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Copper-Catalyzed Cascade Transformation of Homopropargyl Azides into Trifluoromethylated Nitriles via C−C Cleavage

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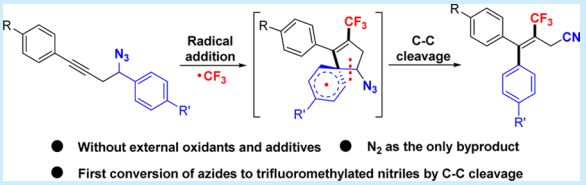
Supporting Information

ABSTRACT: A cascade reaction of homopropargyl azides in the presence of a Cu catalyst was achieved, affording 3-(trifluoromethyl)but-3-enenitriles with good yields and excellent regioselectivity. This reaction appears to be the first direct conversion of homopropargyl azides into trifluoromethylated nitriles. Mechanistic studies indicate that the transformation proceeds by addition of a CF_3 radical to the alkyne, C−C cleavage by 1,4-aryl radical migration, and nitrile formation. This protocol provides a novel strategy for transforming azides into nitriles via C−C cleavage derived from radical migration.



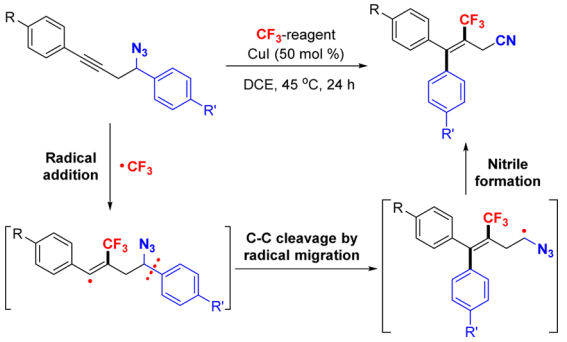
Alkyl nitriles are versatile synthons in organic synthesis; they are widely used to prepare carboxylic acids, amines, and other useful products.[1] The nitrile group within alkyl nitriles is ubiquitous in medicines and functional materials.[2] Nitrile compounds are often synthesized via Sandmeyer reaction[3] or transition-metal-mediated cyanation of aryl halides with cyanide sources,[4] generally toxic cyanide salts. To avoid the use of toxic salts, methods have been developed to convert amides,[5a,b] oximes,[5c−e] amines, and alcohols[5f,g] directly into nitriles. Most of these reactions require stoichiometric or excess amounts of external oxidants to sustain the catalytic cycle.

Azides have emerged as an important source of nitrogen for nitrile synthesis.[6−11] For example, Rozen reported BrF_3-promoted conversion of azides to nitriles,[8a] while Mizuno achieved the aerobic oxidative transformation of primary azides into nitriles using a $Ru_x(OH)/Al_2O_3$ catalytic system.[8b] Ye[9a] and Chibaet[9b] independently reported the oxidative transformation of 2-azido-1-hydroxy-containing compounds or α-azido carbonyl compounds into nitriles. This reaction proceeded via C−C cleavage, leading to the loss of a functional group. Prabhu achieved the oxidation of benzyl azide to nitriles using a catalytic amount of CuI or I_2 in the presence of *tert*-butyl hydroperoxide.[10a,b] Most of these reactions involve oxidative C−H cleavage of azides and require stoichiometric or excess amounts of external oxidants. Much less progress has been made toward cascade transformation of azides into nitriles via C−C cleavage.[9,11]

Alkyne difunctionalization allows two different functional groups to be added in a single step from simple precursors, helping to generate molecular complexity with excellent step economy.[12] One of the most important difunctionalizations is the reaction involving trifluoromethylation for rapidly constructing trifluoromethylated alkenes, which are commonly found in biologically active compounds and featured in pharmaceuticals and agrochemicals.[13−15] Alkyne cyanotrifluoromethylation, which combines trifluoromethylation and cyanation, is increasingly attractive because it leads to valuable CF_3- and CN-containing alkenes.[14,15] In 2014, Liang reported the cyanotrifluoromethylation and carbocyclization of 1,6-enynes to afford CF_3-containing nitriles.[14a] Subsequently, this group achieved Cu-mediated cyanotrifluoromethylation and cyanodifluoroalkylation of terminal alkynes using trimethylsilyl cyanide as a cyanide source, yielding β-trifluoromethylated or β-difluoroalkylated acrylonitriles.[14b,c] The alkyne cyanotrifluoromethylation reactions reported to date have been limited to additions involving terminal alkynes.

Our group is interested in the cascade transformation of alkynes.[16] Here, we describe a Cu-catalyzed cascade reaction of homopropargyl azides to afford 3-(trifluoromethyl)but-3-enenitriles in good yields and excellent regioselectivity (Scheme 1). This reaction appears to be the first direct conversion of homopropargyl azides into trifluoromethylated nitriles. Mechanistic studies indicate that the reaction proceeds via addition of a

Scheme 1. Cascade Transformation of Homopropargyl Azides to Trifluoromethylated Nitriles via C−C Cleavage



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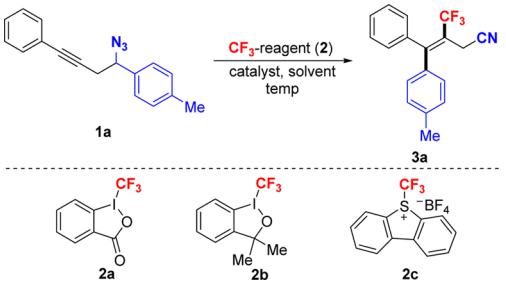
CF_3 radical to the alkyne, C−C cleavage via 1,4-aryl radical migration, and nitrile formation. To the best of our knowledge, this protocol is the first example of transformation of azides to nitriles through C−C cleavage derived from radical migration.

Studies were initiated using homopropargyl azide **1a** as a model substrate (Scheme 1). This substrate was treated with commonly used CF_3-reagent **2a** in the presence of CuBr (20 mol %) in DCM at room temperature for 24 h. Unexpectedly, the product (*E*)-4-phenyl-4-(*p*-tolyl)-3-(trifluoromethyl)but-3-enenitrile (**3a**) was isolated in 25% yield (Table 1, entry 1). To optimize production

Table 1. Optimization of Reaction Conditions[a]



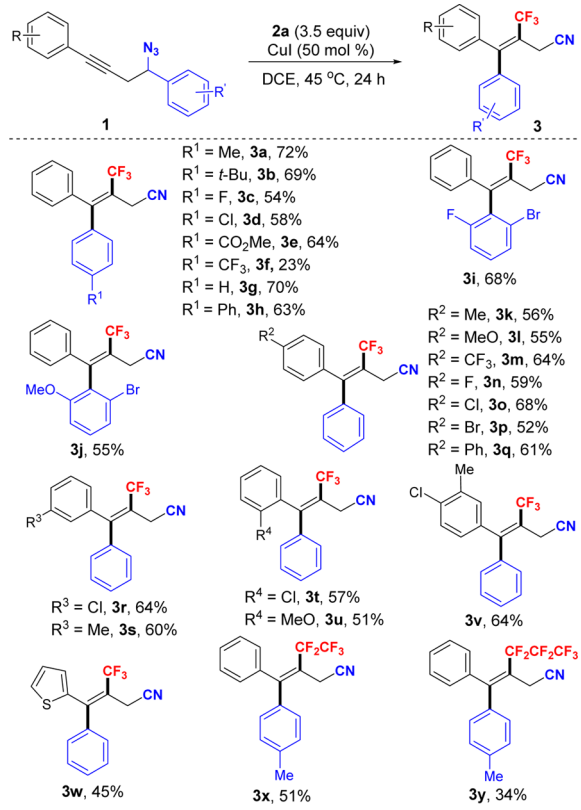
entry	catalyst	solvent	temp (°C)	**2a** (equiv)	yield (%)[b]
1	CuBr	DCM	rt	2	25
2	CuI	DCM	rt	2	40
3	CuCl	DCM	rt	2	35
4	$Cu(OTf)_2$	DCM	rt	2	20
5	CuOAc	DCM	rt	2	15
6	CuI	DCE	rt	2	43
7	CuI	dioxane	rt	2	28
8	CuI	DMF	rt	2	31
9	CuI	toluene	rt	2	trace
10[c]	CuI	DCE	rt	2	48
11[d]	CuI	DCE	rt	2	47
12[c]	CuI	DCE	45	2	59
13[c]	CuI	DCE	80	2	50
14[c]	CuI	DCE	45	3	67
15[c]	CuI	DCE	45	3.5	72
16[c]	CuI	DCE	45	4	69
17[c,e]	CuI	DCE	45	3.5	68
18[c,f]	CuI	DCE	45	3.5	46
19[c,g]	CuI	DCE	45	3.5	ND
20	–	DCE	45	3.5	ND

[a]Reaction conditions: homopropargyl azide **1a** (0.2 mmol), CF_3-reagent **2a** (0.7 mmol), catalyst (0.04 mmol), solvent (4 mL), 24 h under N_2. [b]Isolated yield. [c]CuI (0.1 mmol) was used. [d]CuI (0.2 mmol) was used. [e]Solvent (2 mL) was used. [f]**2b** was used instead of **2a**. [g]**2c** was used instead of **2a**.

of this desirable product, we explored various reaction conditions. CuI proved to be the best catalyst, providing **3a** in 40% yield (entries 2−5). DCE performed better than other common solvents, generating **3a** in 43% yield (entries 6−9). Increasing CuI loading to 50 mol % improved yield to 48% (entry 10), which higher loadings did not improve further (entry 11). Raising the reaction temperature to 45 °C improved the yield to 59% (entry 12), while an even higher temperature reduced the yield (entry 13). Using 3.5 equiv of trifluoromethyl reagent **2a** gave the highest yield of **3a** (entries 14−16). Decreasing the solvent volume to 2 mL did not further improve the yield (entry 17). The alternative CF_3-reagents **2b** and **2c** were less effective or inactive at affording **3a** (entries 18 and 19). No reaction occurred in the absence of a copper catalyst (entry 20).

With the optimized reaction conditions in hand, we began to explore the substrate scope of the cascade transformation of homopropargyl azides into trifluoromethylated nitriles (Scheme 2). First, homopropargyl azides **1** containing electron-donating

Scheme 2. Substrate Scope[a,b]



[a]Reaction conditions: homopropargyl azide **1** (0.2 mmol), CF_3 reagent **2** (0.7 mmol), CuI (0.1 mmol), DCE (4 mL), 45 °C, 24 h, under N_2. [b]Isolated yield.

groups such as Me or *t*-Bu at the R^1 position were found to react with **2a**, giving the products **3a** and **3b** in respective yields of 72% and 69%. Homopropargyl azides **1** carrying F or Cl gave products **3c** and **3d** in moderate yields. Even a homopropargyl azide substituted with an ester group reacted efficiently, generating the desired product **3e** in 64% yield. However, a homopropargyl azide bearing the CF_3 group at the R^1 position gave the desired product **3f** in only 23% yield, which might be due to the instability of the strongly electron-withdrawing group substituted aryl radical intermediate. A homopropargyl azide carrying a hydrogen atom or unsubstituted Ph at the R^1 position reacted with **2a** to give products **3g** and **3h** in good yields. In fact, homopropargyl azides with multiple substitutions at the R^1 position provided the corresponding products **3i** and **3j** in moderate yields.

Next, we investigated reactions involving homopropargyl azides **1** with different substitutions on the aryl ring attached to the triple bond. Homopropargyl azides with electron-donating or -withdrawing groups at the R^2 position underwent the cascade reaction with **2a**, affording the corresponding products **3k−q** in yields of 55−64%. The structure of product **3k** was confirmed by single-crystal X-ray diffraction analysis (Figure 1), and the

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structures of other products were confirmed by analogy and comparison with NMR spectra (see the Supporting Information).

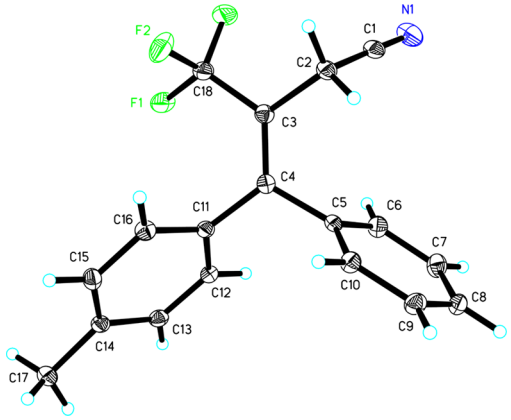


Figure 1. ORTEP diagram of cascade product **3k**.

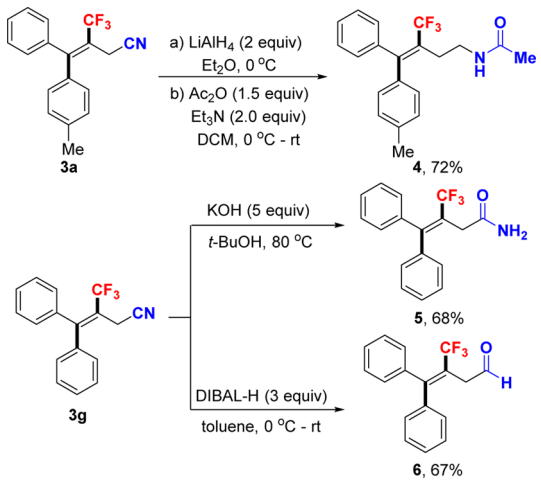
Homopropargyl azides substituted with *meta*-Cl or -Me reacted well with **2a**, producing **3r** in 64% yield and **3s** in 60% yield. Homopropargyl azides substituted with *ortho*-Cl or -MeO also gave the desired products **3t** and **3u** in slightly lower yields. The reaction tolerated simultaneous substitutions at the *meta* and *para* positions, yielding the desired product **3v** in 64% yield.

A heteroaryl-substituted homopropargyl azide reacted with **2a**, giving the corresponding product **3w** in moderate yield. However, aliphatic substituents showed little reactivity, perhaps reflecting the instability of the corresponding radical intermediate generated from the addition of the CF_3 radical to the alkynyl moiety.

Perfluoroalkylated reagents were prepared and applied to the reaction using **1a** as a partner under the standard reactions. The desired products **3x** and **3y** were isolated in 51% and 34% yield, respectively, clearly showing the feasibility of the method for synthesizing perfluoroalkylated nitriles.

To demonstrate the synthetic usefulness of our approach, we performed various downstream transformations of the nitrile groups (Scheme 3). For example, nitrile groups were readily converted to an *N*-acetyl-protected amine (**4**, 72%) by hydride reduction, to an amide (**5**, 68%) by alkaline hydrolysis, and to an aldehyde (**6**, 67%) via DIBAL-H reduction that tolerated a trifluoromethylated alkenyl.

Scheme 3. Transformation of Nitrile Groups

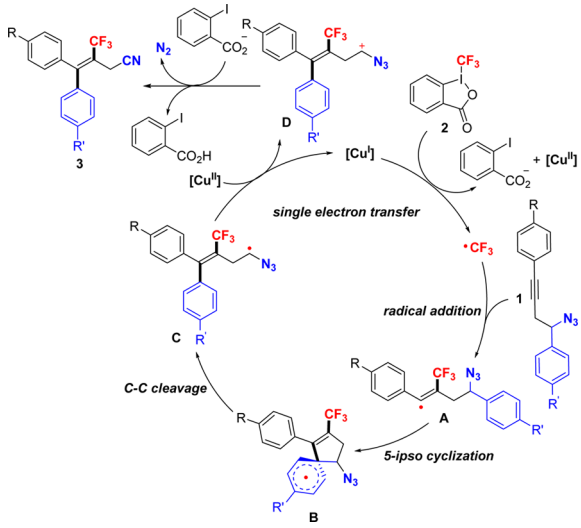


To clarify the mechanism of this cascade reaction, we added the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to the cascade reaction under standard conditions (Scheme 4). No product **3a** formed; instead, compound **7** was obtained in 42% yield (^{19}F NMR δ −55.65; see the Supporting Information). This result indicates that the reaction starts with addition of a CF_3 radical to the alkyne.

Scheme 4. Mechanistic Study

On the basis of our mechanistic study and previous relevant reports,[13h,17] we propose the following mechanism for the cascade transformation of homopropargyl azides into trifluoromethylated nitriles (Scheme 5). First, the CF_3 radical is generated from Togni's reagent in the presence of [Cu^I]. The CF_3 radical adds to the alkynyl moiety of **1**, forming the vinyl radical **A**, which immediately undergoes 5-*ipso* cyclization on the aryl ring, leading to radical **B** and the high regioseletivity.[13h,17] Then 1,4-aryl radical migration leads to C−C cleavage, forming the alkyl radical **C**, which undergoes [Cu^{II}]-promoted single-electron transfer to afford cation **D**[7g] and regenerate [Cu^I]. Finally, cation **D** is deprotonated, giving the desired product **3** and releasing N_2.[10b]

Scheme 5. Proposed Mechanism



In summary, we have developed a novel copper-catalyzed cascade reaction of homopropargyl azides that provides concise access to 3-(trifluoromethyl)but-3-enenitriles in good yields and excellent regioselectivity. This reaction appears to be the first example of direct conversion of homopropargyl azides into trifluoromethylated nitriles. Mechanistic investigations demonstrated that the reaction begins with addition of the CF_3 radical to the alkyne. Subsequent 1,4-aryl radical migration proceeds by 5-*ipso* cyclization, generating nitriles with high regioselectivity. This strategy allows the transformation of azides into nitriles via C−C cleavage derived from radical migration, which might be

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extensively used in the synthesis of medicines and functional materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00571.

Detailed experimental procedures, characterization data of products (NMR, HRMS, etc.), spectra of products (PDF)
X-ray crystal structures of **3k** (CIF)

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Notes

The authors declare no competing financial interest.

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