Supporting Information

Title: 8-hydroxyquinolin-N-oxide Promoted Copper-Catalyzed C-S Cross Coupling of Thiols with Aryl Iodides

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General Experimental Methods: 1H NMR and 13C NMR spectra were recorded on Bruker Avance ARX-400. Anhydrous solvents were obtained as follows: DMSO from CaH2. All other solvents were reagent grade. All moisture sensitive reactions were carried out in flame dried flask under argon atmosphere.

General Procedure: In an argon-filled flask, it was charged with CuI (20 mg, 0.1 mmol, 10 mol%), L5 (32 mg, 0.2 mmol, 20 mol%), Cs2CO3 (652 mg, 2 mmol) and thiophenol (1 mmol). The aryl iodide (1.5 mmol) and DMSO (1 ml) were injected into the flask under argon atmosphere. The contents were then stirred at 80°C for 24 hours. After allowing the mixture to cool to room temperature, the mixture was diluted with ethyl acetate (20 ml) and filtered. The filtrate was washed with water (2 × 10 ml). The organic phase was dried with Na2SO4, filtered, and the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel to give desired aryl sulfide.

Synthesis of phenols from aryl Iodides: Table 2

\[ \text{3a} \]

p-Tolylthiophenol (3a): The general procedure was used to convert 4-iodotoluene and thiophenol to the title product. Purification by flash chromatography (hexane as
the eluent) gave the analytically pure product as a clear oil (183 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31-7.27 (m, 6H), 7.20-7.17 (q, 1H), 7.14-7.12 (d, $J = 8.00$ Hz, 2H), 2.34 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 137.6, 137.1, 132.3, 131.3, 130.0, 129.8, 129.0, 126.4, 21.1.

![Chemical Structure](image)

**o-Tolylthiophenol (3b):** The general procedure was used to convert 2-iodotoluene and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (191 mg, 95% yield). $^1$H NMR (400 MHz, CD$_2$OD): $\delta$ 7.28-7.12 (m, 9H), 2.32 (s, 3H). $^{13}$C NMR (125 MHz, CD$_2$OD): $\delta$ 141.3, 137.6, 134.8, 134.4, 131.7, 130.4, 130.2, 129.3, 127.9, 127.4, 20.7.

![Chemical Structure](image)

**3-chlorophenyl phenyl sulfide (3d):** The general procedure was used to convert 1-Chloro-3-iodobenzene and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (196 mg, 90% yield). $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 7.42-7.31 (m, 5H),
7.24-7.14 (m, 4H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 138.8, 134.9, 133.9, 132.3, 129.5, 127.9, 127.9, 126.7.

4-chlorophenyl phenyl sulfide (3e): The general procedure was used to convert 1-Chloro-4-iodobenzene and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (200 mg, 91% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36-7.27 (m, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$135.1, 134.7, 133.0, 132.0, 131.3, 129.3, 129.3, 127.4.

2-nitrodiphenylsulfide (3f): The general procedure was used to convert 1-Iodo-2-nitrobenzene and thiophenol to the title product. Purification by flash chromatography (hexane / ethyl acetate [20:1] as the eluent) gave the analytically pure product as a yellow oil (210 mg, 91% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22-8.21 (dd, $J$ = 7.20 Hz, 1H), 7.60-7.57 (m, 2H), 7.49-7.47 (dd, $J$ = 3.60 Hz, 3H), 7.35-7.31 (q, $J$ = 6.80 Hz, 1H). 7.23-7.18 (q, $J$ = 7.20 Hz, 1H), 6.87-6.85 (dd, $J$ = 7.20 Hz, 1H) $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 139.4, 135.9, 133.4, 131.1, 130.1, 129.9, 128.3, 125.7, 124.9.

3-nitrodiphenyl sulfide (3g): The general procedure was used to convert 1-Iodo-3-nitrobenzene and thiophenol to the title product. Purification by flash chromatography (hexane / ethyl acetate [20:1] as the eluent) gave the analytically pure product as a yellow oil (200 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$
8.03-7.98 (m, 2H), 7.51-7.47 (m, 3H), 7.43-7.39 (m, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 148.9, 140.6, 134.3, 133.4, 132.4, 129.8, 129.6, 128.9, 123.3, 120.9.

4-nitrodiphenyl sulfide (3h): The general procedure was used to convert 1-Iodo-4-nitrobenzene and thiophenol to the title product. Purification by flash chromatography ((hexane / ethyl acetate [20:1] as the eluent) gave the analytically pure product as a yellow oil (213 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.07-8.05 (d, $J = 8.80$ Hz, 2H), 7.55-7.53 (m, 2H), 7.46-7.45 (m, 3H), 7.19-7.16 (d, $J = 9.20$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 148.3, 145.7, 134.6, 130.9, 130.0, 129.6, 126.9, 124.0.

4-Phenylsulfanyl-benzoic acid methyl ester (3i): The general procedure was used to convert Methyl-4-iodobenzoate and thiophenol to the title product. Purification by flash chromatography (hexane / ethyl acetate [6:1] as the eluent) gave the analytically pure product as a white solid (220 mg, 90% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90-7.88 (d, $J = 8.40$ Hz, 2H), 7.50-7.47 (m, 2H), 7.39-7.38 (m, 3H), 7.21-7.19 (d, $J = 8.40$ Hz, 2H), 3.89 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 166.7, 144.3, 133.6, 132.8, 130.1, 129.6, 128.6, 127.9, 127.8, 51.9.

(4-methyl-2-nitro-phenyl)-phenyl sulfide (3j): The general procedure was used to convert 4-iodo-3-nitrotoluene and thiophenol to the title product. Purification by flash chromatography ((hexane / ethyl acetate [20:1] as the eluent) gave the analytically pure product as a yellow oil (226 mg, 92% yield). $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (s, 1H), 7.57-7.55 (m, 2H), 7.47-7.45 (m, 3H), 7.16-7.13 (m, 1H), 6.77-6.75 (d, $J$
= 8.00 Hz, 1H), 2.35 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 135.6, 135.5, 135.4, 134.3, 131.8, 129.9, 129.6, 128.7, 125.7, 20.3.

**2-aminophenyl phenyl sulfide (3k):** The general procedure was used to convert 2-iodobenzenamine and thiophenol to the title product. Purification by flash chromatography (hexane / ethyl acetate [10:1] as the eluent) gave the analytically pure product as a clear oil (170 mg, 85% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47-7.45 (dd, $J = 7.60$ Hz, 1H), 7.25-7.20 (q, $J = 12.40$ Hz, 3H), 7.13-7.08 (q, $J = 13.60$ Hz, 3H), 6.80-6.74 (q, $J = 15.6$ Hz, 2H), 4.29 (s, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 148.8, 137.4, 136.8, 131.1, 128.9, 126.4, 125.4, 118.7, 115.3, 114.3.

**(p-bromophenyl)-phenyl sulfide (3l):** The general procedure was used to convert 1-Bromo-4-iodobenzene and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (255 mg, 96% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42-7.28 (m, 7H), 7.18-7.16 (d, $J = 8.8$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 135.6, 135.0, 132.3, 132.2, 131.6, 129.4, 127.6, 120.9.

**3-pyridyl phenyl sulfide (3m):** The general procedure was used to convert 3-iodo-pyridine and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (172 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.56-8.55 (s, 1H), 8.46-8.45 (q, $J = 4.8$ Hz, 1H), 7.60-7.58 (d, $J = 8.00$ Hz, 1H), 7.39-7.29 (m, 5H), 7.22-7.19 (q, $J = 4.80$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 151.1, 147.8, 137.9, 133.9, 133.6, 131.7, 129.5, 127.8, 123.9.
2-Brom-4-Chlor-diphenyl sulfide (3n): The general procedure was used to convert 1-chloro-3-bromo-4-iodobenzene and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (263 mg, 88% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57 (s, 1H), 7.45-7.38 (m, 5H), 7.13-7.10 (dd, $J = 2.4$ Hz, 1H), 6.84-6.82 (d, $J = 8.4$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 137.6, 133.3, 132.9, 132.7, 130.8, 129.7, 128.6, 128.1, 123.7.

2-(4-tolylsulfanyl)-phenyl bromide (3o): The general procedure was used to convert 4-Iodotoluene and 2-bromo thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a white solid (260 mg, 93% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.54-7.52 (d, $J = 7.6$ Hz, 1H), 7.40-7.38 (d, $J = 8.00$ Hz, 2H), 7.23-7.21 (d, $J = 8.00$ Hz, 1H), 7.13-7.08 (m, 1H), 7.00-6.96 (m, 1H), 6.82-6.79 (dd, $J = 7.60$ Hz, 1H), 2.38(s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 139.8, 139.0, 134.4, 132.9, 130.5, 128.7, 128.7, 127.7, 126.6, 122.0, 21.3.

2-tolyl-4-tolyl sulfide (3p): The general procedure was used to convert 4-Iodotoluene and 2-Methylbenzenethiol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a white solid (205mg, 96% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23-7.09 (m, 8H), 2.39 (s, 3H), 2.34 (s, 3H) $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 138.8, 136.9, 135.2, 131.7, 131.4, 131.0, 130.4, 130.0, 127.1, 126.6, 21.1, 20.5.
4, 4’-dimethyldiphenyl sulfide (3q): The general procedure was used to convert 4-Iodotoluene and 4-Methylbenzenethiol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a white solid (210mg, 98% yield). \[^1\]H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 7.24-7.22\ (d, J = 8.40\ Hz, 4H), 7.11-7.09\ (d, J = 8.40\ Hz, 4H), 2.32\ (s, 6H)\) \[^1\]C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta 136.9, 132.6, 131.0, 129.9, 21.0.\)

\[\text{3q}\]

1-methoxy-4-[4-methylphenyl]thio] benzene (3r): The general procedure was used to convert 4-Iodotoluene and 4-Methoxybenzenethiol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a white solid (215mg, 95% yield). \[^1\]H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 7.39-7.37\ (d, J = 8.80\ Hz, 2H), 7.16-7.14\ (d, J = 8.00\ Hz, 2H), 7.09-7.07\ (d, J = 8.00\ Hz, 2H), 6.89-6.87\ (d, J = 8.80\ Hz, 2H), 3.81\ (s, 3H), 2.31\ (s, 3H).\) \[^1\]C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta 159.4, 136.1, 134.3, 130.1, 129.7, 129.4, 125.7, 118.6, 114.8, 55.3, 20.9.\)

\[\text{3r}\]

4-[(4-methylphenyl)thio]benzenamine (3s): The general procedure was used to convert 4-Iodotoluene and 4-Aminobenzenethiol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a white solid (195 mg, 90% yield). \[^1\]H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta 7.28-7.26\ (dd, J = 6.40\ Hz, 2H), 7.09-7.02\ (m, 4H), 6.66-6.64\ (d, J = 8.40\ Hz, 2H), 3.76\ (s, 2H), 2.28\ (s, 3H).\) \[^1\]C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta 146.6, 135.5, 135.4, 135.2, 129.6, 128.2, 121.6, 115.7, 20.9.\)

\[\text{3s}\]
2-[(4-methylphenyl)thio]benzenamine (3t): The general procedure was used to convert 4-Iodotoluene and 2-Aminobenzenethiol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a white solid (198 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.44-7.42 (dd, $J = 7.60$ Hz, 1H), 7.23-7.19 (q, $J = 6.40$ Hz, 1H), 7.05-7.00 (m, 4H), 6.78-6.72 (q, $J = 7.60$ Hz, 2H), 4.26 (s, 2H), 2.27 (s, 3H). $^{13}$CNMR (125 MHz, CDCl$_3$): δ 148.5, 137.1, 135.5, 133.0, 130.8, 129.8, 127.1, 118.7, 115.3, 115.3, 20.9.
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Table 2, 3r