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Metal free fluoroamination of allylsilanes: A route to 3-fluoropyrrolidines

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Dedicated to Professor David O'Hagan, recipient of the 2012 ACS Award for Creative Work in Fluorine Chemistry.

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ABSTRACT

The intramolecular fluoroamination of homoallylic amines activated by a triisopropylsilyl or *p*-tolyldiisopropylsilyl group was successfully performed in the presence of Selectfluor® in acetonitrile leading to *anti* or *syn* 3-fluoropyrrolidines. The stereochemical outcome of these fluorocyclizations is dictated by the geometry of the alkene precursor. In comparison with oxygen nucleophile, the use of *N*-tosyl or *N*-Boc nucleophiles benefits from superior control over stereoselectivity but suffers from competitive fluorodesilylation.

1. Introduction

Organosilanes are valuable starting materials for the preparation of fluorinated targets when reacted in the presence of electrophilic sources of fluorine [1]. Arylsilanes are amenable to fluorination upon *ipso*-substitution, a reaction leading to fluorinated aromatics in modest yields [2]. Recently, Ritter and Tang reported an improved regiospecific silver-mediated electrophilic fluorination of aryltriethoxysilanes [3]. Since our first report in 2001, we have expanded significantly the scope of this chemistry to non aromatic systems with the demonstration that vinylsilanes, allylsilanes, allenylsilanes and allenylmethylsilanes are superior to arylsilanes in terms of reactivity and in some cases, product selectivity [4]. When these organosilanes were subjected to fluorination, fluoroalkenes, fluorodienes, allylic and propargylic fluorides became accessible in moderate to excellent yields. Numerous enantiopure products were synthesized including biologically relevant targets [5]. For these applications, the presence of the silyl group is critical to increase the nucleophilicity of the proximal alkene and dictate the regiochemistry of the fluorination [6]. More recently, we exploited a new mode of reactivity for allylsilanes with "F^+" sources by allowing them to act as 1,2-dipoles instead of the equivalent of an allyl anion [7]. For this purpose, the triisopropylsilylmethyl and diisopropylphenylsilylmethyl groups were used as activating groups instead of trimethylsilylmethyl. Based on these principles, the fluoroetherification of silyl-activated homoallylic alcohols was performed in the presence of 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis tetrafluoroborate (Selectfluor®) or *N*-fluorobenzenesulfonimide (NFSI) and led to a series of fluorinated tetrahydrofurans [8]. The stereochemical outcome of these reactions is consistent with an overall *syn* addition to the double bond; this stereospecific transformation led to *syn*- and *anti*-cyclized products using *E*- and *Z*-allylsilanes respectively. The importance of fluorinated *N*-heterocycles encouraged us to expand the scope of these silyl-induced fluoroetherifications by examining the reactivity of allylsilanes substituted with pending *N*-nucleophiles as potential substrates for fluoroamination. Herein, we report that 3-fluoropyrrolidines are accessible upon fluorocyclization of *N*-protected homoallylic amines and we discuss the efficiency of this process *versus* the fluoroetherification of the corresponding homoallylic alcohols (Fig. 1).

2. Results and discussion

We began our studies with the fluorocyclization of the linear homoallylic amines **1a–f**. The purpose of this preliminary investigation was to identify the optimum silyl substituent and *N*-protecting group for fluorocyclization to occur in preference to fluorodesilylation. Based on our previous work [8], we selected the

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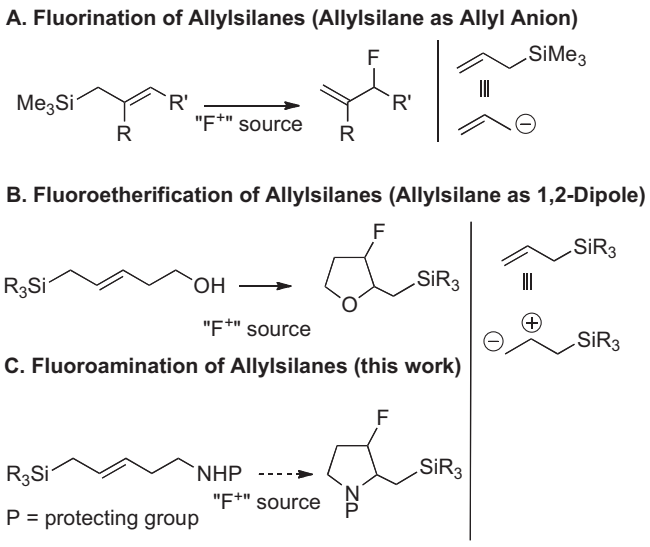
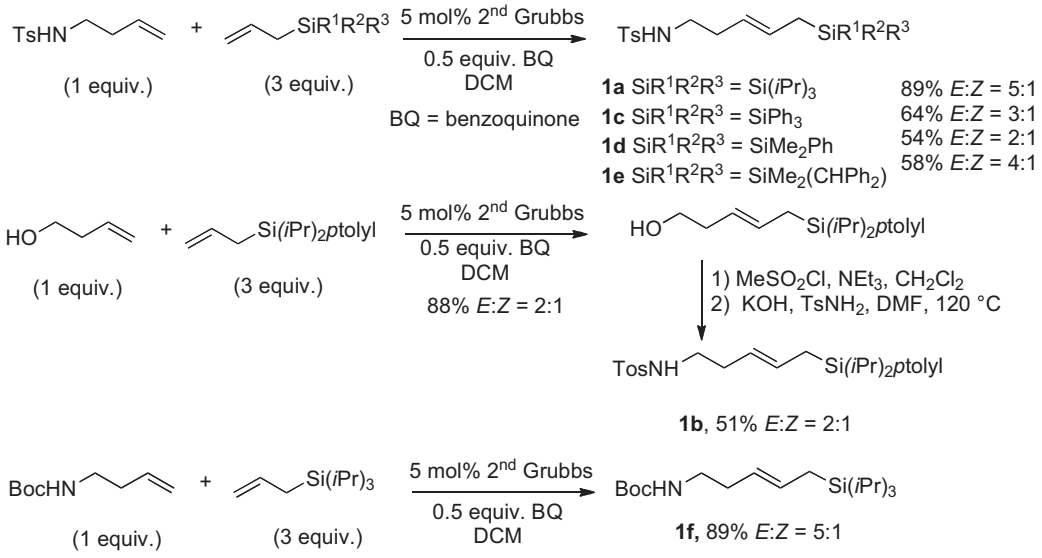


Fig. 1. Fluorination of allylsilanes used as allyl anion or 1,2-dipole equivalent.

triisopropylsilyl, *p*-tolyldimethylsilyl, triphenylsilyl, dimethylphenylsilyl and the benzhydryldimethylsilyl groups as a replacement to trimethylsilyl in order to favor 1,2-dipole reactivity; all these groups with the exception of the triisopropylsilyl group are amenable to oxidative cleavage [9]. Both the tosyl and Boc groups were chosen to protect the pending amino nucleophile towards direct *N*-fluorination [10], yet allowing for cyclization. All homoallylic amines, with the exception of **1b**, were prepared by cross-metathesis of the corresponding allylsilanes with homoallylic tosylamine or *tert*-butyl but-3-en-1-ylcarbamate in the presence of Grubbs catalyst 2nd generation and 1,4-benzoquinone. For **1b**, it was preferable to perform the cross-metathesis reaction with but-3-enol then convert the primary alcohol group into the tosylated amine [11]. The required allylsilanes were either commercially available or obtained by substitution of the chloroallylsilane with the necessary organolithium following literature procedures [12]. All cross-metathesis reactions gave the desired allylsilanes as inseparable mixture of *E* and *Z* geometrical isomers (*E* major) with isolated yields ranging from 54 to 89% (Scheme 1).

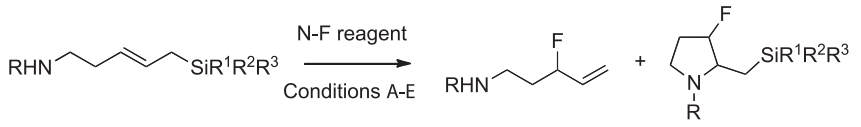
The homoallylic amines **1a–f** were subjected to fluorocyclization in acetonitrile using either Selectfluor (1.1 equiv.) or NFSI (1.1 equiv.). The reactions were typically performed in the presence of $NaHCO_3$ (1.1 equiv.) or K_2CO_3 (1.1 equiv.) to minimize protodesilylation and facilitate cyclization by deprotonation of the protected nitrogen nucleophile. Amines **1c–e** did not undergo fluorination-cyclization but led exclusively to the allylic fluoride **2**. The homoallylic amine **1b** with the pending diisopropyltolylsilyl group gave the cyclized product **4b** in 23% isolated yield along with 50% of the undesired product **2** resulting fluorodesilylation (entry 5). The triisopropylsilyl group was found to be optimum; indeed **1a** gave the pyrrolidine **4a** in isolated yields up to 58% (entries 1–4); competitive fluorodesilylation could however not be avoided. The *N*-Boc protected precursor **1f** underwent cyclization but this protecting group did not lead to a more favorable product distribution towards the fluorinated pyrrolidine **4f** (entry 12). The cyclized products were produced as inseparable mixtures of *syn* and *anti* isomers with diastereomeric ratio superior to the *E*/*Z* ratio of the starting allylsilanes; the *syn* isomer was consistently found to be predominant. The use of Selectfluor® and $NaHCO_3$ in acetonitrile at room temperature gave better results and was retained for further investigation. All together, these results highlight clear differences with the corresponding fluoroetherification of silyl-activated homoallylic alcohols [8]. The fluorocyclization of the *N*-protected homoallylic amines **1a–f** was less efficient as competitive fluorodesilylation could not be eradicated or was the predominant reaction pathway, but the level of stereocontrol for the fluoroamination was superior (Table 1).

To further investigate the difference in reactivity of silyl-activated homoallylic alcohols and amines, we examine the cyclization of (*Z*)-**1a**, (*Z*)-**1b**, (*Z*)-**1g** and (*E*)-**1h**. The synthesis of these allylsilanes is presented in Scheme 2. Compounds (*Z*)-**1a**, (*Z*)-**1b** and (*Z*)-**1g** were prepared by substituting the corresponding activated alcohols with tosyl amine in DMF. The *Z* geometry of all precursors was secured through a key ring closing metathesis as previously reported in the literature [8,13,14]. The preparation of (*E*)-**1h** began with the known (*E*)-2,2-dimethyl-5-(triisopropylsilyl)pent-3-enoic acid [8]. This precursor was obtained by cross-metathesis reaction of deconjugated tiglic acid with triisopropylallylsilane followed by methylation under basic condition applying literature procedures [8]. Amination with tosyl isocyanate gave the amide (*E*)-**5** with no erosion of stereochemistry (*E*:*Z* ratio > 20:1). The reduction of (*E*)-**5** with lithium aluminium



Scheme 1. Synthesis of amines **1a–f**.

Table 1
Fluorocyclization of allylsilanes **1a**–**f**.



1a R = Ts; $SiR^1R^2R^3 = Si(iPr)_3$
1b R = Ts; $SiR^1R^2R^3 = Si(iPr)_2$-p-tolyl
1c R = Ts; $SiR^1R^2R^3 = SiPh_3$
1d R = Ts; $SiR^1R^2R^3 = SiMe_2Ph$
1e R = Ts; $SiR^1R^2R^3 = SiMe_2(CHPh_2)$
1f R = Boc; $SiR^1R^2R^3 = Si(iPr)_3$

2 R = Ts
3 R = Boc

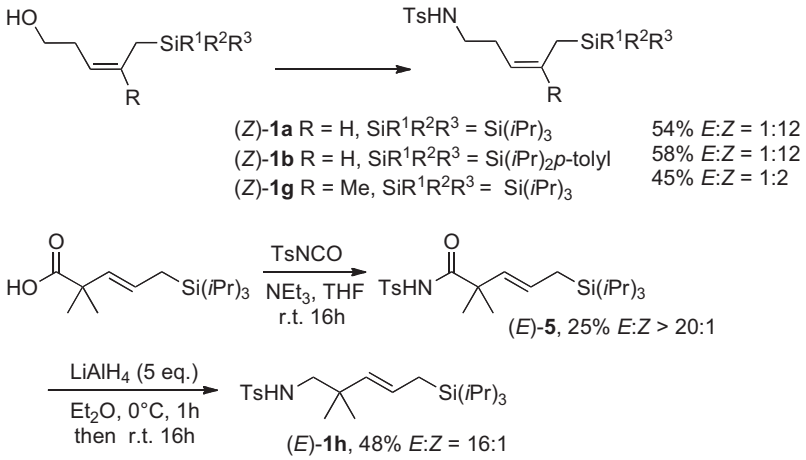
4a R = Ts; $SiR^1R^2R^3 = Si(iPr)_3$
4b R = Ts; $SiR^1R^2R^3 = Si(iPr)_2$p-tolyl
4c R = Ts; $SiR^1R^2R^3 = SiPh_3$
4d R = Ts; $SiR^1R^2R^3 = SiMe_2Ph$
4e R = Ts; $SiR^1R^2R^3 = SiMe_2(CHPh_2)$
4f R = Boc; $SiR^1R^2R^3 = Si(iPr)_3$

Entry	Allylsilanes (*E*:*Z*)	Condition (time)[a]	Yield [%] of **2** or **3**[b]	Yield [%] of **4a-f** (*syn:anti*)[c]
1	**1a** (5:1)	**A** (24 h)	**2**, 34	**4a** 58 (9:1)
2	**1a** (5:1)	**B** (48 h)	**2**, 17	**4a** 55 (7:1)
3	**1a** (5:1)	**C** (48 h)	**2**, 22	**4a** 53 (7:1)
4	**1a** (5:1)	**D** (24 h)	**2**, 18	**4a** 50 (9:1)
5	**1b** (2:1)	**A** (24 h)	**2**, 50	**4b** 23 (5:1)
6	**1c** (3:1)	**A** (16 h)	**2**, 44	–[d]
7	**1c** (3:1)	**E** (72 h)	**2**, 56	–[d]
8	**1d** (2:1)	**A** (16 h)	**2**, 72	–[d]
9	**1d** (2:1)	**E** (16 h)	**2**, 63	–[d]
10	**1e** (4:1)	**A** (48 h)	**2**, 34	–[d]
11	**1e** (4:1)	**E** (72 h)	**2**, 46	–[d]
12	**1f** (5:1)	**A** (24 h)	**3**, 43	**4f** 54 (5:1)

[a] *Conditions*: **A** = Selectfluor (1.1 equiv.), $NaHCO_3$ (1.1 equiv.) CH_3CN, r.t.; **B** = Selectfluor (1.1 equiv.), K_2CO_3 (1.1 equiv.), CH_3CN, r.t.; **C** = Selectfluor (1.1 equiv.), CH_3CN, r.t.; **D** = NFSI (1.1 equiv.), $NaHCO_3$ (1.1 equiv.), CH_3CN, reflux; **E** = NFSI (1.1 equiv.), $NaHCO_3$ (1.1 equiv.), CH_3CN, r.t.
[b] Yield of the isolated product.
[c] d.r., determined by ^{19}F NMR analysis of the crude product.
[d] Fluorodesilylation only.

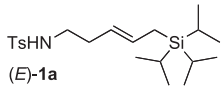
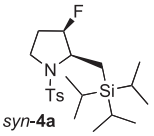
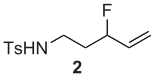
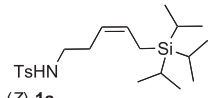
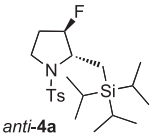
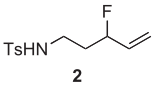
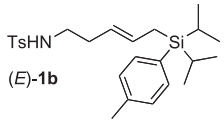
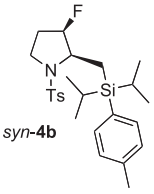
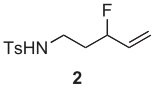
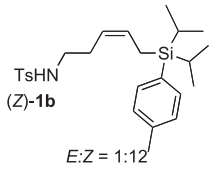
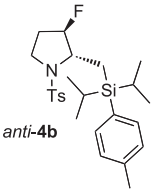
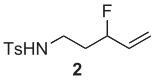
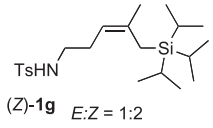
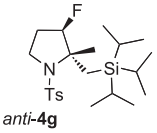
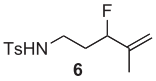
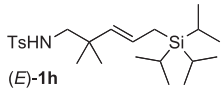
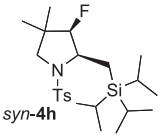
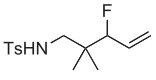
hydride gave (*E*)-**1h** in 48%. This reaction led to detectable isomerization of the double bond (*E*:*Z* ratio = 16:1).

All homoallylic amines were subjected to fluorocyclization using Selectfluor® and $NaHCO_3$ in acetonitrile at room temperature (Table 2). These reactions gave the desired fluorinated pyrrolidines with yields ranging from 14 to 61%. Competitive fluorodesilylation was observed for all substrates; the allylic fluoride side-products could be separated from the desired 3-fluoropyrrolidines **4** by silica gel column chromatography. Several trends emerge from this study. The cyclization of triisopropylallylsilanes was more efficient than the corresponding precursors presenting with the diisopropyltolylsilyl group; this stands true both for the *E* and *Z* series (entries 1 and 2 *vs.* entries 3 and 4). In the *Z* series, the presence of an alkene methyl substituent proximal to the silyl group was beneficial in terms of product distribution. The branched amine (*Z*)-**1g** gave the product of cyclization in 61% yield (entry 5) but in contrast, the linear allylsilane (*Z*)-**1b** gave **4b** with a chemical yield of only 14% (entry 4). The *gem*-dimethyl substitution of (*E*)-**1h** did not encourage further cyclization *vs.* competitive fluorodesilylation (entry 6). For (*E*)-**1h**, the allylic fluoride **7** was isolated as the major product (45%) and the 3-fluoropyrrolidine **4h** was obtained in 36%. The stereochemical outcome of the cyclization is consistent with an overall *syn* addition to the double bond; this stereospecific transformation led to *syn*- and *anti*-cyclized products using *E*- and *Z*-allylsilanes respectively. For the *E* and *Z* linear precursors (*E*)-**1a**, (*E*)-**1b**, (*Z*)-**1a** and (*Z*)-**1b**, the diastereomeric ratio of the products was superior to the *E*:*Z* ratio of the starting allylsilanes (entries 1–4) [8]. In contrast, erosion was observed for the substituted amines (*Z*)-**1g** and (*E*)-**1h** (entries 5 and 6). Steady state NOE/HOESY experiments were conducted for all cyclized products for the assignment of *syn* or *anti*-stereochemistry. A strong NOE interaction was found between the H^3 and



Scheme 2. Synthesis of amines (*Z*)-**1a** and **b**, (*Z*)-**1g** and (*E*)-**1h**.

Table 2
Fluorocyclisation of Allylsilanes **1a** and **b** and **1g** and **h**.[a]

Entry	Allylsilane **1**	Product **4**	Yield (%)[b] d.r. (syn:anti)[c]	Product **2**, **6** or **7**	Yield (%)[b]
1	 (*E*)-**1a** *E*:*Z* = 5:1	 *syn*-**4a**	58% (9:1)	 **2**	34%
2	 (*Z*)-**1a** *E*:*Z* =1:10	 *anti*-**4a**	34% (1:>20)	 **2**	38%
3	 (*E*)-**1b** *E*:*Z* = 2:1	 *syn*-**4b**	23% (5:1)	 **2**	50%
4	 (*Z*)-**1b** *E*:*Z* = 1:12	 *anti*-**4b**	14% (1:23)	 **2**	56%
5	 (*Z*)-**1g** *E*:*Z* = 1:2	 *anti*-**4g**	61% (1:1.3)	 **6**	27%
6	 (*E*)-**1h** *E*:*Z* = 16:1	 *syn*-**4h**	36% (6:1)	 **7**	45%

[a] *Conditions*: Selectfluor® (1.1 equiv.), $NaHCO_3$ (1.1 equiv.), CH_3CN, r.t., up to 48 h.
[b] Yield of isolated product.
[c] The d.r. was determined by ^{19}F NMR analysis on the crude product.

H^2 protons for the *syn*-pyrrolidines. HOESY analysis showed a strong interaction between the fluorine and one the isopropyl substituent of the silyl group. These observations are consistent with a *syn* spatial arrangement of these two substituents. In contrast, the *anti* 3-fluoropyrrolidines showed a strong HOESY interaction between the fluorine and H^2 proton, and a weak NOE interaction between H^3–H^2, which is diagnostic of an *anti* relationship between the fluorine and silylmethyl substituent. This study revealed that the pending nucleophile has a clear influence on the efficiency of the cyclization process. Chemical yields were significantly higher for the *O*-series [8] *vs* the *N*-series. In contrast, control over stereoselectivity was typically superior for the amines with respect to the corresponding alcohols, at least for the linear systems. The branched precursors (*Z*)-**1g** and (*E*)-**1h** led to significant erosion of d.r. upon cyclization. Assuming that the cyclizations are kinetically controlled [15], such stereochemical leakage could arise from two possible pathways. In a first scenario, competitive *syn* addition of the electrophilic fluorination reagent with respect to the silyl group could take place [16]. Alternatively, the fluorinated carbocation resulting from an *anti* attack of "F^+" with respect to the bulky stereodirecting triisopropylsilyl or diisopropyltolylsilyl group could undergo bond rotation prior to ring closure [16].

3. Conclusions

In summary, this work demonstrates that *N*-tosyl and *N*-Boc homoallylic amines activated by a triisopropylsilyl or *p*-tolyldiisopropylsilyl group are amenable to electrophilic fluorocyclization. The *E* or *Z* geometry of the alkene functionality dictates the preferential *syn* or *anti* stereochemical outcome of these kinetically controlled reactions. Important differences have been noted between allylsilanes substituted with oxygen [8] or nitrogen nucleophiles. Competitive fluorination leading to allylic fluorides could not be avoided with homoallylic amines but the level of stereocontrol achieved was superior at least for linear substrates. The fluorocyclization of silyl-activated homoallylic amines provides an alternative route to palladium-catalyzed intramolecular aminofluorination, a method restricted in scope to styrenes and providing no control over *syn* or *anti* selectivity [17]. The work described herein represents a solid foundation for further development; these new metal free fluorocyclizations will however require the development of a new cleavable silyl group to eradicate competitive fluorodesilylation and thereby allowing this strategy to reach its full synthetic potential.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded in deuterated solvents using Bruker DPX200, DPX400, AV400 and AV500 spectrometers, calibrated using residual undeuterated solvent as an internal reference. ^{13}C NMR spectra were recorded in deuterated solvents using Bruker DPX200, DPX400, AV400 and AV500 spectrometers, calibrated using residual undeuterated solvent as an internal reference. ^{19}F spectra were recorded on an AV400 spectrometer, calibrated using fluorotrichloromethane ($CFCl_3$) as a reference. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (J) are measured in hertz (Hz). The following abbreviations are used to describe multiplicities s = singlet; d = doublet; t = triplet; q = quartet; br = broad; m = multiplet; app = apparent. NMR spectra were processed with either MestRe-C or ACD/SpectManager. IUPAC names were obtained using the ACD/I-Lab service. High resolution mass spectra (HMRS; m/z) were recorded on micromass GCT spectrometer using field ionization (FI) or chemical ionization (CI); or on Autospec-oa Tof and Bruker MicroTOF instruments for electrospray ionization (ESI). Infrared spectra were recorded as thin films on NaCl plates in solution in CH_2Cl_2 or as solid on KBr disc on a Bruker Tensor 27 FT-IR spectrometer. Absorptions are measured in wavenumbers (cm^{-1}) and only peaks of interest are reported. Melting points of solids were measured on a Griffin apparatus and are uncorrected. All reactions requiring anhydrous conditions were conducted in dried apparatus under an inert atmosphere of argon. Solvents were dried on a column of alumina or purified before use according to standard procedures. All reactions were monitored by thin layer chromatography (TLC) using Merck Kiesegel 60 F_{254} plates. Visualization of the reaction components was achieved using UV fluorescence (254 nm) and KMnO4 stain. Silica gel chromatography was carried out over Merck silica gel C60 (40–60 μm) using eluent systems as described for each experiment.

4.2. Synthesis of allylsilanes

Allyldimethylphenylsilane [12], allylbenzhydryldimethylsilane [12], and allyl(diisopropyl)(4-methylphenyl)silane [8] were synthesized according to the literature procedures. Allyltriisopropylsilane and allyltriphenylsilane were commercially available and used without further purification.

4.3. Synthesis of organosilanes

General procedure A. To a solution of homoallylic amine (1 equiv.) and allylsilane (3 equiv.) in dry CH_2Cl_2 [0.3 M] was added portion wise over 3 days Grubbs' 2nd generation catalyst (5 mol%) and 1,4-benzoquinone (0.5 equiv.) at reflux. The reaction was maintained at reflux under argon atmosphere until TLC showed complete consumption of the starting material (3–4 days); the reaction was stopped and the solvent removed *in vacuo*. The resulting crude mixture was purified by flash column chromatography on silica gel.

General procedure B. Dry NEt_3 (5 equiv.) was added dropwise at 0 °C to a solution of primary alcohol (1 equiv.) and methane sulfonylchloride (1.2 equiv.) in dry CH_2Cl_2 [0.2 M]. The reaction was stirred at ambient temperature under an atmosphere of argon until TLC showed consumption of the alcohol (2 h). The reaction mixture was quenched with H_2O and extracted three times with CH_2Cl_2. The combined organic phases were washed with H_2O, brine, dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The resulting crude mixture was engaged without further purification to the next step. Finely grinded potassium hydroxide (1.5 equiv.) was dissolved in anhydrous DMF [0.5 M] at 120 °C and tosylamine (1.5 equiv.) added. The mixture was stirred for 30 min, after which a solution of mesylate (1 equiv.) in anhydrous DMF [0.5 M] was added. After complete consumption of the starting material (2–3 h), the reaction mixture was cooled, diluted with H_2O and extracted four times with EtOAc. The combined organic extracts were washed three times with H_2O then brine, dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel.

4.3.1. (E)-4-Methyl-N-(5-(triisopropylsilyl)pent-3-en-1-yl)benzenesulfonamide (E)-**1a**

Following the *general procedure A* on 500 mg (2.2 mmol, 1 equiv.) of *N*-but-3-en-1-yl-4-methylbenzenesulfonamide [18], the reaction yielded 782 mg of (*E*)-**1a** (89%, *E:Z* = 5:1) as a colorless oil after flash column chromatography on silica gel (hexane/Et_2O 8:2–7:3). *Major (E) isomer*: R_f = 0.4 (hexane/Et_2O 6:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.94–1.04 (m, 21H, Si(*i*-Pr)$_3$), 1.49 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, CH_2Si), 2.08 (q, 2H, $^3J_{H-H}$ = 6.9 Hz, NCH$_2$CH_2), 2.40 (s, 3H, CH_3PhNH), 2.88–2.94 (m, 2H, NCH_2CH$_2$), 4.88 (t, 1H, $^3J_{H-H}$ = 5.8 Hz, N*H*), 5.07 (1H, dtt, $^3J_{H-H(trans)}$ = 15.0 Hz, $^3J_{H-H}$ = 6.9 Hz, $^4J_{H-H}$ = 1.4 Hz, NCH$_2$CH$_2$C*H*), 5.45 (dtt, 1H, $^3J_{H-H(trans)}$ = 15.0 Hz, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.4 Hz, C*H*CH$_2$Si), 7.28 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, &&&Ar–*H*), 7.73 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, Ar–*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 10.8 (Si(*C*H(CH$_3$)$_2$)$_3$), 15.3 (*C*H$_2$Si), 18.5 (Si(CH(*C*H$_3$)$_2$)$_3$), 21.5 (*C*H$_3$PhNH), 32.6 (NCH$_2$CH$_2$), 42.8 (NCH$_2$CH$_2$), 123.5 (NCH$_2$CH$_2$*C*H), 127.0 (Ar), 129.5 (Ar), 131.1 (*C*HCH$_2$Si), 136.9 (Ar), 143.1 (Ar); IR (CH_2Cl_2): ν = 2948, 2000, 1699, 1130, 1047, 988, 883; HRMS (CI$^+$) m/z required for $C_{21}H_{38}NO_2SSi$ ([M+H]$^+$): 396.2393, found 396.2400, Δ = 1.9 ppm.

4.3.2. (E)-N-(5-(diisopropyl(p-tolyl)silyl)pent-3-en-1-yl)-4-methylbenzenesulfonamide (E)-**1b**

Following the *general procedure B* on 311.5 mg (1.12 mmol, 1 equiv.) of (*E*)-5-[diisopropyl(4-methylphenyl)silyl]pent-3-en-1-ol [8] the reaction yielded 255.2 mg (51% over two steps, *E:Z* = 2:1) of (*E*)-**1b** as a colorless oil after flash column chromatography on silica gel (hexane/Et_2O 9:1 to 8:2). Note: the synthesis of this product by direct cross-metathesis of the homoallylic tosyl-amine with allyl(diisopropyltolyl)silane gave a mixture of the desired product along up to 50% of the truncated side-product despite the addition of 1,4-benzoquinone. *Major (E) isomer*: R_f = 0.2 (hexane/Et_2O 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.96–1.05 (m, 12H, Si(CH(CH_3)$_2$)$_2$), 1.18–1.30 (m, 2H, Si(C*H*(CH$_3$)$_2$)$_2$), 1.82 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, CH_2Si), 2.05–2.12 (m, 2H, NCH$_2$CH_2), 2.36 (s, 3H, CH_3PhNH), 2.43 (s, 3H, CH_3PhSi), 2.90–2.96 (m, 2H, NCH_2CH$_2$), 4.35–4.42 (m, 1H, N*H*), 5.13 (dt,1H, $^3J_{H-H(trans)}$ = 15.1 Hz, $^3J_{H-H}$ = 7.1 Hz, NCH$_2$CH$_2$C*H*), 5.51 (dtt, 1H, $^3J_{H-H(trans)}$ = 15.1 Hz, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.3 Hz, C*H*CH$_2$Si), 7.19 (d, 2H, $^3J_{H-H}$ = 7.3 Hz, SiAr–*H*), 7.30 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, NHAr–*H*), 7.37 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, SiAr–*H*), 7.72 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, NHAr–*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 10.9 (Si(*C*H(CH$_3$)$_2$)$_2$), 15.6 (*C*H$_2$Si), 18.0 (Si(CH(*C*H$_3$)$_2$)$_2$), 21.4 (*C*H$_3$PhNH), 21.5 (*C*H$_3$PhSi), 32.6 (NCH$_2$CH$_2$), 42.7 (NCH$_2$CH$_2$), 124.3 (NCH$_2$CH$_2$*C*H), 127.0 (NHAr), 128.4 (*C*HCH$_2$Si), 128.5 (SiAr), 129.6 (NHAr), 130.8 (SiAr), 134.8 (SiAr), 137.0 (SiAr), 138.7 (NHAr), 143.2 (NHAr); IR (CH_2Cl_2) ν = 2942, 2864, 1599, 1328, 1100, 882, 814; HRMS (ESI$^+$) m/z required for $C_{25}H_{37}NO_2SSiNa^+$ ([M+Na]$^+$): 466.2206, found 466.2209, Δ = 0.6 ppm.

4.3.3. (E)-4-methyl-N-(5-(triphenylsilyl)pent-3-en-1-yl)benzenesulfonamide (E)-**1c**

Following the *general procedure A* on 200 mg (0.9 mmol, 1 equiv.) of *N*-but-3-en-1-yl-4-methylbenzenesulfonamide [18], the reaction yielded 343 mg of a mixture containing 64% of (*E*)-**1c** (*E:Z* = 3:1) and 15% of the truncated side product, as a white solid

after flash column chromatography on silica gel (hexane/Et_2O 8:2 then 7:3). *Major (E) isomer*: R_f = 0.2 (hexane/Et_2O 7:3); m.p. = 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.98–2.06 (m, 2H, $NHCH_2CH_2$), 2.31 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, CH_2Si), 2.44 (s, 3H, CH_3PhNH), 2.80–2.87 (m, 2H, $NHCH_2CH_2$), 4.16 (t, 1H, $^3J_{H-H}$ = 6.1 Hz, N*H*), 5.08 (dtt, 1H, $^3J_{H-H(trans)}$ = 15.1 Hz, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-H}$ = 1.4 Hz, $NHCH_2CH_2CH$), 5.52 (dtt, 1H, $^3J_{H-H(trans)}$ = 15.1 Hz, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.1 Hz, $CHCH_2Si$), 7.27 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, NHAr–*H*), 7.35–7.55 (m, 15H, SiAr–*H*), 7.66 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, NHAr–*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 19.5 (CH_2Si), 21.5 (CH_3PhNH), 32.8 ($NHCH_2CH_2$), 42.7 ($NHCH_2CH_2$), 126.2 ($NHCH_2CH_2CH$), 127.0 (NHAr–*C*), 127.9 (SiAr–*C*), 129.0 ($CHCH_2Si$), 129.6 (NHAr–*C*), 129.6 (SiAr–*C*), 134.3 (SiAr–*C*), 135.6 (SiAr–*C*), 137.2 (NHAr–*C*), 143.2 (NHAr–*C*); IR (CH_2Cl_2) ν = 3282, 3068, 1428, 1327, 1161, 702; HRMS (ESI$^+$) *m/z* required for $C_{30}H_{31}NO_2SSiNa^+$ ([M+Na]$^+$): 520.1737, found 520.1731, Δ = 1.9 ppm. *Identifiable data for the minor (Z) isomer* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.87–1.94 (m, 2H, $NHCH_2CH_2$), 2.28 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, CH_2Si), 2.41 (s, 3H, CH_3PhNH), 2.73–2.79 (m, 2H, $NHCH_2CH_2$), 4.22 (t, 1H, $^3J_{H-H}$ = 6.1 Hz, N*H*), 5.12–5.24 (m, 1H, $NHCH_2CH_2CH$), 5.58–5.75 (m, 1H, $CHCH_2Si$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 15.4 (CH_2Si), 27.1 ($NHCH_2CH_2$), 42.5 ($NHCH_2CH_2$), 124.6 ($NHCH_2CH_2CH$), 128.0 ($CHCH_2Si$).

4.3.4. (E)-N-(5-(dimethyl(phenyl)silyl)pent-3-en-1-yl)-4-methylbenzenesulfonamide (E)-1d

Following the *general procedure A* on 100 mg (0.4 mmol, 1 equiv.) of *N*-but-3-en-1-yl-4-methylbenzenesulfonamide [18], the reaction yielded 90 mg of (*E*)-**1d** (54%, *E:Z* = 2:1) as a colorless oil after flash column chromatography on silica gel (hexane/Et_2O 8:2 then 7:3). *Major (E) isomer:* R_f = 0.2 (hexane/Et_2O 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.28 (s, 6H, $Si(CH_3)_2$), 1.66 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, CH_2Si), 2.06–2.12 (m, 2H, $NHCH_2CH_2$), 2.44 (s, 3H, CH_3PhNH), 2.88–2.94 (m, 2H, $NHCH_2CH_2$), 4.56 (t, 1H, $^3J_{H-H}$ = 6.1 Hz, N*H*), 5.04 (dtt, 1H, $^3J_{H-H(trans)}$ = 15.2 Hz, $^3J_{H-H}$ = 6.8 Hz, $^4J_{H-H}$ = 1.2 Hz, $NHCH_2CH_2CH$), 5.40 (dtt, 1H, $^3J_{H-H(trans)}$ = 15.2 Hz, $^3J_{H-H}$ = 7.8 Hz, $^4J_{H-H}$ = 1.2 Hz, $CHCH_2Si$), 7.30 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, NHAr–*H*), 7.34–7.40 (m, 3H, SiAr–*H*), 7.47–7.51 (m, 2H, SiAr–*H*), 7.74 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, NHAr–*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ = −3.5 ($Si(CH_3)_2$), 21.4 (CH_3PhNH), 21.9 (CH_2Si), 32.6 ($NHCH_2CH_2$), 42.8 ($NHCH_2CH_2$), 124.5 ($NHCH_2CH_2CH$), 127.0 (NHAr–*C*), 127.7 (SiAr–*C*), 129.0 ($CHCH_2Si$), 129.6 (SiAr–*C*), 129.6 (NHAr–*C*), 133.5 (SiAr–*C*), 137.0 (NHAr–*C*), 138.3 (SiAr–*C*), 143.2 (NHAr–*C*); IR (CH_2Cl_2) ν = 3283, 2956, 1426, 1327, 1161, 836; HRMS (ESI$^+$): *m/z* required for $C_{20}H_{27}NO_2SSiNa^+$ ([M+Na]$^+$) 396.1424, found 396.1416, Δ = 2.0 ppm. *Identifiable data for the minor (Z) isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.27 (s, 6H, $Si(CH_3)_2$), 1.65 (d, 2H, $^3J_{H-H}$ = 8.6 Hz, CH_2Si), 2.01–2.07 (m, 2H, $NHCH_2CH_2$), 2.42 (s, 3H, CH_3PhNH), 2.84–2.90 (m, 2H, $NHCH_2CH_2$), 4.62 (t, 1H, $^3J_{H-H}$ = 6.1 Hz, N*H*), 5.14 (dtt, 1H, $^3J_{H-H(cis)}$ = 10.6 Hz, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-H}$ = 1.3 Hz, $NHCH_2CH_2CH$), 5.51 (dtt, 1H, $^3J_{H-H(cis)}$ = 10.6 Hz, $^3J_{H-H}$ = 8.6 Hz, $^4J_{H-H}$ = 1.5 Hz, $CHCH_2Si$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = −3.4 ($Si(CH_3)_2$), 17.9 (CH_2Si), 27.1 ($NHCH_2CH_2$), 42.7 ($NHCH_2CH_2$), 122.9 ($NHCH_2CH_2CH$), 128.5 ($CHCH_2Si$).

4.3.5. (E)-N-(5-(benzhydryldimethylsilyl)pent-3-en-1-yl)-4-methylbenzenesulfonamide (E)-1e

Following the *general procedure A* on 150 mg (0.6 mmol, 1 equiv.) of *N*-but-3-en-1-yl-4-methylbenzenesulfonamide [18], the reaction yielded 178 mg of (*E*)-**1e** (58%, *E:Z* = 4:1) as a colorless oil after flash column chromatography on silica gel (hexane/Et_2O 8:2 then 7:3). *Major (E) isomer*: R_f = 0.2 (hexane/Et_2O 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.06 (s, 6H, $Si(CH_3)_2$), 1.42–1.49 (m, 2H, CH_2Si), 2.06–2.14 (m, 2H, $NHCH_2CH_2$), 2.42 (s, 3H, CH_3PhNH), 2.86–2.95 (m, 2H, $NHCH_2CH_2$), 3.58 (s, 1H, $SiCH(Ph)_2$), 4.85 (t, 1H, $^3J_{H-H}$ = 6.1 Hz, N*H*), 4.96 (dt, 1H, $^3J_{H-H(trans)}$ = 15.1 Hz, $^3J_{H-H}$ = 6.8 Hz, $NHCH_2CH_2CH$), 5.28 (dt, 1H, $^3J_{H-H(trans)}$ = 15.1 Hz, $^3J_{H-H}$ = 7.7 Hz, $CHCH_2Si$), 7.12–7.19 (m, 2H, $SiCH(Ph\text{–}H)_2$), 7.23–7.34 (m, 10H, $SiCH(Ph\text{–}H)_2$), 7.79 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, NHAr–*H*), 7.74 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, NHAr–*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ = −3.8 ($Si(CH_3)_2$), 20.7 (CH_2Si), 21.3 (CH_3PhNH), 32.5 ($NHCH_2CH_2$), 42.8 ($NHCH_2CH_2$), 44.6 ($SiCH(Ph)_2$), 125.1 ($NHCH_2CH_2CH$), 126.9 (NHAr–*C*), 128.2 ($SiCH(Ph\text{–}C)_2$), 128.2 ($SiCH(Ph\text{–}C)_2$), 128.6 ($SiCH(Ph\text{–}C)_2$), 129.2 ($CHCH_2Si$), 129.5 (NHAr–*C*), 136.8 (NHAr–*C*), 142.2 ($SiCH(Ph\text{–}C)_2$), 143.1 (NHAr–*C*); IR (CH_2Cl_2) ν = 3280, 3090, 1597, 1447; HRMS (CI$^+$) *m/z* required for $C_{27}H_{34}NO_2SSi$ ([M+H]$^+$): 464.2080, found 464.2063, Δ = 3.6 ppm. *Identifiable data for the minor (Z) isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.05 (s, 6H, $Si(CH_3)_2$), 1.98–2.06 (m, 2H, $NHCH_2CH_2$), 4.89 (t, 1H, $^3J_{H-H}$ = 6.1 Hz, N*H*), 5.09 (dt, 1H, $^3J_{H-H(cis)}$ = 10.1 Hz, $^3J_{H-H}$ = 7.3 Hz, $NHCH_2CH_2CH$), 5.40 (dt, 1H, $^3J_{H-H(cis)}$ = 10.1 Hz, $^3J_{H-H}$ = 8.8 Hz, $CHCH_2Si$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = −3.7 ($Si(CH_3)_2$), 16.4 (CH_2Si), 26.9 ($NHCH_2CH_2$), 42.7 ($NHCH_2CH_2$), 44.6 ($SiCH(Ph)_2$), 124.4 ($NHCH_2CH_2CH$).

4.3.6. (E)-tert-butyl (5-(triisopropylsilyl)pent-3-en-1-yl)carbamate (E)-1f

Following the *general procedure A* on 500 mg (2.9 mmol, 1 equiv.) of *tert*-butyl but-3-en-1-ylcarbamate [19], the reaction yielded 887 mg of (*E*)-**1f** (89%, *E:Z* = 5:1) as a yellow oil after flash column chromatography on silica gel (hexane/Et_2O 9:1). *Major (E) isomer*: R_f = 0.7 (hexane/Et_2O 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.04 (s, 21H, $Si(CH(CH_3)_2)_3$), 1.43 (s, 9H, $COC(CH_3)_3$), 1.56 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, CH_2Si), 2.13–2.17 (m, 2H, $NHCH_2CH_2$), 3.11 (m, 2H, $NHCH_2CH_2$), 5.22 (d, 1H, $^3J_{H-H(trans)}$ = 14.8 Hz, $NHCH_2CH_2CH$), 5.55 (d, 1H, $^3J_{H-H(trans)}$ = 14.8 Hz, $CHCH_2Si$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 10.9 ($Si(CH(CH_3)_2)_3$), 15.4 (CH_2Si), 18.7 ($Si(CH(CH_3)_2)_3$), 28.4 (CH_3PhNH), 33.1 ($NHCH_2CH_2$), 40.2 ($NHCH_2CH_2$), 78.0 ($COC(CH_3)_3$), 124.9 ($NHCH_2CH_2CH$), 130.2 ($CHCH_2Si$), 155.9 (*CO*); IR (CH_2Cl_2) ν = 3044, 2322, 1761, 1543; HRMS (CI$^+$) *m/z* required for $C_{19}H_{40}NO_2Si$ ([M+H]$^+$): 342.2828, found 342.2845, Δ = 4.9 ppm.

4.3.7. (Z)-4-methyl-N-(5-(triisopropylsilyl)pent-3-en-1-yl)benzenesulfonamide (Z)-1a

Following the *general procedure B* on 164.5 mg (0.68 mmol, 1 equiv.) of (*Z*)-5-(triisopropylsilyl)pent-3-en-1-ol [8], the reaction yielded 145.4 mg (54% over two steps, *E:Z* = 1:10) of (*Z*)-**1a** as a colorless oil after flash column chromatography on silica gel (hexane/Et_2O 9:1 to 7:3). *Major (Z) isomer*: R_f = 0.5 (hexane/Et_2O 6:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.95–1.05 (m, 21H, $Si(i\text{-}Pr)_3$), 1.45 (d, 2H, $^3J_{H-H}$ = 8.6 Hz, CH_2Si), 2.16–2.23 (m, 2H, NCH_2CH_2), 2.40 (s, 3H, CH_3PhNH), 2.92–2.99 (m, 2H, NCH_2CH_2), 4.86–4.96 (m, 1H, N*H*), 5.02 (dtt, 1H, $^3J_{H-H(cis)}$ = 10.5 Hz, $^3J_{H-H}$ = 7.3 Hz, $^4J_{H-H}$ = 1.5 Hz, NCH_2CH_2CH), 5.57 (dt, 1H, $^3J_{H-H(cis)}$ = 10.5 Hz, $^3J_{H-H}$ = 8.8 Hz, $CHCH_2Si$), 7.28 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, Ar–*H*), 7.76 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, Ar–*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 10.8 (CH_2Si), 10.9 ($Si(CH(CH_3)_2)_3$), 18.5 ($Si(CH(CH_3)_2)_3$), 21.4 (CH_3PhNH), 27.1 (NCH_2CH_2), 42.8 (NCH_2CH_2), 122.0 (NCH_2CH_2CH), 127.0 (Ar), 129.5 (Ar), 130.0 (CHC_2Si), 136.9 (Ar), 143.1 (Ar); IR (CH_2Cl_2) ν = 2942, 2865, 1463, 1328, 1161, 883, 663; HRMS (ESI$^+$) *m/z* required for $C_{21}H_{37}NO_2SSiNa^+$ ([M+Na]$^+$): 418.2206, found 418.2206, Δ = 1 ppm.

4.3.8. (Z)-N-(5-(diisopropyl(p-tolyl)silyl)pent-3-en-1-yl)-4-methylbenzenesulfonamide (Z)-1b

Following the *general procedure B* on 300 mg (1.1 mmol, 1 equiv.) of (*Z*)-5-[diisopropyl(4-methylphenyl)silyl]pent-3-en-1-ol [8], the reaction yielded 277 mg of (*Z*)-**1b** (58% over two steps, *E:Z* = 1:12) as a colorless oil after flash column chromatography on silica gel (hexane/Et_2O 9:1 to 8:2). *Major (Z) isomer*: R_f = 0.2 (hexane/Et_2O 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.96–1.03 (m, 12H,

Si(CH(CH_3)$_2$)$_2$), 1.19–1.29 (m, 2H, Si(CH(CH$_3$)$_2$)$_2$), 1.77 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, CH_2Si), 2.15–2.23 (m, 2H, NCH$_2$CH_2), 2.37 (s, 3H, CH_3PhNH), 2.41 (s, 3H, CH_3PhSi), 2.94–2.99 (m, 2H, NCH_2CH$_2$), 4.60–4.73 (m, 1H, NH), 5.07 (dt, 1H, $^3J_{H-H(cis)}$ = 10.1 Hz, $^3J_{H-H}$ = 7.3 Hz, NCH$_2$CH$_2$CH), 5.65 (dt, 1H, $^3J_{H-H(cis)}$ = 10.1 Hz, $^3J_{H-H}$ = 8.7 Hz, CHCH$_2$Si), 7.18 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, SiAr–H), 7.30 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, NHAr–H), 7.37 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, SiAr–H), 7.77 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, NHAr–H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 10.9 (Si(CH(CH$_3$)$_2$)$_2$), 11.2 (CH_2Si), 17.9 (Si(CH(CH_3)$_2$)$_2$), 21.4 (CH_3PhNH), 21.4 (CH_3PhSi), 27.2 (NCH$_2$CH_2), 42.7 (NCH_2CH$_2$), 122.7 (NCH$_2$CH$_2$CH), 127.0 (NHAr), 128.4 (SiAr), 129.5 (CHCH$_2$Si), 129.6 (NHAr), 130.8 (SiAr), 134.8 (SiAr), 137.0 (SiAr), 138.7 (NHAr), 143.2 (NHAr); IR (CH$_2$Cl$_2$): ν = 2958, 1717, 1630, 1427, 949; HRMS (CI$^+$) m/z required for $C_{25}H_{38}NO_2SSi$ ([M+H]$^+$): 444.2393, found 444.2401, Δ = 1.9 ppm.

4.3.9. (Z)-5-(triisopropylsilyl)-4-methylpent-3-en-1-ol

To a solution of 2,2-diisopropyl-4-methyl-2,3,6,7-tetrahydro-1,2-oxasilepine [8] (791 mg, 3.7 mmol, 1 equiv.) in anhydrous THF at −78 °C under argon, was added dropwise a solution of *sBuLi* ([0.7 M] in pentane, 16 mL, 11.2 mmol, 3 equiv.). The reaction mixture was stirred at 0 °C for 4 h. It was quenched with a saturated $NH_4Cl_{(aq)}$ solution and the aqueous phase was extracted with Et$_2$O. The combined organic phases were washed with brine, dried over MgSO$_4$, filtered and the solvent removed *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel (hexane/Et$_2$O 9:1 to 7:3) to give 405 mg of the corresponding alcohol (42%, *E:Z* = 1:2) as a colorless oil. *Major (Z) isomer*: R_f = 0.3 (hexane/Et$_2$O 7:3); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.85–0.90 (m, 3H, Si(CH(CH$_3$)$_2$)$_3$), 0.99–1.10 (m, 17 H, Si(CH(CH_3)$_2$)$_3$), 1.48–1.52 (m, 1H, OH), 1.58 (s, 2H, CH_2Si), 1.76 (s, 3H, CH_3CCH$_2$Si), 2.24–2.33 (m, 2H, OHCH$_2$CH_2), 3.63 (t, 2H, $^3J_{H-H}$ = 6.5 Hz, OHCH_2CH$_2$), 4.96 (t, 1H, $^3J_{H-H}$ = 7.1 Hz, OHCH$_2$CH$_2$CH); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 11.9 (Si(CH(CH$_3$)$_2$)$_3$), 16.2 (CH_2Si), 18.7 (Si(CH(CH_3)$_2$)$_3$), 26.6 (CH_3CCH$_2$Si), 33.0 (OHCH$_2$CH_2), 62.6 (OHCH_2CH$_2$), 117.7 (OHCH$_2$CH$_2$CH), 137.3 (CCH_2Si); IR (neat) ν = 3329, 2943, 2867, 1465, 1167, 1049, 918; HRMS (FI$^+$) m/z required for $C_{15}H_{32}OSi$ ([M]$^+$) 256.2223, found 256.2228, Δ = 2.2 ppm. *Identifiable data for the minor (E) isomer*: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.62 (s, 2H, CH_2Si), 1.79 (s, 3H, CH_3CCH$_2$Si); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 11.9 (Si(CH(CH$_3$)$_2$)$_3$), 15.3 (CH_2Si), 18.3 (Si(CH(CH_3)$_2$)$_3$), 26.7 (CH_3CCH$_2$Si), 118.1 (OHCH$_2$CH$_2$CH), 137.5 (CH$_3$CCH_2Si).

4.3.10. (Z)-4-methyl-N-(4-methyl-5-(triisopropylsilyl)pent-3-en-1-yl)benzenesulfonamide (Z)-**1g**

Following the *general procedure B* on 405 mg (1.6 mmol, 1 equiv.) of (*Z*)-5-(triisopropylsilyl)-4-methylpent-3-en-1-ol the reaction yielded 306 mg of (*Z*)-**1g** (47% over two steps, *E:Z* = 1:2) as a yellow oil after flash column chromatography on silica gel (hexane/Et$_2$O 9:1 to 7:3). *Major (Z) isomer*: R_f = 0.6 (hexane/Et$_2$O 6:4); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.83–0.86 (m, 3H, Si(CH(CH$_3$)$_2$)$_3$), 0.91–0.97 (m, 18H, Si(CH(CH_3)$_2$)$_3$), 1.41 (s, 2H, CH_2Si), 1.64 (s, 3H, CH_3CCH$_2$Si), 2.06–2.16 (m, 2H, NHCH$_2$CH_2), 2.38 (s, 3H, CH_3PhNH), 2.86–2.96 (m, 2H, NHCH_2CH$_2$), 4.73 (t, 1H, $^3J_{H-H}$ = 6.8 Hz, NHCH$_2$CH$_2$CH), 4.98–5.20 (m, 1H, NH), 7.25 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, Ar–H), 7.75 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, Ar–H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 11.7 (Si(CH(CH$_3$)$_2$)$_3$), 16.0 (CH_2Si), 18.5 (Si(CH(CH_3)$_2$)$_3$), 21.3 (CH_3PhNH), 26.3 (CH_3CCH$_2$Si), 28.5 (NHCH$_2$CH_2), 42.9 (NHCH_2CH$_2$), 117.5 (NHCH$_2$CH$_2$CH), 127.0 (Ar–C), 129.4 (Ar–C), 137.0 (Ar–C), 137.3 (CH$_3$CCH_2Si), 142.9 (Ar–C); IR (CH$_2$Cl$_2$) ν = 2944, 2866, 1464, 1328, 1161, 883; HRMS (ESI$^-$) m/z required for $C_{22}H_{38}NO_2SSi$ ([M–H]$^-$): 408.2398, found 408.2392, Δ = 1.4 ppm. *Identifiable data for the minor (E) isomer*: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.80–0.83 (m, 3H, Si(CH(CH$_3$)$_2$)$_3$), 0.97–1.02 (m, 18H, Si(CH(CH_3)$_2$)$_3$), 1.44 (s, 2H, CH_2Si), 1.66 (s, 2H, CH_3CCH$_2$Si); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 11.6 (Si(CH(CH$_3$)$_2$)$_3$), 15.1 (CH_2Si), 18.0 (Si(CH(CH_3)$_2$)$_3$), 26.4 (CH_3CCH$_2$Si), 28.5 (NHCH$_2$CH_2), 117.8 (NHCH$_2$CH$_2$CH).

4.3.11. (E)-2,2-dimethyl-N-tosyl-5-(triisopropylsilyl)pent-3-enamide (E)-**5**

To a solution of (*E*)-2,2-dimethyl-5-(triisopropylsilyl)pent-3-enoic acid [8] (824 mg, 2,9 mmol, 1 equiv.) in THF (6 mL) under argon was added tosyl isocyanate (0.45 mL, 2.9 mmol, 1 equiv.). After stirring at room temperature for 10 minutes, distilled triethylamine (0.40 mL, 2.9 mmol, 1 equiv.) was added dropwise to the open flask allowing the release of CO_2. The reaction was stirred overnight. The mixture was then diluted with an equal volume of EtOAc, washed twice with 2 M HCl and brine, dried over MgSO$_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane/Et$_2$O 9:1 to 7:3) to yield 322 mg of (*E*)-**5** (25%, *E:Z* = >20:1) as a colorless oil. *(E) isomer*: R_f = 0.3 (hexane/Et$_2$O 7:3); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.03–1.06 (m, 21H, Si(CH(CH_3)$_2$)$_3$), 1.19 (s, 6H, NHCOC(CH_3)$_2$), 1.63 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, CH_2Si), 2.44 (s, 3H, CH_3PhNH), 5.34 (d, 1H, $^3J_{H-H(trans)}$ = 15.6 Hz, CH=CHCH$_2$Si), 5.70 (dt, 1H, $^3J_{H-H(trans)}$ = 15.6 Hz, $^3J_{H-H}$ = 8.3 Hz, CH=CHCH$_2$Si), 7.33 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, Ar–H), 7.92 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, Ar–H), 8.15–8.19 (m, 1H, NH); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 11.0 (Si(CH(CH$_3$)$_2$)$_3$), 16.1 (CH_2Si), 18.6 (Si(CH(CH_3)$_2$)$_3$), 21.7 (CH_3PhNH), 24.6 (NHCOC(CH_3)$_2$), 45.8 (NHCOC(CH$_3$)$_2$), 128.4 (Ar–C), 129.5 (Ar–C), 130.4 (CH=CHCH$_2$Si), 130.5 (CH=CHCH$_2$Si), 135.4 (Ar–C), 144.9 (Ar–C), 174.4 (NHCO); IR (CH$_2$Cl$_2$): ν = 2949, 1699, 1423, 1239, 1165, 964, 853; HRMS (ESI$^+$) m/z required for $C_{23}H_{39}NO_3SSiNa^+$ ([M+Na]$^+$): 460.2312, found 460.2293, Δ = 4 ppm.

4.3.12. (E)-N-(2,2-dimethyl-5-(triisopropylsilyl)pent-3-en-1-yl)-4-methylbenzenesulfonamide (E)-**1h**

In a flask charged with $LiAlH_4$ (83 mg, 2.2 mmol, 5 equiv.) in dry Et$_2$O (9 mL) at 0 °C under argon, a solution of (*E*)-2,2-dimethyl-*N*-tosyl-5-(triisopropylsilyl)pent-3-enamide (*E*)-**5** (193 mg, 0.4 mmol, 1 equiv.) in 1 mL of Et$_2$O was added dropwise. The reaction mixture stirred at 0 °C for 1 h then at room temperature overnight. H_2O was added carefully to the mixture, which was filtered through Celite and then extracted with Et$_2$O. The combined organic layers were washed with brine, dried over MgSO$_4$ and the solvent removed *in vacuo*. Purification of the resulting residue by flash column chromatography on silica gel (hexane/Et$_2$O 8:2) yielded 90.3 mg of the product (*E*)-**1h** (48%, *E:Z* = 16:1) as a colorless oil. *Major (E) isomer*: R_f = 0.5 (hexane/Et$_2$O 6:4); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.95 (s, 6H, NHCH$_2$C(CH_3)$_2$), 0.99–1.04 (m, 21H, Si(CH(CH_3)$_2$)$_3$), 1.52 (d, 2H, $^3J_{H-H}$ = 7.9 Hz, CH_2Si), 2.42 (s, 3H, CH_3PhNH), 2.68 (d, 2H, $^3J_{H-H}$ = 6.3 Hz, NHCH_2), 4.39–4.46 (m, 1H, NH), 5.05 (d, 1H, $^3J_{H-H(trans)}$ = 15.6 Hz, CH=CHCH$_2$Si), 5.42 (dt, 1H, $^3J_{H-H(trans)}$ = 15.6 Hz, $^3J_{H-H}$ = 7.9 Hz, CH=CHCH$_2$Si), 7.30 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, Ar–H), 7.72 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, Ar–H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 10.9 (Si(CH(CH$_3$)$_2$)$_3$), 15.6 (CH_2Si), 18.6 (Si(CH(CH_3)$_2$)$_3$), 21.4 (CH_3PhNH), 25.1 (NHCH$_2$C(CH_3)$_2$), 36.5 (NHCH$_2$C(CH$_3$)$_2$), 53.2 (NHCH$_2$), 126.8 (CH=CHCH$_2$Si), 127.0 (Ar–C), 129.6 (Ar–C), 134.1 (CH=CHCH$_2$Si), 136.9 (Ar–C), 143.1 (Ar–C); IR (neat) ν = 1265, 1162, 739, 705; HRMS (ESI$^-$) m/z required for $C_{23}H_{40}NO_2SSi$ ([M–H]$^-$): 422.2555, found 422.2548, Δ = 1.5 ppm. *Identifiable data for the minor (Z) isomer*: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.45 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, CH_2Si), 2.84 (d, 2H, $^3J_{H-H}$ = 6.6 Hz, NHCH_2), 4.95 (d, 1H, $^3J_{H-H(cis)}$ = 11.9 Hz, CH=CHCH$_2$Si), 5.47–5.56 (m, 1H, CH=CHCH$_2$Si).

4.4. Fluorocyclization of organosilanes

General procedure C. NaHCO$_3$ (1.1 equiv.) was added to a solution of allylsilane (1 equiv.) in dry CH$_3$CN [0.1 M]. Selectfluor

(1.1 equiv.) was added and the reaction was stirred for 48 h at r.t. The solvent was removed *in vacuo* and the reaction mixture was treated with a saturated solution of $NaHCO_3$ and extracted three times with Et_2O. The combined organic phases were washed with H_2O, brine, dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane/Et_2O 8:2).

4.4.1. Syn-3-fluoro-1-tosyl-2-((triisopropylsilyl)methyl)pyrrolidine syn-4a

Following the *general procedure C* on 100 mg (0.25 mmol, 1 equiv.) of (*E*)-**1a**, the reaction gave 62 mg of *syn*-**4a** (58%, d.r. *(syn:anti)* 9:1) as a white solid and 22 mg of allylic fluoride **2** (34%). *Major syn isomer*: R_f = 0.5 (hexane/Et_2O 6:4); m.p. = 73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.06–1.13 (m, 21H, Si(C*H*(CH_3)$_2$)$_3$), 1.23–1.47 (m, 2H, CH_AH$_B$CHF + CH_AH$_B$Si), 1.53 (ddd, 1H, $^2J_{H-H}$ = 14.5 Hz, $^3J_{H-F}$ = 4.3 Hz, $^3J_{H-H}$ = 3.4 Hz, CH$_A$$H_B$Si), 1.95 (td, 1H, *J* = 14.9, 5.3 Hz, CH$_A$$H_B$CHF), 2.43 (s, 3H, C$H_3$PhN), 3.45–3.55 (m, 1H, NCH_AH$_B$), 3.68 (dd, 1H, $^2J_{H-H}$ = 11.4 Hz, $^3J_{H-H}$ = 8.3 Hz, NCH$_A$$H_B$), 3.88 (ddt, 1H, $^3J_{H-F}$ = 25.3 Hz, $^3J_{H-H}$ = 12.7, 3.4 Hz, NC*H*CHF), 4.89 (dt, 1H, $^2J_{H-F}$ = 52.3 Hz, $^3J_{H-H}$ = 3.1 Hz, NCHC*H*F), 7.31 (d, 2 H, $^3J_{H-H}$ = 8.1 Hz, Ar–*H*), 7.73 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, Ar–*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 11.3 (Si(*C*H(CH_3)$_2$)$_3$), 11.4 (*C*H$_2$Si), 11.5 (Si(*C*H(CH_3)$_2$)$_3$), 18.5 (Si(CH(*C*H_3)$_2$)$_3$), 18.8 (Si(CH(*C*H_3)$_2$)$_3$), 21.5 (*C*H$_3$PhN), 32.1 (d, $^2J_{C-F}$ = 22.4 Hz, *C*H$_2$CHF), 46.4 (NCH$_2$), 63.3 (d, $^2J_{C-F}$ = 20.8 Hz, NCHCHF), 94.1 (d, $^1J_{C-F}$ = 182.9 Hz, NCH*C*HF), 127.2 (Ar–*C*), 129.7 (Ar–*C*), 135.6 (Ar–*C*), 143.5 (Ar–*C*); ^{19}F {^{1}H} NMR (377 MHz, $CDCl_3$) δ = −188.59; IR (CH_2Cl_2): ν = 3029, 1900, 1400, 902, 760; HRMS (CI^+) *m*/*z* required for $C_{21}H_{37}FNO_2SSi$ ([M+H]$^+$) 414.2298, found 414.2300, Δ = 4.8 ppm.

4.4.2. Syn-2-((diisopropyl(p-tolyl)silyl)methyl)-3-fluoro-1-tosylpyrrolidine syn-4b

Following the *general procedure C* on 100 mg (0.22 mmol, 1 equiv.) of (*E*)-**1b**, the reaction gave 24 mg of *syn*-**4b** (23%, d.r. *(syn:anti)* 5:1) as a colorless oil and 29 mg (50%) of allylic fluoride **2**. *Major syn isomer:* R_f = 0.4 (hexane/Et_2O 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.08–1.13 (m, 12H, Si(CH(CH_3)$_2$)$_2$), 1.13–1.18 (m, 1H, CH_AH$_B$CHF), 1.29–1.35 (m, 2H, Si(*C*H(CH_3)$_2$)$_2$), 1.56–1.61 (m, 1H, CH_AH$_B$Si), 1.79–1.89 (m, 2H, CH$_A$$H_B$CHF+CH$_A$$H_B$Si), 2.39 (s, 3H, C$H_3$PhSi), 2.42 (s, 3H, C$H_3$PhN), 3.46–3.54 (m, 1H, NCH_AH$_B$), 3.61 (dd, 1H, $^2J_{H-H}$ = 12.0 Hz, $^3J_{H-H}$ = 8.2 Hz, NCH$_A$$H_B$), 3.69 (ddd, 1H, $^3J_{H-F}$ = 25.8 Hz, $^3J_{H-H}$ = 12.6, 3.3 Hz, NC*H*CHF), 4.59 (ddd, 1H, $^2J_{H-F}$ = 52.0 Hz, $^3J_{H-H}$ = 3.5, 2.8 Hz, NCHC*H*F), 7.21 (d, 2H, $^3J_{H-H}$ = 7.2 Hz, SiAr–*H*), 7.25 (d, 2H, $^3J_{H-H}$ = 7.9 Hz, NAr–*H*), 7.47 (*d*, 2H, $^3J_{H-H}$ = 7.9 Hz, SiAr–*H*), 7.61 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, NAr–*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 11.5 (Si(*C*H(CH_3)$_2$)$_2$), 11.6 (Si(*C*H(CH_3)$_2$)$_2$), 12.1 (d, $^3J_{C-F}$ = 10.5 Hz, *C*H$_2$Si), 18.2 (Si(CH(*C*H_3)$_2$)$_2$), 18.3 (Si(CH(*C*H_3)$_2$)$_2$), 21.5 (*C*H$_3$PhSi), 21.5 (*C*H$_3$PhN), 31.9 (d, $^2J_{C-F}$ = 21.9 Hz, *C*H$_2$CHF), 46.6 (NCH$_2$), 63.2 (d, $^2J_{C-F}$ = 21.0 Hz, NCHCHF), 93.7 (d, $^1J_{C-F}$ = 183.1 Hz, NCH*C*HF), 127.3 (NAr–*C*), 128.6 (SiAr–*C*), 129.6 (NAr–*C*), 130.9 (SiAr–*C*), 135.1 (NAr–*C*), 135.2 (SiAr–*C*), 138.7 (SiAr–*C*), 143.4 (NAr–*C*); ^{19}F {^{1}H} NMR (377 MHz, $CDCl_3$) δ = −188.77; IR (CH_2Cl_2) ν = 2944, 2866, 1599, 1349, 1161, 1099, 817, 737; HRMS (ESI^+) *m*/*z* required for $C_{25}H_{36}FNO_2SSiNa^+$ ([M+Na]$^+$): 484.2112, found 484.2096, Δ = 3.2 ppm.

4.4.3. Syn-tert-butyl-3-fluoro-2-((triisopropylsilyl)methyl)pyrrolidine-1-carboxylate syn-4f

Following the *general procedure C* on 100 mg (0.29 mmol, 1 equiv.) of (*E*)-**1f**, the reaction gave 56 mg of *syn*-**4f** (54%, d.r. *(syn:anti)* 5:1) as a colorless oil and 27 mg (43%) of allylic fluoride **3**. *Major syn isomer*: R_f = 0.6 (hexane/Et_2O 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.08 (m, 23H, Si(C*H*(CH_3)$_2$)$_3$ + CH_2Si), 1.48 (s, 9H, COOC(CH_3)$_3$), 1.88 (ddddd, 1H, $^3J_{H-F}$ = 39.1 Hz, $^3J_{H-H}$ = 11.3, 11.0, 8.5, 3.8 Hz, CH_AH$_B$CHF), 2.09 (m, 1H, CH$_A$$H_B$CHF), 3.40 (dd, 1H, $^3J_{H-H}$ = 11.0, 6.0 Hz, NCH_AH$_B$), 3.71 (m, 1H, NCH$_A$$H_B$), 4.01 (m, 1H, NC*H*CHF), 5.04 (ddt, 1H, $^2J_{H-F}$ = 52.9 Hz, $^3J_{H-H}$ = 6.9, 3.8 Hz, NCHC*H*F); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 11.6 (Si(*C*H(CH_3)$_2$)$_3$), 18.7 (*C*H$_2$Si), 18.9 (Si(CH(*C*H_3)$_2$)$_3$), 28.6 (COOC(*C*H_3)$_3$), 31.3 (d, $^3J_{C-F}$ = 21.0 Hz, *C*H$_2$CHF), 44.0 (NCH$_2$), 59.4 (d, $^3J_{C-F}$ = 20 Hz, NCHCHF), 79.7 (COO*C*(CH_3)$_3$), 94.2 (d, $^1J_{C-F}$ = 173.7 Hz, NCH*C*HF), 154.5 (*C*OOC(CH_3)$_3$); ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ = −188.0; ν_{max}/cm^{-1} (DCM): 2800, 1715, 1352; HRMS (CI^+) required for $C_{21}H_{37}FNO_2SSi$ ([M+H]$^+$): 360.2730; found: 360.2734; Δ = 1.1 ppm. *Characteristic data for minor anti-isomer*: ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ = −172.7.

4.4.4. Anti-3-fluoro-1-tosyl-2-((triisopropylsilyl)methyl)pyrrolidine anti-4a

Following the *general procedure C* on 145 mg (0.37 mmol, 1 equiv.) of (*Z*)-**1a**, the reaction gave52 mg of *anti*-**4a** (34%, d.r. *(syn:anti)* 1:21) as a white solid and 36 mg (38%) of allylic fluoride **2**. *Major anti isomer*: R_f = 0.5 (hexane/Et_2O 6:4); m.p. = 70 °C; ^{1}H NMR (400 MHz, C_6D_6) δ = 0.62 (ddd, 1H, $^2J_{H-H}$ = 15.1 Hz, $^3J_{H-H}$ = 13.4 Hz, $^4J_{H-F}$ = 1.5 Hz, CH_AH$_B$Si), 0.91–1.02 (m, 3H, Si(C*H*(CH_3)$_2$)$_3$), 1.02–1.10 (m, 18H, Si(CH(CH_3)$_2$)$_3$), 1.41–1.56 (m, 2H, CH_2CHF), 1.66 (ddd, 1H, $^2J_{H-H}$ = 15.1 Hz, $^4J_{H-F}$ = 4.8 Hz, $^3J_{H-H}$ = 2.8 Hz, CH$_A$$H_B$Si), 1.85 (s, 3H, C$H_3$PhN), 3.11 (ddd, 1H, $^3J_{H-H}$ = 10.6 Hz, $^2J_{H-H}$ = 9.3 Hz, $^3J_{H-H}$ = 7.6 Hz, NCH_AH$_B$), 3.45 (ddd, 1H, $^2J_{H-H}$ = 9.3 Hz, $^3J_{H-H}$ = 7.6, 2.1 Hz, NCH$_A$$H_B$), 4.21 (ddd, 1H, $^3J_{H-F}$ = 25.3 Hz, $^3J_{H-H}$ = 13.1, 2.3 Hz, NC*H*CHF), 4.52 (d, 1H, $^2J_{H-F}$ = 53.1 Hz, NCHC*H*F), 6.84 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, Ar–*H*), 7.88 (d, 2H, $^3J_{H-H}$ = 8.3 Hz, Ar–*H*); ^{13}C NMR (100 MHz, C_6D_6) δ = 11.9 (Si(*C*H(CH_3)$_2$)$_3$), 18.4 (d, $^3J_{C-F}$ = 11.2 Hz, *C*H$_2$Si), 19.2 (Si(CH(*C*H_3)$_2$)$_3$), 21.5 (*C*H$_3$PhN), 30.5 (d, $^2J_{C-F}$ = 21.6 Hz, *C*H$_2$CHF), 46.4 (NCH$_2$), 65.2 (d, $^2J_{C-F}$ = 22.4 Hz, NCHCHF), 97.1 (d, $^1J_{C-F}$ = 179.7 Hz, NCH*C*HF), 128.0 (Ar–*C*), 130.0 (Ar–*C*), 135.7 (Ar–*C*), 143.4 (Ar–*C*); ^{19}F {^{1}H} NMR (377 MHz, C_6D_6) δ = −173.33; IR (CH_2Cl_2) ν = 3002, 1923, 1355, 991; HRMS (CI^+): *m*/*z* required for $C_{21}H_{37}FNO_2SSi$ ([M+H]$^+$) 414.2298, found 414.2310, Δ = 4.5 ppm.

4.4.5. Anti-2-((diisopropyl(p-tolyl)silyl)methyl)-3-fluoro-1-tosylpyrrolidine anti-4b

Following the *general procedure C* on 100 mg (0.22 mmol, 1 equiv.) of (*Z*)-**1b**, the reaction gave 15 mg of *anti*-**4b** (14%, d.r. *(syn:anti)* > 1:20) as a colorless oil and 39 mg (57%) of the allylic fluoride **2**. *Major anti isomer*: R_f = 0.5 (hexane/Et_2O 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.04 (dd, 6H, $^3J_{H-H}$ = 10.4, 7.6 Hz, Si(CH(CH_3)$_2$)$_2$), 1.05 (m, 1H, CH_AH$_B$Si), 1.15 (dd, 6H, $^3J_{H-H}$ = 10.7, 7.6 Hz, Si(CH(CH_3)$_2$)$_2$), 1.26 (p, 1H, $^3J_{H-H}$ = 7.6 Hz, Si(C*H*(CH_3)$_2$)$_2$), 1.41 (p, 1H, $^3J_{H-H}$ = 7.6 Hz, Si(C*H*(CH_3)$_2$)$_2$), 1.74 (ddd, 1H, $^2J_{H-H}$ = 15.1 Hz, $^4J_{H-F}$ = 4.4 Hz, $^3J_{H-H}$ = 3.1 Hz, CH$_A$$H_B$Si), 1.92–2.14 (m, 2H, C$H_2$CHF), 2.37 (s, 3H, C$H_3$PhSi), 2.42 (s, 3H, C$H_3$PhN), 3.11 (ddd, 1H, $^3J_{H-H}$ = 11.4 Hz, $^2J_{H-H}$ = 9.5 Hz, $^3J_{H-H}$ = 6.2 Hz, NCH_AH$_B$), 3.62 (dd, 1H, $^2J_{H-H}$ = 9.5 Hz, $^3J_{H-H}$ = 1.0 Hz, NCH$_A$$H_B$), 3.97 (dddd, 1H, $^3J_{H-F}$ = 25.2 Hz, $^3J_{H-H}$ = 13.2, 3.1, 1.1 Hz, NC*H*CHF), 4.56 (dd, 1H, $^2J_{H-F}$ = 51.7 Hz, $^3J_{H-H}$ = 2.5 Hz, NCHC*H*F), 7.21 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, SiAr–*H*), 7.28 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, NAr–*H*), 7.40 (*d*, 2H, $^3J_{H-H}$ = 7.8 Hz, SiAr–*H*), 7.65 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, NAr–*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 10.8 (Si(*C*H(CH_3)$_2$)$_2$), 11.5 (Si(*C*H(CH_3)$_2$)$_2$), 18.0 (Si(CH(*C*H_3)$_2$)$_2$), 18.2 (Si(CH(*C*H_3)$_2$)$_2$), 18.4 (d, $^3J_{C-F}$ = 11.4 Hz, *C*H$_2$Si), 21.5 (*C*H$_3$PhSi), 21.5 (*C*H$_3$PhN), 30.1 (d, $^2J_{C-F}$ = 21.0 Hz, *C*H$_2$CHF), 45.7 (NCH$_2$), 64.6 (d, $^2J_{C-F}$ = 21.9 Hz, NCHCHF), 96.1 (d, $^1J_{C-F}$ = 179.3 Hz, NCH*C*HF), 127.6 (NAr–*C*), 128.8 (SiAr–*C*), 129.5 (NAr–*C*), 130.5 (SiAr–*C*), 133.8 (NAr–*C*), 134.8 (SiAr–*C*), 139.0 (SiAr–*C*), 143.3 (NAr–*C*); ^{19}F {^{1}H} NMR (377 MHz, $CDCl_3$) δ = −174.06; IR (CH_2Cl_2) ν = 2945, 2866, 1599, 1345, 1161, 1099, 739; HRMS (CI^+) *m*/*z* required for $C_{25}H_{37}FNO_2SSi$ ([M+H]$^+$): 462.2298, found 462.2311, Δ = 2.7 ppm.

*4.4.6. Anti-3-fluoro-2-methyl-1-tosyl-2-((triisopropylsilyl)methyl)pyrrolidine anti-**4g***

Following the *general procedure C* on 163 mg (0.39 mmol, 1 equiv.) of (*Z*)-**1g**, the reaction gave 102 mg of *anti*-**4g** (61%, d.r. (*syn:anti*) 1:1) as a yellow oil and 29 mg (27%) of the allylic fluoride **6**. *Major anti isomer*: R_f = 0.6 (hexane/Et_2O 6:4); ^1H NMR (500 MHz, C_6D_6) δ = 0.78–0.87 (m, 1H, C$H_A$$H_B$Si), 0.89–1.09 (m, 21H, Si(CH(CH_3)$_2$)$_3$), 1.55–1.80 (m, 2H, CH_2CHF), 1.72 (d, 3H, $^3J_{H-H}$ = 4.7 Hz, NC(CH_3)), 1.93 (s, 3H, CH_3PhN), 2.12 (dd, 1H, $^2J_{H-H}$ = 15.1 Hz, $^4J_{H-F}$ = 6.3 Hz, CH$_A$$H_B$Si), 3.34 (ddd, 1H, $^2J_{H-H}$ = 16.8 Hz, $^3J_{H-H}$ = 9.7, 7.3 Hz, NCH_AH$_B$), 3.56 (ddd, 1H, $^2J_{H-H}$ = 16.8 Hz, $^3J_{H-H}$ = 9.1, 2.5 Hz, NCH$_A$$H_B$), 4.59 (ddd, 1H, $^2J_{H-F}$ = 53.0 Hz, $^3J_{H-H}$ = 3.8, 1.9 Hz, NCCHF), 6.83 (d, 2H, $^3J_{H-H}$ = 8.5 Hz, NAr–*H*), 7.80 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, NAr–*H*); ^{13}C NMR (125 MHz, C_6D_6) δ = 12.7 (Si(CH(CH$_3$)$_2$)$_3$), 19.5 (Si(CH(CH_3)$_2$)$_3$), 21.5 (CH_3PhN), 22.4 (d, $^3J_{C-F}$ = 12.4 Hz, NC(CH_3)), 24.4 (d, $^3J_{C-F}$ = 5.7 Hz, CH_2Si), 29.3 (d, $^2J_{C-F}$ = 22.9 Hz, CH_2CHF), 46.4 (NCH$_2$), 72.0 (d, $^2J_{C-F}$ = 19.1 Hz, NC(CH$_3$)), 99.7 (d, $^1J_{C-F}$ = 186.0 Hz, NCCHF), 127.7 (NAr–*C*), 129.9 (NAr–*C*), 140.3 (NAr–*C*), 142.8 (NAr–*C*); ^{19}F {^1H} NMR (377 MHz, $CDCl_3$) δ = −181.97; IR (CH_2Cl_2) ν = 2952, 1464, 1341, 1158, 1011, 814, 711; HRMS (ESI^+) *m/z* required for $C_{22}H_{38}FNO_2SSiNa^+$ ([M+Na]$^+$): 450.2269, found 450.2261, Δ = 1.4 ppm. *Identifiable data for minor syn isomer*: ^1H NMR (500 MHz, C_6D_6) δ = 1.74 (d, 3H, $^3J_{H-H}$ = 5.3 Hz, NC(CH_3)), 2.20 (dd, 1H, $^2J_{H-H}$ = 15.4 Hz, $^4J_{H-F}$ = 6.9 Hz, CH_AH$_B$Si), 4.62 (ddd, 1H, $^2J_{H-F}$ = 53.0 Hz, $^3J_{H-H}$ = 3.5, 1.3 Hz, NCCHF); ^{13}C NMR (125 MHz, C_6D_6) δ = 12.6 (Si(CH(CH$_3$)$_2$)$_3$), 19.4 (Si(CH(CH_3)$_2$)$_3$), 22.3 (d, $^3J_{C-F}$ = 12.4 Hz, NC(CH_3)), 24.3 (d, $^3J_{C-F}$ = 5.7 Hz, CH_2Si), 29.4 (d, $^2J_{C-F}$ = 21.9 Hz, CH_2CHF), 46.4 (NCH$_2$), 72.3 (d, $^2J_{C-F}$ = 18.1 Hz, NC(CH$_3$)), 99.7 (d, $^1J_{C-F}$ = 186.0 Hz, NCCHF); ^{19}F {^1H} NMR (377 MHz, $CDCl_3$) δ = −181.75.

*4.4.7. Syn-3-fluoro-4,4-dimethyl-1-tosyl-2-((triisopropylsilyl)methyl)pyrrolidine syn-**4h***

Following the *general procedure C* on 90 mg (0.22 mmol, 1 equiv.) of (*E*)-**1h**, the reaction gave 35 mg of *syn*-**4h** (36%, d.r. (*syn:anti*) 6.6:1) as a yellow oil and 28 mg (45%) of the allylic fluoride **7**. *Major syn isomer*: R_f = 0.6 (hexane/Et_2O 6:4); ^1H NMR (500 MHz, C_6D_6) δ = 0.43 (d, 3H, $^4J_{H-F}$ = 1.7 Hz, NCH$_2$C(CH_3)$_2$), 0.80 (d, 3H, $^4J_{H-F}$ = 1.9 Hz, NCH$_2$C(CH_3)$_2$), 1.01–1.03 (m, 3H, Si(CH(CH$_3$)$_2$)$_3$), 1.10 (d, 9H, $^3J_{H-H}$ = 6.9 Hz, Si(CH(CH_3)$_2$)$_3$), 1.15 (d, 9H, $^3J_{H-H}$ = 7.2 Hz, Si(CH(CH_3)$_2$)$_3$), 1.41 (dd, 1H, $^2J_{H-H}$ = 13.2 Hz, $^3J_{H-H}$ = 12.9 Hz, CH_AH$_B$Si), 1.85 (s, 3H, CH_3PhN), 1.86–1.92 (m, 1H, CH$_A$$H_B$Si), 3.22 (d, 1H, $^2J_{H-H}$ = 10.7 Hz, NCH_AH$_B$), 3.41 (d, 1H, $^2J_{H-H}$ = 10.4 Hz, NCH$_A$$H_B$), 4.19 (dd, 1H, $^2J_{H-F}$ = 52.6 Hz, $^3J_{H-H}$ = 3.5 Hz, C(CH$_3$)$_2$CHF), 4.36 (ddt, 1H, $^3J_{H-F}$ = 27.4, $^3J_{H-H}$ = 16.6, 3.1 Hz, NCHCHF), 6.81 (d, 2H, $^3J_{H-H}$ = 7.9 Hz, NAr–*H*), 7.84 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, NAr–*H*); ^{13}C NMR (125 MHz, C_6D_6) δ = 11.9 (*d*, $^3J_{C-F}$ = 12.4 Hz, CH_2Si), 12.3 (Si(CH(CH$_3$)$_2$)$_3$), 19.2 (Si(CH(CH_3)$_2$)$_3$), 19.4 (Si(CH(CH_3)$_2$)$_3$), 19.7 (d, $^3J_{C-F}$ = 7.6 Hz, NCH$_2$C(CH_3)$_2$), 21.4 (CH_3PhN), 23.3 (d, $^3J_{C-F}$ = 6.7 Hz, NCH$_2$C(CH_3)$_2$), 42.1 (d, $^2J_{C-F}$ = 19.1 Hz, NCH$_2$C(CH$_3$)$_2$), 58.0 (NCH$_2$), 63.6 (d, $^2J_{C-F}$ = 21.9 Hz, NCHCHF), 101.1 (d, $^1J_{C-F}$ = 189.8 Hz, NCHCHF), 127.9 (NAr–*C*), 130.0 (NAr–*C*), 139.2 (NAr–*C*), 143.1 (NAr–*C*); ^{19}F {^1H} NMR (377 MHz, C_6D_6) δ = −192.61; IR (CH_2Cl_2) ν = 2945, 2868, 1470, 1265, 1156, 739; HRMS (ESI^+) *m/z* required for $C_{23}H_{40}FNO_2SSiNa^+$ ([M+Na]$^+$): 464.2425, found 464.2413, Δ = 2.7 ppm. *Identifiable data for minor anti isomer*: ^{19}F {^1H} NMR (377 MHz, $CDCl_3$) δ = −197.73.

4.5. Allylic fluorides

*4.5.1. N-(3-fluoropent-4-en-1-yl)-4-methylbenzenesulfonamide **2***

R_f = 0.3 (hexane/Et_2O 6:4); m.p. = 73 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.81–1.94 (m, 2H, $^3J_{H-F}$ = 21.2 Hz, NHCH$_2$CH_2), 2.43 (sbr, 3H, CH_3PhNH), 3.05–3.19 (m, 2H, NHCH_2CH$_2$), 4.70 (t, 1H, $^3J_{H-H}$ = 5.7 Hz, N*H*), 4.97 (dddt, 1H, $^2J_{H-F}$ = 48.6 Hz, $^3J_{H-H}$ = 7.2, 5.8 Hz, $^4J_{H-H}$ = 1.3 Hz, CH$_2$=CHCHF), 5.23 (dt, 1H, $^3J_{H-H(cis)}$ = 10.6 Hz, $^2J_{H-H}$ = 1.3 Hz, $^4J_{H-H}$ = 1.3 Hz, CH_AH$_B$=CHCHF), 5.30 (ddt, 1H, $^3J_{H-H(trans)}$ = 17.2 Hz, $^4J_{H-F}$ = 3.3 Hz, $^2J_{H-H}$ = 1.3 Hz, $^4J_{H-H}$ = 1.3 Hz, CH$_A$$H_B$=CHCHF), 5.82 (dddd, 1H, $^3J_{H-F}$ = 14.9 Hz, $^3J_{H-H}$ = 17.2, 10.6, 5.8 Hz, CH$_2$=CHCHF), 7.32 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, NHAr–*H*), 7.76 (d, 2H, $^3J_{H-H}$ = 8.1 Hz, NHAr–*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 21.5 (CH_3PhNH), 35.0 (d, $^2J_{C-F}$ = 21.6 Hz, NHCH$_2$CH$_2$), 39.3 (d, $^3J_{C-F}$ = 4.0 Hz, NHCH$_2$CH$_2$), 91.5 (d, $^1J_{C-F}$ = 167.8 Hz, CH$_2$=CHCHF), 117.6 (d, $^3J_{C-F}$ = 12.0 Hz, CH_2=CHCHF), 127.1 (NHAr–*C*), 129.8 (NHAr–*C*), 135.4 (d, $^2J_{C-F}$ = 19.2 Hz, CH$_2$=CHCHF), 136.7 (NHAr–*C*), 143.6 (NHAr–*C*); ^{19}F {^1H} NMR (377 MHz, $CDCl_3$) δ = −180.3; IR (neat) ν = 3250, 3061, 2821, 1645, 1432; HRMS (Cl^+) *m/z* required for $C_{12}H_{20}FN_2O_2S$ ([M+NH$_4$]$^+$) 275.1230, found 275.1243, Δ = 4.9 ppm.

*4.5.2. N-tert-butyl (3-fluoropent-4-en-1-yl)carbamate **3***

R_f = 0.4 (hexane/Et_2O 7:3); ^1H NMR (400 MHz, $CDCl_3$) δ = 1.44 (sbr, 9H, COOC(CH_3)$_3$), 1.81–1.95 (m, 2H, $^3J_{H-F}$ = 25.7 Hz, NHCH$_2$CH_2), 3.28 (d, 2H, $^3J_{H-H}$ = 6.3 Hz, NHCH_2CH$_2$), 4.74 (sbr, 1H, N*H*), 4.98 (dddd, 1H, $^2J_{H-F}$ = 48.5 Hz, $^3J_{H-H}$ = 11.0, 5.8 Hz, $^4J_{H-H}$ = 1.3 Hz, CH$_2$=CHCHF), 5.24 (dt, 1H, $^3J_{H-H(cis)}$ = 10.9, $^2J_{H-H}$ = 1.3 Hz, $^4J_{H-H}$ = 1.3 Hz, CH_AH$_B$=CHCHF), 5.34 (ddt, 1H, $^3J_{H-H(trans)}$ = 17.2 Hz, $^4J_{H-F}$ = 3.3 Hz, $^2J_{H-H}$ = 1.3 Hz, $^4J_{H-H}$ = 1.3 Hz, CH$_A$$H_B$=CHCHF), 5.89 (dddd, 1H, $^3J_{H-H(trans)}$ = 17.2 Hz, $^3J_{H-F}$ = 14.9 Hz, $^3J_{H-H(cis)}$ = 10.9 Hz, $^3J_{H-H}$ = 5.8 Hz, CH$_2$=CHCHF); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 28.3 (COOC(CH_3)$_3$), 35.3 (d, $^2J_{C-F}$ = 21.6 Hz, NHCH$_2$CH_2), 36.7 (d, $^3J_{C-F}$ = 3.2 Hz, NHCH$_2$CH$_2$), 79.2 (COOC(CH$_3$)$_3$), 91.5 (d, $^1J_{C-F}$ = 167.0 Hz, CH$_2$=CHCHF), 117.1 (d, $^3J_{C-F}$ = 12.0 Hz, CH_2=CHCHF), 135.9 (d, $^2J_{C-F}$ = 19.2 Hz, CH$_2$=CHCHF), 155.9 (COOC(CH$_3$)$_3$); ^{19}F {^1H} NMR (377 MHz, $CDCl_3$) δ = −179.90; IR (neat) ν = 3351, 2979, 1694, 1521, 1367, 1174, 989; HRMS (ESI^+) *m/z* required for $C_{10}H_{18}FNO_2Na^+$ ([M+Na]$^+$) 226.1214, found 226.1214, Δ = 0.2 ppm.

*4.5.3. N-(3-fluoro-4-methylpent-4-en-1-yl)-4-methylbenzene sulfonamide **6***

R_f = 0.2 (hexane/Et_2O 6:4); ^1H NMR (500 MHz, C_6D_6) δ = 1.43 (s, 3H, CH$_2$=C(CH_3)CHF), 1.40–1.61 (m, 2H, NHCH$_2$CH_2), 1.89 (s, 3H, CH_3PhNH), 2.78–2.89 (m, 2H, NHCH_2CH$_2$), 4.49–4.54 (m, 1H, N*H*), 4.57 (ddd, 1H, $^2J_{H-F}$ = 48.0 Hz, $^3J_{H-H}$ = 8.5, 3.8 Hz, CH$_2$=C(CH$_3$)CHF), 4.69 (d, 1H, $^2J_{H-H}$ = 1.6 Hz, CH_AH$_B$=C(CH$_3$)CHF), 4.85 (s, 1H, CH$_A$$H_B$=C(CH$_3$)CHF), 6.79 (d, 2H, $^3J_{H-H}$ = 7.9 Hz, NHAr–*H*), 7.78 (d, 2H, $^3J_{H-H}$ = 8.2 Hz, NHAr–*H*); ^{13}C NMR (125 MHz, C_6D_6) δ = 17.6 (d, $^3J_{C-F}$ = 3.8 Hz, CH$_2$=C(CH_3)CHF), 21.4 (CH_3PhNH), 34.2 (d, $^2J_{C-F}$ = 21.9 Hz, NHCH$_2$CH$_2$), 39.9 (d, $^3J_{C-F}$ = 3.8 Hz, NHCH$_2$CH$_2$), 93.6 (d, $^1J_{C-F}$ = 170.7 Hz, CH$_2$=C(CH$_3$)CHF), 113.1 (d, $^3J_{C-F}$ = 9.5 Hz, CH_2=C(CH$_3$)CHF), 127.8 (NHAr–*C*), 130.1 (NHAr–*C*), 138.6 (NHAr–*C*), 143.3 (d, $^2J_{C-F}$ = 17.2 Hz, CH$_2$=C(CH$_3$)CHF), 143.3 (NHAr–*C*); ^{19}F {^1H} NMR (377 MHz, C_6D_6) δ = −180.54; IR (neat) ν = 3441, 3054, 1641, 1422, 1265, 896, 737; HRMS (Cl^+) *m/z* required for $C_{13}H_{19}FNO_2S$ ([M+H$^+$]) 272.1121, found 272.1133, Δ = 4.6 ppm.

*4.5.4. N-(3-fluoro-2,2-dimethylpent-4-en-1-yl)-4-methylbenzene sulfonamide **7***

R_f = 0.3 (hexane/Et_2O 6:4); m.p. = 81 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 0.89 (d, 3H, $^4J_{H-F}$ = 0.8 Hz, NHCH$_2$C(CH_3)$_2$), 0.90 (d, 3H, $^4J_{H-F}$ = 1.3 Hz, NHCH$_2$C(CH_3)$_2$), 2.43 (s, 3H, CH_3PhNH), 2.79 (dd, 1H, $^2J_{H-H}$ = 12.6 Hz, $^3J_{H-H}$ = 7.1 Hz, NHCH_AH$_B$C(CH$_3$)$_2$), 2.88 (dd, 1H, $^2J_{H-H}$ = 12.6 Hz, $^3J_{H-H}$ = 6.6 Hz, NHCH$_A$$H_B$C(CH$_3$)$_2$), 4.62 (ddt, 1H, $^2J_{H-F}$ = 47.5 Hz, $^3J_{H-H}$ = 6.3 Hz, $^4J_{H-H}$ = 1.3 Hz, CH$_2$=CHCHF), 4.93 (dd, 1H, $^3J_{H-H}$ = 7.1, 6.6 Hz, N*H*), 5.30 (dd, 1H, $^3J_{H-H(cis)}$ =10.9 Hz, $^2J_{H-H}$ = 1.5 Hz, CH_AH$_B$=CHCHF), 5.31 (dddd, 1H, $^3J_{H-H(trans)}$ = 17.2 Hz, $^4J_{H-F}$ = 3.1 Hz, $^2J_{H-H}$ = 1.5 Hz, $^4J_{H-H}$ = 1.3 Hz, CH$_A$$H_B$=CHCHF), 5.83 (dddd, 1H, $^3J_{H-H(trans)}$ = 17.2 Hz, $^3J_{H-F}$ = 15.9 Hz, $^3J_{H-H(cis)}$ = 10.9 Hz, $^3J_{H-H}$ = 6.3 Hz, CH$_2$=CHCHF), 7.31

(d, 2H, $^{3}J_{H-H}$ = 8.4 Hz, NHAr–*H*), 7.75 (d, 2H, $^{3}J_{H-H}$ = 8.4 Hz, NHAr–*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 20.0 (d, $^{3}J_{C-F}$ = 3.2 Hz, $NHCH_2C(CH_3)_2$), 21.5 (CH_3PhNH), 21.5 (d, $^{3}J_{C-F}$ = 6.4 Hz, $NHCH_2C(CH_3)_2$), 38.1 (d, $^{2}J_{C-F}$ = 19.2 Hz, $NHCH_2C(CH_3)_2$), 50.4 (d, $^{3}J_{C-F}$ = 3.2 Hz, $NHCH_2C(CH_3)_2$), 98.1 (d, $^{1}J_{C-F}$ = 174.2 Hz, CH_2=CHCHF), 119.4 (d, $^{3}J_{C-F}$ = 12.8 Hz, CH_2=CHCHF), 127.0 (NHAr–*C*), 129.7 (NHAr–*C*), 132.1 (d, $^{2}J_{C-F}$ = 19.2 Hz, CH_2=CHCHF), CHCHF), 136.9 (NHAr–*C*), 143.3 (NHAr–*C*); ^{19}F {^{1}H} NMR (377 MHz, $CDCl_3$) δ = −186.10; IR (KBr) ν = 3418, 2975, 1644, 1427, 1326, 1161, 664; HRMS (CI^+) *m*/*z* required for $C_{14}H_{24}N_2O_2FS$ ([M+NH_4^+]) 303.1543, found 303.1549, Δ = 3.5 ppm.

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