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Keto-Trifluoromethylation

Combining Photoredox-Catalyzed Trifluoromethylation and Oxidation with DMSO: Facile Synthesis of α-Trifluoromethylated Ketones from Aromatic Alkenes**

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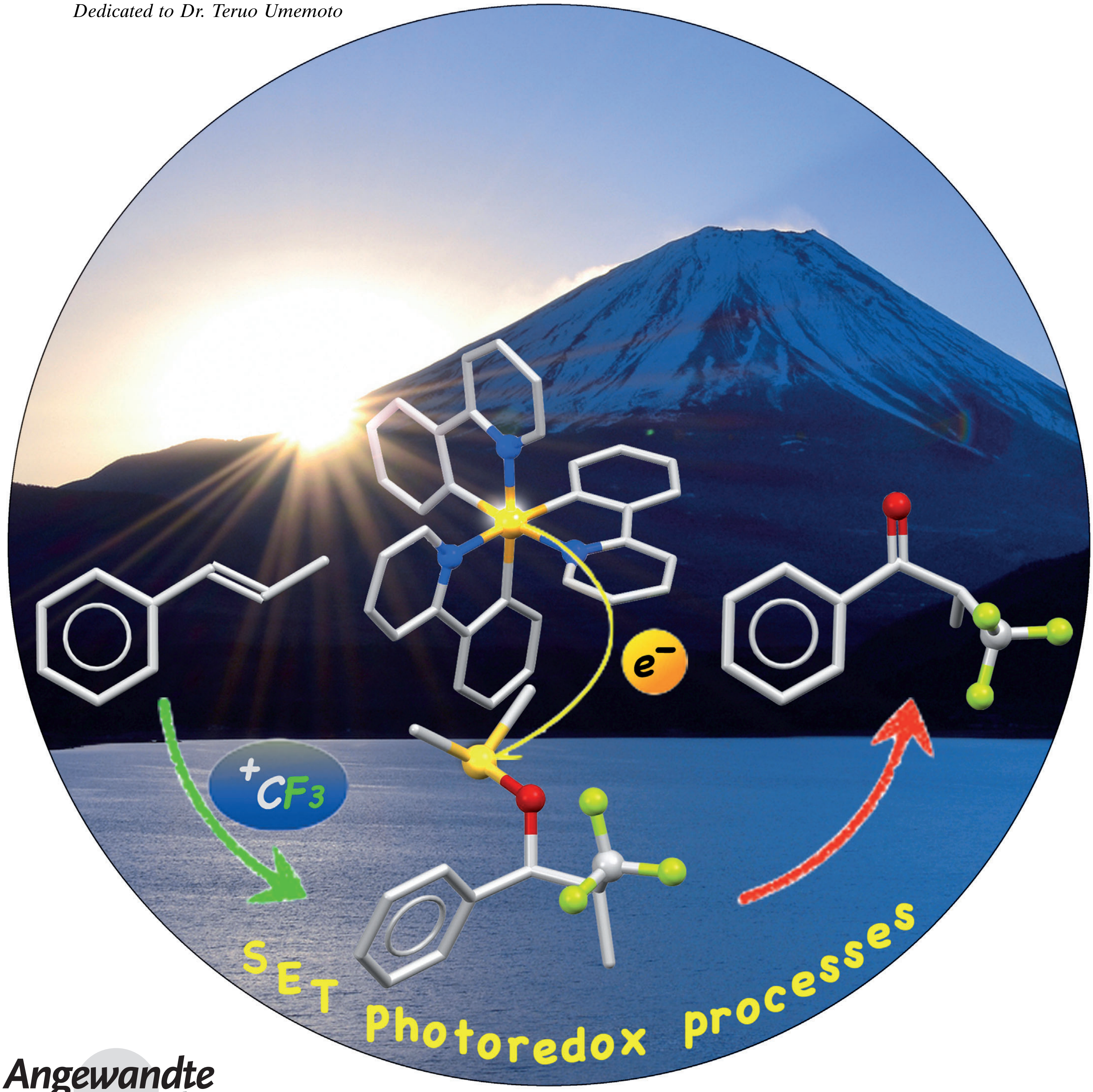
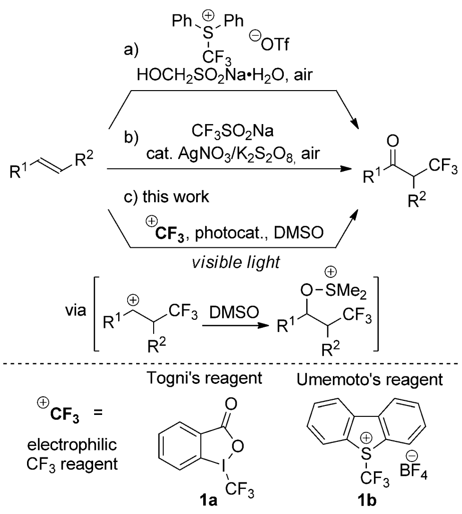
Dedicated to Dr. Teruo Umemoto



Abstract: *Trifluoromethylated ketones are useful building blocks for organic compounds with a trifluoromethyl group. A new and facile synthesis of ketones with a trifluoromethyl substituent in the α-position proceeds through a one-pot photoredox-catalyzed trifluoromethylation–oxidation sequence of aromatic alkenes. Dimethyl sulfoxide (DMSO) serves as a key and mild oxidant under these photocatalytic conditions. Furthermore, an iridium photocatalyst, fac-[Ir(ppy)$_3$] (ppy = 2-phenylpyridine), turned out to be crucial for the present photoredox process.*

The trifluoromethyl group prevails in pharmaceutical and agrochemical compounds as well as in functional organic materials.[1,2] Therefore, the development of new methods for the efficient and selective incorporation of a CF_3 group into diverse molecular architectures has become an important research topic in synthetic organic chemistry.[3] Trifluoromethylated carbonyl compounds are versatile building blocks for the synthesis of a wide variety of fluorinated compounds.[4] In general, electrophilic or radical trifluoromethylation of enolates, which were prepared from the corresponding carbonyl compounds in advance, provides access to valuable α-trifluoromethylated carbonyl compounds.[5] A few other unique methods have also been reported,[6–9] but examples of the "direct" oxidative trifluoromethylation (keto-trifluoromethylation) of alkenes, which are abundant and commonly used feedstocks, have been limited thus far.[10] Xiao and coworkers reported the keto-trifluoromethylation of styrenes with an *S*-(trifluoromethyl)diphenylsulfonium salt and air in the presence of an excess amount of the reducing agent, $HOCH_2SO_2Na$. However, the α-CF_3-substituted ketones were obtained in low yields (Scheme 1 a). More recently, Maiti et al. described a catalytic system consisting of $AgNO_3$ and $K_2S_2O_8$ that is effective for the oxidative trifluoromethylation of alkenes with the Langlois reagent, CF_3SO_2Na, and air (Scheme 1 b). For both processes, the involvement of a trifluoromethyl radical ($^{\bullet}CF_3$) was proposed, and it was implied that the outcome of the reaction is significantly affected by the methods that are used for the generation of the CF_3 radical and oxidation.

Recently, radical trifluoromethylation by photoredox catalysis has emerged; visible-light-driven single-electron transfer (SET) processes are enabled by the well-known ruthenium(II) polypyridine complexes (e.g., $[Ru(bpy)_3]^{2+}$; bpy = 2,2′-bipyridine) and the corresponding cyclometalated iridium(III) derivatives (e.g., *fac*-[Ir(ppy)$_3$]; ppy = 2-phenylpyridine).[5k,m,11–13] Our efforts have been devoted to the development of a photoredox-catalyzed difunctionalization of C=C bonds[13] in the presence of electrophilic trifluoromethylating reagents (**$^+CF_3$**),[5g,14] such as Togni's reagent (**1a**) or Umemoto's reagent (**1b**). In these reactions, a key intermediate is the β-CF_3-substituted carbocation that is generated from SET photoredox processes, and which undergoes subsequent nucleophilic attack to produce difunctionalized products. This is a powerful method for the difunctionalization of alkenes without isolation of the intermediate. We hypothesized that combining the photoredox-catalyzed trifluoromethylation and Kornblum (DMSO) oxidation[15] of the β-CF_3-substituted carbocation would enable the development of a facile and new approach to the synthesis of α-trifluoromethylated ketones by keto-trifluoromethylation (Scheme 1 c), which is the subject of the present contribution. Our strategy provides us with an operationally simple procedure as well as a highly regioselective and efficient transformation. Furthermore, it has been revealed that an alkoxysulfonium species, which is a well-known intermediate in DMSO oxidation,[16] smoothly produces an α-CF_3-substituted ketone without treatment with any base under photoredox reaction conditions.



Scheme 1. Keto-trifluoromethylation of alkenes.

We initially examined the photocatalytic reaction of styrene (**2a**) with Togni's reagent **1a** (1.05 equiv) and the iridium photoredox catalyst *fac*-[Ir(ppy)$_3$][17] (5 mol %) in [D$_6$]DMSO under visible-light irradiation (blue LEDs: λ_{max} = 425 nm) for two hours. To our surprise, the α-CF_3-substituted ketone **3a** was directly formed in 58 % yield together with β-trifluoromethylstyrene (**4a**, 35 % yield; entry 1, Table 1). When Umemoto's reagent **1b** was used in place of **1a**, a similar product mixture (**3a**: 59 %, **4a**: 22 %) to that of the reaction with Togni's reagent **1a** (entry 2) was obtained. The ruthenium photoredox catalyst $[Ru(bpy)_3](PF_6)_2$[18], in contrast, did not promote the present direct keto-trifluoromethylation of **2a** very well (entries 3 and 4). The use of Togni's reagent **1a** resulted in low conversion (12 %; entry 3). Remarkably, the use of Umemoto's reagent **1b** gave alkoxysulfonium salt **5a** in 76 % yield instead of **3a** with concomitant formation of β-trifluoromethylstyrene (**4a**) in 20 % yield

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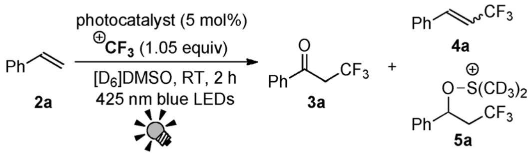
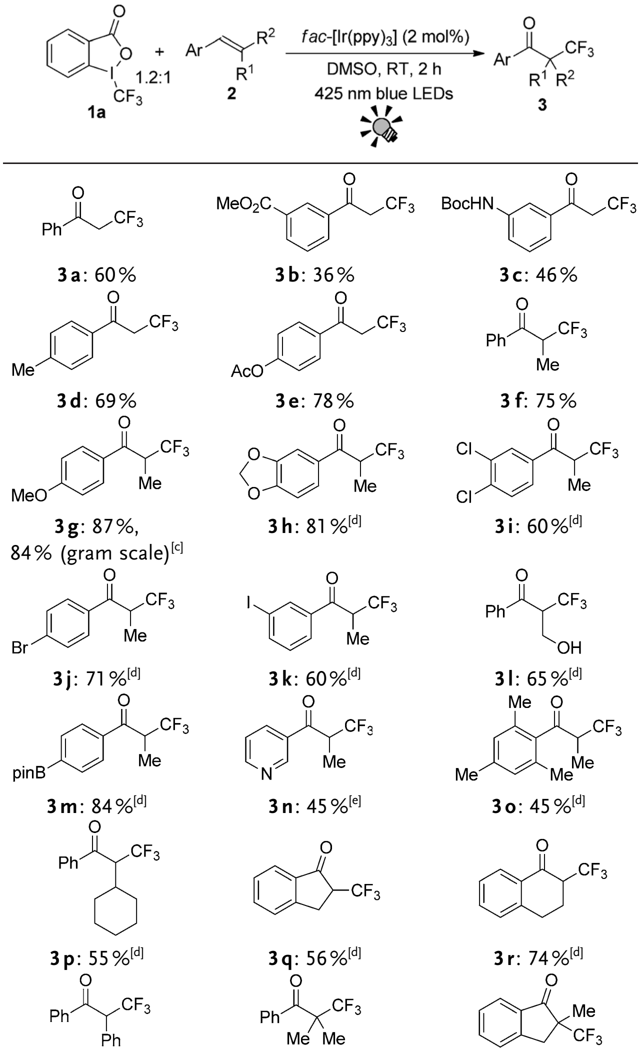
Table 1: Optimization of the photocatalytic keto-trifluoromethylation of styrene (**2a**).[a]



Entry	CF$_3$ reagent	Photocatalyst	Yield of **3a** [%][b]	Yield of **4a** [%][b]
1	**1a**	*fac*-[Ir(ppy)$_3$]	58	35
2	**1b**	*fac*-[Ir(ppy)$_3$]	59	22
3	**1a**	[Ru(bpy)$_3$](PF$_6$)$_2$	5	0
4	**1b**	[Ru(bpy)$_3$](PF$_6$)$_2$	76 (**5a**); 38[c]	20
5[d]	**1a**	*fac*-[Ir(ppy)$_3$]	0	0
6	**1a**	–	0	0

[a] For detailed reaction conditions, see the Supporting Information. [b] Yields were determined by ^{1}H NMR spectroscopy using Si(Et)$_4$ as an internal standard. [c] Yield after treatment of the product mixture with NEt$_3$ (10 equiv). [d] In the dark. bpy = 2,2′-bipyridine, LED = light-emitting diode, ppy = 2-phenylpyridine.

Table 2: Scope of the photocatalytic keto-trifluoromethylation.[a,b]



3a: 60%
3b: 36%
3c: 46%
3d: 69%
3e: 78%
3f: 75%
3g: 87%, 84% (gram scale)[c]
3h: 81%[d]
3i: 60%[d]
3j: 71%[d]
3k: 60%[d]
3l: 65%[d]
3m: 84%[d]
3n: 45%[e]
3o: 45%[d]
3p: 55%[d]
3q: 56%[d]
3r: 74%[d]
3s: 46%[d]
3t: 28%[f]
3u: 56%[f]

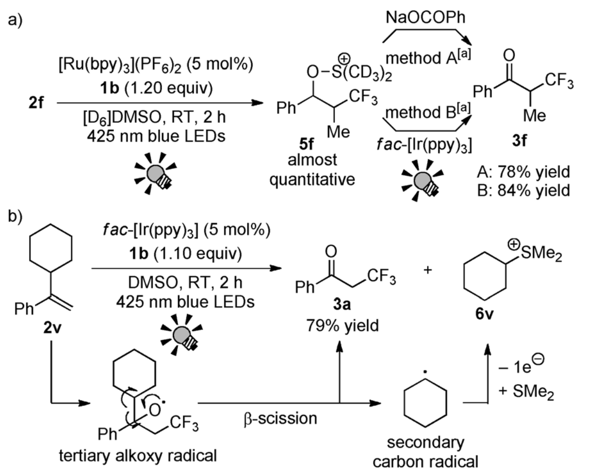
[a] For detailed reaction conditions, see the Supporting Information. [b] Yields of isolated products. [c] Reaction conducted on a gram scale. For details, see the Supporting Information. [d] **1a** (1.30 equiv) was used. [e] *fac*-[Ir(ppy)$_3$] (5 mol%) and **1a** (1.5 equiv) were used. [f] *fac*-[Ir(ppy)$_3$] (5 mol%), **1a** (2.0 equiv), 5 h.

(entry 4). When the salt **5a**, the key intermediate of the DMSO oxidation,[16] was treated with NEt$_3$, the desired α-CF$_3$-substituted ketone **3a** was formed in 38% yield (entry 4). For entries 1 and 2, ketone **3a** was formed in the absence of a base, as is the case in the Kornblum oxidation. On the basis of these results, we have developed the direct keto-trifluoromethylation of alkenes using the iridium photocatalyst without addition of a base. Notably, product **3a** was not obtained either in the dark or in the absence of the photocatalyst (entries 5 and 6), strongly supporting that the photoexcited species of the photoredox catalyst plays key roles in the reaction.

The scope of the present photocatalytic keto-trifluoromethylation is summarized in Table 2. Styrene (**2a**) and styrene derivatives bearing CO$_2$Me (**2b**) and NHBoc groups (**2c**; Boc = *tert*-butoxycarbonyl) on the aryl ring produced the α-CF$_3$-substituted ketones (**3a**–**3c**) in moderate yields (36–60%) because of concomitant formation of β-trifluoromethylstyrene derivatives **4**. In contrast, styrenes with electron-donating substituents, such as methyl (**2d**) and acetoxy groups (**2e**), and (*E*)-β-methylstyrene (**2f**) suppressed the formation of the side product **4** to a significant extent. As a result, the corresponding CF$_3$-substituted ketones were obtained in good yields (**3d**–**f**; 69–78%).

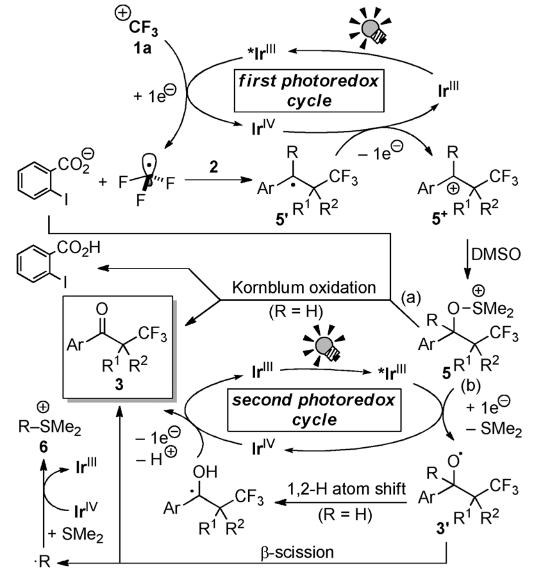
Furthermore, β-methylstyrene derivatives with electron-donating groups on the aromatic ring (**2g** and **2h**) smoothly afforded the corresponding products **3g** and **3h** in a regioselective fashion and in 87% and 81% yield, respectively. To demonstrate the scalability of the present photocatalytic reaction, the keto-trifluoromethylation of **2g** was carried out on a gram scale, and the product **3g** was isolated in 84% yield (1.31 g). Halogen (**2i**–**2k**), hydroxy (**2l**), boronic ester (Bpin; **2m**), and pyridyl groups (**2n**) did not hinder the reaction (45–84%). Alkenes with bulky mesityl or cyclohexyl substituents (**2o** and **2p**), cyclic alkenes (**2q** and **2r**), and *trans*-stilbene (**2s**) were also suitable substrates for this transformation (45–74%). Furthermore, the present catalytic system was amenable to the reaction of β-disubstituted alkenes (**2t** and **2u**). The corresponding α-CF$_3$-substituted ketones that bear a quaternary carbon atom were obtained in 28% and 56% yield, respectively (**3t** and **3u**). The reactions of some alkenes, such as 1-octene and vinylcyclohexane, resulted in an inseparable mixture of products. These results show that aromatic alkenes with a variety of functional groups, such as halogen, ester, acetal, boronic ester, hydroxy, and pyridyl groups, can be applied to the present photocatalytic keto-trifluoromethylation, leading to the corresponding α-CF$_3$-substituted ketones in a highly regioselective fashion.

To gain insight into the reaction mechanism, we conducted some control experiments. As mentioned above, the reaction of (*E*)-β-methylstyrene **2f** gave a better yield than that of styrene **2a** because formation of CF$_3$-substituted alkene **4** was suppressed. Therefore, we conducted the reaction of **2f** with Umemoto's reagent **1b** in the presence of $[Ru(bpy)_3](PF_6)_2$ (5 mol%). As a result, quantitative formation of a diastereomeric mixture of alkoxysulfonium salt **5f** was observed by NMR spectroscopy. In light of these results, side product **4** is possibly formed before formation of **5**. Subsequent treatment of **5f** with sodium benzoate (2.0 equiv; method A) or further photoreaction with addition of *fac*-$[Ir(ppy)_3]$ (5 mol%; method B) provided **3f** in 78% and 84% yield, respectively (yields determined by NMR spectroscopy; Scheme 2a). When *fac*-$[Ir(ppy)_3]$ (5 mol%) was added at the beginning of the reaction, a product mixture of **3f** (31% NMR yield) and **5f** (49% NMR yield) was obtained after ten minutes, and elongated reaction times (30 min) enabled the formation of **3f** in 74% yield as the sole product. A cyclic voltammogram for alkoxysulfonium salt **5f** exhibited a broad irreversible reduction wave at −1.07 V (vs. $[Cp_2Fe]$ in MeCN; Cp = cyclopentadienyl), which is close to the reduction potential of the photoexcited $[Ru(bpy)_3]^{2+}$, indicating that **5f** cannot be easily reduced by the photoexcited $[Ru(bpy)_3]^{2+}$, but only by the photoexcited *fac*-$[Ir(ppy)_3]$.[17,18] These results suggest that the action of benzoate or the iridium photocatalyst can induce the formation of the corresponding ketones **3** from the alkoxysulfonium intermediates **5**. Furthermore, to our surprise, the reactions of α-cyclohexylstyrene **2v** and α-methylstyrene **2w** afforded **3a** in 79% and 44% yield, respectively; these transformations proceed through a C−C bond cleavage process. In the case of the reaction of **2v**, the eliminated alkyl group was detected as the cyclohexyldimethylsulfonium salt **6v** (Scheme 2b). These remarkable C−C bond cleavage processes likely stem from β-scission of the tertiary alkoxy radical intermediate. These results suggest that photoredox catalysis is playing two crucial roles in the present photocatalytic keto-trifluoromethylation: 1) formation of the β-CF_3-substituted carbocation intermediate,[13] and 2) formation of the reactive alkoxy radical intermediate from the alkoxysulfonium intermediate **5**.



Scheme 2. Control experiments. [a] Method A: Sodium benzoate (2 equiv) was added at RT, and the reaction mixture stood for two hours; method B: *fac*-$[Ir(ppy)_3]$ (5 mol%) was added, and the reaction mixture was irradiated with visible light (425 nm blue LEDs) at RT for one hour. Yields were determined by ^1H NMR spectroscopy using $Si(Et)_4$ as an internal standard.

On the basis of these results, a possible reaction mechanism was proposed by combining photoredox-catalyzed trifluoromethylation and oxidation with DMSO (Scheme 3). First, irradiation with visible light excites *fac*-$[Ir^{III}(ppy)_3]$ ($\mathbf{Ir^{III}}$) into *fac*-$[Ir^{III}(ppy)_3]^*$ ($\mathbf{{}^*Ir^{III}}$), which undergoes SET reduction of the electrophilic trifluoromethylating reagent ($\mathbf{{}^+CF_3}$) **1** to generate the CF_3 radical ($^{\bullet}CF_3$), accompanied by formation of the highly oxidized *fac*-$[Ir^{IV}(ppy)_3]^+$ ($\mathbf{Ir^{IV}}$) species. Addition of the CF_3 radical to alkene **2** provides radical intermediate **5′**. A second SET oxidation event of **5′** should occur concurrently with reduction of $\mathbf{Ir^{IV}}$ to the $\mathbf{Ir^{III}}$ ground state, leading to the β-CF_3-substituted carbocationic intermediate $\mathbf{5^+}$. Nucleophilic attack of DMSO to $\mathbf{5^+}$ affords alkoxysulfonium intermediate **5**. In the reaction with Togni's reagent **1a**, *o*-iodobenzoate, which is the byproduct of the reduction of **1a**, should serve as the base. A reaction similar to Kornblum oxidation proceeds to give product **3** (path a).[19] On the other hand, the strong reducing agent $\mathbf{{}^*Ir^{III}}$ can affect the reduction of **5**, which leads to the formation of alkoxy radical **3′** (path b), especially in the reaction with Umemoto's reagent **1b**. Subsequent SET oxidation preceded by 1,2-hydrogen atom shift[20] or β-scission of the alkoxy radical **3′** furnishes the product **3**. In the reactions of **2v** and **2w**, the alkyl groups (R) cannot be removed with the help of a base. This observation is therefore regarded as unequivocal evidence for the hypothesis that at least in the case of α-substituted styrene derivatives, the photoredox mechanism is operating for the conversion of **5** into **3** via **3′**.



Scheme 3. A proposed reaction mechanism.

In conclusion, we have developed a new method for the synthesis of α-CF_3-substituted carbonyl compounds by combining photoredox-catalyzed trifluoromethylation and oxidation mediated by an alkoxysulfonium ion. The iridium photocatalyst *fac*-$[Ir(ppy)_3]$, which can be a strong reducing agent, plays key roles in achieving the direct keto-trifluoromethylation of a C=C bond in a regioselective manner. Furthermore, this iridium-catalyzed reaction is a new type of base-free DMSO oxidation. The present method also enabled the transformation of alkenes with a variety of functional groups into the corresponding α-CF_3-substituted ketones. The development of new photocatalytic multifunctionalization processes that include trifluoromethylation is currently underway in our laboratory.

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[17] The photoexcited state of *fac*-[Ir(ppy)$_3$] is a stronger reductant ($E_{1/2} = -2.14$ V vs. [Cp_2Fe]) than that of [Ru(bpy)$_3$]$^{2+}$; see: L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura, F. Barigelletti, *Top. Curr. Chem.* **2007**, *281*, 143–203.

[18] The photoexcited state of [Ru(bpy)$_3$]$^{2+}$ is a strong reductant ($E_{1/2} = -1.24$ V vs. [Cp_2Fe]); see: K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159–244.

[19] The control experiment (method A, Scheme 2a) suggested that the reaction in the presence of **1a** (entry 1 in Table 1 and Table 2) mainly proceeds through path a.

[20] The reaction in the presence of **1b** (entry 2 in Table 1; method B in Scheme 2a and Scheme 2b) can proceed through path b. We cannot exclude other possibilities. This 1,2-hydrogen atom shift might be induced by adventitious H_2O or O_2 in DMSO; see: K. G. Konya, T. Paul, S. Lin, J. Lusztyk, K. U. Ingold, *J. Am. Chem. Soc.* **2000**, *122*, 7518–7527.