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Photocatalytic access to aromatic keto sulfonyl fluorides from vinyl fluorosulfates†

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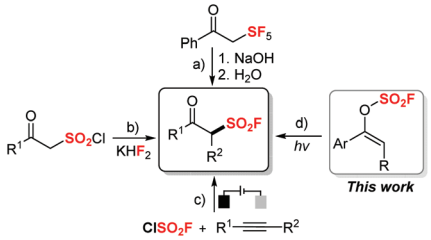
We present herein an efficient photocatalytic transformation of vinyl fluorosulfates to aromatic β-keto sulfonyl fluorides with 1 mol% of iridium catalyst under the irradiation of 3 W blue LEDs. Preliminary mechanistic studies proposed a direct radical fragmentation and recombination of vinyl fluorosulfates through a free fluorosulfonyl radical ($FSO_2^{\bullet}$). 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.

Introduction

Sulfonyl fluorides are valuable motifs not only in organic synthesis but also in chemical biology,[1] medicine[2] 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 aliphatic[5] or aromatic[6] 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 sulfuryl 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



Scheme 1 Synthetic approaches to β-keto sulfonyl fluorides.

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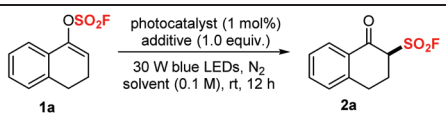
vinyl fluorosulfates is seldom reported. Meanwhile, a sustainable photoredox strategy has witnessed remarkable development during the last few decades and been applied in many research fields.[12] Inspired by all these advances and in connection with our research interest in the synthesis of β-functionalized 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 $[Ir(dFCF_3ppy)_2bbpy]PF_6$ (**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% ^{19}F 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. $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (**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 (K_2CO_3, Na_2CO_3, Et_3N 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, CF_3 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

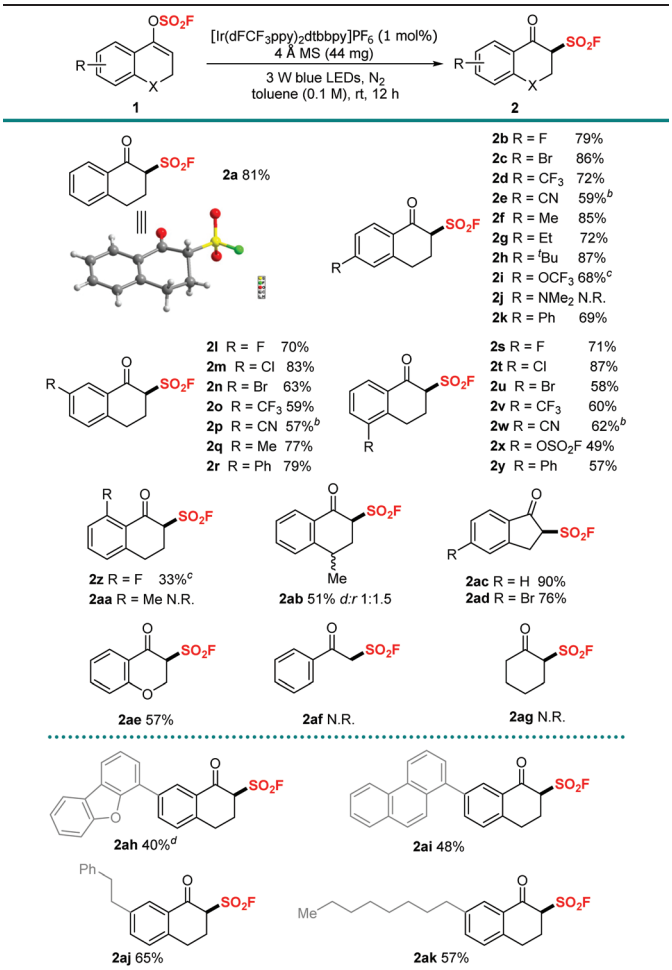
Table 1 Optimization of reaction conditions[a]



Entry	Photocatalyst	Solvent	Additive	**2a**/**1a**[b] (%)
1	**Ir 1**	Et_2O	—	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	$Ru(bpy)_3Cl_2$	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_2CO_3	78/<5
13[c]	**Ir 3**	Toluene	K_2CO_3	51/24
14[c]	**Ir 3**	Toluene	Et_3N	<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 N_2. **Ir 1**: $[Ir(dFCF_3ppy)_2bbpy]PF_6$; **Ir 2**: *fac*-Ir(ppy)$_3$; **Ir 3**: $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$. [b] Determined by crude ^{19}F 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]

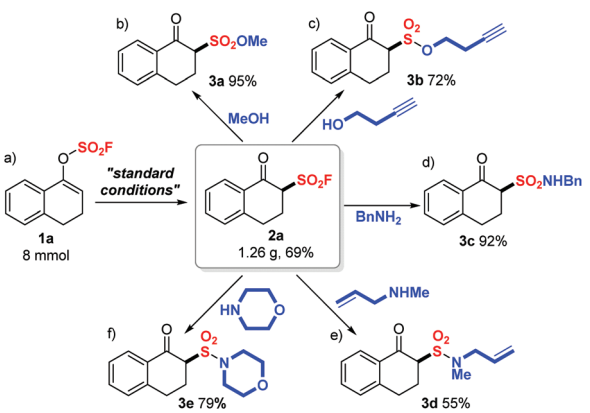


[a] Reaction conditions: **1** (0.2 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.002 mmol, 1 mol%) and 4 Å MS (44 mg) in toluene (2 mL), irradiated using 3 W blue LEDs at room temperature for 12 h under N_2; isolated yields. [b] Irradiated for 24 h. [c] Na_2CO_3 (0.2 mmol, 1.0 equiv.) instead of 4 Å MS (44 mg). [d] THF as the solvent.

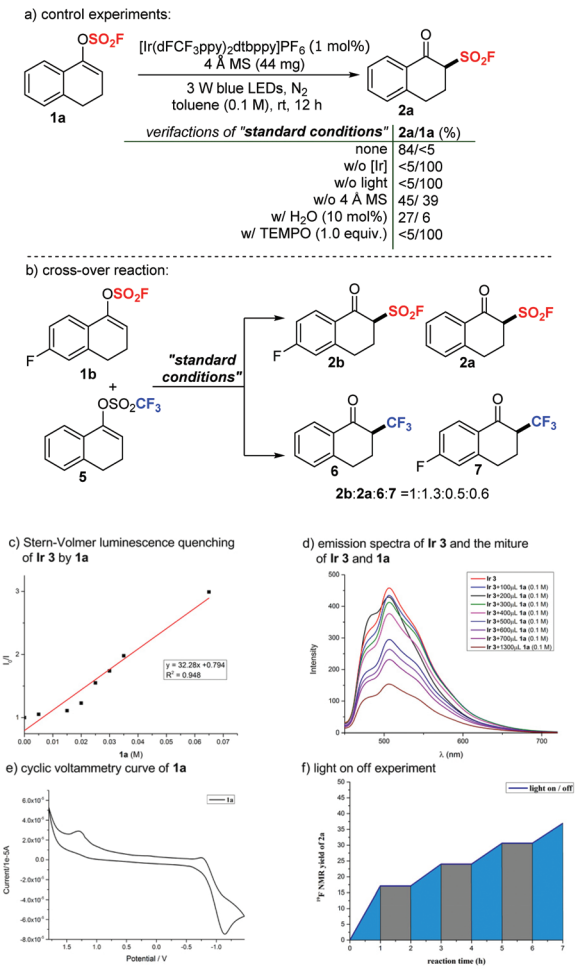
(Table 2, **2b–2e**, **2i–2p** and **2s–2w**). Substrates with alkyl, phenyl, OCF_3 or OSO_2F groups on aromatic rings also reacted smoothly to deliver the corresponding products in good yields of 49%–79% (Table 2, **2f–2i**, **2k**, **2q**, **2r**, **2x** and **2y**). Notably, substrate **1j**, bearing 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 (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 H_2O (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 ^{19}F NMR in a ratio of



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

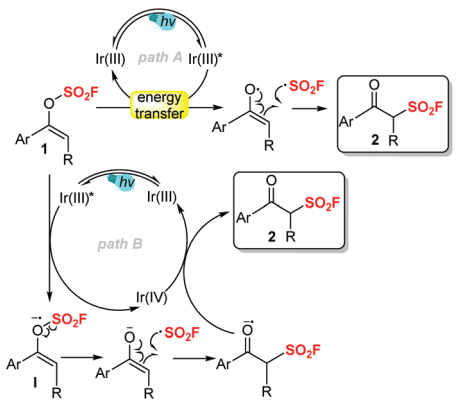


Scheme 3 Mechanistic studies.

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** ($E^{red}_{1/2}$ = +1.30 V *vs.* SCE, as shown in Scheme 3e) is higher than that of **Ir 3** ($E^{*III/II}_{1/2}$ = +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.



Scheme 4 Proposed mechanism.

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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