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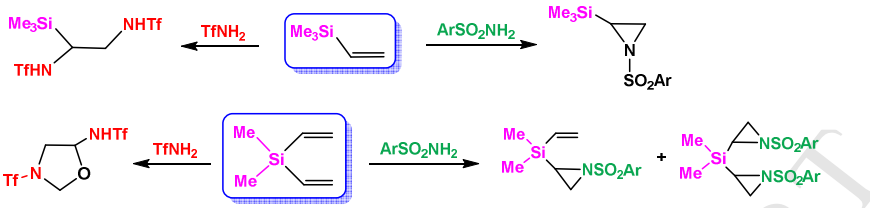
Oxidative Sulfamidation of Vinyl Silanes: A Route to Diverse Silylated N-Heterocycles

Vera V. Astakhova, Bagrat A. Shainyan,* Mikhail Yu. Moskalik, Irina V. Sterkhova



ABSTRACT: The reaction of trimethyl(vinyl)silane **1** and dimethyl(divinyl)silane **2** with various sulfonamides in the oxidative system (*tert*-BuOCl + NaI) has been studied and shown to be an efficient approach for the synthesis of silylated N-heterocycles. Triflamide demonstrated the reactivity principally different from that of arenesulfonamides. With silane **1**, it afforded the products of iodochlorination and bis(triflamidation) (major), whereas arenesulfonamides gave N-arenesulfonylaziridines in up to 91% yield. Silane **2** with arenesulfonamides yielded the products of mono and bis(iodochlorination), mono and bis(aziridination), and 3,5-diiodo-4,4-dimethyl-1-(arylsulfonyl)-1,4-azasilinanes. By contrast, triflamide, apart from the products of halogenation and iodotriflamidation, unexpectedly gave 3-(trifluoromethylsulfonyl)-5-(triflamido)oxazolidine as the main product. The structure of most heterocyclic products is proved by X-ray analysis. The effect of the silyl group in the substrate and of the substituent in the reagent on the course of oxidative sulfamidation is discussed by comparing with all-carbon analogues.

Keywords: sulfonamides · vinyl silanes · oxidative sulfonamidation · aziridines · 1,4-azasilinanes · reaction mechanisms

1. Introduction

The reactions of oxidative sulfamidation of alkenes[1-4] and dienes[5-10] is a mild metal-free method for the synthesis of unsaturated sulfonamides and various N-heterocycles.[11-13] Unsaturated triflamide derivatives (*N*-allyl- and *N*,*N*-diallyltriflamide) have also been examined as substrates in these reactions and showed the formation of different linear, cyclic and bicyclic products in the ratio depending on the reagents and reaction conditions.[14] Oxidative sulfamidation of

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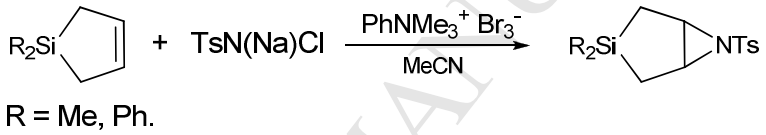
heterodienes is confined to the reactions of triflamide with diallyl sulfide,[15] divinyl sulfoxide and divinyl sulfone.[16] The first substrate affords the sulfur atom oxidation products, first acyclic λ^4-sulfane, *N*,*N*'-(diprop-2-en-1-yl-λ^4-sulfanediyl)bis(triflamide), $(CF_3SO_2NH)_2S(CH_2CH{=}CH_2)_2$. The latter two reactions proceed as heterocyclization resulting in 2,6-diiodo-4-(trifluoromethylsulfonyl)thiomorpholine 1-oxide or 1,1-dioxide.

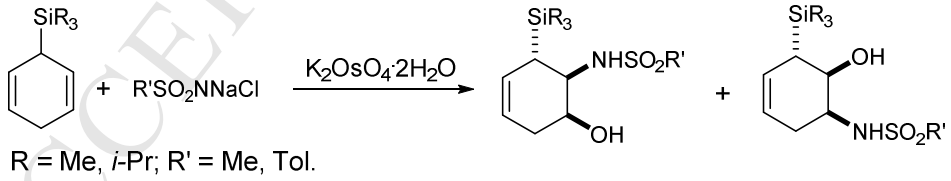
There are very few studies on the reactions of sulfonamidation of vinyl silanes. In early works, free-radical addition of *N*,*N*-dichloroarylsulfonamides to vinyl- and allylsilanes was studied.[17,18] The addition of $TsNCl_2$ to vinyl- and allylsilanes proceeds with different regio-selectivity leading to $Me_3SiCH(Cl)CH_2N(Cl)Ts$ and $Me_3SiCH_2C[N(Cl)Ts]CH_2Cl$, respectively;[17] replacement of hydrogens and/or methyls in $Me_3SiCH{=}CH_2$ by chlorine hinders the reaction.[18]

4-Silacyclopentenes undergo aziridination with chloramine-T in the presence of ammonium tribromide salt.[19] Nucleophilic ring opening of the formed aziridines followed by deprotection provides an efficient and stereoselective route to unnatural cyclic sila-substituted β-amino acids.



Scheme 1. Aziridination of 4-silacyclopentanes with Chloramine T.

The first reaction which can be considered as oxidative sulfamidation of unsaturated silanes was the reaction of 3-silylated cyclohexa-1,4-dienes with chloramines in water or aqueous-organic media in the presence of K_2OsO_4 as an oxidant.[20] The reaction occurs at only one double bond with the major adduct having the sulfonamide residue closer to the silyl group.



Scheme 2. Diastereo- and regioselective hydroxysulfamidation of 3-dialkylsilylcyclohexa-1,4-dienes with Chloramines.

The Rh-catalyzed oxidative intramolecular sulfamidation of 4-silylated (3*Z*)-but-3-en-1-yl sulfamates proceeds with different stereoselectivity for achiral and chiral substrates (Scheme 3).[21]

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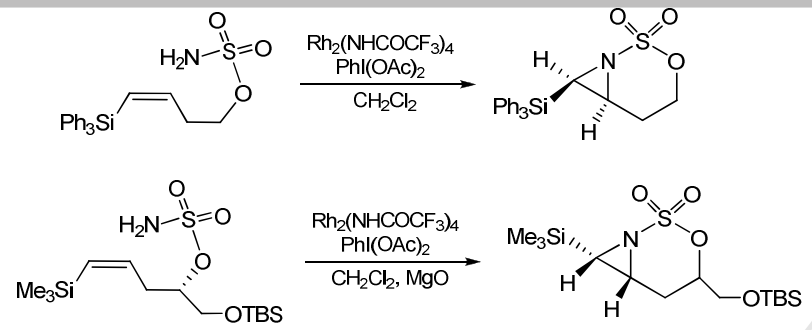

Scheme 3. Intramolecular aziridination of achiral and chiral silylvinyl sulfamates.

Therefore, one can conclude that no reactions of electrophilic oxidative sulfamidation of unsaturated silanes are known; at the same time, vinyl silanes must be active as substrates in electrophilic sulfamidation due to the stabilizing effect of silicon on β-carbocations. In this paper we report the first study of the reactions of oxidative sulfamidation of trimethyl(vinyl)silane **1** and dimethyl(divinyl)silane **2** [and, for comparison, diphenyl(divinyl)silane] with sulfonamides.

Apart from fundamental interest in the chemistry of unsaturated silanes and functionalized sulfonamides, the products of the investigated reactions containing pharmacophoric sulfonamide group and silicon atom may show biological activity. Bioisosteric replacement is a promising molecular design approach successfully used in medicinal chemistry, and the C and Si atoms are classical bioisosteres.[22-27] A lot of nitrogen-containing heterocycles, including those possessing silylated groups in the molecule, display biological activity, that attracts the attention of researchers.[28–31]

2. Results and discussion

The reaction of trimethyl(vinyl)silane **1** with sulfonamides $CF_3SO_2NH_2$ ($TfNH_2$, **3**) and $XC_6H_4SO_2NH_2$ [X = H (**4a**), Me (**4b**), Cl (**4c**), NO_2 (**4d**)] was performed at different temperatures using a 1:1.5 ratio of the reagents amide:silane in the presence of oxidative system (*t*-BuOCl + NaI). This system was successfully used by us for oxidative sulfamidation of alkenes and dienes.[1-10, 14-16]

Silane **1** reacts with triflamide **3** at 10–15°C or –30°C to afford a whole bunch of products of oxidative addition, the main ones being (2-chloro-1-iodoethyl)trimethylsilane **5** and *N*,*N*′-[1-(trimethylsilyl)ethane-1,2-diyl]bis(triflamide) **6**. Also, *N*-[2-iodo-2-(trimethylsilyl)ethyl]triflamide **7** and *N*-[2-chloro-1-(trimethylsilyl)ethyl]triflamide **8** were isolated by column chromatography from the ethereal–hexane eluate as an inseparable mixture of minor products **7**:**8** = 4:3 in 4–13% total yield. 2-Iodo-2-(trimethylsilyl)ethanol **9** was isolated from the hexane eluate in trace amounts (Scheme 4). Different regiochemistry of the products of halotriflamidation **7** and **8** is

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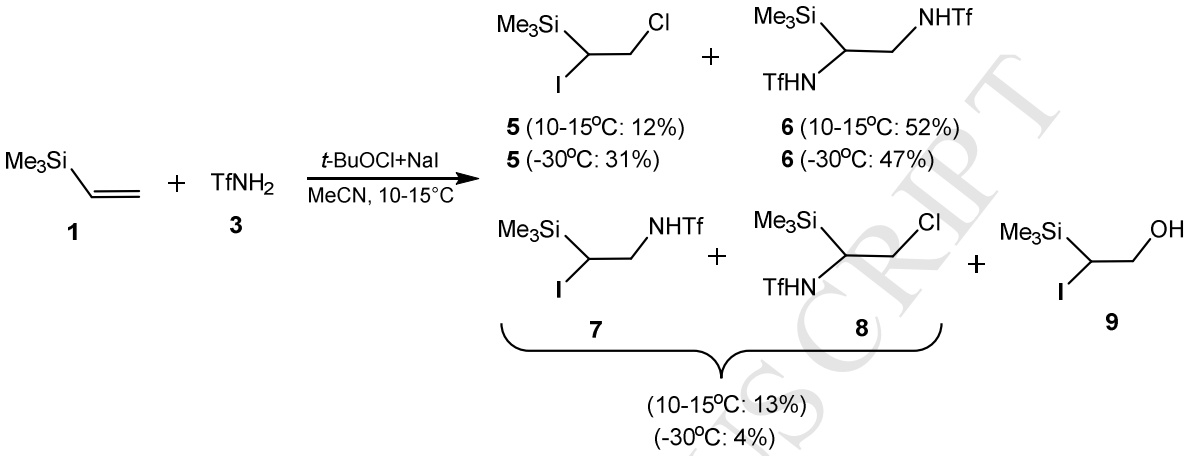
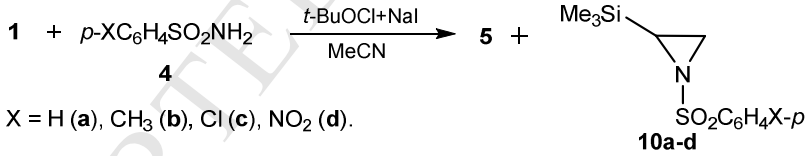
proved by different splitting of the NH proton in the ^{1}H NMR spectrum – triplet in **7** and doublet in **8**, and can be rationalized by different routes of their formation (see Scheme 6 below). The conversion of triflamide increases on cooling from 86 to 98%, as does the total yield from 64 to 78%, apparently due to lower amount of side products at lower temperature.



Scheme 4. Oxidative triflamidation/halogenation of silane **1**.

Arenesulfonamides **4** react with silane **1** in the temperature range from –30 to +45 ºC in a different manner (Scheme 5) resulting in adduct **5** as a minor product and 1-(arylsulfonyl)-2-(trimethylsilyl)aziridines **10a–d** in up to 91% yield (Table 1). The structure of aziridine **10d** was proved by X-ray analysis (Fig. 1).



Scheme 5. Iodochlorination and aziridination of silane **1** with arenesulfonamides **4a**–**d**.

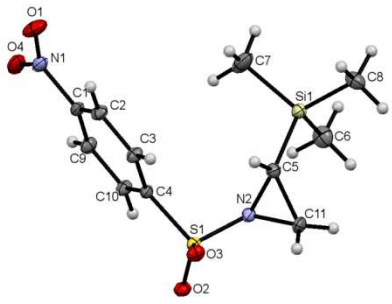


Figure 1. Molecular structure of aziridine **10d**.

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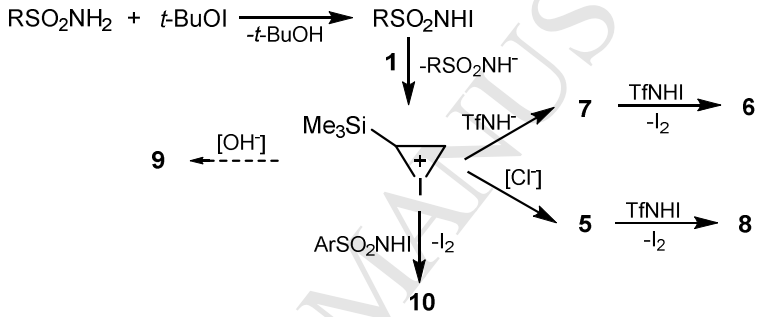
Table 1. Conversion and isolated yields of products **5** and **10** (Scheme 5)

X in *p*-$XC_6H_4SO_2NH_2$	Temperature, °C	Conversion of amide, %	Yield, %	
			5	**10**
H	45	86	31	47
	15	89	19	71
CH_3	–30	32	16	31
	15	98	13	86
Cl	15	95	11	84
NO_2	15	98	6	91

A tentative mechanism of formation of all products in Schemes 4 and 5 can be proposed as follows (Scheme 6). The structure of compounds **5**, **7** and **9** is consistent with the ring opening in the intermediate iodonium cation from the side of less sterically hindered CH_2 group.



Scheme 6. Tentative mechanism of the reaction of trimethyl(vinyl)silane **1** with triflamide **3** and arenesulfonamides **4**.

Although the formation of intermediate iodonium cation in Scheme 6 is fully consistent with the formation of products 5 and 7 as the precursors of 6 and 8, the formation of products 6 and 8 via an independent pathway, through the aziridinium intermediate, cannot be completely ruled out. The 'aziridinium' mechanism was proposed in a series of works on reactions of $TsNCl_2$ with electron-deficient alkenes leading to the products of deamination[32-35] or aziridines.[36]

The reaction of dimethyl(divinyl)silane **2** with sulfonamides **3** and **4a**–**d** was performed under the same conditions as those for silane **1**. The reaction of silane **2** with triflamide proceeds in high total yield as shown in Scheme 7. The main product is 3-(trifluoromethylsulfonyl)-5-(triflamido)oxazolidine **11**, the product of iodotriflamidation **12** is formed in lower yield, and very small amounts of the products of mono- and bis(iodochlorination) **13** and **14** were isolated.

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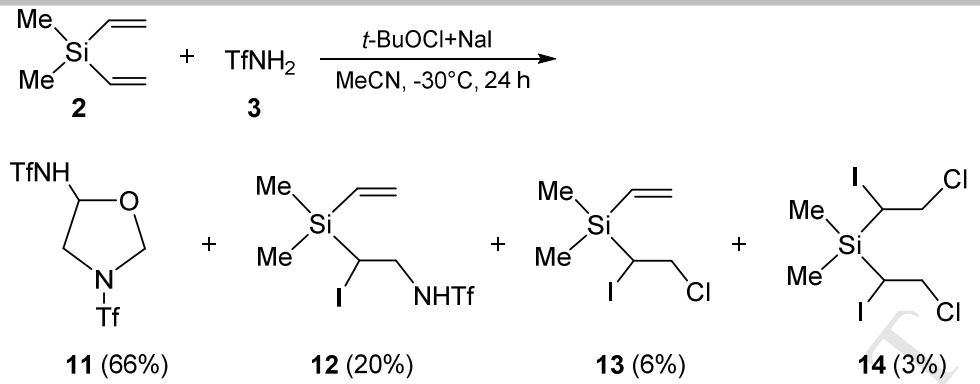
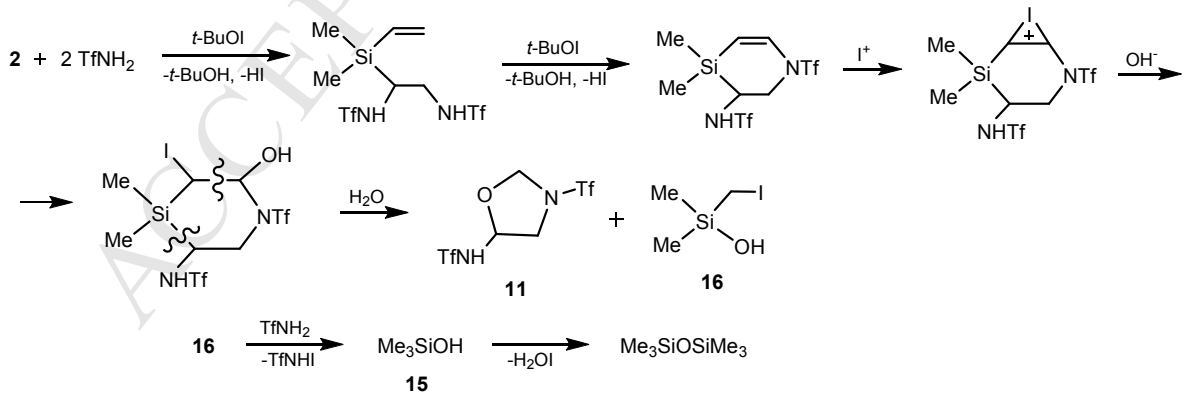


Scheme 7. Oxidative triflamidation/halogenation of dimethyl(divinyl)silane **2**. *Reaction conditions*: solvent MeCN, –30°C, 24 h, **2**:**3** = 1:1. The yields with respect to the converted triflamide are the isolated yields after column chromatography.

While the products of iodotriflamidation and iodochlorination **12**–**14** in Scheme 7 are similar to those obtained earlier and can be expected to be formed, the formation of oxazolidine **11** is surprising since it implies desilylation and the cleavage of the C=C double bond of substrate **2**. The reaction of formation of product **11** is easily balanced assuming the formation of silanol Me_3SiOH **15** (which can be further transformed into siloxane $Me_3SiOSiMe_3$), as follows:

The mechanism of formation of oxazolidine **11** is not clear and deserves special study. Its structure only presumes that one Si–C bond and one of the initially double C=C bonds in **2** are split, apparently hydrolytically, as schematically shown in Scheme 8.



Scheme 8. Tentative mechanism of formation of 3-(trifluoromethylsulfonyl)-5-(triflamido)-oxazolidine **11** *via* desilylation and the C=C double bond cleavage of dimethyl(divinyl)silane **2**.

The structure of oxazolidine **11** was proved by NMR spectroscopy, in particular by the presence of two CF_3 quartets, one methine and two methylene groups in the ^{13}C NMR spectrum,

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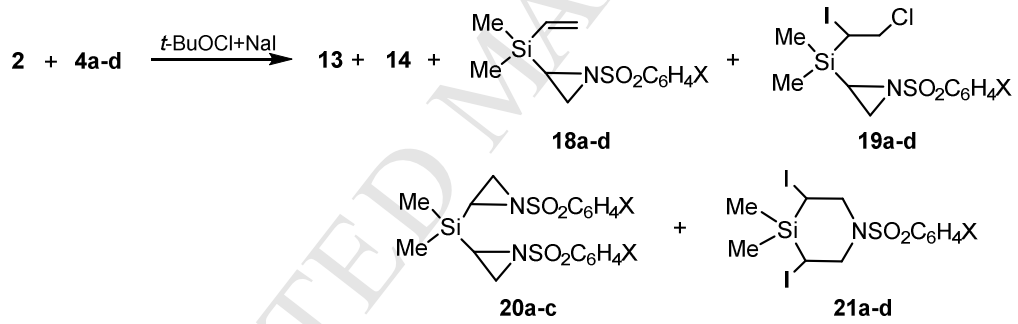
and the corresponding proton signals, which were assigned based on J_{mod}, $^{1}H–^{1}H$ and $^{1}H–^{13}C$ 2D NMR spectra. The ^{1}H and ^{13}C NMR spectra of products **12**, **13** show diastereotopic methyl signals, and compound **14** is formed as two diastereomers in the ratio of 5:4. The formation of silanols **15**, **16** and, apparently, the corresponding siloxanes after their dehydration is confirmed by the presence of a number of signals in the 0–1 ppm region of the ^{1}H NMR spectrum of the reaction mixture.

This unusual reactivity is not specific for silane **2**, because the formation of product **11** was found also in the reaction of diphenyl(divinyl)silane **17** with triflamide under the same conditions. However, it is specific for triflamide as a sulfamidating reagent, since no analogues of oxazolidine **11** or the product of iodotriflamidation **12** were obtained from the reactions of silane **2** with arenesulfonamides **4a**–**d**. Instead, the reaction of **2** with sulfonamides **4** gives rise to the formation of the products of aziridination **18**–**20** and 1,4-azasilinanes **21** (Scheme 9). The only products identical to those formed in the reaction with triflamide (Scheme 7) were the products of iodochlorination **13** and **14**. The reaction conditions and the yields of the products are summarized in Table 2.



Scheme 9. Oxidative sulfonamidation/halogenation/aziridination of dimethyl(divinyl)silane **2** with arenesulfonamides **4**. *Reaction conditions*: solvent MeCN, –30°C, 24 h, **2**:**4** = 1:1. The yields with respect to the converted arenesulfonamides are the isolated yields after column chromatography.

Table 2. Products of the reaction of dimethyl(divinyl)silane **2** with arenesulfonamides **4** (Scheme 9).[a]

Entry	Sulfonamide	Conversion of sulfonamide, %	Product yields[b]					
			13	**14**	**18**	**19** (*dr*)[c]	**20** (*dr*)[c, d]	**21**
1	**4a**	49	28	5	13	25 (65:35)	21 (44:56)	4
2	**4b**	84	27	3	7	29 (67:33)	15 (49:51)	4
3	**4c**	85	14	2	4.5[e]	55 (61:39)	11 (42:58)	4
4	**4d**	58	23	3	54	12 (69:31)	–	2
5	**4d**[f]	66	26	6	42	26	–	–

[a] Reaction conditions: solvent MeCN, –30°C, 24 h, **2**:**4** = 1:1. [b] After column chromatography. [c] *dr* – diastereomeric ratio from relative intensities of the SiMe signals in the ^{1}H NMR spectra. [d] *RS*:(*RR*+*SS*) ratio. [e] Yield determined by ^{1}H NMR spectroscopy. [f] **2**:**4d** = 2:1.

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Oxazolidine **11** and 1,4-azasilinanes **21** are crystalline compounds, whereas the adducts **13**, **14**, and aziridines **18**–**20** are viscous light-yellow oils, slowly solidified upon standing.

The structure of the products of aziridination **18**–**20** was proved by NMR spectroscopy, in particular, by the presence of diastereotopic methyl signals in the ^{1}H and ^{13}C NMR spectra, the formation of diastereomers of compounds **19** and **20** in different ratio, and by the values of $^{1}J_{CH}$ coupling constants falling in the range 170–190 Hz typical for aziridines.[7,37]

Mono and diaziridines **19** and **20** are formed as diastereomeric mixtures as proved by the presence of two sets of signals both in the ^{1}H and ^{13}C NMR spectra, the ratios are given in Table 2. The SiMe groups in monoaziridines **19** show two signals for each diastereomer, whereas symmetrical diaziridines **20** show two signals of one diastereomer and one signal of the second diastereomer, which allows to assign them, respectively, to the (*R*,*R*+*S*,*S*)- and *R*,*S*-diastereomer (*meso*-form). Symmetrical products **21** existing in the *R*,*S*-form (see Figure 3 and Figures SI-3–SI-6) show two SiMe signals due to the axial and equatorial methyls on the azasilinane ring.

For compound **18d** and for all 1,4-azasilinanes **21a–d** the molecular structure was also ascertained by X-ray structural analysis (Figures 2, 3).

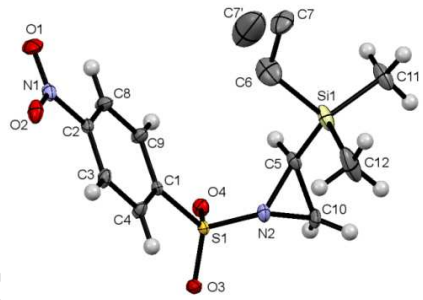

Figure 2. Molecular structure of 2-[1,1-dimethyl(vinyl)silyl]-1-[(4-nitrophenyl)sulfonyl]aziridine **18d**. The terminal olefinic methylene group is disordered over two conformations in 55:45 ratio.

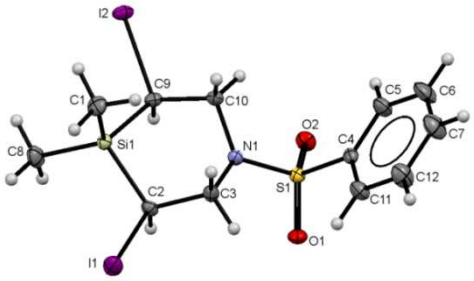

Figure 3. Molecular structure of 3,5-diiodo-4,4-dimethyl-1-(phenylsulfonyl)-1,4-azasilinane **21a**. Molecular structures of its analogues **21b**–**d** are very similar (see Supporting Information).

Note, that azasilinanes **21a**–**d** are formed as *meso*-diastereomers having the iodine atoms in the equatorial positions. The structure of compounds **12**–**14**, **19a**–**d**, **21a**–**d** having the iodine atoms in the α-position to silicon is consistent with the initial electrophilic iodination of

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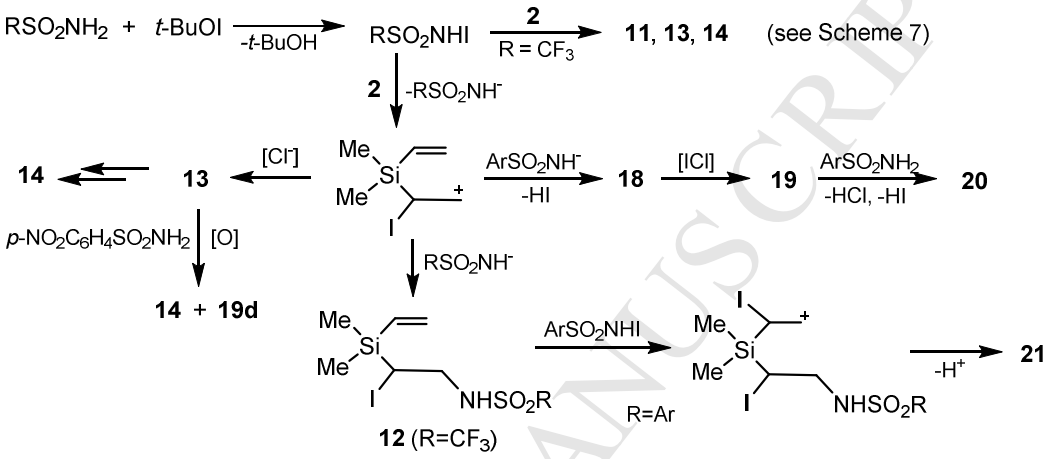
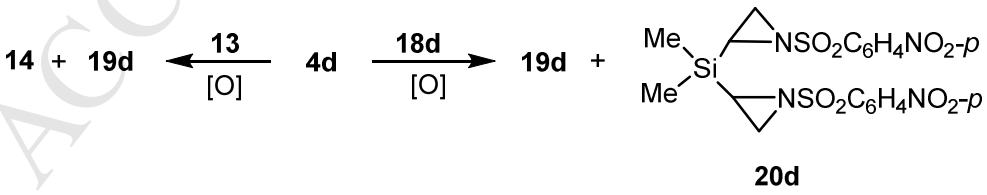
divinylsilanes **2** and **17**. The MP2/6-31G* theoretical calculations[38] showed that the maximum of the electron density in **2** or **17** is located on the internal olefinic CH groups (–0.25e), while the terminal CH_2 groups are practically uncharged (<0.01e). Therefore, the electrophilic attack by iodonium ion must be directed on the internal atoms of the double bonds.

The probable mechanism of the reaction, assuming the presence in the reaction mixture of various species containing the O–I and I–Cl bonds and capable of iodination and chlorination of the double bonds,[39] is outlined in Scheme 10.



Scheme 10. Tentative mechanism of the formation of products of the reaction of dimethyl(divinyl)silane **2** with triflamide **3** and arenesulfonamides **4**.

To confirm the mechanism in Scheme 10, additional experiments were performed using sulfonamide **4d** as the reagent in the same oxidative system (*t*-BuOCl+NaI). Thus, when product **13** was introduced in the reaction with **4d**, diadduct **14** (37%) and aziridine **19d** (16%), were obtained. In the reaction of **4d** with aziridine **18d**, the already known product **19d** and the diaziridine **20d** lacking in the reaction of **4d** with silane **2** were formed in the yield of 80% and 20%, respectively (from ^{1}H NMR analysis) (Scheme 11).



Scheme 11. The products of the reaction of nosylamide **4d** with monoadduct **13** and monoaziridine **18d** in the oxidative system (*t*-BuOCl+NaI).

It would be interesting to compare the reactivity of silanes **1** and **2** with their all-carbon analogues, that is, 3,3-dimethylbutene-1 and 3,3-dimethylpentadiene-1,4. Unfortunately, the two are rarely used as substrates in the reactions of oxidative amidation; thus, for the latter diene we failed to find any examples of such reactions. As to 3,3-dimethylbutene-1, it is aziridinated with

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PhI=NTs in the presence of different Cu-based catalysts in up to 90% yield.[40-42] It also reacts with $H_2NSO_3CH_2CCl_3$ in the presence of PhI=O and Cu(dibenzoylmethanoate) complexes with N-heterocyclic carbenes,[43] or with $TsNH_2$ in the presence of excess $PhI(OAc)_2$, I_2 and *t*-BuOK to give the corresponding aziridines in moderate yield.[44] It could be assumed that in the latter work the aziridine is formed via elimination of HI from the intermediate adduct $RCH(NHTs)CH_2I$ (which was indeed obtained by the reaction of styrene with PhI=NTs) but the authors showed that it does not cyclize to aziridine under the action of *t*-BuOK.[44] No formation of the products of hydroxyamination or haloamination analogous to products **7** or **8** in Scheme 4 was reported for the reactions of oxidative sulfamidation of 3,3-dimethylbutene-1, although the α-amino-β-chloro derivatives can be obtained by the ring opening of N-arylsulfonyl-2-*t*Bu-substituted aziridines with Me_3SiCl catalyzed by chiral 1,2,3-triazolium chlorides.[45]

Therefore, silane **1** shows the reactivity different from its all-carbon analogue: with arenesulfonamides the latter gives only aziridines, whereas silane **1** yields also the product of dihalogenation **5** (Scheme 5). Even more striking dissimilarity was shown for the reaction with triflamide, which gave no aziridine but, instead, the products of dihalogenation, bis-triflamidation, and halotriflamidation with different regioselectivity (Scheme 4).

3. Conclusions

To summarize, we have studied for the first time the oxidative sulfonamidation of trimethylvinylsilane, dimethyl(divinyl)silane and diphenyl(divinyl)silane with triflamide and arenesulfonamides. In the system (*t*-BuOCl+NaI), the reactions of dimethyl(divinyl)silane **2** with arenesulfonamides were shown to give the products of iodochlorination, aziridination and heterocyclization to 1,4-azasilinanes in high total yield. In the same conditions, triflamide reacted with divinylsilanes in a different manner. Both with dimethyl(divinyl)silane and diphenyl(divinyl)silane, the reaction occurred with the rupture of the $Si–C_{sp2}$ and C=C bonds and formation of the same main product, 3-(trifluoromethylsulfonyl)-5-(triflamido)oxazolidine. The main product of the reaction of trimethylvinylsilane **1** with triflamide was linear adduct, *N*,*N*′-[1-(trimethylsilyl)ethane-1,2-diyl)bis(triflamide), whereas arenesulfonamides react with silane **1** via aziridination of the double bond. Therefore, the reaction with silane **2** is not selective but, instead, it allowed to demonstrate diverse reactivity in the reactions of oxidative sulfonamidation leading to numerous and sometimes unexpected products. In contrast, the reactions of oxidative arenesulfonamidation of silane **1** provide a convenient synthetic route to silylated N-arylsulfonyl-aziridines in up to 91% isolated yield. Apart from the demonstrated diverse reactivity patterns, the novelty of this work is the synthesis of more than twenty new compounds, which belong to potentially biologically active silylated N-heterocycles and, thus, deserve further investigation.

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4. Experimental Section

4.1. General

All starting materials reported in the manuscript have been previously described in literature. All products were identified using ^{1}H NMR and ^{13}C analysis and comparison with authentic samples. IR spectra were taken on a Bruker Vertex 70 spectrophotometer in KBr. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and CD_3CN on Bruker DPX 400 spectrometer at working frequencies 400 (^{1}H), 100 (^{13}C), 40.5 (^{15}N), 79.5 (^{29}Si) and 376 (^{19}F) MHz. All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.27 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively) and CD_3CN peak (1.95 (^{1}H), 1.3 and 118 (^{13}C) ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. Melting point was measured on MeltEMP (laboratory devices). All flash chromatography was performed using 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. The plates were visualized using a 254 nm ultraviolet lamp or aqueous $NaIO_4$ solutions. ^{1}H NMR and ^{13}C NMR, IR and X-Ray data are given for all compounds in the Supporting Experimental.

4.2 Synthesis

4.2.1 Reaction of triflamide with vinyltrimethylsilane in the system t-BuOCl+NaI. To the solution of (2.00 g, 13 mmol) of triflamide and (6.04 g, 40 mmol) of NaI in 80 ml of CH_3CN (2.01 g, 20 mmol) of vinyltrimethylsilane was added, the mixture was cooled to +10-15°C, then (4.60 ml, 40 mmol) of *t*-BuOCl was added dropwise in the dark in argon atmosphere. The reaction mixture was kept for 2 h at +10-15°C, then 22 h at room temperature. After the reaction was completed, the solvent was removed at a reduced pressure, the residue dissolved in 80 ml of ethyl acetate and treated with 90 ml of saturated aqueous $Na_2S_2O_3$. The extract was dried with $CaCl_2$, solvent removed in vacuum, 5.44 g of light-yellow residue placed in a column with coarse silica and eluted successively with hexane, hexane–ether 1:1, ether. From the hexane eluate, (0.61 g, 12%) of (2-chloro-1-iodoethyl)trimethylsilane **5** was isolated as a liquid. From ethereal-hexane eluate, yellow precipitate was obtained, which was crystallized from chloroform to give (2.71 g, 52%) of *N*,*N'*-[1-(trimethylsilyl)ethane-1,2-diyl)bis(triflamide) **6** as a white powder.

Products **7**, **8** were isolated from the ethereal-hexane eluate in total yield (1.13 g, 13%). Iodohydrin **9** is formed in trace amounts and was isolated from the hexane eluate, along with product **5**.

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4.2.2. Reaction of arenesulfonamides with vinyltrimethylsilane in the system t-BuOCl+NaI (general procedure). To the solution of 10-13 mmol of arenesulfonamide and three-fold molar excess of NaI 80 ml of CH_3CN 15-19 mmol of trimethylvinylsilane was added, the mixture cooled to +10-15°C, three-fold molar excess of *t*-BuOCl was added dropwise in the dark in argon atmosphere, the reaction mixture kept for 2 h at +10-15°C, then 22 h at room temperature. After completion of the reaction, the solvent was removed at a reduced pressure, the residue dissolved in 80 ml of ethyl acetate and treated with 90 ml of saturated aqueous $Na_2S_2O_3$. The extract was dried with $CaCl_2$, solvent removed in vacuum, the residue (3.5-4.5 g) was placed in a column with coarse silica and eluted successively with hexane, hexane–эфир 1:1, ether. From the hexane eluate, 6–19% of (2-chloro-1-iodoethyl)trimethylsilane was isolated as light liquid, and from the ethereal-hexane eluate 71–91% of 1-arenesulfonyl-2-(trimethylsilyl)aziridine was obtained as light-yellow oil (for X = H, Me, Cl) or white powder (X = NO_2), which was crystallized from chloroform.

4.2.3. Reaction of triflamide with dimethyldivinylsilane in the system t-BuOCl+NaI. To the solution of (0.93 g, 6 mmol) of triflamide and (2.81 g, 19 mmol) of NaI in 60 ml of CH_3CN (0.70 g, 6 mmol) of dimethyldivinylsilane was added, the mixture cooled to –30°C, (2.14 ml, 19 mmol) of *t*-BuOCl 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 under reduced pressure, the residue dissolved in 70 ml of ethyl acetate and treated with 90 ml of aqueous $Na_2S_2O_3$. The extract was dried over $CaCl_2$, solvent removed in vacuum, ~2.58 g of light-yellow residue placed in a column with coarse silica and eluted successively with hexane, mixture hexane–ether 1:1, ether. From hexane eluate, were obtained successively (0.10 g, 6%) of (2-chloro-1-iodoethyl)dimethyl(vinyl)silane **13** as a liquid, then (7 mg, 3%) of dark-orange liquid consisting of the mixture of diastereomers of bis(2-chloro-1-iodoethyl)dimethylsilane **14**. From ether-hexane eluate, 0.11 g of unreacted triflamide and (0.42 g, 20%) of *N*-(2-{[dimethyl(vinyl)silyl]-2-iodoethyl}triflamide **12** (light-yellow oil) were obtained, and from the ethereal eluate – light-yellow crystals which were purified by washing with chloroform to give (0.64 g, 66%) of *N*-(3-(trifluoromethylsulfonyl)oxazolidin-5-yl)triflamide **11** as a white powder.

4.2.4. Reaction of benzenesulfonamide with dimethyldivinylsilane in the system t-BuOCl+NaI. To the solution of (1.40 g, 9 mmol) of benzenesulfonamide and (4.02 g, 27 mmol) of NaI in 70 ml of CH_3CN (1.00 g, 9 mmol) of dimethylvinylsilane was added. The reaction was carried out and treated as above. Light-yellow residue (3.29 g) was dissolved in chloroform, the insoluble solid filtered and analyzed by NMR. The isolated powder was crystallized from chloroform and dried to give 0.71 g of unreacted benzenesulfonamide (from ^{1}H NMR). The yellow oily part soluble in chloroform (2.58 g) was placed in a column with coarse silica and

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eluted as in the previous synthesis. From the hexane eluate, were successively obtained (0.68 g, 28%) of compound **13** and (0.18 g, 5%) of diastereomeric mixture of compound **14**. From ether-hexane eluate, a mixture of crystalline and oily compounds was obtained, which was separated by preparative TLC with eluent hexane–ether 2:1 to give (0.15 g, 13%) of 2-[dimethyl(vinyl)silyl)-1-(phenylsulfonyl)aziridine **18a** as a colorless oil and (0.48 g, 25%) of 2-[(2-chloro-1-iodoethyl)dimethylsilyl]-1-(phenylsulfonyl)aziridine **19a** as a light-yellow oil. The crystalline residue was washed with ether and dried to afford (0.10 g, 4%) of analytically pure 3,5-diiodo-4,4-dimethyl-1-(phenylsulfonyl)-1,4-azasilinane **21a** as a white powder. From the ethereal eluate (0.19 g, 21%) of 2-{dimethyl[1-(phenylsulfonyl)aziridin-2-yl]silyl}-1-(phenylsulfonyl)aziridine **20a** was obtained as a colorless oily compound.

4.2.5. Reaction of tosylamide with dimethyldivinylsilane in the system t-BuOCl+NaI. To the solution of (1.53 g, 9 mmol) of tosylamide and (4.02 g, 27 mmol) of NaI in 70 ml of CH_3CN (1.00 g, 9 mmol) of dimethyldivinylsilane was added. The reaction was carried out and treated as above. The light-yellow residue (3.65 g) was placed in a column with coarse silica and eluted successively with the same eluents as above. From the hexane eluate was isolated (0.65 g, 27%) of compound **13**, then (0.11 g, 3%) of the diastereomeric mixture of compound **14**. From the ether-hexane eluate, a mixture of crystals and light-yellow oil was obtained, which was washed with ether to separate crystals from oil. The crystals were dried to afford (0.12 g, 4%) of analytically pure 3,5-diiodo-4,4-dimethyl-1-tosyl-1,4-azasilinane **21b** as a white powder. The oil was purified on the column with fine silica using hexane and hexane–ether 1:1 as eluents. (0.13 g, 7%) of 2-[dimethyl(vinyl)silyl]-1-tosylaziridine **18b** was isolated as a colorless oil. From the ethereal eluate, the oily mixture of two products was obtained, which was separated by column chromatography on coarse silica eluting with hexane and hexane–ether 1:1. (0.80 g, 29%) of 2-[(2-chloro-1-iodoethyl)dimethylsilyl]-1-tosylaziridine **19b** and (0.21 g, 15%) of 2-{dimethyl[1-(tosylaziridin-2-yl)silyl]-1-tosylaziridine **20b** as colorless oils were obtained.

4.2.6. Reaction of p-chlorobenzenesulfonamide with dimethyldivinylsilane in the system t-BuOCl+NaI. To the solution of (3.42 g, 18 mmol) of *p*-chlorobenzenesulfonamide and (8.04 g, 54 mmol) of NaI in 70 ml of CH_3CN (2.00 g, 18 mmol) of dimethyldivinylsilane was added. The reaction was carried out and treated as above. The light-yellow residue (6.83 g) was placed in a column with coarse silica and eluted successively with the same eluents as above. From the hexane eluate was isolated (0.70 g, 14%) of compound **13**, then (0.11 g, 3%) of the diastereomeric mixture of compound **14**. Then, from the hexane solution white crystals precipitated (0.30 g, 4%), which proved to be 1-(4-chlorophenylsulfonyl)-3,5-diiodo-4,4-dimethyl-1,4-azasilinane **21c**. From ether-hexane eluate, light-yellow oil was obtained, which was purified on a column with coarse silica eluting with hexane and hexane–ether 1:1 to afford

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3.84 g (55%) of 2-[(2-chloro-1-iodoethyl)dimethylsilyl]-1-(4-chlorophenylsulfonyl)aziridine **19c** as a colorless oil. From the ethereal eluate, yellow oil was obtained, which was additionally purified by column chromatography on coarse silica using hexane and hexane–ether 1:1 as eluents. (0.41 g, 11%) of 1-(4-chlorophenylsulfonyl)-2-{[1-(4-chlorophenylsulfonyl)aziridin-2-yl]dimethylsilyl}aziridine **20c** as a colorless oil.

4.2.7. Reaction of p-nitrobenzenesulfonamide with dimethyldivinylsilane in the system t-BuOCl+NaI. To the solution of (1.80 g, 9 mmol) of *p*-nitrobenzenesulfonamide and (4.02 g, 27 mmol) of NaI in 70 ml of CH_3CN (1.00 g, 9 mmol) of dimethyldivinylsilane was added. The reaction was carried out and treated as above. The light-yellow residue (4.46 g) was placed in a column with coarse silica and eluted successively with the same eluents as above. From the hexane eluate was isolated (0.55 g, 23%) of compound **13**, then (0.12 g, 3%) of the diastereomeric mixture of compound **14**. Then, from the hexane eluate, white crystals of 3,5-diiodo-4,4-dimethyl-1-(4-nitrophenylsulfonyl)-1,4-azasilinane **21d** (0.07 g, 2.4%) precipitated. From ether-hexane eluate, light-yellow powder was obtained, which was purified on fine silica using hexane and hexane–ether 1:1 as eluents. (0.87 g, 54%) of 2-[dimethyl(vinyl)silyl]-1-(4-nitrophenylsulfonyl)aziridine **18d** was isolated as a white powder. From the ethereal eluate, yellow powder was obtained and further purified on a column with coarse silica eluted with hexane and hexane–ether 1:1 to afford (0.29 g, 12%) of 2-[(2-chloro-1-iodoethyl)dimethylsilyl]-1-(4-nitrophenylsulfonyl)aziridine **19d** as a white powder.

*4.2.8. Reaction of p-nitrobenzenesulfonamide with (2-chloro-1-iodoethyl)dimethyl(vinyl)-silane **10** in the system t-BuOCl+NaI.* To the solution of (0.51 g, 2.6 mmol) of *p*-nitrobenzene-sulfonamide and (1.15 g, 7.6 mmol) of NaI in 50 ml of CH_3CN (0.70 g, 2.6 mmol) of (2-chloro-1-iodoethyl)dimethyl(vinyl)silane **13** was added, the mixture cooled to –30°C, then (0.87 ml, 7.6 mmol) of *t*-BuOCl was added dropwise in the dark in argon atmosphere. The reaction mixture was 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 $CaCl_2$, solvent removed in vacuum, the light-yellow residue (0.97 g) analyzed by NMR spectroscopy, which showed the presence of products **14** (37%), **19d** (16%) and 10% of unreacted **13** (the yields are given based on the ^{1}H NMR spectroscopy data).

*4.2.9. Reaction of p-nitrobenzenesulfonamide with 2-[dimethyl(vinyl)silyl)-1-(4-nitro-phenylsulfonyl)aziridine **15d** in the system t-BuOCl+NaI.* To the solution of (0.26 g, 1.3 mmol) of *p*-nitrobenzenesulfonamide and (0.58 g, 3.8 mmol) of NaI in 50 ml of CH_3CN (0.40 g, 1.3 mmol) of 2-[dimethyl(vinyl)silyl]-1-(4-nitrophenylsulfonyl)aziridine **18d** was added, the mixture cooled to –30°C and (0.44 ml, 3.8 mmol) of *t*-BuOCl was added dropwise in the dark in argon

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atmosphere. The reaction mixture was 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 $CaCl_2$, solvent removed in vacuum, 0.55 g of light-yellow residue analyzed by NMR spectroscopy, which showed the presence of products **19d** (80%) and 2-{dimethyl[1-(4-nitrophenylsulfonyl)aziridin-2-yl]silyl}-1-(4-nitrophenylsulfonyl)aziridine **20d** (20%) (the yields are given based on the ^{1}H NMR spectroscopy data).

4.2.10. (2-Chloro-1-iodoethyl)trimethylsilane, ***5***. Liquid, yields see in Table 1 in the main text. IR (KBr) 2956, 2104, 1945, 1516, 1420, 1295, 1254, 1137, 1032, 845, 760, 694, 607, 539, 497 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 3.92 (dd, C*H*H, *J* 11.8, 5.9 Hz, 1H), 3.88 (dd, CH*H*, *J* 11.8, 9.2 Hz, 1H), 3.38 (dd, C*H*, *J* 9.2, 5.9 Hz, 1H), 0.22 (s, CH_3, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 48.7 (*C*H_2Cl), 20.1 (*C*HI), -1.5 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$ δ, ppm) 7.21. Anal. calcd for $C_5H_{12}ClISi$: C, 22.87; H, 4.61; I, 48.33; Si, 10.70. Found: C, 22.61; H, 4.51; I, 48.12; Si, 10.51.

4.2.11. N,N'-(1-(Trimethylsilyl)ethane-1,2-diyl)bis(1,1,1-trifluoromethanesulfonamide), ***6***. White solid. Mp 125 °C. 52% yield. IR (KBr) 3384, 3298, 2971, 1453, 1444, 1366, 1231, 1195, 1145, 1059, 960, 907, 853, 760, 727, 609, 572, 487, 441 cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN δ, ppm) 6.72 (br.tr, $NHCH_2$, *J* 5.62 Hz), 6.56 (br.d, NHCH, *J* 9.1 Hz), 3.49 (dtr, CH, *J* 14.1, 3.7 Hz, 1H), 3.32 (dtr, CH*H*, *J* 14.1, 9.1 Hz, 1H), 3.20 (dtr, C*H*H, *J* 9.1, 3.7 Hz, 2H), 0.16 (s, CH_3, 9H). ^{13}C NMR (100 MHz, CD_3CN, δ, ppm) 120.8 (q, *J* 320.9 Hz, CF_3), 120.7 (q, *J* 320.0 Hz, CF_3), 48.3 (*C*H_2), 47.1 (*C*H), –3.1 (CH_3). ^{19}F NMR (376 MHz, CD_3CN, δ, ppm) –77.9, –78.1. ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.34. Anal. calcd for $C_7H_{14}F_6N_2O_4S_2Si$: C, 21.21; H, 3.56; N, 7.07; S, 16.18; F, 28.76; Si, 7.09. Found: C, 21.20; H, 3.51; N, 7.01; S, 16.15; F, 28.43; Si, 7.02.

4.2.12. N-[2-Iodo-2-(trimethylsilyl)ethyl]triflamide, ***7***. Yellow oil. ^{1}H NMR (400 MHz, CD_3CN, δ, ppm) 5.49 (br. tr, NH, *J* ~6 Hz), 3.76-3.61 (m, CH^{B}N in **7** and CHN in **8**), 3.50-3.35 (m, CH^{A}N in **7** and CH^{B}Cl in **8**), 3.21 (dd, C*H*I, *J* 11.2, 3.2 Hz, 1H), 0.21 (s, CH_3, 9H). ^{13}C NMR (100 MHz, CD_3CN, δ, ppm) 119.5 (q, *J* 321.0 Hz, CF_3), 48.1 (*C*H_2N), 19.6 (*C*HI), –2.4 (CH_3). ^{19}F NMR (376 MHz, CD_3CN, δ, ppm) –77.19. ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 6.56.

4.2.13. N-[2-Chloro-1-(trimethylsilyl)ethyl]triflamide, ***8***. Yellow oil. ^{1}H NMR (400 MHz, CD_3CN, δ, ppm) 5.46 (br. d, NH, *J* 5.9 Hz), 3.80-3.68 (m, CHN, 1H), 3.43 (dd, CH^{B}Cl, *J* 11.3, 3.0 Hz, 1H), 3.40-3.35 (m, CH^{A}Cl, 1H), 0.19 (s, CH_3, 9H); ^{13}C NMR (100 MHz, CD_3CN, δ, ppm) 119.5 (q, *J* 321.0 Hz, CF_3), 50.4 (*C*HN), 47.7 (*C*H_2Cl), –3.8 (CH_3). ^{19}F NMR (376 MHz, CD_3CN, δ, ppm) –77.24. ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.11.

4.2.14. 2-Iodo-2-(trimethylsilyl)ethanol, ***9***. Liquid. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 3.67 (dd, C*H*H, *J* 10.2, 7.3 Hz, 1H), 3.61 (dd, CH*H*, *J* 10.0, 5.6 Hz, 1H), 3.22 (dd, C*H*, *J* 7.3, 5.6

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Hz, 1H), 0.17 (s, CH_3, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 73.1 (*C*H_2OH), 20.0 (*C*HI), -1.4 (CH_3); ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 6.01.

4.2.15. 1-(Phenylsulfonyl)-2-(trimethylsilyl)aziridine, ***10a***. Light-yellow oil. 71% yield. IR (KBr): 2957, 1448, 1321, 1252, 1207, 1162, 1091, 954, 904, 846, 738, 690, 662, 595, 542 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.92 (d, *o*-C*H*, *J* 7.8 Hz, 2H), 7.61 (tr, *p*-C*H*, *J* 7.8 Hz, 1H), 7.52 (tr, *m*-C*H*, *J* 7.8 Hz, 2H), 2.69 (d, C*H*HN, *J* 8.7 Hz, 1H), 2.07 (d, CH*H*N, *J* 5.8 Hz, 2H), 2.07 (dd, C*H*N, *J* 8.7, 5.8 Hz, 2H), -0.11 (s, CH_3, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 138.0 (C_i), 133.3 (C_p), 128.8 (C_o), 127.8 (C_m), 30.2 (*C*H_2N), 29.9 (*C*HN), -3.9 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 1.44. Anal. calcd for $C_{11}H_{17}NO_2SSi$: C, 51.73; H, 6.71; N, 5.48; S, 12.55; Si, 11.00. Found: C, 51.70; H, 6.56; N, 5.45; S, 12.49; Si, 10.94.

4.2.16. 1-Tosyl-2-(trimethylsilyl)aziridine, ***10b***. Light-yellow oil, 86% yield. IR (KBr) 2958, 2900, 1921, 1598, 1494, 1451, 1408, 1323, 1299, 1253, 1208, 1158, 1094, 954, 905, 847, 815, 758, 700, 656, 557, 494 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.79 (d, *o*-C*H*, *J* 8.2 Hz, 2H), 7.30 (d, *m*-C*H*, *J* 8.2 Hz, 2H), 2.64 (d, C*H*HN, *J* 8.7 Hz, 1H), 2.41 (s, CH_3Ph, 3H), 2.04 (d, CH*H*N, *J* 5.8 Hz, 1H), 1.87 (dd, C*H*N, *J* 8.7, 5.8 Hz, 1H), -0.11 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 143.9 (C_p), 134.6 (C_i), 129.1 (C_m), 127.6 (C_o), 29.9 (*C*HN), 29.4 (*C*H_2N), 21.0 (CH_3Ph), -4.2 (CH_3); ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 1.49. Anal. calcd for $C_{12}H_{19}NO_2SSi$: C, 53.49; H, 7.11; N, 5.20; S, 11.90; Si, 10.42. Found C, 53.45; H, 7.08; N, 5.20; S, 11.84; Si, 10.40.

4.2.17. 1-(4-Chlorophenylsulfonyl)-2-(trimethylsilyl)aziridine, ***10c***. Light-yellow oil. 84% yield. IR (KBr) 3092, 2958, 1582, 1475, 1396, 1327, 1253, 1208, 1163, 1091, 1014, 954, 905, 846, 761, 707, 673, 626, 544, 482 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.85 (d, *o*-C*H*, *J* 8.4 Hz, 2H), 7.49 (d, *m*-C*H*, *J* 8.4 Hz, 2H), 2.66 (d, C*H*HN, *J* 8.6 Hz, 1H), 2.06 (d, CH*H*N, *J* 5.8 Hz, 1H), 1.93 (dd, CHN, *J* 8.6, 5.8 Hz, 1H), -0.06 (s, CH_3, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 139.6 (C_p), 136.5 (C_i), 129.2 (C_o), 128.9 (C_m), 30.4 (*C*H_2N), 30.0 (*C*HN), -4.0 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 1.71. Anal. calcd for $C_{11}H_{16}ClNO_2SSi$: C, 45.58; H, 5.56; N, 4.83; S, 11.06; Si, 9.69; Cl, 12.23. Found: C, 45.37; H, 5.41; N, 4.46; S, 11.03; Si, 9.57; Cl, 12.19.

4.2.18. 1-(4-Nitrophenylsulfonyl)-2-(trimethylsilyl)aziridine, ***10d***. White solid. Mp 128 (±2) °C. 91% yield. IR (KBr) 3102, 2957, 1606, 1527, 1404, 1305, 1249, 1210, 1170, 1090, 955, 896, 845, 752, 687, 613, 539, 459 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 8.39 (d, *m*-C*H*, *J* 8.7 Hz, 2H), 8.15 (d, *o*-C*H*, *J* 8.7 Hz, 2H), 2.76 (d, CH*H*N, *J* 8.5 Hz, 1H), 2.15 (d, C*H*HN, *J* 6.0 Hz, 1H), 2.09 (dd, C*H*N, *J* 8.5, 6.0 Hz, 1H), -0.04 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 150.5 (C_i), 144.1 (C_p), 129.3 (C_o), 124.1 (C_m), 31.2 (*C*H_2N), 31.0 (*C*HN), -3.8 (CH_3). ^{29}Si

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NMR (79.5 MHz, $CDCl_3$, δ, ppm) 1.90. Anal. calcd for $C_{11}H_{16}N_2O_4SSi$: C, 43.98; H, 5.37; N, 9.33; S, 10.67; Si, 9.35; found: C, 43.95; H, 5.30; N, 9.31; S, 10.60; Si, 9.29.

4.2.19. N-[3-(Trifluoromethylsulfonyl)oxazolidin-5-yl]triflamide, ***11***. White solid. Mp 128 (±2) °C. 66% yield. IR (KBr) 3559, 3303, 2901, 2262, 1445, 1377, 1198, 1075, 1005, 873, 827, 607 cm^{-1}. ^1H NMR (400 MHz, CD_3CN, δ, ppm) 7.87 (br. s, NH), 3.63 (m, NCH_2O and NC*H*O, 3H), 3.93 (dd, ClCH*H*, *J* 11.6, 5.0 Hz, 2H), 3.73 (m, IC*H*, 2H), 0.48 (s, CH_3, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 135.3 (=*C*H), 134.6 (=*C*H_2), 48.7 (*C*H_2Cl), 18.7 (*C*HI), -3.0 (CH_3), -3.4 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, δ, ppm) –78.30, –78.57. Anal. calcd for $C_5H_6F_6N_2O_5S_2$: C, 17.05; H, 1.72; N 7.95; S 18.21; F 32.36. Found: C, 17.00; H, 1.68; N, 7.91; S, 18.09; F, 32.12.

4.2.20. N-{2-[Dimethyl(vinyl)silyl]-2-iodoethyl}triflamide, ***12***. Light-yellow oil. 20% yield. IR (KBr) 3574, 3319, 1636, 1552, 1443, 1397, 1318, 1229, 1197, 1141, 1065, 839, 602 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm) 6.56 (dd, =C*H*, *J* 15.6, 9.0 Hz, 1H), 5.98 (br. s, NH), 4.82 (dd, =C*H*H, *J* 9.0, 2.0 Hz, 1H), 4.74 (dd, =CH*H*, *J* 15.6, 2.0 Hz, 1H), 4.02 (d, CH_2, *J* 8.0 Hz, 2H), 3.51 (tr, C*H*, *J* 8.0 Hz, 1H), 0.41 (s, CH_3, 3H), 0.39 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 129.3 (=*C*H), 119.80 (q, *J* 326.6 Hz, CF_3), 100.7 (=*C*H_2), 49.5 (*C*H_2NH), 11.7 (*C*HI), -1.2 (CH_3), -1.6 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, δ, ppm) –78.9; ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 13.6. Anal. calcd for $C_7H_{13}F_3INO_2SSi$: C, 21.71; H, 3.38; N, 3.62; S, 8.28; Si, 7.25; F, 14.72; I, 32.77. Found: C, 21.66; H, 3.32; N, 3.60; S, 8.15; Si, 7.19; F, 14.59; I, 32.55.

4.2.21. (2-Chloro-1-iodoethyl)dimethyl(vinyl)silane, ***13***. Liquid. Yields see in Scheme 7 and Table 2 in the main text. IR (KBr) 3051, 2956, 1406, 1295, 1253, 1008, 958, 819, 781, 702, 602, 534 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm) 6.24 (dd, =C*H*H, *J* 19.5, 14.8 Hz, 1H), 6.11 (dd, =CH*H*, *J* 14.8, 3.9 Hz, 1H), 5.81 (dd, =C*H*, *J* 19.5, 3.9 Hz, 1H), 3.93 (dd, C*H*H, *J* 11.9, 5.4 Hz, 1H), 3.83 (dd, =CH*H*, *J* 11.9, 9.6 Hz, 1H), 3.38 (dd, =C*H*, *J* 9.6, 5.4 Hz, 1H), 0.31 (s, CH_3, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 135.3 (=*C*H), 134.6 (=*C*H_2), 48.7 (*C*H_2Cl), 18.7 (*C*HI), -3.0 (CH_3), -3.4 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) -1.42. Anal. calcd for $C_6H_{12}ClISi$: C, 26.24; H, 4.40; I, 46.21; Si, 10.23. Found: C, 26.19; H, 4.20; I, 45.87; Si, 10.09.

4.2.22. Bis(2-chloro-1-iodoethyl)dimethylsilane, ***14***. Liquid. Yields see in Scheme 7 and Table 2 in the main text. IR (KBr) 2957, 2929, 1391, 1295, 1256, 1193, 1137, 1030, 922, 816, 789, 719, 594, 494 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm) 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 (100 MHz, $CDCl_3$, δ, ppm), major diastereomer: 47.6 (*C*H_2Cl), 16.7 (*C*HI), -3.3 (CH_3); minor diastereomer: δ47.9 (*C*H_2Cl), 17.0 (*C*HI), -2.1 and -3.8 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 9.59. Anal. calcd for $C_6H_{12}Cl_2I_2Si$: C, 16.49; H, 2.77; I 58.09; Si 6.43. Found: C, 16.15; H, 2.36; I, 56.90; Si, 6.40.

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4.2.23. 2-[Dimethyl(vinyl)silyl]-1-(phenylsulfonyl)aziridine, ***18a***. Colorless oil, 13% yield. IR (KBr) 1714, 1449, 1407, 1321, 1253, 1211, 1162, 1092, 1010, 957, 905, 836, 756, 664, 597 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.95 (d, *o*-C*H*, *J* 7.8 Hz, 2H), 7.64 (tr, *p*-C*H*, *J* 7.8 Hz, 1H), 7.54 (tr, *m*-C*H*, *J* 7.8 Hz, 2H), 5.96 (dd, =C*H*H, *J* 14.6, 4.6 Hz, 1H), 5.90 (dd, =C*H*, *J* 18.2, 14.6 Hz, 1H), 5.67 (dd, =C*H*H, *J* 18.2, 4.6 Hz, 1H), 2.72 (d, C*H*HN, *J* 8.4 Hz, 1H), 2.10 (d, CH*H*N, *J* 5.7 Hz, 1H), 1.98 (dd, C*H*N, *J* 8.4, 5.7 Hz, 1H), -0.02 (s, CH_3, 3H), -0.03 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 134.5 (C_i), 134.4 (C_p), 134.3 (=*C*H), 133.4 (=*C*H_2), 128.9 (C_o), 128.1 (C_m), 30.4 (*C*HNH), 29.4 (*C*H_2N), -5.5 (CH_3), -5.7 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) -6.34. Anal. calcd for $C_{12}H_{17}NO_2SSi$: C, 53.90; H, 6.41; N, 5.24; S, 11.99; Si, 10.50. Found: C, 53.73; H, 6.35; N, 5.20; S, 11.86; Si, 10.32.

4.2.24. 2-(Dimethyl(vinyl)silyl)-1-tosylaziridine, ***18b***. Colorless oil. 7% yield. IR (KBr) 2961, 1597, 1406, 1325, 1254, 1205, 1160, 1091, 1014, 955, 905, 835, 811, 703 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.81 (d, *o*-C*H*, *J* 8.2 Hz, 2H), 7.33 (d, *m*-C*H*, *J* 8.2 Hz, 2H), 5.96 (dd, =C*H*H, *J* 14.7, 6.2 Hz, 1H), 5.92 (dd, =C*H*, *J* 18.0, 14.4 Hz, 1H), 5.67 (dd, =C*H*H, *J* 18.0, 6.2 Hz, 1H), 2.67 (d, C*H*HN, *J* 8.5 Hz, 1H), 2.45 (s, CH_3Ph, 3H), 2.07 (d, CH*H*N, *J* 5.8 Hz, 1H), 1.95 (dd, C*H*N, *J* 8.4, 5.8 Hz, 1H), -0.01 (s, CH_3, 3H), -0.02 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 144.3 (C_p), 135.1 (=*C*H), 134.6 (C_i), 134.1 (=*C*H_2), 129.5 (C_m), 128.1 (C_o), 30.3 (*C*HN), 29.1 (*C*H_2N), 21.5 (CH_3Ph), -5.4 (CH_3), -5.6 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) -6.56. Anal. calcd for $C_{13}H_{19}NO_2SSi$: C, 55.48; H, 6.80; N, 4.98; S, 11.39; Si, 9.98. Found: C, 55.41; H, 6.77; N, 4.92; S, 11.31; Si, 9.90.

4.2.25. 2-[Dimethyl(vinyl)silyl]-1-[(4-chlorophenyl)sulfonyl]aziridine, ***18c***. From the fraction with **19c** as the major component. Yield (from NMR) 45%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.91–7.85 (m, *m*-C*H*, 2H), 7.56–7.47 (m, *o*-C*H*, 2H), 6.0–5.84 (m, =CH_2, 2H), 5.67 (dd, CH=, *J* 19.1, 5.0 Hz, 1H), 2.02–1.95 (m, C*H*N, 1H), 0.05 (s, CH_3, 3H), –0.01 (s, CH_3, 3H); the CH_2 signals of the aziridine ring overlap with the corresponding signals of **19c**.

4.2.26. 2-[Dimethyl(vinyl)silyl]-1-[(4-nitrophenyl)sulfonyl]aziridine, ***18d***. White solid. Mp 96 °C. 54% yield. IR (KBr) 3286, 3107, 2964, 1939, 1605, 1532, 1405, 1346, 1309, 1254, 1206, 1165, 1093, 1012, 957 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 8.39 (d, *m*-C*H*, *J* 8.8 Hz, 2H), 8.13 (d, *o*-C*H*, *J* 8.8 Hz, 2H), 5.98 (dd, =C*H*H, *J* 14.6, 4.5 Hz, 1H), 5.91 (dd, =C*H*, *J* 19.3, 14.6 Hz, 1H), 5.70 (dd, =C*H*H, *J* 19.3, 4.5 Hz, 1H), 2.77 (dd, C*H*HN, *J* 8.2, 0.67 Hz, 1H), 2.16 (d, CH*H*N, *J* 5.9, 0.7 Hz, 1H), 2.12 (dd, C*H*N, *J* 8.1, 5.9 Hz, 1H), 0.03 (s, CH_3, 3H), 0.02 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 150.5 (C_p), 144.0 (C_i), 134.4 (=*C*H), 134.0 (=*C*H_2), 129.3 (C_o), 124.1 (C_m), 31.1 (*C*HN), 30.2 (*C*H_2N), -5.6 and -5.7 (CH_3); ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) -6.35. Anal. calcd for $C_{12}H_{16}N_2O_4SSi$: C, 46.13; H, 5.16; N, 8.97; S, 10.26; Si, 8.99. Found: C, 46.10; H, 5.12; N, 8.94; S, 10.21; Si, 8.95.

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4.2.27. 2-[(2-Chloro-1-iodoethyl)dimethylsilyl]-1-(phenylsulfonyl)aziridine, ***19a***. Light-yellow oil. 25% yield. IR (KBr) 2958, 1705, 1447, 1321, 1255, 1162, 1090, 903, 818, 737 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.95 (d, *o*-C*H*, *J* 7.8 Hz, 2H), 7.67 (tr, *p*-C*H*, *J* 7.8 Hz, 1H), 7.57 (tr, *m*-C*H*, *J* 7.8 Hz, 2H), 3.85 (d, CH_2Cl, *J* 7.2 Hz, 2H), 3.36 (trd, C*H*I, *J* 7.2, 5.5 Hz, 1H), 2.74 (d, C*H*N, *J* 8.4 Hz, 1H), 2.19-2.13 (m, CH_2N, 2H), 0.16 (s, CH_3, 3H), 0.07 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 133.8 (C_i), 132.9 (C_p), 129.1 (C_o), 128.2 (C_m), 47.66 (*C*H_2Cl), 30.88 (*C*H_2N), 28.4 (*C*HN), 14.8 (*C*HI), -4.3 and -5.9 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.87. Anal. calcd for $C_{12}H_{17}ClINO_2SSi$: C, 33.54; H, 3.99; N, 3.26; I, 29.53; S, 7.46; Si, 6.53. Found: C, 33.24; H, 3.98; N, 3.11; I, 28.87; S, 7.30; Si, 6.14.

Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 3.87 (d, C*H*$_2$Cl, *J* 7.3, 1.5 Hz, 2H), 3.42-3.38 (m, C*H*I, 1H), 2.20 (dd, CH_2N, *J* 8.4, 5.7 Hz, 2H), 0.17 (s, CH_3, 3H), 0.04 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 47.74 (*C*H_2Cl), 30.80 (*C*H_2N), 28.7 (*C*HN), 15.0 (*C*HI), -5.28 and -5.34 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.98.

4.2.28. 2-[(2-Chloro-1-iodoethyl)dimethylsilyl]-1-tosylaziridine, ***19b***. Colorless oil. 29% yield. IR (KBr): 3284, 2958, 1593, 1406, 1326, 1160, 1088, 906, 815 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.82 (d, *o*-C*H*, *J* 8.1 Hz, 2H), 7.35 (d, *m*-C*H*, *J* 8.1 Hz, 2H), 3.87-3.76 (m, C*H*$_2$Cl, 2H), 3.38-3.32 (m, C*H*I, 1H), 2.69 (d, C*H*N, *J* 8.5 Hz, 1H), 2.46 (s, CH_3Ph, 3H), 2.15-2.10 (m, C*H*$_2$N, 2H), 0.16 (s, CH_3, 3H), 0.09 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 144.8 (C_p), 143.6 (C_i), 129.7 (C_m), 128.2 (C_o), 47.72 (*C*H_2Cl), 30.65 (*C*H_2N), 28.05 (*C*HN), 21.59 (CH_3Ph), 15.16 (*C*HI), -4.4 and -5.8 (CH_3). ^{29}Si NMR (79.5, $CDCl_3$, δ, ppm) 5.61. Anal. calcd for $C_{13}H_{19}ClINO_2SSi$: C, 35.18; H, 4.32; N, 3.16; I, 28.59; S, 7.23; Si, 6.33. Found: C, 35.15; H, 4.31; N 3.13; I, 28.33; S, 7.03; Si, 6.28.

Minor diastereomer, ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 2.44 (s, CH_3Ph, 3H), 2.18-2.15 (m, C*H*$_2$N, 2H), 0.17 (s, CH_3, 3H), 0.06 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 47.81 (*C*H_2Cl), 30.62 (*C*H_2N), 28.46 (*C*HN), 21.46 (CH_3Ph), 15.28 (*C*HI), -5.1 and -5.5 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.69.

4.2.29. 2-[(2-Chloro-1-iodoethyl)dimethylsilyl]-1-[(4-chlorophenyl)sulfonyl]aziridine, ***19c***. Colorless oil. 55% yield. IR (KBr) 3290, 3090, 2962, 2255, 1581, 1475, 1397, 1327, 1257, 1206, 1162, 1089, 904, 798, 674 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.88 (d, *o*-C*H*, *J* 8.6 Hz, 2H), 7.54 (d, *m*-C*H*, *J* 8.6 Hz, 2H), 3.88 (dd, C*H*HCl, *J* 7.1, 3.7 Hz, 1H), 3.38 (q, CH*H*Cl, *J* 7.1 Hz, 1H), 2.71 (dd, C*H*I, *J* 8.5, 1.5 Hz, 1H), 2.22 (ddd, C*H*HN, *J* 10.9, 5.4, 5.8 Hz, 1H), 2.15 (dd, CH*H*N, *J* 5.8, 1.5 Hz 1H), 0.17 (s, CH_3, 3H), 0.11 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 140.36 (C_p), 136.08 (C_i), 129.6 (C_o), 129.4 (C_m), 47.68 (*C*H_2Cl), 31.15 (*C*H_2N), 28.56 (*C*HN), 14.64 (*C*HI), -4.3 and -6.0 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.71. Anal.

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calcd for $C_{12}H_{16}Cl_2INO_2SSi$: C, 31.05; H, 3.47; N, 3.02; I, 27.34; S, 6.91; Si, 6.05. Found: C, 31.00; H, 3.45; N, 3.01; I, 27.30; S, 6.86; Si, 6.02.

Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 0.17 (s, CH_3, 3H), 0.06 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 140.34 (C_p), 136.15 (C_i), 47.60 (*C*H_2Cl), 31.04 (*C*H_2N), 28.95 (*C*HN), 14.75 (*C*HI), -5.24 and -5.32 (CH_3); ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.83.

4.2.30. 2-([(2-Chloro-1-iodoethyl)dimethylsilyl]-1-[(4-nitrophenyl)sulfonyl]aziridine, ***19d***. White solid. Mp 97 °C. 12% yield. IR (KBr) 3106, 2958, 1608, 1532, 1346, 1309, 1164, 1091, 904, 849, 796, 747 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 8.42 (d, *m*-C*H*, *J* 8.6 Hz, 2H), 8.17 (d, *o*-C*H*, *J* 8.6 Hz, 2H), 3.93 (dd, C*H*HCl, *J* 11.6, 7.0 Hz, 1H), 3.89 (dd, CH*H*Cl, *J* 11.6, 5.5 Hz, 1H), 3.93 (dd, C*H*I, *J* 7.0, 5.5 Hz, 1H), 2.79 (dd, C*H*N, *J* 8.5, 1.5 Hz, 1H), 2.37 (ddd, C*H*HN, *J* 8.5, 5.8, 1.5 Hz, 1H), 2.12 (dd, CH*H*N, *J* 5.8, 1.5 Hz 1H), 0.19 (s, CH_3, 3H), 0.15 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 150.7 (C_p), 143.5 (C_i), 129.5 (C_o), 124.3 (C_m), 47.47 (*C*H_2Cl), 31.84 (*C*H_2N), 29.28 (*C*HN), 14.05 (*C*HI), -4.1 and -6.0 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.88. Anal. calcd for $C_{12}H_{16}ClIN_2O_4SSi$: C, 30.36; H, 3.40; Cl, 7.47; I, 26.73; N, 5.90; S, 6.75; Si, 5.92. Found: C, 30.33; H, 3.39; N 5.88; I, 26.68; S, 6.68; Si, 5.89.

Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 0.20 (s, CH_3, 3H), 0.13 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 47.53 (*C*H_2Cl), 31.66 (*C*H_2N), 29.67 (*C*HN), 14.16 (*C*HI), -5.0 and -5.4 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 6.03.

4.2.31. Dimethylbis[1-(phenylsulfonyl)aziridin-2-yl]silane, ***20a***. Colorless oil. 21% yield. IR (KBr) 2961, 2904, 2256, 1589, 1447, 1320, 1258, 1206, 1163, 1083, 1066, 905, 841, 798, 737, 589 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.92 (d, *o*-C*H*, *J* 7.8 Hz, 2H), 7.63 (tr, *p*-C*H*, *J* 7.8 Hz, 1H), 7.54 (tr, *m*-C*H*, *J* 7.8 Hz, 2H), 2.62 (dd, CH^{B}N, *J* 8.6, 2.8 Hz, 1H), 2.06 (dd, CH^{A}N, *J* 5.7, 2.8 Hz, 1H), 1.90 (dtr, C*H*N, *J* 8.6, 5.7 Hz, 1H), -0.07 and -0.09 (s, CH_3, 6H, major (*R*,*R*+*S*,*S*)-diastereomer), -0.05 (s, CH_3, 6H, minor *R*,*S*-diastereomer). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 138.0 (C_i), 133.5 (C_p), 129.0 (C_o), 128.0 (C_m), 30.2 (*C*H_2N), 29.4 (*C*HNH), -1.37 and 1.42 [CH_3, major (*R*,*R*+*S*,*S*)-diastereomer], -2.1 (CH_3, minor *R*,*S*-diastereomer). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 3.66.

4.2.32. Dimethylbis(1-tosylaziridin-2-yl)silane, ***20b***. Colorless oil. 15% yield. IR (KBr) 2960, 1593, 1401, 1323, 1258, 1161, 1084, 906, 800 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.80 (d, *o*-C*H*, *J* 7.8 Hz, 2H), 7.34 (d, *m*-C*H*, *J* 7.8 Hz, 2H), 2.59 (dd, CH^{B}N, *J* 8.6, 2.0 Hz, 1H), 2.45 (s, CH_3Ph, 3H), 2.04 (d, CH^{A}N, *J* 5.8 Hz, 1H), 1.88 (dtr, C*H*N, *J* 8.6, 5.8 Hz, 1H), -0.04 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 144.4 (C_i), 135.1 (C_p), 129.6 (C_o), 128.1 (C_m), 30.2 (*C*H_2N), 29.3 (*C*HNH), 21.6 (CH_3Ph), -1.33 and 1.37 [CH_3 in (*R*,*R*+*S*,*S*)-diastereomer], -2.1 (CH_3 in *R*,*S*-diastereoisomer). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 3.72. Anal. calcd for

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$C_{20}H_{26}N_2O_4S_2Si$: C, 53.30; H, 5.82; N, 6.22; S, 14.23; Si, 6.23. Found: C, 53.26; H, 5.79; N, 6.21; S, 14.19; Si, 6.22.

4.2.33. Dimethyl{bis[(4-chlorophenyl)sulfonyl]aziridin-2-yl}silane, ***20c***. Colorless oil. 11% yield. IR (KBr) 3286, 3092, 2961, 1581, 1475, 1396, 1327, 1163, 1090, 903, 833, 795, 762, 673, 626 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.84 (d, *o*-C*H*, *J* 8.5 Hz, 2H), 7.51 (d, *m*-C*H*, *J* 8.5 Hz, 2H), 2.58 (d, CH^BN, *J* 8.6 Hz, 1H), 2.09 (d, CH^AN, *J* 5.9 Hz, 1H), 1.94 (trd, C*H*N, *J* 8.0, 6.1 Hz, 1H), -0.09 (s, CH_3, 3H), -0.13 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 140.3 (C_p), 136.1 (C_i), 129.4 (C_o), 129.3 (C_m), 30.58 (*C*H_2N), 27.1 (*C*HN), -7.1 and -7.4 (CH_3); ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 1.55. Anal. calcd for $C_{18}H_{20}Cl_2N_2O_4S_2Si$: C, 43.99; H, 4.10; N, 5.70; S, 13.05; Si, 5.71. Found: C, 43.96; H, 4.08; N, 5.67; S, 12.99; Si, 5.66.

Minor diastereomer, ^1H NMR (400 MHz, $CDCl_3$, δ, ppm) 2.58 (d, CH^BN, *J* 8.6 Hz, 1H), 2.04 (d, CH^AN, *J* 5.8 Hz, 1H), 1.94 (trd, C*H*N, *J* 8.0, 6.1 Hz, 1H), -0.14 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 30.49 (*C*H_2N), 27.5 (*C*HN), -7.5 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 1.31.

4.2.34. Dimethyl{bis[(4-nitrophenylsulfonyl)aziridin-2-yl]silane, ***20d***. Light-yellow oil. ^1H NMR (400 MHz, $CDCl_3$, , δ, ppm, from the reaction mixture) 8.42-8.37 (m, *o*-C*H*, 2H), 8.17-8.12 (m, *m*-C*H*, 2H), 2.70-2.65 (m, CH^BN, 1H), 2.22-2.18 (m, CH^AN, 1H), 2.14-2.11 (m, C*H*N, 1H), -0.03 (s, CH_3, 3H).

4.2.35. 3,5-Diiodo-4,4-dimethyl-1-(phenylsulfonyl)-1,4-azasilinane, ***21a***. White solid. Mp 155 (±2) °C. 4% yield. IR (KBr) 2960, 1451, 1335, 1249, 1161, 1097, 1039, 785, 570 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.78 (d, *o*-C*H*, *J* 7.3 Hz, 2H), 7.61 (tr, *p*-C*H*, *J* 7.3 Hz, 1H), 7.54 (tr, *m*-C*H*, *J* 7.3 Hz, 2H), 4.33 (dd, C*H*I, *J* 13.4, 6.1 Hz, 2H), 3.34 (dd, CH^BN, *J* 13.4, 6.1 Hz, 2H), 2.97 (tr, CH^AN, *J* 13.4 Hz, 2H), 0.41 (s, CH_3, 3H), 0.26 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 139.3 (C_i), 133.0 (C_p), 129.4 (C_o), 126.7 (C_m), 52.6 (*C*H_2N), 6.9 (*C*HI), -4.4 and -5.8 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 4.91. Anal. calcd for $C_{12}H_{17}I_2NO_2SSi$: C, 27.65; H, 3.29; N, 2.69; I, 48.69; S, 6.15; Si, 5.39. Found: C, 27.30; H, 3.27; N, 2.53; I, 48.68; S, 6.01; Si, 5.24.

4.2.36. 3,5-Diiodo-4,4-dimethyl-1-tosyl-1,4-azasilinane, ***21b***. White solid. Mp 169 °C. 4% yield. IR (KBr) 2960, 2922, 1596, 1455, 1337, 1158, 1097, 1038, 923, 813, 779, 546 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.66 (d, *o*-C*H*, *J* 8.3 Hz, 2H), 7.33 (d, *m*-C*H*, *J* 8.3 Hz, 2H), 4.31 (dd, C*H*I, *J* 12.4, 5.9 Hz, 2H), 3.34 (dd, CH^BN, *J* 13.0, 5.9 Hz, 2H), 2.94 (tr, CH^AN, *J* 13.0 Hz, 2H), 2.44 (s, CH_3Ph, 3H), 0.40 (s, CH_3, 3H), 0.26 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 143.9 (C_i), 136.2 (C_p), 130.0 (C_o), 126.8 (C_m), 52.6 (*C*H_2N), 21.5 (CH_3Ph), 7.0 (*C*HI), -4.4 and -5.8 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.47. Anal. calcd for $C_{13}H_{19}I_2NO_2SSi$:

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C, 29.17; H, 3.58; N, 2.62; I, 47.42; S, 5.99; Si, 5.25. Found: C, 29.10; H, 3.50; N, 2.57; I, 47.22; S, 5.89; Si, 5.21.

4.2.37. 3,5-Diiodo-4,4-dimethyl-1-((4-nitrophenyl)sulfonyl)-1,4-azasilinane, ***21c****.* White solid. Mp. 205 (±2) °C. 2% yield. IR (KBr) 2919, 1649, 1579, 1474, 1342, 1248, 1156, 1092, 1032, 927, 839, 778 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 7.72 (d, *m*-C*H*, *J* 8.6 Hz, 2H), 7.51 (d, *o*-C*H*, *J* 8.6 Hz, 2H), 4.29 (dd, C*H*I, *J* 12.6, 5.5 Hz, 2H), 3.34 (dd, $CH^{B}N$, *J* 13.2, 5.5 Hz, 2H), 2.97 (tr, $CH^{A}N$, *J* 13.2 Hz, 2H), 0.42 (s, CH_3, 3H), 0.27 (s, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm) 139.6 (C_p), 137.7 (C_i), 129.7 (C_o), 128.2 (C_m), 52.6 (*C*H_2N), 6.6 (*C*HI), -4.4 and -5.8 (CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$, δ, ppm) 5.30. Anal. calcd. for $C_{12}H_{16}ClI_2NO_2SSi$: C, 25.94; H, 2.90; N, 2.52; I, 45.68; S, 5.77; Si, 5.05; found: C, 25.91; H, 2.88; N, 2.50; I, 45.59; S, 5.69; Si, 5.01.

4.2.38. 3,5-Diiodo-4,4-dimethyl-1-((4-nitrophenyl)sulfonyl)-1,4-azasilinane, ***21d****.* White solid, Mp 244 °C. 2% yield. IR (KBr) 3102, 2922, 1736, 1523, 1459, 1345, 1161, 1096, 1037, 785, 593 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 8.38 (d, *m*-C*H*, *J* 8.6 Hz, 2H), 7.97 (d, *o*-C*H*, *J* 8.6 Hz, 2H), 4.31 (dd, C*H*I, *J* 12.6, 6.0 Hz, 2H), 3.36 (dd, $CH^{B}N$, *J* 13.2, 6.0 Hz, 2H), 3.03 (tr, $CH^{A}N$, *J* 13.0 Hz, 2H), 0.40 (s, CH_3, 3H), 0.29 (s, CH_3, 3H).

4.3. X-ray measurements

Crystal data were collected on a Bruker D8 Venture diffractometer with MoK_α radiation (λ = 0.71073) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set.[46] Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX programs set.[46] The details of all structures can be obtained free of charge from the Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

Conflict of interest

The authors declare no conflict of interest.

Supporting Information

Experimental details, spectroscopic data and X-ray structural information for new compounds (CCDC 1882243 (**10d**), 1859983 (**18d**)**,** 1815954 (**21a**), 1859981 (**21b**), 1874187 (**21c**), 1859982 (**21d**)). This material is available free of charge via the Internet at doi:

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- Vinyl silanes undergo via oxidative addition and heterocyclization when reacting with sulfonamides in oxidative conditions.
- The reactivity of triflamide is principally different from that of arenesulfonamides.
- Silylated mono- and diaziridines, N-sulfonyl-1,4-azasilinanes and 3-(triflyl)-5-(triflamido)oxazolidine are obtained.

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