Trifluoromethylation

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Controlled Trifluoromethylation Reactions of Alkynes through Visible-Light Photoredox Catalysis**

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Abstract: *The control of a reaction that can form multiple products is a highly attractive and challenging concept in synthetic chemistry. A set of valuable CF_3-containing molecules, namely trifluoromethylated alkenyl iodides, alkenes, and alkynes, were selectively generated from alkynes and CF_3I by environmentally benign and efficient visible-light photoredox catalysis. Subtle differences in the combination of catalyst, base, and solvent enabled the control of reactivity and selectivity for the reaction between an alkyne and CF_3I.*

The control of a chemical reaction to selectively produce a set of distinct valuable compounds from the same starting material is a highly attractive concept, but represents a significant synthetic challenge.[1] Selective trifluoromethylation[2,3] processes could be of great benefit as the trifluoromethyl group is widely utilized, for example, in pharmaceuticals and agrochemicals.[4] Recently, visible-light photoredox catalysis has attracted substantial attention because of its environmental compatibility and versatility in promoting a large number of synthetically important reactions.[5] Visible-light photoredox catalysis has also been applied to trifluoromethylations,[6] and further applications of this method will continue to yield important trifluoromethylation reactions. Herein, an environmentally benign and efficient method for controlled trifluoromethylation reactions was exploited to selectively obtain three different valuable alkenyl–CF_3 and alkynyl–CF_3 compounds from the same starting materials, namely an alkyne and CF_3I, by the judicious choice of reaction conditions using different photoredox catalysts, bases, and solvents (Figure 1).

Whereas the formation of aryl–CF_3 bonds has been extensively studied, trifluoromethylation reactions for the synthesis of alkenyl–CF_3 and alkynyl–CF_3 compounds are rather underdeveloped; this prompted us to prepare alkenyl–CF_3 and alkynyl–CF_3 compounds from alkynes.[2,3,7] Alkynes are highly reactive towards atom-transfer radical addition processes and can be converted into a set of distinct compounds depending on the reaction conditions.[8] Subtle differences in the combination of catalyst and base led to totally different outcomes; iodotrifluoromethylation,[9,10] hydrotrifluoromethylation,[11] and trifluoromethylation[12] of alkynes have been described.

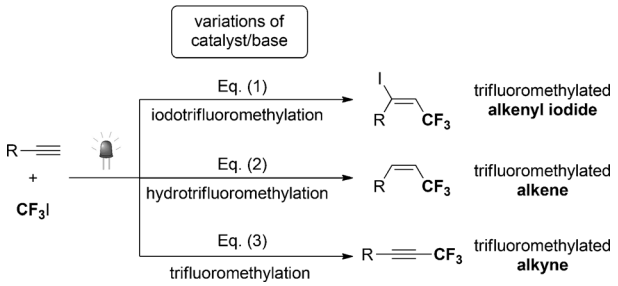

Figure 1. Controlled trifluoromethylation reactions using an unactivated alkyne and CF_3I under visible-light irradiation.

We started our investigation of controlled trifluoromethylations using phenyl acetylene (**1a**) as a model compound with CF_3I. First, iodotrifluoromethylation and hydrotrifluoromethylation were studied with different catalysts and bases. A range of iridium and ruthenium photocatalysts, including *fac*-$[Ir(ppy)_3]$, $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$, $[Ru(bpy)_3]Cl_2$, and $[Ru(phen)_3]Cl_2$, efficiently generated the iodotrifluoromethylation product **2a** in high yields with *E*/*Z* ratios ranging from 17:1 to 20:1 with TMEDA in MeCN under visible-light irradiation (Table 1, entries 3–6). $[Ru(phen)_3]Cl_2$ was chosen as the catalyst for iodotrifluoromethylation because it is inexpensive and displayed a cleaner reaction profile. Both the photocatalyst and visible light were required for the transformation, as demonstrated by control experiments (entries 1 and 2).

For the hydrotrifluoromethylation of **1a** to form the alkenyl–CF_3 product **3a**, iridium catalysts were found to be more effective than ruthenium catalysts. The choice of base was critical for this process, as the base acts not only as a reductive quencher of the activated photocatalyst, but also as a hydrogen donor.[13] For the reaction of **1a** catalyzed by *fac*-$[Ir(ppy)_3]$, the highest reactivity was observed with DBU to yield the alkenyl–CF_3 compound **3a** (Table 1, entries 11–15). The use of THF as a co-solvent improved the reactivity, and **3a** was isolated in a higher yield after a shorter reaction time (entry 18).

With optimized conditions in hand, we next evaluated the iodotrifluoromethylation of a variety of aromatic and aliphatic alkynes (Scheme 1). The mild conditions allowed for the iodotrifluoromethylation of alkynes that contain a range

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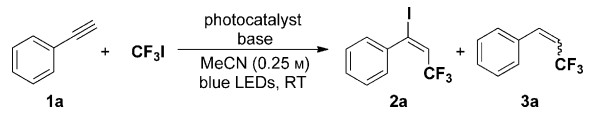
Table 1: Catalyst and base screening with phenyl acetylene (**1a**) for iodo- and hydrotrifluoromethylation.[a]



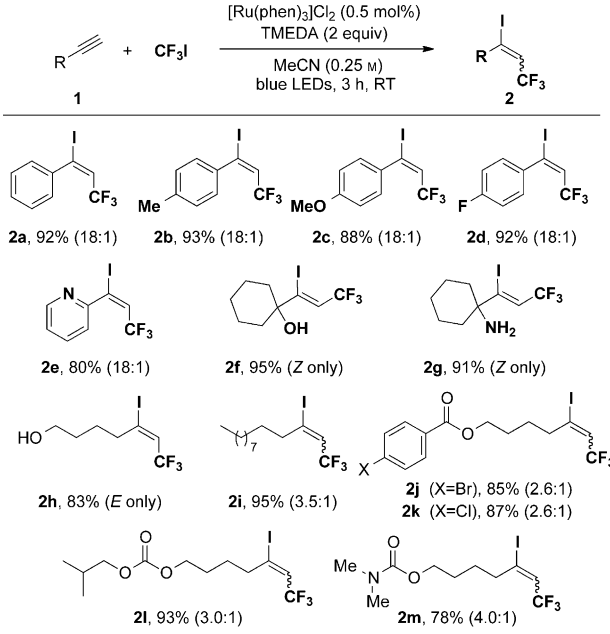
Entry	Photocatalyst (mol%)	Base (2 equiv)	Yield[b] [%] **2a** (*E*/*Z*)	**3a** (*E*/*Z*)
1	–	TMEDA	trace	–
2	$[Ru(phen)_3]Cl_2$ (no light)	TMEDA	trace	–
3	*fac*-$[Ir(ppy)_3]$ (0.5)	TMEDA	92 (19:1)	trace
4	$[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (0.5)	TMEDA	93 (18:1)	trace
5	$[Ru(bpy)_3]Cl_2$ (0.5)	TMEDA	90 (17:1)	trace
6	**$[Ru(phen)_3]Cl_2$ (0.5)**	**TMEDA**	**95 (18:1)**	**trace**
7	$[Ru(phen)_3]Cl_2$ (0.5)	–	trace	–
8	$[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (0.5)	–	80 (8:1)	–
9	$[Ru(phen)_3]Cl_2$ (3.0)	DBU	60 (17:1)	11 (1:3.8)
10	$[Ru(phen)_3]Cl_2$ (3.0)	DBU (5 equiv)	67	24 (1:4.0)
11	*fac*-$[Ir(ppy)_3]$ (3.0)	TMEDA	71 (11:1)	17 (1:2.8)
12	*fac*-$[Ir(ppy)_3]$ (3.0)	DIPEA	79 (11:1)	14 (1:6.4)
13	*fac*-$[Ir(ppy)_3]$ (3.0)	nBu_3N	86 (11:1)	7 (1:2.8)
14	*fac*-$[Ir(ppy)_3]$ (3.0)	TEA	84 (12:1)	11 (1:3.1)
15	*fac*-$[Ir(ppy)_3]$ (3.0)	DBU	53 (only *E*)	36 (1:2.2)
16	*fac*-$[Ir(ppy)_3]$ (3.0)	DBU (5 equiv)	trace	55 (1:2.3)
17[c]	*fac*-$[Ir(ppy)_3]$ (3.0)	DBU (10 equiv)	trace	70 (1:2.3)
18[d]	***fac*-$[Ir(ppy)_3]$ (3.0)**	**DBU (10 equiv)**	**trace**	**75 (1:1.3)**

[a] Reaction conditions: **1a** (0.2 mmol), CF_3I (0.6 mmol). [b] The yield and the *E*/*Z* ratio were determined by gas chromatography and ^{19}F NMR spectroscopy with internal standards, namely dodecane and 4-fluorotoluene, respectively. [c] 2.0 mL of MeCN (0.1 M). [d] MeCN/THF (1:1; 0.1 M). DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DIPEA = diisopropylethylamine, dtb-bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, phen = 1,10-phenanthroline, ppy = 2-phenylpyridine, TEA = triethylamine, TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

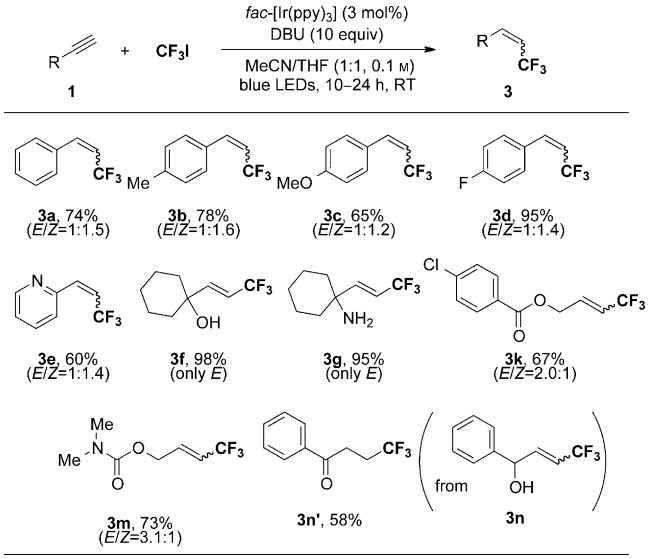
of functional groups. Notably, excellent *E*/*Z* stereoselectivity was observed with selective formation of the *E* isomers, especially in reactions of phenyl acetylene derivatives (**2a**–**2e**).[8b] Alkynes with directing groups at the propargylic position, such as **2f** and **2g**, however, underwent selective iodotrifluoromethylation to exclusively give the *Z* isomers.[14]

The substrate scope of the hydrotrifluoromethylation of alkynes was also investigated (Scheme 2). Reactions in the presence of *fac*-$[Ir(ppy)_3]$ (3 mol%) and DBU (10 equiv) in MeCN (0.1 M) or MeCN/THF (1:1) under visible-light irradiation provided a mixture of the *E* and *Z* alkenyl–CF_3 compounds in good to excellent yields. In general, aliphatic alkynes, except for those with a heteroatom at the propargylic position, did not readily undergo hydrotrifluoromethylation under these conditions.

A plausible mechanism for the hydrotrifluoromethylation of alkynes is proposed in Figure 2. Photoexcitation of $[Ir(ppy)_3]$ by visible light provides $*[Ir(ppy)_3]$, which is then reductively quenched by DBU to produce $[Ir(ppy)_3]^{\bullet-}$ and the ammonium radical cation. The radical anion $[Ir(ppy)_3]^{\bullet-}$ in turn performs a single-electron reduction of the $F_3C{-}I$ bond, which leads to the regeneration of $[Ir(ppy)_3]$ and the formation of a carbon-centered $*CF_3$ radical. Addition of this electron-deficient radical species to an alkyne **1** generates the vinyl radical. The desired alkenyl–CF_3 product **3** is finally generated through direct hydrogen abstraction by the vinyl radical.



Scheme 1. Scope of the iodotrifluoromethylation of alkynes. Reaction conditions: **1** (1.0 mmol), CF_3I (3.0 mmol). Yields of isolated products that are based on the average of two runs are given. The *E*/*Z* ratios were determined by gas chromatography and ^1H NMR spectroscopy of the crude products.



Scheme 2. Scope of the hydrotrifluoromethylation of alkynes. Reaction conditions: **1** (0.5 mmol), CF_3I (1.5 mmol). The given yields either correspond to the yield of isolated product or were determined by ^{19}F NMR spectroscopy because of the volatility of the products. The *E*/*Z* ratios were determined by gas chromatography and ^1H NMR and ^{19}F NMR spectroscopy of the crude products.

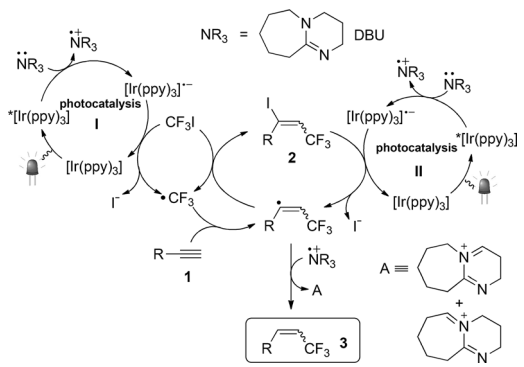
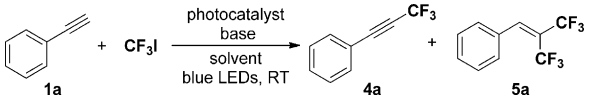


Figure 2. Proposed mechanism for the formation of trifluoromethylated alkenes.

However, the reaction could also proceed by competitive iodide abstraction from CF_3I by the vinyl radical to give the alkenyl iodide **2** as an intermediate, that is, hydrotrifluoromethylation of alkynes might occur through a cascade process where iodotrifluoromethylation is followed by de-iodination of the trifluoromethylated alkenyl iodide intermediate **2**. De-iodination could proceed with the same catalytic system; $[Ir(ppy)_3]^{\bullet-}$ performs a single-electron reduction of the alkenyl–I bond to give a vinyl radical that undergoes hydrogen abstraction to provide the alkenyl–CF_3 product **3**.[15] This was confirmed by an additional experiment; the alkenyl iodide **2** was transformed into **3** under the conditions for the hydrotrifluoromethylation of **1** to yield **3**.[16] Furthermore, the fact that alkenyl iodide **2** was present during the course of the reaction[17] also supports the idea that cascade catalysis through de-iodination of **2** is involved in this hydrotrifluoromethylation.

Next, we investigated the trifluoromethylation reaction that yields trifluoromethylated alkynes (Table 2). The reaction conditions for this process were quite different to the conditions for the iodo- and hydrotrifluoromethylation processes. Phenyl acetylene (**1a**) was converted into the alkynyl–CF_3 compound **4a** when inorganic bases, such as KO*t*Bu and Cs_2CO_3, were used (Table 2). Although this process was less efficient than the iodo- and hydrotrifluoromethylation reactions, the alkynyl–CF_3 product **4a** was obtained in a reasonable yield with *fac*-$[Ir(ppy)_3]$ and KO*t*Bu in DMF (0.1 M). The process also produced approximately 10–20% of the bis(trifluoromethylated) product **5a** and 5% of the alkynyl iodide as side products (entry 2). The process required both a visible-light source and the photocatalyst to give the trifluoromethylated alkyne **4a**, as without light or catalyst, only the alkynyl iodide was formed (entries 7 and 8).[18]

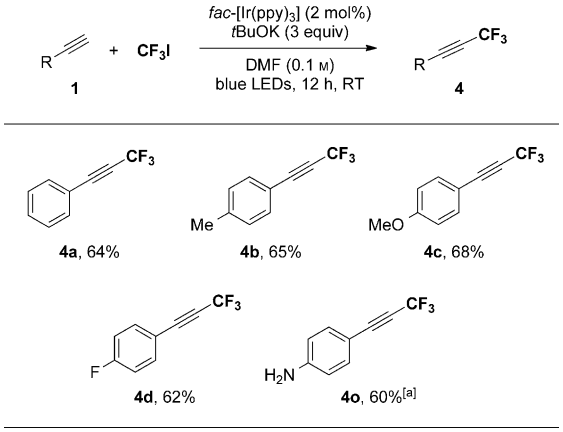
Table 2: Optimization of the reaction conditions for the synthesis of trifluoromethylated alkynes.[a]



Entry	Photocatalyst (2 mol%)	Base (3 equiv)	Solvent (0.1 M)	Yield[b] [%] 4a	5a
1	*fac*-$[Ir(ppy)_3]$	Cs_2CO_3	DMF	58	trace
2	*fac*-$[Ir(ppy)_3]$	**KO*t*Bu**	**DMF**	**64**	**15**
3	*fac*-$[Ir(ppy)_3]$	KO*t*Bu	MeCN	trace	–
4[c]	*fac*-$[Ir(ppy)_3]$	KO*t*Bu	DMSO	–	–
5	$[Ru(phen)_3]Cl_2$	KO*t*Bu	DMF	–	–
6	$[Ir(dFppy)_3]$	KO*t*Bu	DMF	60	16
7[c]	–	KO*t*Bu	DMF	–	–
8[c]	$[Ir(dFppy)_3]$ (no light)	KO*t*Bu	DMF	–	–

[a] Reaction conditions: **1a** (0.2 mmol), CF_3I (0.6 mmol), 7 h. [b] The yield was determined by gas chromatography and ^{19}F NMR spectroscopy. [c] The alkynyl iodide was formed. dFppy = 2-(2,4-difluorophenyl)-pyridine, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide.

Various aromatic alkynes **1** were transformed into the desired alkynyl–CF_3 compounds **4** under the optimized conditions, which was accompanied by the formation of the bis(trifluoromethylated) products **5** (5–20%; Scheme 3). Reactions of both electron-rich (**4b**, **4c**, **4o**) and electron-poor (**4d**) phenyl acetylene derivatives yielded trifluoromethylated alkynes in reasonable yields. Unfortunately, aliphatic alkynes were not suitable substrates for this reaction.



Scheme 3. Scope of the trifluoromethylation of alkynes. Reaction conditions: **1** (0.5 mmol), CF_3I (1.5 mmol). The given yields either correspond to the yield of isolated product or were determined by ^{19}F NMR spectroscopy because of the volatility of the products. [a] With TMEDA (instead of KO*t*Bu) in MeCN after 3 h.

In conclusion, three different CF_3-substituted compounds, namely trifluoromethylated alkenyl iodides, alkenes, and alkynes, were selectively generated from alkynes under similar reaction conditions. Subtle differences in the choice of catalyst and base enabled the control of reactivity and selectivity in the reaction between an alkyne and CF_3I. Trifluoromethylated alkenyl iodides were selectively obtained as the *E* isomers in the presence of $[Ru(phen)_3]Cl_2$ and TMEDA under visible-light irradiation, whereas alkenyl–CF_3 compounds were obtained with *fac*-$[Ir(ppy)_3]$ and DBU by the hydrotrifluoromethylation of alkynes. Alkynyl–CF_3 compounds were generated with *fac*-$[Ir(ppy)_3]$ and KO*t*Bu in DMF under visible-light irradiation. These environmentally friendly and mild reaction conditions enabled the trifluoromethylation of alkynes that bear a variety of functional groups to efficiently provide a highly valuable set of CF_3-containing molecules.

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[16] Isolated **2a** (Scheme 1) was subjected to the conditions described in Scheme 2. See the Supporting Information, Scheme S1.

[17] Alkenyl iodide **2a** was detected during the reaction of **1a**, see the Supporting Information, Figure S1 (kinetic studies of the reaction with **1a**).

[18] It is likely that the reaction proceeded through an alkynyl iodide as the intermediate. For experimental details, see the Supporting Information, Scheme S2. A plausible mechanism for the trifluoromethylation of alkynes is proposed in Figure S2.

