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Difluoro(aryl)(perfluoroalkyl)-λ^4-sulfanes and Selanes: Missing Links of Trichloroisocyanuric Acid/Potassium Fluoride Chemistry

Fabian Brüning,† Cody Ross Pitts,† Jorna Kalim, Dustin Bornemann, Clément Ghiazza,‡ Jean de Montmollin, Nils Trapp, Thierry Billard,‡* and Antonio Togni*

Abstract: The TCICA/KF approach to oxidative fluorination of heteroatoms has emerged as a surprisingly simple, safe, and versatile surrogate to classically challenging fluorination reactions. Although polyfluorination (or chlorofluorination) of diaryl disulfides, diaryl diselenides, diaryl ditellurides, aryl iodides, and aryl(perfluoroalkyl)tellanes has been described, the application of this TCICA/KF methodology to aryl(perfluoroalkyl)sulfanes and selanes remains an area of unexplored chemical space. Accordingly, to address the "missing links" in the developing series of chalcogen-based substrate reactivity, we report mild syntheses of meta-stable difluoro(aryl)(perfluoroalkyl)-λ^4-sulfanes and selanes. As only limited examples of these species exist in the current literature (accessible only by using F_2 or XeF_2/HF), we have carried out detailed structural analyses, primarily using NMR and SC-XRD data. In addition, we investigate the effect of the perfluoroalkyl chain on the outcome of oxidative fluorination, and, finally, we provide preliminary evidence that difluoro(aryl)(trifluoro-methyl)-λ^4-sulfanes may act as fluorinating reagents.

The trichloroisocyanuric acid/potassium fluoride (TCICA/KF) approach to oxidative fluorination has opened up new frontiers in the synthesis and study of highly fluorinated substituents. Recently, TCICA/KF conditions have 1) obviated the reliance on corrosive Cl_2 gas in the synthesis of aryl-SF_4Cl and aryl-SF_3 compounds,[1] 2) replaced XeF_2 in the synthesis of aryl-SeF_3 and aryl-TeF_5 compounds,[1,2] and 3) circumvented extremely hazardous reagents such as F_2, HF, and SF_4 in the synthesis of aryl-IF_2 and aryl-IF_4 compounds,[3] thus demonstrating a powerful ability to make fluorination chemistry more accessible to the broader chemical community. Moreover, this approach has created opportunities to synthesize/study previously unknown fluorinated moieties, including the TeF_4CF_3 group.[3] Beyond academic interest, unknown/underexplored fluorinated groups of the like may find interesting applications in medicinal chemistry, agrochemistry, materials, or reagent design.[4,5]

Following the chalcogen series, the reactivity of diaryl disulfides,[1] diaryl diselenides,[1] and diaryl ditellurides[2] under TCICA/KF conditions has been studied in our laboratory, as well as the behavior of aryl(trifluoromethyl)tellanes (Figure 1).[2] Conversely, *the reactivity of aryl(trifluoromethyl)sulfanes and selanes under similar conditions has yet to be explored*. Herein, we now report an application of the TCICA/KF approach to the synthesis and study of difluoro(aryl)(trifluoromethyl)-λ^4-sulfanes (aryl-SF_2CF_3 compounds) and difluoro(aryl)(trifluoromethyl)-λ^4-selanes (aryl-SeF_2CF_3 compounds) – two virtually unexplored fluorinated species. Only limited examples of each have been synthesized by Yagupol'skii and Savina using XeF_2/HF in 1979,[6] and one example of an aryl-SF_2CF_3 compound has been synthesized by Umemoto and Ishihara (though only as an intermediate) using F_2 gas in 1993.[7] Accordingly, we utilize this newfound accessibility via TCICA/KF chemistry as an opportunity to study the structure and properties of these compounds in detail.

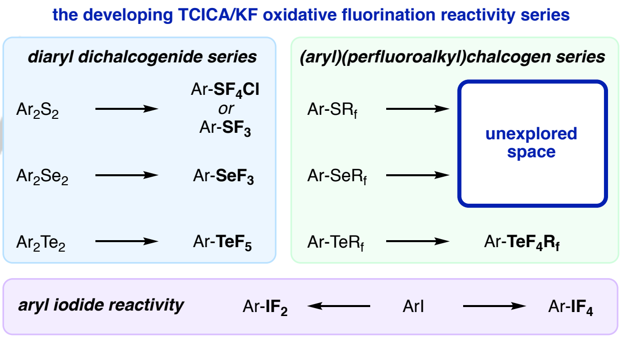

Figure 1. *Identifying a gap in our understanding of the reactivity of substrates in the (aryl)(perfluoroalkyl)chalcogen series under TCICA/KF conditions; reactivity of diaryl dichalcogenides and aryl iodides has been explored previously.*

Adapted from the conditions used for oxidative fluorination of diaryl disulfides,[1] we began screening with phenyl(trifluoromethyl)sulfane using 9.0 equiv. TCICA, 16 equiv. KF, and 10 mol% TFA in MeCN at room temperature overnight. Under these conditions, we found that the substrate is converted to difluoro(phenyl)(trifluoromethyl)-λ^4-sulfane (**1**) in 81% yield by ^{19}F NMR analysis. Further attempts to decrease the amounts of TCICA or KF at room temperature resulted in consistently lower yields; however, the amounts could be decreased to 4.0 equiv. TCICA and 8.0 equiv. KF by heating the reaction mixture to 40 °C (i.e., **1** was obtained in ~80% yield by ^{19}F NMR). Additionally, we found that the reaction proceeds poorly (or not at all) in the

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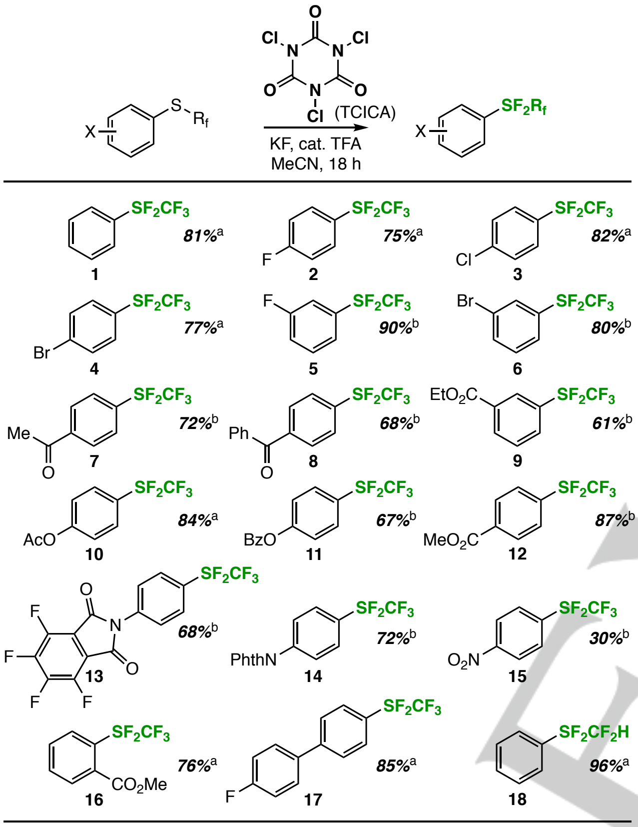
absence of TFA, using increased amounts of TFA, or when replacing it with certain Lewis acid additives. Moreover, it is important to note that tetrafluoro(aryl)(trifluoromethyl)-λ^6-sulfanes was not observed during the screening process.[8-11] See the Supporting Information for additional details regarding reaction screening.

Table 1. *Substrate scope of aryl(trifluoromethyl)sulfanes and aryl(difluoromethyl)sulfanes.*



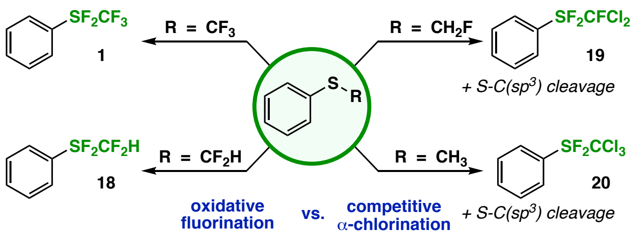
^{19}F NMR yields reported. Yields in parentheses based on conversion. All reactions carried out using 9.0 equiv. TCICA, 16 equiv. KF, and 10 mol% TFA. [a]Reaction was carried out at rt. [b]Reaction was carried out at 40 °C.

Subsequently, we examined the scope of the reaction on a variety of aryl(trifluoromethyl)sulfanes (Table 1). For one, the corresponding difluorinated products containing halogens in the *para*-position (**2**-**4**) were obtained in 75-82% yields by ^{19}F NMR. Yet, the first attempts at synthesizing *meta*-fluoro- and *meta*-bromo-derivatives **5** and **6** resulted in yields below 40%, with the majority of the material balance being unreacted starting material. It is possible that the stronger inductive effect of a halogen in the *meta*-position slows the rate of oxidation of the sulfur atom. We later found that better yields can be obtained overnight by heating to 40 °C. A similar tactic was used to obtain favorable yields of *meta*- or *para*-substituted compounds decorated with ketones (**7**-**8**), esters (**9**-**12**), amides (**13**-**14**), and a nitro group (**15**). However, substrates containing a nitro substituent were particularly finicky, resulting in low yields and/or reproducibility issues.

Initial attempts at difluorinating substrates garnished with fluorine, bromine, or nitro substituents in the *ortho*-position were unsuccessful, though **16**, containing an *ortho*-methyl ester, formed in 76% yield. Another limitation of this method is the use of even mild electron-donating groups, as background ring and/or benzylic chlorination often becomes competitive.[12] For instance, previously, we observed unselective ring chlorination on biphenyl-based substrates.[2] Yet, if the biphenyl moiety sports an electron-withdrawing group, no ring chlorination is observed (**17**).

Although aryl(difluoromethyl)sulfane substrates are less accessible, we were curious about how their reactivity compares to aryl(trifluoromethyl)sulfanes. Fortuitously, (difluoromethyl)-difluoro(phenyl)-λ^4-sulfane **18** was formed from its commercially available starting material in 96% yield. Whereas **1** is identified in the ^{19}F NMR spectrum by diagnostic signals and F-F coupling constants at -14.38 ppm (2F, quartet, $^3J_{F\text{-}F}$ = 18 Hz) and -62.79 ppm (3F, triplet, $^3J_{F\text{-}F}$ = 18 Hz), **18** exhibits additional *J*-couplings to the hydrogen atom and upfield shifts of both signals to -25.14 ppm (2F, td, $^3J_{F\text{-}F}$ = 12 Hz, $^3J_{F\text{-}H}$ = 4 Hz) and -105.84 ppm (2F, dt, $^1J_{F\text{-}H}$ = 55 Hz, $^3J_{F\text{-}F}$ = 12 Hz). To the best of our knowledge, this species has not been reported previously.

Once the difluoromethyl group on the sulfur atom is replaced with a monofluoromethyl group, divergent reactivity occurs (Scheme 1). After subjecting fluoromethyl(phenyl)sulfane to TCICA/KF conditions, a doublet at -3.64 ppm and triplet at -39.16 ppm are observed in the ^{19}F NMR spectrum, each with $^3J_{F\text{-}F}$ = 22.0 Hz (confirmed in the ^{19}F{^{1}H} spectrum). These signals correspond to formation of an SF_2CFCl_2 group (**19**), indicating that α,α-dichlorination of this substrate occurs readily. Taking it one step further, we discovered that the reaction employing thioanisole is notably exothermic, and the major product contains an SF_2CCl_3 group (**20**) with a singlet at +10.14 ppm in the ^{19}F NMR spectrum (the SF_2CH_3 derivative is not formed). Such α-chlorination chemistry on thioanisole has been described using reagents such as Cl_2 and *N*-chlorosuccinimide and may be expected for TCICA;[13,14] however, note that neither di- nor tri-chlorination stifles difluorination of the sulfur atom under our conditions. Additionally, some minor products indicate S–C(sp^3) bond cleavage occurs, including phenyl-SF_3, phenyl-SOF_3, phenyl-SF_4Cl, and C_2Cl_6 (when employing thioanisole). No evidence of S–C(sp^3) bond cleavage was observed for **1** or **18**.

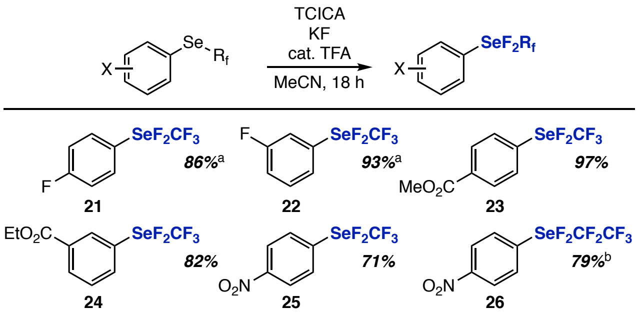


Scheme 1. *Divergent reactivity of sulfane substrates bearing CH_3 vs. CH_2F vs. CF_2H vs. CF_3 groups under TCICA/KF conditions.*

One major reactivity question remained: does the selenium derivative behave more like sulfur or tellurium (i.e. with Se in the +4 or +6 oxidation state in the final product)? A small number of aryl(trifluoromethyl)-selanes were synthesized and subjected to TCICA/KF conditions (Table 2).[15-18] As Yagupol'skii's results with XeF_2/HF suggest,[6] we found that the selanes undergo difluorination similar to sulfanes. Thus, compounds **21**-**26** were formed in good yields. The ^{19}F NMR data of **15**, for instance, can be compared to **25**: in **15**, signals at -11.89 ppm (2F, q, $^3J_{F\text{-}F}$ = 18

Hz) and -61.74 ppm (3F, t, $^3J_{F\text{-}F}$ = 18 Hz) are observed, and in **25**, the corresponding signals appear upfield at -58.30 ppm (3F, t, $^3J_{F\text{-}F}$ = 12 Hz) and -73.21 ppm (2F, q, $^3J_{F\text{-}F}$ = 12 Hz). Additionally, from the ^{77}Se satellite signals, $^1J_{Se\text{-}F}$ = 420 Hz and $^2J_{Se\text{-}F}$ = 52 Hz.

***Table 2.** Showcasing reactivity of aryl(perfluoroalkyl)selanes.*



^{19}F NMR yields reported. Reactions were carried out using 9.0 equiv. TCICA, 16 equiv. KF, and 10 mol% TFA at rt. ^{a}Yield determined based on conversion of material balance by ^{19}F NMR. ^{b}Isolated yield.

Next, we compared the reactivity of substrates with CF_3 versus CF_2CF_3 substituents on the selenium atom. Interestingly, **26** formed in 79% yield, which allows for a comparison between the SeF_2CF_3 group and a novel $SeF_2CF_2CF_3$ group. Evidently, the selenium-bound fluorine atoms have similar ^{19}F NMR shifts (i.e. -73.21 ppm for **25** and -72.10 ppm for **26**) and identical $^1J_{Se\text{-}F}$-values of 420 Hz. The change in perfluoroalkyl chain length also has a minimal effect on the ^{77}Se NMR shifts, which were observed at 1112 ppm for **25** and 1108 ppm for **26**.[19]

On another note, two properties that are often of general interest in polyfluorinated substituents are their lipophilicity and their electron-withdrawing effect.[20] However, the aryl-SF_2CF_3 and aryl-SeF_2CF_3 compounds are unstable in water; they hydrolyze to their aryl-$SOCF_3$ and aryl-$SeOCF_3$ derivatives. Rapid decomposition of these compounds in water renders determining a Hansch lipophilicity parameter somewhat meaningless,[21] and complicates the determination of Hammett parameters using classical techniques.[22] Alternatively, the Hammett parameters can be estimated by adapting the ^{19}F NMR approach developed by Taft.[23,24]

By measuring the chemical shift differences between *meta*- or *para*-substituted fluorobenzenes and a fluorobenzene internal standard at low concentrations, we determined inductive (σ_I) and resonance (σ_R) parameters, and thus *meta*- and *para*-σ constants (σ_m and σ_p), as per Eq. 1-4 in the SI. The electron-withdrawing effect of the SF_2CF_3 group, with $\sigma_m \approx 0.73$ and $\sigma_p \approx 0.79$, is on the order of that of a nitro group (Table 3).[25] These values also can be benchmarked against values for the SCF_3 group ($\sigma_m \approx 0.40$ and $\sigma_p \approx 0.50$)[26] and the SO_2CF_3 group ($\sigma_m \approx 0.83$ and $\sigma_p \approx 0.96$).[22] For the SeF_2CF_3 group, we determined similar values of $\sigma_m \approx 0.75$ and $\sigma_p \approx 0.80$, which likewise sit between those for $SeCF_3$ group ($\sigma_m \approx 0.44$ and $\sigma_p \approx 0.45$)[27] and the SeO_2CF_3 group ($\sigma_m \approx 1.08$ and $\sigma_p \approx 1.21$).[28] Expectedly, the inductive influence of SeF_2CF_3 is slightly greater than that of SF_2CF_3, while the opposite is true for the resonance contributions.

To the best of our knowledge, solid-state structures of neither aryl-SF_2CF_3 nor aryl-SeF_2CF_3 compounds have been reported in the literature to date. Accordingly, after some difficulty, we obtained single crystals of **8** and **25** for X-ray diffraction, as well as other derivatives for comparative analyses (Figures 2 and 3). As anticipated from the ^{19}F NMR data, both **8** and **25** exhibit distorted seesaw geometries with the chalcogen-bound fluorine atoms arranged in the axial positions.

***Table 3.** Estimating Hammett parameters of SF_2CF_3 and SeF_2CF_3 groups.*

X	$\delta_H^{p\text{-}X}$	$\delta_H^{m\text{-}X}$	σ_I	σ_R^0	σ_m^0	σ_p^0
SF_2CF_3	-7.92	-4.08	0.66	0.13	0.73	0.79
SeF_2CF_3	-7.40	-4.39	0.70	0.10	0.75	0.80

Negative values of $\delta_H^{p\text{-}X}$ and $\delta_H^{m\text{-}X}$ denote downfield ^{19}F NMR shifts (deshielding) of para- and meta-substituted fluorobenzene derivatives, respectively, relative to a fluorobenzene standard in $\leq$ 0.02 M solutions in CD_3CN. The σ_I and σ_R^0 parameters were calculated by the method of Taft and used to estimate σ_m^0 and σ_p^0 constants according to Eq. 1-4 in the SI.

With respect to the sulfur-based compounds in Figure 2, some features of the molecular structure of aryl-SF_2CF_3 compound **8** were compared to its aryl-SCF_3 starting material **27**. Although the C_{ipso}–S bond length is virtually unaffected between the S(II) and S(IV) species, the S–CF_3 bond of **8** (ca. 1.874 Å) is 5% longer than that of **27** (ca. 1.785 Å). In addition, the C_{ipso}-S-CF_3 bond angle ($\theta_{C\text{-}S\text{-}C}$) in **8** of ca. 104.5° is 4% greater than that displayed in the bent structure of **27** (ca. 100.3°). Lastly, there are a few important features to highlight regarding the sulfur-bound fluorine atoms of **8**: 1) an average S–F bond length of 1.713 Å was observed, which is significantly longer than, for instance, an S–F bond on a stable SF_5 group on the same benzophenone core (ca. 1.566 Å),[1] 2) the F-S-F bond angle deviates somewhat from linearity ($\theta_{F\text{-}S\text{-}F} \approx 173.5°$), and 3) the average C_{ipso}-S-F bond angle ($\theta_{C\text{-}S\text{-}F} \approx 90.1°$) is near ideal perpendicularity for seesaw-type structures.

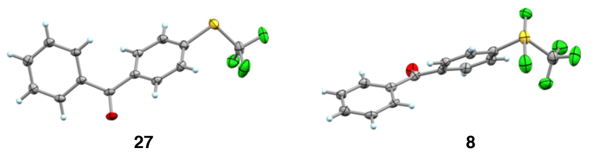


***Figure 2.** Molecular structures of **27** (left) and **8** (right), for comparison of the SCF_3 and SF_2CF_3 groups on the same scaffold, determined by single-crystal X-ray diffraction (displacement ellipsoids depicted at 50% probability level).*

The selenium-based structures in Figure 3 also offer an opportunity to make additional comparisons. For one, the aryl-$SeCF_3$ precursor (**28**) to aryl-SeF_2CF_3 compound **25** has, on average, a slightly shorter C_{ipso}–Se bond length (ca. 1.924 Å vs. 1.943 Å), unlike what we observed when comparing sulfur-based structures **8** and **27**. However, similar to the comparison between **8** and **27**, the Se–CF_3 bond of **25** (ca. 2.009 Å) is 3% longer than that of **28** (ca. 1.953 Å). Additionally, the C_{ipso}-Se-CF_3 bond angle of **25** ($\theta_{C\text{-}Se\text{-}C} \approx 97.5°$) is greater than that of aryl-$SeCF_3$ compound

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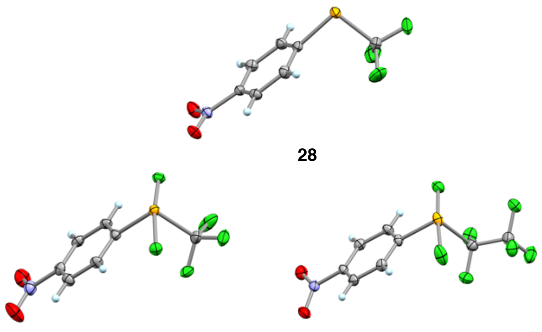
28 ($\theta_{C\text{-}Se\text{-}C} \approx 94.7°$). Here, note that both C_{ipso}-Se-CF_3 angles are significantly smaller than for the sulfur-based structures, due to a larger influence of the selenium lone pairs. Furthermore, the average Se–F bond lengths of 1.857 Å in **25** are unsurprisingly longer than the S–F bonds in **8**, and its average $\theta_{F\text{-}Se\text{-}F}$ of 169.2° deviates further from linearity than the aforementioned $\theta_{F\text{-}S\text{-}F}$ in **8**. Yet, the average C_{ipso}-Se-F bond angle ($\theta_{C\text{-}Se\text{-}F} \approx 89.7°$) is similarly near ideal perpendicularity.

For another vantage point, we also obtained an X-ray crystal structure of aryl-$SeF_2CF_2CF_3$ compound **26** (Figure 3). For the most part, **25** and **26** display similar features. However, the average Se–CF_2CF_3 bond length (ca. 2.034 Å) is slightly longer than the Se–CF_3 bond, the average C_{ipso}-Se-CF_2CF_3 bond angle (ca. 95.8°) is smaller than the C_{ipso}-Se-CF_3 angle, and the F-Se-F bond angle of **26** ($\theta_{F\text{-}Se\text{-}F} \approx 172.2°$) is closer to linearity than the F-Se-F angle of **25**. More detailed comparisons of all SC-XRD data can be found in the Supporting Information.

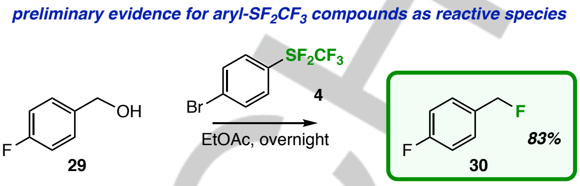


28

25 **26**

Figure 3. *Molecular structures of **28** (top), **25** (bottom left), and **26** (bottom right), for comparison of the $SeCF_3$, SeF_2CF_3 and $SeF_2CF_2CF_3$ groups on the same scaffold, determined by single-crystal X-ray diffraction (displacement ellipsoids depicted at 50% probability level).*

Finally, we present very preliminary evidence that these classes of compounds have potential applications as fluorinating reagents. For one, analogies can be drawn between aryl-SF_2CF_3 compounds and aryl-SF_3 compounds (e.g. Fluolead[29]), which are known nucleophilic fluorinating reagents.[30-32] Although a complete study of the reactivity of the SF_2CF_3 and SeF_2CF_3 groups is beyond the scope of this work, we briefly studied the reactivity of **4** with 4-fluorobenzyl alcohol (**29**) as a simple test substrate. Note that **4** was chosen for this study as it is derived from a fairly inexpensive starting material and proved easily isolable. Thus, we synthesized and isolated **4** on a gram scale in 53% yield via extraction of the crude reaction mixture with n-hexane (without column chromatography). Quickly, we discovered that **4** is capable of deoxyfluorination of **29**, providing 4-fluorobenzyl fluoride (**30**) in 83% yield (Scheme 2). Initial results suggest that the reaction is sensitive to solvent (e.g. favorable results were only obtained using EtOAc or $CHCl_3$) and that there may be an induction period prior to deoxyfluorination. Future work will focus on understanding/exploring the reactivity of these compounds, as well as developing a full scope. It remains to be seen whether aryl-SF_2CF_3 compounds will carry any advantages over aryl-SF_3 compounds as fluorinating reagents at all; however, we hope this initial result will encourage further investigations in due course.



Scheme 2. *Initial result suggesting behavior of aryl-SF_2CF_3 compounds as potential fluorinating reagents.*

In brief, by applying our recently developed TCICA/KF oxidative fluorination strategy to aryl-SCF_3 and aryl-$SeCF_3$ substrates, we unveiled an easy synthetic route to relatively unexplored aryl-SF_2CF_3 and aryl-SeF_2CF_3 compounds, among other derivatives. Straightforward access to these polyfluorinated compounds has also allowed for their detailed characterization in both solution (via ^{19}F, ^{1}H, ^{13}C, and ^{77}Se NMR) and in the solid state (via SC-XRD).[30] Additionally, we have been able to estimate Hammett parameters for the SF_2CF_3 and SeF_2CF_3 groups, and we have preliminary evidence that aryl-SF_2CF_3 compounds can mediate deoxyfluorination chemistry. Given the inherent hydrolytic instability of aryl-SF_2CF_3 and aryl-SeF_2CF_3 compounds on direct contact with water, the utility of these groups (beyond fundamental academic interest) may lie more so in the realm of reagent design.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: heteroatoms • oxidative fluorination • sulfanes • selanes • trichloroisocyanuric acid

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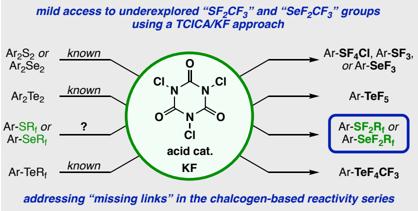

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