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Copper-Catalyzed Intramolecular Carbotrifluoromethylation of Alkynes for the Construction of Trifluoromethylated Heterocycles

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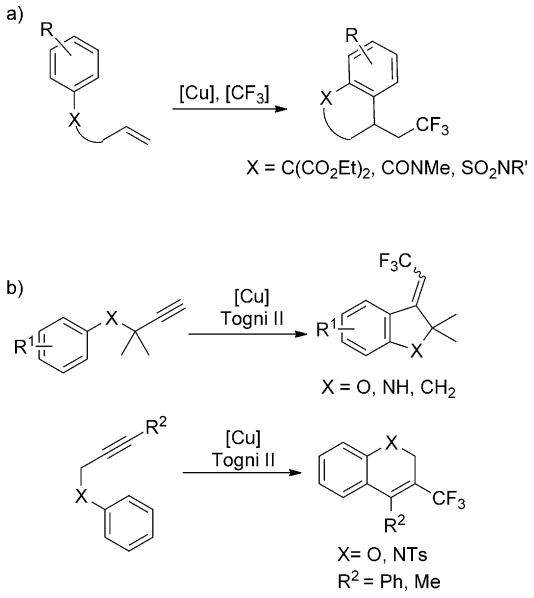
Abstract: A mild and efficient copper-catalyzed intramolecular carbotrifluoromethylation of alkynes has been achieved in the presence of Togni reagent as trifluoromethylating reagent. The reaction tolerates a range of substrates to give a group of trifluoromethylated heterocycles with high selectivities. A plausible mechanism was proposed on the basis of experimental results.

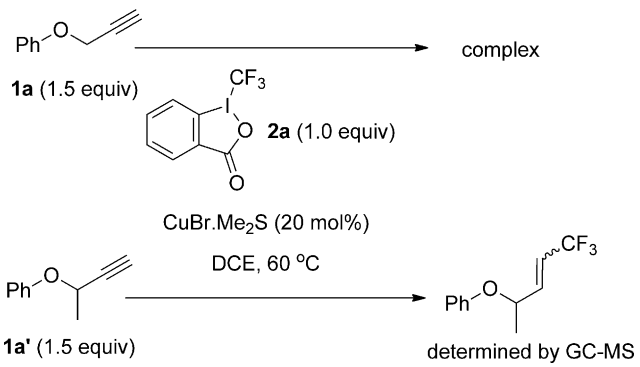
The introduction of trifluoromethyl groups into organic compounds may profoundly change their properties.[1] Owing to their high stabilities, hydrophobicities, metabolic activities, and bioavailabilities, trifluoromethylated compounds have gained more and more interest in a wide range of applications, especially in pharmaceuticals and agrochemicals.[2] Accordingly, the development of efficient methods for the preparation of trifluoromethylated compounds is of great importance. In the past few years, various transition metal-mediated or -catalyzed trifluoromethylation reactions have been developed by many independent research groups to synthesize various CF_3-containing compounds.[3]

The synthesis of heterocyclic compounds catalyzed by transition metal complexes has also attracted significant attention. Transition-metal-catalyzed reactions can directly construct complicated molecules from readily accessible starting materials under mild conditions. Recently, many groups have engaged in the trifluoromethylation of alkenes coupled with intramolecular reactions. For example, Buchwald and co-workers[4] have reported the intramolecular oxytrifluoromethylation of alkenes. Sodeoka's group[5] developed successfully a method of intramolecular aminotrifluomethylation of alkenes. Liang and co-workers[6] have reported the trifluoromethylation of alkenes involving oximes. The groups of Sodeoka,[7] Zhu,[8] and Shi[9] studied the carbotrifluoromethylation of alkenes independently (Scheme 1a). Our group was also interested in the trifluoromethylation of unsaturated alkanes and have developed an efficient copper-catalyzed oxytrifluoromethylation reaction of allenes.[10] However, to our knowledge, studies of carbotrifluoromethylation of alkynes is quite rare.[11] We report herein the copper-catalyzed intramolecular carbotrifluoromethylation of alkynes for the construction of trifluoromethylated heterocycles (Scheme 1b).



Scheme 1. a) Reported carbotrifluoromethylation of alkenes[7–9]; b) Carbotrifluoromethylation of alkynes (this work).

In our preliminary experiments, propargyl phenylether (**1a**) was chosen as the substrate. The reaction was carried out with 1 equivalent of Togni reagent II (**2a**), 1.5 equivalents of **1a** and 20 mol% of $CuBr{\cdot}Me_2S$ in dichloroethane (DCE) at 60 °C. However, ^{19}F NMR spectroscopy showed that the reaction was complicated and no annular product was isolated (Scheme 2).



Scheme 2. The reactions of **1a** and **1a**′ in the presence of Togni reagent II.

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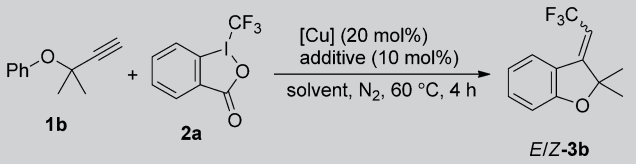
Using **1a**′ with a methyl group at the propargylic position as substrate, a small amount of hydrotrifluoromethylation product was formed, as shown by ^{19}F NMR and GC-MS spectra of the crude reaction mixture (see the Supporting Information).

Considering the Thorpe–Ingold effect,[12] which demonstrates that increasing the size of two substituents on a tetrahedral center leads to enhanced reactions between parts of the other two substituents in the cyclization reaction, we prepared alkyne **1b** with two methyl substituents at the propargyl position and continued to study its carbotrifluoromethylation. Gratifyingly, the corresponding five-membered cyclic products **3b** were obtained as a mixture of two isomers in 61% overall yield with a ratio of 11:1 under the same conditions (Table 1, entry 1). The stereochemistry of the newly formed double bond in the major product was established as *E* by NOE experiments. Inspired by the result, we screened different conditions to find a suitable protocol for the selective formation of cyclization products. Using Togni reagent I (**2b**) instead of **2a**, the total yield of products *E*- and *Z*-**3b** was slightly lowered. Umemoto's reagent (**2c**) failed to give any cyclic product with full recovery of the starting materials (Table 1, entries 2 and 3). Next, we focused on the catalyst and solvent effects. However, various copper salt catalysts, such as CuCl, CuI, $[(CH_3CN)_4Cu][PF_6]$, CuBr, $Cu(OTf)_2$, and $CuBr_2$, could not improve the yield of **3b** in DCE (Table 1, entries 4–9). Using dichloromethane (DCM) as solvent, the CuI-catalyzed reaction afforded **3b** in 63% overall yield with high selectivity, whereas the total yield was only 41% with $CuBr{\cdot}Me_2S$ (Table 1, entries 10 and 11). Therefore, CuI was chosen as the catalyst to further study the solvent effect. Much lower yields were obtained with *N*-methyl-2-pyrrolidone (NMP), acetonitrile, dioxane or dimethyl sulfoxide (DMSO) as solvent (Table 1, entries 12–15). Ethyl acetate and *tert*-butyl alcohol were also less effective for the reaction (Table 1, entries 16 and 17). Therefore, DCM was identified as the best solvent for this reaction among the solvents tested. Further investigation showed that the catalyst loading could be lowered to 10 mol% without any loss in yield or stereoselectivity (Table 1, entry 18). Carrying out the reaction in DCM under reflux and increasing the amount of **1b** to 2.0 equivalents gave isomers *E*- and *Z*-**3b** in 67% combined yield (Table 1, entry 19). Attempts to use PPh_3 or PCy_3 as an additive did not further improve the yield (Table 1, entries 20 and 21). Surprisingly, the total yield of *E*- and *Z*-**3b** was improved to 74% in the presence of B_2Pin_2 (Table 1, entry 22). Control experiments indicated that the copper salt was important for this reaction (Table 1, entries 23 and 24). Thus, the optimal conditions were set to 10 mol% of CuI, 2.0 equivalents of **1b**, and 10 mol% of B_2Pin_2 in DCM under reflux.

With the optimized reaction conditions in hand, we studied the scope of alkyne substrates for this copper-catalyzed carbotrifluoromethylation reaction. As shown in Table 2, a range of terminal alkynes **1** with different substituents in the benzene ring could react with **2a** and give the expected carbotrifluoromethylation products in moderate to good yields. Both electron-rich and electron-deficient alkynes are compatible with

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



Entry	[Cu]	Additive	Solvent	*E*-**3b**/*Z*-**3b** Yield [%][b]
1	$CuBr{\cdot}Me_2S$	—	DCE	56:5
2[c]	$CuBr{\cdot}Me_2S$	—	DCE	53:5
3[d]	$CuBr{\cdot}Me_2S$	—	DCE	NR
4	CuCl	—	DCE	41:4
5	CuI	—	DCE	47:5
6	$[(CH_3CN)_4Cu][PF_6]$	—	DCE	47:5
7	CuBr	—	DCE	54:5
8	$Cu(OTf)_2$	—	DCE	38:4
9	$CuBr_2$	—	DCE	44:4
10	$CuBr{\cdot}Me_2S$	—	DCM	37:4
11	CuI	—	DCM	57:6
12	CuI	—	NMP	13:<5
13	CuI	—	CH_3CN	14:<5
14	CuI	—	dioxane	19:<5
15	CuI	—	DMSO	37:4
16	CuI	—	EA	49:5
17	CuI	—	*t*BuOH	50:5
18[e]	CuI	—	DCM	58:6
19[e,f,g]	CuI	—	DCM	61:6
20[e,f,g]	CuI	PPh_3	DCM	24:<5
21[e,f,g]	CuI	PCy_3	DCM	52:5
22[e,f,g]	CuI	B_2Pin_2	DCM	67:7
23[g]	—	B_2Pin_2	DCM	NR
24[g]	—	—	DCM	NR

[a] Reaction conditions: **1b** (0.15 mmol), **2a** (0.1 mmol), copper catalyst (0.02 mmol), solvent (1 mL), 60 °C, 4 h, under N_2; [b] determined by ^{19}F NMR spectroscopy using hexafluorobenzene as internal standard; [c] Togni reagent I was used as trifluoromethylating reagent; [d] Umemoto reagent was used as trifluoromethylating reagent; [e] 0.1 equivalents of CuI were used; [f] 0.2 mmol of **1b** was used; [g] the reaction was carried out in DCM at reflux.

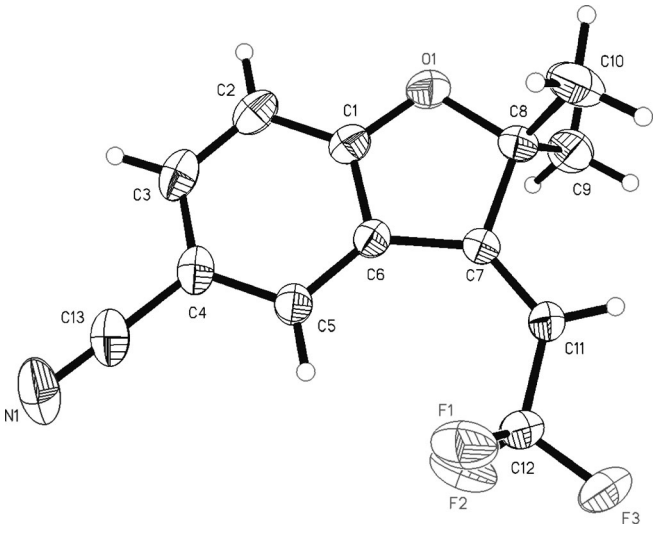
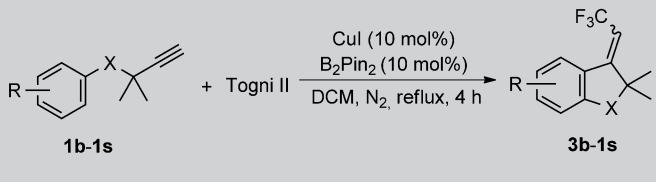
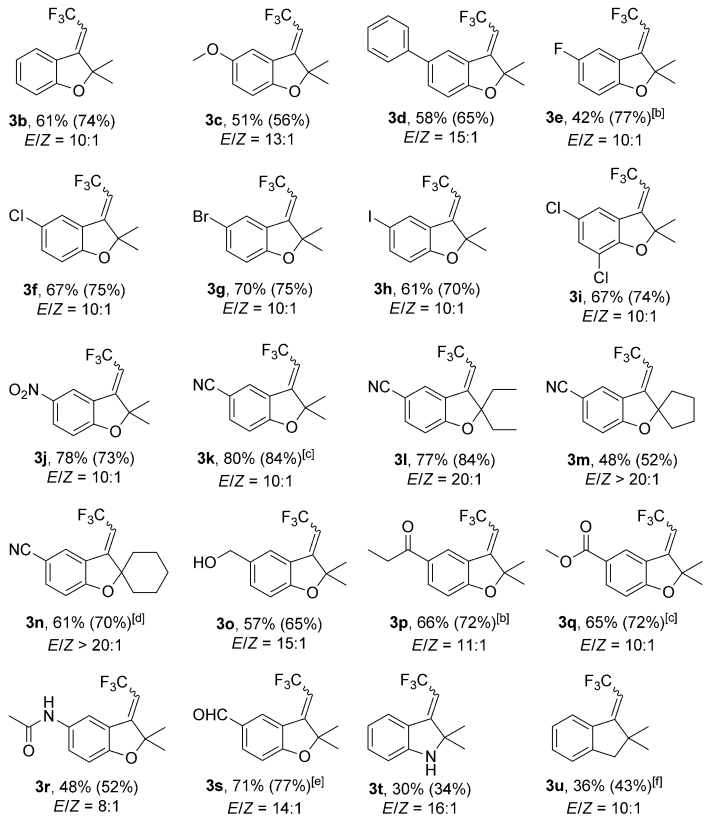


Figure 1. ORTEP representation of major isomer **3k**.

Table 2. Scope of the intramolecular carbotrifluoromethylation of alkynes.[a]





[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.1 mmol), CuI (0.01 mmol), B_2Pin_2 (0.01 mmol), DCM (1 mL), reflux, 4 h, under N_2, yield of isolated product (yield determined by ^{19}F NMR spectroscopy using hexafluorobenzene as internal standard is given in parentheses); [b] reaction time was 7 h; [c] reaction time was 8 h; [d] reaction time was 11 h; [e] reaction time was 17 h; [f] the reaction was conducted in a sealed tube at 80 °C for 12 h.

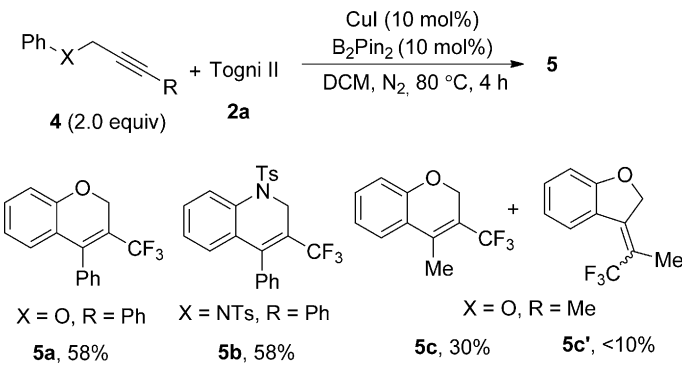
the reaction conditions. The substrates bearing methoxy or aryl substituents gave the cyclic products in moderate yields. Halide-substituted substrates also reacted well to give the cyclic products in good yields. In the case of an iodo-substituted substrate, the iodo substituent remained intact under the reaction conditions, and the corresponding products were obtained in 70% overall yield with an *E*/*Z* ratio of 10:1. The substrates containing an electron-deficient substituent such as *para*-nitro and *para*-cyano afforded the corresponding cyclic products in higher yields. Moderate to good yields were also achieved when the two methyl substituents at the propargylic position were replaced by two ethyl (**3l**), cyclopentyl (**3m**), or cyclohexyl (**3n**) groups. Furthermore, many functional groups, such as hydroxy, ketone, ester, amide, and aldehyde, were tolerated in this carbotrifluoromethylation reaction. When an unprotected amine substrate was used, the reaction could also occur to give the corresponding cyclic product, but the yield was kind of lower (**3t**, 34%), and 6-*endo* carbocyclization product was formed as the major product (see the Supporting Information). It is worth mentioning that the reaction of the substrate with a methylene linkage took place successfully at 80 °C to give the expected products **3u** in 43% yield, along with the hydrotrifluoromethylation product in moderate yield (see the Supporting Information). Furthermore, the X-ray crystal structure of major isomer **3k** was determined (Figure 1; CIF data are presented in the Supporting Information).[13]

Interestingly, when a phenyl group was introduced at the terminal position of the alkyne, six-membered cyclic products were obtained under similar conditions. Using DCM as solvent, the carbotrifluoromethylation reaction of O-tethered alkyne **4a** without two methyl groups at the propargyl position took place smoothly in a sealed tube at 80 °C to give the unexpected 2*H*-chromene derivative **5a**, isolated in 58% yield, and the 5-*exo* carbotrifluoromethylation product was not detected. Similar transformation could be achieved with N-tethered alkyne **4b**, affording the corresponding 1,2-dihydroquinoline derivative **5b**.

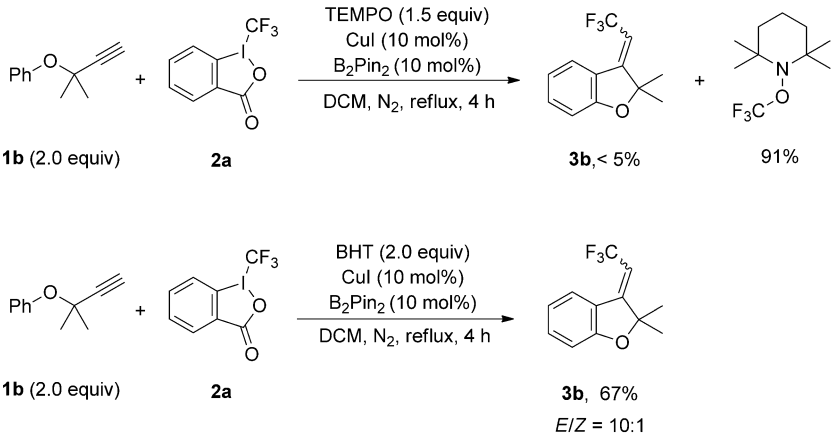
However, if the substituent at the terminal position of alkyne was methyl, 2*H*-chromene **5c** was obtained in 30% yield and less than 10% yield of five-membered cyclic product **5c′** was also detected (Scheme 3).

To gain insight into the reaction mechanism, we performed the reaction in the presence of 1.5 equivalents of 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO). ^{19}F NMR spectroscopy showed that the reaction was inhibited and the radical trapping product TEMPO-CF_3 was obtained in 91% yield (Scheme 4). However, when another radical scavenger, 2,6-di-*tert*-butyl-4-methylphenol (BHT, 2.0 equiv), was added, isomers *E*- and *Z*-**3a** were obtained in 67% total yield. We hypothesized that TEMPO might destroy Togni's reagent under the reaction conditions.[14]

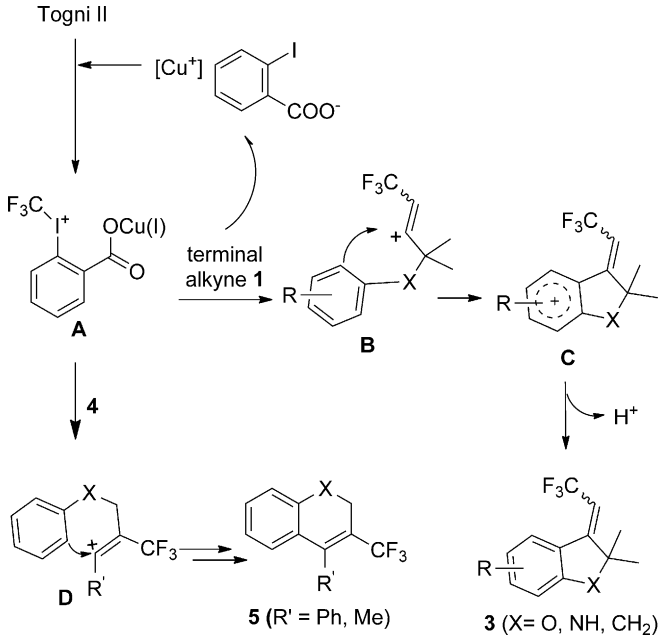
Based on the experimental results, a plausible mechanism is proposed (Scheme 5). Initially, the interaction of



Scheme 3. The reactions of alkynes **4** with Togni reagent II (**2a**).



Scheme 4. Reaction in the presence of TEMPO or BHT



Scheme 5. Proposed mechanism of the carbotrifluoromethylation.

Togni reagent II and Cu catalyst gives the iodine(III) species **A**, which reacts with carbon–carbon triple bond in alkyne **1** to produce the vinyl cation intermediate **B**[15] and regenerate the copper(I) species at the same time. In this step, intermediate **B**, with *E*-configuration, is favored and forms predominantly. Then, intramolecular cyclization[16] of **B** takes place to give the final product **3**. However, when a phenyl group was introduced into the terminal position of alkyne, the addition of trifluoromethyl cation to the inner position of the triple bond would form a more stable cationic intermediate **D**. The subsequent 6-*endo* cyclization[17] of **D** gives compound **5**. If a methyl group is present instead of the phenyl group, two cationic intermediates, **B** and **D**, may be produced at the same time and afford **5c′** and **5c**, respectively.

In conclusion, the copper-catalyzed intramolecular carbotrifluoromethylation of alkynes was achieved under mild conditions. The reaction tolerates a wide range of functional groups, providing a practical method for the synthesis of various trifluoromethylated heterocycles. Further studies regarding the scope, mechanism, and synthetic application of this reaction are in progress in our laboratory.

Experimental Section

General procedure for copper-catalyzed intramolecular carbotrifluoromethylation of alkynes: To a reactor charged with Togni reagent II (0.1 mmol), CuI (0.01 mmol), B_2Pin_2 (0.01 mmol), and dichloromethane (1 mL) was added alkyne (0.2 mmol) under N_2 atmosphere. The mixture was stirred under reflux and monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by column chromatography to give the product (petroleum ether).

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Keywords: alkynes · carbotrifluoromethylation · copper · heterocycles · homogeneous catalysis

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[13] CCDC-1012240 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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