HIGHLIGHT

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Fluorosulfonyl radicals: new horizons for the synthesis of sulfonyl fluorides

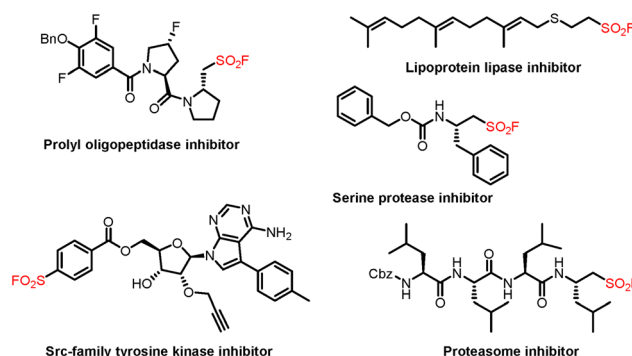Fu-Sheng He,*[a] Yuqing Li[a] and Jie Wu *[a,b,c]

Sulfonyl fluorides have found widespread applications in organic synthesis, chemical biology, drug discovery and materials science. Compared with current methods, direct fluorosulfonylation with fluorosulfonyl radicals has emerged as a concise and efficient approach for producing sulfonyl fluorides. This highlight provides an overview of recent advances in the generation of fluorosulfonyl radicals from different precursors and their participation in the synthesis of diverse functionalized sulfonyl fluorides.

Sulfonyl fluoride is a prevalent structural unit found in biologically active molecules and versatile synthetic intermediates in modern organic synthesis (Fig. 1).[1] Since the concept of Sulfur (VI) Fluoride Exchange (SuFEx) was pioneered by Sharpless and co-workers as the next generation of click chemistry in 2014,[2] sulfonyl fluorides have received considerable attention and continuous interest from the communities of synthetic chemistry and medicinal chemistry. Generally, strategies for the construction of these frameworks mainly focus on the fluoride–chloride exchange from the corresponding sulfonyl chlorides.[3] Other methods, including conjugate addition,[4] electrophilic fluorination of thiols,[5] anodic oxidative fluorination,[6] and SO_2 insertion/fluorination,[7] for the preparation of sulfonyl fluorides have also been reported. Compared with these methods *via* S–F bond formation, direct fluorosulfonylation by using FSO_2-containing reagents represents a concise and effective approach for C–SO_2F bond formation. In this case, the reported fluorosulfonylating reagents such as sulfuryl fluoride gas (SO_2F_2)[2] and other solid reagents (FDIT and AISF)[8] have been widely utilized as the synthetic equivalents of electrophilic "FSO_2^+" synthons to access sulfonyl fluorides. In contrast, fluorosulfonylation of the corresponding fluorosulfonyl radical ($FSO_2^•$) is more challenging and remains less well explored.

As one of the sulfur-centered radicals, the highly active fluorosulfonyl radical has been ignored for a long time owing to its instability and difficulty of generation. It was not until 2013 that Zeng, Beckers, and co-workers first observed the formation of the fluorosulfonyl radical by the flash vacuum pyrolysis of fluorosulfonyl azide.[9] Inspired by this observation, many efforts have been devoted to the development of suitable fluorosulfonyl radical precursors for the direct radical fluorosulfonylation reactions. In this highlight article, we focus on the most recent advances in the fluorosulfonyl radical-involved transformations, with emphasis on the synthesis of sulfonyl fluorides.
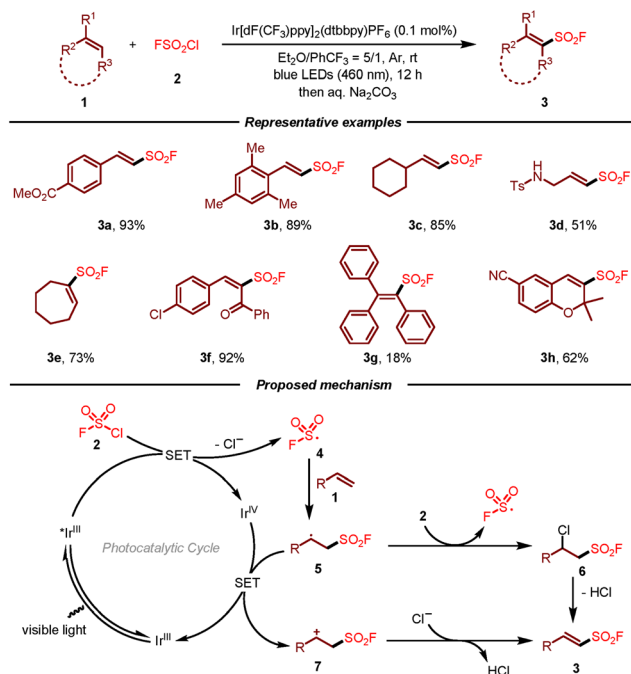
The first radical fluorosulfonylation of alkenes using FSO_2Cl as the fluorosulfonyl radical precursor was reported by Liao and co-workers in 2020 (Scheme 1).[10,11] This photoredox-catalyzed reaction shows a broad substrate scope and excellent functional group compatibility, providing a novel and facile approach for the synthesis of alkenyl sulfonyl fluorides. Notably, the scope of alkenes could be expanded to cyclic, di- and tri-substituted olefins, giving rise to multi-substituted vinyl sulfonyl fluorides that are challenging to be synthesized using established cross-coupling methods. Moreover, the late-stage fluorosulfonylation of natural products including oleic ester, cinnamate, chromene, estrone, pregnenolone, and cholesterol also demonstrated the superiority of this approach. The

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Fig. 1 Selected examples of SO_2F-containing bioactive molecules.

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Scheme 1 Radical fluorosulfonylation of alkenes with FSO$_2$Cl under photoredox conditions.

Scheme 2 Visible light-induced photoredox-catalyzed chloro-fluoro-sulfonylation of alkynes.

reaction mechanism for this visible-light-induced radical fluorosulfonylation of alkenes **1** with FSO$_2$Cl **2** was supported by the experimental and DFT calculation studies. Initially, single-electron reduction of FSO$_2$Cl by the excited Ir(III)* would occur to generate fluorosulfonyl radical **4**, which then attacked the double bond of alkene **1** leading to carbon radical intermediate **5**. In the case of a radical chain process, the radical would react with FSO$_2$Cl to form chlorinated intermediate **6**. Following the loss of HCl, fluorosulfonylation product **3** would be afforded. On the other hand, a redox pathway that involved a single-electron oxidation/deprotonation process could not be excluded.

However, the above radical fluorosulfonylation of multi-substituted alkenes usually suffered from side reactions, low reaction efficiency, and low Z/E selectivity. To address these issues, the same group subsequently developed a photoredox-catalyzed radical chloro-fluorosulfonylation of alkynes for the construction of β-chloro alkenylsulfonyl fluorides (BCASF) (Scheme 2).[12] Under the optimal reaction conditions, both terminal and internal alkynes reacted smoothly in this transformation. More importantly, this protocol provided a novel and powerful class of sulfonyl fluoride hubs, which could be converted to a series of functionalized alkenylsulfonyl fluorides. As a result, BCASF molecules could undergo different types of transformations at the β-chloro site while maintaining the sulfonyl fluoride group intact, such as Suzuki coupling, Sonogashira coupling, selective reduction, and nucleophilic substitution with nitrogen, oxygen, and sulfur nucleophiles. Furthermore, this versatile platform could also be applied in the late-stage modification of peptides and drugs. Similar to their previous work, it was postulated that fluorosulfonyl
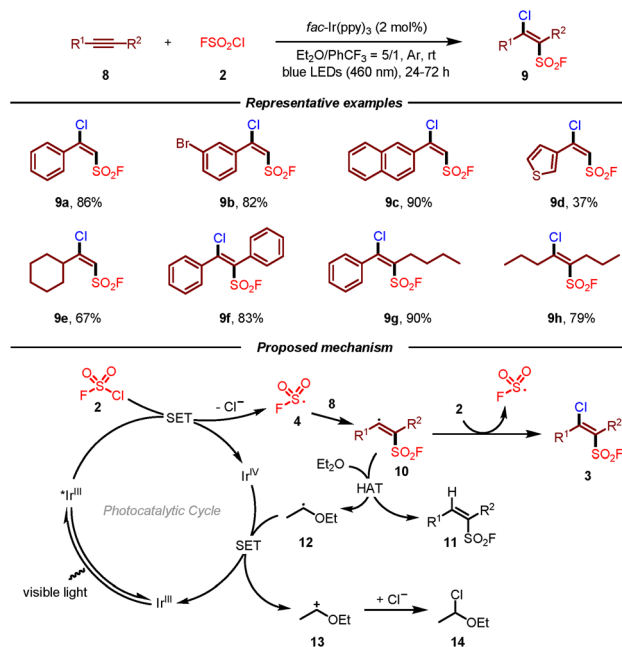
radical **4** could be first generated from FSO$_2$Cl **2** by single-electron reduction. Then, addition of fluorosulfonyl radical **4** to alkyne **8** produced vinyl radical intermediate **10**, which could attack FSO$_2$Cl **2** to deliver the target product **3** and initiate the radical chain process. Meanwhile, vinyl radical **10** might undergo hydrogen-atom transfer from Et$_2$O leading to alkenyl-sulfonyl fluoride **11** and radical **12**. A single-electron transfer of the oxidized Ir(IV) by ether-derived radical **12** would give rise to carbocation intermediate **13** and regenerate the Ir(III) photo-catalyst. Finally, GC-MS detection of α-chlorinated diethyl ether **14** suggested the addition of the chloride anion to the carbocation.

In the same year, Liao, Huang, and co-workers disclosed a practical synthesis of β-keto sulfonyl fluorides by electro-chemical oxo-fluorosulfonylation of alkynes with FSO$_2$Cl (Scheme 3).[13] For the first time, the fluorosulfonyl radical could be generated under electrochemical conditions. This strategy featured mild reaction conditions, broad substrate scope, air as the oxidant and high chemoselectivity. Remarkably, the divergent synthesis of β-keto sulfonyl fluorides and α-chloro β-keto sulfonyl fluorides from the same starting materials was achieved simply by the variation of solvents. Additionally, some β-keto sulfonyl fluoride derivatives showed potent activities toward *Bursaphelenchus xylophilus* and *Colletotrichum gloeosporioides*. Regarding the reaction mechanism, it was suggested that cathodic reduction of FSO$_2$Cl **2** would produce fluorosulfonyl radical **4**, which then attacked the triple bond of alkyne **15** leading to vinyl radical **18**. Vinyl radical **18** would react with O$_2$ to generate peroxy radical **19**, which could be converted to radical **20** according to the Russell mechanism. Subsequently, radical **20** undergoes a
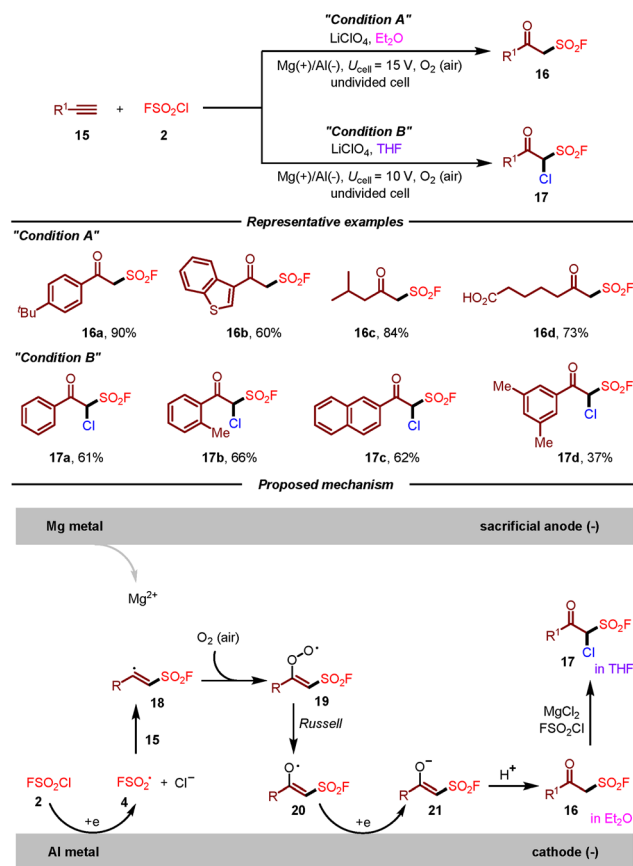
Scheme 3 Electrochemical-induced oxo-fluorosulfonylation of alkynes under air.

cathodic reduction and protonation sequence to furnish β-keto sulfonyl fluoride **16**. In the case of THF as the solvent, α-chloro β-keto sulfonyl fluoride **17** could be obtained through electrophilic chlorination of **16** with $MgCl_2$ and FSO_2Cl. However, the current electrochemical approach was exclusively limited to employing a sacrificial magnesium anode.

After that, the same group developed an electrochemical radical fluorosulfonylation of vinyl triflates with FSO_2Cl by using inexpensive graphite felt as electrodes (Scheme 4).[14] As a result, a broad spectrum of readily available vinyl triflates were well tolerated, giving rise to various β-keto sulfonyl fluoride derivatives in moderate to good yields. Moreover, this metal-free electrosynthetic approach was amenable to be scaled up. On the basis of the results of control experiments, a plausible mechanism for this transformation was proposed. Initially, fluorosulfonyl radical **4** would be generated from FSO_2Cl **2** by cathodic reduction, which would undergo addition to vinyl triflate **22** giving rise to radical **25**. Following β-fragmentation, the final product **24** would be produced with the generation of CF_3SO_2-radical **26**. This F_3SO_2-radical **26** would release SO_2 leading to CF_3 radical **27**, which would undergo hydrogen atom transfer from diethyl ether to afford HCF_3 **28**.

Due to the inherent characteristics of gaseous FSO_2Cl, including inconvenience in storage and handling as well as
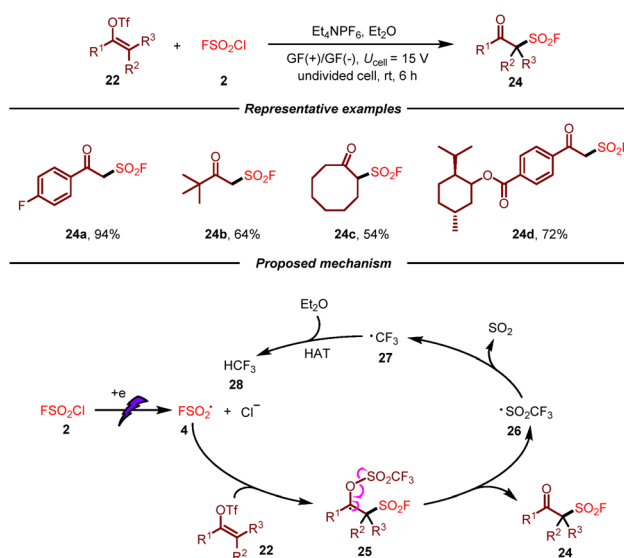

Scheme 4 Electrochemical synthesis of β-keto sulfonyl fluorides *via* radical fluorosulfonylation of vinyl triflates.

moisture sensitiveness, the development of new and practical fluorosulfonyl radical precursors to access sulfonyl fluorides undoubtedly will be more appealing. In this context, Liao and co-workers recently introduced solid state 1-fluorosulfonyl benzoimidazolium triflate (FABI) salts **30** as a convenient and effective redox-active fluorosulfonyl radical precursor (Scheme 5).[15] Compared with the known FSO_2Cl, this reagent was bench-stable and easy to handle, enabling the radical fluorosulfonylation of alkenes with high efficiency. A wide range of electron-rich, cyclic, di- and trisubstituted olefins were compatible with FABI, which fully demonstrated its superiority over FSO_2Cl. Additionally, the photoredox-catalyzed alkoxy-fluorosulfonylation of alkenes with FABI was also developed. By employing suitable alcohols and acids as nucleophiles, the corresponding β-alkoxyl sulfonyl fluorides could be obtained in moderate to good yields. On the basis of the experimental results, a plausible mechanism for this reaction was proposed as shown in Scheme 5. It was reasoned that the redox-active radical precursor **30** underwent single electron transfer by the excited Ir(III)* to give neutral radical **34**, which then converted to fluorosulfonyl radical **4** through a homolytic cleavage of the N–S bond. Addition of fluorosulfonyl radical **4** to alkene substrate **29** would produce a new carbon radical **35**, which underwent single electron oxidation by Ir(IV) to form carbon cation intermediate **36** and regenerate ground-state Ir(III) to close the photocatalytic cycle. Ultimately, the carbon cation could either be deprotonated or trapped by oxygen nucleophiles to furnish the corresponding product.

At the same time, Wang and co-workers reported the same air- and bench-stable benzoimidazolium fluorosulfonate reagent from their previous work on the chemistry of imidazolium sulfonate cationic salts,[16] which successfully applied to the radical fluorosulfonylation of unsaturated hydrocarbons (Scheme 6).[17] Under suitable optimized photocatalytic con-
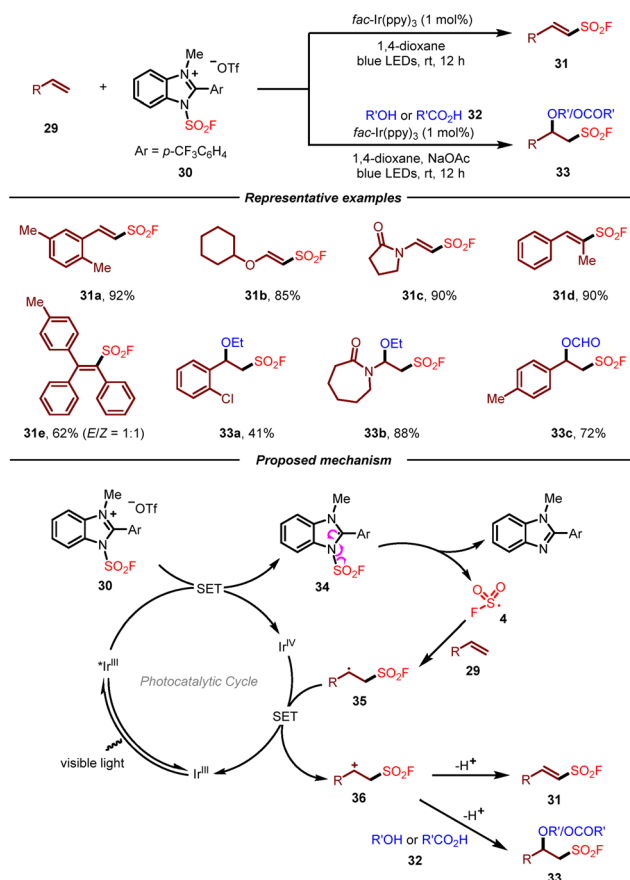
Scheme 5 Photoredox-catalyzed radical fluorosulfonylation of alkenes with a benzoimidazolium-based fluorosulfonyl radical precursor.
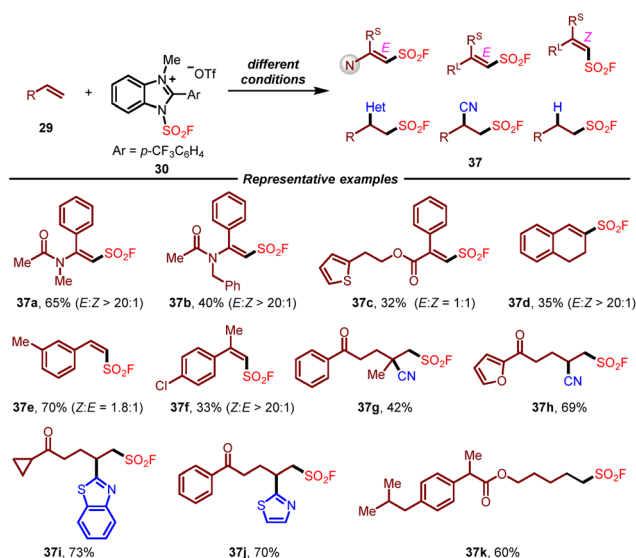

Scheme 6 Synthesis of alkenyl and alkyl sulfonyl fluorides with a benzoimidazolium-based fluorosulfonyl radical precursor.

ditions, this redox-active fluorosulfonyl radical precursor could react with various alkenes smoothly, providing alkenyl sulfonyl fluoride, alkylsulfonyl fluoride, and migratory fluorosulfonylat-

ing products in good yields with high stereoselectivity. This operationally simple protocol enabled the efficient introduction of the FSO$_2$ group into a wide range of complex molecules derived from natural products and drugs. The combination of radical trapping and radical clock experiments demonstrated the generation of the fluorosulfonyl radical during the reaction.

Soon after, using the same 1-fluorosulfonyl benzoimidazolium triflate salt as the fluorosulfonyl radical precursor, the Liao group further developed a radical hydro-fluorosulfonylation of alkenes by employing oxygen-doped anthanthrene (ODA) as the photocatalyst and 1,4-cyclohexadiene (1,4-CHD) as a hydrogen donor (Scheme 7).[18] This method enabled the synthesis of various aliphatic sulfonyl fluorides **40** under mild and metal-free conditions, which could be applied to the late-stage functionalization of natural products, peptides and drugs. Moreover, with (TMS)$_3$SiH as a hydrogen donor, the application of this photocatalytic system to the radical hydro-fluorosulfonylation of alkynes was also demonstrated, allowing the formation of alkenylsulfonyl fluorides **41** with high Z-selectivity.

Given the similar bifunctional radical reactivity between alkynyl sulfonyl fluorides and alkynyl triflones, Studer and co-workers recently disclosed an efficient transition-metal-free radical 1,2-difunctionalization of unactivated alkenes to access various aliphatic β-alkynylfluorosulfonylalkanes (Scheme 8).[19] Notably, alkynyl sulfonyl fluorides could not only be used as highly valuable bifunctional radical trapping reagents but also as the fluorosulfonyl radical precursor. The successful diversification of products with SuFEx click chemistry to sulfonates and sulfonamides also highlighted the practicality of this method. Mechanistically, it was proposed that the reaction was initiated by AIBN to give AIBN-derived cyanopropyl radical **45**. Following the addition to alkyne **43** and radical fragmentation
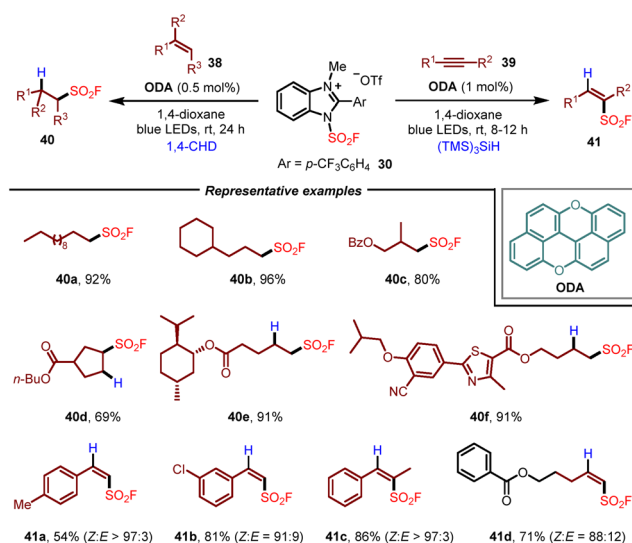
Scheme 7 Photoredox-catalyzed radical hydro-fluorosulfonylation of unactivated alkenes and alkynes.
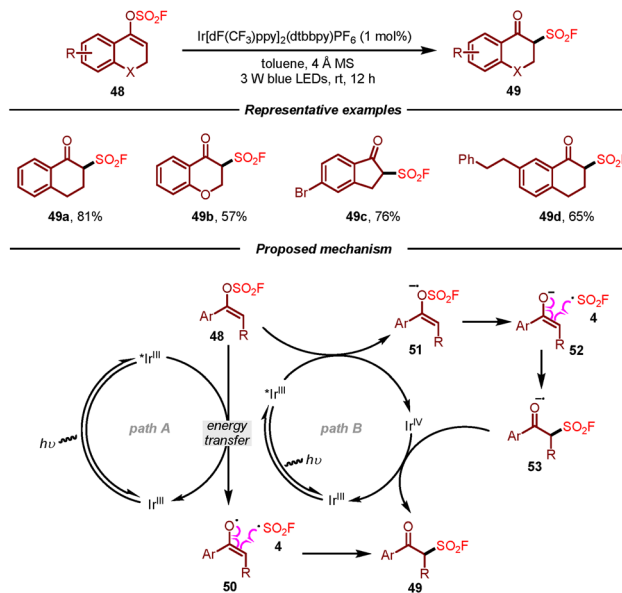
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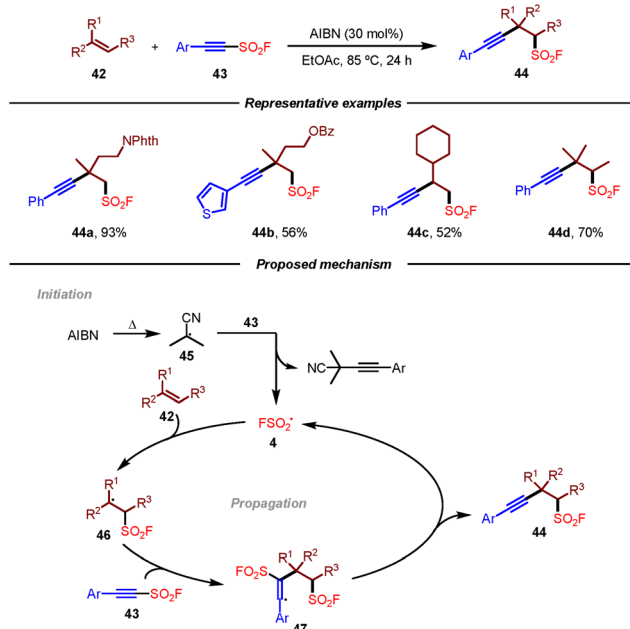
Scheme 8 Radical difunctionalization of unactivated alkenes to access β-alkynyl-fluorosulfonylalkanes.

Scheme 9 Synthesis of β-keto sulfonyl fluorides *via* photocatalytic transformation of vinyl fluorosulfates.

sequence, fluorosulfonyl radical **4** would be generated, which would undergo addition to alkene **42** leading to radical intermediate **46**. This radical intermediate **46** could be trapped by alkynyl sulfonyl fluoride **43** giving rise to vinyl radical **47**, which underwent β-fragmentation to provide the desired product **44** with the regeneration of fluorosulfonyl radical **4**.

Very recently, Li, Su, and co-workers developed a photocatalytic procedure for the preparation of β-keto sulfonyl fluorides from vinyl fluorosulfates (Scheme 9).[20] This methodology featured sustainable conditions and a broad substrate scope, affording aromatic β-keto sulfonyl fluorides in moderate to good yields by using $Ir[dF(CF_3)ppy]_2(dtbbpy)(PF_6)$ (1 mol%) as a photocatalyst under irradiation of 3 W blue LEDs. According to the mechanistic results, two plausible pathways for this photocatalytic transformation of vinyl fluorosulfates were proposed as shown in Scheme 9. In path A, the Ir(III) complex was excited under visible light irradiation to form Ir(III)*, which would then undergo energy transfer with vinyl fluorosulfate **48** to generate enol radical **50** and fluorosulfonyl radical **4**. Subsequently, the corresponding product **49** would be produced through recombination of these two radical species. The authors also suggested another plausible pathway through which the excited Ir(III)* and vinyl fluorosulfate **48** would undergo SET to afford Ir(IV) and a radical anion intermediate **51**. Following radical fragmentation/reconstruction and SET oxidation, product **49** would be formed (path B).

The direct fluorosulfonylation process involving the fluorosulfonyl radical has appeared as an attractive strategy for the rapid assembly of sulfonyl fluorides. In this highlight, the most recent progress in this aspect by utilizing different fluorosulfonyl radical precursors is discussed. Specifically, four types

of radical fluorosulfonylating reagents including FSO_2Cl, benzoimidazolium fluorosulfonates, alkynyl sulfonyl fluorides and vinyl fluorosulfates have been developed and applied to the efficient construction of diverse functionalized sulfonyl fluorides. These achievements would offer new opportunities for SuFEx click chemistry, accelerating the applications of sulfonyl fluorides in chemical biology and drug discovery. There are still some challenges remaining in this field. First, the substrate scope of radical acceptors in the above-mentioned reactions is relatively narrow, which is mostly restricted to alkenes and alkynes. Second, the fluorosulfonyl radical precursors are still limited to the above four types. The development of novel and efficient radical precursors would provide new approaches for the construction of sulfonyl fluorides in a more sustainable way. Therefore, this highly reactive intermediate is worthy of further investigation. Besides that, enantioselective radical fluorosulfonylation involving the fluorosulfonyl radical to deliver chiral sulfonyl fluorides remains undeveloped. The exploration of enantioselective radical flurosulfonylation is highly in demand. Given these challenges and opportunities, further progress can be expected in the near future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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