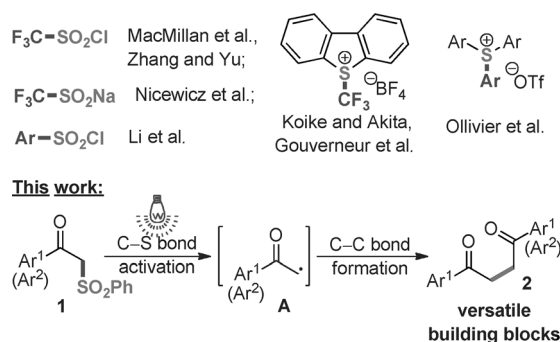


Photoredox Catalysis

Visible-Light-Induced C–S Bond Activation: Facile Access to 1,4-Diketones from β -KetosulfonesJun Xuan,^[a] Zhu-Jia Feng,^[a] Jia-Rong Chen,^[a] Liang-Qiu Lu,^{*[a]} and Wen-Jing Xiao^{*[a, b]}

Abstract: A novel method for the synthesis of 1,4-diketones from β -ketosulfones was developed by means of a visible light-induced C–S bond activation process. Symmetrical and unsymmetrical 1,4-diketones can be easily prepared in moderate to good yields.

Transition-metal catalyzed coupling reactions through C–S bond activation have been established as a useful method to forge new C–C bonds, especially when the traditionally applied organohalides are not readily available or bench-stable.^[1] Recently, visible light-induced photoredox strategy^[2,3] has been introduced to this field due to its mild reaction conditions and high energy economy (solar power). It enables the preparation of valuable synthetic intermediates or bioactive pharmaceutical molecules from easily accessible sulfur-containing organic precursors (Scheme 1).^[4–8] For example, in 2011 MacMillan and co-workers disclosed an elegant example on visible light-induced trifluoromethylation of arenes and heteroarenes using



Scheme 1. Visible light-induced C–S bond activation for C–C bond formation.

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$\text{CF}_3\text{SO}_2\text{Cl}$ as a trifluoromethyl source.^[4a] Later, the activation of C–S bonds in $\text{CF}_3\text{SO}_2\text{Na}$ and ArSO_2Cl through a photocatalytic technology was successfully achieved by groups of Nicewicz^[5] and Li.^[6] Besides sulfonyl-type substrates, the sulfonium salts such as Umemoto's reagent (*S*-(trifluoromethyl)dibenzothio-phenium tetrafluoroborate)^[7] and triarylsulfonium salts^[8] have also been applied to the functionalization of C=C bonds under visible light-induced photocatalytic conditions. In spite of these significant advances, it remains a highly appealing objective to exploit novel and efficient sulfur-containing organic precursors and extend their application to more reactions.

β -Ketosulfones are important synthetic intermediates in organic synthesis,^[9] which can be easily prepared through aerobic difunctionalization and direct oxysulfonylation of commercial available terminal alkynes and alkenes.^[10] However, to our knowledge, it is still quite limited to form new molecule skeleton utilizing β -ketosulfones through visible light-induced photocatalysis. Very recently, we have demonstrated that the N–S bond of tosyl amides can be activated under visible light irradiation in the presence of photosensitizers and a subsequent reductive cleavage reaction finished the desulfonylation process of tosyl amides with high chemoselectivity under very mild conditions.^[11] We therefore reasoned that the C–S bond in the structural analog β -ketosulfone could proceed a similar process under visible light photocatalytic conditions to generate a carbon-centered radical intermediate **A** (Scheme 1). The latter will subsequently undergo a radical–radical coupling reaction to give a 1,4-diketone, an important synthetic building block for the construction of various carbocyclic and heterocyclic structural motifs.^[12] However, a major barrier of this reaction design is that the generated carbon-centered radical intermediate **A** can readily undergo a hydrogen abstraction process to give corresponding ketone as the desulfonylation product (see the mechanistic analysis in Scheme 3).^[13] As a result, the amine reductive quenchers must be chosen carefully to balance the reactivity and selectivity (hydrogen abstraction vs. radical–radical coupling).^[14]

As a consequence of our investigations targeted at the development of useful chemical transformations using visible-light photocatalytic strategy,^[15] we describe herein a novel method for the synthesis of 1,4-diketones from easily prepared β -ketosulfones through a visible light-promoted C–S bond activation process.

Initially, the reaction of β -ketosulfone **1a** in the presence of 2 mol% $[\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}]$ and two equivalents of different amines under the irradiation of 3W white LED was selected to verify our hypothesis. As expected, only acetophenone was ob-

Table 1. Optimization of reaction conditions.^[a]

	Amine	Solvent	Additive	t [h]	Yield [%] ^[b]
1	HEH ^[c]	CH ₃ CN	—	48	0
2	<i>i</i> Pr ₂ NEt	CH ₃ CN	—	48	17
3	<i>n</i> Bu ₃ N	CH ₃ CN	—	48	30
4	Et ₃ N	CH ₃ CN	—	48	40
5	Et ₃ N	DMF	—	48	25
6	Et ₃ N	DMSO	—	48	trace
7	Et ₃ N	MeOH	—	48	39
8	Et ₃ N	CH ₃ CN	Cs ₂ CO ₃	48	50
9	Et ₃ N	CH ₃ CN	Na ₂ CO ₃	24	59
10	Et ₃ N	CH ₃ CN	K ₂ CO ₃	12	75
11	Et ₃ N	CH ₃ CN	DBU	48	42
12	Et ₃ N	CH ₃ CN	TMG	48	62
13 ^[d]	Et ₃ N	CH ₃ CN	K ₂ CO ₃	12	77
14 ^[e]	Et ₃ N	CH ₃ CN	K ₂ CO ₃	36	0
15	—	CH ₃ CN	K ₂ CO ₃	36	0
16 ^[f]	Et ₃ N	CH ₃ CN	K ₂ CO ₃	36	0

[a] Reaction conditions: **1a** (0.5 mmol), [Ru(bpy)₃Cl₂·6H₂O] (2 mol%), amine (2.0 equiv), additive (2.0 equiv), a 3 W white LED, solvent (3 mL), at room temperature. [b] Yield of isolated product. [c] HEH (Hantzsch ester) is diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate. [d] 5 mL CH₃CN is used. [e] In the absence of light source. [f] In the absence of photocatalyst. DBU = 1,8-diazabicycloundec-7-ene, TMG = 1,1,3,3-tetramethylguanidine.

tained as a single product when the Hantzsch ester was applied in the process probably because of its strong hydrogen-donating ability (Table 1, entry 1).^[12] We were pleased to observe that 17 and 30% of C–C bond formation product **2a** were obtained when *i*Pr₂NEt and *n*Bu₃N were used as sacrificial electron donors, respectively (Table 1, entries 2 and 3). Further screening of the amine-type reductive quenchers revealed that Et₃N showed the best balance between reaction activity and selectivity for C–C bond formation process over competitive hydrogen abstraction (Table 1, entry 4). An extensive survey of reaction media revealed that CH₃CN was best solvent of choice (Table 1, entries 5–7).

To further improve the efficiency of this process, various basic additives^[16] were evaluated in order to improve the isomerization of the β-ketosulfones to their enolate form (Scheme 3, process **1** to **B**) and the yield increased to 75% when two equivalents of K₂CO₃ were added to the system (Table 1, entries 8–12). Notably, decreasing the concentration of the mixture slightly enhanced the yield of **2a** to 77% (Table 1, entry 13). Notably, β-ketosulfones bearing other sulfonyl groups, such as 2-(methylsulfonyl)-1-phenylethanone, was also examined and the desired product **2a** was generated in 56% yield after 15 h. No desired 1,4-diketone **2a** was obtained when 2-bromoacetophenone was applied under the best reaction conditions.^[17] In addition, control experiments showed that the light source, photocatalyst, and Et₃N were all required, because no reaction occurred when one or the other was omitted from the reaction (Table 1, entries 14–16).

With the optimal conditions in hand, the scope of substrates that undergo the C–C bond formation reaction was explored.

Both electronically and sterically modified substrates were found to be tolerated in this visible light-induced C–C bond formation process (Table 2). Incorporation of electron-donating groups (Me, OMe) or electron-withdrawing groups (Cl, Br, F) at different positions of the benzene ring does not compromise the reaction efficiency, giving the corresponding symmetrical

Table 2. Construction of symmetrical 1,4-diketones.^[a]

	Ar 1	Product 2	t [h]	Yield [%] ^[b]
1			12	77
2			12	74
3			14	52
4			16	71
5			24	71
6			16	64
7			18	55
8			12	66
9			26	69
10			48	65
11			48	31
12			15	66
13			14	64
14			15	56

[a] Reaction conditions: **1a** (0.5 mmol), [Ru(bpy)₃Cl₂·6H₂O] (2.0 mol%), Et₃N (2.0 equiv), K₂CO₃ (2.0 equiv), a 3W white LED, CH₃CN (5 mL), at room temperature. [b] Yield of isolated product.

1,4-diketones in reasonable yields (Table 2, entries 2–9). Moreover, the disubstituted substrates (Table 2, entry 10) and the substrates bearing a sensitive free hydroxy group (Table 2, entry 11) were also suitable. It is worthy to note that, the benzene ring of the substrate can be replaced by heteroaryl ring to provide furyl-substituted and thienyl-substituted 1,4-diketones in 66 and 64% yields, respectively (Table 2, entries 12 and 13).

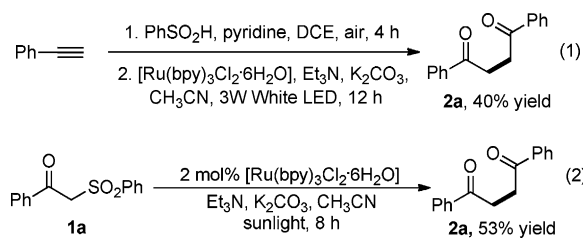
To further expand the substrates scope, we next applied this visible-light photocatalytic C–C bond formation reaction to the construction of unsymmetrical 1,4-diketones. It is noteworthy that an excess of one β -ketosulfone is required under the best reaction conditions in order to compete with undesired self-coupling. As shown in Table 3, substituents with different electronic nature on the aryl ring, are well tolerated during the reaction. Either the unsymmetrical 1,4-diketones bearing two dif-

Table 3. Construction of unsymmetrical 1,4-diketones. ^[a]	
	$2 \text{ mol\% } [\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}]$ $\text{Et}_3\text{N}, \text{K}_2\text{CO}_3, \text{CH}_3\text{CN}$ 3W White LED
	2ca, 14h, 32% 2la, 12h, 40% 2lb, 14h, 44% 2ld, 14h, 50% 2lf, 14h, 40% 2lg, 14h, 34% 2lh, 14h, 46% 2ma, 14h, 45%
[a] Reaction conditions: 1c, 1l–m (0.5 mmol); 1a, b, d, f, and g (0.75 mmol), $[\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}]$ (2.0 mol%), Et_3N (5.0 equiv), K_2CO_3 (5.0 equiv), a 3W white LED, CH_3CN (10 mL), at room temperature. [b] Yield of isolated product.	

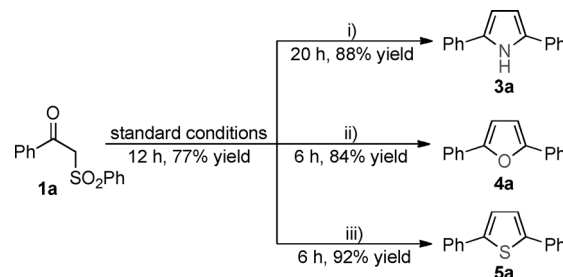
ferent phenyl rings (**2ca**) or the products containing with a heteroaryl ring and a phenyl ring (**2la–ma**) can be successfully prepared, albeit with moderate yields.

Perhaps more important, the 1,4-diketone **2a** could be obtained in 40% yield after a two-step sequential reaction from commercially available phenylethyne without the purification of β -ketosulfone intermediate [Eq. 1]. In addition, direct sunlight irradiation of the reaction of **1a** gave the desired 1,4-diketone **2a** with 53% yield after 8 h [Eq. 2].

According to reported methods,^[17] the formed 1,4-diketone from β -ketosulfone using a visible light photocatalytic strategy



can be easily transferred to various biologically important heterocycles, such as pyrrole **3a**, furan **4a** and thiophene **5a** in excellent isolated yields (Scheme 2).

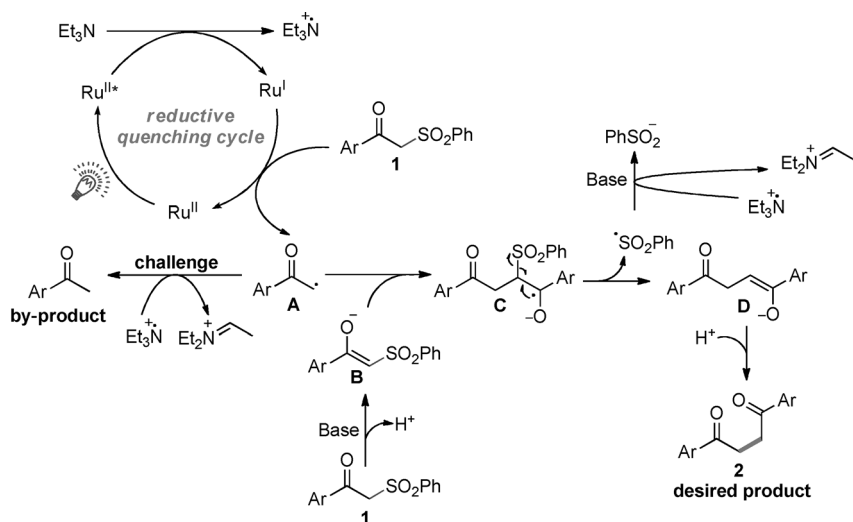


Scheme 2. Two-step construction of heterocycles from β -ketosulfone **1a**. Reaction conditions: i). NH_2OAc , AcOH , reflux; ii). Ac_2O , HCl , 10–60 °C; iii). Lawesson reagent, THF, 55 °C.

To obtain some mechanism insight for this process, we investigated the reaction of **1a** in the presence of radical inhibitor TEMPO under standard conditions. This visible light promoted C–C bond formation reaction is completely inhibited, which indicated that a radical process is presumably involved in the reaction pathway. Furthermore, the results of the reaction of **1a** with and without of light irradiation revealed that a radical chain process is not the major reaction pathway, although it cannot be fully ruled out (see the Supporting Information for details).

Based on these results, a possible reaction pathway is proposed in Scheme 3. The excited state of photoredox catalyst Ru^{II*} was reductively quenched by Et_3N to deliver the strong reductant Ru^I (–1.33 V vs. SCE in CH_3CN). Then single-electron reduction of β -ketosulfone **1** ($\text{Ar}=\text{Ph}$, –0.79 V vs. SCE in CH_3CN)^[19] with Ru^I afforded the key radical intermediate **A** through the breakage of the α -C–S bond (not Ph-SO_2 bonds). To better understand this selectivity, a theoretical calculation was performed and the bond length of CH_2 –S bond (1.835 Å) was found longer than Ph-S bond (1.807 Å), which indicated the former more likely to undergo reductive cleavage process.^[11,13] On the other hand, another molecule of β -ketosulfone **1** would readily isomerize to their enolate form **B** under basic conditions. Subsequently, radical addition of **A** to the α -position of **B** generated radical anion **C**, wherein the elimination of a phenylsulfonyl radical afforded enolate **D**.^[20] Finally, protonation of **D** gave the desired C–C formation product **2**, whereas competitive hydrogen abstraction of **A** would provide acetophenone as the byproduct.

In summary, we have developed an efficient visible light-induced C–S bond activation reaction of β -ketosulfones that operates under mild reaction conditions. It renders this reaction a useful method to various symmetrical and unsymmetrical 1,4-diketones from readily available starting materials. Furthermore, the desired products were well applied to the construction of synthetically significant pyrrole, furan, and thiophene frameworks. The continuous discovery of other stable and easily prepared organosulfur precursors is currently underway in our laboratory.



Scheme 3. Possible mechanism.

Experimental Section

General procedure

To a 10 mL Schlenk flask equipped with a magnetic stir bar was added **1a** (0.5 mmol), Et₃N (1.0 mmol), K₂CO₃ (1.0 mmol), [Ru(bpy)₃Cl₂·6H₂O] (0.01 mmol) and dry CH₃CN (5.0 mL). The resulting mixture was degassed with a freeze-pump-thaw procedure (3 times). Later, the solution was stirred at a distance of approximately 5 cm from a 3W white LED at room temperature. When the reaction was judged to be complete (by TLC), the reaction system was poured into a mixture of H₂O (20 mL) and CH₂Cl₂ (30 mL). The organic layer was separated and aqueous phase was extracted with CH₂Cl₂ (3×20 mL). The combined organic layer was dried over Na₂SO₄ and the crude product was purified by flash chromatography on silica gel (silica: 200–300; eluent: petroleum ether/ethyl acetate (15:1–10:1) to provide product **2a** as a white solid in 77% yield.

Acknowledgements

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Keywords: β-ketosulfones • C–S bond activation • 1,4-diketones • radicals • visible light

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