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# Visible-Light-Induced Three-Component Intermolecular Trifluoromethyl-Alkenylation Reactions of Unactivated Alkenes

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*Dedicated to the 100th anniversary of Chemistry at Nankai University.*

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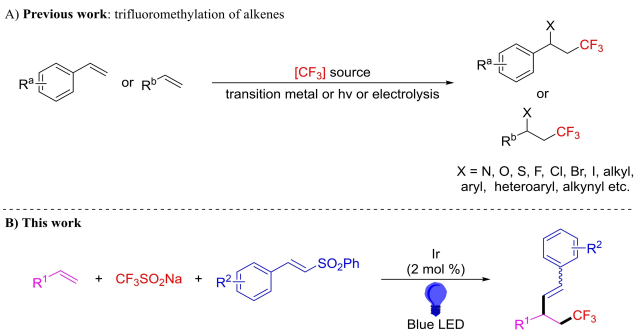
**Abstract:** Herein, we describe a practical protocol for efficient, mild, visible-light-induced three-component intermolecular trifluoromethyl-alkenylation reactions of unactivated alkenes. The protocol has good functional group tolerance and a broad substrate scope. Using this protocol, we not only introduced a trifluoromethyl group into alkenes but also converted unactivated alkenes to styrene-based activated alkenes, in addition to accomplishing late-stage functionalization of pharmaceutical intermediates.

**Keywords:** Photocatalysis; Three components; Unactivated alkenes; Trifluoromethylation; Alkenylation

The development of fluorine chemistry has great significance for organic synthesis because introduction of a fluorine atom or fluorinated moiety into a molecule can improve its physical, chemical, or biological properties.[1] For example, replacing a hydrogen atom or methyl group with a trifluoromethyl group ($CF_3$) markedly alters a molecule's lipophilicity, absorbability, metabolic stability, hydrophobicity, and binding selectivity.[2]

Intermolecular difunctionalization of alkenes, a transformation that forms two chemical bonds in a single reaction, is an efficient, atom-economical method for constructing complex organic molecules from inexpensive, readily available starting materials.[3] Over the past few decades, a number of methods for alkene difunctionalization have been developed, including transition-metal-catalyzed reactions, visible-light-mediated reactions, reactions involving both photoredox and transition-metal catalysts, and electrocatalytic fluoroalkylation reactions.[4] Of these methods, one of the most attractive involves difunctionalization of alkenes with $CF_3$ radical (such as the Umemoto reagent,[5] Togni reagents,[6] Langlois' reagent,[7] $CF_3SO_2Cl$,[8] $CF_3I$,[9] $CF_3Br$,[10] $TMSCF_3$,[11] $CF_3SO_2NHNHBoc$,[12] $(CF_3CO)_2O$[13] and (bpy)$Cu(CF_3)_3$[14]) (Scheme 1A). Using these reagents, many research groups have achieved various difunctional modifications of the styrenes and unactivated alkenes through trifluoromethyl radicals. These research results can be divided into carbo-$CF_3$,[15] amino-$CF_3$,[16] oxo-$CF_3$,[17] thio-$CF_3$,[18] halo-$CF_3$.[19] and so on.

In the past few decades, considerable progress has been made in the development of methods capable of synthesizing $CF_3$-containing molecules, with particular emphasis on the direct trifluoromethylation of alkenes. These remarkable achievements can help us effectively




**Scheme 1.** Trifluoromethylative difunctionalization of alkenes.

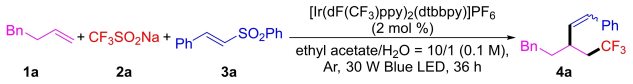
convert alkenes into various trifluoromethyl-containing molecules by forming two chemical bonds in one reaction. However, there is still a lack of effective bifunctional reaction methods that convert unactivated alkenes into styrene-based activated alkenes. This reaction product can be used as an olefin synthon for other types of difunctionalization reactions. Very recently, Yang and co-workers reported iron-catalyzed trifluoromethyl-alkenylation reactions of unactivated olefins with a substituted cinnamic acid as the alkenyl source.[20] Many substrates can undergo trifluoromethyl-alkenylation by means of this method, but the range and quantity of unactivated alkenes are still insufficient. In addition, because of the harsh reaction conditions, the method cannot be used for late-stage functionalization of pharmaceutical intermediates.

We hypothesized that we could use Langlois' reagent ($CF_3SO_2Na$) to achieve visible-light-mediated intermolecular trifluoromethyl-alkenylation reactions between unactivated alkenes and vinyl sulfones under mild conditions. Such a method not only would have a wide substrate scope but also could be used for late-stage functionalization of drug molecules containing unactivated alkenes (Scheme 1B).

To test our hypothesis, we chose 4-phenyl-1-butene (**1a**), $CF_3SO_2Na$ (**2a**), and (*E*)-(2-(phenylsulfonyl) vinyl)benzene (**3a**) as model substrates to optimize the reaction conditions (Table 1). By screening several photocatalysts (entries 1–5), we found that [Ir(dF($CF_3$)ppy)$_2$(dtbbpy)]$PF_6$, *fac*-Ir(ppy)$_3$, and Eosin Y gave target product **4a**. We were delighted to find that irradiation of **1a** (1 equiv.), **2a** (2 equiv.), **3a** (2 equiv.), and [Ir(dF($CF_3$)ppy)$_2$(dtbbpy)]$PF_6$ (2 mol%) in 10:1 (v/v) ethyl acetate/$H_2O$ (0.1 M) under argon afforded an excellent yield of **4a** (see the Supporting Information for screening details). When the solvent mixture was changed to 10:1 (v/v) acetone/$H_2O$ (0.1 M), the yield decreased slightly (entry 6), and different solvent mixtures gave greatly reduced yields (entries 7–9). When the reaction was carried out under air, the yield of the product was low (entry 10), which indicates that oxygen interfered with the reaction. Control experiments showed that in the absence of a photocatalyst or light, none of the desired product was detected (entries 11 and 12).

With the optimized reaction conditions (Table 1, entry 1) in hand, we evaluated the substrate scope with respect to alkene **1** (Scheme 2). Unactivated terminal aliphatic alkenes could be smoothly transformed into the corresponding trifluoromethyl-alkenylation products (**4a–4f**) in moderate to good yields with modest *Z/E* ratios. Enol ethers, enol esters, and common alkyl ethers also afforded the target products (**4g–4k**) in moderate yields with modest *Z/E* ratios. A free hydroxyl group and a tosyl-protected hydroxyl group

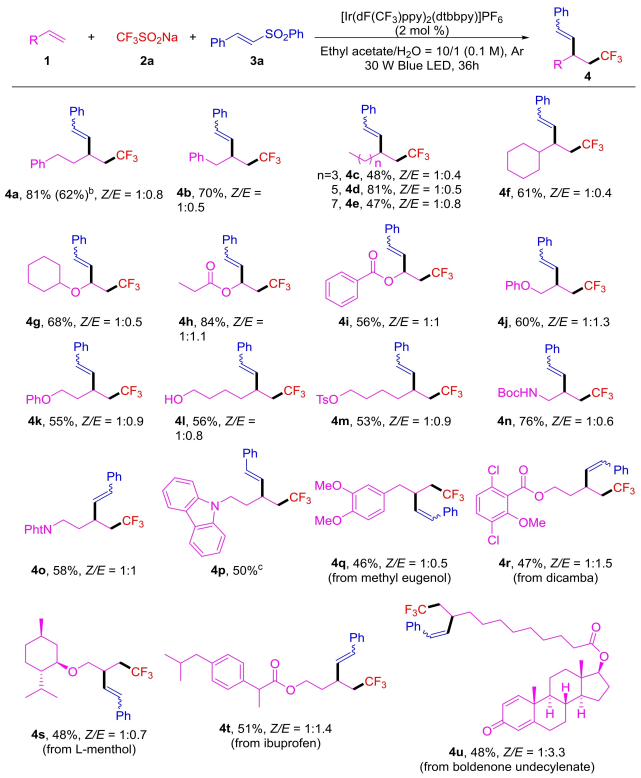
**Table 1.** Optimization of reaction conditions.[a]




1a 2a 3a 4a

| Entry | Variation from standard conditions | Yield (%)[b] |
|---|---|---|
| **1** | **none** | **81** |
| 2 | *fac*-Ir(ppy)$_3$ as photocatalyst | 9[c] |
| 3 | EosinY as photocatalyst | 7[c] |
| 4 | Ru(bpy)$_3$Cl$_2$·6H$_2$O as photocatalyst | NR[c] |
| 5 | Mes-Acr$^+$-Me $ClO_4^-$ as photocatalyst | NR[c] |
| 6 | 10:1 acetone/$H_2O$ as solvent | 78 |
| 7 | 10:1 MeCN/$H_2O$ as solvent | trace |
| 8 | 10:1 THF/$H_2O$ as solvent | 23 |
| 9 | 10:1 toluene/$H_2O$ as solvent | 11 |
| 10 | under air | 20 |
| 11 | no photocatalyst | 0 |
| 12 | no light | 0 |

[a] Reaction conditions, unless otherwise noted: **1a** (0.3 mmol), **2a** (0.6 mmol), **3a** (0.6 mmol), and [Ir(dF($CF_3$)ppy)$_2$(dtbbpy)]$PF_6$ (2 mol%) in 10:1 (v/v) ethyl acetate/$H_2O$ (0.1 M) were irradiated with 30 W blue LEDs at room temperature under argon for 36 h.
[b] Isolated yields are provided. NR = no reaction.
[c] 3 mL DMSO (0.1 M) used as solvent.

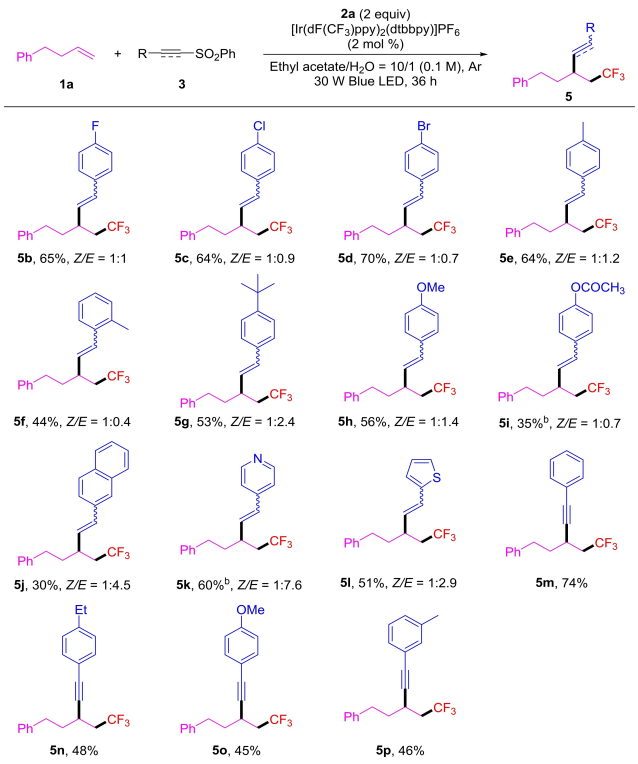



**Scheme 2.** Substrate scope with respect to alkene **1** [a]Reactions were performed under the conditions listed in entry 1 of Table 1, unless otherwise noted; isolated yields are provided. [b]The reaction was carried out with 4 mmol of **1a**. [c]Z-4p was also produced, but it is inseparable from unknown impurities and no pure Z-4p can be obtained.

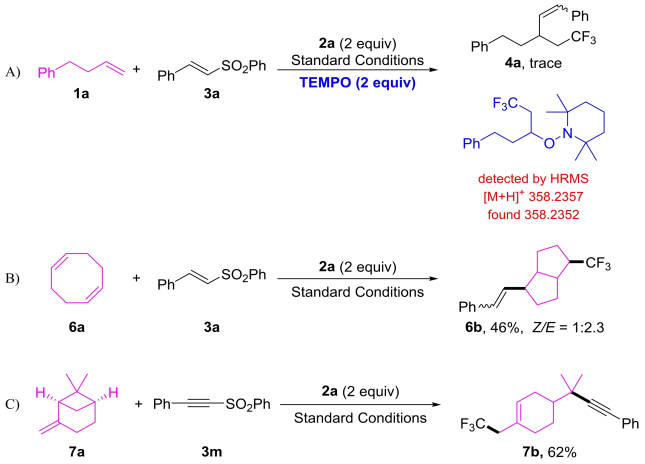
were tolerated (**4 l** and **4 m**). Various nitrogen-containing functional groups-an amide (**4 n**), an imide (**4 o**), and a carbazole (**4 p**)-remained intact under the mild reaction conditions. Unfortunately, however, styrene-type olefins were not amenable to the reaction. To demonstrate the scalability of the protocol, we conducted a reaction using 4 mmol alkene **1 a**, which afforded 0.76 g **4 a** (62% yield). The excellent functional group tolerance of the reaction suggested that it could be used for late-stage functionalization of bioactive molecules. To evaluate this possibility, we selected methyl eugenol, dicamba derivatives, and the drug molecules menthol derivatives, ibuprofen derivatives, and boldenone undecylenate as substrates. Reactions of these molecules gave the corresponding trifluoromethyl-alkenylation products (**4 q**–**4 u**) in moderate yields.

Next we carried out reactions of a broad range of functionalized sulfones **3** with 4-phenyl-1-butene (**1 a**) and $CF_3SO_2Na$ (**2 a**) under the optimized conditions (Scheme 3). Vinyl sulfones with a halogen atom (F, Cl, or Br) in the *para* position smoothly gave the corresponding trifluoromethyl-alkenylation products (**5 b**–**5 d**) in good yields with modest *Z/E* ratios. The reaction also proceeded smoothly with phenylvinyl sulfones bearing an electron-donating group at the *ortho* or *para* position to give the corresponding trifluoromethyl-alkenylation products (**5 e**–**5 i**) in moderate yields with modest *Z/E* ratios. Moreover, fused-ring aromatic-hydrocarbon-, pyridine-, and thiophene-based vinyl sulfones also reacted smoothly to give target products **5 j**–**5 l** in moderate yields. Substrates with an electron-withdrawing atom (–F, –Cl or –Br) in the *para*-position or have an electron-withdrawing pyridine ring gave better yields than electron-donating group (e. g., –Me, –OMe, –$^t$Bu or –OCOMe). We were pleased to find that acetylene sulfones could also be used to achieve the trifluoromethyl-alkynylation reaction, affording target compounds **5 m**–**5 p** in moderate to good yields.

To gain mechanistic insight into the process, we carried out several control experiments. When the radical scavenger TEMPO (2,2,6,6-tetramethyl-piperidine nitroxide) was added to the model reaction system, the desired coupling was completely shut down, and the corresponding radical-trapping product was detected by high-resolution mass spectrometry (Scheme 4A). This result indicates that a trifluoromethyl radical formed from $CF_3SO_2Na$ and rapidly added to the alkene to form a new alkyl radical intermediate. Radical clock experiments using 1,5-cyclooctadiene (**6 a**) and (1*S*)-(−)-β-pinene (**7 a**) under the standard conditions afforded cyclized product **6 b** (Scheme 4B) and ring-opened product **7 b** (Scheme 4C), respectively, results that further support the free-radical mechanism we have proposed. Through controlled experiments, we found that isomer E will be converted to Z isomer, but not completely converted (can see the Supporting Information for more details).[21] We also monitored the changes of the E/Z isomer ratio during the reaction by H NMR. Through H NMR, we found that at the beginning of the reaction, the thermody-




**Scheme 3.** Substrate scope with respect to sulfone **3** [a]Reactions were performed under the conditions listed in entry 1 of Table 1, unless otherwise noted; isolated yields are provided. [b]The solvent was 10:1 (v/v) acetone/$H_2O$ (0.1 M).

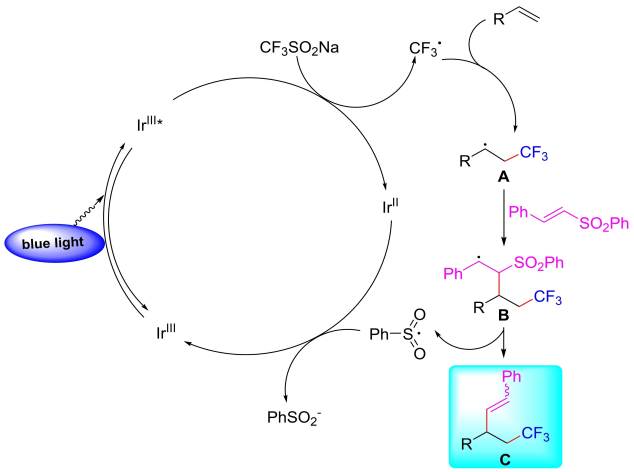



**Scheme 4.** Control experiments [a]Reactions were carried out under the conditions listed in entry 1 of Table 1; isolated yields are provided.

namically more stable E isomer was the main product, but as the reaction progressed, the thermodynamically unstable Z isomer became the main product (can see the Supporting Information for more details). Unfortunately, we have no method to improve stereoselectivity.

On the basis of our mechanistic experiments and literature reports,[22] we propose the mechanism depicted in Scheme 5. Photoexcited *[Ir(dF($CF_3$)ppy)$_2$(dtbbpy)]$PF_6$ [$E_{1/2}^{red}$ ($*Ir^{III}/Ir^{II}$) = +1.21 V vs SCE; τ = 2.3 μs][23] undergoes a single-electron-transfer reaction with $CF_3SO_2Na$ to form a trifluoromethyl radical and $Ir^{II}$. The radical reacts with the alkene to form new alkyl radical intermediate **A**, which then attacks the vinyl sulfone to form benzyl radical **B**. Radical **B** releases the desired product **C** and an open-shell phenyl sulfonyl radical. Finally, the phenyl sulfonyl radical ($E_{1/2}^{red}$ = +0.50 V vs SCE) undergoes a single-electron-transfer reaction with the reduced photocatalyst $Ir^{II}$ ($E_{1/2}$ [$Ir^{III}/Ir^{II}$] = −1.37 V vs SCE) to close the catalytic cycle.[22b] Theoretically, the generated phenylsulfonyl radicals may react with an alkene during the reaction. However, we did not find this addition product, probably because the phenylsulfonyl radicals react with the reduced photocatalyst $Ir^{II}$ at a faster rate than the reaction with an alkene.

In conclusion, we have developed a practical protocol for efficient, mild, visible-light-induced three-component intermolecular trifluoromethyl-alkenylation reactions of unactivated alkenes. Using this protocol, we not only introduced a trifluoromethyl group into alkenes but also converted unactivated alkenes to styrene-based activated alkenes. The excellent functional group tolerance and mild conditions give this protocol a broad substrate scope and make it suitable for late-stage functionalization of pharmaceutical intermediates.




**Scheme 5.** Proposed mechanism.

## Experimental Section

To a 15 mL glass vial was added [Ir(dF($CF_3$)ppy)$_2$(dtbbpy)]$PF_6$ (6.7 mg, 0.006 mmol, 2 mol%), alkene **1** (0.3 mmol, 1 equiv.), **2a** (93.6 mg, 0.6 mmol, 2 equiv.), sulfone **3** (0.6 mmol, 2 equiv.) and ethyl acetate:$H_2O$ (3 mL, V/V = 10:1). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W Blue LED (approximately 5 cm away from the light source) at room temperature for 36 h. When the reaction is completed, extracted with ethyl acetate, washed with brine, dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (hexane/ethyl acetate) to afford the target compound.

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