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Divergent reactivity of divinylsilanes toward sulfonamides in different oxidative systems†

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Oxidative sulfonamidation of divinylsilanes with various sulfonamides in different solvents is reported. With *t*-BuOI as an oxidant, halogenation is the main process, whereas aziridines are the minor products. With NBS in CH_2Cl_2 the products of bromination or bromosulfonamidation were obtained, whereas in MeCN or THF the Ritter-type solvent interception products are formed. The obtained bromosulfonamidation products undergo base-induced cyclization to various heterocycles, including imidazolines, 1,4-oxazocanes, or Si,N-containing heterocycles of a new type, 1,3,5-diazasilinanes, in up to quantitative yield.

Introduction

Unsaturated organosilicon compounds are valuable building blocks, which play an important role in the synthesis of large molecules due to the diverse transformations they can undergo.[1] Thus, alkenyl- and dienyl silanes[2] are excellent reagents in various W, Mo, Re and Ru-catalyzed metathesis reactions.[3] Functionalized allyl- and vinylsilanes obtained by the addition of silyl cuprates to alkenes, dienes or acetylenes are used in the synthesis of natural products (salicylihalamide, tetrahydrolipstatin and ebelactone A), and stereoselective synthesis of di- and trisubstituted alkenes.[4] Vinyl- and alkynylsilanes are important reagents for the synthesis of carbocycles, as well as N- and O-containing heterocycles, including alkaloids.[5] Pd- and Ru-catalyzed cross-coupling of alkenes with vinylsilanes and -siloxanes can proceed with desilylation or with retention of the silyl group to afford π-conjugated systems (stilbenes, styryl halogenides, chalcones).[6] In the presence of Cu and Cs salts, similar reactions occur with desilylation and formation of dienes.[7] Bis-alkynes are hydrosilylated with bis-vinylsilanes in the presence of Rh-catalysts to give conjugated organosilicon chromophores possessing unique optoelectronic properties.[8] A specific type of transformations of unsaturated silanes of great potential interest is their oxidative sulfonamidation, since it allows to introduce not only pharmacophore sulfonamide fragment in the molecule, but also a halogen as a good leaving group, opening the way to further modifications. However, the information on this issue is very scarce. Very recently, oxidative triflamidation of several allylsilanes in different oxidative systems was shown to proceed with desilylation and formation of silicon-free products in the system (*t*-BuOCl + NaI), while no reaction occurred in the presence of *N*-bromosuccinimide (NBS).[9] Also noteworthy are the reactions of trimethyl(vinyl)silane and dimethyl(divinyl)silane in the absence of external oxidant but with pre-oxidized triflamide in the form of *N*,*N*-dichlorotriflamide leading to the products of α-chloro-β-triflamidation in moderate yield.[10] Of particular relevance to the present work are two recent studies on the reactions of trimethyl(vinyl)silane **1** and dimethyl(divinyl)silane **2** with sulfonamides in different oxidative systems.[11] Thus, the reaction in the system (*t*-BuOCl + NaI)[11a] has been proven to be an effective approach to various heterocycles as shown in Scheme 1.

Note, that the reactivity of triflamide is principally different from that of arenesulfonamides. With silane **1**, it gives mainly the product of bis(triflamidation), whereas with arenesulfonamides *N*-sulfonylaziridines were obtained in high yield. With silane **2**, most remarkable is the formation of 3-(triflyl)-5-(triflamido)oxazolidine in the reaction with triflamide.

The course of the NBS-induced reaction of silane **1** with sulfonamides is strongly solvent dependent.[11b] In CH_2Cl_2, the products of α-bromo-β-sulfonamidation were formed regioselectively in good yield. The latter underwent base-induced dehydrobromination to give the corresponding aziridines in a very high yield. In acetonitrile or THF, silane **1** with triflamide affords the solvent interception products, which were converted to 1-triflyl-2-methyl-5-(trimethylsilyl)-2-imidazoline or 4-triflyl-3-(trimethylsilyl)-1,4-oxazocane in almost quantitative yield (Scheme 2).[11b]

As seen from the above literature analysis, two important issues have not been addressed. First, the reactions of NBS-induced oxidative sulfonamidation of silanes **2** and **3** were not studied, although the nature of the oxidant can play a pivotal role in determining the course of the reaction (*vide supra*). Second, the reaction path may change by replacing the methyl by a phenyl substituent at silicon. Unlike in classical organic chemistry, the phenyl group at silicon can be considered as

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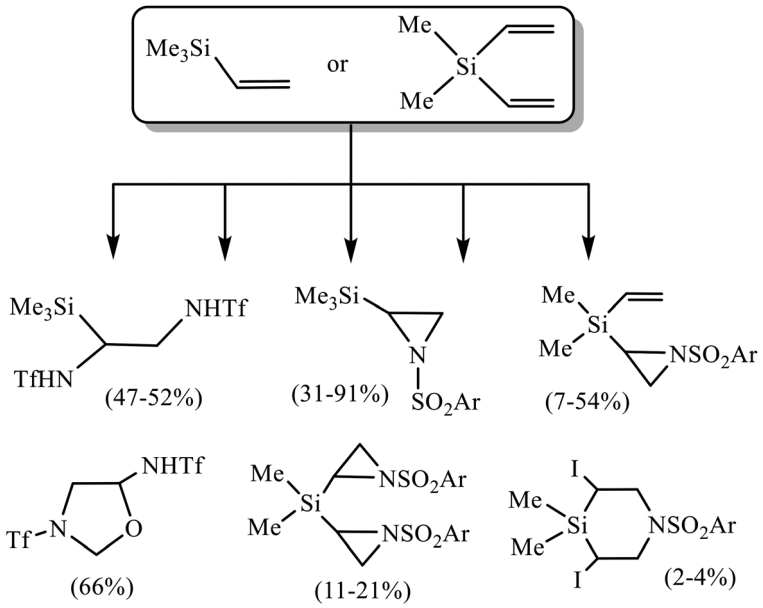


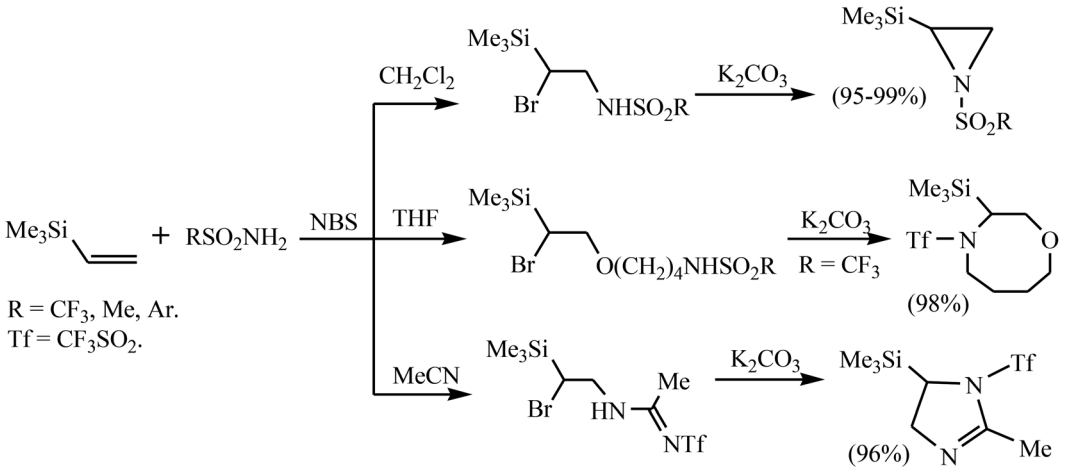
Scheme 1 Products of sulfonamidation of silanes **1** and **2** in the system (*t*-BuOCl + NaI)/MeCN.

a functional group because of the possibility of the Si–C bond cleavage. More feasible splitting of the Si–Ph as compared to the Si–Me bond is consistent with a longer Si–Ph with respect to Si–Me bond in spite of larger C_{sp^3} *vs.* C_{sp^2} covalent radius.[12] Therefore, the second aim of this study was to investigate the effect of substitution of methyl by phenyl groups in silane **2**, and, indeed, as will be shown below, such a replacement in some cases substantially changed the course of the reaction.

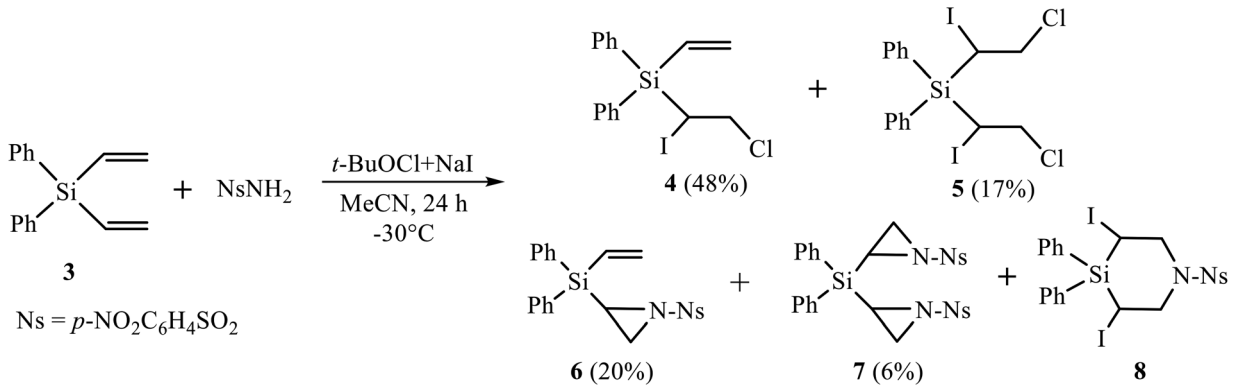
With these two goals in mind, and in order to investigate the dependence of the reaction on the nature of the reagents, the oxidant, and the solvent, we have studied the reactions of silanes **2** and **3** with triflamide ($TfNH_2$), methanesulfonamide ($MsNH_2$) and arenesulfonamides *p*-$RC_6H_4SO_2NH_2$ (R = Me, MeO, NO_2) in the presence of different oxidants [(*t*-BuOCl + NaI) or NBS] in different solvents (MeCN, THF, CH_2Cl_2). The results of this multifactor study as well as of the base-induced reactions of the products of bromosulfonamidation are presented below.

Results and discussion

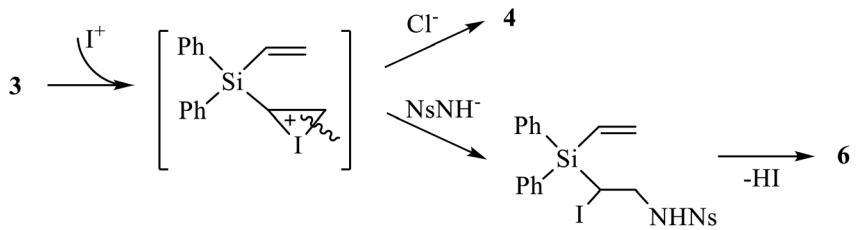
Firstly, we performed the reaction of silane **3** with nosylamide, which was chosen as the most close to triflamide in the NH acidity. However, the reaction with nosylamide proceeded in a different way (Scheme 3). No desilylation, like in Scheme 1, occurred; instead, the products of mono (**4**, major) and bis-α-iodo-β-chlorination (**5**, minor), mono (**6**) and bis-aziridination (**7**), as well as trace amounts of 3,5-diiodo-1-(4-nitrophenylsulfonyl)-4,4-diphenyl-1,4-azasilinane **8** were formed (Scheme 3). Although heterocycles **6–8** are similar to those of the reaction of nosylamide with silane **2**,[11b] their content is drastically different, being, in total, 68% in the



Scheme 2 NBS-induced sulfonamidation of trimethyl(vinyl)silane.



Scheme 3 Reaction of diphenyl(divinyl)silane **3** with nosylamide in the system (*t*-BuOCl + NaI).



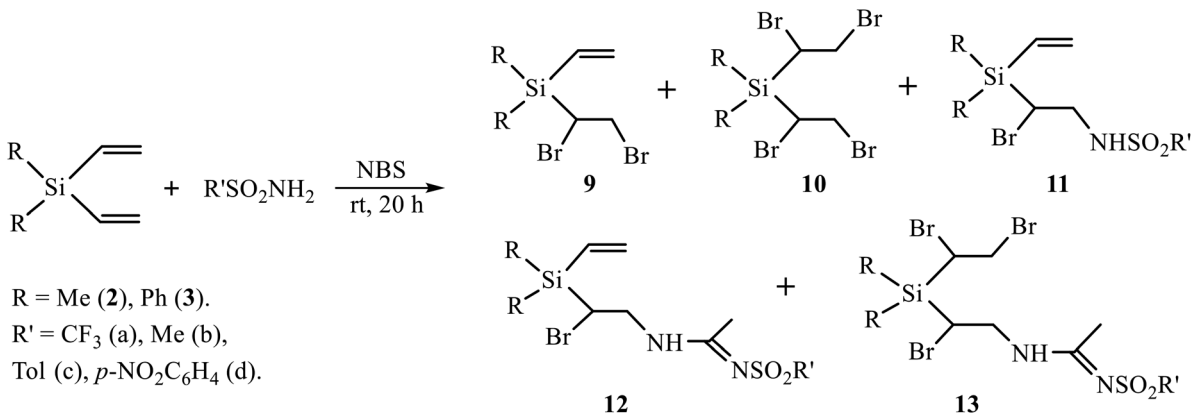
Scheme 4 Possible mechanism of independent halogenation *versus* aziridination *via* the same iodonium ion intermediate.

reaction with silane **2** and only 26% in the reaction with its Si–Ph analogue, silane **3**.

Because of low content of product **8**, we were unable to isolate it from the reaction mixture; however, its formation was proved by the presence of signals, similar to those of azasilinanes shown in Scheme 1 and described earlier,[11b] in the ^{1}H NMR spectrum of the fraction enriched with diaziridine **7** and containing *ca.* 11% of azasilinane **8**.

Next, we tried the reaction of compound **4** with nosylamide in order to replace one or both halogen atoms by the amide residue and obtain, after cyclization, aziridine **6**. However, apart from the unreacted nosylamide, the only product isolated in 76% yield was the product of dihalogenation **5** (Scheme 4). This may be indicative of independent formation of the products of halogenation **4**, **5** and aziridines **6**, **7**, as shown in Scheme 4 on the example of the adducts at one double bond.

A low content of the products of sulfonamidation **6–8** (<30%) as compared to undesired products of halogenation **4**, **5** (65%) when using the oxidative system (*t*-BuOCl + NaI) prompted us to replace it with NBS. The use of NBS as an oxidant in similar reactions was shown to be effective due to the lower resinification of the reaction mixture and the amount of side products.[11] The reaction of silanes **2** and **3** with a series of sulfonamides in the presence of NBS was performed in CH_2Cl_2 and MeCN as solvents and with various ratios of the reagents. The results are summarized in Scheme 5 and Table 1.



Scheme 5 NBS-induced reaction of (divinyl)silanes **2**, **3** with sulfonamides.

Table 1 Products of the reaction of silanes **2** and **3** with sulfonamides (Scheme 5)

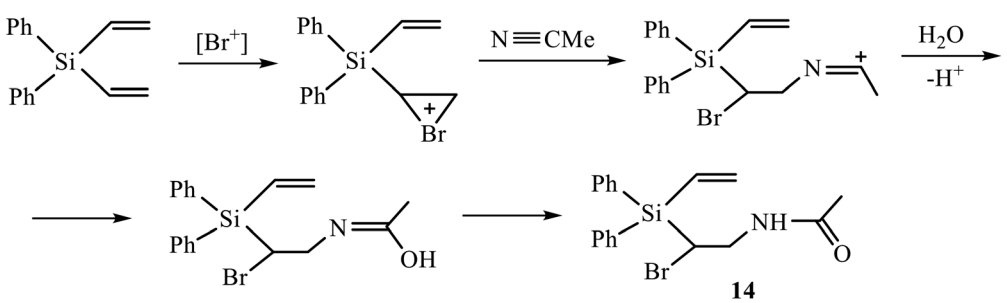
Entry	R	R′	Conversion, %	Solvent	$R'SO_2NH_2$/NBS	Yield[a], %				
						9	**10**	**11**	**12**	**13**
1	Me	CF_3	48	CH_2Cl_2	1 : 1	53	—	39	—	—
2			80	MeCN	1 : 1	6	—	—	88	—
3			37	MeCN	1 : 5	—	2[b]	—	—	46
4		Me	0	MeCN	1 : 1	81	—	—	—	—
5		Tol	42	MeCN	1 : 1	8	—	37	—	—
6		*p*-$NO_2C_6H_4$	38	MeCN	1 : 1	30	—	15	—	—
7	Ph	CF_3	53	CH_2Cl_2	1 : 1	30	—	46	—	—
8			72	MeCN	1 : 1	9	—	—	68	—
9			81	MeCN	1 : 5	—	12	—	—	60
10		*p*-$NO_2C_6H_4$	79	MeCN	1 : 5	—	14	—	—	65

[a] Isolated yields taking into account the conversion. [b] From ^{1}H NMR.

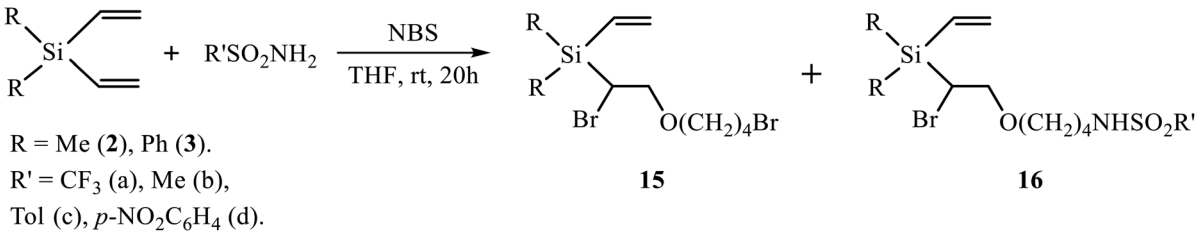
Although the yields in Table 1 seem to vary irregularly, the following conclusions can be made: (i) in the reactions of silanes **2** and **3** with $TfNH_2$ in CH_2Cl_2 the products of monobromination **9** and bromotriflamidation **11** are formed in comparable amounts (entries 1, 7); (ii) dibromination is a minor process with both silanes **2** and **3** and occurs only with large excess of NBS (1 : 5) and only with most acidic sulfonamides $TfNH_2$ and $NsNH_2$, most probably, due to higher electrophilicity of the bromine atom in most acidic intermediate *N*-bromosulfonamides TfNHBr and NsNHBr. The major product in this case is the Ritter-type product of bromosulfonamidation of one double bond **12** and bromination of the other double bond **13** (entries 3, 9, 10). With the equimolar ratio ($R'SO_2NH_2$/NBS = 1 : 1), the major product is the Ritter-type product of bromosulfonamidation of one and retention of the other double bond **12**, and the minor one is the product of bromination of one double bond **9** (entries 2, 8); (iii) silane **2** gives the Ritter-type products **12** and **13** only with $TfNH_2$, and not with $MsNH_2$ or aromatic sulfonamides (entries 4–6), whereas silane **3** gives products **13** with both most acidic sulfonamides, $TfNH_2$ and $NsNH_2$ (entries 9, 10). Formation of the Ritter-type product **13** in the reaction of silane **3** with $NsNH_2$ and its absence in the reaction of silane **2** is another demonstration of substantial influence of the phenyl substituent.

A vivid illustration of strong dependence of the reaction of oxidative sulfonamidation on the nature of the reagent is the change of the reaction course in going to *p*-methoxyphenylsulfonamide. In contrast to the reactions with other sulfonamides in Scheme 5, the reaction of silane **3** with *p*-methoxyphenylsulfonamide in acetonitrile in the presence of five-fold excess of NBS afforded monoadduct **9** (28%), diadduct **10** (11%) and, unexpectedly, as the major product, 40% of *N*-{2-bromo-2-[diphenyl(vinyl)silyl]ethyl}acetamide **14** rather than amidine of the type **12** or **13** having the –CH(Br)CH_2NHC(Me) = NSO_2R' motif. Apparently, the reaction proceeds *via* the intermediate bromonium cation opened by acetonitrile and subsequently quenched with traces of water in the solvent (Scheme 6). Such a specific reactivity can be explained by the presence of a strong basic center in the molecule of the reagent – the methoxy group, which increases the nucleophilicity of water by hydrogen bonding to the ethereal oxygen atom.

THF, when used as the solvent, is a cyclic ether with the oxygen atom more basic than that of the methoxy group in *p*-methoxyphenylsulfonamide, and it directly participates in the reaction of oxidative sulfonamidation in the presence of NBS. Two Ritter-type products of solvent interception with the THF ring opening, with retention of the second double bond, were isolated from the reaction of silanes **2** and **3** with all types of sulfonamides ($TfNH_2$, $MsNH_2$, $ArSO_2NH_2$) – [1-bromo-2-(4-bromobutoxy)ethyl](diorganyl)vinylsilanes **15** and *N*-(4-{2-bromo-2-[diorganyl(vinyl)silyl]ethoxy}butyl)sulfonamides **16** (Scheme 7, Table 2).



Scheme 6 Possible mechanism of formation of β-silylated acetamide **14**.



R = Me (**2**), Ph (**3**).
R' = CF_3 (a), Me (b), Tol (c), *p*-$NO_2C_6H_4$ (d).

15 **16**

Scheme 7 NBS-induced reaction of (divinyl)silanes **2**, **3** with sulfonamides in THF.

Table 2 Products of the reaction of silanes **2** and **3** with sulfonamides in THF (Scheme 7), $R'SO_2NH_2$/NBS = 1 : 1

Entry	R	R′	Conversion, %	Yield[a], % **15**	**16**
1	Me	CF_3	80	8	89
2		Me	27	52	17
3		Tol	55	31	35
4		*p*-$NO_2C_6H_4$	59	9	80
5	Ph	CF_3	92	21	74
6		*p*-$NO_2C_6H_4$	87	18	72

[a] Isolated yields taking into account the conversion.

Table 3 Yields of the products of reaction of arensulfonamides with **12a** or **18** in MeCN (Scheme 10)

Substrate	Ar in $ArSO_2NH_2$	Yield of **19**, %
12a	*p*-ClC_6H_4	99
18	*p*-Tol	97
	p-$NO_2C_6H_4$	98

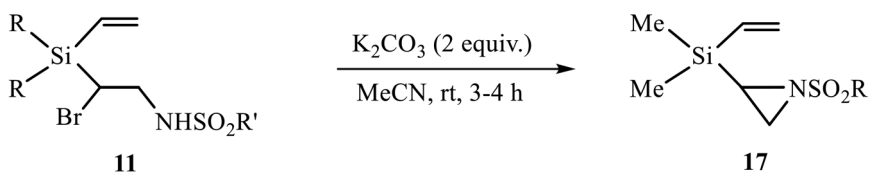
The analysis of Table 2 shows that the highest overall yield of ≥95% with high conversion is obtained in the reactions with triflamide (entries 1, 5). Also, good yields (~90%) are observed for nosylamide, although the conversion is somewhat lower (entries 4, 6). In all these reactions, the products of bromosulfonamidation strongly predominate. With tosylamide, and especially with mesylamide, the conversion and the yield are lower and, remarkably, the ratio of products **16 : 15** changes in favor of the latter. Therefore, both the absolute yield of the Ritter-type product of sulfonamidation **16**, and its predominance (ratio **16 : 15**) decrease with lowering the NH acidity of the reagent (on the example of silane **2**): 11 ($TfNH_2$) > 9 ($NsNH_2$) > 1.1 ($TsNH_2$) > 0.3 ($MsNH_2$).

The products of bromosulfonamidation **11–13**, **16** containing in one molecule simultaneously the bromine atom and the sulfonamide moiety with free NH group are potential precursors for the synthesis of various heterocycles *via* HBr elimination. Indeed, the products of bromoarenesulfonamidation **11** were successfully converted into the corresponding aziridines **17** by the reaction with excess potassium carbonate in almost quantitative yield (Scheme 8). In contrast, the similar product of bromotriflamidation of silane **3** did not enter the reaction. This result clearly demonstrates different reactivity of silanes **2** and **3**, and is in full agreement with the one reported earlier for the substrates similar to **11**, except the silyl substituent was Me_3Si, where no reaction occurred for R′ = CF_3 while for R′ = Ar the yields were practically quantitative.[11a]

The Ritter-type products **12**, **13** and **16** were also examined in the reaction of base-induced heterocyclization. Amidines **12** gave 5-[diorganyl(vinyl)silyl]-2-methyl-1-trifluoromethylsulfonyl-2-imidazolines **18** (Scheme 9).

The reaction in Scheme 9 proceeds under mild conditions and in almost quantitative yield, suggesting that, unlike in adducts **11**, a more remote triflyl group in amidines **12** does not prevent the formation of the product of heterocyclization.

In a hope to involve the second double bond of amidines **12** or imidazolines **18** in the reaction of bromosulfonamidation/heterocyclization, we tried the one-pot reaction by successive addition of amidine **12a** or imidazoline **18** (R = Ph) to the solution of arenesulfonamides and NBS in acetonitrile and two-fold

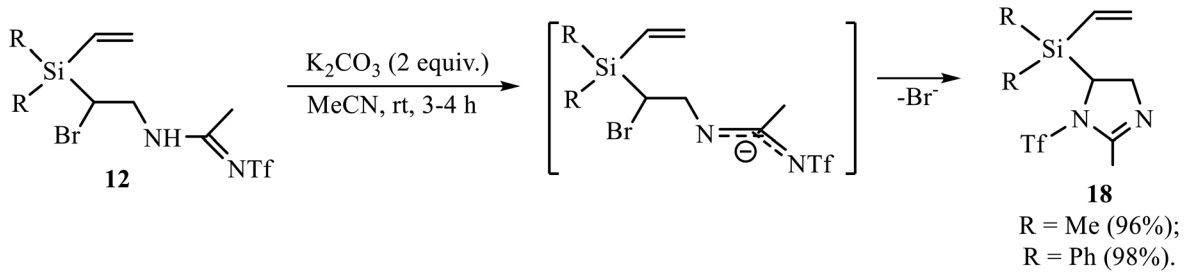


11 **17**

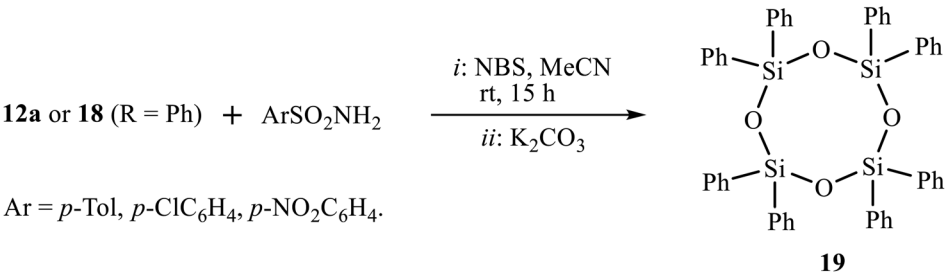
R = Ph, R' = CF_3 (a); R = Me, R' = Tol (c); R = Me, R' = *p*-$NO_2C_6H_4$ (d).

R = Ph, R' = CF_3, 0%; R = Me, R' = Tol, 95%; R = Me, R' = *p*-$NO_2C_6H_4$, 97%.

Scheme 8 Intramolecular dehydrobromination of compounds **11**.



Scheme 9 Dehydrobromination of amidines **12** to imidazolines **18**.

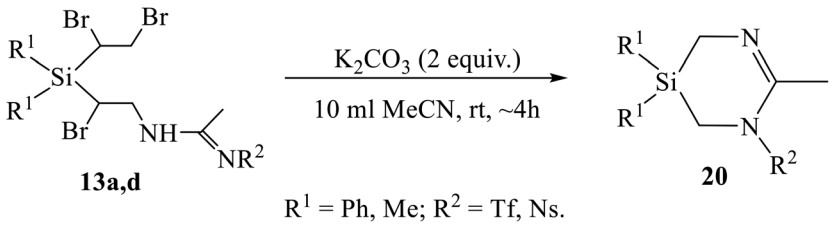


Scheme 10 Desilylation of compounds **12a** and **18** (R = Ph) in the system (NBS + K_2CO_3).

excess K_2CO_3. Surprisingly, instead of the expected bisimidazoline, the only product isolated in almost quantitative yield was 2,2,4,4,6,6,8,8-octaphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane **19** (Scheme 10). Cyclic siloxane **19** is a known compound[13] as a monomer for organosilicon polymers used as a precursor for the synthesis of phase-transfer catalysts. The structure of $(Ph_2SiO)_4$ **19** was proved by NMR spectroscopy, in particular, by comparison of its ^1H and ^{13}C spectra (7.48, 7.35, 7.19 ppm and 134.4, 134.3, 130.0, 127.6 ppm) with those reported in the literature (7.48, 7.36, 7.19 and 134.4, 130.1, 127.7 ppm).[13a] Presumably, fragmentation of the molecule is due to steric overcongestion of the expected product, which would have four bulky substituents at silicon (two phenyl groups and two secondary substituents of isopropyl type). The oxygen atoms, apparently, come from water eliminated from the reaction of the formed HBr with K_2CO_3.

One of the most interesting was the reaction of the Ritter-type products **13a**, **13b**, **13d**, having the 1,2-dibromoethyl substituent instead of the former vinyl group at silicon, with K_2CO_3. The compounds expected to be formed during dehydrobromination were heterocycles similar to azasilinanes (Scheme 3), aziridines (Scheme 8), or imidazolines (Scheme 9). However, neither of these expectations was confirmed. Instead, the previously unknown type of heterocycles, 1,3,5-diazasilinanes **20** were isolated in close to quantitative yield under very mild conditions by stirring amidines **13** with two-fold excess of K_2CO_3 in acetonitrile at room temperature (Scheme 11, Table 4). The structure of compounds **20** was unequivocally proved by the elemental analysis data and the presence of only three signals in the alicyclic part of the ^{13}C NMR spectra belonging to one CH_3 and two CH_2 groups (as proved by J_{mod} and proton-coupled ^{13}C NMR spectra), as well as by the intensity ratio of the signals in the ^1H NMR spectra (see ESI†).

To the best of our knowledge, the only so far known six-membered heterocycles with one silicon and two nitrogen atoms were 1,4,2-diazasilinanes prepared by insertion of N-heterocyclic carbenes into the Si–H bond.[14] The discovery of a new type of heterocycles is one of the most significant results of the present study. Although the detailed mechanism of the reaction in Scheme 11 deserves special consideration, a tentative mechanism including two successive eight- to six-membered ring contraction steps can be proposed (Scheme 12). The reaction starts with β-bromine substitution in **13** and formation of intermediate (**A**). An alternative mechanism with



Scheme 11 Based-induced dehydrobromination/heterocyclization of amidines **13a**, **13d**.

Table 4 Yields of the products of reaction of **13a**, **13d** with K_2CO_3 (Scheme 11)

Entry	R^1	R^2	Yield of **20**, %
1	Me	Tf	94
2	Ph	Tf	97
3		Ns	96

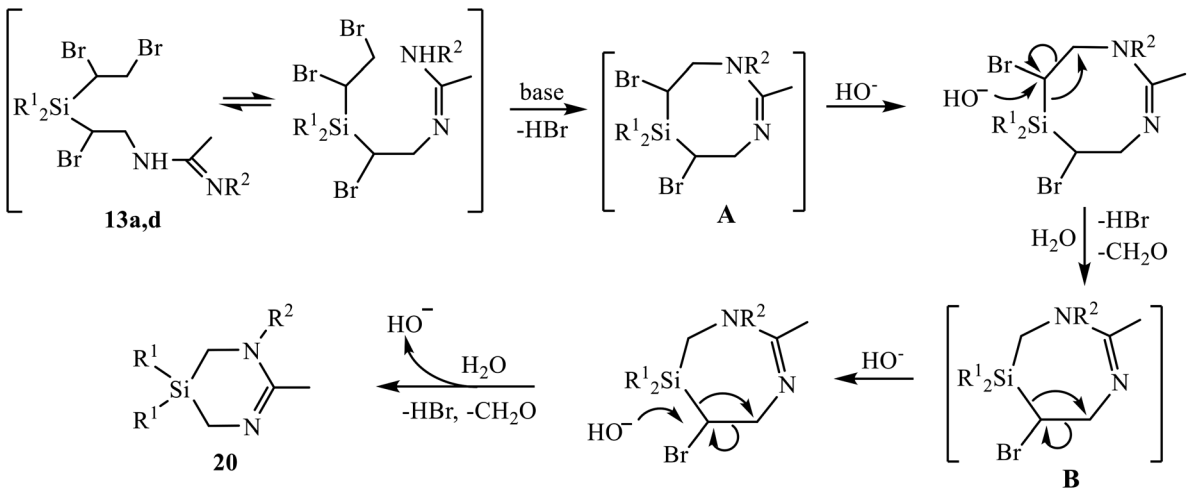
the nucleophile attacking the silicon atom in **A**, which might be preferable due to high oxophilicity of silicon, is sterically hindered by four bulky substituents, two Ph and two CHBr groups at silicon. Intermediate **A** undergoes two similar consecutive steps of nucleophilic attack on the CHBr group with the Si–CHBr bond rupture/Si–CH_2 bond formation/C–CHBr bond rupture, resulting in successive ring contraction **A** → **B** → **20**. This follows from the comparison of the reaction paths for amidines **12** and **13** in Schemes 9 and 11 differing only in one substituent at silicon: the vinyl group in **12** remains intact and the ring closure occurs within the α-bromo-β-amidino structural motif, whereas in adducts **13** the 1,2-dibromoethyl group is involved in heterocyclization. The leaving group $[HOCHBr]^-$ may react with water with elimination of HBr and CH_2O and regeneration of HO^- anion.

In a search for experimental evidences in support of the mechanism in Scheme 12, we performed ^1H NMR and GC-MS monitoring of the reaction mixture (**13d** + K_2CO_3, R^1 = Ph). Although no direct detection of specific structures was observed, the changes in the NMR spectrum (Fig. S73†) indicate the formation of reaction intermediates clearly distinct from the reagent. This is evidenced by disappearance of the multiplets at 3.0, 3.3, 4.3 and 4.4 ppm belonging to amidine **13d**, and the appearance of unresolved signals in the range 3.4–4.2 ppm, *which first increase and then decrease in intensity*, up to complete disappearance (Fig. S73†). Apparently, they belong to numerous methine and diastereotopic methylene protons in intermediates **A** and **B**, having chiral carbon atoms.

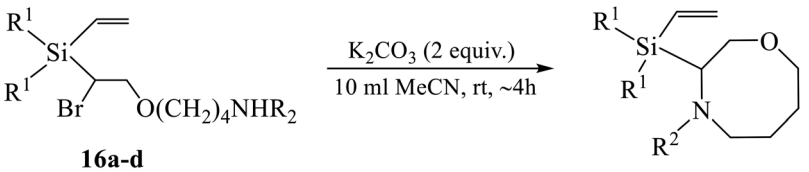
Transformations of intermediates **A** and **B** include the rupture of the Si–CHBr bonds. The possibility of such a process, at least by electron impact in mass spectrometry, is indicated by the presence of a doublet peak at *m*/*z* 261 and 263, belonging to $[Ph_2SiBr]^+$ ion in the mass spectrum.

Similar to Scheme 9, the replacement of the α-bromine atom was found to occur through the base-induced 1,8-cyclization of the THF interception products **16a–d** into the corresponding 1,4-oxazocanes **21** (Scheme 13, Table 5).

Remarkably, the yield of cyclization is practically quantitative for both derivatives of silane **3** (R^2 = Tf, Ns), whereas for the derivative of silane **2** with R^2 = Tf it is also close to 100%, but no reaction occurred with other sulfonamides (mesylamide,



Scheme 12 Tentative mechanism of formation of 1,3,5-diazasilinanes **20** by the based-induced dehydrobromination/heterocyclization of amidines **13a**, **13d**.



R^1 = Ph, Me; R^2 = Ms, Ts, Ns, Tf.

Scheme 13 Dehydrobromination of **16a–d** with potassium carbonate.

Table 5 Yields of the products of the reaction of **16a–d** with potassium carbonate (Scheme 13)

Entry	R^1	R^2	Yield of **21a–d**, %
1	Ph	Tf	99
2		Ns	98
3	Me	Ms	0
4		Ts	0
5		Ns	0
6		Tf	98

tosylamide or nozylamide). Comparison of entries 2 and 5 in Table 5 provides another evidence that the replacement of the methyl by the phenyl groups at silicon may play a decisive role in determining the feasibility of the reaction.

Conclusions

To summarize, divinylsilanes show diverse reactivity in oxidative sulfonamidation reactions, depending on the substituents at silicon, the oxidative system used and the solvent. In the oxidative system (*t*-BuOCl + NaI) the main reaction is halogenation of one or both double bonds; mono- and diaziridines are the minor products. With NBS, as the oxidant, the course of reaction is governed by nature of the substituent in sulfonamide and the solvent: in CH_2Cl_2 the products of bromination or bromosulfonamidation are formed, whereas in MeCN the Ritter-type products with interception of the solvent are formed with triflamide and nosylamide. In THF as the solvent, two Ritter-type products of solvent interception with opening of the THF ring and retention of the second double bond of the substrate were isolated, the major one being the products of bromosulfonamidation – *N*-(4-{2-bromo-2-[diorganyl(vinyl)silyl] ethoxy}butyl)sulfonamides. Such a dramatic change of the reaction course by simple variationof the substituent at silicon from the Me to the Ph group seems to be a striking phenomenon and deserves special consideration. Preliminarily, it can be assumed that is due to a combined action of different bulkiness and electronic effects of the two groups, as well as the Si–C bond lengths.

The base-induced cyclization of the products of bromoarenesulfonamidation gives rise to the corresponding aziridines in close to quantitative yield, whereas no reaction occurs with the similar product of bromotriflamidation. The Ritter-type products of bromotriflamidation formed in MeCN (amidines with the intact vinyl group at silicon) afford 5-silylated 2-methyl-1-(trifluoromethylsulfonyl)-2-imidazolines in almost quantitative yield. In contrast, in the reaction of amidines with the vinyl group at silicon brominated to 1,2-dibromoethyl group, 1,3,5-diazasilinanes, were obtained also in close to quantitative yield. The latter compounds are the first representatives of the so far unknown type of Si,N-containing heterocycles. A trial to involve the second double bond in the formation of the corresponding bisimidazolines led to desilylation and formation of cyclic siloxane D4 [$(Ph_2SiO)_4$] in practically quantitative yield. The base-induced heterocyclization of the Ritter-type products with the ring opening and interception of the THF molecule leads to 3-silylated 1,4-oxazocanes with the yield close to 100% for triflamide or nosylamide derivatives, but no reaction occurred with the mesylamide or tosylamide analogues.

Therefore, the present work, on the one hand, considerably increases the synthetic potential of unsaturated silanes in the reactions of oxidative sulfonamidation, and, on the other hand, when comparing with the previous studies, reveals the pivotal role of the substituent at silicon in determining the course and feasibility of the reactions leading to new heterocyclic and polyfunctional otherwise hardly accessible organosilicon compounds.

Experimental

General information

All starting materials have been previously described in literature. All products were identified by ^1H, ^{13}C, ^{19}F and ^{29}Si NMR spectroscopy and comparison with authentic samples. IR spectra were taken on a Bruker Vertex 70 spectrophotometer in KBr. NMR spectra were recorded in $CDCl_3$ and CD_3CN on Bruker DPX 400 spectrometer at working frequencies 400 (^1H), 100 (^{13}C), 376 (^{19}F) and 79.5 (^{29}Si) MHz. All shifts are reported in ppm relative to residual $CHCl_3$ peak [7.27 (^1H) and 77.2 (^{13}C) ppm] and CD_3CN peak [1.95 (^1H), 1.3 and 118 (^{13}C) ppm]. All coupling constants (*J*) are given in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; br s, broad singlet. Melting points were measured on a Boetius apparatus (VEB Analytik). Flash chromatography was performed on silica gel, 60 Å, 300 mesh. TLC analysis was carried out on aluminum plates coated with silica gel 60 F_{254}, 0.2 mm thickness, visualized by 254 nm UV lamp or aqueous $NaIO_4$ solutions. All NMR spectra are given in the ESI.†

Synthesis and characterization of compounds

Reaction of *p*-nitrobenzenesulfonamide with diphenyl(divinyl)silane 3 in the system t-BuOCl + NaI. To the solution of *p*-nitrobenzenesulfonamide (1.40 g, 7 mmol) and NaI (3.12 g, 21 mmol) in 70 ml CH_3CN diphenyl(divinyl)silane **3** (1.64 g, 7 mmol) was added, the mixture cooled to −30 °C, *t*-BuOCl (2.38 ml, 21 mmol) was added dropwise in the dark, the obtained mixture kept for 1.5 h at −30 °C, then 23 h at room temperature. After completion of the reaction, the solvent was removed at a reduced pressure, the residue dissolved in 50 ml of ethyl acetate and treated with 60 ml of aqueous $Na_2S_2O_3$. The extract was dried over CaCl, solvent removed in vacuum, the light-yellow residue (3.61 g) was placed in a column with coarse silica and eluted successively with hexane, Et_2O : hexane 1 : 1, Et_2O. From the hexane eluate, compounds **4** (1.33 g, 48%) and **5** (0.68 g, 17%) as a mixture of diastereomers were isolated. From ether–hexane eluate, light-yellow powder was obtained, which was purified on fine silica using hexane and hexane–ether 1 : 1 as eluents to give 2-(diphenyl(vinyl)silyl)-1-(4-nitrophenylsulfonyl)aziridine **6** (0.21 g, 20%) as white powder. From the first portion of Et_2O eluate, 0.35 g of unreacted *p*-nitrobenzenesulfonamide precipitated. From the nest portions,

a yellow powder was obtained, which was further purified on a column with coarse silica eluted with hexane and hexane–ether 1 : 1 to afford (0.09 g, 6%) of 1-(4-nitrophenylsulfonyl)-2-((1-(4-nitrophenylsulfonyl)aziridin-2-yl)diphenylsilyl)aziridine **7** as a white powder and 3,5-diiodo-1-(4-nitrophenylsulfonyl)-4,4-diphenyl-1,4-azasilinane **8** (for **8** the yields are given based on the ^{1}H NMR spectroscopy data).

Reaction of *p*-nitrobenzenesulfonamide with (2-chloro-1-iodoethyl)diphenyl(vinyl)silane 4 in the system *t*-BuOCl + NaI. The reaction of the solution of *p*-nitrobenzenesulfonamide (0.35 g, 1.7 mmol) and NaI (0.77 g, 5.1 mmol) with compound **4** (0.68 g, 1.7 mmol) was performed and treated as described above. The obtained light-yellow residue (1.07 g) was analyzed by NMR spectroscopy, which showed the presence of product **5** (76%) and unreacted **4** (8%).

Reaction of triflamide with diphenyl(divinyl)silane 3 and NBS in CH_2Cl_2. To the solution of triflamide (1.00 g, 6.7 mmol) and NBS (1.20 g, 6.7 mmol) in 70 ml CH_2Cl_2 silane **3** (1.58 g, 6.7 mmol) was added, the mixture kept for 20 h. Then, CH_2Cl_2 was removed at a reduced pressure, the residue dissolved in 70 ml of ether, succinimide filtered off, filtrate evaporated, the residue (3.79 g) separated by column chromatography eluting successively with hexane and hexane–ether 1 : 1. From the hexane extract, (1,2-dibromoethyl)diphenyl(vinyl)silane **9** (0.80 g, 30%) was isolated as light-yellow oil, from hexane–ether extract – unreacted triflamide (0.47 g) and yellow oil were obtained, which was purified by column chromatography on fine silica using hexane and hexane–ether 5 : 1 as eluents to give *N*-(2-bromo-2-(diphenyl(vinyl)silyl)ethyl)triflamide **11a** (0.76 g, 46%) (R = Ph) as a colorless oil crystallized upon long standing. The reaction with dimethyl(divinyl)silane **2** and treatment of the reaction mixture was carried out similarly. From hexane, (1,2-dibromoethyl)dimethyl(vinyl)silane **9** (0.97 g, 53%) was isolated as colorless liquid, from hexane–ether extract – unreacted triflamide (0.52 g) and yellow oil were obtained, which was purified on fine silica using hexane and hexane–ether 1 : 1 as eluents, to give *N*-(2-bromo-2-(dimethyl(vinyl)silyl)ethyl) triflamide **11a** (R = Me) (0.42 g, 39%) as a colorless oil.

Reaction of triflamide with diphenyl(divinyl)silane 3 and NBS in CH_3CN. The reaction of the solution of triflamide (1.00 g, 6.7 mmol) and NBS (1.20 g, 6.7 mmol) with silane **3** (1.58 g, 6.7 mmol) was performed and treated as described above. From the hexane extract, compound **9** (R = Ph) (0.23 g, 9%) was isolated, from hexane–ether extract – unreacted triflamide (0.28 g) and yellow oil were obtained. The latter was purified by column chromatography on fine silica using hexane and hexane–ether 2 : 1 as eluents to give *N*-(2-bromo-2-(diphenyl(vinyl)silyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acetamidine **12a** (R = Ph) (1.65 g, 68%) as a light-yellow oil. The reaction with dimethyl(divinyl) silane **2** and treatment of the reaction mixture was carried out similarly. From hexane, compound **9** (R = Me) (0.11 g, 6%) was isolated, from hexane–ether extract – unreacted triflamide (0.20 g) and *N*-(2-bromo-2-(dimethyl(vinyl)silyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acetamidine **12a** (R = Me) (1.82 g, 88%) as a light-yellow oil.

The reaction of triflamide with diphenyl(divinyl)silane 3 and 5-fold excess of NBS in CH_3CN. The reaction of triflamide with diphenyl(divinyl)silane **3** and **5**-fold excess of NBS in CH_3CN was performed as above and eluted successively with hexane and hexane–ether 1 : 1. From the hexane eluate, bis(1,2-dibromoethyl)diphenylsilane **10** (0.43 g, 12%) was isolated as a light-yellow oil, from hexane–ether extract – unreacted triflamide (0.19 g) and yellow oil, which was eluted on fine silica with hexane and hexane–ether–chloroform 1 : 4:1 to give *N*-(2-bromo-2-((1,2-dibromoethyl)diphenylsilyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acetamidine **13a** (R = Ph) (2.17 g, 60%) as an oil crystallized upon long standing. The reaction with silane **2** was performed and treated similarly to afford 0.63 g of unreacted triflamide and *N*-(2-bromo-2-((1,2-dibromoethyl) dimethylsilyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acetamidine **13a** (R = Me) (0.62 g, 46%).

Reaction of sulfonamides with dimethyl(divinyl)silane 2 in the presence of NBS in CH_3CN

General procedure. To a solution of 6.4–11.0 mmol of sulfonamide ($MsNH_2$, $TsNH_2$, $NsNH_2$) and 6.4–11.0 mmol of NBS in 70 ml CH_3CN dimethyl(divinyl)silane **2** (6.4–11.0 mmol) was added, the mixture kept for 20 h. Solvent was removed at a reduced pressure, the residue dissolved in 70 ml of ether, succinimide filtered off, filtrate evaporated, the residue (2.36–3.93 g) separated by column chromatography eluting successively with hexane and hexane–ether 1 : 1 (1 : 2). From the hexane eluate, compound **9** (R = Me) was isolated, from hexane–ether extract – the corresponding *N*-(2-bromo-2-(dimethyl(vinyl)silyl)ethyl)sulfonamide **11c**, **11d** (R = Me) and unreacted sulfonamide.

With $MsNH_2$. Compound **9** (R = Me) **$MsNH_2$.** Yield 2.43 g, 81%.

With $TsNH_2$. Compound **9** (R = Me) (0.18 g, 8%), unreacted tosylamide (0.87 g) and *N*-(2-bromo-2-(dimethyl(vinyl)silyl) ethyl)-4-methylbenzenesulfonamide **11c** (R = Me). (0.49 g, 37%).

With $NsNH_2$. Compound **9** (R = Me) (0.52 g, 30%), unreacted nosylamide (0.81 g) and *N*-(2-bromo-2-(dimethyl(vinyl)silyl) ethyl)-4-nitrobenzenesulfonamide **11d** (R = Me) (0.14 g, 15%).

Reaction of *p*-nitrobenzenesulfonamide with diphenyl(divinyl)silane 3 in the presence of NBS in CH_3CN. To the solution of *p*-nitrobenzenesulfonamide (1.00 g, 5.0 mmol) and NBS (3.52 g, 25 mmol) in 70 ml CH_3CN diphenyl(divinyl)silane **3** (1.17 g, 5.0 mmol) was added, the mixture kept for 20 h, solvent removed at a reduced pressure, the residue dissolved in 70 ml of ether, *N*-succinimide filtered off, filtrate evaporated, the residue (3.42 g) separated by column chromatography eluting successively with hexane and hexane–ether 1 : 2. From the hexane extract bis(1,2-dibromoethyl)diphenylsilane **10** (R = Ph) (0.39 g, 14%) was isolated as a light-yellow oil, from hexane–ether extract – unreacted nosylamide (0.21 g) and yellow oil, which was purified by column chromatography on fine silica with hexane and hexane–ether-chloroform 1 : 3:2 as eluents. *N*-(2-Bromo-2-((1,2-dibromoethyl)diphenylsilyl)ethyl)-*N*′-(4-nitrophenylsulfonyl)acetamidine **13d** (1.81 g, 65%) was obtained as a light-yellow oil crystallized upon long standing.

The reaction of the solution of 4-methoxybenzenesulfonamide (0.80 g, 4.3 mmol) with silane **3** (1.01 g, 4.3 mmol) and NBS (4.00 g, 21 mmol) in 70 ml CH_3CN was

performed and treated as above to afford compounds **9** (0.47 g, 28%) and **10** (0.25 g, 11% of diastereomeric mixture), as well as 0.47 g of unreacted 4-methoxybenzenesulfonamide and *N*-(2-bromo-2-(diphenyl(vinyl)silyl)ethyl)acetamide **14** (0.59 g, 40%) as a white powder.

Reaction of *p*-nitrobenzenesulfonamide with diphenyl(divinyl)silane 3 in the presence of NBS in THF. To the solution of triflamide (0.50 g, 3.4 mmol) or *p*-nitrobenzenesulfonamide (0.7 g, 3.5 mmol) and equimolar amount of NBS in 50 ml THF diphenyl(divinyl)silane **3** was added, the mixture was kept for 20 h, THF removed at a reduced pressure, the residue dissolved in 50 ml of ether, *N*-succinimide was filtered off, the filtrate concentrated, the residue separated by column chromatography eluting successively with hexane and hexane–ether 1 : 1. From hexane eluate, (1-bromo-2-(4-bromobutoxy)ethyl) diphenyl(vinyl)silane **15** (R = Ph) was obtained as colorless oil, from hexane/ether – *N*-(4-[2-bromo-2-(diphenyl(vinyl)silyl) ethoxy]butyl)sulfonamides **16**, which was purified on fine silica using hexane and hexane–ether 1 : 2 as eluents to give *N*-(4-(2-bromo-2-(diphenyl(vinyl)silyl)ethoxy)butyl)trifamide **16a** (R = Ph) (1.23 g, 74%) or *N*-(4-(2-bromo-2-(diphenyl(vinyl)silyl) ethoxy)butyl)-4-nitrobenzenesulfonamide **16d** (R = Ph) (1.28 g, 72%).

The reactions with silane **2** and treatment of the reaction mixture were performed similarly. From hexane eluate, (1-bromo-2-(4-bromobutoxy)ethyl)dimethyl(vinyl)silane **15** (R = Me) was obtained, from hexane/ether – *N*-(4-[2-bromo-2-(dimethyl(vinyl)silyl)ethoxy]butyl)sulfonamides **16**, which was purified on fine silica using hexane and hexane–ether 1 : 2 as eluents, and unreacted $TfNH_2$ (0.20 g), or $MsNH_2$ (0.73 g), $TsNH_2$ (0.68 g), $NsNH_2$ (0.53 g).

Reaction of *N*-((2-bromo-2-(diphenyl or dimethyl)(vinyl)silyl) ethyl)sulfonamides 11a, 11c, 11d with K_2CO_3. To the solution of **11a** (0.160 g, 0.35 mmol), **11c** (0.143 g, 0.51 mmol) or **11d** (0.137 g, 0.44 mmol) in 5 ml MeCN, 2 equiv. K_2CO_3 was added, the obtained mixture stirred for 5 h. The formed precipitate was filtered, solvent removed, the residue was dried in vacuum to give of 2-diphenyl- or -dimethyl(vinyl)silyl-1-(sulfonyl)aziridines **17**. No reaction of **11a** occurred with K_2CO_3, the reagent was recovered. Aziridines **17c** and **17d** are fully characterized in ref. 2.

Reaction of *N*-(2-bromo-2-(diphenyl- or -dimethyl(vinyl)silyl) ethyl)-*N*′-(trifluoromethylsulfonyl)acetamidine 12a with K_2CO_3. To the solution of *N*-(2-bromo-2-(diphenyl(vinyl)silyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acetamidine **12a** (R = Ph) (0.650 g, 1.29 mmol) or *N*-(2-bromo-2-(dimethyl(vinyl)silyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acetamidine **12a** (R = Me) (0.140 g, 0.37 mmol) in 10 ml MeCN, 2 equiv. K_2CO_3 was added, the obtained mixture stirred for 4 h. The formed precipitate was filtered, solvent removed, the residue dried in vacuum to give 5-(dimethyl(vinyl)silyl)-2-methyl-1-(trifluoromethylsulfonyl)-2-imidazoline **18** (R = Me) (0.106 g, 96%) or 5-(diphenyl(vinyl) silyl)-2-methyl-1-(trifluoromethylsulfonyl)-2-imidazoline **18** (R = Ph) (0.535 g, 98%).

Reaction of arensulfonamides with 12a and 18 (R = Ph) in the presence of NBS + K_2CO_3 in MeCN

General procedure. To the solution of arensulfonamides (0.49–1.20 mmol) and equimolar amount of NBS in 15 ml MeCN compound **12a** or **18** (R = Ph) was added and the mixture kept for 15 h. Then, K_2CO_3 (0.99–2.30 mmol) was added, the mixture kept for 4 h, filtered, the solvent removed, the residue dissolved in 50 ml of ether, *N*-succinimide filtered off, the filtrate concentrated, the residue purified by column chromatography eluting successively with hexane and chloroform. From chloroform eluate, 2,2,4,4,6,6,8,8-octaphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane **19** was obtained as white solid in close to quantitative yield (Table 3).

Reaction of (sulfonyl)acetamidines 13a and 13d with K_2CO_3. To the solution of **13a** or **13d** (0.10–0.27 g, 0.15–0.38 mmol) in 10 ml MeCN two-fold excess K_2CO_3 was added and stirred for 4 h. The formed precipitate was filtered, solvent removed, the residue dried in vacuum to give 1,3,5-diazasilinanes **20**: 2-methyl-5,5-diphenyl-1-((trifluoromethyl)sulfonyl)-1,3,5-diazasilinane **20a** (R = Ph) 0.058 g (97%), 2-methyl-1-((4-nitrophenyl)sulfonyl)-5,5-diphenyl-1,3,5-diazasilinane, **20d** (R = Ph) 0.164 g (96%), 2,5,5-trimethyl-1-((trifluoromethyl) sulfonyl)-1,3,5-diazasilinane **20a** (R = Me) 0.047 (94%).

Reaction of *N*-(4-[2-bromo-2-(diphenyl- or -dimethyl(vinyl) silyl)ethoxy]butyl)sulfonamides 16a–d with K_2CO_3. To the solution of *N*-(4-[2-bromo-2-(diphenyl(vinyl)silyl)ethoxy]butyl) sulfonamides **16a–d** (0.120–0.190 g, 0.20–0.35 mmol) in 10 ml MeCN, two-fold excess of K_2CO_3 was added and stirred for 4 h. The formed precipitate was filtered off, solvent removed and the residue dried in vacuum to give 1,4-oxazocane **21a** (0.159 g, 99%) (R = Ph) or 1,4-oxazocane **21d** (0.102 g, 98%) (R = Ph).

The reactions of *N*-(4-[2-bromo-2-(dimethyl(vinyl)silyl) ethoxy]butyl)sulfonamides **16a–d** with K_2CO_3 and treatment of the reaction mixtures were performed similarly to give **16a** (0.520 g, 1.26 mmol), **16b** (0.300 g, 0.84 mmol), **16c** (0.030 g, 0.069 mmol), or **16d** (0.220 g, 0.47 mmol). The residue was dried in vacuum to give 3-(dimethyl(vinyl) silyl)-4-(trifluoromethylsulfonyl)-1,4-oxazocane **21a** (R = Me) (0.411 g, 98%). No reactions occurred with **16b–d** (R = Me).

(2-Chloro-1-iodoethyl)diphenyl(vinyl)silane, 4 (R = Ph). Pink oil. 19% yield. IR (KBr) 3053, 3011, 2938, 1893, 1824, 1655, 1588, 1483, 1427, 1296, 1111, 1008, 964, 703, 645, 549, 495 cm^{-1}. ^1H NMR: 7.69–7.62 (m, C*H*, 4H), 7.51–7.42 (m, C*H*, 6H), 6.68 (dd, =C*H*, *J* 20.2, 14.7 Hz, 1H), 6.39 (dd, =CH*H*, *J* 14.7, 3.2 Hz, 1H), 5.87 (dd, =C*H*H, *J* 20.2, 3.2 Hz, 1H)), 4.05 (dd, *J* 11.6, 3.3 Hz, CH^AHCl, 1H), 3.91 (dd, *J* 11.6, 3.3 Hz, CHH^BCl, 1H), 3.83 (dd, *J* 11.6, 10.6 Hz, C*H*I, 1H). ^{13}C NMR): 138.4 (=CH_2), 135.7 (C_o), 135.4 (C_i), 132.2 (=*C*H), 130.3 (C_p), 128.1 (C_m), 49.0 (CH_2Cl), 15.9 (CHI). ^{29}Si NMR: −15.09. Anal. calcd for $C_6H_{16}ClISi$: C, 48.19; H, 4.04; I, 31.83; Cl, 8.89; Si, 7.04. Found: C, 48.11; H, 4.00; I, 31.06; Cl, 8.71; Si, 6.99.

Bis(2-chloro-1-iodoethyl)dimethylsilane, 5 (R = Me). Dark-orange oil, crystallizes after long standing, mp 107 °C. 8% yield. IR (KBr) 3066, 3018, 2933, 2246, 1963, 1893, 1822, 1588, 1484, 1428, 1294, 1233, 1193, 1112, 1064, 1020, 908, 733, 702, 645, 564, 488 cm^{-1}. ^1H NMR: 3.99 (dd, ClC*H*H, *J* 11.6, 8.6 Hz, 2H), 3.93 (dd, ClCH*H*, *J* 11.6, 5.0 Hz, 2H), 3.78–3.69 (m, IC*H*, 2H), 0.49 (s, CH_3, 6H, major *R*,*S*-diastereomer), 0.462 and 0.457

(s, CH_3, 6H, minor (*R*,*R* + *S*,*S*)-diastereomer). ^{13}C NMR: major diastereomer: 47.6 (CH_2Cl), 16.7 (*C*HI), −3.3 (CH_3); minor diastereomer: *δ* 47.9 (CH_2Cl), 17.0 (*C*HI), −2.1 and −3.8 (CH_3). ^{29}Si NMR: 9.5, 9.6. Anal. calcd for $C_6H_{12}Cl_2I_2Si$: C, 16.49; H, 2.77; Cl, 16.23; I, 58.09; Si, 6.43. Found: C, 16.38; H, 2.70; Cl, 16.11; I, 58.25; Si, 6.55.

Bis(2-chloro-1-iodoethyl)diphenylsilane, 5 (R = Ph). IR (KBr) 3066, 3018, 2933, 1963, 1893, 1822, 1588, 1484, 1428, 1294, 1233, 1193, 1112, 1064, 1020, 908, 733, 702, 645, 564, 488 cm^{-1}. ^{1}H NMR: 7.81–7.76 (m, C*H*, 1H), 7.75–7.66 (m, C*H*, 3H), 7.60–7.52 (m, C*H*, 2H), 7.51–7.43 (m, C*H*, 4H), 4.33 (dd, *J* 9.8, 6.1 Hz, C*H*^{A}H, 1H), 4.29 (dd, *J* 10.2, 5.8 Hz, C*H*$^{A\prime}$H, 1H), 3.88 (dd, *J* 11.8, 5.8 Hz, CH*H*$^{B\prime}$, 1H), 3.85 (dd, *J* 11.8, 6.1 Hz, CH*H*^{B}, 1H), 3.66 (dd, *J* 11.8, 9.8 Hz, C*H*, 1H), 3.62 (dd, *J* 11.8, 10.2 Hz, C*H*′, 1H). ^{13}C NMR: 136.6 (C_o), 136.5 ($C_o^{'}$), 131.29 (C_p), 131.21 ($C_p^{'}$), 131.0 (C_i), 128.4 (C_m), 128.2 ($C_m^{'}$), 47.6 (CH_2Cl), 47.3 (CH_2'Cl), 16.7 (*C*HI), 15.7 (*C*H′I). ^{29}Si NMR: −14.3, −14.7. Anal. calcd for $C_{16}H_{16}Cl_2I_2Si$: C, 34.25; H, 2.87; Cl, 12.64; I, 45.23; Si, 5.01. Found: C, 34.21; H, 2.82; I, 45.02; Cl, 12.19; Si, 4.97.

2-(Diphenyl(vinyl)silyl)-1-(4-nitrophenylsulfonyl)aziridine, 6. White solid. 20% yield. Mp 109 °C. IR (KBr) 3104, 3064, 3009, 1602, 1531, 1427, 1344, 1310, 1206, 1164, 1113, 1009, 960, 898, 856, 815, 747, 695, 617, 548, 497 cm^{-1}. ^{1}H NMR: 8.14 (d, *m*-C*H*, *J* 8.9 Hz, 2H), 7.97 (d, *o*-C*H*, *J* 8.9 Hz, 2H), 7.68–7.54 (m, C*H* (Ph), 4H), 7.48–7.36 (m, C*H* (Ph), 6H), 6.30–6.23 (m, =CH_2, 2H), 5.85–5.74 (m, =C*H*, 1H), 2.97 (d, C*H*HN, *J* 8.4 Hz, 1H), 2.52 (dd, C*H*N, *J* 8.4, 5.8 Hz, 1H), 2.26 (dd, CH*H*N, *J* 5.8 Hz, 1H). ^{13}C NMR: (mixture of diastereomers) 150.5 (C_p (Ns)), 143.6 (C_i (Ns)),139.0 (=*C*H_2), 135.4 (C_o (Ph)), 135.3 ($C_o^{'}$(Ph)), 130.99 (C_i (Ph)), 130.97 ($C_i^{'}$(Ph)), 130.3 (C_p (Ph)), 130.2 ($C_p^{'}$(Ph)), 129.1 (=*C*H), 129.1 (C_o (Ns)), 128.18 (C_m (Ph)), 128.14 ($C_m^{'}$(Ph)), 124.0 (C_m (Ns)), 30.3 (*C*H_2), 29.7 (*C*H). ^{29}Si NMR: −18.4. Anal. calcd for $C_{22}H_{20}N_2O_4SSi$: C, 60.53; H, 4.62; N, 6.42; S, 7.34; Si, 6.43. Found: C, 60.48; H, 4.60; N, 6.39; S, 7.22; Si, 6.35.

1-(4-Nitrophenylsulfonyl)-2-((1-(4-nitrophenylsulfonyl) aziridin-2-yl)diphenylsilyl)aziridine, 7. White solid. 6% yield. Mp 178 °C. IR (KBr) 3103, 3067, 2924, 2862, 1604, 1530, 1427, 1343, 1204, 1164, 1115, 1085, 951, 901, 857, 818, 739, 696, 617, 503 cm^{-1}. ^{1}H NMR: 8.11 (d, *m*-C*H*, *J* 8.9 Hz, 2H), 7.87 (d, *o*-C*H*, *J* 8.9 Hz, 2H), 7.46–7.34 (m, C*H* (Ph), 5H), 7.33–7.28 (m, C*H* (Ph), 3H), 7.24–7.14 (m, C*H* (Ph), 2H), 2.73 (d, C*H*HN, *J* 8.6 Hz, 2H), 2.43 (dd, C*H*N, *J* 8.6, 5.8 Hz, 1H), 2.10 (dd, CH*H*N, *J* 10.6, 5.8 Hz, 1H). ^{29}Si NMR: 5.5. Anal. calcd for $C_{28}H_{24}N_4O_8S_2Si$: C, 52.82; H, 3.80; N, 8.80; S, 10.07; Si, 4.41. Found: C, 52.66; H, 3.73; N, 8.69; S, 9.99; Si, 4.35.

(1,2-Dibromoethyl)dimethyl(vinyl)silane, 9 (R = Me). Colorless liquid. 0.97 g, 53% yield. IR (KBr) 3052, 3011, 2958, 1593, 1407, 1255, 1212, 1123, 1070, 1029, 1009, 959, 871, 840, 818, 789, 708, 628, 596, 542, 513 cm^{-1}. ^{1}H NMR: 6.19 (dd, =C*H*, *J* 18.8, 14.7 Hz, 1H), 6.12 (dd, =CH*H*, *J* 14.7, 5.2 Hz, 1H), 5.83 (dd, =C*H*H, *J* 18.5, 5.2 Hz, 1H), 3.93 (dd, C*H*H, *J* 11.9, 5.4 Hz, 1H), 3.83 (dd, C*H*, *J* 11.9, 9.6 Hz, 1H), 3.38 (dd, CH*H*, *J* 9.6, 5.4 Hz, 1H), 0.30 (s, CH_3, 6H). ^{13}C NMR: 135.0 (=*C*H_2), 134.8 (=*C*H), 41.9 (*C*HBr), 36.5 (*C*H_2Br), −3.8 (CH_3), −4.5 (CH_3). ^{29}Si NMR: −17.1. Anal. calcd for $C_6H_{12}Br_2Si$: C, 26.49; H, 4.45; Br, 58.74; Si, 10.32. Found: C, 26.45; H, 4.44; Br, 58.69; Si, 10.25.

(1,2-Dibromoethyl)diphenyl(vinyl)silane, 9 (R = Ph). Light-yellow oil. 0.80 g, 30% yield. IR (KBr) 3053, 3011, 2938, 1824, 1822, 1655, 1588, 1483, 1428, 1122, 1075, 1007, 963, 703, 645, 549, 495 cm^{-1}. ^{1}H NMR: 7.68–7.53 (m, C*H* (Ph), 4H), 7.53–7.36 (m, C*H* (Ph), 6H), 6.62 (dd, =C*H*, *J* 19.8, 15.1 Hz, 1H), 6.38 (d, =C*H*H, *J* 15.1 Hz, 1H), 5.88 (d, =CH*H*, *J* 19.8 Hz, 1H), 4.11 (d, C*H*H, *J* 11.4 Hz, 1H), 4.01 (d, C*H*H, *J* 11.4 Hz, 1H), 3.69 (tr, C*H*, *J* 11.4 Hz, 1H). ^{13}C NMR: 138.8 (=*C*H_2), 136.2 (C_o), 135.7 (C_p), 131.1 (=*C*H), 130.4 (C_i), 128.2 (C_m), 39.8 (*C*H_2), 37.1 (*C*H). ^{29}Si NMR: −16.4. Anal. calcd for $C_{16}H_{16}Br_2Si$: C, 48.50; H, 4.07; Br, 40.34; Si, 7.09. Found: C, 48.47; H, 4.05; Br, 40.18; Si, 7.00.

Bis(1,2-dibromoethyl)diphenylsilane, 10. Light-yellow oil. 12% yield. IR (KBr) 3064, 2933, 1742, 1700, 1651, 1519, 1425, 1271, 1216, 1115, 1022, 908, 869, 740, 699, 615, 555, 485 cm^{-1}.^{1}H NMR: 7.68 (tr, *m*-C*H*, *J* 7.2 Hz, 2H), 7.56 (d, *p*-C*H*, *J* 7.2 Hz, 1H), 7.48 (tr, *o*-C*H*, *J* 7.2 Hz, 2H), 4.38 (tr, C*H*, *J* 10.7 Hz, 1H), 4.37 (tr, C*H*, *J* 10.7 Hz, 1H), 3.94 (tr, CH*H*, *J* 4.5 Hz, 1H), 3.92 (tr, CH*H*, *J* 4.5 Hz, 1H), 3.51 (tr, C*H*H, *J* 10.9 Hz, 1H), 3.46 (tr, C*H*H, *J* 10.9 Hz, 1H). ^{13}C NMR: 136.3 (C_o), 131.4 (C_p), 128.5 (C_m), 127.1 (C_i), 38.3 (*C*H), 38.0 (*C*H), 35.0 (*C*H_2), 34.8 (*C*H_2). ^{29}Si NMR: −12.9, −13.9. Anal. calcd for $C_{16}H_{16}Br_4Si$: C, 34.56; H, 2.90; Br, 57.48; Si, 5.05. Found: C, 34.55; H, 2.85; Br, 57.39; Si, 5.00.

***N*-(2-Bromo-2-(diphenyl(vinyl)silyl)ethyl) trifluoromethanesulfonamide, 11a (R = Ph).** Colorless oil crystallizes upon long standing. 0.76 g, 46% yield. IR (KBr) 3318, 3063, 3016, 2945, 1962, 1896, 1826, 1724, 1592, 1426, 1374, 1197, 1144, 1115, 1073, 1011, 968, 846, 774, 707, 610, 548, 505 cm^{-1}. ^{1}H NMR: 7.68–7.64 (m, C*H* (Ph), 2H), 7.62–7.57 (m, C*H* (Ph), 2H), 7.53–7.48 (m, C*H* (Ph), 2H), 7.48–7.41 (m, C*H* (Ph), 4H), 6.58 (dd, =C*H*, *J* 20.1, 14.8 Hz, 1H), 6.41 (dd, =C*H*H, *J* 14.8, 3.3 Hz, 1H), 5.92 (dd, =CH*H*, *J* 20.1, 3.3 Hz, 1H), 5.40 (br. dd, N*H*, *J* 7.5, 2.8 Hz, 1H), 3.95 (dd, C*H*H, *J* 12.2, 2.8 Hz, 1H), 3.93 (dd, C*H*H, *J* 11.9, 2.8 Hz, 1H), 3.50 (ddd, C*H*, *J* 12.2, 11.9, 2.8 Hz, 1H). ^{13}C NMR: (mixture diastereomers) 139.3 (=*C*H_2), 135.77 (C_o), 135.70 ($C_o^{'}$), 130.72 (C_p), 130.71 ($C_p^{'}$), 130.45 (=*C*H), 130.2 (C_i), 128.41 (C_m), 128.38 ($C_m^{'}$), 119.57 (q, *J* 320.9 Hz, CF_3), 47.7 (*C*H_2NH), 39.0 (*C*HBr). ^{19}F NMR: −77.3. ^{29}Si NMR: −17.0. Anal. calcd for $C_{17}H_{17}BrF_3NO_2SSi$: C, 43.97; H, 3.69; N, 3.02; Br, 17.21; S, 6.91; F, 12.27; Si, 6.05. Found: C, 43.93; H, 3.66; N, 2.98; Br, 17.11; S, 6.89; F, 11.98; Si, 5.93.

***N*-(2-Bromo-2-(dimethyl(vinyl)silyl)ethyl) trifluoromethanesulfonamide, 11a (R = Me).** Colorless oil. 0.42 g, 39% yield. IR (KBr) 3310, 2960, 1717, 1594, 1427, 1375, 1256, 1233, 1196, 1146, 1072, 1010, 962, 841, 822, 786, 704, 609, 578, 478 cm^{-1}. ^{1}H NMR: 6.1422 (dd, =C*H*H, *J* 14.0, 9.5 Hz, 1H), 6.1421 (dd, =C*H*, *J* 19.3, 14.0 Hz, 1H), 5.85 (ddd, =CH*H*, *J* 19.3, 9.5, 5.7 Hz, 1H), 5.35 (br. s, NH, 1H) 3.79 (ddd, C*H*^{A}H, *J* 14.1, 7.6, 2.6 Hz, 1H), 3.47 (ddd, C*H*, *J* 14.1, 11.1, 3.2 Hz, 1H), 3.37 (dd, CH*H*^{B}, *J* 11.1, 2.6 Hz, 1H), 0.29 (s, CH_3, 3H), 0.28 (s, CH_3, 3H). ^{13}C NMR: 135.8 (=*C*H_2), 133.9 (=*C*H), 119.5 (q, *J* 318.3 Hz, CF_3), 47.6 (*C*H_2N), 41.4 (*C*HBr), −4.5 (CH_3), −4.1 (CH_3). ^{19}F NMR: −77.2. ^{29}Si NMR: −17.7. Anal. calcd for $C_7H_{13}BrF_3NO_2SSi$: C, 24.71; H, 3.85; N, 4.12; Br, 23.49; S, 9.42; F, 16.75.

***N*-(2-Bromo-2-(dimethyl(vinyl)silyl)ethyl)-4-methylbenzenesulfonamide, 11c (R = Me).** Light-yellow oil. 0.49 g, 37% yield. IR (KBr) 3284, 3051, 2956, 2924, 1919, 1597,

1494, 1406, 1330, 1252, 1161, 1091, 1009, 959, 816, 782, 706, 665, 550 cm^{-1}. ^1H NMR: 7.74 (d, *m*-C*H*, *J* 7.9 Hz, 2H), 7.32 (d, *o*-C*H*, *J* 7.9 Hz, 2H), 6.12–6.06 (m, =CH_2, 2H), 5.77 (ddd, =C*H*, *J* 18.8, 10.3, 5.4 Hz, 1H), 4.88 (br. dd, N*H*, *J* 7.1, 4.3 Hz, 1H), 3.47 (ddd, C*H*H, *J* 13.6, 7.9, 2.7 Hz, 1H), 3.26 (dd, C*H*H, *J* 10.1, 2.7 Hz, 1H), 3.16 (ddd, C*H*, *J* 13.6, 10.1, 4.1 Hz, 1H), 2.44 (s, CH_3Ph, 3H), 0.217 (s, CH_3, 3H), 0.211 (s, CH_3, 3H). ^{13}C NMR: 143.7 (C_p), 136.9 (C_i), 135.1 (=CH_2), 134.6 (=*C*H), 129.8 (C_m), 127.1 (C_o), 46.4 (*C*HBr), 41.5 (CH_2NH), 21.6 (*C*H_3Ph), −4.4 (CH_3), −4.9 (CH_3). ^{29}Si NMR: −4.0. Anal. calcd for $C_{13}H_{20}BrNO_2SSi$: C, 43.09; H, 5.56; N, 3.87; Br, 20.05; S, 8.85; Si, 7.75. Found: C, 43.03; H, 5.55; N, 3.82; Br, 19.98; S, 8.80; Si, 7.71.

***N*-(2-Bromo-2-(dimethyl(vinyl)silyl)ethyl)-4-nitrobenzenesulfonamide, 11d.** White solid. 0.14 g, 15% yield. mp 106 °C. IR (KBr) 3308, 3107, 2957, 1607, 1532, 1405, 1350, 1312, 1253, 1168, 1091, 1011, 961, 854, 820, 785, 738, 685, 610, 548, 465 cm^{-1}. ^1H NMR: 8.38 (d, *m*-C*H*, *J* 8.8 Hz, 2H), 8.06 (d, *o*-C*H*, *J* 8.8 Hz, 2H), 6.17–6.03 (m, =CH_2, 2H), 5.88–5.74 (m, 1H), 5.15 (br. dd, N*H*, *J* 6.9, 3.9 Hz, 1H), 3.56 (ddd, C*H*H, *J* 13.1, 7.3, 2.3 Hz, 1H), 3.28 (dd, C*H*H, *J* 10.5, 2.3 Hz, 1H), 3.21 (ddd, C*H*, *J* 13.1, 10.5, 4.1 Hz, 1H), 0.239 (s, CH_3, 3H), 0.231 (s, CH_3, 3H). ^{13}C NMR: 150.2 (C_p), 145.9 (C_i),135.4 (=CH_2), 134.2 (=*C*H), 128.3 (C_o), 124.5 (C_m), 46.5 (*C*HBr), 41.2 (CH_2NH), −4.4 (CH_3), −5.0 (CH_3). ^{29}Si NMR: −3.7. Anal. calcd for $C_{12}H_{17}BrN_2O_4SSi$: C, 36.64; H, 4.36; N, 7.12; Br, 20.31; S, 8.15; Si, 7.14. Found: C, 36.63; H, 4.32; N, 7.09; Br, 20.26; S, 8.04; Si, 7.10.

***N*-(2-Bromo-2-(diphenyl(vinyl)silyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acetamidine, 12a (R = Ph).** Light-yellow oil. 68% yield. IR (KBr) 3333, 3063, 2945, 1582, 1428, 1324, 1210, 1135, 1053, 968, 912, 776, 737, 705, 656, 598, 542, 497 cm^{-1}. ^1H NMR: 7.69–7.64 (m, C*H* (Ph), 2H), 7.63–7.58 (m, C*H* (Ph), 2H), 7.50–7.39 (m, C*H* (Ph), 2H), 6.73 (br. tr, N*H*, *J* 4.7, 1H), 6.58 (dd, =C*H*, *J* 20.2, 14.5 Hz, 1H), 6.39 (dd, =C*H*H, *J* 14.5, 3.3 Hz, 1H), 5.91 (dd, =CH*H*, *J* 20.2, 3.3 Hz, 1H), 4.72 (ddd, CH*H*, *J* 14.7, 6.1, 3.0 Hz, 1H), 4.08 (dd, C*H*H, *J* 10.9, 3.0 Hz, 1H), 3.50 (ddd, C*H*, *J* 14.7, 10.9, 4.7 Hz, 1H), 2.38 (s, CH_3, 3H). ^{13}C NMR: 168.7 (C=N), 139.0 (=CH_2), 135.78 (C_o), 130.6 (=*C*H), 130.5 (C_p), 128.5 (C_i), 128.3 (C_m), 119.4 (q, *J* 319.7 Hz, CF_3), 45.9 (CH_2NH), 36.6 (*C*HBr), 22.0 (CH_3). ^{19}F NMR: −79.0. ^{29}Si NMR: −16.7. Anal. calcd for $C_{19}H_{20}BrF_3N_2O_2SSi$: C, 45.15; H, 3.99; N, 5.54; Br, 15.81; S, 6.34; F, 11.28; Si, 5.56. Found: C, 45.14; H, 3.97; N, 5.52; Br, 15.73; S, 6.29; F, 11.08; Si, 5.50.

***N*-(2-Bromo-2-(dimethyl(vinyl)silyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acetamidine, 12a (R = Me).** Light-yellow oil. 88% yield. IR (KBr) 3332, 2958, 1585, 1560, 1422, 1323, 1254, 1212, 1137, 1052, 961, 844, 823, 773, 740, 660, 598, 476 cm^{-1}. ^1H NMR: 6.44 (br. s, NH, 1H), 6.21–6.08 (m, =CH_2, 2H), 5.84 (ddd, =CH, *J* 17.4, 11.4, 5.1 Hz, 1H), 4.13 (dd, *J* 13.4, 6.2 Hz, 1H), 3.47–3.34 (m, 2H), 2.51 (s, CH_3C=N, 3H), 0.28 (s, CH_3, 3H), 0.27 (s, CH_3, 3H). ^{13}C NMR: 168.6 (C=N), 135.4 (=CH_2), 134.0 (=*C*H), 119.4 (q, *J* 319.4 Hz, CF_3), 45.9 (CH_2N), 39.1 (*C*HBr), 22.1 (*C*H_3C=N), −4.8 (CH_3), −5.2 (CH_3). ^{19}F NMR: −79.2. ^{29}Si NMR: −3.6. Anal. calcd for $C_9H_{16}BrF_3N_2O_2SSi$: C, 28.35; H, 4.23; N, 7.35; Br, 20.96; S, 8.41; F, 14.95; Si, 7.37. Found: C, 28.33; H, 4.20; N, 7.34; Br, 20.87; S, 8.34; F, 14.86; Si, 7.29.

***N*-(2-Bromo-2-((1,2-dibromoethyl)diphenylsilyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acet-amidine, 13a (R = Ph).** Light-yellow oil crystallizes upon long standing. 60% yield. mp 155 °C. IR (KBr) 3332, 3131, 3071, 2943, 1965, 1894, 1825, 1579, 1552, 1428, 1325, 1209, 1133, 1053, 910, 736, 704, 655, 601, 487 cm^{-1}. ^1H NMR: (mixture of diastereomers) 7.80–7.62 (m, C*H* (Ph), 8H), 7.61–7.41 (m, C*H* (Ph), 12H), 6.47–6.33 (br. m, N*H*, 1H), 4.52 (dd, *J* 11.2, 2.9 Hz, 1H), 4.47 (dd, *J* 10.5, 3.1 Hz, 1H), 4.37–4.31 (m, 2H), 4.26 (ddd, *J* 14.8, 6.4, 2.9 Hz, 1H), 4.20 (ddd, *J* 14.8, 5.9, 3.1 Hz, 1H), 3.90 (dd, *J* 11.2, 4.6 Hz, 1H), 3.86 (dd, *J* 11.0, 5.1 Hz, 1H), 3.55 (tr, *J* 10.7 Hz, 1H), 3.49 (tr, *J* 11.1 Hz, 1H), 3.35 (ddd, *J* 15.0, 10.3, 4.9 Hz, 1H), 3.18 (ddd, *J* 14.9, 11.2, 4.5 Hz, 1H), 2.4 (s, CH_3, 3H), 2.36 (s, CH_3, 3H). ^{13}C NMR: 169.3 (C=N), 169.2 (C=N), 136.2 (C_o), 136.1 (C_o'), 131.6 (C_p), 131.5 (C_p'), 128.6 (C_m), 128.5 (C_m'), 127.3 (C_i), 127.2 (C_i'), 119.4 (q, *J* 320.2 Hz, CF_3), 45.3 (CH_2NH), 45.1 (CH_2NH), 37.6 (*C*HBr), 36.6 (*C*HBr), 36.0 (*C*HBr), 35.8 (*C*HBr), 34.7 (CH_2Br), 34.5 (CH_2Br), 21.8 (CH_3). ^{19}F NMR: −78.7, −78.8. ^{29}Si NMR: −11.1, −12.2. Anal. calcd for $C_{19}H_{20}Br_3F_3N_2O_2SSi$: C, 34.30; H, 3.03; N, 4.21; Br, 36.03; S, 4.82; F, 8.57; Si, 4.22. Found: C, 34.26; H, 3.00; N, 4.20; Br, 35.88; S, 4.71; F, 8.40; Si, 4.09.

***N*-(2-Bromo-2-((1,2-dibromoethyl)dimethylsilyl)ethyl)-*N*′-(trifluoromethylsulfonyl)acet-amidine, 13a (R = Me).** Light-yellow oil. 46% yield. IR (KBr) 3040, 2940, 2824, 2546, 2334, 2220, 2120, 1911, 1876, 1704, 1620, 1567, 1490, 1401, 1335, 1250, 1160, 1120, 1000, 950, 811, 773, 706, 544 cm^{-1}. ^1H NMR: 6.82 (br. s, N*H*, 1H), 4.18–4.11 (m, 1H), 3.97–3.88 (m, 1H), 3.86–3.66 (m, 3H), 3.56–3.45 (m, 1H), 2.53 (s, CH_3C=N, 3H), 0.41–0.33 (m, CH_3, 6H). ^{13}C NMR: 168.86 (*C*=N), 168.80 (*C*=N), 119.4 (q, *J* 320.9 Hz, CF_3), 45.59 (CH_2NH), 45.49 (CH_2NH), 38.4 (*C*HBr), 38.1 (*C*HBr), 38.8 (*C*HBr), 37.9 (*C*HBr), 34.6 (CH_2Br), 34.3 (CH_2Br), 22.26 (CH_3), 22.24 (CH_3), −5.2, −5.3, −5.4, −5.6 (CH_3Si). ^{19}F NMR: −78.9, −79.0. ^{29}Si NMR: 6.0, 5.7. Anal. calcd for $C_9H_{16}Br_3F_3N_2O_2SSi$: C, 19.98; H, 2.98; N, 5.18; Br, 44.30; S, 5.93; F, 10.53; Si, 5.19. Found: C, 19.97; H, 2.95; N, 5.15; Br, 44.23; S, 5.89; F, 10.41; Si, 5.14.

***N*-(2-Bromo-2-((1,2-dibromoethyl)diphenylsilyl)ethyl)-*N*′-(4-nitrophenylsulfonyl)acetamidine, 13d (R = Ph).** Light-yellow oil crystallizes upon long standing. 60% yield. mp 79 °C. IR (KBr) 3309, 3103, 3019, 2926, 1774, 1709, 1529, 1428, 1349, 1290, 1148, 1091, 1051, 855, 745, 699, 656, 500, 464 cm^{-1}. ^1H NMR: 8.27 (d, *m*-C*H* (Ns), *J* 8.3 Hz, 2H), 8.04 (d, *o*-C*H* (Ns), *J* 8.3 Hz, 2H), 7.62–7.58 (m, C*H* (Ph), 2H), 7.52–7.46 (m, C*H* (Ph), 3H) 7.45–7.32 (m, C*H* (Ph), 5H), 6.28 (br. tr, NH, *J* 5.2 Hz, 1H), 4.42 (d, *J* 10.2, 1H), 4.22 (dd, *J* 8.7, 3.9 Hz, 1H), 4.10–4.20 (m, 1H), 3.92 (d, *J* 10.2 Hz, 1H), 3.82–3.72 (m, 1H), 3.30–3.19 (m, 1H), 2.35 (s, CH_3, 3H). ^{13}C NMR: (Mixture of diastereomers) 166.5 (C=N), 149.5 (C_p (Ns)), 145.8 (C_i (Ns)), 136.33 (C_o (Ph)), 136.31 (C_o'(Ph)), 131.15 (C_p (Ph)), 131.12 (C_p'(Ph)), 128.32 (C_m (Ph)), 128.29 (C_m'(Ph)), 128.2 (C_i (Ph)), 127.8 (C_i'(Ph)), 127.7 (C_o (Ns)), 124.1 (C_m (Ns)), 44.9 (CH_2NH), 40.2 (*C*HBr), 36.2 (*C*HBr), 29.6 (CH_2Br), 21.4 (CH_3). ^{29}Si NMR: −12.9, −13.9. Anal. calcd for $C_{24}H_{24}Br_3N_3O_4SSi$: C, 40.13; H, 3.37; N, 5.85; Br, 33.37; S, 4.46; Si, 3.91. Found: C, 40.11; H, 3.36; N, 5.82; Br, 33.27; S, 4.38; Si, 3.87.

***N*-(2-Bromo-2-(diphenyl(vinyl)silyl)ethyl)acetamide, 14.** White powder. 40% yield. mp 158 °C. IR (KBr) 3415, 3283, 3064,

2928, 2884, 1653, 1536, 1428, 1366, 1284, 1193, 1145, 1112, 1098, 1007, 961, 911, 705, 606, 544, 513 cm^{-1}. ^1H NMR: 7.66–7.56 (m, C*H*, 4H), 7.50–7.40 (m, C*H*, 6H), 6.57 (dd, =C*H*, *J* 20.1, 14.7 Hz, 1H), 6.38 (dd, =C*H*H, *J* 14.7, 3.2 Hz, 1H), 5.92 (br. s, N*H*, 1H), 5.85 (dd, =CH*H*, *J* 20.1, 3.2 Hz, 1H), 3.84 (d.tr, *J* 9.9, 2.8 Hz, CH, 1H), 3.61–3.49 (m, 1H, C*H*HN), 3.49–3.39 (m, 1H, CH*H*N), 1.86 (s, CH_3, 3H). ^{13}C NMR: 171.7 (C=O), 139.5 (=*C*H), 135.8 (C_o), 135.7 ($C_o^{'}$), 130.7 (C_p), 130.6 ($C_p^{'}$), 130.2 (C_i), 130.1 ($C_i^{'}$), 130.0 (=*C*H), 128.5 (C_m), 128.4 ($C_m^{'}$), 46.2 (*C*H_2N), 42.1 (*C*HBr), 23.0 (CH_3). ^{29}Si NMR: −18.9. Anal. calcd for $C_{18}H_{20}$BrNOSi: C, 57.75; H, 5.39; N, 3.74; Br, 21.34; Si, 7.50. Found: C, 46.37; H, 4.31; N, 4.79; Br, 3.83; Si, 7.50.

(1-Bromo-2-(4-bromobutoxy)ethyl)diphenyl(vinyl)silane, 15 (R = Ph). Colorless oil. Yield 18–21%. IR (KBr) 3053, 3008, 2942, 2861, 1962, 1895, 1825, 1725, 1656, 1590, 1429, 1364, 1255, 1193, 1111, 1007, 962, 706, 652, 549, 501 cm^{-1}. ^1H NMR: 7.70–7.59 (m, C*H* (Ph), 4H), 7.47–7.37 (m, C*H* (Ph), 6H), 6.62 (dd, =C*H*, *J* 20.4, 14.7 Hz, 1H), 6.34 (dd, =C*H*H, *J* 14.7, 3.5 Hz, 1H), 5.84 (dd, =CH*H*, *J* 20.4, 3.5 Hz, 1H), 3.95 (dd, *J* 8.0, 3.5 Hz, 1H), 3.88 (dd, *J* 11.1, 3.5 Hz, 1H), 3.76 (dd, *J* 11.1, 8.0 Hz, 1H), 3.46–3.37 (m, 4H), 1.95–1.86 (m, 2H), 1.72–1.66 (m, 2H). ^{13}C NMR: (Mixture of diastereomers) 137.7 (=*C*H_2), 135.85 (C_o), 135.82 ($C_o^{'}$), 132.3 (=*C*H), 132.18 (C_i), 132.07 ($C_i^{'}$), 130.06 (C_p), 130.05 ($C_p^{'}$), 127.97 (C_m), 127.96 ($C_m^{'}$), 72.8 (CH*C*H_2O), 69.8 (O*C*H_2CH_2), 37.1 (CHBr), 37.1 (CHBr), 33.9 (CH_2Br), 29.5 (OCH_2*C*H_2), 28.1 (CH_2*C*H_2Br). ^{29}Si NMR: −20.0. Anal. calcd for $C_{20}H_{24}Br_2OSi$: C, 51.30; H, 5.17; Br, 34.13; Si, 6.00. Found: C, 51.27; H, 5.10; Br, 33.85; Si, 5.76.

(1-Bromo-2-(4-bromobutoxy)ethyl)dimethyl(vinyl)silane, 15 (R = Me). Colorless liquid. Yield 8–52%. IR (KBr) 3050, 2946, 2867, 1593, 1478, 1439, 1406, 1356, 1251, 1110, 1009, 956, 841, 822, 780, 648, 610, 561, 515 cm^{-1}. ^1H NMR: 6.17 (dd, =C*H*, *J* 19.8, 14.7 Hz, 1H), 6.06 (dd, =C*H*H, *J* 14.7, 4.0 Hz, 1H), 5.78 (dd, =CH*H*, *J* 19.8, 4.0 Hz, 1H), 3.80 (dd, *J* 11.1, 4.0 Hz, 1H), 3.71 (dd, CHBr, *J* 11.1, 8.0 Hz, 1H), 3.55–3.42 (m, 4H), 3.39 (dd, CHBr, *J* 8.0, 4.0 Hz, 1H), 2.01–1.94 (m, 2H), 1.77–1.70 (m, CH_2CH_2, 2H), 0.247 (s, CH_3, 3H), 0.244 (s, CH_3, 3H). ^{13}C NMR: 135.9 (=*C*H), 133.9 (=*C*H_2), 73.0 (CH*C*H_2O), 69.9 (O*C*H_2CH_2), 39.9 (*C*HBr), 33.8 (*C*H_2Br), 29.7 (OCH_2*C*H_2), 28.2 (CH_2*C*H_2N), −4.0 (CH_3), −4.4 (CH_3). ^{29}Si NMR: −4.3. Anal. calcd for $C_{10}H_{20}Br_2OSi$: C, 34.90; H, 5.86; Br, 46.43; Si, 8.16. Found: C, 34.87; H, 5.85; Br, 46.39; Si, 8.13.

***N*-(4-(2-Bromo-2-(diphenyl(vinyl)silyl)ethoxy)butyl) trifluoromethanesulfonamide, 16a (R = Ph).** Colorless oil. 74% yield. IR (KBr) 3320, 3061, 2943, 2868, 1962, 1898, 1827, 1709, 1591, 1429, 1371, 1193, 1112, 966, 860, 709, 609, 549, 503 cm^{-1}. ^1H NMR: 7.66–7.57 (m, C*H* (Ph), 4H), 7.46–7.39 (m, C*H* (Ph), 6H), 6.59 (dd, =C*H*, *J* 20.3, 14.7 Hz, 1H), 6.35 (dd, =C*H*H, *J* 14.7, 3.2 Hz, 1H), 5.84 (dd, =CH*H*, *J* 20.3, 3.2 Hz, 1H), 5.75 (br. tr, N*H*, *J* 5.1 Hz, 1H), 3.97–3.88 (m, 2H), 3.75 (dd, *J* 10.8, 8.9 Hz, 1H), 3.48–3.41 (m, 2H), 3.34–3.25 (m, 2H), 1.71–1.64 (m, 4H). ^{13}C NMR: (mixture of diastereomers) 138.1 (=*C*H_2), 135.78 (C_o), 135.74 ($C_o^{'}$), 131.80 (=*C*H), 131.85 (C_i), 131.76 ($C_i^{'}$), 130.16 (C_p), 130.15 ($C_p^{'}$), 128.04 (C_m), 128.02 ($C_m^{'}$),119.7 (q, *J* 321.3 Hz, CF_3), 72.9 (CH*C*H_2O), 70.4 (O*C*H_2CH_2), 44.0 (CH_2N), 36.9 (CHBr), 27.7 (OCH_2*C*H_2), 26.4 (CH_2*C*H_2N). ^{19}F NMR: −77.1. ^{29}Si NMR: −16.8. Anal. calcd for $C_{21}H_{25}BrF_3NO_3SSi$: C, 47.01; H, 4.70; N, 2.61; Br, 14.89; S, 5.98; F, 10.62; Si, 5.24. Found: C, 47.00; H, 4.65; N, 2.59; Br, 14.52; S, 5.90; F, 10.30; Si, 5.18.

***N*-(4-(2-Bromo-2-(diphenyl(vinyl)silyl)ethoxy)butyl)-4-nitrobenzenesulfonamide, 16d (R = Ph).** Colorless oil. 72% yield. IR (KBr) 3296, 3063, 2940, 2866, 1823, 1601, 1530, 1426, 1347, 1164, 1107, 1009, 966, 911, 854, 736, 613, 548, 503, 466 cm^{-1}. ^1H NMR: 8.33 (d, *m*-C*H* (Ns), *J* 8.6 Hz, 2H), 8.05 (d, *o*-C*H* (Ns), *J* 8.6 Hz, 2H), 7.68–7.54 (m, C*H* (Ph), 4H), 7.48–7.36 (m, C*H* (Ph), 6H), 6.58 (dd, =C*H*, *J* 20.3, 14.7 Hz, 1H), 6.34 (dd, =C*H*H, *J* 14.7, 3.3 Hz, 1H), 5.84 (dd, =CH*H*, *J* 20.3, 3.3 Hz, 1H), 5.32 (br. tr, N*H*, *J* 5.7 Hz, 1H), 3.39 (dd, *J* 8.9, 3.0 Hz, 1H), 3.87 (dd, *J* 11.3, 3.0 Hz, 1H), 3.70 (dd, *J* 11.3, 8.9 Hz, 1H), 3.44–3.32 (m, 2H), 3.11–2.95 (m, 2H), 1.62–1.51 (m, 4H). ^{13}C NMR: 149.9 (C_p (Ns)), 146.2 (C_i (Ns)), 138.1 (=*C*H_2), 135.7 (C_o), 131.8 (=*C*H), 131.7 (C_i), 130.1 (C_p), 128.3 (C_o (Ns)), 128.0 (C_m), 124.3 (C_m (Ns)), 72.8 (CH*C*H_2O), 70.3 (O*C*H_2CH_2), 43.1 (CH_2N), 37.5 (CHBr), 27.1 (OCH_2*C*H_2), 26.6 (CH_2*C*H_2N). ^{29}Si NMR: −16.5. Anal. calcd for $C_{26}H_{29}BrN_2O_5SSi$: C, 52.97; H, 4.96; N, 4.75; Br, 13.55; S, 5.44; Si, 4.76. Found: C, 52.95; H, 4.93; N, 4.70; Br, 13.46; S, 5.39; Si, 4.68.

***N*-(4-(2-Bromo-2-(dimethyl(vinyl)silyl)ethoxy)butyl) trifluoromethanesulfonamide, 16a (R = Me).** Colorless oil. 1.98 g, 89% yield. IR (KBr) 3313, 2952, 2872, 1594, 1434, 1374, 1253, 1231, 1192, 1150, 1105, 1010, 958, 842, 822, 783, 702, 610, 578, 514 cm^{-1}. ^1H NMR: 6.16 (dd, =C*H*, *J* 19.3, 14.7 Hz, 1H), 6.08 (dd, =C*H*H, *J* 14.7, 4.5 Hz, 1H), 5.96 (br. tr, N*H*, *J* 5.3 Hz, 1H), 5.79 (dd, =CH*H*, *J* 19.3, 4.5 Hz, 1H), 3.83 (dd, *J* 11.3, 3.4 Hz, 1H), 3.69 (dd, CHBr, *J* 11.3, 9.2 Hz, 1H), 3.57–3.43 (m, 2H), 3.42–3.33 (m, 3H), 1.77–1.71 (m, CH_2CH_2, 4H), 0.25 (s, CH_3, 3H), 0.24 (s, CH_3, 3H). ^{13}C NMR: 135.3 (=*C*H), 134.2 (=*C*H_2), 119.8 (q, *J* 321.3 Hz, CF_3), 72.8 (CH*C*H_2O), 70.3 (O*C*H_2CH_2), 44.0 (CH_2N), 39.7 (CHBr), 27.6 (OCH_2*C*H_2), 26.4 (CH_2*C*H_2N), −4.3 (CH_3), −4.8 (CH_3). ^{19}F NMR: −77.3. ^{29}Si NMR: −4.6. Anal. calcd for $C_{11}H_{21}BrF_3NO_3SSi$: C, 32.04; H, 5.13; N, 3.40; Br, 19.38; S, 7.78; F, 13.82; Si, 6.81. Found: C, 32.01; H, 5.12; N, 3.35; Br, 19.29; S, 7.70; F, 13.73; Si, 6.74.

***N*-(4-(2-Bromo-2-(dimethyl(vinyl)silyl)ethoxy)butyl) methanesulfonamide, 16b (R = Me).** Light-yellow oil. 0.17 g, 17% yield. IR (KBr) 3289, 2948, 2868, 1733, 1593, 1558, 1541, 1408, 1321, 1252, 1153, 1109, 1010, 972, 841, 823, 782, 702, 611, 522 cm^{-1}. ^1H NMR: 6.13 (dd, =C*H*, *J* 19.7, 14.7 Hz, 1H), 6.03 (dd, =C*H*H, *J* 14.7, 4.1 Hz, 1H), 5.75 (dd, =CH*H*, *J* 19.7, 4.1 Hz, 1H), 4.88 (br. s, N*H*, 1H), 3.77 (dd, *J* 11.2, 3.6 Hz, 1H), 3.66 (dd, CHBr, *J* 11.2, 8.5 Hz, 1H), 3.48–3.37 (m, 3H), 3.15–3.09 (m, 2H), 2.92 (s, *C*H_3SO_2, 3H), 1.67–1.62 (m, CH_2CH_2, 4H), 0.208 (s, CH_3, 3H), 0.204 (s, CH_3, 3H). ^{13}C NMR: 135.5 (=*C*H), 133.9 (=*C*H_2), 72.7 (CH*C*H_2O), 70.1 (O*C*H_2CH_2), 42.8 (CH_2N), 40.0 (*C*H_3SO_2), 39.9 (CHBr), 27.0 (OCH_2*C*H_2), 26.5 (CH_2*C*H_2N), −4.2 (CH_3), −4.6 (CH_3). ^{29}Si NMR: −4.4. Anal. calcd for $C_{11}H_{24}BrNO_3SSi$: C, 36.87; H, 6.75; N, 3.91; Br, 22.30; S, 8.95; Si, 7.84. Found: C, 36.86; H, 6.74; N, 3.89; Br, 22.26; S, 8.92; Si, 7.77.

***N*-(4-(2-Bromo-2-(dimethyl(vinyl)silyl)ethoxy)butyl)-4-methylbenzenesulfonamide, 16c (R = Me).** Colorless oil. 0.72 g, 35% yield. IR (KBr) 3283, 2947, 2868, 1720, 1598, 1407, 1328, 1251, 1161, 1095, 1010, 956, 841, 818, 782, 664, 552 cm^{-1}. ^1H NMR: 7.75 (d, *m*-C*H*, *J* 7.9 Hz, 2H), 7.29 (d, *o*-C*H*, *J* 7.9 Hz, 2H), 6.15 (dd, =C*H*, *J* 19.6, 14.6 Hz, 1H), 6.05 (dd, =C*H*H, *J* 14.6, 4.2 Hz, 1H), 5.77 (dd, =CH*H*, *J* 19.6, 4.2 Hz, 1H), 4.88 (br. tr, N*H*,

J 5.9 Hz, 1H), 3.76 (dd, *J* 11.3, 3.8 Hz, 1H), 3.65 (dd, CHBr, *J* 11.3, 8.5 Hz, 1H), 3.46–3.35 (m, 3H), 3.02–2.92 (m, 2H), 2.43 (s, CH_3Ph, 3H), 1.61–1.54 (m, CH_2CH_2, 4H), 0.228 (s, CH_3, 3H), 0.221 (s, CH_3, 3H). ^{13}C NMR: 143.2 (C_p), 137.1 (C_i), 135.7 (=CH_2), 134.0 (=*C*H), 129.6 (C_m), 127.1 (C_o), 72.8 (CH*C*H_2O), 70.2 (O*C*H_2CH_2), 42.9 (CH_2N), 32.9 (CHBr), 26.7 (OCH_2*C*H_2), 26.6 (CH_2*C*H_2N), 21.5 (*C*H_3Ph), −4.1 (CH_3), −4.5 (CH_3). ^{29}Si NMR: −4.4. Anal. calcd for $C_{17}H_{28}BrNO_3SSi$: C, 47.00; H, 6.50; N, 3.22; Br, 18.39; S, 7.38; Si, 6.46. Found: C, 46.98; H, 6.47; N, 3.20; Br, 18.31; S, 7.34; Si, 6.40.

***N*-(4-(2-Bromo-2-(dimethyl(vinyl)silyl)ethoxy)butyl)-4-nitrobenzenesulfonamide, 16d (R = Me).** Light-yellow oil. 1.42 g, 80% yield. IR (KBr) 3292, 2948, 2869, 1607, 1531, 1349, 1311, 1251, 1165, 1093, 1012, 958, 852, 822, 781, 736, 686, 611, 563 cm^{-1}. ^{1}H NMR: 8.35 (d, *m*-C*H*, *J* 8.9 Hz, 2H), 8.06 (d, *o*-C*H*, *J* 8.9 Hz, 2H), 6.14 (dd, =C*H*, *J* 19.2, 14.7 Hz, 1H), 6.06 (dd, =C*H*H, *J* 14.7, 4.6 Hz, 1H), 5.78 (dd, =CH*H*, *J* 19.2, 4.6 Hz, 1H), 5.40 (br. tr, N*H*, *J* 5.9 Hz, 1H), 3.78 (dd, *J* 11.3, 3.4 Hz, 1H), 3.64 (dd, CHBr, *J* 11.3, 9.1 Hz, 1H), 3.47–3.36 (m, 3H), 3.12–3.01 (m, 2H), 1.67–1.60 (m, CH_2CH_2, 4H), 0.23 (s, CH_3, 3H), 0.22 (s, CH_3, 3H). ^{13}C NMR: 149.9 (C_p), 146.3 (C_i), 135.4 (=*C*H), 134.2 (=*C*H_2), 128.3 (C_o), 124.3 (C_m), 72.8 (CH*C*H_2O), 70.3 (O*C*H_2CH_2), 43.1 (CH_2N), 40.2 (CHBr), 27.1 (OCH_2*C*H_2), 26.7 (CH_2*C*H_2N), −4.1 (CH_3), −4.6 (CH_3). ^{29}Si NMR: −4.5. Anal. calcd for $C_{16}H_{25}BrN_2O_5SSi$: C, 41.29; H, 5.41; N, 6.02; Br, 17.17; S, 6.89; Si, 6.03. Found: C, 41.28; H, 5.37; N, 6.00; Br, 17.13; S, 6.78; Si, 5.94.

5-(Dimethyl(vinyl)silyl)-2-methyl-1-(trifluoromethylsulfonyl)-2-imidazoline, 18 (R = Me). Yellow oil. 96% yield. IR (KBr) 3055, 2960, 2877, 1674, 1594, 1403, 1386, 1286, 1255, 1237, 1203, 1153, 1087, 1052, 1010, 992, 958, 916, 842, 825, 782, 704, 678, 661, 616, 584, 537, 520 cm^{-1}. ^{1}H NMR: 6.14–5.99 (m, 2H), 5.87–5.72 (m, 1H), 4.06–3.98 (m, 1H), 3.89–3.78 (m, 2H), 2.22 (s, CH_3, 3H), 0.21 (s, CH_3, 3H), 0.18 (s, CH_3, 3H). ^{13}C NMR: 154.7 (C=N), 135.2 (=*C*H_2), 133.9 (=*C*H), 121.5 (q, *J* 325.2 Hz, CF_3), 56.2 (*C*H_2), 53.2 (*C*H), 16.6 (*C*H_3), −5.2 (CH_3), −6.0 (CH_3). ^{19}F NMR: −73.9. ^{29}Si NMR: −17.8. Anal. calcd for $C_9H_{15}F_3N_2O_2SSi$: C, 35.99; H, 5.03; N, 9.33; S, 10.68; F, 18.97; Si, 9.35. Found: C, 35.97; H, 5.02; N, 9.31; S, 10.56; F, 18.88; Si, 9.29.

5-(Diphenyl(vinyl)silyl)-2-methyl-1-(trifluoromethylsulfonyl)-2-imidazoline, 18 (R = Ph). Yellow oil. 98% yield. IR (KBr) 3061, 3016, 2949, 2877, 1963, 1896, 1826, 1673, 1589, 1557, 1401, 1286, 1203, 1152, 1113, 960, 918, 790, 708, 614, 506 cm^{-1}. ^{1}H NMR: 7.48–7.38 (m, C*H* (Ph), 5H), 7.37–7.23 (m, C*H* (Ph), 5H), 6.54 (dd, =C*H*, *J* 20.3, 14.7 Hz, 1H), 6.20 (dd, =C*H*H, *J* 14.7, 3.3 Hz, 1H), 5.65 (dd, =CH*H*, *J* 20.3, 3.3 Hz, 1H), 4.36 (dd, CH*H*, *J* 10.4, 3.6 Hz, 1H), 4.0–3.9 (m, C*H*H, 1H), 3.83 (dd, C*H*, *J* 15.2, 3.3 Hz, 1H), 1.86 (s, CH_3, 3H). ^{13}C NMR: 154.7 (C=N), 138.7 (=*C*H_2), 135.7 (C_o), 134.5 (C_i), 134.3 (C_i), 130.8 (=*C*H), 130.4 (C_p), 130.3 (C_p), 128.2 (C_m), 128.1 (C_m), 120.1 (q, *J* 325.8 Hz, CF_3), 56.5 (*C*H_2), 52.4 (*C*H), 16.3 (CH_3). ^{19}F NMR: −74.0. ^{29}Si NMR: −15.2. Anal. calcd for $C_{19}H_{19}F_3N_2O_2SSi$: C, 53.76; H, 4.51; N, 6.60; S, 7.55; F, 13.43; Si, 6.62. Found: C, 53.74; H, 4.49; N, 6.55; S, 7.51; F, 13.02; Si, 6.58.

2,2,4,4,6,6,8,8-Octaphenyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane, 19. White solid. 97–99% yield. mp 184 °C. IR (KBr) 3052, 2925, 2855, 1962, 1892, 1739, 1428, 1122, 1075, 700, 524, 489 cm^{-1}. ^{1}H NMR: 7.48 (d, *o*-C*H*, *J* 7.5 Hz, 4H), 7.35 (tr, *m*-C*H*, *J* 7.5 Hz, 2H), 7.18 (tr, *o*-C*H*, *J* 7.5 Hz, 4H). ^{13}C NMR: 134.5 (C_i), 134.4 (C_m), 130.0 (C_p), 127.6 (C_o). ^{29}Si NMR: −43.1. Anal. calcd for $C_{48}H_{40}O_4Si_4$: C, 72.68; H, 5.08; Si, 14.16. Found: C, 72.66; H, 5.07; Si, 14.11.

2-Methyl-5,5-diphenyl-1-(trifluoromethylsulfonyl)-1,3,5-diazasilinane, 20a (R = Ph). Light-yellow oil. 97% yield. IR (KBr) 2959, 1668, 1554, 1400, 1259, 1201, 1153, 1084, 1052, 961, 914, 835, 802, 673, 615, 587, 533 cm^{-1}. ^{1}H NMR: 7.47 (d, *o*-C*H*, *J* 7.3 Hz, 4H), 7.34 (tr, *p*-C*H*, *J* 7.3 Hz, 2H), 7.18 (tr, *m*-C*H*, *J* 7.3 Hz, 4H), 4.03–3.85 (m, $CHCH_2$, 4H), 2.27 (br. s, CH_3, 3H). ^{13}C NMR: 153.6 (C=N), 134.5 (C_i (Ph)), 134.4 (C_m (Ph)), 130.0 (C_p (Ph)), 127.6 (C_o (Ph)), 121.5 (q, *J* 322.3 Hz, CF_3), 52.8 (*C*H_2), 48.9 (*C*H_2), 16.1 (CH_3). ^{19}F NMR: −75.0. ^{29}Si NMR: −43.0. Anal. calcd for $C_{17}H_{17}F_3N_2O_2SSi$: C, 51.24; H, 4.30; N, 7.03; S, 8.05; F, 14.30; Si, 7.05. Found: C, 51.18; H, 4.19; N, 7.18; S, 8.11; F, 14.70; Si, 7.11.

2-Methyl-1-(4-nitrophenylsulfonyl)-5,5-diphenyl-1,3,5-diazasilinane, 20d (R = Ph). Yellow solid. 96% yield. mp 171 °C. IR (KBr) 3067, 2934, 2879, 1657, 1596, 1532, 1429, 1357, 1235, 1172, 1119, 1020, 970, 927, 857, 739, 696, 612, 580, 526, 495, 464 cm^{-1}. ^{1}H NMR: 8.42 (d, *m*-C*H*, *J* 8.6 Hz, 2H), 8.07 (d, *o*-C*H*, *J* 8.06 Hz, 2H), 7.47 (d, *o*-C*H*, *J* 7.3 Hz, 4H), 7.33 (tr, *p*-C*H*, *J* 7.3 Hz, 2H), 7.17 (tr, *m*-C*H*, *J* 7.3 Hz, 4H), 3.77 (br. s, CH_2, 4H), 2.30 (br. s, CH_3, 3H). ^{13}C NMR: 155.0 (C=N), 150.5 (C_p (Ns)), 144.1 (C_i (Ns)), 134.4 (C_i (Ph)), 134.3 (C_o (Ns)), 130.0 (C_p (Ph)), 128.4 (C_m (Ph)), 127.6 (C_m (Ns)), 124.8 (C_o (Ph)), 52.3 (*C*H_2NNs), 48.2 (*C*H_2), 16.8 (CH_3). ^{29}Si NMR: −42.8. Anal. calcd for $C_{22}H_{21}N_3O_4SSi$: C, 58.52; H, 4.69; N, 9.31; S, 7.10; Si, 6.22. Found: C, 58.60; H, 4.73; N, 9.40; S, 7.14; Si, 6.25.

2,5,5-Trimethyl-1-(trifluoromethylsulfonyl)-1,3,5-diazasilinane, 20a (R = Me). Yellow oil. 94% yield. IR (KBr) 2961, 1671, 1557, 1403, 1261, 1204, 1155, 1087, 1056, 962, 916, 839, 803, 675, 617, 588, 535 cm^{-1}. ^{1}H NMR: 4.05–3.72 (m, CH_2, 4H), 2.25 (br. s, CH_3, 3H), 2.22 (s, CH_3, 3H), 0.25–0.20 (m, CH_3, 6H). ^{13}C NMR: 154.6 (C=N), 55.6 (*C*H_2NTf), 53.3 (*C*H_2), 16.6 (CH_3), −1.3 (CH_3), −1.4 (CH_3), −1.95 (CH_3), −1.97 (CH_3). ^{19}F NMR: −74.1. ^{29}Si NMR: −41.3. Anal. calcd for $C_7H_{13}F_3N_2O_2SSi$: C, 30.65; H, 4.78; F, 20.78; N, 10.21; S, 11.69; Si, 10.24. Found: C, 30.70; H, 4.83; N, 10.25; S, 11.64; F, 20.85; Si, 10.27.

3-(Diphenyl(vinyl)silyl)-4-(trifluoromethylsulfonyl)-1,4-oxazocane, 21a (R = Ph). Yellow oil. 94% yield. IR (KBr) 3055, 2939, 2863, 1961, 1895, 1824, 1591, 1429, 1367, 1241, 1199, 1112, 1006, 964, 910, 706, 614, 548, 505 cm^{-1}. ^{1}H NMR: 7.69–7.55 (m, 5H), 7.41–7.34 (m, 5H), 6.58 (dd, =C*H*, *J* 20.3, 14.7 Hz, 1H), 6.31 (dd, =C*H*H, *J* 14.7, 3.3 Hz, 1H), 5.83 (dd, =CH*H*, *J* 20.3, 3.3 Hz, 1H), 3.99 (dd, *J* 9.2, 2.9 Hz, 1H), 3.85 (dd, *J* 11.5, 2.9 Hz, 1H), 3.70 (dd, *J* 11.5, 9.2 Hz, 1H), 3.40–3.35 (m, 1H), 3.34–3.26 (m, 1H), 2.98 (tr, *J* 6.1 Hz, 2H), 1.56–1.42 (m, 4H). ^{13}C NMR: 138.0 (C_i), 135.8 (=*C*H_2), 135.7 (C_o), 131.9 (=*C*H), 130.1 (C_p), 128.0 (C_m), 122.1 (q, CF_3, *J* 326.9 Hz), 72.6, 70.7, 44.9, 37.6, 29.0, 26.9. ^{19}F NMR: −76.6. ^{29}Si NMR: −16.5. Anal. calcd for $C_{21}H_{24}F_3NO_3SSi$: C, 55.37; H, 5.31; N, 3.07; S, 7.04; F, 12.51; Si, 6.16. Found: C, 55.33; H, 5.28; N, 3.07; S, 7.00; F, 12.32; Si, 6.08.

3-(Diphenyl(vinyl)silyl)-4-(4-nitrophenylsulfonyl)-1,4-oxazocane, 21d (R = Ph). Yellow oil. 98% yield. IR (KBr) 3070, 2943, 2868, 1606, 1530, 1428, 1349, 1311, 1166, 1109, 1012, 965, 854, 737, 701, 612, 547, 503, 464 cm^{-1}. ^{1}H NMR: 8.32 (d, *m*-C*H* (Ns), *J* 8.7 Hz, 2H), 8.04 (d, *o*-C*H* (Ns), *J* 8.7 Hz, 2H), 7.65–7.57 (m,

CH (Ph), 4H), 7.47–7.38 (m, CH (Ph), 6H), 6.58 (dd, *J* 20.3, 14.7 Hz, =CH, 1H), 6.34 (dd, *J* 14.7, 3.3 Hz, =CHH, 1H), 5.83 (dd, *J* 20.3, 3.3 Hz, =CHH, 1H), 3.95 (dd, *J* 8.8, 2.9 Hz, 1H), 3.87 (dd, *J* 11.3, 2.9 Hz, 1H), 3.70 (dd, *J* 11.3, 8.8 Hz, 1H), 3.42–3.33 (m, 2H), 3.07–2.99 (m, 2H), 1.60–1.55 (m, 4H). ^{13}C NMR: 150.0 (C_p (Ns)), 146.3 (C_i (Ns)), 138.1 (=CH_2), 135.8 (C_o), 131.9 (=CH), 131.8 (C_i), 130.2 (C_p), 128.3 (C_o (Ns)), 128.0 (C_m), 124.3 (C_m (Ns)), 72.8, 70.4, 43.1, 37.5, 27.2, 26.7. ^{29}Si NMR: −16.6. Anal. calcd for $C_{26}H_{28}N_2O_5SSi$: C, 61.39; H, 5.55; N, 5.51; S, 6.30; Si, 5.52. Found: C, 61.36; H, 5.51; N, 5.49; S, 6.22; Si, 5.45.

3-(Dimethyl(vinyl)silyl)-4-(trifluoromethylsulfonyl)-1,4-oxazocane, 21a (R = Me). Colorless oil. 98% yield. IR (KBr) 3053, 2946, 2866, 2793, 1637, 1594, 1456, 1407, 1364, 1252, 1201, 1154, 1083, 1009, 987, 958, 910, 842, 822, 782, 735, 615, 515 cm^{-1}. ^{1}H NMR: 6.16 (dd, =CH, *J* 19.6, 14.7 Hz, 1H), 6.06 (dd, =CHH, *J* 14.7, 4.2 Hz, 1H), 5.78 (dd, =CHH, *J* 19.6, 4.2 Hz, 1H), 3.78 (dd, *J* 11.1, 3.4 Hz, 1H), 3.67 (dd, *J* 11.1, 9.6 Hz, CH, 1H), 3.50–3.40 (m, 3H), 3.06–2.99 (m, 2H), 1.63–1.49 (m, 4H), 0.24 (s, CH_3, 3H), 0.23 (s, CH_3, 3H). ^{13}C NMR: 135.5 (=CH_2), 134.1 (=CH), 122.0 (q, CF_3, *J* 328.0 Hz), 72.6 ($CHCH_2O$), 70.7 (OCH_2CH_2), 45.0, 40.3, 29.0, 27.0, −4.2 (CH_3), −4.6 (CH_3). ^{19}F NMR: −77.3. ^{29}Si NMR: −4.5. Anal. calcd for $C_{11}H_{20}F_3NO_3SSi$: C, 39.86; H, 6.08; N, 4.23; S, 9.67; F, 17.20; Si, 8.47. Found: C, 39.85; H, 6.05; N, 4.22; S, 9.61; F, 17.09; Si, 8.43.

Conflicts of interest

There are no conflicts of interests to declare.

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