Si-Fluoro substituted quasisilatranes (N → Si) FYSi(OCH$_2$CH$_2$)$_2$NR

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ABSTRACT

The reaction of fluorosilanes XYSiF$_2$ (X = Y = F; X = F, Y = Ph; X = Ph, Y = Me) with diethanolamines and their *O*-trimethylsilyl derivatives affords novel Si-fluoro substituted quasisilatranes **3**, **5** and **9**. These compounds were characterized by the multinuclear NMR spectroscopy and X-ray diffraction analysis. Experimental and theoretically calculated electron density distribution functions in crystal structure of **9** have shown that the N → Si coordination bond corresponds to polar bond with pronounced ionic contribution. Calculated N → Si bond order in the compound **9** does not exceed 1/3 of the normal Si–N bond. A strong N → Si coordination bond exists in compounds **3**, **5** and **9** the length of which varies in the range 1.98–2.175 Å.

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1. Introduction

Silatranes XSi(OCH$_2$CH$_2$)$_3$N, pentacoordinate tricyclic silyl derivatives of triethanolamine, have been widely studied owing to the peculiarities of their electronic and molecular structure and wide range of biological activity that they possess [1a–e]. These compounds have the N → Si transannular bond the strength of which depends on the nature of X substituent [1e].

The formation of the monocyclic or bicyclic compounds with N → Si coordination bond from mono or dialkanolamines is appreciably affected by the substituent nature at the silicon and the nitrogen atoms [2a–d]. Thus, the intramolecular coordination in compounds R$_{4−n}$Si(OCH$_2$CH$_2$)$_n$NR′$_{3−n}$ (R′ = H, alkyl; n = 1, 2) is completely lacking when R – electron-donating Me groups [2c,3a,3b], while electron-withdrawing phenyl ligands (R = Ph, n = 2) at silicon favors sufficiently strong intramolecular N → Si bonding [4]. It has been also shown the pentacoordination at silicon in phenyldifluoro and trifluoro monocyclic compounds prepared by the transsilylation of phenyltrifluorosilane PhSiF$_3$ (**1**) or tetrafluorosilane SiF$_4$ (**2**) with *O*-trimethylsilyl derivatives of monoalkanolamines [5].

$$XSiF_3 + Me_3SiOCH_2CH_2NR^1R^2 \xrightarrow{-Me_3SiF}$$
1, 2
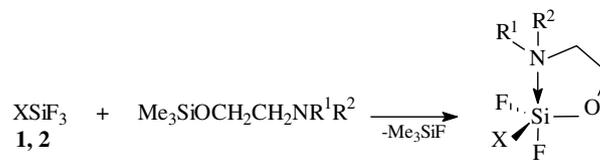
X = Ph (**1**); R^1 = R^2 = H; R^1 = H, R^2 = Me;
X = F (**2**); R^1 = R^2 = H; R^1 = H, R^2 = Me; R^1 = R^2 = Me.

We have recently found that the reaction of PhSiF$_3$ (**1**) with ethanolamine and its *N*-methyl or *N,N*-dimethyl derivatives is a convenient method for the synthesis of the related pentacoordinate fluoro complexes with N → Si coordination bond [6].

$$PhSiF_3 + HOCH_2CH_2NH_{2-n}Me_n \xrightarrow{-PhH}$$
1
n = 0-2
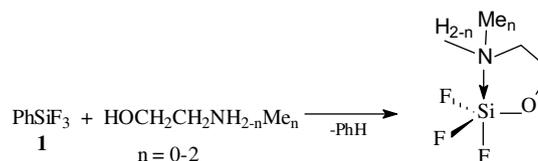
The obtained results prompted us to examine the potential of organylfluorosilanes in the preparation of the related hypervalent silicon compounds. It should be noted that in the above fluoro

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compounds N → Si intramolecular bonding was studied in the solutions and supported by the ^{19}F and ^{29}Si NMR data [5,6]. The structural investigations of bicyclic pentacoordinate derivatives of dialkanolamines are scare and mainly concerned aryl substituted compounds or spirochelates the silicon atom of which is connected with four oxygen atoms [2c]. No X-ray data are available for related compounds bearing a fluoro ligand at the silicon atom.

We report here the synthesis of new pentacoordinate bicyclic fluorosilanes derived from diethanolamine and its N-methyl derivative, their X-ray studies as well as N → Si chemical bonding nature.

2. Results and discussion

2.1. Synthesis

The reaction of PhSiF$_3$ (**1**) with diethanolamine (Scheme 1a) proceeds via the cleavage of the Ph–Si bond under mild conditions to afford a solid product the ^{19}F and ^{29}Si NMR data of which differ from those for pure compound **3**. The latter was obtained by treatment of O,O′-bissilylated diethanolamine with gaseous SiF$_4$ (**2**) in hexane (Scheme 1b). The product of the reaction (Scheme 1a) is found to be a 1:1 mixture of bicyclic pentacoordinate compound **3** and its hydrofluoride **4**. It is suggested by elemental analysis data which are averaged between those for compounds **3** and **4**. In the crude product compound **4** was identified by its typical [29]Si quartet at δ −127.2 ppm (J_{Si-F} = 208 Hz) which is in the range characteristic of related pentacoordinate silicon compounds [5]. A broadened ^{19}F signal (δ −117.4 ppm) was observed in the ^{19}F NMR spectrum of the reaction product supporting the **3** ⇄ **4** rapid equilibrium in DMSO-d_6 solution.

In contrast to the reaction (Scheme 1a), replacement of fluoro atoms takes place by treatment of PhSiF$_3$ with N-Me-diethanolamine or its bissilylated derivative resulting in pentacoordinate compound **5** (Scheme 2).

In a similar way, bicyclic compound **7** was prepared from diphenyldifluorosilane Ph$_2$SiF$_2$ (**6**) in 53% yield (Scheme 3).

Meanwhile, the cleavage of the Ph–Si bond in the initial silane is observed when the phenyl group is replaced by a methyl one (Scheme 4).

Note that the compound **9** is the first example of the related pentacoordinate compounds having an alkyl substituent at the silicon atom.
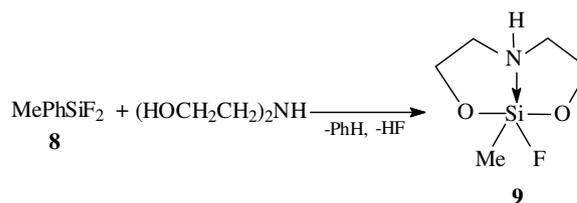
All compounds were isolated as air-sensitive crystals, insoluble in non-polar organic solvents and soluble in polar solvent such as DMF and DMSO only. The latter was used as the solvent for NMR studies.
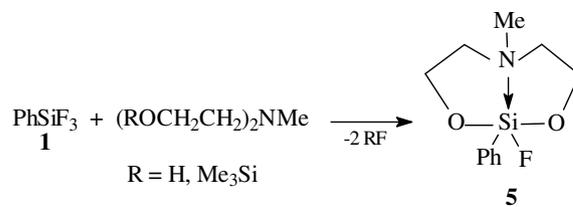
Scheme 2.
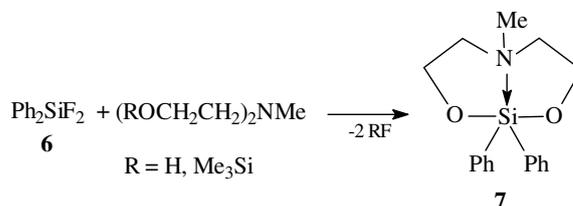
Scheme 3.

Scheme 4.

Obtained compounds were named quasisilatranes [7] (cf. pseudo-silatranes [8a,8b], 2/3-silatrane [9]) because of some their structural similarity with silatranes.

Evidence that all of the new compounds **3**, **5** and **9** have pentacoordinate structure in solution DMSO-d_6 is obtained from the ^{29}Si and ^{19}F NMR spectral data which are within the range typical for pentavalent silicon compounds. From Table 1 follows that the [29]Si signals of **3**, **5** and **9** appear at higher field as the substituent become more electron-withdrawing.

Because of the presence of the intramolecular N → Si bond the diastereotopy of the protons of the CH$_2$N and CH$_2$O groups is observed in the ^{1}H NMR spectra of compounds **3**, **5** and **9**.
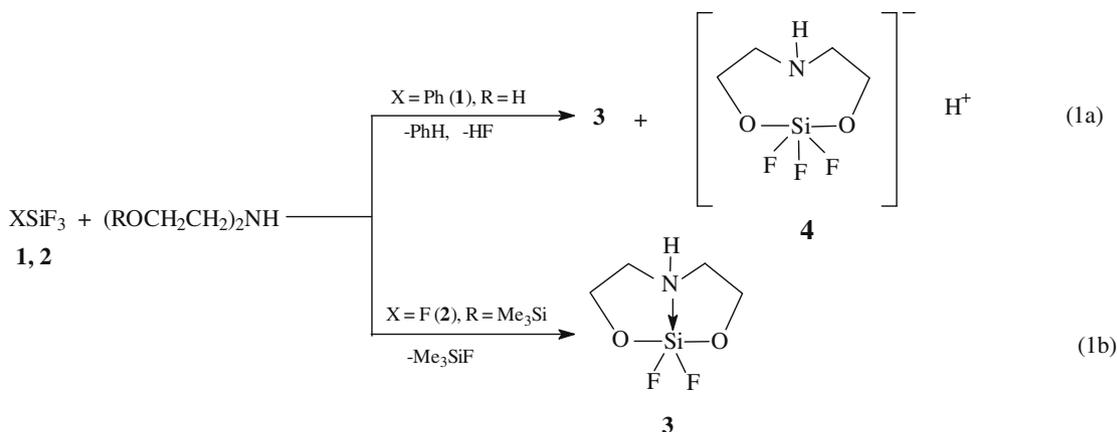
Scheme 1.

Table 1
[29]Si Chemical shifts (ppm) in DMSO-d_6 for quasisilatranes **3**, **5** and **9** and related diphenyl compounds **7** and **10** for comparison

	3	**5**	**7**	**9**	**10**[a]
δ ([29]Si)	−113.4	−80.3	−44.0 −48.1 [10]	−82.1	−62.0 [10]

10[a]: $Ph_2Si(OCH_2CH_2)_2NH$.

2.2. X-Ray structures of crystals **3**, **5** and **9**

The molecular structures of compounds **3**, **5** and **9** are depicted in Figs. 1–3. Selected bond lengths and angles are listed in Table 2. The X-ray crystallographic experimental parameters used for crystal structure analysis are summarized in Table 3.

The geometry of Si atom coordination centre in crystals of quasisilatranes can be described as almost ideal (for **3**) or slightly distorted trigonal bipyramid (TBP) (for **5** and **9**). The axial positions are occupied by N1 and F1 atoms while the equatorial plane is formed by two oxygen atoms and the carbon atom (Me, Ph groups) or F2 atom.

The N–Si distance is in the same range for all compounds and much shorter than the sum of the van der Waals radii of the silicon and nitrogen atoms (3.65 Å) [11], that indicates coordination bonding between them. As expected, the presence of a fluoro substituent in the axial position has profound effect on the N → Si bond length in quasisilatranes. Thus, the N–Si distance in **3** (1.981 Å) is significantly shorter than that in $Ph_2Si(OCH_2CH_2)_2NH$ (2.301 Å) [4]. The N–Si coordination bond become shorter (by 0.505 Å) by replacing one phenyl ligand in $Ph_2Si(OCH_2CH_2)_2NMe$ (2.68 Å) [12] with a fluorine atom.

It is noteworthy that N–Si distance in **3** is noticeably shorter than in 1-fluorosilatrane [13] because of lower total electronega-
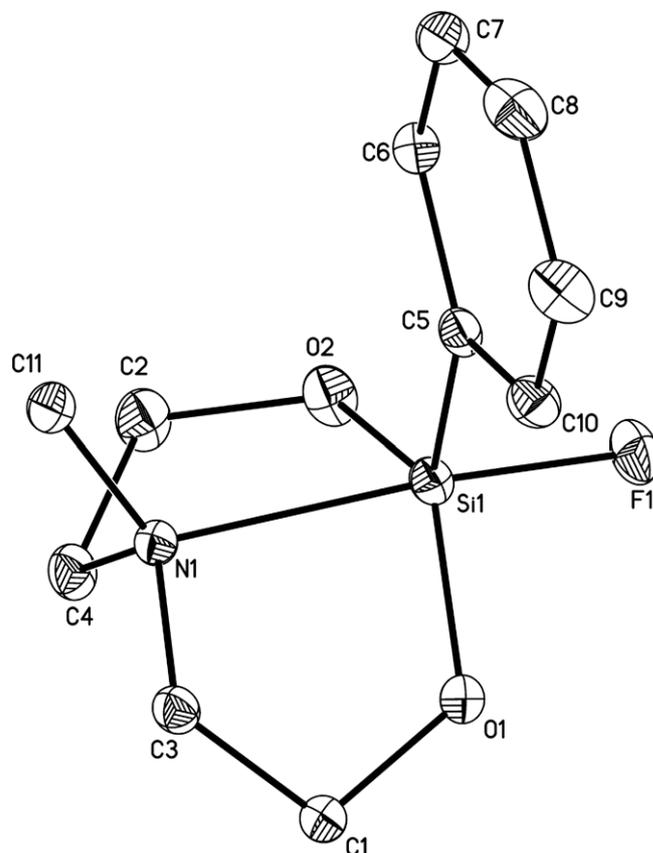
Fig. 2. Molecular structure of **5**. Atoms are presented by thermal ellipsoids with 50% probability. Hydrogen atoms are omitted for clarity.

Fig. 1. Molecular structure of **3**. Atoms are presented by thermal ellipsoids with 50% probability. Hydrogen atoms with exception of H1 are omitted for clarity.
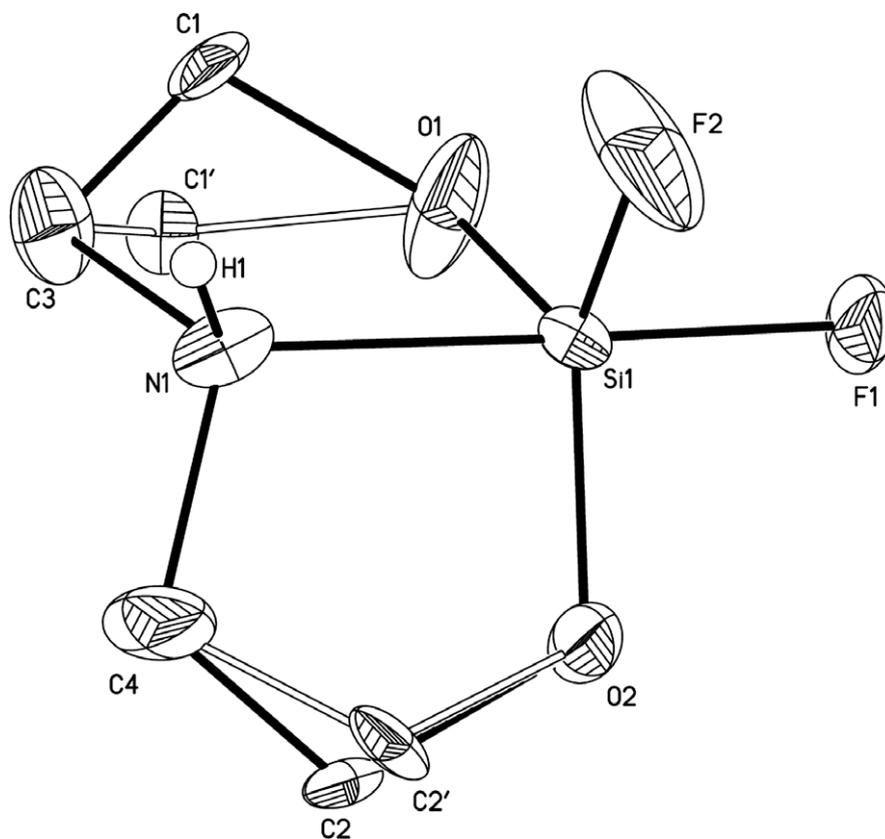
Fig. 3. Molecular structure of **9**. Atoms are presented by thermal ellipsoids with 50% probability. Hydrogen atoms with exception of H1 are omitted for clarity.
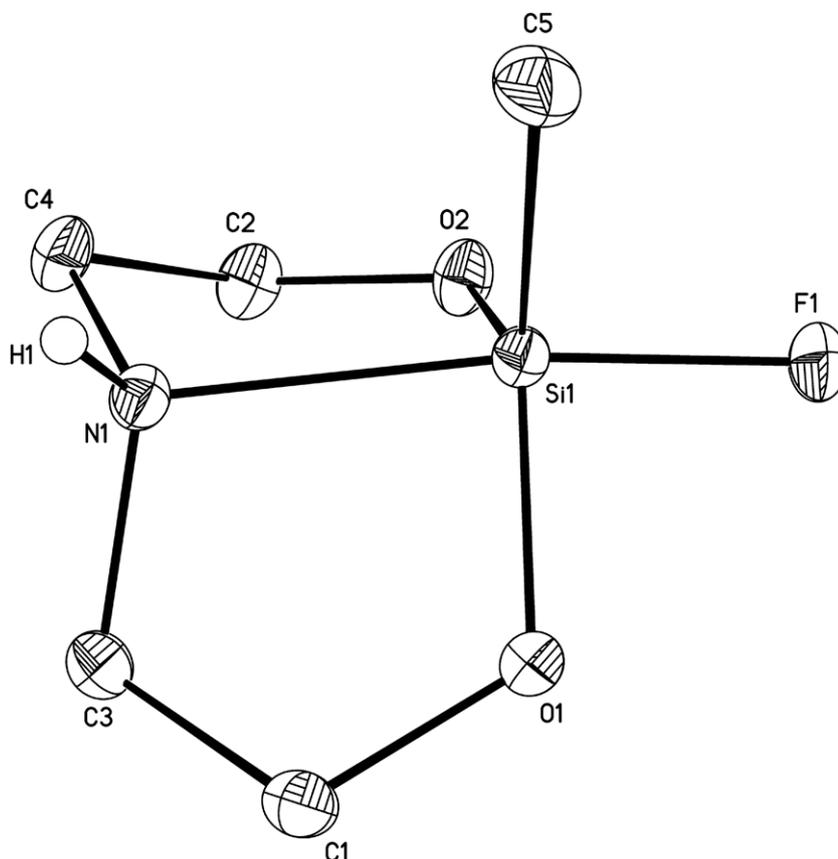
Table 2
Selected bond lengths (Å) and angles (°) in the crystal structures of **3**, **5** and **9**

	3	**5**	**9**	PW91–PW **9**
N1 → Si1	1.981(6)	2.1751(7)	2.0590(4)	2.083
Si1–F1	1.617(4)	1.6452(6)	1.6612(3)	2.083
Si1–F2	1.595(5)	–	–	1.679
Si1–O1	1.635(6)	1.6562(6)	1.6763(4)	1.696
Si1–O2	1.628(5)	1.6569(7)	1.6671(4)	1.685
Si1–C5	–	1.8680(9)	1.8708(5)	1.880
N1–C3	1.492(8)	1.473(1)	1.4756(6)	1.476
N1–C4	1.480(9)	1.483(1)	1.4763(6)	1.475
N1–R	0.92	1.477(1)	0.90	1.029
N1–Si1–F1	178.4(3)	171.98(3)	170.99(2)	170.5
O1–Si1–F1	93.0(3)	93.49(3)	–	89.7
O1–Si1–O2	123.9(3)	124.01(4)	122.28(2)	122.5
O1–Si1–C5	–	115.80(4)	119.29(2)	
O1–Si1–F2	117.5(4)	–	–	118.0
O2–Si1–F2	117.3(4)	–	–	119.0
O2–Si1–C5	–	118.30(4)	117.84(2)	
ΔSi	0.105(3)	0.1367(4)	0.0772 (3)	0.07
ΔN	0.446(4)	0.4473(8)	0.3550 (3)	0.39
%TBP$_e$[a]	96	94	98	

[a] Percent pentacoordination$(\%TBP_{eq}) = \frac{120° - \frac{1}{3}(\sum_{n=1}^{3}\Phi_n)}{120° - 109.5°} \times 100$. Φ_n are the angles Req-Sil-Yeq [14].

tivity of the substituents at silicon in the latter in comparison with quasisilatrane **3**. The N–Si bond length in **3** is very close to that in silatranyl oxonium salt [Me$_2$OSi(OCH$_2$CH$_2$)$_3$N] · BF$_4$, the compound with shortest N–Si distance in silatranes (1.965 Å) [15].

The axial Si1–F1 bond lengths in **3**, **5** and **9** are longer (by 0.016, 0.044 and 0.059 Å, respectively) relative to that for equatorial Si1–F2 bond in **3** (1.595 Å) which is close to typical Si–F bond distance accepted for tetracoordinate silanes (1.601 Å) [11].

The N1–Si1–F1 angles in compounds **5** and **9** are 171–172° (Table 2) which are lower than in 1-fluorosilatrane (179.7°) [13]. The N1–Si1–F1 angle (178.4°) in compound **3** is close to the value for 1-fluorosilatrane. Such a discrepancy in values of N1–Si1–F1 angles in compounds **3**, **5** and **9** are related to the sterical repulsion between equatorial substituent at Si1 atom and substituent at N1 atom. Indeed, the hydrogen atoms of Ph group at Si and Me group at N atoms have short C5...H11C (2.73 Å) and H1A...H5A (2.28 Å) contacts in the crystal structures of **5** and **9**, respectively. The latter values are less than sum of van der Waals radii of the corresponding atoms [11]. Besides, the values of torsional angles C11–N1–Si1–C5 in **5** (29.8°) and H1A–N1–Si1–C5 in **9** (21.6°) is additional proof for repulsive character of above contacts. Thus, the short contacts between substituents at Si1 and N1 atoms in **5** and **9** led to the distortion of geometry of Si1 atom coordination centre and weakening N–Si coordination bond. On the contrary, in **3** the H1...F2 contact may serve as additional factor for shortening Si–N distance and almost ideal TBP geometry of Si1 atom coordination centre.

In all three compounds **3**, **5** and **9** the silicon atom deviates from the equatorial plane toward the axial F1 ligand, the displacement of the silicon atom (Δ_{Si}) being close to 0.1 Å (Table 2). Lesser Δ_{Si} value for **5** (0.14 Å) than that for Ph$_2$Si(OCH$_2$CH$_2$)$_2$NMe (0.38 Å) [12] suggests strengthening the N → Si coordination bond by replacement of one phenyl group at silicon by an electron-withdrawing fluoro ligand. The pentacoordination degree in XPhSi(OCH$_2$CH$_2$)$_2$NMe increases from 50% to 94% (TBP$_{eq}$) on going from X = Ph to X = F.

2.3. Chemical bonding in crystal of **5** and **9**

Above X-ray data reveal the presence of the short and thus strong N → Si coordination bond in crystals of compounds **3**, **5**

Table 3
Crystallographic parameters for **3**, **5** and **9**

	3	5	9
Empirical formula	$C_4H_9NO_2F_2Si$	$C_{11}H_{16}NO_2FSi$	$C_5H_{12}NO_2FSi$
Formula weight	169.14	241.34	165.25
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Crystal size (mm)	$0.7 \times 0.1 \times 0.1$	$0.2 \times 0.2 \times 0.05$	$0.1 \times 0.1 \times 0.1$
Density (calc.) (g cm^{-3})	1.613	1.395	1.446
a (Å)	6.338(2)	7.3149(4)	6.7543(3)
b (Å)	9.531(3)	11.1975(6)	9.6468(5)
c (Å)	6.511(2)	14.0314(8)	11.6465(5)
β (°)	117.7(1)	90.65(1)	90.0
V (Å^3)	348.3(3)	1149.2(1)	758.8(1)
Space group, Z	$P2_1$, 2	$P2_1/c$, 4	$P2_12_12_1$, 4
$2\theta_{max}$ (°)	52.04	66.54	108.72
Scan type		ϕ and ω scans	
Reflections collected	3116	14466	62856
Independent reflections [$R_{(int)}$]	1328 (0.0609)	4400 (0.0251)	9350 (0.0339)
Number of reflections with $I > 2\sigma(I)$	947	3842	7893
Parameters	111	146	92
Linear absorption (cm^{-1})	3.15	2.03	2.69
T_{min}/T_{max}	0.809/0.969	0.961/0.990	0.974/0.974
Goodness-of-fit (GOF)	0.964	1.049	1.039
R_1 [$I > 2\sigma(I)$]	0.0678	0.0303	0.0293
wR_2 (all reflections)	0.1483	0.0899	0.0716
Absolute structure parameter	0.04(1)		0.02(4)
ρ_{min}/ρ_{max}, e	−0.45/0.52	−0.29/0.46	−0.23/0.41

and **9**. However, the nature of chemical bonding cannot be verified without detail knowledge of the electron structure of these molecules which can be extracted from results of quantum chemical calculations. Therefore we carried out the high resolution X-ray diffraction study and the quantum chemical calculations of crystal structure of compounds **5** and **9**. Such type of quantum chemical calculations in terms of DFT theory (PW91 exchange correlation functional and plane wave (PW) basis set allowed one to minimize the possible experimental errors in topological parameters and compare the characteristics of N → Si coordination bond depending on changes of Si1 and N1 atoms coordination environment. The choice of PW91–PW method instead of standard B3LYP and MP2 calculations of isolated molecules is caused by necessity to take into account the crystal packing. The analysis of literature concerning pentacoordinated silicon species has shown that interatomic Si–N distances in isolated molecules [16–18] are in most cases exceed the experimental values (revealed by X-ray diffraction) by 0.2–0.3 Å, that makes difficult direct comparison experimental and theoretical results. Unfortunately, the disorder of C1 and C2 atoms in compound **3** made impossible the experimental study and quantum chemistry calculation of its crystal structure.

Bond lengths and angles calculated by PW91–PW for structure of compounds **5** and **9** are in good agreement with experimental ones (Table 2). The main discrepancies (up to 0.03–0.1 Å) are observed for weak intramolecular contacts H...H, C–H...O and C–H...F. All bonds formed by Si atom are elongated in comparison to experimental values by ca. 0.02 Å, so the precision of PW91–PW calculations is better than that of hybrid functionals [16] and MP2 [17,18] in case of isolated molecules of silatranes.

On the basis of experimental study and PW91–PW calculations of crystal structures of **5** and **9** the electron density distribution function ($\rho(r)$) was obtained. Analysis of chemical bonding pattern was performed using topological analysis of experimental and calculated $\rho(r)$ in terms of R.F. Bader's "Atoms in molecules theory" (AIM) [19]. This approach was successfully utilized for combined experimental and theoretical study of characteristics of the N → Si bonds in crystal structures of 1-methylsilatrane [20] and O,N-chelated silicon difluoride [21].

According to AIM theory [19] the interatomic interactions divided into three types. The first type titled as "shared interactions"

are characterized by domination of potential energy density ($V^e(r)$) in CP(3,−1) ($E^e(r)$ and $\nabla^2\rho(r) < 0$) and correspond to ordinary covalent bonds such as C–C, N–C and C–O. In the case of domination of kinetic energy density in CP(3,−1) ($E^e(r)$ and ($\nabla^2\rho(r) > 0$) interatomic interactions correspond to closed shell type. The examples of latter interactions are highly polar ionic bonds (Na–Cl, Li–F) as well as weak intermolecular contacts. The third type of interatomic interactions titled as "intermediate type" includes the bonds with domination of potential energy density and positive sign of Laplacian in CP(3,−1). Both in 1-methylsilatrane [20] and O,N-chelated silicon difluoride [21] the N → Si bond correspond to intermediate type of interatomic interactions.

Topological analysis of theoretical and experimental $\rho(r)$ in crystal structure of **5** and **9** has revealed the CPs(3,−1) in regions of all chemical bonds including N → Si bond (Table 4). Also, the CPs(3,−1) correspond to weak intramolecular H...H, C–H...O and C–H...F interactions as well as N–H...O and N–H...F bonds were localized. All C–O, C–C and N–C bonds belong to shared (covalent) type of interatomic interactions. All intermolecular interactions correspond to the closed shell type. In CPs(3,−1) of the Si–O and N → Si coordination bonds the positive sign of $\nabla^2\rho(r)$ and negative one of $E^e(r)$ are observed (Table 4). To get further information on the N → Si bonding we estimated the experimental and theoretical λ_1/λ_3 ratio values in **9** and **5** which are equal to 0.346, 0.304 and 0.227, respectively. These values can be considered as extent of covalent character of the coordination bonds in hypervalent organosilicon compounds [16,21]. The λ_1/λ_3 obtained fall within the range typical for most of silatranes. Thus, according to AIM theory we can conclude that N → Si intramolecular bond in quasisilatranes corresponds to highly polar bond with pronounced ionic contribution.

We analyzed the nature of chemical bonding in axial N1–Si1–F1 fragment on the basis of electron localization function (ELF [22]) distribution which is indicative for concentrations of valence electron density in regions of chemical bonds and positions of lone electron pairs. The sections of experimental and theoretical (PW91–PW) ELF in O1–Si1–F1 plane (Figs. 4 and 5) in **9** allowed one to suggest that transfer of electron density from electron pair of N1 to the region of Si1–F1 bond is rather small. Indeed, it can be seen from the Figs. 4 and 5 that in **9** the electron density

Table 4
Topological characteristics of bonds in Si1 atom coordination centre in structures of **5** and **9**

	Experiment	PW91–PW calculation	
$\rho(r)$, e Å^{-3}			
N1 → Si1	0.53	0.41	0.52
Si1–F1	0.99	0.98	0.94
Si1–O1	1.02	1.08	1.02
Si1–O2	1.06	1.07	1.05
Si1–C5	0.83	0.94	0.93
$\nabla^2 \rho(r)$, Å^{-5}			
N1 → Si1	2.24	1.21	2.44
Si1–F1	10.78	22.45	20.86
Si1–O1	7.18	20.24	18.61
Si1–O2	9.33	19.76	18.98
Si1–C5	1	2.47	1.76
$E^e(r)$, Hartree Å^{-3}			
N1 → Si1	−0.15	−0.15	−0.21
Si1–F1	−0.41	−0.25	−0.23
Si1–O1	−0.66	−0.44	−0.4
Si1–O2	−0.66	−0.44	−0.43
Si1–C5	−0.57	−0.67	−0.67
$V^e(r)$, a.u. [E_{bond}, kcal/mol]			
N1 → Si1	−0.09 [28.4]	−0.058 [18.1]	−0.088 [27.7]
Si1–F1	−0.273 [85.4]	−0.308 [96.7]	−0.286[89.6]
Si1–O1	−0.271 [85.3]	0.339 [106.3]	−0.311 [97.4]
Si1–O2	−0.318 [91.9]	−0.336 [105.3]	−0.323 [101.2]
Si1–C5	−0.178 [56.0]	−0.222 [69.6]	−0.217 [67.9]

Bond energies calculated according to ELM scheme [23] are given in square brackets.

maximum in region of N → Si coordination bond is localized at 0.7 Å from N1 atom.

The N → Si bond energy has been estimated semi-qualitatively using correlation formula (ELM) [23]

$$E_{bond} \approx -1/2 V^e(r)[\text{a.u.}]$$

One can see that experimental values are systematically decreased in comparison with theoretical ones. Comparison of obtained values of E_{bond} for **9** (Table 4) with literature data have shown that they are not exceed 1/3 of energy of "normal" N–Si bond in $(Me_3Si)_2NH$ (75.8 kcal mol^{-1} [24]).

The electron-acceptor effect of substituents at Si1 atom was analyzed on the basis of atomic charges (AIM charges, Table 5) calculated for each type of atoms as difference between atomic number and population of respective atomic basin. These charges have physical meaning and they are transferable between molecules with same molecular fragments.

It can be seen from Table 5 that Si1 is characterized by positive charge while N, O and F atoms are negatively charged. The experimental and calculated values of AIM charges are in good agreement with exception for N1 atom. The high negative charge of $FCSiO_2$ moiety (experimental and calculated values 1.21 and 1.09 e, for **9** and **5**, respectively) is indicative for significant Lewis acidity of this fragment.

2.4. Conclusion

In summary the synthesis of quasisilatranes with electron acceptor substituents at Si atom without noticeable steric overcrowding is the fruitful approach for preparation of compounds with strong N → Si bond. It has been shown that the strength of the N → Si coordination is strongly dependent on the number of fluorine ligands at silicon. Detailed study of electron density distribution function reveals that the energy of N → Si bond in quasisilatrane **9** is about 1/3 of normal N–Si bond.

3. Experimental

3.1. General comments

All reactions were carried out under an argon atmosphere. Standard precautions to avoid moisture were taken. Benzene and hexane were purified by distillation from sodium. DMSO-d_6 was kept over 4A molecular sieves.

The ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded on a Brucker DPX-400 spectrometer (^{1}H, 400,13 MHz; ^{13}C, 100.62 MHz; ^{15}N, 40.55 MHz; ^{19}F, 376.50; ^{29}Si, 79.50 MHz) at room temperature. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent resonances, ^{19}F chemical shifts to external CCl$_3$F, and ^{29}Si chemical shifts to external Me$_4$Si.

3.2. X-Ray diffraction studies

X-Ray diffraction measurements for **3**, **5** and **9** were carried out with a Bruker Smart APEX II diffractometer at 100 K using Mo Kα radiation (graphite monochromator, λ[Mo Kα] = 0.71073 Å). The frames were integrated and corrected for absorption by the APEX 2 program suite [25]. Structures were solved by direct methods and non-hydrogen atoms were refined in full-matrix anisotropic approximation. The hydrogen atoms were located from differential Fourier synthesis of the electron density and refined isotropically in rigid body approximation. All calculations were carried out using the SHELXTL 5.1 program package [26]. Details of crystallographic data and experimental conditions are presented in Table 3.

The analytical form of the electron density distribution function in **9** was obtained by a multipole refinement based on Hansen–Coppens [27] formalism using XD program package [28]. Prior to refinement procedure all C–H bonds were normalized to values corresponding to values obtained in neutron diffraction experiments (1.08 Å [29]) while for N–H bond the value 1.03 Å were assumed on the basis of quantum chemical calculations. The level of the multipole expansion was octadecapole for C, O, N, Si, F atoms and dipole for hydrogens. The scattering factor of the hydrogen atoms was calculated from the contracted radial density functions ($\kappa = 1.2$). The refinement was carried out against F with usage of C_2 symmetry for the Si1 and N1 atoms. For hydrogens a cylindrical symmetry was assumed. The refinement is converged to $R = 0.0176$, $Rw = 0.0135$ and GOF = 1.228 for 3854 merged reflections with $I > 3\sigma(I)$ and $F_{obs} > 1.7$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria (the maximum difference of the mean square displacement amplitudes was 6×10^{-4} Å^2). The residual electron density was not more than 0.225 e Å^{-3}. Topological analysis of the experimental $\rho(r)$ function was carried out using the WINXPRO program package [30].

3.3. Details of quantum chemical calculations

The quantum chemical calculations of structure **9** in the crystal were carried out using the VASP 4.6.31 code [31]. Conjugated gradient technique was used for optimizations of the atomic positions (started from experimental data) and minimization of total energy. Projected augmented wave (PAW) method was applied to account for core electrons while valence electrons were approximated by plane-wave expansion with 680 eV cutoffs. Exchange and correlation terms of total energy were described by PW91 [32] exchange-correlation functional. Kohn–Sham equations were integrated with 8 irreducible k-points. Using DFT method was not possible owing to dispersion interactions. For this reason calculated cell parameters may be systematically overestimated or underestimated up to 5%. Thus, the experimental values of cell parameters were used in the calculations. At a final step of our calculations atomic
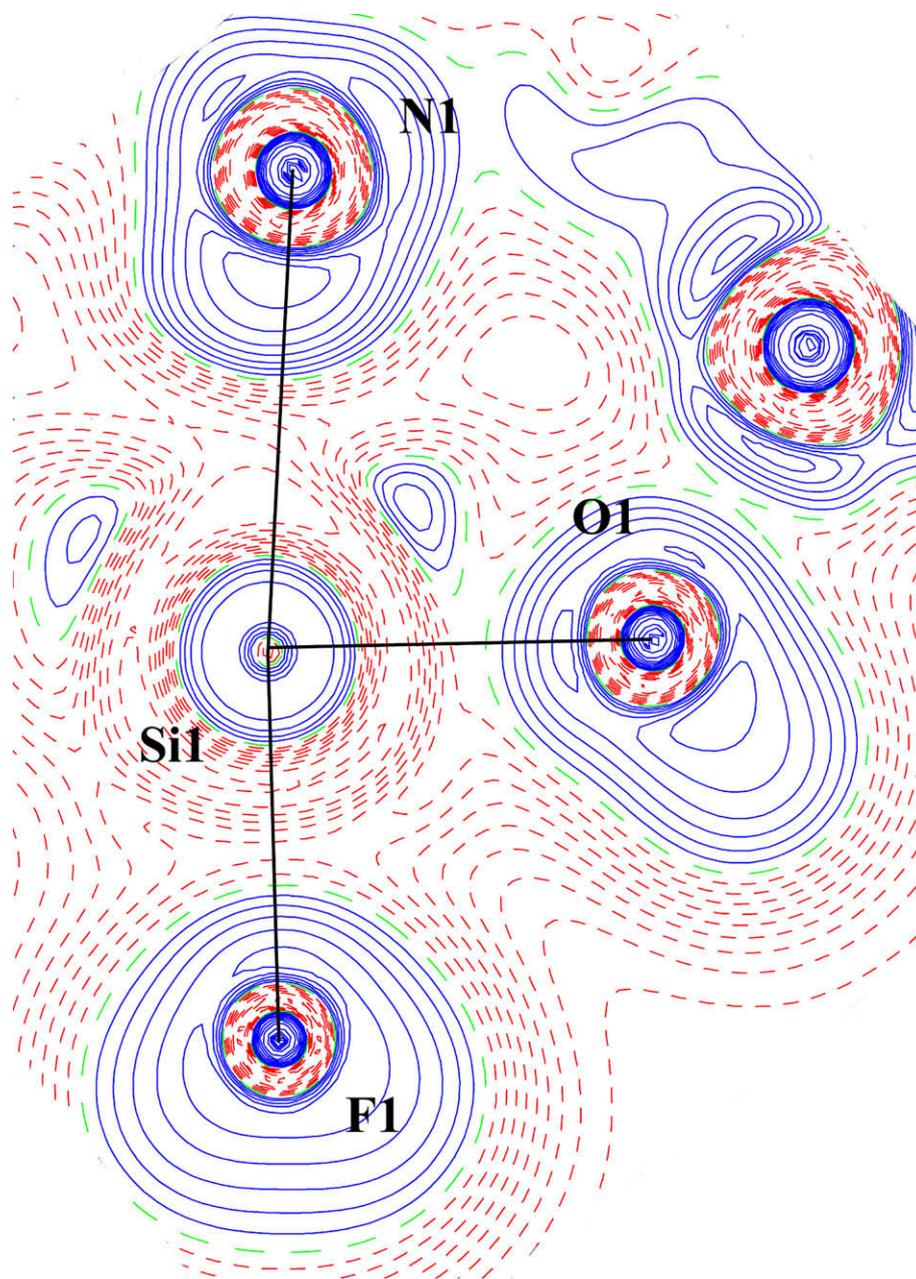
Fig. 4. The section of experimental electron localization functions in O1Si1F1 plane in **9**. Isolines of ELF ($\eta > 0.5$) corresponding to concentrations of valence electron density are drawn by solid lines.

displacements converged were better than 0.01 eV Å^{-1}, as well as energy variations were less than 10^{-3} eV. In order to carry out the topological analysis of electron density distribution function in terms of AIM theory the dense FFT (fast Fourier transformation) grid was used (corresponding to cutoff 1360 eV). The latter was obtained by separate single point calculation of optimized geometry with hard PAWs for each atom type. The topological analysis of electron density distribution function was carried out using AIM program – part of ABINIT software package [33].

3.4. Synthesis of quasisilatranes

3.4.1. From SiF$_4$. 1,1-Difluoroquasisilatrane (**3**)

Gaseous SiF$_4$ (prepared from 37.82 g, 0.02 mol Na$_2$SiF$_6$ and 19.6 g, 0.02 mol conc. H$_2$SO$_4$) was passed through a solution of (Me$_3$SiOCH$_2$CH$_2$)$_2$NH (4.36 g, 0.02 mol) in hexane (10 ml) for 0.5 h at −5–0 °C. Filtration of a solid product followed by sublimation in vacuum gave **3** (1.39 g, 47%), m.p. 180 °C. Anal. Calc. for C$_4$H$_9$NO$_2$F$_2$Si: C, 28.01; H, 5.73; N, 8.39; F, 22.12. Found: C, 28.39; H, 5.36; N, 8.28; F, 22.46%. ^{1}H NMR (DMSO-d_6): δ 2.71, 2.91 (dt, 2H, NCH$_2$, ^3J = 6.1, J_{AB} = 11.6 Hz); 3.61, 3.72 (dt, 2H, OCH$_2$, J_{AB} = 10.2 Hz). ^{13}C NMR (DMSO-d_6): δ 43.63 (NCH$_2$); 57.71 (OCH$_2$, d, $^3J_{CF}$ = 4.6 Hz). ^{29}Si NMR (DMSO-d_6): δ −113.4 dd. ^{19}F NMR (DMSO-d_6): δ −136.1 (F), −137.9 (F′) $J_{Si-F'}$ = 192.4 Hz, $^2J_{FF}$ = 23.5 Hz, J_{Si-F} = 132.2 Hz. ^{15}N NMR (DMSO-d_6): δ −348.0.

3.4.2. From organylfluorosilanes: general procedure
3.4.2.1. 1-Phenyl-1-fluoro-5-methylquasisilatrane (**5**).
(a) Phenyltrifluorosilane **1** (12.17 g, 0.07 mol) was added to a solution of (HOCH$_2$CH$_2$)$_2$NMe (8.96 g, 0.07 mol) in C$_6$H$_6$ (10 ml). After stirring for 30 min at −3–0 °C, the precipitate was filtered, recrystallized from DMF and dried under vacuum to yield **5** (3.51 g, 71%)
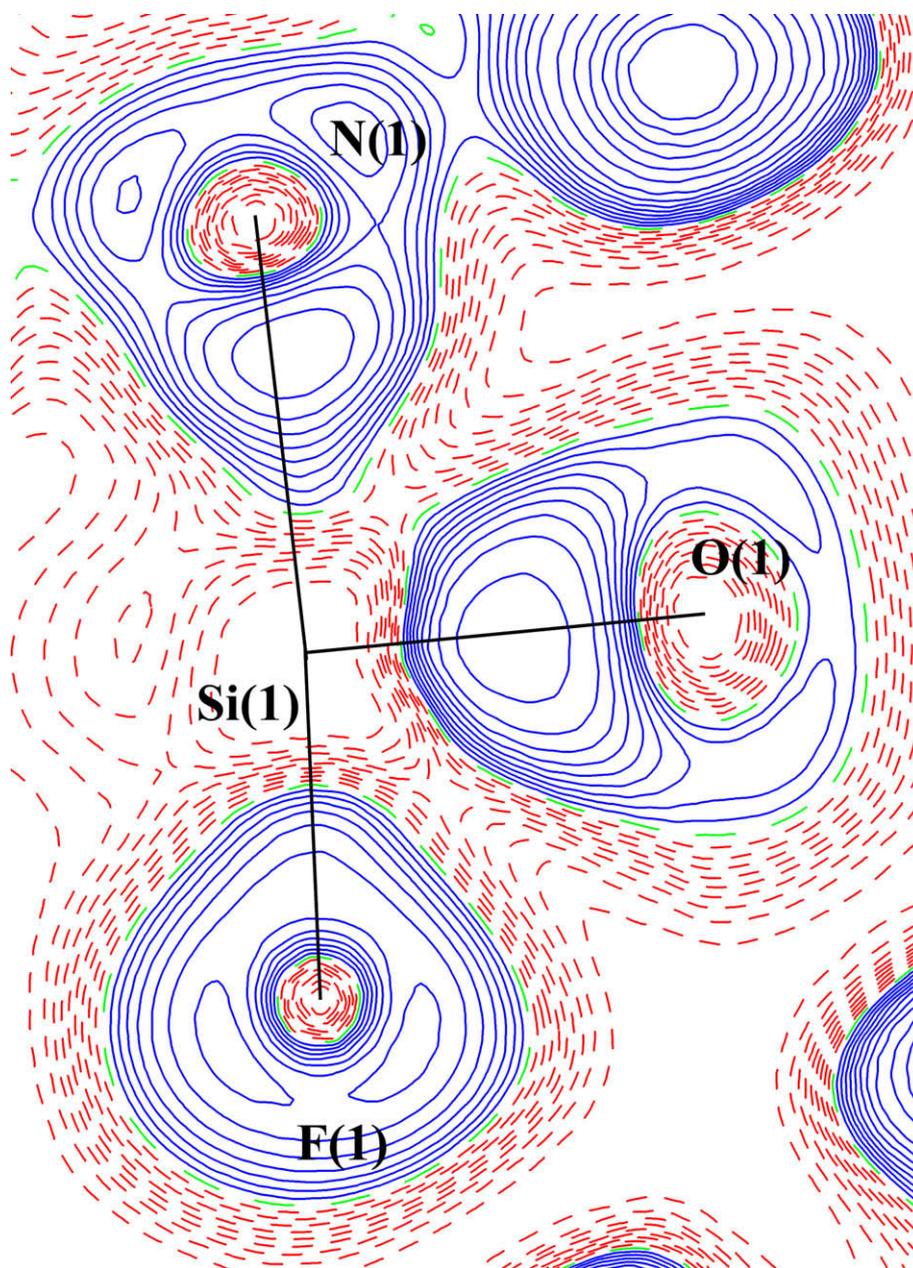
Fig. 5. The section of theoretical electron localization functions in O1Si1N1 plane in **9**. Isolines of ELF ($\eta > 0.5$) corresponding to concentrations of valence electron density are drawn by solid lines.

Table 5
Atomic charges in terms of AIM theory for selected atoms in crystal of **5** and **9**

	Experiment	PW91–PW calculation	
	9	**5**	**9**
Si1	2.46	2.70	2.69
N1	−0.82	−1.07	−0.84
F1	−0.67	−0.85	−0.85
O1	−1.09	−1.26	−1.25
O2	−1.14	−1.25	−1.26
C5	−0.68	−0.56	−0.54
R	0.38	0.37	0.42
C3	0.08	0.34	0.36
C4	0.15	0.33	0.34

as white crystals, m.p. 84 °C. Anal. Calc. for $C_{11}H_{16}NO_2FSi$: C, 54.74; H, 6.68; N, 5.80; F, 7.87. Found: C, 54.51; H, 6.89; N, 6.01; F, 7.62%. ^1H NMR (DMSO-d_6): δ 1.67 (s, 3H, NMe); 7.32, 7.51 (m, 5H, Ph); 2.65, 2.74 (dt, 2H, NCH$_2$, J_{AB} = 12.4, ^3J = 6.04 Hz); 3.95, 4.01 (dt, 2H, OCH$_2$, J_{AB} = 12.1 Hz). ^{13}C NMR (DMSO-d_6): δ 42.95 (NMe); 54.10 (NCH$_2$); 59.83 (OCH$_2$); 127.93 (C$_o$), 128.96 (C$_p$), 131.86 (C$_m$), 134.05 (C$_i$). ^{29}Si NMR (DMSO-d_6): δ −80.3, J_{Si-F} = 214.3 Hz. ^{15}N NMR (DMSO-d_6): δ −345.6.

(b) Compound **5** (14.88 g, 40%) was also obtained from (Me$_3$SiOCH$_2$CH$_2$)$_2$NMe (16.24 g, 0.06 mol) and PhSiF$_3$ (10.00 g, 0.06 mol).

3.4.2.2. 1,1-Diphenyl-5-methylquasisilatrane (7). The compound **7** (1.14 g, 53%) was obtained from Ph$_2$SiF$_2$ (**6**) in benzene (10 ml) using the above procedures and the same initial diethanolamine derivatives (Section 3.4.2.1. (a) and (b)). B.p. 180–182 °C/2 mmHg, m.p. 61 °C. ^1H NMR (DMSO-d_6): δ 1.69 (s, 3H, NMe); 2.65 (t, 4H, NCH$_2$, ^3J = 4.8 Hz); 4.05 (t, 4H, OCH$_2$); 7.34, 7.65 (m, 10H, Ph). ^{13}C NMR (DMSO-d_6): δ 42.28 (NMe); 55.60 (NCH$_2$); 61.51 (OCH$_2$);

127.64 (C_o), 128.63 (C_p), 133.51 (C_m), 138.49 (C_i). ^{29}Si NMR (DMSO-d_6): δ −44.0.

3.4.2.3. 1-Methyl-1-fluoroquasisilatrane (9).

The compound **9** was obtained from MePhSiF$_2$ (11.87 g, 0.07 mol) and (HOCH$_2$CH$_2$)$_2$NH (7.89 g, 0.07 mol) in benzene (10 ml) by procedure mentioned in Section 3.4.2.1. (a). Yield 45% (6.9 g), white crystals, m.p. 60–61 °C (from C$_6$H$_6$). Anal. Calc. for C$_5$H$_{12}$NO$_2$FSi: C, 36.34; H, 7.27; N, 8.48; F, 11.51. Found: C, 36.61; H, 7.20; N, 8.13; F, 11.83%. ^{1}H NMR (DMSO-d_6): δ 0.06 (d, 3H, SiMe, $^3J_{HF}$ = 6.85 Hz); 2.54, 2.87 (ddt, 2H, NCH$_2$, J_{AB} = 12.0, ^3J = 5.6, $^3J_{HNCH}$ = 5.9 Hz); 3.53, 3.69 (dt, 2H, OCH$_2$, J_{AB} = 10.3 Hz). ^{13}C NMR (DMSO-d_6): δ 0.73 (d, SiMe, $^2J_{CF}$ = 45.5); 43.94 (NCH$_2$); 58.51 (d, OCH$_2$, $^3J_{CF}$ = 3.4 Hz). ^{29}Si NMR (DMSO-d_6): δ −82.1. ^{19}F NMR (DMSO-d_6): δ −107.4, J_{Si-F} = 209.9 Hz. ^{15}N NMR (DMSO-d_6): δ −343.0.

Acknowledgment

Appendix A. Supplementary material

CCDC 688265, 675484 and 688266 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.010.

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