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A heterogeneous copper(I)-catalyzed aerobic oxidative cross-dehydrogenative coupling of terminal alkynes with thiols leading to alkynyl sulfides

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Abstract

A heterogeneous copper-catalyzed direct oxidative cross-dehydrogenative coupling of terminal alkynes with thiols was achieved in DMSO at 70 ºC in the presence of an MCM-41-supported bidentate nitrogen copper(I) complex [MCM-41-2N-CuCl] and K_2CO_3 under an atmosphere of O_2, yielding selectively a variety of alkynyl sulfides in good to excellent yields. This heterogeneous copper catalyst can be easily recovered by a simple filtration and recycled for 10 times without any decreases in activity.

Keywords: Copper; Cross-dehydrogenative coupling; Alkynyl sulfide; MCM-41; Heterogeneous catalysis

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Introduction

Alkynyl sulfides are extremely useful intermediates in organic synthesis and have been used as versatile building blocks in a variety of organic transformations, such as hydrostannylation,[1] cycloaddition[2] and cross-coupling reactions.[3] Generally, the most precedent methodologies are based on the transition metal-catalyzed cross-coupling reactions, such as copper-catalyzed coupling of alkynyl bromides with disulfides[4] or

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coupling of terminal alkynes with phenylthio halides,[5] copper or rhodium-catalyzed coupling of terminal alkynes with disulfides.[6] Recently, the transition-metal-free synthesis of alkynyl sulfides has also been reported.[7] However, these methods usually require a prefunctionalization process of terminal alkyne or sulfur nucleophile coupling partners, resulting in the inevitable production of large amounts of byproducts during the preactivation steps. In addition, these protocols lack generality, and suffer from some drawbacks such as strict conditions, low chemoselectivity, and/or limited substrate scope, making them less desirable and impractical.

Metal-catalyzed oxidative cross-dehydrogenative coupling reaction through the direct activation of C–H and/or X–H bonds (X = heteroatom) has received much attention as a powerful and straightforward method for the construction of new C–X bonds.[8] However, the activation of sp C–H bonds of terminal alkynes for their incorporation with heteroatoms into organic molecules remains a challenge because of the inevitable formation of the diyne as a byproduct by the homocoupling of terminal alkyne.[9] In addition, the coupling reaction usually requires the use of stoichiometric oxidants such as Cu(II) or Ag(I) salts, organohalides, $PhI(OAc)_2$, and benzoquinone, which are both environmental and economic concerns. It is therefore of considerable importance to develop aerobic oxidative cross-dehydrogenative coupling reactions from the standpoint of environmentally benign organic synthesis. Recently, a few examples of the direct oxidative cross-dehydrogenative couplings of terminal alkynes with nitrogen nucleophiles and H-phosphonates using air or O_2 as the sole oxidant to produce C–N and C–P acetylenes have been reported.[10]

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Although considerable advances made recently in the copper-catalyzed oxidative C–H bond functionalizations highlight the possibility for the construction of sulfur-incorporated functional acetylenes,[11] the problem with homogeneous catalysis is the difficulty to separate the catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. It is well known that homogeneous catalysis might result in heavy metal contamination of the isolated product. These problems are of particular environmental and economic concerns in large-scale syntheses and in industry. In contrast, heterogeneous catalysts have received more and more attention because of the advantages of high catalytic efficiency and easy recycling.[12] Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes. From the standpoint of green chemistry, the development of highly active and recyclable supported copper catalysts is challenging and important. In spite of tremendous effort dedicated to the immobilization of homogeneous palladium complexes over the last two decades,[13] the supported copper complexes-catalyzed carbon-heteroatom coupling reactions have received less attention.[14] To the best of our knowledge, no heterogeneous copper-catalyzed oxidative cross-dehydrogenative coupling reaction has been reported until now. Herein, we wish to report the successful application of MCM-41-supported bidentate nitrogen copper(I) complex [MCM-41-2N-CuCl] as a highly efficient and recyclable copper catalyst for the direct oxidative cross-dehydrogenative coupling of terminal alkynes with thiols using O_2 as the sole oxidant under mild conditions to selectively afford a variety of alkynyl sulfides in good to excellent yields.

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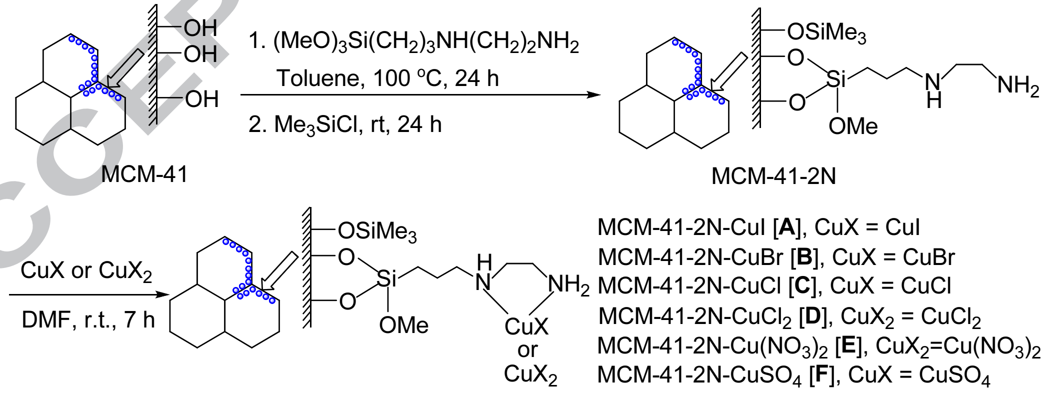
Results and discussion

The discovery of the hexagonally-ordered mesoporous material MCM-41 has given an enormous stimulus to research in heterogeneous catalysis and provided a new possible candidate for a solid support for immobilizing homogeneous catalysts.[15] MCM-41 has extremely high surface areas, large and uniform pore size, big pore volume and rich silanol groups in the inner walls, which provide the opportunity to support or anchor various functional groups by different postsynthetic modification methods.[16] A series of MCM-41-supported bidentate nitrogen copper complexes [MCM-41-2N–CuX(CuX_2)] were conveniently prepared starting from commercially available and inexpensive 3-(2-aminoethylamino)propyltrimethoxysilane and simple copper salts such as CuX or CuX_2 (X = Cl, Br, I, NO_3, SO_4) according to our previous procedure (Scheme 1).[17]



Scheme 1. Preparation of MCM-41-2N-CuX(CuX_2) complexes

In our initial screening experiments, the oxidative cross-dehydrogenative coupling

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of 4-methylphenylacetylene with thiophenol was selected as a model reaction to optimize the reaction conditions, and the results are summarized in Table 1. We first screened various MCM-41-supported bidentate nitrogen copper complexes catalysts with K_2CO_3 as base in DMSO at 70 °C under 1 atm. of oxygen. It was found that all the MCM-41-supported bidentate nitrogen copper complexes [**A**, **B**, **C**, **D**, **E** and **F**] can effectively promote the coupling reaction to afford desired phenyl *p*-tolylethynyl sulfide in good to excellent yields with high selectivity, but MCM-41-2N-CuCl [**C**] gave the best result (Table 1, entries 1-6). Our next studies focused on the effect of solvent on the model reaction and a significant solvent effect was observed. DMF was also suitable solvent and 88% yield was obtained (entry 7). While other solvents such as toluene, THF, 1,2-DCE, and hexane were inefficient and a mixture of (*E*)- and (*Z*)-phenyl styryl sulfides was formed as major products (entries 8-11). When Cs_2CO_3 or Na_2CO_3 was used as an inorganic base, slightly lower yield was obtained (entries 12 and 13). No formation of desired product was observed when Et_3N or pyridine was used as the base, but diphenyldisulfide was produced in good yield due to the oxidation of thiophenol (entries 14 and 15). DBU gave only 43% yield, and diphenyldisulfide was also formed in 48% yield (entry 16). So, K_2CO_3 was finally selected as the base for this coupling reaction. Reducing the amount of K_2CO_3 to 5 mol% resulted in lower activity and selectivity, and no desired product was observed without a base (entries 17 and 18). Lowering the reaction temperature to 30 ºC led to a decreased yield (entry 19). Finally, the amount of supported copper catalyst was also screened, and 5 mol% loading of copper was found to be optimal. A lower yield was observed

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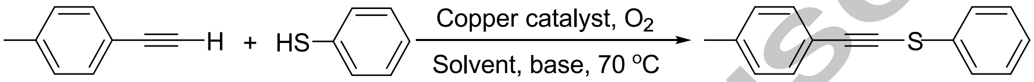
and a longer reaction time was required when the amount of the catalyst was decreased (entries 20 and 21). Thus, the optimized reaction conditions for this transformation are the MCM-41-2N-CuCl (5 mol%) in DMSO using K_2CO_3 (10 mol%) as base at 70 °C under 1 atm. of O_2 for 1 h (Table 1, entry 3).

Table 1 Cross-dehydrogenative coupling reaction of 4-methylphenylacetylene with thiophenol in different conditions.[a]



Entry	Cu catalyst (mol%)	Solvent	Base	Time (h)	Yield [b] (%)
1	**A** (5)	DMSO	K_2CO_3	1	92
2	**B** (5)	DMSO	K_2CO_3	1	91
3	**C** (5)	DMSO	K_2CO_3	1	95
4	**D** (5)	DMSO	K_2CO_3	1	90
5	**E** (5)	DMSO	K_2CO_3	1	89
6	**F** (5)	DMSO	K_2CO_3	1	85
7	**C** (5)	DMF	K_2CO_3	1	88
8	**C** (5)	Toluene	K_2CO_3	12	0
9	**C** (5)	THF	K_2CO_3	12	0
10	**C** (5)	1,2-DCE	K_2CO_3	12	0
11	**C** (5)	Hexane	K_2CO_3	12	0
12	**C** (5)	DMSO	Cs_2CO_3	1	89
13	**C** (5)	DMSO	Na_2CO_3	1	86
14	**C** (5)	DMSO	Et_3N	12	0
15	**C** (5)	DMSO	Pyridine	12	0
16	**C** (5)	DMSO	DBU	2	43
17[c]	**C** (5)	DMSO	K_2CO_3	2	54
18	**C** (5)	DMSO	–	12	0
19[d]	**C** (5)	DMSO	K_2CO_3	3	81
20	**C** (2.5)	DMSO	K_2CO_3	3	78

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21	**C** (1)	DMSO	K_2CO_3	12	61

[a] All reactions were performed using 4-methylphenylacetylene (0.5 mmol), thiophenol (0.55 mmol), base (0.05 mmol), and copper catalyst (0.025 mmol) in solvent (2 mL) at 70 ºC under 1 atm O_2. [b] Isolated yield based on 4-methylphenylacetylene used. [c] 5 mol% K_2CO_3 was used. [d] At 30 ºC.

With the optimized conditions in hand, we subsequently investigated the scope of this heterogeneous copper-catalyzed direct oxidative cross-dehydrogenative coupling reaction using a wide range of 1-alkynes and various thiols as the substrates and the results are outlined in Table 2. As shown in Table 2, phenylacetylene and a variety of substituted phenylacetylenes could effectively couple with thiophenol to selectively afford desired alkynyl sulfides **3a-3d** in excellent yields. The electronic effect of substituents on the benzene ring has limited influence on the coupling reaction and both electron-donating groups and electron-withdrawing groups were tolerated well. It is noteworthy that, in the case of 4-fluorophenylacetylene (**1d**), excellent chemo-selectivity was observed and the desired product **3d** were obtained in 91% yield without the occurrence of defluorination. Aliphatic alkynes and propiolates were also suitable coupling partners in addition to aromatic alkynes. For instance, 1-hexyne (**1e**), 1-octyne (**1f**), 5-chloro-1-pentyne (**1g**), 5-phenyl-1-pentyne (**1h**), methyl propiolate (**1i**) and ethyl propiolate (**1j**) were effectively coupled with thiophenol to provide the corresponding alkynyl sulfides **3e-3j** in good to high yields.

Substituted thiophenols bearing both electron-donating and electron-withdrawing groups could also efficiently couple with terminal alkynes to afford the corresponding alkynyl sulfides **3k-3n** in good to high yields. Reactions of *p*-, *m*-, and *o*-methyl-

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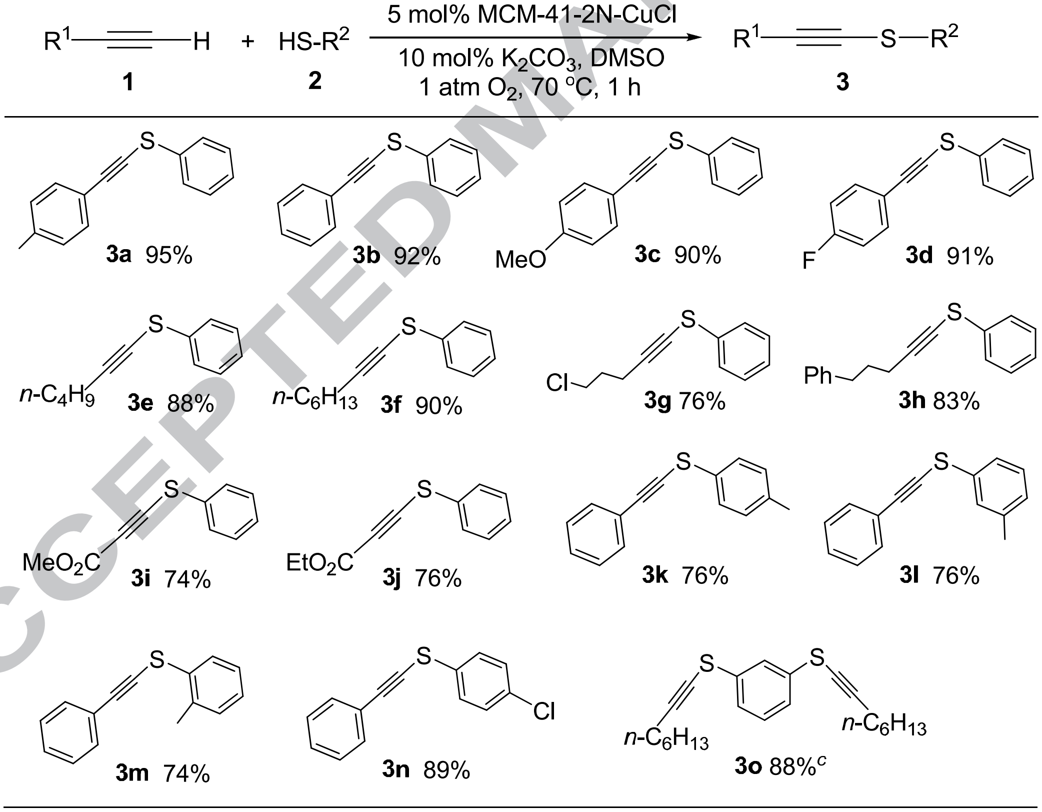
thiophenols (**2k**, **2l** and **2m**) with phenylacetylene proceeded well, and almost equal yields were obtained, indicating that the steric effect of substituents on the benzene ring is negligible. The electron-deficient thiophenol (**2n**) displayed superior reaction efficiency to the electron-rich ones (**2k-2m**) under the same reaction conditions. The coupling reaction between benzene-1,3-dithiol and 2 equivalents of 1-octyne also proceeded smoothly to give the desired product **3o** in 88% yield. The result highlights the power of this protocol for the synthesis of sulfur-rich π-conjugated polymers.

Table 2 Synthesis of alkynyl sulfides by heterogeneous copper-catalyzed aerobic oxidative cross-dehydrogenative coupling reaction.[a,b]



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[a] All reactions were performed using terminal alkyne (0.5 mmol), thiol (0.55 mmol), K_2CO_3 (0.05 mmol), and MCM-41-2N-CuCl (0.025 mmol) in DMSO (2 mL) at 70 ºC under 1 atm O_2 for 1 h. [b] Isolated yield based on terminal alkyne used. [c] 1.0 mmol 1-octyne, 0.55 mmol benzene-1,3-dithiol,

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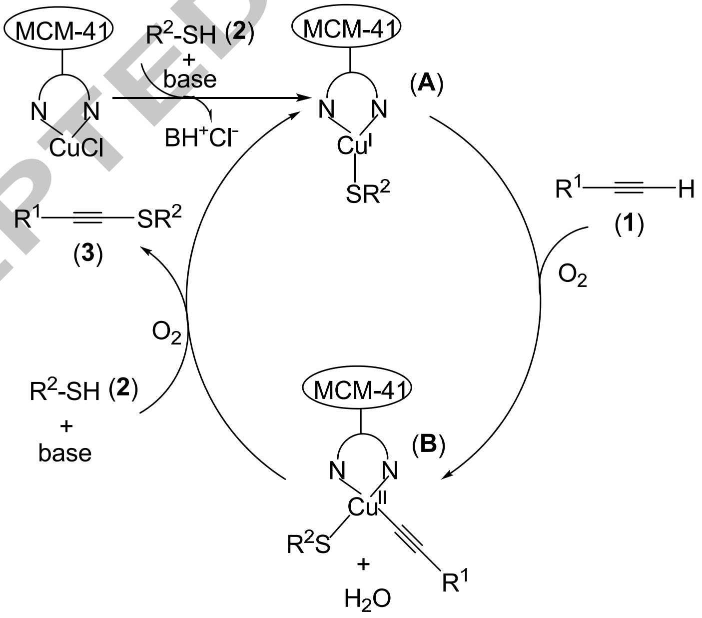
2 h.

To verify whether the observed catalysis was due to the heterogeneous catalyst MCM-41-2N-CuCl or to a leached copper species in solution, we performed the hot filtration test.[18] We focused on the coupling reaction of phenylacetylene with thiophenol. We filtered off the MCM-41-2N-CuCl complex at 70 °C after 30 min of reaction time and allowed the filtrate to react further. We found that, after this hot filtration, no further reaction was observed, indicating that leached copper species from the catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that no copper could be detected in the hot filtered solution.



Scheme 2. Plausible mechanism for heterogeneous copper-catalyzed aerobic cross-dehydrogenative coupling of terminal alkyne with thiol.

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A plausible mechanism for this heterogeneous copper-catalyzed aerobic oxidative cross-dehydrogenative coupling reaction is proposed as shown in Scheme 2. Firstly, the MCM-41-2N-CuCl complex reacts with thiol in the presence of a base to provide an MCM-41-supported bidentate nitrogen copper(I) thiolate (**A**). Subsequent transmetalation of alkyne into the MCM-41-supported bidentate nitrogen copper(I) thiolate (**A**) via activation of terminal alkyne with the assistance of O_2 produces an MCM-41-supported bidentate nitrogen copper(II) intermediate (**B**). Then the newly generated intermediate (**B**) undergoes the reductive elimination in excess of thiol to afford the desired alkynyl sulfide and regenerate the MCM-41-supported bidentate nitrogen copper(I) thiolate (**A**). Molecular oxygen plays a key role in facilitating the formation of the copper(II) intermediate (**B**) via activation of sp C–H bond of terminal alkyne.

For a heterogeneous catalyst, it is important to know its ease of separation and possible reuse. We next investigated the recyclability of the MCM-41-2N-CuCl by using the coupling reaction of 4-methylphenylacetylene (0.5 mmol) with thiophenol (0.55 mmol) in the presence of MCM-41-2N-CuCl (0.025 mmol) and K_2CO_3 (0.05 mmol) in DMSO (2 mL) at 70 °C under 1 atm. of oxygen for 1 h. After carrying out the reaction, the catalyst was separated by simple filtration and washed with distilled water, DMSO and ethanol. After being air-dried, it can be reused directly without any further treatment. The recovered copper catalyst was used in the next run, and almost consistent activity was observed for 10 consecutive cycles (Fig. 1). The high stability and excellent reusability of the catalyst should result from the chelating action of bidentate nitrogen ligand on copper and the mesoporous structure of the MCM-41

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support.

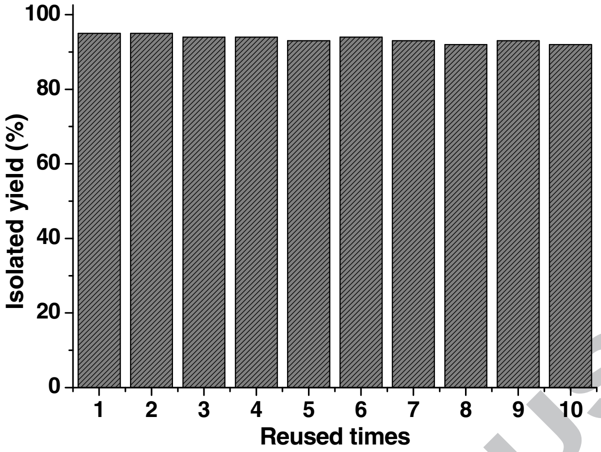

Figure 1. Recycle of the MCM-41-2N-CuCl catalyst

Conclusions

In summary, we have developed a simple, straightforward and atom-economical route to alkynyl sulfides through the direct oxidative cross-dehydrogenative coupling of terminal alkynes with thiols by using a recyclable MCM-41-supported bidentate nitrogen copper(I) complex [MCM-41-2N-CuCl] as catalyst under an atmosphere of oxygen. The reactions generated selectively a variety of alkynyl sulfides in good to excellent yields and were applicable to a wide range of terminal alkynes and various thiols. This heterogeneous copper catalyst can be conveniently prepared by a simple procedure from commercially available and inexpensive reagents and recycled for 10 times without any decreases in activity, thus making this procedure environmentally more acceptable.

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Acknowledgements

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Supplementary data

Supplementary data (experimental procedures for the heterogeneous copper-catalyzed aerobic oxidative cross-dehydrogenative coupling reactions as well as ^{1}H, ^{13}C NMR spectra of the products are described) associated with this article can be found in the Supporting Information.

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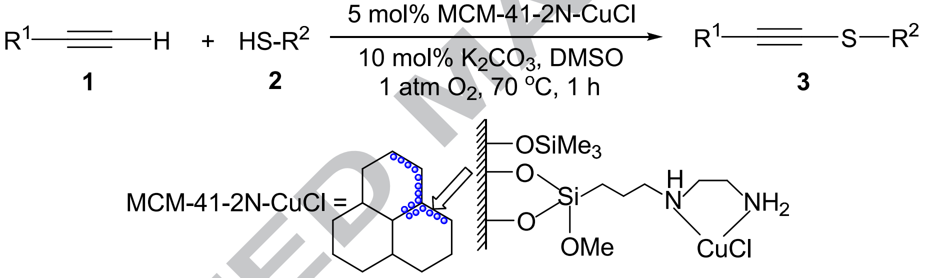
Graphical Abstract

A heterogeneous copper(I)-catalyzed aerobic oxidative cross-dehydrogenative coupling of terminal alkynes with thiols leading to alkynyl sulfides

Zhiqiang Fang, Wen He, Mingzhong Cai,* Yang Lin, Hong Zhao*



A simple and practical method for selective synthesis of alkynyl sulfides has been developed through the direct oxidative cross-dehydrogenative coupling of terminal alkynes with thiols in DMSO by using a recyclable MCM-41-supported bidentate nitrogen copper(I) complex [MCM-41-2N-CuCl] as catalyst under an atmosphere of oxygen.

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Research Highlights

- ► The MCM-41-2N-CuCl complex can be easily prepared by a simple two-step procedure.
- ► Heterogeneous Cu-catalyzed CDC reaction of 1-alkynes with thiols is first reported.
- ► The reaction generates selectively a variety of alkynyl sulfides in high yields.
- ► The Cu catalyst can be recycled for 10 times without any decrease in activity.
- ► Our catalytic system provides a new, simple and practical route to alkynyl sulfides.

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