Supporting Information
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Supporting Information

Efficient Copper-Catalyzed S-Arylation of Thiols with Aryl Bromides and Chlorides

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I General information

All reagents unless otherwise noted were obtained from commercial source (purity>99%) and used without further purification. The reactions were carried out under argon atmosphere and the products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90°C) and ethyl acetate as eluate. Compounds described in the literature were characterized by comparison of their $^1$H NMR, $^{13}$C NMR spectra and MS to the reported data. $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ and chemical shifts were reported in parts per million relative to TMS. Gas chromatography analyses were performed with an FID detector. High resolution mass spectrometric data (HRMS) were performed on HPLC-Q-Tof MS.
II Experimental procedures for all compounds

The 1,2,3,4-tetrahydro-quinoline-8-ol (L) was prepared as literature reported

General Procedure for the Cross-Coupling of Thiols and Aryl Halides

For monothioethers, a flame-dried test tube with a magnetic stirring bar was charged with CuBr (14 mg, 0.1 mmol), ligand (15 mg, 0.1 mmol), Cs₂CO₃ (326 mg, 1.0 mmol), thiol (0.5 mmol), aryl halide (0.75 mmol) and DMF (1.5 mL) under Ar. The mixture reacted at 130 °C for 48 h, then cooled to room temperature and the resulting mixture was extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent of petroleum ether and ethyl acetate.

For symmetrical bis-thioethers, a flame-dried test tube with a magnetic stirring bar was charged with CuBr (7 mg, 0.05 mmol), ligand (15 mg, 0.1 mmol), Cs₂CO₃ (489 mg, 1.5 mmol), thiophenol (1.1 mmol), aryl dihalide (0.5 mmol) and DMF (1.5 mL) under Ar. The mixture reacted at 130 °C for 48 h, then cooled to room temperature and the resulting mixture was extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent of petroleum ether and ethyl acetate.

For unsymmetrical bis-thioethers, firstly synthesized 4-bromophenyl phenyl thioether as previous operation for those of monothioethers, then the residue was purified by column chromatography on silica gel. After that, a flame-dried test tube with a magnetic stirring bar was charged with CuBr (14 mg, 0.1 mmol), ligand (15 mg, 0.1 mmol), Cs₂CO₃ (326 mg, 1.0 mmol), other thiol (0.5 mmol), 4-bromophenyl phenyl thioether (0.75 mmol) and DMF (1.5 mL) under Ar. The mixture reacted at 130 °C for 48 h, then cooled to room temperature and the resulting mixture was extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent of petroleum ether and ethyl acetate.

Diphenyl thioether (2a)
Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving colorless oil. CAS: 139-66-2.

\[ \text{4-Tolyl phenyl thioether (2b)} \]

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving colorless oil. CAS: 3699-01-2.

\[ \text{1-Naphyl phenyl thioether (2f)} \]

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving colorless oil. CAS: 7570-98-1.

\[ \text{4-Aminophenyl phenyl thioether (2c)} \]

Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/3) giving pale solid. mp 95.7-96.2 °C (Lit.\textsuperscript{4b} mp 96-96.5 °C). CAS: 1135-14-4.
6.69 (d, J=8.4 Hz, 2H), 3.98 (brs, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ=146.8, 139.7, 136.1, 128.9, 127.6, 125.4, 121.1, 116.1. GC-MS (EI, m/z): 201 [M]$^+$.  

2-(phenylthio)pyridine (2e)$^{4a}$

![Structure of 2-(phenylthio)pyridine](image)

Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (2/25) giving colorless oil. CAS: 3111-54-4.

$^1$H NMR (400 MHz, CDCl$_3$) δ=8.41 (d, J=4.4 Hz, 1H), 7.60-7.57 (m, 2H), 7.46-7.39 (m, 4H), 6.99-6.96 (t, J=6.2 Hz, 1H), 6.87 (d, J=8.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ=161.6, 149.6, 136.8, 135.0, 131.0, 129.7, 129.2, 121.3, 119.9. GC-MS (EI, m/z): 186 [M]$^+$; MS (API, m/z) 188 [M + H]$^+$.  

2-(phenylthio)benzonitrile (2g)$^{5a,b}$

![Structure of 2-(phenylthio)benzonitrile](image)

Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (3/20) giving slightly yellow solid. mp 56.1-57.1 °C (Lit.$^{5b}$ mp 56.5-58 °C). CAS: 91804-55-6.

$^1$H NMR (400 MHz, CDCl$_3$) δ=7.64 (d, J=8.0 Hz, 1H), 7.49-7.47 (m, 2H), 7.43-7.38 (m, 4H), 7.28-7.24 (m, 1H), 7.13 (d, J=8.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ=142.4, 133.7, 133.6, 133.0, 132.0, 130.0, 129.8, 129.0, 126.5, 117.0, 113.0. GC-MS (EI, m/z): 211 [M]$^+$.  

Phenyl 4-(trifluoromethyl)phenyl sulfide (2h)$^{5a}$

![Structure of Phenyl 4-(trifluoromethyl)phenyl sulfide](image)

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving colorless oil. CAS: 53451-90-4.

$^1$H NMR (400 MHz, CDCl$_3$) δ=7.49-7.47 (m, 4H), 7.41-7.38 (m, 3H), 7.27-7.25 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ=143.0, 133.7 (2C), 132.6, 129.9 (2C), 128.8, 128.4 (2C), 128.3 (q, $^2$J$_{C,F}=32.6$ Hz), 125.9 (d, $^1$J$_{C,F}=3.5$ Hz), 124.2 (q, $^1$J$_{C,F}=271.6$ Hz). GC-MS (EI, m/z): 254 [M]$^+$.  

1-(4-(phenylthio)phenyl)ethanone (2i)$^{4a-b}$

![Structure of 1-(4-(phenylthio)phenyl)ethanone](image)
Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/40) giving white solid. mp 64-64.8 °C (Lit.\textsuperscript{3b} mp 64-66 °C). CAS: 10169-55-8.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta=7.82\) (d, \(J=8.4\) Hz, 1H), 7.51-7.48 (m, 2H), 7.41-7.39 (m, 3H), 7.20 (d, \(J=8.4\) Hz, 2H), 2.55 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta=197.3, 145.1, 134.6, 134.0, 132.2, 129.8, 129.0, 128.9, 127.5, 26.6\). GC-MS (EI, m / z): 228 [M]\(^+\).

\textbf{4-Bromophenyl phenyl thioether}\textsuperscript{6}

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving colorless oil. CAS: 65662-88-6.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta=7.39\) (d, \(J=8.4\) Hz, 2H), 7.36-7.24 (m, 5H), 7.16 (d, \(J=8.4\) Hz, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta=135.7, 135.0, 132.4, 132.2, 131.7, 129.5, 127.7, 121.0\). GC-MS (EI, m / z): 264 [M]\(^+\), 266 [M+2]\(^+\).

\textbf{4-Chlorophenyl phenyl thioether (2j)}\textsuperscript{7}

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving colorless oil. CAS: 13343-26-5.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta=7.35-7.25\) (m, 9H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta=135.3, 134.8, 133.2, 132.2, 131.5, 129.49, 129.48, 127.6\). GC-MS (EI, m / z): 220 [M]\(^+\), 222 [M+2]\(^+\).

\textbf{4-(4-(trifluoromethyl)phenylthio)aniline (2l)}\textsuperscript{8}

Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/6) giving slightly yellow solid. mp 89.6-90.5 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta=7.42\) (d, \(J=8.4\) Hz, 2H), 7.33 (d, \(J=8.4\) Hz, 2H), 7.11 (d, \(J=8.4\) Hz, 2H), 6.72 (d, \(J=8.4\) Hz, 2H), 3.98 (brs, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta=147.8, 145.9, 137.1, 126.1, 125.7, 118.4, 116.3\). GC-MS (EI, m / z): 269 [M]\(^+\).

\textbf{2-(o-tolylthio)benzonitrile (2m)}\textsuperscript{9}
Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/80) giving slightly yellow solid. mp 65-65.6 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$=7.63 (d, $J$=7.6 Hz, 1H), 7.47 (d, $J$=7.6 Hz, 1H), 7.38-7.34 (m, 3H), 7.25-7.18 (m, 2H), 6.84 (d, $J$=8.0 Hz, 1H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=143.0, 142.2, 135.7, 133.8, 133.1, 131.3, 130.2, 130.0, 128.1, 127.4, 125.8, 117.1, 111.7, 20.9. GC-MS (EI, m / z): 225 [M]$^+$.  

1-(4-(o-tolylthio)phenyl)ethanone (2n)

Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate / petroleum ether (1/20) giving slightly yellow solid. mp 57.7-59 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$=7.80 (d, $J$=8.8 Hz, 2H), 7.52 (d, $J$=8.0 Hz, 1H), 7.35-7.34 (m, 2H), 7.25 (m, 1H), 7.08 (d, $J$=8.4 Hz, 2H), 2.54 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=197.2, 145.1, 142.4, 136.0, 134.3, 131.3, 130.5, 129.9, 129.1, 127.3, 126.5, 26.6, 20.8. HRMS (ESI) calcd for C$_{15}$H$_{14}$OS (M+Na)$^+$ 265.0663, found 265.0656.  

1,4-bis(phenylthio)benzene (3a)$^{10a-b}$

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving white solid. mp 81.6-82.1 °C (Lit.$^{10b}$ mp 81.3 °C). CAS: 3459-94-7.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$=7.35 (d, $J$=7.2 Hz, 4H), 7.32-7.28 (t, $J$=7.2 Hz, 4H), 7.27-7.23 (t, $J$=7.2 Hz, 2H), 7.21 (s, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=135.2, 135.1, 131.6, 131.3, 129.5, 127.6. GC-MS (EI, m / z): 294 [M]$^+$.  

1,3-bis(phenylthio)benzene (3b)$^{10a}$

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving colorless oil. CAS: 2974-10-9.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$=7.33 (d, $J$=7.4 Hz, 4H), 7.28-7.20 (m, 7H), 7.18-7.10 (m, 3H); $^{13}$C
NMR (100 MHz, CDCl₃): δ=137.8, 134.6, 132.0, 131.4, 129.8, 129.4, 128.5, 127.7. GC-MS (EI, m/z): 294 [M]+.

1,2-bis(phenylthio)benzene (3c)

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving colorless oil. CAS: 3379-36-0.

^{1}H NMR (400 MHz, CDCl₃) δ=7.37-7.21 (m, 10H), 7.14-7.08 (m, 4H); ^{13}C NMR (100 MHz, CDCl₃): δ=137.5, 134.6, 131.9, 131.5, 129.5, 129.2, 127.6. GC-MS (EI, m/z): 294 [M]+.

1-phenylsulfanyl-4-p-tolylsulfanyl-benzene (4a)

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving white solid. mp 59-60 °C (Lit.^{11b} mp 55.5 °C). CAS: 96802-31-2.

^{1}H NMR (400 MHz, CDCl₃) δ=7.34-7.24 (m, 7H), 7.21 (d, J=8.0 Hz, 2H), 7.16-7.14 (m, 4H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl₃): δ=138.2, 136.7, 135.7, 133.9, 132.9, 131.7, 131.2, 130.6, 130.4, 130.1, 129.4, 127.3, 21.3. GC-MS (EI, m/z): 308 [M]+.

1-phenylsulfanyl-4-o-tolylsulfanyl-benzene (4b)

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving colorless oil.

^{1}H NMR (400 MHz, CDCl₃) δ=7.34-7.28 (m, 5H), 7.24-7.20 (m, 5H), 7.15 (d, J=8.0 Hz, 1H), 7.08 (d, J=8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl₃): δ=140.0, 135.7, 135.6, 133.8, 133.6, 133.1, 131.7, 131.2, 130.9, 129.9, 129.4, 128.5, 127.3, 127.0, 20.8. GC-MS (EI, m/z): 308 [M]+.

(4-chlorophenyl)(4-(phenylthio)phenyl)sulfane (4c)

Following the general procedure, the crude product was purified over a silica gel column using petroleum ether giving white solid. mp 92.3-92.8 °C (Lit.^{12b} mp 92-93 °C). CAS: 60420-81-7.

^{1}H NMR (400 MHz, CDCl₃) δ=7.37 (d, J=8.0 Hz, 2H), 7.32-7.26 (m, 3H), 7.24-7.20 (m, 8H); ^{13}C
NMR (100 MHz, CDCl₃): δ=136.0, 134.7, 134.2, 134.0, 133.5, 132.4, 131.9, 131.7, 131.0, 129.6, 129.5, 127.8. GC-MS (EI, m / z): 328 [M⁺], 330 [M+2⁺].

III Detail information about side-reaction process

Scheme 1. Control experiment of 4-bromoanisole and phenthiol. Reaction Conditions: 4-bromoanisole or anisole (0.75 mmol), thiols (0.5 mmol), CuBr (20 mol%), L (20 mol%), Cs₂CO₃ (1 mmol) and DMF (1.5 mL) stirred at 130 °C for 48 h (1) and 24h (2) under argon. GC yield.

IV References

V Copies of $^1$H NMR, $^{13}$C NMR spectra for all the compounds

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR (400 MHz, CDCl3)

13C NMR (100 MHz, CDCl3)
1H NMR (400 MHz, CDCl₃)

13C NMR (100 MHz, CDCl₃)
1H NMR (400 MHz, CDCl₃)

13C NMR (100 MHz, CDCl₃)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
1H NMR (400 MHz, CDCl₃)

13C NMR (100 MHz, CDCl₃)
**1H NMR (400 MHz, CDCl₃)**

**13C NMR (100 MHz, CDCl₃)**