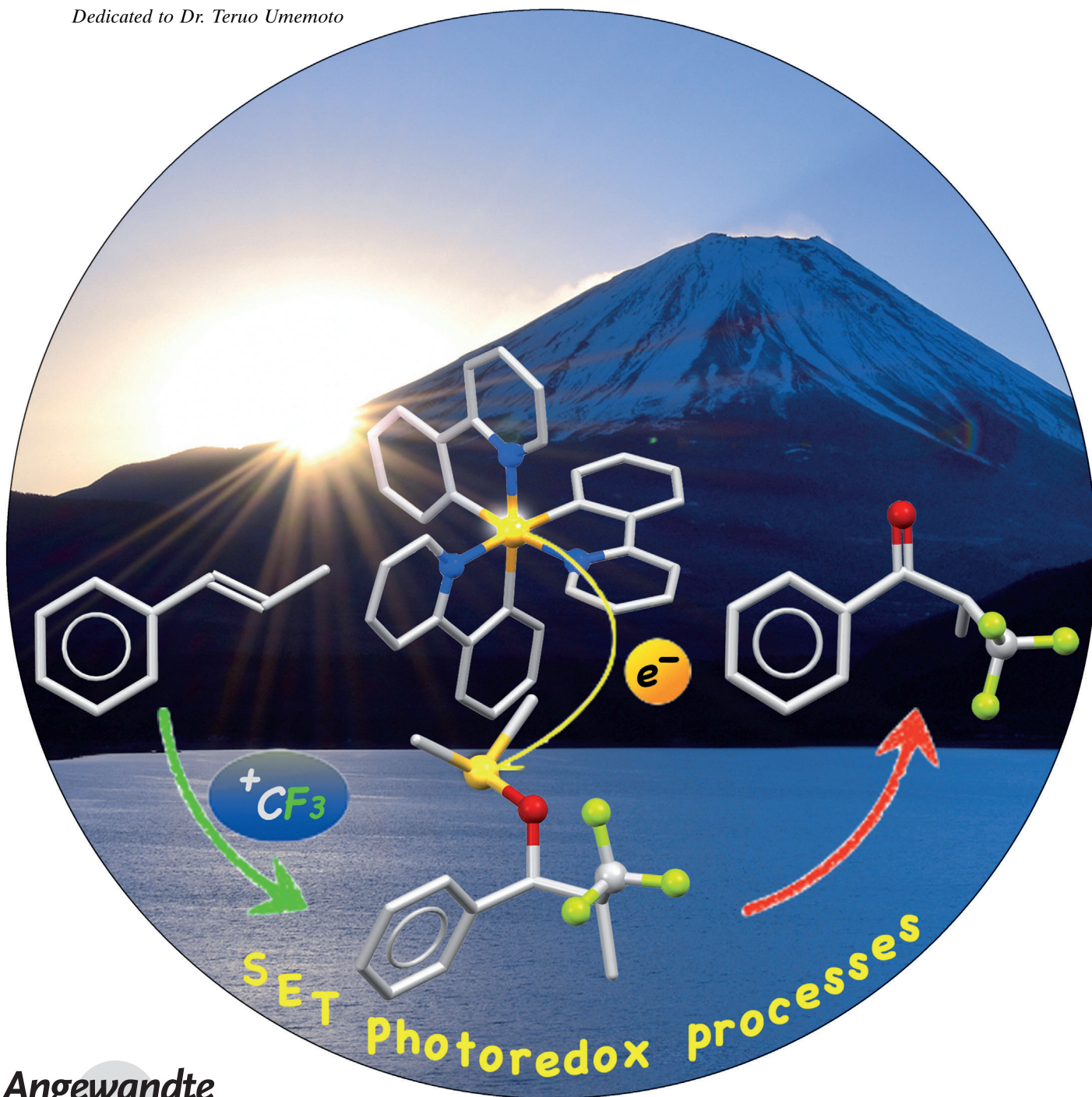


Combining Photoredox-Catalyzed Trifluoromethylation and Oxidation with DMSO: Facile Synthesis of α -Trifluoromethylated Ketones from Aromatic Alkenes**

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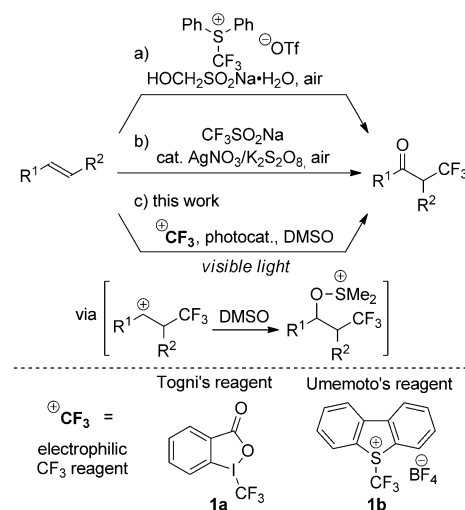
Dedicated to Dr. Teruo Umemoto



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 CF₃ 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 co-workers 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, HOCH₂SO₂Na. However, the α -CF₃-substituted ketones were obtained in low yields (Scheme 1a). More recently, Maiti et al. described a catalytic system consisting of AgNO₃ and K₂S₂O₈ that is effective for the oxidative trifluoromethylation of alkenes with the Langlois reagent, CF₃SO₂Na, and air (Scheme 1b). For both processes, the involvement of a trifluoromethyl radical ($\cdot$ CF₃) 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 CF₃ 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



Scheme 1. Keto-trifluoromethylation of alkenes.

development of a photoredox-catalyzed difunctionalization of C=C bonds^[13] in the presence of electrophilic trifluoromethylating reagents ($^+\text{CF}_3$),^[5g,14] such as Togni's reagent (**1a**) or Umemoto's reagent (**1b**). In these reactions, a key intermediate is the β -CF₃-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 -CF₃-substituted carbocation would enable the development of a facile and new approach to the synthesis of α -trifluoromethylated ketones by keto-trifluoromethylation (Scheme 1c), 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 -CF₃-substituted ketone without treatment with any base under photoredox reaction conditions.

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 [D₆]DMSO under visible-light irradiation (blue LEDs: λ_{max} = 425 nm) for two hours. To our surprise, the α -CF₃-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](PF₆)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	<i>fac</i> -[Ir(ppy) ₃]	58	35
2	1b	<i>fac</i> -[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	<i>fac</i> -[Ir(ppy) ₃]	0	0
6	1a	—	0	0

[a] For detailed reaction conditions, see the Supporting Information.

[b] Yields were determined by ¹H NMR spectroscopy using Si(Et)₄ as an internal standard. [c] Yield after treatment of the product mixture with NEt₃ (10 equiv). [d] In the dark. bpy = 2,2'-bipyridine, LED = light-emitting diode, ppy = 2-phenylpyridine.

(entry 4). When the salt **5a**, the key intermediate of the DMSO oxidation,^[16] was treated with NEt₃, the desired α-CF₃-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 CO₂Me (**2b**) and NHBoc groups (**2c**; Boc = *tert*-butoxycarbonyl) on the aryl ring produced the α-CF₃-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 CF₃-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 ame-

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]

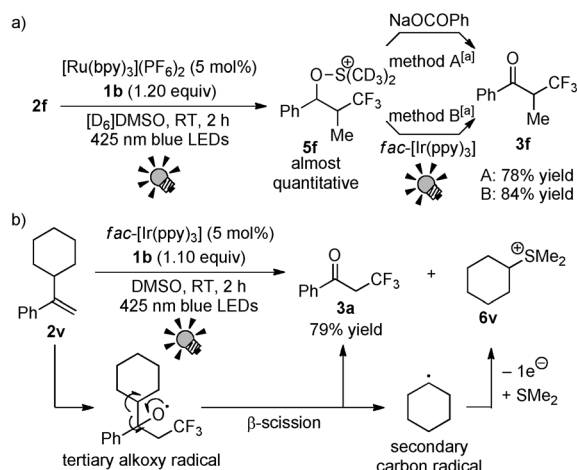
[a] For detailed reaction conditions, see the Supporting Information.

[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.

nable to the reaction of β-disubstituted alkenes (**2t** and **2u**). The corresponding α-CF₃-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-CF₃-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 CF₃-substituted alkene **4** was suppressed. Therefore, we conducted the

reaction of **2f** with Umemoto's reagent **1b** in the presence of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (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*- $[\text{Ir}(\text{ppy})_3]$ (5 mol %; method B) provided **3f** in 78 % and 84 % yield, respectively (yields determined by NMR spectroscopy; Scheme 2a). When *fac*- $[\text{Ir}(\text{ppy})_3]$ (5 mol %) was added at the

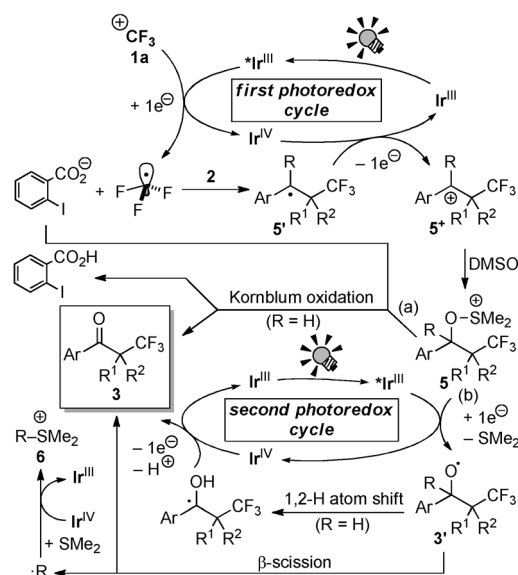


Scheme 2. Control experiments. [a] Method A: Sodium benzoate (2 equiv) was added at RT, and the reaction mixture stood for two hours; method B: *fac*- $[\text{Ir}(\text{ppy})_3]$ (5 mol %) was added, and the reaction mixture was irradiated with visible light (425 nm blue LEDs) at RT for one hour. Yields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

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. $[\text{Cp}_2\text{Fe}]$ in MeCN; Cp = cyclopentadienyl), which is close to the reduction potential of the photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$, indicating that **5f** cannot be easily reduced by the photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$, but only by the photoexcited *fac*- $[\text{Ir}(\text{ppy})_3]$.^[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**.

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*- $[\text{Ir}^{\text{III}}(\text{ppy})_3]$



Scheme 3. A proposed reaction mechanism.

(Ir^{III}) into *fac*- $[\text{Ir}^{\text{III}}(\text{ppy})_3]^*$ ($\text{Ir}^{\text{III}*}$), which undergoes SET reduction of the electrophilic trifluoromethylating reagent ($^+\text{CF}_3$) **1** to generate the CF_3 radical ($\cdot\text{CF}_3$), accompanied by formation of the highly oxidized *fac*- $[\text{Ir}^{\text{IV}}(\text{ppy})_3]^+$ (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 Ir^{IV} to the Ir^{III} ground state, leading to the β - CF_3 -substituted carbocationic intermediate **5'**. Nucleophilic attack of DMSO to **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 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'**.

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*- $[\text{Ir}(\text{ppy})_3]$, which can be a strong reducing agent, plays key roles in achieving the direct keto-trifluor-

omethylation 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 -CF₃-substituted ketones. The development of new photocatalytic multifunctionalization processes that include trifluoromethylation is currently underway in our laboratory.

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