JOURNAL OF THE AMERICAN CHEMICAL SOCIETY



Communication

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*J. Am. Chem. Soc.*, **Just Accepted Manuscript** • DOI: 10.1021/jacs.9b06126 • Publication Date (Web): 13 Jul 2019

# Sulfonyl Fluoride Synthesis through Electrochemical Oxidative Coupling of Thiols and Potassium Fluoride

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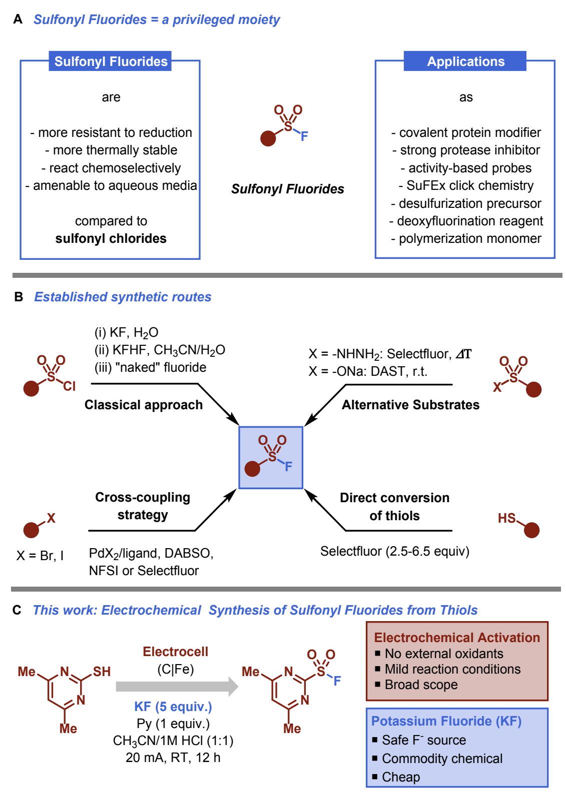
*Supporting Information Placeholder*

**ABSTRACT:** Sulfonyl fluorides are valuable synthetic motifs for a variety of applications, amongst which SuFEx-based click chemistry is currently the most prominent. Consequently, the development of novel and efficient synthetic methods to access these functional groups is of great interest. Herein, we report a mild and environmentally benign electrochemical approach to prepare sulfonyl fluorides using thiols or disulfides, as widely available starting materials, in combination with KF, as an inexpensive, abundant and safe fluoride source. No additional oxidants nor additional catalysts are required and, due to mild reaction conditions, the reaction displays a broad substrate scope, including a variety of alkyl, benzyl, aryl and heteroaryl thiols or disulfides.

Arguably, sulfonyl fluorides can be considered a “privileged moiety” in chemistry, as they can be adopted in a wide variety of applications. This can be attributed to the unique balance between reactivity and stability of these functional groups, which is in sharp contrast with analogous sulfonyl chlorides (Figure 1A).[1] Hence, sulfonyl fluorides have been used in chemical biology as covalent protein modifiers, strong protease inhibitors and activity-based probes.[2] In addition, sulfonyl fluorides have been successfully applied as fluorinating reagents,[3] $^{18}F$ radiolabeling agents[4] and have been engaged in other useful transformations,[5] including polymerizations.[6] However, the breakthrough application for sulfonyl fluorides is the realization of their utility as stable and robust sulfonyl precursors using sulfur(VI) fluoride exchange “click chemistry” (SuFEx).[1, 7]

Due to their evident value, efficient syntheses of sulfonyl fluorides starting from abundant starting materials are highly desired. The classical strategy to access these functional groups involves a chloride/fluoride exchange of sulfonyl chlorides using fluoride salts (Figure 1B).[8] However, sulfonyl chlorides are not widely available and need to be prepared from the corresponding thiols using a combination of oxidizing and chlorinating reagents.[9] In order to avoid toxic and unstable sulfonyl chlorides, new synthetic methods have been developed using alternative starting materials, including sulfonyl hydrazides[8b] or sodium sulfonates.[10] Also palladium-based cross-coupling strategies have been developed which utilize aryl halides in combination with 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) (DABSO) and electrophilic fluorinating reagents, such as Selectfluor[11] and NFSI.[12] Kirihara *et al.* reported a method to transform disulfides and thiols into sulfonyl fluorides using Selectfluor and refluxing conditions.[13] Despite the synthetic value of these approaches, the use of costly and atom-inefficient fluoride sources limits their practicality to small scale applications.

It is, however, evident that the development of a synthetic method which directly uses commodity chemicals, such as thiols and metal alkali fluorides, would be particularly useful given the broad availability and the low cost of these starting materials.




| Entry | Variation from the standard conditions | Isolated Yield (%) |
|---|---|---|
| 1 | none | 74 |
| 2 | no HCl | 0 |
| 3 | 0.3 M HCl | 32 |
| 4 | 1 M *p*-TsOH | 24 |
| 5 | no pyridine | 52 |
| 6 | no electricity | 0 |

**Figure 1. Development of an electrochemical synthesis of sulfonyl fluorides.** (A) Advantages and applications of sulfonyl fluorides. (B) Established synthetic routes to prepare sulfonyl fluorides. (C) Reaction Conditions (Entry 1): 2-mercapto-4,6-dimethylpyrimidine (2 mmol), KF (5 equiv.), Pyridine (1 equiv.), $CH_3CN$/ 1M HCl (20 mL, 1:1 v/v), C anode/Fe cathode, 20 mA (4.1 mA/cm$^2$), 12 h.

Even so, it is immediately clear that a number of challenges need to be overcome to develop such a hitherto elusive transformation. First, fluoride is poorly soluble in organic solvents and is hardly reactive in its solvated form in aqueous media. Second, combining nucleophilic fluorine reagents with thiols to establish a single S–F bond appears unlikely.[14] Nevertheless, based on our recent success in the electrochemical synthesis of sulfonamides,[15] we speculated that the union of these stubborn starting materials would not only be plausible using electrochemical activation[16] but would also facilitate the subsequent oxidation to sulfonyl fluoride via anodic oxidation. Herein, we report the discovery and optimization of an electrochemical method which meets these design criteria. The method utilizes KF as a readily available, safe and cost-efficient fluoride source. Moreover, anodic oxidation allows to avoid stoichiometric amounts of oxidants and enables the direct use of thiols or disulfides as convenient and widely available starting materials.

Initial experiments on a representative thiol, 2-mercapto-4,6-dimethylpyrimidine, revealed that the combination of 5 equivalents of KF, 1 equivalent of pyridine in a $CH_3CN$/1M HCl biphasic reaction mixture using inexpensive graphite/stainless steel electrodes is highly effective, providing the targeted sulfonyl fluoride in 74% isolated yield (Figure 1C, Entry 1). TBAF and other alkali fluorides, such as NaF and CsF, are less effective (See Supporting Information). Selectfluor, an electrophilic fluorine source, is equally potent as KF but was not further considered due to the unfavorable price difference (KF 8 $/mol vs. Selectfluor 407 $/mol).[17] We surmise that KF functions partially as an electrolyte, as the total amount can be lowered when supporting electrolytes are added (See Supporting Information). However, given the low cost of KF in comparison to these supporting electrolytes, we opted to keep a higher concentration of KF. In the absence of acid or at lower concentrations, decreased yields are observed (Figure 1C, Entries 2-4). The addition of one equivalent of pyridine is beneficial (Figure 1C, Entry 5), and is speculated to function as an electron mediator[18] or as a phase transfer catalyst. The reaction was confirmed to be electrochemically driven (Figure 1C, Entry 6).

With the optimal conditions in hand, we next turned our attention to examine the generality of this electrochemical transformation. As shown in Figure 2, a wide variety of structurally and electronically distinct thiols can be transformed into the corresponding sulfonyl fluorides. First, with a diverse set of thiophenols, it was determined that substrates bearing electron–neutral (**1-5**), –donating (**6-7**) and –withdrawing substituents (**8-10**) were all compatible with the reaction conditions; the yields were ranging from 37 to 99%. Due to the volatility of some products,

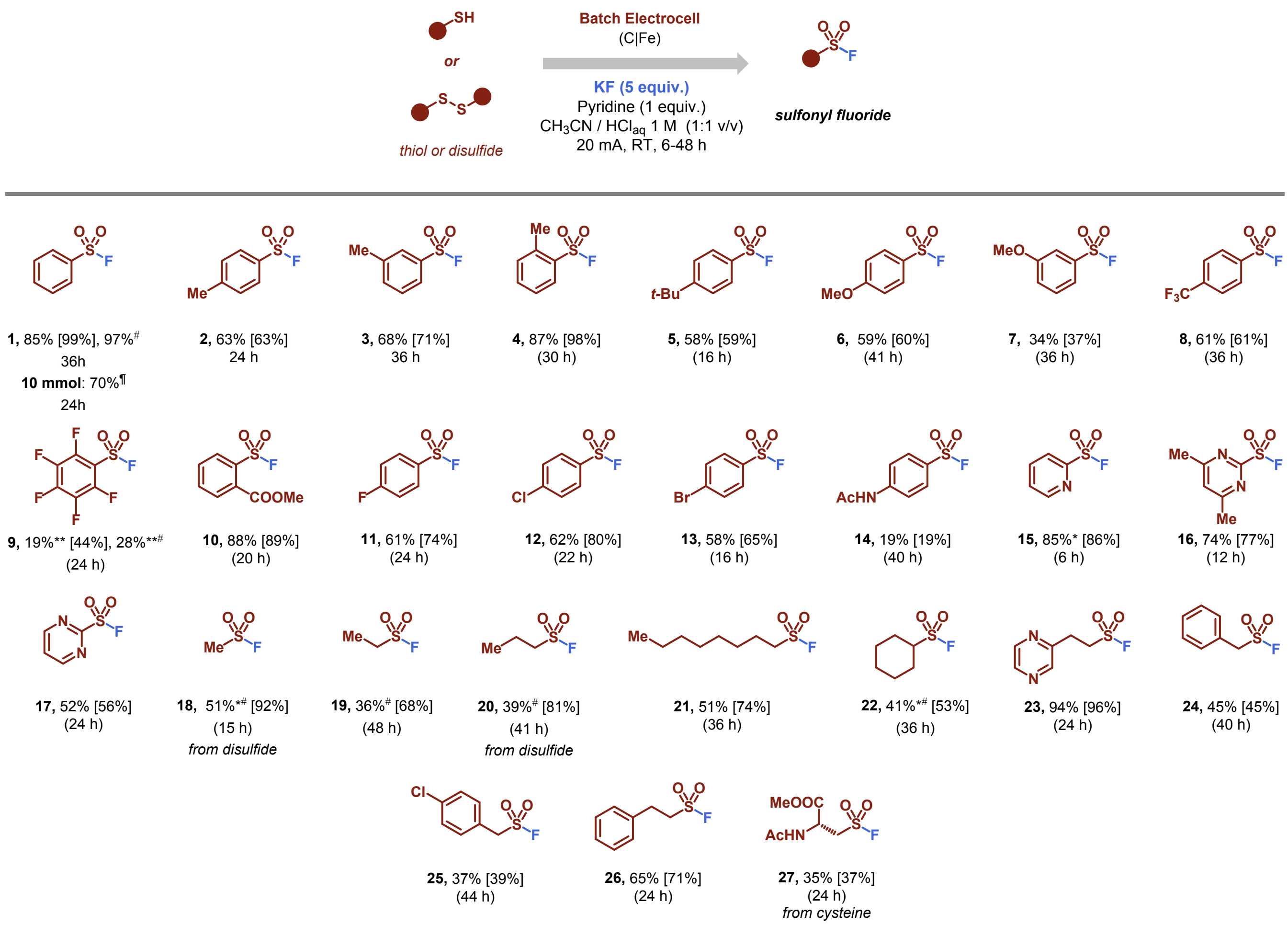



**Figure 2. Synthesis of sulfonyl fluorides.** Substrate scope for the electrochemical sulfonyl fluoride synthesis. Reported yields are isolated and reproduced at least two times. Yields between [brackets] are those referring to $^{19}F$ NMR yields calculated with $PhCF_3$ as internal standard Reaction Conditions (Entry 1): thiol (2 mmol) or disulfide (1 mmol), KF (5 equiv.), Pyridine (1 equiv.), $CH_3CN$/ 1 M HCl (20 mL, 1:1 v/v), C anode/Fe cathode, 20 mA (4.1 mA/cm$^2$). $^*$ 3.2 V applied potential. $^{**}$ 4.0 V applied potential. $^{\#}$ Isolated as a phenyl sulfonate derivative through reaction with phenol. $^{¶}$ Scale-up reaction conditions: thiophenol (10 mmol), KF (5 equiv.), Pyridine (1 equiv.), $CH_3CN$/ 1 M HCl (40 mL, 1:1 v/v), C anode/Fe cathode, 3.2 V applied potential.

isolated yields were in some cases lower than observed with $^{19}F$ NMR. This could be partially avoided by converting the obtained volatile sulfonyl fluoride *in situ* to the corresponding sulfonate through reaction with phenol (e.g. **1**). The electrochemical reaction is not particularly sensitive to sterical hindrance as ortho-substituted thiophenols displayed similar yields to unsubstituted variants (**1** versus **4**). Also, halogenated thiophenols (**11-13**) were suitable reaction partners, providing opportunities to further functionalize the formed sulfonyl fluorides using cross-coupling chemistry. Protected amines (**14**), previously unreactive in our electrochemical sulfonamide chemistry, were tolerated under the current reaction conditions. Heterocyclic thiols (**15-17**), which are among the most widely used moieties in pharmaceutical and agrochemical syntheses, were also effective. Notably, compound **15** is also known as PyFluor, an effective deoxyfluorination reagent reported by Doyle and coworkers.[3] We next examined a variety of different primary and secondary aliphatic thiol substrates, including methanethiol (**18**), ethanethiol (**19**), propanethiol (**20**), *n*-octanethiol (**21**), cyclohexylthiol (**22**), pyrazineethanethiol (**23**), benzylthiol (**24**), *p*-chlorobenzylthiol (**25**), 2-phenylethanethiol (**26**) and cysteine (**27**). All proved to be competent reaction partners yielding the corresponding sulfonyl fluorides in synthetically useful yields (19-96%). The use of the most volatile and odorous thiols could be avoided by using the corresponding disulfide instead (**18-20**). Interestingly, we were able to engage cysteine (**27**) in our electrochemical sulfonyl fluoride protocol, providing opportunities for the preparation of new non-proteinogenic amino acid building blocks.

To obtain insights into the underlying mechanism, a number of additional experiments were carried out (Figure 3). Kinetic experiments revealed a rapid conversion of 4-(trifluoromethyl)thiophenol via anodic oxidation to the corresponding disulfide within 45 minutes (Figure 3A).[19] Next, the disulfide intermediate is consumed and the corresponding sulfonyl fluoride is formed. The pseudo-zero-order behavior suggests that mass transfer limitations from the bulk to the electrode surface occur during the batch electrochemical transformation.

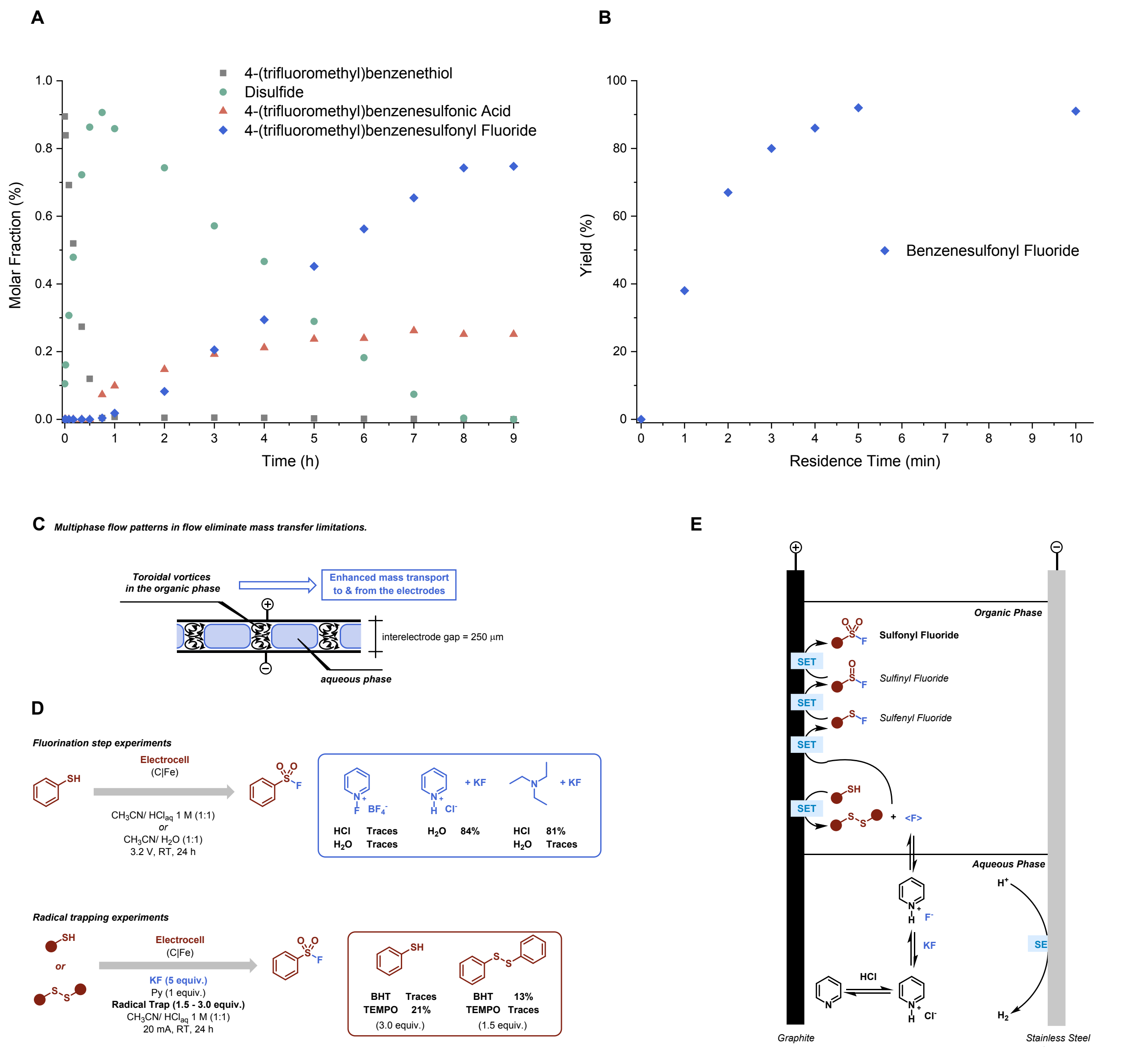



**Figure 3. Mechanistic investigation of the electrochemical sulfonamide synthesis.** (**A**) $^{19}F$ NMR Kinetic batch experiment (see Supporting Information). (**B**) Kinetic experiment carried out in electrochemical microreactor (GC-FID, see Supporting Information). (**C**) Toroidal vortices in segmented flow result in enhanced mass transport to and from the electrodes. (**D**) Fluorination step experiments and radical trapping experiments. GC Yield (biphenyl as internal standard). (**E**) Proposed mechanism.

Indeed, when the reaction is carried out in an electrochemical microflow reactor with a small interelectrode gap (250μm),[20] full conversion is observed in only 5 minutes reaction time (Figure 3B). The reduced reaction times observed in flow can be attributed to (i) the increased electrode surface-to-volume ratio; (ii) a high interfacial area between the organic and the aqueous phase; (iii) an intensified mass transport to and from the electrodes due to multiphase fluid patterns (Figure 3C).[21]

Oxidation of the disulfide results in the formation of a radical cation[22] which can react further with nucleophilic fluoride to yield the corresponding sulfenyl fluoride (Figure 3E). At this point, we still wondered whether a nucleophilic or electrophilic fluorination, with an in-situ generated 1-fluoro-pyridinium reagent,[23] was operative under these reaction conditions. Hence, we carried out the reaction in the presence of 1-fluoro-pyridinium tetrafluoroborate and observed only traces of product formation (Figure 3D). In contrast, using either HCl-pyridine or HCl-$Et_3N$ in combination with KF allowed to obtain isolate the corresponding sulfonyl fluoride in good yields, indicating the presence of a nucleophilic fluorination. Adding TEMPO or BHT as radical scavengers reduces the efficacy of the electrochemical process, substantiating the presence of radical intermediates. Next, two consecutive oxidations steps resulted in the formation of the targeted sulfonyl fluoride. While we cannot formally rule out a nucleophilic attack of fluoride to S-phenyl benzenethiosulfonate, we found for most substrates no formation of the latter compound. In contrast, during our kinetic experiments, traces of other fluorinated intermediates were observed which are tentatively attributed to sulfenyl fluoride and sulfinyl fluoride intermediates (See Supporting Information). These intermediates could unfortunately not be isolated as they are generally perceived as unstable.[24] The main byproduct formed in the electrochemical sulfonyl fluoride synthesis is sulfonic acid, which originates from anodic oxidation of disulfides or through hydrolysis of sulfonyl fluoride.

The electrochemical approach described herein demonstrates the ability to directly convert thiols into sulfonyl fluorides using KF as an ideal fluoride source in terms of cost, safety and availability. In this context, we believe that this green and mild protocol will be of added value to prepare sulfonyl fluorides in both academic and industrial settings.

## ASSOCIATED CONTENT

### Supporting Information

Data and materials availability: additional optimization, mechanistic data, experimental procedures and analytical data ($^1$H, $^{19}$F and $^{13}$C NMR, HRMS) for all new compounds.

The Supporting Information is available free of charge on the ACS Publications website.

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### Author Contributions

§ These authors contributed equally to this work.

### Notes

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

We acknowledge financial support from the Dutch Science Foundation (NWO) for a VIDI grant for T.N. (SensPhotoFlow, No. 14150). A.A.B. and K.T.O. thank the São Paulo Research Foundation for a FAPESP Fellowship Grant (2018/08772-6).

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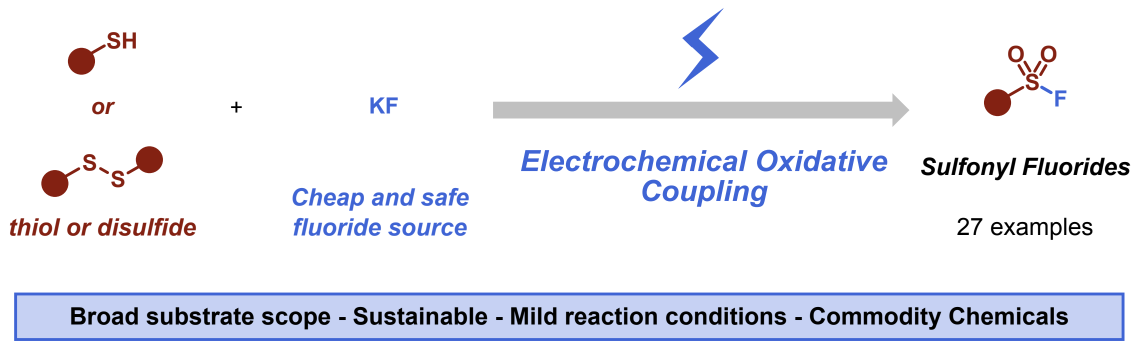
**TOC graphic**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Sulfonyl Fluorides
27 examples
Broad substrate scope - Sustainable - Mild reaction conditions - Commodity Chemicals