

Nano-CuFe₂O₄ as a magnetically separable and reusable catalyst for the synthesis of diaryl/aryl alkyl sulfides *via* cross-coupling process under ligand-free conditions†

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An efficient protocol was developed for the CuFe₂O₄ nanopowder-catalyzed aryl–sulfur bond formation between aryl halide and thiol/disulfide. A variety of aryl sulfides were synthesized in impressive yields with good chemoselectivity and functional group tolerance in the presence of a catalytic amount of CuFe₂O₄, Cs₂CO₃ as base, in nitrogen atmosphere, under ligand-free conditions, in DMSO as solvent at 100 °C. The catalyst is air-stable, inexpensive, magnetically separable and recyclable up to four cycles.

Introduction

The C–S cross-coupling reaction plays a significant role in organic synthesis and constitutes a key step in the synthesis of many molecules that are of biological, chemical, material or pharmaceutical interest.¹ These organosulfur compounds are used in diverse fields with various applications, such as treatment of cancer,² diabetes, inflammation, Alzheimer's and Parkinson's diseases,³ and HIV.⁴ The traditional methods for C–S bond formation were achieved under drastic reaction conditions such as elevated reaction temperatures (>200 °C), with the use of toxic and high boiling polar solvents like quinoline, HMPA or *N,N*-dimethylacetamide. Alternatively, these sulfides can be synthesized by the reduction of aryl sulfones or aryl sulfoxides using strong reducing agents like DIBAL-H or LiAlH₄.⁵ In today's chemical research arena, transition metals play a prominent role in bringing tremendous progress in the field of organosulfur chemistry, even though C–S cross-coupling reactions are less explored when compared to C–N or C–O bond formation due to the deactivation of the metal catalyst in view of the strong coordination properties of organosulfur compounds,⁶ often making the catalytic system ineffective. To overcome these difficulties, several transition metal-catalyzed cross-coupling reactions were developed. Migita *et al.* first reported that palladium catalyzed C–S bond formation, involving the coupling between aryl halides and thiols using Pd(PPh₃)₄ as catalyst.⁷ However, these palladium-catalyzed reactions⁸ also require bidentate phosphine ligands or diverse oxo phosphane derivatives,⁹ as well as high cost palladium

salts. These systems suffer from certain limitations such as moisture sensitive phosphine ligands, tedious synthetic procedures *etc.* Recently, several transition metal-catalyzed coupling systems involving nickel,¹⁰ and cobalt,¹¹ were demonstrated for thioether bond formation between aryl halides and thiols. Often these above mentioned homogeneous methods have limitations of requiring excessive use of reagents, toxic metals, and low turnover numbers.

However, further development of these classical Ullmann coupling reactions,¹² were explored by using easily available and cheap metals like copper¹³ and iron,¹⁴ for the C–S bond formation by the coupling of aryl halides with thiols. The traditional copper-mediated C–S bond formation reactions also involve drawbacks, such as the use of stoichiometric amounts of the catalyst, high reaction temperatures, longer reaction times, as well as sensitivity to functional groups on the aryl halide.^{5b,15} Palomo¹⁶ and co-workers reported C–S cross-coupling reactions by using CuBr and expensive phosphazene base as ligand. Venkataraman¹⁷ and coworkers described an efficient protocol utilizing CuI/neocuproine in the presence of NaO^tBu. Kumar and Engman¹⁸ described a microwave-assisted copper/bipyridyl-catalyzed preparation of diaryl sulfides by employing aryl halides and diaryl disulfide as coupling partners in the presence of Mg as additive. Bolm¹⁹ *et al.*, achieved great success in C–S cross-coupling reactions by utilizing a catalytic amount of FeCl₃ in combination with DMEDA ligand. Sekar²⁰ and coworkers developed an efficient, mild and intermolecular Ullmann-type synthesis of thioethers catalyzed by a diol–copper(i) complex system.

In recent times, several catalytic systems based on metals like Cu,²¹ Cu/Fe,²² In,²³ La²⁴ and Mn²⁵ were explored for C–S cross-coupling reaction with aryl halides and thiols in the presence of various ligands. However, these aforementioned protocols suffer from one or more drawbacks such as the use of various well-designed ligands, lack of recyclability *etc.* Hence, the development

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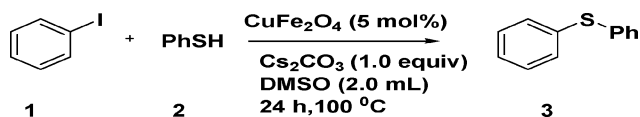
† Electronic supplementary information (ESI) available: ¹H NMR and ¹³C NMR spectroscopic data of all the compounds. See DOI: 10.1039/c1ob05597f

of an alternative inexpensive, ligand-free, air-resistant and recyclable catalyst for the formation of the thioether linkage is highly desirable in the context of environmental and industrial concerns. In the realm of cross-coupling reactions, metal-anchored heterogeneous supported reagents have received paramount attention in recent times in view of their advantages and improved efficacy due to their stable active sites, better steric control of the reaction intermediate and reusability of the catalyst.²⁶ B. C. Ranu²⁷ and coworkers reported reusable heterogeneous supported copper/ Al_2O_3 -catalyzed coupling of thiols with aryl halides under aerobic, ligand-free conditions. Very recently, Rao *et al.*, reported a recyclable iron/graphite,²⁸ catalyst for C–S cross-coupling of thiols with aryl halides under ligand-free conditions to afford cross-coupled products in good to excellent yields. Catalysts in nanoscale are more advantageous due to their greater exposed active surface area to bind the substrates selectively, making it an effective process, allowing genuine advance in relation to traditional methodologies.

Recently, several transition metal oxides like CuO ²⁹ and In_2O_3 ³⁰ in the form of nanoparticles were employed as recyclable catalysts for C–S cross-coupling processes under ligand-free conditions. In general, nanomaterials with natural morphologies containing higher surface area as reactive sites allows them to act as effective catalysts for organic synthesis.³¹ These nanoparticles have provided a simplified isolation procedure for the product, with small amounts of catalyst, affording easy recovery and recyclability of the catalyst. Inspired by the utilization of magnetically separable CuFe_2O_4 nanoparticles as a catalyst for the C–S cross-coupling process and as a part of our continuous interest in the field of cross-coupling reactions,³² herein we describe for the first time inexpensive, air-stable, magnetically separable, recyclable CuFe_2O_4 nanoparticle-catalyzed synthesis of diaryl thioether derivatives from the corresponding aryl halides and benzenethiol under mild ligand-free reaction conditions.

Results and discussion

During our initial studies towards the development of CuFe_2O_4 nanoparticle-catalyzed C–S cross-coupling reactions, iodobenzene and benzenethiol were chosen as model substrates and the reaction was conducted in the presence of Cs_2CO_3 as base and DMSO as solvent at 100 °C (Scheme 1). In this process various parameters were investigated, such as the effect of temperature, base and solvent on the synthesis of the diaryl sulfides.



Scheme 1 Nano- CuFe_2O_4 -catalyzed cross-coupling of aryl iodide with benzenethiol.

The reaction failed to give the desired product when it is at room temperature, instead starting materials were recovered (Table 1, Entry 1). The same reaction at the slightly elevated temperature around 80 °C afforded a low yield of the product (Table 1, Entry 2). Among the several solvents tested, DMF, 1,4-dioxane, toluene, water and CH_3CN were less effective compared to DMSO (Table 1, Entries 4–8). Cs_2CO_3 as base gave impressive yield when compared

Table 1 Nano-copper ferrite-catalyzed cross-coupling of iodobenzene with benzenethiol^a

Entry	Solvent	Base	$T/^\circ\text{C}$	Yield ^b (%)
1	DMSO	Cs_2CO_3	rt	—
2	DMSO	Cs_2CO_3	80	70
3	DMSO	Cs_2CO_3	100	98
4	DMF	Cs_2CO_3	100	71
5	1,4-dioxane	Cs_2CO_3	100	65
6	toluene	Cs_2CO_3	100	70
7	water	Cs_2CO_3	100	—
8	CH_3CN	Cs_2CO_3	100	45
9	DMSO	K_2CO_3	100	75
10	DMSO	K_3PO_4	100	80
11	DMSO	NaOH	100	60
12	DMSO	NaOMe	100	55
13	DMSO	NaO^tBu	100	56
14	DMSO	KO^tBu	100	55



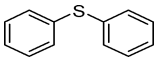
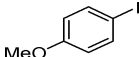

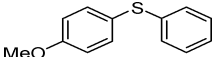
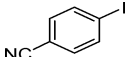

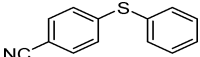
^a Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), CuFe_2O_4 (5 mol%, 12 mg), N_2 , 24 h. ^b Isolated yield.

to other bases such as K_2CO_3 , K_3PO_4 , NaOH , NaOMe , NaO^tBu , KO^tBu (Table 1, Entries 9–14). It is noteworthy to observe that the choice of DMSO as the solvent with Cs_2CO_3 as a base at 100 °C was crucial for the present C–S coupling reaction. Studies were conducted on different metal oxides as catalysts for the synthesis of diaryl sulfides. The coupling reaction did not occur in the absence of catalyst, and the optimal reaction conditions for the desired C–S cross-coupling reaction were found to be 5 mol% CuFe_2O_4 , 1.0 equiv. of Cs_2CO_3 and DMSO (2.0 mL) as solvent at 100 °C to afford the corresponding diphenyl sulfide as product in 98% yield (Table 2, Entry 5).

In the course of optimization studies towards C–S bond formation, different metal oxide nanoparticles, such as SnO_2 , Y_2O_3 , NiFe_2O_4 , ZnFe_2O_4 , CuFe_2O_4 , YFe_2O_4 and Co_3O_4 , were used as catalysts for the C–S cross-coupling process with aryl halides and thiols under ligand-free conditions and the results are summarized in Table 2. After standardization of all the reaction parameters, the proposed catalytic system was employed to cross-couple a wide variety of commercially available aliphatic/aromatic iodides and aryl bromides with aromatic/aliphatic thiols under ligand-free conditions. In general, all the reactions were very clean, neat and the corresponding diaryl sulfides were obtained in good to excellent yields as presented in Table 3. Electron withdrawing groups at the *para*-position of the aryl iodides afforded high yields compared to electron donating groups at the *para*-position. Satisfactory yields were obtained in the case of electron donating and electron withdrawing groups at the *para*-position of the aryl thiols. Using this protocol, various alkyl-substituted iodides reacted with different thiols affording the corresponding products in good to high yields (Table 3, Entries 18–20). It was observed that there is a slight decrease in the product yield as the carbon length chain was increased in the case of the aliphatic thiols.

The sterically demanding *ortho*-substituents underwent aryl thiolation without any difficulty and gave the corresponding diaryl sulfides in good yields (Table 3, Entries 11–12). It is significant to note that the aryl iodide, on reaction with benzenethiol, was

Table 2 Optimization studies on C–S cross-coupling reaction with different nanocatalysts^a

Entry	Aryl halide	Benzenethiol	Diphenyl sulphide	Nanocatalyst (5 mol%)	Yield ^b (%)
1				SnO ₂	58
2				Y ₂ O ₃	75
3				NiFe ₂ O ₄	70
4				ZnFe ₂ O ₄	60
5				CuFe ₂ O ₄	98
6				YFe ₂ O ₄	65
7				CoFe ₂ O ₄	62
8				SnO ₂	54
9				Y ₂ O ₃	52
10				NiFe ₂ O ₄	45
11				ZnFe ₂ O ₄	42
12				CuFe ₂ O ₄	81
13				YFe ₂ O ₄	43
14				CoFe ₂ O ₄	45
15				SnO ₂	56
16				Y ₂ O ₃	50
17				NiFe ₂ O ₄	50
18				ZnFe ₂ O ₄	55
19				CuFe ₂ O ₄	89
20				YFe ₂ O ₄	45
21				CoFe ₂ O ₄	48

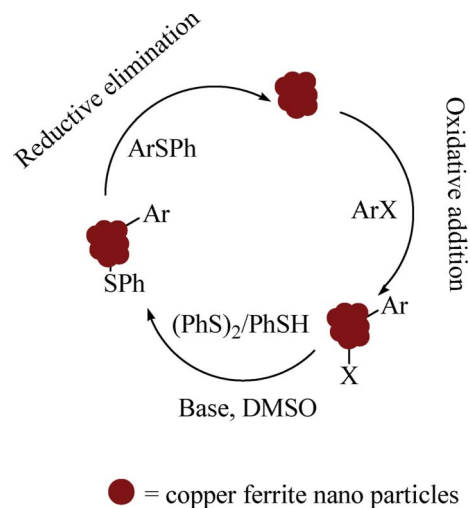
^a Reaction conditions: aryl halide (1.0 mmol), benzenethiol (1.0 mmol), Cs₂CO₃ (1.0 equiv.), DMSO (2.0 mL), N₂, 100 °C, 24 h. ^b Isolated yield.

proved to be more reactive towards the thioetherification process than aryl bromide (Table 3, Entries 21–25), and chlorobenzene did not react in the present reaction conditions (Table 3, Entry 26). In order to extend the scope of the proposed catalytic system, the thioetherification process has been studied with various aryl/alkyl iodides on reaction with various thiols and the results are presented in Table 4. This protocol very efficiently cross-coupled various iodobenzenes with diphenyl disulfide and it was found that the yields of the expected products, were good to excellent as shown in the representative Table 5.

The reusability of the nano-CuFe₂O₄ catalyst was examined and the results are summarized in Table 6. The catalyst was magnetically separated from the reaction mixture after completion of the reaction, washed with ethyl acetate and acetone, air dried and used directly for further catalytic reactions. No significant loss of catalyst (CuFe₂O₄) activity was observed up to four cycles.

Next, the leaching of metal from the CuFe₂O₄ nanopowder was checked. After the separation, the filtrate was tested by the AAS (Atomic Absorption Spectroscopy) technique; it was found that 0.001% of the metal leached into the solution after the second cycle. This study clearly demonstrated that there was no significant amount of leaching. It is also observed from spectral studies that there is no change in the nature of the catalyst even after four cycles. The SEM analysis³⁴ of CuFe₂O₄ nanoparticles before and after the reaction showed identical shape and size (Fig. 1, ESI†). In addition, the powder X-ray diffraction analysis³⁴ exhibited identical peaks for both fresh and recovered CuFe₂O₄ nanoparticles, which were compared with those reported in the literature³³ (Fig. 2, ESI†). These experimental results clearly suggest that there was no significant change in the catalytic activity of nano-CuFe₂O₄ before and after the reaction.

We thought that the proposed mechanism for the CuFe₂O₄ nanoparticle-catalyzed coupling reaction involves a oxidative addition followed by reductive elimination mechanism as illustrated in Scheme 2.

**Scheme 2** Proposed mechanism for C–S cross-coupling.

Conclusions

In summary, we have developed a facile and efficient protocol for the *S*-arylation of aryl/aliphatic halides with aromatic/aliphatic thiols as well as diphenyl disulfide using a heterogeneous CuFe₂O₄ nanoparticle catalyst in the absence of any ligand. This inexpensive, mild and clean procedure provides a convenient route for a variety of substituted organic sulfides, offers significant improvements with regard to operational simplicity, and works efficiently with general applicability giving high yields of the corresponding products. Further investigations on other useful applications of this catalyst are in progress. To the best of our knowledge, this is the first report on magnetically separable recyclable nano-CuFe₂O₄-catalyzed C–S bond formation with aryl/alkyl iodides and aryl/alkyl thiols to afford aryl and alkyl sulfides.

Table 3 Nano-copper ferrite-catalyzed cross-coupling of aryl halides with thiols^a

Entry	Aryl halide	Product	Yield ^b (%)
1			3a 98
2			3b 81
3			3c 82
4			3d 79
5			3e 85
6			3f 84
7			3g 89
8			3h 83
9			3i 80
10			3j 70
11			3k 76
12			3l 75
13			3m 76
14			3n 80
15			3o 86
16			3p 85

Table 3 (Contd.)

Entry	Aryl halide	Product	Yield ^b (%)
17			3q 88
18	$C_{10}H_{21}I$		3r 78
19	$C_8H_{17}I$		3s 80
20	$C_6H_{13}I$		3t 85
21			3a 80
22			3e 75
23			3b 70
24			3g 72
25			3c 70
26			3a —

^a Reaction conditions: aryl halide (1.0 mmol), benzenethiol (1.0 mmol), $CuFe_2O_4$ (5 mol%, 12 mg), Cs_2CO_3 (1.0 equiv.), DMSO (2.0 mL), N_2 , 100 °C, 24 h. ^b Isolated yield.

Experimental section

General information

Aryl halides (99%), diphenyl disulphide (99.5%), benzenethiol (99%), nano- $CuFe_2O_4$ (99.9%) and other aryl halides were purchased from Sigma Aldrich and Fluka and were used without purification. All experiments were carried out under nitrogen atmosphere. Column chromatography was carried out with 60–120 sized mesh silica gel using hexane as eluent. Analytical TLC was performed with Merck silica gel 60 F₂₅₄ plates, and the products were visualized by UV detection. ¹H NMR and ¹³C NMR (Avance 300, Innova 400 MHz and Bruker Gemini 200 MHz) spectra were recorded in $CDCl_3$ using TMS as internal standard. Chemical shifts (δ) are reported in ppm, and spin–spin coupling constants (J) are in Hz. Melting points were determined on a Fischer–Johns melting point apparatus. IR and MS were recorded on a Thermo

Table 4 Nano-copper ferrite catalyzed cross-coupling of aryl iodides with various thiols^a

Entry	Aryl halide	Thiol	Product	Yield ^b (%)
1				89
2				85
3				88
4				81
5				80
6		$C_5H_{11}SH$		79
7		C_4H_9SH		79
8		C_4H_9SH		81
9				80
10				80

^a Reaction conditions: aryl iodide (1.0 mmol), thiol (1.0 mmol), $CuFe_2O_4$ (5 mol%, 12 mg), Cs_2CO_3 (1.0 equiv.), DMSO (2.0 mL), N_2 , 100 °C, 24 h.
^b Isolated yield.

Nicolet Nexus 670 FT-IR spectrometer and Finnegan MAT 1020 mass spectrometer operating at 70 eV.

Representative experimental procedure for the synthesis of diphenyl sulfides using $CuFe_2O_4$ as a catalyst

To a stirred solution of aryl halide (1.0 mmol) and thiol (1.0 mmol) in dry DMSO (2.0 mL) were added $CuFe_2O_4$ nanopowder (5 mol%, 12 mg) and Cs_2CO_3 (1.0 equiv.), and the reaction mixture was heated at 100 °C under nitrogen atmosphere. After the completion of the reaction for 24 h, as monitored by TLC, the reaction mixture was extracted with ethyl acetate (3 × 10 ml). The combined organic layers were dried with anhydrous Na_2SO_4 . The solvent was evaporated under vacuum to give the crude product, which was purified by column chromatography with hexane as eluent to get the expected products in good yields. The purity of the product was confirmed by ¹H and ¹³C NMR and mass spectroscopy.

Table 5 Nano-copper ferrite-catalyzed cross-coupling of aryl halides with diphenyl disulfides^a

Entry	Aryl halide	Product	Yield ^b (%)
1			97
2			89
3			90
4			86
5			85
6			86
7			82
8			80
9			81
10	$C_6H_{13}I$		85
11	$C_{10}H_{21}I$		78
12	$C_8H_{17}I$		80

^a Reaction conditions: aryl iodide (1.0 mmol), diphenyl disulfide (0.5 mmol), $CuFe_2O_4$ (5 mol, 12 mg), Cs_2CO_3 (1.0 equiv.), DMSO (2.0 mL), N_2 , 100 °C, 24 h. ^b Isolated yield.

Table 6 Recyclability of nano- $CuFe_2O_4$ catalyst^a

Entry	Isolated product yield (%)	Catalyst recovery (%)
1	98	95
2	91	90
3	89	85

^a Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), $CuFe_2O_4$ (5 mol %, 12 mg), Cs_2CO_3 (1.0 equiv.), DMSO (2.0 mL), N_2 , 100 °C, 24 h.

Spectral data for representative examples

Diphenylsulfane (3a)²² (Table 3, Entry 1). Colorless oil (98%, 182 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.16 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 135.7, 130.9, 129.1, 126.9, 124.7. IR (neat): ν 3056, 2924, 2853, 1948, 1475, 1078, 908, 739, 690 cm⁻¹. EI-MS: *m/z* 186.

(4-Methoxyphenyl)(phenyl)sulfane (3b)²² (Table 3, Entry 2). Colorless oil (81%, 174 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.24–7.17 (m, 2H), 7.14–7.12 (m, 3H), 6.84 (d, *J* = 8.2 Hz, 2H), 3.77 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 159.5, 138.7, 135.5, 128.9, 128.3, 125.8, 124.2, 115.1, 55.4. IR (neat): ν 3448, 1575, 1490, 1045, 853, 747 cm⁻¹. EI-MS: *m/z* 216.

Phenyl(*p*-tolyl)sulfane (3c)²² (Table 3, Entry 3). Yellowish oil (82%, 164 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.31–7.18 (m, 4H), 7.17–7.07 (m, 3H) 7.01 (d, *J* = 7.5 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 137.7, 137.1, 132.4, 131.3, 130.1, 129.5, 128.5, 126.1, 21.1. IR (neat): ν 3448, 2923, 2854, 1582, 1082, 808, 741, 516 cm⁻¹. EI-MS: *m/z* 200.

(4-*Tert*-butylphenyl)(phenyl)sulfane (3d)^{21b} (Table 3, Entry 4). Yellowish oil (79%, 191 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.37–7.07 (m, 9H), 1.31 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 152.1, 136.5, 131.5, 130.5, 130.2, 129.0, 128.2, 126.6, 124.2, 34.6, 31.3. IR (neat): ν 3055, 2915, 2854, 1022, 842, 736 cm⁻¹. EI-MS: *m/z* 242.

(4-Fluorophenyl)(phenyl)sulfane²³ (3e) (Table 3, Entry 5). Yellowish oil (85%, 173 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.38–7.31 (m, 2H), 7.26–7.12 (m, 5H), 6.98 (t, *J* = 8.3 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 164.0, 160.5, 136.8, 134.1, 134.1, 130.2, 129.8, 129.2, 126.8, 116.4, 116.1. IR (neat): ν 1599, 1576, 1060, 827, 730 cm⁻¹. EI-MS: *m/z* 204.

(4-Chlorophenyl)(phenyl)sulfane (3f)²² (Table 3, Entry 6). Yellowish oil (84%, 184 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.29–7.07 (m, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 132.8, 131.3, 129.5, 127.3. IR (neat): ν 1595, 1570, 1050 cm⁻¹. EI-MS: *m/z* 220.

4-(Phenylthio)benzotrile (3g)²² (Table 3, Entry 7). Colorless oil (89%, 187 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.53–7.44 (m, 4H), 7.32–7.24 (m, 3H), 7.23–7.17 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 140.5, 137.1, 129.0, 127.5, 127.1, 115.6, 108.6. IR (neat): ν 2924, 2250, 1567, 1577, 1403 cm⁻¹. EI-MS: *m/z* 211.

(4-Nitrophenyl)(phenyl)sulfane (3h)^{21b} (Table 3, Entry 8). Yellowish oil (83%, 191 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.05 (d, *J* = 8.9 Hz, 2H), 7.56–7.41 (m, 5H) 7.12 (d, *J* = 8.9 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 148.9, 145.5, 135.0, 130.9, 130.3, 130.2, 127.3, 124.5. IR (neat): ν 3040, 3100, 3090, 2950, 2854, 1570, 930, 845, 725 cm⁻¹. EI-MS: *m/z* 231.

Phenyl(3-(trifluoromethyl)phenyl)sulfane (3i)^{10a} (Table 3, Entry 9). Colorless oil (80%, 203 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.60–7.54 (m, 1H), 7.28–7.16 (m, 4H), 7.01–6.92 (m, 2H), 6.84–6.78 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 138.7, 133.6, 132.6, 129.6, 129.4, 128.2, 126.1, 126.2, 125.5, 123.1. IR (neat): ν 2930, 1577, 1475, 1421, 1320, 1166 cm⁻¹. EI-MS: *m/z* 254.

(3-Methoxyphenyl)(phenyl)sulfane (3j)^{20b} (Table 3, Entry 10). Yellowish oil (70%, 151 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.35–

7.12 (m, 5H), 6.88–6.79 (m, 2H), 6.75–6.69 (m, 1H), 3.74 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 160.1, 137.2, 135.5, 131.3, 129.8, 129.1, 127.1, 123.0, 115.9, 112.8, 55.1. IR (neat): ν 3448, 3050, 1579, 1535, 1490, 1045, 875, 776 cm⁻¹. EI-MS: *m/z* 216.

2-(Phenylthio)phenol (3k)¹⁷ (Table 3, Entry 11). Colorless oil (76%, 153 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.42–7.17 (m, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 162.3, 135.8, 131.0, 129.1, 128.2, 127.0, 125.5, 116.4. IR (neat): ν 3400, 2925, 1599, 1130, 879, 760 cm⁻¹. EI-MS: *m/z* 202.

(2-Nitrophenyl)(phenyl)sulfane (3l)²³ (Table 3, Entry 12). Yellowish oil (75%, 173 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, *J* = 1.6 Hz, 1H), 7.56–7.43 (m, 5H) 7.11 (d, *J* = 9.0 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 148.9, 145.6, 135.2, 130.9, 130.2, 130.1, 127.2, 124.5. IR (neat): ν 3448, 3040, 3100, 3090, 2950, 2854, 845, 725 cm⁻¹. EI-MS: *m/z* 231.

(4-Isopropylphenyl)(phenyl)sulfane (3m)³⁰ (Table 3, Entry 13). Yellowish oil (76%, 173 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.46–7.12 (m, 9H), 3.05–2.78 (m, 1H), 1.27 (d, *J* = 7.2 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 148.5, 136.9, 132.0, 131.8, 130.1, 129.2, 128.1, 127.3, 127.0, 126.5, 33.8, 23.7. IR (neat): ν 3448, 3050, 2915, 2854, 1052, 875, 736 cm⁻¹. EI-MS: *m/z* 228.

(3,5-Dimethylphenyl)(phenyl)sulfane (3n)^{21d} (Table 3, Entry 14). Yellowish oil (80%, 171 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.35–7.15 (m, 4H), 7.12–7.03 (m, 2H), 6.97–6.82 (m, 2H), 2.27 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 138.6, 135.1, 131.6, 130.4, 129.2, 129.0, 128.2, 127.5, 126.5, 125.5, 21.2. IR (neat): ν 3050, 2918, 1570, 809, 727 cm⁻¹. EI-MS: *m/z* 214.

Naphthalen-2-yl(phenyl)sulfane (3o)²³ (Table 3, Entry 15). Yellowish oil (86%, 202 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.0–7.62 (m, 4H), 7.60–7.09 (m, 8H). ¹³C NMR (75 MHz, CDCl₃) δ 135.8, 133.9, 132.8, 132.2, 130.9, 129.7, 129.1, 128.9, 128.5, 127.5, 127.3, 127.0, 126.7, 126.3. IR (neat): ν 3054, 1560, 1510 cm⁻¹. EI-MS: *m/z* 236.

2-(Phenylthio)thiophene (3p)¹⁷ (Table 3, Entry 16). Colorless oil (85%, 163 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.59–7.43 (m, 3H), 7.37–7.18 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 129.0, 127.5, 127.1. IR (neat): ν 3070, 1515, 1470, 1435, 1395 cm⁻¹. EI-MS: *m/z* 192.

1,4-Bis(phenylthio)benzene (3q)²⁸ (Table 3, Entry 17). Colorless oil (88%, 258 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.61–7.54 (m, 3H), 7.40–7.17 (m, 8H), 7.03–6.97 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 139.3, 138.0, 132.0, 131.8, 129.3, 127.5. IR (neat): ν 3449, 2922, 2852, 1469, 1081, 806, 690 cm⁻¹. EI-MS: *m/z* 294.

Decyl(phenyl)sulfane (3r)²³ (Table 3, Entry 18). Colorless oil (78%, 195 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.04 (m, 5H), 2.86 (t, *J* = 7.2 Hz, 2H), 1.71 (p, *J* = 7.1 Hz, 2H), 1.46–1.13 (m, 14H), 0.89 (t, *J* = 7.0 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 137.1, 128.8, 125.5, 33.6, 31.7, 29.4, 29.3, 29.2, 28.7, 22.5, 14.1. IR (neat): ν 3449, 3359, 3010, 2850, 1158 cm⁻¹. EI-MS: *m/z* 250.

Octyl(phenyl)sulfane (3s)^{29a} (Table 3, Entry 19). Colorless oil (80%, 177 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.29–7.19 (m, 4H), 7.14–7.07 (m, 1H), 2.87 (t, *J* = 7.5 Hz, 2H), 1.63 (p, *J* = 7.5 Hz, 2H), 1.48–1.20 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 128.6, 128.5, 125.3, 33.4, 31.7, 29.2, 29.1, 28.7,

22.6. 14.1. IR (neat): ν 3449, 3359, 3010, 2850, 1158 cm^{-1} . EI-MS: m/z 222.

Hexyl(phenyl)sulfane (3t)^{29a} (Table 3, Entry 20). Colorless oil (85%, 164 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.40–7.17 (m, 4H), 7.16–7.06 (m, 1H), 2.89 (t, J = 7.9 Hz, 2H), 1.64 (p, J = 7.9 Hz, 2H), 1.55–1.21 (m, 6H), 0.90 (t, J = 7.5 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 128.7, 128.6, 125.5, 33.5, 31.9, 31.3, 29.6, 29.3, 29.0, 28.5, 22.5, 14.1. IR (neat): ν 3400, 3359, 3010, 2925, 2850, 1579 cm^{-1} . EI-MS: m/z 194.

(4-Bromophenyl)(phenyl)sulfane (4a)^{21b} (Table 4, Entry 2). Colorless oil (85%, 232 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.38–7.22 (m, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 134.9, 134.5, 132.8, 132.0, 131.3, 129.4, 127.1. IR (neat): ν 1595, 1575, 1050 cm^{-1} . EI-MS: m/z 220.

Naphthalen-1-yl(phenyl)sulfane (4b)^{21f} (Table 4, Entry 4). Colorless oil (81%, 190 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.37–8.31 (m, 1H), 7.86–7.79 (m, 2H), 7.65–7.61 (m, 1H), 7.52–7.35 (m, 3H), 7.27–7.07 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 134.2, 133.6, 132.5, 131.2, 130.9, 129.1, 129.0, 128.9, 128.5, 126.8, 126.3, 126.0, 125.7, 125.5. IR (neat): ν 3054, 1560, 1515 cm^{-1} . EI-MS: m/z 236.

Pentyl(*p*-tolyl)sulfane (4c)²³ (Table 4, Entry 6). Colorless oil (79%, 153 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.30–7.19 (m, 4H), 4.30–7.10 (m, 1H), 2.85 (t, J = 7.4 Hz, 2H), 1.62 (p, J = 7.3 Hz, 2H), 1.43–1.25 (m, 4H), 0.90 (t, J = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 128.7, 125.4, 33.5, 30.8, 28.6, 22.0, 13.6. IR (neat): ν 3440, 2923, 2856, 1582, 1082, 820, 745, 516 cm^{-1} . EI-MS: m/z 194.

Butyl(naphthalen-1-yl)sulfane (4d)²⁴ (Table 4, Entry 7). Colorless oil (79%, 170 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.40 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.51–7.40 (m, 3H), 7.31 (t, J = 8.2 Hz, 1H), 2.92 (t, J = 7.8 Hz, 2H), 1.62 (p, J = 7.5 Hz, 2H), 1.42 (sexet, J = 7.8 Hz, 2H), 0.91 (t, J = 7.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 134.3, 133.5, 132.3, 128.3, 127.1, 126.7, 126.2, 126.0, 125.3, 124.8, 33.6, 31.2, 21.7, 13.4. IR (neat): ν 3445, 3359, 3010, 1650, 1350 cm^{-1} . EI-MS: m/z 216.

Butyl(phenyl)sulfane (4e)²⁴ (Table 4, Entry 8). Colorless oil (81%, 134 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.30–7.17 (m, 4H), 7.13–7.07 (m, 1H), 2.88 (t, J = 7.5 Hz, 2H), 1.62 (p, J = 7.5 Hz, 2H), 1.43 (sex, J = 6.7, 7.5 Hz, 2H), 0.93 (t, J = 6.7 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 130.7, 129.3, 128.7, 127.0, 125.5, 33.3, 31.0, 21.7, 13.4. IR (neat): ν 3400, 3359, 3010, 2850, 1650, 1135 cm^{-1} . EI-MS: m/z 166.

Cyclohexyl(phenyl)sulfane (4f)²² (Table 4, Entry 9). Colorless oil (80%, 152 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.40 (d, J = 8.0 Hz, 2H), 7.30–7.15 (m, 3H), 3.15–3.03 (m, 1H), 2.02–1.93 (m, 2H), 1.81–1.74 (m, 2H), 1.64–1.55 (m, 1H), 1.44–1.21 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 135.2, 131.5, 128.7, 126.1, 46.2, 33.2, 26.0, 25.5. IR (neat): ν 3445, 3010, 2950, 1715, 1635, 670 cm^{-1} . EI-MS: m/z 192.

(4-Methylcyclohexyl)(phenyl)sulfane (4g)²² (Table 4, Entry 10). Colorless oil (80%, 164 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.20 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 3.00–2.85 (m, 1H), 2.31 (s, 3H), 1.99–1.49 (m, 5H), 1.40–1.20 (m, 5H). ¹³C NMR

(75 MHz, CDCl₃) δ 136.5, 132.9, 131.2, 129.6, 47.0, 33.1, 26.0, 25.9, 21.1. IR (neat): ν 3340, 2850, 1715, 1640, 1035, 740, 815, 635 cm^{-1} . EI-MS: m/z 206.

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