A New Family of Nucleophiles for Photoinduced, Copper-Catalyzed Cross-Couplings via Single-Electron Transfer: Reactions of Thiols with Aryl Halides Under Mild Conditions (0 °C)

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Supporting Information

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I. General Information

Unless specified otherwise, all reagents were purchased from commercial vendors and used without further purification. CH₃CN was dried and degassed by passage through a column of activated alumina and sparging with N₂ gas. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc.

¹H and ¹³C spectra were collected at room temperature on Varian 300, 400, or 500 MHz NMR spectrometers. ¹H and ¹³C NMR spectra are reported in ppm relative to tetramethylsilane, using the residual solvent resonance as an internal standard.

Single-crystal X-ray diffraction studies were carried out at the Caltech Division of Chemistry and Chemical Engineering X-ray Crystallography Facility on a Bruker KAPPA APEX II diffractometer. Data were collected at 100 K using Mo Kα radiation (λ = 0.71073 Å). Structures were solved by the direct method using SHELXS and refined against F2 on all data by full-matrix least-squares with SHELXL-97.

Elemental analysis was performed by Robertson Microlit Laboratories (Ledgewood, NJ). Fluorescence measurements (excitation and emission spectra) were taken in dry, degassed acetonitrile in a 1-cm quartz cuvette using a Horiba Jobin Yvon Fluorolog-3 instrument in the Beckmann Institute Laser Resource Center at Caltech.
II. Photoinduced, Copper-Catalyzed C-S Cross Couplings

**General procedure, Table 1.** Under an atmosphere of N$_2$, a borosilicate glass tube was charged in turn with CuI (0.033 mmol, 10%), NaO$t$-Bu (0.33 mmol, 1.0 equiv), CH$_3$CN (1.0 mL), 1-iodo-3,5-dimethylbenzene (48 µL, 0.33 mmol, 1.0 equiv), and thiophenol (34 µL, 0.33 mmol, 1.0 equiv). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 5 h, Et$_2$O (10 mL) and dodecane (76 µL) were added, and the reaction was analyzed by GC.

**General procedure, Table 2, 3, and 4.** Under an atmosphere of N$_2$, a borosilicate glass tube was charged in turn with CuI (0.10 mmol, 10%), NaO$t$-Bu (1.0 mmol, 1.0 equiv), CH$_3$CN (3.0 mL), the aryl halide (1.0 mmol, 1.0 equiv), and the aryl thiol (1.0 mmol, 1.0 equiv). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 5–24 h, the volatiles were removed under reduced pressure. The residue was suspended in Et$_2$O, and the mixture was filtered through a short plug of Celite. The filtrate was concentrated, and the residue was purified by column chromatography.

**3,5-Dimethylphenyl phenyl sulfide (Table 2, entry 1) [457625-29-5].** According to the general procedure, 1-iodo-3,5-dimethylbenzene (144 µL, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO$_2$, hexanes). Run 1: 194 mg (91% yield). Run 2: 180 mg (84% yield).

**Gram-scale reaction (Table 2, entry 1).** According to the general procedure, 1-iodo-3,5-dimethylbenzene (1.54 mL, 8.0 mmol, 1.0 equiv) and thiophenol (822 µL, 8.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. After purification by column chromatography (SiO$_2$, hexanes), 1.40 g (82% yield) of 3,5-dimethylphenyl phenyl sulfide was isolated as a colorless oil.

**1-Naphthyl phenyl sulfide (Table 2, entry 2) [7570-98-1].** According to the general procedure, 1-iodonaphthalene (146 µL, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO$_2$, hexanes). Run 1: 198 mg (84% yield). Run 2: 189 mg (80% yield).
2-Fluorophenyl phenyl sulfide (Table 2, entry 3) [61900-51-4]. According to the general procedure, 2-fluoroiodobenzene (117 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO₂, hexanes). Run 1: 161 mg (79% yield). Run 2: 158 mg (77% yield).

2-Aminophenyl phenyl sulfide (Table 2, entry 4) [134-94-7]. According to the general procedure, 2-aminooiodobenzene (219 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 8 h. The product (yellow oil) was purified by column chromatography (SiO₂, hexanes → 1:10 Et₂O:hexanes). Run 1: 149 mg (74% yield). Run 2: 152 mg (76% yield).

2,4-Dimethylphenyl phenyl sulfide (Table 2, entry 5) [16704-47-5]. According to the general procedure, 1-iodo-2,4-dimethylbenzene (144 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO₂, hexanes). Run 1: 172 mg (80% yield). Run 2: 161 mg (75% yield).

2,6-Dimethylphenyl phenyl sulfide (Table 2, entry 6) [54088-93-6]. According to the general procedure, 1-iodo-2,6-dimethylbenzene (144 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 8 h. The product (colorless oil) was purified by column chromatography (SiO₂, hexanes): 158 mg (74% yield). Run 2: 152 mg (71% yield).
4-Nitrophenyl phenyl sulfide (Table 2, entry 7) [952-97-6]. According to the general procedure, 1-iodo-4-nitrobenzene (249 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (pale-yellow oil) was purified by column chromatography (SiO$_2$, hexanes → 1:1 Et$_2$O:hexanes). Run 1: 207 mg (90% yield). Run 2: 206 mg (89% yield).

4-Cyanophenyl phenyl sulfide (Table 2, entry 8) [51238-46-1]. According to the general procedure, 4-iodo-benzonitrile (229 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO$_2$, hexanes → 1:10 Et$_2$O:hexanes). Run 1: 174 mg (82% yield). Run 2: 163 mg (76% yield).

4-Methoxyphenyl phenyl sulfide (Table 2, entry 9) [5633-57-8]. According to the general procedure, 1-iodo-4-methoxybenzene (234 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO$_2$, hexanes). Run 1: 171 mg (79% yield). Run 2: 169 mg (78% yield).

3-(Phenylthio)pyridine (Table 2, entry 10) [28856-77-1]. According to the general procedure, 3-iodopyridine (205 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO$_2$, 1:5 EtOAc:hexanes). Run 1: 155 mg (83% yield). Run 2: 150 mg (80% yield).

5-(Phenylthio)-1H-indole (Table 2, entry 11) [163258-14-8]. According to the general procedure, 5-iodoindole (243 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO$_2$, hexanes). Run 1: 173 mg (81% yield). Run 2: 167 mg (79% yield).
equiv) were reacted at 0 °C for 5 h. The product (colorless solid) was purified by column chromatography (SiO₂, 1:10 EtOAc:hexanes). Run 1: 145 mg (64% yield). Run 2: 138 mg (61% yield).

3-(Phenylthio)thiophene (Table 2, entry 12) [16718-11-9]. According to the general procedure, 3-iodothiophene (210 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless solid) was purified by column chromatography (SiO₂, hexanes). Run 1: 138 mg (72% yield). Run 2: 135 mg (70% yield).

2-(Phenylthio)thiophene (Table 2, entry 13) [16718-12-0]. According to the general procedure, 2-iodothiophene (210 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO₂, hexanes). Run 1: 121 mg (63% yield). Run 2: 126 mg (66% yield).

2-Fluorophenyl phenyl sulfide (Table 3, entry 1) [61900-51-4]. According to the general procedure, iodobenzene (112 µL, 1.0 mmol, 1.0 equiv) and 2-fluorothiophenol (107 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO₂, hexanes). Run 1: 152 mg (74% yield). Run 2: 147 mg (72% yield).

2,6-Dimethylphenyl phenyl sulfide (Table 3, entry 2) [54088-93-6]. According to the general procedure, iodobenzene (112 µL, 1.0 mmol, 1.0 equiv) and 2,6-dimethylbenzenethiol (133 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 8 h. The product (colorless oil) was purified by column chromatography (SiO₂, hexanes). Run 1: 154 mg (72% yield). Run 2: 148 mg (69% yield).
4-Methoxyphenyl phenyl sulfide (Table 3, entry 3) \([5633-57-8]\). According to the general procedure, iodobenzene (112 µL, 1.0 mmol, 1.0 equiv) and 4-methoxythiophenol (123 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO\(_2\), hexanes). Run 1: 172 mg (80% yield). Run 2: 178 mg (82% yield).

3-Methoxyphenyl phenyl sulfide (Table 3, entry 4) \([30723-54-7]\). According to the general procedure, iodobenzene (112 µL, 1.0 mmol, 1.0 equiv) and 3-methoxythiophenol (124 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO\(_2\), 1:50 EtOAc:hexanes). Run 1: 140 mg (65% yield). Run 2: 139 mg (64% yield).

4-(Phenylthio)pyridine (Table 3, entry 5) \([33399-48-3]\). According to the general procedure, iodobenzene (112 µL, 1.0 mmol, 1.0 equiv) and 4-mercaptopyridine (111 mg, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO\(_2\), hexanes → Et\(_2\)O). Run 1: 139 mg (74% yield). Run 2: 136 mg (73% yield).

**Diphenylsulfide (Table 4, entry 1) \([139-66-2]\)**. According to the general procedure, bromobenzene (105 µL, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO\(_2\), hexanes). Run 1: 139 mg (75% yield). Run 2: 131 mg (70% yield).

**Phenyl \(o\)-tolyl sulfide (Table 4, entry 2) \([13963-35-4]\)**. According to the general procedure, 2-bromotoluene (120 µL, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO\(_2\), hexanes). Run 1: 119 mg (59% yield). Run 2: 119 mg (59% yield).
Phenyl 4-trifluoromethylphenyl sulfide (Table 4, entry 3) [53451-90-4]. According to the general procedure, 1-bromo-4-(trifluoromethyl)benzene (140 µL, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO₂, hexanes). Run 1: 178 mg (70% yield). Run 2: 177 mg (70% yield).

4-Methoxyphenyl phenyl sulfide (Table 4, entry 4) [5633-57-8]. According to the general procedure, 4-bromoanisole (187 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 24 h. The product (colorless oil) was purified by column chromatography (SiO₂, hexanes). Run 1: 138 mg (64% yield). Run 2: 135 mg (63% yield).

3,5-Dimethylphenyl phenyl sulfide (Eq. (2)) [457625-29-5]. According to the general procedure, 1-iodo-3,5-dimethylbenzene (144 µL, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at –40 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO₂, hexanes): 170 mg (80% yield).

4-Cyanophenyl phenyl sulfide (Eq. (3)) [51238-46-1]. According to the general procedure, 4-chlorobenzonitrile (138 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 µL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO₂, 1:20 EtOAc:hexanes): 162 mg (77% yield).
III. Cyclization and Isotopic Labeling Experiments [Eq. (4) and Eq. (5)]

Under an atmosphere of N₂, a borosilicate glass tube was charged in turn with CuI (3.8 mg, 0.020 mmol, 10%), NaO-t-Bu (19.2 mg, 0.20 mmol, 1.0 equiv), 2-allyloxy-1-iodobenzene (52.0 mg, 0.20 mmol, 1.0 equiv) in CH₃CN (0.50 mL), and thiophenol (22.0 mg, 0.20 mmol, 1.0 equiv) in CH₃CN (0.50 mL). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 5 h, 1,3,5-trimethoxybenzene (33.6 mg, 0.20 mmol, 1.0 equiv) was added, and the volatiles were removed under reduced pressure. The residue was suspended in Et₂O, and the mixture was filtered through a short plug of Celite. The filtrate was concentrated, and the residue was then suspended in hexanes. The mixture was filtered through a short plug of Celite, and the filtrate was concentrated. Next, the reaction mixture was analyzed by ¹H NMR spectroscopy.

This procedure was repeated in the dark with a reaction time of 72 h at 60 °C.

The procedure above was repeated using the mono-deuterated substrate (2-d).¹ The reaction mixture was analyzed by ²H⁻¹H NMR.

2-(Allyloxy)phenyl phenyl sulfide (3). ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.34 (m, 2 H), 7.34–7.28 (m, 2 H), 7.28–7.23 (m, 1 H), 7.20 (dd, J = 1.8, 7.4, 8.2 Hz, 1 H), 7.09 (dd, J = 1.6, 7.6 Hz, 1 H), 6.93–6.83 (m, 2 H), 6.04–5.90 (m, 1 H), 5.38 (qd, J = 1.7, 17.2 Hz, 1 H), 5.24 (qd, J = 1.5, 10.6 Hz, 1 H), 4.59 (td, J = 1.7, 5.0 Hz, 2 H).

$^{13}$C[$^1$H] NMR (101 MHz, CDCl$_3$) $\delta$ 156.4, 134.7, 133.0, 131.9, 131.6, 129.2, 128.2, 127.2, 125.1, 121.6, 117.6, 112.6, 69.5.

Figure S1. $^1$H NMR spectrum (CDCl$_3$) of 3.

Figure S2. $^{13}$C[$^1$H] NMR spectrum (CDCl$_3$) of 3.
3-(Phenylthiomethyl)-2,3-dihydrobenzofuran (4). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44–7.37 (m, 2 H), 7.36–7.28 (m, 2 H), 7.28–7.19 (m, 2 H), 7.19–7.12 (m, 1 H), 6.88 (dt, \(J = 0.9, 7.5\) Hz, 1 H), 6.81 (d, \(J = 8.1\) Hz, 1 H), 4.63 (t, \(J = 9.0\) Hz, 1 H), 4.45 (dd, \(J = 5.7, 9.2\) Hz, 1 H), 3.64 (tt, \(J = 5.2, 9.4\) Hz, 1 H), 3.33 (dd, \(J = 4.9, 12.7\) Hz, 1 H), 3.02 (dd, \(J = 9.7, 13.0\) Hz, 1 H).

\(^{13}\)C\(^{1}\)H NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.1, 135.6, 130.1, 129.2, 129.0, 126.7, 124.7, 120.7, 110.0, 76.2, 41.8, 39.0.

Figure S3. \(^1\)H NMR spectrum (CDCl\(_3\)) of 4.

Figure S4. \(^{13}\)C\(^{1}\)H NMR spectrum (CDCl\(_3\)) of 4.
Figure S5. $^1$H NMR and $^2$H{$^1$H} NMR spectra (CDCl$_3$/CHCl$_3$) of the unpurified reaction mixture from the cross-coupling of 2-d. Unreacted 2-d is at 5.3 ppm.
IV. Competition Experiment [Eq. (6)]

\[
\begin{align*}
\text{Br} & \quad \text{5.0 equiv} \\
\text{Cl} & \quad \text{5.0 equiv}
\end{align*}
\]

Under an atmosphere of N\(_2\), a borosilicate glass tube was charged in turn with CuI (9.5 mg, 0.050 mmol, 10%), NaO-t-Bu (48.1 mg, 0.50 mmol, 1.0 equiv), 4-chlorobenzonitrile (344 mg, 2.5 mmol, 5.0 equiv), CH\(_3\)CN (1.5 mL), 1-bromonaphthalene (350 \(\mu\)L, 2.5 mmol, 5.0 equiv), and thiophenol (51 \(\mu\)L, 0.50 mmol, 1.0 equiv). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 10 h, Et\(_2\)O (10 mL) and dodecane (114 \(\mu\)L) were added, and then the mixture was analyzed by GC.
V. Synthesis and Reactivity of \([\text{Cu}_5(\text{SPh})_7][\text{Na}(12-\text{crown-4})_2]\)_2

\([\text{Cu}_5(\text{SPh})_7][\text{Na}(12-\text{crown-4})_2]\)_2. Under an atmosphere of N₂, a vial was charged with CuI (190 mg, 1.0 mmol, 1.0 equiv), NaOt-Bu (96.1 mg, 1.0 mmol, 1.0 equiv), CH₃CN (1.0 mL), and thiophenol (103 µL, 1.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 15 min, and then it was filtered through a short plug of Celite. Cedar-4 (352 mg, 2.0 mmol, 2.0 equiv) was added to the filtrate, and then the mixture was filtered through a short plug of Celite. The filtrate (total volume: 2 mL) was allowed to stand at room temperature. After 12 h, X-ray quality crystals of \([\text{Cu}_5(\text{SPh})_7][\text{Na}(12-\text{crown-4})_2]\)_2 had formed (yellow crystalline solid; see Section VI).

\([\text{Cu}_5(\text{SPh})_7][\text{Na}(12-\text{crown-4})_2]\)_2. Under an atmosphere of N₂, a vial was charged with CuCl (99 mg, 1.0 mmol, 1.0 equiv), NaOt-Bu (96.1 mg, 1.0 mmol, 1.0 equiv), CH₃CN (1.0 mL), and thiophenol (103 µL, 1.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 15 min, and then it was filtered through a short plug of Celite. Cedar-4 (352 mg, 2.0 mmol, 2.0 equiv) was added to the filtrate, and then the mixture was filtered through a short plug of Celite. The filtrate (total volume: 2 mL) was allowed to stand at room temperature. After 12 h, analytically pure \([\text{Cu}_5(\text{SPh})_7][\text{Na}(12-\text{crown-4})_2]\)_2 (82 mg, 32% yield) was isolated as a yellow crystalline solid (X-ray quality crystals had the same unit cell as the crystals obtained in the previous paragraph with CuI as the starting material).

Elemental analysis calcd for C₇₄H₉₉Cu₅Na₂O₁₆S₇: C, 48.50; H, 5.44. Found: C, 48.27; H, 5.40.

Reaction of \([\text{Cu}_5(\text{SPh})_7][\text{Na}(12-\text{crown-4})_2]\)_2 with 1-iodo-3,5-dimethylbenzene. Under an atmosphere of N₂, a tube was charged with \([\text{Cu}_5(\text{SPh})_7][\text{Na}(12-\text{crown-4})_2]\)_2 (24.4 mg, 0.013 mmol, 1.0 equiv) and then a solution of 1-iodo-3,5-dimethylbenzene (22.0 mg, 0.093 mmol, 7.0 equiv) in CH₃CN (1.0 mL). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 5 h, Et₂O (10 mL) and dodecane (20 µL) were added, and the reaction was analyzed by GC.
Figure S6. ESI-MS (negative) of [Cu₅(SPh)₇][Na(12-crown-4)]₂ (1) dissolved in CH₃CN.

Figure S7. ESI-MS (negative) of an aliquot of a cross-coupling reaction mixture (PhSH, 1-iodo-3,5-dimethylbenzene, NaOt-Bu, 10% CuI, CH₃CN, 1 h, 0 °C, 100-watt Hg lamp).
VI. X-Ray Crystallographic Data for [Cu$_5$(SPh)$_7$][Na(12-crown-4)$_2$]$_2$

Empirical formula
C$_{74}$H$_{62}$Cu$_5$Na$_2$O$_{16}$S$_7$

Formula weight
1795.34

Temperature/K
373(2)

Crystal system
triclinic

Space group
P-1

a/Å
15.7407(6)
b/Å
15.7841(6)
c/Å
19.5588(8)
α/°
85.530(3)
β/°
71.368(2)
γ/°
61.411(2)

Volume/Å$^3$
4026.9(3)

Z
2

ρcalc/mg/mm$^3$
1.481

m/mm$^{-1}$
1.553

F(000)
1826.0

Crystal size/mm$^3$
0.21 × 0.12 × 0.10

2θ range for data collection
2.96 to 71.26°

Index ranges
-25 ≤ h ≤ 25, -23 ≤ k ≤ 25, -31 ≤ l ≤ 31

Reflections collected
150135

Independent reflections
33743[R(int) = 0.0871]

Data/restraints/parameters
33743/0/874

Goodness-of-fit on F$^2$
1.027

Final R indexes [I≥2σ (I)]
R1 = 0.1403, wR2 = 0.3776

Final R indexes [all data]
R1 = 0.2124, wR2 = 0.4232

Largest diff. peak/hole / e Å$^{-3}$
9.48/-2.26
VII. $^1$H NMR Spectra of Cross-Coupling Products

Figure S8. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 1.

Figure S9. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 2.
Figure S10. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 3.

Figure S11. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 4.
Figure S12. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 5.

Figure S13. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 6.
Figure S14. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 7.

Figure S15. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 8.
Figure S16. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 9.

Figure S17. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 10.
Figure S18. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 11.

Figure S19. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 12.
Figure S20. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 2, entry 13.

Figure S21. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 3, entry 1.
Figure S22. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 3, entry 2.

Figure S23. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 3, entry 3.
Figure S24. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 3, entry 4.

Figure S25. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 3, entry 5.
Figure S26. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 4, entry 1.

Figure S27. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 4, entry 2.
Figure S28. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 4, entry 3.

Figure S29. $^1$H NMR spectrum (CDCl$_3$) for the product in Table 4, entry 4.
Figure S30. $^1$H NMR spectrum (CDCl$_3$) for the product in Eq. (2).

Figure S31. $^1$H NMR spectrum (CDCl$_3$) for the product in Eq. (3).