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Perspective

The Emerging Applications of Sulfur(VI) Fluorides in Catalysis

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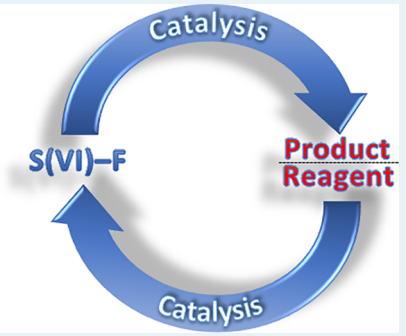
ABSTRACT: The past decade has witnessed remarkable growth of catalytic transformations in organic sulfur(VI) fluoride chemistry. This Perspective concentrates exclusively on foundational examples that utilize catalytic strategies to synthesize and react S(VI) fluorides. Key mechanistic studies that aim to provide insight toward future catalytic systems are emphasized.



KEYWORDS: *catalysis, S(VI) fluorides, sulfur-fluoride exchange (SuFEx), sulfonyl fluorides, fluorosulfates, sulfamoyl fluorides, sulfonimidoyl fluorides*

1. INTRODUCTION

Organic compounds with the SO_2F moiety have a unique and diverse history. The first organic S(VI) fluorides that received significant attention in the literature were sulfonyl fluorides (RSO_2F)—investigated in the 1920s and 30s for their application as dyes and pesticides.[1−5] From these early studies, several key characteristics emerged: the installation of the SO_2F moiety in an organic compound introduces a functional group that is hydrolytically stable, resistant to reduction/oxidation chemistry, and reacts selectively at the sulfur atom.[6,7] These characteristics highlighted a unique stability and reactivity regarding sulfonyl fluorides that was not present among other halogenated analogues. The introduction of the fluorine atom confers significant pi-donation from fluorine to sulfur, as well as strong ionicity between the two atoms. Combined, these factors attenuate the electrophilicity of the sulfur atom and increase the stability of the sulfur(VI) fluoride compared with other sulfur(VI) halides.

Despite these unique properties, interest in sulfur(VI) fluorides waned in the literature for several decades until their brief reappearance in the 1960s as protease inhibitors and chemical probes.[8−10] After another publication lull, the application of sulfur(VI) fluorides in synthesis was reinvigorated by Barry Sharpless in a foundational 2014 *Angewandte Chemie* paper.[9] Since then, over 240 manuscripts have been published on sulfur(VI) fluorides and sulfur-fluoride exchange (SuFEx) chemistry (Figure 1).[11] Notably, a significant portion of this field's dramatic growth can be attributed to catalytic syntheses and transformations of sulfur(VI) fluorides. While numerous reviews provide rigorous and thoughtful accounts of the synthetic developments and applications involving S(VI) fluoride chemistry,[6,10,12−17] to date there has not been an account that focuses solely on organic S(VI) fluorides in catalysis. This Perspective seeks to concentrate exclusively on foundational examples that employ catalysis to react and synthesize S(VI) fluorides. It is organized according to applications of S(VI) fluorides starting with the most robust mechanistic evidence and ending with examples where there has been synthetic innovations but more effort toward their mechanistic understanding is needed. Furthermore, this Perspective will highlight key mechanistic hypotheses and studies that aim to provide insight toward future catalytic systems. We will end the Perspective articulating remaining challenges and areas of growth in this exciting, emerging field.

2. CATALYTIC ACTIVATION OF S(VI) FLUORIDES

2.1. Activation of Sulfonyl Fluorides via Base Catalysis. Early catalytic strategies focused on activation of the sulfur center in S(VI) fluorides for nucleophilic addition. Rooted in acylation chemistry, whereby benzoyl fluorides can be converted to benzoates in the presence of a catalytic

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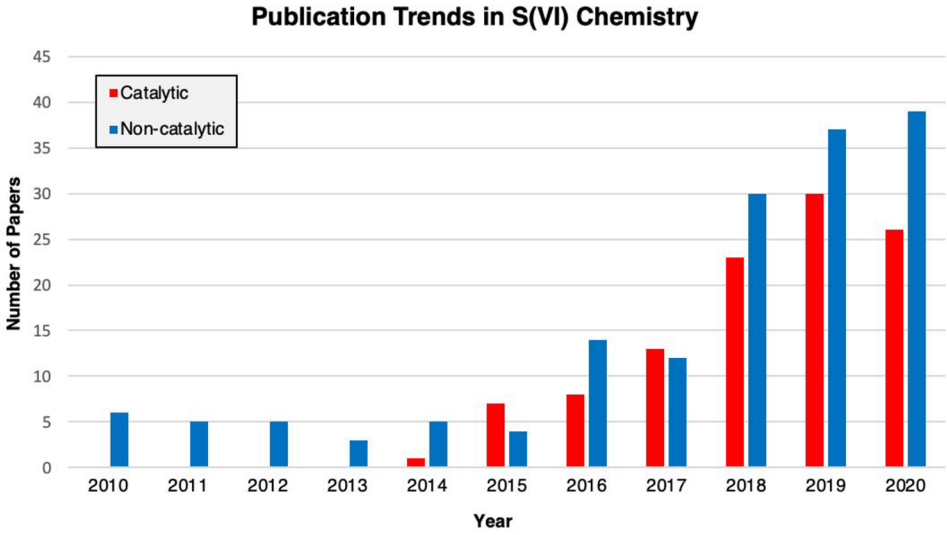
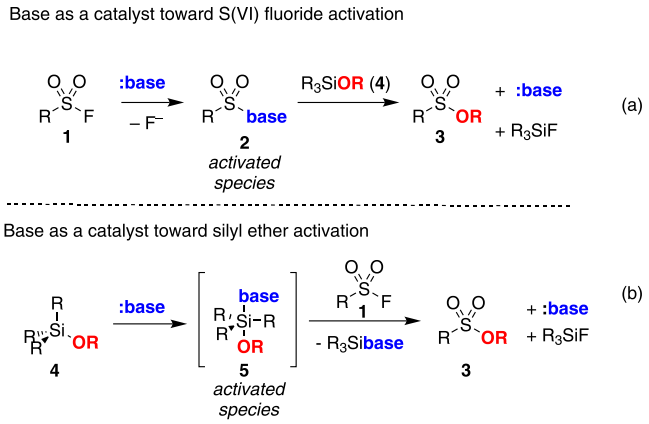


Figure 1. S(VI) fluoride publication trends involving catalytic (red) and noncatalytic (blue) methods over the past decade.

amount of 4-(dimethylamino)pyridine (DMAP) and silyl ethers,[18] nitrogen and phosphorus bases emerged as a sulfonyl fluoride activation strategy. The central mechanistic hypothesis was that a S(VI) fluoride (**1**) could be activated via a reversible addition of a base catalyst yielding activated species **2** (Scheme 1a). The S(VI) species (**2**) is then more reactive to a nucleophile (e.g., a silyl ether) than the parent sulfur(VI) fluoride (**1**) and thus provides a lower activation energy path to the desired product. In the last step, the base is replaced by the oxygen nucleophile, forming a sulfonic ester (**3**). Notably, the fluoride is trapped by silicon, where the strong Si−F bond serves as a thermodynamic sink that drives the reaction forward.[19]

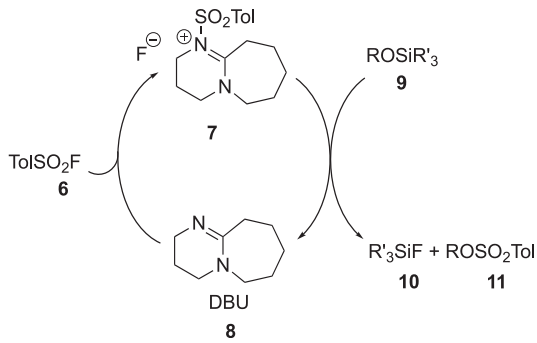
Scheme 1. Modes of Base Catalysis in Reactions with Sulfur(VI) Fluorides and Silyl Ethers: (a) Base Activation of S(VI) Fluorides; (b) Base Activation of Silyl Ethers



Another mechanistic possibility is the base catalyst activates the silyl ether (R_3SiOR, **4**) toward sulfur-fluoride exchange (SuFEx) (Scheme 1b). This mechanism involves the initial coordination of a base to the silicon atom to form a silicate (**5**), followed by release of the OR group that undergoes subsequent SuFEx chemistry with S(VI) fluoride **1**. In both mechanisms, a silicon atom ultimately serves as a fluoride trap and regenerates the base catalyst. This following section highlights key mechanistic considerations regarding reactions of sulfonyl fluorides (RSO_2F), fluorosulfates ($ROSO_2F$), and sulfonimidoyl fluorides ($ROSNR_2F$) in base-catalyzed SuFEx reactions. In these transformations, the base will serve as a nucleophile either for activating the S(VI) fluoride (Scheme 1a) or for activating silyl ethers (Scheme 1b).

The first example of base-catalyzed activation of a sulfonyl fluoride was reported in 1995 by Vorbrüggen and co-workers, who were studying the synthesis of sulfinate esters.[20] They demonstrated that perfluorobutane sulfonyl fluoride can be activated in the presence of organobase 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, **8**) and a silyl-protected alcohol (**9**, Scheme 2). A report in 2008 by Gembus and co-workers demonstrated that substoichiometric amounts of DBU (20 mol %) could be used to catalyze the conversion of *p*-toluenesulfonyl fluoride (**6**) and silyl alcohols (**9**) to silyl fluorides (**10**) and tosylates (**11**).[21] No other combination of base and sulfonyl fluoride substrate in the study afforded any appreciable yield over 24 h. Given the precedence for the use of DBU as a nucleophilic catalyst, Gembus and co-workers postulated that the SuFEx reaction proceeded through an activated arylsulfonyl ammonium fluoride salt (**7**).

Scheme 2. Working Hypothesis by Gembus and Co-workers for the Activation of *p*-Toluenesulfonyl Fluoride That Implicates the Intermediacy of an Activated Arylsulfonyl Ammonium Fluoride Salt[a]



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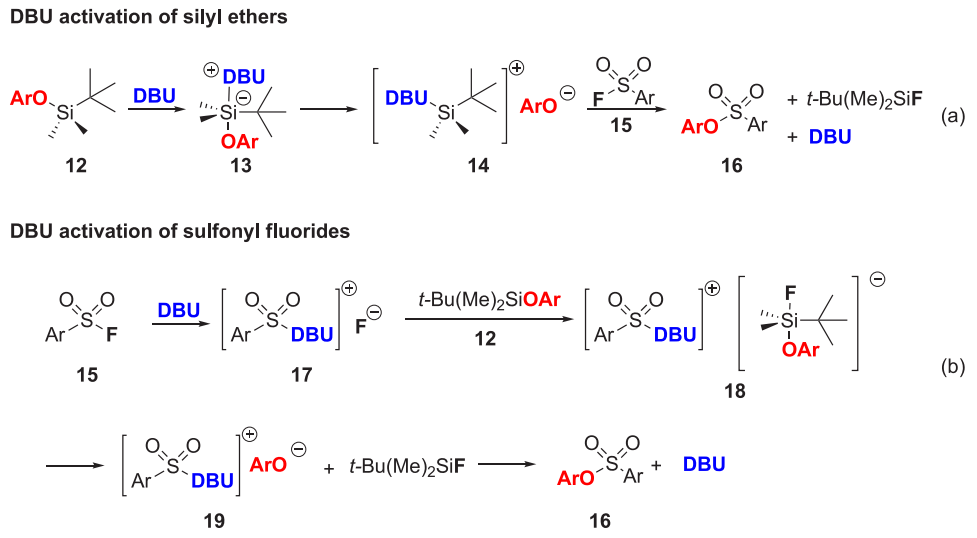
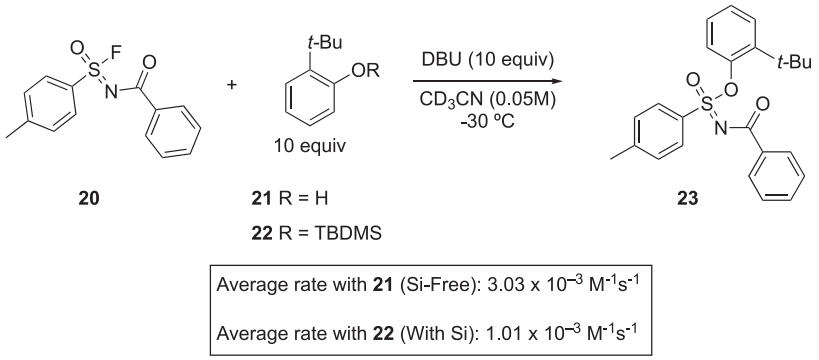
Scheme 3. Two Mechanistic Proposals for the Mechanism of Nucleophilic Catalysis by DBU in SuFEx Reactions: (a) DBU Activation of Silyl Ethers; (b) DBU Activation of Sulfonyl Fluorides



Scheme 4. Bifluoride-Catalyzed Reaction of Phenol (21) or Silyl Protected Phenol (22) and *N*-Benzoyl-4-methylbenzenesulfonimidoyl Fluoride to Form 23



Since the foundational work of Vorbrüggen and Gembus, nucleophilic catalysis with DBU has been used extensively for the synthesis of alkyl and aryl sulfonic esters from the corresponding sulfonyl fluorides and silyl ethers. However, how DBU facilitates Si−F bond formation toward sulfur-fluoride exchange is unclear. Two mechanistic hypotheses have been proposed to explain DBU's catalytic role in these reactions: (1) DBU facilitates silyl ether deprotection (Scheme 3a), and (2) DBU activates the sulfur(VI) fluoride substrate (Scheme 3b).

Substantial evidence for the role of DBU as a means to activate silyl ethers was reported by Zuilhof and co-workers in a study investigating the mechanism of a silicon-free SuFEx reaction with sulfonimidoyl fluoride (**20**) and phenols (Figure 4).[22] In the mechanistic study, they compared the kinetics of the Si-free SuFEx reaction of sulfonimidoyl fluoride **20** with (*t*-butyl)phenol (**21**) to the same reaction replacing the phenol with silyl ether analogue **22**. The aim was to investigate whether the role of DBU in silicon-based SuFEx reactions was to ultimately release phenolate as a nucleophile. While both reactions were completed in 2 min at room temperature, at −30 °C the reaction with silyl ether **22** was approximately 3 times slower with an average rate of 1.01×10^{-3} M^{-1} s^{-1} versus 3.03×10^{-3} M^{-1} s^{-1} using the free phenol. Notably, an induction period was observed for the reaction with silyl ether **22**. To investigate whether this observation was due to the need to generate phenolate from a rate-determining desilylation, they next used an equimolar amount of silyl ether **22** and $(CH_3)_4NF$ at −30 °C. Complete desilylation was detected by ^1H NMR spectroscopy in minutes, suggesting that an accumulation of fluoride in the reaction was needed to initiate the reaction. These results would suggest a dual role for DBU in SuFEx reactions with a silyl ether: (1) DBU activates the silyl ether toward sulfur-fluoride exchange, whereby the resulting fluoride anion can catalyze further desilylation to produce phenolate; and (2) DBU undergoes SuFEx with sulfonimidoyl fluoride **20**, releasing fluoride that goes on to further desilylation and propagation of the reaction. However, DFT calculations suggest that the nucleophilic addition of DBU to the sulfur(VI) fluoride, *N*-benzoyl-4-methylbenzene-sulfonimidoyl fluoride, is not a likely pathway. When the two molecules were calculated using an intermolecular separation of 1.7 Å, the corresponding N−S equilibrium bond length, the electronic repulsion was greater than 19 kcal/mol relative to the reactants. This suggests that DBU primarily catalyzes deprotection and is only minimally involved in the addition to the sulfur center (Scheme 4).

Alternative roles for bases in activation of sulfonyl fluorides have also been reported in literature. In 2020, a computational study by Luy and co-workers of the synthesis of sulfonamides

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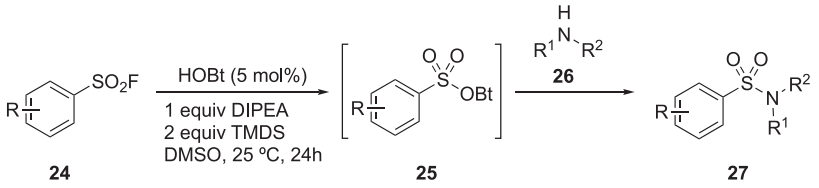
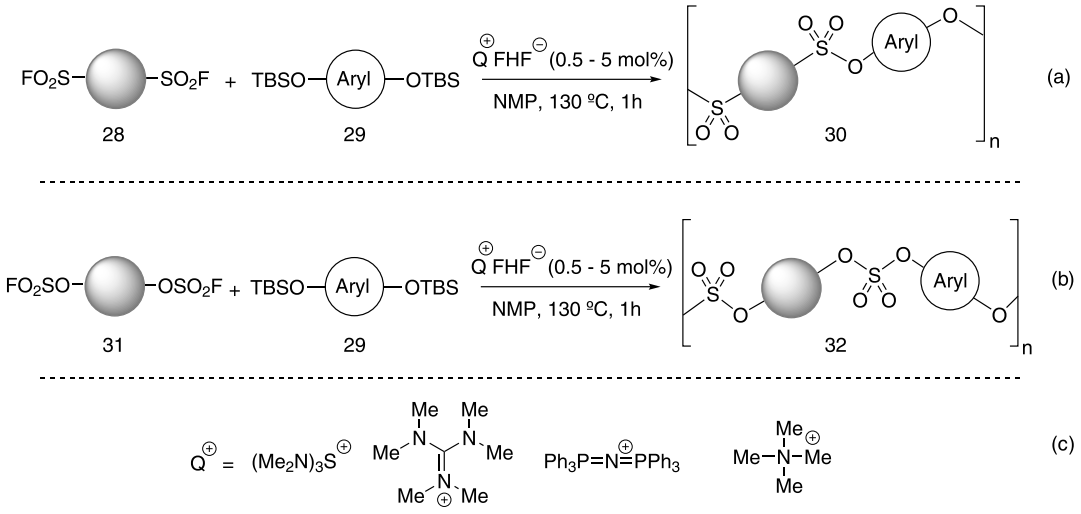
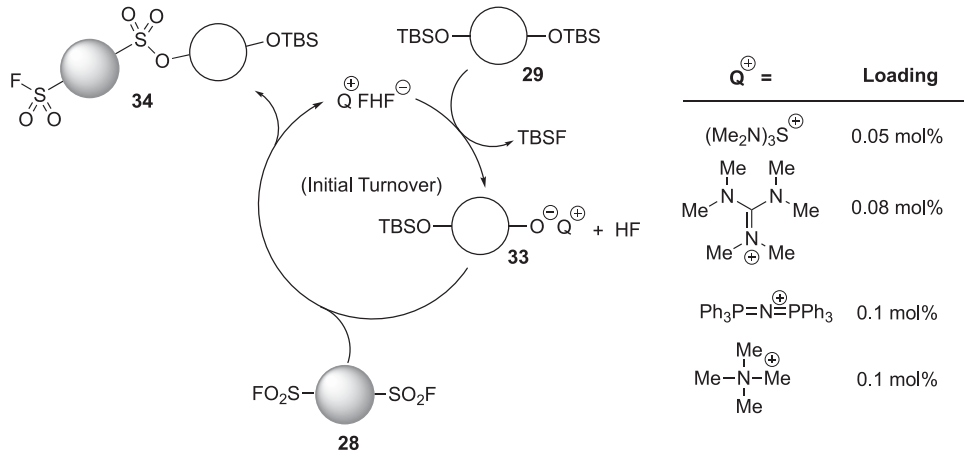
Scheme 5. Nucleophilic Activation of Sulfonyl Fluorides with HOBt



Scheme 6. (a) Bifluoride-Catalyzed Polymerization of Sulfonyl Fluorides and Aryl Silyl Ethers, (b) Bifluoride-Catalyzed Polymerization of Bisfluorosulfates and Bis-Siloxy Aryl Ethers, and (c) Representative Viable Cations (Q^+)



Scheme 7. Initial Turnover of Bifluoride-Salt Catalyzed Polymerization of Sulfonyl Fluorides and Bis-Siloxy Aryl Ethers[a]



[a]A selection of viable cations (Q+) is presented on the right.

starting from amines and methyl sulfonyl fluoride demonstrated that the formation of the N−S bond in the transition state is largely influenced by concerted deprotonation of the amine nucleophile with a complementary base. This hydrogen bonding-like interaction significantly increased the nucleophilicity of the amine and lowered the barrier for the SuFEx reaction.[23] Collectively, these studies suggest that the role of DBU and other nucleophilic bases may be highly dependent on the system (e.g., silyl protected alcohol vs free alcohols).

While the role of DBU as a nucleophilic catalyst for the activation of sulfur(VI) fluorides is still uncertain, Li and coworkers have recently demonstrated an alternative catalytic system to activate sulfonyl fluorides (**24**) and fluorosulfates toward nucleophilic substitution by amines (**26**) (Scheme 5).[24] Utilizing hydroxybenzotriazole (HOBt) as a nucleophilic catalyst, they synthesized a wide variety of sulfonamides (**27**) and sulfamates in high yield at room temperature with sterically hindered amines. Notably, the reaction required a silicon coadditive, 1,1,3,3-tetramethyldisiloxane (TMDS), to enable catalytic loadings of HOBt. While the exact role of the silicon additive is uncertain, they propose TMDS traps the postsubstitution fluoride (**25**). Central to their proposed mechanism is sulfonyl fluoride activation by HOBt forming activated intermediate **25**, which they observed using ^{1}H NMR spectroscopy. Similar to the proposal by Gembus and coworkers with DBU, this serves as another example of a nucleophilic addition of a base-catalyst.

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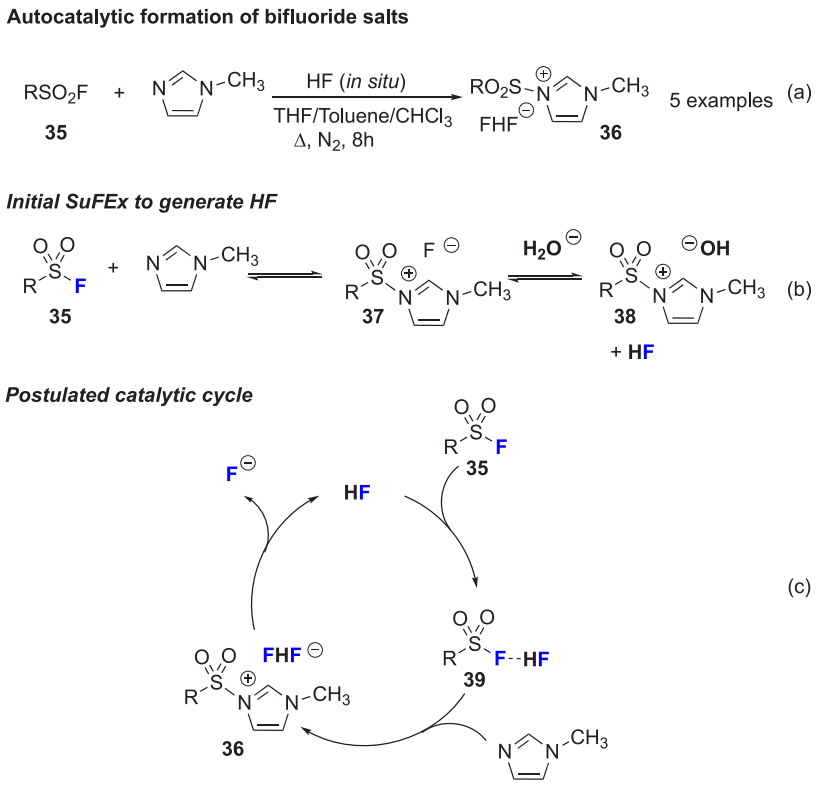
Scheme 8. Autocatalytic SuFEx Reaction between Alkyl and Perfluoroalkyl Sulfonyl Fluorides and 1-Methylimidazole and Working Mechanism: (a) General Transformation; (b) Initial Formation of HF; (c) Catalytic Cycle



As an alternative to amines serving as bases in sulfur-fluoride exchange (SuFEx) reactions, fluoride anions can also be employed as catalysts. In their 2014 account, Sharpless and co-workers suggest that SuFEx with silane coupling partners can be achieved by solely employing fluoride donors as a means to activate sulfur(VI) fluorides toward substitution.[25,26] The highly stable Si−F bond formed between silyl ethers and fluoride was hypothesized to provide a driving force for the overall reaction. In 2017, the Sharpless group utilized these conditions in the syntheses of polysulfonates (**30**) and polysulfates (**32**) using bis-silylethers (**29**) with bisaryl sulfonyl fluorides (**28**) and bisfluorosulfates monomers (**31**) (Scheme 6).[26−28] Initially amidine and phosphazene superbases were tested as catalysts to initiate the deprotection cascade. However, these catalysts also promoted unwanted side reactions that limited the reaction scope and hindered purification. On the basis of the hypothesis that bifluoride salts could serve as a more stable fluoride source versus metal fluoride salts (e.g., CsF), potassium bifluoride (KFHF) was selected as a catalyst. Potassium bifluoride catalyzed the SuFEx reaction, but it proceeded at a slow rate and produced low molecular weight polymers. The addition of organic bifluoride led to rapid and effective catalysis of the SuFEx reaction, affording higher molecular weight polymers in near qualitative yields.

The Sharpless SuFEx polymerization was observed to initiate with the formation of a trialkylfluorosilane, indicating that the initial role of the catalyst is to deprotect the bis-siloxy aryl ethers (**29**) by F^- enabling the formation of a phenolate (**33**) for nucleophilic substitution (Scheme 7). The organic cation of the bifluoride salt is believed to facilitate mobility of fluoride to the silyl ether in organic media, effectively accelerating the reaction. It should be noted that the acidic bifluoride ion could also act as a HF source allowing for concomitant activation of the S(VI) fluoride via hydrogen-bonding. While current data suggests that this mechanism may be a minor factor, the possibility of this mechanistic pathway cannot be excluded.[9]

While the role of bifluoride salts in SuFEx reactions involving silyl ethers is to primarily initiate the deprotection cascade, the formation of the bifluoride anion itself can drive the reaction. In systems with acidic protons, fluoride can form HF, which can then act as a hydrogen-bond donor to activate S(VI) fluorides toward nucleophilic substitution. Akin to how the silanes in SuFEx reactions can serve as a fluoride trap via resulting the strong Si−F bond, the formation of the highly stable bifluoride anion $[FHF]^-$ (~40 kcal/mol)[19] can also serve as a trap for fluoride in protic systems. In 2018, Mirjafari and co-workers utilized the formation of the bifluoride ion to autocatalytically accelerate the SuFEx reaction between *N*-methylimidazole and sulfonyl fluorides (**35**, Scheme 8) to form bifluoride ionic liquids (**36**).[29] While mechanistic experiments were not reported, the activation of the S−F bond may occur via a hydrogen-bonding interaction with HF, where autocatalysis is started by the fluoride released from the initial SuFEx reaction deprotonating adventitious water (Scheme 8b). The resulting HF undergoes hydrogen bonding with the fluorine of another molecule of a sulfonyl fluoride (**39**, Scheme 8c), and the sulfur−fluorine exchange with *N*-methylimidazole results in bifluoride ion ($[FHF]^-$) formation (**36**). Bifluoride dissociation to F^- and HF regenerates the catalytic HF. While HF may play two critical roles—serving toward S−F bond labilization or stabilization of the fluoride as the bifluoride anion—they are indistinguishable without further mechanistic investigation.

2.2. Use of Fluorosulfates as Pseudohalides for Oxidative Addition. Since the seminal discovery that vinyl triflates could be used in palladium catalyzed Heck reactions in

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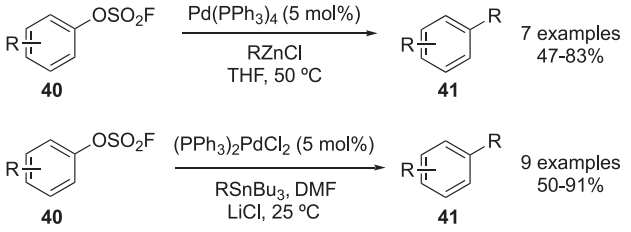
1984,[30,31] sulfonates such as triflates,[32−34] tosylates,[35−38] and mesylates,[39−41] have been used as pseudohalides for a variety of cross-coupling reactions. Their widespread use stems from their ready preparation from phenolic derivatives. Furthermore, the rate of oxidative addition can be tuned through the selection of the sulfate, with triflates reacting more quickly than analogous mesylates or tosylates.[39,42,43] In 1991, Roth and co-workers reported the first example of fluorosulfates (**40**) in Pd-catalyzed Negishi and Stille cross-coupling reactions (Scheme 9).[44] They reported competition studies that demonstrated phenyl fluorosulfate and phenyl triflate have similar reaction rates in Pd-catalyzed Stille couplings.

Scheme 9. Aryl Fluorosulfates in Pd-Catalyzed Negishi and Stille Cross-Coupling Reactions

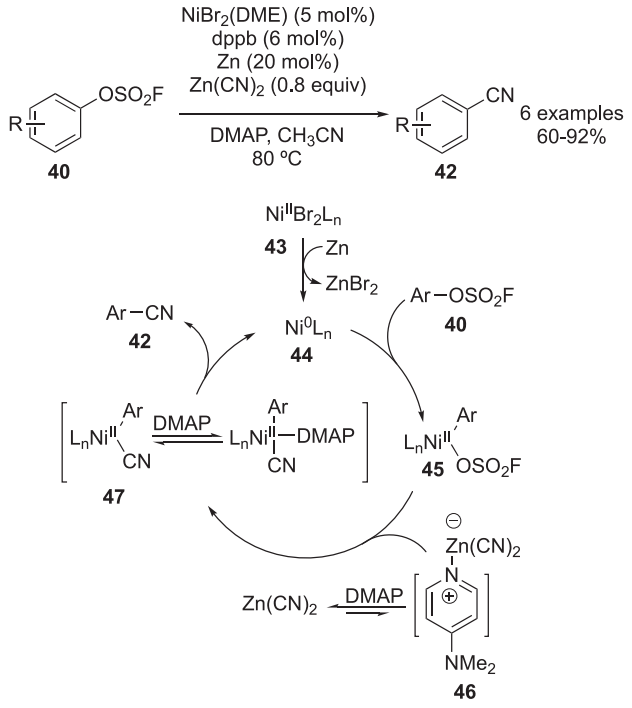


For several decades after the original Roth report,[44] fluorosulfate cross-coupling was largely limited to palladium catalysis. It was not until 2015 that Sharpless[45] and Hanley[46] reported the first examples of fluorosulfates (**40**) cross coupling with nickel catalysts. Since then, there has been increasing interest in these nickel-catalyzed transformations. In a representative example, Liu and co-workers investigated the Ni-catalyzed cyanation of phenol derivatives with $Zn(CN)_2$ in the presence of DMAP as a promoter (Scheme 10).[47] The role of DMAP is to form the $Zn(CN)_2$-DMAP complex (**46**), which increases solubility and reactivity in transmetalation.

2.3. Metal Coordination with Sulfur(VI) Fluorides. The intrinsic Lewis basicity of the fluorosulfuryl group has enabled several catalytic strategies based on metal coordination (Figure 2). The first strategy focuses on using metal chelation, either through the oxygen or the fluorine atoms, to activate the otherwise stable fluorosulfuryl group (Figure 2, part A). The second strategy exploits the Lewis basicity of the fluorosulfuryl oxygens as a directing group (Figure 2, part B).

2.3.1. Lewis Acid Activation of the Fluorosulfuryl Moiety. In 2018, Ball and am Ende reported that calcium triflimide can be used to facilitate the conversion of sulfonyl fluorides (**1**) to the corresponding sulfonamides (**48**, R= alkyl or aryl) (Scheme 11a). While this reaction was not catalytic, $Ca(NTf_2)_2$ is a common catalyst in Ca-catalyzed organic transformations and this work represents its first application in S(VI) fluoride chemistry.[48] They proposed that calcium triflimide coordinates either to the oxygens of the sulfonyl fluoride or the fluorine atom to increase the electrophilicity at sulfur. In 2020, Ball and am Ende[49] (Scheme 11b) and Grygorenko[50] (Scheme 11c) further extended the use of $Ca(NTf_2)_2$ to other S(VI) fluorides, including sulfamoyl fluorides (R = NR^3R^4), fluorosulfates (R = OAr), and sulfonyl fluorides (R = alkyl or aryl). Notably in the second-generation Ball and am Ende $Ca(NTf_2)_2$ system, the introduction of 1,4-diazabicyclo[2.2.2]octane (DABCO) allowed for room-temperature sulfur-fluoride exchange reactions with amines, even with the significantly more stable sulfamoyl fluorides and

Scheme 10. Ni-Catalyzed Cyanation of Phenol Derivatives with $Zn(CN)_2$ in the Presence of DMAP and Associated Mechanistic Hypothesis[a]



[a]Reproduced with permission from ref 47. Copyright 2018 American Chemical Society.

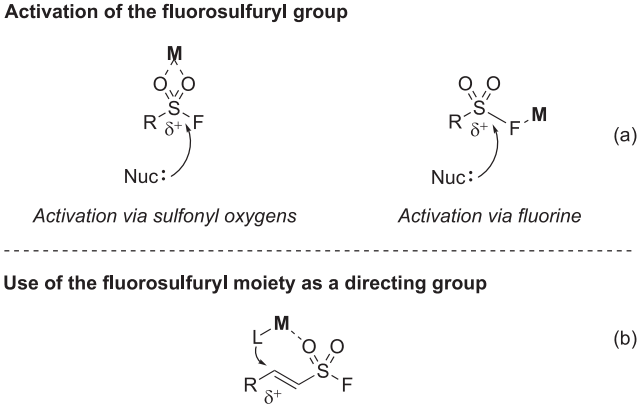


Figure 2. Catalytic strategies based on metal coordination to the fluorosulfuryl group.

fluorosulfates. Additionally, as little as 30 mol % of $Ca(NTf_2)_2$ affected SuFEx reactions between an alkyl sulfamoyl fluoride and a secondary amine, suggesting the potential for these reactions to be catalyzed by Lewis acids.

2.3.2. Using the Fluorosulfuryl Moiety as a Directing Group in Catalysis. In 2019, Leung and co-workers reported Pd-catalyzed asymmetric hydrophosphinations of α,β-unsaturated sulfonyl fluorides (**51**) (Scheme 12a).[51] Their mechanistic investigations were consistent with the hypothesis that the sulfonyl group chelates to the palladium catalyst (**53**) via the sulfonyl oxygens. The resulting chelated intermediate facilitates the intramolecular nucleophilic addition of the phosphine to the olefin. In the same year, Qin and co-workers reported the Rh-catalyzed 1,4-addition of aryl boronic acids to sulfonyl fluoride **54** (Scheme 12b).[52] DFT calculations

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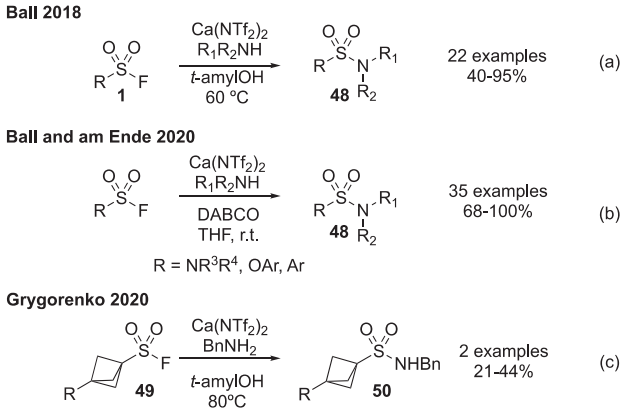
Scheme 11. Metal-Catalyzed Conversion of Sulfonyl Fluorides to the Corresponding Sulfonamide



indicated that 1,4-selectivity predominates over 1,6-selectivity. They attributed these findings to stabilization through a larger Coulomb attraction between the partial positive charge of the SO_2F-bound Rh(I) and partial negative charge α-carbon bound by a bond in the 1,4-selectivity pathway.

3. CATALYTIC SYNTHESES OF SULFUR(VI) FLUORIDES

3.1. Direct Installation of the S(VI) Fluoride Motif. There are numerous effective methods for the direct incorporation of sulfur(VI) fluoride motifs into organic molecules that use stoichiometric reagents.[14,16,53] However, the few catalytic strategies that have been developed are limited to the preparation of sulfonyl fluorides. Two catalytic fluorosulfurylation strategies have been developed to date: metal-catalyzed formation of the C−S bond (Figure 3a), and

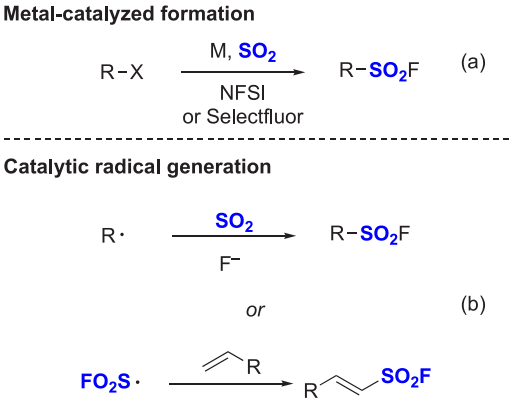
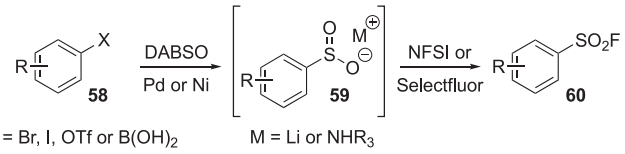
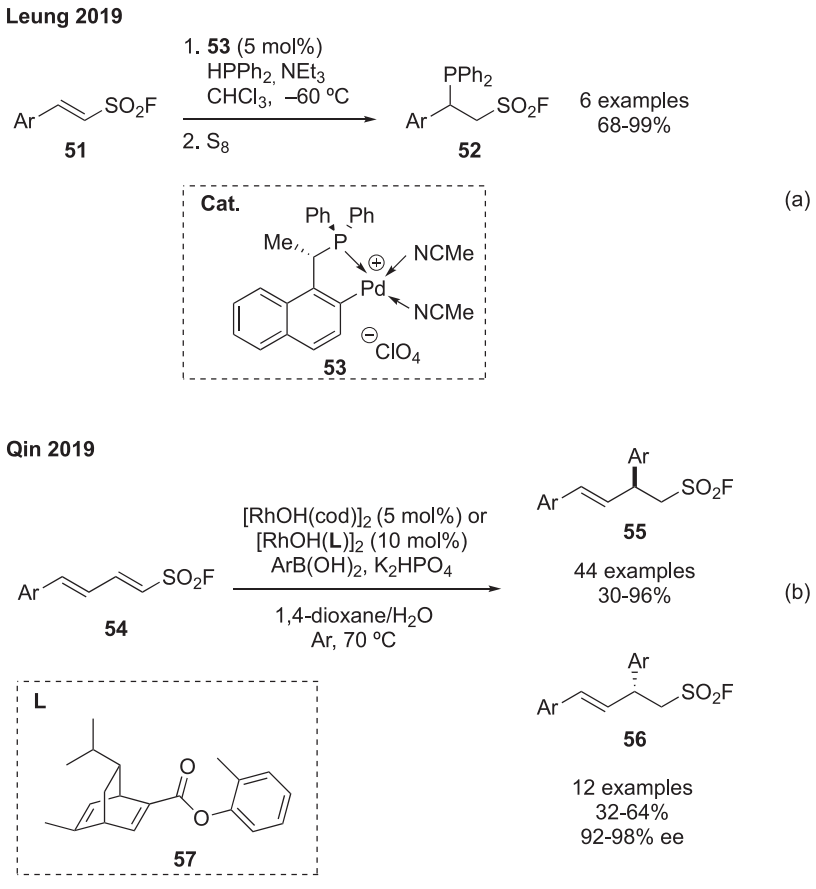


Figure 3. Catalytic fluorosulfurylation strategies.

Scheme 13. General Metal-Catalyzed Strategy for the Direct Installation of the Fluorosulfuryl Group



Scheme 12. Representative Examples on the Use of Fluorosulfuryl Moieties as a Directing Group in Catalysis



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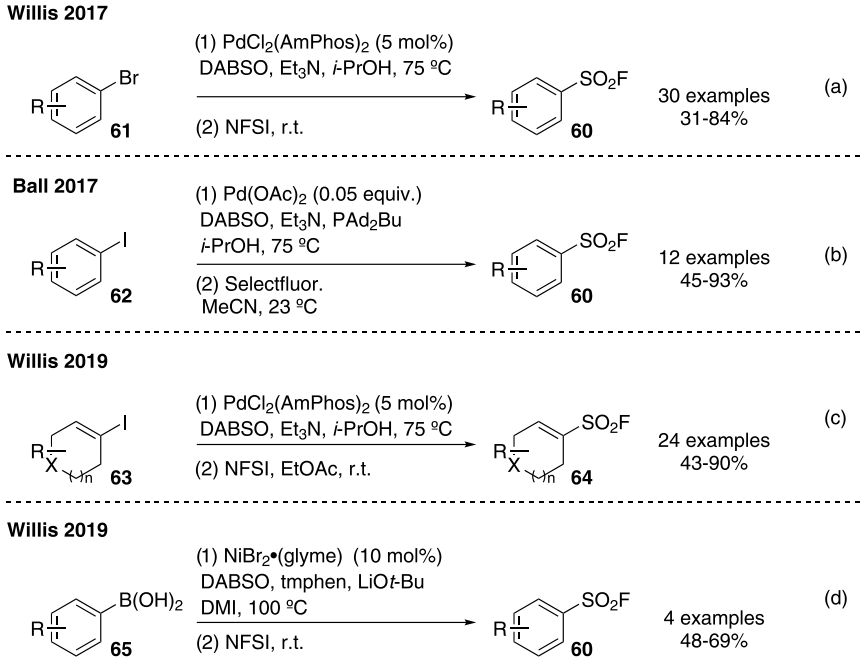
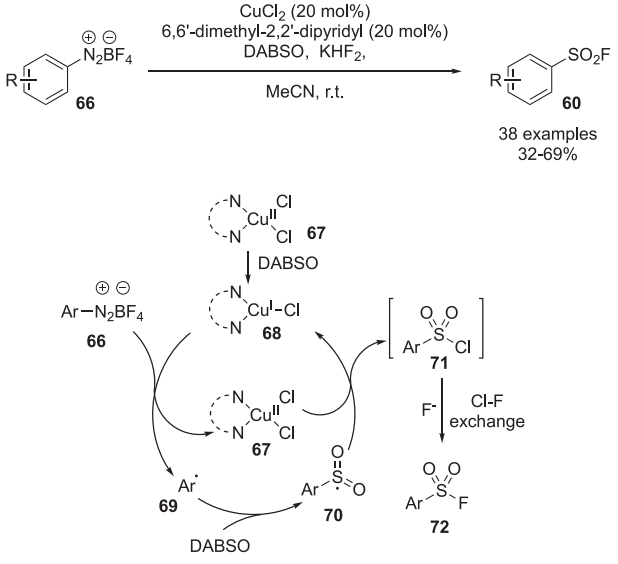
Scheme 14. Metal-Catalyzed Methods for the Preparation of Aryl Sulfonyl Fluorides



Scheme 15. Cu-Catalyzed Fluorosulfonylation of Aryl Diazonium Salts and the Postulated Mechanism[a]



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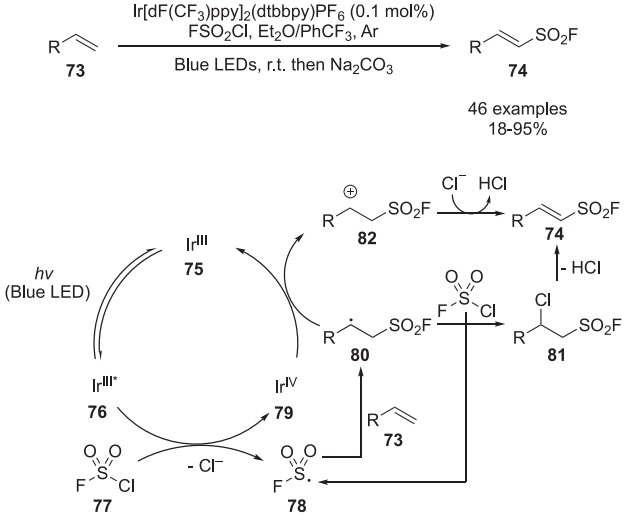
Scheme 16. Photocatalytic Synthesis of Alkenyl Sulfonyl Fluorides and Mechanism[a]



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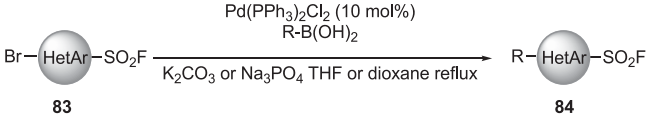

Figure 4. Strategies for the derivatization of organosulfur(VI) fluorides.

catalytic radical generation followed by C−S bond formation (Figure 3b).

All of the metal-catalyzed methods for the direct, catalytic installation of the sulfur(VI) fluoride motif utilize the coupling strategy depicted in Scheme 13. The first step involves the metal-catalyzed coupling of an aryl halide, triflate, or boronic acid (**58**) with 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) (DABSO), an SO_2 surrogate. The resulting sulfinate (**59**) then undergoes oxidation and fluorination with an electrophilic fluorination reagent to afford the desired aryl fluorosulfate (**60**).

In 2017, the Willis group reported one-pot Pd-catalyzed syntheses of aryl sulfonyl fluorides (**60**) from aryl bromides (**61**) (Scheme 14a).[54] The direct installation of the sulfonyl fluoride involved an initial Pd-catalyzed sulfonylation of aryl bromides using DABSO, followed by in situ oxidation and fluorination using *N*-fluorobenzenesulfonimide (NFSI). Concurrently, the Ball group developed a similar Pd-catalyzed method to convert aryl iodides (**62**) to aryl sulfonyl fluorides, except that Selectfluor was used as the oxidant and

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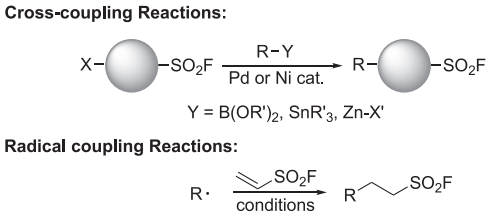
Scheme 17. Suzuki Cross-Coupling for the Synthesis of Heteroaromatic Sulfonyl Fluorides



electrophilic source of fluorine (Scheme 14b).[55] In 2019, the Willis group expanded the substrate scope to the synthesis of cyclic alkenyl sulfonyl fluorides (**64**) using alkenyl triflates (**63**) (Scheme 14c).[56] The Willis group subsequently reported a Ni-catalyzed method to generate sulfonyl fluorides from aryl and heteroaryl boronic acids (**65**) and DABSO (Scheme 14d).[57]

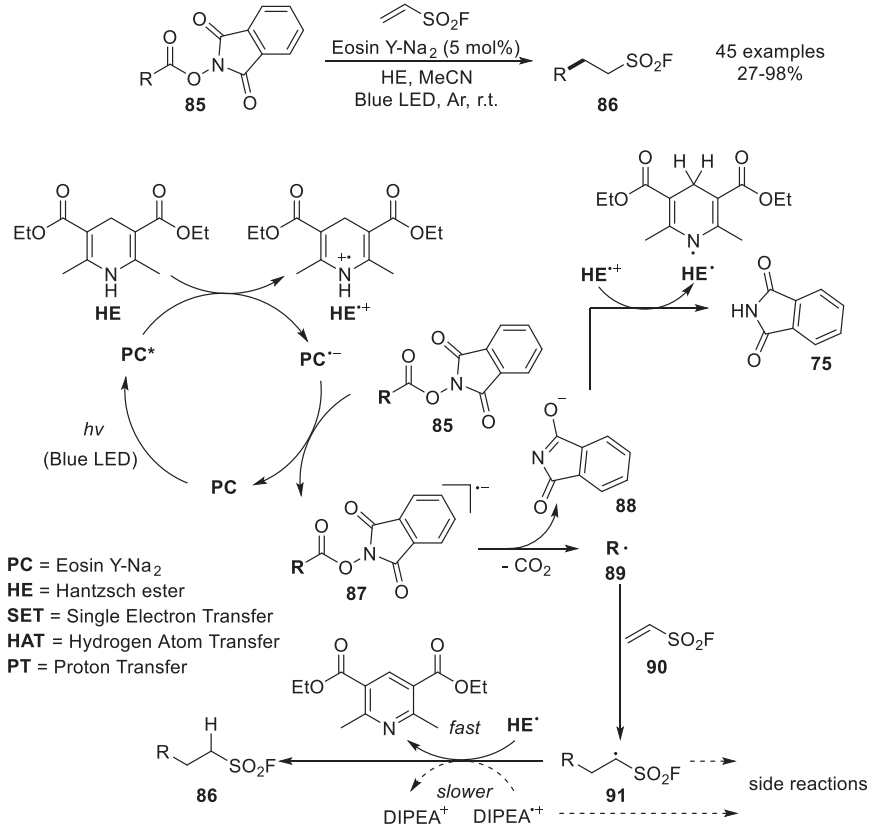
There have been two catalytic radical approaches for the synthesis of sulfonyl fluorides. The first involves catalytic generation of an alkyl radical followed by coupling with a SO_2 equivalent. This strategy is exemplified in the 2020 report by Liu, Chen, and co-workers, who described the Cu-catalyzed fluorosulfurylation of aryl diazonium salts (Scheme 15).[58] $CuCl_2$(DMBP) (**67**) is first reduced to a Cu(I) species (**68**), which reduces the aryl diazonium salt (**66**) to an aryl radical (**69**). The aryl radical then reacts with DABSO to afford an aryl sulfonyl radical (**70**). A subsequent chlorine transfer from $CuCl_2$(DMBP) provides sulfonyl chloride **71**. The desired sulfonyl fluoride was obtained through a subsequent halogen exchange with KFHF. Liu, Chen, and co-workers supported this radical mechanism through radical inhibition and radical probe experiments and identifying the sulfonyl chloride intermediate in the control experiments.

An alternative approach is the catalytic generation of a sulfur-centered radical, followed by addition to an organic substrate. This approach was pioneered by Liao and co-workers in a 2021 report where fluorosulfuryl radicals are utilized to access alkenyl sulfonyl fluorides using photoredox catalysis (Scheme 16).[59] In the proposed mechanism, catalyst **75**, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6([Ir]), is first photoexcited to **76**. It subsequently reduces chlorosulfonyl fluoride (**77**) to afford fluorosulfuryl radical **78** and chloride. The radical then adds to the alkene to form **80**. This radical intermediate either reacts with FSO_2Cl to give a β-chlorinated sulfonyl fluoride (**81**) or loses an electron through single-electron transfer to form a cationic sulfonyl fluoride (**82**). Both **81** or **82** could readily form the alkenyl sulfonyl fluoride product (**74**). Liao and co-workers supported this mechanism through a TEMPO trapping experiment, radical clock experiments, and DFT calculations.

3.2. Catalytic Strategies to Derivatize Sulfonyl Fluoride-Containing Motifs. Instead of direct catalytic incorporation of the sulfur(VI) fluoride functional group, an alternative approach is the derivatization of an organic fragment that already contains the key fluorosulfuryl moiety. This approach has been explored both with cross-coupling reactions and with radical coupling reactions (Figure 4).

In 2018, Grygorenko and co-workers reported a Pd-catalyzed Suzuki (Scheme 17), Stille, and Negishi cross-

Scheme 18. Photocatalytic Method for the Reductive Coupling of Alkyl Radicals with Vinyl Sulfonyl Fluoride[a]



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coupling reactions for the synthesis of heteroaromatic sulfonyl (**84**) using the corresponding organometallic reagents with bromoheteroaromatic sulfonyl fluorides (**83**).[60] In the majority of cases, the SO_2F group is stable to the reaction conditions and does not compete with the aryl bromide coupling.

There are several examples of Heck-type cross-couplings with aryl halides[61,62] or boronic acids,[63,64] and vinyl fluorides. Interestingly, there are also mechanistically distinct photocatalytic examples reported. In 2019, Liao and co-workers reported a photocatalyzed radical-based method for the synthesis of aliphatic sulfonyl fluorides.[65] They postulated the mechanism shown in Scheme 18. Under irradiation of blue LED light, Eosin Y−Na_2 is excited and reduced by the Hantzsch ester. The subsequent radical anion of Eosin Y−Na_2 oxidizes the *N*-acyloxyphthalamide (**85**) to reform the catalyst. The radical anion of the *N*-acyloxyphthalamide (**87**) then undergoes decarboxylation to afford an alkyl radical (**89**), which then adds to vinyl sulfonyl fluoride (**90**) to form alkyl sulfonyl fluoride radical **91**. A subsequent hydrogen atom transfer (HAT) from the Hantzsch ester radical forms the desired product (**86**).

4. FUTURE DIRECTIONS

Over the past decade, the field of S(VI) fluoride chemistry has witnessed incredible growth driven by transformational method development and applications. Essential to this growth are methods that employ nitrogen, oxygen, and phosphorus bases, bifluorides, and transition metals as catalysts in the synthesis and application of S(VI) fluorides. In light of this progress, further mechanistic investigations can broaden innovation in the field. After over 20 years of investigations, nuances regarding the role of base-catalysis are still unclear, especially in silicon-free systems. In transition-metal catalysis, fluorosulfates as an emerging pseudohalide in transition-metal catalyzed cross-coupling reactions are promising; however, the assumed oxidation addition mechanism into the C−S bond needs further elaboration.

The next frontier in metal-catalyzed cross-coupling reactions is the activation and functionalization of more stable S(VI) fluorides (e.g., sulfonyl fluorides, sulfamoyl fluorides, sulfonimidoyl fluorides, etc.) toward C−C, C−N, C−O, and other bond formations.[60] Contributions to this idea will be transformational in expanding their synthetic utility. Lastly, we are just scratching the surface in the exploration of single-electron transformations using S(VI) fluorides. This nascent subfield of S(VI) fluoride chemistry will enable an array of orthogonal transformations that are currently challenging under a two-electron regime.

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Notes

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