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Copper-Catalyzed Three-Component Cyanotrifluoromethylation/Azidotrifluoromethylation and Carbocyclization of 1,6-Enynes

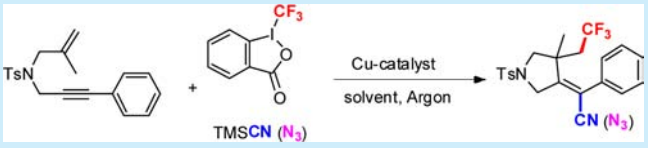
Yu-Tao He,[†] Lian-Hua Li,[†] Zhao-Zhao Zhou,[†] Hui-Liang Hua,[†] Yi-Feng Qiu,[†] Xue-Yuan Liu,[†] and Yong-Min Liang*[,†,‡]

[†]State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China

[‡]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou, 730000, P. R. China

Supporting Information

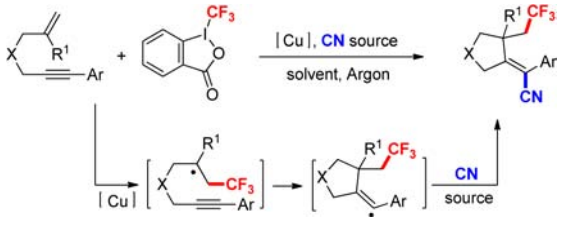
ABSTRACT: A novel three-component strategy for the cyanotrifluoromethylation/azidotrifluoromethylation and carbocyclization of 1,6-enynes is developed. The reaction proceeds smoothly under a moderate temperature by using a copper catalyst, which provides a rapid and concise access to addition−carbocyclization products. Furthermore, the products obtained can be useful building blocks in discoveries of lead compounds and other biologically active CF_3-containing heterocycles.



The cyclization of 1,6-enynes has attracted ever-increasing interest in the field of organic chemistry because of their synthetic utility for accessing complicated carbocyclic and heterocyclic frameworks.[1] Strategies for 1,6-enynes cyclization can be classified into two types, that is, transition-metal-catalyzed cyclization and radical cyclization.[2,3] Such cyclization processes are inherently atom economical in the assembly synthetically versatile compounds, which give an impetus to synthetic chemists to design and develop new synthetic protocols. Important examples of metal-catalyzed reactions include Au-,[4] Ru-,[5] Rh-,[6] Pd-,[7] and Ni-catalyzed[8] cyclization of 1,6-enynes. Although related reactions have been extensively and repeatedly investigated, the metal-catalyzed cyclization reactions of 1,6-enynes are ultimately impeded by the limitation of simple addition−carbocyclization and many of them require a relatively high reaction temperature. Thus, seeking novel linkers, especially for the introduction of two important functional groups into 1,6-enynes in one step, is highly desirable.

Compounds bearing a trifluoromethyl group (CF_3), especially heterocycles, play an important role as pharmaceuticals and functional materials due to their potential improvement in lipophilicity, membrane permeability, and bioactivity.[9,10] Therefore, much attention has been focused on the introduction of the CF_3 group into organic compounds and tremendous progress in the transition-metal-catalyzed trifluoromethylation has been achieved,[11,12] in particular the reactions based on the difunctionalization strategy, such as hydrotrifluoromethylation,[13] carbotrifluoromethylation,[14] oxytrifluoromethylation,[15] and aminotrifluoromethylation.[16] Recently, we reported a new type of copper-catalyzed intermolecular cyanotrifluoromethylation of alkenes to construct two vicinal chemical bonds.[17] The produced cyanotrifluoromethylation products could be used as versatile synthetic intermediates for the reaction of a cyano group. Encouraged by this result and on account of our research in the exploration of novel fluorine-containing pharmaceutical candidates, we envisioned that the cyano group and trifluoromethyl group could be achieved concurrently by catalytic addition−carbocyclization of 1,6-enynes (Scheme 1). Herein, we report a novel three-component cyanotrifluoromethylation/carbocyclization of 1,6-enynes with Togni's reagent (**2a**)[18] and trimethylsilyl cyanide (TMSCN) by copper catalysis at room temperature (rt). This methodology allows a broad substrate scope to access cycloaddition products, and the efficiently constructed cyanotrifluoromethylation/carbocyclization products show great potential in subsequent transformations in organic chemistry.

Scheme 1. Cyanotrifluoromethylation and Carbocyclization of 1,6-Enynes



To probe the feasibility of our envisioned strategy, the commercially available TMSCN was chosen as the CN source. We initially selected 1,6-enyne **1a** as the starting material to react with Togni's reagent **2a** and 1,10-phenanthroline **L1** in the presence of 10 mol % $Cu(OTf)_2$ at rt. Unfortunately, only a

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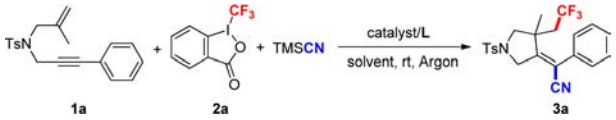
trace amount of the cyanotrifluoromethylation and carbocyclization product **3a** was obtained in DMF (Table 1, entry 1).

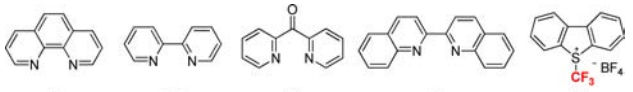
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	catalyst	ligand	solvent	t (h)	yield (%)[b]
1	$Cu(OTf)_2$	**L1**	DMF	6.0	trace
2	$Cu(OTf)_2$	**L1**	CH_3CN	6.0	18
3	$Cu(OTf)_2$	**L1**	DCE	6.0	10
4	$Cu(OTf)_2$	**L1**	1,4-dioxane	6.0	10
5	$Cu(OAc)_2$	**L1**	CH_3CN	6.0	82
6	CuF_2	**L1**	CH_3CN	6.0	65
7	$Cu(MeCN)_4PF_6$	**L1**	CH_3CN	6.0	60
8	$CuSO_4$	**L1**	CH_3CN	6.0	52
9	CuCl	**L1**	CH_3CN	6.0	60
10	$Cu(OAc)_2$	**L2**	CH_3CN	6.0	76
11	$Cu(OAc)_2$	**L3**	CH_3CN	6.0	21
12	$Cu(OAc)_2$	**L4**	CH_3CN	6.0	20
13	$Cu(OAc)_2$	**L1**	CH_3CN	5.0	80
14	$Cu(OAc)_2$	**L1**	CH_3CN	4.0	82
15[c]	$Cu(OAc)_2$	—	CH_3CN	4.0	0
16[d]	—	**L1**	CH_3CN	4.0	0
17[e]	$Cu(OAc)_2$	**L1**	CH_3CN	4.0	trace

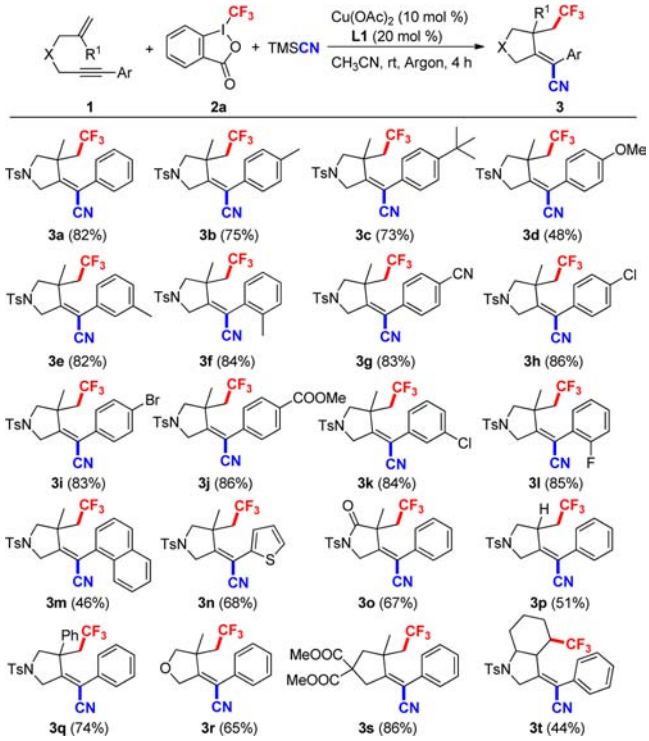
[a]Reaction conditions: **1a** (0.2 mmol), Togni's reagent (0.3 mmol), TMSCN (0.4 mmol), copper catalyst (10 mol %), ligand (20 mol %), solvent (2.0 mL), room temperature, under argon. [b]Isolated yield. [c]Without ligand. [d]Without copper catalyst. [e]Umemoto's reagent **2b** was used.



The screening of the solvents demonstrated that CH_3CN was effective for this transformation and the targeted product was obtained in 18% yield (Table 1, entry 2). Encouraged by this result, we varied the copper catalysts. $Cu(OAc)_2$ was found to be the most effective catalyst which can increase the yield to 82% (Table 1, entry 5), albeit some desired addition−carbocyclization products were obtained by using CuF_2, $Cu(MeCN)_4PF_6$, $CuSO_4$, and CuCl (Table 1, entries 6−9). Compared to 1,10-phenanthroline **L1**, ligands **L2**−**L4** were found to be less efficient for this transformation (Table 1, entries 10−12). Besides, the reaction time could be decreased to 4 h without variation of the outcome (Table 1, entries 14). The control experiments confirmed that no reaction occurred in the absence of a ligand or copper catalyst (Table 1, entries 15−16). However, only a trace of **3a** was observed when Umemoto's reagent **2b** was used as the trifluoromethylation reagent (Table 1, entry 17). Finally, the optimal reaction conditions were established as $Cu(OAc)_2$ (10 mol %), 1,10-phenanthroline **L1** (20 mol %) in CH_3CN at rt under Ar.[19]

Under the optimal reaction conditions, the scope of 1,6-enynes was investigated. As demonstrated in Scheme 2, in most cases, the cyanotrifluoromethylation and carbocyclization proceeded in moderate to good yields with a series of 1,6-enynes, and the substrates bearing electron-withdrawing groups work more efficiently than those bearing electron-donating groups on the aromatic rings. Functionality with the curious

Scheme 2. Substrate Scope of the Cyanotrifluoromethylation and Carbocyclization of 1,6-Enynes[a]



[a]Reaction conditions: **1** (0.2 mmol), Togni's reagent (0.3 mmol), TMSCN (0.4 mmol), $Cu(OAc)_2$ (10 mol %), **L1** (20 mol %), CH_3CN (2 mL), room temperature, 4 h, under argon, isolated yield.

case of the *p*-methoxy gave the desired product **3d** in 48% yield. When *o*-substituted 1,6-enynes (**3f**, **3m**) were used in our reaction, two spatial configuration products could be detected by NMR. The structure of compound **3i** was identified unambiguously by X-ray diffraction. It was worth noting that the addition−carbocyclization was effective with a 2-thiophenyl group (**3n**) attached to the triple bond as well as with methacrylamide (**3o**). Enyne with a phenyl substituent furnished the desired product **3q** in 74% yield. After further investigation of the scope of this reaction, we found that the oxygen- and carbon-tethered 1,6-enynes also reacted well, with the corresponding products obtained in 65% and 86% yield, respectively. Eyne **1t** was converted into the corresponding product in 44% yield.

Encouraged by this successful cyanotrifluoromethylation/carbocyclization reaction, we attempted to broaden this addition−carbocyclization of 1,6-enynes to their azidotrifluoromethylation/carbocyclization reactions with Togni's reagent and $TMSN_3$. During the process of our investigation, we were pleased to find that the desired azidotrifluoromethylation and carbocyclization product could be obtained in good yields. As described in Scheme 3, in the presence of 20 mol % CuBr, the reaction of 1,6-enyne (**1a**, 0.2 mmol) with Togni's reagent (**2a**, 0.36 mmol) and $TMSN_3$ (0.5 mmol) was carried out in CH_3CN (2 mL) at 40 °C for 5 h giving the azidotrifluoromethylation and carbocyclization product **4a** in 75% yield.[19] The substrates **1**, bearing either an electron-donating or -withdrawing group on the aromatic rings, were converted into the corresponding products in moderate to good yields. In contrast with the cyanotrifluoromethylation/carbocyclization, the *p*-methoxy substituent of 1,6-enyne proceed smoothly

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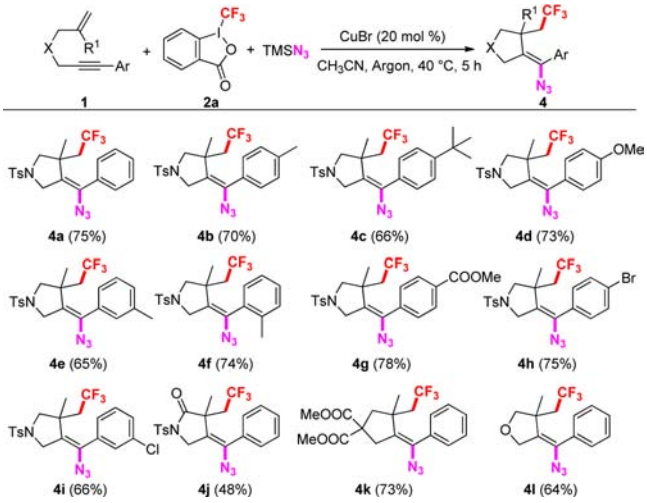
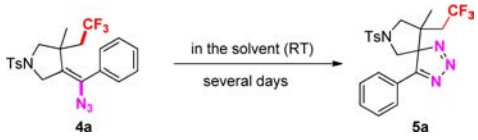
Scheme 3. Substrate Scope of the Azidotrifluoromethylation and Carbocyclization of 1,6-Enynes[a]



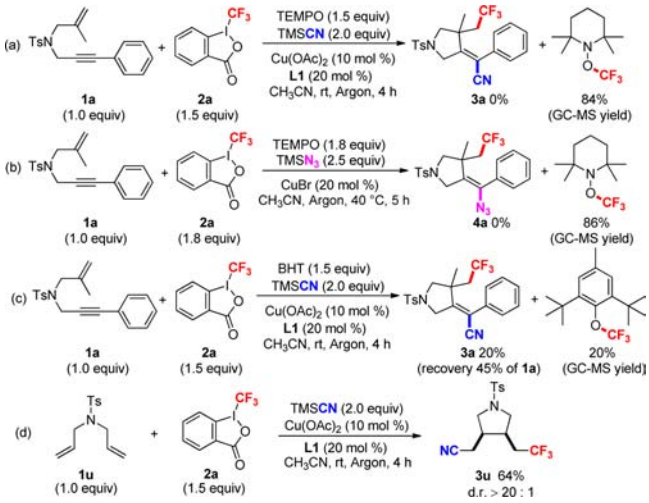
[a]Reaction conditions: **1a** (0.2 mmol), Togni's reagent (0.36 mmol), $TMSN_3$ (0.5 mmol), CuBr (20 mol %), CH_3CN (2.0 mL), under argon, isolated yield.

during this protocol. Furthermore, the product **4j** was unambiguously confirmed by X-ray crystallographic analysis. It should be indicated that when **4a** was dissolved in solvent for several days, part of the product would convert into the spiro compound **5a**. As we know, organic azides were useful nitrogen-containing building blocks, which were widely applied in synthetic chemistry. Thus, this new protocol could hold great potential applications in discoveries of lead compounds and other biologically active CF_3-containing heterocycles in organic chemistry as well as biology.

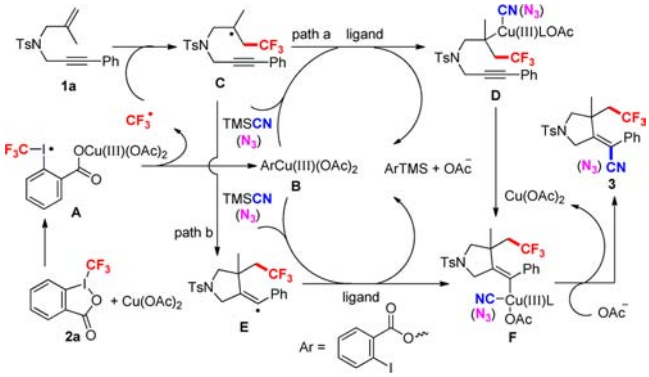


To elucidate the possible mechanism of the above two reactions, a stoichiometric amount of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added as the radical inhibitor. Significantly sluggish reactions were observed, and the TEMPO−CF_3 adducts were detected by GC-MS in 84% and 86% yield, respectively (Scheme 4). When 2,6-di-*tert*-butyl-4-methyl-phenol (BHT) was added under the standard conditions of the reaction, the desired product **3a** was obtained with a decreased yield (20%). The BHT−CF_3 adduct was also observed in 20% yield along with the recovery of 45% of enyne **1a**. In addition, the reaction of *N*,*N*-diallyl-4-methylbenzenesulfonamide **1u**, a radical clock, with Togni's reagent **2a** under the standard reaction conditions resulted in cyclization of cyanotrifluoromethylation product **3u** in 64% yield (d.r. > 20:1). These experiments indicate that a radical pathway might be included in the present reactions. On the basis of these facts and previous studies,[20] we propose a plausible mechanism as depicted in Scheme 5. Togni's reagent **2a** is activated by copper catalysis, leading to the CF_3-containing radical species **A**. A CF_3 radical, releasing from the decomposition of the CF_3-containing radical species **A**, reacts with 1,6-enyne **1a** to give the radical intermediate **C**. In path a, the radical intermediate **C** reacts with (2-iodobenzoyloxy)copper(III) acetate (**B**) and TMSCN to

Scheme 4. Trapping Experiments



Scheme 5. Proposed Reaction Mechanism



afford the copper(III) cyanide complex **D** and nucleophilic attack of the C−C triple bond affords Cu complex **F**. In path b, the radical intermediate **C** attacks the C−C triple bond of 1,6-enyne to give the radical intermediate **E**, which reacts with (2-iodobenzoyloxy)copper(III) acetate (**B**) and TMSCN to generate the copper(III) cyanide complex **F**. Subsequent elimination of the copper(III) cyanide complex **F** would afford the desired cyanotrifluoromethylation and carbocyclization product **3**.

In conclusion, we have finished the first copper-catalyzed three-component cyanotrifluoromethylation/azidotrifluoromethylation accompanied by a carbocyclization reaction of 1,6-enynes. The reaction tolerates a broad substrate scope, and it is a novel protocol for the synthesis of valuable CF_3-containing nitriles and azides, which would be an excellent strategy in 1,6-enynes modification. Further investigations on the scope and synthetic applications of this reaction are currently underway in our group.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, spectral data for all new Compounds, crystallographic data, and CIF information for **3i** and **4j** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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AUTHOR INFORMATION

Corresponding Author

*E-mail: liangym@lzu.edu.cn.

Notes

The authors declare no competing financial interest.

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