

# Perfluorooxosulfate Salts as SOF<sub>4</sub>-Gas-Free Precursors to Multidimensional SuFEx Electrophiles

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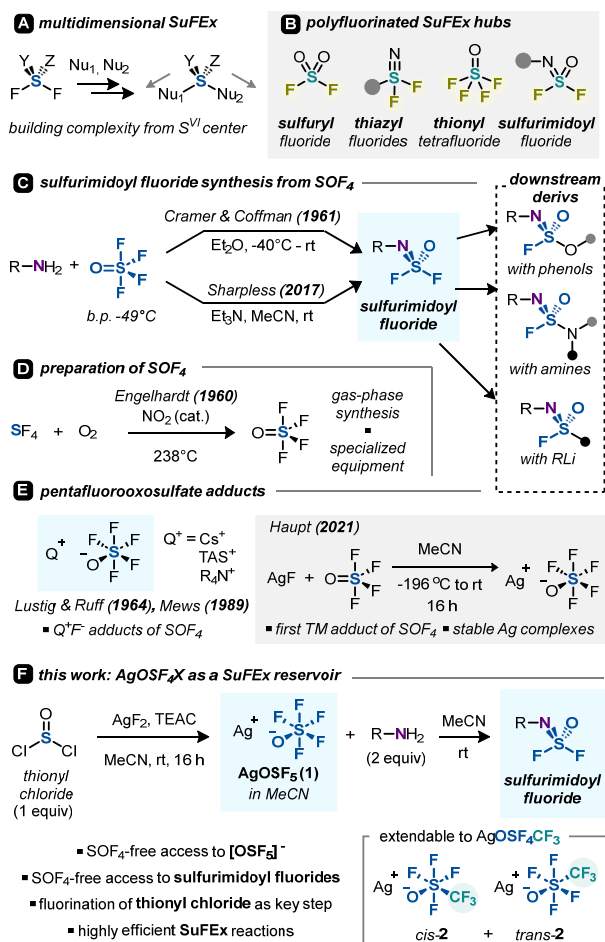
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**Abstract:** Sulfur(VI) Fluoride Exchange (SuFEx) chemistry stands as a well-established method for swiftly constructing complex molecules in a modular fashion. An especially promising segment of this toolbox is reserved for multidimensional SuFEx hubs: three or more substituents pluggable into a singular S<sup>VI</sup> centre to make ‘beyond-linear’ clicked constructions. Sulfurimidoyl difluorides (RNSOF<sub>2</sub>) stand out as the prime example of this, however their preparation from the scarcely available thionyl tetrafluoride (SOF<sub>4</sub>) limits this chemistry to only a few laboratories with access to this gas. In this work, we identify silver pentafluorooxosulfate (AgOSF<sub>5</sub>) as a viable SuFEx hub with reactivity equal to SOF<sub>4</sub>. The AgF<sub>2</sub>-mediated oxidation of SOCl<sub>2</sub> gives rise to the hexacoordinate AgOSF<sub>5</sub> adduct, which in contact with primary amines produces the sulfurimidoyl fluorides in high yields. In addition, we have found this workflow to be fully extendable to the trifluoromethyl homologue, AgOSF<sub>4</sub>CF<sub>3</sub>, and we propose the use of AgOSF<sub>4</sub>X salts as a general route to azasulfur SuFEx electrophiles from commercial starting materials.

## Introduction

S<sup>VI</sup>-F bonds as connective hubs have notably increased interest in high-valent sulfur species.<sup>[1]</sup> In this context, Sulfur(VI)-Fluoride Exchange (SuFEx) chemistry refers to the umbrella of reactions replacing fluoride at the electrophilic sulfur center.<sup>[2]</sup> These sulfur-linked connections serve as a pivotal tool facilitating the synthesis of covalently linked modules through S(VI) hubs (Scheme 1A). In 2014, Sharpless established this branch of click chemistry by exploring the distinctive chemical behavior of sulfonyl fluorides (R-SO<sub>2</sub>F) and fluorosulfates (R-OSO<sub>2</sub>F).<sup>[3]</sup> Later also sulfurimidoyl fluoride (RN=SO<sub>2</sub>F)<sup>[4]</sup> and thiazyl fluoride (NSF<sub>3</sub>)<sup>[5]</sup> compounds were added, a remarkable advancement by merit of their multiple-bonded azasulfur(VI) moiety and multiple interchangeable S-F bonds which easily undergo consecutive nucleophilic exchange (Scheme 1B). A small but growing number of studies has explored the chemistry of [N=S=O]-based SuFExable compounds, unveiling intriguing reactivity patterns across diverse applications from small molecules<sup>[6]</sup> to bioconjugation<sup>[4a, 7]</sup> and polymers.<sup>[8]</sup>

Sulfurimidoyl fluorides,<sup>[9]</sup> as tetravalent azasulfur(VI) species, are prepared by reaction of a primary amine with thionyl tetrafluoride (SOF<sub>4</sub>), a gaseous fluorosulfane boiling at -49°C. This bimolecular reaction was first reported by Cramer and Coffman,<sup>[10]</sup> and the resulting difluorides were found to be stable and resistant towards hydrolysis, a characteristic of many S<sup>VI</sup>



Scheme 1. A) Multidimensional SuFEx; B) Polyfluorinated SuFEx hubs; C) Sulfurimidoyl fluoride synthesis from SOF<sub>4</sub>; D) Preparation of SOF<sub>4</sub>; E) Pentafluorooxosulfate adducts F) This work: AgOSF<sub>4</sub>X as a SuFEx reservoir.

fluorides. These structures then remained virtually absent from the literature after 1970,<sup>[11]</sup> until Sharpless and others greatly expanded the known chemistry of SOF<sub>4</sub> as a SuFEx hub towards sulfurimidoyl fluorides<sup>[4c]</sup> and their further reaction products with phenols,<sup>[8c]</sup> amines,<sup>[4a]</sup> organosilanes<sup>[12]</sup> or organolithiums.<sup>[4b]</sup> (Scheme 1C).

Despite the promising downstream possibilities, the bottleneck lies in the preparation of iminosulfur oxydifluorides. Although their synthesis from SOF<sub>4</sub> gas and primary amines proceeds excellently, the gas is only sparsely available, and even then, comes at high cost.<sup>[13]</sup> This deficit has led some laboratories

to produce it in-house, typically by means of the NO<sub>2</sub>-catalyzed oxygenation of SF<sub>4</sub> gas (Scheme 1D).<sup>[4c, 14]</sup> Recently, another synthesis of SOF<sub>4</sub> was published by direct fluorination of thionyl fluoride.<sup>[15]</sup> For non-specialized laboratories, however, the unfamiliarity of gas-phase syntheses and the lack of equipment to properly condense and store the product, form a hindrance to adopting this otherwise highly promising segment of SuFEx chemistry (Scheme 1A). Clearly, a more expedient preparation of iminosulfur oxydifluorides is needed for these three-dimensional click hubs to reach their full potential.

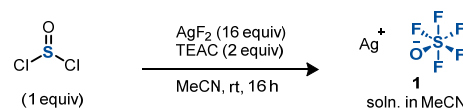
We identified pentafluorooxosulfate (Q<sup>+</sup>OSF<sub>5</sub><sup>-</sup>) salts as potential non-gaseous reservoirs for SOF<sub>4</sub>. Pentafluorooxochalcogenate salts [O(S, Se, Te)F<sub>5</sub>] have long been known in literature, however their stability and accessibility exhibit substantial variation.<sup>[16]</sup> Extensive research has delved into compounds incorporating the [OSeF<sub>5</sub>]<sup>-</sup> anion, and especially [OTeF<sub>5</sub>]<sup>-</sup> and M(OTeF<sub>5</sub>)<sub>n</sub> derivatives.<sup>[17]</sup> However, the exploration of HOSF<sub>5</sub> is limited due to its decomposition at -60 °C.<sup>[18]</sup> Researchers since the 1960s have prepared Q<sup>+</sup>F<sup>-</sup> adducts of SOF<sub>4</sub> such as the partially stable CsOSF<sub>5</sub> (Scheme 1E).<sup>[19]</sup> Later work by Mews and others has demonstrated organic salts of [OSF<sub>5</sub>]<sup>-</sup>, which could even be used for introduction of the functional group in organic molecules.<sup>[20]</sup> In a recent breakthrough in 2021, Haupt, Röschenhaler and coworkers introduced the first transition metal complexes containing [OSF<sub>5</sub>]<sup>-</sup> anions, namely silver pentafluorooxosulfate (Ag<sup>+</sup>OSF<sub>5</sub><sup>-</sup>).<sup>[21]</sup> The synthesis of AgOSF<sub>5</sub> was achieved by quantitatively reacting AgF with OSF<sub>4</sub> in MeCN at -196 °C for 20 h. However important all these advances are, they continue to rely on SOF<sub>4</sub> gas for the preparation of valuable [OSF<sub>5</sub>]<sup>-</sup> structures.

In this work, we aim to overcome this perennial SOF<sub>4</sub> dependence by introducing a novel synthesis method for AgOSF<sub>5</sub> and investigating its potential as an alternative SuFEx hub. Envisaging a broadly useable protocol, our design was to produce AgOSF<sub>5</sub> in an efficient manner from commercially available starting materials. Based on Gatzenmeier and Nozaki's work, we hypothesized that AgOSF<sub>5</sub> could be synthesized via the oxidative fluorination of thionyl chloride (SOCl<sub>2</sub>) using excess of AgF<sub>2</sub> and a tetraalkylammonium halide catalyst.<sup>[22]</sup> Indeed, combining these reagents proved to be a reliable way of preparing MeCN stock solutions of AgOSF<sub>5</sub> in near-quantitative yield (Scheme 1F). Furthermore, a one-pot combination of a primary amine with this hexacoordinate Ag adduct restored the 'parent' SOF<sub>4</sub> reactivity without the need to evolve the gas in a separate step. Both aromatic and aliphatic amines were thus transformed into the otherwise inaccessible sulfurimidoyl fluorides (RNSOF<sub>2</sub>) in high yields. In addition, we could seamlessly translate these findings to AgOSF<sub>4</sub>CF<sub>3</sub>, the not yet reported trifluoromethyl homologue of AgOSF<sub>5</sub>, to make a variety of triflimidoyl fluorides (CF<sub>3</sub>SO(NR)F), demonstrating further the high efficiency and generality of AgOSF<sub>4</sub>X salts as new SuFEx hubs.

## Results and discussion

With the stability of AgOSF<sub>5</sub> established in Haupt's work (Scheme 1E), we envisioned that an alternative generation of AgOSF<sub>5</sub> under mild and safe conditions would offer a pragmatic approach to its use as a novel SuFEx hub. We commenced our study by using SOCl<sub>2</sub>, tetraethylammonium chloride (TEAC), and AgF<sub>2</sub> as an oxidizing agent in anhydrous MeCN to produce AgOSF<sub>5</sub>, as shown in Table 1. An excellent yield was obtained with 2 equiv of TEAC and 16 equiv of AgF<sub>2</sub> after overnight reaction (Table 1, entry 1). Further conditions were screened with the aim to decrease the equivalents of AgF<sub>2</sub> (entries 2-3) and shorten the reaction duration (entries 4-6). Since these changes brought about a decreased yield, we opted to keep the conditions in entry 1 as final. Nevertheless, a respectable yield of 79% and 86% was obtained after only 3 and 6 h, resp. (entries 4 and 5).

**Table 1.** Investigation of the reaction parameters for the synthesis of AgOSF<sub>5</sub><sup>[a]</sup>

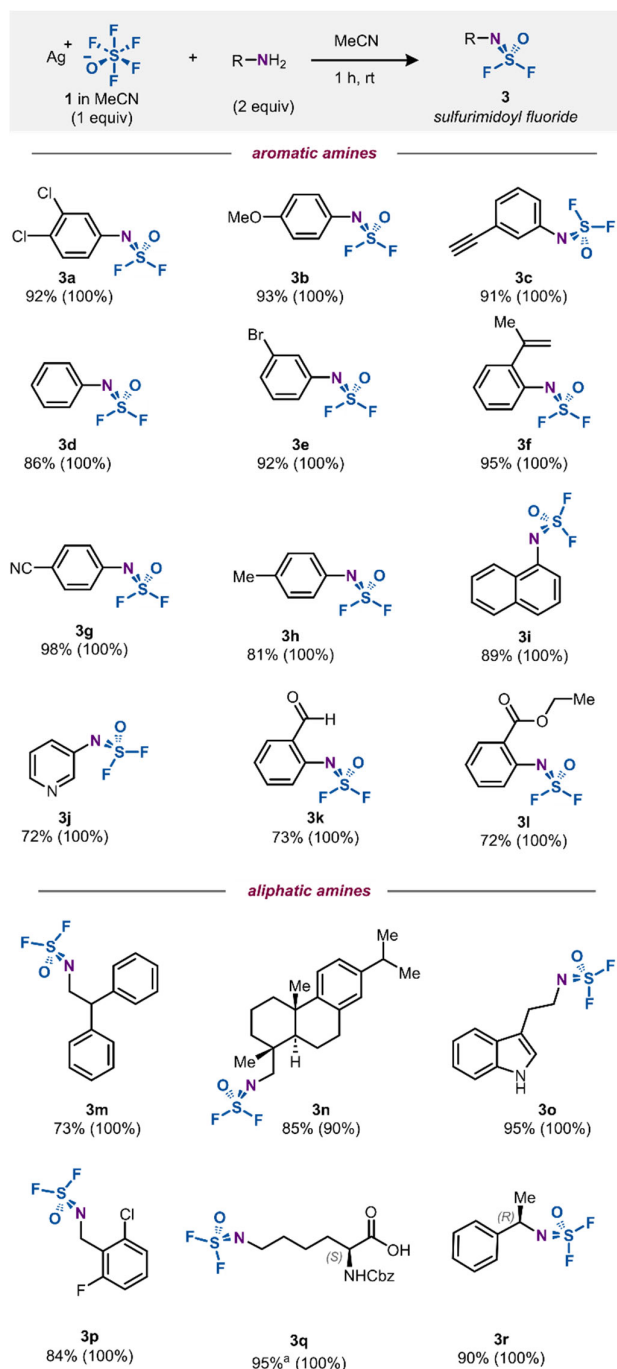


entry	variation from the standard conditions	yield (%) of <b>1</b> <sup>[b]</sup>
1	none	98
2	AgF <sub>2</sub> (12 equiv.)	71
3	AgF <sub>2</sub> (8 equiv.)	38
4	3 hours reaction time	79
5	6 hours reaction time	86
6	AgF <sub>2</sub> (12 equiv.), 3 hours reaction time	68

[a] Reaction conditions. [b] <sup>19</sup>F NMR yield relative to internal standard (PhCF<sub>3</sub>). TEAC = tetraethylammonium chloride.

With this method in hand, we set out to transform AgOSF<sub>5</sub> and apply it as a versatile SuFEx hub. We explored its reactivity with a diverse range of aromatic and aliphatic 1° amines, by simply adding the amine nucleophile to the prepared solution of AgOSF<sub>5</sub> in MeCN. To our delight, these reactions proceeded excellently with typically quantitative conversions within 1 h towards the sulfurimidoyl difluorides (Scheme 2). Anilines bearing either electron-withdrawing or electron-donating groups in *ortho*-, *para*- or *meta*- positions, were successfully transformed to iminosulfur oxydifluorides **3a-3l** as reported in Scheme 2. The mild reaction conditions tolerate the presence of halogens, ethers, cyano, as well as alkenes and alkynes on the aromatic core **3a-i**. Pleasingly, an *N*-heterocyclic ring such as an aminopyridine, was efficiently converted to the desired product **3j**. Moreover, aromatic amines attached with functional groups like aldehyde **3k** and ester **3l** in *ortho* were transformed smoothly to the desired products.

Aliphatic amines equally afforded the *N*-alkyl sulfurimidoyl fluorides in good to high yields. Several linear amines such as **3m**, natural product-derived **3n**, indole-containing **3o** or benzylamine **3p** worked well. Also Lys derivative **3q** and secondary amine **3r** efficiently underwent the SuFEx assembly (Scheme 2).



**Scheme 2.** Synthesis of sulfurimidoyl fluorides using  $\text{AgOSF}_5$  stock solution in MeCN (1 equiv) with amines (2 equiv). Isolated yields shown,  $^{19}\text{F}$  NMR yield based on internal standard ( $\text{PhCF}_3$ ) shown in parentheses. (a) Using Z-Lys-OH as amine starting material but isolated as the methyl ester.

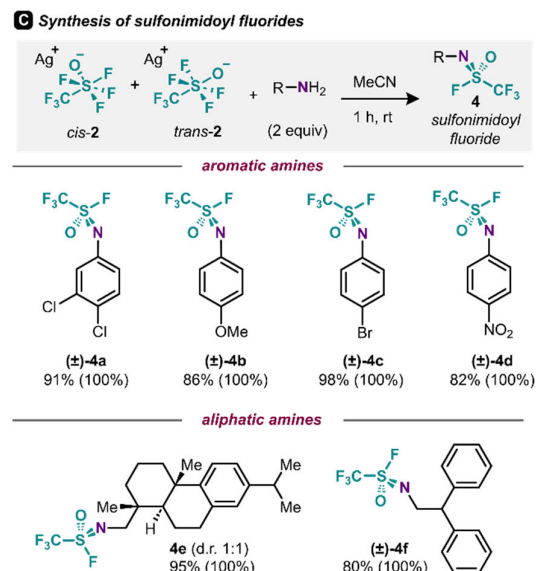
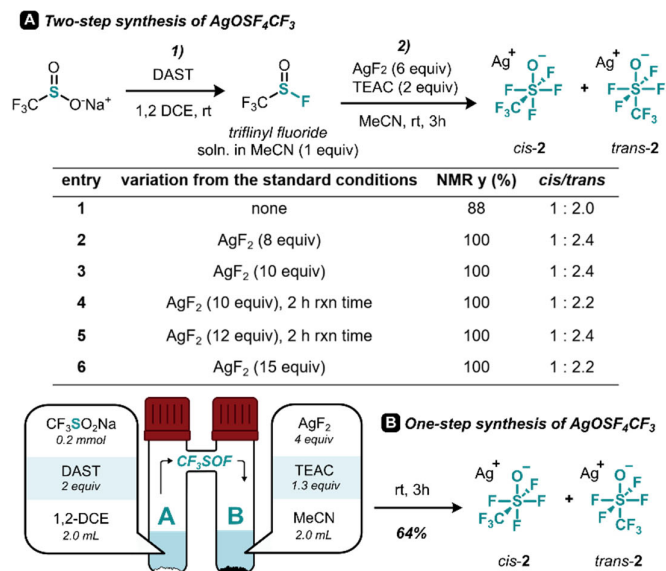
Having explored the synthesis and ‘SuFExability’ of the  $\text{AgOSF}_5$  complex, our focus shifted toward the related  $\text{AgOSF}_4\text{CF}_3$ . More specifically, we set out to investigate whether the same approach to prepare the silver salt from  $\text{SOCl}_2$  as the starting material could be translated to a  $\text{CF}_3\text{SOX}$  derivative. We chose triflinyl fluoride ( $\text{CF}_3\text{SOF}$ ) as the precursor, which we

figured could be evolved in a two-chamber reactor due to its gaseous nature.<sup>[23]</sup> Indeed, a careful addition of DAST as the deoxofluorinating agent to sodium triflinate ( $\text{CF}_3\text{SO}_2\text{Na}$ ) in chamber A proved an efficient way of evolving  $\text{CF}_3\text{SOF}$ . This could then be trapped in MeCN solution for oxidative fluorination in a subsequent step (Scheme 3A), however the most efficient protocol proved to be the same-step preparation of  $\text{AgOSF}_4\text{CF}_3$  with the  $\text{AgF}_2/\text{TEAC}$  combination present chamber B (Scheme 3B). In this way, 64% of the desired complex was obtained with 4 equiv of  $\text{AgF}_2$  in 3.5 h. Interestingly, both the *cis* and *trans* isomers of the complex were isolated together in a 1:2.3 ratio.

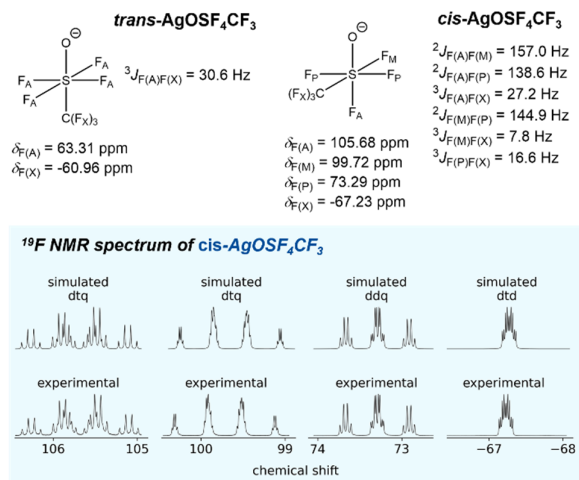
Trifluoromethanesulfonyl (triflimidoyl) fluorides were then investigated as the products of the newly obtained  $\text{AgOSF}_4\text{CF}_3$ . Triflimidoyl fluorides are described in a handful of literature precedents, and are invariably prepared by oxidative halogenation of a S(IV) species with a preexisting S–N bond,<sup>[24]</sup> most notably Oehlrich’s two-step route via the sulfinamide intermediate.<sup>[24d]</sup> A precursor like  $\text{AgOSF}_4\text{CF}_3$ , as a trifluoromethyl homologue of  $\text{AgOSF}_5$ , would offer an attractive alternative by allowing the direct synthesis from a primary amine. To our delight, the simple addition of primary amine to the MeCN solution of the oxosulfate salt delivered the triflimidoyl fluorides in high efficiency (Scheme 3C), entirely comparable to the sulfurimidoyl fluorides above. A set of amines was tested, including anilines (**4a-d**) and aliphatic amines (**4e-f**), demonstrating excellent yields from 82% to 92%.

$\text{AgOSF}_4\text{CF}_3$  is produced as a mixture of *cis-trans* stereo-isomers in a 69:31 ratio as evidenced by  $^{19}\text{F}$  NMR analysis. With the current high NMR spectrometer field strengths in use (e.g. 9.4 Tesla, 377 MHz for  $^{19}\text{F}$ ), both isomers give rise to spectra that can be analyzed in the weak coupling limit. The more symmetrical *trans*-derivative shows up as an  $\text{A}_4\text{X}_3$  spin-system with a  $^3J_{\text{FF}}$  coupling constant of 30.6 Hz, while the *cis*-isomer produces an  $\text{AMP}_2\text{X}_3$  spin system (Figure 1). Peak assignment of the  $^{19}\text{F}$  nuclei in the *cis*-isomer was unambiguous for the  $\text{P}_2\text{X}_3$  part of the spectrum simply using the integration values of the signals. For the AM part of the spectrum a tentative assignment was based on DFT calculated chemical shifts (Figure 1 and SI). Using the chemical shift assignments and the extracted coupling constants from the experimental spectrum, we simulated the  $^{19}\text{F}$  spectra of *cis*- $[\text{OSF}_4\text{CF}_3]^-$  to give an excellent match (Figure 1).

To evaluate the scalability of the method, selected reactions were carried out on a larger scale. 3,4-dichloroaniline as a starting substrate reacted with both  $\text{AgOSF}_4\text{X}$  ( $\text{X}=\text{F}, \text{CF}_3$ ) salts (Scheme 4A). Pleasingly, the desired products **3a** and **4a** were obtained in almost unabated yields compared to the smaller scale reactions. In addition, a few post-transformations were investigated for the triflimidoyl fluorides obtained in the previous section. Since these could be prepared efficiently in one step from the amine, triflimidoyl fluorides can in turn serve as starting materials for other valuable  $\text{CF}_3$ -containing sulfur(VI) species. We focused on two transformations reported for sulfurimidoyl fluorides in order to translate these to the  $\text{CF}_3$  counterparts. First, the reaction with silylated O-nucleophiles was carried out using TBS-protected phenol and catalytic DBU<sup>[4c]</sup> to furnish triflimidate ester **5** in good yield (Scheme 4B).<sup>[24e, 24f]</sup> Next, phenyllithium as C-nucleophile was used to efficiently prepare trifluoromethyl sulfoximine **6**,<sup>[4b]</sup> in



**Scheme 3.** A) Synthesis of  $\text{AgOSF}_4\text{CF}_3$  solution in two-step procedure, with intermediate isolation of  $\text{CF}_3\text{SOF}$ ; B) Synthesis of  $\text{AgOSF}_4\text{CF}_3$  solution in one-step procedure; C) Synthesis of sulfonylimidoyl fluorides using  $\text{AgOSF}_4\text{CF}_3$  stock solution in MeCN (1 equiv) with amines (2 equiv). Isolated yields shown,  $^{19}\text{F}$  NMR yield based on internal standard ( $\text{PhCF}_3$ ) shown in parentheses. TEAC = tetraethylammonium chloride.



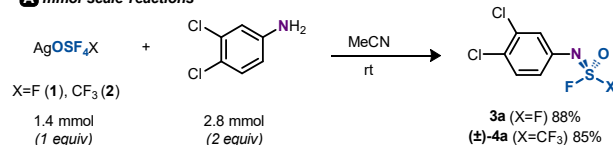
**Figure 1.** Summary of chemical shifts and coupling constants for the *trans*- and *cis*-isomers respectively giving rise to  $\text{A}_4\text{X}_3$  and  $\text{AMP}_2\text{X}_3$  spectra. The labels for the fluorine atoms refer to the Pople spin-system notation and simulated (top) stacked over experimental (bottom)  $\text{AMP}_2\text{X}_3$  spectrum of *cis*- $\text{AgOSF}_4\text{CF}_3$ .

a disconnection that was hitherto undescribed for perfluoroalkyl sulfoximines<sup>[25]</sup> (Scheme 4C).

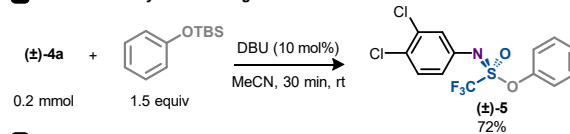
In summary, we have successfully developed a novel method to synthesize  $\text{AgOSF}_5$ , the first preparation of pentafluoroosulfate salts without the need for  $\text{SOF}_4$  gas. This method uses thionyl chloride and  $\text{AgF}_2$  as starting materials and operates under mild reaction conditions. The subsequent reaction with primary amines proves the viability of the  $[\text{OSF}_3]^-$  salt to function as a SuFEx hub, entirely equivalent to its gaseous congener,  $\text{SOF}_4$ . Both aromatic and aliphatic amines proceeded to form sulfonylimidoyl fluorides in excellent yields. Moreover, we found that the findings for  $\text{AgOSF}_5$  uphold very well for carbon-bound analogue  $\text{AgOSF}_4\text{CF}_3$ , which was obtained in a mixture of *cis* and *trans* isomers, with interesting

$^{19}\text{F}$  NMR spectra which we attempted to elucidate. This mixture of isomeric complexes similarly gave rise to sulfonylimidoyl fluorides in high yields. By cutting  $\text{SOF}_4$  gas from the equation, these novel SuFEx hubs enable laboratories worldwide to engage in this branch of multidimensional SuFEx chemistry, which we expect will advance the field with new applications of sulfonylimidoyl fluorides.

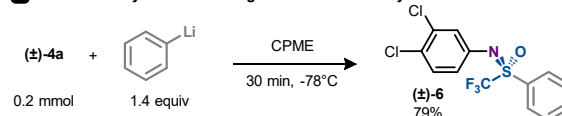
**A mmol scale reactions**



**B sulfonylimidate synthesis using 'silicon click' conditions**



**C sulfoximine synthesis with organolithium chemistry**



**Scheme 4.** A) Scale-up synthesis of iminosulfur oxydifluoride and sulfonylimidoyl fluoride derivative; B) Sulfonylimidate synthesis; C) Sulfoximine synthesis. Isolated yields shown.

**Supporting Information**

The data that support the findings of this study are available in the Supporting Information of this article. The authors have cited

additional references within the Supporting Information.  
[26],[27],[28],[29],[30],[31],[32],[33]

## Acknowledgements

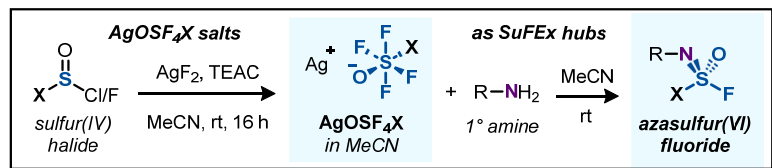
AZ, EI, WMDB and JD acknowledge the Research Foundation - Flanders (FWO) (G0D6221N) and KU Leuven (DOA/2020/013) for funding. KU was supported by Sapienza University of Rome through PhD funding. JD acknowledges FWO for funding received through fellowships 12ZL820N and 12B5024N. EI acknowledges Gipuzkoa Foru Aldundia (Gipuzkoa Fellows Program) for funding received through grant number 2022-000013-01. The High Performance Computing resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by FWO and the Flemish Government. Mass spectrometry was made possible by the support of the Hercules Foundation of the Flemish Government (grant 20100225-7). This research was supported by the FWO through infrastructure grants I002720N and I001920N.

**Keywords:** Perfluorooxosulfate Salts • thionyl tetrafluoride • iminosulfur oxydifluoride • sulfonimidoyl fluoride • synthetic methodology •

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- [9] A note on nomenclature: The RNS(O)F<sub>2</sub> functional group has elsewhere been named iminosulfur oxydifluoride, which is entirely correct as well. Here, we opt to follow a common logic for azasulfur nomenclature, which is to start from the sulfonyl-containing counterpart, and using basename+[imid]+suffix for the nitrogen analogue. In this case, the parent compound is sulfonyl fluoride (SO<sub>2</sub>F<sub>2</sub>) and thus becomes sulfurimidoyl fluoride for the nitrogenated species.
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## Entry for the Table of Contents



Sulfurimidoyl difluorides (RNSOF<sub>2</sub>) are excellent multidimensional SuFEx hubs, however their preparation from the scarcely available thionyl tetrafluoride (SOF<sub>4</sub>) gas limits this chemistry. Here, we propose silver pentafluorooxosulfate (AgOSF<sub>5</sub>) as a viable alternative to SOF<sub>4</sub>. Prepared by the AgF<sub>2</sub>-mediated oxidation of SOCl<sub>2</sub>, we found that the adduct produces sulfurimidoyl fluorides in high yields from primary amines, also extendable to AgOSF<sub>4</sub>CF<sub>3</sub>.

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