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Supplementary Information

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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. *t*BuONa 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%), *t*BuONa (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 ^{o}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. Dicloromethane (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 CH_2Cl_2. 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 *t*BuONa/K_2CO_3

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), *t*BuONa (192.0 mg, 2.0 mmol), K_2CO_3 (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 ^{o}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 *t*BuONa

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), *t*BuONa (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 ^{o}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 *t*BuOK

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), *t*BuOK (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 ^{o}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 *t*BuONa/K_2CO_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%), *t*BuONa (192.0 mg, 2.0 mmol), K_2CO_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 ^{o}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 *t*BuONa 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%), *t*BuONa (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 ^{o}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 *t*BuONa/K_2CO_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%), *t*BuONa (192.0 mg, 2.0 mmol), K_2CO_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 ^{o}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 *t*BuONa 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%), *t*BuONa (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 ^{o}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 *t*BuONa/K_2CO_3 without phen.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), *t*BuONa (192.0 mg, 2.0 mmol), K_2CO_3 (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 ^{o}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 *t*BuONa/K_2CO_3 without phen with 20 mol% TEMPO added.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), *t*BuONa (192.0 mg, 2.0 mmol), K_2CO_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

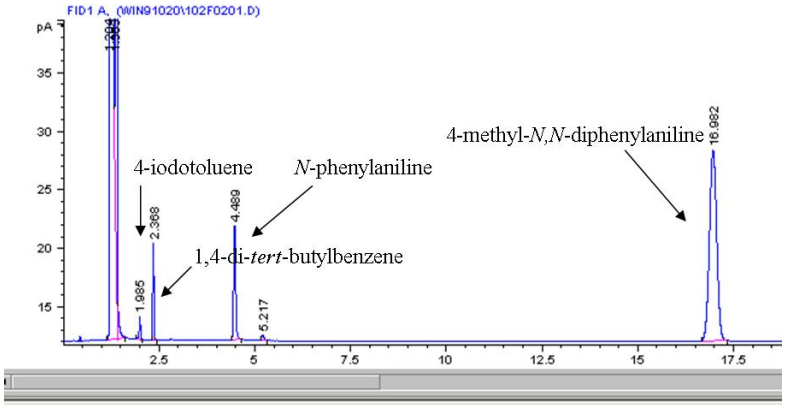
mmol) were then added to the above mixture at room temperature. The mixture was stirred and heated at 120 ^{o}C in an oil bath for 6 h. GC yield**:** 15.5%. 1,4-di-*tert*-butylbenzene was used as the internal standard (correction factor for 4-methyl-*N,N*-diphenylaniline: 0.818).

10. Copper-catalyzed C-N coupling of *N*-phenylaniline with 4-iodotoluene by *t*BuONa/K_2CO_3 without phen with 100 mol% TEMPO added.

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), *t*BuONa (192.0 mg, 2.0 mmol), K_2CO_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 ^{o}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).

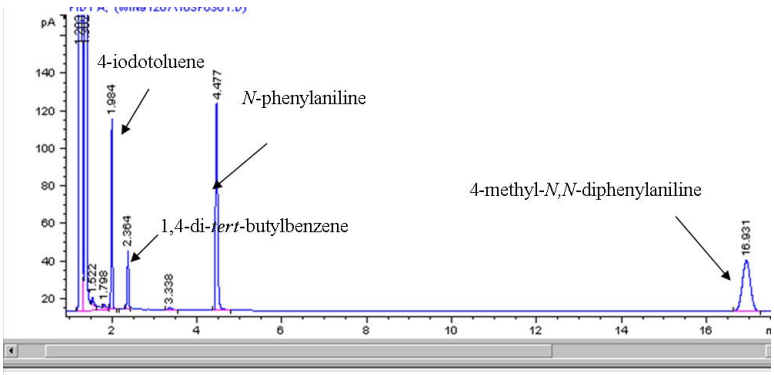
GC data for Copper-Catalyzed C-N Cross-Coupling Reaction

1. Copper-catalyzed C-N coupling of *N*-phenylaniline with 4-iodotoluene by *t*BuONa/K_2CO_3.



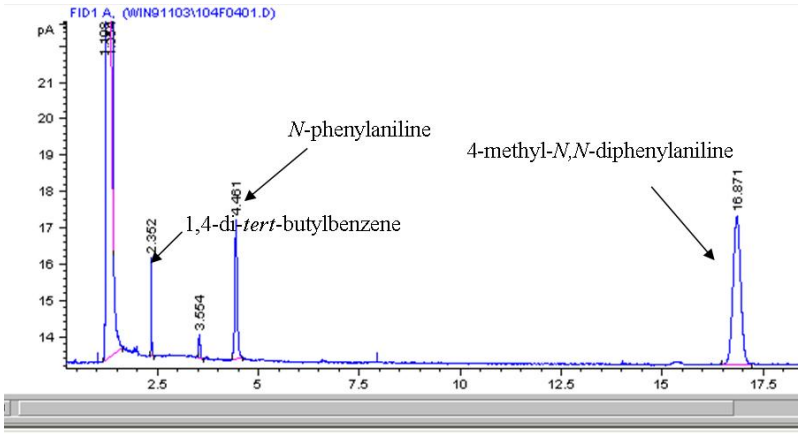
#	Time	Area	Height	Width	Area%	Symmetry
1	1.204	327342.9	168022.6	0.0307	98.830	0.143
2	1.363	3601.3	1878	0.0319	1.087	1.003
3	1.985	4.4	2	0.0328	0.001	1.224
4	2.368	18.9	8.3	0.0362	0.006	1.018
5	4.489	36	9.7	0.0576	0.011	0.874
6	5.217	1.7	4.1E-1	0.0559	0.001	0.793
7	16.982	214.1	16.2	0.1882	0.065	0.984

2. Copper-catalyzed C-N coupling of *N*-phenylaniline with 4-iodotoluene by *t*BuONa.



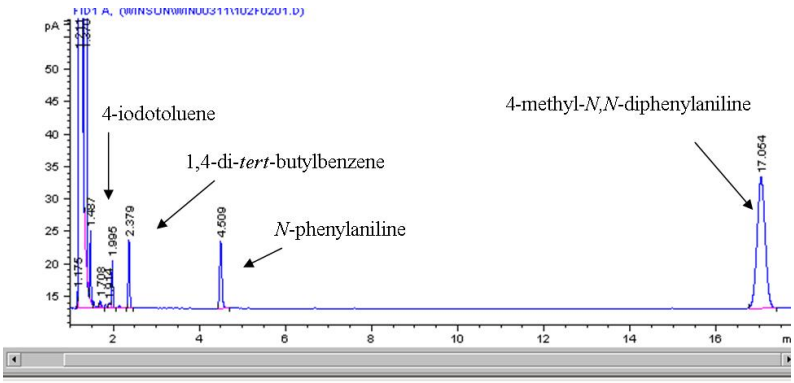
#	Time	Area	Height	Width	Area%	Symmetry
1	1.203	307612.5	158231.6	0.0307	95.503	0.143
2	1.362	13411.8	6657.8	0.0335	4.164	1.146
3	1.522	11.8	4.2	0.0396	0.004	0.365
4	1.798	7.2	2	0.0493	0.002	0.416
5	1.984	207	100.7	0.033	0.064	1.135
6	2.364	77.2	31.1	0.0414	0.024	1.073
7	3.338	7.6	1.2	0.0886	0.002	0.575
8	4.477	404.2	110.6	0.0561	0.125	0.919
9	16.931	356.3	27.2	0.1808	0.111	1.033

3. Copper-catalyzed C-N coupling of *N*-phenylaniline with 4-iodotoluene by *t*BuOK.



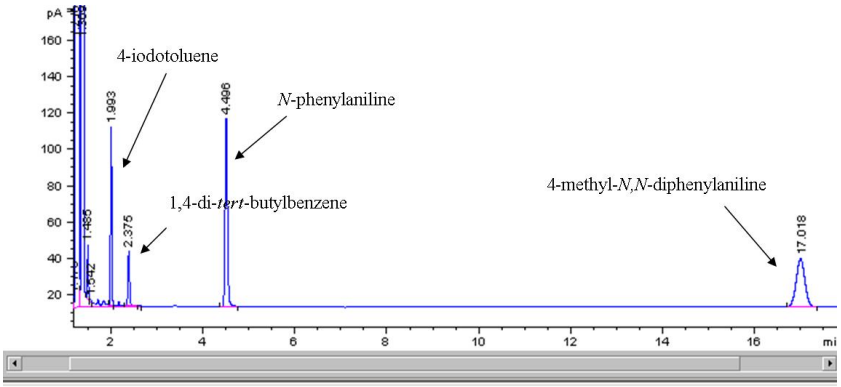
#	Time	Area	Height	Width	Area%	Symmetry
1	1.198	293653.9	160355.5	0.0289	99.611	0.152
2	1.354	1070.4	609.8	0.029	0.363	1.022
3	2.352	6	2.7	0.0337	0.002	1.051
4	3.554	1.9	6.4E-1	0.0421	0.001	0.92
5	4.461	15.9	3.8	0.0603	0.005	0.844
6	16.871	53.9	4.1	0.1554	0.018	1.025

4. Copper-catalyzed C-N coupling of *N*-phenylaniline with 4-iodotoluene by *t*BuONa/K_2CO_3 with 20 mol% TEMPO added.



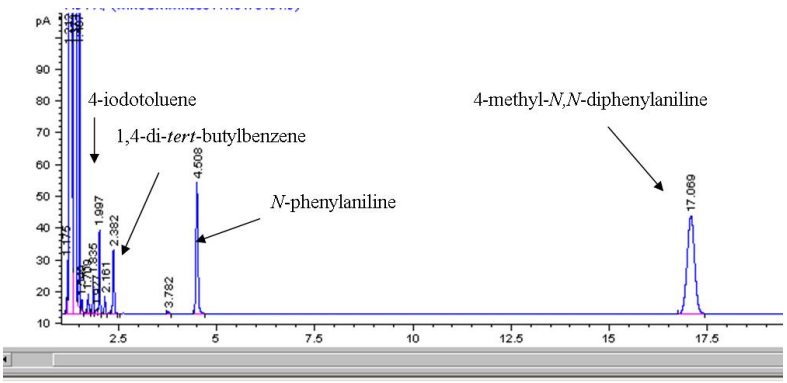
#	Time	Area	Height	Width	Area%	Symmetry
1	1.175	3.3	2.5	0.0203	0.001	0.821
2	1.211	321328.3	171427.2	0.0279	98.549	0.134
3	1.37	4362.2	2312.8	0.031	1.338	0.989
4	1.487	18.5	10.9	0.0274	0.006	0.983
5	1.708	2.5	9.8E-1	0.0358	0.001	0.65
6	1.914	2.2	7E-1	0.0416	0.001	0.446
7	1.995	14.7	7.3	0.032	0.005	1.028
8	2.379	25.2	10.6	0.0373	0.008	0.939
9	4.509	37.9	10.2	0.0576	0.012	0.874
10	17.054	263.5	20.2	0.1835	0.081	0.973

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



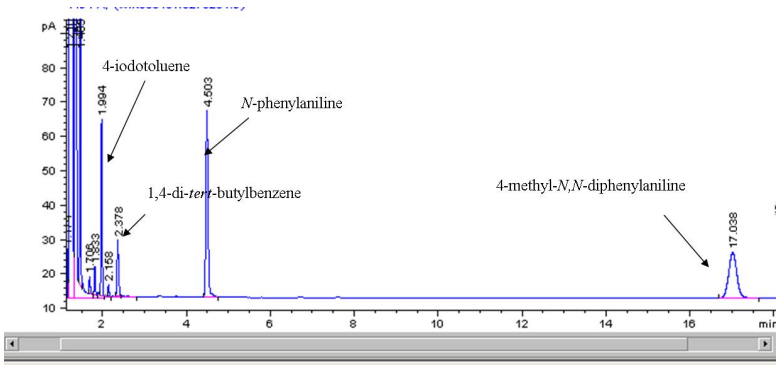
#	Time	Area	Height	Width	Area%	Symmetry
1	1.175	7.9	6	0.0199	0.002	0.927
2	1.21	311850.8	161162.8	0.0296	96.017	0.142
3	1.369	11889.5	6290.5	0.0311	3.661	1.076
4	1.485	47.7	29.8	0.0252	0.015	0.997
5	1.542	2.6	1.2	0.0343	0.001	0.607
6	1.993	188.7	98.1	0.0299	0.058	1.065
7	2.375	75	30.5	0.0377	0.023	0.932
8	4.496	375.8	104	0.0556	0.116	0.869
9	17.018	347.6	26.7	0.1902	0.107	1.018

6. Copper-catalyzed C-N coupling of *N*-phenylaniline with 4-iodotoluene by *t*BuONa/K_2CO_3 with 100 mol% TEMPO added.



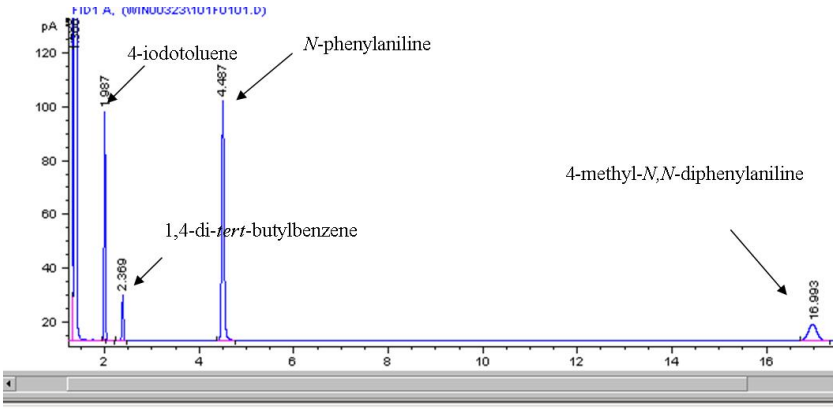
#	Time	Area	Height	Width	Area%	Symmetry
6	1.709	13.4	5.8	0.0348	0.004	0.803
7	1.835	19.4	11	0.0275	0.006	0.992
8	1.927	3.5	1.2	0.0407	0.001	1.298
9	1.997	50.4	26.2	0.0299	0.015	1.048
10	2.161	10	5.2	0.0299	0.003	0.997
11	2.382	51.4	20	0.0395	0.016	0.817
12	3.782	2.4	8.2E-1	0.0428	0.001	0.983
13	4.508	146.9	41.4	0.0549	0.045	0.86
14	17.069	405.2	30.6	0.1739	0.123	1.103

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



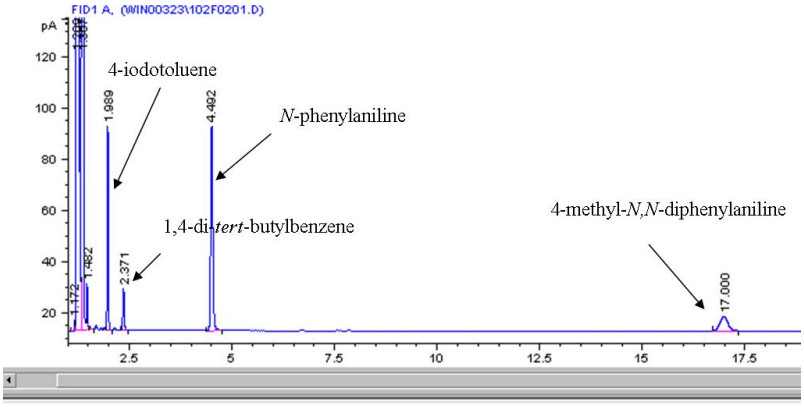
#	Time	Area	Height	Width	Area%	Symmetry
1	1.174	18.2	14	0.0202	0.006	0.831
2	1.21	319191.8	165439.2	0.0295	97.798	0.144
3	1.369	6485.8	3545.2	0.0302	1.987	0
4	1.485	138.5	81.1	0.0264	0.042	1.034
5	1.706	11.1	5.1	0.0336	0.003	0.765
6	1.833	16	8.4	0.0293	0.005	1.065
7	1.994	98.3	51.3	0.0304	0.030	1.025
8	2.158	6.6	3.5	0.0297	0.002	0.998
9	2.378	41.9	16.1	0.0434	0.013	0.86
10	4.503	195.2	54.2	0.0555	0.060	0.87
11	17.038	176.4	13.2	0.2231	0.054	1.01

8. Copper-catalyzed C-N coupling of *N*-phenylaniline with 4-iodotoluene without phen by *t*BuONa.



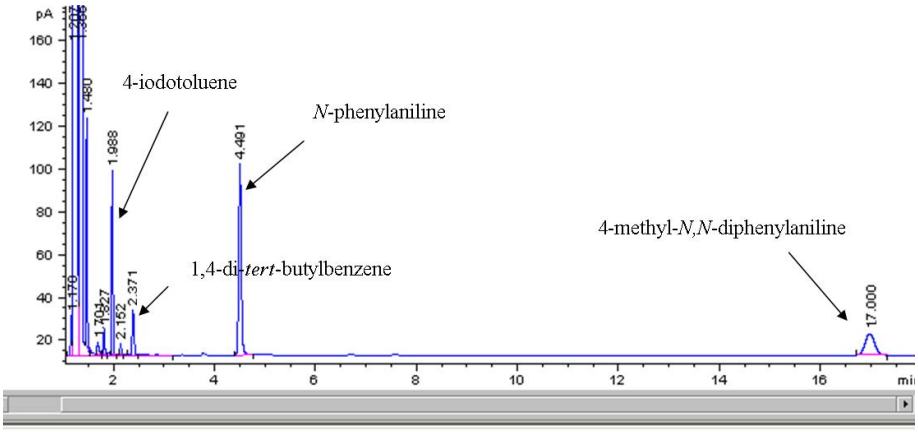
#	Time	Area	Height	Width	Area%	Symmetry
1	1.208	321600.3	168811.8	0.0287	97.826	0.138
2	1.366	6546.9	3662.1	0.0292	1.991	0
3	1.987	162.5	84.5	0.032	0.049	0.969
4	2.369	38.9	17.2	0.0354	0.012	1.01
5	4.487	320.6	89.1	0.0565	0.098	0.876
6	16.993	79	6	0.163	0.024	1.09

9. Copper-catalyzed C-N coupling of *N*-phenylaniline with 4-iodotoluene without phen by *t*BuONa with 20 mol% TEMPO added.



#	Time	Area	Height	Width	Area%	Symmetry
1	1.172	5.4	4.2	0.0195	0.002	0.742
2	1.209	313842.8	164188.3	0.0283	97.712	0.148
3	1.367	6770	3675.5	0.03	2.108	1.041
4	1.482	26.3	16.2	0.0254	0.008	0.953
5	1.989	150.3	79.2	0.0296	0.047	0.997
6	2.371	38.8	16.5	0.0359	0.012	0.943
7	4.492	286	79.5	0.0555	0.089	0.87
8	17	73.3	5.5	0.1615	0.023	1.014

10. Copper-catalyzed C-N coupling of *N*-phenylaniline with 4-iodotoluene without phen by *t*BuONa with 100 mol% TEMPO added.

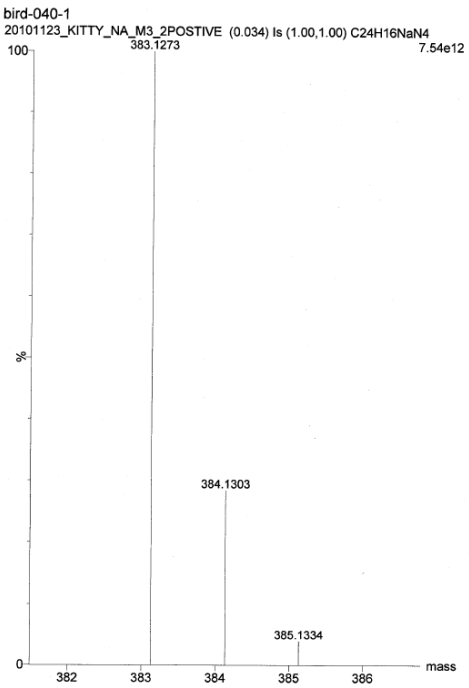


#	Time	Area	Height	Width	Area%	Symmetry
1	1.17	23.9	18.8	0.0194	0.007	0.828
2	1.207	317929.3	165600	0.0294	97.162	0.139
3	1.366	8372.7	4686.6	0.0292	2.559	0
4	1.48	179.8	107.9	0.0259	0.055	1.072
5	1.701	13.5	5.8	0.0357	0.004	0.752
6	1.827	20.4	11.7	0.0274	0.006	1.03
7	1.988	162	86	0.0295	0.050	1.019
8	2.152	9.9	5.3	0.0296	0.003	1
9	2.371	56.1	20.9	0.0448	0.017	0.781
10	4.491	318.1	89.2	0.0541	0.097	0.894
11	17	129.2	10	0.2161	0.039	1.08

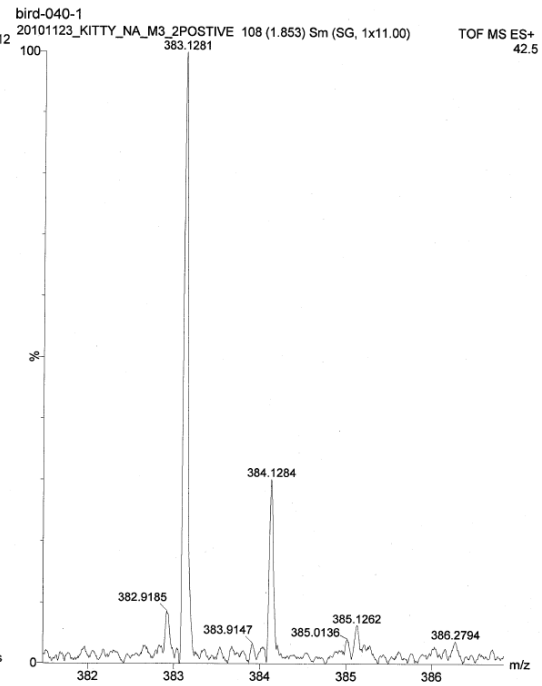
In situ ESI-MS Spectra and Isotope Distributions of Intermediates

Experimental and theoretical isotopic distributions of $[Na(phen)_2]^+$, $[Cu(phen)_2]^+$, $K[Cu(phen)(NPh_2)(p\text{-tolyl})]^+$, $[Cu(NPh_2)_2]^-$ and $[Cu(NPh_2)I]^-$ (from the ESI-MS spectra of the reaction solution of *N*-phenylaniline with 4-iodotoluene using *t*BuONa/K_2CO_3 as the base system in the presence of CuI and phen in toluene at 120°C)

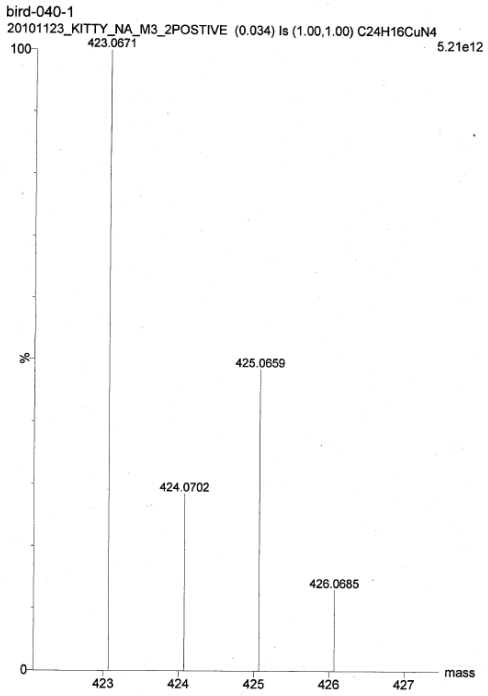
Theoretical isotopic distributions of $[Na(phen)_2]^+$



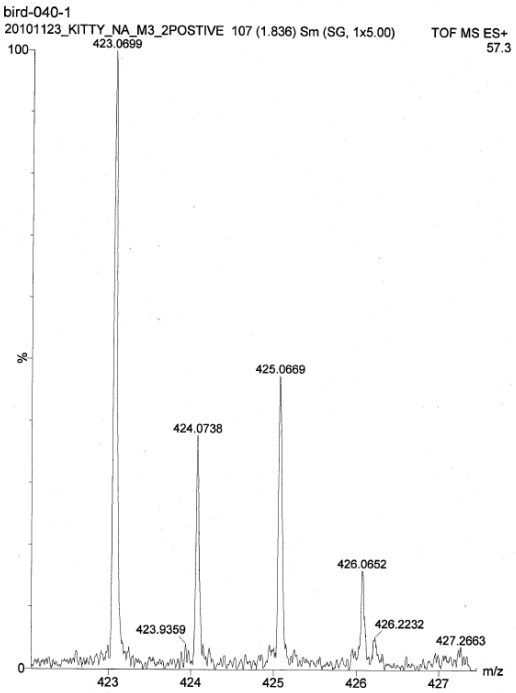
Experimental isotopic distributions of $[Na(phen)_2]^+$



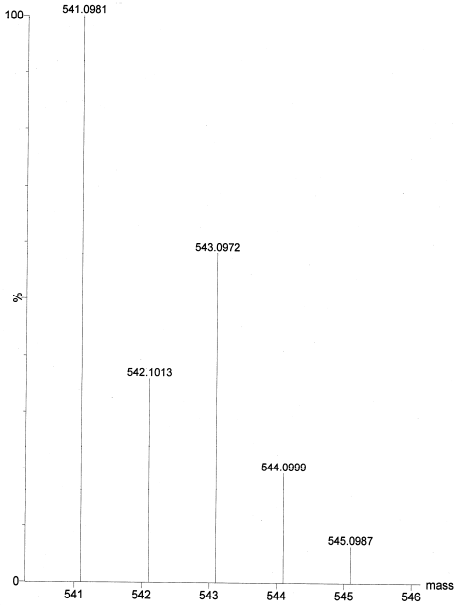
Theoretical isotopic distributions of $[Cu(phen)_2]^+$



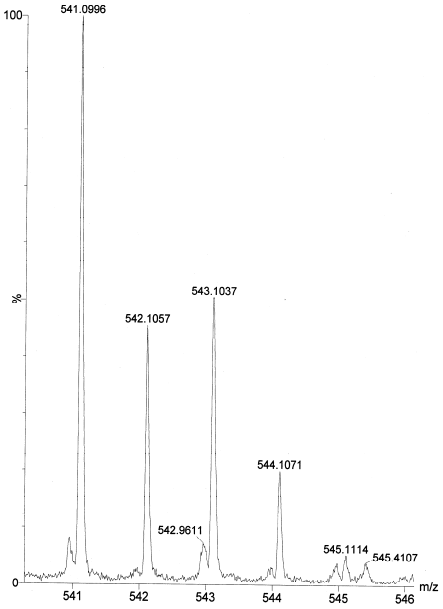
Experimental isotopic distributions of $[Cu(phen)_2]^+$



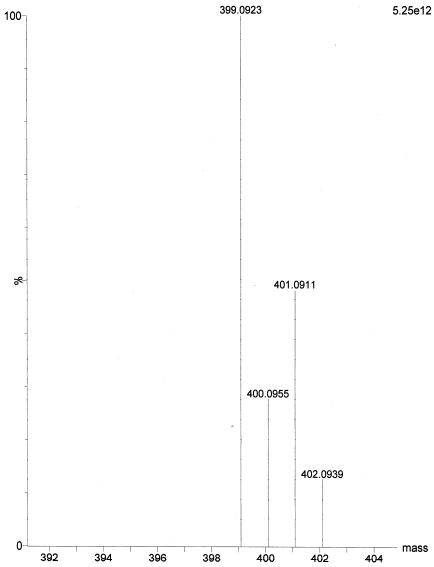
Theoretical isotopic distributions of $K[Cu(phen)(NPh_2)(p\text{-tolyl})]^+$



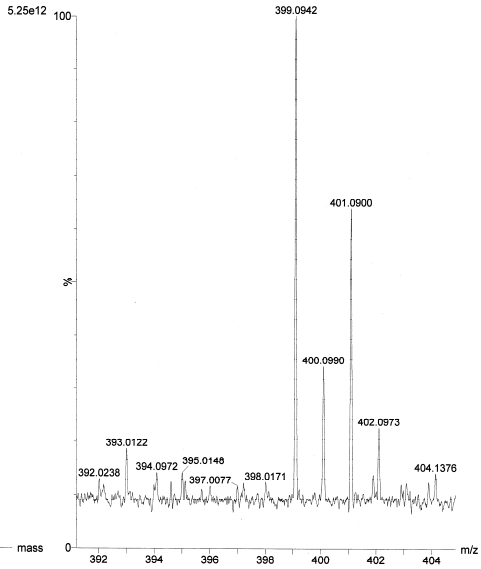
Experimental isotopic distributions of $K[Cu(phen)(NPh_2)(p\text{-tolyl})]^+$



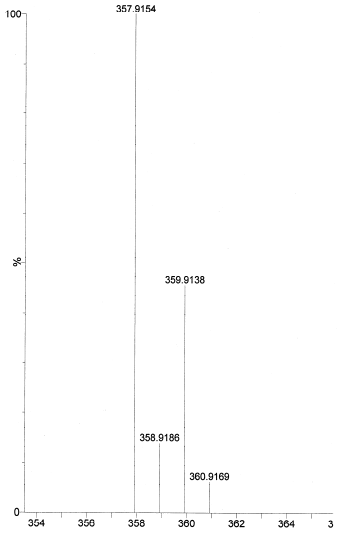
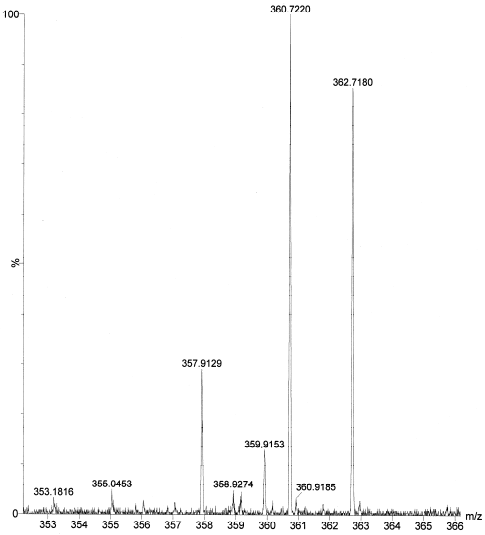
Theoretical isotopic distributions of $[Cu(NPh_2)_2]^-$



Experimental isotopic distributions of $[Cu(NPh_2)_2]^-$



Theoretical isotopic distributions of $[Cu(NPh_2)I]^-$



Experimental isotopic distributions of $[Cu(NPh_2)I]^-$