Supporting Information

Copper nanopowder catalyzed cross-coupling of diaryl disulfides with aryl iodides in PEG-400

Xiang-mei Wu* and Guo-bing Yan

Department of Chemistry, College of ecology, Lishui University, Lishui, Zhejiang 323000, China. E-mail: lsxxm7162@163.com

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**Materials and Methods**

All commercial reagents were used as received without purification, and all solvents were of reagent grade. $^1$H NMR and $^{13}$C NMR spectra were recorded at 300 MHz and 75 MHz with Bruker Avance 300 spectrometer using CDCl$_3$ as solvent and tetramethyldisilane as internal standard. Melting points were obtained of a XT4A melting point apparatus and were uncorrected. Gas chromatography mass spectra (GC/MS) were recorded on a Saturn 2000GC/MS instrument. Detailed experimental procedures, $^1$H, $^{13}$C NMR spectra and GCMS for all compounds are available in the supporting information. Copper nanopowder was purchased from Aldrich, with an average diameter of 30-40 nm, as shown in technical information.

**General procedure for the coupling of aryl iodides and diaryl disulfides**

Copper nanopowder (0.05 mmol), aryl iodides (1.0 mmol), diaryl disulfides (0.5 mmol), KOH (2.0 mmol) and PEG-400 (2.0 mL) were taken in a 25 mL two-neck flask. The reaction mixture was stirred at 110 °C for 12 hours in air. After cooling to room temperature, the product was diluted with H$_2$O (5 mL) and extracted with EtOAc (4×10 mL). The extracts were combined and washed by brine (3×10 mL), dried over MgSO$_4$, filtered, and evaporated, and purified by chromatography on silica gel to obtain the desired products with ethyl acetate/hexane (v/v=1:5 ~ 1:100). The products were characterized by their spectral and analytical data and compared with those of the known compounds.

**Recycling of copper nanopowder and PEG-400**

The aforementioned procedure was used with 4-methoxyiodobenzene (1.0 mmol) and diphenyl disulfide (0.5 mmol), copper nanopowder (0.05 mmol), KOH (2.0 mmol) and PEG-400 (2.0 mL) in a 25 mL two-neck flask. The reaction mixture was stirred at 110 °C for 12 hours in air. After completion of the reaction, the desired products can be conveniently obtained by extraction with diethyl ether (5×10 mL). Then the reaction mixture was subjected to the vacuum for 1 hour to eliminate the moisture and trace organic solvents and reused for the next coupling reaction.

**Characterization data**

**Diphenyl sulfide (Table 2, entry 1)**

![Diphenyl sulfide](image)

Yield: 89%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.36-7.23 (m, 10H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 135.8, 131.0, 129.2, 127.0. GC-MS (EI, m/z): 186 [M+].

**4-Methylphenyl phenyl sulfide (Table 2, entry 2)**

![4-Methylphenyl phenyl sulfide](image)

Yield: 86%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.31-7.11 (m, 9 H), 2.33 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 137.6, 137.1, 132.3, 131.3, 130.1, 129.8, 129.1, 126.4,

3-Methylphenyl phenyl sulfide (Table 2, entry 3) [2]

Yield: 87%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.33-7.03 (m, 9 H), 2.30 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 139.1, 136.1, 135.3, 131.9, 130.8, 129.8, 128.4, 128.0, 126.9, 21.3. GC-MS (EI, m/z): 200 [M]+.

4-Methoxyphenyl phenyl sulfide (Table 2, entry 4) [1]

Yield: 84%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.40 (d, $J$ = 8.7 Hz, 2 H), 7.21-7.11 (m, 5 H), 6.87 (d, $J$ = 8.7 Hz, 2 H), 3.78 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 159.9, 138.6, 135.4, 129.0, 128.3, 125.8, 124.4, 115.0, 55.4. GC-MS (EI, m/z): 216 [M]+.

2-Methoxyphenyl phenyl sulfide (Table 2, entry 5) [3]

Yield: 73%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.35-7.24 (m, 6H), 7.08 (d, $J$ = 7.6 Hz, 1H), 6.92-6.85 (m, 2 H), 3.87 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 157.3, 134.4, 131.5, 129.2, 128.3, 127.1, 124.0, 121.2, 110.8, 55.9. GC-MS (EI, m/z): 216 [M]+.

3-Methoxynaphthyl phenyl sulfide (Table 2, entry 6) [4]

Yield: 83%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.38-7.19 (m, 6H), 6.91-6.85 (m, 2H), 6.79-6.74 (m, 1H), 3.73 (s, 3H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 160.1, 137.3, 135.3, 131.4, 130.0, 129.3, 127.3, 123.0, 116.0, 112.8, 55.3. GC-MS (EI, m/z): 216 [M]+.

3-Methylthiophenyl phenyl sulfide (Table 2, entry 7)

Yield: 82%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.37-7.07 (m, 9 H), 2.40 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 139.8, 137.0, 135.1, 131.5, 129.4, 129.3, 128.0, 127.4, 127.2, 125.0, 15.6. GC-MS (EI, m/z): 232 [M]+. Anal calcd for C$_{13}$H$_{12}$S$_2$ C, 67.20; H, 5.21. Found C, 67.12; H, 5.15.

3-Bromophenyl phenyl sulfide (Table 2, entry 8) [5]

Yield: 90%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.40-7.10 (m, 9 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 139.1, 134.0, 132.4, 132.3, 130.4, 129.7, 129.5, 128.4, 128.0,
123.0. GC-MS (EI, m/z): m/z = 264 [M]+.

2-Bromophenyl phenyl sulfide (Table 2, entry 9) \[^1\]

\[
\begin{array}{c}
\text{Br} \\
\text{S} \\
\text{H} \\
\end{array}
\]

Yield: 65%; pale yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.54 (d, \(J = 7.8\) Hz, 1 H), 7.46-7.35 (m, 5 H), 7.11 (d, \(J = 7.5\) Hz, 1 H), 7.01 (s, 1 H), 6.91 (d, \(J = 7.8\) Hz, 1 H). \(^1\)\(^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) 138.8, 133.5, 133.1, 132.9, 129.7, 129.6, 128.5, 127.9, 127.3, 123.1. GC-MS (EI, m/z): 264 [M]+.

4-Bromophenyl phenyl sulfide (Table 2, entry 10) \[^1\]

\[
\begin{array}{c}
\text{Br} \\
\text{S} \\
\text{H} \\
\end{array}
\]

Yield: 91%; pale yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.39-7.13 (m, 9 H). \(^1\)\(^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) 135.5, 134.8, 132.3, 132.1, 131.6, 129.4, 127.6, 120.9. GC-MS (EI, m/z): 264 [M]+.

4-Chlorophenyl phenyl sulfide (Table 2, entry 11) \[^1\]

\[
\begin{array}{c}
\text{Cl} \\
\text{S} \\
\text{H} \\
\end{array}
\]

Yield: 92%; pale yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.32-7.24 (m, 9 H). \(^1\)\(^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) 135.2, 134.7, 133.0, 132.0, 131.3, 129.3, 127.5. GC-MS (EI, m/z): 220 [M]+.

3-Fluorophenyl phenyl sulfide (Table 2, entry 12)

\[
\begin{array}{c}
\text{F} \\
\text{S} \\
\text{H} \\
\end{array}
\]

Yield: 90%; pale yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.43-7.30 (m, 5 H), 7.22-7.20 (m, 1 H), 7.04-7.02 (m, 1H), 6.95-6.87 (m, 2H). \(^1\)\(^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) 163.0 (164.7, 161.4, d, \(J = 246.8\) Hz), 139.3, 133.8, 132.6, 130.3, 129.5, 128.1, 125.1, 116.4 (116.5, 116.2, d, \(J = 22.5\) Hz), 113.5 (113.6, 113.3, d, \(J = 22.5\) Hz). GC-MS (EI, m/z): 204 [M]+. Anal calecd for C\(_{12}\)H\(_9\)SF C, 70.56; H, 4.44. Found C, 70.53; H, 4.39.

4-Fluorophenyl phenyl sulfide (Table 2, entry 13) \[^6\]

\[
\begin{array}{c}
\text{F} \\
\text{S} \\
\text{H} \\
\end{array}
\]

Yield: 91%; pale yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.40-7.35 (m, 2 H), 7.31-7.22 (m, 5 H), 7.05-7.00 (m, 2 H). \(^1\)\(^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) 162.4 (164.0, 160.8, d, \(J = 240.0\) Hz), 136.7, 134.2, 134.1, 130.1, 129.9, 129.2, 126.8, 116.5 (116.6, 116.3, d, \(J = 22.5\) Hz). GC-MS (EI, m/z): 204 [M]+.

4-Nitrophenyl phenyl sulfide (Table 2, entry 14) \[^1\]

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{H} \\
\end{array}
\]

4
Yield: 68%; pale yellow solid. mp: 54-56 °C (lit. 54.8-55.5 °C ). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.05 (d, $J = 8.8$ Hz, 2 H), 7.55-7.44 (m, 5 H), 7.16 (d, $J = 8.8$ Hz, 2 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 148.5, 145.4, 138.7, 134.7, 130.5, 130.0, 129.7, 126.7, 124.8, 124.0. GC-MS (EI, m/z): 231 [M]+.

2-thiophenyl phenyl sulfide (Table 2, entry 15) $^{[3]}$

Yield: 64%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.51-7.48 (m, 1 H), 7.32-7.18 (m, 7 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 138.6, 136.0, 131.2, 129.0, 127.9, 127.6, 127.2, 126.1. GC-MS (EI, m/z): 231 [M]+.

4-Methoxyphenyl 4-methylphenyl sulfide (Table 2, entry 16) $^{[1,4]}$

Yield: 89%; white solid. mp 45-46 °C (lit. 46 °C ). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.34 (d, $J = 8.4$ Hz, 2 H), 7.12 (d, $J = 7.9$ Hz, 2 H), 7.04 (d, $J = 7.9$ Hz, 2 H), 6.84 (d, $J = 8.4$ Hz, 2 H), 3.77 (s, 3 H), 2.28 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 159.5, 136.1, 134.3, 129.8, 129.4, 125.7, 114.9, 55.3, 20.9. GC-MS (EI, m/z): 231 [M]+.

4-Methoxyphenyl 4-chlorophenyl sulfide (Table 2, entry 17) $^{[7]}$

Yield: 86%; pale yellow oil. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.38 (d, $J = 8.4$ Hz, 2 H), 7.18 (d, $J = 8.4$ Hz, 2 H), 7.06 (d, $J = 8.4$ Hz, 2 H), 6.88 (d, $J = 8.4$ Hz, 2 H), 3.80 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 160.1, 137.4, 135.5, 135.4, 131.7, 129.5, 129.0, 124.0, 115.2, 55.3. GC-MS (EI, m/z): 231 [M]+.

4-Methoxyphenyl 4-bromophenyl sulfide (Table 2, entry 18) $^{[8]}$

Yield: 85%; pale yellow solid, mp 57-59 °C (lit. 60 °C ). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.38 (d, $J = 7.2$ Hz, 2 H), 7.31 (d, $J = 7.2$ Hz, 2 H), 6.98 (d, $J = 7.2$ Hz, 2 H), 6.88 (d, $J = 7.2$ Hz, 2 H), 3.80 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 160.1, 138.2, 135.6, 131.9, 129.5, 127.3, 126.2, 123.5, 119.4, 115.1, 55.4. GC-MS (EI, m/z): 296 [M]+.

3-Pyridi 4-methoxyphenyl sulfide (Table 2, entry 19) $^{[4,7]}$

Yield: 76%; white solid, mp 50-52 °C (lit. 51-52 °C ). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.40-8.39 (m, 1 H), 7.53 (d, $J = 7.8$ Hz, 2 H), 7.41 (m, 1 H), 6.95 (d, $J = 7.8$ Hz, 3 H), 6.78 (d, $J = 8.1$ Hz, 1 H), 3.85 (s, 3 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 162.8, 160.7, 149.4, 137.2, 136.6, 121.1, 120.4, 119.4, 115.3, 55.4. GC-MS (EI, m/z): 231 [M]+.
3-Pyridi phenyl sulfide (Table 2, entry 20) \[^9\]

![Structure](attachment:image.png)

Yield: 78%; pale yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 8.42 (d, \(J = 4.0\) Hz, 1 H), 7.60-7.57 (m, 2 H), 7.46-7.40 (m, 4 H), 7.00-6.96 (m, 1 H), 6.89-6.87 (m, 1 H). \(^13\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) 161.5, 149.5, 136.7, 134.9, 131.1, 129.6, 129.1, 121.4, 119.9. GC-MS (EI, m/z): 231 [M]+.

2-Aminophenyl phenyl sulfide (Table 2, entry 21) \[^11\]

![Structure](attachment:image.png)

Yield: 80%; pale yellow oil. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.49 (d, \(J = 6.9\) Hz, 1 H), 7.29-7.10 (m, 6 H), 6.78 (d, \(J = 7.0\) Hz, 2 H), 4.30 (s, 2 H). \(^13\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) 148.8, 137.6, 136.8, 131.4, 129.1, 126.4, 125.5, 118.9, 115.5, 114.3. GC-MS (EI, m/z): 201 [M]+.

References