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Carbotrifluoromethylation of Allylic Alcohols *via* 1,2-Aryl Migration Promoted by Visible-Light-Induced Photoredox Catalysis**

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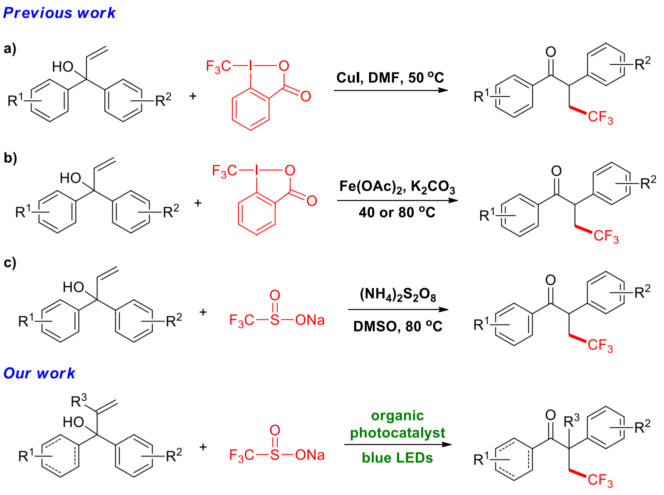
Abstract: Visible-light-enabled photocatalytic carbotrifluoromethylations of allylic alcohols and sodium triflinate were explored through 1,2-migration of an aryl group, affording an efficient method for synthesis of β-trifluoromethyl-α-substituted carbonyl compounds under mild reaction conditions. This catalyst system is well tolerant of various synthetically useful functional groups.

Keywords: Photocatalysis; visible light; carbotrifluoromethylation; trifluoromethyl radical; Langlois reagent; 1,2-aryl migration

Incorporation of the trifluoromethyl (CF_3) group into organic molecules has become an increasingly crucial subject in modern organic synthetic chemistry because it is capable of improving the biological properties of small molecules through increasing their metabolic stability, elevated electronegativity, and lipophilicity.[1] Consequently, an explosion of research efforts has been triggered to develop efficient methods for the introduction of the trifluoromethyl group into small molecules.[2-3] Many effective strategies have been developed, leveraging various “CF_3^+” or “CF_3^-” reagents such as Umemoto’s reagent, and Togni’s reagent, etc.[4] However, these established methods generally restrict their practical usage due to the high cost and/or scarce availability of these trifluoromethylation reagents. As a response to this problem, it is more appealing to take advantage of CF_3SO_2Na (Langlois reagent), which is a stable, inexpensive, and easy-to-handle trifluoromethyl source, to develop new and efficient catalytic variants for trifluoromethylation of alkenes under mild reaction conditions.

In recent years, photoredox catalysis[5,6] enabled by visible light irradiation has been demonstrated to be a powerful synthetic protocol to produce trifluoromethyl radical species. In particular, utilizing this strategy, a number of trifluoromethylations of C=C bonds have been successfully established with the concomitant formation of C–N, C–O, C–X and C–S bonds employing various CF_3 reagents, affording a facile approach to a variety of synthetically useful and biologically significant CF_3-containing frameworks.[7]

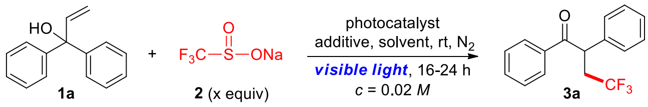
In 2013, Wu and co-workers reported an inspirational β-trifluoromethyl-α-aryl ketones synthesis *via* copper-catalyzed trifluoromethylation-triggered radical 1,2-migration of an aryl group in α,α-diaryl allylic alcohols (Scheme 1a).[8a] Subsequently, other transition-metal catalysts were also demonstrated to be effective in similar scenarios. $Fe(OAc)_2$-catalyzed carbotrifluoromethylation of allylic alcohols and Togni’s reagent was discovered by Sodeoka and co-workers for the preparation of β-trifluoromethyl-α-aryl ketones (Scheme 1b).[8b] Alternatively, a metal-free protocol for the direct aryltrifluoromethylation of allylic alcohols with CF_3SO_2Na was disclosed by Yang and Xia for β-trifluoromethyl-α-aryl ketones synthesis by using $(NH_4)_2S_2O_8$ as the oxidant (Scheme 1c). However, the established protocols[8] generally suffer from drawbacks such as the employment of transition metal catalysts, as well as unstable and expensive trifluoromethyl sources or/and strong oxidants. Therefore, a strong need remains for uncovering new and straightforward methods for the facile generation of β-trifluoromethyl-α-aryl ketones *via* visible-light-enabled photocatalytic radical 1,2-migration, with simpler substrate structures under transition-metal-free conditions.



Scheme 1. Synthetic routes to β-trifluoromethyl-α-aryl ketones

Owing to our sustaining research interest in the design and discovery of robust synthetic reactions relying on visible-light-enabled photoredox catalysis,[9] we disclose herein our recent achievement in radical carbotrifluoromethylation of allylic alcohols, which illustrates an approach for the convenient preparation of β-trifluoromethyl-α-aryl ketones using CF_3SO_2Na as the trifluoromethyl source (Scheme 1c). The event of radical abstraction might be triggered on CF_3SO_2Na [$E^{ox}_{1/2}$ = +1.05 V][6i] under the synergistic actions of an organic fluorophores 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) [$E^{red}_{1/2}(*P/P^-)$ = +1.35 V][10] and visible light irradiation, thereby leading to the formation of trifluoromethyl radical species. Subsequent of radical addition and 1,2-aryl migration would take place to yield β-trifluoromethyl-α-aryl ketones.

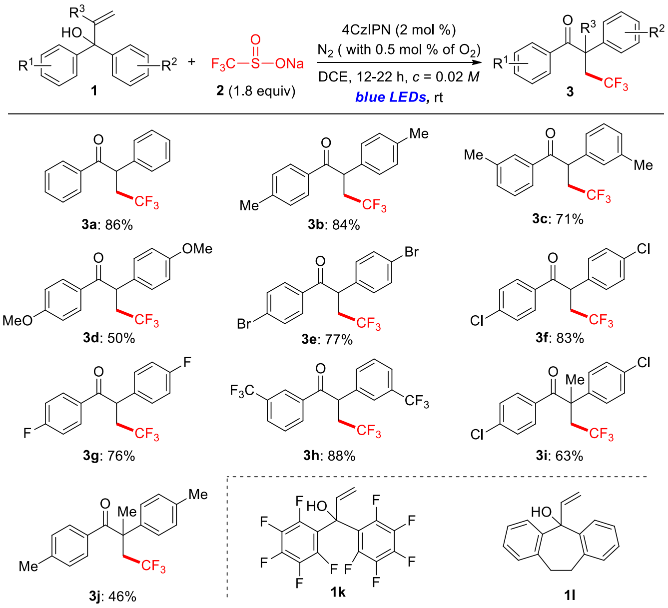
Table 1. Screenings of reaction conditions



entry	2a (equiv)	PC (x mol%)^h	solvent	yield (%)^g
1^a	1.5	eosin Y (2)	ACN	trace
2^a	1.5	4CzIPN (2)	ACN	10
3^b	1.5	4CzIPN (2)	ACN	41
4^b	1.5	4CzIPN (2)	MeOH	24
5^b	1.5	4CzIPN (2)	DMF	31
6^b	1.5	4CzIPN (2)	NMP	decomp
7^b	1.5	4CzIPN (2)	DCE	65
8^b	1.5	4CzIPN (2)	DCM	54
9^{b,c}	1.5	4CzIPN (2)	DCE	79
10^{b,c}	**1.8**	**4CzIPN (2)**	**DCE**	**86**
11^{b,c}	2.0	4CzIPN (2)	DCE	81
12^{b,c}	1.8	eosin Y (2)	DCE	trace
13^{b,c}	1.8	rose bengal (2)	DCE	trace
14^{b,c,d}	1.8	[Ir-cat. 1] (2)	DCE	45
15^{b,c,e}	1.8	[Ir-cat. 2] (2)	DCE	68
16^{b,c}	1.8	[$Ru(bpy)_3Cl_2$] (2)	DCE	trace
17^{c,f}	1.8	4CzIPN (2)	DCE	NR
18^{b,c}	1.8	/	DCE	NR

[a] Irradiation with white LED. [b] Irradiation with blue LED. [c] Reaction mixture was degassed. [d] [**Ir-cat.1**] = $Ir(ppy)_2(dtbpy)PF_6$. [e] [**Ir-cat. 2**] = $[Ir[dF(CF_3)ppy]_2(dtbbpy)]PF_6$. [f] No light was employed. [g] Yield of isolated product. [h] 4CzIPN = 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene.

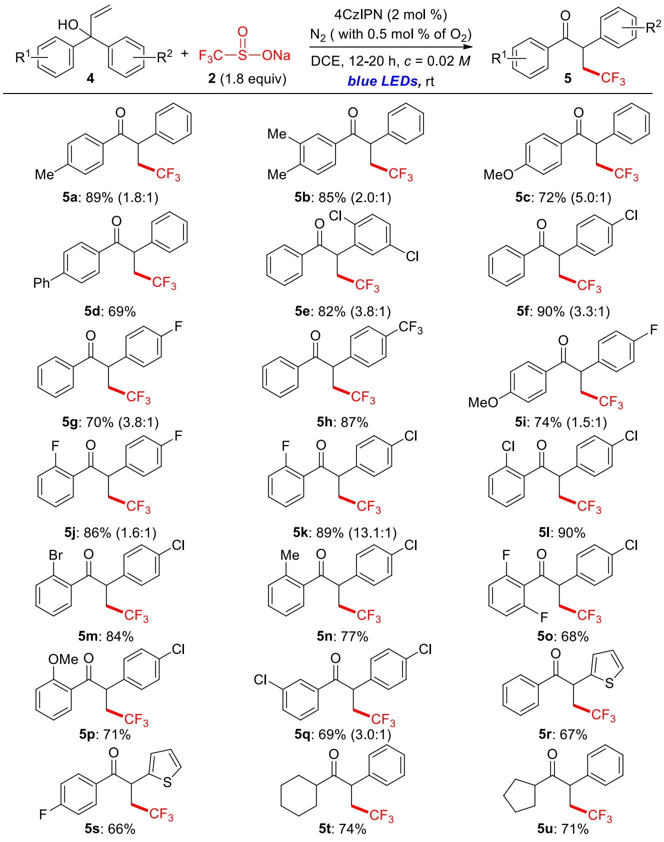
Allylic alcohol **1a** and sodium triflinate **2** were employed as the model substrates for screening the optimal reaction conditions (Table 1). Eventual success demonstrated that the capacity to deliver the β-trifluoromethyl-α-aryl ketones in synthetically meaningful efficiency relies heavily on the synergistic effects of photocatalyst, light source, and solvent. Using a catalytic amount of eosin Y as photocatalyst under white light emitting diode (LED) irradiation, no desired product was detected when the reaction was performed in MeCN under a balloon-nitrogen atmosphere at room temperature (entry 1, Table 1). Fortunately, the desired β-trifluoromethyl-α-aryl ketone **3a** was obtained in 10% isolated yield by employing 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) [$E^{red}_{1/2}(*P/P^-) = +1.35$ V, $E^{ox}_{1/2}(P/P^-) = -1.21$ V *vs.* SCE],[10] in place of eosin Y (entry 2). Under otherwise identical reaction conditions, a simple switch of the light source white LED to blue LED exhibited great improvement of the reactivity (41% isolated yield, entry 3). A number of solvents, including methanol (MeOH), dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), 1,2-dichloroethane (DCE), or dichloromethane (DCM) were next screened, from which the DCE stood out for its remarkable capacity to afford the desired product in moderate isolated yield (65%, entry 7). These results indicated that the trace amout of oxygen in the reaction system might serve as the oxidant in this migration. It merits attention that, in some of the above cases, accompanying **3a** was the formation of benzophenone as the major byproduct, arising possibly from the excess oxygen in the reaction system promoted cleavage of the C=C double bond of **1a**.[11] Indeed, when the reaction mixture was purged carefully with a stream of nitrogen (with 0.5 mol% of oxygen) for half an hour, we were pleased to find that **3a** could be obtained in an improved yield (79%, entry 9), thus suggesting that 0.5 mol% of oxygen in nitrogen was chosen as a practically simple source of oxidant. Fortunately, a satisfactory 86% yield of desired product was obtained by increasing the loading of **2a** (1.8 equiv) (entry 10). Further increasing the amount of **2a** was found to be detrimental for the product yield (entry 11). The choice of a photocatalyst was proven to be extremely significant, since the use of eosin Y, rose bengal, $Ru(bpy)_3Cl_2$, $Ir(ppy)_2(dtbpy)PF_6$ (**Ir-cat. 1**), or even $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (**Ir-cat. 2**) only resulted in critical reductions or complete inhibitions in reactivities (entries 13-16). Finally, reactions carried out under the absence of either visible light irradiation or a photocatalyst confirmed definitely that the reproducible synthesis of **3a** requires both (entries 17 and 18).



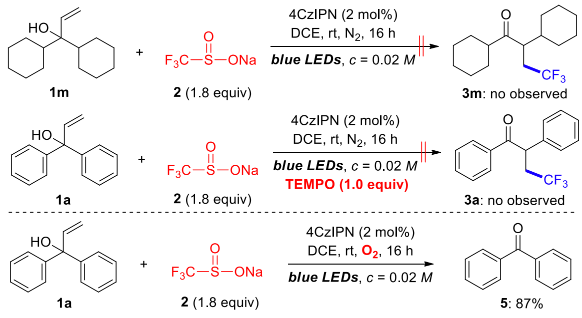
Scheme 2. Reactivity screenings on symmetrical allylic alcohols

A range of symmetrical α,α-diaryl allylic alcohols **1** were next exposed to the above-identified optimal reaction conditions; the results were summarized in Scheme 2. The substitution patterns on the aryl rings appeared to have posed little effect on the reaction efficiency. Substrates **1** bearing a *para-* and a *meta*-methyl substituent on the aromatic ring proceeded smoothly to furnish the corresponding products **3b** and **3c** in 84 and 71% isolated yields, respectively. Both electron-donating (**3d**) and electron-withdrawing (**3e-3h**) substituents on the aromatic ring were well tolerated, and the desired products were generated in good-to-excellent yield. It should be noted that β-trifluoromethyl ketones (**3i** and **3j**) containing a quaternary carbon center could also be obtained by this method. However, pentafluorophenyl **1k** was found to be almost inert in our conditions. The conformational effects were demonstrated to have a vital influence on the reactivity, in which complicated mixtures were detectable with the substrate having a tricyclic moiety (**1l**).

To expand the substrate scope of this method further, a variety of structurally variable, unsymmetrical allylic alcohols **4** next attempted to react with Langlois reagent **2**. As exemplified in Scheme 3, the reactivity seems to be general, smoothly producing the corresponding β-trifluoromethyl-α-aryl ketones **5** in good-to-excellent isolated yields (66-90%) with high chemoselectivity in each case. Substrates possessing electron-donating groups, e.g., methyl (**4a** and **4b**), methoxy (**4c**), and phenyl (**4d**) groups on the aromatic ring, afforded the corresponding products with the migration of the phenyl group in a preferential manner. When unsymmetrical allylic alcohols **4** having electron-withdrawing substituents on the aromatic ring were employed as the substrates, the more electron-deficient aryl group was found to migrate preferentially to generate the β-trifluoromethyl-α-aryl ketones **5e**-**5i** in each case. The results, in conjunction with the previous reports,[8] strongly suggested that radical intermediates should be involved in this migration. It is interesting that substitution patterns on the aryl rings in unsymmetrical allylic alcohols **4** were demonstrated to be significant. When the substrate **4j**, which carries 2-fluorophenyl and 4-fluorophenyl groups, was subjected to the standard reaction conditions, two inseparable isomers were obtained in a 1:1.6 ratio and 86% yield. Notably, a switch of a 4-fluorophenyl group to a 4-chlorophenyl group in the case of **4k** was found to improve the chemoselectivity dramatically, from which migration of 4-chlorophenyl ring was faster than that of the 2-fluorophenyl group. Furthermore, preferential migration of a *para*-substituted aryl ring was also recorded in the cases of **5l**-**5q**, regardless of whether the *ortho*- or *meta*-substituent was electron-withdrawing or electron-donating. It is worth noting that the reactions were also successful with α-heterocyclic or alkyl-substituted allylic alcohols; the corresponding β-trifluoromethyl-α-aryl ketones (**5r**-**5u**) were thus yielded in 66-74% yield.

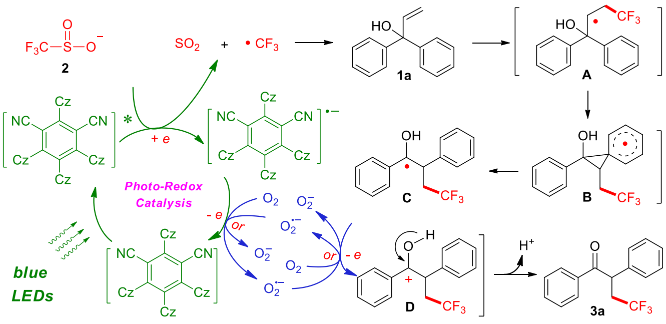


Scheme 3. Reactivity screenings on unsymmetrical allylic alcohols **4**



Scheme 4. Control experiments

To elucidate the potential reaction pathways, several control experiments were performed (see the Supporting Information), and some results are shown in Scheme 4. When α,α-dicyclohexyl allylic alcohol **1m** was exposed to the standard reaction conditions to react with Langlois reagent **2**, no desired β-trifluoromethyl-α-cyclohexyl ketone **3m** was yielded at all. Next, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was consciously added into the reaction mixture as a radical scavenger, and complete inhibition in reactivity was observed. These collected results also supported that the reaction should be a radical pathway.12 Interestingly, when the reaction was performed in the presence of a ballooned O_2 atmosphere under otherwise identical reaction conditions, benzophenone **5** was furnished in excellent isolated yield, but no migratory product **3a** was observed.[13] Finally, to identify the effect of photostimulation, we explored on-off switching of the light source in the reaction of **1f** with CF_3SO_2Na under standard reaction conditions, in which a full consumption of **1f** required continuous irradiation of visible light, thus suggesting that a radical chain process might be ruled out in this migration.[14]



Scheme 5. Proposed mechanistic network

A plausible mechanistic network enabled by these observations is illustrated in Scheme 5. Upon exposure to visible light irradiation, sulfinate anion **2** would be reductively quenched by the excited-state species 4CzIPN to generate SO_2 and a relatively stable trifluoromethyl radical, which should react with alkene **1a** to give rise to the key radical **A**.[8] Subsequent 1,2-aryl migration *via* spiro[2,5]octadienyl[8a] radical **B** yields the radical intermediate **C**. Finally, intermediate **C** would undergo a sequence of oxidation and deprotonation to deliver the final β-trifluoromethyl-α-aryl ketone product, **3a**.

In conclusion, by subjecting a series of α,α-diaryl allylic alcohols and Langlois reagent to visible-light photoredox catalysis under mild reaction conditions, we disclosed a novel technology for β-trifluoromethyl-α-aryl ketones synthesis through photocatalytic radical 1,2-aryl migration. This catalyst system is tolerant of various synthetically useful functional groups, including bromo, chloro, fluoro, trifluoromethoxy, methoxy, and phenyl. Compared with the previous established methods, this method, not requiring any strong oxidants and transition-metal catalysts and using easily accessible and relatively low cost starting materials, adds further to its applications in organic synthesis.

Experimental Section

A flame-dried round bottom flask (25 mL) was equipped with magnetic stir bar and charged with α,α-diaryl allylic alcohols **1** (0.145 mmol, 1.0 equiv), CF_3SO_2Na **2** (0.261 mmol, 1.8 equiv), 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) (0.0029 mmol, 0.02 equiv), and DCE (7.5 mL). The reaction mixture was degassed carefully by purging thoroughly with nitrogen (with 0.5 mol % of oxygen) for half an hour, then irradiated by blue LED (18 *W*) under a balloon nitrogen (with 0.5 mol % of oxygen) atmosphere at room temperature until the starting material disappeared from the TLC. After that, the reaction mixture was directly concentrated under reduced pressure and the crude product was purified by silica gel column chromatography to afford the desired product.

Acknowledgments

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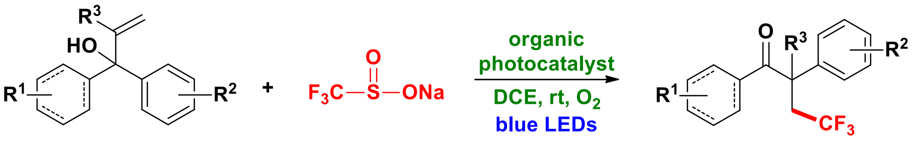
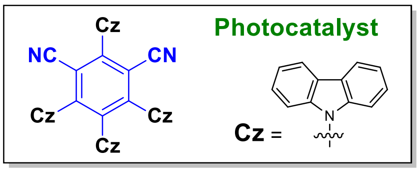
[13] For the mechanistic proposal for benzophenone **5** formation, see the Supporting Information.

[14] C. J. Wallentin, J. D. Nguyen, P. Finkbeiner, C. R. Stephenson, *J. Am. Chem. Soc.* **2012**, *134*, 8875.

10.1002/adsc.201800726

Graphical Abstract





- ***strong-oxidant-free***
- ***transition-metal-free***
- ***good functional group tolerance***
- ***readily available starting materials***