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Copper-Mediated Trifluoromethylation of Terminal Alkynes by *S*-(Trifluoromethyl)diarylsulfonium Salt

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The copper-mediated trifluoromethylation of terminal alkynes with *S*-(trifluoromethyl)diarylsulfonium salt has been carefully investigated. The reactions proceeded smoothly to afford trifluoromethylated acetylenes in moderate to good yields. This approach is a convenient method to synthesize a variety of functional trifluoromethylated acetylenes.

Keywords copper, alkynes, trifluoromethylation, *S*-(trifluoromethyl)diarylsulfonium salt

Introduction

Trifluoromethylated organic compounds are becoming increasingly important in the fields of polymers, agrochemicals, and pharmaceuticals due to the unique characteristics of the trifluoromethyl group (CF_3), such as metabolic stability and hydrophobicity.[1] As a consequence, the development of efficient methods for trifluoromethylation has been of great synthetic interest for organic chemists and medicinal chemists recently.[1c,2] Traditional methods, which involve radical, nucleophilic or electrophilic trifluoromethylation reagents and usually focus on non-catalytic trifluoromethylation reactions, suffer from harsh reaction conditions and limited substrate scope.[1a,1b] Recently, considerable progress has been made on the transition metal-mediated coupling reactions for trifluoromethylation.[3] In these approaches, copper has been shown to be one of the most efficient transition metals for trifluoromethylation.[3q-3w]

Trifluoromethylated acetylenes are a class of important fluorinated building blocks and have found widespread applications in medicinal chemistry, agrochemistry and material science.[4] The first copper-mediated oxidative trifluoromethylation of terminal alkynes with Me_3SiCF_3 was reported by Qing and coworkers.[5] This approach is a straightforward and functional group compatible method for a broad range of trifluoromethylated acetylenes, but the limitations such as high reaction temperature and the use of large amount of $TMSCF_3$ prompted them to find a better way to achieve the trifluoromethylation under milder conditions.[6] Recently, it was found that electrophilic trifluromethylating reagent, Togni's reagent or Umemoto's reagent, could also achieve trifluoromethylation of terminal alkynes by utilizing copper complex as catalyst.[7] While in the case of Umemoto's reagent, only moderate yields were obtained for aliphatic alkynes and low yields were obtained for aromatic alkynes.[7a]

S-(Trifluoromethyl)diarylsulfonium salts, which were first prepared by Yagupolskii and then developed by Umemoto, Shreeve and Shibata, have been successfully used for the electrophilic trifluoromethylation of nucleophiles.[8] We have shown that one of these reagents could be able to achieve trifluoromethylation of heteroaromatic compounds, arylboronic acids and styrenes.[3r,9] We then further investigated the use of this reagent in the copper-mediated trifluoromethylation of terminal alkynes.

Experimental

^1H and ^{13}C NMR spectra were recorded at 300 and 100 MHz, respectively, with TMS as the internal standard. ^{19}F NMR spectra were recorded at 282 MHz with $CFCl_3$ (positive for downfield shifts) as the external standards. High resolution mass data were recorded on a Waters Micromass GCT Preminer instrument. Melting points were obtained on SYP1008-3 instrument. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300—400 mesh silica gel.

General procedure for the trifluoromethylation of terminal alkynes: into the solution of terminal alkyne (0.2 mmol) in DMF (6 mL) was added $[Ph_2SCF_3]^+[OTf]^-$ (160.0 mg, 0.40 mmol), followed by CuI (39.1 mg, 0.2

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mmol), 2,2'-bipyridine (33.0 mg, 0.2 mmol) and K_3CO_3 (32.0 mg, 0.2 mmol). The reaction mixture was stirred at 60 ℃ for 6—11 h. After cooling to room temperature, the mixture was diluted with diethyl ether, washed with H_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [eluent: petroleum ether/ethyl acetate (20∶1, *V*∶*V*)] to give the desired product.

(3,3,3-Trifluoroprop-1-yn-1-yl)benzene (**2a**):[10a] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.56 (d, J=7.6 Hz, 2H), 7.47 (d, J=7.4 Hz, 1H), 7.40 (t, J=7.6 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –48.77 (s, 3F).

1-Propyl-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2b**):[10b] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, J=7.8 Hz, 2H), 7.20 (d, J=7.8 Hz, 2H), 2.62 (t, J=7.8 Hz, 2H), 1.71—1.49 (m, 2H), 0.94 (t, J=7.5 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.55 (s, 3F).

1-(*tert*-Butyl)-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2c**):[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.49 (d, J=8.1 Hz, 2H), 7.41 (d, J=8.1 Hz, 2H), 1.32 (s, 9H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.18 (s, 3F).

4-(3,3,3-Trifluoroprop-1-yn-1-yl)-1,1'-biphenyl (**2d**):[10c] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64—7.59 (m, 6H), 7.50—7.40 (m, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.33 (s, 3F).

2-(3,3,3-Trifluoroprop-1-yn-1-yl)-9*H*-fluorene (**2e**): A white solid. M.p. 99—100 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.79 (t, J=7.3 Hz, 2H), 7.72 (s, 1H), 7.57 (d, J=7.7 Hz, 2H), 7.48—7.30 (m, 2H), 3.91 (s, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.47 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.39 (s), 143.74 (s), 143.26 (s), 140.37 (s), 131.40 (s), 128.96 (s), 127.95 (s), 127.09 (s), 125.18 (s), 120.61 (s), 119.97 (s), 116.11 (q, J=1.8 Hz), 114.97 (q, J=256.6 Hz), 87.48 (q, J=6.4 Hz), 75.53 (q, J=52.3 Hz), 36.68 (s); IR (KBr) ν: 2265, 2229, 1610, 1485, 1466, 1456, 1420, 1398, 1339, 1321, 1297, 1235, 1191, 1180, 1131, 1103, 862, 770, 735, 698, 600 cm^{-1}. GC-MS: 258 (M^+). HRMS calcd for $C_{16}H_9F_3$: 258.0656; found 258.0652.

1-Methoxy-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2f**):[10a] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.49 (d, J=8.7 Hz, 2H), 6.89 (d, J=8.7 Hz, 2H), 3.83 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.36 (s, 3F).

1-Ethoxy-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2g**): A colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46 (d, J=8.7 Hz, 2H), 6.68 (d, J=8.7 Hz, 2H), 4.05 (q, J=6.9 Hz, 2H), 1.43 (t, J=6.9 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.32 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.02, 134.16 (q, J=1.5 Hz), 115.13 (q, J=254.5 Hz), 114.79, 110.11, 87.22 (q, J=5.8 Hz), 74.75 (q, J=51.8 Hz), 63.73, 14.58; IR (KBr) ν: 2990, 2250, 1606, 1510, 1478, 1291, 1254, 1135, 1044, 836, 772, 577, 537 cm^{-1}. GC-MS: 214 (M^+). HRMS calcd for $C_{11}H_9F_3O$: 214.0605; found 214.0604.

1-Bromo-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**2h**):[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.55 (d, J=7.5 Hz, 2H), 7.42 (d, J=7.5 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.76 (s, 3F).

Methyl 2-(3,3,3-trifluoroprop-1-yn-1-yl)benzoate (**2i**):[6a] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.03—7.95 (m, 1H), 7.59—7.28 (m, 3H), 3.88 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.78 (s, 3F).

Methyl 4-(3,3,3-trifluoroprop-1-yn-1-yl)benzoate (**2j**):[10d] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.00 (d, J=8.1 Hz, 2H), 7.57 (d, J=8.1 Hz, 2H), 3.88 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.48 (s, 3F).

4-(3,3,3-Trifluoroprop-1-yn-1-yl)benzonitrile (**2k**):[10e] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.66—7.22 (m, 4H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.76 (s, 3F).

5-(3,3,3-Trifluoroprop-1-yn-1-yl)-1*H*-indole (**2l**): A white solid. M.p. 109—110 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.30 (s, 1H), 7.90 (s, 1H), 7.40—7.27 (m, 3H), 6.58 (s, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –48.96 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.70, 127.74, 126.30 (q, J=2.1 Hz), 125.81 (q, J=1.5 Hz), 125.70, 115.32 (q, J=254.4 Hz), 111.51, 109.54 (q, J=1.4 Hz), 103.3, 88.93 (q, J=6.6 Hz), 73.92 (q, J=51.8 Hz); IR (KBr) ν: 3404, 2243, 1324, 1327, 1307, 1263, 1208, 1109, 1088, 898, 814, 766, 732, 607 cm^{-1}. GC-MS: 209 (M^+). HRMS calced for $C_{11}H_6F_3N$: 209.0452; found 209.0451.

1-(5-(3,3,3-Trifluoroprop-1-yn-1-yl)thiophen-2-yl)-ethanone (**2m**): A yellow solid. M.p. 49—50 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.60 (d, J=3.9 Hz, 1H), 7.44 (d, J=3.9 Hz, 1H), 2.61 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –48.78 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.81, 147.90, 136.17 (q, J=1.6 Hz), 131.50, 124.93 (q, J=2.3 Hz), 114.58 (q, J=256.7 Hz), 81.43 (q, J=53.7 Hz), 79.23 (q, J=6.3 Hz), 26.89; IR (KBr) ν: 3085, 2242, 1663, 1449, 1262, 1132, 821, 749, 650, 608, 587 cm^{-1}. GC-MS: 218 (M^+). HRMS calcd for $C_9H_5F_3OS$: 218.0013; found 218.0016.

N-Benzyl-4,4,4-trifluoro-*N*-methylbut-2-yn-1-amine (**2n**):[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39—7.24 (m, 5H), 3.58 (s, 2H), 3.42 (q, J=2.9 Hz, 2H), 3.38 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.60 (s, 3F).

Results and Discussion

The trifluoromethylation of phenylacetylene (**1a**) with $[Ph_2SCF_3]^+[OTf]^-$(**3**) was selected as a model reaction (Table 1). The reactions were performed in the presence of copper complex and sodium acetate in DMF at 60 ℃ for 6 h (Entries 1—13). Of the copper complexes screened, Cu(I) was found to be more effective than copper(II) or copper powder (Entries 1—6). Copper powder could lead to the reduction of $[Ph_2SCF_3]^+$ $[OTf]^-$ but only trace amount of desired product was detected by ^{19}F NMR (Entry 5). The ligand is quite important for the reaction (Entries 7—13). It was found that 1 equiv. of bipy (2,2'-bipyridine) as ligand gave better result (Entry 4 vs. Entries 7—13). Worse results were obtained if the reaction temperature was varied (Entry 4 vs. Entries 14 and 15). Based on these first results, we decided to further screen the reaction condi-

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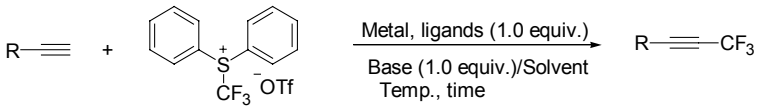
Table 1 Screening for optimal conditions for the trifluoromethylation of phenylacetylene by $[Ph_2SCF_3]^+[OTf]^-$ [a]



1a **3** **2a**

Entry	**1a**∶**3**∶**M** (equiv.)[b]	Ligand	Base	Solvent	Temp., Time	Yield (**2a**, %)[c]
1	1∶1∶CuCl (1.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	34
2	1∶1∶CuBr (1.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	36
3	1∶1∶$CuCl_2$ (1.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	4
4	1∶1∶CuI (1.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	47
5	1∶1∶Cu (1.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	complex
6	1∶1∶CuOTf (1.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	22
7	1∶1∶CuI (1.0)	—	NaOAc	DMF	60 ℃, 6 h	12
8	1∶1∶CuI (1.0)	Benzo[h]quinoline	NaOAc	DMF	60 ℃, 6 h	10
9	1∶1∶CuI (1.0)	Py	NaOAc	DMF	60 ℃, 6 h	18
10	1∶1∶CuI (1.0)	Phen	NaOAc	DMF	60 ℃, 6 h	40
11	1∶1∶CuI (1.0)	2,6-Dimethylpyridine	NaOAc	DMF	60 ℃, 6 h	15
12	1∶1∶CuI (1.0)	DPPP	NaOAc	DMF	60 ℃, 6 h	30
13	1∶1∶CuI (1.0)	DPPF	NaOAc	DMF	60 ℃, 6 h	16
14	1∶1∶CuI (1.0)	Bipy	NaOAc	DMF	80 ℃, 6 h	43
15	1∶1∶CuI (1.0)	Bipy	NaOAc	DMF	R.T., 6 h	40
16	1∶1∶CuI (1.0)	Bipy	NaOAc	CH_3CN	60 ℃, 6 h	20
17	1∶1∶CuI (1.0)	Bipy	NaOAc	THF	60 ℃, 6 h	complex
18	1∶1∶CuI (1.0)	Bipy	NaOAc	DMSO	60 ℃, 6 h	15
19	1∶1∶CuI (0.1)	Bipy	NaOAc	DMF	60 ℃, 6 h	6
20	1∶1∶CuI (2.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	48
21	1∶2∶CuI (1.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	70
22	1∶3∶CuI (1.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	75
23	1∶4∶CuI (1.0)	Bipy	NaOAc	DMF	60 ℃, 6 h	68
24	1∶2∶CuI (1.0)	Bipy	$NaHCO_3$	DMF	60 ℃, 6 h	66
25	1∶2∶CuI (1.0)	Bipy	K_3PO_4	DMF	60 ℃, 6 h	52
26	1∶2∶CuI (1.0)	Bipy	K_2CO_3	DMF	60 ℃, 6 h	90
27	1∶2∶CuI (1.0)	Bipy	DABCO	DMF	60 ℃, 6 h	trace
28	1∶2∶CuI (1.0)	Bipy	DMAP	DMF	60 ℃, 6 h	20
29	1∶1∶CuI (1.0)	Bipy	—	DMF	60 ℃, 6 h	10
30	1∶2∶CuI (1.0)	Bipy	K_2CO_3	DMF	60 ℃, 3 h	85
31	1∶2∶CuI (1.0)	Bipy	K_2CO_3	DMF	60 ℃, 10 h	90

[a] Reaction conditions: **1a** (0.1 mmol), **3** (0.1 mmol), DMF (3 mL). [b] Molar ratio. [c] Yield of **2a** determined by ^{19}F NMR. Bipy＝2,2'-bipyridine, DPPP＝1,3-bis(diphenylphosphino)propane, DPPF＝1,1'-bis(diphenylphosphino)ferrocene.

tions in the presence of CuI and 1 equiv. of bipy at 60 ℃.

Some other polar solvents, such as CH_3CN, THF, DMSO, were also investigated (Entries 16－18). Of these solvents, DMF was the best choice (Entry 4 vs. Entries 16－18). Reducing the amount of CuI led to dramatic decrease of the yield (Entry 19). Increasing its amount to 2 equiv. did not increase the yield (Entry 20 vs. Entry 4). So 1 equiv. of CuI was adopted to be the optimal amount.

The effect of the amount of $[Ph_2SCF_3]^+[OTf]^-$ on the reaction was examined (Entries 21－23). When 2 equiv. of this salt was used, the yield was improved (Entry 21 vs. 4). 3 equiv. of salt gave slightly better yield (Entry 22). But further increasing the amount of salt gave lower yield (Entry 23). Obviously, 2 equiv. of salt was a better choice than 3 equiv. because of the similar result and the cost.

Both of inorganic bases and organic bases were screened (Entries 24－28). Inorganic bases gave moderate to excellent yields but organic bases gave very low yields. The low yields might be because the presence of

organic base would lead to the decomposition of $[Ph_2SCF_3]^+[OTf]^-$. Without the presence of any base, only small amount of desired product was detected (Entry 29). It can be clearly seen that K_2CO_3 was the best choice.

The reaction time shows some effect on the yield (Entries 30 and 31). Shortening the time led to lower yield (Entry 30). Prolonging the time to 10 h gave the same yield as that of 6 h (Entry 31 vs. 26), which means the reaction was complete in 6 h. After the screening of the reaction condition, we determined that the optimal reaction condition was that 1∶2∶1 ratio of akyn∶$[Ph_2SCF_3]^+[OTf]^-$∶CuI, 1 equiv. of bipy as ligand, K_2CO_3 as base, DMF as solvent, reaction at 60 ℃ for 6 h.

With the optimized conditions in hand, we further investigated the scope of the CuI-mediated trifluoromethylation of terminal alkynes and, as shown in Figure 1, found that the reaction could tolerate various functional groups. Substrates with electron-donating groups were converted smoothly into the products with moderate to good yields (**2b**—**2g**). We have found that iodobenzene could be trifluoromethylated by $[Ph_2SCF_3]^+[OTf]^-$ in the presence of copper powder.[3r] So we were concerned that bromine substituent on the phenyl group might interfere with the desired reaction. However, to our surprise, not any sign of trifluoromethylated phenyl product was detected in ^{19}F NMR. The desired product was obtained in 67% of isolated yield (**2h**). In the case of other substrates with electron-withdrawing groups, the reactions also proceeded smoothly to give the expected products in moderate to good yields (**2i**—**2k**). It was found that the steric effect shows no side effect on the reaction (**2i**).

Examples of heteroaromatic and aliphatic substrates were also examined (**2l**—**2n**). When screening the reaction conditions, we found that the strong organic base would lead to the decomposition of $[Ph_2SCF_3]^+[OTf]^-$ (Table 1, Entries 27 and 28). But no obvious negative effect was observed for the substrates containing weaker basic group (**2n**). The desired products could still be obtained in good yield.

The ^{19}F NMR of all of the reaction mixtures before work-up showed that there were four signals: expected products, CF_3I, CF_3H and OTf. If CuBr or CuCl was used instead of CuI, CF_3Br or CF_3Cl would be obtained. If KI was used instead of CuI, no CF_3I was detected. Combined with the results achieved above, the mechanism for this reaction was proposed in Scheme 1. Copper complex (**I**) is oxidated to a Cu(III)-complex (**III**) intermediate, which undergoes reductive elimination to give CF_3I or ligand exchange to give intermediate **IV**. Another possibility is that the ligand exchange of iodine substituent in intermediate **I** with alkyne anion would give intermediate **IV**. The reductive elimination of intermediate **IV** affords the desired product.

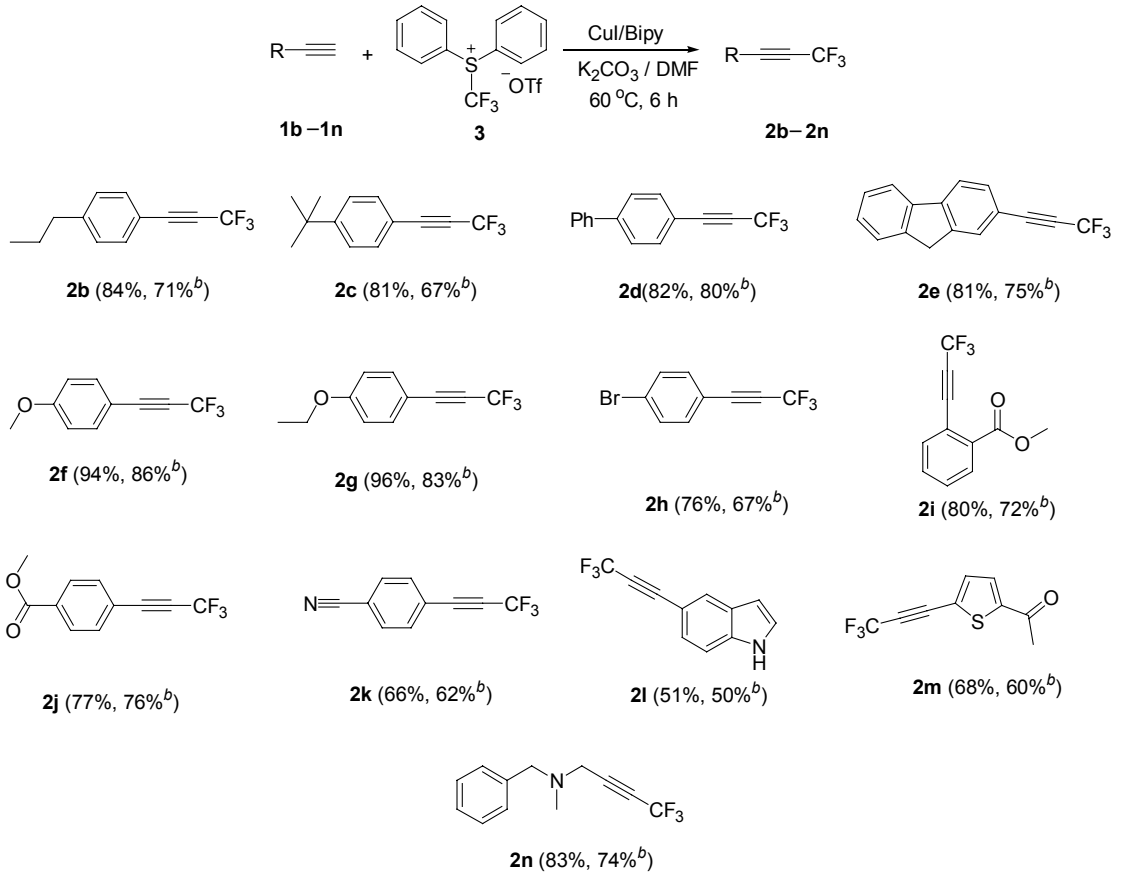
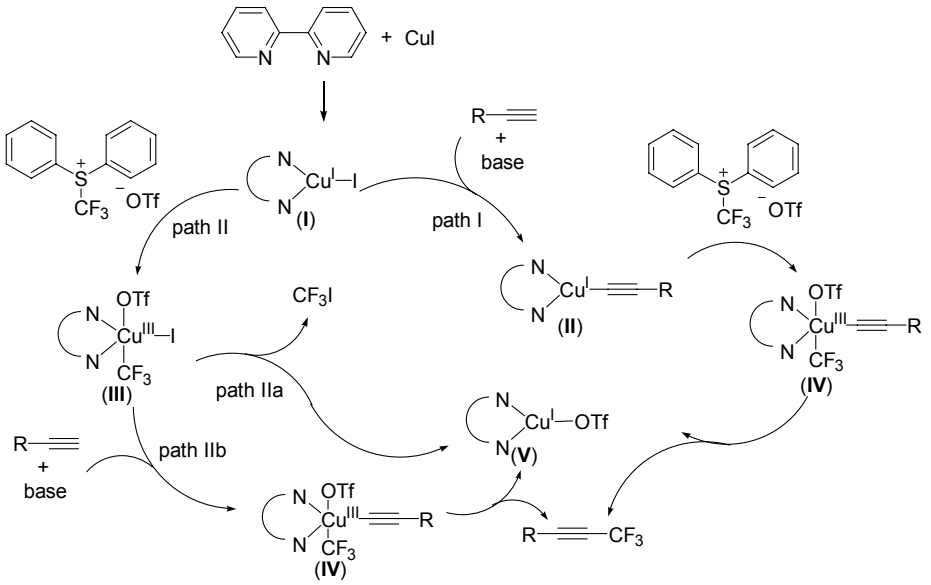


Figure 1 CuI-mediated trifluoromethylation of terminal alkynes (the molar ratio of **1b**—**1n**∶**3**∶CuI∶Bipy∶K_2CO_3 was 1∶2∶1∶1. The yield was determined by ^{19}F NMR. *b* Isolated yield).

Scheme 1 Proposed mechanism for the trifluoromethylation of terminal alkynes



Conclusions

In summary, we have developed a convenient method for the trifluoromethylation of a variety of terminal alkynes with *S*-(trifluoromethyl)diarylsulfonium triflate in the presence of copper iodide. The reaction could tolerate various functional groups. In the case of substrates substituted by weak basic groups, the reaction still proceeded smoothly to give the desired products. Investigation on the application of the trifluoromethylation method to the synthesis of pharmaceuticals and agrochemicals is currently underway.

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