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# Access to chiral β-sulfonyl carbonyl compounds *via* photoinduced organocatalytic asymmetric radical sulfonylation with sulfur dioxide†

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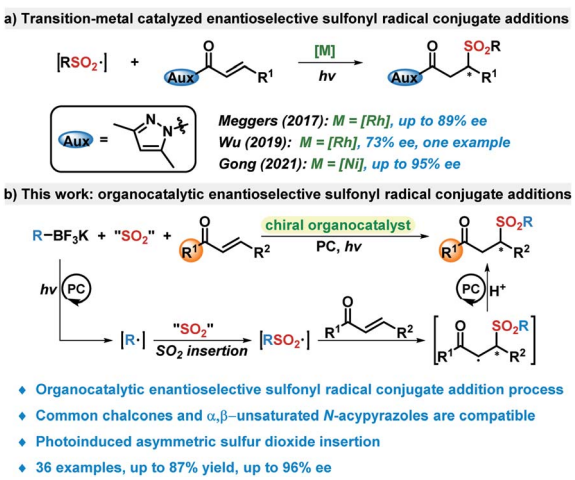
An organocatalytic enantioselective radical reaction of potassium alkyltrifluoroborates, DABCO·$(SO_2)_2$ and α,β-unsaturated carbonyl compounds under photoinduced conditions is developed, which provides an efficient pathway for the synthesis of chiral β-sulfonyl carbonyl compounds in good yields with excellent enantioselectivity (up to 96% ee). Aside from α,β-unsaturated carbonyl compounds with auxiliary groups, common chalcone substrates are also well compatible with this organocatalytic system. This method proceeds through an organocatalytic enantioselective radical sulfonylation under photoinduced conditions, and represents a rare example of asymmetric transformation involving sulfur dioxide insertion.

## Introduction

The catalytic asymmetric conjugate addition of α,β-unsaturated carbonyl compounds is one of the most powerful synthesis strategies for the synthesis of chiral β-substituted carbonyl compounds.[1] Compared with the well-developed classic Michael addition, the photoinduced radical addition process provides more promising opportunities since the high activity of radical species can overcome the inherent deficiencies of the traditional pathway in terms of substrate activity and steric hindrance. Since the pioneering work of Bach in photoinduced catalytic enantioselective radical addition,[2] research in this field has developed rapidly. Various carbon-centered radicals or N-centered radicals are compatible in this transformation, leading to diverse chiral β-substituted carbonyl compounds.[3,4]

Chiral sulfur-containing molecules are ubiquitous in market drugs and bioactive molecules.[5] Great attention has been devoted to the catalytic asymmetric synthesis of enantioenriched sulfones and considerable progress has been made in recent years.[6] However, construction of chiral sulfones through a catalytic enantioselective radical process remains challenging. There are few reports on catalytic asymmetric sulfonyl radical conjugate addition to α,β-unsaturated carbonyl compounds, which would afford biologically interesting enantioenriched β-sulfonyl carbonyl compounds (Scheme 1a). In 2017, Meggers and co-workers described a photoinduced, chiral Rh catalyzed enantioselective reaction of allyl sulfones with α,β-unsaturated *N*-acylpyrazoles, affording a sulfonyl radical asymmetric addition product.[7] In 2019, Wu and co-workers reported one example to access a chiral β-sulfonyl carbonyl compound using sulfinic acid as a sulfonyl radical source.[8] Recently, Gong and co-workers demonstrated a photoinduced asymmetric sulfonyl radical addition to α,β-unsaturated carbonyl compounds under chiral nickel catalysis.[9] The sulfonyl radical was generated *in situ* from the reaction of the C($sp^3$)–H precursor and




Scheme 1 Catalytic asymmetric sulfonyl radical conjugate addition to α,β-unsaturated carbonyl compounds.

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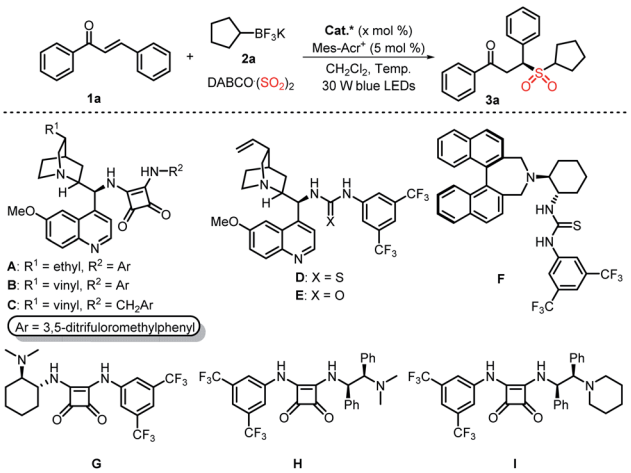
DABCO·$(SO_2)_2$ in this transformation. Despite significant advances, the aforementioned metal-catalyzed radical additions still suffer from substrate limitations, where the coordination of an auxiliary group to the metal center is essential for substrate activation and stereochemical control. The development of a novel catalytic system for the asymmetric synthesis of chiral β-sulfonyl carbonyl compounds with excellent enantioselectivity and broader substrate scope is still highly desirable.

On the other hand, construction of a sulfonyl nucleus through the radical-based sulfur dioxide insertion strategy has been developed rapidly.[10,11] Based on our continuous interest in radical-based sulfur dioxide insertion and recent success in squaramide catalyzed asymmetric addition of sulfonyl radicals to VQMs (vinylidene *ortho*-quinone methides),[12] we develop an organocatalytic enantioselective radical reaction of α,β-unsaturated carbonyl compounds, potassium alkyltrifluoroborates, and DABCO·$(SO_2)_2$ under visible light irradiation, affording chiral β-sulfonyl carbonyl compounds in good yields with excellent enantioselectivity (up to 96% ee). This method proceeds through a photoinduced organocatalytic enantioselective sulfonyl radical conjugate addition process, and represents a rare example of asymmetric transformation involving sulfur dioxide insertion (Scheme 1b).

## Results and discussion

We commenced this study by using commercially available chalcone **1a** and potassium cyclopentyltrifluoroborate **2a** as

Table 1 Initial studies for the reaction of chalcone **1a**, potassium cyclopentyltrifluoroborate **2a** and DABCO·$(SO_2)_2$[a]




| Entry | PC (mol%) | Cat* (mol%) | $T$ (°C) | Solvent | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|---|---|
| 1 | Mes-Acr$^+$$ClO_4^-$ | **A** (5) | −5 | $CH_2Cl_2$ | 80 | −68 |
| 2 | Mes-Acr$^+$$ClO_4^-$ | **B** (5) | −5 | $CH_2Cl_2$ | 78 | −73 |
| 3 | Mes-Acr$^+$$ClO_4^-$ | **C** (5) | −5 | $CH_2Cl_2$ | 78 | −60 |
| 4 | Mes-Acr$^+$$ClO_4^-$ | **D** (5) | −5 | $CH_2Cl_2$ | 78 | −60 |
| 5 | Mes-Acr$^+$$ClO_4^-$ | **E** (5) | −5 | $CH_2Cl_2$ | 88 | −68 |
| 6 | Mes-Acr$^+$$ClO_4^-$ | **F** (5) | −5 | $CH_2Cl_2$ | 84 | −46 |
| 7 | Mes-Acr$^+$$ClO_4^-$ | **G** (5) | −5 | $CH_2Cl_2$ | 72 | 60 |
| 8 | Mes-Acr$^+$$ClO_4^-$ | **H** (5) | −5 | $CH_2Cl_2$ | 84 | 80 |
| 9 | Mes-Acr$^+$$ClO_4^-$ | **I** (5) | −5 | $CH_2Cl_2$ | 78 | 80 |
| 10 | *fac*-Ir(ppy)$_3$ | **H** (5) | −5 | $CH_2Cl_2$ | n.r. | — |
| 11 | [Ir(dFCF$_3$ppy)$_2$bpy]PF$_6$ | **H** (5) | −5 | $CH_2Cl_2$ | n.r. | — |
| 12 | Ru(bpy)$_3$Cl$_2$ | **H** (5) | −5 | $CH_2Cl_2$ | n.r. | — |
| 13 | Mes-Acr$^+$$ClO_4^-$ | **H** (5) | −20 | $CH_2Cl_2$ | 54 | 89 |
| 14 | Mes-Acr$^+$$ClO_4^-$ | **H** (5) | −20 | $CHCl_3$ | 70 | 87 |
| 15 | Mes-Acr$^+$$ClO_4^-$ | **H** (5) | −20 | EtOAc | 30 | 93 |
| 16 | Mes-Acr$^+$$ClO_4^-$ | **H** (5) | −20 | $^i$PrOH | 20 | 86 |
| 17 | Mes-Acr$^+$$ClO_4^-$ | **H** (5) | −20 | MTBE | 32 | 73 |
| 18 | Mes-Acr$^+$$ClO_4^-$ | **H** (5) | −20 | MeCN | 56 | 93 |
| 19 | Mes-Acr$^+$$ClO_4^-$ | **H** (1) | −20 | MeCN | 64 (60) | 95 |
| 20 | Mes-Acr$^+$$ClO_4^-$ | — | −20 | MeCN | Trace | — |
| 21[d] | Mes-Acr$^+$$ClO_4^-$ | **H** (1) | −20 | MeCN | n.r. | — |
| 22[e] | Mes-Acr$^+$$ClO_4^-$ | **H** (1) | −20 | MeCN | n.r. | — |

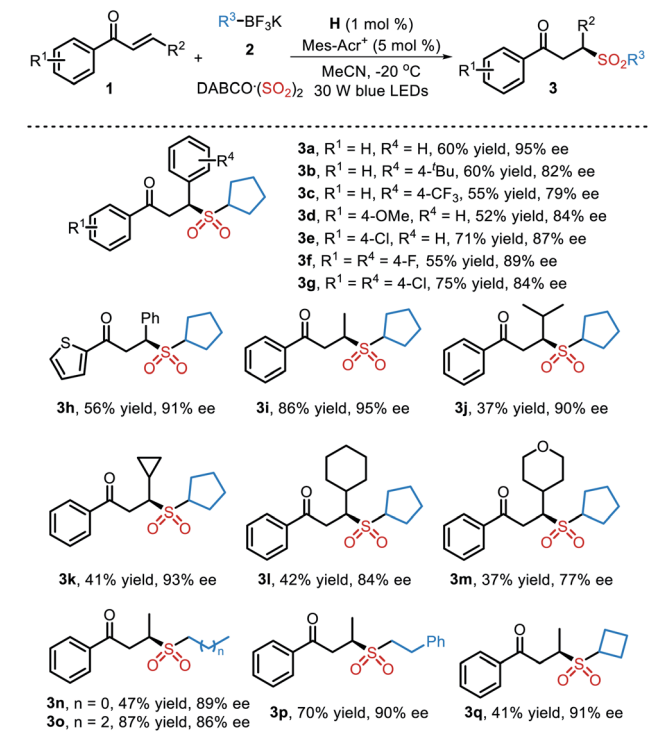
[a] Reaction conditions: chalcone **1a** (0.1 mmol), potassium cyclopentyltrifluoroborate **2a** (0.2 mmol), DABCO·$(SO_2)_2$ (0.1 mmol), Mes-Acr$^+$$ClO_4^-$ (5 mol%), solvent (2.0 mL), 30 W blue LED, 72 h. [b] Determined by $^1$H NMR analysis (isolated yield in parentheses). [c] Determined by HPLC analysis on a chiral stationary phase. [d] In the dark. [e] In the absence of Mes-Acr$^+$.

model substrates with DABCO·$(SO_2)_2$ as the sulfur dioxide surrogate to explore suitable reaction conditions (Table 1). Pleasingly, the reaction proceeded smoothly with **A** as the organocatalyst, and Mes-Acr$^+ClO_4^-$ as the photocatalyst in $CH_2Cl_2$ at −5 °C, providing the desired product **3a** in 80% NMR yield with −68% ee (Table 1, entry 1). Encouraged by this result, we then examined the reaction with other bifunctional organocatalysts **B–I** (Table 1, entries 2–9). It was found that **H** was the optimal oraganocatalyst in terms of yield and enantioselectivity (Table 1, entry 8). No reaction occurred when other Ir or Ru photocatalysts were used in this reaction (Table 1, entries 10–12). Lowering the reaction temperature to −20 °C resulted in an improvement of enantioselectivity, albeit with a slightly decreased yield (Table 1, entry 13). Furthermore, the screening of solvents including $CHCl_3$, EtOAc, $^i$PrOH, MTBE, and MeCN showed that MeCN was the ideal solvent for this transformation (Table 1, entries 14–18). Remarkably, when the loading of catalyst **H** was decreased to 1 mol%, an improved yield and ee value of **3a** was obtained (Table 1, entry 19). Control experiments without an organocatalyst, light irradiation, or a photocatalyst suggested that these components were all essential to achieve a product with excellent enantioselectivity (Table 1, entries 20 and 21).

Under optimal reaction conditions, the substrate scope of this organocatalytic asymmetric three-component reaction with respect to α,β-unsaturated ketones **1** and potassium alkyltrifluoroborates **2** was investigated (Table 2). In general, the reaction proceeded smoothly with a wide range of substrates to give the desired products in moderate to good yields with universally high enantioselectivities. For example, α,β-unsaturated ketones bearing both electron-donating or -withdrawing substituents on the phenyl group participated in the reaction well to furnish the corresponding products **3b–3g**. Changing the aryl group of $R^2$ to an alkyl group had little effect on the enantioselectivities (**3i–3m**). Moreover, the reaction was also compatible with primary potassium alkyltrifluoroborates, leading to the chiral sulfones **3n–3p** in 47–87% yields with 86–90% ee. The absolute configuration of **3d** was determined to be *S* by single-crystal X-ray diffraction analysis.[13] No product was obtained when phenyltrifluoroborate was utilized in this reaction under the standard reaction conditions.

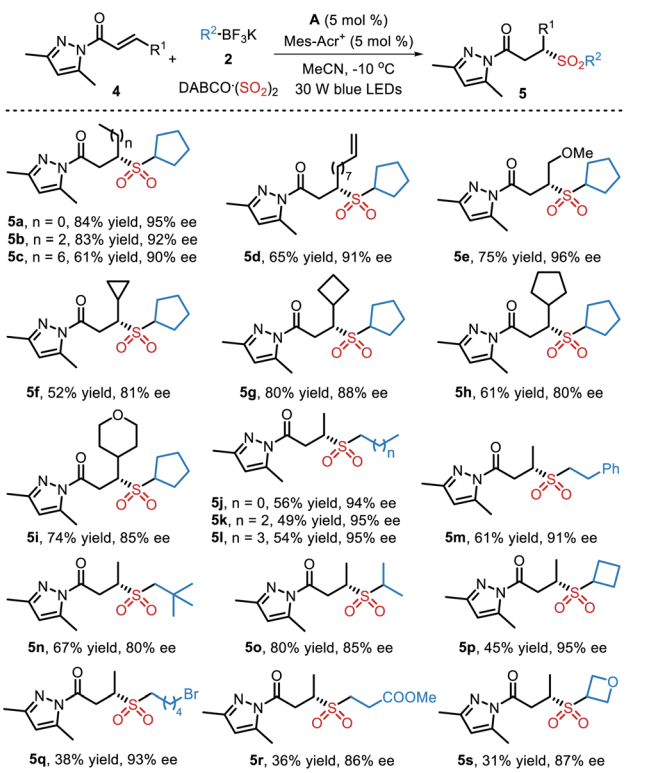
Subsequently, the generality of this transformation utilizing α,β-unsaturated *N*-acylpyrazoles as radical acceptors was also explored. As summarized in Table 3, a variety of structurally diverse chiral sulfones were afforded under slightly modified reaction conditions (see the ESI for details). It was found that α,β-unsaturated *N*-acylpyrazoles with different substituents ($R^1$) were all suitable for this reaction, providing the chiral products **5a–5i** in moderate to good yields with high ee values. The absolute configuration of **5a** was assigned as *S* by comparison with Gong's work.[9] Additionally, both primary and secondary potassium alkyltrifluoroborates worked well and delivered the target products **5j–5q** in 31–80% yields with 80–95% ee.

Table 2 Scope exploration for the reaction of α,β-unsaturated ketones **1**, potassium alkyltrifluoroborates **2** and DABCO·$(SO_2)_2$[a]

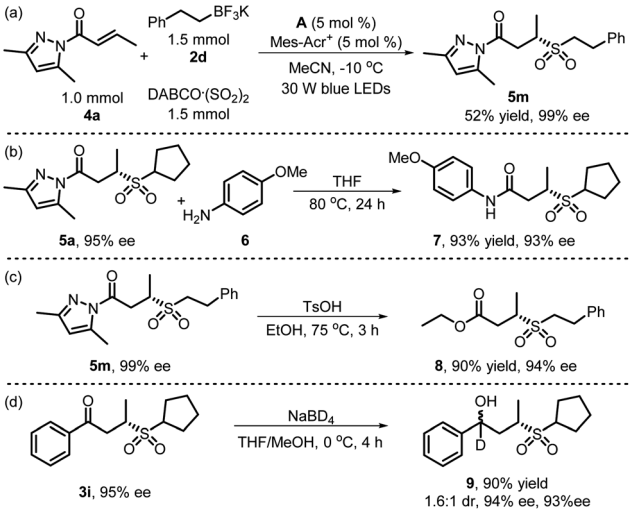



[a] Isolated yield based on α,β-unsaturated ketone **1**.

Table 3 Scope exploration for the reaction of α,β-unsaturated *N*-acylpyrazoles **4**, potassium alkyltrifluoroborates **2** and DABCO·$(SO_2)_2$[a]



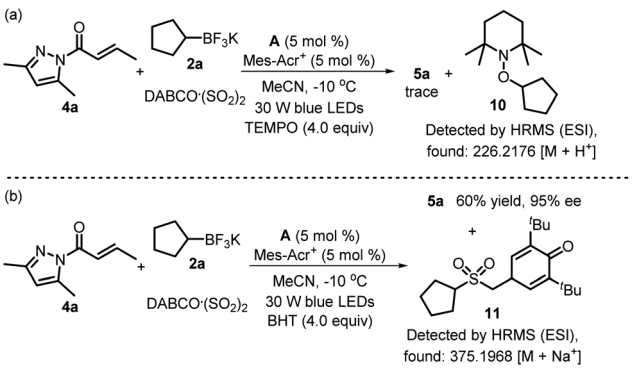

[a] Isolated yield based on α,β-unsaturated *N*-acylpyrazole **4**.



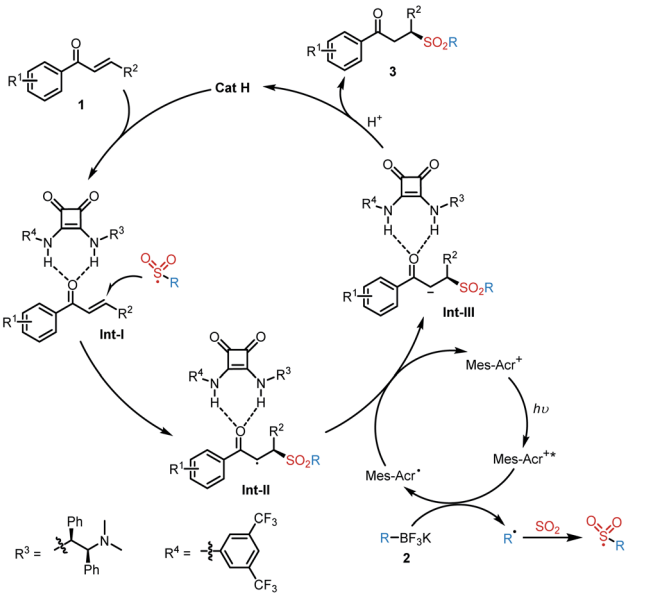

Scheme 2 (a) Large-scale synthesis. (b)–(d) Synthetic transformations.

To further evaluate the practicality of this method, a 1 mmol scale reaction of α,β-unsaturated *N*-acylpyrazole **4a**, potassium phenethyltrifluoroborate **2d** and DABCO·$(SO_2)_2$ was carried out under standard conditions, affording the desired product **5m** in 52% yield and with 99% ee (Scheme 2a). In addition, the pyrazole moiety of chiral sulfone product **5a** could be substituted by 4-methoxyaniline **6** and delivered the amide derivative **7** in 91% yield with 93% ee (Scheme 2b). Furthermore, esterification product **8** could be generated in 90% yield with 94% ee from the reaction of chiral sulfone product **5m** with ethanol (Scheme 2c). Next, a γ-hydroxy sulfone product could be constructed by the hydrogenation of the carbonyl group of chiral sulfone product **3i**, and γ-hydroxy sulfone product **9** could be obtained in 90% yield with 1.6 : 1 dr (94% ee, 93% ee) (Scheme 2d).

Next, two control experiments were performed to elucidate the reaction mechanism. As shown in Scheme 3a, the reaction of α,β-unsaturated *N*-acylpyrazole **4a**, potassium cyclopentyltrifluoroborate **2a** and DABCO·$(SO_2)_2$ was completely suppressed in the presence of 4.0 equiv. of radical scavenger TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) under standard conditions, and radical trapping adduct **10** was detected by




Scheme 3 (a) Radical trapping with TEMPO. (b) Radical trapping with BHT.




Scheme 4 Proposed mechanism.

HRMS (high-resolution mass spectrometry). Moreover, the addition of 4.0 equiv. of another radical scavenger BHT (butylated hydroxytoluene) led to a decreased yield of product **5a** with retention of enantioselectivity, and confirmed the existence of a sulfonyl radical upon the detection of compound **11** (Scheme 3b). Taken together, these results suggested that the organocatalytic asymmetric reaction involved a radical process.

Based on the above experiment results and previous reports on the organocatalytic asymmetric radical transformations,[14] a plausible reaction pathway for this photoinduced enantioselective radical sulfonylation with sulfur dioxide is shown in Scheme 4. Initially, potassium alkyltrifluoroborate **2** could be oxidized by a photocatalyst under visible light irradiation to afford the alkyl radical, which would react with sulfur dioxide to generate the alkylsulfonyl radical. The asymmetric addition of a sulfonyl radical to substrate **1** was achieved by the hydrogen-bond interaction in the presence of chiral squaramide catalyst **H**, giving rise to the chiral radical intermediate **Int II** in the *S* configuration. Subsequently, **Int II** would undergo single electron transfer (SET) reduction to produce the anion intermediate **Int-III**. The desired product **3** was obtained by the protonation of **Int-III** and regeneration of the organocatalyst **H**.

## Conclusions

In conclusion, we have developed a photoinduced enantioselective organocatalytic radical conjugate addition to access enantioenriched β-sulfonyl carbonyl compounds through a three-component reaction of potassium alkyltrifluoroborates, DABCO·$(SO_2)_2$ and α,β-unsaturated carbonyl compounds. Chiral β-sulfonyl carbonyl compounds were achieved with excellent enantioselectivity and good yields. This process features mild reaction conditions and broad substrate scope. Not only α,β-unsaturated carbonyl compounds with auxiliary

groups, but also common chalcone substrates were workable in this reaction. This method represents a rare example of asymmetric transformation involving sulfur dioxide insertion as well.

## Data availability

The data supporting this study are available within the article and the ESI.† The X-ray crystallographic coordinates for the structure of **3d** have been deposited at the Cambridge Crystallographic Data Center (CCDC: 2165683).

## Author contributions

F.-S. H. and C. Z. contributed equally to this work. S. Y. conceived the study. F.-S. H. and C. Z. conducted the experiments and analysed the data. M. J. and L. L. conducted the preparation of the starting materials. S. Y. and J. W. directed the project. S. Y. and F.-S. H. prepared the manuscript. C. Z. prepared the ESI.† All authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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