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Synthesis of Unsymmetrical Sulfides Using Ethyl Potassium Xanthogenate and Recyclable Copper Catalyst under Ligand-Free Conditions

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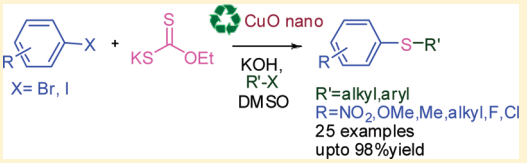
Supporting Information

ABSTRACT: The synthesis of unsymmetrical sulfides has been achieved in good to excellent yields with inexpensive ethyl potassium xanthogenate via cross-coupling reaction using recyclable CuO nanoparticles under ligand-free conditions.The copper oxide nanoparticles can be recovered and reused up to five cycles without loss of activity.



The construction of biological and synthetically important C−S bond through cross-coupling reactions using various transition metals such as Pd,[1] Cu,[2] Fe,[3] Co,[4] In,[5] Ni,[6] etc. has been well explored over the years owing to various developments in the area of cross-coupling reactions. Most of these methods require metal reagents in combination with different ligands for achieving smooth conversions. The disadvantages, like metal accumulations and organic waste generation associated with these methods, make them less adoptable for the sustainable synthesis of various sulfide molecules. In view of these drawbacks, the development of efficient protocols using recyclable catalysts devoid of ligands would address the problems associated with the metal accumulation and toxic waste generation in the environment. This is the main focus in the current organic research due to the growing concern for sustainable chemistry. Cross-coupling reactions using copper oxide nanoparticles (CuO nps) have the advantages of recyclability and absence of external ligands that minimize the organic waste generation as compared with the conventional catalytic systems. So in continuation of our sustainable approach using CuO nps for cross-coupling reactions,[7] we report herein the synthesis of unsymmetrical sulfides utilizing ethyl potassium xanthogenate,[8] CuO nps, and aryl halides under ligand-free conditions.

Initially, we studied the reaction of phenyl iodide with potassium ethyl xanthogenate for the formation of diaryl sulfide in DMSO at 85 °C. Phenyl iodide reacted completely within 15 h as monitored by GC to form phenylxanthogenate ester in situ, which, upon addition of KOH and 4-methyliodobenzene, afforded the C−S cross-coupled product (summarized in Table1). The solvents like 1,4-dioxane, toluene, NMP, DMF, and acetonitrile, in combination with the bases such as Cs_2CO_3, Li_2CO_3, K_2CO_3, Na_2CO_3, *t*-BuOK, and *t*-BuOLi, were found to be inefficient in achieving a good conversion of the coupled product. We observed 97% yield of the aryl sulfide formation with DMSO and KOH as the solvent and base, respectively. The optimum amount of CuO required was found to be 7 mol % to obtain the maximum yield of the coupled product, whereas nearly the same yield was obtained when 10 and 7 mol % of CuO was used. However, 5 mol % resulted in a slight decrease in the yield, and hence, 7 mol % of the catalyst was used for further reactions. The catalytic activity of bulk CuO as catalyst was significantly low as compared to the CuO nps (19, Table 1). From this we infer that the reaction might be taking place over the surface of the nanoparticles, whereas the reaction did not take place in the absence of the copper catalyst (18, Table 1). This has clearly proved that the presence of a copper catalyst was crucial for the reaction.[9]

We further tested various aryl halides viz. bromo- and iodobenzenes with the optimized conditions. The yields of aryl sulfides after two iterations were remarkably high with aryl iodides when compared to aryl bromides (Table 2, entries 1, 2). Unfortunately, the yields of the coupling between Ar-Br and Ar′-Br are discouraging (Table 2, entry 3). Aryl iodides with different substituents like nitro, methoxy, isopropyl, *tert*-butyl, chloro, and fluoro were tested for their reactivities. The reaction of 4-nitroiodobenzene was faster as expected followed by chloro, fluoro, alkyl, and methoxy substituents, which after the second iteration with the respective aryl halides, gave good to excellent yields of the coupled products (Table 2). Moreover, the double thiolation of *p*-diiodobenzene required 2 equiv each of xanthogenate, KOH, and iodobenzene to form the desired cross-coupled product in 78% yield (entry 6, Table 2).

We also succeeded in obtaining the heterothioethers in moderate yields with 2-bromothiophene and 2-bromopyridine in 73% and 66% yields, respectively (entries 14 and 15, Table 2). To broaden the substrate scope, we investigated the synthesis of various thioethers using alkyl halides in the second iteration. Interestingly, alkyl halides such as cyclohexyl-, *n*-hexyl-, *n*-pentyl-, *n*-decyl-, and 2-bromoethanol gave the desired products in moderate to excellent yields. Nevertheless, the yields of the products were moderate in the case of 2-bromonaphthalene with both aryl and alkyl halides (Tables 2 and 3). To expand the utility of this methodology, a reaction on a higher scale was performed

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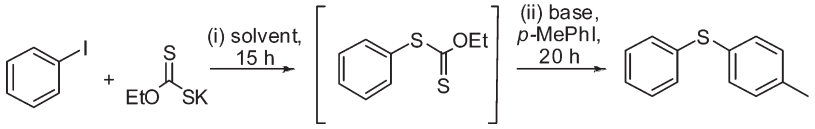
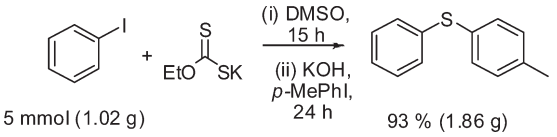
Table 1. Optimization of Solvents and Bases for CuO Nano Catalyzed Synthesis of Thioethers[a]



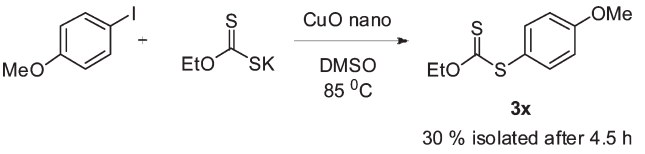
entry	copper	solvent	base	yield (%)
1	CuO nano	DMF	KOH	88
2	CuO nano	dioxane	KOH	75
3	CuO nano	DMSO	K_2CO_3	43
4	CuO nano	DMSO	Li_2CO_3	38
5	CuO nano	DMSO	*t*-BuOK	58
6	CuO nano	DMSO	*t*-BuOLi	55
7	CuO nano	DMSO	K_3PO_4	46
8	CuO nano	DMSO	KOH	95[b]
9	CuO nano	DMSO	KOH	97[c]
10	CuO nano	DMSO	KOH	89[d]
11	CuO nano	DMSO	Cs_2CO_3	32
12	CuO nano	DMF	Cs_2CO_3	24
13	CuO nano	THF	KOH	29
14	CuO nano	CH_3CN	KOH	25
15	CuO nano	Toluene	KOH	14
16	CuO nano	NMP	KOH	67
17	CuO nano	H_2O	KOH	
18		DMSO	KOH	<5
19	CuO	DMSO	KOH	39

[a] Reaction conditions: iodobenzene (1 mmol), CuO nanopowder (7 mol %), solvent (2 mL), base (3.0 equiv), *p*-MePhI (1.0 equiv), ethyl potassium xanthogenate (1.0 equiv), 85 °C. [b] 5 mol % CuO nano. [c] 7 mol % CuO nano. [d] 10 mol % CuO nano.

Scheme 1. CuO Nano Catalyzed Synthesis of Thioethers on 5 mmol Scale



Scheme 2. Evidence for the Formation of the Aryl Xanthogenate Ester



with 5 mmol of substrates. It is noteworthy that this reaction was successful on an increased scale affording 93% yield of the product (Scheme 1). Though a laboratory-scale procedure, this indicates that it has a potential for further increased scale.

We suggest a possible mechanistic pathway based on the one suggested by Zhang et al. in the arylation of heterocyclic C−H bonds catalyzed by CuO nano.[10] First, the aryl halide forms a C−S bond with the xanthogenate followed by the hydrolysis of the aryl xanthogenate ester to generate the aryl thiol salt. This then undergoes a second cross-coupling reaction with the aryl halide to form the final product (Figure 1). The formation of the aryl xanthogenate ester during the reaction was confirmed by a control experiment in which 4-methoxyiodobenzene was reacted with potassium ethylxanthogenate in the presence of CuO nps (Scheme 2). To isolate the intermediate, *O*-ethyl-*S*-4-methoxyphenyl carbonodithioate, the reaction was arrested after 4.5 h, and the product was isolated as pale yellow oil in 30% yield, which was completely characterized by ^{1}H and ^{13}C NMR (Scheme 2).

In the case of alkyl halides, the control experiment in the absence of copper for the second iteration was found to be base catalyzed and noncatalytic with respect to the copper catalyst. To find out whether the reaction was catalyzed by CuO nano particles or leached copper species,[11] we carefully analyzed the reaction mixtures after each iteration (iterations 1 and 2) using ICP-AES. It was found that around 0.8 and 1.2 ppm of copper had leached into the solution after the first and second iterations, respectively. Another control experiment was performed to elucidate the extent to which the leached species can catalyze the reaction. The catalyst was separated by centrifugation from the reaction mixture after 6.5 h to get 50% conversion of the iodobenzene with potassium ethyl xanthogenate. The filtered reaction mixture was further continued to react after removal of the catalyst, and the conversion was monitored by GC. There was no progress in the conversion of iodobenzene even after 10 h. Hence, from these experiments we conclude that the true catalyst was the heterogeneous CuO nps and not the leached copper species. In another experiment, the *O*-ethyl-*S*-4-methoxyphenyl carbonodithioate was allowed to react with iodobenzene in the absence of copper, with KOH as the base. The progress of the reaction was monitored by GC. It was found that only the ester

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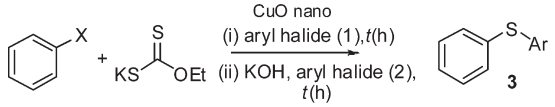
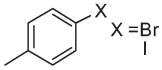
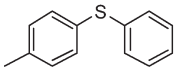
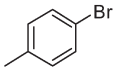
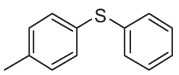
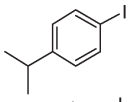
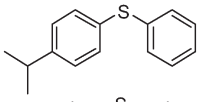
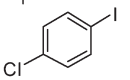
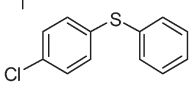
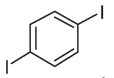
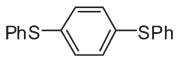
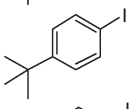
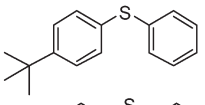
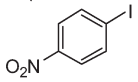
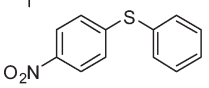
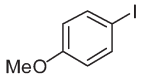
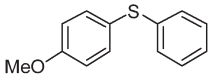
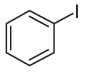
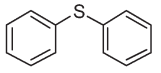
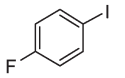
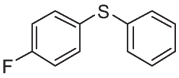
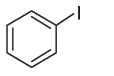
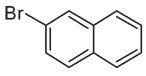
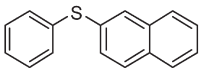
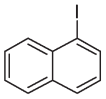
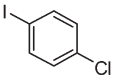
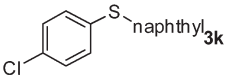
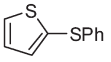
Table 2. CuO Nano Catalyzed Synthesis of Thioethers with Various Aryl Halides[a]



entry	aryl halide (1)	aryl halide (2)	product (3)		t(h)	yield (%)
1				3a	20/24	68
2					15/20	97
3					24/24	41
4				3b	16/12	85
5				3c	12/14	80
6				3d	24/20	78[b]
7				3e	15/13	93
8				3f	10/11	84
9				3g	17/15	75
10				3h	14/10	98
11				3i	14/12	88
12				3j	12/28	66
13				3k	15/13	87
14				3l	22/10	73
15				3m	21/10	76

[a] Reaction conditions: (i) iteration 1: CuO nanopowder (7 mol %), aryl halide (1) (1 mmol), ethylpotassium xanthogenate (1.0 equiv), DMSO (2 mL) stirred for specified time at 85 °C; (ii) iteration 2: KOH (3.0 mmol), aryl halide (2) (1.0 mmol), 85 °C. [b] Ethyl potassium xanthogenate (2.0 mmol), KOH (6.0 mmol), aryl halide (2) (2.0 mmol).

underwent hydrolysis generating the thiol, and no aryl sulfide formation was detected in the reaction mixture. This further confirmed that both the steps of the cross-coupling reaction, as shown in Table 1, are catalyzed by copper.

Furthermore, we tested the recyclability of CuO nps to ascertain the sustainability of this methodology. The aqueous layer containing CuO nps was carefully centrifuged and washed several times with water and acetone after workup. The nanoparticles were retrieved, oven-dried at 80 °C for 5 h, and used for the next cycle. Likewise, the recovered CuO nps were recyclable up to five cycles (Table 4).

The native and used CuO nanoparticles were analyzed by powder XRD and TEM analysis. It was observed from the TEM studies that the used CuO nanoparticles were intact in size and shape even after five cycles as compared with the native catalyst. The powder XRD spectra also confirmed the intactness of the particles after five cycles (see the Supporting Information).

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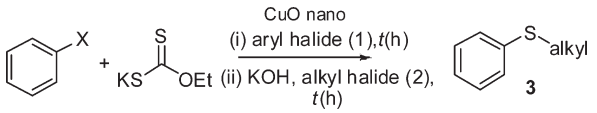
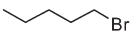
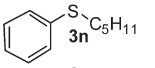
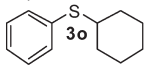
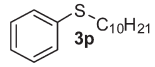
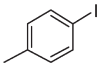
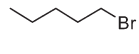
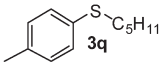
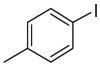
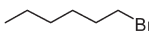
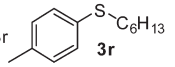
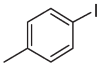
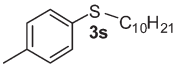
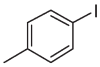
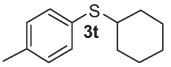
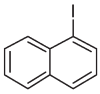
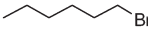
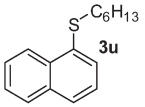
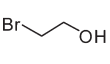
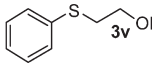
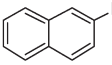
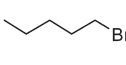
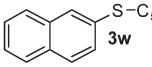
Table 3. CuO Nano Catalyzed Synthesis of Thioethers with Various Alkyl Halides[a]

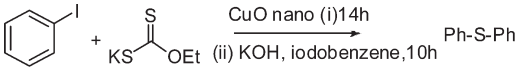


entry	aryl halide(1)	alkyl halide(2)	product(3)	t (h)	yield (%)
1			 **3n**	12/2	93
2			 **3o**	12/4	88
3		$C_{10}H_{21}Br$	 **3p**	12/5	81
4			 **3q**	15/2	86
5			 **3r**	15/3	81
6		$C_{10}H_{21}Br$	 **3s**	15/5	77
7			 **3t**	15/4	81
8			 **3u**	15/6	84
9			 **3v**	12/2	92
10			 **3w**	22/6	65

[a] Reaction conditions: iteration 1: CuO nanopowder (7 mol %), aryl halide (1) (1 mmol), ethyl potassium xanthogenate (1.0 equiv), DMSO (2 mL) stirred for specified time at 85 °C, iteration 2: KOH (3.0 equiv), alkyl halide (2) (1.0 mmol), 50 °C.

In conclusion, we have developed an efficient synthesis of unsymmetrical thioethers using copper oxide nanoparticles without the use of any external ligands. The copper oxide nanoparticles can be easily recovered and reused up to five cycles without loss of activity. The ligand-free and reusable copper combination makes this a sustainable method for the synthesis of unsymmetrical thioethers.

Table 4. Recycle of Copper Oxide Nanoparticles[a]



entry	CuO recovered (%)	yield (%)
cycle 1	99	95
cycle 2	97	94
cycle 3	96	92
cycle 4	95	90
cycle 5	92	89

[a] Reaction conditions: iteration 1: CuO nanopowder (7 mol %), iodobenzene (1 mmol), ethyl potassium xanthogenate (1.0 equiv), DMSO (2 mL); iteration 2: KOH (3.0 equiv), iodobenzene (1.0 mmol), 85 °C.

EXPERIMENTAL SECTION

General Information. Aryl halides, alkyl halides, CuO nanopowder (<50 nm), and dry solvents were purchased from commercial sources. Column chromatography was carried out using silica gel (60−120 mesh size). Visualization was accomplished with UV lamp, I_2 stain. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ using TMS as the internal standard. Chemical shifts were reported in parts per million (ppm) downfield from TMS.

Typical Procedure for Phenyl *p*-Tolylsulfane Synthesis Using Ethyl Potassium Xanthogenate. A mixture of iodobenzene (204 mg, 1 mmol), CuO nanopowder (5.5 mg, 7 mol %), and ethyl potassium xanthogenate (160.30 mg, 1 mmol) was stirred in DMSO (2 mL) in a 25 mL round-bottom flask equipped with a reflux condenser at 85 °C under nitrogen atmosphere. After complete conversion of the iodobenzene as monitored by GC−MS, the reaction mixture was allowed to cool to room temperature, 4-iodotoluene (218.1 mg, 1 mmol) and KOH (168 mg, 3 mmol) were added, and the mixture was heated at 85 °C for 20 h. The reaction mixture was allowed to cool to room temperature, water (5 mL) was added, and the product was extracted with ethyl acetate (2 × 5 mL). The combined organic extracts were dried with anhydrous Na_2SO_4, and the solvent and the volatiles were completely removed under vacuum to give the crude product, which was purified by column chromatography on silica gel (petroleum

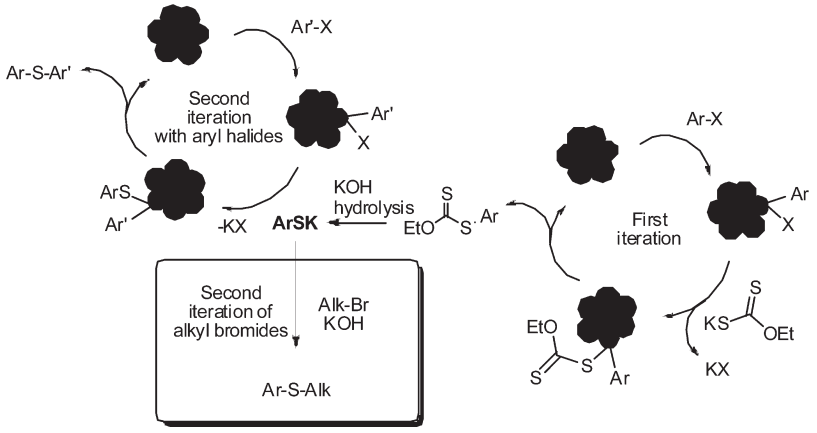


Figure 1. Possible mechanistic pathway for the synthesis of sulfides with xanthogenate.

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ether/ethyl acetate) to afford the corresponding coupling product in 97% yield. **Phenyl (*p*-tolyl) sulfane (3a)**:[4] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.28 (d, J = 8.0 Hz, 2H), 7.25−7.14 (m, 5H), 7.10 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 137.5, 137.0, 132.2, 131.2, 130.0, 129.7, 129.0, 126.3, 21.1

Typical Procedure for Pentyl Phenylsulfane Synthesis Using Ethyl Potassium Xanthogenate. A mixture of iodobenzene (204 mg, 1 mmol), CuO nanopowder (5.5 mg, 7 mol %), and ethyl potassium xanthogenate (160.30 mg, 1 mmol) was stirred in DMSO (2 mL) in a 25 mL round-bottom flask equipped with a reflux condenser at 85 °C under nitrogen atmosphere. After complete conversion of the iodobenzene as monitored by GC−MS, the reaction mixture was allowed to cool to room temperature, 1-bromopentane (151 mg, 1 mmol) and KOH (168 mg, 3 mmol) were added, and the mixture was heated at 50 °C for 2 h. The reaction mixture was allowed to cool to room temperature, water (5 mL) was added, and the product was extracted with ethyl acetate (2 × 5 mL). The combined organic extracts were dried with anhydrous Na_2SO_4, and the solvent and the volatiles were completely removed under vacuum to give the crude product, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding coupling product in 93% yield. **Pentyl phenylsulfane (3n)**:[5a] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.27−7.17 (m, 4H), 7.14−7.05 (m, 1H), 2.86 (t, 2H, J = 7.5 Hz), 1.63 (m, 2H), 1.45−1.25 (m, 4H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 136.9, 128.6, 125.5, 33.4, 30.9, 28.7, 22.1, 13.8

Experimental Procedure for Recycling of CuO Nanoparticles. The aqueous layer containing CuO nanoparticles was carefully centrifuged at 10000 rpm for 60 min and washed several times with water and acetone after workup of the reaction mixture. The retrieved nanoparticles were oven-dried at 80 °C for 5 h and used for the next cycle.

(4-Isopropylphenyl)phenylsulfane (3b):[5a] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.44− 7.11 (m, 9H), 3.03−2.76 (m, 1H), 1.28 (d, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 148.3, 136.8, 131.9, 131.7, 130.0, 129.0, 128.1, 127.3, 127.1, 126.4, 33.7, 23.8.

(4-Chlorophenyl)phenylsulfane (3c):[2e] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.40−7.22 (m, 7H), 7.16 (d, J = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 135.4, 134.7, 132.1, 132.0, 131.4, 129.3, 127.5.

1, 4-Bis(phenylthio)benzene (3d):[12] white solid; mp 73−74 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.73 (s, 6H), 7.50−7.43 (m, 2H), 7.32−7.23 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 133.3, 133.2, 130.5, 130.4, 129.4, 127.6.

(4-*tert*-Butylphenyl)phenylsulfane (3e):[5a] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.35−7.08 (m, 9H), 1.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 150.5, 136.7, 131.4, 130.4, 130.2, 129.0, 126.7, 126.2, 35.0, 31.2.

(4-Nitrophenyl)phenylsulfane (3f):[2d] yellow solid; mp 52−55 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 8.05 (d, J = 9.0 Hz, 2H), 7.54 (m, 2H), 7.46 (m, 3H), 7.16 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 148.4, 145.2, 134.6, 130.3, 129.9, 129.5, 126.6, 123.9.

(4-Methoxyphenyl)phenylsulfane (3g):[4] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.42 (d, J = 8.0 Hz, 2H), 7.23−7.19 (m, 2H), 7.16−7.12 (m, 3H), 6.82 (d, J = 8.0 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 159.7, 138.5, 135.3, 128.8, 128.1, 125.7, 124.2, 114.9, 55.3.

Diphenylsulfane (3h):[4] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.34−7.14 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 135.7, 131.0, 129.1, 127.0.

(4-Fluorophenyl)phenylsulfane (3i):[4] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.36−7.30 (m, 2H), 7.26−7.13 (m, 5H), 6.99 (t, J = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 163.9, 160.6, 136.6, 134.0, 133.9, 130.1, 129.8, 129.1, 126.7, 116.5, 116.2.

(Naphthalen-2-yl)phenylsulfane (3j):[4] white solid; mp 49 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.96−7.62 (m, 4H), 7.58−7.05 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 135.7, 133.7, 132.9, 132.2, 130.8, 129.8, 129.1, 128.8, 128.6, 127.6, 127.3, 126.9, 126.5, 126.1.

(4-Chlorophenyl)naphthalen-1-ylsulfane (3k):[5a] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 8.31 (dd, J = 3.0 Hz, 1H), 7.87−7.84 (m, 2H), 7.68−7.66 (m, 1H), 7.49 (dd, J = 3.0, 3.7 Hz, 2H), 7.42 (t, J = 8.5 Hz, 1H), 7.14 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 135.7, 134.2, 133.5, 133.0, 131.8, 130.3, 129.7, 129.6, 129.1, 128.6, 127.1, 126.5, 125.8, 125.4.

2-(Phenylthio)thiophene (3l):[3c] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.05 (t, J = 7.2 Hz, 1H), 7.05−7.19 (m, 3H), 7.20−7.26 (m, 3H), 7.43 (d, J = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 124.3, 125.9, 127.0, 127.9, 128.9, 131.2, 135.9, 138.6.

2-(Phenylthio)pyridine (3m):[3c] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 6.93 (d, 1H), 6.60−6.99 (m, 1H), 7.39−7.45 (m, 4H), 7.56−7.60 (m, 2H), 8.41 (d, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 119.9, 121.3, 129.1, 129.6 (2C), 131.1, 134.9 (2C), 136.7, 149.6, 161.5.

Cyclohexylphenylsulfane (3o):[1e] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.38 (d, J = 8.0 Hz, 2H), 7.30−7.17 (m, 3H), 3.14−3.05 (m, 1H), 2.01−1.92 (m, 2H), 1.81−1.74 (m, 2H), 1.65−1.57 (m, 1H), 1.44−1.20 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 135.1, 131.8, 128.7, 126.5, 46.5, 33.3, 26.0, 25.7.

***n*-Decylphenylsulfane (3p):**[5b] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.31− 7.04 (m, 5H), 2.87 (t, J = 7.0, 2H), 1.70 (m, 2H), 1.44−1.12 (m, 14H), 0.88 (t, J = 7.0, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 137.4, 129.4, 125.9, 33.6, 31.9, 29.5, 29.3, 29.2, 28.8, 22.7, 14.1

***n*-Pentyl-*p*-tolylsulfane (3q):**[5b] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.17 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 2.82 (t, J = 7.5 Hz, 2H), 2.31 (s, 3H), 1.60 (m, 2H), 1.43−1.25 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 135.7, 133.1, 129.7, 129.5, 34.3, 30.9, 28.9, 22.2, 20.9, 13.9

***n*-Hexyl-*p*-tolylsulfane (3r):**[5b] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.15 (d, J = 7.5 Hz, 2H), 6.99 (d, J = 7.5 Hz, 2H), 2.80 (t, J = 7.0 Hz, 2H), 2.29 (s, 3H), 1.64−1.51 (m, 2H), 1.45−1.16 (m, 6H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 135.8, 133.1, 131.0, 129.7, 129.6, 34.4, 31.4, 29.2, 28.0, 22.6, 20.98, 14.0.

***n*-Decyl-*p*-tolylsulfane (3s):**[5a] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.17 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 2.82 (t, J = 7.5 Hz, 2H), 2.31 (s, 3H), 1.59 (m, 2H), 1.42−1.17 (m, 14H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 135.7, 133.1, 129.7, 129.5, 34.3, 31.8, 29.5, 29.3, 29.2, 29.1, 28.8, 22.6, 20.9, 14.1.

Cyclohexyl-*p*-tolylsulfane (3t):[4] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.23 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 3.01−2.85 (m, 1H), 2.32 (s, 3H), 1.98−1.51 (m, 5H), 1.42−1.20 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 136.7, 132.7, 131.1, 129.4, 47.0, 33.3, 26.0, 25.7, 21.0

Hexylnaphthalen-1-ylsulfane (3u):[5a] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 8.34 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.48 (q, J = 7.2 Hz, 3H), 7.35 (t, J = 7.5 Hz, 1H), 2.93 (t, J = 7.5 Hz, 2H), 1.65 (m, 2H), 1.49−1.20 (m, 6H), 0.88 (t, J = 7.0 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 134.2, 133.8, 132.8, 128.4, 127.2, 126.7, 126.19, 126.1, 125.5, 124.9, 34.1, 31.3, 29.1, 28.5, 22.5, 14.0.

2-(Phenylthio)ethanol (3v): pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.35−7.33 (m, 2H), 7.27−7.22 (m, 2H), 7.18−7.14 (m, 1H), 3.68 (m, 2H), 3.05 (t, J = 6.1 Hz, 2H), 2.38 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 134.8, 129.7, 128.9, 126.3, 60.2, 36.7. Anal. Calcd for $C_8H_{10}S$: C, 62.30; H, 6.54; S, 20.79. Found: C, 62.00; H, 6.51; S, 20.21.

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(Naphthalene-2-yl)pentylsulfane (3w):[5a] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.73−7.66 (m, 4H), 7.42−7.33 (m, 3H), 2.97 (t, J = 7.5 Hz, 2H), 1.68 (m, 2H), 1.48 − 1.24 (m, 4H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 134.2, 133.8, 132.8, 128.5, 127.3, 126.7, 126.2, 126.1, 125.5, 124.9, 34.1, 31.0, 28.8, 22.2, 13.9

***O*-Ethyl *S*-4-methoxyphenyl carbonodithioate (3x):** pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 7.48 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 2.76 (q, J = 7.8, 2H), 1.32 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 159.4, 133.9, 131.6, 114.5, 55.4, 32.5, 29.7, 14.1. Anal. Calcd for $C_{10}H_{12}S_2$: C, 52.60; H, 5.30; S, 28.09. Found: C, 52.45; H, 5.12; S, 27.89.

■ ASSOCIATED CONTENT

Supporting Information. General experimental procedures, catalyst charaterization (TEM images, powder XRD of native and used CuO nano), and ^{1}H, ^{13}C NMR for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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