## Electronic Supplementary Information

# Efficient recyclable CuI-nanoparticles-catalyzed S-arylation of thiols with aryl halides on water under mild conditions

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#### I. General considerations

All reactions were carried out in an oven-dried flask under a pure and dry nitrogen atmosphere. CuI nanoparticles were synthesized in our laboratory. Tetra-*n*-alkylammonium hydroxides water solution was purchased from Sinopharm Chemical Reagent Co. without further purification. These solvents were transferred by syringe to the reaction flask. Generally, thiols, aryl iodides and aryl bromides were purchased from commercial sources (Aldrich, Acros, Alfa Aesar, Fluka, Lancaster) and distilled when necessary. Analytical thin layer chromatography (TLC) was performed using Merck silica gel GF254 plates. Flash column chromatography was performed with silica gel (200-300 mesh). NMR spectra were recorded using a Bruker Avance 300 instruments. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2014 Series GC System. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. The samples were characterized by powder X-ray diffraction (XRD) on a D/Max-rB X-ray diffractometer with monochromatized Cu K $\alpha$  ( $\lambda = 1.5406$  Å) incident radiation. XRD patterns were recorded from 20° to 80° (2 $\theta$ ) with a scanning rate of 6°/min. The morphologies of the samples were analyzed by TEM on an H-800 transmission electron microscope operated at 200 kV.

#### **II.** Preparation of the catalyst

CuI nanoparticles were prepared by the reaction of Cu(dmg)<sub>2</sub> and KI in the autoclave with ethanol as solvent, solvothermal method. Firstly, 0.464 g (4 mmol) of dimethylglyoxime (dmgH) and 0.400 g (2 mmol) of Cu(OAc)<sub>2</sub>•H<sub>2</sub>O 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)<sub>2</sub>. Then the collected precipitates dispersed in 50 ml of absolute ethanol again. Secondly, 0.664g (4 mmol) KI was added and stirred vigorously for 2 h. After that, the mixture was transferred into 60mL 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 is then dried in a vacuum oven at room temperature for 12 h.

#### **III.** Catalyst characterization

The XRD pattern of the product is shown in *Figure S1(c, d)*. All diffraction peaks in the XRD pattern can be perfectly indexed to pure CuI (JCPDS, 06-0246). No impurity was detected, indicating that the as-synthesized product was of high purity.

The average crystalline size of the product can be estimated by Scherrer equation:

$$D=(K\lambda)/\beta \cos\theta$$

where D is the mean diameter of the nanoparticles, K is a constant (0.94),  $\lambda$  is the

X-ray wavelength (0.15406 nm in the present case),  $\beta$  is the corrected X-ray diffraction broadening ( $\beta$ =B-b, B stands for full width at half maximum and b is the



**Figure 1** (a) TEM image of fresh CuI nanoparticles; (b) TEM image of CuI nanoparticles after the fourth catalytic cycle; (c) XRD pattern of fresh CuI nanoparticles; (d) XRD pattern of CuI nanoparticles after the fourth catalytic cycle.

instrumental line broadening), and  $\theta$  is the Bragg angle of the X-ray diffraction peak. Calculation made on the strongest peak of fresh CuI nanoparticals at  $2\theta=25.40^{\circ}$  is 52.3 nm, and 57.5 nm for CuI nanoparticles after the third catalytic cycle.

The morphologies of the as-prepared CuI crystals were studied by TEM. *Figure S1 (a, b)* shows that the CuI crystals are nanoparticals with diameters ranging from 30 to 80 nm, which is coincident with the value measured by XRD.

#### **IV.** General experimental procedures for examples described in Table 1

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 tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counter flow of argon, benzenethiol (1.2 mmol, 124µl), halogenated benzene (1 mmol) and degassed 40% tetra-*n*-butyl-ammonium 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 24h or 48h.. The reaction mixture was then allowed to cool to ambient temperature. Then, the mixture was quenched by the addition of a saturated NH<sub>4</sub>Cl solution (3 mL) and extracted with ethyl acetate (3×10 mL). Organic layers were gathered, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered. Then he filtrate was analyzed by gas chromatography.

#### V. General experimental procedures for examples described in Scheme 1

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 mol%, 2.9 mg), the aryl iodides if a solid (1 mmol, 1 equiv), aryl thiols if a liquid (1.2 mmol). The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counter flow of argon, aryl iodides if a liquid (1 mmol, 1 equiv), aryl thiols if a liquid (1 mmol, 1 equiv), 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.-50°C for 24h. The reaction mixture was then allowed to cool to ambient temperature. Then, the mixture was quenched by the addition of a saturated NH<sub>4</sub>Cl solution (3 mL) and extracted with ethyl acetate ( $3 \times 10$  mL). Organic layers were gathered, dried over Na<sub>2</sub>SO<sub>4</sub>, 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):**<sup>8a</sup> iodobenzene was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (173 mg, 93% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.35-7.30 (m, 5H), 7.29-7.19 (m, 5H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  135.8, 131.0, 129.2, 127.0 ppm. HRMS calcd for C<sub>12</sub>H<sub>10</sub>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%.

(4-methoxyphenyl)(phenyl)sulfane (5b):<sup>7y</sup> iodobenzene was allowed to react with 4-methoxybenzenethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (197 mg, 91% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.34-7.31 (d, *J* = 8.7 Hz, 2H), 7.16-7.05 (m, 5H), 6.82-6.79 (dd, *J* = 2.1, 6.6 Hz, 2H), 3.73 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  159.8, 138.2, 135.3, 128.9, 128.3, 125.8, 116.4, 115.0, 55.3 ppm. HRMS calcd for C<sub>12</sub>H<sub>10</sub>S (M+): 216.0609; found: 216.0598.

(4-chlorophenyl)(phenyl)sulfane (5c):<sup>7a</sup> iodobenzene was allowed to react with 4-chlorobenzenethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a pale yellow liquid (209 mg, 95% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.52-7.50 (d, *J* = 7.2 Hz, 2H), 7.34-7.27 (m, 7H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  132.0, 131.3, 129.4, 129.3, 129.1, 127.6, 127.4, 127.2 ppm. HRMS calcd for C<sub>12</sub>H<sub>9</sub>ClS (M+): 220.0113; found: 220.0115.

**phenyl**(*o*-tolyl)sulfane (5d):<sup>7ab</sup> 1-iodo-2-methylbenzene was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (196 mg, 89% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.48-7.46 (m, 3H), 7.23-7.18 (m, 6H), 2.36 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  133.1, 130.6, 129.7, 129.2, 129.1, 127.9, 127.6, 127.2, 126.8, 126.4, 20.6 ppm. HRMS calcd for C<sub>12</sub>H<sub>13</sub>S (M+): 220.0660; found: 220.0679.

(4-methoxyphenyl)(*p*-tolyl)sulfane (5e):<sup>7f</sup> 1-iodo-4-methylbenzene was allowed to react with 4-methoxybenzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (200 mg, 87% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.38-7.38 (d, *J* = 9.0 Hz, 2H), 7.16-7.13 (d, *J* = 8.4 Hz, 2H), 7.08-7.06 (d, *J* = 7.8 Hz, 2H), 6.89-6.86 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.31 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  158.4, 135.0, 133.2, 128.7, 128.3, 124.6, 113.8, 54.3, 19.9

ppm. HRMS calcd for  $C_{14}H_{14}S$  (M+): 230.0765; found: 230.0773.

(3-chlorophenyl)(phenyl)sulfane (5f):<sup>7m</sup> iodobenzene was allowed to react with 3-chlorobenzenethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a pale yellow liquid (189 mg, 86% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.41-7.30 (m, 6H), 7.29-7.11 (m, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  138.8, 134.9, 133.9, 132.3, 130.0, 129.4, 129.0, 128.0, 127.9, 126.7 ppm. HRMS calcd for C<sub>12</sub>H<sub>9</sub>ClS (M+): 220.0113; found: 220.0121.

(2,6-dimethylphenyl)(phenyl)sulfane (5g):<sup>7k</sup> iodobenzene was allowed to react with 2,6-dimethylbenzenethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (199 mg, 93% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.24-7.16 (m, 5H), 7.09-7.07 (d, *J* = 7.2 Hz, 1H), 6.95-6.93 (d, *J* = 7.2 Hz, 2H), 2.44 (s, 6H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  143.9, 138.0, 130.5, 129.2, 128.9, 128.4, 125.6, 124.6, 21.8 ppm. HRMS calcd for C<sub>14</sub>H<sub>14</sub>S (M+): 214.0816; found: 214.0837.

**bis**(4-methoxyphenyl)sulfane (5h):<sup>3g</sup> 1-iodo-4-methoxybenzene was allowed to react with 4-methoxybenzenethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (209 mg, 85% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.27-7.25 (d, *J* = 8.7 Hz, 4H), 6.83-6.80 (d, *J* = 8.7 Hz, 4H), 3.75 (s, 6H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  159.0, 132.7, 132.6, 114.7, 55.3 ppm. HRMS calcd for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>S (M+): 246.0715; found: 246.0718.

(3,4-dimethylphenyl)(phenyl)sulfane (5i):<sup>15a</sup> 4-iodo-1,2-dimethylbenzene was allowed to react with benzenethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (207 mg, 97% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.51-7.48 (m, 1H), 7.26-7.14 (m, 6H), 7.09-7.06 (d, *J* = 7.8 Hz, 1H), 2.24-2.21 (m, 6H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  137.7, 137.4, 136.4, 133.5, 130.6, 130.0, 129.6, 129.0, 127.6, 126.2, 19.7, 19.4 ppm. HRMS calcd for C<sub>14</sub>H<sub>14</sub>S (M+): 214.0816; found: 214.0832.

(4-chlorophenyl)(4-methoxyphenyl)sulfane (5j):<sup>8b</sup> 1-chloro-4-iodobenzene was allowed to react with 4-methoxybenzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a white solide (240 mg, 96% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.42-7.39 (d, J = 9.0 Hz, 2H), 7.21-7.18 (d, J = 8.7 Hz, 2H), 7.09-7.06 (d, J = 8.7 Hz, 2H), 6.92-6.89 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  160.0, 137.3, 135.4, 131.6, 129.3, 129.0, 123.8, 115.1, 55.3 ppm. HRMS calcd for C<sub>13</sub>H<sub>11</sub>ClOS (M+): 250.0219; found: 250.0236.

(2-chlorophenyl)(phenyl)sulfane (5k):<sup>15b</sup> 1-chloro-2-iodobenzene was allowed to react with benzenethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (179 mg, 81% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.47-7.45 (d, *J* = 7.5 Hz, 1H), 7.42-7.38 (m, 2H), 7.36-7.27 (m, 2H), 7.23-7.18 (t, *J* = 9.0 Hz, 1H), 7.11-7.03 (m, 2H), 6.96-6.93 (m, 1H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):

 $\delta$  136.5, 133.2, 132.8, 130.2, 129.8, 129.6, 129.1, 128.3, 127.6, 127.3, 127.2 ppm. HRMS calcd for  $C_{12}H_9ClS$  (M+): 220.0113; found: 220.0159.

**phenyl**(*p*-tolyl)sulfane (51):<sup>7a</sup> 1-iodo-4-methylbenzene was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (174 mg, 87% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.49-7.47 (d, J = 7.5 Hz, 2H), 7.30-7.23 (m, 5H), 7.12-7.10 (d, J = 8.4 Hz, 2H), 2.32 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 137.6, 132.3, 130.1, 129.8, 129.1, 127.6, 127.2, 126.4, 21.2 ppm. HRMS calcd for C<sub>13</sub>H<sub>12</sub>S (M+): 200.0660; found: 200.0655.

(4-fluorophenyl)(phenyl)sulfane (5m):<sup>4</sup> The general procedure was used to convert 4-fluoroiodobenzene and benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (196 mg, 96% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.39-7.35 (t, *J* = 9.0 Hz, 2H), 7.28-7.22 (m, 5H), 7.05-6.99 (t, *J* = 8.7 Hz, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  160.8, 134.1, 130.0, 129.1, 127.6, 127.2, 126.8, 116.3 ppm. HRMS calcd for C<sub>12</sub>H<sub>9</sub>FS (M+): 204.0409; found: 204.0444.

(2-methoxyphenyl)(phenyl)sulfane (5n):<sup>7d</sup> iodobenzene was allowed to react with 2-methoxybenzenethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (189 mg, 87% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.36-7.20 (m, 6H), 7.10-7.07 (dd, *J* = 1.8, 7.5 Hz, 1H), 6.90-6.83 (dd, *J* = 7.2, 13.5 Hz, 2H), 3.85 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  157.4, 134.6, 131.7, 131.4, 129.1, 128.3, 127.0, 124.1, 121.2, 110.9, 55.9 ppm. HRMS calcd for C<sub>13</sub>H<sub>12</sub>OS (M+): 216.0609; found: 216.0622.

**4-(***m***-tolylthio)aniline** (50):<sup>71</sup> 4-iodoaniline was allowed to react with 3-methylbenzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a brown solid (188 mg, 87% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.33-7.30 (d, J = 8.7 Hz, 2H), 7.14-7.09 (t, J = 7.5 Hz, 1H), 7.00 (s, 1H), 6.96-6.92 (m, 2H), 6.69-6.66 (d, J = 8.7 Hz, 2H), 3.79 (s, 2H), 2.28 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  146.9, 139.3, 138.6, 135.9, 128.6, 128.0, 126.2, 124.5, 120.7, 115.8, 21.3 ppm. HRMS calcd for C<sub>13</sub>H<sub>13</sub>NS (M+): 215.0769; found: 215.0764.

**phenyl**(*m*-tolyl)sulfane (5p):<sup>7a</sup> 1-iodo-3-methylbenzene was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (185 mg, 92% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.32-7.28 (m, 3H), 7.24-7.19 (m, 2H), 7.16-7.10 (m, 3H), 7.04-7.02 (d, *J* = 6.9 Hz, 1H), 2.28 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  139.0, 136.1, 135.3, 131.8, 130.8, 129.1, 128.3, 128.0, 127.5, 126.8, 21.3 ppm. HRMS calcd for C<sub>13</sub>H<sub>12</sub>S (M+): 200.0660; found: 200.0663.

**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. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>19</sub>H<sub>16</sub>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 chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a white solid (290 mg, 98% yield). M.p.=122-125°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.55-7.50 (t, *J* = 8.4 Hz, 4H), 7.43-7.32 (m, 5H), 7.30-7.19 (m, 4H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>18</sub>H<sub>13</sub>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-(4-methoxyphenylthio)pyridine (5s):**<sup>15c</sup> 3-iodopyridine was allowed to react with 4-methoxybenzenethiol, column chromategraphy (petroleum ether/ethyl acetate 10/1), isolated as a colorless oil (189 mg, 87% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.41-8.35 (d, *J* = 19.2 Hz, 2H), 7.42-7.39 (m, 3H), 7.13-7.09 (m, 1H), 6.90-6.87 (d, *J* = 9.0 Hz, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  160.2, 148.8, 146.7, 136.0, 135.6, 123.6, 122.6, 115.2, 55.3 ppm. HRMS calcd for C<sub>12</sub>H<sub>11</sub>NOS (M+): 217.0561; found: 217.0578.

**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). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>12</sub>H<sub>11</sub>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%.

**2-(phenylthio)thiophene** (**5u**):<sup>7k</sup> 2-iodothiophene was allowed to react with benzenethiol, column chromategraphy (petroleum ether/ethyl acetate 20/1), isolated as a colorless oil (166 mg, 86% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.46-7.43 (d, *J* = 5.4 Hz, 1H), 7.28-7.27 (d, *J* = 2.4 Hz, 1H), 7.23-7.13 (m, 5H), 7.07-7.04 (dd, *J* = 3.6, 5.4 Hz, 1H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  138.6, 136.0, 131.3, 131.2, 129.0, 127.9, 127.2, 126.1 ppm. HRMS calcd for C<sub>10</sub>H<sub>8</sub>S<sub>2</sub> (M+): 192.0067; found: 192.0070.

2-(phenylthio)benzo[d]thiazole (5v):<sup>8d</sup> iodobenzene was allowed to react with

benzo[*d*]thiazole-2-thiol, column chromategraphy (petroleum ether/ethyl acetate 5/1), isolated as a colorless oil (175 mg, 72% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.80-7.77 (d, *J* = 8.1 Hz, 1H), 7.65-7.63 (d, *J* = 7.5 Hz, 2H), 7.56-7.53 (d, *J* = 7.8 Hz, 1H), 7.41-7.27 (m, 4H), 7.19-7.14 (t, *J* = 8.7 Hz, 1H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 168.5, 152.8, 134.5, 134.3, 129.4, 128.9, 128.8, 125.1, 123.3, 120.9, 119.7 ppm. HRMS calcd for C<sub>13</sub>H<sub>9</sub>NS<sub>2</sub> (M+): 243.0176; found: 243.0178.

**naphthalen-1-yl(phenyl)sulfane** (**5**w):<sup>7a</sup> 1-iodonaphthalene was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (170 mg, 72% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.38-8.36 (t, *J* = 3.0 Hz, 1H), 7.85-7.80 (dd, *J* = 3.9, 6.9 Hz, 2H), 7.65-7.63 (d, *J* = 6.9 Hz, 1H), 7.49-7.46 (dd, *J* = 3.3, 6.3 Hz, 2H), 7.41-7.36 (t, *J* = 7.5 Hz, 1H), 7.19-7.11 (m, 5H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  137.0, 134.3, 133.6, 132.6, 131.3, 129.2, 129.1, 129.0, 128.6, 127.0, 126.4, 126.2, 125.8, 125.7 ppm. HRMS calcd for C<sub>16</sub>H<sub>12</sub>S (M+): 236.0660; found: 236.0660.

#### VI. General experimental procedures for examples described in Scheme 2

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 mol%, 2.9 mg), the aryl iodides if a solid (1 mmol, 1 equiv). The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counter flow of argon, aryl iodides if a liquid (1 mmol, 1 equiv), alkyl thiols (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.-50°C for 24h. The reaction mixture was then allowed to cool to ambient temperature. Then, the mixture was quenched by the addition of a saturated NH<sub>4</sub>Cl solution (3 mL) and extracted with ethyl acetate (3×10 mL). Organic layers were gathered, dried over Na<sub>2</sub>SO<sub>4</sub>, 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 0.5h.

**benzyl(phenyl)sulfane** (6a):<sup>7y</sup> iodobenzene was allowed to react with phenylmethanethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (194 mg, 97% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.31-7.16 (m, 10H), 4.10 (s, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  137.5, 136.5, 129.9, 129.5, 128.9, 128.5, 127.2, 126.4, 39.1 ppm. HRMS calcd for C<sub>13</sub>H<sub>12</sub>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**(*p***-tolyl)sulfane** (**6b**):<sup>3j</sup> 1-iodo-4-methylbenzene was allowed to react with phenylmethanethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1),

isolated as a colorless oil (200 mg, 93% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.30-7.21 (m, 7H), 7.19-7.18 (d, *J* = 2.1 Hz, 2H), 4.05 (s, 2H), 2.29 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  137.8, 136.5, 132.6, 130.7, 129.6, 128.9, 128.4, 127.1, 39.8, 21.1 ppm. HRMS calcd for C<sub>14</sub>H<sub>14</sub>S (M+): 214.0816; found: 214.0820.

**benzyl(4-methoxyphenyl)sulfane** (6c):<sup>71</sup> 1-iodo-4-methoxybenzene was allowed to react with phenylmethanethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (210 mg, 91% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.26-7.19 (m, 7H), 6.80-6.75 (m, 2H), 3.98 (s, 2H), 3.76 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  158.1, 137.0, 132.9, 127.8, 127.2, 125.9, 125.0, 113.3, 54.1, 40.1 ppm. HRMS calcd for C<sub>14</sub>H<sub>14</sub>OS (M+): 230.0765; found: 230.0787.

**benzyl(4-chlorophenyl)sulfane (6d):**<sup>8d</sup> 1-chloro-4-iodobenzene was allowed to react with phenylmethanethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a white solid (225 mg, 96% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.30-7.26 (m, 3H), 7.25-7.22 (m, 2H), 7.21-7.18 (m, 4H), 4.05 (s, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  137.1, 134.8, 132.5, 131.4, 129.0, 128.8, 128.6, 127.3, 39.3 ppm. HRMS calcd for C<sub>13</sub>H<sub>11</sub>ClS (M+): 234.0270; found: 234.0254.

**benzyl**(*o*-tolyl)sulfane (6e):<sup>15d</sup> 1-iodo-2-methylbenzene was allowed to react with phenylmethanethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (191 mg, 89% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.34-7.27 (m, 6H), 7.20-7.09 (m, 3H), 4.10 (s, 2H), 2.35 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  138.0, 137.4, 135.8, 130.0, 129.1, 128.9, 128.5, 127.2, 126.4, 126.2, 38.4, 20.3 ppm. HRMS calcd for C<sub>14</sub>H<sub>14</sub>S (M+): 214.0816; found: 214.0816.

**benzyl(2-chlorophenyl)sulfane (6f):**<sup>15e</sup> 1-chloro-2-iodobenzene was allowed to react with phenylmethanethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (206 mg, 88% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.35-7.27 (m, 4H), 7.24-7.20 (m, 3H), 7.14-7.04 (m, 2H), 4.11 (s, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  136.4, 135.8, 129.6, 129.4, 128.9, 128.6, 128.5, 127.4, 127.1, 126.9, 37.5 ppm. HRMS calcd for C<sub>13</sub>H<sub>11</sub>ClS (M+): 234.0270; found: 234.0788.

**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). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.45-7.34 (m, 6H), 7.23-7.14 (m, 2H), 4.21 (s, 2H), 2.34 (s, 6H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>15</sub>H<sub>16</sub>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%.

**benzyl(naphthalen-1-yl)sulfane (6h):**<sup>3j</sup> 1-iodonaphthalene was allowed to react with phenylmethanethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1),

isolated as a colorless oil (243 mg, 97% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.43-8.40 (d, *J* = 8.1 Hz, 1H), 7.84-7.82 (d, *J* = 7.5 Hz, 1H), 7.73-7.71 (d, *J* = 8.1 Hz, 1H), 7.56-7.46 (m, 3H), 7.35-7.22 (m, 6H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  137.4, 133.9, 133.0, 129.4, 129.2, 128.9, 128.5, 128.4, 127.6, 127.1, 126.4, 126.2, 125.5, 125.1, 39.4 ppm. HRMS calcd for C<sub>17</sub>H<sub>14</sub>S (M+): 250.0816; found: 250.0818.

**butyl(phenyl)sulfane (6i):**<sup>7y</sup> iodobenzene was allowed to react with butane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (155 mg, 93% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.32-7.22 (m, 4H), 7.15-7.11 (t, *J* = 7.2 Hz, 1H), 2.92-2.88 (m, 2H), 1.64-1.59 (t, *J* = 7.5 Hz, 2H), 1.47-1.40 (m, 2H), 0.92-0.88 (t, *J* = 6.9 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  137.1, 128.9, 128.8, 125.6, 33.3, 31.2, 21.9, 13.6 ppm. HRMS calcd for C<sub>10</sub>H<sub>14</sub>S (M+): 166.0816; found: 166.0816.

**pentyl(phenyl)sulfane (6j):**<sup>6a</sup> iodobenzene was allowed to react with pentane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (172 mg, 95% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.32-7.22 (m, 4H), 7.15-7.10 (t, *J* = 7.2 Hz, 1H), 2.92-2.87 (t, *J* = 7.5 Hz, 2H), 1.69-1.59 (m, 2H), 1.42-1.27 (m, 4H), 0.90-0.86 (t, *J* = 6.9 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  137.1, 128.9, 128.8, 125.6, 33.6, 31.0, 28.8, 22.2, 13.9 ppm. HRMS calcd for C<sub>11</sub>H<sub>16</sub>S (M+): 180.0973; found: 180.0978.

**hexyl(phenyl)sulfane (6k):**<sup>7y</sup> 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). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>12</sub>H<sub>18</sub>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%.

**heptyl(phenyl)sulfane (6l):**<sup>12f</sup> iodobenzene was allowed to react with heptane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (192 mg, 92% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.32-7.23 (m, 4H), 7.16-7.11 (t, J = 7.2 Hz, 1H), 2.92-2.87 (t, J = 7.2 Hz, 2H), 1.68-1.59 (m, 2H), 1.43-1.38 (m, 2H), 1.36-1.26 (m, 6H), 0.89-0.85 (t, J = 6.6 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 137.1, 128.8, 125.6, 33.5, 31.7, 29.1, 28.9, 28.8, 22.6, 14.0 ppm. HRMS calcd for C<sub>13</sub>H<sub>20</sub>S (M+): 208.1286; found: 208.1286.

octyl(*o*-tolyl)sulfane (6m):<sup>15m</sup> 1-iodo-2-methylbenzene was allowed to react with octane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (206 mg, 87% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.36-7.33 (d, *J* = 7.8 Hz, 1H), 7.27-7.18 (m, 2H), 7.11-7.06 (t, *J* = 7.8 Hz, 1H), 2.95-2.90 (t, *J* = 7.2 Hz, 2H), 1.74-1.64 (m, 2H), 1.50-1.41 (m, 2H), 1.35-1.28 (m, 8H), 0.90-0.86 (t, *J* =

6.3 Hz, 3H) ppm.  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  136.6, 133.1, 129.6, 127.8, 127.0, 126.0, 32.4, 32.2, 31.7, 29.1, 28.9, 28.6, 22.6, 14.0 ppm. HRMS calcd for C<sub>15</sub>H<sub>24</sub>S (M+): 236.1599; found: 236.1607.

(2-chlorophenyl)(octyl)sulfane (6n):<sup>15g</sup> 1-chloro-2-iodobenzene was allowed to react with octane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (208 mg, 81% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.36-7.33 (d, J = 7.8 Hz, 1H), 7.27-7.18 (m, 2H), 7.11-7.06 (t, J = 7.8 Hz, 1H), 2.95-2.90 (t, J = 7.2 Hz, 2H), 1.74-1.64 (m, 2H), 1.50-1.41 (m, 2H), 1.35-1.28 (m, 8H), 0.90-0.86 (t, J = 6.3 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  136.6, 133.1, 129.6, 127.8, 127.0, 126.0, 32.4, 32.2, 31.7, 29.1, 28.9, 28.6, 22.6, 14.0 ppm. HRMS calcd for C<sub>14</sub>H<sub>21</sub>ClS (M+): 256.1052; found: 256.1069.

(3,4-dimethylphenyl)(octyl)sulfane (60): 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). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>16</sub>H<sub>26</sub>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%.

**dodecyl**(*o*-tolyl)sulfane (6p):<sup>15h</sup> 1-iodo-2-methylbenzene was allowed to react with dodecane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (237 mg, 81% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.25-7.23 (d, J = 7.2 Hz, 1H), 7.15-7.11 (t, J = 7.5 Hz, 2H), 7.07-7.02 (m, 1H), 2.90-2.85 (t, J = 7.5 Hz, 2H), 2.52-2.47 (m, 1H), 2.35 (s, 3H), 1.70-1.58 (m, 2H), 1.55-1.38 (m, 3H), 1.36-1.25 (m, 14H), 0.90-0.85 (t, J = 6.3 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  137.2, 136.4, 129.9, 127.4, 126.3, 125.2, 32.8, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 29.0, 22.7, 20.3, 14.1 ppm. HRMS calcd for C<sub>19</sub>H<sub>32</sub>S (M+): 292.2225; found: 292.210.

**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). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>14</sub>H<sub>20</sub>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. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>18</sub>H<sub>20</sub>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%.

**cyclohexyl(phenyl)sulfane** (6s):<sup>6a</sup> iodobenzene was allowed to react with cyclohexanethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (179 mg, 93% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.40-7.37 (dd, J = 1.5, 8.4 Hz, 2H), 7.29-7.19 (m, 3H), 3.13-3.05 (m, 1H), 1.99-1.96 (d, J = 9.9 Hz, 2H), 1.78-1.74 (m, 2H), 1.39-1.25 (m, 6H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  135.2, 131.8, 128.7, 126.5, 46.5, 33.3, 26.0, 25.7 ppm. HRMS calcd for C<sub>12</sub>H<sub>16</sub>S (M+): 192.0973; found: 192.0961.

**cyclohexyl**(*o*-tolyl)sulfane (6t):<sup>15i</sup> 1-iodo-2-methylbenzene was allowed to react with cyclohexanethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (190 mg, 92% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.57 (s, 1H), 8.41-8.40 (d, *J* = 3.9 Hz, 1H), 7.64-7.61 (d, *J* = 8.1 Hz, 1H), 7.21-7.17 (m, 1H), 2.94-2.89 (t, *J* = 7.2 Hz, 2H), 1.69-1.59 (m, 2H), 1.47-1.37 (m, 2H), 1.30-1.28 (m, 4H), 0.90-0.86 (t, *J* = 6.9 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  139.4, 134.7, 131.3, 130.2, 126.4, 126.2, 45.9, 33.4, 26.1, 25.8, 20.8 ppm. HRMS calcd for C<sub>13</sub>H<sub>18</sub>S (M+): 206.1129; found: 206.1112.

**3-(hexylthio)pyridine** (**6u**):<sup>15j</sup> 3-iodopyridine was allowed to react with hexane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (197 mg, 93% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.29-7.26 (m, 1H), 7.10-7.06 (m, 1H), 7.04-7.00 (m, 2H), 3.03-2.95 (m, 1H), 2.31 (s, 3H), 1.91-1.86 (m, 2H), 1.70-1.66 (m, 2H), 1.54-1.51 (m, 1H), 1.33-1.17 (m, 4H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  150.0, 146.8, 136.5, 134.1, 123.5, 33.7, 31.2, 29.0, 28.3, 22.4, 13.9 ppm. HRMS calcd for C<sub>11</sub>H<sub>17</sub>NS (M+): 195.1082; found: 195.1072.

#### VII. General experimental procedures for examples described in Scheme 3

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 (3.0 mol%, 5.7 mg), the aryl bromides if a solid (1 mmol, 1 equiv), aryl thiols or alkyl thiols if a liquid (1.2 mmol). The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counter flow of argon, aryl bromides if a liquid (1 mmol, 1 equiv), aryl thiols or alkyl thiols if a liquid (1 mmol, 1 equiv), aryl thiols or alkyl thiols if a liquid (1 mmol, 1 equiv), aryl thiols or alkyl 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 80°C for 48h. 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.

**phenyl(4-(trifluoromethyl)phenyl)sulfane** (5aa):<sup>6b</sup> 1-bromo-4-(trifluoromethyl)benzene was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (231 mg, 91% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.49-7.42 (m, 4H), 7.38-7.34 (m, 3H), 7.27-7.19 (m, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  142.8, 133.5, 132.5, 129.6, 129.0, 128.6, 128.3, 127.5, 125.8-125.7 (dd, *J* = 3.825, 7.575 Hz, 1C) ppm. HRMS calcd for C<sub>13</sub>H<sub>9</sub>F<sub>3</sub>S (M+): 254.0377; found: 254.0378.

**2-(phenylthio)benzoic acid (5ab):**<sup>8a</sup> 2-bromobenzoic acid was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 20/1), isolated as a white solid (200 mg, 87% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.77 (br-s, 1H), 8.15-8.12 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.60-7.57 (m, 2H), 7.45-7.43 (t, *J* = 3.6 Hz, 3H), 7.30-7.25 (m, 1H), 7.17-7.12 (m, 1H), 6.82-6.79 (dd, *J* = 0.9, 8.7 Hz, 1H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  171.6, 144.6, 135.8, 133.1, 132.2, 132.1, 129.8, 129.2, 127.2, 125.3, 124.3 ppm. HRMS calcd for C<sub>13</sub>H<sub>10</sub>O<sub>2</sub>S (M+): 230.0402; found: 230.0400.

**4-(phenylthio)benzoic acid (5ac):**<sup>8d</sup> 4-bromobenzoic acid was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 20/1), isolated as a white solid (216 mg, 94% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.96-7.93 (d, *J* = 8.7 Hz, 2H), 7.53-7.50 (dd, *J* = 4.5, 7.5 Hz, 2H), 7.42-7.40 (m, 3H), 7.22-7.19 (d, *J* = 8.7 Hz, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  171.6, 145.9, 134.0, 131.8, 130.6, 129.7, 128.9, 127.2, 126.3 ppm. HRMS calcd for C<sub>13</sub>H<sub>10</sub>O<sub>2</sub>S (M+): 230.0402; found: 230.0402.

**3-(phenylthio)benzoic acid (5ad):** <sup>3j</sup> 3-bromobenzoic acid was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 20/1), isolated as a yellow solid (189 mg, 82% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  10.05 (br-s, 1H), 8.05 (s, 1H), 7.96-7.93 (d, *J* = 7.5 Hz, 1H), 7.52-7.50 (d, *J* = 7.8 Hz, 1H), 7.42-7.29 (m, 6H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  171.4, 137.7, 135.7, 134.2, 132.0, 131.6, 130.3, 129.5, 129.2, 128.4, 127.8 ppm. HRMS calcd for C<sub>13</sub>H<sub>10</sub>O<sub>2</sub>S (M+): 230.0402; found: 230.0414.

**1-(4-(phenylthio)phenyl)ethanone (5ae):**<sup>7w</sup> 1-(4-iodophenyl)-ethanone was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a yellow solid (187 mg, 82% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):

δ 7.82-7.79 (d, J = 8.4 Hz, 2H), 7.49-7.47 (d, J = 3.3 Hz, 2H), 7.41-7.36 (m, 3H), 7.21-7.15 (d, J = 8.4 Hz, 2H), 2.53 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 197.0, 144.8, 134.5, 133.8, 132.1, 129.6, 128.9, 128.7, 127.5, 26.4 ppm. HRMS calcd for C<sub>14</sub>H<sub>12</sub>OS (M+): 228.0609; found: 228.0601.

**3-(phenylthio)benzonitrile** (**5af**):<sup>71</sup> 3-bromobenzonitrile was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a pale yellow liquid (186 mg, 88% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.48-7.41 (m, 4H), 7.40-7.31 (m, 5H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  140.0, 133.3, 132.8, 132.2, 131.6, 129.8, 129.6, 129.5, 128.8, 118.2, 113.3 ppm. HRMS calcd for C<sub>13</sub>H<sub>9</sub>NS (M+): 211.0456; found: 211.0455.

**4-(phenylthio)benzonitrile (5ag):**<sup>4</sup> 4-bromobenzonitrile was allowed to react with benzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a yellow liquid (197 mg, 92% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.52-7.48 (m, 3H), 7.46-7.41 (m, 4H), 7.18-7.15 (d, *J* = 8.7 Hz, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  145.7, 134.4, 132.3, 130.9, 129.9, 129.3, 127.3, 118.7, 108.7 ppm. HRMS calcd for C<sub>13</sub>H<sub>9</sub>NS (M+): 211.0456; found: 211.0458.

**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). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 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<sub>15</sub>H<sub>14</sub>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%.

(4-*tert*-butylphenyl)(phenyl)sulfane (5ai):<sup>6a</sup> bromobenzene was allowed to react with 4-*tert*-butylbenzenethiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (176 mg, 73% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.35-7.28 (m, 4H), 7.26-7.21 (m, 5H), 1.30 (s, 9H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  150.6, 136.6, 131.6, 131.5, 130.2, 129.1, 126.6, 34.6, 31.3 ppm. HRMS calcd for C<sub>16</sub>H<sub>18</sub>S (M+): 242.1129; found: 242.1138.

(4-*tert*-butylphenyl)(*p*-tolyl)sulfane (5aj):<sup>15k</sup> 1-bromo-4-methylbenzene was allowed to react with 4-*tert*-butylbenzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (192 mg, 75% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.30-7.21 (m, 6H), 7.11-7.08 (d, *J* = 8.4 Hz, 2H), 2.31 (s, 3H), 1.29 (s, 9H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  149.9, 137.1, 131.6, 130.2, 129.9, 129.1, 126.1, 125.8, 34.5, 31.3, 21.1 ppm. HRMS calcd for C<sub>17</sub>H<sub>20</sub>S (M+): 256.1286; found: 256.1286.

**2-(***o***-tolylthio)pyridine** (**5ak**):<sup>151</sup> 2-bromopyridine was allowed to react with 2-methylbenzenethiol, column chromatography (petroleum ether/ethyl acetate 10/1), isolated as a colorless oil (139 mg, 69% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.41-8.40 (d, *J* = 4.2 Hz, 1H), 7.61-7.58 (d, *J* = 7.5 Hz, 1H), 7.43-7.38 (t, *J* = 9.6 Hz, 1H), 7.35-7.33 (m, 2H), 7.28-7.21 (m, 1H), 6.97-6.94 (t, *J* = 6.6 Hz, 1H), 6.71-6.69 (d, *J* = 8.1 Hz, 1H), 2.40 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  161.2, 149.6, 142.7, 136.7, 136.6, 131.0, 129.9, 129.8, 127.1, 120.4, 119.5, 20.8 ppm. HRMS calcd for C<sub>12</sub>H<sub>11</sub>NS (M+): 201.0612; found: 201.0612.

(4-chlorophenyl)(naphthalen-1-yl)sulfane (5al):<sup>7e</sup> 1-bromonaphthalene was allowed to react with 4-chlorobenzenethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (240 mg, 89% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.39-8.36 (m, 1H), 7.91-7.89 (d, *J* = 7.2 Hz, 2H), 7.74-7.71 (d, *J* = 7.2 Hz, 1H), 7.57-7.53 (m, 2H), 7.49-7.44 (t, *J* = 7.8 Hz, 1H), 7.21-7.18 (d, *J* = 8.7 Hz, 2H), 7.13-7.10 (d, *J* = 8.7 Hz, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  135.8, 134.3, 133.6, 133.0, 132.0, 130.5, 129.9, 129.7, 129.2, 128.6, 127.1, 126.5, 125.8, 125.5 ppm. HRMS calcd for C<sub>16</sub>H<sub>11</sub>ClS (M+): 270.0270; found: 270.0264.

**1-(4-(benzylthio)phenyl)ethanone** (6aa):<sup>7g</sup> 1-(4-bromophenyl)-ethanone was allowed to react with phenylmethanethiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (198 mg, 82% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.83-7.80 (d, J = 8.4 Hz, 2H), 7.35-7.25 (m, 7H), 4.20 (s, 2H), 2.54 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 197.0, 144.1, 136.3, 134.2, 128.8, 128.7, 127.5, 126.9, 37.2, 26.4 ppm. HRMS calcd for C<sub>15</sub>H<sub>14</sub>OS (M+): 242.0765; found: 242.0762.

naphthalen-1-yl(octyl)sulfane (6ab):<sup>15m</sup> 1-iodonaphthalene was allowed to react with octane-1-thiol, column chromatography (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (223 mg, 82% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.45-8.43 (d, J = 7.8 Hz, 1H), 7.87-7.84 (d, J = 9.0 Hz, 1H), 7.74-7.72 (d, J = 8.1 Hz, 1H), 7.59-7.49 (m, 3H), 7.45-7.40 (t, J = 7.8 Hz, 1H), 3.03-2.98 (t, J = 7.2 Hz, 2H), 1.75-1.65 (m, 2H), 1.53-1.42 (m, 2H), 1.40-1.25 (m, 8H), 0.93-0.89 (t, J = 5.7 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 134.3, 133.9, 132.9, 128.5, 127.4, 126.8, 126.2, 126.1, 125.5, 125.0, 34.2, 31.8, 29.2, 28.9, 22.6, 14.1 ppm. HRMS calcd for C<sub>18</sub>H<sub>24</sub>S (M+): 272.1599; found: 272.1587.

(4-chlorophenyl)(dodecyl)sulfane (6ac):<sup>15n</sup> 1-bromo-4-chlorobenzene was allowed to react with dodecane-1-thiol, column chromategraphy (petroleum ether/ethyl acetate 100/1), isolated as a colorless oil (221 mg, 71% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.24 (s, 4H), 2.91-2.86 (t, *J* = 7.2 Hz, 2H), 1.67-1.58 (m, 2H), 1.43-1.36 (m, 2H), 1.33-1.6 (m, 16H), 0.91-0.86 (t, *J* = 6.6 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  135.6, 131.5, 130.2, 128.9, 39.2, 33.8, 31.9, 29.7, 29.6, 29.5, 29.3, 29.1, 29.0, 28.8, 22.7, 14.1 ppm. HRMS calcd for C<sub>18</sub>H<sub>29</sub>ClS (M+): 312.1678; found: 312.1660.

**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). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>11</sub>H<sub>17</sub>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%.

**2-(cyclohexylthio)pyridine (6ae):**<sup>150</sup> 2-bromopyridine was allowed to react with cyclohexanethiol, column chromatography (petroleum ether/ethyl acetate 10/1), isolated as a colorless oil (153 mg, 79% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.45-8.40 (d, *J* = 3.0 Hz, 1H), 7.46-7.41 (t, *J* = 8.1 Hz, 1H), 7.15-7.12 (d, *J* = 8.1 Hz, 1H), 6.96-6.91 (t, *J* = 6.0 Hz, 1H), 3.84-3.78 (m, 1H), 2.10-2.04 (m, 2H), 1.78-1.29 (m, 8H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  158.2, 148.4, 134.8, 121.8, 118.2, 41.8, 32.2, 24.9, 24.8 ppm. HRMS calcd for C<sub>11</sub>H<sub>15</sub>NS (M+): 193.0925; found: 193.0922.

#### VIII. General experimental procedures for examples described in Scheme 4

## Synthesis of 1,4-bis(phenylthio)benzene, 1,4-bis(hexylthio)benzene and 1,4-bis-

#### (cyclohexylthio)benzene

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 mol%, 2.9 mg), 1,4-diiodobenzene (1 mmol, 1 equiv). The tube was evacuated and backfilled with argon (this procedure was repeated three times). Under a counter flow of argon, benzenethiol or hexane-1-thiol or cyclohexanethiol (2.4 mmol, 1.2 equiv) 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 50°C for 24h. The reaction mixture was then allowed to cool to ambient temperature. Then, the mixture was quenched by the addition of a saturated NH<sub>4</sub>Cl solution (3 mL) and extracted with ethyl acetate ( $3 \times 10$  mL). Organic layers were gathered, dried over Na<sub>2</sub>SO<sub>4</sub>, 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 0.5 h, affording the pure product.

# Synthesis of 1,6-bis(phenylthio)-hexane, 1,6-bis(naphthalen-1-ylthio)hexane and 1,6-bis(pyridin-2-ylthio)hexane

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 mol%, 2.9 mg). The tube was evacuated and backfilled with argon

(this procedure was repeated three times). Under a counter flow of argon, hexane-1,6-dithiol (1 mmol, 1 equiv), iodobenzene or 1-iodonaphthalene or 2-iodopyridine (2.4 mmol, 1.2 equiv) 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 50°C for 24h. The reaction mixture was then allowed to cool to ambient temperature. Then, the mixture was quenched by the addition of a saturated NH<sub>4</sub>Cl solution (3 mL) and extracted with ethyl acetate (3×10 mL). Organic layers were gathered, dried over Na<sub>2</sub>SO<sub>4</sub>, 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 0.5 h, affording the pure product.

**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. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.37-7.31 (m, 5H), 7.30-7.23 (m, 5H), 7.21 (s, 4H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  135.1, 134.9, 131.4, 131.2, 129.3, 127.4 ppm. HRMS calcd for C<sub>18</sub>H<sub>14</sub>S<sub>2</sub> (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. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  134.4, 129.6, 33.9, 31.3, 29.0, 28.4, 22.4, 13.9 ppm. HRMS calcd for C<sub>18</sub>H<sub>30</sub>S<sub>2</sub> (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. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  133.5, 131.8, 46.5, 33.2, 25.9, 25.6 ppm. HRMS calcd for C<sub>18</sub>H<sub>26</sub>S<sub>2</sub> (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. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  135.8, 127.9, 127.7, 124.6, 32.4, 27.9, 27.2 ppm. HRMS calcd for C<sub>18</sub>H<sub>22</sub>S<sub>2</sub> (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 (358 mg, 89% yield). M.p.=100-101°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>26</sub>H<sub>26</sub>S<sub>2</sub> (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 (268 mg, 89% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  159.3, 149.3, 135.6, 122.0, 119.0, 29.8, 29.1, 28.3 ppm. HRMS calcd for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub> (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%.

#### Reference

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### IX. Copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra

### diphenylsulfane

















#### (4-methoxyphenyl)(p-tolyl)sulfane





(3-chlorophenyl)(phenyl)sulfane

















#### (2-chlorophenyl)(phenyl)sulfane







#### (4-fluorophenyl)(phenyl)sulfane

100

150

200 ppm (t1) 0

0

50



(2-methoxyphenyl)(phenyl)sulfane





#### 4-(*m*-tolylthio)aniline



#### phenyl(*m*-tolyl)sulfane

ppm (t1)





biphenyl-4-yl(p-tolyl)sulfane


biphenyl-4-yl(4-chlorophenyl)sulfane







-0

S38





# 3-(o-tolylthio)pyridine



## 2-(phenylthio)thiophene









## naphthalen-1-yl(phenyl)sulfane



S42



## benzyl(phenyl)sulfane



## benzyl(p-tolyl)sulfane



benzyl(4-methoxyphenyl)sulfane



benzyl(4-chlorophenyl)sulfane



benzyl(o-tolyl)sulfane



benzyl(2-chlorophenyl)sulfane





50 150 100 200 ppm (t1)

- 0

0





benzyl(naphthalen-1-yl)sulfane



## butyl(phenyl)sulfane

















## cyclohexyl(3,4-dimethylphenyl)sulfane













phenyl(4-(trifluoromethyl)phenyl)sulfane



## 2-(phenylthio)benzoic acid



4-(phenylthio)benzoic acid



## 3-(phenylthio)benzoic acid

100

50

0

150

200 ppm (t1)





## 3-(phenylthio)benzonitrile

100

50

0

150

200

ppm (t1)

- 0



## 4-(phenylthio)benzonitrile



ppm (t1)
















## naphthalen-1-yl(octyl)sulfane



(4-chlorophenyl)(dodecyl)sulfane







1,4-bis(phenylthio)benzene

## 1,4-bis(hexylthio)benzene



## 1,4-bis(cyclohexylthio)benzene









## 1,6-bis(naphthalen-1-ylthio)hexane



S85



# 1,6-bis(pyridin-2-ylthio)hexane