Chemistry of Heterocyclic Compounds, Vol. 47, No. 12, March, 2012 (Russian Original Vol. 47, No. 12, December, 2011)

PENTACOORDINATED CHLOROSILANES WITH *C,O*-CHELATE LIGANDS DERIVED FROM *N*-METHYL-*N*'-ORGANOSULFONYL-PROLINAMIDES*

A. A. Nikolin[1], D. E. Arkhipov[2], A. G. Shipov[1], E. P. Kramarova[1], N. A. Koval'chuk[2], A. A. Korlyukov[2], V. V. Negrebetsky[1], Yu. I. Baukov[1]**, A. R. Bassindale[3], P. G. Taylor[3], A. Bowden[3], and S. Yu. Bylikin[1,3]**

The reaction of amides RSO_2-Pro-NHMe with $ClCH_2SiMe_2Cl$ in the presence of $(Me_3Si)_2NH$ gave pentacoordinated chlorosilanes RSO_2-Pro-N(Me)CH_2SiMe_2Cl with an organosulfonyl group (R = Me, Ph, 4-ClC_6H_4, 4-BrC_6H_4, 4-MeC_6H_4, and 4-$O_2NC_6H_4$) attached to the proline nitrogen atom. An alternative method for the preparation of these compounds comprises the cyclosilylmethylation of proline methylamide by dimethylchloromethylchlorosilane to give the previously unreported heterocyclic 2-sila-5-piperazinone system in the first step. The bicyclic silacyclane synthesized is 2-sila-5-piperazinone condensed with a proline residue. The action of sulfonyl chlorides RSO_2Cl leads to cleavage of the sila ring Si–N bond to give the desired chlorosilanes. The hydrolysis of these products, depending on the reaction conditions, gives either silyloxonium chlorides [RSO_2-Pro-N(Me)$CH_2SiMe_2OH_2$]Cl or disiloxanes [RSO_2-Pro-N(Me)CH_2SiMe_2]$_2$O. X-ray diffraction structural analysis showed that the silicon atom in the chlorides and silyloxonium chlorides is pentacoordinated due to an intramolecular O→Si bond and has distorted trigonal-bipyrimidal configuration. ^{29}Si NMR spectroscopy showed that the disiloxanes and bicyclic sila-5-piperazinone have a tetracoordinated silicon atom.

Keywords: silacyclanes, pentacoordinated silicon compounds, X-ray structural analysis, synthesis.

*Dedicated to the shining memory of our friend, Edmunds Lukevics, whom we knew, appreciated, and loved, a bright, energetic, multifaceted personality, a scientist with a capital S, brilliant leader, highly erudite chemist, who made a definitive contribution to the creation and development of a new area in silicon chemistry, namely, silicon bioorganic chemistry.

**To whom correspondence should be addressed, e-mail: alex@xrlab.ineos.ac.ru, baukov@rgmu.ru.

[1]Russian State Medical University, 1 Ostrovityanova St, Moscow 117997, Russia.
[2]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilova St. , Moscow 119991, Russia.
[3]Open University, Walton Hall, Milton Keynes, MK7 6AA, Great Britain; e-mail: a.bassindale@open.ac.uk.

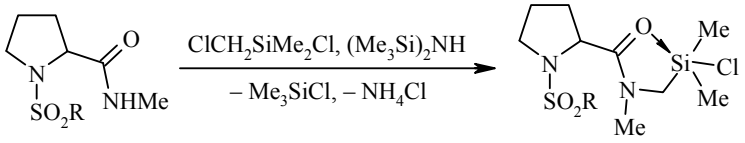
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1869-1890, December, 2011. Original article submitted June 28, 2011.

Pentacoordinated *C,O*-chelates containing amidomethyl and related bidentate monoanionic ligands (LCH_2), which are typical representatives of silicon compounds with nonstandard coordination, have been classified as hypercoordination complexes. Such complexes have been studied rather extensively [1-4]. The strength of the intramolecular O→Si coordination bond in these compounds varies in a rather broad range depending on the nature of the monodentate ligands at the silicon atom and substituents in the five-membered chelate ring [1-11]. Investigation of the structure features of pentacoordinated *C,O*-chelates with the SiC_3OX coordination unit (X = Hal, OAlk, OAr, ½O, and Otf) [5, 10, 12-17] allows using these compounds as models for studying hypervalence problem [1, 18, 19] and modeling pathways for S_N reactions at the silicon atom [1-5, 7-10, 20, 21].

Chlorosilanes, especially monochlorosilanes of LCH_2SiMe_2Cl type occupy an important place among *C,O*-chelate complexes. Rather efficient methods have been developed for the preparation of such monochlorosilanes [2, 12-17]. Furthermore, the synthesis of other derivatives of pentacoordinated silicon is carried out starting from monochlorosilanes. At present, the Cambridge Crystallographic Data Center [22] has information on about 50 neutral and ionic pentacoordinated *C,O*-mono- and bichelate silicon complexes with amidomethyl and related ligands, 20 of which are chlorosilanes.

Nevertheless, we should note that no *C,O*-chelates with amino acid fragments within the substituent at the amide carbon atom have been reported among the various types of pentacoordinated chlorosilanes known up to date. In the present communication, data are given on the synthesis and chemical properties of pentacoordinated chlorosilanes RSO_2-Pro-N(Me)CH_2SiMe_2Cl with an organosulfonyl group attached to the proline nitrogen atom as well as X-ray structural analysis data for these compounds. The products of the partial hydrolysis of these proline derivatives, namely silyloxonium chlorides [RSO_2-Pro-N(Me)$CH_2SiMe_2OH_2$]Cl are also reported.

We have used the direct *N*-dimethylchlorosilylmethylation of amides and lactams by the $ClCH_2SiMe_2Cl$–$(Me_3Si)_2NH$ system under thermodynamic control conditions for the synthesis of the desired *N*-methyl-*N*-(dimethylchlorosilylmethyl)-*N*'-organosulfonylprolinamides [17]. Such reactions with 2-amino acid derivatives, with the exception of 2,5-piperazinedione [23], have not yet been examined.



1a,f, (*S*)-**1b–e** **2a,f,** (*S*)-**2b–e**

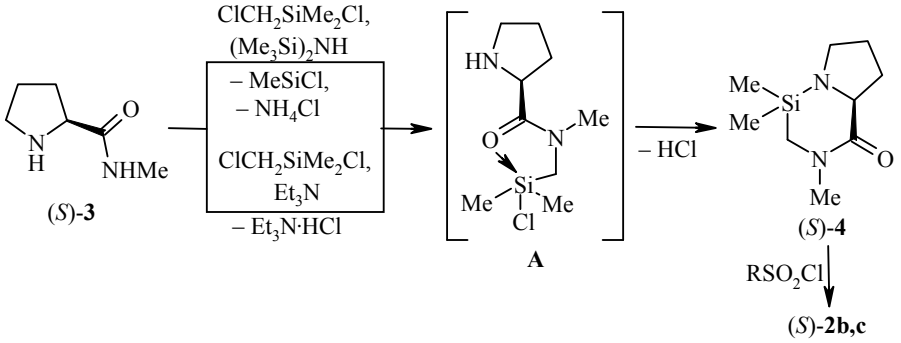
a R = Me, **b** R = Ph, **c** R = 4-MeC_6H_4, **d** R = 4-ClC_6H_4, **e** R = 4-BrC_6H_4, **f** R = 4-$O_2NC_6H_4$

IR monitoring of the course of *N*-methyl-*N*'-(organosulfonyl)prolinamides **1a-f** reactions with $ClCH_2SiMe_2Cl$ in the presence of $(Me_3Si)_2NH$ showed that the reaction of these compounds upon refluxing in benzene or toluene for 7-14 h when the ratio of the amide and $ClCH_2SiMe_2Cl$ was 1:1 leads to the formation of a mixture of starting amide **1** ($\nu_{(NCO)}$ ~ 1680 cm^{-1}) and chloride **2** ($\nu_{(NCO)}$ ~ 1605 cm^{-1}). Chlorosilanes **2a-f** were isolated preparatively using an amide to $ClCH_2SiMe_2Cl$ ratio equal to 1:2. The reaction of methylamide (*S*)-**1c** with $ClCH_2SiMe_2Cl$ was also carried out in the presence of Et_3N according to Hillyard et al. [13]. IR spectral monitoring of the course of this reaction showed that it proceeds over 3 h in benzene at reflux with the methylamide to $ClCH_2SiMe_2Cl$ ratio equal to 1:1. However, the yield of compound (*S*)-**2c** was lower than when the $ClCH_2SiMe_2Cl$–$(Me_3Si)_2NH$ system was used. Retention of configuration in the case of enantiomers of proline derivatives was confirmed by X-ray structural analysis of the monocrystals.

The composition and structure of hygroscopic chlorosilanes **2**, which are readily hydrolyzed even upon brief contact with the air, were established by elemental analysis (except compounds (*S*)-**2b** and (*S*)-**2f**), IR ^1H, ^{13}C, and ^{29}Si NMR spectroscopy (for compound (*S*)-**2c**), and X-ray structural analysis.

The low-frequency shift of the absorption band corresponding to the NCO fragment in the IR spectra of chlorosilanes **2** (to ~1605 cm^{-1}) relative to starting methylamides **1** and the presence of a second, less intense absorption band at ~1510 cm^{-1} indicate the (O→Si)-chelate structure of chlorosilanes **2** [15].

We have proposed still another pathway to *C,O*-chelates of type **2** realized for (*S*)-proline methylamide ((*S*)-**3**), which, in contrast to prolinamides **1**, have a free proline NH group. The silylmethylation of amide (*S*)-**3** by the $ClCH_2SiMe_2Cl$–$(Me_3Si)_2NH$ system or its treatment with $ClCH_2SiMe_2Cl$ in the presence of Et_3N led to previously unreported bicyclic silacyclane (*S*)-**4**. We may assume that the product of *N*-dimethylchlorosilylmethylation at the amide nitrogen atom, chlorosilane **A** (or/and its *N*'-TMS derivative using hexamethyldisilazane) is initially formed in these reactions and then undergoes thermal decomposition with the loss of HCl (respectively, Me_3SiCl) during fractionation, leading to the desired silacyclane (*S*)-**4**.



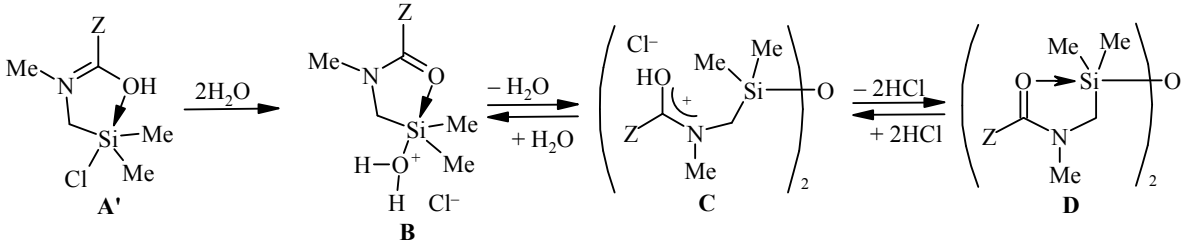
The IR spectrum of silacyclane (*S*)-**4** features a stretching vibrational band for the NCO group at ~1640 cm^{-1}, while its ^{29}Si NMR spectrum shows a silicon chemical shift (~4 ppm) typical for the tetracoordinated silicon atom in a comparable environment [4, 24-26].

The subsequent reaction of silacyclane (*S*)-**4** with sulfonyl chlorides led to (O→Si)-chelate chlorosilanes (*S*)-**2b,c** in yields comparable to those for previously prepared derivatives **2**.

We have already noted the high tendency of chlorosilanes **2** to undergo hydrolysis, which is markedly greater than for previously reported *C,O*-chelate pentacoordinated chlorosilanes [15, 28]. Thus, recrystallization in the air led to the formation of silyloxonium chlorides $[RSO_2$-Pro-N(Me)$CH_2SiMe_2OH_2]Cl$ **5a-f**. The general sequence of transformations presented below has been proposed for describing the formation of various compounds in the hydrolysis of pentacoordinated *C,O*-chelate chlorosilanes **A'** on the basis of the structures established for the intermediate and final hydrolysis products [25, 28].

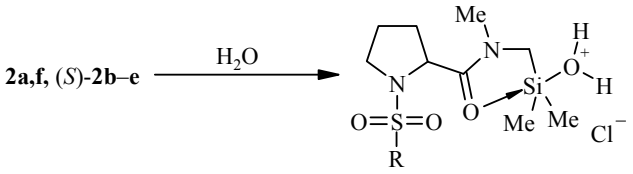
The first step of hydrolysis is the formation of a silyloxonium chloride (silanol hydrochloride) **B**, which loses water to give protonated disiloxane **C**. The loss of HCl (generally occurring upon the addition of an HCl acceptor) leads to the conversion of protonated disiloxane **C** into disiloxane **D**.

Some time after dissolving chlorosilanes **2** in $CDCl_3$, the ^1H NMR spectrum of this solution shows a broad signal at 6-8 ppm, which we assigned to the $–OH_2^+$ group. The C=O group signal in the ^{13}C NMR spectra of these compounds at 170-172 ppm is much broadened, which makes its precise observation impossible in most cases.



Z = *N*-(organosulphonyl)proline residue

Taking account of the upfield position of the signal in the ^{29}Si NMR spectrum (from -33 to -36 ppm), this data, in our opinion, indicate the formation of the products of the first step in the hydrolysis of chlorosilanes **2**, namely, silyloxonium chlorides **5**, under these conditions.

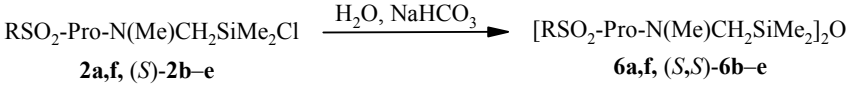


5a,f, (*S*)-**5b–e**

The chemical shift of the signal in the ^{29}Si NMR spectra (from -33 to -36 ppm, in $CDCl_3$) indicates a pentacoordinated state for silicon in solutions of chlorosilanes **2**, which corresponds to the shift for *C,O*-chelate pentacoordinated monochlorosilanes with similar structure [4, 26]. We have found using the ^{29}Si NMR CP/MAS method for complexes **5a**, **5f**, and (*S*)-**5c** that silyloxonium chlorides **5** in the solid phase, as should have been expected, have an even stronger upfield silicon signal shift (-40.2, -42.2, and -43.4, respectively).

We established the nature of the O→Si coordination interaction in silyloxonium chlorides **5** in solution on the basis of the "coordination contribution" values, which permit to evaluate this interaction by using the difference in the chemical shifts between the pentacoordinated complex and a model compound containing a tetracoordinated silicon atom: $-\Delta\delta = \delta Si(V) - \delta Si(IV)$ [4, 26, 27]. Me_3SiCl ($\delta Si(IV)$ 29.9 ppm) was taken as the model compound. Comparison of the calculated values of $-\Delta\delta$ for complexes **5a**, (*S*)-**5b-e**, and **5f** (62.7, 63.4, 63.9, 62.9, 65.9, and 66.7 ppm, respectively) with the analogous values for *C,O*-chelate *N*-(monochlorosilylmethyl)amides with a pentacoordinated silicon atom (65-75 ppm) [4, 27] indicates realization of an O→Si coordination interaction in solutions of silyloxonium chlorides **5**. The extent of this coordination interaction is similar to that in the case of the above-mentioned neutral *C,O*-chelate silylmethyl amide derivatives of type **A**.

The products of the final step of these transformations, namely, disilyloxanes **6**, were obtained by the hydrolysis of monochlorosilanes **2** in the presence of $NaHCO_3$ as a base.



2a,f, (*S*)-**2b–e** **6a,f,** (*S,S*)-**6b–e**

The composition and structure of the obtained disiloxanes **6a-f** were established using elemental analysis (except for (*S,S*)-**6b** and **6f**) and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy as well as infrared spectroscopy. The IR spectra of disiloxanes **6** showed a strong absorption band for the free amide group at 1650 cm^{-1}. The signal of the tetracoordinated silicon atom in the ^{29}Si NMR spectra appeared in the narrow region (4-5 ppm) characteristic for disiloxanes [4, 29].

We have found that disiloxanes **6** readily react with electrophilic agents. For example, the reaction of compounds (*S,S*)-**6c** and **6f** with $SOCl_2$ proceeds readily even at room temperature and leads to the formation of chlorosilanes (*S*)-**2c** and **2f**, respectively, in high yield. The synthesis of these chlorosilans by other means was described above.

The structures of chlorosilanes **2a-f** and silyloxonium chlorides **5a,c,d,f** were established by X-ray structural analysis. The silicon atom in all these structures has distorted trigonal-bipyramidal (TBP) geometry. The deviation of the silicon atom from the plane of the equatorial atoms is in the range 0.01-0.08 Å (Tables 1 and 2, Figs. 1-10). Thus, in the framework of the structural correlation method, the geometry of the silicon atom coordination unit corresponds to a transition state of S_N2 reactions at a tetrahedral silicon atom.

TABLE 1. Bond Lengths (*l*) in the Silicon Coordination Polyhedron and Amide Fragment, Valence Angle (ω) O(1)-Si(1)-Cl(1) and Deviation of the Silicon Atom from the Plane (Δ_{Si}) of the Equatorial Substituents in Compounds **2a-f**

Compound	*l*, Å						ω, deg	Δ_{Si}, Å*
	Si(1)–Cl(1)	Si(1)–O(1)	Si(1)–$Me_{av.}$	Si(1)–C(3)	C(4)–O(1)	C(4)–N(1)	O(1)–Si(1)–Cl(1)	
2a	2.353(1)	1.927(2)	1.859(3)	1.891(3)	1.266(3)	1.317(3)	170.35(6)	0.045(1)
(*S*)-**2b**	2.283(1)	2.007(2)	1.860(2)	1.891(2)	1.267(3)	1.311(3)	170.56(5)	0.070(1)
(*S*)-**2c**	2.312(1)	1.945(1)	1.860(2)	1.895(2)	1.273(2)	1.319(2)	172.20(4)	0.066(1)
(*S*)-**2d**	2.256(2)	1.983(2)	1.843(4)	1.891(4)	1.272(4)	1.308(4)	170.69(9)	0.066(1)
(*S*)-**2e**	2.271(1)	1.969(1)	1.858(2)	1.895(2)	1.265(2)	1.315(2)	170.69(5)	0.061(1)
2f	2.292(1)	1.971(1)	1.862(1)	1.900(1)	1.271(1)	1.317(1)	171.15(3)	0.081(1)

*A positive value for the deviation of the silicon atom from the plane of equatorial substituents indicates deviation toward the chlorine atom.

TABLE 2. Bond Lengths (*l*) in the Silicon Coordination Polyhedron and Amide Fragment, Valence Angle (ω) O(1W)-Si(1)-O(1) and Deviation of the Silicon Atom from the Plane (Δ_{Si}) of the Equatorial Substituents in Compounds **5a,c,d, f**

Compound	*l*, Å						ω, deg	Δ_{Si}, Å*
	Si(1)–O(1W)	Si(1)–O(1)	Si(1)–$Me_{av.}$	Si(1)–C(3)	C(4)–O(1)	C(4)–N(1)	O(1W)–Si(1)–O(1)	
5a	1.953(1)	1.907(1)	1.855(2)	1.886(1)	1.274(2)	1.314(2)	172.41(4)	0.006(1)
(*S*)-**5c**	1.925(3)	1.911(3)	1.863(4)	1.891(4)	1.261(4)	1.314(4)	167.43(15)	0.032(1)
(*S*)-**5d**	1.878(4)	1.961(3)	1.852(5)	1.869(5)	1.249(5)	1.321(6)	171.18(17)	0.038(1)
5f	1.914(1)	1.912(1)	1.857(1)	1.900(1)	1.274(1)	1.315(1)	170.56(4)	0.007(1)

*A positive value for the deviation of the silicon atom from the plane of equatorial substituents indicates deviation toward the oxonium oxygen atom.

In the framework of this approach, atom O(1) is considered as a nucleophile, while the exocyclic substituent (X = OH_2, Cl) is considered as a leaving group. The difference between the standard values of the Si–O (1.64 Å) and Si–Cl (2.07 Å) bond lengths [30] and the experimental values for compounds **2a-f** and **5a,c,d,f**, i.e., the relative lengthening of the bonds, is 0.23-0.31 Å (X = OH_2) and 0.20-0.29 Å (X = Cl). In turn, the length of the Si(1)–O(1) coordination bond varies in the range 1.91-2.01 Å. Analysis of the Si(1)–O(1) bonds lengths in chlorosilanes **2a-f** indicates the absence of a direct relationship between the lengths of these bonds and the electron-withdrawing (inductive) effect of the *N*-organosulfonylproline substituent. The shortest Si–O bond is found for compound **2a**, while the longest Si–O bond is found for (*S*)-**2b**. Weak intermolecular interactions in the crystal also apparently have a significant effect on this bond length in addition to the inductive effect in the structures of chlorosilanes **2a-f**.

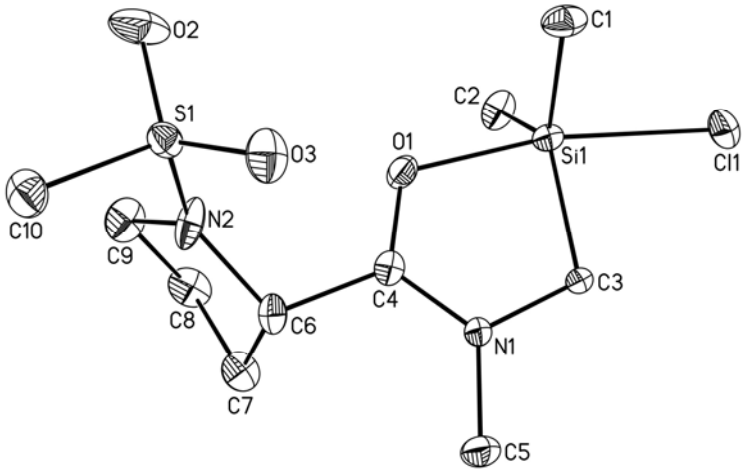


Fig. 1. General view of complex **2a**. The atoms are represented by 50%-probability thermal vibration ellipsoids. The hydrogen atoms are not shown.

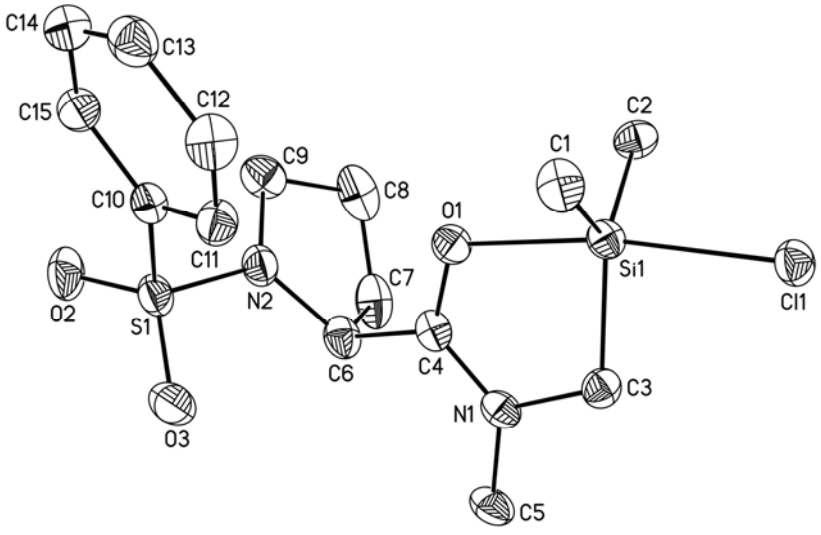


Fig. 2. General view of complex (*S*)-**2b**. The atoms are represented by 50%-probability thermal vibration ellipsoids. The hydrogen atoms are not shown.

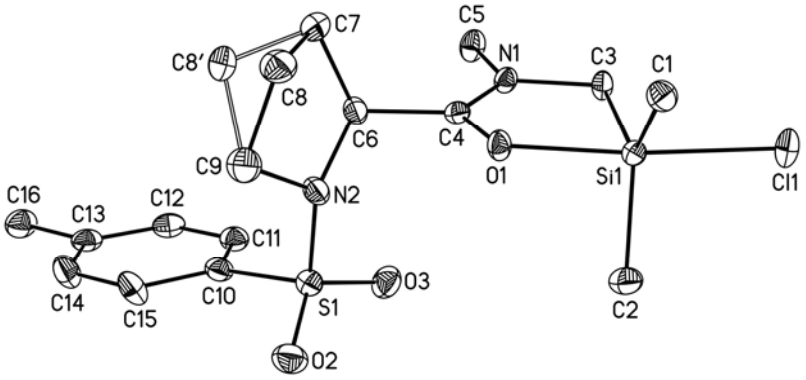


Fig. 3. General view of complex (*S*)-**2c**. The atoms are represented by 50%-probability thermal vibration ellipsoids. The hydrogen atoms are not shown.

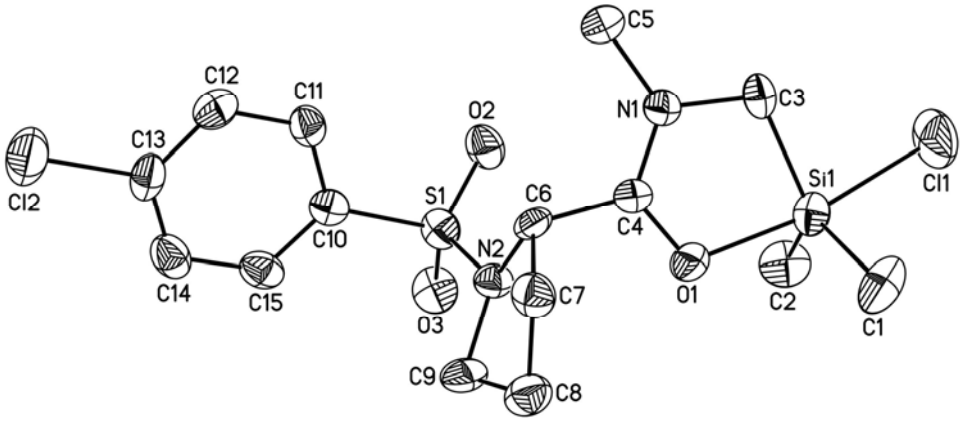


Fig. 4. General view of complex (*S*)-**2d**. The atoms are represented by 50%-probability thermal vibration ellipsoids. The hydrogen atoms are not shown.

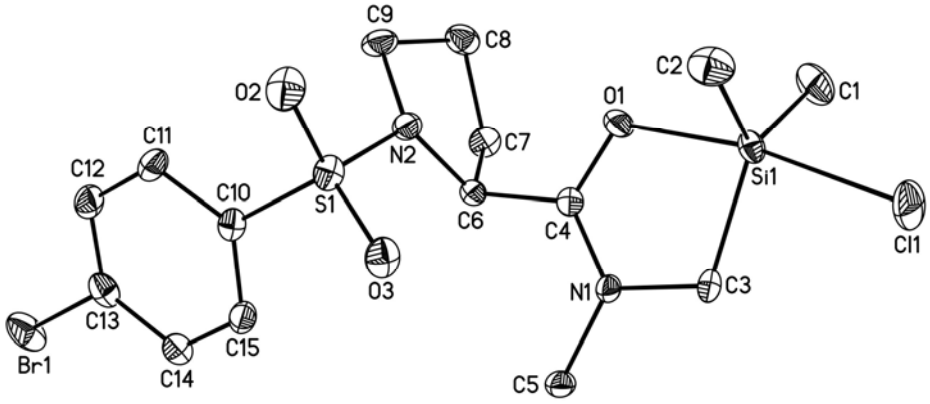


Fig. 5. General view of complex (*S*)-**2e**. The atoms are represented by 50%-probability thermal vibration ellipsoids. The hydrogen atoms are not shown.

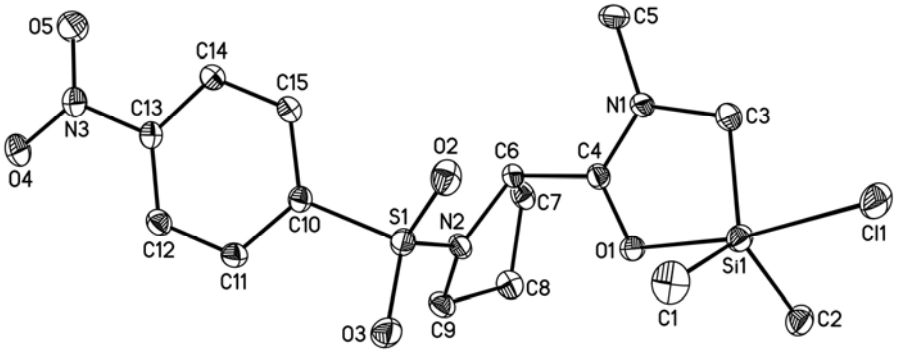


Fig. 6. General view of complex **2f**. The atoms are represented by 50%-probability thermal vibration ellipsoids. The hydrogen atoms are not shown.

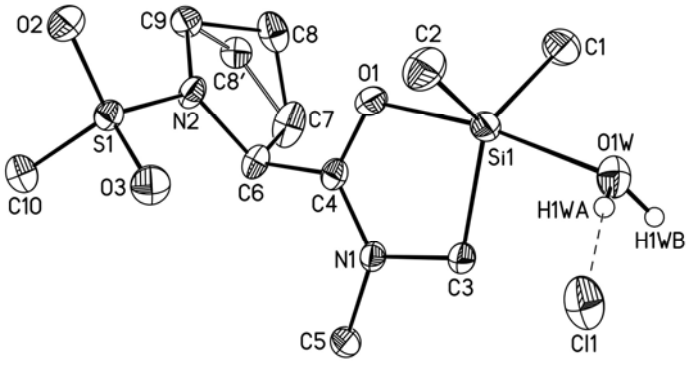


Fig. 7. General view of complex **5a**. The atoms are represented by 50%-probability thermal vibration ellipsoids. Only the hydrogen atoms of the oxonium fragment are shown.

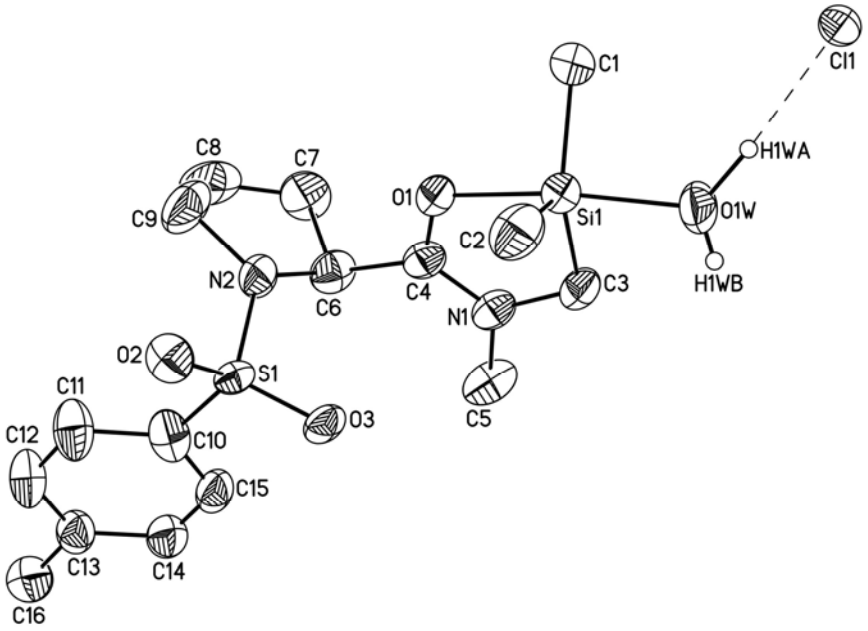


Fig. 8. General view of complex (*S*)-**5c**. The atoms are represented by 50%-probability thermal vibration ellipsoids. Only the hydrogen atoms of the oxonium fragment are shown.

Structures analogous to complexes **5a-d** were discussed in our previous work [28] for two salts with the (benzoylamido)methyl ligand. The lengths of the Si(1)–O(1) bonds in these salts are 0.03-0.08 Å greater than in **5a-d**, while the Si(1)–O(1) bond length varies only slightly (by 0.01-0.03 Å). This latter finding can be attributed to the effect of the crystal packing and observed differences in the hydrogen bond system. Indeed, hydrogen-bonded dimers are observed in the structure of compound **5f**, while a spiral along the crystallographic 6_5 axis is noted in the structure of compound (*S*)-**5c** due to O–H···Cl bonds. The interatomic O···Cl and H···Cl distances are 2.83-3.06 and 2.00-2.21 Å, respectively.

Coordination polyhedra may be seen in the Holmes formalism [31] as points on the potential energy surface of a hypothetical polytopic rearrangement. The silicon atom coordination polyhedron changes during the rearrangement from ideal TBP to an ideal square pyramid (SP). The general scheme for evaluating the of pseudorotation coordinate comprises 1) calculation of all the dihedral angles between the faces of the given polyhedron (nine angles), 2) calculation of the difference between the corresponding angles of the given polyhedron and the ideal TBP and SP polyhedron, 3) summation of the deviations for TBP and SP, and 4) plotting a curve in coordinates of the deviation from TBP vs. (100 – deviation from SP).

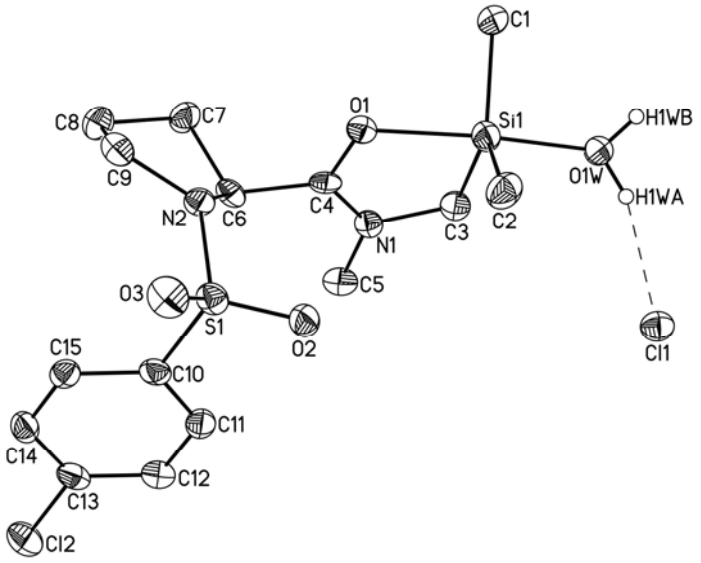


Fig. 9. General view of complex (*S*)-**5d**. The atoms are represented by 50%-probability thermal vibration ellipsoids. Only the hydrogen atoms of the oxonium fragment are shown.

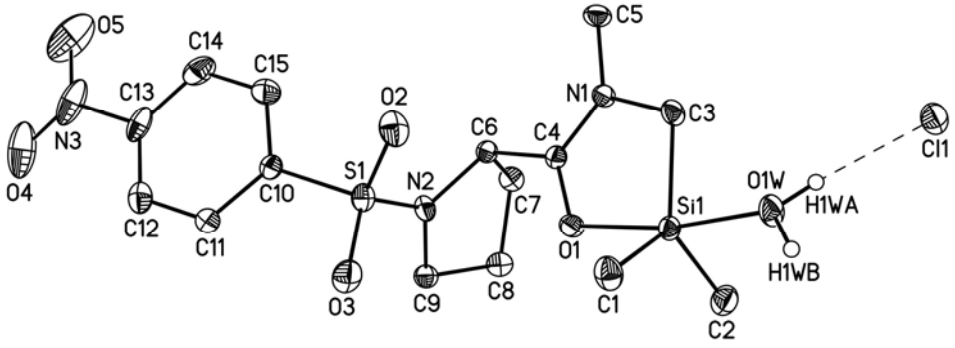


Fig. 10. General view of complex **5f**. The atoms are represented by 50%-probability thermal vibration ellipsoids. Only the hydrogen atoms of the oxonium fragment are shown.

TABLE 3. Deviations from TBP and SP for Complexes **2a-f, 5a,c,d,f**

Polyhedron	Deviation from TBP, %	100 – deviation from SP, %	Δ, %
2a_1*	15.10	14.89	0.20
2a_2*	13.38	11.74	1.64
2b	14.32	7.75	6.57
2c	10.21	9.90	0.31
2d	12.22	6.79	5.44
2e	12.06	7.00	5.06
2f	14.38	9.01	5.37
5a	10.98	7.87	3.12
5c	18.23	18.23	0.00
5d	10.15	10.15	0.00
5f	13.25	13.09	0.16

*Numbers 1 and 2 indicate two crystallographically independent silicon atoms.

A part of the pseudorotation trajectory may be described by examining a series of complexes with the same coordination polyhedron. The deviation values from TBP and SP are given in Table 3. A direct dependence of the deviations from TBP and SP is not observed for all the complexes studied. The difference (Δ) for chloride **2b** reaches 6.57%. It should be noted that the silicon coordination polyhedra of silyl chlorides (Δ_{max} 6.57%) deviate more significantly from the Berry coordinate than in the case of the corresponding silyloxonium polyhedra (Δ_{max} 3.12%). The deviation of the silicon atom polyhedra from ideal TBP lies in a rather narrow range (10-18%). Thus, complexes **2a,c, 5a,c,d,f** with small Δ describe the initial step of a Berry pseudorotation.

EXPERIMENTAL

The IR spectra were recorded in various solvents and in solid phase (using the incomplete internal reflection modulus) on a Bruker Tensor-27 spectrometer. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker Avance II 300 spectrometer at 300, 75, and 60 MHz, respectively and Bruker Avance II 600 spectrometer at 600, 151, and 119 MHz, respectively. Some of the ^{29}Si NMR spectra were recorded on a Jeol JNM-EX400 spectrometer at 80 MHz in a pulse mode using Fourier transformation, ^{2}H-stabilization of the resonance conditions, and TMS as internal standard. The ^{29}Si NMR spectra were recorded using the ^{1}H-^{29}Si HSQC pulse sequence provided in the mathematical package for the Bruker Avance II 600 spectrometer [32]. The ^{29}Si CP/MAS spectra in the solid state were recorded on a Jeol JNM-EX400 spectrometer.

Starting *N*-tosyl-(*S*)-proline monohydrate ((*S*)-**7c**) [33], racemic *N*-(4-nitrophenylsulfonyl)proline (**7f**), *N*-(4-chlorophenylsulfonyl)-(*S*)-proline ((*S*)-**7d**) [34], *N*-(4-bromophenylsulfonyl)-(*S*)-proline ((*S*)-**7e**) [35], and (*S*)-proline *N*-methylamide ((*S*)-**3**) [36] were prepared by reported procedures. The physicochemical properties of these proline derivatives corresponded to the literature data.

***N*-Mesylproline Ethyl Ester (7a).** A mixture of proline hydrochloride (75.8 g, 0.5 mol), absolute ethanol (200 ml), and Me_3SiCl (140.0 g, 1.3 mol) was heated at reflux for 9 h. After cooling to room temperature, the lower layer was separated and evaporated in vacuum. The residue was mixed with ice water (20 ml) and ether (100 ml). A solution of KOH (28.0 g, 0.5 mol) in water (20 ml) was added over 5 min with stirring and ice cooling followed by calcinated K_2CO_3 (250 g) until a thick, difficult to stir mass formed in the bottom layer. The ethereal layer was separated and the thick mass was washed with ether (2×50 ml). The combined ethereal layers were dried with calcinated $MgSO_4$. Ether was removed in vacuum and

TABLE 4. The Main Crystallographic Parameters for the Complexes **2a–f, 5a,c,d,f**

Parametrs	**2a**	(*S*)-**2b**	(*S*)-**2c**	(*S*)-**2d**	(*S*)-**2e**	**2f**	**5a**	(*S*)-**5c**	(*S*)-**5d**	**5f**
Empirical formula	$C_{10}H_{21}ClN_2O_3SSi$	$C_{15}H_{23}ClN_2O_3SSi$	$C_{16}H_{25}ClN_2O_3SSi$	$C_{15}H_{22}Cl_2N_2O_3SSi$	$C_{15}H_{22}BrClN_2O_3SSi$	$C_{15}H_{22}ClN_3O_5SSi$	$C_{10}H_{23}ClN_2O_4SSi$	$C_{16}H_{27}ClN_2O_4SSi$	$C_{15}H_{24}Cl_2N_2O_4SSi$	$C_{17}H_{27}ClN_4O$
Molecular weight	312.89	374.95	388.98	409.40	453.86	419.96	330.90	407.00	427.41	479.03
T, K	100	120	100	120	100	100	100	100	100	100
Crystal system	Monoclinic	Rhombic	Rhombic	Rhombic	Rhombic	Triclinic	Rhombic	Hexagonal	Rhombic	Triclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	P-1	Pccn	$P6_5$	$P2_12_12_1$	P-1
Z	8	4	4	4	4	2	8	6	4	2
a, Å	27.313(3)	8.9868(12)	8.9215(7)	6.1905(13)	6.2013(2)	7.6960(6)	17.5647(11)	20.236(2)	7.347(3)	7.2288(2)
b, Å	6.4692(7)	10.2203(14)	9.8213(7)	15.954(3)	16.0629(6)	10.5853(7)	22.2442(13)	20.236(2)	12.831(5)	12.6485(4)
c, Å	17.758(2)	19.500(3)	22.0035(17)	19.724(4)	19.7753(8)	12.4199(9)	8.3790(5)	8.9741(11)	20.613(8)	13.9453(4)
α, deg	90.00	90.00	90.00	90.00	90.00	98.187(2)	90.00	90.00	90.00	66.9260(10
β, deg	108.730(2)	90.00	90.00	90.00	90.00	103.452(2)	90.00	90.00	90.00	82.6030(10
γ, deg	90.00	90.00	90.00	90.00	90.00	91.136(2)	90.00	120.00	90.00	74.1310(10
V, $Å^3$	2971.6(6)	1791.0(4)	1928.0(3)	1948.1(7)	1969.83(13)	972.52(12)	3273.8(3)	3182.4(7)	1943.2(13)	1128.02(6)
d_{calc}, $g·cm^{-3}$	1.399	1.391	1.340	1.396	1.530	1.434	1.343	1.274	1.461	1.410
μ, cm^{-1}	4.8	4.12	3.85	5.18	24.05	3.96	4.44	3.56	5.26	3.56
F(000)	1328	792	824	856	928	440	1408	1296	896	504
$2\theta_{max}$, deg.	61.28	60.06	61.04	56.00	61.14	64.24	63.94	52.00	55.98	62.32
Number of measured reflections	38819	21007	25070	24230	26299	13858	44778	4165	15119	20933
Number of independent reflections	9079	5195	5873	4713	6032	6703	5669	4165	4705	7268
Number of reflections with $I > 2\sigma(I)$	8048	4439	5327	2590	5142	5554	4456	3921	2841	6033
Number of refined parameters	334	211	231	220	220	238	181	243	229	276
*R*1	0.0448	0.0392	0.0339	0.0498	0.0311	0.0322	0.0335	0.0533	0.0609	0.0355
w*R*2	0.1186	0.0809	0.0789	0.1027	0.0606	0.0863	0.0938	0.1498	0.1206	0.0963
GOOF	1.031	1.019	1.046	0.836	0.965	1.003	1.004	1.070	1.005	1.019
Residual electron density, $e·Å^{-3}$ (d_{min}/d_{max})	0.489/-0.669	0.345/-0.290	0.530/-0.359	0.530/-0.331	0.429/-0.372	0.490/-0.373	0.490/-0.283	0.458/-0.473	0.425/-0.452	0.621/-0.35

the residue was fractionated. Yield 50.0 g (70%); bp 78-80ºC (13 mm Hg) (lit. bp 82-83ºC (17 mm Hg) [38]). n_D^{20} 1.4484. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.15 (3H, t, ^3J = 7.3, $CH_2C\underline{H}_3$); 1.58-1.81 and 1.96-2.10 (4H, m, 3,4-CH_2); 2.40 (1H, br. s, NH); 2.75–2.85 and 2.95–3.05 (2H, m, 5-CH_2); 3.39–3.58 (1H, m, 2-CH); 4.10 (2H, q, ^3J = 7.3, $C\underline{H}_2CH_3$).

$MeSO_2Cl$ (5.73 g, 50 mmol) was added dropwise with stirring and cooling to a mixture of the prepared proline ethyl ester (7.15 g, 50 mmol) and Et_3N (5.05 g, 50 mmol) in ether (40 ml). The mixture was stirred for 2 h. The precipitate formed was filtered off and washed with 15 ml ether. The filtrate was evaporated in vacuum. Fractionation of the residue gave 8.30 g (72%) compound **7a**. Bp 176-177°C (9 mm Hg); mp 31-32°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1745 (C=O), 1360 and 1160 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.25 (3H, t, ^3J = 7.3, $CH_2C\underline{H}_3$); 1.85–2.11 and 2.14-2.37 (4H, m, 3,4-CH_2); 2.98 (3H, s, CH_3S); 3.31-3.61 (2H, m, 5-CH_2); 4.16 (2H, q, ^3J = 7.3, $C\underline{H}_2CH_3$); 4.37-4.51 (1H, m, 2-CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 8.9 ($CH_2\underline{C}H_3$); 19.4 (C-4); 25.7 (C-3); 32.7 (CH_3S); 43.0 (C-5); 55.3 ($\underline{C}H_2CH_3$); 56.2 (C-2); 173.8 (C=O). Found, %: C 43.41; H 6.98; N 6.31. $C_8H_{15}NO_4S$. Calculated, %: C 43.42; H 6.83; N 6.33.

***N*-Phenylsulfonyl-(*S*)-proline Ethyl Ester ((*S*)-7b).** $PhSO_2Cl$ (8.83 g, 50 mmol) was added dropwise with stirring and cooling with water to (*S*)-proline ethyl ester (7.15 g, 50 mmol) and Et_3N (5.05 g, 50 mmol) in ether (40 ml). The reaction mixture was stirred for 2 h. The precipitate formed was filtered off and washed with ether (15 ml). The filtrate was evaporated in vacuum and the oily residue was crystallized by trituration in heptane. Yield 12.56 g (89%); mp 53-55°C. $[\alpha]_D^{25}$ -87.0° (*c* 3.0, $CHCl_3$). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1750 (C=O), 1590 (Ph), 1360 and 1160 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.24 (3H, t, ^3J = 7.3, $CH_2C\underline{H}_3$); 1.60-2.17 (4H, m, 3,4-CH_2); 3.25–3.55 (2H, m, 5-CH_2); 4.11-4.20 (2H, m, $C\underline{H}_2CH_3$); 4.25-4.44 (1H, m, 2-CH); 7.45-7.67 (3H, m, H Ph); 7.87 (2H, d, ^3J = 7.7, H Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.0 ($CH_2\underline{C}H_3$); 24.5 (C-4); 30.8 (C-3); 48.3 (C-5); 60.4 ($\underline{C}H_2CH_3$); 61.2 (C-2); 127.3 (C-3,5 Ph); 128.9 (C-2,6 Ph); 132.7 (C-1 Ph); 138.3 (C-4 Ph); 171.9 (C=O). Found, %: C 55.23; H 6.08; N 5.01. $C_{13}H_{17}NO_4S$. Calculated, %: C 55.11; H 6.05; N 4.94.

***N*-Arylsulfonylproline Ethyl Esters 8c-f (General Method)**. Freshly distilled $SOCl_2$ (23.8 g, 0.2 mol) was added dropwise with vigorous stirring and cooling to -15°C to absolute ethanol (75 ml). Then, *N*-aryl-sulfonylproline **7c-f** (0.1 mol) was added in portions. The reaction mixture was slowly brought to reflux, heated at reflux for 1.5 h, and cooled to 0°C. The crystalline precipitate was filtered off, recrystallized from aqueous ethanol, and dried in the air.

***N*-Tosyl-(*S*)-proline Ethyl Ester ((*S*)-8c).** Yield 25.3 g (85%); mp 98-99°C (EtOH), $[\alpha]_D^{25}$ -93.1° (*c* 3.47, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1654 (s, C=O), 1600 (w, Ar), 1360 (s), 1160 (s, SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.27 (3H, t, ^3J = 7.3, $CH_2C\underline{H}_3$,); 1.67–2.14 (4H, m, 3,4-CH_2); 2.43 (3H, s, CH_3); 3.24–3.39 and 3.41–3.57 (2H, m, 5-CH_2); 4.08–4.24 (2H, m, $C\underline{H}_2CH_3$); 4.25–4.35 (1H, m, 2-CH); 7.34 (2H, d, ^3J = 8.3, H Ar); 7.75 (2H, d, ^3J = 8.3, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 8.8 ($CH_2\underline{C}H_3$); 16.3 ($\underline{C}H_3C_6H_4$); 19.4 (C-4); 25.7 (C-3); 43.1 (C-5); 55.3 ($\underline{C}H_2CH_3$); 56.0 (C-2); 127.1 (C-3,5 Ar); 128.3 (C-2,6 Ar); 144.2 (C-1 Ar); 156.4 (C-4 Ar); 173.8 (C=O). Found, %: C 56.47; H 6.33; N 4.61. $C_{14}H_{19}NO_4S$. Calculated, %: C 56.55; H 6.44; N 4.71.

***N*-(4-Chlorophenylsulfonyl)-(*S*)-proline Ethyl Ester ((*S*)-8d).** Yield 28.4 g (89%); mp 84-84.5°C (EtOH), $[\alpha]_D^{25}$ -96.9° (*c* 1.4, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1751 and 1569 (NCO), 1585 (Ar), 1346 and 1162 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.23 (3H, t, ^3J = 7.3, $CH_2C\underline{H}_3$); 1.68–2.12 (4H, m, 3,4-CH_2); 3.22-3.45 (2H, m, 5-CH_2); 4.03-4.19 (2H, m, $C\underline{H}_2CH_3$); 4.23–4.31 (1H, m, 2-CH); 7.45 (2H, d, ^3J = 8.7, H Ar); 7.78 (2H, d, ^3J = 8.7, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 8.9 ($CH_2\underline{C}H_3$); 19.4 (C-4); 25.7 (C-3); 43.0 (C-5); 55.3 ($\underline{C}H_2CH_3$); 56.2 (C-2); 127.1 (C-3,5 Ar); 128.3 (C-2,6 Ar); 144.2 (C-1 Ar); 156.4 (C-4 Ar); 173.8 (C=O). Found, %: C 49.22; H 5.13; N 4.35; S 9.91. $C_{13}H_{16}ClNO_4S$. Calculated, %: C 49.13; H 5.07; N 4.41; S 10.09.

***N*-(4-Bromophenylsulfonyl)-(*S*)-proline Ethyl Ester ((*S*)-8e).** Yield 33.7 g (93%); mp 71-72°C (EtOH), $[\alpha]_D^{25}$ -69.5° (*c* 2.72, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1753 (NCO), 1585 (Ar, NCO), 1346 and 1162 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.21 (3H, t, ^3J = 7.3, $CH_2C\underline{H}_3$); 1.68-2.18 (4H, m, 3,4-CH_2); 3.25-3.51 (2H, m, 5-CH_2); 4.03–4.19 (2H, m, $C\underline{H}_2CH_3$); 4.23-4.31 (1H, m, 2-CH); 7.63 (2H, d, ^3J = 8.7,

H Ar); 7.73 (2H, d, ^3J = 8.7, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.97 ($CH_2\underline{C}H_3$); 24.5 (C-4); 30.8 (C-3); 48.2 (C-5); 60.4 ($\underline{C}H_2CH_3$); 61.3 (C-2); 127.6 (C-4 Ar); 128.9 (C-3,5 Ar); 132.1 (C-2,6 Ar); 137.5 (C-1 Ar); 171.8 (C=O). Found, %: C 43.28; H 4.46; N 3.76; S 8.55. $C_{13}H_{16}BrNO_4S$. Calculated, %: C 43.10; H 4.45; N 3.87; S 8.85.

***N*-(4-Nitrophenylsulfonyl)proline Ethyl Ester (8f).** Yield 29.1 g (88%); mp 94-95°C (EtOH). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1747 (CO), 1600 (Ar), 1525 (NO_2), 1360 (NO_2, SO_2), 1160 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.26 (3H, t, ^3J = 7.3, $CH_2C\underline{H}_3$); 1.80-2.32 (4H, m, 3,4-CH_2); 3.46 (2H, t, ^3J = 6.2, 5-CH_2); 4.06-4.27 (2H, m, $C\underline{H}_2CH_3$); 4.38–4.52 (1H, m, 2-CH); 8.08 (2H, d, ^3J = 8.7, H Ar); 8.36 (2H, d, ^3J = 8.7, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 9.1 ($CH_2\underline{C}H_3$); 24.3 (C-4); 28.9 (C-3); 48.9 (C-5); 59.4 ($\underline{C}H_2CH_3$); 61.4 (C-2); 124.6 (C-3,5 Ar); 128.9 (C-2,6 Ar); 142.6 (C-1 Ar); 149.8 (C-4 Ar); 172.5 (C=O). Found, %: C 47.49; H 4.35; N 8.60. $C_{13}H_{16}N_2O_6S$. Calculated, %: C 47.55; H 4.19; N 8.53.

***N*'-(Arylsulfonyl)-*N*-methylprolinamides 1a-f (General Method).** A mixture of *N*-arylsulfonylproline ethyl ester **8a-f** (30 mmol) and 40% aqueous $MeNH_2$ (30 ml) was stirred at room temperature for seven days. The precipitate formed was filtered off and dried in the air.

***N*'-Mesyl-*N*-methylprolinamide (1a).** Yield 6.2 g (95%); mp 152-153°C (EtOH). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1670 and 1527 (NCO), 1360 and 1160 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.81-2.20 and 2.22-2.49 (4H, m, 3,4-CH_2); 2.83 (3H, d, ^3J = 4.5, CH_3N); 2.87 (3H, s, CH_3S); 3.29-3.42 and 3.44–3.63 (2H, m, 5-CH_2); 4.08-4.24 (1H, m, 2-CH); 6.76 (1H, br. s, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.8 (C-4); 26.5 (CH_3N); 30.8 (C-3); 34.6 (CH_3S); 49.6 (C-5); 62.5 (C-2); 171.8 (C=O). Found, %: C 40.88; H 6.81; N 13.50. $C_7H_{14}N_2O_3S$. Calculated, %: C 40.76; H 6.84; N 13.58.

***N*-Methyl-*N*'-phenylsulfonyl-(*S*)-prolinamide ((*S*)-1b).** Yield 6.6 g (82%); mp 130-131°C (EtOH), $[\alpha]_D^{25}$ -159.6° (*c* 2.8, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1643 and 1570 (NCO), 1360 and 1160 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.46-1.67 and 2.10-2.20 (4H, m, 3,4-CH_2); 2.84 (3H, d, ^3J = 4.8, CH_3N); 3.12-3.18 and 3.52-3.57 (2H, m, 5-CH_2); 4.05-4.09 (1H, m, 2-CH); 6.92 (1H, br. s, NH); 7.55 (2H, t, ^3J = 7.7, H Ar); 7.62 (1H, t, ^3J = 7.7, H Ar); 7.67 (2H, d, ^3J = 7.7, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.2 (C-4); 26.4 (CH_3N); 29.9 (C-3); 49.8 (C-5); 62.6 (C-2); 127.7 (C-3,5 Ar); 129.3 (C-2,6 Ar); 133.4 (C-1 Ar); 135.6 (C-4 Ar); 171.6 (C=O). Found, %: C 53.49; H 6.02; N 10.33. $C_{12}H_{16}N_2O_3S$. Calculated, %: C 53.71; H 6.01; N 10.44.

***N*-Methyl-*N*'-tosyl-(*S*)-prolinamide ((*S*)-1c).** Yield 8.5 g (96%); mp 123-125°C (EtOAc–hexane, 1:5) (lit. mp 122-124 °C [39]), $[\alpha]_D^{25}$ -168.6° (*c* 3.71, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1697 (Ar), 1654 and 1531 (NCO), 1360, 1160 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.14–1.83 and 2.04-2.28 (4H, m, 3,4-CH_2); 2.45 (3H, s, CH_3); 2.87 (3H, d, ^3J = 5.2, CH_3N); 3.07-3.26 and 3.47-3.66 (2H, m, 5-CH_2); 4.01-4.13 (1H, m, 2-CH); 6.95 (1H, br. s, NH); 7.36 (2H, d, ^3J = 8.3, H Ar); 7.72 (2H, d, ^3J = 8.3, H Ar).

***N*'-(4-Chlorophenylsulfonyl)-*N*-methyl-(*S*)-prolinamide ((*S*)-1d).** Yield 8.7 g (95%); mp 176-177°C (EtOH), $[\alpha]_D^{25}$ -157.4° (*c* 4.4, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1651 and 1568 (NCO), 1360 and 1160 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.45-1.75 and 2.10-2.22 (4H, m, 3,4-CH_2); 2.81 (3H, d, ^3J = 4.9, CH_3N); 3.09-3.18 and 3.45-3.57 (2H, m, 5-CH_2); 3.95-4.08 (1H, m, 2-CH); 6.80 (1H, br. s, NH); 7.48 (2H, d, ^3J = 8.8, H Ar); 7.72 (2H, d, ^3J = 8.8, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 19.1 (C-4); 21.4 (CH_3N); 24.9 (C-3); 44.7 (C-5); 57.4 (C-2); 127.1 (C-3,5 Ar); 128.3 (C-2,6 Ar); 142.1 (C-1 Ar); 154.8 (C-4 Ar); 174.6 (C=O). Found, %: C 47.50; H 4.98; N 9.30. $C_{12}H_{15}ClN_2O_3S$. Calculated, %: C 47.60; H 4.99; N 9.25.

***N*'-(4-Bromophenylsulfonyl)-*N*-methyl-(*S*)-prolinamide ((*S*)-1e).** Yield 9.9 g (95%); mp 151-153°C (EtOH), $[\alpha]_D^{25}$ -146.3° (*c* 4.3, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1650 (s) and 1534 (m, NCO), 1600 (m, Ar), 1360 (s) and 1160 (s, SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.45-1.80 and 2.10-2.25 (4H, m, 3,4-CH_2); 2.81 (3H, d, ^3J = 4.9, CH_3N); 3.05-3.21 and 3.45-3.61 (2H, m, 5-CH_2); 3.95-4.08 (1H, m, 2-CH); 6.87 (1H, br. s, NH); 7.69 (4H, m, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.4 (C-4); 26.4 (CH_3N); 30.2 (C-3); 50.1 (C-5); 62.8 (C-2); 128.8 (C-4 Ar); 129.3 (C-3,5 Ar); 132.8 (C-2,6 Ar); 134.8 (C-1 Ar); 171.4 (C=O). Found, %: C 41.60; H 4.39; N 8.15. $C_{12}H_{15}BrN_2O_3S$. Calculated, %: C 41.51; H 4.35; N 8.07.

***N*-Methyl-*N*'-(4-nitrophenylsulfonyl)prolinamide (1f).** Yield 8.7 g (92%); mp 172-174°C (EtOH). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1670 (NCO), 1600 (Ar), 1525 (NCO, NO_2), 1360 (NO_2, SO_2), 1160 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.48-2.00 and 2.15-2.34 (4H, m, 3,4-CH_2); 2.89 (3H, d, ^3J = 4.9, CH_3N); 3.09-3.28 and 3.53-3.72 (2H, m, 5-CH_2); 4.04-4.18 (1H, m, 2-CH); 6.76 (1H, br. s, NH); 8.05 (2H, d, ^3J = 8.7, H Ar); 8.42 (2H, d, ^3J = 8.7, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.3 (C-4); 26.5 (CH_3N); 30.3 (C-3); 49.9 (C-5); 62.7 (C-2); 124.6 (C-3,5 Ar); 129.0 (C-2,6 Ar); 141.6 (C-1 Ar); 150.5 (C-4 Ar); 170.9 (C=O). Found, %: C 46.03; H 4.80; N 13.42. $C_{12}H_{15}N_3O_5S$. Calculated, %: C 46.00; H 4.83; N 13.41.

***N*'-Mesyl-*N*-(dimethylchlorosilylmethyl)-*N*-methylprolinamide (2a).** A mixture of methylamide **1a** (2.17 g, 10 mmol), $(Me_3Si)_2NH$ (1.61 g, 10 mmol) and $Me_2Si(Cl)CH_2Cl$ (2.86 g, 20 mmol) in toluene (10 ml) was heated at reflux for 4 h and filtered while hot. The filtrate was cooled to room temperature. The crystalline precipitate was filtered off, washed with ether (5 ml), and dried. Yield 2.91 g (90%); mp 115-118°C (MeCN). IR spectrum (KBr), ν, cm^{-1}: 1607, 1508 (NCO), 1325 and 1143 (SO_2). Found, %: C 38.44; H 6.99; N 8.69. $C_{10}H_{21}ClN_2O_3SSi$. Calculated, %: C 38.39; H 6.76; N 8.95.

Crystallization of a portion of hygroscopic amide **2a** from benzene–acetonitrile without protection from a moist air gave (*N*'-mesyl-*N*-methylprolinamidomethyl)dimethylsilyloxonium chloride (**5a**); mp 88-90°C (C_6H_6–MeCN, 5:1). IR spectrum (KBr), ν, cm^{-1}: 1612, 1509 (NCO), 1325 and 1143 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.51 (6H, s, $Si(CH_3)_2$); 1.89-2.06 and 2.06-2.23 (4H, m, 3,4-CH_2); 2.84 (2H, m, NCH_2Si); 2.93 (3H, s, CH_3S); 3.15 (3H, s, CH_3N); 3.45-3.53 (2H, m, 5-CH_2); 4.79 (1H, m, 2-CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 6.7, 6.9 ($Si(CH_3)_2$); 24.9 (C-4); 30.8 (C-3); 37.6 (CH_3N); 38.6 (CH_3S); 41.1 (CH_2Si); 48.2 (C-5); 56.9 (C-2); 172.1 (C=O). ^{29}Si NMR spectrum ($CDCl_3$), δ, ppm: -32.8. ^{29}Si NMR spectrum CP/MAS, δ, ppm: -40.3. Found, %: C 36.21; H 6.98; N 8.59. $C_{10}H_{23}ClN_2O_4SSi$. Calculated, %: C 36.30; H 7.01; N 8.47.

***N*-(Dimethylchlorosilylmethyl)-*N*-methyl-*N*'-phenylsulfonyl-(*S*)-prolinamide ((*S*)-2b).** A. A mixture of compound (*S*)-**1b** (2.68 g, 10 mmol), $(Me_3Si)_2NH$ (1.61 g, 10 mmol), and $Me_2Si(Cl)CH_2Cl$ (2.68 g, 20 mmol) in toluene (10 ml) was refluxed for 4 h and filtered while hot. The filtrate was cooled to room temperature. The solvent was evaporated in vacuum. The oily residue was crystallized by trituration with ether (15 ml). The crystals were washed with ether (3 ml) and dried**.**, Yield 3.2 g (87%); mp 102-105 °C (C_6H_6–heptane, 1:1). IR spectrum (KBr), ν, cm^{-1}: 1606 (s), 1516 (w, NCO), 1344 (s) and 1155 (s, SO_2).

B. A mixture of silacyclane (*S*)-**4** (1.00 g, 5 mmol) and PhSO2Cl (0.88 g, 5 mmol) in absolute benzene (10 ml) was stirred for 8 h. The solvent was removed in vacuum. The oily residue crystallized upon standing. The crystals were washed with absolute ether. Yield 1.46 g (75%); mp 102-105°C (benzene). A mixed probe did not give a depressed melting point. IR spectrum (solid, $CHCl_3$), ν, cm^{-1}: 1606 (s), 1516 (w, NCO), 1344 (s) and 1155 (s, SO_2).

Crystallization of a part of hygroscopic amide (*S*)-**2b** from benzene–heptane mixture without protection from a moist air gave (O→Si)-chelate (*N*-methyl-*N*'-phenylsulfonyl-(*S*)-prolinamidomethyl)dimethylsilyl-oxonium chloride ((*S*)-**5b**); mp 83-85°C (C_6H_6–heptane, 1:1), $[\alpha]_D^{25}$ -115.4° (*c* 0.57, MeCN). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3100–2900 (OH, CH), 1609, 1508 (NCO), 1330 and 1155 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.52 (6H, br. s, $Si(CH_3)_2$); 1.78-2.23 (4H, m, 3,4-CH_2); 2.86 (2H, s, CH_2Si); 3.27 (3H, s, CH_3N); 3.26–3.49 (2H, m, 5-CH_2); 4.72 (1H, br. s, 2-CH); 7.48–7.73 (3H, m, H Ar); 7.56 (2H, d, ^3J = 7.7, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 6.3 ($Si(CH_3)_2$); 25.0 (C-4); 30.6 (C-3); 37.0 (CH_3N); 44.7 (CH_2Si); 48.3 (C-5); 55.5 (C-2); 127.2 (C-2,6 Ar); 128.3 (C-1 Ar); 129.2 (C-3,5 Ar); 133.1 (C-4 Ar). The carbon atom signal for the C=O group is not observed due to extensive broadening. ^{29}Si NMR spectrum ($CDCl_3$), δ, ppm: -33.5. Found, %: C 46.04; H 6.41; N 6.96. $C_{15}H_{25}ClN_2O_4SSi$. Calculated, %: C 45.85; H 6.41; N 7.13.

***N*-(Dimethylchlorosilylmethyl)-*N*-methyl-*N*'-tosyl-(*S*)-prolinamide ((*S*)-2c).** A. A mixture of methylamide (*S*)-**1c** (2.80 g, 10 mmol), $(Me_3Si)_2NH$ (1.61 g, 10 mmol), $Me_2Si(Cl)CH_2Cl$ (2.86 g, 20 mmol) in toluene (15 ml) was refluxed for 8 h. The hot reaction mixture was filtered and the filtrate was cooled to room temperature. The solvent was evaporated in vacuum. The oily residue was recrystallized by stirring with ether. The crystals were washed with ether (3 ml) and dried. Yield 3.4 g (88%); mp 100-102°C (C_6H_6). IR spectrum (KBr), ν, cm^{-1}: 1608, 1510 (NCO), 1347 and 1156 (SO_2). ^1H NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 0.90 and

0.91 (6H, two s, $Si(CH_3)_2$); 1.28-1.73 (4H, m, 3,4-CH_2); 2.11 (3H, s, CH_3); 2.63 (3H, s, CH_3N); 2.75 (2H, q, ^2J = 12.4, CH_2Si); 3.17-3.28 (2H, m, 5-CH_2); 4.45-4.49 (1H, m, 2-CH); 7.07 (2H, d, ^3J = 8.1, H Ar); 7.82 (2H, d, ^3J = 8.1, H Ar). ^{13}C NMR spectrum (C_6D_6), δ, ppm: 8.0 ($Si(CH_3)_2$); 21.6 ($\underline{C}H_3C_6H_4$); 25.4 (C-4); 30.7 (C-3); 36.6 (CH_3N); 45.7 (CH_2Si); 48.8 (C-5); 56.0 (C-2); 128.0 (C-2,6 Ar); 130.4 (C-3,5 Ar); 136.7 (C-1 Ar); 144.4 (C-4 Ar); 174.7 (C=O). ^{29}Si NMR spectrum (C_6D_6), δ, ppm: -36.8. Found, %: C 49.17; H 6.55; N 6.98. $C_{16}H_{25}ClN_2O_3SSi$. Calculated, %: C 49.40; H 6.48; N 7.20.

B. $Me_2Si(Cl)CH_2Cl$ (1.43 g, 10 mmol) in benzene (5 ml) was added dropwise with stirring to methylamide (*S*)-1c (2.80 g, 10 mmol) and Et3N (1.01 g, 10 mmol) in benzene. The reaction mixture was refluxed for 3 h and then cooled to 20°C. The precipitate formed was filtered off and washed with ether (15 ml). The solvent was evaporated in vacuum. The oily residue was crystallized upon stirring with ether. The crystals were washed with ether (2 ml) and recrystallized from benzene. Yield 2.5 g (65%); mp 100–102°C. IR spectrum (KBr), ν, cm^{-1}: 1608, 1510 (NCO), 1347 and 1156 (SO_2).

C. A mixture of silacyclane (*S*)-**4** (1.00 g, 5 mmol) and *p*-toluenesulfonyl chloride (0.96 g. 5 mmol) in absolute benzene (10 ml) was stirred for 8 h. The solvent was evaporated in vacuum. The oily residue was crystallized by stirring in ether. The crystals were washed with absolute ether. Yield 1.6 g (81%). IR spectrum (KBr), ν, cm^{-1}: 1608, 1510 (NCO), 1347 and 1156 (SO_2).

D. $SOCl_2$ (0.178 g, 1.5 mmol) was added dropwise to a solution of disiloxane (*S,S*)-**6c** (0.720 g, 1.0 mmol) in benzene (5 ml) and stirred for 30 min. The reaction mixture was evaporated in vacuum. The oily residue was crystallized upon stirring in ether. The crystals were washed with ether (1 ml) and dried Yield 0.65 g (83%); mp 100-102°C (C_6H_6); mp of mixed probe 100-102°C.

Crystallization of crude chloride (*S*)-**2c** (0.78 g, 2 mmol) from *o*-xylene (3 ml) without protection from a moist air gave 0.75 g (92%) (*N*-methyl-*N*'-tosyl-(*S*)-prolinamidomethyl)dimethylsilyloxonium chloride ((*S*)-**5c**); mp 86-89°C (*o*-xylene), $[\alpha]_D^{25}$ -55.1° (*c* 1.48, $CHCl_3$). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3000–2800 (OH, CH), 1611, 1509 (NCO), 1351, 1158 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.50 (6H, s, $Si(CH_3)_2$); 1.76-1.98 and 2.04-2.21 (4H, m, 3,4-CH_2); 2.45 (3H, s, CH_3); 2.87 (2H, s, CH_2Si); 3.27 (3H, s, CH_3N); 3.36-3.50 (2H, m, 5-CH_2); 4.66-4.77 (1H, m, 2-CH); 7.33 (2H, d, ^3J = 8.5, H Ar); 7.73 (2H, d, ^3J = 8.5, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 5.0 ($Si(CH_3)_2$); 21.5 ($\underline{C}H_3C_6H_4$); 25.0 (C-4); 30.6 (C-3); 37.0 (CH_3N); 44.7 (CH_2Si); 48.3 (C-5); 55.5 (C-2); 127.3 (C-2,6 Ar); 128.3 (C-1 Ar); 129.8 (C-3,5 Ar); 135.4 (C-4 Ar). The carbon atom signal of the C=O group was not observed. ^{29}Si NMR spectrum ($CDCl_3$) δ, ppm: -34.0. ^{29}Si NMR spectrum CP/MAS, δ, ppm: -43.4. Found, %: C 47.93; H 6.65; N 6.44. $C_{16}H_{27}ClN_2O_4SSi$. Calculated, %: C 47.22; H 6.69; N 6.88.

***N*'-(4-Chlorophenylsulfonyl)-*N*-(dimethylchlorosilylmethyl)-*N*-methyl-(*S*)-prolinamide ((*S*)-2d)**. A mixture of methylamide (*S*)-**1d** (3.03 g, 10 mmol), $(Me_3Si)_2NH$ (1.61 g, 10 mmol), and $Me_2Si(Cl)CH_2Cl$ (2.86 g, 20 mmol) in toluene (15 ml) was refluxed for 5 h and filtered while hot. The filtrate was cooled to room temperature and the solvent was removed in vacuum. The oily residue was crystallized by stirring in ether. The crystals were filtered off, washed with ether (2 ml), and dried. Yield 3.3 g (80%); mp 89-93°C (C_6H_6–heptane, 1:1). IR spectrum (KBr), ν, cm^{-1}: 1605, 1500 (NCO), 1316 and 1152 (SO_2). Found, %: C 44.26; H 5.35; N 6.95; S 7.94. $C_{15}H_{22}Cl_2N_2O_3SSi$. Calculated, %: C 44.01; H 5.42; N 6.84; S 7.83.

Crystallization of hygroscopic amide (*S*)-**2d** (0.82 g, 2 mmol) from 1:1 benzene–heptane mixture (3 ml) without protection from a moist air gave 0.80 g (94%) (*N*-methyl-*N*'-chlorophenylsulfonyl-(*S*)-prolinamidomethyl)dimethylsilyloxonium chloride ((*S*)-**5d**); mp 126-128°C (C_6H_6–heptane, 1:1), $[\alpha]_D^{25}$ -22.2° (*c* 1.01, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 3000-2800 (OH, CH), 1610, 1501 (NCO), 1316 and 1152 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.50 (6H, s, $Si(CH_3)_2$); 1.76-1.95 and 2.00-2.20 (4H, m, 3,4 CH_2); 2.90 (2H, s, CH_2Si); 3.25 (3H, s, CH_3N); 3.40-3.55 (2H, m, 5-CH_2); 4.70 (1H, br. s, 2-CH); 7.45 (2H, d, ^3J = 8.5, H Ar); 7.79 (2H, d, ^3J = 8.5, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 3.9 ($Si(CH_3)_2$); 24.8 (C-4); 30.5 (C-3); 37.0 (CH_3N); 43.2 (CH_2Si); 48.2 (C-5); 55.8 (C-2); 128.5 (C-2,6 Ar); 129.4 (C-3,5 Ar); 136.6 (C-1 Ar); 139.4 (C-4 Ar); 173.7 (C=O). ^{29}Si NMR spectrum ($CDCl_3$) δ, ppm: -36.0. Found, %: C 42.28; H 5.54; N 6.30; S 7.41. $C_{15}H_{24}Cl_2N_2O_4SSi$. Calculated, %: C 42.15; H 5.66; N 6.55; S 7.50.

***N*'-(4-Bromophenylsulfonyl)-*N*-(dimethylchlorosilylmethyl)-*N*-methyl-(*S*)-prolinamde ((*S*)-2e).** A mixture of methylamide (*S*)-**1e** (3.47 g, 10 mmol), $(Me_3Si)_2NH$ (1.61 g, 10 mmol), and $Me_2Si(Cl)CH_2Cl$ (2.86 g, 20 mmol) in toluene (15 ml) was refluxed for 3 h and filtered while hot to remove the precipitate formed. The filtrate was cooled to room temperature. The crystalline precipitate was filtered off, washed with ether (5 ml), and dried. Yield 3.85 g (85%); mp 127-129°C (C_6H_6). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1605, 1572 (Ar), 1519 (NCO), 1344 and 1156 (SO_2). Found, %: C 39.85; H 4.91; N 6.06; S 7.15. $C_{15}H_{22}BrClN_2O_3SSi$. Calculated, %: C 39.70; H 4.89; N 6.17; S 7.07.

Crystallization of hygroscopic amide (*S*)-**2e** (0.91 g, 2 mmol) from benzene (3 ml) without protection from a moist air gave 0.9 g (95%) (*N*'-(4-bromophenylsulfonyl)-*N*-methyl-(*S*)-prolinamidomethyl)dimethylsilyloxonium chloride (*S*)-**5e**; mp 95-97°C (C_6H_6), $[\alpha]_D^{25}$ -12.4° (*c* 3.25, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 3000-2800 (OH, CH), 1609, 1571 (Ar), 1510 (NCO), 1344 and 1156 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.52, 0.58 (6H, two s, $Si(CH_3)_2$); 1.80-1.90 and 2.10-2.25 (4H, m, 3,4-CH_2); 2.82 (1H, d, ^2J = 14.8) and 2.92 (2H, d, ^2J = 14.8, CH_2Si); 3.27 (3H, s, CH_3N); 3.38–3.49 (2H, m, 5-CH_2); 4.78 (1H, br. s, 2-CH); 7.68 (2H, d, ^3J = 8.3, H Ar); 7.78 (2H, d, ^3J = 8.3, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 7.8 (br. s, $Si(CH_3)_2$); 25.0 (C-4); 30.6 (C-3); 37.8 (br. s, CH_3N); 40.5 (br. s, CH_2Si); 48.2 (C-5); 55.5 (C-2); 128.8 (C-2,6 Ar); 132.4 (C-3,5 Ar). The signals for C-1,4 Ar and the C=O group are not observed due to broadening. ^{29}Si NMR spectrum ($CDCl_3$), δ, ppm: -32.8. Found, %: C 38.44; H 5.19; N 6.07. $C_{15}H_{24}BrClN_2O_4SSi$. Calculated, %: C 38.18; H 5.13; N 5.94.

***N*-(Dimethylchlorosilylmethyl)-*N*-methyl-*N*'-(4-nitrophenylsulfonyl)prolinamide (2f).** A. A mixture of methylamide **1f** (3.12 g, 10 mmol), $(Me_3Si)_2NH$ (1.61 g, 10 mmol), and $Me_2Si(Cl)CH_2Cl$ (2.86 g, 20 mmol) in toluene (15 ml) was refluxed for 2 h. The filtrate was cooled to room temperature. The crystalline precipitate was filtered off, washed with ether (3 ml), and dried. Yield 3.99 g (95%); mp 84-88°C. IR spectrum (KBr), ν, cm^{-1}: 1606 (NCO), 1525 (NO_2, NCO), 1349 (NO_2, SO_2), 1160 (SO_2).

B. $SOCl_2$ (0.30 g, 2.5 mmol) was added dropwise with stirring to a solution of disiloxane **6f** (1.57 g, 2.0 mmol) in benzene (10 ml). The precipitate formed was filtered off and washed with absolute ether. Yield 1.5 g (90%); mp 84-88°C; mp of mixed probe 84-88°C. ^{29}Si NMR spectrum CP/MAS, δ, ppm: -43.3.

Crystallization of crude chloride **2f** (0.84 g, 2 mmol) from acetonitrile (3 ml) without protection from a moist air gave 0.91 g (95%) the acetonitrile monosolvate of [*N*-methyl-*N*'-(4-nitrophenylsulfonyl)prolinamidomethyl]dimethylsilyloxonium chloride (**5f**); mp 98-102°C (MeCN). IR spectrum (KBr), ν, cm^{-1}: 3000-2800 (OH, CH), 2260 (CN, MeCN), 1609 (NCO), 1527 (NO_2, NCO), 1348 (NO_2, SO_2), 1156 (SO_2). ^1H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): 0.42 (6H, s, $Si(CH_3)_2$); 1.68–2.15 (4H, m, 3,4-CH_2); 2.80 (2H, s, CH_2Si); 3.18 (3H, s, CH_3N); 3.33-3.49 (2H, m, 5-CH_2); 4.70 (1H, m, 2-CH); 8.05 (2H, d, ^3J = 8.8, H Ar); 8.37 (2H, d, ^3J = 8.8, H Ar). ^{13}C NMR spectrum (CD_3CN), δ, ppm: 1.4 ($Si(CH_3)_2$); 25.5 (C-4); 31.4 (C-3); 37.5 (CH_3N); 45.2 (CH_2Si); 49.7 (C-5); 57.5 (C-2); 125.6 (C-2,6 Ar); 128.2 (C-3,5 Ar); 129.6 (C-1 Ar); 137.5 (C-4 Ar); 171.2 (C=O). ^{29}Si NMR spectrum (CD_3CN), δ, ppm: -36.8. ^{29}Si NMR spectrum CP/MAS, δ, ppm: -42.2. Found, %: C 42.57; H 5.28; N 11.56. $C_{17}H_{27}ClN_4O_6SSi$. Calculated, %: C 42.62; H 5.68; N 11.70.

1,1,3,3-Tetramethyl-1,3-bis(*N*-methyl-*N*'-organosulfonylprolinamidomethyl)-1,3-disiloxanes 6a-f (General Method). A solution of $NaHCO_3$ (1.26 g, 15 mmol) in water (10 ml) was added with stirring to chloride **2** (10 mmol) in chloroform (10 ml) and stirred for 24 h. The organic layer was separated and the aqueous layer was extracted with chloroform (10 ml). The organic extract was evaporated in vacuum. The residue was crystallized by trituration with heptane (15 ml). The crystals were separated and dried.

1,3-Bis(*N*'-mesyl-*N*-methylprolinamidomethyl)-1,1,3,3-tetramethyl-1,3-disiloxane (6a). Yield 2.65 g (93%); mp 110-114°C (hexane). IR spectrum (KBr), ν, cm^{-1}: 1640 (NCO), 1311 and 1145 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.00-0.34 (12H, m, $2Si(CH_3)_2$); 1.77-2.38 (8H, m, two 3,4-CH_2); 2.88 (4H, s, $2CH_2Si$); 2.99 (6H, s, $2CH_3S$); 3.06 (6H, s, $2CH_3N$); 3.38-3.67 (4H, m, two 5-CH_2); 4.73–4.92 (2H, m, 2H-2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 0.6 ($Si(CH_3)_2$); 24.8 (C-4); 30.8 (C-3); 37.7 (CH_3N); 39.2 (CH_3S); 41.9 (CH_2Si); 47.8 (C-5); 58.9 (C-2); 170.6 (C=O). ^{29}Si NMR spectrum ($CDCl_3$) δ, ppm: 4.8. Found, %: C 42.21; H 7.32; N 9.99. $C_{20}H_{42}N_4O_7S_2Si_2$. Calculated, %: C 42.08; H 7.42; N 9.81.

1,1,3,3-Tetramethyl-1,3-bis(*N*-methyl-*N*'-phenylsulfonyl-(*S*)-prolinamidomethyl)-1,3-disiloxane ((*S*,*S*)-6b). Yield 3.3 g (95%), oil, n_D^{20} 1.5077, $[\alpha]_D^{25}$ -39.3° (*c* 1.57, $CHCl_3$). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1642 (NCO), 1571 and 1470 (Ar), 1348 and 1155 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.10-0.30 (12H, m, $2Si(CH_3)_2$); 1.77-2.18 (8H, m, two 3,4-CH_2); 2.78 (4H, s, $2CH_2Si$); 3.06 (6H, s, $2CH_3N$); 3.38-3.47 (4H, m, two 5-CH_2); 4.80-4.89 (2H, m, two 2-CH) 7.55 (4H, t, ^3J = 7.7, H Ar); 7.62 (2H, t, ^3J = 7.7, H Ar); 7.67 (4H, d, ^3J = 7.7, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 0.4 ($Si(CH_3)_2$); 24.8 (C-4); 30.8 (C-3); 37.7 (CH_3N); 41.9 (CH_2Si); 48.2 (C-5); 57.5 (C-2); 127.6 (C-2,6 Ar); 129.6 (C-3,5 Ar); 132.5 (C-1 Ar); 139.1 (C-4 Ar); 170.3 (C=O). ^{29}Si NMR spectrum ($CDCl_3$) δ, ppm: 4.8.

1,1,3,3-Tetramethyl-1,3-Bis(*N*-methyl-*N*'-tosyl-(*S*)-prolinamidomethyl)-1,3-disiloxane ((*S*,*S*)-6c). Yield 3.24 g (90%); mp 125-126°C (hexane), $[\alpha]_D^{25}$ -58.2° (*c* 2.16, $CHCl_3$). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1640 (NCO), 1600 and 1460 (Ar), 1336 and 1164 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.05-0.31 (12H, m, $2Si(CH_3)_2$); 1.63-2.19 (8H, m, two 3,4-CH_2); 2.41 (6H, s, $2C\underline{H}_3C_6H_4$); 2.81-2.98 (4H, m, $2CH_2Si$); 3.16 (6H, s, $2CH_3N$); 3.32-3.54 (4H, m, two 5-CH_2); 4.79 (2H, br. s, two 2-CH); 7.28 (4H, d, ^3J = 7.6, H Ar); 7.78 (4H, d, ^3J = 7.6, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 0.4 ($Si(CH_3)_2$); 21.6 ($\underline{C}H_3C_6H_4$); 25.0 (C-4); 30.8 (C-3); 37.9 (CH_3N); 42.0 (CH_2Si); 48.4 (C-5); 57.5 (C-2); 127.6 (C-2,6 Ar); 129.6 (C-3,5 Ar); 136.2 (C-1 Ar); 143.4 (C-4 Ar); 170.3 (C=O). ^{29}Si NMR spectrum ($CDCl_3$) δ, ppm: 4.8. Found, %: C 53.01; H 7.19; N 7.60; S 8.75. $C_{32}H_{50}N_4O_7S_2Si_2$. Calculated, %: C 53.15; H 6.97; N 7.75; S 8.87.

1,3-Bis[*N*'-(4-chlorophenylsulfonyl)-*N*-methyl-(*S*)-prolinamidomethyl]-1,1,3,3-tetramethyl-1,3-disiloxane ((*S*,*S*)-6d). Yield 3.55 g (93%); mp 120-124°C (heptane), $[\alpha]_D^{25}$ -10.6° (*c* 3.41, $CHCl_3$). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1649 and 1585 (NCO), 1470 (Ar), 1336 and 1164 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.10-0.25 (12H, m, $2Si(CH_3)_2$); 1.79–2.19 (8H, m, two 3,4-CH_2); 2.82–2.90 (4H, m, $2CH_2Si$); 3.12 (6H, s, $2CH_3N$); 3.32-3.48 (4H, m, two 5-CH_2); 4.84 (2H, br. s, two 2-CH); 7.44 (4H, d, ^3J = 7.6, H Ar); 7.85 (4H, d, ^3J = 7.6, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 0.5 ($Si(CH_3)_2$); 25.0 (C-4); 30.7 (C-3); 37.8 (CH_3N); 41.9 (CH_2Si); 48.1 (C-5); 57.8 (C-2); 129.0 (C-2,3,5,6 Ar); 137.9 (C-1 Ar); 139.0 (C-4 Ar); 170.0 (C=O). ^{29}Si NMR spectrum ($CDCl_3$) δ, ppm: 4.8. Found, %: C 47.28; H 5.93; N 7.47. $C_{30}H_{44}Cl_2N_4O_7S_2Si_2$. Calculated, %: C 47.17; H 5.81; N 7.33.

1,3-Bis[*N*'-(4-bromophenylsulfonyl)-*N*-methyl-(*S*)-prolinamidomethyl]-1,1,3,3-tetramethyl-1,3-disiloxane ((*S*,*S*)-6e). Yield 4 g (94%); mp 117-118°C (hexane), $[\alpha]_D^{25}$ +0.45° (*c* 2.66, $CHCl_3$). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1643 (NCO), 1573 (NCO), 1470 (Ar), 1348 and 1155 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.15-0.30 (12H, m, $2Si(CH_3)_2$); 1.81-2.19 (8H, m, two 3,4-CH_2); 2.82-2.94 (4H, m, $2CH_2Si$); 3.18 (6H, s, $2CH_3N$); 3.35-3.48 (4H, m, two 5-CH_2); 4.88 (2H, br. s, two 2-CH); 7.64 (4H, d, ^3J = 7.6, H Ar); 7.82 (4H, d, ^3J= 7.6, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 0.5 ($Si(CH_3)_2$); 24.8 (C-4); 30.9 (C-3); 37.8 (CH_3N); 42.2 (CH_2Si); 48.1 (C-5); 57.8 (C-2); 127.5 (C-1 Ar); 129.1 and 132.1 (C-2,3,5,6 Ar); 138.5 (C-4 Ar); 170.0 (C=O). ^{29}Si NMR spectrum ($CDCl_3$) δ, ppm: 3.9. Found, %: C 42.05; H 5.15; N 6.41. $C_{30}H_{44}Br_2N_4O_7S_2Si_2$. Calculated, %: C 42.25; H 5.20; N 6.57.

1,1,3,3-Tetramethyl-1,3-bis[*N*-methyl-*N*'-(4-nitrophenylsulfonyl)propylamidomethyl]-1,3-disiloxane (6f). Yield 3.8 g (96%); mp 141-146°C (heptane). IR spectrum (KBr), ν, cm^{-1}: 1647 (NCO), 1525 (NO_2), 1350 (NO_2, SO_2), 1160 (SO_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.03-0.33 (12H, m, $2Si(CH_3)_2$); 1.78-2.35 (8H, m, two 3,4-CH_2); 2.76-2.91 (4H, m, $2CH_2Si$); 3.13 (6H, s, $2CH_3N$); 3.29-3.45 and 3.49-3.67 (4H, m, two 5-CH_2); 4.94 (2H, br. s, two 2-CH); 8.12 (4H, d, ^3J = 4.2, H Ar); 8.34 (4H, d, ^3J = 4.2, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 0.6 ($Si(CH_3)_2$); 25.0 (C-4); 30.9 (C-3); 37.8 (CH_3N); 41.9 (CH_2Si); 48.2 (C-5); 58.5 (C-2); 124.0 (C-2,6 Ar); 128.9 (C-3,5 Ar); 145.5 (C-1 Ar); 150.0 (C-4 Ar); 170.0 (C=O). ^{29}Si NMR spectrum ($CDCl_3$) δ, ppm: 4.8.

2,2,4-Trimethyl-1,4-diaza-2-silabicyclo[4.3.0]nonan-5-one ((*S*)-4). A. $Me_2Si(Cl)CH_2Cl$ (15.7 g, 110 mmol) in absolute ether (10 ml) was added dropwise to a mixture of absolute ether (50 ml), methylamide (*S*)-**3** (12.8 g, 100 mmol) and abs. Et_3N (11.0 g, 110 mmol) and refluxed for 4 h. The precipitate formed was filtered off and the residue was fractionated. Yield 10 g (50%), a thick oil; bp 138-140°C (12 mm Hg). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1641 (NCO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.00-0.30 (6H, s, $Si(CH_3)_2$); 1.56-2.56 (4H, m, 7,8-CH_2); 2.75 (2H, s, CH_2Si); 2.98 (3H, s, CH_3N); 3.26-3.38 (2H, m, 9-CH_2); 3.55–3.65 (1H,

m, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 0.5 ($Si(CH_3)_2$); 26.5 (C-8); 30.8 (C-7); 37.0 (CH_3N); 41.6 (C-3); 47.9 (C-9); 58.1 (C-6); 173.2 (C=O). ^{29}Si NMR spectrum ($CDCl_3$) δ, ppm: 4.3. Found, %: C 54.20; H 9.22; N 14.00. $C_9H_{18}N_2OSi$. Calculated, %: C 54.50; H 9.15; N 14.12.

B. A mixture of methylamide (*S*)-**3** (12.80 g, 100 mmol) and $(Me_3Si)_2NH$ (24.15 g, 150 mmol) was refluxed for 6 h. Then, $Me_2Si(Cl)CH_2Cl$ (15.73 g, 110 mmol) and $(Me_3Si)_2NH$ (12.07 g, 75 mmol) were added and the mixture was refluxed for an additional 6 h. After cooling to room temperature, the mixture was evaporated in vacuum and the residue was fractionated. Yield 8.0 g (40%); bp 138–142°C (12 mm Hg), $[\alpha]_D^{25}$ -50.6° (*c* 4.57, CH_2Cl_2). The spectral data for the samples of (*S*)-**4** obtained by both procedures were identical.

X-ray Structural Analysis of 2a-f, 5a,s,d,f. Monocrystals for X-ray structural analysis were obtained by crystallization of samples of **2a** and **5f** from acetonitrile, (*S*)-**2b**, (*S*)-**2d**, and (*S*)-**5d** from 5:1 benzene-heptane mixture, silyl chlorides (*S*)-**2c,** and (*S*)-**2e** from benzene, silyloxonium chloride **5a** from 5:1 benzene–acetonitrile mixture, and (*S*)-**5c** from *o*-xylene. In the case of silyl chloride **2f**, crystals precipitated directly from the reaction mixture were used.

The major crystallographic data and refinement results for the 10 complexes analyzed are given in Table 4. The structures were solved by the direct method and refined anisotropically by the full-matrix method of least squares for the non-hydrogen atoms. The hydrogen atoms of the alkyl and aryl fragments were calculated from geometrical considerations and included in the refinement with equivalent thermal parameters dependent on the attached carbon atoms ($U_{eq}(H) = 1.2U_{eq}(C)$, $1.5U_{eq}(C_{Me})$). The hydrogen atoms in the oxonium fragments were revealed in the electron density Fourier difference maps. Their thermal parameters were refined analogously ($U_{eq}(H) = 1.5U_{eq}(O)$). All the calculations were carried out using the SHELTX-97 V.5.10 software package [37]. The atomic coordinates and their temperature parameters for compounds **2a-g, 5a,s,d,f** were deposited in the Cambridge Crystallographic Data Center (CCDC 833653-833662).

This work was carried out with the financial support of the Russian Foundation for Fundamental Investigations (projects Nos. 09-03-00669, 10-03-00824, and 11-03-00655) as part of the activities of the Russian State Medical University Scientific Educational Center.

REFERENCES

1. D. Kost and I. Kalikhman, in: Z. Rappoport and Y. Apeloig (editors), *The Chemistry of Organic Silicon Compounds*, Vol. 2, Part 1, J. Wiley, Chichester (1998), p. 1339.
2. M. G. Voronkov, V. A. Pestunovich, and Yu. I. Baukov, *Metalloorg. Khim.*, **4**, 1210 (1991).
3. C. Chuit, R. J. P. Corriu, C. Reyé, and J. C. Young, *Chem. Rev.*, **93**, 1371 (1993).
4. V. V. Negrebetsky and Yu. I. Baukov, *Izv. Akad. Nauk, Ser. Khim.*, **11**, 1912 (1997).
5. A. A. Macharashvili, V. E. Shklover, Yu. T. Struchkov, G. I. Oleneva, E. P. Kramarova, A. G. Shipov, and Yu. I. Baukov, *J. Chem. Soc., Chem. Commun.*, 683 (1988).
6. D. Kummer and S. H. Abdel Halim, *Z. Anorg. Allg. Chem.*, **622**, 57 (1996).
7. V. F. Sidorkin, V. V. Vladimirov, M. G. Voronkov, and V. A. Pestunovich, *J. Mol. Struct. (Theochem.)*, **228**, 1 (1991).
8. Yu. E. Ovchinnikov, A. A. Macharashvili, Yu. T. Struchkov, A. G. Shipov, and Yu. I. Baukov, *Zh. Strukt. Khim.*, **35**, 1 (1994).
9. A. R. Bassindale, M. Borbaruah, S. J. Glynn, D. J. Parker, and P. G. Taylor, *J. Organomet. Chem.*, **606**, 125 (2000).
10. A. R. Bassindale, D. J. Parker, P. G. Taylor, N. Auner, and B. Herrschaft, *J. Organomet. Chem.*, **667**, 66 (2003).
11. B. Gostevskii, G. Silbert, K. Adear, A. Sivaramakrishna, D. Stalke, S. Deuerlein, N. Kocher, M. G. Voronkov, I. Kalikhman, and D. Kost, *Organometallics*, **24**, 2913 (2005).

12. K. D. Onan, A. T. McPhail, C. H. Yoder, and R. W. Hillyard, *J. Chem. Soc., Chem. Commun.*, 209 (1978).
13. R. W. Hillyard, C. M. Ryan, and C. H. Yoder, *J. Organomet. Chem.*, **153**, 369 (1978).
14. C. H. Yoder, C. M. Ryan, G. F. Martin, and P. S. Ho, *J. Organomet. Chem.*, **190**, 1 (1980).
15. Yu. I. Baukov, E. P. Kramarova, A. G. Shipov, G. I. Oleneva, O. B. Artamkina, A. I. Albanov, M. G. Voronkov, and V. A. Pestunovich, *Zh. Obshch. Khim.*, **59**, 127 (1989).
16. V. V. Negrebetsky, P. G. Taylor, E. P. Kramarova, S. Yu. Bylikin, I. Yu. Belavin, A. G. Shipov, A. R. Bassindale, and Yu. I. Baukov, *J. Organomet. Chem.*, **691**, 3976 (2006).
17. A. G. Shipov, E. P. Kramarova, and Yu. I. Baukov, *Zh. Obshch. Khim.*, **64**, 1220 (1994).
18. V. F. Sidorkin, E. F. Belogolova, and V. A. Pestunovich, *J. Mol. Struct.*, **538**, 59 (2001).
19. V. A. Pestunovich, V. F. Sidorkin, and M. G. Voronkov, in: *Progress in Organosilicon Chemistry*, Gordon and Breach, New York (1995), p. 69.
20. A. R. Bassindale, M. Borbaruah, S. J. Glynn, D. J. Parker, and P. G. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2099 (1999).
21. A. R. Bassindale, S. J. Glynn, P. G. Taylor, N. Auner, and B. Herrschaft, *J. Organomet. Chem.*, **619**, 132 (2001).
22. Cambridge Structural Database (CSD), Release 2010.
23. A. O Mozzhukhin, M. Yu. Antipin, Yu. T. Struchkov, A. G. Shipov, E. P. Kramarova, and Yu. I. Baukov, *Metalloorg. Khim.*, **5**, 906 (1992).
24. I. D. Kalikhman, A. I. Albanov, O. B. Bannikova, L. I. Belousova, M. G. Voronkov, V. A. Pestunovich, A. G. Shipov, E. P. Kramarova, and Yu. I. Baukov, *J. Organomet. Chem.*, **361**, 147 (1989).
25. V. A. Pestunovich, S. V. Kirpichenko, N. F. Lazareva, A. I. Albanov, and M. G. Voronkov, *J. Organomet. Chem.*, **692**, 2160 (2007).
26. V. A. Pestunovich, *Author's Abstract of Chem. Sci. Doct. Diss.*, Irkutsk (1985).
27. V. V. Negrebetsky, S. N. Tandura, and Yu. I. Baukov, *Usp. Khim.*, **78**, 24 (2009).
28. A. A. Korlyukov, S. A. Pogozhikh, Yu. E. Ovchinnikov, K. A. Lyssenko, M. Yu. Antipin, A. G. Shipov, O. A. Zamyshlyaeva, E. P. Kramarova, Vad. V. Negrebetsky, I. P. Yakovlev, and Yu. I. Baukov, *J. Organom. Chem.*, **691**, 3962 (2006).
29. Vad. V. Negrebetsky, A. G. Shipov, E. P. Kramarova, V. V. Negrebetsky, and Yu. I. Baukov, *J. Organomet. Chem.*, **530**, 1 (1997).
30. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, S1 (1987).
31. R. R. Holmes and J. A. Deiters, *J. Am. Chem. Soc.*, **99**, 3318 (1977).
32. W. S. Brey, *Pulse Methods in 1D and 2D Liquid-Phase NMR*, Academic Press, New York (1988), p. 561.
34. N. Izumiya, *Bull. Chem. Soc. Japan*, **26**, 53 (1953).
34. J. De Ruiter, A. N. Brubaker, M. A. Garner, J. M. Barksdale, and C. A. Mayfield, *J. Pharm. Sci.*, **76**, 149 (1987).
35. R. Korukonda, N. Guan, J. T. Dalton, J. Liu, and I. O. Donkor, *J. Med. Chem.*, **49**, 5282 (2006).
36. J. K. Chang, H. Sievertsson, B. Currie, and K. Folkers, *J. Med. Chem.*, **14**, 484 (1971).
37. G. M. Sheldrick, *Acta Crystallogr.* **A64**, 112 (2008).
38. A. A. Potekhin, *Handbook of Properties of Organic Compounds* [in Russian], Khimiya, Leningrad (1984), p. 298.
39. R. R. Hill, S. A. Moore, and D. R. Roberts, *Photochem. Photobiol.*, **81**, 1439 (2005).