

## Supporting Information

Hydrodehalogenation of aryl chlorides and aryl bromides using a microwave-assisted, copper-catalyzed concurrent tandem catalysis methodology

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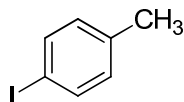
**General Considerations.** All manipulations were carried out using standard nitrogen drybox techniques. Anhydrous acetonitrile and copper(I) iodide were purchased from Acros and used as received. *trans-N,N'*-dimethylcyclohexane-1,2-diamine was purchased from Aldrich and used as received. Microwave reactions were performed in a CEM Discover microwave reactor. GC/MS analysis was performed on a Shimadzu GCMS-QP5050A with a Restek Rxi-5ms capillary column (30 m, 0.25 mm ID, 0.25  $\mu$ m film thickness, 5% diphenyl / 95% dimethylpolysiloxane) or Varian Saturn 2900 GC/3100 GC/MS/MS with a Varian VF-5ms Factor Four capillary column (30 m, 0.25 mm ID, 0.25  $\mu$ m film thickness, 5% diphenyl / 95% dimethylpolysiloxane).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL ECX-400 spectrometer and were referenced to residual protio solvent peaks. Melting points were measured on an Electrothermal Mel-temp melting point device.

## **Experimental Procedures.**

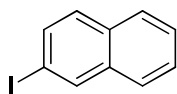
### **General Procedure for the Copper-Catalyzed Conversion of Aryl Bromides into**

**Aryl Iodides.** In a nitrogen-filled glove box, CuI (15 mg, 0.079 mmol, 5 mol%), NaI (450 mg, 3.00 mmol), and an aryl bromide (1.5 mmol) were weighed into an oven-dried microwave tube containing a small stir bar. Acetonitrile (0.6 mL) was added by syringe and then *trans-N,N'*-dimethylcyclohexane-1,2-diamine (23.7  $\mu$ L, 0.1 mmol, 10 mol%) was added by positive displacement pipet, the sample was stirred, and a septum-lined cap was added. The initial reaction mixture appeared as a yellow or yellow-green liquid over a white solid. After removing the tube from the box, the reaction was performed in a CEM Discover microwave reactor for 30-120 minutes at 100  $^{\circ}\text{C}$  and 250 W (with power

adjustments to maintain temperature), with a 2 minute ramp time. After cooling, the reaction mixture contained a turquoise-blue liquid over a solid. The product mixture was purified by column chromatography on silica. The yields reported did not take into account the trace amount of aryl bromide present in the isolated products.

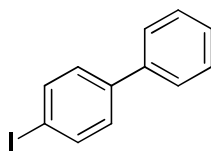


**4-Iodotoluene (Table 1, entry 1).** Following the general procedure, 4-bromotoluene (187  $\mu$ L, 1.5 mmol) was converted to 4-iodotoluene in 60 minutes. The product was purified by column chromatography on silica gel (10:90 v/v EtOAc : hexanes) to provide the desired product as a clear liquid that was further purified by rotary evaporation into white crystals (90% yield, 96% purity). Mp: 34 – 37  $^{\circ}$ C (lit: 33-35  $^{\circ}$ C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J$  = 7.8 Hz, 2H), 6.92 (d,  $J$  = 8.3 Hz, 2H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  137.44, 137.19, 131.18, 90.18, 21.02.<sup>1</sup>

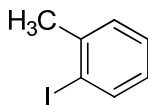


**2-Iodonaphthalene (Table 1, entry 2).** Following the general procedure, 2-bromonaphthalene (311 mg, 1.5 mmol) was converted to 2-iodonaphthalene in 60 minutes. Purification of the crude product was accomplished by column chromatography on silica gel (100% hexanes), which provided the desired product as a clear liquid that was further purified by rotary evaporation into white crystals (97% yield, 96% purity). Mp: 50.5 – 51.5  $^{\circ}$ C (lit: 53-54  $^{\circ}$ C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (s, 1H), 7.81-7.77 (m, 1H),

7.73-7.69 (m, 2H), 7.57 (d,  $J = 8.7$  Hz, 1H), 7.51-7.47 (m 2H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  136.73, 135.08, 134.47, 132.19, 129.60, 127.97, 126.90, 126.80, 126.58, 91.63.<sup>2</sup>



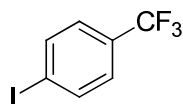
**4-Iodobiphenyl (Table 1, entry 3).** Following the general procedure, 4-bromobiphenyl (351 mg, 1.51 mmol) was converted to 4-iodobiphenyl in 60 minutes. Purification of the crude product by column chromatography on silica gel (10:90 v/v EtOAc : hexanes) provided the desired product as a clear liquid that was further purified by rotary evaporation into white crystals (96% yield, 98% purity). Mp: 113.0 – 115.0 °C (lit: 112.5 – 113.5 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 6.9$  Hz, 2H), 7.55 (d,  $J = 7.8$  Hz, 2H), 7.44 (t,  $J = 7.3$  Hz, 2H), 7.39 – 7.28 (m, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  140.81, 140.15, 137.94, 129.12, 129.01, 127.80, 127.00, 93.15.<sup>3,4</sup>



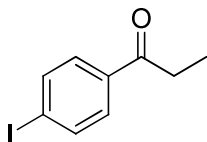
**2-Iodotoluene (Table 1, entry 4).** Following the general procedure, 2-bromotoluene (184  $\mu\text{L}$ , 1.5 mmol) was converted to 2-iodotoluene in 60 minutes at 150 °C. The product was purified by column chromatography on silica gel (10:90 v/v EtOAc : hexanes) to provide the desired product as a clear liquid that was further purified by rotary evaporation into a colorless oil (89% yield, 95% purity).  $^1\text{H}$  NMR (400 MHz,

$\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 7.4$  Hz, 1H), 7.28-7.24 (m, 2H), 6.90-6.88 (m, 1H), 2.46 (s, 3H);

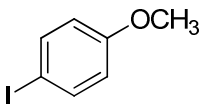
$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3, 138.8, 129.7, 128.1, 127.3, 101.2, 28.1.<sup>1</sup>



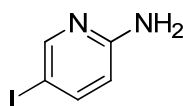
**4-Iodobenzotrifluoride (Table 1, entry 5).** Following the general procedure, 4-bromobenzotrifluoride (210.9  $\mu\text{L}$ , 1.5 mmol) was converted to 4-iodobenzotrifluoride in 60 minutes. The product was purified by column chromatography on silica gel (10:90 v/v EtOAc : hexanes) to provide the desired product as a clear liquid that was further purified by rotary evaporation (84% yield, 96% purity).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 8.3$  Hz, 2H), 7.34 (d,  $J = 8.2$  Hz, 2H).  $^{19}\text{F}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.93 (s).<sup>5</sup>



**4-Iodopropiophenone (Table 1, entry 6).** Following the general procedure, 4-bromopropiophenone (320 mg, 1.5 mmol) was converted to 4-iodopropiophenone in 30 minutes. Purification of the crude product was accomplished by column chromatography on silica gel (10:90 v/v EtOAc : hexanes), which provided the desired product as a clear liquid that was further purified by rotary evaporation into white crystals (94% yield, 98% purity). Mp: 62.0 – 64.0  $^{\circ}\text{C}$  (lit: 57-58  $^{\circ}\text{C}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.3$  Hz, 2H), 7.66 (d,  $J = 8.7$  Hz, 2H), 2.95 (q,  $J = 7.3$  Hz, 2H), 1.20 (t,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  200.16, 137.96, 136.19, 129.52, 100.88, 31.83, 8.21.<sup>6</sup>



**4-Iodoanisole (Table 1, entry 7).** Following the general procedure, 4-bromoanisole (187  $\mu$ L, 1.5 mmol) was converted to 4-iodoanisole in 75 minutes. The product was purified by column chromatography on silica gel (10:90 v/v EtOAc : hexanes) to provide the desired product as a clear liquid that was further purified by rotary evaporation into white crystals (95% yield, 98% purity). Mp: 51.0 – 53.0  $^{\circ}$ C (lit: 51 - 53  $^{\circ}$ C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J$  = 8.7 Hz, 2H), 6.68 (d,  $J$  = 8.7 Hz, 2H), 3.77 (s, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  159.52, 138.28, 116.44, 82.80, 55.42.<sup>7</sup>



**2-Amino-5-iodopyridine (Table 1, entry 8).** Following the general procedure, 2-amino-5-bromopyridine (261 mg, 1.5 mmol) was converted to 2-amino-5-iodopyridine in 120 minutes. The product was purified by column chromatography on silica gel using 3:2 v/v EtOAc:hexanes as eluent to provide the desired product as a white solid (94% yield, 99% purity).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (s, 1H), 7.61 (dd,  $J$  = 1.8, 8.7 Hz, 1H), 6.35 (d,  $J$ =8.7 Hz, 1H), 4.45 (br s, 2H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  157.17, 153.38, 145.38, 110.96, 77.32.<sup>4</sup>

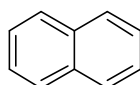
### General Procedure for the Copper-Catalyzed Conversion of Aryl Chlorides into

**Aryl Iodides.** In a nitrogen-filled glove box, CuI (10 mg, 0.047 mmol, 5 mol%), NaI (300 mg, 2.00 mmol), and an aryl chloride (1.0 mmol) were weighed into an oven-dried

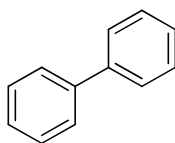
microwave tube containing a small stir bar. Acetonitrile (0.5 mL) was added by syringe and then *trans*-*N,N'*-dimethylcyclohexane-1,2-diamine (23.7  $\mu$ L, 0.1 mmol, 10 mol%) was added by positive displacement pipet, the sample was stirred, and a septum-lined cap was added. The initial reaction mixture appeared as a yellow or greenish liquid over a white solid. After removing the tube from the box, the reaction was performed in a CEM Discover microwave reactor for 30-120 minutes at 100 °C and 250 W (with power adjustments to maintain temperature), with a 2 minute ramp time. After cooling, the crude reaction mixture appeared as a yellow or brown solution. An equimolar amount (versus ArCl) of either hexadecane or decane was added to the solution. The solution was then quenched with 2 mL water and 2 mL EtOAc. The resulting solution was a dark brown, cloudy organic layer over a purple aqueous layer. A drop was removed from the organic layer and diluted with 10 drops of EtOAc in order to determine the GC yield.

**General Procedure for the Copper-Catalyzed Conversion of Aryl Bromides and Aryl Chlorides into Arenes.** In a nitrogen-filled glove box, CuI (40 mg, 0.21 mmol, 20 mol%), NaI (300 mg, 2.00 mmol, 2 equiv), and an aryl bromide or aryl chloride (1.0 mmol) were weighed into an oven-dried microwave tube containing a small stir bar. Acetonitrile (0.5 mL) was added by syringe and then *trans*-*N,N'*-dimethylcyclohexane-1,2-diamine (237  $\mu$ L, 1.5 mmol, 1.5 equiv) was added by positive displacement pipet, the sample was stirred, and a septum-lined cap was added. The initial reaction mixture appeared as a yellow or greenish liquid over a white solid. After removing the tube from the dry box, the reaction was performed in a CEM Discover microwave reactor for 1-2 hours at 200 °C and 250-300 W (with power adjustments to maintain temperature), with a

5-10 minute ramp time. Most reactions reached 200 °C after ~2 minutes. After the desired reaction time was reached and the tube cooled, the crude reaction mixture appeared as a dark brown liquid over some solids. The product mixture was either spiked with ~1.0 mmol decane for GC yield determination or purified by column chromatography on silica gel. Products purified by column chromatography routinely contained a small percentage of the corresponding aryl iodide and reported yields were adjusted to account for this impurity.



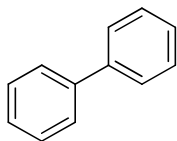
**Naphthalene (Table 4, entry 2).** Following the general procedure, 2-bromonaphthalene (207 mg, 1.0 mmol) was converted to naphthalene in 2 hours at 200 °C. The product was purified by column chromatography on silica gel (hexanes, loaded crude product by dissolving in a minimum of CH<sub>2</sub>Cl<sub>2</sub>) to provide the desired product as a crystalline white solid (87% yield, adjusted for the presence of ~4 mol % 2-iodonaphthalene). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91-7.83 (m, 4H), 7.54-7.46 (m, 4H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 133.42, 127.88, 125.82. <sup>8</sup>



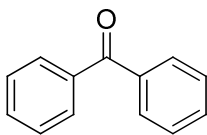
**Biphenyl (Table 4, entry 3).** Following the general procedure, 4-bromobiphenyl (233 mg, 1.0 mmol) was converted to biphenyl in 2 hours at 200 °C. The product was purified by column chromatography on silica gel (hexanes, loaded crude product by dissolving in



a minimum of CH<sub>2</sub>Cl<sub>2</sub>) to provide the desired product as a white crystalline solid (77% yield, adjusted for the presence of ~10 mol % 4-iodobiphenyl). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63-7.57 (m, 4H), 7.48-7.41 (m, 4H), 7.38-7.32 (m, 2H); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 141.32, 128.85, 127.35, 127.27.<sup>9</sup>



**Biphenyl (Table 4, entry 4).** CuI (80 mg, 0.42 mmol, 40 mol%), NaI (600 mg, 4.00 mmol, 4 equiv), and 4, 4'-dibromobiphenyl (312 mg, 1.0 mmol) were weighed into an oven-dried microwave tube containing a small stir bar. *trans*-*N,N'*-Dimethylcyclohexane-1,2-diamine (474 μL, 3.0 mmol, 3.0 equiv) and acetonitrile (0.5 mL) were added. The general procedure was then followed to produce biphenyl in 2 hours at 200 °C. The product was purified by column chromatography on silica gel (hexanes, loaded crude product by dissolving in a minimum of CH<sub>2</sub>Cl<sub>2</sub>) to provide the desired product as a white solid (72% yield, adjusted for the presence of ~8 mol % 4-iodobiphenyl). Spectral data was consistent with the biphenyl product produced from 4-bromobiphenyl.<sup>9</sup>



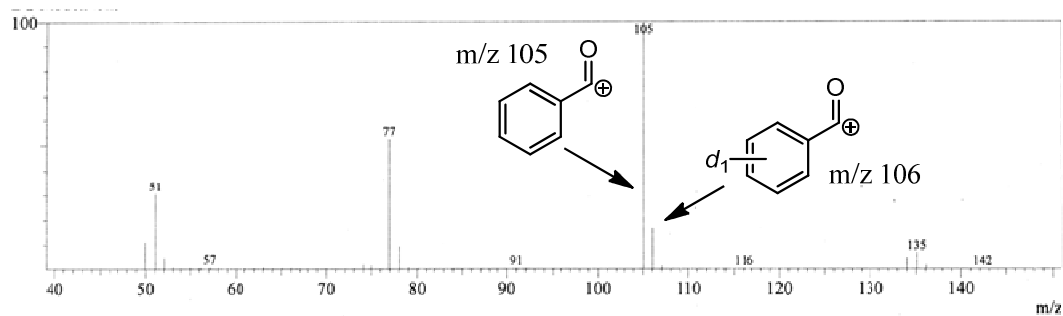
**Benzophenone (Table 4, entry 6).** Following the general procedure, but with only 20 mg CuI (0.10 mmol, 10 mol%), 4-bromobenzophenone (261 mg, 1.0 mmol) was converted to benzophenone in 2 hours at 200 °C. The product was purified by column

chromatography on silica gel (1:10 v/v EtOAc : hexanes, loaded column by adsorbing crude product onto silica gel) to provide the desired product as a yellow oil (77% yield, adjusted for the presence of ~4 mol % 4-iodobenzophenone).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82-7.77 (m, 4H), 7.61-7.54 (m, 2H), 7.51-7.45 (m, 4H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  196.90, 137.66, 132.53, 130.18, 128.37.<sup>10</sup>

### **Procedure for the Deuterium-Labeling Experiments:**

In a nitrogen-filled glove box, CuI (10 mg, 0.05 mmol, 10 mol%), NaI (150 mg, 1.00 mmol, 2 equiv), and 4-chloropropiophenone (88 mg, 0.5 mmol) were weighed into an oven-dried microwave tube containing a small stir bar. Acetonitrile- $d_3$  (0.25 mL) was added by syringe and then *trans*- $N,N'$ -dimethylcyclohexane-1,2-diamine (118.5  $\mu\text{L}$ , 0.75 mmol, 1.5 equiv) was added by positive displacement pipet, the sample was stirred, and a septum-lined cap was added. After removing the tube from the dry box, the reaction was performed in a CEM Discover microwave reactor for 1 hour at 200 °C and 250-300 W (with power adjustments to maintain temperature), with a 10 minute ramp time. Most reactions reached 200 °C after ~3-4 minutes. After the desired reaction time was reached and the tube cooled, the product mixture was diluted in ethylacetate and analyzed by GC-MS.

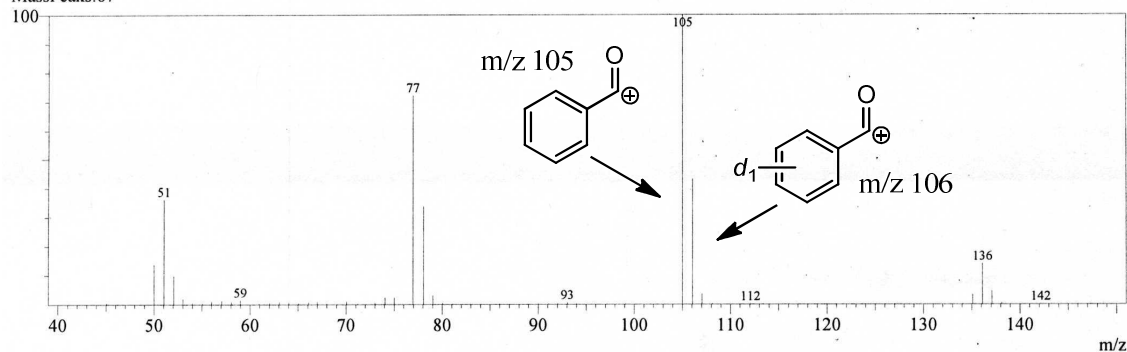
Mass spectra from GC-MS analysis:  
Arene peak after 5 min:



m/z 105 : 91%  
m/z 106 : 9%

Arene peak, after 10 min:

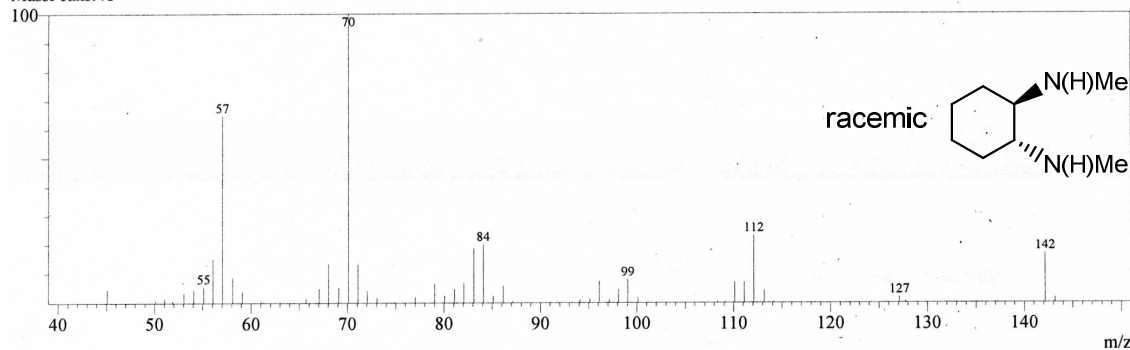
R.Time:8.5(Scan#:976)  
MassPeaks:67



m/z 105 : 80%  
m/z 106 : 20%

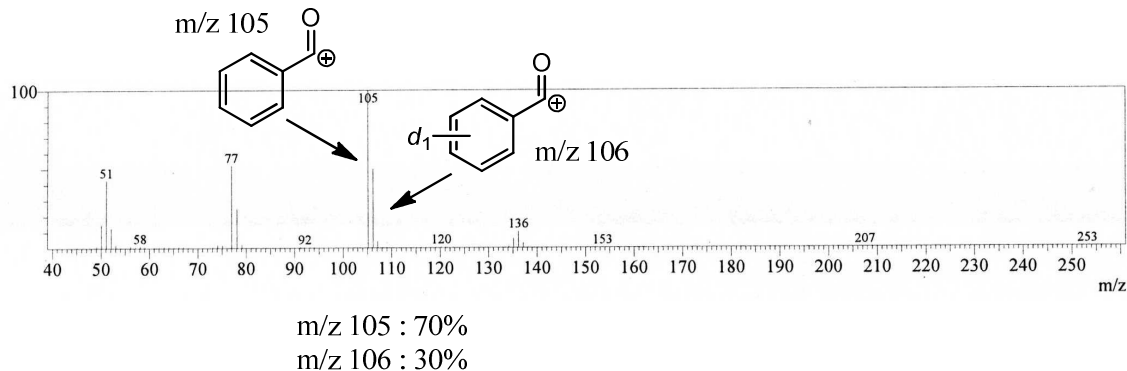
Ligand peak, after 10 min:

R.Time:8.2(Scan#:931)  
MassPeaks:48



m/z 142 : 100%

Arene peak after 2 hours:



## References

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