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Cu-Catalyzed C−H Trifluoromethylation of 3-Arylprop-1-ynes for the Selective Construction of Allenic Csp^2−CF_3 and Propargyl Csp^3−CF_3 Bonds

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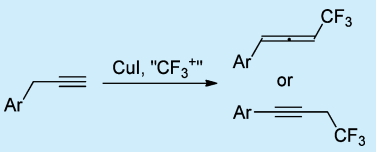
Supporting Information

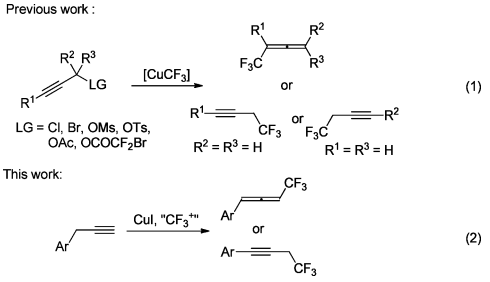
ABSTRACT: A new method has been developed for the Cu-catalyzed C−H trifluoromethylation of 3-arylprop-1-ynes for the selective construction of allenic Csp^2−CF_3 and propargyl Csp^3−CF_3 bonds. The selective formation of allenic Csp^2−CF_3 and propargyl Csp^3−CF_3 bonds can be controlled by modifying the reaction conditions.



The trifluoromethyl group has proven to be a valuable functionality in medicinal chemistry and agrochemistry, where it is generally used to modify the physiochemical and biological properties of target molecules through steric and electronic effects.[1] In light of its importance, considerable research efforts have been directed toward the development of efficient methods for the trifluoromethylation of a wide range of different substrates.[2] The trifluoromethylation of alkynes has received considerable interest from researchers working in a number of different fields because this reaction is a valuable tool for the construction of various C−CF_3 bonds, including olefinic Csp^2−CF_3,[3] and alkynyl Csp−CF_3 bonds.[4] However, the C−H trifluoromethylation of alkynes for the construction of allenic Csp^2−CF_3 and alkyl Csp^3−CF_3[5] bonds remains a significant challenge. In continuation of our research interest in trifluoromethylation chemistry,[6] we have now investigated the trifluoromethylation of terminal alkynes for the selective formation of allenic Csp^2−CF_3 and propargyl Csp^3−CF_3 bonds by modifying the reaction conditions, allowing access to (trifluoromethyl)allenes and propargyltrifluoromethanes, respectively.

A variety of different methods have already been developed for the construction of allenic Csp^2−CF_3[6d,7] and propargyl Csp^3−CF_3[7b−f] bonds. The trifluoromethylation of propargyl halides or esters with [$CuCF_3$] reagent, which can be prepared in advance or generated in situ, can lead to the formation of either of these two bonds (eq 1, Scheme 1). However, the type of bond formed by these reactions is heavily dependent on the nature of the substrate used in the reaction. In most cases, it is not possible to vary the selectivity of these reactions by modifying the reaction conditions. Szabó and co-workers reported that the reaction temperature can be used to control the selectivity of these trifluoromethylation reactions, although a stoichiometric amount of copper was required to affect these reactions.[7c] Notably, however, the authors failed to provide an explanation for this temperature-mediated variation in the selectivity. More recently, Altman et al. found that the nature of

Scheme 1. Construction of Allenic Csp^2−CF_3 and Propargyl Csp^3−CF_3 Bonds



the ligand is an important factor for the selective formation of allenic Csp^2−CF_3 bonds.[7b] However, the selectivity of this reaction for the construction of propargyl Csp^3−CF_3 bonds was low.[7f] In addition to the selectivity issues associated with these reactions, their application has also been limited by the need for the prefunctionalization of the substrates. These prefunctionalization processes can be operationally inconvenient and are generally associated with poor atom economy and low reaction efficiency. In contrast, C−H trifluoromethylation is a straightforward and attractive alternative. Herein, we describe the development of a new method for the Cu-catalyzed C−H trifluoromethylation of 3-arylprop-1-ynes with an electrophilic trifluoromethylating reagent for the selective construction of allenic Csp^2−CF_3 and propargyl Csp^3−CF_3 bonds. This is the first reported example for effectively controlling the selectivity for the formation of allenic Csp^2−CF_3 and propargyl Csp^3−CF_3 bonds by modifying the reaction conditions (eq 2).

Although the Cu-catalyzed trifluoromethylation of 3-phenylprop-1-yne **1a** with Togni's reagent **I** has been reported to provide facile access to the (trifluoromethyl)alkyne **4a**,[4c] our initial attempt at this reaction in DMF afforded the

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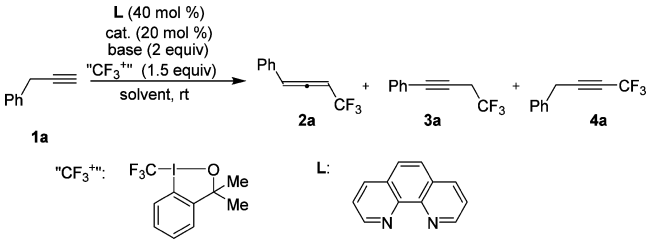
Org. Lett. XXXX, XXX, XXX−XXX

(trifluoromethyl)allene **2a** together with propargyl trifluoromethanes **3a**, without any of the previously reported product **4a** (Table 1, entry 1). We then investigated the use of reagent **I** to screen a variety of other conditions for the selective construction of allenic Csp^2-CF_3 and propargyl Csp^3-CF_3 bonds, starting with the former. The reaction in DCM completely suppressed the production of **3a**, although the (trifluoromethyl)alkyne **4a** was produced as a major product,[4h] which indicated that the reaction solvent plays an important role in determining the selectivity of the reaction (Table 1, entry 2). Several other solvents were also examined (Table 1, entries 3 and 4), and NMP was found to be the most suitable choice (Table 1, entry 4). The reaction was also screened against a variety of different copper salts (Table 1, entries 5–9), and the results revealed that CuI provided the best results (Table 1, entry 4). Surprisingly, increasing the reaction temperature led to a shift in the selectivity of the reaction toward the propargyl trifluoromethane product **3a** (Table 1, entries 10–12), which showed that the reaction performed much more effectively at room temperature for the selective construction of allenic Csp^2-CF_3 bonds. Pleasingly, the evaluation of various bases (Table 1, entries 13–18) revealed that the use of KF afforded the desired product **2a** in a high yield, with only trace quantities of **3a** and **4a** being detected (Table 1, entry 16). Interestingly, **2a** still could be obtained in 70% yield without the external addition of base (entry 19).

Table 1. Screening Reaction Conditions



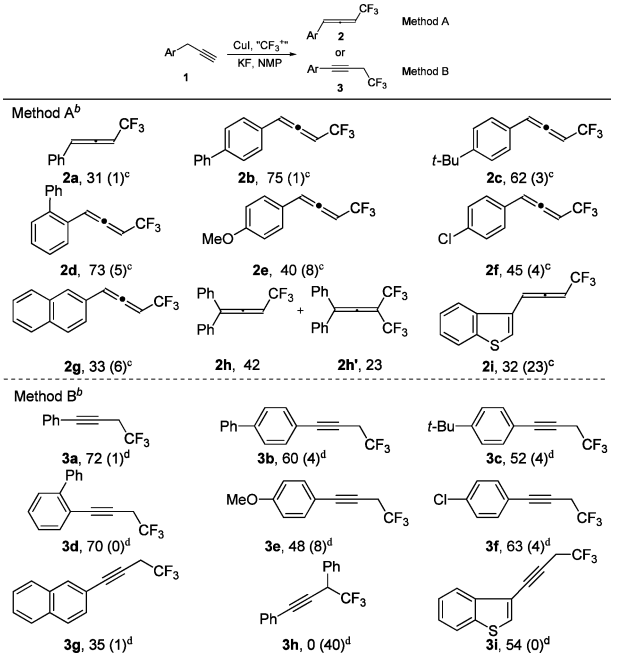
				yield[a] (%)		
entry	solvent	cat.	base	**2a**	**3a**	**4a**
1	DMF	CuI	K_2CO_3	32	13	0
2	DCM	CuI	K_2CO_3	20	0	63
3	DMA	CuI	K_2CO_3	56	10	0
4	NMP	CuI	K_2CO_3	78	3	0
5	NMP	CuCl	K_2CO_3	63	6	0
6	NMP	CuBr	K_2CO_3	67	3	0
7	NMP	CuP[b]	K_2CO_3	54	1	0
8	NMP	$CuCl_2$	K_2CO_3	trace	0	0
9	NMP	$Cu(OAc)_2$	K_2CO_3	30	13	0
10[c]	NMP	CuI	K_2CO_3	51	29	0
11[d]	NMP	CuI	K_2CO_3	32	50	0
12[e]	NMP	CuI	K_2CO_3	1	44	0
13	NMP	CuI	K_3PO_4	81	4	1
14	NMP	CuI	KOAc	49	11	0
15	NMP	CuI	Na_2CO_3	74	3	0
16	NMP	CuI	KF	91	1	trace
17	NMP	CuI	CsF	0	28	0
18	NMP	CuI	Et_3N	36	3	0
19	NMP	CuI		70	0	13
20[f]	NMP	CuI	KF	1	80	0

[a]Yields were determined by ^{19}F NMR. [b]CuP = $(MeCN)_4CuPF_6$. [c]The reaction was performed at 30 °C. [d]The reaction was performed at 40 °C. [e]The reaction was performed at 60 °C. [f]The resulting solution obtained under the reaction conditions as shown in entry 16 was further stirred at 80 °C for another 8 h.

Having identified the optimal conditions for the selective construction of allenic Csp^2-CF_3 bond, we turned our attention to identifying the optimal conditions for the selective construction of propargyl Csp^3-CF_3 bond leading to **3a**. On the basis of the results obtained above for changing the selectivity by increasing the reaction temperature (entries 10–12), it was envisaged that the allenic product **2a** could be converted to the propargyl trifluoromethane **3a** via a one-pot thermal rearrangement process, a process which has been reported by the group of Szabó.[7c] Indeed, **2a** disappeared while the yield of **3a** increased dramatically when a solution of **2a** obtained under the conditions shown in entry 16 was further heated (Table 1, entry 20) (see the Supporting Information for more reaction conditions).

With the optimal reaction conditions for the construction of allenic Csp^2-CF_3 (entry 16, Table 1) and propargyl Csp^3-CF_3 (entry 20, Table 1) bonds in hand, we proceeded to investigate the substrate scope for each conversion.[8] As shown in Scheme 2, the reactions proceeded well in most cases to give the desired products in moderate to good yields with excellent selectivity. It is noteworthy that product **2a** was isolated in a low yield of 31% because of its high volatility and that the actual reaction yield was determined to be 91% by ^{19}F NMR prior to its purification. Interestingly, product **3a** was much less volatile and was consequently isolated in good yield. Given that the propargyl product **3** was produced from the corresponding allenic

Scheme 2. Selective Construction of Allenic Csp^2-CF_3 and Propargyl Csp^3-CF_3 Bonds[a]



[a]Method A: **1** (0.1 mmol), **L1** (40 mol %), CuI (20 mol %), Togni's reagent **I** (1.5 equiv), and KF (2 equiv) at rt in NMP (1 mL) for 8–12 h. Method B: the solution obtained under the conditions described for method A was further stirred at 80 °C for another 8–12 h. [b]Isolated yields. [c]The yields in parentheses are the yields of **3** determined by ^{19}F NMR with the use of CF_3CH_2OH as an internal standard. [d]The yields in parentheses are the yields of **2** determined by ^{19}F NMR using CF_3CH_2OH as an internal standard.

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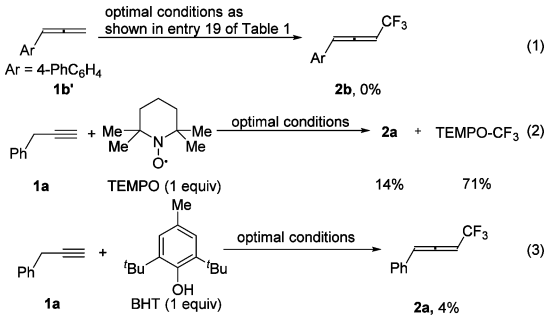
product **2**, the yield of **3** was always lower than that of **2** (e.g., **3a**–**d** vs **2a**–**d**). The reversal observation in the cases of **2e**/**3e** and **2f**/**3f** was attributed to the lower reactivity of **1e** and **1f** toward trifluoromethylation at room temperature. The unreacted starting materials **1e** and **1f** were also transformed into the desired products **3e** and **3f**, respectively, after the heating process. The disubstituted substrate **1h** was also examined. Surprisingly, the reaction for the construction of the allenic Csp^2–CF_3 bond not only gave the desired product **2h** but also furnished the ditrifluoromethylation product **2h′**. This side product may have been derived from **2h**, with the allene unit being activated by the two phenyl groups. Stirring the resulting solution of **2h** and **2h′** for an extended period at 80 °C did not result in the formation of **3h** via the migration of one of the phenyl groups. Although the heteroaromatic allene **2i** was obtained in low yield and low selectivity, excellent selectivity was observed for the conversion of **2i** to **3i**. No desired product **2** was observed for trifluoromethylation of aliphatic substrate such as 4-phenyl-1-butyne.

It is well-known that the presence of base can result in the rapid rearrangement of 3-arylprop-1-ynes to give the corresponding phenyl allenes.[9] The observation that allene **1b′** remained intact under the optimal conditions ruled out the possibility of a pathway involving the rearrangement of 3-arylprop-1-yne to give a phenyl allene prior to the trifluoromethylation step (eq 1, Scheme 3). Based on our

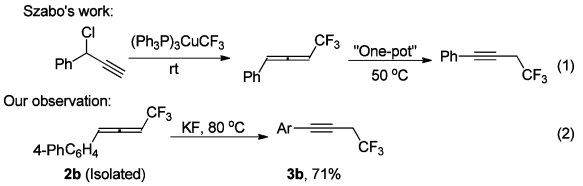
Scheme 3. Experimental Evidence To Elucidate the Reaction Mechanism



previous experiences with Togni's reagent **I**, we became convinced that the trifluoromethylation step occurred through a radical pathway. This hypothesis was subsequently supported by a series of radical-trapping experiments (eqs 2 and 3). The inclusion of the well-known radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (eq 2) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) (eq 3) led to a dramatic decrease in the conversion of **1a** to **2a**. Furthermore, the major byproduct formed in the presence of TEMPO was TEMPO–CF_3 (eq 2).

It would be necessary to figure out how the (trifluoromethyl)allenes **2** was converted to propargyl trifluoromethanes **3**. A review of the literature revealed that Szabó and co-workers had previously reported the same conversion (eq 1, Scheme 4),[7c] although they failed to provide an adequate explanation for their observation. Instead, they proposed that an unknown Cu(I) complex could be responsible for mediating their reported reaction. Fortunately, we found that the isolated allene **2b** could be converted to the propargyl trifluoromethane **3b** in the presence of KF at 80 °C (eq 2, Scheme 4), which

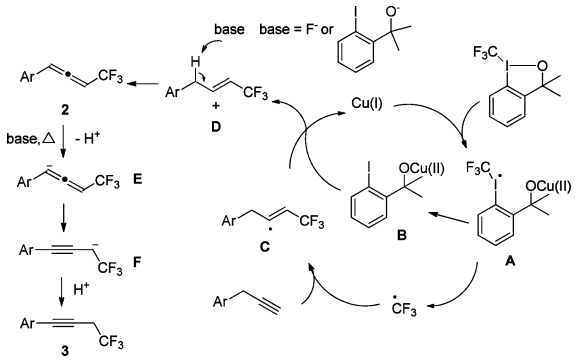
Scheme 4. Conversion of 2 to 3



suggested that the presence of a base and the temperature were important factors for this reaction.

Based on the results provided above and the results of related reports,[10] we have proposed a mechanism for this reaction, which is shown in Scheme 5. Briefly, the redox reaction of

Scheme 5. Proposed Reaction Mechanism



Togni's reagent with Cu(I) would afford the radical species **A**, which would undergo a dissociation reaction to give the Cu(II) intermediate **B** together with a trifluoromethyl radical. The trifluoromethyl radical would then be trapped by 3-arylprop-1-yne to produce the radical intermediate **C**. The subsequent oxidization of intermediate **C** by species **B** would then release the catalyst Cu(I) together with the cationic intermediate **D**. The benzyl proton in intermediate **D** would be highly activated by the neighboring carbocation, which would allow it to be readily deprotonated by the base (fluoride or alkoxide generated from Togni's reagent) to give the allenic product **2**. The subsequent deprotonation of allene **2** by KF at high temperature would generate anion **E**, which would be converted to anion **F** through a resonance effect. Protonation of intermediate **F** would then furnish the final product **3**.

In conclusion, we have developed a new method for the selective construction of allenic Csp^2–CF_3 and propargyl Csp^3–CF_3 bonds via the Cu-catalyzed C–H trifluoromethylation of 3-arylprop-1-ynes. These reactions proceeded smoothly to afford the desired (trifluoromethyl)allenes and propargyltrifluoromethanes, respectively, in good yields. This work represents the first reported example of a method for effectively controlling the selectivity for the formation of allenic Csp^2–CF_3 and propargyl Csp^3–CF_3 bonds by modifying the reaction conditions. Furthermore, this method shows good atom economy and high reaction efficiency by avoiding the requirement for the prefunctionalization of the substrates.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and characterization for new compounds (PDF)

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Author Contributions

§Y.-L.J. and J.-J.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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