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1-Organosulfonyl-2-sila-5-piperazinones: synthesis, molecular and crystal structure, and chemical transformations into 2-aminoacid derivatives

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Abstract

The reaction of chloro(chloromethyl)dimethylsilane and hexamethyldisilazane with *N*-methylamides of *N'*-organosulfonyl-2-amino acids (**1a–e**), the derivatives of *N*-mesylglycine (**a**), *N*-tosylglycine (**b**), *N*-nosylglycine (**c**), *N*-nosylalanine (**d**) and *N*-nosylleucine (**e**), affords new type of silacyclanes, 1-organosulfonyl-2-sila-5-piperazinones **2a–e**. The presence of very labile Si–N bonds in compounds **2** can be utilised in a variety of synthetic applications. The hydrolysis of **2a–e** yields disiloxanes **3a–e**, which can be subsequently transformed into fluorosilanes, such as **4a**, by the reaction with boron trifluoride. Ring-opening reactions of piperazinones **2b** with 1-chloromethyl-2-pyrrolidone and acetyl bromide lead to previously unknown silyloxonium chloride **6b** and silyloxonium bromide **8b**, respectively, containing fragments of 2-amino acids as C,O-chelate ligands.

Crystal structures of *N*-methylamide **1b**, piperazinones **2a**, **d**, **e**, disiloxanes **3c**, **e**, fluorosilane **4a**, silyloxonium chloride **6b** and silyloxonium bromide **8b** have been determined by X-ray diffraction study. The silicon atom in piperazinones and disiloxanes is tetracoordinated while compounds **4a**, **6b** and **8b** contain pentacoordinated Si atoms.

Keywords: 2-sila-5-piperazinones, pentacoordinate silicon compounds, synthesis, X-ray diffraction study.

1. Introduction

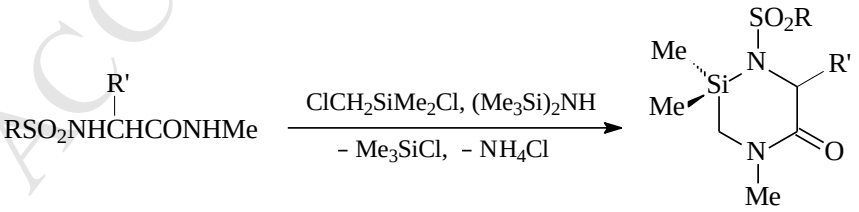
Silacyclanes, a diverse group of chemically and biologically active compounds, have recently become the focus of extensive studies [1]. Polyfunctional silicon-containing heterocycles, such as silapiperazines and their derivatives, are particularly interesting as potential precursors in organic synthesis due to the presence of very labile Si–N bonds in their molecules [2]. At the same time, certain classes of such compounds, including 2-sila-5-piperazinones, are virtually unknown — the only silacyclane of this type described in literature is a bicyclic derivative of proline [3].

Earlier, we studied the cyclosilylmethylation reaction of 2-hydroxyamides and the properties of the reaction products, 2-sila-5-morpholinones [4][5]. Recently, we have extended the scope of this synthetic approach towards the derivatives of 2-amino acids [3]. In the present paper, we report the general strategy of the synthesis of 1-organosulfonyl-2-sila-5-piperazinones by the reaction of *N'*-organosulfonyl-2-amino-*N*-methylamides with chloro(chloromethyl)dimethylsilane and the use of the resulting silacyclanes for the preparation of *N'*-(organosulfonyl)-2-amino acids derivatives.

2. Results and discussion

Cyclosilylmethylation of substituted amides of glycine **1a**–**c**, alanine (*S*)-**1d** and leucine **1e** was achieved by their reaction with a mixture of chloro(chloromethyl)dimethylsilane and hexamethyldisilazane — a versatile system that allows a one-pot synthesis involving both *N*-trimethylsilylation and subsequent *N*-dimethylchlorosilylmethylation [6]. For 2-sila-5-piperazinones **2a**, **2b**, (*S*)-2**d** and **2e**, the target products were isolated with yields of 53, 90, 65 and 68%, respectively. Piperazinone **2c** was used in further transformations without purification (Scheme 1).

Scheme 1



1a–c, (*S*)-**1d**, **1e** **2a–c**, (*S*)-**2d**, **2e**

R = Me, R' = H (**a**); R = 4-MeC_6H_4, R' = H (**b**); R = 4-$NO_2C_6H_4$, R' = H (**c**);
R = 4-$NO_2C_6H_4$, R' = Me (**d**), R = 4-$NO_2C_6H_4$, R' = CH_2CHMe_2 (**e**)

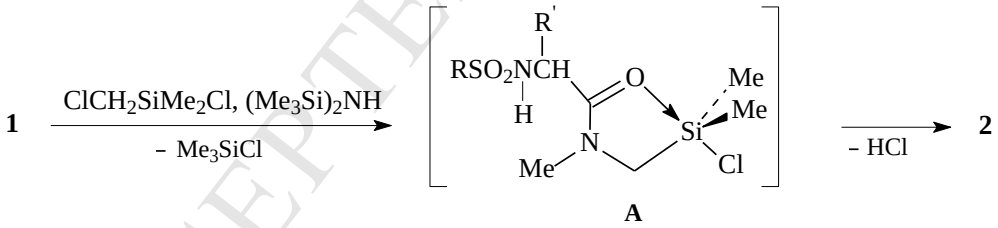
The composition and structures of hydrolytically labile 2-sila-5-piperazinones **2** were confirmed by elemental analysis, IR, NMR ^{1}H, ^{13}C and ^{29}Si spectra. In addition, the crystal structures of compounds **2a**, (*S*)-**2d** and **2e** were determined by X-ray diffraction study. All isolated

piperazinones **2a**, **2b**, (*S*)-**2d** and **2e** had a characteristic absorption at 1630–1650 cm^{-1} (NCO fragment) in the IR spectra and the chemical shift of the central atom in their NMR ^{29}Si spectra at 4–7 ppm, which is typical for a tetracoordinate silicon with similar environments [4][5][7][8]. The $SiMe_2$ and $SiCH_2$ groups in the ^1H NMR spectra of piperazinones (*S*)-2**d** and **2e** were non-equivalent due to the presence of chiral centres in these molecules.

According to X-ray data, the absolute configuration of the alanine derivative (*S*)-**1d** was retained during its cyclosilylmethylation into silapiperazinone (*S*)-**2d**.

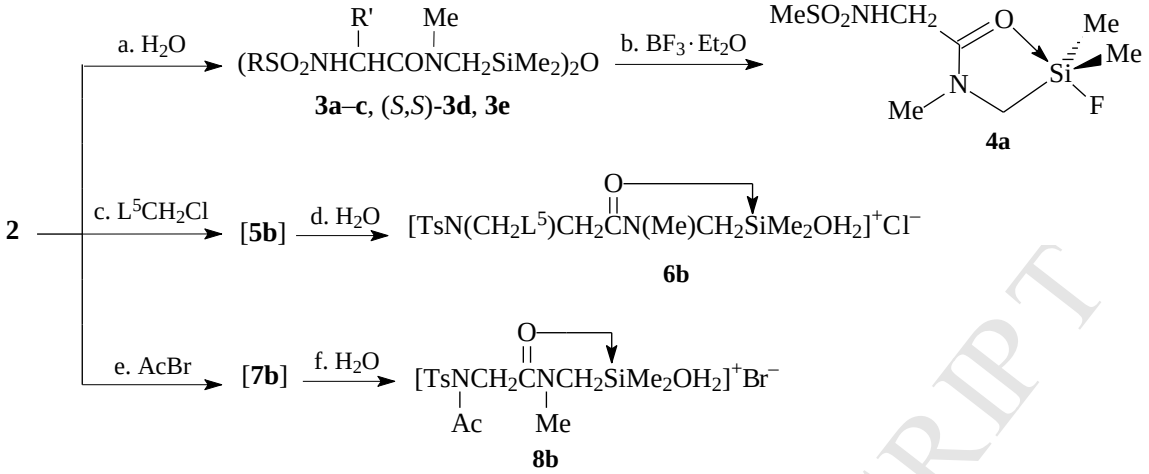
Earlier, we established a route for the formation of 2-sila-5-morpholinones from *O*-trimethylsilyloxy-*N*-methylamides and $ClCH_2SiMe_2Cl$ in the presence of Et_3N. The process involved intermediate pentacoordinated chlorosilanes, which subsequently underwent intramolecular elimination of Me_3SiCl and heterocyclisation into the final products [4][5]. Similarly, we propose that the formation of 2-sila-5-piperazinones, **2**, proceeds through initial *N*-dimethylchlorosilylmethylation of the amide nitrogen atom and the formation of pentacoordinate C,O-chelate chlorosilanes **A** (or their *N'*-trimethylsilyl derivatives), with subsequent elimination of HCl (or Me_3SiCl) and cyclisation into final compounds **2** (Scheme 2). At the same time, the process could also involve the initial trans-silylation of hexamethyldisilazane with $ClCH_2SiMe_2Cl$ and subsequent reaction of the resulting $Me_2SiNHSiMe_2CH_2Cl$ [9] with methylamides **1** affording the final 2-sila-5-piperazinones **2**.

Scheme 2



From the synthetic point of view, the lability of the Si–N bond in 2-sila-5-piperazinones **2** makes these compounds very useful intermediates for further chemical transformations at silicon. In aqueous ethanol, compounds **2a–c**, (*S*)-**2d** and **2e** readily undergo hydrolysis even at ambient temperature and afford disiloxanes **3a–c**, (*S,S*)-**3d** and **3e**, respectively (Scheme 3, reaction *a*). Disiloxanes **3b** and **3c** have been prepared by a simplified one-pot method, where 2-sila-5-piperazinones formed according to Scheme 1 were hydrolysed "*in situ*". The yields of disiloxanes, **3**, in all cases varied from moderate to good (46–72%).

Scheme 3



A typical transformation of disiloxanes into fluorosilanes was achieved by the reaction of **3a** with $BF_3 \bullet Et_2O$, which afforded pentacoordinate fluoride **4a** in a 75% yield (Scheme 3, reaction *b*).

Chloride **5b** and bromide **7b**, the expected products of the reaction of 2-sila-5-piperazinone **2b** with 1-chloromethyl-2-pyrrolidone (L^5CH_2Cl) and acetyl bromide (Scheme 3, reactions *c* and *e*) were hydrolytically unstable and could not be isolated. Instead, the C,O-chelate silyloxonium chloride **6b** and bromide **8b** were obtained (Scheme 3, reactions *d* and *f*).

The composition and structures of disiloxanes **3** and halides **4a**, **6b, 8b** were confirmed by elemental analysis, IR, ^1H, ^{13}C, ^{19}F (for **4a**) and ^{29}Si NMR spectra. The crystal structures of compounds **3c, 3e**, **4a**, **6b** and **8b** were determined by X-ray diffraction study.

The presence of the O→Si coordination in compounds **4–8** and the absence of such interaction in disiloxanes **3** were confirmed by IR spectroscopy. The two absorption bands at 1615–1640 cm^{-1} (strong) and 1450–1520 cm^{-1} (weak) observed in the IR spectra of compounds **4**–**8** were typical for pentacoordinate (O→Si)-chelates [10][11]. At the same time, the IR spectra of disiloxanes **3** contained only one strong absorption at 1625–1645 cm^{-1}.

The chemical shifts of fluorine (–136.4 ppm) and silicon (+2.3 ppm) in the NMR ^{19}F and ^{29}Si spectra of fluorosilane **4a** are similar to those in a previously reported derivative of *N*-mesylproline, Ms-Pro-N(Me)CH_2SiMe_2F (–126.4 and –3.3 ppm, respectively) [12]. Therefore, the O→Si intramolecular coordination in solutions of **4a** must be relatively weak. In contrast, the ^{29}Si signal of silyloxonium chloride **6b** in solution has a chemical shift of –30.0 ppm, which indicates the presence of a much stronger O→Si coordination in this compound. A similar chemical shift of ^{29}Si (–32.8 ppm) was observed for another cyclic proline derivative, [Ms-Pro-N(Me)$CH_2SiMe_2OH_2]^+Cl^-$ [3].

3. Single crystal X-ray studies

*3.1. N-tosylglycinemethylamide **1b***

The compound crystallized in two polymorph modifications (**1b** and **1b'**). Both modifications are colourless crystals with approximately equal cell volumes. In the crystal packing of the triclinic polymorph, two independent molecules are assembled into a three-dimensional network via weak N–H…O bonds. The monoclinic polymorph contains infinite chains along the *c* direction of the unit cell, with additional stacking interaction between the phenyl groups (the interplanar distance and the distance between centroids of the Ph groups are 3.478(5) and 4.40 Å, respectively). Further details are given in the supplementary materials.

*3.2. 2-Sila-5-piperazinones **2a**, (S)-**2d** and **2e***

Compounds **2a**, (*S*)-**2d** and **2e** are the first structurally characterised examples of organosilicon species with a Si–N bond in a six-membered ring. The heterocyclic fragments in all silapiperazinones adopt distorted boat conformations with the following deviations of C3 and C6 atoms, respectively: 0.619(3) and 0.572(3) for **2a**, 0.663 and 0.492(2) for (*S*)-**2d**, 0.693(2) and 0.518(2) for **2e**. The Si1–N2 distances are almost the same in all compounds; the longest bond is observed for **2e** where a relatively short intermolecular contact Si…O (3.594(2) Å) is present. The Si1N2S1O2 moieties are nearly planar in all cases, which is in line with other sulfonamides reported in literature (CSD [13] ref. codes: DUGWEH01, FACZIS, HIJGOW, SUQBIP, SUQQUQ, VEDDOX, VEDGEQ, VOGJUW, XINXOH, YILFOP, YILGAC, YILGEG).

Figure 1 shows the structure of 2-sila-5-piperazinone **2a**; selected geometrical parameters of structures **2a**, (*S*)-**2d** and **2e** are given in Table 1.

Table 1

Selected bond lengths and angles (Å and °) in structures **2a,** (*S*)-**2d** and **2e**.

Bond	**2a**	(*S*)-**2d**	**2e**
Si1–N2	1.774(2)	1.776(2)	1.779(2)
Si–C	1.863(3)	1.857(2)	1.859(2)
O1–C5	1.227(3)	1.222(2)	1.231(3)
S–O	1.437(2)	1.439(2)	1.435(2)
N2–C6	1.468(3)	1.491(2)	1.491(3)
N2Si1C3	97.46(11)	97.98(8)	97.28(10)

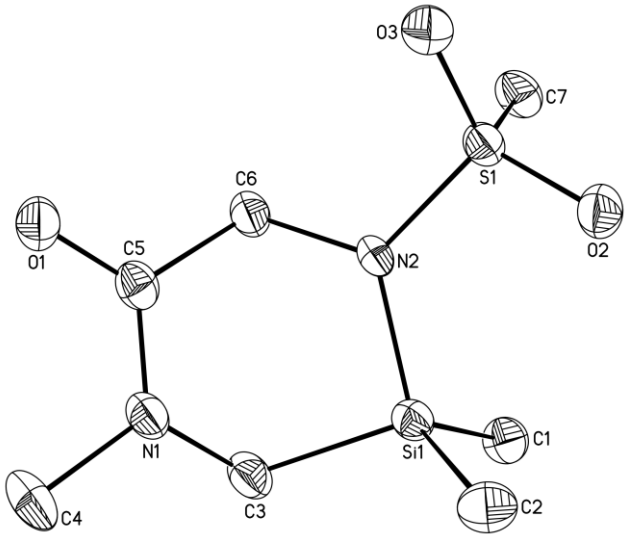


Fig. 1. Molecular structure of **2a** presented with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

*3.3. Disiloxanes **3c** and **3e***

To date, the structures of four disiloxanes similar to **3c** and **3e** have been reported in the literature [14][15][16]. In three published structures of this type, short Si…O intramolecular contacts between the silicon atom and the oxygen atom of a carbonyl or hydroxyl moiety were observed. The only exception was 1,1,3,3-tetramethyl-1,3-bis(2-oxo-1-pyrrolidinomethyl)-1,3-disiloxane, where the Si…O interatomic distance (3.959 Å) was greater than the sum of van-der-Waals radii of respective atoms (3.48 Å [17]). The structure of disiloxane **3c** contains two carbonyl groups, with the C2A=O2A group involved in an intermolecular N–H…O interaction with an adjacent molecule. Intermolecular distances Si1…O2, Si1A…O2 [-x+1,-y+1,-z+1] and the intramolecular contact Si1A…O2A (3.961(3), 3.978(3) and 4.017(3) Å, respectively) exceed the sum of van-der-Waals radii of corresponding elements. In addition, the $C_6H_4NO_2$ moieties participate in weak stacking interactions (the distances between the planes of the six-membered rings and their centroids are 3.468(4) and 4.916 Å, respectively). Another interesting feature of the structure **3c** is a linear SiOSi fragment. The analysis of anisotropic displacement parameters has shown that each of the O1 and O1A atoms is disordered over two positions with equivalent populations.

In disiloxane **3e**, both carbonyl oxygen atoms participate in the N–H…O interactions but the Si1…O2, Si1'…O2 and Si2…O7 distances are shorter than those in **3c** (3.487(4), 3.822(6) and 3.674(4) Å, respectively). The NO_2 moieties participate in peak-hole interactions O…N (the distances between the planes of nitro groups are 2.887(11) and 2.951(6) Å).

Representative structures of disiloxanes **3c** and **3e** are shown in Figures 2 and 3.

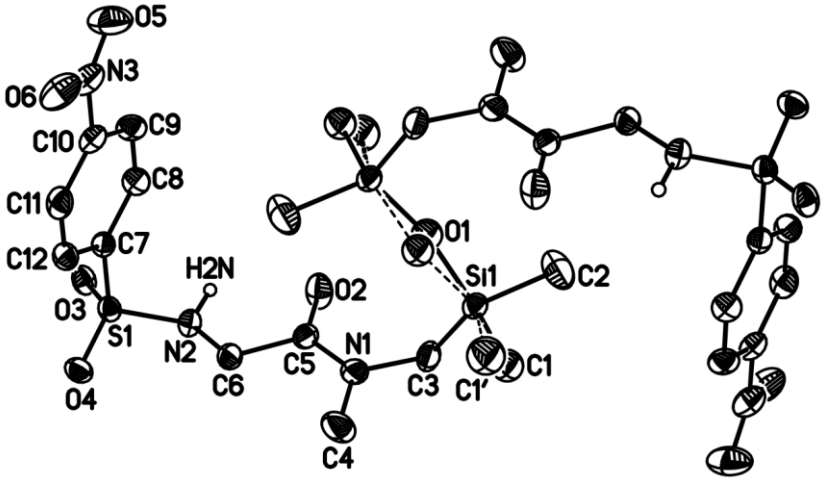


Fig. 2. Molecular structure of **3c** presented with thermal ellipsoids at 50% probability. Hydrogen atoms (except H2N) are omitted for clarity.

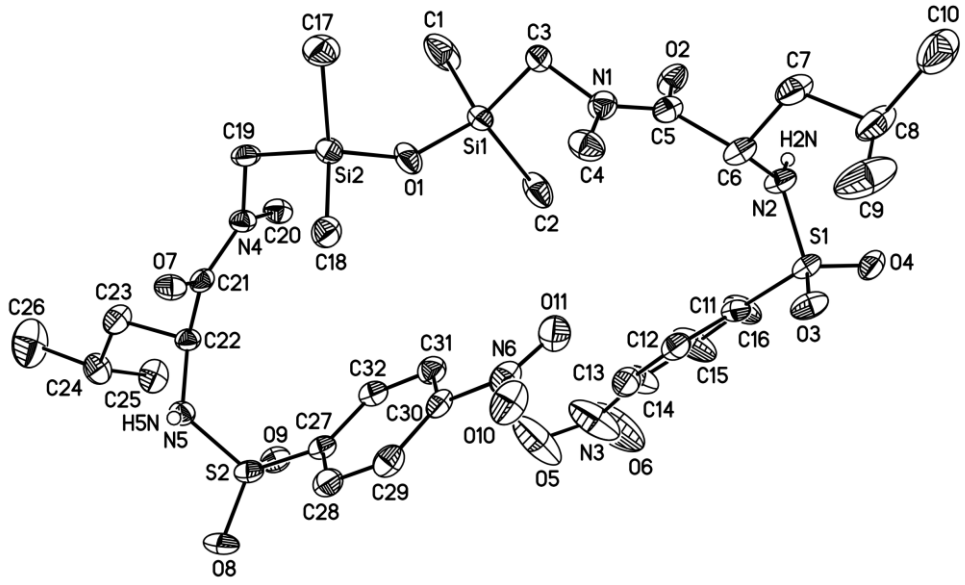


Fig. 3. Molecular structure of **3e** presented with thermal ellipsoids at 50% probability. Hydrogen atoms (except H2N and H5N) and minor positions of the disordered atoms are omitted for clarity.

*3.4. Fluoride **4a**, silyloxonium halides **6b** and **8b***

Table 2

Selected geometrical parameters (Å and °) of structures **4a**, **6b** and **8b**.

	Si1–X, Å	**Si1–O1, Å**	**O1–Si1–X, °**	**Δ_{Si}*, Å**
4a (X = F1)	1.6699(8)	2.1949(9)	171.39(4)	0.2204(3)
6b (X = O1W)	1.888(3)	1.943(3)	174.35(14)	0.0637(12)
8b (X = O1W)	1.9765(13)	1.8924(12)	173.24(6)	–0.0094(6)

* The deviation of the Si atom from the plane of equatorial substituents C1, C2, C3; a positive value means deviation towards X fragment.

Organosilicon compounds containing $OSiC_3F$ coordination polyhedra are often described in the literature as snapshots of the S_N2 reaction potential surface [18][19]. The Si…O interatomic distances in such compounds are strongly affected by the inductive effects of substituents at the C and N atoms of the five-membered ring. The shortest Si…O distance and the longest Si–F bond (2.065(1) and 1.675(1) Å, respectively) have been found in a quinolinone complex [19], which is probably a result of the –M effect of the vicinal C=C bond. In the derivative of 1,3-oxazin-4-one [16], the Si…O distance exceeds that in the quinolinone complex by 0.16 Å while the Si–F bond is only 0.01 Å shorter. The same Si–F bond lengths were observed in *N*,*N*-bis(dimethylfluorosilylmethyl)acetamide [20] and (*N*-acetyl-*N*-((*S*)-1-phenylethyl)amino-methyl)dimethylfluorosilane [21]. The Si…O distances in these compounds were also very similar (2.147 and 2.187 Å, respectively). Such minor variations of the Si–F and Si–O bond lengths are in good agreement with the nature of the F atom, which is a poor leaving group in the S_N2 reactions. In **4a** the Si atom has a strongly distorted trigonal bipyramidal (TBP) configuration with a deviation from the plane of the equatorial substituents (Δ_{Si}) of 0.2204(3) Å (see Table 2 for selected geometrical parameters of structures **4a**, **6b** and **8b**). The F1 and O1 atoms occupy axial positions (Fig. 4), the angle F1-Si1-O1 is 171.39(4)°. The lengths of the Si1–F1 and Si1–O1 bonds are 1.6699(8) and 2.1949(9) Å respectively. The five-membered chelate ring Si1C3N1C4O1 is almost planar (maximum deviation from the plane is 0.03 Å). The molecules of **4a** are assembled into chains via N–H…OSO bonds, the F1 and O1 atoms are not involved in H-bonding.

In **6b** and **8b**, the configurations of Si atoms correspond to slightly distorted TBP (Figs. 5, 6) with Δ_{Si} of 0.0637(12) and –0.0094(6) Å respectively. The O1 and O1W atoms occupy axial positions, the O1-Si1-O1W angles are 174.35(14) and 173.24(6)° in **6b** and **8b**, respectively. The chelate ring in **6b** adopts an envelope conformation while in **8b** it is almost planar. It should be noted that the average Δ_{Si} values in **6b** and **8b** are close to zero and the axial angles O1-Si1-O1W are more close to 180° than the axial angle O1-Si1-F1 in fluoride **4a**. The published data [3][22][23][24] provide the ranges for the axial Si1–O1 and Si1–O1W bond lengths: 1.878–1.960 and 1.907–2.009 Å respectively; the values for **6b** and **8b** (Table 2) slightly expand the above ranges. Thus the structures **6b** and **8b** correspond to the steps within the middle stage of an S_N2 process. The chlorine and bromine atoms in **6b** and **8b** reside in the outer sphere with respect to Si atoms and do not form interatomic contacts with it (the shortest Si…Cl and Si…Br distances are 4.058 and 4.320 Å respectively). In **6b**, the cations and Cl^- are assembled into chains via O–H…Cl bonds, and in **8b**, the cations and Br^- form centrosymmetric dimers.

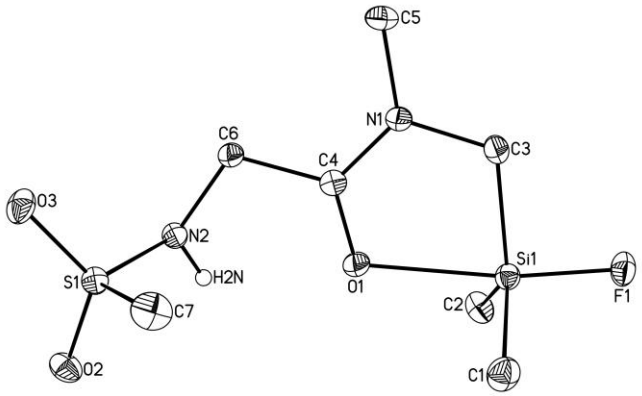


Fig. 4. Molecular structure of **4a** presented with thermal ellipsoids at 50% probability. Hydrogen atoms (except H2N) are omitted for clarity.

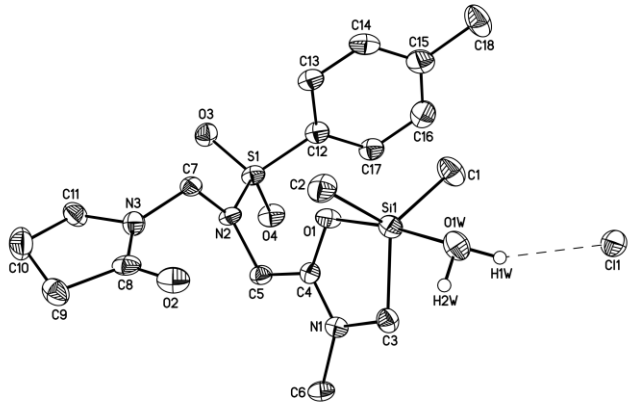


Fig. 5. Molecular structure of **6b** presented with thermal ellipsoids at 50% probability. Hydrogen atoms (except H1W and H2W) are omitted for clarity.

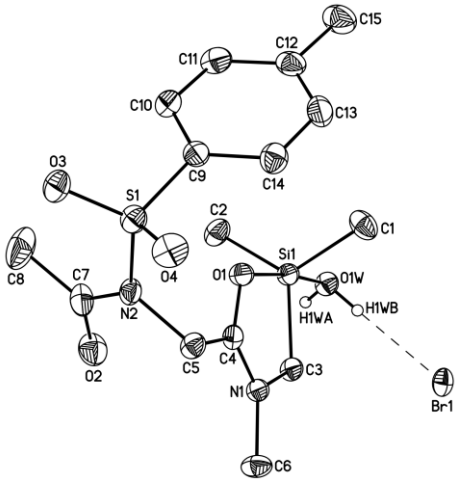


Fig. 6. Molecular structure of **8b** presented with thermal ellipsoids at 50% probability. Hydrogen atoms (except H1WA and H1WB) are omitted for clarity.

Thus, a new type of silacyclanes, 1-organosulfonyl-2-sila-5-piperazinones, were prepared from *N*-methylamides of *N'*-organosulfonyl-2-amino acids and used in a variety of synthetic applications, including the synthesis of disiloxanes, fluorosilanes and silyloxonium halides containing fragments of 2-amino acids as C,O-chelate ligands. These synthetic applications illustrate the versatility and high reactivity of the silacyclanes due to the presence of labile Si–N bonds in their molecules. The structures of most compounds in solutions and in the solid state were confirmed by multinuclear NMR spectra and X-ray diffraction study.

4. Experimental

IR spectra of compounds in KBr pressings were recorded on Specord M80 instrument. IR spectra of neat solid samples were recorded on Bruker Tensor-27 instrument using attenuated internal reflection module.

Multinuclear NMR spectra of compounds in $CDCl_3$ and CD_3CN were recorded on Bruker AC-200 (^{1}H, 200 MHz), Bruker Avance II 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{19}F, 282 MHz; ^{29}Si, 59.63 MHz) and Bruker Avance II 600 (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{29}Si 119.2 MHz) instruments using a pulse sequence with Fourier transformation and ^{2}H-stabilization of the resonance conditions. Tetramethylsilane and $CFCl_3$ were used as internal and external references, respectively. In some cases, ^{29}Si NMR spectra were recorded using 2D NMR techniques (pulse sequence ^{1}H–^{29}Si HSQC) [25].

Optical rotations of compounds were measured in 10 cm cuvettes using a Perkin Elmer 341 instrument.

The starting materials and solvents were obtained from commercial sources (*Acros* and *Sigma-Aldrich*).

N-Nosylglycine [26], *N*-Nosyl-(*S*)-alanine [27], *N*-methylamides of *N'*-mesylglycine (**1a**) [28] and *N'*-tosylglycine (**1b**) [29], and 3-tosyl-4-methyl-5-oxazolidinone [30] were prepared by common synthetic methods.

Synthetic details and spectroscopic data for *N*-methylamides **1** are given in the supplementary materials.

Single crystals suitable for X-ray diffraction analysis were obtained by recrystallisation from: **1b** (triclinic), (*S*)-**2d**, **3d** and **6b** – benzene; **1b'** (monoclinic) and **2e** – toluene; **3c** – ethanol; **4a** – heptane/benzene mixture; **8b** – acetonitrile; **2a** – directly from the reaction mixture.

X-ray diffraction measurements were carried out using SMART 1000 CCD and Smart APEX II diffractometers. The frames were integrated and corrected for absorption by the APEX 2 program package [31]. The details of crystallographic data and experimental conditions are given in Tables 3 and 4 as supplementary materials. The structures were solved by direct method and refined by full-

matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the difference Fourier maps and refined in a rigid body model. All calculations were performed using the APEX 2 program package [31]. Crystallographic data for the structural analysis of **1b**, **1b'**, **2a**, (*S*)-**2d**, **2e**, **3c**, **3d**, **4a**, **6b** and **8b** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 826708–826710, 826713–826717, 911025, 911027.

4.1. Preparation of N-methylamides of 2-amino acids

The syntheses of *N*-methylamides of 2-amino acids are described in the Supplementary materials.

4.2. Preparation of 2-sila-5-piperazinones

*4.2.1. 2,2,4-Trimethyl-1-mesyl-2-sila-5-piperazinone (**2a**)*

A mixture of methylamide **1a** (13.1 g, 80 mmol) [28], hexamethyldisilazane (11.4 g, 70 mmol), chloro(chloromethyl)dimethylsilane (11.3 g, 80 mmol) and benzene (100 mL) was refluxed for 3 h, allowed to cool down, the precipitate formed filtered out, the volatiles removed *in vacuo*, and the residue distilled to afford 9.9 g (53%) of piperazinone **2a**, b. p. 205–206 °C/3 mm Hg, m. p. 81–85 °C.

Found, %: C 35.26, H 6.54, N 11.64. $C_7H_{16}N_2O_3SSi$. Calculated, %: C 35.57, H 6.82, N 11.85.

IR spectrum (KBr, *v*, cm^{-1}): 1632 s (NCO), 1316 s and 1152 s (SO_2).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.30 (s, 6H, $SiMe_2$), 2.69 (s, 2H, CH_2Si), 2.81 (s, 3H, CH_3S), 2.87 (s, 3H, NCH_3), 3.74 (s, 2H, NCH_2).

^{13}C NMR ($CDCl_3$, δ, ppm): –2.0 ($SiMe_2$), 37.29 (NCH_3), 39.91 (CH_2Si), 40.25 (CH_3S), 48.94 (NCH_2), 168.35 (C=O).

^{29}Si NMR ($CDCl_3$, δ, ppm): 4.0.

*4.2.2. 2,2,4-Trimethyl-1-tosyl-2-sila-5-piperazinone (**2b**)*

A mixture of methylamide **1b** (2.3 g, 10 mmol) [29], hexamethyldisilazane (1.4 g, 9 mmol), chloro(chloromethyl)dimethylsilane (1.4 g, 10 mmol) and benzene (20 mL) was refluxed for 3 h, allowed to cool down, the precipitate formed filtered out, the volatiles removed *in vacuo*, and the residue dried *in vacuo* for 2 h at 100 °C/20 mm Hg to afford 2.8 g (90%) of crude piperazinone **2b** as a yellow oil.

Found, %: C 49.23, H 6.61, N 9.91. $C_{13}H_{20}N_2O_3SSi$. Calculated, %: C 49.97, H 6.45, N 8.96.

IR spectrum (KBr, *v*, cm^{-1}): 1648 s (NCO), 1596 w, 1496 m (Ar), 1336 s and 1164 s (SO_2).

*4.2.3. 2,2,4,6-Tetramethyl-1-nosyl-2-sila-5-piperazinone ((S)-**2d**)*

A mixture of methylamide (*S*)-**1d** (5.9 g, 20 mmol), $[\alpha]_D^{25}$ +16.2° (*c* 2.00, CH_3CN), hexamethyldisilazane (3.2 g, 20 mmol), chloro(chloromethyl)dimethylsilane (2.9 g, 20 mmol) and toluene (80 mL) was refluxed for 3 h, allowed to cool down, the precipitate formed filtered out, and the volatiles removed *in vacuo*. The remaining solid was washed with dry ether and re-crystallised from benzene to afford 4.5 g (65%) of piperazinone (*S*)-**2d**, m. p. 128–130 °C (benzene), $[\alpha]_D^{25}$ +4.4° (*c* 5.62, CH_3CN).

Found, %: C 49.25, H 5.39, N 10.60. Calculated for $C_{13}H_{19}N_3O_5SSi \times 0.5C_6H_6$, %: C 48.47, H 5.59, N 10.60.

IR spectrum (KBr, *v*, cm^{-1}): 1648 s (NCO), 1526 s (Ar, NO_2), 1333 s (NO_2, SO_2), 1161 s (SO_2).

^{1}H NMR (CD_3CN, δ, ppm): 0.51 (s, 3H, SiMe), 0.55 (s, 3H, SiMe), 1.34 (d, 3H, CH<u>CH</u>$_3$, $^3J_{HH}$ 7 Hz), 2.77 and 3.09 (two d, 2H, $SiCH_2$, $^3J_{HH}$ 16 Hz, $^3J_{HH}$ 16.5 Hz), 2.89 (s, 3H, NCH_3), 3.98 (br, 1H, NCH), 8.06 (d, 2H, Ar, $^3J_{HH}$ 9 Hz), 8.32 (d, 2H, Ar, $^3J_{HH}$ 8 Hz).

^{13}C NMR (CD_3CN, δ, ppm): 1.24 ($SiMe_2$), 19.95 (<u>CH</u>$_3$CH), 37.82 (NCH_3), 41.75 (NCH_2), 49.75 (<u>CH</u>CH_3), 125.19 (C(2), C(6) Ar), 129.22 (C(3), C(5) Ar), 147.17 (C(1), Ar), 151.06 (C(4), Ar), 170.40 (C=O).

^{29}Si NMR (CD_3CN, δ, ppm): 4.8.

*4.2.4. 2,2,4-Trimethyl-6-isobutyl-1-nosyl-2-sila-5-piperazinone (**2e**)*

Piperazinone **2e** was prepared in the same manner as (*S*)-**2d** from methylamide **1e** (6.6 g, 20 mmol), hexamethyldisilazane (3.2 g, 20 mmol), chloro(chloromethyl)dimethylsilane (2.9 g, 20 mmol) and toluene (80 mL). Yield 5.4 g (68%), m. p. 130–135 °C (benzene).

Found, %: C 47.52, H 6.31, N 10.15. $C_{16}H_{25}N_3O_5SSi$. Calculated, %: C 48.10, H 6.31, N 10.51.

IR spectrum (solid, *v*, cm^{-1}): 1647 s (NCO), 1525 s (Ar, NO_2), 1347 s (NO_2, SO_2), 1157 s (SO_2).

^{1}H NMR (CD_3CN, δ, ppm): 0.57 (s, 3H, SiMe), 0.62 (s, 3H, SiMe), 0.95 (d, 6H, CH(<u>CH</u>$_3$)$_2$, $^3J_{HH}$ 7 Hz), 1.54 (br, 1H, <u>CH</u>Me_2), 1.86 (br, 2H, <u>CH</u>$_2$CH), 2.82 and 3.23 (two d, 2H, $SiCH_2$, $^3J_{HH}$ 16 Hz, $^3J_{HH}$ 16.5 Hz), 2.98 (s, 3H, NCH_3), 4.04 (br, 1H, NCH), 8.12 (d, 2H, Ar, $^3J_{HH}$ 9 Hz), 8.42 (d, 2H, Ar, $^3J_{HH}$ 8 Hz).

^{13}C NMR (CD_3CN, δ, ppm): 0.45 ($SiMe_2$), 20.97, 22.44 (<u>Me</u>$_2$CH), 24.91 (<u>CH</u>Me_2), 37.35 (NCH_3), 37.8 (NCH_2), 42.06 (<u>CH</u>$_2$CH), 60.65 (NCH), 124.75 (C(2), C(6) Ar), 128.61 (C(3), C(5) Ar), 146.12 (C(1) Ar), 150.45 (C(4), Ar), 168.67 (C=O).

^{29}Si NMR (CD_3CN, δ, ppm): 7.0.

4.3. Preparation of disiloxanes

*4.3.1. 1,1,3,3-Tetramethyl-1,3-bis(2-mesylamido-N-methylacetamidomethyl)-1,3-disiloxane (**3a**)*

A solution of 2-sila-5-piperazinone **2a** (1 g, 4.2 mmol) and water (2 mL, 0.11 mol) in ethanol (20 mL) was stirred at ambient temperature for 24 h. The crystals formed were isolated by filtration and dried in the open air to afford 0.47 g (46%) of disiloxane **3a**, m. p. 139–141 °C (ethanol).

Found, %: C 33.44, H 7.09, N 11.02. $C_{14}H_{34}N_4O_7S_2Si_2$. Calculated, %: C 33.72, H 6.87, N 11.27.

IR spectrum (KBr, *v*, cm^{-1}): 2904 w (NH), 1632 s (NCO), 1316 s and 1152 s (SO_2).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.11 (s, 12H, $2SiMe_2$), 2.74 and 2.90 (two d, 4H, $2SiCH_2$, $^3J_{HH}$ 15 Hz), 2.91 (s, 6H, $2CH_3S$), 2.93 (s, 6H, $2NCH_3$), 3.91 (s, 4H, $2CH_2CO$), 5.51 (br, 2H, 2NH).

^{13}C NMR ($CDCl_3$, δ, ppm): 0.63 ($SiMe_2$), 26.42 (CH_3S), 39.41 (NCH_3), 40.34 ($NHCH_2$), 41.61 ($SiCH_2$), 150.09 (C=O).

^{29}Si NMR ($CDCl_3$, δ, ppm): 4.0.

*4.3.2. 1,1,3,3-Tetramethyl-1,3-bis(2-tosylamido-N-methylacetamidomethyl)-1,3-disiloxane (**3b**)*

A mixture of methylamide **1b** (4.8 g, 20 mmol), hexamethyldisilazane (2.2 g, 13 mmol), chloro(chloromethyl)dimethylsilane (2.9 g, 20 mmol) and benzene (40 mL) was refluxed for 3 h, allowed to cool down, the precipitate formed was filtered out, and the volatiles were removed *in vacuo*. The remaining oil was treated with a mixture of ethanol (30 mL) and water (0.5 mL). The crystals formed were re-dissolved in 50 mL of a mixture of ethyl acetate and acetonitrile (3 : 1) and filtered through silica. The volatiles were removed *in vacuo*, the residue was washed with ethanol and dried in the open air to afford 4.6 g (72%) of disiloxane **3b**, m. p. 162–164 °C (ethanol).

Found, %: C 48.61, H 6.57, N 8.59. $C_{26}H_{42}N_4O_7S_2Si_2$. Calculated, %: C 48.57, H 6.58, N 8.71.

IR spectrum (KBr, *v*, cm^{-1}): 3192 (NH), 1640 s (NCO), 1595 m and 1495 m (Ar), 1336 s and 1164 s (SO_2).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.08 (s, 12H, $2SiMe_2$), 2.55 (s, 6H, $2\underline{CH_3}Ar$), 2.66 and 2.81 (two d, 4H, $2SiCH_2$, $^3J_{HH}$ 15 Hz), 2.85 (s, 6H, $2NCH_3$), 3.65 (s, 4H, $2CH_2CO$), 5.65 (br, 2H, 2NH), 7.23 (d, 4H, Ar, $^3J_{HH}$ 8 Hz), 7.69 (d, 4H, Ar, $^3J_{HH}$ 8 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 0.43 ($SiMe_2$), 21.47 ($\underline{CH_3}Ar$), 36.36 (CH_2Si), 41.58 (NCH_3), 43.44 ($NHCH_2$), 124.92, 127.14, 143.50, 145.28 (Ar), 150.19 (C=O).

^{29}Si NMR ($CDCl_3$, δ, ppm): 4.0.

*4.3.3. 1,1,3,3-Tetramethyl-1,3-bis(2-nosylamido-N-methylacetamidomethyl)-1,3-disiloxane (**3c**)*

A mixture of methylamide **1c** (2.7 g, 10 mmol), hexamethyldisilazane (1.6 g, 10 mmol), chloro(chloromethyl)dimethylsilane (1.4 g, 10 mmol) and toluene (40 mL) was refluxed for 3 h, allowed to cool down, the precipitate formed filtered out, and the volatiles removed *in vacuo*. The residue was washed with a mixture of ethanol (30 mL) and water (0.5 mL), the crystalline material isolated by filtration and dried in the open air to afford 1.8 g (52%) of disiloxane **3c**, m. p. 150–151 °C (ethanol).

Found, %: C 40.75, H 5.07, N 11.87. $C_{24}H_{36}N_6O_{11}S_2Si_2$. Calculated, %: C 40.89, H 5.15, N 11.92.

IR spectrum (solid, *ν*, cm^{-1}): 3202 br (NH), 1647 s (NCO), 1526 s (Ar, NO_2), 1348 s (NO_2, SO_2), 1168 s (SO_2).

^{1}H NMR ($CDCl_3$, δ, ppm): –0.08 (s, 12H, $2SiMe_2$), 2.62 and 2.77 (two d, 4H, $2SiCH_2$, $^3J_{HH}$ 15 Hz), 2.87 (s, 6H, $2NCH_3$), 3.79 (s, 4H, $2CH_2CO$), 6.28 (br, 2H, 2NH), 8.08 (d, 4H, Ar, $^3J_{HH}$ 8 Hz), 8.29 (d, 4H, Ar, $^3J_{HH}$ 8 Hz).

^{13}C NMR (CD_3CN, δ, ppm): –0.16 and –0.02 ($SiMe_2$), 40.25 ($SiCH_2$), 40.74 ($NHCH_2$), 43.65 (NCH_3), 124.22 (C(2), C(6) Ar), 128.43 (C(3), C(5) Ar), 145.47 (C(1) Ar), 150.09 (C(4) Ar), 165.28 (C=O).

^{29}Si NMR ($CDCl_3$, δ, ppm): 3.9.

*4.3.4. (S,S)-1,1,3,3-Tetramethyl-1,3-bis(2-nosylamido-N-methylpropanamidomethyl)-1,3-disiloxane ((S,S)-**3d**)*

A solution of piperazinone (*S*)-**2d** (1.8 g, 5 mmol) and water (5 mL) in 25 mL of ethanol was stirred for 24 h. The crystals formed were isolated by filtration and dried in the open air to afford 1.0 g (54%) of disiloxane *(S,S)*-**3d**, m. p. 146–147 °C (ethanol), $[\alpha]_D^{25}$ +5.6° (*c* 3.36, CH_3CN).

Found, %: C 42.18, H 5.55, N 11.27. $C_{26}H_{40}N_6O_{11}S_2Si_2$. Calculated, %: C 42.60, H 5.50, N 11.46.

IR spectrum (solid, *ν*, cm^{-1}): 3111 br (NH), 1625 s (NCO), 1527 s (Ar, NO_2), 1348 s (NO_2, SO_2), 1166 s (SO_2).

^{1}H NMR ($CDCl_3$, δ, ppm): –0.08 (s, 6H, 2SiMe), 0.16 (s, 6H, 2SiMe), 1.17 (d, 6H, $2\underline{CH_3}CH$, $^3J_{HH}$ 6.9 Hz), 2.43 and 2.71 (two d, 4H, $2SiCH_2$, $^3J_{HH}$ 6.9 Hz), 2.88 (s, 6H, $2NCH_3$), 3.65 (m, 2H, CHCO), 6.45 (br, 2H, 2NH), 8.02 (d, 4H, Ar, $^3J_{HH}$ 8.8 Hz), 8.3 (d, 4H, Ar, $^3J_{HH}$ 8.8 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 0.38 and 0.41 ($SiMe_2$), 19.77 ($\underline{CH_3}CH$), 37.34 (NCH_3), 48.61 ($SiCH_2$), 49.09 ($\underline{CH}CH_3$), 124.19 (C(2), C(6) Ar), 128.17 (C(3), C(5) Ar), 146.19 (C(1), Ar), 149.95(C(4), Ar), 169.53 (C=O).

^{29}Si NMR ($CDCl_3$, δ, ppm): 3.8.

*4.3.5. 1,1,3,3-Tetramethyl-1,3-bis(2-nosylamido-4-methyl-N-methylpentanamidomethyl)-1,3-disiloxane (**3e**)*

A solution of piperazinone **2e** (1.3 g, 3.3 mmol) and water (0.5 mL) in 30 mL of ethanol was stirred for 24 h. The crystals formed were isolated by filtration and dried in the open air to afford 0.65 g (49%) of disiloxane **3e**, m. p. 153–154 °C (ethanol).

Found, %: C 47.03, H 6.37, N 10.14. $C_{38}H_{56}N_4O_{10}S_2Si_2$. Calculated, %: C 47.04, H 6.41, N 10.29.

IR spectrum (solid, *v*, cm^{-1}): 3177 s (NH), 1630 s (NCO), 1529 s (Ar, NO_2), 1348 s (NO_2, SO_2), 1163 s (SO_2).

^{1}H NMR ($CDCl_3$, δ, ppm): –0.25 and 0.08 (two s, 12H, $2SiMe_2$), 0.93 and 0.96 (two d, 12H, $2(\underline{CH_3})_2CH$, $^3J_{HH}$ 6.9 Hz), 1.48 (br, 2H, $2\underline{CH}Me_2$), 1.89 (br, 4H, $2\underline{CH_2}CH$), 2.69 (d, 4H, $2SiCH_2$, $^3J_{HH}$ 16 Hz), 2.92 (s, 6H, $2NCH_3$), 4.26 (br, 2H, $2\underline{CH}NH$), 6.12 (br, 2H, $\underline{NH}CH$), 8.18 (d, 4H, Ar, $^3J_{HH}$ 9 Hz), 8.32 (d, 4H, Ar, $^3J_{HH}$ 9 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 0.29 ($SiMe_2$), 23.18 ($\underline{Me_2}CH$), 24.09 ($\underline{CH}Me_2$), 37.12 (NCH_3), 41.48 ($\underline{CH_2}CH$), 42.24 ($SiCH_2$), 51.56 ($\underline{CH}NH$), 124.00 (C(2), C(6) Ar), 128.31 (C(3), C(5) Ar), 146.08 (C(1), Ar), 149.90 (C(4), Ar), 169.65 (C=O).

^{29}Si NMR ($CDCl_3$, δ, ppm): 3.8.

*4.4. Preparation of (O→Si)-chelates: fluorosilane **4a**, silyloxonium chloride **6b** and silyloxonium bromide **8b***

*4.4.1. N-(dimethylfluorosilylmethyl)-N-methyl-2-(mesylamido)acetamide (**4a**)*

A solution of disiloxane **3a** (0.95 g, 1.96 mmol) in acetonitrile (8 mL) was heated up to 60 °C, and BF_3–Et_2O complex (0.10 g, 0.72 mmol) was added. The reaction mixture was refluxed for 1 h, cooled down, the volatiles removed *in vacuo*, and the remaining mixture extracted with 15 mL of boiling benzene. The extract was filtered, the volatiles removed *in vacuo*, and the remaining oil washed with heptane to afford 0.77 g (75%) of fluoride **4a**, m. p. 109–111 °C (benzene–heptane, 3 : 2).

Found, %: C 32.67, H 6.77, N 10.77. $C_7H_{17}F_1N_2O_3S_1Si_1$. Calculated, %: C 32.79, H 6.68, N 10.92.

IR spectrum (KBr, *v*, cm^{-1}): 2960 br (NH), 1640 s (NCO), 1494 br (NCO), 1330 s and 1160 m (SO_2).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.25 (d, 6H, $SiMe_2$, $^3J_{HF}$ 5.4 Hz), 2.55 (s, 2H, CH_2Si), 2.93 (s, 3H, NCH_3), 2.97 (s, 3H, CH_3S), 3.95 (s, 2H, CH_2CO), 5.15 (br, 1H, NH).

^{13}C NMR ($CDCl_3$, δ, ppm): 6.94 ($SiMe_2$), 36.42 ($SiCH_2$), 39.44 (NCH_3), 40.7 (CH_3S), 42.99 (CH_2NH), 168.09 (C=O).

^{19}F NMR ($CDCl_3$, δ, ppm): –136.4.

^{29}Si NMR ($CDCl_3$, δ, ppm): 2.3 (d, $^1J_{SiF}$ 256 Hz).

*4.4.2. {2-[N-(2-oxopyrrolidinylmethyl)tosylamido]-(N'-methylacetamido)methyl}dimethylsilyl-oxonium chloride (**6b**)*

A solution of **1b** (2.4 g, 10 mmol), hexamethyldisilazane (1.6 g, 10 mmol) and chloro(chloromethyl)dimethylsilane (1.4 g, 10 mmol) in toluene (40 mL) was refluxed for 5 hrs, cooled down, filtered and evaporated *in vacuo* to afford 2.5 g (8 mmol) of 2-sila-5-piperazinone **2b**. The intermediate **2b** was dissolved in benzene (15 mL) and a solution of 1-chloromethyl-2-pyrrolidone (1.1 g, 8.5 mmol) in benzene (5 mL) was added dropwise. The mixture was stirred 5 days at room temperature. The crystals formed were filtered, washed with 2 mL of benzene and dried over phosphorus(V) oxide to afford 2.8 g (75%) of silyloxonium chloride **6b**, m. p. 102–104 °C (CH_3CN).

Found, %: C 46.58, H 6.39, N 9.26. $C_{18}H_{30}Cl_1N_3O_5S_1Si_1$. Calculated, %: C 46.58, H 6.51, N 9.05.

IR spectrum (KBr, *v*, cm^{-1}): 1690 s (NCO lactam), 1615 m and 1490 w (NCO→Si), 1340 s and 1160 s (SO_2).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.44 (s, 6H, $SiMe_2$). 2.02–2.13 (m. 2H, C^4H_2 lactam), 2.40 (t, 2H, C^3H_2 lactam, J^3 8.08 Hz), 2.45 (s, 3H, CH_3), 2.78 (s, 2H, $SiCH_2$), 3.06 (s, 3H, MeN), 3.56–3.64 (m, 2H, C^5H_2 lactam), 4.25 (s, 2H, NCH_2 lactam), 4.77 (s, 2H, NCH_2CO), 7.33 and 7.71 (two d, 4H, J^3 8.08 Hz, Ar).

^{13}C NMR ($CDCl_3$, δ, ppm): 6.17 ($SiMe_2$), 17.88 (C^4 lactam), 21.52 (CH_3Ar), 30.67 (C^3 lactam), 127.17 (C^2 and C^6 Ar), 129.83 (C^3 and C^5 Ar), 136.62 (C^1 Ar), 144.26 (C^4 Ar), 170.56 (C=O amide), 177.2 (C=O lactam).

^{29}Si NMR ($CDCl_3$, δ, ppm): –30.0.

*4.4.3. [2-(N-tosylacetamido)-(N'-methylacetamido)methyl]dimethylsilyloxonium bromide (**8b**)*

A solution of **1b** (2.4 g, 10 mmol), hexamethyldisilazane (1.6 g, 10 mmol) and chloro(chloromethyl)dimethylsilane (1.4 g, 10 mmol) in toluene (40 mL) was refluxed for 5 hrs, cooled down, filtered and evaporated *in vacuo* to afford 2.5 g (8 mmol) of 2-sila-5-piperazinone **2b**. The intermediate **2b** was dissolved in benzene (15 mL) and a solution of acetyl bromide (4.9 g, 40 mmol) in benzene (5 mL) was added dropwise. The mixture was allowed to stand for 5 days at room temperature. The crystals formed were filtered and re-crystallised from absolute CH_3CN (4 mL) to afford 1.3 g (37%) of silyloxonium bromide **8b**, m. p. 118–120 °C (CH_3CN).

Found, %: 39.99, H 5.78, N 5.93. $C_{15}H_{25}N_2O_5Br_1S_1Si_1$. Calculated, %: C 39.73, H 5.56, N 6.18.

IR spectrum (KBr, *v*, cm^{-1}): 1700 s ($O{=}CNSO_2$), 1644 s and 1491 s ($NCO{\rightarrow}Si$), 1598 w (Ar), 1370 s and 1168 s (SO_2).

^1H NMR (DMSO-d^6, δ, ppm): 0.13 (s, 6H, $SiMe_2$), 2.04 (s, 3H, MeCO), 2.39 (s, 3H, Me), 2.79 (s, 2H, $SiCH_2$), 3.11 (s, 3H, MeN), 4.67 (s, 2H, NCH_2CO), 5.98 (br, 2H, H_2O), 7.36 and 7.86 (two d, 4H, Ar, *J* 8 Hz).

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