Arenesulfenyl Fluorides: Synthesis, Structure, and Reactivity

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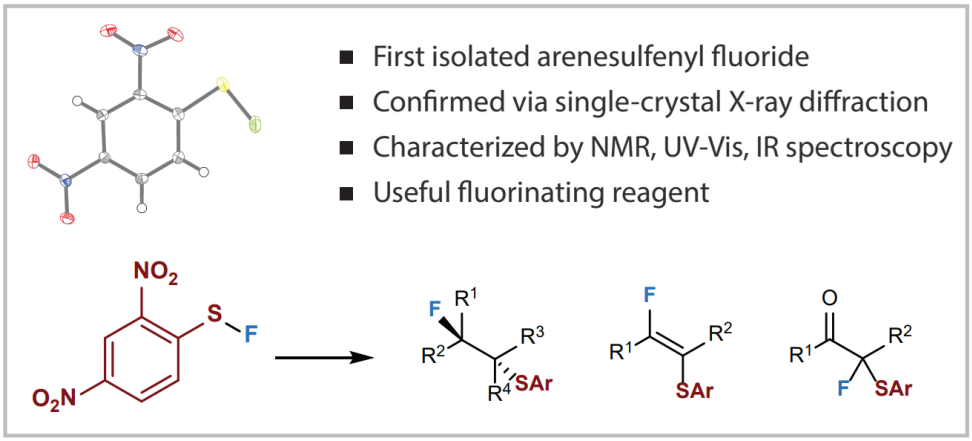
Abstract

Sulfenyl fluorides are organic compounds of sulfur in formal oxidation state +2 with the formula R–S–F. Although the chloride, bromide, and iodide analogues have been extensively described in the literature, organic sulfenyl fluorides remain essentially unstudied. These structures have been implicated as putative intermediates in established processes to access polyfluorinated sulfur species; however, definitive and direct evidence of their existence has not been achieved, nor has a systematic understanding of their reactivity. Here, we report the synthesis, isolation, and spectroscopic characterization of several arenesulfenyl fluorides, including structural analysis of 2,4-dinitrobenzenesulfenyl fluoride by single-crystal X-ray diffraction. The functional group undergoes direct, efficient, and highly regioselective *anti*-addition to alkenes and alkynes, as well as insertion by carbenes. The resulting α- or β-fluoro thioether adducts can be readily transformed into useful fluorinated motifs, for example by modification of the sulfur groups (to sulfonamides or sulfonyl fluorides), by sulfur elimination (to generate formal C–H fluorination products), or by Julia–Kocienski olefination (to form vinyl fluorides). Thus, we establish that sulfenyl fluorides are unexpectedly accessible and stable compounds. Further, they serve as versatile reagents for the production of fluorinated organic compounds.



Introduction

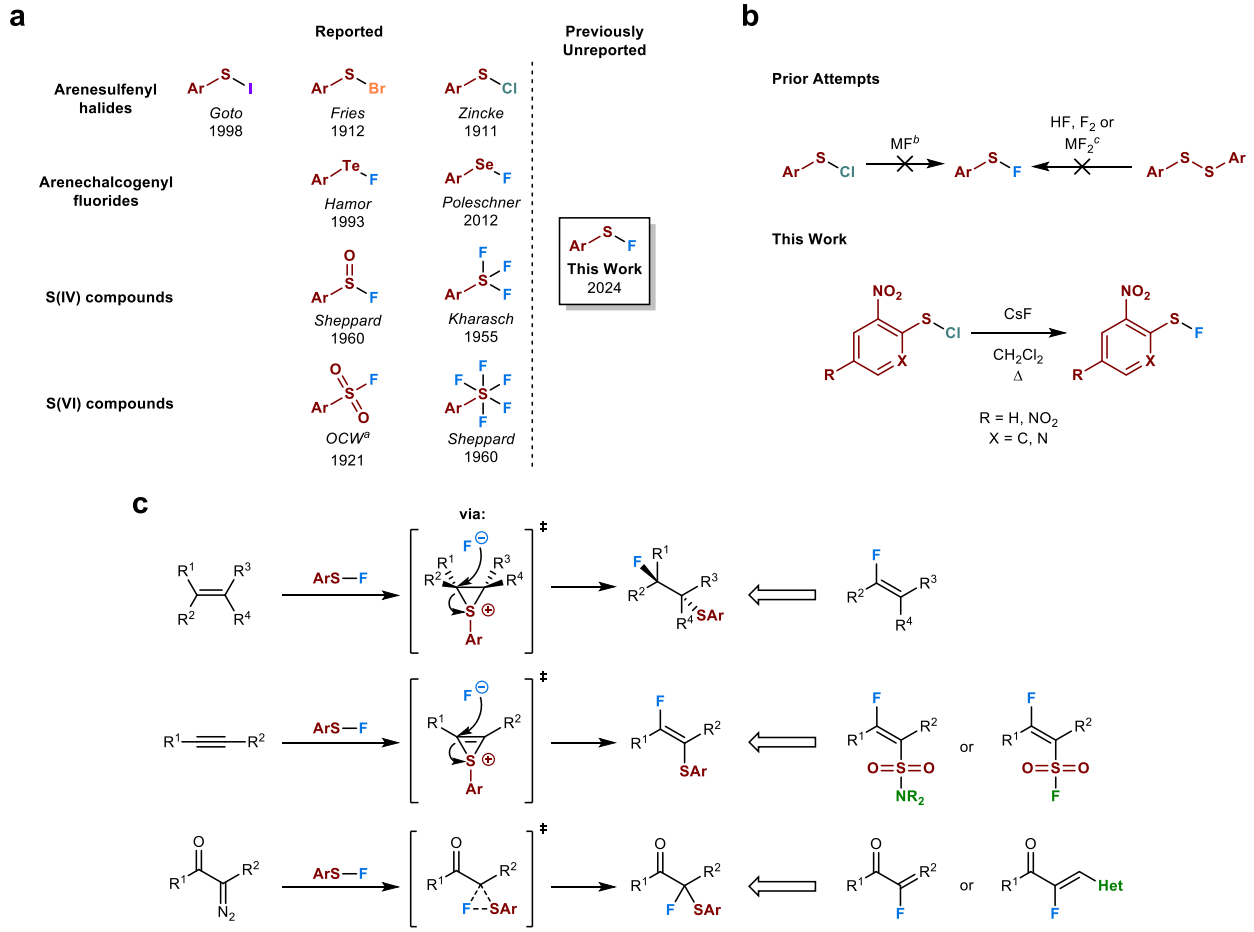
Discovered by Theodore Zincke in 1911, arenesulfenyl halides are significant if somewhat unusual class of compounds in organic chemistry.[1-3] Most notably, they have been employed as reagents for the protection of cysteine side chains[4] and for the difunctionalization of alkenes,[5-6] alkynes,[7] and diazo compounds.[8] Arenesulfenyl halides suffer from limited stability and are prone to decomposition by disproportionation to aryl disulfides and elemental halogens. Therefore, only sufficiently electron-deficient arenesulfenyl halides can be stored for more than a few days.[9,10] Intriguingly, while organic sulfenyl chlorides, bromides, and iodides have been reported in the literature, studies of organic sulfenyl fluorides are conspicuously scarce.[11-14] This disparity is especially striking given that, from a thermodynamic perspective, the typical disproportionation reaction might be expected to be the least favorable for the fluoride compared to other halides.[15] Moreover, organic sulfur trifluorides, tetrafluorides, and pentafluorides have been well known for decades – so, why do the corresponding monofluorides remain known?[16,17]

To date, the vast majority of discussions involving arenesulfenyl fluorides have evoked them as hypothetical and unobserved reactive intermediates. Nevertheless, significant effort has been devoted to attempted preparations.[18,19] In 1946, Heal reported some of the earliest endeavors using various arenesulfenyl chlorides with AgF, HgF_2, HgF, or HF, but in these, only undesired fluorinated products were obtained.[20] Following this work, Kharasch reinvestigated the reaction of arenesulfenyl chlorides and aryl disulfides with HF(*l*) and F_2 (*g*), obtaining only the trifluoride ($ArSF_3$).[21] The same study found that direct fluorination of thiophenols with elemental fluorine gas was unsuccessful, as was the treatment of arenesulfenyl chlorides with SbF_3 and HgF_2. Later, Seel suggested that a species with a characteristic ^{19}F NMR chemical shift of -150 ppm, formed upon mixing phenyl disulfide with SF_4 might correspond to a sulfenyl fluoride, but he was unable to isolate the compound.[22] Purrington proposed that treatment of benzenesulfenyl chloride with AgF results in the *in situ* formation of benzenesulfenyl fluoride, which was again too unstable to isolate, but was associated with a ^{19}F NMR chemical shift of -173 ppm.[23] By comparison with our own NMR data provided below, we believe that neither of the species (Seel and Purrington) were correctly assigned. A final example from Furin claims that reaction of perfluorinated aryl disulfides with AgF_2 furnished the corresponding sulfenyl fluorides in >70% yield; however, based on comparison with multiple literature sources, [24-26] we propose that the procedure instead generated the sulfinyl fluorides.

Aside from these attempts to synthesize organic sulfenyl fluorides, several intriguing studies have also been published on perhaloalkyl and amino analogues, which are considered to be extremely unstable.[27] The first example, trichloromethanesulfenyl fluoride (Cl_3CSF), was reported by Kober and coworkers.[28] However, compelling evidence was later uncovered that contradicts the structural assignment in this work.[29,30] Later, several perfluoroalkyl and dialkylaminosulfenyl halides had been reported, with ^{19}F NMR spectroscopy as the main structural evidence.[31]

It is notable that several areneselenyl- and tellurenyl fluorides have been synthesized, isolated, and characterized.[32-35] Therefore, the absence of synthetic methods for accessing organic sulfenyl fluorides appears specific to this combination sulfur and fluorine, as compounds bearing heavier analogues of either atom are easily prepared. As part of our research on organosulfur compounds, we became interested in reexamining the status of organic sulfenyl fluorides as isolable species. Here, we describe the first synthesis, isolation, and unequivocal characterization of

arenesulfenyl fluorides. Additionally, we report observations on the reactivity of these compounds, which exhibit promising fluorination capabilities towards a variety of alkenes, alkynes, and diazo compounds.



Scheme 1. Discovery and exploration of arenesulfenyl fluorides. (a) Summary of the current progress in arenechalcogenyl halides; (b) Synthesis of arenesulfenyl fluorides; (c) Reactivity of arenesulfenyl fluorides with putative reaction mechanisms included [a]Odenberger Chemischen Werke.[60] [b]M = Pb, Hg, Ag. [c]M = Ag, Hg.

Results and Discussion

Synthesis

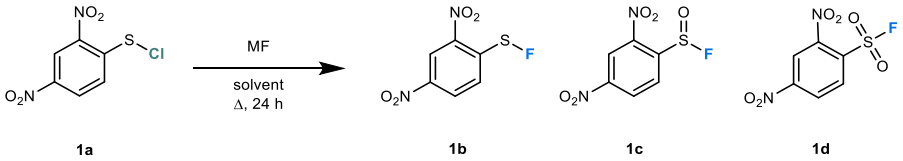
At the outset, we explored several types of approaches to synthesize arenesulfenyl fluorides. All strategies involving oxidative transformations from thiophenols or aryl disulfides were unsuccessful, resulting in the formation of sulfinyl fluorides, sulfur trifluorides, and/or sulfonyl fluorides.[36] The Hu group recently reported some reactions of aryl diselenides (and a few disulfides and ditellurides) that could proceed through a monofluoride intermediate upon oxidation by the mild oxidant *N*-fluorobenzenesulfonimide (NFSI).[37] Starting with various disulfides, we attempted to stop these transformation at the point of sulfenyl fluoride formation, but were ultimately unsuccessful, obtaining only further oxidized products.

To avoid the risks of overoxidation associated with common oxidative halogenation strategies, we chose to attempt a halogen exchange (Halex) strategy, involving substitution at the sulfur of arenesulfenyl halides effected by

nucleophilic fluoride reagents. Prior work by Jensen and coworkers demonstrated the bifunctional utility of thallium fluoride (TlF) which serves as a fluorine source and a chloride scavenger due to the relative insolubility of thallium chloride (TlCl).[38,39] When we treated 2,4-dinitrobenzenesulfenyl chloride (**1a**) with TlF (Table 1, Entry 1) at rt, near quantitative conversion to the sulfenyl fluoride (**1b**) was observed after 24 h. Though precautions were taken to exclude oxygen, a small amount of sulfinyl (**1c**) and sulfonyl fluorides (**1d**) were each observed. When a sulfenyl bromide was instead used as starting material, only trace **1b** was detected by ^{19}F NMR analysis of the crude mixture (Table 1, Entry 2). Encouraged by the efficiency of Halex with TlF, we turned our attention to evaluating alternative and more practical fluoride sources with lower toxicity, though Purrington had previously reported negative results with a variety of fluoride salts.[22] In our hands, **1a** was unreactive to LiF, KF, RbF, and AgF (Table 1, Entries 3-6) but engaged in a Halex reaction with CsF in modest yield (Table 1, Entries 7 and 8). Excess CsF appeared to be important: decreasing the quantity of CsF to a single equivalent (Table 1, Entry 9) resulted in low reactivity and incomplete conversion. In the case of soluble organic fluorides (M = *n*-Bu_4N, Me_4N[40]), rapid decomposition of sulfenyl chloride **1a** to a complex mixture took place (Table 1, Entries 10 and 11).

The Halex reaction with CsF occurred with similar yields in ethereal (THF, 2-MeTHF, Et_2O, and MTBE) and chlorinated (CH_2Cl_2, $CHCl_3$) solvents, with CH_2Cl_2 providing best results (97% yield at 75 °C). When ethereal solvents were used, additional side products from fluorinative cleavage of the ether were observed, and the use of 1,2-dichloroethane led to unproductive decomposition of the starting material. We elected to use CH_2Cl_2 for subsequent reactivity studies. We note that the purification of arenesulfenyl chlorides by recrystallization prior to use appears to be important. Batches of sulfenyl chlorides, both commercially available and prepared in our laboratory have been found to contain impurities not easily detected by ^{1}H NMR but which can cause diminished yields for the preparation of arenesulfenyl fluorides with either TlF or CsF (see Supporting Information for arenesulfenyl fluoride decomposition).

Table 1. Optimization of the Halex reaction conditions



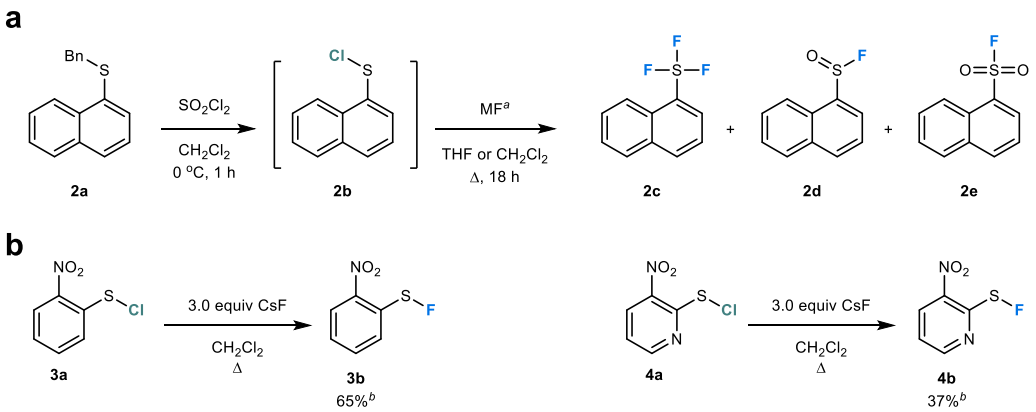
1a **1b** **1c** **1d**

entry[a,b]	MF	equiv MF	solvent	1b	1c	1d
1[c]	TlF	2.0	MTBE	94	3	1
2[c]	TlF	1.0	THF	<1	0	0
3	LiF	5.0	MTBE	0	0	0
4	KF	5.0	MTBE	<1	0	0
5	AgF	5.0	MTBE	0	0	0
6	RbF	5.0	MTBE	4	0	<1
7	CsF	3.0	MTBE	87	5	2
8[e]	**CsF**	**3.0**	**CH_2Cl_2**	**97**	**3**	**<1**
9	CsF	1.0	CH_2Cl_2	13	<1	<1
10	TMAF	5.0	MTBE	0	0	0

11	TBAF	5.0	MTBE	0	0	<1

[a]Calculated yields based on ^{19}F NMR spectroscopy using a 0.5 mL aliquot passed through a syringe filter and 10 µL of 1,3,5-trifluorobenzene as an external standard. [b]Entry 1 was performed on 10.0 mmol scale, entries 2-4 and entries 9-11 were performed on 1.0 mmol scale, entries 5-7 were performed on 0.5 mmol scale, and entry 8 was performed on 25.0 mmol scale. [c]rt, 12 h. [d]2,4-dinitrobenzenesulfenyl bromide was used. [e]60 h, 75 °C.

Efforts to generalize this Halex method to prepare various arenesulfenyl fluorides were met with mixed success (see Supporting Information). In several cases (e.g., from 1-napthalenesulfenyl chloride or 4-nitrobenzenesulfenyl chlorides), significant quantities of oxidized products such as **2c**, **2d**, and **2e** were observed based on ^{19}F NMR analysis. These results suggest that the corresponding sulfenyl fluorides do in fact form *in situ*, but they react too rapidly to form overoxidized species, presumably through a disproportionation pathway. In general, substrates containing an *ortho*-NO_2 group reacted well to form sulfenyl fluorides such as **3a** and **4a** in modest yield. Despite the currently limited scope of accessible sulfenyl fluorides, these characterizable examples establish the definitive existence of the functional group and provide a convenient starting point for the rigorous study of diverse reactivity of sulfenyl fluorides.



Scheme 2. Preparation of additional arenesulfenyl fluorides. (a) Unsuccessful attempts to synthesize 1-naphthalenesulfenyl fluoride. (b) Synthesis of arenesulfenyl fluorides **3b** and **4b**. [a]M = Li, Na, K, Ag, Cs, and Tl [b]Calculated yields based on ^{19}F NMR spectroscopy using 10 µL of 1,3,5-trifluorobenzene ($C_6H_3F_3$) as an internal standard.

In their pure form or as highly concentrated solutions, arenesulfenyl fluorides are significantly more sensitive than their chloride counterparts. Although it is possible to isolate such compounds in crystalline form (*vide infra*), bulk concentration of reaction mixtures under reduced pressure led to significant decomposition to a complex mixture of products, even when conducted with exclusion of oxygen. With prolonged storage at above concentrations of *ca.* 0.8 mol L^{-1}, spontaneous and unpredictable decomposition can occur (usually over the course of days), accompanied by visible darkening of the solution. This instability complicated most attempts at solvent swapping after initial preparation. Fortunately, we discovered that solutions of the arenesulfenyl fluoride below 0.8 mol L^{-1} could be stored in a -20 °C freezer for at least 1 to 2 months in glassware pretreated with a small quantity of slurried CsF. The

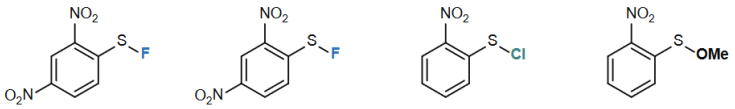
arenesulfenyl fluorides we prepared appear sensitive to atmospheric moisture and prolonged exposure to light below 420 nm.

Structure

Structural determination of the arenesulfenyl fluorides (**1b**, **3b**, and **4b**) were based on routine ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy. The sulfur-bound fluorine atom displayed characteristically upfield ^{19}F NMR chemical shifts of –206 to –222 ppm, consistent with predicted chemical shifts from GIAO calculations (–193 ppm for **1b**). ^{1}H–^{19}F PANSY COSY experiments provided additional support for our assignment based on the expected scalar couplings between the ^{19}F and aromatic ^{1}H nuclei. The ^{19}F chemical shifts we observed are incompatible with those reported by Seel, Purington, and Furin, which appear closer to those of sulfinyl fluorides.[21-25]

With care, it is possible to prepare single crystals of 2,4-dinitrobenzenesulfenyl fluoride (**1b**) suitable for X-ray diffraction analysis (monoclinic, $P2_1/n$). The S–F bond length of 1.66 Å is longer than observed in $ArSF_5$ compounds (1.56 - 1.58 Å)[41-43] and comparable to the theoretical model (1.70 Å at B3LYP/6-311+G(d,p)). The enhanced stability of arenesulfenyl fluorides bearing an *ortho*-nitro group may result from attractive donor-acceptor interactions involving the sulfenyl fluoride and oxygen atom of the nitro group.[44,45] In the crystal structure, an S---O distance of 2.25 Å (well below the sum of covalent radii, 3.32 Å), a nearly linear ∠O---S-F angle of 175.16°, and near planarity of the entire molecule are consistent with significant n(O) to σ*(S–F) donation

a



	1b	1b (DFT)	3a[44]	ArS–OMe[45]
S1---O1 (Å)	2.25	2.27	2.38–2.41	2.46
S–X bond (Å)	1.66	1.70	2.04–2.05	1.65
∠C1–S1–X1 (°)	95.6	95.5	100.5	100.1
∠O1···S1–X1 (°)	175.2	174.9	176.9–177.8	176.4

b

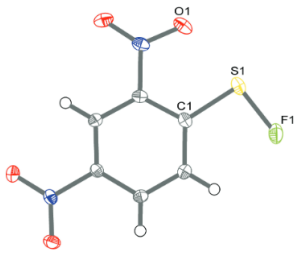


Figure 1. Summary of X-ray diffraction data for arenesulfenyl fluoride (**1b**) and related compounds. (a) Comparison of key bond lengths, bond angles, and S1—O1 distances. Ar = 2-nitrophenyl, DFT calculations performed using B3LYP/6-311+G(d,p). (b) Perspective view of **1b** showing 50% probability displacement

Comparative UV-Vis spectrophotometry of 2,4-dinitrobenzenesulfenyl fluoride (**1b**), chloride (**1-Cl**), and bromide (**1-Br**) in solution revealed a notable shift of the peak absorption at 402 nm for **1b** compared to the same transition in **1-Cl** (384 nm) and **1-Br** (390 nm)**.** By time-dependent density functional theory (TD-DFT), this transition is attributed to a □ to □* transition, whose bathochromic shift may reflect a stronger degree of charge transfer in the n(O) to □*(S–X) interaction. Greater absorbance of **1b** in the visible range is consistent with its elevated proclivity for decomposition by ambient light.

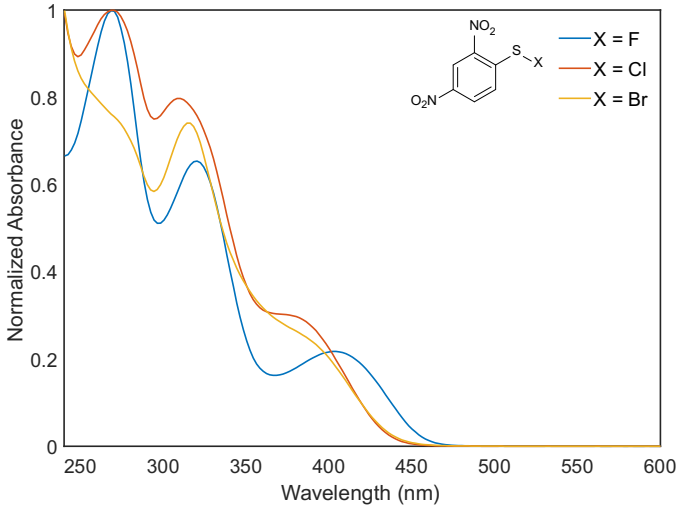
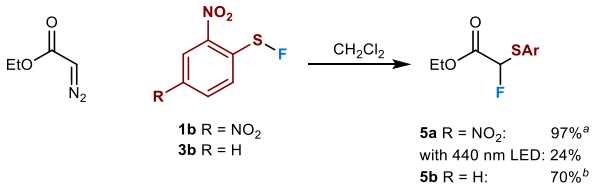


Figure 2. UV-Vis spectra of 2,4-dinitrobenzenesulfenyl halides in THF.

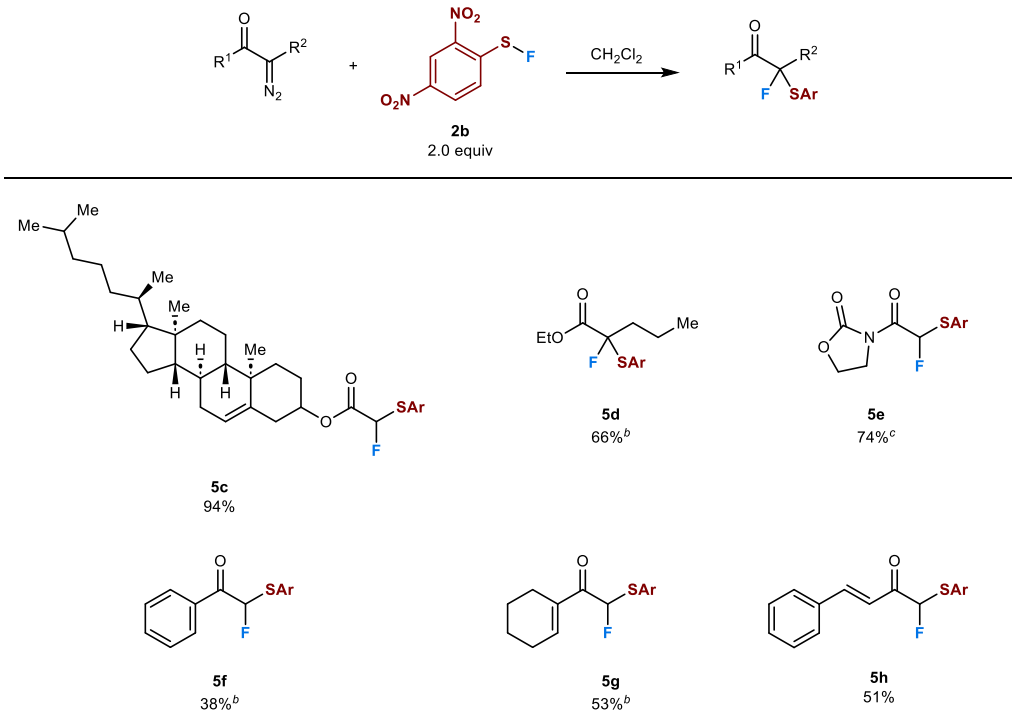
Reactivity

Arenesulfenyl fluorides display rich reactivity towards numerous common functional groups. In this study, we chose to focus on diazo compounds (carbene precursors), alkenes, and alkynes, as the corresponding transformations involved addition of both the fluorine and the sulfur component and may have synthetic utility for the preparation of diverse fluorinated structures. We evaluated the reactivity of sulfenyl fluorides **1b** and **3b** with carbenes and carbenoids using ethyl α-diazoacetate as a precursor under photochemical, thermal, and transition-metal activation. Thermal activation appeared to be the most effective, producing the S–F insertion product **5a** in up to 97% yield at 45 °C. Interestingly, this adduct was not observed when the reaction was conducted with catalytic $Rh_2(OAc)_4$. Sulfenyl fluoride **3b** is generally more reactive than the dinitro version **3a**, and the carbene insertion reaction proceeded at rt in high yield.



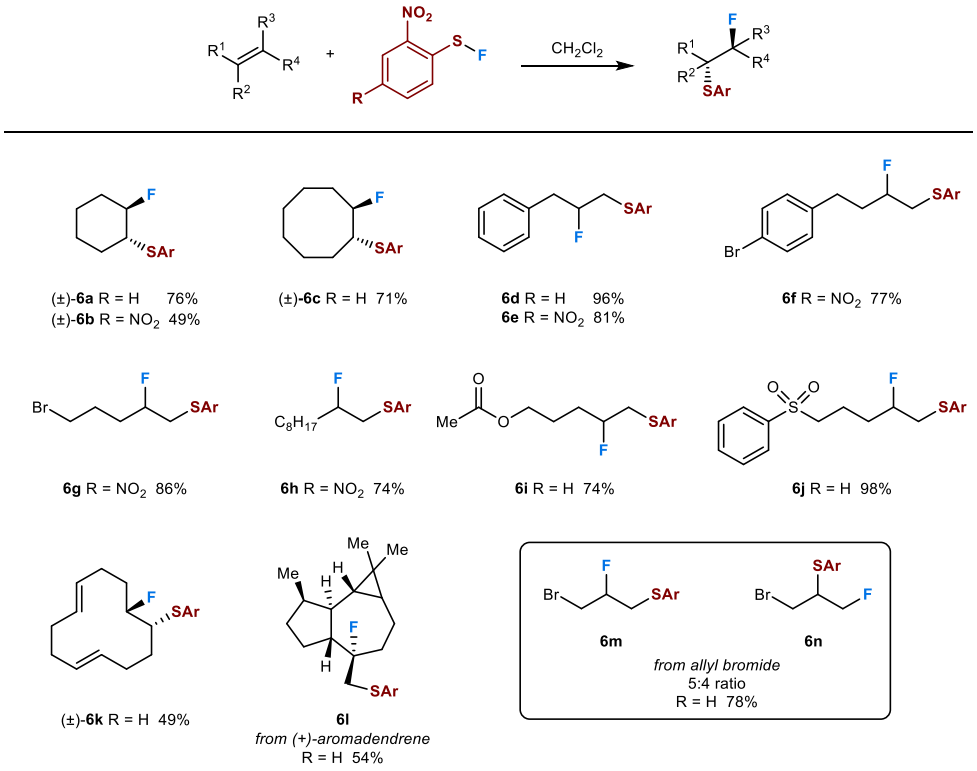
Scheme 3. Arenesulfenyl fluoride addition to ethyl diazoacetate. [a]2.0 equiv, 45 °C. [b]1.0 equiv, rt.

This synthesis of fluorinated thioethers functions well on a range of α-diazo carbonyl compounds, although some optimization of the reaction temperature was required for each example. Common electron-withdrawing groups, including esters, ketones, imides, and their α,β-unsaturated versions were tolerated by the reaction conditions. In the case of cholesteryl acetate, the trisubstituted alkene was preserved during the transformation (**5c**). Cyclic diazo ketones did not successfully convert under these conditions due to competing Wolff rearrangement.



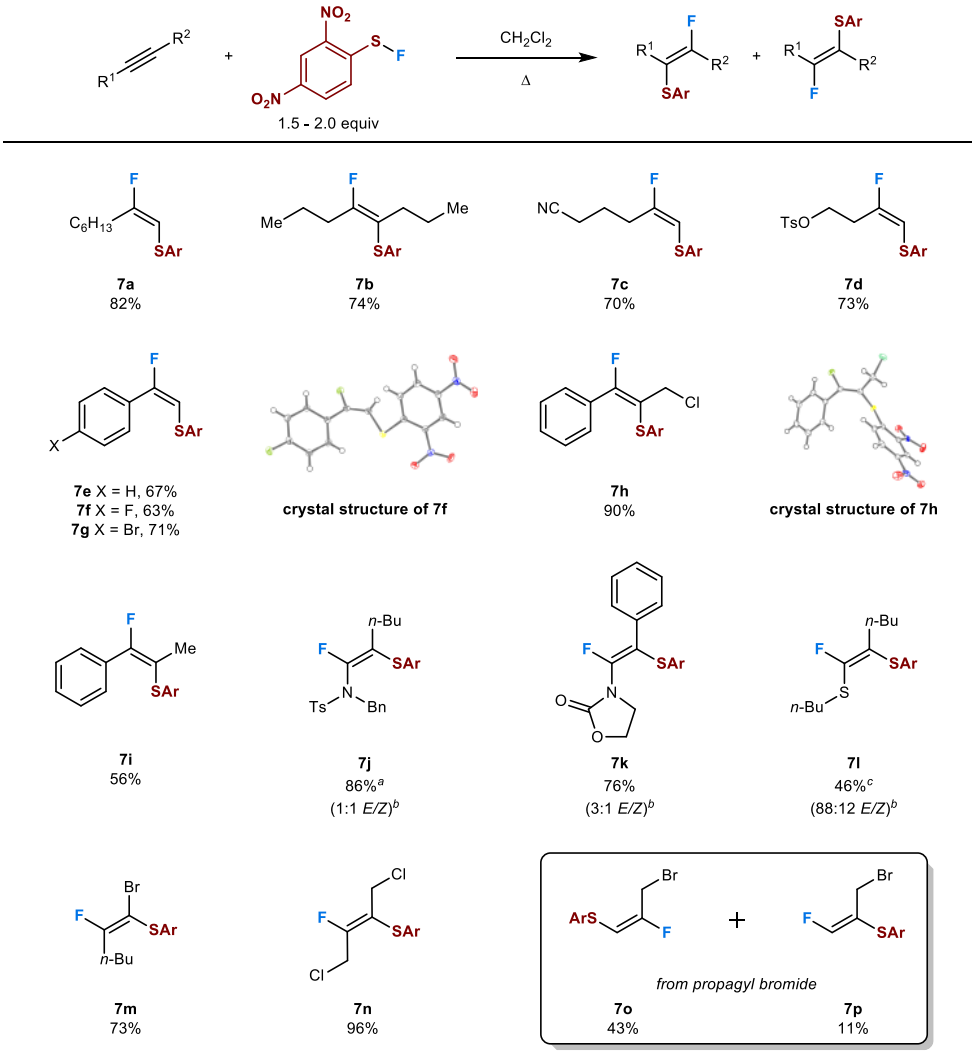
Scheme 4. Substrate scope for the addition of arenesulfenyl fluorides to α-diazo carbonyl compounds. [a]Isolated yields. [b]60 °C. [c]70 °C.

Arenesulfenyl fluorides react with alkenes with exclusive *anti*-selectivity, presumably through the intermediacy of an *epi*-sulfonium intermediate, and typically with high regioselectivity. The sense of regioselectivity is consistent with S_N2-type ring opening of an *epi*-sulfonium species at the more substituted carbon. In most cases, elevated temperatures are required for reaction with 2,4-dinitrobenzenesulfenyl fluoride (**1b**), and the more reactive, 2-nitro version **3b** could be used at rt to better effect.



Scheme 5. Substrate scope for the addition of arenesulfenyl fluorides to alkenes.

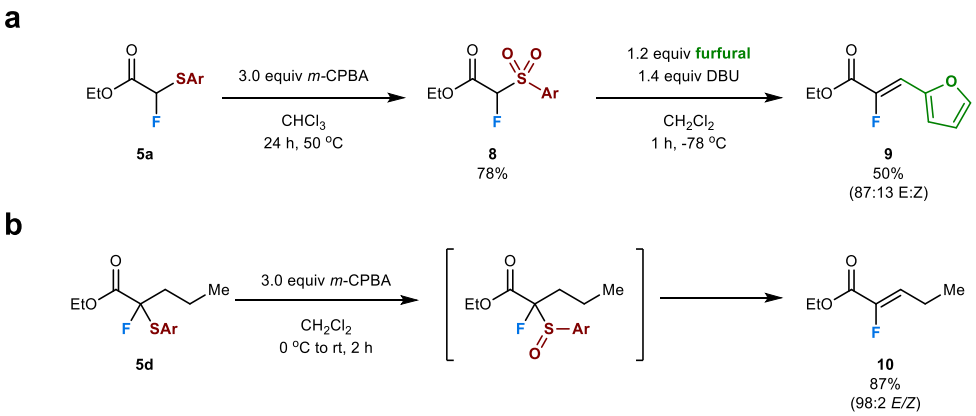
Similar *trans*-selective, 1,2-addition reactivity towards alkynes was observed, providing fluoroalkenes with high stereo- and regiochemical purity. Although the exact mechanism, and whether a sulfonium intermediate is involved, is less definite, we consistently observed fluorine addition occurring at the terminus more capable of stabilizing partial carbocation character. Interestingly, the observed regioselectivity for sulfenyl fluorides is in direct contrast to the outcomes observed by their chloride analogues, in which the chloride adds to the less-substituted carbon.[46,47] The reaction works well with a range of alkynes and, because it does not generate a large concentration of nucleophilic fluoride, tolerates potentially electrophilic groups such as an alkyl chloride, an alkyl tosylate, a nitrile, and an allylic bromide. The stereo- and regiochemical assignments were confirmed by single crystal X-ray diffraction analysis for representative products **7f** and **7h**. Alkynes directly bonded to some heteroatomic substituents, such as ynamides **7j** and **7k** as well as alkynyl thioether **7l**, reacted to form a mixture of E/Z isomers. The loss of stereospecificity potentially originates from intermediate formation of a stabilized vinyl cation adjacent to the electron-donating substituents.[48-50] Evidently, bromine is insufficiently donating by resonance to cause this erosion of stereospecificity, as an alkynyl bromide reacted in good yield and with high *E*-selectivity (**7m**). Interestingly, the addition of **1b** to parent propargyl bromide resulted in a separable mixture of regioisomers (**7o** and **7p**), both as exclusively the *E* stereoisomer.



Scheme 6. Substrate scope for the addition of arenesulfenyl fluorides to alkynes. [a]14% recovered starting material. [b]*E/Z* stereochemical assignments were determined by ^{1}H-^{19}F 2D NOESY correlations. [c]41% recovered starting material.

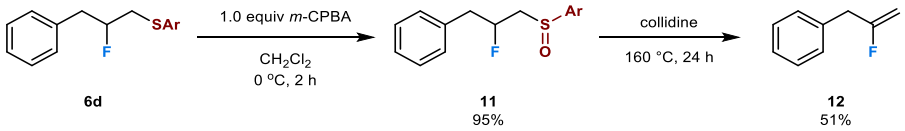
Derivatization

Having established the reactivity of arenesulfenyl fluorides with α-diazo compounds, alkenes, and alkynes, we wondered whether the products could be easily converted to useful fluorinated compounds. Although the scope of isolable arenesulfenyl fluoride reagents appears limited to those with *ortho*-nitro substituents, we found that the resulting electron-deficient –SAr group provides convenient opportunities for further synthetic elaboration. As an example, oxidation of **5a**, derived from ethyl α-diazoacetate, with excess *m*-CPBA yielded sulfone **8**, which was employed in a Julia olefination to synthesize vinyl fluoride **10** with modest stereocontrol.[51,52] Alternatively, thioether **5d**, was oxidized with *m*-CPBA, and the resulting sulfoxide rapidly eliminated to furnish fluoroalkenoate **10** in good yield and with high stereoselectivity.[53]



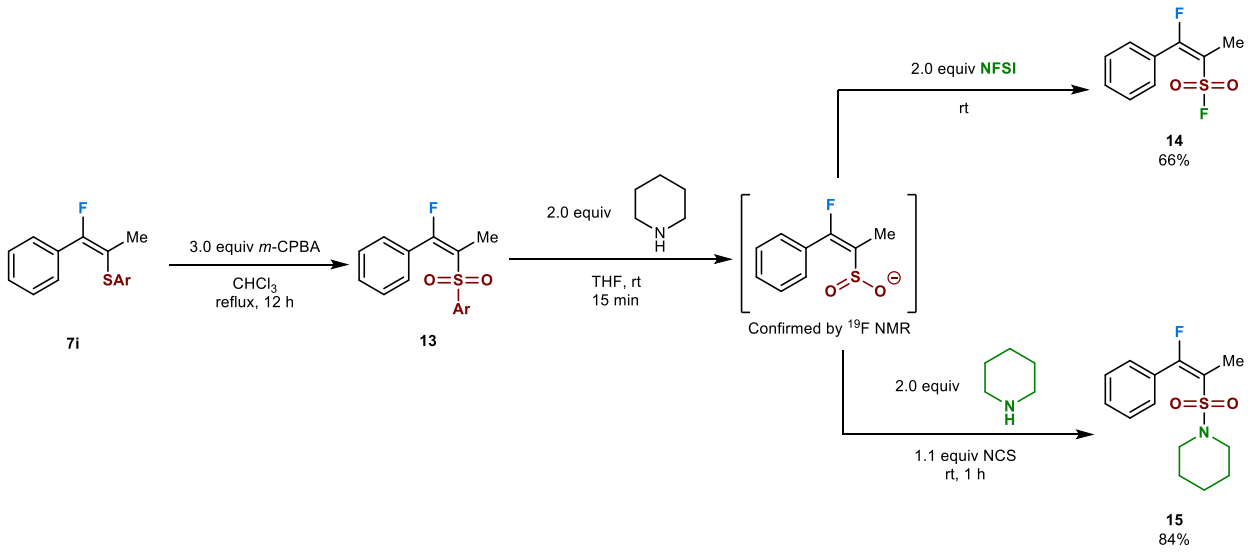
Scheme 7. Synthetic elaboration of α-diazo carbonyl adducts. (a) Julia-Kocienski olefination approach. (b) *syn*-Thermal elimination approach. Ar = 2,4-dinitrophenyl.

Thermal elimination of the aryl thioether was also possible with the adducts derived from sulfenyl fluoride addition to alkenes. Oxidation of thioether **6d** with *m*-CPBA provided the corresponding sulfoxide as a mixture of diastereomers, which upon heating afforded fluorinated olefin **12**.[54] To avoid isomerization of the double bond to the internal alkene, presumably catalyzed by evolved hydrofluoric or arylsulfenic acid, use of a mild base (collidine) was required.



Scheme 8. Synthetic elaboration of alkene adduct 6d via a *syn*-thermal elimination strategy. Ar = 2-nitrophenyl.

Finally, taking advantage of the electron-deficient nature of the aryl thioethers prepared by our procedure, we proposed that the arene could be efficiently removed by nucleophilic aromatic substitution, allowing for the installation of other sulfur functional groups.[55-59] After oxidation of alkyne-derived adduct **7i** to the sulfone, treatment with piperidine at room temperature resulted in rapid dearylation to form the fluorinated sulfinate, which was identified by ^{19}F NMR spectroscopy (δ = -97.0 ppm) but not isolated. Through addition of an appropriate electrophile, either NFSI or the combination of NCS with a secondary amine, this sulfinate could be transformed into a sulfonyl fluoride or sulfonamide, retaining the previously installed fluorine and its stereochemical relationships.



Scheme 9. Synthetic elaboration of alkyne adduct **7i**. Ar = 2,4-dinitrophenyl.

Conclusions

In summary, we report the first isolation and definitive characterization of organic sulfenyl fluorides. These compounds were found to engage in addition reactions with carbenes, alkenes, and alkynes to afford thiofluorinated adducts with excellent regio- and stereoselectivity where applicable. The thioether products could be conveniently elaborated into a variety of useful fluorinated motifs. The promising synthetic potential of arenesulfenyl fluorides as reagents warrants further study, and a systematic exploration of additional reactivity is ongoing in our group.

Supporting Information

The Supporting Information is available free of charge at http://pubs.acs.org. Experimental procedures, computational data, and compound characterization data are available in the Supporting Information. Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 2359079 (**1b**), 2359081 (**7f**), and 2359080 (**7h**). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/.

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Notes

The authors declare no competing interests.

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