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Copper-catalyzed trifluoromethylation of terminal alkynes using Umemoto's reagent

Dong-Fen Luo, Jun Xu, Yao Fu *, Qing-Xiang Guo *

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

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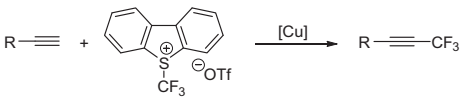
ABSTRACT

A copper-catalyzed method for trifluoromethylation of terminal alkynes with Umemoto's reagent has been developed. The reaction is conducted at room temperature and shows good tolerance to a variety of functional groups.

Trifluoromethyl-containing organic compounds constitute an important class of biologically active molecules.[1,2] The introduction of a CF_3 group into organic compounds often enhances the chemical and metabolic stability, lipophilicity, and binding selectivity.[2] Due to this reason, the development of efficient methods for the incorporation of trifluoromethyl group into organic structures has received much attention recently.[3] Traditional methods in this area usually focused on non-catalytic trifluomethylation reactions, mostly forming C(sp3)–CF_3 bond.[4] However, these methods suffer from harsh reaction conditions and limited substrates scope. Recently, more attention has been paid to transition metal-catalyzed methods[5] to make CF_3-containing building blocks. Examples include: (1) Pd-catalyzed trifluoromethylation of C(sp2)–H and C(sp2)–halide bonds;[6–9] (2) copper-mediated[10] or copper-catalyzed[11] trifluoromethylation of C(sp2)–X (X = halide, boronic acid) moieties; and (3) copper-catalyzed allylic C–H bond activation/trifluoromethylation reactions.[12] In comparison to the previous trifluoromethylation methods, these newly developed reactions employ mild reaction conditions and enjoy a broader substrate scope.

Trifluoromethylated acetylenes are a class of building blocks for the synthesis of agrochemicals, pharmaceuticals, and functional materials.[13] Traditional methods for the synthesis of trifluoromethylated acetylenes include: Pd-catalyzed coupling of trifluoropropynyl metal reagents with aryl iodides; dehalogenation of trifluoromethylethenes; and electrophilic trifluoromethylation of alkynyl metal reagents.[14,15] However, these methods usually involve tedious procedures or use toxic substrates. Recently, Chu and Qing, developed the first example of Cu-mediated protocol for oxidative trifluoromethylation of terminal alkynes with Me_3SiCF_3.[16] This method is very useful for the synthesis of a broad range of trifluoromethylated acetylenes. However, this method also has some limitations, such as the requirement of a high reaction temperature, use of an excess amount (5.0 equiv) of Me_3SiCF_3, and use of a stoichiometric amount of copper reagents. Herein, we want to report a mild copper-catalyzed trifluoromethylation of terminal alkynes using Umemoto's reagent (Eq. (1)).



(1)

We began our study by examining the trifluoromethylation reaction of but-3-ynyl 4-methylbenzene-sulfonate (**1a**) with (trifluoromethyl)dibenzothiophenium triflate (**2a**). At first, a catalytic amount of CuTc (20% mmol) and a cheap ligand (2,4,6-trimethylpridine, **L1**) were tested. To our delight, the desired trifluoromethylation alkyne **3a** was detected, although the yield was still low (Table 1, entry1). To optimize the reaction, we changed **L1** to other related ligands but observed only poorer performance (entries 2 and 3). In particular, the often used ligand (1,10-phenanthroline, **L4**) generated no desired product (entry 4). Furthermore, the best reaction temperature was 30 °C (entry 5), because a higher reaction temperature decreases the yield of **3a** (entry 1). To improve the yield, we then tried different Cu(I) salts (entries 6–10) until we found that CuCl increased the yield to 75%. Under the same optimized conditions, the use of (trifluoromethyl)dibenzothiophenium tetrafluoroborate (**2b**, entry 11) produces **3a** in a similar

* Corresponding authors.
E-mail address: fuyao@ustc.edu.cn (Y. Fu).

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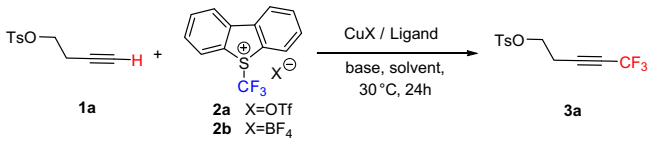
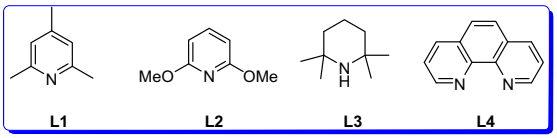
Table 1
Optimization of the Cu-catalyzed trifluoromethylation reaction[a]



1a **2a** X=OTf **2b** X=BF_4 **3a**



L1 **L2** **L3** **L4**

Entry	CuX (equiv)	Ligand (equiv)	Base (equiv)	Solvent	Yield of **3a**
1[b]	CuTc[c] (0.2)	**L1** (2.0)	—	DMAc	35
2[b]	CuTc (0.2)	**L2** (2.0)	—	DMAc	2
3[b]	CuTc (0.2)	**L3** (2.0)	—	DMAc	0
4[b]	CuTc (0.2)	**L4** (2.0)	K_3PO_4(2.0)	DMAc	0
5	CuTc (0.2)	**L1** (2.0)	—	DMAc	55
6	CuBr (0.2)	**L1** (2.0)	—	DMAc	61
7	CuI (0.2)	**L1** (2.0)	—	DMAc	46
8	CuOAc (0.2)	**L1** (2.0)	—	DMAc	53
9	[Cu(OTf)]·C_6H_6 (0.1)	**L1** (2.0)	—	DMAc	12
10	CuCl (0.2)	**L1** (2.0)	—	DMAc	75
11[d]	CuCl (0.2)	**L1** (2.0)	—	DMAc	73
12	CuCl (0.2)	**L1** (2.0)	—	DCE	30
13	CuCl (0.2)	**L1** (2.0)	—	THF	26
14	—	**L1** (2.0)	—	DMAc	0

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.12 mmol), [Cu] (20 mol %), solvent (0.5 mL), 30 °C, 24 h under Ar atmosphere, GC yields with biphenyl as an internal standard.
[b] Reaction was conducted at 60 °C.
[c] TcCu = (thiophene-2-carbonyloxy) Cu(I).
[d] **2a** was instead of **2b**.

yield. Moreover, we optimized the solvent and found *N*,*N*-dimethylacetamide (DMAc) to be optimal (entries 10, 12 and 13). Note that in the absence of copper salt we did not observe any trifluoromethylation product (entry 14).

With the optimized set of reaction conditions in hand, we examined the scope of the new transformation (Table 2). We found that various terminal alkynes can be transformed to the corresponding products in modest to good yields. Many synthetically important functional groups, such as sulfonate, nitro, ester, amide, ether, and even hydroxyl are well-tolerated under the conditions. Moreover, arene rings carrying chloro and iodo groups do not interfere with the transformation (entries 2 and 3), making additional modifications possible at the halogenated positions. A high reactivity was also observed with substrates bearing sulfonate group (entries 1–5). The 4-nitro-substituted phenylacetylene and 3-ester-substituted phenylacetylene also smoothly underwent the reaction in good yield (entries 6 and 7). It should be noted that 2-(prop-2-ynyl) isoindoline-1,3-dione (entry 8) could be employed as substrate to afford the target product in a moderate yield. Ether-containing alkynes can also be trifluomethylated (entry 9). Same as the sulfonate, benzoate can also be tolerated in this reaction and successfully converted to the product in a moderated yield (entry 10). Finally, undec-10-yn-1-ol was suitable in this reaction to afford corresponding product in a good yield (entry 11). Thus, both of the aliphatic (entries 1–5 and 8–11) and aromatic alkynes (entries 6 and 7) can afford the desired trifluoromethylated products in moderate to good yields under the reaction conditions.

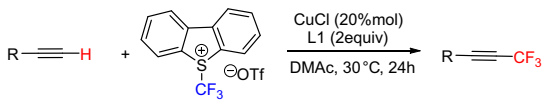
A plausible reaction pathway for trifluoromethylation of alkynes with CF_3^+ is presented in Scheme 1. A ligated complex **A** would be generated in situ by the reaction of CuCl with 2,4,6-trimethylpyridine in DMAc. Subsequently, coordination/deprotonation of the alkyne occurs to form a copper species **B** in the presence of 2,4,6-trimethylpyridine as a base. Oxidative addition of CF_3^+ to species **B** then took place to form a Cu (alkynyl)(trifluoromethyl)complex **C**, which affords the product alkynyl-CF_3 through reductive elimination.[17] Alternatively, **C** may cause an S_N2-type substitution (or σ-bond metathesis) reaction at the CF_3 center to form the product alkynyl-CF_3. Finally, Cu(I) was released regenerating the starting copper species **A**.

In conclusion, we have developed an efficient copper-catalyzed trifluoromethylation reaction of terminal alkynes with Umemoto's reagent. The reaction is carried out under mild conditions and shows good functional group compatibility even with unprotected OH groups. The reaction provides a straightforward way to prepare various trifluoromethylated alkynes.

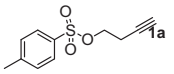
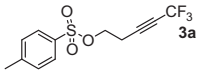
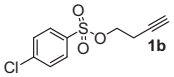
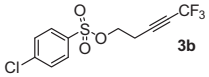
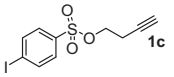
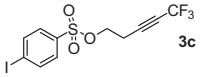
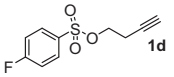
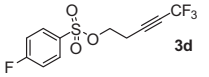
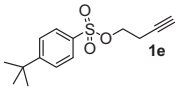
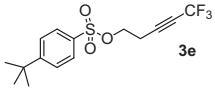
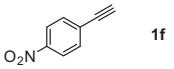
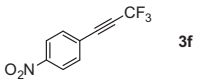
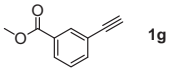
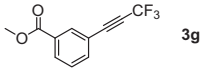
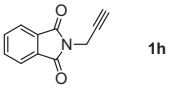
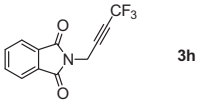
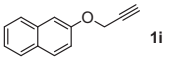
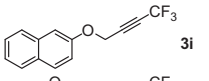
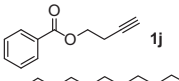
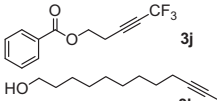
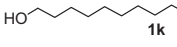
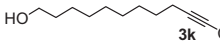
Experimental

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts of ^{1}H NMR spectra were reported in parts per million relative to tetramethylsilane (δ = 0). ^{19}F NMR spectra ($CFCl_3$ as outside standard and low field is positive) were recorded with ^{1}H-coupling on a Bruker 376 MHz spectrometer. ^{13}C NMR spectra were recorded with ^{1}H-decoupling on a Brucker 100 MHz spectrometer. Chemical shifts of ^{1}C NMR spectra were reported in parts per million relative to the solvent resonance as the internal standard ($CDCl_3$, δ 77.00 ppm). Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (200–300 mesh).

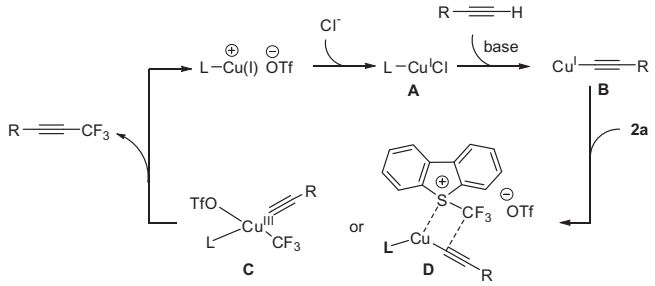
Table 2
CuCl catalyzed trifluoromethylation of terminal alkynes[a]



1 2a 3

Entry	Substrate	Product	Yield (%)
1	 1a	 3a	65
2	 1b	 3b	65
3	 1c	 3c	69
4	 1d	 3d	75
5	 1e	 3e	75
6	 1f	 3f	44
7	 1g	 3g	58
8	 1h	 3h	38
9	 1i	 3i	26
10	 1j	 3j	54
11	 1k	 3k	79

[a] The reactions were conducted under the optimized conditions.



Scheme 1. A possible mechanism for the catalytic trlfluoromethylation reaction.

General procedure for copper-catalyzed trifluoromethylation of terminal alkenes

CuCl (0.04 mmol), 2,4,6-trimethylpyridine (0.4 mmol), trifluoromethylating reagent **2a** (0.24 mmol) and terminal alkynes (0.2 mmol) were added to a Schlenk tube which was equipped with a stirring bar. DMAc (1 mL) was added under argon atmosphere to this tube. After the addition of all materials, the reaction mixture was kept for 24 h at 30 °C. After the reaction, ethyl acetate was added. The organic layer was separated, and washed with water. The combined organic extracts were washed with brine, and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by chromatography on silica gel to give the product.

5,5,5-Trifluoropent-3-ynyl 4-methylbenzenesulfonate (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H), 4.14 (t, J = 6.6 Hz, 2H), 2.70 (d, J = 3.1 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.39, 132.50, 130.04, 127.99, 111.14 (q, J = 254.8 Hz), 83.29 (q, J = 6.5 Hz), 70.24 (q, J = 52.6 Hz), 65.72, 21.66, 19.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.28 (t, J = 3.1 Hz).

5,5,5-Trifluoropent-3-ynyl 4-chlorobenzenesulfonate (3b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 8.6 Hz, 2H), 4.19 (q, J = 6.4 Hz, 2H), 2.74 (tq, J = 6.7, 3.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.06, 134.01, 129.82, 129.37, 113.66 (q, J = 257.3 Hz), 83.07 (q, J = 6.3 Hz), 70.41 (q, J = 52.8 Hz), 66.12, 19.31. ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.30 (t, J = 3.4 Hz).

5,5,5-Trifluoropent-3-ynyl 4-iodobenzenesulfonate (3c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.91 (m, 2H), 7.66–7.60 (m, 2H), 4.21–4.15 (m, 2H), 2.80–2.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.77, 135.18, 129.14, 113.65 (q, J = 257.2 Hz), 102.10, 83.04 (q, J = 6.3 Hz), 70.40 (q, J = 52.7 Hz), 66.11, 19.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.26 (t, J = 3.3 Hz).

5,5,5-Trifluoropent-3-ynyl 4-fluorobenzenesulfonate (3d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.90 (m, 2H), 7.30–7.21 (m, 2H), 4.18 (t, J = 6.5 Hz, 2H), 2.73 (tq, J = 6.8, 3.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.03 (d, J = 257.4 Hz), 131.57 (d, J = 3.3 Hz), 130.81 (d, J = 9.6 Hz), 116.82 (d, J = 22.9 Hz), 113.65 (q, J = 257.2 Hz), 83.13 (q, J = 6.3 Hz), 70.33 (q, J = 52.7 Hz), 65.97 (d, J = 1.5 Hz), 19.28 (d, J = 1.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.30 (t, J = 3.4 Hz), −102.32 (s).

5,5,5-Trifluoropent-3-ynyl 4-tert-butylbenzene-sulfonate (3e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 4.19–4.13 (m, 2H), 2.78–2.64 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.31, 132.38, 127.85, 126.47, 113.71 (q, J = 257.1 Hz), 83.45 (q, J = 6.4 Hz), 70.19 (q, J = 52.7 Hz), 65.78, 35.36, 31.00, 19.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.21 (t, J = 3.4 Hz).

1-Nitro-4-(3,3,3-trifluoroprop-1-ynyl)benzene (3f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 7.9 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.47, 129.07, 122.83, 122.64, 113.38 (q, J = 258.2 Hz), 82.65 (q, J = 6.0 Hz), 78.39 (q, J = 53.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.60.

2-Methyl 3-(3,3,3-trifluoroprop-1-ynyl)benzoate (3g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.65, 135.32, 132.58, 130.80, 130.13, 129.93, 127.89, 112.38 (q, J = 257.1 Hz), 84.23 (q, J = 6.4 Hz), 75.11, 51.46. ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.12.

2-(4,4,4-Trifluorobut-2-ynyl)isoindoline-1,3-dione (3h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.88 (m, 2H), 7.81–7.74 (m, 2H), 4.63–4.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.52, 134.55, 131.80, 123.87, 113.66 (q, J = 258.0 Hz), 80.98 (q, J = 6.5 Hz), 70.36 (q, J = 53.2 Hz), 26.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.76 (t, J = 3.2 Hz).

2-(4,4,4-Trifluorobut-2-ynyloxy)naphthalene (3i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.73 (m, 3H), 7.47 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.39 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.20–7.15 (m, 2H), 4.90 (q, J = 3.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.08, 134.18, 129.93, 129.62, 127.73, 127.01, 126.73, 124.44, 118.39, 113.78 (q, J = 258.0 Hz), 107.54, 82.15 (q, J = 6.4 Hz), 74.18 (q, J = 53.2 Hz), 55.08. ^{19}F NMR (376 MHz, $CDCl_3$) δ −50.83 (t, J = 3.4 Hz).

5,5,5-Trifluoropent-3-ynyl benzoate (3j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.01 (m, 2H), 7.63–7.55 (m, 1H), 7.50–7.42 (m, 2H), 4.47 (t, J = 6.6 Hz, 2H), 2.81 (tq, J = 7.0, 3.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.13, 132.32, 128.67, 128.52, 127.47, 112.86 (q, J = 256.8 Hz), 83.78 (q, J = 6.4 Hz), 68.79 (q, J = 52.4 Hz), 60.01, 17.92. ^{19}F NMR (376 MHz, $CDCl_3$) δ −49.99 (t, J = 3.5 Hz).

12,12,12-Trifluorododec-10-yn-1-ol (3k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (t, J = 6.6 Hz, 2H), 2.29–2.17 (m, 2H), 1.56–1.42 (m, 4H), 1.35–1.20 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.17 (q, J = 255.9 Hz), 88.33 (q, J = 6.3 Hz), 67.35 (q, J = 51.8 Hz), 61.99, 31.75, 28.31, 28.30, 27.86, 27.65, 26.18, 24.69, 17.09. ^{19}F NMR (376 MHz, $CDCl_3$) δ −49.38 (t, J = 3.7 Hz).

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