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Photocatalytic access to aromatic keto sulfonyl fluorides from vinyl fluorosulfates†

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We present herein an efficient photocatalytic transformation of vinyl fluorosulfates to aromatic β -keto sulfonyl fluorides with 1 mol% of iridium catalyst under the irradiation of 3 W blue LEDs. Preliminary mechanistic studies proposed a direct radical fragmentation and recombination of vinyl fluorosulfates through a free fluorosulfonyl radical (FSO_2^\cdot). This methodology provides a facile approach to aromatic β -keto sulfonyl fluorides, featuring sustainable conditions and a broad substrate scope (32 examples) with 33%–90% isolated yields.

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Introduction

Sulfonyl fluorides are valuable motifs not only in organic synthesis but also in chemical biology,¹ medicine² and materials science.³ Due to their special stability and reactivity pattern, sulfonyl fluorides have been widely utilized in Sulfur(vi) Fluoride Exchange (SuFEx) as the latest reaction for click chemistry, which is pioneered by Sharpless and applied widely to many research fields.⁴ Thus, there are increasing demands to develop efficient methods for the synthesis of various sulfonyl fluoride compounds, especially with highly-valued functionalities.

β -Keto sulfonyl fluorides have drawn special attention as they are highly functionalized with both fluorosulfonyl motifs and carbonyl groups, enabled with further possibility of post-functionalizations. Yet, compared to the well-developed methods to synthesize aliphatic⁵ or aromatic⁶ sulfonyl fluorides, strategies to prepare β -keto sulfonyl fluorides remain less explored. Early in 1990, Seppelt and co-workers reported a useful synthesis of β -keto sulfonyl fluoride through a multiple-step procedure with ketene (g) and SF_5Cl (g) (Scheme 1a).⁷ Recently, a facile strategy to synthesize β -keto sulfonyl fluoride that relied on F–Cl exchange between β -keto sulfonyl chloride and KH_2F was demonstrated by Hirai and co-workers

(Scheme 1b).⁸ Notably, a novel synthetic method involving the formation of the FSO_2 radical was developed most recently on the basis of an electrochemical oxidative process.⁹ The Huang and Liao groups demonstrated that β -keto sulfonyl fluorides can be synthesized through oxofluorosulfonylation of alkynes with sulfonyl chlorofluoride as the radical fluorosulfonyl source under electrochemical conditions with air as the oxidant (Scheme 1c). While impressive progress has been made to develop novel and diverse synthetic tools for the generation of β -keto sulfonyl fluorides, many of the reported examples generally require harsh conditions or usage of gaseous starting materials. Therefore, the development of new and efficient methods to synthesize β -keto fluorosulfones still remains highly desirable, especially with a broader substrate scope, milder reaction conditions and easier handling.

Vinyl fluorosulfates, as versatile substrates, have been used in transition-metal-catalyzed cross-coupling processes to form C–C bonds.¹⁰ Most recently, Michaudel and co-workers reported an elegant modular synthesis of β -keto sulfonamides from alkenyl sulfamates which are rapidly generated through SuFEx chemistry with vinyl fluorosulfates.¹¹ However, to the best of our knowledge, radical transformations directly with

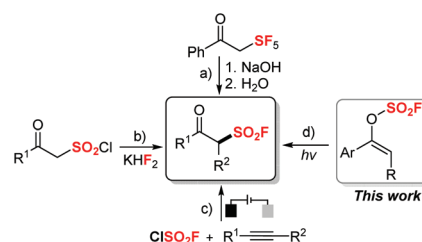
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Scheme 1 Synthetic approaches to β -keto sulfonyl fluorides.

vinyl fluorosulfates is seldom reported. Meanwhile, a sustainable photoredox strategy has witnessed remarkable development during the last few decades and been applied in many research fields.¹² Inspired by all these advances and in connection with our research interest in the synthesis of β -functionalized ketones from enolates *via* a radical fragmentation/recombination strategy,¹³ we envisioned that an efficient approach to various aromatic β -keto sulfonyl fluorides might be realized through photocatalytic radical rearrangement of vinyl fluorosulfates (Scheme 1d). Herein, we report our efforts on this approach.

Results and discussion

We initially investigated suitable reaction conditions by using vinyl fluorosulfate (**1a**) as the model substrate. The use of 1 mol% of [Ir(dFCF₃ppy)₂dtbbpy]PF₆ (**Ir 1**) as the photocatalyst, 30 W blue LEDs as the light source, and ethyl ether as the solvent at room temperature for 12 hours successfully delivered 6% ¹⁹F NMR yield of the target product **2a** along with 69% of unreacted **1a** (Table 1, entry 1). We then carried out further solvent screening. While reactions in ethyl acetate or toluene generated **2a** almost equally (33% in EA and 30% in toluene), toluene was chosen to be the optimal solvent as the substrate **1a** is more stable in toluene. By applying toluene as the preferred solvent, several photoredox catalysts, such as transition-metal catalysts (Ir or Ru) and organophotocatalysts (4-CzIPN or 9-fluorenone), were then screened. [Ir(dFCF₃ppy)₂dtbbpy]PF₆ (**Ir 3**) emerged as the leading catalyst

that improved the yield of **2a** to 48%. Upon careful evaluation of other parameters such as light sources, additives (K₂CO₃, Na₂CO₃, Et₃N and 4 Å MS), the reaction time and the reaction concentration (see the ESI† for details), the optimized conditions were as follows: **1a** (0.2 mmol), **Ir 3** (1 mol%) and 4 Å MS (44 mg) irradiated using 3 W blue LEDs at room temperature for 12 h (Table 1, entry 15). The desired product **2a** was generated in a good isolated yield of 81%, and the starting vinyl fluorosulfate **1a** was almost consumed.

With the optimized conditions in hand, we proceeded to investigate the broad applicability of this new approach for a library of vinyl fluorosulfates. As shown in Table 2, a variety of aromatic vinyl fluorosulfates with diverse electronic and steric properties have displayed satisfactory to good reactivity. Functional groups such as halogens, CF₃ and CN at the 3-, 4- or 5-position of the aromatic rings were well tolerated and the corresponding products were generated in 57%–87% yields

Table 1 Optimization of reaction conditions^a

Entry	Photocatalyst	Solvent	Additive	2a/1a ^b (%)
1	Ir 1	Et ₂ O	—	6/69
2	Ir 1	THF	—	18/54
3	Ir 1	DMF	—	<5/51
4	Ir 1	EA	—	33/36
5	Ir 1	Toluene	—	30/63
6	Ir 2	Toluene	—	<5/93
7	Ir 3	Toluene	—	48/21
8	Ru(bpy) ₃ Cl ₂	Toluene	—	<5/96
9	4-CzIPN	Toluene	—	21/60
10	9-Fluorenone	Toluene	—	33/60
11 ^c	Ir 3	Toluene	—	48/39
12 ^c	Ir 3	Toluene	Na ₂ CO ₃	78/<5
13 ^c	Ir 3	Toluene	K ₂ CO ₃	51/24
14 ^c	Ir 3	Toluene	Et ₃ N	<5/99
15 ^{c,d}	Ir 3	Toluene	4 Å MS	84(81)/<5

^a Reaction conditions: **1a** (0.2 mmol), photocatalyst (0.002 mmol, 1 mol%) and additive in solvent (2 mL), irradiated using 30 W blue LEDs at room temperature for 12 h under N₂. **Ir 1**: [Ir(dFCF₃ppy)₂bbpy]PF₆; **Ir 2**: *fac*-Ir(ppy)₃; **Ir 3**: [Ir(dFCF₃ppy)₂dtbbpy]PF₆. ^b Determined by crude ¹⁹F NMR analysis; isolated yield in parentheses. ^c Irradiated using 3 W blue LEDs. ^d 4 Å MS (44 mg) as an additive.

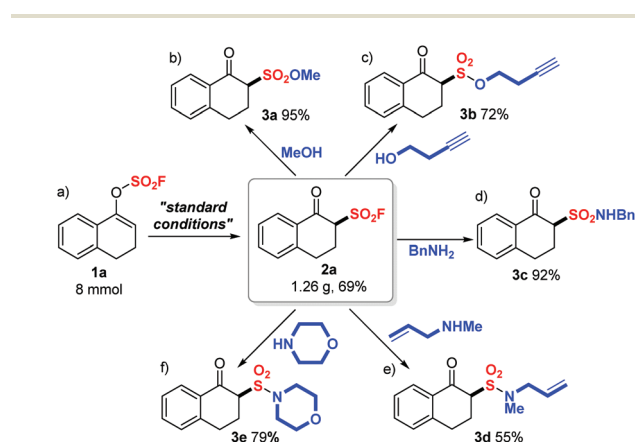
Table 2 Scope of substrates^a

Substrate	Yield (%)
1 (General structure)	Reaction conditions: [Ir(dFCF ₃ ppy) ₂ dtbbpy]PF ₆ (1 mol%), 4 Å MS (44 mg), 3 W blue LEDs, N ₂ , toluene (0.1 M), rt, 12 h
2a (81%)	
2b R = F	79%
2c R = Br	86%
2d R = CF ₃	72%
2e R = CN	59% ^b
2f R = Me	85%
2g R = Et	72%
2h R = ^t Bu	87%
2i R = OCF ₃	68% ^c
2j R = NMe ₂	N.R.
2k R = Ph	69%
2l R = F	70%
2m R = Cl	83%
2n R = Br	63%
2o R = CF ₃	59%
2p R = CN	57% ^b
2q R = Me	77%
2r R = Ph	79%
2s R = F	71%
2t R = Cl	87%
2u R = Br	58%
2v R = CF ₃	60%
2w R = CN	62% ^b
2x R = OSO ₂ F	49%
2y R = Ph	57%
2z R = F	33% ^c
2aa R = Me	N.R.
2ab	51% <i>dtr</i> 1:1.5
2ac R = H	90%
2ad R = Br	76%
2ae	57%
2af	N.R.
2ag	N.R.
2ah	40% ^d
2ai	48%
2aj	65%
2ak	57%

^a Reaction conditions: **1** (0.2 mmol), [Ir(dFCF₃ppy)₂dtbbpy]PF₆ (0.002 mmol, 1 mol%) and 4 Å MS (44 mg) in toluene (2 mL), irradiated using 3 W blue LEDs at room temperature for 12 h under N₂; isolated yields. ^b Irradiated for 24 h. ^c Na₂CO₃ (0.2 mmol, 1.0 equiv.) instead of 4 Å MS (44 mg). ^d THF as the solvent.

(Table 2, **2b–2e**, **2i–2p** and **2s–2w**). Substrates with alkyl, phenyl, OCF₃ or OSO₂F groups on aromatic rings also reacted smoothly to deliver the corresponding products in good yields of 49%–79% (Table 2, **2f–2i**, **2k**, **2q**, **2r**, **2x** and **2y**). Notably, substrate **1j**, bearing the dimethylamino group at the 4-position on the aromatic ring, is unsuitable for this transformation, and no desired product was formed with 60% of **1j** remaining. To our delight, substrate **1z**, which possessed an F group at the sterically hindered 6-position of the aromatic ring, underwent this transformation with a moderate yield of 33%. However, the reaction was totally hindered with substrate **1aa** harbouring a methyl group at the 6-position of the aromatic ring, and we reasoned that hydrogen abstraction at the benzylic C–H position was probably the main cause. Then we focused on the modifications to the enol motifs. To our delight, substrate **1ab** bearing a β-methyl group at the enol motif could render the expected product **2ab** in a synthetically useful yield of 51% with dr of 1 : 1.5. 1*H*-Inden-3-yl fluorosulfonates performed as good candidates, giving the desired products (**2ac** 90% and **2ad** 76%) without loss of efficiencies. Moreover, our attempt to construct 4-oxochromane-3-sulfonyl fluoride was also successful and the target β-keto sulfonyl fluoride **2ae** was formed in 57% yield. However, to our great disappointment, substrates derived from acyclic ketone (**1af**) or aliphatic ketone (**1ag**) could not generate the desired products. Additionally, substrates with sterically hindered substituents (**1ah–1ak**) were amenable for the transformation and the corresponding products were obtained in synthetically useful yields (40%–65%).

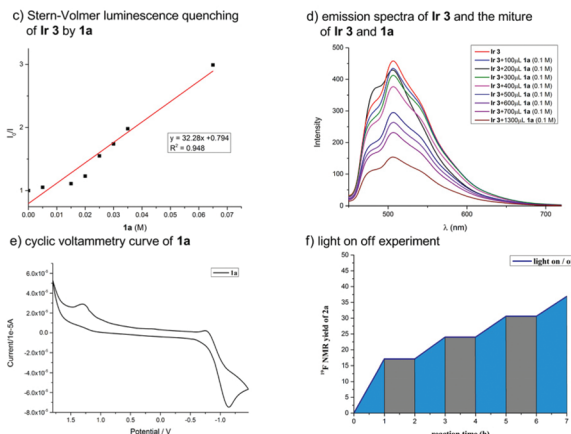
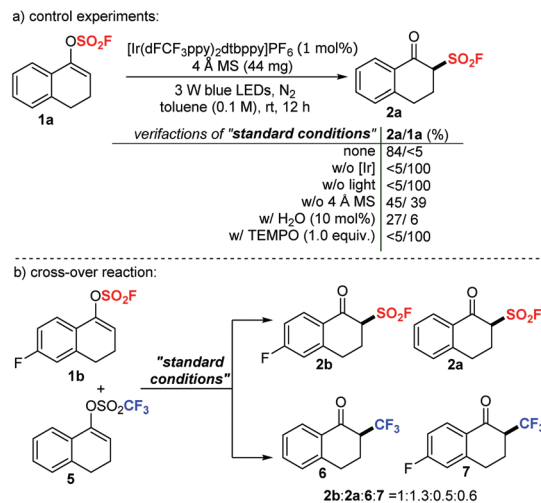
After the successful preparation of **2a** on an 8 mmol scale with a slightly decreased yield (1.26 g, 69%) (Scheme 2a), we then investigated the diversification of **2a** through SuFEx click reactions. As illustrated in Scheme 2b and c, β-keto sulfonyl fluoride **2a** readily underwent SuFEx with methanol or 3-butynol, affording the corresponding sulfonate esters **3a** and **3b** in good to quantitative yields (95% and 72%). Furthermore, sulfonamides **3c** (92%, Scheme 2d), **3d** (55%, Scheme 2e) and **3e** (79%, Scheme 2f) were generated smoothly through S–N bond formation reactions between **2a** and a primary amine



Scheme 2 Gram-scale synthesis and derivatizations of **2a**.

(benzyl amine) or secondary amines (*N*-methyl allyl amine or morphine).

To gain some mechanistic insights into this transformation, we carried out several experiments. Control experiments indicated that light irradiation and a photocatalyst were essential for the success of this transformation. In the absence of an additive, a much lower yield was obtained. Notably, **1a** decomposed readily with extra addition of H₂O (10 mol%); therefore, the desired product **2a** was formed in a dramatically decreased yield of 27%. According to these mechanistic results, we assumed that 4 Å MS could act partially as a drying agent that prevented vinyl fluorosulfates **1** from decomposition, and 4 Å MS could also work as a weak base to accelerate the transformation of vinyl fluorosulfates **1** to β-keto sulfonyl fluorides **2**. A typical radical scavenger TEMPO (1.0 equiv.) was introduced to the standard reaction system with **1a** and completely inhibited the reaction, suggesting the involvement of a radical mechanism (Scheme 3a). We then performed a crossover experiment by applying an equimolar amount of **1b** and **5** to the standard conditions (Scheme 3b). Four possible crossover products (**2b**, **2a**, **6** and **7**) were detected by crude ¹⁹F NMR in a ratio of



Scheme 3 Mechanistic studies.

1:1.3:0.5:0.6, suggesting the involvement of a free radical procedure.

To further clarify the mechanism, we applied DFT calculations on the triplet energy of vinyl fluorosulfate (**1a**) (for more details, see the ESI†). The calculated triplet energy of **1a** is 134 kJ mol⁻¹ which is much lower than the reported E_T of **Ir 3** (251 kJ mol⁻¹).^{14a,c} Therefore, a possibility of energy transfer between the initiator and the substrate is supported. We then carried out the fluorescence quenching experiments (Stern–Volmer studies) of **Ir 3**. As shown in Scheme 3c, the fluorescence intensity of the photocatalyst **Ir 3** decreased with increasing concentration of **1a**. A clear linear relationship was observed between I_0/I (I_0 is the fluorescence intensity of **Ir 3** before the addition of **1a** and I is the fluorescence intensity after the addition) and the concentration of **1a** (Scheme 3d). These fluorescence quenching results are consistent with the DFT calculations and supported a possibility of energy transfer or electron transfer between the photoexcited state **Ir 3** and **1a** at the initial stage. However, a reductive quenching cycle is also favored, based on the fact that the oxidation potential of **1a** ($E_{1/2}^{\text{red}} = +1.30$ V vs. SCE, as shown in Scheme 3e) is higher than that of **Ir 3** ($E_{1/2}^{*\text{III}/\text{II}} = +1.21$ V vs. SCE).^{14b} Light on/off experiments with **1a** under the standard conditions are shown in Scheme 3f. The fact that the reaction proceeded under the irradiation of light and almost stopped without light verified the possibility of a photocatalytic mechanism. Furthermore, the apparent quantum efficiency of the model transformation with **1a** was calculated to be 0.86, which indicates a photocatalytic mechanism (details in the ESI†).

According to the mechanistic studies and our previous work,¹³ we proposed a possible reaction pathway as follows (Scheme 4). Through energy transfer from the excited iridium(III) catalyst, vinyl fluorosulfate **1** underwent homolytic decomposition to generate the enol radical and the fluorosulfonyl radical. Subsequent radical reconstruction of the fluorosulfonyl radical and the enol radical would eventually form the desired product **2** (path A). Alternatively, a redox pathway *via* the reduction of **1** to a radical anion **I** by Ir(III)*, followed by radical fragmentation/reconstruction and oxidation, may also

be involved to some extent (path B). At this stage, we could not eliminate either of these two pathways.

Conclusions

In conclusion, a photocatalytic procedure to synthesize β -keto sulfonyl fluorides has been developed *via* radical fragmentation and recombination of vinyl fluorosulfates. 3 W blue LEDs were applied as the light source with 1 mol% of iridium(III) catalyst. This sustainable strategy enables the rapid and efficient transformation of a number of vinyl fluorosulfates into various valuable β -keto sulfonyl fluorides which would be widely utilized in SuFEx chemistry. We anticipate that this sustainable rearrangement reaction will provide an efficient strategy to synthesize various potentially valuable β -keto sulfonyl fluorides and contribute to their advanced studies and applications.

Author contributions

Dr X. S. and Dr Y. L. conceived the project and designed the experiments. J. C., S. W. and W. L. carried out the experiments. J. C., S. K. and J. Z. analysed the experimental data. S. X. performed the DFT calculations. Dr Y. L. and J. C. wrote the manuscript. All the authors discussed the results and commented on the manuscript.

Conflicts of interest

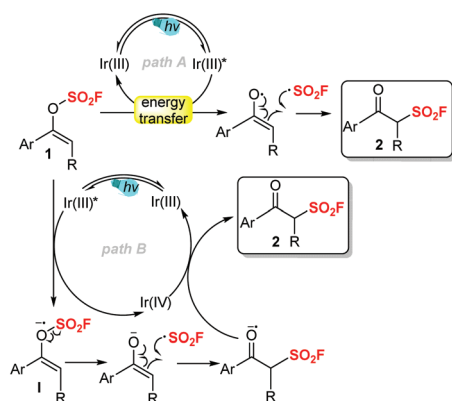
There are no conflicts to declare.

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Notes and references

- (a) A. M. Gold, Sulfonyl Fluorides as Inhibitors of Esterases. III. Identification of Serine as the Site of Sulfonylation in Phenylmethanesulfonyl α -Chymotrypsin, *Biochemistry*, 1965, **4**, 897–901; (b) A. J. Brouwer, T. Ceylan, A. M. Jonker, T. van der Linden and R. M. J. Liskamp, Synthesis and Biological Evaluation of Novel Irreversible Serine Protease Inhibitors Using Amino Acid Based Sulfonyl Fluorides as an Electrophilic Trap, *Bioorg. Med. Chem.*, 2011, **19**, 2397–2406; (c) A. J. Brouwer, N. H. Álvarez, A. Ciaffoni, H. van de Langemheen and R. M. J. Liskamp, Proteasome Inhibition by New Dual Warhead Containing Peptido Vinyl Sulfonyl Fluorides, *Bioorg. Med. Chem.*, 2016,



Scheme 4 Proposed mechanism.

- 24, 3429–3435; (d) J. M. Hatcher, G. Wu, C. Zeng, J. Zhu, F. Meng, S. Patel, W. Wang, S. B. Ficarro, A. L. Leggett, C. E. Powell, J. A. Marto, K. Zhang, J. C. K. Ngo, X.-D. Fu, T. Zhang and N. S. Gray, SRPKIN-1: A Covalent SRPK1/2 Inhibitor that Potently Converts VEGF from Pro-Angiogenic to Anti-Angiogenic Isoform, *Cell Chem. Biol.*, 2018, **25**, 460–470.
- 2 (a) A. J. Brouwer, A. Jonker, P. Werkhoven, E. Kuo, N. Li, N. Gallastegui, J. Kemmink, B. I. Florea, M. Groll, H. S. Overkleeft and R. M. J. Liskamp, Peptido Sulfonyl Fluorides as New Powerful Proteasome Inhibitors, *J. Med. Chem.*, 2012, **55**, 10995–11003; (b) L. H. Jones, Emerging Utility of Fluorosulfate Chemical Probes, *ACS Med. Chem. Lett.*, 2018, **9**, 584–586; (c) C. Baggio, P. Udompholkul, L. Gambini, A. F. Salem, J. Jossart, J. J. P. Perry and M. Pellicchia, Aryl-fluorosulfate-Based Lysine Covalent Pan-Inhibitors of Apoptosis Protein (IAP) Antagonists with Cellular Efficacy, *J. Med. Chem.*, 2019, **62**, 9188–9200.
- 3 (a) S. Tschan, A. J. Brouwer, P. R. Werkhoven, A. M. Jonker, L. Wagner, S. Knittel, M. N. Aminake, G. Pradel, F. Joanny, R. M. Liskamp and B. Mordmuller, Broad-Spectrum Antimalarial Activity of Peptido Sulfonyl Fluorides, a New Class of Proteasome Inhibitors, *Antimicrob. Agents Chemother.*, 2013, **57**, 3576–3584; (b) C. Yang, J. P. Flynn and J. Niu, Facile Synthesis of Sequence-Regulated Synthetic Polymers Using Orthogonal SuFEx and CuAAC Click Reactions, *Angew. Chem., Int. Ed.*, 2018, **57**, 16194–16199; (c) Q. Zheng, H. Xu, H. Wang, W.-G. H. Du, N. Wang, H. Xiong, Y. Gu, L. Noodleman, K. B. Sharpless, G. Yang and P. Wu, Sulfur [18F]Fluoride Exchange Click Chemistry Enabled Ultrafast Late-Stage Radiosynthesis, *J. Am. Chem. Soc.*, 2021, **143**, 3753–3763; (d) N. Suto, S. Kamoshita, S. Hosoya and K. Sakurai, Exploration of the Reactivity of Multivalent Electrophiles for Affinity Labeling: Sulfonyl Fluoride as a Highly Efficient and Selective Label, *Angew. Chem., Int. Ed.*, 2021, **60**, 17080–17087.
- 4 For reviews: (a) H. C. Kolb, M. G. Finn and K. B. Sharpless, Click Chemistry: Diverse Chemical Function from a Few Good Reactions, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021; (b) P. K. Chinthakindi and P. I. Arvidsson, Sulfonyl Fluorides (SFs): More Than Click Reagents?, *Eur. J. Org. Chem.*, 2018, 3648–3666; (c) A. S. Barrow, C. J. Smedley, Q. Zheng, S. Li, J. Dong and J. E. Moses, The Growing Applications of SuFEx Click Chemistry, *Chem. Soc. Rev.*, 2019, **48**, 4731–4758; (d) L. Xu and J. Dong, Click Chemistry: Evolving on the Fringe, *Chin. J. Chem.*, 2020, **38**, 414–419. For selected examples: (e) S. Li, P. Wu, J. E. Moses and K. B. Sharpless, Multidimensional SuFEx Click Chemistry: Sequential Sulfur(vi) Fluoride Exchange Connections of Diverse Modules Launched from an SOF4 Hub, *Angew. Chem., Int. Ed.*, 2017, **56**, 2903–2908; (f) B. Gao, S. Li, P. Wu, J. E. Moses and K. B. Sharpless, SuFEx Chemistry of Thionyl Tetrafluoride (SOF4) with Organolithium Nucleophiles: Synthesis of Sulfonimidoyl Fluorides, Sulfoximines, Sulfonimidamides and Sulfonimidates, *Angew. Chem., Int. Ed.*, 2018, **57**, 1939–1943; (g) D. E. Mortenson, G. J. Brighty, L. Plate, G. Bare, W. Chen, S. Li, H. Wang, B. F. Cravatt, S. Forli, E. T. Powers, K. B. Sharpless, I. A. Wilson and J. W. Kelly, “Inverse Drug Discovery” Strategy to Identify Proteins That Are Targeted by Latent Electrophiles as Exemplified by Aryl Fluorosulfates, *J. Am. Chem. Soc.*, 2018, **140**, 200–210; (h) C. Lee, A. J. Cook, J. E. Elisabeth, N. C. Friede, G. M. Sammis and N. D. Ball, The Emerging Applications of Sulfur(vi) Fluorides in Catalysis, *ACS Catal.*, 2021, **11**, 6578–6589; (i) C. J. Smedley, J. A. Homer, T. L. Gialelis, A. S. Barrow, R. A. Koelln and J. E. Moses, Accelerated SuFEx Click Chemistry for Modular Synthesis, *Angew. Chem.*, 2022, **61**, e202112375.
- 5 (a) J. Dong, L. Krasnova, M. G. Finn and K. B. Sharpless, Sulfur(vi) Fluoride Exchange (SuFEx): Another Good Reaction for Click Chemistry, *Angew. Chem., Int. Ed.*, 2014, **53**, 9430–9448; (b) H.-L. Qin, Q. Zheng, G. A. L. Bare, P. Wu and K. B. Sharpless, A Heck-Matsuda Process for the Synthesis of β -Arylethenesulfonyl Fluorides: Selectively Addressable Bis-electrophiles for SuFEx Click Chemistry, *Angew. Chem., Int. Ed.*, 2016, **55**, 14155–14158; (c) A. Shavnya, S. B. Coffey, K. D. Hesp, S. C. Ross and A. S. Tsai, Reaction of Alkyl Halides with Rongalite: One-Pot and Telescoped Syntheses of Aliphatic Sulfonamides, Sulfonyl Fluorides and Unsymmetrical Sulfones, *Org. Lett.*, 2016, **18**, 5848–5851; (d) P. K. Chinthakindi, K. B. Govender, A. S. Kumar, H. G. Kruger, T. Govender, T. Naicker and P. I. Arvidsson, A Synthesis of “Dual Warhead” β -Aryl Ethenesulfonyl Fluorides and One-Pot Reaction to β -Sultams, *Org. Lett.*, 2017, **19**, 480–483; (e) A. Talko and M. Barbasiewicz, Nucleophilic Fluorination with Aqueous Bifluoride Solution: Effect of the Phase-Transfer Catalyst, *ACS Sustainable Chem. Eng.*, 2018, **6**, 6693–6701; (f) G. Laudadio, A. de A. Bartolomeu, L. M. H. M. Verwijlen, Y. Cao, K. T. de Oliveira and T. Noël, Sulfonyl Fluoride Synthesis through Electrochemical Oxidative Coupling of Thiols and Potassium Fluoride, *J. Am. Chem. Soc.*, 2019, **141**, 11832–11836; (g) C. J. Smedley, G. Li, A. S. Barrow, T. L. Gialelis, M.-C. Giel, A. Ottonello, Y. Cheng, S. Kitamura, D. W. Wolan, K. B. Sharpless and J. E. Moses, Diversity Oriented Clicking (DOC): Divergent Synthesis of SuFExable Pharmacophores from 2-Substituted-Alkynyl-1-Sulfonyl Fluoride (SASF) Hubs, *Angew. Chem., Int. Ed.*, 2020, **59**, 12460–12469; (h) X. Nie, T. Xu, J. Song, A. Devaraj, B. Zhang, Y. Chen and S. Liao, Radical Fluorosulfonylation: Accessing Alkenyl Sulfonyl Fluorides from Alkenes, *Angew. Chem., Int. Ed.*, 2021, **60**, 3956–3960; (i) X. Nie, T. Xu, Y. Hong, H. Zhang, C. Mao and S. Liao, Introducing A New Class of Sulfonyl Fluoride Hubs via Radical Chloro-Fluorosulfonylation of Alkynes, *Angew. Chem., Int. Ed.*, 2021, **60**, 22035–22042; (j) N. L. Frye, C. G. Daniliuc and A. Studer, Radical 1-Fluorosulfonyl-2-alkynylation of Unactivated Alkenes, *Angew. Chem.*, 2022, **61**, e202115593.
- 6 (a) L. Tang, Y. Yang, L. Wen, X. Yang and Z. Wang, Catalyst-Free Radical Fluorination of Sulfonyl Hydrazides in Water,

- Green Chem.*, 2016, **18**, 1224–1228; (b) L. Revathi, L. Ravindar, J. Leng, K. P. Rakesh and H.-L. Qin, Synthesis and Chemical Transformations of Fluorosulfates, *Asian J. Org. Chem.*, 2018, **7**, 662–682; (c) C. Lee, N. D. Ball and G. M. Sammis, One-pot Fluorosulfurylation of Grignard Reagents Using Sulfuryl Fluoride, *Chem. Commun.*, 2019, **55**, 14753–14756; (d) L. Wang and J. Cornella, A Unified Strategy for Arylsulfur(vi) Fluorides from Aryl Halides: Access to Ar-SOF₃ Compounds, *Angew. Chem., Int. Ed.*, 2020, **59**, 23510–23515; (e) Y. Liu, D. Yu, Y. Guo, J. C. Xiao, Q. Y. Chen and C. Liu, Arenesulfonyl Fluoride Synthesis via Copper-Catalyzed Fluorosulfonylation of Arenediazonium Salts, *Org. Lett.*, 2020, **22**, 2281–2286; (f) T. Zhong, J. Yi, Z. Chen, Q. Zhuang, Y. Li, G. Lu and J. Weng, Photoredox-catalyzed Aminofluorosulfonylation of Unactivated Olefins, *Chem. Sci.*, 2021, **7**, 9359–9365; (g) M. Magre and J. Cornella, Redox-Neutral Organometallic Elementary Steps at Bismuth: Catalytic Synthesis of Aryl Sulfonyl Fluorides, *J. Am. Chem. Soc.*, 2021, **143**, 21497–21502; (h) Z. Ma, Y. Liu, X. Ma, X. Hu, Y. Guo, Q.-Y. Chen and C. Liu, Aliphatic Sulfonyl Fluoride Synthesis via Reductive Decarboxylative Fluorosulfonylation of Aliphatic Carboxylic Acid NHPI Esters, *Org. Chem. Front.*, 2022, **9**, 1115–1120.
- 7 T. Henkel, T. Krgerke and K. Seppelt, Isomerization of Benzoylalkylidene Sulfur Tetrafluorides C₆H₅-CO-CR-SF₄ to Dihydrooxathietes, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1128–1129.
- 8 (a) T. Hirai, D. Jomuta and C. Tamitsuji, Fluorosulfonyl Group-Containing Compound, Fluorosulfonyl Group-Containing Monomer and Their Production Methods, US 2020/0190025 A1, 2020; (b) T. Hirai, H. Watabe and S. Saito, Sulfonic Acid Group-Containing Polymer, Fluorosulfonyl Group-Containing Polymer and Liquid Coposition, US 2021/0380732 A1, 2021.
- 9 D. Chen, X. Nie, Q. Feng, Y. Zhang, Y. Wang, Q. Wang, L. Huang, S. Huang and S. Liao, Electrochemical Oxo-Fluorosulfonylation of Alkynes under Air: Facile Access to β -Keto Sulfonyl Fluorides, *Angew. Chem., Int. Ed.*, 2021, **60**, 27271–27276.
- 10 (a) P. S. Hanley, M. S. Ober, A. L. Krasovskiy, G. T. Whiteker and W. J. Kruper, Nickel- and Palladium-Catalyzed Coupling of Aryl Fluorosulfonates with Aryl Boronic Acids Enabled by Sulfuryl Fluoride, *ACS Catal.*, 2015, **5**, 5041–5046; (b) Q. Liang, P. Xing, Z. Huang, J. Dong, K. B. Sharpless, X. Li and B. Jiang, Palladium-Catalyzed, Ligand-Free Suzuki Reaction in Water Using Aryl Fluorosulfates, *Org. Lett.*, 2015, **17**, 1942–1945;
- (c) A. Markos, S. Voltrová, V. Motornov, D. Tichý, B. Klepetářová and P. Beier, Stereoselective Synthesis of (Z)- β -Enamido Triflates and Fluorosulfonates from N-Fluoroalkylated Triazoles, *Chem. – Eur. J.*, 2019, **25**, 7640–7644; (d) M. Mendel, I. Kalvet, D. Hupperich, G. Magnin and F. Schoenebeck, Site-Selective, Modular Diversification of Polyhalogenated Aryl Fluorosulfates (ArOSO₂F) Enabled by an Air-Stable PdI Dimer, *Angew. Chem., Int. Ed.*, 2020, **59**, 2115–2119.
- 11 F. C. S. Silva, K. Doktor and Q. Michaudel, Modular Synthesis of Alkenyl Sulfamates and β -Ketosulfonamides via Sulfur(vi) Fluoride Exchange (SuFEx) Click Chemistry and Photomediated 1,3-Rearrangement, *Org. Lett.*, 2021, **23**, 5271–5276.
- 12 (a) N. A. Romero and D. A. Nicewicz, Organic Photoredox Catalysis, *Chem. Rev.*, 2016, **116**, 10075–10166; (b) C. S. Wang, P. H. Dixneuf and J. F. Soule, Photoredox Catalysis for Building C–C Bonds from C(sp²)-H Bonds, *Chem. Rev.*, 2018, **118**, 7532–7585; (c) X.-Y. Yu, J.-R. Chen and W.-J. Xiao, Visible Light-Driven Radical-Mediated C–C Bond Cleavage/Functionalization in Organic Synthesis, *Chem. Rev.*, 2021, **121**, 506–561; (d) N. H. Douglas and D. A. Nicewicz, Photoredox-Catalyzed C–H Functionalization Reactions, *Chem. Rev.*, 2022, **122**, 1925–2016; (e) A. Y. Chan, I. B. Perry, N. B. Bissonnette, B. F. Buksh, G. A. Edwards, L. I. Frye, O. L. Garry, M. N. Lavagnino, B. X. Li, Y. Liang, E. Mao, A. Millet, J. V. Oakley, N. L. Reed, H. A. Sakai, C. P. Seath and D. W. C. MacMillan, Metallaphotoredox: The Merger of Photoredox and Transition Metal Catalysis, *Chem. Rev.*, 2022, **122**, 1485–1542.
- 13 (a) X. Su, H. Huang, Y. Yuan and Y. Li, Radical Desulfur-Fragmentation and Reconstruction of Enol Triflates: Facile Access to α -Trifluoromethyl Ketones, *Angew. Chem., Int. Ed.*, 2017, **56**, 1338–1341; (b) L. Xie, X. Zhen, S. Huang, X. Su, M. Lin and Y. Li, Photoinduced Rearrangement of Vinyl Tosylates to β -Ketosulfones, *Green Chem.*, 2017, **19**, 3530–3534.
- 14 (a) J. I. Day, K. Teegardin, J. Weaver and J. Chan, Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations, *Org. Process Res. Dev.*, 2016, **20**, 1156–1163; (b) N. A. Romero and D. A. Nicewicz, Organic Photoredox Catalysis, *Chem. Rev.*, 2016, **116**, 10075–10166; (c) M. R. Becker, E. R. Wearing and C. S. Schindler, Synthesis of Azetidines via Visible-Light-Mediated Intermolecular [2+2] Photocycloaddition, *Nat. Chem.*, 2020, **12**, 898–905.