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PAPER

Efficient recyclable CuI-nanoparticle-catalyzed *S*-arylation of thiols with aryl halides on water under mild conditions†

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CuI nanoparticles efficiently catalyzed the C–S cross coupling of aryl and alkyl thiols with aryl halides in the absence of ligands on water under mild conditions. A wide range of diaryl sulfides and aryl alkyl sulfides are synthesized in good to excellent yields utilizing this protocol. This procedure is particularly noteworthy given its mild conditions, avoiding the undesired formation of disulfides through oxidation of thiols. The recovery and successful reutilization of the catalyst is described. Furthermore, the directed synthesis of bisarylated product is presented.

Introduction

Catalytic methods for the formation of carbon–sulfur bonds are of great important in general organic synthesis as well as in materials science applications and in the pharmaceutical industry.[1] Transition-metal-catalyzed cross-coupling of aryl halides with thiols for the formation of aryl sulfides is one of the most powerful tools.[2] A variety of Pd,[3] Co,[4] Ni,[5] In,[6] Cu[7] and Fe[8] catalysts have been studied for the development of efficient, beneficial and environmentally friendly conditions for *S*-arylation. However, *S*-arylation has been comparatively less studied than *N*-arylation and *O*-arylation due to the tendency of thiols to undergo oxidative homocoupling S–S reactions.[8a]

From an industrial viewpoint, the development of Cu-catalyzed methods for arylation of thiols with aryl halides is still attractive owing to the advantages of copper over other metals, like its ready availability and low toxicity.[9] The traditional copper-mediated reactions suffer from many drawbacks such as high reaction temperature, the usual requirement of stoichiometric copper salts, long reaction time, sensitivity to functional groups on the aryl halide and irreproducibility. In fact, only in recent years have considerable efforts been made to improve the efficiency of this reaction and they have made a great contribution with the use of copper salts in the presence of several ligands.[7a–q] Some ligand-free copper-catalyzed C–S coupling reactions have also been developed.[7r–ad] However, many of these ligand-free methods still have certain shortcomings, as of the requirement of microwave irradiation,[7r–t] poor efficiency with aliphatic thiols,[7u–w] and more critical is that the majority of them do not suitable for aryl bromide.[7s–t,w–ad] Otherwise, of the limited number of methods available employing copper catalysts, most involve the use of a non-reusable catalytic system and toxic organic solvents.

Metal nanoparticles have received much attention due to the advantages offered by these "semi-heterogeneous catalysts". They both have the characteristics of heterogeneous catalysis (recovery and recyclability) and those of homogeneous catalysis (relatively low catalyst loadings and good selectivity). In addition, because of their large surface area, metal nanoparticles usually showed enhanced reactivity under mild conditions.[10] Thus, transition-metal nanoparticles have been used widely as catalyst for organic synthesis.[11]

The development of environmentally friendly catalytic systems, in particular using water as the reaction medium, has drawn much attention in recent years due to this green solvent being non-toxic, low cost, widely available and giving greater chemoselectivity, as compared with organic solvents.[12] Considering our experience in this field with the application of "on-water chemistry" to selective synthesis of phenols, anilines and thiophenols from aryl halides catalyzed by CuI nanoparticles,[13] we judged it certainly appealing to explore and extend the scope of such advantageous protocol. Herein, we report that CuI nanoparticles efficiently catalyzed the C–S cross-coupling of aryl and alkyl thiols with aryl halides on water under mild conditions.

Results and discussion

In the first stage of the study, the coupling reaction was carried out with iodobenzene and benzenethiol in the presence of 1.5 mol% CuI nanoparticles using nBu_4NOH as the base on water at room temperature for 24 h, and the corresponding

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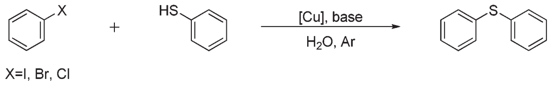
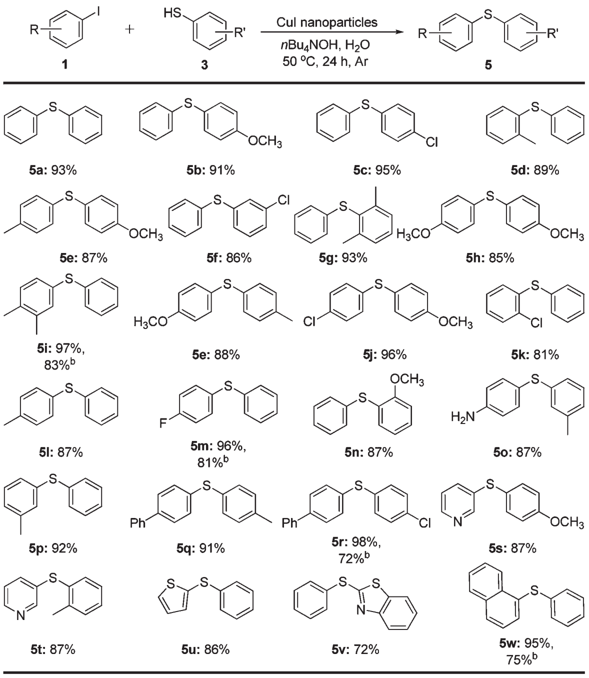
Table 1 CuI nanoparticles catalyzed C–S cross-coulping of thiophenol with aryl halides on water[a]

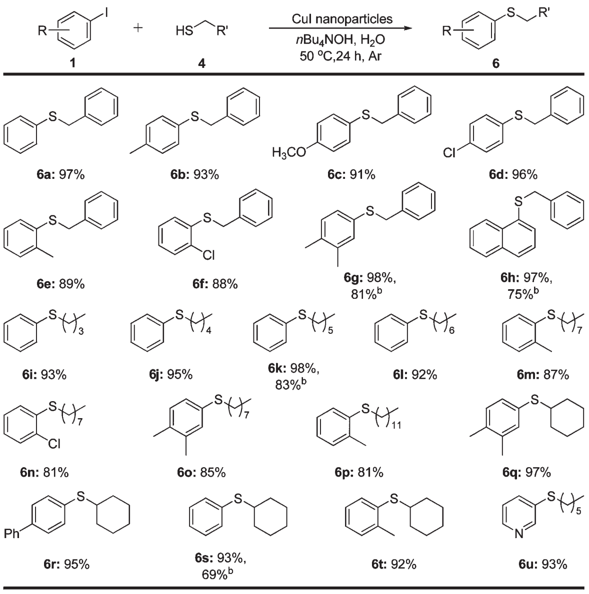


Entry	X	[Cu] (mol%)	Base	*T* (°C)	Yield[b] (%)
1	I	CuI (np(1.5))	nBu_4NOH	r.t.	51
2	I	CuI (np(1.5))	nBu_4NOH	40	79
3	**I**	**CuI (np(1.5))**	**nBu_4NOH**	**50**	**93**
4	I	CuI (np(1.5))	CsOH	50	11
5	I	CuI (np(1.5))	KOH	50	9
6	I	CuI (np(1.5))	Cs_2CO_3	50	Trace
7	I	CuI (np(1.5))	NEt_3	50	7
8	I	CuI (np(1.5))	Me_4NOH	50	67
9	I	CuI (np(1.5))	Et_4NOH	50	78
10	I	CuI (10)	nBu_4NOH	50	27
11	I	CuBr (10)	nBu_4NOH	50	19
12	I	CuCl (10)	nBu_4NOH	50	17
13	I	Cu_2O (10)	nBu_4NOH	50	21
14	I	—	nBu_4NOH	50	Trace
15[c]	Br	CuI (np(3.0))	nBu_4NOH	50	21
16[c]	Br	CuI (np(3.0))	nBu_4NOH	80	61
17[c]	Br	CuI (np(5.0))	nBu_4NOH	90	45
18[c]	Br	CuI (10)	nBu_4NOH	80	trace
19[c]	Cl	CuI (np(5))	nBu_4NOH	80	trace

[a] Reaction conditions: halogenated benzene (1.0 mmol), benzenethiol (1.2 mmol), base (3.0 equiv), H_2O (2.0 mL) under Ar for 24 h. [b] Determined by GC (average of two GC runs). [c] Reaction time is 48 h. np = nanoparticles. r.t. = room temperature.



Scheme 1 CuI nanoparticle catalyzed *S*-arylation of aryl iodides with aryl thiols on water. CuI nanoparticles (1.5 mol%), Ar–I (1.0 mmol), Ar–SH (1.2 mmol), 40% nBu_4NOH aq. (2.0 mL/3.0 equiv) at 50 °C under Ar for 24 h; isolated yield. At room temperature.

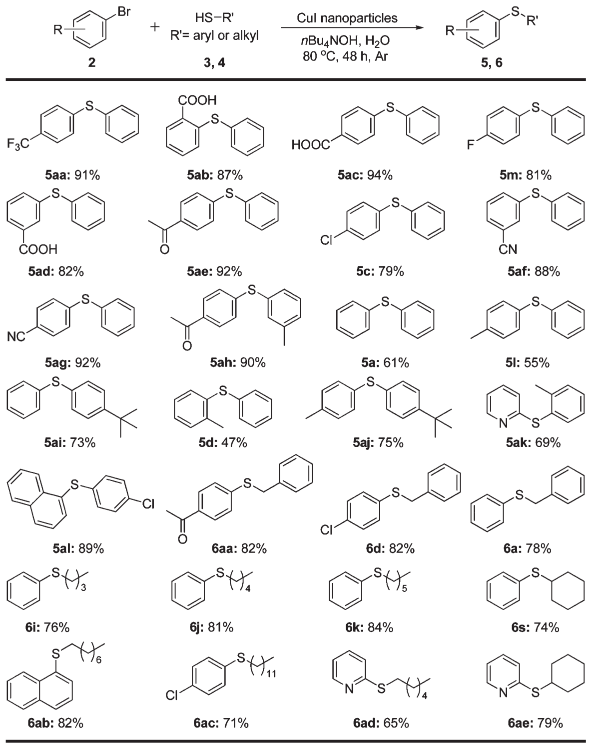


Scheme 2 CuI nanoparticle catalyzed *S*-arylation of aryl iodides with alkyl thiols on water. CuI nanoparticles (1.5 mol%), Ar–I (1.0 mmol), R′-CH_2SH (1.2 mmol), 40% nBu_4NOH aq. (2.0 mL/3.0 equiv) at 50 °C under Ar for 24 h; isolated yield. At room temperature.

coupling product was obtained in 51% yield (Table 1, entry 1). Surprisingly, when the temperature was elevated to 50 °C, the yield increased to 93% (Table 1, entry 3). It's noteworthy that the low temperature presumably greatly reduced the amount of disulfide byproducts (<4%) through the facile oxidation of thiols.[14] Among the bases studied, CsOH, KOH, Cs_2CO_3, NEt_3, Me_4NOH and Et_4NOH, provided lower yields than nBu_4NOH (Table 1, entries 4–9). Of the copper catalysts investigated, CuI nanoparticles were significantly superior to CuI, CuBr, CuCl and Cu_2O (Table 1, entries 10–13). Only a trace amount of the product was observed in the absence of the catalyst (Table 1, entry 14).

In order to extend the scope of this catalytic system, we examined a wide array of aryl iodides and aryl thiols. As shown in Scheme 1, the presence of electron donating methyl or methoxy groups or electron withdrawing carboxyl or chloro groups on the phenyl rings both in the aryl iodides and the aryl thiols did not cause significant changes in yields. Sterically more hindered substrates such as 2-methyliodobenzene, 2-chloro-iodobenzene and 2,6-dimethylbenzenethiol were also proved to be excellent substrates. In addition, the coupling reaction between heteroaryl iodides and aryl thiols were successfully performed and the corresponding heteroaromatic sulfides in excellent yields were obtained. 4-iodo-1,2-dimethylbenzene, 4-fluoroiodo-benzene, 4-iodobiphenyl and 1-iodonaphthalene can react with aryl thiols even at room temperature in moderate to good yields.

Interestingly, the methodology described herein was not limited to the use of aryl thiols. Indeed, these reaction conditions were also suitable for the coupling of alkyl thiols with aryl iodides. Butane-, pentane-, hexane-, heptanes-, octane-, and dodecanethiol all afforded the corresponding products (Scheme 2). However, an increase in the size of the alkyl chain led to a slight decrease in the yield of the aryl alkyl sulfides. Aliphatic secondary thiols also reacted. For example, cyclohexanethiol reacted with 2-methyliodobenzene to give the product in 92% yield. Aryl iodides containing heteroatoms also reacted to

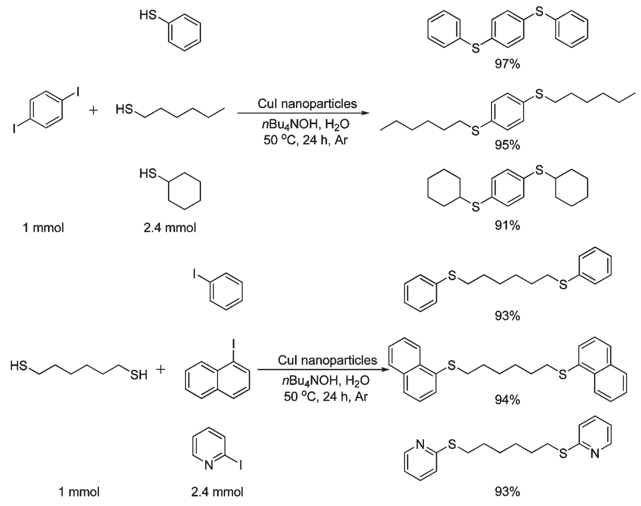


Scheme 3 CuI nanoparticle catalyzed *S*-arylation of aryl bromides with aryl thiols and alkyl thiols on water. CuI nanoparticles (3.0 mol%), Ar–Br (1.0 mmol), R′-SH (1.2 mmol), 40% nBu_4NOH aq. (2.0 mL/3.0 equiv) at 80 °C under Ar for 48 h; isolated yield.

give the corresponding aryl alkyl sulfides. The C–S bond formation of iodobenzene with hexane-1-thiol and cyclohexanethiol can be accomplished at room temperature in 83% and 69% yields respectively.

With regard to aryl bromides, elevation of the reaction temperature to 80 °C, accretion of the amount of the catalyst to 3 mol % and prolongation of the reaction time to 48 h were required to obtain satisfactory yields. Under these revised conditions, aryl bromides could couple with a variety of aryl thiols in yields between 47% and 94% (Scheme 3). For electron-poor aryl bromides, such as 4-trifluoromethylbromobenzene, 4-fluoro-bromobenzene and 4-bromobenzoic acid, high yields were obtained. In the case of electron-rich aryl bromides, moderate isolated yields could be obtained. The coupling reaction of sterically hindered aryl bromides with aryl thiols could occur, although the yields were lower than those of iodides analogs. To our delight, aryl bromides also could be coupled successfully with alkyl thiols in moderate to good yields under this improved condition. Butanethiol, pentanethiol, hexanethiol and phenyl-methanethiol were *S*-arylated in good yields. An *ortho*-substituted bromobenzene and heteroaryl bromide were compatible in this coupling reaction.

Unfortunately, when aryl chlorides were employed, very low yields were obtained. For example, the reactions of 4-trifluoromethylchlorobenzene and 4-nitrochlorobenzene with phenthiol with 5 mol% CuI nanoparticles at 80 °C for 72 h giving the corresponding product in only 21% and 16% yields, respectively.



Scheme 4 Synthesis of bisarylated product.

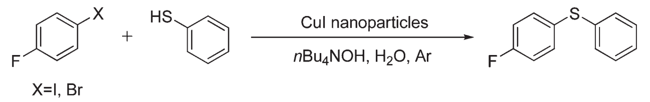
This catalytic system can also be applied to synthesis of bisarylated product (Scheme 4). Both iodine groups of 1,4-didiiodobenzene underwent the cross-coupling reaction with phenthiol, hexane-1-thiol and cyclohexanethiol to give 1,4-bis-(phenylthio)benzene, 1,4-bis(hexylthio)benzene and 1,4-bis-(cyclohexylthio)benzene in 97%, 95% and 91% yield. The two mercapto groups of hexane-1,6-dithiol could react with iodobenzene, 1-iodonaphthalene and 2-iodopyridine to product 1,6-bis(phenylthio)-hexane, 1,6-bis(naphthalen-1-ylthio)hexane and 1,6-bis(pyridin-2-ylthio)hexane in 93%, 94% and 93% yield, respectively.

Finally, the catalyst was recyclable with slight loss of activity (Table 2). We consider the loss of catalyst during the separation process was the main factor responsible for the slight decrease of catalytic activity during the recycling tests, and thus the runs were made in 10 mmol scale in order to facilitate the catalyst recovery. After completion of *S*-arylation of phenthiol with 4-fluoroiodobenzene, the catalyst was recovered from the reaction mixture by centrifugation and reused for the fresh reaction. It was found that the catalyst could be reused at least four times with a slight decrease in activity. In case of cross-coupling of phenthiol with 4-fluorobromobenzene, the reuse runs also proceeded well for each cycle. In the TEM analysis of CuI nanoparticles (Fig. S1a, b†), interestingly, the shape and size of the nanoparticles remained unchanged before and after the reaction. Furthermore, the XRD analysis exhibited identical peaks for both the fresh and recovered CuI nanoparticles (Fig. S1c, d†).

Conclusions

To sum up, we have developed a reusable and efficient CuI nanoparticle catalytic system for the C–S bond formation of both aryl and alkyl thiols with aryl iodides and aryl bromides without ligand assisted on water under relative low temperature (no higher than 80 °C). A variety of diaryl sulfides and aryl alkyl sulfides are synthesized with good chemoselectivity and functional group tolerance. Many aryl iodides could translate even at room temperature. The formation of disulfide side product through the facile oxidation of thiols was repressed efficiently due to the very mild conditions. Synthesis of bisarylated product

Table 2 Reuse studies of CuI nanoparticles in 10 mmol scale[a]



Run	Catalyst recovery (%)		Product yield[c] (%)	
	X = I	X = Br	X = I	X = Br
1	96	97	94	86
2[b]	94	94	92	84
3[b]	93	93	92	84
4[b]	92	93	90	84

[a] X = I: CuI nanoparticles (1.5 mol%), 4-fluoroiodobenzene (10 mmol), phenthiol (12 mmol), 40% nBu_4NOH aq. (20 mL/3.0 equiv) at 50 °C under Ar for 24 h; X = Br: CuI nanoparticles (3.0 mol%), 4-fluorobromobenzene (10 mmol), phenthiol (12 mmol), 40% nBu_4NOH aq. (20 mL/3.0 equiv) at 80 °C under Ar for 48 h. [b] The recovered catalyst was used under identical reaction conditions to those for the first run. [c] Determined by GC.

has also been demonstrated. The catalyst can be easily recovered and reused.

Experimental section

General procedure for preparation of CuI nanoparticles

0.464 g (4 mmol) of dimethylglyoxime (dmgH) and 0.400 g (2 mmol) of $Cu(OAc)_2 \cdot H_2O$ were added into 50 ml of absolute ethanol in sequence, which was stirred at 0 °C for 30 min to get brown precipitates $Cu(dmg)_2$. Then the collected precipitates dispersed in 50 ml of absolute ethanol again, 0.664 g (4 mmol) KI was added and stirred vigorously for 2 h. After that, the mixture was transferred into 60 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C for 6 h, and then the reactor bomb is allowed to cool to room temperature. Black precipitates were obtained, then centrifugalized and washed with ethanol and deionized water for three times to ensure the removal of the impurities. The final product was then dried in a vacuum oven at room temperature for 12 h.

General procedure for C–S coupling catalyzed by CuI nanoparticles on water

After standard cycles of evacuation and back-filling with dry and pure argon, an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI nanoparticles (1.5–5 mol %), the aryl halides if a solid (1 mmol), aryl thiols if a solid (1.2 mmol). The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counter flow of argon, aryl halides if a liquid (1 mmol), aryl thiols if a liquid (1.2 mmol) and degassed 40% tetra-n-butylammonium hydroxides water solution (2.0 mL, 3.0 equiv) were added by syringe. The tube was sealed and the mixture was allowed to stir at r.t. −80 °C for 24–72 h. The reaction mixture was then allowed to cool to ambient temperature. Then, the mixture was quenched by the addition of a saturated NH_4Cl solution (3 mL) and extracted with ethyl acetate (3 × 10 mL). Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product. The obtained crude was purified by column chromatography on silica gel and the product was dried under vacuum for at least 0.5 h.

Diphenylsulfane (5a).[8a] Iodobenzene was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (173 mg, 93% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.35–7.30 (m, 5H), 7.29–7.19 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.8, 131.0, 129.2, 127.0 ppm. HRMS calcd for $C_{12}H_{10}S$ (M+): 186.0503; found: 186.0541. Elemental analysis: calcd C, 77.37; H, 5.41; S, 17.21%; found C, 77.35; H, 5.37; S, 17.16%.

Biphenyl-4-yl(p-tolyl)sulfane (5q). 4-Iodobiphenyl was allowed to react with 4-methylbenzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a white solid (252 mg, 91% yield). M.p. = 106–108 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.59–7.56 (d, J = 7.2 Hz, 2H), 7.53–7.50 (d, J = 8.4 Hz, 2H), 7.47–7.42 (t, J = 7.5 Hz, 2H), 7.38–7.34 (m, 5H), 7.19–7.17 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.4, 139.4, 137.7, 136.3, 132.4, 131.3, 130.2, 130.1, 128.8, 127.7, 127.4, 126.9, 21.2 ppm. HRMS calcd for $C_{19}H_{16}S$ (M+): 276.0973; found: 276.0976. Elemental analysis: calcd C, 82.56; H, 5.83; S, 11.60%; found C, 82.47; H, 5.71; S, 11.53%.

Biphenyl-4-yl(4-chlorophenyl)sulfane (5r). 4-Iodobiphenyl was allowed to react with 4-chlorobenzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a white solid (290 mg, 98% yield). M.p. = 122–125 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.55–7.50 (t, J = 8.4 Hz, 4H), 7.43–7.32 (m, 5H), 7.30–7.19 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.4, 140.2, 134.6, 134.2, 133.1, 132.1, 131.6, 129.4, 128.9, 128.0, 127.6, 127.0 ppm. HRMS calcd for $C_{18}H_{13}ClS$ (M+): 296.0426; found: 296.0432. Elemental analysis: calcd C, 72.84; H, 4.41; Cl, 11.94; S, 10.80%; found C, 72.76; H, 4.35; Cl, 11.83; S, 10.70%.

3-(*o*-Tolylthio)pyridine (5t). 3-Iodopyridine was allowed to react with 2-methylbenzenethiol, column chromatography (petroleum ether/ethyl acetate 20/1), isolated as a colorless oil (175 mg, 87% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.44–8.39 (m, 2H), 7.44–7.40 (m, 1H), 7.35–7.32 (d, J = 7.5 Hz, 1H), 7.27–7.22 (m, 2H), 7.19–7.13 (m, 2H), 2.38 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 147.1, 140.5, 136.3, 134.0, 133.7, 131.8, 130.9, 128.7, 127.0, 123.8, 20.6 ppm. HRMS calcd for $C_{12}H_{11}NS$ (M+): 201.0612; found: 201.0612. Elemental analysis: calcd C, 71.60; H, 5.51; N, 6.96; S, 15.93%; found C, 71.33; H, 5.45; N, 6.48; S, 15.82%.

Benzyl(phenyl)sulfane (6a).[7y] Iodobenzene was allowed to react with phenylmethanethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (194 mg, 97% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.31–7.16 (m, 10H), 4.10 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.5, 136.5, 129.9, 129.5, 128.9, 128.5, 127.2, 126.4, 39.1 ppm. HRMS calcd for $C_{13}H_{12}S$ (M+): 200.0660; found: 200.0662. Elemental analysis: calcd C, 77.95; H, 6.04; S, 16.01%; found C, 77.40; H, 6.17; S, 16.33%.

Benzyl(3,4-dimethylphenyl)sulfane (6g). 4-Iodo-1,2-dimethylbenzene was allowed to react with phenylmethanethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (224 mg, 98% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.34 (m, 6H), 7.23–7.14 (m, 2H), 4.21 (s, 2H), 2.34 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 137.2, 135.2, 131.8, 130.1, 129.4, 128.9, 128.4, 128.0, 127.0, 39.7, 19.6, 19.3 ppm. HRMS calcd for $C_{15}H_{16}S$ (M+): 228.0973; found: 228.0975. Elemental analysis: calcd C, 78.90; H, 7.06; S, 14.04%; found C, 78.77; H, 7.18; S, 14.06%.

Hexyl(phenyl)sulfane (6k).[7y] Iodobenzene was allowed to react with hexane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (190 mg, 98% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32–7.24 (m, 4H), 7.16–7.12 (t, J = 7.2 Hz, 1H), 2.93–2.88 (t, J = 7.2 Hz, 2H), 1.69–1.59 (m, 2H), 1.46–1.37 (m, 2H), 1.30–1.25 (m, 4H), 0.90–0.85 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.1, 128.9, 128.8, 125.6, 33.6, 31.3, 29.1, 28.5, 22.5, 14.0 ppm. HRMS calcd for $C_{12}H_{18}S$ (M+): 194.1129; found: 194.1136. Elemental analysis: calcd C, 74.16; H, 9.34; S, 16.50%; found C, 74.28; H, 9.17; S, 16.30%.

(3,4-Dimethylphenyl)(octyl)sulfane (6o). 4-Iodo-1,2-dimethylbenzene was allowed to react with octane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (213 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14 (s, 1H), 7.11–7.08 (d, J = 7.8 Hz, 1H), 7.06–7.03 (d, J = 7.8 Hz, 1H), 2.90–2.85 (t, J = 7.5 Hz, 2H), 2.24–2.23 (d, J = 3.3 Hz, 6H), 1.68–1.58 (m, 2H), 1.45–1.27 (m, 10H), 0.91–0.86 (t, J = 6.3 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.1, 134.4, 133.4, 131.0, 130.1, 127.1, 34.3, 31.8, 29.3, 29.2, 29.1, 28.8, 22.6, 19.7, 19.2, 14.0 ppm. HRMS calcd for $C_{16}H_{26}S$ (M+): 250.1755; found: 250.1757. Elemental analysis: calcd C, 76.73; H, 10.46; S, 12.80%; found C, 76.37; H, 10.31; S, 12.59%.

Cyclohexyl(3,4-dimethylphenyl)sulfane (6q). 4-Iodo-1,2-dimethylbenzene was allowed to react with cyclohexanethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (214 mg, 97% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (s, 1H), 7.19–7.16 (d, J = 7.8 Hz, 1H), 7.07–7.05 (d, J = 7.8 Hz, 1H), 3.06–2.98 (m, 1H), 2.24 (s, 6H), 1.99–1.96 (m, 2H), 1.79–1.75 (m, 2H), 1.38–1.25 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.0, 135.5, 134.0, 131.4, 130.2, 130.0, 47.0, 33.4, 26.1, 25.8, 19.7, 19.4 ppm. HRMS calcd for $C_{14}H_{20}S$ (M+): 220.1286; found: 220.1286. Elemental analysis: calcd C, 76.30; H, 9.15; S, 14.55%; found C, 76.40; H, 9.16; S, 14.28%.

Biphenyl-4-yl(cyclohexyl)sulfane (6r). 4-Iodobiphenyl was allowed to react with cyclohexanethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a white solid (255 mg, 95% yield). M.p. = 36–37 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60–7.58 (d, J = 7.2 Hz, 2H), 7.55–7.52 (d, J = 8.4 Hz, 2H), 7.48–7.42 (m, 4H), 7.37–7.32 (t, J = 7.2 Hz, 1H), 3.20–3.13 (m, 1H), 2.06–2.03 (d, J = 11.1 Hz, 2H), 1.83–1.80 (m, 2H), 1.48–1.26 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.5, 139.5, 134.4, 132.1, 128.8, 127.4, 127.3, 126.9, 46.6, 33.4, 26.1, 25.8 ppm. HRMS calcd for $C_{18}H_{20}S$ (M+): 268.1286; found: 268.1288. Elemental analysis: calcd C, 80.54; H, 7.51; S, 11.95%; found C, 80.44; H, 7.37; S, 11.98%.

1-(4-(*m*-Tolylthio)phenyl)ethanone (5ah). 1-(4-Iodophenyl)-ethanone was allowed to react with 3-methylbenzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a yellow solid (218 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82–7.80 (d, J = 8.7 Hz, 2H), 7.32 (s, 1H), 7.30–7.28 (d, J = 5.4 Hz, 2H), 7.22–7.19 (d, J = 8.7 Hz, 3H), 2.54 (s, 3H), 2.36 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.0, 145.2, 139.6, 134.5, 134.4, 131.6, 130.9, 129.6, 129.5, 128.8, 127.3, 26.4, 21.2 ppm. HRMS calcd for $C_{15}H_{14}OS$ (M+): 242.0765; found: 242.0742. Elemental analysis: calcd C, 74.34; H, 5.82; O, 6.60; S, 13.23%; found C, 74.22; H, 5.93; O, 6.25; S, 13.17%.

2-(Hexylthio)pyridine (6ad). 2-Bromopyridine was allowed to react with hexane-1-thiol, column chromatography (petroleum ether/ethyl acetate 10/1), isolated as a colorless oil (127 mg, 65% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41–8.39 (d, J = 6.3 Hz, 1H), 7.46–7.34 (t, J = 8.1 Hz, 1H), 7.15–7.13 (d, J = 8.1 Hz, 1H), 6.95–6.91 (t, J = 4.8 Hz, 1H), 3.17–3.12 (t, J = 7.2 Hz, 2H), 1.74–1.64 (m, 2H), 1.48–1.39 (m, 2H), 1.33–1.25 (m, 4H), 0.90–0.85 (t, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 148.3, 134.7, 121.1, 118.0, 30.3, 29.0, 28.3, 27.6, 21.5, 12.9 ppm. HRMS calcd for $C_{11}H_{17}NS$ (M+): 195.1082; found: 195.1080. Elemental analysis: calcd C, 67.64; H, 8.77; N, 7.17; S, 16.42%; found C, 67.38; H, 8.77; N, 7.15; S, 16.31%.

1,4-Bis(phenylthio)benzene. 1,4-Diiodobenzene was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a white solid (286 mg, 97% yield). M.p. = 86–89 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.31 (m, 5H), 7.30–7.23 (m, 5H), 7.21 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.1, 134.9, 131.4, 131.2, 129.3, 127.4 ppm. HRMS calcd for $C_{18}H_{14}S_2$ (M+): 294.0537; found: 294.0532. Elemental analysis: calcd C, 73.43; H, 4.79; S, 21.78%; found C, 73.16; H, 4.83; S, 21.95%.

1,4-Bis(hexylthio)benzene. 1,4-Diiodobenzene was allowed to react with hexane-1-thiol, column chromatography (petroleum ether/ethyl acetate 50/1), isolated as a white solid (295 mg, 95% yield). M.p. = 33–34 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (s, 4H), 2.76–2.71 (t, J = 6.6 Hz, 4H), 1.54–1.44 (m, 4H), 1.32–1.22 (m, 4H), 1.21–1.07 (m, 8H), 0.76–0.72 (t, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.4, 129.6, 33.9, 31.3, 29.0, 28.4, 22.4, 13.9 ppm. HRMS calcd for $C_{18}H_{30}S_2$ (M+): 310.1789; found: 310.1796. Elemental analysis: calcd C, 69.61; H, 9.74; S, 20.65%; found C, 69.28; H, 9.82; S, 20.73%.

1,4-Bis(cyclohexylthio)benzene. 1,4-Diiodobenzene was allowed to react with cyclohexanethiol, column chromatography (petroleum ether/ethyl acetate 50/1), isolated as a white solid (278 mg, 91% yield). M.p. = 66–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (s, 4H), 3.11–3.04 (m, 2H), 2.05–1.91 (m, 4H), 1.77–1.68 (m, 4H), 1.62–1.55 (m, 2H), 1.42–1.22 (m, 10H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.5, 131.8, 46.5, 33.2, 25.9, 25.6 ppm. HRMS calcd for $C_{18}H_{26}S_2$ (M+): 306.1476;

found: 306.1470. Elemental analysis: calcd C, 70.53; H, 8.55; S, 20.92%; found C, 70.47; H, 8.39; S, 20.98%.

1,6-Bis(phenylthio)hexane. Iodobenzene was allowed to react with hexane-1,6-dithiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a white solid (281 mg, 93% yield). M.p. = 62–64 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24–7.16 (m, 8H), 7.10–7.05 (t, J = 6.9 Hz, 2H), 2.84–2.79 (t, J = 7.2 Hz, 4H), 1.58–1.54 (m, 4H), 1.38–1.33 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.8, 127.9, 127.7, 124.6, 32.4, 27.9, 27.2 ppm. HRMS calcd for $C_{18}H_{22}S_2$ (M+): 302.1163; found: 302.1163. Elemental analysis: calcd C, 71.47; H, 7.33; S, 21.20%; found C, 71.27; H, 7.35; S, 21.17%.

1,6-Bis(naphthalen-1-ylthio)hexane. 1-Iodonaphthalene was allowed to react with hexane-1,6-dithiol, column chromatography (petroleum ether/ethyl acetate 30/1), isolated as a white solid (373 mg, 94% yield). M.p. = 100–101 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45–8.43 (d, J = 8.1 Hz, 2H), 7.87–7.85 (d, J = 7.8 Hz, 2H), 7.75–7.72 (d, J = 8.4 Hz, 2H), 7.59–7.49 (m, 6H), 7.44–7.39 (t, J = 8.1 Hz, 2H), 3.00–2.95 (t, J = 7.2 Hz, 4H), 1.70–1.60 (m, 4H), 1.49–1.44 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.0, 133.8, 132.8, 128.4, 127.5, 126.8, 126.1, 126.0, 125.4, 124.9, 34.0, 28.9, 28.2 ppm. HRMS calcd for $C_{26}H_{26}S_2$ (M+): 402.1476; found: 402.1476. Elemental analysis: calcd C, 77.56; H, 6.51; S, 15.93%; found C, 77.66; H, 6.52; S, 15.83%.

1,6-Bis(pyridin-2-ylthio)hexane. 2-Iodopyridine was allowed to react with hexane-1,6-dithiol, column chromatography (petroleum ether/ethyl acetate 20/1), isolated as a colorless oil (282 mg, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40–8.38 (d, J = 4.8 Hz, 2H), 7.45–7.39 (t, J = 7.5 Hz, 2H), 7.14–7.12 (d, J = 8.1 Hz, 2H), 6.94–6.90 (t, J = 6.3 Hz, 2H), 3.17–3.12 (t, J = 7.2 Hz, 4H), 1.75–1.66 (m, 4H), 1.50–1.45 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 149.3, 135.6, 122.0, 119.0, 29.8, 29.1, 28.3 ppm. HRMS calcd for $C_{16}H_{20}N_2S_2$ (M+): 304.1068; found: 304.1082. Elemental analysis: calcd C, 63.12; H, 6.62; N, 9.20; S, 21.06%; found C, 63.17; H, 6.86; N, 9.26; S, 21.47%.

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