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Photoredox-Catalysed Redox-Neutral Trifluoromethylation of Vinyl Azides for the Synthesis of *α*–Trifluoromethylated Ketones

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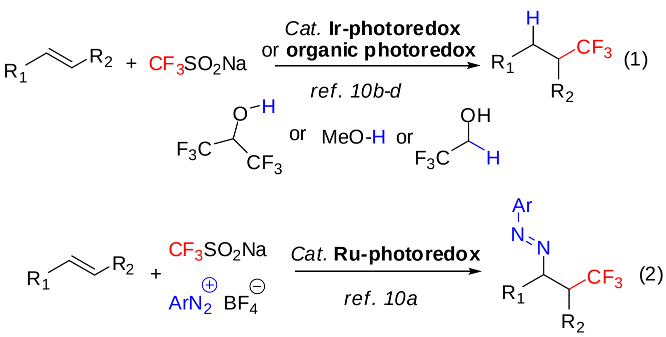
A redox-neutral, mild, and simple protocol is developed for the synthesis of *α*-trifluoromethylated ketones from vinyl azides under transition-metal-free conditions. In the presence of organic photoredox catalyst *N*-methyl-9-mesityl acridinium and sodium trifluoromethanesulfinate, a broad range of substituted vinyl azides were found to react smoothly upon visible-light irradiation, readily furnishing the corresponding products in satisfied yields.

The trifluoromethyl (CF_3) moiety, with chemical stability and electron withdrawing character, is a useful substituent for organic compounds.[1] For example, Introduction of a CF_3 group can lead to profound changes on the metabolic stability, lipophilicity, and bioavailability of potential drug candidates.[1] Therefore, the development of novel methods for efficient, selective and mild incorporation of a CF_3 group into diverse skeletons has emerged as a pivotal objective in organic synthesis.[2] Radical trifluoromethylation, especially, via photoredox catalysis, has received great attention. A variety of agents, such as CF_3I,[3] CF_3SO_2Cl,[4] Togni reagent,[2b,5] Umemoto reagent,[6] Langlois/Baran reagents (CF_3SO_2Na,[7] $(CF_3SO_2)_2Zn$[8]), and Ruppert-Prakash reagent[9] ($TMSCF_3$) could serve as CF_3 radical precursors. Among these reagents, the commercially available, low cost, and easy-handling Langlois reagent has been extensively utilized as the source of CF_3 radical by single electron oxidation.[7,10] However, there have been only few reports referring to a photoredox catalyst in combination with Langlois reagent towards generating a CF_3 radical to date (Scheme 1).[10] The oxidation potential of Langlois reagent is 1.05 V (*vs.* SCE).[10d,11] Organic dyes, such as Fukuzumi acridiniums,[10d,12] have been widely adopted as catalytic visible-light photoredox systems. *N*-Methyl-9-mesityl acridinium (**Mes-Acr**$^+$, **3**) with excited-state reduction potential ($E_{1/2}^{red}$*) > 1.8 V (*vs.* SCE),[12,13] as one of the acridinium species, is actually sufficient for single electron oxidation of the Langlois reagent. We wondered if it was possible to achieve *α*-trifluoromethylated ketones using Langlois reagent and mesityl acridinium with visible-light irradiation.



Scheme 1 Visible-light-induced trifluoromethylation with CF_3SO_2Na.

As versatile building blocks, in general, *α*-trifluoromethylated carbonyl compounds are prepared by electrophilic or radical trifluoromethylation of enolates, silyl enol ethers, or enamines which are obtained from corresponding carbonyl compounds in advance or in situ,[14] or via oxidative keto-trifluoromethylation of alkenes[5b,7f,15] in a radical process. A few other unique protocols were also established.[16] Vinyl azides[17] with high intrinsic reactivity have been used as versatile synthons for various transformations.[9a-b,18] For example, radical trifluoromethylation of vinyl azides with $TMSCF_3$ and $PhI(OAc)_2$ allows preparation of *α*-trifluoromethyl azines, followed by hydrolysis to give *α*-trifluoromethylated ketones.[9a] In this reaction, the iminyl radical intermediate was generated, followed by immediate dimerization to yield the azines (Scheme 2). It should be noted that the above method requires super-stoichiometric amounts of strong oxidant $PhI(OAc)_2$ which is often not compatible with sensitive functional groups. In

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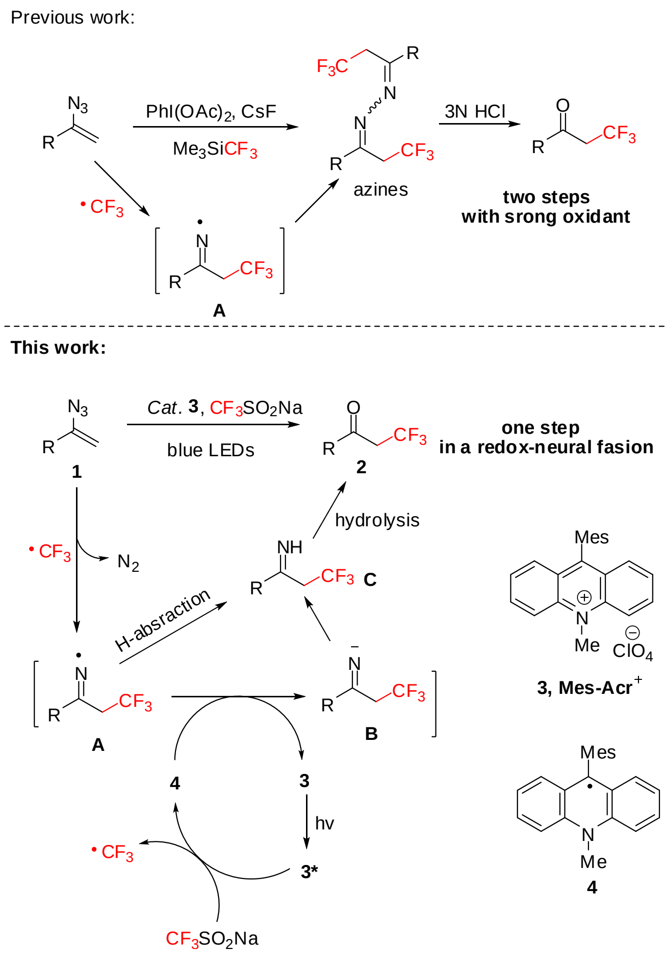
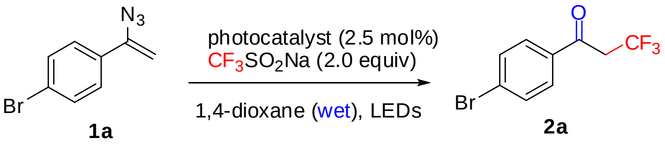
continuation of our research interest in transformation of vinyl azides[19] and radical trifluoromethylation,[20] it was envisioned that a redox-neutral radical trifluoromethylation of vinyl azides could serve as a useful methodology to achieve α-trifluoromethylated ketones directly in a mild redox process in which Langlois reagent acts as reductant and the iminyl radical intermediate generated from vinyl azides could play as oxidant, though an H-atom abstraction process would also happen. Consequently, we believed that the interception of the iminyl radical **A** via single electron reduction by **4** to circumvent dimerization would furnish α-trifluoromethylated ketones when using *N*-Methyl-9-mesityl acridinium perchlorate (**3**) as the photoredox catalyst (Scheme 2).



Scheme 2 Radical trifluoromethylation of vinyl azides.

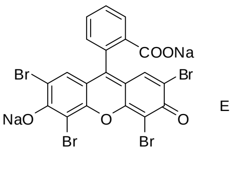
The hypothesis was first examined using 4-bromopheny vinyl azide **1a** as the model substrate. Initially, various solvents (used directly without dehydration) were screened upon irradiation by white LEDs (light emitting diodes) in the presence of catalytic amount of **3** (2.5 mol%), as might be expected, affording the desired α-trifluoromethylated ketone **2a** in various yields, as well as identifying 1,4-dioxane as the best solvent in terms of chemical yield (see supporting information). An increase in the loading of **Mes-Acr⁺** did not improve the chemical yield but shortening the reaction time (Table 1, entry 2). It should be noted that this protocol did also work well under the air, only leading to a slight decrease of the yield (Table 1, entry 3). We next examined the influence of light source. The results showed that blue LEDs gave the highest yield (Table 1, entries 1, 4 and 5). In order to quench the iminyl anion **B** (Scheme 2), various weak base or weak acids as proton donor were added. To our surprise, the chemical yields dropped (Table 1, entries 6–9). Other photocatalyst, such as Na_2-Eosin Y, Rhodamine B, or Riboflavin was also tested, affording **2a** in much lower yields (Table 1, entry 5 *vs.* entries 10–12). Control experiments were performed in the absence of the photoredox catalyst or in the dark revealed that both the catalyst and photoirradiation are crucial for this radical trifluoromethylation (Table 1, entries 13 and 14).

Table 1 Optimization of reaction conditions [a]

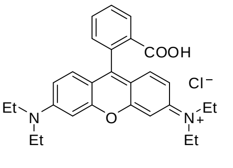


entry	LEDs	photocatalyst	additive[b]	yield (%)[c]
1	white	Mes-Acr⁺	–	65
2[d]	white	Mes-Acr⁺	–	65
3[e]	white	Mes-Acr⁺	–	52
4	green	Mes-Acr⁺	–	53
5	**blue**	**Mes-Acr⁺**	**–**	**72**
6	blue	Mes-Acr⁺	$KHCO_3$	< 5
7	blue	Mes-Acr⁺	HOAc	55
8	blue	Mes-Acr⁺	NH_4OAc	37
9	blue	Mes-Acr⁺	NH_4Cl	63
10	blue	Na_2-Eosin Y	–	33
11	blue	Rhodamine B	–	25
12	blue	Riboflavin	–	29
13[f]	–	Mes-Acr⁺	–	0
14[g]	blue	–	–	0

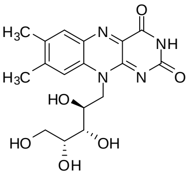
[a] **1a** (0.20 mmol), catalyst (2.5 mol%), CF_3SO_2Na (0.4 mmol), 1,4-dioxane (2 mL), Argon balloon, 5 W LEDs, 36-60 h. [b] 2.0 equivalent of additive [c] Isolated yield. [d] Mes-Acr⁺ (5 mol%), 24 h. [e] Open flask, under the air. [f] In the dark. [g] No photoredox catalyst.



Na_2-Eosin Y

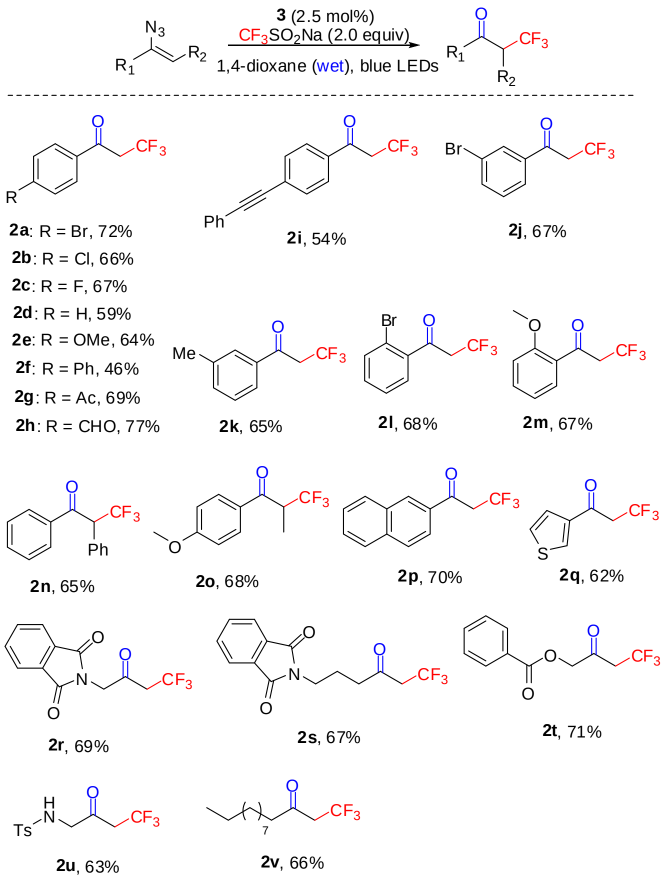


Rhodamine B



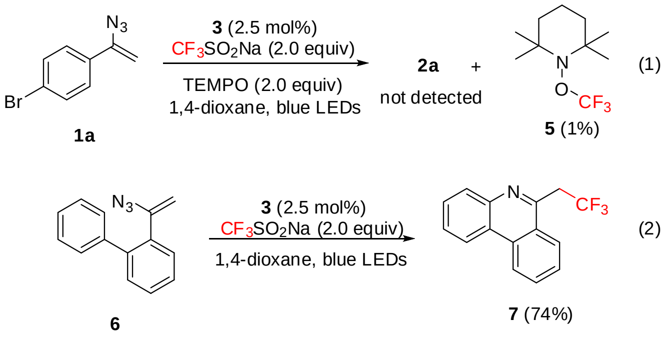
Riboflavin

With the optimal reaction conditions in hand, we aimed to define the scope of this protocol. As shown in Scheme 3, a broad range of substituted *α*-trifluoromethylated ketones were readily furnished in moderate to good yields. The reaction was found to tolerate a series of different functional groups on phenyl ring, giving the corresponding *α*-trifluoromethylated acetophenone derivatives in satisfactory yields (46–77% yield, **2a–p**). Investigations of the substrate scope also demonstrated that both electron-rich and electron-deficient arenes bearing diverse groups at *para*, *meta*, or *ortho* position, ranging from OMe (**2e**, **2m** and **2o**) to Ac (**2g**) and CHO (**2h**), could be employed in good yields. In addition, the steric effect did not hinder the reaction (**2l** and **2m**) and this protocol could be extended to non-terminal vinyl azides (**2n** and **2o**), giving the desired products in good yields. It is of note that substrates containing alkynyl (**2i**) or thienyl moiety (**2q**) were compatible with the reaction conditions. Not only aryl but alkyl vinyl azides could be subject to this radical trifluoromethylation, achieving the corresponding *α*-trifluoromethylated ketones in useful yields (63–71% yield, **2r–v**). Furthermore, the chemical yields were not compromised when functionalized groups were installed (**2r–u** *vs.* **2v**).



Scheme 3 Substrate scope for *α*-trifluoromethylated ketones. Reaction conditions: A mixture of **1** (0.20 mmol), CF_3SO_2Na (0.4 mmol) and Mes-Acr$^+$ **3** (0.005 mmol, 2.5 mol%) in 1,4-dioxane (2 mL) was irradiated by blue LEDs at rt for 36-60 h. Isolated yields.

Control experiments were performed to gain more insights on the reaction mechanism (Scheme 4). In the presence of radical scavenger TEMPO, no desired product was found from the reaction mixture, along with the formation of the adduct TEMPO-CF_3 **5** only in 1% yield based on ^{19}F NMR (Scheme 4, eq 1).[10b,21] This observation supports the involvement of a radical process. We further conducted the reaction of **6** under the standard conditions, affording the cyclization product **7** in 74% (Scheme 4, eq 2). The result could confirm that this reaction involves the *α*-CF_3 iminyl radical **A** intermediate.



Scheme 4 Control experiments.

In conclusion, we have outlined a novel and simple protocol for the preparation of *α*-trifluoromethylated ketones from vinyl azides via organic photoredox catalysis upon visible-light irradiation in a redox-neutral manner. The commercially available, low cost, and easy-handling Langlois reagent serves as CF_3 radical source. This mild catalytic reaction demonstrates a broad substrate scope and high functional group tolerance, as well as displaying potential for further applications in medicinal and agrochemical research.

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