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Hydroamination of Triisopropylsilyl Acetylene Sulfur Pentafluoride – a Bench-top Route to Pentafluorosulfanylated Enamines

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Dedicated to Prof. Roger Alberto on the occasion of his 65th birthday

Synthetic access to a variety of aliphatic and vinylic pentafluorosulfanylated building blocks remains a major challenge in contemporary organofluorine chemistry hampering its investigation in the context of medicinal chemistry, agrochemistry and functional materials. Herein, we report a bench-top protocol to access the virtually unknown class of α-SF_5-enamines under mild reaction conditions in good to excellent yields (up to 95%). This reaction combines the protodesilylation of the commercially available precursor **TASP** with the *in situ* hydroamination of HC≡C–SF_5. The on-site use of highly toxic gases or corrosive reagents is avoided, making access to this motif applicable to a wide chemical audience. The excellent *E*-diastereoselectivity of this two-step cascade reaction is suggested to be the result of the convergence of the fast *Z*-/*E*-isomerization of a vinyl anion as well as the isomerization of the iminium ion. The remarkable thermal stability of these SF_5-enamines encourages further studies of their synthetic utility.

Introduction

Since its initial discovery in the 1950s, the pentafluorosulfanyl (SF_5) group has been proposed as a promising structural motif for applications in medicinal chemistry and functional materials. For instance, the strongly lipophilic SF_5 moiety is suggested to act as a bioisosteric replacement of CF_3, tBu, NO_2, or halogen substituents and is therefore expected to have potential indications on modern drug discovery.[1] Despite the increasing interest in organic molecules bearing the SF_5 group,[2] the synthesis of small non-aromatic SF_5 building blocks remains challenging due to the lack of broadly applicable and robust synthetic methodologies. The general dependence on the use of the highly toxic mixed sulfur fluorides SF_5Cl or SF_5Br significantly hampered building blocks from being explored. Recently, a variety of inventive solutions have been proposed to circumvent the problem of accessibility of vinyl- and alkyl SF_5 compounds, comprising the single electron activation of SF_6[2h,3] or the *in situ* generation of SF_5Cl from S_8 or SF_6.[4]

In this light, the increased inclusion of SF_5 arenes into routine screening processes in modern academic and industrial research programs seems to be largely attributable to commercial availability of prefunctionalized aromatic SF_5-building blocks.[5] Only recent progress in fundamental methodology enabled the commercialization of these compounds, which ultimately relieved the experimentalist from the burden to employ hazardous or synthetically challenging fluorination or pentafluorosulfanylation chemistry on-site. We found triisopropyl acetylene sulfur pentafluoride (**TASP** or **1**) (air-stable, tolerates ambient conditions, liquid) to be a promising precursor for SF_5 chemistry.[1] A more detailed analysis of literature revealed that today **TASP** exclusively had been investigated in the context of cycloaddition reactions.[6] Interestingly, even reports on the parent compound HC≡C–SF_5 (**2**) in the context of synthetic organic chemistry remain scarce, mainly covering cycloaddition reactions[6a,7] and its deprotonation[8] as well as single reports of various reactivity.[9] This situation is even more astonishing since preliminary studies by Hoover and Coffman on the parent acetylene sulfur pentafluoride in 1969 already hinted on a possible more widespread chemistry based on its electronic properties. In this work the authors showcased the addition of methanol to the free acetylene under strongly basic conditions.[7c]

Our initial considerations were focused on the negative hyperconjugation of the SF_5 group, which adds some π-accepting properties to the structural motif. While the low-lying σ^*_{SF} orbitals are responsible for the low stability of the corresponding enolates, we became curious in exploiting reactivity enabled by this feature.[10] We therefore anticipated **TASP** (**1**) to be a

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[1] TASP was/is commercially available from at least one provider at the time of execution of this work and submission of this manuscript, respectively.

precious precursor to access the corresponding enamines by an unprecedented *in situ* deprotection/-hydroamination sequence paralleling the reactivity of conventional π-acceptors. The spontaneous addition of secondary amines to π-acceptor substituted alkynes[11] has been extensively reported and found application in the preparation of polymers.[12] In contrast, the uncatalyzed addition of amines to non-π-acceptor substituted alkynes at room temperature has been described scarcely and is only applicable to intramolecular cyclization reactions.[13] SF_5 substituted acetylenes have been shown to undergo gold-catalyzed hydrofluorination and hydration reactions.[14] Fascinated by the so far out of reach α-SF_5-enamine motif and the potential impact of a method to access this class of molecules, we became interested in the hydroamination of **2** starting from **1**. While the base catalyzed intramolecular hydroamination of (2-aminoaryl)-substituted SF_5-acetylenes has been reported in 2021, the parent α-substituted motif has not been conclusively described until the pre-disclosure of this contribution at the end of 2022 and has been soon followed by a similar report on the hydroelementation of internal acetylenes by Bizet in 2023, interestingly yielding inverse diastereoselectivity, which highlights the importance of these finding.[15] To the best of our knowledge, the only reports of the putative existence of α-SF_5 enamines trace back to the reports of Welch investigating the stereochemical control by the SF_5 group in 2013 and 2018. Therein, the formation of two putative enamine species was suggested, which were either not or only partially characterized by NMR spectroscopy.[16] Herein, we report a protocol for the hydroamination of commercially available **1** to access α-SF_5-enamines under bench-top conditions with high diastereoselectivity and short reaction times (see Figure 1).

Results and Discussion

We started our investigations by the initial addition of 1.50 eq. of pyrrolidine (**3**) to a solution of TIPS–C≡C–SF_5 (**TASP**, **1**) at ambient temperature in $CDCl_3$ which did not show any

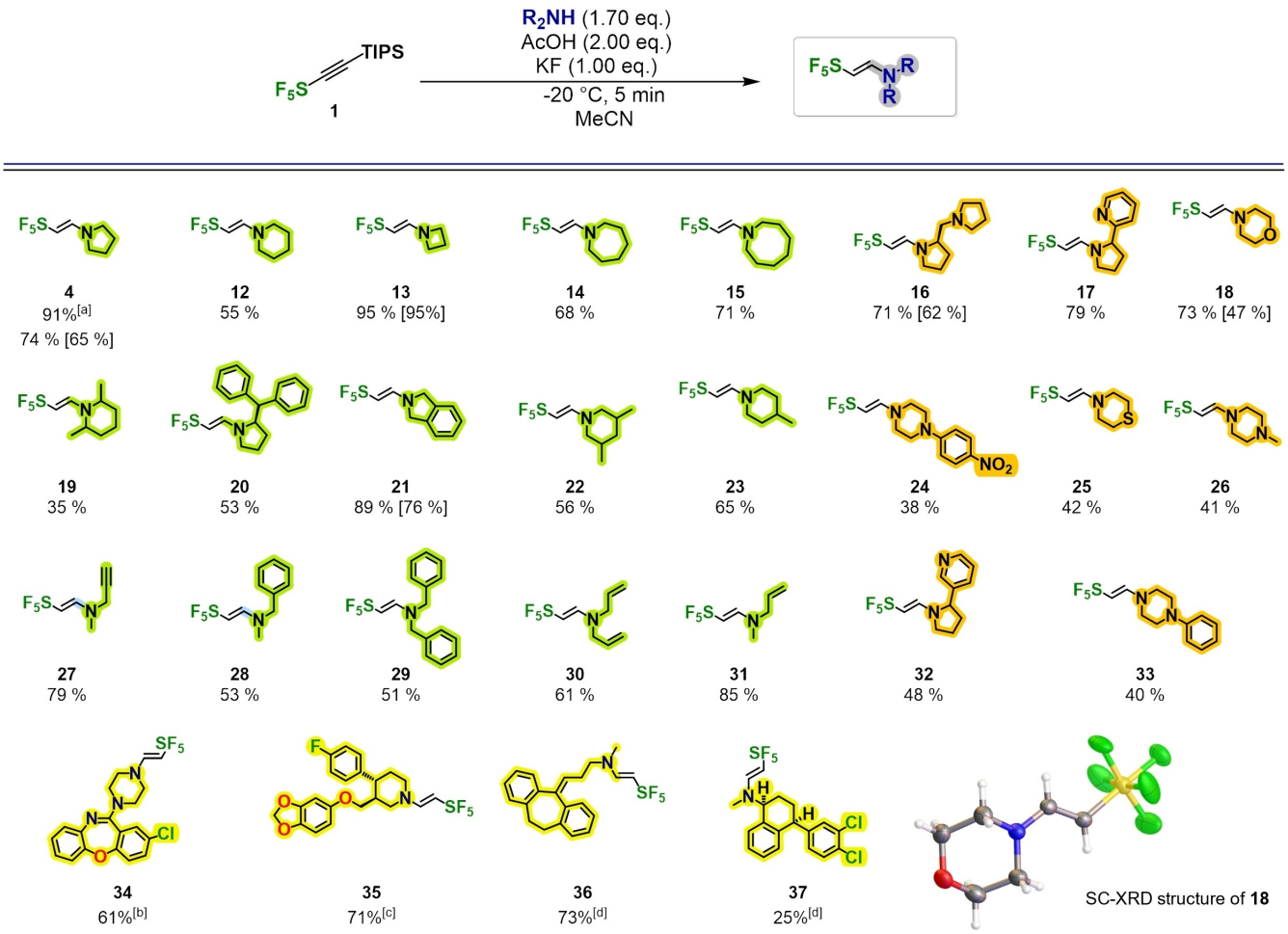

Figure 1. Substrate scope of enamines. *green:* cyclic aliphatic amines and amines with unsaturated side chains. *orange:* amines with heteroatoms in the side chains. *yellow:* drugs and drug-like substrates. ^{19}F NMR-yields given. Isolated yields given in square brackets. Reaction conditions: 175 μmol **1**, 0.28 M.[a] 34.9 μmol.[b] 0.70 mmol, CsF, MeCN/DMSO (4:1), 16 h, rt.[c] 4 h,[d] 0.35 mmol, MeCN/DMSO,16 h, rt. Representative isolated yields were given where the products could be flawlessly purified and were not significantly volatile. In all other cases a validated ^{19}F NMR quantification procedure was applied. Deposition Number 2232894 for **18** contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

reactivity after 10 min according to ^{19}F NMR spectroscopy. However, after 15.5 h at room temperature a new SF_5-species was observed. Interestingly, the apical fluorine substituent was found to resonate in an untypical chemical shift range at $\delta = 96.7$ ppm (p) in ^{19}F NMR spectroscopy. Thrilled by the unusual ability of the amine to deprotect the acetylene *in situ*, a careful analysis of the ^{19}F NMR spectrum revealed the partial degradation of the SF_5 moiety under formation of a Si–F bond as the thermodynamic sink due to the lack of an external fluoride source.

On the other hand, mixing **1** with 1.00 eq. of tetra-*n*-butylammonium fluoride (TBAF) as well as 1.00 eq. of pyrrolidine **3** at −78 °C in CH_2Cl_2 showed immediately deep brown colorization of the reaction mixture and formation of **4-E** in only 37 % ^{19}F NMR yield after 50 min. The deep colorization of the reaction mixture hinted on a competing decomposition of **6** under formation of C_2 during its lifetime $\mathbf{\Delta t_1}$ (see ESI, Figure S248).[9b] The addition of a proton source was suggested to increase the yield by suppression of this loss channel.[17] Indeed, under addition of 2.00 eq. of acetic acid (**10**) in MeCN caused a dramatic increase of the yield of the enamine from 33 % to 83 % due to fast trapping of acetylide **6** (see ESI, Figure S244&S248 $\mathbf{\Delta t_2}$). Supporting the deprotection step by TBAF, CsF or even KF was found to have a beneficial effect on the reaction outcome (see ESI, Figure S242&S246). Furthermore, a strong dependence on the reaction temperature was observed. Carrying out the reaction at −11 °C showed further increase of the yield of **4-E** to up to 91 %. However, severe reproducibility issues led us to the observation of a negative correlation of the yield with increasing time between deprotection of **TASP** and addition of the secondary amine (see ESI, Figure S247&S248, $\mathbf{\Delta t_1}$). Finally, we found optimized reaction conditions by subjecting a solution of **1** to deprotection by the fluoride source (1.00 eq.) in the presence of 2.00 eq. of acetic acid and immediate addition of the amine (1.70 eq.) at about −20 °C. Under these conditions the formation of the colorful side product was effectively suppressed, and **4-E** was formed in up to 91 % ^{19}F NMR yield in 5 min.

Next, we turned to an investigation of the substrate scope of the reaction. A broad variety of functionalized secondary amines including alkenes (**30**, **31**), alkynes (**27**), sulfur- (**25**), oxygen- (**18**) and nitrogen- containing heterocycles (**16**, **17**, **32**), acetals and ethers (**34**&**35**) could be subjected to the reaction conditions. In particular, several approved drugs and drug-like molecules, namely amoxapine, paroxetine, nortriptyline, and sertraline (**34**–**37**, yellow) delivered the corresponding enamines in moderate to good yields (25 %–73 %) as determined by ^{19}F NMR spectroscopy. A combined ^{19}F NMR as well as an IR spectroscopic study employing dibenzylamine **39** as nucleophile and deprotection agent, confirmed a stepwise reaction mechanism under initial protodesilylation of **1**, followed by hydroamination of **2** by the amine (see ESI, Section 5.1&5.3). The observation of an initial induction period of the deprotection of **1** by dibenzylamine hinted on an autocatalytic reaction attributed to the reactivity of SF_4 forming several fluoride anion equivalents as well as the overall consumption of protons shifting the pyrrolidinium/pyrrolidine equilibrium towards the free base which has been observed to be crucial for the deprotection step (see ESI, Figure S310). Furthermore, enamine formation only ramps up after a significant build-up of the free alkyne, excluding a mechanism initiated by the direct addition of **3** to the terminal carbon center of the acetylene **1** (see ESI, Figure S286). Remarkably, no deprotection of **1** by *in situ* generated HF was observed at all after 1 h, once more highlighting the necessity of free fluoride anions in the reaction mixture which is intrinsically compromised by the essential requirement of a proton source to trap the reactive intermediates. Hofmann elimination of tetrabutyl ammonium (TBA) cation **43** has been identified as a significant source of the α-proton of **4-E** during the deprotection step (see ESI, Figure S314). Interestingly, incubation of **1** with acetic acid and KF at room temperature revealed the formation of the enol acetate as well as multiple unidentified species. Addition of the secondary amine after 21 h caused convergence of almost all transiently formed SF_5 species to the enamine (see ESI, Figure S296).

An *in-silico* analysis of the proposed reaction mechanism indicated the formation of a precomplex between **3** and **2**. The attack of **3** was found to require only a very low barrier of $\Delta G_{TS\text{-}1}^{\ddagger} = 8.1$ kcal/mol to form zwitterion **44-Z** compared to **44-E** ($\Delta G_{TS\text{-}2}^{\ddagger} = 8.4$ kcal/mol (see Figure 2).

The distinct *E*-diastereoselectivity of the reaction therefore cannot be explained by the very small difference in transition state Gibbs free energies of the primary attack of **3** on the free alkyne. A potential interconversion of **44-Z** to the thermodynamically more stable *E*-zwitterion (**44-E**, $\Delta G_{TS\text{-}3}^{\ddagger} = 23.1$ kcal/mol, $t_{1/2} = 2.7$ h) or interconversion of the putative primary reaction product **4-Z** by a twist-mechanism ($\Delta G_{TS\text{-}5}^{\ddagger} = 27.0$ kcal/mol, $t_{1/2} = 81$ days) (see Figure 3) turned out to be unpassable under the reaction conditions. However, zwitterion (**44-Z**) has a slightly higher pKa than CH_3COOH resulting in an equilibrium situation ($K = 3.8 \cdot 10^{-3}$) with acetate to form the corresponding anion (**45-Z**) and acetic acid. This anion was found to be capable of passing to **45-E** via a very low-lying transition state for isomerization ($\Delta G_{TS\text{-}4}^{\ddagger} = 3.4$ kcal/mol, $t_{1/2} = 34$ ps). Additionally, enamine **4-Z** was found to be in equilibrium with a preassembled acetic-acid complex **52** ($K = 1.2 \cdot 10^{-5}$ mol^{-1} L). The barrier for proton transfer of this assembly was found to be easily overcome at room temperature ($\Delta G_{TS\text{-}6}^{\ddagger} = 8.1$ kcal/mol, $t_{1/2} = 97$ ns) to form iminium ion **46** ($\Delta G_r = 8.7$ kcal/mol) with $K_0 = 4.2 \cdot 10^{-7}$ opening a window for bond rotation and deprotonation to form **4-E**.

Interestingly, aligned with experimental results, acetate anion **48** was found to be able to slowly undergo direct addition to the acetylene at room temperature to form vinyl anions **49-Z** ($\Delta G_{TS\text{-}8}^{\ddagger} = 17.1$ kcal/mol) and **49-E** ($\Delta G_{TS\text{-}7}^{\ddagger} = 22.4$ kcal/mol), respectively. However, due to the very different rate constants compared to the attack of **3**, a significant contribution of the two-step mechanism involving enol acetate **47** only seems to be important during the initial phase of the deprotection period in the presence of a significant amount of protonated pyrrolidine **3-H**. This is also aligned with a ^{19}F NMR spectroscopic investigation proving that the formation of side products exclusively happens during the initial phase of the reaction, namely during the deprotection step.

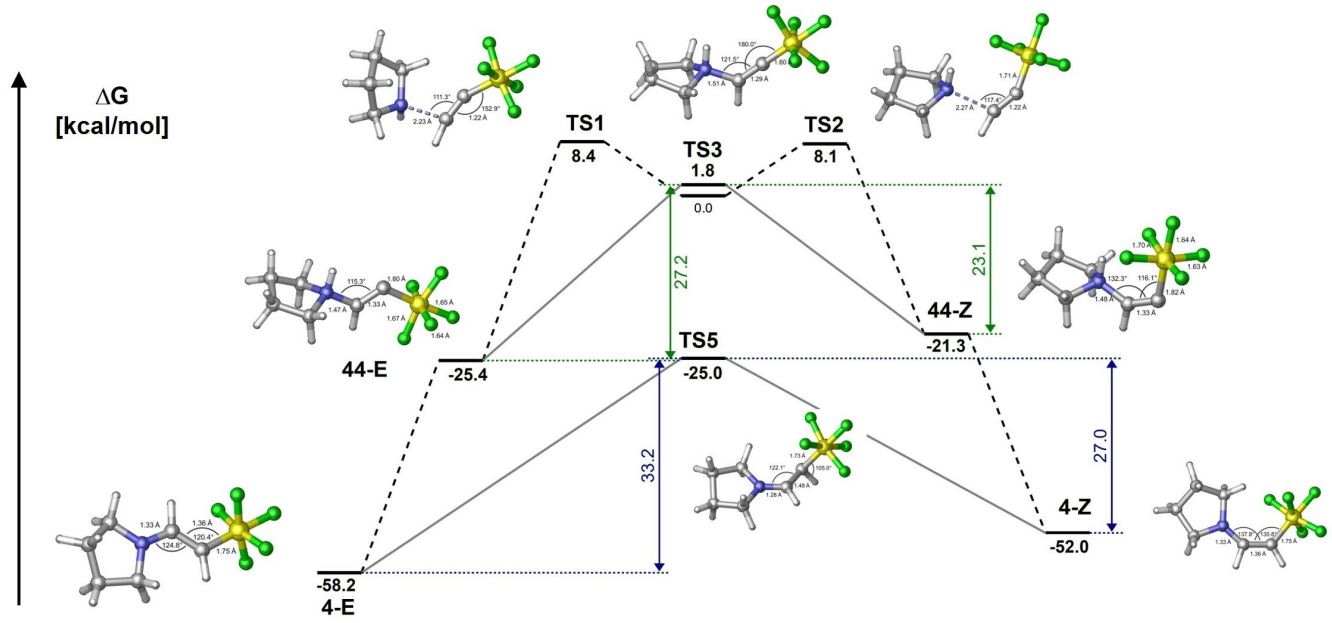

Figure 2. Relative energies of intermediates and transition states and energy differences along the reaction coordinates to **4-E** and **4-Z**. Precomplex between **2** and **3** was taken as reference point (0.0 kcal/mol). Furthermore, interconversion pathways of the zwitterions **44** and products **4** have been calculated. Gibbs free energies have been calculated on the DLPNO-CCSD(T)/M062X/6-311++G(d,p)/CPCM level of theory. All energies are given in kcal/mol.

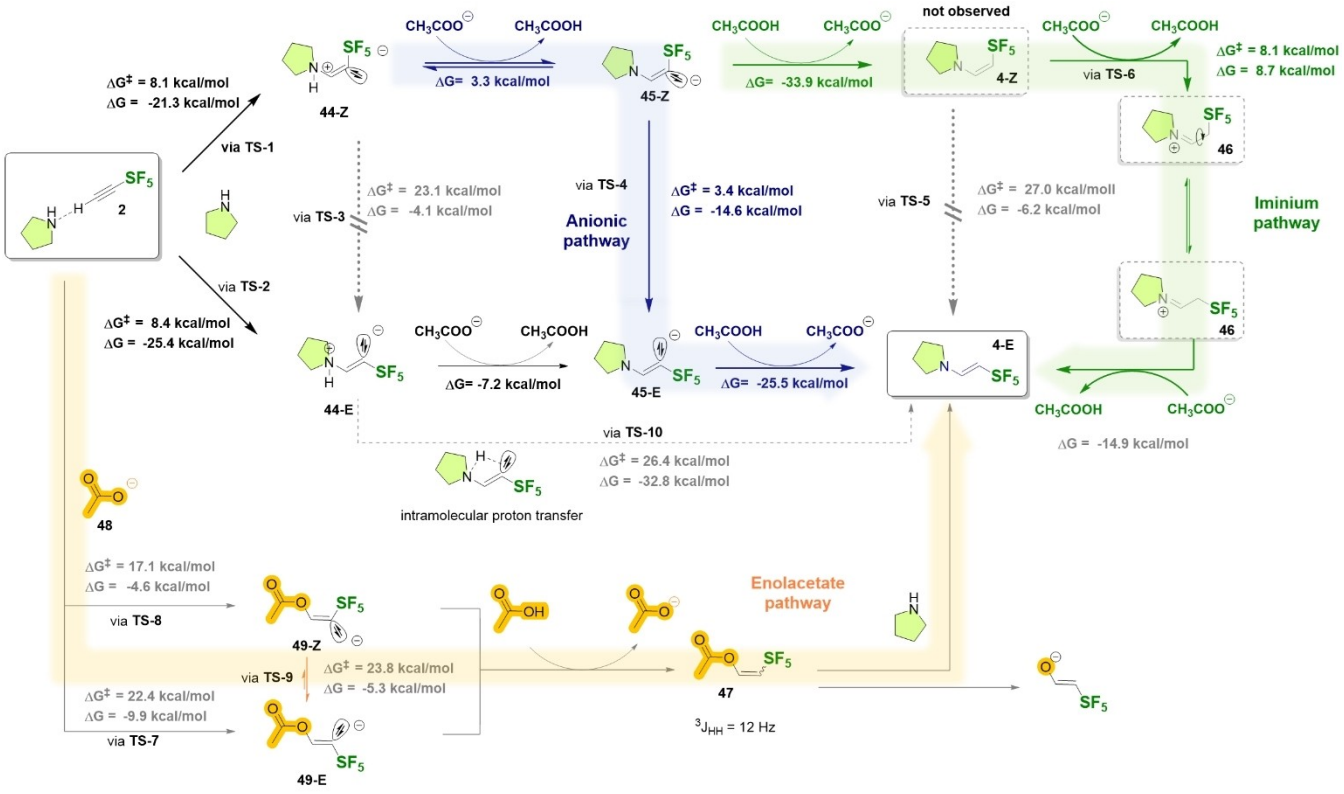

Figure 3. Mechanistic overview. The proposed main reaction pathways are highlighted. *Blue*: Isomerization of anion **45-Z**. *Green*: Isomerization of iminium ion **46**. Orange: Product formation via enol acetate **47**. Energies have been calculated on the DLPNO-CCSD(T)/M062X/6-311++G(d,p)/CPCM level of theory. All energies are given in kcal/mol.

Conclusions

In conclusion, we report a robust and facile bench-top protocol that allows reliable access to α-pentafluorosulfanylated enamines in moderate to excellent yields from commercially available triisopropylsilyl acetylene sulfur pentafluoride (**TASP** or **1**) under bench-top conditions in very short reaction times. This versatile motif in organic chemistry has so far only been described as a putative side product relying on the necessity to employ SF_5Cl on-site. We want to highlight that the commercially available triisopropylsilyl acetylene sulfur pentafluoride (**TASP**) can be used as a precious precursor to access unprecedented pentafluorosulfanylated motifs, playing a central role in synthetic organic chemistry, under bench-top conditions. We predict this reagent being capable of opening-up a more widespread use of vinylic and aliphatic SF_5 containing molecules in the future. Furthermore, we shone light on the operating reaction mechanism revealing a cascade of a protodesilylation and hydroamination on a fine line between decomposition of the primarily formed acetylide anion and sufficient nucleophilicity. The excellent *E*-diastereoselectivity could be attributed to the convergence of the isomerization of the Z-configured vinyl anion or formation of an iminium ion. This method complements the reported cycloaddition reactivity of **TASP** and adds to the toolbox of modern pentafluorosulfanyl chemistry by allowing the downstream processing of a non-aromatic building block to access the central structural enamine motif. Furthermore, inspired by the spontaneous hydroamination of **1**, we became interested in the reaction of **1** with S-nucleophiles. We were delighted to find aromatic as well as aliphatic thiols to afford the corresponding (*Z*)-β-SF_5 vinyl sulfides in excellent yields under similar reaction conditions, underlining the value of TASP for charting fluorinated chemical space.[15c] The separation of the addition step of SF_5Cl to industrial suppliers will significantly broaden the accessibility of small SF_5-containing motifs to non-specialized laboratories, rendering the on-site use of highly toxic reagents or the employment of strictly inert conditions superfluous.

Supporting Information

The authors have cited additional references within the Supporting Information.[17–18]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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