), 73 (47), 59 (23), 55 (70). HR-EI-MS: 476.12135 (M^+, $C_{17}H_{28}N_4O_6S_2Si^+$; calc. 476.1220).

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