

RESEARCH ARTICLE

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Based on a radical sulfur dioxide insertion and fluorination strategy, we have developed an efficient method for aliphatic sulfonyl fluoride synthesis using abundant carboxylic acids, a reductant, a sulfur dioxide surrogate and the electrophilic fluorination reagent *N*-fluorobenzenesulfonylimide (NFSI) under reduction conditions. This protocol provides a convenient synthetic pathway for various aliphatic sulfonyl fluorides and tolerates a wide range of functional groups.

Introduction

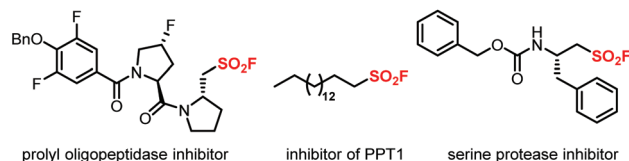
The last two decades have witnessed the rapid development of click chemistry introduced by Sharpless and co-workers in many research fields.¹ Since sulfonyl fluorides have a special stability–reactivity pattern, Sulfur(vi) Fluoride Exchange (SuFEx) as the latest reaction identified for click chemistry has attracted enormous attention and has been widely utilized in not only organic synthesis but also chemical biology, medicine, and materials science,² which has led to a fast-growing demand for chemists to develop reliable methods for the incorporation of this highly valued sulfonyl fluoride group (SO₂F) into various organic compounds.

Conventional approaches for the formation of sulfonyl fluorides typically involve the fluorosulfonylation of thiols and their derivatives or utilization of FSO₂-containing synthons.³ These approaches do not involve the formation of the C–SO₂F bond. An alternative attractive and straightforward strategy for the introduction of the sulfonyl fluoride group would be the direct formation of a new C–SO₂F bond. In recent years, several elegant methods based on transition-metal catalyzed cross-coupling,⁴ electrophilic fluorosulfonylating reagents,⁵ fluorosulfonyl radical addition⁶ or radical sulfur dioxide insertion and fluorination^{7,8} have emerged for

the effective incorporation of SO₂F into a variety of organic small molecules. However, the reactions typically lead to the formation of Csp²–SO₂F bonds, whereas processes that involve the formation of Csp³–SO₂F bonds remain largely unexplored.

Although aliphatic sulfonyl fluorides may have highly selective peptide-type inhibition activity (Fig. 1A) and high potential

(A) Selected examples of aliphatic sulfonyl fluoride inhibitors



(B) Synthetic approaches to aliphatic sulfonyl fluorides

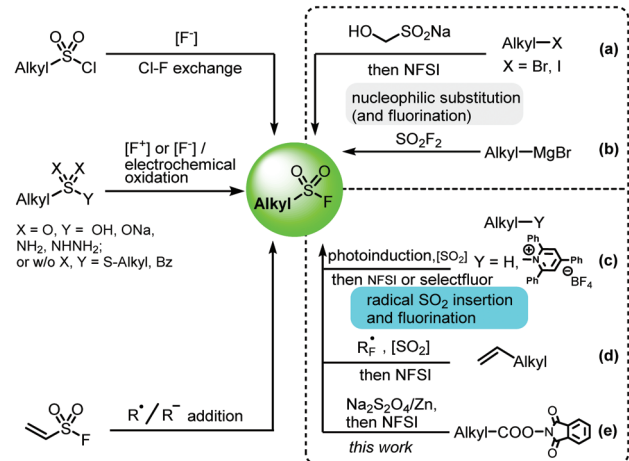


Fig. 1 Aliphatic sulfonyl fluoride inhibitors and the synthetic approaches to aliphatic sulfonyl fluorides.

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in SuFEx chemistry,² their limited availability significantly hampered their study and application. As can be seen in Fig. 1B, the main synthetic approaches without the formation of the C–SO₂F bond for aliphatic sulfonyl fluorides rely on F–Cl exchange of the corresponding aliphatic sulfonyl chlorides,^{2a,9} oxidative fluorination of thiols and their derivatives,¹⁰ and various addition reactions of ethenesulfonyl fluoride (ESF).¹¹ Notably, two novel synthetic methods involving the formation of Csp³–SO₂F bonds were developed recently on the basis of the nucleophilic substitution process.¹² Shavnya and co-workers reported that aliphatic sulfonyl fluorides can be synthesized from nucleophilic substitution of alkyl halides with cheap rongalite as the sulfonyl source followed by fluorination with *N*-fluorobenzenesulfonylimide (NFSI) (Fig. 1Ba).^{12a,b} More recently, Sammis and co-workers demonstrated that aliphatic sulfonyl fluoride synthesis can be realized through the nucleophilic substitution of sulfuryl fluoride (SO₂F₂) by Grignard reagents (Fig. 1Bb).^{12c} Furthermore, based on the new strategy of radical sulfur dioxide insertion and fluorination,⁷ we reported several new methods to efficiently synthesize various aliphatic sulfonyl fluorides through perfluoroalkyl radical addition with a variety of alkenes followed by radical sulfur dioxide insertion and oxidative fluorination by NFSI (Fig. 1Bd).^{7a–c} Very recently, the MacMillan group reported the direct conversion of aliphatic C(sp³)–H bonds into the corresponding alkyl sulfinic acids *via* decatungstate photocatalysis, and that fluorination of sulfinic acids with selectfluor can result in the desired aliphatic sulfonyl fluorides (Fig. 1Bc).¹³ The Willis group reported that versatile alkyl sulfinates can be prepared from readily available amines, using Katritzky pyridinium salt intermediates by a photoinduced or thermally induced single-electron transfer (SET) process, and fluorination of alkyl sulfinates with NFSI can lead to the desired aliphatic sulfonyl fluorides as well (Fig. 1Bc).¹⁴ Despite these invaluable advances, the development of general and efficient methods for aliphatic sulfonyl fluoride synthesis is still in high demand.

Aliphatic carboxylic acids are abundant and easily available feedstocks, and have been widely utilized as an ideal type of building block in organic synthesis.¹⁵ In recent years, their important and valuable utilization is as a convenient radical source *via* reductive decarboxylation after activation in the form of *N*-hydroxyphthalimide (NHPI) esters.^{15d–g} Inspired by this progress and in connection with our research interest in sulfonyl fluoride synthesis *via* a radical sulfur dioxide insertion and fluorination strategy,⁷ we envisioned that the combination of aliphatic carboxylic acid as a radical source with an appropriate SO₂ and fluorine source would forge a general and efficient approach to various aliphatic sulfonyl fluorides (Fig. 1Be). Herein, we report our effort on this approach. The wide availability of carboxylic acids and practical reaction conditions allow for a fast construction of a variety of diverse aliphatic sulfonyl fluorides. Further diversification of the products is also demonstrated and utilization of this method for the preparation of some pharmaceutically important motifs would be expected.

Results and discussion

We commenced our study of the desired decarboxylative fluorosulfonylation of aliphatic carboxylic acids *via* the oxidative decarboxylation process by using cyclohexane carboxylic acid as the model substrate, the 1,4-diazabicyclo[2.2.2]-octane-bis(sulfur dioxide) adduct (DABSO) as the sulfur dioxide surrogate, NFSI or KF as the fluoride source and K₂S₂O₈ as the oxidant with a catalytic amount of AgNO₃ in *N,N*-dimethylformamide (DMF)/H₂O (3 : 1 v/v) at 80 °C for 9 h (Fig. 2a). But no formation of the desired fluorosulfonylation product **2m** was observed, which might be due to the complicated and incompatible oxidation and reduction process existing in the reaction system. We then turned our attention toward the reductive decarboxylation process for the desired decarboxylative fluorosulfonylation of aliphatic carboxylic acids by using the corresponding cyclohexane carboxylic acid NHPI ester **1m** as the model substrate and Na₂S₂O₄ as both the sulfur dioxide surrogate and reductant¹⁶ in DMF/H₂O (3 : 1 v/v) at 80 °C for 9 h (Fig. 2b). To our delight, following rapid fluorination with NFSI, the reaction successfully provided the desired fluorosulfonylation product **2m** in 30% ¹⁹F NMR yield.

Encouraged by this result, subsequent extensive screening of the reaction conditions revealed that the optimized conditions for the desired decarboxylative fluorosulfonylation of aliphatic carboxylic acids were as follows: aliphatic carboxylic acid NHPI ester (1.0 equiv.), Na₂S₂O₄ (1.5 equiv.), Zn (2.0 equiv.), *N,N*-dimethylpropionamide (DMPPr)/H₂O (5 : 1 v/v), Ar atmosphere, 80 °C, 9 h; then NFSI (3.0 equiv.), room temperature, 4 h (Table S8,† entry 1). Replacement of Na₂S₂O₄ with other sulfur dioxide surrogates including DABSO or K₂S₂O₅ resulted in a lower yield of the desired product (Table S8,† entries 2 and 3). Though Na₂S₂O₄ can act as both the sulfur dioxide surrogate and reductant, it was found that zinc powder played an important role in the reaction since the reaction gave a lower yield of **2m** by switching zinc with other metals including copper and manganese or in the absence of zinc (Table S8,† entries 4–6). Notably, replacement of DMPPr with other common solvents, such as DMF or CH₃CN, afforded lower yields of **2m** (Table S8,† entries 7 and 8), demonstrating the unique solvent effect of DMPPr. Moreover, water was found to be vital for the desired reaction because no formation of **2m** was observed in its absence (Table S8,† entry 9). Finally,

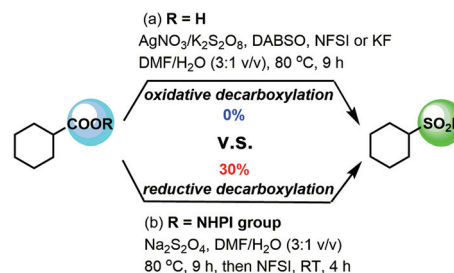


Fig. 2 Initial decarboxylative fluorosulfonylation attempt on aliphatic carboxylic acids.

further examination of reaction temperatures showed that lower or higher reaction temperatures had a deleterious effect on the reaction because 20 °C, 60 °C or 100 °C led to lower yields of the target product **2m** (Table S8,† entries 10–12). Detailed screening information on the reaction conditions can be found in the ESI.†

With the optimal reaction conditions successfully established, we next engaged in investigating the substrate scope of the reductive decarboxylative fluorosulfonylation of aliphatic carboxylic acids and the results are presented in Fig. 3. A wide range of aliphatic carboxylic acids including various primary, secondary, and tertiary aliphatic carboxylic acids can be applied to this transformation, providing the target aliphatic sulfonyl fluorides in good yields. For example, a number of

primary aliphatic carboxylic acids underwent smooth reductive decarboxylative fluorosulfonylation to give the desired aliphatic sulfonyl fluorides in modest to good yields (**2a–l**). When secondary aliphatic carboxylic acids were utilized as the substrates, the target products were successfully produced in nice yields (**2m–p**). Tertiary aliphatic carboxylic acids could also be applied to the reactions to provide the corresponding products in acceptable yields (**2q–t**). Gratifyingly, the reaction showed good compatibility with a variety of functional groups, including ether (**2g**, **2i**, **2n**, **2y**), halide (**2e**, **2k**, **2l**, **2u**), ketone (**2d**, **2w**, **2x**, **2bb**), ester (**2t**), alkenyl (**2z**), and hydroxyl (**2bb**) groups. Notably, substrates derived from benzyl carboxylic acids are suitable candidates for the protocol and various benzylic sulfonyl fluorides (**2h–2l**, **2p**, **2u–2y**) were obtained in good yields. Interestingly, benzylic sulfonyl fluorides **2x**, **2y**, and **2z** are not very stable, and cannot be subjected to column chromatography purification. Consequently, their corresponding derivatives were generated from their reactions with 1-naphthol to unambiguously characterize them. Finally, the superiority of this transformation was further demonstrated in the decarboxylative fluorosulfonylation of various natural or pharmaceutical molecules. The carboxylic groups of drugs such as flurbiprofen, ibuprofen, loxoprofen, ketoprofen, and naproxen could be smoothly transformed into the sulfonyl fluoride group in high yields by this decarboxylative fluorosulfonylation approach (**2u–2y**). Additionally, the reductive decarboxylative fluorosulfonylation of several natural carboxylic acids (**2z**, **2aa**, **2bb**) also permits efficient introduction of a sulfonyl fluoride group in good yields.

To broaden the scope and utility of this protocol, we decided to investigate the derivatization reactions of the aliphatic sulfonyl fluorides acquired. As shown in Fig. 4, the desired aliphatic sulfonyl fluoride **2v** was obtained in 70% isolated yield on a 6.0 mmol scale under the standard conditions *via* reductive decarboxylative fluorosulfonylation of ibuprofen, demonstrating the good viability of the transformation for scale-up. The aliphatic sulfonyl fluoride **2v** obtained was then treated with different N- or O-nucleophiles to give the corresponding products in good yields (**3–6**), which might be potentially useful molecules for organic synthesis or drug research.

Next, we conducted several preliminary control experiments to shed light on the mechanism of this transformation (Fig. 5).

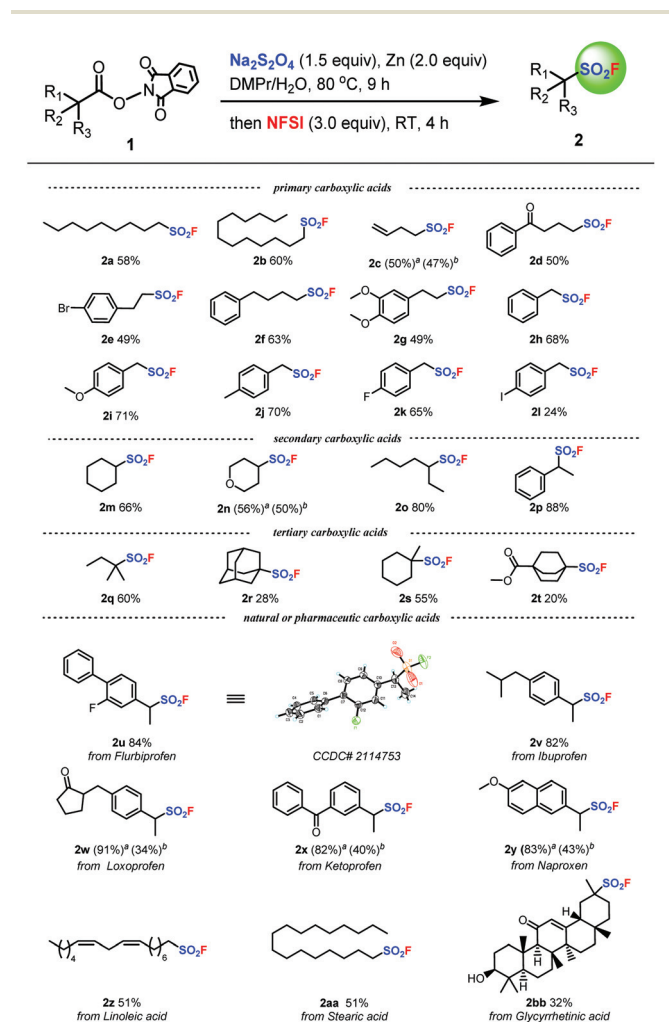


Fig. 3 Reaction conditions: **1** (0.4 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (0.6 mmol) and zinc (0.8 mmol) were reacted in a solvent system at 80 °C under the protection of Ar for 6–9 h, and then NFSI (3 equiv.) was added at room temperature for 4 h. Unless noted otherwise, the yields are of the isolated material. ^a Due to the high volatility or instability of the products, the yields were determined by ¹⁹F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard. ^b Derivatization of the desired sulfonyl fluorides with 1-naphthol was carried out in one pot and the isolated yields of the corresponding derivatives are reported.

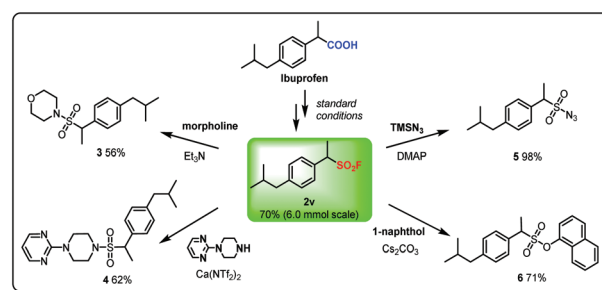


Fig. 4 Scale-up and derivatization reactions of the aliphatic sulfonyl fluoride **2v** achieved *via* reductive decarboxylative fluorosulfonylation of ibuprofen.

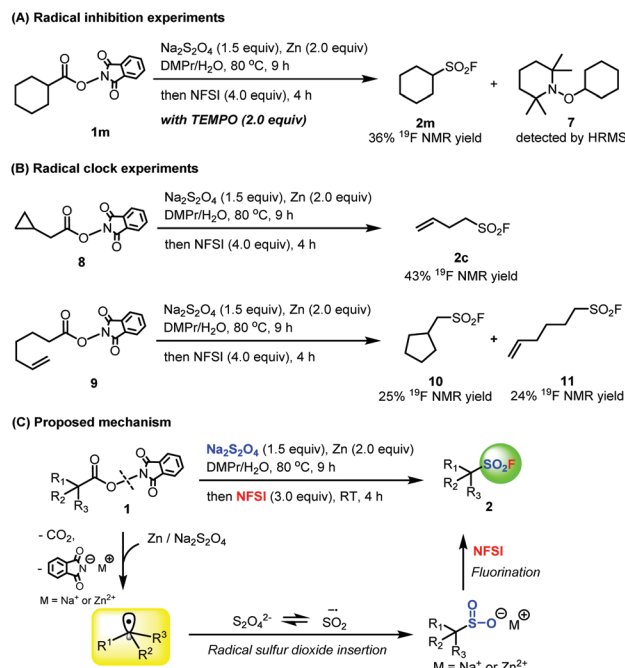


Fig. 5 Control experiments and the proposed mechanism.

First, a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the reductive decarboxylative fluorosulfonation reaction of **1a** under the standard reaction conditions, resulting in an obvious decrease in the yield and the observation of TEMPO-trapped complex **7** (Fig. 5A). Second, compound **8** as a radical probe was subjected to the standard reaction conditions, and the corresponding ring-opened fluoro-sulfonation product **2c** was obtained in 43% ^{19}F NMR yield (Fig. 5B). When compound **9** was utilized as a radical probe in the reaction to monitor if a radical intermediate was involved in the reaction, in addition to the desired product **11**, the alkyl radical formed *in situ* by reductive decarboxylation did undergo irreversible intramolecular cyclization to successfully produce the ring-closed product **10** (Fig. 5B). All these observations suggested that the reaction might proceed *via* a free radical pathway. On the basis of all the experimental results presented above and the literature,^{16,17} the plausible reaction mechanism is proposed as shown in Fig. 5C. Reductive decarboxylation of aliphatic carboxylic acid NHPI ester **1** by zinc or $\text{Na}_2\text{S}_2\text{O}_4$ generates the corresponding alkyl radical. This is rapidly trapped by the SO_2 radical anion generated from $\text{Na}_2\text{S}_2\text{O}_4$ to form the corresponding alkyl sulfinate. The desired aliphatic sulfonyl fluoride **2** was finally produced by subsequent rapid fluorination of the resulting alkyl sulfinate by NFSI.

Conclusions

In conclusion, a reductive decarboxylative fluorosulfonation reaction of aliphatic carboxylic acid NHPI ester has been developed *via* a radical sulfur dioxide insertion and fluorination strategy. Cheap and convenient $\text{Na}_2\text{S}_2\text{O}_4$ was used as the sulfur

dioxide surrogate. This method enables rapid and efficient transformation of a number of abundant aliphatic carboxylic acids, including primary, secondary, and tertiary ones, as well as several natural and pharmaceutical carboxylic acids, into various valuable aliphatic sulfonyl fluorides. We anticipate that this reductive decarboxylative fluorosulfonation reaction will provide a useful method to synthesize various potentially important aliphatic sulfonyl fluorides and promote their further study and application.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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