Supplementary Information

Contents of the supplementary information:

1. Experimental Section........................................................................................................S2

2. GC data for Copper-Catalyzed C-N Cross-Coupling Reaction.......................................S7

3. In situ ESI-MS Spectra and Isotope Distributions of Intermediates....................................S12
Experimental Section

All reagents were purchased from commercial sources and used without further purification. Copper(I) iodide (fine grey powder), N-phenylaniline, 4-iodotoluene, 1,10-phenanthroline, 1,4-di-tert-butylbenzene were purchased from ACROS. tBuONa was purchased from Alfa Aesar. Toluene (dried, seccoSolv®) was purchased from Merck and purged with argon for 15 min before use. All reagents were transferred to the reaction vessel (Pyrex tube with a Teflon screw cap) in a glove box. GC experiments were performed on an Agilent 6890N gas chromatograph equipped with a 30 m X 0.53 mm X 3.0 μm HP-1 capillary column and a FID detector. High resolution ESI-Q-TOF-MS were measured using a Waters HDMS in the Mass Spectrometry Facility in the Institute of Chemistry, Academia Sinica. Leucine Enkephalin [M+H]+ 556.277 was used as a reference standard.

Typical Procedure of Copper(I) Catalyzed C-N Coupling Reaction: In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), tBuONa (288.0 mg, 3.0 mmol) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. After stirring for 5 min, N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were added, and the resulting mixture was stirred for additional 20 min at room temperature. The mixture was then heated at 120 °C in an oil bath for 6 h. The tube was removed from the oil bath, and the resulting solution was allowed to cool to room temperature. Dichloromethane (10 mL) was added into the resulting solution, and the mixture was filtered to remove any insoluble residues by Celite. The solvent was diluted with CH2Cl2. GC quantitative analysis was carried out by using 1,4-di-tert-butylbenzene as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).
1. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa/K₂CO₃

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), tBuONa (192.0 mg, 2.0 mmol), K₂CO₃ (138.0 mg, 1.0 mmol) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h. GC yield: 92.7%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).

2. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), tBuONa (288.0 mg, 3.0 mmol) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h. GC yield: 37.8%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).

3. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuOK

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), tBuOK (336.0 mg, 3.0 mmol) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h. GC yield: 73.5%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).
4. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa/K$_2$CO$_3$ with 20 mol% TEMPO added.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), tBuONa (192.0 mg, 2.0 mmol), K$_2$CO$_3$ (138.0 mg, 1.0 mmol), TEMPO (31.2 mg, 0.2 mmol, 20 mol%) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h. GC yield: 85.4%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).

5. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa with 20 mol% TEMPO added.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), tBuONa (288.0 mg, 3.0 mmol), TEMPO (31.2 mg, 0.2 mmol, 20 mol%) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h. GC yield: 37.9%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).

6. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa/K$_2$CO$_3$ with 100 mol% TEMPO added.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), tBuONa (192.0 mg, 2.0 mmol), K$_2$CO$_3$ (138.0 mg, 1.0 mmol), TEMPO (156.0 mg, 1.0 mmol, 100 mol%) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h.
GC yield: 64.4%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).

7. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa with 100 mol% TEMPO added.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), tBuONa (288.0 mg, 3.0 mmol), TEMPO (156.0 mg, 1.0 mmol, 100 mol%) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h. GC yield: 34.5%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).

8. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa/K₂CO₃ without phen.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), tBuONa (192.0 mg, 2.0 mmol), K₂CO₃ (138.0 mg, 1.0 mmol), and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h. GC yield: 16.6%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).

9. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa/K₂CO₃ without phen with 20 mol% TEMPO added.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), tBuONa (192.0 mg, 2.0 mmol), K₂CO₃ (138.0 mg, 1.0 mmol), TEMPO (31.2 mg, 0.2 mmol, 20 mol%) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0
mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h. GC yield: 15.5%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).

10. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa/K$_2$CO$_3$ without phen with 100 mol% TEMPO added.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), tBuONa (192.0 mg, 2.0 mmol), K$_2$CO$_3$ (138.0 mg, 1.0 mmol), TEMPO (156.0 mg, 1.0 mmol, 100 mol%) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. N-phenylaniline (203.0 mg, 1.2 mmol) and 4-iodotoluene (218.0 mg, 1.0 mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 °C in an oil bath for 6 h. GC yield: 18.4%. 1,4-di-tert-butylbenzene was used as the internal standard (correction factor for 4-methyl-N,N-diphenylaniline: 0.818).
GC data for Copper-Catalyzed C-N Cross-Coupling Reaction

1. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa/K$_2$CO$_3$.

2. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa.
3. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuOK.

4. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa/K$_2$CO$_3$ with 20 mol% TEMPO added.
5. Copper-catalyzed C-N coupling of $N$-phenylaniline with 4-iodotoluene by $t$BuONa with 20 mol% TEMPO added.

6. Copper-catalyzed C-N coupling of $N$-phenylaniline with 4-iodotoluene by $t$BuONa/K$_2$CO$_3$ with 100 mol% TEMPO added.
7. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene by tBuONa with 100 mol% TEMPO added.

8. Copper-catalyzed C-N coupling of N-phenylaniline with 4-iodotoluene without phen by tBuONa.
9. Copper-catalyzed C-N coupling of \( N \)-phenylaniline with 4-iodotoluene without phen by \( t \)BuONa with 20 mol% TEMPO added.

10. Copper-catalyzed C-N coupling of \( N \)-phenylaniline with 4-iodotoluene without phen by \( t \)BuONa with 100 mol% TEMPO added.
**In situ ESI-MS Spectra and Isotope Distributions of Intermediates**

Experimental and theoretical isotopic distributions of $[\text{Na(phen)}_2]^+$, $[\text{Cu(phen)}_2]^+$, $K[\text{Cu(phen)(NPh}_2)(p\text{-tolyl})]^+$, $[\text{Cu(NPh}_2)_2]^-$ and $[\text{Cu(NPh}_2)\text{I}]^-$ (from the ESI-MS spectra of the reaction solution of $N$-phenylaniline with 4-iodotoluene using $t\text{BuONa/K}_2\text{CO}_3$ as the base system in the presence of CuI and phen in toluene at 120$^\circ$C)
Theoretical isotopic distributions of $[\text{Cu(phen)}_2]^+$

Experimental isotopic distributions of $[\text{Cu(phen)}_2]^+$

Theoretical isotopic distributions of $[\text{Cu(phen)}(\text{NPh}_2)(\text{p-tolyl})]^+$

Experimental isotopic distributions of $[\text{Cu(phen)}(\text{NPh}_2)(\text{p-tolyl})]^+$
Theoretical isotopic distributions of 
$[\text{Cu} (\text{NPh}_2)_2]$ 

Experimental isotopic distributions of 
$[\text{Cu} (\text{NPh}_2)_2]$ 

---

Theoretical isotopic distributions of 
$[\text{Cu} (\text{NPh}_2)_2]$ 

Experimental isotopic distributions of 
$[\text{Cu} (\text{NPh}_2)_2]$