Trifluoromethylation

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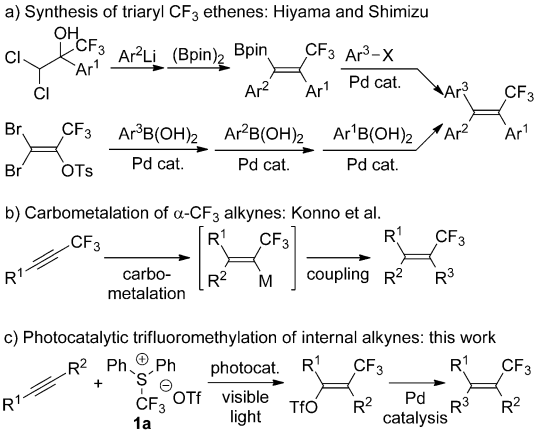
Photoredox-Catalyzed Stereoselective Conversion of Alkynes into Tetrasubstituted Trifluoromethylated Alkenes

Ren Tomita, Takashi Koike, and Munetaka Akita**

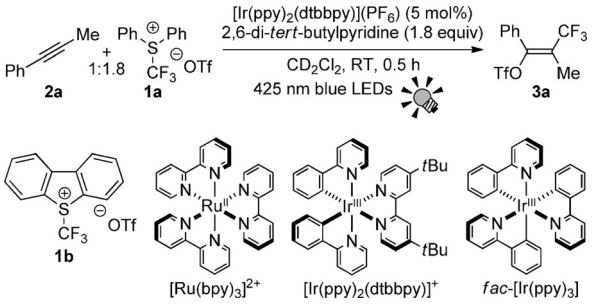
Abstract: *A regio- and stereoselective synthesis of trifluoromethylated alkenes bearing four different substituents has been developed. Stereocontrolled sulfonyloxytrifluoromethylation of unsymmetric internal alkynes with an electrophilic CF_3 reagent, namely the triflate salt of the Yagupol'skii–Umemoto reagent, in the presence of an Ir photoredox catalyst under visible-light irradiation afforded trifluoromethylalkenyl triflates with well-predictable stereochemistry resulting from anti addition of the trifluoromethyl and triflate groups. Subsequent palladium-catalyzed cross-couplings led to tetrasubstituted trifluoromethylated alkenes in a highly stereoselective manner. The present method is the first example of a facile one-pot synthesis of tetrasubstituted trifluoromethylated alkenes from simple alkynes.*

Tetrasubstituted alkenes represent a useful structural motif that is found in biologically active natural products, drugs, and functional materials.[1] Therefore, the development of new and reliable methods for the stereoselective synthesis of tetrasubstituted alkenes is in high demand.[2] Owing to the unique properties of the trifluoromethyl (CF_3) group, CF_3-substituted alkenes have great potential in the pharmaceutical, agrochemical, and material sciences.[3] Step-economic and versatile stereoselective synthetic methods towards tetrasubstituted trifluoromethylated alkenes, however, have been extremely limited thus far.[4] Hiyama and Shimizu reported the synthesis of CF_3-substituted triarylethenes starting from CF_3-substituted dichlorohydrin and 1,1-dibromo-3,3,3-trifluoro-2-tosyloxypropene (Scheme 1a). Konno et al. developed methods based on the carbometalation of CF_3-substituted alkynes (Scheme 1b). However, these excellent methods require CF_3-substituted precursors, reducing their versatility and simplicity. In contrast, the direct trifluoromethylation of alkynes is regarded as one of the most straightforward strategies for the synthesis of CF_3-substituted alkenes. Nevertheless, highly stereoselective trifluoromethylations of simple internal alkynes are still a great challenge in spite of the recent development of various trifluoromethylation methods.[5,6] Herein, we describe a novel stereoselective



Scheme 1. Stereoselective synthesis of tetrasubstituted trifluoromethylated alkenes.

Table 1: Optimization of the photocatalytic trifluoromethyltriflation of **2a**.



Entry	Deviations from the standard conditions[a]	**3a**[b] [%]	*E*/*Z*[c]
1	–	84	99:1
2	10 min	74[d]	99:1
3	2 h	84	96:4
4	**1a** (1 equiv)	62[e]	98:2
5	**1b**, 1 h	75	94:6
6	$[Ru(bpy)_3](PF_6)_2$, 10 h	80	99:1
7	*fac*-[Ir(ppy)$_3$], 2 h	70	99:1
8	CD_3CN	47	95:5
9	[D_6]acetone	13	–
10	2,6-lutidine	79	98:2
11	Na_2CO_3	77	98:2
12	no base	77	98:2
13	no light	0	–
14	no photocatalyst	0	–

[a] For detailed reaction conditions, see the Supporting Information. [b] Yields were determined by ^{1}H NMR spectroscopy using $SiEt_4$ as an internal standard. [c] The *E*/*Z* ratios were determined by ^{19}F NMR spectroscopy. [d] Unreacted **2a** (13%) was observed. [e] Unreacted **2a** (23%) was observed. bpy = 2,2′-bipyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, LED = light-emitting diode, ppy = 2-pyridylphenyl.

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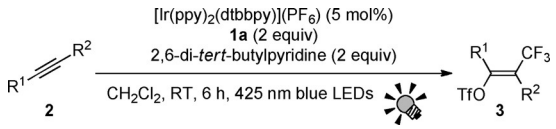
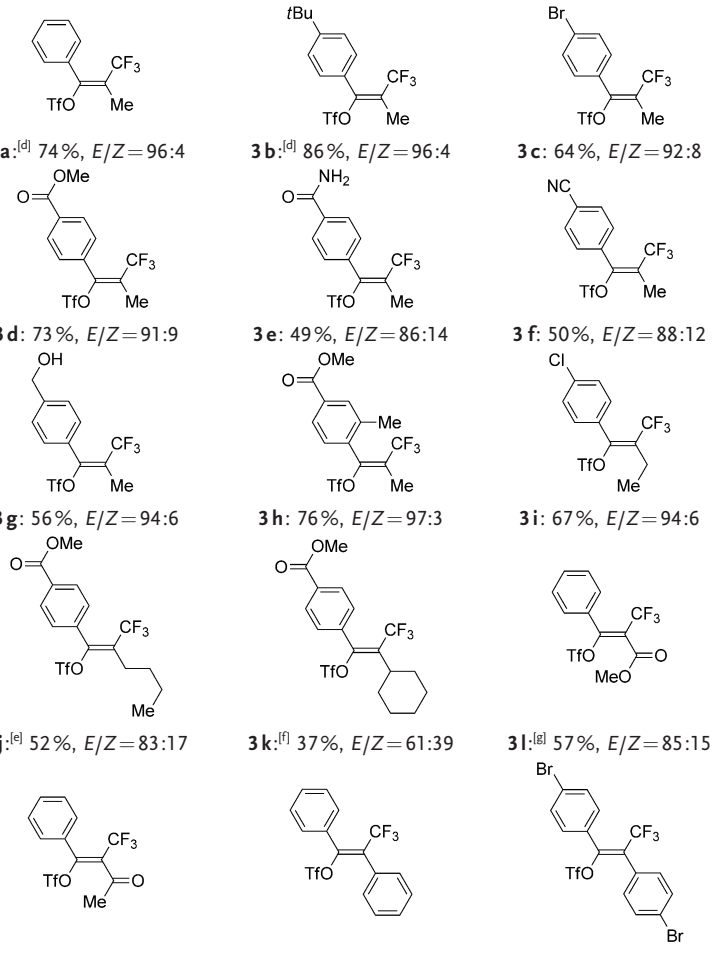
Table 2: Scope of the photocatalytic trifluoromethyltriflation of alkynes.[a,b,c]





[a] For detailed reaction conditions, see the Supporting Information. [b] Yields of isolated products. [c] The *E*/*Z* ratios were determined by ^{19}F NMR spectroscopy of the crude product mixtures. [d] **1a** and base (1.8 equiv each). [e] **1a** and base (2.8 equiv each), 10 h. [f] **1a** and base (3.0 equiv each), 12 h. [g] **1a** and base (2.2 equiv each).

sulfonyloxytrifluoromethylation of internal unsymmetric alkynes mediated by visible-light photoredox catalysis.[7] A shelf-stable and easy-to-use electrophilic CF_3 reagent, *S*-(trifluoromethyl)diphenylsulfonium trifluoromethanesulfonate (**1a**; Yagupol'skii–Umemoto reagent),[8] was found to be a key compound for the difunctionalization of alkynes. The obtained trifluoromethylalkenyl triflates were readily converted into tetrasubstituted trifluoromethylated alkenes in a stereocontrolled manner by well-established Pd-catalyzed coupling reactions. This method thus enables the facile one-pot synthesis of CF_3-substitued alkenes bearing four different substituents (Scheme 1c).

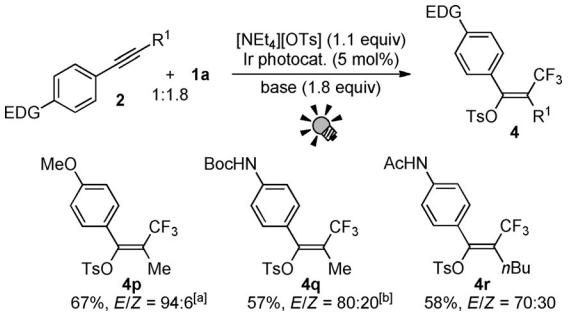
Previously, we had developed a regiospecific trifluoromethylating difunctionalization reaction of alkenes mediated by photoredox catalysis.[9] The experience accumulated during these earlier projects prompted us to design a method for the trifluoromethylating difunctionalization of alkynes through photoredox single electron transfer (SET) processes. Initially, we examined the photocatalytic trifluoromethanesulfonyloxy-trifluoromethylation (trifluoromethyltriflation) of 1-phenyl-1-propyne (**2a**), an unsymmetric internal alkyne, with the Yagupol'skii–Umemoto reagent (**1a**). To our delight, the reaction of alkyne **2a** with 1.8 equivalents of **1a** in CD_2Cl_2 in the presence of an Ir photoredox catalyst, namely $[Ir(ppy)_2(dtbbpy)](PF_6)$ (5 mol%), and 2,6-di-*tert*-butylpyridine under visible-light irradiation (425 nm blue LEDs) for 0.5 h afforded the desired product **3a** in an NMR yield of 84% in a highly regio- and stereoselective manner (*E*/*Z* = 99:1). Shorter (10 min) or longer reaction times (2 h) did not lead to a significant deterioration of the stereoselectivity (Table 1, entries 1–3), indicating that an isomerization process is not involved in the present reaction as a major reaction pathway. Reducing the amount of **1a** led to a lower conversion of **2a** (entry 4). The use of Umemoto's reagent (**1b**) lowered the yield and the efficiency owing to the degradation of **1b** under the reaction conditions (entry 5). Other photocatalysts turned out to be inefficient (entries 6 and 7). Other solvent systems, such as CD_3CN and $[D_6]$acetone, gave complicated mixtures of products (entries 8 and 9). The addition of a bulky organic base, 2,6-di-*tert*-butylpyridine, made the reaction cleaner, improving the yield of **3a** (entries 10–12).[10] Finally, irradiation with visible light and the photoredox catalyst were shown to be essential for the present reaction (entries 13 and 14).

The tetrasubstituted trifluoromethylalkenyl triflates that were obtained through this photocatalytic trifluoromethylation are shown in Table 2. The reactions of 1-phenyl-1-propyne (**2a**) and various derivatives (**2b**–**2g**) afforded the corresponding trifluoromethylalkenyl triflates (**3a**–**3g**) in 49–86% yield in a highly stereoselective manner (*E*/*Z* = 86:14–96:4). Remarkably, the present reaction tolerates a variety of functional groups on the arene ring, such as halide (**2c**), ester (**2d**), primary amide (**2e**), nitrile (**2f**), and hydroxy (**2g**) groups. Furthermore, a substituent in the *ortho* position of the arene ring (**2h**) did not induce a deterioration of yield and stereoselectivity (**3h**: 76%, *E*/*Z* = 97:3).

Aryl alkyl acetylenes (Ar–C≡C–R), such as **2i**, **2j**, and **2k**, can also be trifluoromethylated under these reaction conditions. Substrates with alkyl groups bulkier than a methyl group, such as ethyl and *n*-butyl groups, still afforded the *E* stereoisomer selectively (**3i**: 67%, *E*/*Z* = 94:6; **3j**: 52%, *E*/*Z* = 83:17). An even bulkier substituent, namely a cyclohexyl group, had a significant harmful effect on the efficiency and stereoselectivity (**3k**: 37%, *E*/*Z* = 61:39). The reactions of methyl 3-phenyl-2-propynoate (**2l**) and 4-phenyl-3-butyn-2-one (**2m**) also proceeded in a stereoselective manner to give useful α-CF_3-substituted enones (**3l**: 57%, *E*/*Z* = 85:15; **3m**: 63%, *E*/*Z* = 86:14).[6o] Furthermore, diaryl acetylenes (**2n** and

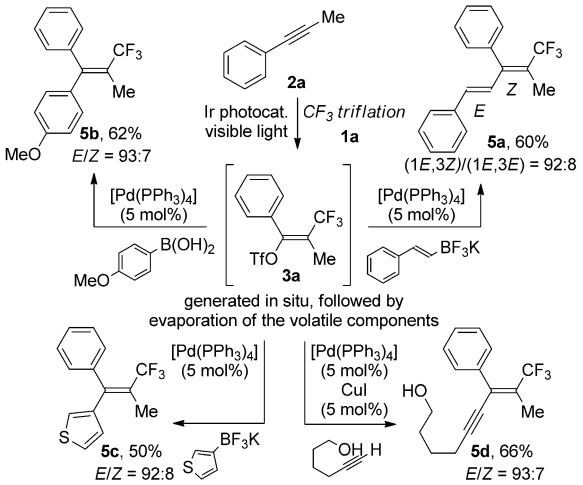
2o) afforded the corresponding diaryl trifluoromethylalkenyl triflates in moderate yields and stereoselectivities (**3n**: 30%, $E/Z = 89{:}11$; **3o**: 30%, $E/Z = 85{:}15$). A simple aliphatic alkyne, 6-dodecyne, did not afford the corresponding product. These results show that the present photocatalytic reaction can be used for the regio- and highly stereoselective difunctionalization of aryl acetylenes with trifluoromethyl and triflate groups.

While investigating the scope, we found that the reaction products of 1-aryl-1-propynes bearing an electron-donating group (EDG) on the aryl ring could not be isolated presumably owing to their susceptibility to hydrolysis. Therefore, the trifluoromethylating sulfonyloxylation of alkynes with other external nucleophiles was examined. The reaction with a tetraalkylammonium tosylate (1.1 equiv) yielded the corresponding trifluoromethylalkenyl tosylates **4** as isolable products. The tosylate system is amenable to the synthesis of anisyl and *N*-protected aminophenyl trifluoromethylalkenyl tosylates (**4p**: 67%, $E/Z = 94{:}6$; **4q**: 57%, $E/Z = 80{:}20$; **4r**: 58%, $E/Z = 70{:}30$). The tosylate system also exhibited a high stereoselectivity as the trifluoromethyl and tosylate groups were added to the alkyne in an *anti* fashion (Scheme 2).



Scheme 2. Photocatalytic trifluoromethyltosylation of alkynes bearing an electron-donating group (EDG). Reaction conditions: $[Ir(ppy)_2(dtbbpy)](PF_6)$ (5 mol%), 2,6-di-*tert*-butylpyridine (1.8 equiv). [a] **1a** and base (1.5 equiv each) were used. [b] $[NMe_4][OTs]$ was used. EDG = electron-donating group.

Next, we examined the stereocontrolled synthesis of trifluoromethylalkenes bearing four different substituents through Pd-catalyzed coupling reactions of the trifluoromethylalkenyl triflates. As shown in Scheme 3, CF_3-substituted alkenyl triflate **3a**, generated in situ by the photoredox-catalyzed reaction, was directly subjected to various Pd-catalyzed reactions without purification and after solvent exchange. As a result, the tetrasubstituted CF_3-substituted alkene **5a** was obtained in 60% yield in a highly stereoselective manner ($(1E,3Z)/(1E,3E) = 92{:}8$) in a one-pot process. The present, highly programmable strategy enabled the stereocontrolled synthesis of a variety of tetrasubstituted CF_3-substituted alkenes **5a**–**5d** in facile one-pot reactions. It turned out that the stereochemistry of **3a** was almost retained during the Pd-catalyzed reactions under mild conditions (RT–40 °C). Furthermore, trifluoromethylalkenyl tosylate **4p** also underwent a Pd-catalyzed coupling with phenylboronic acid

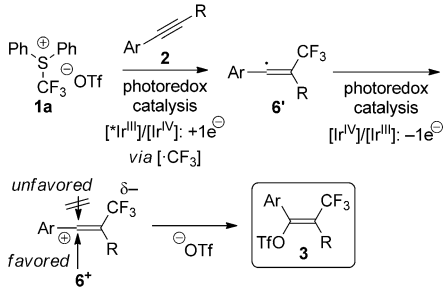


Scheme 3. One-pot stereocontrolled synthesis of tetrasubstituted trifluoromethylated alkenes from alkynes. Yields of **5** are based on **2a**.

to afford **5b** ($E/Z = 8{:}92$) in 49% yield (see the Supporting Information).

A possible reaction mechanism for the photocatalytic sulfonyloxytrifluoromethylation is illustrated in Scheme 4. Up to the regiospecific generation of the α-styryl-type trifluoromethylalkenyl radical **6′**, which is stabilized by delocalization to the π orbitals of the phenyl ring,[11a,c] the reaction appears to proceed through a mechanism similar to that of the previously reported photoredox-catalyzed trifluoromethylation of olefins.[9,12] Key intermediate **6′** can undergo 1e oxidation by the highly oxidizable Ir photocatalyst (Ir^{IV})[11b,12] to give trifluoromethylalkenyl cation **6**$^+$. The highly stereoselective formation of trifluoromethylalkenyl triflate **3** can be interpreted in terms of the strongly electronegative properties of the CF_3 group:[4a,13] Nucleophilic attack of the triflate anion favors *anti* addition with respect to the CF_3 group owing to electrostatic repulsion, as supported by the electrostatic potential map of **6a**$^+$ (see the Supporting Information). We also suggest that another possible mechanism proceeds through direct addition of the triflate anion to **6′** followed by 1e oxidation (see the Supporting Information). We cannot determine the exact reaction pathway at present.

In conclusion, we have developed novel trifluoromethyltriflation and -tosylation reactions of alkynes mediated by photoredox catalysis. The present photocatalytic system



Scheme 4. Possible reaction mechanism.

turned out to be powerful for the regio- and highly stereocontrolled synthesis of trifluoromethylalkenes from simple alkynes bearing a wide variety of functional groups. Furthermore, by combining this process with well-established palladium catalysis, various tetrasubstituted CF_3-substituted alkenes were obtained in a highly stereoselective manner in a facile one-pot process. The synthesis of new and functional multisubstituted trifluoromethylated alkenes is currently underway in our laboratory.

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[10] The present reaction gave a small amount of 1-phenylprop-1-en-1-yl trifluoromethanesulfonate, a product of the addition of TfOH to the alkyne, as a side product in the absence of a base.

The addition of a base effectively prevents formation of this side product.

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