Supporting Information

Copper-Catalyzed Carbonylative Suzuki Coupling of Aryl iodides with Arylboronic Acids under Ambient Pressure of Carbon Monoxide

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1. General Information

**Reagent Information.** All the aryl halides and the arylboronic acids were purchased from Alfa Aesar and Accela ChemBio Co., Ltd. and were used as received. PEG-400 (bought from Acros) was pre-dried (toluene azeotrope) and pre-deoxygenated. The following nanocopper, bases, and tBuCOOH were used: nanocopper (99.9%, aladdin; 10-30 nm), K$_3$PO$_4$ (99%, Alfa Aesar), KF (99%, Accela), and tBuCOOH (99%, Alfa Aesar).

**Analytical methods.** $^1$H and $^{13}$C NMR spectra of solutions in CDCl$_3$ were recorded on a Bruker Avance 400 instrument. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals (CDCl$_3$: H 7.24 and C 77.0 ppm). The signals of water were observed at about 1.58 ppm in CDCl$_3$, respectively. Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; ddd, doublet of doublet of doublets; tdd, doublet of doublet of triplets. Coupling constants, $J$, were reported in hertz unit (Hz). Infrared spectra of neat substances were recorded on a Thermo Nicolet Corporation GC-FTIR NEXUS670 spectrometer. HRMS was performed on a Bruker's solarix 94 (ESI-FTICR-MS) mass spectrometer.

2. General Procedures for Copper-Catalyzed Carbonylative Suzuki Reactions

**General Procedure A:** A 25 mL Schlenk flask was charged with arylboronic acid (0.75mmol), nanocopper (0.1 mmol, 6.4 mg), K$_3$PO$_4$ (1.0 mmol, 218.8 mg), tBuCOOH (0.25 mmol, 25.8 mg), and PEG-400 (2.0 mL) before standard cycles of evacuation and back-filling with dry and pure carbon monoxide. Corresponding aryl iodide (0.5 mmol) was added successively. The mixture was stirred at 80 °C for the indicated time. At the end of the reaction, the reaction mixture was poured into a saturated aqueous NaCl
solution (15 mL) and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel (petroleum ether: diethyl ether = 25 : 1).

In the recycling experiment, the reaction mixture was extracted with ethyl acetate (2 × 15 mL), and the residue was subjected to a second run by charging it with the same substrates as mentioned above without further addition of Pd(OAc)$_2$ and PEG 400 under 1 atm of carbon monoxide. In the third, sixth, and eighth runs, another 0.5 mL of PEG-400 was added to the reaction mixture.

**General Procedure B**: A 25 mL Schlenk flask was charged with arylboronic acid (0.75 mmol), nanocopper (0.1 mmol, 6.4 mg), K$_3$PO$_4$ (0.5 mmol, 109.4 mg), KF (0.25 mmol, 14.7 mg), $t$BuCOOH (0.25 mmol, 25.8 mg), and PEG-400 (2.0 mL) before standard cycles of evacuation and back-filling with dry and pure carbon monoxide. Corresponding aryl iodide (0.5 mmol) was added successively. The mixture was stirred at 100 °C for the indicated time. At the end of the reaction, the reaction mixture was poured into a saturated aqueous NaCl solution (15 mL) and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel (petroleum ether: diethyl ether = 25 : 1).

3. Analytical Data of Products

The products, 3aa-3fa, 3ha-3na, 3pa-3qa, 3ab-3ae, 3ii-3ij, 3ie, 3ki-3kj, 3ke, and 3kh were identified by comparison of their spectral data with those of our previous reports.[S1-S2]
4-Benzoylbenzonitrile (3ga): Following general procedure B, 3ga was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref.[S3] $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.85 (d, $J=8.0$ Hz, 2 H), 7.77 (d, $J=8.0$ Hz, 2 H), 7.76-7.75 (m, 2 H), 7.62 (tt, $J=8.0$, 1.2 Hz, 1 H), 7.51-7.47 ppm (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.0, 141.2, 136.3, 133.3, 132.1, 130.2, 130.0, 128.6, 117.9, 115.6, 116.6 ppm.

(3,5-Dimethylisoxazol-4-yl)(phenyl)methane (3oa): Following general procedure B, 3oa was isolated as a colorless liquid. Known compound; the NMR spectroscopic data agree with those described in ref.[S4] $^1$H NMR (400 MHz, CDCl$_3$): $\delta$7.70–7.68 (m, 2 H), 7.59 (tt, $J=8.0$, 1.2 Hz, 1H), 7.50–7.46 (m, 2 H), 2.31 (s, 3 H), 2.28 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.4, 172.3, 159.6, 138.4, 133.2, 128.9, 128.7, 116.4, 13.3, 11.3 ppm.

3-(4'-Chlorobenzoyl)benzaldehyde (3cf): Following general procedure B, 3cf was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref.[S5] $^1$H NMR (400 MHz, CDCl$_3$): $\delta$10.07 (s, 1 H), 8.22 (t, $J=4.0$ Hz, 1 H), 8.10 (dt, $J=8.0$, 4.0 Hz, 1 H), 8.03 (dt, $J=8.0$, 4.0 Hz, 1 H), 7.74 (d, $J=8.0$ Hz, 2 H), 7.67 (t, $J=8.0$ Hz, 1 H), 7.47 ppm (d, $J=8.0$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 194.2, 191.2, 139.6, 138.1, 136.4, 135.2, 135.1, 132.9, 131.4, 131.0, 129.4, 128.9 ppm;
mp 93.5-94.3 °C.

4-(4-Chlorobenzoyl)benzonitrile (3cg): Following general procedure B, 3cg was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref.[S3] \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J=8.0\) Hz, 2 H), 7.78 (d, \(J=8.0\) Hz, 2 H), 7.72 (d, \(J=8.0\) Hz, 2 H), 7.47 ppm (d, \(J=8.0\) Hz, 2 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.8, 140.8, 139.9, 134.6, 132.3, 131.4, 130.1, 129.0, 117.9, 115.9 ppm.

(4-Chlorophenyl)(4-methoxyphenyl)methanone (3ch): Following general procedure B, 3ch was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref.[S6] \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.78 (d, \(J=8.0\) Hz, 2 H), 7.69 (d, \(J=8.0\) Hz, 2 H), 7.43 (d, \(J=8.0\) Hz, 2 H), 6.95 (d, \(J=8.0\) Hz, 2 H), 3.87 ppm (s, 3 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 194.3, 163.4, 138.3, 136.6, 132.4, 131.1, 129.8, 128.5, 113.7, 55.5 ppm; mp 123.3-124.0 °C.

4,4'-Carbonyldibenzonitrile (3gg): Following general procedure A, 3gg was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref.[S7] \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J=8.0\) Hz, 4 H), 7.81 ppm (d, \(J=8.0\) Hz, 4 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.4, 139.7, 132.5, 130.2, 117.7, 116.6 ppm.
4-(2-Methylbenzoyl)benzonitrile (3ig): Following general procedure B, 3ig was isolated as a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J$=8.0 Hz, 2 H), 7.74 (d, $J$=8.0 Hz, 2 H), 7.44–7.40 (m, 1 H), 7.31–7.23 (m, 3 H), 2.34 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.8, 141.1, 137.5, 136.9, 132.3, 131.4, 131.2, 130.3, 128.9, 125.4, 117.9, 116.2, 20.1 ppm.

4-(4-Methylbenzoyl)benzonitrile (3kg): Following general procedure B, 3kg was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref.[53] $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J$=8.0 Hz, 2 H), 7.76 (d, $J$=8.0 Hz, 2 H), 7.67 (d, $J$=8.0 Hz 2 H), 7.29 (d, $J$=8.0 Hz, 2 H), 2.43 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.8, 144.4, 141.6, 133.6, 132.1, 130.3, 130.1, 129.3, 118.0, 115.3, 21.7 ppm.

Naphthalen-1-yl(naphthalen-2-yl)methanone (3nk): Following general procedure B, 3nk was isolated as a white solid. Known compound; the NMR spectroscopic data agree with those described in ref.[58] $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.24 (s, 1 H), 8.10 (d, $J$=8.0 Hz, 1 H), 8.07 (dd, $J$=8.0, 2.0 Hz, 1 H), 8.03 (d, $J$=8.0 Hz, 1 H), 7.95-7.92 (m, 2 H), 7.89 (d, $J$=8.0 Hz, 1 H), 7.82 (d, $J$=8.0 Hz, 1 H), 7.64 (dd, $J$=8.0, 1.2 Hz, 1 H), 7.61-7.57 (m, 1 H), 7.55 (d, $J$=8.0 Hz, 1 H), 7.53 (d, $J$=8.0 Hz, 1 H), 7.51-7.46 ppm (m, 2 H); $^{13}$C
NMR (100 MHz, CDCl₃): δ 198.0, 136.6, 135.7, 135.6, 133.7, 132.9, 132.3, 131.2, 131.0, 129.7, 128.7, 128.42, 128.4, 127.8, 127.7, 127.3, 126.8, 126.5, 125.7, 125.4, 124.4 ppm; mp 132.7-133.2 °C.

Dibenzofuran-4-yl(p-tolyl)methanone (3km): Following general procedure B, 3km was isolated as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.11 (dd, J=8.0, 1.2 Hz, 1 H), 7.97 (d, J=8.0 Hz, 1 H), 7.81 (d, J=8.0 Hz, 2 H), 7.67 (dd, J=8.0, 1.2 Hz, 1 H), 7.52 (d, J=8.0 Hz, 1 H), 7.46-7.39 (m, 2 H), 7.37-7.33 (m, 1 H), 7.26 (d, J=8.0 Hz, 2 H), 2.43 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 156.3, 153.7, 144.0, 134.9, 130.4, 129.0, 128.4, 127.7, 125.4, 123.8, 123.5, 123.3, 123.1, 122.4, 120.6, 112.1, 21.7 ppm; IR νmax (KBr)/cm⁻¹ 3065, 2915, 2915, 1594, 1487, 1449, 1419, 1377, 1292, 1179, 846, 746; HRMS (ESI) calcd. for C₂₀H₁₅O₂ [M + H] 287.1072, found 287.1065; mp 96.5-97.1 °C.

4. Hg(0) Poisoning Test

As general procedure B, a reactions of 4-iodotoluene 1k (0.5 mmol, 66.3 µL), phenylboronic acid 2a (0.75 mmol, 92.4 mg), nanocopper (0.1 mmol, 6.4 mg), K₃PO₄ (0.5 mmol, 109.4 mg), KF (0.25 mmol, 14.7 mg), and tBuCO₂H (0.25 mmol, 25.8 mg) in PEG-400 (2.0 mL), with the addition of elemental mercury (20 mmol, 4.0 g) (relative to copper) was conducted. Following the reaction for 9 h at 100 °C, the isolated yield of the desired product 3aa was less than 5%, suggesting that the reaction is inhibited by the introduction of Hg(0).
5. References


6. NMR Spectra for Products

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

$^{13}C$ NMR (400 MHz, CDCl$_3$)
$\text{Figure S10: NMR Spectra for Compound 3oa}$

$\text{1H NMR (400 MHz, CDCl$_3$)}$

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

$^{13}$C NMR (400 MHz, CDCl$_3$)
$\text{Cl}$

3ch

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

$\text{Me}$

$\text{Cl}$

$\text{O}$

3ch

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

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

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

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

$^{13}$C NMR (400 MHz, CDCl$_3$)