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Copper-Catalyzed Direct Trifluoromethylation of Propiolates: Construction of Trifluoromethylated Coumarins

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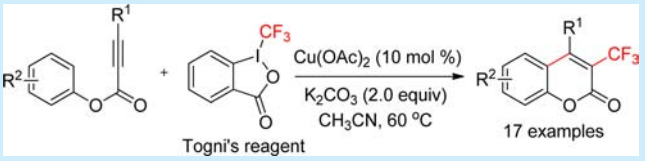
Supporting Information

ABSTRACT: A novel copper-catalyzed direct trifluoromethylation of internal alkynes was developed, obtaining a series of trifluoromethylated coumarins in good yields. The cyclization was proposed to proceed via a radical mechanism under copper-catalyzed conditions with good functional group tolerance.



Coumarin and its derivatives rank among the most important heterocycles in many naturally occurring heterocyclic products and pharmaceutically active molecules.[1] They have extensive applications as anticancer, antibacterial, anti-inflammatory, anti-HIV, antipsoriasis, anticoagulant, or enzymatic inhibitors in medicinal chemistry,[2] or as fluorescent probes and in illumination light source material sciences.[3] Since it is generally accepted that smuggling a trifluoromethyl group (CF_3) into a potentially useful organic molecule could improve its physical and chemical as well as biological evaluations,[4] some attention has been given to the trifluoromethyl substituted coumarins as anticancer agents, fluorescent markers, optical molecular sensors, and polymer wavelength-tuning agents.[5] Nonetheless, such applications are restricted to the easily available 4-trifluoromethyl substituted coumarins, which were prepared by Lewis acid catalyzed condensation reactions from phenols.[6] The limited successful but low yielding preparations of 3-trifluoromethyl substituted coumarins reported so far involve the reaction of coumarins with bis(trifluoroacetyl)-peroxide and that of coumarin-3-carboxylic acids with sulfur tetrafluoride.[7] Additionally, the Bi group reported the copper-(I)-catalyzed regioselective C−H 3-trifluoromethylation of hymecromone (an antispasmodic drug) using Togni's reagent.[8] Therefore, the development of a general and practical protocol to afford 3-trifluoromethyl substituted coumarins from accessible starting materials under mild reaction conditions remains highly desirable and equally challenging.

It has been of great synthetic interest to develop new methods for highly efficient and selective incorporation of the CF_3 group into diverse skeletal structures.[9] Recently, many efforts have been focused toward the development of efficient means to access C−CF_3 bonds via direct trifluoromethylation of alkenes using various CF_3 reagents.[8,10,11] Additionally, regioselective difunctionalization of alkenes also provided a straightforward access to the $C_{(sp^3)}$−CF_3 bond.[12] Furthermore, the CF_3 group could be incorporated into many carbocycles and heterocycles using $TMSCF_3$ or Togni's reagent, such as oxindole, indoline, and isoquinoline-1,3-dione derivatives.[13] Meanwhile, the 2-trifluoromethylated indole and 6-(trifluoromethyl)phenanthridine derivatives have been synthesized through oxidative cyclization of corresponding isocyanide derivatives with CF_3 reagents under metal-free conditions.[14] However, to the best of our knowledge, only very few direct trifluoromethylations of alkynes have been reported.[11a,12b,15] Direct construction of $C_{(sp^2)}$−CF_3 bonds through difunctionalization (oxy-trifluoromethylation) of terminal alkynes has been developed by the groups of Szabó[12b] [Scheme 1, eq 1], Sodeoka[11a] and Cho[15c] [Scheme 1, eq 2] independently. During preparation of this Letter, three other groups reported the direct trifluoromethylation of internal alkynes.[15d−f] Liu and Tan and co-workers described the transformation of propargylic alcohols into α-CF_3 enones using Togni's reagent [Scheme 1, eq 3].[15d] The Liang group reported the direct conversion of homopropargylic alcohols into CF_3-containing 3-butenal or 3-buten-1-one derivatives in a regioselective manner [Scheme 1, eq 4].[15e] The group of Ding and Hou developed the CuBr-catalyzed domino cyclization−trifluoromethylation of homopropargyl amines using Umemoto's reagent [Scheme 1, eq 5].[15f] Based on our recent efforts on the synthesis of trifluoromethylthiolated heterocycles,[16] we herein present the direct trifluoromethylation of propiolates **1** to obtain trifluoromethylated coumarins **3** using Togni's reagents [Scheme 1, eq 6].

To verify the feasibility of the projected direct trifluoromethylation of propiolates illustrated in Scheme 1, we started to explore the practicability of this transformation. Initially, the substrate *p*-tolyl 3-phenylpropiolate **1a** was selected as the model. It has been reported that radicals can be generated from $TMSCF_3$ with $PhI(OAc)_2$ and the Togni reagent in the

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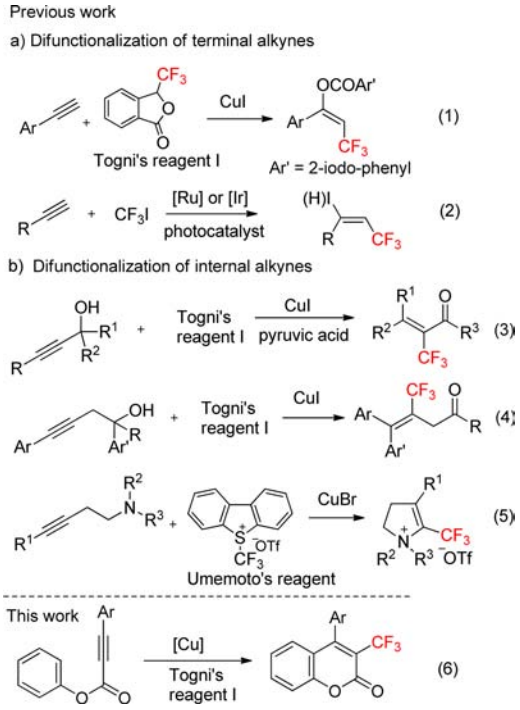
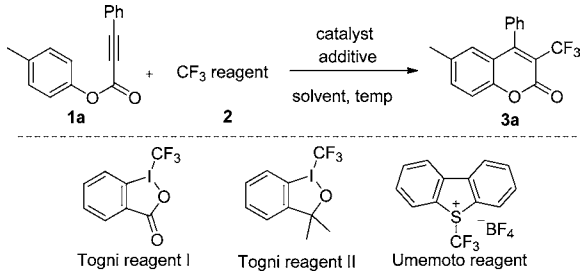
Scheme 1. Direct Trifluoromethylation of Alkynes



presence of copper.[13d] Based on these previous results, the reaction of **1a** with $TMSCF_3$ in the presence of $PhI(OAc)_2$ in CH_3CN at 90 °C was performed (Table 1, entry 1). Only a trace amount of the desired product **3a** was detected. Pleasingly, the targeted product **3a** was obtained in 15% yield when **1a** reacted with Togni's reagent I in the presence of CuI. Then various catalysts were surveyed, revealing that $Cu(OAc)_2$ is best suited to running this reaction to provide **3a** in 30% yield (Table 1, entries 3−8). To our delight, the yield was increased sharply when 2.0 equiv of K_2CO_3 were added in the reaction (Table 1, entry 9). Then we transferred our attention on other CF_3 reagents (Table 1, entries 10 and 11), but observed only poorer results. Changing the temperature of the reaction, we found the slightly effective temperature was at 60 °C with 55% yield (Table 1, entry 14). Gratifyingly, a satisfied yield (60%) was obtained when the quantity of Togni's reagent I was increased to 1.5 equiv. Unfortunately, the result could not be enhanced any more by switching the additive or solvent (see the Supporting Information).

With the optimized reaction conditions in hand, we started to explore the substrate scope of this transformation. The results are shown in Scheme 2. In general, 3-arylpropiolate substrates **1** containing either electron-withdrawing or -donating groups reacted smoothly with Togni's reagent I to give the corresponding trifluoromethylated coumarins in moderate to good yields. The effects of the substituent group R^1 were obvious. Results indicated that the substrates with electron-donating groups showed better reactivity (**3c**, **3f**−**g** vs **3d**−**e**). Additionally, phenyl 3-cyclopropylpropiolate **1h** (R^1 = cyclopropyl) was also found to be suitable for the reaction under the standard conditions, providing the corresponding product in a relative low yield (**3h**). Subsequently, substrates (**1i**−**k**) bearing a methyl group (R^2 = Me) in the *para*-, *meta*-, or *ortho*-position of the phenyl were subjected to the optimized reaction conditions. The results showed that the steric effect was also significant. Substrate **1i** (R^2 = *p*-Me) was converted into the

Table 1. Optimization of the Reaction Conditions[a]



entry	CF_3 reagent	catalyst	temp	yield (%)
1	$PhI(OAc)_2 + TMSCF_3$	−	90	trace
2	Togni reagent I	CuI	90	15
3	Togni reagent I	CuBr	90	23
4	Togni reagent I	CuOAc	90	17
5	Togni reagent I	$[Cu(CN)_4]PF_6$	90	nd
6	Togni reagent I	Cu_2O	90	28
7	Togni reagent I	$CuBr_2$	90	24
8	Togni reagent I	$Cu(OAc)_2$	90	30
9[b]	Togni reagent I	$Cu(OAc)_2$	90	45
10[b]	Togni reagent II	$Cu(OAc)_2$	90	35
11[b]	Umemoto reagent	$Cu(OAc)_2$	90	34
12[b]	Togni reagent I	$Cu(OAc)_2$	80	47
13[b]	Togni reagent I	$Cu(OAc)_2$	70	53
14[b]	Togni reagent I	$Cu(OAc)_2$	60	55
15[b]	Togni reagent I	$Cu(OAc)_2$	45	45
16[b,c]	Togni reagent I	$Cu(OAc)_2$	60	60
17[b,c,d]	Togni reagent I	$Cu(OAc)_2$	60	58

[a]Unless otherwise noted, the reaction conditions are as follows: **1a** (0.2 mmol), **2** (1.2 equiv, 0.24 mmol), catalyst (10 mol %), additive (2.0 equiv), solvent (4 mL), reaction time 12 h. ^{19}F NMR yield of the isolated product. Isolated yield based on methyl 2-(phenylethynyl)-benzoate **1a**. [b]2.0 equiv of K_2CO_3 were added. [c]Togni reagent I (1.5 equiv, 0.3 mmol). [d]5 mol % catalyst $Cu(OAc)_2$ was used.

corresponding product **3i** in good yield. While two isomers **3j** and **3j′** were obtained in a ratio of 5:2 in a moderate total yield, and no desired product **3k** was formed under the standard conditions. Furthermore, we also investigated the effects of substituent group R^2. Different functional groups, including methyl, tertiary butyl, methoxyl, and halogen, were all compatible during the reaction process with good yields (**3l**−**q**). Painfully, no reaction took place when the activated alkyne was replaced by unactivated alkyne [1-methoxy-4-(3-phenoxy-prop-1-yn-1-yl)benzene, **1r**].

To probe into the possible reaction mechanism, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), an effective radical scavenger, was added in the reaction under the standard conditions. As expected, a trace of the desired product (**3a**) was detected, and a distinctive compound **4** (^{19}F NMR δ −56.06; see the Supporting Information) was observed instead. This result indicated that a CF_3 radical intermediate might be involved in the reactions. Thus, a plausible mechanism is proposed in Scheme 3. First, CF_3 radical **A** would be afforded under the proper conditions from Togni's reagent in the presence of copper(II). The CF_3 radical **A** would be easily trapped by phenyl 3-phenylpropiolate **1**, which would undergo a radical addition leading to imdoyl radical **B**. Subsequently, there are two possible ways for the formation of cyclohexadienyl cation **E** from the imdoyl radical **B**. In path a, imdoyl radical **B** undergoes radical addition to generate cyclohexadienyl radical **C**, which would be oxidized by

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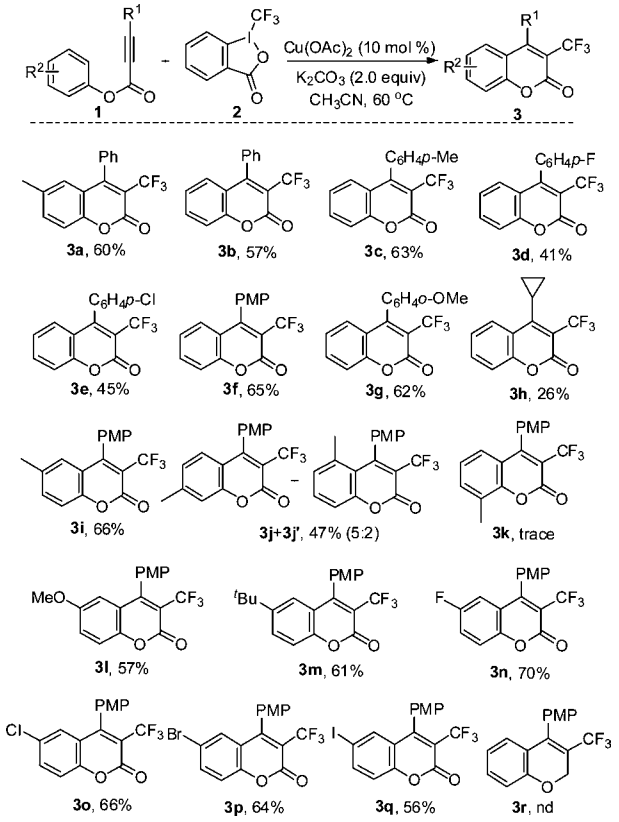
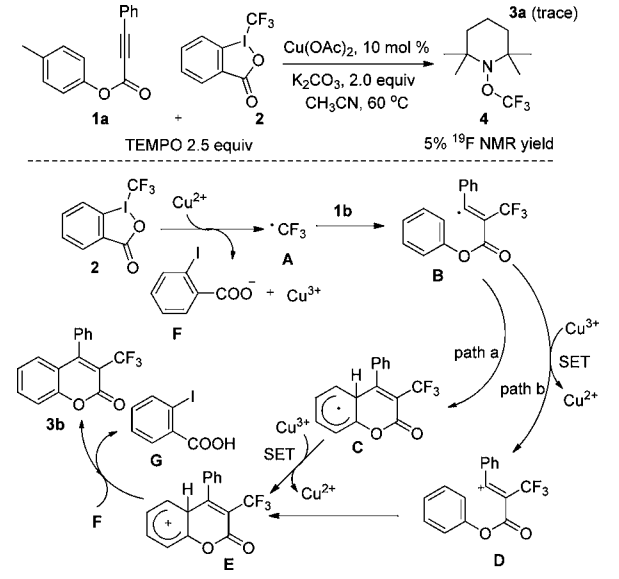
Scheme 2. Scope of the Trifluoromethylation Reaction of Propiolates 1 with Togni Reagent I



Scheme 3. Investigation of the Mechanism and the Proposed Mechanism



copper(III) to give cyclohexadienyl cation **E**. And in path b, the imdoyl radical **B** initially went through a single electron transfer (SET), followed by a Friedel–Crafts reaction also producing intermediate **E**. Finally, **E** underwent deprotonation to produce the targeted product **3**.

In conclusion, we have reported a copper-catalyzed direct trifluoromethylation of activated alkynes, providing a rapid access to trifluoromethylated coumarins in good yields. Preliminary mechanistic studies indicate that the reaction proceeds through a CF_3 radical addition to activated alkynes, followed by sequential oxidation cyclization to target products. Further investigations on direct trifluoromethylation of internal alkynes for the synthesis of other heterocycles with privileged structures are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, Table S1, and product characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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